Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information

Microwave-assisted construction of triazole-linked amino acid - glucoside conjugates as novel PTP1B inhibitors

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General procedure for the *O*-propargylation. To a solution of alcohol in anhydrous DMF at 0 °C, NaH (3-5 equiv) was added. After 20 min stirring, propargyl bromide (3-5 equiv) was slowly added. After 20 min, the reaction mixture was warmed to rt and stirred for another 12 h. After which, DMF was evaporated and the resulting residue was diluted with EtOAc, washed successively with water and brine, dried over $MgSO_4$, filtered and concentrated to give a crude product which was purified by column chromatography.

Methyl 3,4-di-*O*-benzyl-2,6-di-*O*-propargyl-α-D-glucopyranoside (8). From compound **6** (245.5 mg, 0.66 mmol), column chromatography (petroleum ether/EtOAc, 4:1) afforded **8** as a yellow-brown syrup (267.2 mg, 90.5 %). R_f = 0.70 (petroleum ether/EtOAc, 1:1). $[\alpha]_D$ = +70.0 (c = 0.1/CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.26 (m, 10H), 4.96 (d, 1H, J = 10.8 Hz), 4.78 (d, 1H, J = 12.4 Hz), 4.66 (t, 2H, J = 12.4 Hz), 4.58-4.10 (m, 5H), 3.88 (t, 1H, J = 9.6 Hz), 3.83 (dd, 1H, J = 3.6, 10.4 Hz), 3.73-3.70 (m, 1H), 3.65 (dd, 1H, J = 2.0, 10.4 Hz), 3.56 (t, 1H, J = 9.6 Hz), 3.49 (dd, 1H, J = 3.6, 9.6 Hz), 3.34 (s, 3H), 2.45 (t, 1H, J = 2.4 Hz), 2.38 (t, 1H, J = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.1, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 98.1, 81.7, 80.4, 79.6, 79.5, 76.9, 75.2, 75.1, 74.3, 73.4, 69.7, 68.0, 60.5, 58.6, 55.2. HR-ESI-MS m/z: calcd for $C_{27}H_{30}O_6$+Na 473.1940, found 473.1929.

Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-propargyl-α-D-glucopyranoside (9). From **7** (466.8 mg, 1.20 mmol), column chromatography (petroleum ether/EtOAc, 15:1 to 10:1) afforded **9** as a yellow-brown syrup (468.7 mg, 84.0 %). R_f = 0.65 (petroleum ether/EtOAc, 3:1). $[\alpha]_D$ = +96.8 (c = 1.2/CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 10H), 4.96 (d, 1H, J = 10.8 Hz), 4.82 (d, 1H, J = 10.8 Hz), 4.78 (d, 1H, J = 12.0 Hz), 4.64 (d, 1H, J = 12.0 Hz), 4.59 (d, 1H, J = 3.2 Hz), 4.46-4.13 (m, 2H), 4.26-3.96 (m, 2H), 3.94 (t, 1H, J = 9.2 Hz), 3.83 (dd, 1H, J = 4.0, 10.4 Hz), 3.75-3.71 (m, 2H), 3.51-3.47 (m, 2H), 3.38 (s, 3H), 2.45-2.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 138.0, 128.5, 128.4, 128.2, 128.1, 128.0, 127.0, 98.2, 81.8, 80.1, 79.6, 79.3, 77.0, 75.8, 75.0, 74.3, 73.4, 69.5, 68.1, 60.1, 58.6, 55.3. HR-ESI-MS m/z: calcd for $C_{27}H_{30}O_6$+K 489.1679, found 489.1682.

Methyl 2,6-di-*O*-tert-butyldimethylsilyl-3,4-di-*O*-propargyl-α-D-glucopyranoside (26). From compound **25** (422 mg, 1 mmol), column chromatography (EtOAc/petroleum ether, 1:10) afforded **26** as a yellow syrup (368 mg, 74 %). R_f = 0.71 (EtOAc/cyclohexane, 1:10). $[\alpha]_D$ = +64.9 (c = 3.5/CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.91 (d, 1H, J = 3.7 Hz), 4.42-4.16 (m, 4H), 3.95-3.79 (m, 2H), 3.52 (m, 2H), 3.38 (m, 1H), 3.36 (s, 3H), 3.22 (t, 1H, J = 9.3 Hz), 2.44 (m, 2H), 0.85 (m, 18H), 0.06 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 97.4, 80.1, 79.9, 79.8, 78.6, 74.5, 74.0, 73.5, 70.8, 62.4, 59.9, 58.3, 54.5, 25.9, 25.8, 25.7, 18.2, 17.9, -4.2, -4.5, -5.2, -5.4, -5.5.

