β-Branched α-Halo Carboxylic Acid Derivatives via Stereoselective 1,4 Addition of Dialkylaluminum Chlorides to α,β-Unsaturated *N*-Acyloxazolidinones

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The stereoselective synthesis of β-branched α-halo carboxylic acids containing two newly formed chiral centers is accomplished by a reaction cascade consisting of the 1,4 addition of dialkylaluminum chlorides to α,β-unsaturated *N*-acyloxazolidinones and subsequent reaction of the intermediate aluminum enolates with *N*-halosuccinimide. The most efficient stereocontrol in these tandem processes has been achieved with oxazolidinones derived from glucosamine. Not only aryl substituted but also purely aliphatic β-branched α-halo carboxylic acids can be stereoselectively synthesized by this method. However, the reactions of β-aryl α,β-unsaturated *N*-acyloxazolidinones show the highest diastereoselectivity and give one out of four possible diastereomers in high excess.

Introduction

Numerous natural compounds, e.g. isoprenoids, alkaloids, and macrolides, contain chiral branched chain skeletons. The Michael addition[1] and analogous 1,4 additions to readily available α,β-unsaturated carbonyl compounds[2] provide a general method for the introduction of carbon chain branchings. For the 1,4 addition of σ-localized carbanions, i.e. the introduction of alkyl or aryl groups, organocuprates are commonly applied.[3] As a rule, they react with high regioselectivity. Stereoselective 1,4 additions of organocuprates have been achieved using α,β-unsaturated carboxylic acid derivatives containing a stereodifferentiating auxiliary in the ester or amide position.[4] Although their reactions often are less regioselective, Grignard reagents have also been successfully applied for stereoselective 1,4 additions.[5] While 1,4 additions of alkyl aluminum reagents to enones had been achieved only in isolated cases and under special conditions,[6] we had found a general access to β-branched carboxylic acids which consists in the 1,4 addition of dialkylaluminum chlorides to α,β-unsaturated *N*-acyl urethanes.[7] Using tetrahydrooxazinones,[7] oxazolidinones derived from carbohydrates[8,9] or an Evans auxiliary[10] as the stereodifferentiating tool in this conjugate additions, β-branched carboxylic acid derivatives are obtained in good[7,11] or even excellent diastereoselectivity.[8,9] It is noteworthy in this context, that ethylaluminum dichloride did not add to α,β-unsaturated *N*-acyl sultams but was used as the catalyst in organocuprate additions to these substrates.[12] An interesting feature of the 1,4 additions of organoaluminum chlorides is the contrasting behavior of dimethylaluminum chloride on the one hand and higher dialkylaluminum chlorides on the other.[8,9,11] Diethylaluminum chloride, for example, undergoes a smooth 1,4 addition to the *N*-cinnamoyloxazolidinone **1** at −78 °C to yield the 3-phenylvaleric acid derivative. Dimethylaluminum chloride does not react with **1** under identical conditions even in 6-fold excess and at temperatures up to −20 °C as long as oxygen or air are excluded.[11] However, the 1,4 addition of a methyl group of dimethylaluminum chloride to **1** proceeds after photochemical activation ($\lambda = 254$ nm) to give the 3-phenylbutyric acid derivative.[11] The intermediates formed from **1** and diethylaluminum chloride on the one hand and dimethylaluminum chloride on the other obviously are structurally different, as was shown by trapping reactions with oxidizing reagents.[11] The reaction cascades consisting of the 1,4 addition of dialkylaluminum chlorides to α,β-unsaturated *N*-acyl urethanes and the subsequent oxidation of the intermediates provide synthetic routes to β-branched α-hydroxy carboxylic acid derivatives and involve the introduction of two chiral centers at the former double bond with promising stereoselectivity.[11]

We here report on the extension of this principle to the synthesis of β-branched α-halo carboxylic acids. By nucleophilic substitution reactions, these compounds can be transformed to a number of interesting products, for instance, to unnatural amino acids required for the construction of peptide derivatives and peptidomimetics.[13]

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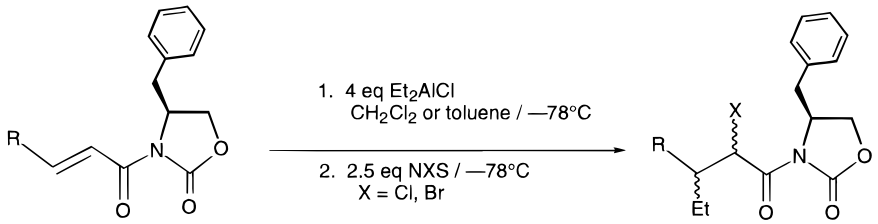
Table 1. Diastereoselective Synthesis of *β*-Branched α-Halo Carboxylic Acid *N*-Acyloxazolidinones Derived from Phenylalanine



1 R = Ph
2 R = Me

3 R = Ph, X = Cl
4 R = Ph, X = Br
5 R = Me, X = Cl

product	solvent	reaction time	dr[b,d] of 1,4 addition[c]	yield[a] (%)	(2*S*,3*S*), (2*R*,3*S*), (2*S*,3*R*), (2*R*,3*R*): $J_{CHR,CHX}$ dr;[b,d] (Hz)
3	CH_2Cl_2	(1) 3.5 h, (2) 20 h	88:12	72	79.1:9.5:6.8:4.6; 10.6, 9.1, 9.1, 10.6
3	toluene	(1) 4 h, (2) 15 h	89:11	79	79.9:9.4:8.1:2.6; 10.6, 9.1, 9.1, 10.6
4	CH_2Cl_2	(1) 3.5 h, (2) 20 h	88:12	54	49.2:37.5:7.3:6.0;[d] 10.5, 11.1, 10.5, 11.2
5	CH_2Cl_2	(1) 4 h, (2) 15 h	84:16	87	52.9:22.5:19.9:4.7;[d] 7.9, 4.9, 6.4, ~7.5

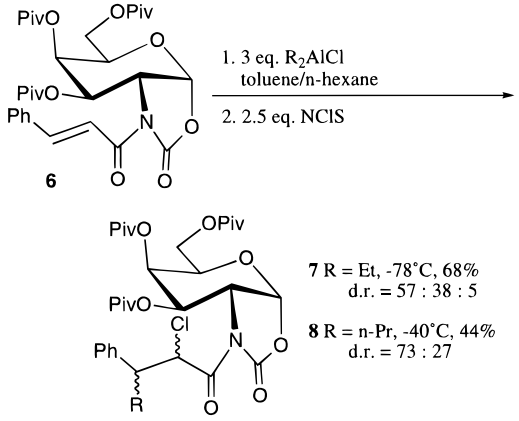
[a] Yield after flash chromatography [b] Diastereomeric ratio determined by analytical HPLC. [c] (*S*):(*R*). [d] Diastereomeric ratio determined by analysis of 400 MHz ^{1}H NMR spectra of the crude reaction mixtures.

β-Branched α-Halo Carboxylic Acids Formed on Evans[10] Auxiliary

In analogy to the synthesis of the branched α-hydroxy carboxylic acid derivatives,[11] the polar 1,4 addition of diethylaluminum chloride to **1** and its crotonyl analogue **2** was coupled to the subsequent trapping of the intermediate aluminum enolates with *N*-chloro- and *N*-bromosuccinimide (Table 1).

The results quoted in Table 1 show that in each of these cascade processes all four of the possible diastereomers are formed. In general, the stereoselection observed is unsatisfactory and considerably lower than that achieved in the 1,4 addition.[9] In particular, the bromination to yield **4** and the conversion of the crotonyl oxazolidinone **2** to give **5** show only low stereoselectivity during the halogenation step. Unfortunately, the diastereomers cannot be separated or enriched by chromatographic methods. The absolute configuration of the diastereomers of **5** could be elucidated in comparison with reference compound **5a** synthesized from L-isoleucine, i.e. (2*S*,3*S*)- and (2*R*,3*S*)-2-chloro-3-methylpentanoic acid (dr 92:8),[14] and their coupling to the Evans auxiliary. The two major diastereomers of **5** are obviously formed from chlorination of the major diastereomer of the initial 1,4 adduct with opposing influence of the auxiliary (1,4 induction) and the newly generated chiral center in *β*-position (1,2 induction). The anti-product (2*S*,3*S*)-**5** showing the larger coupling constant $J_{CHR,CHCl}$ in the proton NMR spectrum is slightly preferred. Comparison of the analogous coupling constants suggests that this also holds true for the 2-halo-3-phenylvaleric acid derivatives **3** and **4**. However, a stringent extrapolation is not justified from these data because the preferred conformation of the different diastereomers of **3** and **4** is not known. Nevertheless, it can be concluded from the diastereomeric ratios (dr) for **3** and **4** in relation of the diastereomeric ratios to the corresponding 1,4 adducts[9] (Table 1) together with the comparison of the coupling constants[15] that the two major diastereomers of **3** and **4** contain diastereomers of the branched 2-halo carboxylic acids with identical configuration in the *β*-position (3*R*).

Scheme 1



The lower stereoselections in these organoaluminum-based cascade reactions[11,16] in comparison to analogous organocuprate reactions on acceptors linked to a modified Evans auxiliary[13] are traced back to the strong complexation and probably aggregation of the intermediate aluminum enolates. Therefore we investigated carbohydrate-derived oxazolidinones in these conversions.

β-Branched α-Chloro Carboxylic Acid Derivatives Formed on Galactosamine-Derived Oxazolidinones

Since the galactosamine-derived oxazolidinone proved to be very efficient as stereodifferentiating tool in the 1,4 addition of dialkylaluminum chlorides to its α,*β*-unsaturated *N*-acyl derivatives,[8,9] we first investigated the *N*-cinnamoyl acceptor **6** in the combination of this 1,4 addition with the trapping of the aluminum enolate intermediate with *N*-chlorosuccinimide (Scheme 1).

