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Synthesis and cytotoxic activity of the *N*-acetylglucosamine-bearing triterpenoid saponins

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ABSTRACT

Fourteen ursolic acid and oleanolic acid saponins with *N*-acetyl-β-D-glucosamine, and (1→4)-linked and (1→6)-linked *N*-acetyl-β-D-glucosamine oligosaccharide residues were synthesized in a convergent manner. The structures of all compounds were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy and by mass spectrometry, and their cytotoxic activities were assayed in three cancer cell lines. Only oleanolic acid-3-yl β-D-GluNAc showed significant cytotoxicity against HL-60 and BGC-823.

1. Introduction

Triterpenoid and steroidal saponins isolated from various natural medicinal plants have many biological and physiological activities such as anti-HIV activity, inhibition of β-glucosidase and cytotoxicity.[1–3] A common feature of saponins is their inhibitory activity against the growth of tumour cells with the potency being highly dependent on the structure of the 3-*O*-sugar residue.[4–6] It is well known that the naturally occurring *N*-acetylglucosamine-bearing triterpenoid saponins are rare; however, most of these show remarkable cytotoxicity or antiproliferative activity.[7] These findings indicate that the *N*-acetylglucosamine-bearing sugar chain dramatically boosts the bioactivity of triterpenoid. Several reviews on the synthesis of steroids/triterpene saponins have been published.[8] In a previous paper, we reported the synthesis of an ursolic acid saponin with an *N*-acetylglucosamine-containing sugar chain, which was the active sugar moiety attached to the oleanolic acid saponin isolated from the Suriname rainforest plants, *Acacia tenuifolia* and *Albizia subdimidiata*.[9] In continuing work on further probing the mode of linkage of the *N*-acetylglucosamine oligosaccharide residue on the cytotoxic activity of oleanolic acid and ursolic acid saponins, we have designed and synthesized β-D-(1→4)- and (1→6)-linked mono- to tetra-(*N*-acetylglucosamine) derivatives of ursolic acid and oleanolic acid (Fig. 1) and have carried out a preliminary evaluation of their cytotoxicity against HL-60, BGC-823 and HeP-2.

2. Results and discussion

2.1. Chemistry

It is considered essential to develop a concise procedure to prepare saponins in high overall yield for evaluation in pharmacological research. A convergent synthesis for the two series of target saponins was adopted in this paper. The β-(1→4)-linked glycosyl donors that are involved in the synthesis were prepared as shown in Scheme 1. To increase the nucleophilic activity of the 4-OH benzyl-protected disaccharide, acceptor, **19** was designed at the outset to synthesize trisaccharide and tetrasaccharide donors. So the key monosaccharide acceptor **16**[10] and donor **17**[11] were selected as the basic building blocks for preparing the disaccharide unit. Starting from known materials, glycosylation of **16** with donor **17** under the promotion of TMSOTf (0.2 equiv) yielded β-(1→4)-linked disaccharide **18** (81%). Deacetylation of **18** in NaOMe–MeOH at pH 12 without removal of Phth afforded the key disaccharide acceptor **19**. The literature reported that if benzyl-protected glycosyl donor was used in a reaction with the acceptor **19** for the preparation of β-(1→4)-linked trisaccharide and tetrasaccharide donors, the conditions required for the removal of the benzyl groups (Pd/C, H_2, 1:1→1:2 0.1 M HCl–MeOH) and the acetyl groups[12] (LiOH–30%H_2O_2–THF) after coupling with ursolic acid or oleanolic acid will destroy the carbon–carbon double bonds of the aglycon. To address this problem the known acetyl-protected glycosyl donor **15**[13] was employed in the coupling reaction with disaccharide acceptor **19** to give the β-(1→4)-linked trisaccharide **20** in 73% yield. Subsequent removal of the anomeric *O*-MP protection by

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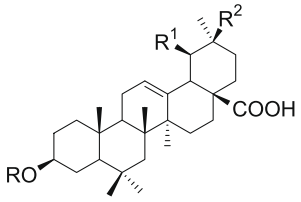


	R	R^1	R^2
1	β-D-GlcNAc	H	CH_3
2	β-D-GlcNAc	CH_3	H
3	β-D-GlcNAc-(1→4)-β-D-GlcNAc	H	CH_3
4	β-D-GlcNAc-(1→4)-β-D-GlcNAc	CH_3	H
5	β-D-GlcNAc-(1→4)-β-D-GlcNAc-(1→4)-β-D-GlcNAc	H	CH_3
6	β-D- GlcNAc-(1→4)-β-D-GlcNAc-(1→4)-β-D-GlcNAc	CH_3	H
7	β-D-GlcNAc-(1→4)-β-DGlcNAc-(1→4)-β-D-GlcNAc-(1→4)-β-D-GlcNAc	H	CH_3
8	β-D-GlcNAc-(1→4)-β-D-GlcNAc-(1→4)-β-D-GlcNAc-(1→4)-β-D-GlcNAc	CH_3	H
9	β-D-GlcNAc-(1→6)-β-D-GlcNAc	H	CH_3
10	β-D-GlcNAc-(1→6)- β-D-GlcNAc	CH_3	H
11	β-D-GlcNAc-(1→6)-β-D-GlcNAc-(1→6)-β-D-GlcNAc	H	CH_3
12	β-D-GlcNAc-(1→6)-β-D-GlcNAc-(1→6)-β-D-GlcNAc	CH_3	H
13	β-D-GlcNAc-(1→6)-β-D-GlcNAc-(1→6)-β-D-GlcNAc-(1→6)-β-D-GlcNAc	H	CH_3
14	β-D-GlcNAc-(1→6)-β-D-GlcNAc-(1→6)-β-D-GlcNAc-(1→6)-β-D-GlcNAc	CH_3	H

Figure 1. Structures of target saponins.

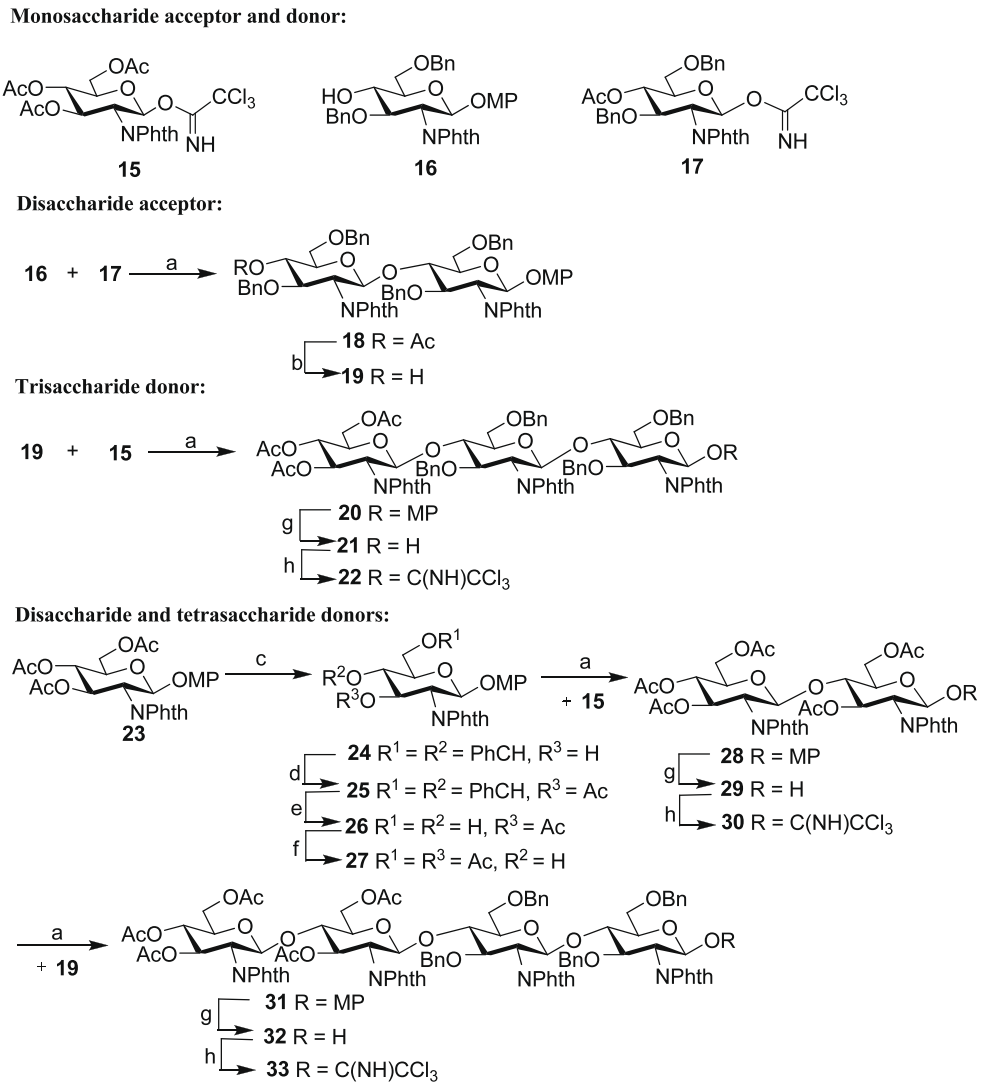
oxidative cleavage[14] with ammonium cerium(IV) nitrate (CAN) yielded **21**, which was then reacted with CCl_3CN–DBU to produce the trisaccharide donor **22**. Herein, acetyl-protected disaccharide donor **30** was prepared for the synthesis of the (1→4)-linked tetrasaccharide donor. Starting from **23**,[15] compound **24** was obtained by deacetylation of **23** with NaOMe–MeOH, followed by protection of the 4,6-OHs with a benzylidene group. The free hydroxyl group (HO-3) was then acetylated to give **25**. Subsequent full debenzylidenation of **25** afforded **26,** and selective acetylation gave **27**. Compound **27** was coupled with donor **15** under standard glycosylation conditions to afford **28** in good yield. Removal of the anomeric *O*-MP protection and then reaction of the HO-1 group with CCl_3CN produced disaccharide donor **30**. Coupling of **30** with **19** under standard conditions afforded the β-(1→4)-linked tetrasaccharide **31** in 41% yield. Tetrasaccharide donor **33** was obtained in the same manner as in the previous case. So β-(1→4)-linked acetylglucosamine oligosaccharide donors **15**, **22**, **30** and **33** were produced in moderate to good yields and were designed to provide effective glycosyl donors for the preparation of target saponins in the next part of the work.

The synthetic route to β-(1→6)-linked glycosyl donors is shown in Scheme 2. Compound **34** was selected as the key glycosyl acceptor, which was coupled with donor **15,** with promotion by TMSOTf, to produce disaccharide **35**. In a concise process **35** was converted into glycosyl donor **38** and acceptor **36**. Herein, the coupling of glycosyl donor **15** and acceptor **36** gave trisaccharide **39**, while the coupling of donor **38** and acceptor **36** produced tetrasaccharide **42**. Removal of the C-1-OMP group of **35**, **39** and **42** produced β-(1→6)-linked di-, tri- and tetrasaccharide hemiacetals **37**, **40** and **43**, respectively, in good yields. During the subsequent preparation of the Schmidt donors, only trace amounts of products were detected by TLC when 6 equiv of trichloroacetonitrile were added, but trichloroacetimidates **38**, **41** and **44** were obtained in acceptable yields when the amount of trichloroacetonitrile was increased to 15.0 equiv.

With these protected glycosyl donors **15**, **22**, **30**, **33, 38**, **41** and **44** in hand, the coupling of donors with trityl ursolate or trityl oleanolate was performed at −70 °C under the promotion of TMSOTf (0.2 equiv), followed by removal of the trityl ester group by warming the reaction solutions to room temperature and adding MeOH and TsOH (pH 2) to generate the intermediates **45**–**58**. These products were then treated with hot ethylenediamine–butanol[16] (90 °C) and Ac_2O–pyridine, and finally with NaOMe–MeOH to produce the target saponins **1–4** and **9**–**14**. Target compounds **5**–**8** were obtained by hydrogenolysis of **49**–**52** under Pd/C (10%) in the presence of HOAc (Scheme 3).

2.2. Bioactivity assays

The antitumour activities of these synthetic saponins against HL-60, BGC-823 and HeP-2 tumour cell were determined in vitro by the standard MTT assay (HL-60) and SRB assay (BGC-823 and HeP-2). As shown in Table 1, the cytotoxicity of all oleanolic acid saponins were better than that of the corresponding ursolic acid saponins. Only oleanolic acid saponin **1** displayed prominent inhibition activity against HL-60 and BGC-823 with an IC_{50} value at 4.70 μM against HL-60. The counterpart of ursolic acid **2** showed weaker antitumour activity against HL-60 and no cytotoxicity against BGC-823 and Hep-2. All other saponins with di- to tetrasaccharide chains did not show distinct cytotoxicity. These results indicate that some *N*-acetylglucosamine-containing sugar chains are important for inducing the antitumour activity of triterpene saponins and branched sugar chains with specific linkages may be essential for this pharmacological effect.[7] So there is still a lot of work to do in searching for such active sugar residues.



Scheme 1. Preparation of β-(1→4)-linked glycosyl donors. Reagents and conditions: (a) TMSOTf (0.2 equiv), 4 Å MS, 81% for **18**, 85% for **28**, 73% for **20**, 41% for **31**; (b) NaOMe, MeOH, rt, quant; (c) (i) NaOMe, MeOH, rt; (ii) $PhCH(OCH_3)_2$, TsOH, DMF, 60 °C, 0.1 MPa, 89.0% for two steps; (d) Ac_2O, Py, rt, quant; (e) 80% HOAc, 50 °C, 92.8%; (f) Ac_2O (1.05 equiv), Py, 0 °C→rt, 76%; (g) CAN, $CH_3CN–H_2O$, 89% for **29**, 88% for **21**, 83% for **32**; (h) DBU, $CNCCl_3$, CH_2Cl_2, 0 °C→rt, 72% for **30**, 82% for **22**, 84% for **33**.

3. Conclusions

In summary, 14 ursolic acid and oleanolic acid saponins bearing *N*-acetyl-D-glucosamine, (1→4)-linked and (1→6)-linked *N*-acetyl-D-glucosamine oligosaccharide residues were synthesized using a convergent strategy. Significant antitumour activity was demonstrated for only saponin **1**. Further searching for active sugar chains that can induce antitumour activity of oleanolic acid and ursolic acid are in progress and will be reported in due course.

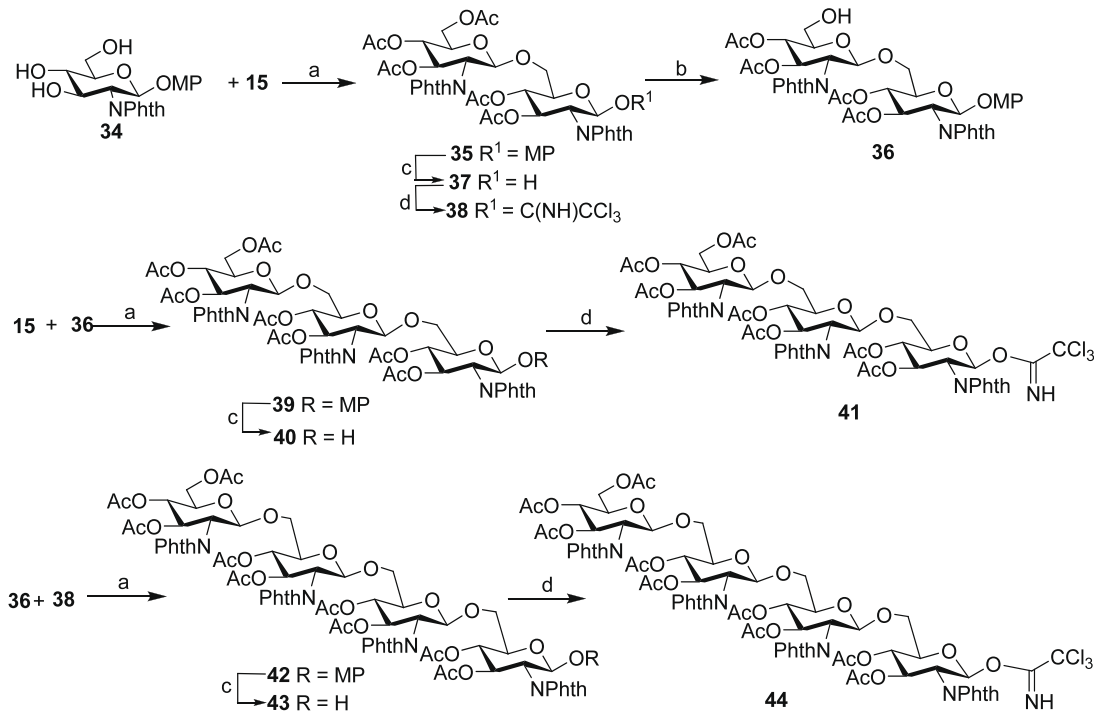
4. Experimental

4.1. General procedures

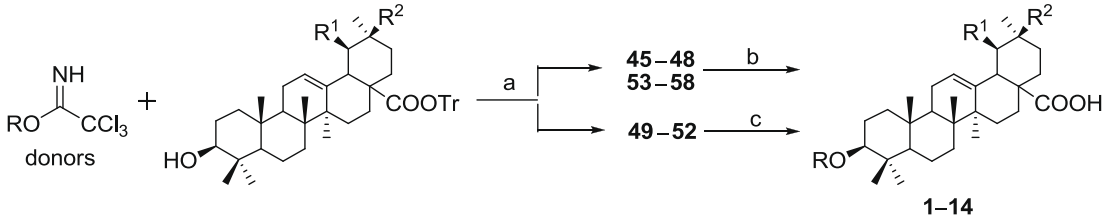
Solvents were purified in the usual way. Thin-layer chromatography (TLC) was performed on pre-coated E. Merck Silica Gel 60 F_{254} plates. Flash column chromatography was performed on silica gel (200–300 mesh, Qingdao, China). Optical rotations were determined with a Perkin–Elmer Model 241 MC polarimeter. ^1H NMR and ^{13}C NMR spectra were taken on a JEOL JNM-ECP 600 spectrometer with tetramethylsilane as the internal standard and chemical shifts are recorded in δ units. Mass spectra were recorded on a Q-TOF Global mass spectrometer.

