Supporting Information

Stereoselective Assembly of Complex Oligosaccharides Using Anomeric Sulfonium Ions as Glycosyl Donors

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1. Preparations and characterizations of prepared compounds

Reagents and General Procedures. Reagents were obtained from commercial sources and used as purchase. Dichloromethane (DCM) was freshly distilled using standard procedures. Other organic solvents were purchased anhydrous and used without further purification. Unless otherwise noted, all reactions were carried out at room temperature in oven-dried glassware with magnetic stirring. Molecular sieves were flame dried *in vacuo* prior to use. Organic solutions were concentrated under diminished pressure with bath temperature < 40 ^{o}C. Flash column chromatography was carried out on silica gel G60 (Silicycle, 60-200 μm, 60 Å). Thin-layer chromatography (TLC) was carried out on Silica gel 60 F_{254} (EMD Chemicals Inc.) and detection was performed by UV absorption (254 nm) where applicable, and by spraying with 20% sulfuric acid in ethanol followed by charring at ~150 ^{o}C, or by spraying with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}H_2O$ (25 g/L) in 10% sulfuric acid in ethanol followed by charring at ~150 ^{o}C. Optical rotations were measured by ATAGO POLAX-2L with 1 ml (5 cm) micro observation tube at 589 nm. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova-300 (300/75 MHz), a Varian Inova-500 (500 MHz) and a Varian Inova-600 (600/150 MHz) spectrometer equipped with sun workstations. Multiplicities are quoted as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), or multiplet (m). All NMR signals were assigned on the basis of 1H NMR, 13C NMR, gCOSY, and gHSQC experiments. All chemical shifts are quoted on the δ-scale in parts per million (ppm). Signals marked with a superscript Roman numeral I were the reducing end, whereas II and III were the second and the third sugar from the reducing end, and IV is the branching sugar. Residual solvent signals were used as an internal reference. Mass spectra were recorded on an Applied Biosystems 5800 MALDI-TOF

mass spectrometer. The matrix used was 2,5-dihydroxy-benzoic acid (DHB). Reverse-Phase HPLC was performed on an Aglient 1200 series system equipped with an auto-sampler, fraction-collector, UV-detector, and eclipse XDB-C18 column (5 µm, 4.6 × 250 mm or 9.4 × 250 mm).

2-(*S*)-Phenyl-(1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (2). Compound **1** (11 g, 35 mmol) was dissolved in anhydrous CH_3CN (400 mL) and hexamethyldisiloxane (TMS_2O) (44 mL, 0.21 mol) and TMSOTf (6.6 mL, 37 mmol) were added. After 30 min, Et_3SiH (46 mL, 0.29 mol) was added and the reaction mixture was stirred for another 4 h before quenching by the addition of MeOH (50 mL) and Et_3N (10 mL). The solution was concentrated *in vacuo* and the resulting yellow oil was purified by flash chromatography over silica gel (toluene/acetone, 3/1→1/1, v/v) to give **2** (7.7 g, 74%). Proton chemical shifts are identical to reported data.[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.09 (m, 5H, Ar*H*), 4.67 (dd, *J* = 10.6, 1.6 Hz, 1H, SCH_2CHPh), 4.35 (d, *J* = 8.2 Hz, 1H, H-1), 3.84 – 3.71 (m, 2H, H-$6_{a,b}$), 3.70 – 3.43 (m, 3H, H-2, H-3, H-4), 3.43 – 3.29 (m, 1H, H-5), 3.00 (dd, *J* = 13.9, 10.8 Hz, 2H, SC*H*HCHPh), 2.69 (d, *J* = 12.4 Hz, 1H, SCH*H*CHPh).

2-(*S*)-Phenyl-(4,6-*O*-benzylidene-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (3). Compound **2** (3.3 g, 11 mmol) was dissolved in DMF (60 mL) and benzaldehyde dimethyl acetal (2.5 mL, 17 mmol) and camphorsulfonic acid (40 mg, 0.17 mmol) were added. The reaction mixture was heated at 50 ^{o}C under reduced pressure (~15 mm Hg) for 16 h after which it was quenched by adding Et_3N (0.5 mL). The mixture was diluted with DCM (300 mL) and the organic solution was washed with water (2 × 200 mL) and brine (150 mL). The organic phase was dried ($MgSO_4$), filtered and the

filtrate was concentrated *in vacuo*. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/5→1/2, v/v) to give **3** (3.7 g, 87 %). R_f = 0.26 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{26}$ (deg cm^3 g^{-1} dm^{-1}) = +157.1 (*c* = 0.7 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 – 7.27 (m, 10H, Ar*H*), 5.56 (s, 1H, PhC*H*<), 4.73 (dd, *J* = 10.7, 2.0 Hz, 1H, SCH_2CHPh), 4.54 (d, *J* = 8.9 Hz, 1H, H-1), 4.37 (dd, *J* = 10.3, 4.6 Hz, 1H, H-6_a), 3.91 (t, *J* = 8.8 Hz, 1H, H-3), 3.85 – 3.56 (m, 4H, H-4, H-5, H-2, H-6_b), 3.09 (dd, *J* = 14.1, 10.8 Hz, 1H, SC*H*HCHPh), 2.77 (dd, *J* = 14.0, 2.0 Hz, 1H, SCH*H*CHPh); ^{13}C NMR (75 MHz, $CDCl_3$): δ140.20, 137.09, 129.49, 128.86, 128.60, 128.54, 126.56, 126.20, 102.28, 84.67, 81.15, 80.89, 77.69, 77.26, 76.84, 76.47, 72.34, 72.04, 68.64, 35.98; HR MALDI-TOF MS: m/z: calcd for $C_{21}H_{22}O_5S$ $[M+Na]^+$: 409.1086; found: 409.1097.

2-(*S*)-Phenyl-(3-*O*-acetyl-4,6-*O*-benzylidene-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (4). Compound **3** (1.35 g, 3.50 mmol) was dissolved in pyridine (10 mL) and acetic anhydride (5 mL) was added. After stirring for 16 h, the reaction mixture was diluted with DCM (120 mL) and washed with saturated $NaHCO_3$ (2 × 100 mL) and brine (90 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/Toluene, 1 /16→1/8, v/v) to give **4** (1.47 g, 98%). R_f = 0.53 (EtOAc/Toluene, 1/8, v/v); $[\alpha]^{d}_{26}$ (deg cm^3 g^{-1} dm^{-1}) = +40.0 (*c* = 0.5 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 – 7.16 (m, 10H, Ar*H*), 5.53 (s, 1H, PhC*H*<), 5.42 (t, *J* = 9.4 Hz, 1H, H-3), 4.72 (dd, *J* = 10.6, 1.9 Hz, 1H, SCH_2CHPh), 4.62 (d, *J* = 8.9 Hz, 1H, H-1), 4.39 (dd, *J* = 9.9, 4.1 Hz, 1H, H-6_a), 3.87 – 3.65 (m, 4H, H-2, H-4, H-5, H-6_b), 3.02 (dd, *J* = 14.0, 10.6 Hz, 1H, SC*H*HCHPh), 2.84 (dd, *J* = 14.0, 2.1 Hz, 1H, SCH*H*CHPh), 2.04 (s, 3H); ^{13}C NMR (75

MHz, $CDCl_3$): δ170.29, 140.18, 137.03, 129.34, 128.72, 128.47, 128.09, 126.36, 125.52, 101.84, 82.67, 80.10, 79.38, 77.66, 77.24, 76.93, 76.82, 72.48, 71.80, 68.61, 36.10, 21.17; HR MALDI-TOF MS: m/z: calcd for $C_{23}H_{24}O_6S$ $[M+Na]^+$: 451.1192; found: 451.1201.

2-(*S*)-Phenyl-(3-*O*-acetyl-4,6-*O*-benzylidene-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (5). Levulinic acid (464 µL, 4.56 mmol), *N*,*N*'-dicyclohexylcarbodiimide (DCC) (940 mg, 4.56 mmol) and 4-dimethylaminopyridine (DMAP) (44 mg, 0.36 mmol) were added to a stirred solution of **3** (440 mg, 1.14 mmol) in DCM (8 mL). After stirring for 16 h, the reaction mixture was filtered and the organic layer was concentrated *in vacuo*. The resulting oil was purified by flash chromatography over silica gel (toluene/acetone, 15/1→5/1, v/v) to give **5** (436 mg, 79%). R_f = 0.5 (toluene/acetone, 6/1, v/v); $[\alpha]^d_{26}$ (deg cm^3 g^{-1} dm^{-1}) = +66.7 (*c* = 1.2 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 – 7.16 (m, 10H, Ar*H*), 5.53 (s, 1H, PhC*H*<), 5.38 (t, *J* = 9.4 Hz, 1H, H-3), 4.71 (dd, *J* = 10.5, 1.9 Hz, 1H, SCH_2CHPh), 4.61 (d, *J* = 8.9 Hz, 1H, H-1), 4.39 (dd, *J* = 10.0, 4.3 Hz, 1H, H-5), 3.87 – 3.61 (m, 4H, H-2, H-4, H-$6_{a,b}$), 3.02 (dd, *J* = 14.0, 10.6 Hz, 1H, SC*H*HCHPh), 2.83 (dd, *J* = 14.0, 2.1 Hz, 1H, SCH*H*CHPh), 2.71 – 2.45 (m, 4H, 2×CH_2 Lev), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.24, 172.27, 140.12, 137.01, 129.29, 128.68, 128.44, 128.11, 126.37, 125.61, 101.78, 82.67, 80.13, 79.31, 77.67, 77.25, 76.86, 76.83, 72.47, 72.11, 68.59, 38.45, 36.00, 29.82, 28.39.; HR MALDI-TOF MS: m/z: calcd for $C_{21}H_{21}O_4S$ $[M+Na]^+$: 392.1059; found: 392.1051.

2-(*S*)-Phenyl-(3-*O*-allyloxycarbonyl-4,6-*O*-benzylidene-1,2-dideoxyl-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (6). Allyl chloroformate (274 µL, 2.56 mmol), tetramethylethylenediamine (TMEDA) (200 µL, 1.22 mmol) and 4-dimethylaminopyridine (DMAP) (50 mg, 0.41 mmol) were added to a stirred solution of

3 (470 mg, 1.22 mmol) in DCM (10 mL). After stirring for 16 h, the reaction mixture was diluted with DCM (100 mL) and washed with saturated $NaHCO_3$ (2 × 100 mL), brine (90 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The resulting yellow oil was purified by flash chromatography over silica gel (toluene/acetone, 20/1→8/1, v/v) to give **6** (500 mg, 87%). R_f = 0.56 (toluene/acetone, 8/1, v/v); $[\alpha]^d_{26}$ (deg cm^3 g^{-1} dm^{-1}) = +53.8 (*c* = 1.3 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.54 – 7.19 (m, 10H, Ar*H*), 5.91 – 5.70 (m, 1H, CH alloc), 5.53 (s, 1H, PhC*H*<), 5.28 – 5.13 (m, 2H, C*H*H alloc, H-3), 5.08 (d, *J* = 10.5 Hz, 1H, CH*H* alloc), 4.72 (dd, *J* = 10.6, 1.8 Hz, 1H, SCH_2CHPh), 4.63 (d, *J* = 8.9 Hz, 1H, H-1), 4.57 (d, *J* = 5.7 Hz, 1H, CH_2 alloc), 4.40 (dd, *J* = 10.0, 4.1 Hz, 1H, H-6_a), 3.90 – 3.65 (m, 4H, H-2, H-4, H-5, H-6_b), 3.05 (dd, *J* = 14.0, 10.7 Hz, 1H, SC*H*HCHPh), 2.83 (dd, *J* = 14.0, 2.0 Hz, 1H, SCH*H*CHPh); ^{13}C NMR (75 MHz, $CDCl_3$): δ154.59, 140.05, 136.94, 131.41, 129.35, 128.62, 128.43, 128.13, 126.42, 125.70, 119.03, 101.89, 82.57, 80.18, 79.16, 77.66, 77.44, 77.24, 76.82, 76.73, 76.03, 72.35, 68.92, 68.56, 35.98; HR MALDI-TOF MS: m/z: calcd for $C_{25}H_{26}O_7S$ $[M+Na]^+$: 493.1297; found: 493.1288.

2-(*S*)-Phenyl-(3-*O*-benzyl-4,6-*O*-benzylidene-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (7). Benzyl bromide (246 µL, 2.08 mmol) and sodium hydride (124 mg, 3.12 mmol) were added to a stirred solution of **3** (400 mg, 1.04 mmol) in DMF (5 mL). After stirring for 16 h, the reaction mixture was quenched with MeOH (2 mL), diluted with DCM (100 mL) and washed with 1 M HCl solution (100 mL), saturated $NaHCO_3$ (100 mL), and brine (90 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The resulting yellow oil was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/4 → 1/2, v/v) to give **7** (390 mg, 79%).

R_f = 0.28 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{26}$ (deg cm^3 g^{-1} dm^{-1}) = +54.5 (*c* = 1.1 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 – 7.16 (m, 15H, Ar*H*), 5.60 (s, 1H, PhC*H*<), 4.85 (s, 2H, C*H*$_2$Ph), 4.78 (d, *J* = 10.6 Hz, 1H, SCH$_2$C*H*Ph), 4.53 (d, *J* = 8.8 Hz, 1H, H-1), 4.37 (dd, *J* = 10.4, 4.8 Hz, 1H, H-4), 3.88 – 3.72 (m, 4H, H-2, H-3, H-6$_{a,b}$), 3.61 (td, *J* = 9.5, 4.9 Hz, 1H, H-5), 3.06 (dd, *J* = 13.9, 10.9 Hz, 1H, SC*H*HCHPh), 2.81 (d, *J* = 13.9 Hz, 1H, SCH*H*CHPh); ^{13}C NMR (75 MHz, $CDCl_3$): δ140.55, 138.58, 137.42, 129.22, 128.68, 128.46, 128.40, 128.23, 127.76, 126.28, 125.91, 101.65, 84.99, 81.71, 80.40, 78.79, 77.66, 77.24, 76.99, 76.82, 74.83, 72.37, 68.68, 36.09; HR MALDI-TOF MS: m/z: calcd for $C_{28}H_{28}O_5S$ $[M+Na]^+$: 499.1555; found: 499.1562.

2-(*S*)-Phenyl-(3,4-di-*O*-acetyl-6-*O*-benzyl-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (9). A mixture of **4** (550 mg, 1.29 mmol) and activated molecular sieves (4Å) in DCM (5 mL) was stirred for 1 h under an atmosphere of argon. After cooling to -78 ^{o}C, triethylsilane (408 μL, 2.58 mmol) and trifluoromethanesulfonic acid (171 μL, 1.94 mmol) were added. After 1 h, the reaction was quenched by the addition of MeOH (1 mL) and Et_3N (0.5 mL). The mixture was diluted with DCM (10 mL), filtered and the filtrate was concentrated *in vacuo*. The residue was redissolved in pyridine (5 mL) and acetic anhydride (5 mL) was added. After stirring for 16 h, the solvent was removed *in vacuo* and the resulting residue was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/6 → 1/2, v/v) to afford **9** (516 mg, 85%). R_f = 0.37 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{26}$ (deg cm^3 g^{-1} dm^{-1}) = +141.7 (*c* = 1.2 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.18 (m, 10H, Ar*H*), 5.34 – 5.10 (m, 2H, H-3, H-4), 4.69 (dd, *J* = 10.5, 1.8 Hz, 1H, SCH$_2$C*H*Ph), 4.58 – 4.44 (m, 3H, C*H*$_2$Ph, H-1), 3.86 – 3.66 (m, 2H, H-5, H-2), 3.62 – 3.50 (m, 2H, H-6$_{a,b}$), 2.97 (dd, *J* = 14.0, 10.6 Hz, 1H, SC*H*HCHPh), 2.80 (dd, *J*

= 14.0, 2.1 Hz, 1H, SCH*H*CHPh), 1.99 (s, 3H), 1.92 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.65, 169.83, 140.32, 137.84, 128.69, 128.61, 128.22, 128.07, 128.00, 125.57, 81.30, 79.75, 78.81, 77.71, 77.29, 76.86, 76.01, 73.84, 73.38, 69.62, 68.89, 35.86, 21.03, 20.89; HR MALDI-TOF MS: m/z: calcd for $C_{25}H_{28}O_7S$ $[M+Na]^+$: 495.1454; found: 495.1463.

2-(*S*)-Phenyl-(3-*O*-acetyl-4,6-di-*O*-benzyl-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (10). A mixture of **4** (430 mg, 1.00 mmol) and activated molecular sieves (4 Å) in DCM (5 mL) was stirred for 1 h under an atmosphere of argon. After cooling to -78 ^{o}C, triethylsilane (316 μL, 2.00 mmol) and trifluoromethanesulfonic acid (132 μL, 1.50 mmol) were added. After 1 h, the reaction was quenched by the addition of MeOH (1 mL) and Et_3N (0.5 mL). The mixture was diluted with DCM (10 mL), filtered and the filtrate was concentrated *in vacuo.* The resulting residue was loaded onto a small plug of silica gel and product fractions were collected and concentrated. The residue was redissolved in DMF (5 mL) followed by the addition of benzyl bromide (356 μL, 3.00 mmol) and Ag_2O (1.2 g, 5.2 mmol). After stirring for 16 h, the reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The resulting residue was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/6 → 1/3, v/v) to afford **10** (287 mg, 55%). R_f = 0.45 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{26}$ (deg cm^3 g^{-1} dm^{-1}) = +66.7 (*c* = 0.3 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 – 7.09 (m, 15H, Ar*H*), 5.30 (dd, *J* = 11.0, 7.9 Hz, 1H, H-3), 4.72 – 4.50 (m, 5H, 2×C*H*$_2$Ph, SCH_2CHPh), 4.46 (d, *J* = 8.9 Hz, 1H, H-1), 3.83 (t, *J* = 9.5 Hz, 1H, H-4), 3.76 (d, *J* = 2.8 Hz, 2H, H-6$_{a,b}$), 3.72 – 3.55 (m, 2H, H-2, H-5), 2.95 (dd, *J* = 14.0, 10.5 Hz, 1H, SC*H*HCHPh), 2.79 (dd, *J* = 14.0, 2.1 Hz, 1H, SCH*H*CHPh) 1.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ170.34, 140.49, 138.13, 137.99, 128.65, 128.21, 128.10, 128.06, 127.98, 127.91, 125.49, 81.77, 80.59, 79.57, 77.66, 77.24,

76.81, 76.18, 75.93, 75.27, 74.84, 73.85, 68.59, 35.86, 21.21; HR MALDI-TOF MS: m/z: calcd for $C_{30}H_{32}O_6S$ $[M+Na]^+$: 543.1818; found: 543.1824.

2-(*S*)-Phenyl–{3-*O*-acetyl-6-*O*-benzyl-4-*O*-(9-fluorenylmethyloxycarbonyl)-1,2-dideoxy-ß-D-glucopyranoso}[1,2-*e*]-1,4-oxathiane (11). A mixture of **4** (1.05 g, 2.45 mmol) and activated molecular sieves (4 Å) in DCM (10 mL) was stirred for 1 h under an atmosphere of argon. After cooling to -78 ^oC, triethylsilane (0.78 mL, 4.90 mmol) and trifluoromethanesulfonic acid (323 µL, 3.68 mmol) were added. After 1 h, the reaction was quenched by the addition of MeOH (1 mL) and Et_3N (0.5 mL). The resulting mixture was diluted with DCM (10 mL), filtered and the filtrate was concentrated *in vacuo*. The resulting residue was redissolved in a mixture of pyridine and DCM (10 mL, 1/1, v/v) and FmocCl (0.95 g, 3.70 mmol) was added. After stirring for 16 h, the reaction mixture was diluted with DCM (50 mL), poured into an aqueous 1 M HCl solution (100 mL) and washed with H_2O (100 mL) and brine (100 mL). The organic layer dried ($MgSO_4$) and concentrated *in vacuo*. The resulting residue was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/6 → 1/3, v/v) to afford **11** (1.06 g, 66%). R_f = 0.47 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{26}$ (deg cm^3 g^{-1} dm^{-1}) = +47.5 (c = 0.6 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.88 – 7.08 (m, 18H), 5.40 (t, J = 9.5 Hz, 1H, H-3), 5.07 (t, J = 9.7 Hz, 1H, H-4), 4.70 (d, J = 9.3 Hz, 1H, SCH_2CHPh), 4.64 – 4.45 (m, 3H, H-1, CH_2Ph), 4.45 – 4.08 (m, 3H, CH Fmoc, CH_2 Fmoc), 3.98 – 3.83 (m, 1H, H-5), 3.83 – 3.61 (m, 3H, H-2, H-$6_{a,b}$), 2.98 (dd, J = 14.0, 10.7 Hz, 1H, SCHHCHPh), 2.81 (dd, J = 13.9, 1.7 Hz, 1H, SCHHCHPh), 1.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ171.85, 140.45, 137.87, 128.73, 128.70, 128.12, 128.07, 125.61, 81.28, 80.01, 79.73, 77.77, 77.35, 76.92, 76.03, 75.98, 74.02, 70.95, 70.06, 35.85, 21.29; HR MALDI-TOF MS: m/z: calcd for

$C_{38}H_{36}O_8S$ $[M+Na]^+$: 675.2029; found: 675.2017.

2-(*S*)-Phenyl-(3,6-di-*O*-acetyl-4-*O*-benzyl-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (13). A mixture of **4** (610 mg, 1.43 mmol) and activated molecular sieves (4Å) in DCM (8 mL) was stirred for 1 h under an atmosphere of argon. After cooling to -78 ^oC, triethylsilane (451 µL, 2.86 mmol) and dichlorophenylborane (280 µL, 2.15 mmol) were added. After 30 min, the reaction was quenched by the addition of MeOH (1 mL) and Et_3N (0.5 mL). The resulting mixture was diluted with DCM (10 mL), filtered and the filtrate was concentrated *in vacuo*. The residue was redissolved in pyridine (5 mL) and acetic anhydride (5 mL) was added. After stirring for 16 h, the mixture was concentrated *in vacuo* and the resulting residue was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/4 → 1/3, v/v) to afford **13** (525 mg, 78%). R_f = 0.43 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{26}$ (deg cm^3 g^{-1} dm^{-1}) = +80.0 (c = 0.3 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.18 (m, 10H, Ar*H*), 5.36 (t, J = 9.3 Hz, 1H), 4.73 – 4.53 (m, 3H, SCH_2CHPh, $PHCH_2$), 4.48 (d, J = 8.9 Hz, 1H, H-1), 4.38 (dd, J = 12.2, 1.8 Hz, 1H, H-6_a), 4.22 (dd, J = 12.1, 4.6 Hz, 1H, H-6_b), 3.81 – 3.54 (m, 3H, H-5, H-4, H-2), 2.95 (dd, J = 14.0, 10.5 Hz, 1H, SC*H*HCHPh), 2.80 (dd, J = 14.0, 2.1 Hz, 1H, SCH*H*CHPh), 2.08 (s, 3H), 1.98 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.85, 170.20, 140.34, 137.44, 128.80, 128.69, 128.37, 128.27, 128.00, 125.46, 81.70, 79.62, 78.46, 77.70, 77.28, 76.86, 76.17, 75.80, 75.24, 74.91, 63.18, 35.80, 21.23, 21.12; HR MALDI-TOF MS: m/z: calcd for $C_{25}H_{28}O_7S$ $[M+Na]^+$: 495.1454; found: 495.1447.

2-(*S*)-Phenyl-(4-*O*-acetyl-6-*O*-benzyl-3-*O*-levulinoyl-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (14). A mixture of **5** (300 mg, 0.62 mmol) and activated molecular sieves (4 Å) in DCM (5 mL) was stirred for 1 h under an atmosphere

of argon. After cooling to -78 ^{o}C, triethylsilane (196 µL, 1.24 mmol) and trifluoromethanesulfonic acid (82 µL, 0.93 mmol) were added. After 1 h, the reaction was quenched by the addition of MeOH (1 mL) and Et_3N (0.5 mL). The resulting mixture was diluted with DCM (10 mL), filtered and the filtrate was concentrated *in vacuo*. The residue was redissolved in pyridine (5 mL) and acetic anhydride (5 mL) was added. After stirring for 16 h, the mixture was removed *in vacuo*. The resulting residue was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/4 → 1/2, v/v) to afford **14** (259 mg, 79%). R_f = 0.29 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{26}$ (deg cm^3 g^{-1} dm^{-1}) = +105.3 (*c* = 1.9 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.18 (m, 10H, Ar*H*), 5.23 (t, *J* = 9.6 Hz, 1H, H-3), 5.17 (t, *J* = 9.6 Hz, 1H, H-4), 4.67 (dd, *J* = 10.5, 1.8 Hz, 1H, SCH_2CHPh), 4.63 – 4.43 (m, 3H, CH_2Ph, H-1), 3.86 – 3.66 (m, 2H, H-2, H-5), 3.61 – 3.48 (m, 2H, H-$6_{a,b}$), 2.96 (dd, *J* = 14.0, 10.6 Hz, 1H, SC*H*HCHPh), 2.79 (dd, *J* = 14.0, 2.1 Hz, 1H, SCH*H*CHPh), 2.76 – 2.31 (m, 4H, 2×CH_2 Lev), 2.07 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ206.19, 172.23, 170.06, 140.28, 137.86, 128.66, 128.60, 128.21, 128.06, 127.98, 125.60, 81.39, 79.74, 78.93, 77.69, 77.26, 76.84, 75.94, 73.85, 73.38, 69.20, 68.95, 38.10, 35.80, 29.80, 28.25, 20.92; HR MALDI-TOF MS: m/z: calcd for $C_{23}H_{25}O_5S$ $[M+Na]^+$: 436.1321; found: 436.1329.

2-(*S*)-Phenyl-(4-*O*-acetyl-3-*O*-allyloxycarbonyl-6-*O*-benzyl-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (15). A mixture of **6** (300 mg, 0.64 mmol) and activated molecular sieves (4 Å) in DCM (5 mL) was stirred for 1 h under an atmosphere of argon. After cooling to -78 ^{o}C, triethylsilane (202 µL, 1.28 mmol) and trifluoromethanesulfonic acid (85 µL, 0.96 mmol) were added. After 1 h, the reaction was quenched by the addition of MeOH (1 mL) and Et_3N (0.5 mL), diluted by DCM (10 mL)

and filtered. The filtrate was concentrated *in vacuo*. The residue was redissolved in pyridine (5 mL) and acetic anhydride (5 mL) was added. After stirring for 16 h, the solvent was removed. The resulting residue was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/8 → 1/2, v/v) to afford **15** (302 mg, 92%). R_f = 0.58 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +94.4 (*c* = 3.6 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 – 7.17 (m, 10H, Ar*H*), 5.79 (ddd, *J* = 22.7, 10.8, 5.6 Hz, 1H, C*H* alloc), 5.29 – 4.99 (m, 4H, H-3, H-4, CH_2 alloc), 4.69 (dd, *J* = 10.5, 1.8 Hz, 1H, SCH$_2$C*H*Ph), 4.64 – 4.45 (m, 5H, CH_2Ph, CH_2 alloc, H-1), 3.89 – 3.71 (m, 2H, H-2, H-5), 3.61 – 3.51 (m, 2H, H-6$_{a,b}$), 2.99 (dd, *J* = 14.0, 10.6 Hz, 1H, SC*H*HCHPh), 2.80 (dd, *J* = 14.0, 2.0 Hz, 1H, SCH*H*CHPh), 1.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.69, 154.84, 140.19, 137.83, 131.45, 128.61, 128.60, 128.21, 128.10, 128.00, 125.77, 125.73, 118.89, 81.32, 79.79, 78.84, 77.70, 77.46, 77.28, 76.85, 75.80, 73.88, 69.45, 69.10, 68.84, 35.72, 20.90; HR MALDI-TOF MS: m/z: calcd for $C_{27}H_{30}O_8S$ $[M+Na]^+$: 537.1559; found: 537.1551.

2-(*S*)-Phenyl-(4,6-di-*O*-acetyl-3-*O*-benzyl-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (16). TsOH·H_2O (80 mg, 0.42 mmol) and EtSH (31 µL, 0.42 mmol) were added to a stirred solution of **7** (200 mg, 0.42 mmol) in DCM (5 mL). After stirring for 2 h, the solvent was removed *in vacuo* and the residue was redissolved in pyridine (5 mL) and acetic anhydride (5 mL). After stirring for 16 h, the reaction mixture was concentrated under reduced pressure. The resulting residue was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/5 → 1/4, v/v) to afford **16** (167 mg, 84%). R_f = 0.21 (EtOAc/hexanes, 1/4, v/v); $[\alpha]^{d}_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +80.0 (*c* = 0.4 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ7.50 – 7.09 (m, 10H, Ar*H*), 5.11 (t, *J* = 9.7 Hz,

1H, H-4), 4.80 (t, *J* = 12.2 Hz, 2H, C*H*HPh, SCH_2CHPh), 4.63 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.44 (d, *J* = 8.9 Hz, 1H, H-1), 4.25 – 4.04 (m, 2H, H-$6_{a,b}$), 3.84 (t, *J* = 9.0 Hz, 1H, H-2), 3.75 – 3.55 (m, 2H, H-5, H-3), 3.05 (dd, *J* = 13.9, 10.7 Hz, 1H, SC*H*HCHPh), 2.81 (dd, *J* = 13.9, 1.6 Hz, 1H, SCH*H*CHPh), 2.08 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ171.00, 169.67, 140.51, 138.40, 128.74, 128.49, 128.28, 128.14, 127.87, 125.82, 84.59, 80.05, 79.98, 77.65, 77.55, 77.23, 76.80, 75.92, 74.87, 69.62, 62.68, 35.67, 21.03, 21.00; HR MALDI-TOF MS: m/z: calcd for $C_{25}H28O7S$ $[M+Na]^+$: 495.1454; found: 495.1463.

2-(*S*)-phenyl-(3,4-di-*O*-acetyl-6-benzyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (*R*,*S*)-*S*-oxide (17). Compound **17** (1.4 g, 92 %, *R*/*S* = 1.3/1) was prepared according to the general procedure for the preparation of sulfoxide donors starting from **9** (1.5 g, 3.2 mmol) and using *m*-CPBA (0.79 g, ≤77%, 3.5 mmol). **17*S***: R_f = 0.24 (EtOAc/hexanes, 1/1, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 – 7.19 (m, 10H, Ar*H*), 5.55 – 5.30 (m, 2H, H-3, SCH_2CHPh), 5.05 (t, *J* = 9.8 Hz, 1H, H-4), 4.59 – 4.45 (m, 3H, CH_2Ph, H-2), 4.14 (d, *J* = 9.7 Hz, 1H, H-1), 3.96 – 3.81 (m, 1H, H-5), 3.73 – 3.52 (m, 2H, H-$6_{a,b}$), 3.21 (dd, *J* = 14.5, 1.6 Hz, 1H, $SCH_{eq}HCHPh$), 2.71 (dd, *J* = 14.4, 11.3 Hz, 1H, $SCH_{ax}CHPh$), 2.01 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ170.59, 169.72, 138.87, 137.72, 128.94, 128.65, 128.38, 128.22, 128.07, 125.70, 85.41, 79.27, 77.68, 77.26, 76.83, 73.98, 73.37, 69.40, 69.33, 69.16, 68.51, 53.01, 21.01, 20.82; HR MALDI-TOF MS: m/z: calcd for $C_{25}H_{28}O_8S$ $[M+Na]^+$: 511.1403; found: 511.1397. **17*R***: R_f = 0.18 (EtOAc/hexanes, 1/1, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 – 7.19 (m, 10H, Ar*H*), 5.47 – 5.20 (m, 2H, H-3, H-4), 4.70 (d, *J* = 10.9 Hz, 1H, SCH_2CHPh), 4.62 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.48 (d, *J* = 12.0 Hz, 1H, CH*H*Ph) 4.31 (d, *J* = 10.0 Hz, 1H, H-1), 3.84

– 3.54 (m, 5H, H-2, H-5, H-$6_{a,b}$, SC*H*$_{eq}$HCHPh), 3.05 (dd, *J* = 12.7, 11.8 Hz, 1H, SCH*H*$_{ax}$CHPh), 1.99 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ170.32, 169.60, 138.03, 137.69, 129.08, 128.94, 128.81, 128.62, 128.29, 128.21, 128.04, 125.69, 125.60, 95.26, 78.74, 77.65, 77.23, 76.81, 75.74, 75.45, 73.95, 73.47, 68.60, 67.92, 57.81, 20.96, 20.81; HR MALDI-TOF MS: m/z: calcd for $C_{25}H_{28}O_8S$ $[M+Na]^+$: 511.1403; found: 511.1404.