The extent of conversion in both the formation of **7** and **8** was about 80%, although the cascade to furnish **8** was carried out at higher temperatures (−40 °C) and longer reaction times for both the 1,4 addition (**7**, 3 h; **8**, 5 h) as well as for the electrophilic chlorination (**7**, 5 h; **8**, 21 h). The ratios of diastereomers were determined by 400 MHz ^{1}H NMR spectroscopy of the crude and purified products. As was shown in previous investigations,[8,9] the 1,4

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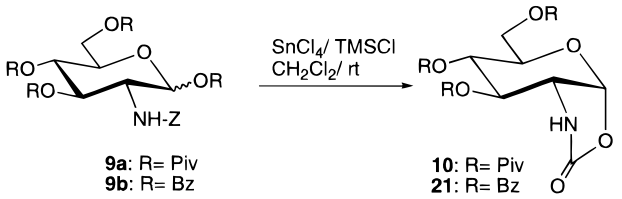
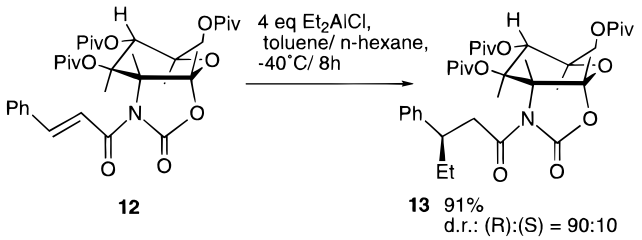
Scheme 2



Scheme 3



addition of diethyl- and di-*n*-propylaluminum chloride to **6** proceeds with high diastereoselectivity (96:4 and 97:3, respectively). The results obtained in the cascade-type reactions suggest that again in the second step, the chlorination of the intermediate enolates, only a low diastereoselectivity is achieved. It is concluded that in the second step, the 1,2 induction exhibited by the new stereogenic center formed in the first step strongly mismatches with the stereodifferentiation caused by the oxazolidinone auxiliary. Actually, it is not clear which influence is stronger, because all diastereomers of **7** and **8** show a rather large coupling constant $J_{CHR,CHCl} \approx 10.5$ Hz for the α-chloro carboxylic acid side chain, but obviously differ in the preferred conformation. The different conformations of the major and the minor diastereomers of each, **7** and **8**, are indicated by significantly different chemical shifts of the anomeric protons of the major diastereomers ($\delta \approx 5.0$ ppm) and minor diastereomers ($\delta \approx 6.0$ ppm). The fact that the high stereodifferentiation in the first step, i.e. the 1,4 addition, parallels a low stereodifferentiation in the second one was surprising. We assume that the rigid bicyclic oxazolidinone not only exhibits a strong exo versus endo differentiation during the 1,4 attack but also hinders the rotation of the newly formed chiral side chain of the coordinatively fixed aluminum enolate intermediate. As a consequence, the allylic strain[17] in the enolate cannot be minimized by a rotational movement of the phenyl substituent toward the endo position. In order to modify the flexibility we have varied the carbohydrate oxazolidinone structure.

O-Pivaloylglucosamine-Derived Oxazolidinone as the Auxiliary

The synthesis of a bicyclic oxazolidinone derived from glucosamine[16] is readily accomplished starting from *N*-(benzyloxycarbonyl)glucosamine[18] by its pivaloylation in pivaloyl chloride/pyridine to give **9a** and subsequent anomeric activation with tin tetrachloride and trimethylsilyl chloride (Scheme 2). By deprotonation with methyl magnesium bromide (Cerevitinov reagent) and acylation with the appropriate acid chlorides, the glucooxazolidinone **10** is converted to the α,β-unsaturated acceptors **11** and **12** (Scheme 2, Table 2).

The *N*-cinnamoyl derivative **12** was subjected to the 1,4 addition of diethylaluminum chloride and gave the β-branched adduct **13** in high yield and a diastereomeric ratio of 90:10 (Scheme 3). The analogous reaction with the galactosamine-derived auxiliary had shown a diastereoselectivity of 96:4.[8,9]

The lower stereofacial differentiation of the glucopyranosidooxazolidinone **10** in the 1,4 addition should be accompanied by a less opposing influence on the subsequent α-halogenation of the intermediate enolate. To prove this expectation, the acceptors **11** and **12** were used in reaction cascades consisting in the 1,4 addition of diethylaluminum chloride or diisobutylaluminum chloride (the latter reaction was promoted by 1 equiv of dimethylaluminum chloride[7,9]) and subsequent trapping with *N*-chloro- or *N*-bromosuccinimide (Table 2).

The results are quoted in Table 2. Yields given refer to purified compounds, whereas the diastereomeric ratios have been determined by analytical HPLC and/or 400 MHz ^{1}H NMR spectroscopy of the crude products. In order to estimate the stereoselectivity of the second step (halogenation), the stereoselectivity of the plain 1,4 addition has also been determined by analytical HPLC and/or 400 MHz ^{1}H NMR spectroscopy of samples taken after completion of the first step. In all cases examined in which analysis with both analytical HPLC and ^{1}H NMR spectroscopy could be performed, the obtained results were in good coincidence.

In most of the cascade-type conversions, one out of the four possible diastereomers was formed in high diastereoselectivity (**14**−**16**). As a rule the major diastereomer can be enriched by flash chromatography. The pure major diastereomer of **16** was isolated after a single recrystallization. The reactions of the crotonyl acceptor **11** are less selective. However, in the formation of both, the α-chloro-β-methylpentanoic acid derivative **17** and the α-chloro-β,δ-dimethylhexanoic acid derivative **18** only two out of four possible diastereomers have been found. Among them, the 3(*R*) diastereomer is formed preferably in a ratio of 4:1 for **17** and 5−6:1 for **18**. These ratios completely reflect the diastereoselectivity of the initial 1,4 addition. Thus, it has to be concluded that the chlorination of the intermediate enolates in these two conversions proceeds with almost complete stereoselectivity. By comparison of the NMR data of the diastereomeric mixture **17** with those of a diastereomer **17a** synthesized from L-isoleucine as described before for **5a**, the configuration of the major diastereomer was assigned to (2*R*,3*R*).[19] As the 1,4 addition of diethylaluminum chloride to **11** gives a diastereomeric ratio of 4:1, the minor component was assigned to (2*R*,3*S*) configuration. Additional evidence for the configurational assignments is given by the optical rotation value of the 2-chloro-3-methylpentanoic acid (**19**) obtained from hydrolysis of **17** (Scheme 4) and comparison with those reported for known stereoisomers of this compound in the literature.[19]

Since the configuration of the stereogenic center carrying only aliphatic substituents has a small influence as was demonstrated for the formation of **17**, the stereochemical course of the chlorination is controlled by the auxiliary.

In the conversions of the cinnamoyl acceptor **12**, three out of four possible diastereomers of **14**, **15**, and **16** were found. However, in contrast to the corresponding reac-

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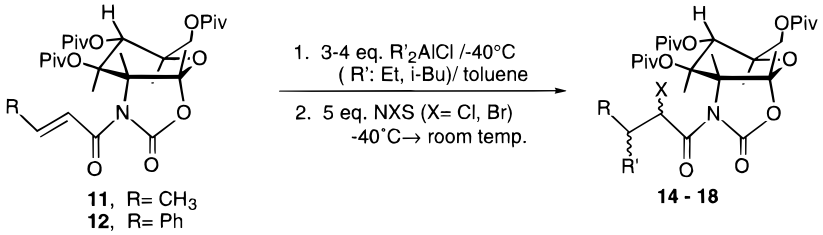
Table 2. Synthesis of β-Branched α-Hydroxy Acyl O-Pivaloylated Glucopyranosidooxazolidinones 14−18



11, R= CH_3
12, R= Ph

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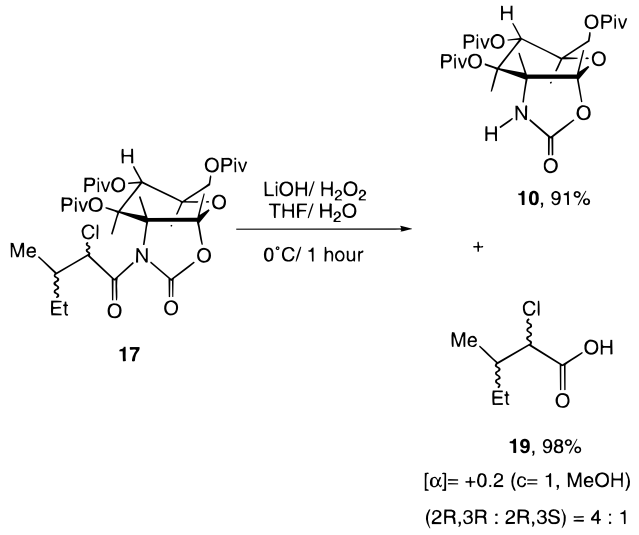
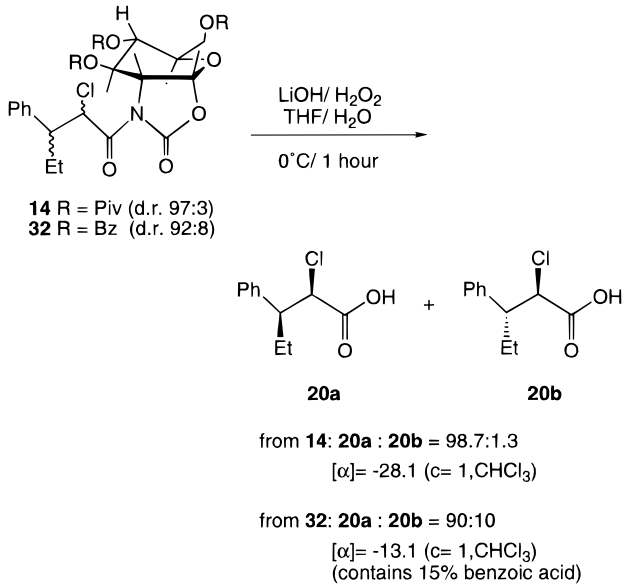
R	R′	X	reaction time	dr[b] of 1,4 addition[c]	yield[a] (%)	product	dr[d]; $J_{CHR,CHX}$ (Hz)
Ph	Et	Cl	(1) 36 h, (2) 48 h	90:10	64	**14**	91.8(2*R*,3*S*):7.1(2*R*,3*R*):1.1; 10.6, 6.5, 10.9
Ph	Et	Br	(1) 28 h, (2) 64 h	90:10	51	**15**	90.0(2*R*,3*S*):5.3:4.7; 11.6, 11.6, 8.0
Ph	iBu	Cl	(1) 32 h, (2) 36 h	92:8	48	**16**	91.1(2*R*,3*S*):6.3:2.6; 10.5, 10.9, 7.6
Me	Et	Cl	(1) 30 h, (2) 48 h	80:20	77	**17**	80(2*R*,3*R*):20(2*R*,3*S*); 7.5, 5.2
Me	iBu	Cl	(1) 30 h, (2) 66 h	85:15	57	**18**	84(2*R*,3*R*):16(2*R*,3*S*); 6.7, 5.6

[a] Yield after purification by flash chromatography or crystallization. [b] Diastereomeric ratio of plain 1,4 addition determined by analytical HPLC or NMR spectroscopy. [c] (*R*):(*S*). [d] Diastereomeric ratio determined by analytical HPLC or NMR spectroscopy.

