Stereoselective Conjugate Addition of Mixed Organoaluminum Reagents to α,β-Unsaturated *N*-Acyloxazolidinones Derived from Carbohydrates

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Dedicated to Professor Herbert Meier on the occasion of his 65th birthday.

Abstract: The stereoselective synthesis of β-branched carboxylic acid derivatives was accomplished by conjugate addition of mixed organoaluminum reagents to chiral α,β-unsaturated *N*-acyloxazolidinones. Mixed organoaluminum reagents were generated in situ by transmetalation of Grignard or organolithium compounds with methylaluminum dichloride. Efficient stereocontrol was achieved using different bicyclic glycosamine-derived oxazolidinones, yielding alternatively (*R*)- or (*S*)-configured β-branched carboxylic acid derivatives.

Key words: stereoselective Michael additions, organoaluminum compounds, chiral carboxylic acids, carbohydrates, auxiliaries

The synthesis of carboxylic acids branched at the β-position can efficiently be accomplished by Michael addition or analogous 1,4-addition reactions of carbon nucleophiles to enone systems. Whereas organoaluminum compounds play an important role as Lewis acids and catalysts in the polymerization of olefins,[1] conjugate addition reactions of organoaluminum reagents have only rarely been reported, in contrast to analogous reactions of organocuprates and Grignard compounds. The conjugate addition of organoaluminum reagents obviously suffers from decreased reactivity and regioselectivity of these nucleophiles.[2] A few examples of conjugate addition reactions of alkenyl groups from organoaluminum reagents have been reported. Hexenyl diisobutylalane, for example, transfers the alkenyl moiety to α,β-unsaturated ketones in 35% yield.[3] The conjugate addition of alkynyl groups was also achieved by the application of mixed organoaluminum compounds.[4]

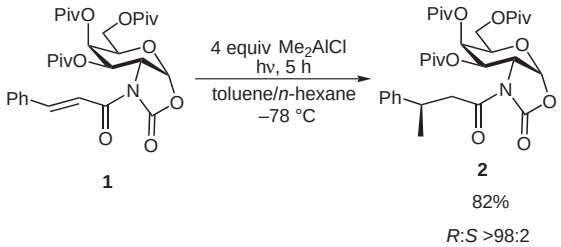
Recent studies have shown that the chemoselective 1,4-addition of dialkylaluminum chlorides to alkylidenemalonic acid esters is efficiently accomplished.[5] The stereoselective version of this reaction was successfully performed by applying chiral oxazolidinones derived from amino acids[6] or carbohydrates.[7–9] In the latter case, β-branched carboxylic acid derivatives were obtained with excellent stereoselectivity, especially when an *O*-pivaloyl protected bicyclic galactosamine-derived oxazolidinone (**9**) was used as the auxiliary.

Mixed methylalkylaluminum chlorides and trimethylalkylaluminates, generated by transmetalation of organolithium or Grignard compounds with $MeAlCl_2$ or Me_3Al, respectively, proved to be useful reagents in 1,4-addition reactions, thereby extending the methodology beyond the limited number of commercially available dialkylaluminum chlorides.[10]

In this article, the stereoselective conjugate addition of mixed organoaluminum reagents to α,β-unsaturated acceptors is described. The given conversions are based on bicyclic carbohydrate oxazolidinones as efficient stereodifferentiating tools.

Among organoaluminum compounds, the dialkylaluminum chlorides have shown the most favourable reactivity and selectivity in 1,4-addition reactions to the *N*-acyloxazolidinone acceptors (for example, **1**).[8,9] The reaction was restricted by the fact that only a few dialkylaluminum chlorides are commercially available and that syntheses of these air-sensitive compounds are often rather demanding, requiring, for example, the use of organomercury or organotin compounds.[11]

Under the reaction conditions for conjugate addition to **1** (toluene, –78 to –45 °C), the Me-Al bond shows no reactivity. It was demonstrated, in detailed studies, that even at elevated temperature (–20 °C) and with larger excess, dimethylaluminum chloride fails to deliver a methyl group to α,β-unsaturated acceptors, whereas this reaction proceeds efficiently under UV-irradiation (Scheme 1).[9]



Scheme 1 1,4-Addition of dimethylaluminum chloride[9]

Mixed organoaluminum species selectively transfer non-methyl groups in 1,4-addition reactions.[5,9,10]

In transmetalation processes, various alkyl, alkenyl (vinyl), aryl and alkynyl aluminum compounds **3a–f** can be generated by subjecting commercially available $MeAlCl_2$

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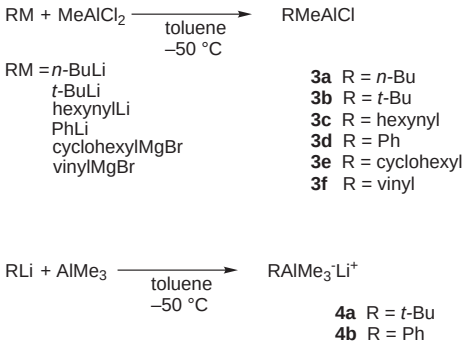
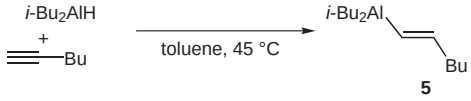
to reaction with organolithium or Grignard compounds in toluene at –50 °C. In an analogous manner, aluminates **4** can be produced as Michael reagents from Me_3Al (Scheme 2).



Scheme 2 Generation of mixed organoaluminum reagents by transmetalation reactions

A more general access to organoaluminum compounds for the transfer of alkenyl groups is the hydroalumination of alkynes, yielding *trans*-configured alkenyl aluminum compounds.[12] Accordingly, an appropriate diisobutylalane **5** was synthesized from 1-hexyne and diisobutyl aluminum hydride at 45 °C in toluene (Scheme 3).



Scheme 3 Synthesis of mixed organoaluminum reagent by hydroalumination of 1-hexyne

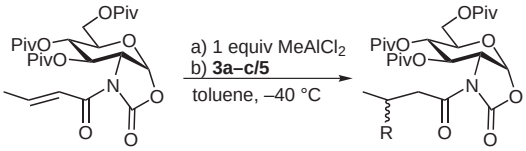
With the exception of commercially available Et_2AlCl and $(i\text{-}Bu)_2AlCl$, the reagents investigated in the following conjugate addition reactions were prepared in situ, according to Scheme 2 and Scheme 3, prior to the 1,4-addition reaction.

Among the glycosamine-derived oxazolidinones efficient in 1,4-addition reactions of dialkylaluminum chlorides, the glucosamine-derived Michael acceptor **6** was first investigated in reactions with mixed diorganyl (**3**) and triorganyl aluminum (**5**) reagents.

The reactions were carried out at –40 °C with toluene as the solvent. Prior to the 1,4-addition reaction, the α,β-unsaturated acceptor was subjected to one equivalent of a strong Lewis acid ($MeAlCl_2$) to form a chelating complex with the acyl and oxazolidinone carbonyl groups. The mixed aluminum reagent used for 1,4-addition should also form a chelating complex with substrate **6**, but our investigations have shown that subjecting the acceptor to $MeAlCl_2$ prior to the conjugate addition significantly increases the stereoselectivity.[9]

As shown in Table 1, conjugate addition reactions of aluminum nucleophiles **3a**, **3b** and **5** to Michael acceptor **6** yielded the β-branched carboxylic derivatives **7a**–**c** with diastereomeric ratios in the range of 70:30, whereas the

Table 1 Conjugate Addition of Mixed Aluminum Reagents to Glucose-Derived *N*-Acyloxazolidinones **6**



6 **7**

Product	Reagent (equiv)	R	Yield (%)	Conversion (%)	dr[a] (3*R*):(3*S*)
7a	**3a** (10)	*n*-Bu	55	85	75:25[b]
7b	**3b** (10)	*t*-Bu	31	90	34:66[c]
7c	**5** (8)	hexenyl	38	75	33:67
7d	**3c** (5)	hexynyl	40	68	46:54

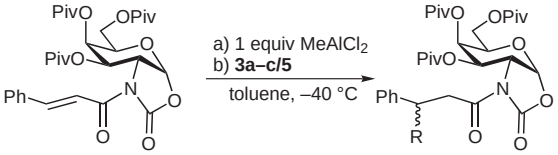
[a] Determined by ^1H NMR, unless otherwise indicated.
[b] Determined by ^{13}C NMR.
[c] Determined by HPLC.

1,4-addition of hexynylmethylaluminum chloride **3c** proceeded with lower selectivity (**7d**).

Galactosamine-derived chiral template **1**[9] was shown to be a more efficient stereodifferentiating tool in comparison to the glucosamine auxiliary in acceptor **6**. In addition, sterically more demanding cinnamic acid acceptors like **1** should be superior to crotonic acid derivatives such as **6**. In order to enhance the stereoselectivity of the addition, the application of acceptor **1** was investigated (Table 2).

Indeed, the conjugate addition to α,β-unsaturated *N*-acyloxazolidinone **1** proceeded with significantly higher diastereoselectivity (Table 2). β-Branched carboxylic acid derivatives were formed in diastereomeric ratios from 84:16 up to almost enantiomerically pure products (**8a**). In

Table 2 1,4-Addition Reactions of Mixed Aluminum Reagents to Galactose-Based Acceptor **1**



1 **8**

Product	Reagent (equiv)	R	Yield (%)	Conversion (%)	dr[a] (3*R*):(3*S*)
8a	**3a** (10)	*n*-Bu	77	quant.	99:1
8b	**3b**[b] (10)	*t*-Bu	58	90	11:89
8c	**5** (10)	hexenyl	44	85	11:89
8d	**3c** (10)	hexynyl	33	83	16:84

[a] Determined by ^1H NMR.
[b] BF_3 was added to minimize β-H elimination.

order to reduce the competing β-hydrogen transfer, which was observed in the transfer of sterically demanding groups,[5,10] BF_3 was added for the preparation of **8b**.

In general, the products from transfer of the *n*-butyl group (**7a**, **8a**) were obtained in the highest stereoselectivity and yield. The transfer of hexenyl and *tert*-butyl moieties resulted in similar yield and selectivity using acceptor **1** as well as acceptor **6** (adducts **7b**, **7c** and **8b**, **8c**). As shown in Table 1 and Table 2, various carbon nucleophiles, even those containing sterically demanding (adducts **7b**, **8b**) and unsaturated substituents (adducts **7c**, **7d**, **8c** and **8d**), can be introduced in the β-position of the carboxylic acid by this method. The absolute configuration of the major diastereomers of type **7** and **8** was deduced by comparing the optical rotation data of known free carboxylic acids obtained after release from the auxiliary (see also Scheme 6) with compounds described in the literature.[9] Unfortunately, some reactions suffered from incomplete conversion even when ten equivalents of the reagent were used.

Our next interest concerned the expansion of the described method to access the opposite enantiomers of the β-branched carboxylic acids. Since preparation of the bicyclic oxazolidinone from L-galactose was not a realistic option, D-arabinose was used as the source for the auxiliary.[13] The only difference between L-galactose and D-arabinose is the absence of the C-5 hydroxymethyl group in D-arabinose. However, as the 1,4-addition occurs in proximity of C-2, C-3 and C-4,[9] the missing substituent should have only a marginal effect on the stereodifferentiating potential of the D-arabinose auxiliary **10** (Figure 1).

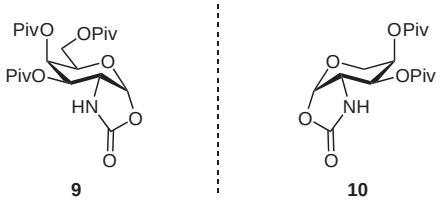
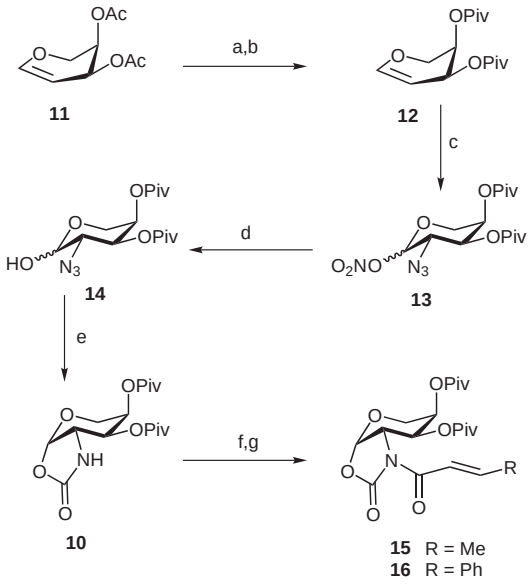


Figure 1 Bicyclic carbohydrate auxiliaries

Synthesis of **10** was accomplished in analogy to that of chiral auxiliary **9**[9] (Scheme 4). From readily accessible acetylated arabinal **11**,[14] *O*-acetyl groups were replaced by *O*-pivaloyl groups under Zemplen conditions for deprotection, and subsequently esterified with pivaloyl chloride (**12**). After azidonitration according to Lemieux[15] (**13**) and hydrolysis of the nitrate[16] using aqueous sodium nitrite (**14**), the bicyclic oxazolidinone **10** was formed in a Staudinger–aza-Wittig reaction sequence with triphenyl phosphine and carbon dioxide. The α,β-unsaturated acyl oxazolidinones **15** and **16** were obtained by deprotonation of **10** with methylmagnesium chloride, followed by treatment with crotonoyl or cinnamoyl chloride, respectively.

The conjugate addition of various aluminum nucleophiles to these Michael acceptors **15** and **16** were examined under standard conditions at –55 °C (Table 3). The α,β-unsaturated acceptor was treated with 1.5 equivalents of $MeAlCl_2$ prior to the reaction. Commercially available Et_2AlCl and $(i\text{-}Bu)_2AlCl$ gave excellent yield and stereoselectivity (adducts **18a**, **18b**). The sterically more demanding and less reactive $(i\text{-}Bu)_2AlCl$ chloride reacted smoothly under these conditions (**17a**, **18b**).