4.2. *p*-Methoxyphenyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (24)

Compound **23** (16.8 mmol, 9.09 g) was dissolved in 1:5 MeOH–CH_2Cl_2 (100 mL) and then 1:1 NaOMe–MeOH was added to adjust the solution to pH 9. After stirring at rt for 2 h, the solution was neutralized with cation-exchange resin (H^+) and then filtered and concentrated to afford an amorphous solid. To a solution of the above-mentioned compound and $PhCH(OMe)_2$ (32.5 mmol, 4.95 g) in dry DMF (50 mL) was added $TsOH·H_2O$ (1.5 mmol, 0.26 g). The resulting mixture was stirred at 40 °C under reduced pressure for 6 h, neutralized by Et_3N (3 mL), diluted with EtOAc (200 mL) and then successively washed with water (2 × 50 mL), satd $NaHCO_3$ (2 × 50 mL) and brine (2 × 50 mL). The organic layer was dried over anhyd Na_2SO_4 and then concentrated under vacuum. The residue was purified by silica gel column chromatography (4:1–3:1 petroleum ether–EtOAc) to yield **24** (8.3 g, 92%) as a white solid with R_f 0.70 (15:1 $CHCl_3$–MeOH); $[\alpha]_D^{20}$ +11.4 (*c* 0.67, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.87–7.27 (m, 4H, Phth), 7.51–7.38 (m, 5H, Ph), 6.83–6.73 (m, 4H, Ph), 5.81 (d, 1H, *J* 8.4 Hz, H-1), 5.60 (s, 1H, PhC*H*), 4.71 (dd, 1H, *J* 10.6, 8.5 Hz, H-3), 4.51 (dd, 1H, *J* 10.6, 8.4 Hz, H-2), 4.41 (dd, 1H, *J* 10.6, 4.4 Hz, H-6_i), 3.90–3.82 (m, 1H, H-6_{ii}), 3.78–3.69 (m, 5H, H-4, H-5 and OCH_3), 1.86



Scheme 2. Preparation of β-(1→6)-linked glycosyl donors. Reagents and conditions: (a) TMSOTf (0.2 equiv), 4 Å MS, 99% for **35**, 92% for **39**, 91% for **42**; (b) (i) NaOMe, MeOH, rt, quant; (ii) TrCl (5 equiv), DMAP, Py, 80 °C; (iii) Ac_2O, Py, 92%; (iv) $FeCl_3{\cdot}6H_2O$, 79%; (c) CAN, CH_3CN–H_2O, 96% for **37**, 88% for **40**, 92% for **43**; (d) DBU, $CNCCl_3$, CH_2Cl_2, 0 °C→rt, 74% for **38**, 66% for 4**1**, 65% for **44**.



Glycosyl donor	R^1	R^2	Protected saponin	Yield	Target saponin	Yield
15	H	CH_3	**45**	78%	**1**	69%
	CH_3	H	**46**	77%	**2**	69%
30	H	CH_3	**47**	69%	**3**	61%
	CH_3	H	**48**	72%	**4**	59%
22	H	CH_3	**49**	89%	**5**	74%
	CH_3	H	**50**	86%	**6**	71%
33	H	CH_3	**51**	82%	**7**	73%
	CH_3	H	**52**	84%	**8**	71%
38	H	CH_3	**53**	62%	**9**	64%
	CH_3	H	**54**	64%	**10**	60%
41	H	CH_3	**55**	69%	**11**	60%
	CH_3	H	**56**	61%	**12**	56%
44	H	CH_3	**57**	54%	**13**	47%
	CH_3	H	**58**	51%	**14**	46%

Scheme 3. Preparation of the target saponins. Reagents and conditions: (a) TMSOTf, TsOH; (b) (i) $NH_2CH_2CH_2NH_2$, BuOH, 90 °C; (ii) Ac_2O, Py; (iii) NaOMe, MeOH; (c) (i) $NH_2CH_2CH_2NH_2$, BuOH, 90 °C; (ii) Ac_2O, Py; (iii) NaOMe, MeOH; (iv) Pd/C, AcOH, MeOH.

Table 1
Inhibition rate at 10 μM (%) of the synthetic compounds **1**–**14** against different tumour cell lines

Compound	OL[a]	1	3	5	7	9	11	13
HL-60	13.18	82.62	31.70	18.17	48.31	12.81	4.31	6.52
BGC-823	17.00	68.99	39.17	22.55	35.46	16.29	8.42	14.78
HeP-2	26.99	23.34	23.64	13.30	37.84	2.02	10.47	21.80
Compound	UA[b]	2	4	6	8	10	12	14
HL-60	7.57	51.04	31.22	4.11	10.99	15.52	3.11	Nt[c]
BGC-823	12.49	5.43	−4.35	5.99	3.90	0.65	7.48	Nt[c]
HeP-2	10.77	4.06	−6.39	6.84	−12.01	3.44	2.52	Nt[c]

[a] OL = oleanolic acid.
[b] UA = ursolic acid.
[c] nt = not tested.

(br s, 1H, OH); ESIMS: calcd for $C_{28}H_{25}NNaO_8$ 526.1, found 526.0 $[M+Na]^+$.

4.3. General procedure for the preparation of compounds 21, 29, 32, 37, 40 and 43

To a stirred solution of precursor compound (1 mmol) in 4:1 CH_3CN–H_2O (10 mL) was added ammonium cerium(IV) nitrate (5 mmol). After stirring at rt for 1 h, the mixture was diluted with EtOAc (100 mL) and successively washed with water (3 × 50 mL) and brine (3 × 50 mL). The organic layer was dried over anhyd Na_2SO_4 and then concentrated in vacuum to give a yellow syrup that was purified by column chromatography to afford the pure compound.

4.3.1. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose (29)

Yield 89%; R_f 0.23 (2:3 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +23.5 (*c* 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.88–7.72 (m, 8H, Phth), 5.79 (dd, 1H, *J* 8.7, 10.0 Hz, H-3), 5.73 (dd, 1H, *J* 9.2, 10.6 Hz, H-3′), 5.56 (d, 1H, *J* 8.3 Hz, H-1), 5.47 (d, 1H, *J* 8.7 Hz, H-1′), 5.15 (dd, 1H, *J* 9.2, 10.1 Hz, H-4′), 4.43 (dd, 1H, *J* 4.1, 12.4 Hz, H-6_i′), 4.33 (dd, 1H, *J* 1.8, 11.9 Hz, H-6_i), 4.26 (dd, 1H, *J* 8.2, 10.5 Hz, H-2′), 4.11 (dd, 1H, *J* 8.7, 10.5 Hz, H-2), 4.08 (dd, 1H, *J* 2.3, 12.4 Hz, H-6_{ii}′), 3.96 (dd, 1H, *J* 9.2, 9.6 Hz, H-4), 3.83 (ddd, 1H, *J* 2.3, 3.7, 10.1 Hz, H-5′), 3.73 (ddd, 1H, *J* 1.8, 4.1, 10.1 Hz, H-5), 3.68 (dd, 1H, *J* 4.1, 11.9 Hz, H-6_{ii}), 3.33 (br s, 1H, OH), 2.10, 2.00, 1.96, 1.91, 1.82 (s each, 3H each, 5 × COCH_3); ESIMS: calcd for $C_{38}H_{38}N_2NaO_{18}$ 833.2, found 833.3 $[M+Na]^+$.

4.3.2. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranose (21)

Yield 88%; R_f 0.14 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +9.1 (*c* 0.1.15, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.96–7.61 (m, 12H, Phth), 7.33–6.69 (m, 20H, *Ph*CH_2), 5.78 (dd, 1H, *J* 9.1, 10.6 Hz, H-3″), 5.52 (d, 1H, *J* 8.4 Hz, H-1″), 5.12 (t, 1H, *J* 9.2 Hz, H-4″), 5.11 (d, 1H, *J* 9.5 Hz, H-1), 5.10 (d, 1H, *J* 8.0 Hz, H-1′), 4.88–4.37 (m, 8H, PhCH_2), 4.32 (dd, 1H, *J* 8.5, 10.6 Hz, H-2″), 4.26 (dd, 1H, *J* 8.0, 9.5 Hz, H-4′), 4.21 (dd, 1H, *J* 3.7, 12.1 Hz, H-6_i″), 4.18–4.10 (m, 3H, H-3, H-2′, H-3′), 4.07 (t, 1H, *J* 9.5 Hz, H-4), 3.95 (dd, 1H, *J* 8.4, 10.3 Hz, H-2), 3.91 (dd, 1H, *J* 1.9, 12.1 Hz, H-6_{ii}″), 3.48–3.43 (m, 3H, H-6_i, H-6_i′, H-5″), 3.33–3.29 (m, 2H, H-5, H-6_{ii}), 3.22 (dd, 1H, *J* 2.9, 11.0 Hz, H-6_{ii}′), 3.06 (d, 1H, *J* 3.7 Hz, OH), 2.93 (dd, 1H, *J* 1.4, 9.9 Hz, H-5′), 1.98, 1.89, 1.84 (s each, 3H each, 3 × COCH_3); ESIMS: calcd for $C_{76}H_{71}N_3NaO_{22}$ 1400.3, found 1400.4 $[M+Na]^+$.

4.3.3. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-ph-thalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranose (32)

Yield 83%; R_f 0.45 (2:1 petroleum ether–EtOAc); ^1H NMR ($CDCl_3$): δ 7.94–7.54 (m, 16H, Phth), 7.22–6.68 (m, 20H, *Ph*CH_2), 5.79–5.67 (m, 2H, H-3″, H-3‴), 5.42 (d, 1H, *J* 8.5 Hz, H-1″), 5.35 (d, 1H, *J* 8.4 Hz, H-1‴), 5.13 (t, 1H, *J* 9.5 Hz, H-4‴), 5.09 (br s, 1H, H-1), 5.05 (d, 1H, *J* 8.0 Hz, H-1′), 4.77 (d, 1H, *J* 12.8 Hz, PhCH_2), 4.71 (d, 1H, *J* 12.8 Hz, PhCH_2), 4.49–4.29 (m, 7H, H-6_i‴, 6 × PhCH_2), 4.21 (dd, 1H, *J* 8.5, 10.6 Hz, H-2‴), 4.16–3.88 (m, 9H, H-2, H-3, H-4, H-2′, H-3′, H-4′, H-2″, H-6_i″, H-6_i‴), 3.75 (ddd, 1H, *J* 2.2, 3.3, 10.3 Hz, H-5‴), 3.45–3.39 (m, 3H, H-6_I, H-6_i′, H-6_i″), 3.30–3.27 (m, 2H, H-5, H-6_{ii}), 3.19 (dd, 1H, *J* 2.9, 11.3 Hz, H-6_{ii}′), 3.13 (dt, 1H, *J* 2.2, 9.9 Hz, H-5″), 2.99 (br s, 1H, OH), 2.90 (d, 1H, *J* 7.4 Hz, H-5′), 2.05, 1.97, 1.89, 1.80, 1.75 (s each, 3H each, 5 × COCH_3); ESIMS: calcd for $C_{94}H_{88}N_4NaO_{30}$ 1775.5, found 1775.5 $[M+Na]^+$.

4.3.4. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose (37)

Yield 88%; R_f 0.20 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +29.0 (*c* 0.71, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.88–7.73 (m, 8H, Phth), 5.81 (dd, 1H, *J* 8.8, 10.6 Hz, H-3′), 5.70 (d, 1H, *J* 8.4 Hz, H-1′), 5.57 (dd, 1H, *J* 8.8, 10.6 Hz, H-3), 5.24 (d, 1H, *J* 8.0 Hz, H-1), 5.17 (dd, 1H, *J* 9.2, 10.6 Hz, H-4′), 4.84 (dd, 1H, *J* 9.2, 10.3 Hz, H-4), 4.35–4.31 (m, 2H, H-2′, H-6_i′), 4.22–4.17 (m, 2H, H-2, H-6_{ii}′), 3.90 (ddd, 1H, *J* 2.2, 4.4, 10.3 Hz, H-5′), 3.81 (dd, 1H, *J* 8.5, 12.8 Hz, H-6_i), 3.71 (dd, 1H, *J* 1.9, 12.8 Hz, H-6_{ii}), 3.53 (m, 1H, H-5), 2.15, 2.04, 1.93, 1.88, 1.81 (s each, 3H each, 5 × COCH_3); ESIMS: calcd for $C_{38}H_{38}N_2NaO_{18}$ 833.2, found 833.2 $[M+Na]^+$.

4.3.5. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose (40)

Yield 88%; R_f 0.23 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +36.8 (*c* 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$):δ 7.92–7.73 (m, 12H, Phth), 5.78 (dd, 1H, *J* 9.2, 10.6 Hz, H-3″), 5.66 (dd, 1H, *J* 9.2, 11.0 Hz, H-3), 5.56 (dd, 1H, *J* 9.1, 10.6 Hz, H-3′), 5.52 (d, 2H, *J* 8.5 Hz, H-1, H-1″), 5.25 (d, 1H, *J* 8.5 Hz, H-1′), 5.18 (t, 1H, *J* 9.5 Hz, H-4″), 4.92 (t, 1H, *J* 9.1 Hz, H-4), 4.85 (dd, 1H, *J* 9.2, 10.3 Hz, H-4′), 4.38–4.34 (m, 2H, H-2″, H-6_i″), 4.23–4.19 (m, 2H, H-2, H-6_{ii}″), 4.17 (dd, 1H, *J* 8.4, 11.0 Hz, H-2′), 3.92–3.87 (m, 2H, H-6_i, H-5″), 3.75–3.64 (m, 5H, H-5, H-6_{ii}, H-6_i′, H-6_{ii}′, OH), 3.47 (m, 1H, H-5′), 2.16, 2.03, 1.91, 1.88, 1.86, 1.80, 1.80 (s, 3H each, 7 × COCH_3); ESIMS: calcd for $C_{56}H_{55}N_3NaO_{26}$ 1208.3, found 1208.4 $[M+Na]^+$.

4.3.6. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose (43)

Yield 92%; R_f 0.14 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +35.1 (*c* 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.95–7.72 (m, 16H, Phth), 5.80 (dd, 1H, *J* 9.1, 10.6 Hz, H-3‴), 5.65 (dd, 1H, *J* 9.2, 10.6 Hz, H-3′), 5.61–5.58 (m, 2H, H-3, H-3″), 5.50 (d, 1H, *J* 8.4 Hz, H-1‴), 5.46 (d, 1H, *J* 8.4 Hz, H-1″), 5.35 (d, 1H, *J* 8.5 Hz, H-1′), 5.28 (d, 1H, *J* 8.4 Hz, H-1), 5.20 (dd, 1H, *J* 9.2, 10.3 Hz, H-4‴), 4.39–4.35 (m, 2H, H-4′), 4.89 (dd, 1H, *J* 8.8, 10.3 Hz, H-2‴, H-6_i‴), 4.23–4.10 (m, 4H, H-2, H-2′, H-2″, H-6_i‴), 3.93–3.89 (m, 2H, H-6_i′, H-5‴), 3.79–3.66 (m, 5H, H-6_I, H-6_{ii}, H-5′, H-6_{ii}′, H-6_i″), 3.53–3.44 (m, 3H, H-5, H-5″, H-6_{ii}″), 2.14, 2.04, 1.95, 1.89, 1.88, 1.86, 1.80, 1.79 (some overlap, 27H, 9 × COCH_3); ESIMS: calcd for $C_{74}H_{72}N_4NaO_{34}$ 1583.4, found 1583.6 $[M+Na]^+$.

4.4. General procedure for preparation of the glycosyl donors 30, 22, 33, 38, 41 and 44

To a stirred solution of carbohydrate precursor compound (1 mmol) in dry CH_2Cl_2 (15 mL) at 0 °C were added CCl_3CN (6 mmol–15 mmol) and DBU (0.5 mmol). The mixture was then allowed to warm up to rt and stir for 2 h, after which time it was concentrated in vacuo. The resulting residue was purified by flash column chromatography to afford the pure product.

4.4.1. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (30)

Yield 72%; R_f 0.25 (2:3 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +31.2 (*c* 0.73, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.58 (s, 1H, NH), 7.88–7.71 (m, 8H, Phth), 6.53 (d, 1H, *J* 9.2 Hz, H-1), 5.87 (dd, 1H, *J* 8.8, 10.3 Hz, H-3) 5.75 (dd, 1H, *J* 9.2, 10.6 Hz, H-3′), 5.48 (d, 1H, *J* 8.5 Hz, H-1′), 5.15 (dd, 1H, *J* 9.2, 10.3 Hz, H-4′), 4.48 (dd, 1H, *J* 9.2, 10.6 Hz, H-2), 4.44 (dd, 1H, *J* 4.7, 12.4 Hz, H-6$_i$′), 4.36 (dd, 1H, *J* 1.5, 12.1 Hz, H-6$_i$), 4.28 (dd, 1H, *J* 8.5, 10.6 Hz, H-2′), 4.14–4.06 (2H, H-4, H-6$_{ii}$′), 3.89 (ddd, 1H, *J* 1.8, 3.7, 9.9 Hz, H-5′), 3.86 (ddd, 1H, *J* 2.2, 4.4, 10.3 Hz, H-5), 3.75 (dd, 1H, *J* 3.7, 12.5 Hz, H-6$_{ii}$), 2.13, 2.01, 1.94, 1.91, 1.83 (s, 15H each, 5 × COC*H*$_3$); ESIMS: calcd for $C_{40}H_{38}Cl_3N_3NaO_{18}$ 976.1, found 976.0 $[M+Na]^+$.

4.4.2. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (22)

Yield 82%; R_f 0.27 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +5.5 (*c* 0.65, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.38 (s, 1H, NH), 7.97–7.62 (m, 12H, Phth), 7.35–6.68 (m, 20H, *Ph*CH_2), 6.18 (d, 1H, *J* 8.8 Hz, H-1), 5.78 (dd, 1H, *J* 9.2, 10.6 Hz, H-3″), 5.53 (d, 1H, *J* 8.5 Hz, H-1″), 5.13 (t, 1H, *J* 9.1 Hz, H-4″), 5.12 (d, 1H, *J* 8.1 Hz, H-1′), 4.89–4.40 (m, 8H, PhC*H*$_2$), 4.34–4.10 (m, 8H, H-2, H-3, H-4, H-2′, H-3′, H-4′, H-2″, H-6$_i$″), 3.92 (dd, 1H, *J* 2.2, 12.1 Hz, H-6$_{ii}$″), 3.54 (d, 1H, *J* 10.2, H-6$_i$′), 3.24 (dd, 1H, *J* 2.9, 11.3 Hz, H-6′), 3.46 (ddd, 1H, *J* 2.2, 3.7, 10.3 Hz, H-5), 3.44–3.42 (m, 2H, H-6$_i$, H-5″), 3.35 (dd, 1H, *J* 3.3, 11.0 Hz, H-6$_{ii}$), 3.23 (dd, 1H, *J* 2.9, 11.4 Hz, H-6$_{ii}$′), 2.91 (d, 1H, *J* 8.4 Hz, H-5′), 1.98, 1.90, 1.84 (s each, 3H each, 3 × COC*H*$_3$); ESIMS: calcd for $C_{78}H_{71}Cl_3N_4NaO_{22}$ 1543.4, found 1543.5 $[M+Na]^+$.

