Electronic Supplementary Material (ESI) for Chemical Communications.

Anomeric alkylations and acylations of unprotected mono- and disaccharides mediated by pyridoneimine in aqueous solution

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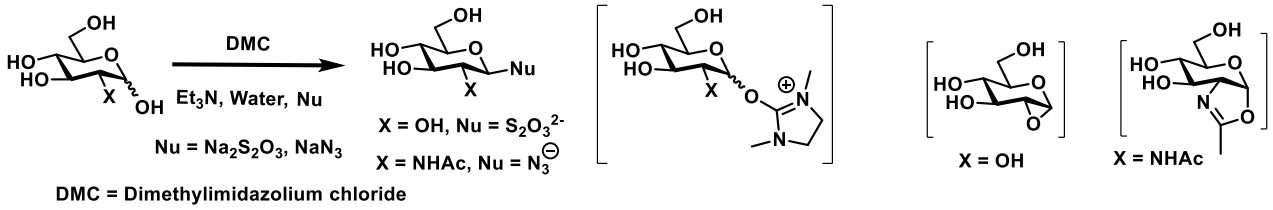
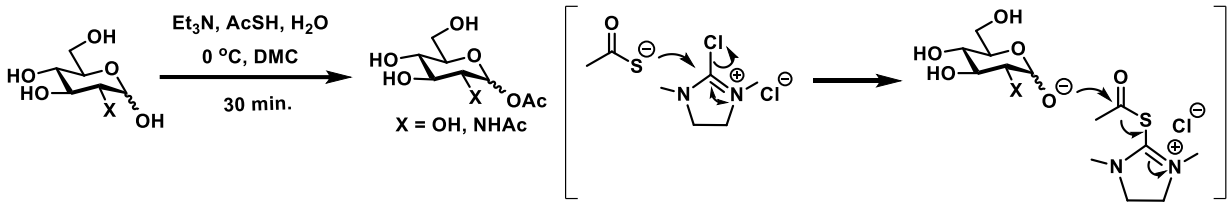
Supporting Information

Contents

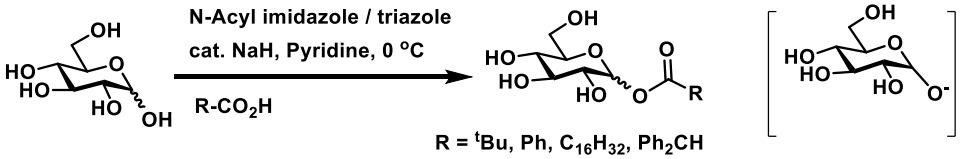
A brief survey of the reported reactions of free sugars:



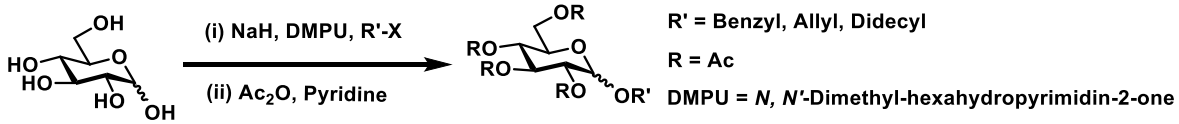
Scheme S1. Formation of glycosyl azide and thiosulfate reported by Shoda and co-workers. Suggested intermediates are given in parenthesis.[1]



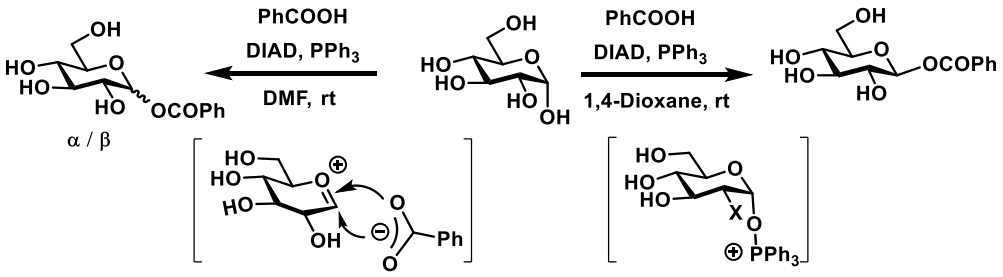
Scheme S2. Formation of glycosyl ester reported by Fairbanks and co-workers. Suggested intermediates are given in parenthesis.[2]



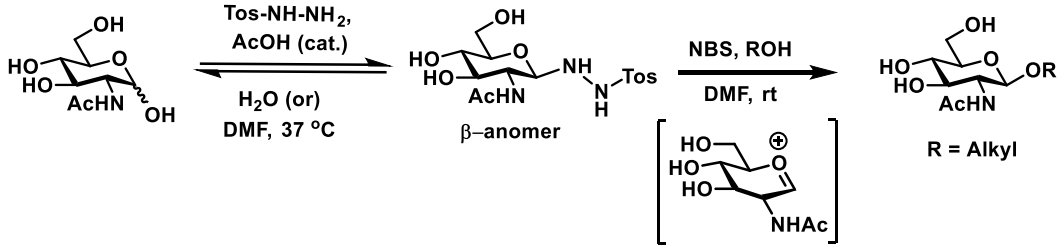
Scheme S3. Formation of glycosyl esters reported by Pfander and Läderach. Suggested intermediate is given in parenthesis.[3]



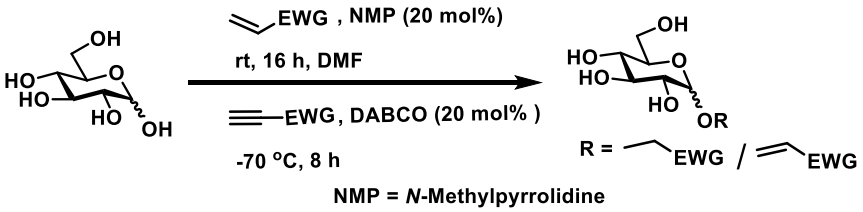
Scheme S4. Formation of glycosides reported by Klotz and Schmidt. The reaction is suggested to proceed through hemiacetal anion.[4]



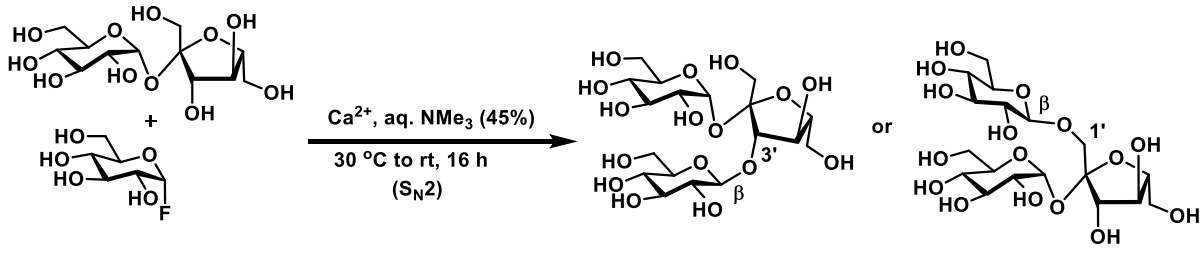
Scheme S5. Formation of glycosyl esters reported by Kawabata and co-workers. Suggested intermediates are given in parenthesis.[5]



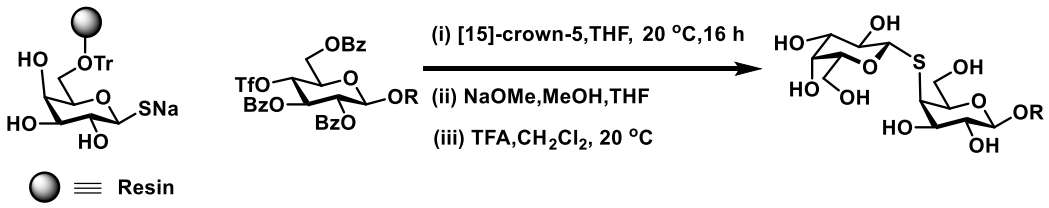
Scheme S6. Formation of glycosides reported by Nitz and co-workers. Suggested intermediate is given in parenthesis.[6]



Scheme S7. Formation of glycosides reported by Mahrwald and co-workers. The reaction is suggested to proceed through hemiacetal anion formation.[7]



Scheme 8. Reaction of sucrose with glycosyl fluoride reported by Miller, Schepartz and co-workers. The reaction is suggested to proceed in an S_N2 manner.[8]



Scheme 9. Formation of thia-linked disaccharides reported by Himmel and Hindsgaul. The reaction is suggested to proceed in an S_N2 manner.[9]

References

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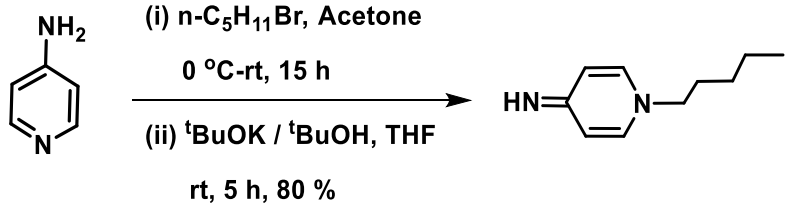
General Methods

Unless otherwise noted, all reagents were purchased commercially and used as received. Solvents were dried and distilled according to literature procedures. Analytical TLC was performed on commercial Merck plates coated with silica gel. Visualization of the spots on the TLC plates was achieved by UV radiation or spraying 5% sulfuric acid in ethanol or ninhydrin in ethanol solution or by using I_2 as staining agent. Silica gel (100-200 and 230-400 mesh size) was used for column chromatography. The IR spectra were recorded as neat samples. Mass spectral characterizations were performed on ESI-QTOF, operating in the positive ion mode, on samples in either MeCN/water or MeOH/water solution. ^{1}H and ^{13}C NMR spectral analyses were performed on a spectrometer operating at 400 and 100 MHz, respectively. Processing of the FID data was performed on Bruker TopSpin™ and Mnova software, with default settings. Chemical shifts are reported with respect to tetramethylsilane for ^{1}H NMR and the central line (77.0 ppm) of $CDCl_3$ for ^{13}C NMR spectra. Coupling constants (*J*) are reported in Hertz. Standard abbreviations s, d, t, dd, br s, m, and app refer to singlet, doublet, triplet, doublet of doublet, broad singlet, multiplet, and apparent, respectively.

1-Pentyl pyridone-4-imine (1).



A solution of 4-aminopyridine (5 g, 53.2 mmol) in acetone (50 mL), 1-bromopentane (13 mL, 106.4 mmol) was added dropwise at 0 °C and the reaction mixture stirred overnight at rt.[1] The resulting white precipitate filtered, washed with acetone and dried *in vacuo* to secure *n*-pentyl

pyridine-4-iminium bromide. Yield: 10.4 g (80%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 (d, J = 7.2 Hz, 2 H), 6.83 (d, J = 7.2 Hz, 2 H), 4.08 (t, J = 7.2 Hz, 2 H), 1.71 (m, 2 H), 1.27 (m, 2 H), 1.15 (m, 2 H), 0.82 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.8, 143.1, 109.7, 57.4, 30.2, 27.8, 21.9, 14.1. ESI-MS *m/z*: $[M]^+$ Calcd. for $C_{10}H_{17}N_2$, 165.1392; found 165.1395.

Resulting 1-pentyl pyridine-4-iminium bromide (10.4 g, 42.6 mmol) in THF (25 mL) was treated with potassium *tert*-butoxide in ^{t}BuOH (1 M) (41.9 mL, 42.6 mmol), stirred at room temperature for 5 h and solvents removed *in vacuo*. The crude residue was dissolved in PhMe (40 mL), filtered, solvents removed *in vacuo* and dried to secure 1-pentyl pyridone-4-imine, as a brown oil. Yield: 5.85 g (83%). ^{1}H NMR (400 MHz, CD_3CN) δ 6.81 (d, J = 7.8 Hz, 2 H), 5.85 (d, J = 7.8 Hz, 2 H), 4.36 (br, 1 H), 3.50 (t, J = 7.0 Hz, 2 H), 1.65-1.58 (m, 2 H), 1.36-1.19 (m, 4 H), 0.88 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, CD_3CN) δ 164.9, 137.6, 113.5, 55.7, 30.8, 28.9, 22.8, 14.1. ESI-MS *m/z*: $[M+H]^+$ Calcd. for $C_{10}H_{16}N_2H$, 165.1392; found 165.1394.

General procedure for anomeric alkylation

The alkylating agent (2 mol. equiv.) in acetonitrile (minimum amount to solubilize) was added to a solution of free sugar (1 mol. equiv.) and pyridoneimine **1** (1 mol. equiv.) in water (final water/acetonitrile 1:1), stirred at room temperature for 12 h, solvents evaporated *in vacuo* and the resulting residue purified by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH, linear gradient) to afford the glycoside product.

Characterization of anomeric alkylation products:

Allyl α/β-D-glucopyranoside (3). A mixture of D-glucose (50 mg, 0.27 mmol), allyl bromide (48 µL, 0.54 mmol) and **1** (45 mg, 0.27 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Allyl glycoside **3**[2] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 92:8), as a colorless foamy solid (46 mg, 76 %) and as an inseparable of α/β-anomers (22:78). ^{1}H NMR (400 MHz, D_2O) δ 6.02-5.92 (m, 1.16 H), 5.37 (m, 1.19 H), 5.28 (d, J = 10.4 Hz, 1 H), 4.96 (d, J = 4 Hz, 0.28 H), 4.4 (d, J = 8 Hz, 1 H), 4.38 (dd, J = 12.6, 5.6 Hz, 1 H), 4.21 (dd, J = 12.6, 6.4 Hz, 1.2 H), 3.90 (dd, J = 12.0, 2 Hz, 1 H), 3.75-3.83 (m, 0.5 H), 3.73-3.68 (m, 1.6 H), 3.55-3.57 (m, 0.3 H), 3.50-3.42 (m, 2 H), 3.38 (dd, J = 12.0, 3.2 Hz, 1.2 H), 3.24-3.25 (m, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 133.5, 133.2, 118.7, 118.1, 101.1, 97.3, 75.8, 75.7, 73.0, 71.8, 71.1, 70.6, 69.6, 69.5, 68.4, 60.7, 60.4. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_9H_{16}O_6Na$ 243.0845; found 243.0846.

Benzyl α/β-D-glucopyranoside (4). A mixture of D-glucose (50 mg, 0.27 mmol), benzyl bromide (65 µL, 0.54 mmol) and **1** (45 mg, 0.27 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Benzyl glycoside **4**[2] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 92:8), as a colorless foamy solid (49 mg, 65 %) and as an inseparable α/β-anomers (20:80). ^{1}H NMR (400 MHz, D_2O) δ 7.50-7.45 (m, 6 H), 5.05 (d, J = 3.2 Hz, 0.25 H), 4.97 (d, J = 11.6 Hz, 1 H), 4.66 (d, J = 12 Hz, 0.2 H), 4.55 (d, J = 8 Hz, 1 H), 3.96 (d, J = 12.4 Hz, 1 H), 3.76 (dd, J = 12.4, 5.2 Hz, 2 H), 3.56 (dd, J = 10.0, 3.2 Hz, 0.3 H), 3.51-3.39 (m, 3.5 H), 3.34 (app. t, 8.4 Hz, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 136.7,

136.6, 128.9, 128.8, 128.7, 128.6, 128.5, 101.2, 100.6, 75.9, 75.8, 73.2, 73.1, 71.9, 71.5, 70.1, 71.4, 69.7, 68.3, 64.2, 60.8. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{18}O_6Na$, 293.1001; found 293.1002.

Propargyl α/β-D-glucopyranoside (5). A mixture of D-glucose (50 mg, 0.27 mmol), propargyl bromide (52 µL, 0.54 mmol) and **1** (45 mg, 0.27 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Propargyl glycoside **5**[3] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 90:10), as a colorless foamy solid (37.5 mg, 62 %) and as an inseparable α/β-anomers (14:86). ^{1}H NMR (400 MHz, D_2O) δ 5.12 (d, J = 3.6 Hz, 0.3 H), 4.66 (d, J = 8 Hz, 1 H), 4.50 (s, 2 H), 4.36 (s, 0.47 H), 3.94 (d, J = 12.4 Hz, 1 H), 3.80-3.72 (m, 1.74 H), 3.55-3.49 (m, 2 H), 3.43 (app. t, J = 12 Hz, 1.20 H), 3.32 (app. t, J = 8.6 Hz, 1 H), 2.93 (br, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 100.6, 99.6, 79.1, 78.9, 78.8, 76.3, 76.2, 76.0, 75.9, 75.7, 75.6, 73.0, 72.9, 69.6, 69.5, 60.7, 60.6, 56.6, 56.3. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_9H_{14}O_6Na$, 241.0688; found 241.0689.

Allyl α/β-D-galactopyranoside (6). A mixture of D-galactose (50 mg, 0.27 mmol), allyl bromide (48 µL, 0.54 mmol) and **1** (45 mg, 0.27 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Allyl glycoside **6**[2] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 92:8), as a colorless foamy solid (46 mg, 75 %) and as an inseparable α/β-anomers (20:80). ^{1}H NMR (400 MHz, D_2O) δ 6.03-5.92 (m, 1 H), 5.39 (d, J = 16.4 Hz, 1 H), 5.28 (d, J = 9.2 Hz, 1 H), 4.44 (d, J = 8 Hz, 1 H), 4.39 (d, J = 6.0 Hz, 0.22 H), 4.23 (dd, J = 12.8, 6.0 Hz, 1.28 H), 4.16-4.06 (m, 1.22 H), 3.96-3.98 (m, 0.47 H), 3.92 (d, J = 3.2 Hz, 1 H), 3.85-3.80 (m, 0.69 H), 3.79-3.70 (m, 2.54 H), 3.70-3.63 (m, 2.30 H), 3.53 (dd, J = 10.0, 8.0

Hz, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 133.6, 133.4, 118.6, 118.1, 101.8, 97.5, 76.3, 75.1, 74.4, 72.8, 70.7, 70.6, 69.4, 69.2, 68.6, 68.1, 62.1, 60.9. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_9H_{16}O_6Na$, 243.0845; found 243.0844.

Benzyl β-D-galactopyranoside (7). A mixture of D-galactose (50 mg, 0.27 mmol), benzyl bromide (65 µL, 0.54 mmol) and **1** (45 mg, 0.27 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Benzyl glycoside **7**[2] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 92:8), as a colorless foamy solid (37.5 mg, 50 %). ^{1}H NMR (400 MHz, D_2O) δ 7.50-7.43 (m, 5 H), 4.97 (d, *J* = 11.6 Hz, 1 H), 4.48 (d, *J* = 7.6 Hz, 1 H), 3.93 (d, *J* = 2.8 Hz, 1 H), 3.85-3.82 (m, 1 H), 3.80-3.75 (m, 2 H), 3.69 (dd, *J* = 7.6, 5.2 Hz, 1 H), 3.64-3.54 (m, 2 H). ^{13}C NMR (100 MHz, D_2O) δ 136.7, 128.8, 128.7, 128.5, 101.8, 75.2, 72.8, 71.4, 70.8, 68.7, 61.0. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{18}O_6Na$, 293.1001; found 293.1005.

Propargyl α/β-D-galactopyranoside (8). A mixture of D-galactose (50 mg, 0.27 mmol), propargyl bromide (52 µL, 0.54 mmol) and **1** (45 mg, 0.27 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Propargyl glycoside **8** was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 92:8), as a colorless foamy solid (33.3 mg, 55 %) and as an inseparable α/β-anomers (20:80). ^{1}H NMR (400 MHz, D_2O) δ 4.60 (d, *J* = 7.6 Hz, 1.2 H), 4.51 (t, *J* = 3.2 Hz, 2 H), 4.39-4.35 (m, 1 H), 3.96 (d, *J* = 3.2 Hz, 1.36 H), 3.88 (br, 0.6 H), 3.82 (br, 0.5 H), 3.80-3.78 (m, 2 H), 3.76-3.72 (m, 2.31 H), 3.69 (dd, *J* = 10.0, 3.2 Hz, 1.37 H), 3.56 (dd, *J* = 9.6, 8.0 Hz, 1.22 H), 2.94 (t, *J* = 2.4 Hz, 1.25 H). ^{13}C NMR (100 MHz, D_2O)

δ 101.1, 98.6, 79.1, 79.0, 76.2, 75.9, 75.3, 72.8, 71.3, 70.6, 70.5, 69.4, 69.2, 68.6, 61.4, 60.9, 56.6. 56.5. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_9H_{14}O_6Na$, 241.0688; found 241.0688.

Allyl α/β-D-mannopyranoside (9). A mixture of D-mannose (50 mg, 0.27 mmol), allyl bromide (48 µL, 0.54 mmol) and **1** (45 mg, 0.27 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Allyl glycoside **9**[2] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 92:8), as a colorless foamy solid (38.5 mg, 63 %) and as an inseparable α/β-anomers (64:36). ^{1}H NMR (400 MHz, D_2O) δ 6.02-5.97 (m, 1.35 H), 5.38 (app. d, *J* = 17.2 Hz, 1.5 H), 5.30 (d, *J* = 10.4 Hz, 1.4 H), 4.93 (s, 1 H), 4.72 (s, 0.6 H), 4.39 (dd, *J* = 12.6, 5.0 Hz, 0.4 H), 4.38-4.24 (m, 1.4 H), 4.09 (dd, *J* = 12.4, 6.0 Hz, 1 H), 4.01-3.89 (m, 2.85 H), 3.82-3.73 (m, 2.54 H), 3.67 (app. d, *J* = 4.8 Hz, 2.4 H), 3.59 (t, *J* = 9.6 Hz, 0.6 H), 3.40-3.37 (m, 0.6 H). ^{13}C NMR (100 MHz, D_2O) δ 133.5, 133.3, 118.5, 118.4, 99.0, 98.9, 76.3, 73.0, 72.8, 70.6, 70.1, 70.0, 68.1, 66.9, 66.8, 61.1, 60.9. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_9H_{16}O_6Na$, 243.0845; found 243.0847.

Benzyl α/β-D-mannopyranoside (10). A mixture of D-mannose (50 mg, 0.27 mmol), benzyl bromide (65 µL, 0.54 mmol) and **1** (45 mg, 0.27 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Benzyl glycoside **10**[2] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 92:8), as a colorless foamy solid (53 mg, 71 %) and as an inseparable α/β-anomers (60:40). ^{1}H NMR (400 MHz, D_2O) δ 7.44-7.39 (m, 8 H), 4.96 (d, *J* = 1.6 Hz, 1 H), 4.89 (d, *J* = 12 Hz, 1 H), 4.74 (br, 1 H), 4.70-4.66 (m, 1 H), 4.56 (d, *J* = 11.2 Hz, 1 H), 3.93-3.90 (m, 2.28 H), 3.85 (dd, *J* = 11.2, 1.2 Hz, 1 H), 3.8-3.71 (m, 2.76 H), 3.67-

3.62 (m, 2 H), 3.56-3.55 (m, 1 H), 3.34-3.30 (m, 0.68 H). ^{13}C NMR (100 MHz, D_2O) δ 136.7, 136.6, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 99.3, 98.5, 76.2, 72.9, 72.8, 70.7, 70.5, 70.0, 69.4, 66.8, 66.7, 61.0, 60.8. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{18}O_6Na$, 293.1001; found 293.1005.

Propargyl α/β-D-mannopyranoside (11). A mixture of D-mannose (50 mg, 0.27 mmol), propargyl bromide (52 µL, 0.54 mmol) and **1** (45 mg, 0.27 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Propargyl glycoside **11**[3] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 90:10), as a colorless foamy solid (35 mg, 58 %) and as an inseparable α/β-anomers (68:32). ^{1}H NMR (400 MHz, D_2O) δ 5.02 (d, *J* = 1.2 Hz, 1 H), 4.85 (s, 0.46 H), 4.45 (d, *J* = 2.4 Hz, 0.8 H), 4.37 (d, *J* = 2.4 Hz, 0.20 H), 4.33 (d, *J* = 2.4 Hz, 0.8 H), 4.31 (d, *J* = 2.4 Hz, 0.8 H), 4.27 (d, *J* = 2.4 Hz, 0.22 H), 3.99 (d, *J* = 3.1 Hz, 0.44 H), 3.94 (dd, *J* = 3.2, 1.7 Hz, 1.21 H), 3.91-3.89 (m, 0.68 H), 3.86 (s, 0.68 H), 3.80-3.76 (m, 1.65 H), 3.74-3.69 (m, 0.72 H), 3.65 (dd, *J* = 7.2, 5.6 Hz, 2.3 H), 2.90 (s, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 98.6, 97.9, 78.8, 78.7, 76.3, 76.1, 76.0, 73.0, 72.8, 70.4, 69.8, 66.7, 66.5, 60.9, 60.7, 55.9, 54.5. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_9H_{14}O_6Na$, 241.0688; found 241.0693.

Allyl (1→4)-α-D-glucopyranosyl-α/β-D-glucopyranoside (12). A mixture of D-maltose (50 mg, 0.15 mmol), allyl bromide (25 µL, 0.29 mmol) and **1** (24 mg, 0.15 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Allyl glycoside **12**[4] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 86:14), as a colorless foamy solid

(42.4 mg, 76 %) and as β-anomer. ^{1}H NMR (400 MHz, D_2O) δ 6.01-5.92 (m, 1 H), 5.39-5.35 (m, 2 H), 5.27 (d, *J* = 9.2 Hz, 1 H), 4.51 (d, *J* = 9.2 Hz, 1 H), 4.38 (dd, *J* = 12.8, 5.6 Hz, 1 H), 4.21 (dd, *J* = 12.2, 6.4 Hz, 1 H), 3.92 (d, *J* = 12 Hz, 1 H), 3.84 (d, *J* = 12.2 Hz, 1 H), 3.78-3.72 (m, 3 H), 3.69-3.54 (m, 5 H), 3.42-3.37 (m, 1 H), 3.33-3.28 (m, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 133.2, 118.7, 100.9, 99.5, 76.6, 76.2, 74.5, 72.9, 72.8, 72.6, 71.6, 70.6, 69.3, 60.7, 60.4. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{15}H_{26}O_{11}Na$, 405.1373; found 405.1371.

Benzyl (1→4)-α-D-glucopyranosyl-β-D-glucopyranoside (13). A mixture of D-maltose (50 mg, 0.15 mmol), benzyl bromide (35 µL, 0.29 mmol) and **1** (24 mg, 0.15 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Benzyl glycoside **13**[5] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 82:18), as a colorless foamy solid (46 mg, 73 %). ^{1}H NMR (400 MHz, D_2O) δ 7.44-7.39 (m, 5 H), 5.38 (d, *J* = 3.6 Hz, 1 H), 4.92 (d, *J* = 11.6 Hz, 1 H), 4.52 (d, *J* = 8 Hz, 1 H), 3.92 (d, *J* = 10.8 Hz, 1 H), 3.84 (d, *J* = 10.8 Hz, 1 H), 3.78-3.74 (m, 2 H), 3.72-3.68 (m, 3 H), 3.63 (dd, *J* = 9.6, 6.8 Hz, 2 H), 3.57-3.54 (m, 2 H), 3.39-3.30 (m, 2 H). ^{13}C NMR (100 MHz, D_2O) δ 136.5, 128.7, 128.6, 128.5, 128.4, 100.9, 99.5, 76.7, 76.2, 74.5, 72.9, 72.7, 72.6, 71.6, 71.4, 69.3, 60.7, 60.4. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{28}O_{11}Na$, 455.1529; found 455.1527.

Propargyl (1→4)-α-D-glucopyranosyl-α/β-D-glucopyranoside (14). A mixture of D-maltose (50 mg, 0.15 mmol), propargyl bromide (27 µL, 0.29 mmol) and **1** (24 mg, 0.15 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Propargyl glycoside **14**[3] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 82:18), as a colorless

foamy solid (36 mg, 61 %) and as an inseparable α/β-anomers (20:80). ^{1}H NMR (400 MHz, D_2O) δ 5.39 (d, J = 3.6 Hz, 1 H), 5.21 (d, J = 3.6 Hz, 0.44 H), 5.08 (d, J = 3.6 Hz, 0.36 H), 4.64 (d, J = 8 Hz, 1 H), 4.46 (t, J = 2 Hz, 2 H), 4.41 (s, 0.45 H), 4.32 (d, 2.8 Hz, 0.48 H), 3.94-3.89 (m, 1.8 H), 3.85-3.80 (m, 4 H), 3.78-3.74 (m, 3.34 H), 3.74-3.70 (m, 2 H), 3.69-3.66 (m, 3 H), 3.64-3.61 (m, 3 H), 3.56 (dd, J = 12, 4 Hz, 2 H), 3.52-3.37 (m, 4 H), 3.31 (t, J = 8 Hz, 1.29 H), 3.20 (t, J = 9.2 Hz, 0.64 H), 2.90-2.87 (m, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 100.3, 99.5, 97.0, 95.8, 78.7, 76.6, 76.5, 76.3, 76.1, 76.0, 75.9, 75.7, 74.6, 74.0, 73.4, 72.8, 72.7, 71.6, 71.7, 71.6, 71.4, 71.3, 69.6, 69.5, 69.4, 69.2, 60.7, 60.6, 60.4, 56.5. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{15}H_{24}O_{11}Na$, 403.1216; found 403.1216.

Allyl (1→4)-β-D-glucopyranosyl-α/β-D-glucopyranoside (15).

A mixture of D-cellobiose (50 mg, 0.15 mmol), allyl bromide (26 µL, 0.29 mmol) and **1** (24 mg, 0.15 mmol) in 1 mL water acetonitrile (1:1) was stirred at room temperature for 12 h and worked-up as given in the general procedure for the anomeric alkylation reaction. Allyl glycoside **15**[5] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 85:15), as a colorless solid (45.5 mg, 72 %) as an inseparable α/β- anomers (26:74). ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.94-5.84 (m, 1 H), 5.70-5.60 (m, 0.37 H), 5.31 (d, J = 17.2 Hz, 1.14 H), 5.13 (d, J = 10.8 Hz, 1.17 H), 4.24 (d, J = 7.6 Hz, 1 H), 4.21 (d, J = 8 Hz, 1 H), 4.05 (d, J = 5.6 Hz, 0.5 H), 4.02 (d, J = 5.6 Hz, 0.40 H), 3.73 (d, J = 10 Hz, 1.17 H), 3.69 (d, J = 10 Hz, 1.4 H), 3.60 (dd, J = 12.4, 4.8 Hz, 2.32 H), 3.31-3.29 (m, 4.52 H), 3.24 (br, 3.1 H), 3.19-3.17 (m, 1 H), 3.16-3.12 (m, 1.43 H), 3.06-2.95 (m, 4 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.3, 135.1, 117.0. 116.9, 103.5, 102.2, 97.2, 92.6, 80.6, 77.1, 76.8, 75.4, 75.3, 75.2, 73.7, 73.6, 73.4, 72.6, 72.3, 71.3, 71.1, 70.9, 70.6, 70.4, 69.3, 67.6, 66.8, 61.4, 61.3, 60.6. ESI-MS *m/z*: $[M + Na]^+$ calcd. for $C_{15}H_{26}O_{11}Na$, 405.1373; found 405.1372.

Benzyl (1→4)-β-D-glucopyranosyl-β-D-glucopyranoside (16). A mixture of D-cellobiose (50 mg, 0.15 mmol), benzyl bromide (35 µL, 0.29 mmol) and **1** (24 mg, 0.15 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Benzyl glycoside **16**[5] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 82:18), as a colorless foamy solid (45.5 mg, 72 %). ^{1}H NMR (400 MHz, D_2O) δ 7.45-7.39 (m, 5 H), 7.91 (d, *J* = 11.6 Hz, 1 H), 4.73 (d, *J* = 11.6 Hz, 1 H), 4.52 (d, *J* = 8 Hz, 1 H), 4.48 (d, *J* = 8 Hz, 1 H), 3.96 (dd, *J* = 12.4, 4 Hz, 1 H), 3.88 (dd, 12.4, 4 Hz, 1 H), 3.79 (dd, *J* = 11.8, 4.4 Hz, 1 H), 3.70 (dd, 11.8, 5.6 Hz, 1 H), 3.64-3.59 (m, 2 H), 3.57-3.50 (m, 2 H), 3.48-3.44 (m, 1 H), 3.40-3.48 (m, 1 H), 3.28 (dd, *J* = 12, 8 Hz, 2 H). ^{13}C NMR (100 MHz, D_2O) δ 136.5, 128.7, 128.5, 128.4, 102.5, 101.0, 78.6, 75.9, 75.4, 74.7, 74.3, 73.1, 72.8, 71.4, 69.4, 60.5, 60.0. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{28}O_{11}Na$, 455.1529; found 455.1530.

Propargyl (1→4)-β-D-glucopyranosyl-α/β-D-glucopyranoside (17). A mixture of D-cellobiose (50 mg, 0.15 mmol), propargyl bromide (27 µL, 0.29 mmol) and **1** (24 mg, 0.15 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Propargyl glycoside **14**[3] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 80:20), as a colorless foamy solid (44 mg, 74 %) and as an inseparable α/β-anomers (18:82). ^{1}H NMR (400 MHz, D_2O) δ 4.65 (d, *J* = 8 Hz, 1 H), 4.49 (d, *J* = 7.8 Hz, 1.17 H), 4.46 (t, *J* = 2.8 Hz, 2 H), 4.39 (d, *J* = 7.8 Hz, 0.21 H), 3.98-3.95 (m, 1.25 H), 3.93-3.86 (m, 1.66 H), 3.80 (dd, *J* = 12.4, 4.8 Hz, 1.38 H), 3.71 (dd, *J* = 12.4, 5.6 Hz, 1.35 H), 3.65-3.62 (m, 2 H), 3.61-3.59 (m, 1.24 H), 3.56 (br, 0.85 H), 3.51-3.45 (m, 3 H), 3.42-3.37 (m, 1.61 H), 3.30-3.27 (m, 1.20 H), 2.90 (t, *J* = 2.4 Hz, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 103.0, 102.5, 100.3, 99.4, 78.7, 78.6, 78.5, 77.4, 76.3,

75.9, 75.4, 75.3, 74.8, 74.7, 74.3, 74.2, 73.1, 72.9, 72.8, 72.6, 71.3, 69.4, 68.1, 64.9, 60.5, 59.9, 59.8, 57.1, 56.5. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{15}H_{24}O_{11}Na$, 403.1216; found 403.1216.

Allyl (1→4)-β-D-galactopyranosyl-β-D-glucopyranoside (18). A mixture of D-lactose (50 mg, 0.15 mmol), allyl bromide (25 µL, 0.29 mmol) and **1** (24 mg, 0.15 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Allyl glycoside **18**[4] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 75:25), as a colorless foamy solid (41 mg, 74 %). ^{1}H NMR (400 MHz, D_2O) δ 6.02-5.92 (m, 1 H), 5.38 (d, J = 17.2 Hz, 1 H), 5.28 (d, J = 10.4 Hz, 1 H), 4.53 (d, J = 8 Hz, 1 H), 4.44 (d, J = 8 Hz, 1 H), 4.22 (dd, J = 12.8, 6.8 Hz, 1 H), 3.99-3.91 (m, 2 H), 3.81-3.75 (m, 4 H), 3.72-3.64 (m, 4 H), 3.59 (br, 1 H), 3.53 (t, J = 8.8 Hz, 1 H), 3.33 (t, J = 5.2 Hz, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 133.2, 118.7, 102.9, 101.0, 78.3, 75.3, 74.7, 74.4, 72.8, 72.4, 70.9, 70.6, 68.5, 61.0, 60.0. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{15}H_{26}O_{11}Na$, 405.1373; found 405.1371.