Scheme 4 Synthesis of D-arabinose-derived bicyclic oxazolidinone acceptors **15** and **16**. *Reagents and conditions:* (a) NaOMe, MeOH, 20 °C; (b) pivaloyl chloride, pyridine, 20 °C, 88% over two steps; (c) NaN_3, $Ce(NH_4)_2(NO_3)_6$, MeCN, –25 °C, 33%; (d) $NaNO_2$, dioxane–H_2O, 61%; (e) PPh_3, CO_2, dioxane, 20 °C, 64%; (f) MeMgCl, THF, 0 °C; (g) 1.1 equiv crotonoyl chloride (**15**) or cinnamoyl chloride (**16**), –78 °C→0 °C, 74–82%.

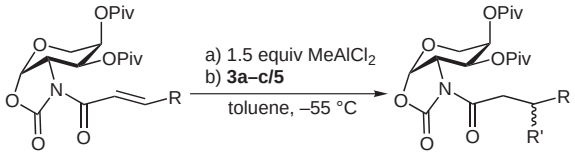
Mixed organoaluminum reagents showed lower reactivity as they required ten equivalents of reagent for high rates of conversion. Indeed, good yields could be achieved, especially with alkyl nucleophiles (**17a**, **17b**, **18a**–**c**). Use of cyclohexylmagnesium bromide in Et_2O, instead of the lithium compound (in hexane), for transmetalation with $MeAlCl_2$ resulted in lower diastereoselectivity (**18e**). The more nucleophilic aluminate **4a** gave a slightly higher yield in the addition reaction to the cinnamoyl acceptor **16**, compared to the product obtained by reaction with dialkylaluminum chloride **3b**, but in this case the diastereoselectivity was lower.

Analogous addition reactions of methylphenylaluminum chloride (**3d**) and methylvinylaluminum chloride (**3f**) to α,β-unsaturated acceptor **15** or **16** failed. In both cases, the starting material was recovered.

In order to increase the reactivity of the phenyl alane, addition with phenyltrimethylaluminate **4b** was examined. Even after prolonged reaction times, HPLC analysis of the crude reaction mixture showed only 50% conversion, and a mixture of products from phenyl addition (**18h**) and methyl addition (**19**) was formed in a ratio of 1:2.3 (Scheme 5).

To confirm the stereochemical outcome of the reaction performed with bicyclic oxazolidinone **10**, the product of

Table 3 Conjugate Addition of Mixed Organoaluminum Compounds to Arabinose-Derived α,β-Unsaturated Acceptors **15** and **16**

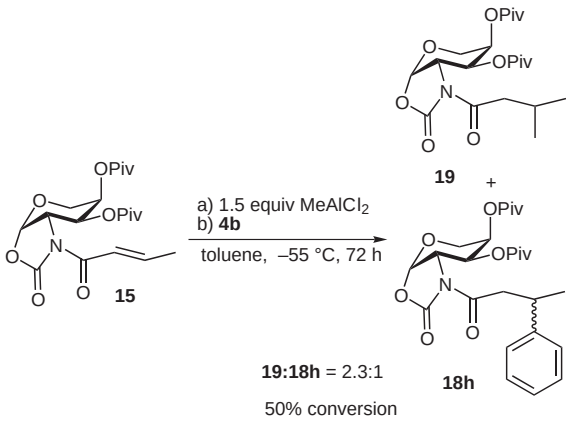


15 R = Me
16 R = Ph

17a-e R = Me
18a-i R = Ph

Reagent	Equiv	Acceptor	R	R^1	Reaction time (h)	Product	Yield/ Conversion (%)	dr (3*S*):(3*R*)
i-Bu_2AlCl	10	**15**	Me	*i*-Bu	3	**17a**	75	73:27[a]
3a (*n*-BuMeAlCl)	10	**15**	Me	*n*-Bu	10	**17b**	71	72:28[b]
3b (*t*-BuMeAlCl)	10	**15**	Me	*t*-Bu	16	**17c**	42	28:72[a]
5 [hexenyl(*i*-Bu)$_2$Al]	10	**15**	Me	hexenyl	18	**17d**	46/90	25:75[b]
3c (hexynylMeAlCl)	12	**15**	Me	hexynyl	72	**17e**	41	35:65[b]
Et_2AlCl	3	**16**	Ph	Et	18	**18a**	83	96:4[c]
i-Bu_2AlCl	6	**16**	Ph	*i*-Bu	5	**18b**	76	95:5[c]
3a (*n*-BuMeAlCl)	10	**16**	Ph	*n*-Bu	18	**18c**	69	96:4[c]
3b (*t*-BuMeAlCl)	10	**16**	Ph	*t*-Bu	18	**18d**	54	5:95[c]
4a (*t*-$BuMe_3Al^-Li^+$)	10	**16**	Ph	*t*-Bu	16	**18d**	57	9:91[c]
3e (cyclohexylMeAlCl)	10	**16**	Ph	cyclohexyl	16	**18e**	50/75	29:71[c]
5 [hexenyl(*i*-Bu)$_2$Al]	10	**16**	Ph	hexenyl	40	**18f**	41/90	19:81[b]
3c (hexynylMeAlCl)	10	**16**	Ph	hexynyl	72	**18g**	16/55	19:81[b]
3d (PhMeAlCl)	10	**15**	Me	Ph	72	**18h**	–	–
3f (vinylMeAlCl)	10	**16**	Ph	vinyl	72	**18i**	–	–

[a] Determined by ^{13}C NMR.
[b] Determined by ^1H NMR.
[c] Determined by HPLC.

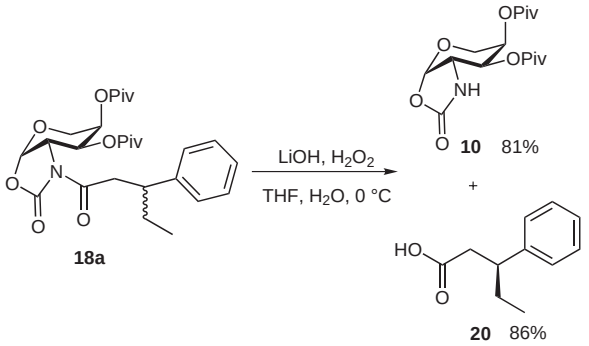


Scheme 5 Reaction of lithium phenyltrimethylalanate **4b** with acceptor **15**

ethyl addition (**18a**, dr = 97:3) was subjected to hydrolysis with LiOH–H_2O_2 in THF–H_2O (Scheme 6).[8,17] Auxiliary **10** and carboxylic acid **20** were readily isolated from the reaction mixture by aqueous extraction. Comparison of the optical rotation value with that of an authentic sample of carboxylic acid **20** described in the literature[18] proved the absolute configuration of **20** to be *S*. Thus, the arabinose-derived oxazolidinone **10** serves as pseudo-enantiomeric auxiliary to **9** and, therefore, leads to the (*S*)-enantiomer of the β-branched carboxylic acid as the major stereoisomer (Scheme 6).

In summary, concerning yield and stereoselectivity, comparable results in the synthesis of the enantiomeric β-branched carboxylic acids can be achieved by applying either the galactose- or arabinose-derived bicyclic oxazolidinones. The glucose-derived auxiliary is somewhat less efficient.

The results described herein show that a great variety of aluminum carbon nucleophiles, particularly mixed organoaluminum reagents, can be utilized in 1,4-addition reactions. The β-branched carboxylic acids can be synthesized with high stereoselectivity. Chiral auxiliaries derived



Scheme 6 Detachment of β-branched carboxylic acid **20** from the chiral template and confirmation of the absolute configuration

from D-galactose on the one hand and D-arabinose on the other hand offer an alternative access to either (*R*)- or (*S*)-configured β-branched carboxylic acids.

Solvents were dried and distilled before use. Analytical TLC was performed on aluminum-backed TLC plates coated with silica gel $60F_{254}$ (E. Merck, Darmstadt). Column chromatography was performed on silica (63–200 μm, Baker or 40-63 μm, E. Merck, Darmstadt). Melting points were measured on a Dr. Tottoli apparatus (Büchi) and are uncorrected. Optical rotation values were measured on a Perkin-Elmer 241 polarimeter. NMR spectra were recorded on a Bruker WT-200 and a Bruker AM 400 spectrometer; chemical shifts are given in ppm downfield from tetramethylsilane. FD-MS spectra were measured on a MAT 95-spectrometer (Finnigan). ESI-MS were measured on a Navigator (ThermoQuest) between 200 and 1300 amu at a cone voltage of 70 eV using a flow rate of 0.75 mL/min MeCN–H_2O (70:30 v/v) and a nitrogen flow of 300 L/h. A basic marathon autosampler was employed for sample injection (20 μL at 0.1 g/L). Analytical HPLC analyses were performed on a Knauer system (LKB 2150) equipped with a diode array detection (LKB2140) and a LUNA C18-2 column (Phenomenex, 250 × 4.6 mm, 5 μm particle size) in MeCN–H_2O using a flow rate of 1 mL/min. HPLC-MS analysis was performed on a Navigator system described above and Knauer HPLC system with a LUNA C18-2 column (Phenomenex, 75 × 4.6 mm, 3 μm particle size) in combination with a flow splitter (ratio 10:1). Preparative HPLC was performed on a Knauer system equipped with a LUNA C18-2 column (Phenomenex, 250 × 50 mm, 10 μm particle size) and a diode array UV detector at a flow rate of 20 mL/min. Light petroleum ether is abbreviated throughout as LPE.

Synthesis of chiral auxiliary 10 and acceptors 15 and 16: 1,5-Anhydro-3,4-di-*O*-pivaloyl-2-deoxy-D-erythro-pent-1-enitol (12)

To a solution of arabinal **11**[14] (94.6 g, 470 mmol) in dry MeOH (440 mL) was added NaOMe in dry MeOH (0.5 M, 266 mL, 133 mmol) at 0 °C. After 15 min, the ice bath was removed and the solution was stirred for additional 3 h at 20 °C. Then the solvent was removed in vacuo. The deacetylated crude product was dissolved in pyridine (5 L). Pivaloyl chloride (180 mL, 1.5 mol) was added at 0 °C under argon atmosphere. After 3 d, additional pivaloyl chloride (20 mL, 167 mmol) was added and stirring was continued for 1 d. Then, pyridine was removed in vacuo. The residue was dissolved in CH_2Cl_2 (2 L) and washed with 2 N HCl (3 × 350 mL), sat. $NaHCO_3$ (3 × 500 mL) and sat. NaCl (1 L). The organic layer was dried with $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash chromatography in LPE–EtOAc (12:1).

Yield: 118 g (415 mmol, 88%); colourless oil; R_f = 0.51 (LPE–EtOAc, 9:1); $[\alpha]_D^{21}$ +160.1 (c = 1.0, $CHCl_3$).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.16, 1.18 (2 s, 18 H, C(C*H*$_3$)$_3$), 3.96 (m, 2 H, H-5a, H-5b), 4.85 (dd, 1 H, *J* = 5.9, 5.4 Hz, H-2), 5.13 (q, 1 H, *J* = 4.9, 4.4, 3.9 Hz, H-4), 5.35 (dd, 1 H, *J* = 4.9, 3.9 Hz, H-3), 6.45 (d, 1 H, *J* = 6.3 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 26.50, 27.15 [C(*C*H$_3$)$_3$], 38.72, 38.86 [*C*(CH$_3$)$_3$], 62.71 (C-5), 62.88, 66.22 (C-3, C-4), 97.74 (C-2), 147.51 (C-1), 177.27, 177.56 (*C*O, pivaloyl).

Anal. Calcd for $C_{15}H_{24}O_5$ (284.36): C, 63.36; H, 8.51. Found: C, 63.72; H, 8.73.

FD-MS (+): *m/z* = 284.7 $[M]^+$, 183.5 $[M - PivOH]^+$.

2-Azido-2-deoxy-3,4-di-*O*-pivaloyl-D-arabinopyranosyl nitrate (13)[15]

To **12** (46 g, 161 mmol) in dry degassed MeCN (800 mL), NaN_3 (15.5 g, 238 mmol) and $Ce(NH_4)_2(NO_3)_6$ (300 g, 547 mmol) was added at –50 °C under argon atmosphere. The yellow solution was stirred overnight at –25 °C. The reaction mixture was diluted with ice-cold Et_2O (900 mL) and ice-cold H_2O (900 mL). The organic layer was separated, washed with ice-cold H_2O (3 × 900 mL), dried with $MgSO_4$ and concentrated in vacuo (bath temperature <35 °C). The crude product was purified by flash chromatography in LPE–EtOAc (15:1).

Yield: 20.7 g (53.3 mmol, 33%); colourless oil; R_f = 0.48 (LPE–EtOAc, 6:1); $[\alpha]_D^{21}$ –117.7 (c = 1.0, $CHCl_3$).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.19, 1.23 [s, 18 H, C(C*H*$_3$)$_3$], 3.83 (dd, 1 H, *J* = 13.2, 2.0 Hz, H-5a), 4.13 (m, 2 H, *J* = 13.2, 3.4 Hz, H-2, H-5b), 5.22 (dd, 1 H, *J* = 3.4, 11.2 Hz, H-3), 5.36 (d, 1 H, *J* = 1.5 Hz, H-4), 6.34 (d, 1 H, *J* = 3.9 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 26.50, 26.96 [C(*C*H$_3$)$_3$], 38.86, 40.19 [*C*(CH$_3$)$_3$], 56.97 (C-2), 63.31 (C-5), 67.46, 68.21 (C-3, C-4), 97.8 (C-1), 177.0 (*C*O, pivaloyl).

$C_{15}H_{24}N_4O_8$ (388.38).

FD-MS (+): *m/z* = 389.1 $[M + H]^+$.

2-Azido-2-deoxy-3,4-di-*O*-pivaloyl-D-arabinopyranose (14)[16]

To a solution of **13** (20 g, 51.4 mmol) in dioxane (233 mL) was added $NaNO_2$ (12.85 g, 186 mmol) in H_2O (42 mL), and the reaction mixture was stirred at 80 °C for 5 h. Then, H_2O (150 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 150 mL). The organic layer was dried with $MgSO_4$, concentrated in vacuo, and the crude product was purified by flash chromatography in LPE–EtOAc (8:1).

