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Synthesis of β-*C*-Glycosyl Amino Acids by Ring Opening of Donor-Acceptor Spiro-cyclopropanecarboxylated Sugars

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Abstract: The electrophilic ring opening of donor-acceptor spiro-cyclopropanecarboxylated sugars are shown to provide easy access to the stereoselective synthesis of β-*C*-glycosyl D- and L-alanine derivatives. A possible mechanism is proposed for the ring-opening reaction based on the obtained crystal structure of one of the spiro-cyclic sugar moieties.

Keywords: amino acids · carboxylation · donor-acceptor systems · glycoproteins · ring opening

1. Introduction

In the last two decades, the crucial role of glycoproteins in key cellular processes, such as cell recognition, signaling, and immune response, has been understood significantly.[1] In these bio-molecules, the sugar unit is attached to the peptide or protein through either oxygen (as in *O*-glycoproteins) or nitrogen (as in *N*-glycoproteins) atoms. Biological studies on the evaluation of glycopeptides as carbohydrate antigens,[2] enzyme inhibitors,[3] and novel therapeutics[4] has opened a new avenue in drug discovery. In this context, the attachment of the glycan to the peptide through a C–C bond has become one of the strategic approaches in achieving glycopeptide analogues that are more stable to acidic or enzymatic hydrolysis conditions.[5] This has necessitated the stereoselective synthesis of various *C*-glycosyl amino acid precursors. To date, the majority of the methodologies reported have been on the synthesis of the α-*C*-glycosyl analogues of serine, threonine, and asparagine moieties.[5e] Apart from these, a few methods for the synthesis of *C*-glycosyl alanine are also described. The motivation behind the linking of the sugar moiety and the α-amino acid, D- or L-alanine, through a C–C bond is to increase the proximity between the glycan and the peptide or protein backbone, which could influence the overall structure of the glycopeptide/protein.

One of the earlier reports for the synthesis of α-*C*-glycosylated DL-alanine derivatives involved the generation of a radical at the anomeric position, followed by its trapping with various dehydroalanine precursors.[6] This protocol was applied to achieve the synthesis of α-*C*-glycosyl DL-alanine derivatives of D-Glc, D-Gal, and D-Lac. Recently, Dondoni *et al.*[7] cleverly utilized the asymmetric α-amination reaction catalyzed by D- or L-proline on *C*-glycosylalkyl aldehydes to achieve the α- and β-*C*-(D)-glycosyl D- and L-amino acids. Apart from these, an asymmetric Strecker reaction on α-*C*-(D)-glycosyl acetaldehyde,[8] and a cross-metathesis of a gluco-heptenitol derivative with protected allyl or vinyl glycine, followed by Hg(II) mediated cyclization,[9] are also reported to obtain α-*C*-(D)-glycosyl D-alanine derivatives. Consequently, the Claisen-Ireland rearrangement of 2-*O*-glycynyl *exo*-methylene glycals was shown to provide α-*C*-glycoamino acid glycals.[10] On the other hand, α-*C*-allyl-(D)-glucopyranoside was converted to the α-*C*-(D)-glucosyl D- and L-alanine derivatives in a stereoselective fashion involving Sharpless asymmetric dihydroxylation as the key step to incorporate the chirality on the olefin.[11] Very recently, this protocol was successfully extended to achieve the β-*C*-(D)-galactosyl D- and L-alanine derivatives from the corresponding β-*C*-allyl-(D)-galactopyranoside, obtained by a stereoselective Grignard addition to α-(D)-galactosyl iodide.[12] Another approach for the stereoselective preparation of 2-deoxy-β-*C*-(D)-galactosyl D-alanine derivative was also reported, involving a Wittig reaction of 2-deoxy (D)-galactosyl phosphoranes with a Garner aldehyde, followed by palladium-catalyzed hydrogenation.[13] However, to the best of our knowledge, the application of donor-acceptor (DA) cyclopropanes, obtained by the cyclopropanation of *exo*-methylene glycals, has not been explored towards the synthesis of *C*-glycosyl D- and L-alanine derivatives. In continuation of our research in the use of DA cyclopropanes[14] in the synthesis of various glycoamino acids (GAAs),[15] herein we report the synthesis of β-

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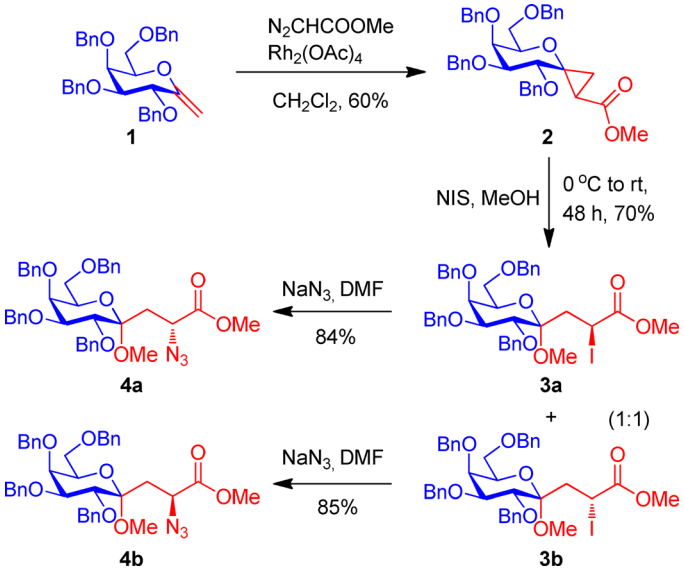
C-(D)-glycosyl D- and L-alanine scaffolds from sugar-derived spiro-cyclopropanecarboxylates.

2. Results and Discussion

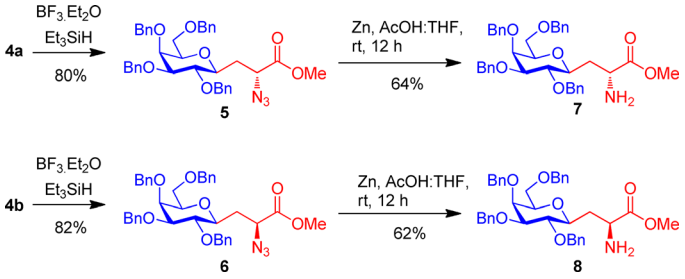
Our initial efforts were focused on the preparation of *C*-(D)-galactosyl alanine from the D-galactose-derived *exo*-glycal **1**.[16] Thus, **1** was cyclopropanated with methyldiazoacetate in the presence of a catalytic amount of $Rh_2(OAc)_4$ in dichloromethane to afford the spiro-cyclopropanecarboxylate **2**[17] in 60% yield, as a mixture of four diastereomers. Interestingly, *N*-iodosuccinimide (NIS) mediated solvolytic ring opening of **2** in methanol provided the iodoketals **3a** and **3b**, which were separable as single diastereomers by silica-gel column chromatography. Subsequent reaction of iodoketals **3a** and **3b** with sodium azide in DMF gave the azido ketals **4a** and **4b**,[18] respectively, in good yield (Scheme 1).