Benzyl (1→4)-β-D-galactopyranosyl- α/β-D-glucopyranoside (19).[5] A mixture of D-lactose (50 mg, 0.15 mmol), benzyl bromide (35 µL, 0.29 mmol) and **1** (24 mg, 0.15 mmol) in 1 mL water acetonitrile (1:1) was stirred at room temperature for 12 h and worked-up as given in the general procedure for the anomeric alkylation reaction. Benzyl glycoside **19**[5] was secured after purification by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 84:16), as a colorless foamy solid (47 mg, 74 %) and as an inseparable α/β-anomers (12:88). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.38-7.36 (m, 5.67 H), 4.81 (d, J =12.4 Hz, 1 H), 4.75 (d, J = 4 Hz, 0.4 H), 4.66 (d, J = 12.4 Hz, 1.25 H), 4.57 (d, J = 12.4 Hz, 2.46 H), 4.44 (d, J = 12 Hz, 1.29 H), 4.30 (d, J = 8 Hz, 1 H), 4.22-4.19 (m, 1.2 H), 3.76 (d, J = 10.8 Hz, 0.96 H), 3.65-

3.60 (m, 3.4 H), 3.55-3.46 (m, 5 H), 3.12-3.04 (m, 1.15 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 138.0, 137.9, 128.3, 128.2, 127.7, 127.6, 127.5, 127.4, 103.8, 101.8, 97.7, 96.9, 80.6, 76.74, 76.70 77.0, 76.7, 75.5, 75.0, 74.9, 74.8, 73.3, 73.2, 73.0, 72.2, 71.9, 71.6, 70.9, 70.6, 70.3, 69.7, 68.2, 68.1, 60.4, 60.3, 60.0. ESI-MS *m/z*: $[M + Na]^+$ calcd. for $C_{19}H_{28}O_{11}Na$, 455.1529; found 455.1528.

Propargyl (1→4)-β-D-galactopyranosyl-β-D-glucopyranoside (20). A mixture of D-lactose (50 mg, 0.15 mmol), propargyl bromide (27 µL, 0.29 mmol) and **1** (24 mg, 0.15 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Propargyl glycoside **20**[3] was secured as a colorless foamy solid (36.6 mg, 66 %), by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 80:20). ^{1}H NMR (400 MHz, D_2O) δ 4.67 (d, J = 8 Hz, 1 H), 4.47 (br, 2 H), 4.45 (d, J = 8 Hz, 1 H), 3.98 (d, J = 11.2 Hz, 1 H), 3.92 (br, 1 H), 3.81 (dd, J = 7.6, 3.6 Hz, 2 H) , 3.76 (d, J = 4 Hz, 2 H), 3.72 (d, J = 9.6 Hz, 2 H), 3.68-3.65 (m, 3 H), 3.56-3.52 (m, 1 H), 2.90 (s, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 102.9, 100.4, 78.2, 76.3, 75.4, 74.8, 74.4, 72.6, 72.5, 71.9, 70.9, 68.5, 61.0, 60.0, 56.6. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{15}H_{24}O_{11}Na$, 403.1216; found 403.1216.

Allyl β-D-ribopyranoside/ribofuranoside (21). A mixture of D-ribose (50 mg, 0.33 mmol), allyl bromide (58 µL, 0.65 mmol) and **1** (54.6 mg, 0.33 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Allyl glycoside **21** was secured after purification by column chromatography (SiO_2) (eluant: hexane/EtOAc = 20:80), as a colorless foamy solid (38 mg, 60 %) and as an inseparable mixture of β-pyranoside/β-furanoside (1:1). ^{1}H NMR (400 MHz, D_2O) δ 5.99-5.86 (m, 1.51 H), 5.36-5.29 (m, 1.55 H), 5.25 (d, J = 10.8 Hz, 1.55 H), 4.27 (d, J = 5.6 Hz,

0.5 H), 4.24 (d, *J* = 5.6 Hz, 1 H), 4.20-4.15 (m, 1.4 H), 4.14-4.09 (m, 2.1 H), 4.06-4.03 (m, 1 H), 4.01-3.98 (m, 2 H), 3.90-3.83 (m, 3.44 H), 3.81-3.76 (m, 2 H), 3.67 (dd, *J* = 11.6, 6.8 Hz, 2.16 H), 3.61-3.56 (m, 2 H). ^{13}C NMR (100 MHz, D_2O) δ 133.3, 118.6, 118.5, 106.0, 99.5, 82.8, 74.3, 70.8, 70.2, 69.6, 69.5, 68.8, 67.7, 63.1, 62.8. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_8H_{14}O_5Na$, 213.0739; found 213.0743.

Benzyl α/β-D-ribopyranoside (22). A mixture of D-ribose (50 mg, 0.33 mmol), benzyl bromide (79 µL, 0.65 mmol) and **1** (54.6 mg, 0.33 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Benzyl glycoside **22** was secured column chromatography (SiO_2) (eluant: hexane/EtOAc = 20:80), as a colorless foamy solid (48 mg, 60 %) and as an inseparable α/β-anomers (60:40). ^{1}H NMR (400 MHz, D_2O) δ 7.42-7.40 (m, 8.44 H) 5.22 (br, 0.27 H), 5.08 (br, 0.44 H) 4.87 (d, *J* = 4.8 Hz, 1 H), 4.72 (d, *J* = 1.2 Hz, 0.47 H), 4.65 (d, *J* = 3.2 Hz, 0.46 H), 4.62 (d, *J* = 10.8 Hz, 1 H), 4.54 (d, *J* = 11.2 Hz, 1 H), 4.48 (d, *J* = 12 Hz, 0.28 H), 4.36-4.31 (m, 0.37 H), 4.19-4.16 (m, 0.54 H), 4.04-4.01 (m, 0.9 H), 3.98 (s, 0.96 H), 3.86 (d, *J* = 9 Hz, 1.94 H), 3.80 (d, *J* = 8.8 Hz, 1 H), 3.70 (dd, *J* = 12.8, 6.8 Hz, 1 H), 3.64-3.53 (m, 1.87 H). ^{13}C NMR (100 MHz, D_2O) δ 136.6, 136.5, 128.72, 128.70, 128.6, 128.5, 128.4, 106.1, 99.6, 82.7, 74.2, 70.8, 70.6, 70.1, 69.8, 67.8, 67.3, 63.2, 62.8. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{12}H_{16}O_5Na$, 263.0895; found 263.0894.

Propargyl α/β-D-ribopyranoside (23). A mixture of D-ribose (50 mg, 0.33 mmol), propargyl bromide (62.5 µL, 0.65 mmol) and **1** (54.6 mg, 0.33 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Propargyl glycoside **23** was secured by column chromatography (SiO_2) (eluant: hexane/EtOAc = 20:80), as a colorless foamy solid (40 mg, 57 %) and as an inseparable α/ β-

anomers (72:28). ^{1}H NMR (400 MHz, D_2O) δ 5.18 (br, 0.22 H), 4.97 (d, *J* = 4.8 Hz, 1 H), 4.44 (br, 0.20 H), 4.40-4.39 (m, 2.11 H), 4.34 (d, *J* = 10.4 Hz, 0.77 H), 4.24-4.21 (m, 0.39 H), 4.10 (d, *J* = 4.4 Hz, 0.34 H), 4.04 (br, 1.20 H), 3.93-3.88 (m, 2.30), 3.84 (dd, *J* = 12.0, 2.8 Hz, 0.4 H), 3.75 (dd, *J* = 12.0, 6 Hz, 1.27 H), 3.68 (br, 1.23 H), 3.64 (d, *J* = 6.4 Hz, 0.18 H), 2.94 (d, *J* = 1.6 Hz, 1.06 H). ^{13}C NMR (100 MHz, D_2O) δ 105.5, 99.2, 83.0, 78.9, 76.2, 76.1, 74.4, 70.7, 70.0, 67.8, 67.3, 63.4, 62.6, 55.7, 54.8. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_8H_{12}O_5Na$, 211.0582; found 211.0583.

Allyl α/β-D-arabinopyranoside/arabinofuranoside (24). A mixture of D-arabinose (50 mg, 0.33 mmol), allyl bromide (58 μL, 0.65 mmol) and **1** (54.6 mg, 0.33 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Allyl glycoside **24** was secured by column chromatography (SiO_2) (eluant: hexane/EtOAc = 20:80), as a colorless foamy solid (37 mg, 58 %) and as an inseparable mixture of α/β-anomers of pyranoside (41%) (78:22) and α/β-anomers of furanoside (17%) (1:1). ^{1}H NMR (400 MHz, D_2O) δ 6.01-5.91 (m, 1.42 H), 5.36 (d, *J* = 17.2 Hz, 1.37 H), 5.27 (d, *J* = 10.4 Hz, 1.41 H), 5.04 (d, *J* = 4.8 Hz, 0.18 H), 4.97 (d, *J* = 3.2 Hz, 0.18 H), 4.61 (d, *J* = 9.2 Hz, 0.18 H), 4.37 (d, *J* = 7.6 Hz, 1 H), 4.35-4.31 (m, 0.88 H), 4.19 (dd, *J* = 12.8, 6.8 Hz, 1.29 H), 4.14-3.96 (m, 1.44 H), 3.92-3.81 (m, 2.44 H), 3.85-3.73 (m, 1 H), 3.66-3.62 (m, 2.33 H), 3.55-3.51 (m, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 133.6, 133.5, 133.3, 118.6, 118.4, 118.2, 118.0, 106.5, 102.1, 100.2, 97.9, 83.6, 81.9, 81.1, 76.3, 76.2, 74.6, 73.7, 72.4, 72.3, 70.7, 70.6, 68.9, 68.8, 68.7, 68.6, 68.2, 68.1, 66.2, 63.1, 62.7, 59.2. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_8H_{14}O_5Na$, 213.0739; found 213.0748.

Benzyl α/β-D-arabinopyranoside/arabinofuranoside (25). A mixture of D-arabinose (50 mg, 0.33 mmol), benzyl bromide (79 µL, 0.65 mmol) and **1** (54.6 mg, 0.33 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Benzyl glycoside **25** was secured by column chromatography (SiO_2) (eluant:hexane/EtOAc = 20:80), as a colorless foamy solid (56 mg, 70 %) and as an inseparable mixture of α/β-anomers of pyranoside (53%) (2:8) and α/β-anomers of furanoside (17%) (1:1). ^{1}H NMR (400 MHz, D_2O) δ 7.45-7.39 (m, 6.9 H), 5.08 (d, J = 7.2 Hz, 0.12 H), 5.01 (d, J = 3.2 Hz, 0.16 H), 4.88 (d, J = 11.6 Hz, 1.19 H), 4.70 (d, J = 11.6 Hz, 1.20 H), 4.58 (d, J = 1.6 Hz, 0.23 H), 4.40 (d, J = 7.2 Hz, 1 H), 4.14-3.95 (m, 0.9 H), 3.94-3.89 (m, 2.16 H), 3.85-3.67 (m, 0.77 H), 3.65-3.60 (m, 2.29 H), 3.58-3.53 (m, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 137.0, 136.9, 136.6, 128.7, 128.6, 128.5, 128.45, 128.42, 128.3, 128.26, 128.24, 106.6, 102.1, 100.2, 98.1, 83.6, 82.0, 81.1, 76.3, 74.6, 73.7, 72.4, 72.3, 71.4, 70.7, 69.7, 69.6, 68.9, 68.8, 68.2, 68.1, 66.2, 63.2, 61.0, 59.2. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{12}H_{16}O_5Na$, 263.0895; found 263.0895.

Propargyl α/β-D-arabinopyranoside/arabinofuranoside (26). A mixture of D-arabinose (50 mg, 0.33 mmol), propargyl bromide (62.5 µL, 0.65 mmol) and **1** (54.6 mg, 0.33 mmol) in water/acetonitrile (1:1) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Propargyl glycoside **26** was secured column chromatography (SiO_2) (eluant: hexane/EtOAc = 20:80), as a colorless foamy solid (36 mg, 57 %) and as an inseparable mixture of α/β-anomers of pyranoside (40%) (1:3) and α/β-anomers of furanoside (17%) (1:1). ^{1}H NMR (400 MHz, D_2O) δ 5.16 (aap. d, J = 5.2 Hz, 0.18 H), 5.09 (d, J = 3.2 Hz, 0.17 H), 4.60 (d, J = 9.2 Hz, 0.19 H), 4.49 (d, J = 7.6 Hz, 1 H), 4.41 (t, J = 3.2 Hz, 2 H), 4.34-4.22 (m, 1.37 H), 4.19-4.01 (m, 0.52 H), 3.99-3.95 (m, 0.5 H), 3.92-3.88 (m, 2.39 H), 3.83 (d, J = 1.2 Hz, 0.39 H), 3.78-3.73 (m, 0.46 H), 3.67-3.64 (m, 2.38 H), 3.55-3.51 (m, 1

H), 2.89-2.86 (m, 1.08 H). ^{13}C NMR (100 MHz, D_2O) δ 105.9, 101.4, 99.5, 97.7, 84.4, 82.1, 81.1, 80.9, 78.9, 78.8, 76.6, 76.1, 76.0, 75.9, 75.8, 74.2, 73.7, 72.3, 72.1, 70.4, 68.8, 68.6, 68.0, 67.8, 66.1, 63.1, 61.1, 59.1, 56.4, 54.9, 54.6, 54.4. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_8H_{12}O_5Na$, 211.0582; found 211.0583.

Allyl α/β-D-xylopyranoside (27). A mixture of D-xylose (50 mg, 0.33 mmol), allyl bromide (58 µL, 0.65 mmol) and **1** (54.6 mg, 0.33 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Allyl glycoside **27**[6] was secured column chromatography (SiO_2) (eluant: hexane/EtOAc = 20:80), as a colorless foamy solid (48 mg, 76 %) and as an inseparable mixture of α/β-anomers (23:77). ^{1}H NMR (400 MHz, D_2O) δ 6.04-5.95 (m, 1 H), 5.41 (d, *J* = 17.6 Hz, 1 H), 5.31 (d, *J* = 9.2 Hz, 1 H), 4.97 (d, *J* = 3.2 Hz, 0.32 H), 4.63 (d, *J* = 8.4 Hz, 1 H), 4.50-4.46 (m, 1 H), 4.39-4.36 (m, 1 H), 4.25 (d, *J* = 5.9 Hz, 1 H), 4.12 (br, 0.52 H), 3.73-3.57 (m, 2 H), 3.49-3.43 (m, 1 H), 3.38-3.28 (m, 2 H). ^{13}C NMR (100 MHz, D_2O) δ 133.6, 133.4, 118.9, 118.7, 102.1, 96.2, 80.4, 75.8, 73.3, 73.1, 73.0, 72.2, 70.8, 69.4, 69.2, 58.9. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_8H_{14}O_5Na$, 213.0739; found 213.0748.

Benzyl α/β-D-xylopyranoside (28). A mixture of D-xylose (50 mg, 0.33 mmol), benzyl bromide (79 µL, 0.65 mmol) and **1** (54.6 mg, 0.33 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Benzyl glycoside **28**[7] was secured after column chromatography (SiO_2) (eluant: hexane/EtOAc = 20:80), as a colorless foamy solid (56 mg, 70 %), as an inseparable α/β-anomers (25:75). ^{1}H NMR (400 MHz, D_2O) δ 7.45-7.40 (m, 6.34 H), 4.97 (d, *J* = 3.6 Hz, 0.34 H), 4.88 (d, *J* = 11.6 Hz, 1.31 H), 4.71 (d, *J* = 11.6 Hz, 1.33 H), 4.58 (d, *J* = 11.6 Hz,

0.28 Hz), 4.47 (d, *J* = 7.6 Hz, 1 H), 3.97-3.90 (m, 1.23 H), 3.70-3.52 (m, 2.22 H), 3.39 (t, *J* = 9.2 Hz, 1 H), 3.33-3.25 (m, 1.45 H). ^{13}C NMR (100 MHz, D_2O) δ 137.0, 136.6, 128.8, 128.7, 128.5, 128.3, 102.1, 97.7, 75.8, 73.2, 73.0, 71.7, 71.3, 69.6, 69.4, 69.2, 65.2, 61.3. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{12}H_{16}O_5Na$, 263.0895; found 263.0898.

Propargyl α/β-D-xylopyranoside (29). A mixture of D-xylose (50 mg, 0.33 mmol), propargyl bromide (62.5 µL, 0.65 mmol) and **1** (54.6 mg, 0.33 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Propargyl glycoside **29**[8] was secured after column chromatography (SiO_2) (eluant: hexane/EtOAc = 20:80), as a colorless foamy solid (35 mg, 56 %) and as an inseparable α/β-anomers (11:89). ^{1}H NMR (400 MHz, D_2O) δ 5.05 (d, *J* = 3.6 Hz, 0.13 H), 4.70-4.62 (m, 0.29 H), 4.55 (d, *J* = 7.6 Hz, 1 H), 4.42 (s, 2 H), 4.38-4.29 (m, 0.52 H), 3.97-3.89 (m, 1 H), 3.63-3.57 (m, 1 H), 3.45-3.40 (m, 1 H), 3.28 (m, 2 H), 2.89 (t, *J* = 2 Hz, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 101.4, 97.2, 80.3, 78.7, 76.2, 75.9, 75.6, 73.0, 72.7, 72.0, 70.9, 69.0, 65.1, 58.7, 56.6, 54.8. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_8H_{12}O_5Na$, 211.0582; found 211.0585.

General procedure for anomeric acylation. Benzoic / phthalic anhydride (1 mol. equiv.) in acetonitrile was added to a solution of free sugar (1 mol. equiv.) and **1** (1 mol. equiv.) in water (final water/acetonitrile 1:1), stirred at room temperature for 12 h, solutions were evaporated *in vacuo* and the resulting residue purified by column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH) to afford the anomeric benzoates/phthalates.

Characterization of anomeric acylation products

1-*O*-Benzoyl-α/β-D-glucopyranose (30). A mixture of D-glucose (50 mg, 0.27 mmol), benzoic anhydride (62 mg, 0.27 mmol) and **1** (0.45 g, 0.27 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Anomeric benzoate **30**[9] was isolated after column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 94:6), as a colorless foamy solid (57 mg, 72 %) and as an inseparable α/β-anomers (35:65). ^{1}H NMR (400 MHz, D_2O) δ 8.06-8.02 (m, 2.7 H), 7.69-7.62 (m, 1.4 H), 7.53-7.49 (m, 2.7 H), 5.77 (d, J = 7.2 Hz, 1 H), 5.46 (d, J = 3.6 Hz, 0.22 H), 4.06 (m, 0.3 H), 3.92-3.82 (m, 2 H), 3.80-3.70 (m, 2.25 H), 3.67-3.60 (m, 3 H), 3.56-3.46 (m, 2 H). ^{13}C NMR (100 MHz, D_2O) δ 167.7, 166.8, 134.5, 134.0, 129.8, 129.6, 128.7, 128.6, 128.5, 128.0, 94.5, 94.2, 76.8, 76.0, 75.4, 73.9, 72.6, 71.9, 69.6, 69.1, 60.4, 60.3. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{16}O_7Na$, 307.0794; found 307.0793.

1-*O*-Benzoyl-α/β-D-galactopyranose (31). A mixture of D-galactose (50 mg, 0.27 mmol), benzoic anhydride (62 mg, 0.27 mmol) and **1** (0.45 g, 0.27 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Anomeric benzoate **31** was isolated after column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 94:6), as a colorless solid (54 mg, 68 %) and as an inseparable mixture of α/β-anomers (27:73). ^{1}H NMR (400 MHz, D_2O) δ 8.14-8.08 (m, 2 H), 7.76-7.70 (m, 1.45 H), 7.59-7.56 (m, 2.1 H), 5.78 (d, J = 8 Hz, 1 H), 5.56 (d, J = 3.6 Hz, 0.37 H), 4.13 (br, 0.64 H), 4.04 (br, 1.5 H), 3.99-3.92 (m, 1.8 H), 3.85-3.79 (m, 3.27 H). ^{13}C NMR (100 MHz, D_2O) δ 167.0, 134.5, 129.9, 129.7, 129.6, 129.5, 128.9, 128.8, 128.2, 95.1, 94.8, 76.2, 75.4, 72.6, 72.0, 69.7, 69.5, 68.9, 68.4, 61.1, 60.8. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{16}O_7Na$, 307.0794; found 307.0793.

1-*O*-Benzoyl-α/β-D-mannopyranose (32). A mixture of D-mannose (53 mg, 0.29 mmol), benzoic anhydride (65.5 mg, 0.29 mmol) and **1** (47.5 mg, 0.29 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Anomeric benzoate **32** was isolated after column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 94:6), as a colorless solid (60 mg, 72 %) and as an inseparable mixture of α/β-anomers (23:77). ^{1}H NMR (400 MHz, D_2O) δ 8.10-8.05 (m, 2.52 H), 7.71-7.65 (m, 1.29 H), 7.56-7.53 (m, 2.56 H), 5.32 (d, *J* = 9.2 Hz, 1 H), 5.15 (dd, *J* = 12.0, 9.2 Hz, 0.3 H), 4.20 (br, 1.06 H), 4.14-4.04 (m, 1.08 H), 4.00-3.87 (m, 2.88 H), 3.84-3.76 (m, 1.40 H), 3.70-3.66 (m, 0.25 H), 3.55 (app. t, *J* = 9.2 Hz, 0.43 H). ^{13}C NMR (100 MHz, D_2O) δ 167.9, 167.8, 134.0, 133.9, 129.7, 129.6, 129.5, 128.9, 129.8, 128.7, 93.8, 93.2, 76.2, 75.9, 74.3. 72.4, 69.1, 68.7, 64.5, 64.4, 60.8, 60.7. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{13}H_{16}O_7Na$, 307.0794; found 307.0793.

1-*O*-Phthaloyl-α/β-D-mannopyranose (33). A mixture of D-mannose (30 mg, 0.16 mmol), phthalic anhydride (23 mg, 0.16 mmol) and **1** (26.2 mg, 0.16 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Anomeric phthalate **33** was isolated after column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 80:20), as a colorless foamy solid (34 mg, 62 %) and as an inseparable mixture of α/ β-anomers (40:60). ^{1}H NMR (400 MHz, D_2O) δ 7.89-7.82 (m, 1.6 H), 7.69 (dd, *J* = 5.6, 3.2 Hz, 1 H), 7.65-7.60 (m, 2 H), 7.55 (dd, *J* = 5.6, 3.2 Hz, 1.31 H), 7.52-7.50 (m, 2 H), 7.47-7.44 (m, 1.7 H), 6.17 (d, *J* = 2 Hz, 1 H), 5.30 (d, *J* = 4 Hz, 0.2 H), 5.14 (app. s, 0.4 H), 4.06 (dd, *J* = 3.6, 2.4 Hz, 1 H), 4.0 (dd, *J* = 9.2, 3.6 Hz, 1.4 H), 3.89 (dd, *J* = 5.2, 2.4 Hz, 0.7 H), 3.87-3.85 (m, 1.5 H), 3.82 (br, 1 H), 3.80 (d, *J* = 3.2 Hz, 0.7 H), 3.78-3.77 (m, 2 H), 3.74 (br, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 176.5, 174.0, 170.1, 167.0, 140.2, 133.6, 133.3,

132.4, 1307, 129.9, 129.0, 128.7, 128.6, 126.8, 126.7, 125.7, 94.8, 94.0, 93.9, 93.6, 76.1, 75.2, 73.0, 72.3, 71.4, 71.1, 70.6, 70.2, 70.0, 69.9, 69.0, 68.4, 67.4, 66.8, 66.5, 66.0, 64.5, 60.9, 60.5, 52.8. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{16}O_9Na$, 351.0692; found 351.0690.

1-*O*-Benzoyl (1→4)-α-D-glucopyranosyl-β-D-glucopyranose (34). A mixture of D-maltose (55 mg, 0.160 mmol), benzoic anhydride (36 mg, 0.160 mmol) and **1** (26.2 mg, 0.160 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Anomeric benzoate **34** was isolated after column chromatography (SiO_2) (eluant: $CHCl_3$/ MeOH = 88:12), as a colorless foamy solid (51.6 mg, 72%) as the β-anomer. ^{1}H NMR (400 MHz, D_2O) δ 8.13-8.08 (m, 2 H), 7.75-7.69 (m, 1 H), 7.59-7.55 (m, 2 H), 5.83 (d, *J* = 8 Hz, 1 H), 5.44 (d, *J* = 4 Hz, 1 H), 3.94 (app. t, *J* = 8.4 Hz, 2 H), 3.87-3.85 (m, 2 H), 3.82-3.77 (m, 2 H), 3.76-3.73 (m, 2 H), 3.70 (dd, *J* = 8.8, 3.6 Hz, 2 H), 3.60 (dd, *J* = 9.6, 3.6 Hz, 1 H), 3.39-3.34 (m, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 166.9, 134.6, 129.9, 129.6, 128.8, 128.7, 128.1, 99.6, 94.4, 76.2, 75.9, 75.5, 72.8, 72.7, 71.9, 71.7, 69.3, 66.6, 60.5, 60.4. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{26}O_{12}Na$, 469.1322; found 469.1325.

1-*O*-Benzoyl (1→4)-β-D-glucopyranosyl-β-D-glucopyranose (35). A mixture of D-cellobiose (53 mg, 0.155 mmol), benzoic anhydride (35 mg, 0.155 mmol) and **1** (25.4 mg, 0.154 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Anomeric benzoate **35** was isolated after column chromatography (SiO_2) (eluant: $CHCl_3$/ MeOH = 85:15), as a colorless foamy solid (50 mg, 72%) and as the β-anomer. ^{1}H NMR (400 MHz, D_2O) δ 8.14-8.09 (m, 2 H), 7.77-7.70 (m, 1 H), 7.60-7.55 (m, 2 H), 5.85 (d, *J* = 7.8 Hz, 1 H), 4.56 (d, *J* = 7.8 Hz, 1 H), 4.01-3.94 (m, 2 H), 3.87 (dd, *J* = 12.0, 4 Hz, 2 H), 3.82-3.80 (m, 2 H), 3.78-3.73 (m, 2 H), 3.57-

3.51 (m, 2 H), 3.46 (app. t, J = 9.2 Hz, 1 H), 3.37 (app. t, J = 8.6 Hz, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 166.9, 134.6, 129.9, 128.9, 128.8, 128.1, 102.6, 94.4, 78.0, 76.0, 75.7, 74.1, 73.2, 71.8, 69.5, 60.6, 59.7. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{26}O_{12}Na$, 469.1322; found 469.1325.

1-*O*-Benzoyl (1→4)-β-D-galactopyranosyl-α/β-D-glucopyranose (36). A mixture of D-lactose (50 mg, 0.15 mmol), benzoic anhydride (33 mg, 0.15 mmol) and **1** (24 mg, 0.15 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Anomeric benzoate **36** was isolated after column chromatography (SiO_2) (eluant: $CHCl_3$/MeOH = 85:15), as a colorless solid (46 mg, 70 %) and as an inseparable α/β-anomers (40:60). ^{1}H NMR (400 MHz, D_2O) δ 8.15-8.10 (m, 2.8 H), 7.77-7.71 (m, 1.5), 7.61-7.56 (m, 2.8 H), 5.86 (d, J = 7.8 Hz, 1 H), 4.51 (d, J = 7.8 Hz, 1.7 H), 4.01-3.95 (m, 4.32 H), 3.89-3.87 (m, 3 H), 3.86-3.84 (m, 2 H), 3.82-3.80 (m, 4 H), 3.77-3.74 (m, 4.30 H), 3.70 (dd, J = 10.0, 2.8 Hz, 2.24 H), 3.60 (dd, J = 10.0, 8 Hz, 2.31 H). ^{13}C NMR (100 MHz, D_2O) δ 167.7, 166.9, 134.6, 134.2, 129.9, 129.8, 129.7, 128.9, 128.8, 128.1, 102.9, 102.8, 94.4, 94.2, 78.2, 77.9, 77.8, 75.7, 75.4, 75.1, 74.1, 73.6, 72.7, 72.6, 71.8, 71.0, 70.1, 69.4, 68.6, 61.0, 60.0, 59.9, 59.7. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{19}H_{26}O_{12}Na$, 469.1322; found 469.1320.

1-*O*-benzoyl-β-D-ribopyranose/ribofuranose (37). A mixture of D-ribose (50 mg, 0.33 mmol), benzoic anhydride (74.5 mg, 0.33 mmol) and **1** (54.1 mg, 0.33 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Anomeric benzoate **37** was isolated after column chromatography (SiO_2) (eluant: EtOAc/hexane = 80:20), as a colorless solid (56 mg, 66 %)

and as an inseparable mixture of β-pyranose/β-furanose (1:2). ^{1}H NMR (400 MHz, D_2O) δ 8.10-8.02 (m, 3 H), 7.68-7.65 (m, 1.57 H), 7.54-7.50 (m, 3.49 H), 5.18 (d, *J* = 6.4 Hz, 0.46 H), 5.05 (d, *J* = 7.2 Hz, 1 H), 4.32 (br, 0.72 H), 3.92 (dd, *J* = 11.6, 4.4 Hz, 1.62 H), 3.85-3.79 (m, 1.38 H), 3.72 (td, *J* = 12.8, 9.6 Hz, 2 H). ^{13}C NMR (100 MHz, D_2O) δ 167.9, 167.4, 134.1, 134.0, 129.7, 129.6, 128.8, 128.7, 128.6, 94.0, 91.7, 73.2, 73.0, 69.7, 66.4, 65.7, 63.6, 62.9. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{12}H_{14}O_6Na$, 277.0688; found 277.0685.

1-*O*-Benzoyl-α/β-D-arabinopyranose (38). A mixture of D-arabinose (56 mg, 0.37 mmol), benzoic anhydride (84.3 mg, 0.37 mmol) and **1** (60.6 mg, 0.37 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Anomeric benzoate **38** was isolated after column chromatography (SiO_2) (eluant: EtOAc/hexane = 80:20), as a colorless foamy solid (70 mg, 74 %) and as an inseparable mixture of α/β-anomers (1:9). ^{1}H NMR (400 MHz, D_2O) δ 8.7-8.03 (m, 2.3 H), 7.69-7.65 (m, 1.3 H), 7.53-7.49 (m, 2.3 H), 6.32 (d, *J* = 3.2 Hz, 0.1 H), 5.64 (d, *J* = 7.6 Hz, 1 H), 4.06 (br, 1 H), 3.97 (d, *J* = 2.1 Hz, 0.4 H), 3.95-3.93 (m, 1 H), 3.90 (d, *J* = 8 Hz, 1 H), 3.83-3.78 (m, 2.17 H). ^{13}C NMR (100 MHz, D_2O) δ 167.0, 164.8 134.4, 133.9, 129.8, 129.7, 129.6, 128.7, 128.6, 128.0, 96.6, 95.2, 72.1, 71.8, 71.0, 69.4, 68.5, 67.8, 67.1, 66.9. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{12}H_{14}O_6Na$, 277.0688; found 277.0686.

1-*O*-Benzoyl-α/β-D-xylopyranose (39). A mixture of D-xylose (55 mg, 0.36 mmol), benzoic anhydride (83 mg, 0.36 mmol) and **1** (0.59 g, 0.30 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Anomeric benzoate **39** was isolated after column chromatography (SiO_2) (eluant: EtOAc/hexane = 80:20), as a colorless solid (63 mg, 68 %) and as an inseparable α/β-

anomers (1:9). ^{1}H NMR (400 MHz, D_2O) δ 8.01 (d, J = 7.6 Hz, 2 H), 7.93 (d, J = 7.2 Hz, 0.3 H), 7.67-7.60 (m, 1.1 H), 7.51-7.44 (m, 2.2 H), 6.26 (d, J = 3.6 Hz, 0.11 H), 5.67 (d, J = 7.6 Hz, 1 H), 3.99 (dd, J = 11.6, 5.2 Hz, 1 H), 3.89-3.74 (m, 0.64 H), 3.6 (m, 2.18 H), 3.49-3.44 (m, 1 H). ^{13}C NMR (100 MHz, D_2O) δ 167.0, 166.8, 134.5, 133.6, 129.8, 129.7, 129.5, 128.7, 128.6, 127.9, 95.1, 92.8, 75.2, 73.9, 73.1, 71.7, 70.3, 68.8, 65.8, 63.3. ESI-MS *m/z*: $[M+Na]^+$ Calcd. for $C_{12}H_{14}O_6Na$, 277.0688; found 277.0684.

1-*O*-Benzoyl-β-L-fucopyranose (40). A mixture of L-fucose (0.50 g, 0.30 mmol), benzoic anhydride (69 mg, 0.30 mmol) and **1** (0.50 g, 0.30 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Anomeric benzoate **40** was isolated after column chromatography (SiO_2) (eluant: EtOAc/hexane = 80:20), as a colorless foamy solid (61 mg, 75 %) and as the β-anomer. ^{1}H NMR (400 MHz, acetone-d_6) δ 8.09-8.02 (m, 2 H), 7.67-7.59 (m, 1 H), 7.54-7.47 (m, 2 H), 5.67 (d, J = 8 Hz, 1 H), 3.86 (dd, J = 9.2, 2.8 Hz, 2 H), 3.73-3.66 (m, 2 H), 1.26 (d, J = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, acetone-d_6) δ 165.4, 133.9, 133.3, 130.2, 130.0, 129.0, 128.9, 96.0, 74.4, 72.0, 71.8, 70.6, 16.4. ESI-MS *m/z*: $[M + Na]^+$ calcd. for $C_{13}H_{16}O_6Na$, 291.0845; found 291.0842.

1-*O*-Benzoyl-α/β-L-rhamnopyranose (41). A mixture of L-rhamnose (52 mg, 0.32 mmol), benzoic anhydride (72.3 mg, 0.32 mmol) and **1** (52.4 mg, 0.32 mmol) in water/acetonitrile (1:1) (1 mL) was stirred at room temperature for 12 h and worked-up as given in the general procedure. Anomeric benzoate **41**[11] was isolated after column chromatography (SiO_2) (eluant: EtOAc/hexane = 80:20,) as a colorless solid (57 mg, 67 %) and as an inseparable α/β-anomers (1:2). ^{1}H NMR (400 MHz, D_2O) δ 8.06 (d, J = 7.2 Hz, 3.1 H), 7.68-7.65 (m, 1.35 H), 7.54-7.50 (m, 3.3 H), 5.25 (dd, J = 10, 2.8 Hz, 1 H), 5.05 (dd, J = 10, 2.8 Hz, 0.58 H),

4.12-3.95 (m, 2 H), 3.80 (m 1 H), 3.73 (m, 0.6 H), 3.65-3.52 (m, 1 H), 1.32 (m, 4.1 H). ^{13}C NMR (100 MHz, D_2O) δ 167.9, 167.8, 134.0, 133.9, 129.6, 129.5, 129.0, 128.9, 128.6, 93.8, 93.1, 76.0, 74.0, 71.9, 69.8, 69.6, 69.3, 68.9, 68.3, 16.8, 16.7. ESI-MS *m/z*: $[M + Na]^+$ calcd. for $C_{13}H_{16}O_6Na$, 291.0845; found 291.0842.

