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Combinatorial Synthesis of Deoxyhexasaccharides Related to the Landomycin A Sugar Moiety, Based on an Orthogonal Deprotection Strategy

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Abstract: In this report, we describe the stereoselective synthesis of a combinatorial library comprised of 16 deoxyhexasaccharides that are related to a landomycin A sugar moiety, based on an orthogonal deprotection strategy. The use of an olivosyl donor containing a benzyl ether at the C3 position and benzoyl ester at the C4 position, and the olivosyl donor, a naphthylmethyl ether, and a *p*-nitrobenzylethyl or benzyl sulfonyl ester enabled the synthesis of a set of four diolivosyl units containing a hydroxyl group at the C3 or C4 position by a simple glycosylation and deprotection procedure. Using a phenylthio 2,3,6-trideoxyglycoside, α-selective glycosidation proceeded without anomerization of the 2,6-dideoxy-β-glycosides. In addition, alkylhydroquinone and levulinoyl groups were found to be an effective set of orthogonal protecting groups for the anomeric position and a hydroxyl group. The coupling of all combinations of trisaccharide units in a β-selective manner was accomplished by activation of the glycosyl imidate with I_2 and Et_3SiH. No cleavage of the acid-labile 2,3,6-trideoxyglycoside was observed under the conditions used for the reactions. Finally, all of the protected hexasaccharides were deprotected by hydrolysis of the esters, microwave (MW) assisted cleavage of the 2-trimethylsilylethoxymethoxy (SEM) ether, and a Birch reduction.

Keywords: combinatorial chemistry · 2-deoxyglycoside · glycosyl imidates · glycosylation · saccharides

Introduction

2-Deoxysaccharides are key components of biologically active natural products. The application of combinatorial synthesis for preparing 2-deoxyoligosaccharides is an attractive way to provide effective resources for the preparation of new biologically active compounds.[1] However, they represent difficult and challenging synthetic targets:[2] neighboring group participation for stereoselective glycosidation is not possible and the absence of electron-withdrawing substituents on saccharide units permits the interconversion of thermodynamically unstable β-glycosides to α-glycosides by anomerization and cleavage of the β-glycosidic linkage during the glycosidation. In addition, the stereoselectivity of glycosidation of 2-deoxyglycosides is strongly dependent on the nature of the protecting groups used for the reaction. We recently reported our development of direct α- and β-selective glycosidation methods using glycosyl imidates, which are key reactions for the synthesis of combinatorial libraries of anomeric stereoisomers of deoxyoligosaccharides.[3,4] Therein, protection of a C4 hydroxyl group with a strongly electron-withdrawing protecting group such as benzylsulfonyl and 2-(*p*-nitrobenzyl)ethylsulfonyl (Npes) esters, improved the desired stereoselectivity. Our next challenge is to develop a method for the assembly of their regioisomers. An orthogonal deprotection strategy is known to be an effective method for the synthesis of regioisomers of oligosaccharides and for minimizing the number of building blocks and/or synthetic intermediates required.[5] However, stereoselective glycosidation and orthogonal deprotection of 2-deoxyglycosides requires further careful selection of these pro-

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tecting groups. In this report, we describe the combinatorial synthesis of deoxyhexasaccharides related to the landomycin A sugar moiety, based on an orthogonal deprotection strategy.

Landomycin A (**1**) (Figure 1), an angucylic-type antitumor antibiotic, exhibits potent antitumor and antibacterial activity, and inhibits G1/S cell cycle progression, which results in the induction of apoptosis.[6] It is composed of a tetracyclic aglycon and a structurally unique, complex deoxyhexasaccharide. The deoxyhexasaccharide is made up of a head-to-tail dimer of a repeating trisaccharide subunit (L-rhodinoside-β-(1,3)-D-olivoside-β(1,4)-D-olivoside). This structure appears to be required for the biological activity of the molecule, since that of naturally occurring landomycin derivatives that contain shorter glycan chains is significantly lower.[6f] However, the number of naturally occurring landomycin A derivatives are limited and mainly vary in the number of saccharide units. Therefore, a chemical synthesis of the deoxyoligosaccharide and derivatives thereof would facilitate identification of their biological roles.

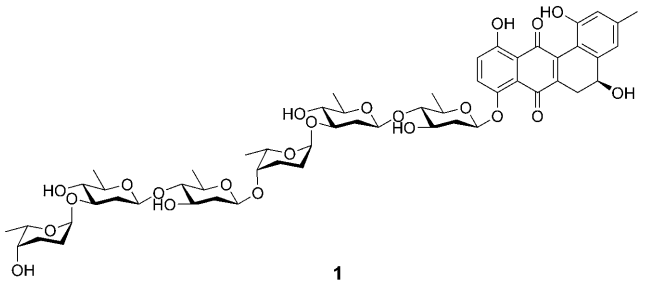
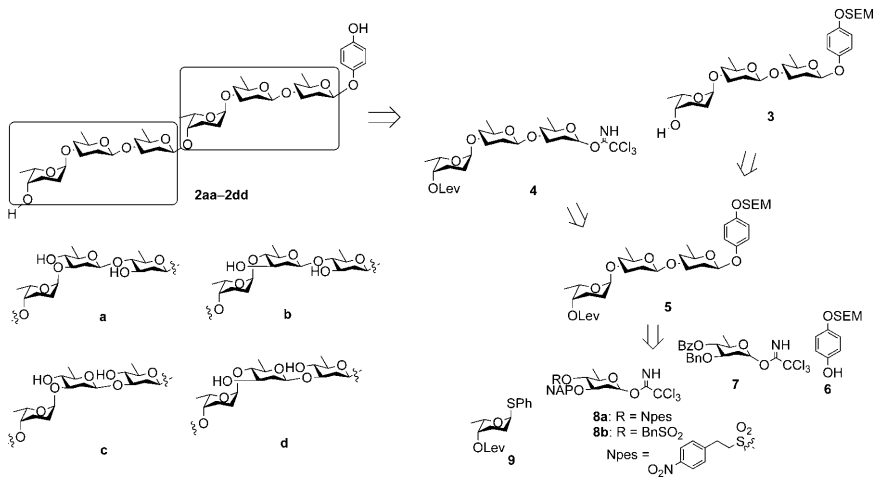


Figure 1. The structure of landomycin A (**1**).

Sulikowski and Guo reported the first chemical synthesis of the landomycin deoxyhexasaccharide by a direct head-to-tail coupling of the repeating trisaccharide units using glycosyl phosphites and tetrazoles.[7] The direct dimerization was difficult to achieve in a stereoselective manner and resulted in a moderate coupling yield and stereoselectivity. Indirect approaches using olivosides, in which stereodirecting substituents were attached to the C2 position, have been reported as alternative methods for the synthesis of the deoxyhexasaccharide.[8,9,10] However, in all of these methods it was difficult to completely prevent anomerization and cleavage of the 2,3,6-trideoxyglycoside. In addition, these methods are based on target oriented synthetic strategy. Therefore, an effective method for the systematic synthesis of deoxyoligosaccharides related to the landomycin A hexasaccharide moiety continues to be a subject of attention in terms of both chemical and biological interests.

Results and Discussion

The hydroquinone substituted landomycin A hexasaccharide **2aa** and their 15 regioisomers **2ab–dd** constitute the target library of compounds (Scheme 1). The hydroquinone moiety serves not only as a partial structure of the landomycin aglycon, but also as a protecting group at the anomeric position for further coupling with various aglycons. The strategy for the synthesis of the hexasaccharide library **2aa–dd** involves direct and stereoselective head-to-tail coupling of the trisaccharide glycosyl acceptors **3a–d** and donors **4a–d**. These building blocks **3a–d** and **4a–d** could be prepared from the hydroquinone derivative **6**, three olivosides **7**, **8a**, and **8b**, and rhodinoside **9** based on an orthogonal deprotection strategy. The first glycosyl donor **7** contained two orthogonal protecting groups; a benzyl ether at the C3 position and a benzoate at the C4 position. A combination of an electron-withdrawing protecting group at the C4 hydroxyl that participates in the reaction and an electron-donating protecting group at the C3 hydroxyl could be effective for achieving selective, direct β glycosylation.[11] The second glycosyl donor



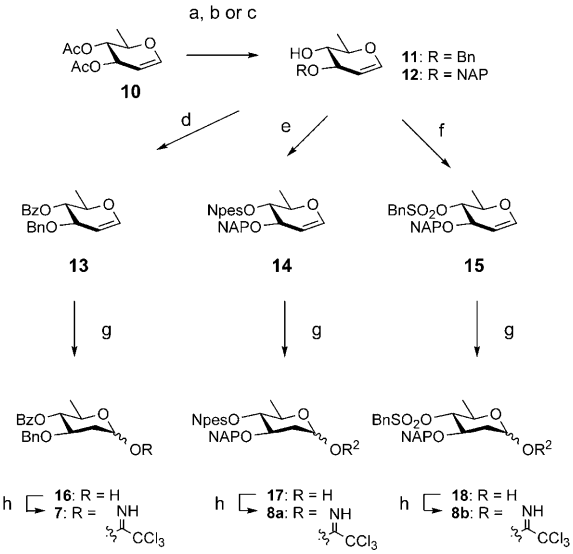
Scheme 1. Strategy for the synthesis of a combinatorial library of a landomycin sugar moiety.

Abstract in Japanese:

直接的かつ立体選択的なグリコシル化反応を利用するランドマイシン6糖部のコンビナトリアル合成を行った。オルソゴナル脱保護法と当研究室で開発した2-デオキシ糖の直接的グリコシル化を組み合わせることによりすべての3糖位置異性体の合成を達成した。さらに、得られた4種の3糖体の組み合わせからなる16種類の6糖ライブラリーの合成を達成した。

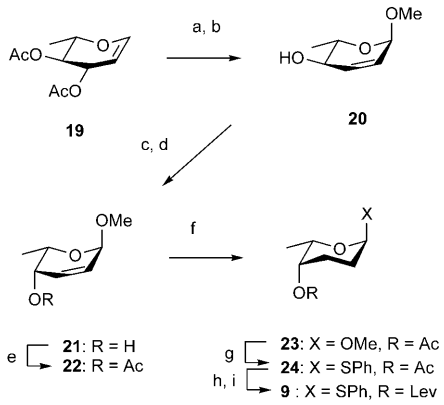
8a was protected by a 2-naphthylmethyl (NAP) ether and an Npes ester at the C3 and C4 positions, respectively. An alternative olivoside **8b**, with a benzylsulfonyl ester protecting group in place of the Npes ester at C4, was also used. The protecting groups of **8a** and **8b** are orthogonally deprotectable without affecting the benzyl ether and benzoate protecting groups of **7**. Introduction of the α-rhodinoside should be possible without decomposition of the β-linked disaccharides. We selected the thiorhodinoside **9** containing a levulinoyl (Lev) ester at the C4 position as a glycosyl donor because it is a chemically stable compound and could undergo glycosidation under oxidative activation conditions. The trisaccharides **5a–d** were converted to the corresponding glycosyl acceptors **3a–d** and donors **4a–d** by removing the Lev protecting groups and the *p*-(trimethylethoxymethoxy)phenyl group.

Preparation of olivosyl donors **7**, **8a**, and **8b** is outlined in Scheme 2. Hydrolysis of the acetyl groups of the diacetyl glycal **10**, followed by regioselective *O*-alkylation with benzyl and 2-naphthylmethyl bromides, via a tin acetal, provided alcohols **11** and **12**. The remaining hydroxyl group of **11** was protected with benzoyl chloride to afford glycal **13**. The remaining hydroxyl group of **12** was protected with 2-(*p*-nitrophenyl)ethylsulfonyl and benzylsulfonyl chlorides providing sulfonyl esters **14** and **15**. Hydration of the glycols **13**, **14**, and **15** provided the hemiacetals **16**-**18**, respectively. The hemiacetals **16**, **17**, and **18** were converted to the corresponding glycosyl imidates **7**, **8a**, and **8b** under conventional conditions for the synthesis of trichloroacetimidates. The imidates were used for the next reactions without purification by chromatography on silica gel.



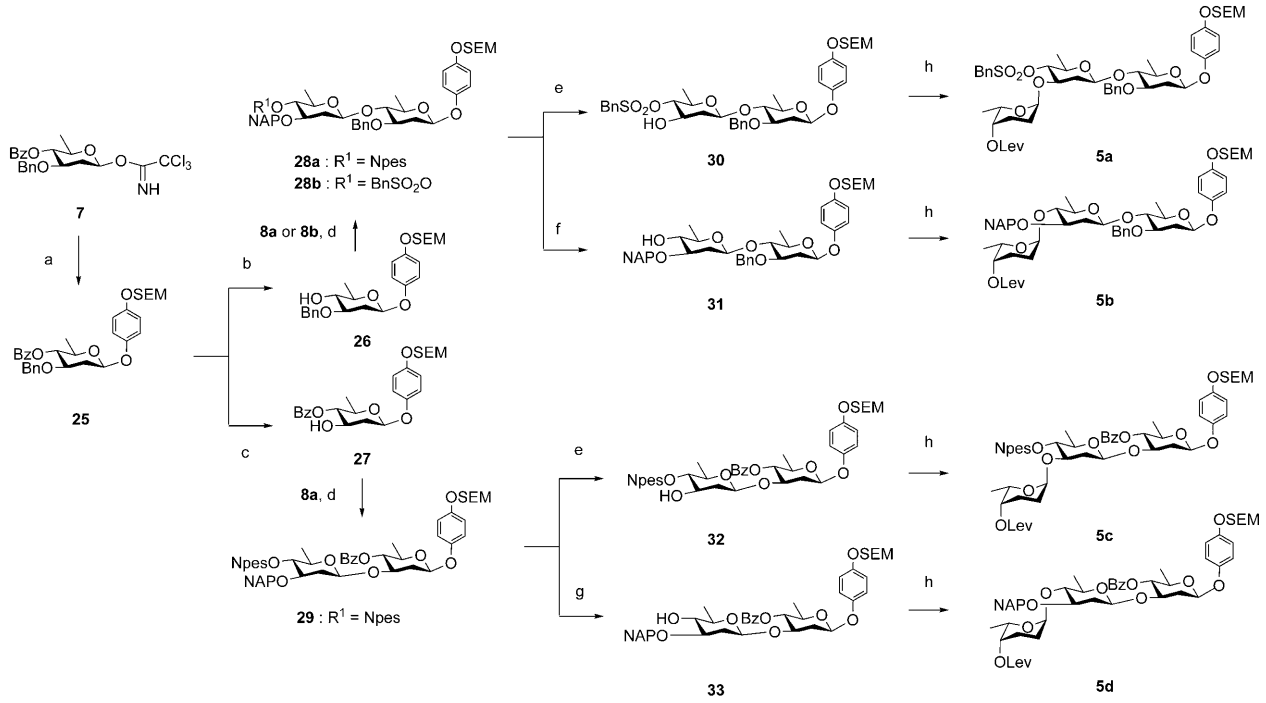
Scheme 2. Reagents and conditions: (a) K_2CO_3, MeOH, RT; (b) Bu_2SnO, toluene, 140 °C, then TBAI, BnBr; (c) Bu_2SnO, toluene, 140 °C, then TBAI, NAPBr, 75% from **10**; (d) BzCl, DMAP, TMEDA, RT; (e) $BnSO_2Cl$, DMAP, Py, RT, 95%; (f) NpesCl, DMAP, Py, RT; (g) LiBr, Dowex, CH_3CN, H_2O, 85% from **10** for **16**, 99% from **12** for **17**, 70% from **12** for **18**; (h) CCl_3CN, Cs_2CO_3, CH_2Cl_2, RT.

Preparation of phenylthio D-rhodinoside **9** is outlined in Scheme 3. Treatment of diacetylglycal **19** with $FeCl_3$ in the presence of MeOH provided the α-methyl glycoside.[12] Subsequently, hydrolysis of the remaining acetyl group provided alcohol **20** in 50% yield. Inversion of the stereochemistry of the hydroxyl group was achieved by Mitsunobu reaction, and was followed by hydrolysis of the generated ester to provide secondary alcohol **21** in 70% yield. The resulting alcohol **21** was protected with acetic anhydride to afford the allylic acetate **22** in 55% yield. Hydrogenation of the double bond of **22**, followed by treatment of the methyl glycoside **23** with thiophenol in the presence of $Sc(OTf)_3$ provided the phenylthio α-glycoside **24** in 50% yield from **22**. Hydrolysis of the acetate, followed by acylation with levulic acid provided the D-rhodinosyl donor **9** in 80% yield.



Scheme 3. Reagents and conditions: (a) $FeCl_3$, MeOH, CH_3CN, 0 °C to RT, 3 h; (b) K_2CO_3, MeOH, 50% from **19**; (c) *p*-nitrobenzoic acid, PPh_3, DEAD, THF, 0 °C to RT, 2 h; (d) NaOMe, THF/MeOH (1:1), RT, 2 h, 70% from **20**; (e) Ac_2O, NEt_3, DMAP, CH_2Cl_2, RT, 6 h, 55%; (f) H_2 (1 atm), Pd/C, EtOAc; (g) PhSH, $Sc(OTf)_3$, CH_2Cl_2, 50% from **22**; (h) NaOMe, MeOH, RT, 3 h; (i) LevOH, EDCI, DMAP, DIEA, CH_2Cl_2, 80% from **24**.

Scheme 4 shows the synthesis of four trisaccharides **5a–d** from imidate **7**. Treatment of the olivosyl imidate **7** and 1.5 equivalents of phenol **6** with I_2 and a catalytic amount of Et_3SiH at −78 °C provided the phenyl glycoside **25** in 79% yield with β/α > 90:10. Treatment of benzoate **25** with NaOMe in MeOH provided **26**, with an unprotected C4 hydroxyl, in quantitative yield. Alternatively, hydrogenation of the benzyl ether of glycoside **25** using a Pd catalyst led to **27**, with an unprotected C3 hydroxyl, in 80% yield. Glycosylation of the C4 and C3 hydroxyls **26** and **27** with olivoside **8a** was then examined. Treatment of acceptor **27** with 1.5 equivalents of the Npes protected olivoside **8a**, I_2 and a catalytic amount of Et_3SiH at −94 to −78 °C gave the disaccharide **29** in 79% yield with β/α = 90:10. However, the Npes protected olivoside **8a** did not undergo glycosidation at the C4 hydroxyl of **26** under the same glycosidation conditions and resulted in decomposition of the donor **8a** and



Scheme 4. Synthesis of the four trisaccharides **5a–d**. *Reagents and conditions*: (a) **6**, I_2, cat Et_3SiH, MS 4 Å, toluene, −78 °C, 2.0 h, 79 % β/α = > 90:10; (b) NaOMe, MeOH, RT, 3 h, quant.; (c) H_2 (1 atm), Pd/C, MeOH/THF = 1:1, RT, 12 h, 80 %; (d) I_2, cat Et_3SiH, MS 4 Å, toluene, −94 to −78 °C, 0% for **28a**, 75 % β/α = 93:7 for **28b**, 79 % β/α = 90:10 for **29**; (e) DDQ, $NaHCO_3$ aq., CH_2Cl_2, 3 h, 71 % for **15**, 71 % for **17**; (f) NH_2Na, DMF, 24 h, 99 %; (g) DBU, CH_2Cl_2, 71 %; (h) **9**, Bu_4NOTf, NBS, CH_2Cl_2, MS 4 Å, −78 to −40 °C, 95 %, β/α = > 95:5 for **5a**, 76 %, β/α = > 90:10 for **5b**, 76 %, β/α = > 95:5 for **5c**, 90 %, β/α = > 90:10 for **5d.**

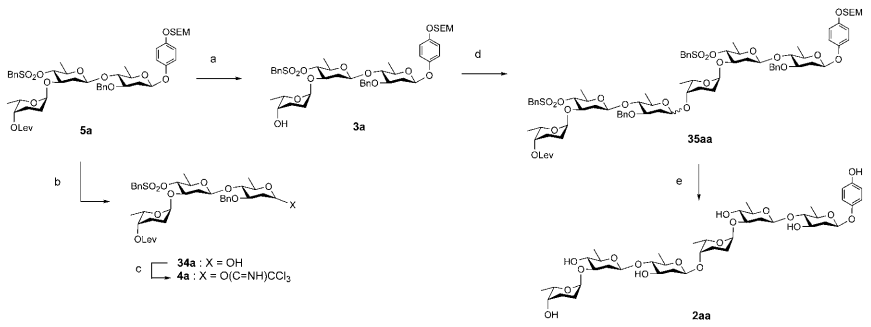
recovery of the acceptor **26**. In a subsequent experiment, we used olivoside **8b**, which has a benzylsulfonyl ester at the C4 position, as the glycosyl donor. Treatment of acceptor **26** and 1.5 equivalents of olivoside **8b** with I_2 and a catalytic amount of Et_3SiH at −94 to −78 °C provided the disaccharide **28b** in 75 % yield with β/α = 93:7. Reasons for the difference in the glycosidation reactions of the Npes and benzylsulfonyl protected donors **8a** and **8b** are not clear. Oxidative removal of the NAP group of disaccharides **28b** and **29** was accomplished by treatment with DDQ to provide the corresponding alcohols **30** and **32**, each in 71 % yield and without any detectable cleavage of the dialkylhydroquinone moiety. Additionally, the benzylsulfonyl ester of **28b** and the Npes group of **29** were removed by treatment with $NaNH_2$ and DBU, respectively, to provide the corresponding disaccharides **31** and **33**, with free hydroxyl groups at C4 in 99% yield for **31**and 71 % yieldfor **33**.

The glycosylation of disaccharide **30** with D-rhodinoside **9** was then examined (Table 1). Treatment of disaccharides **30** with 2.0 equivalents of rhodinoside **9**, NBS and Bu_4NOTf at −78 to −40 °C provided the trisaccharides **5a** in 95 % yield (α/β > 95:5). Bu_4NOTf enhanced the rate of activation of the thioglycoside without reducing α-selectivity (Table 1).[13] Use of IBr as an activator resulted in the decomposition of the product. By the same method, the remaining disaccharide acceptors **31–33** were converted to the corresponding trisaccharides **5b–d** in 76 % (α/β > 90:10), 76 % (α/β > 95:5) and 90 % (α/β > 90:10) yields, respectively. No evidence of anomerization or cleavage of glycosidic linkages was observed in the α-glycosidation.

Table 1. Glycosylation of diolivoside **30** with thiorhodinoside **9**.

