Supporting Information

for

Design and synthesis of multivalent neoglycoconjugates by click conjugations

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Experimental

All solvents were distilled under nitrogen from the following drying agents immediately before use: tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl; dichloromethane and 1,2-dichloroethane were distilled from calcium hydride. Anhydrous acetonitrile (MeCN) was purchased from commercial suppliers and used without further purification. $BF_3{\cdot}OEt_2$ was distilled from calcium hydride before use. The compounds **1a**, **1d**, **3a**, $TsNH_2$ and propargyl alcohol were purchased from commercial suppliers and used without further purification. The compounds **1b** [1], **1c** [1], **1e** [1], **3a**–**3h** [2-6], and **5a** and **5b** [7-9] were prepared according to literature reported procedures. All the catalysts and additives were purchased from commercial suppliers and used without further purification. High resolution mass spectra (HRMS) were recorded on a Waters Q-Tof premier^{TM} mass spectrometer. Microwave experiments were conducted in a CEM Discover^{TM} system.

General procedure for the synthesis of propagyl 3-tosylamino-2,3-dideoxysugars 2a–2d [10]. To a solution of glycal **1** (1.0 equiv) and *p*-methylbenzenesulfonamide (1.1 equiv) in DCE (0.1 M) was added propagyl alcohol (1.1 equiv) under N_2 atmosphere. $BF_3{\cdot}OEt_2$ (2.2 equiv) was then added to this mixture. The reaction mixture was stirred for 20 min at room temperature, quenched with saturated $NaHCO_3$ and subsequently extracted with CH_2Cl_2 (3 × 15 mL). The extract was dried under Na_2SO_4 and

concentrated. The residue was subjected to column chromatography (silica gel, hexane/EtOAc) to obtain pure 3-tosylamino-2,3-dideoxysugars **2**.

Propargyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-allo-hexopyranoside (**2a**): Compound **2a** (gummy liquid, 640 mg, 81% yield) was prepared according to the general procedure for the synthesis of propargyl 3-tosylamino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (500 mg, 1.8 mmol), *p*-methylbenzenesulfonamide (342 mg, 2.0 mmol), and propargyl alcohol (210 μL, 2.0 mmol) and purified by column chromatography (hexane/ethyl acetate = 5 : 1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.82 (d, *J* = 8.8 Hz, 1H), 5.05 (d, *J* = 3.2 Hz, 1H), 4.65 (dd, *J* = 10.4, 4.0 Hz, 1H), 4.32 (dd, *J* = 12.0, 4.4 Hz, 1H), 4.09-4.27 (m, 3H), 3.91 (q, *J* = 3.6 Hz, 1H), 3.38-3.40 (m, 1H), 2.46 (s, 1H), 2.42 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.87 (dt, *J* = 14.8, 4.0 Hz, 1H), 1.50 (dd, *J* = 18.4, 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100MHz): δ 170.7, 170.4, 143.4, 137.8, 129.8, 126.9, 95.7, 78.1, 75.5, 66.8, 64.7, 62.6, 54.8, 47.8, 32.7, 21.5, 21.0, 20.8; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{20}H_{25}NO_8SNa$ 462.1199, found 462.1201.

Propargyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-galacto-pyranoside (**2b**): Compound **2b** (gummy liquid, 66 mg, 84% yield) was prepared according to the general procedure for the synthesis of propargyl 3-tosylamino-2,3-dideoxysugars from tri-*O*-acetyl-D-galactal **1c** (50 mg, 0.18 mmol), *p*-methylbenzenesulfonamide (34 mg, 0.2 mmol), and propargyl alcohol (21 μL, 0.2 mmol) and purified by column chromatography

(hexane/ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.94 (d, *J* = 8.0 Hz, 1H), 5.10 (d, *J* = 3.6 Hz, 1H), 4.79 (d, *J* = 3.2 Hz, 1H), 4.22-4.32 (m, 3H), 4.00-4.10 (m, 2H), 3.58-3.68 (m, 1H), 2.49 (t, *J* = 2.4 Hz, 1H), 2.42 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.03 (dt, *J* = 14.8, 4.0 Hz, 1H), 1.47 (dd, *J* = 14.8, 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100MHz): δ 170.6, 170.4, 143.6, 137.5, 129.8, 127.1, 95.3, 78.3, 75.4, 67.8, 63.5, 62.7, 54.5, 47.4, 28.4, 21.6, 21.5, 20.8; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{20}H_{25}NO_8SNa$ 462.1199, found 462.1195.

Propargyl 3-*p*-toluenesulfonamido-4-*O*-acetyl-2,3,6-trideoxy-α-L-ribo-hexopyranoside (**2c**): Compound **2c** (gummy liquid, 51 mg, 74% yield) was prepared according to the general procedure for the synthesis of propargyl 3-tosylamino-2,3-dideoxysugars from di-*O*-acetyl-D-rhamnal **1d** (39 mg, 0.18 mmol), *p*-methylbenzenesulfonamide (34 mg, 0.2 mmol), and propargyl alcohol (21 μL, 0.2 mmol) and purified by column chromatography (hexane/ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.84 (d, *J* = 8.8 Hz, 1H), 4.97 (d, *J* = 3.6 Hz, 1H), 4.35 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.24 (t, *J* = 2.4 Hz, 2H), 4.02-4.06 (m, 1H), 3.83-3.86 (m, 1H), 2.47 (t, *J* = 2.4 Hz, 1H), 2.41 (s, 3H), 2.08 (s, 3H), 1.83 (dt, *J* = 15.6, 4.0 Hz, 1H), 1.47 (dd, *J* = 14.8, 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100MHz): δ 170.7, 143.2, 138.0, 129.7, 126.9, 95.4, 78.4, 75.2, 72.3, 62.3, 54.5, 47.8, 33.0, 21.5, 21.0, 17.3; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{23}NO_6SNa$ 404.1144, found 404.11153.

Propargyl 3-*p*-toluenesulfonamido-4-(2',3',4',6',-tetra-*O*-acetyl-α-D-gluco-pyranoside)-6-*O*-acetyl-2,3-dideoxy-α-D-allopyranoside (**2d**) [10]: Compound **2d** (gummy liquid, 88 mg, 67% yield) was prepared according to the general procedure for the synthesis of propargyl 3-tosylamino-2,3-dideoxysugars from hexa-*O*-acetyl-D-maltal **1e** (101 mg, 0.18 mmol), *p*-methylbenzene sulfonamide (34 mg, 0.2 mmol), and propargyl alcohol (21 μL, 0.2 mmol) and purified by column chromatography (hexane/ethyl acetate = 5:1); analytical data of **2d** were in all respect identical with the published data [10]: ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.69 (d, *J* = 10.0 Hz, 1H), 5.42-5.46 (m, 1H), 5.24 (dd, *J* = 10.4, 2.4 Hz, 1H), 5.12 (t, *J* = 10.0 Hz, 1H), 4.93 (d, *J* = 1.6 Hz, 1H), 4.47 (dd, *J* = 12.0, 2.4 Hz, 1H), 4.19-4.33 (m, 3H), 4.09-4.17 (m, 4H), 3.95-3.98 (m, 1H), 3.75 (dd, *J* = 9.6, 4.0 Hz, 1H), 2.49 (t, *J* = 2.4 Hz, 1H), 2.43 (s, 3H), 2.20 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.61 (dt, *J* = 14.4, 3.6 Hz, 1H), 1.31 (dd, *J* = 14.8, 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.6, 170.4, 170.3, 170.0, 169.6, 143.6, 138.1, 129.9, 126.8, 95.7, 92.1, 78.2, 75.4, 70.0, 68.6, 68.4, 68.1, 66.1, 62.9, 61.7, 60.4, 54.9, 46.2, 31.5, 21.5, 20.9, 20.8, 20.7, 20.6, 14.2; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{32}H_{41}NO_{16}SNa$ 750.2044, found 750.2042.

General procedures for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates.

Method A: To a propargyl 3-tosylamino-2,3-dideoxysugar **2** (0.05 mmol, 1.0 equiv) and azide **3** (1.5 equiv) in DMF (2 mL) was added $CuSO_4 \cdot 5H_2O$ solution (1 mol %) and sodium ascorbate solution (10 mol %). The reaction mixture was stirred for 12 hours at 70 °C, quenched with water (10 mL) and subsequently extracted with EA (10 mL × 3). The extract was dried and concentrated. The residue was subjected to column chromatography (silica gel, hexane/EtOAc) to obtain pure 3-tosylamino-2,3-dideoxyneoglycoconjugates **4**.

Method B: To a 3-amino-2,3-dideoxysugar **4** (0.05 mmol, 1.0 equiv) and azide **5** (1.5 equiv) in DMF (2 mL) was added $CuSO_4 \cdot 5H_2O$ solution (1.0 M) (10 mol %) and sodium ascorbate solution (1.0 M) (10 mol %). The reaction vessel was sealed and irradiated in a microwave reactor (CEM Discover™ system) at a temperature of 70 °C for 15 minutes at a maximum power of 200 W. The reaction mixture was cooled to room temperature and quenched with water (10 mL) and subsequently extracted with EA (10 mL × 3). The extract was dried and concentrated. The residue was subjected to column chromatography (silica gel, hexane/EtOAc) to obtain pure 3-tosylamino-2,3-dideoxyneoglyco conjugates **4.**

1-Benzyl-4-(3'-*p*-toluenesulfonamido-4',6'-di-*O*-acetyl-2',3'-dideoxy-α-D-allo-pyranosyloxymethyl)-1*H*-1,2,3-triazol (**4a**): Compound **4a** (gummy liquid, 27 mg, 97% yield) was prepared according to the general procedure

(method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), benzyl azide **3a** (10 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL). The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **4a** (28 mg, 98% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (gummy liquid, 22 mg, 0.05 mmol), benzyl azide (**3a**, 10 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.51 (s, 1H) , 7.31-7.41 (m, 5H), 7.24 (d, *J* = 8.4 Hz, 2H), 5.94 (d, *J* = 9.2 Hz, 1H), 5.56 (s, 2H), 4.95 (d, *J* = 7.2 Hz,1H), 4.81 (d, *J* = 12.4 Hz, 1H), 4.60-4.65 (m, 2H), 4.29 (dd, *J* = 12.0, 4.4 Hz, 1H), 4.11-4.17 (m, 2H), 3.88-3.91 (m, 1H), 2.40 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.83 (dt, *J* = 9.6, 3.6 Hz, 1H), 1.51 (dd, *J* = 14.8, 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 170.7, 170.3, 143.9, 143.3, 137.9, 134.4, 129.7, 129.3, 128.9, 128.2, 126.9, 122.5, 96.3, 66.9, 64.6, 62.6, 60.7, 54.3, 47.9, 32.8, 21.5, 20.9, 20.8; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{27}H_{32}N_4O_8SNa$ 595.1839, found 595.1838.

1-Benzyl-4-(3'-*p*-toluenesulfonamido-4',6'-di-*O*-acetyl-2',3'-dideoxy-α-D-galactopyranosyloxymethyl)-1*H*-1,2,3-triazol (**4b**): Compound **4b** (gummy liquid, 25 mg, 89% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglyco conjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2b** (22 mg, 0.05 mmol), benzyl azide (**3a**, 10 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 µL, 1.0 M), and sodium ascorbate solution (5 µL, 1.0 M) in DMF (2 mL), which was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **4b** (26 mg, 93% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxy sugar **2b** (gummy liquid, 22 mg, 0.05 mmol), benzyl azide (**3a**, 10 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 µL, 1.0 M), and sodium ascorbate solution (5 µL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.53 (s, 1H), 7.37-7.43 (m, 3H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.01 (d, *J* = 8.0 Hz, 1H), 5.57 (s, 2H), 5.01 (d, *J* = 3.2 Hz, 1H), 4.82 (d, *J* = 12.4 Hz, 1H), 4.75 (d, *J* = 2.8 Hz, 1H), 4.62 (d, *J* = 12.4 Hz,1H), 4.30 (t, *J* = 6.0 Hz,1H), 3.98-4.07 (m, 2H), 3.59-3.60 (m, 1H), 2.41(s, 3H), 2.06 (s, 3H), 2.04 (d, *J* = 4.0 Hz,1H), 2.01 (s, 3H), 1.47 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 170.5, 169.5, 144.1, 143.5, 137.6, 134.4, 129.8, 129.3,

128.9, 128.2, 127.1, 122.5, 96.1, 67.7, 63.4, 62.8, 60.5, 54.3, 47.5, 28.6, 21.6, 20.8, 20.7; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{27}H_{32}N_4O_8SNa$ 595.1839, found 595.1843.

1-Benzyl-4-(3'-*p*-toluenesulfonamido-4'-*O*-acetyl-2',3',6'-trideoxy-α-L-ribo hexopyranosyloxymethyl)-1*H*-1,2,3-triazol (4c): Compound **4c** (gummy liquid, 17 mg, 74% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2c** (19 mg, 0.05 mmol), benzyl azide (**3a**, 10 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **4c** (gummy liquid, 21 mg, 81% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxy sugar **2c** (19 mg, 0.05 mmol), benzyl azide (**3a**, 10 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.50 (s,1H), 7.34-7.42 (m, 3H), 7.30-7.33 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.95 (d, *J* = 9.2 Hz, 1H), 5.55 (s, 2H), 4.86 (d, *J* =3.2 Hz, 1H), 4.80 (d, *J* = 12.4 Hz, 1H),4.58 (d, *J* = 12.4

Hz, 1H), 4.32 (dd, *J* = 10.0, 4.0 Hz, 1H),4.02 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.79-3.84 (m, 1H), 2.39 (s, 3H), 2.02 (s, 3H), 1.77 (dt, *J* = 14.8, 4.0 Hz, 1H), 1.47 (dd, *J* = 14.8, 2.0 Hz, 1H), 1.17 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 170.7, 144.2, 143.2, 138.0, 134.4, 129.7, 129.3, 128.9, 128.2, 126.9, 122.4, 96.2, 72.5, 62.2, 60.6, 54.3, 48.0, 33.1, 21.5, 21.0, 17.4; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{25}H_{30}N_4O_6SNa$ 537.1784, found 537.1781.

1-Benzyl-4-(4'-(2'',3'',4'',6''-tetra-O-acetyl-α-D-allopyranoside)-6'-*O*-acetyl -2',3'-dideoxy-α-D-allopyranosyloxymethyl)-1*H*-1,2,3-triazol (**4d**): Compound **4d** (gummy liquid, 30 mg, 71% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxy neoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2d** (36 mg, 0.05 mmol), benzyl azide (**3a**, 10 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 µL, 1.0 M), and sodium ascorbate solution (5 µL, 1.0 M) in DMF (2 mL). The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **4d** (gummy liquid, 34 mg, 78% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2d** (36 mg, 0.05 mmol), benzyl azide **3a** (10 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 µL, 1.0 M), and sodium ascorbate solution (5 µL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1);

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.64-7.69 (m, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.46-7.50 (m, 2H), 7.37-7.41 (m, 1H), 7.32-7.34 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 5.77 (d, *J* = 9.6 Hz, 1H), 5.58 (s, 2H), 5.44 (d, *J* = 10.0 Hz, 1H), 5.40 (d, *J* = 4.0 Hz, 1H), 5.24 (dd, *J* = 10.4, 3.6 Hz, 1H), 5.11 (t, *J* = 9.6 Hz, 1H), 4.86 (s, 1H), 4.78 (d, *J* = 12.4 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.44 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.28 (dd, *J* = 12.0, 4.4 Hz, 1H), 4.21 (dd, *J* = 12.4, 4.0 Hz, 1H), 4.09-4.13 (m, 3H), 3.96 (d, *J* = 10.0 Hz, 1H), 3.84-3.88 (m, 1H), 3.72 (dd, *J* = 9.6, 4.0 Hz, 1H), 2.40 (s, 3H), 2.19 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.52-1.56 (m, 1H), 1.32-1.36 (m, 1H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 170.6, 170.4, 170.3, 170.0, 169.5, 143.9, 143.5, 138.0, 134.4, 132.1, 131.9, 129.9, 129.3, 128.2, 126.7, 122.5, 96.5, 92.0, 70.0, 68.7, 68.4, 68.1, 65.9, 62.9, 61.7, 61.1, 54.3, 46.2, 31.5, 21.5, 21.0, 20.8, 20.7, 20.6, 14.2; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{39}H_{48}N_4O_{16}SNa$ 883.2684, found 883.2686.

1-Cinnamyl-4-(3'-*p*-toluenesulfonamido-4',6'-di-*O*-acetyl-2',3'-dideoxy-α-D-allopyranosyloxymethyl)-1*H*-1,2,3-triazol (**4e**): Compound **4e** (gummy liquid, 24 mg, 82% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), cinnamyl azide (**3b**, 12 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL). The crude product was purified by

column chromatography (hexane/ethyl acetate = 1:1); compound **4e** (gummy liquid, 26 mg, 85% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxy sugar **2a** (22 mg, 0.05 mmol), cinnamyl azide (**3b**, 12 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.64 (d, *J* = 10.4 Hz, 3H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.26-7.35 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.38 (dt, *J* = 16.0, 6.8 Hz, 1H), 5.96 (d, *J* = 8.8 Hz, 1H), 5.17 (d, *J* = 6.8 Hz, 2H), 4.97 (d, *J* = 3.2 Hz, 1H), 4.84 (d, *J* = 12.4, 1H), 4.61-4.66 (m, 2H), 4.30 (dd, *J* = 12.4, 4.8 Hz,1H), 4.18 (d, *J* = 10.4 Hz, 2H), 3.88-3.91(m, 1H), 2.37 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.83 (dt, *J* = 14.8, 4.0 Hz, 1H), 1.53 (dd, *J* = 14.8, 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 170.7, 170.4, 143.8, 143.3, 137.8, 136.0, 135.4, 129.7, 128.8, 128.7, 126.9, 126.8, 122.4, 121.5, 96.3, 66.9, 64.6, 62.6, 60.7, 52.5, 47.9, 32.9, 21.5, 20.9, 20.8; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{29}H_{34}N_4O_8SNa$ 621.1995, found 621.1994.