4.4.3. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (33)

Yield 84%; R_f 0.55 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +9.0 (*c* 0.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.37 (s, 1H, NH), 7.93–7.49 (m, 16H, Phth), 7.22–6.68 (m, 20H, *Ph*CH_2), 6.16 (d, 1H, *J* 8.8 Hz, H-1), 5.71–5.67 (m, 2H, H-3″, H-3‴), 5.43 (d, 1H, *J* 8.1 Hz, H-1″), 5.36 (d, 1H, *J* 8.1 Hz, H-1‴), 5.13 (dd, 1H, *J* 9.2, 10.3 Hz, H-4‴), 5.07 (d, 1H, *J* 8.0 Hz, H-1′), 4.77 (d, 1H, *J* 13.2 Hz, PhC*H*$_2$), 4.71 (d, 1H, *J* 12.8 Hz, PhC*H*$_2$), 4.50–4.30 (m, 8H, H-2‴, H-6$_i$‴, 6 × PhC*H*$_2$), 4.23–4.06 (m, 7H, H-2, H-3, H-4, H-2′, H-3′, H-4′, H-2″), 4.01–3.97 (m, 2H, H-6$_i$″, H-6$_i$‴), 3.76 (ddd, 1H, *J* 2.2, 3.7, 10.3 Hz, H-5‴), 3.51 (d, 1H, *J* 9.8 Hz, H-6$_i$), 3.41–3.38 (m, 3H, H-5, H-6$_i$′, H-6$_{ii}$″), 3.32 (dd, 1H, *J* 3.3, 11.0 Hz, H-6$_{ii}$″), 3.20 (dd, 1H, *J* 2.5, 11.0 Hz, H-6$_{ii}$′), 3.13 (ddd, 1H, *J* 1.8, 2.9, 9.9 Hz, H-5″), 2.88 (d, 1H, *J* 5.9 Hz, H-5′), 2.05, 1.97, 1.89, 1.81, 1.76 (s each, 3H each, COC*H*$_3$ × 5); ESIMS: calcd for $C_{96}H_{88}Cl_3N_5NaO_{30}$ 1918.4, found 1918.5 $[M+Na]^+$.

4.4.4. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (38)

Yield 74%; R_f 0.25 (2:3 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +43.2 (*c* 1.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.36 (s, 1H, NH), 7.87–7.70 (m, 8H, Phth), 6.49 (d, 1H, *J* 8.8 Hz, H-1), 5.80 (dd, 1H, *J* 8.8, 10.6 Hz, H-3), 5.76 (dd, 1H, *J* 8.3, 10.6 Hz, H-3′), 5.47 (d, 1H, *J* 8.5 Hz, H-1′), 5.17 (dd, 1H, *J* 9.1, 10.2 Hz, H-4′), 5.04 (dd, 1H, *J* 8.8, 9.9 Hz, H-4), 4.50 (dd, 1H, *J* 8.8, 10.6 Hz, H-2), 4.37–4.34 (m, 2H, H-2′, H-6$_i$′), 4.18 (dd, 1H, *J* 2.2, 12.1 Hz, H-6$_{ii}$′), 3.98–3.95 (m, 2H, H-5, H-6$_i$), 3.85 (ddd, 1H, *J* 2.6, 4.8, 10.3 Hz, H-5′), 3.70 (dd, 1H, *J* 6.2, 11.3 Hz, H-6$_{ii}$), 2.14, 2.03, 1.94, 1.85, 1.82 (s each, 3H each, 5 × COC*H*$_3$); ESIMS: calcd for $C_{40}H_{38}Cl_3N_3NaO_{18}$ 976.1, found 976.1 $[M+Na]^+$.

4.4.5. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (41)

Yield 66%; R_f 0.34 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +28.8 (*c* 0.45, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.46 (s, 1H, NH), 7.93–7.70 (m, 12H, Phth), 6.46 (d, 1H, *J* 8.8 Hz, H-1), 5.78 (dd, 1H, *J* 9.2, 10.6 Hz, H-3″), 5.74 (dd, 1H, *J* 9.2, 10.6 Hz, H-3), 5.62 (dd, 1H, *J* 8.8, 10.6 Hz, H-3′), 5.50 (d, 1H, *J* 8.5 Hz, H-1″), 5.32 (d, 1H, *J* 8.4 Hz, H-1′), 5.19 (dd, 1H, *J* 9.2, 10.3 Hz, H-4″), 4.91–4.88 (m, 2H, H-4, H-4′), 4.47 (dd, 1H, *J* 8.8, 10.6 Hz, H-2), 4.38 (dd, 1H, *J* 4.8, 12.1 Hz, H-6$_i$″), 4.34 (dd, 1H, *J* 8.4, 10.6 Hz, H-2″), 4.22 (dd, 1H, *J* 8.4, 11.0 Hz, H-2′), 4.19 (dd, 1H, *J* 2.2, 11.8 Hz, H-6$_{ii}$″), 3.90 (ddd, 1H, *J* 2.2, 4.8, 10.3 Hz, H-5″), 3.88 (dd, 1H, *J* 1.8, 11.0 Hz, H-6$_i$′), 3.74 (dd, 1H, *J* 3.3, 11.0 Hz, H-6$_i$), 3.72–3.64 (m, 3H, H-5, H-5′, H-6$_{ii}$′), 3.40 (dd, 1H, *J* 4.7, 11.0 Hz, H-6$_{ii}$), 2.15, 2.04, 1.94, 1.92, 1.86, 1.80, 1.78 (s each, 3H each, 7 × COC*H*$_3$); ESIMS: calcd for $C_{58}H_{55}Cl_3N_4NaO_{26}$ 1351.2, found 1351.2 $[M+Na]^+$.

4.4.6. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (44)

Yield 65%; R_f 0.22 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +8.7 (*c* 0.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.47 (s, 1H, NH), 7.93–7.70 (m, 16H, Phth), 6.46 (d, 1H, *J* 8.8 Hz, H-1), 5.79 (dd, 1H, *J* 9.2, 10.6 Hz, H-3‴), 5.74 (dd, 1H, *J* 9.2, 10.6 Hz, H-3), 5.65 (dd, 1H, *J* 8.8, 10.6 Hz, H-3′), 5.56 (dd, 1H, *J* 9.1, 10.6 Hz, H-3″), 5.49 (d, 1H, *J* 8.5 Hz, H-1‴), 5.30 (d, 1H, *J* 8.4 Hz, H-1′), 5.23 (d, 1H, *J* 8.4 Hz, H-1″), 5.19 (dd, 1H, *J* 9.2, 9.9 Hz, H-4‴), 4.91 (t, 2H, *J* 9.1 Hz, H-4, H-4′), 4.78 (dd, 1H, *J* 9.2, 9.8 Hz, H-4″), 4.46 (dd, 1H, *J* 9.2, 11.0 Hz, H-2), 4.38 (dd, 1H, *J* 4.8, 12.5 Hz, H-6$_i$‴), 4.35 (dd, 1H, *J* 9.4, 10.6 Hz, H-2‴), 4.22–4.16 (m, 3H, H-2′, H-2″, H-6$_{ii}$‴), 3.93–3.89 (m, 2H, H-6$_i$′, H-5‴), 3.78–3.65 (m, 4H, H-6$_i$, H-5′, H-6$_{ii}$′, H-6$_i$″), 3.49 (ddd, 1H, *J* 3.2, 5.2, 10.3 Hz, H-5″), 3.42–3.38 (m, 2H, H-6$_{ii}$, H-6$_{ii}$″), 2.16, 2.04, 1.94, 1.93, 1.91, 1.86, 1.79, 1.78, 1.77 (s each, 3H each, 9 × COC*H*$_3$); ESIMS: calcd for $C_{76}H_{72}Cl_3N_5NaO_{34}$ 1726.3, found 1726.3 $[M+Na]^+$.

4.5. General procedure for preparing compounds 18, 28, 20, 31, 35, 39 and 42

A mixture of glycosyl acceptor (1 mmol), glycosyl donor (1.2 mmol) and powdered 4 Å molecular sieves (300 mg) in dried CH_2Cl_2 (40 mL) was stirred for 1 h at room temperature. The mixture was cooled to −40 °C for 30 min, followed by the dropwise addition of TMSOTf (0.2 mmol). After it was stirred at −40 °C for 30 min, the reaction mixture was warmed up naturally to room temperature and quenched with Et_3N. The solid was then filtered

off. The filtrate was concentrated under vacuum to produce a yellow syrup that was purified by column chromatography to afford the pure compound.

4.5.1. *p*-Methoxyphenyl 3,6-di-*O*-benzyl-4-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (18)

Yield 81%; R_f 0.18 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +43.7 (*c* 1.65, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.85–7.65 (m, 8H, Phth), 7.36–6.83 (m, 20H, Ph), 6.70–6.58 (m, 4H, Ph), 5.44 (d, 1H, *J* 8.4 Hz, H-1), 5.33 (d, 1H, *J* 8.4 Hz, H-1′), 5.16 (t, 1H, *J* 9.18 Hz, H-4′), 4.86 (d, 1H, *J* 12.4 Hz, PhCH_2), 4.61 (d, 1H, *J* 12.1 Hz, PhCH_2), 4.53–4.40 (m, 6H, H-3′, 5 × PhCH_2), 4.35 (dd, 1H, *J* 8.4, 10.3 Hz, H-2), 4.32 (d, 1H, *J* 12.1 Hz, PhCH_2), 4.29 (dd, 1H, *J* 8.1, 10.6 Hz, H-2′), 4.23 (t, 1H, *J* 8.5 Hz, H-3), 4.20 (t, 1H, *J* 8.8 Hz, H-4), 3.65 (s, 3H, OCH_3), 3.61–3.56 (m, 2H, H-5′, H-6_i′), 3.52–3.46 (m, 2H, H-6_i, H-6_{ii}′), 3.43–3.39 (m, 2H, H-5, H-6_{ii}), 1.92 (s, 3H, COCH_3); ESIMS: calcd for $C_{65}H_{60}N_2NaO_{15}$ 1131.4, found 1131.5 $[M+Na]^+$.

4.5.2. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (28)

Yield 85%; R_f 0.18 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +13.8 (*c* 0.60, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.88–7.73 (m, 8H, Phth), 6.77–6.67 (m, 4H, *Ph*OCH_3), 5.81 (dd, 1H, *J* 8.8, 10.3 Hz, H-3), 5.75 (d, 1H, *J* 8.4 Hz, H-1), 5.74 (dd, 1H, *J* 9.1, 11.0 Hz, H-3′), 5.47 (d, 1H, *J* 8.1 Hz, H-1′), 5.16 (t, 1H, *J* 10.3 Hz, H-4′), 4.45 (dd, 1H, *J* 4.1, 12.1 Hz, H-6_i′), 4.41 (dd, 1H, *J* 8.4, 10.3 Hz, H-2), 4.31 (dd, 1H, *J* 1.5, 11.7 Hz, H-6_i), 4.27 (dd, 1H, *J* 8.8, 10.6 Hz, H-2′), 4.09 (dd, 1H, *J* 2.2, 12.1 Hz, H-6_{ii}′), 4.03 (t, 1H, *J* 9.1 Hz, H-4), 3.85 (ddd, 1H, *J* 2.2, 4.0, 9.8 Hz, H-5′), 3.77 (ddd, 1H, *J* 1.9, 4.4, 9.9 Hz, H-5), 3.74 (dd, 1H, *J* 7.3, 12.1 Hz, H-6_{ii}), 3.69 (s, 3H, OCH_3), 2.11, 2.01, 1.97, 1.93, 1.83 (s each, 3H each, 5 × COCH_3); ^{13}C NMR ($CDCl_3$): δ 170.6, 170.1, 170.0, 169.8, 169.4 (5 × *C*OCH_3), 155.6–114.3 (Ph), 97.4 (C-1, C-1′), 75.6 (C-4), 72.4 (C-5), 71.9 (C-5′), 70.6, 70.3 (C-3, C-3′), 68.4 (C-4′), 62.0 (C-6), 61.6 (C-6′), 68.4 (C-4′), 55.6 (PhO*C*H_3), 54.9 (C-2), 54.8 (C-2′), 20.7, 20.6, 20.5, 20.3 (5 × COCH_3); ESIMS: calcd for $C_{45}H_{44}N_2NaO_{19}$ 939.2, found 939.2 $[M+Na]^+$.

4.5.3. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (20)

Yield 73%; R_f 0.23 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +13.0 (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.97–7.61 (m, 12H, Phth), 7.35–6.70 (m, 20H, Ph), 6.68–6.56 (m, 4H, *Ph*OCH_3), 5.79 (dd, 1H, *J* 8.8, 10.6 Hz, H-3″), 5.52 (d, 1H, *J* 8.5 Hz, H-1″), 5.40 (d, 1H, *J* 8.4 Hz, H-1), 5.13 (t, 1H, *J* 9.5 Hz, H-4″), 5.12 (d, 1H, *J* 8.0 Hz, H-1′), 4.87 (d, 1H, *J* 12.5 Hz, PhCH_2), 4.81 (d, 1H, *J* 12.8 Hz, PhCH_2), 4.59 (d, 1H, *J* 12.1 Hz, PhCH_2), 4.50–4.37 (m, 5H, PhCH_2), 4.32 (dd, 1H, *J* 8.5, 10.6 Hz, H-2″), 4.30–4.26 (m, 2H, H-2, H-4′), 4.21 (dd, 1H, *J* 3.7, 12.1 Hz, H-6_i″), 4.20–4.10 (m, 4H, H-3, H-4, H-2′, H-3′), 3.92 (dd, 1H, *J* 1.9, 12.1 Hz, H-6_{ii}″), 3.63 (s, 3H, PhO*C*H_3), 3.48–3.44 (m, 3H, H-6_i, H-6_i′, H-5″), 3.36–3.31 (m, 2H, H-5, H-6_{ii}), 3.24 (dd, 1H, *J* 2.9, 11.3 Hz, H-6_{ii}′), 2.98 (dd, 1H, *J* 1.4, 9.8 Hz, H-5′), 1.98, 1.90, 1.84 (s each, 3H each, 3 × COCH_3); ^{13}C NMR ($CDCl_3$): δ 170.6, 170.1, 169.5 (3 × *C*OCH_3), 168.3–114.2 (Ph), 97.4 (C-1), 96.8 (C-1′, C-1″), 76.8 (C-3′), 76.7 (C-3), 75.9 (C-4′), 75.6 (C-4), 74.6 (C-5), 74.4 (PhCH_2), 74.2 (C-5′), 72.5, 72.4 (PhCH_2), 71.4 (C-5″), 70.7 (C-3″), 68.7 (C-4″), 68.0 (C-6), 67.0 (C-6′), 61.4 (C-6″), 56.2 (C-2′), 55.6, 55.5, 55.3 (C-2, C-2″, OCH_3), 20.6, 20.4 (3 × COCH_3); ESIMS: calcd for $C_{83}H_{77}N_3NaO_{23}$ 1506.5, found 1506.5 $[M+Na]^+$.

4.5.4. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (31)

Yield 41%; R_f 0.54 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +17.3 (*c* 0.33, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.94–7.49 (m, 16H, Phth), 7.22–6.68 (m, 20H, *Ph*CH_2), 6.67–6.55 (m, 4H, *Ph*OCH_3), 5.69 (dd, 2H, *J* 9.2, 10.5 Hz, H-3″, H-3‴), 5.42 (d, 1H, *J* 8.2 Hz, H-1″), 5.38 (d, 1H, *J* 8.7 Hz, H-1), 5.36 (d, 1H, *J* 8.3 Hz, H-1‴), 5.13 (t, 1H, *J* 9.6 Hz, H-4‴), 5.07 (d, 1H, *J* 7.7 Hz, H-1′), 4.78 (d, 1H, *J* 12.8 Hz, PhCH_2), 4.70 (d, 1H, *J* 12.8 Hz, PhCH_2), 4.49 (d, 1H, *J* 11.9 Hz, PhCH_2), 4.46 (1H, dd, *J* 4.1, 12.4 Hz, H-6_i‴), 4.38–4.33 (m, 4H, PhCH_2), 4.27 (dd, 1H, *J* 8.7, 10.5 Hz, H-2), 4.22 (dd, 1H, *J* 8.2, 10.6 Hz, H-2‴), 4.16–4.07 (m, 6H, H-3, H-4, H-2′, H-3′, H-4′, H-2″), 4.00 (dd, 1H, *J* 2.3, 11.9 Hz, H-6_i‴), 3.98 (dd, 1H, *J* 1.9, 12.1 Hz, H-6_i″), 3.90 (dd, 1H, *J* 8.7, 10.1 Hz, H-4″), 3.76 (ddd, 1H, *J* 2.8, 3.2, 10.1 Hz, H-5‴), 3.63 (s, 3H, PhO*C*H_3), 3.45–3.42 (m, 2H, H-6_i, H-6_i′), 3.40 (dd, 1H, *J* 3.2, 11.9 Hz, H-6_{ii}″), 3.34–3.28 (m, 2H, H-5, H-6_{ii}), 3.21 (dd, 1H, *J* 2.8, 11.0 Hz, H-6_{ii}′), 3.12 (ddd, 1H, *J* 1.9, 3.2, 10.1 Hz, H-5″), 2.94 (d, 1H, *J* 8.2 Hz, H-5′), 2.05, 1.97, 1.89, 1.81, 1.76 (s each, 3H each, 5 × COCH_3); ^{13}C NMR ($CDCl_3$): δ 170.5, 170.1, 169.8, 169.7, 169.3 (5 × *C*OCH_3), 168.2–114.1 (Ph), 97.7 (C-1‴), 97.4 (C-1), 96.8 (C-1″), 96.5 (C-1′), 76.6 (C-4′), 75.7 (C-4, C-4″), 74.6 (C-5), 74.2 (C-5′), 72.5 (PhCH_2), 72.3 (PhCH_2), 72.5, 72.4 (PhCH_2), 71.7 (C-5″, C-5‴, PhCH_2), 70.9 (C-3″), 70.5 (C-3‴), 68.2 (C-4‴), 67.9 (C-6), 66.9 (C-6′), 61.8 (C-6″), 61.4 (C-6‴), 56.2 (C-2′), 55.7 (C-2″), 55.5 (C-2, OCH_3), 54.7 (C-2‴), 20.3–20.7 (5 × *C*OCH_3); ESIMS: calcd for $C_{101}H_{94}N_4NaO_{31}$ 1881.6, found 1881.6 $[M+Na]^+$.