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NMR Spectra

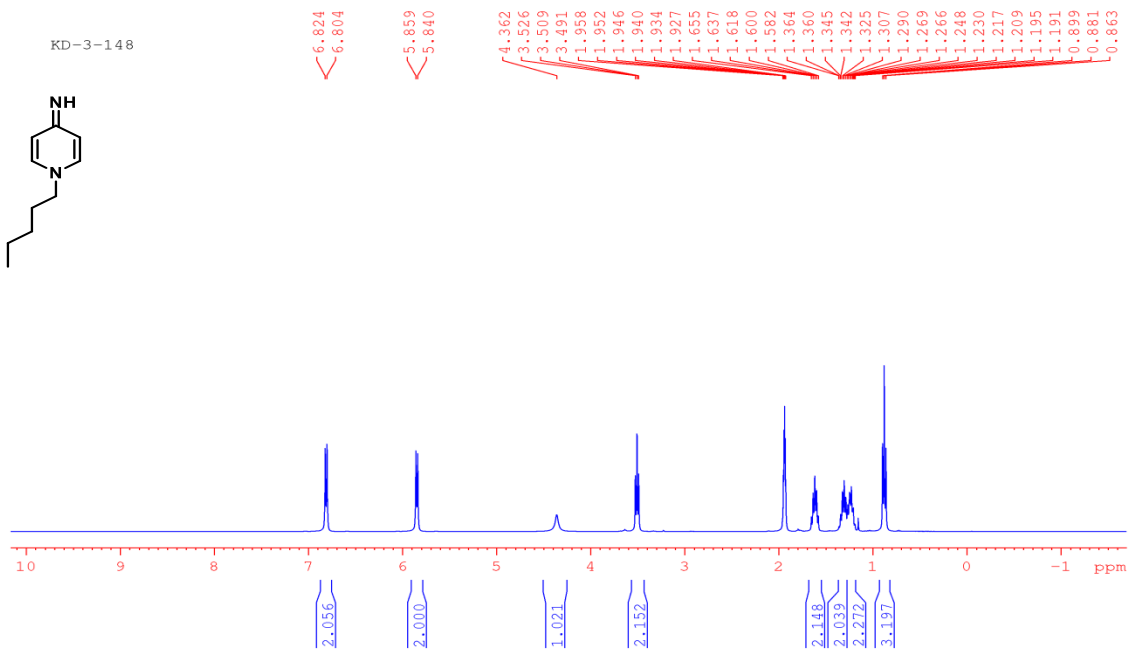

Figure S1. ^{1}H NMR spectrum of 1-pentyl pyridone-4-imine **1** (CD_3CN, 400 MHz).

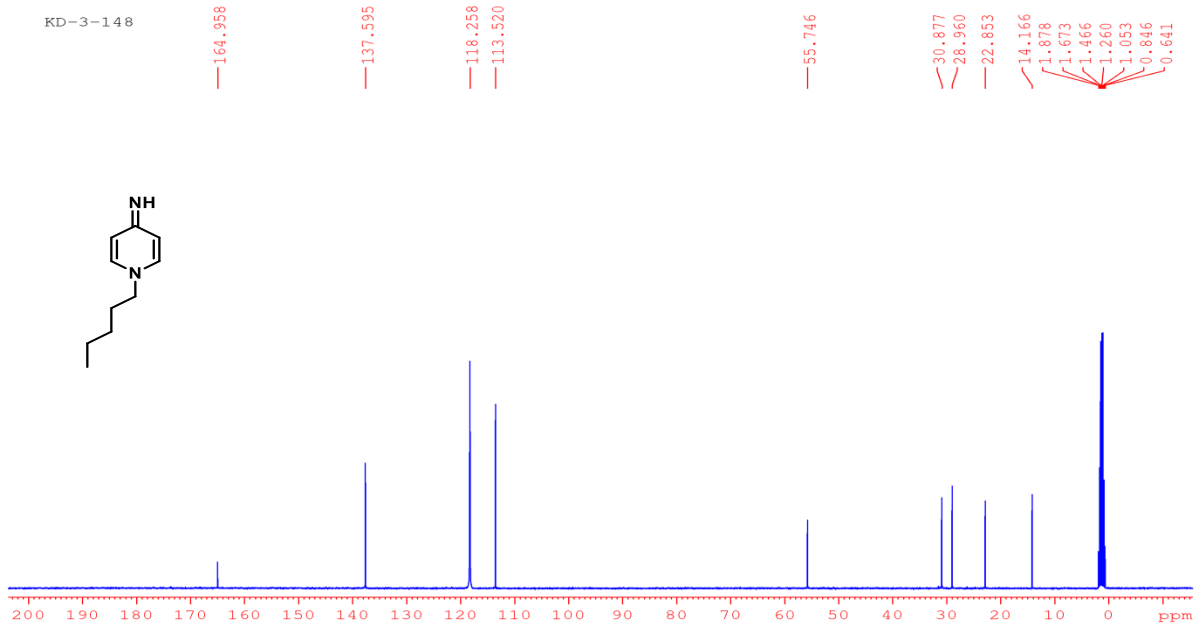

Figure S2. ^{13}C NMR spectrum of 1-pentylpyridine-4-imine **1** (CD_3CN, 100 MHz).

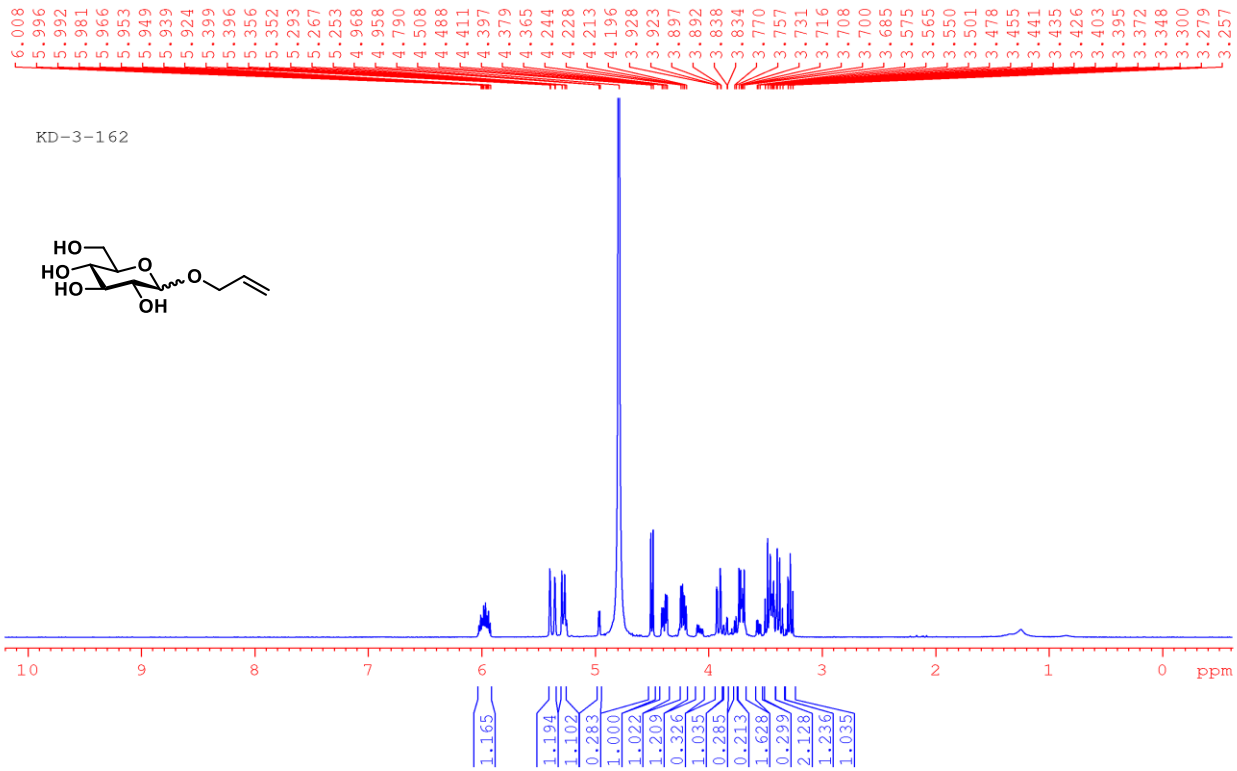

Figure S3. ^{1}H NMR spectrum of **3** (D_2O, 400 MHz).

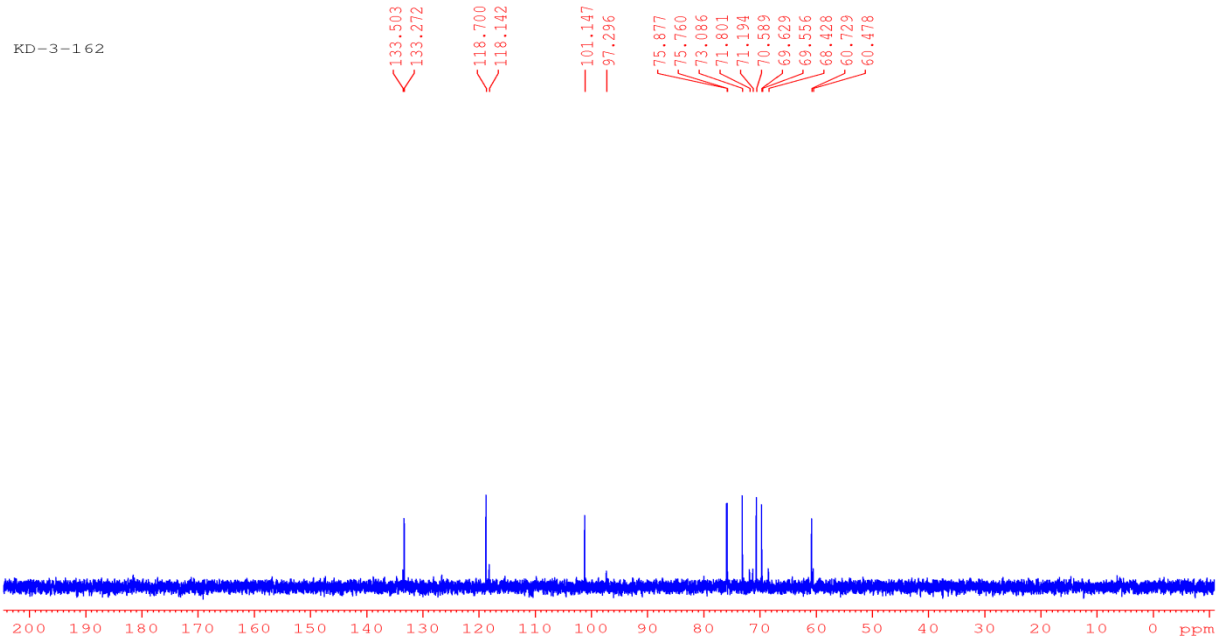

Figure S4. ^{13}C NMR spectrum of **3** (D_2O, 100 MHz).

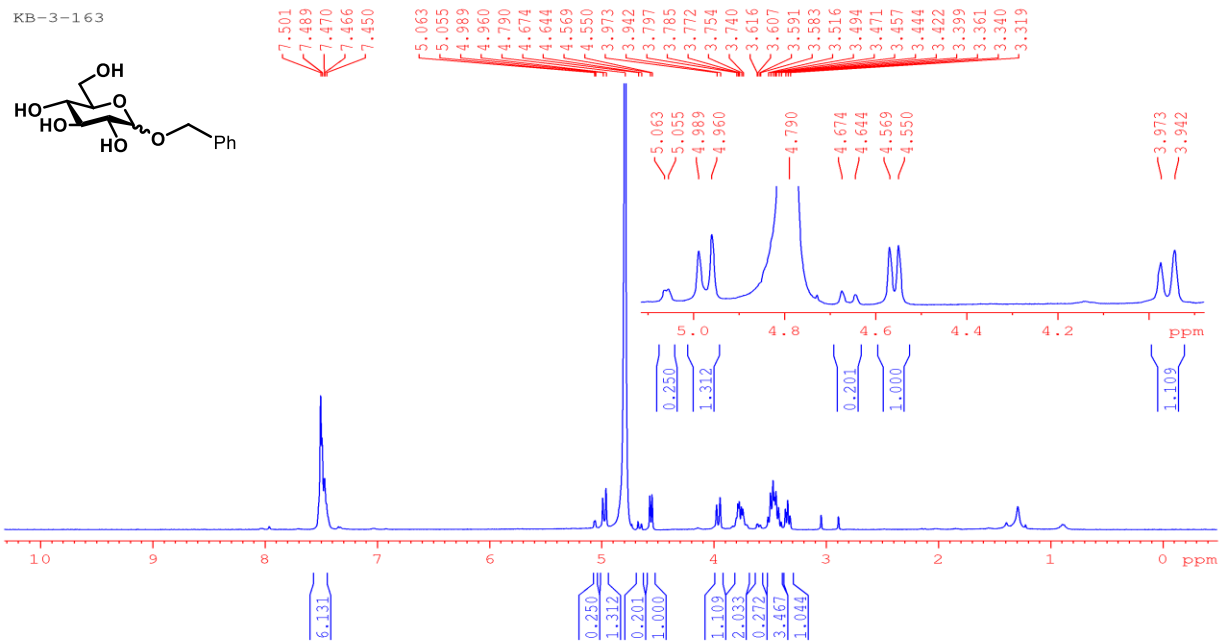

Figure S5. ^{1}H NMR spectrum of **4** (D_2O, 400 MHz).

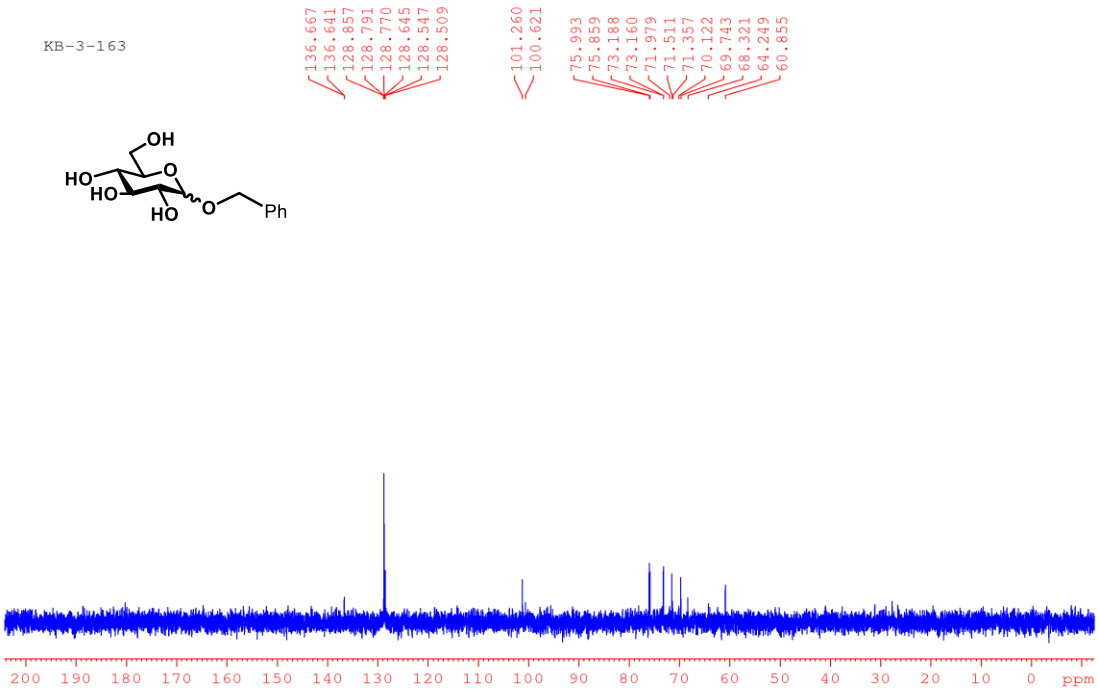

Figure S6. ^{13}C NMR spectrum of **4** (D_2O, 100 MHz).

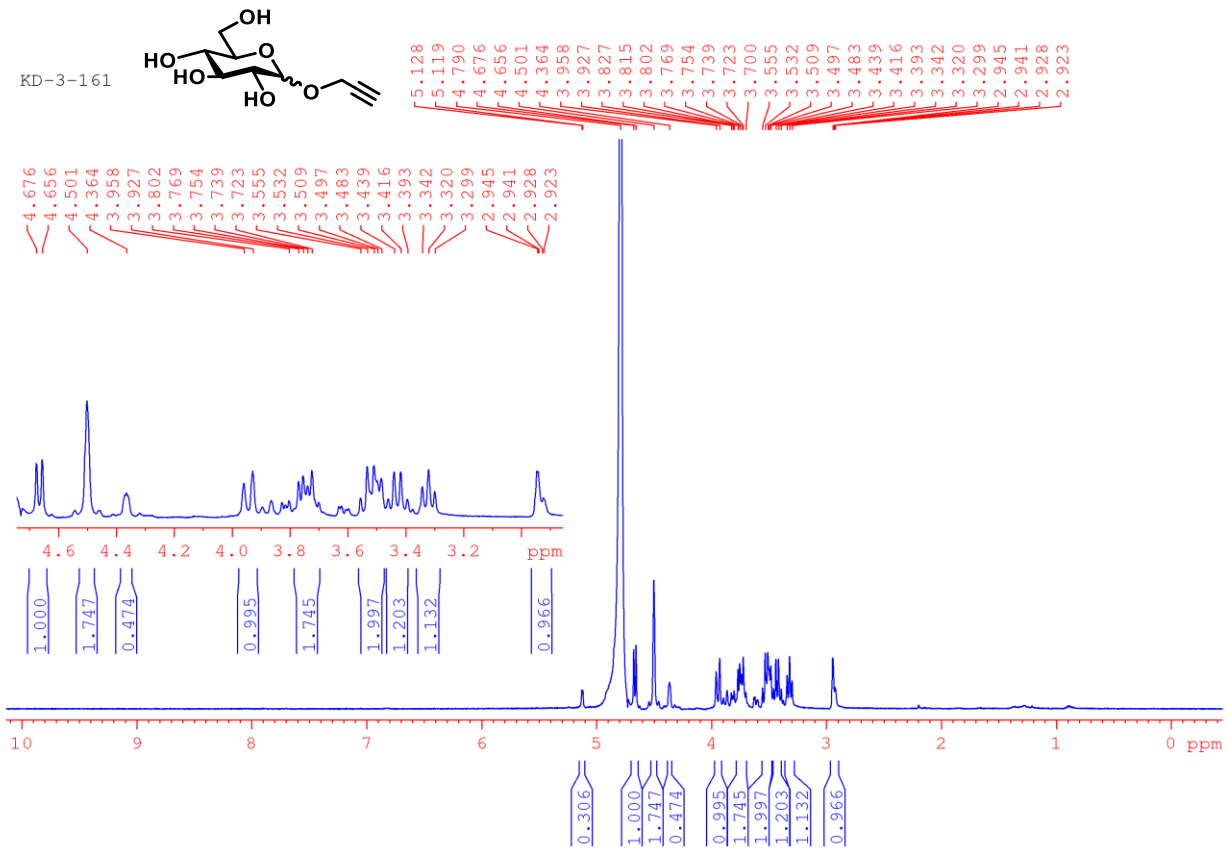

Figure S7. ^{1}H NMR spectrum of **5** (D_2O, 400 MHz).

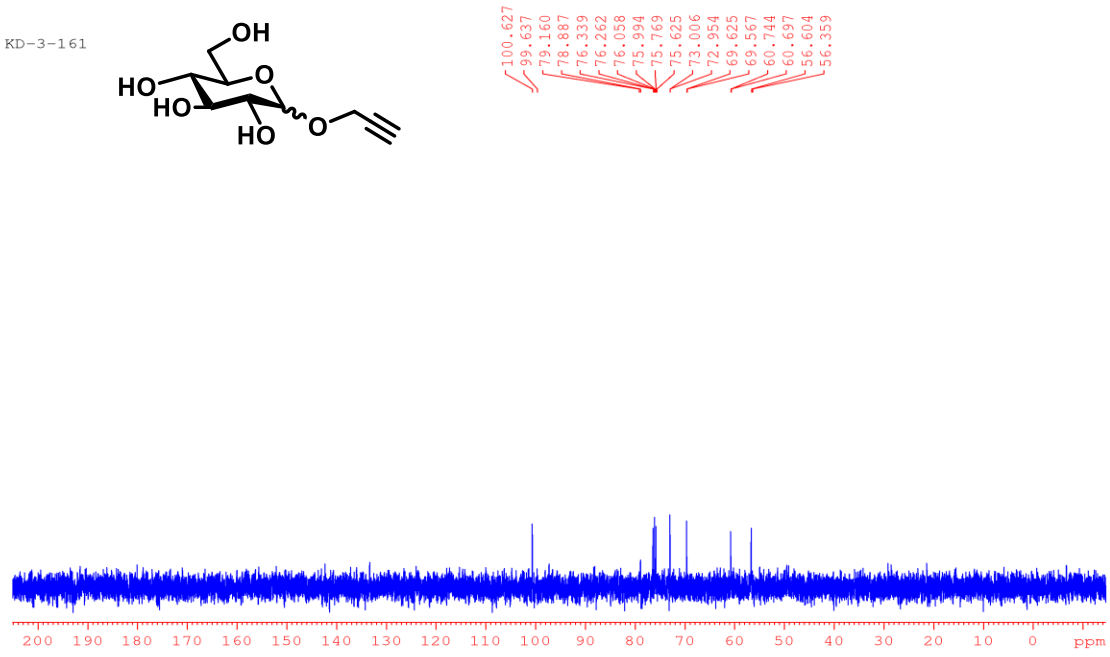

Figure S8. ^{13}C NMR spectrum of **5** (D_2O, 100 MHz).

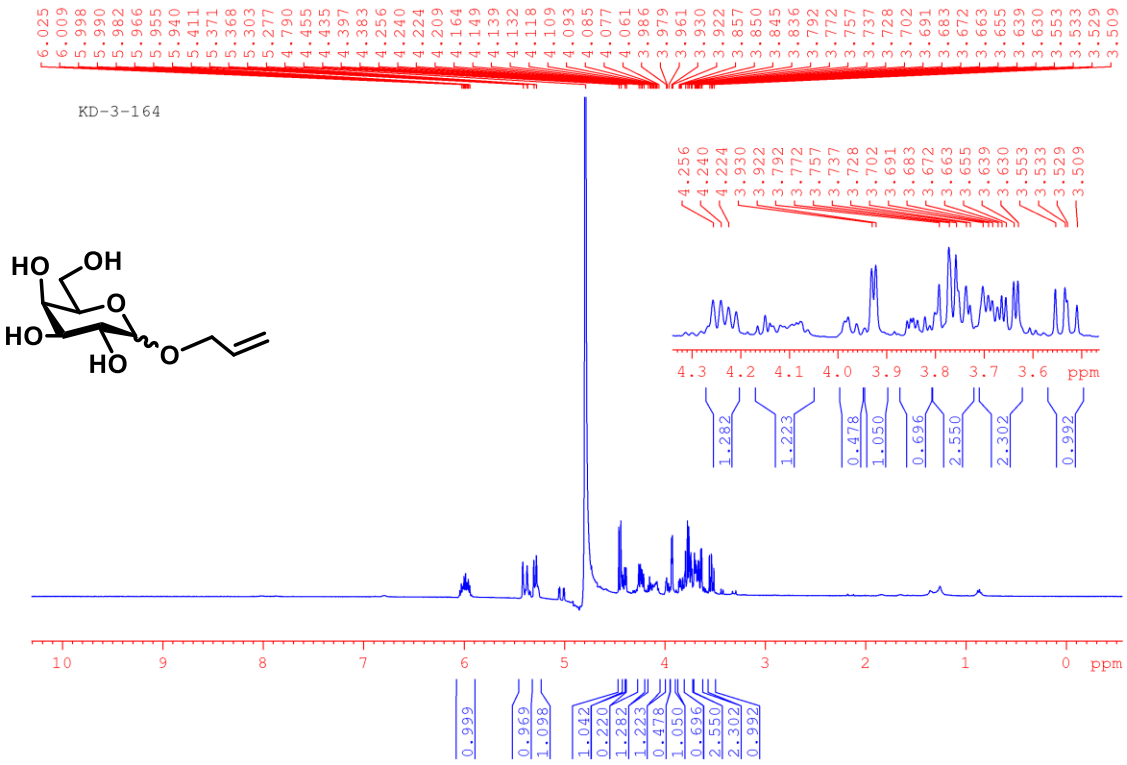

Figure S9. ^{1}H NMR spectrum of **6** (D_2O, 400 MHz).

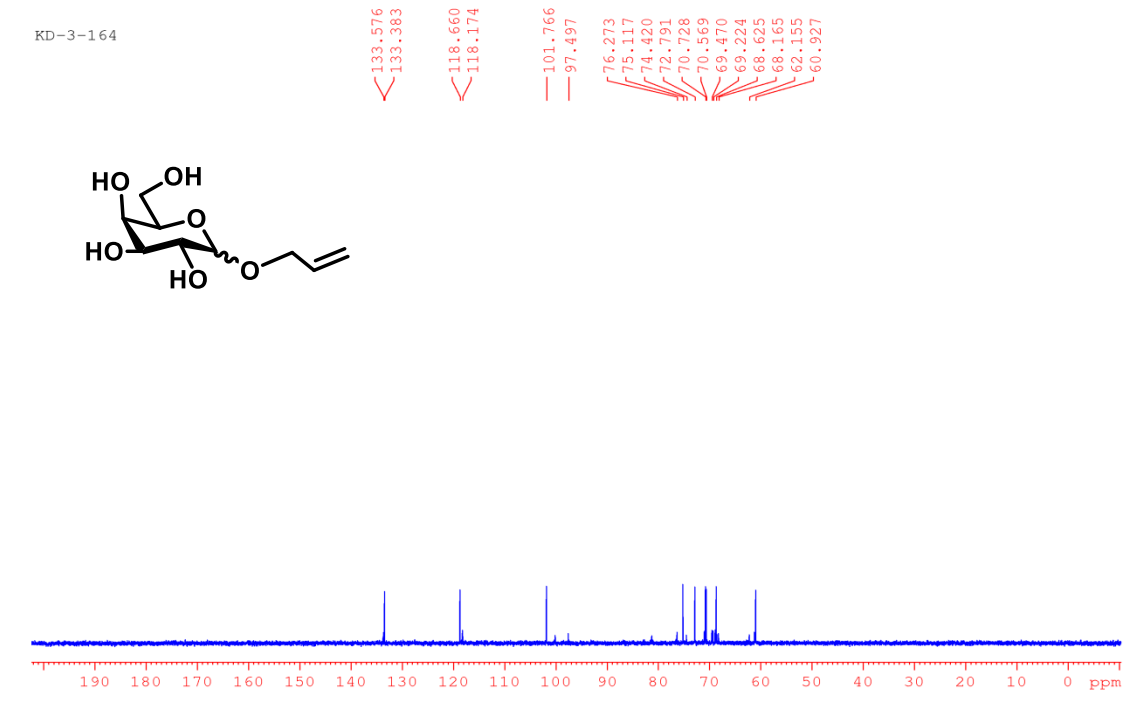

Figure S10. ^{13}C NMR spectrum of **6** (D_2O, 100 MHz).

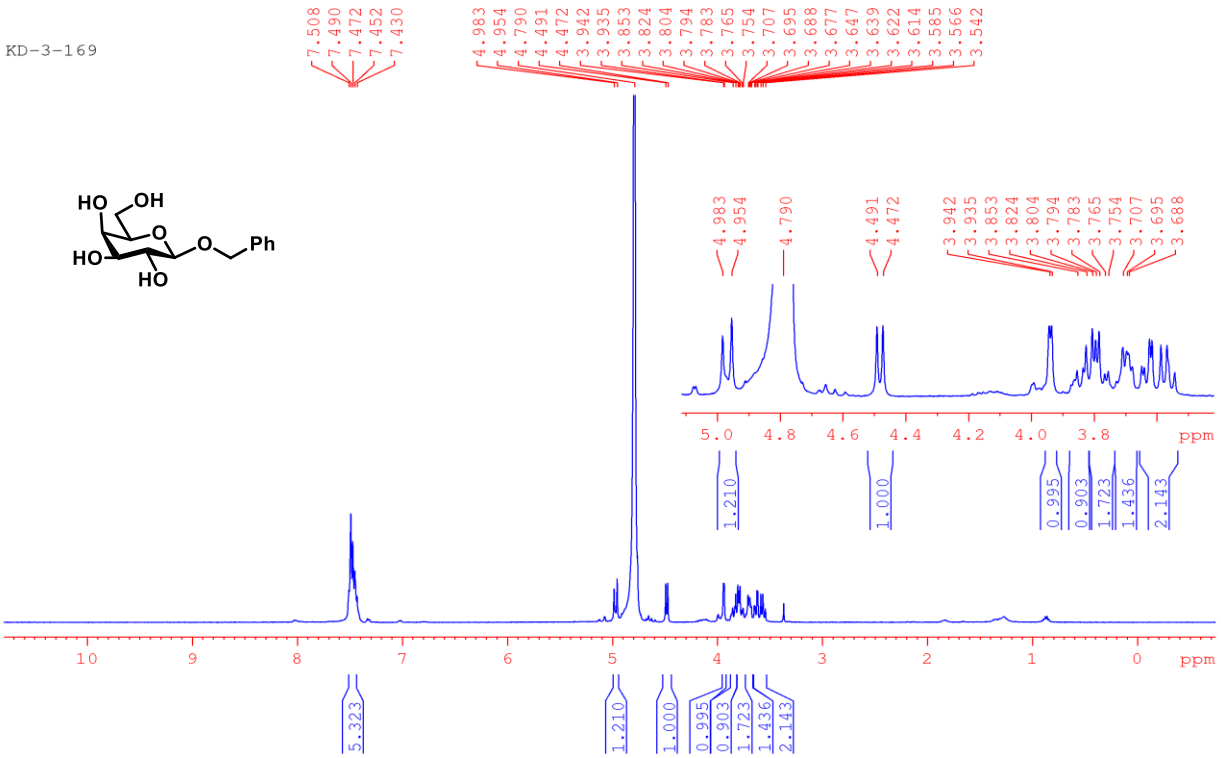

Figure S11. ^{1}H NMR spectrum of 7 (D_2O, 400 MHz).

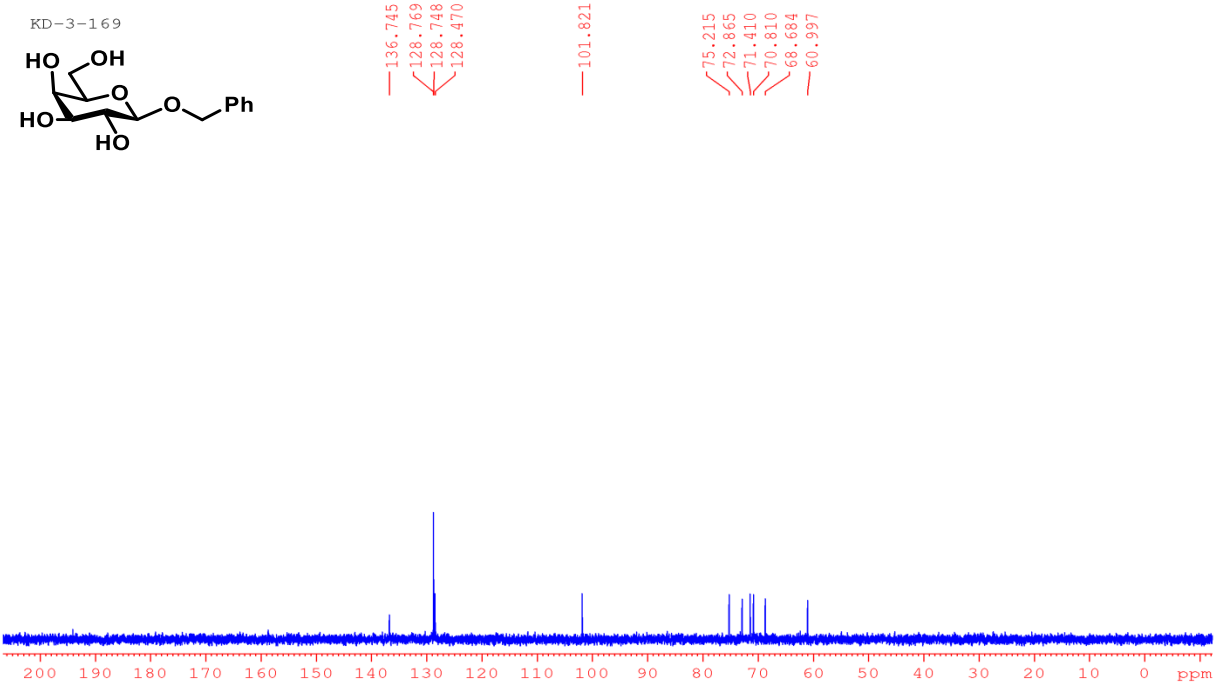

Figure S12. ^{13}C NMR spectrum of **7** (D_2O, 100 MHz).

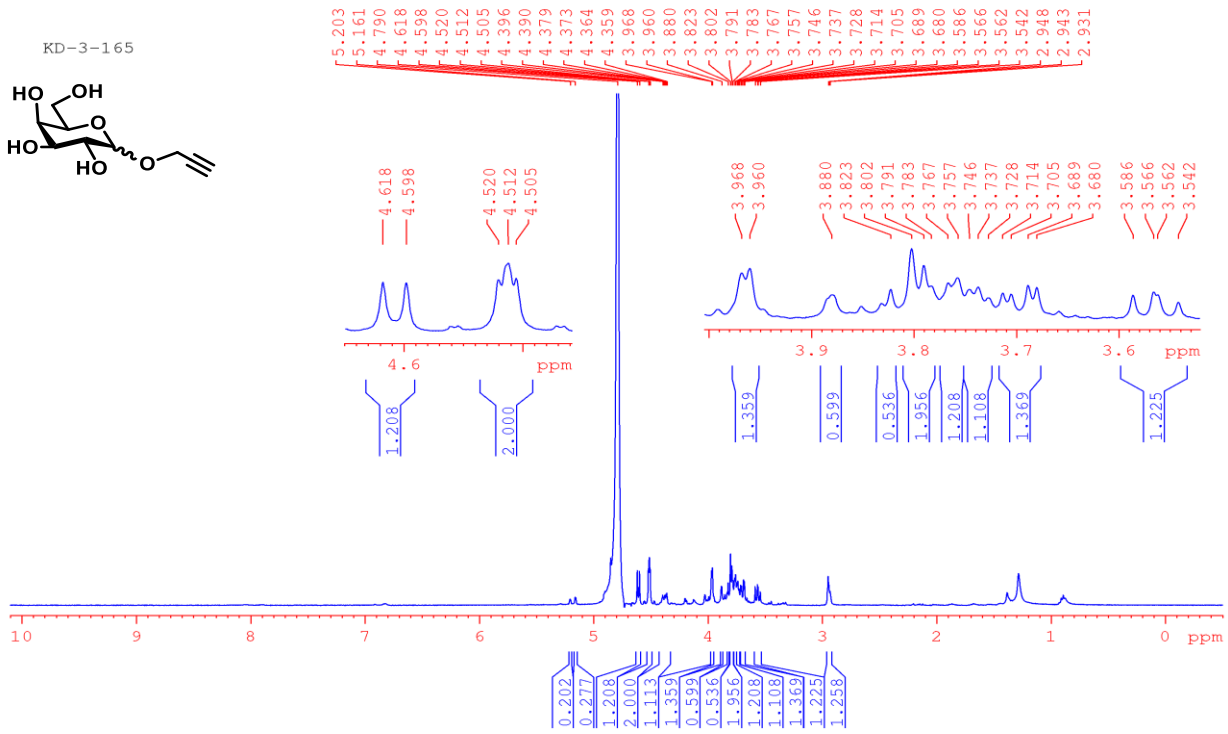

Figure S13. ^{1}H NMR spectrum of **8** (D_2O, 400 MHz).