2-(*S*)-Phenyl–(3-*O*-acetyl-4,6-di-*O*-benzyl-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane(*R*,*S*)-*S*-oxide (18). Compound **18** (0.17 g, 96 %, *R*/*S* = 1.1/1) was prepared according to the general procedure for the preparation of sulfoxide donors starting from **10** (0.17 g, 0.33 mmol) and using *m*-CPBA (0.82 g, ≤ 77%, 0.36 mmol). **18*S***: R_f = 0.24 (EtOAc/hexanes, 1/1, v/v); $[\alpha]^d_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +48.0 (*c* = 0.6 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 – 7.13 (m, 15H, Ar*H*), 5.45 (t, *J* = 9.4 Hz, 1H, H-3), 5.35 (d, *J* = 11.1 Hz, 1H, SCH_2CHPh), 4.66 – 4.49 (m, 4H, 2×CH_2Ph), 4.42 (t, *J* = 9.6 Hz, 1H, H-2), 4.11 (d, *J* = 9.6 Hz, 1H, H-1), 3.80 – 3.64 (m, 4H, H-4, H-5, H-$6_{a,b}$), 3.20 (d, *J* = 14.5 Hz, 1H, SC*H*$_{eq}$HCHPh), 2.70 (dd, *J* = 14.3, 11.4 Hz, 1H, SCH*H*$_{ax}$CHPh), 1.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.11, 138.87, 137.81, 137.40, 128.69, 128.49, 128.43, 128.02, 128.00, 127.78, 125.38, 85.27, 80.83, 77.23, 77.01, 76.80, 75.47, 75.15, 74.81, 73.72, 69.53, 68.60, 68.00, 52.80, 20.98.; HR MALDI-TOF MS: m/z: calcd for $C_{30}H_{32}O_7S$ $[M+Na]^+$: 559.1767; found: 559.1779. **18*R***: R_f = 0.21 (EtOAc/hexanes, 1/1, v/v); $[\alpha]^d_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +80.0 (*c* = 0.5 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 – 7.12 (m, 15H, Ar*H*), 5.41 (t, *J* = 9.3 Hz, 1H, H-3), 4.77 – 4.44 (m, 5H, 2×CH_2Ph, SCH_2CHPh), 4.28 (d, *J* = 9.6 Hz, 1H, H-1), 3.95 – 3.81 (m, 3H, H-4, H-$6_{a,b}$), 3.64 (dd, *J* = 19.2, 11.4 Hz, 2H, H-5, SC*H*$_{eq}$HCHPh), 3.52 (t, *J* = 9.6 Hz, 1H, H-2), 3.02

(t, J = 12.2 Hz, 1H, SCHH_{ax}CHPh), 1.90 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.72, 137.96, 137.59, 128.79, 128.76, 128.45, 128.44, 128.40, 128.29, 128.05, 128.01, 127.89, 127.86, 125.24, 125.21, 95.05, 80.39, 77.19, 76.98, 76.77, 75.73, 75.26, 74.92, 74.84, 74.73, 73.81, 67.65, 57.46, 20.85; HR MALDI-TOF MS: m/z: calcd for $C_{30}H_{32}O_7S$ $[M+Na]^+$: 559.1767; found: 559.1759.

2-(*S*)-Phenyl–{3-*O*-acetyl-6-*O*-benzyl-4-*O*-(9-fluorenylmethyloxycarbonyl)-1,2-dideoxy-ß-D-glucopyranoso}[1,2-*e*]-1,4-oxathiane(*R*,*S*)-*S*-oxide (19). Compound **19** (1.9 g, 98 %, *R*/*S* = 1/1) was prepared according to the general procedure for the preparation of sulfoxide donors starting from **11** (1.9 g, 2.9 mmol) and using *m*-CPBA (712 mg, ≤77%, 3.2 mmol). **19*S***: R_f = 0.18 (EtOAc/hexanes, 1/1, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 – 7.08 (m, 18H, Ar*H*), 5.47 (t, J = 9.5 Hz, 1H, H-3), 5.30 (d, J = 10.9 Hz, 1H, SCH_2CHPh), 4.86 (t, J = 9.7 Hz, 1H, H-4), 4.60 – 4.38 (m, 3H, H-2, CH_2Ph), 4.36 – 4.02 (m, 4H, C*H* Fmoc, CH_2 Fmoc, H-1), 3.98 – 3.81 (m, 1H, H-5), 3.70 – 3.52 (m, 2H, H-$6_{a,b}$), 3.15 (d, J = 14.1 Hz, 1H, SCH_{eq}HCHPh), 2.64 (dd, J = 14.4, 11.3 Hz, 1H, SCHH_{ax}CHPh), 1.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ170.44, 154.34, 143.38, 143.24, 141.51, 141.49, 138.84, 137.77, 128.97, 128.63, 128.39, 128.24, 128.22, 128.05, 128.03, 127.52, 127.47, 125.69, 125.37, 125.31, 120.36, 120.33, 85.34, 78.88, 77.76, 77.33, 76.91, 74.00, 73.28, 73.11, 70.65, 69.42, 69.37, 68.50, 52.93, 46.77, 21.05; HR MALDI-TOF MS: m/z: calcd for $C_{38}H_{36}O_9S$ $[M+Na]^+$: 691.1978; found: 691.1971. **19*R***: R_f = 0.15 (EtOAc/hexanes, 1/1, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 – 7.18 (m, 18H), 5.51 (t, J = 9.4 Hz, 1H, H-3), 5.16 (t, J = 9.7 Hz, 1H, H-4), 4.71 (d, J = 11.0 Hz, 1H, SCH_2CHPh), 4.55 (dd, J = 28.1, 12.1 Hz, 2H, CH_2Ph), 4.45 – 4.10 (m, 4H, H-1, C*H* Fmoc, CH_2 Fmoc), 3.96 – 3.86 (m, 1H, H-5), 3.86 – 3.55 (m, 4H, H-$6_{a,b}$, H-2,

SCH_{eq}HCHPh), 3.06 (dd, J = 12.4, 12.0 Hz, 1H, SCHH_{ax}CHPh), 1.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ169.89, 154.01, 143.15, 143.03, 141.27, 137.79, 137.52, 128.87, 128.59, 128.36, 127.99, 127.96, 127.84, 127.75, 127.29, 127.24, 125.34, 125.11, 120.10, 95.02, 78.25, 77.44, 77.22, 77.01, 76.59, 75.52, 75.29, 73.80, 72.93, 72.37, 70.45, 67.85, 57.63, 53.80, 46.51, 30.93, 29.71, 29.28, 20.74; HR MALDI-TOF MS: m/z: calcd for $C_{38}H_{36}O_9S$ $[M+Na]^+$: 691.1978; found: 691.1973.

2-(*S*)-phenyl-(3,6-di-*O*-acetyl-4-benzyl-2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (*R*,*S*)-*S*-oxide (20). Compound **20** (245 mg, 93 %, *R*/*S* = 1/1) was prepared according to the general procedure for the preparation of sulfoxide donors starting from **13** (250 mg, 0.54 mmol) and using *m*-CPBA (133 mg, ≤ 77%, 0.60 mmol). **20*S***: R_f = 0.15 (EtOAc/hexanes, 1/1, v/v); $[\alpha]^d_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +60.0 (c = 0.5 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 – 7.20 (m, 10H, Ar*H*), 5.49 (t, J = 9.4 Hz, 1H, H-3), 5.35 (d, J = 10.5 Hz, 1H, SCH_2CHPh), 4.65 (d, J = 11.2 Hz, 1H, C*H*HPh), 4.58 (d, J = 11.2 Hz, 1H, CH*H*Ph), 4.47 – 4.37 (m, 2H, H-2, H-6$_a$), 4.21 (dd, J = 12.2, 5.5 Hz, 1H, H-6$_b$), 4.14 (d, J = 9.7 Hz, 1H, H-1), 3.82 (ddd, J = 9.8, 5.5, 2.0 Hz, 1H, H-5), 3.65 (t, J = 9.5 Hz, 1H, H-4), 3.22 (dd, J = 14.5, 1.6 Hz, 1H, SCH_{eq}HCHPh), 2.71 (dd, J = 14.4, 11.3 Hz, 1H, SCHH_{ax}CHPh), 2.07 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ170.82, 170.23, 138.94, 137.17, 128.95, 128.85, 128.48, 128.34, 128.28, 125.56, 85.36, 78.79, 77.67, 77.24, 76.82, 75.52, 75.36, 75.14, 69.67, 68.25, 63.12, 52.98, 21.21, 21.08; HR MALDI-TOF MS: m/z: calcd for $C_{25}H_{28}O_8S$ $[M+Na]^+$: 511.1403; found: 511.1408. **20*R***: R_f = 0.12 (EtOAc/hexanes, 1/1, v/v); $[\alpha]^d_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +26.7 (c = 0.4 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 – 7.10 (m, 10H, Ar*H*), 5.48 (t, J = 9.1 Hz, 1H, H-3), 4.69 (d, J = 11.3 Hz, 1H, SCH_2CHPh), 4.60 (q, J = 11.2 Hz, 2H, CH_2Ph), 4.43 (dd, J = 12.4, 1.9 Hz,

1H, H-6_a), 4.31 (dd, *J* = 13.0, 3.4 Hz, 2H, H-6_b, H-1), 3.85 – 3.73 (m, 1H, H-5), 3.73 – 3.59 (m, 2H, H-4, SC*H*$_{eq}$HCHPh), 3.52 (t, *J* = 9.7 Hz, 1H, H-2), 3.12 – 2.96 (m, 1H, SCH*H*$_{ax}$CHPh), 2.08 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.73, 169.82, 138.08, 137.15, 129.08, 128.85, 128.72, 128.50, 128.29, 125.46, 94.99, 78.47, 77.67, 77.25, 76.82, 75.85, 75.62, 75.34, 75.11, 75.07, 62.67, 57.74, 21.13, 21.07; HR MALDI-TOF MS: m/z: calcd for $C_{25}H_{28}O_8S$ $[M+Na]^+$: 511.1403; found: 511.1411.

2-(*S*)-phenyl-(4-*O*-acetyl-6-benzyl-3-levulinoyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (*R*,*S*)-*S*-oxide (21). Compound **21** (0.41 g, 98 %, *R*/*S* = 1.3/1) was prepared according to the general procedure for the preparation of sulfoxide donors using *m*-CPBA (0.24 g, ≤ 77%, 1.1 mmol) and starting from **14** (0.4 g, 0.97 mmol). **21*S***: R_f = 0.19 (EtOAc/hexanes, 1/1, v/v); $[\alpha]^d_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +87.5 (*c* = 0.6 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 – 7.17 (m, 10H, Ar*H*), 5.42 (t, *J* = 9.6 Hz, 1H, H-3), 5.36 (d, *J* = 11.0 Hz, 1H, SCH_2CHPh), 5.06 (t, *J* = 9.8 Hz, 1H, H-4), 4.60 – 4.41 (m, 3H, H-2, CH_2Ph), 4.14 (d, *J* = 9.7 Hz, 1H, H-1), 3.97 – 3.79 (m, 1H, H-5), 3.66 (dd, *J* = 11.0, 6.0 Hz, 1H, H-6_a), 3.57 (dd, *J* = 11.0, 2.8 Hz, 1H, H-6_b), 3.21 (d, *J* = 13.5 Hz, 1H, SC*H*$_{eq}$HCHPh), 2.83 – 2.36 (m, 5H, SCH*H*$_{ax}$CHPh, 2×CH_2 Lev), 2.08 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.04, 171.97, 169.81, 138.01, 137.72, 129.04, 128.77, 128.61, 128.28, 128.02, 125.63, 95.22, 78.85, 77.66, 77.24, 76.81, 75.68, 75.56, 73.96, 73.47, 68.19, 68.01, 57.73, 37.97, 29.79, 28.14, 20.86; HR MALDI-TOF MS: m/z: calcd for $C_{23}H_{25}O_6S$ $[M+Na]^+$: 452.1270; found: 452.1277. **21*R***: R_f = 0.18 (EtOAc/hexanes, 1/1, v/v); $[\alpha]^d_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +56.0 (*c* = 0.7 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ7.47 – 7.17 (m, 10H, Ar*H*), 5.38 (t, *J* = 9.4 Hz, 1H, H-3), 5.29 (t, *J* = 9.7 Hz, 1H, H-4), 4.70 (d, *J* = 11.2 Hz, 1H, SCH_2CHPh), 4.61 (d, *J* = 12.0 Hz, 1H,

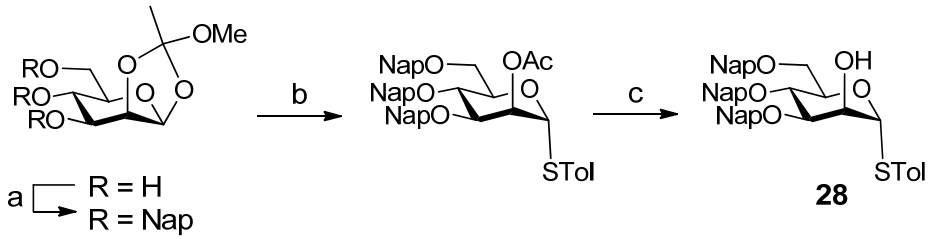
C*H*HPh), 4.49 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.31 (d, *J* = 10.0 Hz, 1H, H-1), 3.83 – 3.75 (m, 1H, H-5), 3.72 (dd, *J* = 11.1, 2.9 Hz, 1H, H-6_a), 3.69 – 3.53 (m, 3H, H-6_b, H-2, SCH_{eq}HCHPh), 3.05 (dd, *J* = 12.8, 11.8 Hz, 1H, SCHH_{ax}CHPh), 2.78 – 2.37 (m, 4H, 2×CH_2 Lev), 2.08 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ206.12, 172.12, 170.01, 138.84, 137.74, 128.92, 128.64, 128.36, 128.21, 128.06, 125.71, 85.39, 79.41, 77.66, 77.44, 77.23, 76.81, 73.99, 73.35, 69.43, 68.71, 68.46, 52.98, 38.01, 29.79, 28.22, 20.87; HR MALDI-TOF MS: m/z: calcd for $C_{23}H_{25}O_6S$ $[M+Na]^+$: 452.1270; found: 452.1268.

2-(*S*)-phenyl-(3-allyoxycarbonyl-4-*O*-acetyl-6-*O*-benzyl-1,2-dideoxyl-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (*R*,*S*)-*S*-oxide (22). Compound **22** (0.42 g, 82 %, *R*/*S* = 1.5/1) was prepared according to the general procedure for the preparation of sulfoxide donors using *m*-CPBA (0.24 g, ≤ 77%, 0.97 mmol) and starting from **15** (0.50 g, 0.97 mmol). **22*S***: R_f = 0.33 (EtOAc/hexanes, 1/1, v/v); $[\alpha]^d_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +78.0 (*c* = 4.1 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 – 7.21 (m, 10H, Ar*H*), 5.92 – 5.64 (m, 1H, CH alloc), 5.37 (d, *J* = 10.0 Hz, 1H, SCH_2C*H*Ph), 5.30 – 5.17 (m, 2H, H-3, C*H*H alloc), 5.17 – 5.00 (m, 2H, H-4, CH*H* alloc), 4.63 – 4.48 (m, 5H, H-2, CH_2 alloc, CH_2Ph), 4.15 (d, *J* = 9.7 Hz, 1H, H-1), 3.97 – 3.81 (m, 1H, H-5), 3.73 – 3.47 (m, 2H, H-$6_{a,b}$), 3.21 (dd, *J* = 14.5, 1.6 Hz, 1H, SCH_{eq}HCHPh), 2.72 (dd, *J* = 14.4, 11.3 Hz, 1H, SCHH_{ax}CHPh), 1.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.60, 154.76, 138.75, 137.72, 131.35, 128.86, 128.65, 128.40, 128.22, 128.08, 125.86, 119.01, 85.23, 79.27, 77.73, 77.60, 77.31, 76.89, 73.99, 69.52, 69.40, 69.01, 68.95, 68.57, 52.87, 20.84.; HR MALDI-TOF MS: m/z: calcd for $C_{27}H_{30}O_9S$ $[M+Na]^+$: 553.1509; found: 553.1500. **22*R***: R_f = 0.31 (EtOAc/hexanes, 1/1, v/v); $[\alpha]^d_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +81.3 (*c* = 1.6 in $CHCl_3$);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 – 7.19 (m, 10H, Ar*H*), 5.90 – 5.68 (m, 1H, C*H* alloc), 5.42 – 5.05 (m, 4H, CH_2 alloc, H-3, H-4), 4.71 (d, *J* = 11.0 Hz, 1H, SCH_2CHPh), 4.66 – 4.43 (m, CH_2 alloc, CH_2Ph), 4.32 (d, *J* = 10.0 Hz, 1H, H-1), 3.87 – 3.49 (m, 4H, H-5, H-6, H-2, SCH_{eq}HCHPh), 3.07 (t, *J* = 12.0 Hz 1H, SCH_{ax}CHPh), 1.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.45, 154.56, 137.93, 137.69, 131.29, 128.99, 128.83, 128.62, 128.28, 128.04, 125.76, 119.07, 95.07, 78.72, 77.69, 77.62, 77.26, 76.84, 75.81, 75.44, 73.97, 69.01, 68.48, 68.15, 57.71, 20.83; HR MALDI-TOF MS: m/z: calcd for $C_{27}H_{30}O_9S$ $[M+Na]^+$: 553.1509; found: 553.1514.

2-(*S*)-phenyl-(4,6-di-*O*-acetyl-3-*O*-benzyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (*R*,*S*)-*S*-oxide (23). Compound **23** (142 mg, 96 %, *R*/*S* = 1.7/1) was prepared as an inseparable mixture of diastereomers according to the general procedure for the preparation of sulfoxide donors using *m*-CPBA (75 mg, ≤77%, 0.33 mmol) and starting from **16** (140 mg, 0.30 mmol). R_f = 0.27 (EtOAc/hexanes, 2/1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 – 7.12 (m, 20H, Ar*H*), 5.43 (d, *J* = 10.3 Hz, 1H, SCH_2CHPh^S), 5.12 (t, *J* = 12.0 Hz, 1H, H-4^R), 5.08 (t, *J* = 12.0 Hz, 1H, H-4^S), 4.85 – 4.74 (m, 3H, SCH_2CHPh^R, 2×C*H*HPh), 4.68 – 4.57 (m, 3H, H-2^S, 2×CH*H*Ph), 4.35 – 4.13 (m, 5H, H-1^R, 2×H-$6_{a,b}$) 4.10 (d, *J* = 9.7 Hz, 1H, H-1^S), 3.85 – 3.62 (m, 6H, H-3^S, H-3^R, H-2^R, H-5^S, H-5^R, SC*H*HCHPh^R), 3.20 (dd, *J* = 14.5, 1.5 Hz, 1H, SC*H*HCHPh^S), 3.14 – 3.05 (m, 1H, SCH*H*CHPh^R), 2.79 (dd, *J* = 14.4, 11.3 Hz, 1H, SCH*H*CHPh^S), 2.13 – 2.02 (2×s, 6H), 1.99 – 1.86 (2×s, 6H); selected ^{13}C NMR (gHSQC, $CDCl_3$): δ 94.98 (C-1^R), 85.40 (C-1^S), 79.91, 78.33, 77.58, 75.90, 75.08, 74.42, 68.84, 68.41, 62.66, 61.84, 57.34, 52.51; HR MALDI-TOF MS: m/z: calcd for $C_{25}H_{28}O_8S$ $[M+Na]^+$: 511.1403; found: 511.1411.

Scheme S1. Preparation of **28**



Reagents and conditions: (a) NaH, NapBr, DMF (95%); (b) HgBr (cat.), TolSH, DCE, 60 ^{o}C, 16 h (81%); (c) NaOMe, MeOH (quantitive).

***p*-toluene 3,4,6-tri-*O*-(2-naphthyl)-α-thiomannoside (28):** R_f = 0.53 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +141.5 (*c* = 1.6 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 6.89 (m, 25H, Ar*H*), 5.58 (s, 1H, H-1), 5.00 (d, *J* = 11.2 Hz, 1H, NapC*H*H), 4.90 (d, *J* = 11.7 Hz, 1H, NapC*H*H), 4.84 (d, *J* = 11.7 Hz, 1H, NapCH*H*), 4.78 (d, *J* = 12.2 Hz, 1H, NapC*H*H), 4.67 (d, *J* = 11.2 Hz, 1H, NapCH*H*), 4.59 (d, *J* = 12.2 Hz, 1H, NapCH*H*), 4.37 (dd, *J* = 9.1, 2.8 Hz, 1H, H-5), 4.32 (s, 1H, H-2), 4.10 – 3.94 (m, 2H, H-3, H-4), 3.87 (dd, *J* = 10.9, 4.5 Hz, 1H, H-6$_a$), 3.75 (dd, *J* = 10.8, 1.8 Hz, 1H, H-6$_b$), 2.25 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.90, 135.91, 135.87, 135.30, 133.49, 133.46, 133.43, 133.32, 133.21, 133.14, 132.44, 130.16, 130.04, 128.67, 128.32, 128.24, 128.21, 128.14, 127.95, 127.91, 127.84, 127.05, 126.91, 126.60, 126.47, 126.33, 126.27, 126.25, 126.19, 126.05, 126.03, 126.01, 87.96, 80.60, 77.68, 77.26, 76.83, 75.41, 74.84, 73.73, 72.51, 72.43, 70.11, 69.07, 21.29; HR MALDI-TOF MS: m/z: calcd for $C_{46}H_{42}O_5S$ $[M+Na]^+$: 729.2651; found: 729.2638.

Methyl 3,4-di-*O*-acetyl-6-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-

D-glucopyranoside (29). Compound **29** was prepared according to the general glycosylation procedure using glycosyl donor **17** (45 mg, 0.09 mmol) and glycosyl acceptor **24** (39 mg, 0.08 mmol). Purification by LH20 size exclusion chromatography afforded compound **29** (80 mg, 91%). R_f = 0.45 (acetone/toluene, 1/9, v/v); $[\alpha]^{d}_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +86.7 (*c* = 3.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 – 6.98 (m, 25H, Ar*H*), 6.18 (t, *J* = 9 Hz, 1H, H-3^{I}), 6.04 (s, 2H, Ar*H*), 5.51 (d, *J* = 3.3 Hz, 1H, H-1^{II}), 5.44 (t, *J* = 9 Hz, 1H, H-4^{I}), 5.38 (t, *J* = 9 Hz, 1H, H-3^{II}), 5.30 – 5.16 (m, 2H, H-1^{I}, H-2^{I}), 4.99 (t, *J* = 9.7 Hz, 1H, H-4^{II}), 4.66 – 4.36 (m, 4H, C*H*$_2$Ph, H-5^{I}, SCH$_2$C*H*Ph), 4.30 – 4.08 (m, 2H, H-5^{II}), 4.03 – 3.91 (m, 2H, H-$6^{I}_{a,b}$), 3.81 (s, 3H, OMe), 3.74 (s, 6H, 2 × OMe), 3.66 – 3.37 (m, 6H, OMe, H-2^{II}, H-$6^{II}_{a,b}$), 2.99 – 2.71 (m, 2H, SC*H*$_2$CHPh), 1.83 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.26, 169.79, 165.89, 165.67, 165.54, 161.68, 161.60, 142.02, 137.88, 133.29, 133.14, 132.97, 129.95, 129.79, 129.64, 129.34, 129.15, 128.74, 128.39, 128.32, 128.22, 128.15, 127.94, 127.61, 127.41, 126.20, 101.82, 97.36, 96.50, 90.89, 84.33, 78.82, 77.44, 77.22, 77.02, 76.60, 73.39, 72.42, 72.04, 70.67, 69.86, 69.47, 68.83, 68.30, 67.98, 67.08, 55.89, 55.47, 55.34, 43.33, 20.68, 20.32; HR MALDI-TOF MS: m/z: calcd for $C_{62}H_{64}O_{19}S$ $[M+Na]^+$: 1167.3660; found: 1167.3655.

Methyl 3,4-di-*O*-acetyl-6-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-*O*-benzyl-α-D-glucopyranoside (30). Compound **30** was prepared according to the general procedure using glycosyl donor **17** (50 mg, 0.10 mmol) and glycosyl acceptor **25** (31 mg, 0.083 mmol). Purification by LH20 size exclusion chromatography afforded compound **30** (52 mg, 62%). R_f = 0.34 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +75.0 (*c* = 1.6 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 – 6.87 (m, 15H, Ar*H*), 6.12 (s,

2H, Ar*H*), 5.77 (d, *J* = 3.2 Hz, 1H, H-1^{II}), 5.72 (t, *J* = 9.2 Hz, 1H, H-3^{I}), 5.23 (t, *J* = 9.8 Hz, 1H, H-3^{II}), 5.04 – 4.79 (m, 3H, H-1^{I}, H-2^{I}, H-4^{II}), 4.61 (s, 2H, C*H*$_2$Ph), 4.48 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.33 (d, *J* = 11.8 Hz, 1H, CH*H*Ph), 4.27 – 4.12 (m, 2H, H-4^{I}, SCH$_2$C*H*Ph), 4.12 – 3.90 (m, 3H, H-5^{I}, H-5^{II}, H-6$^{I}_{a}$), 3.84 (s, 3H, OMe), 3.79 (s, 7H, 2 × OMe, H-6$^{I}_{b}$), 3.66 (dd, *J* = 10.2, 3.2 Hz, 1H, H-2^{II}), 3.41 (s, 3H, OMe), 3.39 – 3.29 (m, 2H, H-6$^{II}_{a,}$ H-6$^{II}_{b}$), 3.02 (dd, *J* = 13.9, 3.8 Hz, 1H, SC*H*HCHPh), 2.77 (dd, *J* = 14.0, 8.7 Hz, 1H, SCH*H*CHPh), 2.08 (s, 3H), 2.06 (s, 3H), 1.84 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.70, 170.30, 170.16, 170.08, 162.11, 162.01, 142.30, 138.46, 138.07, 128.53, 128.50, 128.39, 128.22, 128.06, 127.83, 127.64, 127.53, 127.49, 126.22, 100.99, 96.97, 96.90, 91.16, 84.30, 79.90, 77.70, 77.48, 77.27, 76.85, 74.29, 73.61, 73.58, 72.33, 72.16, 71.17, 69.97, 69.72, 69.25, 68.94, 68.43, 56.21, 55.59, 55.49, 42.99, 21.67, 21.11, 20.94, 20.31; HR MALDI-TOF MS: m/z: calcd for $C_{52}H_{62}O_{18}S$ $[M+Na]^+$: 1029.3555; found: 1029.3541.

N$^{\alpha}$-(9-Fluorenylmethyloxycarbonyl)-*O*-{3,4-di-*O*-acetyl-6-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl}-*L*-threonine benzyl ester (31). Compound **31** was prepared according to the general glycosylation procedure using glycosyl donor **17** (35 mg, 0.070 mmol) and glycosyl acceptor **26** (26 mg, 0.060 mmol). Purification by LH20 size exclusion chromatography afforded compound **31** (57 mg, 89%). R_f = 0.23 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +53.3 (*c* = 1.9 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 – 6.97 (m, 23H, Ar*H*), 6.25 (d, *J* = 7.7 Hz, 1H, N*H*Fmoc), 6.15 (s, 2H, Ar*H*), 5.70 (d, *J* = 3.5 Hz, 1H, H-1), 5.34 (t, *J* = 9.8 Hz, 1H, H-3), 5.27 (s, 2H, C*H*$_2$Ph), 4.95 (t, *J* = 9.8 Hz, 1H, H-4), 4.58 – 4.17 (m, 8H, C*H*$_2$Ph, 2 × C*H*^{Thr}, C*H*$_2^{Fmoc}$, C*H*^{Fmoc}, SCH$_2$C*H*Ph), 4.07 (d, *J* = 10.1 Hz, 1H, H-5), 3.85 –

3.81 (2s, 10H, 3 × OMe, H-2), 3.64 – 3.39 (m, 2H, H-6_a, H-6_b), 3.09 (dd, *J* = 14.0, 2.6 Hz, 1H, SC*H*HCHPh), 2.86 (dd, *J* = 14.0, 9.6 Hz, 1H, SCH*H*CHPh), 1.87 (s, 3H), 1.40 (d, *J* = 6.4 Hz, 3H, CH_3^{Thr}), 1.18 (d, *J* = 13.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.25, 170.07, 169.87, 161.95, 161.79, 156.78, 144.05, 143.91, 142.38, 141.19, 141.15, 137.84, 135.49, 128.50, 128.41, 128.31, 128.23, 127.80, 127.65, 127.55, 127.18, 125.66, 125.41, 125.33, 119.81, 100.97, 98.93, 91.01, 84.72, 80.40, 77.44, 77.22, 77.02, 76.59, 75.93, 73.45, 72.67, 69.59, 69.08, 68.27, 67.61, 67.41, 59.44, 55.96, 55.37, 47.09, 43.20, 30.13, 20.69, 19.93, 19.35; HR MALDI-TOF MS: m/z: calcd for $C_{60}H_{63}NO_{15}S$ $[M+Na]^+$: 1092.3816; found: 1092.3808.

***p*-Methylphenyl 3,4-di-*O*-acetyl-6-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→4)- 2,3-di-*O*-acetyl-6-*O*-benzyl-1-thio-ß-D-glucopyranoside (32)**. Compound **32** was prepared according to the general glycosylation procedure using glycosyl donor **17** (45 mg, 0.090 mmol) and glycosyl acceptor **27** (35 mg, 0.080 mmol). Purification by LH20 size exclusion chromatography afforded compound **32** (63 mg, 75%). R_f = 0.25 (acetone/toluene, 1/9, v/v); $[\alpha]^d_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +68.6 (*c* = 0.9 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 – 6.96 (m, 19H, Ar*H*), 6.12 (s, 2H, Ar*H*), 5.64 (d, *J* = 3.2 Hz, 1H, H-1^{II}), 5.43 (t, *J* = 9.0 Hz, 1H, H-3^{I}), 5.18 (t, *J* = 9.7 Hz, 1H, H-3^{II}), 4.92 (t, *J* = 9 Hz, 2H, H-2^{I}, H-4^{II}), 4.68 (d, *J* = 10.0 Hz, 1H, H-1^{I}), 4.56 (s, 2H, CH_2Ph), 4.45 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.30 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.19 (dd, *J* = 8.3, 4.2 Hz, 1H, SCH_2C*H*Ph), 4.10 (t, *J* = 9.4 Hz, 1H, H-4^{I}), 4.03 – 3.87 (m, 2H, H-5^{I}, H-5^{II}), 3.82 (s, 3H, OMe), 3.78 (s, 6H, 2 × OMe), 3.74 – 3.56 (m, 3H, H-2^{II}, H-$6^{I}_{a,}$ H-6^{I}_{b}), 3.32 (dd, *J* = 10.7, 2.4 Hz, 1H, H-6^{II}_{a}), 3.25 (dd, *J* = 10.7, 3.4 Hz, 1H, H-6^{II}_{b}), 2.99 (dd, *J* = 13.9, 4.1 Hz, 1H, SC*H*HCHPh), 2.82 (dd, *J* =

13.9, 8.3 Hz, 1H, SCH*H*CHPh), 2.31 (s, 3H, C*H*$_3$), 2.09 (s, 3H), 2.04 (s, 3H), 1.82 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.16, 169.99, 169.76, 169.67, 161.91, 161.78, 141.96, 138.42, 138.31, 137.81, 133.57, 129.65, 128.27, 128.23, 128.13, 128.02, 127.86, 127.60, 127.44, 127.39, 127.31, 126.10, 116.18, 100.98, 96.79, 91.03, 85.36, 83.75, 79.16, 79.11, 77.44, 77.22, 77.02, 76.59, 75.26, 73.39, 73.34, 73.18, 72.05, 71.12, 69.34, 69.06, 68.93, 68.05, 56.02, 55.37, 42.76, 30.15, 21.40, 21.16, 20.89, 20.67, 20.14.; HR MALDI-TOF MS: m/z: calcd for $C_{58}H_{66}O_{17}S_2$ $[M+Na]^+$: 1121.3639; found: 1121.3630.

***p*-Methylphenyl 3,4-di-*O*-acetyl-6-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→2)-3,4,6-tri-*O*-(2-ethylnaphthyl)-1-thio-α-D-mannopyranoside (33)**. Compound **33** was prepared according to the general glycosylation procedure using glycosyl donor **17** (56 mg, 0.11 mmol) and glycosyl acceptor **28** (68 mg, 0.10 mmol). Purification by LH20 size exclusion chromatography afforded compound **33** (93 mg, 72%). R_f = 0.23 (EtOAc/hexanes, 1/3, v/v); $[\alpha]^d_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +100 (c = 0.5 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 – 6.83 (m, 35H, Ar*H*), 6.05 (s, 2H, Ar*H*), 5.88 (d, J = 3.5 Hz, 1H, H-1^{II}), 5.83 (s, 1H, H-1^{I}), 5.47 (t, J = 9.6 Hz, 1H, H-3^{II}), 5.22 – 5.06 (m, 2H, C*H*HNap, C*H*HNap), 4.96 (t, J = 9.8 Hz, 1H, H-4^{II}), 4.82 (d, J = 11.8 Hz, 1H, CH*H*Nap), 4.72 (dd, J = 16.6, 11.8 Hz, 2H, CH*H*Nap, C*H*HNap), 4.67 – 4.55 (m, 2H, H-2^{I}, CH*H*Nap), 4.47 (d, J = 12.2 Hz, 1H, C*H*HPh), 4.42 – 4.26 (m, 4H, CH*H*Ph, SCH$_2$C*H*Ph^{II}, H-5^{I}, H-5^{II}), 4.23 (t, J = 9.2 Hz, 1H, H-4^{I}), 4.12 (d, J = 8.6 Hz, 1H, H-3^{I}), 3.91 – 3.64 (m, 12H, H-2^{II}, H-6$^{I}_a$, H-6$^{I}_b$, 3 ×OMe), 3.48 – 3.33 (m, 2H, H-6$^{II}_a$, H-6$^{II}_b$), 3.01 (dd, J = 13.8, 4.0 Hz, 1H, SCH*H*CHPh^{II}), 2.76 (dd, J = 13.7, 8.7 Hz, 1H, SC*H*HCHPh^{II}), 2.23 (s, 3H),

1.69 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.44, 170.17, 161.97, 161.88, 142.31, 138.19, 137.63, 136.29, 136.26, 136.20, 133.59, 133.49, 133.20, 133.16, 133.10, 132.77, 132.37, 130.94, 130.01, 129.95, 128.54, 128.48, 128.36, 128.28, 128.23, 128.21, 128.13, 128.09, 128.04, 127.87, 127.76, 127.74, 127.45, 126.80, 126.77, 126.59, 126.44, 126.36, 126.20, 126.13, 126.05, 125.98, 125.89, 125.86, 125.82, 101.69, 99.23, 91.20, 87.52, 84.36, 79.77, 79.44, 77.68, 77.50, 77.25, 76.83, 75.33, 73.38, 72.92, 72.88, 71.24, 69.81, 69.58, 69.03, 68.22, 56.17, 55.55, 43.45, 30.35, 21.27, 20.81, 20.38; HR MALDI-TOF MS: m/z: calcd for $C_{80}H_{80}O_{15}S_2$ $[M+Na]^+$: 1367.4836; found: 1367.4829.