Scheme 4



Scheme 5



tions of the acceptor **6** linked to the galactopyranosidooxazolidinone, one of the diastereomers is formed in high diastereoselectivity. According to the coupling constants ($J_{CHR,CHCl} = 10.5-11.5$ Hz) of the halo carboxylic portion, one would assume that the major diastereomer as well as one of the minor diastereomers have anti configurations.[15]

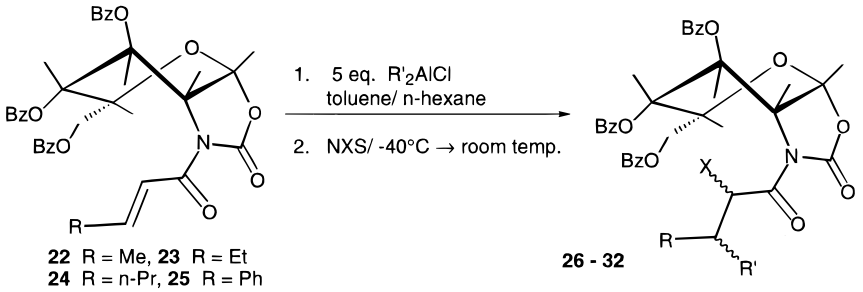
However, this conclusion is not convincing since the stereoisomers of **7** and **8** containing diastereomeric α-chloro carboxylic acid moieties showed very similar coupling constants in their NMR spectra (vide supra). Therefore, the configurational assignment for the diastereomers of **14**−**16** demands additional proof and can be achieved from the following reflection. The configuration of the β-carbon of the major diastereomers of **14**−**16** is given by the stereochemistry of the plain 1,4 addition to yield **13** and is (3*S*) (reversal of the notation after α-chlorination). For the halogenation of the minor diastereomer of the enolate formed by 1,4 addition (Scheme 3), both the newly formed stereogenic center and the auxiliary favour the exo attack (Re side) of the *N*-halosuccinimide to yield the minor diastereomer with anti configuration (2*R*,3*R*). To elucidate the configuration of the major diastereomer, a sample of **14** purified by flash chromatography (diastereomeric ratio 97:3) was subjected to detachment of the 2-chloro-3-phenylvaleric acid (**20**) from the auxiliary **10** (Scheme 5).

The 400 MHz ^{1}H NMR spectrum indicated that not enantiomers but two diastereomers of **20** with a dr of 98.7:1.3 were obtained. Logically, the major diastereomers of **14** and **20** have (2*R*,3*S*) configuration. The same assignment should apply to the major diastereomers of **15** and **16** (Table 2). From these results, the conclusion can be drawn that the halogenation of the intermediate aluminum enolate in this series is sterically directed by the carbohydrate auxiliary. The domination of the influence of the auxiliary in comparison to the situation in the galactosamine-derived series is considered a consequence of the higher flexibility of the enolate side chain in the less rigid glucosamine-derived substrates. As an extension in this direction, we have also studied the *O*-benzoyl-protected glucopyranosidooxazolidinone.

O-Benzoyl-Protected Glucosamine-Derived Oxazolidinone as the Auxiliary

The *O*-benzoyl-protected glucosamine-derived oxazolidinone **21** and the α,β-unsaturated acceptors **22**−**25** were synthesized in close analogy to the construction of **10** and its derivatives (Scheme 2, Table 3). After deprotonation with methylmagnesium bromide, acylation was carried out using α,β-unsaturated acyl chlorides to yield the acceptors **22**−**25**. Different from the *O*-pivaloyl ana-

Table 3. β-Branched α-Halo Carboxylic Acid Derivatives via Stereoselective 1,4 Addition of Dialkylaluminum Chlorides



22 R = Me, **23** R = Et
24 R = n-Pr, **25** R = Ph

26 - 32

R	R′	X	reaction conditions[a]	dr of 1,4 addition[d]	conversion[b]	yield[c] (%)	product	dr[d]	dr[c,f]
Me	Et	Cl	10 equiv of NCS/7 days	92:8		30	**26**	73.4:16.6:10	90.5(2*R*,3*R*):9.5(2*R*,3*S*)
Me	Et	Br	10 equiv of NBS/7 days	92:8	quantitative	70	**27**	76:17:7	93(2*R*,3*R*):7(2*R*, 3*S*)
Pr	Et	Cl	10 equiv of NCS/7 days	89:11	85%	65	**28**	75:19:6	86(2*R*,3*S*):14(2*R*,3*R*)
Pr	Et	Br	10 equiv of NBS/7 days	89:11	quant.	50	**29**	77:18.5:4.5	83(2*R*,3*S*):17(2*R*,3*R*)
Et	Pr	Cl	8 equiv of NCS/7 days	83:17	90%	60	**30**	81:19	77(2*R*,3*R*):23(2*R*,3*S*)
Et	Pr	Br	8 equiv of NCS/7 days	83:17	80%	45	**31**	74:15:7:4	77(2*R*,3*R*):23(2*R*,3*S*)
Ph	Et	Cl	5 equiv of NCS/64 h[e]	93:7	quantitative	51	**32**	92:8	96(2*R*,3*S*):4(2*R*,3*R*)

[a] First step: 5 equiv of Et_2AlCl/−40 °C/24 h. [b] Conversion monitored by NMR spectroscopy of the crude reaction product. [c] After flash chromatography. [d] Ratios determined by ^1H NMR spectroscopy of the crude reaction product. [e] First step: 3 equiv of Et_2AlCl/−40 °C/29 h [f] ^1H NMR spectroscopy.

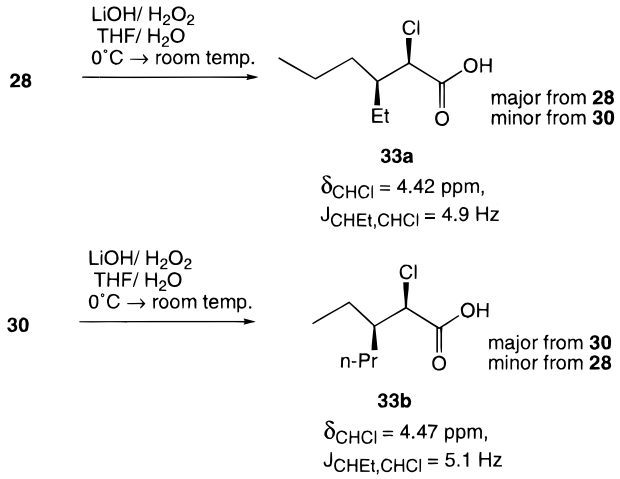
logues **11** and **12**, and indicating an increased flexibility, the *O*-benzoylated *N*-acyloxazolidinones prefer a twisted $^OS_2$ conformation in solution proven by a significant ^4J coupling ($^4J \approx 1.3$ Hz) between H-2 and H-4 (Table 3).

The cascade of 1,4 addition of dialkylaluminum chlorides to the acceptors **22**−**25** and subsequent reaction of the enolates with *N*-halosuccinimides have been carried out in analogy to the corresponding conversions of the *O*-pivaloylated acceptors **11** and **12**. The 1,4 addition of diethylaluminum chloride for example to the crotonyl derivative **22** proceeded readily at −60 °C with a diastereoselectivity of >20:1. However, the halogenation reactions of the intermediate aluminum enolates of this series are distinctly slower. Therefore, a higher temperature (−40 °C), longer reaction times and a large excess of the NXS reagents were applied (for **26**−**31**). Nevertheless, even after 7 days the conversions remained incomplete in most cases. The yields in Table 3 are given for the isolated products and are respectable. Out of the four possible diastereomers one is formed preferentially (Table 3) and can be enriched or even purified by chromatography.

In some cases only two of the four possible diastereomers have been found. It is noteworthy that for the formations of **26**−**32** the ratio of the major diastereomer and the main minor component almost corresponds to the selectivity of the initial 1,4 addition. Only in the conversion of the crotonyl derivative **22**, the selectivity in the 1,4 addition step is much higher than the ratio of the two major diastereomers of **26** and **27**, respectively. According to the results obtained from the pivaloyl-protected substrates **11** and **12** and to the ^1H NMR spectra, **30** should show the reverse ratio of diastereomers in comparison to **28**, and **31** the reverse preference in comparison to **29**. This was confirmed by hydrolytic release of the 2-chloro-3-ethylhexanoic acid **33** from the auxiliary (Scheme 6).

While the detachment from **28** (dr 86:14) gave a mixture of diastereomers of **33** in which the (2*R*,3*S*) isomer **33a** was predominant, hydrolysis of **30** (dr 77:23) yielded a mixture with prevailing **33b** (2*R*,3*R*). The configuration of the diastereomers of **26** and **27** was assigned by comparison with **19** and with the known 2-bromo-3-methylvaleric acid.[19]

Scheme 6



As for the cascade reactions on the acceptors linked to the *O*-pivaloyl-protected glucooxazolidinone **10**, the highest overall stereodifferentiation is found for the cinnamoyl derivative **25**. The configuration of the formed diastereomers of **32** (dr 92:8) was elucidated by hydrolysis to give the diastereomers of 2-chloro-3-phenylvaleric acid (**20**) of identical stereochemistry and in a ratio similar to that obtained from **14** (Scheme 5). The carbohydrate auxiliary was recovered from the hydrolysis reactions in almost quantitative yield (92−97%).

In this context it is interesting to note, that for 1,4 additions of cuprates to α,β-unsaturated acceptors bound to Evans-type auxiliaries and subsequent reactions with NXS exclusively methyl transfer to β-aryl acryloyl acceptors or aryl transfer to crotonyl acceptors has been studied so far.[20,21] Boron enolates of β-chiral branched *N*-acyloxazolidinones show a modest stereoselection in reactions with NXS, which becomes even lower if the methyl group bound to the phenyl methine center is substituted by an ethyl group.[22]

(20) Nicholas, E.; Russel, K. C.; Hruby, V. J. *J. Org. Chem.* **1993**, *58*, 766.
(21) Li, G.; Jarosinski, M. A.; Hruby. V. J. *Tetrahedron Lett.* **1993**, *34*, 2561.
(22) Li, G.; Patel, D.; Hruby, V. J. *Tetrahedron Lett.* **1994**, *35*, 2301.

