Electronic Supplementary Information (ESI)

for

A compatibility study on the glycosylation of 4,4'-dihydroxyazobenzene

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Synthesis

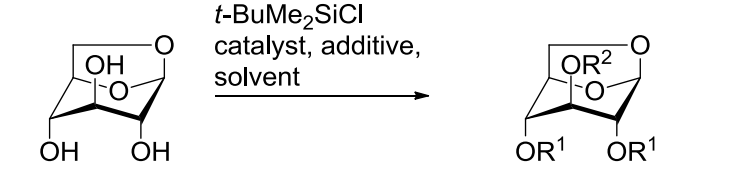
General methods

All reagents were used as received from chemical suppliers without further purification. Moisture sensitive reactions were carried out in flame-dried glassware and under positive pressure of nitrogen, unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on silica gel plates (GF 254 Merck). Visualization was achieved by UV light and/or by charring with 10 % sulfuric acid in ethanol, vanillin or PPh_3/CH_3Ph and ninhydrin, followed by heat treatment at ca. 400 °C. Acetonitrile was dried over calcium hydride, dichloromethane and THF over aluminum oxide columns, and pyridine over potassium hydroxide. Optical rotations were measured with a PerkinElmer 241 polarimeter with a sodium D-line (589 nm) and a cuvette of 10 cm path length, in the solvents indicated. Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance spectra were recorded on a Bruker DRX-500 spectrometer. Chemical shifts are referenced to internal tetramethylsilane (TMS), or to the residual proton of the NMR solvent. Data are presented as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, and bs=broad singlet), coupling constant in Hz and integration. Full assignment of the signals was achieved by using 2D NMR techniques (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and HMBC). All NMR spectra of the *E*-isomer of azobenzene derivatives were recorded after they were kept in the dark for 20 h at 45 °C. Infrared spectra were recorded a Perkin Elmer FT-IR Paragon 1000 (ATR) spectrometer. ESI mass spectra were recorded on an Esquire-LC instrument from Bruker Daltonics.

Preparation of the glycosyl donors

Donors **1**,[1a] **2**,[1b] **4**,[1c] **5**[1d] and **6**[1d,1e] were prepared starting from D-glucose according to known procedures.

Optimisation of the persilylation of Levoglucosan 10



Levoglucosan 10

13 $R^1 = R^2$ = TBS

S1 R^1 = TBS, R^2 = H

Table S1 Optimisation of the conditions for the persilylation of levoglucosan.

Entry	Me_2*t*-BuSiCl (eq)	Catalyst (eq)	Additive (eq)	Solvent	Temp.	Time	Yield (%) 13 : S1
1	5	Imidazole (7)	–	THF	0 °C to rt	20 h	15 : ND
2	6	DMAP (1.6)	–	Pyr/CH_2Cl_2	0 °C to rt	72 h	0 : 50
3	6	Imidazole (7)	–	Pyr	0 °C to rt	48 h	38 : ND
4	6	NMI (7)	I_2 (2.5)	Pyr	rt	24 h	80 : ND

NMI = *N*-methylimidazole; ND: not determined

1,6-anhydro-2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-β-D-glucopyranose (13). To a mixture of levoglucosan (162 mg, 1.00 mmol) and *N*-methylimidazole (559 μL, 7.00 mmol, 7 eq) in dry pyridine (2.00 mL) was added Me_2*t*-BuSiCl (904 mg, 6.00 mmol, 6 eq). The mixture was stirred at RT for 30 min and then iodine (634 mg, 2.50 mmol, 2.5 eq) was added. The mixture was stirred for 24 h, and then was diluted in EtOAc. It was washed with satd. aq. $Na_2S_2O_3$ solution until the organic phase was colorless. Then it was washed with 1N HCl (3x), satd. aq. $NaHCO_3$ (1x) and brine (1x) before being

dried over $MgSO_4$ and concentrated in *vacuo*. Column chromatography (cyclohexane:EtOAc 1:0 to 9:1) afforded the title compound **13** (405 mg, 80 %) as a white amorphous solid. The obtained analytical data are in agreement with reported literature.[2]

1,6-anhydro-2,4-di-*O*-((*tert*-butyldimethyl)silyl)-β-D-glucopyranose (S1). To levoglucosan (200 mg, 1.23 mmol) in dry CH_2Cl_2 (17.0 mL) were added pyridine (4.20 mL, 51.7 mmol) and 4-dimethylaminopyridine (297 mg, 1.97 mmol, 1.6 eq). The resulting suspension was cooled to 0 °C, and Me_2*t*-BuSiCl (1.11 g, 7.38 mmol, 6 eq) was added as a solution in dry CH_2Cl_2 (17.0 mL). The mixture was stirred at 0 °C for 10 min, and then was allowed to stir at RT for 3 days. After that time, the solvent was removed in *vacuo*, the resulting residue was triturated in toluene, the insoluble materials were filtered and the filtrate concentrated. Column chromatography (cyclohexane:CH_2Cl_2:Et_2O 1:0:0 to 7:1.5:1.5) afforded the title compound **S1** (240 mg, 50 %) as a white amorphous solid. The obtained analytical data are in agreement with reported literature.[2]

(6-azido-6-deoxy-2,3,4-tri-*O*-acetyl-α,β-D-glucopyranosyl)-1-(*N*-phenyl)-2,2,2-trifluoroacetimidate (6). To a solution of 6-azido-6-deoxy-2,3,4-tri-*O*-acetyl-α,β-D-glucopyranose[1e] (993 mg, 3.00 mmol) and cesium carbonate (1.47 g, 4.50 mmol, 1.5 eq) in dry CH_2Cl_2 (30.0 mL) was added 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (713 µL, 4.50 mmol, 1.5 eq) at RT. The mixture was stirred 1.5 h at RT, then it was diluted with CH_2Cl_2 and filtered through celite. The celite pad was washed with CH_2Cl_2 and the filtrate was concentrated in *vacuo*. Column chromatography (cyclohexane:EtOAc 8:2 to 7:3) afforded an anomeric mixture of the title compound **6** (1.35 g, 90 %) as a white foam. **β-6** (major anomer): ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32 (t, *J* = 7.6 Hz, 2H, 2Ar-H_{ortho}), 7.14 (t, *J* = 7.6 Hz, 1H, Ar-H_{para}), 6.86 (d, *J* = 7.6 Hz, 2H, 2Ar-H_{meta}), 5.85 (bs, 1H, H-1), 5.26 (bs, 2H, H-2, H-3), 5.12-5.04 (m, 1H, H-4), 3.79 (bs, 1H, H-5), 3.41 (dd, $J_{6a,6b}$ = 13.6 Hz, $J_{6a,5}$ = 6.7 Hz, 1H, H-6a), 3.25 (dd, $J_{6b,6a}$ = 13.6 Hz, $J_{6b,5}$ = 2.6 Hz, 1H, H-6), 2.09 (s, 3H, CH_3CO), 2.04 (s, 3H, CH_3CO), 2.03 (s, 3H, CH_3CO) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.3, 169.5, 169.1 (3C, $3CH_3\underline{C}O$), 143.1 (Ar-C_{ipso}), 129.0 (2C, 2Ar-C_{ortho}), 124.8 (Ar-C_{para}), 119.4 (2Ar-C_{meta}), 74.5 (C-1), 72.5 (C-2), 70.7 (C-3), 70.2(C-4), 69.2 (C-5), 51.0 (C-6), 20.7, 20.6 (3C, $3\underline{C}H_3CO$) ppm; ESI HRMS: *m/z*: calcd for $C_{20}H_{21}F_3O_8N_4 + Na^+$: 552.1204 [M + Na^+] found: 552.1208.

1,6-anhydro-2,3,4-tri-*O*-benzoyl-β-D-glucopyranose (11). To a cold solution (0 °C) of levoglucosan (2.00 g, 12.3 mmol) in dry pyridine (20.0 mL) was added benzoyl chloride (8.57 mL, 73.8 mmol, 6 eq). The mixture was allowed to stir 1 h at RT then water was added and the resulting suspension was extracted with CH_2Cl_2 (3x20 mL). The combined organic layers were successively washed with aq. 1N HCl (3x), satd. aq. $NaHCO_3$ (1x) and brine (1x). The organic phase was dried over $MgSO_4$, concentrated in *vacuo* and the remaining pyridine was co-evaporated with toluene. The residue was then triturated with the minimum amount of toluene, filtered and washed three times with cold toluene, to afford **11** (5.36 g, 92 %) as white crystals. The obtained analytical data are in agreement with reported literature.[3]

Phenyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (12). To **11** (235 mg, 0.500 mmol) in CH_2Cl_2 (5 mL) were added zinc iodide (640 mg, 2.00 mmol, 4 eq) and trimethyl(phenylthio)silane (240 µL, 1.25 mmol, 2.5 eq). The mixture was stirred under micro-wave irradiation (200 W) at 120 °C for 25 min. The resulting suspension was filtered through celite, diluted with methanol and treated with Amberlite IR 120 H^+. The resin was filtered-off and the solvents removed in *vacuo*. The residue was purified by column chromatography (cyclohexane:EtOAc 9:1 to 7:3) to afford the title compound **12**

(286 mg, 98 %) as a white foam. The obtained analytical data are in agreement with reported literature.[4]

Phenyl-6-azido-6-deoxy-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (3). To a solution of **12** (2.67 g, 4.57 mmol) in dry THF (23.0 mL) was added triphenylphosphine (1.80 g, 6.85 mmol, 1.5 eq). The solution was cooled to -15 °C and diisopropyl azodicarboxylate (2.25 mL, 11.4 mmol, 2.5 eq) was added dropwise. The mixture was stirred for 15 min at -15 °C. It was then allowed to warm to -5 °C. After formation of a precipitate, diphenylphosphoryl azide (1.48 mL, 6.85 mmol, 1.5 eq) was added dropwise. The mixture was then allowed to warm slowly to RT and stirred for 14 h. Then, the solvent was removed in *vacuo* and the residue was purified by column chromatography (cyclohexane:EtOAc 9:1 to 8:2) to afford the title compound **3** (1.99 g, 71 %) as a white foam. The obtained analytical data are in agreement with reported literature.[5]

(6-azido-6-deoxy-2,3,4-tri-*O*-benzoyl-α,β-D-glucopyranosyl)-1-(*N*-phenyl)-2,2,2-trifluoroacetimidate (7). To a solution of **3** (1.36 g, 2.24 mmol) in acetone:water (9:1, 67.0 mL) was added trichlorocyanuric acid (546 mg, 2.35 mmol, 1.05 eq) at RT. The mixture was stirred at RT for 30 min, and then the acetone was evaporated. The resulting residue was dissolved in CH_2Cl_2 and washed with satd. aq. $NaHCO_3$ (1x), brine (1x), and dried over $MgSO_4$. The solvent was evaporated in *vacuo* and the crude was purified by column chromatography (cyclohexane:EtOAc 9:1 to 7:3) to afford an α,β mixture of hemiacetals as a white foam. This mixture (978 mg, 1.94 mmol) was dissolved in dry CH_2Cl_2 (19.0 mL) and Cs_2CO_3 (1.11 g, 2.91 mmol, 1.5 eq) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (465 µL, 2.91 mmol, 1.5 eq) were added sequentially at RT. The mixture was stirred for 4 h, then diluted with CH_2Cl_2 and filtered through celite, and the filtrate concentrated. The crude residue was purified by column chromatography (cyclohexane:EtOAc 9:1 to 7:3) to afford an anomeric mixture of the title compound **7** (1.03 g, 76 %) as a white foam. **β-7** (major anomer): ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 7.6 Hz, 2H, 2Ar-H), 7.92 (d, *J* = 7.6 Hz, 2H, 2Ar-H), 7.85 (d, *J* = 7.6 Hz, 2H, 2Ar-H), 7.58-7.51 (m, 2H, 2Ar-H), 7.46 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.44-7.36 (m, 4H, 4Ar-H), 7.34-7.28 (m, 4H, 4Ar-H), 7.13 (t, *J* = 7.4 Hz, 1H, Ar-H), 6.81 (d, *J* = 7.4 Hz, 2H, 2Ar-H), 6.22 (bs, 1H, H-1), 5.92 (bs, 1H, H-3), 5.76 (dd, $J_{1,2}$ = $J_{2,3}$ = 8.3 Hz, 1H, H-2), 5.57 (t, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, 1H, H-4), 4.12 (bs, 1H, H-5), 3.59 (dd, $J_{6a,6b}$ = 13.1 Hz, $J_{6a,5}$ = 7.2 Hz, 1H, H-6a), 3.40 (dd, $J_{6b,6a}$ = 13.1 Hz, $J_{6b,5}$ = 2.6 Hz, 1H, H-6b) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 165.6, 165.2, 164.8 (3C, 3 Ph<u>C</u>O), 143.0, 133.8, 133.6, 133.5, 129.9, 129.8, 128.8, 128.6, 128.5, 128.4, 124.6, 119.3 (24 C, 24 Ar-C), 74.9 (C-5), 72.3 (2C, C-1, C-3), 70.7 (C-2), 69.6 (C-4), 51.1 (C-6) ppm; ESI HRMS: *m/z*: calcd for $C_{35}H_{27}F_3N_4O_8$ + Na^+: 711.1679 [M + Na^+] found: 711.1671.

Phenyl-2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-1-thio-α,β-D-glucopyranoside (14). To a mixture of **13** (1.50 g, 2.97 mmol) and zinc iodide (3.80 g, 11.9 mmol, 4 eq) in dry CH_2Cl_2 (30.0 mL) was added trimethyl(phenylthio)silane (1.40 mL, 7.43 mmol, 2.5 eq) at RT. The mixture was stirred for 1.5 h at RT then it was filtered through celite. The filtrate was diluted with methanol (20.0 mL) and the solvents removed in *vacuo* (concentration of the crude mixture in presence of MeOH is sufficient for removing the 6-*O*-TMS groups). The crude was purified by column chromatography (cyclohexane:CH_2Cl_2:Et_2O 95:2.5:2.5 to 8:1:1) to afford **α-14** (350 mg, 19 %) and **β-14** (1.42 g, 77 %) as colorless syrups. For characterization purposes, both anomers were separated, but mixtures were used in the further steps. **α-14**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.53-7.49(m, 2H, 2Ar-H_{ortho}), 7.32-2.27 (m, 2H, 2Ar-H_{meta}), 7.25-7.20 (m, 1H, Ar-H_{para}), 5.58 (d, $J_{1,2}$ = 4.2 Hz, 1H, H-1), 4.20 (ddd, $J_{5,4}$ = 8.8 Hz, $J_{5,6a}$ = 6.0 Hz, $J_{5,6b}$ = 2.6 Hz, 1H, H-5), 4.08 (m, 1H, H-2), 3.86-3.79 (m, 2H, H-3, H-6a), 3.72 (d, *J* = 8.8 Hz,

1H, H-4), 3.60-3.53 (dd, $J_{6b,6a}$ = 11.5 Hz, $J_{6b,5}$ = 2.6 Hz, 1H, H-6b), 0.99 (s, 9H, $C(CH_3)_3$), 0.89 (s, 9H, $C(CH_3)_3$), 0.87 (s, 9H, $C(CH_3)_3$), 0.22 (s, 3H, CH_3), 0.14 (s, 3H, CH_3), 0.13 (s, 3H, CH_3), 0.11 (s, 3H, CH_3), 0.10 (s, 3H, CH_3), 0.09 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 136.4 (Ar-C_{ipso}), 131.5 (2C, 2Ar-C_{ortho}), 129.0 (2C, 2Ar-C_{meta}), 126.9 (Ar-C_{para}), 87.4 (C-1), 76.4 (C-3), 73.6 (C-4), 73.5 (C-5), 72.9 (C-2), 63.2 (C-6), 26.2, 26.1, 25.9 (9C, 3 C($\underline{C}H_3)_3$), 18.4, 18.2, 18.0 (3C, 3$\underline{C}(CH_3)_3$), -3.5, -3.6, -3.9, -4.3, -4.9, -5.0 (6C, 6CH_3) ppm; ESI HRMS: *m/z*: calcd for $C_{30}H_{58}O_5SSi_3 + Na^+$: 637.3205 [M + Na^+] found: 637.3196.

β-14: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.48-7.44 (m, 2H, 2Ar-H_{ortho}), 7.31-7.26 (m, 2H, 2Ar-H_{meta}), 7.23-7.19 (m, 1H, Ar-H_{para}), 4.98 (d, $J_{1,2}$ = 6.4 Hz, 1H, H-1), 3.92,3.88 (m, 1H, H-5), 3.86-3.81 (m, 2H, H-2,H-3), 3.80-3.75 (m, 2H, H-2, H-6_a), 3.72 (dd, $J_{6b,6a}$ = 11.4 Hz, $J_{6b,5}$ = 3.7 Hz, 1H, H-6b), 2.31 (bs, 1H, OH), 0.92 (s, 9H, $C(CH_3)_3$), 0.89 (s, 9H, $C(CH_3)_3$), 0.88 (s, 9H, $C(CH_3)_3$) , 0.13 (s, 3H, CH_3), 0.11 (s, 6H, 2CH_3), 0.09 (s, 3H, CH_3), 0.08 (s, 3H, CH_3), 0.07 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 135.7 (Ar-C_{ipso}), 130.4 (2C, 2Ar-C_{ortho}), 129.0 (2C, 2Ar-C_{meta}), 126.8 (Ar-C_{para}), 87.2 (C-1), 83.0 (C-5), 77.3 (C-3), 75.5 (C-2), 71.3 (C-4), 64.2 (C-6), 26.1, 26.0 (9C, 3C($\underline{C}H_3)_3$), 18.2, 18.1 (3C, 3$\underline{C}(CH_3)_3$), -4.1, -4.2, -4.3, -4.8 (6C, 6CH_3) ppm; ESI HRMS: *m/z*: calcd for $C_{30}H_{58}O_5SSi_3 + Na^+$: 637.3205 [M + Na^+] found: 637.3198.

Phenyl-6-*O*-acetyl-2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-1-thio-α,β-D-glucopyranoside (8). To **α,β-14** (420 mg, 683 μmol) in pyridine (6.8 mL) were added DMAP (16.4 mg, 137 μmol, 0.2 eq) and Ac_2O (970 μL, 1.02 mmol, 1.5 eq) at RT. The mixture was stirred for 2 h at RT, and the pyridine was co-evaporated with toluene. The remaining residue was dissolved in EtOAc, and washed with HCl 1N (3x), $NaHCO_3$ (1x) and brine (1x). The organic layer was dried over $MgSO_4$, filtered and concentrated in *vacuo*. The crude was purified by column chromatography (cyclohexane:EtOAc 95:5) to afford the title compound **8** (426 mg, 95 %) as a colorless syrup. **α-8**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57-7.54 (m, 2H, 2Ar-H_{ortho}), 7.29-7.24 (m, 2H, 2Ar-H_{meta}), 7.24-7.18 (m, 1H, Ar-H_{para}), 5.50 (d, $J_{1,2}$ = 4.3 Hz, 1H, H-1), 4.40-4.24 (m, 2H, H-5, H-6a), 4.15 (dd, $J_{6b,6a}$ = 11.8 Hz, $J_{6b,5}$ = 7.0 Hz, 1H, H-6b), 4.09-4.02 (m, 1H, H-2), 3.87-3.82 (m, 1H, H-3), 3.75-3.67 (m, 1H, H-4), 2.04 (s, 3H, CH_3CO), 0.99 (s, 9H, $C(CH_3)_3$), 0.89 (s, 9H, $C(CH_3)_3$), 0.87 (s, 9H, $C(CH_3)_3$), 0.22 (s, 3H, CH_3), 0.14 (s, 3H, CH_3), 0.12 (s, 3H, CH_3), 0.11 (s, 3H, CH_3), 0.09 (s, 3H, CH_3), 0.07 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.1 ($CH_3\underline{C}O$), 136.2 (Ar-C_{ipso}), 132.1 (2Ar-C_{ortho}), 128.9 (2Ar-C_{meta}), 127.0 (Ar-C_{para}), 87.4 (C-1), 76.2 (C-3), 73.7 (C-4), 72.7 (C-2), 71.5 (C-5), 64.4 (C-6), 26.3, 26.1 (9C, 3C($\underline{C}H_3)_3$), 21.0 ($\underline{C}H_3CO$), 18.5, 18.2 (3C, 3$\underline{C}(CH_3)_3$), -3.4, -3.9, -4.1, -4.3, -4.9 (6C, 6 CH_3) ppm; ESI HRMS: *m/z*: calcd for $C_{32}H_{60}O_6SSi_3 + Na^+$: 679.3311 [M + Na^+] found: 679.3311.

β-8: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.50-7.46 (m, 2H, 2Ar-H_{ortho}), 7.30-7.24 (m, 2H, 2Ar-H_{meta}), 7.23-7.18 (m, 1H, Ar-H_{para}), 5.00 (d, $J_{1,2}$ = 7.0 Hz, 1H, H-1), 4.29 (dd, $J_{6a\text{-}6b}$ = 11.3 Hz, $J_{6a,5}$ = 7.2 Hz, 1H, H-6a), 4.23 (dd, $J_{6b\text{-}6a}$ = 11.3, $J_{6b,5}$ = 6.2 Hz, 1H, H-6b), 4.03-3.98 (m, 1H, H-5), 3.86-3.80 (m, 3H, H-2, H-3, H-4), 2.06 (s, 3H, CH_3CO), 0.91 (s, 9H, $C(CH_3)_3$), 0.89 (s, 9H, $C(CH_3)_3$), 0.88 (s, 9H, $C(CH_3)_3$), 0.11 (s, 3H, CH_3), 0.10 (s, 3H, CH_3), 0.09 (s, 3H, CH_3), 0.08 (s, 3H, CH_3), 0.08 (s, 6H, 2CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.8 ($CH_3\underline{C}O$), 135.7 (Ar-C_{ipso}), 130.5 (2C, 2Ar-C_{ortho}), 128.8 (2C, 2Ar-C_{meta}), 126.8 (Ar-C_{para}), 86.6 (C-1), 80.0 (C-5), 77.4 (C-2), 75.5 (C-3), 70.9 (C-4), 65.5 (C-6), 26.0, 25.9 (9C, 3C($\underline{C}H_3)_3$), 21.0 ($\underline{C}H_3CO$), 18.1, 18.0 (3C, 3$\underline{C}(CH_3)_3$), -3.6, -4.0, -4.2, -4.4, -5.0 (6C, 6CH_3) ppm; ESI HRMS: *m/z*: calcd for $C_{32}H_{60}O_6SSi_3 + Na^+$: 679.3311 [M + Na^+] found: 679.3311.

Phenyl-6-azido-6-deoxy-2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-1-thio-α,β-D-glucopyranoside (9). To **α,β-14** (1.12 g, 1.82 mmol) in dry THF (7.30 mL) was added triphenylphosphine (716 mg, 2.73 mmol, 1.5 eq) at RT. The mixture was cooled down to -15 °C, and diisopropylazodicarboxylate (896 μL, 4.55 mmol, 2.5 eq) was added. The temperature was allowed to raise to -5 °C over 30 min, and upon apparition of a precipitate, diphenylphosphorylazide (588 μL, 2.73 mmol, 1.5 eq) was added. The

reaction was then stirred at RT for 16 h, then the solvent was removed in *vacuo*, and the resulting residue was purified by column chromatography (cyclohexane:CH_2Cl_2 1:0 to 9:1) to afford the title compound **9** (995 mg, 85 %) as a colorless oil. For characterization purposes, both anomers were separated, but mixtures were used in the further steps. **α-9**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56-7.52 (m, 2H, 2Ar-H_{ortho}), 7.31-7.26 (m, 2H, 2Ar-H_{meta}), 7.23-7.18 (m, 1H, Ar-H_{para}), 5.59 (d, $J_{1,2}$ = 4.2 Hz, 1H, H-1), 4.30 (ddd, $J_{5,4}$ = 9.0 Hz, $J_{5,6b}$ = 5.9 Hz, $J_{5,6a}$ = 2.6 Hz, 1H, H-5), 4.09 (m, 1H, H-2), 3.84 (d, $J_{3,2}$ = 3.6 Hz, 1H, H-3), 3.73 (d, $J_{4,5}$ = 9.0 Hz, 1H, H-4), 3.52 (dd, $J_{6a,6b}$ = 13.1 Hz, $J_{6a,5}$ = 2.6 Hz, 1H, H-6a), 3.22 (dd, $J_{6b,6a}$ = 13.1 Hz, $J_{6b,5}$ = 5.9 Hz, 1H, H-6b), 0.98 (s, 9H, $C(CH_3)_3$), 0.89 (s, 9H, $C(CH_3)_3$), 0.88 (s, 9H, $C(CH_3)_3$), 0.22 (s, 3H, CH_3), 0.14 (s, 6H, $2CH_3$), 0.12 (s, 3H, CH_3), 0.09 (s, 3H, CH_3), 0.09 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 136.7 (Ar-C_{ipso}), 130.8 (2Ar-C_{ortho}), 128.9 (2Ar-C_{meta}), 126.5 (Ar-C_{para}), 87.2 (C-1), 76.3 (C-3), 74.6 (C-4), 73.0 (C-2), 72.8 (C-5), 52.5 (C-6), 26.2, 26.1, 25.9 (3C, 3C($\underline{C}H_3)_3$), 18.4, 18.1, 18.0 (3C, 3$\underline{C}(CH_3)_3$), -3.4, -3.6, -3.8, -4.4, -4.9, -5.0 (6C, $6CH_3$) ppm; ESI HRMS: *m/z*: calcd for $C_{30}H_{57}O_4N_3Si_3$ + Na^+: 662.3270 [M + Na^+] found: 662.3262.

β-9: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.52-7.48 (m, 2H, 2Ar-H_{ortho}), 7.31-7.26 (m, 2H, 2Ar-H_{meta}), 7.24-7.19 (m, 1H, Ar-H_{para}), 5.01 (d, $J_{1,2}$ = 6.3 Hz, 1H, H-1), 3.94,3.89 (m, 1H, H-5), 3.88-3.84 (m, 1H, H-2), 3.84,3.82 (m, 1H, H-3), 3.78-3.74 (m, 1H, H-4), 3.56 (dd, $J_{6a,6b}$ = 12.5 Hz, $J_{6a,5}$ = 7.3 Hz, 1H, H-6a), 3.38 (dd, $J_{6b,6a}$ = 12.5 Hz, $J_{6b,5}$ = 5.9 Hz, 1H, H-6b), 0.92 (s, 9H, $C(CH_3)_3$), 0.89 (s, 9H, $C(CH_3)_3$), 0.88 (s, 9H, $C(CH_3)_3$), 0.13 (s, 3H, CH_3), 0.11 (s, 3H, CH_3), 0.10 (s, 3H, CH_3), 0.09 (s, 3H, CH_3), 0.08 (s, 3H, CH_3), 0.08 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 135.5 (Ar-C_{ipso}), 130.8 (2Ar-C_{ortho}), 128.9 (2Ar-C_{meta}), 126.9 (Ar-C_{para}), 87.0 (C-1), 80.5 (C-5), 77.5 (C-3), 75.4 (C-2), 71.6 (C-4), 53.5 (C-6), 26.1, 26.0, 25.9 (3C, 3C($\underline{C}H_3)_3$), 18.2, 18.1, (3C, 3$\underline{C}(CH_3)_3$), -4.1, -4.2, -4.3, -4.8 (6C, $6CH_3$) ppm; ESI HRMS: *m/z*: calcd for $C_{30}H_{57}O_4N_3Si_3$ + Na^+: 662.3270 [M + Na^+] found: 662.3262.

Glycosylations

Procedure A: $BF_3.OEt_2$ promoted glycosylation.