General Procedure for the desilylation and *O*-benzylation. To a solution of silylated compound in MeOH, AcCl (0.5 equiv) was added dropwise. After over night stirring at rt, the mixture was then evaporated, dissolved in CH_2Cl_2, then washed with $NaHCO_3$ sat. and brine. The organic layer was dried over $MgSO_4$, filtered, and evaporated to give a crude product which was directly used for the *O*-benzylation. To a solution of alcohol in anhydrous DMF at 0 °C, NaH (5 equiv) was added. After 20 min stirring, BnBr (5 equiv) was carefully added. After 20 min, the reaction mixture was warmed to rt and stirred for another 12 h. After which, DMF was evaporated and the resulting residue was diluted with EtOAc, washed successively with water and brine, dried over $MgSO_4$, filtered and concentrated to give the crude product which was purified by column chromatography.

Methyl 4,6-di-*O*-benzyl-2,3-di-*O*-propargyl-α-D-glucopyranoside (11). To a solution of **10** (306 mg, 0.82 mmol) in CH_2Cl_2, TFA (0.45 mL, 5.74 mmol) was added. After stirring for 5h at rt, the mixture was neutralized with $NaHCO_3$, extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuum to give the crude product which was used directly to the O-benzylation according to the General procedure. Purification by column chromatography (petroleum ether/EtOAc, 15:1 to 10:1) afforded **11** as a yellow-brown syrup (491 mg, 70.4 % for 2 steps). R_f = 0.56 (petroleum ether/EtOAc, 3:1). $[\alpha]_D$ = +96.8 (c = 1.2/CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.23 (m, 10H), 4.94 (d, 1H, J = 3.2 Hz), 4.91 (d, 1H, J = 11.2 Hz), 4.65 (d, 1H, J = 12.0 Hz), 4.54-4.38 (m, 6H), 3.87 (t, 1H, 9.2 Hz), 3.77-3.41 (m, 5H), 3.42 (s, 3H), 2.47 (t, 1H, J = 2.0 Hz), 2.44 (t, 1H, J = 2.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 137.9, 128.4, 128.3, 128.2, 128.0, 127.8, 98.0, 81.6, 80.2, 79.8, 79.3, 77.3, 75.2, 75.0, 74.3, 73.5, 70.0, 68.3, 60.4, 58.7, 55.1. HR-ESI-MS m/z: calcd for $C_{27}H_{30}O_6$+Na 473.1940, found 473.1941.

Methyl 2,6-di-*O*-benzyl-3,4-di-*O*-propargyl-α-D-glucopyranoside (27). Compound **26** (553 mg, 1.11 mmol) was desilylated and benzylated according to the General procedures. Column chromatography (petroleum ether/EtOAc, 20 :1) afforded **27** as a yellow-brown syrup (374.8 mg, 75.0 % for 2 steps). R_f = 0.45 (petroleum ether/EtOAc, 4:1). $[\alpha]_D$ = +76.4 (c = 0.1/CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 10H), 4.94 (d, 1H, J = 3.6 Hz), 4.88 (d, 1H, J = 11.2 Hz), 4.79 (d, 1H, J = 10.8 Hz), 4.65 (d, 1H, J = 12.0 Hz), 4.57 (d, 1H, J = 12.0 Hz), 4.41-4.30 (m, 3H), 4.23 (dd, 1H, J = 2.0, 13.2 Hz), 3.92 (t, 1H, J = 9.2 Hz), 3.76-3.72 (m, 3H), 3.66 (dd, 1H, J = 3.6 Hz, 6.0 Hz), 3.56 (t, 1H, J = 9.2 Hz), 3.44 (s, 3H), 2.44 (brs, 1H), 2.40 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.0, 128.5, 128.4, 128.2, 128.2, 128.4, 128.0, 127.8, 127.7, 98.1, 81.8, 80.0, 79.9, 79.4, 77.4, 75.7, 75.0, 74.4, 73.5, 69.8, 68.7, 60.0, 58.8, 55.2. HR-ESI-MS m/z: calcd for $C_{27}H_{30}O_6$+K 489.1679, found 489.1686.