Scheme 1. Synthesis and solvolytic ring opening of D-galactose-derived spiro-cyclopropanecarboxylate.

Reaction of the obtained azido ketals **4a** and **4b** with Et_3SiH, $BF_3.Et_2O$ in CH_2Cl_2 provided β-*C*-(D)-galactosyl azido esters **5**[12] and **6**,[12] which were further converted to the corresponding β-*C*-(D)-galactosyl alanine derivatives **7** and **8**, respectively, using Zn/AcOH-mediated azide reduction (Scheme 2).

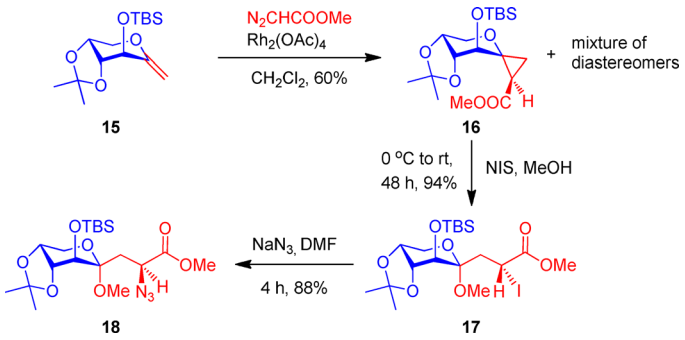
Encouraged by this result, spiro-cyclopropanecarboxylates **9**[17] and **10**,[17b] synthesized from the corresponding *exo*-glycals, were subjected to a pyranose oxygen-assisted solvolytic ring-opening reaction in methanol using NIS to provide the iodoketals **11** and **12**, respectively, as a mixture of diastereomers. Substitution of the iodide with azide led to the formation of azido ketals **13** and **14** in excellent yield as mixture of diastereomers (Table 1).



Scheme 2. Synthesis of β-*C*-(D)-galactosyl L- and D-alanine derivatives.

Table 1. Solvolytic ring opening of spiro-cyclopropanecarboxylated sugar derivatives.

DA Cyclopropane	Iodide (%)	Azide (%)
9	**11** (72 (1:1))	**13** (92 (1:1))
10	**12** (73 (6:1))	**14** (70 (4:1))

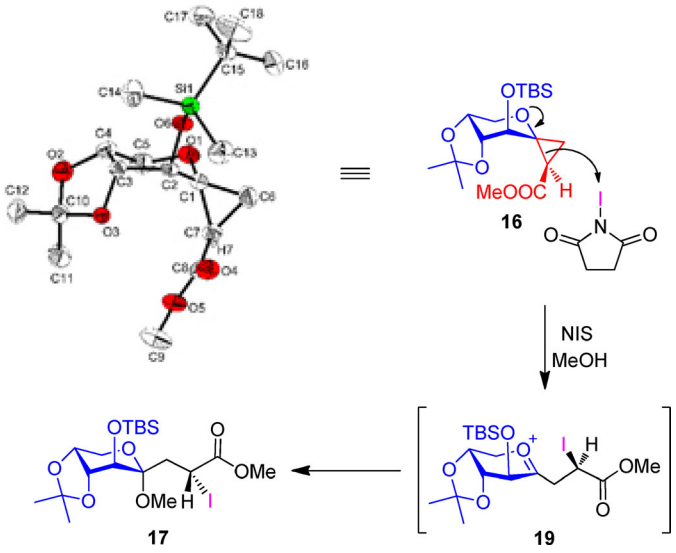


Scheme 3. Ring opening of D-fructose-derived spiro-cyclopropanecarboxylate.

To further explore the ring opening of DA spiro-cyclopropanecarboxylated sugar derivatives, D-fructose-derived *exo*-glycal **15**[19] was cyclopropanated with methyldiazoacetate to provide a mixture of diastereomeric DA cyclopropanes. Interestingly, purification of this mixture by column chromatography allowed us to isolate one of the diastereomers **16**, in its pure form, as a solid. Crystallizing **16**[20] and subjecting it to single crystal X-ray diffraction studies provided the support to assign the exact stereochemistry at the newly formed stereocenters. Subjecting **16** to NIS in methanol provided the iodoketal **17** as a single diastereomer, which was further converted to the azido ketal **18** (Scheme 3). This clearly indicates that

the ring-opening reaction that provides the iodoketal as a single diastereomer is highly stereospecific.

Based on the above observations, a possible mechanism for the electrophilic ring opening of spiro-cyclopropane-carboxylated sugar **16** is proposed. Thus, stereospecific "edge attack" of iodine through the less hindered side of **16** generates an oxocarbenium ion intermediate **19**. Trapping of **19** with methanol via a stereoelectronically favored axial trajectory provides iodoketal **17,** as a single diastereomer, which was converted to the azido ketal **18** through an SN_2 reaction (Scheme 4). The stereochemistry of **18** at the anomeric position was further confirmed by a 2D NOESY NMR experiment.[21]

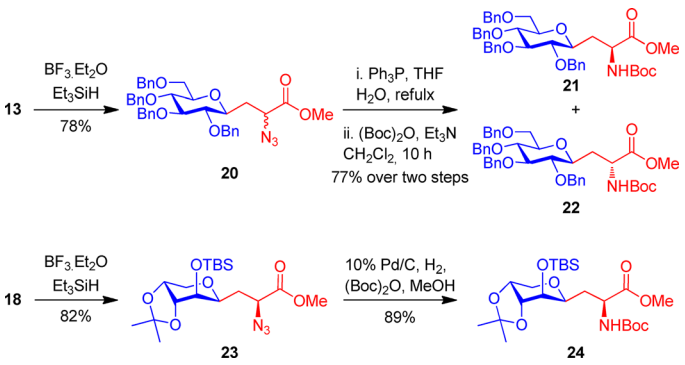


Scheme 4. Proposed mechanism for the NIS mediated ring opening of DA spiro-cyclopropane carboxylate **16**.