To a solution of DHAB (1 eq) and donor (2.2 eq) in dry MeCN (45 mM) was added freshly activated molecular sieves (10mg/mg acceptor). The mixture was stirred for 30 min at RT and $BF_3.OEt_2$ (1.1 eq) was added. After stirring for 2 h at RT, the mixture was diluted with CH_2Cl_2, filtered through celite, and the filtrate washed with satd. aq. $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by column chromatography to afford bis- (**15a, 16a** or **17a**) and monoglycosylated (**16b** or **17b**) compounds (see Table 1 for yields) respectively.

Procedure B: MeOTf promoted glycosylation.

To a suspension of DHAB (1 eq) and glycosyl donor (2.2-2.5 eq) in the appropriate dry solvent (see Table 1 for solvent and concentration) was added freshly activated molecular sieves (10mg/mg acceptor). The mixture was stirred at RT for 30 min and the base (see Table 1; 2.2 eq) was added. Then MeOTf (5.5-6.6 eq) was added and the reaction was stirred at RT until completion. The mixture was then diluted with CH_2Cl_2 and filtered through celite. The filtrate was subsequently washed with satd. aq. $NaHCO_3$ solution and brine. The aqueous phase was extracted with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$ and concentrated in *vacuo*. The resulting residue was purified by column chromatography to afford bis- (**18a** or **19a**) and monoglycosylated (**18b** or **19b**) compounds (see Table 1 for yields) respectively.

Procedure C: BSP/Tf_2O promoted glycosylation.

To a solution of glycosyl donor (0.1 mmol), 2,6-di-*tert*-butyl-4-methylpyridine (0.11 mmol), 1-(phenylsulfinyl)piperidine (BSP) (0.1 mmol) and freshly activated molecular sieves (10mg/mg acceptor) in dry CH_2Cl_2 (0.5 mL) was added Tf_2O (0.1 mmol) at -90 °C. The mixture was stirred for 10 min at -90 °C and DHAB (45.0 µmol) was added as a solution in a 4:1 CH_2Cl_2/[bmim][OTf] mixture (0.5 mL). The mixture was stirred for 1 h between -90 °C and -40 °C then it was allowed to warm to RT and filtered through celite. The filtrate was washed with satd. aq. $NaHCO_3$, the aqueous phase was extracted with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by column chromatography to afford bis- (**18a**) and monoglycosylated (**18b**) compounds (see Table 1 for yields) respectively.

For symmetrical azobenzene bis-glycosides, assignments of NMR data for the azobenzene signals were reported as H_{ortho}, H_{meta}, C_{ipso}, C_{ortho}, C_{meta}, C_{para}, regarding to the position of the azo bond. In the case of unsymmetrical compounds (mono-glycosides or αβ isomers), the following numbering was used (Figure S1).

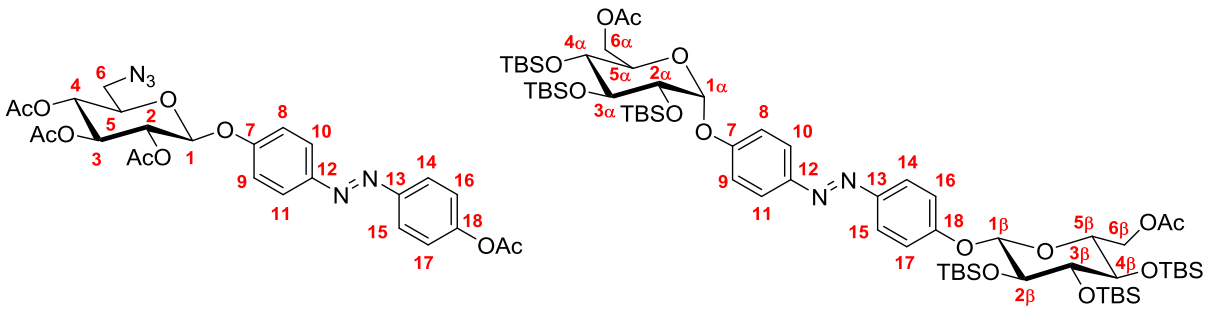


Figure S1. Numbering of unsymmetrical glycosides for assignment of NMR data.

Screening of bases in the glycosylation with silylated donor 8

Table S2 Screening of glycosylation conditions of DHAB with donors **8**.[a]

Entry	Donor[b]	Promoter (eq/donor)	Base (eq/DHAB)	Solvent	Temp.	Bis-glycoside, yield, αβ:ββ Mono-glycoside, yield, α:β
4[d]	**9**	MeOTf (2.5)	DBU (2.2)	DCM	rt	**19a**, 20%, 1:5 **19b**, 30%, 1:10
5[c, e]	**9**	MeOTf (2.5)	Cs_2CO_3 (2.2)	DCM	rt	**19a**, 27%, 1:5 **19b**, 21%, 1:10
6[c, e]	**9**	MeOTf (2.5)	*t*-BuOK (2.2)	DCM	rt	**19a**, 7%, 1:5 **19b**, 25%, 1:10
7	**9**	MeOTf (2.5)	Collidine (2.2)	DCM	rt	**19a**, 20%, 1:3 **19b**, 35%, 1:6

[a] All reactions were performed with [DHAB] = 0.05 mol.L^{-1} unless otherwise stated.
[b] 2.2 eq of donor were used in each glycosylation unless otherwise stated.
[c] 2.5 eq of donor were used
[d] [DHAB] = 0.03 mol.L^{-1}
[e] [DHAB] = 0.04 mol.L^{-1}

(*E*)-p,p'-Bis-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy) azobenzene (15a). General procedure A was applied to DHAB (10.0 mg, 45.0 µmol) and donor **5** (52.0 mg, 100 µmol, 2.2 eq). Reagents and conditions: boron trifluoride etherate (6.30 µL, 50.0 µmol, 1.1 eq), molecular sieves (100 mg), acetonitrile (1.00 mL, *c* = 45 mM). Column chromatography (cyclohexane:EtOAc 1:1) afforded the title compound **15a** (27.0 mg, 68 %) as an orange foam. $[\alpha]^{20}_{D}$ = -22.3 (*c* = 0.5 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 9.0 Hz, 4H, 4Ar-H_{ortho}), 7.09 (d, *J* = 9.0 Hz, 4H, 4Ar-H_{meta}), 5.35-5.28 (m, 4H, 2H-2, 2H-3), 5.21-5.16 (m, 4H, 2H-1, 2H-4), 4.30 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{6a,5}$ = 5.5 Hz, 2H, 2H-6a), 4.19 (dd, $J_{6b,6a}$ = 12.3 Hz, $J_{6b,5}$ = 2.3 Hz, 2H, 2H-6b), 3.92 (ddd, $J_{5,4}$ = 10.0 Hz, $J_{5,6a}$ = 5.5 Hz, $J_{5,6b}$ = 2.3 Hz, 2H, 2H-5), 2.08 (s, 3H, CH_3CO), 2.07 (s, 3H, CH_3CO), 2.06 (s, 3H, CH_3CO), 2.04 (s, 3H, CH_3CO) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.7, 170.4, 169.5, 169.4 (8C, 8$CH_3\underline{C}O$), 158.8 (2C, 2Ar-C_{para}), 148.7 (2C, 2Ar-C_{ipso}), 124.5 (4C, 4Ar-C_{ortho}), 117.2 (4C, 4Ar-C_{meta}), 98.8 (C-1), 72.8 (C-2), 72.4 (C-5), 71.3 (C-3), 68.4 (C-4), 62.1 (C-6), 20.8, 20.7 (8C, 8$\underline{C}H_3CO$) ppm; ESI HRMS: *m/z*: calcd for $C_{40}H_{46}N_2O_{20}$ + H^+: 875.2717 [M + H^+] found: 875.2690.

(*E*)-p,p'-Bis-(2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-β-D-glucopyranosyloxy) azobenzene (16a). General procedure A was applied to DHAB (193 mg, 900 µmol) and donor **6** (1.04 g, 2.00 mmol, 2.2 eq). Reagents and conditions: boron trifluoride etherate (126 µL, 1.00 mmol, 1.1 eq), molecular sieves (1.93 g), acetonitrile (20.0 mL, *c* = 45 mM). Column chromatography (cyclohexane:EtOAc 9:1 to 1:1) afforded the title compound **16a** (367 mg, 48 %) as an orange foam as well as the monoglycosylated compound. Since the latter was eluted in the same time as the hydrolysis products of the corresponding donor, acetylation of these fractions needed to be performed to isolate the pure compounds. Column chromatography (cyclohexane:EtOAc 9:1 to 7:3) afforded the monoglycosylated compound **16b** (72.0 mg, 14 %) as an orange foam. The obtained analytical data for **16a** are in agreement with reported literature.[1e]

(*E*)-p-(2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-β-D-glucopyranosyloxy)-p´-acetoxy azobenzene (16b). $[\alpha]^{20}_{D}$ = -60.0 (*c* = 1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.94-7.89 (m, 4H, H-10, H-11, H-14, H-15), 7.24 (d, *J* = 8.9 Hz, 2H, H-16, H-17), 7.13 (d, *J* = 9.0 Hz, 2H, H-8, H-9), 5.35-5.27 (m, 2H, H-2, H-3), 5.20

(d, $J_{1,2}$ = 7.6 Hz, 1H, H-1), 5.12-5.06 (m, 1H, H-4), 3.83 (ddd, $J_{5,4}$ = 10 Hz, $J_{5,6a}$ = 7.3 Hz, $J_{5,6b}$ = 2.7 Hz, 1H, H-5), 3.45 (dd, $J_{6a,6b}$ = 13.3 Hz, $J_{6a,5}$ = 7.3 Hz, 1H, H-6a), 3.35 (dd, $J_{6b,6a}$ = 13.3 Hz, $J_{6b,5}$ = 2.7 Hz, 1H, H-6b), 2.33 (s, 3H, Ar-CH_3CO), 2.08 (s, 3H, CH_3CO), 2.07 (s, 3H, CH_3CO), 2.05 (s, 3H, CH_3CO) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.3, 169.6, 169.4, 169.3 (4C, 4$CH_3\underline{C}O$), 158.9 (C-7), 152.6 (C-18), 150.34 (C-13), 148.7 (C-12), 124.8 (2C, C-14, C-15), 124.1 (2C, C-10, C-11), 122.3 (2C, C-16, C-17), 117.4 (2C, C-8, C-9), 98.8 (C-1), 73.8 (C-5), 72.6, 71.2 (C-2, C-3), 69.5 (C-4), 51.4 (C-6), 21.3 (Ar-$\underline{C}H_3CO$), 20.8, 20.7 (3C, $\underline{C}H_3CO$) ppm; ESI HRMS: *m/z*: calcd for $C_{26}H_{27}N_5O_{10}$ + H^+: 570.1831 [M + H^+] found: 570.1829.

(*E*)-p,p'-Bis-(2,3,4-tri-*O*-benzoyl-6-azido-6-deoxy-β-D-glucopyranosyloxy) azobenzene (17a). General procedure A was applied to DHAB (97.0 mg, 450 µmol) and donor **7** (690 mg, 1.00 mmol, 2,2 eq). Reagents and conditions: boron trifluoride etherate (63.0 µL, 500 µmol, 1.1 eq), molecular sieves (970 mg), acetonitrile (10.0 mL, *c* = 45 mM). Column chromatography (PhMe:EtOAc 9:1 to 8:2 to separate mono- from bis-glycosylated products; then cyclohexane:acetone 8:2) afforded the title compound **17a** (213 mg, 38 %) as an orange foam as well as the monoglycosylated compound. Since the latter was eluted in the same time as the hydrolysis products of the corresponding donor, acetylation of these fractions needed to be performed to isolate the pure compound. Column chromatography (cyclohexane:EtOAc 8:2) afforded **17b** (85.0 mg, 25 %) as an orange foam. **17a**: $[\alpha]^{20}_D$ = +61.7 (*c* = 1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98-7.92 (m, 8H, 8Ar-H_{Bz}), 7.87-7.83 (m, 8H, 4Ar-H_{Bz} + 4Ar-H_{ortho}), 7.56-7.49 (m, 4H, 4Ar-H_{Bz}), 7.47-7.42 (m, 2H, 2Ar-H_{Bz}), 7.41-7.35 (m, 8H, 8Ar-H_{Bz}), 7.33-7.28 (m, 4H, 4Ar-H_{Bz}), 7.14 (d, *J* = 9.1 Hz, 4H, 4Ar-H_{meta}), 6.00 (dd, $J_{3,2}$ = $J_{3,4}$ = 9.6 Hz, 2H, 2H-3), 5.81 (dd, $J_{2,3}$ = 9.6 Hz, $J_{2,1}$ = 7.8 Hz, 2H, 2H-2), 5.58 (dd, $J_{4,3}$ = $J_{4,5}$ = 9.6 Hz, 2H, 2H-4), 5.49 (d, $J_{1,2}$ = 7.8 Hz, 2H, 2H-1), 4.13 (ddd, $J_{5,4}$ = 9.6 Hz, $J_{5,6a}$ = 7.5 Hz, $J_{5,6b}$ = 2.6 Hz, 2H, 2H-5), 3.62 (dd, $J_{6a,6b}$ = 13.5 Hz, $J_{6a,5}$ = 7.5 Hz, 2H, 2H-6a), 3.48 (dd, $J_{6b,6a}$ = 13.5 Hz, $J_{6b,5}$ = 2.6 Hz, 2H, 2H-6b) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 165.9, 165.5, 165.2 (6C, 6Ph$\underline{C}$O), 158.8 (2C, 2Ar-C_{para}), 148.8 (2C, 2Ar-C_{ipso}), 133.9, 133.6, 133.5 (6C, 6Ar-C_{Bz}), 130.0, 129.9 (12C, 12Ar-C_{Bz}), 129.1 (2C, 2Ar-C_{Bz}), 128.8, 128.7 (6C, 6Ar-C_{Bz}) 128.6 (6C, 6ArC_{Bz}) 128.5 (4C, 4Ar-C_{Bz}), 124.6 (4C, 4Ar-C_{ortho}), 117.6 (4C, 4Ar-C_{meta}), 99.5 (2C-1), 74.4 (2C-5), 72.6 (2C-3), 71.7 (2C-2), 70.2 (2C-4), 51.6 (2C-6) ppm; ESI HRMS: *m/z*: calcd for $C_{66}H_{52}O_{16}N_8$ + H^+: 1213.3574 [M + H^+] found: 1213.3579.

(*E*)-p-(2,3,4-tri-*O*-benzoyl-6-azido-6-deoxy-β-D-glucopyranosyloxy)-p´-acetoxy azobenzene (17b). $[\alpha]^{20}_D$ = +20.2 (*c* = 1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.99-7.93 (m, 4H, 4Ar-H_{Bz}), 7.92 (d, *J* = 9.0 Hz, 2H, H-14, H-15), 7.89 (d, *J* = 9.0 Hz, 2H, H-10, H-11), 7.88-7.84 (m, 2H, 2Ar-H_{Bz}), 7.57-7.50 (m, 2H, 2Ar-H_{Bz}), 7.48-7.43 (m, 1H, Ar-H_{Bz}), 7.43-7.36 (m, 4H, 4Ar-H_{Bz}), 7.34-7.28 (m, 2H, 2Ar-H_{Bz}), 7.24 (d, *J* = 9.0 Hz, 2H, H-16, H-17), 7.16 (d, *J* = 9.0 Hz, 2H, H-8, H-9), 5.99 (dd, $J_{3,2}$ = $J_{3,4}$ = 9.6 Hz, 1H, H-3), 5.83 (dd, $J_{2,3}$ = 9.6 Hz, $J_{2,1}$ = 7.8 Hz, 1H, H-2), 5.59 (dd, $J_{4,3}$ = $J_{4,5}$ = 9.6 Hz, 1H, H-4), 5.50 (d, $J_{1,2}$ = 7.8 Hz, 1H, H-1), 4.14 (ddd, $J_{5,4}$ = 9.6 Hz, $J_{5,6a}$ = 7.5 Hz, $J_{5,6b}$ = 2.6 Hz, 1H, H-5), 3.62 (dd, $J_{6a,6b}$ = 13.5 Hz, $J_{6a,5}$ = 7.5 Hz, 1H, H-6a), 3.49 (dd, $J_{6b,\ 6a}$ = 13.5 Hz, $J_{6b,5}$ = 2.6 Hz, 1H, H-6b), 2.33 (s, 3H, CH_3CO) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.3 ($CH_3\underline{C}O$), 165.9, 165.5, 165.2 (3C, 3Ph$\underline{C}$O), 159.0 (C-7), 152.6 (C-18), 150.3 (C-13), 148.8 (C-12), 133.9, 133.6, 133.5 (3C, 3Ar-C_{Bz}), 130.0, 130.0, 129.9 (6C, 6Ar-C_{Bz}), 129.1, 128.7, 128.7, 128.6, 128.6, 128.5 (9C, 9Ar-C_{Bz}), 124.8 (2C, C-11, C-10), 124.1 (2C, C-14, C-15), 122.3 (2C, C-16, C-17), 117.6 (2C, C-8, C-9), 99.5 (C-1), 74.4 (C-5), 72.6 (C-3), 71.7 (C-2), 70.2 (C-4), 51.6 (C-6), 21.3 ($\underline{C}H_3CO$) ppm; ESI HRMS: *m/z*: calcd for $C_{41}H_{35}O_{10}N_5$ + H^+: 756.2300 [M + H^+] found: 756.2297.

(*E*)-p,p'-Bis-(2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-6-*O*-acetyl-β-D-glucopyranosyloxy) azobenzene (ββ-18a).

Route 1. General procedure B was applied to DHAB (10.0 mg, 45.0 µmol) and donor **8** (66.0 mg, 100 µmol, 2.2 eq). Reagents and conditions: methyl trifluoromethanesulfonate (33.0 µL, 304 µmol, 6.6 eq), 2,6-di-*tert*-butyl-4-methylpyridine (20.0 mg, 100 µmol, 2.2 eq), molecular sieves (100 mg), dichloromethane (1.00 mL, *c* = 45 mM). Column chromatography (cyclohexane:CH_2Cl_2 1:1 to 0:1 then cyclohexane:EtOAc 7:3) afforded an αβ:ββ (1:5) anomeric mixture of the title compound **18a** (30 mg, 50 %) as well as an α:β (1:10) anomeric mixture of monoglycosylated compound **18b** (7 mg, 20 %).

Route 2. General procedure C was applied to DHAB (10.0 mg, 45.0 µmol) and donor **9** (66.0 mg, 100 µmol, 2.2 eq). Reagents and conditions: 1-(phenylsulfinyl)piperidine (21.0 mg, 100 µmol, 2.2 eq), trifluoromethansulfonic anhydride (17.0 µL, 100 µmol, 2.2 eq), 2,6-di-*tert*-butyl-4-methylpyridine (23 mg, 110 µmol, 2.5 eq), molecular sieves (100 mg), CH_2Cl_2:bmimOTf (9:1, 1.00 mL, *c* = 45 mM). Column chromatography (cyclohexane:CH_2Cl_2 1:1 to 0:1 then cyclohexane:EtOAc 7:3) afforded an αβ:ββ (1:10) anomeric mixture of the title compound **18a** (11 mg, 18 %) as well as an α:β (1:5) anomeric mixture of monoglycosylated compound **18b** (7 mg, 20 %).

For a proper characterisation of the αβ anomer, the αβ,ββ mixture isolated after the glycosylation was enriched in αβ isomer after silica gel chromatography (see figures S24-S29).

ββ-18a: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 9.0 Hz 4H, 4Ar-H_{ortho}), 7.06 (d, *J* = 9.0 Hz 4H, 4Ar-H_{meta}), 5.50 (d, $J_{1,2}$ = 6.0 Hz, 2H, 2H-1), 4.31 (dd, $J_{6a,6b}$ = 11.1 Hz, $J_{6a,5}$ = 7.3 Hz, 2H, 2H-6a), 4.26 (dd, $J_{6b,6a}$ = 11.1 Hz, $J_{6b,5}$ = 6.2 Hz, 2H, 2H-6b), 4.21-4.16 (m, 2H, 2H-5), 3.96 (d, $J_{2,1}$ = 6.0 Hz, 2H, 2H-2), 3.90-3.83 (m, 4H, 2H-3, 2H-4), 2.00 (s, 6H, $2CH_3CO$), 0.94 (s, 18H, $2C(CH_3)_3$), 0.92 (s, 18H, $2C(CH_3)_3$), 0.86 (s, 18H, $2C(CH_3)_3$), 0.18 (s, 6H, $2CH_3$), 0.16 (s, 6H, $2CH_3$), 0.13 (s, 6H, $2CH_3$), 0.12 (s, 6H, $2CH_3$), 0.12 (s, 6H, $2CH_3$), 0.02 (s, 6H, $2CH_3$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.7 (2C, $2CH_3\underline{C}O$), 159.1 (2C, 2Ar-C_{para}), 148.0 (2C, 2Ar-C_{ipso}), 124.4 (4C, 4Ar-C_{ortho}), 116.2 (4C, 4Ar-C_{meta}), 99.0 (2C-1), 79.0 (2C-5), 78.0 (2C-3), 76.5 (2C-2), 70.6 (2C-4), 65.1 (2C-6), 26.0, 25.9 (18C, $6C(\underline{C}H_3)_3$), 20.9 (2C, $2\underline{C}H_3CO$), 18.2, 18.1 (6C, $\underline{C}(CH_3)_3$), -4.0, -4.3, -4.4, -4.6, -4.7, -4.9 (12C, $12CH_3$) ppm; ESI HRMS: *m/z*: calcd for $C_{64}H_{118}N_2O_{14}Si_6 + H^+$: 1307.7271 [M + H^+] found: 1307.7257.

(*E*)-p-(2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-6-*O*-acetyl-α-D-glucopyranosyloxy)-p'-(2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-6-*O*-acetyl-β-D-glucopyranosyloxy) azobenzene (αβ-18a).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89-7.84 (m, 4H, 4Ar-H_{ortho}), 7.19 (d, *J* = 9.0 Hz, 2H, H-8, H-9), 7.06 (d, *J* = 9.0 Hz, 2H, H-16, H-17), 5.52 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1_α), 5.50 (d, $J_{1,2}$ = 6.0 Hz, 1H, H-1_β), 4.34-4.24 (m, 4H, H-5_α, H-$6a_\alpha$, H-$6a_\beta$, H-$6b_\beta$), 4.22-4.16 (m, 2H, H-$6b_\alpha$, H-5_β), 4.06-4.03 (m, 1H, H-2_α), 3.99-3.93 (m, 2H, H-3_α, H-2_β), 3.90-3.83 (m, 2H, H-3_β , H-4_β), 3.70-3.67 (m, 1H, H-4_α), 2.0 (s, 3H, CH_3CO_β), 1.95 (s, 3H, CH_3CO_α), 0.96 (s, 9H, $C(CH_3)_3$), 0.93 (s, 9H, $C(CH_3)_3$), 0.92 (s, 9H, $C(CH_3)_3$), 0.92 (s, 9H, $C(CH_3)_3$), 0.89 (s, 9H, $C(CH_3)_3$), 0.86 (s, 9H, $C(CH_3)_3$), 0.20 (s, 3H, CH_3), 0.18 (s, 3H, CH_3), 0.16 (s, 3H, CH_3), 0.15 (s, 3H, CH_3), 0.14 (s, 3H, CH_3), 0.13 (s, 3H, CH_3), 0.12 (s, 3H, CH_3), 0.12 (s, 3H, CH_3), 0.11 (s, 3H, CH_3), 0.08 (s, 3H, CH_3), 0.02 (s, 3H, CH_3), 0.02 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.0 ($CH_3\underline{C}O_\alpha$), 170.7 ($CH_3\underline{C}O_\beta$), 159.6 (C-7), 159.1 (C18), 148.0 (C-13), 147.9 (C-12), 124.4 (2C, C-14, C-15), 124.3 (2C, C-10, C-11), 117.1 (2C, C-8, C-9), 116.2 (2C, C-16, C-17), 99.0 (C-1_β), 94.9 (C-1_α), 79.2 (C-5_β), 78.0 (C-3_β), 76.6 (C-2_β), 76.0 (C-3_α), 73.1 (C-4_α), 72.8 (C-5_α), 71.6 (C-2_α), 70.6 (C-4_β), 65.1 (C-6_β), 64.0 (C-6_α), 26.1, (9C, $3C(\underline{C}H_3)_3$, α-side), 26.0, 25.9 (9C, $3C(\underline{C}H_3)_3$, β-side), 21.0 ($\underline{C}H_3CO$, α-side), 20.9 ($\underline{C}H_3CO$, β-side), 18.5, 18.2, 18.1 (6C, $6\underline{C}(CH_3)_3$), -3.2, -3.7, -4.0, -4.1, -4.3, -4.4, -4.6, -4.7, -4.8, -4.9 (12C, CH_3) ppm; ESI HRMS: *m/z*: calcd for $C_{64}H_{118}N_2O_{14}Si_6 + H^+$: 1307.7271 [M + H^+] found: 1307.7257.

(*E*)-p-(2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-6-*O*-acetyl-β-D-glucopyranosyloxy)-p´-hydroxy azobenzene (β-18b). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87-7.79 (m, 4H, H-10, H-11, H-14, H-15), 7.06 (d,

J = 9.1 Hz, 2H, H-8, H-9), 6.91 (d, *J* = 9.1 Hz, 2H, H-16, H-17), 5.91 (bs, 1H, Ar-OH), 5.52 (d, $J_{1,2}$ = 6.0 Hz, 1H, H-1), 4.34 (dd, $J_{6a\text{-}6b}$ = 11.2 Hz, $J_{6a,5}$ = 7.5 Hz, 1H, H-6a), 4.28 (dd, $J_{6b\text{-}6a}$ = 11.2 Hz, $J_{6b,5}$ = 6.3 Hz, 1H, H-6b), 4.23,4.18 (m, 1H, H-5), 3.97 (d, $J_{2,1}$ = 6.0 Hz, 1H, H-2), 3.90 (d, $J_{3,4}$ = 3.3 Hz, 1H, H-3), 3.87 (d, $J_{4,3}$ = 3.3 Hz, 1H, H-4), 2.00 (s, 3H, CH_3CO), 0.94 (s, 9H, $C(CH_3)_3$), 0.93 (s, 9H, $C(CH_3)_3$), 0.86 (s, 9H, $C(CH_3)_3$, 0.18 (s, 3H, CH_3), 0.17 (s, 3H, CH_3), 0.13 (s, 3H, CH_3), 0.13 (s, 3H, CH_3), 0.12 (s, 3H, CH_3) 0.02 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.1 ($CH_3\underline{C}O$), 159.0 (C-7), 158.3 (C-18), 147.9 (C-12), 147.2 (C-13), 124.8 (2C, C-14, C-15), 124.4 (2C, C-10, C-11), 116.2 (2C, C-8, C-9), 115.9 (2C, C-16, C-17), 98.9 (C-1), 78.9 (C-5), 77.9 (C-3), 76.4 (C-2), 70.6 (C-4), 65.2 (C-6), 26.0, 25.9 (9C, $3C(\underline{C}H_3)_3$), 20.9 ($\underline{C}H_3CO$), 18.2, 18.1 (3C, $3\underline{C}(CH_3)_3$), -4.1, -4.3, -4.4, -4.6, -4.7, -4.9 (6C, $6CH_3$) ppm; ESI HRMS: *m/z*: calcd for $C_{38}H_{64}O_8N_2Si_3 + H^+$: 761.4043 [M + H^+] found: 761.4017.