General procedure for the saponification. To a solution of methyl ester in MeOH (5 mL) and water (5 mL) were added LiOH (1.5 equiv./ester). The mixture was stirred at rt for 3-12 h, then acidified with resin H^+, filtered and evaporated to give the free acid. If the residue was chromatographically not uniform, it was purified by column chromatography.

3-Phenyl-2(*S*)-[4-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosid-6-yloxy)-methyl-1*H*-1,2,3-triazole-1-yl]propanoic acid (4). From compound **2** (250.0 mg, 0.35 mmol), column chromatography (EtOAc/EtOH = 5:1) afforded **4** as a white solid (194.1 mg, 79.2 %). R_f = 0.67 (EtOAc/EtOH = 3:1). $[\alpha]_D$ = +21.7 (c = 0.3/MeOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (s, 1H), 7.34-7.26 (m, 15H), 7.16-7.11 (m, 5H), 5.58 (brs, 1H), 4.85 (d, 1H, J = 11.2 Hz), 4.81-4.80 (m, 1H), 4.72 (d, 2H, J = 11.6 Hz), 4.66 (brs, 2H), 4.55-4.48 (m, 3H), 3.78 (t, 1H, J = 9.2 Hz), 3.61-3.46 (m, 7H), 3.31 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 170.8, 142.7, 138.7, 138.4, 138.3, 137.9, 128.6, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.4, 127.3, 126.2, 123.6, 96.7, 81.0, 79.5, 77.4, 74.4, 74.0, 71.3, 69.6, 68.5, 66.6, 63.9, 54.5, 38.2. HR-ESI-MS m/z: calcd for $C_{40}H_{43}N_3O_8$+H 694.3128, found 694.3118.

3-p-Hydroxyphenyl-2(*S*)-[4-(methyl

2,3,4-tri-*O*-benzyl-α-D-glucopyranosid-6-yloxy)-methyl-1*H*-1,2,3-triazole-1-yl]propanoic acid (5). From compound **3** (120.0 mg, 0.17 mmol), column chromatography (EtOAc/EtOH = 5:1) afforded **5** as a white solid (88.3 mg, 75.0 %). R_f = 0.4 (EtOAc/EtOH = 3:1). $[\alpha]_D$ = +24.1 (*c* = 0.3/MeOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (s, 1H), 7.34-7.25 (m, 15H), 6.85 (d, 2H, *J* = 8.0 Hz), 6.59-6.56 (m, 2H), 5.22-5.11 (m, 1H), 4.84 (d, 1H, *J* = 11.6 Hz), 4.81 (d, 1H, *J* = 3.6 Hz), 4.76-4.71 (m, 2H), 4.65 (brs, 2H), 4.57 (d, 1H, *J* = 11.2 Hz), 4.51 (d, 1H, *J* = 12.4 Hz), 4.48 (d, 1H, *J* = 12.4 Hz), 3.79 (t, 1H, *J* = 9.2 Hz), 3.50-3.38 (m, 5H), 3.31 (s, 3H), 3.23-3.16 (m, 2H). ^{13}C NMR (100 MHz, DMSO-*d*6) δ 170.9, 155.8, 138.7, 138.5, 138.3, 129.6, 128.2, 128.1, 127.7, 127.7, 127.6, 127.6, 127.5, 127.3, 123.6, 114.9, 96.8, 81.1, 79.5, 77.4, 74.4, 74.1, 71.4, 69.7, 68.5, 66.6, 63.9, 54.5, 37.3. HR-ESI-MS *m*/*z*: calcd for $C_{40}H_{43}N_3O_9$+H 710.3078, found 710.3064.