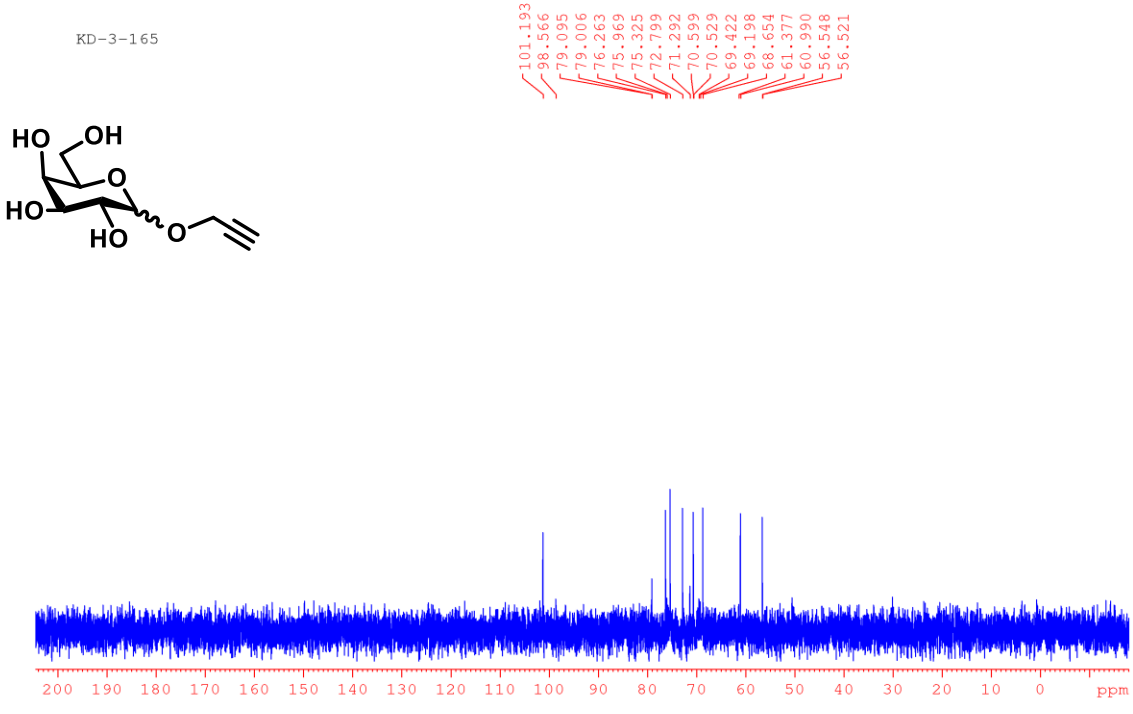

Figure S14. ^{13}C NMR spectrum of **8** (D_2O, 100 MHz).

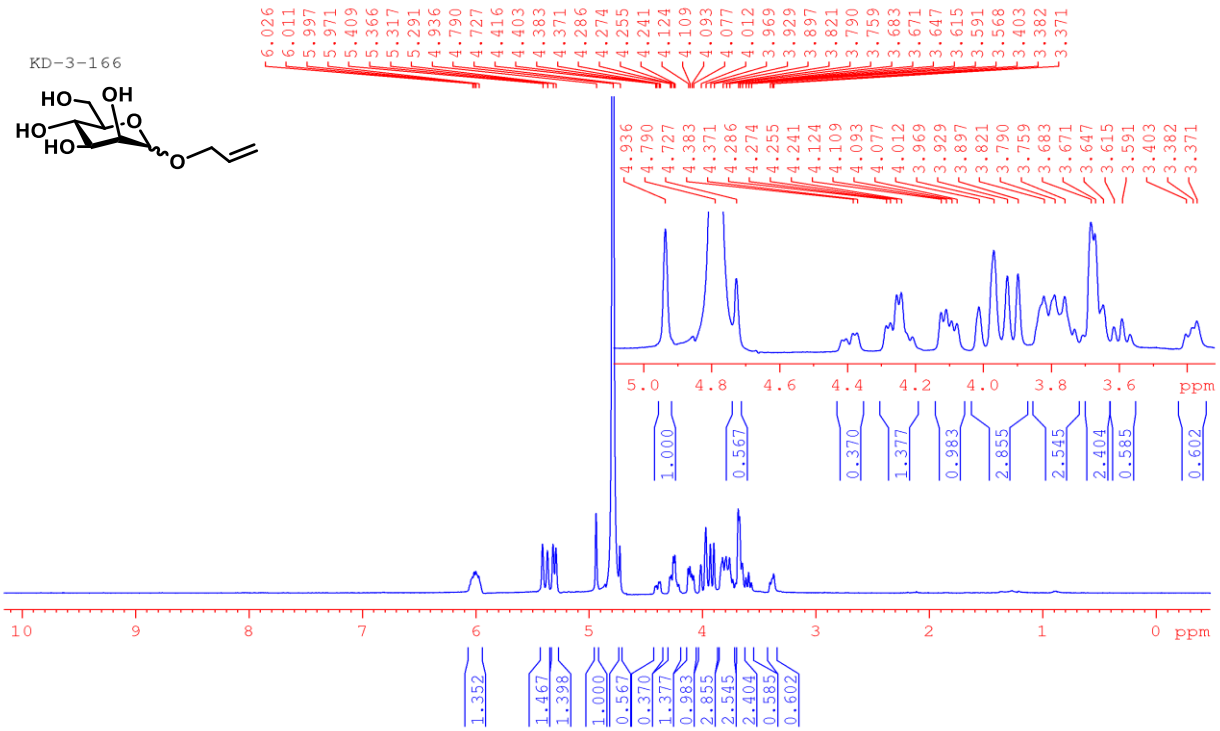

Figure S15. ^{1}H NMR spectrum of **9** (D_2O, 400 MHz).

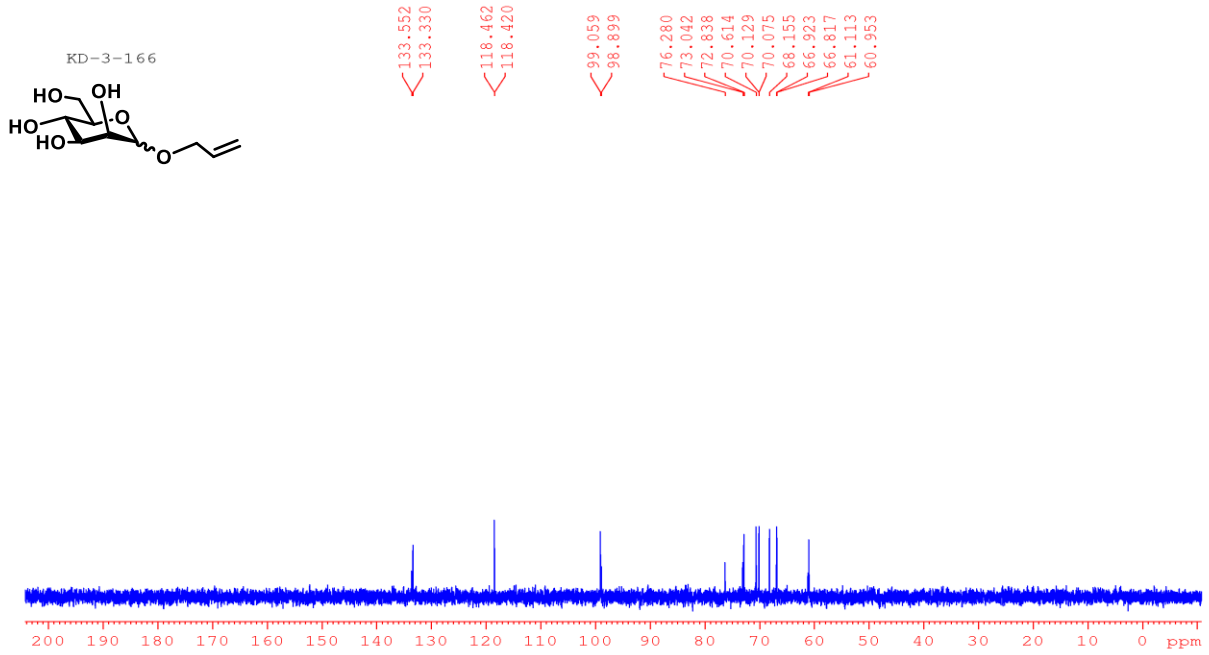

Figure S16. ^{13}C NMR spectrum of **9** (D_2O, 100 MHz).

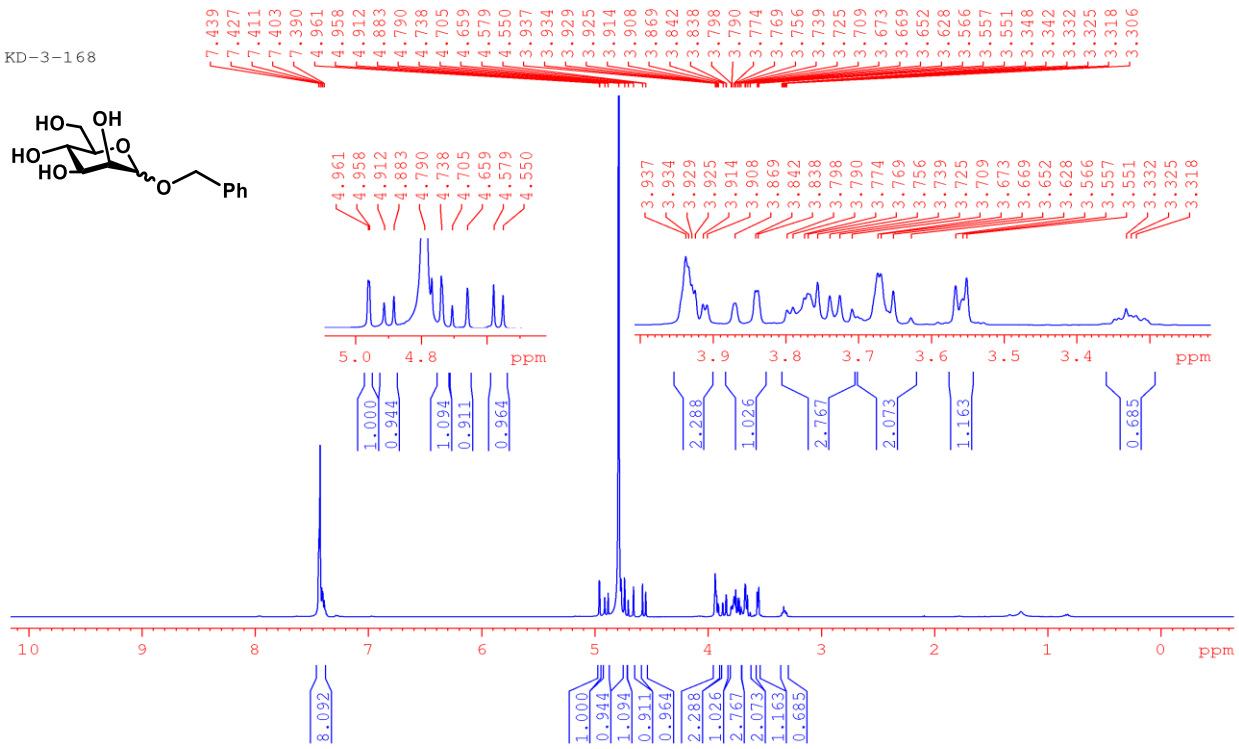

Figure S17. ^{1}H NMR spectrum of **10** (D_2O, 400 MHz).

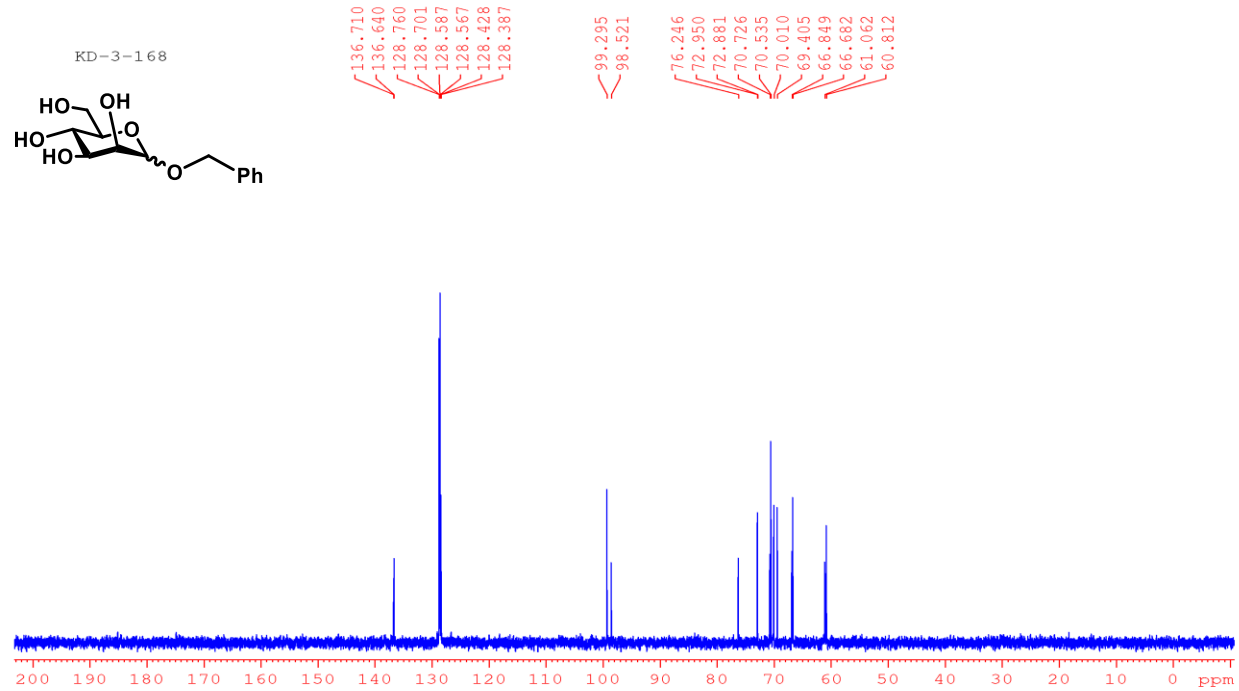

Figure S18. ^{13}C NMR spectrum of **10** (D_2O, 100 MHz).

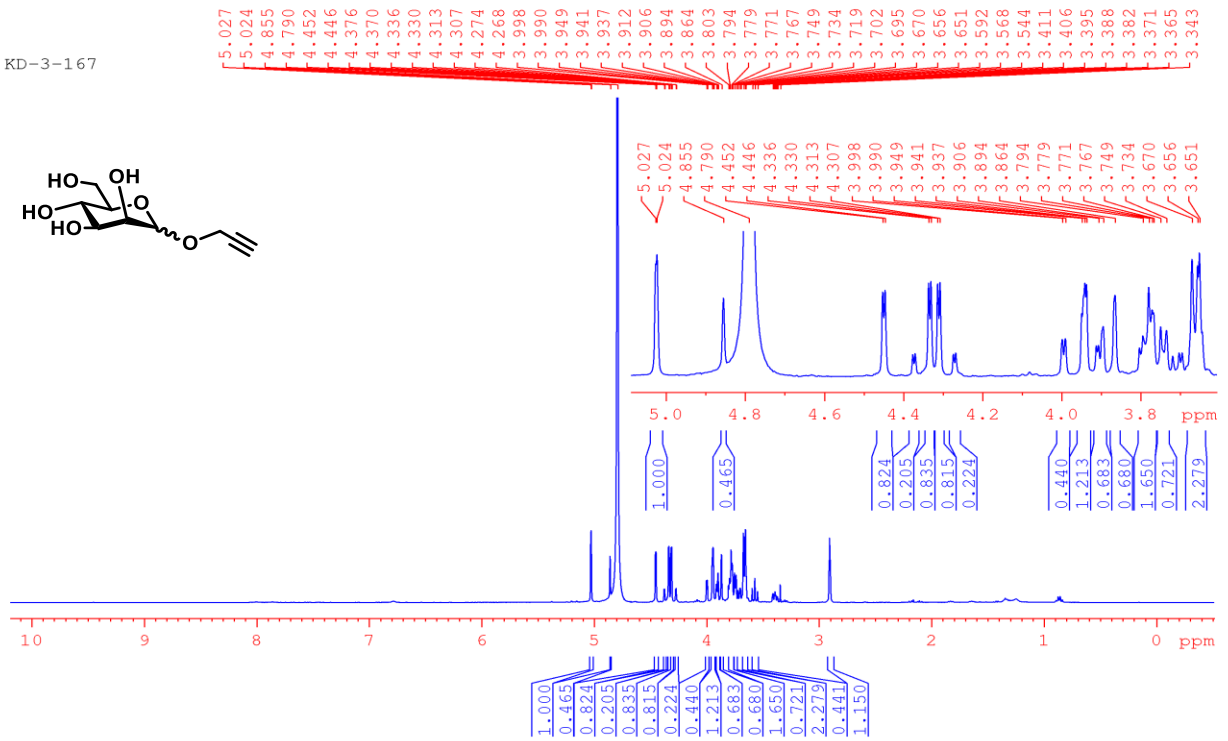

Figure S19. ^{1}H NMR spectrum of **11** (D_2O, 400 MHz).

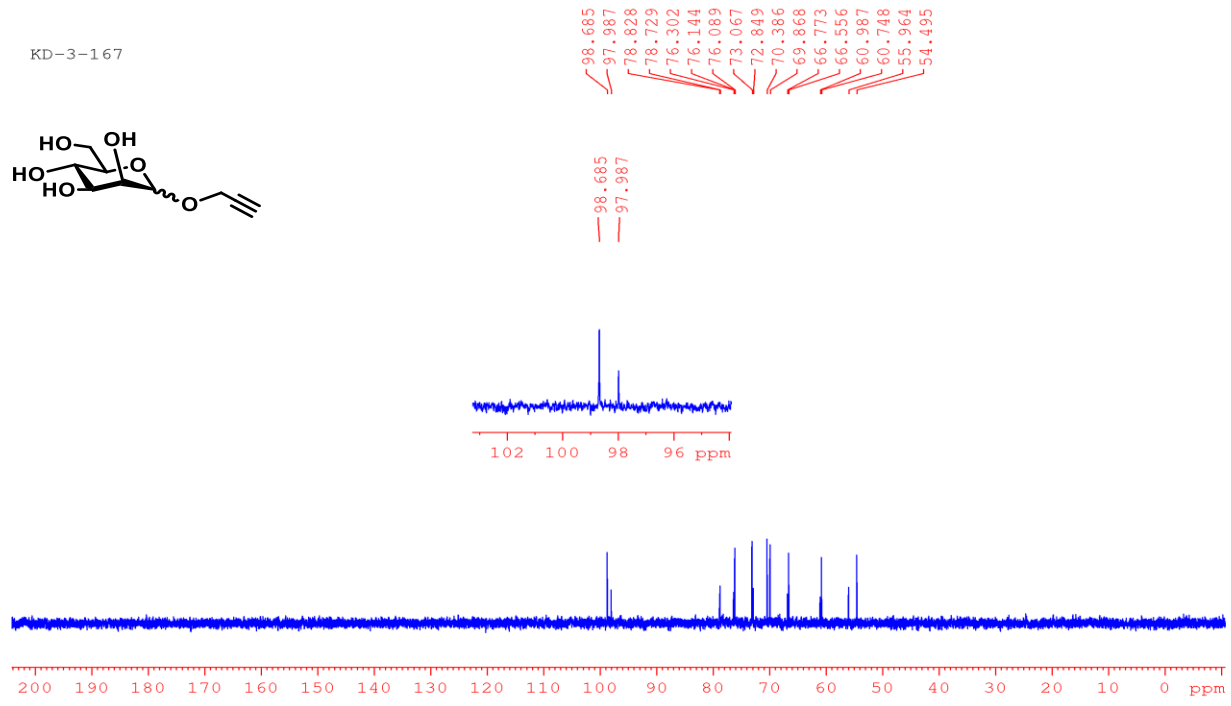

Figure S20. ^{13}C NMR spectrum of **11** (D_2O, 100 MHz).

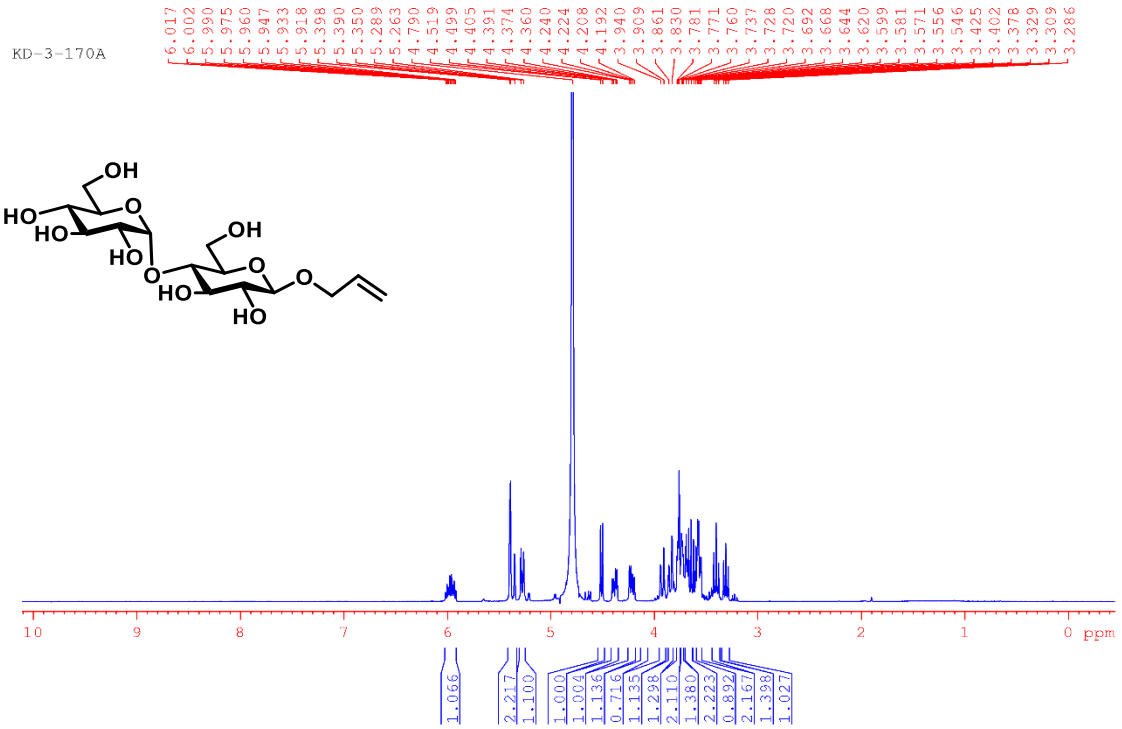

Figure S21. ^{1}H NMR spectrum of **12** (D_2O, 400 MHz).

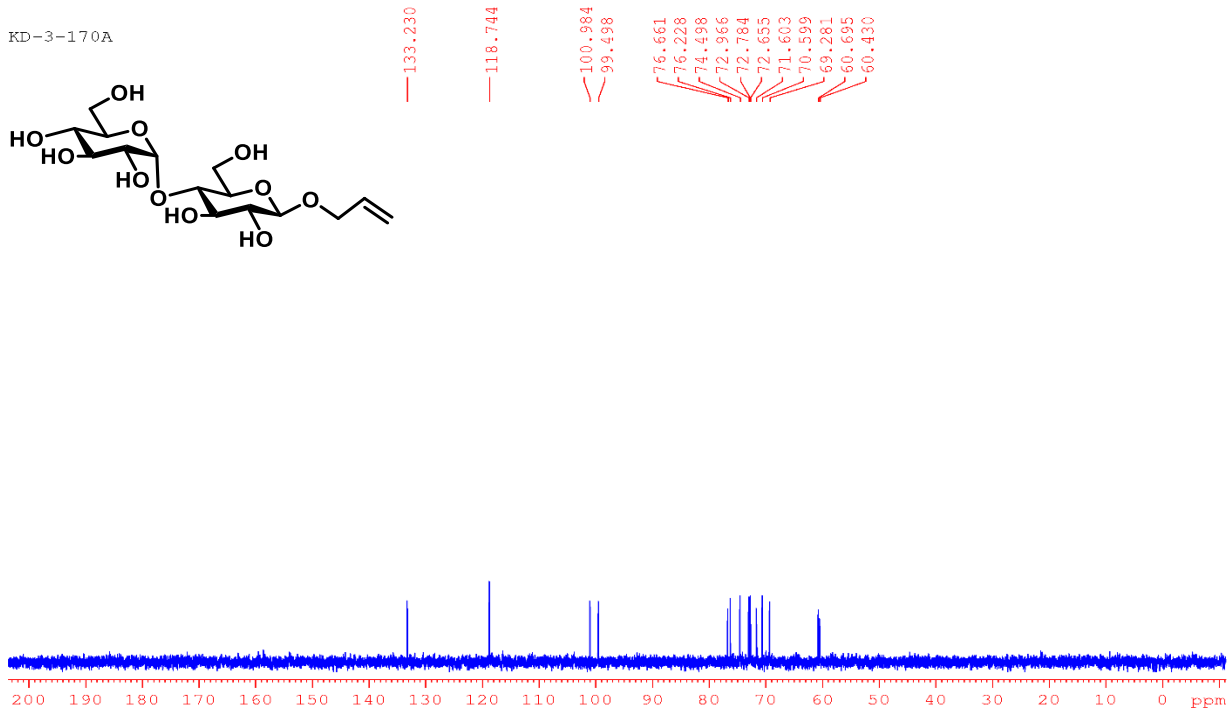

Figure S22. ^{13}C NMR spectrum of **12** (D_2O, 100 MHz).

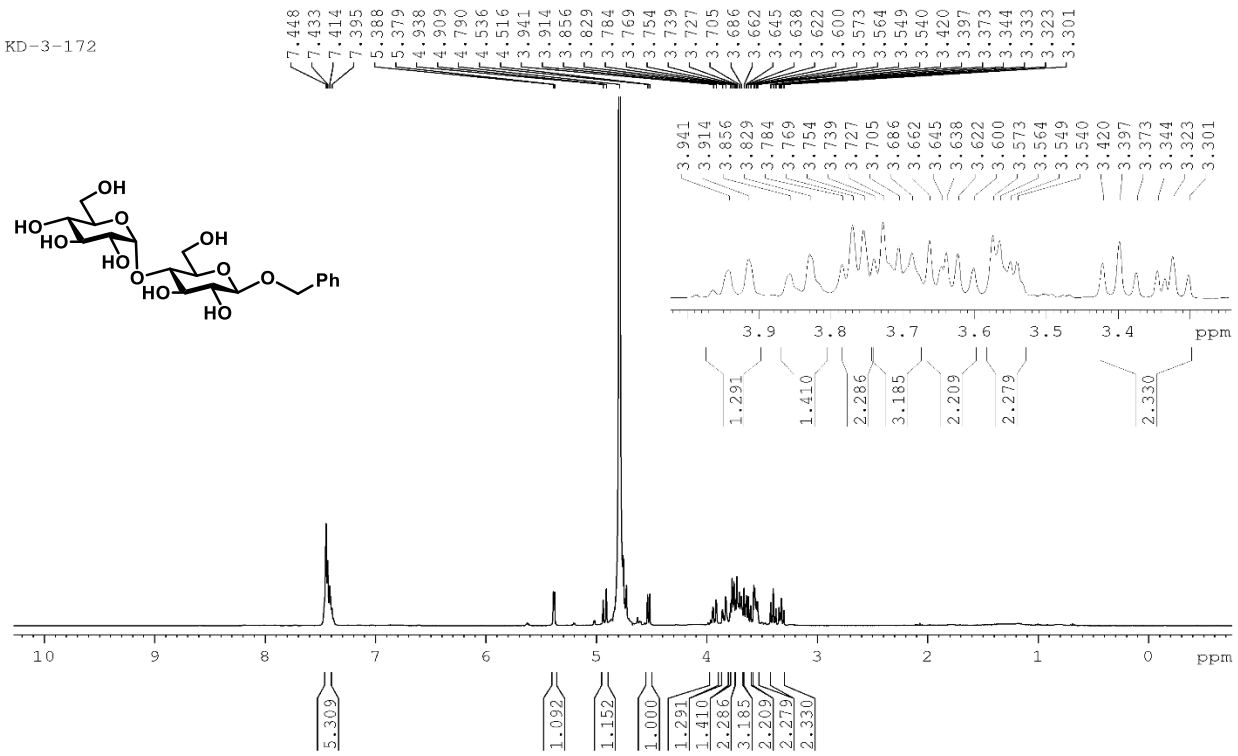

Figure S23. ^{1}H NMR spectrum of **13** (D_2O, 400 MHz).

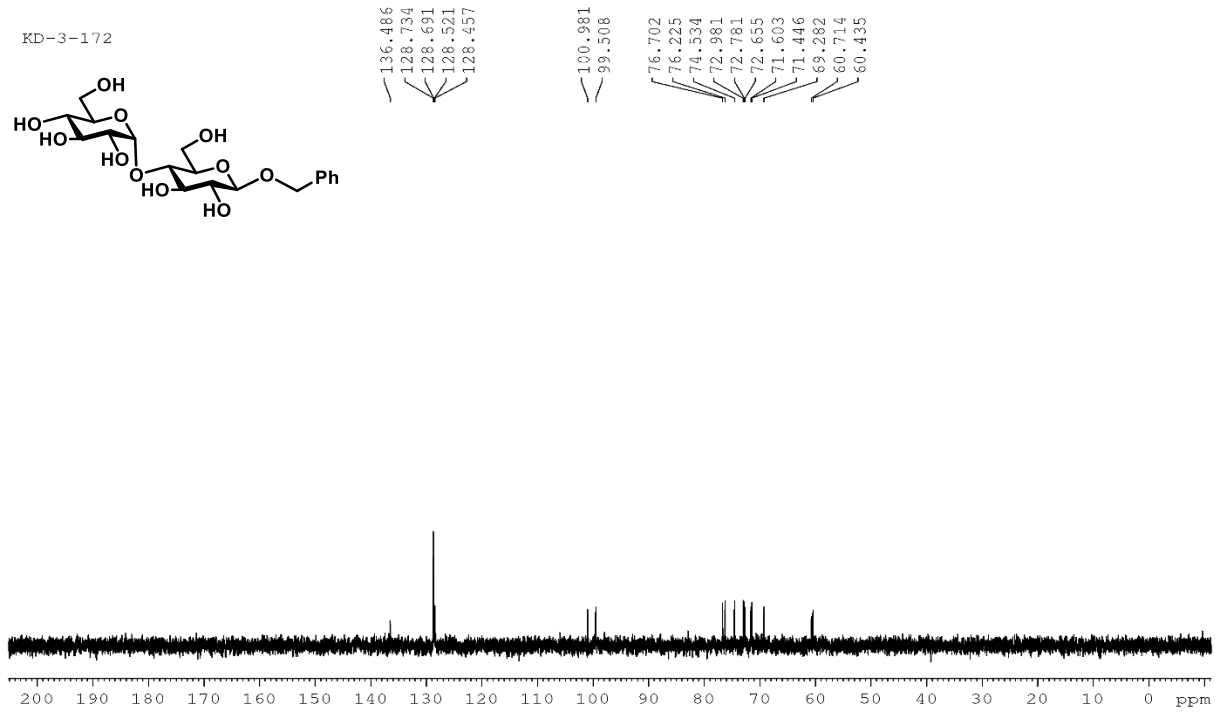

Figure S24. ^{13}C NMR spectrum of **13** (D_2O, 100 MHz).

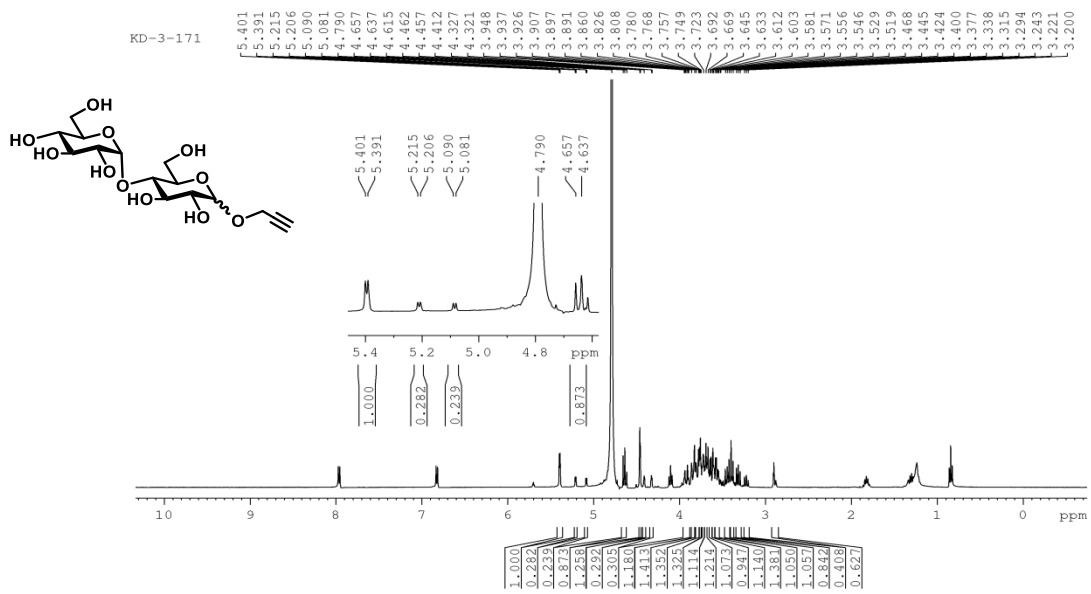

Figure S25. ^{1}H NMR spectrum of **14** (D_2O, 400 MHz). Resonances at 7.96, 6.82, 4.10, 1.82, 1.25 and 0.84 correspond to reagent **1**.

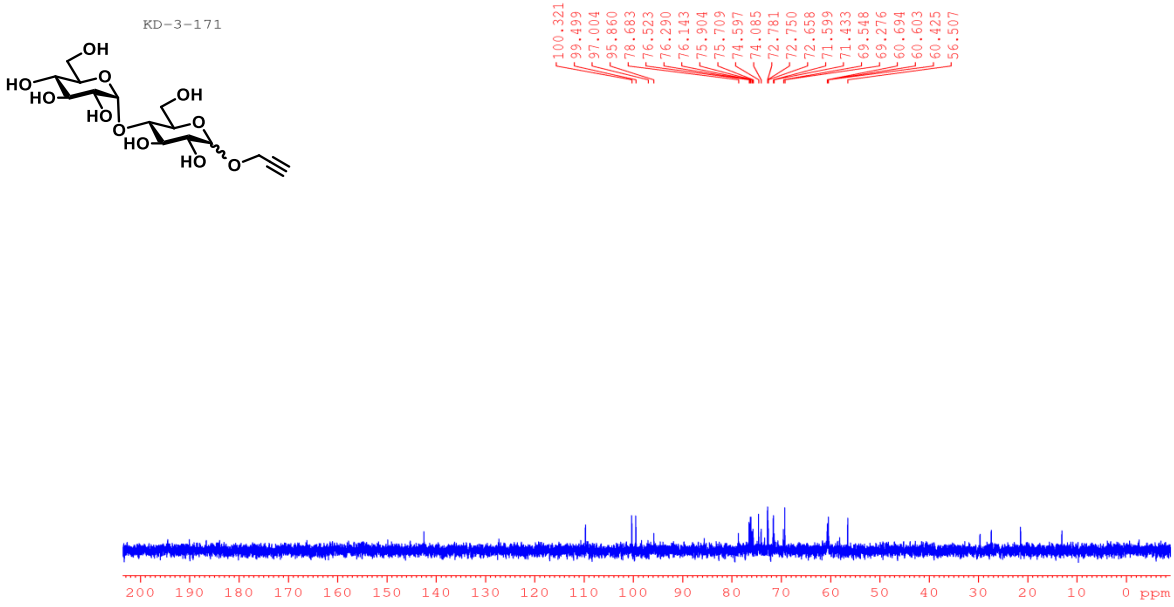

Figure S26. ^{13}C NMR spectrum of **14** (D_2O, 100 MHz). Resonances at 142.5, 109.7, 58.1, 29.6, 27.4, 21.4 and 13.0 correspond to reagent **1**.