Finally, the synthesized azido ketals **13** and **18** were subjected to $BF_3.Et_2O/Et_3SiH$ to provide *C*-glycoside derivatives **20** (as a 1:1 mixture of diastereomers) and **23** (as a single diastereomer), which were further converted to β-*C*-(D)-glucosyl L-alanine derivative **21**[7] and β-*C*-(D)-glucosyl D-alanine derivative **22**,[7] and β-*C*-(D)-arabinosyl L-alanine derivative **24**, respectively (Scheme 5).

3. Conclusion

In conclusion, a general methodology for the stereoselective synthesis of β-*C*-(D)-glycosyl D- and L-alanine derivatives from donor-acceptor spiro-cyclopropanecarboxylated sugars was revealed. The approach of the *O*-nucleophilic, MeOH, via the axial trajectory due to the anomeric effect was utilized as a tool to achieve the formation of a β-*C*-glycosidic bond in the electrophilic ring opening of spiro-cyclopropanecarboxylated donors. The developed



Scheme 5. Synthesis of β-*C*-(D)-glycosyl D- and L-alanine derivatives.

methodology was successfully applied to the preparation of D-Gal-, D-Glc-, and D-Ara-derived β-*C*-(D)-glycosyl alanine derivatives. Further, application of the synthesized GAAs in the preparation of glycopeptide analogues is in progress.

4. Experimental Section

All the reactions were carried out under nitrogen atmosphere and monitored by thin layer chromatography (TLC) using silica-gel GF_{254} plates with detection by charring with 5% (v/v) H_2SO_4 in methanol or by phosphomolybdic acid (PMA) stain or by ultra violet (UV) detection. All the chemicals were purchased from local suppliers and Sigma-Aldrich. Solvents used in the reactions were distilled over dehydrated agents. Silica gel (100–200 mesh) was used for column chromatography. ^1H, ^{13}C, DEPT, COSY, and NOESY spectra were recorded on Bruker 400 MHz and 500 MHz spectrometers in $CDCl_3$ and C_6D_6. ^1H NMR chemical shifts were reported in ppm (δ) with TMS as internal standard (δ 0.00) and ^{13}C NMR were reported in chemical shifts with solvent reference ($CDCl_3$, δ 77.00). High resolution mass spectra (HRMS) were obtained in the ESI mode using a Bruker maXis QTOF spectrometer.

(3*R*,5*R*,6*S*,7*S*,8*R*)-Methyl 6,7,8-tris(benzyloxy)-5-(benzyloxymethyl)-4-oxaspiro[2.5]octane-1-carboxylate (**2**): To a stirred suspension of *exo*-glycal **1** (4.4 g, 8.20 mmol) and $Rh_2(OAc)_4$ (72 mg, 0.16 mmol) in anhydrous CH_2Cl_2 (30 mL), over a period of 1 h, a solution of methyl diazoacetate (2.28 mL, 24.6 mmol) in CH_2Cl_2 (70 mL) was added dropwise. After completion of the reaction, the reaction mixture was concentrated *in vacuo* and the obtained crude product was purified by silica-gel column chromatography, which gave the desired spiro-cyclopropanecarboxylate **2** (2.9 g, 60%) as a mixture of four diastereomers. IR (neat): ν_{max} 3063, 3030, 2947, 2871, 1736, 1495, 1452, 1364 cm^{-1}. HRMS calcd. for $C_{38}H_{40}O_7+Na$ 631.2672, found 631.2670.

(*S*)-Methyl 2-iodo-3-((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-methoxytetrahydro-2*H*-pyran-2-yl)propanoate (**3a**) and (*R*)-Methyl 2-iodo-3-((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)-methyl)-2-methoxytetrahydro-2*H*-pyran-2-yl)propanoate (**3b**): To a stirred solution of D-galactose-derived spirocyclopropane carboxylate **2** (3.3 g, 5.42 mmol) in methanol (20 mL) at 0 °C under nitrogen, *N*-iodosuccinimide (NIS) (1.45 g, 6.5 mmol) was added. The reaction mixture was stirred for 48 h at room temperature. After complete conversion of the starting material, confirmed by TLC, the reaction was quenched with saturated sodium thiosulfate. Methanol was evaporated under reduced pressure and the obtained residue was extracted with dichloromethane (3×100 mL). Finally, the combined organic layer was washed with water and brine solution, and concentrated on a rotary evaporator. The obtained crude product was purified by silica-gel column chromatography to afford the ring-opened iodo-carboxylates **3a** and **3b** (2.9 g, 70 %) as a colorless gum. **(3a)**: IR (neat): ν_{max} 3062, 3035, 2920, 2865, 1747, 1632, 1500, 1451, 1363 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.27–7.41 (m, 20H), 5.03 (d, 1H, *J* = 12.0 Hz), 4.97 (d, 1H, *J* = 11.0 Hz), 4.74–4.80 (m, 3H), 4.58 (d, 1H, *J* = 11.5 Hz), 4.48 (d, 1H, *J* = 11.5 Hz), 4.41 (d, 1H, *J* = 12.0 Hz), 4.00–4.09 (m, 4H), 3.68 (dt, 1H, *J* = 2.0 Hz, *J* = 7.0 Hz), 3.50–3.54 (m, 4H), 3.40 (dd, 1H, *J* = 5.5 Hz, *J* = 9.0 Hz), 3.26 (s, 3H), 2.97 (dd, 1H, *J* = 12.5 Hz, *J* = 14.0 Hz), 2.39 (dd, 1H, *J* = 2.5 Hz, *J* = 14.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9, 139.1, 138.3, 137.7, 128.9, 128.7, 128.4, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.2, 127.1, 102.0, 80.6, 75.5, 75.0, 74.6, 74.3, 73.5, 72.4, 70.4, 68.3, 52.3, 48.3, 38.6, 13.9. HRMS (ESI) calcd. for $C_{39}H_{43}IO_8$ + Na 789.1900, found 789.1902. **(3b)**: IR (neat): ν_{max} 3059, 3032, 2924, 2859, 1742, 1629, 1495, 1455, 1360, 1252, 1215, 1060 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.27–7.37 (m, 20H), 5.01 (d, 1H, *J* = 11.2 Hz), 4.96 (d, 1H, *J* = 10.8 Hz), 4.78 (d, 1H, *J* = 10.8 Hz), 4.75 (d, 1H, *J* = 5.2 Hz), 4.72 (d, 1H, *J* = 11.6 Hz), 4.54 (d, 1H, *J* = 3.6 Hz), 4.52 (d, 1H, *J* = 4.4 Hz), 4.49 (d, 1H, *J* = 10.0 Hz), 4.47 (d, 1H, *J* = 19.2 Hz), 3.92–4.01 (m, 3H), 3.72 (t, 1H, *J* = 6.8 Hz), 3.59 (dd, 1H, *J* = 7.2 Hz, *J* = 7.6 Hz), 3.50 (dd, 1H, *J* = 5.6 Hz, *J* = 9.2 Hz), 3.37 (s, 3H), 3.21 (s, 3H), 2.83 (dd, 1H, *J* = 11.6 Hz, *J* = 15.2 Hz), 2.42 (dd, 1H, *J* = 3.6 Hz, *J* = 15.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 138.9, 138.4, 138.2, 137.9, 128.6, 128.4, 128.3, 128.1, 127.8, 127.8, 127.7, 127.6, 127.5, 127.4, 100.8, 80.8, 78.9, 77.2, 75.7, 74.7, 73.6, 72.5, 70.7, 68.5, 52.4, 48.4, 41.1, 14.8. HRMS calcd. for $C_{39}H_{43}IO_8$ + Na 789.1900, found 789.1904.