In conclusion, the reaction cascade consisting of the 1,4 addition of dialkylaluminum chlorides to *N*-acyloxazolidinones derived from glucosamine and subsequent halogenation provides a stereoselective access not only to aryl substituted but also to purely aliphatic β-branched α-halo carboxylic acids. Depending upon the choice of the group R residing in the acceptor and R′ transferred from the organoaluminum chloride alternative stereoselective formations of different diastereomers of the branched α-halo carboxylic acids can be achieved as was demonstrated in the synthesis of **28**−**31**. In general, the reactions of aryl substituted α,β-unsaturated acceptors **12** and **25** are more stereoselective and give one out of four diastereomers (**14**, **15**, **26**, or **32**) in high diastereoselectivity.

Experimental Section

General experimental conditions and details of instrumentation have been previously reported.[9] All reactions were carried out in flame-dried glassware under an argon atmosphere.

***β*-Branched α-Halo Carboxylic Acid Derivatives via 1,4 Addition of Dialkylaluminum Chlorides to α,*β*-Unsaturated *N*-Acyloxazolidinones and Subsequent Reaction with *N*-Halosuccinimides. General Procedure.** A solution of the corresponding *N*-acyloxazolidinone **1** or **2** (1−2 mmol, 0.03 M) or **6**, **11**, **12** (0.5−1.2 mmol, 0.01 M) was cooled to the temperature quoted in Table 1, Scheme 1, or Table 2. Subsequently the addition of R'_2AlCl was conducted as has already been described.[9] After complete consumption of the starting material (monitoring by TLC) an excess of neat *N*-chloro- or *N*-bromosuccinimide (quoted in Table 1, Scheme 1, and Table 2) was added. The solution was stirred until the corresponding 1,4 addition product was no longer detectable by TLC in samples taken from the reaction mixture. The reaction was then quenched by addition of saturated NH_4Cl (20 mL/mmol **1** or **2**) or by pouring the solution into saturated NH_4Cl (100 mL, **6**, **11**, **12**). After dilution with HCl (10 mL, 1 N solution), the aqueous layer was extracted with CH_2Cl_2 (100 mL, three times). The combined organic layer was washed with $Na_2S_2O_3$ (50 g of $Na_2S_2O_3$/300 mL of H_2O; 80 mL, two times) and H_2O (80 mL, two times) and dried with $MgSO_4$. The solution was concentrated in vacuo affording colorless oils or colorless amorphous solids. Further purification was carried out by flash chromatography in light petroleum ether/EtOAc (8:1) for **3**, **4**, **5** and (18:1) for compounds **7**, **8** and **14**−**18**.

(4*S*)-3-(3′-Phenyl-2′-chloropentanoyl)-4-(phenylmethyl)-2-oxazolidinone (3): colorless oil; yield 72%; $[\alpha]_D^{25} = +78.4$ (c = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer 7.38−7.11 (m, 10H), 5.98 (d, 1H, J = 10.6 Hz, CHCl), 4.14−4.09 (m, 1H), 3.93 (dd, 1H, J = 2.3 Hz, J = 8.9 Hz), 3.58 (dd, 1H, J = 3.6 Hz, J = 8.2 Hz), 3.13 (dd, 1H, J = 3.4 Hz), 2.68 (dd, 1H, J = 9.6 Hz, J = 13.5 Hz), 2.33−2.27 (m, 1H), 1.65−1.76 (m, 2H), 0.81−0.74 (m, 3H); minor diastereomer 5.96 (d, 1H, J = 9.1 Hz, CHCl), 4.70 (m, 1H), 3.23−4.20 (m, 2H), 3.11 (dd, 1H, J = 3.3 Hz), 2.66 (dd, 1H, J = 13.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ major diastereomer 168.8, 152.4, 139.2, 134.8, 129.4, 128.9, 128.6, 127.4, 127.3, 65.9, 57.7 (CHCl), 55.3, 51.9, 37.2, 24.9, 11.4; minor diastereomers 168.9, 152.8, 139.3, 134.9, 66.5, 58.0 (CHCl), 55.9, 51.1, 37.9, 26.2, 11.9; 56.7 (CHCl), 54.9, 51.4, 36.7, 25.3. Anal. Calcd for $C_{21}H_{22}NO_3Cl$: C, 67.83; H, 5.96; N, 3.77. Found: C, 67.40; H, 6.01; N, 3.81.

(4*S*)-3-(2′-Chloro-3′-methylpentanoyl)-4-(phenylmethyl)-2-oxazolidinone (5): colorless oil; yield 87%; $[\alpha]_D^{25} = +49.6$ (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer 7.34−7.16 (m, 5H), 5.53 (d, 1H, J = 7.9 Hz, CHCl), 4.76−4.42 (m, 1H), 4.27−4.09 (m, 2H), 3.27 (dd, 1H, J = 3.1 Hz, J = 13.4 Hz), 2.81 (dd, 1H, J = 8.9 Hz, J = 13.4 Hz), 2.17−2.05 (m, 1H), 1.81−1.65 (m, 1H), 1.40−1.22 (m, 1H), 1.00−0.87 (m, 6H); minor diastereomers 5.63 (d, 1H, J = 4.9 Hz, CHCl); 5.64 (d, 1H, J = 6.4 Hz, C*H*Cl); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ major diastereomer 169.0, 152.6, 134.8, 129.4, 128.9, 127.4, 66.2, 59.7 (*C*HCl), 55.4, 47.7, 37.2, 24.5, 15.9, 10.6; minor diastereomers 66.6, 55.5, 61.1 (CHCl), 66.3, 55.6, 60.8 (CHCl). Anal. Calcd for $C_{16}H_{20}NO_3Cl$: C, 62.03; H, 6.51; N, 4.52; Cl, 11.44. Found: C, 61.93; H, 6.63; N, 4.61; Cl, 11.26.

(4*S*)-3-(2′(*S*)-Chloro-3′(*S*)-methylpentanoyl)-4-(phenylmethyl)-2-oxazolidinone (5a). Compound **5a** was prepared via the acid chloride of 2′-chloro-3′-methylpentanoic acid ($[\alpha]_D^{25} = +3.74$ (c = 1.0, benzene) starting from L-isoleucine by following the procedure published by Birnbaum and Greenstein.[15] According to the procedure described before,[9] acylation of the Evans auxiliary (0.9 g, 4.8 mmol) by applying MeMgBr afforded **5a** after flash chromatography (eluent petroleum ether/EtOAc 8:1) as a colorless oil: yield 1.15 g (77%); $[\alpha]_D^{25} = +62.1$ (c = 1.0, $CHCl_3$), dr 98:2; R_f = 0.43 (petroleum ether/EtOAc 5:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ major diastereomer 7.35−7.13 (m, 5H), 5.53 (d, 1H, J = 7.9 Hz, C*H*Cl), 4.76−4.42 (m, 1H), 4.27−4.09 (m, 2H), 3.27 (dd, 1H, J = 3.1 Hz, J = 13.4 Hz), 2.81 (dd, 1H, J = 8.9 Hz, J = 13.4 Hz), 2.17−2.05 (m, 1H), 1.81−1.65 (m, 1H), 1.40−1.22 (m, 1H), 1.00−0.87 (m, 6H); minor diastereomer 5.62 (d, 1H, $J \approx$ 5.0 Hz, C*H*Cl). Anal. Calcd for $C_{16}H_{20}NO_3Cl$: C, 62.03; H, 6.51; N, 4.52; Cl, 11.44. Found: C, 62.09; H, 6.54; N, 4.56; Cl, 11.29.

3′-(2″-Chloro-3″-phenylpentanoyl)-3,4,6-tri-*O*-pivaloyl-1,2-dideoxy-α-D-galactopyranosido[1,2:5′,4′]oxazolidin-2′-one (7): colorless amorphous solid; yield 68%; $[\alpha]_D^{25} = -19.9$ (c = 1, $CHCl_3$); R_f = 0.61 (petroleum ether/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer 7.33−7.12 (m, 5H), 5.78 (d, 1H, $J_{CHCl,CHPh}$ = 10.74 Hz, C*H*Cl), 5.35 (d, 1H, $J_{H4,H3}$ = 3.0 Hz, H-4), 5.01 (m, 2 H, $J_{H3,H4}$ = 3.0 Hz, $J_{H3,H2}$ = 8.6 Hz, $J_{H1,H2}$ = 5.1 Hz, H-3, H-1), 4.26 (m, 1H, J = 6.7 Hz, H-5), 4.16 (dd, 1H, $J_{H2,H1}$ = 5.5 Hz, $J_{H2,H3}$ = 8.9 Hz, H-2), 4.05 and 3.95 (dd, 2H, $J_{H6a,H5}$ = 7.1 Hz, $J_{H6b,H5}$ = 6.5 Hz, J_{gem} = 11.4 Hz, H-6a, H-6b), 2.98 (ddd, 1H, J = 3.2 Hz, J = 2.9 Hz, J = 11.1 Hz), 2.28−2.22 (m, 1H), 1.68 −1.53 (m, 1H), 1.19, 1.14 and 1.11 (s, 9H), 0.73−0.64 (m, 3H); minor diastereomer 6.02 (d, 1H, $J_{H1,H2}$ = 5.6 Hz, H-1), 5.74 (d, 1H, $J_{CHCl,CHPh}$ = 10.8 Hz, C*H*Cl), 5.41 (d, 1H, J = 3.2 Hz, H-4), 5.26 (dd, 1H, $J_{H3,H4}$ = 3.3 Hz, $J_{H3,H2}$ = 8.4 Hz, H-3), 4.69 (dd, 1H, $J_{H2,H1}$ = 5.7 Hz, $J_{H2,H3}$ = 8.4 Hz, H-2), 4.40 (m, 1H, J = 6.7 Hz, H-5), 4.13−4.09 (m, 2H, H-6a, H-6b), 3.06 (ddd, 1H, J = 3.6 Hz, CHPh), 1.25, 1.17, and 1.16 (s, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ major diastereomer 177.7, 177.1, 176.6, 167.7, 149.3, 139.9, 128.7, 128.4, 127.7, 97.2, 70.5, 70.4, 64.5, 60.9, 57.3 (C-Cl), 53.1, 52.2, 39.1, 38.7, 38.65, 27.10, 26.9, 26.8, 24.9, 13.4; minor diastereomer 176.5, 168.6, 149.7, 139.6, 128.5, 128.3, 127.2, 97.4, 70.5, 70.2, 64.5, 60.9, 57.3 (C-Cl), 54.4, 51.3, 39.0, 38.7, 27.0, 26.2, 11.9. Anal. Calcd for $C_{33}H_{46}NO_{10}Cl$: C, 60.78; H, 7.11; N, 2.15. Found: C, 59.14; H, 6.99; N, 2.16.