1-*tert*-Butylacetyl-4-(3'-*p*-toluenesulfonamido-4',6'-di-*O*-acetyl-2',3'-dide-oxy-α-D-allopyranosyloxymethyl)-1*H*-1,2,3-triazol (**4f**): Compound **4f** (gummy liquid, 27 mg, 91% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent

3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), azide **3c** (8 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL). The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **4f** (gummy liquid, 28 mg, 92% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), azide **3c** (8 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.72 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.96 (d, *J* = 8.8 Hz, 1H), 5.08 (s, 2H), 4.96 (d, *J* = 3.2 Hz, 1H), 4.84 (d, *J* = 12.4 Hz, 1H),4.67 (d, *J* = 12.4 Hz, 1H), 4.63 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.29 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.17 (d, *J* = 10.4 Hz, 2H), 3.87-3.90 (m, 1H), 2.39 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.82 (dt, *J* = 14.4, 4.0 Hz, 1H), 1.52 (d, *J* = 2.4 Hz, 1H),1.49 (s, 9H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 170.7, 170.4, 165.2, 143.7, 143.3, 137.9, 129.8, 126.9, 124.2, 96.2, 84.0, 67.0, 64.6, 62.7, 60.6, 51.5, 47.9, 32.8, 28.0, 21.5, 20.9, 20.8; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{26}H_{36}N_4O_{10}SNa$ 619.2050, found 619.2053.

1-(Hept-6'-en-1-yl)-4-(3''-*p*-toluenesulfonamido-4'',6''-di-*O*-acetyl-2'',3''-dideoxy-α-D-allopyranosyloxymethyl)-1*H*-1,2,3-triazol (**4g**): Compound **4g**

(gummy liquid, 25 mg, 86% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglyco conjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), azide **3d** (11 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL). The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **4g** (gummy liquid, 26 mg, 89% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), azide **3d** (11 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.57 (s, 1H), 7.27 (d, *J* = 6.8 Hz, 2H), 5.97 (d, *J* = 8.8 Hz, 1H), 5.76-5.79 (m, 1H), 4.93-5.01 (m, 3H), 4.84 (d, *J* = 12.4 Hz, 1H), 4.65 (d, *J* = 12.4 Hz, 2H), 4.38 (t, *J* = 7.2 Hz, 2H), 4.32 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.19 (d, *J* = 11.2 Hz, 2H), 3.88-3.92 (m, 1H), 2.40 (s, 3H), 2.07 (s, 3H), 2.03-2.05 (m, 2H), 2.01 (s, 3H), 1.95 (t, *J* = 7.2 Hz, 2H), 1.85 (dt, *J* = 14.4, 4.0 Hz, 1H), 1.24-1.48 (m, 5H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 170.7, 170.4, 143.4, 143.3, 138.3, 137.8, 129.8, 126.9, 122.4, 114.8, 96.3. 67.0, 64.6,

62.7, 60.7, 50.5, 48.0, 33.4, 32.9, 30.1, 28.2, 25.9, 21.5, 20.9, 20.8; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{27}H_{38}N_4O_8SNa$ 601.2308, found 601.2308.

1-(6'-Acetylthiohexyl)-4-(3''-*p*-toluenesulfonamido-4'',6''-di-*O*-acetyl-2'', 3''-dideoxy-α-D-allopyranosyloxymethyl)-1*H*-1,2,3-triazol (**4h**): Compound **4h** (gummy liquid, 28 mg, 87% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), azide **3e** (10 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL). The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **4h** (gummy liquid, 30 mg, 92% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), azide **3e** (10 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.58 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.97 (d, *J* = 8.8 Hz, 1H), 5.75-5.81 (m, 1H), 4.93-5.01 (m, 3H), 4.84 (d, *J* = 12.4 Hz, 1H), 4.62-4.65 (m, 2H), 4.38 (t, *J* = 7.2 Hz, 2H), 4.30 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.17-4.20 (m, 1H), 3.88-3.91 (m, 1H), 2.40 (s, 3H), 2.07 (s, 3H), 2.03

(s, 3H), 1.99 (s, 3H), 1.95 (t, *J* = 7.2 Hz, 2H), 1.85 (dt, *J* = 14.4, 4.0 Hz, 1H), 1.54-1.64 (m, 3H), 1.38-1.40 (m, 4H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 171.2, 170.7, 170.3, 143.5, 143.4, 137.8, 129.8, 126.9, 122.4, 96.3. 67.0, 64.6, 64.2, 62.6, 60.7, 50.4, 48.0, 32.9, 30.2, 28.4, 26.1, 25.4, 21.5, 21.0, 20.9, 20.8; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{28}H_{40}N_4O_9S_2Na$ 663.2134, found 663.2130.

1-(2',3',4',6'-Tetra-*O*-acetyl-α-D-allopyranosyl)-4-(3''-*p*-tosamido-4'',6''-di-*O*-acetyl-2'',3''-dideoxy-α-D-allopyranosyloxymethyl)-1*H*-1,2,3-triazol (**4i**): Compound **4i** (gummy liquid, 31 mg, 76% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), azide **3f** (28 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL). The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **4i** (gummy liquid, 33 mg, 80% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), azide **3f** (28 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR

($CDCl_3$, 400MHz): δ 7.84 (s, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.92 (dd, *J* = 13.6, 9.2 Hz, 2H), 5.40-5.48 (m, 2H), 5.27 (t, *J* = 9.6 Hz, 1H), 4.92 (d, *J* = 3.2 Hz, 1H), 4.85 (d, *J* = 12.4 Hz, 1H), 4.66 (d, *J* = 12.4 Hz, 2H), 4.31-4.38 (m, 2H), 4.16-4.21 (m, 3H), 4.02-4.04 (m, 1H), 3.90-3.92 (m, 1H), 2.41 (s, 3H), 2.07-2.09 (m, 9H), 2.03-2.05 (m, 9H), 1.85 (dt, *J* = 14.8, 4.0 Hz, 1H), 1.53 (dd, *J* = 10.4, 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 170.7, 170.5, 170.3, 169.9, 169.4, 169.0, 144.1, 143.3, 138.0, 129.7, 126.9, 121.2, 96.1, 85.9, 75.3, 72.4, 70.4, 67.7, 66.9, 64.6, 62.7, 61.5, 60.2, 47.9, 32.8, 21.5, 20.9, 20.8, 20.7, 20.5, 20.2, 14.2; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{34}H_{44}N_4O_{17}SNa$ 835.2320, found 835.2314.

1-(2'-*N*-Acetyl-3',4',6'-tri-*O*-acetyl-α-D-allopyranosyl)-4-(3''-*p*-toluenesul-fonamido-4'',6''-di-*O*-acetyl-2'',3''-dideoxy-α-D-allopyranosyloxymethyl)-1*H*-1,2,3-triazol (**4j**): Compound **4j** (gummy liquid, 38 mg, 93% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), azide **3g** (28 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL). The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **4j** (gummy liquid, 39 mg, 95% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl

3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), azide **3g** (28 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.89 (d, *J* = 28.4 Hz, 1H), 5.58 (d, *J* = 8.0 Hz, 2H) , 7.21 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.72 (d, *J* = 9.2 Hz, 1H), 6.14 (d, *J* = 10.0 Hz, 1H), 5.98 (d, *J* = 9.2 Hz, 1H), 5.51 (t, *J* = 10.4 Hz, 1H), 5.24 (t, *J* = 10.0 Hz, 1H), 5.16 (t, *J* = 9.6 Hz, 1H), 5.01 (t, *J* = 9.6 Hz, 1H), 4.86 (d, *J* = 2.8 Hz, 1H), 4.81 (d, *J* = 9.6 Hz, 1H), 4.76 (d, *J* = 12.4 Hz, 1H), 4.54-4.59 (m, 2H), 4.17-4.29 (m, 1H), 4.05-4.14 (m, 2H), 3.78-3.90 (m, 1H), 2.33 (s, 3H), 1.88-2.01 (m, 18H), 1.70-1.80 (m, 1H), 1.40-1.50 (m, 1H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 171.2, 170.8, 170.6, 170.4, 170.3, 169.4, 162.7, 143.7, 137.8, 129.8, 126.8, 121.8, 96.0, 88.3, 85.7, 74.7, 72.2, 68.4, 67.0, 64.6, 62.6, 61.9, 60.3, 53.9, 48.0, 36.5, 32.6, 22.7, 21.4, 20.8, 20.4, 14.1; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{34}H_{45}N_5O_{16}SNa$ 834.2480, found 834.2484.

1-(2'-*N*-Acetyl-3',4',6'-tri-*O*-acetyl-α-D-glucopyranosyl)-4-(4'-(2'',3'',4'',6''-tetra-*O*-acetyl-α-D-glucopyranoside)-6'-*O*-acetyl-2',3'-dideoxy-α-D-allopyranosyloxymethyl)-1*H*-1,2,3-triazol (**4k**): Compound **4k** (gummy liquid, 44 mg, 80% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2d** (36 mg, 0.05 mmol), benzyl azide **3g** (28 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and

sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL). The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **4k** (gummy liquid, 45 mg, 82% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2d** (36 mg, 0.05 mmol), azide **3g** (28 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.95 (s, 1H), 7.53(d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 9.6 Hz, 2H), 6.40 (d, *J* = 8.4 Hz, 1H), 6.31 (d, *J* = 10.0 Hz, 1H), 5.95 (d, *J* = 10.0 Hz, 1H), 5.62 (d, *J* = 9.2 Hz, 1H), 5.43 (dd, *J* = 10.0, 9.2 Hz, 1H), 5.37 (d, *J* = 3.6 Hz, 1H), 5.19-5.28 (m, 2H), 5.06-5.13 (m, 1H), 4.86 (s, 1H), 4.76-4.82 (m, 2H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.50 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.07-4.28 (m, 8H), 3.90-3.97 (m, 1H), 3.78-3.88 (m, 1H), 3.74 (dd, *J* = 10.4, 3.6 Hz, 1H), 2.41 (s, 3H), 2.14 (s, 3H), 1.96-2.10 (m, 25H), 1.49-1.54 (m, 1H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 171.0, 170.6, 170.5, 170.4, 170.3, 170.0, 169.5, 169.4, 169.3, 144.1, 143.7, 137.9, 130.0, 126.7, 121.4, 96.4, 88.4, 85.6, 75.0, 73.9, 72.2, 71.6, 69.9, 68.7, 68.4, 68.1, 65.7, 63.1, 61.8, 60.5, 60.4, 54.7, 54.1, 46.2, 31.3, 23.2, 22.8, 21.5, 21.1, 20.9, 20.7, 20.6, 20.5, 20.4; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{46}H_{61}N_5O_{24}SNa$ 1122.3325, found 1122.3322.

1-(2',2',7',7'-Tetramethyltetrahydro-bis([1,3]dioxolo)pyranylmethyl)-4-(3''-*p*-toluenesulfonamido-4'',6''-di-*O*-acetyl-2'',3''-dideoxy-α-D-allo-pyrano-syloxymethyl)-1*H*-1,2,3-triazol (**4l**): Compound **4l** (gummy liquid, 26 mg, 72% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), azide **3h** (22 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL). The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **4l** (gummy liquid, 28 mg, 78% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (22 mg, 0.05 mmol), azide **3h** (22 mg, 0.075 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.76 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 5.95 (d, *J* = 8.8 Hz, 1H), 5.52 (d, *J* = 5.2 Hz, 1H), 4.93 (d, *J* = 3.6 Hz, 1H), 4.84 (d, *J* = 12.4 Hz, 1H), 4.63-4.69 (m, 4H), 4.48 (dd, *J* = 10.0, 8.8 Hz, 1H), 4.31-4.35 (m, 2H), 4.19-4.24 (m, 4H), 3.88-3.91 (m, 1H), 2.41 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 1.82 (dt, *J* = 14.8, 4.0 Hz, 1H), 1.51 (s, 3H), 1.49 (dd, *J* = 9.2, 2.4 Hz, 1H), 1.41 (s, 3H), 1.38 (s, 3H), 1.29 (s, 3H); ^{13}C NMR ($CDCl_3$,

400MHz): δ 170.7, 170.4, 143.3, 137.9, 129.7, 126.9, 124.2, 110.0, 109.1, 96.2, 96.0, 71.2, 70.8, 70.3, 67.2, 67.0, 64.6, 62.7, 60.6, 50.7, 47.9, 32.8, 26.0, 24.9, 24.4, 21.5, 21.1, 20.9, 20.8, 14.2; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{32}H_{44}N_4O_{13}SNa$ 747.2523, found 747.2531.

1,3-Bis{4'-(3''-*p*-toluenesulfonamido-4'',6''-di-*O*-acetyl-2'',3''-dideoxy-α-D-allopyranosyloxymethyl)-1'*H*-1',2',3'-triazol-1'-methyl}-benzene (**6a**): Compound **6a** (gummy liquid, 44 mg, 83% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (44 mg, 0.1 mmol), diazide **5a** (10 mg, 0.05 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL). The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **6a** (gummy liquid, 46 mg, 86% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (44 mg, 0.1 mmol), diazide **5a** (10 mg, 0.05 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.59-7.62 (m, 6H), 7.40-7.44 (m, 1H), 7.23-7.30 (m, 7H) , 5.99 (d, *J* = 8.8 Hz, 2H), 5.55 (s, 4H), 4.98 (d, *J* = 3.2 Hz, 2H), 4.82 (d, *J* = 12.0

Hz, 2H), 4.57-4.65 (m, 4H), 4.26-4.36 (m, 2H), 4.12-4.17 (m, 4H), 3.86-3.89 (m, 2H), 2.40 (s, 6H), 2.04 (s, 6H), 1.98 (s, 6H), 1.83 (dt, *J* = 14.8, 4.0 Hz, 2H), 1.56 (d, *J* = 2.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 170.7, 170.2, 143.4, 137.7, 135.8, 129.8, 128.5, 127.6, 126.9, 122.7, 96.6, 66.9, 64.7, 62.6, 60.8, 60.4, 54.3, 48.0, 32.9, 21.5, 21.0, 20.8, 20.7, 14.2; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{48}H_{58}N_8O_{16}S_2Na$ 1089.3310, found 1089.3312.

1,3-Bis{4'-(3''-*p*-toluenesulfonamido-4''-*O*-acetyl-2'',3'',6''-trideoxy-α-L-ribohexopyranosyloxymethyl)-1'*H*-1',2',3'-triazol-1'-methyl}benzene (**6b**): Compound **6b** (gummy liquid, 28 mg, 61% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2c** (38 mg, 0.1 mmol), diazide **5a** (10 mg, 0.05 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL). The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **6b** (gummy liquid, 30 mg, 65% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2c** (38 mg, 0.1 mmol), diazide **5a** (10 mg, 0.05 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR

($CDCl_3$, 400MHz): δ 7.62 (d, *J* = 8.0 Hz, 4H), 7.54 (s, 2H), 7.41-7.44 (m, 2H), 7.23-7.34 (m, 6H), 5.97 (d, *J* = 8.8 Hz, 2H), 5.58 (s, 4H), 4.88 (d, *J* = 2.4 Hz, 2H), 4.82 (d, *J* = 12.0 Hz, 2H), 4.59 (d, *J* =12.4 Hz, 2H), 4.32-4.61 (m, 2H), 3.99-4.07 (m, 2H), 3.80-3.83 (m, 2H), 2.40 (s, 6H), 2.01 (s, 6H), 1.76-1.81 (m, 2H), 1.51 (d, *J* = 14.4 Hz, 2H), 1.18 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 170.6, 144.4, 143.2, 137.9, 136.7, 135.2, 129.8, 129.7, 129.6, 128.6, 128.0, 127.8, 126.9, 122.4, 96.2, 72.5, 62.3, 60.6, 54.3, 54.0, 48.0, 33.1, 21.5, 21.0, 17.4, 14.2; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{44}H_{55}N_8O_{12}S_2$ 951.3381, found 951.3361.

2,4,6-Tris{2-[4'-(3''-*p*-toluenesulfonamido-4'',6''-di-*O*-acetyl-2'',3''-dide-oxy-α-D-allopyranosyloxymethyl)-1'*H*-1',2',3'-triazol-1'-yl]ethoxy}-1,3,5-triazine (**6c**): Compound **6c** (gummy liquid, 54 mg, 66% yield) was prepared according to the general procedure (method A) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (66 mg, 0.15 mmol), triazide **5b** (17 mg, 0.05 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL). The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); compound **6c** (gummy liquid, 56 mg, 68% yield) was also prepared according to the general procedure (method B) for the synthesis of multivalent 3-tosylamino-2,3-dideoxyneoglycoconjugates from propargyl 3-tosylamino-2,3-dideoxysugar **2a** (66 mg, 0.15 mmol), triazide **5b** (17 mg,

0.05 mmol), $CuSO_4 \cdot 5H_2O$ solution (5 μL, 1.0 M), and sodium ascorbate solution (5 μL, 1.0 M) in DMF (2 mL) under microwave irradiation. The crude product was purified by column chromatography (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.78 (s, 3H), 7.66 (d, *J* = 8.4 Hz, 6H), 7.29 (d, *J*= 8.8 Hz, 6H), 5.93 (d, *J* = 9.2 Hz, 3H), 4.98 (d, *J* = 3.2 Hz, 3H), 4.83-4.87 (m, 6H), 4.62-4.65 (m, 3H), 4.56 (t, *J* = 4.8 Hz, 6H), 4.31 (dd, *J* = 12.0, 4.8 Hz, 3H), 4.18-4.20 (m, 6H), 3.86-3.89 (m, 3H), 3.65 (t, *J* = 4.8 Hz, 6H), 2.41 (s, 9H), 2.08 (s, 9H), 2.01 (s, 9H), 1.84 (dt, *J* = 14.8, 4.0 Hz, 3H), 1.56 (dd, *J* = 12.0, 2.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 400MHz): δ 173.1, 171.8, 171.6, 170.8, 170.4, 143.4, 137.7, 129.8, 126.9, 96.4, 67.4, 66.9, 64.6, 62.6, 60.6, 49.4, 48.9, 47.9, 32.8, 21.5, 20.9; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{69}H_{87}N_{15}O_{27}S_3Na$ 1676.4956, found 1676.4979.