(*R*)-Methyl 2-azido-3-((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-methoxytetrahydro-2*H*-pyran-2-yl)propanoate (**4a**): To a stirred solution of **3a** (1.3 g, 1.69 mmol) in *N*,*N*-dimethylformamide (10 mL), sodium azide (0.505 g, 8.47 mmol) was added and the reaction mixture was stirred at room temperature for 4 h. After completion of the reaction, monitored by TLC, the solvent was removed under reduced pressure and the obtained residue was extracted with dichloromethane (3× 50 mL). The combined organic layer was washed with water and brine, dried over anhydrous $MgSO_4$ and concentrated. The obtained crude product was purified by silica-gel column chromatography to provide the corresponding azido carboxylate **4a** (0.98 g, 85 %) as a colorless liquid. IR (neat): ν_{max} 3084, 3068, 3024, 2915, 2871, 2104, 1742, 1495, 1463, 1358 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.28–7.42 (m, 20H), 5.02 (d, 1H, *J* = 10.5 Hz), 5. 01 (d, 1H, *J* = 12.0 Hz), 4.74–4.80 (m, 3H), 4.61 (d, 1H, *J* = 11.5 Hz), 4.53 (d, 1H, *J* = 11.5 Hz), 4.46 (d, 1H, *J* = 11.5 Hz), 4.09 (bs, 2H), 4.07 (bs, 1H), 3.94 (dd, 1H, *J* = 4.0 Hz, *J* = 7.5 Hz), 3.81 (t, 1H, *J* = 6.5 Hz), 3.70 (t, 1H, *J* = 4.5 Hz), 3.65 (s, 3H), 3.61 (dd, 1H, *J* = 5.5 Hz, *J* = 9.0 Hz), 3.28 (s, 3H), 2.43 (dd, 1H, *J* = 4.5 Hz, *J* = 15.0 Hz), 2.24 (dd, 1H, *J* = 8.0 Hz, *J* = 15.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 139.0, 138.4, 138.2, 138.0, 128.4 128.4, 128.3, 128.2, 127.7, 127.6, 127.6, 127.5, 127.4, 127.3, 100.7, 80.8, 77.2, 75.6, 74.6, 74.4, 73.5, 72.4, 70.8, 68.8, 58.6, 52.5, 48.1, 33.4. HRMS calcd. for $C_{39}H_{43}N_3O_8$ + Na 704.2948, found 704.2948.

(*S*)-Methyl 2-azido-3-((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-methoxytetrahydro-2*H*-pyran-2-yl)propanoate (**4b**): Compound **4b** was synthesized from 3b (1.2 g, 1.56 mmol) according to the procedure described for compound **4a**. Yield (0.89 g, 84 %). $[\alpha]_D^{25}$ +11.2 (*c* 0.86, $CHCl_3$); IR (neat): ν_{max} 3089, 3058, 3029, 2921, 2847, 2105, 1745, 1506, 1452, 1360 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.28–7.40 (m 20H), 5.03 (d, 1H, *J* = 9.5 Hz), 5.00 (d, 1H, *J* = 9.5 Hz), 4.80 (d, 1H, *J* = 11.5 Hz), 4.79 (d, 1H, *J* = 16.5 Hz), 4.75 (d, 1H, *J* = 11.5 Hz), 4.56 (d, 1H, 11.5 Hz), 4.50 (d, 1H, *J* = 12.0 Hz), 4.44 (d, 1H, *J* = 12.0 Hz), 4.17 (d, 1H, *J* = 10.0 Hz), 4.08 (dd, 1H, *J* = 2.5 Hz, *J* = 9.5 Hz), 4.01 (d, 1H, *J* = 1.0 Hz), 3.73–3.77 (m, 2H), 3.59 (s, 3H), 3.56 (dd, 1H, *J* = 8.0 Hz, *J* = 9.5 Hz), 3.48 (dd, 1H, *J* = 5.5 Hz, *J* = 9.0 Hz), 3.25 (s, 3H), 2.38 (dd, 1H, *J* = 7.0 Hz, *J* = 14.5 Hz), 2.03 (dd, 1H, *J* = 6.5 Hz, *J* = 14.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 139.0, 138.3, 138.0, 137.8, 128.6, 128.4, 128.3, 128.1, 127.7, 127.7, 127.6, 127.5, 127.4, 127.3, 100.1, 80.9, 77.2, 76.3, 75.2, 74.5, 74.4, 73.5, 72.4, 70.5, 68.5, 58.2, 52.3, 48.0, 32.3. HRMS calcd. for $C_{39}H_{43}N_3O_8$ + Na 704.2948, found 704.2948.

