Supporting Information for the Paper entitled

Synthesis of a β-glucan polysaccharide analogue by an iterative cupper-catalyzed azide-acetylene coupling reaction.

Hiroshi Tanaka,* Hiroaki Tago, Yohiyuki Adachi, Naohito Ohno, Takashi Takahashi*

Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-H-101 Ookayama, Meguro, Tokyo 152-8552 Japan.

Fax: +81-3-5734-2884
E-mail: thiroshi@apc.titech.ac.jp

Experimental Section

General Techniques

NMR spectra were recorded on a JEOL Model EX-270 (270 MHz for ^{1}H, 67.8 MHz for ^{13}C) or a JEOL Model ECP-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) instrument in the indicated solvent. Chemical shifts are reported in units parts per million (ppm) relative to the signal (0.00 ppm) for internal tetramethylsilane for solutions in $CDCl_3$. ^{1}H NMR spectrum data are reported as follows: $CDCl_3$ (7.26 ppm), CD_3OD (3.30 ppm), Acetone-d_6 (2.04 ppm) or D_2O (HOD (4.7015 ppm at 303 K, 4.5977 ppn at 313 K)). ^{13}C NMR spectrum data are reported as follows: $CDCl_3$ (77.0 ppm), CD_3OD (49.3 ppm) or Acetone-d_6 (30.3 ppm) as internal standard for D_2O. Multiplicities are reported by using the following abbreviations: s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, br; broad, *J*; coupling constants in Hertz.

IR spectra was recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Only the strongest and/or structurally important peaks are reported as the IR data given in cm^{-1}.

Optical rotations were measured with JASCO model P-1020 polarimeter.

All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) with UV light, visualized by 10% ethanolic phosphomolybdic acid, *p*-anisaldehyde solution or 0.5% ninhydrin *n*-butanol solution.

Merck silica gel was used for column chromatography.

Gel permeation chromatography (GPC) for qualitative analysis were performed on Japan Analytical Industry Model LC908 (recycling preparative HPLC), on a Japan Analytical Industry Model RI-5 refractive index detector and on a Japan Analytical Industry Model 310 ultra violet detector with a polystyrene gel column (JAIGEL-1H, 20mm x 600 mm), using chloroform as solvent (3.5 mL/min).

ESI-TOF Mass spectra were measured with Waters LCT Premier^{TM} XE. HRMS (ESI-TOF) were calibrated with leucine enkephalin.

Dry THF, dry CH_2Cl_2, dry toluene, dry CH_3CN were purified by GlassContour. Dry EtOH was distilled from $Mg(OEt)_2$.

1-[2,4,6-Tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilyl-prop-2-yn-1-yl)-β-D-glucopyranosyl]-4-phenyl-1*H*-1,2,3-triazole(11)

A mixture of 2,4,6-tri-*O*-benzoyl-3-[*O*-(3-*tert*-butyldimethylsilyl)prop-2-yn-1-yl]-β-D-glucopyranosyl azide (**10**) (151 mg, 213 μmol, 1.00 eq.) and phenylacetylene (68.7 μL, 639 μmol, 3.00 eq.) in CH_2Cl_2 (854 μL) was added Na ascorbate (427 μL, 0.500 M solution in H_2O, 213 μmol, 1.00 eq.) and $CuSO_4$ (427 μL, 0.500 M solution in H_2O, 213 μmol, 1.00 eq.) at room temperature. After being stirred at the same temperature for 2 days, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 97:3 toluene:acetone to give phenyltriazole **11** (108 mg, 133 μmol, 63%).

R_f = 0.40 (hexane/ethyl acetate = 1/1).

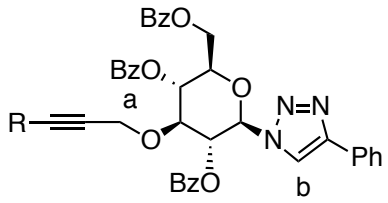
$[\alpha]_D^{30}$ = -93.7 (*c* = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H, b), 7.32-8.11 (m, 20H, aromatic), 6.16 (d, 1H, H-1, *J* = 9.3 Hz), 5.81 (dd, 1H, H-2, *J* = 9.3, 9.3 Hz), 5.69 (dd, 1H, H-4, *J* = 9.8, 9.8 Hz), 4.63-4.68 (m, 2H, H-3, H-6), 4.45 (dd, 1H, H-6, *J* = 5.4, 12.7 Hz), 4.32-4.34 (m, 3H, H-5, a), 0.91 (s, 9H, *t*-Bu), 0.05 (s, 3H, SiC*H*$_3$), 0.04 (s, 3H, SiC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.0, 164.6, 148.4, 133.7, 133.2, 130.0, 129.9, 129.7, 129.4, 128.9, 128.7, 128.6, 128.5, 128.4, 125.9, 117.9, 100.2, 92.1, 86.3, 77.7, 75.5, 72.3, 70.3, 62.9, 60.2, 25.9, 16.4, -4.9.

FT-IR (neat) 3785, 2956, 2858, 1723, 1602, 1452, 1361, 1316, 1259, 1178, 1096, 1070, 1027, 825, 709 cm^{-1}.

HRMS (ESI-TOF) calcd for $C_{44}H_{46}N_3O_8Si$ $[M+H]^+$ 772.3054, found 772.3053.



1-[2,4,6-Tri-*O*-benzoyl-3-*O*-(prop-2-yn-1-yl)-β-D-glucopyranosyl]-4-phenyl-1*H*-1,2,3-triazole (12)

To a stirred solution of the silyl alkyne **11** (131 mg, 162 μmol, 1.00 eq.) in THF (757 μL) was added TBAF (243 μL, 1.00 M solution in THF, 243 μmol, 1.50 eq.) at 0 °C. After being stirred at the same temperature for 2 h, the reaction mixture was poured into H_2O. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 95:5 toluene:ethyl acetate to give terminal acetylene **12** (103 mg, 149 μmol, 92%).

R_f = 0.33 (toluene/ethyl acetate = 9/1).

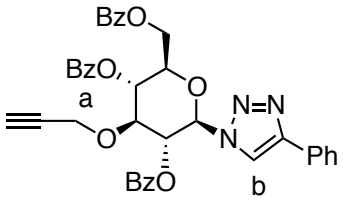
$[\alpha]_D^{30}$ = -139 (*c* = 0.310, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H, b), 7.32-8.11 (m, 20H, aromatic), 6.18 (d, 1H, H-1, *J* = 9.3 Hz), 5.81 (dd, 1H, H-2, *J* = 9.3, 9.3 Hz), 5.69 (dd, 1H, H-4, *J* = 9.3, 9.3 Hz), 4.45 (dd, 1H, H-6, *J* = 2.4, 9.8 Hz), 4.43-4.49 (m, 2H, H-3, H-6), 4.33-4.38 (m, 1H, H-5), 4.25 (d, 2H, a, *J* = 2.4 Hz), 2.12 (t, 1H, CC*H*, *J* = 2.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.6, 148.4, 133.7, 133.2, 130.0, 129.9, 129.8, 129.4, 128.8, 128.6, 128.4, 125.9, 117.8, 86.2, 79.0, 78.7, 75.7, 75.5, 72.2, 70.2, 62.9, 59.8.

FT-IR (neat) 3286, 3066, 1720, 1602, 1584, 1484, 1451, 1412, 1358, 1316, 1263, 1178, 1097, 1071, 1027, 976, 914, 839, 765, 709 cm^{-1}.

HRMS (ESI-TOF) calcd for $C_{38}H_{32}N_3O_8$ $[M+H]^+$ 658.2189, found 658.2181.



2,4,6-Tri-*O*-benzoyl-3-*O*-{1-[2,4,6-tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-β-D-glucopyranosyl]-1*H*-1,2,3-triazol-4-yl}methyl-β-D-glucopyranosyl 4-phenyl-1*H*-[1,2,3]triazole (13)

A mixture of terminal acetylene **12** (6.20 mg, 8.92 μmol, 1.00 eq.) and glycosyl azide **10** (7.60 mg, 10.7 μmol, 1.20 eq.) in H_2O (0.946 mL) and CH_2Cl_2 (1.00 mL) was added Na ascorbate (36.0 μL, 0.500 M solution in H_2O, 18.0 μmol, 2.00 eq.) and $CuSO_4$ (18.0 μL, 0.500 M solution in H_2O, 9.00 μmol, 1.00 eq.) at room temperature. After being stirred at the same temperature for 1 d, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 70:30 toluene:ethyl acetate to give ditriazole (**13**) (10.7 mg, 7.63 μmol, 86%).

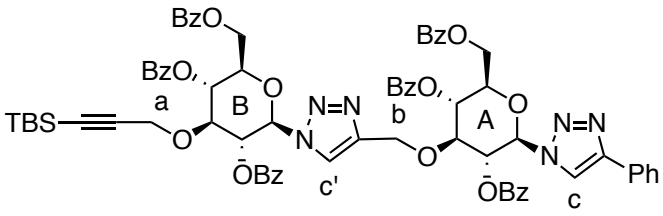
R_f = 0.42 (toluene/ethyl acetate = 4/1).

$[\alpha]_D^{29}$ = -67.9 (*c* = 0.780, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-8.14 (m, 37H, aromatic), 6.22 (d, 1H, H-A1 or H-B1, *J* = 9.8 Hz), 5.89 (dd, 1H, H-A2 or H-B2, *J* = 9.2, 9.2 Hz), 5.82 (d, 1H, H-A1 or H-B1, *J* = 9.3 Hz), 5.72 (dd, 1H, H-A4 or H-B4, *J* = 9.7, 9.7 Hz), 5.51 (dd, 1H, H-A4 or H-B4, *J* = 9.7, 9.7 Hz), 5.35 (dd, 1H, H-A2 or H-B2, *J* = 9.7, 9.7 Hz), 4.14-4.64 (m, 12H, H-A3, H-B3, H-A5, H-B5, H-A6, H-B6, a, b), 0.91 (s, 9H, *t*-Bu), 0.04 (s, 6H, SiC*H*$_3$).

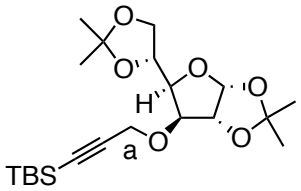
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.1, 164.9, 148.3, 144.7, 134.0, 133.6, 133.2, 130.0, 129.9, 129.7, 129.4, 129.2, 128.7, 128.6, 128.5, 128.3, 125.9, 121.1, 117.8, 100.2, 86.1, 79.1, 77.2, 75.4, 72.8, 72.4, 70.3, 65.6, 63.0, 62.8, 60.1, 29.6, 25.9, 16.4, -4.9.

FT-IR (neat) 2955, 1730, 1602, 1452, 1361, 1316, 1262, 1178, 1095, 1070, 1027, 826, 709 cm^{-1}.
HRMS (ESI-TOF) calcd for $C_{74}H_{71}N_6O_{16}Si$ $[M+H]^+$ 1327.4696, found 1327.4690.



1,2,5,6-Bis-*O*-isopropylidene-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-α-D-glucofuranose (15)

To a stirred solution of 1,2,5,6-bis-*O*-isopropylidene-3-*O*-(prop-2-yn-1-yl)-α-D-glucofuranose (**14**) (7.70 g, 25.8 mmol, 1.00 eq.) in THF (62.5 mL) was added dropwise *n*-BuLi (16.4 mL, 1.65 M solution in hexane, 27.1 mmol, 1.05 eq.) at -78 °C. After being stirred at the same temperature for 5 min, TBSCl (4.28 g, 28.4 mmol, 1.10 eq.) in THF (15.0 mL) was added dropwise. After being stirred at 0 °C for 1 h, the reaction mixture was poured into saturated aq. NH_4Cl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. NH_4Cl and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 97:3 hexane:ethyl acetate to give alkynylsilane **15** (9.46 g, 22.9 mmol, 89%).
R_f = 0.46 (hexane/ethyl acetate = 4/1).
$[\alpha]_D^{22}$ = -5.76 (*c* = 1.15, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (d, 1H, H-1, *J* = 3.9 Hz), 4.67 (d, 1H, H-2, *J* = 3.9 Hz), 4.19-4.29 (m, 3H, H-6, a), 4.12 (dd, 1H, H-5, *J* = 2.9, 7.8 Hz), 4.03-4.07 (m, 2H, H-3, H-6), 3.97 (dd, 1H, H-4, *J* = 5.4, 8.8 Hz), 1.47 (s, 3H, Me), 1.39 (s, 3H, Me), 1.31 (s, 3H, Me), 1.27 (s, 3H, Me), 0.92 (s, 9H, *t*-Bu), 0.10 (s, 6H, SiCH_3).
^{13}C NMR (100 MHz, $CDCl_3$) δ 111.7, 108.9, 105.2, 101.8, 90.2, 82.7, 81.6, 81.0, 72.6, 67.0, 58.8, 26.8, 26.2, 26.0, 25.3, 16.4, -4.8.
FT-IR (neat) 2988, 2934, 2859, 1463, 1372, 1252, 1209, 1166, 1080, 1029, 841, 826, 812, 683 cm^{-1}.
HRMS (ESI-TOF) calcd for $C_{21}H_{37}O_6Si$ $[M+H]^+$ 413.2359, found 413.2351.



1,2,4,6-Tetra-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-α/β-D-glucopyranose (16)

To a stirred solution of diacetal **15** (3.41 g, 8.26 mmol, 1.00 eq.) in THF (50.0 mL) and H_2O (20.0 mL) was added trifluoroacetic acid (50.0 mL) at room temperature. After being stirred at 60 °C for 5 h, the

reaction mixture was evaporated *in vacuo*. The residue was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with three portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was used for the next reaction without further purification.

To a stirred solution of the residue in pyridine (30.0 mL) was added benzoyl chloride (5.52 mL, 47.9 mmol, 5.80 eq.) and a catalytic amount of DMAP at room temperature. After being stirred at the same temperature for 13 h, the reaction mixture was quenched with MeOH and 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl and saturated aq. $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 95:5 hexane:ethyl acetate to give the benzoyl glycoside **16** (5.19 g, 6.94 mmol, 2 steps 84%, α:β = 56:44).

R_f = 0.39, 0.44 (hexane/ethyl acetate = 2/1).