4.5.5. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (35)

Yield 99%; R_f 0.18 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +37.8 (*c* 0.27, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.84–7.69 (m, 8H, Phth), 6.84–6.77 (m, 4H, *Ph*OCH_3), 5.91 (d, 1H, *J* 8.8 Hz, H-1), 5.80 (dd, 1H, *J* 9.4, 11.0 Hz, H-3), 5.64 (dd, 1H, *J* 9.4, 10.4 Hz, H-3′), 5.53 (d, 1H, *J* 8.2 Hz, H-1′), 5.12 (dd, 1H, *J* 8.8, 9.9 Hz, H-4′), 4.96 (dd, 1H, *J* 8.8, 9.8 Hz, H-4), 4.46 (dd, 1H, *J* 8.3, 10.4 Hz, H-2), 4.30 (dd, 1H, *J* 8.8, 11.0 Hz, H-2′), 4.22 (dd, 1H, *J* 4.4, 12.1 Hz, H-6_i′), 4.10 (dd, 1H, *J* 2.2, 12.1 Hz, H-6_{ii}′), 4.93 (dt, 1H, *J* 4.4, 9.3 Hz, H-5), 3.80 (d, 2H, *J* 4.4 Hz, H-6_i, H-6_{ii}), 3.77 (s, 3H, OCH_3), 3.89 (ddd, 1H, *J* 2.2, 4.4, 9.9 Hz, H-5′), 2.13, 2.03, 1.98, 1.85, 1.84 (s each, 3H each, 5 × COCH_3); ^{13}C NMR ($CDCl_3$): δ 170.7–169.2 (5 × *C*OCH_3), 155.5–114.5 (Ph), 97.2 (C-1′), 95.9 (C-1), 73.7 (C-5), 71.9 (C-5′), 70.9 (C-3′), 70.5 (C-3), 69.5 (C-4), 68.7 (C-4′), 67.6 (C-6), 61.7 (C-6′), 55.6 (OCH_3), 55.4 (C-2, C-2′), 20.8–20.4 (5 × COCH_3); ESIMS: calcd for $C_{45}H_{44}N_2NaO_{19}$ 939.2, found 939.2 $[M+Na]^+$.

4.5.6. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (39)

Yield 92%; R_f 0.28 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +46.0 (*c* 0.40, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.89–7.65 (m, 12H, Phth), 6.77–6.76 (m, 4H, *Ph*OCH_3), 5.80 (d, 1H, *J* 8.5 Hz, H-1), 5.77 (dd, 1H, *J* 8.8, 10.6 Hz, H-3″), 5.72 (dd, 1H, *J* 9.2, 10.6 Hz, H-3), 5.51 (dd, 1H, *J* 9.2, 10.6 Hz, H-3′), 5.48 (d, 1H, *J* 8.8 Hz, H-1″), 5.32 (d, 1H, *J* 8.4 Hz, H-1′), 5.20 (dd, 1H, *J* 9.2, 9.9 Hz, H-4″), 4.88 (dd, 1H, *J* 9.2, 10.3 Hz, H-4′), 4.86 (dd, 1H, *J* 9.2, 10.3 Hz, H-4), 4.41 (dd, 1H, *J* 8.4, 10.6 Hz, H-2), 4.37 (dd, 1H, *J* 4.4, 12.1 Hz, H-6_i″), 4.35 (dd, 1H, *J* 8.5, 10.6 Hz, H-2″), 4.19 (dd, 1H, *J* 1.9, 12.1 Hz, H-6_{ii}″), 4.18 (dd, 1H, *J* 8.8, 11.0 Hz, H-2′), 3.89 (ddd, 1H, *J* 2.2, 4.4, 10.3 Hz, H-5″), 3.81 (dd, 1H, *J* 2.2, 11.4 Hz, H-6_i′), 3.75 (s, 3H, OCH_3), 3.72 (dd, 1H, *J* 2.6, 11.0 Hz, H-6_i), 3.67 (ddd, 1H, *J* 2.6, 6.2, 9.9 Hz, H-5), 3.62 (dd, 1H, *J* 6.2, 11.3 Hz, H-6_{ii}′), 3.50 (dd, 1H, *J* 6.2, 11.0 Hz,

H-6_{ii}), 3.37 (ddd, 1H, *J* 2.2, 6.2, 9.9 Hz, H-5′), 2.14, 2.04, 1.96, 1.93, 1.86, 1.83, 1.78 (s each, 3H each, 7 × Ac); ^{13}C NMR ($CDCl_3$): δ 170.8–169.4 (7 × *C*OCH$_3$), 155.5–114.5 (Ph), 97.9 (C-1″), 97.1 (C-1′), 96.5 (C-1), 73.2, 73.0 (C-5, C-5′), 72.0 (C-5″), 70.8, 70.6 (C-3, C-3′, C-3″), 69.4 (C-4, C-4′), 69.0 (C-4″), 67.7 (C-6′), 67.6 (C-6), 61.9 (C-6″), 55.5 (OCH$_3$), 54.2 (C-2, C-2′, C-2″), 20.6–20.4 (7 × CO*C*H$_3$); ESIMS: calcd for $C_{63}H_{61}N_3NaO_{27}$ 1314.3, found 1314.3 [M+Na]$^+$.

4.5.7. *p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (42)

Yield 91%; R_f 0.19 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +30.8 (*c* 0.33, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.90–7.65 (m, 16H, Phth), 6.76–6.72 (m, 4H, *Ph*OCH$_3$), 5.80 (dd, 1H, *J* 9.1, 10.6 Hz, H-3‴), 5.75 (d, 1H, *J* 8.4 Hz, H-1), 5.72 (dd, 1H, *J* 9.2, 11.0 Hz, H-3), 5.64 (dd, 1H, *J* 9.1, 10.6 Hz, H-3′), 5.50 (dd, 1H, *J* 9.2, 10.6 Hz, H-3″), 5.49 (d, 1H, *J* 8.5 Hz, H-1‴), 5.32 (d, 1H, *J* 8.4 Hz, H-1′), 5.29 (d, 1H, *J* 8.8 Hz, H-1″), 5.20 (dd, 1H, *J* 9.5, 10.3 Hz, H-4‴), 4.93 (dd, 1H, *J* 9.2, 9.9 Hz, H-4′), 4.88 (dd, 1H, *J* 9.5, 10.3 Hz, H-4), 4.80 (dd, 1H, *J* 9.1, 10.3 Hz, H-4″), 4.40–4.36 (m, 3H, H-2, H-2‴, H-6_i‴), 4.21 (dd, 1H, *J* 8.4, 10.6 Hz, H-2′), 4.21 (dd, 1H, *J* 2.2, 12.4 Hz, H-6_{ii}‴), 4.16 (dd, 1H, *J* 8.5, 10.6 Hz, H-2″), 3.94–3.90 (m, 2H, H-6_i′, H-5‴), 3.77–3.63 (m, 8H, H-5, H-6_i, H-5′, H-6_{ii}′, H-6_i″, PhOC*H*$_3$), 3.50 (dd, 1H, *J* 6.2, 11.0 Hz, H-6_{ii}), 3.41 (dd, 1H, *J* 5.9, 11.3 Hz, H-6_{ii}″), 3.28 (ddd, 1H, *J* 2.9, 5.5, 9.9 Hz, H-5″), 2.16, 2.04, 1.97, 1.94, 1.86, 1.83, 1.78, 1.77 (some overlap, 27H, 9 × CO*CH*$_3$); ^{13}C NMR ($CDCl_3$): δ 170.8–169.4 (9 × *C*OCH$_3$), 167.9–114.5 (Ph), 98.0 (C-1‴), 97.6 (C-1′), 97.2 (C-1″), 96.7 (C-1), 73.5 (C-5), 72.9 (C-5′), 72.0 (C-5″), 72.0 (C-5‴), 70.8, 70.7, 70.6 (C-3, C-3′, C-3″, C-3‴), 69.6 (C-4′), 69.4 (C-4, C-4″), 68.9 (C-4‴), 68.1 (C-6′), 67.4 (C-6, C-6″), 62.0 (C-6‴), 55.5 (OCH$_3$), 54.4, 54.3 (C-2, C-2′, C-2″, C-2‴), 20.6–20.4 (9 × CO*C*H$_3$); ESIMS: calcd for $C_{81}H_{78}N_4NaO_{35}$ 1689.4, found 1689.4 [M+Na]$^+$.

4.6. *p*-Methoxyphenyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (19)

Compound **18** (1.44 mmol, 1.60 g) was dissolved in MeOH–CH_2Cl_2 (1:5, 60 mL) and then NaOMe in MeOH (50%) was added to pH 12. After stirring at rt for 2 h, the solution was neutralized with cation-exchange resin (H^+) and then filtered and concentrated to afford **19** as an amorphous solid (1.59 g, 100%) with R_f 0.21 (10:1 $CHCl_3$–CH_3OH); ^{1}H NMR ($CDCl_3$): δ 7.74–7.63 (m, 8H, Phth), 7.37–6.83 (m, 20H, *Ph*CH_2), 6.72–6.58 (m, 4H, *Ph*OCH$_3$), 5.45 (d, 1H, *J* 8.8 Hz, H-1), 5.31 (d, 1H, *J* 8.4 Hz, H-1′), 4.81 (d, 1H, *J* 11.8 Hz, PhC*H*$_2$), 4.79 (d, 1H, *J* 12.1 Hz, PhC*H*$_2$), 4.54–4.49 (m, 5H, 5 × PhC*H*$_2$), 4.43 (d, 1H, *J* 11.7 Hz, PhC*H*$_2$), 4.34 (dd, 1H, *J* 8.4, 10.6 Hz, H-2), 4.26 (dd, 1H, *J* 8.4, 11.0 Hz, H-3′), 4.21–4.18 (m, 2H, H-3, H-4), 4.17 (dd, 1H, *J* 8.5, 10.6 Hz, H-2′), 3.83 (dd, 1H, *J* 8.4, 9.5 Hz, H-4′), 3.72 (dd, 1H, *J* 4.4, 9.5 Hz, H-6_i), 3.65 (s, 3H, OCH$_3$), 3.58–3.53 (m, 2H, H-6_i, H-6_{ii}′), 3.45–3.40 (m, 3H, H-5, H-6_{ii}, H-5′), 3.14 (br s, 1H, OH); ESIMS: calcd for $C_{63}H_{58}N_2NaO_{14}$ 1089.4, found 1089.5 [M+Na]$^+$.

4.7. *p*-Methoxyphenyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (25)

To a solution of compound **24** (0.236 mmol, 115 mg) in pyridine (5 mL) was added Ac_2O (2 mL). The reaction mixture was stirred at rt for 3 h, then co-evaporated with toluene under reduced pressure to afford a syrup that was purified by silica gel column chromatography (2:1 hexane–EtOAc) to yield compound **25** (125 mg, 100%) as a white solid with R_f 0.45 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +23.9 (*c* 0.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.88–7.73 (m, 4H, Phth), 7.47–7.36 (m, 5H, *Ph*CH), 6.86–6.74 (m, 4H, *Ph*OCH$_3$), 5.97 (d, 1H, *J* 8.5 Hz, H-1), 5.95 (dd, 1H, *J* 9.1, 10.3 Hz, H-3), 5.57 (s, 1H, PhC*H*), 4.55 (dd, 1H, *J* 8.4, 10.3 Hz, H-2), 4.43 (dd, 1H, *J* 4.7, 10.6 Hz, H-6_i), 3.90–3.81 (3H, m, H-4, H-5, H-6_{ii}), 3.72 (s, 3H, OC*H*$_3$), 1.92 (3H, s, CO*CH*$_3$); ESIMS: calcd for $C_{30}H_{27}KNO_9$ 584.1, found 584.1 [M+K]$^+$.

4.8. *p*-Methoxyphenyl 3-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (26)

A solution of **25** (0.229 mmol, 125 mg) in 80% AcOH (5 mL) was stirred at 60 °C for 2 h and then concentrated in vacuum. The residue was directly purified by silica gel column chromatography (20:1 $CHCl_3$–MeOH) to afford **26** (97 mg, 93%) as a white solid: R_f 0.23 (20:1 $CHCl_3$–MeOH); $[\alpha]_D^{20}$ +36.0 (*c* 0.40, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.87–7.74 (m, 4H, Phth), 6.85–6.73 (m, 4H, *Ph*OCH$_3$), 5.93 (d, 1H, *J* 8.5 Hz, H-1) 5.72 (dd, 1H, *J* 9.1, 10.6 Hz, H-3), 4.48 (dd, 1H, *J* 8.5, 10.6 Hz, H-2), 4.01 (ddd, 1H, *J* 3.2, 5.8, 11.8 Hz, H-5), 3.93–3.89 (m, 2H, H-6_i, H-6_{ii}), 3.75–3.73 (m, 4H, H-4, OCH$_3$), 2.90 (br s, 1H, OH), 2.11 (br s, 1H, OH), 1.98 (s, 3H, CO*CH*$_3$); ESIMS: calcd for $C_{23}H_{23}KNO_9$ 496.1, found 496.1 [M+K]$^+$.

4.9. *p*-Methoxyphenyl 3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (27)

To a solution of compound **26** (11.7 mmol, 5.34 g) in pyridine (30 mL) and CH_2Cl_2 (100 mL) was added dropwise Ac_2O (12.26 mmol, 1.16 mL) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was allowed to warm to rt and stir at rt for 12 h. The solution was then diluted with EtOA*c* (300 mL) and successively washed with 5% HCl (2 × 100 mL), satd $NaHCO_3$ (2 × 100 mL) and brine (2 × 100 mL). The organi*c* layer was dried over anhyd Na_2SO_4 and then concentrated under vacuum. The residue was purified by silica gel column chromatography (4:3 petroleum ether–EtOAc) to afford compound **27** (4.96 g, 85%) as a white solid with R_f 0.23 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +16.0 (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.86–7.73 (m, 4H, Phth), 6.87–6.72 (m, 4H, *Ph*OCH$_3$), 5.88 (d, 1H, *J* 8.4 Hz, H-1), 5.74 (dd, 1H, *J* 8.8, 10.6 Hz, H-3), 4.54 (dd, 1H, *J* 4.1, 11.8 Hz, H-6_i), 4.49 (dd, 1H, *J* 8.5, 10.6 Hz, H-2), 4.40 (dd, 1H, *J* 1.9, 12.1 Hz, H-6_{ii}), 3.85 (ddd, 1H, *J* 2.6, 4.8, 9.9 Hz, H-5), 3.75 (t, 4H, *J* 9.5 Hz, H-4), 3.72 (s, 3H, OCH$_3$), 3.28 (br s, 1H, OH), 2.14, 1.95 (s each, 3H each, 2 × CO*CH*$_3$); ESIMS: calcd for $C_{25}H_{25}NNaO_{10}$ 522.1, found 522.1 [M+Na]$^+$.

4.10. General procedure for protected saponins 45–58

A mixture of trityl oleanolic ester or trityl ursolic ester (1 mmol), glycosyl donor (1.5 mmol) and powdered 4 Å molecular sieves (300 mg) in dried CH_2Cl_2 (40 mL) was stirred for 0.5 h at room temperature. The mixture was cooled to −70 °C for 30 min, followed by the dropwise addition of TMSOTf (0.2 mmol) under Ar protection. After stirring at −70 °C for 45 min, the mixture was quenched with MeOH. The reaction mixture was allowed to warm up to room temperature, TsOH was added until the solution was adjusted to pH 2, and stirring was continued at rt for 30 min. The solid was then filtered off, and the filtrate was concentrated under vacuum to afford a yellow syrup that was purified by silica gel column chromatography to yield the pure saponin.

4.10.1. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopranosyl)oleanolic acid (45)

Yield 78%; R_f 0.59 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +51.4 (*c* 0.65, $CHCl_3$); ^{1}H NMR (DMSO-d_6): δ 12.02 (br s, 1H, COOH), 7.89–7.87 (m, 4H, Phth), 5.69 (dd, 1H, *J* 9.1, 11.0 Hz, H-3′), 5.31 (d, 1H, *J* 8.2 Hz, H-1′), 5.14 (t, 1H, *J* 3.2 Hz, H-12), 4.96 (t,

1H, *J* 9.1 Hz, H-4′), 4.28 (dd, 1H, *J* 5.0, 11.9 Hz, H-6$_i$′), 4.08 (dd, 1H, *J* 8.3, 10.6 Hz, H-2′), 4.04–4.01 (m, 2H, H-5′, H-6$_{ii}$′), 3.04 (dd, 1H, *J* 4.6, 11.9 Hz, H-3), 2.72 (dd, 1H, *J* 3.7, 12.8 Hz, H-18), 2.05–0.59 (m, 22H), 2.03, 2.00, 1.80 (s each, 3H each, 3 × COC*H*$_3$), 1.05, 0.87, 0.86, 0.79, 0.66, 0.46, 0.34 (s each, 3H each, 7 × Me); ESIMS: calcd for $C_{50}H_{66}NO_{12}$ 872.4585, found 872.4588 $[M-H]^-$.

4.10.2. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopranosyl)ursolic acid (46)

Yield 77%; R_f 0.59 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +16.4 (*c* 0.30, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.88–7.72 (m, 4H, Phth), 5.83 (dd, 1H, *J* 9.2, 11.0 Hz, H-3′), 5.37 (d, 1H, *J* 8.4 Hz, H-1′), 5.21 (t, 1H, *J* 3.7 Hz, H-12), 5.13 (dd, 1H, *J* 9.1, 9.8 Hz, H-4′), 4.36 (dd, 1H, *J* 8.5, 10.6 Hz, H-2′), 4.31 (dd, 1H, *J* 5.5, 12.1 Hz, H-6$_i$′), 4.15 (dd, 1H, *J* 2.6, 12.1 Hz, H-6$_{ii}$′), 3.88 (ddd, 1H, *J* 2.2, 5.5, 9.9 Hz, H-5′), 3.04 (dd, 1H, *J* 4.4, 11.8 Hz, H-3), 2.15 (d, 1H, *J* 11.3 Hz, H-18), 2.06–0.56 (m, 22H), 2.10, 2.04, 1.87 (s each, 3H each, 3 × COC*H*$_3$), 1.01 (s, 3H), 0.93 (d, 3H, *J* 6.5 Hz), 0.85 (d, 3H, *J* 6.6 Hz), 0.84 (s, 3H), 0.70 (s, 3H), 0.55 (s, 3H), 0.41 (s, 3H); ESIMS: calcd for $C_{50}H_{66}NO_{12}$ 872.4585, found 872.4557 $[M-H]^-$.