Entry	Conditions	*T* [°C]	Yield [%]	α/β
1	NBS, Bu_4NOTf	−78 to −40	95	> 95:5
2	NBS	−78 to −25	72	> 95:5
3	I_2, Bu_4NOTf	−78 to 0	35	> 95:5
4	IBr, Bu_4NOTf	−78	–	–

The synthesis of the landomycin A hexasaccharide **2aa** from trisaccharide **5a** was then carried out as shown in Scheme 5. Treatment of trisaccharide **5a** with NH_2NH_2 and AcOH provided glycosyl acceptor **3a** in 80 % yield. For the synthesis of the glycosyl donor **4a**, oxidative cleavage of the dialkylhydroquinone moiety of **5a** by treatment with CAN afforded the hemiacetal **34a**, which when treated with CCl_3CN under basic conditions provided the glycosyl imidate **4a**. The imidate **4a** was used for the subsequent glycosylation without purification by column chromatography on silica gel. Hexasaccharide formation was achieved by treating the acceptor **3a** and the imidate **4a**, prepared from 2.0 equivalents of **5a**, with I_2 and a catalytic amount of Et_3SiH in toluene at −94 °C for 1 h to provide a mixture of the hexasaccharides β- and α-**35aa** in 93 % yield based on **3a**. The ratio of the anomeric isomers β- and α-**35aa** was determined by HPLC analysis based on IR detection to be β/α = 82:18. Anomerization of the β-2,6-dideoxyglycosides and/or cleav-



Scheme 5. Synthesis of the hexasaccharide **2aa**. *Reagents and conditions*: (a) NH_2NH_2, AcOH, H_2O, Py., RT, 80%; (b) CAN, H_2O, CH_3CN, RT, 10 min; (c) CCl_3CN, Cs_2CO_3, CH_2Cl_2, RT, 3 h; (d) I_2, cat Et_3SiH, MS 4 Å, toluene, −94 °C, 1.0 h, 93%, β/α = 82:18; (e) (i) NaOMe, MeOH/THF = 1:1, 50 °C, 6 h; (ii) TBAF in THF, DMF, MW (300W), 100 °C, 15 min; (iii) Na, NH_3(l), THF, −78 °C, 30 min, then MeOH, 70% overall yield from β-**35aa**.

age of 2,3,6-trideoxyglycosides were not observed. The β- and α-isomers of **35aa** were separated by HPLC. Deprotection of the purified β-**35aa** was achieved as follows: (1) removal of the ester and sulfonyl ester protecting groups under basic conditions; (2) cleavage of the SEM ether with TBAF under MW irradiation; and (3) deprotection of the benzyl ether protecting group by Birch reduction to afford the fully deprotected hexasaccharide β-**2aa** in 70% yield based on β-**35aa**. Removal of the SEM group prior to the Birch reduction was important to prevent reduction of the hydroquinone moiety.[14] In addition, MW irradiation was effective in terms of minimizing the reaction time required for removal of the SEM group.

The synthesis of regioisomers **2ab–dd** (Figure 2 was then carried out (entries 2–16 in Tables 2 and 3). The acceptors **3b–d** and donors **4b–d** were prepared from **5b–d** using established procedures. Coupling of all remaining combinations of the glycosyl acceptors **3a–d** and donors **4a–d** provided all of the desired hexasaccharides **35ab–35dd** in good yields. The use of the glycosyl donors **4c** and **4d**, containing a benzoate at the C4 position of the olivoside, resulted in good β-selectivity (β/α = 83:17 to >90:10). On the other hand, the glycosyl donors **4a** and **4b**, which contain a benzyl ether at the C3 position, underwent only moderately β-selective glycosylation (β/α = 65:35 to 77:23). Deprotection of the protected oligosaccharides **35ab–35dd** provided a set of regioisomers of the landomycin hexasaccharide isomers **2ab–2dd** in moderate total yields.[15]

Conclusions

In conclusion, we report herein an efficient combinatorial synthesis of deoxyhexasaccharides related to the landomycin sugar moiety, based on an orthogonal deprotection strategy. The orthogonal deprotection approach is effective for as-

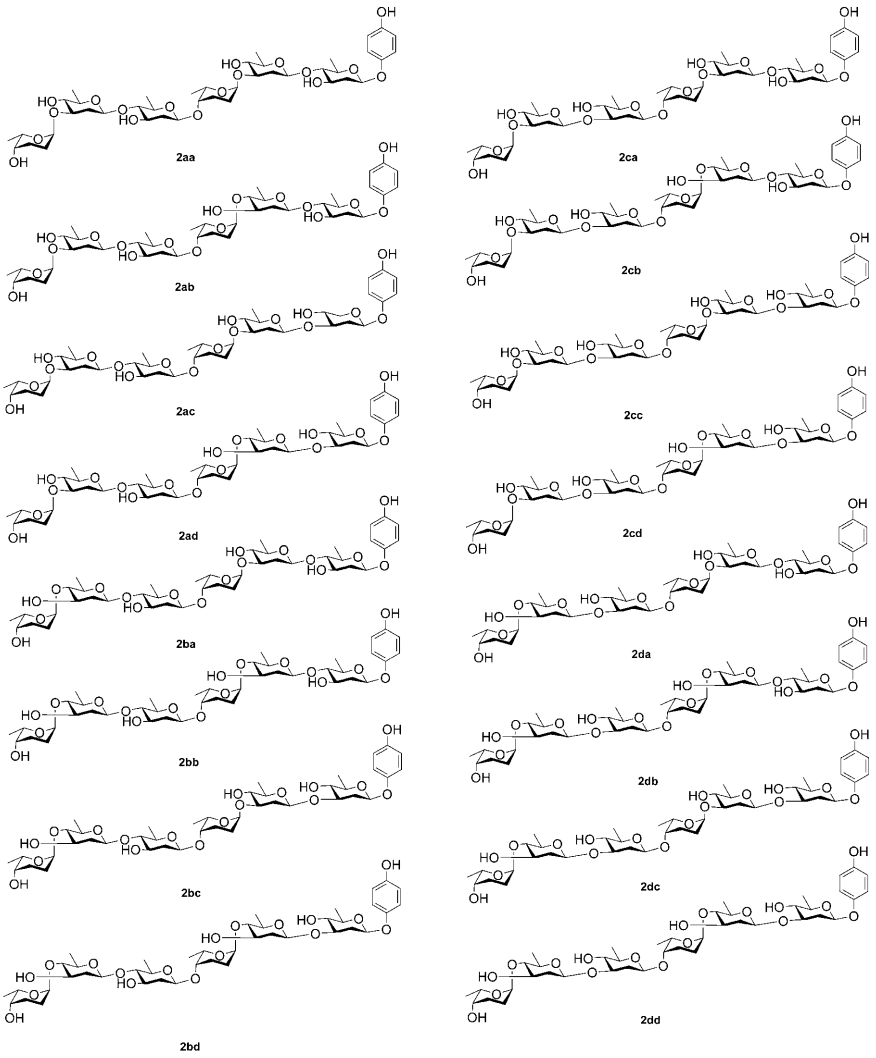


Figure 2. The hexasaccharide library **2** based on the strucutre of the landomycin sugar part.

Table 2. Coupling of two deoxytrisaccharide units via direct β-selective glycosylation.

Entry	Donor[a]	Acceptor	Product	Yield [%]	β/α[b]
1	**3a**	**4a**	**35aa**	95	82:18
2	**3a**	**4b**	**35ab**	95	77:23
3	**3a**	**4c**	**35ac**	72	77:23
4	**3a**	**4d**	**35ad**	90	69:31
5	**3b**	**4a**	**35ba**	67	77:23
6	**3b**	**4b**	**35bb**	93	70:30
7	**3b**	**4c**	**35bc**	76	70:30
8	**3b**	**4d**	**35bd**	88	65:35
9	**3c**	**4a**	**35ca**	86	90:10
10	**3c**	**4b**	**35cb**	80	>90:10
11	**3c**	**4c**	**35cc**	71	>90:10
12	**3c**	**4d**	**35cd**	72	>90:10
13	**3d**	**4a**	**35da**	90	90:10
14	**3d**	**4b**	**35db**	82	85:15
15	**3d**	**4c**	**35dc**	79	>90:10
16	**3d**	**4d**	**35dd**	93	73:17

[a] The donors, prepared from 2.0 equivalents of the corresponding **5a–d**, were used. [b] The ratio was determined by HPLC based on RI.

Table 3. Deprotection of the protected oligosaccharides **35aa–dd**.

Entry	Substrates	Products	Overall yield [%]
1	**35aa**	**2aa**	70
2	**35ab**	**2ab**	55
3	**35ac**	**2ac**	45
4	**35ad**	**2ad**	34
5	**35ba**	**2ba**	65
6	**35bb**	**2bb**	71
7	**35bc**	**2bc**	39
8	**35bd**	**2bd**	68
9	**35ca**	**2ca**	55
10	**35cb**	**2cb**	72
11	**35cc**	**2cc**	71
12	**35cd**	**2cd**	57
13	**35da**	**2da**	49
14	**35db**	**2db**	80
15	**35dc**	**2dc**	44
16	**35dd**	**2dd**	77

sembling the various regioisomers of deoxyoligosaccharides and involves the use of a small set of building blocks. Further biological evaluation of the hexasaccharide library, and the total synthesis of landomycin A are currently in progress.

Experimental Section

General

NMR spectra were recorded on a JEOL Model EX-270 (270 MHz for ^{1}H, 67.8 MHz for ^{13}C) or a JEOL Model ECP-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) in the specified solvent. Chemical shifts are reported in parts per million (ppm) relative to the signal (0.00 ppm) for internal tetramethylsilane in $CDCl_3$. ^{1}H NMR spectral data are reported as follows: $CDCl_3$ (7.26 ppm) or CD_2Cl_2 (5.30 ppm). ^{13}C NMR spectral data are reported as follows: $CDCl_3$ (77.1 ppm). NMR multiplicities are reported using the following abbreviations. (s: singlet, d: doublet, t: triplet, q: quartet m: multiplet, br: broad, *J*: coupling constants in Hertz.). Infrared spectra (IR) were recorded on a Perkin–Elmer Spectrum 1. Only the strongest and/or structurally important absorbances are reported as the IR data given in cm^{-1}. Optical rotations were measured on a JASCO model P-1020 polarimeter. The reactions were monitored by thin layer chromatography carried out on Merck precoated TLC plates (60F-254) using UV light and *p*-anisaldehyde/H_2SO_4/ethanol solution. Flash column chromatography separations were performed using silica gel (KANTO, silica gel 60 N, spherical, neutral, 40–100 um). NH column chromatography separations were performed using silica gel (FUJI SILYSIA, NH-functionalized silica gel, 100–200 mesh). Gel permeation chromatography (GPC) for qualitative analysis was performed on Japan Analytical Industry Model LC908 (recycling preparative HPLC) using a polystyrene gel column (JAIGEL-1 H, 20 mm × 600 mm). Detection of products was made by UV detector (Japan Analytical Industry Model 310) and refractive index detector (Japan Analytical Industry Model RI-5). ESI-TOF Mass spectra were measured with P. E. Biosystems TK-3500 Biospectrometry Workstation. Dry THF, dry toluene, and dry ether were distilled from sodium wire in the presence of a catalytic amount of benzophenone. Dry CH_2Cl_2 was distilled from P_2O_5. Dry DMF and dry triethylamine were distilled from CaH_2. Dry methanol and dry ethanol were distilled from magnesium in the presence of a catalytic amount of iodine.

Synthesis

16: To a solution of **10** (1.42 g, 6.65 mmol) in methanol (20.0 mL) was added K_2CO_3 (9.00 mg, 0.0665 mmol) at room temperature. After stirring at room temperature for 1 h, the reaction mixture was concentrated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in toluene (66.5 mL) was added Bu_2SnO (4.58 g, 18.4 mmol) at room temperature. The reaction mixture was stirred at 140 °C for 6 h, then cooled to room temperature. Bu_4NI (6.84 g, 18.4 mmol) and benzyl bromide (2.98 mL, 25.1 mmol) were added to the reaction mixture at room temperature. After stirring at 100 °C for 18 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in CH_2Cl_2 (33.3 mL) was added benzoyl chloride (0.926 mL, 7.98 mmol), TMEDA (6.65 mL), and a catalytic amount of DMAP at 0 °C under argon. After stirring at room temperature for 2 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 3 M HCl, saturated aq. $NaHCO_3$, brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in acetonitrile (33.3 mL) and water (6.65 mL) was added lithium bromide (1.74 g, 20.0 mmol) and a catalytic amount of Dowex at room temperature. After stirring at room temperature for 1 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 70:30 hexane/ethyl acetate to give **16** (1.91 g, 5.59 mmol, 4 steps 84%, α/β = 72:28). The α/β ratio was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05–7.15 (m, 20H), 5.40 (br s, 1H), 5.04 (t, 1H, *J* = 9.2 Hz), 5.03 (t, 1H, *J* = 9.2 Hz), 4.85 (br d, 1H, *J* = 9.7 Hz), 4.62–4.46 (m, 4H), 4.21–4.04 (m, 2H), 3.73–3.54 (m, 2H), 3.03 (br s, 1H), 2.46 (m, 1H), 2.34 (dd, 1H, *J* = 13.0 Hz, *J* = 4.8 Hz), 2.04 (br s, 1H), 1.82 (t, 1H, *J* = 13.0 Hz), 1.71 (ddd, 1H, *J* = 11.6 Hz, *J* = 9.7 Hz), 1.26 (d, 3H, *J* = 7.2 Hz), 1.21 ppm (d, 3H, *J* = 6.3 Hz); IR (neat): $\tilde{\nu}$ = 1723, 1272, 1126, 772 cm^{-1}.

7: To a stirred solution of **16** (50.0 mg, 0.150 mmol) in CH_2Cl_2 (1.50 mL) was added trichloroacetonitrile (44.0 μL, 0.440 mmol) and a catalytic amount of Cs_2CO_3 at room temperature under argon. After stirring at room temperature for 3 h, the reaction mixture was filtered through celite, and concentrated in vacuo. After ion exchange chromatography on NH-functionalized silica gel with CH_2Cl_2, the residue was used for the next reaction without further purification.

12: To a solution of **10** (3.30 g, 15.4 mol) in methanol (50.0 mL) was added K_2CO_3 (21.3 mg, 0.154 mmol) at room temperature. After stirring

at room temperature for 1 h, the reaction mixture was concentrated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in toluene (50.0 mL) was added Bu_2SnO (4.22 g, 16.9 mmol) at room temperature under argon. The reaction mixture was stirred under 140 °C for 5 h, then cooled to room temperature. Then Bu_4NI (6.30 g, 16.9 mmol) and naphthyl bromide (5.11 g, 23.1 mmol) were added to the reaction mixture at room temperature. After stirring at 100 °C for 18 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 80:20 hexane/ethyl acetate to give **12** (3.12 g, 11.5 mmol, 2 steps 75%). $[\alpha]_D^{26} = -83.6$ ($c = 1.05$, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.84$–7.46 (m, 7H), 6.34 (d, 1H, $J = 6.3$ Hz), 4.87–4.83 (m, 2H), 4.69 (br d, 1H, $J = 11.6$ Hz), 4.08 (br d, 1H, $J = 7.3$ Hz), 3.87 (m, 1H), 3.64 (t, 1H, $J = 8.2$ Hz), 2.43 (br s, 1H, OH), 1.37 ppm (d, 3H, $J = 6.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 145.0, 135.7, 133.2, 132.9, 128.3, 127.8, 12.7, 126.5, 126.2, 125.9, 125.7, 99.7, 76.8, 74.4, 72.7, 70.6, 17.1 ppm; IR (neat): $\tilde{\nu} = 3406$, 2974, 1646, 1509, 1451, 1387, 1230, 1056, 856, 817, 743, 476 cm^{-1}.

17: To a stirred solution of **12** (47.0 mg, 0.174 mmol) in pyridine (0.870 mL) was added (*p*-nitrobenzyl)ethylsulfonyl chloride (49.9 mg, 0.261 mmol) and a catalytic amount of DMAP at 0 °C under argon. After stirring at room temperature for 2 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 3 M HCl, saturated aq. $NaHCO_3$, brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in acetonitrile (0.870 mL) and water (0.174 mL) was added lithium bromide (45.0 mg, 0.524 mmol) and a catalytic amount of Dowex at room temperature. After stirring at 50 °C for 3 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 70:30 hexane/ethyl acetate to give **17** (84.4 mg, 0.173 mmol, 2 steps 99%, $\alpha/\beta = 79{:}21$). The α/β ratio was determined by ^1H NMR. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.75$–6.65 (m, 22H), 5.42 (br s, 1H), 4.92–4.83 (m, 3H), 4.47 (d, 1H, $J = 10.6$ Hz), 4.45 (d, 1H, $J =$ 10.6 Hz), 4.36 (t, 1H, $J = 9.2$ Hz), 4.36 (t, 1H, $J = 9.2$ Hz), 4.20–4.13 (m, 2H), 3.81 (ddd, 1H, $J = 11.6$ Hz, $J = 4.8$ Hz, $J = 9.2$ Hz), 3.59 (m, 1H), 3.40–2.95 (m, 8H), 2.68–2.63 (m, 2H), 2.55 (dd, 1H, $J = 13.0$ Hz, $J =$ 4.8 Hz), 1.77 (m, 1H), 1.69 (ddd, 1H, $J = 11.6$ Hz, $J = 13.0$ Hz, $J = 9.7$ Hz), 1.44 (d, 3H, $J = 5.8$ Hz), 1.39 ppm (d, 3H, $J = 6.3$ Hz); IR (neat): $\tilde{\nu} = 3020$, 1730, 1523, 1349, 1218, 771 cm^{-1}.

18: To a stirred solution of **12** (770 mg, 2.85 mmol) in pyridine (14.2 mL) was added benzylsulfonyl chloride (815 mg, 4.28 mmol) and a catalytic amount of DMAP at 0 °C under argon. After stirring at room temperature for 2 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 3 M HCl, saturated aq. $NaHCO_3$, and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in acetonitrile (14.2 mL) and water (2.85 mL) was added lithium bromide (735 mg, 8.55 mmol) and a catalytic amount of Dowex at room temperature. After stirring at room temperature for 1 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 70:30 hexane/ethyl acetate to give **18** (900 mg, 2.00 mmol, 2 steps 70%, $\alpha/\beta = 73{:}27$). The α/β ratio was determined by ^1H NMR analysis. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.78$–7.16 (m, 24H), 5.33 (br s, 1H), 4.83–4.62 (m, 4H), 4.77 (br d, 1H, $J = 9.2$ Hz), 4.45–4.36 (m, 4H), 4.27 (d, 1H, $J = 14.2$ Hz), 4.27 (d, 1H, $J = 14.2$ Hz), 4.16 (ddd, 1H, $J = 11.1$ Hz, $J =$ 4.8 Hz, $J = 9.7$ Hz), 4.11 (m, 1H), 3.76 (ddd, 1H, $J = 11.6$ Hz, $J = 4.8$ Hz, $J = 9.2$ Hz), 3.68 (m, 1H), 3.49 (dq, 1H, $J = 6.3$ Hz, $J = 9.2$ Hz), 3.00 (br s, 1H), 2.50 (ddd, 1H, $J = 1.5$ Hz, $J = 12.6$ Hz, $J = 4.8$ Hz), 2.43 (dd, 1H, $J =$ 13.1 Hz, $J = 4.8$ Hz), 1.76–1.61 (m, 2H), 1.33 (d, 3H, $J = 6.3$ Hz), 1.29 ppm (d, 3H, $J = 6.3$ Hz); IR (neat): $\tilde{\nu} = 3020$, 1730, 1351, 1217, 998, 759 cm^{-1}.

8b: To a stirred solution of **28** (2.42 g, 5.47 mmol) in CH_2Cl_2 (54.7 mL) was added trichloroacetonitrile (1.65 mL, 16.4 mmol) and a catalytic amount of Cs_2CO_3 at room temperature under argon. After stirring at room temperature for 3 h, the reaction mixture was filtered through celite and concentrated in vacuo. After ion exchange chromatography on NH-functionalized silica gel with CH_2Cl_2, the residue was used for the next reaction without further purification.

20: To a stirred solution of **19** (11.2 g, 52.2 mmol) in acetonitrile (261 mL) was added methanol (21.1 mL, 52.2 mmol) and a catalytic amount of $FeCl_3$ at 0 °C. After stirring at room temperature for 3 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in methanol (261 mL) was added a catalytic amount of sodium methoxide at room temperature under argon. After stirring at room temperature for 12 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 80:20 hexane/ethyl acetate to give **20** (4.06 g, 26.1 mmol, 2 steps 50%, $\alpha/\beta = > 99{:}1$) as a colorless oil. The α/β ratio was determined by ^1H NMR analysis. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 5.88$ (br d, 1H, $J = 10.6$ Hz), 5.68 (ddd, 1H, $J = 10.2$ Hz, $J = 2.4$ Hz), 4.78 (br s, 1H), 3.87–3.54 (m, 2H), 3.39 (s, 3H), 2.55 (m, 1H), 1.29 ppm (d, 3H, $J = 5.8$ Hz); IR (neat): $\tilde{\nu} = 3018$, 1584, 1478, 1439, 1375, 1219, 1105, 1014, 969, 771 cm^{-1}.

22: To a stirred solution of **20** (0.510 g, 3.54 mmol) in THF (8.85 mL) was added 4-nitrobenzoic acid (0.887 g, 5.31 mmol) and PPh_3 (1.36 g, 7.79 mmol) at 0 °C. After stirring at room temperature for 30 min, the reaction mixture was added dropwise a 2.20 M toluene solution of DEAD (3.54 mL, 7.79 mmol) in THF (8.85 mL) at 0 °C. After stirring at room temperature for 2 h, the reaction mixture was concentrated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in THF (17.7 mL) and methanol (17.7 mL) was added a catalytic amount of sodium methoxide at room temperature under argon. After stirring at room temperature for 12 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in CH_2Cl_2 (17.7 mL) was added acetic anhydride (0.401 mL, 4.25 mmol), triethylamine (3.54 mL), and a catalytic amount of DMAP at room temperature. After stirring at room temperature for 6 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 80:20 hexane/ethyl acetate to give **22** (0.253 g, 1.36 mmol, 3 steps 39%, $\alpha/\beta = > 99{:}1$). The α/β ratio was determined by ^1H NMR analysis. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.10$–5.99 (m, 2H), 4.92 (br s, 2H), 4.28 (m, 1H), 3.43 (s, 3H), 2.10 (s, 3H), 1.22 ppm (d, 3H, $J = 6.8$ Hz); IR (neat): $\tilde{\nu} = 3018$, 1735, 1584, 1478, 1439, 1375, 1219, 1105, 1014, 969, 771 cm^{-1}.

24: To a stirred solution of **22** (0.739 g, 3.97 mmol) in ethyl acetate (19.9 mL) was added Pd/C (100 mg/mmol) at room temperature. After stirring at room temperature for 75 min, the reaction mixture was concentrated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in CH_2Cl_2 (19.9 mL) was added thiophenol (0.814 mL, 7.94 mmol) and a catalytic amount of $Sc(OTf)_3$ at 0 °C. After stirring at room temperature for 3 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was chromatographed on silica gel with 80:20 hexane/ethyl acetate to give **24** (0.528 g, 1.99 mmol, 2 steps 50%,

α/β = >99:1). The α/β ratio was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.19 (m, 5H), 5.66 (brs, 1H, J = 5.3 Hz), 4.88 (brs, 1H), 4.49 (q, 1H, J = 6.8 Hz), 2.35 (m, 1H), 2.13 (s, 3H), 2.06 (tt, 1H, J = 14.5 Hz, J = 3.4 Hz), 1.92 (m, 1H), 1.81 (brd, 1H, J = 14.0 Hz), 1.12 ppm (d, 3H, J = 6.8 Hz); IR (neat): $\tilde{\nu}$ = 3016, 1729, 1447, 1367, 1247, 1065, 770, 669 cm^{-1}.