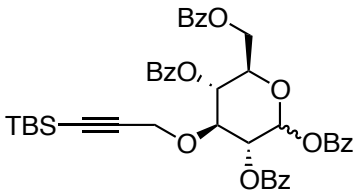
$[\alpha]_D^{24}$ = -6.51 (*c* = 1.07, $CHCl_3$).

^{1}H NMR (270 MHz, $CDCl_3$) δ 7.99-8.11 (m, 8H, aromatic), 7.38-7.54 (m, 12H, aromatic), 6.78 (d, 0.56H, H-1α, *J* = 4.0 Hz), 6.15 (d, 0.44H, H-1β, *J* = 7.6 Hz), 5.60-5.70 (m, 1.44H, H-2β, H-4α, H-4β), 5.48 (dd, 0.56H, H-2α, *J* = 4.6, 10.5 Hz), 4.79 (t, 0.56H, H-3α, *J* = 8.1 Hz), 4.22-4.65 (m, 5.44H, H-3β, H-5α, H-5β, H-6α, H-6β, aα, aβ), 0.88 (s, 9H, *t*-Bu), 0.03 (s, 6H, SiC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.2, 165.1, 165.0, 164.8, 164.3, 133.7, 133.5, 133.4, 133.0, 130.2, 129.9, 129.8, 129.7, 129.6, 129.3, 129.2, 128.6, 128.5, 128.3, 100.9, 100.6, 92.6, 91.1, 90.1, 77.2, 74.6, 73.1, 72.4, 72.0, 70.3, 62.9, 62.7, 60.0, 59.8, 25.9, 16.4, 16.3, -4.8, -4.9.

FT-IR (neat) 3065, 2954, 2929, 2858, 1734, 1602, 1452, 1362, 1316, 1266, 1178, 1094, 1069, 1027, 840, 826, 754, 709, 686, 581 cm^{-1}.

HRMS (ESI-TOF) calcd for $C_{43}H_{45}O_{10}Si$ $[M+H]^+$ 749.2782, found 749.2772.



2,4,6-Tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-D-glucopyranose (17)

A mixture of benzoyl glycoside (8.00 g, 10.7 mmol, 1.00 eq.) and acetic acid (1.20 mL) in DMF (42.8 mL) was added hydrazine monohydrate (1.00 mL) at 0 °C. After being stirred at the same temperature for 4 h, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with three portions of ethyl acetate. The combined extract was washed with 1 M HCl and H_2O and saturated aq. $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 97:3 toluene:ethyl acetate to give hemicatal **17** (6.10 g, 9.48 mmol, 89%).

R_f = 0.34 (hexane/ethyl acetate = 2/1).

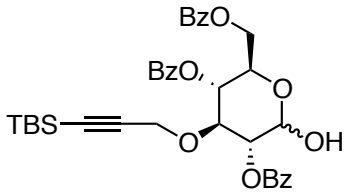
$[\alpha]_D^{31}$ = +45.8 (*c* = 0.640, $CHCl_3$).

^{1}H NMR (270 MHz, $CDCl_3$) α anomer (major); δ 8.02-8.13 (m, 6H, aromatic), 7.36-7.58 (m, 9H, aromatic), 5.65 (d, 1H, H-1, *J* = 3.3 Hz), 5.52 (dd, 1H, H-4 or H-6, *J* = 9.6, 9.6 Hz), 5.12 (dd, 1H, H-2, *J* = 4.1, 9.9 Hz), 4.69 (dd, 1H, H-4 or H-6, *J* = 9.6, 9.6 Hz), 4.61 (dd, 1H, H-6, *J* = 2.6, 12.2 Hz), 4.33-4.54 (m, 4H, H-3, H-5, a), 0.88 (s, 9H, *t*-Bu), 0.03 (s, 6H, SiC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.7, 165.2, 133.3, 133.0, 129.8, 129.7, 129.6, 129.5, 129.0, 128.4, 128.2, 125.2, 101.2, 90.8, 90.2, 77.2, 75.0, 74.1, 70.7, 67.6, 62.9, 60.4, 25.9, 16.3, -4.9.

FT-IR (neat) 3684, 2955, 2858, 1728, 1602, 1452, 1316, 1270, 1178, 1110, 1070, 1027, 826, 777, 710, 686 cm^{-1}.

HRMS (ESI-TOF) calcd for $C_{36}H_{41}O_9Si$ $[M+H]^+$ 645.2520, found 645.2523.



O-[2,4,6-Tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-α,β-D-glucopyranosyl] trichloroacetimidate (6)

A mixture of hemiacetal **17** (6.10 g, 9.48 mmol, 1.00 eq.) and a catalytic amount of Cs_2CO_3 in CH_2Cl_2 (37.9 mL) was added Cl_3CCN (5.90 mL, 56.9 mmol, 6.00 eq.) at 0 °C. After being stirred at room temperature for 2 h, the reaction mixture was filtered through a pad of Celite. The filtrate mixture was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 99:1 toluene:ethyl acetate to give glycosyl imidate **6** (7.18 g, 9.10 mmol, 96%).

R_f = 0.49 (hexane/ethyl acetate = 2/1).

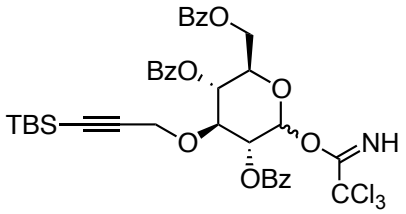
$[\alpha]_D^{22}$ = +59.0 (*c* = 1.03, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) α anomer (major); δ 8.60 (s, 1H, N*H*), 8.00-8.10 (m, 6H, aromatic), 7.52-7.59 (m, 3H, aromatic), 7.38-7.47 (m, 6H, aromatic), 6.73 (d, 1H, H-1, *J* = 3.9 Hz), 5.60 (dd, 1H, H-4, *J* = 10.2, 10.2 Hz), 5.42 (dd, 1H, H-2, *J* = 3.9, 9.8 Hz), 4.75 (dd, 1H, H-3, *J* = 9.3, 9.3 Hz), 4.59 (dd, 1H, H-6, *J* = 2.4, 12.4 Hz), 4.46-4.51 (m, 1H, H-5), 4.33-4.43 (m, 3H, H-6, a), 0.90 (s, 9H, *t*-Bu), 0.05 (s, 3H, SiC*H*$_3$), 0.05 (s, 3H, SiC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.1, 160.3, 137.7, 133.4, 132.9, 129.9, 129.8, 129.7, 129.2, 129.0, 128.9, 128.4, 128.2, 128.1, 125.2, 100.8, 93.1, 91.0, 90.8, 74.5, 72.6, 70.4, 69.9, 62.6, 60.0, 25.9, 21.3, 16.3, -4.8.

FT-IR (neat) 3344, 2954, 2858, 1732, 1677, 1602, 1452, 1268, 1108, 1028, 908, 839, 796, 710, 647 cm^{-1}.

HRMS (ESI-TOF) calcd for $C_{38}H_{41}Cl_3NO_9Si$ $[M+H]^+$ 788.1616, found 788.1614.



Ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2,4,6-tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranoside (20)

A mixture of diol **18** (1.86 g, 2.79 mmol, 1.10 eq.), the glycoyl imidate **6** (2.00 g, 2.54 mmol, 1.00 eq.) and pulverized activated MS-4A (7.60 g) in dry CH_2Cl_2 (508 mL) was stirred at room temperature for 1 h under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 °C. To the mixture was added a catalytic amount of TMSOTf. After being stirred at the same temperature for 2 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was evaporated *in vacuo*. The residue was used for the next reaction without further purification.

To a stirred solution of the residue in pyridine (10.5 mL) was added acetic anhydride (2.00 mL, 21.0 mmol, 8.27 eq.) and a catalytic amount of DMAP at room temperature. After being stirred at the same temperature for 7 h, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 95:5 toluene:ethyl acetate to give ethylthio glycoside **20** (1.44 g, 1.08 mmol, 2 steps 43%).

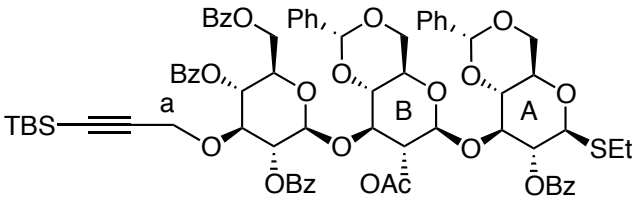
R_f = 0.41 (toluene/ethyl acetate = 9/1).

$[\alpha]_D^{25}$ = -14.3 (*c* = 0.935, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, 2H, aromatic, *J* = 7.3 Hz), 7.94-8.03 (m, 6H, aromatic), 7.11-7.65 (m, 22H, aromatic), 5.52 (s, 1H, benzylidene), 5.49 (dd, 1H, H-C4, *J* = 9.8, 9.8 Hz), 5.34 (dd, 1H, H-C2, *J* = 7.8, 7.8 Hz), 4.98 (d, 1H, H-C1, *J* = 7.8 Hz), 4.83-4.85 (m, 2H, H-A2, H-B2), 4.72 (s, 1H, benzylidene), 4.68 (d, 1H, H-A1, *J* = 5.4 Hz), 4.47-4.49 (m, 2H, H-B1, H-C6), 4.31-4.36 (m, 2H, H-C3, H-A6), 4.23-4.27 (m, 3H, H-C6, a), 4.08-4.14 (m, 2H, H-A3, H-B6), 4.00 (dd, 1H, H-B4, *J* = 8.8, 10.3 Hz), 3.76-3.86 (m, 2H, H-B3, H-C5), 3.67 (dd, 1H, H-A6, *J* = 10.4, 10.4 Hz), 3.37-3.54 (m, 3H, H-A5, H-B5, H-B6), 3.23 (dd, 1H, H-A4, *J* = 10.0, 10.0 Hz), 2.60-2.68 (m, 2H, S*CH*$_2$CH$_3$), 1.63 (s, 3H, COC*H*$_3$), 1.19 (t, 3H, SCH$_2$C*H*$_3$, *J* = 7.3 Hz), 0.86 (s, 9H, t-Bu), -0.01 (s, 6H, Si*CH*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 169.1, 166.1, 164.9, 137.2, 133.5, 133.3, 132.9, 129.9, 129.7, 129.4, 129.2, 129.0, 128.7, 128.5, 128.4, 128.2, 127.9, 126.3, 125.9, 101.6, 100.5, 98.5, 98.4, 84.3, 78.4, 77.9, 77.8, 75.8, 73.2, 72.9, 72.0, 71.1, 68.5, 65.4, 63.2, 59.5, 25.9, 24.3, 20.3, 16.4, 14.7, -4.9.

FT-IR (neat) 3675, 2929, 2859, 1732, 1603, 1452, 1374, 1316, 1266, 1178, 1096, 1070, 1027, 839, 749, 710 cm^{-1}.



2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl azide (21)

A mixture of ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**7**) (4.00 g, 4.64 mmol, 1.00 eq.) and pulverized activated MS-4A (9.30 g, 2.00 g/mmol) in dry CH_2Cl_2 (46.2 mL, 10.0 mL/mmol) was stirred at room temperature for 1 h under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 °C. To the mixture was added IBr (5.56 mL, 1.00 M solution in CH_2Cl_2, 5.56 mmol, 1.20 eq.). After being stirred at 0 °C for 30 min, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was poured into 10% aq. $Na_2S_2O_3$ and saturated aq. $NaHCO_3$. The aqueous layer was extracted with three portions of ethyl acetate. The combined extract was washed with 10% aq. $Na_2S_2O_3$ and saturated aq. $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was used for the next reaction without further purification.

To a stirred solution of the residue in DMF (23.1 mL) was added sodium azido (756 mg, 11.6 mmol, 2.50 eq.) at room temperature. After being stirred at the same temperature for 3 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl and H_2O and saturated aq. $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 95:5 toluene:acetone to give 2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl azide (**21**) (3.21 g, 3.81 mmol, 2 steps 82%).

R_f = 0.46 (toluene/ethyl acetate = 2/1).

$[\alpha]_D^{25}$ = -68.3 (*c* = 0.835, $CHCl_3$).

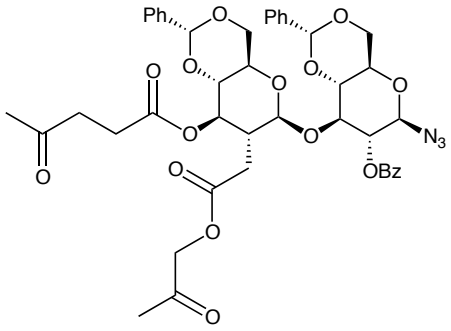
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, 2H, aromatic, *J* = 7.8 Hz), 7.16-7.65 (m, 13H, aromatic), 5.59 (s, 1H, benzylidene), 5.38 (s, 1H, benzylidene), 5.25 (dd, 1H, H-A2, *J* = 9.3, 9.3 Hz), 5.10 (dd, 1H, H-B3, *J* = 9.8, 9.8 Hz), 5.01 (dd, 1H, H-B2, *J* = 7.8, 7.8 Hz), 4.71 (d, 1H, H-B1, *J* = 8.8 Hz), 4.69 (d, 1H, H-A1, *J* = 8.8 Hz), 4.42 (dd, 1H, H-A6, *J* = 4.4, 10.2 Hz), 4.25 (dd, 1H, H-B6, *J* = 4.9, 10.8 Hz), 4.19 (dd, 1H, H-A3, *J* = 9.3, 9.3 Hz), 3.77-3.88 (m, 2H, H-A4, H-A6), 3.61-3.68 (m, 3H, H-B4, H-A5, H-B6), 3.36-3.42 (m, 1H, H-B5), 2.31-2.68 (m, 8H, a, b, c, d), 2.08 (s, 6H, COC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 171.6, 171.2, 164.8, 136.9, 136.6, 133.7, 129.7, 129.1, 128.8, 128.7,

128.1, 128.0, 126.0, 125.9, 101.1, 101.0, 100.8, 88.4, 78.2, 78.1, 77.2, 72.8, 71.5, 71.4, 68.7, 68.3, 68.0, 66.1, 37.6, 37.5, 29.5, 27.7, 27.2.

FT-IR (neat) 2872, 2119, 1721, 1371, 1268, 1152, 1099, 1028, 700 cm^{-1}.