(*E*)-p-(2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-6-*O*-acetyl-α-D-glucopyranosyloxy)-p´-hydroxy azobenzene (α-18b). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88-7.79 (m, 4H, 4Ar-H_{ortho}), 7.18 (d, *J* = 9.0 Hz, 2H, H-8, H-9), 6.91 (d, *J* = 9.0 Hz, 2H, H-16, H-17), 5.53 (d, $J_{1,2}$ = 3.7 Hz, 1H, H-1), 4.32-4.27 (m, 2H, H-5, H-6a), 4.25,4.21 (m, 1H, H-6b), 4.07-4.03 (m, 1H, H-2), 3.97-3.93 (m, 1H, H-3), 3.72,3.68 (m, 1H, H-4), 1.97 (s, 3H, CH_3CO), 0.96 (s, 9H, $C(CH_3)_3$), 0.93 (s, 9H, $C(CH_3)_3$), 0.90 (s, 9H, $C(CH_3)_3$), 0.20 (s, 3H, CH_3), 0.16 (s, 3H, CH_3), 0.14 (s, 3H, CH_3), 0.13 (s, 3H, CH_3), 0.12 (s, 3H, CH_3), 0.09 (s, 3H, CH_3) ppm; ESI HRMS: *m/z*: calcd for $C_{38}H_{64}O_8N_2Si_3 + H^+$: 761.4043 [M + H^+] found: 761.4017. Since the isolated amount of **α,β-18b** (α minor anomer) was too small, no proper ^{13}C-NMR characterization of the α species could be achieved.

(*E*)-p,p'-bis-(2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-6-azido-6-deoxy-β-D- glucopyranosyloxy) azobenzene (ββ-19a). General procedure B was applied to DHAB (21.0 mg, 97.0 µmol) and donor **9** (136 mg, 212 µmol, 2.2 eq). Reagents and conditions: methyl trifluoromethanesulfonate (70.0 µL, 636 µmol, 6.6 eq), 2,6-di-*tert*-butyl-4-methylpyridine (44.0 mg, 212 µmol, 2.2 eq), molecular sieves (210 mg), dichloromethane (2.12 mL, *c* = 45 mM). Column chromatography (cyclohexane:CH_2Cl_2 9.1 to 7:3 then cyclohexane:EtOAc 7:3) afforded an αβ:ββ (1:4) anomeric mixture of the title compound **19a** (13 mg, 10 %) as well as an α:β (1:8) anomeric mixture of monoglycosylated compound **19b** (11 mg, 14 %). For a proper characterisation of the αβ anomer, the αβ,ββ mixture isolated after the glycosylation was enriched in αβ isomer after silica gel chromatography (see figures S32 – S36).
ββ-19a: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 9.0 Hz, 4H, 4Ar-H_{ortho}), 7.07 (d, *J* = 9.0 Hz, 4H, 4Ar-H_{meta}), 5.50 (d, $J_{1,2}$ = 5.8 Hz, 2H, 2H-1), 4.11-4.05 (m, 2H, 2H-5), 3.96 (d, $J_{2,1}$ = 5.8 Hz, 2H, 2H-2), 3.89, (bs, 2H, 2H-3), 3.85 (bs, 2H, 2H-4), 3.61 (dd, $J_{6a,5}$ = 6.9 Hz, $J_{6a\text{-}6b}$ = 12.2 Hz, 2H, 2H-6a), 3.48 (dd, $J_{6b,5}$ = 7.4 Hz, $J_{6b\text{-}6a}$ = 12.2 Hz, 2H, 2H-6b), 0.94 (s, 18H, $2C(CH_3)_3$), 0.92 (s, 18H, $2C(CH_3)_3$), 0.86 (s, 18H, $2C(CH_3)_3$), 0.18 (s, 3H, CH_3), 0.17 (s, 3H, CH_3), 0.14 (s, 3H, CH_3), 0.14 (s, 3H, CH_3), 0.12 (s, 3H, CH_3), 0.02 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 159.0 (2C, 2Ar-C_{para}), 148.1 (2C, 2Ar-C_{ipso}), 124.5 (4C, 4Ar-C_{ortho}), 116.2 (4C, 4Ar-C_{meta}), 99.1 (2C-1), 79.8 (2C-5), 78.2 (2C-3), 76.5 (2C-2), 70.9 (2C-4), 53.2 (2C-6), 26.0, 25.9 (18C, $C(\underline{C}H_3)_3$), 18.2, 18.1, 18.0 (6C, $C(\underline{C}H_3)_3$), -4.1, -4.3, -4.5, -4.7, -4.8 (12C, CH_3) ppm; ESI HRMS: *m/z*: calcd for $C_{60}H_{112}O_{10}N_8Si_6 + H^+$: 1273.7190 [M + H^+] found: 1273.7193.

(*E*)-p-(2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-6-azido-6-deoxy-α-D-glucopyranosyloxy)-p'-(2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-6-azido-6-deoxy-β-D-glucopyranosyloxy) azobenzene (αβ-19a).
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90-7.85 (m, 4H, 4Ar-H_{ortho}), 7.18 (d, *J* = 9.1 Hz, 2H, H-8, H-9), 7.07 (d, *J* = 9.0 Hz, 2H, H-16, H-17), 5.57 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1_α), 5.50 (d, $J_{1,2}$ = 6.0 Hz, 1H, H-1_β), 4.36-4.32 (m, 1H, H-5_α), 4.11-4.05 (m, 2H, H-5_β, H-2_α), 3.96 (d, $J_{2,1}$ = 6.0 Hz, 1H, H-2_β), 3.94,3.91 (m, 1H, H-3_α), 3.91-3.88 (m, 1H, H-3_β), 3.87-3.83 (m, 1H, H-4_β), 3.75 (m, 1H, H-4_α), 3.61 (dd, $J_{6a,6b}$ 12.3 Hz, $J_{6a,5}$ = 6.9 Hz,

1H, H-6a$_\beta$), 3.52,3.45 (m, 2H, H-6b$_\beta$, H-6a$_\alpha$), 3.20 (dd, $J_{6a,6b}$ = 13.3 Hz, $J_{6a,5}$ = 5.5 Hz, 1H, H-6b$_\alpha$), 0.96 (s, 9H, C(CH$_3$)$_3$), 0.94 (s, 9H, C(CH$_3$)$_3$), 0.92 (s, 9H, C(CH$_3$)$_3$), 0.92 (s, 9H, C(CH$_3$)$_3$), 0.88 (s, 9H, C(CH$_3$)$_3$), 0.86 (s, 9H, C(CH$_3$)$_3$), 0.22 (s, 3H, CH$_3$), 0.18 (s, 3H, CH$_3$), 0.17 (s, 3H, CH$_3$), 0.16 (s, 3H, CH$_3$), 0.14 (s, 3H, CH$_3$), 0.14 (s, 3H, CH$_3$), 0.12 (s, 3H, CH$_3$), 0.12 (s, 3H, CH$_3$), 0.09 (s, 3H, CH$_3$), 0.07 (s, 3H, CH$_3$), 0.02 (s, 3H, CH$_3$), 0.02 (s, 3H, CH$_3$) ppm; ESI HRMS: *m/z*: calcd for $C_{60}H_{112}O_{10}N_8Si_6$ + H^+: 1273.7190 [M + H^+] found: 1273.7193; Since the isolated amount of **αβ,ββ-19a** (αβ minor isomer) was too small, no proper ^{13}C-NMR characterization of the α,β species by could be achieved.

(*E*)-p-(2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-6-deoxy-6-azido-β-D-glucopyranosyloxy)-p´-hydroxy azobenzene (β-19b). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 9.0 Hz, 2H, H-10, H-11), 7.83 (d, *J* = 8.9 Hz, 2H, H-14, H-15), 7.07 (d, *J* = 9.0 Hz, 2H, H-8, H-9), 6.93 (d, *J* = 8.9 Hz, 2H, H-16, H-17), 5.51 (d, $J_{1,2}$ = 5.9 Hz, 1H, H-1), 4.11-4.06 (m, 1H, H-5), 3.96 (d, $J_{2,1}$ = 5.9 Hz, 1H, H-2), 3.90-3.88 (m, 1H, H-3), 3.86-3.83 (m, 1H, H-4), 3.61 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{6a,5}$ = 6.9 Hz, 1H, H-6a), 3.48 (dd, $J_{6b,6a}$ = 12.4 Hz, $J_{6b,5}$ = 7.4 Hz, 1H, H-6b), 0.94 (s, 9H, C(CH$_3$)$_3$), 0.92 (s, 9H, C(CH$_3$)$_3$), 0.86 (s, 9H, C(CH$_3$)$_3$), 0.18 (s, 3H, CH$_3$), 0.17 (s, 3H, CH$_3$), 0.14 (s, 6H, 2CH$_3$), 0.12 (s, 3H, CH$_3$), 0.02 (s, 3H, CH$_3$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 159.0 (C-7), 158.0 (C-18), 148.0 (C-12), 147.4 (C-13), 124.8 (2C, C-14, C-15), 124.4 (2C, C-10, C-11), 116.2 (2C, C-8, C-9), 115.9 (2C, C-14, C-15), 99.1 (C-1), 79.8 (C-5), 78.2 (C-3), 76.5 (C-2), 70.9 (C-4), 53.2 (C-6), 26.0, 25.9 (9C, 3C($\underline{C}$H$_3$)$_3$), 18.2, 18.1, 18.0 (3C, 3$\underline{C}$(CH$_3$)$_3$), -4.1, -4.3, -4.5, -4.7, -4.8 (6C, 6CH$_3$) ppm; ESI HRMS: *m/z*: calcd for $C_{38}H_{61}O_6N_5Si_3$ – H^+: 742.3857 [M - H^+] found: 742.3861.

(*E*)-p-(2,3,4-tri-*O*-((*tert*-butyldimethyl)silyl)-6-deoxy-6-azido-α-D-glucopyranosyloxy)-p´-hydroxy azobenzene (α-19b). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89-7.81 (m, 4H, H-10, H-11, H-14, H-15), 7.18 (d, *J* = 9.1 Hz, 2H, C-8, C-9), 6.93 (d, *J* = 9.1 Hz, 2H, H-16, H-17), 5.57 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1), 4.34 (ddd, $J_{5,4}$ = 8.9 Hz, $J_{5,6b}$ = 5.5 Hz, $J_{5,6a}$ = 2.7 Hz, 1H, H-5), 4.11-4.07 (m, 1H, H-2), 3.94,3.91 (m, 1H, H-3), 3.75 (d, $J_{4,5}$ = 8.9 Hz, 1H, H-4), 3.48 (dd, $J_{6a,6b}$ = 13.3 Hz, $J_{6a,5}$ = 2.7 Hz, 1H, H-6a), 3.21 (dd, $J_{6b,6a}$ = 13.3 Hz, $J_{6b,5}$ = 5.5 Hz, 1H, H-6b), 0.96 (s, 9H, C(CH$_3$)$_3$), 0.93 (s, 9H, C(CH$_3$)$_3$), 0.88 (s, 9H, C(CH$_3$)$_3$), 0.22 (s, 3H, CH$_3$), 0.16 (s, 3H, CH$_3$), 0.14 (s, 3H, CH$_3$), 0.12 (s, 3H, CH$_3$), 0.11 (s, 3H, CH$_3$), 0.09 (s, 3H, CH$_3$) ppm; ESI HRMS: *m/z*: calcd for $C_{38}H_{61}O_6N_5Si_3$ – H^+: 742.3857 [M - H^+] found: 742.3861; Since the isolated amount of **α,β-20b** (α minor anomer) was too small, no proper ^{13}C-NMR characterization of the α species by could be achieved.

O-methylated azobenzenes

To a suspension of DHAB (214 mg, 1.00 mmol) in acetonitrile (10 mL) were added diisopropylethylamine (0.348 mL, 2.00 mmol) and methyltrifluoromethanesulfonate (0.164 mL, 1.50 mmol) at RT. The mixture was stirred for 2 h at this temperature and then was concentrated and purified by column chromatography (cyclohexane-ethyl acetate) to afford 4,4´-dimethoyazobenzene **S2** (34 mg, 11 %) and 4-hydroxy-4´-methoxyazobenzene **S3** (72.8 mg, 32 %).

p,p´-dimethoxyazobenzene (S2). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.93-7.78 (m, 4H, 4-H$_{ortho}$), 7.05-6.87 (m, 4H, 4-H$_{meta}$), 3.89 (s, 6H, OMe) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 161.7 (2C, Ar-C$_{para}$), 147.2 (2C, Ar-C$_{ipso}$), 124.5 (4C, Ar-C$_{ortho}$), 111.3 (4C, Ar-C$_{meta}$), 55.7 (2C, OCH$_3$) ppm; ESI HRMS: *m/z*: calcd for $C_{14}H_{14}O_2N_2$ + H^+: 243.1128 [M + H^+] found: 243.1124.

p-methoxy-p´-hydroxyazobenzene (S3). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90-7.80 (m, 4H, 4-H$_{ortho}$), 7.02-6.98 (m, 2H, 2-H$_{meta}$, OMe side), 6.94-6.90 (m, 2H, 2-H$_{meta}$, OH side), 5.51, (bs, 1H, OH), 3.88 (s, 3H, OMe) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 161.8 (1Ar-C$_{para}$, OMe side), 157.9 (1Ar-C$_{para}$, OH side), 147.3 (1Ar-C$_{ipso}$, OH side), 147.1 (1Ar-C$_{ipso}$, OMe side), 124.7 (2C, 2Ar-C$_{ortho}$, OH side), 124.5 (2C, 2Ar-

C_{ortho}, OMe side), 115.9 (2C, 2Ar-C_{meta}, OH side), 114.3 (2C, 2Ar-C_{meta}, OH side), 55.7 (OCH_3) ppm; ESI HRMS: *m/z*: calcd for $C_{13}H_{12}O_2N_2 + H^+$: 229.0972 [M + H^+] found: 229.0968.

NMR spectra of the synthesized compounds

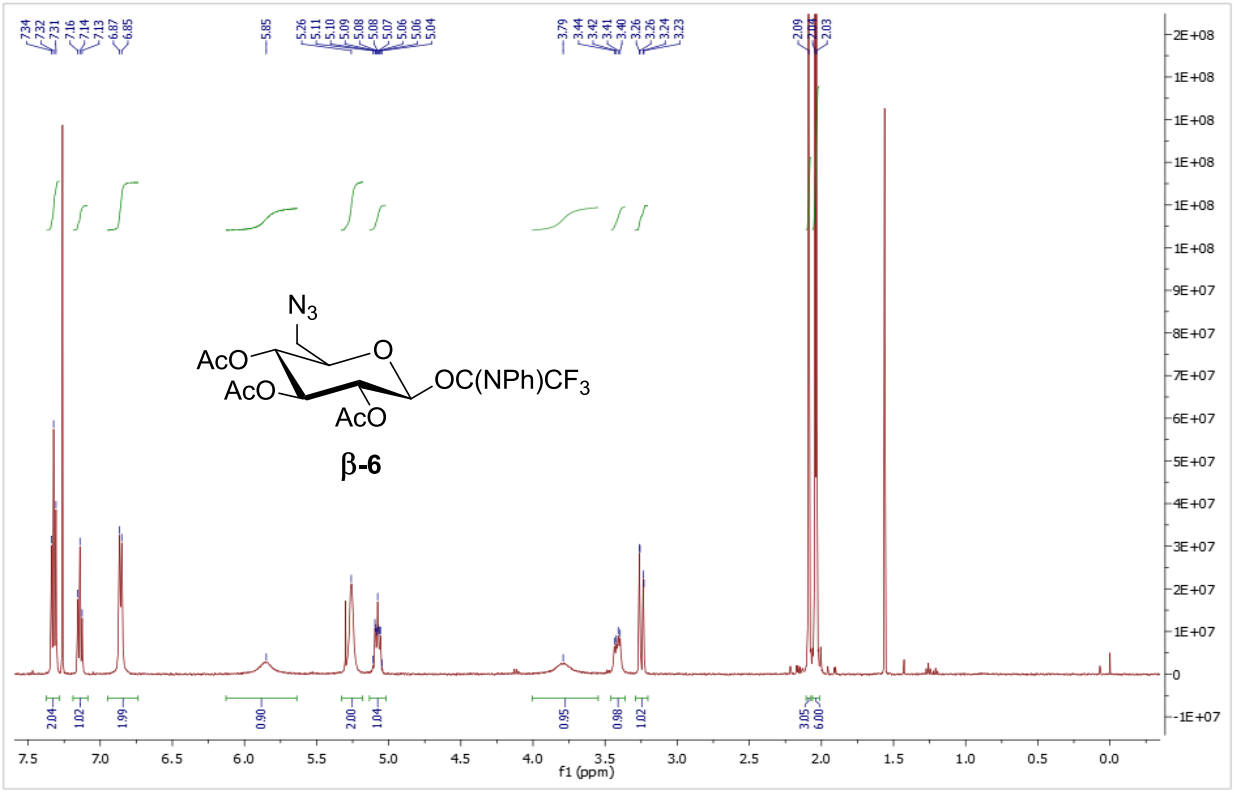


Figure S2: ^{1}H NMR spectrum of **β-6** (500 MHz, $CDCl_3$, 300 K).

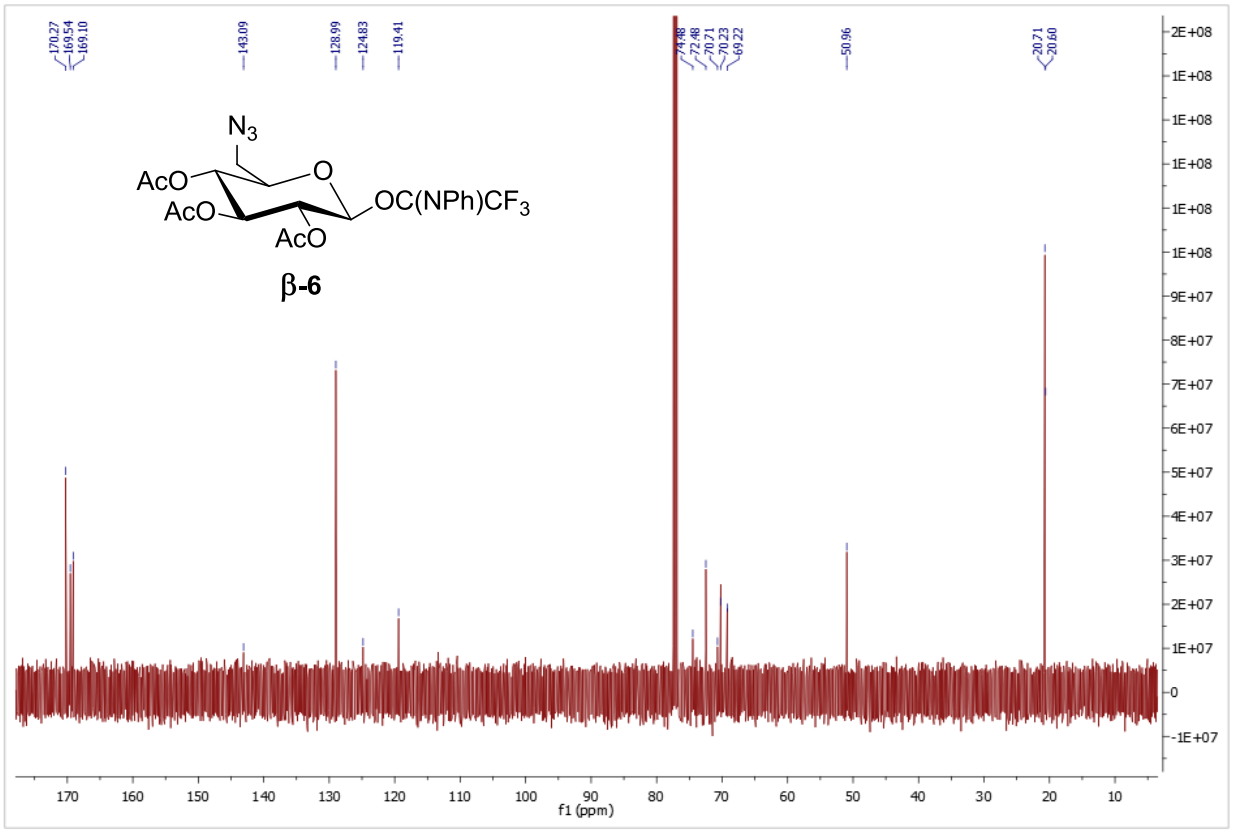


Figure S3: ^{13}C NMR spectrum of **β-6** (126 MHz, $CDCl_3$, 300 K).

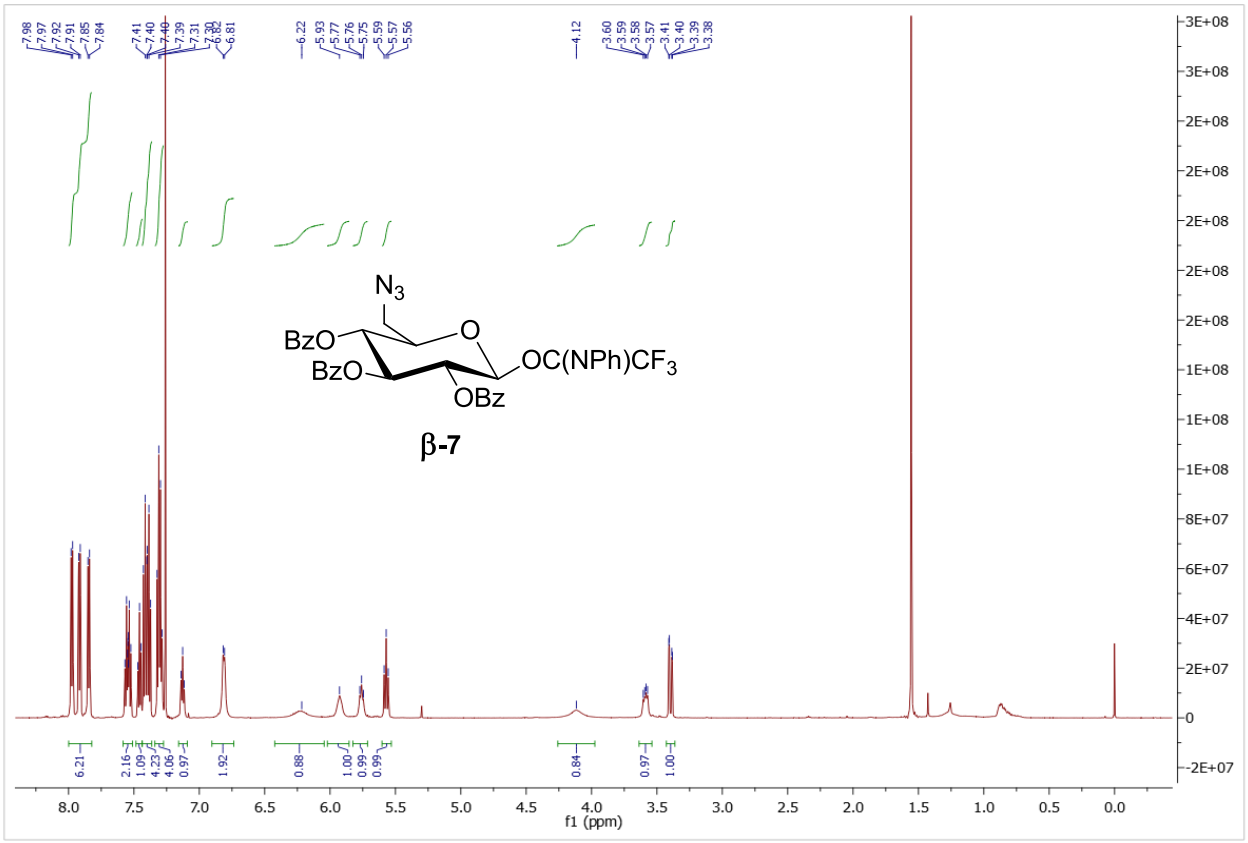


Figure S4: ^{1}H NMR spectrum of **β-7** (500 MHz, $CDCl_3$, 300 K).

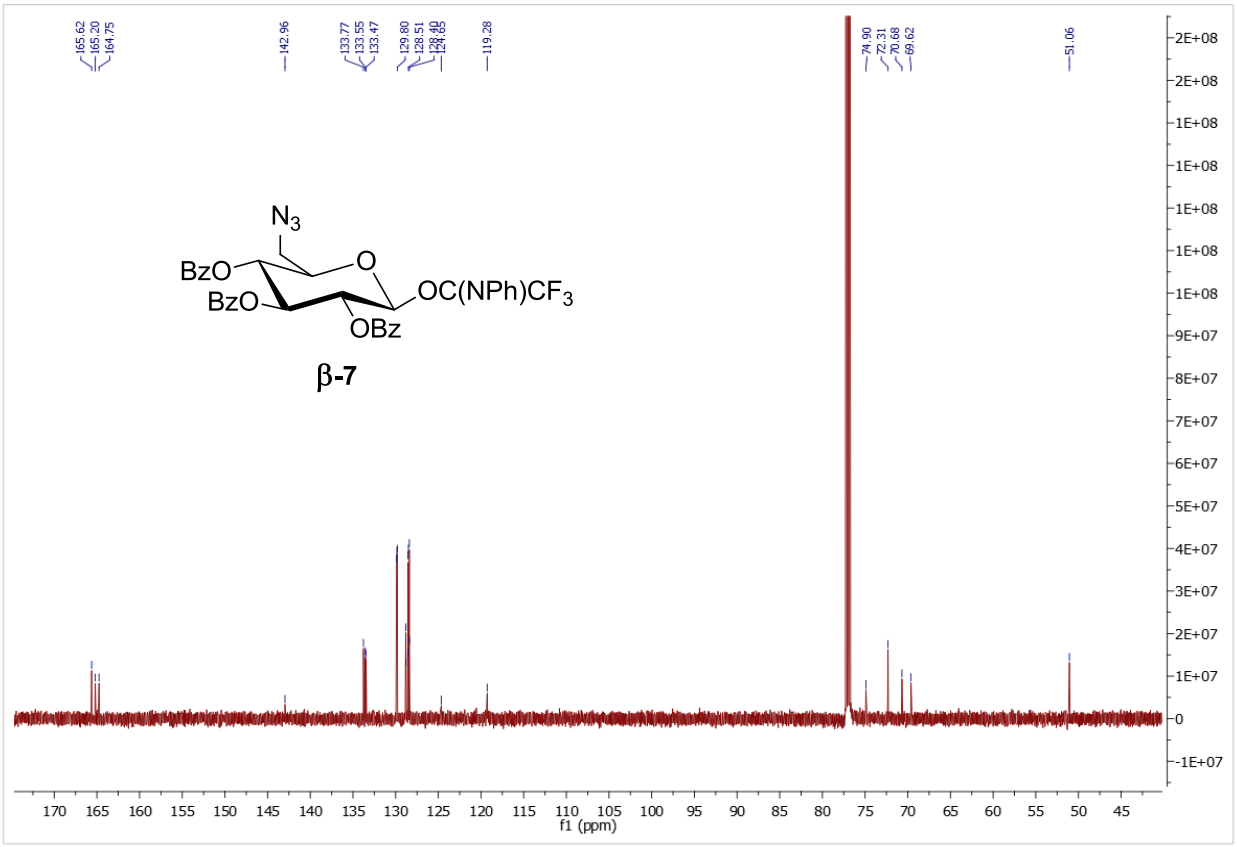


Figure S5: ^{13}C NMR spectrum of **β-7** (126 MHz, $CDCl_3$, 300 K).

