Supporting Information

Identification of 3,6-Di-*O*-acetyl-1,2,4-*O*-orthoacetyl-α-D-glucopyranose as a Direct Evidence for the 4–*O*-Acyl Group Participation in Glycosylation

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General Remarks for the Synthesis

All solvents were purchased from commercial sources and were used as received unless otherwise stated. Crushed 4Å molecular sieves were activated through flame-drying immediately prior to use. Optical rotations were measured at room temperature with a Perkin–Elmer 241 MC polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 instrument at 400 and 100 MHz, respectively, in $CDCl_3$. TMS was used as the internal standard and all *J* values are given in hertz. High-resolution mass spectra (ESI) were recorded with APEXIII 7.0 TESLA FTMS.

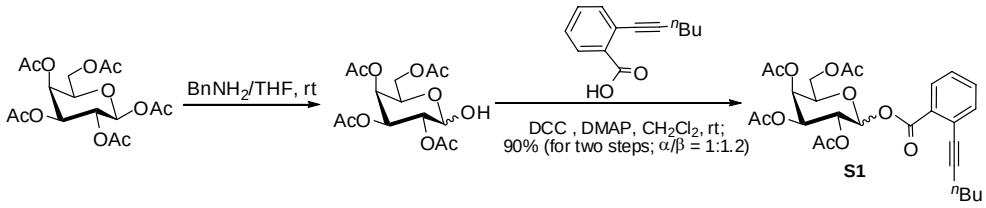
Flash column chromatography was performed on silica gel H (10-40 μ). Analytical thin layer chromatography (TLC) was performed on glass plates pre-coated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with ethanol/ sulfuric acid (10%, v/v).

Preparation of Glycosyl *ortho*-Hexynylbenzoates

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl *ortho*-hexynylbenzoate (1).

To a solution of penta-*O*-acetyl-β-D-glucopyranose (8.0 g, 20.5 mmol) in CH_2Cl_2 (50 mL), 33% HBr/HOAc (10.6 mL, 61.5 mmol) was added slowly at 0 ^{o}C. The temperature was allowed to warm up to rt. After 21 h, the mixture was poured into a freshly prepared cold solution of sodium hydroxide. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, and then concentrated. The crude product was stirred with *ortho*-hexynylbenzoic acid (5.4 g, 26.7 mmol), $BnNEt_3Cl$ (1.3 g, 4.1 mmol), and K_2CO_3 (14.2 g, 102.5 mmol) in a mixed solvent of dichloromethane and distilled water (120 mL, 1:1) for 24 h at rt. The resulting mixture was diluted with brine. The aqueous layer was extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel column chromatography (hexane-ethyl acetate, 7:1 to 5:1) to give **1** (9.8 g, 90% for two steps) as a white solid: $[\alpha]_D^{25}$ = -27.1 (*c* 2.8, $CHCl_3$); ^{1}H NMR (75 MHz, $CDCl_3$) δ 7.95 (d, 1 H, *J* = 8.1 Hz), 7.58–7.24 (m, 2 H), 7.33 (t, *J* = 7.5 Hz, 1 H), 5.97 (d, *J* = 6.6 Hz, 1 H), 5.40-5.28 (m, 2 H), 5.26-5.14 (m, 2 H), 4.34 (dd, *J* = 3.9, 12.6 Hz, 1 H), 4.13 (d, *J* = 12.6 Hz, 1 H), 3.94 (d, *J* = 9.6 Hz, 1 H), 2.51 (t, *J* = 6.6 Hz, 2 H), 2.08 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 2.00 (s, 3 H), 1.73–1.42 (m, 4 H), 0.96 (t, *J* = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.9, 169.3, 169.2, 163.2, 134.6, 132.5, 130.7, 129.0, 127.2, 125.8, 97.3, 92.0, 78.9, 72.7, 72.6, 70.1, 67.8, 61.4, 30.5, 21.9, 20.5, 20.43, 20.39, 19.4, 13.5; HRMS (MALDI) *m/z* calcd $C_{27}H_{32}O_{11}Na$ $[M+Na]^+$ 555.1837, found 555.1843.

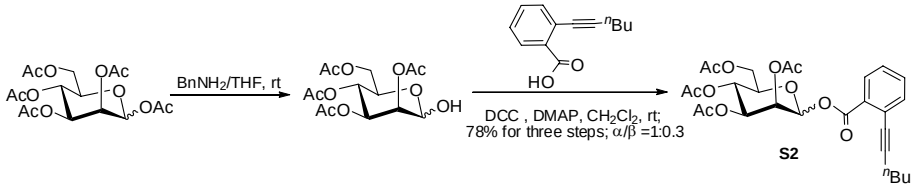
2,3,4,6-Tetra-*O*-acetyl-D-galactopyranosyl *ortho*-hexynylbenzoate (S1).



A solution of galactose pentacetate (4.00 g, 10.14 mmol) and $BnNH_2$ (1.66 mL, 15.22 mmol) in THF (20 mL) was stirred at rt for 14 h. After addition of 8.0 mL of 1 N HCl, the reaction mixture was stirred for one more hour. The reaction mixture was diluted with 1 N HCl (100 mL) and extracted with CH_2Cl_2. The combined extracts were dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by chromatography on silica gel (hexane-ethyl acetate, 3:2) to give 2,3,4,6-tetra-*O*-acetyl-D-galactopyranose (3.30 g) as a colorless syrup.

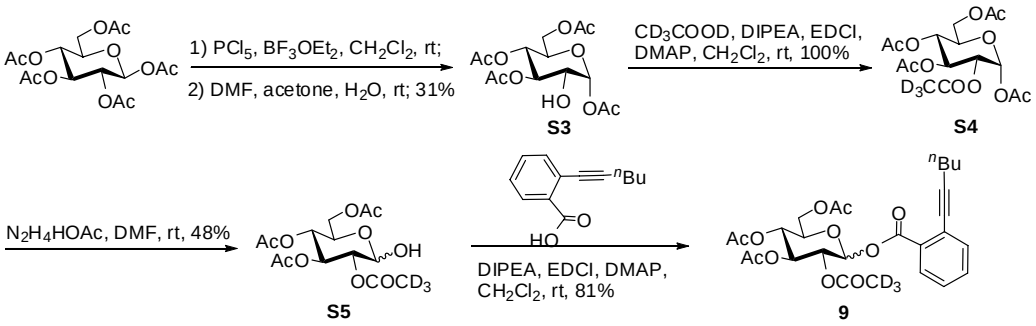
A solution of the above lactol (3.23 g, 9.3 mmol) and *ortho*-hexynylbenzoic acid (2.24 g, 11.1 mmol) in dry CH_2Cl_2 (15 mL) was added DMAP (1.68 g, 13.8 mmol) and DCC (2.84 g, 13.8 mmol). After being stirred at rt for 3 h, the mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_3$ and brine. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated. The residue was purified by silica gel column chromatography (hexane-ethyl acetate, 5:1) to provide **S1** (4.76 g, 90% for two steps; α/β = 1:1.2) as a white solid. A small portion of the α/β-anomer was separated for characterization. The α-anomer: $[\alpha]^{25}_D$ = 94.9 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1 H), 7.55 (d, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.4 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 6.66 (d, *J* = 2.8 Hz, 1 H), 5.55 (br s, 1 H), 5.48-5.40 (m, 2 H), 4.53 (t, *J* = 6.8 Hz, 1 H), 4.17 (dd, *J* = 7.0, 11.4 Hz, 1 H), 4.07 (dd, *J* = 6.4, 11.2 Hz, 1 H), 2.49 (m, 2 H), 2.16 (s, 3 H), 2.00 (s, 3 H), 1.992 (s, 3 H), 1.988 (s, 3 H), 1.61 (m, 2 H), 1.49 (m, 2 H), 0.94 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 170.1, 170.0, 169.9, 164.1, 135.1, 132.3, 130.7, 129.9, 127.3, 125.1, 96.9, 90.5, 79.7, 69.1, 67.7, 67.3, 66.6, 61.1, 30.6, 22.0, 20.6, 20.5, 19.4, 13.6; HRMS (ESI) *m/z* calcd $C_{27}H_{32}O_{11}Na$ $[M+Na]^+$ 555.1837, found 555.1837. The β-anomer: $[\alpha]^{25}_D$ = -9.6 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.53 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.47 (dt, *J* = 1.2, 7.6 Hz, 1 H), 7.32 (dt, *J* = 1.2, 7.6 Hz, 1 H), 5.94 (d, *J* = 8.0 Hz, 1 H), 5.53-5.47 (m, 2 H), 5.15 (dd, *J* = 3.2, 10.4 Hz, 1 H), 4.19-4.11 (m, 3 H), 2.51 (t, *J* = 7.0 Hz, 2 H), 2.18 (s, 3 H), 2.05 (s, 3 H), 2.01 (s, 3 H), 1.99 (s, 3 H), 1.63 (m, 2 H), 1.51 (m, 2 H), 0.95 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.1, 169.8, 169.6, 163.1, 134.5, 132.3, 130.4, 129.7, 127.0, 125.7, 97.2, 90.7, 78.7, 73.2, 70.7, 68.4, 65.6, 62.1, 30.6, 22.0, 20.74, 20.68, 20.65, 20.52, 19.4, 13.6; HRMS (ESI) *m/z* calcd $C_{27}H_{32}O_{11}Na$ $[M+Na]^+$ 555.1837, found 555.1837.

2,3,4,6-Tetra-*O*-acetyl-D-mannopyranosyl *ortho*-hexynylbenzoate (S2)



D-Mannopyranose pentacetate was synthesized as reported.[S1] Compound **S2** was prepared following a procedure similar to that for the preparation of **S1**. Thus, silica gel chromatography gave **S2** (4.83 g, 78% for three steps; α/β= 1:0.3) as a white solid. A small portion of the α/β-anomer was separated for characterization. The α-anomer: $[\alpha]^{25}_{D}$ = 57.1 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 1 H), 7.54 (d, *J* = 8.4 Hz, 1 H), 7.47 (t, *J* = 7.4 Hz, 1 H), 7.34 (t, *J* = 7.4 Hz, 1 H), 6.34 (d, *J* = 1.2 Hz, 1 H), 5.50 (dd, *J* = 3.4, 10.2 Hz, 1 H), 5.40 (m, 2 H), 4.31 (dd, *J* = 4.4, 12.4 Hz, 1 H), 4.24-4.20 (m, 1 H), 4.12-4.08 (m, 1 H), 2.49 (m, 2 H), 2.07 (s, 3 H), 2.03(s, 3 H), 2.01 (s, 3 H), 1.99 (s, 3 H), 1.60 (m, 2 H), 1.47 (m, 2 H), 0.93 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.7, 169.6, 169.4, 163.4, 135.0, 132.4, 130.7, 129.7, 127.3, 125.1, 97.0, 91.4, 79.5, 70.9, 68.8, 68.5, 65.6, 61.9, 30.6, 22.0, 20.7, 20.6, 20.55, 20.52, 19.4, 13.6; HRMS (ESI) *m/z* calcd $C_{27}H_{32}O_{11}Na$ $[M+Na]^+$ 555.1837, found 555.1837. The β-anomer: $[\alpha]^{25}_{D}$ = -27.4 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.57-7.47 (m, 2 H), 7.37 (dt, *J* = 1.2, 7.6 Hz, 1 H), 3.36 (d, *J* = 1.2 Hz, 1 H), 5.52 (dd, *J* = 3.6, 10.4 Hz, 1 H), 5.44-5.39 (m, 2 H), 4.33 (dd, *J* = 4.8, 12.4 Hz, 1 H), 4.26-4.22 (m, 1 H), 4.12 (dd, *J* = 2.4, 12.4 Hz, 1 H), 2.51 (t, *J* = 7.6 Hz, 2 H), 2.21 (s, 3 H), 2.05 (s, 3 H), 2.09 (s, 3 H), 2.05 (s, 3 H), 2.01 (s, 3 H), 1.63 (m, 2 H), 1.50 (m, 2 H), 0.95 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.1, 169.9, 169.5, 163.2, 134.6, 132.5, 130.8, 129.1, 127.2, 125.9, 97.4, 92.5, 78.9, 71.7, 70.8, 67.8, 66.8, 60.9, 30.6, 22.0, 20.6, 20.5, 19.5, 13.6; HRMS (ESI) *m/z* calcd $C_{27}H_{32}O_{11}Na$ $[M+Na]^+$ 555.1837, found 555.1837.