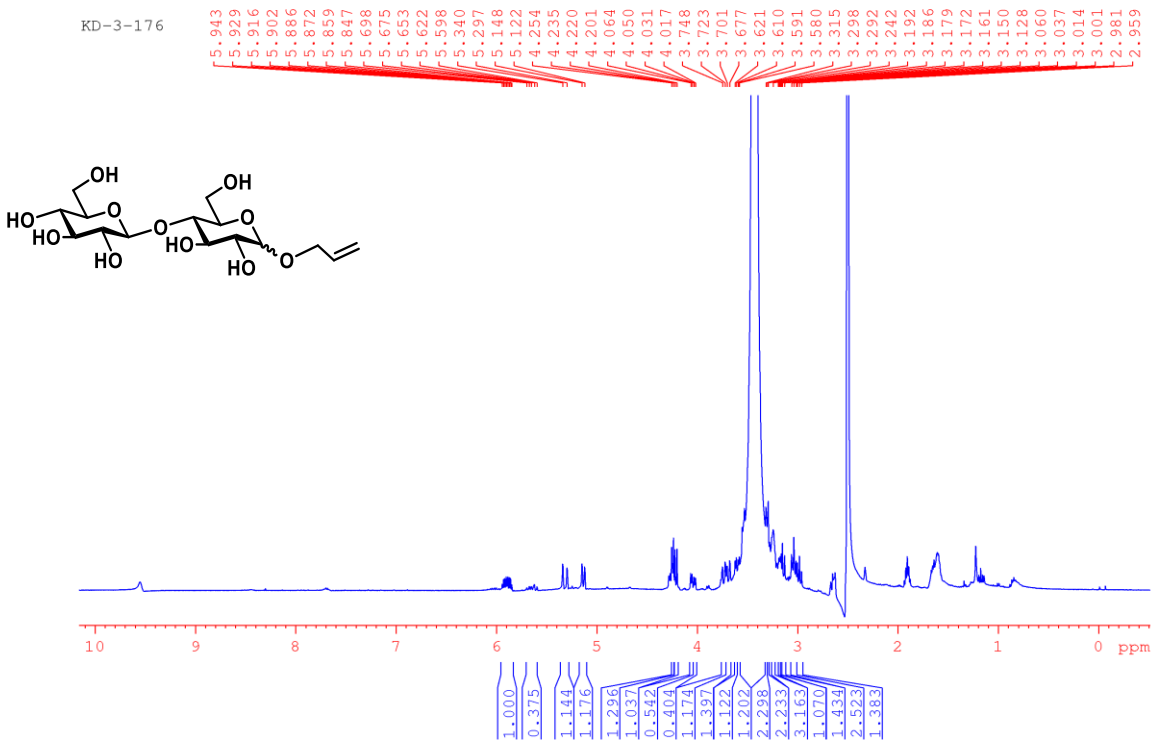

Figure S27. ^{1}H NMR spectrum of **15** (DMSO-d_6, 400 MHz).

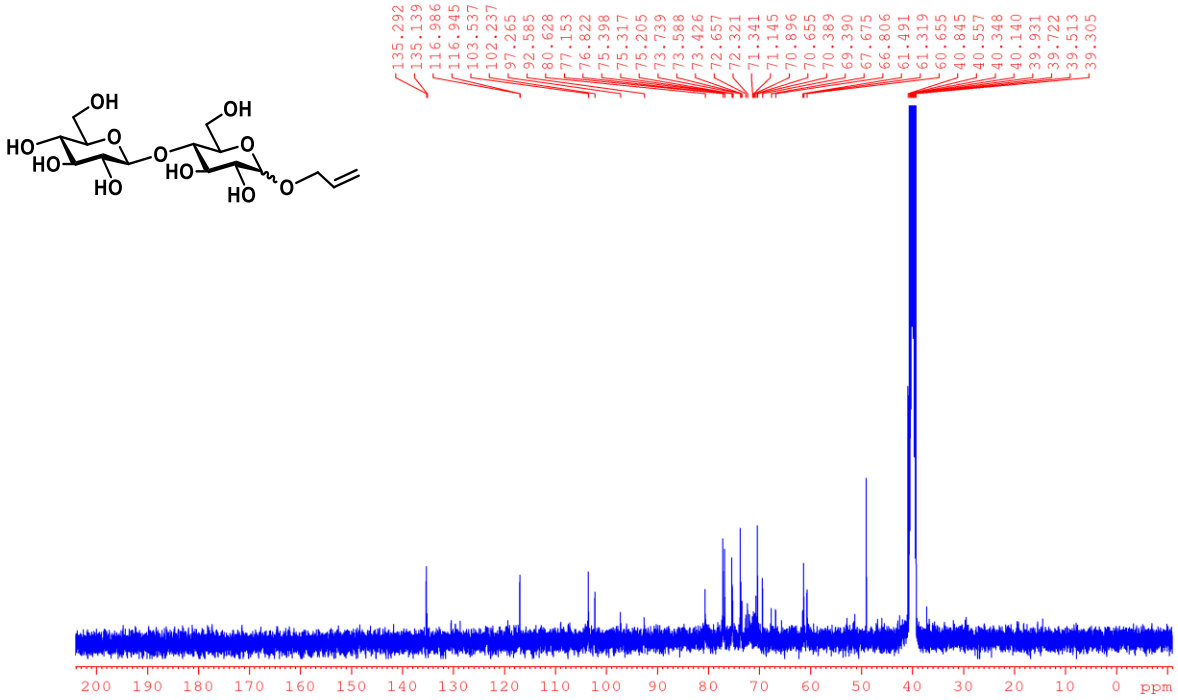

Figure S28. ^{13}C NMR spectrum of **15** (DMSO-d_6, 100 MHz).

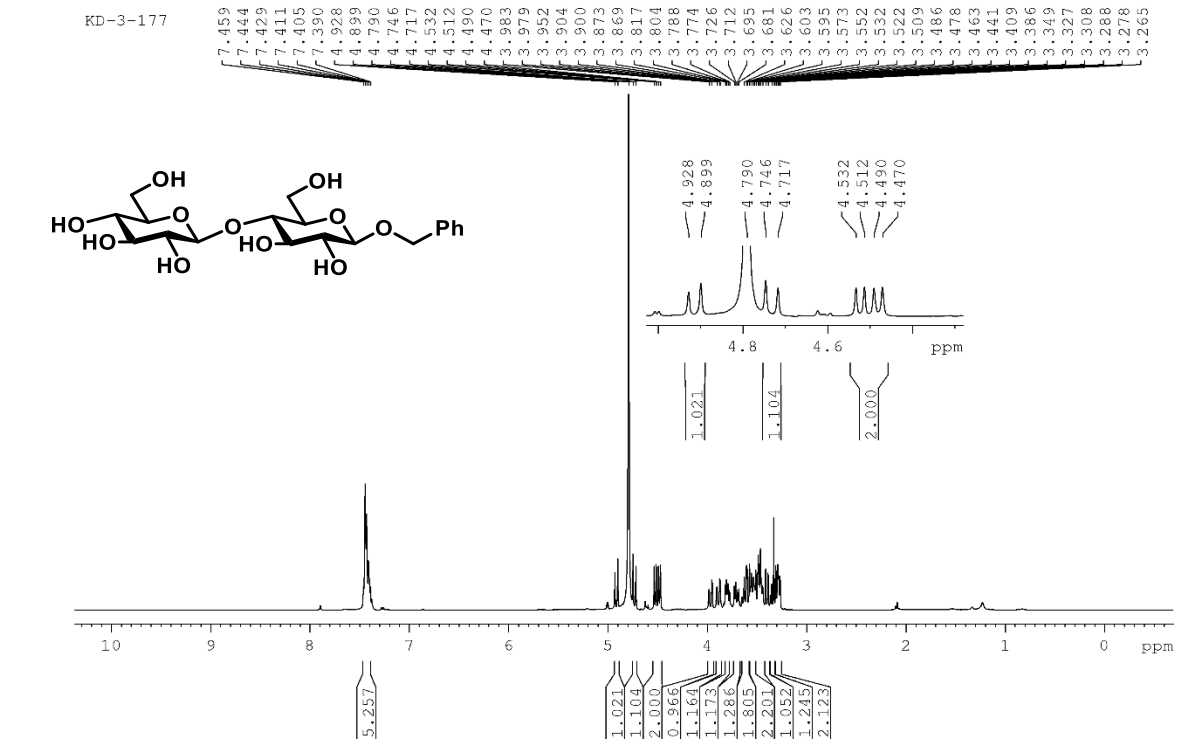

Figure S29. ^{1}H NMR spectrum of **16** (D_2O, 400 MHz).

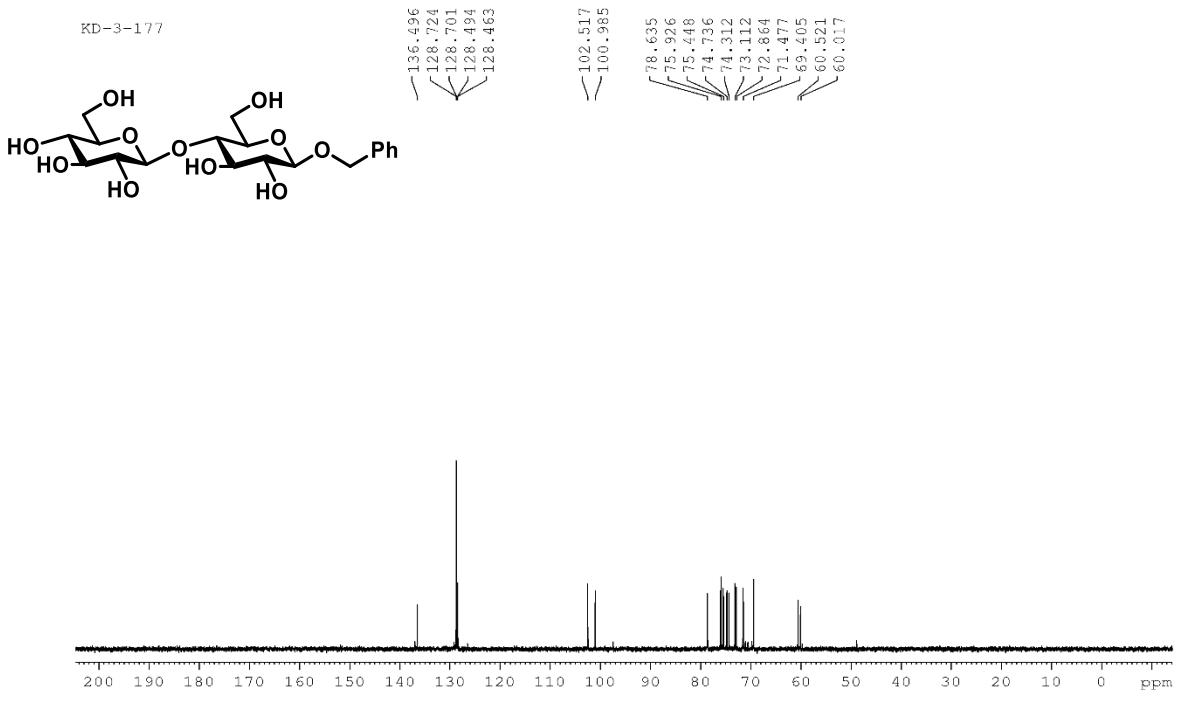

Figure S30. ^{13}C NMR spectrum of **16** (D_2O, 100 MHz).

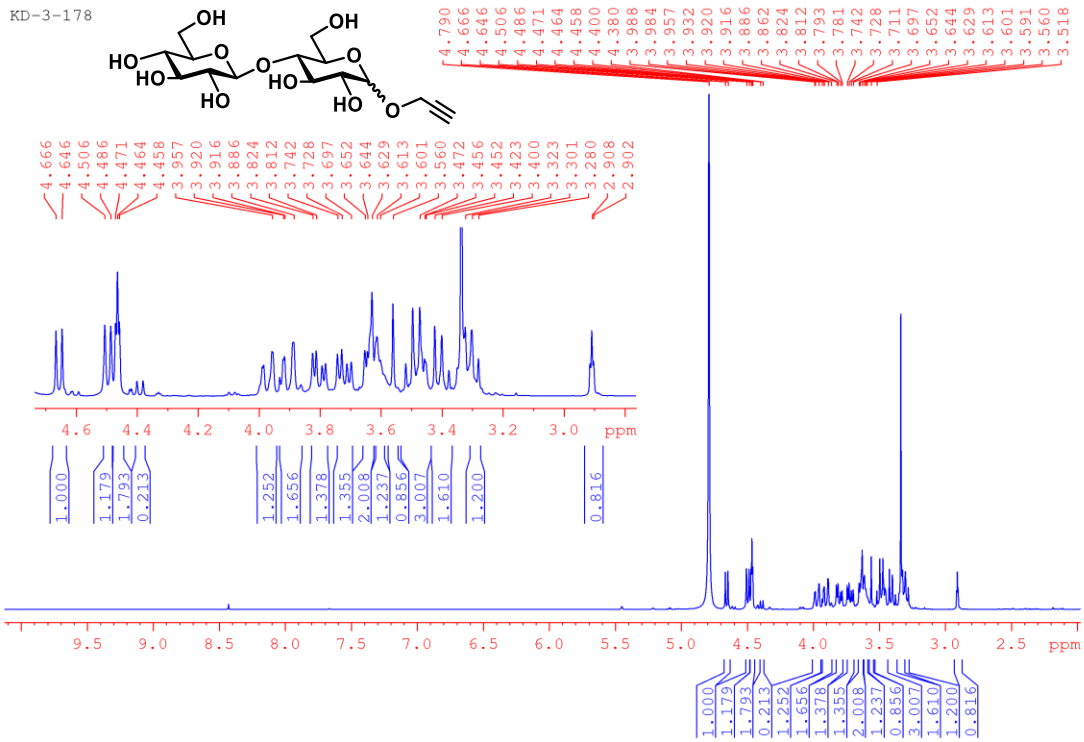

Figure S31. ^{1}H NMR spectrum of **17** (D_2O, 400 MHz).

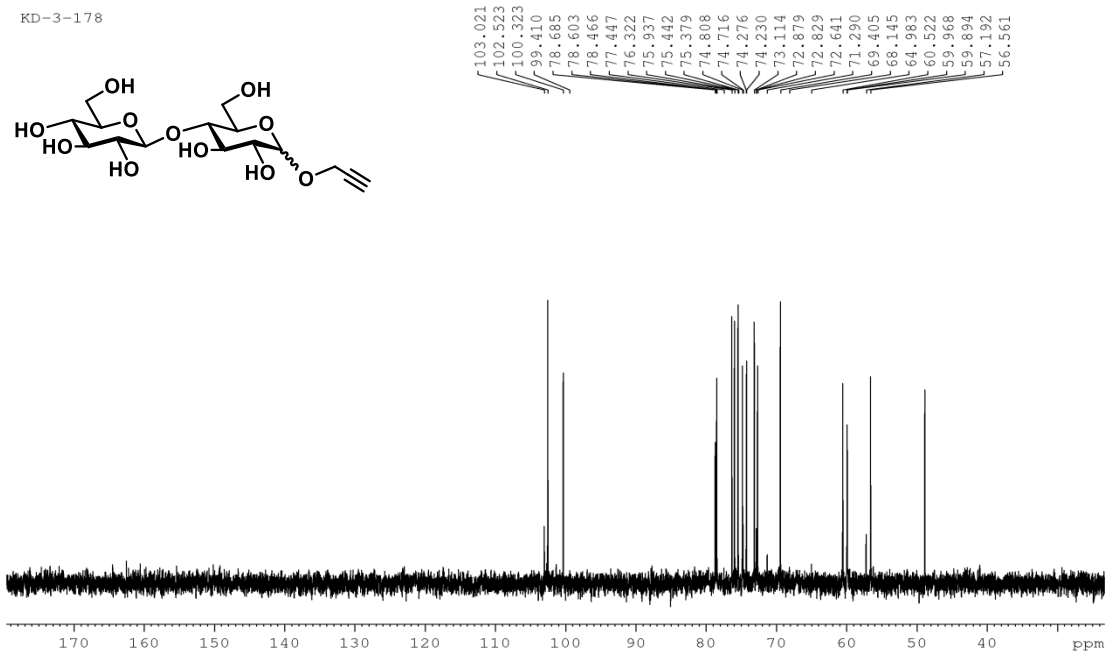

Figure S32. ^{13}C NMR spectrum of **17** (D_2O, 100 MHz).

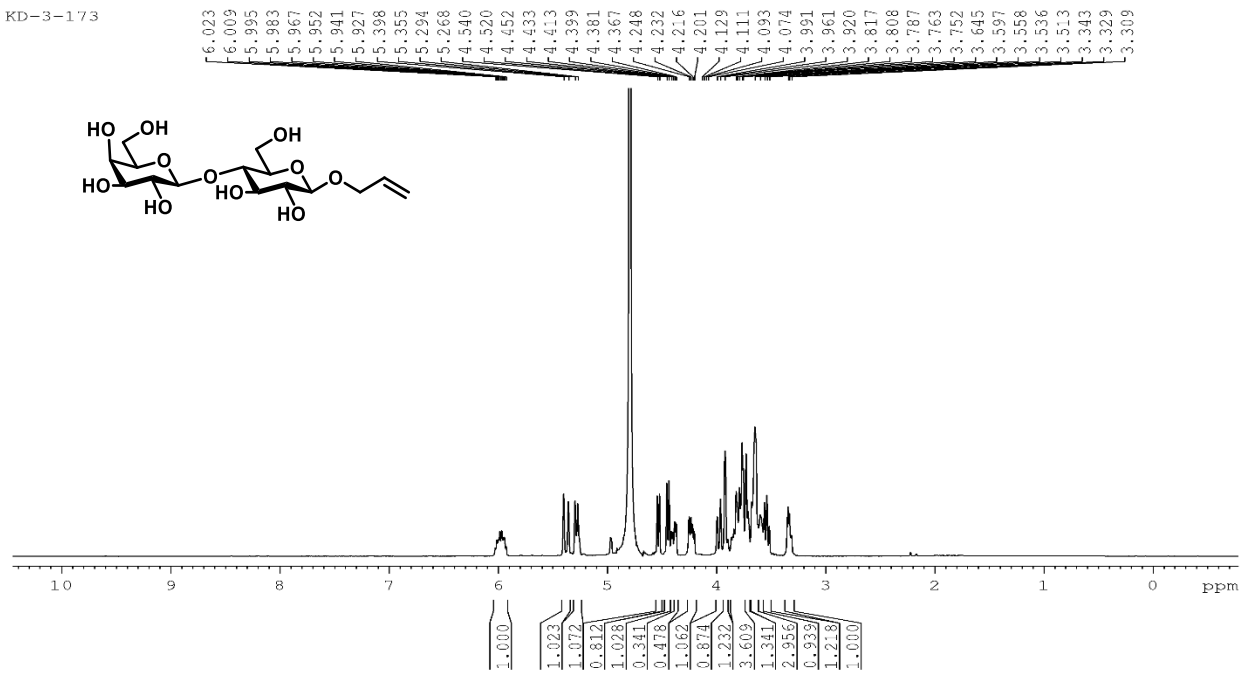

Figure S33. ^{1}H NMR spectrum of **18** (D_2O, 400 MHz).

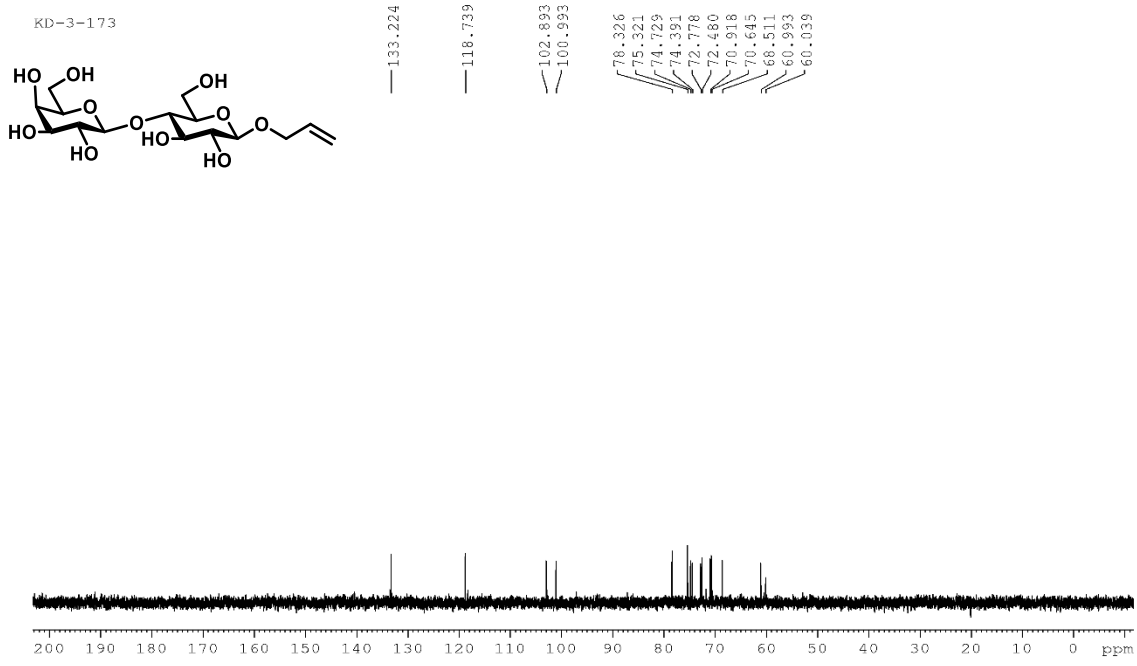

Figure S34. ^{13}C NMR spectrum of **18** (D_2O, 100 MHz).

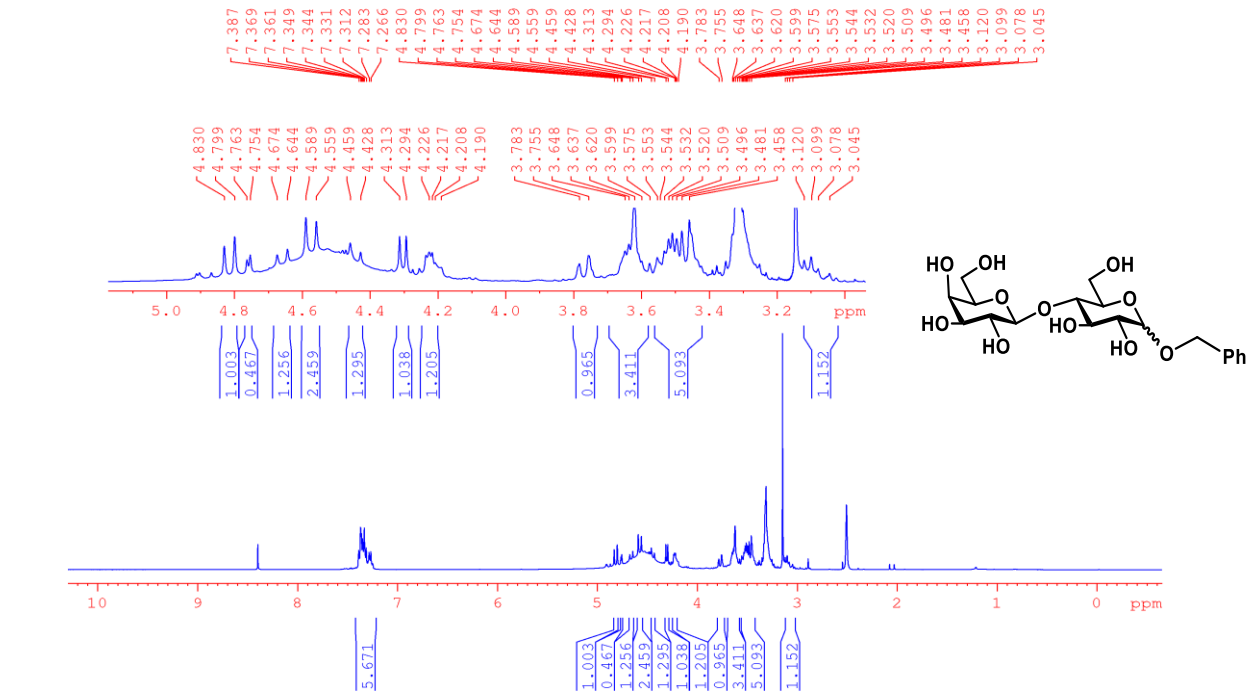

Figure S35. ^{1}H NMR spectrum of **19** (DMSO-d_6, 400 MHz).

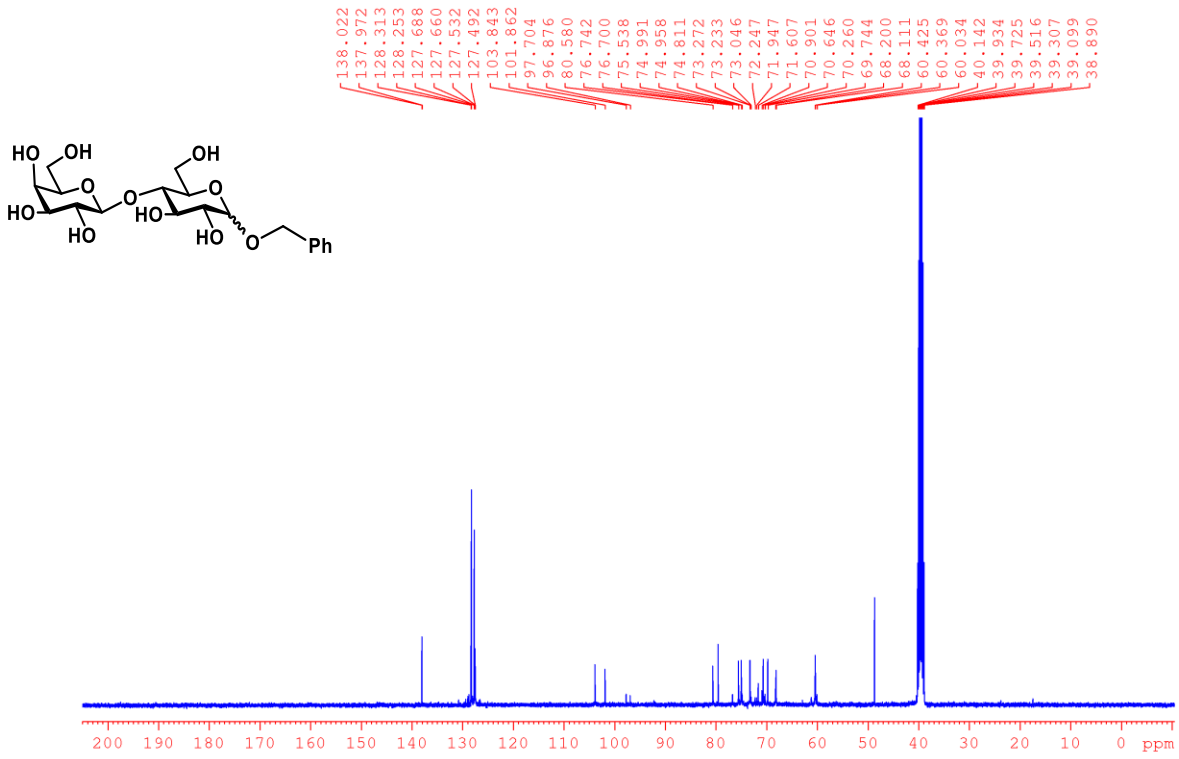

Figure S36. ^{13}C NMR spectrum of **19** (DMSO-d_6, 100 MHz).

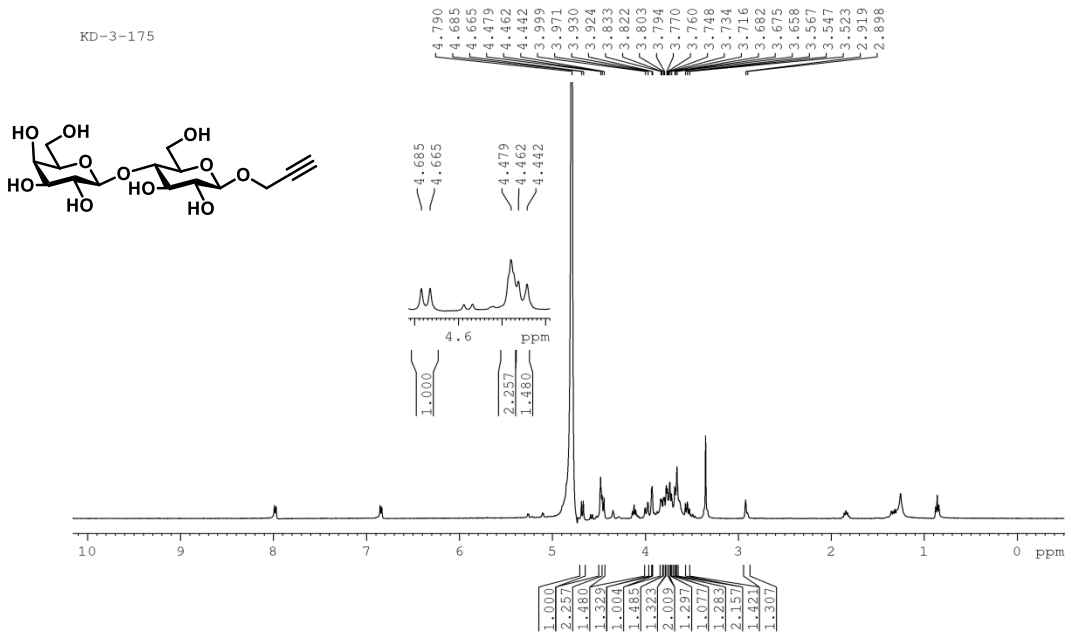

Figure S37. ^{1}H NMR spectrum of **20** (D_2O, 400 MHz). Resonances at 7.96, 6.82, 4.10, 1.82, 1.25 and 0.84 correspond to reagent **1**.

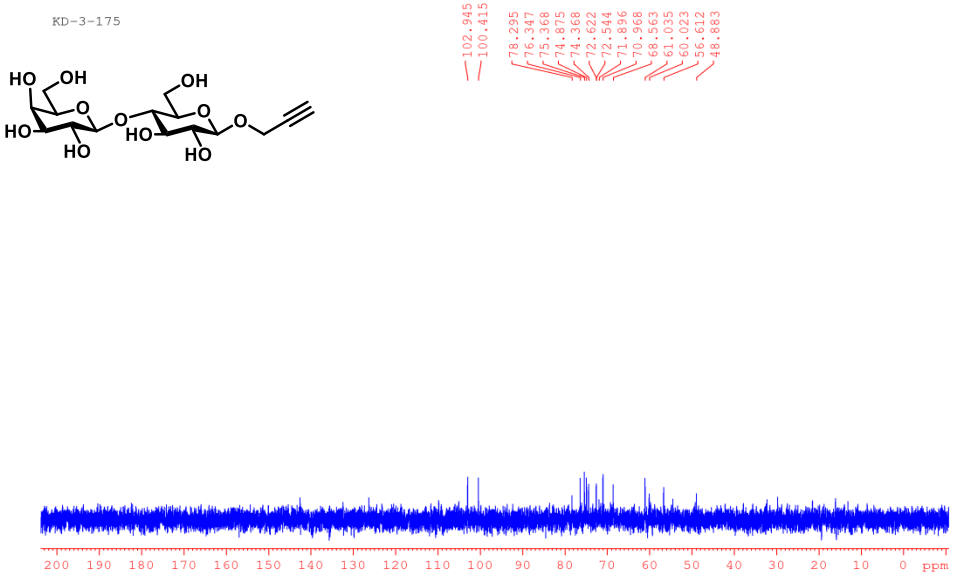

Figure S38. ^{13}C NMR spectrum of **20** (D_2O, 100 MHz). Resonances at 142.5, 109.7, 58.1, 29.6, 27.4, 21.4 and 13.0 correspond to reagent **1**.

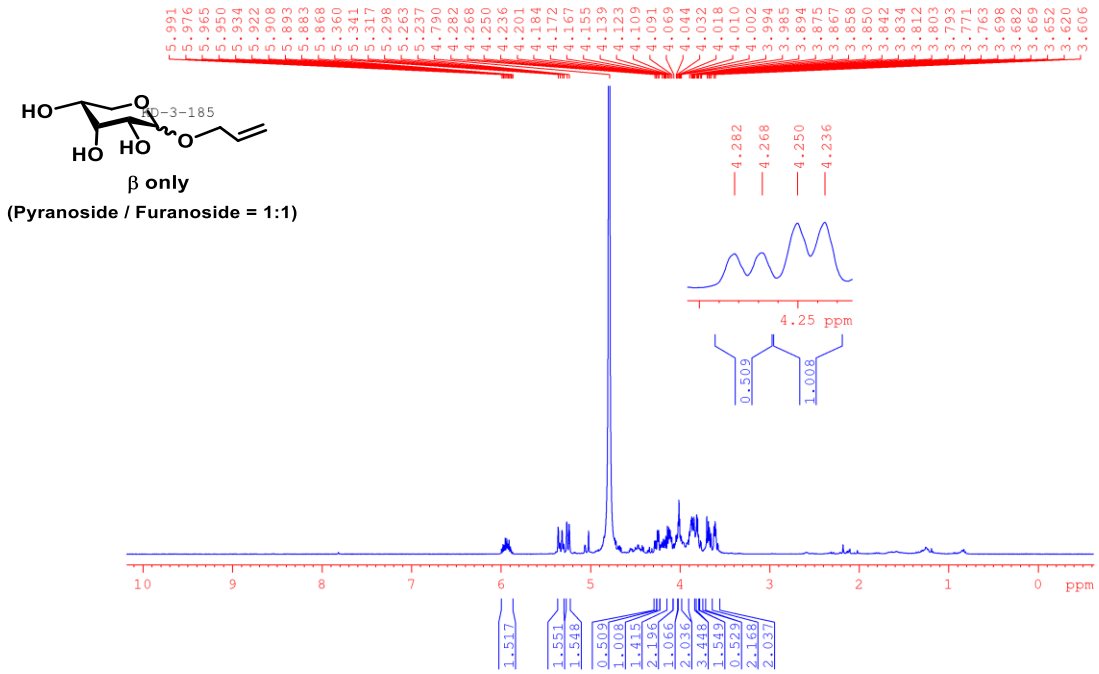

Figure S39. ^{1}H NMR spectrum of **21** (D_2O, 400 MHz).