(*R*)-Methyl 2-azido-3-((2*S*,3*S*,4*R*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-propanoate (**5**): To a solution of azido carboxylate **4a** (700 mg, 1.02 mmol) in dry dichloromethane (10 mL), freshly distilled triethyl silane (3.25 mL, 20.55 mmol) was added and the reaction mixture was cooled to −78 °C, then freshly distilled $BF_3.Et_2O$ (1.29 mL, 10.30 mmol) was added dropwise, over a period of 10 minutes, via syringe. The reaction was warmed to −50 °C, and allowed to stir for an additional 4 h. After completion of the reaction, checked by TLC, the reaction mixture was quenched by the addition of saturated aqueous $NaHCO_3$ solution (10 mL). The mixture was taken into a separating funnel

and the aqueous layer was extracted with dichloromethane (3×50 mL). The combined organic layer was washed with water and brine solution, and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure, and purification of the crude product by silica-gel column chromatography, afforded compound **5** (540 mg, 80%) as a colorless liquid. $[\alpha]_D^{25}$ −14.8 (*c* 0.5, $CHCl_3$); IR (neat): ν_{max} 3085, 3066, 3030, 2923, 2854, 2111, 1743, 1496, 1454, 1436, 1363 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.28–7.40 (m, 20H), 4.99 (d, 1H, *J* = 4.8 Hz), 4.96 (d, 1H, *J* = 5.2 Hz), 4.78 (d, 1H, *J* = 12.0 Hz), 4.69 (dd, 2H, *J* = 6.4 Hz, *J* = 13.6 Hz), 4.65 (d, 1H, *J* = 2.8 Hz), 4.47 (q, 2H, *J* = 12.0 Hz), 4.17 (dd, 1H, *J* = 3.2 Hz, *J* = 11.2 Hz), 4.05 (d, 1H, *J* = 2.4 Hz), 3.76 (s, 3H), 3.70 (d, 1H, *J* = 9.2 Hz), 3.65 (dd, 1H, *J* = 2.4 Hz, *J* = 9.2 Hz), 3.55–3.59 (m, 3H), 3.43–3.48 (m, 1H), 2.16–2.23 (m, 1H), 1.93–2.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 138.6, 138.2, 138.2, 137.9, 128.4, 128.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 84.7, 78.5, 76.9, 75.3, 74.7, 73.7, 73.5, 72.3, 68.7, 58.6, 52.5, 33.9. HRMS calcd. for $C_{38}H_{41}N_3O_7$ + Na 674.2842, found 674.2843.

(*S*)-Methyl 2-azido-3-((2*S*,3*S*,4*R*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl) tetrahydro-2*H*-pyran-2-yl)-propanoate (**6**): Compound **6** was synthesized from **4b** (600 mg, 0.88 mmol) following the procedure described for compound **5**. Yield (480 mg, 82%). $[\alpha]_D^{25}$ −15.2 (*c* 0.5, $CHCl_3$); IR (neat): ν_{max} 3066, 3030, 2923, 2853, 2106, 1743, 1541, 1496, 1454, 1362 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.28–7.37 (m, 20H), 4.96 (dd, 2H, *J* = 9.6 Hz, *J* = 11.2 Hz), 4.75 (d, 1H, *J* = 11.6 Hz), 4.61–4.68 (m, 3H), 4.44 (q, 2H, *J* = 12.0 Hz), 4.10 (dd, 1H, *J* = 5.2 Hz, *J* = 7.6 Hz), 4.01 (d, 1H, *J* = 2.8 Hz), 3.75 (dd, 1H, *J* = 7.2 Hz, *J* = 13.2 Hz), 3.71 (s, 3H), 3.60 (dd, 1H, *J* = 2.8 Hz, *J* = 9.2 Hz), 3.51–3.56 (m, 3H), 3.36–3.42 (m, 1H), 2.34 (ddd, 1H, *J* = 2.8 Hz, *J* = 7.2 Hz, *J* = 14.0 Hz), 1.93–2.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 138.7, 138.2, 138.1, 137.9, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 84.7, 78.1, 76.8, 75.7, 75.3, 74.6, 73.6, 73.5, 72.2, 68.5, 59.0, 52.4, 33.8. HRMS calcd. for $C_{38}H_{41}N_3O_7$ + Na 674.2842, found 674.2845.

(*R*)-Methyl 2-amino-3-((2*S*,3*S*,4*R*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-(benzyloxymethyl) tetrahydro-2*H*-pyran-2-yl)-propanoate (**7**): To a stirred solution of azide **5** (30 mg, 0.04 mmol) in AcOH/THF (3 mL, 1:1), Zn dust (3.0 mg, 0.04 mmol) was added, and the reaction mixture was stirred for 12 h at room temperature. After completion of the reaction, Zn was removed by filtration, then the solvent was removed under vacuum. The obtained residue was dissolved in ethyl acetate (20 mL). The solution was washed with saturated $NaHCO_3$ solution, water and brine, dried over anhydrous Na_2SO_4, and concentrated. Purification of the crude product by silica-gel column chromatography gave the β-*C*-(D)-galactosyl L-alanine derivative **7** (18 mg, 64%) as a colorless gum.$[\alpha]_D^{25}$ −3.2 (*c* 0.6, $CHCl_3$); IR (neat): ν_{max} 2920, 2854, 1742, 1463, 1364 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.26–7.34 (m, 20H), 4.95 (d, 1H, *J* = 4.0 Hz), 4.92 (d, 1H, *J* = 5.0 Hz), 4.74 (d, 1H, *J* = 11.5 Hz), 4.66 (d, 1H, *J* = 11.5 Hz), 4.63 (d, 1H, *J* = 2.0 Hz), 4.61 (d, 1H, *J* = 3.0 Hz), 4.43 (q, 2H, *J* = 11.5 Hz), 3.98 (d, 1H, *J* = 3.0 Hz), 3.69 (t, 1H, *J* = 3.5 Hz), 3.67 (s, 3H), 3.61 (dd, 1H, *J* = 2.5 Hz, *J* = 9.0 Hz), 3.52–3.55 (m, 3H), 3.46–3.50 (m, 1H), 1.98–2.07 (m, 1H), 1.91–1.97 (m, 2H), 1.70 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6, 138.6, 138.2, 137.9, 128.4, 128.3, 128.2, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 84.7, 78.6, 77.2, 76.1, 75.3, 74.5, 73.7, 73.4, 72.3, 68.9, 51.9, 51.2, 36.3. HRMS calcd. for $C_{38}H_{43}NO_7$ + H 626.3118, found 626.3117.