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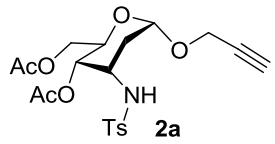
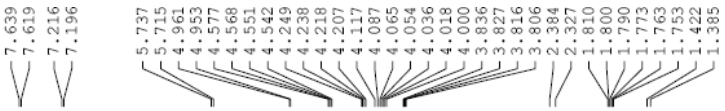
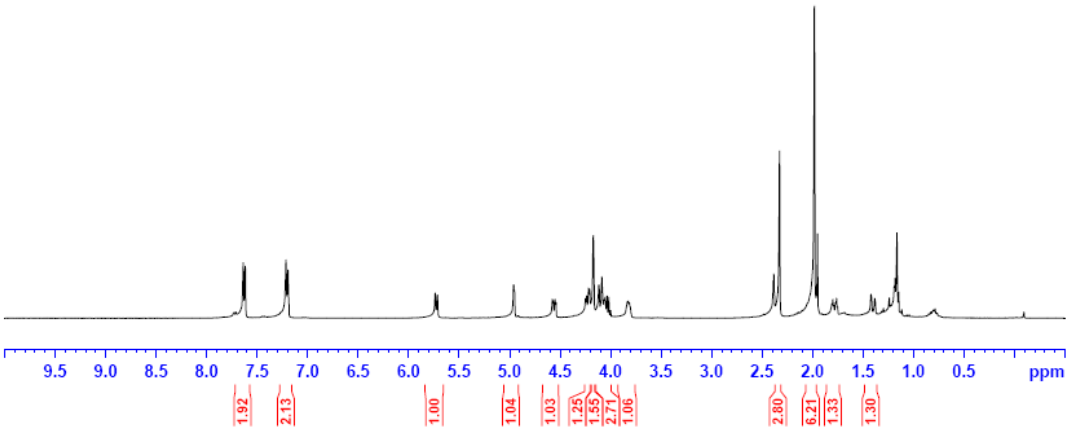
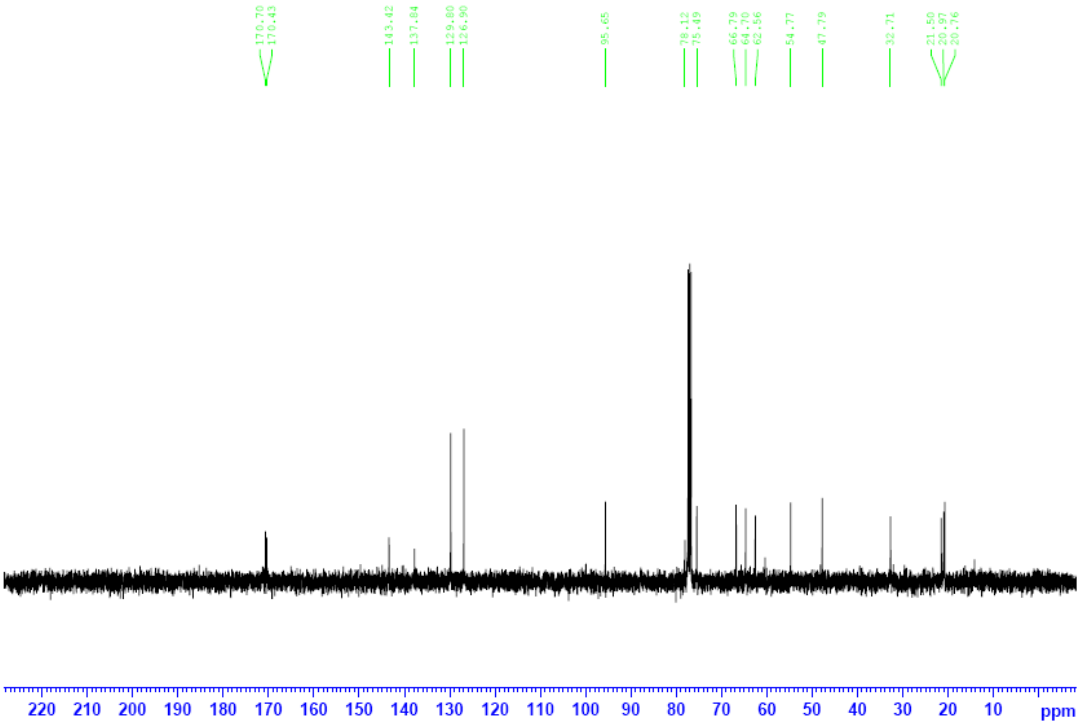
NMR spectra for all compounds.

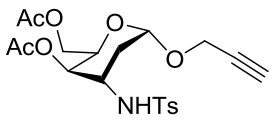


2a



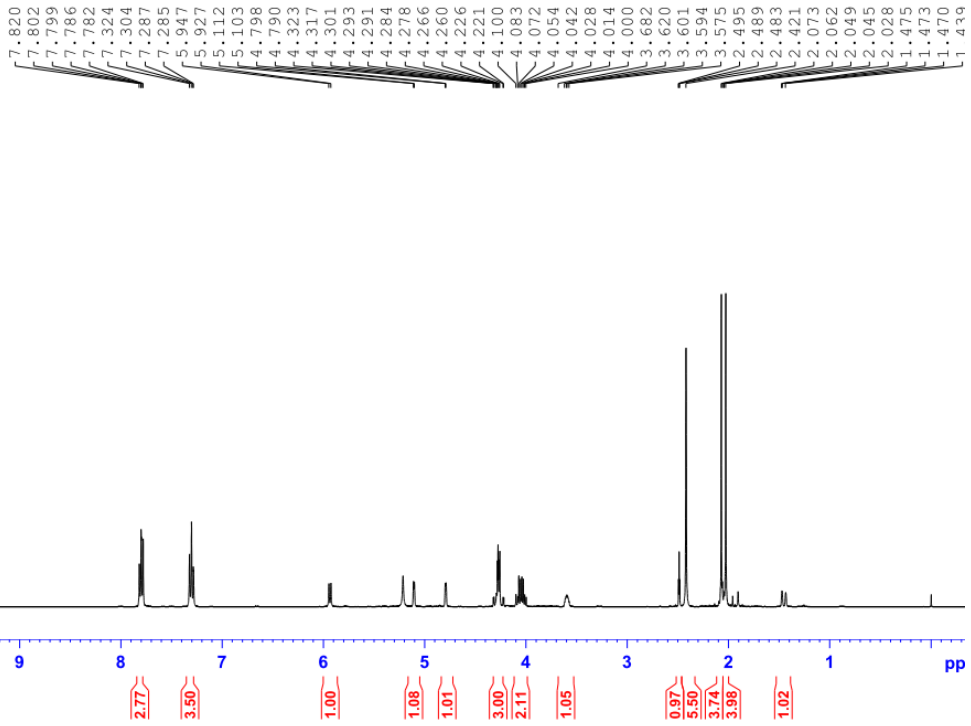




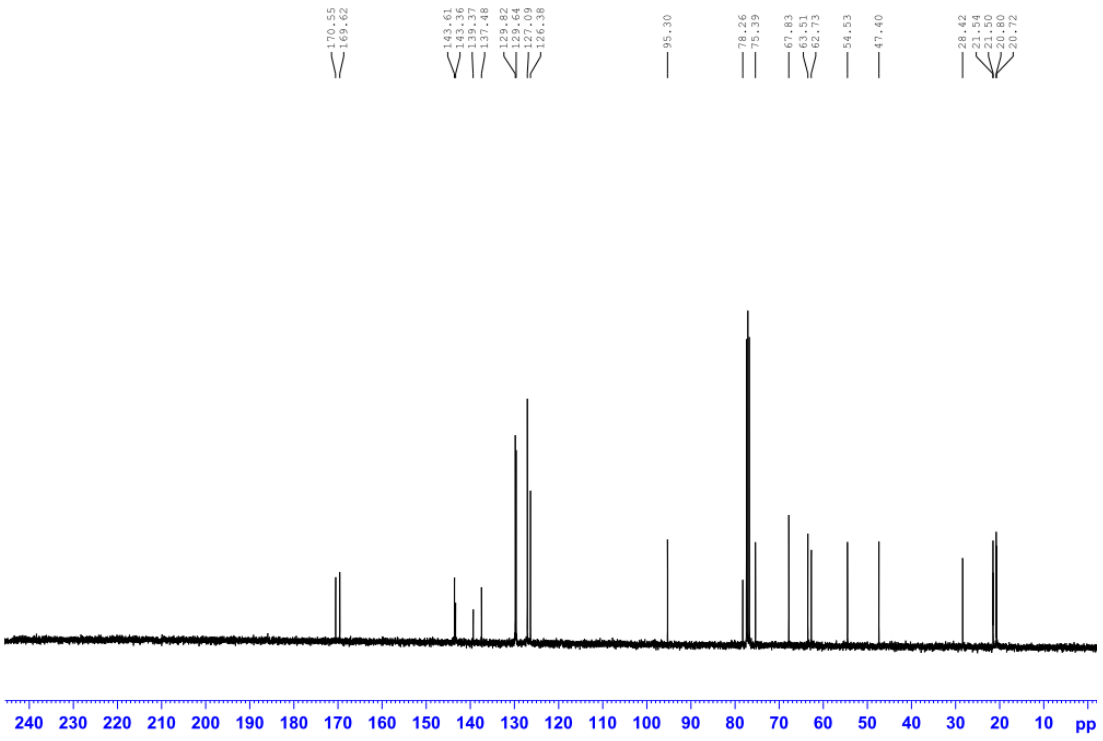


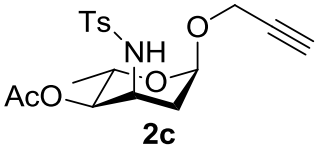
2b

D2-142-1p,1H NMR, JUL, BBFO1 400HZ



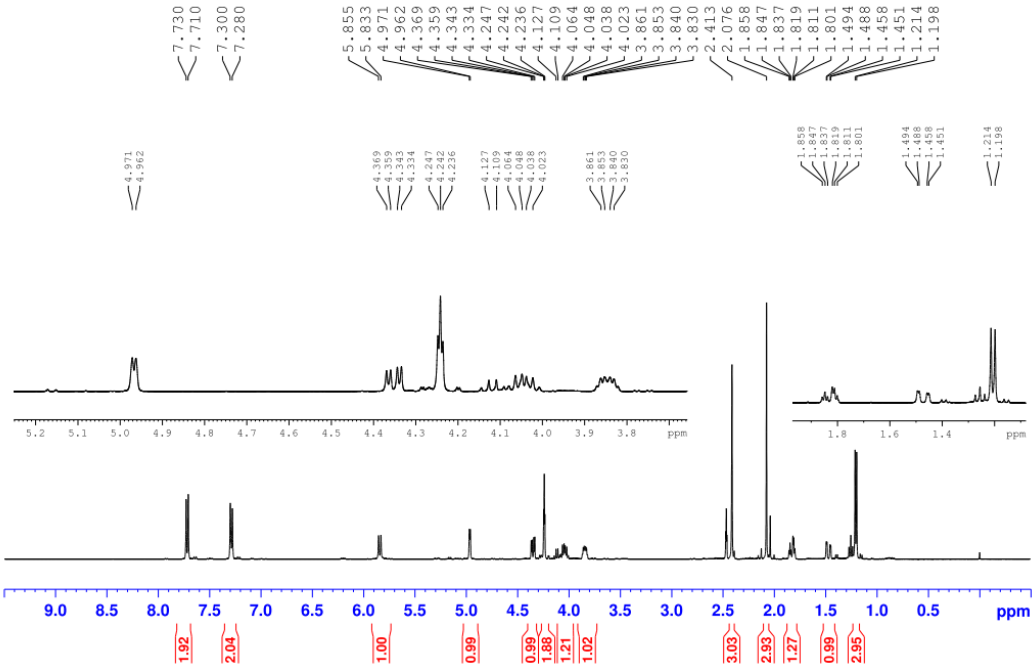
D2-142-1p,13C NMR, JUL, BBFO1 400HZ



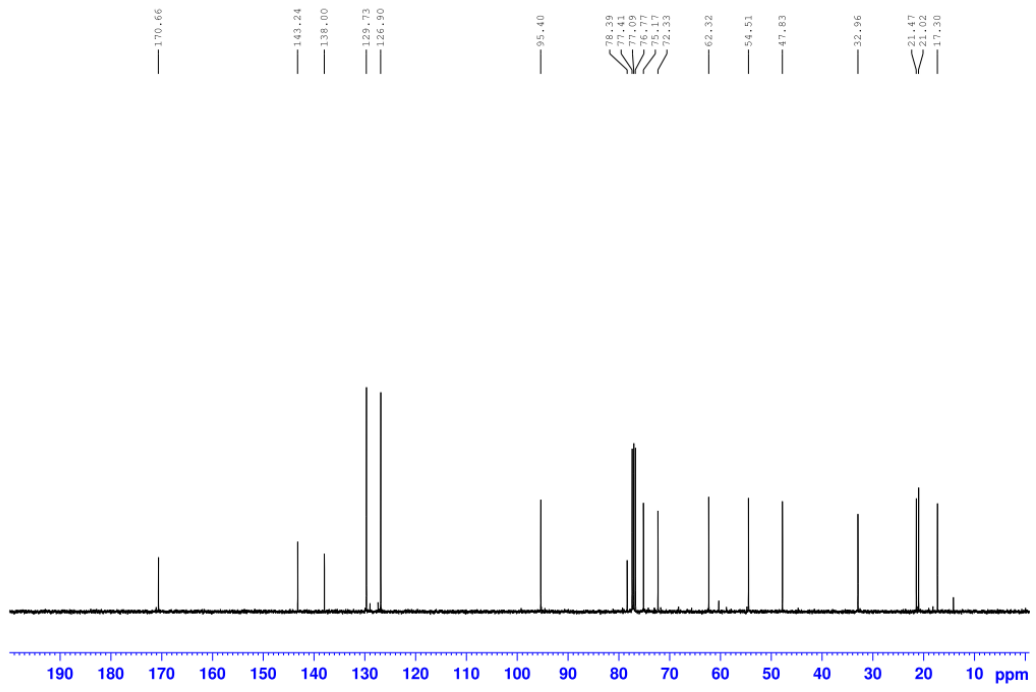


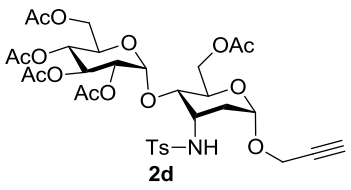
2c

D2-114-1p, 1H NMR, AV400MHz, CDCl3



D2-114-1p, 13C NMR, AV400MHz, CDCl3

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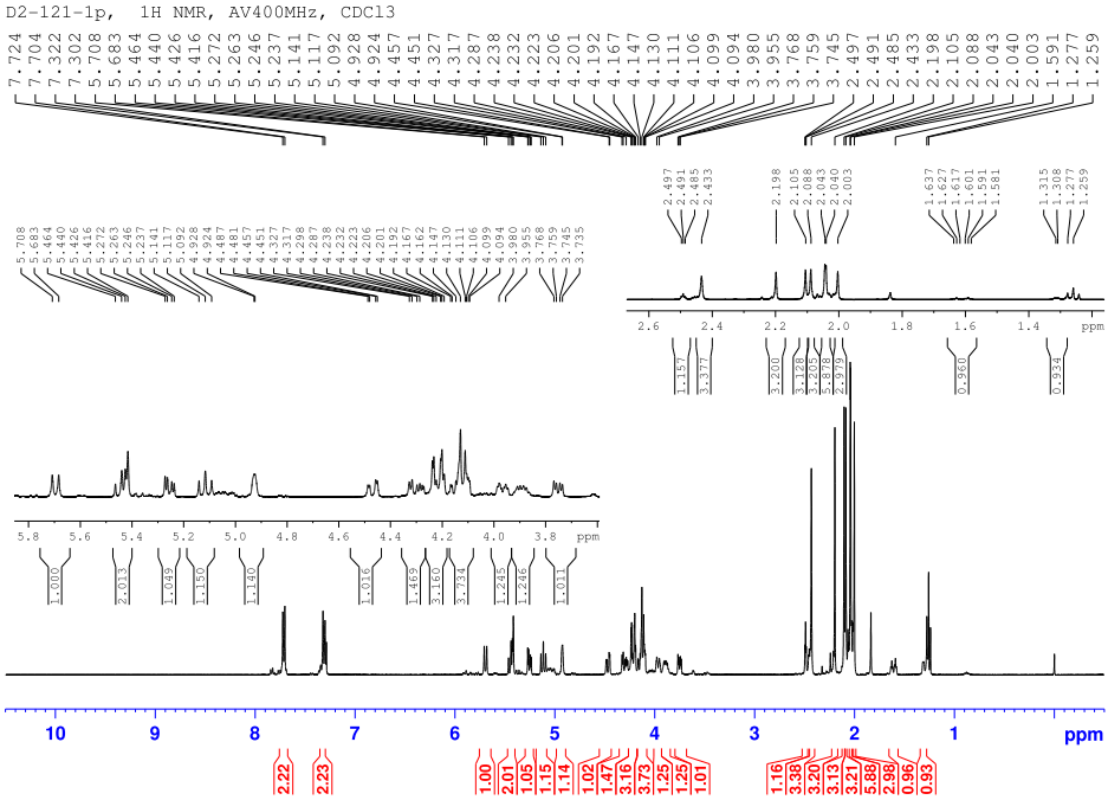
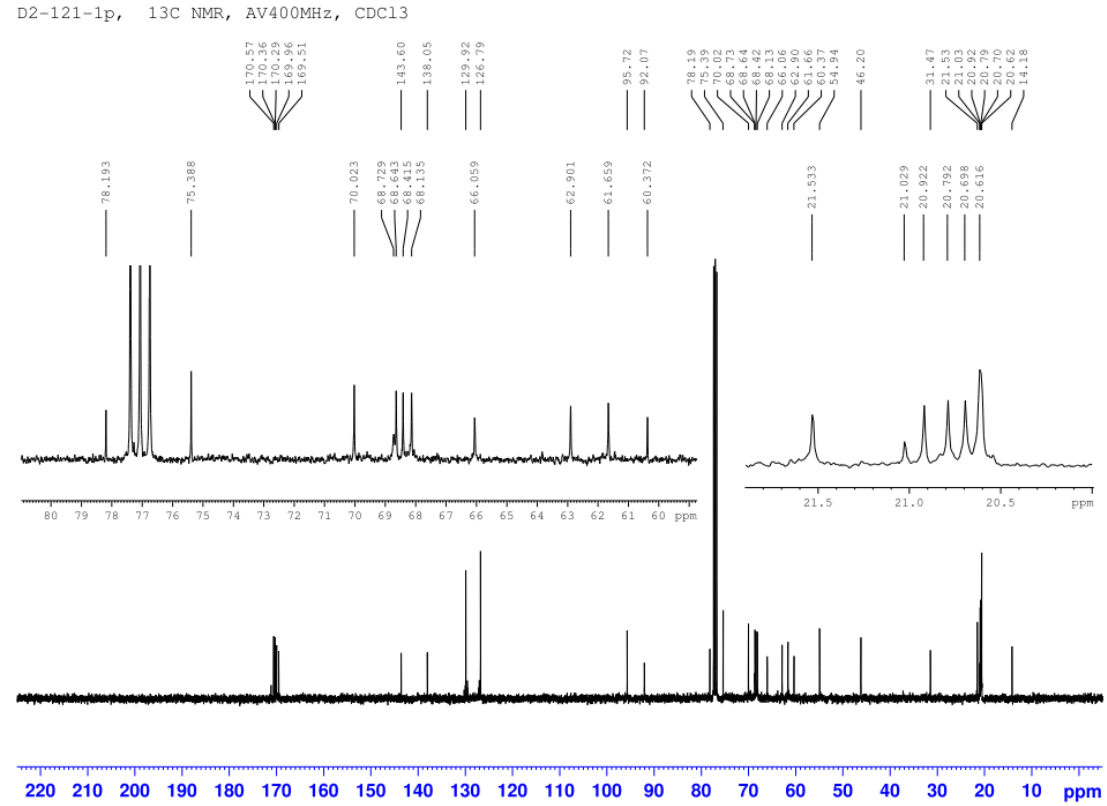
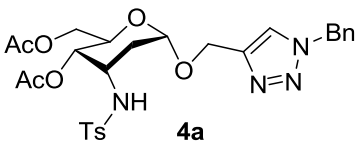
AcO
AcO
AcO
O
OAc
O
O
Ts–NH
O