HRMS (ESI-TOF) calcd for $C_{43}H_{46}N_3O_{15}$ $[M+H]^+$ 844.2929, found 844.2917.



2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl azide (22)

A mixture of dilevulinoyl ester **21** (3.11 g, 3.69 mmol, 1.00 eq.) and acetic acid (3.00 mL) in CH_2Cl_2 (18.4 mL) was added hydrazine monohydrate (1.00 mL) at 0 °C. After being stirred at the same temperature for 4 h, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl and H_2O and saturated aq. $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 92:8 toluene:acetone to give diol **22** (2.14 g, 3.31 mmol, 90%).

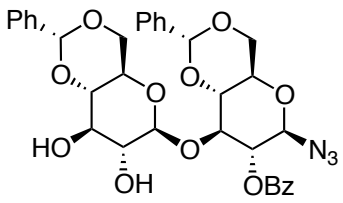
R_f = 0.36 (toluene/acetone = 4/1).

$[\alpha]_D^{25}$ = -56.3 (*c* = 1.15, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, 2H, aromatic, *J* = 7.3 Hz), 7.18-7.61 (m, 13H, aromatic), 5.62 (s, 1H, benzylidene), 5.42 (s, 1H, benzylidene), 5.26 (dd, 1H, H-A2, *J* = 8.8, 8.8 Hz), 4.87 (d, 1H, H-A1, *J* = 8.8 Hz), 4.43-4.48 (m, 2H, H-B1, H-A6), 4.21 (dd, 1H, H-A3, *J* = 9.3, 9.3 Hz), 3.80-3.90 (m, 3H, H-A4, H-A6, H-B6), 3.58-3.68 (m, 2H, H-B3, H-A5), 3.43-3.48 (m, 3H, H-B2, H-B4, H-B6), 3.26-3.32 (m, 1H, H-B5), 2.86 (d, 1H, O*H*, *J* = 2.9 Hz), 2.08 (brs, 1H, O*H*).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 136.8, 136.4, 133.7, 129.9, 129.5, 129.2, 128.6, 128.3, 126.2, 126.0, 102.9, 101.8, 88.7, 80.1, 78.7, 77.9, 73.3, 72.7, 68.7, 68.3, 66.6.

FT-IR (neat) 3477, 2875, 2119, 1727, 1603, 1452, 1384, 1317, 1270, 1181, 1098, 1029, 1008, 918, 752, 711, 700, 547 cm^{-1}.



2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-[4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2,4,6-tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl azide (23)

A mixture of ethyl glycoside **20** (976 mg, 0.731 mmol, 1.00 eq.), diol **22** (520 mg, 0.804 mmol, 1.10 eq.) and pulverized activated MS-4A (2.19 g) in dry CH_2Cl_2 (73.1 mL) was stirred at room temperature for 1 h under argon to remove a trace amount of water. Then the reaction mixture was cooled to 0 °C. To the mixture was added MeOTf (827 μL, 7.31 mmol, 10.0 eq.). After being stirred at room temperature for 1 day, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was evaporated *in vacuo*. The residue was chromatographed on silica gel with 94:6 toluene:ethyl acetate to give pentasaccharide **23** (1.15 g, 0.598 mmol, 82%).

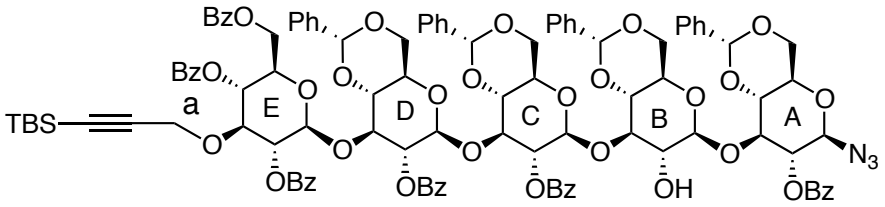
R_f = 0.39 (toluene/ethyl acetate = 5/1).

$[\alpha]_D^{32}$ = -15.3 (*c* = 0.130, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-8.11 (m, 10H, aromatic), 7.16-7.99 (m, 35H, aromatic), 5.58 (s, 1H, benzylidene), 5.47-5.52 (m, 2H, H-E4, benzylidene), 5.33 (t, 1H, H-E2, *J* = 7.8 Hz), 5.19 (dd, 1H, H-A2, *J* = 8.8, 8.8 Hz), 3.25-5.01 (m, 36H, H-A1, H-B1, H-C1, H-D1, H-E1, H-B2, H-C2, H-D2, H-A3, H-B3, H-C3, H-D3, H-E3, H-A4, H-B4, H-C4, H-D4, H-A5, H-B5, H-C5, H-D5, H-E5, H-A6, H-B6, H-C6, H-D6, H-E6, a, benzylidene), 2.70 (brs, 1H, O*H*) 1.71 (s, 3H, COC*H*$_3$), 0.86 (s, 9H, *t*-Bu), -0.01 (s, 6H, SiC*H*$_3$).

FT-IR (neat) 3851, 3568, 3446, 2927, 2376, 2345, 2118, 1731, 1633, 1384, 1266, 1096, 1028, 756, 712 cm^{-1}.

HRMS (ESI-TOF) calcd for $C_{104}H_{106}N_3O_{31}Si$ $[M+H]^+$ 1920.6580, found 1920.6592.



2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2,4,6-tri-*O*-benzoyl-3-*O*-(prop-3-*tert*-butyldimethylsilyl-2-yn-1-yl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl azide (4)

To a stirred solution of pentasaccahride **23** (1.15 g, 0.598 mmol, 1.00 eq.) in pyridine (3.00 mL) was added acetic anhydride (565 μL, 5.98 mmol, 10.0 eq.) and a catalytic amount of DMAP at room temperature. After being stirred at the same temperature for 2 h, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl and saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 92:8 toluene:ethyl acetate to give acetate **4** (971 mg,

0.495 mmol, 83%).

R_f = 0.60 (toluene/ethyl acetate = 4/1).

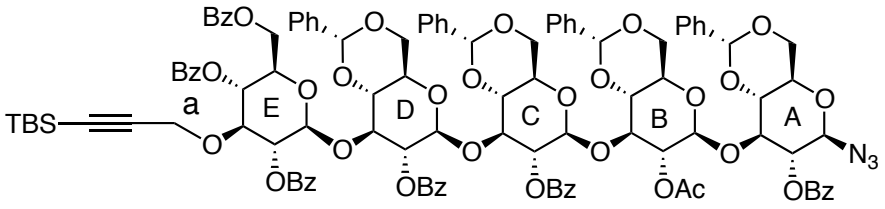
$[\alpha]_D^{31}$ = -21.5 (*c* = 0.990, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-8.15 (m, 10H, aromatic), 7.16-7.67 (m, 35H, aromatic), 5.56 (s, 1H, benzylidene), 5.51 (dd, 1H, H-E4, *J* = 9.6, 9.6 Hz), 5.38 (dd, 1H, H-E2, *J* = 8.8, 8.8 Hz), 5.18 (s, 1H, benzylidene), 5.33 (d, 1H, H-E1, *J* = 7.8 Hz), 3.17-4.91 (m, 36H, H-A1, H-B1, H-C1, H-D1, H-A2, H-B2, H-C2, H-D2, H-A3, H-B3, H-C3, H-D3, H-E3, H-A4, H-B4, H-C4, H-D4, H-A5, H-B5, H-C5, H-D5, H-E5, H-A6, H-B6, H-C6, H-D6, H-E6, a, benzylidene), 1.77 (s, 3H, COC*H*$_3$), 1.65 (s, 3H, COC*H*$_3$), 0.89 (s, 9H, *t*-Bu), 0.02 (s, 6H, SiC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.0, 164.7, 137.1, 136.9, 133.8, 133.6, 132.8, 129.8, 129.7, 129.4, 129.1, 129.0, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 126.3, 126.1, 125.9, 125.2, 101.8, 101.0, 100.8, 98.5, 98.4, 90.9, 88.2, 78.0, 71.9, 71.8, 71.1, 68.8, 65.4, 65.3, 59.5, 25.9, 21.4, 20.4, 20.3, 16.4, -5.0.

FT-IR (neat) 2930, 2861, 2119, 1733, 1603, 1452, 1375, 1316, 1266, 1179, 1097, 1028, 915, 840, 753, 712 cm^{-1}.

HRMS (ESI-TOF) calcd for $C_{106}H_{108}N_3O_{32}Si$ $[M+H]^+$ 1962.6685, found 1962.6730.



1-{2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2,4,6-tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-4-*N*-(*tert*-butoxycarbonyl)aminomethyl-1*H*-1,2,3-triazole (24)

To a solution of glycosyl azide **4** (264 mg, 0.134 mmol, 1.00 eq.) and *N*-(*tert*-butoxycarbonyl)-prop-2-ynylamine (62.4 mg, 0.402 mmol, 3.00 eq.) in H_2O (2.00 mL) and CH_2Cl_2 (2.00 mL) was added Na ascorbate (0.538 mL, 0.500 M solution in H_2O, 0.269 mmol, 2.00 eq.) and $CuSO_4$ (0.269 mL, 0.500 M solution in H_2O, 0.134 mmol, 1.00 eq.) at room temperature. After being stirred at the same temperature for 2 d, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 89:11 toluene:acetone to give triazole **24** (284 mg, 0.134 mmol, quant.).

R_f = 0.42 (toluene/acetone = 5/1).

$[\alpha]_D^{32}$ = -24.3 (*c* = 0.830, $CHCl_3$).

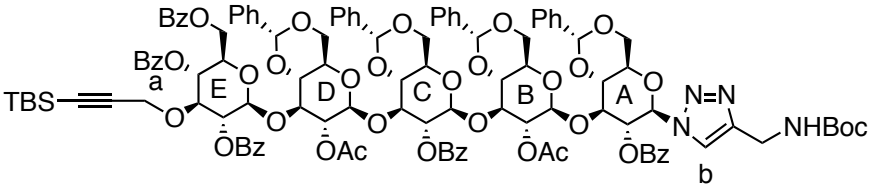
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-8.09 (m, 46H, aromatic), 5.84 (d, 1H, H-A1, *J* = 9.3 Hz), 3.19-5.62 (m,

42H, H-B1, H-C1, H-D1, H-E1, H-A2, H-B2, H-C2, H-D2, H-E2, H-A3, H-B3, H-C3, H-D3, H-E3, H-A4, H-B4, H-C4, H-D4, H-E4, H-A5, H-B5, H-C5, H-D5, H-E5, H-A6, H-B6, H-C6, H-D6, H-E6, a, b, benzylidene), 1.71 (s, 3H, COC*H*$_3$), 1.61 (s, 3H, COC*H*$_3$), 1.47 (s, 9H, Boc), 0.86 (s, 9H, *t*-Bu), -0.02 (s, 6H, SiC*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 168.9, 166.0, 165.0, 164.9, 164.6, 137.1, 136.8, 133.7, 133.3, 132.8, 129.8, 129.7, 129.4, 129.0, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 126.3, 126.2, 126.1, 125.9, 125.2, 101.9, 101.4, 101.0, 100.5, 98.5, 98.2, 91.0, 78.0, 77.9, 77.8, 74.2, 73.1, 71.9, 71.8, 71.0, 69.9, 68.6, 68.4, 68.0, 65.9, 65.3, 63.1, 59.5, 28.4, 25.9, 21.4, 20.4, 20.2, 16.4, -5.0.

FT-IR (neat) 2930, 1733, 1603, 1500, 1452, 1373, 1316, 1265, 1178, 1097, 1070, 914, 840, 712 cm^{-1}.

HRMS (ESI-TOF) calcd for $C_{114}H_{121}N_4O_{34}Si$ $[M+H]^+$ 2117.7632, found 2117.7661.



1-{2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2,4,6-tri-*O*-benzoyl-3-*O*-(prop-2-yn-1-yl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-4-*N*-(*tert*-butoxycarbonyl)aminomethyl-1*H*-1,2,3-triazole (25)

To a stirred solution of 1alkynylsilane **24** (302 mg, 143 μmol, 1.00 eq.) in THF (4.30 mL) was added TBAF (214 μL, 1.00 M solution in THF, 214 μmol, 1.50 eq.) at 0 °C. After being stirred at room temperature for 30 min, the reaction mixture was poured into H_2O. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 92:8 toluene:acetone to give terminal acetylene **25** (276 mg, 138 μmol, 96%).

R_f = 0.53 (toluene/ethyl acetate = 2/1).

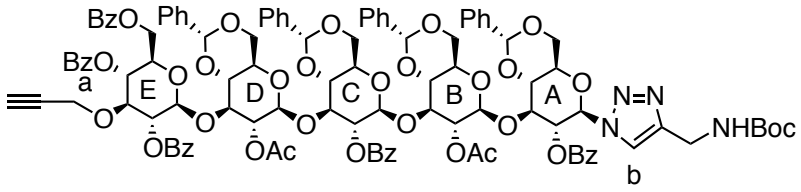
$[\alpha]_D^{33}$ = -29.5 (*c* = 0.780, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-8.14 (m, 46H, aromatic), 5.83 (d, 1H, H-A1, *J* = 9.8 Hz), 3.08-5.61 (m, 42H), 2.02 (t, 1H, CC*H*, *J* = 2.4 Hz), 1.70 (s, 3H, COC*H*$_3$), 1.62 (s, 3H, COC*H*$_3$), 1.47 (s, 9H, Boc).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 169.0, 166.0, 164.9, 164.8, 164.7, 164.2, 137.8, 137.0, 136.8, 133.9, 133.7, 133.3, 132.8, 129.8, 129.7, 129.5, 129.4, 129.2, 129.0, 128.8, 128.5, 128.3, 128.2, 128.0, 127.8, 126.3, 126.1, 125.9, 125.2, 101.6, 100.3, 98.0, 97.7, 86.2, 79.3, 79.1, 78.0, 77.7, 74.9, 74.5, 74.3, 73.2, 71.8, 71.7, 71.0, 69.9, 68.5, 68.4, 68.0, 65.9, 65.1, 63.1, 59.2, 28.4, 21.4, 20.4, 20.3.