9: To a stirred solution of **24** (386 mg, 1.72 mmol) in methanol (8.60 mL) was added a catalytic amount of NaOMe at room temperature. After stirring at room temperature for 3 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in CH_2Cl_2 (8.60 mL) was added EDCI (490 mg, 2.58 mmol), LevOH (264 μL, 2.58 mmol), and DIEA (591 μL, 3.44 mmol) at 0 °C. After stirring at room temperature for 3 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 80:20 hexane/ethyl acetate to give **9** (665 mg, 2.06 mmol, 2 steps 80%, α/β = >99:1). The α/β ratio was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.20 (m, 5H), 5.65 (brd, 1H), 4.87 (brs, 1H), 4.48 (q, 1H), 2.79–2.63 (m, 4H), 2.34 (m, 1H), 2.19 (s, 3H), 2.04 (m, 1H), 1.92 (m, 1H), 1.81 (brd, 1H, J = 14.0 Hz), 1.12 ppm (d, 3H, J = 6.8 Hz); IR (neat): $\tilde{\nu}$ = 3016, 1729, 1447, 1367, 1247, 1065, 770, 669 cm^{-1}.

25: To a stirred solution of **7** in toluene (3.00 mL) was added *p*-(2-(trimethylsilyl)ethoxymethoxy)phenol **6** (35.0 mg, 0.150 mmol), and pulverized activated 4 Å molecular sieves (MS 4 Å) (150 mg). After stirring at room temperature for 30 min under argon to remove a trace amount of water, the reaction mixture was cooled to −94 °C. After 10 min, I_2 (56.0 mg, 0.220 mmol) and a catalytic amount of triethylsilane were added to the reaction mixture at the same temperature. After stirring for 3 h, the reaction mixture was neutralized with triethylamine, filtered through Celite, and poured into aq. $NaHCO_3$ and aq. $Na_2S_2O_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 80:20 hexane/ethyl acetate and GPC to give **25** (64.0 mg, 0.115 mmol, 79%, α/β = 10:>90). The α/β ratio was determined by ^{1}H NMR analysis. $[\alpha]_D^{21} = -42.3$ (c = 0.260, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07–7.20 (m, 10H), 6.99 (brs, 4H), 5.18 (s, 2H), 5.13 (t, 1H, J = 9.2 Hz), 5.07 (dd, 1H, J = 9.7 Hz, J = 1.9 Hz), 4.66 (d, 1H, J = 12.1 Hz), 4.52 (d, 1H, J = 12.6 Hz), 3.82–3.75 (m, 3H), 3.66 (m, 1H), 2.57 (ddd, 1H, J = 1.9 Hz, J = 12.6 Hz, J = 4.8 Hz), 2.04 (ddd, 1H, J = 12.6 Hz, J = 9.7 Hz), 1.33 (d, 3H, J = 6.8 Hz), 0.98 (t, 2H, J = 8.2 Hz), 0.00 ppm (s, 9H,); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 152.9, 151.8, 137.8, 133.1, 129.9, 129.7, 128.4, 128.2, 127.5, 117.8, 117.2, 98.3, 93.4, 77.2, 76.0, 75.4, 70.8, 70.4, 66.0, 36.5, 18.0, 17.8, −1.49 ppm; IR (neat): $\tilde{\nu}$ = 3019, 1711, 1506, 1364, 1218, 1119, 1090, 1056, 923, 771, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 582.2887, found: 582.2897.

26: To a stirred solution of **25** (100 mg, 0.177 mmol) in methanol (1.77 mL) was added a catalytic amount of sodium methoxide at 0 °C under argon. After stirring at room temperature for 2 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 70:30 hexane/ethyl acetate to give **26** (81.6 mg, 0.177 mmol, quant.). $[\alpha]_D^{21} = -39.9$ (c = 0.150, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.31 (m, 5H), 6.97–6.93 (brs, 4H), 5.16 (s, 2H), 5.00 (dd, 1H, J = 9.7 Hz, J = 1.9 Hz), 4.73 (d, 1H, J = 11.6 Hz), 4.52 (d, 1H, J = 11.6 Hz), 3.76 (t, 2H, J = 8.2 Hz), 3.48 (ddd, 1H, J = 11.6 Hz, J = 4.8 Hz, J = 8.7 Hz), 3.41 (m, 1H), 3.30 (t, 1H, J = 9.2 Hz), 2.61 (s, 1H), 2.50 (ddd, 1H, J = 1.9 Hz, J = 12.6 Hz, J = 4.8 Hz), 1.84 (ddd, 1H, J = 11.6 Hz, J = 12.6 Hz, J = 9.7 Hz), 1.38 (d, 3H, J = 6.3 Hz), 0.97 (t, 2H, J = 8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 151.9, 137.9, 128.6, 127.9, 127.8, 117.7, 117.2, 98.2, 93.5, 78.7, 77.2, 75.4, 71.8, 70.9, 66.0, 35.9, 18.0, 17.9, −1.47 ppm; IR (neat): $\tilde{\nu}$ = 3018, 1719, 1507, 1451, 1365, 1270, 1219, 1035, 1000, 861, 772, 528 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 478.2625, found: 478.2625.

27: To a stirred solution of **25** (100 mg, 0.177 mmol) in THF (0.885 mL) and methanol (0.855 mL) was added Pd/C (17.7 mg). After stirring at room temperature for 12 h under H_2, the reaction mixture was filtered and concentrated in vacuo. The residue was chromatographed on silica gel with 70:30 hexane/ethyl acetate to give **27** (66.7 mg, 0.142 mmol, 80%). $[\alpha]_D^{26} = -0.95$ (c = 0.575, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–7.41 (m, 5H), 6.98 (brs, 4H), 5.16 (s, 2H), 5.07 (dd, 1H, J = 9.7 Hz, J = 1.9 Hz), 4.82 (t, 1H, J = 9.2 Hz), 3.93 (ddd, 1H, J = 9.2 Hz, J = 5.3 Hz, J = 11.6 Hz), 3.75 (t, 2H, J = 8.2 Hz), 3.68 (m, 1H), 3.15 (brs, 1H), 2.45 (ddd, 1H, J = 1.9 Hz, J = 12.6 Hz, J = 5.3 Hz), 2.01 (ddd, 1H, J = 11.6 Hz, J = 12.6 Hz, J = 9.7 Hz), 1.32 (d, 3H, J = 5.8 Hz), 0.96 (t, 2H, J = 8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 152.8, 151.8, 133.4, 129.7, 129.4, 128.4, 117.8, 117.2, 98.1, 93.4, 78.7, 77.3, 70.1, 69.8, 65.9, 39.3, 17.9, 17.8, −1.52 ppm; IR (neat): $\tilde{\nu}$ = 3019, 1710, 1506, 1364, 1218, 1070, 1001, 772, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 492.2418, found: 492.2416.

28b: To a stirred solution of **7** in toluene (109 mL) was added **26** (1.73 g, 3.76 mmol), and pulverized activated MS 4 Å (1.00 g $mmol^{-1}$). After stirring at room temperature for 30 min under argon to remove a trace amount of water, the reaction mixture was cooled to −94 °C. After 10 min, I_2 (2.00 g, 8.21 mmol) and a catalytic amount of triethylsilane were added to the reaction mixture at the same temperature. After stirring for 3 h, the reaction mixture was neutralized with triethylamine, filtered through celite, and poured into a mixture of aq. $NaHCO_3$ and aq. $Na_2S_2O_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 80:20 hexane/ethyl acetate and GPC to give **28b** (2.48 g, 2.82 mmol, 75%, α/β = 7:93). The α/β ratio was determined by ^{1}H NMR analysis. $[\alpha]_D^{21} = -29.3$ (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.19 (m, 17H), 7.00–6.94 (m, 4H), 5.18 (s, 2H), 4.98 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 4.85 (d, 1H, J = 11.6 Hz), 4.77 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 4.70 (brs, 2H), 4.67 (d, 1H, J = 11.6 Hz), 4.44 (t, 1H, J = 9.2 Hz), 4.41 (d, 1H, J = 13.5 Hz), 4.29 (d, 1H, J = 13.5 Hz), 3.78 (m, 1H), 3.77 (t, 2H, J = 8.2 Hz), 3.67 (ddd, 1H, J = 12.1 Hz, J = 5.3 Hz, J = 8.7 Hz), 3.51–3.36 (m, 3H), 2.52–2.47 (m, 2H), 1.90 (ddd, 1H, J = 12.1 Hz, J = 12.6 Hz, J = 9.7 Hz), 1.73 (ddd, 1H, J = 12.1 Hz, J = 12.6 Hz, J = 9.7 Hz), 1.34 (d, 3H, J = 5.8 Hz), 1.33 (d, 3H, J = 5.8 Hz), 0.98 (t, 2H, J = 8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 151.9, 138.4, 134.7, 133.2, 133.0, 130.4, 128.7, 128.6, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 126.7, 126.3, 126.1, 125.6, 117.7, 117.2, 99.8, 98.1, 93.4, 83.8, 82.6, 77.2, 76.0, 71.7, 71.1, 70.7, 70.2, 66.0, 57.4, 36.9, 36.8, 18.3, 18.0, 17.9, −1.47 ppm; IR (neat): $\tilde{\nu}$ = 3020, 1732, 1506, 1359, 1216, 1085, 980, 758, 668 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 902.3969, found: 902.3975.

29: To a stirred solution of **8b** in toluene (49.2 mL) was added **27** (1.14 g, 2.40 mmol) and pulverized activated MS 4 Å (246 mg). After stirring at room temperature for 30 min under argon to remove a trace amount of water, the reaction mixture was cooled to −94 °C. After 10 min, I_2 (938 mg, 3.70 mmol) and a catalytic amount of triethylsilane was added to the reaction mixture at the same temperature. After stirring for 3 h, the reaction mixture was neutralized with triethylamine, filtered through celite, and poured into a mixture of aq. $NaHCO_3$ and aq. $Na_2S_2O_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 80:20 hexane/ethyl acetate and GPC to give **29** (1.07 g, 1.95 mmol, 79%, α/β = 10:90). The α/β ratio was determined by ^{1}H NMR analysis. $[\alpha]_D^{21} = -28.3$ (c = 1.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09–6.61 (m, 16H), 6.98 (brs, 4H), 5.17 (s, 2H), 5.10 (dd, 1H, J = 9.7 Hz, J = 1.9 Hz), 5.00 (t, 1H, J = 9.2 Hz), 4.75 (d, 1H, J = 10.6 Hz), 4.65 (dd, 1H, J = 9.7 Hz, J = 1.9 Hz), 4.34 (d, 1H, J = 10.6 Hz), 4.18 (m, 1H), 4.16 (t, 1H, J = 9.2 Hz), 3.76 (t, 2H, J = 8.2 Hz), 3.76–3.68 (m, 2H), 3.43 (m, 1H), 3.34–2.94 (m, 4H), 2.52 (ddd, 1H, J = 1.9 Hz, J = 12.6 Hz, J = 5.3 Hz), 2.47 (ddd, 1H, J = 1.9 Hz, J = 12.6 Hz, J = 4.8 Hz), 2.03 (ddd, 1H, J = 12.6 Hz,

J=12.1 Hz, J=9.7 Hz), 1.64 (ddd, 1H, J=12.6 Hz, J=12.1 Hz, J=9.7 Hz), 1.34 (d, 3H, J=6.3 Hz), 1.22 (d, 3H, J=6.3 Hz), 0.96 (t, 2H, J=8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=165.9, 153.0, 151.8, 146.5, 144.3, 134.2, 133.1, 132.9, 130.2, 129.8, 128.3, 127.6, 126.6, 126.5, 126.4, 125.4, 123.4, 117.9, 117.3, 98.2, 96.1, 93.5, 84.3, 76.3, 74.9, 74.0, 70.5, 70.1, 66.1, 51.5, 36.6, 36.4, 28.9, 18.0, 17.9, 17.6, −1.46 ppm; IR (neat): $\tilde{\nu}$=3020, 1729, 1506, 1349, 1217, 771, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 975.3769, found: 975.3788.

30: To a stirred solution of **28b** (633 mg, 0.715 mmol) in CH_2Cl_2 (3.58 mL) and $NaHCO_3$ aq. (0.715 mL) was added DDQ (324 mg, 1.43 mmol) at 0 °C under argon. After stirring at room temperature for 3 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 70:30 hexane/ethyl acetate to give **30** (378 mg, 0.508 mmol, 71%). $[\alpha]_D^{20}=-25.3$ (c=0.770, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.42–7.28 (m, 10H), 6.96 (brs, 4H), 5.15 (s, 2H), 4.95 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 4.73 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 4.68 (brs, 2H), 4.49 (brs, 2H), 4.20 (t, 1H, J=9.2 Hz), 3.76–3.71 (m, 3H), 3.63 (ddd, 1H, J=12.1 Hz, J=5.3 Hz, J=9.2 Hz), 3.44 (m, 1H), 3.34 (t, 1H, $J=J$=9.2 Hz), 3.27 (m, 1H), 2.68 (d, 1H, J=3.9 Hz), 2.45 (ddd, 1H, J=1.9 Hz, J=12.5 Hz, J=5.3 Hz), 2.31 (ddd, 1H, J=1.9 Hz, J=12.5 Hz, J=5.3 Hz), 1.86 (ddd, 1H, J=12.1 Hz, J=12.5 Hz, J=9.7 Hz), 1.67 (ddd, 1H, J=12.1 Hz, J=12.5 Hz, J=9.7 Hz), 1.34 (d, 3H, J=5.8 Hz), 1.10 (d, 3H, J=6.3 Hz), 0.96 (t, 2H, J=8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=152.9, 151.9, 138.5, 130.7, 129.2, 128.9, 128.3, 127.7, 127.6, 127.5, 117.7, 117.2, 100.0, 98.2, 93.5, 85.2, 82.9, 71.8, 71.2, 69.6, 69.1, 66.0, 57.2, 39.3, 36.9, 18.3, 18.0, 17.5 ppm; IR (neat): $\tilde{\nu}$=3020, 1732, 1506, 1359, 1216, 1085, 980, 758, 668 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 762.3343, found: 762.3345.

31: To a stirred solution of **28b** (547 mg, 0.620 mmol) in DMF (6.20 mL) was added a large excess of sodium amide at 0 °C under argon. After stirring at room temperature for 12 h, the reaction mixture was poured into H_2O. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 70:30 hexane/ethyl acetate to give **31** (446 mg, 0.611 mmol, 99%). $[\alpha]_D^{21}=-20.9$ (c=1.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.86–7.27 (m, 12H), 6.98 (brs, 4H), 5.16 (s, 2H), 4.96 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 4.77 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 4.86–4.64 (m, 4H), 3.76 (t, 2H, J=8.2 Hz), 3.67 (ddd, 1H, J=11.6 Hz, J=5.3 Hz, J=9.2 Hz), 3.50–3.42 (m, 2H), 3.37 (t, 1H, J=9.2 Hz, J=9.2 Hz), 3.27–3.22 (m, 2H), 2.48–2.44 (m, 2H), 2.38 (ddd, 1H, J=1.9 Hz, J=12.6 Hz, J=4.8 Hz), 1.88 (ddd, 1H, J=11.6 Hz, J=12.6 Hz, J=9.7 Hz), 1.60 (ddd, 1H, J=11.6 Hz, J=12.6 Hz, J=9.7 Hz), 1.34 (d, 3H, J=6.3 Hz), 1.30 (d, 3H, J=5.3 Hz), 0.97 (t, 2H, J=8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=153.0, 152.1, 138.7, 135.6, 133.4, 133.2, 128.4, 128.0, 127.8, 127.7, 126.7, 126.4, 125.7, 117.9, 117.4, 100.3, 98.3, 93.6, 82.3, 79.0, 77.7, 77.3, 75.8, 72.0, 71.9, 71.4, 71.2, 66.1, 37.0, 36.6, 18.5, 18.2, 18.1, −1.32 ppm; IR (neat): $\tilde{\nu}$=3018, 1505, 1370, 1218, 1060, 929, 771, 670 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 748.3881, found: 748.3879.

32: To a stirred solution of **29** (777 mg, 0.810 mmol) in CH_2Cl_2 (4.05 mL) and $NaHCO_3$ aq. (0.810 mL) was added DDQ (184 mg, 1.62 mmol) at 0 °C under argon. After stirring at room temperature for 3 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 70:30 hexane/ethyl acetate to give **32** (471 mg, 0.575 mmol, 71%). $[\alpha]_D^{21}=-24.7$ (c=1.49, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.14–7.35 (m, 9H), 6.96 (brs, 4H), 5.16 (s, 2H), 5.08 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 4.95 (t, 1H, J=9.2 Hz, J=9.2 Hz), 4.60 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 4.13 (ddd, 1H, J=12.1 Hz, J=5.3 Hz, J=9.2 Hz), 4.00 (t, 1H, J=9.2 Hz, J=9.2 Hz), 3.81–3.68 (m, 2H), 3.75 (t, 2H, J=8.2 Hz), 3.61 (m, 1H), 3.46 (m, 1H), 3.32 (m, 1H), 3.27–3.22 (m, 2H), 2.68 (d, 1H, J=4.8 Hz), 2.50 (ddd, 1H, J=1.5 Hz, J=12.6 Hz, J=5.3 Hz), 2.21 (ddd, 1H, J=1.5 Hz, J=12.6 Hz, J=5.3 Hz), 1.99 (ddd, 1H, J=12.1 Hz, J=12.6 Hz, J=9.7 Hz), 1.57 (ddd, 1H, J=12.1 Hz, J=12.6 Hz, J=9.7 Hz), 1.31 (d, 3H, J=5.8 Hz), 1.12 (d, 3H, J=5.8 Hz), 0.95 (t, 2H, J=8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.1, 153.0, 151.7, 147.0, 145.0, 133.2, 130.0, 129.7, 129.4, 128.3, 123.9, 117.8, 117.3, 98.1, 96.0, 93.5, 86.0, 77.2, 75.0, 74.2, 70.4, 69.5, 69.2, 66.0, 51.7, 40.0, 36.6, 29.6, 18.0, 17.9, 17.4, −1.48 ppm; IR (neat): $\tilde{\nu}$=3020, 1726, 1506, 1349, 1216, 1064, 838, 772, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 835.3143, found: 835.3143.

33: To a stirred solution of **29** (315 mg, 0.329 mmol) in CH_2Cl_2 (1.65 mL) was added a large excess of DBU at 0 °C under argon. After stirring at room temperature for 6 h, the reaction mixture was poured into H_2O. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 70:30 hexane/ethyl acetate to give **33** (223 mg, 0.296 mmol, 90%). $[\alpha]_D^{21}=-48.6$ (c=0.360, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.12–7.39 (m, 12H), 7.00 (brs, 4H), 5.09 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 5.01 (t, 1H, J=9.2 Hz, J=9.2 Hz), 4.74 (d, 1H, J=11.6 Hz), 4.57–4.52 (m, 2H), 4.16 (ddd, 1H, J=12.6 Hz, J=5.3 Hz, J=9.2 Hz), 3.78 (t, 2H, J=8.2 Hz), 3.70 (m, 1H), 3.37 (ddd, 1H, J=13.0 Hz, J=4.8 Hz, J=8.7 Hz), 3.16 (m, 1H), 3.06 (t, 1H, J=8.5 Hz, J=8.7 Hz), 2.63 (s, 1H), 2.50 (ddd, 1H, J=1.5 Hz, J=11.1 Hz, J=4.8 Hz), 2.26 (ddd, 1H, J=1.5 Hz, J=11.1 Hz, J=4.8 Hz), 2.03 (ddd, 1H, J=13.0 Hz, J=11.1 Hz, J=9.7 Hz), 1.50 (ddd, 1H, J=13.0 Hz, J=11.1 Hz, J=9.7 Hz), 1.35 (d, 3H, J=5.8 Hz), 1.12 (d, 3H, J=5.8 Hz), 0.99 (t, 2H, J=8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=165.8, 152.9, 151.8, 135.3, 133.1, 132.9, 132.8, 130.3, 129.8, 128.3, 128.1, 127.8, 127.6, 126.4, 126.1, 125.9, 125.5, 117.8, 117.2, 98.2, 96.5, 93.4, 78.5, 77.2, 75.4, 75.1, 73.5, 71.5, 70.5, 70.4, 65.9, 36.7, 36.0, 18.0, 17.9, 17.6, −1.50 ppm; IR (neat): $\tilde{\nu}$=3018, 1725, 1506, 1219, 1070, 1001, 772, 670 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 762.3674, found: 762.3688.

5a: A mixture of **9** (13.8 mg, 0.0420 mmol), **30** (12.5 mg, 0.0168 mmol) and pulverized activated MS 4 Å in dry CH_2Cl_2 (1.00 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Bu_4NOTf (8.23 mg, 0.0210 mmol) and NBS (11.2 mg, 0.0630 mg) were added to the reaction mixture at −78 °C. The reaction mixture was warmed to −40 °C, neutralized with triethylamine, then filtered through celite, and poured into a mixture of aq. $NaHCO_3$ and aq. $Na_2S_2O_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel with 60:40 hexane/ethyl acetate, and gel permeation chromatography (GPC) to give **5a** (16.1 mg, 0.0169 mmol, 95%, α/β=>95:5). The α/β ratio was determined by ^{1}H NMR analysis. $[\alpha]_D^{22}=-29.3$ (c=1.00, $CHCl_3$) ; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.38–7.27 (m, 10H), 6.98–6.90 (m, 4H), 5.15 (brs, 2H), 5.04 (brs, 1H), 4.95 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 4.77–4.73 (m, 2H), 4.68 (brs, 2H), 4.41–4.30 (d, 2H, J=13.5 Hz), 4.38 (t, 1H, J=9.7 Hz, J=9.7 Hz), 4.03 (q, 1H, J=6.3 Hz), 3.81 (ddd, 1H, J=11.6 Hz, J=4.8 Hz, J=9.7 Hz), 3.74 (t, 2H, J=8.2 Hz), 3.63 (ddd, 1H, J=11.6 Hz, J=4.8 Hz, J=9.7 Hz), 3.43 (m, 1H), 3.38–3.30 (m, 2H), 2.81–2.61 (m, 4H), 2.47 (ddd, 1H, J=1.9 Hz, J=12.1 Hz, J=4.8 Hz), 2.45 (ddd, 1H, J=1.9 Hz, J=12.1 Hz, J=4.8 Hz), 2.19 (s, 3H), 2.20–1.49 (m, 6H), 1.33 (d, 3H, J=5.8 Hz), 1.16 (d, 3H, J=5.8 Hz), 1.03 (d, 3H, J=6.3 Hz), 0.97 (t, 2H, J=8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=206.4, 172.3, 152.9, 151.9, 138.6, 130.7, 129.1, 128.9, 128.3, 127.7, 127.5, 127.4, 117.7, 117.2, 99.9, 98.2, 93.5, 91.7, 82.8, 82.4, 71.8, 71.2, 70.2, 69.8, 69.7, 66.0, 65.1, 57.9, 38.0, 36.9, 35.6, 29.8, 28.1, 23.8, 22.2, 18.4, 18.0, 17.9, 16.9, −1.46 ppm; IR (neat): $\tilde{\nu}$=3019, 1720, 1506, 1362, 1216, 1084, 769, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 974.4392, found: 974.4402.