Methyl 3,4-di-*O*-benzyl-2,6-di-*O*-{1-[(1(*S*)-carboxy-2-phenylethyl)]-4-methyl-1*H*-1,2,3-triazole-4-yl}-α-D-glucopyranoside (14). From compound **12** (86.0 mg, 0.10 mmol), column chromatography (EtOAc/EtOH, 1:1) afforded **14** as a white solid (67.0 mg, 80.7 %). R_f = 0.50 (CH_2Cl_2/MeOH, 1:1). $[\alpha]_D$ = +30.0 (*c* = 0.1/MeOH). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 7.94-7.87 (m, 2H), 7.37-7.27 (m, 10H), 7.10-7.03 (m, 10H), 5.22-5.20 (m, 2H), 4.89-4.86 (m, 1H), 4.81-4.71 (m, 3H), 4.69-4.62 (m, 2H), 4.54-4.47 (m, 2H), 4.43 (d, 1H, *J* = 12.0 Hz), 3.76 (t, 1H, *J* = 8.8 Hz), 3.58-3.45 (m, 6H), 3.29 (s, 3H), 3.29-3.19 (m, 3H). ^{13}C NMR (100 MHz, DMSO-*d*6) δ 171.5, 171.4, 143.3, 143.2, 142.7, 142.6, 138.5, 138.0, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 128.01, 127.6, 127.4, 126.2, 123.5, 123.2, 96.9, 81.0, 79.3, 77.0, 73.9, 71.5, 69.6, 68.5, 66.6, 65.1, 63.9, 62.8, 54.9, 38.4. HR-ESI-MS *m*/*z*: calcd for $C_{45}H_{48}N_6O_{10}$-H 831.3354, found 831.3367.

Methyl 3,4-di-*O*-benzyl-2,6-di-*O*-{1-[(1(*S*)-carboxy-2-p-hydroxyphenylethyl)]-4-methyl-1*H*-1,2,3-triazole-4-yl}-α-D-glucopyranoside (15). From compound **13** (92.0 mg, 0.10 mmol), column chromatography (EtOAc/EtOH, 1:2) afforded **15** as a white solid, (74.0 mg, 87.1 %). R_f = 0.34 (EtOAc/EtOH, 6:1). $[\alpha]_D$ = +14.5 (*c* = 0.1/MeOH). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 7.90-7.84 (m, 2H), 7.37-7.27 (m, 10H), 6.81-6.67 (m, 4H), 6.55-6.53 (m, 4H), 5.08 (brs, 2H), 4.89-4.85 (m, 1H), 4.81-4.60 (m, 5H), 4.55-4.43 (m, 2H), 4.42 (d, 1H, *J* = 12.0 Hz), 3.75 (t, 1H, *J* = 9.2 Hz) 3.58-3.40 (m, 6H), 3.29 (s, 3H), 3.19-3.04 (m, 3H). ^{13}C NMR (100 MHz, DMSO-*d*6) δ 171.3, 155.9, 155.8, 143.1, 142.6, 138.5, 129.5, 129.4, 128.3, 128.2, 128.0, 127.9, 127.9, 127.7, 127.6, 127.5, 123.4, 123.0, 114.9, 96.9, 81.1, 79.4, 77.0, 74.0, 71.6, 69.6, 68.5, 67.3, 66.0, 65.0, 64.0, 54.5, 37.8. HR-ESI-MS *m*/*z*: calcd for $C_{45}H_{48}N_6O_{12}$+H 865.3408, found 865.3420.

Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-{1-[(1(*S*)-carboxy-2-phenylethyl)]-4-methyl-1*H*-1,2,3-triazole-4-yl}-α-D-glucopyranoside (19). From compound **17** (128.9 mg, 0.15 mmol), column chromatography (EtOAc/EtOH, 1:1) afforded **19** as a white solid (124.3 mg, 99.6 %). R_f = 0.28 (EtOAc/EtOH, 1:1). $[\alpha]_D$ = +15.5 (*c* = 0.8/MeOH). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 8.11-8.08 (m, 2H), 7.35-7.29 (m, 10H), 7.17-7.13 (m, 10H), 5.82-5.63 (m, 2H), 4.83-4.79 (m, 3H), 4.65-4.50 (m, 5H), 3.77-3.73 (m, 1H), 3.68-3.52 (m, 4H), 3.47-3.29 (m, 9H); ^{13}C NMR (100 MHz, CD_3OD) 171.4, 138.5, 137.9, 135.9, 135.2, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 127.3, 127.0, 126.5, 97.4, 81.3, 79.7, 77.2, 74.9, 73.9, 72.3, 69.7, 68.4, 66.7, 60.6, 59.9, 54.0, 37.4. HR-ESI-MS *m*/*z*: calcd for $C_{45}H_{48}N_6O_{10}$-H 831.3354, found 831.3361.

Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-{1-[(1(*S*)-carboxy-2-p-hydroxyphenylethyl)]-4-methyl-1*H*-1,2,3-triazole-4-yl}-α-D-glucopyranoside (20). From compound **18** (131.2 mg, 0.15 mmol), column chromatography (EtOAc/EtOH, 1:1) afforded **20** as a white solid (125.9 mg, 99.0 %). R_f = 0.19 (EtOAc/EtOH, 1:1). $[\alpha]_D$ = -20.7 (*c* = 0.6/MeOH). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 8.07 (s, 1H), 8.04 (s, 1H), 7.35-7.26 (m, 10H), 6.93-6.90 (m, 4H), 6.61-6.59 (m, 4H), 5.36-5.53 (m, 2H), 4.84-4.76 (m, 4H), 4.65 (brs, 2H), 4.62 (d, 1H, *J* = 11.6 Hz), 4.54-4.51 (m, 2H), 3.78-3.73 (m, 2H), 3.48-3.41 (m, 5H), 3.39-3.32 (m, 3H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 171.5, 169.6, 157.0, 144.0, 143.8, 138.5, 138.0, 129.5, 127.9, 127.8, 127.6, 127.55, 127.49, 127.4, 127.1, 126.1, 124.2, 124.1, 123.9, 114.8, 114.7, 97.4, 81.3, 79.9, 77.2, 74.9, 72.5, 69.7, 68.4, 66.7, 64.9, 64.3, 63.5, 54.0, 36.7, 36.5. HR-ESI-MS *m*/*z*: calcd for $C_{45}H_{48}N_6O_{12}$+Na 887.3228, found 887.3221.

Methyl 4,6-di-*O*-benzyl-2,3-di-*O*-{1-[(1(*S*)-carboxy-2-phenylethyl)]-4-methyl-1*H*-1,2,3-triazole-4-yl}-α-D-glucopyranoside (23). From compound **21** (128.9 mg, 0.15 mmol), column chromatography (EtOAc/EtOH, 1:1) afforded **23** as a white solid (124.2 mg, 99.5 %). R_f = 0.23 (EtOAc/EtOH, 1:1). $[\alpha]_D$

= +25.6 (*c* = 0.7/MeOH). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 8.17-8.04 (m, 2H), 7.34-7.10 (m, 20H), 5.65 (brs, 2H), 4.86-4.71 (m, 3H), 4.69-4.61 (m, 3H), 4.54-4.44 (m, 3H), 3.75-3.69 (m, 2H), 3.65-3.44 (m, 5H), 3.41-3.40 (m, 3H), 3.27-3.24 (m, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 169.6, 169.5, 138.1, 137.9, 137.8, 135.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.79, 127.71, 127.76, 127.5, 127.2, 126.6, 126.5, 124.3, 123.9, 97.3, 81.1, 79.2, 77.1, 77.1, 74.4, 72.8, 69.9, 68.3, 66.7, 65.5, 64.0, 62.8, 53.9, 37.3, 37.1. HR-ESI-MS *m*/*z*: calcd for $C_{45}H_{48}N_6O_{10}$+H 833.3510, found 833.3518.