2-*O*-(Acetyl-d$_3$)-3,4,6-tri-*O*-acetyl-D-glucopyranosyl *ortho*-hexynylbenzoate (9).



To a solution of penta-*O*-acetyl-β-D-glucopyranose (80.0 g, 0.20 mmol) and PCl_5 (47.2 g, 0.227 mol) in CH_2Cl_2 (400 mL) was added $BF_3{\cdot}OEt_2$ (210 μL, 3.3 mmol). The mixture was stirred at rt overnight and then washed with water, saturated $NaHCO_3$, and brine, respectively. The organic layer was dried over anhydrous Na_2SO_4 and concentration. The resulting pale yellow solid was dissolved in a mixed solvent of acetone (400 mL), DMF (16.0 mL), and water (36.9 mL). After being stirred at rt for 24h, the solvent was removed by rotary evaporator. The residue was dissolved with CH_2Cl_2 and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated. The residue was crystallized from diethyl ether to give **S3** (21.9 g, 31%) as a white solid.[S2]

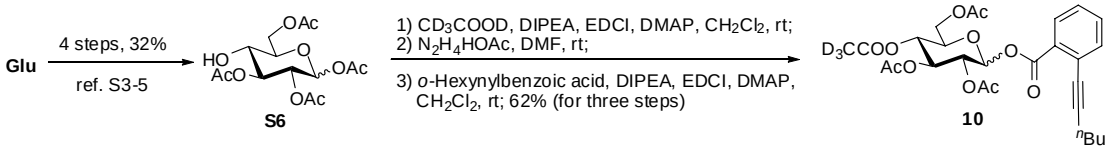
To a solution of **S3** (3.48 g, 10.0 mmol) and acetic acid-d$_4$ (0.85 mL, 15.0 mmol) in dry

CH_2Cl_2 (50 mL) was added DMAP (1.46 g, 15.0 mmol), EDCI (2.48 g, 13.0 mmol), and DIPEA (2.2 mL, 13.0 mmol). After being stirred at rt for 3 h, the mixture was diluted with CH_2Cl_2. The mixture was washed with saturated $NaHCO_3$ and brine. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated. The residue was purified by silica gel column chromatography (hexane-ethyl acetate, 5:1) to provide **S4** (3.93 g, 100%) as a white solid: $[\alpha]^{25}_D$ = 93.5 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (d, *J* = 4.0 Hz, 1 H), 5.47 (t, *J* = 10 Hz, 1 H), 5.16-5.08 (m, 2 H), 4.26 (dd, *J* = 4.4, 12.4 Hz, 1 H), 4.13-4.07 (m, 2 H), 2.18 (s, 3 H), 2.09 (s, 3 H), 2.04 (s, 3 H), 2.02 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.5, 170.1, 169.6, 169.3, 168.7, 89.0, 69.7, 69.1, 67.8, 61.4, 20.8, 20.6, 20.55, 20.45; HRMS (ESI) *m/z* calcd $C_{16}H_{19}D_3O_{11}Na$ $[M+Na]^+$ 416.1243, found 416.1253.

To a solution of the above **S4** in DMF (15.0 mL) was added hydrazine monoacetate (1.11 g, 12.0 mmol). The mixture was stirred at 60 ^{o}C under Ar. The reaction was monitored by TLC. After **S4** was completely consumed, the mixture was cooled to rt, which was then diluted with ethyl acetate. The resulting mixture was washed with 5% NaCl solution and water. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated to provide the crude **S5** as a pale yellow syrup, which was used in the next step without further purification.

Glucopyranosyl *ortho*-hexynylbenzoate **9** was prepared from **S5** following a procedure similar to that for the preparation of **S1**. Thus, treatment of lactol **S5** with DMAP, EDCI, and DIPEA, after silica gel chromatography gave **9** (2.06 g, 39% for two steps; α:β = 1:3) as a white solid. A small portion of the α/β-anomer was separated for characterization. **9α**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H) 7.38 (t, *J* = 8.0 Hz, 1 H), 6.63 (d, *J* = 3.6 Hz, 1 H), 5.61 (t, *J* = 9.8 Hz, 1 H), 5.23-5.20 (m, 2 H), 4.34-4.29 (m, 2 H), 4.14-4.09 (m, 1 H), 2.60-2.46 (m, 2 H), 2.09 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H), 1.67-1.60 (m, 2 H), 1.55-1.45 (m, 2 H), 0.96 (t, *J* = 7.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.0, 169.7, 169.2, 163.9, 135.1, 132.3, 130.7, 129.7, 127.3, 125.2, 97.0, 89.8, 79.6, 70.2, 70.0, 69.3, 67.9, 59.3, 30.6, 22.0, 20.5, 20.4, 19.4, 13.5; HRMS (ESI) *m/z* calcd $C_{27}H_{29}D_3O_{11}Na$ $[M+Na]^+$ 558.2025, found 558.2042. **9β**: $[\alpha]^{25}_D$ = -25.2 (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1 H), 7.53 (d, *J* = 8.0 Hz, 1 H), 7.46 (t, *J* = 7.2 Hz, 1 H), 7.32 (t, *J* = 7.2 Hz, 1 H), 5.97 (d, *J* = 7.6 Hz, 1 H),5.33-5.31 (m, 2 H), 5.21-5.16 (m, 1 H), 4.33 (dd, *J* = 4.4, 12.4Hz, 1 H), 4.13 (d, *J* = 13.2 Hz, 1 H), 3.93 (qd, *J* = 2.4, 10.0 Hz 1 H), 2.50 (t, *J* = 7.6 Hz, 2 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 2.03 (s, 3 H), 1.67-1.60 (m, 2 H), 1.55-1.46 (m, 2 H), 0.96 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.9, 169.3, 169.2, 163.2, 134.6, 132.5, 130.7, 129.1, 127.2, 125.8, 97.3, 92.0, 78.9, 72.7, 72.7, 70.2, 67.8, 61.4, 30.6, 21.9, 20.5, 20.4, 19.4, 13.5; HRMS (ESI) *m/z* calcd $C_{27}H_{29}D_3O_{11}Na$ $[M+Na]^+$ 558.2025, found 558.2041.

4-*O*-(Acetyl-d$_3$)-2,3,6-tri-*O*-acetyl-D-glucopyranosyl *ortho*-hexynylbenzoate (10).

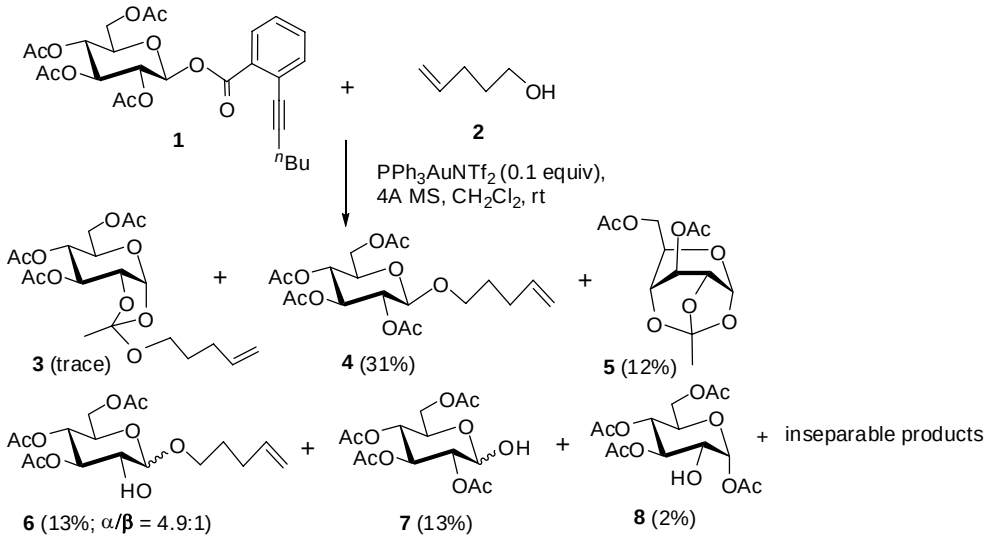


1,2,3,6-Tetra-*O*-acetyl-D-glucopyranose **S6** was prepared from D-glucose following literature transformations (4 steps, 32% total yield).[S3-S5] Compound **10** was prepared from **S6** (3 steps, 62% total yield) following a procedure similar to that for **S3→9**. **10α**: $[\alpha]^{25}_{D}$ = 102.0 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.38 (t, *J* = 8.0 Hz, 1 H), 6.61 (d, *J* = 3.9 Hz, 1 H), 5.60 (t, *J* = 10.1 Hz, 1 H), 5.24-5.17 (m, 2 H), 4.34-4.27 (m, 2 H), 4.11-4.06 (m, 1 H), 2.55-2.46 (m, 2 H), 2.08 (s, 3 H), 2.02 (s, 3 H), 1.99 (s, 3 H), 1.65-1.60 (m, 2 H), 1.55-1.45 (m, 2 H), 0.94 (t, *J* = 7.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.0, 169.8, 169.3, 164.0, 135.2, 132.4, 130.7, 129.8, 127.3, 125.2, 97.1, 89.8, 79.7, 70.2, 70.0, 69.3, 67.9, 61.3, 30.7, 22.1, 20.6, 20.4, 19.8, 19.5, 13.6; HRMS (ESI) *m/z* calcd $C_{27}H_{29}D_3O_{11}Na$ $[M+Na]^+$ 558.2025, found 558.2042. **10β**: $[\alpha]^{25}_{D}$ = -25.7 (*c* 2.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.46 (t, *J* = 7.2 Hz, 1 H), 7.32 (t, *J* = 7.2 Hz, 1 H), 5.97 (d, *J* = 7.6 Hz, 1 H), 5.33-5.31 (m, 2 H), 5.20-5.15 (m, 1 H), 4.33 (dd, *J* = 4.4, 12.4 Hz, 1 H), 4.13 (dd, *J* = 2.1, 13.2 Hz, 1 H), 3.93 (qd, *J* = 2.4, 10.0 Hz 1 H), 2.49 (t, *J* = 7.6 Hz, 2 H), 2.07 (s, 3 H), 2.03 (s, 3 H), 1.98 (s, 3 H), 1.67-1.60 (m, 2 H), 1.55-1.46 (m, 2 H), 0.94 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.1, 169.4, 169.3, 163.2, 134.7, 132.6, 130.8, 129.0, 127.3, 125.9, 97.4, 92.1, 79.0, 72.8, 72.7, 70.2, 67.8, 61.4, 30.6, 22.0, 20.6, 20.5, 19.5, 13.6; HRMS (ESI) *m/z* calcd $C_{27}H_{29}D_3O_{11}Na$ $[M+Na]^+$ 558.2025, found 558.2042.

Glycosylation of 4-Pentenol with Peracetyl Glycosyl *ortho*-Hexynylbenzoates.

A Typical procedure. To a mixture of a peracetyl glycosyl *ortho*-hexynylbenzoate (128 mg, 0.24 mmol), 4-penten-1-ol (20 μL, 0.20 mmol), and 4 Å MS (200 mg) in dry CH_2Cl_2 (10 mL) was added a solution of PPh_3AuNTf_2 in CH_2Cl_2 (0.05 N, 0.4 mL). After being stirred at rt for 3 h, the mixture was filtered through a pad of Celite. The filtrate was concentrated. The residue was subjected to silica gel column chromatography (petroleum ether-EtOAc) to provide the described products.

With Peracetyl Glucopyranosyl *ortho*-Hexynylbenzoate 1.

