

Carbohydrates as Chiral Templates: Diastereoselective Synthesis of *N*-Glycosyl-*N*-homoallyl amines and β -Amino Acids from Imines

Sabine Laschat and Horst Kunz*

Institut für Organische Chemie, Johannes Gutenberg-Universität Mainz, J. J. Becher Weg 18-22,
D-6500 Mainz, Federal Republic of Germany

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Complexing properties and chirality of carbohydrates were utilized in diastereoselective reactions of *O*-pivaloylated *N*-galactosylimines with allylsilanes and -stannanes. With allyltrimethylsilane in the presence of SnCl₄, imines **2** of aromatic and heteroaromatic aldehydes were converted to homoallyl amines **3**, giving ratios of diastereomers higher than 7:1. No addition products derived from α -anomeric aromatic imines were formed. Aliphatic homoallyl amines **3** were synthesized by using allyltributylstannane in the presence of SnCl₄. Both α - and β -anomeric aliphatic imines reacted with the allylstannane. They gave the same ratio of diastereomers and showed the same sense of asymmetric induction.

Introduction

Chiral homoallyl amines are synthons for further transformations, for example, to 1,3-amino alcohols, 1-amino 3,4-epoxides, and β -amino acids. Nonproteinogenic β -amino acids are receiving interest, e.g., for the synthesis of β -lactam antibiotics.¹ Only few investigations of the asymmetric addition of allylic organometallic compounds to imines have been published.² This is in contrast to the numerous studies on allylic addition to aldehydes.^{3,4} Yamamoto and co-workers⁵ have found that the addition of allylic organometallic compounds to imines derived from 2-phenylethylamine and aldehydes proceeds with high diastereoselectivity only if 9-allyl-BBN is used as the reagent. However, there is no report on the addition of allylsilanes to imines so far, although the Sakurai reaction, i.e., the corresponding addition of allylsilanes to carbonyl compounds, is a well-established method.⁶

Recently, we reported that *S*-configured homoallyl amines can be synthesized diastereoselectively by the Lewis acid induced addition of allylsilanes to Schiff bases of 2,3,4,6-tetra-*O*-pivaloyl- β -D-galactopyranosylamine (**1**) (Scheme I).⁸ This chiral auxiliary has already been used in diastereoselective Strecker,⁷ Ugi,⁸ Mannich,⁹ and tandem Mannich-Michael reactions.^{10,11} The stereocontrol in these reactions is caused by the complexing ability of the oxygen functions of the carbohydrate toward Lewis acids in combination with the pronounced chirality of the carbohydrate. Analogously, the (*R*)-homoallyl amines **6** are available by using the corresponding 2,3,4-tri-*O*-pivaloyl- β -L-fucopyranosylamine (**4**) as the template.¹²

Table I. Reaction of Aromatic *N*-Galactosylimines **2** with 1 Equiv of Allyltrimethylsilane in THF in the Presence of 2.2 Equiv of SnCl₄ [(1) 0 °C, 1 h; (2) rt]

imine	R	time, days	product	yield, %	dr ^a
2a	4-ClC ₆ H ₄	2	3a	49	22:1
2b	2-ClC ₆ H ₄	3	3b	82	27:1
2c	3-ClC ₆ H ₄	2.5	3c	47	7:1
2d	C ₆ H ₅	3	3d	65	14:1
2e	4-NO ₂ C ₆ H ₄	2.5	3e	73	8:1
2f	2-NO ₂ C ₆ H ₄	6	3f	26	1.2:1
2g	4-MeC ₆ H ₄	4.5	3g	55	22:1
2h	3-pyridyl	5	3h	28	11:1
2i	2-naphthyl	5	3i	49	16:1
2k	2-MeOC ₆ H ₄	2	3k	37	2.8:1
2l	CH=CHC ₆ H ₅	2	3l	76	15:1
2m	4-CNC ₆ H ₄	3	3m	49	15:1
2n	4-MeO ₂ CC ₆ H ₄	2	3n	44	15:1
2o	4-FC ₆ H ₄	3.5	3o	54	21:1

^aDiastereomeric ratio, which was determined by analytical HPLC.

Results and Discussion

Lewis Acid Induced Addition of Allylsilanes and Allylstannanes to *O*-Pivaloylated *N*-Galactosylimines. Since the nucleophilicity of allylsilanes is low and the electrophilicity of imines is only moderate, the reaction between these compounds requires activation by a Lewis acid to proceed. In this sense, various Lewis acids were tested in the reaction of the *O*-pivaloylated *N*-galactosylimine **2a** (R = 4-ClC₆H₄) with allyltrimethylsilane in THF (see Scheme I). The results revealed that SnCl₄ [1.0 equiv of SnCl₄; 1 h at 0 °C, then 5.5 days at room temperature; 29% yield; ratio of diastereomers (dr) 96:4] and BF₃·OEt₂ [1.0 equiv of BF₃·OEt₂; mixed at -78 °C, then room temperature within 13 h, then 24 h at room temperature; 27% yield; dr 89:11] were able to catalyze the addition. Other Lewis acids tested (e.g., ZnCl₂, SnCl₄/LiBr, TBAF, SnCl₄/TBAF), only caused anomericization of the Schiff base **2a**, and TiCl₄ led to *E/Z* isomerization. Since SnCl₄ gave the higher diastereoselectivity (25:1) compared with BF₃·OEt₂ (9:1), it was used in further investigations.

To determine the optimal conditions, imine **2a** was reacted with 1.2 equiv of allyltrimethylsilane in the presence of different concentrations of SnCl₄ in THF at 0 °C for 1 h, followed by warming to room temperature. An increase in the concentration of Lewis acid (2 equiv) resulted in shorter reaction times (2 days), a higher yield of **3a** (50%), and a slight decrease of the diastereoselectivity (20:1). A further increase of the concentration (5 and 10 equiv) had no significant effect on the reaction time, the yield, or the selectivity.

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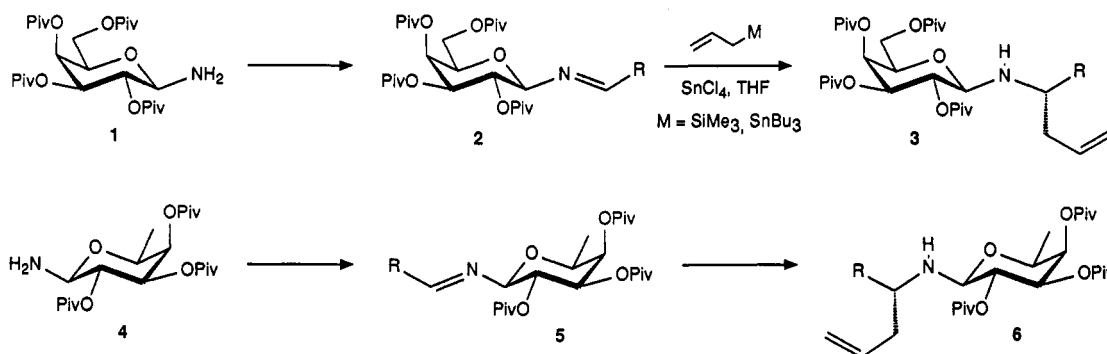
Scheme I. Synthesis of *N*-Glycosyl-*N*-homoallylamines

Table II. Reaction of Aliphatic *N*-Galactosylimines **2** with 1 Equiv of Allyltributylstannane in THF in the Presence of 1.2 Equiv of SnCl_4 (-78°C , 7 h)

imine	R	yield, %	product	dr (β) ^a	dr (α) ^a	β : α
2p	<i>n</i> -C ₃ H ₇	32	3p	>24:1	>24:1	4:1
2q	<i>n</i> -C ₉ H ₁₉	37	3q	8:1	2:1	3.5:1

^aDiastereomeric ratio, which was determined by 100.6-MHz ¹³C NMR spectroscopy.

The nucleophilicity of the allylic organometallic compound can be enhanced by changing the metal from silicon to tin. Therefore imine **2a** was converted to homoallylamine **3a** by using allyltributylstannane instead of allyltrimethylsilane under identical conditions, resulting in an increased yield (68%), but reduced asymmetric induction (10:1).

From these experiments it was concluded that SnCl_4 catalyzes not only the addition of the allyl compound but also the anomerization of the Schiff base **2**. For an optimal outcome, suitable reaction conditions had to be found which favor sufficient activation of the imine and suppression of the anomerization. It should also be noted that the imines **2** of aromatic aldehydes gave no α -anomeric homoallylamines **3**, as was proven by analytical HPLC and NMR spectroscopy.

The allylic addition reaction to imines of various aromatic and heteroaromatic aldehydes (Scheme I) gave the results summarized in Table I. The diastereoselection achieved in most cases was higher than 7:1. The Schiff bases of 2-nitrobenzaldehyde **2f** and 2-methoxybenzaldehyde **2k** showed low selectivities, caused probably by steric and/or electronic interactions between the ortho substituents and the Lewis acid.

Schiff bases **2** of aliphatic aldehydes with allyltrimethylsilane under identical conditions did not undergo allylic addition. Even at low temperature (-78°C), only anomerization and decomposition occurred. However, these imines **2** were converted to the corresponding homoallylamines **3** by using allyltributylstannane instead of the silane at -78°C (Table II). To activate the imine, 1.2 equiv of SnCl_4 was sufficient. In contrast to the above-mentioned results with aromatic imines **2**, both α - and β -anomeric aliphatic Schiff bases reacted with the allyl-stannane.

Assignment of the Absolute Configuration of the Homoallylamines. In order to determine the stereochemical course of the allylic addition to *N*-galactosylimines, the *N*-galactosyl-*N*-homoallylamines **3** were converted to β -amino acids with known configuration. The oxidation of the allylic side chain linked to the carbohydrate failed. Neither ozonolysis^{13,14} of **3d** nor application

Table III. Oxidation of *N*-Terminally Protected Homoallylamines **9**

amine	Y ^a	meth ^b	time, h	acid (yield, %)	aldehyde (yield, %)
9a	Boc	A	16.0	10a (86)	11a (-)
9a	Boc	B	2.5	10a (27)	11a (29)
9b	NZ	A	29.5	10b (71)	11b (-)
9b	NZ	B	3.5	10b (87)	11b (-)

^aBoc = *tert*-butoxycarbonyl, NZ = 4-nitrobenzyloxycarbonyl.
^bMethod A: $\text{NaIO}_4/\text{KMnO}_4$, H_2O , rt. Method B: $\text{NaIO}_4/\text{RuCl}_3$ (H_2O), CH_3CN , CCl_4 , H_2O , rt.