3′-(2″-Chloro-3″-phenylpentanoyl)-3,4,6-tri-*O*-pivaloyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (14): colorless crystals; mp 149 °C; yield 64%; $[\alpha]_D^{25} = -37.9$ (c = 1, $CHCl_3$). dr 94.2:4.7:1.1; R_f = 0.65 (petroleum ether/EtOAc 5:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ major diastereomer 7.32−7.10 (m, 5H), 5.80 (d, 1H, $J_{CHCl,CHPh}$ = 10.6 Hz, CHCl), 5.20 (dd, 1H, $J_{H3,H4}$ = 7.5 Hz, $J_{H3,H2}$ = 5.6 Hz, H-3), 5.04 (d, 1H, $J_{H1,H2}$ = 6.6 Hz, H-1), 4.96 (d, 1H, J = 7.7 Hz, H-4), 4.14 (m, 2H), 4.11−3.93 (m, 2H), 3.04−2.92 (ddd, 1H, J = 10.8 Hz), 2.30−2.21 (m, 1H), 1.75−1.62 (m, 1H), 1.17, 1.14 and 1.11 (s, 9H), 0.72 (t, 3H, J = 7.4 Hz); minor diastereomers 5.95 (d, 1H, $J_{CHCl,CHPh}$ = 10.9 Hz, CHCl), 5.71 (d, 1H, $J_{CHCl,CHPh}$ = 6.5 Hz, CHCl); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 177.8, 176.5, 176.4, 168.2, 149.7, 138.8, 128.7, 128.6, 127.6, 95.6, 70.3, 70.2, 65.2, 61.6, 57.8 (CHCl), 55.8, 52.6, 38.8, 38.7, 38.69, 27.03, 27.01, 26.92, 24.7, 11.4. Anal. Calcd for $C_{33}H_{46}NO_{10}Cl$: C, 60.78; H, 7.11; N, 2.15; Cl, 5.44. Found: C, 60.98; H, 7.17; N, 2.16; Cl, 5.30.

3′-(2″-Bromo-3″-phenylpentanoyl)-3,4,6-tri-*O*-pivaloyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (15): colorless amorphous solid; yield 51%; $[\alpha]_D^{25} = -18.9$ (c = 1, $CHCl_3$), dr 90.0:5.3:4.7; R_f = 0.65 (petroleum ether/EtOAc 5:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ major diastereomer 7.33−7.09 (m, 5H), 5.86 (d, 1H, $J_{CHBr,CHPh}$ = 11.0 Hz, CHBr), 5.24−5.15 (m, 2H, $J_{H3,H4}$ = 7.7 Hz, $J_{H3,H2}$ = 5.6 Hz, $J_{H1,H2}$ =

6.2 Hz, H-1, H-3), 5.00 (t, 1H, J = 7.7 Hz, J = 8.8 Hz, H-4), 4.23−4.09 (m, 3H), 4.04−3.96 (m, 1H), 3.07 (ddd, 1H, J = 11.3 Hz, J = 3.1 Hz), 2.37−2.25 (m, 1H), 1.72−1.55 (m, 1H), 1.18, 1.17, and 1.13 (s, 9H), 0.72 (t, 3H, J = 7.3 Hz); minor diastereomers 5.76 (d, 1H, $J_{CHBr,CHPh}$ = 11.6 Hz, CHBr); 5.95 (d, 1H, $J_{CHBr,CHPh}$ = 8.0 Hz, CHBr); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 177.8, 176.5, 176.4, 167.9, 149.7, 139.1, 128.6, 128.4, 127.5, 95.8, 70.6, 70.2, 65.3, 61.4, 55.9, 51.6 (CHBr), 47.8, 38.8, 38.7, 38.6, 27.0, 27.1, 26.9, 26.1, 11.5. Anal. Calcd for $C_{33}H_{46}NO_{10}$-Br: C, 56.90; H, 6.66; N, 2.01; Br, 11.47. Found: C, 56.91; H, 6.59; N, 2.11; Br, 11.88.

3′-(2″-Chloro-5″-methyl-3″-phenylhexanoyl)-3,4,6-tri-*O*-pivaloyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (16): colorless amorphous solid; mp 72 °C; yield 48%/36% pure major diastereomer; $[\alpha]_D^{25}$ = −31.2 (c = 1.0, $CHCl_3$), major diastereomer; R_f = 0.49 (petroleum ether/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer 7.30−7.13 (m, 5H), 5.76 (d, 1H, $J_{CHCl,CHPh}$ = 10.5 Hz, CHCl), 5.19−5.16 (dd, 1H, $J_{H3,H4}$ = 7.6 Hz, $J_{H3,H2}$ = 5.8 Hz, H-3), 4.99−4.95 (m, 2H, J = 8.2 Hz, $J_{H1,H2}$ = 6.4 Hz, H-1, H-4), 4.13 (d, 2H, J = 3.8 Hz, H-6a, H-6b), 4.10−3.94 (m, 2H, J = 6.5 Hz, J = 4.3 Hz, J = 8.1 Hz, H-5, H-2), 3.19−3.13 (ddd, 1H, J = 3.3 Hz, J = 12.0 Hz, J = 10.6 Hz, CHPh), 1.95−1.88 (ddd, 1H, J = 3.3 Hz, J = 10.7 Hz), 1.77−1.70 (ddd, 1H, J = 3.0 Hz, J = 12.7 Hz), 1.25−1.18 (m, 1H), 1.17, 1.16, and 1.10 (s, 9H), 0.80 (t, 6H, J = 7.0 Hz); minor diastereomer 5.68 (d, 1H, $J_{CHCl,CHPh}$ = 10.9 Hz, CHCl); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 177.8, 176.5, 176.4, 168.3, 149.7, 138.9, 128.7, 128.6, 127.6, 95.6, 70.4, 70.1, 65.1, 61.6, 58.1 (CHCl), 55.7, 49.3, 40.5, 38.7, 27.1, 27.0, 26.9, 25.1, 23.9, 20.8. Anal. Calcd for $C_{35}H_{50}NO_{10}Cl$: C, 61.80; H, 7.41; N, 2.06; Cl, 5.21. Found: C, 61.81; H, 7.44; N, 2.12; Cl, 4.78.

3′-(2″-Chloro-3″-methylpentanoyl)-3,4,6-tri-*O*-pivaloyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (17): colorless crystals; mp 198 °C; yield 77%; $[\alpha]_D^{25}$ = −23.0 (c = 1.0, $CHCl_3$), dr 83:17; R_f = 0.50 (petroleum ether/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer: 5.96 (d, 1H, $J_{H1,H2}$ = 6.78 Hz, H-1), 5.41−5.37 (m, 2H, $J_{H3,H4}$ = 6.0 Hz, $J_{H3,H2}$ = 4.8 Hz, $J_{CHCl,CHCH3}$ = 7.5 Hz, H-3, CHCl), 5.06 (d, 1H, $J_{H4,H3}$ = 6.0 Hz, $J_{H4,H5}$ = 8.6 Hz, H-4), 4.64 (dd, 1H, $J_{H2,H3}$ = 4.7 Hz, $J_{H2,H1}$ = 6.8 Hz, H-2), 4.23 (dd, 1H, $J_{H6a,H5}$ = 7.8 Hz, J_{gem} = 12.4 Hz, H-6a), 4.19 (dd, 1H, $J_{H6b,H5}$ = 5.4 Hz, J_{gem} = 12.1 Hz, H-6b), 4.04 (m, 1H, J = 8.6 Hz, J = 5.4 Hz, J = 2.8 Hz, H-5), 2.02 (m, 1H), 1.65 (m, 1H), 1.25 (m, 1H), 1.19, 1.18, and 1.14 (s, 9H), 0.97−0.85 (m, 6H); minor diastereomer 5.49 (d, 1H, $J_{CHCl,CHCH3}$ = 5.2 Hz, CHCl); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ major diastereomer 177.8, 177.5, 176.3, 168.3, 150.3, 95.3, 69.9, 69.7, 65.7, 61.9, 60.0 (CHCl), 55.4, 38.8, 38.7, 37.8, 27.1, 27.0, 26.9, 24.4, 16.0, 10.7; minor diastereomer 62.0, 60.9 (CHCl), 55.2, 37.5, 14.3. Anal. Calcd for $C_{28}H_{44}NO_{10}Cl$: C, 56.99; H, 7.52; N, 2.37; Cl, 6.01. Found: C, 56.84; H, 7.45; N, 2.48; Cl, 5.88.

2-Chloro-3-methylpentanoic Acid (19). The cleavage experiment with $LiOH/H_2O_2$ was performed following the literature procedure.[9,10] Compound **17** (250 mg, 0.4 mmol) dissolved in THF/H_2O (3:1, 8.5 mL) was reacted with H_2O_2 (8 equiv, 30% solution; 0.1 mL) and LiOH (2 equiv, 20 mg). After stirring for 1 h (TLC monitoring) the reaction mixture was worked up.[9] (The isolation of the glucosamine-derived auxiliary[8,9] was achieved in a yield of 91% (160 mg). The acid was isolated by extraction using EtOAc yielding after removal of the solvent, **19** as a colorless oil: yield 59 mg (98%); $[\alpha]_D^{25}$ = −3.35 (c = 1.0, Benzol); $[\alpha]_D^{25}$ = +0.2 (c = 1.0, MeOH); lit.[18] (*S,S*) $[\alpha]_D^{27}$ = −2.9 (MeOH), lit.[18] (*S,R*) $[\alpha]_D^{27}$ = −7.3 (MeOH); ^{1}H NMR (200 MHz, $CDCl_3$) δ major diastereomer 11.10 (br s, 1H), 4.20 (d, 1H, $J_{CHCl,CHCH3}$ = 6.5 Hz), 2.19−1.99 (m, 1H), 1.70−1.55 (m, 1H), 1.51−1.18 (m, 1H), 1.04 (d, 3H, J = 6.8 Hz), 0.98- 0.92 (m, 3H); minor diastereomer 4.38 (d, 1H, J = 4.6 Hz).