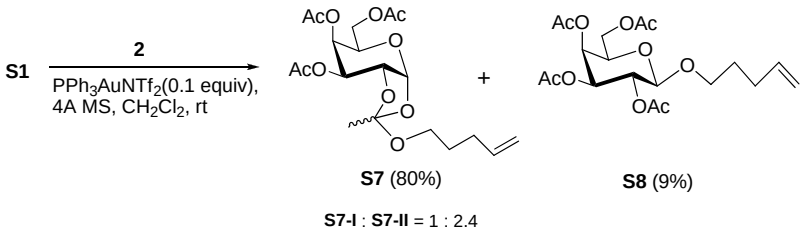


The analytical data of compounds **4**,[S6] **6**,[S4] **7**,[S7] and **8**[S2] are in good agreement with those reported in the literatures. The yields are calculated based on the donor **1**.

1,2-*O*-(4-Penten-1-yl)-orthoacetyl-3,4,6-tri-*O*-acetyl-α-D-glucopyranose (3): $[\alpha]^{25}_D$ = 30.5 (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (m, 1 H), 5.70 (d, *J* = 4.8 Hz, 1 H), 5.19 (t, *J* = 2.6 Hz, 1 H), 5.04-4.88 (m, 3 H), 4.32-4.30 (m, 1 H), 4.21-4.19 (m, 2 H), 3.96-3.92 (m, 1 H), 3.48 (t, *J* = 6.4 Hz, 2 H), 2.11 (s, 3 H), 2.093 (s, 3 H), 2.087 (s, 3 H), 1.71 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.6, 169.1, 137.8, 121.2, 115.0, 96.8, 73.0, 70.1, 68.1, 66.9, 63.0, 62.8, 30.1, 28.7, 20.71 (2C), 20.67, 20.61; HRMS (ESI) *m/z* calcd $C_{19}H_{28}O_{10}Na$ $[M+Na]^+$ 439.1575, found 439.1577.

1,2,4-Orthoacetyl-3,6-di-*O*-acetyl-α-D-glucopyranose (5): $[\alpha]^{25}_D$ = 27.9 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (d, *J* = 4.8 Hz, 1 H, H-1), 5.20 (d, *J* = 4.6 Hz, 1 H, H-3), 4.64 (t, *J* = 6.9 Hz, 1 H, H-5), 4.51 (m, 1 H, H-2), 4.31 (dd, *J* = 6.9, 11.3 Hz, 1 H, H-6), 4.21 (m, 2 H, H-4, H-6'), 2.13 (s, 3 H), 2.10 (s, 3 H), 1.66 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 168.4, 118.3, 96.5 (C-1), 73.8 (C-5), 71.1 (C-2), 69.3 (C-3), 63.8 (C-4), 62.6 (C-6), 19.8, 19.7, 19.0; HRMS (ESI) *m/z* calcd $C_{12}H_{16}O_8Na$ $[M+Na]^+$ 311.0737, found 311.0735.

With Peracetyl Galactopyranosyl *ortho*-Hexynylbenzoate S1.

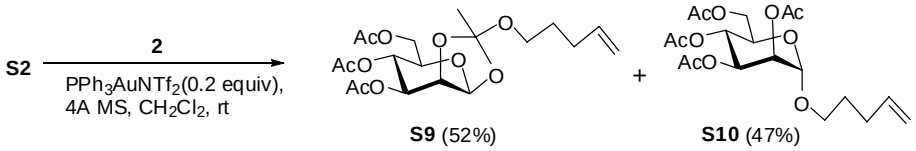


The analytical data of **S8** was in good agreement with those reported in the literature.[S8]

1,2-*O*-(4-Penten-1-yl)-orthoacetyl-3,4,6-tri-*O*-acetyl-α-D-galactopyranose (S7). A pair of the diastereoisomers of the 1,2-orthoesters were isolated and assigned by COSY, HMQC, and HMBC analysis. **S7-I**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (m, 1 H), 5.67 (d, *J* = 4.8 Hz, 1 H), 5.45 (m, 1 H), 5.42 (m, 1 H), 5.05 (dd, *J* = 4.8, 17 Hz, 1 H), 4.97 (d, *J* = 10.4 Hz, 1 H), 4.36 (t, *J* = 6.4 Hz, 1

H), 4.20 (dd, *J* = 5.6, 6.4 Hz, 1 H), 4.14 (m, 2 H), 3.59 (m, 2 H), 2.15 (m, 2 H), 2.12 (s, 3 H), 2.07(s, 3 H), 2.06 (s, 3 H), 1.71 (m, 2 H), 1.59 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.9 (2C), 138.0, 121.6, 114.9, 98.0, 73.2, 71.6, 69.0, 66.2, 63.0, 61.5, 30.1, 28.6, 23.0, 20.71, 20.69, 20.58; HRMS (ESI) *m/z* calcd $C_{19}H_{28}O_{10}Na$ $[M+Na]^+$ 439.1578, found 439.1575. **S7-II**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (m, 2 H), 5.43 (t, *J* = 2.6 Hz, 1 H), 5.07 (m, 1 H), 5.03 (d, *J* = 18.0 Hz, 1 H), 4.97 (d, *J* = 10.0 Hz, 1 H), 4.31 (m, 2 H), 4.15 (m, 2 H), 3.51 (m, 2 H), 2.12 (m, 5 H), 2.073 (s, 3 H), 2.066 (s, 3 H), 1.69-1.62 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.0, 169.7, 137.9, 121.0, 114.9, 97.4, 73.6, 71.3, 69.0, 65.9, 62.1, 61.3, 30.1, 28.6, 23.5, 20.61, 20.60, 20.8; HRMS (ESI) *m/z* calcd $C_{19}H_{28}O_{10}Na$ $[M+Na]^+$ 439.1578, found 439.1575.

With Peracetyl Mannopyranosyl *ortho*-Hexynylbenzoate S2.



The analytical data of **S10** was in good agreement with those reported in the literature.[S9,S2]

1,2-*O*-(4-Penten-1-yl)-orthoacetyl-3,4,6-tri-*O*-acetyl-β-D-mannopyranose (S9): $[\alpha]^{25}_D$ = -10.8 (*c* 3.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (m, 1 H), 5.45 (d, *J* = 2.0 Hz, 1 H), 5.27 (t, *J* = 9.6 Hz, 1 H), 5.13 (dd, *J* = 3.8, 9.8 Hz, 1 H), 5.01-4.92 (m, 2 H), 4.57 (t, *J* = 3.0 Hz, 1 H), 4.21 (dd, *J* = 4.8, 12.0 Hz, 1 H), 4.11 (dd, *J* = 3.8, 12.2 Hz, 1 H), 3.66 (m, 1 H), 3.47(m, 2 H), 2.09 (s, 3 H), 2.09-2.06 (m, 2 H), 2.05 (s, 3 H), 2.03 (s, 3 H), 1.72 (s, 3 H), 1.62 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.2, 169.3, 137.8, 124.1, 114.8, 97.2, 76.2, 71.2, 70.4, 65.4, 62.2, 61.7, 29.9, 28.5, 24.4, 20.57, 20.54, 20.51; HRMS (ESI) *m/z* calcd $C_{19}H_{28}O_{10}Na$ $[M+Na]^+$ 439.1575, found 439.1577.

With 4-*O*-(Acetyl-d$_3$)-2,3,6-tri-*O*-acetyl-D-glucopyranosyl *ortho*-Hexynylbenzoate (10).

1,2,4-*O*-(Orthoacetyl-d^3)-3,6-di-*O*-acetyl-α-D-glucopyranose (11): $[\alpha]^{25}_D$ = 27.7 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (d, *J* = 4.8 Hz, 1 H, H-1), 5.20 (d, *J* = 4.6 Hz, 1 H, H-3), 4.64 (t, *J* = 6.9 Hz, 1 H, H-5), 4.51 (m, 1 H, H-2), 4.31 (dd, *J* = 6.9, 11.3 Hz, 1 H, H-6), 4.21 (m, 2 H, H-4, H-6'), 2.13 (s, 3 H), 2.10 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 168.4, 118.3, 96.5 (C-1), 73.8 (C-5), 71.1 (C-2), 69.3 (C-3), 63.8 (C-4), 62.6 (C-6), 19.8, 19.7, 19.0; HRMS (ESI) *m/z* calcd $C_{12}H_{13}D_3O_8Na$ $[M+Na]^+$ 314.0926, found 314.0930.

Reference

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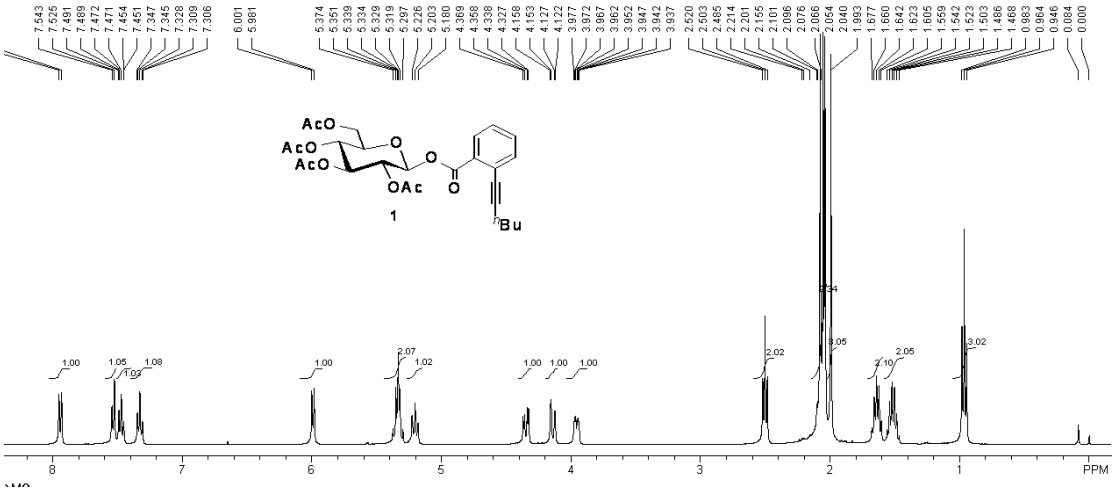
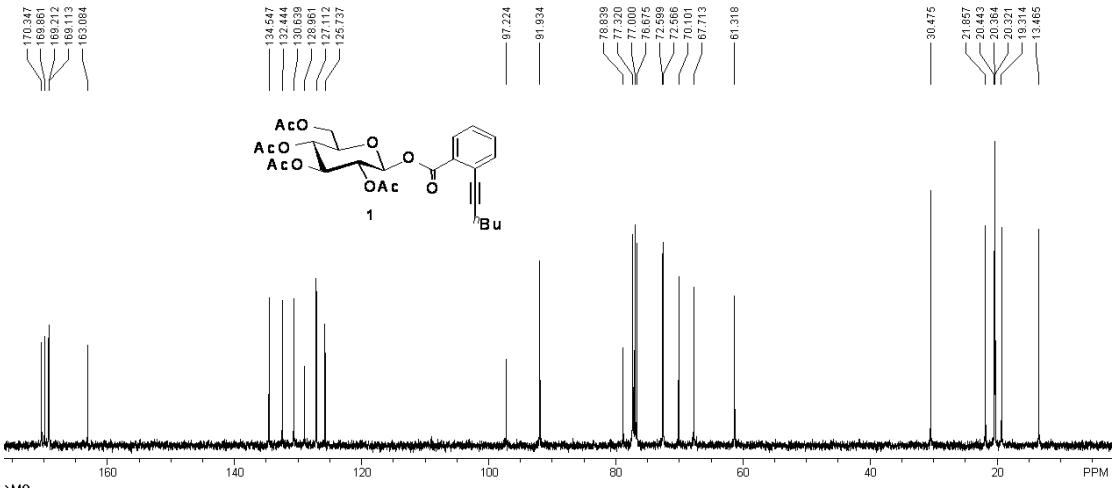
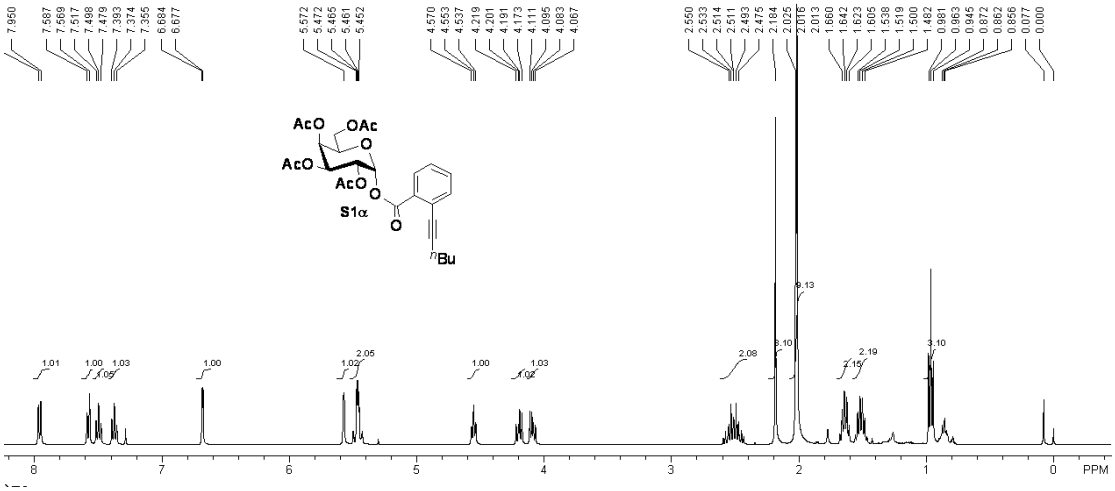
^{1}H NMR and ^{13}C NMR Spectra of New Compounds