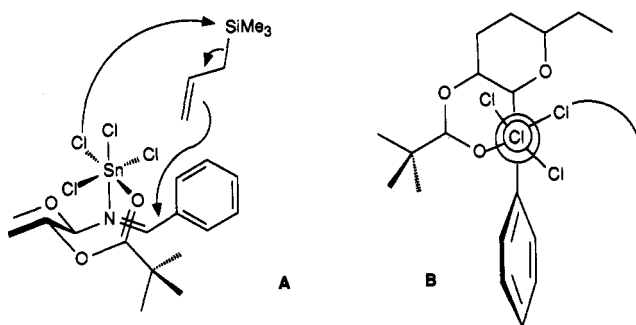


Figure 1.

of $\text{NaIO}_4/\text{KMnO}_4$ ¹⁵ or $\text{NaIO}_4/\text{RuCl}_3$ ^{16,17} was successful. Since the low reactivity of the *N*-galactosyl-*N*-homoallylamine did not allow introduction of the *tert*-butoxycarbonyl¹⁸ or benzyloxycarbonyl group¹⁹ at the galactosyl nitrogen, oxidations of *N*-protected derivatives of compounds **3** could not be realized. After release of the homoallylamine from the carbohydrate template using aqueous HCl in methanol, the homoallylamine hydrochloride **8** could easily be *N*-protected (Scheme II, Table III). The *N*-protected homoallylamines were then oxidized to yield the *N*-protected β -amino acids **10**. Oxidation of the Boc-homoallylamine **9a** with $\text{RuCl}_3/\text{NaIO}_4$ resulted in the accompanying formation of the Boc-protected aldehyde **11a**. After deprotection of **10**, the amino acid β -phenyl- β -alanine (**12**) was isolated in an overall yield of 58% based on **3d**. By comparison of its optical rotation with that of the *R*-configured enantiomer reported in the literature, the configuration was assigned as *S*.^{20,21} Thus,

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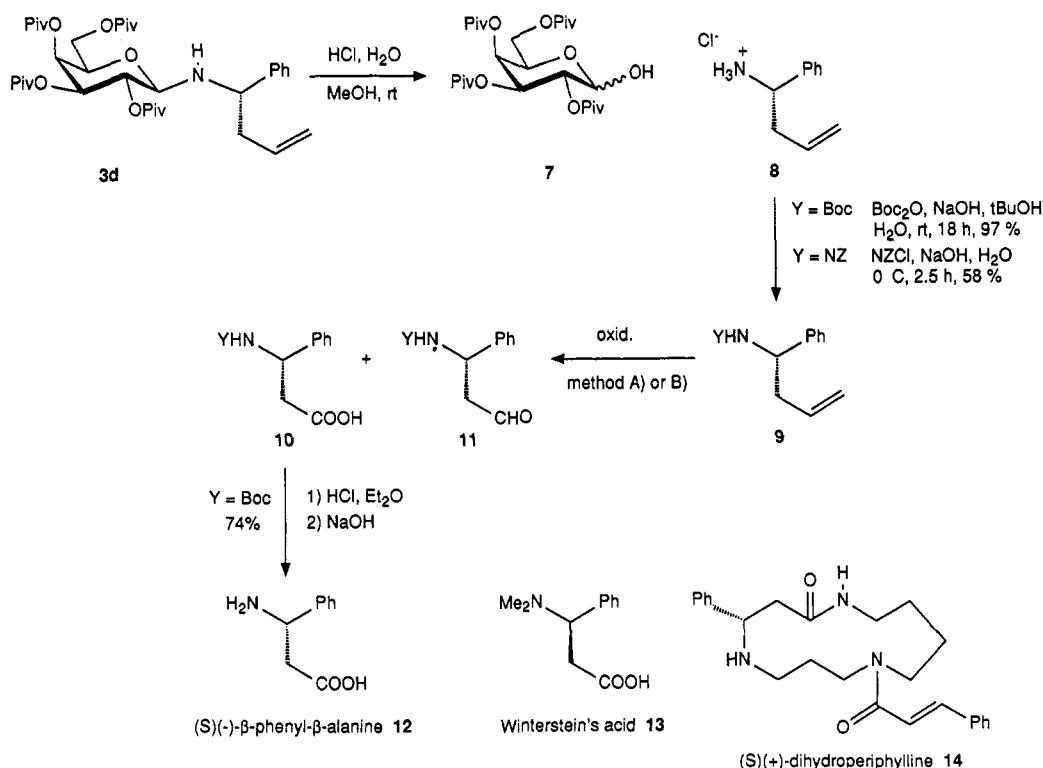
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Scheme II. Conversion of *N*-Galactosyl-*N*-homoallylamines to β -Amino Acids

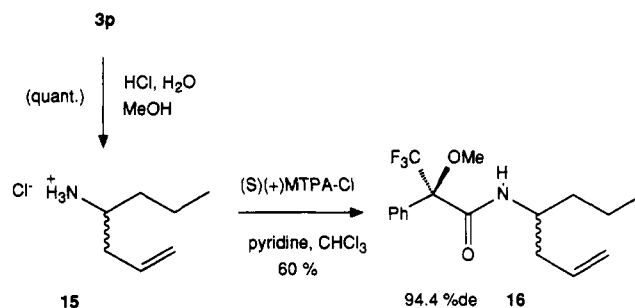
the β -phenyl- β -alanine (12) obtained has a configuration identical with that of the β -phenyl- β -alanine moiety occurring in the spermine alkaloid (S)(+)-dihydroperiphylline²⁰ (14) and opposite that of the taxine alkaloid Winterstein's acid²¹ (13).

Mechanistic Considerations. The preferred formation of the *S*-configured diastereomers of the homoallylamines 3 can be rationalized by an attack of the allylsilane from the *Si* side, i.e., the side facing the ring oxygen.

In the transition state (Figure 1, structure A) the tin should have octahedral coordination. Two coordination sites of the tin(IV) chloride are occupied by the imine nitrogen and the carbonyl oxygen of the (C-2) pivaloyloxy group, respectively. According to this rationalization, the $\text{S}_{\text{N}}2'$ -type attack of the allylic compound from the back side of the imine is initiated by the interaction of one chlorine with the silyl group. From the top view of the transition state (Figure 1, structure B) it is obvious that, for steric reasons, only one of the four chlorine ligands is able to undergo an interaction with the allylsilane. The two other equatorial chlorines are hindered because of steric and/or electronic interactions with the anomeric carbon or the phenyl group, respectively. The axial chlorine ligand is remote from the reaction site.

Asymmetric Induction in the Addition to Aliphatic Imines. In additions of allylstannanes to aliphatic Schiff bases 2, both α - and β -anomeric *n*-butanimines 2p reacted with allyltributylstannane to give the homoallylamines 3p. The question arose as to whether the α - and β -anomer display the same direction of asymmetric induction. This was proven by acidic release of the homoallylamine from the *N*-galactosyl derivative 3p and its conversion to the amide 16 of Mosher's acid (Scheme III). 16 showed a diastereomeric excess of 94.4% determined by NMR. The high diastereomeric ratio displayed by 16 is only explainable by a mechanism in which both α - and β -anomeric imines 2p yield preferably the addition products 3p with

Scheme III



identical absolute configuration.

In conclusion, the *O*-pivaloylated galactosylamine 1 is an effective chiral template in the synthesis of chiral homoallylamines 3. Both aromatic and aliphatic derivatives were synthesized with high asymmetric induction. The homoallylamines can be detached easily from the carbohydrate template, which can be recycled.

Experimental Section

Material and Methods. For measurement of 200-MHz ^1H and 50.3-MHz ^{13}C NMR spectra and 400-MHz ^1H and 100.6-MHz ^{13}C NMR spectra, see ref 8. All melting points are uncorrected. Visualization in analytical TLC (silica gel 60-F₂₅₄) was achieved by spraying with a mixture of a 0.2% solution of 3-methoxyphenol in ethanol/2 N H_2SO_4 (1:1) or a 0.3% solution of ninhydrin in methanol/acetic acid (97:3) and heating. Carboxylic acids were visualized with a 0.1% solution of bromocresol green in 2-propanol. Analytical HPLC was carried out with diode array detection (190–370 nm) on reversed-phase columns in acetonitrile/water (75:25, flow 1.00 mL/min) as eluent. The *O*-pivaloylated galactosylamine 1 was purchased from Merck-Schuchardt, München.

General Procedure for the Preparation of Aromatic *N*-Galactosyl-*N*-homoallylamines 3a–o. A solution of *N*-galactosylimine 2 (0.50 mmol) in THF (5 mL) was cooled to 0°C , and allyltrimethylsilane (0.10 mL, 0.60 mmol) and SnCl_4 (0.13 mL, 1.10 mmol) were added. The mixture was stirred for 1 h at 0°C and warmed up to room temperature. After the time given in Table I, the mixture was hydrolyzed with 2 N aqueous NaOH

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(50 mL). The solvent was evaporated in vacuo, and the residue was triturated three times with CHCl_3 (50 mL). The organic solutions were extracted with a saturated NaHCO_3 solution (100 mL), dried with MgSO_4 , and concentrated in vacuo to yield the crude products 3, which were purified by flash chromatography [petroleum ether/ethyl acetate, 8:1 (v/v)].

General Procedure for the Preparation of Aliphatic *N*-Galactosyl-*N*-homoallylamines 3p-q. A solution of *N*-galactosylimine 2 (0.50 mmol) in THF (5 mL) was cooled to -78°C , and allyltritylstannane (0.19 mL, 0.60 mmol) and SnCl_4 (0.07 mL, 0.60 mmol) were added. The mixture was stirred for 7 h at -78°C and 7.5 days at -30°C . Hydrolysis and purification were carried out as described above for aromatic *N*-galactosyl-*N*-homoallylamines.

***N*-(2,3,4,6-Tetra-*O*-pivaloyl- β -D-galactopyranosyl)-1-amino-1-(4-chlorophenyl)-3-butene (3a):** yield, 170 mg (50%), colorless, amorphous solid; $[\alpha]_D^{22} = -4.2^\circ$ ($c = 1.02$; CHCl_3).