4.10.3. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)oleanolic acid (47)

Yield 69%; R_f 0.28 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +28.8 (*c* 0.40, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.87–7.71 (m, 8H, Phth), 5.77 (dd, 1H, *J* 8.8, 10.6 Hz, H-3′), 5.74 (dd, 1H, *J* 9.2, 10.6 Hz, H-3″), 5.45 (d, 1H, *J* 8.0 Hz, H-1″), 5.27 (d, 1H, *J* 8.5 Hz, H-1′), 5.22 (t, 1H, *J* 3.7 Hz, H-12), 5.15 (t, 1H, *J* 9.8 Hz, H-4″), 4.43 (dd, 1H, *J* 4.4, 12.4 Hz, H-6$_i$″), 4.27–4.24 (m, 2H, H-6$_i$′, H-2″), 4.19 (dd, 1H, *J* 8.5, 10.6 Hz, H-2′), 4.08 (dd, 1H, *J* 2.2, 12.5 Hz, H-6$_{ii}$″), 3.90 (t, 1H, *J* 9.5 Hz, H-4′), 3.83 (ddd, 1H, *J* 2.2, 4.0, 10.3 Hz, H-5″), 3.71–3.66 (m, 2H, H-5′, H-6$_{ii}$′), 2.94 (dd, 1H, *J* 4.4, 11.8 Hz, H-3), 2.76 (dd, 1H, *J* 4.0, 13.5 Hz, H-18), 2.13–0.51 (m, 22H), 2.11, 2.00, 1.96, 1.91, 1.83 (s each, 3H each, 5 × COC*H*$_3$), 1.04, 0.89, 0.88, 0.76, 0.63, 0.49, 0.35 (s each, 3H each, 7 × Me); ESIMS: calcd for $C_{68}H_{83}N_2O_{20}$ 1247.5539, found 1247.5588 $[M-H]^-$.

4.10.4. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O* -acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)ursolic acid (48)

Yield 72%; R_f 0.28 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +12.2 (*c* 0.60, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.87–7.71 (m, 8H, Phth), 5.78 (dd, 1H, *J* 9.2, 10.6 Hz, H-3′), 5.73 (dd, 1H, *J* 9.2, 10.3 Hz, H-3″), 5.45 (d, 1H, *J* 8.0 Hz, H-1″), 5.27 (d, 1H, *J* 8.5 Hz, H-1′), 5.17 (t, 1H, *J* 3.7 Hz, H-12), 5.15 (dd, 1H, *J* 9.5, 9.8 Hz, H-4″), 4.42 (dd, 1H, *J* 4.4, 12.5 Hz, H-6$_i$″), 4.27 (d, 1H, *J* 10.6 Hz, H-6$_i$′), 4.26 (dd, 1H, *J* 8.5, 10.6 Hz, H-2″), 4.19 (dd, 1H, *J* 8.5, 10.3 Hz, H-2′), 4.08 (dd, 1H, *J* 2.2, 12.4 Hz, H-6$_{ii}$″), 3.90 (t, 1H, *J* 9.5 Hz, H-4′), 3.84 (ddd, 1H, *J* 2.2, 4.0, 9.9 Hz, H-5″), 3.72–3.66 (m, 2H, H-5′, H-6$_{ii}$′), 2.94 (dd, 1H, *J* 4.4, 11.7 Hz, H-3), 2.13 (d, 1H, *J* 11.0 Hz, H-18), 2.04–0.49 (m, 22H), 2.11, 2.00, 1.96, 1.91, 1.83 (s each, 3H each, 5 × COC*H*$_3$), 0.92 (d, 3H, *J* 6.2 Hz), 0.82 (d, 3H, *J* 6.2 Hz), 0.98, 0.78, 0.65, 0.49, 0.36 (s each, 3H each, 5 × Me); ^{13}C NMR ($CDCl_3$): δ 182.7, 170.6–169.4 (5 × *C*OCH$_3$), 137.8, 134.4–123.4 (Ph), 125.7, 99.7 (C-1′), 97.3 (C-1″), 90.6, 75.9 (C-4′), 72.1 (C-5′), 71.9 (C-5″), 70.7 (C-3′), 70.6 (C-3″), 68.4 (C-4″), 62.3 (C-6′), 61.6 (C-6″), 55.3 (C-2′), 55.0, 54.8 (C-2″), 52.5, 47.8, 47.3, 41.8, 39.3, 39.0, 38.8, 38.3, 36.6, 32.7, 30.5, 27.9, 27.4, 25.3, 24.0, 23.5, 23.2, 21.1, 20.7–20.3 (5 × *C*OCH$_3$), 17.9, 17.0, 16.3, 15.3; ESIMS: calcd for $C_{68}H_{83}N_2O_{20}$ 1247.5539, found 1247.5538 $[M-H]^-$.

4.10.5. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)oleanolic acid (49)

Yield 89%; R_f 0.46 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +22.7 (*c* 1.20, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.95–7.49 (m, 12H, Phth), 7.34–6.70 (m, 20H, *Ph*CH$_2$), 5.78 (dd, 1H, *J* 9.1, 10.3 Hz, H-3‴), 5.51 (d, 1H, *J* 8.5 Hz, H-1‴), 5.18 (t, 1H, *J* 3.3 Hz, H-12), 5.13 (d, 1H, *J* 8.8 Hz, H-1″), 5.12 (t, 1H, *J* 10.1 Hz, H-4‴), 4.88 (d, 1H, *J* 9.6 Hz, H-1′), 4.87 (d, 1H, *J* 12.9 Hz, PhC*H*$_2$), 4.79 (d, 1H, *J* 12.9 Hz, PhC*H*$_2$), 4.57 (d, 1H, *J* 12.1 Hz, PhC*H*$_2$), 4.47–4.42 (m, 3H, PhC*H*$_2$), 4.36–4.30 (m, 3H, 2 × PhC*H*$_2$, H-2‴), 4.27 (dd, 1H, *J* 8.5, 9.8 Hz, H-4″), 4.22–4.07 (m, 5H, H-2′, H-3′, H-2″, H-3″, H-6$_i$‴), 3.97–3.91 (m, 2H, H-4′, H-6$_{ii}$‴), 3.47–3.44 (m, 2H, H-6$_{ii}$″, H-5‴), 3.39 (d, 1H, *J* 9.1 Hz, H-6$_i$′), 3.27–3.24 (m, 3H, H-5′, H-6$_i$′, H-6$_{ii}$″), 3.02 (d, 1H, *J* 9.1, H-5″), 2.77–2.73 (m, 2H, H-3, H-18), 1.98, 1.91, 1.84 (s each, 3H each, 3 × COC*H*$_3$), 1.76–0.41 (m, 22H), 0.98, 0.87, 0.85, 0.71, 0.59, 0.38, 0.24 (s each, 3H each, 7 × Me); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.1, 169.5 (*C*OCH$_3$ × 3), 168.3–167.6 (NCOPh), 138.7–122.5 (Ph), 134.5, 123.7, 100.0 (C-1′), 97.0 (C-1″), 96.8 (C-1‴), 89.7, 76.3 (C-4′), 76.0 (C-4″), 74.4 (C-5″), 74.3 (C-5′), 74.2 (PhCH_2 × 2), 72.5 (PhCH_2), 72.4 (PhCH_2), 71.4 (C-5‴), 70.7 (C-3‴), 68.8 (C-4‴), 68.3 (C-6′), 67.1 (C-6″), 61.5 (C-6‴), 56.6 (C-2″), 56.0 (C-2′), 55.3, 55.0 (C-2‴), 47.4, 46.5, 45.9, 41.5, 40.9, 39.1, 38.2, 38.1, 36.6, 33.8, 33.0, 32.4, 30.6, 29.4, 27.6, 27.3, 25.8, 25.4, 23.5, 23.3, 22.9, 20.6–20.4 (3 × *C*OCH$_3$), 17.9, 17.0, 16.2, 15.1; ESIMS: calcd for $C_{106}H_{116}N_3O_{24}$ 1814.7949, found 1814.7915 $[M-H]^-$.

4.10.6. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)ursolic acid (50)

Yield 86%; R_f 0.44 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +5.5 (*c* 0.65, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.96–7.49 (m, 12H, Phth), 7.34–6.69 (m, 20H, *Ph*CH$_2$), 5.79 (dd, 1H, *J* 9.2, 10.5 Hz, H-3‴), 5.51 (d, 1H, *J* 8.3 Hz, H-1‴), 5.14–5.11 (m, 3H, H-12, H-1″, H-4‴), 4.88 (d, 1H, *J* 8.7 Hz, H-1′), 4.86 (d, 1H, *J* 13.3 Hz, PhC*H*$_2$), 4.79 (d, 1H, *J* 12.8 Hz, PhC*H*$_2$), 4.58 (d, 1H, *J* 11.9 Hz, PhC*H*$_2$), 4.47–4.42 (m, 3H, PhC*H*$_2$), 4.36–4.30 (m, 3H, 2 × PhC*H*$_2$, H-2‴), 4.27 (t, 1H, *J* 9.6 Hz, H-4″), 4.23–4.05 (m, 5H, H-2′, H-3′, H-2″, H-3″, H-6$_i$‴), 3.97–3.91 (m, 2H, H-4′, H-6$_{ii}$‴), 3.47–3.43 (m, 2H, H-6$_{ii}$″, H-5‴), 3.39 (d, 1H, *J* 8.7 Hz, H-6$_i$′), 3.27–3.23 (m, 3H, H-5′, H-6$_i$′, H-6$_{ii}$″), 3.02 (d, 1H, *J* 9.6 Hz, H-5″), 2.76 (dd, 1H, *J* 4.1, 11.5 Hz, H-3), 2.10 (d, 1H, *J* 11.0 Hz, H-18), 1.98, 1.91, 1.84 (s each, 3H each, 3 × COC*H*$_3$), 1.94–0.42 (m, 22H), 0.90 (d, 3H, *J* 6.4 Hz), 0.79 (d, 3H, *J* 5.9 Hz), 0.93, 0.73, 0.61, 0.39, 0.25 (s each, 3H each, 5 × Me); ^{13}C NMR ($CDCl_3$): δ 183.0, 170.7, 170.1, 169.5 (3 × *C*OCH$_3$), 168.3–167.6 (NCOPh), 138.7–122.9 (Ph), 137.8, 125.7, 100.0 (C-1′), 97.0 (C-1″), 96.8 (C-1‴), 89.6, 76.3 (C-4′), 76.0 (C-4″), 74.4 (C-5″), 74.3 (C-5′), 74.2 (2 × PhCH_2), 72.4 (2 × PhCH_2), 71.4 (C-5‴), 70.7 (C-3‴), 68.8 (C-4‴), 68.3 (C-6′), 67.1 (C-6″), 61.4 (C-6‴), 56.6 (C-2″), 56.0 (C-2′), 55.3, 55.0 (C-2‴), 52.5, 47.9, 47.3, 41.8, 39.3, 39.0, 38.7, 38.3, 38.2, 36.6, 36.5, 32.7, 30.6, 27.9, 27.3, 25.5, 24.0, 23.4, 23.2, 21.1, 20.6–20.4 (3 × *C*OCH$_3$), 17.9, 16.9, 16.2, 15.2; ESIMS: calcd for $C_{106}H_{116}N_3O_{24}$ 1814.7949, found 1814.7929 $[M-H]^-$.

4.10.7. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)oleanolic acid (51)

Yield 82%; R_f 0.65 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +14.5 (*c* 1.10, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.92–7.47 (m, 16H, Phth), 7.22–6.67 (m, 20H, *Ph*CH$_2$), 5.69–5.67 (m, 2H, H-3‴, H-3⁗), 5.41 (d, 1H, *J* 8.4 Hz, H-1‴), 5.36 (d, 1H, *J* 8.4 Hz, H-1⁗), 5.18 (t, 1H, *J* 3.3 Hz, H-12), 5.13 (t, 1H, *J* 9.9 Hz, H-4⁗), 5.08 (d, 1H, *J* 8.4 Hz,

H-1″), 4.87 (d, 1H, *J* 8.1 Hz, H-1′), 4.75 (d, 1H, *J* 13.1 Hz, PhC*H*$_2$), 4.70 (d, 1H, *J* 12.8 Hz, PhC*H*$_2$), 4.49–4.48 (m, 7H, 6 × PhC*H*$_2$, H-6$_i$‴), 4.22 (dd, 1H, *J* 8.5, 10.6 Hz, H-2⁗), 4.16–3.86 (m, 10H, H-2′, H-3′, H-4′, H-2″, H-3″, H-4″, H-2‴, H-4‴, H-6‴, H-6⁗), 3.76 (ddd, 1H, *J* 2.6, 3.3, 10.3 Hz, H-5⁗), 3.43–3.34 (m, 3H, H-6$_i$′, H-6$_i$″, H-6$_{ii}$‴), 3.24–3.20 (m, 3H, H-5′, H-6$_{ii}$′, H-6$_{ii}$″), 3.11 (dt, 1H, *J* 3.3, 9.5 Hz, H-5‴), 2.98 (d, 1H, *J* 7.3 Hz, H-5″), 2.76–2.71 (m, 2H, H-3, H-18), 2.05, 1.97, 1.89, 1.81, 1.77 (3H each, s each, 5 × COC*H*$_3$), 1.76–0.40 (m, 22H), 0.98, 0.87, 0.85, 0.71, 0.59, 0.38, 0.22 (s each, 3H each, 7 × Me); ^{13}C NMR (CDCl$_3$): δ 182.8, 170.5, 170.1, 169.9, 169.7, 169.3 (5 × *C*OCH$_3$), 168.2–167.5 (N*C*OPh), 138.7–123.5 (Ph), 134.5, 123.6, 99.8 (C-1′), 97.7 (C-1⁗), 96.9 (C-1″), 96.6 (C-1‴), 89.6, 76.1 (C-4″), 75.7 (C-4′, C-4‴), 74.2 (2 × PhCH$_2$), 74.1 (C-5′,C-5″), 72.4 (PhCH$_2$), 72.2 (PhCH$_2$), 71.7 (C-5‴, C-5⁗), 70.9 (C-3⁗), 70.5 (C-3‴), 68.8 (C-4⁗), 68.2 (C-6′), 66.9 (C-6″), 61.8 (C-6‴), 61.4 (C-6⁗), 56.5 (C-2″), 56.0 (C-2′), 55.7 (C-2‴), 55.0, 54.7 (C-2⁗), 47.4, 43.4, 45.8, 41.4, 40.8, 39.1, 38.1, 36.5, 33.7, 33.0, 32.4, 30.6, 29.3, 27.5, 27.2, 25.7, 25.4, 23.5, 23.3, 22.8, 20.6–20.3 (5 × COCH$_3$), 17.8, 16.9, 16.1, 15.1.

4.10.8. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)ursolic acid (52)

Yield 84%; R_f 0.47 (1:2 petroleum ether–EtOAc); ^{1}H NMR (CDCl$_3$): δ 7.92–7.47 (m, 16H, Phth), 7.22–6.68 (m, 20H, *Ph*CH$_2$), 5.71–5.67 (m, 2H, H-3‴, H-3⁗) 5.41 (d, 1H, *J* 8.2 Hz, H-1‴), 5.36 (d, 1H, *J* 8.7 Hz, H-1⁗), 5.15–5.12 (m, 2H, H-12, H-4⁗), 5.08 (d, 1H, *J* 8.2 Hz, H-1″), 4.86 (d, 1H, *J* 7.8 Hz, H-1′), 4.75 (d, 1H, *J* 12.8 Hz, PhC*H*$_2$), 4.70 (d, 1H, *J* 12.8 Hz, PhC*H*$_2$), 4.49–4.28 (m, 7H, 6 × PhC*H*$_2$, H-6$_i$⁗), 4.22 (dd, 1H, *J* 8.3, 10.6 Hz, H-2⁗), 4.17–3.86 (m, 10H, H-2′, H-3′, H-4′, H-2″, H-3″, H-4″, H-2‴, H-4‴, H-6‴, H-6⁗), 3.76 (dt, 1H, *J* 2.8, 10.8 Hz, H-5⁗), 3.43–3.33 (m, 3H, H-6$_i$′, H-6$_i$″, H-6$_{ii}$‴), 3.24–3.20 (m, 3H, H-5′, H-6$_{ii}$′, H-6$_{ii}$″), 3.11 (d, 1H, *J* 9.6 Hz, H-5‴), 2.98 (d, 1H, *J* 7.7 Hz, H-5″), 2.75 (dd, 1H, *J* 4.1, 11.5 Hz, H-3), 2.09 (d, 1H, *J* 11.5 Hz, H-18), 2.05, 1.97, 1.89, 1.81, 1.77 (s each, 3H each, 5 × COC*H*$_3$), 1.79–0.38 (m, 22H), 0.90 (d, 3H *J* 5.9 Hz), 0.79 (d, 3H, *J* 6.4 Hz), 0.92, 0.72, 0.61, 0.38, 0.24 (s each, 3H each, 5 × Me); ^{13}C NMR (CDCl$_3$): δ 182.8, 170.6–169.4 (5 × *C*OCH$_3$), 168.3–167.5 (N*C*OPh), 138.7–122.8 (Ph), 137.8, 125.7, 100.0 (C-1′), 97.7 (C-1⁗), 97.0 (C-1″), 96.6 (C-1‴), 89.5, 76.2 (C-4″), 75.7 (C-4′, C-4‴), 74.2 (2 × PhCH$_2$), 74.1 (C-5′,C-5″), 72.4 (PhCH$_2$), 72.3 (PhCH$_2$), 71.8 (C-5⁗), 71.8 (C-5‴), 70.9 (C-3⁗), 70.5 (C-3‴), 68.8 (C-4⁗), 68.2 (C-6′), 66.9 (C-6″), 61.8 (C-6‴), 61.4 (C-6⁗), 56.5 (C-2″), 56.0 (C-2′), 55.7 (C-2‴), 55.0, 54.7 (C-2⁗), 52.4, 47.8, 47.3, 41.8, 39.3, 39.0, 38.7, 38.3, 38.2, 36.6, 36.5, 32.7, 30.5, 27.9, 27.3, 25.5, 24.0, 23.4, 23.2, 21.2, 20.7–20.4 (5 × COCH$_3$), 17.8, 16.9, 16.2, 15.2.