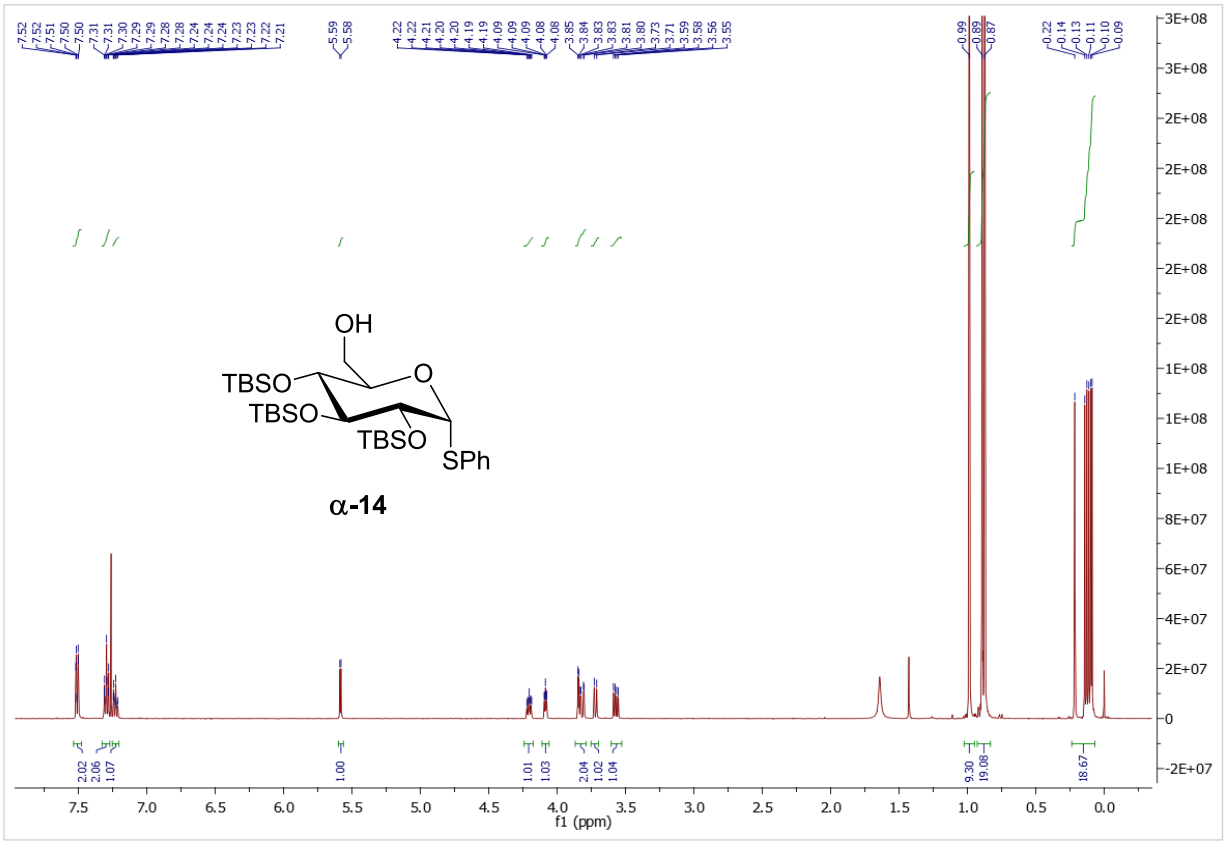


Figure S6: ^{1}H NMR spectrum of **α-14** (500 MHz, $CDCl_3$, 300 K).

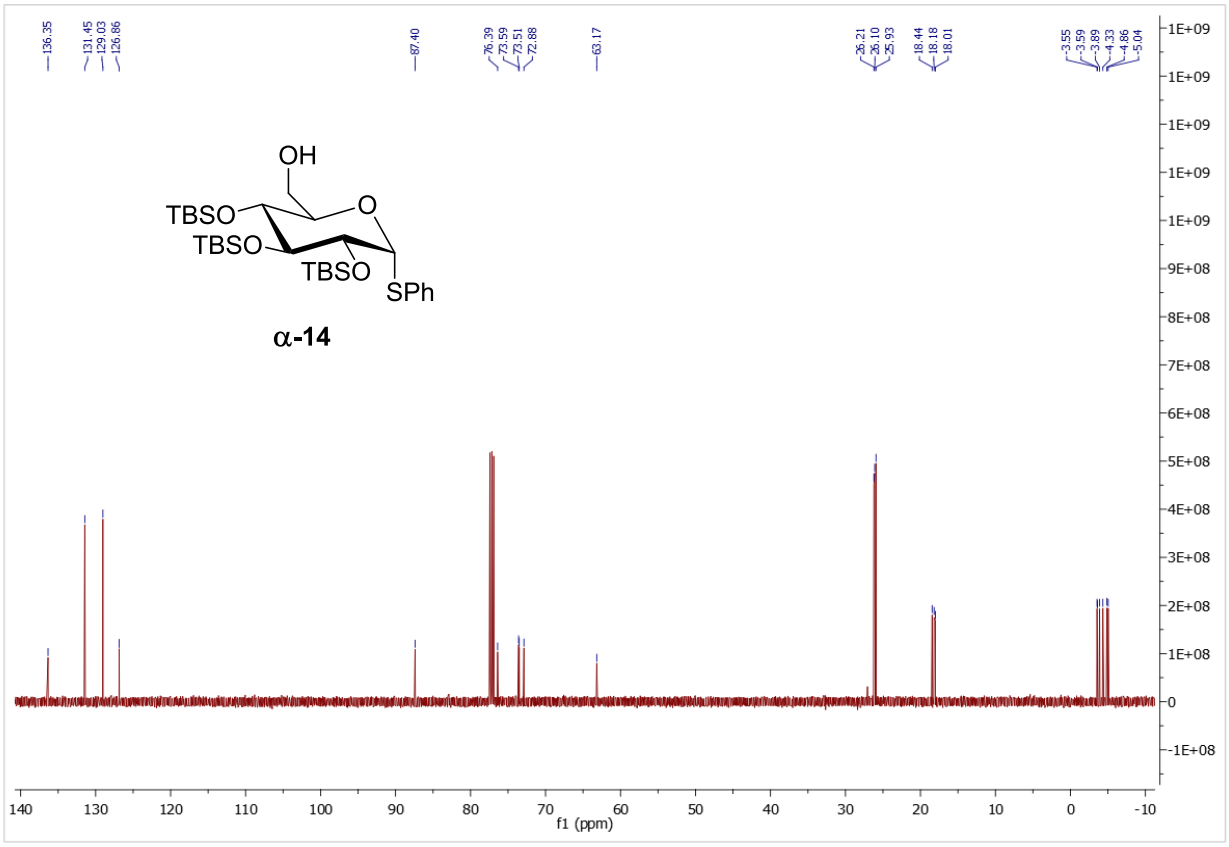


Figure S7: ^{13}C NMR spectrum of **α-14** (126 MHz, $CDCl_3$, 300 K).

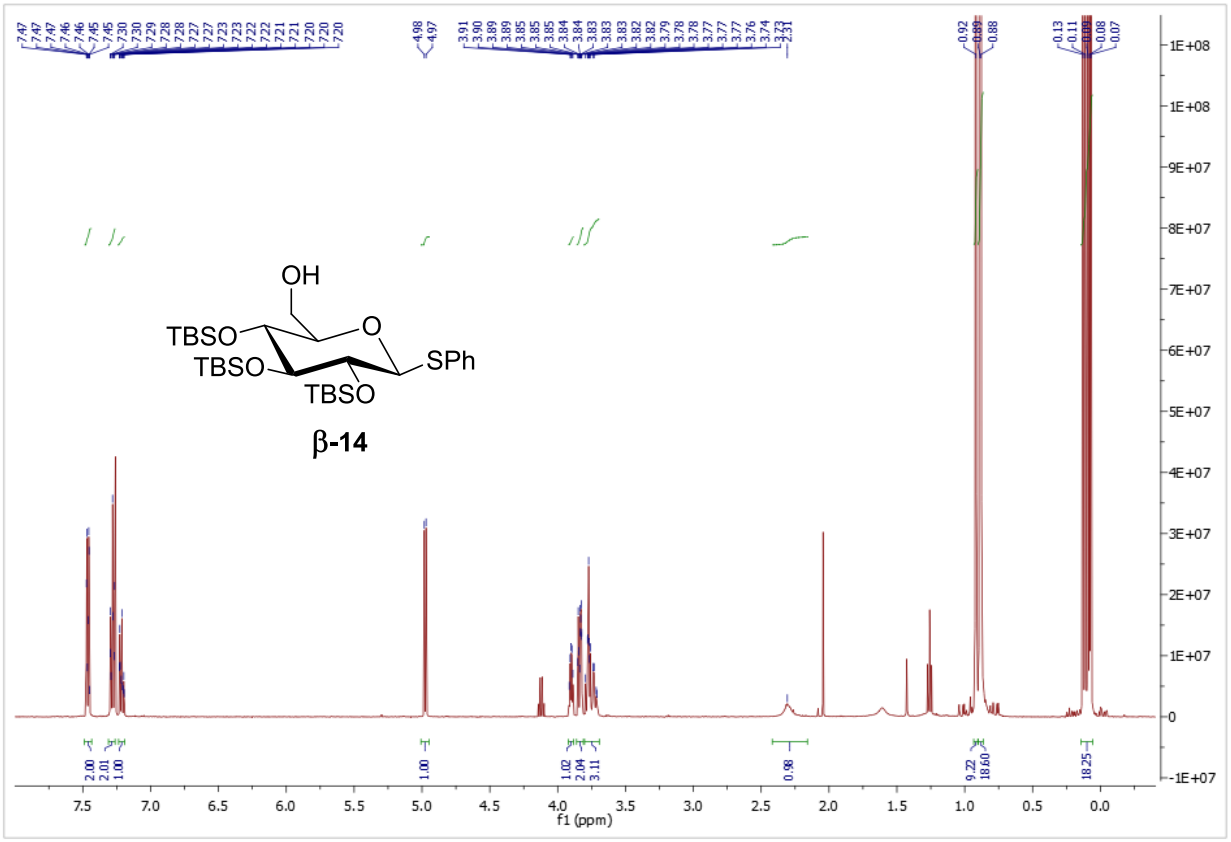


Figure S8: ^{1}H NMR spectrum of **β-14** (500 MHz, $CDCl_3$, 300 K).

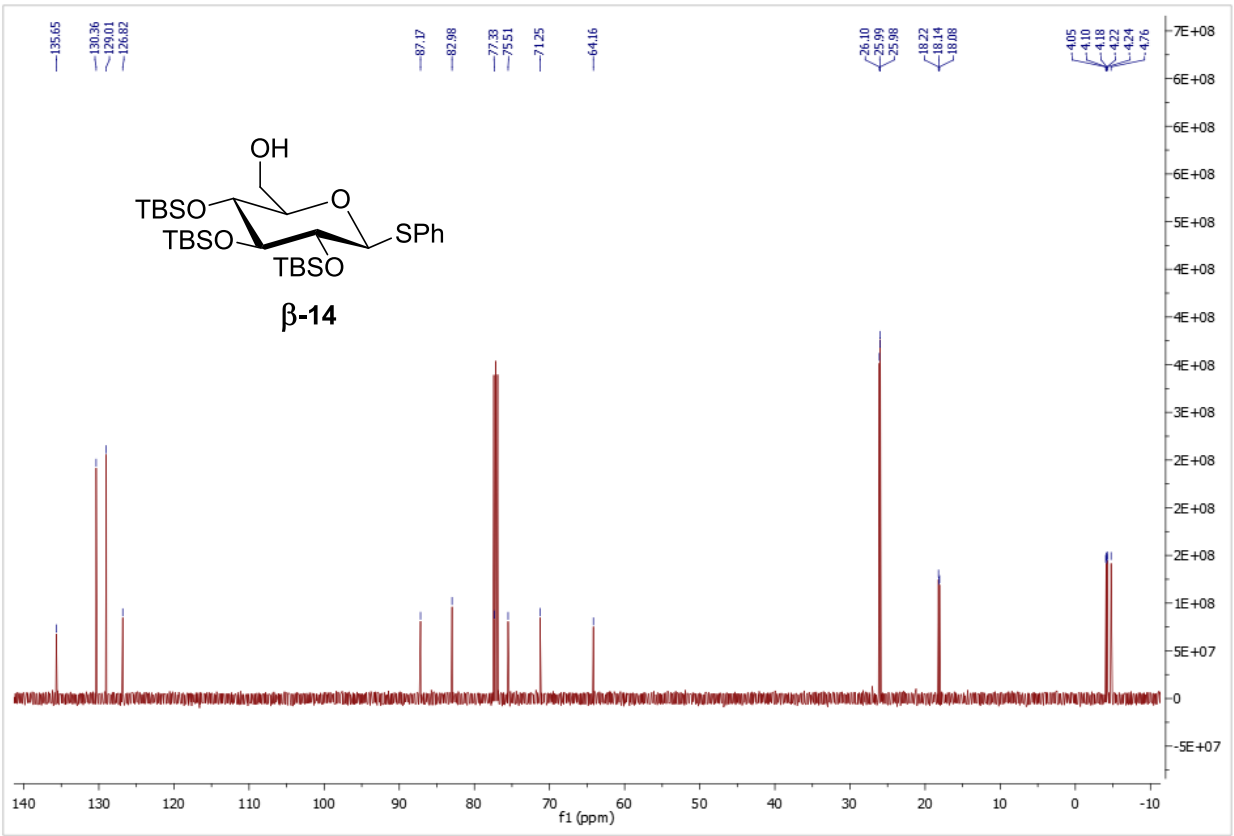


Figure S9: ^{13}C NMR spectrum of **β-14** (126 MHz, $CDCl_3$, 300 K).

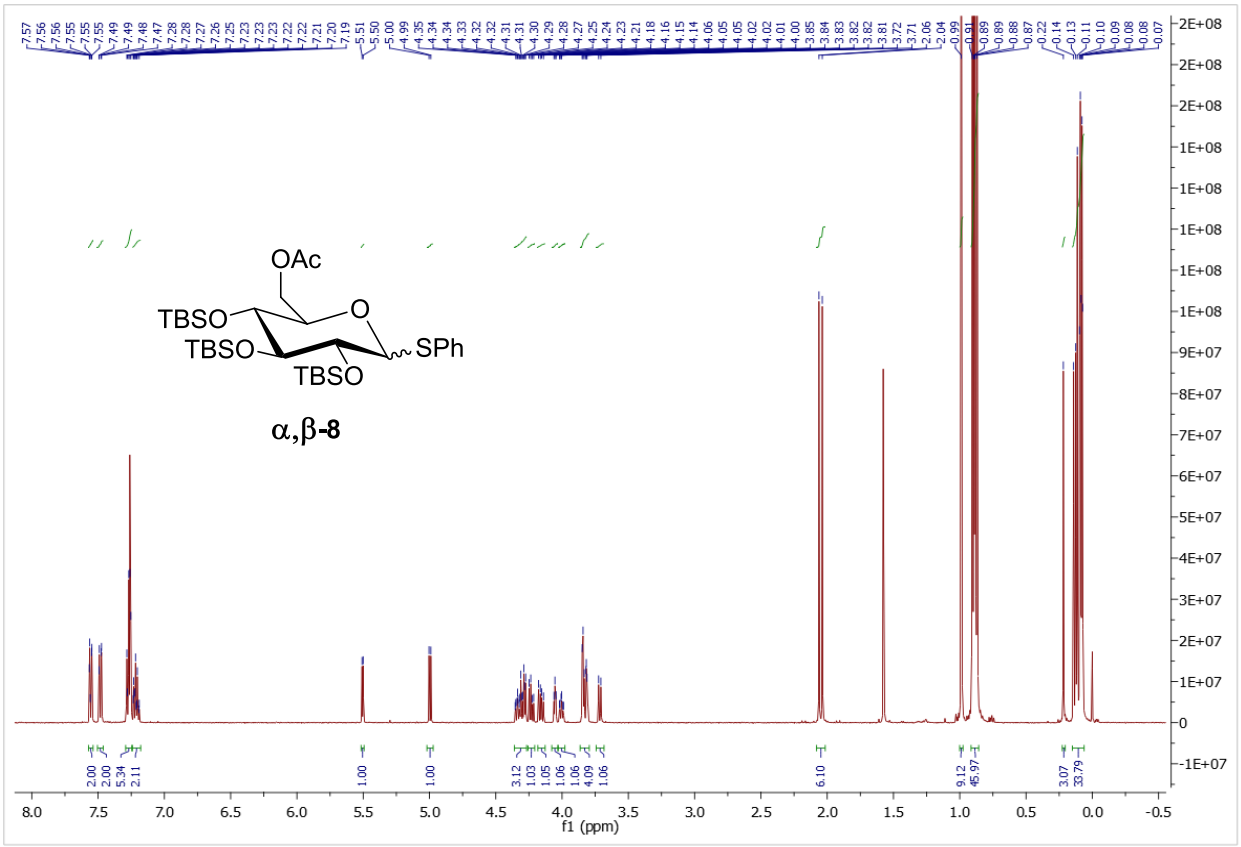


Figure S10: ^{1}H NMR spectrum of **α,β-8** (500 MHz, $CDCl_3$, 300 K).

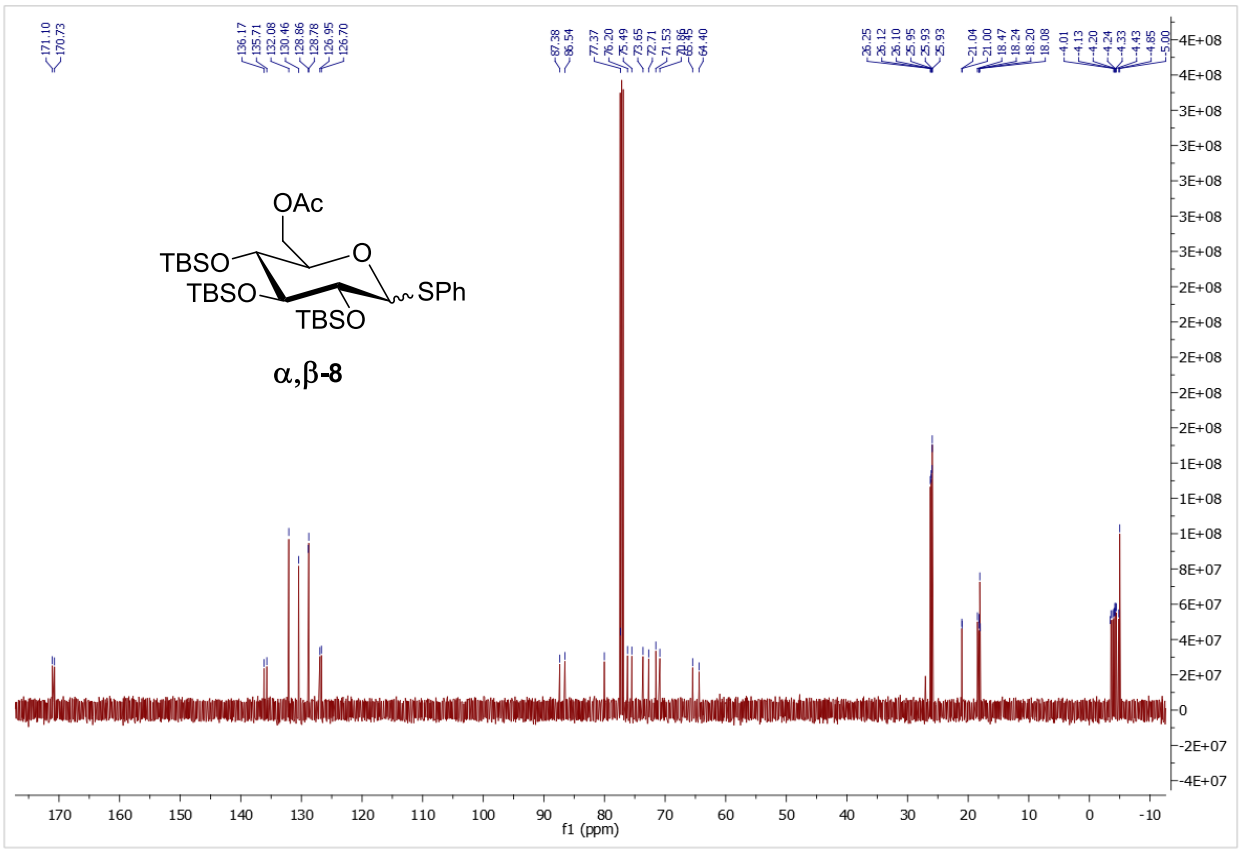


Figure S11: ^{13}C NMR spectrum of **α,β-8** (126 MHz, $CDCl_3$, 300 K).

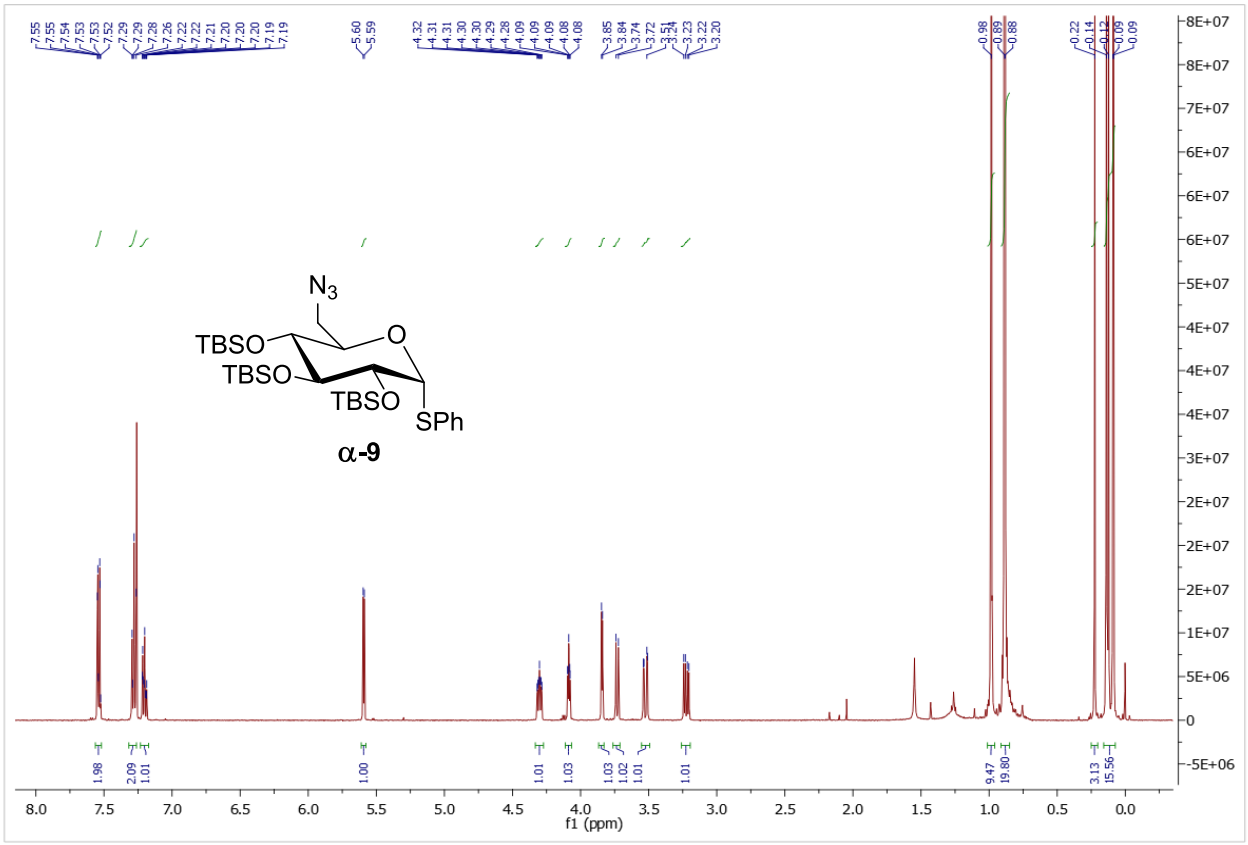


Figure S12: ^{1}H NMR spectrum of **α-9** (500 MHz, $CDCl_3$, 300 K).

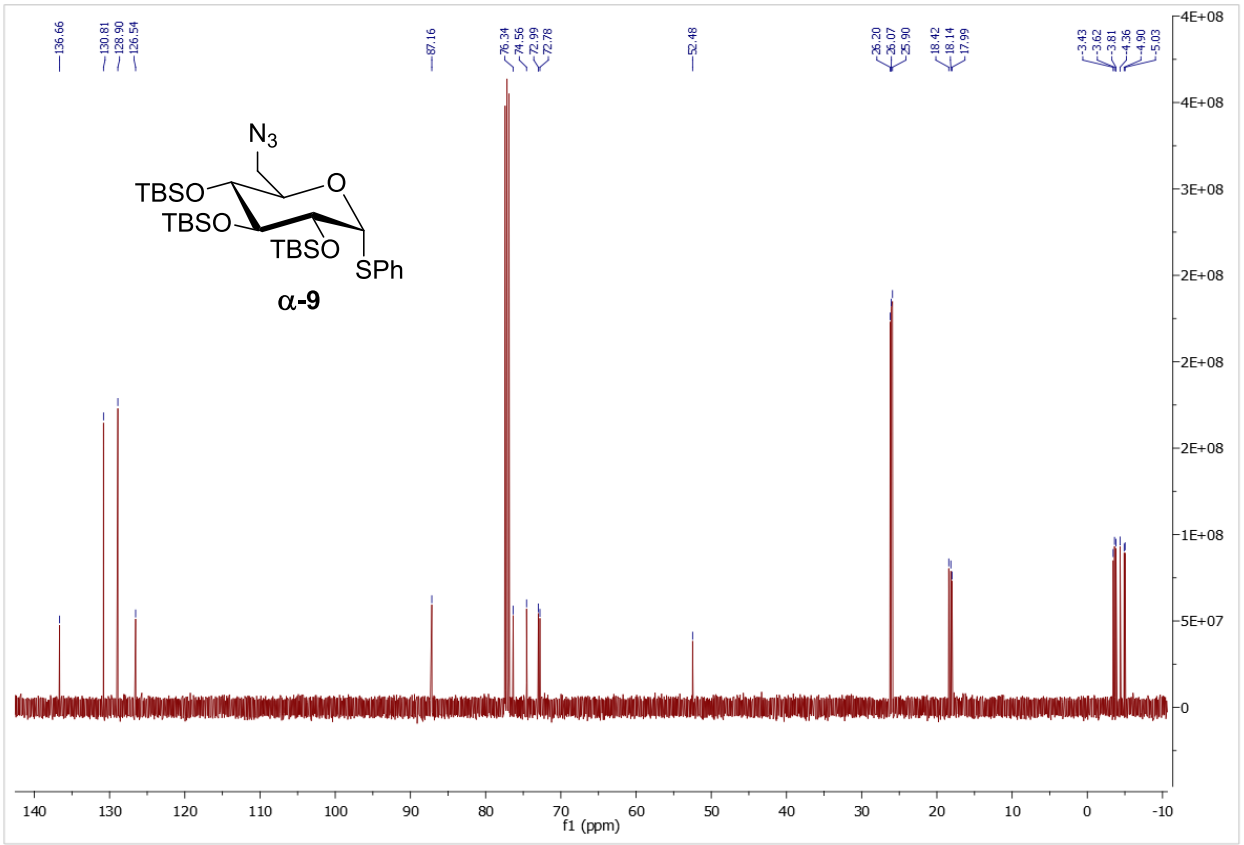


Figure S13: ^{13}C NMR spectrum of **α-9** (126 MHz, $CDCl_3$, 300 K).