$^1\text{H NMR}$ (400 MHz) (CDCl_3): $\delta = 1.06$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.16 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.17 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.23 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.18 (d, br, $J_{1,\text{NH}} = 12.4$ Hz, 1 H, NH), 2.29 (m, 2 H, 2'-H), 3.64 (dd, $J_{5,6a} = 6.9$ Hz, $J_{5,6b} = 6.6$ Hz, 1 H, 5-H), 3.74 (dd, $J_{1,\text{NH}} = 12.2$ Hz, $J_{1,2} = 8.5$ Hz, 1 H, 1-H), 3.93 (dd, $J_{6a,6b} = 11.2$ Hz, $J_{5,6a} = 6.6$ Hz, 1 H, 6a-H), 4.05 (dd, $J_{6a,6b} = 11.2$ Hz, $J_{5,6b} = 7.0$ Hz, 1 H, 6b-H), 4.09 (dd, $J_{1,2a'} = 12.9$ Hz, $J_{1,2b'} = 6.8$ Hz, 1 H, 1'-H), 5.03 (m, 4 H, 2-H, 3-H, 4'-H), 5.31 (d, $J_{3,4} = 3.1$ Hz, 1 H, 4-H), 5.58 (m, 1 H, 3'-H), 7.17 (d, $J_{\text{ortho}} = 8.5$ Hz, 2 H, 3''-H, 5''-H), 7.25 (d, $J_{\text{ortho}} = 8.5$ Hz, 2 H, 2''-H, 6''-H).

$^{13}\text{C NMR}$ (100.6 MHz) (CDCl_3): $\delta = 27.10$, 27.13, 27.22, 27.28 [$\text{C}(\text{CH}_3)_3$], 38.71, 38.81, 39.06 [$\text{C}(\text{CH}_3)_3$], 42.93 (C-2'), 56.04 (C-1'), 61.78 (C-6), 67.46, 68.81, 71.37, 71.69 (C-2, C-3, C-4, C-5), 86.31 (C-1), 118.21 (C-4'), 128.47 (C-2'', C-6''), 129.06 (C-3'', C-5''), 133.03 (C-4''), 134.05 (C-3'), 140.68 (C-1''), 176.86, 177.08, 177.58, 177.88 (CO).

Anal. Calcd for $\text{C}_{36}\text{H}_{54}\text{NO}_9\text{Cl}$: C, 63.58; H, 7.95; N, 2.06. Found: C, 63.67; H, 7.72; N, 2.04.

***N*-(2,3,4,6-Tetra-*O*-pivaloyl- β -D-galactopyranosyl)-1-amino-1-(2-chlorophenyl)-3-butene (3b):** yield, 280 mg (82%), colorless, amorphous solid; $[\alpha]_D^{22} = +6.8^\circ$ ($c = 1.00$; CHCl_3).

$^1\text{H NMR}$ (400 MHz) (CDCl_3): $\delta = 1.06$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.13 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.15 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.23 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.17 (s, br, 1 H, NH), 2.25 (m, 1 H, 2a'-H), 2.41 (m, 1 H, 2b'-H), 3.73 (dd, $J_{5,6a} = 7.1$ Hz, $J_{5,6b} = 6.8$ Hz, 1 H, 5-H), 3.80 (d, br, $J_{1,2} = 7.7$ Hz, 1 H, 1-H), 3.95 (dd, $J_{6a,6b} = 11.1$ Hz, $J_{5,6a} = 7.1$ Hz, 1 H, 6a-H), 4.06 (dd, $J_{6a,6b} = 11.1$ Hz, $J_{5,6b} = 6.8$ Hz, 1 H, 6b-H), 4.70 (dd, $J_{1,2a'} = 7.5$ Hz, $J_{1,2b'} = 5.5$ Hz, 1 H, 1'-H), 5.01 (m, 4 H, 2-H, 3-H, 4'-H), 5.31 (d, $J_{3,4} = 1.8$ Hz, 1 H, 4-H), 5.66 (m, 1 H, 3'-H), 7.11-7.26 (m, 2 H, 4''-H, 5''-H), 7.28 (dd, $J_{5',6'} = 7.6$ Hz, $J_{4',5'} = 1.6$ Hz, 1 H, 6''-H), 7.44 (dd, $J_{3',4'} = 7.5$ Hz, $J_{3'',4''} = 2.0$ Hz, 1 H, 3''-H).

$^{13}\text{C NMR}$ (100.6 MHz) (CDCl_3): $\delta = 27.06$, 27.17, 27.23 [$\text{C}(\text{CH}_3)_3$], 38.66, 38.76, 39.00 [$\text{C}(\text{CH}_3)_3$], 41.27 (C-2'), 52.05 (C-1'), 61.55 (C-6), 67.37, 68.92, 71.46, 71.62 (C-2, C-3, C-4, C-5), 86.81 (C-1), 118.11 (C-4'), 126.56 (C-4''), 128.07 (C-6''), 128.63 (C-3''), 129.43 (C-5''), 133.67 (C-2''), 134.02 (C-3'), 139.91 (C-1''), 176.78, 177.07, 177.46, 177.86 (CO).

Anal. Calcd for $\text{C}_{36}\text{H}_{54}\text{NO}_9\text{Cl}$: C, 63.58; H, 7.95; N, 2.06. Found: C, 63.54; H, 8.08; N, 2.04.

***N*-(2,3,4,6-Tetra-*O*-pivaloyl- β -D-galactopyranosyl)-1-amino-1-(3-chlorophenyl)-3-butene (3c):** yield, 160 mg (47%), colorless, amorphous solid; $[\alpha]_D^{22} = +4.9^\circ$ ($c = 1.01$; CHCl_3).

$^1\text{H NMR}$ (400 MHz) (CDCl_3): $\delta = 0.99$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.09 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.12 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.17 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.18 (d, br, $J_{1,\text{NH}} = 6.8$ Hz, 1 H, NH), 2.22 (m, 2 H, 2'-H), 3.60 (dd, $J_{5,6a} = 7.1$ Hz, $J_{5,6b} = 6.5$ Hz, 1 H, 5-H), 3.71 (m, br, 1 H, 1-H), 3.88 (dd, $J_{6a,6b} = 11.1$ Hz, $J_{5,6a} = 6.5$ Hz, 1 H, 6a-H), 3.99 (dd, $J_{6a,6b} = 11.1$ Hz, $J_{5,6b} = 7.1$ Hz, 1 H, 6b-H), 4.04 (dd, $J_{1,2a'} = 6.9$ Hz, $J_{1,2b'} = 6.8$ Hz, 1 H, 1'-H), 4.94 (m, 4 H, 2-H, 3-H, 4'-H), 5.24 (d, $J_{3,4} = 2.9$ Hz, $J_{2,3} = 0.6$ Hz, 1 H, 4-H), 5.52 (m, 1 H, 3'-H), 7.01-7.19 (m, 4 H, Ph).

$^{13}\text{C NMR}$ (100.6 MHz) (CDCl_3): $\delta = 27.07$, 27.10, 27.19, 27.29 [$\text{C}(\text{CH}_3)_3$], 38.68, 38.80, 39.02 [$\text{C}(\text{CH}_3)_3$], 42.92 (C-2'), 56.16 (C-1'), 61.78 (C-6), 67.45, 68.74, 71.38, 71.71 (C-2, C-3, C-4, C-5), 86.30 (C-1), 118.26 (C-4'), 125.99 (C-6''), 127.50 (C-4''), 127.55 (C-2''), 129.46 (C-5''), 133.93 (C-3'), 134.37 (C-3''), 144.55 (C-1''), 176.82, 177.05, 177.61, 177.83 (CO). Signals of the minor diastereomer: $\delta = 41.91$ (C-2'), 61.16 (C-6), 65.31 (C-1'), 67.03, 68.21, 69.48, 72.83

(C-2, C-3, C-4, C-5), 127.07 (C-6''), 128.33 (C-2''), 129.80 (C-5'').

Anal. Calcd for $\text{C}_{36}\text{H}_{54}\text{NO}_9\text{Cl}$: C, 63.58; H, 7.95; N, 2.06. Found: C, 63.28; H, 8.02; N, 2.07.

***N*-(2,3,4,6-Tetra-*O*-pivaloyl- β -D-galactopyranosyl)-1-amino-1-phenyl-3-butene (3d):** yield, 210 mg (65%), colorless, amorphous solid; $[\alpha]_D^{22} = +4.2^\circ$ ($c = 1.02$; CHCl_3).

$^1\text{H NMR}$ (400 MHz) (CDCl_3): $\delta = 1.06$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.17 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.18 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.24 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.18 (s, br, 1 H, NH), 2.29 (m, 1 H, 2a'-H), 2.35 (m, 1 H, 2b'-H), 3.63 (dd, $J_{5,6a} = 7.1$ Hz, $J_{5,6b} = 6.6$ Hz, 1 H, 5-H), 3.77 (d, br, $J_{1,2} = 7.7$ Hz, 1 H, 1-H), 3.94 (dd, $J_{6a,6b} = 11.2$ Hz, $J_{5,6a} = 6.6$ Hz, 1 H, 6a-H), 4.07 (dd, $J_{6a,6b} = 11.2$ Hz, $J_{5,6b} = 7.1$ Hz, 1 H, 6b-H), 4.12 (dd, $J_{1,2a'} = 6.9$ Hz, $J_{1,2b'} = 6.9$ Hz, 1 H, 1'-H), 5.02 (m, 4 H, 2-H, 3-H, 4'-H), 5.29 (d, $J_{3,4} = 2.9$ Hz, 1 H, 4-H), 5.61 (m, 1 H, 3'-H), 7.21-7.29 (m, 5 H, Ph).

$^{13}\text{C NMR}$ (100.6 MHz) (CDCl_3): $\delta = 27.07$, 27.11, 27.20, 27.26 [$\text{C}(\text{CH}_3)_3$], 38.68, 38.78, 39.03 [$\text{C}(\text{CH}_3)_3$], 43.01 (C-2'), 56.61 (C-1'), 61.81 (C-6), 67.52, 68.80, 71.40, 71.60 (C-2, C-3, C-4, C-5), 86.38 (C-1), 117.82 (C-4'), 127.34 (C-4''), 127.74 (C-2'', C-6''), 128.22 (C-3'', C-5''), 134.52 (C-3'), 142.09 (C-1''), 176.86, 177.07, 177.58, 177.86 (CO).

Anal. Calcd for $\text{C}_{36}\text{H}_{56}\text{NO}_9$: C, 66.97; H, 8.53; N, 2.17. Found: C, 67.03; H, 8.47; N, 2.19.

***N*-(2,3,4,6-Tetra-*O*-pivaloyl- β -D-galactopyranosyl)-1-amino-1-(4-nitrophenyl)-3-butene (3e):** yield, 250 mg (73%), pale yellow, amorphous solid; $[\alpha]_D^{22} = +1.2^\circ$ ($c = 1.00$; CHCl_3).