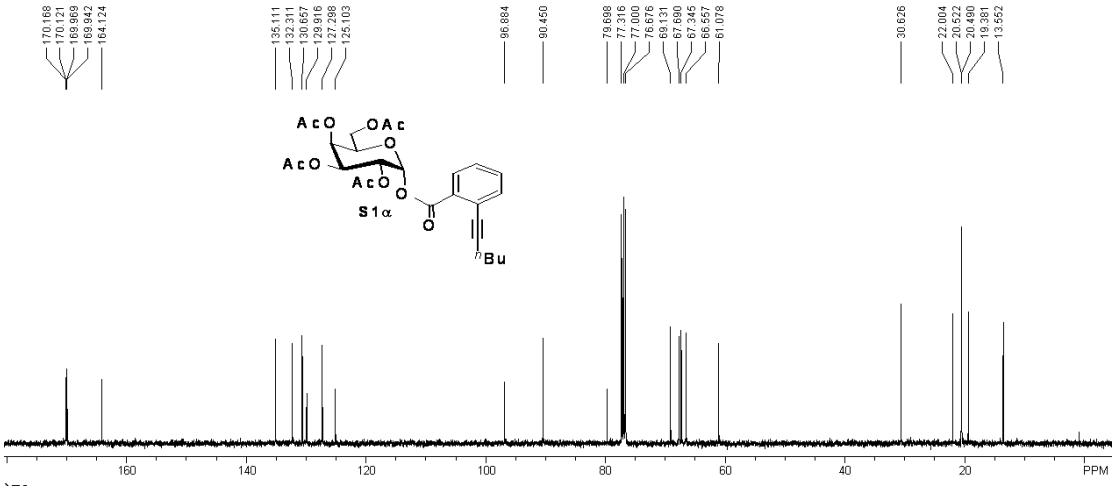
^{1}H NMR of **1** ($CDCl_3$)



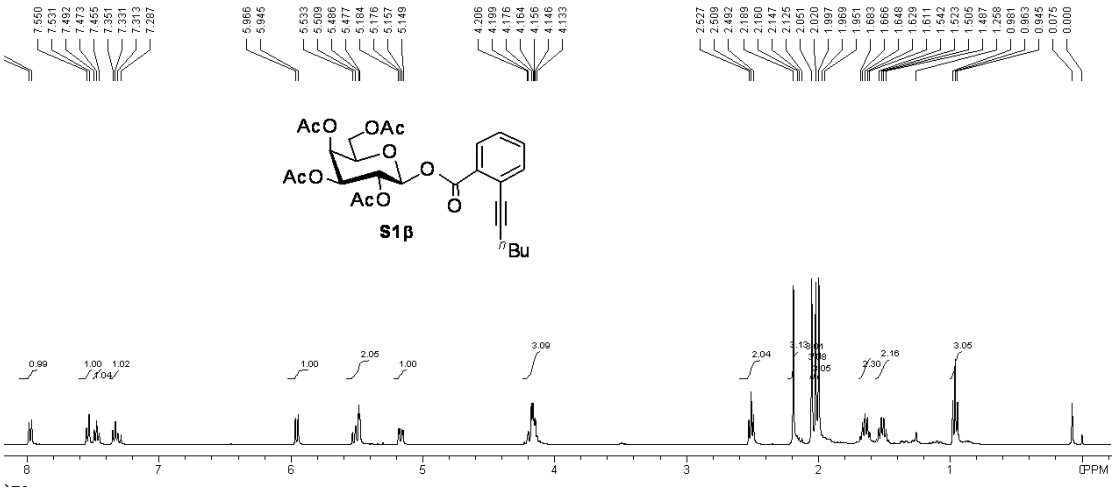
^{13}C NMR of **1** ($CDCl_3$)



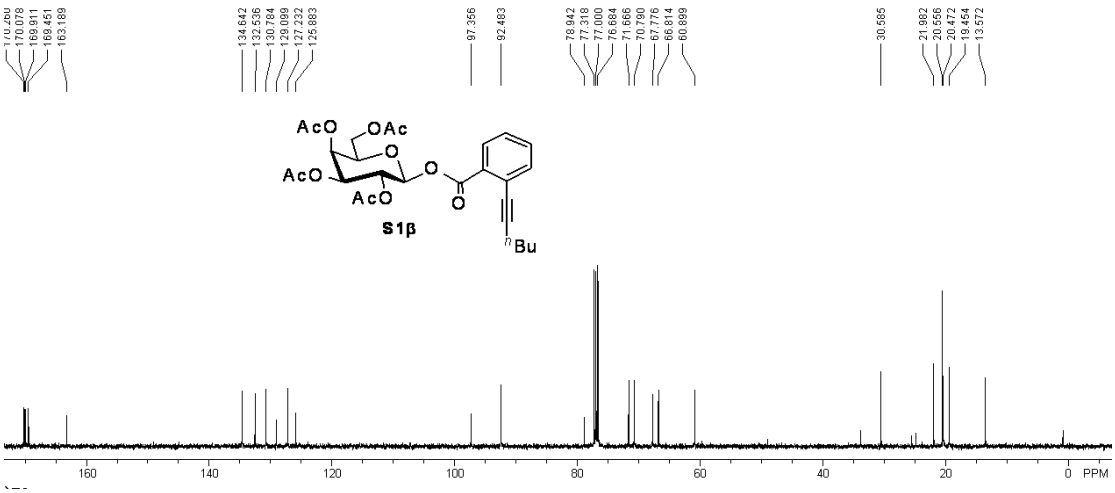
^{1}H NMR of **S1α** ($CDCl_3$)



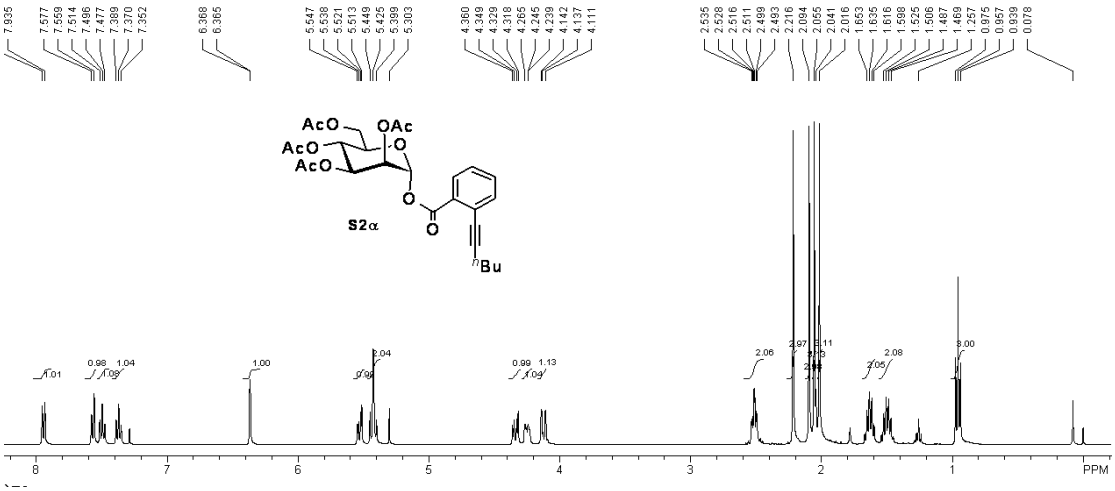
^{13}C NMR of **S1α** ($CDCl_3$)



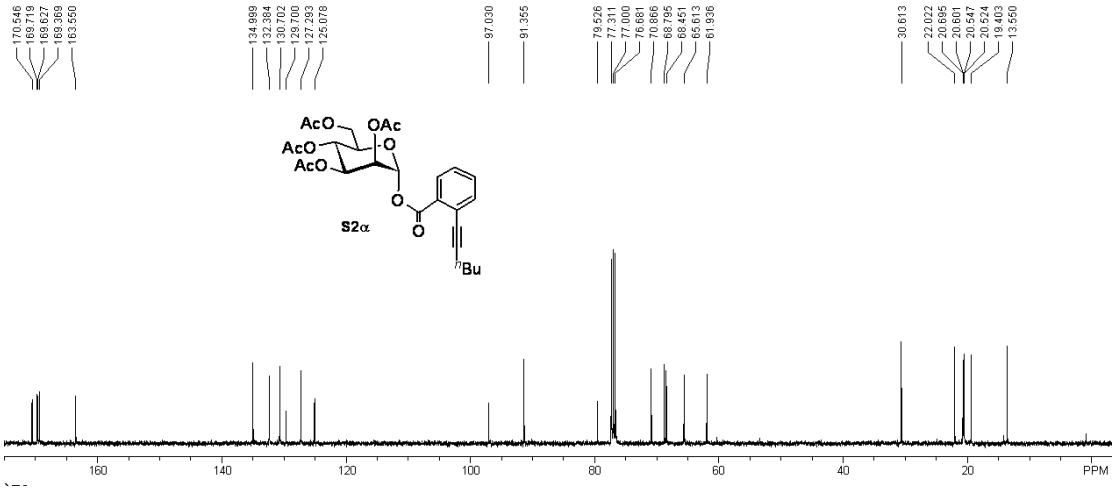
^{1}H NMR of **S1β** ($CDCl_3$)



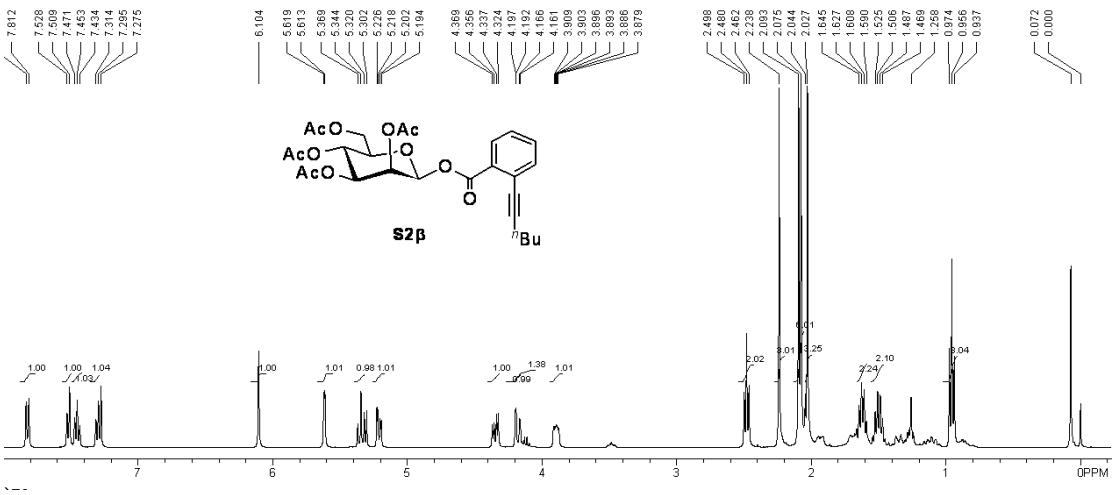
^{13}C NMR of **S1β** ($CDCl_3$)