5b: According to the method for the synthesis of **5a**, a mixture of **9** (137 mg, 0.425 mmol), **31** (212 mg, 0.289 mmol), and pulverized activated MS 4 Å in dry CH_2Cl_2 (4.30 mL) was treated with Bu_4NOTf (83.3 mg, 0.213 mmol) and NBS (113 mg, 0.638 mg) to provide **5b** (243 mg, 0.323 mmol, 76%, α/β=>90:10). $[\alpha]_D^{21}=-31.2$ (c=0.500, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82–7.24 (m, 12H), 6.97–6.90 (m, 4H), 5.15 (brs, 2H), 5.02 (brs, 1H), 4.94 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 4.79–4.60 (m, 5H), 4.59 (brs, 1H), 4.30 (q, 1H, J=6.8 Hz), 3.74 (t, 2H, J=

8.2 Hz), 3.63 (ddd, 1H, J=11.6 Hz, J=4.8 Hz, J=8.2 Hz), 3.53 (ddd, 1H, J=11.6 Hz, J=4.8 Hz, J=8.7 Hz), 3.47–3.23 (m, 3H), 3.25 (m, 1H), 2.72–2.58 (m, 4H), 2.48–2.37 (m, 1H), 2.16 (s, 3H), 2.03–1.52 (m, 6H), 1.31 (d, 3H, J=5.8 Hz), 1.26 (d, 3H, J=6.3 Hz), 0.95 (t, 2H, J=8.2 Hz), 0.67 (d, 3H, J=6.8 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 206.5, 172.3, 152.9, 151.9, 138.7, 135.6, 133.2, 133.0, 128.3, 128.1, 127.8, 127.7, 127.5, 126.7, 126.2, 126.0, 125.9, 117.8, 117.2, 100.2, 98.2, 97.1, 93.5, 82.4, 79.7, 77.5, 72.3, 72.0, 71.3, 71.2, 69.9, 66.0, 65.2, 38.0, 37.0, 29.8, 28.2, 24.0, 18.6, 18.3, 18.1, 16.6, −1.45 ppm; IR (neat): $\tilde{\nu}$=3020, 1731, 1506, 1374, 1249, 1216, 1161, 1059, 910, 758, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 960.4929, found: 960.4940.

5c: According to the method for the synthesis of **5a**, a mixture of **9** (221 mg, 0.685 mmol), **32** (422 mg, 0.515 mmol), and pulverized activated MS 4 Å in dry CH_2Cl_2 (6.85 mL) was treated with Bu_4NOTf (134 mg, 0.343 mmol) and NBS (182 mg, 1.03 mmol) to provide **5c** (402 mg, 0.390 mmol, 76%, α/β=>95:5). $[\alpha]_D^{23}$=−35.9 (c=0.550, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.19–7.35 (m, 9H), 6.98 (brs, 4H), 5.16 (s, 2H), 5.07 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 4.95 (t, 1H, J=9.2 Hz, J= 9.2 Hz), 4.91 (brs, 1H), 4.67 (brs, 1H), 4.59 (dd, 1H, J=9.7 Hz, J= 1.5 Hz), 4.17 (t, 1H, J=9.2 Hz, J=9.2 Hz), 4.15 (ddd, 1H, J=11.6 Hz, J=4.8 Hz, J=9.6 Hz), 4.00 (q, 1H, J=6.8 Hz), 3.78–3.65 (m, 4H), 3.48–3.23 (m, 5H), 2.75–2.60 (m, 4H), 2.47 (ddd, 1H, J=1.5 Hz, J=12.6 Hz, J=4.8 Hz), 2.30 (ddd, 1H, J=1.5 Hz, J=12.0 Hz, J=4.8 Hz), 2.18 (s, 3H), 2.00 (ddd, 1H, J=4.8 Hz, J=12.6 Hz, J=9.7 Hz), 1.93–1.37 (m, 5H), 1.31 (d, 3H, J=6.3 Hz), 1.11 (d, 3H, J=5.3 Hz), 1.05 (d, 3H, J= 6.8 Hz), 0.97 (t, 2H, J=8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=206.5, 172.2, 165.7, 153.0, 151.8, 147.2, 144.7, 133.1, 130.2, 129.8, 129.3, 128.3, 124.1, 117.9, 117.3, 98.1, 96.3, 93.5, 91.9, 83.4, 77.2, 75.0, 74.1, 70.5, 70.0, 69.8, 69.3, 66.0, 65.4, 52.5, 37.9, 36.7, 35.5, 29.8, 29.4, 28.1, 23.9, 22.2, 18.0, 17.9, 16.8, −1.46 ppm; IR (neat): $\tilde{\nu}$=3020, 1728, 1506, 1349, 1216, 1087, 770, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 1047.4192, found: 1047.4200.

5d: According to the method for the synthesis of **5a**, a mixture of **9** (109 mg, 0.330 mmol), **33** (223 mg, 0.299 mmol) and pulverized activated MS 4 Å in dry CH_2Cl_2 (6.85 mL) was treated Bu_4NOTf (65.0 mg, 0.165 mmol) and NBS (88.0 mg, 0.495 mmol) to provide **5d** (287 mg, 0.297 mmol, 90%, α/β=>90:10). $[\alpha]_D^{21}$=−44.7(c 0.650, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.08–7.37 (m, 12H), 6.97 (brs, 4H), 5.17 (s, 2H, a), 5.08 (dd, 1H, J=9.6 Hz, J=1.9 Hz), 4.97 (t, 1H, J=9.2 Hz), 4.91 (brs, 1H), 4.70 (d, 1H, J=11.1 Hz), 4.56 (brs, 1H), 4.55 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 4.50 (d, 1H, J=11.1 Hz), 4.26 (q, 1H, J=6.8 Hz), 4.14 (ddd, 1H, J=11.6 Hz, J=4.8 Hz, J=9.2 Hz), 3.74 (t, 2H, J=8.2 Hz), 3.75 (m, 1H), 3.49 (ddd, 1H, J=12.1 Hz, J=5.3 Hz, J=8.2 Hz), 3.22–3.18 (m, 2H), 2.72–2.55 (m, 4H), 2.48 (ddd, 1H, J=1.9 Hz, J=12.6 Hz, J= 4.8 Hz), 2.30 (ddd, 1H, J=1.5 Hz, J=12.0 Hz, J=5.3 Hz), 2.15 (s, 3H), 2.00 (ddd, 1H, J=12.1 Hz, J=12.6 Hz, J=9.6 Hz), 2.00–1.47 (m, 5H), 1.33 (d, 3H, J=5.8 Hz), 1.07 (d, 3H, J=5.3 Hz), 0.97 (t, 2H, J=8.2 Hz), 0.62 (d, 3H, J=6.8 Hz), 0.00 ppm (s, 9H, TMS); ^{13}C NMR (100 MHz, $CDCl_3$): δ=206.5, 172.4, 165.9, 152.9, 151.8, 135.4, 133.2, 133.0, 130.4, 129.9, 128.2, 128.1, 127.8, 127.7, 126.8, 126.2, 126.1, 126.0, 117.9, 117.3, 98.3, 96.9, 96.5, 93.5, 79.5, 77.2, 75.1, 73.5, 72.0, 70.8, 70.6, 70.0, 66.1, 65.2, 38.0, 36.8, 36.5, 29.8, 28.2, 23.9, 22.6, 18.3, 18.1, 18.0, 16.6, −1.45 ppm; IR (neat): $\tilde{\nu}$=2933, 1702, 1506, 1366, 1016, 857, 756, 522 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 974.4722, found: 974.4731.

3a: To a stirred solution of **5a** (100 mg, 0.119 mmol) in pyridine (0.595 mL) and AcOH (0.893 mL) was added $H_2NNH_2{\cdot}H_2O$ (28.8 μL, 0.595 mmol) at 0 °C under argon. After stirring at the same temperature for 3 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 70:30 hexane/ethyl acetate to give **3a** (74.4 mg, 0.0952 mmol, 80%). $[\alpha]_D^{22}$=−22.2 (c=1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.39–7.27 (m, 10H), 6.97–6.91 (m, 4H), 5.15 (brs, 2H), 5.00 (brs, 1H), 4.95 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 4.76 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 4.69 (brs, 2H), 4.41–4.30 (d, 2H, J=13.5 Hz), 4.36 (t, 1H, J=9.2 Hz, J=9.2 Hz), 4.01 (q, 1H, J=6.6 Hz), 3.83 (ddd, 1H, J=11.6 Hz, J=4.8 Hz, J= 9.2 Hz), 3.74 (t, 2H, J=8.2 Hz), 3.63 (ddd, 1H, J=11.6 Hz, J=4.8 Hz, J=9.2 Hz), 3.53 (brs, 1H), 3.46–3.33 (m, 3H), 2.50 (ddd, 1H, J=1.9 Hz, J=12.1 Hz, J=4.8 Hz), 2.46 (ddd, 1H, J=1.9 Hz, J=12.1 Hz, J=4.8 Hz), 2.12–1.49 (m, 6H), 1.35 (d, 3H, J=5.8 Hz), 1.18 (d, 3H, J=6.3 Hz), 1.13 (d, 3H, J=6.6 Hz), 0.95 (t, 2H, J=8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=152.8, 151.9, 138.5, 130.6, 129.1, 128.9, 128.3, 127.6, 127.5, 127.4, 117.7, 117.2, 99.9, 98.1, 93.5, 91.8, 82.7, 82.6, 71.8, 71.2, 70.2, 69.7, 67.2, 66.3, 66.0, 57.8, 36.9, 35.6, 25.2, 23.1, 18.4, 18.0, 17.0 ppm; IR (neat): $\tilde{\nu}$=3020, 1732, 1506, 1359, 1216, 1085, 980, 758, 668 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4024, found: 876.4033.

3b: According to the method for the synthesis of **3a**, a solution of **5b** (54.2 mg, 0.0520 mmol) in pyridine (0.263 mL) and AcOH (0.390 mL) was treated with $H_2NNH_2{\cdot}H_2O$ (12.6 μL, 0.260 mmol) to provide **3b** (36.0 mg, 0.0426 mmol, 82%) $[\alpha]_D^{21}$=−33.5 (c=0.740, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.84–7.26 (m, 12H), 6.96–6.90 (m, 4H), 5.15 (brs, 2H), 4.98 (brs, 1H), 4.95 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 4.73 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 4.80–4.63 (m, 4H), 4.24 (q, 1H, J=6.3 Hz), 3.74 (t, 2H, J=8.2 Hz), 3.63 (ddd, 1H, J=12.1 Hz, J=5.3 Hz, J=8.7 Hz), 3.55 (ddd, 1H, J=11.6 Hz, J=4.8 Hz, J=8.7 Hz), 3.47–3.23 (m, 4H), 3.35 (brs, 1H), 2.46–2.38 (m, 1H), 1.99–1.52 (m, 6H), 1.32–1.26 (m, 6H), 0.95 (t, 2H, J=8.2 Hz), 0.75 (d, 3H, J=6.3 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=152.8, 151.9, 138.7, 135.7, 133.3, 133.0, 128.3, 128.1, 127.7, 127.6, 127.5, 126.8, 126.2, 126.1, 126.0, 117.8, 100.2, 98.2, 97.2, 93.5, 82.4, 79.7, 77.7, 77.5, 77.2, 72.3, 72.0, 71.4, 71.3, 67.4, 66.5, 66.0, 37.1, 25.6, 23.4, 18.6, 18.3, 18.1, 16.7, −1.44 ppm; IR (neat): $\tilde{\nu}$=3018, 1505, 1370, 1218, 1060, 929, 771, 670 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 862.4530, found: 862.4567.

3c: According to the method for the synthesis of **3a**, a solution of **5c** (54.2 mg, 0.0520 mmol) in pyridine (0.263 mL) and AcOH (0.390 mL) was treated with $H_2NNH_2{\cdot}H_2O$ (12.6 μL, 0.260 mmol) to provide **3c** (34.4 mg, 0.0442 mmol, 85%). $[\alpha]_D^{23}$=−49.1 (c=1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.18–7.35 (m, 9H), 6.96 (brs, 4H), 5.16 (s, 2H), 5.07 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 4.95 (t, 1H, J=9.2 Hz, J=9.2 Hz), 4.87 (brs, 1H), 4.60 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 4.14 (t, 1H, J= 9.2 Hz, J=9.2 Hz), 4.10 (ddd, 1H, J=11.6 Hz, J=4.8 Hz, J=9.2 Hz), 3.92 (q, 1H, J=6.3 Hz), 3.78–3.67 (m, 4H), 3.49–3.20 (m, 6H), 2.46 (ddd, 1H, J=1.5 Hz, J=12.6 Hz, J=4.8 Hz), 2.33 (ddd, 1H, J=1.5 Hz, J=12.6 Hz, J=4.8 Hz), 2.00 (ddd, 1H, J=11.6 Hz, J=12.6 Hz, J=9.7 Hz), 1.90–1.36 (m, 5H), 1.31 (d, 3H, J=5.8 Hz), 1.13–1.11 (m, 6H), 0.95 (t, 2H, J= 8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=165.7, 153.0, 151.7, 147.2, 144.8, 133.0, 130.2, 129.8, 129.3, 128.3, 124.0, 117.9, 117.2, 98.1, 96.4, 93.5, 92.0, 83.6, 77.2, 75.0, 74.1, 70.5, 70.0, 69.8, 66.9, 66.6, 66.0, 52.4, 36.7, 35.4, 29.4, 25.2, 23.0, 18.0, 17.9, 17.8, 16.9, −1.47 ppm; IR (neat): $\tilde{\nu}$=3020, 1729, 1506, 1349, 1216, 1087, 770, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 949.3824, found: 949.3858.

3d: According to the method for the synthesis of **3a**, a solution of **5d** (54.2 mg, 0.0520 mmol) in pyridine (0.263 mL) and AcOH (0.390 mL) was treated with $H_2NNH_2{\cdot}H_2O$ (12.6 μL, 0.260 mmol) to provide **3d** (34.6 mg, 0.0442 mmol, 85%). $[\alpha]_D^{23}$=−55.3 (c=0.810, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.08–7.38 (m, 12H), 6.97 (brs, 4H), 5.17 (s, 2H), 5.08 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 4.98 (t, 1H, J=9.2 Hz, J=9.2 Hz), 4.87 (brs, 1H), 4.70 (d, 1H, J=11.1 Hz), 4.55 (dd, 1H, J=9.7 Hz, J= 1.5 Hz), 4.53 (d, 1H, J=11.1 Hz), 4.20 (q, 1H, J=6.3 Hz), 4.15 (ddd, 1H, J=11.6 Hz, J=4.8 Hz, J=9.2 Hz), 3.75 (t, 2H, J=8.2 Hz), 3.70 (m, 1H), 3.50 (ddd, 1H, J=12.1 Hz, J=4.8 Hz, J=8.2 Hz), 3.32 (brs, 1H), 3.20–3.17 (m, 2H), 2.49 (ddd, 1H, J=1.9 Hz, J=12.5 Hz, J=4.8 Hz), 2.30 (ddd, 1H, J=1.5 Hz, J=12.5 Hz, J=4.8 Hz), 2.05–1.47 (m, 6H), 1.33 (d, 3H, J=6.3 Hz), 1.08 (d, 3H, J=5.3 Hz), 0.96 (t, 2H, J=8.2 Hz), 0.69 (d, 3H, J=6.3 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 165.8, 152.9, 151.8, 135.5, 133.2, 132.9, 130.3, 129.8, 128.2, 128.0, 127.7, 127.6, 126.8, 126.1, 125.9, 117.8, 98.2, 97.0, 96.4, 93.5, 79.4, 77.2, 75.1, 73.4, 72.0, 70.9, 70.5, 67.3, 66.4, 66.0, 36.8, 36.5, 25.3, 23.3, 18.3, 18.0, 17.9, 16.6, −1.46 ppm; IR (neat): $\tilde{\nu}$=3019, 1713, 1506, 1217, 1064, 979, 771, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4354, found: 876.4365

35aa: To a stirred solution of **5a** (77.5 mg, 0.0920 mmol) in CH_3CN (1.00 mL) and water (1.00 mL) was added CAN (75.5 mg, 0.138 mmol) at 0 °C under argon. After stirring at room temperature for 1 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was

extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. After short pass chromatography, the residue was used for the next reaction without further purification. To a stirred solution of the residue in CH_2Cl_2 (0.920 mL) were added trichloroacetonitrile (27.5 μL, 0.276 mmol, 3.00 equiv) and a catalytic amount of Cs_2CO_3 at room temperature under argon. After stirring at room temperature for 3 h, the reaction mixture was filtered through celite and concentrated in vacuo. After ion exchange chromatography on NH-functionalized silica gel with CH_2Cl_2 as eluent, the residue was used for the next reaction without further purification. To a stirred solution of the residue in toluene (1.84 mL) was added **3a** (65.0 mg, 0.0750 mmol), and pulverized activated MS 4 Å (1.00 g mmol^{-1}). After stirring at room temperature for 30 min under argon to remove a trace amount of water, the reaction mixture was cooled to −94 °C. After 10 min, I_2 and a catalytic amount of triethylsilane were added to the reaction mixture at the same temperature. After stirring for 3 h, the reaction mixture was neutralized with triethylamine, filtered through celite, and poured into aq. $NaHCO_3$ and aq. $Na_2S_2O_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica gel chromatography with 70:30 hexane/ethyl acetate and GPC to give **35aa** (87.3 mg, 0.0553 mmol, 93 %, β/α = 82:18). The β/α ratio was determined by HPLC analysis (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 20.5 min, α-isomer = 22.0 min). **β-isomer**: $[\alpha]_D^{22} = -27.3$ ($c = 0.875$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.40$–7.15 (m, 20H), 6.96–6.90 (m, 4H), 5.15 (brs, 2H), 5.03 (brs, 2H), 4.95 (dd, 1H, $J = 9.7$ Hz, $J = 1.5$ Hz), 4.77–4.72 (m, 3H), 4.68 (brs, 2H), 4.64 (brs, 2H), 4.45–4.29 (m, 7H), 4.02 (q, 1H, $J = 6.8$ Hz), 3.96 (q, 1H, $J = 6.8$ Hz), 3.87–3.78 (m, 2H), 3.74 (t, 2H, $J = 8.2$ Hz), 3.64 (ddd, 1H, $J = 11.6$ Hz, $J = 4.8$ Hz, $J = 9.2$ Hz), 3.55 (ddd, 1H, $J = 11.6$ Hz, $J = 4.8$ Hz, $J = 9.2$ Hz), 3.43–3.24 (m, 7H), 2.77–2.62 (m, 4H), 2.51–2.43 (m, 3H), 2.35 (m, 1H), 2.18 (s, 3H), 2.04–1.46 (m, 12H), 1.34–1.14 (m, 12H), 1.10 (d, 3H, $J = 6.8$ Hz), 1.02 (d, 3H, $J = 6.8$ Hz), 0.95 (t, 2H, $J = 8.2$ Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 206.7$, 172.5, 153.2, 152.3, 139.5, 139.4, 131.1, 129.4, 129.2, 128.6, 128.5, 128.4, 127.9, 127.8, 127.7, 118.0, 117.7, 101.6, 100.1, 98.4, 94.0, 92.4, 92.2, 83.8, 83.3, 83.2, 83.0, 77.9, 77.8, 77.4, 76.4, 72.1, 71.8×2, 71.4, 70.5, 70.2, 70.0, 66.7, 66.4, 65.5, 58.2, 38.3, 37.6, 37.4, 36.3, 36.2, 30.1, 29.9, 28.6, 24.6, 24.3, 22.7, 18.4, 18.3, 17.1, −1.41 ppm; IR (neat): $\tilde{\nu} = 3019$, 1720, 1506, 1362, 1216, 1084, 769, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 1592.6891, found 1592.6887. **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.39$–7.15 (m, 20H), 6.96–6.90 (m, 4H), 5.15 (brs, 2H), 5.04 (brs, 2H), 4.97–4.94 (m, 2H), 4.77–4.69 (m, 6H), 4.60 (d, 1H, $J = 11.1$ Hz), 4.44–4.29 (m, 6H), 4.06–3.99 (m, 2H), 3.92 (ddd, 1H, $J = 10.1$ Hz, $J = 3.9$ Hz, $J = 8.2$ Hz), 3.89–3.77 (m, 2H), 3.74 (t, 2H, $J = 8.2$ Hz), 3.74 (m, 1H), 3.63 (m, 1H), 3.49 (brs, 1H), 3.43–3.26 (m, 5H), 2.78–2.62 (m, 4H), 2.51–2.44 (m, 3H), 2.26 (m, 1H), 2.19 (s, 3H), 1.96–1.43 (m, 12H), 1.33 (d, 3H, $J = 5.8$ Hz), 1.22 (d, 3H, $J = 6.3$ Hz), 1.22–1.02 (m, 12H), 0.95 (t, 2H, $J = 8.2$ Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, $CDCl_3$): $\delta = 206.5$, 172.3, 152.8, 151.9, 138.9, 138.5, 130.7, 129.1, 128.9, 128.3, 128.2, 127.7, 127.6, 127.5, 127.4, 127.3, 117.7, 117.2, 100.0×2, 98.2, 93.5, 92.7, 91.7, 83.5, 82.9, 82.8, 82.5, 77.3, 77.2, 72.1, 71.8, 71.2, 70.2, 69.8, 69.7, 69.6, 68.9, 67.1, 66.6, 66.0, 65.1, 57.9, 38.0, 36.9, 35.9, 35.6, 35.5, 29.8, 28.1, 23.8, 23.5, 22.2, 19.4, 18.4, 18.2, 18.0, 17.9, 17.5, 17.0, −1.45 ppm; IR (neat): $\tilde{\nu} = 3020$, 1731, 1374, 1216, 1000, 772, 668 cm^{-1}.