$^1\text{H NMR}$ (400 MHz) (CDCl_3): $\delta = 1.05$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.14 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.17 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.23 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.25 (d, $J_{1,\text{NH}} = 12.3$ Hz, 1 H, NH), 2.31 (m, 2 H, 2-H), 3.65 (ddd, $J_{5,6a} = 6.9$ Hz, $J_{5,6b} = 6.7$ Hz, $J_{4,5} = 0.6$ Hz, 1 H, 5-H), 3.74 (dd, br, $J_{1,\text{NH}} = 12.3$ Hz, $J_{1,2} = 8.6$ Hz, 1 H, 1-H), 3.92 (dd, $J_{6a,6b} = 11.1$ Hz, $J_{5,6a} = 6.7$ Hz, 1 H, 6a-H), 4.07 (dd, $J_{6a,6b} = 11.1$ Hz, $J_{5,6b} = 6.9$ Hz, 1 H, 6b-H), 4.25 (dd, $J_{1,2a'} = 6.8$ Hz, $J_{1,2b'} = 6.7$ Hz, 1 H, 1'-H), 5.02 (m, 4 H, 2-H, 3-H, 4'-H), 5.30 (dd, $J_{3,4} = 3.1$ Hz, $J_{2,3} = 0.9$ Hz, 1 H, 4-H), 5.54 (m, 1 H, 3'-H), 7.40 (d, $J_{\text{ortho}} = 8.8$ Hz, 2 H, 2''-H, 6''-H), 8.13 (d, $J_{\text{ortho}} = 8.8$ Hz, 2 H, 3''-H, 5''-H).

$^{13}\text{C NMR}$ (100.6 MHz) (CDCl_3): $\delta = 27.02$, 27.05, 27.14, 27.23 [$\text{C}(\text{CH}_3)_3$], 38.64, 38.78, 38.99 [$\text{C}(\text{CH}_3)_3$], 42.71 (C-2'), 56.13 (C-1'), 61.57 (C-6), 67.24, 68.76, 71.21, 71.73 (C-2, C-3, C-4, C-5), 86.38 (C-1), 118.82 (C-4'), 123.51 (C-3'', C-5''), 128.34 (C-2'', C-6''), 133.18 (C-3'), 147.35 (C-4''), 150.09 (C-1''), 176.72, 176.98, 177.48, 177.74 (CO).

Anal. Calcd for $\text{C}_{36}\text{H}_{54}\text{N}_2\text{O}_{11}$: C, 62.61; H, 7.83; N, 4.05. Found: C, 62.69; H, 7.14; N, 3.93.

***N*-(2,3,4,6-Tetra-*O*-pivaloyl- β -D-galactopyranosyl)-1-amino-1-(2-nitrophenyl)-3-butene (3f):** yield, 90 mg (26%), yellow, amorphous solid; $[\alpha]_D^{22} = +14.3^\circ$ ($c = 1.03$; CHCl_3).

$^1\text{H NMR}$ (400 MHz) (CDCl_3): $\delta = 1.05$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.12 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.13 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.21 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.26 (m, 1 H, 2a'-H), 2.45 (m, 1 H, 2b'-H), 3.70 (dd, $J_{5,6a} = 6.9$ Hz, $J_{5,6b} = 6.6$ Hz, 1 H, 5-H), 3.75 (d, $J_{1,2} = 7.1$ Hz, 1 H, 1-H), 3.94 (dd, $J_{6a,6b} = 11.0$ Hz, $J_{5,6a} = 7.5$ Hz, 1 H, 6a-H), 4.03 (dd, $J_{6a,6b} = 11.0$ Hz, $J_{5,6b} = 6.6$ Hz, 1 H, 6b-H), 4.54 (m, br, 1 H, NH), 4.67 (dd, $J_{1,2a'} = 7.4$ Hz, $J_{1,2b'} = 5.6$ Hz, 1 H, 1'-H), 4.99 (m, 4 H, 2-H, 3-H, 4'-H), 5.30 ("d", 1 H, 4-H), 5.62 (m, 1 H, 3'-H), 7.35 (m, 1 H, 6''-H), 7.49 (m, 1 H, 4''-H), 7.66 (m, 1 H, 5''-H), 7.72 (m, 1 H, 3''-H). Signals of the minor diastereomer: $\delta = 4.19$ ("dd", br, 1 H, NH), 4.39 ("dd", br, 1 H, 1-H).

$^{13}\text{C NMR}$ (100.6 MHz) (CDCl_3): $\delta = 27.05$, 27.12, 27.16, 27.23 [$\text{C}(\text{CH}_3)_3$], 38.63, 38.66, 38.75, 39.00 [$\text{C}(\text{CH}_3)_3$], 42.18 (C-2'), 50.87 (C-1'), 61.25 (C-6), 67.21, 68.90, 71.40, 71.68 (C-2, C-3, C-4, C-5), 86.84 (C-1), 118.70 (C-4'), 123.63 (C-3''), 127.86 (C-6''), 129.43 (C-6''), 132.16 (C-5''), 133.54 (C-3'), 137.43 (C-1''), 150.27 (C-2''), 176.71, 177.04, 177.40, 177.81 (CO). Signals of the minor diastereomer: $\delta = 41.11$ (C-2'), 54.27 (C-1'), 60.84 (C-6), 66.95, 71.33 (C-2, C-3, C-4, C-5), 88.38 (C-1), 118.00 (C-4'), 123.83 (C-3''), 127.52 (C-4''), 129.07 (C-6''), 132.24 (C-5''), 133.93 (C-3'), 139.29 (C-1''), 149.11 (C-2''), 176.66, 177.31, 177.52, 177.70 (CO).

Anal. Calcd for $\text{C}_{36}\text{H}_{54}\text{N}_2\text{O}_{11}$: C, 62.61; H, 7.83; N, 4.05. Found: C, 62.89; H, 7.82; N, 3.92.

***N*-(2,3,4,6-Tetra-*O*-pivaloyl- β -D-galactopyranosyl)-1-amino-1-(4-methylphenyl)-3-butene (3g):** yield, 120 mg (36%), colorless, amorphous solid; $[\alpha]_D^{22} = +15.4^\circ$ ($c = 1.00$; CHCl_3).

$^1\text{H NMR}$ (400 MHz) (CDCl_3): $\delta = 1.07$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.16 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.17 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.23 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.15 (s, 1 H, NH), 2.30 (m, 2 H, 2-H), 2.32 (s, 3 H, CH_3), 3.63 (dd,

$J_{5,6a} = 6.7$ Hz, $J_{5,6b} = 6.7$ Hz, 1 H, 5-H), 3.75 (d, $J_{1,2} = 8.5$ Hz, 1 H, 1-H), 3.94 (dd, $J_{6a,6b} = 11.1$ Hz, $J_{5,6a} = 6.6$ Hz, 1 H, 6a-H), 4.06 (dd, $J_{6a,6b} = 11.1$ Hz, $J_{5,6b} = 6.7$ Hz, 1 H, 6b-H), 4.09 (d, $J_{1,2} = 6.4$ Hz, 1 H, 1'-H), 4.99 (m, 4 H, 2-H, 3-H, 4'-H), 5.28 (d, $J_{3,4} = 3.1$ Hz, 1 H, 4-H), 5.60 (m, 1 H, 3'-H), 7.08 (d, $J_{ortho} = 8.0$ Hz, 2 H, 2''-H, 6''-H), 7.12 (d, $J_{ortho} = 8.0$ Hz, 2 H, 3''-H, 5''-H).

^{13}C NMR (100.6 MHz) (CDCl_3): $\delta = 20.95$ (CH_3), 26.98, 27.02, 27.11, 27.17 [$\text{C}(\text{CH}_3)_3$], 38.58, 38.68, 38.94 [$\text{C}(\text{CH}_3)_3$], 42.91 (C-2''), 56.21 (C-1'), 61.76 (C-6), 67.49, 68.72, 71.35, 71.51 (C-2, C-3, C-4, C-5), 86.25 (C-1), 117.58 (C-4'), 127.58 (C-2'', C-6''), 128.84 (C-3'', C-5''), 134.58 (C-3'), 136.79 (C-4''), 138.87 (C-1''), 176.74, 176.94, 177.45, 177.73 (CO). Signals of the minor diastereomer: $\delta = 21.46$ (CH_3), 68.02, 68.59, 69.14 (C-2, C-3, C-4, C-5), 126.79 (C-2'', C-6''), 129.34 (C-3'', C-5'').

Anal. Calcd for $\text{C}_{37}\text{H}_{57}\text{NO}_9$: C, 67.38; H, 8.65; N, 2.12. Found: C, 67.10; H, 8.77; N, 2.07.

N-(2,3,4,6-Tetra-O-pivaloyl- β -D-galactopyranosyl)-1-amino-1-(3-pyridyl)-3-butene (3h). The purification procedure described above was modified as follows: the column for flash chromatography was conditioned with a 10% solution of triethylamine in petroleum ether. Mixtures of petroleum ether/ethyl acetate [first 4:1 (v/v), then 2:1 (v/v)] were used as eluent.

Yield: 90 mg (28%), colorless, amorphous solid; $[\alpha]_D^{25} = +2.2^\circ$ ($c = 1.03$; CHCl_3).

^1H NMR (400 MHz) (CDCl_3): $\delta = 1.04$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.15 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.15 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.22 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.21 (d, $J_{1,\text{NH}} = 12.5$ Hz, 1 H, NH), 2.33 (m, 2 H, 2-H), 3.65 (ddd, $J_{5,6a} = 7.0$ Hz, $J_{5,6b} = 6.8$ Hz, $J_{4,5} = 0.6$ Hz, 1 H, 5-H), 3.73 (d, $J_{1,\text{NH}} = 12.5$ Hz, $J_{1,2} = 8.8$ Hz, 1 H, 1-H), 3.94 (dd, $J_{6a,6b} = 11.3$ Hz, $J_{5,6a} = 6.8$ Hz, 1 H, 6a-H), 4.05 (dd, $J_{6a,6b} = 11.3$ Hz, $J_{5,6b} = 7.0$ Hz, 1 H, 6b-H), 4.15 (dd, $J_{1,2a'} = 5.6$ Hz, $J_{1,2b'} = 5.6$ Hz, 1 H, 1'-H), 5.00 (m, 4 H, 2-H, 3-H, 4'-H), 5.30 (dd, $J_{3,4} = 3.0$ Hz, $J_{4,5} = 0.7$ Hz, 1 H, 4-H), 5.58 (m, 1 H, 3'-H), 7.22 (dd, $J_{4',5'} = 7.8$ Hz, $J_{6',6''} = 4.8$ Hz, 1 H, 5'-H), 7.55 (m, 1 H, 4''-H), 8.44 (m, 1 H, 6''-H), 8.48 (d, $J_{2',2''} = 3.7$ Hz, 1 H, 2''-H).