FT-IR (neat) 2976, 2872, 1734, 1603, 1496, 1452, 1373, 1316, 1266, 1178, 1097, 1028, 916, 753, 712 cm^{-1}.

HRMS (ESI-TOF) calcd for $C_{108}H_{107}N_4O_{34}$ $[M+H]^+$ 2003.6767, found 2003.6766.



1-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-{2,4,6-tri-*O*-benzoyl-3-*O*-[({2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2,4,6-tri-*O*-benzoyl-3-*O*-(prop-2-yn-1-yl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosy}-1*H*-1,2,3-triazol-4-yl)methyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*N*-(*tert*-butoxycarbonyl)aminomethyl-1*H*-1,2,3-triazole (27)

A mixture of the terminal acetylene **25** (276 mg, 138 μmol, 96%). (89.2 mg, 0.0445 mmol, 1.00 eq.) and glycosyl azide **6** (95.8 mg, 0.0488 mmol, 1.10 eq.) in H_2O (1.23 mL) and CH_2Cl_2 (1.50 mL) was added Na ascorbate (0.178 mL, 0.500 M solution in H_2O, 0.0890 mmol, 2.00 eq.) and $CuSO_4$ (0.0890 mL, 0.500 M solution in H_2O, 0.0445 mmol, 1.00 eq.) at room temperature. After being stirred at the same temperature for 5 h, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was used for the next reaction without further purification.

To a stirred solution of the residue in THF (1.50 mL) was added TBAF (73.0 μL, 1.00 M solution in THF, 66.8 μmol, 1.50 eq.) at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was poured into H_2O. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 90:10 toluene:acetone to give the terminal acetylene **27** (139 mg, 36.0 μmol, 2 steps 81%).

R_f = 0.30 (toluene/acetone = 4/1).

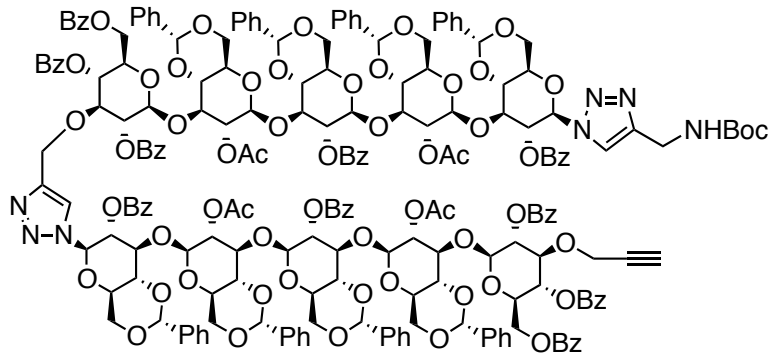
$[\alpha]_D^{36}$ = -33.3 (*c* = 1.39, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09-8.13 (m, 92H, aromatic), 5.83 (d, 1H, H-A1, *J* = 9.3 Hz), 3.03-5.62 (m, 83H), 2.02 (t, 1H, CC*H*, *J* = 2.4 Hz), 1.72 (s, 3H, COC*H*$_3$), 1.68 (s, 3H, COC*H*$_3$), 1.62 (s, 3H, COC*H*$_3$), 1.60 (s, 3H, COC*H*$_3$), 1.47 (s, 9H, Boc).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 169.0, 168.9, 166.0, 165.9, 164.9, 164.8, 164.7, 164.1, 145.3, 137.1, 136.8, 133.6, 133.2, 132.8, 129.8, 129.6, 129.5, 129.4, 129.1, 129.0, 128.8, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 126.3, 126.1, 125.9, 100.8, 100.3, 98.4, 97.9, 97.5, 86.2, 80.7, 79.2, 79.1, 78.0, 77.8, 77.6, 77.2, 76.5, 75.4, 74.9, 74.2, 73.1, 71.8, 71.7, 71.6, 71.0, 69.8, 68.5, 68.4, 67.9, 65.9, 65.3, 65.0, 63.1, 59.2, 28.3, 20.3, 20.2.

FT-IR (neat) 2873, 1733, 1603, 1494, 1452, 1373, 1316, 1265, 1178, 1096, 915, 751, 712 cm^{-1}.

HRMS (ESI-TOF) calcd for $C_{208}H_{200}N_7O_{66}$ $[M+H]^+$ 3851.2509, found 3851.2561.



1-[2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2,4,6-tri-*O*-benzoyl-3-*O*-{[(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-{2,4,6-tri-*O*-benzoyl-3-*O*-[({2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2,4,6-tri-*O*-benzoyl-3-*O*-(prop-2-yn-1-yl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosy}-1*H*-1,2,3-triazol-4-yl)methyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl]methyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosy]-4-*N*-(*tert*-butoxycarbonyl)aminomethyl-1*H*-1,2,3-triazole (28)

A mixture of terminal acetylene **28** (53.4 mg, 13.9 μmol, 1.00 eq.) and the glycosyl azide **6** (29.9 mg, 15.3 μmol, 1.10 eq.) in H_2O (2.00 mL) and CH_2Cl_2 (2.00 mL) was added Na ascorbate (56.0 μL, 0.500 M solution in H_2O, 28.0 μmol, 2.00 eq.) and $CuSO_4$ (28 μL, 0.500 M solution in H_2O, 14.0 μmol, 1.00 eq.) at room temperature. After being stirred at the same temperature for 2 d, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl and saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was used for the next reaction without further purification.

To a stirred solution of the residue in THF (1.00 mL) was added TBAF (15.0 μL, 1.00 M solution in THF, 15.0 μmol, 1.10 eq.) at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was poured into H_2O. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by GPC to give terminal acetylene **28** (49.6 mg, 8.70 μmol, 2 steps 63%).

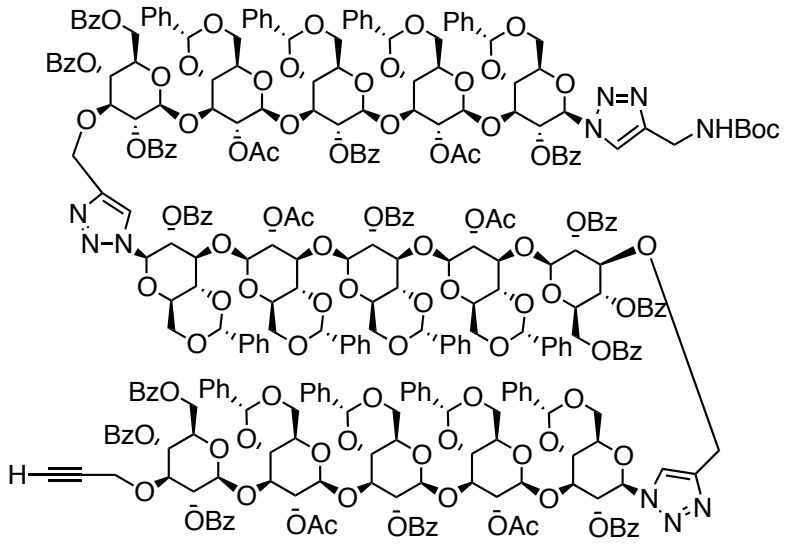
R_f = 0.33 (toluene/acetone = 3/1).

$[\alpha]_D^{29}$ = -35.0 (*c* = 0.990, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09-8.13 (m, 138H, aromatic), 5.83 (d, 1H, H-A1, *J* = 9.3 Hz), 3.00-5.62 (m, 124H), 2.02 (t, 1H, CC*H*, *J* = 2.0 Hz), 1.72 (s, 3H, COCH_3), 1.69 (s, 3H, COCH_3), 1.69 (s, 3H, COCH_3), 1.65 (s, 3H, COCH_3), 1.61 (s, 3H, COCH_3), 1.60 (s, 3H, COCH_3), 1.47 (s, 9H, Boc).

FT-IR (neat) 2875, 1732, 1602, 1493, 1452, 1374, 1316, 1265, 1178, 1070, 1027, 913, 802, 753, 712, 532 cm^{-1}.

HRMS (ESI-TOF) calcd for $C_{308}H_{293}N_{10}O_{98}$ $[M+H]^+$ 5698.8251, found 5698.8438.



1-[3-*O*-(3-*O*-{3-*O*-[3-*O*-(2,4,6-tri-*O*-benzoyl-3-*O*-{[(3-*O*-{3-*O*-[3-*O*-(3-*O*-{-*O*-[({3-*O*-[3-*O*-(3-*O*-{3-*O*-[3-*O*-(prop-2-yn-1-yl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosy}-1*H*-1,2,3-triazol-4-yl)methyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl]methyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosy]-4-*N*-(*tert*-butoxycarbonyl)aminomethyl-1*H*-1,2,3-triazole (3)

To a stirred solution of the protected oligosaccahride (**28**) (29.8 mg, 5.23 μmol, 1.00 eq.) in CH_2Cl_2 (970 μL) was added trifluoroacetic acid (30.0 μL) and a catalytic amount of H_2O at 0 °C. After being stirred at room temperature for 3 h, the reaction mixture was neutralized with triethylamine and evaporated *in vacuo*. The residue was used for the next reaction without further purification.

To a stirred solution of the residue in MeOH (4.00 mL) and THF (4.00 mL) was added a catalytic amount of NaOMe at room temperature. After being stirred at the same temperature for 2 d, the reaction mixture was neutralized with DOWEX 50W-X2 and filtered through a pad of Celite. The filtrate mixture was evaporated *in vacuo*. The residue was purified by reverse-phase column chromatography (Bond Elut-C18) to give the trimer of the pentasaccharide (**3**) (5.40 mg, 1.98 μmol, 2 steps 38%).

R_f = 0.00 (acetic acid/*n*-butanol/H_2O = 4/4/1).

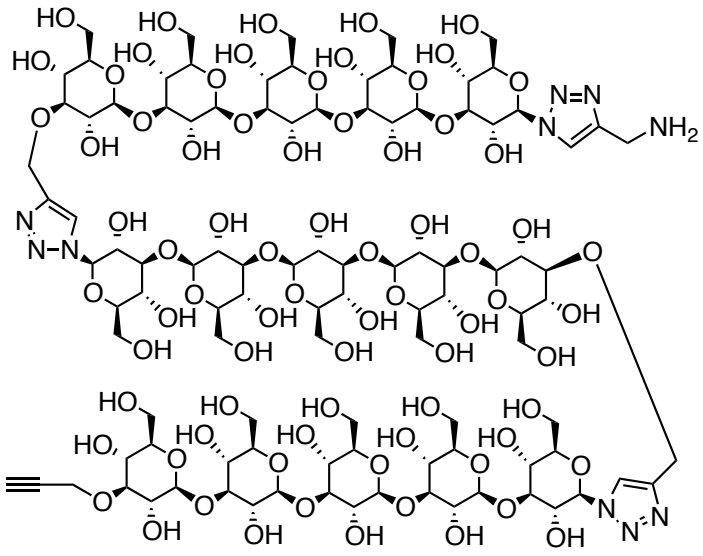
$[\alpha]_D^{25}$ = -5.19 (*c* = 0.270, H_2O).

^{1}H NMR (400 MHz, D_2O) δ 8.44 (s, 1H, aromatic), 8.29 (s, 1H, aromatic), 8.11 (s, 1H, aromatic), 5.75-5.81 (m, 3H), 3.34-5.07 (m, 110H).

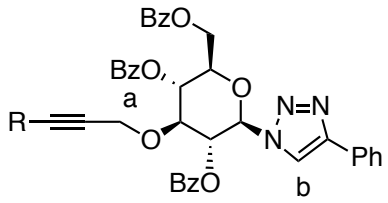
FT-IR (neat) 3860, 3821, 3780, 3762, 3410, 3310, 3290, 3277, 3250, 2906, 2528, 1965, 1593, 1378, 1050,

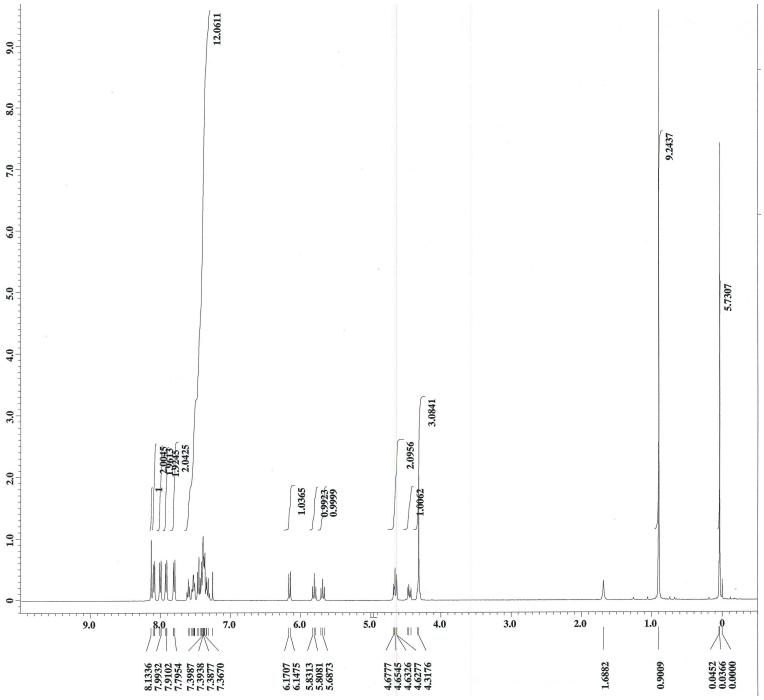
905, 598 cm^{-1}.