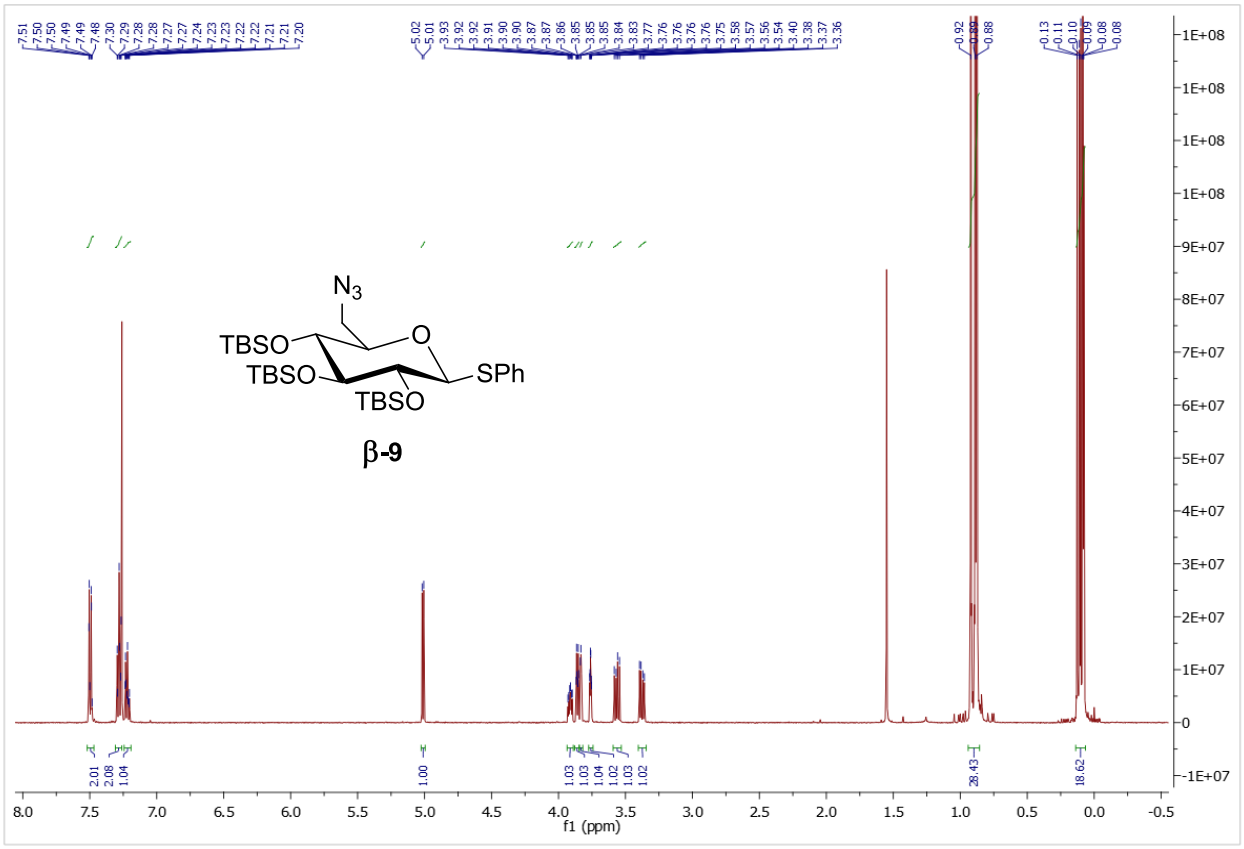


Figure S14: ^{1}H NMR spectrum of **β-9** (500 MHz, $CDCl_3$, 300 K).

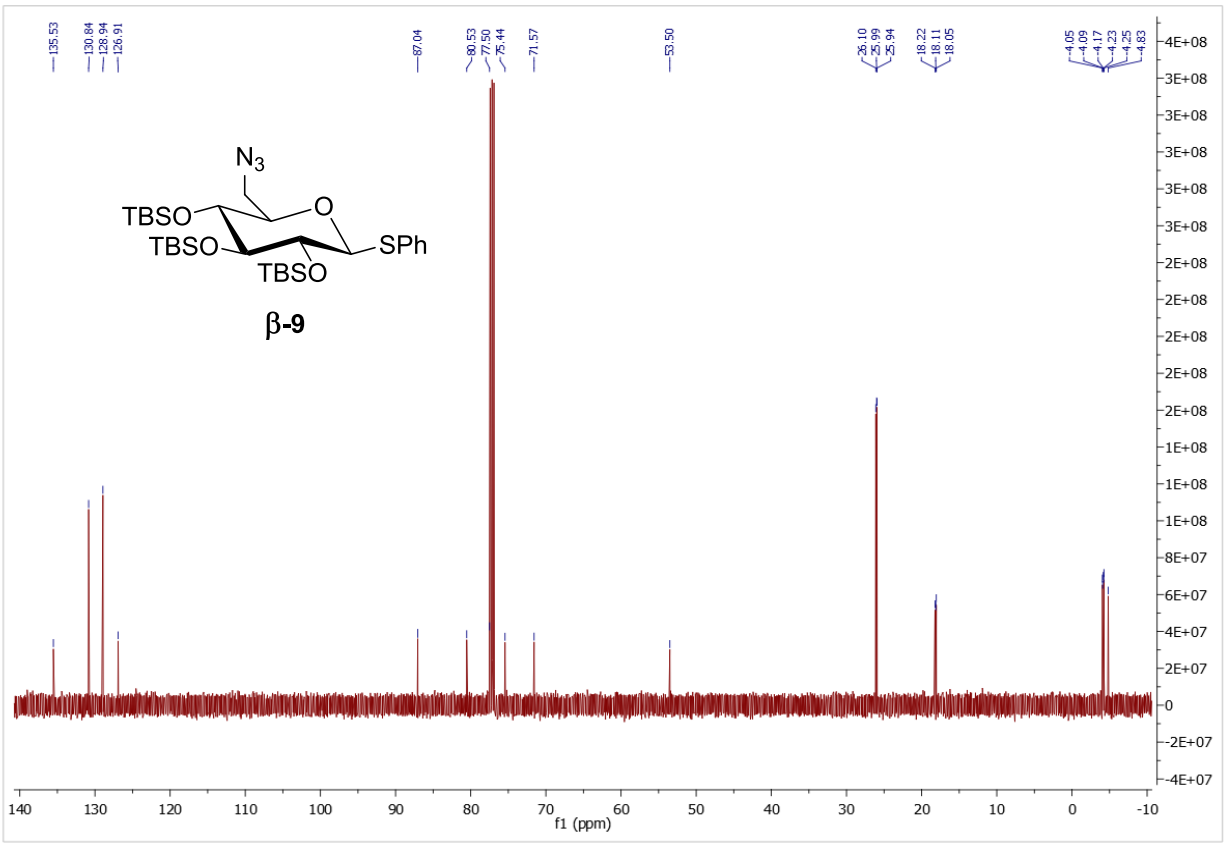


Figure S15: ^{13}C NMR spectrum of **β-9** (126 MHz, $CDCl_3$, 300 K).

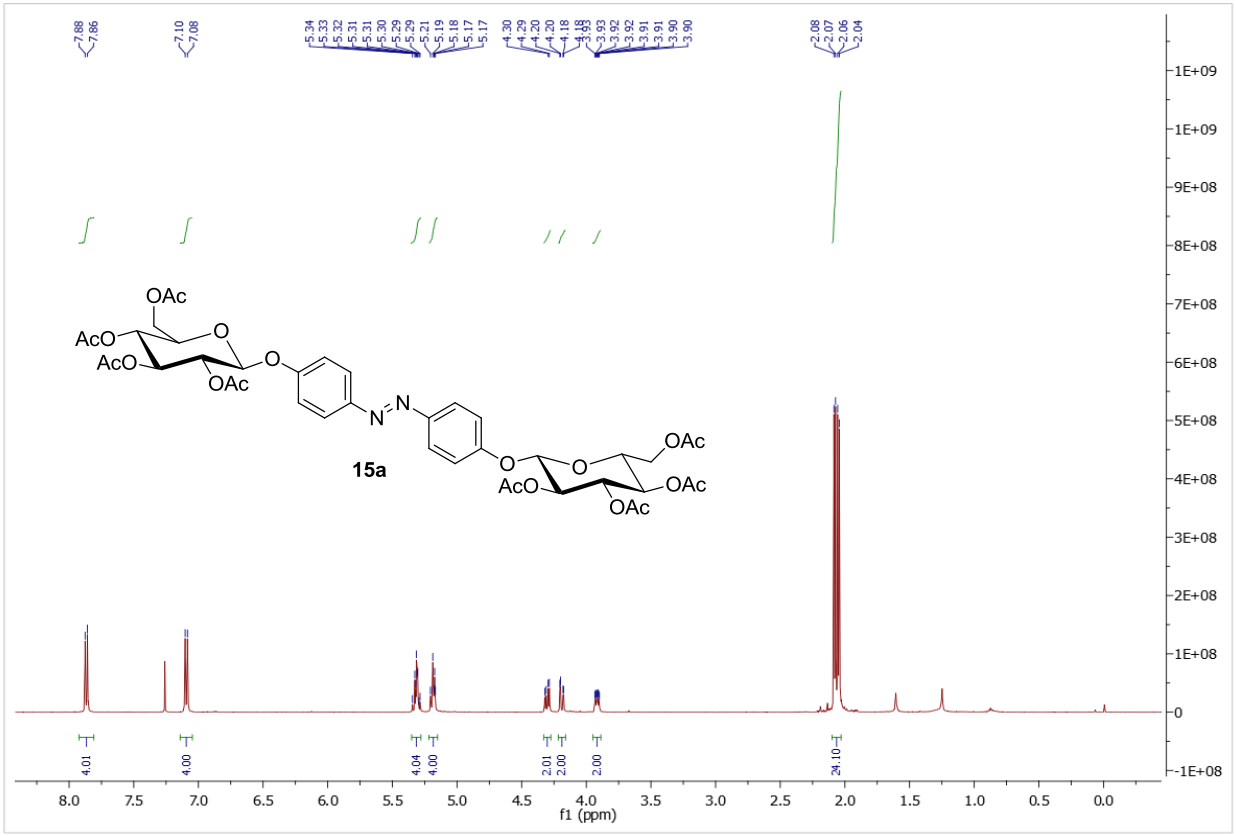


Figure S16: ^{1}H NMR spectrum of **15a** (500 MHz, $CDCl_3$, 300 K).

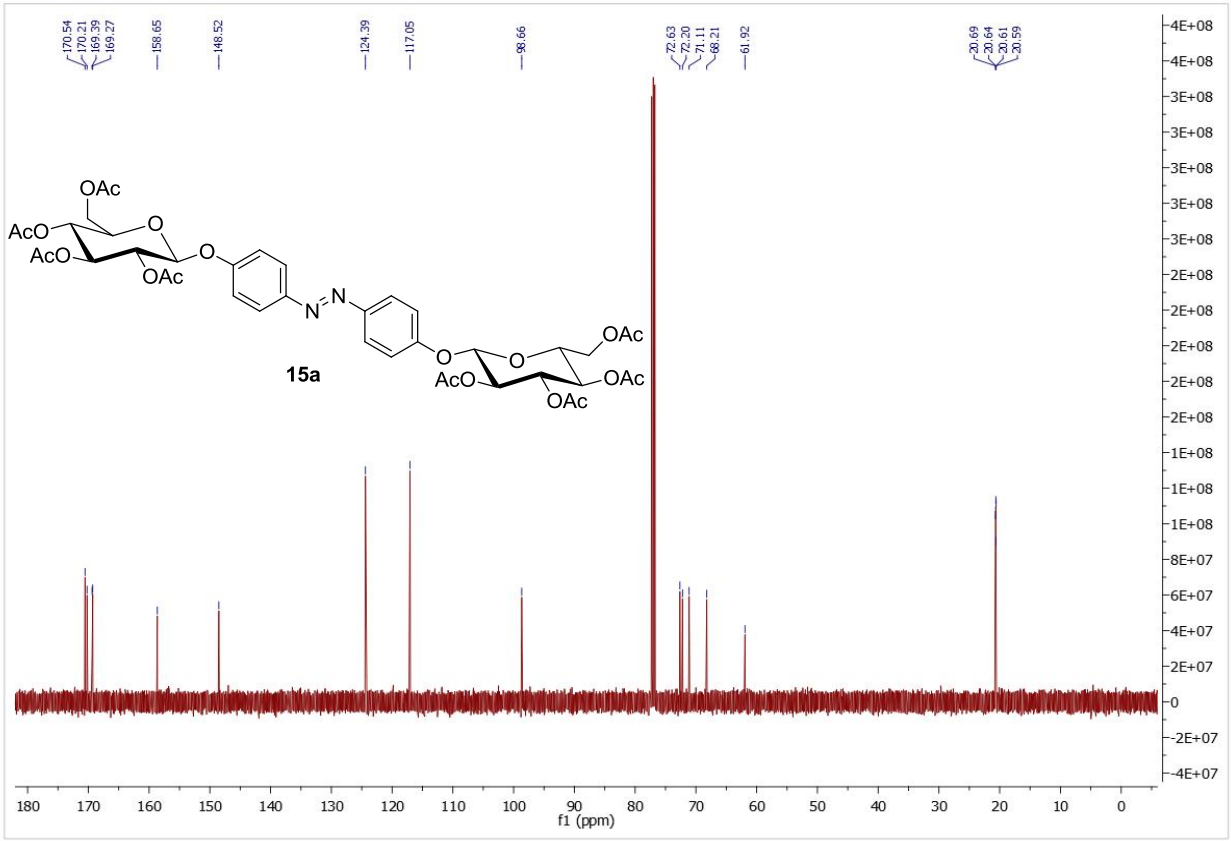


Figure S17: ^{13}C NMR spectrum of **15a** (126 MHz, $CDCl_3$, 300 K).

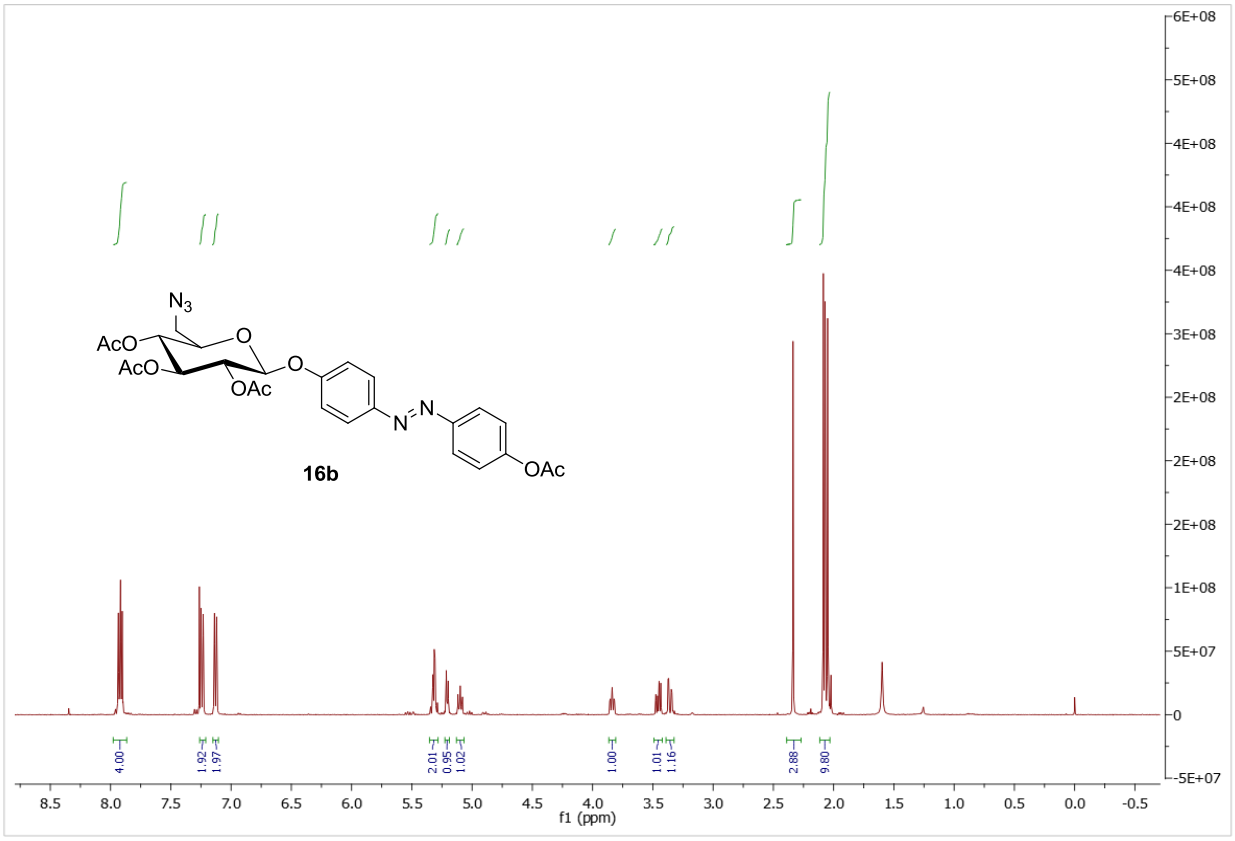


Figure S18: ^{1}H NMR spectrum of **16b** (500 MHz, $CDCl_3$, 300 K).

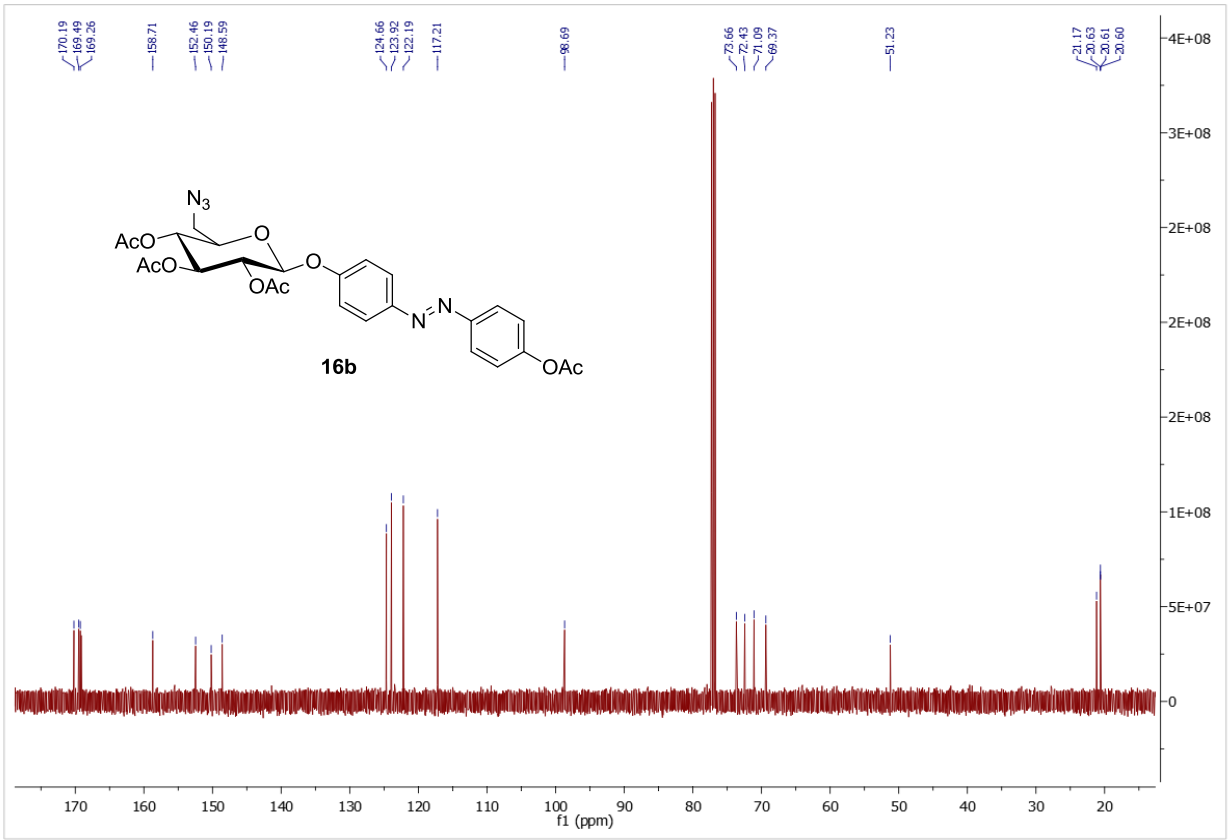


Figure S19: ^{13}C NMR spectrum of **16b** (126 MHz, $CDCl_3$, 300 K).

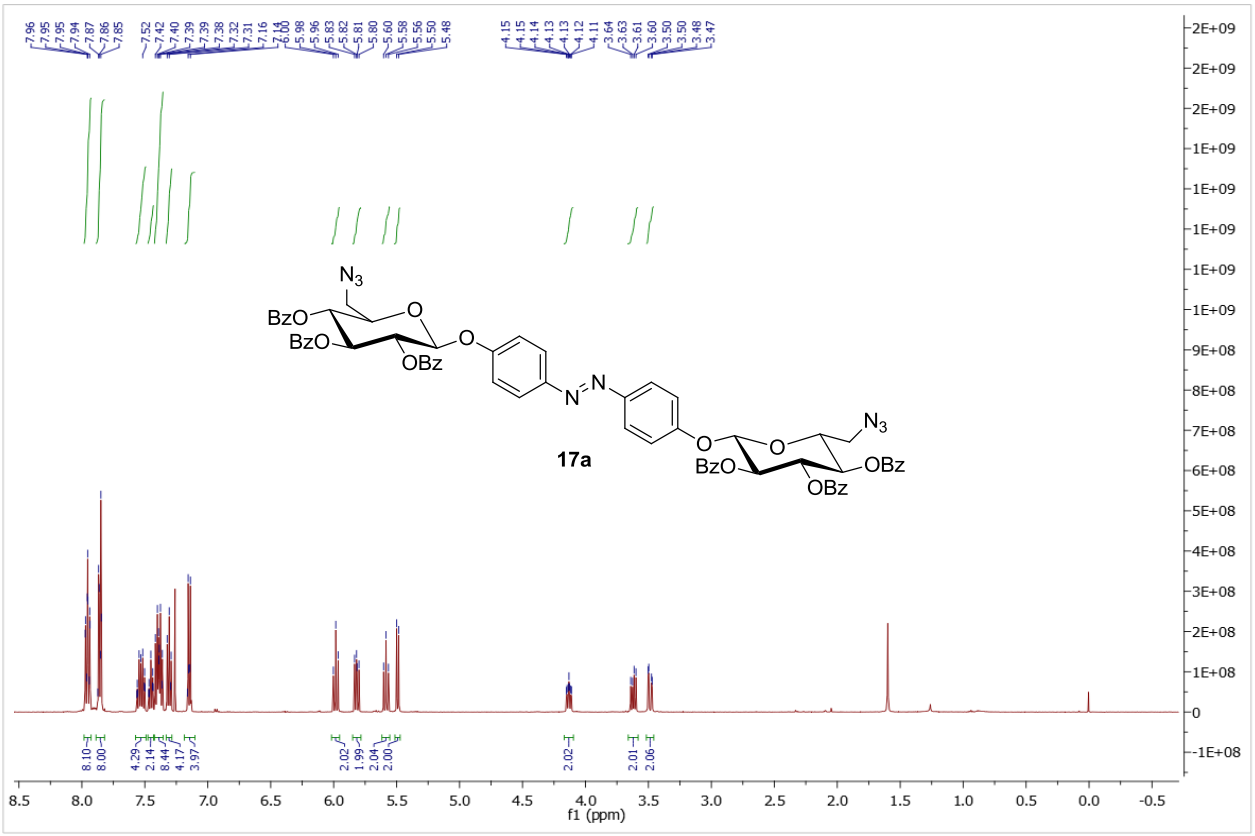


Figure S20: ^{1}H NMR spectrum of **17a** (500 MHz, $CDCl_3$, 300 K).

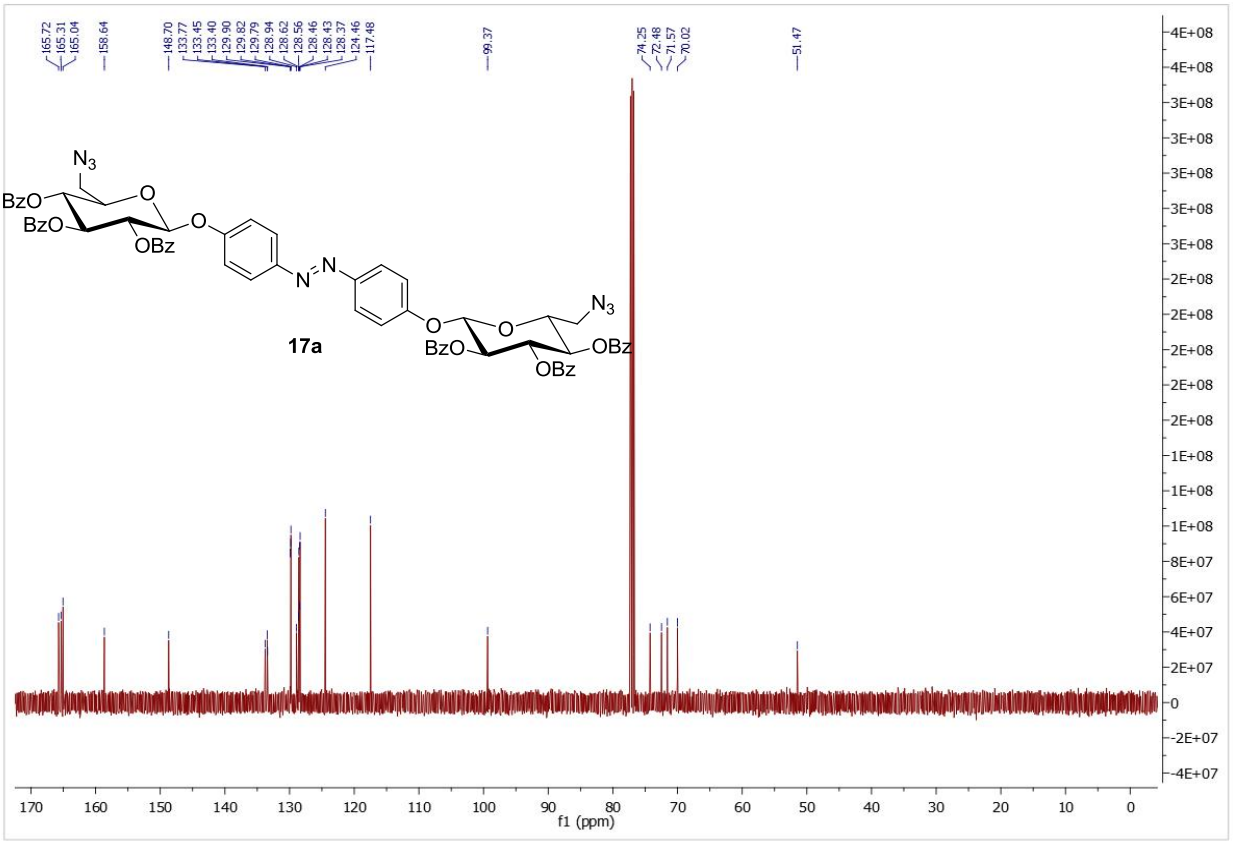


Figure S21: ^{13}C NMR spectrum of **17a** (126 MHz, $CDCl_3$, 300 K).