2d

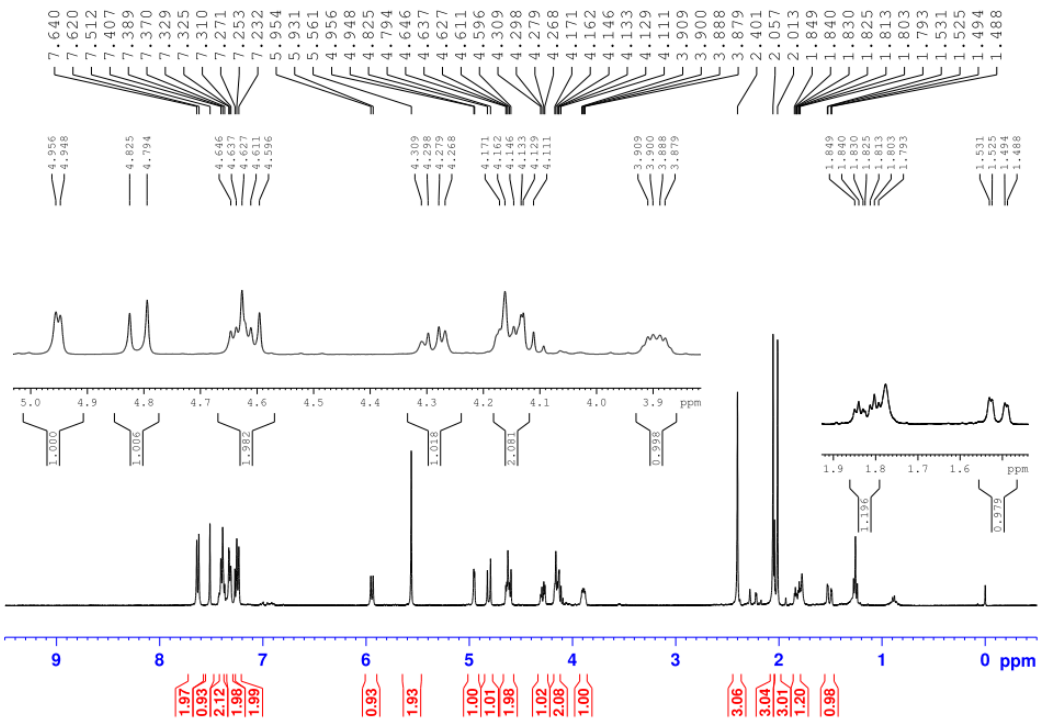

D2-121-1p, 1H NMR, AV400MHz, CDCl3
ppm


D2-121-1p, 13C NMR, AV400MHz, CDCl3
ppm

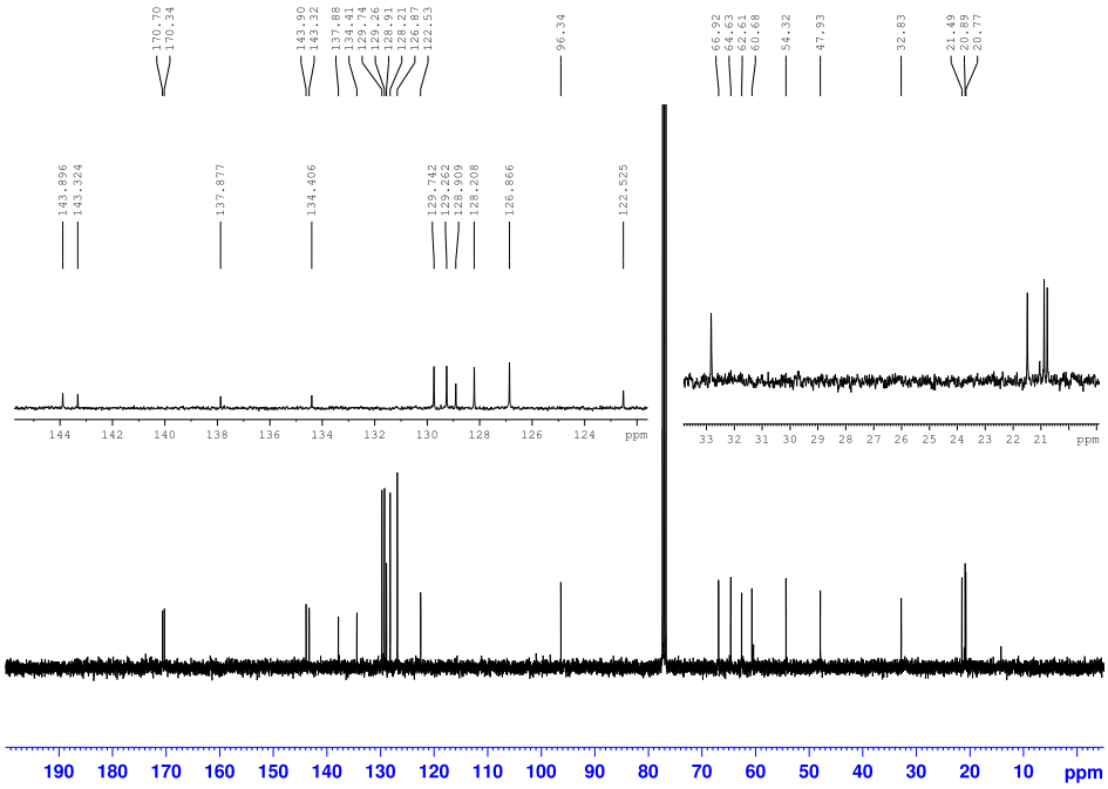


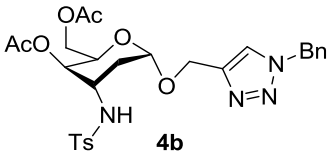
4a

D2-112-2p, 1H NMR, AV400MHz, CDCl3



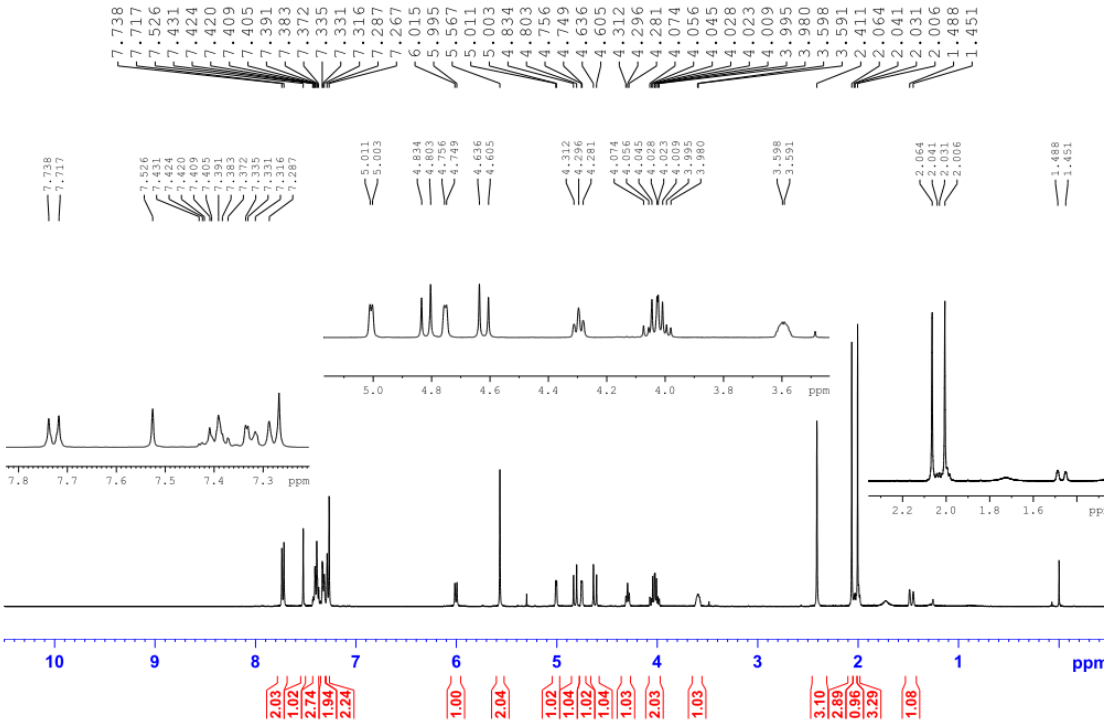
D2-112-2p, 13C NMR, AV400MHz, CDCl3



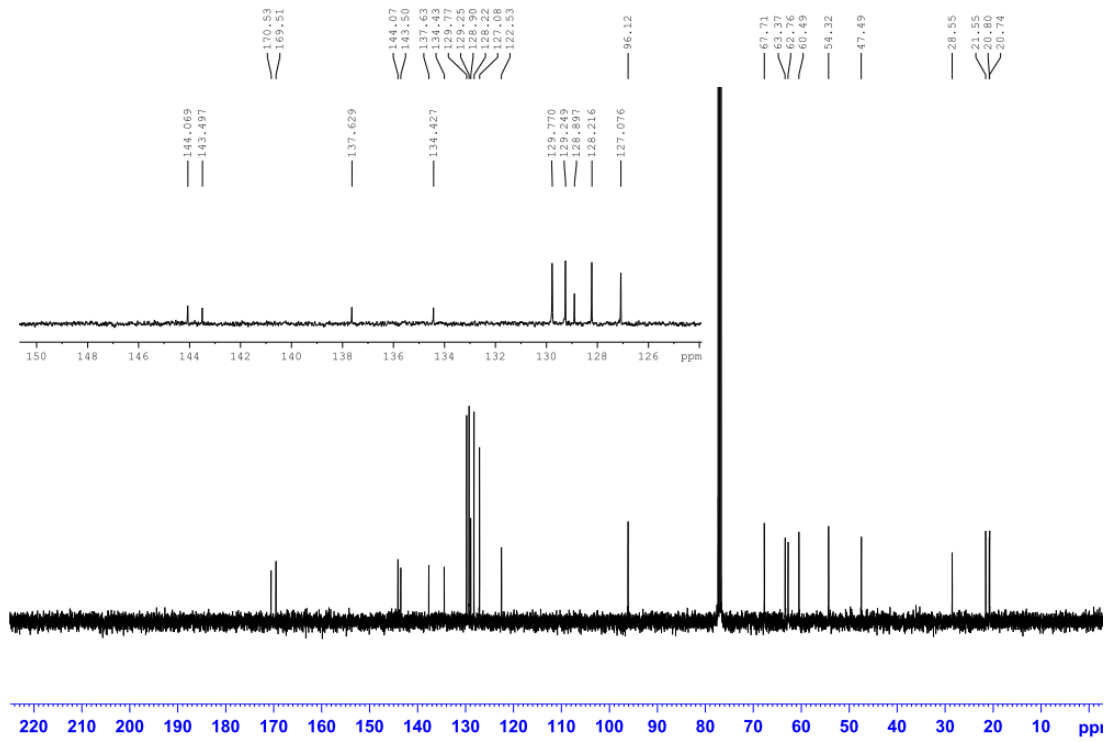


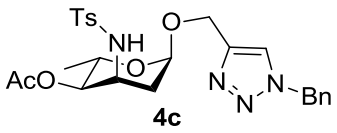
4b

D2-150-1P,1H, BBFO1,400 Hz, CDCl3



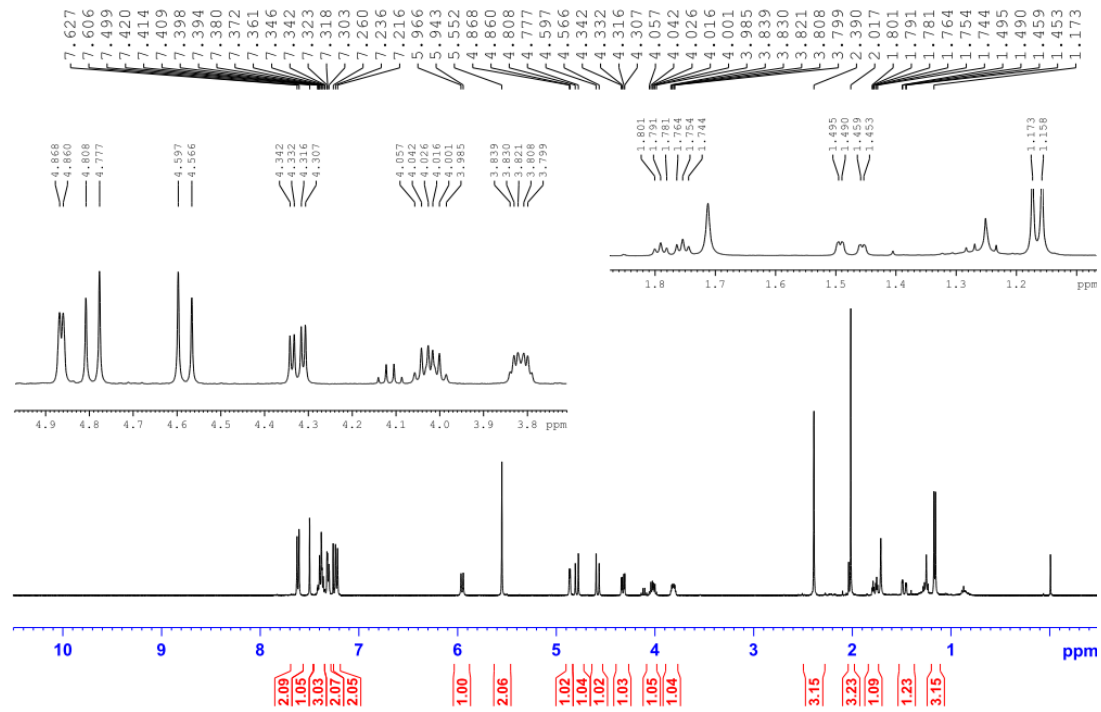
D2-150-1P,13C, BBFO1,400 Hz, CDCl3





4c

D2-123-1P,1H, BBFO1,400 Hz, CDCl3



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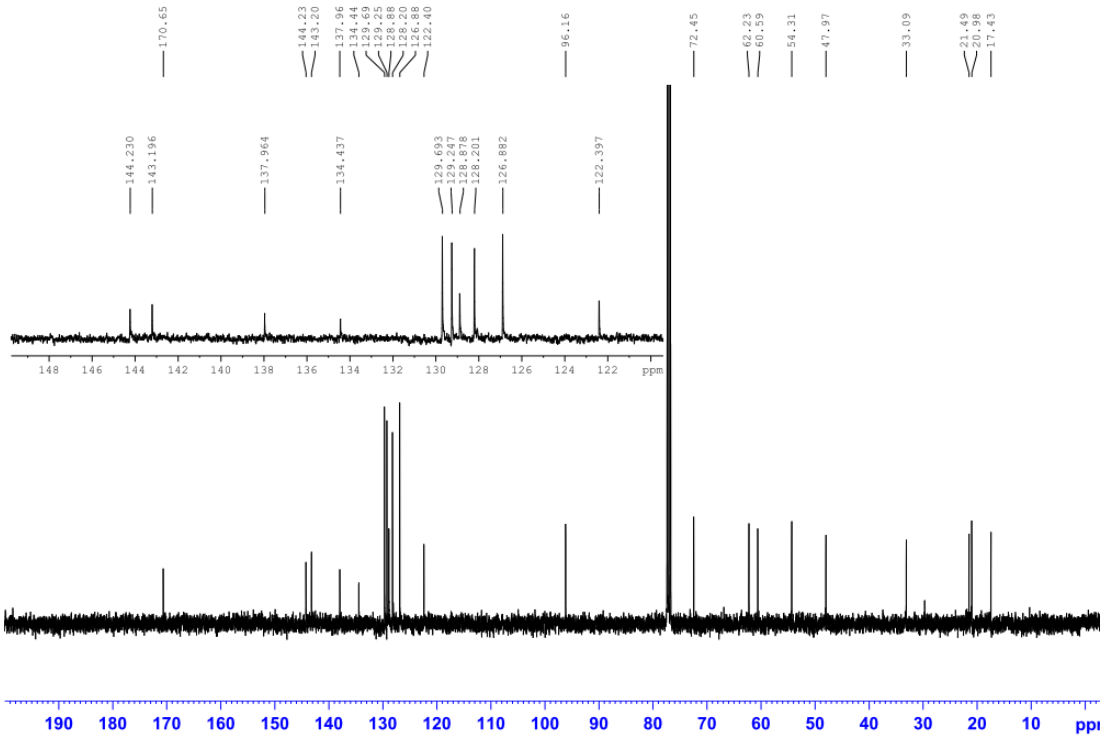