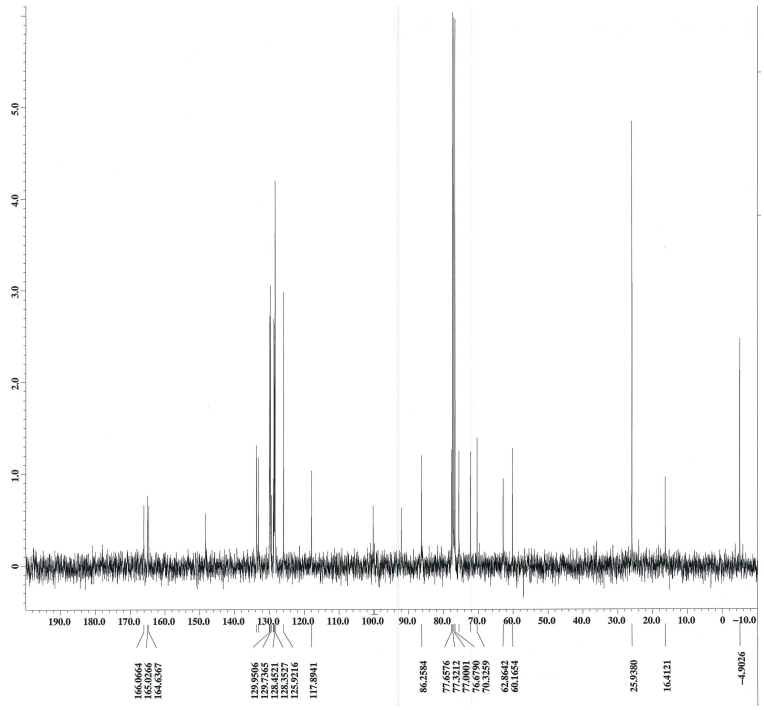
HRMS (ESI-TOF) calcd for $C_{102}H_{165}N_{10}O_{75}$ $[M+H]^+$ 2729.9405, found 2729.9482.



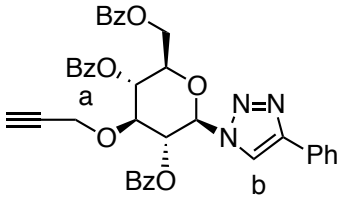
1-[2,4,6-Tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilyl-prop-2-yn-1-yl)-β-D-glucopyranosyl]-4-phenyl-1*H*-1,2,3-triazole(11)

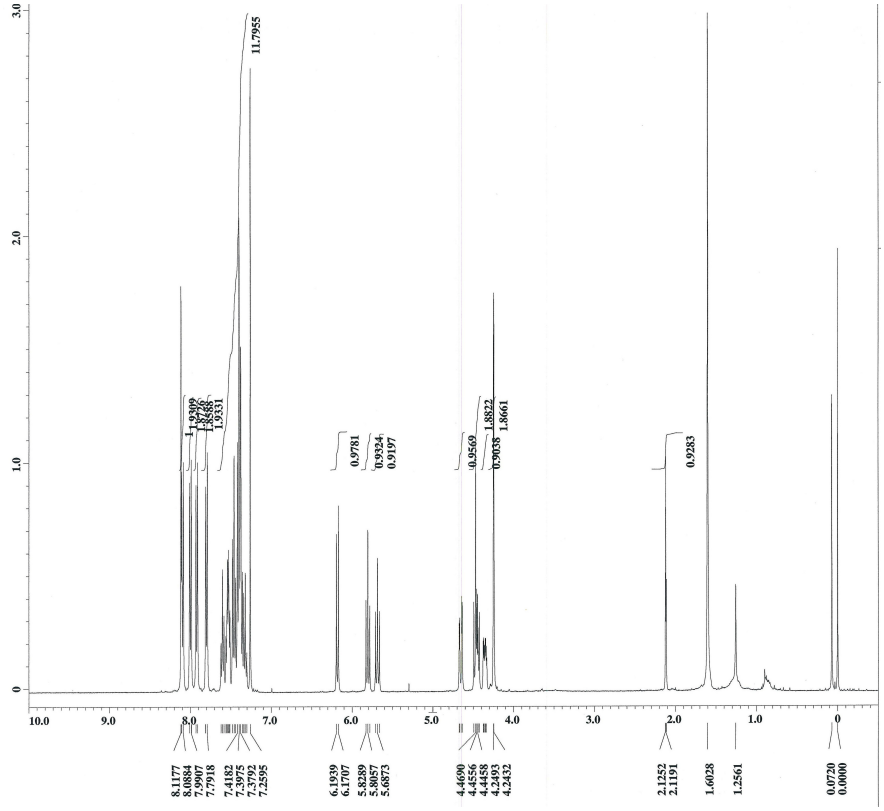


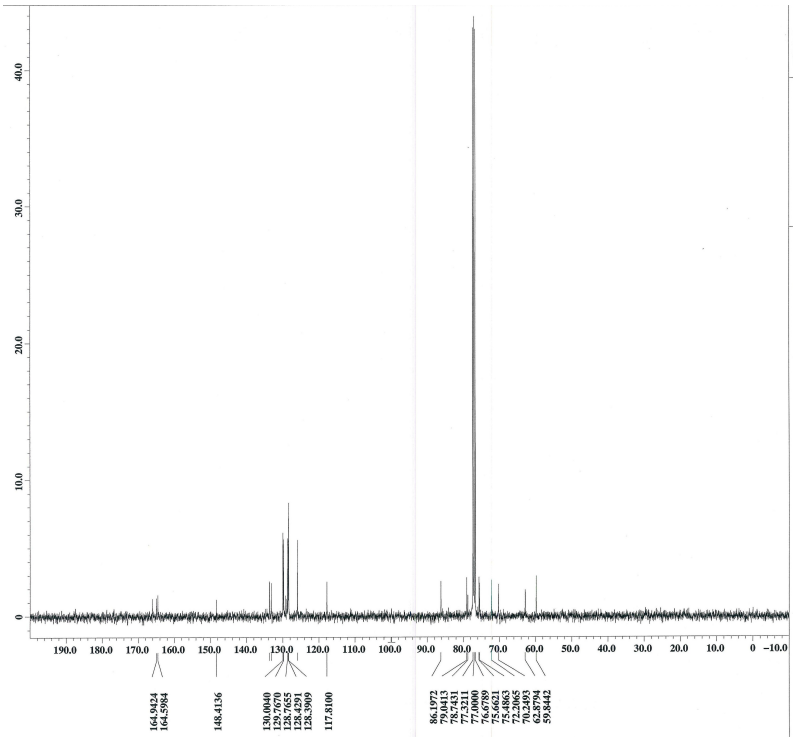




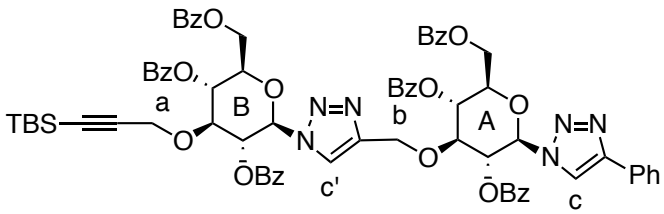
1-[2,4,6-Tri-*O*-benzoyl-3-*O*-(prop-2-yn-1-yl)-β-D-glucopyranosyl]-4-phenyl-1*H*-1,2,3-triazole (12)

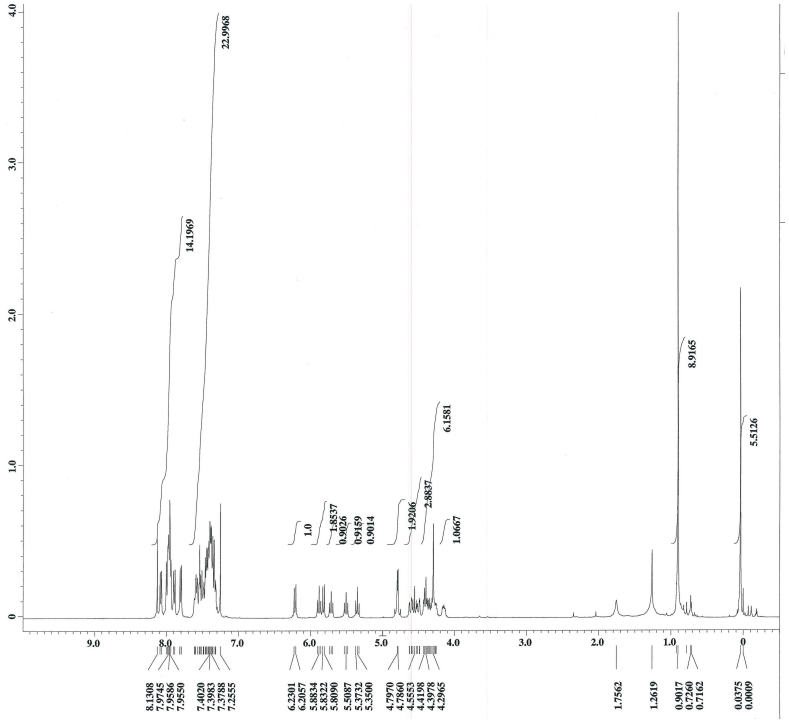


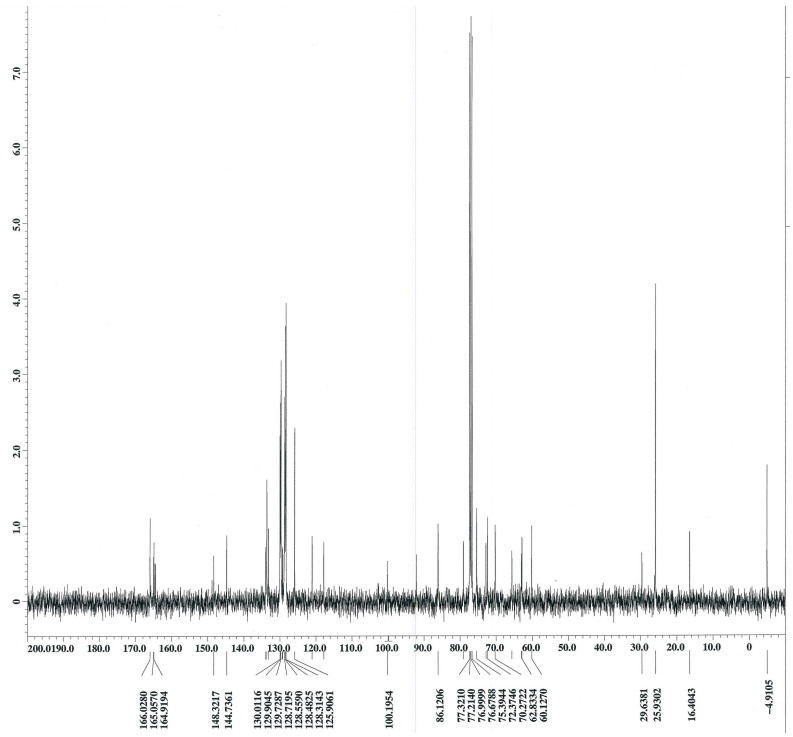




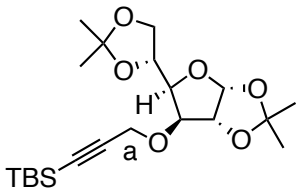
2,4,6-Tri-*O*-benzoyl-3-*O*-{1-[2,4,6-tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-β-D-gluco pyranosyl]-1*H*-1,2,3-triazol-4-yl}methyl-β-D-glucopyranosyl 4-phenyl-1*H*-[1,2,3]triazole (13)

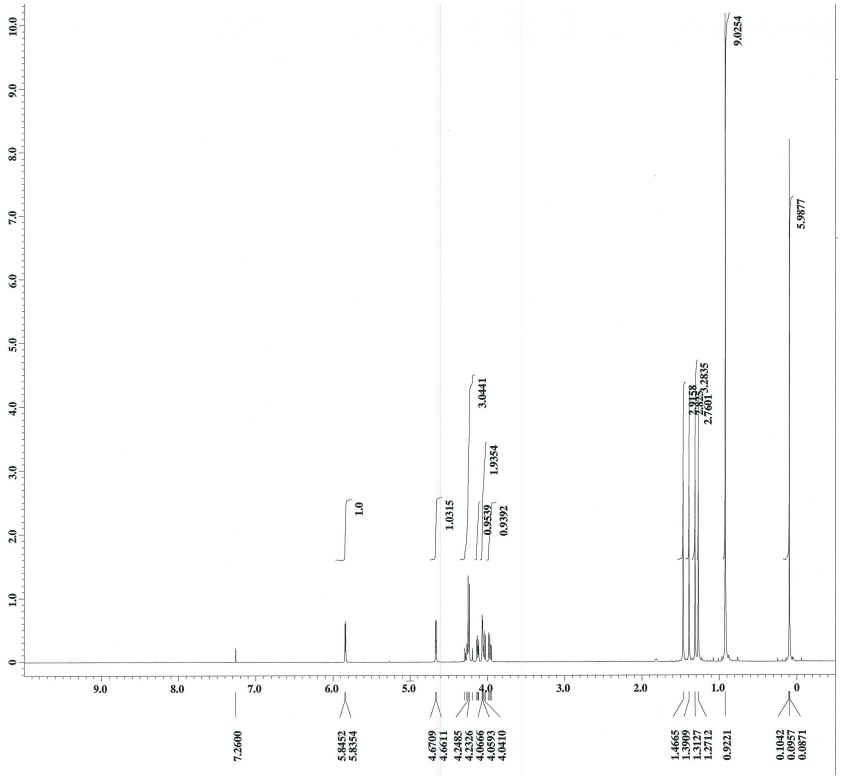


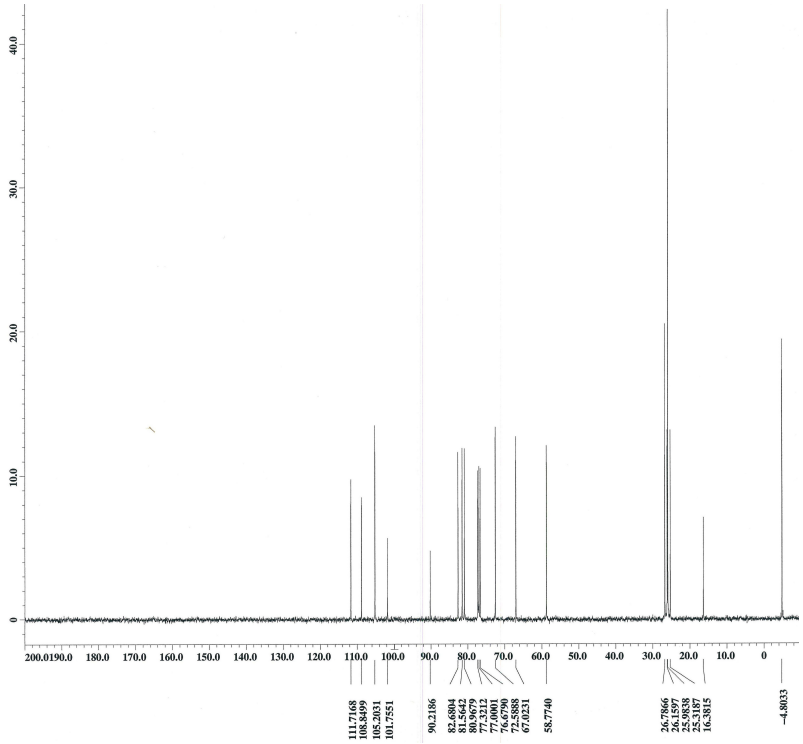




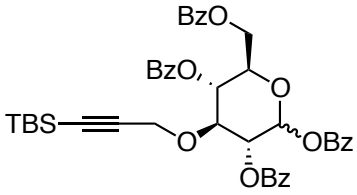
1,2,5,6-Bis-*O*-isopropylidene-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-α-D-glucofuranose (15)