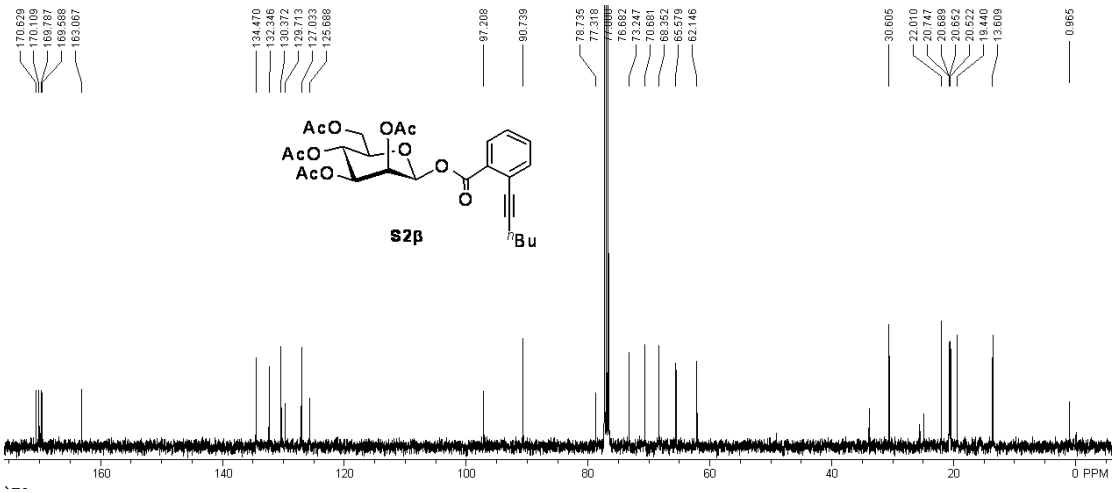
^{1}H NMR of **S2α** ($CDCl_3$)



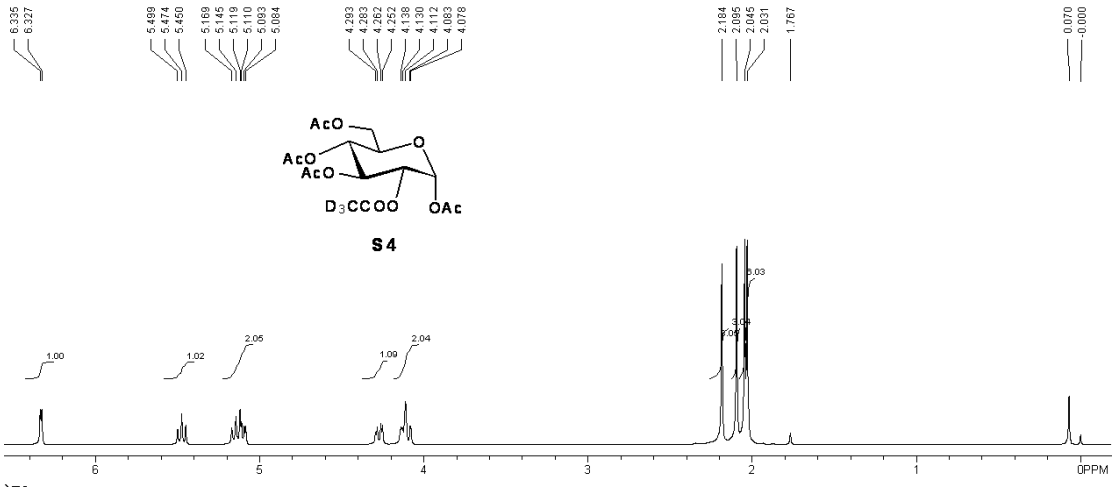
^{13}C NMR of **S2α** ($CDCl_3$)



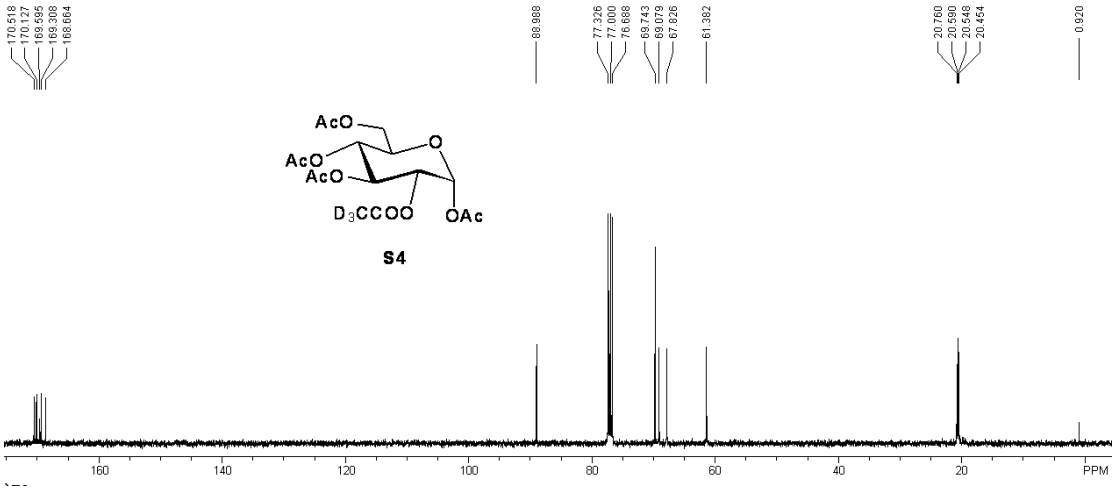
^{1}H NMR of **S2β** ($CDCl_3$)



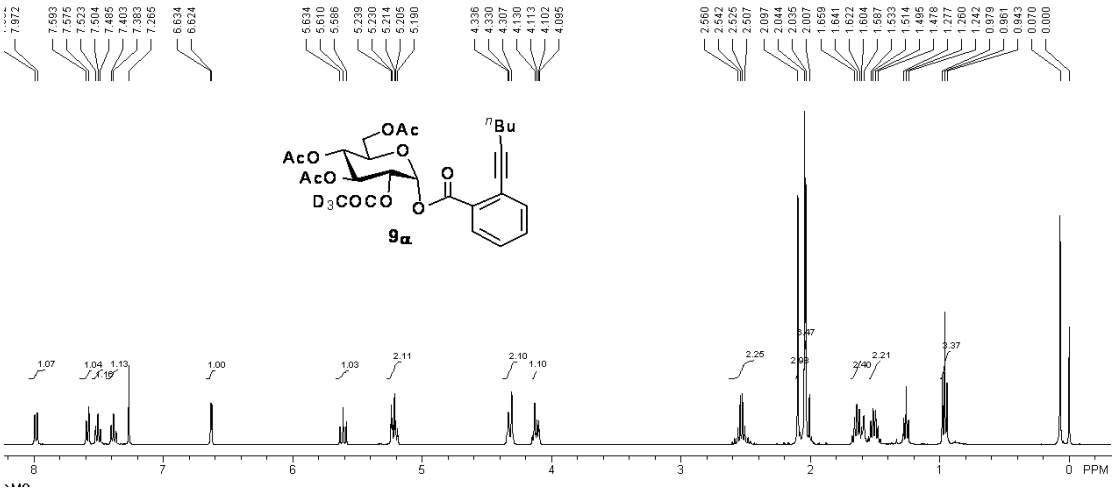
^{13}C NMR of **S2β** ($CDCl_3$)



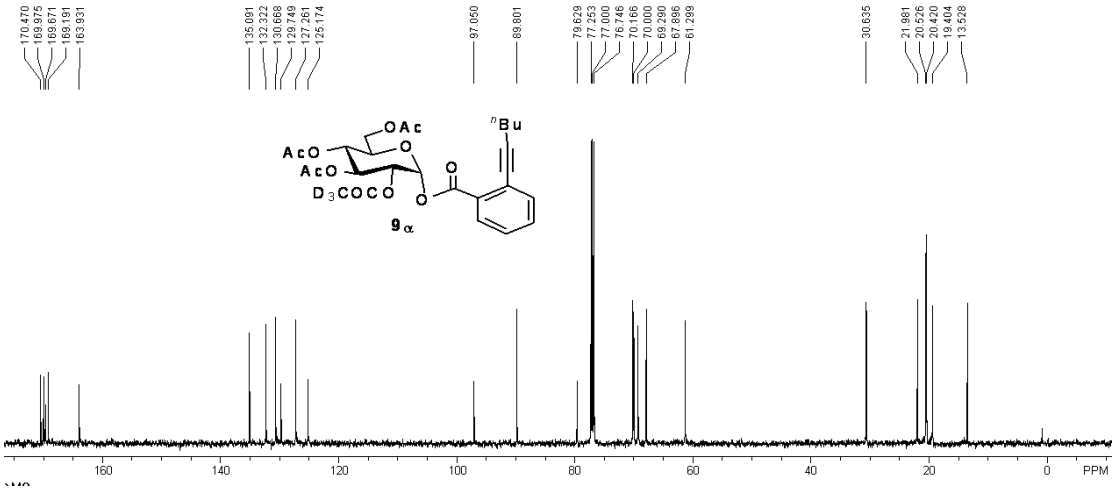
^{1}H NMR of **S4** ($CDCl_3$)



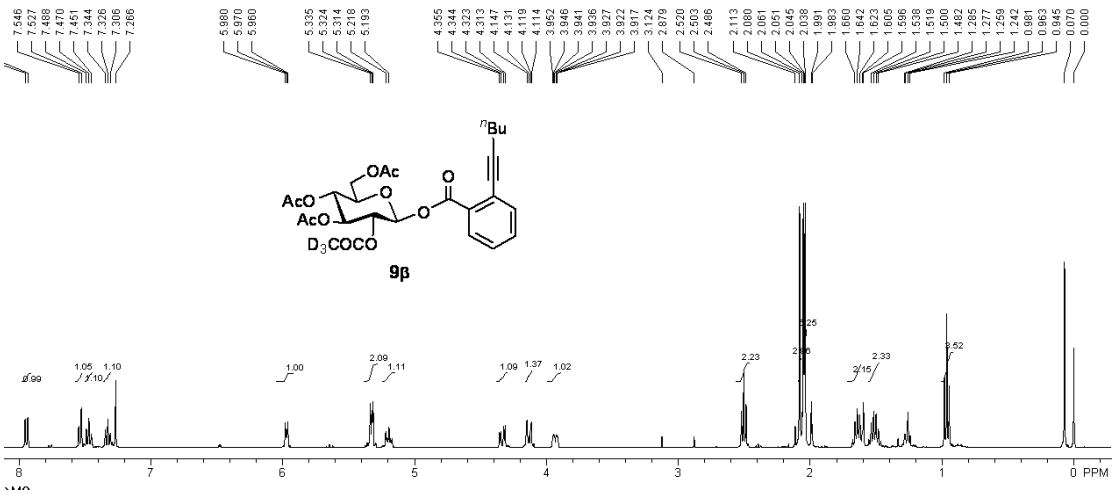
^{13}C NMR of **S4** ($CDCl_3$)