4.10.9. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)oleanolic acid (53)

Yield 62%; R_f 0.28 (1:1 petroleum ether–EtOAc); ^{1}H NMR (CDCl$_3$): δ 7.90–7.72 (m, 8H, Phth), 5.72 (dd, 1H, *J* 8.8, 10.4 Hz, H-3′), 5.71 (dd, 1H, *J* 8.8, 10.4 Hz, H-3″), 5.56 (d, 1H, *J* 8.7 Hz, H-1″), 5.31 (d, 1H, *J* 8.2 Hz, H-1′), 5.27 (t, 1H, *J* 3.3 Hz, H-12), 5.16 (t, 1H, *J* 9.6 Hz, H-4″), 4.90 (t, 1H, *J* 9.6 Hz, H-4′), 4.33–4.29 (m, 2H, H-2″, H-6$_i$″), 4.25 (dd, 1H, *J* 8.2, 10.6 Hz, H-2′), 4.20 (dd, 1H, *J* 2.3, 12.4 Hz, H-6$_{ii}$″), 3.85 (ddd, 1H, *J* 2.3, 5.0, 10.1 Hz, H-5″), 3.82–3.72 (m, 3H, H-5′, H-6$_i$′, H-6$_{ii}$′), 3.08 (dd, 1H, *J* 4.6, 11.9 Hz, H-3), 2.80 (dd, 1H, *J* 3.7, 13.7 Hz, H-18), 2.13–0.58 (m, 22H), 2.15, 2.03, 1.96, 1.85, 1.82(s each, 3H each, 5 × COC*H*$_3$), 1.07, 0.92, 0.89, 0.75, 0.67, 0.44, 0.36 (s each, 3H each, 7 × Me); ^{13}C NMR (CDCl$_3$): δ 170.7–169.5 (3 × *C*OCH$_3$), 134.3–122.5 (Ph), 123.7, 99.7 (C-1′), 97.5 (C-1″), 90.3, 73.1 (C-5′), 72.1 (C-5″), 71.0 (C-3″), 70.6 (C-3′), 69.9 (C-4′), 68.9 (C-4″), 68.0 (C-6′), 62.1 (C-6″), 55.0, 54.8 (C-2′), 54.4 (C-2″), 47.4, 46.5, 45.9, 41.5, 40.9, 39.2, 38.3, 38.1, 36.7, 33.8, 33.1, 32.4, 30.6, 29.7, 27.6, 27.3, 25.8, 25.2, 23.6, 23.5, 22.9, 20.8–20.4(5 × COCH$_3$), 17.9, 17.1, 16.2, 15.2.

4.10.10. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)ursolic acid (54)

Yield 64%; R_f 0.28 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +50.8 (*c* 0.28, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.90–7.72 (m, 8H, Phth), 5.73 (dd, 1H, *J* 8.8, 10.4 Hz, H-3′), 5.72 (dd, 1H, *J* 8.8, 10.4 Hz, H-3″), 5.59 (d, 1H, *J* 8.8 Hz, H-1″), 5.31 (d, 1H, *J* 8.2 Hz, H-1′), 5.22 (t, 1H, *J* 3.3 Hz, H-12), 5.16 (t, 1H, *J* 9.9 Hz, H-4″), 4.88 (t, 1H, *J* 9.3 Hz, H-4′), 4.32–4.29 (m, 2H, H-2″, H-6$_i$″), 4.26 (dd, 1H, *J* 8.8, 11.0 Hz, H-2′), 4.20 (dd, 1H, *J* 1.7, 12.1 Hz, H-6$_{ii}$″), 3.84 (ddd, 1H, *J* 2.2, 4.9, 10.4 Hz, H-5″), 3.78–3.75 (m, 3H, H-5′, H-6$_i$′, H-6$_{ii}$′), 3.16 (dd, 1H, *J* 4.4, 11.5 Hz, H-3), 2.16 (d, 1H, *J* 11.6 Hz, H-18), 2.05–0.61 (m, 22H), 2.15, 2.02, 1.96, 1.84, 1.82 (s each, 3H each, 5 × COC*H*$_3$), 0.93 (d, 3H, *J* 6.6 Hz), 0.84 (d, 3H, *J* 6.1 Hz), 1.03, 0.78, 0.70, 0.44, 0.40 (s each, 3H each, 5 × Me); ^{13}C NMR (CDCl$_3$): δ 170.7–169.4 (5 × *C*OCH$_3$), 137.9, 134.3–123.6 (Ph), 125.7, 99.8 (C-1′), 97.4 (C-1″), 90.1, 73.4 (C-5′), 72.0 (C-5″), 70.8 (C-3″), 70.5 (C-3′), 69.8 (C-4′), 68.9 (C-4″), 67.7 (C-6′), 62.0 (C-6″), 54.9, 54.7 (C-2′), 54.4 (C-2″), 52.5, 47.9, 47.3, 41.8, 39.3, 39.0, 38.7, 38.3, 38.2, 36.7, 36.6, 32.7, 30.6, 27.9, 27.3, 25.3, 24.0, 23.4, 23.3, 21.1, 20.8–20.4 (5 × COCH$_3$), 17.9, 17.0, 16.9, 16.2, 15.4; ESIMS: calcd for $C_{68}H_{83}N_2O_{20}$ 1247.5539, found 1247.5544 $[M-H]^-$.

4.10.11. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)oleanolic acid (55)

Yield 69%; R_f 0.39 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +29.9 (*c* 0.70, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.93–7.71 (m, 12H, Phth), 5.59 (dd, 1H, *J* 9.2, 10.6 Hz, H-3‴), 5.66 (dd, 1H, *J* 9.2, 10.5 Hz, H-3′), 5.59 (dd, 1H, *J* 9.2, 10.6 Hz, H-3″), 5.50 (d, 1H, *J* 8.8 Hz, H-1‴), 5.42 (d, 1H, *J* 8.3 Hz, H-1″), 5.27 (t, 1H, *J* 3.2 Hz, H-12), 5.23 (d, 1H, *J* 8.7 Hz, H-1′), 5.20 (t, 1H, *J* 9.7 Hz, H-4‴), 4.92 (t, 1H, *J* 9.7 Hz, H-4″), 4.74 (t, 1H, *J* 9.2 Hz, H-4′), 4.38 (dd, 1H, *J* 4.6, 12.4 Hz, H-6$_i$‴), 4.35 (dd, 1H, *J* 8.3, 10.6 Hz, H-2‴), 4.23–4.16 (m, 3H, H-2′, H-2″, H-6$_{ii}$‴), 3.91 (ddd, 1H, *J* 2.3, 5.0, 10.6 Hz, H-5‴), 3.87 (d, 1H, *J* 8.7 Hz, H-6″), 3.73–3.68 (m, 2H, H-5″, H-6$_{ii}$″), 3.63 (dd, 1H, *J* 2.2, 12.4 Hz, H-6$_i$′), 3.55–3.49 (m, 2H, H-5′, H-6$_{ii}$′), 3.10 (dd, 1H, *J* 4.6, 11.9 Hz, H-3), 2.80 (dd, 1H, *J* 4.1, 13.7 Hz, H-18), 2.16, 2.05, 1.99, 1.94, 1.86, 1.83, 1.78 (3H each, s each, 7 × COC*H*$_3$), 2.17–0.59 (m, 22H), 1.07, 0.92, 0.89, 0.76, 0.68, 0.43, 0.38 (s each, 3H each, 7 × Me); ^{13}C NMR (CDCl$_3$): δ 170.8–169.5 (7 × *C*OCH$_3$), 168.2–167.3 (N*C*OPh), 143.5, 134.6–122.6 (Ph), 123.8, 99.6 (C-1′), 98.0 (C-1‴), 97.2 (C-1″), 89.8, 73.1 (C-5′), 73.0 (C-5″), 72.1 (C-5‴), 70.8 (C-3″, C-3‴), 70.5 (C-3′), 69.9 (C-4′), 69.6 (C-4″), 68.9 (C-4‴), 68.0 (C-6″), 67.8 (C-6′), 62.0 (C-6‴), 54.9 (C-2′), 54.8 (C-2″), 54.4 (C-5, C-2‴), 47.4, 46.5, 45.9, 41.5, 41.0, 39.2, 38.3, 38.2, 36.7, 33.8, 33.1, 32.4, 30.6, 29.7, 27.6, 27.3, 25.8, 25.2, 23.6, 23.5, 22.7, 20.9–20.4 (7 × COCH$_3$), 18.0, 17.1, 16.2, 15.2; ESIMS: calcd for $C_{86}H_{100}N_3O_{28}$ 1622.6493, found 1622.6415 $[M-H]^-$.

4.10.12. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)ursolic acid (56)

Yield 61%; R_f 0.39 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +45.3 (*c* 0.41, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.94–7.71 (m, 12H, Phth), 5.79 (dd, 1H, *J* 9.1, 10.5 Hz, H-3‴), 5.67 (dd, 1H, *J* 9.1, 10.5 Hz, H-3′), 5.60 (dd, 1H, *J* 9.2, 10.6 Hz, H-3″), 5.50 (d, 1H, *J* 8.7 Hz, H-1‴), 5.45 (d, 1H, *J* 8.2 Hz, H-1″), 5.23 (d, 1H, *J* 8.3 Hz, H-1′), 5.22 (t, 1H, *J* 3.3 Hz, H-12), 5.20 (t, 1H, *J* 9.6 Hz, H-4‴), 4.92 (t, 1H, *J*

9.6 Hz, H-4″), 4.74 (t, 1H, *J* 9.7 Hz, H-4′), 4.39 (dd, 1H, *J* 4.6, 12.4 Hz, H-6$_i$‴), 4.35 (dd, 1H, *J* 8.3, 10.6 Hz, H-2‴), 4.22–4.19 (m, 2H, H-2′, H-6$_{ii}$‴), 4.17 (dd, 1H, *J* 8.7, 11.0 Hz, H-2″), 3.91 (ddd, 1H, *J* 2.3, 5.0, 10.5 Hz, H-5‴), 3.87 (d, 1H, *J* 9.2 Hz, H-6$_i$″), 3.72–3.68 (m, 2H, H-5″, H-6$_{ii}$″), 3.62–3.56 (m, 2H, H-6$_i$′, H-6$_{ii}$′), 3.50 (ddd, 1H, *J* 3.2, 5.9, 10.1 Hz, H-5′), 3.17 (dd, 1H, *J* 4.1, 11.9 Hz, H-3), 2.15 (d, 1H, *J* 11.9 Hz, H-18), 2.16, 2.05, 1.99, 1.93, 1.86, 1.83, 1.77 (3H each, s each, 7 × COC*H*$_3$), 2.04–0.61 (m, 22H), 0.92 (d, 3H, *J* 5.9 Hz), 0.83 (d, 3H, *J* 6.4 Hz), 1.02, 0.77, 0.70, 0.43, 0.40 (s each, 3H each, 5 × Me); ^{13}C NMR ($CDCl_3$): δ 182.9, 170.8–169.4 (7 × *C*OCH$_3$), 168.2–167.3 (NCOPh), 134.5–123.4 (Ph), 137.9, 125.7, 99.7 (C-1′), 97.9 (C-1‴), 97.0 (C-1″), 89.9, 73.3 (C-5′), 73.1 (C-5″), 72.0 (C-5‴), 70.8 (C-3″), 70.7 (C-3‴), 70. (C-3′), 69.9 (C-4′), 69.6 (C-4″), 68.9(C-4‴), 67.9 (C-6″), 67.5 (C-6′), 61.9 (C-6‴), 54.9 (C-2′), 54.8 (C-2″), 54.4 (C-5, C-2‴), 52.5, 47.9, 47.3, 41.8, 39.4, 39.0, 38.8, 38.3, 38.2, 36.7, 36.6, 32.8, 30.6, 28.0, 27.4, 25.3, 24.1, 23.4, 23.3, 21.2, 20.8–20.4 (7 × COC*H*$_3$), 18.0, 17.1, 17.0, 16.2, 15.4; ESIMS: calcd for $C_{86}H_{100}N_3O_{28}$ 1622.6493, found 1622.6470 $[M-H]^-$.

4.10.13. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)oleanolic acid (57)

Yield 54%; R_f 0.29 (1:2 petroleum ether–EtOAc); ^{1}H NMR ($CDCl_3$): δ 7.92–7.71 (m, 16H, Phth), 5.79 (dd, 1H, *J* 9.2, 10.6 Hz, H-3‴′), 5.67–5.64 (m, 2H, H-3′, H-3‴), 5.56 (dd, 1H, *J* 9.1, 10.6 Hz, H-3″), 5.49 (d, 1H, *J* 8.8 Hz, H-1‴′), 5.37 (d, 1H, *J* 8.5 Hz, H-1″), 5.32 (d, 1H, *J* 8.8 Hz, H-1‴), 5.23–5.18 (m, 3H, H-12, H-1′, H-4‴), 4.93 (t, 1H, *J* 9.9 Hz, H-4′), 4.83 (t, 1H, *J* 9.9 Hz, H-4″), 4.74 (t, 1H, *J* 9.5 Hz, H-4‴), 4.39–4.36 (m, 2H, H-2‴′, H-6$_i$‴′), 4.22–4.12 (m, 4H, H-2′, H-2″, H-2‴,H-6$_{ii}$‴′), 3.98–3.90 (m, 2H, H-5‴′, H-6$_i$′), 3.78–3.67 (m, 3H, H-5′, H-6$_{ii}$′, H-6$_i$‴), 3.61–3.45 (m, 5H, H-5″, H-6$_i$″, H-6$_{ii}$″, H-5‴, H-6$_{ii}$‴), 3.09 (dd, 1H, *J* 4.0, 11.3 Hz, H-3), 2.81 (dd, 1H, *J* 3.7, 13.3 Hz, H-3), 2.16, 2.04, 1.99, 1.94, 1.86, 1.82, 1.78, 1.77 (some overlap, 27H, 9 × COC*H*$_3$), 2.02–0.58 (m, 22H), 1.08, 0.92, 0.89, 0.75, 0.69, 0.43, 0.38 (s each, 3H each, 7 × Me); ^{13}C NMR ($CDCl_3$): δ 182.5, 170.8–169.4 (9 × *C*OCH$_3$), 168.2–167.4 (NCOPh), 143.7, 134.5–113.9 (Ph), 123.8, 99.6 (C-1′), 98.1 (C-1‴′), 97.7 (C-1‴), 97.2 (C-1″), 89.9, 73.3 (C-5‴), 73.0 (C-5′), 72.8 (C-5″), 72.1 (C-5‴′), 70.8 (C-3″, C-3‴′), 70.7 (C-3′), 70.6 (C-3‴), 69.6 (C-4‴), 69.7 (C-4′, C-4″), 69.0 (C-4‴′), 68.2 (C-6′), 67.6 (C-6″), 67.3 (C-6‴), 62.0 (C-6‴′), 55.0, 54.9 (C-2′), 54.4 (C-2″, C-2‴, C-2‴′), 47.5, 46.5, 46.0, 41.7, 41.1, 39.2, 38.3, 38.2, 36.7, 33.9, 33.1, 32.5, 30.7, 29.7, 27.7, 27.3, 25.8, 25.2, 23.6, 23.5, 22.7, 20.8–20.4 (9 × COC*H*$_3$), 18.0, 17.1, 16.3, 15.2; ESIMS: calcd for $C_{104}H_{117}N_4O_{36}$ 1997.7448, found 1997.7445 $[M-H]^-$.

4.10.14. 3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)ursolic acid (58)

Yield 51%; R_f 0.29 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ +16.7 (*c* 0.85, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.92–7.71 (m, 16H, Phth), 5.79 (dd, 1H, *J* 9.2, 10.3 Hz, H-3‴′), 5.68–5.64 (m, 2H, H-3′, H-3‴), 5.56 (dd, 1H, *J* 9.2, 10.3 Hz, H-3″), 5.49 (d, 1H, *J* 8.4 Hz, H-1‴′), 5.41 (d, 1H, *J* 8.4 Hz, H-1″), 5.33 (d, 1H, *J* 8.4 Hz, H-1‴), 5.23–5.19 (m, 3H, H-12, H-1′, H-4‴), 4.93 (t, 1H, *J* 9.5 Hz, H-4′), 4.83 (t, 1H, *J* 9.8 Hz, H-4″), 4.74 (t, 1H, *J* 9.5 Hz, H-4‴), 4.39–4.36 (m, 2H, H-2‴′, H-6$_i$‴′), 4.23–4.16 (m, 3H, H-2′, H-2‴,H-6$_{ii}$‴′), 4.14 (dd, 1H, *J* 8.8, 10.6 Hz, H-2″), 3.98–3.90 (m, 2H, H-5‴′, H-6$_i$′), 3.78–3.67 (m, 3H, H-5′, H-6$_{ii}$′, H-6$_i$‴), 3.61–3.45 (m, 5H, H-5″, H-6$_i$″, H-6$_{ii}$″, H-5‴, H-6$_{ii}$‴), 3.15 (dd, 1H, *J* 4.0, 11.7 Hz, H-3), 2.16, 2.04, 1.99, 1.94, 1.86, 1.83, 1.78, 1.77 (some overlap, 27H, 9 × COC*H*$_3$), 2.16–0.60 (m, 23H), 0.93 (d, 3H, *J* 6.5 Hz), 0.84 (d, 3H, *J* 6.2 Hz), 1.03, 0.77, 0.71, 0.43, 0.39 (s each, 3H each, 5 × Me); ^{13}C NMR ($CDCl_3$): δ 182.9, 170.8–169.4 (9 × *C*OCH$_3$), 168.2–167.3 (NCOPh), 138.0, 134.4–113.9 (Ph), 125.8, 99.7 (C-1′), 98.1 (C-1‴′), 97.7 (C-1‴), 97.0 (C-1″), 89.9, 73.3 (C-5‴), 73.0 (C-5′), 72.8 (C-5″), 72.1 (C-5‴′), 70.8 (C-3″), 70.7 (C-3′,C-3‴′), 70.5 (C-3‴), 69.8 (C-4‴), 69.7 (C-4″), 69.6 (C-4′), 69.0 (C-4‴′), 68.2 (C-6′), 67.6 (C-6″), 67.3 (C-6‴), 62.0 (C-6‴′), 55.0, 54.8 (C-2′), 54.4 (C-2″, C-2‴, C-2‴′), 52.6, 47.9, 47.3, 41.9, 39.4, 39.1, 38.8, 38.3, 38.2, 36.7, 36.6, 32.8, 30.6, 28.0, 27.4, 25.3, 24.1, 23.4, 23.3, 21.2, 20.8–20.4 (9 × COC*H*$_3$), 18.0, 17.1, 17.0, 16.2, 15.4; ESIMS: calcd for $C_{104}H_{117}N_4O_{36}$ 1997.7448, found 1997.7440 $[M-H]^-$.

4.11. General procedure for target saponins 1–14

Compounds **45**–**58** (0.1 mmol) were each mixed in BuOH (10 mL) and $NH_2CH_2CH_2NH_2$ (5 mL) was added. After stirring overnight at 80–90 °C, the mixture was concentrated to afford a yellow syrup, which was co-evaporated with toluene twice and then dissolved in 1:1 pyridine–Ac_2O (5 mL). The resulting mixture was stirred at rt overnight and then concentrated to yield a yellow solid, which was dissolved in 5:1 MeOH–CH_2Cl_2 (30 mL) and then NaOMe (20 mg, 50%) in MeOH was added to adjust to pH 10. After stirring at rt for 1 h, the solution was neutralized with cation-exchange resin (H^+), and then filtered and concentrated to give a syrup. The resulting residues of **45**–**48** and **53**–**58** were purified by column chromatography to afford the pure target saponins. The resulting residue of **49**–**52** was dissolved in MeOH (10 mL) and then HOAc (200 μL) and Pd/C (100 mg) was added. [*Caution*! Extreme fire hazard.] The mixture was vigorously stirred at room temperature under a hydrogen atmosphere (balloon) until the debenzylation was complete as determined by TLC. The catalyst was removed by filtration through Celite, and the filter was washed with EtOAc and MeOH. The filtrate was concentrated and purified by column chromatography to give the target saponin.