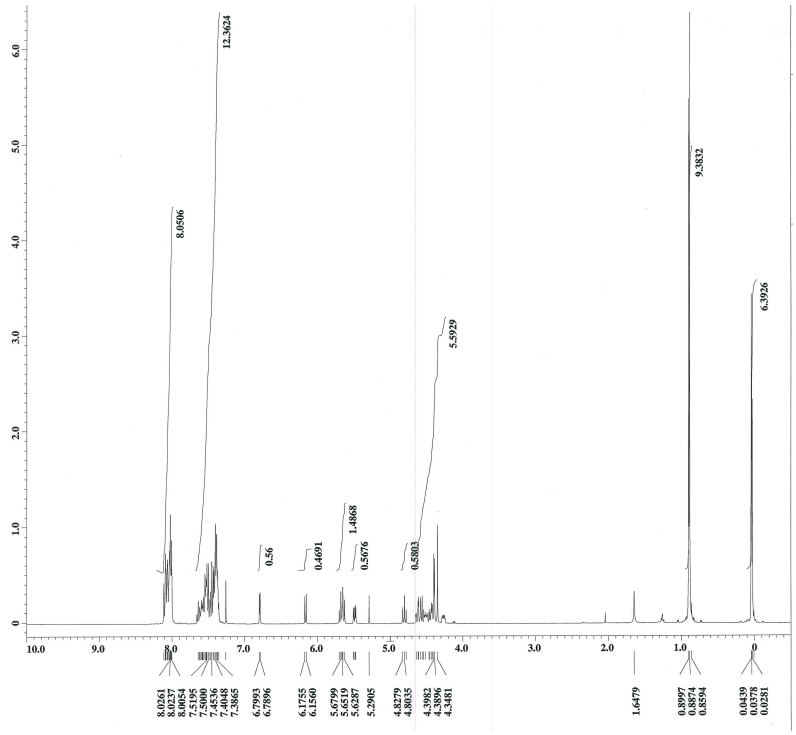


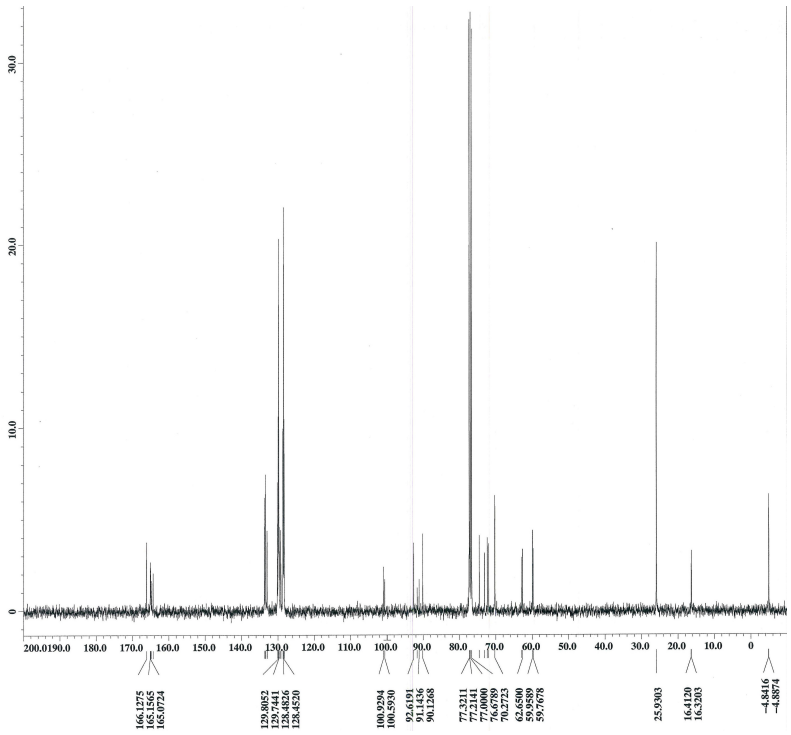




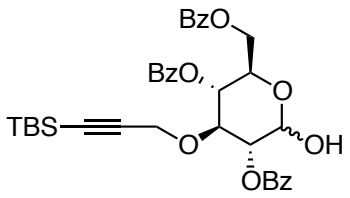
1,2,4,6-Tetra-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-α/β-D-glucopyranose (16)

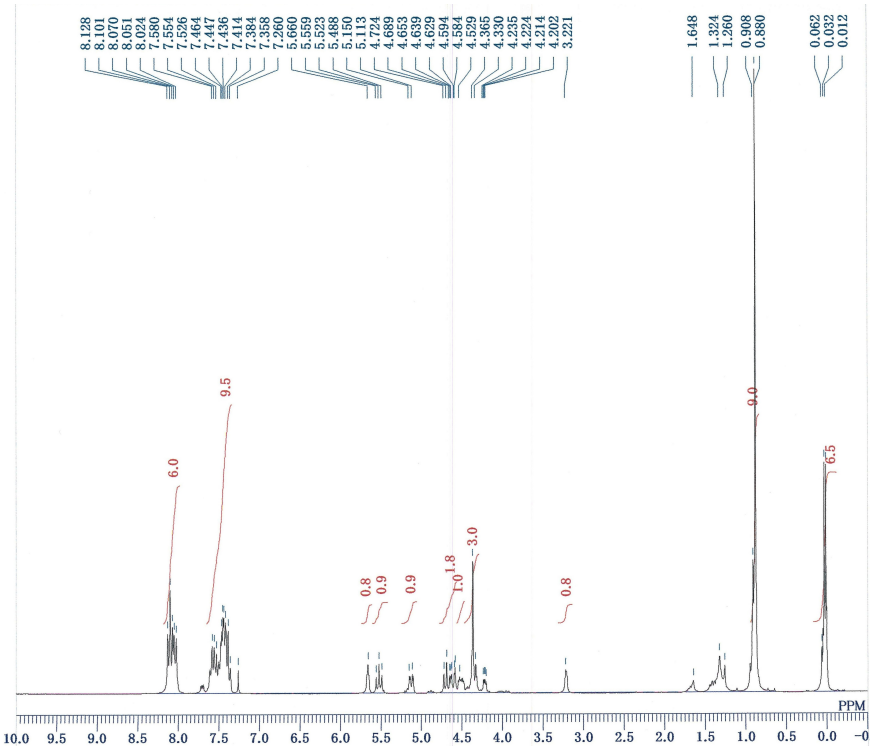


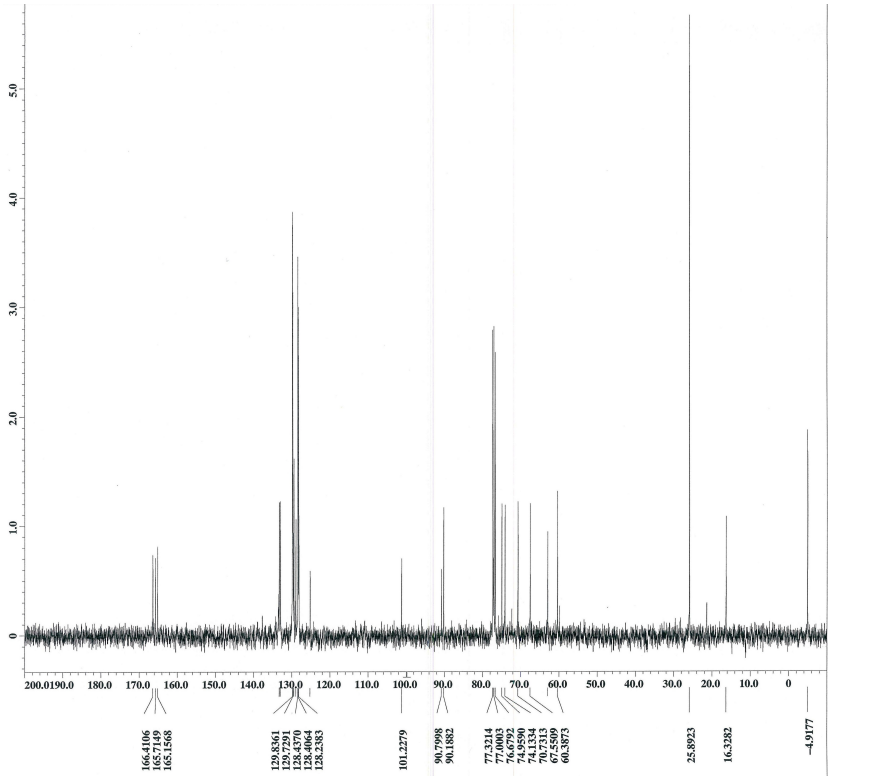




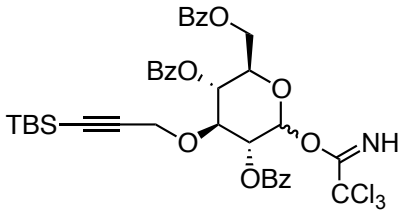
2,4,6-Tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-D-glucopyranose (17)

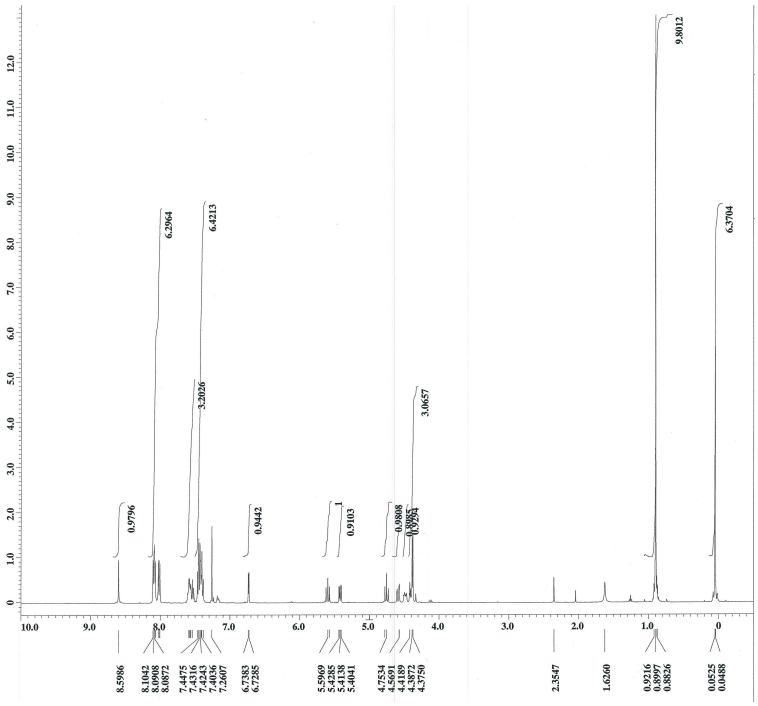


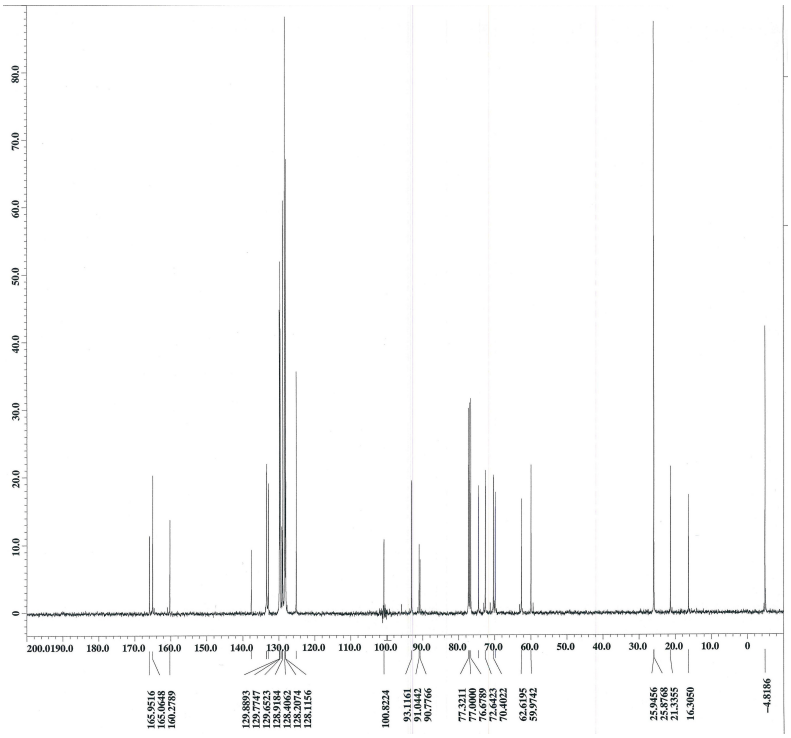




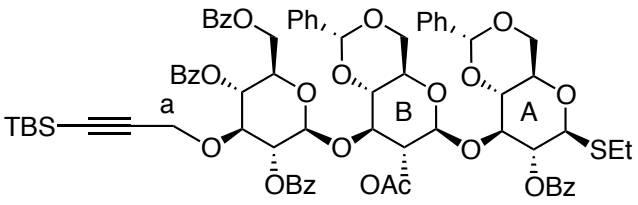
O-[2,4,6-Tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-α,β-D-glucopyranosyl] trichloroacetimidate (6)