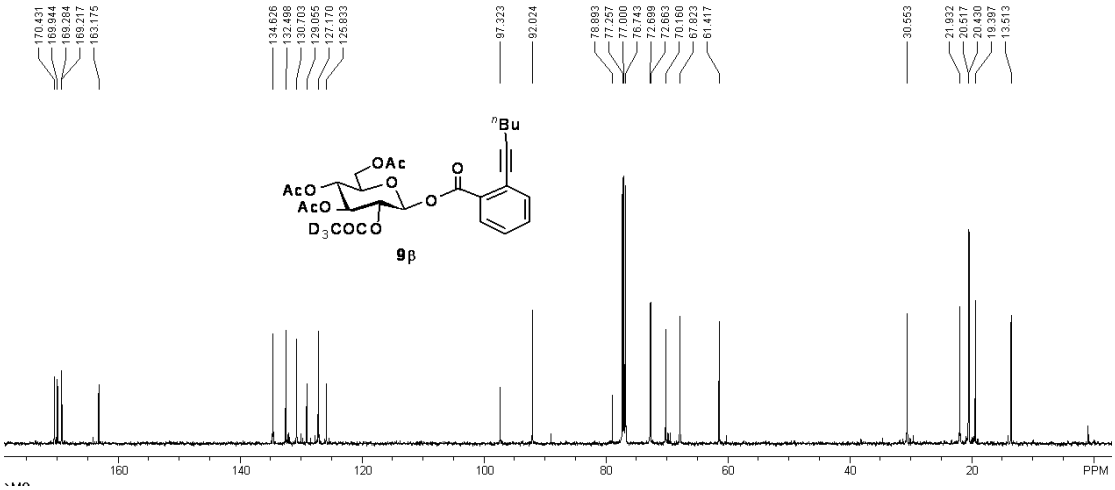
^{1}H NMR of **9α** ($CDCl_3$)



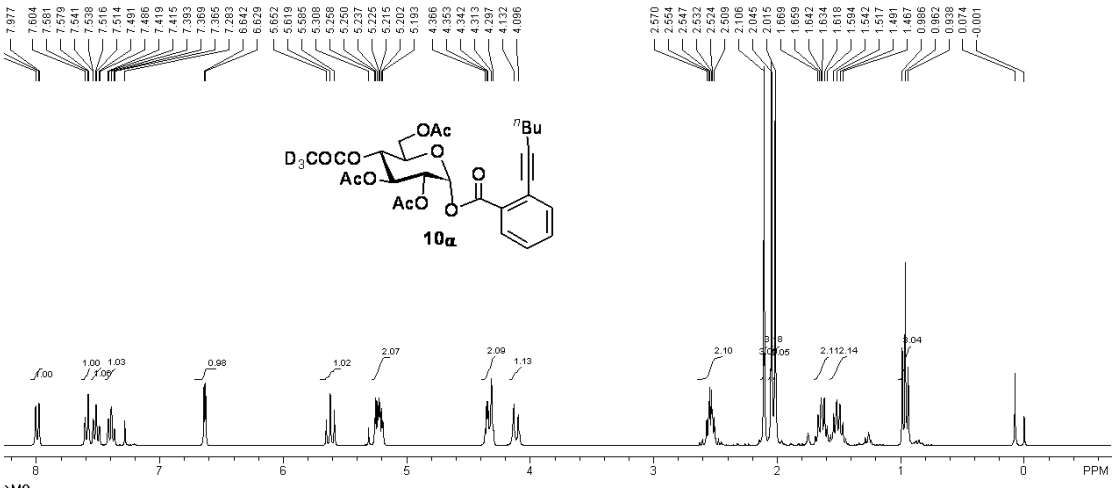
^{13}C NMR of **9α** ($CDCl_3$)



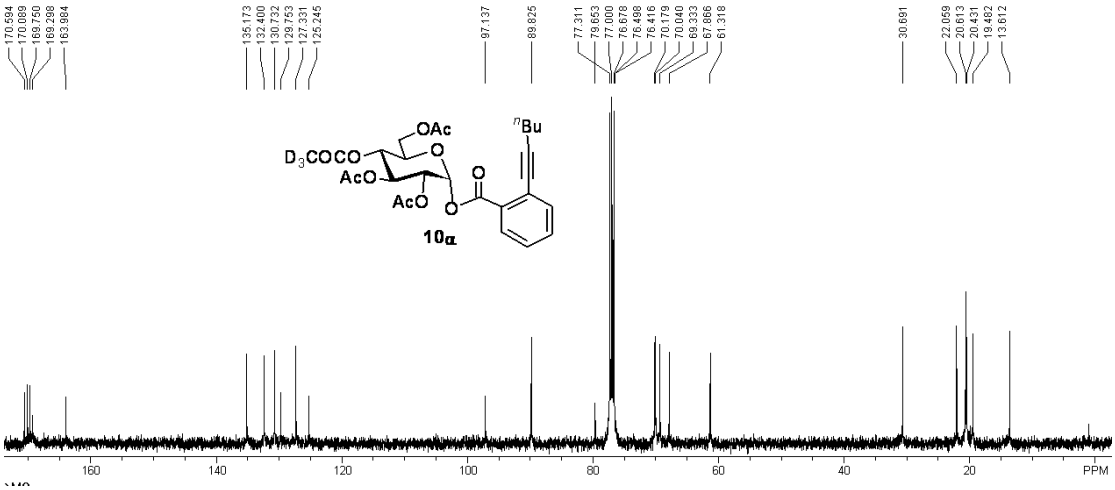
^{1}H NMR of **9β** ($CDCl_3$)



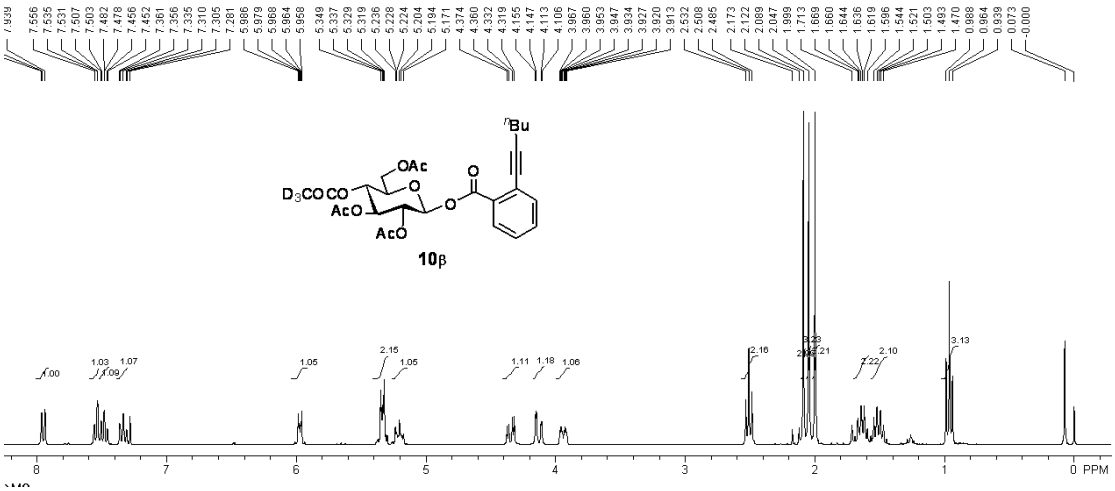
^{13}C NMR of **9β** ($CDCl_3$)



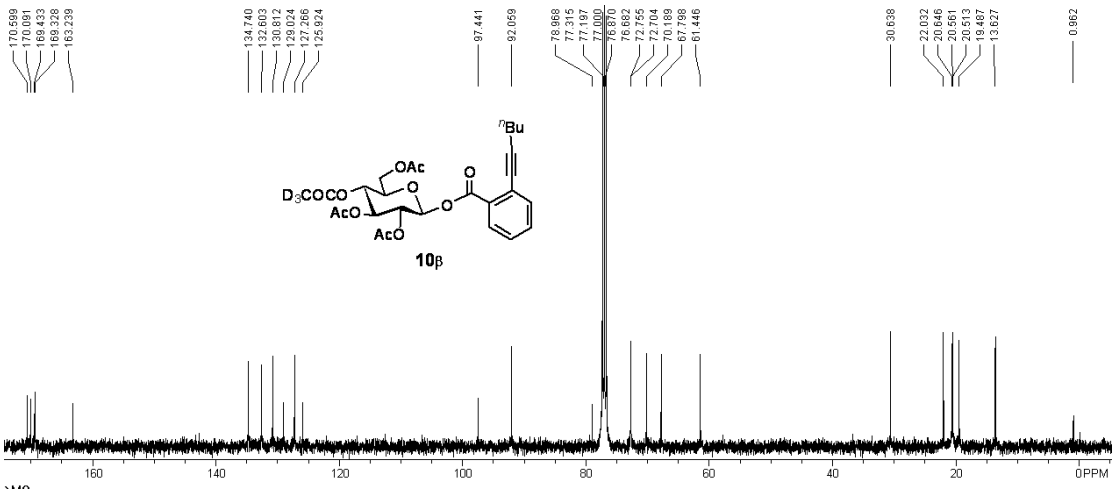
^{1}H NMR of **10α** ($CDCl_3$)



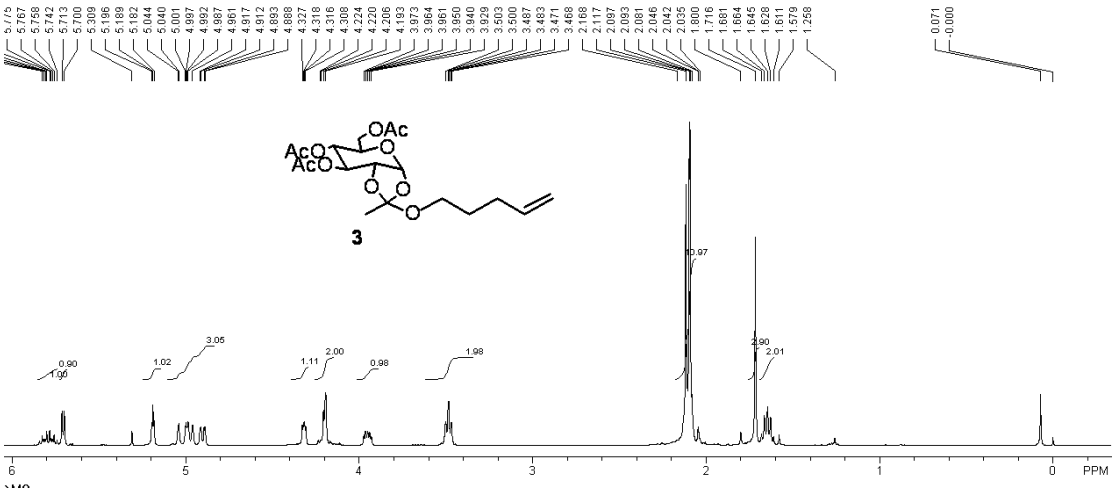
^{13}C NMR of **10α** ($CDCl_3$)



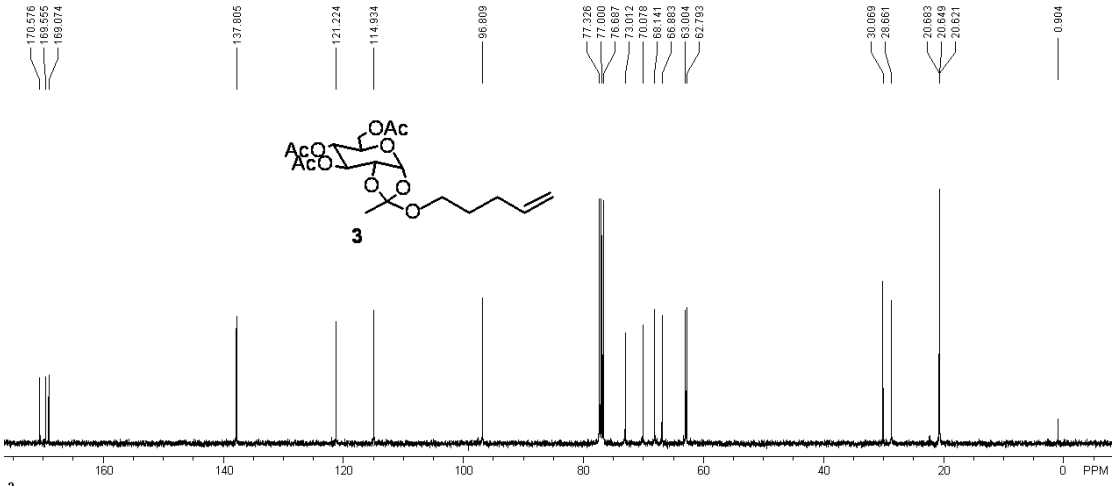
^{1}H NMR of **10β** ($CDCl_3$)