35ab: According to the method for the synthesis of **35aa**, a solution of **5a** (61.1 mg, 0.0725 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (12.6 mg, 0.260 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (21.8 μL, 0.218 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3b** (40.2 mg, 0.0470 mmol) with the imidate in toluene (1.45 mL) by activation with I_2 (27.6 mg, 0.109 mmol) provided the hexasaccharide **35ab** (82.2 mg, 0.0520 mmol, 95 %, β/α = 73:27). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 18.0 min, α-isomer = 19.5 min). **β-isomer**: $[\alpha]_D^{21} = -36.9$ ($c = 1.17$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.84$–7.26 (m, 22H), 6.97–6.90 (m, 4H), 5.15 (s, 2H), 5.03–5.00 (m, 2H), 4.95 (dd, 1H, $J = 9.7$ Hz, $J = 1.5$ Hz), 4.81–4.55 (m, 9H), 4.38 (d, 1H, $J = 14.0$ Hz), 4.34 (t, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 4.33 (d, 1H, $J = 14.0$ Hz), 4.22 (brd, 1H, $J = 9.6$ Hz), 4.13 (q, 1H, $J = 6.3$ Hz), 4.02 (q, 1H, $J = 5.8$ Hz), 3.78 (ddd, 1H, $J = 11.6$ Hz, $J = 4.8$ Hz, $J = 9.2$ Hz), 3.74 (t, 2H, $J = 8.2$ Hz), 3.63 (ddd, 1H, $J = 11.6$ Hz, $J = 4.8$ Hz, $J = 9.2$ Hz), 3.55–3.20 (m, 9H), 3.17 (brs, 1H), 2.77–2.62 (m, 4H), 2.48–2.37 (m, 3H), 2.29 (m, 1H), 2.19 (s, 3H), 2.04–1.48 (m, 12H), 1.32–1.14 (m, 12H), 1.02 (d, 3H, $J = 5.8$ Hz), 0.95 (t, 2H, $J = 8.2$ Hz), 0.71 (d, 3H, $J = 6.3$ Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 206.5$, 172.3, 152.8, 151.9, 138.7, 135.8, 133.2, 132.9, 130.0, 129.1, 128.9, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 126.6, 126.5, 126.3, 126.1, 126.0, 125.9, 125.6, 117.7, 117.2, 101.3, 100.2, 99.9, 98.2, 97.1, 93.5, 91.7, 82.8, 82.5, 82.3, 82.2, 79.2, 78.9, 77.7, 77.6, 77.4, 77.2, 76.2, 75.7, 72.4, 72.0, 71.8, 71.4, 71.1, 70.8, 70.1, 69.8, 69.7, 66.2, 66.0, 65.1, 57.8, 38.0, 37.1, 37.0, 36.9, 36.4, 35.6, 29.8, 28.1, 24.6, 24.2, 23.8, 22.2, 18.6, 18.3, 18.0, 17.9, 16.9, 16.8, −1.46 ppm; IR (neat): $\tilde{\nu} = 2935$, 1729, 1506, 1364, 1213, 1064, 1019, 987, 835, 754, 698 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 1578.7428, found 1578.7479. **α-isomer:** ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.84$–7.26 (m, 22H), 6.96–6.90 (m, 4H), 5.15 (s, 2H), 5.01 (brs, 2H), 4.95 (dd, 1H, $J = 9.7$ Hz, $J = 1.5$ Hz), 4.92 (brs, 1H), 4.81–4.54 (m, 9H), 4.40–4.29 (m, 3H), 4.24 (q, 1H, $J = 6.3$ Hz), 4.03 (q, 1H, $J = 6.3$ Hz), 3.85 (ddd, 1H, $J = 10.6$ Hz, $J = 5.3$ Hz, $J = 8.2$ Hz), 3.79 (m, 1H), 3.74 (t, 2H, $J = 8.2$ Hz), 3.64 (ddd, 1H, $J = 11.6$ Hz, $J = 4.8$ Hz, $J = 8.2$ Hz), 3.57 (m, 2H), 3.47–3.33 (m, 2H), 3.29–3.20 (m, 5H), 2.77–2.62 (m, 4H), 2.46–2.42 (m, 3H), 2.25–2.19 (s, 4H), 1.90–1.44 (m, 12H),1.31 (d, 3H, $J = 5.8$ Hz), 1.26 (d, 3H, $J = 5.3$ Hz), 1.11 (d, 3H, $J = 6.3$ Hz), 1.09 (d, 3H, $J = 6.3$ Hz), 1.03 (d, 3H, $J = 6.3$ Hz), 0.95 (t, 2H, $J = 8.2$ Hz), 0.73 (d, 3H, $J = 6.3$ Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, $CDCl_3$): $\delta = 206.5$, 172.3, 152.8, 151.9, 138.9, 138.7, 135.7, 133.2, 132.9, 130.7, 129.1, 128.9, 128.3, 128.2, 128.1, 127.7, 127.6×2, 127.5, 127.4, 126.8, 126.2, 126.1, 126.0, 117.7, 117.2, 100.2, 99.8, 98.2, 96.9, 93.5, 92.6, 91.7, 83.4, 82.6, 82.3, 79.2, 77.2, 75.7, 72.4, 72.1, 72.0, 71.4, 71.3, 70.2, 69.8, 69.7, 68.7, 66.0, 65.1, 57.9, 38.0, 29.8, 28.2, 19.8, 18.6, 18.4, 18.1, 18.0, 17.9, 17.1, 17.0, −1.44 ppm; IR (neat): $\tilde{\nu} = 2935$, 1729, 1506, 1364, 1213, 1064, 1019, 987, 835, 754, 698 cm^{-1}.

35ac: According to the method for the synthesis of **35aa**, a solution of **5a** (60.5 mg, 0.0725 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (59.9 mg, 0.110 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (22.0 μL, 0.219 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3c** (51.2 mg, 0.0540 mmol) with the imidate in toluene (1.46 mL) by activation with I_2 (28.0 mg, 0.110 mmol) provided the hexasaccharide **35ac** (65.3 mg, 0.0540 mmol, 72 %, β/α = 73:27). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 26.5 min, α-isomer = 37.5 min). **β-isomer**: $[\alpha]_D^{17} = -43.6$ ($c = 1.14$, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 8.16$–7.24 (m, 19H), 6.94 (brs, 4H), 5.14 (s, 2H), 5.07 (brd, 1H, $J = 9.7$ Hz), 5.01 (brs, 1H), 4.89 (t, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 4.84 (brs, 1H), 4.72–4.59 (m, 5H), 4.42 (d, 1H, $J = 14.0$ Hz), 4.35–4.28 (m, 3H), 4.15–4.06 (m, 2H), 4.02 (q, 1H, $J = 6.3$ Hz), 3.86–3.63 (m, 4H), 3.73 (t, 2H, $J = 8.2$ Hz), 3.50–3.21 (m, 10H), 2.74–2.55 (m, 4H), 2.50–2.46 (m, 2H), 2.35–2.28 (m, 2H), 2.13 (s, 3H), 2.09–1.35 (m, 12H), 1.26 (d, 3H, $J = 6.3$ Hz), 1.23 (d, 3H, $J = 5.8$ Hz), 1.15–1.09 (m, 6H), 1.03 (d, 3H, $J = 6.3$ Hz), 0.90 (d, 3H, $J = 6.3$ Hz), 0.93 (t, 2H, $J = 8.2$ Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, CD_2Cl_2): $\delta = 206.8$, 172.5, 166.0, 153.3, 152.1, 147.5, 145.6, 139.4, 133.4, 131.1, 130.6, 130.1, 129.8, 129.4, 129.2, 128.6, 128.5, 128.3, 127.7, 127.6, 124.2, 118.0, 117.6, 101.5, 100.1, 98.3, 96.9, 93.8, 92.4, 92.1, 84.2, 83.2, 83.1, 77.6, 76.0, 75.3, 74.5, 71.8, 71.4, 70.7, 70.4, 70.2, 70.1, 69.9, 66.9, 66.4, 65.4, 58.1, 54.4, 54.0, 53.6, 52.7, 38.3, 37.5, 37.1, 36.1, 36.0, 30.0, 29.9, 29.8, 28.5, 24.5, 24.4, 24.2, 22.6, 18.5, 18.3, 18.2, 18.1, 18.0, 17.1, 16.9, −1.45 ppm; IR (neat): $\tilde{\nu} = 3020$, 1723, 1506, 1349, 1216, 1087, 1019, 756, 668 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 1665.6691, found 1665.6721. **α-isomer**: ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 8.16$–7.25 (m, 19H), 6.94 (brs, 4H), 5.14 (s, 2H), 5.08 (dd, 1H, $J = 9.7$ Hz, $J = 1.9$ Hz), 5.01 (brs, 1H), 4.88 (t, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 4.86 (brs, 2H), 4.73–4.68 (m, 3H), 4.62–4.57 (m, 2H), 4.42 (d, 1H, $J = 14.0$ Hz), 4.34 (d, 1H, $J = 14.0$ Hz), 4.30 (t, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 4.15–4.08 (m, 2H), 4.02 (q, 1H, $J = 6.3$ Hz), 3.93 (q, 1H, $J = 6.8$ Hz), 3.86–3.79 (m, 3H), 3.73 (t, 2H, $J = 8.2$ Hz), 3.69–3.64 (m, 2H), 3.53–3.22 (m, 8H), 2.74–2.55 (m, 4H), 2.50–2.46 (m, 2H), 2.34 (ddd, 1H, $J = 4.8$ Hz, $J = 12.1$ Hz, $J = 1.9$ Hz), 2.19–2.05 (m, 4H), 1.97–1.34 (m, 12H), 1.26 (d, 3H, $J =$

6.3 Hz), 1.18 (d, 3H, J=5.8 Hz), 1.15–1.09 (m, 9H), 0.99 (d, 3H, J=6.3 Hz), 0.93 (t, 2H, J=8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, CD_2Cl_2): δ=206.8, 176.8, 172.5, 166.0, 153.3, 152.1, 147.5, 145.5, 139.2, 133.4, 131.1, 130.7, 130.1, 129.7, 129.4, 129.2, 128.6, 128.5, 128.3, 127.7, 127.6, 124.3, 118.0, 117.6, 100.1, 98.3, 96.9, 93.9, 93.4, 92.2, 92.1, 84.0, 83.7, 83.2, 75.8, 75.3, 74.6, 72.2, 70.8, 70.4, 70.3, 70.2, 70.1, 69.9, 69.4, 67.6, 67.3, 66.4, 65.4, 58.1, 53.6, 52.7, 38.3, 37.0, 36.1, 29.9, 29.8, 28.5, 24.2, 22.6, 18.3, 18.2, 18.1, 18.0, 17.2, 17.1, −1.45 ppm; IR (neat): $\tilde{\nu}$=3020, 1723, 1506, 1349, 1216, 1087, 1019, 756, 668 cm^{-1}.

35ad: According to the method for the synthesis of **35aa**, a solution of **5a** (66.5 mg, 0.0790 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (64.8 mg, 0.119 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (23.9 μL, 0.237 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3d** (28.8 mg, 0.0330 mmol) with the imidate in toluene (1.20 mL) by activation with I_2 (27.0 mg, 0.119 mmol) provided the hexasaccharide **35ad** (46.0 mg, 0.0297 mmol, 90%, β/α=69:31). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate=60:40, 2.0 mL min^{-1}; Retention time: β-isomer=19.0 min, α-isomer=17.0 min). **β-isomer**: $[\alpha]_D^{22}$=−43.8 (c=0.825, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.07–7.31 (m, 22H), 6.96 (brs, 4H), 5.16 (s, 2H), 5.08 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 5.02 (brs, 1H), 4.96 (t, 1H, J=9.2 Hz, J=9.2 Hz), 4.90 (brs, 1H), 4.75–4.50 (m, 7H), 4.40–4.29 (m, 3H), 4.20 (m, 1H), 4.13 (m, 1H), 4.10 (m, 1H), 4.02 (q, 1H, J=6.3 Hz), 3.81–3.66 (m, 4H), 3.48 (ddd, 1H, J=12.1 Hz, J=4.4 Hz, J=8.2 Hz), 3.48 (ddd, 1H, J=12.1 Hz, J=4.4 Hz, J=8.2 Hz), 3.29 (m, 1H), 3.25–3.19 (m, 4H), 3.14 (brs, 1H), 2.78–2.62 (m, 4H), 2.50–2.43 (m, 2H), 2.30–2.25 (m, 2H), 2.19 (s, 3H), 2.04–1.41 (m, 12H), 1.32 (d, 3H, J=6.3 Hz), 1.24 (d, 3H, J=6.8 Hz), 1.14 (d, 3H, J=6.3 Hz), 1.07 (d, 3H, J=5.3 Hz), 1.02 (d, 3H, J=6.3 Hz), 0.96 (t, 2H, J=8.2 Hz), 0.65 (d, 3H, J=6.3 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=206.5, 172.3, 165.9, 152.9, 151.7, 138.6 135.7, 133.2, 132.9, 130.6, 130.4, 129.9, 129.1, 128.9, 128.2, 128.0, 127.8×2, 127.7, 127.6, 127.5, 127.3, 126.6, 126.1, 126.0, 125.8, 117.9, 117.3, 101.3, 99.9, 98.3, 96.9, 96.4, 93.5, 91.7, 82.8, 82.5, 79.0, 78.6, 77.7, 77.2, 76.7, 76.1, 75.5, 75.1, 73.6, 73.4, 72.1, 71.4, 70.9, 70.8, 70.6, 70.1, 69.8, 69.7, 66.0, 65.1, 60.3, 57.9, 38.0, 36.9, 36.8, 36.7, 36.6, 35.6, 29.8, 28.1, 24.1, 23.8, 22.2, 18.3, 18.1, 18.0, 17.9, 16.9, 16.7, 14.2, −1.45 ppm; IR (neat): $\tilde{\nu}$=3436, 1643, 1219, 772 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 1592.7221, found 1592.7222. **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.08–7.26 (m, 22H), 6.97 (brs, 4H), 5.17 (s, 2H), 5.08 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 5.01 (brs, 1H), 4.97 (t, 1H, J=9.2 Hz, J=9.2 Hz), 4.90 (brs, 2H), 4.75 (brs, 1H), 4.72–4.49 (m, 6H), 4.38 (d, 1H, J=14.0 Hz), 4.32 (t, 1H, J=9.2 Hz, J=9.2 Hz), 4.29 (d, 1H, J=14.0 Hz), 4.20 (q, 1H, J=5.8 Hz), 4.14 (m, 1H), 4.03 (q, 1H, J=6.8 Hz), 3.86–3.67 (m, 5H), 3.57–3.46 (m, 2H), 3.31–3.19 (m, 5H), 2.78–2.62 (m, 4H), 2.51–2.41 (m, 2H), 2.29 (m, 1H), 2.23–2.13 (s, 4H), 2.04–1.39 (m, 12H), 1.33 (d, 3H, J=5.8 Hz), 1.11–1.04 (m, 12H), 0.96 (t, 2H, J=8.2 Hz), 0.67 (d, 3H, J=5.8 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, $CDCl_3$): δ=206.5, 172.3, 165.9, 152.9, 151.8, 139.0, 135.5, 133.2, 132.9, 130.7, 130.3, 129.9, 129.1, 128.9, 128.2, 128.0, 127.7, 127.6, 127.4, 126.9, 126.2, 125.9, 117.8, 117.2, 99.8, 98.3, 96.7, 96.4, 93.5, 92.6, 91.7, 83.4, 82.6, 79.0, 77.2, 75.7, 75.1, 73.4, 72.1, 71.0, 70.6, 70.1, 69.8, 69.7, 68.6, 66.9, 66.4, 66.1, 65.1, 57.9, 38.0, 36.8, 36.6, 36.0, 35.5, 29.8, 29.7, 28.2, 23.8, 23.5, 22.2, 19.8, 18.4, 18.1, 17.9, 17.1, 17.0, −1.45 ppm; IR (neat): $\tilde{\nu}$=3019, 1714, 1216, 756 cm^{-1}.

35ba: According to the method for the synthesis of **35aa**, a solution of **5b** (82.8 mg, 0.100 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (82.1 mg, 0.150 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (30.0 μL, 0.300 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3a** (56.7 mg, 0.0650 mmol) with the imidate in toluene (2.00 mL) by activation with I_2 (38.1 mg, 0.150 mmol) provided the hexasaccharide **35ad** (69.0 mg, 0.0442 mmol, 67%, β/α=77:23). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate=60/40, 2.0 mL min^{-1}; Retention time: β-isomer=18.0 min, α-isomer=19.0 min). **β-isomer**: $[\alpha]_D^{15}$=−37.2 (c=0.725, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82–7.26 (m, 22), 6.97–6.90 (m, 4H), 5.15 (s, 2H), 5.04–5.01 (m, 2H), 4.95 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 4.77–4.62 (m, 8H), 4.59 (brs, 1H), 4.46–4.27 (m, 5H), 3.96 (q, 1H, J=6.8 Hz), 3.83 (ddd, 1H, J=12.1 Hz, J=5.3 Hz, J=10.2 Hz), 3.74 (t, 2H, J=8.2 Hz), 3.64 (ddd, 1H, J=11.6 Hz, J=5.3 Hz, J=8.2 Hz), 3.60–3.50 (m, 2H), 3.49–3.21 (m, 8H), 2.72–2.56 (m, 4H), 2.52–2.43 (m, 2H), 2.42–2.31 (m, 2H), 2.16 (s, 3H), 2.04–1.47 (m, 12H), 1.33 (d, 3H, J=5.8 Hz), 1.28–1.19 (m, 9H), 1.10 (d, 3H, J=6.8 Hz), 0.95 (t, 2H, J=8.2 Hz), 0.66 (d, 3H, J=6.8 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=206.4, 172.3, 152.8, 151.9, 138.8, 138.5, 135.5, 133.2, 132.9, 130.7, 129.2, 129.0, 128.9, 128.3, 128.2, 128.1, 127.7, 127.6, 127.5, 127.4, 126.7, 126.2, 126.0, 125.9, 117.7, 117.2, 101.4, 100.1, 100.0, 98.2, 97.0, 93.5, 91.9, 85.2, 83.2, 82.9, 82.8, 82.4, 79.7, 77.8, 77.4, 77.2, 76.0, 72.2, 71.8, 71.6, 71.2, 71.0, 70.2, 69.9, 69.7, 69.6, 69.1, 66.3, 66.0, 65.2, 60.3, 57.8, 57.2, 39.3, 37.9, 37.2, 36.9, 35.7, 29.8, 28.2, 24.2, 24.0, 23.9, 22.6, 21.0, 18.5, 18.3, 18.2, 18.1, 18.0, 17.5, 17.0, 16.6, 14.1, −1.47 ppm; IR (neat): $\tilde{\nu}$=2935, 1729, 1506, 1364, 1213, 1064, 1019, 987, 835, 754, 698 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 1578.7428, found 1578.7428. **α-isomer:** ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83–7.24 (m, 22H), 6.97–6.90 (m, 4H), 5.15 (s, 2H), 5.03–5.01 (m, 2H), 4.96–4.94 (m, 2H), 4.80–4.58 (m, 9H), 4.44–4.29 (m, 4H), 4.01 (q, 1H, J=6.8 Hz), 3.93 (ddd, 1H, J=10.6 Hz, J=4.8 Hz, J=8.7 Hz), 3.83 (ddd, 1H, J=11.1 Hz, J=4.8 Hz, J=8.7 Hz), 3.76–3.71 (m, 3H), 3.63 (ddd, 1H, J=12.1 Hz, J=5.3 Hz, J=8.2 Hz), 3.52 (m, 1H), 3.49 (brs, 1H), 3.43–3.33 (m, 4H), 3.30–3.21 (m, 2H), 2.72–2.56 (m, 4H), 2.52–2.40 (m, 3H), 2.24 (m, 1H), 2.16 (s, 3H), 2.04–1.42 (m, 12H), 1.33 (d, 3H, J=5.8 Hz), 1.26–1.14 (m, 12H), 0.95 (t, 2H, J=8.2 Hz), 0.66 (d, 3H, J=6.3 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, $CDCl_3$): δ=206.5, 172.4, 152.9, 151.9, 139.0, 138.6, 135.6, 133.2, 132.9, 130.7, 129.1, 128.9, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 127.3, 126.7, 126.2, 126.0, 125.9, 117.8, 117.2, (100.2, 100.0, 98.2, 97.1, 93.5, 92.8, 91.7, 83.1, 82.9, 79.7, 77.3, 77.2, 76.0, 72.2, 71.8, 71.2, 70.2, 70.0, 69.7, 68.8, 67.3, 66.6, 66.0, 65.2, 57.9, 38.0, 36.9, 35.6, 29.8, 28.2, 24.0, 23.5, 22.7, 18.5, 18.4, 18.1, 18.0, 17.4, 16.6, −1.45 ppm; IR (neat): $\tilde{\nu}$=3020, 1731, 1216, 1047, 758, 669 cm^{-1}.