In complete analogy were synthesized **20** (from **14** and**32**) and **33** (from **28** and **30**):

2-Chloro-3-phenylpentanoic Acid (20). The acid was obtained from **14** (326 mg, 0.5 mmol; dr 97:3) in 88% yield (94 mg) as a colorless oil: $[\alpha]_D^{23}$ = −28.1 (c = 1, $CHCl_3$), dr 98.3:1.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer 7.7 (br, s, 1H), 7.3−7.14 (m, 5H), 4.45−4.44 (d, 1H, J = 8.9 Hz, CHCl), 3.08−3.02 (m, 1H), 2.13−2.07 (m, 1H), 1.74−1.62 (m, 1H), 0.76−0−73 (m, 3H); minor diastereomer 4.43−4.46 (d, 1H, CHCL); yield of recovered auxiliary **10** 214 mg (94%).

Starting from **32** (250 mg, 0.35 mmol; dr 92:8) **20** was obtained as already described: yield 65.6 mg (88%, according to the ^{1}H NMR spectrum, the material contains 15% benzoic acid, yield of **20** 75%); $[\alpha]_D^{23}$ = −13.1 (c = 1, $CHCl_3$); ^{1}H NMR spectroscopy; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 174.4, 138.9, 128.5, 128.3, 127.6, 61.8, 61.5*, 51.0, 25.9*, 24.5, 11.9*, 11.4 (*minor diastereomer); yield of recovered auxiliary **21** 172 mg (95%).

2-Chloro-3-ethylhexanoic acid (33). According to the procedure described for **19** compound **33** was obtained from **28** (175 mg, 0.36 mmol, dr 86:14) in 87% yield (40 mg) as a colorless oil containing about 5% of benzoic acid (^{1}H NMR): $[\alpha]_D^{20}$ = −2.1 (c = 1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ major diastereomer 11.10 (br s, 1H), 4.42 (d, 1H, J = 5.10 Hz, CHCl), 2.03 (m, 1H), 1.55−1.10 (m, 6H), 0.95−0.80 (M, 6H); minor diastereomer 4.47 (d, 1H, J = 4.94 Hz, CHCl); yield of recovered auxiliary **21** 133 mg (95%).

Starting from **30** (183 mg, 0.27 mmol, dr 77:23) the acid **33** was isolated in 82% (39.5 mg) as a colorless oil containing about 5% benzoic acid (^{1}H NMR): $[\alpha]_D^{20}$ = +1.5 (c = 1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ major diastereomer 10.7 (br s, 1H), 4.46 (d, 1H, J = 4.79 Hz, CHCl), 2.0 (m, 1H); 1.50−1.10 (m, 6H), 0.95−0.80 (m, 6H); minor diastereomer 4.42 (d, 1H, J = 5.14 Hz); yield of recovered auxiliary **21** 133 mg (95%).

1,3,4,6-Tetra-*O*-pivaloyl-2-[*N*-(benzyloxycarbonyl)amino-2-deoxy-β-D-glucopyranose (9a). *N*-(Benzyloxycarbonyl) protected glucosamine[18] (36.8 g, 118 mmol) was dissolved in pyridine. The reaction mixture was cooled to 0 °C and pivaloyl chloride (75 mL, 0.63 mol) was added dropwise. The solution was then warmed up to 40 °C and stirred until the starting material was no longer detectable by TLC. The solvent was removed in vacuo, and the concentrate was diluted with CH_2Cl_2 (400 mL) and then extracted with HCl (80 mL, 1 N solution, two times), saturated $NaHCO_3$ (80 mL, two times), and brine (80 mL). The organic layer was dried with $MgSO_4$ and evaporated in vacuo. Finally recrystallization (ethanol/H_2O) gave compound **9a** as colorless crystals (mp 148 °C): yield 55 g (72%); $[\alpha]_D^{25}$ = +17.1 (c = 1.0, $CHCl_3$); R_f = 0.69 (petroleum ether/EtOAc 2:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36−7.23 (m, 5H), 5.54 (d, 1H, $J_{H1,H2}$ = 8.8 Hz, H-1), 5.20−4.91 (m, 5H), 4.10−3.77 (m, 4H), 1.18, 1.11, 1.10, and 1.04 (s, 9H). Anal. Calcd for $C_{34}H_{51}NO_{11}$: C, 62.85; H, 7.91; N, 2.16. Found: C, 62.86; H, 8.05; N, 2.24.

***O*-Acylated Glucosylpyranosidooxazolidinones. General Procedure.** To a solution of **9** (0.05 mol) in CH_2Cl_2 (500 mL) were added $SnCl_4$ (0.09 mol, 10.6 mL) and Me_3SiCl (0.11 mol, 14 mL). The mixture was stirred until the reaction was completed (TLC monitoring). After dilution with CH_2Cl_2 (300 mL), the organic layer was washed with H_2O (150 mL, five times), $NaHCO_3$ (150 mL, 50% solution) and brine (150 mL), dried over $MgSO_4$ and concentrated in vacuo. Finally, recrystallization afforded pure compounds **10** and **21**.

2′-Oxo-3,4,6-tri-*O*-pivaloyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidine (10). colorless crystals; mp 129 °C (*n*-hexane, CH_2Cl_2 15:1 v/v); yield 22 g (96%); $[\alpha]_D^{25}$ = +44.3 (c = 1, $CHCl_3$); R_f = 0.30 (petroleum ether/EtOAc 2:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.63 (br s, 1H), 5.93 (d, 1H, $J_{H1,H2}$ = 6.8 Hz, H-1), 5.12−4.97 (m, 2H, J = 7.5 Hz, J = 4.9 Hz, H-3, H-4), 4.19 (m, 3H, H-6a, H-6b, H-5), 3.78 (dd, 1H, $J_{H2,H1}$ = 6.7 Hz, $J_{H2,H3}$ = 5.0 Hz, H-2), 1.19, 1.17, 1.15 (s, 9H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 178.2, 177.9, 176.4, 156.6, 97.1, 75.2, 69.0, 65.4, 61.6, 55.7, 38.8, 38.7, 27.0, 26.9. Anal. Calcd for $C_{22}H_{35}NO_9$: C, 57.76; H, 7.71; N, 3.06. Found: C, 57.61; H, 7.60; N, 3.14.

2′-Oxo-3,4,6-tri-*O*-benzoyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidine (21): colorless crystals; mp 196−198 °C (petroleum ether/CH_2Cl_2 5:1 v/v); yield 24 g (92%); $[\alpha]_D^{20}$ = −0.67 (c = 1, $CHCl_3$); R_f = 0.25 (petroleum ether/EtOAc 2:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.01−7.93 (m, 6H), 7.55−7.23 (m, 9H), 6.43 (s, 1H, NH), 6.05 (d, 1H, J = 6.9 Hz, H-1), 5.65 (dd, 1H, J = 5.5 Hz, J = 8.16 Hz, H-4) 5.37 (m, 1H,

J = 5.08 Hz, J = 4.15 Hz, H-3) 4.71−4.43 (m, 3H), 4.11 (dd, 1H, J = 6.9 Hz, J = 4.1 Hz, H-2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 166.0, 165.9, 165.1, 156.4, 133.9, 133.7, 133.1, 129.9, 129.8, 129.7, 128.6, 128.5, 128.3, 96.5, 73.9, 68.5, 67.0, 63.1, 54.1. Anal. Calcd for $C_{28}H_{23}NO_9$: C, 64.99; H, 4.48; N, 2.71. Found: C, 64.83; H, 4.35; N, 2.88.

α,*β*-Unsaturated *O*-Pivaloylated Glucosylpyranosidooxazolidinones. According to the general procedure described previously,[9] compound **10** was reacted with MeMgBr and the appropriate acid chloride. Column chromatography (petroleum ether/EtOAc 8:1) for **11** and crystallization from *n*-hexane/CH_2Cl_2 for **12** afforded pure compounds.

3′-[(2″*E*)-Butenoyl]-3,4,6-tri-*O*-pivaloyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (11): colorless crystals; mp 128 °C; yield 92%; $[\alpha]_D^{25}$ = −49.5 (c = 1.0, $CHCl_3$); R_f = 0.31 (petroleum ether/EtOAc 5:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.14 (d, 2H, $J_{CH,CH3}$ = 2.5 Hz), 5.94 (d, 1H, $J_{H1,H2}$ = 7.0 Hz, H-1), 5.43 (t, 1 H, J = 9.5 Hz, H-4), 5.02 (dd, 1H, $J_{H3,H2}$ = 4.9 Hz, $J_{H3,H4}$ = 8.0 Hz, H-3), 4.61 (dd, 1H, $J_{H2,H3}$ = 4.2 Hz, $J_{H2,H1}$ = 7.0 Hz, H-2), 4.20 (m, 2H), 4.02−3.97 (m, 1H), 1.92 (dd, 3H, J = 2.4 Hz), 1.20, 1.19, and 1.10 (s, 9H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 177.9, 176.4, 176.3, 164.2, 151.3, 148.1, 121.7, 94.6, 69.6, 68.6, 65.9, 62.5, 54.4, 38.8, 38.7, 38.6, 27.0, 26.9, 26.8, 18.5. Anal. Calcd for $C_{26}H_{39}NO_{10}$: C, 59.42; H, 7.48; N, 2.66. Found: C, 59.43; H, 7.48; N, 2.88.

3′-[(2″*E*)-3″-Phenylpropenoyl]-3,4,6-tri-*O*-pivaloyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (12): colorless crystals; mp 204−211 °C, yield 85%; $[\alpha]_D^{25}$ = +0.8 (c = 1.0, $CHCl_3$); R_f = 0.42 (petroleum ether/EtOAc 5:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.81 (dd, 2H), 7.61 (m, 2H), 7.39 (m, 3H), 5.99 (d, 1H, $J_{H1,H2}$ = 7.0 Hz, H-1), 5.52 (t, 1H, $J_{H3,H4}$ = 4.3 Hz, H-3), 5.04 (dd, 1H, J = 4.9 Hz, J = 7.8 Hz, H-4), 4.69 (dd, 1H, $J_{H2,H3}$ = 4.0 Hz, $J_{H2,H1}$ = 6.9 Hz, H-2), 4.25 (m, 2H), 4.05 (m, 1H), 1.22, 1.21, and 1.10 (s, 9H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 176.9, 176.4, 176.3, 164.5, 151.4, 147.4, 134.2, 130.9, 128.9, 128.6, 116.6, 94.6, 69.6, 68.4, 65.8, 62.5, 54.4, 38.8, 38.7, 38.6, 27.0, 26.9, 26.8. Anal. Calcd for $C_{31}H_{41}NO_{10}$: C, 63.36; H, 7.03; N, 2.38. Found: C, 63.15; H, 7.05; N, 2.47.