Methyl 4,6-di-*O*-benzyl-4,6-di-*O*-{1-[(1(*S*)-carboxy-2-p-hydroxyphenylethyl)]-4-methyl-1*H*-1,2,3-triazole-4-yl}-α-D-glucopyranoside (24). From compound **22** (131.2 mg, 0.15 mmol), column chromatography (EtOAc/EtOH, 1:1) afforded **24** as a white solid (125.5 mg, 98.7 %). R_f = 0.12 (EtOAc/EtOH, 1:1). $[\alpha]_D$ = +3.5 (*c* = 0.6/MeOH). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 8.19-8.05 (m, 2H), 7.33-7.24 (m, 10H), 6.94-6.90 (m, 4H), 6.62-6.58 (m, 4H), 5.58-5.51 (m, 2H), 4.89 (dd, 1H, *J* = 4.8, 11.2 Hz), 4.82-4.77 (m, 2H), 4.74-4.70 (m, 2H), 4.66-4.64 (m, 1H), 4.54-4.47 (m, 3H), 3.78-3.72 (m, 1H), 3.67-3.60 (m, 3H), 3.47-3.32 (m, 6H), 3.27-3.26 (m, 3H). ^{13}C NMR (100 MHz, DMSO-*d*6) δ 170.3, 169.9, 156.0, 143.9, 143.8, 138.3, 138.2, 129.8, 128.2, 128.1, 127.9, 127.6, 127.5, 127.4, 126.2, 126.1, 124.1, 123.8, 115.1, 115.0, 97.0, 81.3, 79.0, 77.2, 74.0, 72.2, 69.6, 68.6, 65.6, 63.7, 63.3, 59.7, 54.4, 36.0. HR-ESI-MS *m*/*z*: calcd for $C_{45}H_{48}N_6O_{12}$+H 865.3408, found 865.3403.

Methyl 2,6-di-*O*-benzyl-3,4-di-*O*-{1-[(1(*S*)-carboxy-2-phenylethyl)]-4-methyl-1*H*-1,2,3-triazole-1,4-diyl}-α-D-glucopyranoside (30). From compound **28** (150.0 mg, 0.17 mmol), column chromatography (EtOAc/EtOH, 1:1) afforded **30** as a yellow solid (133.9 mg, 92.0 %). R_f = 0.40 (EtOAc/EtOH, 1:2). $[\alpha]_D$ = +23.0 (*c* = 0.1/MeOH). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 8.00 (s, 1H), 7.89 (s, 1H), 7.36-7.25 (m, 10H), 7.15-7.04 (m, 10H), 5.40-5.35 (m, 2H), 4.81-4.80 (m, 3H), 4.67-4.63 (m, 3H), 4.56 (dd, 1H, *J* = 5.6, 11.6 Hz), 4.51-4.44 (m, 2H), 3.73-3.66 (m, 3H), 3.44-3.28 (m, 6H), 3.22 (s, 3H), 3.25-3.19 (m, 1H). ^{13}C NMR (100 MHz, DMSO-*d*6) δ 170.5, 143.3, 143.1, 138.7, 138.4, 137.4, 137.3, 128.7, 128.6, 128.2, 128.1, 128.1, 127.5, 127.4, 126.4, 123.6, 96.9, 81.0, 78.6, 77.2, 74.4, 74.2, 72.3, 69.6, 68.8, 65.4, 63.2, 63.1, 54.3, 37.7, 37.5. HR-ESI-MS *m*/*z*: calcd for $C_{45}H_{48}N_6O_{10}$+Na 855.3330, found 855.3356.

Methyl 2,6-di-O-benzyl-3,4-di-O-{1-[(1(S)-carboxy-2-p-hydroxyphenylethyl)]-4-methyl-1H-1,2,3-triazole-4-yl}-α-D-glucopyranoside (31). From compound 29 (165.0 mg, 0.18 mmol), column chromatography (EtOAc/EtOH, 1:2) afforded 31 as a yellow solid (148.0 mg, 92.6 %). R_f = 0.40 (EtOAc/EtOH, 1:2). $[\alpha]_D$ = -9.1 (*c* = 0.1/MeOH). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 7.97 (s, 1H), 7.85 (s, 1H), 7.40-7.25 (m, 10H), 6.86-6.82 (m, 4H), 6.59-6.57 (m, 4H), 5.24 (brs, 2H), 4.85-4.78 (m, 3H), 4.75-4.65 (m, 3H), 4.59-4.45 (m, 3H), 3.78-3.40 (m, 6H), 3.29-3.12 (m, 7H). ^{13}C NMR (100 MHz, DMSO-*d*6) δ 170.9, 155.9, 143.1, 142.9, 138.7, 138.4, 129.5, 128.2, 128.0, 127.7, 127.5, 127.4, 127.3, 123.4, 115.0, 97.0, 81.1, 79.2, 78.8, 77.2, 74.4, 72.3, 69.6, 68.8, 66.7, 65.4, 63.5, 54.3, 37.5, 37.4. HR-ESI-MS *m*/*z*: calcd for $C_{45}H_{48}N_6O_{12}$+H 865.3408, found 865.3401.