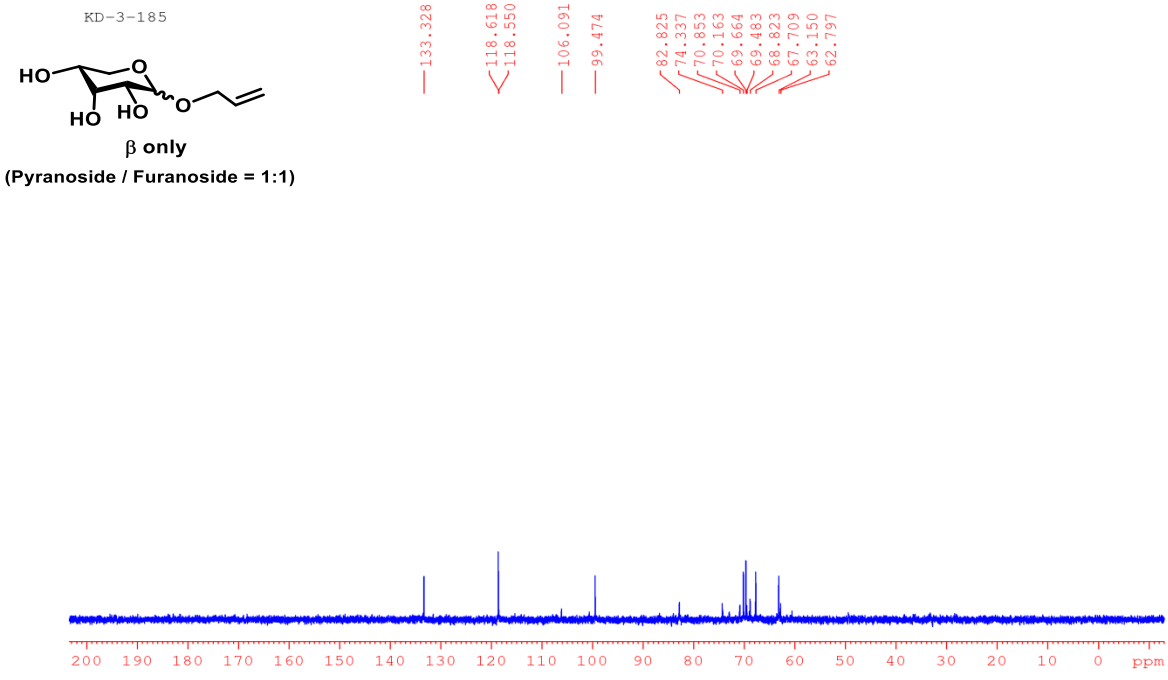

Figure S40. ^{13}C NMR spectrum of **21** (D_2O, 100 MHz).

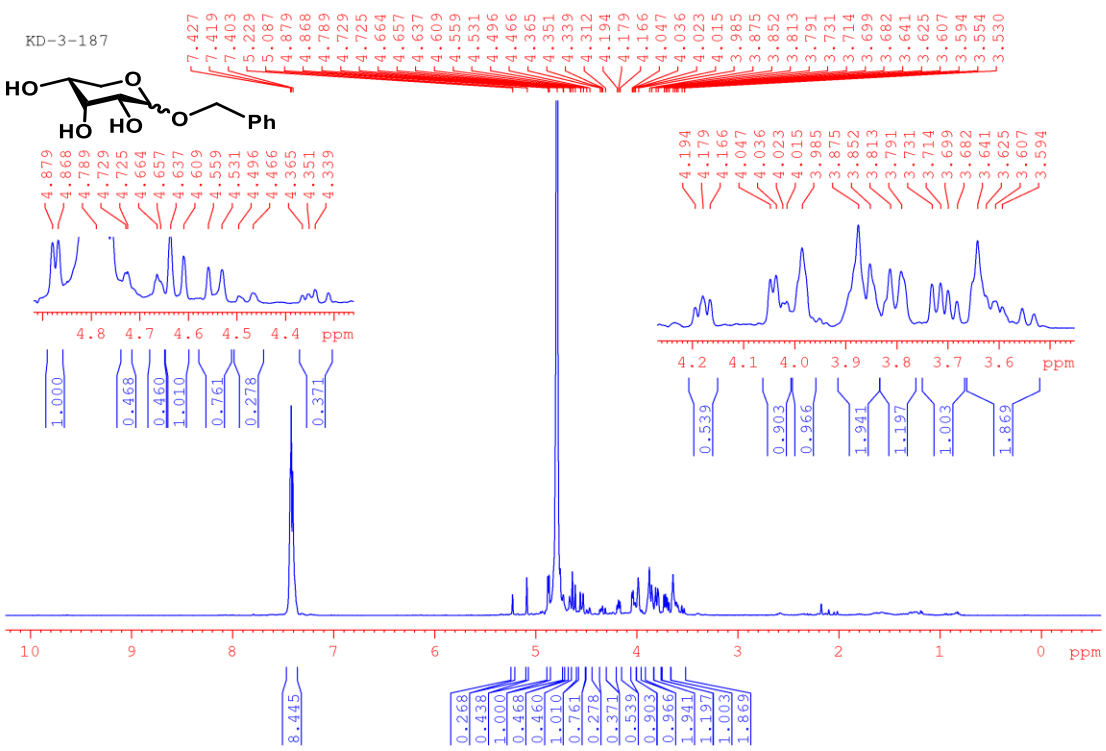

Figure S41. ^{1}H NMR spectrum of **22** (D_2O, 400 MHz).

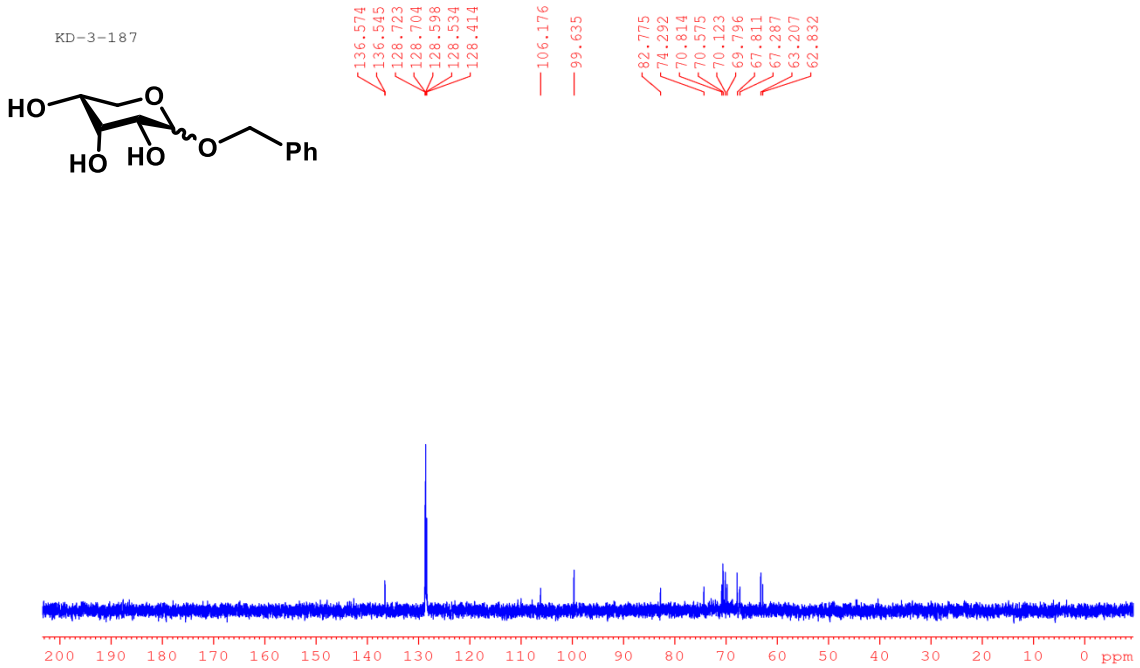

Figure S42. ^{13}C NMR spectrum of **22** (D_2O, 100 MHz).

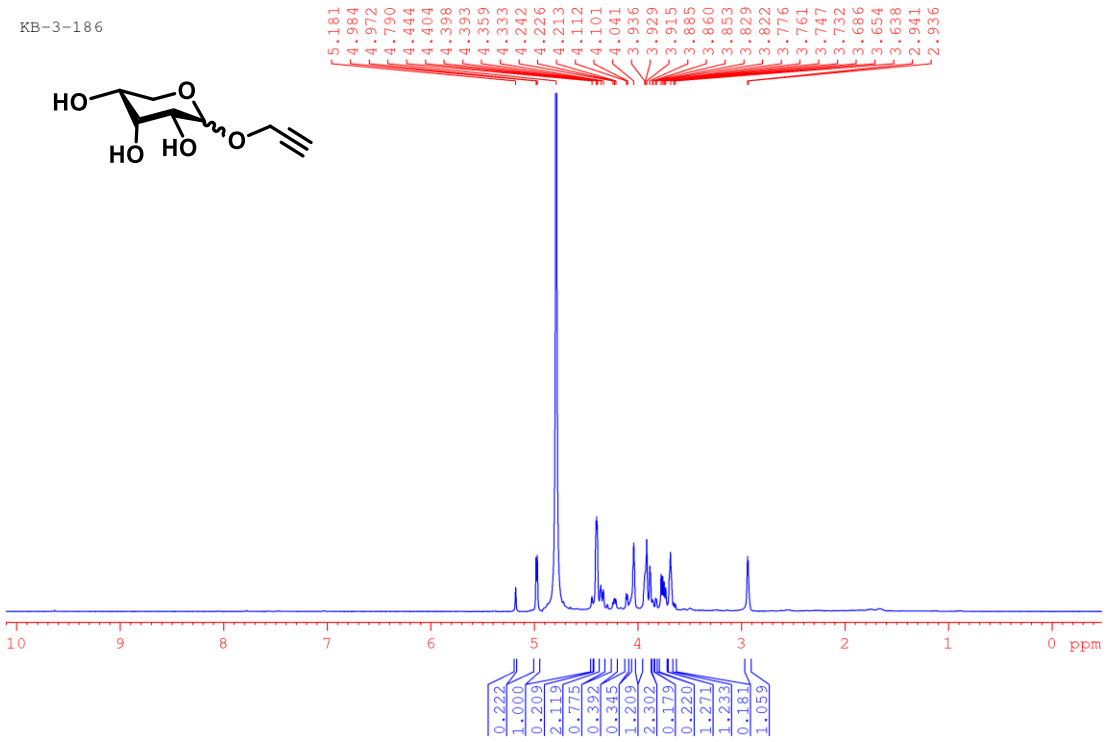

Figure S43. ^{1}H NMR spectrum of **23** (D_2O, 400 MHz).

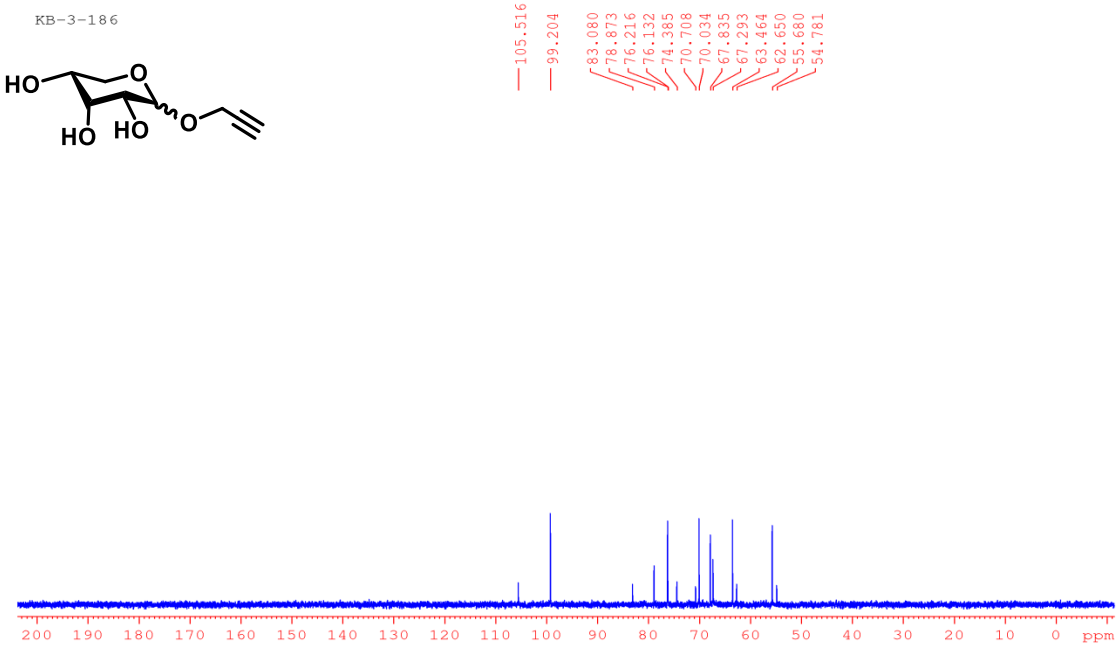

Figure S44. ^{13}C NMR spectrum of **23** (D_2O, 100 MHz).

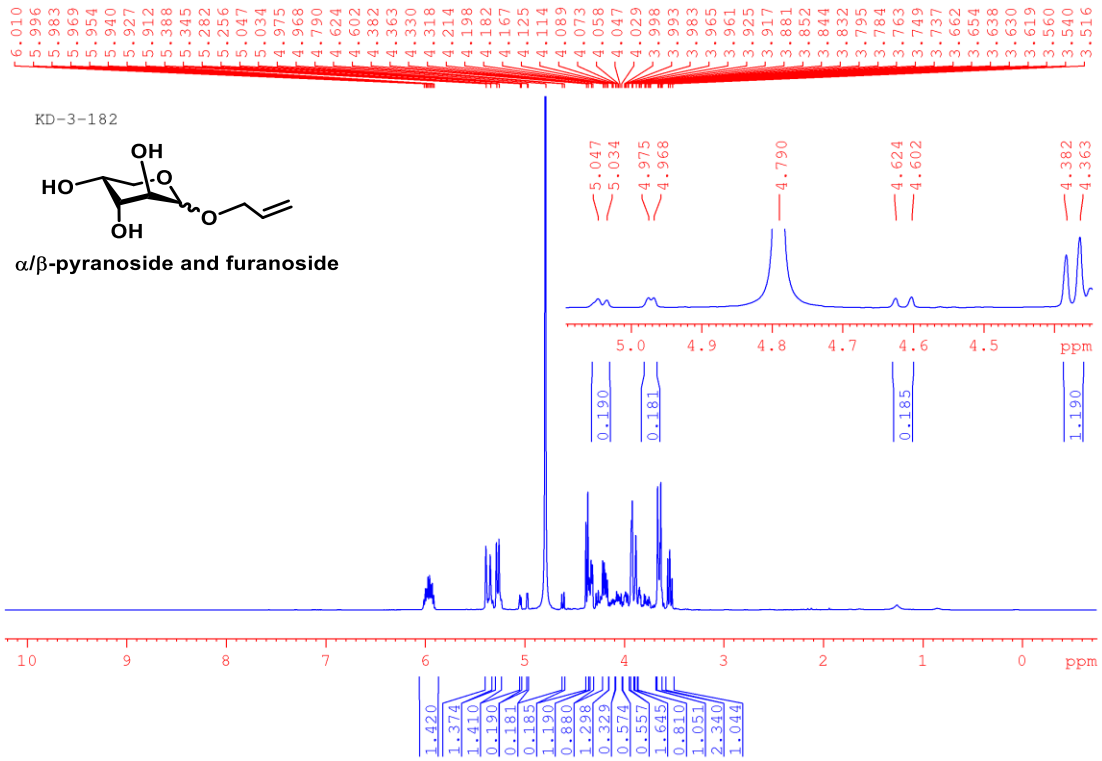

Figure S45. ^{1}H NMR spectrum of **24** (D_2O, 400 MHz).

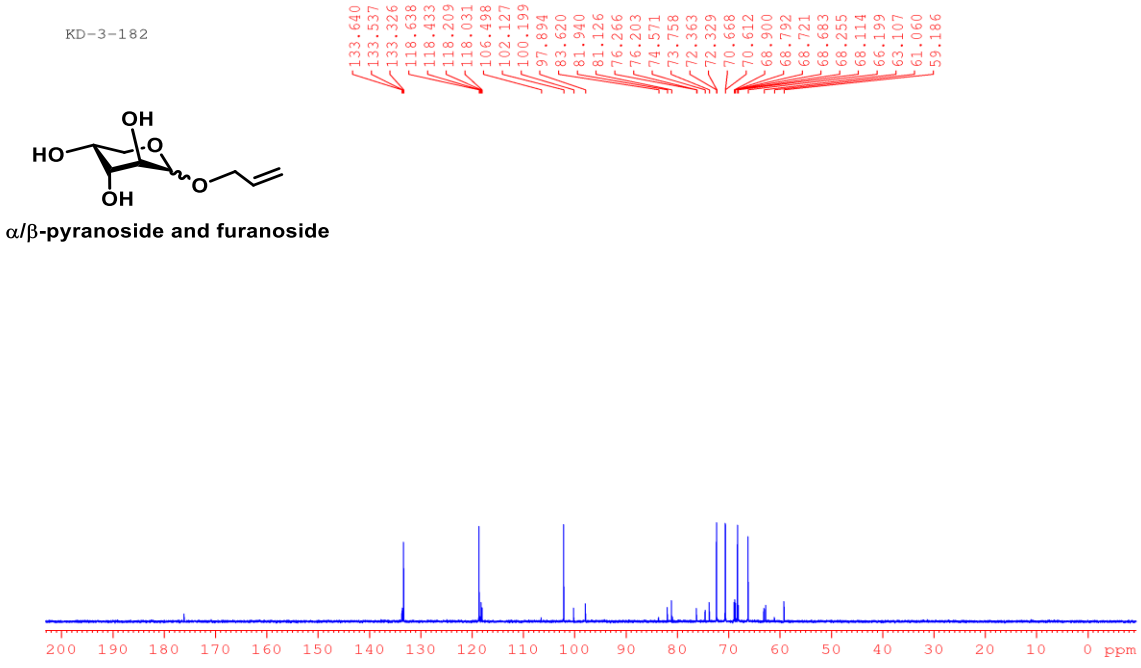

Figure S46. ^{13}C NMR spectrum of **24** (D_2O, 100 MHz).

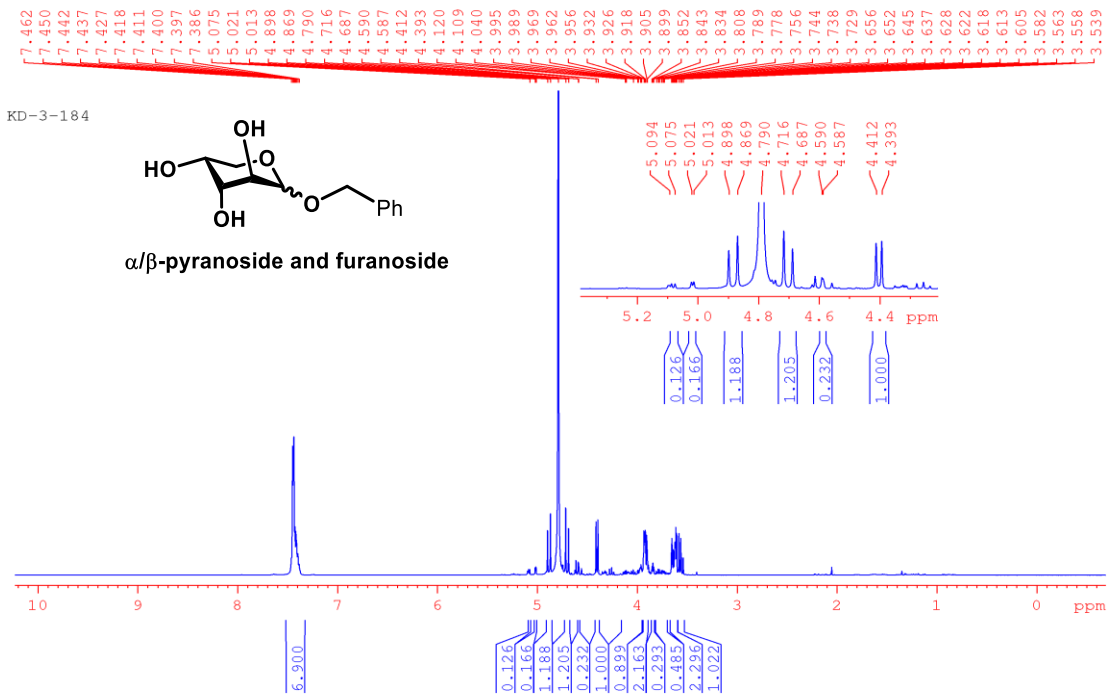

Figure S47. ^{1}H NMR spectrum of **25** (D_2O, 400 MHz).

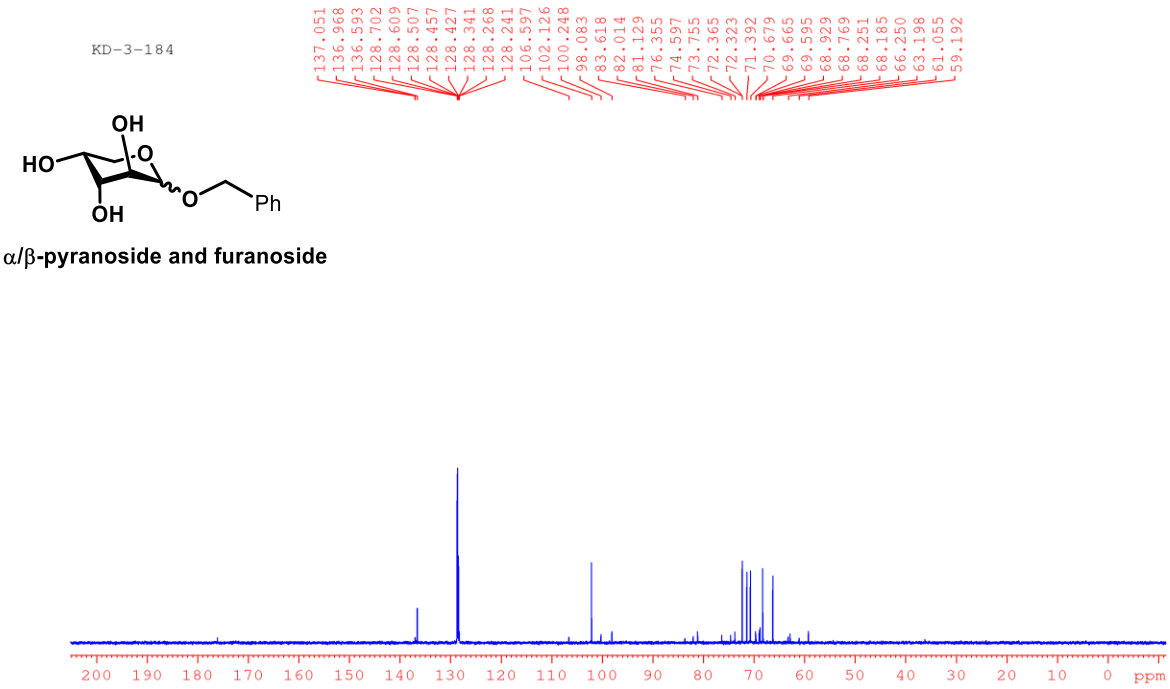

Figure S48. ^{13}C NMR spectrum of **25** (D_2O, 100 MHz).

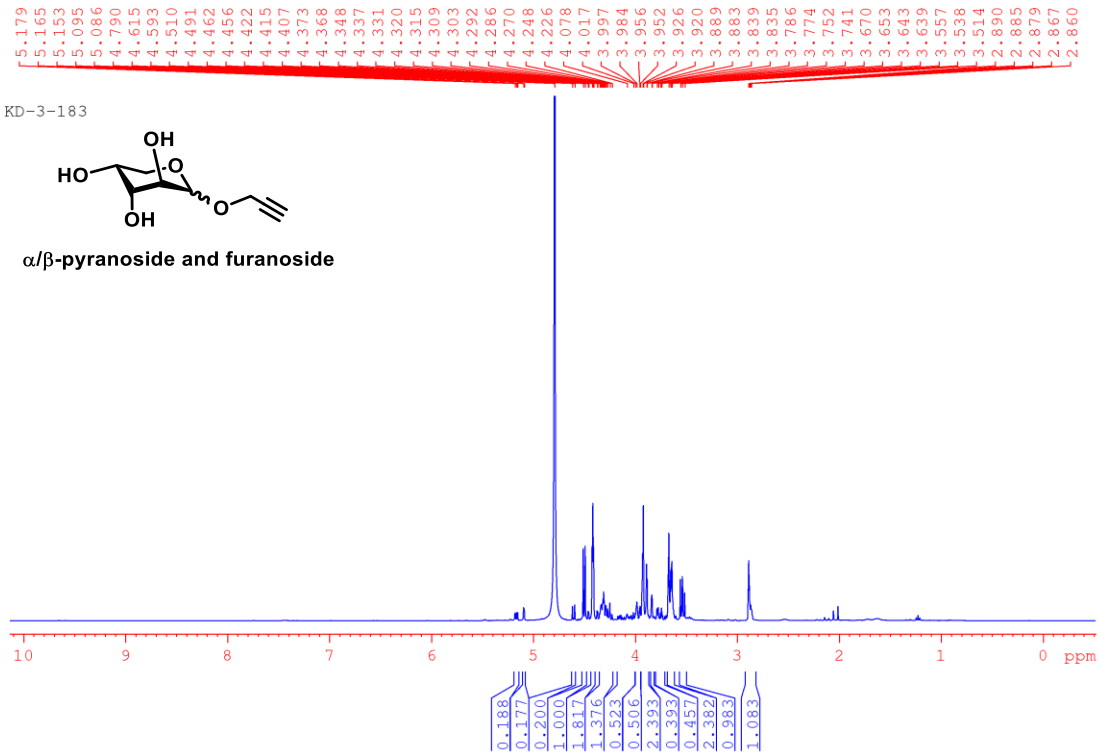

Figure S49. ^{1}H NMR spectrum of **26** (D_2O, 400 MHz).

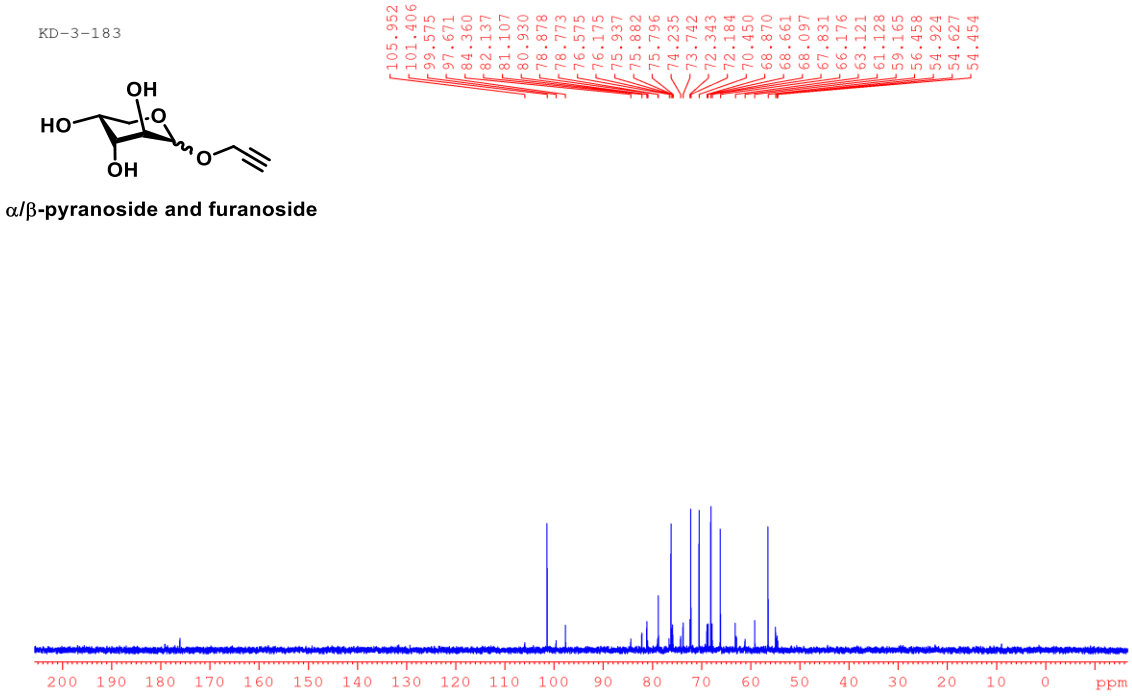

Figure S50. ^{13}C NMR spectrum of **26** (D_2O, 100 MHz).

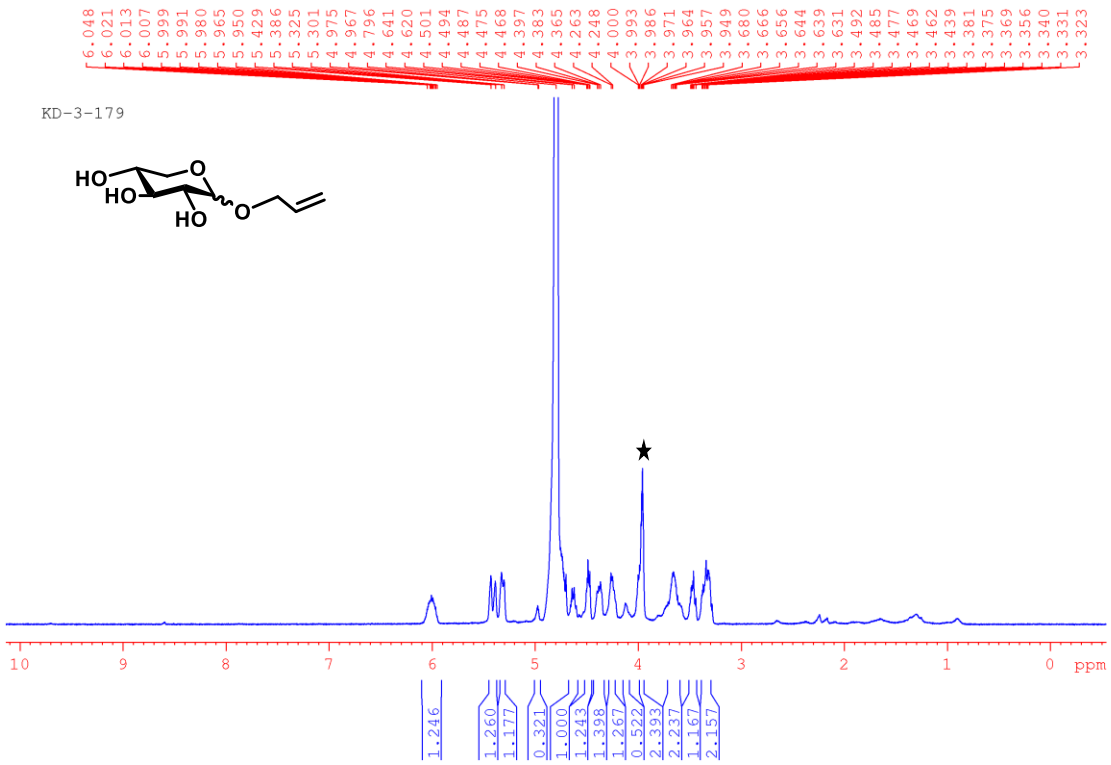

Figure S51. ^{1}H NMR spectrum of **27** (D_2O, 400 MHz).

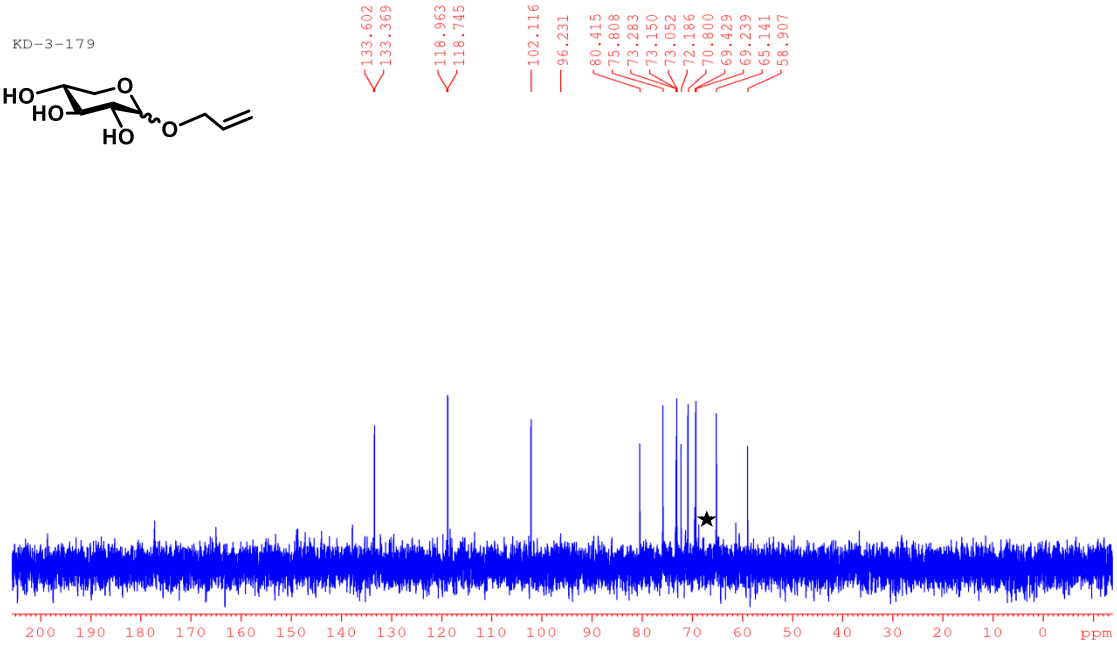

Figure S52. ^{13}C NMR spectrum of **27** (D_2O, 100 MHz).

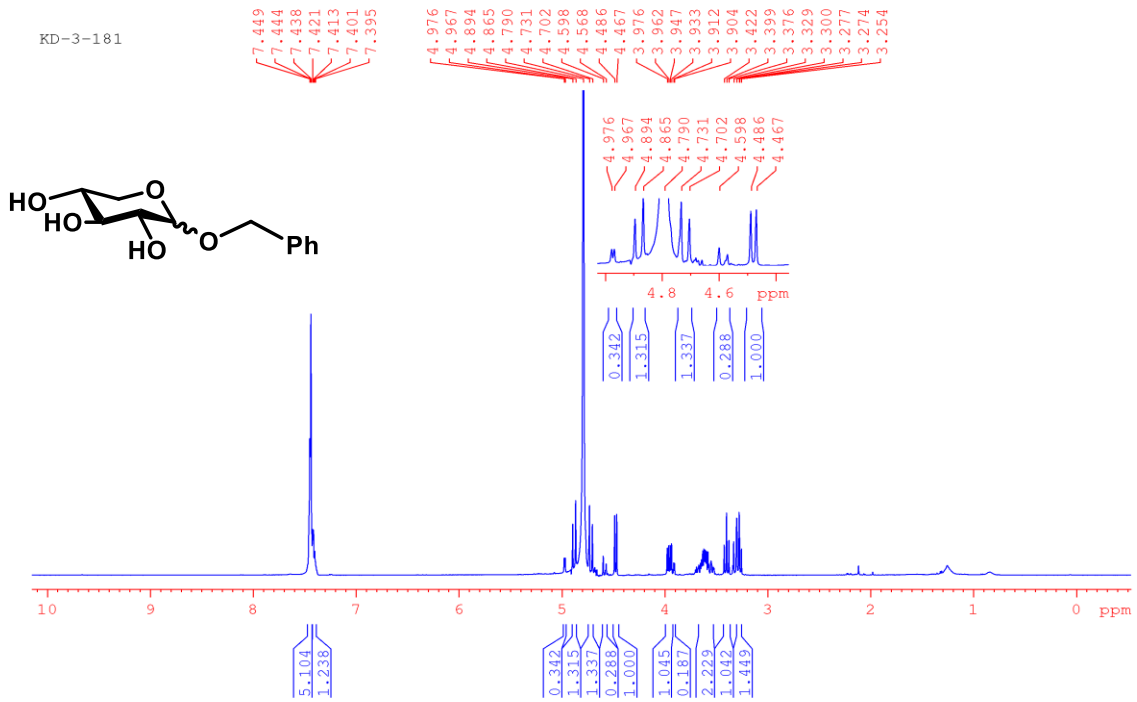

Figure S53. ^{1}H NMR spectrum of **28** (D_2O, 400 MHz).