3′-(3″-Phenylpentanoyl)-3,4,6-tri-*O*-pivaloyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (13). This compound was prepared according to the general method already published (conditions quoted in Scheme 3):[9] colorless crystals; mp 64 °C; yield 91%; $[\alpha]_D^{25}$ = −39.2 (c = 1.0, $CHCl_3$), dr 90:10; R_f = 0.57 (petroleum ether/EtOAc 5:1); ^{1}H NMR (200 MHz, $CDCl_3$), δ major diastereomer 7.30−7.15 (m, 5H), 5.63 (d, 1H, $J_{H1,H2}$ = 6.7 Hz, H-1), 5.32 (dd, 1 H, $J_{H3,H4}$ = 6.9 Hz, $J_{H3,H2}$ = 5.2 Hz, H-3), 5.04 (d, 1H, $J_{H4,H3}$ = 7.0 Hz, $J_{H4,H5}$ = 8.5 Hz, H-4), 4.39 (dd, 1H, $J_{H2,H3}$ = 5.5 Hz, $J_{H2,H1}$ = 6.5 Hz, H-2), 4.19−4.11 (m, 2H), 4.02 (m, 1H, J = 6.7 Hz), 3.43 (dd, 1H, J_{vic} = 10.1 Hz, J_{gem} = 18.4 Hz), 3.01 (m, 2H), 1.72−1.56 (m, 2H), 1.20, 1.19, and 1.15 (s, 9H), 0.76 (t, 3H, J = 7.3 Hz); minor diastereomer 5.89 (d, 1H, $J_{H1,H2}$ = 6.5 Hz, H-1), 4.55 (dd, 1H, H-2); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 177.8, 177.6, 176.2, 171.1, 150.7, 143.7, 128.2, 127.6, 126.4, 95.2, 70.3, 69.8, 65.3, 61.8, 55.3, 43.3, 41.8, 38.7, 38.6, 38.5, 29.1, 27.0, 26.9, 26.85, 11.9. Anal. Calcd for $C_{33}H_{47}NO_{10}$: C, 64.17, H, 7.67; N, 2.27. Found: C, 63.95; H, 7.79; N, 2.28.

α,*β*-Unsaturated O-Benzoylated Glucopyranosidooxazolidinones. The acceptors were prepared by employing the typical experimental procedure of Evans as described previously.[9] A solution of **21** (10.3 g, 20 mmol) dissolved in THF (400 mL) was applied. Chromatography on silica gel (eluent petroleum ether/EtOAc 10:1) followed by recrystallization from petroleum ether/CH_2Cl_2 (5:1) provided pure compounds **22**−**25**.

3′-[2″(*E*)Pentenoyl]-3,4,6-tri-*O*-benzoyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (23): colorless needles; mp 159−161 °C; yield 7.65 g (65%); $[\alpha]_D^{20}$ = −132.1 (c = 1; $CHCl_3$); R_f = 0.53 (petroleum ether/EtOAc 2:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.95 (m, 6H), 7.37 (m, 11H), 6.18 (d, 1H, $J_{H-1,H-2}$ = 7.27 Hz, H-1), 6.18 (t, 1H, J = 2.86 Hz, H-3), 5.59 (m, 1H, $J_{H-4,H-2}$ = 1.12 Hz, $J_{H-4,H-3}$ = 2.8 Hz, $J_{H-4,H-5}$ = 6.7 Hz, H-4), 4.82 (m, 1H, $J_{H-2,H-4}$ = 1.11 Hz, $J_{H-2,H-3}$ = 2.94 Hz, $J_{H-2,H-1}$ = 7.26 Hz, H-2), 4.73 (dd, 1H, $J_{H-6a,H-5}$ = 3.17 Hz, J_{gem}=12.03 Hz, H-6a), 4.59 (dd, 1H, $J_{H-6b,H-5}$ = 5.46 Hz, J_{gem} = 12.02 Hz, H-6b), 4.35 (m, 1H, J = 3.2 Hz), 2.28 (m, 2H), 1.07 (t, 3H, J = 7.37 Hz); ^{1}H NMR (400 MHz, toluene-d_8) δ 8.17 (m, 6H), 7.70 (dt, 1H, J = 15.32 Hz, J = 1.68 Hz), 7.24 (m, 10H), 6.42 (t, 1H, J = 3.72 Hz, H-3), 5.83 (ddd, 1H, $J_{H-4,H-2}$ = 1.21 Hz, $J_{H-4,H-3}$ = 3.7 Hz, $J_{H-4,H-5}$ = 6.97 Hz, H-4), 5.49 (d, 1H, $J_{H-1,H-2}$ = 7.18 Hz, H-1), 4.77 (dd, 1H, $J_{H-6a,H-5}$ = 3.01 Hz, J_{gem}=12.16 Hz, H-6a), 4.58 (dd, 1H, $J_{H-6b,H-5}$ = 5.20 Hz, J_{gem} = 12.17 Hz, H-6b), 4.32 (ddd, 1H, $J_{H-2,H-4}$ = 1.23 Hz, $J_{H-2,H-3}$ = 3.7 Hz, $J_{H-2,H-1}$ = 7.20 Hz, H-2), 4.19 (m, 1H, J = 3.03 Hz, J = 5.21 Hz, H-5), 2.18 (m, 2H, J =1.65 Hz, J = 7.48 Hz), 1.05 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100,6 MHz, toluene-d_8) δ 165.6, 164.9, 164.6, 164.3, 153.5, 151.8, 137.5, 133.3, 132.8, 130.3, 130.25, 130.0, 129.8, 129.4, 129.1, 128.9, 128.6, 128.4, 128.2, 128.0, 127.7, 125.4, 125.1, 124.9, 120.2, 94.4, 70.2, 67.6, 67.5, 63.8, 53.6, 25.9, 12.1. Anal. Calcd for $C_{33}H_{29}NO_{10}$ C, 66.11; H, 4.87; N, 2.34. Found: C, 66.14; H, 4.93; N, 2.29.

3′-[2″(*E*)Hexenoyl]-3,4,6-tri-*O*-benzoyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (24): colorless needles; mp 169−170 °C; yield 8.25 g (70%); $[\alpha]_D^{20}$ = −150.2 (c = 1, $CHCl_3$); R_f = 0.60 (petroleum ether/EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95(m, 6H), 7.36 (m, 11H), 6.17 (d, 1H, $J_{H-1,H-2}$ = 7.29 Hz, H-1), 6.07 (t, 1H, J = 3.02 Hz, J = 2.95 Hz, H-3), 5.58 (m, 1H, $J_{H-4,H-2}$ = 1.40 Hz, $J_{H-4,H-3}$ = 2.67 Hz, $J_{H-4,H-5}$ = 6.62 Hz, H-4), 4.81 (m, 1H, $J_{H-2,H-4}$ = 1.31 Hz, $J_{H-2,H-3}$ = 3.06 Hz, $J_{H-2,H-1}$ = 7.26 Hz, H-2), 4.71 (dd, 1H, $J_{H-6a,H-5}$ = 3.12 Hz, J_{gem}=12.10 Hz, H-6a), 4.59 (dd, 1H, $J_{H-6b,H-5}$ = 5.61 Hz, J_{gem} = 12.04 Hz, H-6b), 4.35 (m, 1H, J = 3.18 Hz, J = 5.90 Hz, J = 6.10 Hz, H-5), 2.23 (m, 2H), 1.51 (m, 2H), 0.91 (t, 3H); ^{13}C NMR (100,6 MHz, $CDCl_3$) δ 166.0, 164,8, 164.7, 164.3, 153.3, 151.8, 133.6, 133.1, 130.0, 129.6, 129.2, 128.7, 128.6, 128.5, 128.3, 128.2, 120.2, 93.9, 69.6, 67.1, 66.4, 64.0, 53.1, 34.7, 21.2, 13.7. Anal. Calcd for $C_{34}H_{31}NO_{10}$: C, 66.55; H, 5.09; N, 2.28. Found: C, 66.48; H, 5.26; N, 2.27.

***β*-Branched α-Halo Carboxylic Acid Derivatives Derived from 22−25.** The method employed was the same as the procedure for the transformation of **1**, **2** and **6**, **11**, **12** respectively, with the variation that the acceptors **22**−**25** (1 g) were dissolved in toluene (250 mL). Refer to Table 3 for the experimental details. Purification of **26**−**31** was accomplished by flash chromatography (petroleum ether/EtOAc 10:1) and 2-fold recrystallization from petroleum ether/CH_2Cl_2 5:1. Flash chromatography (petroleum ether/EtOAc 20:1) afforded pure compound **32**.

3′-(3″-Ethyl-2″-chlorohexanoyl)-3,4,6-tri-*O*-benzoyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (28): colorless needles; mp 174 °C; yield 65%; $[\alpha]_D^{20}$ = −105.2 (c = 1, $CHCl_3$), dr 86:14; R_f = 0.73 (petroleum ether/EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer 7.98 (m, 6H), 7.41 (m, 9H), 6.19 (d, 1H, $J_{H-1,H-2}$ = 7.23 Hz, H-1), 6.05 (t, 1H, J = 3.37 Hz, J = 3.41 Hz, H-3), 5.65 (d, 1H, J = 6.88 Hz, CHCl), 5.57 (ddd, 1H, $J_{H-4,H-3}$ = 3.40 Hz, $J_{H-4,H-5}$ = 6.79 Hz, $J_{H-4,H-2}$ = 0.98 Hz, H-4), 4.78 (ddd, 1H, $J_{H-2,H-4}$ = 1.15 Hz, $J_{H-2,H-3}$ = 3.18 Hz, $J_{H-1,H-2}$ = 7.24 Hz, H-2), 4.72 (dd, 1H, $J_{H-6a,H-5}$ = 3.19 Hz, J_{gem}=12.14 Hz, H-6a), 4.60 (dd, 1H, $J_{H-6b,H-5}$ = 5.75 Hz, J_{gem} = 12.16 Hz, H-6b), 4.40 (m, 1H, J = 3.17 Hz, J = 6.0 Hz, H-5), 1.95 (m, 1H); 1.5−1.23 (m, 6H), 0.87 (m, 6H); minor diastereomer 5.64 (d, 1H, CH-Cl); ^{13}C NMR (100,6 MHz, $CDCl_3$) δ 169.0, 166.0, 165.2, 164.3, 150.7, 133.8, 133.7, 133.2, 130.1, 130.0, 129.7, 129.4, 128.7, 128.6, 128.5, 128.3, 94.4, 69.9, 67.1, 66.8, 63.7, 59.2 (CH-Cl), 54.0, 41.9, 30.8, 23.8, 19.6, 14.3, 11.0. Anal. Calcd for $C_{36}H_{36}ClNO_{10}$: C, 63.76; H, 5.35; N, 2.07; Cl, 5.23. Found: C, 63.56; H, 5.57; N, 1.58; Cl, 4.58.