Yield: 11.3 g (32.9 mmol, 61%); colourless oil; R_f = 0.63 (LPE–EtOAc, 1:1); $[\alpha]_D^{22}$ –81.8 (c = 1.0, $CHCl_3$); anomeric ratio 2.5:1 (200 MHz ^{1}H NMR).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.18, 1.21, 1.22, 1.24 [s, 18 H, C(C*H*$_3$)$_3$], 3.44 (br s, 1 H, O*H*), 3.59–3.76 (m, 2 H, *J* = 12.7, 7.8, 1.5 Hz, H-2, H-5a), 4.14 (dd, 1 H, *J* = 12.7, 1.0 Hz, H-5b), 4.60 (d, 1 H, *J* = 7.8 Hz, α-H-1), 4.82 (dd, 1 H, *J* = 3.4, 0.7 Hz, α-H-3), 5.16 (m, α-H-4), 5.30 (br d, 1 H, *J* = 1.5 Hz, β-H-4), 5.34–5.40 (m, 2 H, *J* = 3.4 Hz, $^3J_{1,2}$ = 7.8 Hz, β-H-3, β-H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 26.97, 27.04, 27.13, 27.45 [C(*C*H$_3$)$_3$], 38.86, 38.94, [*C*(CH$_3$)$_3$], 59.16, 63.07 (C-2), 60.66, 64.48 (C-5), 67.37, 68.05, 68.50, 71.14 (C-3, C-4), 92.67, 96.66 (C-1), 177.34, 177.62 (*C*O, pivaloyl).

Anal. Calcd for $C_{15}H_{25}N_3O_6$ (343.38): C, 52.47; H, 7.34; N, 12.24. Found: C, 52.52; H, 7.39; N, 12.28.

ESI-MS: *m/z* = 366.2 $[M + Na]^+$, 382.3 $[M + K]^+$.

1,2-Dideoxy-1,2-(epoxycarbonylimino)-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (10)

A solution of **14** (4.52 g, 13.2 mmol) in dry degassed dioxane (135 mL) was treated with a stream of dry CO_2 gas at 20 °C. After 1 h,

PPh_3 (3.9 g, 14.9 mmol) in dry dioxane (23 mL) was added dropwise over 30 min. Treatment with CO_2 was continued for 8 h, then the reaction mixture was stirred overnight. The solvent was removed in vacuo and the product was purified by flash chromatography in LPE–EtOAc (8:1).

Yield: 2.86 g (64%); colourless, amorphous solid; R_f = 0.28 (LPE–EtOAc, 4:1); mp 195 °C; $[\alpha]_D^{22}$ –82.6 (c = 1.0, $CHCl_3$).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.19, 1.21 [s, 18 H, C(CH_3)$_3$], 3.76 (dd, 1 H, *J* = 7.3, 6.3 Hz, H-2), 3.94 (dd, 1 H, *J* = 12.7, 2.9 Hz, H-5a), 4.26 (q, 1 H, *J* = 12.7 Hz, H-5b), 5.21 (m, 1 H, H-4), 5.28 (dd, 1 H, *J* = 7.3, 3.9 Hz, H-3), 5.92 (d, 1 H, *J* = 6.4 Hz, H-1), 6.98 (s, 1 H, N-*H*).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 26.96, 27.09 [C(*C*H$_3$)$_3$], 38.85, 38.94 [*C*(CH$_3$)$_3$], 53.39 (C-2), 63.14 (C-5), 65.99, 71.69 (C-3, C-4), 98.34 (C-1), 157.96 (*C*O, urethane), 177.15, 177.85 (*C*O, pivaloyl).

Anal. Calcd for $C_{16}H_{25}NO_7$ (343.38): C, 55.97; H, 7.34; N, 4.08. Found: C, 55.91; H, 7.35; N, 4.03.

ESI-MS: *m/z* = 366.2 $[M + Na]^+$, 709.4 $[2 M + Na]^+$.

1,2-Dideoxy-1,2-[(*E*)-*N*-(2-butenoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (15)

To a solution of **10** (3 g, 8.7 mmol) in THF (140 mL) at 0 °C was added methylmagnesium chloride (3.2 mL, 9.7 mmol, 3 M in THF, 1.1 equiv). After 15 min the reaction mixture was cooled to –78 °C, and freshly distilled crotonoyl chloride (0.92 mL, 9.61 mmol) was added via syringe. Stirring was continued for 15 min at this temperature. After raising the temperature to 0 °C, stirring was continued until complete conversion was detected (ca. 1 h). The reaction mixture was poured into sat. NH_4Cl (35 mL) and the THF was removed under reduced pressure. Et_2O (200 mL) was added to the mixture, then the organic layer was washed with sat. $NaHCO_3$ and dried with $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography in LPE–EtOAc (10:1).

Yield: 2.65 g (74%); colourless, amorphous solid; R_f = 0.55 (LPE–EtOAc, 4:1); mp 143 °C; $[\alpha]_D^{22}$ +11.3 (c = 1.0, $CHCl_3$).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.16, 1.23 [s, 18 H, C(CH_3)$_3$], 1.93 (d, 3 H, *J* = 5.4 Hz, CH_3), 3.97 (dd, 1 H, *J* = 12.7, 3.4 Hz, H-5a), 4.11 (dd, 1 H, *J* = 12.7, 2.0 Hz, H-5b), 4.73 (dd, 1 H, *J* = 5.9, 7.8 Hz, H-2), 5.17 (dd, 1 H, *J* = 3.4, 2.0 Hz, H-4), 5.25 (dd, 1 H, *J* = 7.3, 3.9 Hz, H-3), 5.89 (d, 1 H, *J* = 6.4 Hz, H-1), 7.11 (m, 2 H, C*H*=C*H*).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 18.53 (=CH-*C*H$_3$), 26.86, 27.09 [C(*C*H$_3$)$_3$], 38.70, 38.94 [*C*(CH$_3$)$_3$], 53.74 (C-2), 62.96 (C-5), 65.80, 69.33 (C-3, C-4), 96.78 (C-1), 121.77 (MeCH=*C*H), 147.59 (Me*C*H=CH), 150.65 (*C*O, urethane), 164.06 (*C*O, acyl), 177.18 (*C*O, pivaloyl).

Anal. Calcd for $C_{20}H_{29}NO_8$ (411.46): C, 58.38; H: 7.10; N: 3.40. Found: C, 58.24; H, 7.24; N, 3.30.

FD-MS (+): *m/z* = 413.0 $[M + H]^+$.

1,2-Dideoxy-1,2-[(*E*)-*N*-(3-phenyl-2-propenoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (16)

The synthesis of **16** was accomplished in analogy to that of **15** from **10** (1.3 g, 3.79 mmol) and freshly distilled cinnamoyl chloride (694 mg, 3.9 mmol). The product was purified by flash column chromatrography in LPE–EtOAc (10:1).

Yield: 1.42 g (82%); colourless, amorphous solid; R_f = 0.57 (LPE–EtOAc, 4:1); mp 126 °C; $[\alpha]_D^{22}$ –11.4 (c = 1.0, $CHCl_3$).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.18, 1.27 [s, 18 H, C(CH_3)$_3$], 3.97 (dd, 1 H, *J* = 12.7, 2.9 Hz, H-5a), 4.11 (dd, 1 H, *J* = 12.7, 1.96 Hz, H-5b), 4.73 (dd, 1 H, *J* = 7.8, 5.9 Hz, H-2), 5.17 (ddd, 1 H, *J* = 3.4, 2.9, 1.96 Hz, H-4), 5.25 (dd, 1 H, *J* = 7.8, 3.4 Hz, H-3), 5.89 (d, 1 H, *J* = 5.9 Hz, H-1), 7.37 (m, 3 H, *m*-Ar, *p*-Ar), 7.58 (m, 2 H, *o*-Ar), 7.80 (m, 2 H, C*H*=C*H*).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 26.89, 27.10 [C(*C*H$_3$)$_3$], 38.74, 38.97 [*C*(CH$_3$)$_3$], 53.88 (C-2), 63.02 (C-5), 65.83, 69.41 (C-3, C-4), 96.89 (C-1), 116.84 (PhCH=*C*H), 128.71, 128.90, 130.85 (C-Ar), 134.38 (C-ipso), 147.00 (Ph*C*H=CH), 150.78 (*C*O, urethane), 164.38 (*C*O, acyl), 177.21 (*C*O, pivaloyl).

Anal. Calcd for $C_{25}H_{31}NO_8$ (473.53): C, 63.41; H, 6.60; N, 2.96. Found: C, 63.34; H, 6.76; N, 3.12.

FD-MS (+): *m/z* = 474.0 $[M + H]^+$.

1,4-Addition Reactions, General Procedures: Preparation of Organoaluminum Reagents 3–5

Method A (mixed dialkylaluminum chlorides **3**): Toluene was cooled to –40 °C in a dried flask under argon atmosphere. $MeAlCl_2$ (1 M in hexane) and equimolar amounts of the Grignard or organolithium reagent were added through a rubber septum using a syringe. The mixture was stirred for 1 h at this temperature.

Method B (ate-complexes **4**): In a dried flask, toluene and Me_3Al (2 M in pentane) were placed at –50 °C under argon atmosphere. Organolithium or Grignard compound was added and the mixture was stirred for 1 h.

Method C (hexenyldiisobutylalane **5**): Dry toluene, DIBAL-H and 1-hexyne were placed in a dried flask and stirred at 45 °C for 2 h under argon atmosphere.

1,4-Addition of Organoaluminum Reagents to α,β-Unsaturated *N*-Acyl Oxazolidinones 1, 6, 15 and 16:

The α,β-unsaturated acceptor (**1**, **6**, **15** or **16**) in toluene (details are quoted for every compound) was cooled to –55 °C and 1–1.25 equiv $MeAlCl_2$ (1 M in hexane) were added via syringe. After stirring for 1 h, the aluminum reagent [prepared in a separate flask according to method A-C or commercially available Et_2AlCl or (i-Bu_2)AlCl] was added rapidly via syringe. The reaction mixture was stirred at –55 °C or –40 °C, typically for 18–20 h. The reaction was terminated by addition of sat. NH_4Cl (100 mL) and then extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with aq sat. NH_4Cl (40 mL) and then dried with $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by flash chromatography (LPE–EtOAc, 15:1) except for **7c**, **8c**, **17d** and **18f**, which were purified by preparative HPLC.

1,2-Dideoxy-1,2-[*N*-(3-methylheptanoyl)epoxycarbonylimino]-3,4,6-tri-*O*-pivaloyl-α-D-glucopyranose (7a)

According to general procedure, method A. Reagents: $MeAlCl_2$ (1 M in hexane, 5.7 mL, 5.7 mmol), *n*-BuLi (1.6 M in pentane, 3.6 mL, 5.76 mmol), toluene (50 mL); **6** (300 mg, 0.57 mmol), $MeAlCl_2$ (1.0 M in hexane, 0.6 mL, 0.6 mmol), toluene (50 mL).

Yield: 182 mg (55%); colourless, amorphous solid; R_f = 0.62 (LPE–EtOAc, 5:1); $[\alpha]_D^{22}$ –24.4 (c = 1.0, $CHCl_3$); diastereomeric ratio 75:25 (*C*HN, 100.6 MHz ^{13}C NMR).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.91 [m, 6 H, (CH$_2$)$_3$CH_3, CHCH_3], 1.12, 1.16, 1.18 [s, 27 H, C(CH_3)$_3$], 1.10–1.34 [m, 6 H, (CH_2)$_3$], 1.91–2.00 (m, 1 H, C*H*CH$_3$), 2.68 (dd, 1 H, *J* = 17.0, 7.9 Hz, CH_2CO), 2.80 (dd, 1 H, *J* = 17.0, 5.3 Hz, CH_2CO), 4.00–4.04 (m, 1 H, H-5), 4.16 (dd, 1 H, *J* = 12.3, 5.3 Hz, H-6a), 4.22 (dd, 1 H, *J* = 12.3, 2.6 Hz, H-6b), 4.58 (dd, 1 H, *J* = 6.8, 5.0 Hz, H-2), 5.04 (dd, 1 H, *J* = 8.7, 6.3 Hz, H-4), 5.35 (dd, 1 H, *J* = 6.5, 5.0 Hz, H-3), 5.90 (d, 1 H, *J* = 7.0 Hz, H-1).

(minor diastereomer) δ = 2.65 (dd, 1H, *J* = 17.0, 7.9 Hz, CH_2CO), 5.34 (dd, 1H, *J* = 6.5, 4.7 Hz, H-2).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 13.99 [(CH$_2$)$_3$*C*H$_3$], 19.72 (CH*C*H$_3$), 22.71 (*C*H$_2$), 26.94, 26.98, 27.04 (C(*C*H$_3$)$_3$), 29.12 (*C*H$_2$), 29.20 (*C*HCH$_3$), 36.39 (CH*C*H$_2$CH$_2$), 38.66, 38.80 [*C*(CH$_3$)$_3$], 42.72 (*C*H$_2$CO), 55.18 (C-2), 62.01 (C-6), 65.73, 69.71, 70.21 (C-3, C-4, C-5), 95.08 (C-1), 150.88 (*C*O, urethane), 171.86 (*C*O, acyl), 176.23, 176.45, 177.46 (*C*O, pivaloyl).

(minor diastereomer) δ = 19.66 (CH*C*H$_3$), 29.04, 36.44 (CH*C*H$_2$*C*H$_2$), 55.26 (C-2).

Anal. Calcd for $C_{30}H_{49}NO_{10}$ (583.73): C, 61.73; H, 8.46; N, 2.40. Found: C, 61.74; H, 8.54; N, 2.20.

1,2-Dideoxy-1,2-[*N*-(3,4,4-trimethylpentanoyl)epoxycarbonylimino]-3,4,6-tri-*O*-pivaloyl-α-D-glucopyranose (7b)

According to general procedure, method A. Reagents: $MeAlCl_2$ (5.7 mL, 5.7 mmol, 1.0 M in hexane), *t*-BuLi (3.8 mL, 5.7 mmol, 1.7 M in hexane), toluene (50 mL), **6** (300 mg, 0.57 mmol), $MeAlCl_2$ (0.6 mL, 0.6 mmol, 1.0 M in hexane), toluene (50 mL). The product was purified by preparative HPLC in MeCN–H_2O (75:25).