^{13}C NMR (100.6 MHz) (CDCl_3): $\delta = 26.97$, 27.00, 27.10, 27.14 [$\text{C}(\text{CH}_3)_3$], 38.59, 38.70, 38.94 [$\text{C}(\text{CH}_3)_3$], 42.58 (C-2'), 54.30 (C-1'), 61.59 (C-6), 67.28, 68.66, 71.21, 71.67 (C-2, C-3, C-4, C-5), 86.23 (C-1), 118.52 (C-4'), 123.20 (C-5''), 133.47 (C-3'), 135.03 (C-4''), 137.42 (C-3''), 148.85 (C-6''), 149.48 (C-2''), 176.68, 176.91, 177.45, 177.69 (CO). Signals of the minor diastereomer: $\delta = 61.17$ (C-6), 67.08 (C-2, C-3, C-4, C-5), 85.38 (C-1).

Anal. Calcd for $\text{C}_{38}\text{H}_{55}\text{N}_2\text{O}_9$: C, 65.02; H, 8.36; N, 4.33. Found: C, 64.66; H, 8.57; N, 3.72.

N-(2,3,4,6-Tetra-O-pivaloyl- β -D-galactopyranosyl)-1-amino-1-(2-naphthyl)-3-butene (3i): yield, 170 mg (49%), colorless, amorphous solid; $[\alpha]_D^{25} = +7.3^\circ$ ($c = 1.00$; CHCl_3).

^1H NMR (400 MHz) (CDCl_3): $\delta = 1.08$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.20 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.25 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.27 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.29 (s, 1 H, NH), 2.40 (m, 1 H, 2a'-H), 2.45 (m, 1 H, 2b'-H), 3.64 (dd, $J_{5,6a} = 6.8$ Hz, $J_{5,6b} = 6.8$ Hz, 1 H, 5-H), 3.86 (m, br, 1 H, 1-H), 3.98 (dd, $J_{6a,6b} = 11.1$ Hz, $J_{5,6a} = 6.5$ Hz, 1 H, 6a-H), 4.12 (dd, $J_{6a,6b} = 11.1$ Hz, $J_{5,6b} = 7.1$ Hz, 1 H, 6b-H), 4.33 (dd, $J_{1,2a'} = 6.8$ Hz, $J_{1,2b'} = 6.8$ Hz, 1 H, 1'-H), 4.96 (dd, $J_{2,3} = 10.3$ Hz, $J_{3,4} = 2.8$ Hz, 1 H, 3-H), 5.07 (m, 3 H, 2-H, 4'-H), 5.31 (d, $J_{3,4} = 2.8$ Hz, 1 H, 4-H), 5.65 (m, 1 H, 3'-H), 7.45 (m, 3 H, 3''-H, 6''-H, 7''-H), 7.70 (s, 1 H, 1''-H), 7.79 (m, 3 H, 4''-H, 5''-H, 8''-H).

^{13}C NMR (100.6 MHz) (CDCl_3): $\delta = 27.00$, 27.09, 27.15, 27.28 [$\text{C}(\text{CH}_3)_3$], 38.59, 38.63, 38.75, 38.96 [$\text{C}(\text{CH}_3)_3$], 42.88 (C-2'), 56.68 (C-1'), 61.76 (C-6), 67.46, 68.79, 71.33, 71.57 (C-2, C-3, C-4, C-5), 86.28 (C-1), 117.87 (C-4'), 125.53, 125.62, 125.96, 126.58, 127.54, 127.62, 127.98 (C-1'', C-3'', C-4'', C-5'', C-6'', C-7'', C-8''), 133.00 (C-9''), 133.24 (C-10''), 134.34 (C-3'), 139.52 (C-2''), 176.75, 176.89, 177.50, 177.71 (CO). Signals of the minor diastereomers: $\delta = 41.82$ (C-2'), 58.25 (C-1'), 61.38 (C-6), 67.36, 68.16, 68.29 (C-2, C-3, C-4, C-5), 85.25 (C-1), 125.09 (naphthyl), 134.59 (C-3').

Anal. Calcd for $\text{C}_{40}\text{H}_{57}\text{NO}_9$: C, 69.07; H, 8.20; N, 2.01. Found: C, 69.33; H, 8.26; N, 2.05.

N-(2,3,4,6-Tetra-O-pivaloyl- β -D-galactopyranosyl)-1-amino-1-(2-methoxyphenyl)-3-butene (3k): yield, 250 mg (37%), colorless, amorphous solid; $[\alpha]_D^{25} = +4.2^\circ$ ($c = 1.04$; CHCl_3).

^1H NMR (400 MHz) (CDCl_3): $\delta = 1.06$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.14 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.16 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.24 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.13 (s, br, 1 H, NH), 2.21 (m, 1 H, 2a'-H), 2.42 (m, 1 H, 2b'-H), 3.73 (m, 1 H, 1-H), 3.76 (s, 3 H, OCH_3), 3.91 (m, 2 H, 5-H, 6a-H), 4.11 (dd, $J_{6a,6b} = 11.0$ Hz, $J_{5,6a} = 7.0$ Hz, 1 H, 6b-H), 4.59 (dd, $J_{1,2a'}$

$= 5.7$ Hz, $J_{1,2b'}$ = 5.7 Hz, 1 H, 1'-H), 5.03 (m, 4 H, 2-H, 3-H, 4'-H), 5.31 (d, $J_{3,4} = 2.5$ Hz, 1 H, 4-H), 5.64 (m, 1 H, 3'-H), 6.80 (m, 1 H, 3''-H), 6.86 (m, 1 H, 5''-H), 7.17 (m, 1 H, 4''-H), 7.37 (m, 1 H, 6''-H).

^{13}C NMR (100.6 MHz) (CDCl_3): $\delta = 27.02$, 27.05, 27.16, 27.21 [$\text{C}(\text{CH}_3)_3$], 38.64, 38.74, 39.00 [$\text{C}(\text{CH}_3)_3$], 41.35 (C-2'), 49.53 (C-1'), 55.30 (OCH_3), 61.53 (C-6), 67.43, 69.01, 71.39, 71.62 (C-2, C-3, C-4, C-5), 87.28 (C-1), 110.31 (C-3''), 117.23 (C-4'), 120.14 (C-5''), 127.59 (C-4''), 127.66 (C-6''), 130.88 (C-1''), 135.07 (C-3'), 157.24 (C-2''), 176.83, 177.09, 177.47, 177.81 (CO). Signals of the minor diastereomer: $\delta = 39.68$ (C-2'), 54.49 (C-1'), 55.19 (OCH_3), 60.79 (C-6), 67.70, 68.54, 68.29, 68.45 (C-2, C-3, C-4, C-5), 84.21 (C-1), 110.76 (C-3''), 117.44 (C-4'), 120.40 (C-5''), 128.13 (C-4''), 127.80 (C-6''), 135.39 (C-3').

Anal. Calcd for $\text{C}_{37}\text{H}_{57}\text{NO}_{10}$: C, 65.78; H, 8.44; N, 2.07. Found: C, 65.85; H, 8.38; N, 2.09.

N-(2,3,4,6-Tetra-O-pivaloyl- β -D-galactopyranosyl)-3-amino-1-phenyl-1,5-hexadiene (3l): yield, 235 mg (70%), colorless, amorphous solid; $[\alpha]_D^{25} = -3.6^\circ$ ($c = 1.03$; CHCl_3).

^1H NMR (400 MHz) (CDCl_3): $\delta = 1.07$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.16 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.17 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.23 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.18–2.30 (m, 3 H, 4'-H, NH), 3.67 (dd, $J_{2,3} = 8.3$ Hz, $J_{3,4} = 6.3$ Hz, 1 H, 3'-H), 3.76 (s, 3 H, OCH_3), 3.82 (dd, $J_{5,6a} = 6.3$ Hz, $J_{5,6b} = 6.3$ Hz, 1 H, 5-H), 3.97 (dd, $J_{6a,6b} = 11.2$ Hz, $J_{5,6a} = 6.3$ Hz, 1 H, 6a-H), 4.11 (dd, $J_{6a,6b} = 11.2$ Hz, $J_{5,6a} = 6.3$ Hz, 1 H, 6b-H), 4.13 (d, $J_{1,2} = 8.8$ Hz, 1 H, 1-H), 4.96 (dd, $J_{2,3} = 10.0$ Hz, $J_{1,2} = 8.8$ Hz, 1 H, 2-H), 5.04 (m, 2 H, 6'-H), 5.08 (dd, $J_{2,3} = 11.3$ Hz, $J_{3,4} = 3.8$ Hz, 1 H, 3-H), 5.35 (d, $J_{3,4} = 3.8$ Hz, 1 H, 4-H), 5.71 (m, 1 H, 5'-H), 5.83 (dd, $J_{1,2} = 15.9$ Hz, $J_{2,3} = 8.3$ Hz, 1 H, 2'-H), 6.43 (d, $J_{1,2} = 15.9$ Hz, 1 H, 1'-H), 7.28–7.33 (m, 5 H, Ph).

^{13}C NMR (100.6 MHz) (CDCl_3): $\delta = 27.04$, 27.10, 27.14, 27.16 [$\text{C}(\text{CH}_3)_3$], 38.69 [$\text{C}(\text{CH}_3)_3$], 40.93 (C-4'), 55.43 (C-3'), 61.74 (C-6), 67.49, 68.73, 71.38, 71.67 (C-2, C-3, C-4, C-5), 86.90 (C-1), 117.81 (C-6'), 126.22 (C-2'', C-6''), 127.53 (C-4''), 128.56 (C-3'', C-5''), 131.34 (C-1'), 131.79 (C-2'), 134.19 (C-5'), 176.85, 176.90, 177.03, 177.81 (CO).

Anal. Calcd for $\text{C}_{38}\text{H}_{57}\text{NO}_9$: C, 67.96; H, 8.49; N, 2.09. Found: C, 67.94; H, 8.65; N, 1.81.

N-(2,3,4,6-Tetra-O-pivaloyl- β -D-galactopyranosyl)-1-amino-1-(4-cyanophenyl)-3-butene (3m): yield, 165 mg (49%), colorless, amorphous solid; $[\alpha]_D^{25} = -0.5^\circ$ ($c = 1.01$; CHCl_3).