3,4,6-tri-*O*-acetyl-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (38). Compound **38** was prepared according to the general glycosylation procedure using glycosyl donor **34** (55 mg, 0.13 mmol) and glycosyl acceptor **36** (27 mg, 0.10 mmol). Purification by LH20 size exclusion chromatography afforded compound **38** (71 mg, 80%). R_f = 0.14 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +36.4 (c = 2.2 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 – 7.01 (m, 5H, Ar*H*), 6.14 (s, 2H, Ar*H*), 5.58 – 5.47 (m, 2H, H-1^I, H-1^{II}), 5.33 (t, J = 9.6 Hz, 1H, H-3^{II}), 4.94 – 4.76 (m, 1H, H-4^{II}), 4.64 (dd, J = 7.9, 2.3 Hz, 1H, H-3^I), 4.45 – 3.94 (m, 8H, H-4^I, H-2^I, SCH_2CHPh, H-5^I, H-5^{II}, H-6$_{a,b}^{II}$, H-6$_a^I$), 3.94 – 3.74 (m, 10H, 3×OMe, H-6$_b^I$), 3.62 (dd, J = 10.0, 3.6 Hz, 1H, H-2^{II}), 3.01 (dd, J = 13.8, 4.4 Hz, 1H, SC*H*HCHPh), 2.90 (dd, J = 13.8, 8.2 Hz, 1H, SCH*H*CHPh), 2.05 (s, 3H), 1.95 (s, 3H), 1.60 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.35 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.94, 170.31, 170.13, 161.96, 161.89, 142.09, 128.34, 127.67, 126.49, 109.48, 108.92, 101.77, 98.63, 96.51, 91.21, 84.38, 79.21, 77.68, 77.25, 76.83, 72.28, 71.33, 70.91, 70.88, 69.15, 68.98, 67.38, 67.22, 62.46, 56.16, 55.60,

42.91, 26.41, 26.24, 25.25, 24.71, 20.98, 20.88, 20.44; HR MALDI-TOF MS: m/z: calcd for $C_{46}H_{58}O_{16}S$ $[M+Na]^+$: 873.2979; found: 873.2991.

Methyl 3,4,6-tri-*O*-acetyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (39). Compound **39** was prepared according to the general glycosylation procedure using glycosyl donor **34** (50 mg, 0.11 mmol) and glycosyl acceptor **24** (48 mg, 0.095 mmol). Purification by LH20 size exclusion chromatography afforded compound **39** (62 mg, 59%). R_f = 0.12 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +50.0 (c = 1.0 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 – 6.97 (m, 20H), 6.19 (t, J = 9.3 Hz, 1H, H-2^I), 6.07 (s, 2H, Ar*H*), 5.56 (d, J = 3.1 Hz, 1H, H-1^{II}), 5.45 (t, J = 9.9 Hz, 1H, H-3^I), 5.40 (t, J = 9.7 Hz, 1H, H-3^{II}), 5.32 – 5.20 (m, 2H, H-1^I, H-2^I), 4.83 (t, J = 9.7 Hz, 1H, H-4^{II}), 4.57 – 4.46 (m, 1H, H-5^I), 4.36 – 4.16 (m, 3H, SCH_2CHPh, H-5^{II}, H-6$_a^{II}$), 4.08 (d, J = 12.0 Hz, 1H, H-6$_b^{II}$), 4.01 – 3.90 (m, 2H, H-6$_{a,b}^I$), 3.84 (s, 3H, OMe), 3.77 (s, 6H, 2×OMe), 3.64 – 3.51 (m, 4H, OMe, H-2^{II}), 2.96 – 2.79 (m, 2H, SCH_2CHPh), 2.09 (s, 3H), 1.95 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 184.56, 184.53, 184.51, 184.50, 184.48, 175.63, 175.04, 174.88, 170.81, 170.62, 170.51, 166.61, 166.58, 146.93, 138.25, 138.14, 137.94, 134.89, 134.74, 134.58, 134.22, 134.05, 133.61, 133.34, 133.20, 133.17, 133.14, 132.41, 131.07, 109.95, 106.66, 102.28, 101.97, 101.47, 95.84, 89.59, 84.03, 82.95, 82.94, 82.16, 81.95, 81.74, 77.28, 76.64, 75.53, 74.76, 73.97, 73.74, 72.21, 72.17, 67.23, 60.81, 60.43, 60.31, 48.31, 34.64, 25.74, 25.60, 25.17; HR MALDI-TOF MS: m/z: calcd for $C_{57}H_{60}O_{20}S$ $[M+Na]^+$: 1119.3296; found: 1119.3288.

Methyl 3,4,6-tri-*O*-acetyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (40).

Compound **40** was prepared according to the general glycosylation procedure using glycosyl donor **34** (68 mg, 0.15 mmol) and glycosyl acceptor **37** (60 mg, 0.13 mmol). Purification by LH20 size exclusion chromatography afforded compound **40** (65 mg, 48%). R_f = 0.32 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +35.0 (*c* = 0.3 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 6.80 (m, 20H, Ar*H*), 6.19 – 6.05 (m, 3H, Ar*H*, H-1^{II}), 5.35 (t, *J* = 9.7 Hz, 1H, H-3^{II}), 5.06 (s, 2H, C*H*$_2$Ph), 4.80 (t, *J* = 9.8 Hz, 1H, H-4^{II}), 4.70 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.64 (d, *J* = 3.5 Hz, 1H, H-1^{I}), 4.63 – 4.54 (m, 3H, C*H*$_2$Ph, CH*H*Ph), 4.29 – 4.08 (m, 4H, H-3^{I}, H-4^{I}, H-5^{II}, SC*H*HCHPh), 4.03 (dd, *J* = 10.7, 3.5 Hz, 1H, H-6$^{I}_{a}$), 3.98 (dd, *J* = 12.2, 3.3 Hz, 2H, H-5^{I}, H-6$^{II}_{a}$), 3.90 – 3.71 (m, 11H, 3×OMe, H-6$^{I}_{b}$, H-6$^{II}_{b}$), 3.67 – 3.53 (m, 2H, H-2^{I}, H-2^{II}), 3.40 (s, 3H, OMe), 2.90 (dd, *J* = 13.9, 4.0 Hz, 1H, SCH*H*CHPh), 2.77 (dd, *J* = 13.9, 8.7 Hz, 1H, SC*H*HCHPh), 1.96 (s, 3H), 1.91 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.38, 170.13, 169.79, 161.89, 161.77, 142.08, 139.55, 138.21, 138.16, 128.40, 128.27, 128.12, 128.10, 127.84, 127.40, 127.23, 126.86, 126.74, 126.08, 101.15, 97.77, 95.91, 90.98, 84.39, 80.60, 80.10, 79.78, 77.68, 77.23, 77.02, 76.80, 74.18, 73.87, 73.47, 73.27, 71.91, 69.54, 69.21, 69.12, 67.55, 62.04, 55.85, 55.35, 42.77, 20.67, 20.64, 19.97; HR MALDI-TOF MS: m/z: calcd for $C_{57}H_{66}O_{17}S$ $[M+Na]^+$: 1077.3918; found: 1077.3926.

3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (41). Compound **41** was prepared according to the general glycosylation procedure using glycosyl donor **20** (60 mg, 0.12 mmol) and glycosyl acceptor **36** (27 mg, 0.10 mmol). Purification by LH20 size exclusion chromatography afforded compound **41** (79 mg, 84%). R_f = 0.25 (EtOAc/hexanes, 1/2, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 – 7.06

(m, 10H, Ar*H*), 6.10 (s, 2H, Ar*H*), 5.52 – 5.44 (m, 2H, H-1^{I}, H-3^{II}), 5.37 (d, *J* = 3.5 Hz, 1H, H-1^{II}), 4.62 (dd, *J* = 7.9, 2.3 Hz, 1H, H-3^{I}), 4.54 – 4.40 (m, 2H, CH_2Ph), 4.37 (dd, *J* = 7.9, 1.7 Hz, 1H, H-4^{I}), 4.35 – 4.20 (m, 4H, H-2^{I}, H-6^{II}_{a}, H-6^{II}_{b}, SCH_2CH), 4.16 (dd, *J* = 10.1, 2.9 Hz, 1H, H-5^{II}), 4.06 (t, *J* = 5.4 Hz, 1H, H-5^{I}), 3.97 – 3.92 (m, 1H, H-6^{I}_{a}), 3.88 – 3.79 (m, 10H, 3×OMe, H-6^{I}_{b}), 3.51 – 3.34 (m, 2H, H-2^{II}, H-4^{II}), 3.01 (d, *J* = 6.5 Hz, 2H, SCH_2CH), 2.04 (s, 3H), 1.55 (s, 3H), 1.48 (s, 3H), 1.44 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (75 MHz, CDCl3): δ 170.91, 170.01, 161.89, 161.79, 141.83, 137.81, 128.61, 128.25, 128.22, 128.04, 127.75, 126.91, 109.41, 108.92, 101.95, 98.24, 96.51, 91.15, 83.80, 79.03, 77.67, 77.45, 77.24, 76.82, 76.38, 73.25, 73.08, 71.23, 70.91, 70.88, 68.46, 68.02, 67.12, 63.39, 56.16, 55.59, 42.30, 30.37, 26.40, 26.26, 25.21, 24.72, 21.12, 20.92; HR MALDI-TOF MS: m/z: calcd for $C_{46}H_{58}O_{16}S$ $[M+Na]^+$: 921.3343; found: 921.3337.

Methyl 3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (42). Compound **42** was prepared according to the general glycosylation procedure using glycosyl donor **20** (40 mg, 0.082 mmol) and glycosyl acceptor **37** (32 mg, 0.069 mmol). Purification by LH20 size exclusion chromatography afforded compound **42** (45 mg, 59%). R_f = 0.2 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +23.0 (*c* = 0.3 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 – 6.80 (m, 25H, Ar*H*), 6.07 (s, 2H, Ar*H*), 5.94 (d, *J* = 3.4 Hz, 1H, H-1^{II}), 5.46 (t, *J* = 6.0 Hz, 1H, H-3^{II}), 5.01 (s, 2H, CH_2Ph), 4.70 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.63 (d, *J* = 3.5 Hz, 1H, H-1^{I}), 4.60 – 4.52 (m, 3H, CH*H*Ph, CH_2Ph), 4.43 (d, *J* = 11.0 Hz, 1H, C*H*HPh), 4.36 (d, *J* = 11.0 Hz, 1H, CH*H*Ph), 4.18 (t, *J* = 12.0 Hz, 1H, SCH_2CHPh), 4.14 – 3.89 (m, 7H, H-3^{I}, H-5^{II}, H-5^{I}, H-4^{I}, H-$6_{a,b}{}^{II}$, H-$6_{a}{}^{I}$), 3.79 (s, 3H, OMe), 3.77 – 3.68 (m, 7H, 2×OMe, H-$6_{b}{}^{I}$),

3.62 – 3.54 (m, 1H, H-2^{I}), 3.40 (dd, *J* = 10.1, 3.4 Hz, 1H, H-2^{II}), 3.38 (s, 3H, OMe), 3.36 – 3.31 (m, 1H, H-4^{II}), 2.94 (dd, *J* = 13.7, 7.4 Hz, 1H, SC*H*HCHPh), 2.87 (dd, *J* = 13.6, 5.8 Hz, 1H, SCH*H*CHPh), 1.95 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.38, 169.74, 161.78, 161.60, 141.50, 139.59, 138.19, 138.13, 137.54, 128.44, 128.38, 128.17, 128.13, 128.09, 128.06, 128.01, 127.99, 127.93, 127.85, 127.81, 127.76, 127.43, 127.30, 127.28, 126.86, 126.80, 126.68, 101.35, 97.77, 95.86, 90.83, 83.63, 80.83, 80.34, 79.03, 77.23, 77.02, 76.80, 76.42, 74.06, 74.04, 73.31, 73.29, 73.15, 69.56, 69.03, 68.69, 62.87, 55.81, 55.31, 55.23, 42.10, 20.82, 20.56; HR MALDI-TOF MS: m/z: calcd for $C_{62}H_{70}O_{16}S$ $[M+Na]^+$: 1125.4282; found: 1125.4275.

3,4-di-*O*-acetyl-6-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (43). Compound **43** was prepared according to the general glycosylation procedure using glycosyl donor **17** (70 mg, 0.14 mmol) and glycosyl acceptor **36** (31 mg, 0.12 mmol). Purification by LH20 size exclusion chromatography afforded compound **43** (101 mg, 94%). R_f = 0.33 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{27}$ (deg cm^3 g^{-1} dm^{-1}) = +62.5 (*c* = 1.6 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.01 (m, 10H, Ar*H*), 6.21 – 6.01 (m, 2H, Ar*H*), 5.52 (d, *J* = 4.7 Hz, 1H, H-1^{I}), 5.45 (d, *J* = 3 Hz, 1H, H-2^{II}), 5.31 (t, *J* = 9.7 Hz, 1H, H-3^{II}), 4.98 (t, *J* = 9.7 Hz, 1H, H-4^{II}), 4.63 (dd, *J* = 7.9, 2.2 Hz, 1H, H-3^{I}), 4.57 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.45 – 4.38 (m, 2H, C*H*HPh, H-4^{I}), 4.31 (dd, *J* = 4.9, 2.3 Hz, 1H, H-2^{I}), 4.27 (dd, *J* = 7.9, 4.9 Hz, 1H, SCH_2CHPh), 4.19 – 4.00 (m, 2H, H-5^{I}, H-5^{II}), 3.99 – 3.86 (m, 2H, H-6^{II}_a, H-6^{II}_b), 3.83 (s, 3H, OMe), 3.81 (s, 6H, 2 × OMe), 3.63 (dd, *J* = 10.1, 3.5 Hz, 1H, H-2^{II}), 3.56 (dd, *J* = 10.7, 2.5 Hz, 1H, H-6^{I}_a), 3.46 (dd, *J* = 10.8, 3.6 Hz, 1H, H-6^{I}_b), 3.02 (dd, *J* = 13.7, 4.8 Hz, 1H, SC*H*HCHPh), 2.91 (dd, *J* = 13.8, 7.9 Hz, 1H,

SCH*H*CHPh), 1.84 (s, 3H), 1.60 (s, 3H), 1.48 – 1.21 (4s, 12H).; ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.29, 169.83, 161.73, 161.62, 141.85, 137.93, 128.27, 128.05, 127.91, 127.56, 127.40, 126.37, 116.19, 109.20, 108.67, 101.53, 98.34, 96.30, 90.94, 83.76, 78.64, 77.45, 77.23, 77.03, 76.60, 73.38, 72.39, 70.97, 70.80, 70.62, 69.52, 68.22, 68.08, 67.99, 66.83, 55.96, 55.36, 42.47, 30.16, 26.24, 26.05, 25.04, 24.53, 20.70, 20.31; HR MALDI-TOF MS: m/z: calcd for $C_{46}H_{58}O_{16}S$ $[M+Na]^+$: 921.3343; found: 921.3351.

Methyl 3,4-di-*O*-acetyl-6-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (44). Compound **44** was prepared according to the general glycosylation procedure using glycosyl donor **17** (45 mg, 0.09 mmol) and glycosyl acceptor **37** (36 mg, 0.08 mmol). Purification by LH20 size exclusion chromatography afforded compound **44** (57 mg, 67%). R_f = 0.43 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +50.0 (*c* = 0.8 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 – 6.78 (m, 25H, Ar*H*), 6.07 (s, 3H, Ar*H*, H-1^{II}), 5.33 (t, *J* = 9.7 Hz, 1H, H-3^{II}), 5.05 (s, 2H, CH_2Ph), 4.96 (t, *J* = 9.8 Hz, 1H, H-4^{II}), 4.78 – 4.49 (m, 5H, 2 × CH_2Ph, H-1^{I}), 4.41 – 4.32 (m, 2H, CH_2Ph), 4.22 – 4.11 (m, 3H, SCH_2CHPh, H-3^{I}, H-4^{I}), 4.10 – 3.85 (m, 3H, H-5^{I}, H-5^{II}, H-6$^{I}_{a}$,), 3.80 (s, 1H, OMe), 3.76 – 3.69 (m, 7H, 2 × OMe, H-6$^{I}_{b}$), 3.64 (m, 2H, H-2^{I}, H-2^{II}), 3.39 (s, 3H, OMe), 3.28 (d, *J* = 10.6 Hz, 1H, H-6$^{II}_{a}$), 3.12 (d, *J* = 10.9 Hz, 1H, H-6$^{II}_{b}$), 2.89 (dd, *J* = 13.9, 4.3 Hz, 1H, SC*H*HCHPh), 2.78 (dd, *J* = 13.9, 8.2 Hz, 1H, SCH*H*CHPh), 1.81 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.52, 169.94, 162.08, 161.91, 142.24, 139.73, 138.55, 138.40, 138.23, 128.62, 128.43, 128.40, 128.35, 128.31, 128.28, 128.03, 127.70, 127.49, 127.43, 127.36, 127.09, 126.37, 101.28, 97.97, 96.08, 91.09, 84.18, 80.95, 80.49, 79.57, 77.66, 77.43, 77.23, 76.81, 74.26, 73.91, 73.52,

72.46, 69.81, 69.69, 69.51, 68.95, 68.15, 56.10, 55.53, 42.84, 30.38, 20.91, 20.31; HR MALDI-TOF MS: m/z: calcd for $C_{62}H_{70}O_{16}S$ $[M+Na]^+$: 1125.4282; found: 1125.4292.

3-*O*-allyloxycarbonyl-4-*O*-acetyl-6-*O*-benzyl-2-*O*-[(1S)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (45). Compound **45** was prepared according to the general glycosylation procedure using glycosyl donor **22** (76 mg, 0.14 mmol) and glycosyl acceptor **36** (31 mg, 0.12 mmol). Purification by LH20 size exclusion chromatography afforded compound **45** (76 mg, 67%). R_f = 0.3 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +70.0 (*c* = 0.3 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 – 7.06 (m, 10H, Ar*H*), 6.10 (s, 2H, Ar*H*), 5.77 – 5.61 (m, 1H, C*H* alloc), 5.52 (d, *J* = 5.0 Hz, 1H, H-1^I), 5.46 (d, *J* = 3.5 Hz, 1H, H-1^{II}), 5.26 – 5.09 (m, 2H, CH_2 alloc), 5.04 (t, *J* = 9.7 Hz, 1H, H-4^{II}), 4.64 (dd, *J* = 7.9, 2.2 Hz, 1H, H-3^I), 4.54 (d, *J* = 11.8 Hz, 1H, CH*H*Ph), 4.50 – 4.39 (m, 2H, C*H*HPh, H-4^I), 4.36 – 4.29 (m, 2H, H-2^I, SCH_2CH), 4.27 (dd, *J* = 13.1, 5.8 Hz, 1H, CH*H* alloc), 4.09 (t, *J* = 6.6 Hz, 1H, H-5^I), 4.08 – 3.99 (m, 2H, H-5^{II}, C*H*H alloc), 3.98 – 3.85 (m, 2H, H-6^I_a, H-6^I_b), 3.83 – 3.80 (2s, 9H, 3×OMe), 3.73 (dd, *J* = 9.9, 3.5 Hz, 1H, H-2^{II}), 3.57 (dd, *J* = 10.8, 2.7 Hz, 1H, H-6$^{II}_a$), 3.47 (dd, *J* = 10.8, 3.8 Hz, 1H, H-6$^{II}_b$), 3.02 (dd, *J* = 13.9, 4.3 Hz, 1H, SC*H*HCH), 2.85 (dd, *J* = 13.9, 8.2 Hz, 1H, SCH*H*CH), 1.86 (s, 3H), 1.60 (s, 3H), 1.45 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.61, 161.74, 161.66, 154.09, 141.63, 137.94, 131.61, 128.26, 127.95, 127.92, 127.54, 127.21, 126.23, 118.19, 109.20, 108.66, 101.31, 98.48, 96.30, 95.09, 90.95, 83.31, 78.35, 78.09, 78.07, 77.22, 77.01, 76.80, 73.40, 70.92, 70.77, 70.61, 69.36, 68.30, 68.13, 67.82, 66.75, 55.93, 55.36, 42.75, 26.24, 26.05, 25.03, 24.56, 20.70; HR MALDI-TOF MS: m/z: calcd for $C_{48}H_{60}O_{17}S$ $[M+Na]^+$: 963.3449; found:

963.3456.

Methyl 3-*O*-allyoxylcarbonyl-4-*O*-acetyl-6-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (46). Compound **46** was prepared according to the general glycosylation procedure using glycosyl donor **22** (50 mg, 0.094 mmol) and glycosyl acceptor **24** (40 mg, 0.079 mmol). Purification by LH20 size exclusion chromatography afforded compound **46** (73 mg, 78%). R_f = 0.24 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +60.0 (*c* = 0.3 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 – 6.97 (m, 25H, Ar*H*), 6.18 (t, *J* = 9.4 Hz, 1H, H-3^{I}), 6.04 (s, 2H, Ar*H*), 5.77 – 5.60 (m, 1H, C*H* alloc), 5.53 – 5.42 (m, 2H, H-1^{II}, H-4^{I}), 5.31 – 5.22 (m, 2H, H-1^{I}, H-2^{I}), 5.22 – 5.10 (m, 3H, H-3^{II}, CH_2 alloc), 5.04 (dd, *J* = 18.4, 8.9 Hz, 1H, H-4^{II}), 4.59 – 4.39 (m, 3H, CH_2Ph, H-5^{I}), 4.31 – 4.23 (m, 2H, SCH$_2$C*H*Ph, C*H*H alloc), 4.19 – 4.11 (m, 1H, H-5^{II}), 4.07 (dd, *J* = 13.2, 5.5 Hz, 1H, CH*H* alloc), 3.98 (dd, *J* = 10.6, 8.3 Hz, 1H, H-6$_a^{I}$), 3.91 (dd, *J* = 10.6, 1.7 Hz, 1H, H-6$_b^{I}$), 3.82 (s, 3H, OMe), 3.77 – 3.65 (m, 7H, 2×OMe, H-2^{II}), 3.61 – 3.51 (m, 4H, OMe, H-6$_a^{II}$), 3.45 (dd, *J* = 10.8, 3.7 Hz, 1H, H-6$_b^{II}$), 2.87 (ddd, *J* = 22.8, 14.1, 6.2 Hz, 2H, SCH_2CHPh), 1.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 179.57, 179.54, 179.51, 169.54, 165.85, 165.67, 165.48, 161.65, 161.60, 154.03, 141.67, 137.87, 133.28, 133.17, 132.97, 131.56, 129.93, 129.80, 129.63, 129.29, 129.12, 128.74, 128.37, 128.28, 128.24, 128.21, 127.99, 127.90, 127.56, 127.18, 126.03, 118.15, 97.36, 96.49, 90.87, 83.84, 78.47, 77.97, 77.20, 76.98, 76.77, 73.37, 72.37, 70.62, 69.77, 69.29, 68.75, 68.33, 68.15, 68.11, 66.93, 55.86, 55.43, 55.32, 43.43, 20.66; HR MALDI-TOF MS: m/z: calcd for $C_{64}H_{66}O_{20}S$ $[M+Na]^+$: 1209.3766; found: 1209.3752.

4-*O*-acetyl-3-*O*-levulinoyl-6-*O*-benzyl-2-*O*-[(1S)-phenyl-2-(2,3,5-

trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (47). Compound **47** was prepared according to the general glycosylation procedure using glycosyl donor **21** (40 mg, 0.074 mmol) and glycosyl acceptor **36** (16 mg, 0.062 mmol). Purification by LH20 size exclusion chromatography afforded compound **47** (51 mg, 85%). R_f = 0.14 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{26}$ (deg cm^3 g^{-1} dm^{-1}) = +27.5 (*c* = 0.5 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 – 7.00 (m, 10H, Ar*H*), 6.10 (s, 2H, Ar*H*), 5.52 (d, *J* = 5.0 Hz, 1H, H-1^I), 5.45 (d, *J* = 3.4 Hz, 1H, H-1^{II}), 5.34 (t, *J* = 9.7 Hz, 1H, H-3^{II}), 4.98 (t, *J* = 9.8 Hz, 1H, H-4^{II}), 4.62 (dd, *J* = 7.9, 2.2 Hz, 1H, H-3^I), 4.59 – 4.36 (m, 3H, C*H*$_2$Ph, H-4^I), 4.31 (dd, *J* = 4.9, 2.3 Hz, 1H, H-2^I), 4.25 (dd, *J* = 7.7, 4.8 Hz, 1H, SCH$_2$C*H*Ph), 4.17 – 3.97 (m, 2H, H-5^I, H-5^{II}), 3.97 – 3.72 (m, 11H, H-6^I_a, H-6^I_b, 3×OMe), 3.63 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2^{II}), 3.59 – 3.36 (m, 2H, H-6^{II}_a, H-6^{II}_b), 3.02 (dd, *J* = 13.7, 4.9 Hz, 1H, SC*H*HCHPh), 2.90 (dd, *J* = 13.7, 7.8 Hz, 1H, SCH*H*CHPh), 2.44 – 2.08 (m, 3H, 3×C*H*H Lev), 2.06 (s, 3H), 1.88 (s, 3H), 1.68 – 1.62 (m, 1H, C*H*H Lev), 1.59 (s, 3H)1.45 (s, 3H), 1.34 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.39, 172.00, 170.15, 161.94, 161.86, 142.07, 138.15, 128.48, 128.22, 128.15, 127.87, 127.77, 127.52, 126.66, 109.41, 108.87, 101.61, 98.58, 96.51, 91.16, 83.84, 78.85, 77.66, 77.44, 77.23, 76.81, 73.62, 72.57, 71.15, 71.00, 70.83, 69.43, 68.57, 68.37, 68.08, 66.96, 56.18, 55.58, 42.60, 37.83, 29.94, 27.75, 26.46, 26.26, 25.24, 24.76, 20.92; HR MALDI-TOF MS: m/z: calcd for $C_{49}H_{62}O_{17}S$ $[M+Na]^+$: 977.3605; found: 977.3597.

Methyl 4-*O*-acetyl-6-*O*-benzyl-3-*O*-levulinoyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (48). Compound **48** was prepared according to the general

glycosylation procedure using glycosyl donor **21** (50 mg, 0.093 mmol) and glycosyl acceptor **37** (36 mg, 0.078 mmol). Purification by LH20 size exclusion chromatography afforded compound **48** (57 mg, 64%). R_f = 0.11 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +40.0 (*c* = 0.8 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 – 6.83 (m, 20H, Ar*H*), 6.07 (s, 3H, Ar*H*, H-1^{II}), 5.38 (t, *J* = 9.8 Hz, 1H, H-3^{II}), 5.04 (s, 2H, C*H*$_2$Ph), 4.95 (dd, *J* = 19.0, 9.3 Hz, 1H, H-4^{II}), 4.70 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.63 (d, *J* = 3.5 Hz, 1H, H-1^{I}), 4.60 – 4.52 (m, 3H, CH*H*Ph, C*H*$_2$Ph), 4.38 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.27 (d, *J* = 11.9 Hz, 1H, CH*H*Ph), 4.19 – 4.10 (m, 3H, H-3^{I}, H-4^{I}, SCH$_2$C*H*Ph), 4.07 – 3.90 (m, 3H, H-5^{I}, H-5^{II}, H-6$_a^{II}$), 3.85 – 3.68 (m, 10H, 3×OMe, H-6$_b^{II}$), 3.65 – 3.56 (m, 1H, H-2^{I}), 3.39 (s, 3H, OMe), 3.29 (dd, *J* = 10.7, 2.5 Hz, 1H, H-6$_a^{II}$), 3.13 (dd, *J* = 10.8, 3.4 Hz, 1H, H-6$_b^{II}$), 2.87 (dd, *J* = 13.9, 4.6 Hz, 1H, SC*H*HCHPh), 2.78 (dd, *J* = 13.9, 8.2 Hz, 1H, SCH*H*CHPh), 2.42 – 2.30 (m, 1H, C*H*H Lev), 2.21 – 2.09 (m, 1H, CH*H* Lev), 2.06 (s, 3H), 2.04 – 1.95 (m, 1H, C*H*H Lev), 1.87 (s, 3H), 1.41 (dt, *J* = 17.4, 6.1 Hz, 1H, CH*H* Lev); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.36, 172.06, 170.05, 162.07, 161.93, 142.22, 139.74, 138.55, 138.42, 138.24, 128.62, 128.43, 128.39, 128.35, 128.29, 128.23, 128.05, 127.70, 127.47, 127.37, 127.31, 127.16, 127.07, 126.49, 101.20, 97.99, 96.27, 91.10, 84.05, 80.87, 80.70, 79.55, 77.67, 77.45, 77.24, 76.82, 74.35, 74.00, 73.52, 72.35, 69.76, 69.48, 69.11, 68.28, 56.10, 55.52, 42.75, 37.83, 29.95, 27.54, 20.92; HR MALDI-TOF MS: m/z: calcd for $C_{65}H_{74}O_{17}S$ $[M+Na]^+$: 1181.4545; found: 1181.4556.

4,6-di-*O*-acetyl-3-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (49). Compound **49** was prepared according to the general glycosylation procedure using glycosyl donor **23** (60 mg, 0.12 mmol) and glycosyl acceptor **36** (26 mg, 0.10 mmol).

Purification by LH20 size exclusion chromatography afforded compound **49** (88 mg, 98%). R_f = 0.19 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +13.5 (*c* = 0.3 in $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 – 7.05 (m, 10H, Ar*H*), 6.09 (s, 2H, Ar*H*), 5.54 (d, *J* = 5.0 Hz, 1H, H-1^{I}), 5.21 (d, *J* = 3.4 Hz, 1H, H-1^{II}), 4.89 (t, *J* = 9.9 Hz, 1H, H-4^{II}), 4.67 (dd, *J* = 7.9, 2.3 Hz, 1H, H-3^{I}), 4.60 – 4.54 (m, 2H, C*H*HPh, SCH_2C*H*Ph), 4.48 – 4.41 (m, 2H, CH*H*Ph, H-4^{I}), 4.34 (dd, *J* = 5.0, 2.4 Hz, 1H, H-2^{I}), 4.22 (dd, *J* = 12.3, 4.4 Hz, 1H, H-6$^{II}_{a}$), 4.10 (br t, *J* = 5.8 Hz, 1H, H-5^{I}), 4.05 – 3.71 (m, 14H, H-5^{II}, H-6$^{II}_{b}$, H-6$^{I}_{a}$, H-6$^{I}_{b}$ H-3^{II}, 3 × OMe), 3.58 (dd, *J* = 9.5, 3.5 Hz, 1H, H-2^{II}), 3.12 (dd, *J* = 13.3, 7.0 Hz, 1H, SC*H*HCHPh), 3.01 (dd, *J* = 13.3, 5.6 Hz, 1H, SCH*H*CHPh), 2.04 (s, 3H), 1.86 (s, 3H), 1.59 (s, 3H), 1.47 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.08, 169.87, 161.83, 161.79, 141.09, 138.99, 128.36, 128.30, 127.91, 127.85, 127.45, 127.16, 109.53, 108.83, 102.16, 98.24, 96.55, 91.20, 81.73, 79.05, 78.58, 77.66, 77.44, 77.24, 76.81, 75.17, 71.36, 70.92, 70.88, 70.04, 68.28, 67.76, 67.09, 62.61, 56.17, 55.57, 42.37, 30.37, 26.40, 26.31, 25.24, 24.84, 21.02, 20.99; HR MALDI-TOF MS: m/z: calcd for $C_{46}H_{58}O_{16}S$ $[M+Na]^+$: 921.3344; found: 921.3352.