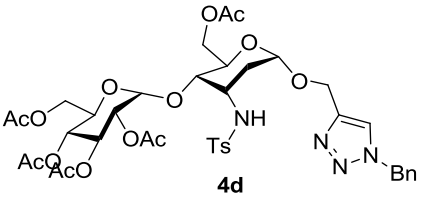
OAc
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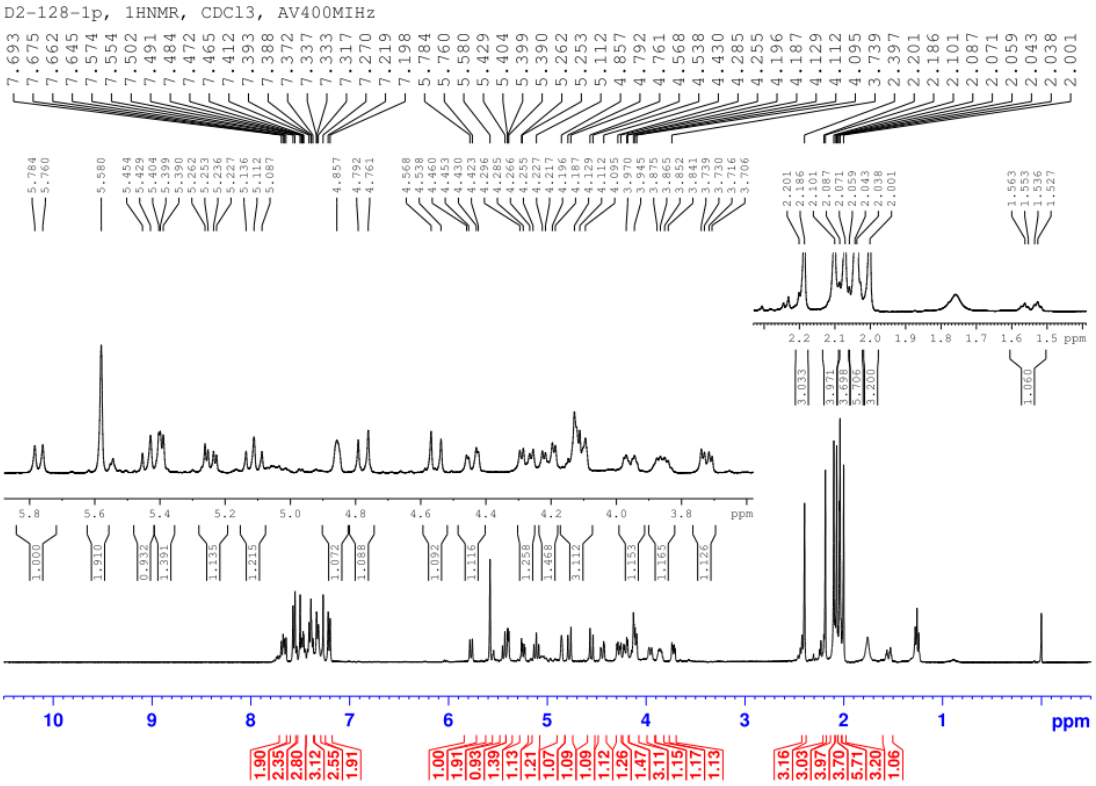
Ts
OAc
AcO
AcO
N
N
N
Bn

4d


D2-128-1p, 1HNMR, CDCl3, AV400MIHz
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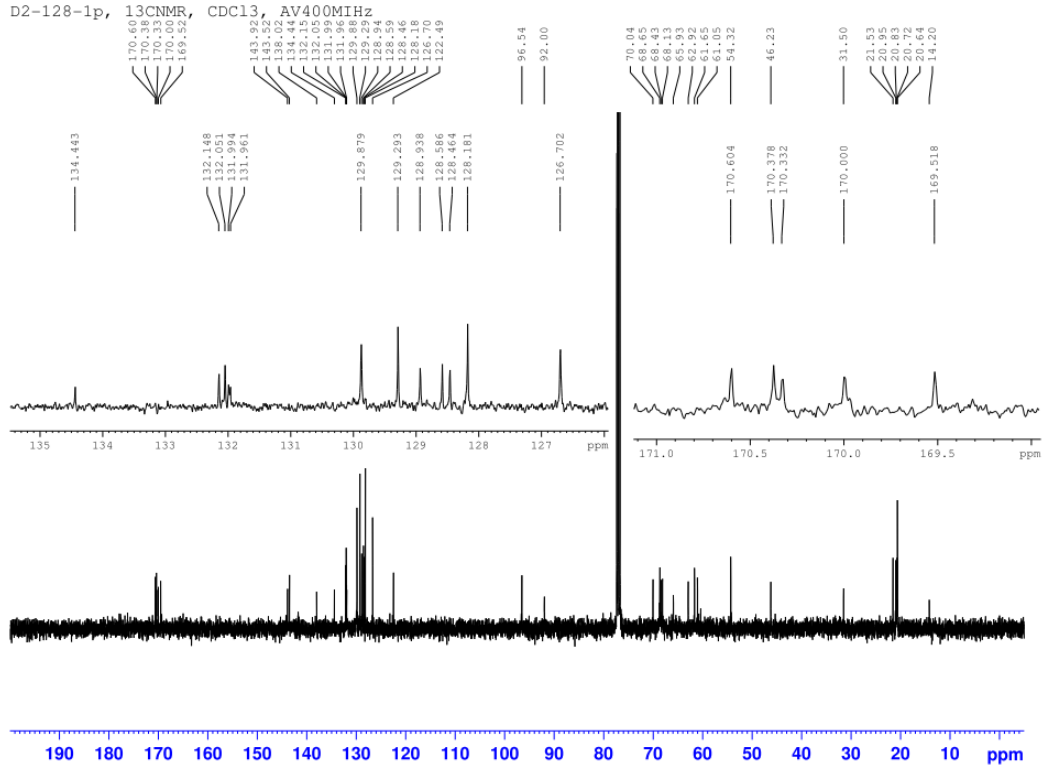
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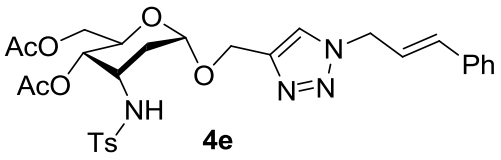
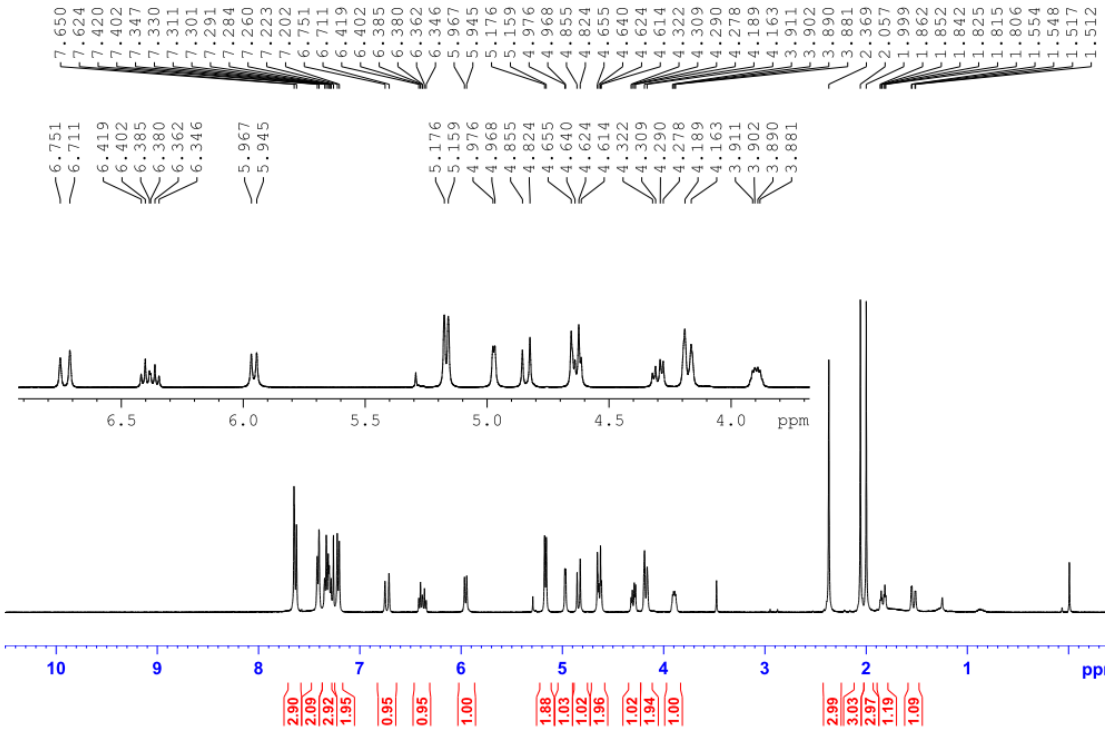
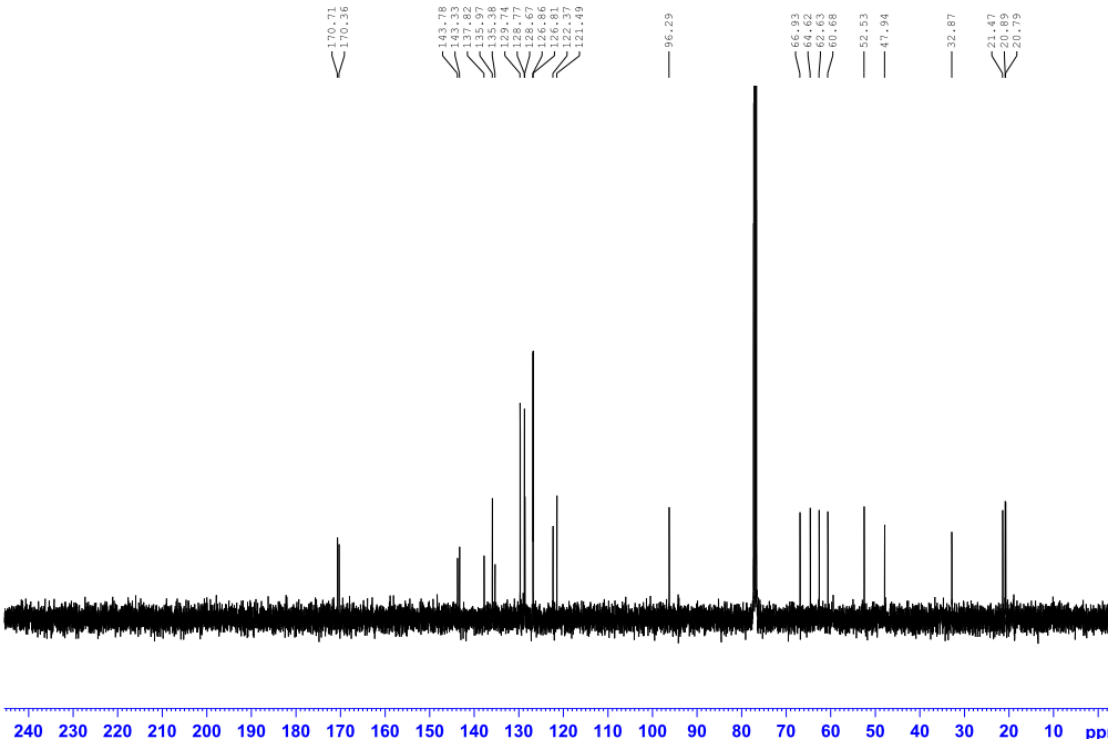