^1H NMR (400 MHz) (CDCl_3): $\delta = 1.07$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.16 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.17 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.24 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.25 (s, br, 1 H, NH), 2.30 (m, 1 H, 2a'-H), 2.33 (m, 1 H, 2b'-H), 3.66 (dd, $J_{5,6a} = 7.5$ Hz, $J_{5,6b} = 6.7$ Hz, 1 H, 5-H), 3.73 (dd, $J_{1,\text{NH}} = 26.5$ Hz, $J_{1,2} = 22.2$ Hz, 1 H, 1-H), 3.92 (dd, $J_{6a,6b} = 11.1$ Hz, $J_{5,6a} = 6.7$ Hz, 1 H, 6a-H), 4.09 (dd, $J_{6a,6b} = 11.1$ Hz, $J_{5,6b} = 6.9$ Hz, 1 H, 6b-H), 4.18 (dd, $J_{1,2a'} = 6.7$ Hz, $J_{1,2b'} = 6.7$ Hz, 1 H, 1'-H), 5.02 (m, 4 H, 2-H, 3-H, 4'-H), 5.32 (dd, $J_{3,4} = 3.0$ Hz, $J_{4,5} = 0.9$ Hz, 1 H, 4-H), 5.58 (m, 1 H, 3'-H), 7.36 (d, $J_{ortho} = 8.3$ Hz, 2 H, 2''-H, 6''-H), 7.58 (d, $J_{ortho} = 8.3$ Hz, 2 H, 3''-H, 5''-H).

^{13}C NMR (100.6 MHz) (CDCl_3): $\delta = 27.08$, 27.10, 27.20, 27.27 [$\text{C}(\text{CH}_3)_3$], 38.70, 38.82, 39.05 [$\text{C}(\text{CH}_3)_3$], 42.74 (C-2'), 56.42 (C-1'), 61.62 (C-6), 67.29, 68.80, 71.26, 71.75 (C-2, C-3, C-4, C-5), 86.43 (C-1), 111.33 (C-4''), 118.71 (C-4'), 118.77 (CN), 128.37 (C-2'', C-6''), 132.15 (C-3'', C-5''), 133.36 (C-3'), 148.07 (C-1''), 176.80, 177.07, 177.54, 177.84 (CO).

Anal. Calcd for $\text{C}_{37}\text{H}_{54}\text{N}_2\text{O}_9$: C, 66.27; H, 8.06; N, 4.18. Found: C, 65.83; H, 8.10; N, 3.78.

N-(2,3,4,6-Tetra-O-pivaloyl- β -D-galactopyranosyl)-1-amino-1-(4-carbomethoxyphenyl)-3-butene (3n): yield, 155 mg (44%), colorless, amorphous solid; $[\alpha]_D^{25} = +0.9^\circ$ ($c = 1.00$; CHCl_3).

^1H NMR (400 MHz) (CDCl_3): $\delta = 1.05$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.15 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.17 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 1.23 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.22 (d, br, $J_{1,\text{NH}} = 9.3$ Hz, 1 H, NH), 2.30 (m, 1 H, 2a'-H), 2.34 (m, 1 H, 2b'-H), 3.63 (dd, $J_{5,6a} = 6.8$ Hz, $J_{5,6b} = 6.9$ Hz, 1 H, 5-H), 3.74 (m, br, 1 H, 1-H), 3.88 (s, 3 H, COOCH_3), 3.92 (dd, $J_{6a,6b} = 11.2$ Hz, $J_{5,6a} = 6.6$ Hz, 1 H, 6a-H), 4.06 (dd, $J_{6a,6b} = 11.2$ Hz, $J_{5,6b} = 7.0$ Hz, 1 H, 6b-H), 4.19 (dd, $J_{1,2a'} = 6.8$ Hz, $J_{1,2b'} = 6.8$ Hz, 1 H, 1'-H), 4.95 (dd, $J_{2,3} = 10.4$ Hz, $J_{3,4} = 3.2$ Hz, 1 H, 3-H), 5.00 (m, 3 H, 2-H, 4'-H), 5.29 (dd, $J_{3,4} = 3.2$ Hz, 1 H, 4-H), 5.57 (m, 1 H, 3'-H), 7.31 (d, $J_{ortho} = 8.2$ Hz, 2 H, 2''-H, 6''-H), 7.94 (d, $J_{ortho} = 8.2$ Hz, 2 H, 3''-H, 5''-H).

¹³C NMR (100.6 MHz) (CDCl₃): δ = 27.05, 27.09, 27.18, 27.26 [C(CH₃)₃], 38.67, 38.80, 39.02 [C(CH₃)₃], 42.80 (C-2'), 52.01 (CO-OCH₃), 56.41 (C-1'), 61.73 (C-6), 67.39, 68.77, 71.31, 71.67 (C-2, C-3, C-4, C-5), 86.40 (C-1), 118.32 (C-4'), 127.67 (C-2'', C-6''), 129.37 (C-4''), 129.60 (C-3'', C-5''), 133.85 (C-3'), 147.64 (C-1''), 166.96 (COOCH₃), 176.82, 177.02, 177.57, 177.83 (CO). Signals of the minor diastereomer: δ = 68.10 (C-2, C-3, C-4, C-5), 126.99 (C-2'', C-6''), 129.30 (C-3'', C-5'').

Anal. Calcd for C₃₃H₅₇NO₁₁: C, 64.86; H, 8.11; N, 1.99. Found: C, 64.71; H, 7.95; N, 1.87.

N-(2,3,4,6-Tetra-O-pivaloyl-β-D-galactopyranosyl)-1-amino-1-(4-fluorophenyl)-3-butene (3o): yield, 180 mg (54%), colorless crystals; mp 97° C; [α]²²_D = -0.1° (c = 1.01; CHCl₃).

¹H NMR (400 MHz) (CDCl₃): δ = 1.06 [s, 9 H, C(CH₃)₃], 1.17 [s, 9 H, C(CH₃)₃], 1.18 [s, 9 H, C(CH₃)₃], 1.24 [s, 9 H, C(CH₃)₃], 2.19 (s, br, 1 H, NH), 2.28 (m, 2 H, 2'-H), 3.63 (ddd, J_{5,6a} = 6.7 Hz, J_{5,6b} = 6.6 Hz, J_{4,5} = 1.0 Hz, 1 H, 5-H), 3.72 (m, br, 1 H, 1-H), 3.92 (dd, J_{6a,6b} = 11.2 Hz, J_{5,6a} = 6.7 Hz, 1 H, 6a-H), 4.08 (m, 2 H, 1'-H, 6b-H), 5.01 (m, 4 H, 2-H, 3-H, 4'-H), 5.29 (dd, J_{3,4} = 3.1 Hz, J_{4,5} = 1.0 Hz, 1 H, 4-H), 5.56 (m, 1 H, 3'-H), 6.94 (dd, J_{ortho} = 8.7 Hz, J_{3',F} = 8.7 Hz, 2 H, 3'-H, 5'-H), 7.18 (dd, J_{ortho} = 8.7 Hz, J_{2',F} = 5.5 Hz, 2 H, 2'-H, 6'-H).

¹³C NMR (100.6 MHz) (CDCl₃): δ = 27.04, 27.07, 27.16, 27.21 [C(CH₃)₃], 38.65, 38.74, 39.00 [C(CH₃)₃], 43.01 (C-2'), 55.89 (C-1'), 61.71 (C-6), 67.40, 68.73, 71.32, 71.59 (C-2, C-3, C-4, C-5), 86.21 (C-1), 115.06 (d, ²J_{F,C} = 21.3 Hz, C-3'', C-5''), 118.02 (C-4'), 129.12 (d, ³J_{F,C} = 7.8 Hz, C-2'', C-6''), 134.17 (C-3'), 137.67 (d, ⁴J_{F,C} = 2.4 Hz, C-1''), 162.04 (d, ¹J_{F,C} = 245.2 Hz, C-4''), 176.80, 177.02, 177.50, 177.80 (CO). Signals of the minor diastereomer: δ = 42.00 (C-2'), 60.89 (C-6), 67.23, 68.21, 69.02, 73.06 (C-2, C-3, C-4, C-5), 85.24 (C-1), 118.84 (C-4'), 134.36 (C-3').

Anal. Calcd for C₃₆H₅₄N₂O₉F: C, 65.16; H, 8.14; N, 2.11. Found: C, 65.07; H, 8.16; N, 2.07.

The diastereomeric ratios of the aliphatic homoallylamines **3p,q** were determined by integration of the signals in the spin-echo 100.6-MHz ¹³C NMR spectra. It was demonstrated that integration of the spin-echo and the inverse gated decoupled ¹³C NMR spectrum resulted in the same diastereomeric ratios.

N-(2,3,4,6-Tetra-O-pivaloyl-β-D-galactopyranosyl)-4-amino-1-heptene (3p): yield, 100 mg (32%), colorless oil; [α]²²_D = +26.5° (c = 1.03; CHCl₃).

¹H NMR (400 MHz) (CDCl₃): δ = 0.83 (m, 3 H, 7'-H), 1.07 [s, 9 H, C(CH₃)₃], 1.11 [s, 9 H, C(CH₃)₃], 1.13 [s, 9 H, C(CH₃)₃], 1.21 [s, 9 H, C(CH₃)₃], 1.22 (m, 2 H, 6'-H), 1.24 (m, 2 H, 5'-H), 1.65 (s, br, 1 H, NH), 2.09 (m, 2 H, 3'-H), 2.85 (m, 1 H, 4'-H), 3.85 (dd, J_{5,6a} = 6.8 Hz, J_{5,6b} = 6.8 Hz, 1 H, 5-H), 3.91-3.96 (m, 1 H, 6a-H), 4.04-4.15 (m, 2 H, 6b-H, 1-H), 4.94-5.03 (m, 3 H, 2-H, 4'-H), 5.11 (dd, J_{2,3} = 10.3 Hz, J_{3,4} = 3.0 Hz, 1 H, 3-H), 5.35 (d, J_{3,4} = 3.0 Hz, 1 H, 4-H), 5.68 (m, 1 H, 6'-H).