Yield: 102 mg (31%); 90% conversion; colourless, amorphous solid; R_f = 0.62 (LPE–EtOAc, 5:1); $[\alpha]_D^{22}$ –15.3 (c = 1.0 $CHCl_3$); diastereomeric ratio 66:34 (HPLC, MeCN–H_2O, 75:25).

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.83 [s, 9 H, C(C*H*$_3$)$_3$], 0.80–0.91 (m, 3 H, C*H*$_3$CH), 1.11, 1.16, 1.18 [s, 27 H, C(C*H*$_3$)$_3$], 1.79–1.88 (m, 1 H, *C*HCH$_3$), 2.61 (dd, 1 H, *J* = 17.3, 10.6 Hz, C*H*$_2$CO), 2.94 (dd, 1 H, *J* = 17.5, 2.5 Hz, C*H*$_2$CO), 4.00–4.08 (m, 1 H, H-5), 4.17 (dd, 1 H, *J* = 12.3, 5.0 Hz, H-6a), 4.22 (dd, 1 H, *J* = 12.3, 2.6 Hz, H-6b), 4.59 (dd, 1 H, *J* = 6.8, 5.0 Hz, H-2), 5.06 (dd, 1 H, *J* = 8.7, 7.2 Hz, H-4), 5.33 (dd, 1 H, *J* = 6.9, 5.1 Hz, H-3), 5.90 (d, 1 H, *J* = 6.7 Hz, H-1).

(minor diastereomer) δ = 0.84 [s, 9 H, CHC(C*H*$_3$)$_3$], 2.68 (dd, 1 H, *J* = 17.2, 11.0 Hz, C*H*$_2$CO), 2.88 (dd, 1 H, *J* = 17.2, 2.2 Hz, C*H*$_2$CO), 5.03 (dd, 1 H, *J* = 8.4, 6.3 Hz, H-4), 5.35 (dd, 1 H, *J* = 6.0, 4.8 Hz, H-3).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 15.00 (CH*C*H$_3$), 26.94, 26.98, 27.04, 27.08 [C(*C*H$_3$)$_3$], 32.73 (*C*H$_2$CO), 38.40 (*C*HCH$_3$), 38.57, 38.66, 38.80 [*C*(CH$_3$)$_3$], 55.55 (C-2), 61.85 (C-6), 65.70, 69.76, 70.78 (C-3, C-4, C-5), 95.23 (C-1), 150.74 (*C*O, urethane), 172.62 (*C*O, acyl), 176.23, 176.49, 177.75 (*C*O, pivaloyl).

(minor diastereomer) δ = 27.12 (CH*C*H$_3$), 32.68 (*C*H$_2$CO), 38.49 (*C*HCH$_3$), 55.13 (C-2), 62.06 (C-6), 94.99 (C-1), 150.89 (*C*O, urethane), 172.72 (*C*O, acyl).

Anal. Calcd for $C_{30}H_{49}NO_{10}$ (583.73): C, 61.73; H, 8.46; N, 2.40. Found: C, 61.89; H, 8.51; N, 2.31.

1,2-Dideoxy-1,2-[*N*-(3-methylnon-4-enoyl)epoxycarbonylimino]-3,4,6-tri-*O*-pivaloyl-α-D-glucopyranose (7c)

According to general procedure (method C). Reagents: DIBAL-H (3.0 mL, 4.5 mmol, 1.5 M in CH_2Cl_2), 1-hexyne (0.5 mL, 4.44 mmol), toluene (50 mL), **6** (300 mg, 0.57 mmol), $MeAlCl_2$ (0.6 mL, 0.6 mmol, 1.0 M in hexane), toluene (50 mL).

Yield: 132 mg (38%); 75% conversion; colourless, amorphous solid; R_f = 0.48 (LPE–EtOAc, 5:1); $[\alpha]_D^{22}$ –25.5 (c = 1.0, $CHCl_3$); diastereomeric ratio 67:33 (H-1, 400 MHz ^{1}H NMR).

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.81–0.88 [m, 3 H, (CH$_2$)$_2$C*H*$_3$], 0.98 (d, 3 H, *J* = 6.5 Hz, CHC*H*$_3$), 1.10, 1.16, 1.18 [s, 27 H, C(C*H*$_3$)$_3$], 1.10–1.32 [m, 4 H, (C*H*$_2$)$_2$], 1.87–1.92 (m, 2 H, CH=CHC*H*$_2$), 2.58–2.66 (m, 1 H, *C*HCH$_3$), 2.68 (dd, 1 H, *J* = 16.6, 6.9 Hz, C*H*$_2$CO), 2.79 (dd, 1 H, *J* = 16.6, 6.0 Hz, C*H*$_2$CO), 4.00–4.04 (m, 1 H, H-5), 4.15 (dd, 1 H, *J* = 12.3, 5.3 Hz, H-6a), 4.21 (dd, 1 H, *J* = 12.3, 2.3 Hz, H-6b), 4.55 (dd, 1 H, *J* = 6.8, 5.0 Hz, H-2), 5.04 (dd, 1 H, *J* = 8.5, 6.8 Hz, H-4), 5.26–5.41 (m, 3 H, H-3, C*H*=C*H*), 5.89 (d, 1 H, *J* = 7.1 Hz, H-1).

(minor diastereomer) δ = 0.99 (d, 3 H, *J* = 6.5 Hz, CHC*H*$_3$), 2.84 (dd, 1 H, *J* = 16.6, 7.5 Hz, C*H*$_2$CO), 2.99 (dd, 1 H, *J* = 16.4, 6.5 Hz, C*H*$_2$CO), 5.02 (dd, 1 H, *J* = 8.5, 6.5 Hz, H-4), 5.87 (d, 1 H, *J* = 6.8 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 13.77 (CH$_2$*C*H$_3$), 20.31 (CH*C*H$_3$), 22.03 (*C*H$_2$), 26.84, 26.90, 26.95 [C(*C*H$_3$)$_3$], 31.52, 31.98 (*C*H$_2$), 32.69 (*C*HCH$_3$), 38.58, 38.72 [*C*(CH$_3$)$_3$], 42.40 (*C*H$_2$CO), 55.15 (C-2), 61.91 (C-6), 65.60, 69.66, 70.09 (C-3, C-4, C-5), 95.01 (C-1), 129.50, 133.82 (*C*H=), 150.75 (*C*O, urethane), 171.23 (*C*O, acyl), 176.15, 176.38, 177.66 (*C*O, pivaloyl).

(minor diastereomer) δ = 20.26 (CH*C*H$_3$), 22.00 (*C*H$_2$), 32.44 (*C*HCH$_3$), 42.73 (*C*H$_2$CO), 55.11 (C-2), 61.94 (C-6), 65.67, 69.62, 70.21 (C-3, C-4, C-5), 129.43 (*C*H=), 171.11 (*C*O, acyl).

Anal. Calcd for $C_{32}H_{51}NO_{10}$ (609.77): C, 63.03; H, 8.43; N, 2.30. Found: C, 63.13; H, 8.41; N, 2.09.

1,2-Dideoxy-1,2-[*N*-(3-methylnon-4-ynoyl)epoxycarbonylimino]-3,4,6-tri-*O*-pivaloyl-α-D-glucopyranose (7d)

According to general procedure (method A). Reagents: $MeAlCl_2$ (2.9 mL, 2.9 mmol, 1.0 M in hexane), 1-hexynyllithium (2.9 mmol, from 1-hexyne in toluene and 1.05 equiv *n*-BuLi), **6** (300 mg, 0.57 mmol), $MeAlCl_2$ (0.6 mL, 0.6 mmol, 1.0 M in hexane), toluene (50 mL).

Yield: 161 mg (40%); 68% conversion; colourless, amorphous solid; diastereomeric ratio 54:46 (C*H*$_2$CO, 400 MHz ^{1}H NMR).

major diastereomer: R_f = 0.53 (LPE–EtOAc, 5:1); $[\alpha]_D^{22}$ –45.1 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 [t, 3 H, *J* = 7.2 Hz, (CH$_2$)$_3$C*H*$_3$], 1.14, 1.18, 1.19 [s, 27 H, C(C*H*$_3$)$_3$], 1.13–1.46 [m, 7 H, CHC*H*$_3$, (C*H*$_2$)$_2$], 2.10 (dt, 2 H, *J* = 6.9, 1.7 Hz, C*H*$_2$C≡), 2.86–3.00 (m, 2 H, C*H*$_2$CO,C*H*CH$_3$), 3.06 (dd, 1 H, *J* = 16.8, 7.4 Hz, C*H*$_2$CO), 4.04 (ddd, 1 H, *J* = 8.2, 5.5, 2.7 Hz, H-5), 4.18 (dd, 1 H, *J* = 12.1, 5.5 Hz, H-6a), 4.23 (dd, 1 H, *J* = 12.1, 2.7 Hz, H-6b), 4.58 (dd, 1 H, *J* = 7.0, 4.7 Hz, H-2), 5.05 (dd, 1 H, *J* = 8.4, 6.5 Hz, H-4), 5.36 (dd, 1 H, *J* = 6.3, 4.7 Hz, H-3), 5.93 (d, 1 H, *J* = 6.7 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.54 [(CH$_2$)$_3$*C*H$_3$], 18.36 (*C*H$_2$), 21.35 (CH*C*H$_3$), 21.86 (*C*H$_2$), 21.87 (*C*HCH$_3$), 26.94, 26.99, 27.05 [C(*C*H$_3$)$_3$], 31.05 (*C*H$_2$), 38.62, 38.82 [*C*(CH$_3$)$_3$], 42.96 (*C*H$_2$CO), 55.08 (C-2), 62.09 (C-6), 65.70, 69.87, 69.87 (C-3, C-4, C-5), 80.99, 82.66 (*C*≡), 95.14 (C-1), 150.82 (*C*O, urethane), 170.23 (*C*O, acyl), 176.29, 176.41, 177.78 (*C*O, pivaloyl).

minor diastereomer: R_f = 0.58 (LPE–EtOAc 5:1); $[\alpha]_D^{22}$ –36.6 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 [t, 3 H, *J* = 7.0 Hz, (CH$_2$)$_3$C*H*$_3$], 1.13, 1.17, 1.19 [s, 27 H, C(C*H*$_3$)$_3$], 1.13–1.44 [m, 7 H, CHC*H*$_3$, (C*H*$_2$)$_2$], 2.08 (dt, 2 H, *J* = 6.9, 2.0 Hz, C*H*$_2$C≡), 2.83 (dd, 1 H, *J* = 17.0, 6.5 Hz, C*H*$_2$CO), 2.92 (tq, 1 H, *J* = 6.7, 2.1 Hz, *C*HCH$_3$), 3.21 (dd, 1 H, *J* = 16.8, 7.0 Hz, C*H*$_2$CO), 4.05 (ddd, 1 H, *J* = 8.4, 5.5, 2.7 Hz, H-5), 4.18 (dd, 1 H, *J* = 12.5, 5.5 Hz, H-6a), 4.23 (dd, 1 H, *J* = 12.1, 2.7 Hz, H-6b), 4.60 (dd, 1 H, *J* = 6.9, 4.9 Hz, H-2), 5.06 (dd, 1 H, *J* = 8.6, 6.7 Hz, H-4), 5.34 (dd, 1 H, *J* = 6.7, 5.1 Hz, H-3), 5.92 (d, 1 H, *J* = 6.7 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.52 [(CH$_2$)$_3$*C*H$_3$], 18.33 (*C*H$_2$), 21.34 (CH*C*H$_3$), 21.83 (*C*H$_2$), 22.04 (*C*HCH$_3$), 26.94, 26.98, 27.04 [C(*C*H$_3$)$_3$], 31.05 (*C*H$_2$), 38.67, 38.82 [*C*(CH$_3$)$_3$], 42.79 (*C*H$_2$CO), 55.32 (C-2), 61.98 (C-6), 65.63, 69.90, 70.31 (C-3, C-4, C-5), 80.82, 82.92 (*C*≡), 95.27 (C-1), 150.74 (*C*O, urethane), 170.44 (*C*O, acyl), 176.22, 176.54, 177.78 (*C*O, pivaloyl).

Anal. Calcd for $C_{32}H_{49}NO_{10}$ (607.75): C, 63.24; H, 8.13; N, 2.30. Found: C, 63.19; H, 8.16; N, 2.08.

1,2-Dideoxy-1,2-[*N*-(3-phenylheptanoyl)epoxycarbonylimino]-3,4,6-tri-*O*-pivaloyl-α-D-galactopyranose (8a)

According to general procedure (method A). Reagents: $MeAlCl_2$ (5.1 mL, 5.1 mmol, 1.0 M in hexane), *n*-BuLi (3.2 mL, 5.12 mmol, 1.6 M in pentane), toluene (50 mL), **1** (300 mg, 0.51 mmol), $MeAlCl_2$ (0.6 mL, 0.6 mmol, 1.0 M in hexane), toluene (50 mL).

Yield: 253 mg (77%); colourless, amorphous solid; R_f = 0.46 (LPE–EtOAc, 5:1); $[\alpha]_D^{22}$ –30.5 (c = 1.0, $CHCl_3$); diastereomeric ratio 99:1 (H-3, 400 MHz ^{1}H NMR).

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.78 (t, 3 H, *J* = 7.0 Hz, C*H*$_3$), 0.99–1.38 [m, 4 H, (C*H*$_2$)$_2$], 1.13, 1.15, 1.21 [s, 27 H, C(C*H*$_3$)$_3$], 1.55–1.67 (m, 2 H, C*H*$_2$), 2.96 (dd, 1 H, *J* = 16.1, 5.6 Hz, C*H*$_2$CO), 2.97–3.06 (m, 1 H, C*H*Ph), 3.36 (dd, 1 H, *J* = 16.1, 8.2 Hz, C*H*$_2$CO), 4.00 (dd, 1 H, *J* = 11.5, 6.5 Hz, H-6a), 4.09 (dd, 1 H, *J* = 11.5, 7.0 Hz,H-6b), 4.31 (t, 1 H, *J* = 6.8 Hz, H-5), 4.43 (dd, 1 H *J* = 8.5, 5.6 Hz, H-2), 5.10 (dd, 1 H, *J* = 8.5, 3.2 Hz, H-3), 5.34 (d, 1 H, *J* = 2.9 Hz, H-4), 5.52 (d, 1 H, *J* = 5.6 Hz, H-1), 7.13–7.26 (m, 5 H, Ar).