4.11.1. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl)oleanolic acid (1)

Yield 69%; R_f 0.13 (6:1 $CHCl_3$–CH_3OH); $[\alpha]_D^{20}$ +18.8 (*c* 1.73, CH_3OH); ^{1}H NMR (DMSO-d_6): δ 12.05 (br s, 1H, COOH), 7.70 (d, 1H, *J* 9.2 Hz, NH′), 5.15 (t, 1H, *J* 2.9 Hz H-12), 4.94 (d, 1H, *J* 4.7 Hz, OH), 4.83 (d, 1H, *J* 5.1 Hz, OH), 4.41 (t, 1H, *J* 5.5 Hz, OH), 4.25 (d, 1H, *J* 8.4 Hz, H-1′), 3.66 (dd, 1H, *J* 5.5, 10.6 Hz, H-6$_i$′), 3.43 (dd, 1H, *J* 3.7, 10.3 Hz, H-6$_{ii}$′), 3.38 (t, 1H, *J* 9.5 Hz, H-2′), 3.27 (dd, 1H, *J* 8.1, 10.3 Hz, H-3′), 3.04–3.01 (m, 2H, H-4′, H-5′), 2.97 (dd, 1H, *J* 4.4, 11.7 Hz, H-3), 2.74 (dd, 1H, *J* 4.0, 14.3 Hz, H-18), 1.91–0.68 (m, 22H), 1.76 (s, 3H, COC*H*$_3$), 1.09, 0.89, 0.89, 0.85, 0.71, 0.65, 0.42 (s each, 3H each, 7 × Me); ^{13}C NMR (DMSO-d_6): δ 178.3, 169.2 (*C*OCH$_3$), 144.4, 122.0.4, 104.1 (C-1′), 88.6, 77.3 (C-5′), 74.6 (C-3′), 71.3 (C-4′), 61.7 (C-6′), 56.4 (C-2′), 55.4, 47.6, 46.3, 46.0, 41.8, 41.4, 39.4, 38.8, 38.6, 36.9, 33.9, 33.4, 33.0, 32.7, 31.0, 28.1, 27.8, 26.1, 25.9, 23.9, 23.7 (*C*OCH$_3$), 23.5, 23.0, 18.3, 17.5, 16.9, 15.6; ESIMS: calcd for $C_{38}H_{60}NO_8$ 658.4319, found 658.4337 $[M-H]^-$.

4.11.2. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl)ursolic acid (2)

Yield 69%; R_f 0.13 (6:1 $CHCl_3$–MeOH); $[\alpha]_D^{20}$ −11.0 (*c* 0.17, CH_3OH); ^{1}H NMR (DMSO-d_6): δ 11.89 (br s, 1H, COOH), 7.71 (d, 1H, *J* 9.1 Hz, NH′), 5.13 (t, 1H, *J* 2.9 Hz H-12), 4.94 (br s, 1H, OH), 4.84 (d, 1H, *J* 5.2 Hz, OH), 4.39 (t, 1H, *J* 5.5 Hz, OH), 4.25 (d, 1H, *J* 8.5 Hz, H-1′), 3.65 (dd, 1H, *J* 4.4, 8.1 Hz, H-6$_i$′), 3.43 (dd, 1H, *J* 5.9, 9.9 Hz, H-6$_{ii}$′), 3.39 (t, 1H, *J* 9.1 Hz, H-2′), 3.30 (m, 1H, H-3′), 3.05–3.02 (m, 2H, H-4′, H-5′), 2.98 (dd, 1H, *J* 4.4, 11.7 Hz, H-3), 2.11 (d, 1H, *J* 11.4 Hz, H-18), 1.93–0.68 (m, 22H), 1.76 (s, 3H, COC*H*$_3$), 0.91 (d, 3H, *J* 6.6 Hz), 0.81 (d, 3H, *J* 6.6 Hz), 1.04, 0.89, 0.87, 0.74, 0.65, (s each, 3H each, 5 × Me); ^{13}C NMR (DMSO-d_6): δ

178.3, 168.7 (*C*OCH$_3$), 138.2, 124.5, 103.5 (C-1′), 88.0, 76.7 (C-5′), 74.0 (C-3′), 70.7 (C-4′), 61.2 (C-6′), 55.8 (C-2′), 54.9, 52.4, 47.0, 46.8, 41.6, 40.4, 38.5, 38.4, 38.3, 38.1, 36.3, 36.2, 32.6, 30.2, 27.6, 27.5, 25.3, 23.8, 23.2, 23.1 (CO*C*H$_3$), 22.8, 21.1, 17.7, 17.0, 16.9, 16.3, 15.2; ESIMS: calcd for $C_{38}H_{60}NO_8$ 658.4319, found 658.4302 $[M-H]^-$.

4.11.3. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl)oleanolic acid (3)

Yield 61%; R_f 0.50 (4:1 $CHCl_3$–MeOH); ^{1}H NMR (DMSO-d_6): δ 12.02 (br s, 1H, COOH), 7.80 (d, 1H, *J* 8.4 Hz, NH), 7.77 (d, 1H, *J* 9.5 Hz, NH), 5.15 (br s, 1H, H-12), 5.10 (br s, 1H, OH), 5.00 (br s, 1H, OH), 4.72 (dt, 1H, *J* 5.1 Hz, OH), 4.68 (br s, 1H, OH), 4.48 (t, 1H, *J* 5.9 Hz, OH), 4.33 (d, 1H, *J* 8.4 Hz, H-1″), 4.26 (d, 1H, *J* 7.7 Hz, H-1′), 3.73 (d, 1H, *J* 12.5 Hz, H-6$_i$″), 3.58 (d, 1H, *J* 7.3 Hz, H-6$_i$′), 3.49–3.42 (m, 4H, H-2′, H-3′, H-6$_{ii}$′, H-2″), 3.35 (1H, H-6$_{ii}$″), 3.27 (t, 1H, *J* 9.1 Hz, H-3″), 3.22 (t, 1H, *J* 9.1 Hz, H-4′), 3.17 (dt, 1H, *J* 2.2, 8.4 Hz, H-5″), 3.12 (dt, 1H, *J* 2.9, 6.3 Hz, H-5′), 3.03 (t, 1H, *J* 9.2 Hz, H-4″), 2.99 (dd, 1H, *J* 4.0, 11.3 Hz, H-3), 2.74 (dd, 1H, *J* 3.7, 13.6 Hz, H-18), 1.94–0.68 (m, 22H), 1.82 (s, 3H, COC*H*$_3$), 1.75 (s, 3H, COC*H*$_3$), 1.09, 0.89, 0.89, 0.87, 0.85, 0.71, 0.65 (s each, 3H each, 7 × Me); ^{13}C NMR (DMSO-d_6): δ 169.1, 168.5 (2 × *C*OCH$_3$), 143.9, 121.4, 103.4 (C-1′), 102.2 (C-1″), 88.2, 81.7 (C-4′), 76.9 (C-5″), 74.6 (C-5′), 74.1 (C-3″), 72.4 (C-3′), 70.7 (C-4″), 61.0 (C-6″), 60.0 (C-6′), 55.4 (C-2″), 55.0 (C-2′), 54.8, 47.0, 45.7, 45.4, 41.3, 40.8, 38.9, 38.4, 38.0, 36.3, 33.3, 32.8, 32.4, 32.1, 30.4, 27.5, 27.2, 25.5, 25.3, 23.4, 23.0 (2 × CO*C*H$_3$), 22.9, 22.6, 17.8, 16.9, 16.3, 15.1; ESIMS: calcd for $C_{46}H_{73}N_2O_{13}$ 861.5113, found 861.5086 $[M-H]^-$.

4.11.4. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl)ursolic acid (4)

Yield 59%; R_f 0.50 (4:1 $CHCl_3$–MeOH); $[\alpha]_D^{20}$ −1.9 (*c* 0.09, CH_3OH); ^{1}H NMR (CD_3OD): δ 5.21 (t, 1H, *J* 3.3 Hz, H-12), 4.48 (d, 1H, *J* 8.4 Hz, H-1″), 4.41 (d, 1H, *J* 8.4 Hz, H-1′), 3.89 (dd, 1H, *J* 2.2, 12.1 Hz, H-6$_i$″), 3.78 (dd, 1H, *J* 1.9, 12.1 Hz, H-6$_i$′), 3.75–3.69 (m, 2H, H-2′, H-2″), 3.64–3.61 (m, 2H, H-6$_{ii}$′, H-6$_{ii}$″), 3.59 (dd, 1H, *J* 8.4, 10.3 Hz, H-3′), 3.51 (t, 1H, *J* 8.4 Hz, H-4′), 3.43 (dd, 1H, *J* 8.8, 10.3 Hz, H-3″), 3.36–3.28 (m, 3H, H-5′, H-4″, H-5″), 3.09 (dd, 1H, *J* 4.4, 12.1 Hz, H-3), 2.19 (d, 1H, *J* 11.3 Hz, H-18), 2.05–0.74 (m, 22H), 2.00 (s, 3H, COC*H*$_3$), 1.93 (s, 3H, COC*H*$_3$), 1.10, 0.96, 0.95, 0.83, 0.75 (s each, 3H each, 5 × Me), 0.94 (d, 3H, *J* 6.2 Hz), 0.87 (d, 3H, *J* 6.2 Hz); ^{13}C NMR (CD_3 OD): δ 173.8, 173.3 (2 × COCH3), 139.7, 126.8, 104.9 (C-1′), 103.3 (C-1″), 91.2, 81.5 (C-4′), 78.2 (C-5″), 76.2 (C-5′), 75.9 (C-3″), 74.2 (C-3′), 72.0 (C-4″), 62.5 (C-6″), 61.8 (C-6′), 57.3 (C-2″), 57.0 (C-2′), 56.9, 54.4, 43.2, 40.8, 40.4, 39.9, 39.8, 38.1, 37.8, 34.3, 31.8, 29.2, 28.6, 26.8, 25.3, 24.4, 24.1, 23.1 (2 × CO*C*H$_3$), 21.6, 19.3, 17.9, 17.7, 17.1, 16.0; ESIMS: calcd for $C_{46}H_{73}N_2O_{13}$ 861.5113, found 861.5116 $[M-H]^-$.

4.11.5. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopranosyl)oleanolic acid (5)

Yield 74%; R_f 0.26 (1:1 $CHCl_3$–MeOH); $[\alpha]_D^{20}$ −8.0 (*c* 0.15, CH_3OH); ^{1}H NMR (CD_3OD): δ 5.22 (t, 1H, *J* 3.3 Hz, H-12), 4.50 (d, 2H, *J* 8.4 Hz, H-1″, H-1‴), 4.41 (d, 1H, *J* 8.5 Hz, H-1′), 3.90 (dd, 1H, *J* 1.9, 11.8 Hz, H-6$_i$‴), 3.81 (dd, 1H, *J* 1.9, 12.1 Hz, H-6$_i$′), 3.78–3.75 (m, 2H, H-2″, H-6$_i$‴), 3.73 (dd, 1H, *J* 8.8, 10.6 Hz, H-2′), 3.70 (dd, 1H, *J* 8.4, 10.3 Hz, H-2‴), 3.64–3.57 (m, 5H, H-3′ H-6$_{ii}$′, H-3″, H-6$_{ii}$″, H-6$_{ii}$‴), 3.52 (t, 1H, *J* 8.8 Hz, H-4′), 3.50 (t, 1H, *J* 8.1 Hz, H-4″), 3.45 (dd, 1H, *J* 8.5, 10.3 Hz, H-3‴), 3.40 (ddd, 1H, *J* 2.2, 5.5, 9.5 Hz, H-5′), 3.36–3.33 (m, 1H, H-5‴), 3.29–3.27 (m, 2H, H-5″, H-4‴), 3.08 (dd, 1H, *J* 4.4, 11.7 Hz, H-3), 2.84 (dd, 1H, *J* 4.0, 13.9 Hz, H-18), 2.05–0.76 (m, 22H), 2.00, 1.99, 1.94 (s each, 3H each, 3 × COC*H*$_3$), 1.14, 0.95, 0.93, 0.92, 0.89, 0.80, 0.74 (s each, 3H each, 7 × Me); ^{13}C NMR (CD_3OD): δ 173.8, 173.7, 173.3 (3 × *C*OCH$_3$), 145.4, 123.4, 104.9 (C-1′), 103.0 (C-1‴), 91.1, 81.5 (C-4′), 81.2 (C-4″), 78.2 (C-5‴), 76.5 (C-5″), 76.2 (C-5′), 75.8 (C-3‴′), 74.2 (C-3′, C-3″), 72.0 (C-4‴), 62.6 (C-6‴), 61.7 (C-6′), 61.6 (C-6″), 57.3 (C-2‴), 57.0 (C-2′), 56.9, 56.6 (C-2″), 47.8, 45.4, 42.9, 42.8, 40.6, 39.9, 39.6, 37.9, 35.0, 34.0, 33.6, 31.6, 28.9, 28.6, 26.8, 26.4, 24.5, 24.2, 24.0, 23.1, 23.0, 22.9 (3 × CO*C*H$_3$), 19.3, 17.9, 17.0, 15.9; ESIMS: calcd for $C_{54}H_{86}N_3O_{18}$ 1064.5906, found 1064.5942 $[M-H]^-$.

4.11.6. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopranosyl)ursolic acid (6)

Yield 71%; R_f 0.26 (1:1 $CHCl_3$–MeOH); $[\alpha]_D^{20}$ −2.3 (*c* 0.10, CH_3OH); ^{1}H NMR (CD_3OD): δ 5.20 (br s, 1H, H-12), 4.48 (dd, 2H, *J* 8.4, 8.4 Hz, H-1″, H-1‴), 4.40 (d, 1H, *J* 8.5 Hz, H-1′), 3.89 (dd, 1H, *J* 1.9, 11.8 Hz, H-6$_i$‴), 3.81 (d, 1H, *J* 10.6 Hz, H-6$_i$′), 3.79–3.75 (m, 2H, H-2″, H-6$_i$‴), 3.73 (dd, 1H, *J* 8.8, 10.3 Hz, H-2′), 3.69 (dd, 1H, *J* 8.8, 10.3 Hz, H-2‴), 3.64–3.56 (m, 5H, H-3′ H-6$_{ii}$′, H-3″, H-6$_{ii}$″, H-6$_{ii}$‴), 3.52 (t, 1H, *J* 9.2 Hz, H-4′), 3.50 (t, 1H, *J* 8.1 Hz, H-4″), 3.44 (dd, 1H, *J* 8.8, 10.3 Hz, H-3‴), 3.40 (ddd, 1H, *J* 1.5, 4.8, 8.8 Hz, H-5′), 3.36–3.33 (m, 1H, H-5‴), 3.30–3.27 (m, 2H, H-5″, H-4‴), 3.09 (dd, 1H, *J* 4.1, 11.4 Hz, H-3), 2.19 (d, 1H, *J* 11.3 Hz, H-18), 2.04–0.75 (m, 22H), 2.00, 1.99, 1.93 (s each, 3H each, 3 × COC*H*$_3$), 1.10, 0.95, 0.95, 0.84, 0.75 (s each, 3H each, 5 × Me), 0.94 (d, 3H, *J* 6.2 Hz), 0.87 (d, 3H, *J* 6.2 Hz); ^{13}C NMR(CD_3OD): δ 173.8, 173.7, 173.3 (3 × *C*OCH$_3$), 139.8, 126.7, 104.9 (C-1′), 103.2 (C-1″), 103.1 (C-1‴), 91.1, 81.4 (C-4′), 81.2 (C-4″), 78.2 (C-5‴), 76.5 (C-5″), 76.2 (C-5′), 75.8 (C-3‴), 74.2 (C-3′, C-3″), 72.0 (C-4‴), 62.6 (C-6‴), 61.7 (C-6′), 61.6 (C-6″), 57.4 (C-2‴), 57.0 (C-2′), 56.9, 56.6 (C-2″), 54.4, 43.3, 40.8, 40.5, 40.4, 39.9, 39.8, 38.2, 37.8, 34.3, 31.9, 29.3, 28.6, 26.8, 25.4, 24.4, 24.1, 23.1, 23.0(3 × CO*C*H$_3$), 21.6, 19.3, 17.9, 17.7, 17.1, 16.0; ESIMS: calcd for $C_{54}H_{86}N_3O_{18}$ 1064.5906, found 1064.5907 $[M-H]^-$.

4.11.7. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopranosyl)oleanolic acid (7)

Yield 73%; R_f 0.18 (1:1 $CHCl_3$–MeOH); ^{1}H NMR (DMSO-d_6 and D_2O): δ 5.09 (br s, 1H, H-12), 4.38 (d, 2H, *J* 8.1 Hz, H-1″, H-1‴), 4.35 (d, 1H, *J* 8.4 Hz, H-1⁗), 4.28 (br s, 1H, H-1′), 3.73–3.14 (m, 23H), 3.04–3.03 (m, 2H, H-4⁗, H-3), 1.85–0.68 (m, 22H), 1.83, 1.82, 1.75, 1.72 (s each, 3H each, 4 × COC*H*$_3$), 1.06, 0.94, 0.88, 0.87, 0.85, 0.73, 0.64 (s each, 3H each, 7 × Me); ^{13}C NMR (DMSO-d_6 and D_2O): δ 169.5–169.2 (4 × *C*OCH$_3$), 145.0, 120.8, 103.3 (C-1′), 102.1, 101.9, 101.8 (C-1″, C-1‴, C-1⁗), 88.3, 81.7, 81.5, 81.4 (C-4′, C-4″, C-4‴), 77.0, 74.8, 74.7, 73.9, 72.4 (C-3′, C-3″, C-3‴, C-3⁗, C-5′, C-5″, C-5‴, C-5⁗), 70.6 (C-4⁗), 61.0, 60.1 (C-6′, C-6″, C-6‴, C-6⁗), 55.4, 55.1, 54.7, 54.6 (C-3′, C-3″, C-3‴, C-3⁗, C-5), 47.3, 46.5, 45.7, 41.5, 41.3, 39.0, 38.4, 38.1, 36.4, 33.9, 33.2 (C-7, C-29), 32.6, 30.6, 27.6, 27.5, 25.6, 25.3, 23.7, 23.2–22.9 (C-11, C-16, 4 × CO*C*H$_3$), 17.9, 17.4, 16.4, 15.2; ESIMS: calcd for $C_{62}H_{99}N_4O_{23}$ 1267.6700, found 1267.6747 $[M-H]^-$.