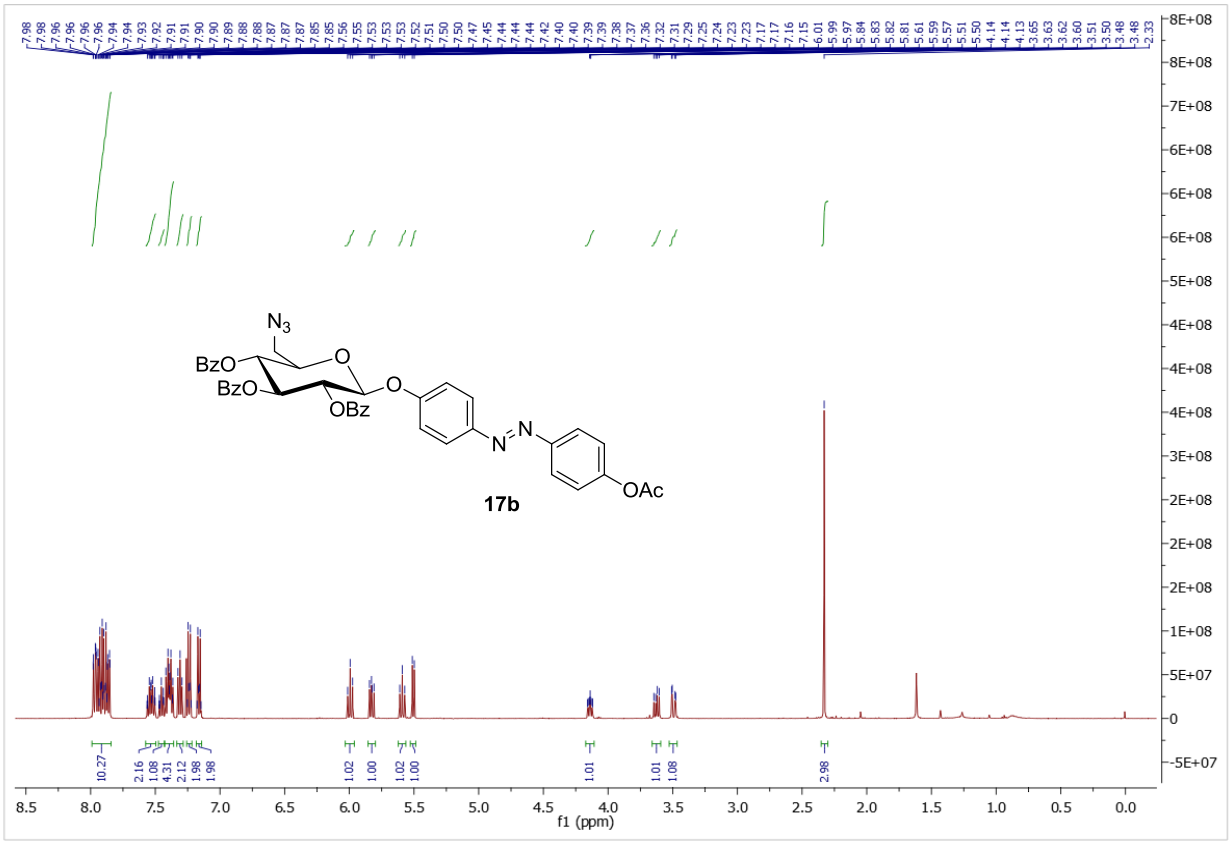


Figure S22: ^{1}H NMR spectrum of **17b** (500 MHz, $CDCl_3$, 300 K).

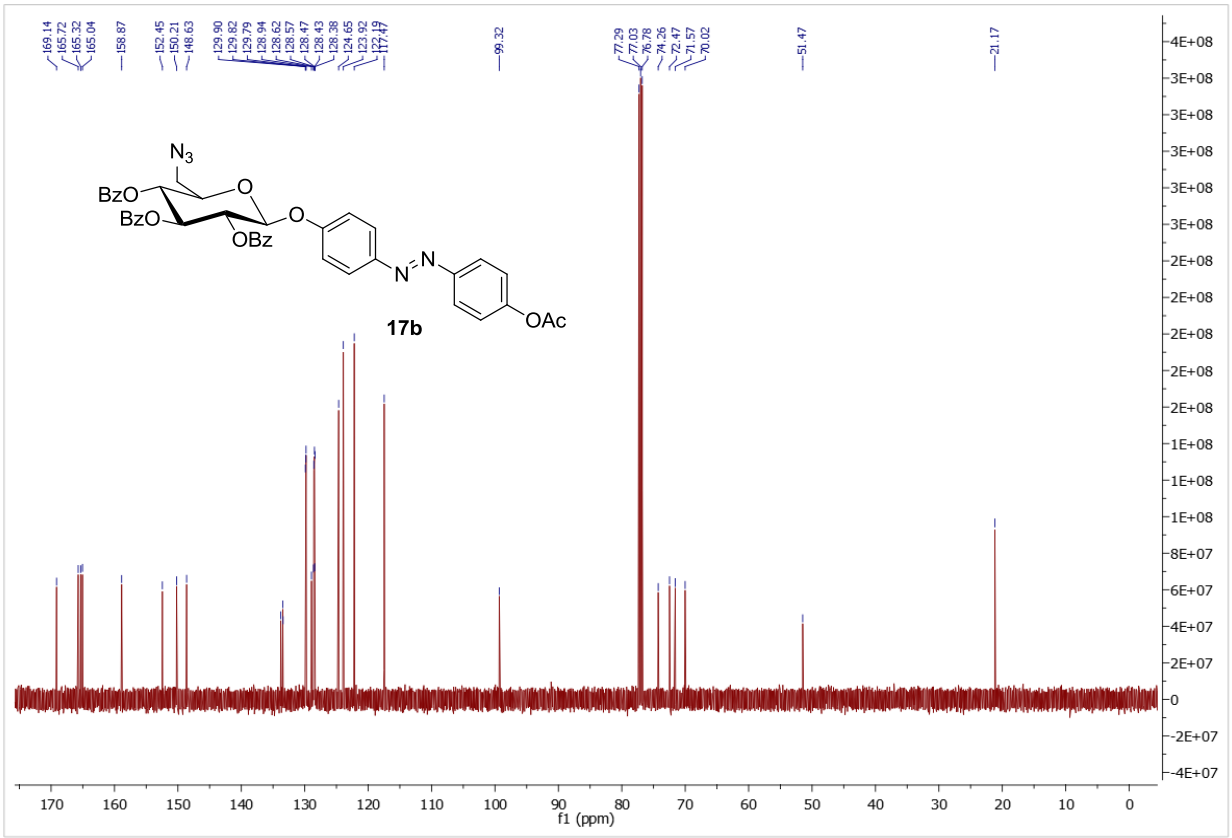


Figure S23: ^{13}C NMR spectrum of **17b** (126 MHz, $CDCl_3$, 300 K).

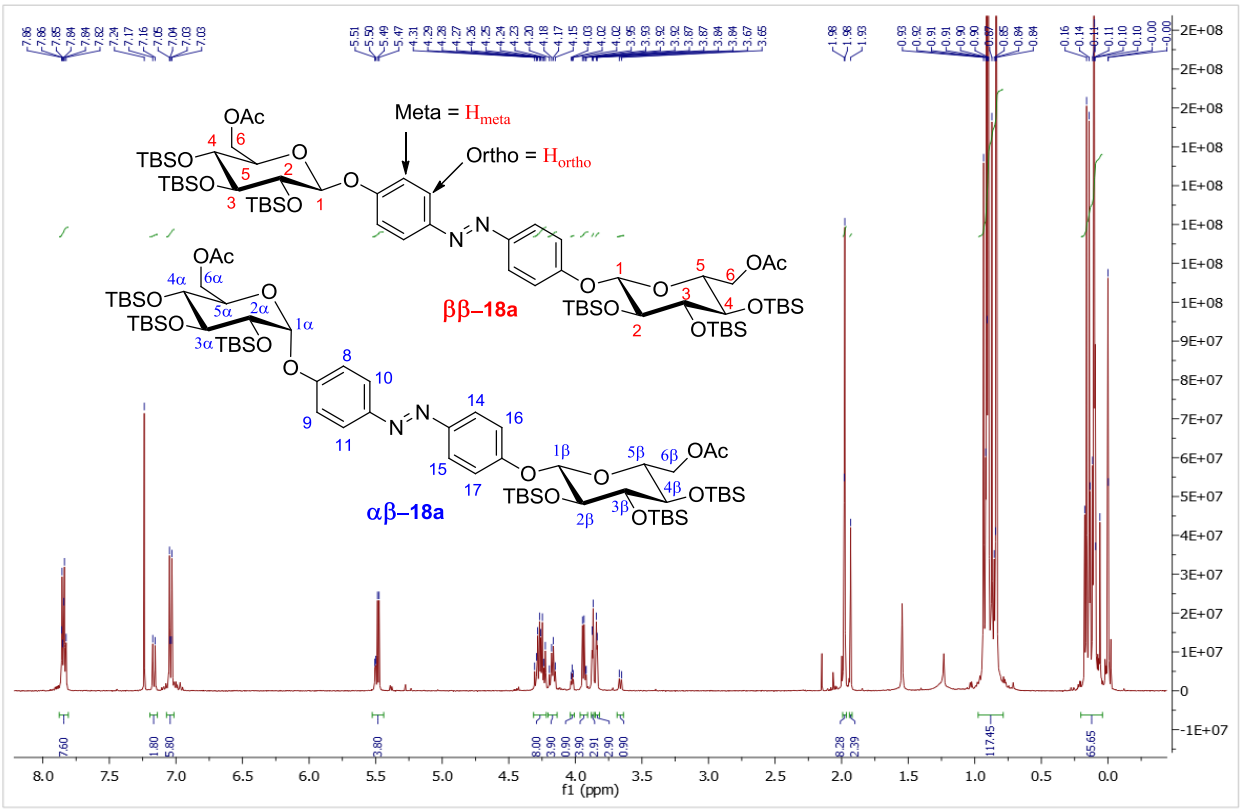


Figure S24: ^{1}H NMR spectrum of a mixture (**αβ**:**ββ**; 47:53) of **18a**, (500 MHz, $CDCl_3$, 300 K).

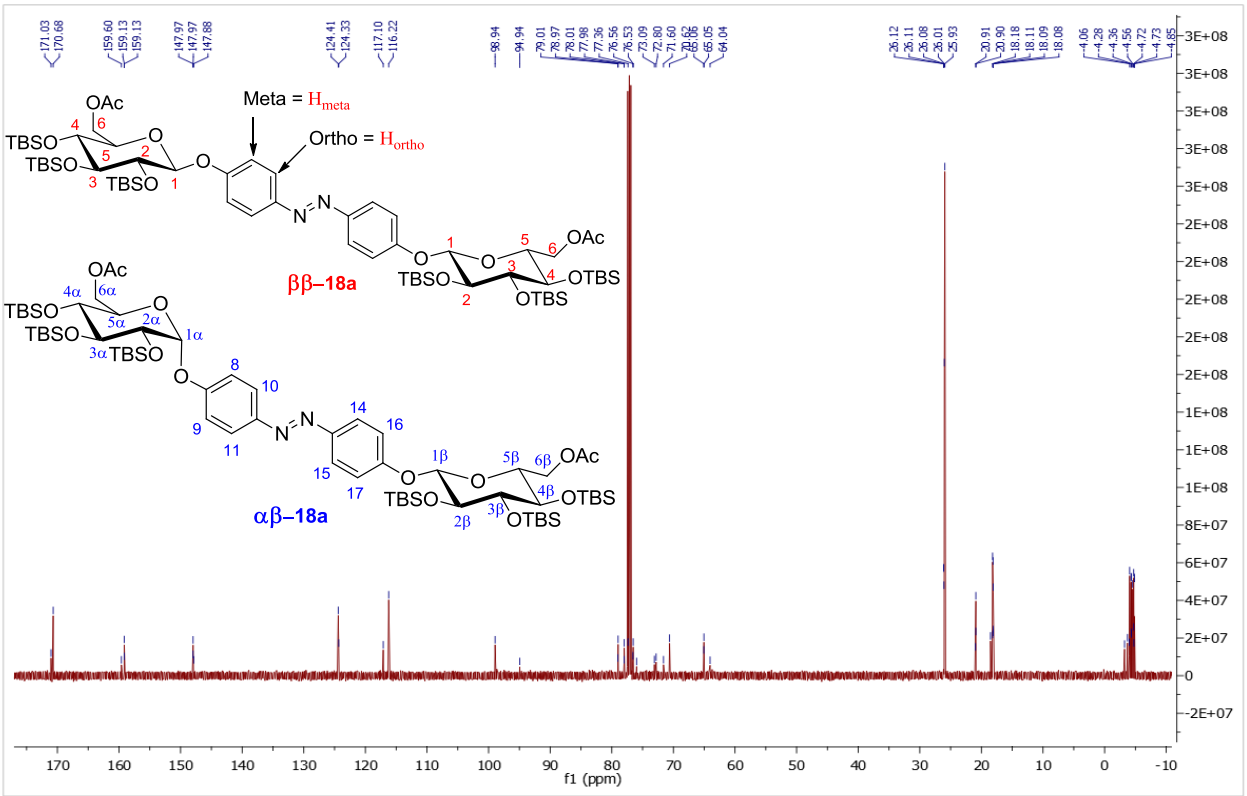


Figure S25: ^{13}C NMR spectrum of a mixture (**αβ**:**ββ**; 47:53) of **18a**, (126 MHz, $CDCl_3$, 300 K).

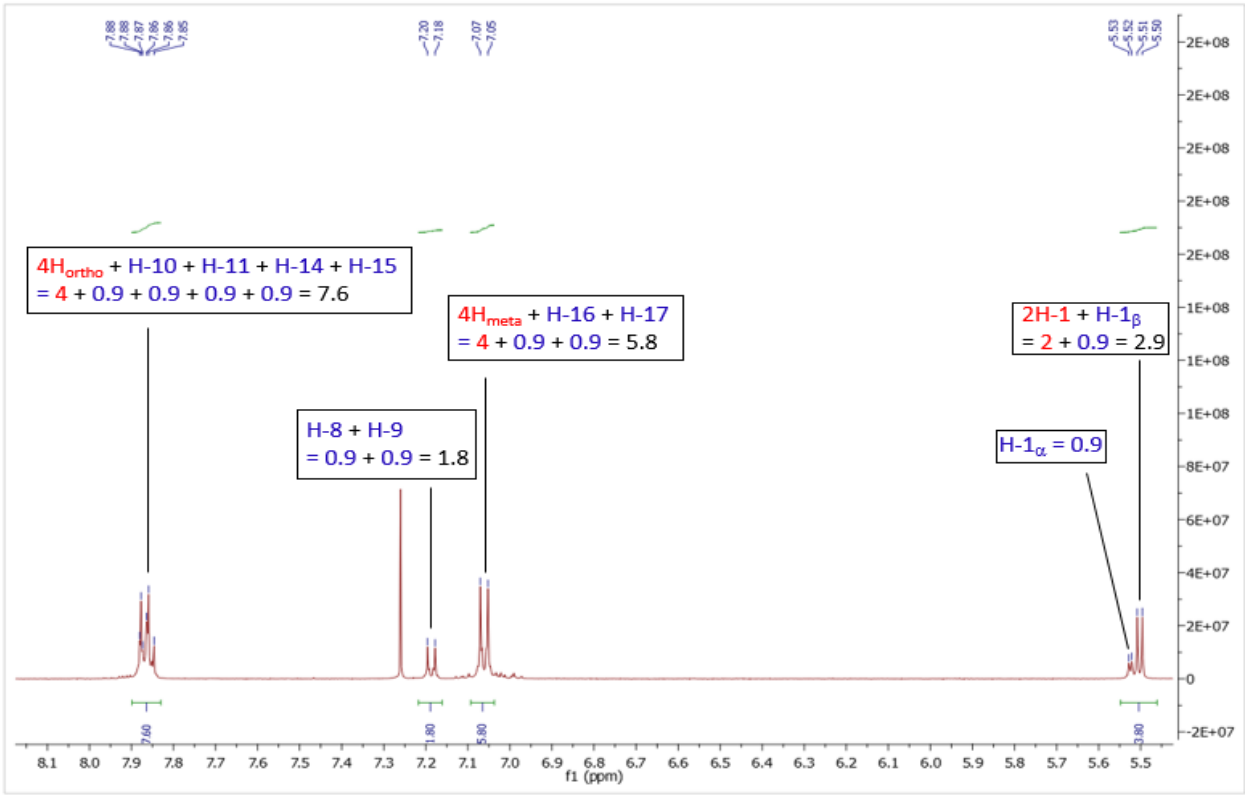


Figure S26: Expansion of the ^{1}H NMR spectrum of a mixture (**αβ**:**ββ**; 47:53) of **18a** in the aromatic region, (500 MHz, $CDCl_3$, 300 K).

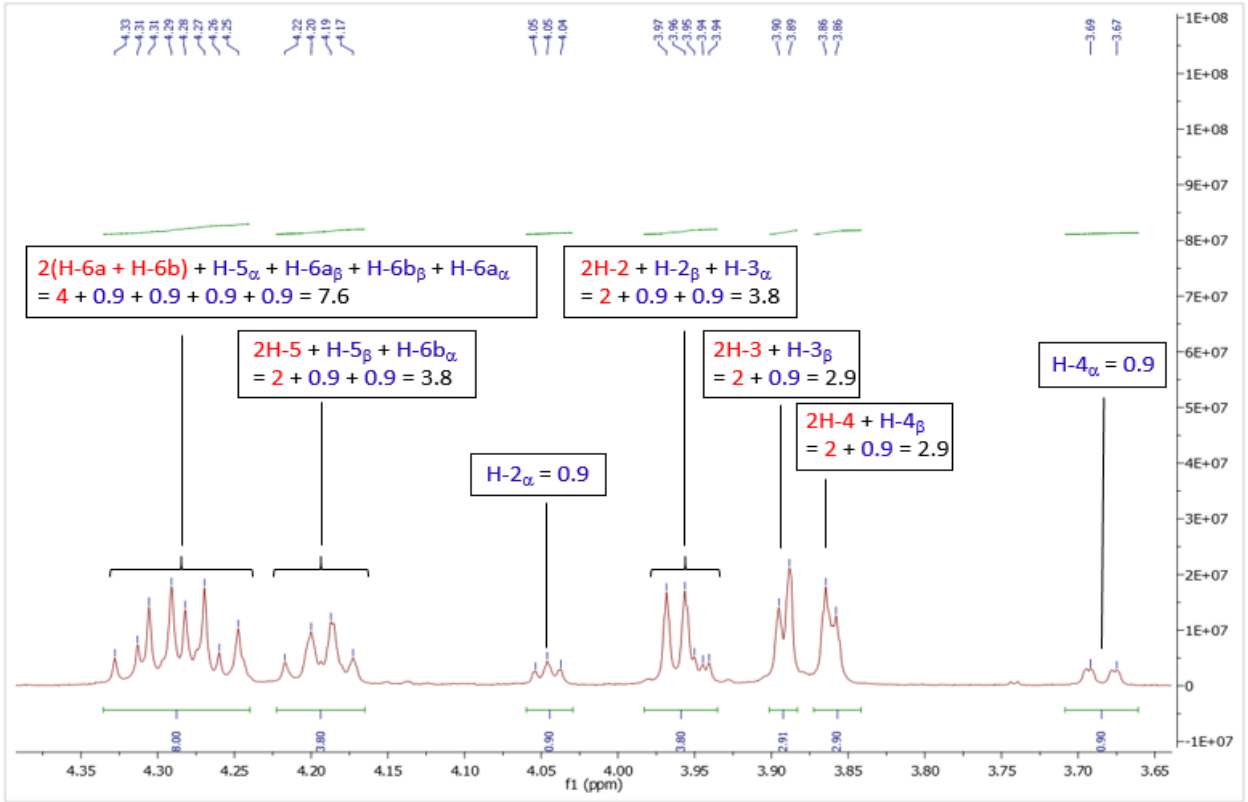


Figure S27: Expansion of the ^{1}H NMR spectrum of a mixture (**αβ**:**ββ**; 47:53) of **18a** in the carbohydrate region, (500 MHz, $CDCl_3$, 300 K).

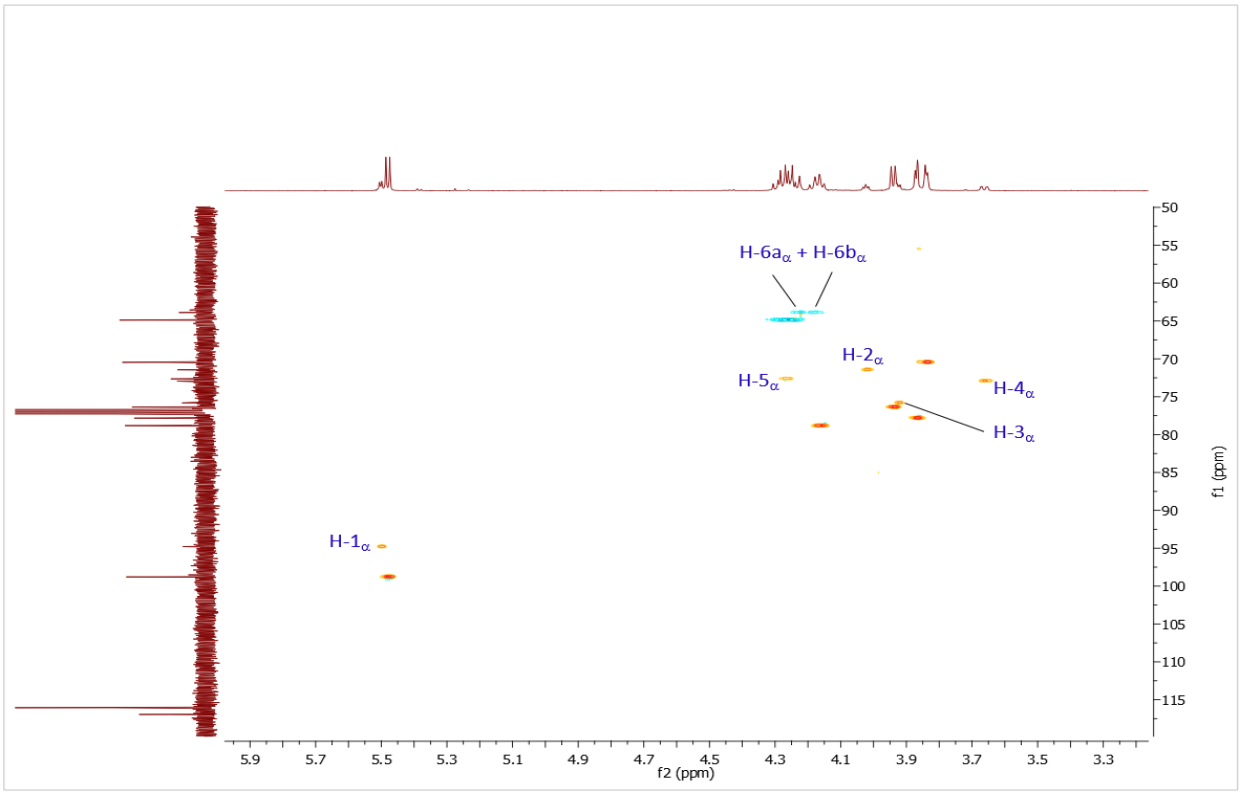


Figure S28: Expansion of the ^{1}H-^{13}C HSQC spectrum of a mixture (**αβ**:**ββ**; 47:53) of **18a** in the carbohydrate region, (500 MHz, $CDCl_3$, 300 K).

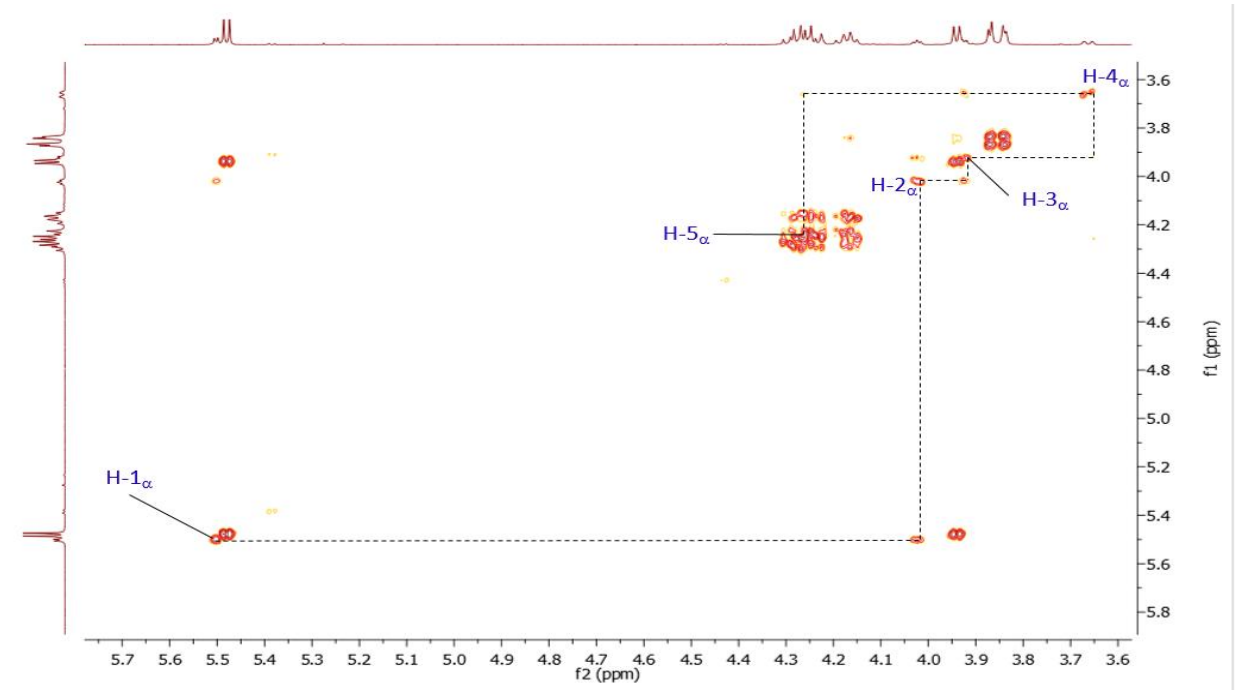


Figure S29: Expansion of the ^{1}H-^{1}H COSY spectrum of a mixture (**αβ**:**ββ**; 47:53) of **18a** in the carbohydrate region, (500 MHz, $CDCl_3$, 300 K).

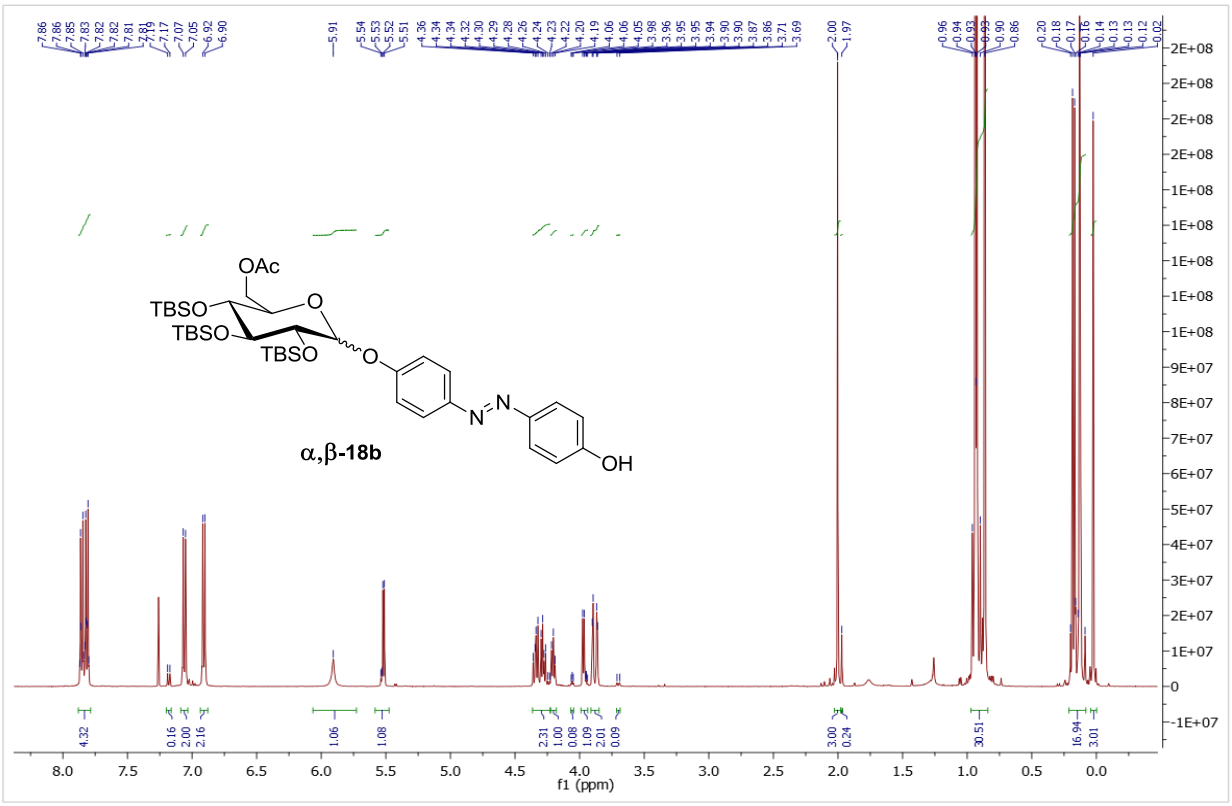


Figure S30: ^{1}H NMR spectrum of a mixture (**α**:**β**; 7:93) of **18b**, (500 MHz, $CDCl_3$, 300 K).