(minor diastereomer) δ = 5.04 (dd, 1 H, *J* = 8.5, 3.2 Hz, H-3).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 13.85 [(CH$_2$)$_3$*C*H$_3$], 22.45 (*C*H$_2$), 26.82, 26.98, 27.08 [C(*C*H$_3$)$_3$], 29.52, 35.94 [(*C*H$_2$)$_2$], 38.65, 38.68, 39.03 [*C*(CH$_3$)$_3$], 41.90 (*C*H$_2$CO), 41.96 (*C*HPh), 53.38 (C-2), 60.69 (C-6), 64.72, 70.36, 70.73 (C-3, C-4, C-5), 96.93 (C-1), 126.41, 127.62, 128.30 (C-Ar), 144.09 (C-ipso), 150.20 (*C*O, urethane), 171.10 (*C*O, acyl), 176.52, 177.21, 177.66 (*C*O, pivaloyl).

Anal. Calcd for $C_{35}H_{51}NO_{10}$ (645.80): C, 65.10; H, 7.96; N, 2.17. Found: C, 64.93; H, 8.01; N, 2.01.

1,2-Dideoxy-1,2-[*N*-(4,4-dimethyl-3-phenylpentanoyl)epoxycarbonylimino]-3,4,6-tri-*O*-pivaloyl-α-D-galactopyranose (8b)

According to general procedure (method A). Reagents: $MeAlCl_2$ (5.1 mL, 5.1 mmol, 1.0 M in hexane), *t*-BuLi (3.4 mL, 2.1 mmol, 1.7 M in hexane), toluene (50 mL), BF_3·OEt_2 (0.61 mL, 4.96 mmol), **1** (300 mg, 0.51 mmol), $MeAlCl_2$ (0.6 mL, 0.6 mmol, 1.0 M in hexane), toluene (50 mL).

Yield: 192 mg (58%); colourless, amorphous solid; R_f = 0.51 (LPE–EtOAc, 5:1); $[\alpha]_D^{22}$ –24.5 (c = 1.0, $CHCl_3$, major diastereomer); diastereomeric ratio 89:11 (H-1, 400 MHz ^{1}H NMR).

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.87 [s, 9 H, C(C*H*$_3$)$_3$], 1.13, 1.17, 1.19 [s, 27 H, C(C*H*$_3$)$_3$], 2.92 (dd, 1 H, *J* = 16.9, 3.1 Hz, C*H*$_2$CO), 2.97 (dd, 1 H, *J* = 11.4, 2.9 Hz, C*H*Ph), 3.77 (dd, 1 H, *J* = 16.7, 11.2 Hz, C*H*$_2$CO), 4.00 (dd, 1 H, *J* = 11.4, 6.5 Hz, H-6a), 4.08 (dd, 1 H, *J* = 11.4, 7.0 Hz, H-6b), 4.33 (t, 1 H, *J* = 6.7 Hz, H-5), 4.41 (dd, 1 H, *J* = 8.5, 5.6 Hz, H-2), 5.10 (dd, 1 H, *J* = 8.5, 3.2 Hz, H-3), 5.34 (d, 1 H, *J* = 2.9 Hz, H-4), 5.52 (d, 1 H, *J* = 5.6 Hz, H-1), 7.14–7.25 (m, 5 H, Ar).

(minor diastereomer) δ = 0.83 [s, 9 H, C(C*H*$_3$)$_3$], 3.25 (dd, 1 H, *J* = 17.6, 3.5 Hz, C*H*$_2$CO), 3.43 (dd, 1 H, *J* = 17.9, 10.9 Hz, C*H*$_2$CO), 4.30 (t, 1 H, *J* = 6.7 Hz, H-5), 4.47 (dd, 1 H, *J* = 8.5, 5.6 Hz, H-2), 4.93 (dd, 1 H, *J* = 8.5, 3.2 Hz, H-3), 5.30 (d, 1 H, *J* = 2.9 Hz, H-4), 5.82 (d, 1 H, *J* = 5.6 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 26.84, 26.99, 27.07 [C(*C*H$_3$)$_3$], 28.05 [CHC(*C*H$_3$)$_3$], 33.68 [*C*HC(CH$_3$)$_3$], 36.16 (*C*H$_2$CO), 38.65, 38.69, 39.02 [*C*(CH$_3$)$_3$], 52.03 (*C*HPh), 53.36 (C-2), 60.98 (C-6), 64.76, 70.42, 70.74 (C-3, C-4, C-5), 96.90 (C-1), 126.37, 127.65, 129.21 (C-Ar), 141.86 (C-ipso), 150.35 (*C*O, urethane), 171.74 (*C*O, acyl), 176.45, 177.21, 177.59 (*C*O, pivaloyl).

Anal. Calcd for $C_{35}H_{51}NO_{10}$ (645.80): C, 65.10; H, 7.96; N, 2.17. Found: C, 65.34; H, 7.89; N, 2.13.

1,2-Dideoxy-1,2-[*N*-(3-phenylnon-4-enoyl)epoxycarbonylimino]-3,4,6-tri-*O*-pivaloyl-α-D-galactopyranose (8c)

According to general procedure (method C). Reagents: DIBAL-H (3.4 mL, 5.1 mmol, 1.5 M in CH_2Cl_2), 1-hexyne (0.55 mL, 4.89 mmol), toluene (50 mL); **1** (300 mg, 0.51 mmol), $MeAlCl_2$ (0.6 mL, 0.6 mmol, 1.0 M in hexane), toluene (50 mL).

Yield: 151 mg (44%); 85% conversion; colourless, amorphous solid; R_f = 0.46 (LPE–EtOAc, 5:1); $[\alpha]_D^{22}$ –26.6 (c = 1.0, $CHCl_3$); diastereomeric ratio 89:11 (C*H*$_2$CO, 400 MHz ^{1}H NMR).

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.83 [t, 3 H, *J* = 7.0 Hz, (CH$_2$)$_2$C*H*$_3$], 1.02, 1.17, 1.23 [s, 27 H, C(C*H*$_3$)$_3$], 1.12–1.28 [m, 4 H, (C*H*$_2$)$_2$], 1.91–1.96 (m, 2 H, =CHC*H*$_2$), 3.12 (dd, 1 H, *J* = 17.0, 6.5 Hz, C*H*$_2$CO), 3.46 (dd, 1 H, *J* = 17.0, 8.2 Hz, C*H*$_2$CO), 3.75–3.82 (m, 1 H, C*H*Ph), 4.02 (dd, 1 H, *J* = 11.5, 6.5 Hz, H-6a), 4.12 (dd, 1 H, *J* = 11.5, 7.0 Hz, H-6b), 4.35 (t, 1 H, *J* = 6.7 Hz, H-5), 4.62 (dd, 1 H, *J* = 8.5, 5.6 Hz, H-2), 5.09 (dd, 1 H, *J* = 8.5, 3.2 Hz, H-3), 5.36 (d, 1 H, *J* = 2.6 Hz, H-4), 5.36–5.59 (m, 2 H, C*H*=C*H*), 5.87 (d, 1 H, *J* = 5.9 Hz, H-1), 7.13–7.27 (m, 5 H, Ar).

(minor diastereomer) δ = 1.14, 1.16, 1.22 [s, 27 H, C(C*H*$_3$)$_3$], 3.06 (dd, 1 H, *J* = 16.4, 6.2 Hz, C*H*$_2$CO), 3.51 (dd, 1 H, *J* = 16.3, 9.0 Hz, C*H*$_2$CO), 4.46 (dd, 1 H, *J* = 8.5, 5.6 Hz, H-2).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 13.85 [(CH$_2$)$_3$*C*H$_3$], 22.14 (*C*H$_2$), 26.76, 27.02, 27.12 [C(*C*H$_3$)$_3$], 31.44, 32.06 [(*C*H$_2$)$_2$], 38.58, 38.73, 39.07 [*C*(CH$_3$)$_3$], 41.15 (*C*H$_2$CO) 44.11 (*C*HPh), 53.38 (C-2), 61.02 (C-6), 64.75, 70.50, 70.83 (C-3, C-4, C-5), 97.04 (C-1), 126.41, 127.45, 128.52 (C-Ar), 131.25, 132.04 (*C*H=), 143.29 (C-ipso), 150.37 (*C*O, urethane), 170.50 (*C*O, acyl), 176.53, 177.15, 177.71 (2 C, *C*O, pivaloyl).

Anal. Calcd for $C_{37}H_{53}NO_{10}$ (671.84): C, 66.15; H, 7.95; N, 2.08. Found: C, 65.70; H, 7.83; N, 1.84.

1,2-Dideoxy-1,2-[*N*-(3-phenylnon-4-ynoyl)epoxycarbonylimino]-3,4,6-tri-*O*-pivaloyl-α-D-galactopyranose (8d)

According to general procedure (method A). Reagents: $MeAlCl_2$ (5.1 mL, 5.1 mmol, 1.0 M in hexane), 1-hexynyllithium (5.1 mmol, from 1-hexyne in toluene and 1.05 equiv *n*-BuLi); toluene (50 mL); **1** (300 mg, 0.51 mmol), $MeAlCl_2$ (0.6 mL, 0.6 mmol, 1.0 M in hexane), toluene (50 mL).

Yield: 114 mg (33%); 83% conversion; colourless, amorphous solid; R_f = 0.48 (LPE–EtOAc, 5:1); $[\alpha]_D^{22}$ –19.9 (c = 1.0, $CHCl_3$); diastereomeric ratio 84:16 (H-2, 400 MHz ^{1}H NMR).

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.86 [t, 3 H, *J* = 7.2 Hz, (CH$_2$)$_3$C*H*$_3$], 1.11, 1.17, 1.24 [s, 27 H, C(C*H*$_3$)$_3$], 1.26–1.48 [m, 4 H, (C*H*$_2$)$_2$CH$_3$], 2.15 (dt, 2 H, *J* = 7.0, 2.1 Hz, C*H*$_2$C≡), 3.00 (dd, 1 H, *J* = 17.2, 4.6 Hz, C*H*$_2$CO), 3.55 (dd, 1 H, *J* = 17.0, 9.7 Hz, C*H*$_2$CO), 4.04 (dd, 1 H, *J* = 11.4, 6.5 Hz, H-6a), 4.02–4.11 (m, 1 H, C*H*Ph), 4.13 (dd, 1 H, *J* = 11.4, 7.0, H-6b), 4.36 (t, 1 H, *J* = 6.9 Hz, H-5), 4.70 (dd, 1 H, *J* = 8.5, 5.6 Hz, H-2), 5.13 (dd, 1 H, *J* = 8.5, 3.2 Hz, H-3), 5.39 (d, 1 H, *J* = 2.6 Hz, H-4), 5.91 (d, 1 H, *J* = 5.6 Hz, H-1), 7.18–7.36 (m, 5 H, Ar).

(minor diastereomer) δ = 0.87 [t, 3H, *J* = 7.5 Hz, (CH$_2$)$_3$C*H*$_3$], 3.25 (dd, 1 H, *J* = 16.4, 7.0 Hz, C*H*$_2$CO), 3.41 (dd, 1 H, *J* = 16.6, 7.5 Hz, C*H*$_2$CO), 4.55 (dd, 1 H, *J* = 8.5, 5.9 Hz, H-2), 5.72 (d, 1 H, *J* = 5.9 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 13.48 [(CH$_2$)$_3$*C*H$_3$], 18.45, 21.85 (*C*H$_2$), 26.79, 26.96, 27.07 [C(C*H*$_3$)$_3$], 30.91 (*C*H$_2$), 33.42 (*C*HPh), 38.63, 38.68, 39.04 [*C*(CH$_3$)$_3$], 44.03 (*C*H$_2$CO), 53.49 (C-2), 60.96 (C-6), 64.74, 70.53, 70.79 (C-3, C-4, C-5), 80.38, 83.61 (*C*≡), 97.16 (C-1), 126.97, 127.37, 128.56 (C-Ar), 141.07 (C-ipso), 150.20 (*C*O, urethane), 169.84 (*C*O, acyl), 176.55, 177.33, 177.72 (*C*O, pivaloyl).

$C_{37}H_{51}NO_{10}$ (669.82); ESI-MS: *m/z* = 692.8 $[M + Na]^+$.

1,2-Dideoxy-1,2-[*N*-(3,5-dimethylhexanoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (17a)

According to general procedure (reaction time 3 h). Reagents: diisobutylaluminum chloride (2.4 mL, 2.4 mmol, 1 M in toluene); **15** (100 mg, 0.243 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (20 mL).

Yield: 85.8 mg (75%); colourless, amorphous solid; R_f = 0.53 (LPE–EtOAc, 5:1); mp 95 °C; $[\alpha]_D^{22}$ –11.5 (c = 1.0, $CHCl_3$); diastereomeric ratio 73:27 (*C*H_2CH, ^{13}C NMR).

Analytical HPLC: R_t = 12.13 min (MeCN–H_2O, 85:15).

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.82–0.90 [m, 9 H, CHC*H*$_3$, CH(C*H*$_3$)$_2$], 1.05–1.10 [m, 1 H, C*H*(CH$_3$)$_2$], 1.16, 1.23 [s, 18 H, C(C*H*$_3$)$_3$], 1.61 [m, 2 H, *J* = 6.3 Hz, C*H*$_2$CH(CH$_3$)$_2$], 2.05 (m, 1 H, *J* = 7.8, 6.3 Hz, C*H*CH$_2$CO), 2.63 (dd, 1 H *J* = 16.8, 8.2 Hz, C*H*$_2$CO), 2.76 (m, 1 H, *J* = 16.8, 7.8 Hz, C*H*$_2$CO), 3.97 (dd, 1 H, *J* = 12.9, 3.1 Hz, H-5a), 4.08 (dd, 1 H, *J* = 12.9, 1.6 Hz, H-5b), 4.69 (dd, 1 H, *J* = 7.8, 5.8 Hz, H-2), 5.16 (d, 1 H, *J* = 1.6 Hz, H-4), 5.19 (dd, 1 H, *J* = 7.3, 3.9 Hz, H-3), 5.87 (d, 1 H, *J* = 5.5 Hz, H-1).

(minor diastereomer) δ = 2.73 (m, 1 H, C*H*$_2$CO).