(*S*)-Methyl 2-amino-3-((2*S*,3*S*,4*R*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-(benzyloxymethyl) tetrahydro-2*H*-pyran-2-yl)-propanoate (**8**): Compound **8** was synthesized using azido carboxylate **6** (25 mg, 0.03 mmol), Zn (2.5 mg, 0.03 mmol) and acetic acid/tetrahydrofuran (1:1) (2 mL) following the procedure described for compound **7**. Compound **8** (15.0 mg, 62%) was obtained as a colorless gum. $[\alpha]_D^{25}$ +0.3 (*c* 0.7, $CHCl_3$); IR (neat): ν_{max} 2958, 2926, 2854, 1742, 1452, 1369 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.27–7.36 (m, 20H), 4.95 (d, 1H, *J* = 5.0 Hz), 4.92 (d, 1H, *J* = 5.5 Hz), 4.74 (d, 1H, *J* = 11.5 Hz), 4.67 (d, 1H, *J* = 7.0 Hz), 4.64 (d, 1H, *J* = 6.5 Hz), 4.60 (d, 1H, *J* = 7.50 Hz), 4.45 (d, 1H, *J* = 11.5 Hz), 4.40 (d, 1H, *J* = 11.5 Hz), 3.97 (d, 1H, *J* = 2.5 Hz), 3.69 (d, 1H, *J* = 6.5 Hz), 3.68 (d, 1H, *J* = 5.0 Hz), 3.66 (s, 3H), 3.58 (dd, 1H, *J* = 2.5 Hz, *J* = 9.0 Hz), 3.50–3.55 (m, 3H), 3.40 (dt, 1H, *J* = 2.0 Hz, *J* = 9.0 Hz, *J* = 18.5 Hz), 2.29 (ddd, 1H, *J* = 2.0 Hz, *J* = 5.5 Hz, *J* = 14.0 Hz), 2.02 (bs, 2H), 1.78 (ddd, 1H, *J* = 6.5 Hz, *J* = 9.5 Hz, *J* = 15.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 138.7, 138.2, 137.8, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 84.6, 78.7, 77.5, 76.8, 75.4, 74.5, 73.7, 73.5, 72.2, 68.8, 52.4, 51.9. 37.0. HRMS calcd. for $C_{38}H_{43}NO_7$ + H 626.3118, found 626.3116.

Methyl 2-iodo-3-((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-methoxy tetrahydro-2*H*-pyran-2-yl)propanoate (**11**): Compound **11** was synthesized from **9** (2.0 g, 3.28 mmol) by following the procedure described for compound **3a**. Compound **11** (1.8 g, 72%) was obtained as an inseparable diastereomeric mixture in 1:1 ratio. IR (neat): ν_{max} 3062, 3035, 2920, 2865, 1747, 1632, 1500, 1451, 1363 cm^{-1}. HRMS calcd. for $C_{39}H_{43}IO_8$ + Na 789.1900, found 789.1902.

Methyl 2-azido-3-((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-(benzyloxymethyl)-2-methoxy tetrahydro-2*H*-pyran-2-yl)propanoate (**13**): Compound **13** was synthesized from **11** (1.0 g, 1.39 mmol) by following the procedure described for compound **4a**. Compound **13** (0.82 g, 92%) was obtained as an inseparable diastereomeric mixture in 1:1 ratio. IR (neat): ν_{max} 3095, 3063, 3024, 2926, 2854, 2109, 1747, 1501, 1457, 1364 cm^{-1}. HRMS calcd. for $C_{39}H_{43}N_3O_8$ + Na 704.2948, found 704.2951.

Methyl 2-azido-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-(benzyloxymethyl)tetrahydro-2*H*-pyran-2-yl)propanoate (**20**): Compound **20** was synthesized from **13**

(300 mg, 0.44 mmol) by following the procedure described for compound **5**. Compound **20** (225 mg, 78 %) was obtained as an inseparable diastereomeric mixture in 1:1 ratio. IR (neat): ν_{max} 3095, 3063, 3024, 2926, 2854, 2109, 1747, 1501, 1457, 1364 cm^{-1}. HRMS calcd. for $C_{38}H_{41}N_3O_7+Na$ 674.2842, found 674.2844.

(*S*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (**21**)[7] and (*R*)-methyl 2-(*tert*-butoxycarbonylamino)-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-(benzyloxymethyl) tetrahydro-2*H*-pyran-2-yl)propanoate (**22**):[7] Triphenyl phosphine (16 mg, 0.06 mmol) was added to a solution of azide **20** (40 mg, 0.06 mmol) in dry THF (3 mL) under nitrogen atmosphere and the solution was stirred for 8 h. After complete formation of iminophosphorane was confirmed by TLC, water was added and the solution was refluxed for 6 h. The reaction mixture was washed with brine solution and extracted with chloroform. The organic extract was dried over anhydrous Na_2SO_4 and evaporated. The obtained residue was co-evaporated with toluene twice *in vacuo* and dried. The residue was dissolved in CH_2Cl_2 (3 mL) and Et_3N (18.7 μL), Boc_2O (65.17 μL, 0.27 mmol) was added successively and the reaction mixture was stirred overnight. After complete conversion of the reaction mixture, checked by TLC, the solvent was removed *in vacuo*, diluted with water, extracted with EtOAc (25 mL × 3), washed with water (30 mL), and brine (30 mL), and dried over anhydrous Na_2SO_4, concentrated. Purification of the crude product by column chromatography afforded the β-*C*-(D)-glucosyl L-alanine derivative **21** and β-*C*-(D)-glucosyl D-alanine derivative **22** as single diastereomers (1:1 ratio) in 77 % overall yield. **21**: IR (neat): ν_{max} 3391, 3084, 3057, 3030, 2920, 2854, 1797, 1720, 1495, 1452, 1364 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.05–7.38 (m, 20H), 5.9 (d, 1H, J = 8.8 Hz), 4.87–4.93 (m, 1H), 4.82 (d, 1H, J = 11.2 Hz), 4.79 (d, 1H, J = 11.2 Hz), 4.77 (d, 1H, J = 11.2 Hz), 4.75 (d, 1H, J = 11.2 Hz), 4.56 (d, 1H, J = 11.6 Hz), 4.55 (d, 1H, J = 12.4 Hz), 4.42 (d, 1H, J = 12.4 Hz), 4.37 (d, 1H, J = 11.2 Hz), 3.53–3.68 (m, 4H), 3.43 (t, 1H, J = 9.2 Hz), 3.29–3.36 (m, 1H), 3.26 (s, 3H), 3.10 (t, 1H, J = 9.2 Hz), 2.23 (m, 1H), 1.80 (m, 1H) ppm. HRMS calcd. for $C_{43}H_{51}NO_9+Na$ 748.3462, found 748.3460. (The spectral data is completely in agreement with the reported values). **22**: IR (neat): ν_{max} 3389, 3079, 3051, 3028, 2923, 2857, 1792, 1715, 1488, 1454 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.06–7.30 (m, 20H), 5.60 (d, 1H, J = 6.8 Hz), 4.82 (d, 1H, J = 11.2 Hz), 4.80 (d, 1H, J = 6.0 Hz), 4.75 (d, 1H, J = 14.8 Hz), 4.69 (d, 1H, J = 11.6 Hz), 4.67 (d, 1H, J = 4.4 Hz), 4.59 (d, 1H, J = 11.6 Hz), 4.42 (d, 1H, J = 11.6 Hz), 4.39 (d, 1H, J = 12.4 Hz), 4.28 (d, 1H, J = 12.0 Hz), 3.71 (t, 1H, J = 9.2 Hz), 3.56–3.60 (m, 2H), 3.52 (t, 1H, J = 8.8 Hz), 3.38–3.41 (m, 1H), 3.36 (s, 3H), 3.10 (t, 1H, J = 8.8 Hz), 2.52 (m, 1H), 1.90 (m, 1H), 1.42 (s, 9H). HRMS calcd. for $C_{43}H_{51}NO_9+Na$ 748.3462, found 748.3460. (The spectral data is completely in agreement with the reported values).