Methyl 4,6-di-*O*-acetyl-3-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranose (50). Compound **50** was prepared according to the general glycosylation procedure using glycosyl donor **23** (30 mg, 0.074 mmol) and glycosyl acceptor **37** (24 mg, 0.063 mmol). Purification by LH20 size exclusion chromatography afforded compound **50** (25 mg, 46%, α/β=7/1). **50α**: R_f = 0.23 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +20.0 (*c* = 0.5 in $CHCl_3$); ^{1}H NMR (500 MHz, CDCl3): δ 7.50 – 6.92 (m, 25H, Ar*H*), 6.06 (s, 2H, Ar*H*), 5.86 (d, *J* = 3.4 Hz, 1H, H-1^{II}), 5.09 (d, *J* = 11.9 Hz, 1H,

C*H*HPh), 5.02 (d, *J* = 13.5 Hz, 1H, CH*H*Ph), 4.83 (t, *J* = 10.0 Hz, 1H, H-4^{II}), 4.69 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.65 (d, *J* = 3.5 Hz, 1H, H-1^{I}), 4.62 – 4.52 (m, 3H, CH*H*Ph, C*H*$_2$Ph), 4.48 (t, *J* = 6.4 Hz, 1H, SCH$_2$C*H*Ph), 4.42 (d, *J* = 11.6 Hz, 1H, C*H*HPh), 4.34 (d, *J* = 11.6 Hz, 1H, CH*H*Ph), 4.17 (t, *J* = 9.1 Hz, 1H, H-3^{I}), 4.04 (t, *J* = 9.2 Hz, 1H, H-4^{I}), 3.99 (dd, *J* = 12.3, 4.1 Hz, 1H, H-6$^{I}_{a}$), 3.96 – 3.83 (m, 3H, H-5^{I}, H-5^{II}, H-6$^{II}_{a}$), 3.83 – 3.77 (m, 4H, OMe, H-6$^{I}_{b}$), 3.77 – 3.67 (m, 7H, 2×OMe, H-6$^{II}_{b}$), 3.61 (dd, *J* = 9.4, 3.5 Hz, 1H, H-2^{I}), 3.50 (dd, *J* = 9.6, 3.4 Hz, 1H, H-2^{II}), 3.40 (s, 3H, OMe), 3.06 (dd, *J* = 13.3, 6.5 Hz, 1H, SC*H*HCHPh), 2.87 (dd, *J* = 13.3, 6.4 Hz, 1H, SCH*H*CHPh), 1.98 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.62, 169.48, 161.58, 161.55, 140.85, 139.13, 138.55, 138.03, 138.01, 128.59, 128.40, 128.31, 128.25, 128.12, 128.06, 127.99, 127.87, 127.53, 127.45, 127.32, 127.21, 127.09, 126.93, 126.83, 101.36, 97.72, 95.95, 90.88, 81.80, 81.24, 80.36, 78.62, 78.14, 78.09, 77.21, 77.00, 76.78, 74.76, 74.06, 73.40, 73.24, 72.79, 70.02, 69.54, 69.12, 68.10, 62.33, 55.80, 55.27, 55.24, 41.56, 20.77, 20.74.; HR MALDI-TOF MS: m/z: calcd for $C_{62}H_{70}O_{16}S$ $[M+Na]^+$: 1125.4283; found: 1125.4276. The ß anomer was purified by reversed phase HPLC on an analytical C-18 column using a gradient of 40→100% acetonitrile in H_2O over 40 min. **50β**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 – 7.08 (m, 25H, Ar*H*), 6.06 (s, 2H, Ar*H*), 4.99 (t, *J* = 6.7 Hz, 1H, SCH$_2$C*H*Ph), 4.90 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.84 – 4.68 (m, 3H, H-4^{II}, 2×C*H*HPh), 4.68 – 4.54 (m, 4H, H-1^{I}, 2×CH*H*Ph, C*H*HPh), 4.54 – 4.40 (m, 2H, 2×CH*H*Ph), 4.32 (d, *J* = 7.2 Hz, 1H, H-1^{II}), 4.22 (d, *J* = 8.2 Hz, 1H, H-6$^{I}_{a}$), 4.07 – 3.96 (m, 2H, H-4^{I}, H-6$^{II}_{a}$), 3.89 – 3.81 (m, 3H, H-6$^{II}_{b}$, H-3^{I}, H-5^{I}), 3.78 (s, 9H, 3×OMe), 3.71 (d, *J* = 11.0 Hz, 1H, H-6$^{I}_{b}$), 3.51 (dd, *J* = 9.6, 3.8 Hz, 1H, H-2^{I}), 3.42 (s, 3H, OMe), 3.30 (dd, *J* = 13.2, 6.3 Hz, 1H, SC*H*HCHPh), 3.26 – 3.15 (m, 2H, H-2^{II}, H-3^{II}), 3.11 (d, *J* = 8.5 Hz, 1H, H-5^{II}), 2.82

(dd, *J* = 13.2, 6.8 Hz, 1H, SCH*H*CHPh), 1.92 (s, 3H), 1.85 (s, 3H); selected ^{13}C NMR (gHSQC, $CDCl_3$): δ 102.01 (C-1^{II}), 98.90 (C-1^{I}), 82.61, 82.16, 81.94, 81.66, 80.63, 78.75, 78.02, 75.76, 75.26, 73.72, 70.31, 69.87, 68.27, 67.85, 62.24, 55.92, 55.64, 41.89; HR MALDI-TOF MS: m/z: calcd for $C_{62}H_{70}O_{16}S$ $[M+Na]^+$: 1125.4283; found: 1125.4272.

3-*O*-acetyl-4,6-di-*O*-benzyl-2-*O*-[(1S)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (51). Compound **51** was prepared according to the general procedure using glycosyl donor **18** (40 mg, 0.075 mmol) and glycosyl acceptor **36** (16 mg, 0.062 mmol). Purification by LH20 size exclusion chromatography afforded compound **51** (56 mg, 95 %). R_f = 0.34 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +21.5 (*c* = 0.5 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 – 7.01 (m, 15H, Ar*H*), 6.06 (s, 2H, Ar*H*), 5.50 (d, *J* = 5.0 Hz, 1H, H-1^{I}), 5.39 (t, *J* = 9.7 Hz, 1H, H-3^{II}), 5.32 (d, *J* = 3.5 Hz, 1H, H-1^{II}), 4.61 (dd, *J* = 7.4, 2.9 Hz, 2H, H-3^{I}, C*H*HPh), 4.46 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.39 (s, 3H, CH_2Ph, H-4^{I}), 4.29 (dd, *J* = 5.0, 2.3 Hz, 1H, H-2^{I}), 4.25 (t, *J* = 6.6 Hz, 1H, SCH_2C*H*Ph), 4.10 – 4.00 (m, 1H, H-6_a^{I}), 3.97 – 3.92 (m, 1H, H-5^{II}), 3.89 (dd, *J* = 9.9, 7.2 Hz, 1H, H-6_b^{I}), 3.86 – 3.71 (m, 11H, 3×OMe, H-5^{I}, H-6_a^{II}), 3.66 (dd, *J* = 10.8, 1.8 Hz, 1H, H-6_b^{II}), 3.57 (t, *J* = 9.7 Hz, 1H, H-4^{II}), 3.45 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2^{II}), 3.02 (d, *J* = 6.6 Hz, 2H, SCH_2CHPh), 1.55 (s, 3H), 1.44 (2s, 6H), 1.34 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 179.61, 179.58, 179.57, 169.89, 161.60, 161.47, 141.44, 138.04, 137.98, 128.32, 128.25, 127.95, 127.90, 127.75, 127.66, 127.54, 127.45, 126.79, 109.09, 108.63, 101.58, 98.11, 96.24, 90.81, 83.16, 78.39, 78.03, 78.02, 77.20, 76.99, 76.78, 76.23, 73.72, 73.44, 73.18, 70.79, 70.77, 70.53, 69.66, 68.32, 67.64, 66.57, 55.91, 55.32, 41.63, 26.21, 26.00, 24.96, 24.45, 20.70; HR MALDI-TOF MS: m/z: calcd for

$C_{51}H_{62}O_{15}S$ $[M+Na]^+$: 969.3707; found: 969.3718.

Methyl 3-*O*-acetyl-4,6-di-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-D-glucopyranosyl-(1→4)- 2,3,6-tri-*O*-benzyl-D-glucopyranoside (52). Compound **52** was prepared according to the general glycosylation procedure using glycosyl donor **18** (50 mg, 0.093 mmol) and glycosyl acceptor **37** (36 mg, 0.078 mmol). Purification by LH20 size exclusion chromatography afforded compound **52** (59 mg, 66%, α/β=10/1). **52α**: R_f = 0.39 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +48.0 (*c* = 0.6 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 – 6.90 (m, 30H, Ar*H*), 6.03 (s, 2H, Ar*H*), 5.95 (d, *J* = 3.4 Hz, 1H, H-1^{II}), 5.39 (t, *J* = 9.7 Hz, 1H, H-3^{II}), 5.03 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.94 (d, *J* = 11.8 Hz, 1H, CH*H*Ph), 4.71 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.63 (d, *J* = 3.5 Hz, 1H, H-1^{I}), 4.58 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.50 (q, *J* = 12.2 Hz, 2H, CH_2Ph), 4.43 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.36 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.31 (d, *J* = 11.2 Hz, 1H, CH*H*Ph), 4.27 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.21 (t, *J* = 6.7 Hz, 1H, SCH_2C*H*Ph), 4.15 – 4.08 (m, 2H, H-4^{I}, H-3^{I}), 3.96 (dd, *J* = 10.7, 3.4 Hz, 1H, H-$6_a{}^{I}$), 3.94 – 3.90 (m, 1H, H-5^{I}), 3.81 (d, *J* = 10.0 Hz, 1H, H-5^{II}), 3.76 (s, 3H, OMe), 3.71 (s, 7H, 2×OMe, H-$6_b{}^{I}$), 3.60 (dd, *J* = 9.2, 3.5 Hz, 1H, H-2^{I}), 3.52 (t, *J* = 9.6 Hz, 1H, H-4^{II}), 3.43 (dd, *J* = 10.2, 3.4 Hz, 1H, H-2^{II}), 3.37 (s, 3H, OMe), 3.33 (d, *J* = 1.9 Hz, 2H, H-$6_{a,b}{}^{II}$), 1.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.09, 161.98, 161.78, 161.66, 141.61, 139.65, 138.56, 138.44, 138.30, 128.79, 128.63, 128.52, 128.46, 128.37, 128.35, 128.33, 128.17, 128.06, 127.93, 127.85, 127.75, 127.64, 127.38, 127.36, 127.28, 127.14, 127.00, 101.59, 97.96, 95.91, 91.04, 83.32, 81.17, 80.89, 78.80, 77.68, 77.46, 77.26, 76.83, 76.54, 74.36, 73.54, 73.51, 73.35, 72.86, 70.63, 69.70, 69.37, 68.32, 56.23, 56.09, 55.48, 55.43, 42.10, 20.85; HR MALDI-TOF MS: m/z: calcd for

$C_{67}H_{74}O_{15}S$ $[M+Na]^+$: 1173.4646; found:1173.4638. The ß anomer was purified by reversed phase HPLC on an analytical C-18 column using a gradient of 50→100% acetonitrile in H_2O over 40 min. **52ß**: ^1H NMR (600 MHz, $CDCl_3$): δ 7.48 – 7.03 (m, 30H, Ar*H*), 6.01 (s, 2H, Ar*H*), 5.00 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.96 (t, *J* = 9.4 Hz, 1H, H-3^{II}), 4.79 (d, *J* = 12.2 Hz, 1H, C*H*HPh), 4.77 – 4.74 (m, 1H, SCH_2CHPh), 4.71 (d, *J* = 11.4 Hz, 1H, CH*H*Ph), 4.66 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.63 – 4.58 (m, 2H, H-1^I, CH*H*Ph), 4.49 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.45 – 4.33 (m, 5H, 2×CH_2Ph, H-1^{II}), 4.09 – 4.02 (m, 1H, H-4^I), 3.96 (dd, *J* = 11.0, 2.6 Hz, 1H, H-6_a^I), 3.87 (t, *J* = 9.4 Hz, 1H, H-3^I), 3.80 – 3.73 (m, 10H, H-5^I, 3×OMe), 3.63 (dd, *J* = 11.2, 1.7 Hz, 1H, H-6_a^{II}), 3.61 (dd, *J* = 11.0, 1.7 Hz, 1H, H-6_b^I), 3.50 – 3.43 (m, 2H, H-2^I, H-6_b^{II}), 3.43 – 3.35 (m, 4H, H-4^{II}, OMe), 3.21 – 3.09 (m, 3H, H-5^{II}, H-2^{II}, SC*H*HCHPh), 2.93 (dd, *J* = 13.3, 8.6 Hz, 1H, SCH*H*CHPh), 1.70 (s, 3H); ^{13}C NMR (gHSQC, 150 MHz, $CDCl_3$): δ; HR MALDI-TOF MS: m/z: calcd for $C_{67}H_{74}O_{15}S$ $[M+Na]^+$: 1173.4646; found:1173.4641.

3,4,6-tri-*O*-benzyl-2-*O*-[(1S)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (53). Compound **53** was prepared according to the general glycosylation procedure using glycosyl donor **35** (50 mg, 0.086 mmol) and glycosyl acceptor **36** (18 mg, 0.070 mmol). Purification by LH20 size exclusion chromatography afforded compound **53** (68 mg, 98%). R_f = 0.39 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +6.7 (*c* = 1.5 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.49 – 6.98 (m, 20H, Ar*H*), 6.06 (s, 2H, Ar*H*), 5.53 (d, *J* = 5.0 Hz, 1H, H-1^I), 5.10 (d, *J* = 3.5 Hz, 1H, H-1^{II}), 4.86 – 4.50 (m, 7H, CH_2Ph, C*H*HPh, C*H*HPh, SCH_2CH, H-4^I, H-3^I), 4.49 – 4.37 (m, 2H, C*H*HPh, C*H*HPh), 4.32 (dd, *J* = 5.0, 2.3 Hz, 1H, H-2^I), 4.18 – 3.98 (m, 1H, H-5^I), 3.98 – 3.68 (m, 15H, 3×OMe, H-3^{II},

H-5^{II}, H-6$^{I}_{a}$, H-6$^{I}_{b}$, H-6$^{II}_{a}$, H-6$^{II}_{b}$), 3.62 (dd, *J* = 10.6, 1.9 Hz, 1H, H-4^{II}), 3.57 – 3.44 (m, 1H, H-2^{II}) 3.19 (dd, *J* = 13.1, 6.4 Hz, 1H, SC*H*HCH), 3.02 (dd, *J* = 13.1, 6.5 Hz, 1H, SCH*H*CH), 1.56 (s, 3H), 1.47 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.76, 161.64, 140.94, 139.37, 138.71, 138.25, 128.53, 128.48, 128.30, 128.15, 128.02, 127.88, 127.82, 127.73, 127.44, 127.40, 116.41, 109.39, 108.81, 102.33, 98.07, 96.54, 91.16, 81.79, 80.92, 78.21, 77.80, 77.68, 77.46, 77.25, 76.83, 75.49, 75.08, 73.65, 71.10, 71.01, 70.84, 70.37, 68.72, 67.27, 66.48, 56.15, 55.53, 41.84, 30.38, 26.46, 26.35, 25.21, 24.91; HR MALDI-TOF MS: m/z: calcd for $C_{56}H_{66}O_{14}S$ $[M+Na]^+$: 1017.4071; found: 1017.4063.

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranoside (54). Compound **54** was prepared according to the general glycosylation procedure using glycosyl donor **35** (50 mg, 0.086 mmol) and glycosyl acceptor **37** (33 mg, 0.071 mmol). Purification by LH20 size exclusion chromatography afforded compound **54** (49 mg, 57%, α/β=1.5/1). **54α**: R_f = 0.43 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +21.4 (*c* = 1.4 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 – 7.00 (m, 35H, Ar*H*), 6.01 (s, 2H, Ar*H*), 5.81 (d, *J* = 3.3 Hz, 1H, H-1^{II}), 5.09 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.98 (d, *J* = 11.8 Hz, 1H, CH*H*Ph), 4.75 – 4.55 (m, 8H, H-1^{I}, C*H*HPh, C*H*$_2$Ph×3), 4.53 – 4.47 (m, 2H, SCH$_2$C*H*Ph, C*H*HPh), 4.45 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.36 (d, *J* = 11.0 Hz, 1H, CH*H*Ph), 4.26 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.15 (t, *J* = 9.1 Hz, 1H, H-3^{I}), 4.07 (t, *J* = 9.2 Hz, 1H, H-4^{I}), 3.92 – 3.64 (m, 14H, H-5^{I}, H-3^{II}, H-5^{II}, H-6$_{a,b}^{I}$, 3×OMe), 3.61 (dd, *J* = 9.4, 3.5 Hz, 1H, H-2^{I}), 3.51 – 3.46 (m, 1H, H-4^{II}), 3.46 – 3.40 (m, 1H, H-6$_{a}^{II}$), 3.40 – 3.33 (m, 5H, OMe, H-2^{II}, H-6$_{b}^{II}$), 3.18 (dd, *J* = 13.0, 5.5 Hz, 1H, SC*H*HCHPh),

2.83 (dd, J = 13.0, 7.6 Hz, 1H, SCH*H*CHPh); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.57, 161.43, 140.61, 139.15, 139.07, 138.64, 138.21, 138.14, 138.04, 128.41, 128.33, 128.28, 128.26, 128.17, 128.15, 128.09, 128.04, 128.01, 127.91, 127.87, 127.71, 127.57, 127.53, 127.49, 127.43, 127.27, 127.25, 127.16, 127.10, 127.02, 101.53, 97.74, 95.70, 90.93, 90.87, 81.77, 81.44, 80.89, 80.52, 77.69, 77.45, 77.26, 77.05, 76.84, 75.07, 74.77, 74.17, 73.37, 73.26, 73.07, 71.43, 70.82, 69.53, 69.03, 68.33, 56.00, 55.81, 55.21, 55.15, 41.15; HR MALDI-TOF MS: m/z: calcd for $C_{72}H_{78}O_{14}S$ $[M+Na]^+$: 1221.5010; found: 1221.5001. The ß anomer was purified by reversed phase HPLC on an analytical C-18 column using a gradient of 50→100% acetonitrile in H_2O over 40 min. **54β**: R_f = 0.35 (EtOAc/hexanes, 1/2, v/v); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.03 (m, 30H, Ar*H*), 6.05 (s, 2H, Ar*H*), 5.04 (t, J = 6.7 Hz, 1H, SCH_2CHPh), 4.93 (d, J = 11.2 Hz, 1H, C*H*HPh), 4.79 (d, J = 12.4 Hz, 2H, C*H*HPh, CH*H*Ph), 4.73 – 4.57 (m, 6H, H-1^I, 2×CH_2Ph, CH*H*Ph), 4.52 (d, J = 12.0 Hz, 1H, CH*H*Ph), 4.49 – 4.42 (m, 2H, C*H*HPh, C*H*HPh), 4.37 (d, J = 7.8 Hz, 1H, H-1^{II}), 4.33 (d, J = 12.3 Hz, 1H, CH*H*Ph), 4.12 (d, J = 8.7 Hz, 1H, H-6$_a^I$), 4.06 (t, J = 9.7 Hz, 1H), 3.90 – 3.82 (m, 2H, H-3^I, H-5^I), 3.77 (s, 6H, 2×OMe), 3.75 (s, 3H, OMe), 3.71 – 3.62 (m, 2H, H-6$_b^I$, H-6$_a^{II}$), 3.51 – 3.39 (m, 5H, H-6$_b^{II}$, H-2^I, OMe), 3.38 – 3.27 (m, 3H, H-3^{II}, H-4^{II}, SC*H*HCH), 3.25 – 3.16 (m, 2H, H-2^{II}, H-5^{II}), 2.82 (dd, J = 13.3, 7.1 Hz, 1H, SCH*H*CHPh).; ^{13}C NMR (150 MHz, $CDCl_3$): δ 179.72, 179.71, 179.71, 179.69, 179.69, 179.68, 179.67, 179.65, 179.61, 179.60, 161.36, 161.32, 140.27, 139.51, 138.92, 138.66, 138.45, 138.31, 137.84, 128.47, 128.30, 128.24, 128.17, 128.14, 128.05, 127.96, 127.90, 127.88, 127.74, 127.70, 127.68, 127.52, 127.49, 127.32, 127.19, 127.02, 102.85, 102.05, 98.76, 97.05, 97.05, 90.92, 84.68, 84.22, 82.04, 80.81, 78.67, 78.13, 78.09, 78.08, 77.20, 76.99, 76.77, 75.47, 75.42, 75.38, 75.22, 74.64,

73.73, 73.41, 73.34, 70.12, 68.93, 68.20, 55.98, 55.69, 55.29, 41.82; HR MALDI-TOF MS: m/z: calcd for C72H78O14S [M+Na]+: 1221.5010; found: 1221.4998.

4-*S*-(2,3,5-trimethoxylphenyl)-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzoyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathianium triflate (56). Compound **56** was prepared according to the general procedure as descripted in the paper. Selected ^{1}H NMR (500 MHz, gHSQC, $CDCl_3$): δ 5.99 (H-3), 5.81 (d, *J* = 10 Hz, H-1), 5.74 (H-4), 4.88 (SCH_2CHPh), 4.50 (H-$6_{a,b}$), 4.37 (H-2), 4.30 (H-5), 4.35 (SC*H*HCHPh), 4.19 (SCH*H*CHPh); ^{13}C NMR (125 MHz, gHSQC, $CDCl_3$): δ 81.60 (C-1), 78.68 (C-2), 78.25 (C-5), 76.00 (SCH_2CHPh), 72.79 (C-3), 68.93 (C-4), 62.55 (C-6), 45.44 (SCH_2CHPh).

4-*S*-(2,3,5-trimethoxylphenyl)-2-(*S*)-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathianium triflate (57). Compound **57** was prepared according to the general procedure as descripted in the paper. Selected ^{1}H NMR (500 MHz, gHSQC, $CDCl_3$): δ 5.66 (d, *J* = 10 Hz, H-1), 5.47 (H-3), 5.22 (H-4), 5.07 (SCH_2CHPh), 4.26 (SC*H*HCHPh), 4.17 (H-$6_{a,b}$), 4.13 (SCH*H*CHPh, H-2), 3.92 (H-5); ^{13}C NMR (125 MHz, gHSQC, $CDCl_3$): δ 81.54 (C-1), 78.23 (C-2), 77.59 (C-5), 76.64 (SCH_2CHPh), 72.72 (C-3), 68.06 (C-4), 62.55 (C-6), 45.60 (SCH_2CHPh).

4-*S*-(2,3,5-trimethoxylphenyl)-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathianium triflate (58). Compound **58** was prepared according to the general procedure as descripted in the paper. Selected ^{1}H NMR (500 MHz, gHSQC, $CDCl_3$): δ 5.61 (d, *J* = 10 Hz, 1H, H-1), 5.24 (d, *J* = 15H, 1H, SCH_2CHPh), 4.92 – 4.78 (m, 3H, $PhCH_2$, PhCH*H*), 4.57 (d, *J* = 15 Hz, 1H, SCH_2CHPh), 4.49 – 4.36 (m, 3H, $PhCH_2$, SC*H*HCHPh), 3.99 – 3.97 (m, 3H, H-2, H-3, SCH*H*CHPh), 3.80 (H-4), 3.68 (H-$6_{a,b}$), 3.66 (H-5); ^{13}C NMR (125 MHz, gHSQC, $CDCl_3$): δ 82.53 (C-2,

C-3), 81.70 (C-1), 81.39 (C-5), 77.82 (SCH_2*C*HPh), 76.39 (C-4, Ph*C*H_2<), 75.53 (Ph*C*H_2<), 73.96 (Ph*C*H_2<), 67.82 (C-6), 44.69 (S*C*H_2CHPh).

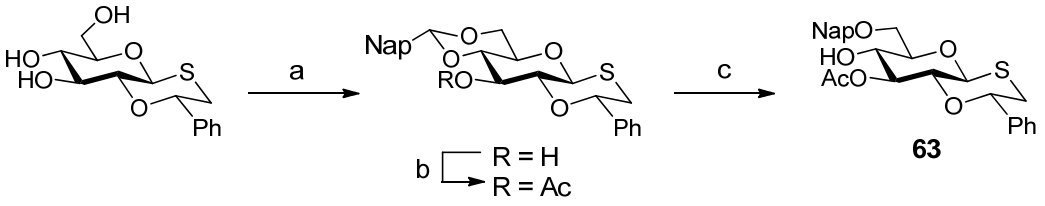
4-*S*-methyl-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzoyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathianium triflate (59). Compound **59** was prepared according to the general procedure as descripted in the paper. Selected ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 – 7.16 (Ar*H*, 20H), 5.99 (t, *J* = 9 Hz, 1H, H-3), 4.81 – 4.74 (m, 2H, H-1, H-4), 5.06 (d, *J* = 10 Hz, 1H, SCH_2C*H*Ph), 4.69 – 4.65 (m, 1H, H-6_a), 4.56 – 4.50 (m, 2H, H-5, H-6_b), 4.30 – 4.27 (m, 2H, H-2, SC*H*HCHPh), 3.72 (t, *J* = 12 Hz, 1H, SCH*H*CHPh); ^{13}C NMR (125 MHz, gHSQC, $CDCl_3$): δ 83.70 (C-1), 78.26 (C-2, C-5), 76.84 (SCH_2*C*HPh), 72.92 (C-3), 68.78 (C-4), 62.35 (C-6), 46.12 (S*C*H_2CHPh).

4-*S*-methyl-2-(*S*)-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathianium triflate (60). Compound **60** was prepared according to the general procedure as descripted in the paper. Selected ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.47 (H-1), 5.42 (H-3), 5.15 (H-4), 4.97 (SCH_2C*H*Ph), 4.25 (H-6_a), 4.16 (SC*H*HCHPh), 4.14 (H-6_b), 4.12 (H-5), 3.99 (H-2), 3.63 (SCH*H*CHPh); ^{13}C NMR (125 MHz, gHSQC, $CDCl_3$): δ 83.35 (C-1), 78.05 (C-5, C-2), 76.47 (SCH_2*C*HPh), 72.35 (C-3), 68.03 (C-4), 62.53 (C-6), 45.85 (S*C*H_2CHPh).

4-*S*-methyl-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathianium triflate (61). Compound **61** was prepared according to the general procedure as descripted in the paper. Selected ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 – 7.21 (Ar*H*, 20H), 5.31 (d, *J* = 12 Hz, 1H, H-1), 4.89 (d, *J* = 12H, 1H, SCH_2C*H*Ph), 4.83 – 4.78 (m, 2H, PhC*H*H, PhC*H*H), 4.70 (d, *J* = 12 Hz, 1H, PhCH*H*), 4.55 – 4.42 (m, 3H, PhCH_2, PhCH*H*), 4.07 (d, *J* = 12H, 1H, SC*H*HCHPh), 3.94 – 3.68 (m, 7H, H-2, H-3, H-4, H-5,

H-$6_{a,b}$, SCH*H*CHPh); ^{13}C NMR (150 MHz, gHSQC, $CDCl_3$): δ 83.73 (C-1), 82.70 (C-3), 80.91 (C-2), 80.44 (C-4), 76.50 (SCH_2*C*HPh), 76.03 (C-5), 75.91 (Ph*C*H_2<), 75.55 (Ph*C*H_2<), 73.53 (Ph*C*H_2<), 67.93 (C-6), 44.94 (S*C*H_2CHPh).

Scheme S2. Preparation of **63**



Reagents and conditions: (a) $NapCH(OMe)_2$, DMF, $TsOH \cdot H_2O$, reduced pressure (78%); (b) Ac_2O, Pyridine; (c) Et_3SiH, TfOH, -78 ^oC (83%, 2 steps).

2-(*S*)-Phenyl-(3-*O*-acetyl-6-*O*-(2-naphthyl)-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (63): R_f = 0.25 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +60.0 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.12 (m, 12H, Ar*H*), 5.11 (t, *J* = 9.3 Hz, 1H, H-3), 4.76 (2H, Nap*C*H_2), 4.67 (dd, *J* = 10.5, 1.7 Hz, 1H, SCH_2C*H*Ph), 4.47 (d, *J* = 8.9 Hz, 1H, H-1), 3.88 – 3.74 (m, 3H, H-4, H-$6_{a,b}$), 3.74 – 3.60 (m, 2H, H-2, H-5), 2.95 (dd, *J* = 14.0, 10.6 Hz, 1H, SC*H*HCHPh), 2.77 (dd, *J* = 14.0, 2.0 Hz, 1H, SCH*H*CHPh), 2.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.90, 140.44, 135.29, 133.47, 133.29, 128.69, 128.56, 128.16, 128.06, 127.94, 126.95, 126.42, 126.24, 125.91, 125.61, 81.24, 80.01, 79.74, 77.71, 77.29, 76.87, 76.08, 76.01, 74.10, 71.03, 70.06, 35.86, 21.27; HR MALDI-TOF MS: m/z: calcd for $C_{27}H_{28}O_6S$ $[M+Na]^+$: 503.1504; found: 503.1521.

2-(*S*)-Phenyl–(3,4-di-*O*-acetyl-6-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-(2-methylnaphthyl)-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (64). Compound **64** was prepared according to the general procedure using glycosyl donor **17** (53 mg, 0.11 mmol) and glycosyl acceptor **63** (43 mg, 0.091 mmol). Purification by LH20 size exclusion chromatography afforded compound **64** (69 mg, 68 %). R_f = 0.27 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +75.0 (*c* = 1.6 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 – 6.94 (m, 22H, Ar*H*), 6.08 (s, 2H, Ar*H*), 5.82 (d, *J* = 3.3 Hz, 1H, H-1^{II}), 5.52 (t, *J* = 9.5 Hz, 1H, H-3^{I}), 5.25 (t, *J* = 9.7 Hz, 1H, H-3^{II}), 4.92 (t, *J* = 9.5 Hz, 1H, H-4^{II}), 4.77 – 4.69 (m, 3H, SCH_2CHPh^{II}, CH_2Nap), 4.54 (d, *J* = 9.0 Hz, 1H, H-1^{I}), 4.45 – 4.30 (m, 2H, H-4^{I}, C*H*HPh), 4.30 – 4.18 (m, 2H, SCH_2CHPh^{I}, CH*H*Ph), 4.11 (dd, *J* = 11.5, 3.8 Hz, 1H, H-6$^{I}_{a}$), 4.06 – 3.91 (m, 2H, H-6$^{I}_{b}$, H-5^{II}), 3.84 (m, 1H, H-5^{I}), 3.81 (s, 3H, OMe), 3.77 (s, 6H, 2× OMe), 3.71 – 3.67 (m, 2H, H-2^{I}, H-2^{II}), 3.35 (dd, *J* = 10.6, 2.6 Hz, 1H, H-6$^{II}_{a}$), 3.26 (dd, *J* = 10.7, 3.7 Hz, 1H, H-6$^{II}_{b}$), 3.07 – 2.67 (m, 4H, SCH_2CHPh^{I}, SCH_2CHPh^{II}), 2.05 (s, 3H), 1.83 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.46, 170.23, 170.04, 162.13, 161.96, 142.19, 140.53, 138.03, 136.09, 133.50, 133.11, 128.66, 128.48, 128.37, 128.18, 128.17, 128.03, 127.96, 127.85, 127.80, 127.53, 126.33, 126.30, 126.15, 125.89, 125.86, 125.45, 101.43, 97.11, 91.17, 84.20, 82.15, 80.71, 79.61, 79.47, 77.67, 77.25, 76.82, 75.64, 74.15, 73.78, 73.50, 72.35, 69.70, 69.29, 69.19, 68.47, 56.21, 55.57, 43.33, 35.76, 21.80, 20.91, 20.39; HR MALDI-TOF MS: m/z: calcd for $C_{61}H_{66}O_{16}S_2$ $[M+Na]^+$: 1141.3690; found: 1141.3697.

2-(*S*)-Phenyl 3-*O*-acetyl-6-*O*-benzyl-4-*O*(9-fluorenylmethyloxycarbonyl)-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→4)-

3-*O*-acetyl-6-*O*-(2-methylnaphthyl)-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (65). Compound **65** was prepared according to the general glycosylation procedure using glycosyl donor **19** (67 mg, 0.09 mmol) and glycosyl acceptor **63** (40 mg, 0.08 mmol). Purification by LH20 size exclusion chromatography afforded compound **65** (60 mg, 56%). R_f = 0.33 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +56.0 (*c* = 2.5 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 – 6.97 (m, 30H, Ar*H*), 6.08 (s, 2H, Ar*H*), 5.86 (d, *J* = 3.1 Hz, 1H, H-1^{II}), 5.55 (t, *J* = 9.5 Hz, 1H, H-3^{I}), 5.41 (t, *J* = 9.7 Hz, 1H, H-3^{II}), 4.94 – 4.64 (m, 4H, SCH_2CHPh^{I}, CH_2Nap, H-4^{II}), 4.55 (d, *J* = 8.9 Hz, 1H, H-1^{I}), 4.48 – 4.19 (m, 5H, SCH_2CHPh^{II}, H-4^{I}, CH_2Ph, C*H*H Fmoc), 4.18 – 4.05 (m, 4H, H-5^{II}, C*H* Fmoc, CH*H* Fmoc, H-6$_a^{I}$), 3.97 (d, *J* = 11.1 Hz, 1H, H-6$_b^{I}$), 3.92 – 3.61 (m, 12H, H-5^{I}, H-2^{I}, H-2^{II}, 3×OMe), 3.51 – 3.29 (m, 2H, H-6$_{a,b}^{II}$), 3.05 – 2.75 (m, 4H, SCH_2CHPh^{I}, SCH_2CHPh^{II}), 2.07 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.19, 169.79, 161.91, 161.73, 154.28, 143.28, 143.18, 141.95, 141.20, 141.16, 140.30, 137.83, 135.86, 133.27, 132.90, 128.43, 128.20, 128.15, 127.98, 127.85, 127.65, 127.62, 127.51, 127.29, 127.25, 127.21, 126.16, 126.08, 125.89, 125.70, 125.64, 125.25, 125.21, 125.15, 119.96, 101.13, 96.82, 90.93, 84.09, 81.98, 80.41, 79.38, 77.45, 77.02, 76.60, 75.37, 73.95, 73.66, 73.58, 73.32, 71.69, 70.18, 68.90, 68.85, 68.38, 55.97, 55.33, 46.54, 43.11, 35.51, 21.58, 20.16; HR MALDI-TOF MS: m/z: calcd for $C_{74}H_{74}O_{17}S_2$ $[M+Na]^+$: 1321.4265; found: 1321.4659.