100.6 MHz ^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 19.87 (CH*C*H$_3$), 22.06, 23.16 [CH(*C*H$_3$)$_2$], 25.19 [*C*H(CH$_3$)$_2$], 26.91 [C(*C*H$_3$)$_3$], 27.01 [*C*H(CH$_3$)], 27.09 [C(*C*H$_3$)$_3$], 38.72, 38.98 [*C*(CH$_3$)$_3$], 42.95 (*C*H$_2$CO), 46.14 [*C*H$_2$CH(CH$_3$)$_2$], 53.69 (C-2), 62.95 (C-5), 65.85, 69.58 (C-3, C-4), 96.90 (C-1), 150.61 (*C*O, urethane), 171.92 (*C*O, acyl), 177.16, 177.21 (*C*O, pivaloyl).

(minor diastereomer) δ = 19.73 (CH*C*H$_3$), 21.96, 23.26 [CH(*C*H$_3$)$_2$], 42.89 (*C*H$_2$CO), 46.23 [*C*H$_2$CH(CH$_3$)$_2$], 96.82 (C-1).

$C_{24}H_{39}NO_8$ (469.58); ESI-MS: *m/z* = 492.3 $[M + Na]^+$, 533.5 $[M + Na + CH_3CN]^+$.

1,2-Dideoxy-1,2-[*N*-(3-methylheptanoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (17b)

According to general procedure (method A; reaction time 10 h). Reagents: $MeAlCl_2$ (2.4 mL, 2.4 mmol, 1 M in hexane), *n*-BuLi (1.5 mL, 2.4 mmol, 1.6 M in pentane), toluene (10 mL); **15** (100 mg, 0.243 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (10 mL).

Yield: 81 mg (71%); colourless, amorphous solid; R_f = 0.45 (LPE–EtOAc, 5:1); mp 97 °C; $[\alpha]_D^{22}$ –11.5 (c = 1.0, $CHCl_3$); diastereomeric ratio 73:27 (*C*H_2CH, 100.6 MHz ^{13}C NMR), 72:28 (C*H*$_2$CO, C*H*-Me, 400 MHz ^{1}H NMR).

Analytical HPLC: R_t = 18.38 min (MeCN–H_2O, 85:15).

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.84–0.91 [m, 6 H, *J* = 6.7 Hz, (CH$_2$)$_3$C*H*$_3$, CHC*H*$_3$], 1.15, 1.22 [s, 18 H, C(C*H*$_3$)$_3$], 1.24–1.33 [m, 6 H, (C*H*$_2$)$_3$], 1.91–1.99 (m, 1 H, *J* = 6.7 Hz, C*H*CH$_3$), 2.62 (dd, 1 H, *J* = 16.8, 7.2 Hz, C*H*$_2$CO), 2.83 (dd, 1 H, *J* = 16.8, 5.4 Hz, C*H*$_2$CO), 3.97 (dd, 1 H, *J* = 12.9, 3.1 Hz, H-5a), 4.07 (dd, 1 H, *J* = 12.5, 1.1 Hz, H-5b), 4.69 (dd, 1 H, *J* = 7.8, 5.5 Hz, H-2), 5.15 (m, 1 H, H-4), 5.20 (dd, 1 H, *J* = 7.8, 3.1 Hz, H-3), 5.87 (d, 1 H, *J* = 5.5 Hz, H-1).

(minor diastereomer) δ = 2.71 (m, 1 H, C*H*$_2$CO), 4.68 (dd, 1 H, *J* = 7.8, 5.9 Hz, H-2).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 13.94 [(CH$_2$)$_3$*C*H$_3$], 19.73 (CH*C*H$_3$), 22.78 (*C*H$_2$), 26.91, 27.10 [C(*C*H$_3$)$_3$], 29.14 (*C*H$_2$), 29.40 (*C*HCH$_3$), 36.39 (CH*C*H$_2$CH$_2$), 38.72, 38.97 [*C*(CH$_3$)$_3$], 42.69 (*C*H$_2$CO), 53.67 (C-2), 62.93 (C-5), 65.82, 69.53 (C-3, C-4), 96.87 (C-1), 150.62 (*C*O, urethane), 171.99 (*C*O, ac yl), 177.18 (2C, *C*O, pivaloyl).

(minor diastereomer) δ = 19.66 (CH*C*H$_3$), 36.47 (CH*C*H$_2$CH$_2$), 42.58 (*C*H$_2$CO).

Anal. Calcd for $C_{24}H_{39}NO_8$ (469.58): C, 61.39; H, 8.37; N, 2.83. Found: C, 61.37; H, 8.44; N, 2.93.

ESI-MS: *m/z* = 448.5 $[M + Na – CO_2]^+$; 492.4 $[M + Na]^+$; 508.5 $[M + K]^+$.

1,2-Dideoxy-1,2-[*N*-(3,4,4-trimethylpentanoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (17c)

According to general procedure (method A). Reagents: $MeAlCl_2$ (2.4 mL, 2.4 mmol, 1.0 M in hexane), *t*-BuLi (1.4 mL, 2.4 mmol, 1.7 M in hexane), toluene (10 mL); **15** (100 mg, 0.243 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (10 mL).

Yield: 47 mg (42%); colourless, amorphous solid; R_f = 0.45 (LPE–EtOAc, 5:1); mp 146 °C; $[\alpha]_D^{22}$ –4.2 (c = 1.0, $CHCl_3$); diastereomeric ratio 72:28 (C-2, 100.6 MHz ^{13}C NMR).

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.86 [s, 9 H, C(C*H*$_3$)$_3$], 0.87–0.94 (m, 3 H, CHC*H*$_3$), 1.15, 1.23 [s, 18 H, C(C*H*$_3$)$_3$], 1.77–1.90 (m, 1 H, *C*HCH$_3$), 2.64 (dd, 1 H, *J* = 14.1, 5.9 Hz, C*H*$_2$CO), 2.91 (dd, 1 H, *J* = 14.1, 2.7 Hz, C*H*$_2$CO), 3.98 (dd, 1 H, *J* = 12.9, 3.1 Hz, H-5a), 4.08 (dd, 1 H, *J* = 12.9, 1.2 Hz, H-5b), 4.72 (dd, 1 H, *J* = 5.9, 2.0 Hz, H-2), 5.16 (m, 1 H, *J* = 3.1 Hz, H-4), 5.20 (dd, 1 H, *J* = 7.8, 3.1 Hz, H-3), 5.87 (d, 1 H, *J* = 5.9 Hz, H-1).

(minor diastereomer) δ = 0.85, 1.16 [s, 18 H, C(C*H*$_3$)$_3$], 2.66 (dd, 1 H, *J* = 16.8, 6.8 Hz, C*H*$_2$CO).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 15.10 (CH*C*H$_3$), 26.91, 27.10, 27.17 [C(*C*H$_3$)$_3$], 32.77 (*C*H$_2$CO), 38.41 (*C*HCH$_3$), 38.61, 38.64, 38.74 [*C*(CH$_3$)$_3$], 53.72 (C-2), 62.99 (C-5), 65.85, 69.58 (C-3, C-4), 96.86 (C-1), 150.57 (*C*O, urethane), 172.90 (*C*O, acyl), 177.18 (2C, *C*O, pivaloyl).

(minor diastereomer) δ = 14.99 (CH*C*H$_3$), 32.81 (*C*H$_2$CO), 53.78 (C-2).

Anal. Calcd for $C_{24}H_{39}NO_8$ (469.58): C, 61.39; H, 8.37; N, 2.83. Found: C, 61.25; H, 8.45; N, 2.85.

ESI-MS: *m/z* = 448.4 $[M + Na – CO_2]^+$, 492.4 $[M + Na]^+$, 533.6 $[M + Na + CH_3CN]^+$.

1,2-Dideoxy-1,2-[*N*-(3-methylnon-4-enoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (17d)

According to general procedure (method C). Reagents: DIBAL-H (2.4 mL, 2.4 mmol, 1.0 M in CH_2Cl_2), 1-hexyne (0.3 mL, 2.7 mmol), toluene (10 mL); **15** (100 mg, 0.243 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (10 mL).

Yield: 53 mg (46%); 90% conversion; colourless, amorphous solid; R_f = 0.39 (LPE–EtOAc, 6:1); mp 109 °C; $[\alpha]_D^{22}$ +1.5 (c = 1.0, $CHCl_3$); diastereomeric ratio 75:25 (H-1, 400 MHz ^{1}H NMR).

Analytical HPLC: R_t = 16.45 min (MeCN–H_2O, 85:15).

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.85 [m, 3 H, (CH$_2$)$_2$C*H*$_3$], 1.02 (d, 3 H, *J* = 6.7 Hz, CHC*H*$_3$), 1.16, 1.22 [s, 18 H, C(C*H*$_3$)$_3$], 1.26 [m, 4 H, (C*H*$_2$)$_2$], 1.92 (m, 2 H, CH=CHC*H*$_2$], 2.62 (m, 1 H, *J* = 7.1 Hz, *C*HCH$_3$), 2.75 (dd, 1 H, *J* = 15.4, 7.1 Hz, C*H*$_2$CO), 2.95 (dd, 1 H, *J* = 15.4, 7.1 Hz, C*H*$_2$CO), 3.96 (dd, 1 H, *J* = 12.9, 3.1 Hz, H-5a), 4.08 (dd, 1 H, *J* = 12.9, 0.9 Hz, H-5b), 4.66 (dd, 1 H, *J* = 7.4, 5.9 Hz, H-2), 5.15 (m, 1 H, H-4) 5.19 (dd, 1 H, *J* = 7.4, 3.1 Hz, H-3), 5.28–5.43 (m, 2 H, C*H*=C*H*), 5.83 (d, 1 H, *J* = 5.9 Hz, H-1).

(minor diastereomer) δ = 2.82 (m, 1 H, C*H*$_2$CO), 5.86 (d, 1 H, *J* = 4.7 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 13.94 (CH$_2$*C*H$_3$), 20.51 (CH*C*H$_3$), 22.17 (*C*H$_2$), 26.91, 27.10 [C(*C*H$_3$)$_3$], 31.63, 32.11 (*C*H$_2$), 33.02 (*C*HCH$_3$), 38.74, 38.97 [*C*(CH$_3$)$_3$] 42.41 (*C*H$_2$CO), 53.74 (C-2), 62.91 (C-5), 65.80, 69.41 (C-3, C-4), 96.81 (C-1), 129.65, 134.03 (*C*H=), 150.64 (*C*O, urethane), 171.43 (*C*O, acyl), 177.18 (2C, *C*O, pivaloyl).

(minor diastereomer) δ = 20.43 (CH*C*H$_3$), 129.56 (*C*H=).

Anal. Calcd for $C_{26}H_{41}NO_8$ (495.62): C, 63.01; H, 8.34; N, 2.83. Found: C, 62.96; H, 8.26; N, 2.75.

ESI-MS: *m/z* = 474.4 $[M + Na – CO_2]^+$, 518.5 $[M + Na]^+$, 559.5 $[M + Na + CH_3CN]^+$.

1,2-Dideoxy-1,2-[*N*-(3-methylnon-4-ynoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (17e)

According to general procedure (method A; reaction time 72 h). Reagents: $MeAlCl_2$ (2.91 mmol, 1.0 M in hexane), 1-hexynyllithium (2.9 mmol, from 1-hexyne in toluene and 1.05 equiv *n*-BuLi); **15** (100 mg, 0.243 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (10 mL).

Yield: 50 mg (41%); colourless, amorphous solid; R_f = 0.47 (LPE–EtOAc, 5:1); mp 107 °C; $[\alpha]_D^{22}$ –20.2 (c = 1.0, $CHCl_3$); diastereomeric ratio 65:35 (C*H*$_2$CO, 400 MHz ^{1}H NMR).

Analytical HPLC: R_t = 25.12 min (MeCN–H_2O, 80:20).

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.86 [t, 3 H, *J* = 7.4 Hz, $(CH_2)_3CH_3$] 1.15, 1.21 [s, 18 H, $C(CH_3)_3$], 1.16 (m, 3 H, $CHCH_3$), 1.31–1.44 (m, 4 H, *J* = 4.3 Hz, CH_2), 2.07 (dt, 2 H, *J* = 2.0, 7.0 Hz, $CH_2C{\equiv}$), 2.83–2.96 (m, 2 H, *J* = 16.0, 2.0 Hz, CH_2CO, $CHCH_3$), 3.03 (dd, 1 H, *J* = 16.0, 7.0 Hz, CH_2CO), 3.96 (dd, 1 H, *J* = 12.7, 2.7 Hz, H-5a), 4.07 (d, 1 H, *J* = 12.1 Hz, H-5b), 4.68 (dd, 1 H, *J* = 7.4, 5.9 Hz, H-2), 5.16–5.20 (m, 2 H, H-4, H-3), 5.87 (d, 1 H, *J* = 5.9 Hz, H-1).

(minor diastereomer) δ = 1.14 [s, 9 H, $C(CH_3)_3$], 3.13 (dd, 1 H, *J* = 16.0, 7.0 Hz, CH_2CO), 4.74 (dd, 1 H, *J* = 7.8, 5.9 Hz, H-2), 5.86 (d, 1 H, *J* = 5.9 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 13.60 $[(CH_2)_3CH_3]$, 18.37 (CH_2), 21.42 ($CHCH_3$), 21.90 (CH_2), 22.12 ($CHCH_3$), 26.89, 27.08 $[C(CH_3)_3]$, 31.08 (CH_2), 38.70, 38.94 $[C(CH_3)_3]$, 42.71 (CH_2CO), 53.66 (C-2), 62.96 (C-5), 65.76, 69.54 (C-3, C-4), 81.07, 82.69 (C≡), 96.95 (C-1), 150.54 (*C*O, urethane), 170.30 (*C*O, acyl), 177.13, 177.19 (*C*O, pivaloyl).

(minor diastereomer) δ = 22.19 ($CHCH_3$), 53.80 (C-2), 97.02 (C-1).

Anal. Calcd for $C_{26}H_{39}NO_8$ (493.60): C, 63.27; H, 7.96; N, 2.84. Found: C, 62.98; H, 8.07; N, 2.59.