4.11.8. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopranosyl)ursolic acid (8)

Yield 71%; R_f 0.26 (1:1 $CHCl_3$–MeOH); ^{1}H NMR (DMSO-d_6 and D_2O): δ 5.11 (br s, 1H, H-12), 4.41 (d, 2H, *J* 8.4 Hz, H-1″, H-1‴), 4.38 (d, 1H, *J* 8.4 Hz, H-1⁗), 4.32 (d, 1H, *J* 7.3 Hz, H-1′), 3.73–3.14 (m, 23H), 3.09 (t, 1H, *J* 9.2 Hz, H-4⁗), 3.02 (br s, 1H, H-3), 2.14 (d, 1H, *J* 10.3 Hz, H-18), 2.01–0.69 (m, 22H), 1.88, 1.87, 1.81, 1.74 (s each, 3H each, 4 × COC*H*$_3$), 1.03, 0.89, 0.88 0.76, 0.66 (s each, 3H each, 5 × Me), 0.95 (d, 3H, *J* 4.7 Hz), 0.82 (d, 3H, *J* 4.7 Hz); ^{13}C NMR (DMSO-d_6 and D_2O): δ 177.0, 170.9–170.2 (4 × *C*OCH$_3$), 139.2, 124.6, 103.6 (C-1′), 102.4, 102.1, 102.0 (C-1″, C-1‴, C-1⁗), 89.1, 81.8, 81.6, 81.5 (C-4′, C-4″, C-4‴), 77.2, 75.2, 75.0, 72.8

(C-3′, C-3″, C-3‴, C-3′′′′, C-5′, C-5″, C-5‴, C-5′′′′), 70.9 (C-4′′′′), 61.4, 60.4 (C-6′, C-6″, C-6‴, C-6′′′′), 55.8, 55.5, 55.1, 55.0 (C-3′, C-3″, C-3‴, C-3′′′′, C-5), 53.2, 47.7 (C-9, C-17), 42.2, 38.8, 37.1, 36.8, 323.3, 31.0, 28.2, 28.0, 25.8, 24.9, 24.6, 23.7, 23.4–23.2 ($4 \times COCH_3$), 21.7, 18.3, 17.7, 16.9, 15.7; ESIMS: calcd for $C_{62}H_{99}N_4O_{23}$ 1267.6700, found 1267.6726 $[M-H]^-$.

4.11.9. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranosyl)oleanolic acid (9)

Yield 64%; R_f 0.21 (2:1 $CHCl_3$–MeOH); $[\alpha]_D^{20}$ −12.8 (*c* 0.11, CH_3OH); ^1H NMR (CD_3OD): δ 5.23 (t, 1H, *J* 3.3 Hz, H-12), 4.49 (d, 1H, *J* 8.4 Hz, H-1″), 4.41 (d, 1H, *J* 8.0 Hz, H-1′), 4.12 (dd, 1H, *J* 1.8, 11.0 Hz, H-6$_i$′), 3.88 (dd, 1H, *J* 2.2, 12.1 Hz, H-6$_i$″), 3.71–3.62 (m, 4H, H-2′, H-6$_{ii}$′, H-2″, H-6$_{ii}$″), 3.45 (dd, 1H, *J* 8.8, 10.3 Hz, H-3″), 3.43 (dd, 1H, *J* 8.8, 10.3 Hz, H-3′), 3.39 (ddd, 1H, *J* 1.8, 5.5, 9.9 Hz, H-5′), 3.34–3.26 (m, 3H, H-4′, H-4″, H-5″), 3.08 (dd, 1H, *J* 4.8, 11.2 Hz, H-3), 2.85 (dd, 1H, *J* 3.3, 13.6 Hz, H-18), 2.05–0.76 (m, 22H), 2.00 (s, 3H, COC*H*$_3$), 1.94 (s, 3H, COC*H*$_3$), 1.14, 0.95, 0.93, 0.92, 0.90, 0.81, 0.75 (s each, 3H each, 7 × Me); ^{13}C NMR (CD_3OD): δ 173.9, 173.4 (2 × *C*OCH$_3$), 145.4, 123.5, 104.8 (C-1′), 102.8 (C-1″), 91.1, 78.0 (C-5″), 76.5 (C-5′), 76.3 (C-3″), 75.8 (C-3′), 72.2 (C-4′), 72.1 (C-4″), 70.0 (C-6′), 62.8 (C-6″), 57.8 (C-2′), 57.4 (C-2″), 56.9, 49.9, 47.8, 47.4, 42.9, 42.8, 40.6, 39.9, 39.8, 37.9, 35.0, 34.0, 33.9, 33.6, 31.6, 28.9, 28.6, 26.7, 26.4, 24.6, 24.1, 24.0, 23.2 (3 × COC*H*$_3$), 19.4, 17.9, 17.1, 15.9; ESIMS: calcd for $C_{46}H_{73}N_2O_{13}$ 861.5113, found 861.5104 $[M-H]^-$.

4.11.10. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranosyl)ursolic acid (10)

Yield 60%; R_f 0.21 (2:1 $CHCl_3$–MeOH); $[\alpha]_D^{20}$ −4.3 (*c* 0.14, CH_3OH); ^1H NMR (CD_3OD): δ 5.21 (t, 1H, *J* 3.3 Hz, H-12), 4.48 (d, 1H, *J* 8.4 Hz, H-1″), 4.41 (d, 1H, *J* 8.5 Hz, H-1′), 4.13 (dd, 1H, *J* 1.9, 11.0 Hz, H-6$_i$′), 3.88 (dd, 1H, *J* 2.2, 11.9 Hz, H-6$_i$″), 3.70–3.62 (m, 4H, H-2′, H-6$_{ii}$′, H-2″, H-6$_{ii}$″), 3.45 (dd, 1H, *J* 8.5, 10.3 Hz, H-3″), 3.44 (dd, 1H, *J* 8.8, 10.3 Hz, H-3′), 3.39 (ddd, 1H, *J* 1.8, 5.5, 9.8 Hz, H-5′), 3.32 (t, 1H, *J* 9.5 Hz, H-4″), 3.29–3.26 (m, 2H, H-4′, H-5″), 3.08 (dd, 1H, *J* 4.4, 11.7 Hz, H-3), 2.19 (d, 1H, *J* 11.0 Hz, H-18), 2.05–0.76 (m, 22H), 2.00 (s, 3H, COC*H*$_3$), 1.94 (s, 3H, COC*H*$_3$), 1.10, 0.95, 0.94, 0.83, 0.75 (s each, 3H each, 5 × Me), 0.94 (d, 3H, *J* 6.6 Hz), 0.87(d, 3H, *J* 6.6 Hz); ^{13}C NMR (CD_3OD): δ 173.9, 173.5 (2 × *C*OCH$_3$), 139.7, 126.8, 104.9 (C-1′), 102.8 (C-1″), 91.1, 78.0 (C-5″), 76.4 (C-5′), 76.3 (C-3″), 75.8 (C-3′), 72.2 (C-4′), 72.1 (C-4″), 70.0 (C-6′), 62.8 (C-6″), 57.7 (C-2′), 57.4 (C-2″), 56.9, 54.4, 43.3, 40.8, 40.5, 40.4, 39.9, 38.2, 37.9, 34.3, 31.8, 29.2, 28.6, 26.7, 25.4, 24.4, 24.1, 23.2 (2 × COC*H*$_3$), 21.6, 19.3, 17.9, 17.7, 17.2, 16.1; ESIMS: calcd for $C_{46}H_{73}N_2O_{13}$ 861.5113, found 861.5184 $[M-H]^-$.

4.11.11. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopranosyl)oleanolic acid (11)

Yield 60%; R_f 0.31 (1:1 $CHCl_3$–MeOH); $[\alpha]_D^{20}$ 2.9 (*c* 0.47, CH_3OH); ^1H NMR (CD_3OD): δ 5.23 (t, 1H, *J* 3.3 Hz, H-12), 4.46 (d, 1H, *J* 8.1 Hz, H-1″), 4.45 (d, 1H, *J* 8.0 Hz, H-1‴), 4.44 (d, 1H, *J* 8.0 Hz, H-1′), 4.10 (dd, 1H, *J* 1.9, 11.8 Hz, H-6$_i$″), 4.05 (dd, 1H, *J* 1.9, 11.8 Hz, H-6$_i$′), 3.89 (dd, 1H, *J* 1.9, 11.7 Hz, H-6$_i$‴), 3.75–3.66 (m, 5H, H-2′, H-6$_{ii}$′, H-2″, H-6$_{ii}$″, H-6$_{ii}$‴), 3.62–3.58 (m, 2H, H-5′, H-2‴), 3.53 (dt, 1H, *J* 1.9, 8.6 Hz, H-5″), 3.47 (dd, 1H, *J* 8.8, 10.3 Hz, H-3′), 3.45–3.41 (m, 2H, H-3″, H-3‴), 3.36 (t, 1H, *J* 8.8 Hz, H-4‴), 3.29–3.27 (m, 1H, H-5‴), 3.22 (t, 1H, *J* 9.5 Hz, H-4′), 3.19 (t, 1H, *J* 9.5 Hz, H-4″), 3.07 (dd, 1H, *J* 4.0, 11.3 Hz, H-3), 2.84 (dd, 1H, *J* 4.0, 13.9 Hz, H-18), 2.00–0.73 (m, 22H), 2.00, 1.98, 1.96 (s each, 3H each, 3 × COC*H*$_3$), 1.14, 0.95, 0.93, 0.90, 0.81, 0.81, 0.75 (s each, 3H each, 7 × Me); ^{13}C NMR (CD_3OD): δ 173.8, 173.6 (3 × *C*OCH$_3$), 145.3, 123.6, 104.5 (C-1′), 103.9 (C-1″), 103.0 (C-1‴), 91.1, 78.0 (C-5‴), 76.9 (C-5″), 76.5 (C-3″), 76.1 (C-3′, C-3‴), 75.9 (C-5′), 72.8 (C-4′), 72.7 (C-4″), 71.9 (C-4‴), 71.3 (C-6″), 71.1 (C-6′), 62.8 (C-6‴), 57.7 (C-2′), 57.5 (C-2‴), 57.3 (C-2″), 57.1, 47.7, 47.4, 42.9, 42.8, 40.6, 39.9, 39.8, 38.0, 34.9, 34.1, 33.9, 33.6, 31.6, 28.9, 28.6, 26.4, 24.6, 24.1, 24.0, 23.3 (3 × COC*H*$_3$), 19.3, 17.8, 17.1, 15.9; ESIMS: calcd for $C_{54}H_{86}N_3O_{18}$ 1064.5906, found 1064.5903 $[M-H]^-$.

4.11.12. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopranosyl)ursolic acid (12)

Yield 56%; R_f 0.31 (1:1 $CHCl_3$–MeOH); ^1H NMR (CD_3OD): δ 5.21 (t, 1H, *J* 3.3 Hz, H-12), 4.46 (d, 1H, *J* 8.4 Hz, H-1″), 4.45 (d, 1H, *J* 8.4 Hz, H-1‴), 4.44 (d, 1H, *J* 8.4 Hz, H-1′), 4.10 (dd, 1H, *J* 1.9, 11.8 Hz, H-6$_i$″), 4.06 (dd, 1H, *J* 1.9, 11.0 Hz, H-6$_i$′), 3.88 (dd, 1H, *J* 2.2, 12.1 Hz, H-6$_i$‴), 3.74–3.66 (m, 5H, H-2′, H-6$_{ii}$′, H-2″, H-6$_{ii}$″, H-6$_{ii}$‴), 3.62–3.57 (m, 2H, H-5′, H-2‴), 3.51 (dt, 1H, *J* 1.4, 8.8 Hz, H-5″), 3.47 (dd, 1H, *J* 8.8, 10.3 Hz, H-3′), 3.45–3.41 (m, 2H, H-3″, H-3‴), 3.35 (t, 1H, *J* 9.5 Hz, H-4‴), 3.29–3.27 (m, 1H, H-5‴), 3.22 (t, 1H, *J* 9.5 Hz, H-4′), 3.19 (t, 1H, *J* 9.5 Hz, H-4″), 3.07 (dd, 1H, *J* 4.4, 11.7 Hz, H-3), 2.19 (d, 1H, *J* 11.7 Hz, H-18), 2.09–0.73 (m, 22H), 2.00, 1.98, 1.96 (s each, 3H each, 3 × COC*H*$_3$), 1.10, 0.96, 0.94, 0.84, 0.75 (s each, 3H each, 5 × Me), 0.94 (d, 3H, *J* 6.6 Hz), 0.88 (d, 3H, *J* 6.6 Hz); ^{13}C NMR (CD_3OD): δ 173.8, 173.6, 173.5 (3 × *C*OCH$_3$), 139.8, 126.9, 104.4 (C-1′), 103.9 (C-1″), 103.0 (C-1‴), 91.1, 78.0 (C-5‴), 76.9 (C-5″), 76.4 (C-3″), 76.1 (C-3′, C-3‴), 76.0 (C-5′), 72.8 (C-4′), 72.7 (C-4″), 72.0 (C-4‴), 71.3 (C-6″), 71.1 (C-6′), 62.8 (C-6‴), 57.8 (C-2′), 57.5 (C-2‴), 57.4 (C-2″), 57.1, 54.4, 43.2, 40.8, 40.5, 40.4, 40.0, 39.8, 38.1, 37.9, 34.3, 31.8, 29.2, 28.7, 26.4, 25.3, 24.4, 24.1, 23.3, 23.1 (3 × COC*H*$_3$), 21.6, 19.3, 17.9, 17.7, 17.1, 16.0; ESIMS: calcd for $C_{54}H_{86}N_3O_{18}$ 1064.5906, found 1064.5880 $[M-H]^-$.

4.11.13. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopranosyl)oleanolic acid (13)

Yield 47%; R_f 0.21 (1:1 $CHCl_3$–MeOH); ^1H NMR (CD_3OD): δ 5.23 (t, 1H, *J* 3.7 Hz, H-12), 4.55 (d, 1H, *J* 8.4 Hz), 4.51 (d, 1H, *J* 8.4 Hz), 4.40 (d, 1H, *J* 8.0 Hz), 4.39 (d, 1H, *J* 8.4 Hz, 4.02–3.10 (m, 24H), 3.07 (dd, 1H, *J* 4.4, 11.8 Hz, H-3), 2.85 (dd, 1H, *J* 4.0, 13.6 Hz, H-18), 2.10–0.71 (m, 22H), 2.01, 2.00, 1.99, 1.98 (s each, 3H each, 4 × COC*H*$_3$), 1.15, 0.93, 0.89, 0.89, 0.81, 0.81, 0.75 (s each, 3H each, 7 × Me), ^{13}C NMR (CD_3OD): δ 174.8, 173.8, 173.2 (4 × *C*OCH$_3$), 145.3, 123.7, 104.9, 104.5, 104.1, 103.0 (C-1′, C-1″, C-1‴, C-1′′′′), 91.1, 78.0, 77.3, 76.7, 76.6, 76.5, 76.1, 75.4, 75.1 (C-3′, C-3″, C-3‴, C-3′′′′, C-5′, C-5″, C-5‴, C-5′′′′), 73.6, 73.5, 72.9, 72.7, 72.6, 72.1, 71.8 (C-4′, C-4″, C-4‴, C-4′′′′, C-6′, C-6″, C-6‴), 62.8 (C-6′′′′), 57.8, 57.4, 57.3, 57.2 (C-5, C-2′, C-2″, C-2‴, C-2′′′′), 47.7, 47.4, 42.9, 42.8, 40.6, 40.0, 39.8, 38.0, 34.9, 34.1, 33.9, 33.6, 31.6, 28.9, 28.6, 26.4, 24.6, 24.1, 24.0, 23.2–23.1 (4 × COC*H*$_3$), 19.4, 17.8, 17.1, 15.9; ESIMS: calcd for $C_{62}H_{99}N_4O_{23}$ 1267.6700, found 1267.6736 $[M-H]^-$.

4.11.14. 3-*O*-(2-Acetamido-2-deoxy-β-D-glucopranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopranosyl)ursolic acid (14)

Yield 46%; R_f 0.21 (1:1 $CHCl_3$–MeOH); ^1H NMR (CD_3OD): δ 5.21 (t, 1H, *J* 3.7 Hz, H-12), 4.54 (d, 1H, *J* 8.4 Hz), 4.50 (d, 1H, *J* 8.5 Hz), 4.41 (d, 1H, *J* 8.8 Hz), 4.39 (d, 1H, *J* 8.4 Hz), (H-1′, H-1″, H-1‴, H-1′′′′), 4.02–3.11 (m, 24H), 3.08 (dd, 1H, *J* 4.4, 11.7 Hz, H-3), 2.20 (d, 1H, *J* 11.0 Hz, H-18), 2.08–0.73 (m, 22H), 2.01, 2.00, 1.98 (s, 12H each, 4 × COC*H*$_3$), 1.10, 0.95, 0.94, 0.84, 0.75 (s each, 3H each, 5 × Me), 0.94 (d, 3H, *J* 6.6 Hz), 0.88 (d, 3H, *J* 6.6 Hz); ^{13}C NMR (CD_3OD): δ 174.1, 173.7, 173.3 (4 × *C*OCH$_3$), 139.9, 126.7, 104.8, 104.3, 104.1, 103.0 (C-1′, C-1″, C-1‴, C-1′′′′), 91.1, 78.0, 77.2, 76.7, 76.6, 76.4, 76.1, 75.6, 75.2 (C-3′, C-3″, C-3‴, C-3′′′′, C-5′, C-5″, C-5‴, C-5′′′′), 73.5, 73.3, 72.8, 72.7, 72.5, 72.0, 71.8 (C-4′, C-4″, C-4‴,

C-4‴′, C-6′, C-6″, C-6‴), 62.8 (C-6‴′), 57.8, 57.7, 57.4, 57.3 (C-5, C-2′, C-2″, C-2‴, C-2‴′), 54.5, 43.2, 40.8, 40.5, 40.4, 40.1, 39.8, 38.2, 37.9, 34.4, 31.9, 29.3, 28.7, 26.2, 25.4, 24.4, 24.1, 23.2–23.1 ($4 \times COCH_3$), 21.6, 19.3, 17.9, 17.8, 17.2, 16.1; ESIMS: calcd for $C_{62}H_{99}N_4O_{23}$ 1267.6700, found 1267.6700 $[M-H]^-$.

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Supplementary data

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