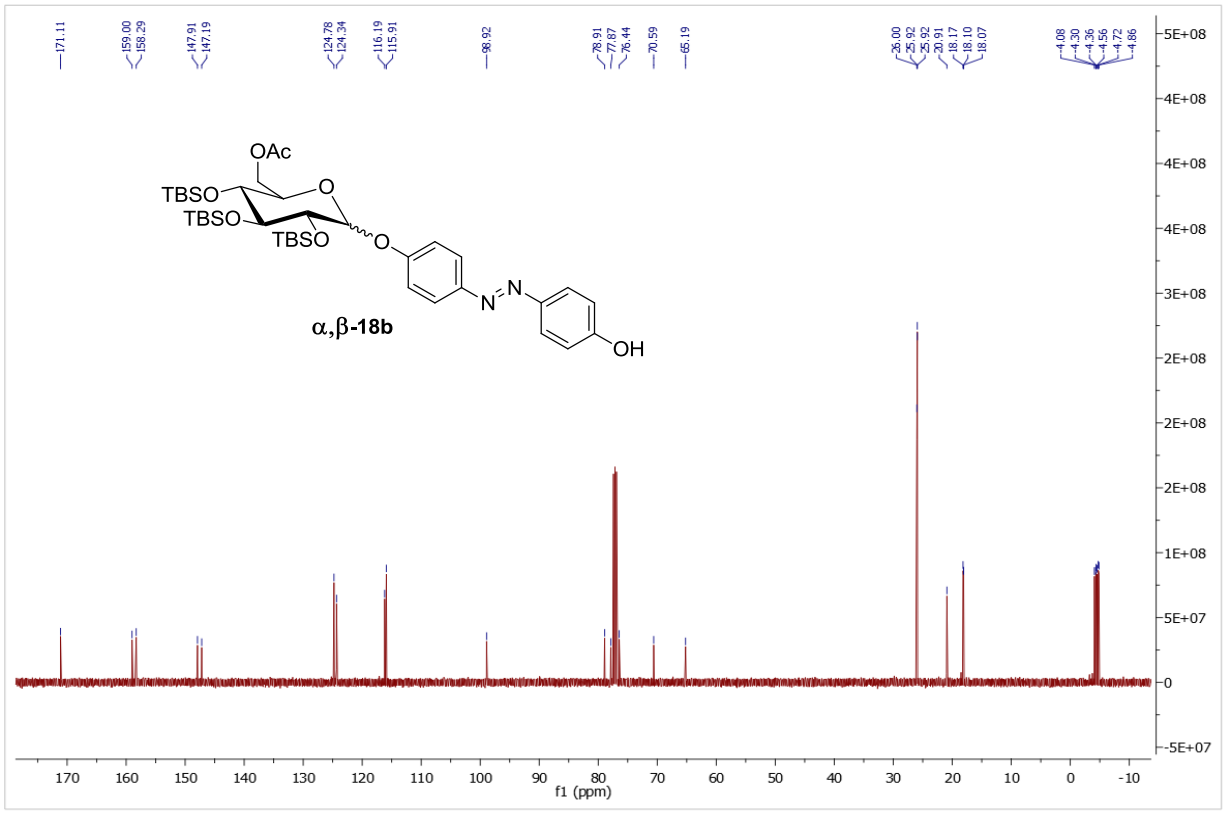


Figure S31: ^{13}C NMR spectrum of a mixture (**α**:**β**; 7:93) of **18b**, (126 MHz, $CDCl_3$, 300 K).

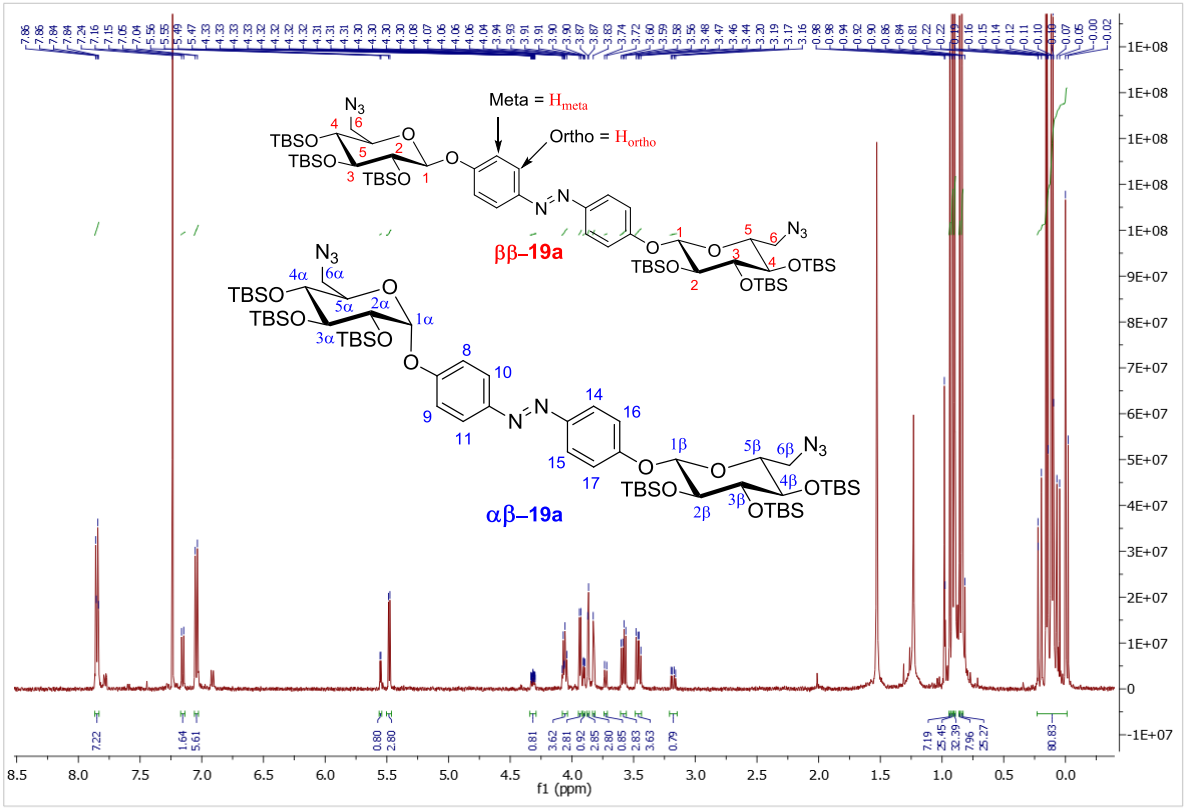


Figure S32: ^{1}H NMR spectrum of a mixture (**αβ:ββ**; 44:56) of **19a**, (500 MHz, $CDCl_3$, 300 K).

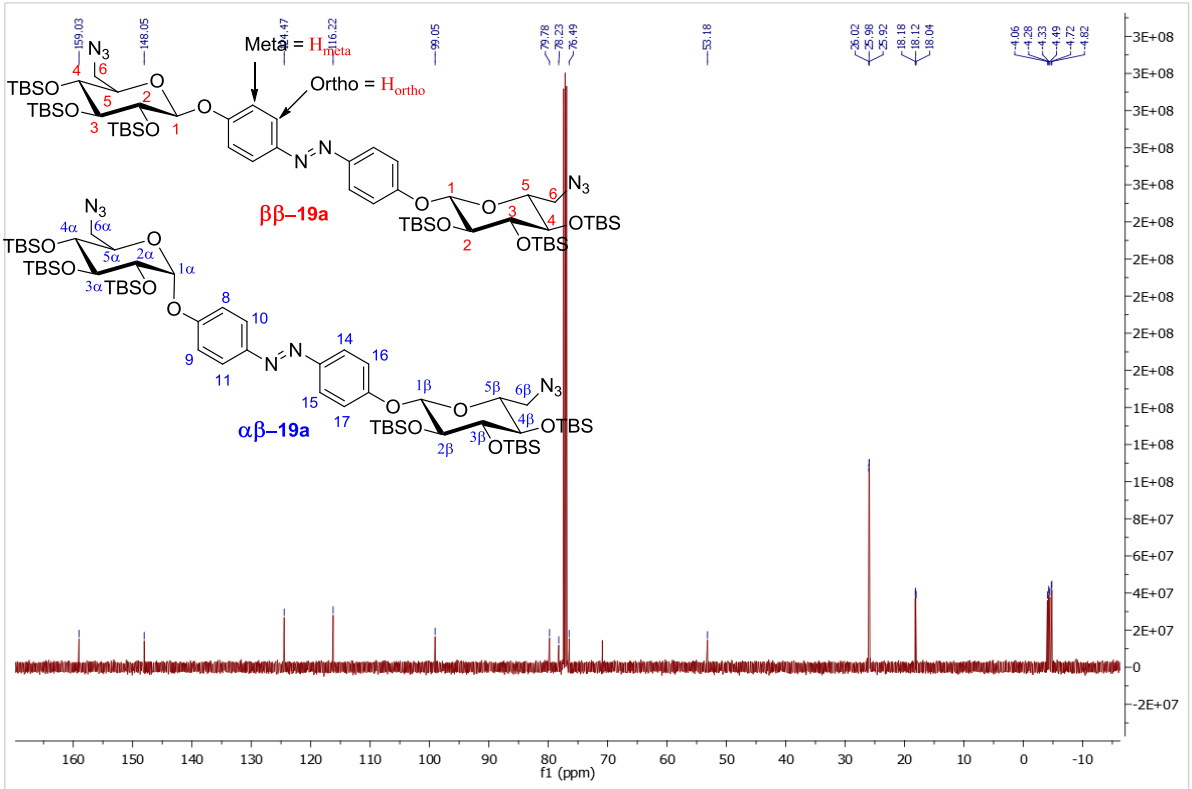


Figure S33: ^{13}C NMR spectrum of a mixture (**αβ:ββ**; 44:56) of **19a**, (126 MHz, $CDCl_3$, 300 K).

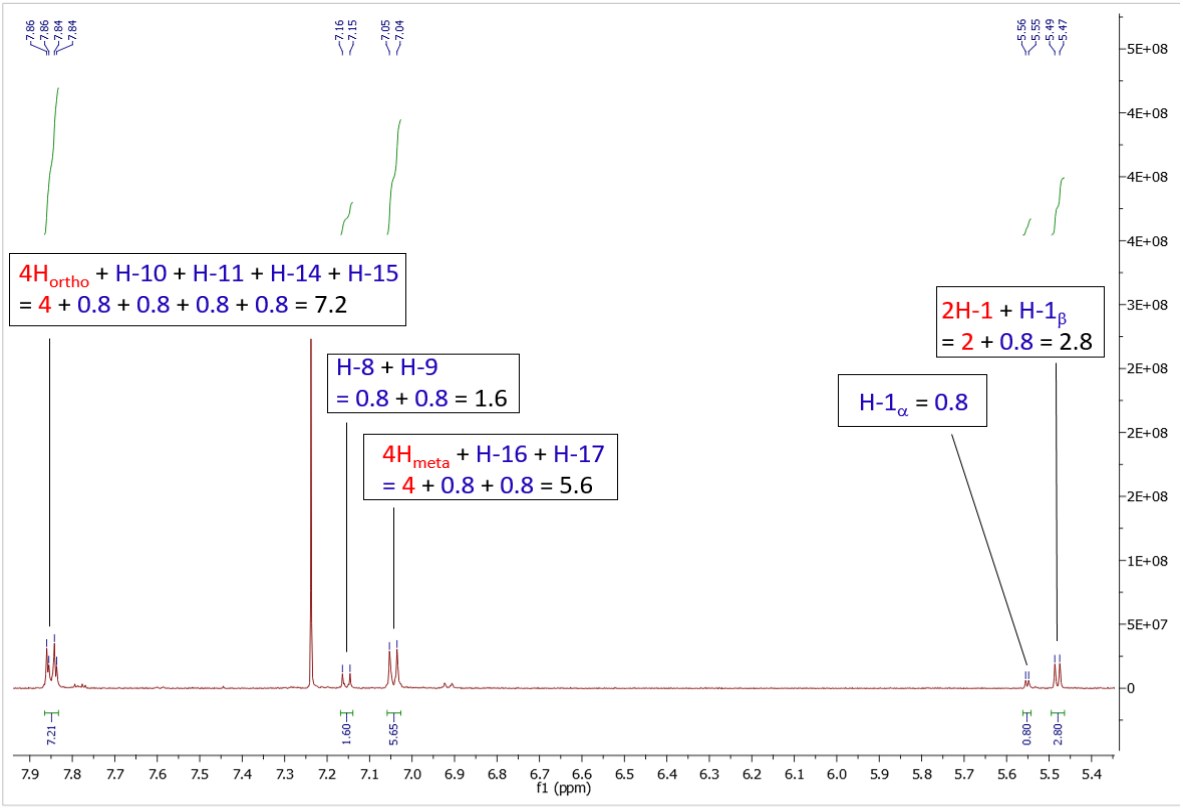


Figure S34: Expansion of the ^{1}H NMR spectrum of a mixture (**αβ:ββ**; 44:56) of **19a** in the aromatic region, (500 MHz, $CDCl_3$, 300 K).

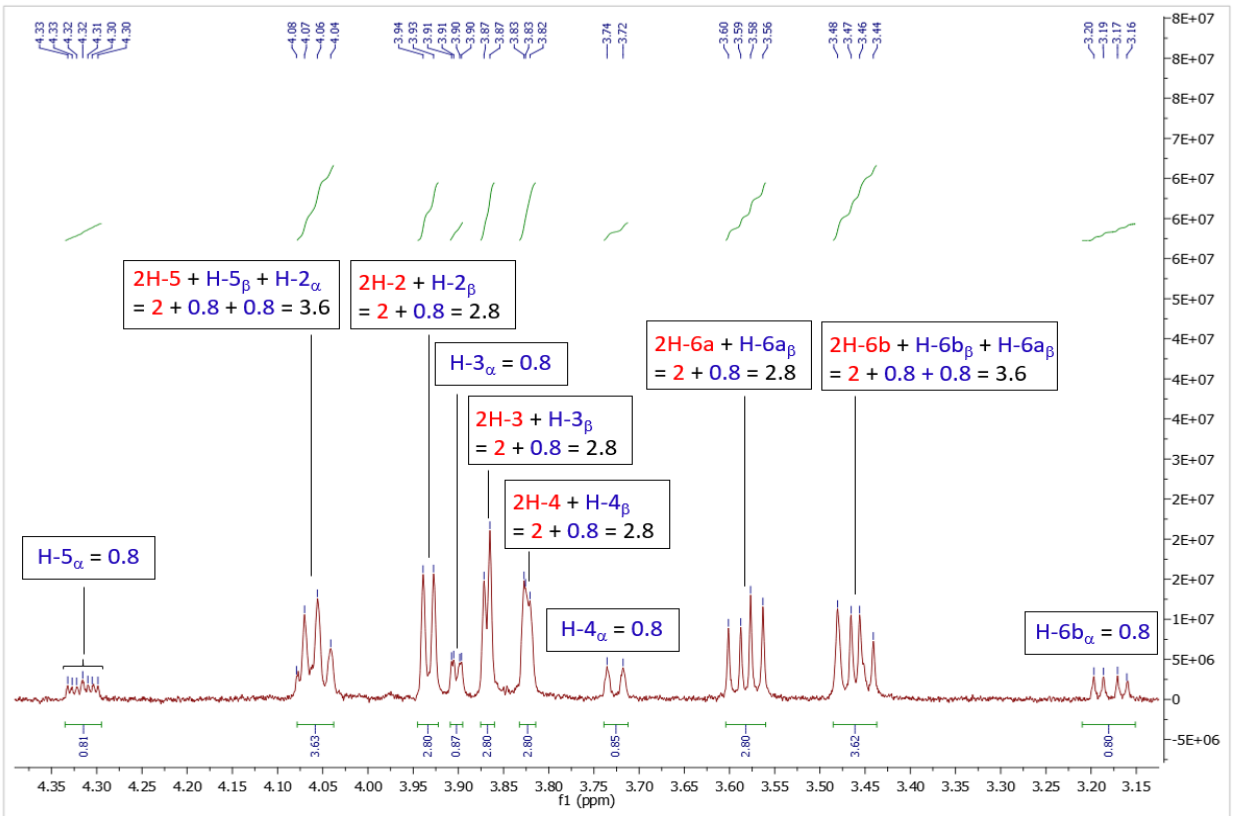


Figure S35: Expansion of the ^{1}H NMR spectrum of a mixture (**αβ:ββ**; 44:56) of **19a** in the carbohydrate region, (500 MHz, $CDCl_3$, 300 K).

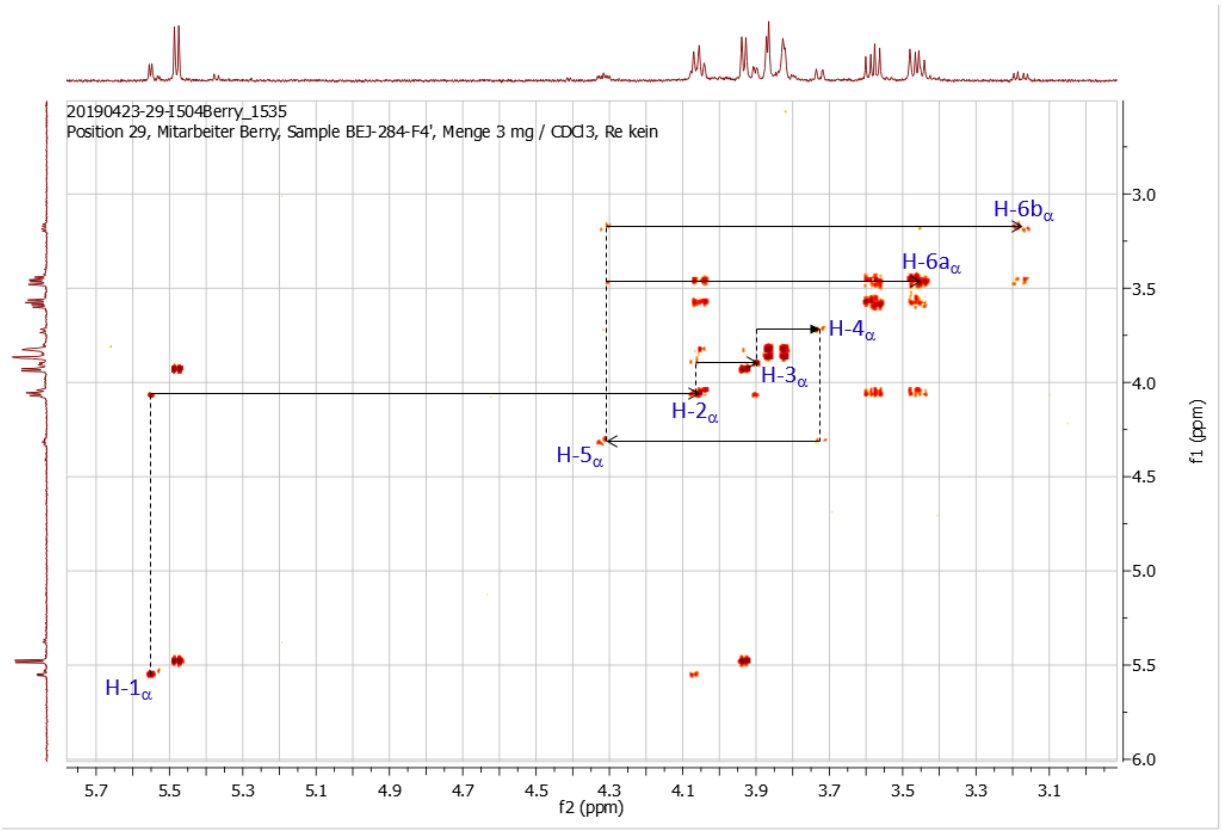


Figure S36: Expansion of the ^{1}H-^{1}H COSY spectrum of a mixture (**αβ:ββ**; 44:56) of **19a** in the carbohydrate region, (500 MHz, $CDCl_3$, 300 K).

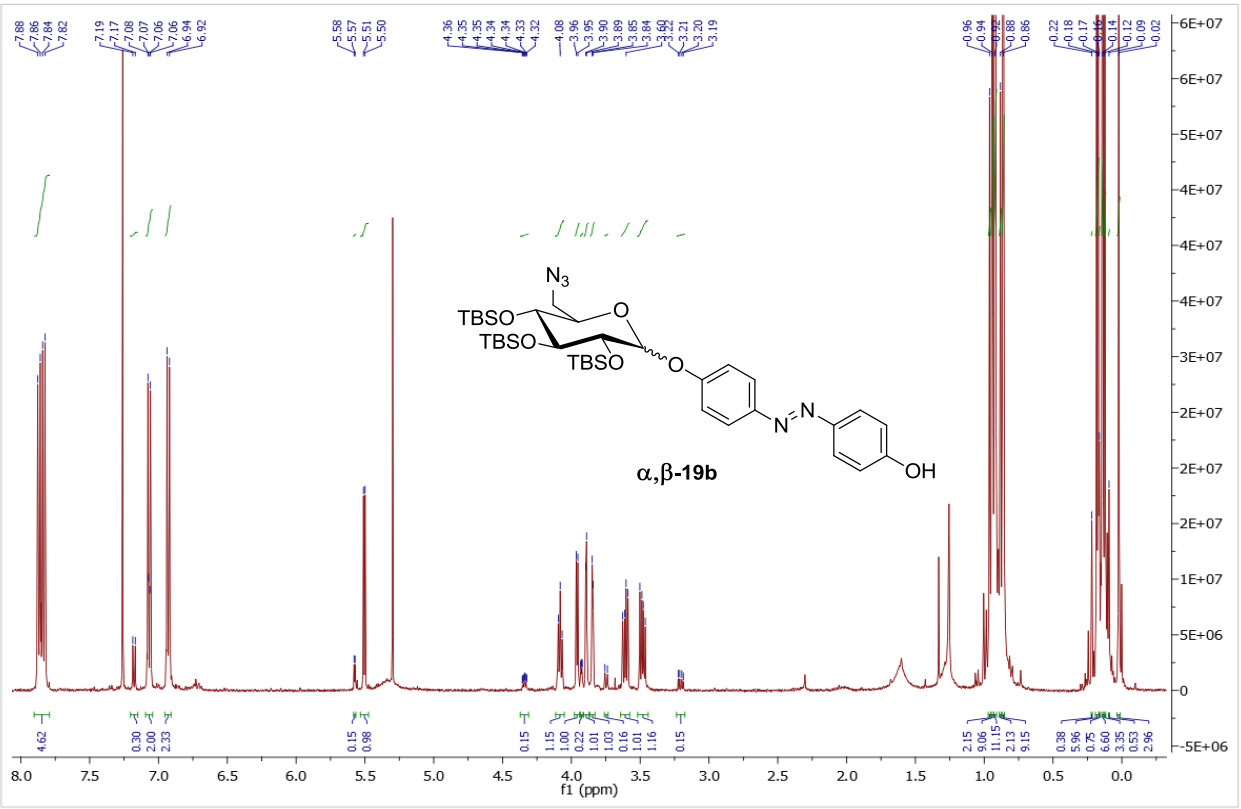


Figure S37: ^{1}H NMR spectrum of a mixture (**α**:**β**; 13:87) of **19b**, (500 MHz, $CDCl_3$, 300 K).

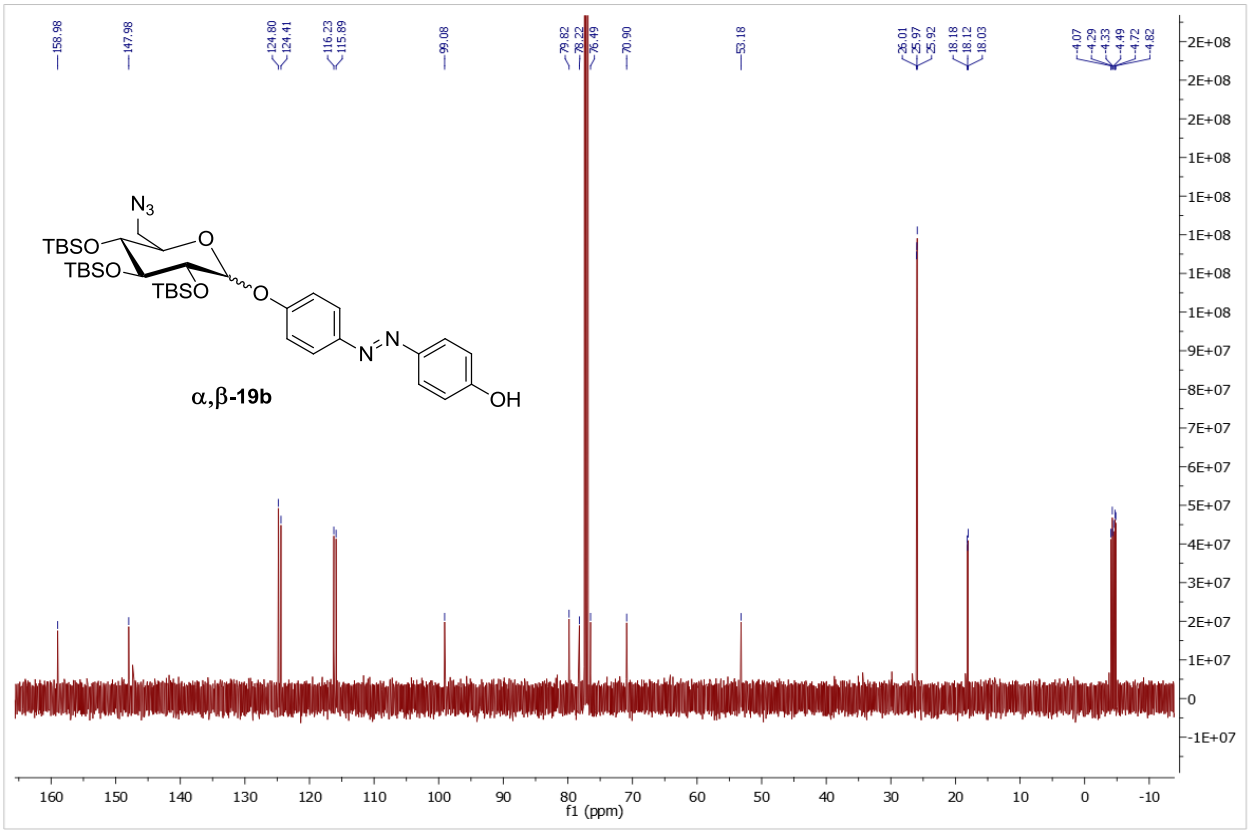


Figure S38: ^{13}C NMR spectrum of a mixture (**α:β**; 13:87) of **19b**, (126 MHz, $CDCl_3$, 300 K).