2-(*S*)-Phenyl 3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-(2-methylnaphthyl)-1,2-dideoxy-ß-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (66). Compound **66** was prepared according to the general glycosylation procedure using

glycosyl donor **20** (40 mg, 0.082 mmol) and glycosyl acceptor **63** (33 mg, 0.069 mmol). Purification by LH20 size exclusion chromatography afforded compound **66** (42 mg, 55%). R_f = 0.25 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +36.4 (*c* = 1.1 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92 – 7.03 (m, 22H, Ar*H*), 6.09 (s, 2H, Ar*H*), 5.71 (d, *J* = 3.3 Hz, 1H, H-1^{II}), 5.47 (t, *J* = 9.5 Hz, 1H, H-3^{I}), 5.39 (t, *J* = 9.5 Hz, 1H, H-3^{II}), 4.76 (s, 2H, CH_2Nap), 4.69 (d, *J* = 9.3 Hz, 1H, SCH_2CHPh^{II}), 4.51 (d, *J* = 8.9 Hz, 1H, H-1^{I}), 4.46 (d, *J* = 11.1 Hz, 1H, C*H*HPh), 4.39 (d, *J* = 11.1 Hz, 1H, CH*H*Ph), 4.34 – 4.20 (m, 2H, H-4I, SCH_2CHPh^{I}), 4.19 – 4.09 (m, 2H, H-$6^{II}_{a,b}$), 4.09 – 4.01 (m, 2H, H-5^{II}, H-6^{I}_{a}), 3.96 (d, *J* = 10.3 Hz, 1H, H-6^{I}_{b}), 3.87 – 3.75 (m, 10H, 3×OMe, H-5^{I}), 3.66 (t, *J* = 9.3 Hz, 1H, H-2^{I}), 3.46 (dd, *J* = 10.0, 3.3 Hz, 1H, H-2^{II}), 3.33 (t, *J* = 9.5 Hz, 1H, H-4^{II}), 3.06 – 2.89 (m, 3H, SCH_2CHPh^{I}, $SCHHCHPh^{II}$), 2.82 (dd, *J* = 13.9, 1.8 Hz, 1H, $SCHHCHPh^{II}$), 2.08 (s, 3H), 1.96 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.62, 170.46, 169.72, 162.13, 161.92, 141.85, 140.56, 137.71, 135.97, 133.49, 133.11, 128.65, 128.40, 128.21, 128.17, 128.11, 127.87, 127.84, 127.76, 126.78, 126.40, 126.10, 125.89, 125.85, 125.49, 101.85, 96.72, 91.20, 84.11, 82.03, 80.82, 79.57, 79.41, 77.68, 77.46, 77.26, 76.84, 76.53, 75.76, 74.55, 73.93, 73.76, 73.18, 69.30, 68.99, 63.25, 56.22, 55.61, 43.12, 35.80, 21.66, 21.03, 20.83; HR MALDI-TOF MS: m/z: calcd for $C_{61}H_{66}O_{16}S_2$ $[M+Na]^+$: 1141.3690; found: 1141.3685.

2-(*S*)-Phenyl 2,3-di-*O*-acetyl-6-*O*-benzyl-4-*O*- (9-fluorenylmethyloxycarbonyl)- α-D-glucopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-(2-methylnaphthyl)-1,2-dideoxy- ß -D-glucopyranoso)[1,2-e]-1,4-oxathiane (67). C-2 auxiliary of **65** was removed using general procedure. Then the residue was redissolved in pyridine and an equal volume of acetic anhydride was added. After stirring for 16 h, the solvents were removed and the

product was purified by silica column chromatography to afford **67** (89%, 2 steps). R_f = 0.35 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^d_{26}$ (deg cm^3 g^{-1} dm^{-1}) = +23.5 (*c* = 0.8 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.99 – 7.00 (m, 25H, Ar*H*), 5.57 (d, *J* = 3.9 Hz, 1H, H-3^{II}), 5.52 (t, *J* = 9.9 Hz, 1H, H-3^{II}), 5.39 (t, *J* = 9.4 Hz, 1H, H-3^{I}), 5.04 (t, *J* = 9.9 Hz, 1H, H-4^{II}), 4.93 – 4.75 (m, 2H, H-2^{II}, C*H*HNap), 4.75 – 4.61 (m, 2H, CH*H*Nap, SCH_2C*H*Ph), 4.51 (d, *J* = 8.9 Hz, 1H, H-1^{I}), 4.41 – 3.95 (m, 8H, H-4^{I}, CH_2 Fmoc, CH Fmoc, CH_2Ph, H-5^{II}, H-6^{I}_a), 3.86 (d, *J* = 10.9 Hz, 1H, H-6^{I}_b), 3.75 (d, *J* = 9.5 Hz, 1H, H-5^{I}), 3.61 (t, *J* = 9.3 Hz, 1H, H-2^{I}), 3.40 – 3.14 (m, 2H, H-6^{II}_a, H-6^{II}_b), 2.96 (dd, *J* = 14.0, 10.5 Hz, 1H, SC*H*HCHPh), 2.82 (dd, *J* = 13.9, 2.0 Hz, 1H, SCH*H*CHPh), 2.07 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.81, 170.57, 170.15, 154.24, 143.47, 143.34, 141.47, 140.28, 137.77, 135.79, 133.49, 133.24, 128.70, 128.39, 128.37, 128.21, 128.17, 127.93, 127.84, 127.74, 127.51, 127.46, 126.77, 126.35, 126.15, 126.12, 125.36, 125.32, 120.30, 120.28, 95.25, 81.96, 80.30, 79.74, 77.67, 77.45, 77.25, 76.83, 75.95, 75.83, 74.24, 73.56, 73.07, 71.11, 70.58, 70.53, 69.75, 69.00, 68.76, 67.81, 60.62, 46.77, 35.73, 21.31, 20.94, 20.86; HR MALDI-TOF MS: m/z: calcd for $C_{59}H_{58}O_{15}S$ $[M+Na]^+$: 1061.3394; found: 1061.3387.

3-azidopropyl 2,3-di-*O*-acetyl-6-*O*-benzyl-4-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-glucopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-(2-methylnaphthyl)-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranoside (70). Compound **67** was oxidized to give sulfoxide donor **68** according to the general procedure. Compound **70** was prepared according to the general glycosylation procedure using glycosyl donor **68** (45 mg, 0.04 mmol) and glycosyl acceptor **69** (22 mg, 0.22 mmol). Purification by LH20 size exclusion chromatography afforded compound **70** (48 mg, 86%). R_f = 0.26

(EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +80.0 (*c* = 0.8 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 – 6.97 (m, 25H, Ar*H*), 6.11 (s, 2H, Ar*H*), 5.55 – 5.35 (m, 3H, H-1^{I}, H-3^{I}, H-3^{II}), 5.29 (d, *J* = 3.8 Hz, 1H, H-1^{II}), 4.97 (t, *J* = 9.9 Hz, 1H, H-4^{II}), 4.81 (dd, *J* = 10.5, 3.8 Hz, 1H, H-2^{II}), 4.72 (q, *J* = 12.2 Hz, 2H, C*H*$_2$Nap), 4.44 – 4.11 (m, 5H, SCH$_2$C*H*Ph, C*H*$_2$Ph, C*H*H Fmoc, C*H* Fmoc), 4.07 – 3.90 (m, 4H, CH*H* Fmoc, H-5^{I}, H-4^{I}, H-5^{II}), 3.83 (s, 10H, 3×OMe, H-6^{I}_{a}), 3.76 – 3.57 (m, 3H, H-6^{I}_{b}, C*H*$_2$ linker), 3.57 – 3.40 (m, 3H, H-2^{I}, C*H*$_2$ linker), 3.27 (d, *J* = 2.8 Hz, 2H, H-6^{II}_{a}, H-6^{II}_{b}), 2.94 (qd, *J* = 13.8, 6.3 Hz, 2H, SC*H*$_2$CHPh), 2.02 (s, 3H), 2.00 – 1.95 (m, 2H, C*H*$_2$ linker), 1.92 (s, 3H) 1.44 (s, 3H); ^{13}C NMR (75 MHz, CDCl3): δ 170.59, 169.82, 161.85, 161.77, 154.03, 143.23, 143.14, 141.46, 141.23, 137.56, 135.61, 133.24, 132.94, 128.22, 128.13, 128.07, 127.91, 127.88, 127.71, 127.54, 127.47, 127.26, 127.21, 126.69, 126.14, 126.11, 125.89, 125.56, 125.13, 120.04, 101.72, 97.24, 94.86, 90.96, 83.93, 78.97, 77.44, 77.22, 77.01, 76.59, 73.76, 73.65, 73.32, 73.07, 71.83, 70.26, 70.19, 69.67, 69.50, 68.86, 68.69, 67.92, 65.31, 56.02, 55.37, 48.53, 46.53, 42.74, 29.00, 20.73, 20.69, 20.67; HR MALDI-TOF MS: m/z: calcd for $C_{71}H_{75}N_3O_{19}S$ $[M+Na]^+$: 1328.4613; found: 1328.4622.

3-azidopropyl 2,3-di-*O*-acetyl-6-*O*-benzyl-4-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-glucopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-(2-methylnaphthyl)-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranoside (71). The C-2 auxiliary of **70** was removed using the general procedure. The residue was redissolved in pyridine and an equal volume of acetic anhydride was added. After stirring for 16 h, the solvent was removed and the product was purified by silica column chromatography to afford **71** (98%, 2 steps). R_f = 0.44 (EtOAc/hexanes, 1/2, v/v); $[\alpha]^{d}_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +64.7 (*c* = 1.7 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 – 6.98 (m, 20H, Ar*H*), 5.65 – 5.39

(m, 3H, H-1^{I}, H-3^{I}, H-3^{II}), 5.09 – 4.99 (m, 2H, H-1^{II}, H-4^{II}), 4.91 – 4.80 (m, 2H, H-2^{I}, H-2^{II}), 4.74 (dd, *J* = 28.2, 9.5 Hz, 2H, C*H*$_2$Nap), 4.43 – 4.11 (m, 5H, CH*H* Fmoc, C*H* Fmoc, C*H*$_2$Ph, H-4^{I}), 4.08 – 3.88 (m, 3H, C*H*H Fmoc, H-5^{I}, H-5^{II}), 3.88 – 3.67 (m, 3H, H-6^{I}_{a}, C*H*$_2$ linker), 3.58 – 3.37 (m, 3H, H-6^{I}_{b}, C*H*$_2$ linker), 3.27 (s, 2H, H-6^{II}_{a}, H-6^{II}_{b}), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.95 (s, 3H), 1.93 – 1.86 (m, 2H, C*H*$_2$ linker); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.56, 170.33, 170.01, 169.90, 154.01, 143.23, 143.10, 141.25, 137.55, 135.48, 133.25, 133.00, 128.16, 127.94, 127.71, 127.57, 127.51, 127.27, 127.22, 126.34, 126.15, 125.93, 125.70, 125.11, 120.07, 95.86, 95.15, 77.43, 77.21, 77.01, 76.59, 73.90, 73.32, 72.89, 72.75, 71.59, 71.52, 70.44, 70.29, 69.87, 69.46, 68.83, 68.50, 67.73, 65.03, 48.14, 46.54, 28.75, 21.01, 20.70, 20.66, 20.65; HR MALDI-TOF MS: m/z: calcd for $C_{56}H_{59}N_3O_{17}$ $[M+Na]^+$: 1068.3742; found: 1068.3738.

3-azidopropyl 2,3-di-*O*-acetyl-6-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-(2-methylnaphthyl)-α-D-glucopyranoside (72). *N*-methyl-2-pyrrolidone (NMP) (0.8 mL) was added to a stirred solution of **71** (130 mg, 0.022 mmol) in DCM (4 mL). After stirring for 1 h, the reaction mixture was diluted with DCM (20 mL) and washed H_2O (2 × 20 mL) and brine (20 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel (EtOAc/hexanes, 1/4→1/2, v/v) to give **72** (93 mg, 91%). R_f = 0.24 (EtOAc/hexanes, 1/2, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 – 7.06 (m, 12H, Ar*H*), 5.68 – 5.43 (m, 1H, H-3^{II}), 5.38 (d, *J* = 3.9 Hz, 1H, H-1^{I}), 5.28 – 5.09 (m, 1H, H-3^{I}), 5.01 (d, *J* = 3.7 Hz, 1H, H-1^{II}), 4.93 – 4.63 (m, 4H, H-2^{I}, H-2^{II}, CH_2Nap), 4.28 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.22 – 4.06 (m, 2H, H-4^{II}, CH*H*Ph), 3.92 (d, *J* = 9.2 Hz, 2H, H-5^{I}, H-6^{I}_{a}), 3.87 – 3.59 (m, 4H, H-6^{I}_{b}, H-4^{I}, H-5^{I}, C*H*H linker), 3.57 – 3.36 (m, 4H, C*H*H

linker, CH_2 linker, H-6$^{II}_a$), 3.32 (d, J = 10.1 Hz, 1H, H-6$^{II}_b$), 2.63 (s, 1H, OH), 2.08 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.00 (s, 2H), 1.97 – 1.81 (m, 2H, CH_2 linker); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.41, 170.97, 170.54, 170.20, 137.72, 135.73, 133.46, 133.19, 128.60, 128.40, 128.13, 127.98, 127.93, 127.78, 126.39, 126.15, 125.75, 96.06, 95.48, 77.66, 77.43, 77.23, 76.81, 73.84, 73.73, 73.09, 72.33, 71.76, 71.63, 70.95, 70.65, 70.44, 69.96, 69.57, 68.70, 65.22, 48.36, 28.95, 21.22, 21.12, 20.92, 20.88; HR MALDI-TOF MS: m/z: calcd for $C_{41}H_{49}N_3O_{15}$ $[M+Na]^+$: 846.3061; found: 846.3077.

3-azidopropyl 3,4-di-*O*-acetyl-6-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-(2-methylnaphthyl)-α-D-glucopyranoside (73). Compound **73** was prepared according to the general glycosylation procedure using glycosyl donor **17** (20 mg, 0.041 mmol) and glycosyl acceptor **72** (28 mg, 0.034 mmol). Purification by LH20 size exclusion chromatography afforded compound **73** (32 mg, 65%). R_f = 0.51 (acetone/toluene, 1/4, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ7.99 – 6.96 (m, 22H, ArH), 6.10 (s, 2H, ArH), 5.69 (d, J = 3.4 Hz, 1H, H-1^{III}), 5.64 (t, J = 10.1 Hz, 1H, H-3^{I}), 5.55 (t, J = 9.6 Hz, 1H, H-3^{II}), 5.42 (d, J = 3.9 Hz, 1H, H-1^{I}), 5.25 (t, J = 9.8 Hz, 1H, H-3^{III}), 5.00 (d, J = 3.7 Hz, 1H, H-1^{II}), 4.93 (t, J = 9.8 Hz, 1H, H-4^{III}), 4.81 (dd, J = 10.1, 3.7 Hz, 2H, H-2^{I}, H-2^{II}), 4.76 – 4.63 (m, 2H, CH_2Nap), 4.39 (d, J = 11.9 Hz, 1H, CHHPh), 4.31 – 4.13 (m, 6H, CHHPh, CH_2Ph SCH$_2$CHPh, H-4^{I}, H-4^{II}), 4.06 – 3.85 (m, 5H, H-5^{I}, H-5^{II}, H-5^{III}, H-6$^{III}_a$, H-6$^{III}_b$), 3.85 – 3.63 (m, 12H, 3×OMe, H-2^{III}, CHH linker, H-6$^{I}_a$), 3.53 – 3.34 (m, 4H, CH_2 linker, CHH linker, H-6$^{I}_b$), 3.27 (d, J = 10.8 Hz, 1H, H-6$^{II}_a$), 3.15 (dd, J = 10.6, 3.3 Hz, 1H, H-6$^{II}_b$), 3.00 (dd, J = 13.8, 4.0 Hz, 1H, SCHHCHPh), 2.86 (dd, J = 13.6, 8.6 Hz, 1H, SCHHCHPh), 2.07 (s,

3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.92 – 1.80 (m, 5H, CH_2 linker, C*H*$_3$), 1.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ171.02, 170.57, 170.23, 169.94, 162.07, 161.93, 142.11, 138.30, 137.96, 135.89, 133.51, 133.21, 128.46, 128.35, 128.28, 128.21, 128.12, 127.91, 127.83, 127.49, 127.31, 126.43, 126.33, 126.20, 125.92, 101.54, 97.21, 96.10, 95.43, 91.17, 83.52, 78.82, 77.65, 77.43, 77.23, 76.81, 73.85, 73.54, 73.25, 73.05, 72.75, 72.44, 71.83, 71.66, 71.49, 69.99, 69.22, 68.76, 68.18, 65.19, 56.16, 55.56, 48.37, 43.04, 28.96, 21.73, 21.25, 20.90, 20.50; HR MALDI-TOF MS: m/z: calcd for $C_{78}H_{87}N_3O_{25}S$ $[M+Na]^+$: 1484.5247; found: 1484.5251.

3-azidopropyl 2,3,4-tri-*O*-acetyl-6-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-benzyl-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-(2-methylnaphthyl)-α-D-glucopyranoside (74). The C-2 auxiliary of **73** was removed using general procedure as described. The residue was redissolved in pyridine and equal volume of acetic anhydride was added. After stirring for 16 h, the solvents were removed and the product was purified by silica column chromatography to afford **74** (76%, 2 steps). R_f = 0.57 (EtOAc/hexanes, 1/1, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ7.95 – 7.03 (m, 17H, Ar*H*), 5.54 (t, *J* = 9.6 Hz, 1H, H-3^{I}), 5.49 – 5.29 (m, 4H, H-1^{II}, H-1^{III}, H-3^{II}, H-3^{III}), 5.15 (t, *J* = 9.9 Hz, 1H, H-4^{III}), 5.01 (d, *J* = 3.7 Hz, 1H, H-1^{I}), 4.88 – 4.64 (m, 5H, H-2^{III}, H-2^{II}, H-2^{I}, C*H*$_2$Nap), 4.42 (d, *J* = 12.1 Hz, 1H, CH*H*Ph), 4.23 – 3.88 (m, 7H, C*H*$_2$Ph, C*H*HPh, H-6$_a^{I}$, H-5^{I}, H-4^{II}, H-4^{I}), 3.88 – 3.64 (m, 4H, C*H*H linker, H-6$_b^{I}$, H-5^{III}, H-5^{II}), 3.64 – 3.37 (m, 4H, H-6$_a^{II}$, C*H*$_2$ linker, C*H*H linker), 3.28 (d, *J* = 10.8 Hz, 1H, H-6$_b^{II}$), 3.17 – 3.07 (m, 2H, H-6$_{a,b}^{III}$), 2.09 – 1.97 (4×s, 18H), 1.96 – 1.80 (m, 5H, C*H*$_2$ linker overlap); ^{13}C NMR (75 MHz, CDCl3): δ170.91, 170.74, 170.56, 170.46, 170.18, 170.15, 169.52, 138.17, 137.75, 135.83, 133.51, 133.24, 128.48, 128.42, 128.36, 128.20,

128.17, 127.92, 127.88, 127.67, 127.39, 126.54, 126.30, 126.07, 125.97, 96.12, 95.46, 95.12, 77.66, 77.44, 77.24, 76.81, 74.12, 73.54, 72.85, 72.49, 72.13, 71.75, 71.27, 70.99, 70.81, 70.53, 70.11, 69.15, 69.00, 68.79, 68.48, 67.47, 65.22, 48.35, 28.97, 21.21, 20.96, 20.86, 20.83; HR MALDI-TOF MS: m/z: calcd for $C_{60}H_{71}N_3O_{23}$ $[M+Na]^+$: 1224.4376; found: 1224.4370.

3-azidopropyl 2,3,4-tri-*O*-acetyl-6-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-benzyl-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-α-D-glucopyranoside (75). 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (9.4 mg, 0.066 mmol) was added to a stirred solution of **74** (27 mg, 0.022 mmol) in DCM (2 mL) and H_2O (0.2 mL). After stirring for 2 h, the reaction mixture was diluted with DCM (20 mL) and washed with saturated $NaHCO_3$ (2 × 20 mL), brine (20 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel (EtOAc/hexanes, 2/1→1/1, v/v) to give **74** (22 mg, 92%). R_f = 0.37 (EtOAc/hexanes, 1/1, v/v); ^{1}H NMR (300 MHz, $CDCl_3$): δ7.41 – 7.16 (m, 10H), 5.55 (t, *J* = 9.6 Hz, 1H, H-3^{II}), 5.46 – 5.25 (m, 3H, H-1^{I}, H-1^{III}, H-3^{III}), 5.08 (t, *J* = 9.8 Hz, 1H, H-4^{III}), 4.97 (d, *J* = 3.7 Hz, 1H, H-1^{II}), 4.83 (dd, *J* = 10.5, 4.0 Hz, 1H, H-2^{III}), 4.80 – 4.69 (m, 2H, H-2^{I}, H-2^{II}), 4.55 (s, 2H, C*H*$_2$Ph), 4.50 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.27 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.01 – 3.88 (m, 3H, C*H*$_2$ linker, H-4^{I}), 3.88 – 3.65 (m, 5H, H-5^{II}, H-5^{III}, H-6^{I}_a, C*H*$_2$ linker), 3.58 – 3.38 (m, 3H, H-6^{I}_b, H-6^{III}_a, H-6^{III}_b), 3.33 – 3.19 (m, 2H, H-6^{II}_a, H-6^{II}_b), 2.72 (dd, *J* = 7.7, 4.9 Hz, 1H, O*H*), 2.04 – 1.9 (6s, 23H, 7×Me, C*H*$_2$ linker overlap); ^{13}C NMR (75 MHz, CDCl3): δ170.95, 170.73, 170.50, 170.32, 170.14, 170.08, 169.57, 137.70, 137.47, 128.69, 128.58, 128.17, 128.14, 128.07, 128.02, 96.20, 95.76, 95.60, 77.65, 77.43, 77.23, 76.80, 74.04, 73.72,

73.11, 72.46, 72.35, 71.86, 71.58, 70.84, 70.76, 70.33, 70.23, 70.04, 69.59, 69.02, 68.92, 67.77, 65.20, 60.84, 48.35, 28.98, 21.22, 21.16, 20.90, 20.86, 20.84, 20.80; HR MALDI-TOF MS: m/z: calcd for $C_{49}H_{63}N_3O_{23}$ $[M+Na]^+$: 1084.3750; found: 1084.3759.

3-azidopropyl 2,3,4-tri-*O*-acetyl-6-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-benzyl-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-{3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-[(1*S*)-phenyl-2-(2,3,5-trimethoxyphenylsulfanyl)-ethyl]-α-D-glucopyranosyl}-α-D-glucopyranoside (76). Compound **76** was prepared according to the general glycosylation procedure using glycosyl donor **20** (35 mg, 0.072 mmol) and glycosyl acceptor **75** (25 mg, 0.024 mmol). Purification by LH20 size exclusion chromatography afforded compound **76** (28 mg, 70%). R_f = 0.19 (EtOAc/hexanes, 1/1, v/v); $[\alpha]^d_{29}$ (deg cm^3 g^{-1} dm^{-1}) = +80.0 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.05 (m, 15H, Ar*H*), 6.14 (s, 2H, Ar*H*), 5.77 (d, *J* = 3.4 Hz, 1H, H-1^{IV}), 5.58 – 5.40 (m, 4H, H-3^{II}, H-3^{I}, H-3^{IV}, H-1^{III}), 5.37 – 5.26 (m, 2H, H-1^{I}, H-3^{III}), 5.17 (t, *J* = 9.9 Hz, 1H, H-4^{III}), 4.98 (d, *J* = 3.8 Hz, 1H, H-1^{II}), 4.87 – 4.77 (m, 3H, H-2^{I}, H-2^{II}, H-2^{III}), 4.64 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.48 – 4.37 (m, 2H, CH*H*Ph, C*H*HPh), 4.34 – 4.16 (m, 5H, SCH_2CHPh, H-4^{II}, H-4^{I}, CH_2Ph), 4.09 – 3.94 (m, 7H, H-5^{I}, H-5^{II}, H-5^{IV}, CH*H*Ph, H-6^{I}_{a}, H-$6^{IV}_{a,b}$), 3.94 – 3.78 (m, 13H, 3×OMe, H-5^{III}, H-6^{I}_{b}, C*H*H linker, H-6^{II}_{a}), 3.68 (dd, *J* = 10.2, 3.4 Hz, 1H, H-2^{IV}), 3.54 – 3.34 (m, 5H, CH_2 linker, CH*H* linker, H-6^{II}_{b}, H-4^{IV}), 3.22 – 3.05 (m, 3H, SC*H*HCHPh, H-$6^{III}_{a,b}$), 2.82 (dd, *J* = 14.1, 8.8 Hz, 2H, SCH*H*CHPh), 2.12 – 1.85 (m, 20H, 6×OAc, CH_2 linker), 1.76 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (150 MHz, CDCl3): δ 179.62, 179.60, 179.58, 179.57, 179.55, 170.67, 170.55, 170.45, 170.05, 170.01, 169.91, 169.47, 169.37, 161.79, 161.57, 142.26, 138.62, 137.64, 137.48, 128.33, 128.19, 128.13, 128.11, 127.95, 127.90, 127.82, 127.53,

127.46, 127.27, 127.18, 125.93, 101.25, 98.11, 95.89, 95.54, 95.06, 90.89, 84.21, 80.22, 77.99, 77.21, 76.99, 76.78, 76.52, 74.00, 73.71, 73.64, 73.54, 73.19, 72.56, 72.53, 71.53, 71.16, 71.08, 71.04, 70.25, 70.22, 70.09, 68.87, 68.81, 68.49, 68.43, 66.83, 65.05, 65.00, 63.02, 55.87, 55.36, 48.22, 42.89, 28.70, 20.99, 20.98, 20.84, 20.70, 20.67, 20.64, 20.60, 20.52, 20.31. HR MALDI-TOF MS: m/z: calcd for $C_{83}H_{101}N_3O_{33}S$ $[M+Na]^+$: 1722.5936; found: 1722.5947.

3-azidopropyl 2,3,4-tri-*O*-acetyl-6-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-benzyl-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-(3,4-di-*O*-acetyl-6-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (78). Compound **77** was prepared according to the general glycosylation procedure using glycosyl donor **17** (19 mg, 0.039 mmol) and glycosyl acceptor **75** (21 mg, 0.020 mmol). Purification by LH20 size exclusion chromatography afforded compound **77** (25 mg, 73%, α/β=8/1). The resulting tetrasaccharide was subjected to general C-2 auxiliary removal condition to give **78** (17 mg, 85%). Isomers were separated by silica gel chromatography. **78α**: R_f = 0.14 (EtOAc/hexanes, 1/1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ7.41 – 7.14 (m, 15H, Ar*H*), 5.50 (t, *J* = 9.5 Hz, 1H, H-3^{II}), 5.45 (d, *J* = 4.0 Hz, 1H, H-1^{III}), 5.40 (t, *J* = 9.6 Hz, 1H, H-3^{I}), 5.35 (d, *J* = 4.0 Hz, 1H, H-1^{I}), 5.31 (t, *J* = 9.6 Hz, 1H, H-3^{III}), 5.25 (t, *J* = 9.7 Hz, 1H, H-3^{IV}), 5.19 – 5.08 (m, 3H, H-1^{IV}, H-4^{III}, H-4^{IV}), 4.96 (d, *J* = 3.8 Hz, 1H, H-1^{II}), 4.83 (dd, *J* = 10.5, 4.0 Hz, 1H, H-2^{III}), 4.76 – 4.70 (m, 2H, H-2^{I}, H-2^{II}), 4.60 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.57 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.51 – 4.40 (m, 3H, CH*H*Ph, CH*H*Ph, C*H*HPh), 4.16 – 4.08 (m, 2H, CH*H*Ph, H-4^{I}), 4.04 – 4.00 (m, 1H, H-5^{IV}), 4.00 – 3.80 (m, 8H, H-5^{I}, H-5^{II}, H-4^{II}, H-5^{III}, CH_2 linker, H-6$^{I}_{a}$, H-6$^{II}_{a}$), 3.76 – 3.67 (m, 2H, H-2^{IV}, H-6$^{I}_{b}$), 3.57 – 3.42 (m, 5H, H-6$^{IV}_{a,b}$, CH_2 linker, H-6$^{II}_{b}$), 3.26 – 3.05

(m, 2H, H-$6^{III}_{a,b}$), 2.60 (d, *J* = 10.7 Hz, 1H, O*H*), 2.06 – 1.99 (6s, 21H), 1.97 – 1.90 (m, 2H, CH_2 linker), 1.89 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.00, 170.95, 170.52, 170.29, 170.14, 169.86, 169.80, 169.54, 169.30, 138.04, 137.68, 137.50, 128.33, 128.31, 128.30, 128.26, 128.25, 127.97, 127.95, 127.88, 127.87, 127.67, 127.60, 127.41, 127.40, 98.10, 95.75, 95.53, 95.04, 77.20, 76.99, 76.77, 73.92, 73.69, 73.45, 73.44, 73.32, 72.14, 72.08, 71.36, 71.12, 71.10, 71.01, 70.87, 70.22, 69.87, 69.68, 69.03, 68.93, 68.63, 68.59, 68.07, 67.12, 65.11, 48.11, 28.66, 20.94, 20.90, 20.69, 20.64, 20.58; HR MALDI-TOF MS: m/z: calcd for $C_{66}H_{83}N_3O_{30}$ $[M+Na]^+$: 1420.4959; found: 1420.4950. **78β**: R_f = 0.12 (EtOAc/hexanes, 1/1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 – 7.16 (m, 15H, Ar*H*), 5.50 (t, *J* = 9.0, 1H, H-3^I), 5.44 – 5.37 (m, 3H, H-1^{II}, H-1^{III}, H-3^{II}), 5.40 (t, *J* = 9.6, 1H, H-3^{III}), 5.14 (t, *J* = 9.3 Hz, 1H, H-4^{III}), 5.10 (t, *J* = 9.5 Hz, 1H, H-3^{IV}), 4.99 – 4.91 (m, 2H, H-1^I, H-4^{IV}), 4.84 (dd, *J* = 10.5, 4.0 Hz, 1H, H-2^{III}), 4.80 (dd, *J* = 10.2, 3.8 Hz, 1H, H-2^I), 4.65 (dd, *J* = 10.2, 3.8 Hz, 1H, H-2^{II}), 4.59 – 4.45 (m, 5H, 2×CH_2Ph, C*H*HPh), 4.42 (d, *J* = 7.9 Hz, 1H, H-1^{IV}), 4.23 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.12 (dd, *J* = 11.5, 1.9 Hz, 1H, H-6_a^I), 4.07 – 3.96 (m, 4H, H-6_b^I, H-4^{II}, H-5^{II}, H-4^I), 3.93 – 3.85 (m, 2H, H-5^I, H-5^{III}), 3.83 – 3.75 (m, 2H, C*H*H linker, H-6_a^{II}), 3.72 (d, *J* = 10.9 Hz, 1H, H-6_b^{II}), 3.67 – 3.60 (m, 1H, H-5^{IV}), 3.60 – 3.50 (m, 2H, H-2^{IV}, H-6_a^{IV}), 3.47 – 3.38 (m, 3H, CH_2 linker, C*H*H linker), 3.37 (d, *J* = 3.8 Hz, 1H, H-6_b^{IV}), 3.31 – 3.22 (m, 2H, H-$6_{a,b}^{III}$), 2.07 – 1.99 (7×s, 21H), 1.91 – 1.86 (2×s, 8H, CH_2 linker overlap); selected ^{13}C NMR (150 MHz, gHSQC, $CDCl_3$): δ 102. 46 (C-1^{IV}), 95.90 (C-1^I), 95.02 (C-1^{II}, C-1^{III}), 74.80 (C-3^{IV}), 73.42 (C-4^I), 73.32 (C-5^{IV}), 72.00 (C-3^{II}), 71.71 (C-3^I, C-2^{II}), 71.24 (C-4^{II}), 71.05 (C-2^I), 70.10 (C-2^{III}), 69.62 (C-3^{III}), 69.43 (C-4^{IV}, C-5^{II}, C-5^{III}), 69.96 (C-2^{IV}), 68.77 (C-4^{III}), 65.26 (*C*H_2), 48.46 (*C*H_2), 21.41 (*C*H_2) ; HR MALDI-TOF MS: m/z: calcd

for $C_{66}H_{83}N_3O_{30}$ $[M+Na]^+$: 1420.4959; found: 1420.4962.