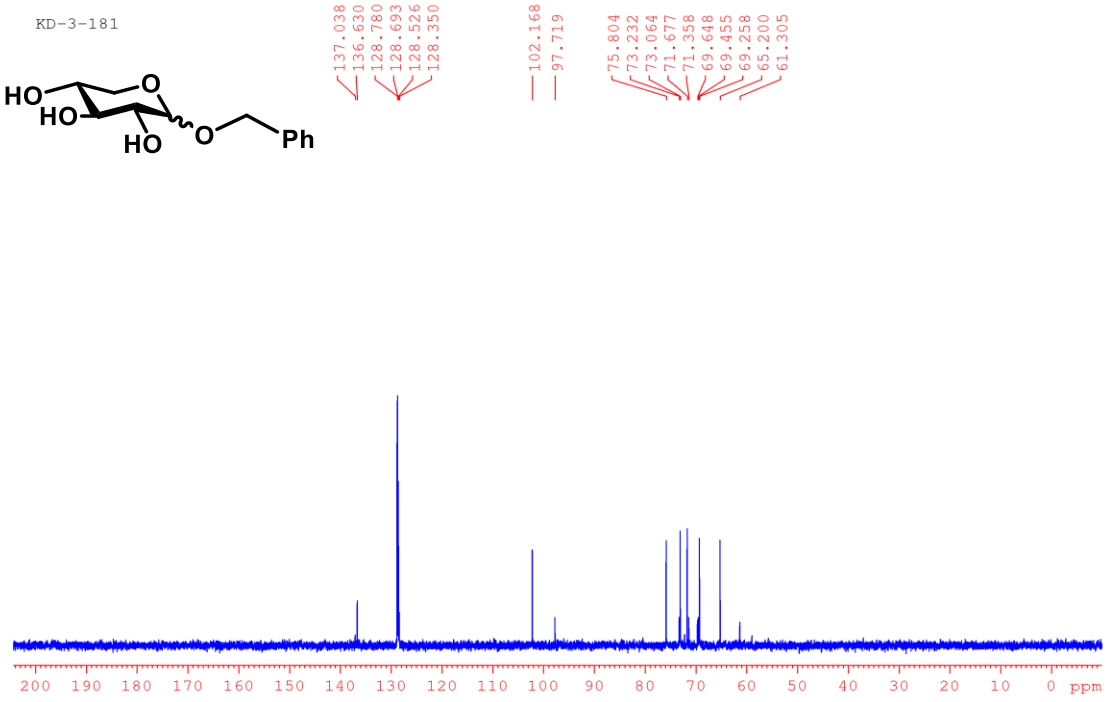

Figure S54. ^{13}C NMR spectrum of **28** (D_2O, 100 MHz).

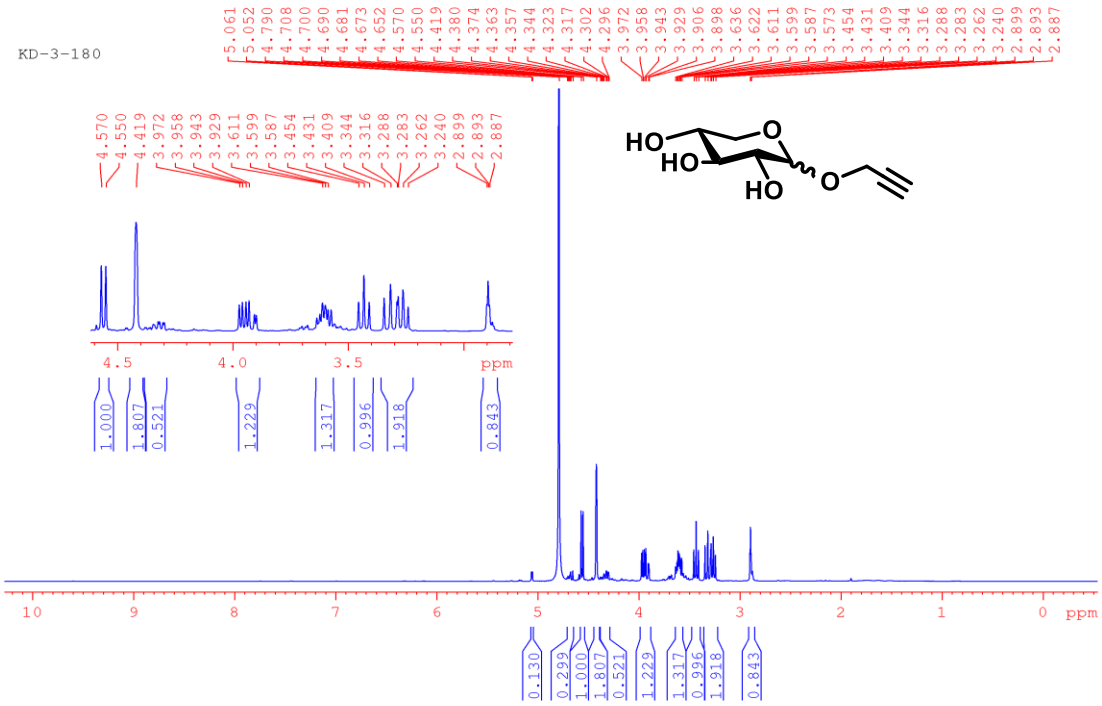

Figure S55. ^{1}H NMR spectrum of **29** (D_2O, 400 MHz).

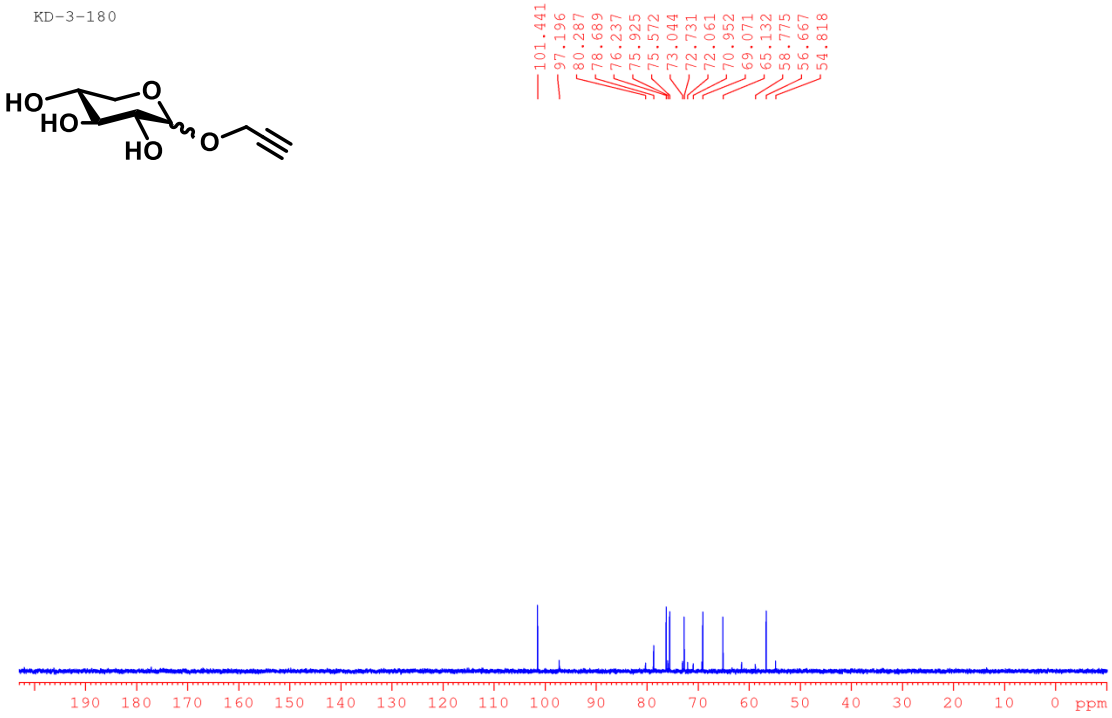

Figure S56. ^{13}C NMR spectrum of **29** (D_2O, 100 MHz).

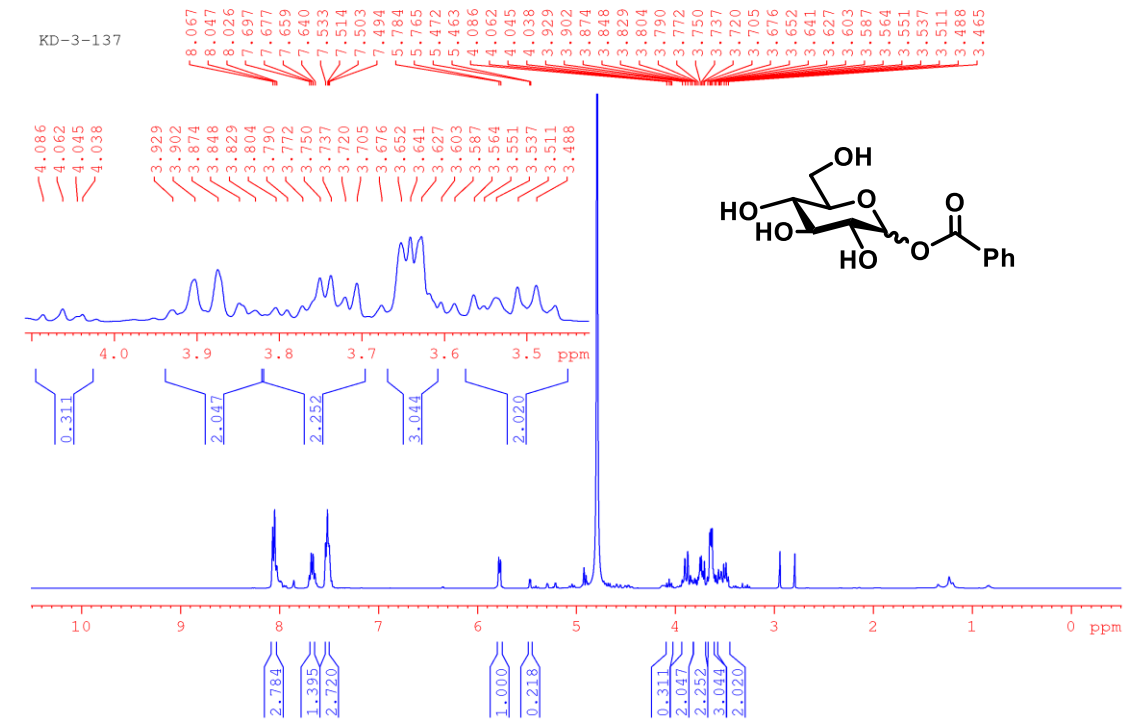

Figure S57. ^{1}H NMR spectrum of **30** (D_2O, 400 MHz).

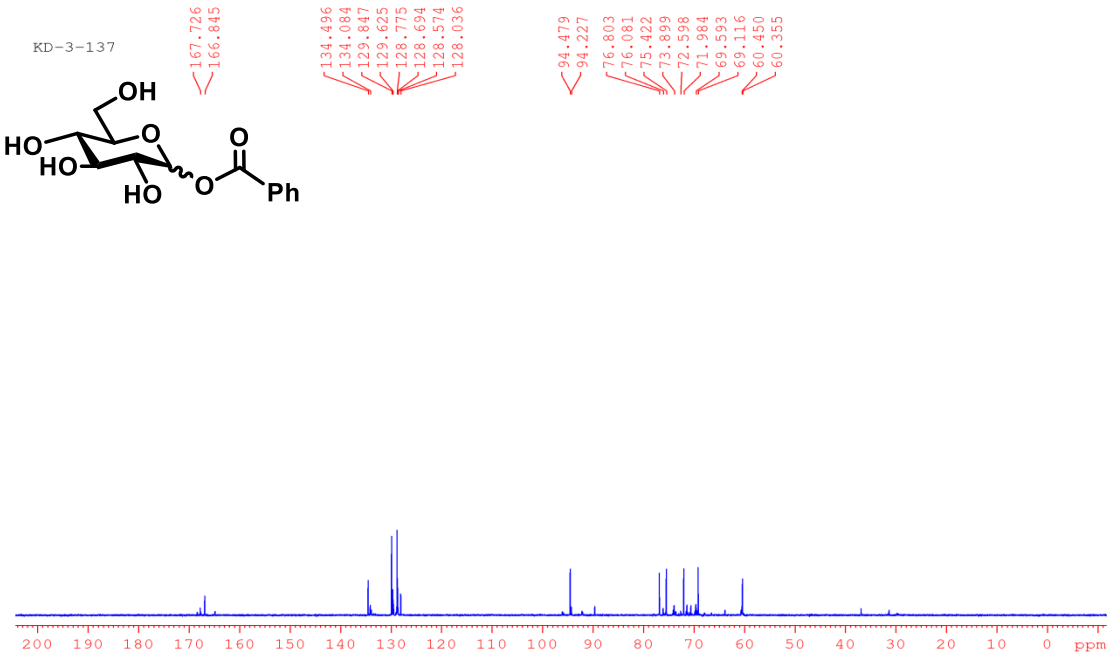

Figure S58. ^{13}C NMR spectrum of **30** (D_2O, 100 MHz).

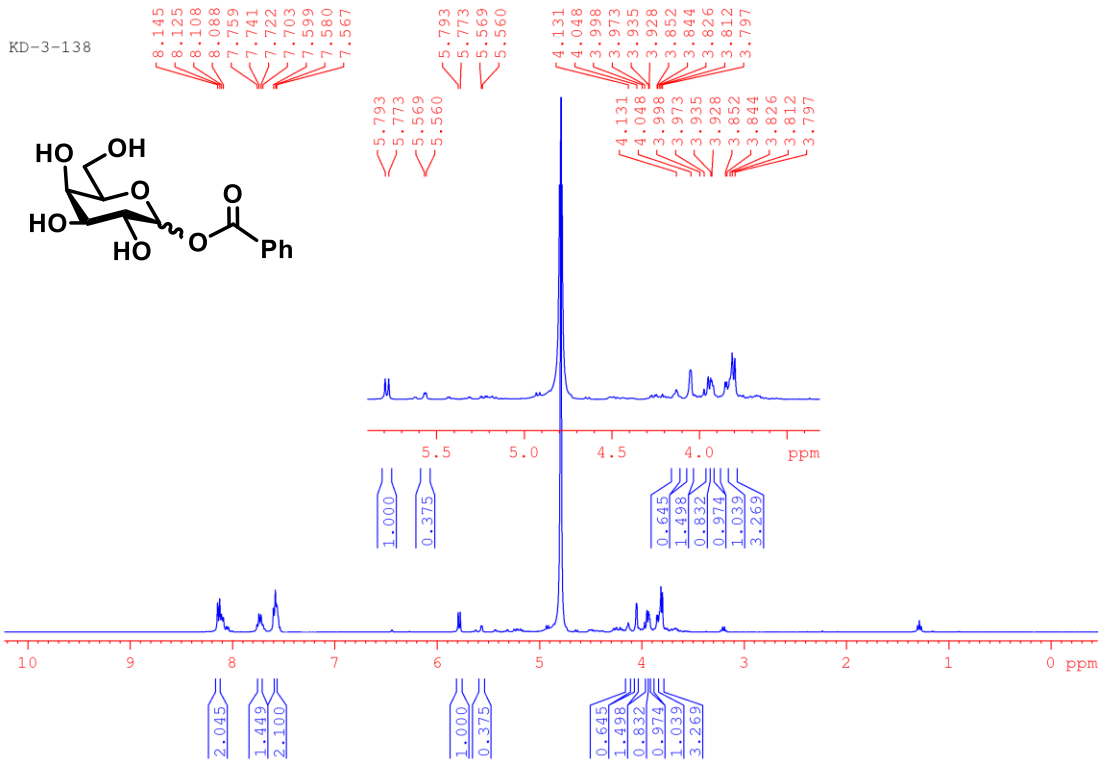

Figure S59. ^{1}H NMR spectrum of **31** (D_2O, 400 MHz).

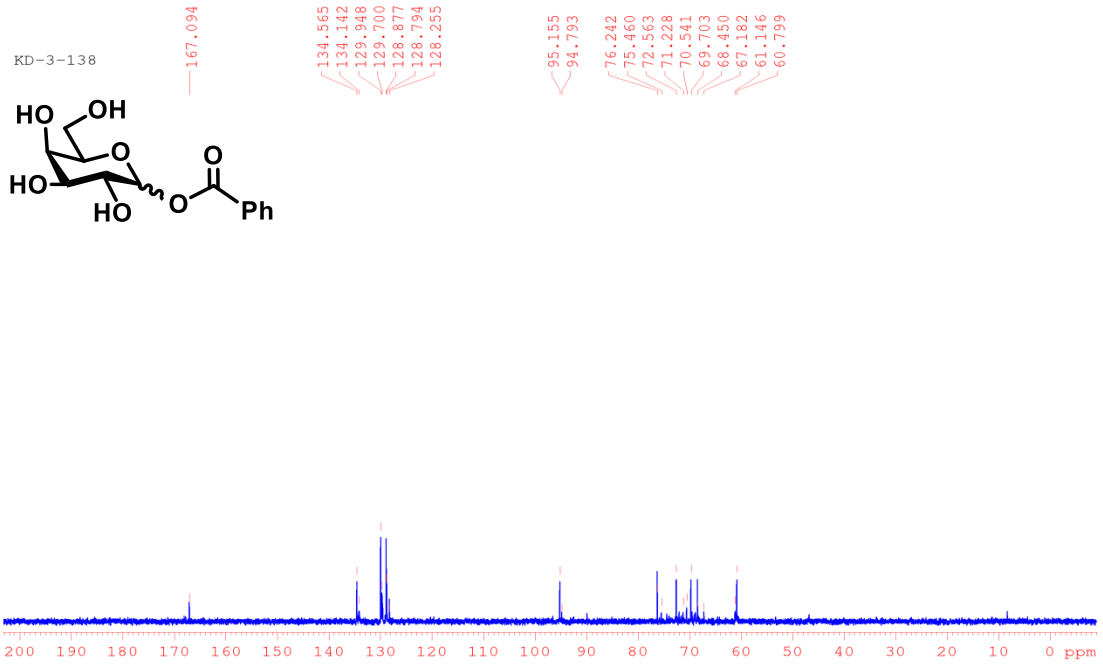

Figure S60. ^{13}C NMR spectrum of **31** (D_2O, 100 MHz).

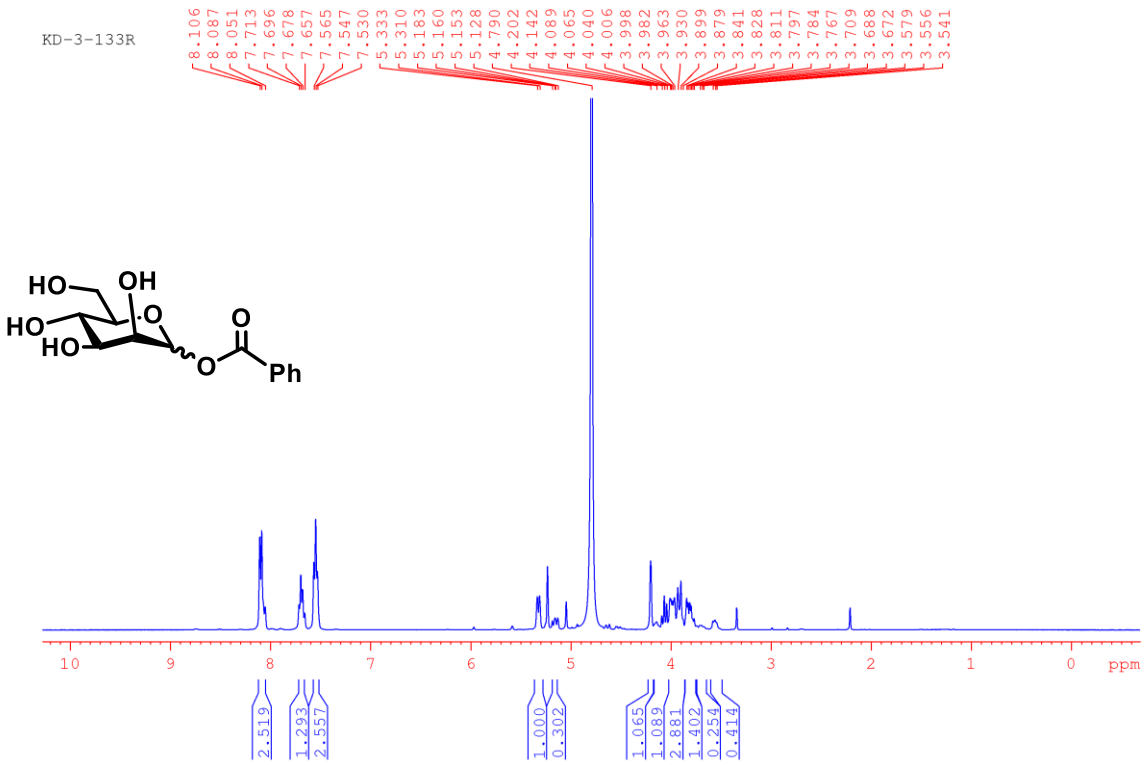

Figure S61. ^{1}H NMR spectrum of **32** (D_2O, 400 MHz).

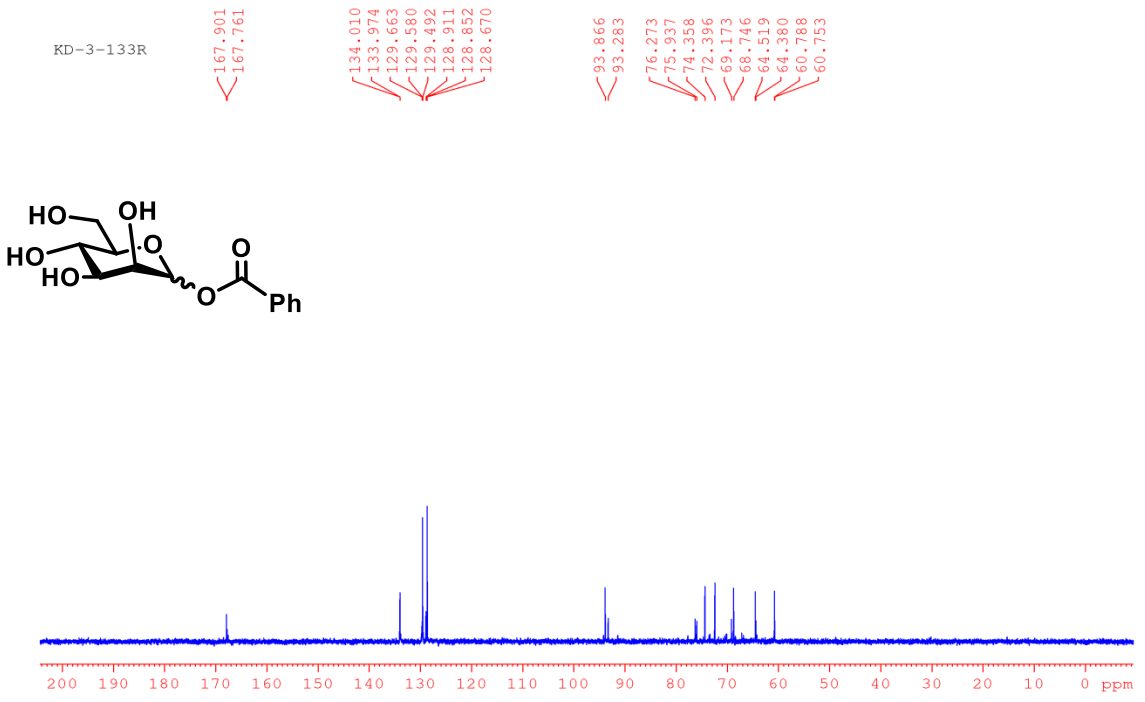

Figure S62. ^{13}C NMR spectrum of **32** (D_2O, 100 MHz).

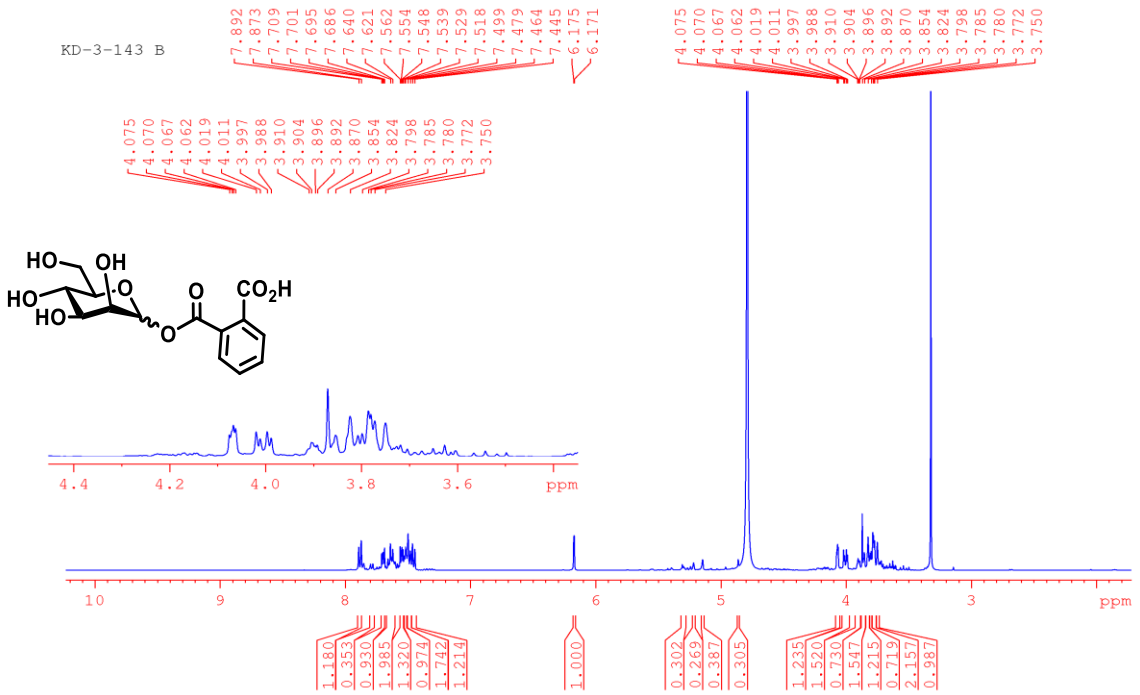

Figure S63. ^{1}H NMR spectrum of **33** (D_2O, 400 MHz).

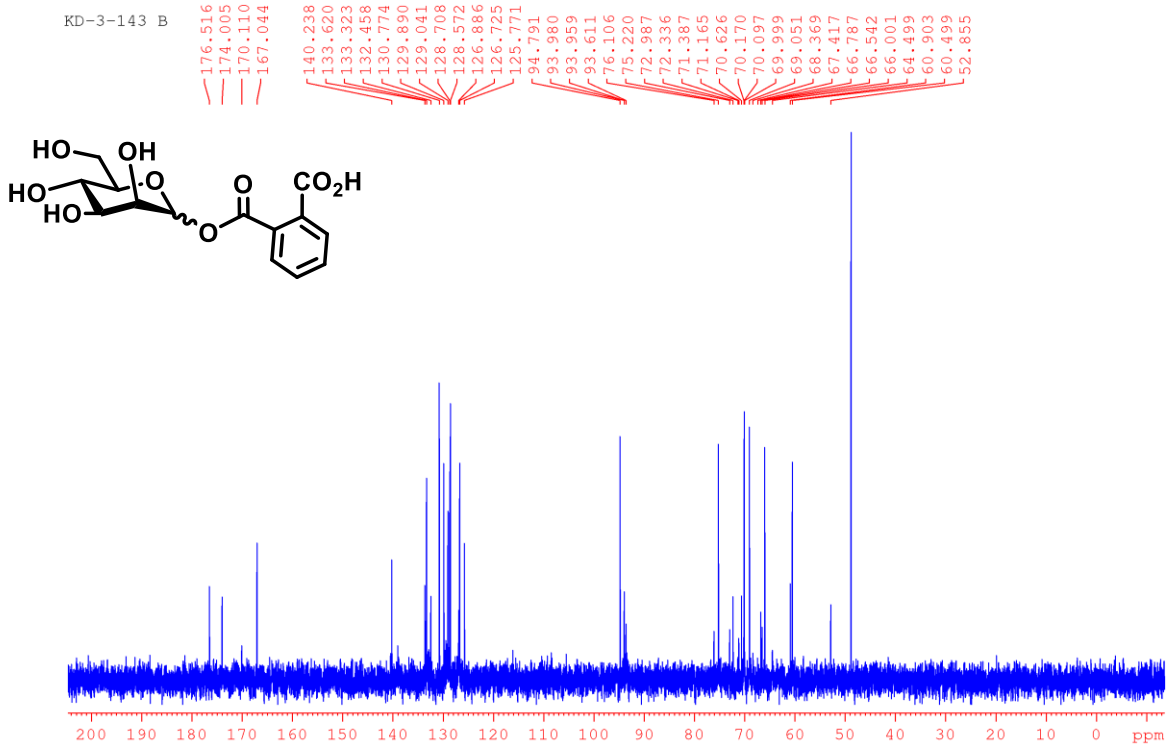

Figure S64. ^{13}C NMR spectrum of **33** (D_2O, 100 MHz).

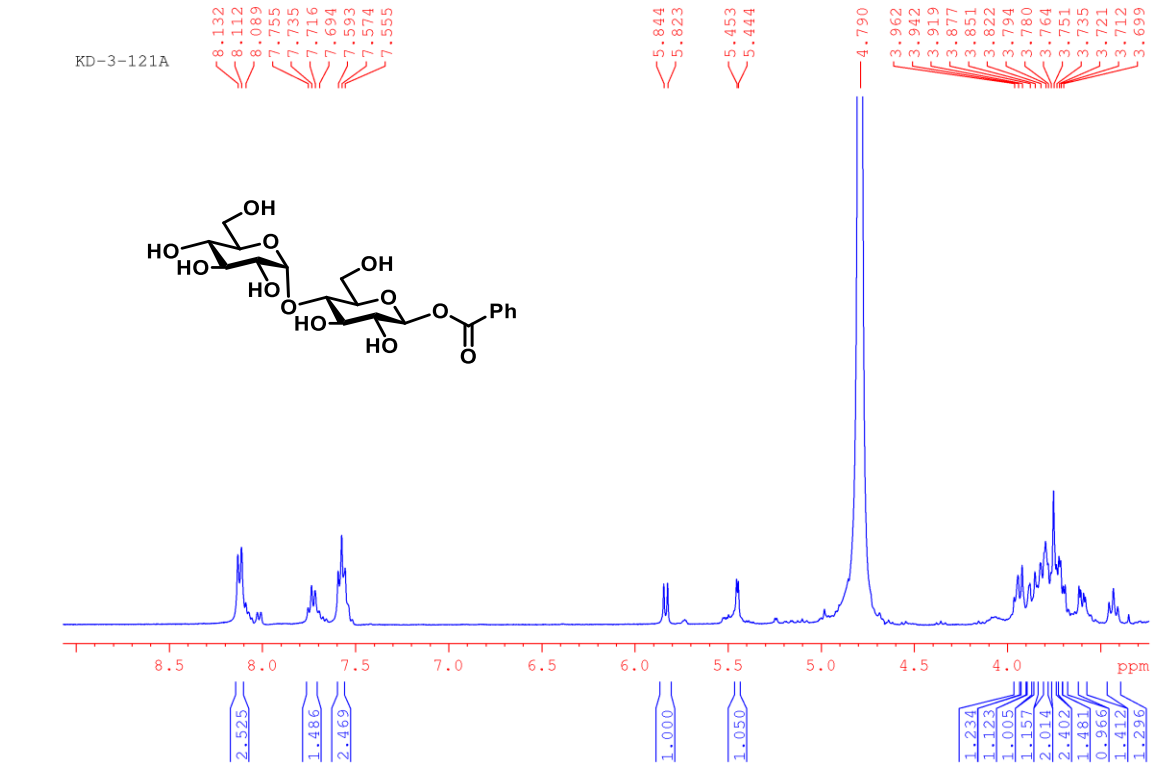

Figure S65. ^{1}H NMR spectrum of **34** (D_2O, 400 MHz).

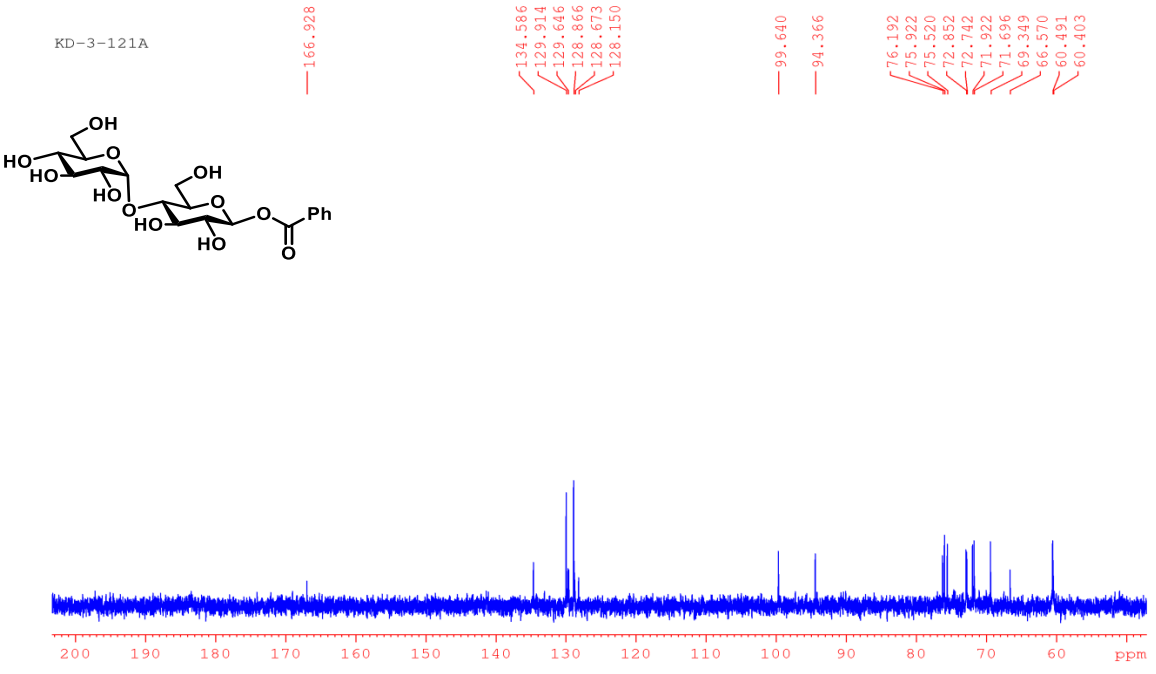

Figure S66. ^{13}C NMR spectrum of **34** (D_2O, 100 MHz).