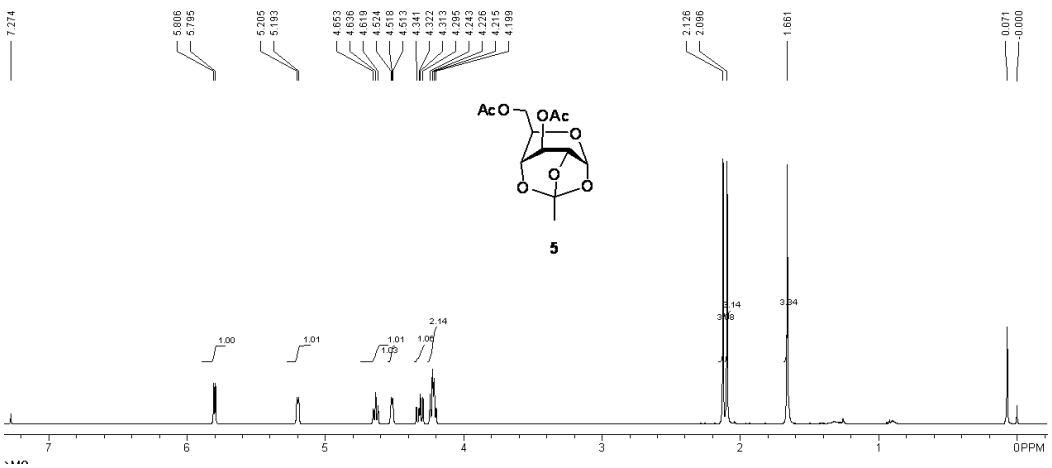
^{13}C NMR of **10β** ($CDCl_3$)



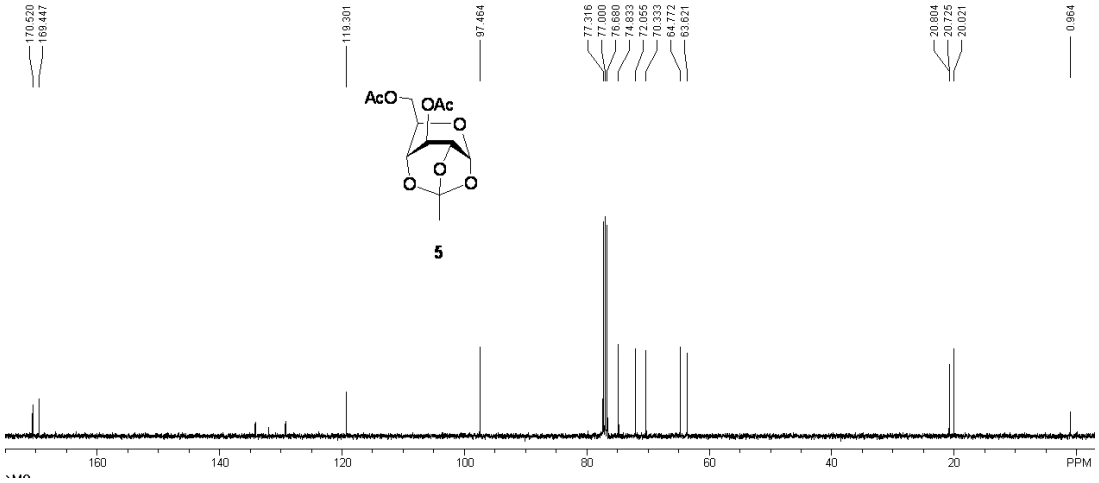
^{1}H NMR of **3** ($CDCl_3$)



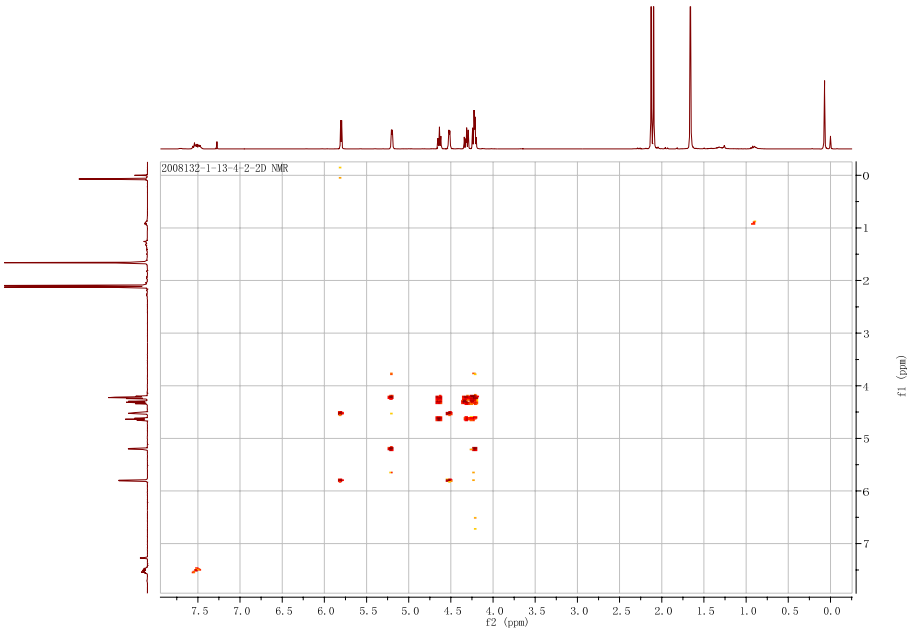
^{13}C NMR of **3** ($CDCl_3$)



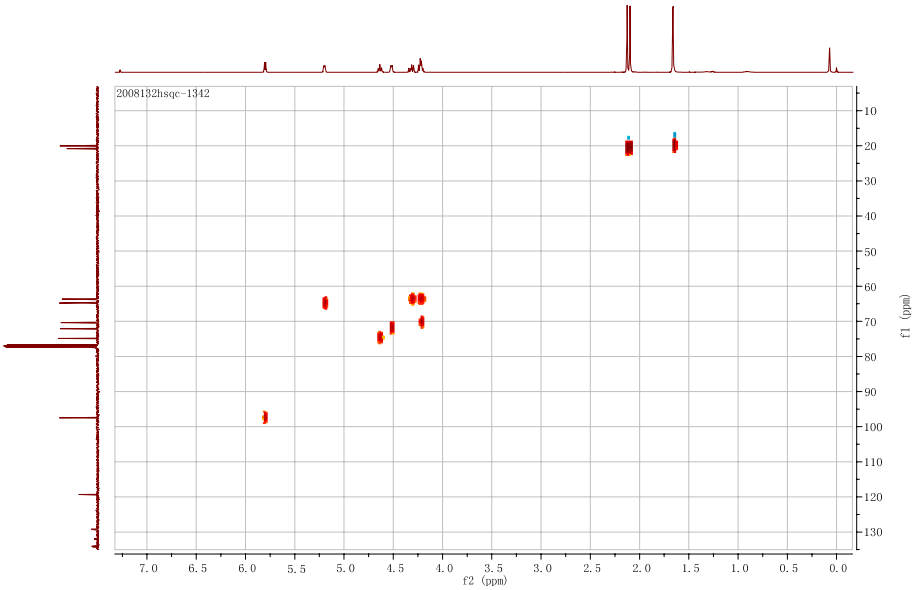
^{1}H NMR of **5** ($CDCl_3$)



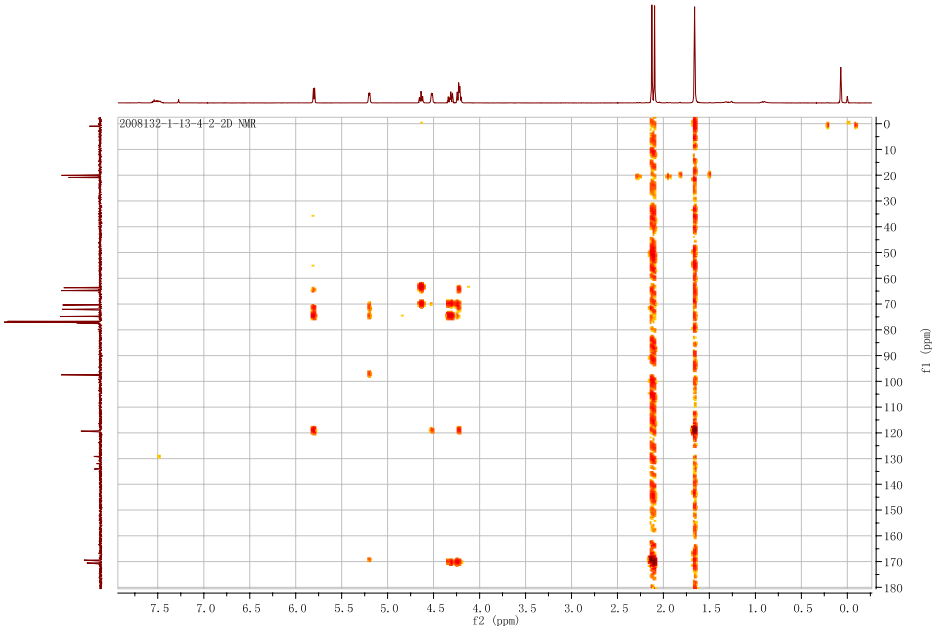
^{13}C NMR of **5** ($CDCl_3$)



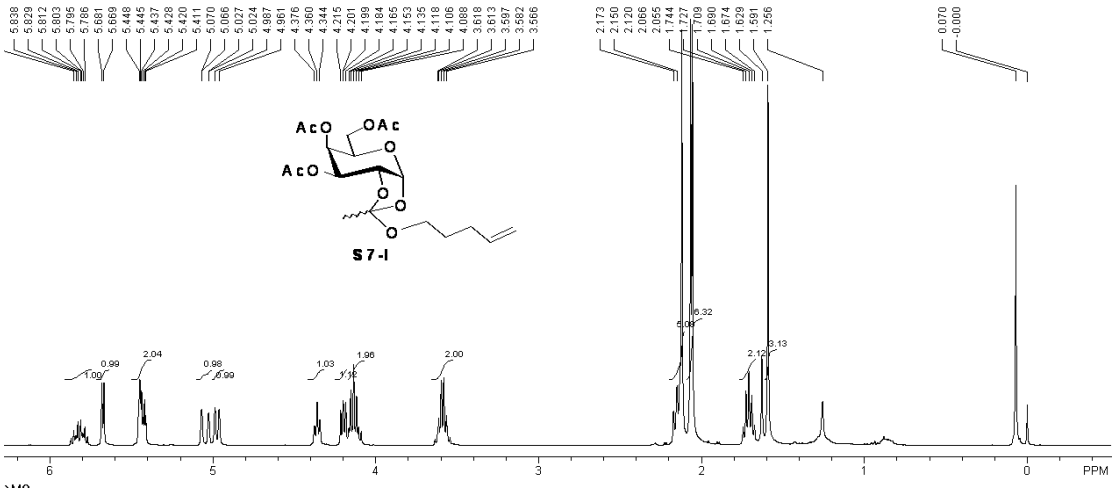
COSY of **5** ($CDCl_3$)