Methyl 3-((2*R*,3*S*,4*R*)-3,4-bis(benzyloxy)-2-methoxytetrahydro-2*H*-pyran-2-yl)-2-iodopropanoate (**12**): Compound **12** was synthesized from **10** (870 mg, 2.27 mmol) by following the procedure described for compound **3a**. Compound **12** (0.9 g, 73 %) was obtained as an inseparable diastereomeric mixture. IR (neat): ν_{max} 3063, 3030, 2953, 2882, 1736, 1495, 1452, 1435, 1364 cm^{-1}. HRMS calcd. for $C_{24}H_{29}IO_6+Na$ 563.0907, found 563.0909.

Methyl 2-azido-3-((2*R*,3*S*,4*R*)-3,4-bis(benzyloxy)-2-methoxytetrahydro-2*H*-pyran-2-yl)propanoate (**14**): Compound **14** was synthesized from **12** (830 mg, 1.53 mmol) by following the procedure described for compound **4a**. Compound **14** (489 mg, 70 %) was obtained as an inseparable diastereomeric mixture in 4:1 ratio. IR (neat): ν_{max} 3090, 3068, 3035, 2926, 2865, 1720, 1501, 1457 cm^{-1}. Data for the major isomer: ^1H NMR (500 MHz, $CDCl_3$): δ 7.28–7.39 (m, 10 H), 5.06 (d, 1H, J = 11.5 Hz), 4.82 (d, 1H, J = 11.5 Hz), 4.67 (q, 2H, J = 11.5 Hz), 4.01–4.07 (m, 1H), 3.76–3.79 (m, 1H), 3.74 (s, 3H), 3.58–3.64 (m, 2H), 3.49–3.54 (m, 1H), 3.24 (s, 3H), 2.33 (dd, 1H, J = 6.5 Hz, J = 14.5 Hz), 2.05–2.13 (m, 2H), 1.66 (ddd, 1H, J = 5.5 Hz, J = 13.0 Hz, J = 24.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 138.4, 138.2, 128.4, 128.3, 128.3, 128.2, 127.6, 127.5, 100.3, 80.7, 76.6, 75.0, 71.6, 59.0, 58.3, 52.4, 47.5, 32.6, 31.4. HRMS calcd. for $C_{24}H_{29}N_3O_6+Na$ 478.1954, found 478.1954.

(1′*R*,2′*R*,3a*R*,7*S*,7a*R*)-Methyl 7-((*tert*-butyldimethylsilyl)-oxy)-2,2-dimethyltetrahydrospiro[[1,3] dioxolo[4,5-*c*]pyran-6,1′-cyclopropane]-2′-carboxylate (**16**): Compound **16** was synthesized from **15** (1.0 g, 3.33 mmol) by following the procedure described for compound **2**. Compound **16** (150 mg, 12 %) was obtained as a colorless solid. Overall yield of the 4 diastereomers (0.73 g, 58 %). Data for compound **16**: $[\alpha]_D^{25}$ +1.8 (*c* 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 4.35 (ddd, 1H, J = 6.0 Hz, J = 8.4 Hz, J = 14.4 Hz), 4.15 (d, 1H, J = 2.4 Hz), 4.10 (dd, 1H, J = 2.4 Hz, J = 5.6 Hz), 3.90 (dd, 1H, J = 6.4 Hz, J = 11.6 Hz), 3.67 (s, 3H), 3.43 (dd, 1H, J = 8.4 Hz, J = 11.2 Hz), 1.95 (dd, 1H, J = 7.2 Hz, J = 8.8 Hz), 1.46 (s, 3H), 1.35–1.42 (m, 2H), 1.32 (s, 3H), 0.90 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 109.6, 75.7, 69.1, 66.4, 65.7, 65.5, 51.7, 27.5, 26.8, 26.0, 25.7, 19.0, 18.0, −4.4, −4.8, −5.1. HRMS calcd. for $C_{18}H_{32}O_6+Na$ 395.1866, found 395.1866.

(*R*)-Methyl 3-((3a*R*,6*S*,7*S*,7a*R*)-7-(*tert*-butyldimethylsilyloxy)-6-methoxy-2,2-dimethyltetra-hydro-3a*H*-[1,3]dioxolo[4,5-*c*]pyran-6-yl)-2-iodopropanoate (**17**): Compound **17** was synthesized from **16** (120 mg, 0.32 mmol) by following the procedure described for compound **3a**. Compound **17** (160 mg, 94 %) was obtained as a colorless liquid. IR (neat): ν_{max} 2931, 2865, 1742, 1457, 1435, 1364 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.49 (dd, 1H, J = 3.6 Hz, J = 10.8 Hz), 4.15–4.18 (m, 1H), 4.06 (dd, 1H, J = 6.0 Hz, J = 6.8 Hz), 3.80–3.86 (m, 2H), 3.71 (s, 3H),

3.59 (d, 1H, J=7.2 Hz), 3.27 (s, 3H), 2.82 (dd, 1H, J=10.8 Hz, J=15.2 Hz), 2.52 (dd, 1H, J=4.0 Hz, J=15.6 Hz), 1.49 (s, 3H), 1.31 (s, 3H), 0.90 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 108.6, 100.6, 75.8, 73.3, 60.4, 52.7, 49.8, 40.9, 28.12, 26.2, 25.9, 18.2, 13.8, −3.8, −5.1. HRMS calcd. for $C_{19}H_{35}IO_7Si+Na$ 553.1094, found 553.1095.