1,2-Dideoxy-1,2-[*N*-(3-phenyl-pentanoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (18a)

According to general procedure. Reagents: Et_2AlCl (0.35 mL, 0.64 mmol, 1.8 M in toluene); **16** (100 mg, 0.212 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (20 mL).

Yield: 88 mg (83%); colourless, amorphous solid; R_f = 0.47 (LPE–EtOAc, 5:1); mp 151 °C; $[\alpha]_D^{22}$ +14.6 (c = 1.0, $CHCl_3$); diastereomeric ratio 97:3 (H-2, 400 MHz ^{1}H NMR), 96:4 (HPLC).

Analytical HPLC: R_t = 15.31 (minor diastereomer), 16.24 min (major diastereomer) [MeCN–H_2O, 80:20].

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.76 (t, 3 H, *J* = 7.4 Hz, CH_3), 1.16, 1.21 [s, 18 H, $C(CH_3)_3$], 1.55–1.75 (m, 2 H, *J* = 8.6 Hz, CH_2CH_3), 2.94–3.06 (m, 2 H, *J* = 16.4, 8.6 Hz, C*H*Ph, CH_2CO), 3.36 (dd, 1 H, *J* = 16.4, 8.6 Hz, CH_2CO), 3.93 (dd, 1 H, *J* = 12.9, 3.1 Hz, H-5a), 4.03 (m, 1 H, H-5b), 4.48 (dd, 1 H, *J* = 7.8, 5.5 Hz, H-2), 5.11 (m, 1 H, H-4), 5.14 (dd, 1 H, *J* = 7.8, 3.5 Hz, H-3), 5.48 (d, 1 H, *J* = 5.5 Hz, H-1), 7.15–7.27 (m, 5 H, Ar).

(minor diastereomer) δ = 1.03 [s, 9 H, $C(CH_3)_3$], 3.18 (dd, 1 H, *J* = 14.5, 7.8 Hz, CH_2CO), 4.48 (dd, 1 H, *J* = 5.5, Hz, H-2), 5.82 (d, 1 H, *J* = 5.5 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 11.99 (CH_2CH_3), 26.91, 27.09 $[C(CH_3)_3]$, 29.27 (CH_2CH_3), 38.73, 38.94 $[C(CH_3)_3]$, 41.72 (*C*HPh), 43.65 (CH_2CO), 53.78 (C-2), 62.88 (C-5), 65.85, 69.38 (C-3, C-4), 96.86 (C-1), 126.48, 127.75, 128.36 (C-Ar), 143.87 (C-ipso), 150.57 (*C*O, urethane), 171.30 (*C*O, acyl), 177.15, 177.22 (*C*O, pivaloyl).

Anal. Calcd for $C_{27}H_{37}NO_8$ (503.60): C, 64.40; H, 7.41; N, 2.78. Found: C, 64.08; H, 7.65; N, 2.73.

ESI-MS: *m/z* = 482.4 $[M + Na - CO_2]^+$, 526.5 $[M + Na]^+$, 544.6 $[M + K]^+$.

1,2-Dideoxy-1,2-[*N*-(5-methyl-3-phenylhexanoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (18b)

According to general procedure (reaction time 5 h). Reagents: $(i\text{-}Bu)_2AlCl$ (1.3 mL, 1.3 mmol, 1.0 M in toluene); **16** (100 mg, 0.212 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (20 mL).

Yield: 87 mg (76%); colourless, amorphous solid; R_f (LPE–EtOAc, 5:1) = 0.54; mp 166 °C; $[\alpha]_D^{22}$ +11.4 (c = 1.0, $CHCl_3$); diastereomeric ratio: 98:2 (H-2, 400 MHz ^{1}H NMR), 95:5 (HPLC).

Analytical HPLC: R_t = 14.87 (minor diastereomer), 15.37 min (major diastereomer) [MeCN–H_2O, 85:15].

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.80, 0.85 [d, 6 H, *J* = 6.7 Hz, $CH(CH_3)_2$], 1.17, 1.21 [s, 18 H, $C(CH_3)_3$], 1.36–1.63 (m, 3 H, CH_2CH), 2.93 (dd, 1 H, *J* = 16.4, 5.5 Hz, CH_2CO), 3.19 (dd, 1 H, *J* = 9.4, 5.5 Hz, C*H*Ph), 3.39 (dd, 1 H, *J* = 16.4, 9.4 Hz, CH_2CO), 3.93 (dd, 1 H, *J* = 12.9, 2.7 Hz, H-5a), 4.02 (d, 1 H, *J* = 12.9 Hz, H-5b), 4.46 (dd, 1 H, *J* = 7.4, 5.9 Hz, H-2), 5.12 (m, 2 H, H-3, H-4), 5.50 (d, 1 H, *J* = 5.5 Hz, H-1), 7.17–7.28 (m, 5 H, Ar).

(minor diastereomer) δ = 1.04 [s, 9 H, $C(CH_3)_3$], 4.60 (dd, 1 H, *J* = 5.9, 13.3 Hz, H-2), 5.78 (d, 1 H, *J* = 5.9 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 21.64, 23.27 $[CH(CH_3)_2]$, 25.30 $[CH(CH_3)_2]$, 26.93, 27.09 $[C(CH_3)_3]$, 38.74, 38.96 $[C(CH_3)_3]$, 39.60 (*C*HPh), 42.35 (CH_2CO), 45.42 $[CH_2CH(CH_3)_2]$, 53.77 (C-2), 62.88 (C-5), 65.85, 69.41 (C-3, C-4), 96.87 (C-1), 126.46, 127.72, 128.39 (C-Ar), 144.08 (C-ipso), 150.53 (*C*O, urethane), 171.26 (*C*O, acyl), 177.18, 177.25 (*C*O, pivaloyl).

(minor diastereomer) δ = 26.81 $[C(CH_3)_3]$, 96.80 (C-1).

Anal. Calcd for $C_{29}H_{41}NO_8$ (531.65): C, 65.52; H, 7.77; N, 2.63. Found: C, 65.55; H, 7.98; N, 2.67.

ESI-MS: *m/z* = 510.4 $[M + Na - CO_2]^+$, 554.5 $[M + Na]^+$, 595.4 $[M + Na + CH_3CN]^+$.

1,2-Dideoxy-1,2-[*N*-(3-phenyl-heptanoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (18c)

According to general procedure (method A). Reagents: $MeAlCl_2$ (2.1 mL, 2.1 mmol, 1.0 M in hexane), *n*-BuLi (1.3 mL, 2.1 mmol, 1.6 M in pentane), toluene (10 mL); **16** (100 mg, 0.212 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (10 mL).

Yield: 78 mg (69%); colourless, amorphous solid; R_f = 0.43 (LPE–EtOAc, 5:1); mp 133 °C; $[\alpha]_D^{22}$ +12.1 (c = 1.0, $CHCl_3$); diastereomeric ratio 95:5 (H-1, 400 MHz ^{1}H NMR), 96:4 (HPLC).

Analytical HPLC: R_t = 22.85 (minor diastereomer), 23.35 min (major diastereomer) [MeCN–H_2O, 80:20].

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.79 (t, 3 H, *J* = 6.0 Hz, CH_3), 1.00–1.32 [m, 4 H, $(CH_2)_2$], 1.16, 1.20 [s, 18 H, $C(CH_3)_3$], 1.55–1.70 (m, 2 H, *J* = 5.9 Hz, CH_2), 2.97–3.10 (m, 2 H, *J* = 18.0, 5.5, 8.6, 5.9 Hz, C*H*Ph, CH_2CO), 3.37 (dd, 1 H, *J* = 16.0, 8.6 Hz, CH_2CO), 3.92 (dd, 1 H, *J* = 12.9, 3.1 Hz, H-5a), 4.03 (d, 1 H, *J* = 12.9 Hz, H-5b), 4.47 (dd, 1 H, *J* = 7.4, 5.9 Hz, H-2), 5.11 (m, 1 H, H-4), 5.14 (m, 1 H, H-3), 5.52 (d, 1 H, *J* = 5.9 Hz, H-1), 7.15–7.27 (m, 5 H, Ar).

(minor diastereomer) δ = 1.03 [s, 9 H, $C(CH_3)_3$], 3.17 (dd, 1 H, *J* = 7.4, 2.2 Hz, CH_2CO), 4.60 (dd, 1 H, *J* = 7.4, 5.8 Hz, H-2), 5.82 (d, 1 H, *J* = 5.8 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 13.94 $[(CH_2)_3CH_3]$, 22.52 (CH_2), 26.91, 27.09 $[C(CH_3)_3]$, 29.59, 36.07 (CH_2), 38.72, 38.94 $[C(CH_3)_3]$, 38.72 (CH_2CO), 38.94 (*C*HPh), 53.77 (C-2), 62.88 (C-5), 65.83, 69.38 (C-3, C-4), 96.86 (C-1), 126.44, 127.69, 128.37 (C-Ar), 144.17 (C-ipso), 150.57 (*C*O, urethane), 171.27 (*C*O, acyl), 177.16, 177.22 (*C*O, pivaloyl).

Anal. Calcd for $C_{29}H_{41}NO_8$ (531.65): C, 65.52; H, 7.77; N, 2.63. Found: C, 65.49; H, 7.70; N, 2.57.

ESI-MS: *m/z* = 510.5 $[M + Na - CO_2]^+$, 554.6 $[M + Na]^+$, 570.5 $[M + K]^+$.

1,2-Dideoxy-1,2-[*N*-(4,4-dimethyl-3-phenylpentanoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (18d)

a) According to general procedure (method A). Reagents: $MeAlCl_2$ (2.1 mL, 2.1 mmol, 1.0 M in hexane), *t*-BuLi (1.2 mL, 2.1 mmol, 1.7 M in hexane), toluene (10 mL); **16** (100 mg, 0.212 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (10 mL).

Yield: 61 mg (54%); colourless, amorphous solid; R_f = 0.53 (LPE–EtOAc, 5:1); mp 160 °C; $[\alpha]_D^{22}$ +14.7 (c = 1.0, $CHCl_3$); diastereomeric ratio 97:3 (HPLC), 96:4 (H-1, 400 MHz ^{1}H NMR).

b) According to general procedure (method B). Reagents: 1.05 mL (2.1 mmol) Me_3Al (2 M in toluene), 1.2 mL (2.1 mmol) *tert*-butyllithium (1.7 M in hexane), 10 mL toluene; 100 mg (0.212 mmol) **16**, 0.3 mL (0.3 mmol) $MeAlCl_2$ (1.0 M in hexane), 10 mL toluene.

Yield: 66 mg (57%); diastereomeric ratio 91:9 (H-1, 400 MHz ^{1}H NMR), 93:7 (HPLC).

Analytical HPLC: R_t = 13.93 (minor diastereomer), 14.70 min (major diastereomer) [MeCN–H_2O, 85:15].

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.88 [s, 9 H, C(CH_3)$_3$], 1.14, 1.18 [s, 18 H, C(CH_3)$_3$], 2.98 (m, 2 H, *J* = 18.0 Hz, C*H*Ph, CH_2CO), 3.75 (dd, 1 H, *J* = 18.0, 5.5 Hz, CH_2CO), 3.92 (dd, 1 H, *J* = 12.5, 3.5 Hz, H-5a), 4.03 (dd, 1 H, *J* = 12.5, 1.2 Hz, H-5b), 4.44 (dd, 1 H, *J* = 7.4, 5.9 Hz, H-2), 5.08 (dd, 1 H *J* = 3.1, 1.2 Hz, H-4), 5.10 (dd, 1 H, *J* = 7.4, 3.1 Hz, H-3), 5.52 (d, 1 H, *J* = 5.9 Hz, H-1), 7.14–7.25 (m, 5 H, Ar).

(minor diastereomer) δ = 0.86 [s, 9 H, C(CH_3)$_3$], 3.20 (dd, 1 H, *J* = 17.2, 3.5 Hz, CH_2CO), 3.51 (dd, 1 H, *J* = 17.6, 6.6 Hz, CH_2CO), 4.51 (m, 1 H, H-2), 4.95 (d, 1 H, *J* = 5.5 Hz, H-3), 5.78 (d, 1 H, *J* = 5.5 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 26.91, 27.05 [C(CH_3)$_3$], 28.08 [CHC(CH_3)$_3$], 33.72 [CHC(CH$_3$)$_3$], 36.26 (CH_2CO), 38.72, 38.93, 38.94 [C(CH$_3$)$_3$], 51.93 (CHPh), 53.74 (C-2), 62.96 (C-5), 65.87, 69.26 (C-3, C-4), 96.81 (C-1), 126.42, 127.75, 129.30 (C-Ar), 141.88 (C-ipso), 150.77 (CO, urethane), 171.99 (CO, acyl), 177.17, 177.27 (CO, pivaloyl).

(minor diastereomer) δ = 26.70 [C(CH_3)$_3$].

Anal. Calcd for $C_{29}H_{41}NO_8$ (531.65): C, 65.52; H, 7.77; N, 2.63. Found: C, 65.60; H, 7.73; N, 2.52.

ESI-MS: *m/z* = 510.4 $[M + Na - CO_2]^+$, 554.5 $[M + Na]^+$, 570.4 $[M + K]^+$.

1,2-Dideoxy-1,2-[*N*-(3-cyclohexyl-3-phenylpropanoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (18e)

According to general procedure (method A). Reagents: $MeAlCl_2$ (2.1 mL, 2.1 mmol, 1.0 M in hexane), cyclohexylmagnesium bromide (1.05 mL, 2.12 mmol, 2.0 M in Et_2O), toluene (10 mL); **16** (100 mg, 0.212 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (10 mL).

Yield: 59 mg (50%); 75% conversion (H-1, 400 MHz ^{1}H NMR); colourless, amorphous solid; R_f = 0.53 (LPE–EtOAc, 5:1); mp 148 °C; $[\alpha]_D^{22}$ +14.5 (c = 1.0, $CHCl_3$); diastereomeric ratio 74:26 (H-2, 400 MHz ^{1}H NMR), 71:29 (HPLC).

Analytical HPLC: R_t = 21.07 (minor diastereomer), 22.43 min (major diastereomer) [MeCN–H_2O, 85:15].