3-aminopropyl-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-6-*O*-(ß-D-glucopyranosyl)-α-D-glucopyranoside (79). Freshly prepared NaOMe in a methanolic solution (0.2 mL, 1.5 M) was added to a stirred solution of **78α** (8 mg, 5.7 μmol) in methanol (1.5 mL). The reaction mixture was stirred for 2 h and then neutralized by the addition of Dowex® 50W X8-200 H^+ resin. The resin was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was dissolved in a mixture of *t*BuOH (4 mL), H_2O (0.1 mL), and AcOH (0.1 mL) and a catalytic amount of 20 wt% $Pd(OH)_2/C$ was added. The reaction mixture was purged with H_2 gas for 2 min followed by stirring for 6 h under and atmosphere of H_2. The progress of the reaction was monitored by MALDI-TOF mass spectrometer. Upon completion, the reaction mixture was purged with Ar gas followed by filtration through a plug of Celite. The filtrate was concentrated *in vacuo* to afford **79** (3.2 mg, 83% over two steps). ^{1}H NMR (600 MHz, D_2O): δ 5.25 (d, *J* = 3.9 Hz, 1H), 5.19 (d, *J* = 3.9 Hz, 1H), 4.82 (d, *J* = 3.6 Hz, 1H), 4.78 (d, *J* = 3.8 Hz, 1H), 3.87 – 3.20 (m, 26H), 3.11 – 2.94 (m, 2H), 1.91 – 1.81 (m, 2H); selected ^{13}C NMR (150 MHz, gHSQC, $CDCl_3$): δ 99.80 (C-1), 98.44 (C-1), 98.02 (C-1), 78.14, 76.79, 73.66, 72.81, 72.39, 71.96 (C-2), 71.46 (C-2), 71.03, 69.51, 66.21 (*C*H_2, linker), 60.46 (C-6), 37.70 (*C*H_2, linker), 26.70 (*C*H_2, linker). HR MALDI-TOF MS: m/z: calcd for $C_{27}H_{49}NO_{21}$ $[M+Na]^+$: 746.2695; found: 746.2683.

2. NMR analysis of sulfonium ion 55

Sulfonium ions were prepared according to general procedures. As an example, detailed analysis for 4-*S*-(2,3,5-trimethoxylphenyl)-2-(*S*)-phenyl-(3,4-di-acetyl-6-*O*-benzyl-1,2-

dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathianium triflate (**55**) was discussed here.

A mixture of *R*/*S* sulfoxide **17** (5.0 mg, 10 μmol), 1,3,5-trimethoxybenzene (2.6 mg, 16 μmol), 2,6-di-*tert*-butyl-4-methylpyridine (4.2 mg, 21 μmol) and activated molecular sieves (4 Å, pellets) in $CDCl_3$ (1 mL) was shaken for 30 min under an atmosphere of argon at room temperature. Then 0.5 mL of the solution was taken out and injected into a 5 mm NMR tube and sealed. After cooling to 0 ^oC, trifluoromethanesulfonic anhydride stock solution (25 μL, 0.23 M in $CDCl_3$) was added. After 3 min, NMR spectra of the reaction mixture were recorded (^1H, gCOSY, gHSQC and HMBC were recorded at 25 ^oC, **Fig. S1**); ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.09 (m, Ar*H*), 6.31 – 6.18 (m, 2H, Ar*H*), 5.63 (d, *J* = 9.7 Hz, 1H, H-1), 5.45 (t, *J* = 9.4 Hz, 1H, H-3), 5.30 (d, *J* = 10.7 Hz, 1H, SCH_2CHPh), 5.22 (t, *J* = 9.7 Hz, 1H, H-4), 4.47 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.38 (d, *J* = 11.8 Hz, 1H, CH*H*Ph), 4.28 (t, *J* = 11.6 Hz, 1H, $SCH_{ax}HCHPh$), 4.14 – 3.96 (m, 8H, $SCH_{eq}CHPh$, 2×OMe, H-2), 3.95 – 3.82 (m, 4H, OMe, H-5), 3.67 – 3.46 (m, 2H, H-$6_{a,b}$), 2.02 (s, 3H), 1.94 (s, 3H); selected ^{13}C NMR (200 MHz, gHSQC, $CDCl_3$): δ 81.50 (C-1), 79.38 (C-5), 78.02 (C-2), 76.74 (SCH_2CHPh), 73.62 ($PhCH_2$), 72.02 (C-3), 67.94 (C-4), 67.62 (C-6), 44.33 (SCH_2CHPh). The ^1H NMR spectrum showed that two sets of peaks corresponding to the mixture of *R*/*S* sulfoxide converted into a single set of peaks. Specifically, the anomeric proton (H-1) signal of *R*-sulfoxide (δ = 4.31, d, *J* = 10 Hz) and *S*-sulfoxide (δ = 4.14, d, *J* = 9.7 Hz) shifted downfield (δ = 5.63, d, *J* = 9.7 Hz). The retaining of β anomeric configuration and the shift of H-1 chemical shift indicated that the sulfoxide donors had completely transformed to a new intermediate within 3 min after activation. The rest of the proton signals were assigned from 2D spectra. The HMBC spectrum indicated the presence of three-bond coupling between C-1 and H-8_{eq}, which

confirmed the formation of *trans*-decalin sulfonium ion as the reactive intermediate.

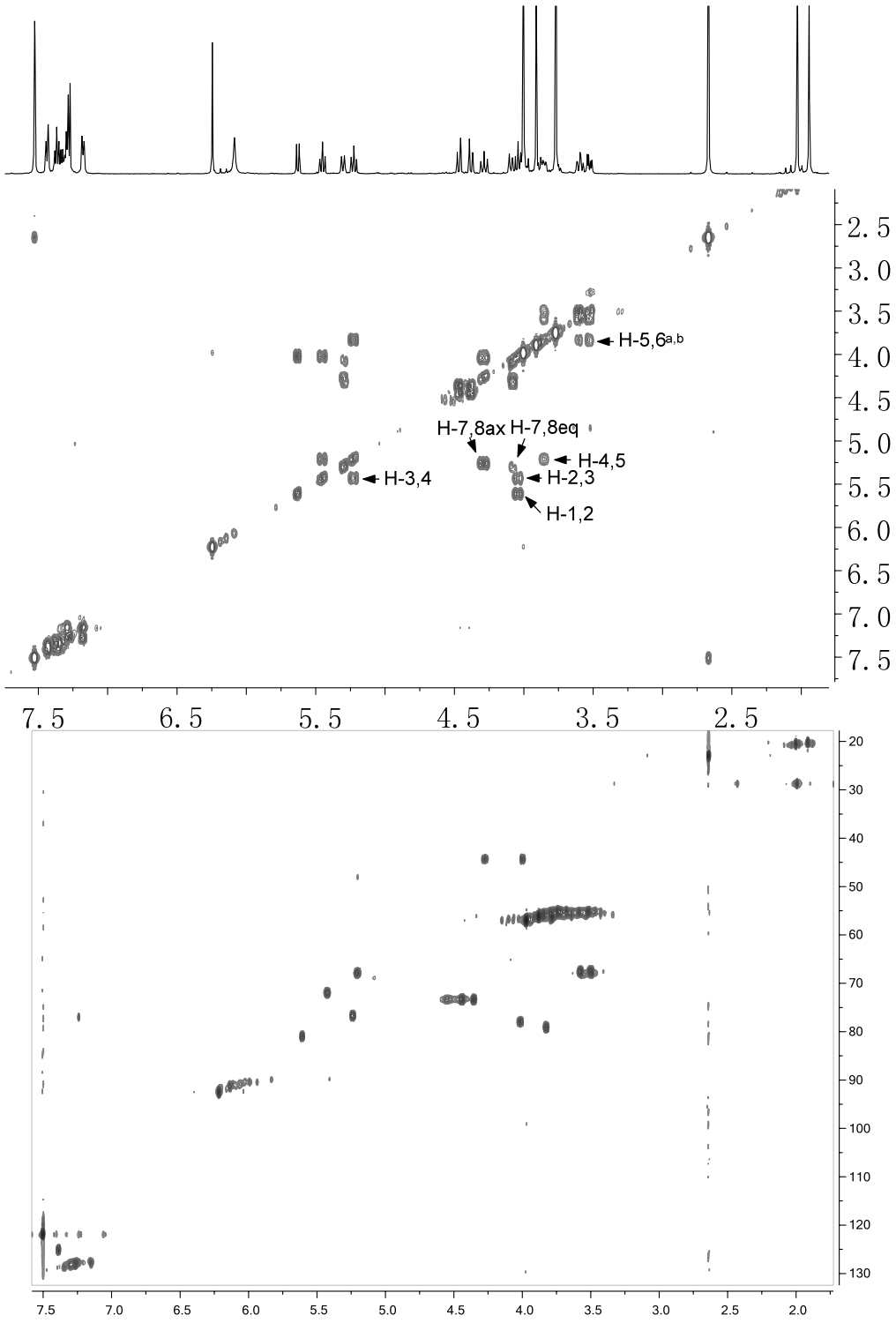


Figure S1. 1H, gCOSY, gHSQC spectra of sulfonium ion **55**.

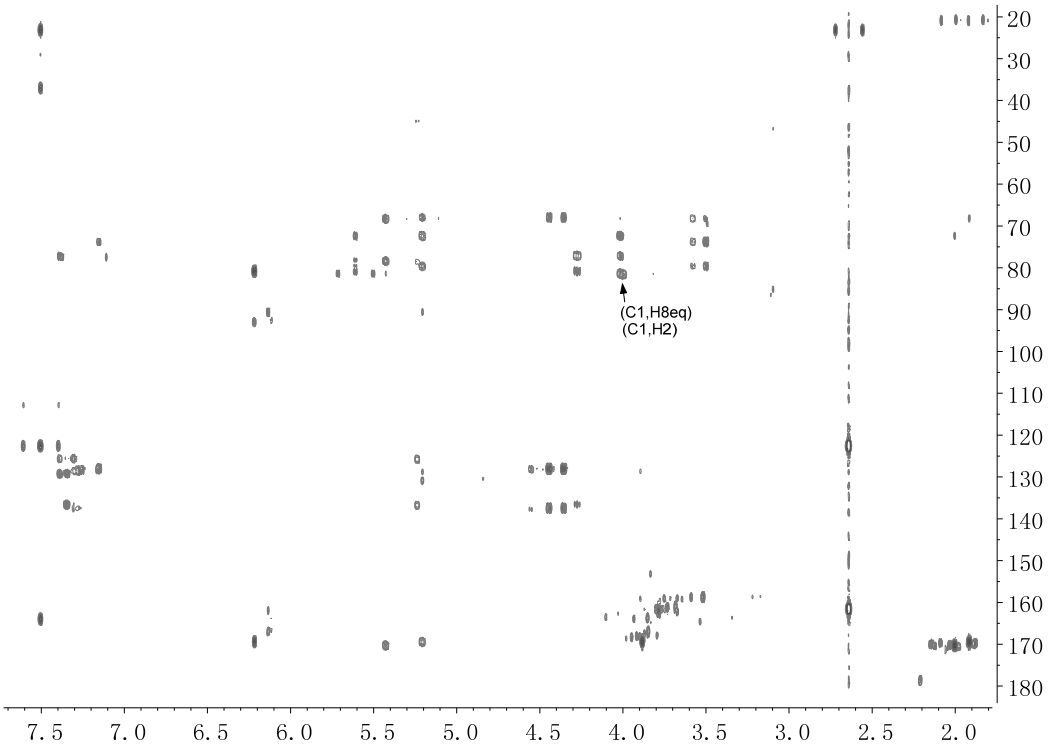


Figure S1 (cont'd). HMBC spectrum of sulfonium ion **55**.

Since sulfonium ion was proposed to be the reactive intermediate and responsible for the high stereoselectivity in glycosylations, its stability therefore is of great interest for the purpose of optimizing reaction conditions. So, the above obtained sulfonium ion **55** was continually monitored by NMR at room temperature (**Fig. S2**). Surprisingly, **55** was stable at this temperature for at least 9 h. During this period of time, the intensity of characteristic sugar peaks remained unchanged while aromatic signal (δ = 6.08) corresponding to trimethoxybenzene decreased. Subsequent heating to 45 ^{o}C in 5 min resulted prompt decomposition of the sulfonium ion. The temperature sensitivity of the sulfonium ion has also been observed when the glycosylation reaction was heated and resulted in low yield and poor stereoselectivity.

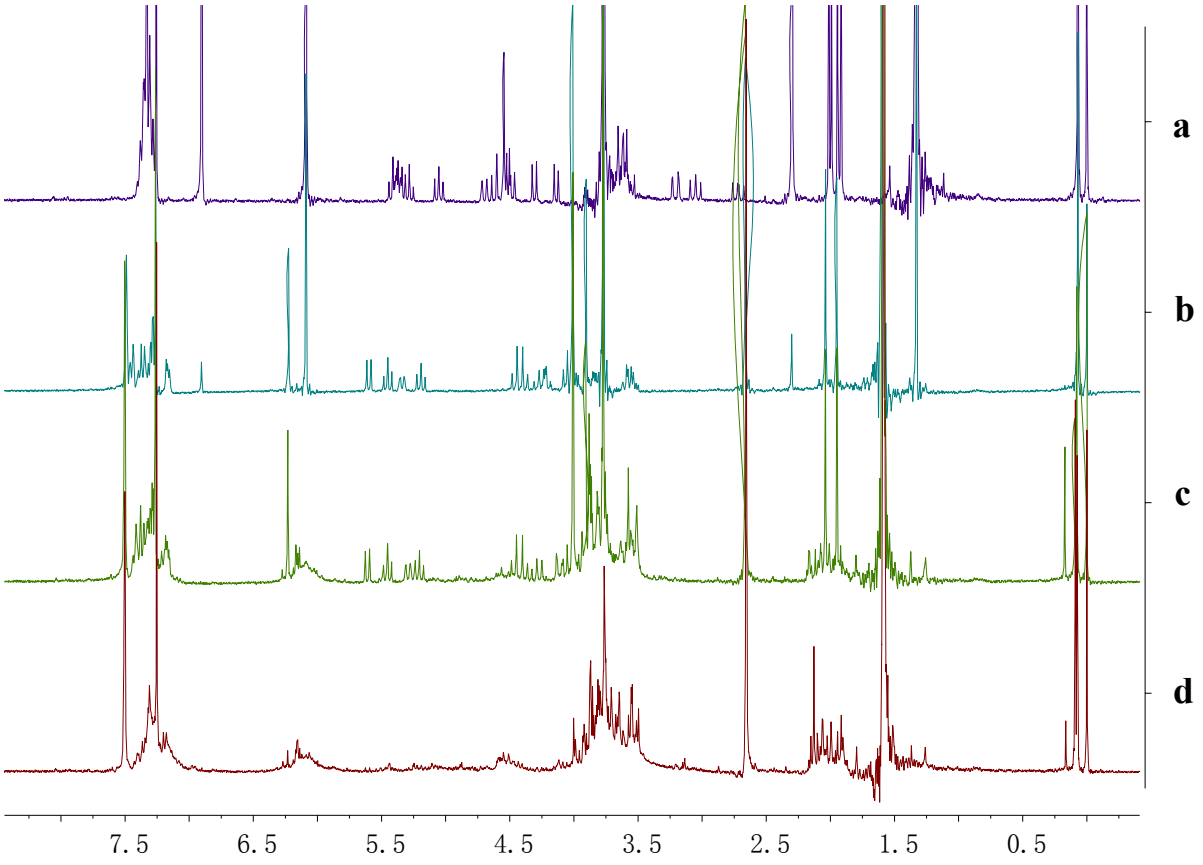


Figure S2. Thermostability of sulfonium ion **55**. a) ^{1}H spectrum of a mixture of *R/S* sulfoxide with 1,3,5-trimethoxylbenzene and DTBMP; b) ^{1}H spectrum of the activated reaction mixture after 3 min at 25 ^{o}C; c) ^{1}H spectrum of the activated reaction mixture after 9 h at 25 ^{o}C; d) ^{1}H spectrum recorded after raising to 45 ^{o}C in 5 min.

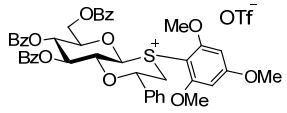
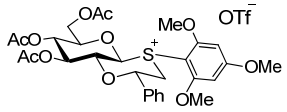
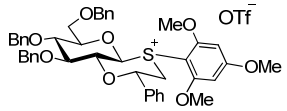
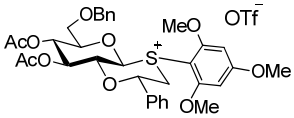
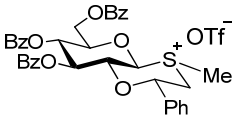
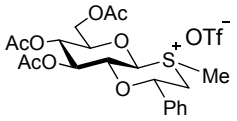
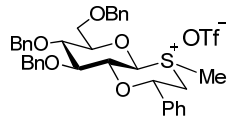
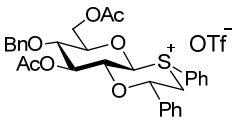
3. Assignment and conformational analysis of diastereomeric sulfonium ions

Various criteria have been applied to the assignment of diastereomeric sulfur subsitutents in a six-member ring system[2]. Usually employed methods include the comparison of the midpoint of chemical shifts for δ_{H8eq} and δ_{H8ax} or the geminal coupling constant for the AB quartet of H8eq and H8ax (**Fig. S3**). Because the substituents on heteroatoms or

elsewhere on the ring alter, the chemical shift criteria can be overridden. But coupling constant criterion has been proven to hold true regardless of the substitution in the ring[3]. Assignments have also been made for similar oxathiane sulfonium ion systems[4-6]. Generally, the equatorial diastereomer with axial lone pair has a smaller geminal coupling constant (~12 Hz) than that of the axial diastereomer with equatorial lone pair (~15 Hz). This trend has also been tested and proven to be effective for similar systems such as sulfoxide donors **17-23**, where both diastereomers are available. Therefore, similar rule was applied to the assignment of distereomeric sulfonium ions **55-61** (**Table S1**).

Figure S3. Schematic presentation for the interpretation of stereochemistry at sulfur atom using geminal coupling constant of H8eq and H8ax.

Table S1. List of δ_{H8eq}, δ_{H8ax} and $J_{eq,ax}$

Entry	Sulfonium Ion[a]	δ_{H8eq} (ppm) doublet	δ_{H8ax} (ppm) triplet	$J_{eq,ax}$ (Hz)	
1	 **56**	4.19	4.35	10.0	
2	 **57**	4.13	4.26	12.5	δ_{Heq} < δ_{Hax}
3	 **58**	3.97	4.36	11.8	
4	 **55**	3.98	4.28	11.6	
5	 **59**	4.27	3.72	11.5	
6	 **60**	4.16	3.63	12.0	δ_{Heq} > δ_{Hax}
7	 **61**	4.07	3.88	10.5	
8[6]		4.32	3.66	11.0	

Once the stereochemistry at sulfur atom was identified, we could make sure we were comparing sulfonium ions with the same stereochemistry. Then the assignment of the rest of the proton signals can be taken out. Due to the large coupling of H8ax-H9 and small coupling of H8eq-H9, they are showing characteristic splittings that give a triplet and a doublet respectively. Therefore, both H8ax and H8eq can be easily assinged on ^{1}H spectra or gHSQC spectra if there are overlaps of peaks in 1D experiment.

As shown in **Table S1**, there is a clear trend that the relative proton chemical shifts (H8ax *vs.* H8eq) of trimethoxylbenzene substituted sulfonium ions reversed when compared to methyl or the phenyl substituted sulfonium ions. This large relative chemical shift change should not be introduced by merely the inductive effect from the changing of sulfur substitutions, since H8 is three bonds away from the substitution and there is no dramatic change of the electronegativity of substitutions. However, one obvious difference between phenyl and trimethoxylbenzene is their steric effect, which may change the orientation of aromatic substitutions and therefore change the orientation of shielding/deshielding environment [7] (**Figure S4**). So, the different relative chemical shifts of H8ax and H8eq may indicate different orientations of sulfur substitutions in space, which may contribute to the slight difference when comparing phenyl and trimethoxybenzene substituted systems in regard of stereoselectivity in glycosylations.

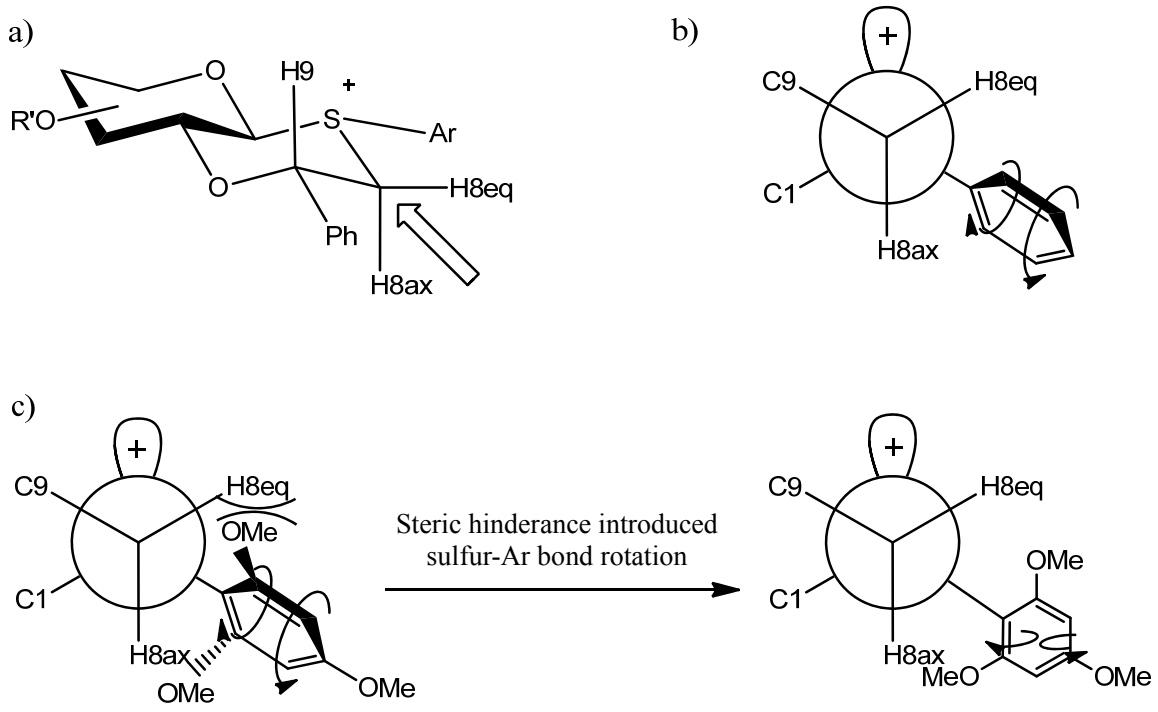
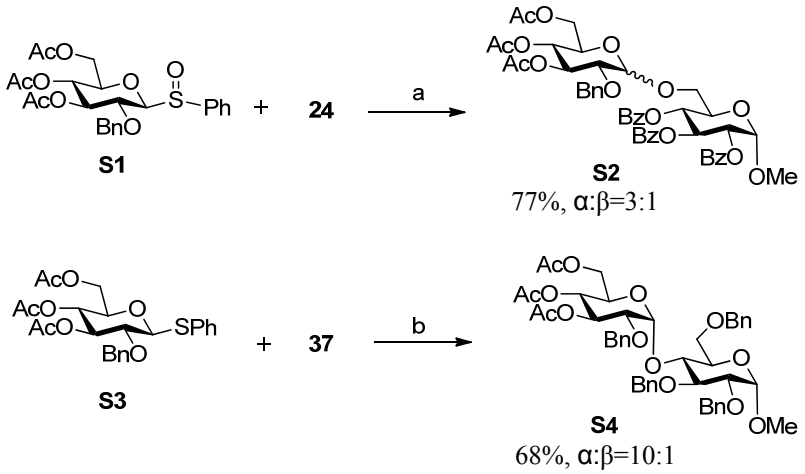


Figure S4. Schematic presentation of Sulfur-Ar bond rotation and shielding/deshielding changes for H8eq and H8ax in phenyl and trimethoxybenzene substituted sulfonium ions. a) Sight angle for the Newman projections; b) Proposed orientation of phenyl group, H8ax is located in the shielded space and H8eq is located in the deshielded space; c) Due to the steric hinderance, the favored coordination for trimethoxybenzene changed making the shielded space rotated toward H8eq.

4. Control glycosytions using donors without C-2 auxiliary

Scheme S2. Glycosylations using donors without C-2 participation



Reagents and conditions: a) TMSOTf, TEP, - 60 ^{o}C to 0 ^{o}C, 2 h[8]; b) NIS, TfOH, 0 ^{o}C.

Methyl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl-(1→6)- 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (S2). A mixture of glycosyl donor **S1**[5] (60 mg, 0.12 mmol), acceptor **24** (30 mg, 0.059 mmol) and activated molecular sieves (4 Å) in DCM (3 mL) was stirred for 60 min under an atmosphere of argon at room temperature. After cooling to -60 ^{o}C, triethyl phosphite (TEP)[9] (32 μL, 0.20 mmol) and TMSOTf (22 μL, 0.10 mmol) were added and the reaction mixture was allowed to warm to -30 ^{o}C over a period of 30 min. TLC showed donor was not fully consumed. Another 22 μL TMSOTf was added at -30 ^{o}C. Then the reaction mixture was allowed to warm to 0 ^{o}C over 2 h. After diluting with DCM (10 mL), aqueous saturated $NaHCO_3$ (10 mL) was added and the organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by sephadex® LH20 size exlusion chromatography (DCM/MeOH, 1/1) to afford the pure disaccharide **S2** (40 mg, 77%, α:β=3:1). R_f = 0.17 (EtOAc/hexanes,

1/2, v/v); **S2α:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 – 7.05 (m, 20H, Ar*H*), 6.17 (t, *J* = 9.4 Hz, 1H, H-3^{I}), 5.53 – 5.38 (m, 2H, H-5^{II}, H-4^{I}), 5.24– 5.21 (m, 2H, H-1^{I,} H-2^{I}), 4.95 (t, *J* = 9.4 Hz, 1H, H-4^{II}), 4.74 (d, *J* = 3.5 Hz, 1H, H-1^{II}), 4.65 (d, *J* = 12.5 Hz, 1H, C*H*HPh), 4.55 (d, *J* = 12.5 Hz, 1H, CH*H*Ph), 4.43 – 4.29 (m, 1H, H-5^{I}), 4.19 (q, *J* = 4.2 Hz, 2H, H-5^{II}, H-6a^{II}), 4.02 (dd, *J* = 14.2, 4.3 Hz, 1H, H-6$_b^{II}$), 3.83 (dd, *J* = 10.7, 7.6 Hz, 1H, H-6$_a^{I}$), 3.60 – 3.46 (m, 5H, H-2^{II}, H-6$_b^{I}$, OMe), 2.07 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 184.54, 175.60, 175.00, 174.83, 170.77, 170.67, 170.31, 142.70, 138.50, 138.30, 138.03, 134.87, 134.84, 134.60, 134.12, 133.97, 133.72, 133.43, 133.41, 133.35, 133.21, 132.95, 132.76, 101.60, 101.50, 82.94, 82.16, 81.95, 81.83, 81.74, 78.10, 77.12, 76.63, 75.33, 74.58, 73.55, 73.49, 72.29, 71.69, 66.94, 60.54, 25.79, 25.70, 25.63; HR MALDI-TOF MS: m/z: calcd for $C_{47}H_{48}O_{17}$ $[M+Na]^+$: 907.2789; found: 907.2799. The ß anomer was purified by reversed phase HPLC on an analytical C-18 column using a gradient of 50→100% acetonitrile in H_2O over 40 min. **S2ß:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 – 7.21 (m, 20H, Ar*H*), 6.16 (t, *J* = 9.8 Hz, 1H, H-3^{I}), 5.45 (t, *J* = 9.9 Hz, 1H, H-4^{I}), 5.29 – 5.20 (m, 2H, H-2^{I}, H-1^{I}), 5.14 (t, *J* = 9.5 Hz, 1H, H-3^{II}), 4.97 – 4.88 (m, 2H, H-4^{II}, C*H*HPh), 4.59 (dd, *J* = 15.2, 9.8 Hz, 2H, CH*H*Ph, H-1^{II}), 4.37 (t, *J* = 7.9 Hz, 1H, H-5^{I}), 4.23 (dd, *J* = 12.2, 5.2 Hz, 1H, H-6$_a^{II}$), 4.05 (t, *J* = 13.3 Hz, 2H, H-6$_b^{II}$, H-6$_a^{I}$), 3.86 (dd, *J* = 11.2, 7.5 Hz, 1H, H-6$_b^{I}$), 3.73 – 3.59 (m, 1H, H-5^{II}), 3.42 (s, 4H, H-2^{II}, OMe), 2.00 (s, 3H), 1.99 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 184.48, 184.45, 184.43, 184.42, 175.60, 175.05, 174.64, 170.75, 170.69, 170.39, 142.93, 138.48, 138.32, 138.04, 134.85, 134.79, 134.57, 134.10, 133.94, 133.90, 133.75, 133.56, 133.42, 133.35, 133.31, 133.21, 132.93, 132.71, 118.04, 108.77, 101.95, 101.83, 83.60, 82.96, 82.94, 82.94, 82.16, 81.95, 81.73, 79.33, 78.66, 76.94, 76.50, 75.26, 74.75, 74.01, 73.97,

73.57, 67.06, 60.59, 34.64, 25.63, 25.58; HR MALDI-TOF MS: m/z: calcd for $C_{47}H_{48}O_{17}$ $[M+Na]^+$: 907.2789; found: 907.2781.

Methyl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl-(1→4)- 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (S4). A mixture of glycosyl donor **S3**[5] (60 mg, 0.12 mmol), acceptor **37** (48 mg, 0.10 mmol) and activated molecular sieves (4 Å) in DCM (2 mL) was stirred for 60 min under an atmosphere of argon at room temperature. After cooling to 0 ^oC, NIS (42 mg, 0.31 mmol) was added followed by the addition of TfOH (4 μL, 0.056 mmol). The reaction mixture was stirred for 2 h at 0 ^oC before quenching by the addition of pyridine (0.1 mL) and diluting with DCM (10 mL). The reaction mixture was filtered, and the filtrate was washed with 10% $Na_2S_2O_3$ (20 mL) and brine (50 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The residue was purified by sephadex® LH20 size exlusion chromatography (DCM/MeOH, 1/1) to afford the pure disaccharide **S4** (73 mg, 68%). R_f = 0.16 (EtOAc/hexanes, 1/2, v/v); ^1H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.01 (m, 20H, Ar*H*), 5.69 (d, *J* = 3.7 Hz, 1H, H-1^{II}), 5.41 (t, *J* = 9.7 Hz, 1H, H-3^{II}), 5.03 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.93 (t, *J* = 9.7 Hz, 1H, H-4^{II}), 4.75 (d, *J* = 11.8 Hz, 1H, CH*H*Ph), 4.68 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.65 – 4.53 (m, 4H, H-1^I, CH*H*Ph, CH_2Ph), 4.44 (d, *J* = 12.2 Hz, 1H, C*H*HPh), 4.33 (d, *J* = 12.2 Hz, 1H, CH*H*Ph), 4.12 – 4.04 (m, 2H, H-3^I, H-6_a^{II}), 4.04 – 3.97 (m, 2H, H-5^{II}, H-4^I), 3.92 – 3.84 (m, 2H, H-5^I, H-6_a^I), 3.80 (dd, *J* = 12.4, 2.1 Hz, 1H, H-6_b^{II}), 3.67 (dd, *J* = 10.9, 1.6 Hz, 1H, H-6_b^{II}), 3.58 (dd, *J* = 9.4, 3.5 Hz, 1H, H-2^I), 3.47 (dd, *J* = 10.1, 3.7 Hz, 1H, H-2^{II}), 3.39 (s, 3H, OMe), 2.00 (s, 3H), 1.99 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ170.51, 170.02, 169.66, 139.05, 137.92,

137.88, 137.50, 128.56, 128.50, 128.43, 128.37, 128.33, 128.31, 128.20, 128.14, 127.93, 127.76, 127.63, 127.52, 127.39, 127.05, 126.58, 97.70, 96.39, 81.59, 80.13, 77.31, 77.09, 76.88, 76.60, 74.27, 73.47, 73.44, 73.26, 72.93, 71.72, 69.47, 68.93, 68.48, 67.72, 61.81, 55.23, 20.78, 20.72, 20.68; HR MALDI-TOF MS: m/z: calcd for $C_{47}H_{54}O_{14}$ $[M+Na]^+$: 865.3412; found: 865.3403.

5. References and notes

1. Fascione, M. A.; Adshead, S. J.; Stalford, S. A.; Kilner, C. A.; Leach, A. G.; Turnbull, W. B. *Chem. Commun.* **2009**, 5841-5843.

2. Lambert, J.B.; Featherman, S. I. *Chem. Rev*. **1975**, *75*, 611-626.

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4. Fascione, M. A.; Kilner, C. A.; Leach, A. G.; Turnbull B. W. *Chem. Eur. J.* **2012**, *18*, 321–333.

5. Mydock, L. K.; Kamat, M. N.; Demchenko, A. V. *Org. Lett*. **2011**, *13*, 2928–2931.

6. Kim, J. H.; Yang, H.; Park, J.; Boons, G. J. *J. Am. Chem. Soc.* **2005**, *127*, 12090–12097.

7. Wannere, C. S.; Schleyer, P. v. R. *Org. Lett*. **2003**, *5*, 605-608.

8. Sliedregt, L.A.J.M.; van der Mare1, G.A.; van Boom, J.H. *Tetrahedron Lett.* **1994**, *35*, 4015-4018.

9. Note: Initially, Tf_2O/DTBMP was employed as activator but the use of this reagent did not provide the desired coupling product probably due to sulfenylation as a major side reaction. Lewis acid alone was also examined as glycosylation promoters but the product yields were low probably due to the *in-situ* dimerization of generated sulfenic acid.

However, a combination of TMSOTf and TEP gave good yields of product. Probably, TEP functions as an effective acid scavenger and quencher of ionic species generated by Lewis acid activated phenylsulfenyl trimethylsilyl ester.