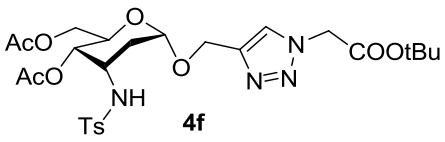
4e

D2-147-1p,1H NMR, JUL, BBFO1 400HZ



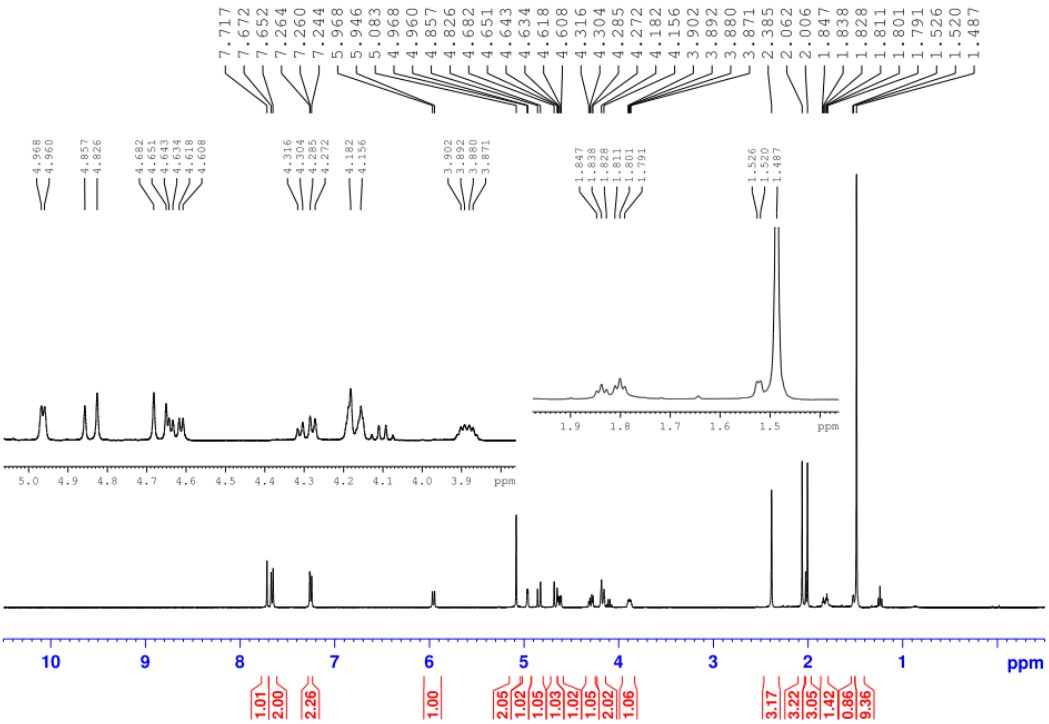
D2-147-1p,13C NMR, JUL, BBFO1 400HZ



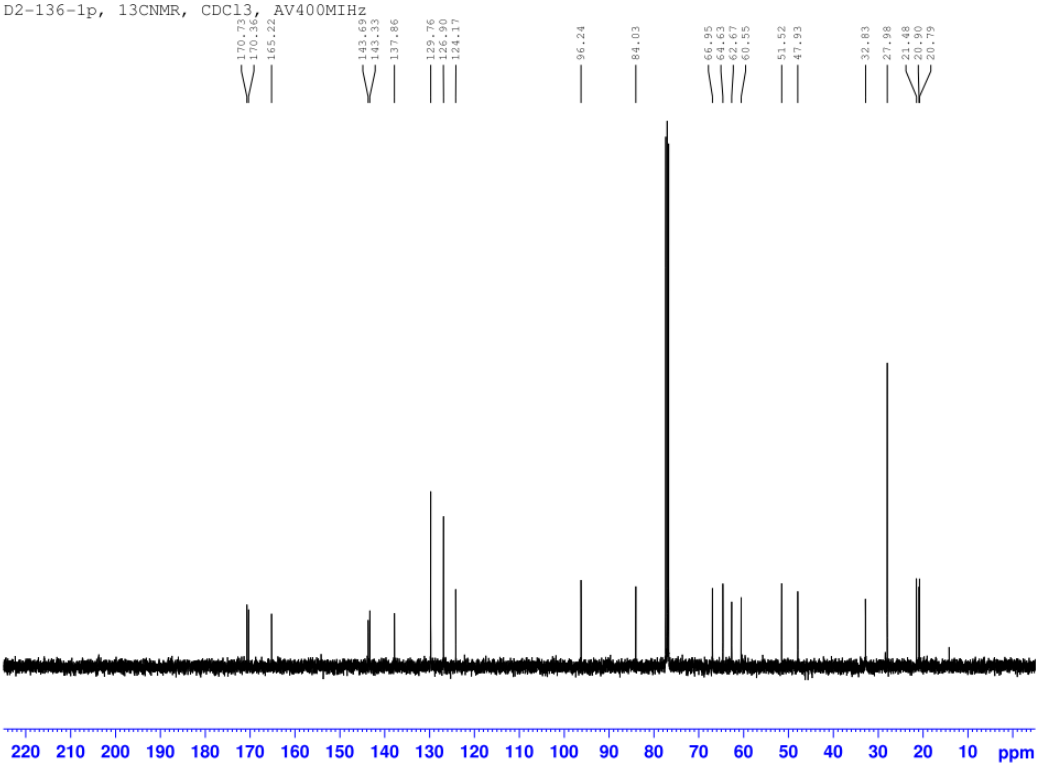


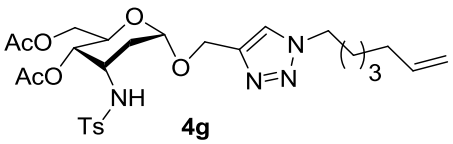
4f

D2-136-1p, 1HNMR, CDCl3, AV400MIHz



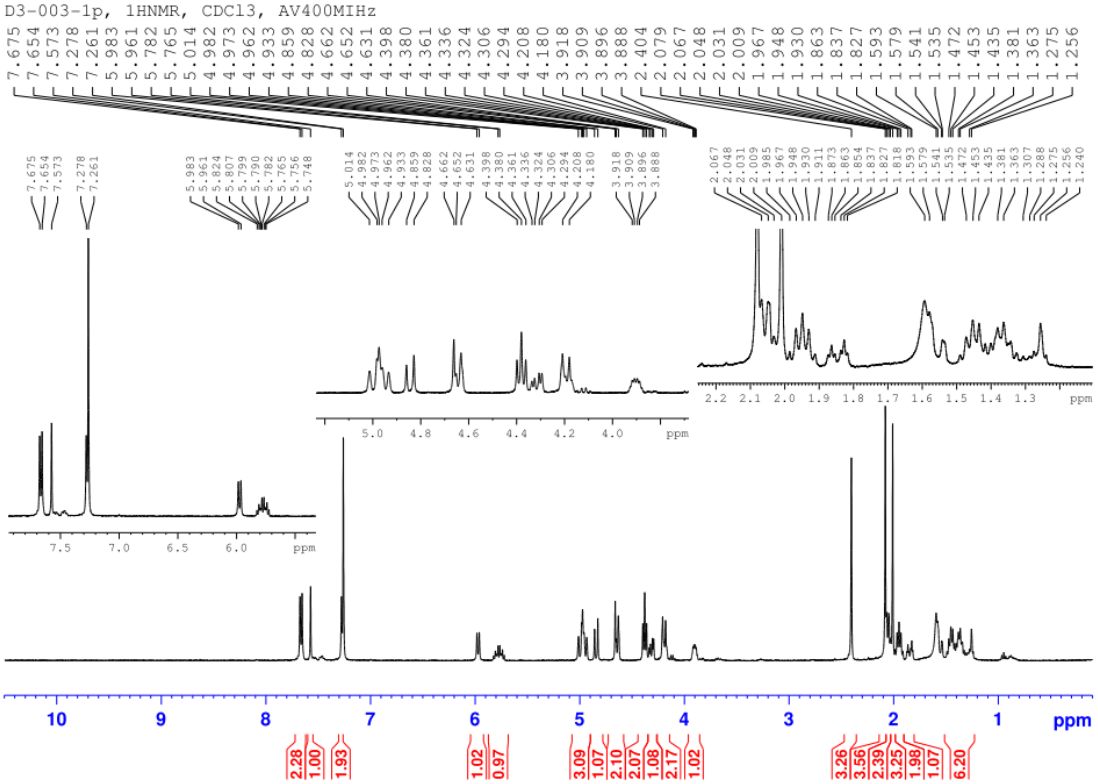
D2-136-1p, 13CNMR, CDCl3, AV400MIHz



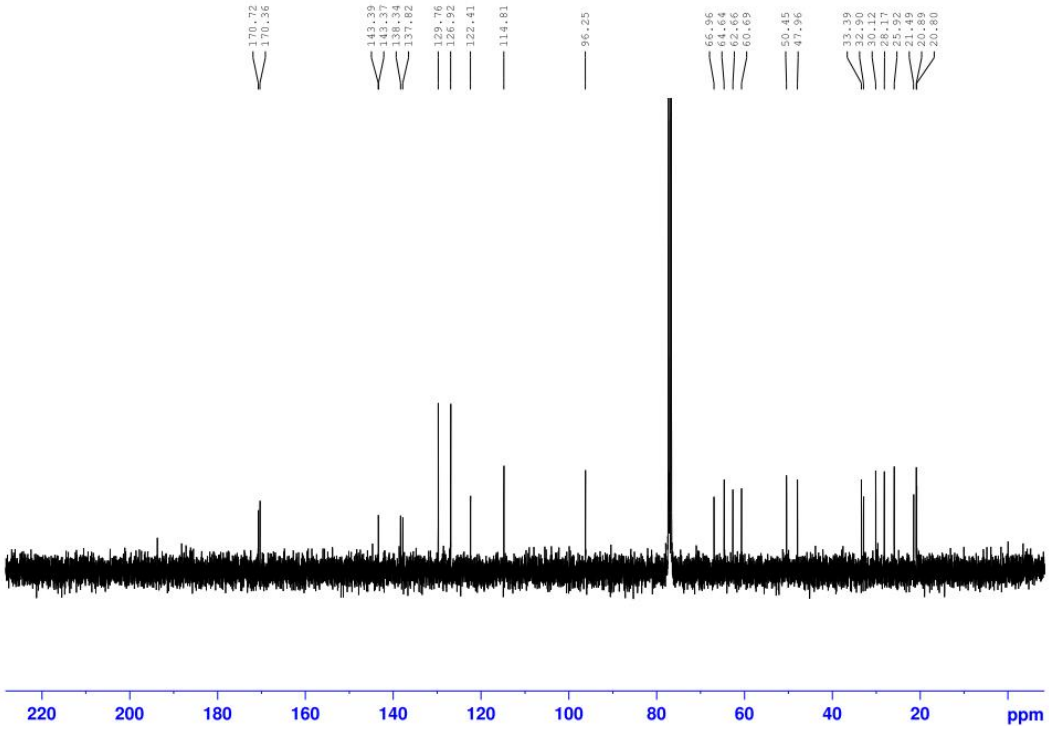


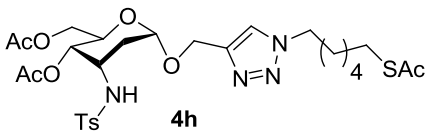
4g

D3-003-1p, 1HNMR, CDCl3, AV400MIHz



D3-003-1p, 13C NMR, CDCl3, AV400MIHz

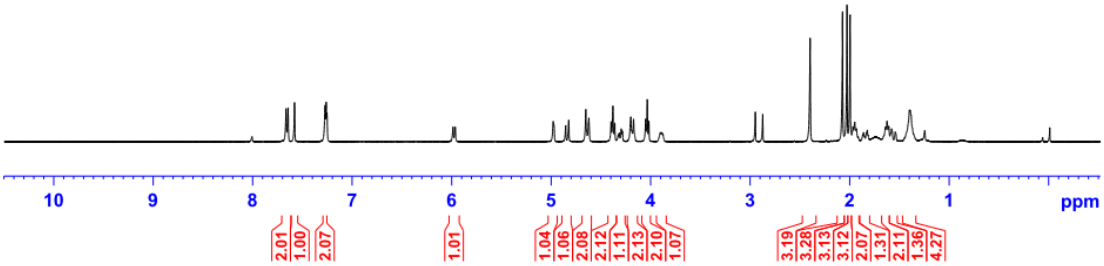




4h

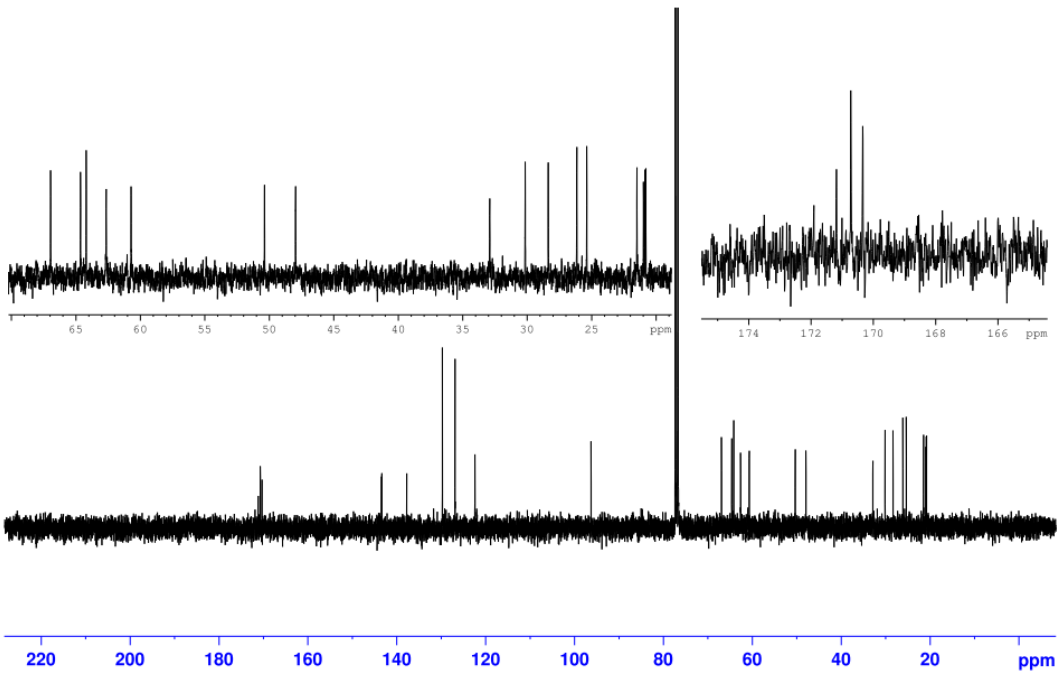
D3-048-1p 1H NMR Av 400 MHz CDCl3, oct-2011

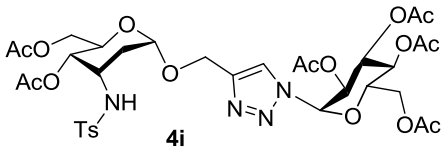
7.664 7.643 7.578 7.272 7.260 7.252 5.985 5.963 4.978 4.971 4.853 4.822 4.651 4.641 4.620 4.396 4.378 4.360 4.325 4.313 4.294 4.283 4.199 4.187 4.171 4.049 4.033 4.016 3.905 3.896 3.885 3.875 2.396 2.070 2.026 1.994 1.965 1.948 1.930 1.868 1.859 1.849 1.831 1.822 1.812 1.737 1.640 1.623 1.605 1.587 1.577 1.540 1.398 1.390 1.381



D3-048-1p 13c NMR Av 400 MHz CDCl3, oct-2011

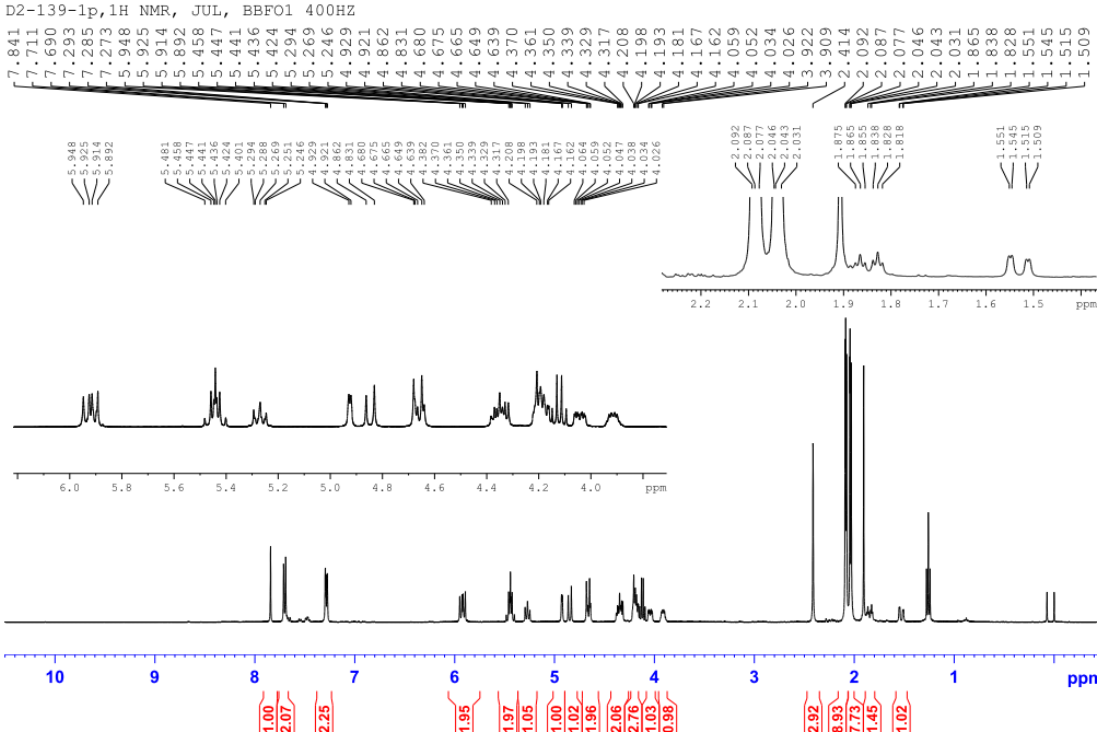
171.15 170.72 170.34 143.46 143.39 137.79 129.76 126.91 122.43 96.30 66.95 64.64 64.19 62.54 60.71 50.36 47.95 32.90 30.15 28.36 26.14 25.37 21.49 20.99 20.88 20.80