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.74–1.87 (m, 11 H, C*H*, CH_2, cyclohexyl), 1.15, 1.19 [s, 18 H, C(CH_3)$_3$], 2.87 (m, 1 H, C*H*Ph), 3.04 (dd, 1 H, *J* = 16.4, 3.9 Hz, CH_2CO), 3.54 (dd, 1 H, *J* = 16.4, 5.9 Hz, CH_2CO), 3.90 (dd, 1 H, *J* = 12.9, 1.95 Hz, H-5a), 4.02 (dd, 1 H, *J* = 12.9, 4.3 Hz, H-5b), 4.38 (dd, 1 H, *J* = 5.5, 7.4 Hz, H-2), 5.09 (m, 2 H, H-4, H-3), 5.39 (d, 1 H, *J* = 5.5 Hz, H-1), 7.10–7.26 (m, 5 H, Ar).

(minor diastereomer) δ = 0.97 [s, 9 H, C(CH_3)$_3$], 2.95 (m, 1 H, C*H*Ph), 3.29 (m, 2 H, CH_2CO), 4.52 (dd, 1 H, *J* = 7.3, 5.9 Hz, H-2), 4.96 (d, 1 H, *J* = 1.95 Hz, H-4), 5.01 (dd, 1 H, *J* = 7.44, 1.9 Hz, H-3), 5.79 (d, 1 H, *J* = 5.9 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 26.35, 30.93, 31.15 (CH_2-Cyclohexyl), 26.93, 27.06 [C(CH_3)$_3$], 38.61 (CH_2CO), 38.72, 38.94 [C(CH$_3$)$_3$], 42.61 (CH-Cyclohexyl), 48.15 (CHPh), 53.77 (C-2), 62.88 (C-5), 65.82, 69.26 (C-3, C-4), 96.79 (C-1), 126.36, 128.14, 128.42 (C-Ar), 143.06 (C-ipso), 150.63 (CO, urethane), 171.83 (CO, acyl), 177.22 (2C, CO, pivaloyl).

(minor diastereomer) δ = 26.77 [C(CH_3)$_3$], 38.86 (CH_2CO), 43.17 (CH, cyclohexyl), 47.00 (CHPh), 53.71 (C-2), 96.65 (C-1).

Anal. Calcd for $C_{31}H_{43}NO_8$ (557.69): C, 66.76; H, 7.77; N, 2.51. Found: C, 66.60; H, 7.91; N, 2.38.

ESI-MS: *m/z* = 536.6 $[M + Na - CO_2]^+$, 580.5 $[M + Na]^+$, 596.5 $[M + K]^+$.

1,2-Dideoxy-1,2-[*N*-(3-phenylnon-4-enoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (18f)

According to general procedure (method C; reaction time 40 h). Reagents: DIBAL-H (2.1 mL, 2.1 mmol, 1.0 M in CH_2Cl_2), 1-hexyne (0.3 mL, 2.7 mmol), toluene (10 mL); **16** (100 mg, 0.212 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (10 mL).

Yield: 48 mg (41%); 90% conversion; colourless, amorphous solid; R_f = 0.53 (LPE–EtOAc, 5:1); mp 98 °C; $[\alpha]_D^{21}$ +9.0 (c = 1.0, $CHCl_3$); diastereomeric ratio 81:19 (H-2, 400 MHz ^{1}H NMR).

Analytical HPLC: R_t = 20.85 min (MeCN–H_2O, 85:15).

^{1}H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.84 [m, 3 H, ^{3}J = 7.0 Hz, (CH$_2$)$_2$CH_3], 1.06, 1.21 [s, 18 H, C(CH_3)$_3$], 1.26 [m, 4 H, (CH_2)$_2$], 1.94 (m, 2 H, *J* = 6.7 Hz, =CHCH_2), 3.18 (dd, 1 H, *J* = 16.8, 6.3 Hz, CH_2CO), 3.44 (dd, 1 H, *J* = 16.8, 7.3 Hz, CH_2CO), 3.82 (m, 1 H, *J* = 7.3, 7.0 Hz, C*H*Ph), 3.94 (dd, 1 H, *J* = 12.9, 3.9 Hz, H-5a), 4.04 (dd, 1 H, *J* = 12.9, 0.7 Hz, H-5b), 4.63 (dd, 1 H, *J* = 7.4, 5.9 Hz, H-2), 5.06 (d, 1 H, *J* = 3.1 Hz, H-4), 5.13 (dd, 1 H, *J* = 7.4, 3.1 Hz, H-3), 5.40–5.74 (dd, 2 H, *J* = 15.3, 6.7 Hz, C*H*=C*H*), 5.83 (d, 1 H, *J* = 5.9 Hz, H-1), 7.14–7.28 (m, 5 H, Ar).

(minor diastereomer) δ = 1.17, 1.21 [s, 18 H, C(CH_3)$_3$], 2.93 (dd, 1 H, *J* = 16.8 Hz, CH_2CO), 4.46 (dd, 1 H, *J* = 7.8, 5.8 Hz, H-2).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 13.92 [(CH$_2$)$_3$CH$_3$], 22.20 (CH_2), 26.83, 27.09 [C(CH_3)$_3$], 31.46, 32.13 (CH_2), 38.66, 38.94 [C(CH$_3$)$_3$], 41.26 (CH_2CO), 44.24 (CHPh), 53.75 (C-2), 62.94 (C-5), 65.73, 69.17 (C-3, C-4), 96.79 (C-1), 126.46, 127.48, 128.55 (C-Ar), 131.33, 131.97 (CH=), 143.28 (C-ipso), 150.72 (CO, urethane), 170.72 (CO, acyl), 177.11 (2C, CO, pivaloyl).

(minor diastereomer) δ = 26.94 [C(CH_3)$_3$], 62.90 (C$_2$).

$C_{31}H_{43}NO_8$ (557.69).

ESI-MS: *m/z* = 536.5 $[M + Na - CO_2]^+$, 580.5 $[M + Na]^+$, 621.4 $[M + Na + CH_3CN]^+$.

1,2-Dideoxy-1,2-[*N*-(3-phenylnon-4-ynoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (18g)

According to general procedure (method A; reaction time 72 h). Reagents: $MeAlCl_2$ (2.1 mL, 2.1 mmol, 1.0 M in hexane), 1-hexynyllithium (2.1 mmol, from 1-hexyne in toluene and 1.05 equiv *n*-BuLi); toluene (10 mL); **16** (100 mg, 0.212 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (10 mL).

Yield: 22 mg (16%); conversion: 59% (H-1, 400 MHz ^{1}H NMR); colourless, amorphous solid; R_f = 0.48 (LPE–EtOAc, 4:1);

$[\alpha]_D^{22}$ +4.8 (c = 1.0, $CHCl_3$); diastereomeric ratio 81:19 (H-1, 400 MHz ^1H NMR).

Analytical HPLC: R_t = 14.63 min (MeCN–H_2O, 85:15).

^1H NMR (400 MHz, $CDCl_3$): (major diastereomer) δ = 0.88 [t, 3 H, *J* = 7.0 Hz, $(CH_2)_3CH_3$], 1.14, 1.23 [s, 18 H, $C(CH_3)_3$)], 1.30–1.40 (m, 2 H, *J* = 7.0, 4.7 Hz, CH_2), 1.42–1.49 (m, 2 H, *J* = 5.1, 4.7 Hz, CH_2), 2.16 (dt, 2 H, *J* = 5.1, 2.0 Hz, $CH_2C{\equiv}$), 3.06 (dd, 1 H, *J* = 16.8, 7.4 Hz, CH_2CO), 3.53 (dd, 1 H, *J* = 16.8, 9.8 Hz, CH_2CO), 3.97 (dd, 1 H, *J* = 12.9, 3.1 Hz, H-5a), 4.07 (dd, 1 H, *J* = 13.3, 1.6 Hz, H-5b), 4.13 (m, 1 H, *J* = 9.8, 7.0, 2.0 Hz, CHPh), 4.72 (dd, 1 H, *J* = 7.4, 5.9 Hz, H-2), 5.14 (m, 1 H, H-4), 5.18 (dd, 1 H, *J* = 7.4, 3.1 Hz, H-3), 5.87 (d, 1 H, *J* = 5.9 Hz, H-1), 7.19–7.37 (m, 5 H, Ar).

(minor diastereomer) δ = 3.27 (dd, 1 H, *J* = 16.4, 7.1 Hz, CH_2CO), 3.43 (dd, 1 H, *J* = 16.4, 7.4 Hz, CH_2CO), 4.57 (dd, 1 H, *J* = 8.6, 5.9 Hz, H-2), 5.70 (d, 1 H, *J* = 5.9 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): (major diastereomer) δ = 13.62 [$(CH_2)_3CH_3$], 18.55 (CH_2), 21.98 (CH_2), 26.91, 27.10 [$C(CH_3)_3$], 31.01 (CH_2), 33.53 (CHPh), 38.97, 38.73 [$C(CH_3)_3$], 44.22 (CH_2CO), 53.90 (C-2), 63.04 (C-5), 65.80, 69.26 (C-3, C-4), 80.32, 83.76 (C≡), 97.02 (C-1), 127.04, 127.43, 128.60 (C-Ar), 141.08 (C-ipso), 155.39 (CO, urethane), 170.03 (CO, acyl), 177.16 (2C, CO, pivaloyl).

$C_{31}H_{41}NO_8$ (555.67).

ESI-MS: *m/z* = 534.5 $[M + Na - CO_2]^+$, 578.5 $[M + Na]^+$.

1,2-Dideoxy-1,2-[*N*-(3-methylbutanoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (19)

According to general procedure (method B). Reagents: Me_3Al (1.2 mL, 2.4 mmol, 2.0 M in pentane), PhLi (1.35 mL, 2.12 mmol, 1.8 M in cyclohexane–Et_2O, 70:30), toluene (10 mL); **15** (100 mg, 0.243 mmol), $MeAlCl_2$ (0.3 mL, 0.3 mmol, 1.0 M in hexane), toluene (10 mL).

Yield: 23.8 mg (23%, isolated); conversion: 50% (200 MHz ^1H NMR); colourless, amorphous solid; R_f = 0.50 (LPE–EtOAc, 5:1); mp 111 °C; $[\alpha]_D^{22}$ –13.6 (c = 1.0, $CHCl_3$).

Analytical HPLC-MS: Phenomenex LUNA C18-2 (75 × 4.6 mm, 3µm), MeCN–H_2O gradient 80:20 → 100:0 in 10 min, ELS-detection: ratio **18h**:**19** = 1:2.3.

R_t = 3.12 min: 1,2-Dideoxy-1,2-[*N*-(3-phenyl-butanoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (**18h**) ($C_{26}H_{35}NO_8$, 489.24); *m/z* = 406.5 $[M + Na - CO_2]^+$, 450.4 $[M + Na]^+$, 491.4 $[M + Na + CH_3CN]^+$.

R_t = 3.75 min: 1,2-Dideoxy-1,2-[*N*-(3-methyl-butanoyl)epoxycarbonylimino]-3,4-di-*O*-pivaloyl-β-D-arabinopyranose (**19**) ($C_{21}H_{33}NO_8$, 427.22); *m/z* = 468.4 $[M + Na - CO_2]^+$, 512.4 $[M + Na]^+$, 553.5 $[M + Na + CH_3CN]^+$.

19: ^1H NMR (200 MHz, $CDCl_3$): δ = 0.94 [d, 6 H, *J* = 6.4 Hz, $CH(CH_3)_2$], 1.16, 1.23 [s, 18 H, $C(CH_3)_3$], 2.03–2.17 (m, 1 H, $CH(CH_3)_2$], 2.73 (m, 2 H, CH_2CO), 3.97 (dd, 1 H, *J* = 12.7, 3.0 Hz, H-5a), 4.09 (dd, 1 H, *J* = 12.7, 1.0 Hz, H-5b), 4.69 (dd, 1 H, *J* = 7.3, 5.8 Hz, H-2), 5.16–5.28 (m, 2 H, *J* = 7.3 Hz, H-3, H-4), 5.88 (d, 1 H, *J* = 5.4 Hz, H-1).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 22.44, 22.47 (CH_3), 24.88 [$CH(CH_3)_2$], 26.91, 27.10 [$C(CH_3)_3$], 29.27 (CH_2CH_3), 38.72, 38.99 [$C(CH_3)_3$], 44.08 (CH_2CO), 53.66 (C-2), 62.93 (C-5), 65.82, 69.55 (C-3, C-4), 96.89 (C-1), 150.62 (CO, urethane), 171.78 (CO, acyl), 177.18 (2C, CO, pivaloyl).

3-Phenylvaleric Acid (20)[17]

To a solution of **18a** (198 mg, 0.393mmol) in THF/H_2O (3:1, 80 mL), H_2O_2 (0.3 mL, 35% in H_2O) and LiOH (19 mg, 0.79 mmol) were added at 0 °C. The solution was stirred at r.t. until TLC showed complete conversion (3 h). $NaHSO_3$ (1.5 M, 2 mL) was added, the pH of the solution was adjusted to 9 by addition of sat. $NaHCO_3$, and THF was removed in vacuo. The aqueous layer was extracted with CH_2Cl_2. The organic layer was dried with $MgSO_4$ and the solvent was removed in vacuo, yielding the chiral auxiliary **10**. The aqueous solution was adjusted to pH 1–2 by the addition of 1 N HCl, and carboxylic acid **20** was extracted with CH_2Cl_2.

Yield: 109 mg (81%) oxazolidinone **13**, 60 mg (86%) acid **20**; $[\alpha]_D^{22}$ +42.3 (c = 5.0, benzene), Lit.[18] $[\alpha]_D^{25}$ +46.3 (benzene).

^1H NMR (200 MHz, $CDCl_3$): δ [ppm] = 0.76 (t, 3 H, *J* = 7.3 Hz, CH_3), 1.52–1.80 (dd, 2 H, *J* = 7.3, 6.8 Hz, CH_2CH_3), 2.61–2.66 (m, 2 H, CH_2CO), 2.88–3.06 (dd, 1 H, *J* = 7.8, 6.8 Hz, CHPh), 7.15–7.34 (m, 5 H, Ar), 10.78 (broad s, 1 H, COOH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.86 (CH_3), 29.13 (CH_2), 41.15 (CH_2CO), 43.52 (CHPh), 126.54, 127.50, 128.45 (C-Ar), 143.62 (C-ipso), 178.90 (COOH).

$C_{11}H_{14}O_2$ (178.10).

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