(*S*)-Methyl 2-azido-3-((3a*R*,6*S*,7*S*,7a*R*)-7-(*tert*-butyldimethylsilyloxy)-6-methoxy-2,2-dimethyltetrahydro-3a*H*-[1,3]dioxolo[4,5-*c*]pyran-6-yl)propanoate (**18**): Compound **18** was synthesized from **17** (150 mg, 0.28 mmol) by following the procedure described for compound **4a**. Compound **18** (110 mg, 88%) was obtained as a colorless liquid. IR (neat): ν_{max} 2988, 2958, 2926, 2860, 2098, 1747, 1457, 1430, 1375 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.18–4.21 (m, 1H), 4.10 (t, 1H, J=7.2 Hz), 3.96 (q, 1H, J=6.8 Hz), 3.88 (dd, 1H, J=0.8 Hz, J=13.2 Hz), 3.81 (d, 1H, J=7.2 Hz), 3.78 (s, 3H), 3.75 (dd, 1H, J=3.2 Hz, J=8.0 Hz), 3.25 (s, 3H), 2.38 (dd, 1H, J=8.0 Hz, J=14.0 Hz), 2.17 (dd, 1H, J=6.4 Hz, J=14.0 Hz), 1.53 (s, 3H), 1.33 (s, 3H), 0.90 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 108.6, 99.6, 76.6, 73.5, 73.4, 60.3, 58.0, 52.5, 48.5, 33.0, 28.1, 26.2, 25.9, 25.6, 18.1, −3.7, −5.3. HRMS calcd. for $C_{19}H_{35}N_3O_7Si+Na$ 468.2142, found 468.2142.

(*S*)-Methyl 2-azido-3-((3a*R*,6*S*,7*R*,7a*R*)-7-((*tert*-butyldimethylsilyl)oxy)-2,2-dimethyltetrahydro-3a*H*-[1,3]dioxolo[4,5-*c*]pyran-6-yl)propanoate (**23**): Compound **23** was synthesized from **18** (100 mg, 0.22 mmol) by following the procedure described for compound **5**. Compound **23** (76 mg, 82%) was obtained as a colorless gum. $[\alpha]_D^{25}$ −29.5 (*c* 1, $CHCl_3$); IR (neat): ν_{max} 2991, 2958, 2931, 2854, 2104, 1747, 1468, 1435, 1380 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.10–4.20 (m, 3H), 3.89 (t, 1H, J=6.4 Hz), 3.75 (s, 3H), 3.63 (dd, 1H, J=2.4 Hz, J=13.6 Hz), 3.40 (dd, 1H, J=6.8 Hz, J=16.4 Hz), 3.08 (dt, 1H, J=2.0 Hz, J=9.6 Hz), 2.33 (ddd, 1H, J=2.0 Hz, J=7.6 Hz, J=14.0 Hz), 1.83–1.91 (m, 1H), 1.51 (s, 3H), 1.34 (s, 3H), 0.88 (s, 9H), 0.14 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 109.2, 79.7, 75.5, 74.4, 74.0, 66.3, 58.9, 52.4, 33.9, 29.6, 28.1, 26.3, 25.8, 18.0, −3.9, −5.0. HRMS calcd. for $C_{18}H_{33}N_3O_6Si+Na$, 438.2036 found 438.2035.

(*S*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-((3a*R*,6*S*,7*R*,7a*R*)-7-((*tert*-butyldimethylsilyl)oxy)-2,2-dimethyltetrahydro-3a*H*-[1,3]dioxolo[4,5-*c*]pyran-6-yl)propanoate (**24**): To a stirred solution of azido carboxylated sugar **23** (20 mg, 0.048 mmol) in methanol (3 mL), Boc_2O (57 μL, 0.24 mmol) and 10% Pd/C (5 mg) was added. The reaction mixture was degassed and stirred under hydrogen atmosphere for 2 h. After completion of the reaction, the catalyst was removed by filtration and the filtrate was concentrated. Purification of the obtained crude product using silica-gel column chromatography afforded the compound **24** (21 mg, 89%) as a colorless gum. $[\alpha]_D^{25}$ −1.4 (*c* 1, $CHCl_3$); IR (neat): ν_{max} 2926, 2860, 1720, 1490, 1441, 1364, 1260, 1216, 1167, 1090 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.30 (d, 1H, J=6.8 Hz), 4.38 (q, 1H, J=5.6 Hz), 4.12 (dd, 1H, J=2.0 Hz, J=5.6 Hz), 4.09 (d, 1H, J=13.6 Hz), 3.88 (t, 1H, J=6.0 Hz), 3.68 (s, 3H), 3.59 (dd, 1H, J=2.0 Hz, J=13.2 Hz), 3.36 (dd, 1H, J=6.8 Hz, J=9.6 Hz), 3.06 (t, 1H, J=9.2 Hz), 2.34 (dd, 1H, J=4.8 Hz, J=14.4 Hz), 1.71–1.78 (m, 1H), 1.50 (s, 3H), 1.41 (s, 9H), 1.33 (s, 3H), 0.86 (s, 9H), 0.12 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 154.9, 109.1, 79.8, 79.6, 76.1, 74.1, 74.0, 66.5, 52.2, 51.2, 34.2, 28.3, 28.1, 26.3, 25.8, 17.9, −3.9, −5.0. HRMS calcd. for $C_{23}H_{43}NO_8Si+Na$, 512.2656 found 512.2660.

The supporting information contains ^{1}H, ^{13}C and ^{13}C DEPT NMR spectra of all new compounds.

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[21] The stereochemistry α to the ester is tentatively assigned based on the proposed mechanism.

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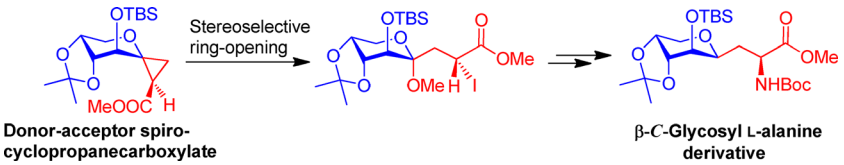

Donor-acceptor spiro-cyclopropanecarboxylate

β-*C*-Glycosyl L-alanine derivative

*B. Ramakrishna, C. Sudharani, P. R. Sridhar**

■■–■■

Synthesis of β-*C*-Glycosyl Amino Acids by Ring Opening of Donor-Acceptor Spiro-cyclopropanecarboxylated Sugars