35bb: According to the method for the synthesis of **35aa**, a solution of **5b** (54.7 mg, 0.0660 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (54.1 mg, 0.138 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (20.0 μL, 0.198 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3b** (39.1 mg, 0.0462 mmol) with the imidate in toluene (1.32 mL) by activation with I_2 (25.0 mg, 0.0990 mmol) provided the hexasaccharide **22ad** (66.5 mg, 0.0420 mmol, 93%, β/α=70:30). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate=60:40, 2.0 mL min^{-1}; Retention time: β-isomer=18.0 min, α-isomer=19.5 min). **β-isomer**: $[\alpha]_D^{21}$=−37.3 (c=1.48, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83–7.26 (m, 22H), 6.97–6.90 (m, 4H), 5.15 (s, 2H), 5.01 (brs, 2H), 4.95 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 4.81–4.59 (m, 11H), 4.30 (q, 1H, J=6.8 Hz), 4.22 (brd, 1H, J=9.7 Hz), 4.13 (m, 1H), 3.74 (t, 2H, J=8.2 Hz), 3.64 (ddd, 1H, J=11.6 Hz, J=5.3 Hz, J=8.2 Hz), 3.56–3.17 (m, 12H), 2.72–2.56 (m, 4H), 2.46–2.38 (m, 3H), 2.27 (m, 1H), 2.16 (s, 3H), 2.04–1.46 (m, 12H), 1.32–1.24 (m, 12H), 0.95 (t, 2H, J=8.2 Hz), 0.72 (d, 3H, J=6.8 Hz), 0.67 (d, 3H, J=6.8 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, $CDCl_3$): δ=206.5, 172.3, 152.8, 151.9, 138.7, 138.6, 138.5, 135.8, 135.5, 135.4, 133.2, 133.0, 132.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6×2, 127.5, 127.4, 126.7, 126.6, 126.5, 126.3, 126.2, 126.1, 126.0×2, 125.9×2, 125.8, 125.6, 117.7, 117.2, 101.4, 100.2, 100.1, 98.2, 97.0, 93.5, 82.3, 82.2, 79.7, 79.2, 78.9, 77.9, 77.7, 77.2, 76.1, 75.6, 72.4, 72.3, 72.0, 71.8, 71.7, 71.6, 71.4, 71.3×2, 71.2, 71.1, 70.9, 69.9, 66.2, 66.0, 65.2, 60.3, 37.9, 37.0, 36.4, 29.8, 28.2, 24.6, 24.2, 24.0, 22.6, 18.6, 18.5, 18.4, 18.3, 18.2, 18.0, 17.9, 16.8, 16.6, 14.2, −1.46 ppm; IR (neat): $\tilde{\nu}$=3019, 1721, 1506, 1366, 1216, 1063, 771, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 1546.7622, found 1546.7622. **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83–7.24 (m, 24H), 6.96–6.90 (m, 4H), 5.15 (s, 2H), 5.01 (brs, 2H), 4.95 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 4.92 (brs, 1H), 4.81–4.54 (m, 11H), 4.29 (q, 1H, J=6.3 Hz), 4.25 (q, 1H, J=6.8 Hz), 3.86 (ddd, 1H, J=11.1 Hz, J=5.3 Hz, J=9.2 Hz), 3.74 (t, 2H, J=8.2 Hz), 3.63 (ddd, 1H, J=11.6 Hz, J=3.4 Hz, J=8.2 Hz), 3.30 (brs, 1H), 3.58–3.20 (m, 10H), 2.74–2.56 (m, 4H), 2.46–2.38 (m, 3H), 2.21 (ddd, 1H, J=5.3 Hz, J=12.6 Hz, J=1.5 Hz), 2.16 (s, 3H), 2.01–1.44 (m, 12H), 1.31 (d, 3H, J=6.3 Hz), 1.26 (d, 3H, J=5.8 Hz), 1.20 (d, 3H, J=5.8 Hz), 1.09 (d, 3H, J=6.3 Hz), 0.95 (t, 2H, J=8.2 Hz), 0.75 (d, 3H, J=6.8 Hz), 0.65 (d, 3H, J=6.3 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=206.5, 172.4, 152.8, 151.9, 139.1, 138.7, 135.7, 135.6, 133.2, 132.9, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7×2, 127.5×2, 127.3, 126.8, 126.7, 126.2×2,

126.0, 125.9, 117.8, 117.2, 100.2, 100.0, 98.2, 97.0, 96.9, 93.5, 92.6, 83.0, 82.3, 79.7, 79.3, 77.6, 77.2, 75.8, 72.4, 72.3, 72.0, 71.4, 71.3, 71.1, 70.0, 68.6, 67.1, 66.6, 66.0, 65.2, 38.0, 37.1, 37.0, 36.9, 36.0, 29.8, 24.0, 23.6, 22.7, 19.8, 18.6, 18.5, 18.3, 18.1, 18.0, 17.2, 16.6, −1.45 ppm; IR (neat): $\tilde{\nu}$ = 3019, 1721, 1506, 1366, 1216, 1063, 771, 669 cm^{-1}

35bc: According to the method for the synthesis of **35aa**, a solution of **5b** (61.3 mg, 0.0740 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (60.7 mg, 0.111 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (22.5 μL, 0.222 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3c** (32.3 mg, 0.0340 mmol) with the imidate in toluene (1.50 mL) by activation with I_2 (28.2 mg, 0.111 mmol) provided the hexasaccharide **35bc** (42.3 mg, 0.0259 mmol, 76%, β/α = 70:30). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 20.0 min, α-isomer = 23.5 min). **β-isomer**: $[\alpha]_D^{17} = -45.8$ (c = 0.625, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19–7.26 (m, 21H), 6.97 (m, 4H), 5.16 (s, 2H), 5.07 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 5.00 (brs, 1H), 4.95 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 4.88 (brs, 1H), 4.78–4.59 (m, 7H), 4.31 (m, 1H), 4.29 (q, 1H, J = 6.8 Hz), 4.15–4.07 (m, 2H), 3.85 (q, 1H, J = 6.8 Hz), 3.77–3.66 (m, 4H), 3.56–3.21 (m, 12H), 2.72–2.57 (m, 4H), 2.48 (ddd, 1H, J = 5.3 Hz, J = 12.1 Hz, J = 1.5 Hz), 2.40 (ddd, 1H, J = 4.4 Hz, J = 12.6 Hz, J = 1.9 Hz), 2.33–2.30 (m, 2H), 2.16 (s, 3H), 2.04–1.41 (m, 12H), 1.31 (d, 3H, J = 6.3 Hz), 1.27–1.12 (m, 9H), 1.07 (d, 3H, J = 6.8 Hz), 0.96 (t, 2H, J = 8.2 Hz), 0.66 (d, 3H, J = 6.8 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.5, 172.4, 165.8, 153.0, 151.8, 147.2, 144.9, 138.8, 135.6, 133.2, 133.1, 133.0, 130.2, 129.8, 129.3, 128.3, 128.2, 128.1, 127.8, 127.7, 127.5, 126.8, 126.2, 126.1, 126.0, 124.0, 117.9, 117.3, 101.2, 100.1, 98.2, 97.1, 96.4, 93.5, 92.3, 85.9, 84.0, 82.4, 79.7, 77.6, 77.5, 77.2, 75.6, 75.0, 74.2, 72.3, 71.7, 71.2, 70.5, 70.2, 70.0, 69.9, 66.7, 66.1, 65.2, 52.4, 38.0, 37.2, 37.0, 36.7, 35.7, 29.8, 29.7, 29.6, 29.5, 28.2, 24.2, 24.0, 22.7, 18.6, 18.2, 18.1, 17.9, 17.8, 16.8, 16.6, 14.2, −1.44 ppm; IR (neat): $\tilde{\nu}$ = 3019, 1720, 1506, 1349, 1217, 1066, 772, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 1651.7228, found 1651.7229. **α-isomer:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20–7.23 (m, 21H), 6.97 (brs, 4H), 5.17 (s, 2H), 5.07 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 5.00 (brs, 1H), 4.96 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 4.89 (brs, 2H), 4.69 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 4.79–4.58 (m, 5H), 4.61 (brs, 1H), 4.30 (q, 1H, J = 6.3 Hz), 4.16–4.07 (m, 2H), 3.96 (q, 1H, J = 6.8 Hz), 3.96 (ddd, 1H, J = 11.1 Hz, J = 5.3 Hz, J = 8.7 Hz), 3.81–3.65 (m, 3H), 3.75 (t, 2H, J = 8.2 Hz), 3.55–3.43 (m, 2H), 3.40 (brs, 1H), 3.40–3.21 (m, 7H), 2.73–2.57 (m, 4H), 2.48 (ddd, 1H, J = 4.8 Hz, J = 11.1 Hz, J = 1.5 Hz), 2.42 (ddd, 1H, J = 4.3 Hz, J = 12.1 Hz, J = 1.5 Hz), 2.34 (ddd, 1H, J = 4.8 Hz, J = 12.1 Hz, J = 1.5 Hz), 2.21 (ddd, 1H, J = 5.3 Hz, J = 13.1 Hz, J = 1.5 Hz), 2.16 (s, 3H), 2.04–1.38 (m, 12H), 1.32 (d, 3H, J = 6.3 Hz), 1.25 (d, 3H, J = 5.8 Hz), 1.18 (d, 3H, J = 6.3 Hz), 1.14 (d, 3H, J = 6.8 Hz), 1.12 (d, 3H, J = 6.3 Hz), 0.96 (t, 2H, J = 8.2 Hz), 0.66 (d, 3H, J = 6.3 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, $CDCl_3$): δ = 206.6, 172.4, 165.8, 153.0, 151.8, 147.2, 144.8, 139.0, 135.5, 133.2, 133.1, 132.9, 130.2, 129.8, 129.3, 128.3, 128.2, 128.1, 127.8, 127.7, 127.4, 127.3, 126.7, 126.2, 126.0, 125.9, 124.1, 117.9, 117.3, 100.3, 98.1, 97.1, 96.4, 93.5, 93.0, 91.9, 83.7, 82.9, 79.7, 77.2, 76.0, 75.0, 74.2, 72.3, 72.2, 71.2, 70.5, 70.0, 69.9, 69.8, 68.9, 67.3, 67.0, 66.1, 65.2, 60.4, 52.4, 37.9, 36.9, 36.7, 35.8, 35.6, 29.8, 29.7, 29.4, 28.2, 24.0, 22.6, 19.7, 18.5, 18.1, 18.0, 17.9, 17.8, 17.1, 16.6, 14.2, −1.44 ppm; IR (neat): $\tilde{\nu}$ = 3019, 1720, 1506, 1349, 1217, 1066, 772, 669 cm^{-1}.

35bd: According to the method for the synthesis of **35aa**, a solution of **5b** (41.4 mg, 0.0500 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (41.0 mg, 0.0750 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (15.5 μL, 0.150 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3d** (29.8 mg, 0.0340 mmol) with the imidate in toluene (1.30 mL) by activation with I_2 (20.0 mg, 0.0750 mmol) provided the hexasaccharide **35bd** (47.7 mg, 0.0300 mmol, 88%, β/α = 65:35). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 19.0 min, α-isomer = 17.5 min). **β-isomer**: $[\alpha]_D^{16} = -55.9$ (c = 0.420, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07–7.22 (m, 24H), 6.96 (brs, 4H), 5.17 (s, 2H), 5.07 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 5.00 (brs, 1H), 4.96 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 4.89 (brs, 1H), 4.77–4.50 (m, 9H), 4.29 (q, 1H, J = 6.8 Hz), 4.19 (brd, 1H, J = 9.7 Hz), 4.14 (m, 1H), 4.08 (q, 1H, J = 6.8 Hz), 3.75 (t, 2H, J = 8.2 Hz), 3.70 (m, 1H), 3.53–3.43 (m, 3H), 3.36 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 3.25–3.15 (m, 5H), 3.14 (brs, 1H), 2.72–2.57 (m, 4H), 2.47 (ddd, 1H, J = 4.4 Hz, J = 11.6 Hz, J = 1.5 Hz), 2.39 (ddd, 1H, J = 4.8 Hz, J = 12.6 Hz, J = 1.5 Hz), 2.30–2.22 (m, 2H), 2.16 (s, 3H), 2.02–1.41 (m, 12H), 1.32 (d, 3H, J = 6.3 Hz), 1.25–1.06 (m, 9H), 0.96 (t, 2H, J = 8.2 Hz), 0.67–0.64 (m, 6H), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, $CDCl_3$): δ = 206.6, 172.4, 165.9, 152.9, 151.8, 138.7, 135.7, 135.5, 133.2, 132.9, 132.9, 130.3, 129.9, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.4, 126.7, 126.6, 126.2, 126.1 × 2, 126.0 × 2, 125.9, 117.8, 117.2, 101.4, 100.1, 98.2, 97.1, 96.9, 96.4, 93.5, 82.2, 79.7, 78.9, 77.9, 77.2, 76.1, 75.1, 73.3, 72.2, 72.1, 71.5, 71.1, 70.9, 70.5, 69.9, 66.1, 65.2, 37.9, 36.9, 36.8, 29.8, 28.2, 24.0, 22.6, 18.5, 18.3 × 2, 18.1, 17.9, 16.7, 16.6, −1.44 ppm; IR (neat): $\tilde{\nu}$ = 2933, 1720, 1506, 1366, 1016, 857, 756, 522 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 1578.7758, found 1578.7816. **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08–7.22 (m, 24H), 6.97 (brs, 4H), 5.17 (s, 2H), 5.08 (dd, 1H, J = 9.7 Hz, J = 1.9 Hz), 5.00 (brs, 1H), 4.97 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 4.90 (m, 2H), 4.77–4.50 (m, 6H), 4.63 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 4.59 (brs, 1H), 4.55 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 4.29 (q, 1H, J = 6.3 Hz), 4.20 (q, 1H, J = 6.3 Hz), 4.14 (m, 1H), 3.83 (ddd, 1H, J = 11.1 Hz, J = 5.3 Hz, J = 8.7 Hz), 3.75 (t, 2H, J = 8.2 Hz), 3.70 (m, 1H), 3.57–3.46 (m, 3H), 3.35 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 3.27 (brs, 1H), 3.25–3.17 (m, 4H), 2.73–2.57 (m, 4H), 2.48 (ddd, 1H, J = 4.8 Hz, J = 12.6 Hz, J = 1.9 Hz), 2.38 (ddd, 1H, J = 4.8 Hz, J = 12.6 Hz, J = 1.5 Hz), 2.28 (ddd, 1H, J = 4.8 Hz, J = 12.6 Hz, J = 1.5 Hz), 2.22–2.16 (m, 4H), 2.04–1.39 (m, 12H), 1.33 (d, 3H, J = 6.3 Hz), 1.20–1.06 (m, 9H), 0.96 (t, 2H, J = 8.2 Hz), 0.69 (d, 3H, J = 6.3 Hz), 0.65 (d, 3H, J = 6.3 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, CD_2Cl_2): δ = 206.8, 172.6, 166.2, 153.3, 152.2, 139.8, 136.4, 136.3, 133.6, 133.3, 130.8, 130.1, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.5, 127.1, 127.0, 126.7, 126.6, 126.5, 126.4, 126.2, 118.0, 117.6, 100.1, 98.4, 97.5, 97.4, 96.9, 93.9, 92.9, 83.6, 80.4, 79.8, 77.9, 77.6, 75.8, 75.5, 73.8, 72.5, 72.4, 71.3, 71.2, 70.8, 70.2, 69.8, 69.2, 67.5, 66.8, 66.4, 65.5, 54.4, 53.6, 38.2, 37.4, 37.1, 37.0, 36.4, 29.9, 28.5, 24.4, 24.0, 23.0, 20.2, 18.6, 18.5, 18.3, 18.2, 18.1, 17.3, 16.8, −1.43 ppm; IR (neat): $\tilde{\nu}$ = 2933, 1720, 1506, 1366, 1016, 857, 756, 522 cm^{-1}.

35ca: According to the method for the synthesis of **35aa**, a solution of **5c** (44.2 mg, 0.0483 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (39.6 mg, 0.0725 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (14.5 μL, 0.145 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3a** (39.8 mg, 0.0462 mmol) with the imidate in toluene (1.30 mL) by activation with I_2 (18.4 mg, 0.0725 mmol) provided the hexasaccharide **35ca** (66.2 mg, 0.0401 mmol, 86%, β/α = 90:10). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 21.0 min, α-isomer = 23.5 min). $[\alpha]_D^{16} = -58.5$ (c = 1.56, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20–7.29 (m, 19H), 6.96 (brs, 4H), 5.15 (s, 2H), 5.05 (brs, 1H), 4.95 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 4.91 (brs, 1H), 4.86 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 4.76 (dd, 1H, J = 9.2 Hz, J = 1.5 Hz), 4.69 (brs, 2H), 4.67 (brs, 1H), 4.55 (brd, 1H, J = 8.7 Hz), 4.50 (brd, 1H, J = 9.2 Hz), 4.44 (d, 1H, J = 13.5 Hz), 4.36 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 4.33 (d, 1H, J = 13.5 Hz), 4.14 (t, 1H, H-E4, $J_{4,3}$ = 9.2 Hz, J = 9.2 Hz), 4.04–3.95 (m, 3H), 3.84 (ddd, 1H, J = 11.1 Hz, J = 4.8 Hz, J = 9.2 Hz), 3.77–3.71 (m, 3H), 3.63 (ddd, 1H, J = 12.1 Hz, J = 5.3 Hz, J = 8.7 Hz), 3.51–3.23 (m, 11H), 2.72–2.56 (m, 4H), 2.53–2.43 (m, 2H), 2.37–2.28 (dd, 2H), 2.19 (s, 3H), 2.07–1.37 (m, 12H), 1.33 (d, 3H, J = 5.8 Hz), 1.21 (d, 3H, J = 6.3 Hz), 1.20 (d, 3H, J = 6.3 Hz), 1.13 (d, 3H, J = 6.8 Hz), 1.10 (d, 3H, J = 6.3 Hz), 1.05 (d, 3H, J = 6.3 Hz), 0.95 (t, 2H, J = 8.2 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, $CDCl_3$): δ = 206.5, 172.2, 165.8, 152.8, 151.9, 147.2, 144.7, 138.5, 133.0, 130.7, 130.3, 129.7, 129.3, 129.1, 128.9, 128.3, 128.2, 127.7, 127.6, 127.4, 124.1, 117.7, 117.2, 101.2, 100.0, 98.2, 96.3, 93.5, 91.9, 91.8, 83.5, 83.2, 82.8, 77.3, 77.2, 76.3, 75.2, 74.6, 71.8, 71.2, 70.1, 70.0, 69.7, 69.3, 66.2, 66.0 × 2, 65.4, 57.9, 52.5, 37.9, 36.9, 35.7, 35.5, 29.8, 29.6, 29.4, 28.1, 24.1, 24.0, 23.9, 22.2, 18.4, 18.0, 17.9, 17.8, 17.0, 16.8, −1.46 ppm; IR (neat): $\tilde{\nu}$ = 3020, 1723, 1506, 1349, 1216, 1087, 1019, 756, 668 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 1665.6691, found: 1665.6711.

35cb: According to the method for the synthesis of **35aa**, a solution of **5c** (43.0 mg, 0.0470 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (38.6 mg, 0.0705 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (14.5 μL, 0.145 mmol) in

CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3b** (36.2 mg, 0.0420 mmol) with the imidate in toluene (1.30 mL) by activation with I_2 (17.9 mg, 0.0705 mmol) provided the hexasaccharide **35cb** (54.6 mg, 0.0330 mmol, 80%, β/α = >90:10). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 17.0 min). $[\alpha]_D^{21} = -51.5$ ($c = 0.560$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.20$–7.24 (m, 21H), 6.94 (brs, 4H), 5.15 (s, 2H), 5.02 (brs, 1H), 4.95 (dd, 1H, $J = 9.7$ Hz, $J = 1.9$ Hz), 4.90 (brs, 1H), 4.88–4.62 (m, 6H), 4.65 (brs, 1H), 4.51 (dd, 1H, $J = 9.7$ Hz, $J = 1.5$ Hz), 4.35 (brd, 1H, $J = 9.2$ Hz), 4.17–4.09 (m, 2H), 3.99 (q, 1H, $J = 6.3$ Hz), 3.94 (ddd, 1H, $J = 12.1$ Hz, $J = 5.3$ Hz, $J = 9.2$ Hz), 3.74 (t, 2H, $J = 8.2$ Hz), 3.71 (m, 1H), 3.64 (ddd, 1H, $J = 11.6$ Hz, $J = 5.3$ Hz, $J = 8.7$ Hz), 3.54 (ddd, 1H, $J = 11.1$ Hz, $J = 4.4$ Hz, $J = 8.7$ Hz), 3.43–3.23 (m, 11H), 2.77–2.58 (m, 4H), 2.46–2.41 (m, 2H), 2.40–2.19 (m, 2H), 2.18 (s, 3H), 2.04–1.30 (m, 12H), 1.31 (d, 3H, $J = 5.8$ Hz), 1.26 (d, 3H, $J = 7.3$ Hz), 1.23 (d, 3H, $J = 6.3$ Hz), 1.10 (d, 3H, $J = 6.3$ Hz), 1.04 (d, 3H, $J = 6.3$ Hz), 0.95 (t, 2H, $J = 8.2$ Hz), 0.74 (d, 3H, $J = 6.3$ Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 206.5$, 172.2, 165.8, 152.8, 151.9, 147.2, 144.7, 138.0, 135.8, 133.2, 133.0, 132.9, 130.3, 129.7, 129.2, 128.3, 128.2, 128.0, 127.8, 127.7, 127.5, 126.6, 126.1, 125.9, 124.1, 117.7, 117.2, 101.2, 100.2, 98.2, 97.1, 96.2, 93.5, 91.8, 83.5, 82.3, 79.2, 77.6, 77.2, 76.3, 75.2, 74.4, 72.4, 71.9, 71.3, 70.0, 69.7, 69.3, 66.1, 66.0, 65.4, 60.3, 52.5, 37.9, 37.1, 37.0, 36.7, 35.5, 29.8, 29.6, 29.4, 28.1, 24.7, 24.1, 23.9, 22.2, 18.6, 18.3, 18.0, 17.9, 16.8, 16.7, 14.2, −1.46 ppm; IR (neat): $\tilde{\nu} = 3019$, 1720, 1506, 1349, 1216, 1062, 759, 668 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 1651.7228, found: 1651.7247.

35cc: According to the method for the synthesis of **35aa**, a solution of **5c** (45.7 mg, 0.0500 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (41.0 mg, 0.0750 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (15.0 μL, 0.150 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3c** (32.5 mg, 0.0340 mmol) with the imidate in toluene (1.20 mL) by activation with I_2 (19.0 mg, 0.0750 mmol) provided the hexasaccharide **35cc** (41.6 mg, 0.0241 mmol, 71%, β/α = >90:10). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 24.5 min). $[\alpha]_D^{17} = -56.8$ ($c = 1.20$, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2); 8.16–7.31 (m, 18H), 6.94 (brs, 4H), 5.14 (brs, 2H), 5.07 (dd, 1H, $J = 9.7$ Hz, $J = 1.9$ Hz), 4.91–4.85 (m, 3H), 4.77 (t, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 4.62–4.55 (m, 3H), 4.43 (dd, 1H, $J = 9.7$ Hz, $J = 1.5$ Hz), 4.12 (m, 1H), 4.10 (t, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 4.10 (t, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 4.02–3.93 (m, 2H), 3.85 (q, 1H, $J = 6.3$ Hz), 3.80–3.62 (m, 3H), 3.73 (t, 2H, $J = 8.2$ Hz), 3.55–3.21 (m, 12H), 2.71–2.53 (m, 4H), 2.48 (ddd, 1H, $J = 5.3$ Hz, $J = 12.5$ Hz, $J = 1.9$ Hz), 2.35–2.28 (m, 3H), 2.13 (s, 3H), 2.00–1.34 (m, 12H), 1.26 (d, 3H, $J = 6.3$ Hz), 1.17 (d, 3H, $J = 6.3$ Hz), 1.12–1.08 (m, 6H), 1.05 (d, 3H, $J = 6.3$ Hz), 1.00 (d, 3H, $J = 6.3$ Hz), 0.93 (t, 2H, $J = 8.2$ Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, CD_2Cl_2): $\delta = 206.8$, 172.5, 166.1, 166.0, 153.3, 152.1, 147.5, 147.4, 145.6, 145.5, 133.4, 133.3, 130.8, 130.7, 130.1, 129.8, 129.7, 128.7, 128.6, 124.3, 124.2, 118.1, 117.7, 101.4, 98.3, 96.9×2, 93.9, 92.6, 92.2, 84.2, 83.8, 77.9, 76.4, 75.6, 75.3, 74.9, 74.5, 70.8, 70.5×2, 70.4, 70.3, 70.2, 69.6, 67.0, 66.4, 65.7, 54.6, 54.4, 54.2, 54.0, 53.8, 53.6, 53.4, 53.0, 52.8, 52.7, 38.2, 37.3, 37.1, 36.1, 35.9, 29.9, 29.8, 28.5, 24.6, 24.5, 24.2, 22.6, 18.3, 18.1, 18.0×2, 16.9, 16.9, −1.43 ppm; IR (neat): $\tilde{\nu} =$ 3020.2, 1728.7, 1505.9, 1349.2, 1216.0, 1086.7, 770.2, 669.3 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 1738.6491, found: 1738.6481

35cd: According to the method for the synthesis of **35aa**, a solution of **5c** (33.8 mg, 0.0370 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (30.4 mg, 0.0555 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (11.0 μL, 0.111 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3d** (26.0 mg, 0.0300 mmol) with the imidate in toluene (1.20 mL) by activation with I_2 (14.0 mg, 0.0555 mmol) provided the hexasaccharide **35cd** (35.5 mg, 0.0215 mmol, 72%, β/α = >90:10). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 20.0 min). $[\alpha]_D^{20} = -69.7$ ($c = 0.230$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.20$–7.35 (m, 21H), 6.96 (brs, 4H), 5.16 (s, 2H), 5.08 (dd, 1H, $J = 9.7$ Hz, $J = 1.5$ Hz), 4.96 (t, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 4.90 (brs, 2H), 4.82 (t, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 4.71 (d, 1H, $J = 11.6$ Hz), 4.66 (brs, 1H), 4.56–4.50 (m, 3H), 4.33 (dd, 1H, $J = 9.7$ Hz, $J = 1.5$ Hz), 4.17–4.09 (m, 3H), 3.99 (q, 1H, $J = 6.3$ Hz), 3.92 (ddd, 1H, $J = 12.6$ Hz, $J = 5.8$ Hz, $J = 9.2$ Hz), 3.77–3.67 (m, 4H), 3.52–3.19 (m, 10H), 2.77–2.58 (m, 4H), 2.48 (m, 1H), 2.30–2.23 (m, 3H), 2.19 (s, 3H), 2.04–1.46 (m, 12H), 1.33–1.03 (m, 15H), 0.96 (t, 2H, $J = 8.2$ Hz), 0.67 (d, 3H, $J = 6.3$ Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 206.5$, 172.2, 165.9, 153.0, 151.9, 147.3, 144.7, 135.8, 135.3, 133.2, 132.9, 130.3, 129.9, 129.8, 129.3, 128.4, 128.2, 128.0, 127.8, 127.6, 126.6, 126.5, 126.2, 126.1, 126.0, 125.8, 125.6, 124.1, 117.9, 117.3, 101.2, 98.3, 96.9, 96.5, 96.2, 93.5, 91.9, 83.5, 79.0, 78.6, 77.2, 76.3, 75.5, 75.3, 75.2, 74.4, 73.6, 73.4, 72.1, 71.5, 70.9, 70.6, 70.1, 69.8, 69.4, 66.0, 65.4, 60.3, 52.5, 37.9, 36.7, 36.0, 35.6, 29.8, 29.4, 28.1, 24.7, 24.1, 23.9, 22.2, 18.1, 17.9, 17.8, 16.8, 14.2, −1.45 ppm; IR (neat): $\tilde{\nu} = 3020$, 1725, 1506, 1350, 1216, 1064, 1017, 771, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 1665.7021, found: 1665.7079.