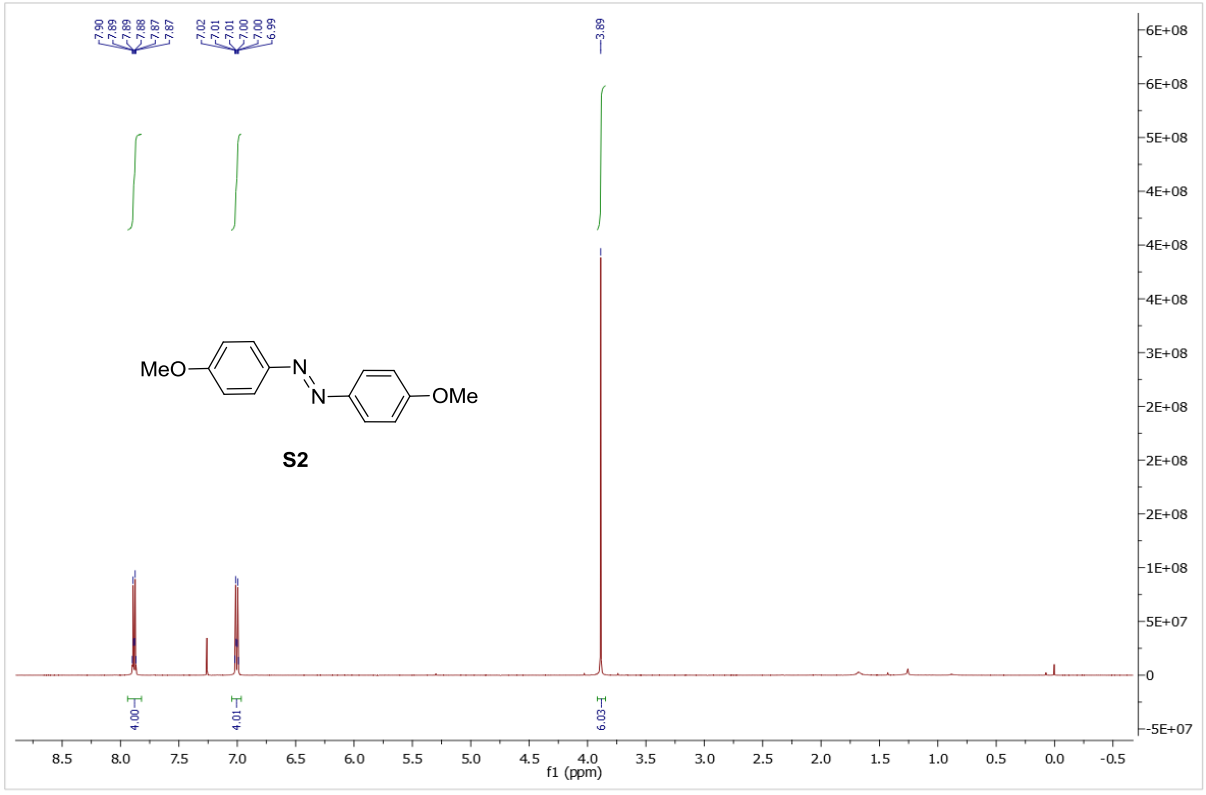


Figure S39: ^{1}H NMR spectrum of *p,p´*-dimethoxyazobenzene **S2** (500 MHz, $CDCl_3$, 300 K).

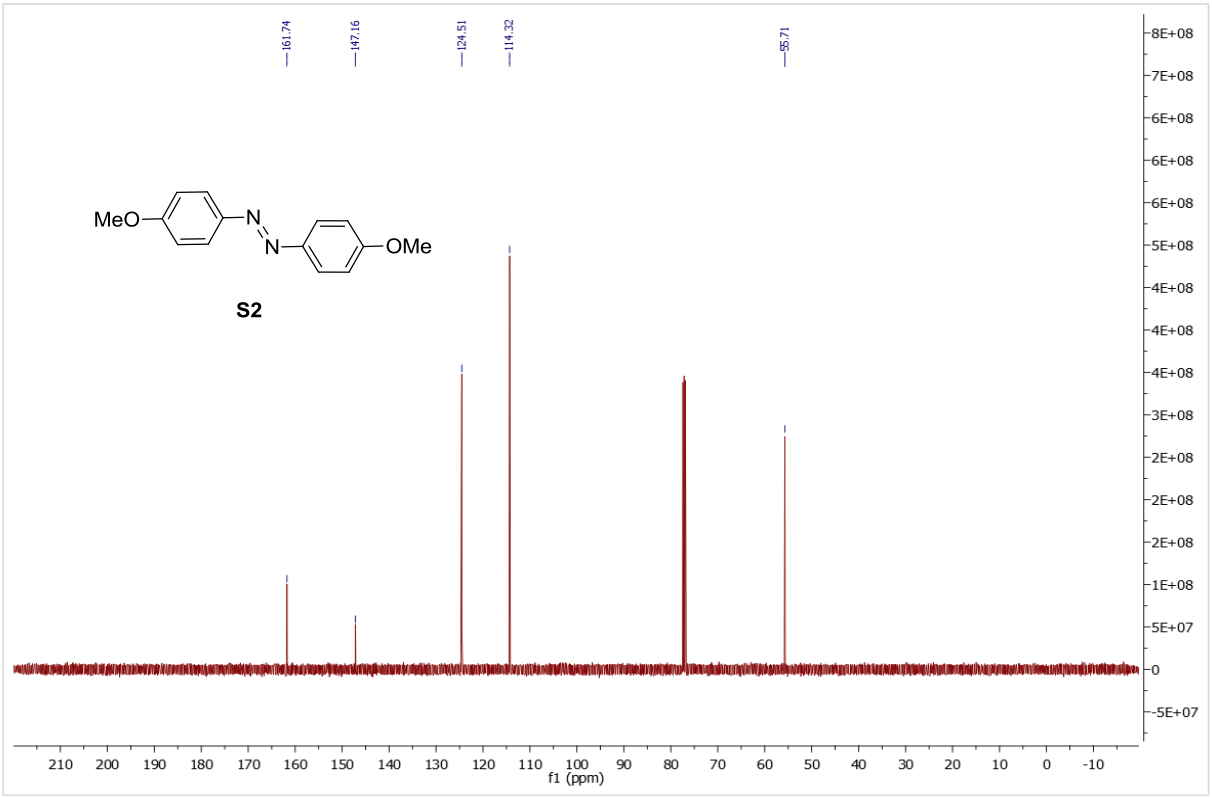


Figure S40: ^{13}C NMR spectrum of *p,p´*-dimethoxyazobenzene **S2** (126 MHz, $CDCl_3$, 300 K).

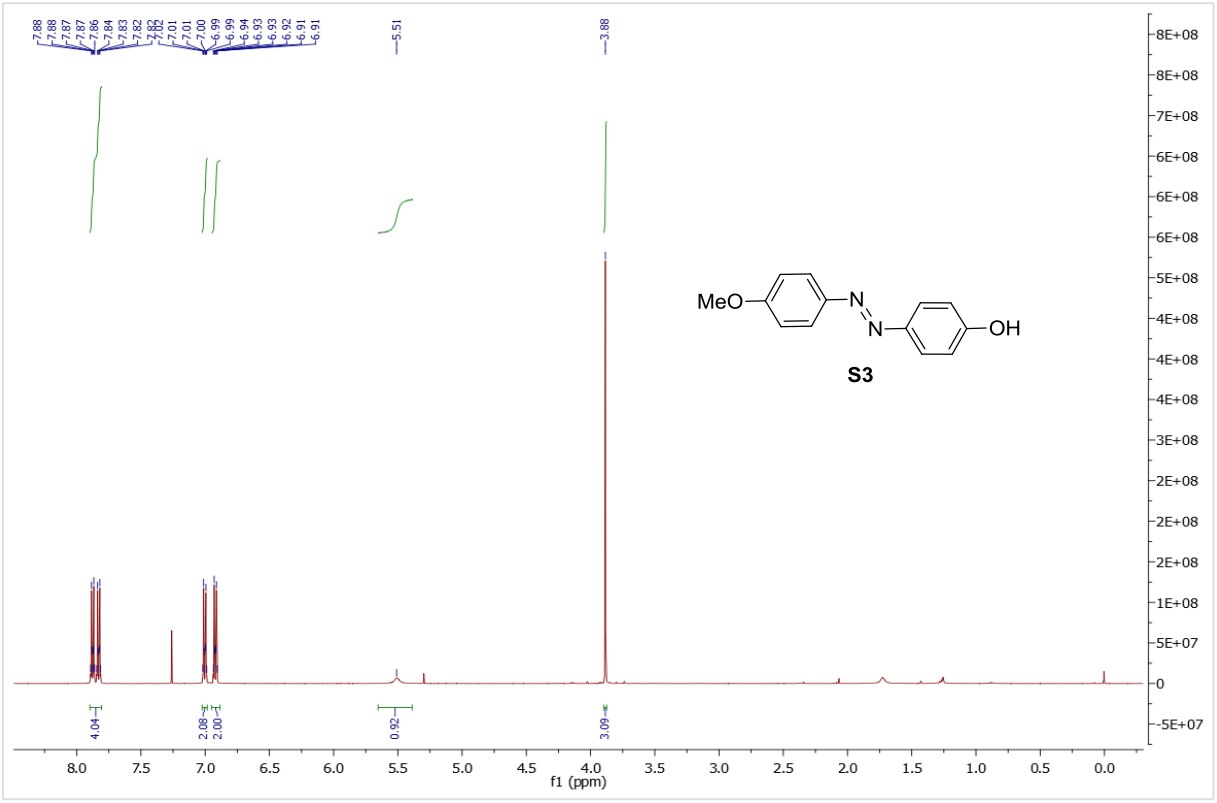


Figure S41: ^{1}H NMR spectrum of *p*-methoxy-*p´*-hydroxyazobenzene **S3** (500 MHz, $CDCl_3$, 300 K).

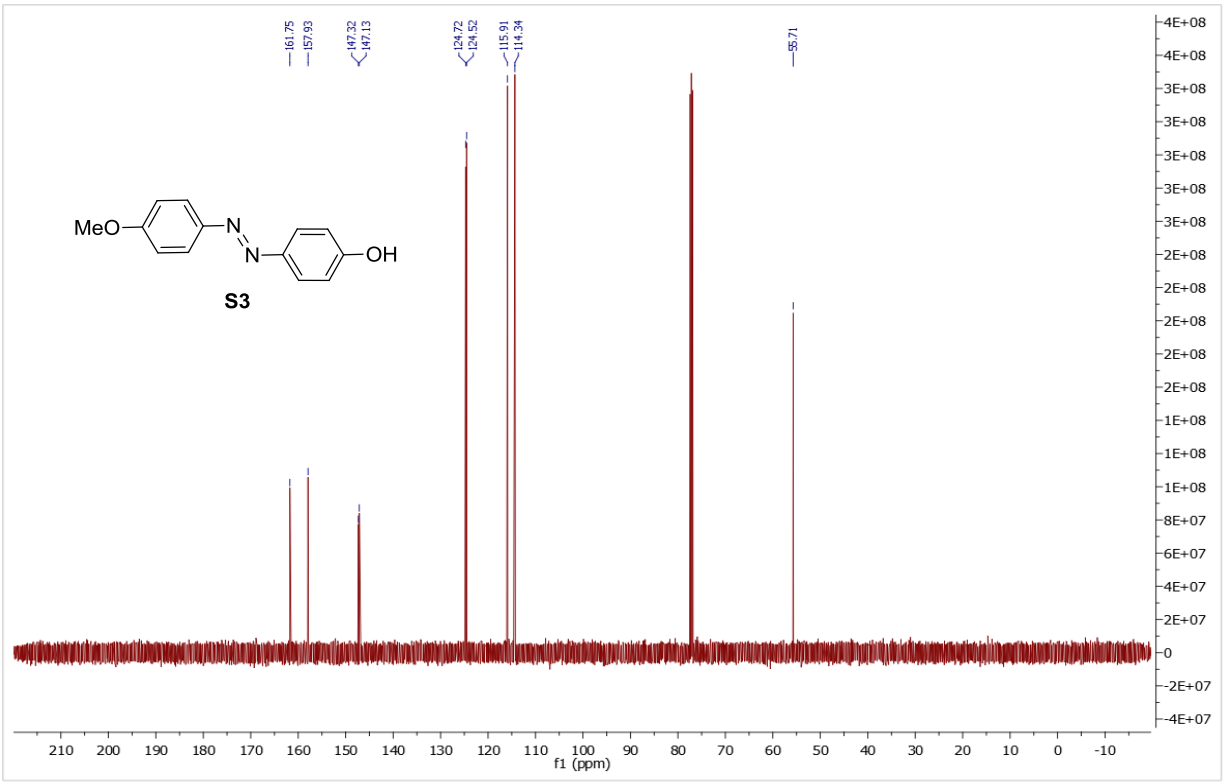


Figure S42: ^{13}C NMR spectrum of *p*-methoxy-*p´*-hydroxyazobenzene **S3** (126 MHz, $CDCl_3$, 300 K).

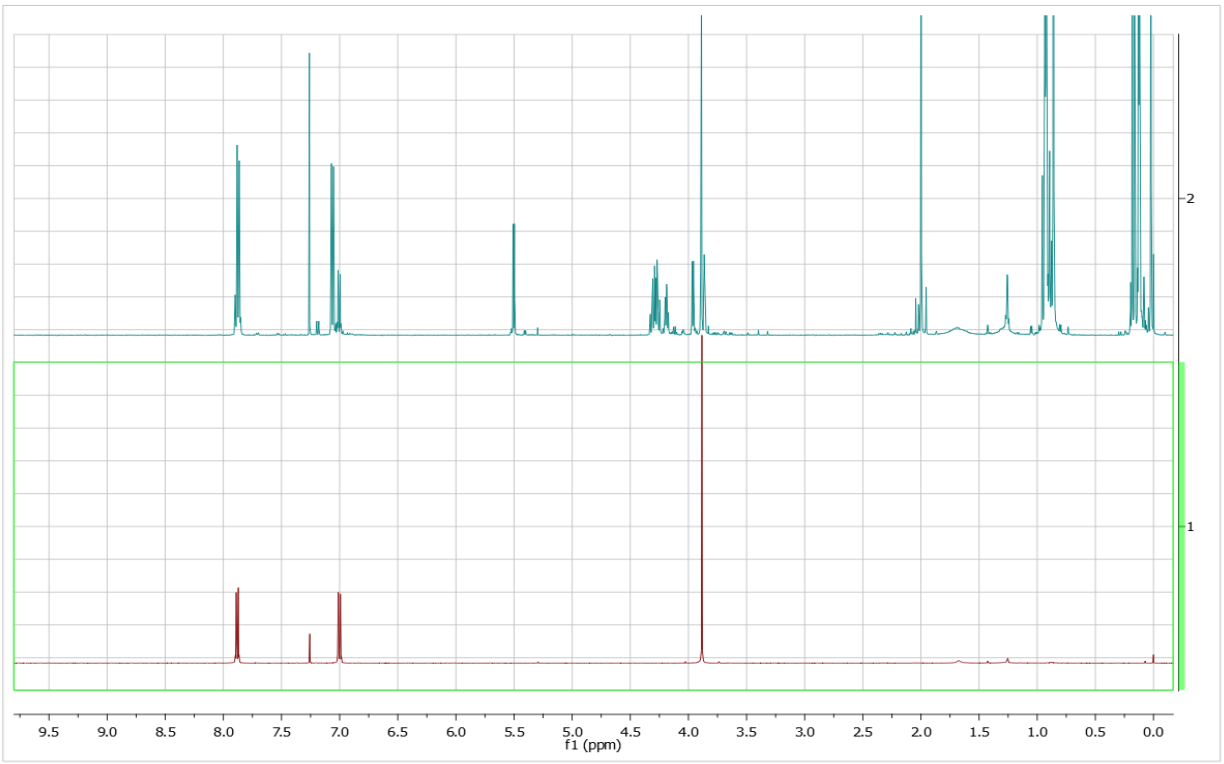
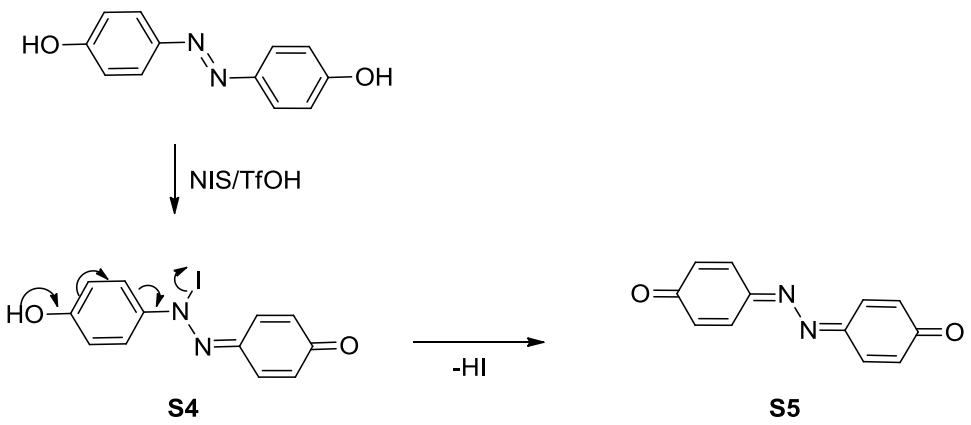


Figure S43: Superimposition of the ^{1}H spectrum of a mixture of **αβ/ββ-18a** and p,p´-dimethoxyazobenzene (top, green) with the spectrum of pure p,p´-dimethoxyazobenzene (bottom, red).

Analytical proofs of the formation of *N*-dehydro-*N*-iodo-*p*-hydroxyphenylhydrazoquinone S4

DHAB, upon treatment with NIS/TfOH gave compound **S4**, which after isolation was undergoing the following rearrangement:



S4 **S5**

The following data are thus concerning compound **S5**, however, the peak corresponding to **20** was observed in HRMS.

S4: ESI HRMS: *m/z*: calcd for $C_{12}H_9IN_2O_2$ - H^+: 338.9636 [M - H^+] found: 338.9636

S5: ESI HRMS: *m/z*: calcd for $C_{12}H_8N_2O_2$ + H^+: 213.0659 [M + H^+] found: 213.0663

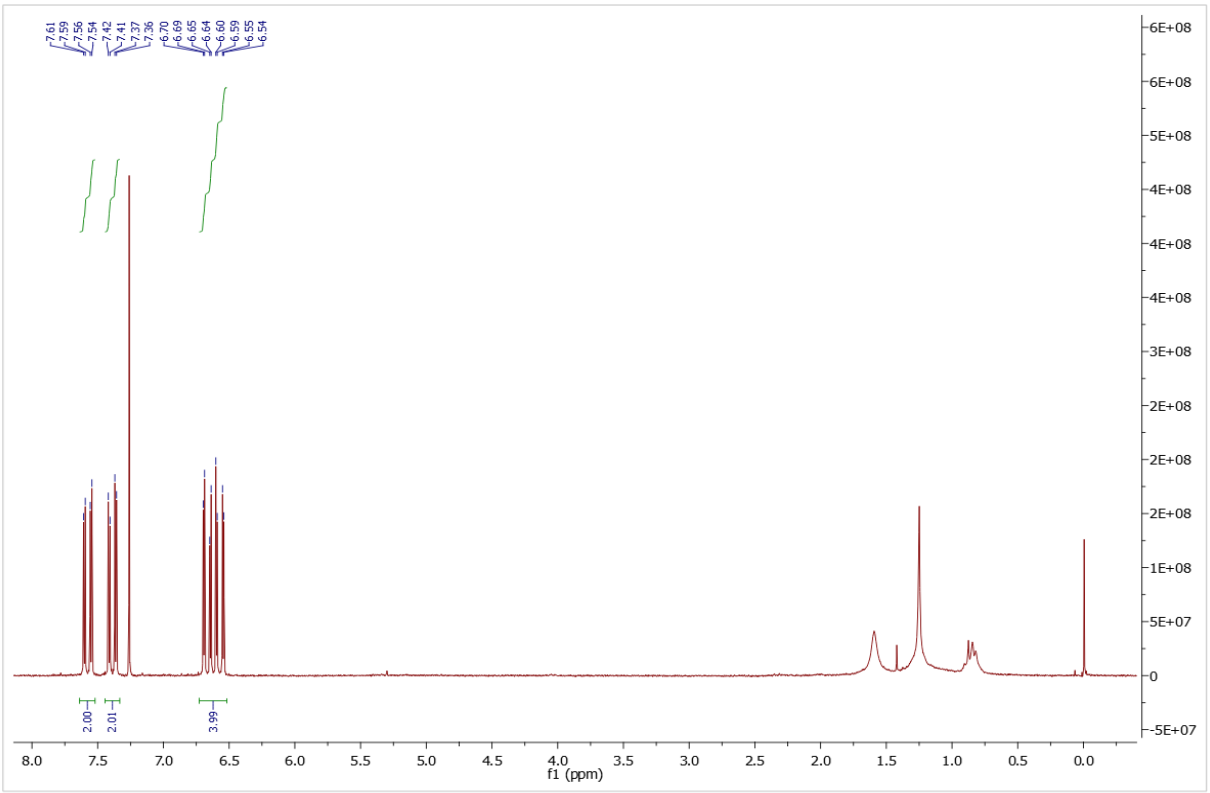


Figure S44: ^{1}H NMR spectrum of **S5**, (500 MHz, $CDCl_3$, 300 K).

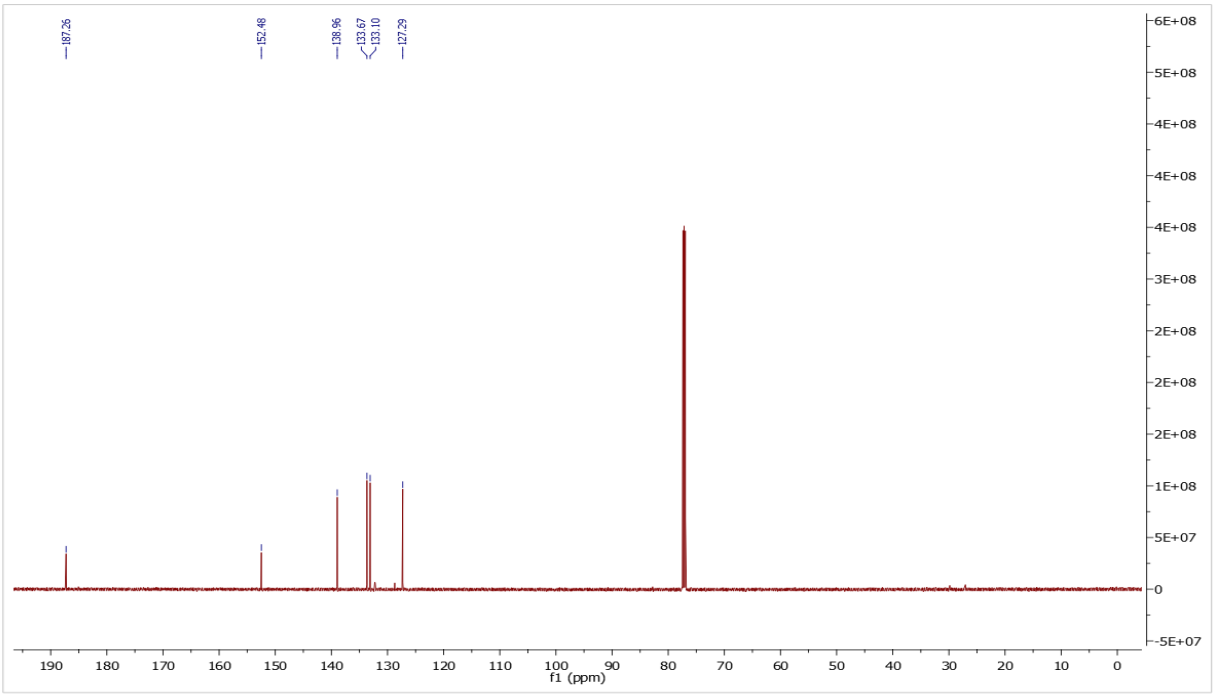


Figure S45: ^{13}C NMR spectrum of **S5**, (126 MHz, $CDCl_3$, 300 K).

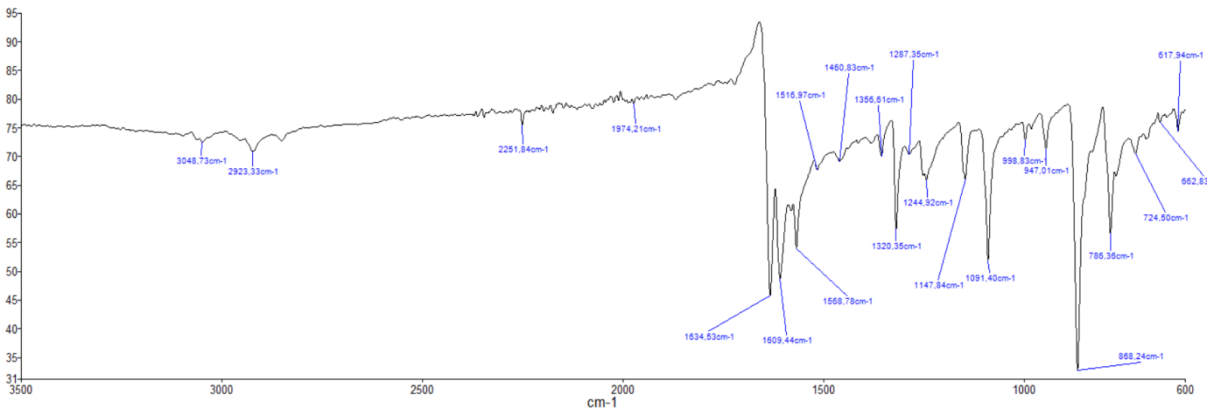


Figure S46: FTIR spectrum of **S5**.

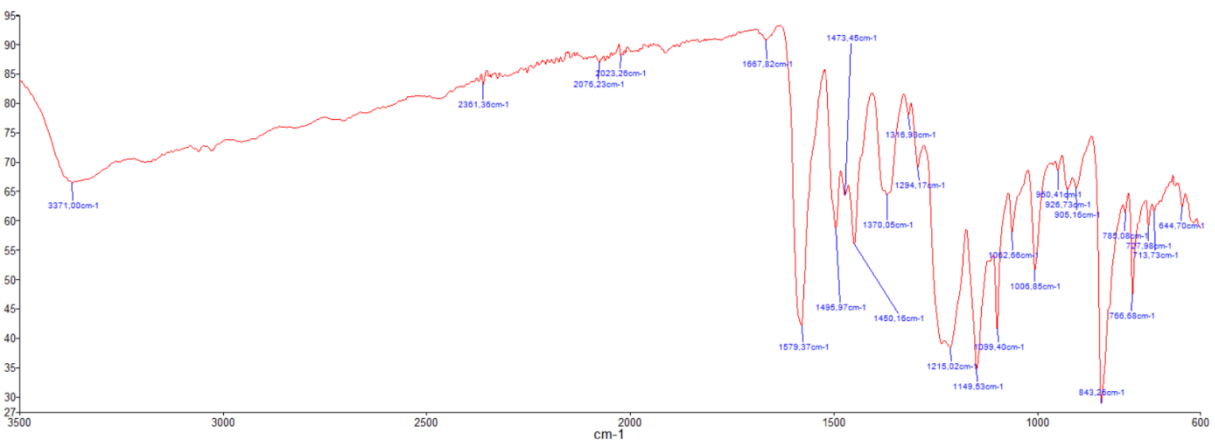


Figure S47: FTIR spectrum of **DHAB**.

Literature references

1. (a) K. P. R. Kartha and H. J. Jennings, *J. Carbohydrate Chemistry*, 1990, **9**, 777–781; (b) *Carbohydrate Research*, 2002, **337**, 1247–1259 (c) R. Kakarla, R. G. Dulina, N. T. Hatzenbuhler, Y. W. Hui and M. J. Sofia, *J. Org. Chem.*, 1996**, 61***,* 8347–8349; (d) B. Yu and H. Tao, *Tetrahedron Letters*, 2001, **42**, 2405–2407; (e) A. Müller and T. K. Lindhorst, *Eur. J. Org. Chem.*, 2016, 1669–1672
2. J. P. Henschke, P.-Y. Wu, C.-W. Lin, S.-F. Chen, P.-C. Chiang and C.-N. Hsiao, *J. Org. Chem.*, 2015, **80**, 2295–2309.
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