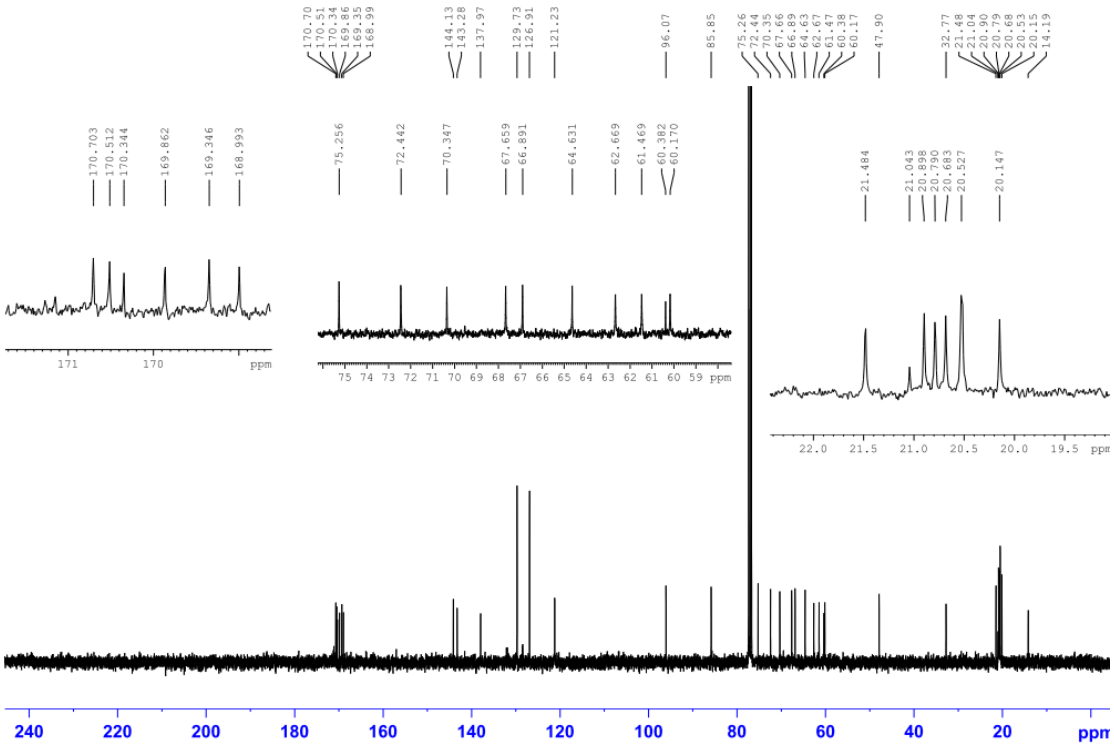


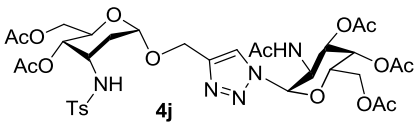
4i

D2-139-1p,1H NMR, JUL, BBFO1 400HZ



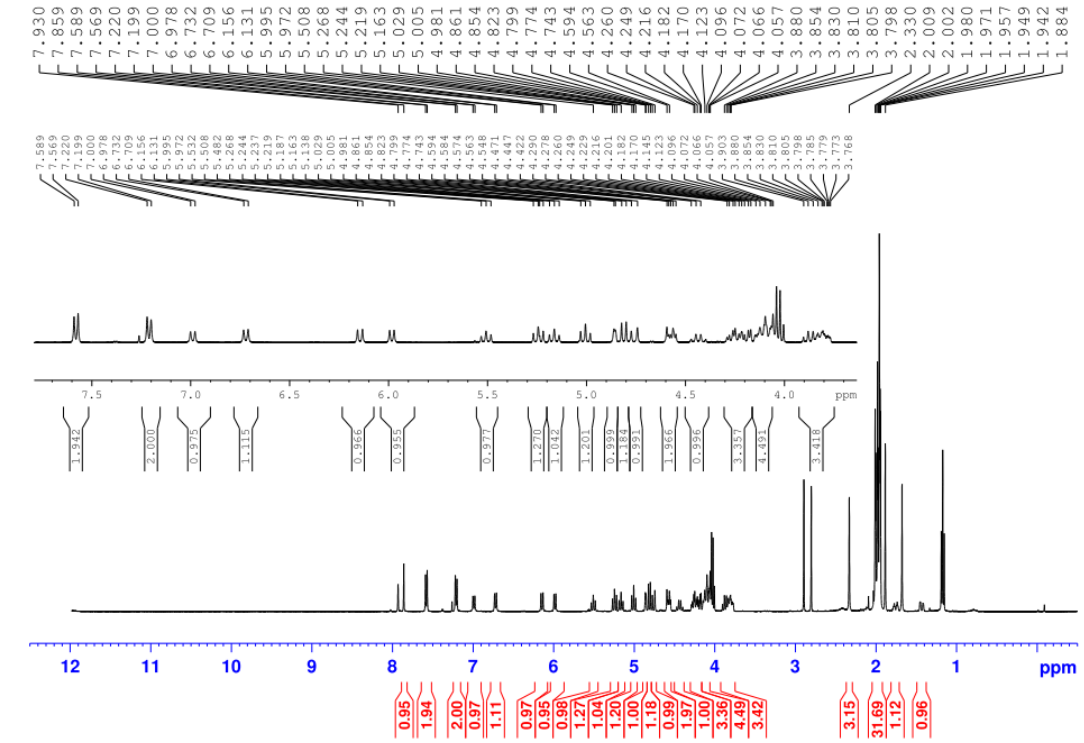
D2-139-1p,13C NMR, JUL, BBFO1 400HZ



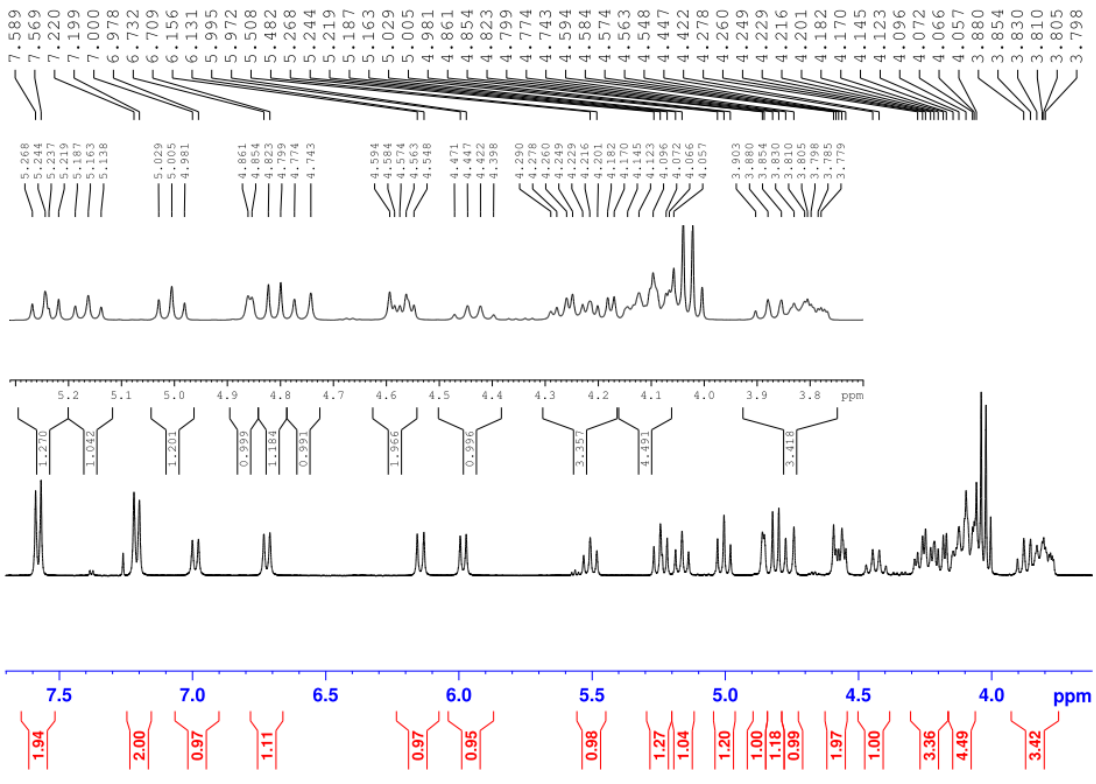


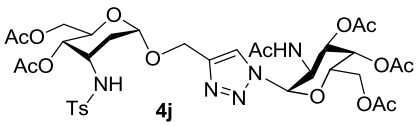
4j

D2-124-1p, 1H NMR, AV400MHz, CDCl3

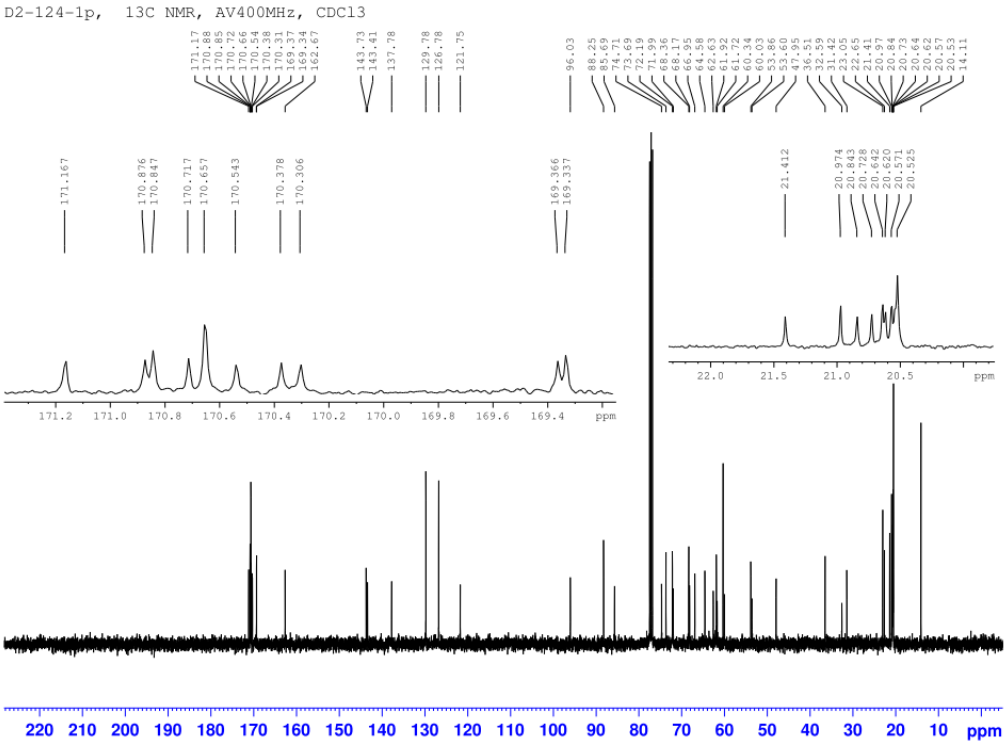


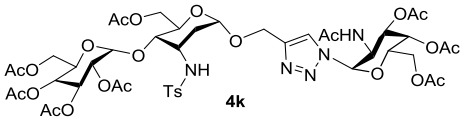
D2-124-1p, 1H NMR, AV400MHz, CDCl3




AcO
AcO
O
NH
Ts
O
AcHN
N
N
N
O
OAc
OAc
OAc

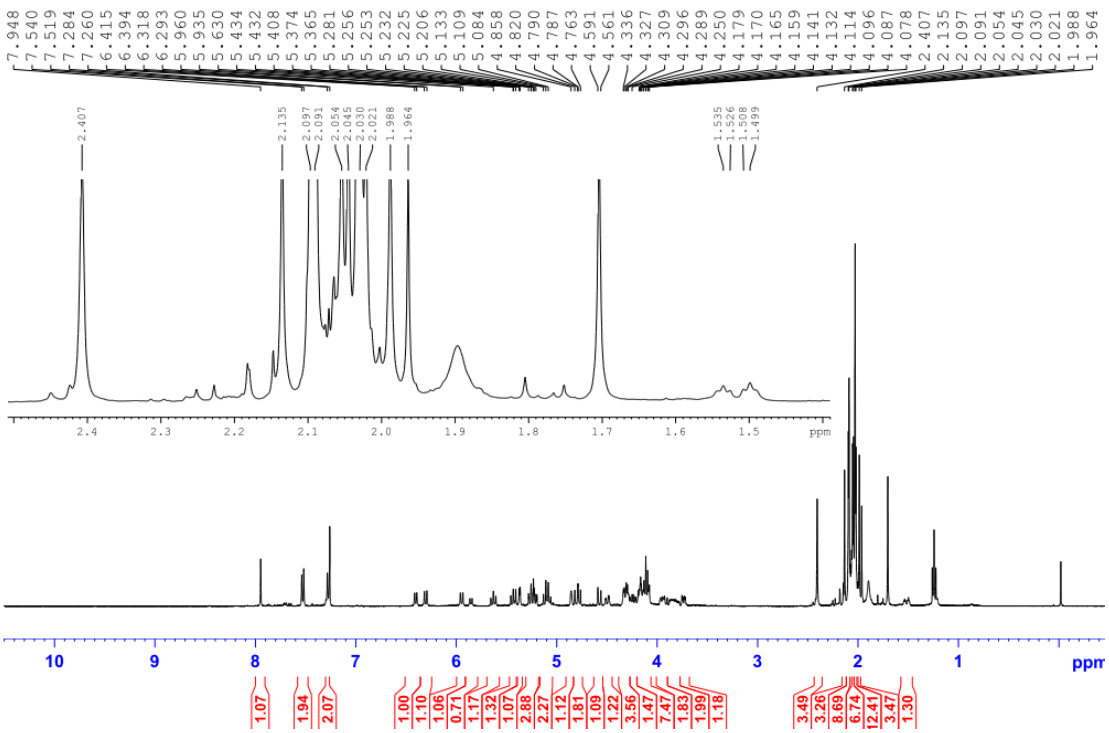
4j


D2-124-1p, 13C NMR, AV400MHz, CDCl3
171.17
170.88
170.85
170.72
170.66
170.64
170.54
170.38
170.31
169.37
169.34
162.67
143.73
143.41
137.78
129.78
126.78
121.75
96.03
88.25
85.69
74.71
73.69
72.19
71.99
68.16
68.17
66.95
64.58
62.63
61.92
61.72
60.34
60.03
53.86
53.60
47.95
36.51
32.59
31.42
31.05
22.65
21.41
20.97
20.84
20.73
20.64
20.62
20.57
20.53
14.11
171.167
170.876
170.847
170.717
170.657
170.543
170.378
170.306
169.366
169.337
21.412
20.974
20.843
20.728
20.642
20.620
20.571
20.525
171.2
171.0
170.8
170.6
170.4
170.2
170.0
169.8
169.6
169.4
ppm
22.0
21.5
21.0
20.5
ppm
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

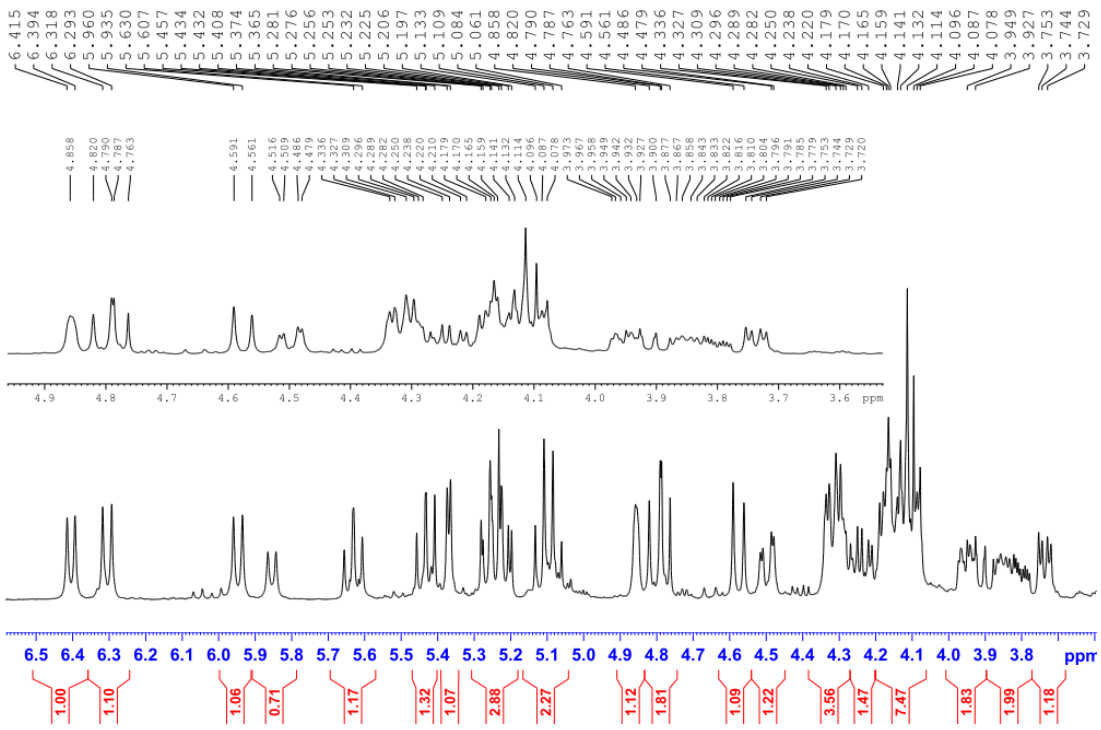


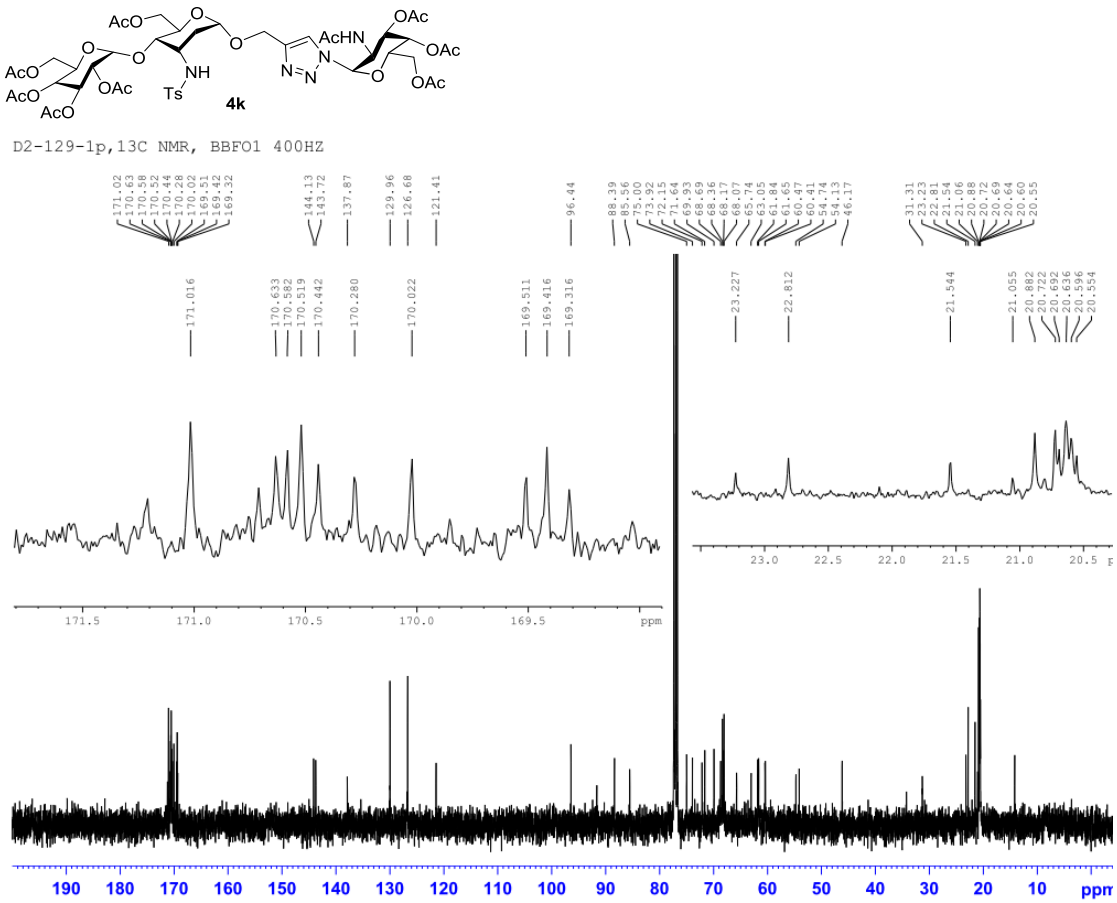
4k

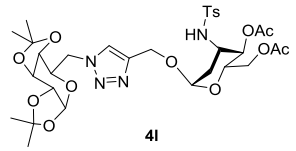
D2-129-1p,1H NMR, BBFO1 400HZ



D2-129-1p,1H NMR, BBFO1 400HZ

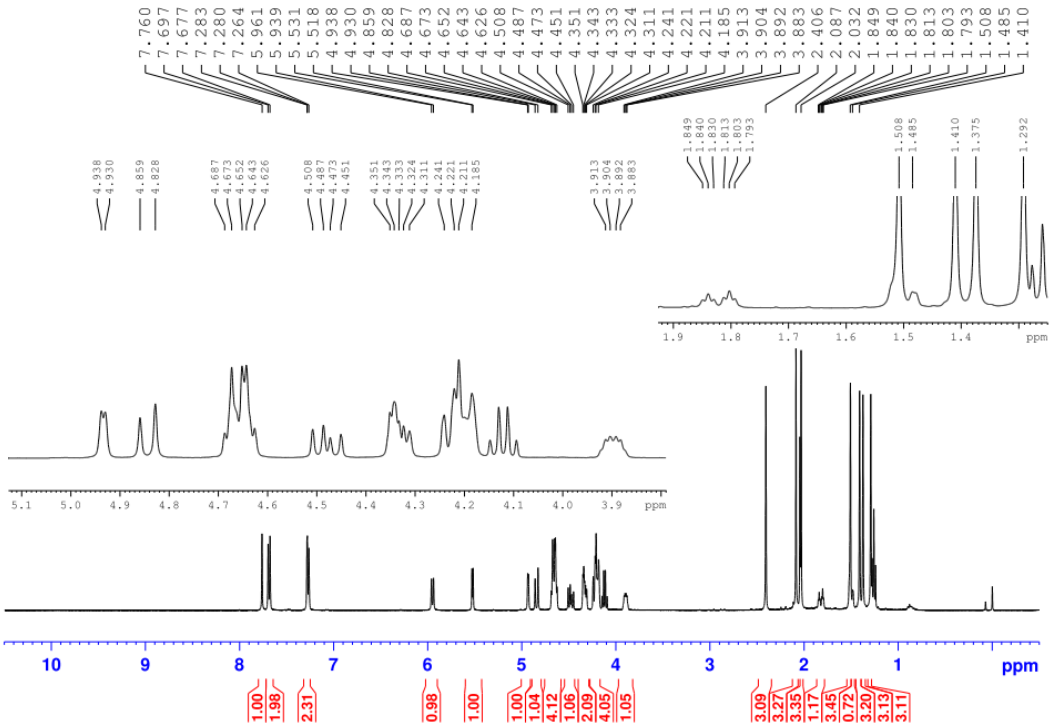



AcO
AcO
AcO
AcO
OAc
NH
Ts
AcHN
OAc
OAc
OAc
4k
D2-129-1p,13C NMR, BBFO1 400HZ
171.02
170.63
170.58
170.32
170.44
170.28
170.02
169.51
169.42
169.32
144.13
143.72
137.87
129.96
126.68
121.41
96.44
88.39
85.56
75.00
73.92
72.15
71.64
69.93
68.69
68.36
68.17
68.07
65.74
63.05
61.84
61.65
60.47
60.41
54.74
54.13
46.17
31.31
23.23
22.81
21.54
21.06
20.88
20.72
20.69
20.64
20.60
20.55
171.016
170.633
170.582
170.519
170.442
170.280
170.022
169.511
169.416
169.316
23.227
22.812
21.544
21.055
20.882
20.722
20.692
20.636
20.596
20.554
171.5
171.0
170.5
170.0
169.5
ppm
23.0
22.5
22.0
21.5
21.0
20.5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