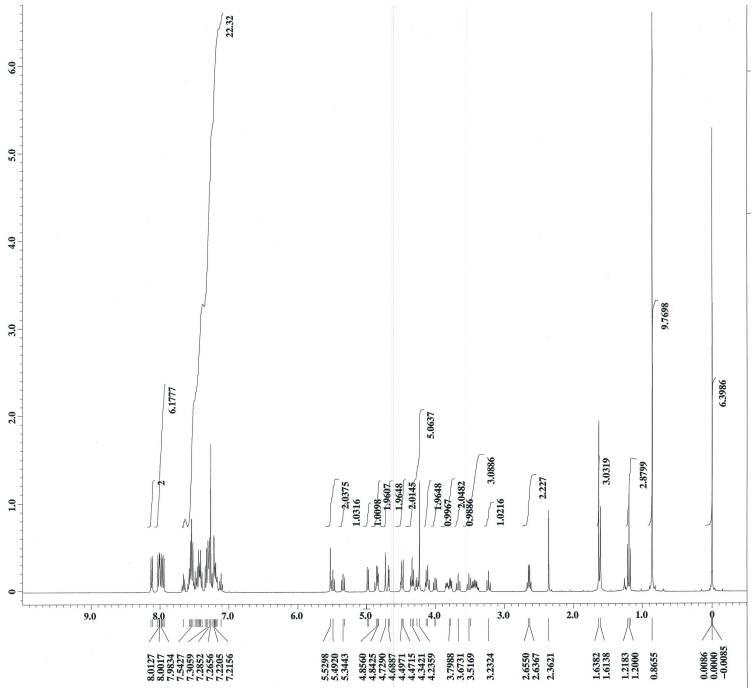


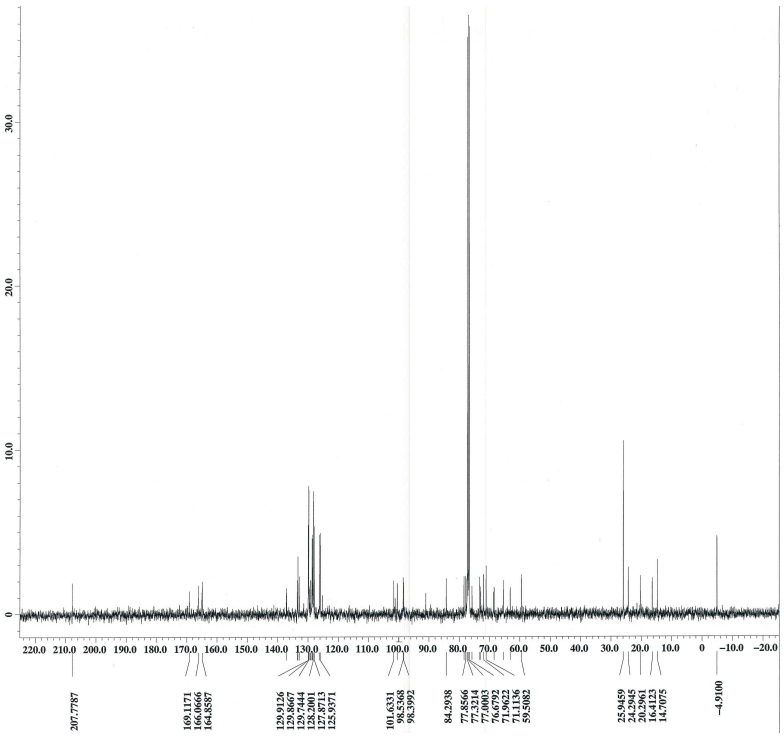




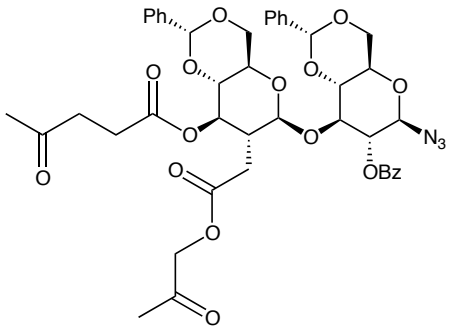
Ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2,4,6-tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranoside (20)

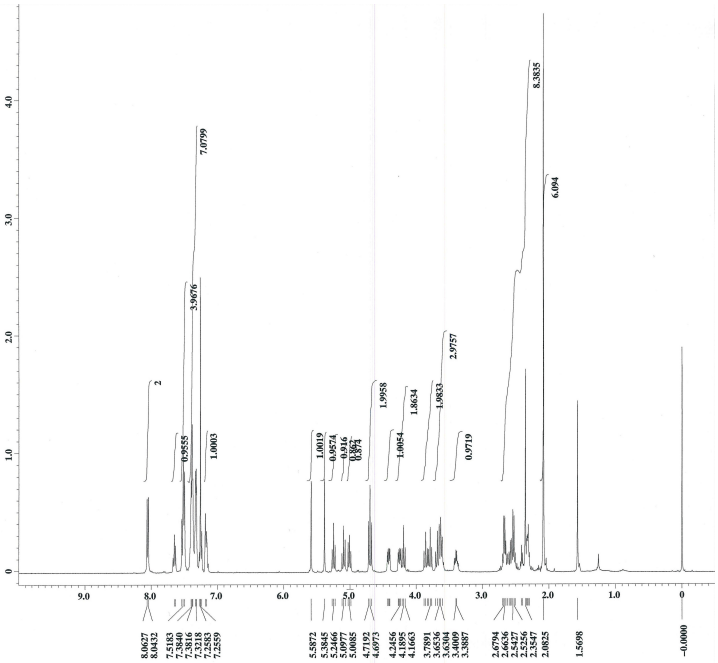


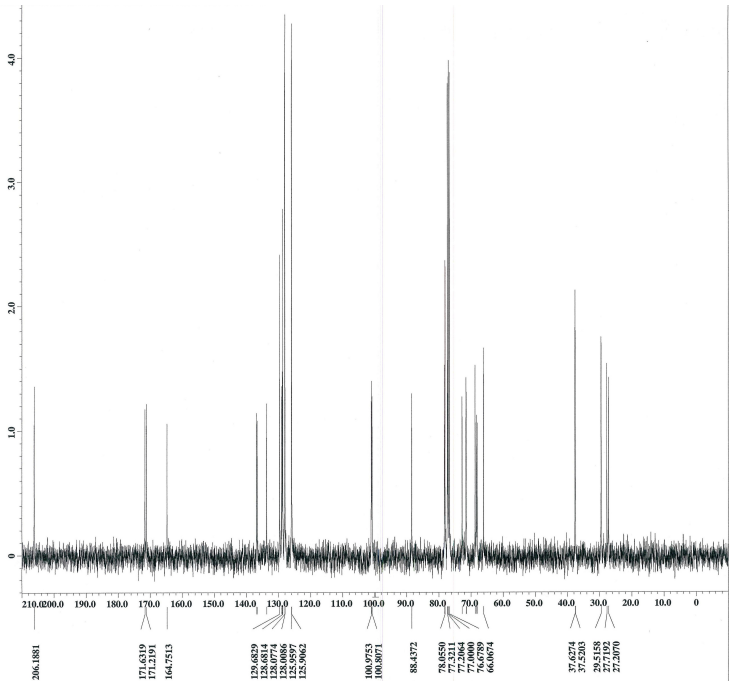




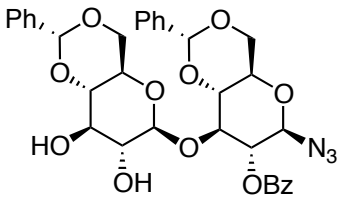
2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl azide (21)

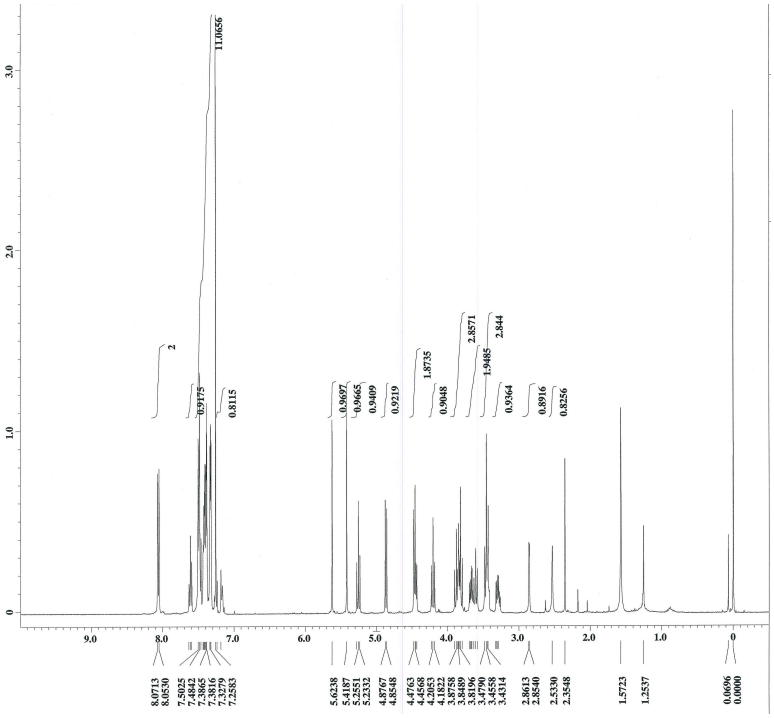


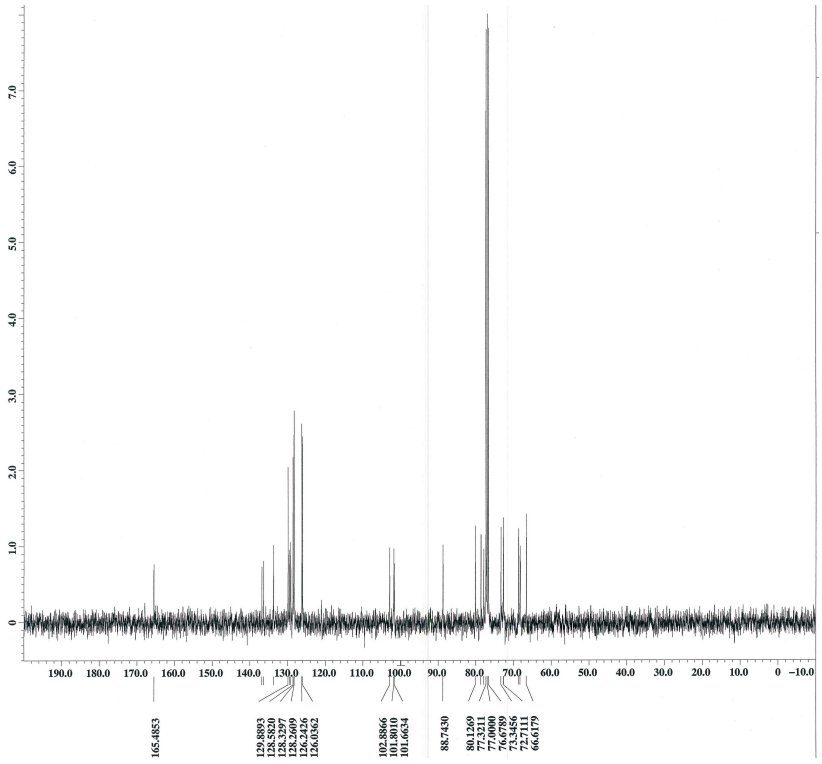




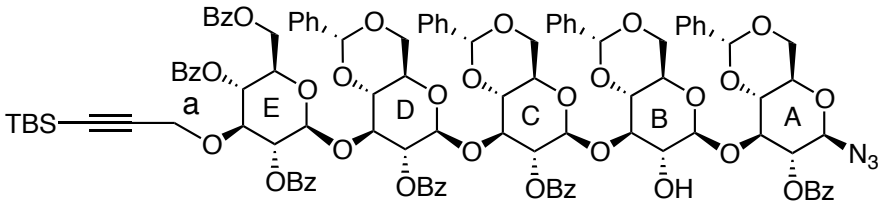
2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl azide (22)