35da: According to the method for the synthesis of **35aa**, a solution of **5d** (61.1 mg, 0.0725 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (59.5 mg, 0.109 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (22.0 μL, 0.218 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3a** (43.4 mg, 0.0500 mmol) with the imidate in toluene (1.46 mL) by activation with I_2 (27.8 mg, 0.109 mmol) provided the hexasaccharide **35da** (71.1 mg, 0.0451 mmol, 90%, β/α = 90:10). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 18.0 min, α-isomer = 19.0 min). $[\alpha]_D^{22} = -51.9$ ($c = 0.825$, $CHCl_3$) ; ^{1}H NMR (400 MHz, $CDCl_3$) 8.05–7.26 (m, 22H), 6.97–6.91 (m, 4H), 5.15 (s, 2H), 5.05 (brs, 1H), 4.96 (dd, 1H, $J = 9.7$ Hz, $J = 1.9$ Hz), 4.90 (brs, 1H), 4.87 (t, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 4.76 (brd, 1H, $J = 9.2$ Hz), 4.56 (brs, 1H), 4.71–4.49 (m, 4H), 4.51 (m, 1H), 4.50 (m, 1H), 4.44 (d, 1H, $J = 13.5$ Hz), 4.36 (t, 1H, $J = 9.2$ Hz, $J = 9.2$ Hz), 4.34 (d, 1H, $J = 13.5$ Hz), 4.26 (q, 1H, $J = 6.3$ Hz), 4.05–3.97 (m, 2H), 3.84 (ddd, 1H, $J = 12.1$ Hz, $J = 5.3$ Hz, $J = 9.2$ Hz), 3.74 (t, 2H, $J = 8.2$ Hz), 3.63 (ddd, 1H, $J = 12.6$ Hz, $J = 5.3$ Hz, $J = 8.2$ Hz), 3.52–3.34 (m, 6H), 3.20–3.12 (m, 2H), 2.72–2.56 (m, 4H), 2.53–2.44 (m, 2H), 2.35 (dd, 1H, $J = 5.3$ Hz, $J = 12.6$ Hz, $J = 1.9$ Hz), 2.27 (dd, 1H, $J = 5.3$ Hz, $J = 12.1$ Hz, $J = 1.9$ Hz), 2.15 (s, 3H), 2.07–1.47 (m, 12H), 1.34–1.20 (m, 9H), 1.13 (d, 3H, $J = 6.3$ Hz), 1.06 (d, 3H, $J = 6.3$ Hz), 0.95 (t, 2H, $J = 8.2$ Hz), 0.61 (d, 3H, $J = 6.3$ Hz), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 206.4$, 172.3, 165.9, 152.9, 151.9, 138.6, 135.4, 133.2, 132.9, 132.8, 130.7, 130.5, 129.8, 129.2, 129.1, 128.9, 128.3, 128.1, 127.8, 127.6, 127.5, 127.4, 126.8, 126.1, 125.9, 117.8, 117.2, 101.3, 100.0, 98.2, 96.9, 96.4, 93.5, 92.0, 83.2, 82.8, 79.5, 77.2, 76.2, 75.3, 73.9, 71.9, 71.8, 71.2, 70.7, 70.2, 69.9, 69.8, 66.3, 66.0, 65.1, 57.9, 57.2, 37.9, 37.0, 36.9, 36.5, 35.7, 29.8, 28.2, 24.2, 24.0, 23.9, 22.6, 18.4, 18.3, 18.0, 17.8, 17.1, 16.5, −1.46; IR (neat): $\tilde{\nu} = 3019$, 1720, 1506, 1364, 1217, 1066, 1018, 770, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 1592.7221, found 1592.7217.

35db: According to the method for the synthesis of **35aa**, a solution of **5d** (81.2 mg, 0.149 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (81.2 mg, 0.149 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (24.0 μL, 0.297 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3a** (44.4 mg, 0.0520 mmol) with the imidate in toluene (2.00 mL) by activation with I_2 (37.7 mg, 0.0149 mmol) provided the hexasaccharide **35db** (66.4 mg, 0.0425 mmol, 82%, β/α = 85:15). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 20.0 min, α-isomer = 23.5 min). **β-isomer**: $[\alpha]_D^{21} = -63.1$ ($c = 1.65$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.05$–7.26 (m, 24H), 6.97–6.90 (m, 4H), 5.15 (brs, 2H), 5.03 (brs, 1H), 4.95 (dd, 1H, $J = 9.7$ Hz, $J = 1.5$ Hz), 4.90 (brs, 1H), 4.89–4.63 (m, 8H), 4.56 (brs, 1H), 4.51–4.46 (m, 2H), 4.36 (brd, 1H, $J = 8.7$ Hz), 4.26 (q, 1H, $J = 6.8$ Hz), 4.16 (q, 1H, $J = 6.3$ Hz), 3.97 (ddd, 1H, $J = 12.6$ Hz, $J = 5.3$ Hz, $J = 10.1$ Hz), 3.75 (t, 2H, $J = 8.2$ Hz), 3.64 (ddd, 1H, $J = 11.6$ Hz, $J = 5.3$ Hz, $J = 8.2$ Hz), 3.55 (ddd, 1H, $J = 11.6$ Hz, $J = 4.4$ Hz, $J = 8.7$ Hz), 3.48–3.33 (m, 4H), 3.29–3.24 (m, 2H), 3.18–3.14 (m, 2H), 2.71–2.56 (m, 4H), 2.47–2.38 (m, 2H), 2.31–2.26 (m, 2H), 2.15 (s, 3H), 2.04–1.47 (m, 12H), 1.33–1.23 (m, 9H), 1.05 (d, 3H, $J = 5.3$ Hz), 0.96 (t, 2H, $J = 8.2$ Hz), 0.75 (d, 3H, $J = 6.3$ Hz), 0.60 (d, 3H, $J = 6.8$ Hz), 0.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 206.5$, 172.3, 165.9, 152.8, 151.9, 138.6, 135.9, 135.4, 133.3, 133.2, 132.9, 132.8, 130.5, 129.8,

128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 126.8, 126.6, 126.3, 126.1, 125.9, 117.4, 117.2, 101.3, 100.2, 98.2, 97.1, 96.9, 96.3, 93.5, 82.3, 79.5, 79.2, 77.7, 77.4, 77.2, 76.2, 75.4, 73.8, 72.4, 71.9, 71.8, 70.7, 70.1, 69.9, 66.2, 66.0, 65.1, 60.3, 37.9, 37.1, 37.0, 36.8, 36.5, 29.8, 28.2, 24.7, 24.2, 23.9, 22.6, 21.0, 18.6, 18.3, 18.0, 17.9, 16.8, 16.5, 14.2, −1.46 ppm; IR (neat): $\tilde{\nu}$ = 2933, 1720, 1506, 1366, 1016, 857, 756, 522 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 1578.7758, found 1578.7816. **α-isomer**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–7.26 (m, 24H), 6.97–6.91 (m, 4H), 5.15 (brs, 2H), 5.03 (brs, 1H), 4.97 (brs, 1H), 4.96 (dd, 1H, J = 9.7 Hz, J = 1.9 Hz), 4.85 (brs, 1H), 4.55 (brs, 1H), 4.44 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 4.87–4.50 (m, 8H), 4.29 (q, 1H, J = 6.3 Hz), 4.27–4.18 (m, 2H), 3.74 (t, 2H, J = 8.2 Hz), 3.74 (m, 1H), 3.67 (ddd, 1H, J = 12.1 Hz, J = 5.3 Hz, J = 8.2 Hz), 3.56 (ddd, 1H, J = 11.1 Hz, J = 4.9 Hz, J = 8.7 Hz), 3.47–3.26 (m, 6H), 3.15–3.09 (m, 2H), 2.70–2.55 (m, 4H), 2.48–2.40 (m, 2H), 2.24 (ddd, 1H, J = 4.8 Hz, J = 11.1 Hz, J = 1.5 Hz), 2.19–2.14 (m, 4H), 1.95–1.48 (m, 12H), 1.32 (d, 3H, J = 5.8 Hz), 1.27 (d, 3H, J = 5.8 Hz), 1.06 (d, 3H, J = 6.3 Hz), 0.95 (t, 2H, J = 8.2 Hz), 0.91 (d, 3H, J = 6.3 Hz), 0.78 (d, 3H, J = 6.3 Hz), 0.58 (d, 3H, J = 6.8 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, $CDCl_3$): δ = 206.5, 172.4, 152.8, 151.9, 138.6, 135.6, 135.5, 133.2, 133.1, 132.9, 132.8, 132.7, 130.5, 129.9, 128.3, 128.1, 127.8, 127.7, 127.6, 127.5, 126.9, 126.7, 126.2, 126.1, 126.1, 126.0, 125.9, 117.7, 117.2, 100.2, 98.2, 97.3, 96.9 × 2, 93.5, 93.0, 82.3, 79.5, 79.2, 77.2, 72.9, 72.4, 72.0, 71.7, 71.5, 71.3, 70.8, 70.7, 70.0, 69.3, 66.4, 66.3, 66.0, 65.1, 37.9, 37.1, 37.0, 36.9, 36.3, 29.8, 23.9, 22.6, 18.7, 18.4, 18.1, 18.0, 17.5, 17.1, 16.5, −1.45 ppm; IR (neat): $\tilde{\nu}$ = 3020, 1728, 1375, 1216, 1064, 756, 669 cm^{-1}.

35dc: According to the method for the synthesis of **35aa**, a solution of **5d** (65.7 mg, 0.0780 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (64.0 mg, 0.117 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (23.5 μL, 0.234 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3c** (33.0 mg, 0.0350 mmol) with the imidate in toluene (1.56 mL) by activation with I_2 (30.0 mg, 0.117 mmol) provided the hexasaccharide **35dc** (46.0 mg, 0.0270 mmol, 79%, β/α = > 90:10). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 18.5 min). $[\alpha]_D^{21}$ = −61.7 (c = 1.39, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19–7.37 (m, 21H), 6.97 (brs, 4H), 5.16 (brs, 2H), 5.07 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 4.96 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 4.89 (brs, 2H), 4.86 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 4.69 (d, 1H, J = 11.6 Hz), 4.60 (brd, 1H, J = 9.7 Hz), 4.56 (brs, 1H), 4.50 (d, 1H, J = 11.6 Hz), 4.49 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 4.45 (brd, 1H, J = 9.7 Hz), 4.26 (q, 1H, J = 6.3 Hz), 4.14 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 4.12 (m, 1H), 4.00 (ddd, 1H, J = 12.6 Hz, J = 4.8 Hz, J = 9.2 Hz), 3.88 (q, 1H, J = 4.8 Hz), 3.75 (t, 2H, J = 8.2 Hz), 3.77–3.65 (m, 2H), 3.54–3.46 (m, 3H), 3.40–3.33 (m, 2H), 3.29–3.16 (m, 5H), 2.71–2.56 (m, 4H), 2.47 (m, 1H), 2.33–2.25 (m, 3H), 2.15 (s, 3H), 2.03–1.42 (m, 12H), 1.32 (d, 3H, J = 6.3 Hz), 1.22 (d, 3H, J = 6.3 Hz), 1.13 (d, 3H, J = 6.3 Hz), 1.09 (d, 3H, J = 6.8 Hz), 1.05 (d, 3H, J = 4.8 Hz), 0.96 (t, 2H, J = 8.2 Hz), 0.61 (d, 3H, J = 6.3 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, $CDCl_3$): δ = 206.6, 172.3, 165.9, 165.7, 153.0, 151.7, 147.1, 144.9, 135.4, 133.2, 133.1, 133.0, 132.9, 132.8, 130.4, 130.1, 129.8, 129.7, 129.3, 128.3, 128.2, 128.1, 127.8, 127.7, 126.8, 126.1, 126.0, 125.9, 124.0, 117.8, 117.2, 101.2, 98.1, 96.9, 96.4, 93.4, 92.4, 83.9, 79.5, 77.2, 52.4, 37.9, 37.0, 36.7, 36.5, 35.7, 29.8, 29.6, 29.4, 28.1, 24.2, 24.1, 23.9, 22.6, 18.2, 18.0, 17.9, 17.8, 16.8, 16.5, −1.46 ppm; IR (neat): $\tilde{\nu}$ = 3020, 1722, 1349, 1216, 1018, 757, 668 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 1665.7021, found 1665.7061.

35dd: According to the method for the synthesis of **35aa**, a solution of **5d** (53.1 mg, 0.0630 mmol) in H_2O (0.100 mL) and CH_3CN (1.00 mL) was treated with CAN (51.7 mg, 0.0945 mmol) to provide a hemiacetal. The hemiacetal was treated with trichloroacetonitrile (20.0 μL, 0.189 mmol) in CH_2Cl_2 (1.00 mL) to provide imidate. Glycosylation of acceptor **3d** (33.2 mg, 0.0380 mmol) with the imidate in toluene (1.20 mL) by activation with I_2 (24.0 mg, 0.0945 mmol) provided the hexasaccharide **35dd** (56.2 mg, 0.0352 mmol, 93%, β/α = 83:17). The β,α isomers were separated by HPLC (Senshu Pak Silica-3301-N, Eluent: Hexane/Ethyl acetate = 60:40, 2.0 mL min^{-1}; Retention time: β-isomer = 18.0 min, α-isomer = 19.0 min). $[\alpha]_D^{22}$ = −71.5 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08–7.35 (m, 24H), 6.97 (brs, 4H), 5.17 (s, 2H), 5.08 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 4.97 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 4.91–4.89 (brs, 2H), 4.84 (t, 1H, J = 9.2 Hz, J = 9.2 Hz), 4.73–4.44 (m, 7H), 4.33 (dd, 1H, J = 9.7 Hz, J = 1.5 Hz), 4.25 (q, 1H, J = 6.8 Hz), 4.18–4.09 (m, 2H), 3.95 (ddd, 1H, J = 12.1 Hz, J = 5.3 Hz, J = 9.2 Hz), 3.75 (t, 2H, J = 8.2 Hz), 3.70 (m, 1H), 3.53–3.42 (m, 3H), 3.23–3.10 (m, 5H), 2.72–2.56 (m, 4H), 2.48 (ddd, 1H, J = 5.8 Hz, J = 12.6 Hz, J = 1.5 Hz), 2.30–2.21 (m, 3H), 2.15 (s, 3H), 2.04–1.44 (m, 12H), 1.33 (d, 3H, J = 5.8 Hz), 1.23 (d, 3H, J = 6.3 Hz), 1.08 (d, 3H, J = 5.3 Hz), 1.04 (d, 3H, J = 5.3 Hz), 0.96 (t, 2H, J = 8.2 Hz), 0.67 (d, 3H, J = 6.8 Hz), 0.59 (d, 3H, J = 6.8 Hz), 0.00 ppm (s, 9H); ^{13}C NMR (68.7 MHz, $CDCl_3$): δ = 206.5, 172.3, 165.9, 152.9, 151.8, 135.7, 135.4, 133.2, 133.1, 132.9 × 2, 132.8, 130.4, 130.3, 129.8, 129.8, 128.2, 128.1 × 2, 128.0, 127.8, 127.7, 126.8, 126.6, 126.1 × 2, 126.0, 125.9, 125.8, 117.8, 117.2, 101.3, 98.2, 97.0, 96.9, 96.4, 96.3, 93.5, 79.5, 79.0, 77.2, 76.2, 75.4, 75.1, 73.8, 73.4, 72.1, 71.9, 70.9, 70.7, 70.5, 70.1, 69.9, 66.1, 66.0, 65.1, 60.3, 37.9, 36.8, 36.7, 36.6, 36.5, 29.8, 28.2, 24.7, 24.1, 23.9, 22.6, 18.3, 18.2, 18.0, 17.9, 17.8, 16.8, 16.5, 14.2, −1.46 ppm; IR (neat): $\tilde{\nu}$ = 2933, 1702, 1506, 1366, 1016, 857, 756, 522 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 1572.7415, found 1572.7415.

2aa: To a stirred solution of the hexasaccharides **35aa** (8.13 mg, 5.16 μmol) in THF/MeOH (1:1 2 mL) was added a catalytic amount of sodium methoxide at room temperature under argon. After stirring at 50 °C for 24 h, the reaction mixture was poured into water. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. After short pass chromatography, the residue was used for the next reaction without further purification. To a stirred solution of the residue in HMPA (103 μL) was added a 1.00 M THF solution of tetrabutylammonium fluoride (15.5 μL, 15.5 μM) at room temperature. After microwave irradiation (300 W, 100 °C, 30 min) reaction, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was used for the next reaction without further purification. To a stirred solution of the residue in THF (1.00 mL) was added a large amount of liq. NH_3 (5.00 mL) and Na (50.0 mg) at −78 °C. After stirring at the same temperature for 1 h, the reaction mixture was quenched by methanol, and poured into brine. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with 95:5 chloroform/methanol to give hexasaccharide **2aa** (3.10 mg, 3.61 μmol, 3 steps 70%). $[\alpha]_D^{27}$ = −54.5 (c = 0.155, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.89 (d, 2H, J = 8.7 Hz), 6.74 (d, 2H, J = 8.7 Hz), 5.03–4.94 (m, 4H), 4.55–4.48 (m. 5H), 4.38 (brs, 1H), 4.26 (brs, 1H), 4.12 (q, 1H, J = 6.8 Hz), 4.07 (q, 1H, J = 6.8 Hz), 3.68–3.34 (m, 7H), 3.62 (brs, 1H), 3.54 (brs, 1H), 3.30 (m, 1H), 3.13–3.03 (m, 3H), 2.97 (dd, 1H, J = 9.7 Hz, J = 9.7 Hz), 2.37 (ddd, 1H, J = 5.3 Hz, J = 12.5 Hz, J = 1.9 Hz), 2.28–2.24 (m, 3H), 2.08–1.52 (m, 12H), 1.37–1.15 ppm (m, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 151.2, 151.1, 118.0, 115.8, (101.4, 100.9 × 2, 98.3, 97.8, 97.5, 88.5, 88.1, 80.5, 80.3, 75.9, 75.3, 72.3, 72.2, 70.6, 70.4, 69.6, 69.4, 67.7, 67.1, 38.5, 38.4, 37.1, 37.0, 29.7, 25.6, 25.1, 24.5, 17.7, 16.8, 16.7 ppm; IR (neat): $\tilde{\nu}$ = 3417, 3020, 2400, 1510, 1216, 770, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4596.

2ab: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35ab** (8.61 mg, 5.51 μmol) in THF/MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1 M THF solution of TBAF (16.5 μL, 16.5 μmol) in HMPA (110 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2ab** (2.60 mg, 3.03 μmol, 3 steps 55%). $[\alpha]_D^{23}$ = −48.1 (c = 0.130, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.85 (d, 2H, J = 8.7 Hz), 6.71 (d, 2H, J = 8.7 Hz), 5.00–4.80 (m, 5H), 4.52–4.45 (m. 5H), 4.22 (brs, 1H), 4.12–4.04 (m, 2H), 3.66–3.23 (m, 8H), 3.59 (brs, 1H), 3.51 (brs, 1H), 3.09–2.92 (m, 4H), 2.34 (m, 1H), 2.27–2.20 (m, 3H), 2.05–1.52 (m, 12H), 1.33–1.13 ppm (m, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 152.3, 151.1, 118.3, 116.2, 101.7, 101.5, 101.3, 100.2, 98.7, 97.9, 88.8, 88.5, 88.3, 80.6, 76.1, 75.7, 72.6, 71.2, 70.9, 70.8, 70.3, 69.9, 69.8, 68.4, 68.1, 67.4, 38.9, 38.7, 38.6, 37.3, 37.0, 36.9, 30.1, 25.9, 25.5, 24.7, 18.1, 17.9, 17.1, 17.0 ppm; IR (neat): $\tilde{\nu}$ = 3400, 3019, 2400, 1509, 1218, 772, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4591.

2ac: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35ac** (16.0 mg, 9.82 μmol) in THF-MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1 M THF solution of TBAF (16.5 μL, 16.5 μmol) in HMPA (196 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2ac** (3.80 mg, 4.42 μmol, 3 steps 45%). $[\alpha]_D^{26} = -31.2$ ($c = 0.180$, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 6.86$ (d, 2H, $J = 9.2$ Hz), 6.71 (d, 2H, $J = 8.7$ Hz), 4.94 (dd, 1H, $J = 9.7$ Hz, $J = 1.9$ Hz), 4.91–4.90 (m, 2H), 4.55–4.43 (m. 3H), 4.12–4.01 (m, 2H), 3.58–3.25 (m, 10H), 3.09–2.92 (m, 4H), 2.29–2.19 (m, 4H,), 2.05–1.46 (m, 12H), 1.33–1.03 ppm (m, 18H); ^{13}C NMR (68.7 MHz, CD_2Cl_2): $\delta = 151.5$, 118.4, 116.2, (101.8, 101.3, 100.1, 98.5, 98.1, 97.9 (anomeric)), 88.8, 82.2, 80.8, 80.7, 76.3, 75.7, 75.6, 75.3, 72.6, 72.5, 72.4, 70.8, 70.0, 69.9, 68.1, 68.0, 67.4, 46.5, 38.8, 37.7, 37.6, 37.4, 36.1, 30.1, 25.9, 24.5, 18.2, 18.0, 17.9, 17.1, 17.0 ppm; IR (neat): $\tilde{\nu} = 3408$, 3019, 1218, 1063, 771, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4594.