¹³C NMR (100.6 MHz) (CDCl₃), signals of the major β-diastereomer: δ = 14.17 (C-7'), 18.67 (C-6'), 27.17 [C(CH₃)₃], 36.51 (C-5'), 38.70 [C(CH₃)₃], 40.05 (C-3'), 53.46 (C-4'), 61.83 (C-6), 67.47, 69.06, 71.47, 71.60 (C-2, C-3, C-4, C-5), 88.68 (C-1), 117.24 (C-1'), 135.21 (C-2'), 176.90, 177.19, 177.50, 177.88 (CO). Signals of the minor β-diastereomer: δ = 14.05 (C-7'), 18.67 (C-6'), 37.04 (C-5'), 38.68 [C(CH₃)₃], 39.01 (C-3'), 53.04 (C-4'), 61.75 (C-6), 87.92 (C-1), 116.57 (C-1'), 135.71 (C-2'), 176.90, 177.50, 177.89 (CO). Signals of the major α-diastereomer: δ = 14.10 (C-7'), 19.21 (C-6'), 37.04 (C-5'), 37.10 [C(CH₃)₃], 39.03 (C-3'), 53.27 (C-4'), 61.97 (C-6), 82.57 (C-1), 117.80 (C-1'), 134.78 (C-2'), 176.95, 177.37, 177.56 (CO). Signals of the minor α-diastereomer: δ = 14.05 (C-7'), 18.81 (C-6'), 36.01 (C-5'), 37.76 [C(CH₃)₃], 39.57 (C-3'), 54.01 (C-4'), 62.01 (C-6), 83.36 (C-1), 117.11 (C-1'), 135.54 (C-2'), 176.95, 177.37, 177.56 (CO).

Anal. Calcd for C₃₃H₅₇NO₉: C, 64.81; H, 9.33; N, 2.29. Found: C, 64.77; H, 9.24; N, 2.18.

N-(2,3,4,6-Tetra-O-pivaloyl-β-D-galactopyranosyl)-4-amino-1-tridecene (3q): yield, 130 mg (37%), colorless oil; [α]²²_D = +19.2° (c = 1.00; CHCl₃).

¹H NMR (400 MHz) (CDCl₃): δ = 0.82 (t, J_{12',13'} = 6.5 Hz, 3 H, 13'-H), 1.05 [s, 9 H, C(CH₃)₃], 1.10 [s, 9 H, C(CH₃)₃], 1.11 [s, 9 H, C(CH₃)₃], 1.20 [s, 9 H, C(CH₃)₃], 1.02-1.24 (s, 16 H, 5'-H...12'-H), 1.70 (s, br, 1 H, NH), 2.10 (m, 1 H, 3a'-H), 2.16 (m, 1 H, 3b'-H), 2.80 (m, 1 H, 4'-H), 3.83 (dd, J_{5,6b} = 7.1 Hz, J_{5,6a} = 6.7 Hz, 1 H, 5-H), 3.92 (dd, J_{6a,6b} = 11.1 Hz, J_{5,6a} = 6.7 Hz, 1 H, 6a-H), 4.05 (dd, J_{6a,6b} = 11.1 Hz, J_{5,6b} = 7.1 Hz, 1 H, 6b-H, 1-H), 4.09 (d, J_{1,2} = 8.8 Hz, 1 H, 1-H), 4.95 (m, 3 H, 2-H, 1'-H), 5.10

(dd, J_{2,3} = 10.3 Hz, J_{3,4} = 3.4 Hz, 1 H, 3-H), 5.34 (d, J_{3,4} = 3.1 Hz, 1 H, 4-H), 5.66 (m, 1 H, 2'-H).

¹³C NMR (100.6 MHz) (CDCl₃), signals of the major β-diastereomer: δ = 13.99 (C-13'), 22.57 (C-12'), 25.46 (C-11'), 27.03, 27.11, 27.13 [C(CH₃)₃], 29.23 (C-10'), 29.53 (C-9'), 29.58 (C-8'), 29.86 (C-7'), 31.80 (C-6'), 34.17 (C-5'), 37.73, 38.65 [C(CH₃)₃], 39.95 (C-3'), 53.57 (C-4'), 61.77 (C-6), 67.43, 69.02, 71.43, 71.58 (C-2, C-3, C-4, C-5), 88.57 (C-1), 117.20 (C-1'), 135.17 (C-2'), 176.84, 177.13, 177.44, 177.81 (CO). Signals of the minor β-diastereomer: δ = 25.60 (C-11'), 29.48 (C-10'), 29.61 (C-8'), 29.80 (C-7'), 34.81 (C-5'), 53.24 (C-4'), 61.68 (C-6), 65.38, 68.10, 68.18, 68.27 (C-2, C-3, C-4, C-5), 87.88 (C-1), 116.52 (C-1'), 135.17 (C-2'). Signals of the major α-diastereomer: δ = 25.60 (C-11'), 34.87 (C-5'), 53.51 (C-4'), 82.61 (C-1), 117.74 (C-1'), 134.76 (C-2'). Signals of the minor α-diastereomer: δ = 25.46 (C-11'), 33.64 (C-5'), 53.51 (C-4'), 83.30 (C-1), 117.05 (C-1'), 135.51 (C-2').

Anal. Calcd for C₃₃H₅₇NO₉: C, 67.34; H, 9.93; N, 2.01. Found: C, 67.75; H, 10.57; N, 1.89.

1-Phenyl-3-butenylamine Hydrochloride (8). To a solution of *N*-galactosyl-*N*-homoallylamine **3d** (2.83 g, 4.39 mmol) in methanol (44 mL) was added 1 N HCl (6.59 mL, 6.59 mmol). The precipitate formed was dissolved by the addition of CH₂Cl₂ (5 mL). After being stirred for 1 day at room temperature, the reaction mixture was evaporated in vacuo. The residue was dissolved in 0.5 N HCl (100 mL) and extracted three times with *n*-pentane (100 mL). Concentration of the aqueous solution yielded 805 mg (quantitative) of the hydrochloride **8** as a pale brown solid (mp >210° C dec). After the pentane solution was dried with MgSO₄ and the solvent was evaporated, the *O*-pivaloylated galactopyranose **7** was isolated as colorless crystals: 2.27 g (quantitative); [α]²²_D = -11.4° (c = 1.01; H₂O).

Anal. Calcd for C₁₀H₁₄NCl: C, 63.40; H, 7.63; N, 7.63. Found: C, 63.36; H, 7.44; N, 7.68.

2,3,4,6-Tetra-O-pivaloyl-α/β-D-galactopyranose (7): mp 71° C (MeOH/H₂O); [α]²²_D = +48.5° (c = 1.02; CHCl₃).

Anal. Calcd for C₂₆H₄₄NO₁₀: C, 60.47; H, 8.53. Found: C, 59.91; H, 8.55.

N-(tert-Butyloxycarbonyl)-1-phenyl-3-butenylamine (9a). A solution of hydrochloride **8** (620 mg, 3.38 mmol) was dissolved in *tert*-butyl alcohol (2.5 mL), and 1 N aqueous NaOH (3.7 mL, 3.70 mmol) and di-*tert*-butyl dicarbonate (737 mg, 3.38 mmol) were added during 30 min, the pH being kept at 9. After being stirred for 18 h at room temperature, the mixture was extracted three times with *n*-pentane (50 mL). The pentane solution was washed three times with a saturated NaHCO₃ solution (50 mL), dried with MgSO₄, and concentrated in vacuo to give the crude product, which was used for the further transformations.

Yield: 810 mg (97%), colorless crystals; mp 71° C; [α]²²_D = -48.4° (c = 1.00; CHCl₃).

¹H NMR (200 MHz) (CDCl₃): δ = 1.40 [s, 9 H, C(CH₃)₃], 2.50 (m, br, 2 H, 2-H), 4.72 (s, br, 1 H, 1-H), 4.86 (s, br, 1 H, NH), 5.05 (dddd, J_{3,4} = 10.1 Hz, J_{4a,4b} = 1.4 Hz, J_{2a,4a} = 1.4 Hz, J_{2b,4b} = 1.4 Hz, 1 H, 4a-H), 5.09 (dddd, J_{3,4b} = 17.1 Hz, J_{4a,4b} = 1.4 Hz, J_{2a,4b} = 1.4 Hz, J_{2b,4b} = 1.4 Hz, 1 H, 4b-H), 5.65 (dddd, J_{3,4b} = 17.1 Hz, J_{3,4a} = 10.1 Hz, J_{2a,3} = 7.1 Hz, J_{2b,3} = 7.1 Hz, 1 H, 3-H), 7.24 (m, 5 H, Ph).

¹³C NMR (50.3 MHz) (CDCl₃): δ = 28.33 [C(CH₃)₃], 54.61 (C-1), 41.21 (C-2), 78.06 [C(CH₃)₃], 118.12 (C-3), 126.22 (C-p), 127.10 (C-o), 128.46 (C-m), 133.98 (C-4), 143.94 (C-i), 155.12 (CO).

Anal. Calcd for C₁₅H₂₁NO₂: C, 72.87; H, 8.50; N, 5.67. Found: C, 72.82; H, 8.37; N, 6.29.

N-(4-Nitrobenzyloxycarbonyl)-1-phenyl-3-butenylamine (9b). To an ice-cooled solution of hydrochloride **8** (430 mg, 2.34 mmol) in 1 N aqueous NaOH (2.34 mL, 2.34 mmol) and water (10 mL) was added 4-nitrobenzyl chloroformate (504 mg, 2.34 mmol). The mixture was stirred for 3 h at 0° C and extracted four times with CH₂Cl₂ (50 mL). After washing of the organic phase with a saturated NaHCO₃ solution (100 mL), drying with MgSO₄, and evaporation of the solvent, the resulting oil was purified by flash chromatography using petroleum ether/ethyl acetate [5:1 (v/v)] as the eluent.

Yield: 440 mg (58%), colorless crystals; mp 81-82° C; [α]²²_D = -27.6° (c = 1.00; CHCl₃).

¹H NMR (200 MHz) (CDCl₃): δ = 2.55 (dd, J_{1,2} = 6.3 Hz, J_{2,3} = 6.3 Hz, 2 H, 2-H), 4.79 (m, 1 H, 1-H), 5.16 (m, 5 H, 4-H, CH₂, NH), 5.68 (m, 1 H, 3-H), 7.29 (m, 5 H, Ph), 7.47 (d, J_{ortho} = 8.0

Hz, 2 H, 2''-H, 6''-H), 8.18 (d, $J_{ortho} = 8.0$ Hz, 2 H, 3''-H, 5''-H). ^{13}C NMR (50.3 MHz) (CDCl_3): $\delta = 41.02$ (C-2), 54.89 (C-1), 65.21 (CH_2), 118.48 (C-4), 123.62, 126.18, 127.47, 128.00, 128.63 (Ph, aryl), 133.57 (C-3), 143.92 (C-4''), 155.15 (CO).

Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_4$: C, 66.26; H, 5.52; N, 8.59. Found: C, 66.26; H, 5.46; N, 8.49.

General Procedure for the Oxidation of N-Protected Homoallylamines 9. **Method A.** To a solution of KMnO_4 (167 mg, 1.05 mmol) and NaIO_4 (8.93 g, 47.8 mmol) in water (220 mL) was added N-protected homoallylamine 9 (6.96 mmol), and the suspension was stirred at room temperature (see Table III). During the reaction, the color of the mixture turned from violet to red. After the conversion was completed, the reaction mixture was extracted six times with ether (100 mL). The combined organic solutions were dried with MgSO_4 and evaporated in vacuo, and the residue was purified by flash chromatography.

Method B. To a suspension of N-protected homoallylamine 9 (0.57 mmol) in CCl_4 (1.14 mL), acetonitrile (1.14 mL), and water (1.71 mL) were added NaIO_4 (501 mg, 2.34 mmol) and $\text{RuCl}_3(\text{H}_2\text{O})$ (4 mg, 0.0125 mmol) sequentially. After being stirred for 2.5–3.5 h at room temperature (see Table III), the mixture was diluted with CH_2Cl_2 (20 mL) and the aqueous layer was extracted four times with CH_2Cl_2 (20 mL). The combined organic solutions were dried and evaporated to yield the crude product, which was purified by flash chromatography.

N-(tert-Butyloxycarbonyl)- β -phenyl- β -alanine (10a). Method A delivered the analytically pure product: yield, 85%, colorless needles; mp 108–111 °C; $[\alpha]^{22}_D = -45.6^\circ$ ($c = 1.00$; MeOH).

The crude product from method B was purified by flash chromatography [eluent: (1) petroleum ether/ethyl acetate, 5:1 (v/v); (2) petroleum ether/ethyl acetate/acetic acid, 78:17:5 (v/v/v)], which yielded the aldehyde 11 as the first fraction and the carboxylic acid 10 as the second fraction: yield, 27%, pale green crystals; mp 113–116 °C; $[\alpha]^{22}_D = -45.6^\circ$ ($c = 1.00$; MeOH).

IR (KBr): $\nu = 3370$ cm $^{-1}$ (s, NH), 3500–2500 (br, OH), 3030, 3005 (m, CH aromatic), 2980 (s, CH), 1705 (s, C=O), 1680 (vs, C=O, amide), 1510 (s, C=C), 765 (s), 705 [vs, $\delta(\text{CH aromatic})$].

^1H NMR (200 MHz) ($\text{DMSO}-d_6$): $\delta = 1.35$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.62 (m, 2 H, 2-H), 4.88 (m, 1 H, 3-H), 7.30 (m, 5 H, Ph), 7.47 (d, $J_{3,NH} = 8.6$ Hz, NH), 12.26 (s, br, COOH).

^{13}C NMR (50.3 MHz) ($\text{DMSO}-d_6$): $\delta = 28.12$ [$\text{C}(\text{CH}_3)_3$], 41.22 (C-2), 51.20 (C-3), 77.75 [$\text{C}(\text{CH}_3)_3$], 126.25 (C-o), 126.72 (C-p), 18.06 (C-m), 143.12 (C-i), 154.63 (CO, Boc), 171.68 (COOH).

Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_4$: C, 63.40; H, 7.17; N, 5.28. Found: C, 63.38; H, 6.90; N, 5.28.

N-(tert-Butyloxycarbonyl)-3-amino-3-phenylpropanal (11a): yield, 29%, colorless crystals; mp 89–91 °C; $[\alpha]^{22}_D = -27.3^\circ$ ($c = 1.01$; CHCl_3).

IR (KBr): $\nu = 3370$ cm $^{-1}$ (s, NH), 3040 (w, CH aromatic), 2980, 2930 (m, CH), 2820, 2730 (w, CH, aldehyde), 1722 (s, C=O), 1680 (s, C=O, amide), 1510 (s, C=C), 765 (s), 705 [vs, $\delta(\text{CH aromatic})$].

^1H NMR (200 MHz) (CDCl_3): $\delta = 1.40$ [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.93 (m, 2 H, 2-H), 5.18 (m, 2 H, 3-H, NH), 7.30 (m, 5 H, Ph), 9.73 (dd, $J_{1,2a} = 1.8$ Hz, $J_{1,2b} = 1.8$ Hz, 1 H, CHO).

^{13}C NMR (50.3 MHz) (CDCl_3): $\delta = 28.29$ [$\text{C}(\text{CH}_3)_3$], 49.87 (C-2), 50.39 (C-3), 80.07 [$\text{C}(\text{CH}_3)_3$], 126.26 (C-o), 127.67 (C-p), 128.53 (C-i), 128.78 (C-m), 155.19 (CO, Boc), 199.91 (CHO).

Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: C, 67.47; H, 7.63; N, 5.62. Found: C, 67.26; H, 7.39; N, 5.62.

N-(4-Nitrobenzyloxycarbonyl)- β -phenyl- β -alanine (10b). The crude product was purified by flash chromatography [eluent:

(1) $\text{CHCl}_3/\text{MeOH}$, 5:1; (2) MeOH].

Method A: yield, 71%, colorless crystals; mp 186 °C dec; $[\alpha]^{22}_D = -4.9^\circ$ ($c = 1.00$; MeOH).

Method B: yield, 87%, colorless crystals; mp >186 °C dec; $[\alpha]^{22}_D = -5.0^\circ$ ($c = 1.00$; MeOH).

IR (KBr): $\nu = 3400$ (s, NH), 3600–2800 (br, OH), 3060 (m, CH aromatic), 2960, 2930 (m, CH), 1705 (vs, C=O), 1685 (vs, C=O, amide), 1345 (s, NO), 745 (m), 705 [s, $\delta(\text{CH aromatic})$].

^1H NMR (200 MHz) ($\text{DMSO}-d_6$): $\delta = 2.50$ (m, 1 H, 3-H), 3.85 (m, 2 H, 2-H), 5.05 (m, 3 H, CH_2 , NH), 7.25 (m, 5 H, Ph), 7.52 (d, $J_{ortho} = 8.0$ Hz, 2 H, 2''-H, 6''-H), 8.15 (d, $J_{ortho} = 8.0$ Hz, 2 H, 3''-H, 5''-H).

^{13}C NMR (50.3 MHz) ($\text{DMSO}-d_6$): $\delta = 44.09$ (C-2), 52.55 (C-3), 63.94 (CH_2), 123.29, 126.27, 127.64 (C-2, C-2'', C-3', C-3'', C-4', C-5', C-5'', C-6', C-6''), 144.37, 145.11, 146.61 (C-1', C-1'', C-4''), 154.95 (CO), 176.25 (COOH).

(S)-(-)- β -Phenyl- β -alanine Hydrochloride (12a). To a solution of Boc- β -phenyl- β -alanine (10a) (1.58 g, 5.96 mmol) in dry ether (30 mL) was added HCl in ether (20 mL). After the mixture was stirred for 18 h at room temperature, the yellow precipitate was collected, washed with dry ether (50 mL), and dried in vacuo.

Yield: 890 mg (74%); mp 195–200 °C dec; $[\alpha]^{22}_D = +1.5^\circ$ ($c = 1.00$; MeOH).

Anal. Calcd for $\text{C}_9\text{H}_{12}\text{NO}_2\text{Cl}$: C, 53.60; H, 5.96; N, 6.95. Found: C, 53.60; H, 6.02; N, 6.97.

(S)- β -Phenyl- β -alanine (12). The hydrochloride 12a (800 mg, 3.97 mmol) was dissolved in water (10 mL) and filtered through a column (15 \times 1.5 cm) with strong acidic ion-exchange resin using first water (200 mL) and then 1 N ammonia (100 mL) as eluent. Evaporation of the ammonia delivered the free amino acid 12.

Yield: 660 mg (quantitative), colorless solid; mp 226–228 °C; $[\alpha]^{22}_D = -6.3^\circ$ ($c = 0.80$; H_2O).

Anal. Calcd for $\text{C}_9\text{H}_{11}\text{NO}_2$: C, 65.46; H, 6.67; N, 8.48. Found: C, 65.42; H, 6.50; N, 8.33.

4-Aminoheptene Hydrochloride (15). 15 was synthesized according to the procedure described for 8. The crude product was used without further purification and characterization: yield, quantitative brown oil.

N-[(R)-Methoxy(trifluoromethyl)phenylacetyl]-4-heptenylamine (16). To a suspension of hydrochloride 15 (370 mg, 2.48 mmol) in dry CHCl_3 (32 mL) were added dry pyridine (3.2 mL) and, subsequently, (S)-(+)-methoxy(trifluoromethyl)phenylacetyl chloride (642 mg, 2.54 mmol). After stirring for 2 days at room temperature, the brown reaction mixture was washed with 2 N HCl (100 mL) and the aqueous layer was extracted three times with CHCl_3 (50 mL). The combined organic solutions were washed with 2 N HCl (100 mL) and a saturated NaHCO_3 solution (100 mL), dried with MgSO_4 , and evaporated to yield 650 mg of a brown oil.

^1H NMR (200 MHz) (CDCl_3): $\delta = 0.85$ (t, $J_{6,7} = 7.1$ Hz, 3 H, 7-H), 1.23 (m, 2 H, 6-H), 1.42 (m, 2 H, 5-H), 2.23 (m, 2 H, 3-H), 3.40 (d, $^5J_{H,F} = 1.4$ Hz, 3 H, OCH_3), 4.07 (m, 1 H, 4-H), 5.05 (m, 1 H, 1a-H), 5.11 (m, 1 H, 1b-H), 5.74 (m, 1 H, 2-H), 6.50 (d, br, $J_{4,NH} = 8.7$ Hz, 1 H, NH), 7.35–7.53 (m, 5 H, Ph). Signal of the minor diastereomer: $\delta = 3.52$ (d, $^5J_{H,F} = 1.4$ Hz, OCH_3).

^{13}C NMR (50.3 MHz) (CDCl_3): $\delta = 13.68$ (C-7), 19.02 (C-6), 36.29 (C-5), 39.03 (C-3), 48.68 (OCH_3), 54.98 (C-4), 84.98 [q, $^2J_{C,F} = 26.1$ Hz, C(CF_3)], 117.91 (C-1), 123.80 [d, $^1J_{C,F} = 289.8$ Hz, C(CF_3)], 127.61 (C-p), 128.35 (C-m), 129.30 (C-o), 132.99 (C-i), 134.04 (C-2), 165.58 (CO).