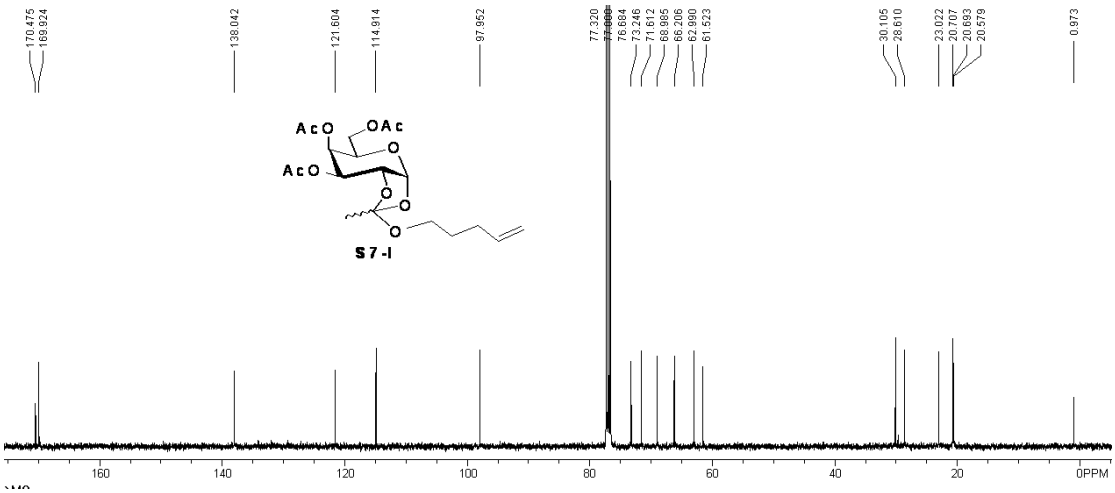
HSQC of **5** ($CDCl_3$)



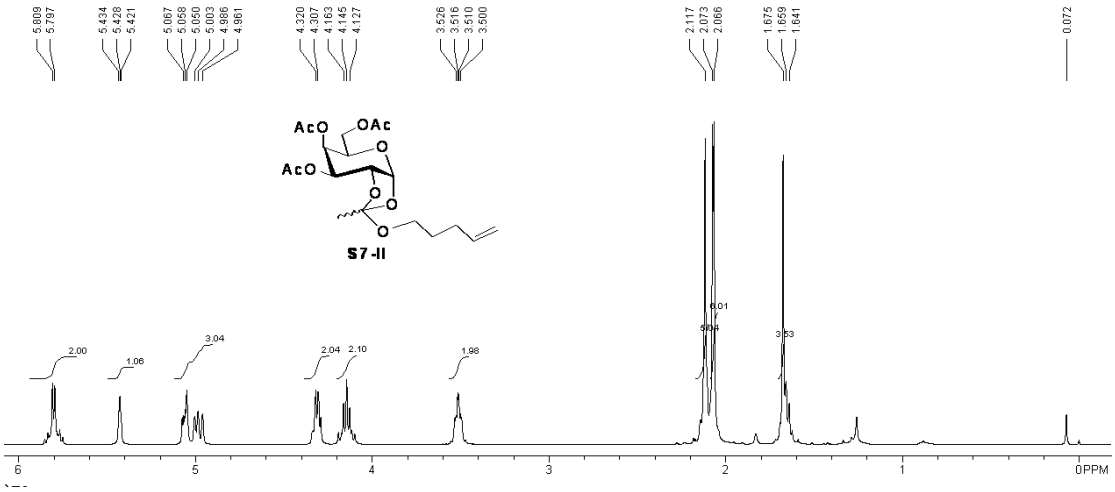
HMBC of **5** ($CDCl_3$)



^{1}H NMR of **S7-I** ($CDCl_3$)



^{13}C NMR of **S7-I** ($CDCl_3$)



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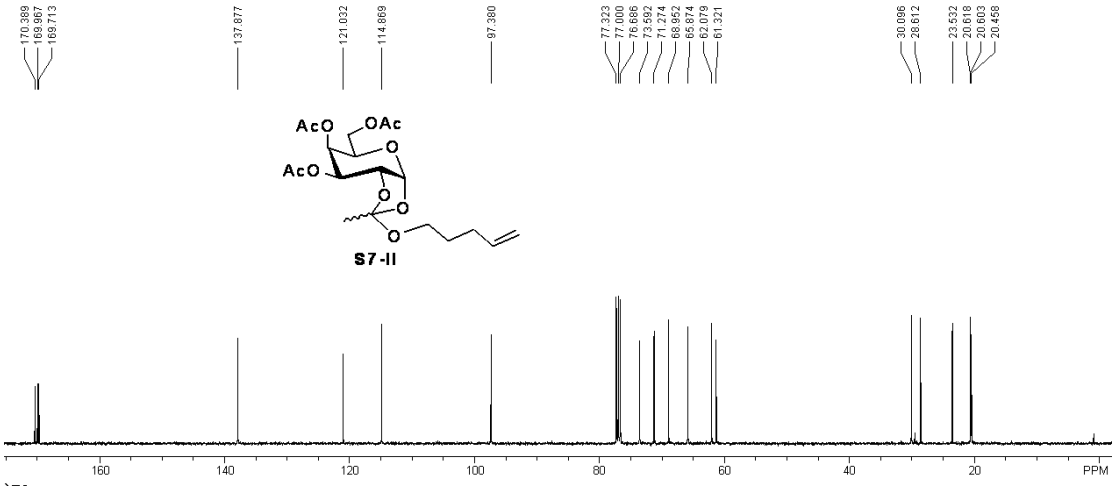

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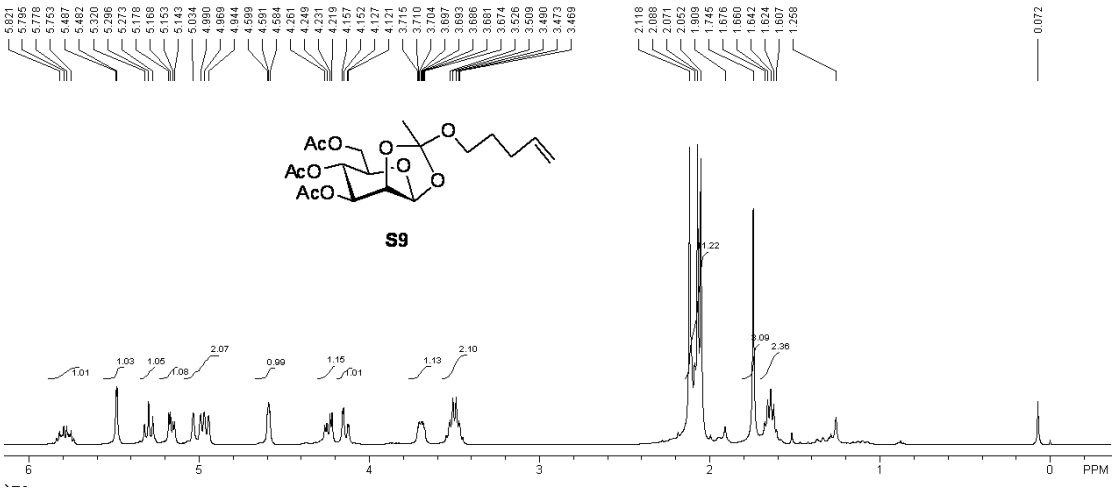
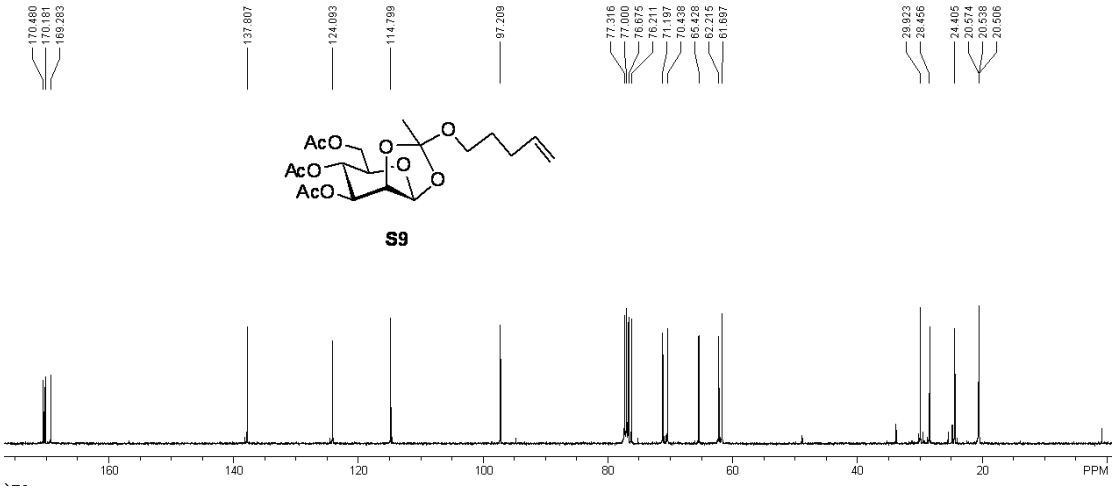
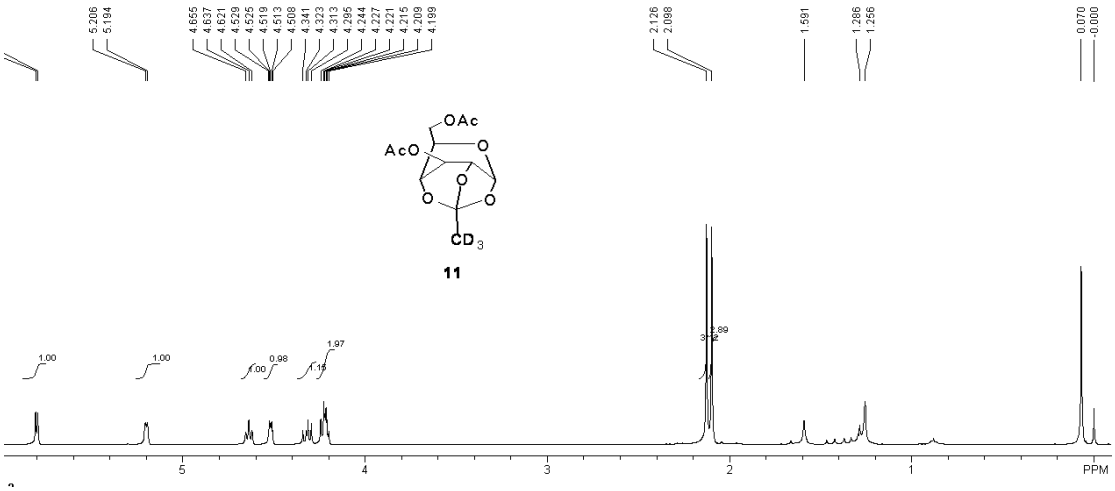


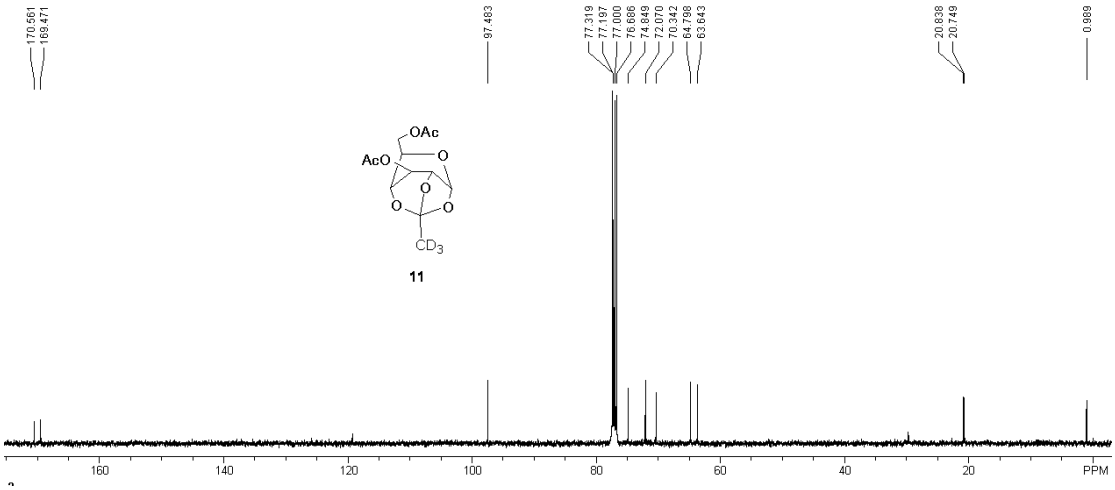
^{1}H NMR of **S9** ($CDCl_3$)



^{13}C NMR of **S9** ($CDCl_3$)



^{1}H NMR of **11** ($CDCl_3$)



^{13}C NMR of **11** ($CDCl_3$)