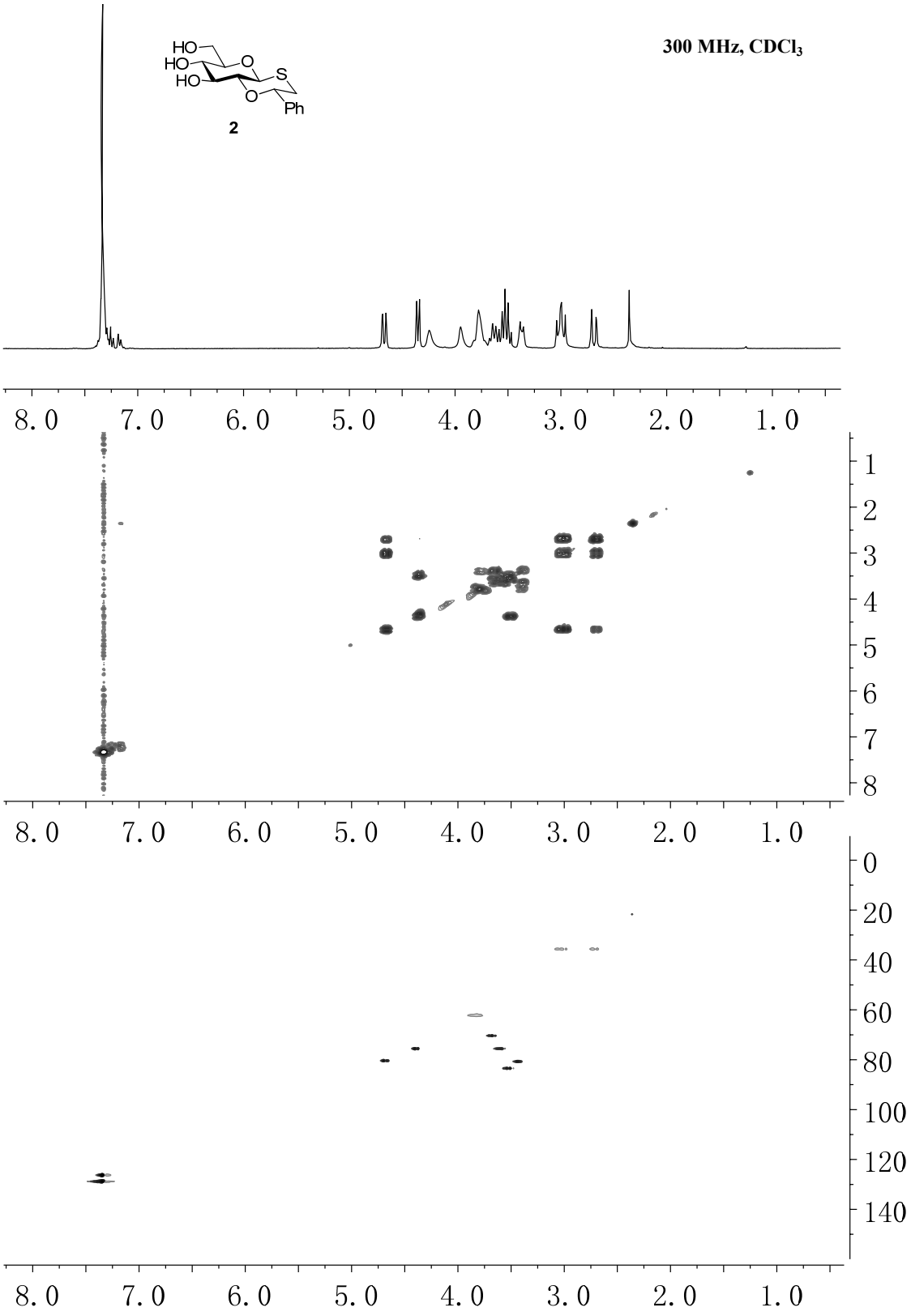
For more information, please see:

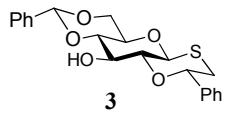
a) Ito, Y.; Ogawa, T. *Tetrahedron Lett.* **1987**, 28, 4701-4704.

b) Alonso, I.; Khiar, N.; Martin-Lomas, M. *Tetrahedron Lett.* **1996**, *37*, 1477-1480.

c) Gildersleeve, J.; Smith, A.; Sakurai, K.; Raghavan, S.; Kahne, D. *J. Am. Chem. Soc.* **1999**, *121*, 6167– 6175.

6. Copies of ^{1}H and ^{13}C NMR spectra


HO
HO
HO
O
S
O
Ph
2
300 MHz, CDCl3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
1
2
3
4
5
6
7
8
0
20
40
60
80
100
120
140



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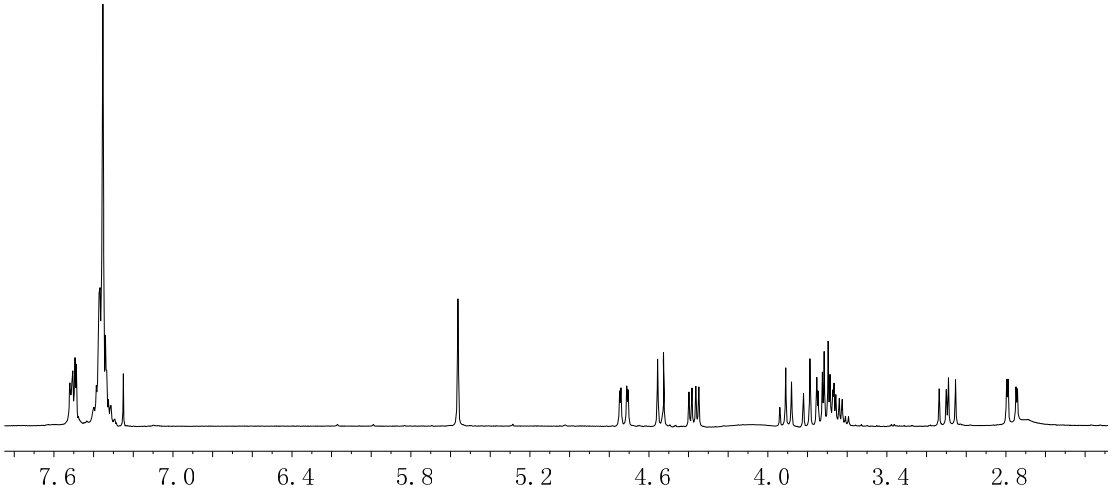
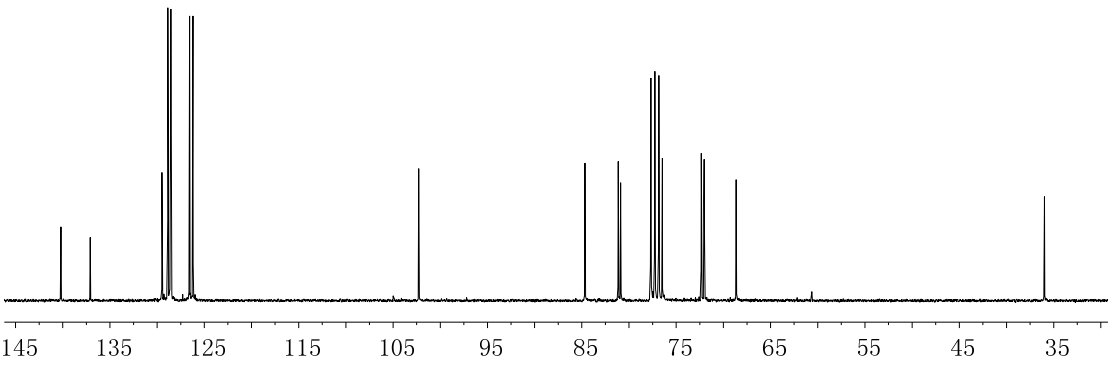
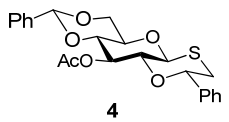
300 MHz, $CDCl_3$



75 MHz, $CDCl_3$





4

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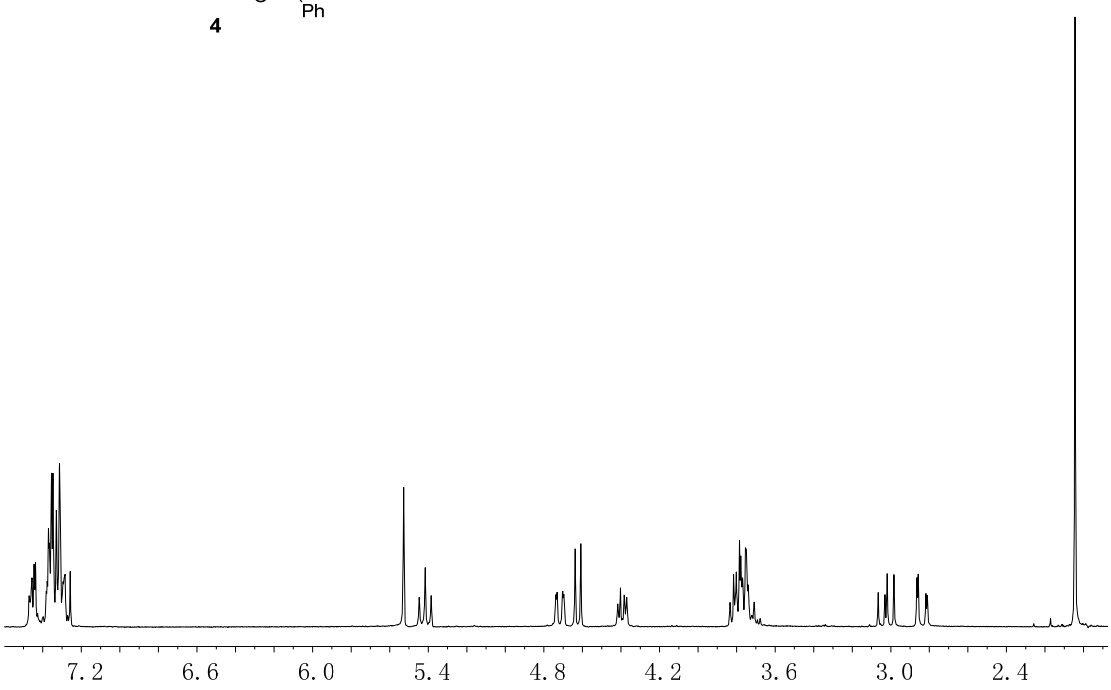

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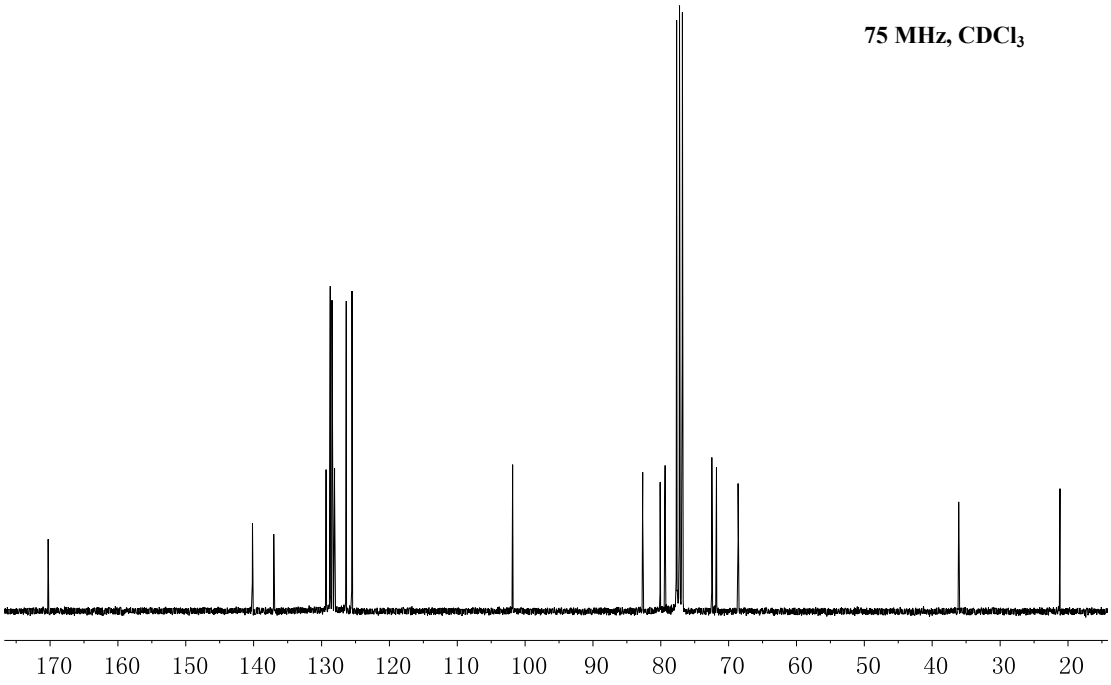

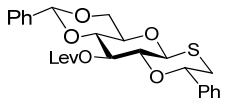

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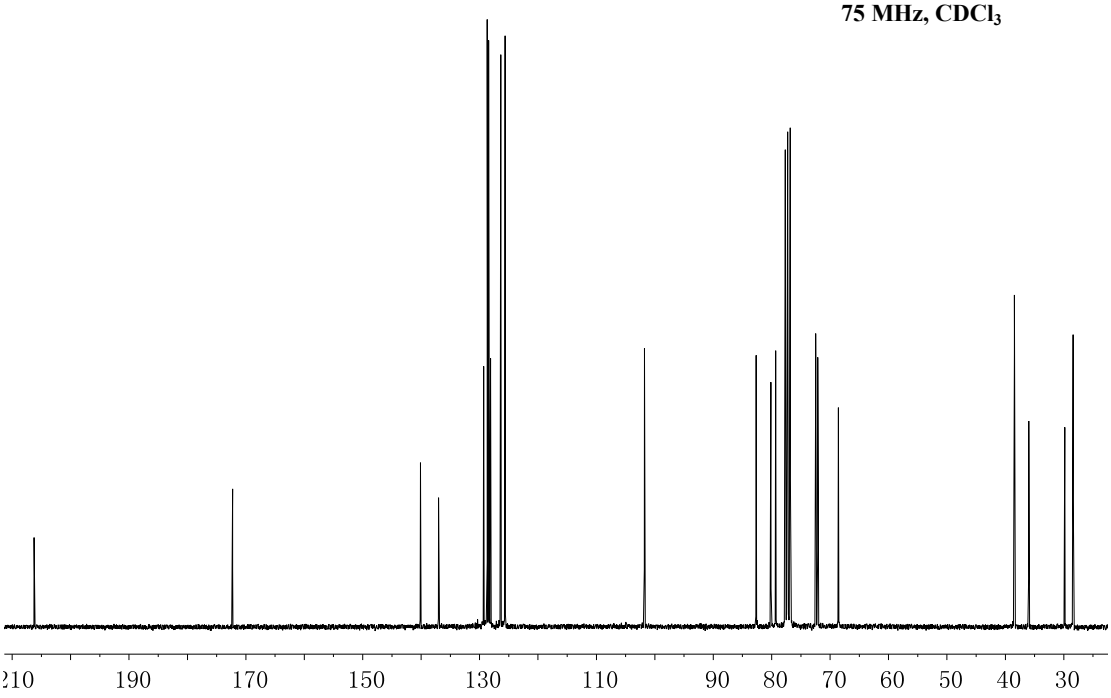
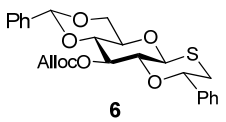
300 MHz, $CDCl_3$

75 MHz, $CDCl_3$





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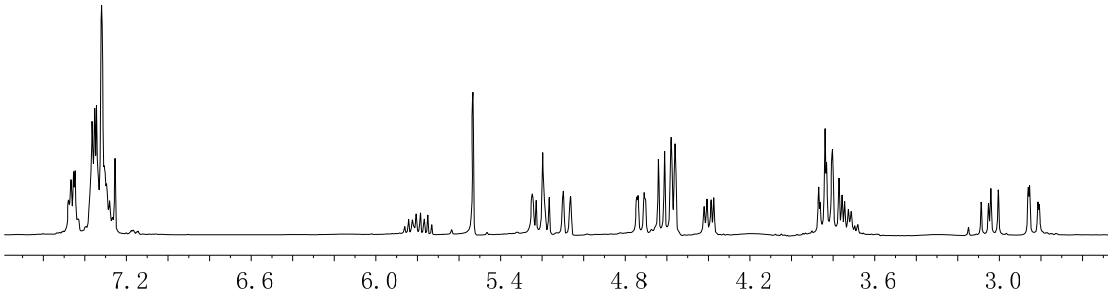
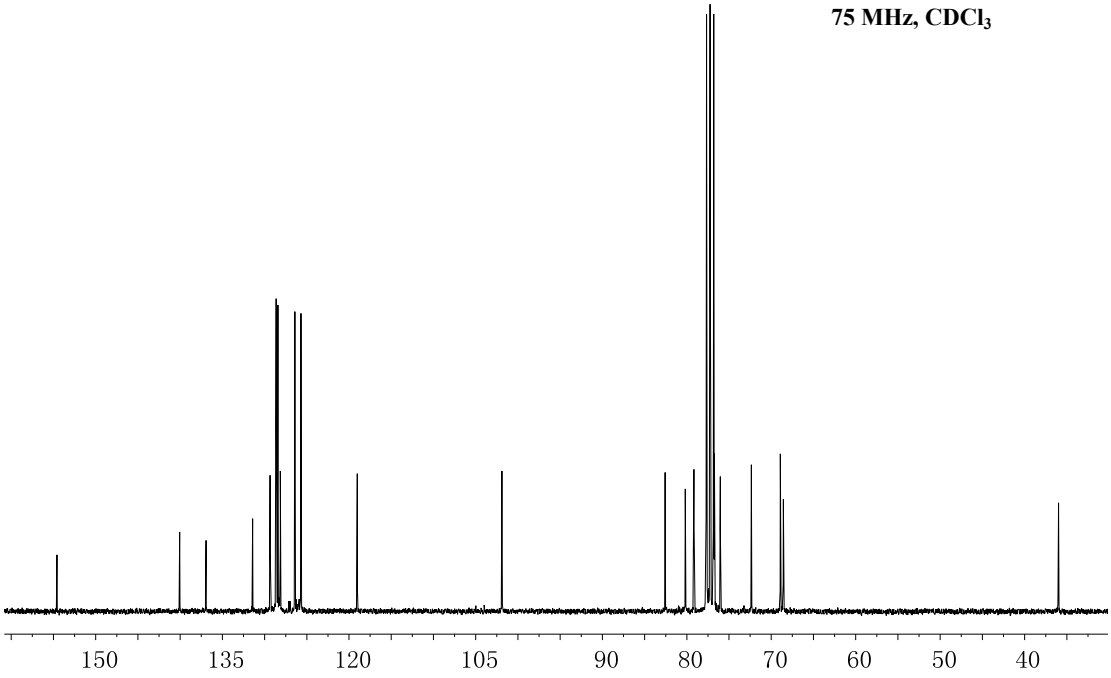
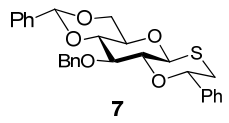