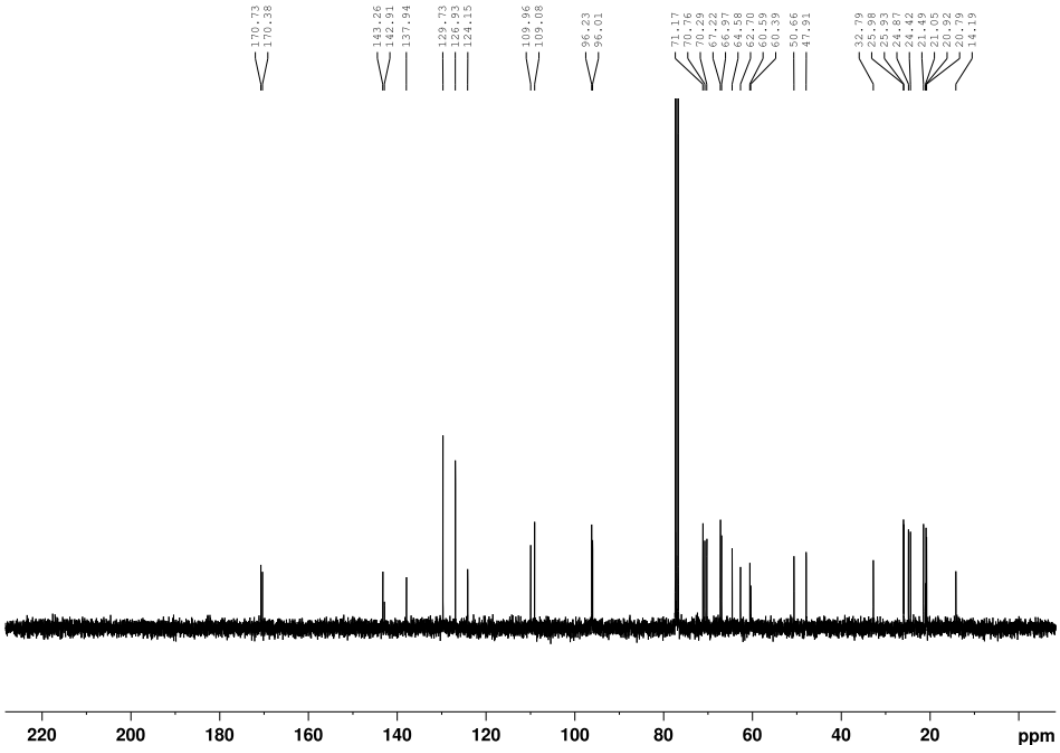


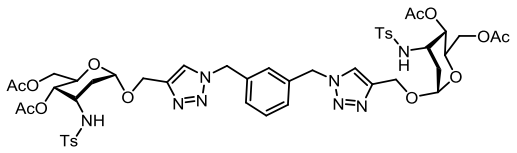
4l

D3-030-1p, 1H Av 400 MHz CDCl3, sep11



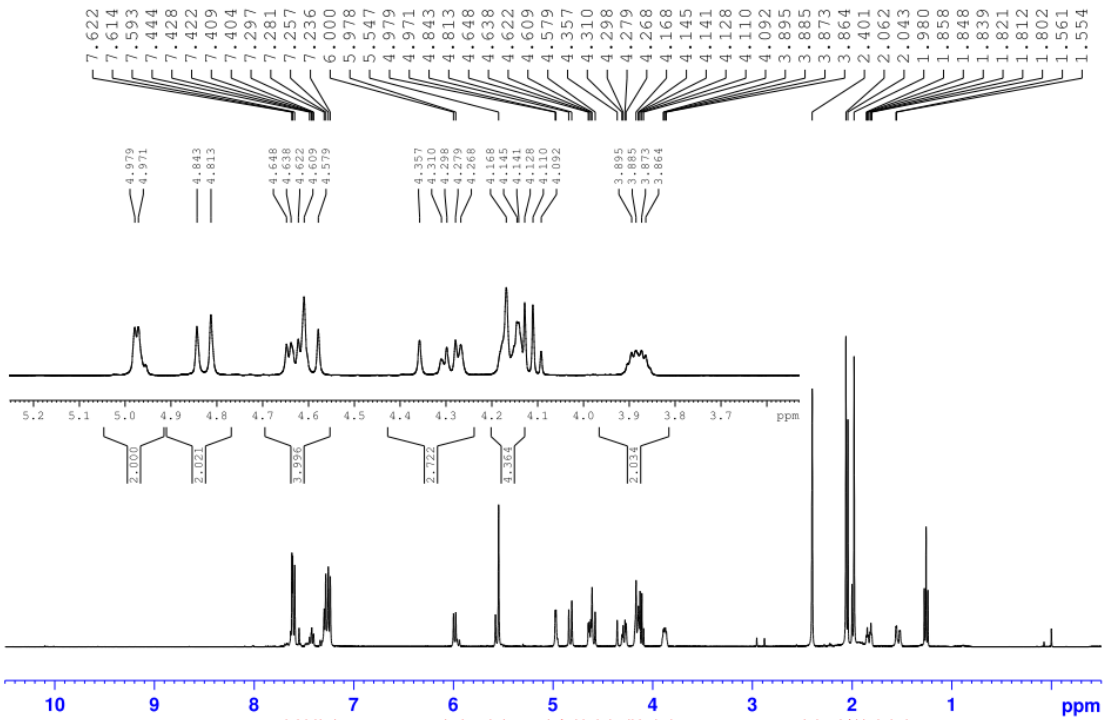
D3-030-1p, 13C Av 400 MHz CDCl3, sep11



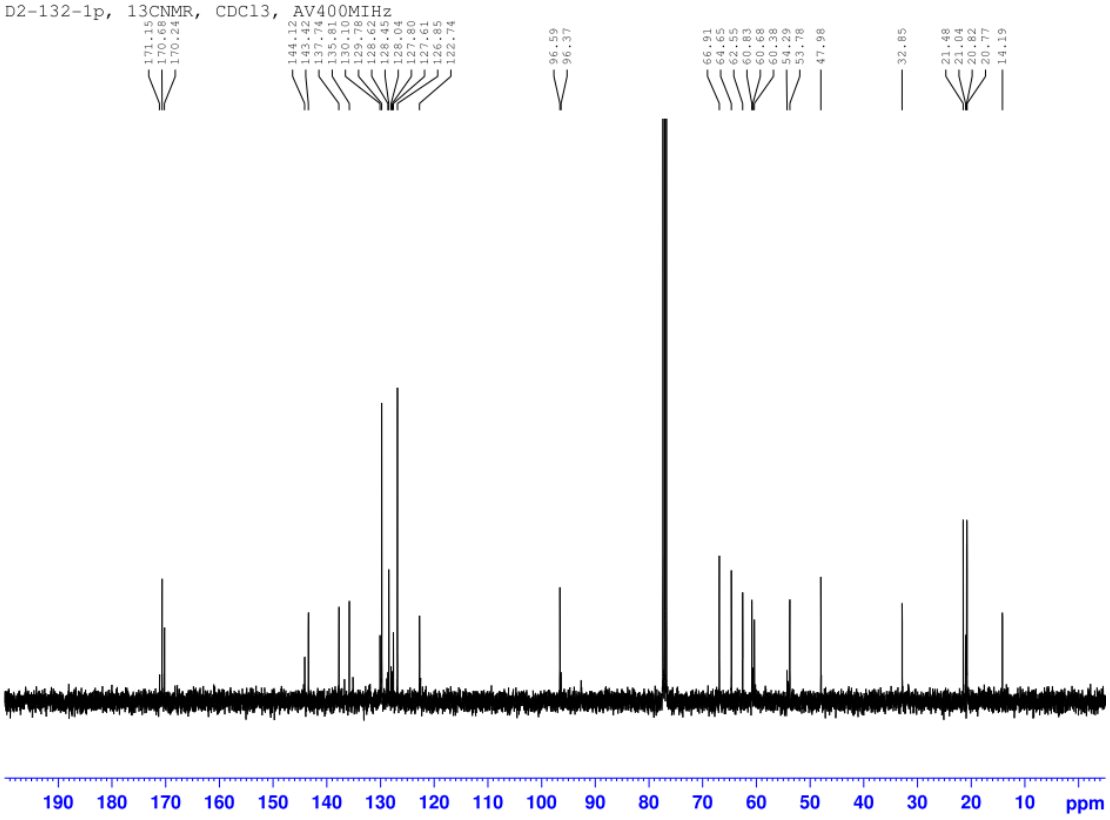


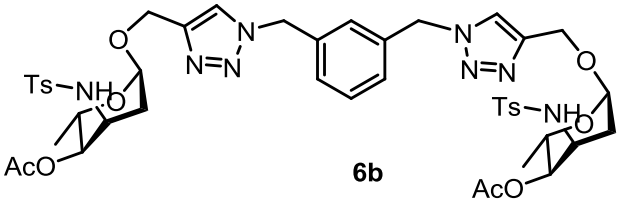
6a

D2-132-1p, 1HNMR, CDCl3, AV400MIHz



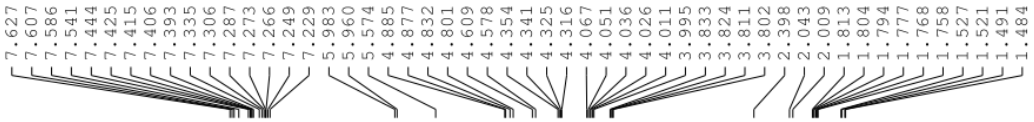
D2-132-1p, 13CNMR, CDCl3, AV400MIHz

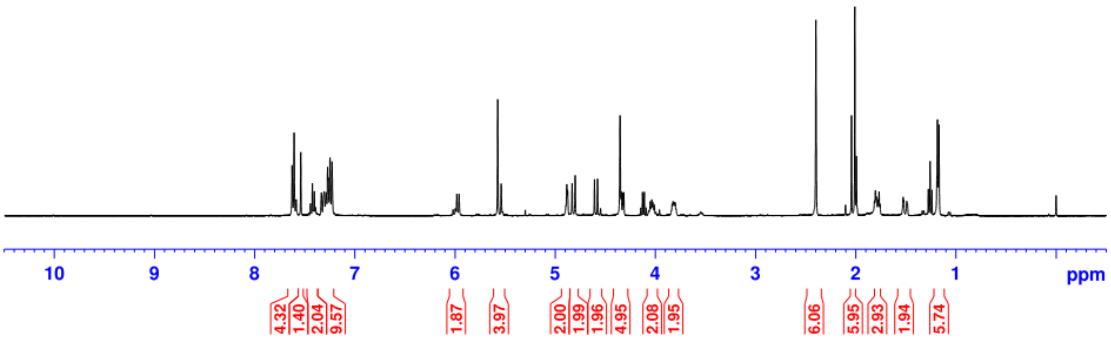




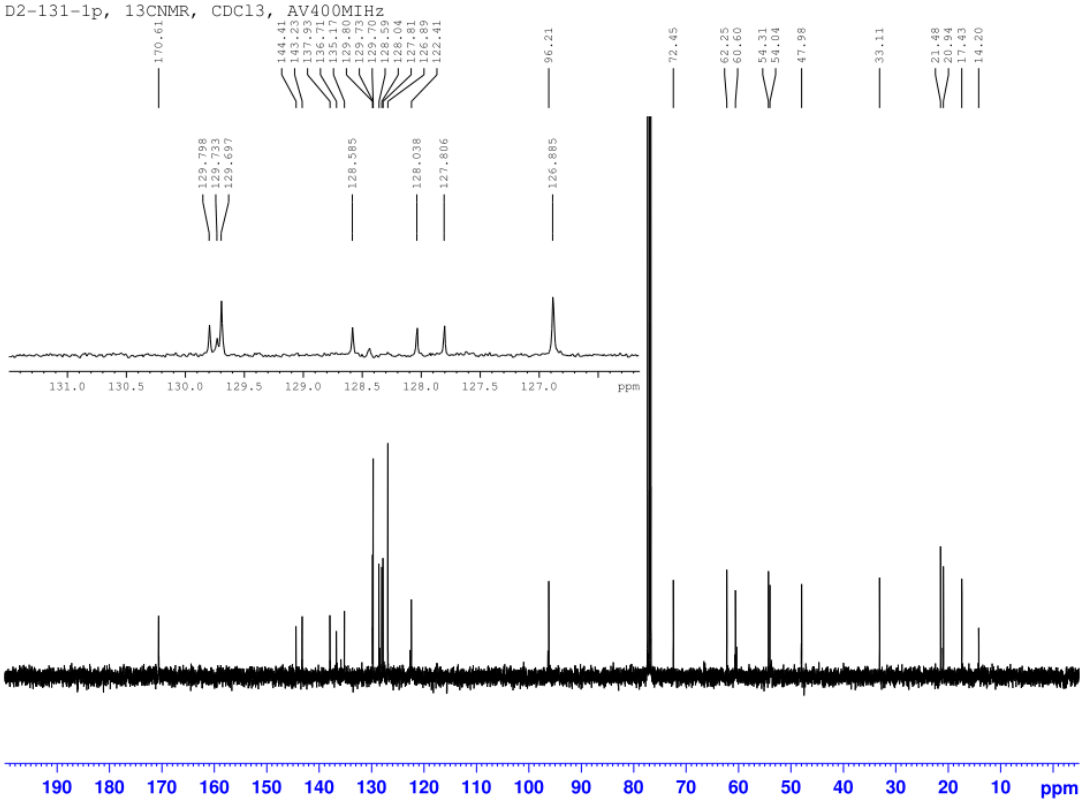
6b

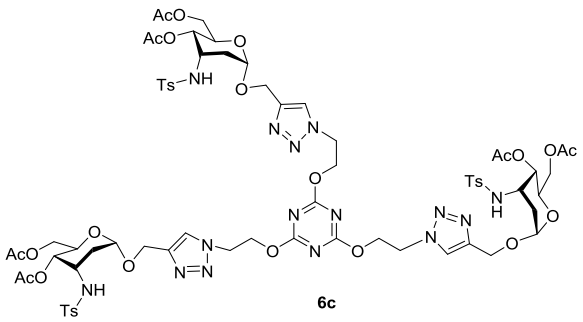
D2-131-1p, 1HNMR, CDCl3, AV400MIHz





D2-131-1p, 13CNMR, CDCl3, AV400MIHz

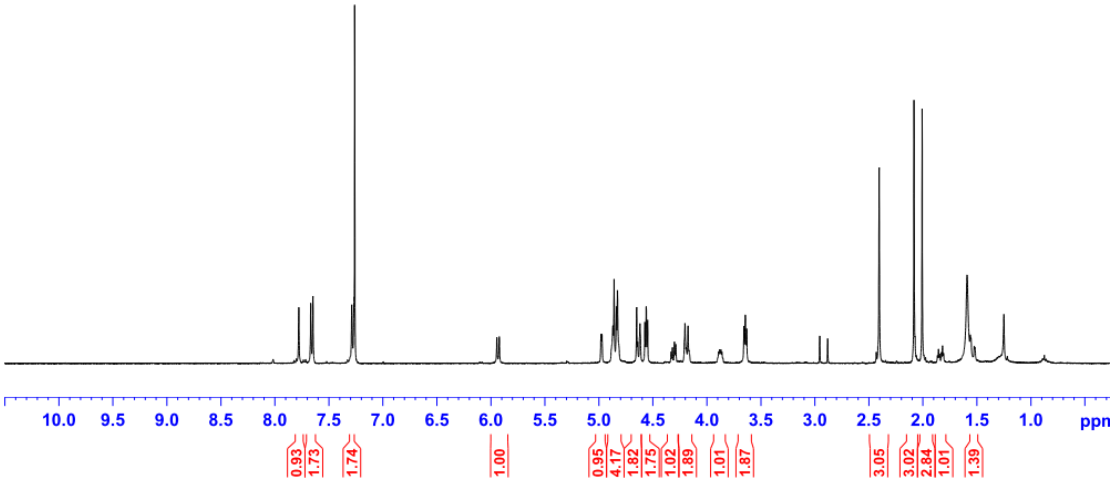




6c

D3-018-1p, 1H, BBFO1-400MHZ, AUG11,CDCl3

7.778 7.668 7.647 7.288 5.944 5.921 4.980 4.972 4.870 4.860 4.839 4.829 4.651 4.642 4.620 4.575 4.563 4.549 4.331 4.320 4.301 4.289 4.204 4.192 4.175 3.892 3.884 3.871 3.862 3.658 3.645 3.632 2.406 2.083 2.007 1.866 1.856 1.846 1.829 1.819 1.809 1.562 1.555



D3-018-1p, 13C, BBFO1-400MHZ, AUG11,CDCl3

173.06 171.84 171.55 170.75 170.37 143.40 137.71 129.79 126.94 96.39 67.44 66.95 66.92 64.64 62.62 60.55 49.39 48.92 47.90 32.84 21.50 20.89 20.81