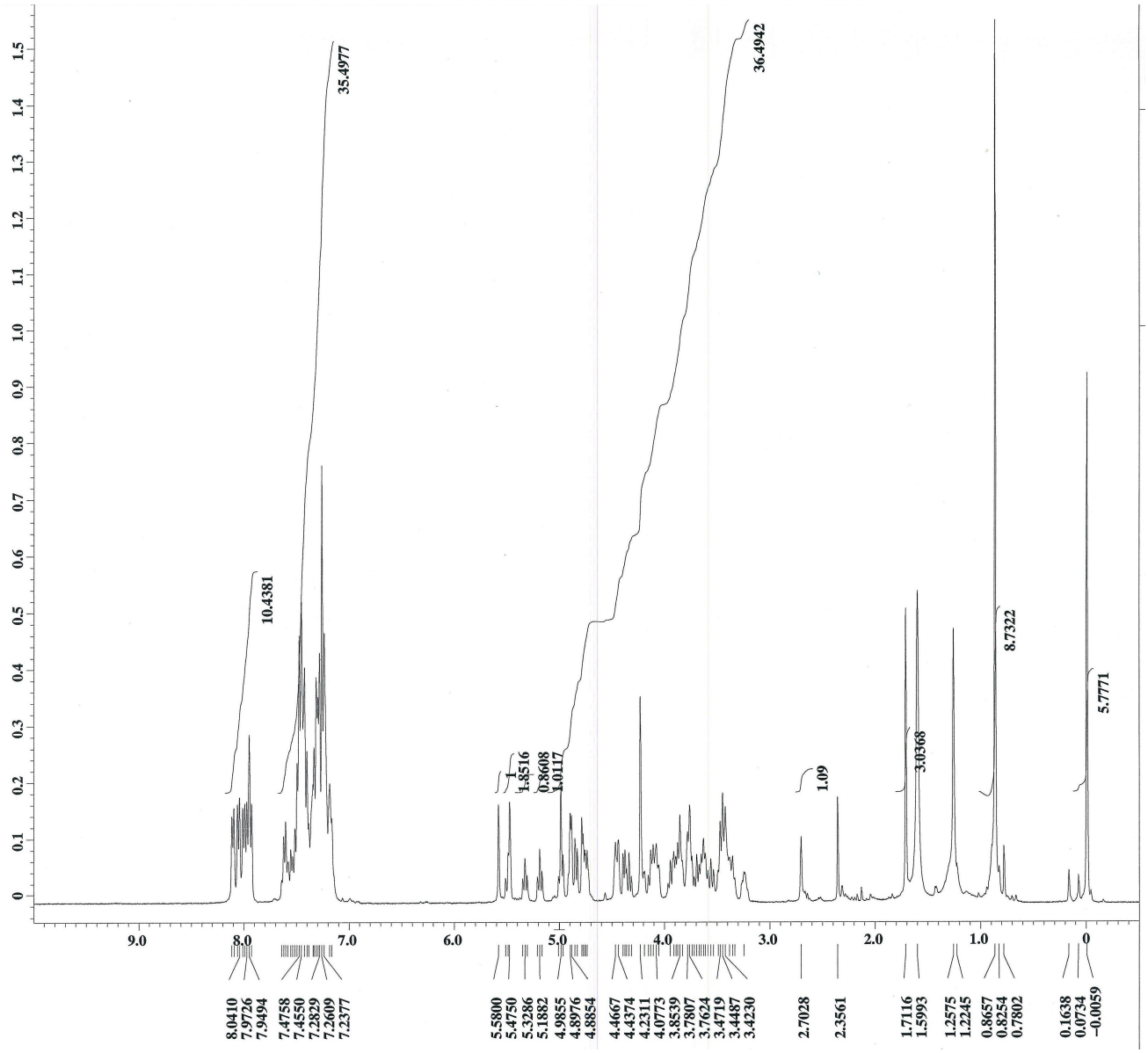




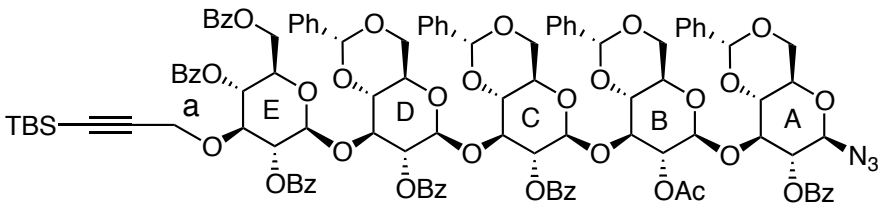


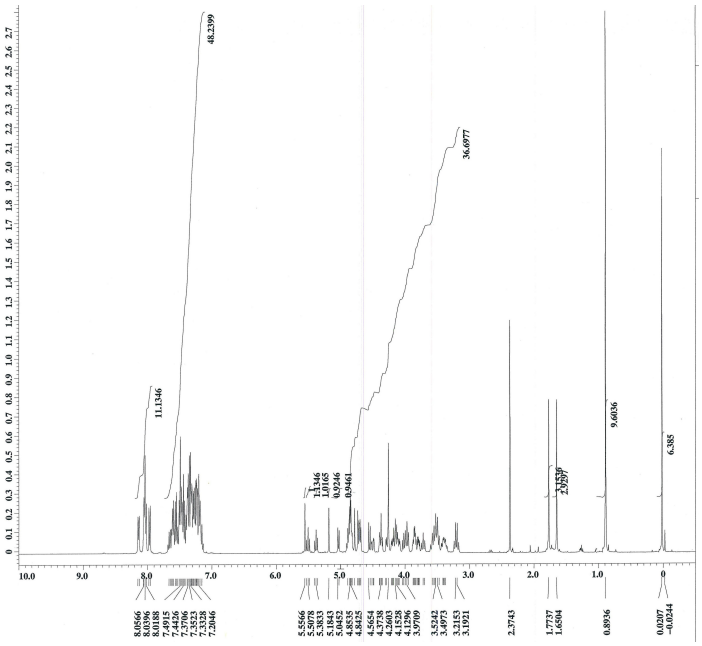
2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-[4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2,4,6-tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl azide (23)

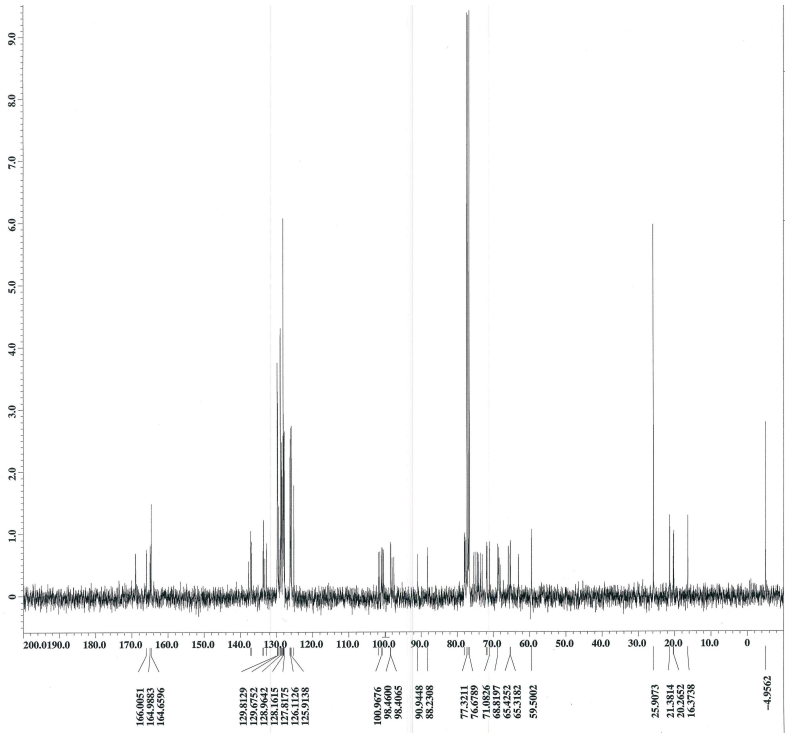




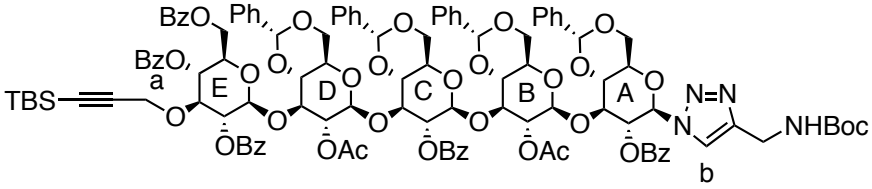
2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2,4,6-tri-*O*-benzoyl-3-*O*-(prop-3-*tert*-butyldimethylsilyl-2-yn-1-yl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl azide (4)

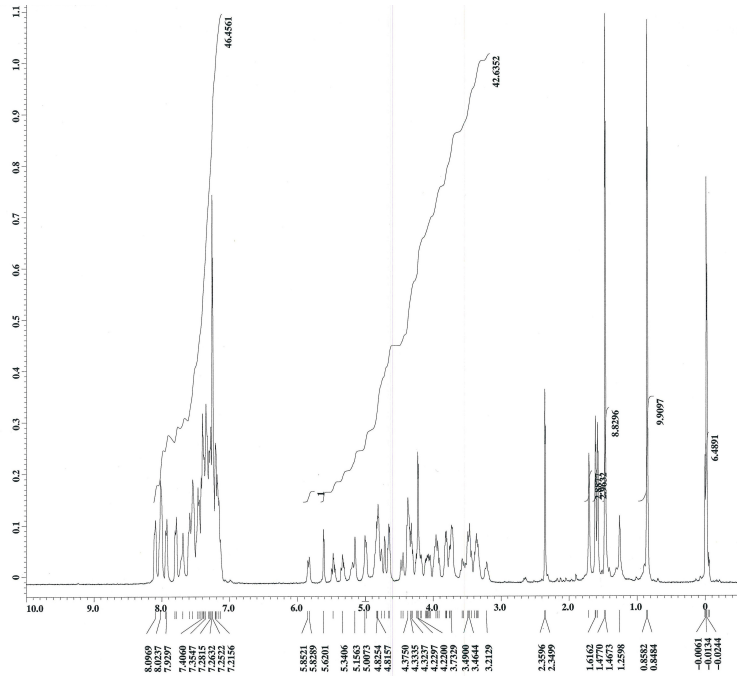


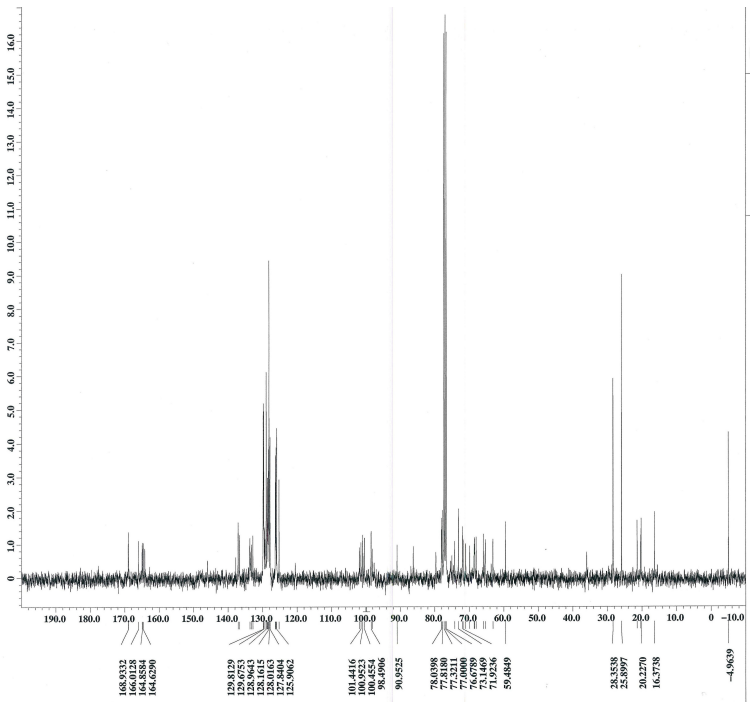




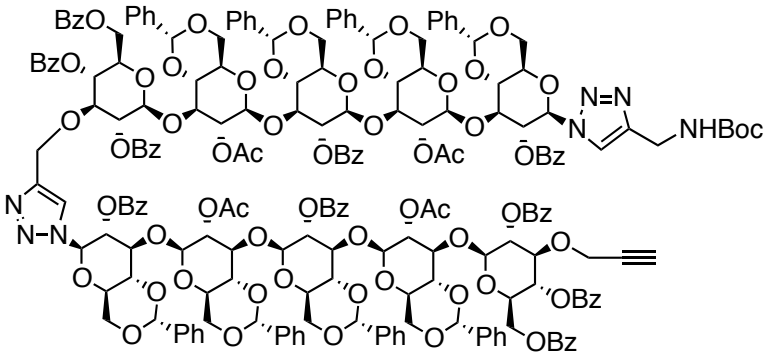
1-{2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2,4,6-tri-*O*-benzoyl-3-*O*-(3-*tert*-butyldimethylsilylprop-2-yn-1-yl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-4-*N*-(*tert*-butoxycarbonyl)aminomethyl-1*H*-1,2,3-triazole (24)

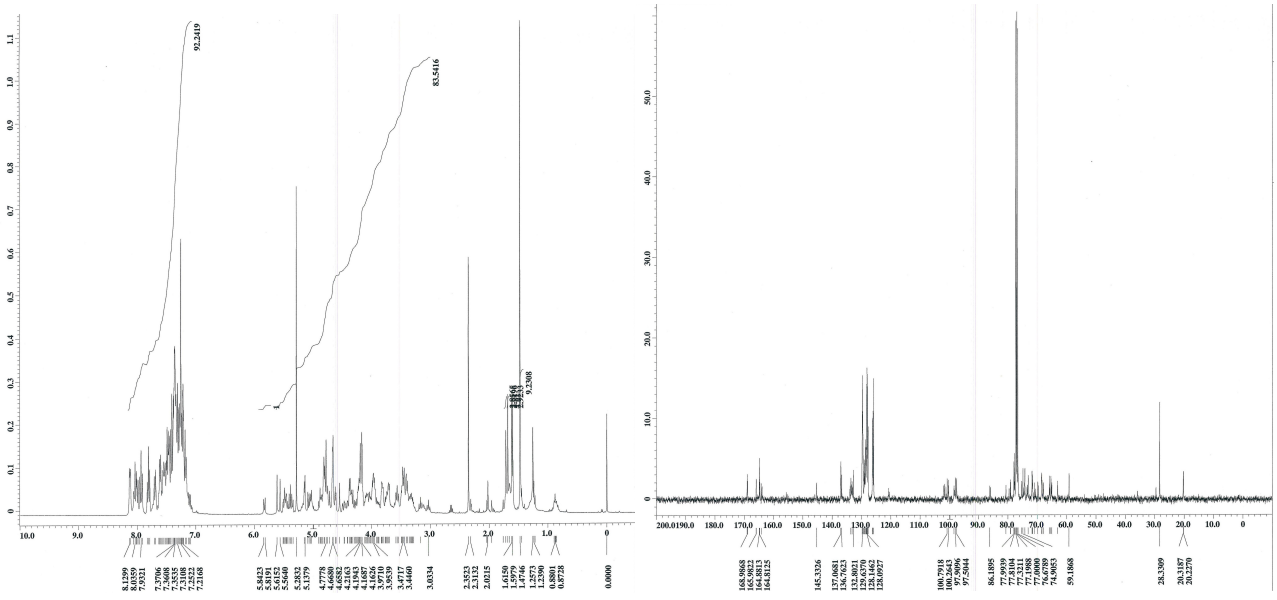






1-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-{2,4,6-tri-*O*-benzoyl-3-*O*-[({2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2,4,6-tri-*O*-benzoyl-3-*O*-(prop-2-yn-1-yl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosy}-1*H*-1,2,3-triazol-4-yl)methyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*N*-(*tert*-butoxycarbonyl)aminomethyl-1*H*-1,2,3-triazole (27)





1-[2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2,4,6-tri-*O*-benzoyl-3-*O*-{[(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-{2,4,6-tri-*O*-benzoyl-3-*O*-[({2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-[2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-{2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-[2,4,6-tri-*O*-benzoyl-3-*O*-(prop-2-yn-1-yl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosy}-1*H*-1,2,3-triazol-4-yl)methyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl]methyl}-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl)-β-D-glucopyranosy]-4-*N*-(*tert*-butoxycarbonyl)aminomethyl-1*H*-1,2,3-triazole (28)