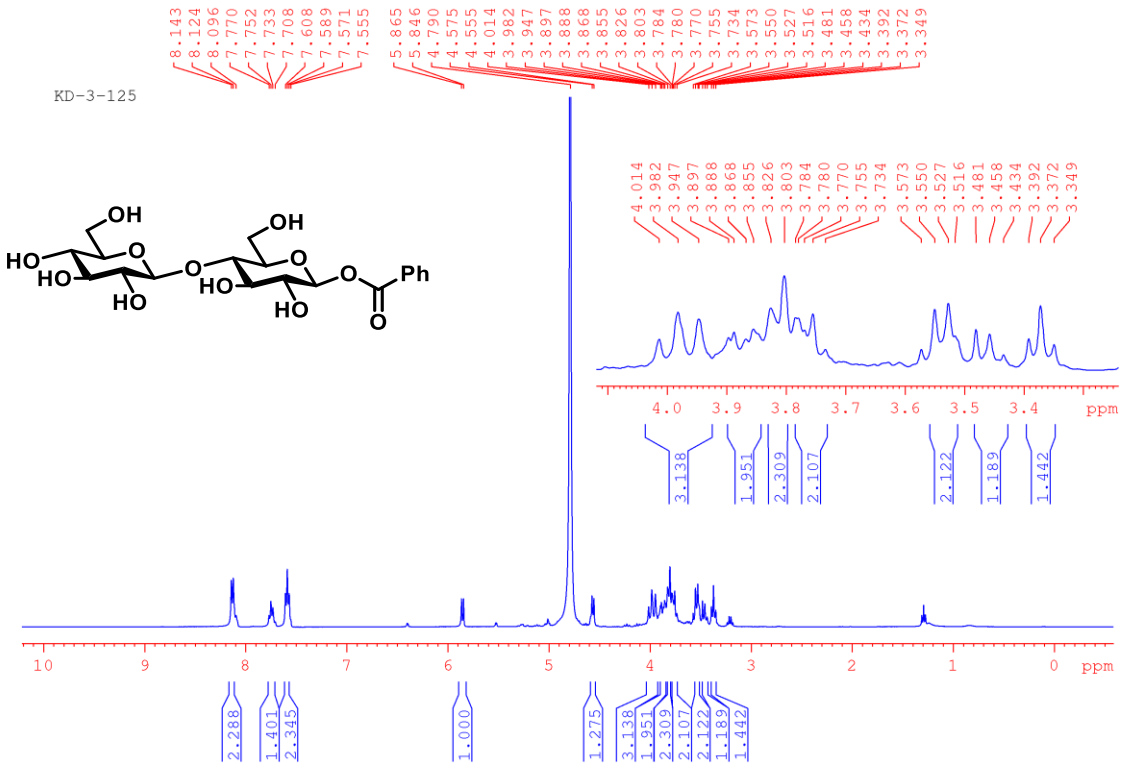

Figure S67. ^{1}H NMR spectrum of **35** (D_2O, 400 MHz).

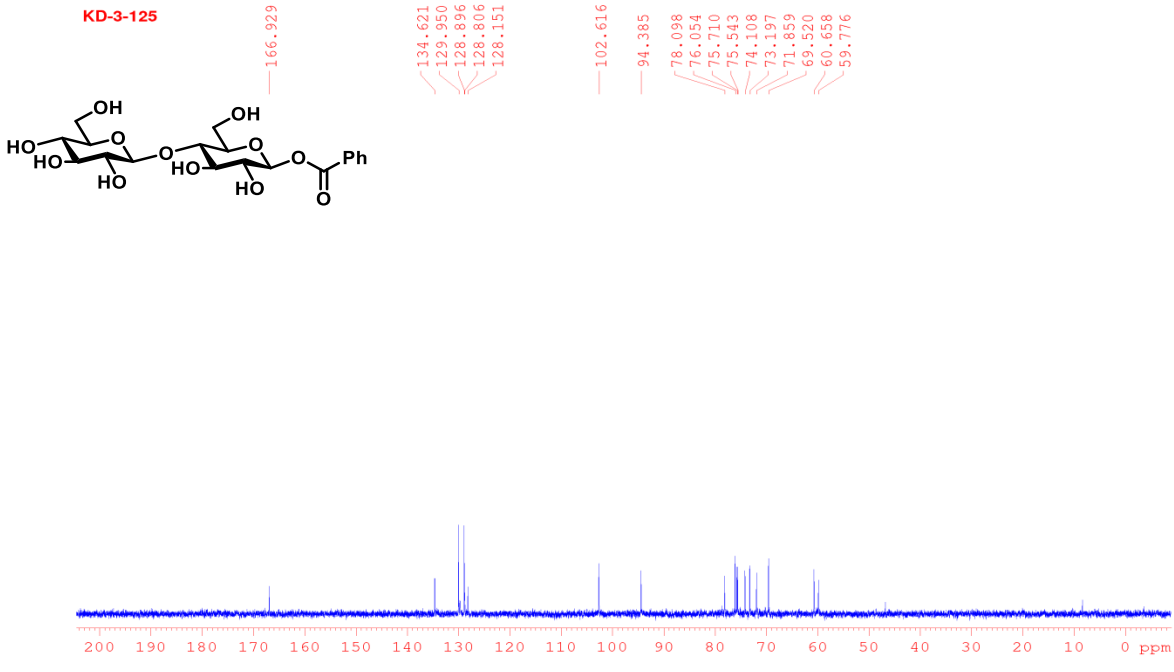

Figure S68. ^{13}C NMR spectrum of **35** (D_2O, 100 MHz).

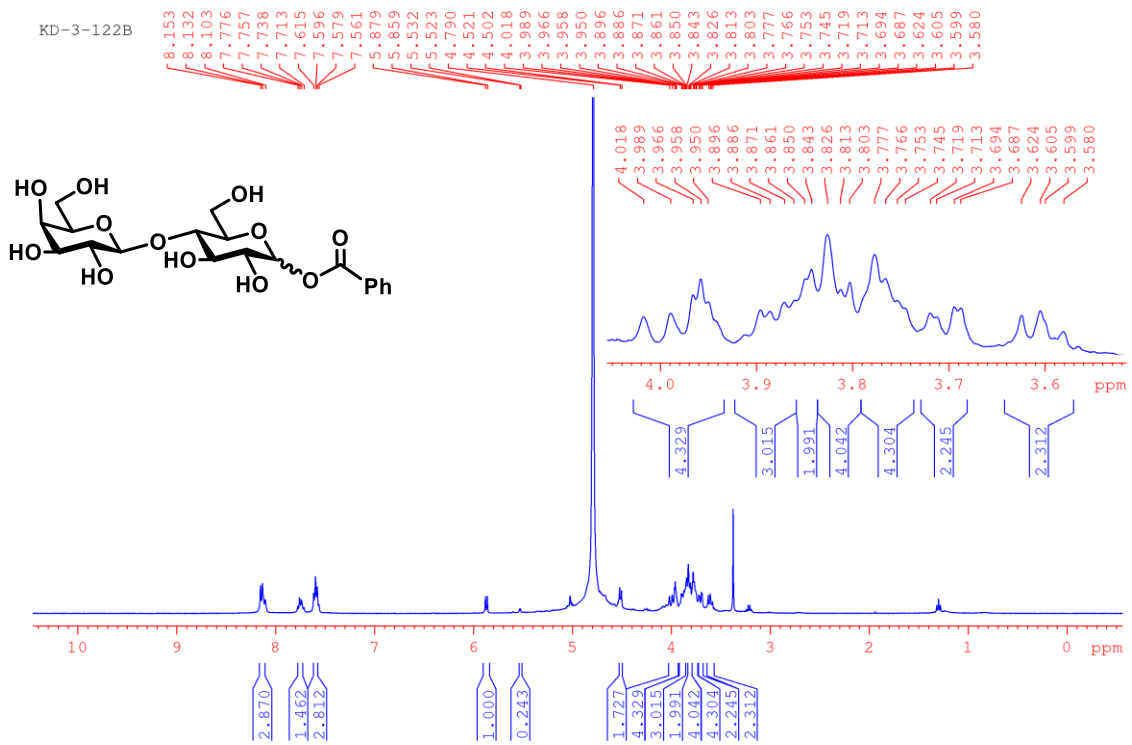

Figure S69. ^{1}H NMR spectrum of **36** (D_2O, 400 MHz).

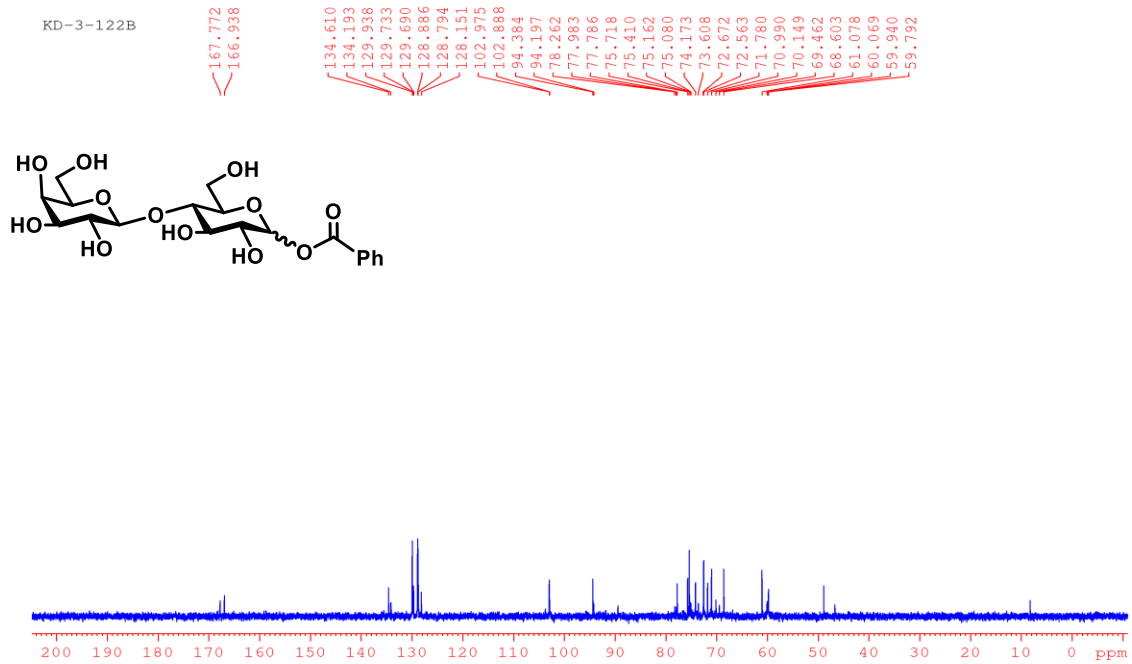

Figure S70. ^{13}C NMR spectrum of **36** (D_2O, 100 MHz).

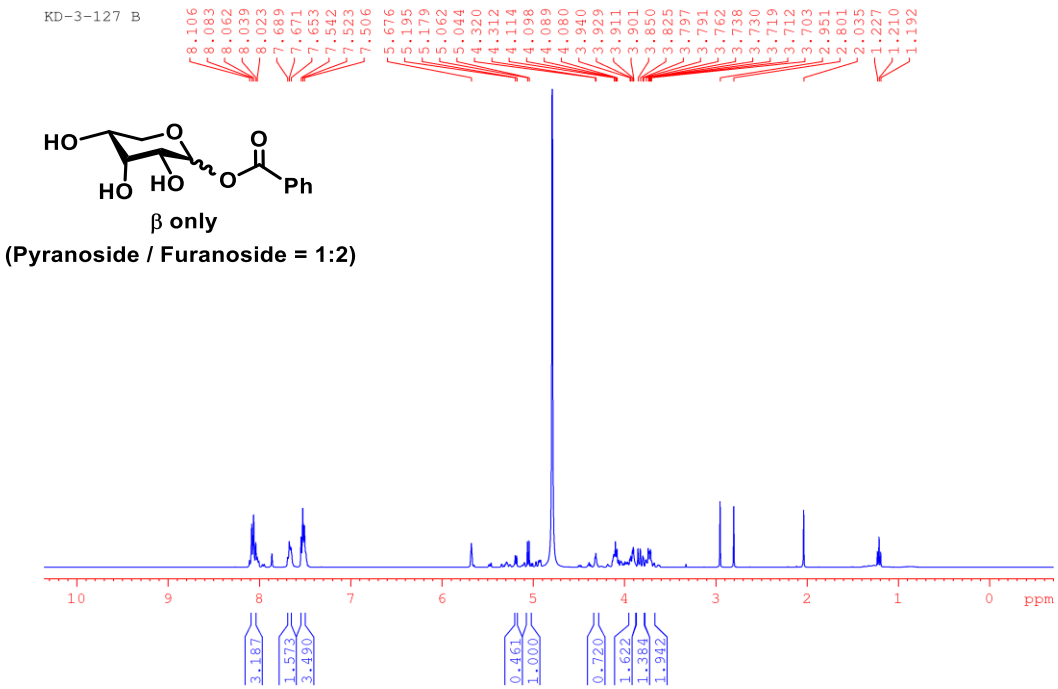

Figure S71. ^{1}H NMR spectrum of **37** (D_2O, 400 MHz).

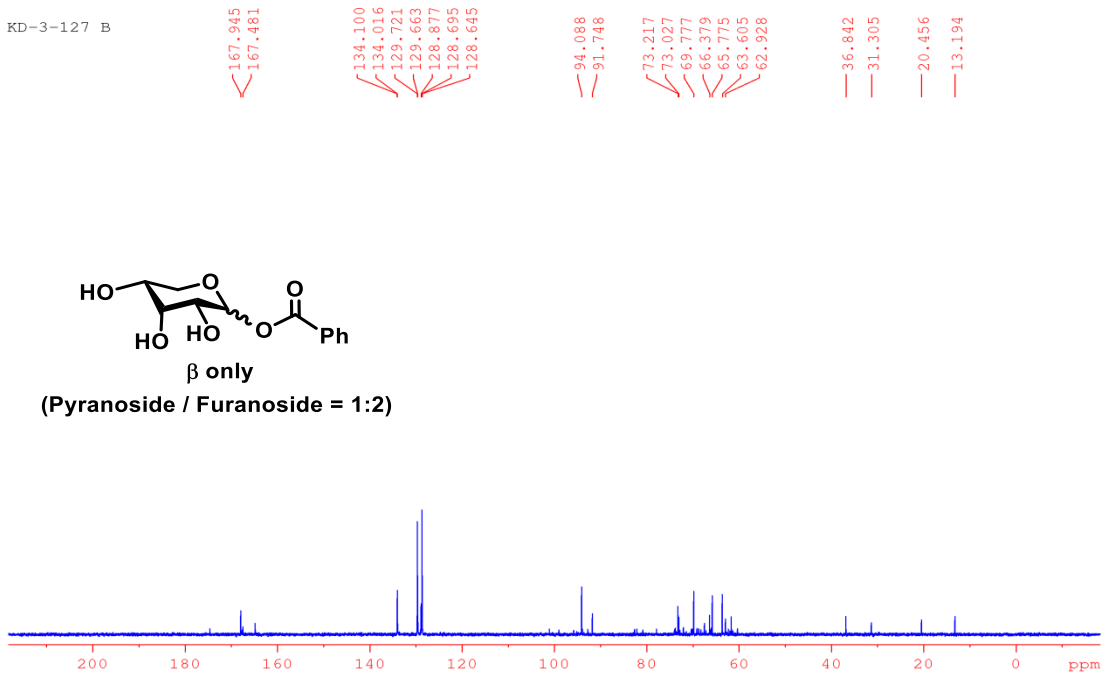

Figure S72. ^{13}C NMR spectrum of **37** (D_2O, 100 MHz).

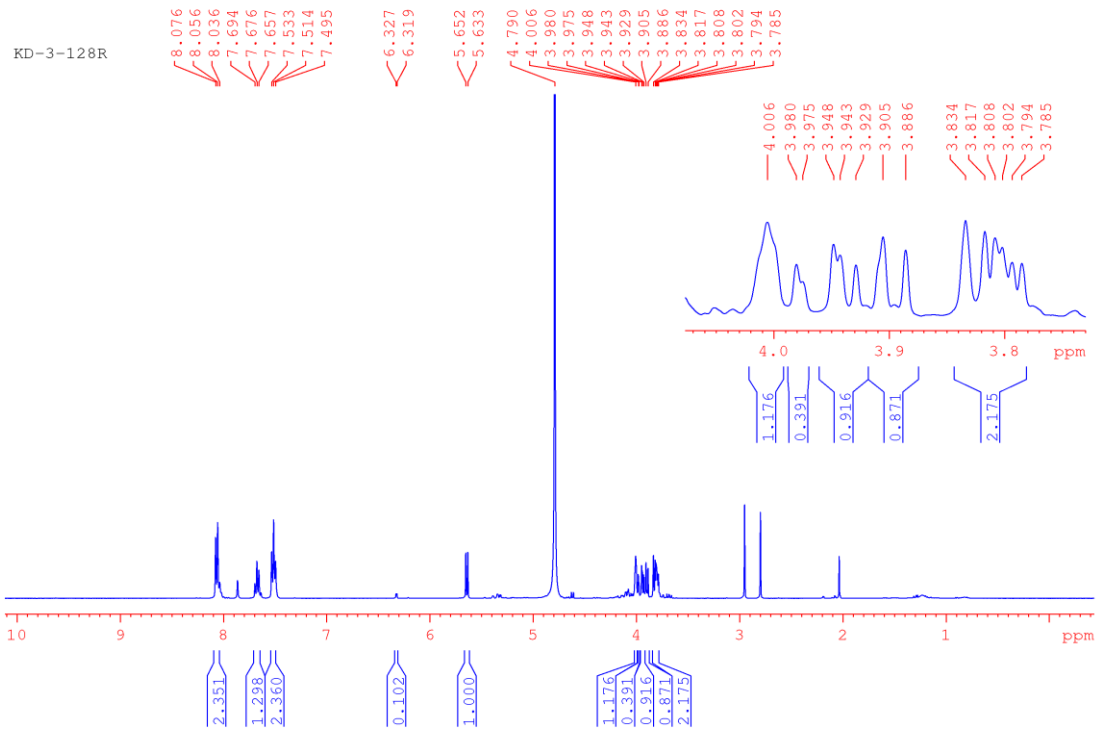

Figure S73. ^{1}H NMR spectrum of **38** (D_2O, 400 MHz).

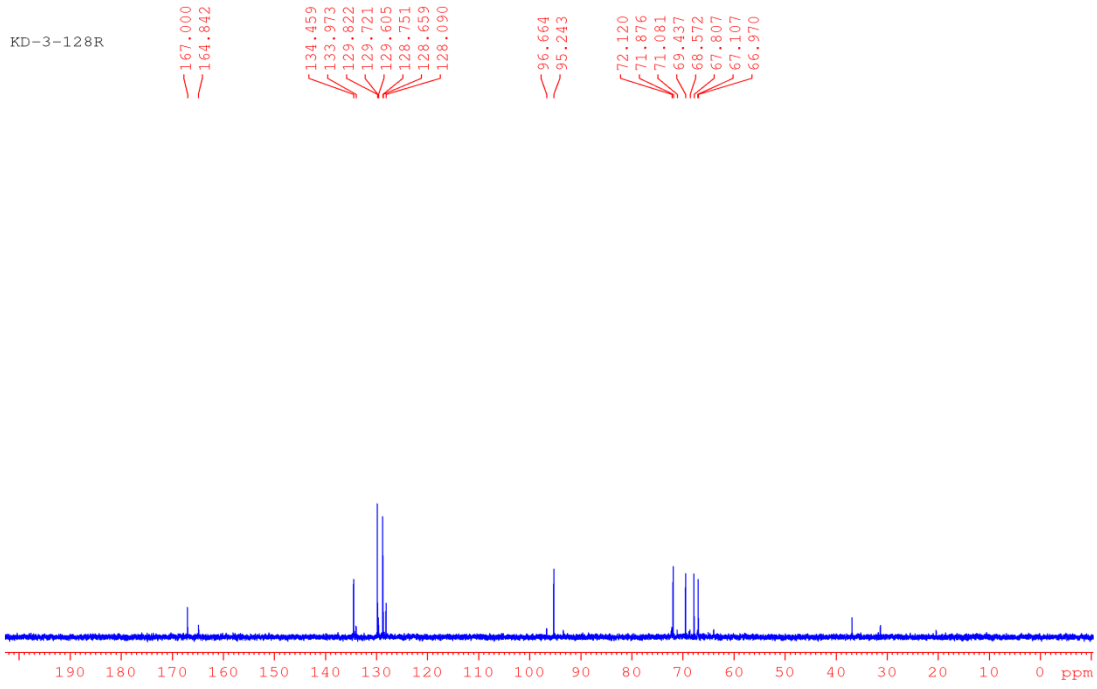

Figure S74. ^{13}C NMR spectrum of **38** (D_2O, 100 MHz).

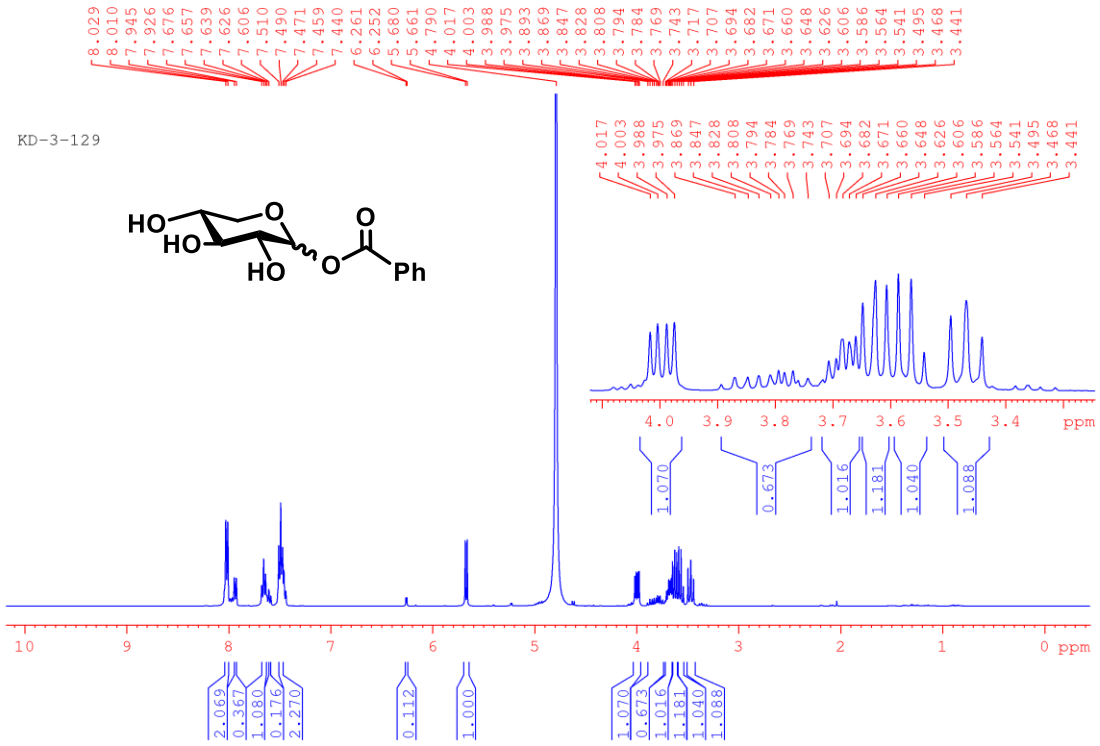

Figure S75. ^{1}H NMR spectrum of **39** (D_2O, 400 MHz).

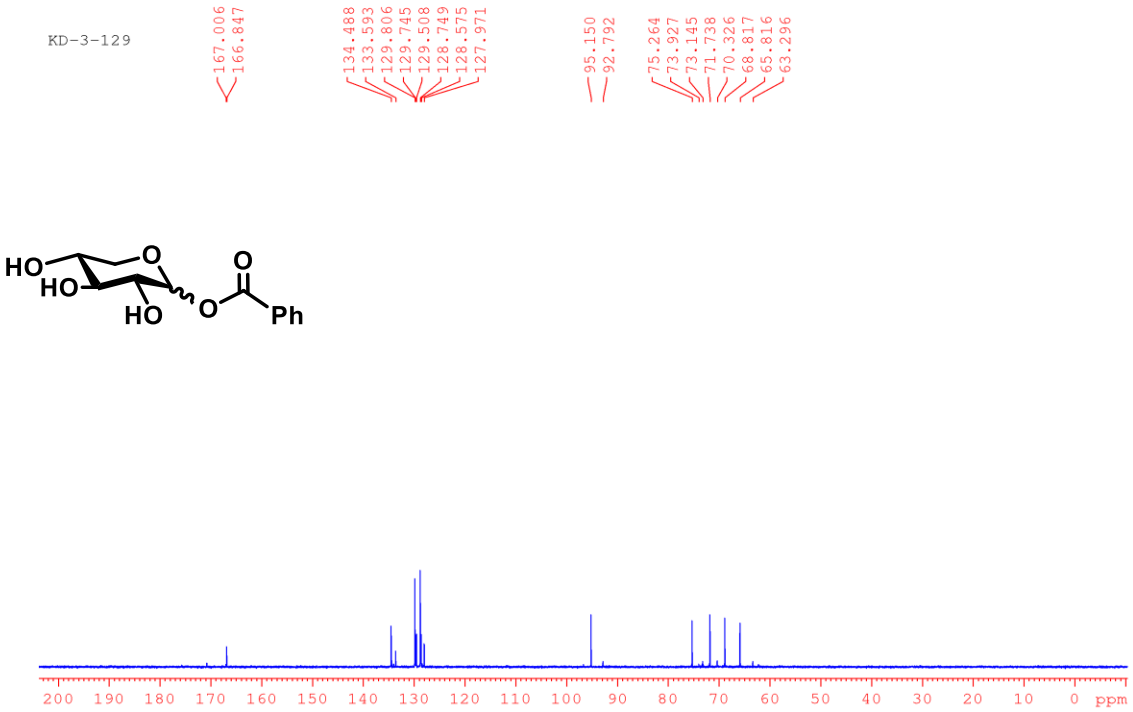

Figure S76. ^{13}C NMR spectrum of **39** (D_2O, 100 MHz).

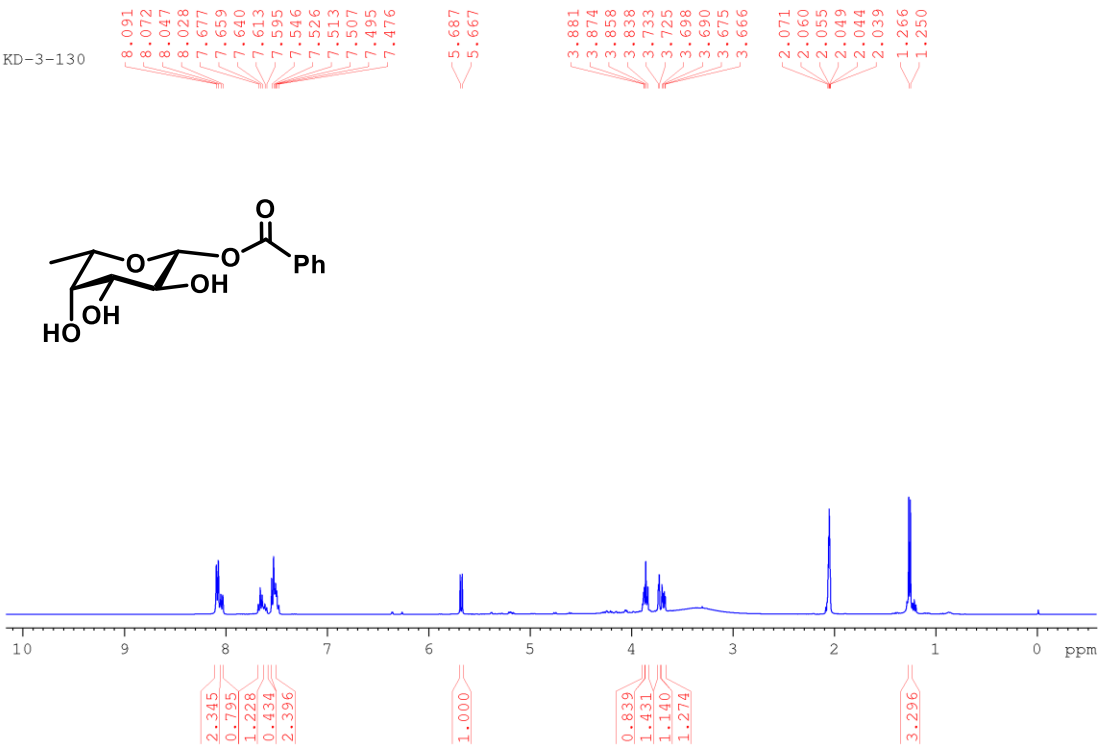

Figure S77. ^{1}H NMR spectrum of **40** (Acetone-d_6, 400 MHz).

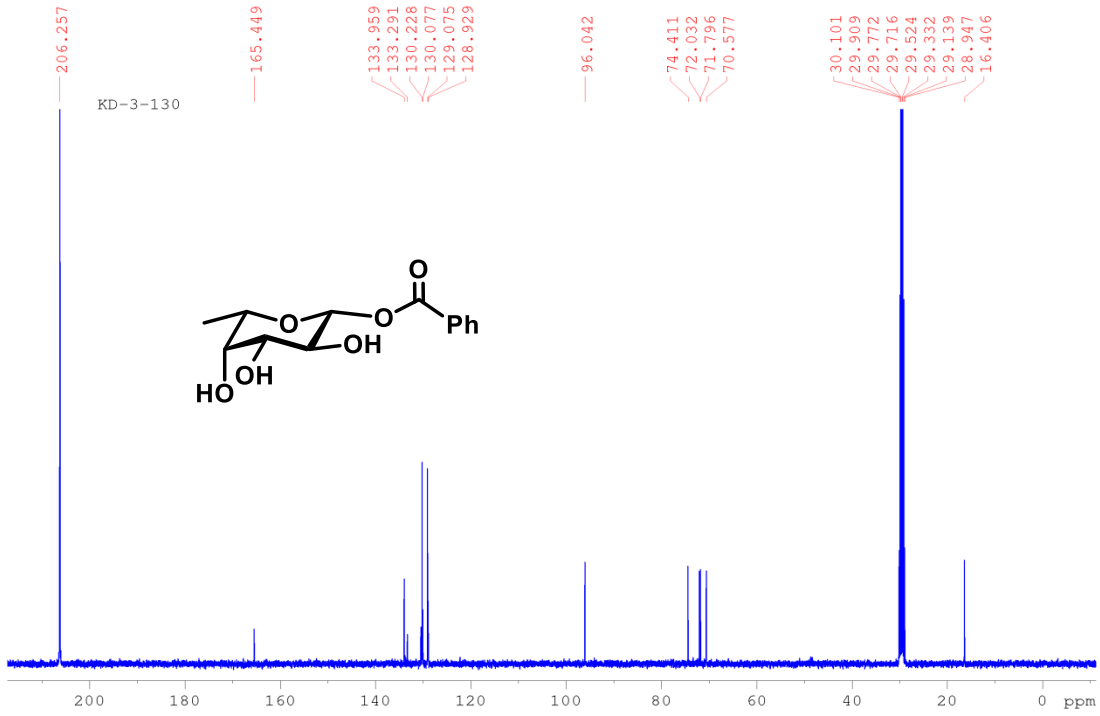

Figure S78. ^{13}C NMR spectrum of **40** (Acetone-d_6, 100 MHz).

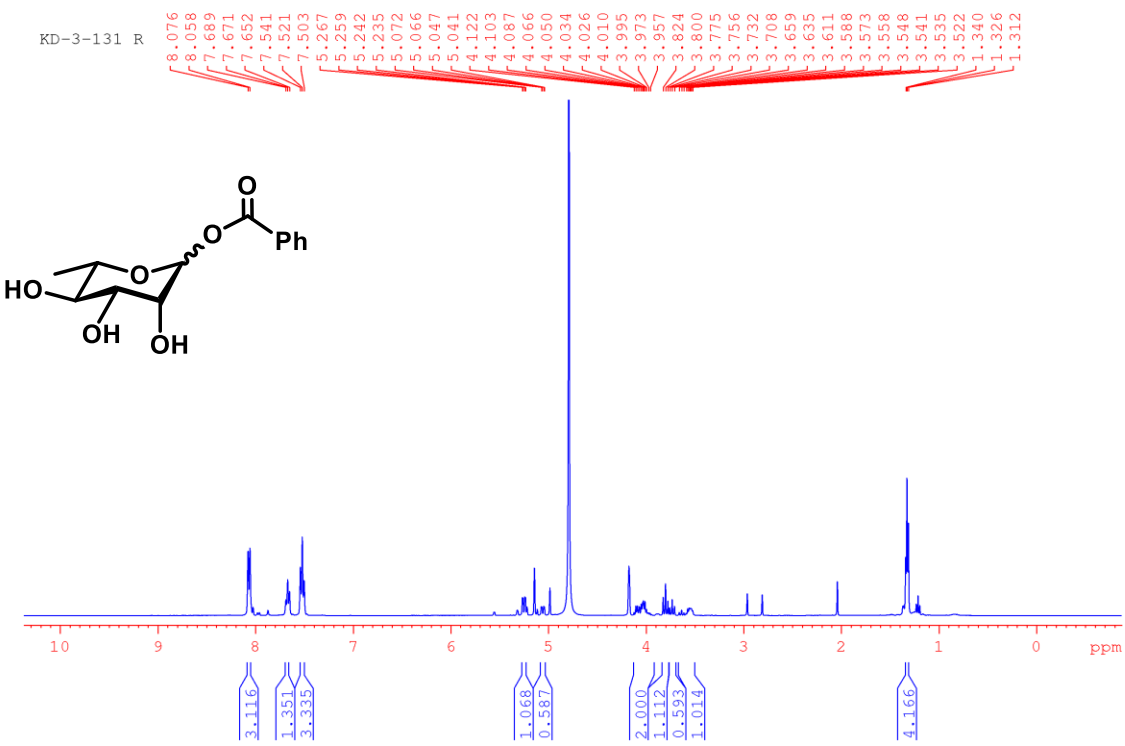

Figure S79. ^{1}H NMR spectrum of **41** (D_2O, 400 MHz).

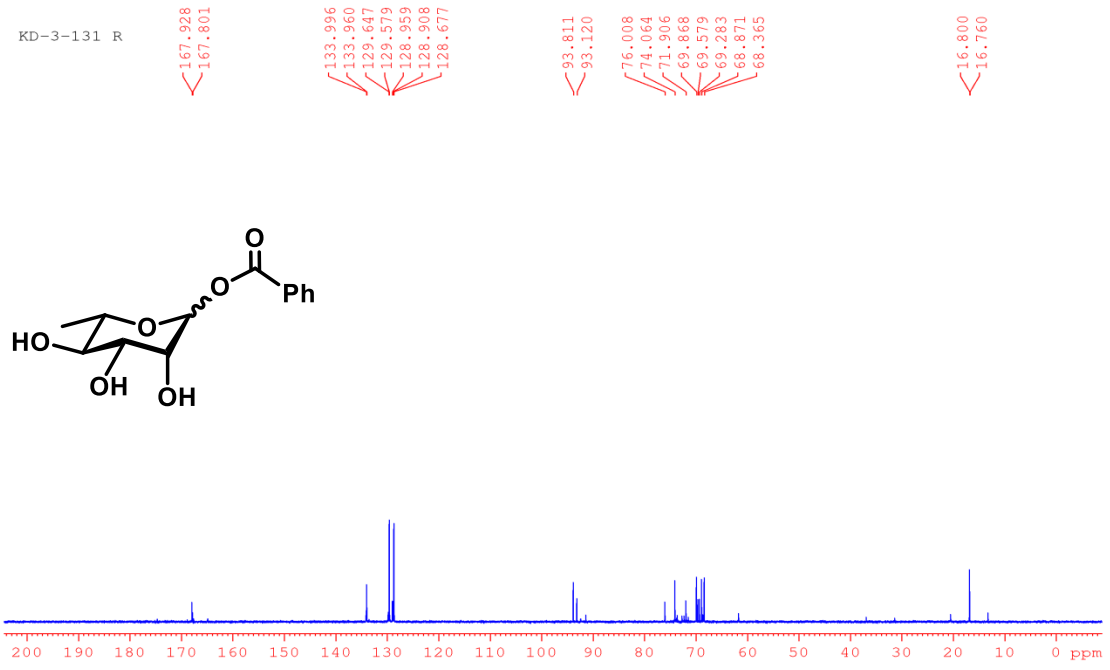

Figure S80. ^{13}C NMR spectrum of **41** (D_2O, 100 MHz).