2ad: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35ad** (10.3 mg, 6.51 μmol) in THF/MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1 M THF solution of TBAF (19.5 μL, 19.5 μmol) in HMPA (130 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2ad** (1.90 mg, 2.21 μmol, 3 steps 34%). $[\alpha]_D^{28} = -39.8$ ($c = 0.100$, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 6.86$ (d, 2H, $J = 9.2$ Hz), 6.71 (d, 2H, $J = 8.7$ Hz), 4.94 (dd, 1H, $J = 9.7$ Hz, $J = 1.9$ Hz), 4.92–4.86 (m, 2H), 4.75 (brs, 1H), 4.55–4.44 (m. 4H), 4.12–4.04 (m, 2H), 3.58–3.23 (m, 10H), 3.09–2.92 (m, 4H), 2.32–2.19 (m, 4H), 2.10–1.48 (m, 12H), 1.33–1.00 ppm (m, 18H); ^{13}C NMR (68.7 MHz, CD_2Cl_2): $\delta = 151.6$, 118.4, 116.2, 101.7, 101.3, 100.2, 100.1, 98.6, 97.9, 88.8, 88.4, 82.2, 80.6, 76.1, 75.7, 75.3, 72.6, 72.5, 71.7, 71.2, 70.9, 70.8, 70.3, 69.9, 68.4, 68.1, 67.4, 46.6, 38.9, 38.8, 37.7, 37.4, 30.1, 25.9, 25.6, 25.0, 24.7, 18.2, 18.0, 17.1, 17.0, 11.5 ppm; IR (neat): $\tilde{\nu} = 3409$, 3019, 2400, 1217, 1063, 771, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4592.

2ba: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35ba** (11.8 mg, 7.52 μmol) in THF-MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1 M THF solution of TBAF (22.6 μL, 22.6 μmol) in HMPA (150 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2ba** (4.20 mg, 4.89 μmol, 3 steps 65%). $[\alpha]_D^{25} = -19.4$ ($c = 0.210$, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 6.85$ (d, 2H, $J = 8.7$ Hz), 6.71 (d, 2H, $J = 8.7$ Hz), 4.98 (dd, 1H, $J = 10.2$ Hz, $J = 1.5$ Hz), 4.91–4.85 (m, 3H), 4.75 (brs, 1H), 4.51–4.45 (m. 5H), 4.39 (brs, 1H), 4.34 (brs, 1H), 4.11 (q, 1H, $J = 6.8$ Hz), 4.04 (q, 1H, $J = 6.3$ Hz), 3.62–3.32 (m, 7H), 3.58 (brs, 1H), 3.51 (brs, 1H), 3.28 (m, 1H), 3.08–2.91 (m, 4H), 2.34 (ddd, 1H, $J = 5.8$ Hz, $J = 12.6$ Hz, $J = 1.5$ Hz), 2.25–2.21 (m, 3H), 2.03–1.45 (m, 12H), 1.34–1.13 ppm (m, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 151.5$, 151.3, 118.3, 116.1, 101.7, 101.4, 101.3, 100.1, 98.6, 98.1, 88.8, 88.4, 80.8, 76.2, 75.6, 72.6, 71.1, 70.9, 70.7, 70.3, 69.8, 69.7, 68.5, 68.0, 67.3, 38.8, 38.7, 38.6, 37.4, 30.1, 25.8, 25.4, 24.8, 24.5, 18.1, 18.0, 17.9×2, 17.1×2 ppm; IR (neat): $\tilde{\nu} = 3412$, 3020, 2401, 1509, 1217, 771, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4598.

2bb: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35bb** (17.5 mg, 11.3 μmol) in THF/MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1 M THF solution of TBAF (33.9 μL, 33.9 μmol) in HMPA (226 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2bb** (6.90 mg, 8.03 μmol, 3 steps 71%). $[\alpha]_D^{24} = -50.4$ ($c = 0.350$, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 6.85$ (d, 2H, $J = 9.2$ Hz), 6.71 (d, 2H, $J = 9.2$ Hz), 4.98 (dd, 1H, $J = 9.7$ Hz, $J = 1.5$ Hz), 4.88–4.77 (m, 4H), 4.52–4.41 (m. 5H), 4.11 (q, 1H, $J = 6.8$ Hz), 4.06 (q, 1H, $J = 6.3$ Hz), 3.66–3.38 (m, 9H 4), 3.28 (m, 1H), 3.04–2.91 (m, 4H), 2.34 (ddd, 1H, $J = 5.3$ Hz, $J = 12.5$ Hz, $J = 1.5$ Hz), 2.26–2.21 (m, 3H), 2.10–1.39 (m, 12H), 1.29–1.13 ppm (m, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 151.5$, 151.4, 118.3, 116.2, 101.7, 101.4×2, 100.2×2, 98.6, 88.8, 88.5, 88.3, 76.1, 71.2, 71.1, 71.0, 70.8, 70.3, 70.2, 69.9, 69.7, 68.5, 68.4, 67.3, 38.8, 38.7, 38.6, 30.1, 25.8, 25.5, 24.7, 24.5, 18.1, 17.9, 17.1, 17.0 ppm; IR (neat): $\tilde{\nu} = 3401$, 3019, 2401, 1509, 1219, 1038, 772, 668 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4593.

2bc: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35bc** (8.30 mg, 5.08 μmol) in THF-MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1 M THF solution of TBAF (15.2 μL, 15.2 μmol) in HMPA (102 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2bc** (1.70 mg, 1.98 μmol, 3 steps 39%). $[\alpha]_D^{22} = -60.3$ ($c = 0.105$, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 6.86$ (d, 2H, $J = 9.2$ Hz), 6.71 (d, 2H, $J = 9.2$ Hz), 4.94 (dd, 1H, $J = 9.7$ Hz, $J = 1.5$ Hz), 4.91–4.88 (m, 2H), 4.75 (brs, 1H), 4.55–4.45 (m. 3H), 4.40 (brs, 1H), 4.37 (brs, 1H), 4.33 (brs, 1H), 4.11 (q, 1H, $J = 6.8$ Hz), 4.04 (q, 1H, $J = 6.8$ Hz), 3.62–3.24 (m, 10H), 3.08–2.91 (m, 4H), 2.29–2.19 (m, 4H), 2.10–1.45 (m, 12H), 1.33–1.12 ppm (m, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 151.5$, 118.4, 116.2, 101.8, 101.5, 100.2, 100.1, 98.6, 98.1, 88.8, 88.5, 82.2, 80.8, 76.3, 75.7, 75.3, 72.6, 72.5, 71.2, 70.8, 70.3, 69.9, 68.5, 68.0, 67.4, 60.6, 46.4, 38.9, 38.6, 37.7, 37.6, 30.1, 25.8, 25.4, 24.8, 24.6, 18.2, 18.1, 18.0, 17.9, 17.1 ppm; IR (neat): $\tilde{\nu} = 3401$, 2933, 1509, 1370, 1219, 1067, 772 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 876.4593, found 876.4594.

2bd: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35bd** (12.8 mg, 8.22 μmol) in THF/MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1 M THF solution of TBAF (24.7 μL, 24.7 μmol) in HMPA (164 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2bd** (4.80 mg, 5.59 μmol, 3 steps 68%). $[\alpha]_D^{16} = -55.9$ ($c = 0.420$, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 6.86$ (d, 2H, $J = 8.7$ Hz), 6.71 (d, 2H, $J = 8.7$ Hz), 4.94 (dd, 1H, $J = 9.7$ Hz, $J = 1.9$ Hz), 4.89–4.85 (m, 2H), 4.77–4.75 (m, 2H), 4.55–4.33 (m. 5H), 4.11 (q, 1H, $J = 6.8$ Hz), 4.06 (q, 1H, $J = 6.8$ Hz), 3.60–3.24 (m, 10H), 3.09–2.91 (m, 4H), 2.30–2.21 (m, 3H), 2.10–1.39 (m, 12H), 1.32–1.13 ppm (m, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 151.5$, 118.4, 116.2, 101.7, 101.5, 100.2×3, 98.6, 88.8, 88.4, 88.2, 76.1, 75.3, 72.6, 72.5, 71.2, 70.8, 70.3, 69.9, 68.5, 68.4, 67.4, 38.9, 38.8, 38.7, 38.6, 37.7, 30.1, 26.0, 25.8, 24.7, 24.6, 23.3, 18.2, 18.1, 18.0, 17.1, 17.0, 15.0 ppm; IR (neat): $\tilde{\nu} =$ 3392, 2931, 1724, 1509, 1371, 1217, 1064, 769, 667 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4595.

2ca: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35ca** (14.9 mg, 9.05 μmol) in THF/MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1 M THF solution of TBAF (27.2 μL, 27.2 μmol) in HMPA (181 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2ca** (3.50 mg, 4.07 μmol, 3 steps 45%). $[\alpha]_D^{27} = -45.1$ ($c = 0.225$, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 6.85$ (d, 2H, $J = 8.7$ Hz), 6.71 (d, 2H, $J = 8.7$ Hz), 4.98 (dd, 1H, $J = 9.7$ Hz, $J = 1.9$ Hz), 4.91–4.90 (m, 2H), 4.53–4.49 (m, 3H), 4.43 (dd, 1H, $J = 9.7$ Hz, $J = 1.9$ Hz), 4.12–4.02 (m, 2H), 3.65–3.29 (m, 9H), 3.17 (m, 1H), 3.09–2.96 (m, 4H), 2.34 (ddd, 1H, $J = 5.3$ Hz, $J = 12.5$ Hz, $J = 1.9$ Hz), 2.25–2.14 (m, 3H), 2.09–1.48 (m, 12H), 1.34–1.03 ppm (m, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 151.5$, 118.4, 116.2, 101.6, 101.3, 100.1, 98.7, 98.2, 97.9, 88.5, 82.4, 80.9, 80.7, 76.2, 75.7, 75.5, 72.7, 72.6, 72.4, 71.0, 69.8, 68.1, 68.0, 67.4, 46.5, 38.7, 37.9, 37.5, 30.1, 25.9, 25.5, 24.9, 24.5, 18.2, 18.0×2, 17.9, 17.1, 17.0 ppm; IR (neat): $\tilde{\nu} = 3330$, 3019, 1216, 1062, 757, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4596.

2cb: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35cb** (19.0 mg, 11.6 μmol) in THF/MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1 M THF solution of TBAF (34.8 μL, 34.8 μmol) in HMPA (232 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2cb** (7.20 mg, 8.38 μmol, 3 steps 72%). $[\alpha]_D^{24} = -64.5$ ($c = 0.325$, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 6.85$ (d, 2H, $J = 8.7$ Hz), 6.71 (d, 2H, $J = 8.8$ Hz), 4.98 (dd, 1H, $J = 9.7$ Hz, $J = 1.9$ Hz), 4.91–4.81 (m, 3H), 4.52–4.47 (m. 2H), 4.43 (dd, 1H, $J = 10.2$ Hz, $J = 1.9$ Hz), 4.29 (brs, 1H), 4.24 (brs, 1H), 4.18–4.03 (m, 2H), 3.66–3.28 (m, 9H), 3.17 (m, 1H), 3.09–2.93 (m, 4H), 2.34 (ddd, 1H, $J = 5.3$ Hz, $J = 12.6$ Hz, $J = 1.9$ Hz), 2.26–2.13 (m, 3H), 2.08–1.52 (m,

12H), 1.32–1.13 ppm (m, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ=151.5, 118.3, 116.2, 101.5, 101.4, 100.2, 100.0, 98.6, 97.9, 88.5, 88.3, 82.4, 80.7, 76.0, 75.7, 75.4, 72.5, 72.3, 71.2, 70.9, 70.3, 69.7, 68.4, 68.0, 67.4, 38.7, 38.6, 37.9, 37.5, 30.1, 25.9, 25.5, 24.7, 24.5, 18.2, 18.1, 18.0, 17.9, 17.1, 17.0 ppm; IR (neat): $\tilde{\nu}$=3400, 2934, 1731, 1510, 1217, 1064, 760, 627 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd. 876.4593, found 876.4594.

2cc: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35cc** (21.7 mg, 12.6 μmol) in THF/MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1M THF solution of TBAF (37.8 μL, 37.8 μmol) in HMPA (252 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2cc** (7.70 mg, 8.96 μmol, 3 steps 71%). $[\alpha]_D^{23}=-47.6$ (c=0.385, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=6.86 (d, 2H, J=8.7 Hz), 6.71 (d, 2H, J=8.7 Hz), 4.94 (brd, 1H, J=9.7 Hz), 4.90 (brs, 1H), 4.90 (brs, 1H), 4.55–4.50 (m. 2H), 4.43 (brd, 1H, J=9.7 Hz), 4.38 (brs, 1H), 4.36 (brs, 1H), 4.29 (brs, 1H,), 4.23 (bs, 1H), 4.09 (q, 1H, J=6.3 Hz), 4.04 (q, 1H, J=6.3 Hz), 3.59–3.27 (m, 9H), 3.17 (m, 1H), 3.09–2.96 (m, 4H), 2.29–2.14 (m, 4H), 2.10–1.49 (m, 12H), 1.33–1.12 ppm (m, 18H); ^{13}C NMR (100 MHz CD_2Cl_2): δ=151.5, 151.4, 118.3, 116.2, 101.6, 100.1, 100.0, 98.5, 98.1, 97.8, 82.4, 82.2, 80.9, 80.7, 76.2, 75.7, 75.5, 75.3, 72.6, 72.5, 72.3, 68.1, 68.0, 67.4, 37.9, 37.7, 37.6, 37.5, 30.1, 25.9, 25.4, 24.8, 24.5, 18.2, 18.0, 17.1 ppm; IR (neat): $\tilde{\nu}$=3369, 2934, 1510, 1366, 1220, 1065, 772 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4592.

2cd: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35cd** (7.06 mg, 4.28 μmol) in THF/MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1M THF solution of TBAF (85.6 μL, 85.6 μmol) in HMPA (85.6 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2cd** (2.10 mg, 2.44 μmol, 3 steps 57%). $[\alpha]_D^{22}=-63.3$ (c=0.0500, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=6.88 (d, 2H, J=9.2 Hz), 6.71 (d, 2H, J=8.7 Hz), 4.94 (brd, 1H, J=9.7 Hz, J=1.9 Hz), 4.90–4.86 (m, 3H), 4.75 (brs, 1H), 4.55–4.49 (m, 2H), 4.42 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 4.32 (brs, 1H), 4.28 (brs, 1H), 4.23 (brs, 1H), 4.12–4.04 (m, 2H), 3.58–3.13 (m, 10H), 3.09–2.93 (m, 4H), 2.30 (m, 1H), 2.27–2.13 (m, 3H), 2.10–1.52 (m, 12H), 1.32–1.24 (m, 12H), 1.16–1.13 ppm (m, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ=151.5, 118.4, 116.2, 101.5, 100.2, 100.1, 100.0, 98.6, 97.9, 88.4, 82.4, 82.2, 80.7, 76.0, 75.7, 75.5, 75.3, 72.6, 72.3, 72.0, 70.9, 70.3, 68.4, 68.0, 67.4, 38.8, 37.9, 37.7, 37.5, 32.3, 30.1, 25.9, 25.5, 24.8, 24.5, 18.2, 18.1, 18.0, 17.1, 17.0 ppm; IR (neat): $\tilde{\nu}$=3401, 3018, 2399, 1509, 1219, 772, 670 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4595.

2da: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35da** (7.85 mg, 4.98 μmol) in THF-MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1M THF solution of TBAF (14.9 μL, 14.9 μmol) in HMPA (99.6 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2da** (2.10 mg, 2.44 μmol, 3 steps 49%). $[\alpha]_D^{24}=-48.2$ (c=0.105, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=6.85 (d, 2H, J=8.7 Hz), 6.71 (d, 2H, J=8.7 Hz), 4.98 (dd, 1H, J=10.2 Hz, J=1.5 Hz), 4.90–4.88 (m, 2H), 4.70 (brs, 1H), 4.53–4.49 (m. 3H), 4.42 (dd, 1H, J=9.7 Hz, J=1.5 Hz), 4.36 (brs, 1H), 4.25 (brs, 1H), 4.11 (q, 1H, J=6.3 Hz), 4.04 (q, 1H, J=6.3 Hz), 3.65–3.32 (m, 7H), 3.58 (brs, 1H), 3.51 (brs, 1H), 3.17 (m, 1H), 3.08–2.93 (m, 4H), 2.34 (ddd, 1H, J=5.3 Hz, J=13.1 Hz, J=1.5 Hz), 2.25–2.15 (m, 3H), 2.10–1.48 (m, 12H), 1.34–1.13 ppm (m, 18H); ^{13}C NMR (100 MHz CD_2Cl_2): δ=151.6, 151.4, 118.3, 116.2, 101.6, 100.3, 100.2, 100.1, 98.7, 98.2, 88.5, 82.5, 80.9, 76.2, 75.7, 72.7, 71.1, 70.9, 70.4, 69.8, 68.5, 68.0, 67.4, 38.8, 38.7, 37.9, 37.5, 30.1, 25.8, 25.4, 24.8, 24.6, 18.2, 18.1, 18.0, 17.9, 17.1 ppm; IR (neat): $\tilde{\nu}$=3406, 3020, 2400, 1509, 1217, 772, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4589.

2db: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35db** (33.4 mg, 21.4 μmol) in THF/MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1M THF solution of TBAF (64.2 μL, 64.2 μmol) in HMPA (428 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2db** (14.7 mg, 17.1 μmol, 3 steps 80%). $[\alpha]_D^{23}=-53.3$ (c=0.735, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=6.85 (d, 2H, J=8.7 Hz), 6.71 (d, 2H, J=8.7 Hz), 4.98 (brd, 1H, J=9.7 Hz), 4.88–4.83 (m, 3H), 4.74 (brs, 1H), 4.53–4.49 (m, 3H), 4.43 (brd, 1H, J=9.2 Hz), 4.11 (q, 1H, J=6.3 Hz), 4.06 (q, 1H, J=6.3 Hz), 3.66–3.35 (m, 9H), 3.17 (m, 1H), 3.04–2.93 (m, 4H), 2.34 (m, 1H), 2.27–2.14 (m, 3H), 2.10–1.53 (m, 12H), 1.29–1.13 ppm (m, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ=151.6, 118.3, 116.2, 101.5, 101.4, 100.2×2, 100.1, 98.6, 89.2, 88.5, 88.3, 82.4, 76.0, 75.4, 72.3, 71.2, 71.1, 70.9, 70.3, 69.7, 68.5, 68.4, 67.3, 38.8, 38.7, 38.6, 37.8, 30.1, 25.8, 25.5, 24.7, 24.5, 24.3, 18.2, 18.1, 18.0, 17.9, 17.1, 17.0 ppm; IR (neat): $\tilde{\nu}$=3394, 3018, 1505, 1220, 1012, 772, 670 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4590.

2dc: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35dc** (23.1 mg, 14.0 μmol) in THF-MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1M THF solution of TBAF (42.0 μL, 42.0 μmol) in HMPA (280 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2dc** (5.30 mg, 6.17 μmol, 3 steps 44%). $[\alpha]_D^{21}=-61.5$ (c=0.265, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=6.86 (d, 2H, J=9.2 Hz), 6.71 (d, 2H, J=9.2 Hz), 4.94 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 4.90–4.85 (m, 3H), 4.72 (brs, 1H), 4.55–4.50 (m, 2H), 4.42 (dd, 1H, J=9.7 Hz, J=1.9 Hz), 4.38 (brs, 1H), 4.36 (brs, 1H), 4.25 (brs, 1H), 4.11 (q, 1H, J=6.8 Hz), 4.04 (q, 1H, J=6.8 Hz), 3.60–3.27 (m, 9H), 3.17 (m, 1H), 3.08–2.93 (m, 4H), 2.29–2.14 (m, 4H), 2.06–1.48 (m, 12H), 1.32–1.12 ppm (m, 18H); ^{13}C NMR (100 MHz CD_2Cl_2): δ=151.6, 151.4, 118.3, 116.2, 101.6, 100.1×3, 98.5, 98.2, 88.5, 82.5, 82.2, 80.9, 76.2, 75.7, 75.5, 75.3, 72.6, 72.5, 72.3, 71.1, 70.4, 68.5, 68.0, 67.3, 38.8, 37.9, 37.7, 37.6, 30.1, 25.8, 25.4, 24.8, 24.5, 18.2, 18.1, 18.0, 17.1 ppm; IR (neat): $\tilde{\nu}$=3393, 3019, 2400, 1415, 1219, 1096, 1019, 772, 669 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4589.

2dd: According to the method for the synthesis of **2aa**, hydrolysis of the ester group of **35dd** (17.1 mg, 10.7 μmol) in THF/MeOH (1:1 2.00 mL) with a catalytic amount of sodium methoxide, removal of the SEM ether with a 1M THF solution of TBAF (32.1 μL, 32.1 μmol) in HMPA (214 μL) under microwave irradiation, and reduction of the benzyl ethers under Birch reduction conditions provided **2dd** (7.10 mg, 8.27 μmol, 3 steps 77%). $[\alpha]_D^{24}=-51.5$ (c=0.355, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=6.86 (d, 2H, J=8.7 Hz), 6.72 (d, 2H, J=8.7 Hz), 4.94 (brd, 1H, J=9.7 Hz), 4.87–4.72 (m, 4H), 4.55–4.50 (m. 2H), 4.43 (brd, 1H, J=9.7 Hz), 4.34 (brs, 1H), 4.26 (brs, 1H), 4.14–4.03 (m, 2H), 3.60–3.13 (m, 10H), 3.10–2.93 (m, 4H), 2.30–2.15 (m, 4H), 2.10–1.50 (m, 12H), 1.32–1.13 ppm (m, 18H); ^{13}C NMR (100 MHz CD_2Cl_2): δ=151.5, 118.4, 116.2, 101.5, 100.2×2, 100.1×2, 98.5, 88.5, 88.3, 82.4, 82.2, 75.9, 75.4, 75.3, 72.5, 72.3, 71.2, 71.1, 70.4, 68.5, 68.4, 67.3, 38.8, 37.9, 37.7, 30.1, 25.8, 25.5, 24.7, 24.5, 18.2, 18.1, 18.0, 17.1, 17.0 ppm; IR (neat): $\tilde{\nu}$=3401, 2934, 1670, 1509, 1369, 1218, 1067, 771, 667 cm^{-1}; HRMS (ESI-TOF) $[M+NH_4]^+$ calcd.: 876.4593, found: 876.4590.

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[15] The cytotoxic effects of the 16 compounds **2** against three cancer cell lines (human cervical carcinoma HeLa cells, human malignant pleural mesothelioma ACC-MESO-1 cells[16] and human acute myelogenous leukemia HL-60 cells) were determined by WST-8 colorimetric assay kit (Dojindo, Kumamoto, Japan). These compounds did not show any cytotoxic effects even at a concentration of 50 μM for 48 h.
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