3′-(3″-Ethyl-2″-bromohexanoyl)-3,4,6-tri-*O*-benzoyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (29): colorless needles; mp 168 °C; yield 50%; $[\alpha]_D^{20}$ = −86.19 (c = 1, $CHCl_3$), dr 83:17; R_f = 0.73 (petroleum ether/EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer 7.98 (m, 6H), 7.41 (m, 9H), 6.18 (d, 1H, $J_{H-1,H-2}$ = 7.27 Hz, H-1), 5.99 (t, 1H, J = 3.40 Hz, J = 3.44 Hz, H-3), 5.65 (d, 1H, J = 7.45Hz, CHBr), 5.56 (ddd, 1H, J = 2.7Hz, J = 7.1Hz, H-4), 4.80 (ddd, 1H, $J_{H-2,H-4}$ = 0.95 Hz, $J_{H-2,H-3}$ = 3.20 Hz, $J_{H-1,H-2}$ = 7.23 Hz, H-2), 4.70 (dd, 1H, $J_{H-6a,H-5}$ = 3.27 Hz, J_{gem}=12.12 Hz, H-6a), 4.59 (dd, 1H, $J_{H-6b,H-5}$ = 5.76 Hz, J_{gem} = 12.11 Hz, H-6b), 4.42 (m, 1H, J = 3.30 Hz), 1.91 (m, 1H), 1.59−1.18 (m,

6H), 0.85 (m, 6H); minor diastereomer 6.19 (d, 1H, H-1), 5.55 (d, 1H, CHBr); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 168.9, 166.0, 165.2, 164.3, 150.7, 133.8, 133.7, 133.2, 130.2, 130.0, 129.7, 129.4, 128.8, 128.6, 128.4, 128.3, 94.4, 69.8, 67.3, 67.2, 63.5, 54.1, 49.7, 41.4, 32.2, 23.9, 19.2, 14.2, 11.0. Anal. Calcd for $C_{36}H_{36}BrNO_{10}$: C, 59.84; H, 5.02; N, 1.94; Br, 11.06. Found: C, 59.96; H, 5.34; N, 1.57; Br, 11.20.

3′-(3″-Ethyl-2″-chlorohexanoyl)-3,4,6-tri-*O*-benzoyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (30): colorless needles; mp 165 °C; yield 60%; $[\alpha]_D^{20} = -106.4$ (c = 1, $CHCl_3$), dr 77:23; R_f = 0.66 (petroleum ether/EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer 7.93 (m, 6H), 7.38 (m, 9H), 6.17 (d, 1H, $J_{H-1,H-2}$ = 7.29 Hz, H-1), 6.01 (t, 1H, J = 3.26 Hz, J = 3.22 Hz, H-3), 5.54 (ddd, 1H, $J_{H-4,H-3}$ = 3.28 Hz , $J_{H-4,H-5}$ = 6.85 Hz, $J_{H-4,H-2}$ = 1.13 Hz, H-4), 5.59 (d, 1H, J = 6.58 Hz, CHCl), 4.76 (ddd, 1H, $J_{H-2,H-4}$ = 1.20 Hz, $J_{H-2,H-3}$ = 3.14 Hz, $J_{H-1,H-2}$ = 7.29 Hz, H-2), 4.69 (dd, 1H, $J_{H-6a,H-5}$ = 3.12 Hz, J_{gem}=12.12 Hz, H-6a), 4.57 (dd, 1H, $J_{H-6b,H-5}$ = 5.74 Hz, J_{gem} = 12.14 Hz, H-6b), 4.36 (m, 1H, J = 3.26 Hz, J = 6.2 Hz, H-5), 1.96 (m, 1H), 1.6−1.1 (m, 6H), 0.80 (m, 6H); minor diastereomer 5.62 (d, 1H, CH-Cl); ^{13}C NMR (100,6 MHz, $CDCl_3$), δ 169.1, 165.9, 165.2, 164.3, 150.8, 133.8, 133.7, 133.2, 130.1, 130.0, 129.8, 129.7, 129.3, 128.7, 128.6, 128.5, 128.3, 128.2, 94.3, 69.8, 67.1, 66.8, 63.6, 58.8 (CHCl), 53.9, 41.6, 32.4, 21.4, 19.9, 14.2, 10.2. Anal. Calcd for $C_{36}H_{36}ClNO_{10}$: C, 63.76; H, 5.35; N, 2.07; Cl, 5.23. Found: C, 63.68; H, 5.51; N, 1.68; Cl, 4.69.

3′-(3″-Ethyl-2″-bromohexanoyl)-3,4,6-tri-*O*-benzoyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (31): colorless needles; mp 167 °C; yield 45%; $[\alpha]_D^{20} = -88.52$ (c = 1, $CHCl_3$), dr 77:23; R_f = 0.66 (petroleum ether/EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer 7.96 (m, 6H), 7.38 (m, 9H), 6.16 (d, 1H, $J_{H-1,H-2}$ = 7.27 Hz, H-1), 5.95 (t, 1H, J = 3.34 Hz, J = 3.30 Hz, H-3), 5.59 (d, 1H, J = 8.1 Hz, CHBr), 5.53 (ddd, 1H, $J_{H-4,H-3}$ = 3.39 Hz , $J_{H-4,H-5}$ = 7.0 Hz , $J_{H-4,H-2}$ = 0.9 Hz , H-4), 4.78 (ddd, 1H, $J_{H-2,H-4}$ = 0.9 Hz, $J_{H-2,H-3}$ = 3.17 Hz, $J_{H-1,H-2}$ = 7.2 Hz, H-2), 4.67 (dd, 1H, $J_{H-6a,H-5}$ = 3.3 Hz, J_{gem}=12.1 Hz, H-6a), 4.56 (dd, 1H, $J_{H-6b,H-5}$ = 5.7 Hz, J_{gem} = 12.1 Hz, H-6b), 4.38 (m, 1H, J = 3.3 Hz, J = 6.2 Hz, H-5), 1.94 (m, 1H), 1.61 (m, 1H), 1.46 (m, 1H), 1.23 (m, 4H), 0.82 (m, 6H); minor diastereomer 6.19 (d, 1H, H-1), 5.62 (d, 1H, CHBr); ^{13}C NMR (100,6 MHz, $CDCl_3$) δ 168.9, 166.0, 165.2, 164.3, 150.7, 133.8, 133.7, 133.2, 130.3, 130.0, 129.7, 129.4, 128.8, 128.6, 128.5, 128.3, 94.3, 69.7, 67.2, 67.2, 63.6, 53.9, 49.7 (CHBr), 41.0, 32.5, 22.8, 20.0, 14.2, 9.7. Anal. Calcd for $C_{36}H_{36}BrNO_{10}$: C, 59.84; H, 5.32; N, 1.94; Br, 11.06. Found: C, 59.79; H, 5.32; N, 1.58; Br, 11.51.

3′-(2″-Chloro-3″-phenylpentanoyl)-3,4,6-tri-*O*-benzoyl-1,2-dideoxy-α-D-glucopyranosido[1,2:5′,4′]oxazolidin-2′-one (32): colorless crystals; mp 76 °C; yield 51%; $[\alpha]_D^{25}$ = −106.9 (c = 1.0, $CHCl_3$), dr 96:4; R_f = 0.66 (petroleum ether/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ major diastereomer 8.00−7.14 (m, 20H), 5.93 (d, 1H, $J_{CHCl,CHPh}$ = 10.6 Hz, CHCl), 5.82 (t, 1H, $J_{H3,H4}$ = 4.1 Hz, H-3), 5.49 (d, 1H, $J_{H1,H2}$ = 7.0 Hz, H-1), 5.45 (m, 1H, $J_{H4,H2}$ = 1.1 Hz, $J_{H4,H3}$ = 4.5 Hz, $J_{H4,H5}$ = 6.3 Hz, H-4), 4.65 (dd, 1H, $J_{H6a,H5}$ = 3.1 Hz, J_{gem} = 12.1 Hz, H-6a), 4.53 (dd, 1H, $J_{H6b,H5}$ = 6.1 Hz, J_{gem} = 12.1 Hz, H-6b), 4.33−4.29 (m, 1H, J = 3.1 Hz, J = 6.1 Hz, H-5), 4.10 (m, 1H, J = 7.1 Hz, J = 3.6 Hz, $J_{H2,H4}$ = 1.1 Hz, H-2), 3.03 (dd, 1H, J = 11.0 Hz, J = 3.2 Hz, CHPh), 2.33−2.24 (m, 1H, J = 3.3 Hz, J = 7.4 Hz, J = 12.9 Hz), 1.72−1.66 (m, 1H, J = 7.2 Hz, J = 11.7 Hz), 0.72 (t, 3H, J = 7.3 Hz); minor diastereomer 4.02 (m, 1H, H-2); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ major diastereomer 168.8, 165.9, 165.1, 164.3, 150.3, 138.8, 129.3, 128.2, 133.8, 133.6, 133.2, 130.1, 129.9, 129.7, 128.7, 128.6, 128.6, 128.5, 128.3, 127.7, 94.4, 70.4, 67.2, 66.6, 63.5, 57.8, 54.1, 52.3, 24.8, 11.4. Anal. Calcd for $C_{39}H_{34}NO_{10}Cl$: C, 65.78; H, 4.81; N, 1.97; Cl, 4.98. Found: C, 65.70; H, 4.86; N, 2.04; Cl, 4.63.

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Supporting Information Available: Experimental details (**9b**) and the full listing of spectroscopic and microanalytical data for compounds **22** and **25** as well as the diastereomers **4**, **8**, **17a**, **18**, **26**, and **27**, and X-ray crystal structures of compound **10a**,**b** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information

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