Methyl 3,4-di-O-{1-[(1(S)-carboxy-2-p-hydroxyphenylethyl)]-4-methyl-1H-1,2,3-triazole-4-yl}-α-D-glucopyranoside (33). Saponification of compound **32** (103.7 mg, 0.15 mmol) afforded **33** as a white solid (95.6 mg, 99.6 %) without column chromatography. R_f = 0.45 (petroleum ether/EtOAc, 1:4). $[\alpha]_D$ = +26.0 (*c* = 0.1/MeOH). ^{1}H NMR (400 MHz, CD_3OD) δ 8.73 (s, 1H), 8.64 (s, 1H), 7.38-7.32 (m, 4H), 7.02-6.98 (m, 4H), 5.72-5.63 (m, 2H), 4.73-4.35 (m, 5H), 3.56 (t, 1H, *J* = 12.0 Hz), 3.35-3.31 (m, 1H), 3.21-2.02 (m, 6H), 2.90 (s, 3H), 2.88-2.79 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 187.6, 170.2, 155.6, 155.3, 137.1, 133.2, 132.1, 130.6, 130.4, 130.2, 118.8, 118.7, 97.0, 74.2, 72.4, 72.3, 66.7, 63.5, 56.1, 54.3, 54.2, 51.1, 42.6, 21.2, 21.2. HR-ESI-MS *m*/*z*: calcd for $C_{31}H_{36}N_6O_{12}$+H 685.2469, found 685.2498.

Preparation of compound 32. To a biphasic solution of **26** (150.0 mg, 0.30 mmol) and **b** (166.5 mg, 0.75 mmol) in CH_2Cl_2 (5 mL) and H_2O (5 mL), Na ascorbate (298.2 mg, 1.51 mmol) and $CuSO_4 \cdot 5H_2O$ (225.8 mg, 0.90 mmol) were added. After stirring for 8 h at rt. (until TLC indicated the disappearance of the starting materials), the mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, filtered and evaporated to give a crude residue which was purified by column chromatography (petroleum ether/EtOAc = 2:1 to 1:1) to afford the corresponding triazole (282.8 mg, 81.4%). This product (150.0 mg, 0.16 mmol) was then desilylated according to the general procedure. Further purification by column chromatography (CH_2Cl_2/MeOH, 12:1) afforded **32** as a white solid (103.7 mg, 91.2 %). R_f = 0.29 (CH_2Cl_2/MeOH, 10:1). $[\alpha]_D$ = +50.3 (*c* = 0.1/MeOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (brs, 1H), 8.83 (brs, 1H), 7.76 (s, 1H), 7.63 (s, 1H), 6.78-6.56 (m, 8H), 5.68 (dd, 1H, *J* = 5.0, 11.9

Hz), 5.47 (dd, 1H, *J* = 4.2, 12.4 Hz), 5.02 (d, 1H, *J* = 13.3 Hz), 4.82 (d, 1H, *J* = 13.7 Hz), 4.76 (d, 1H, *J* = 3.7 Hz), 4.70 (d, 1H, *J* = 13.7 Hz), 4.56 (d, 1H, *J* = 13.8 Hz), 3.84 (s, 3H), 3.83 (s, 3H), 3.78-3.77 (m, 2H), 3.70 (t, 1H, *J* = 13.7 Hz), 3.58 (dd, 1H, *J* = 4.6, 15.1 Hz), 3.52-3.46 (m, 2H), 3.35 (s, 3H), 3.34-3.25 (m, 2H), 3.02 (dd, 1H, *J* = 3.7, 9.2 Hz), 2.79 (t, 1H, *J* = 9.2 Hz), 2.47 (brs, 1H), 2.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 156.5, 144.9, 129.5, 124.8, 124.4, 116.2, 115.9, 96.6, 77.5, 76.8, 72.9, 72.3, 69.9, 64.9, 63.4, 62.0, 61.8, 60.5, 59.8, 55.3, 55.2, 53.5, 38.3, 37.7. HR-ESI-MS *m*/*z*: calcd for $C_{33}H_{40}N_6O_{12}$+H 713.2782, found 713.2781.