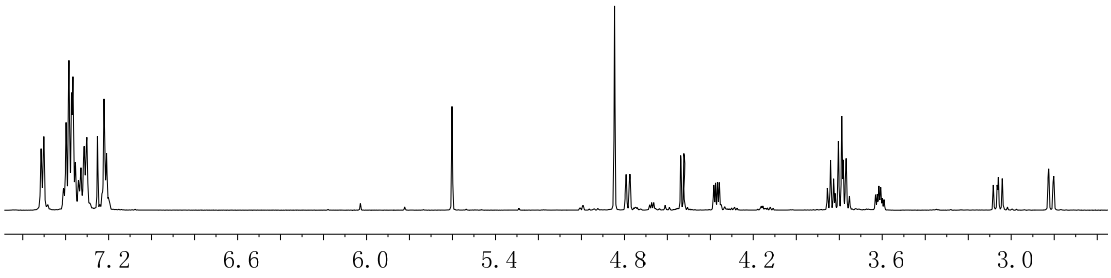
75 MHz, $CDCl_3$



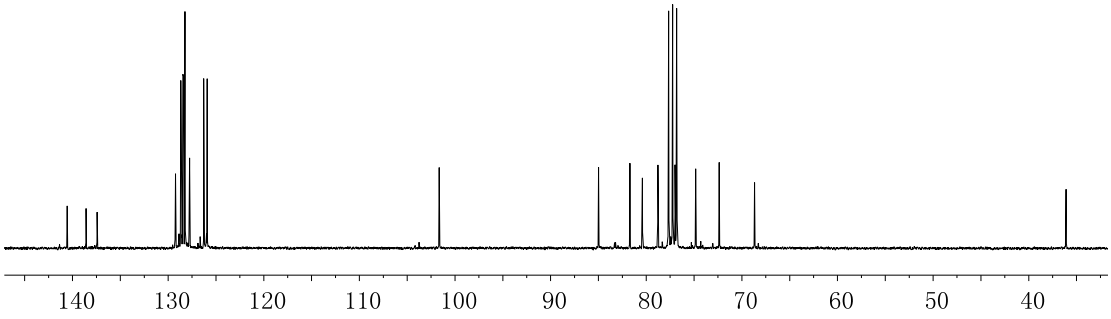


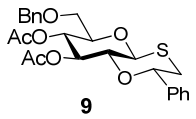
7

600 MHz, $CDCl_3$



75 MHz, $CDCl_3$

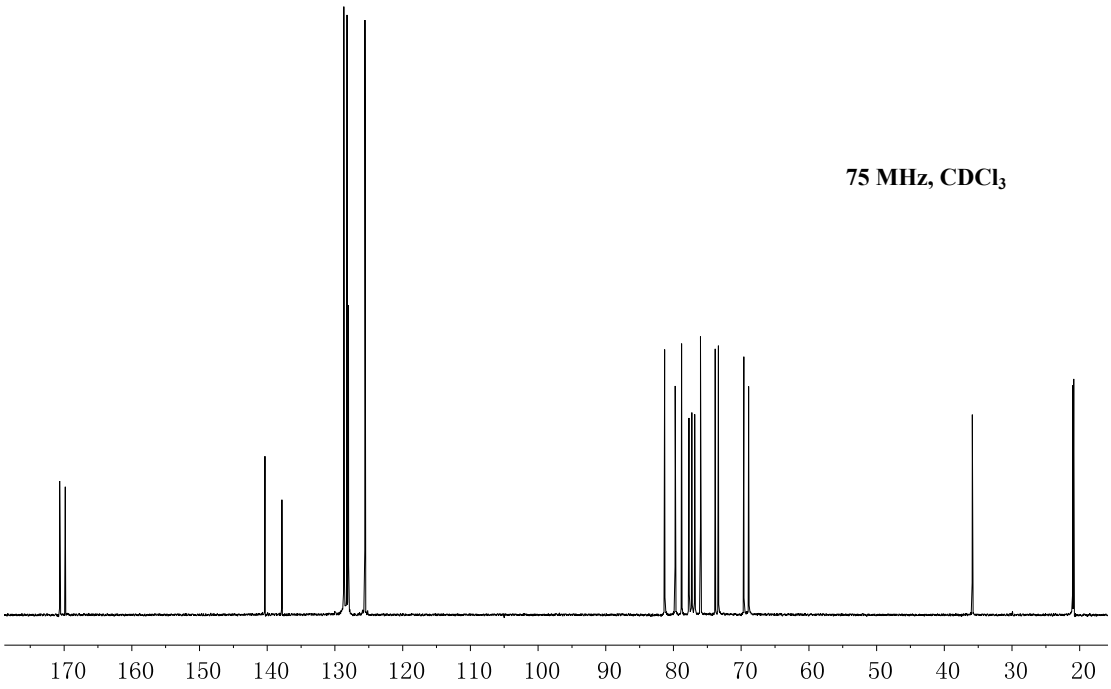


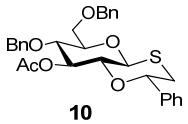


9

300 MHz, $CDCl_3$

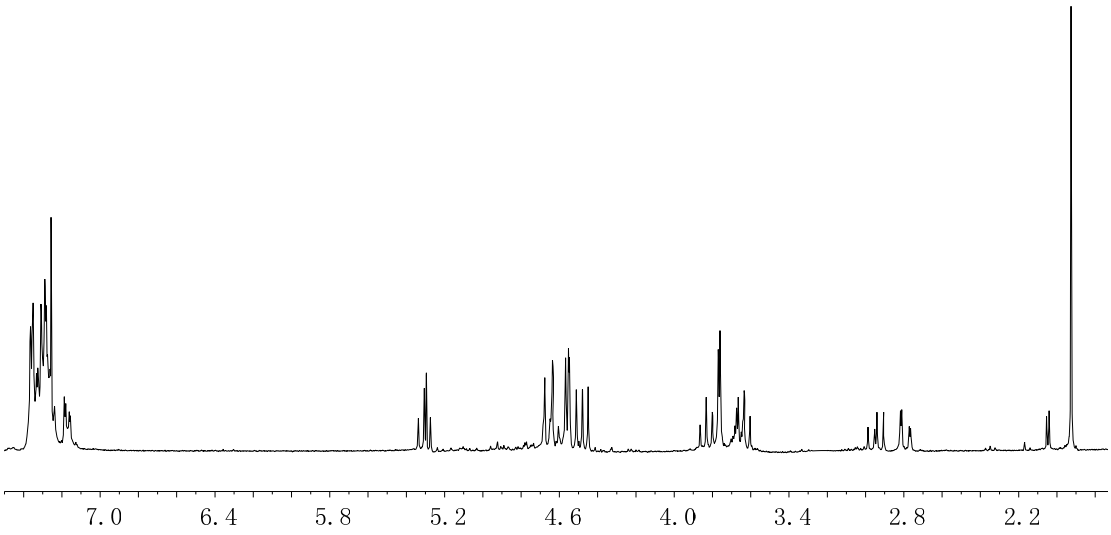
75 MHz, $CDCl_3$



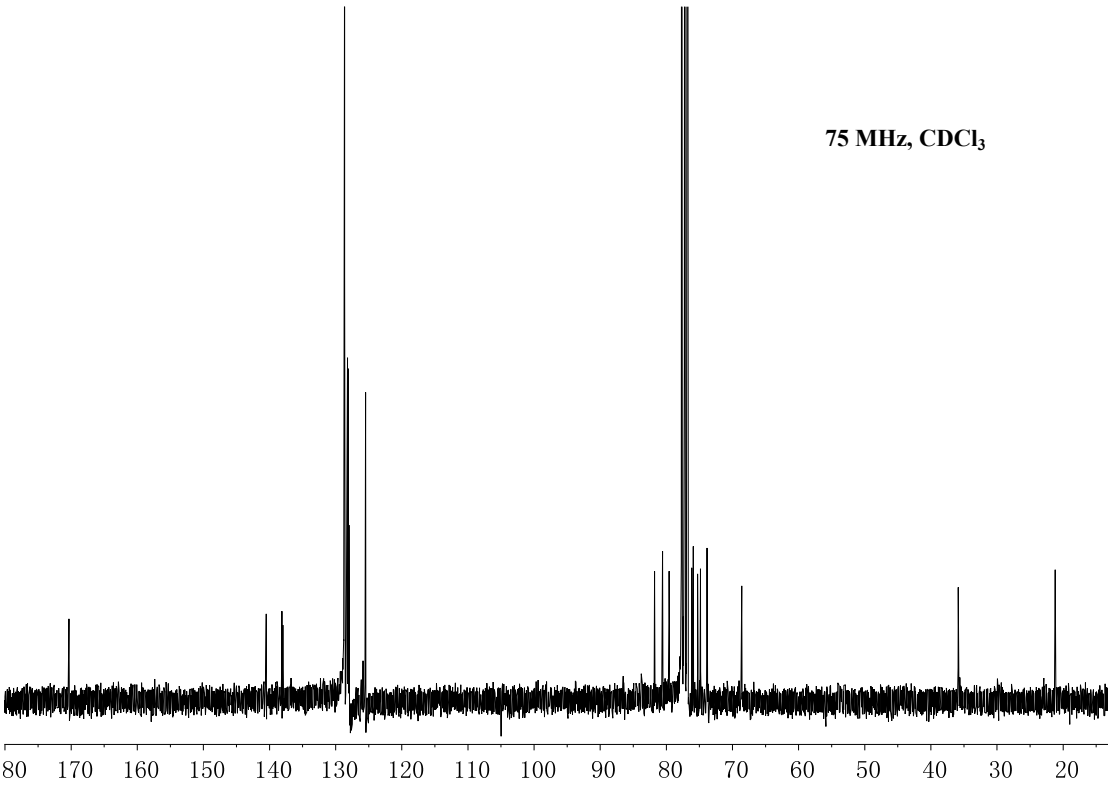


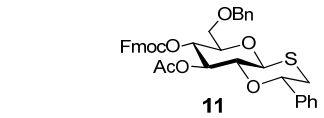
10

300 MHz, $CDCl_3$



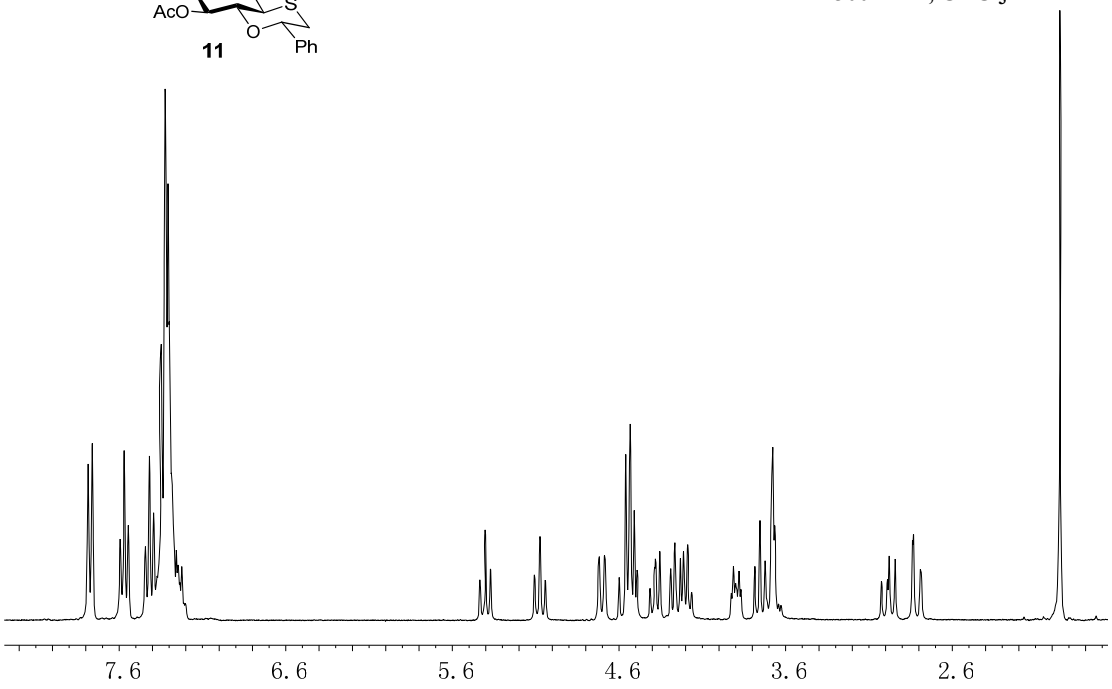
75 MHz, $CDCl_3$



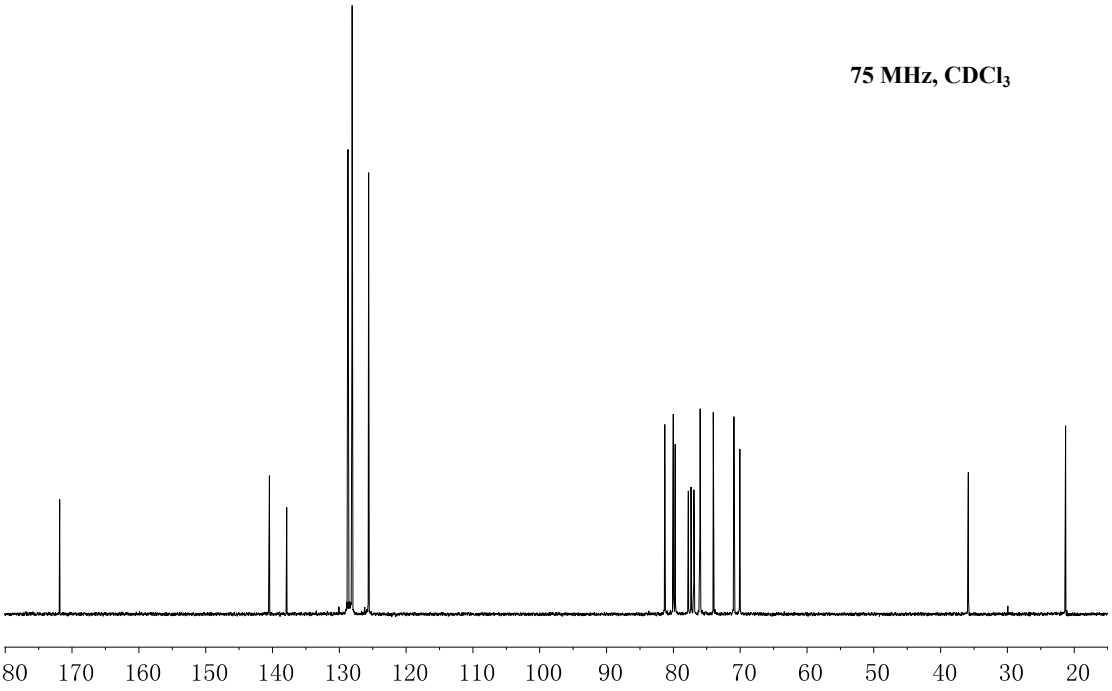


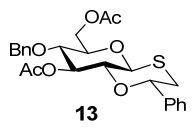
11

300 MHz, $CDCl_3$



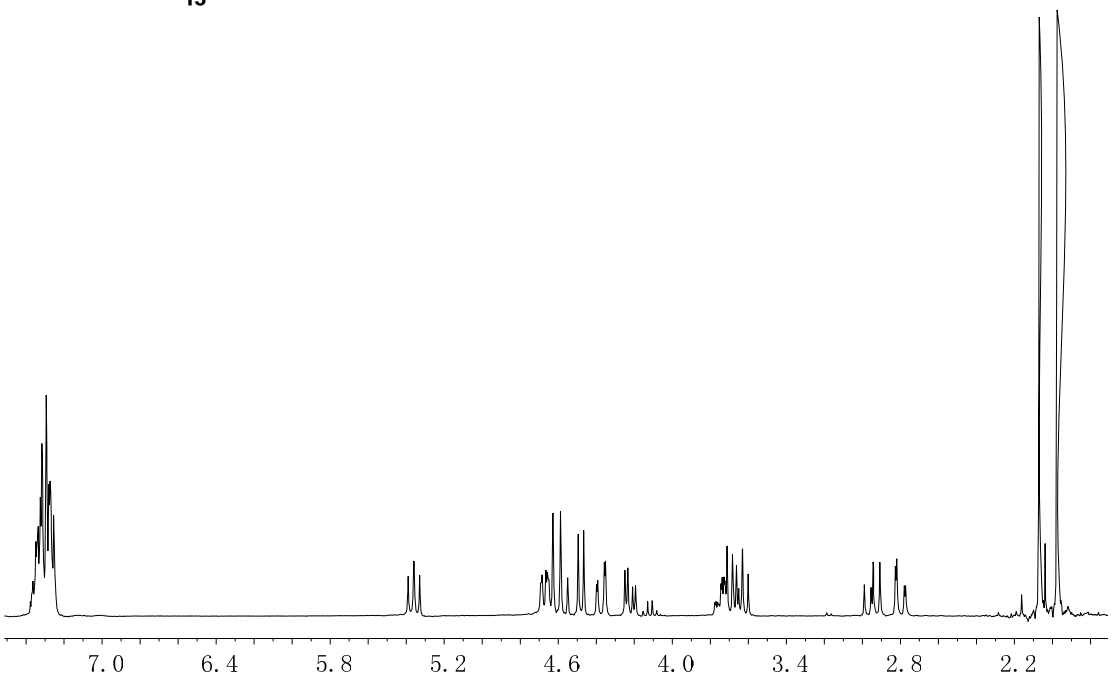
75 MHz, $CDCl_3$



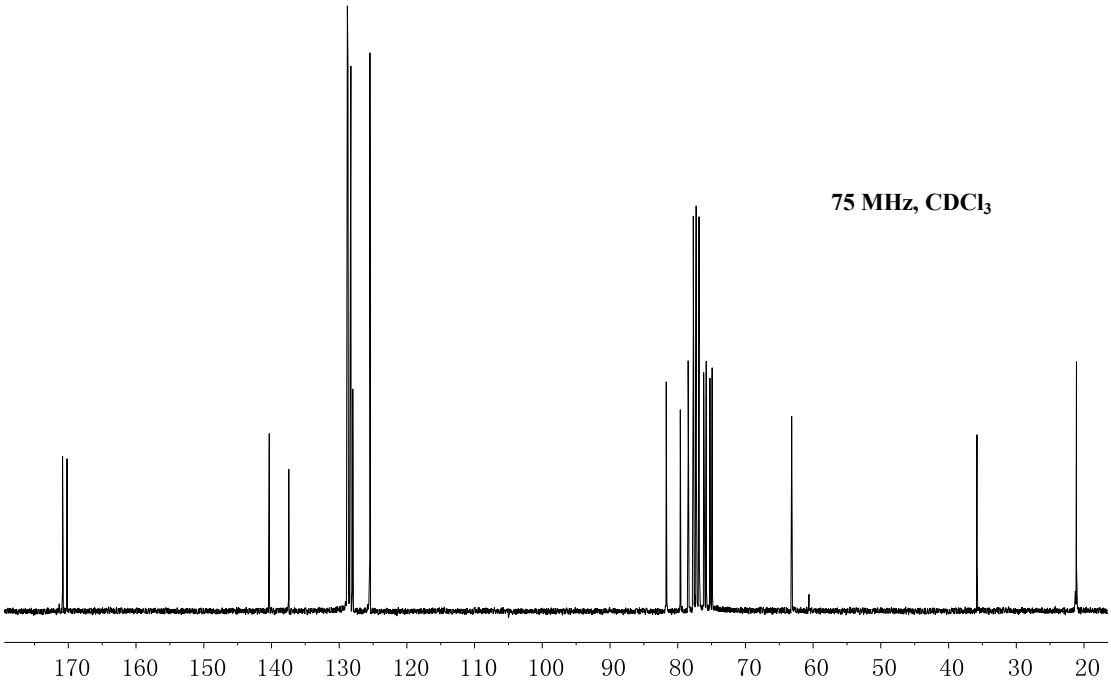


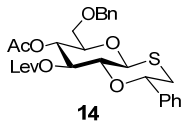
13

300 MHz, $CDCl_3$



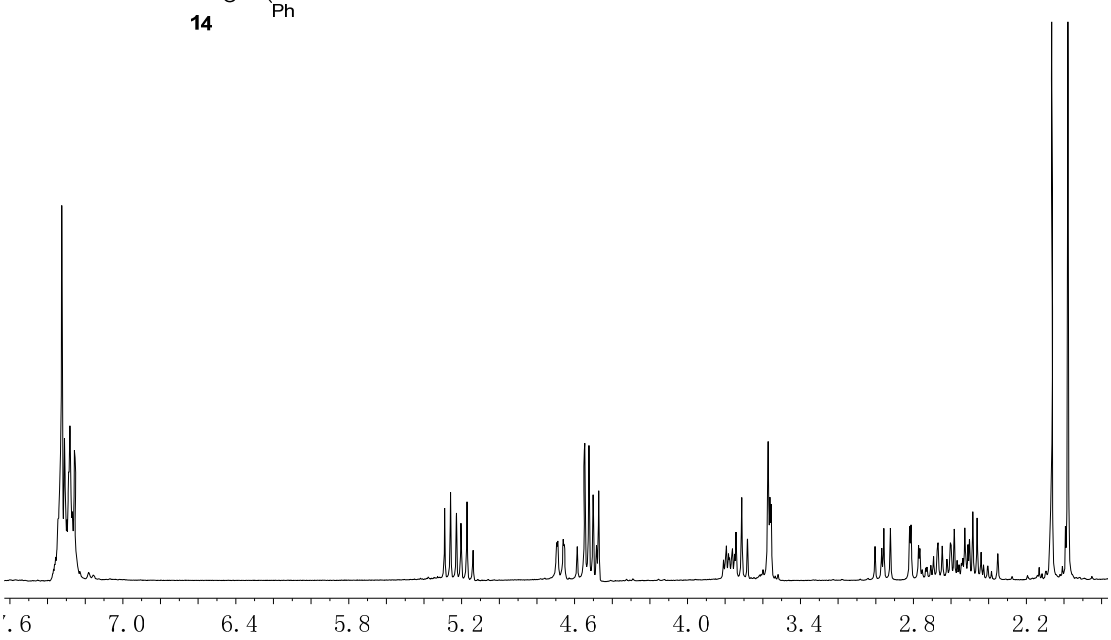
75 MHz, $CDCl_3$



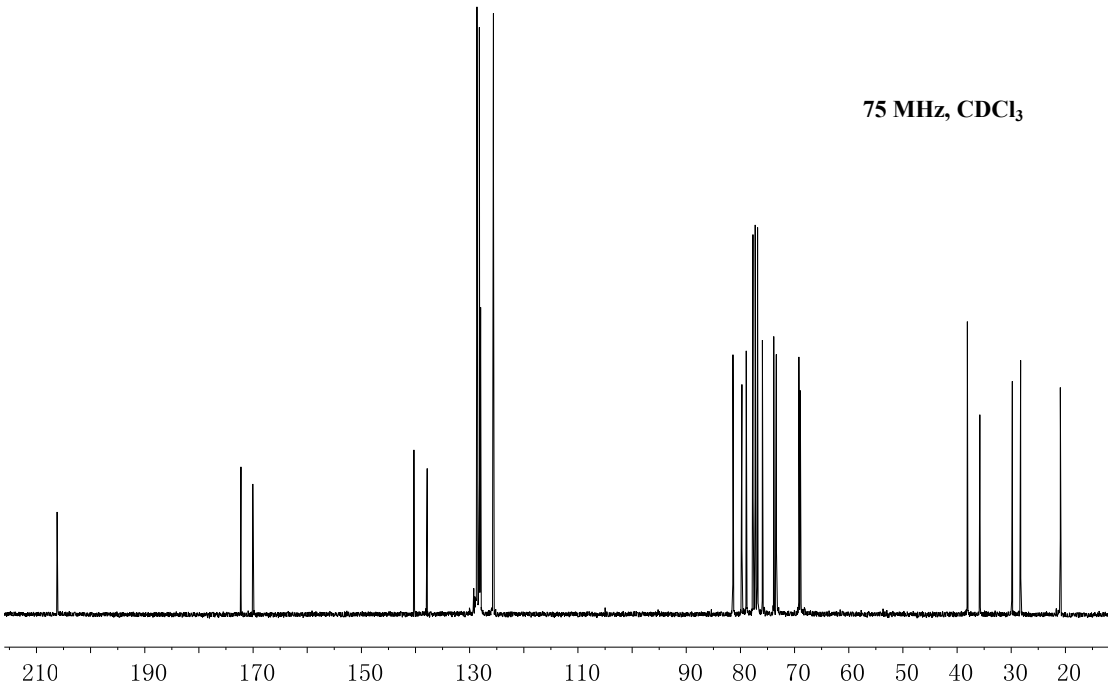


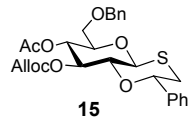
14

300 MHz, $CDCl_3$



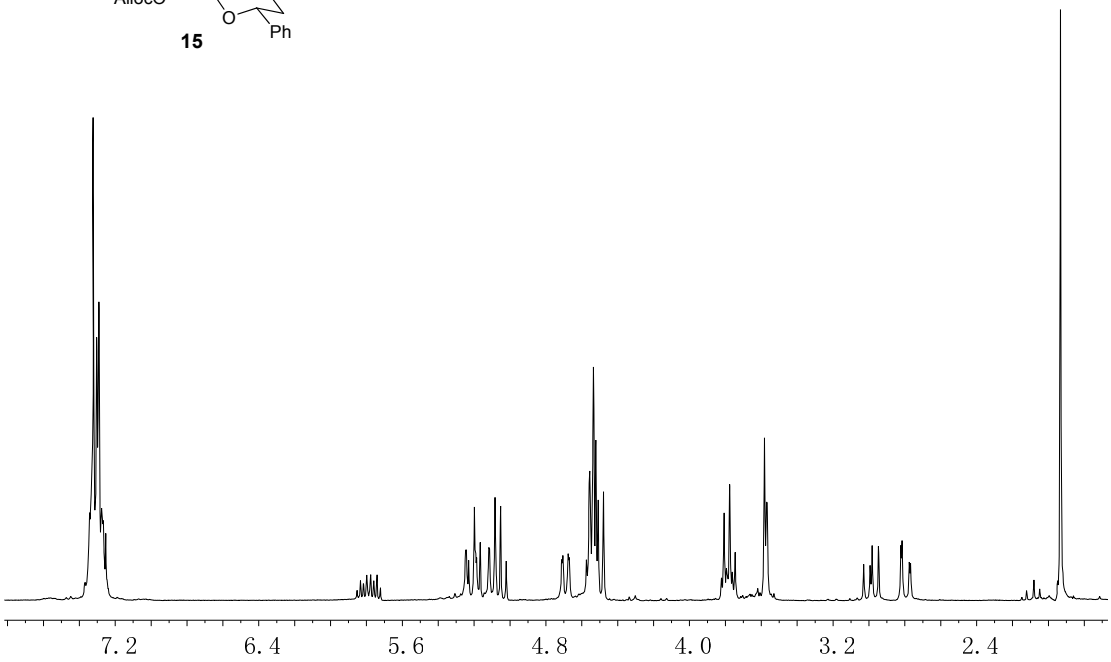
75 MHz, $CDCl_3$



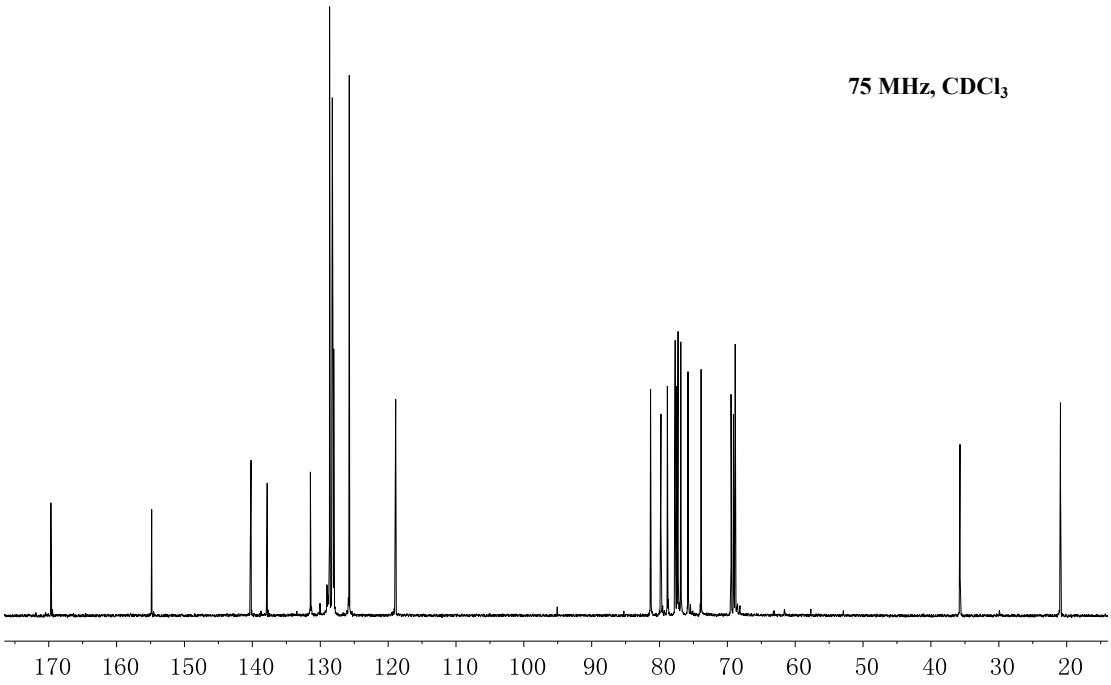


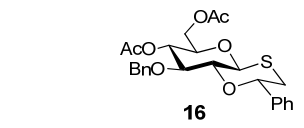
15

300 MHz, $CDCl_3$



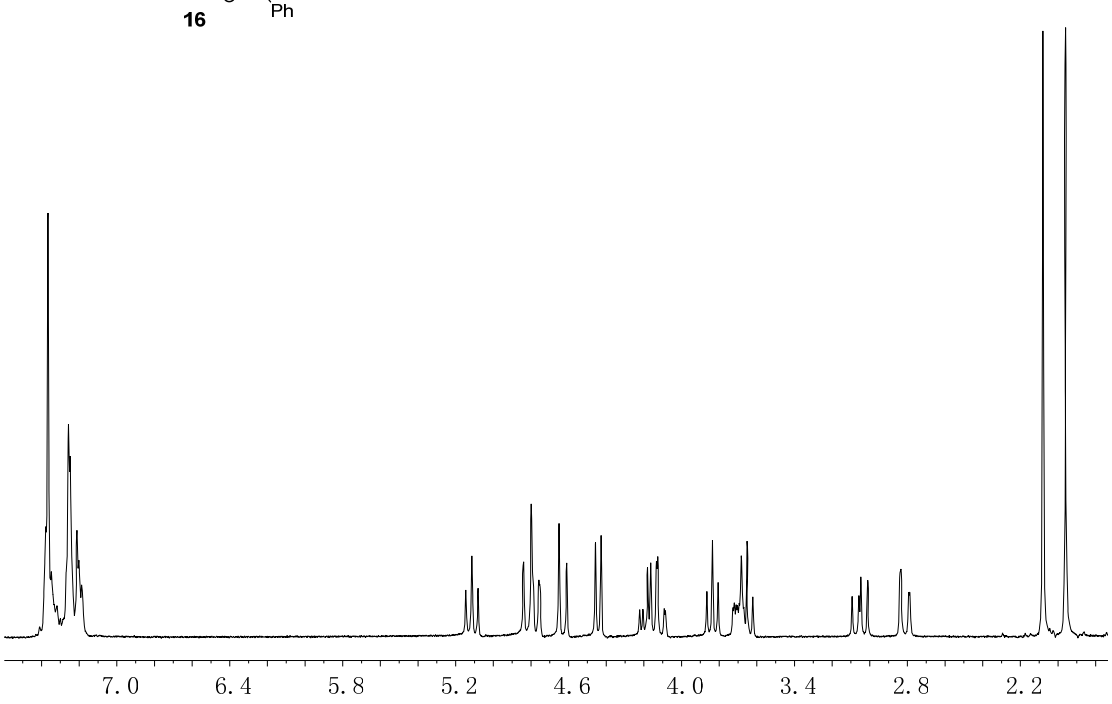
75 MHz, $CDCl_3$



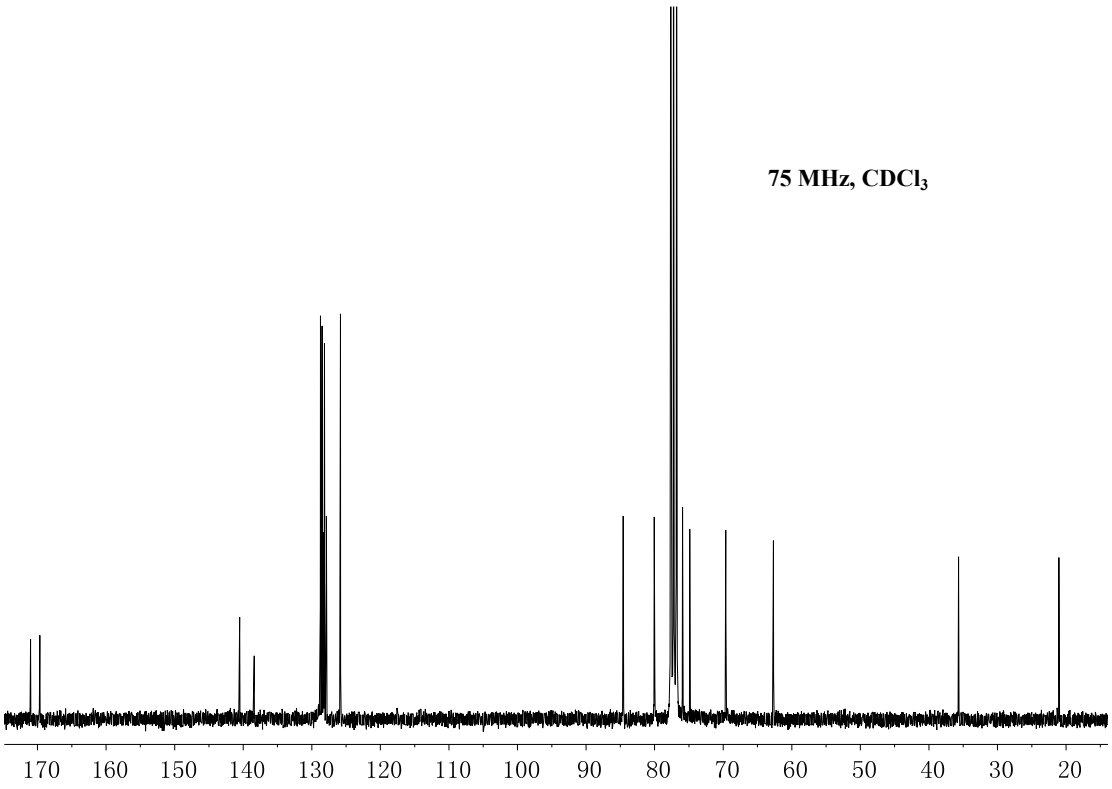


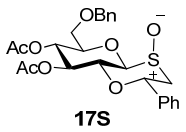
16

300 MHz, $CDCl_3$



75 MHz, $CDCl_3$

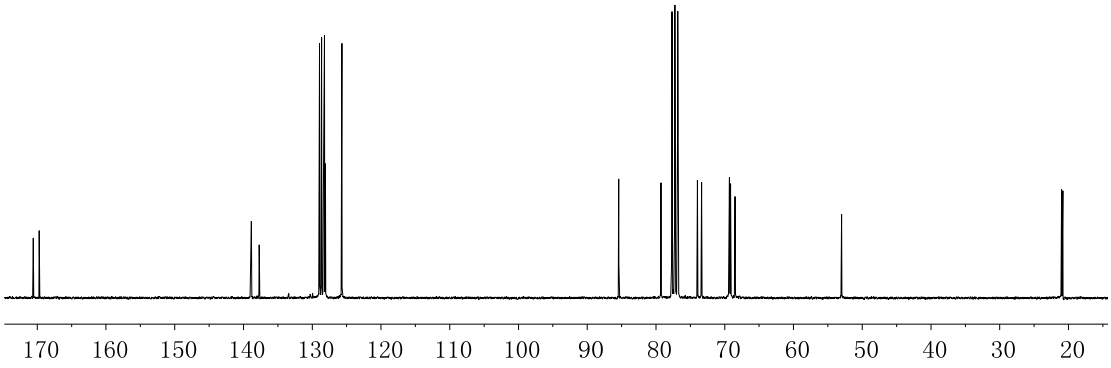


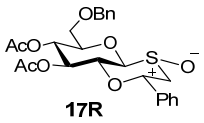


17S

300 MHz, $CDCl_3$

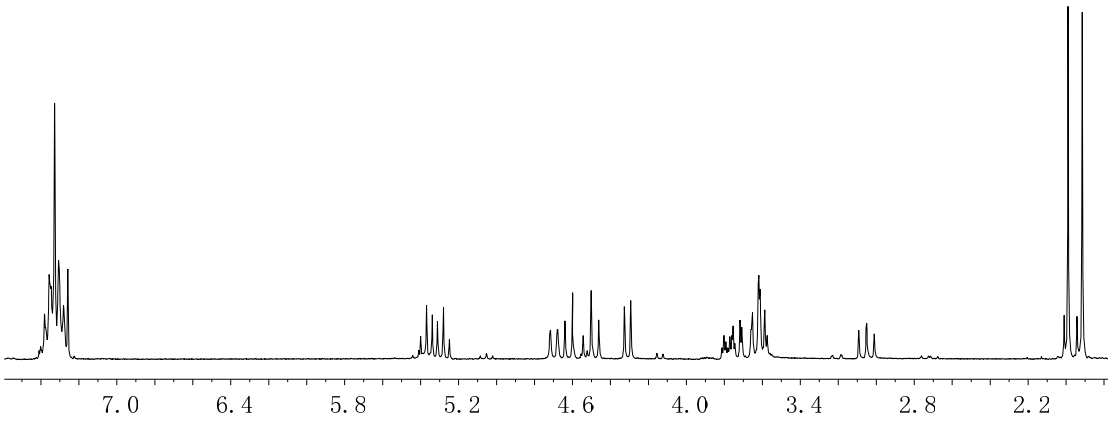
75 MHz, $CDCl_3$



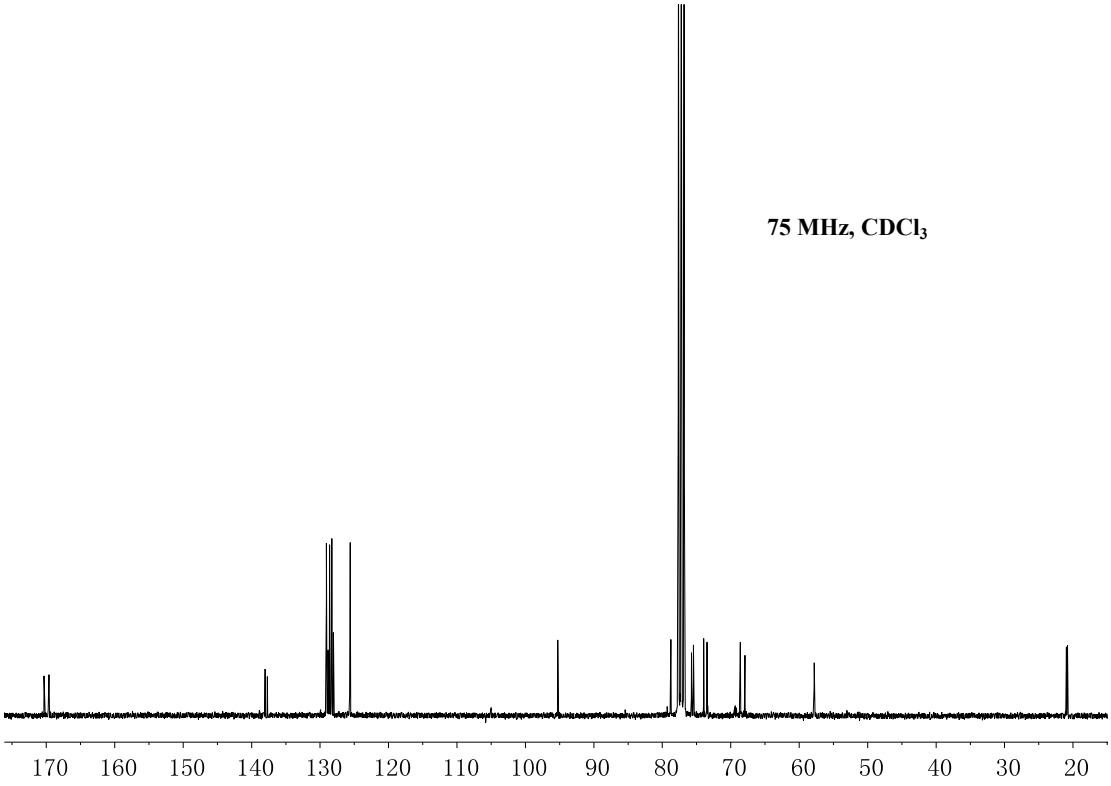


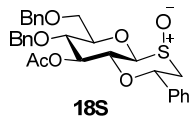
17R

300 MHz, $CDCl_3$



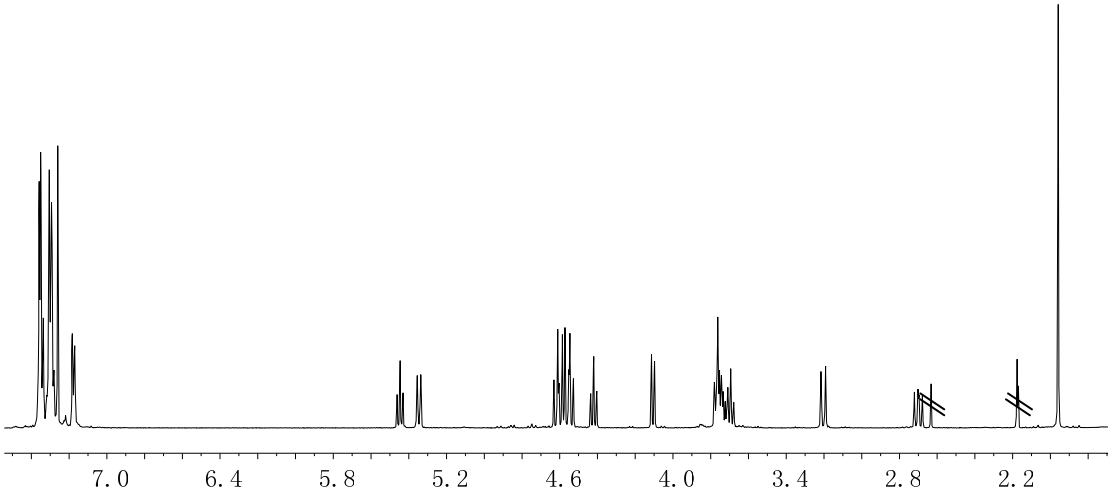
75 MHz, $CDCl_3$



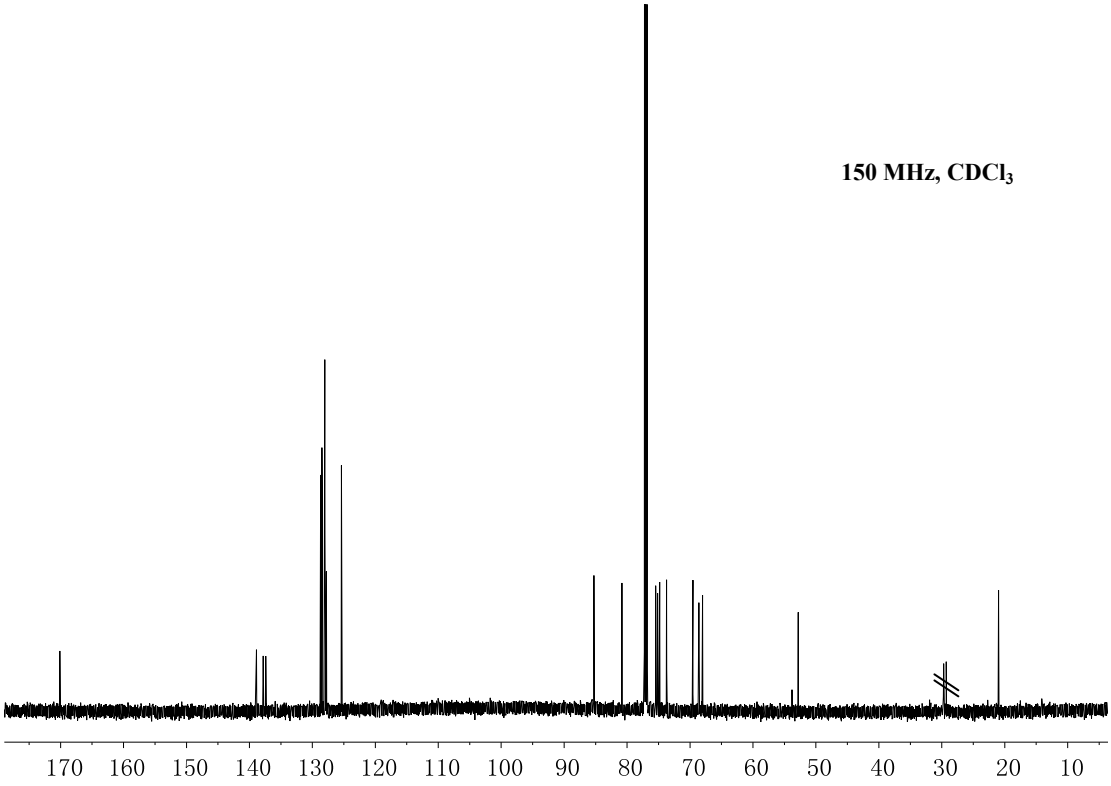


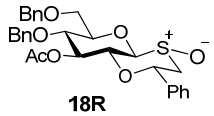
18S

600 MHz, $CDCl_3$



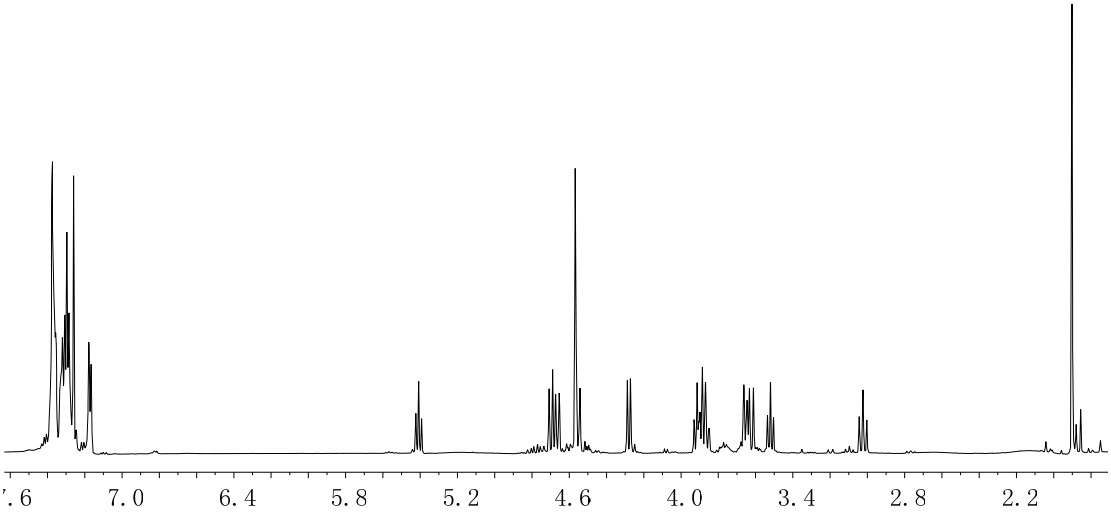
150 MHz, $CDCl_3$



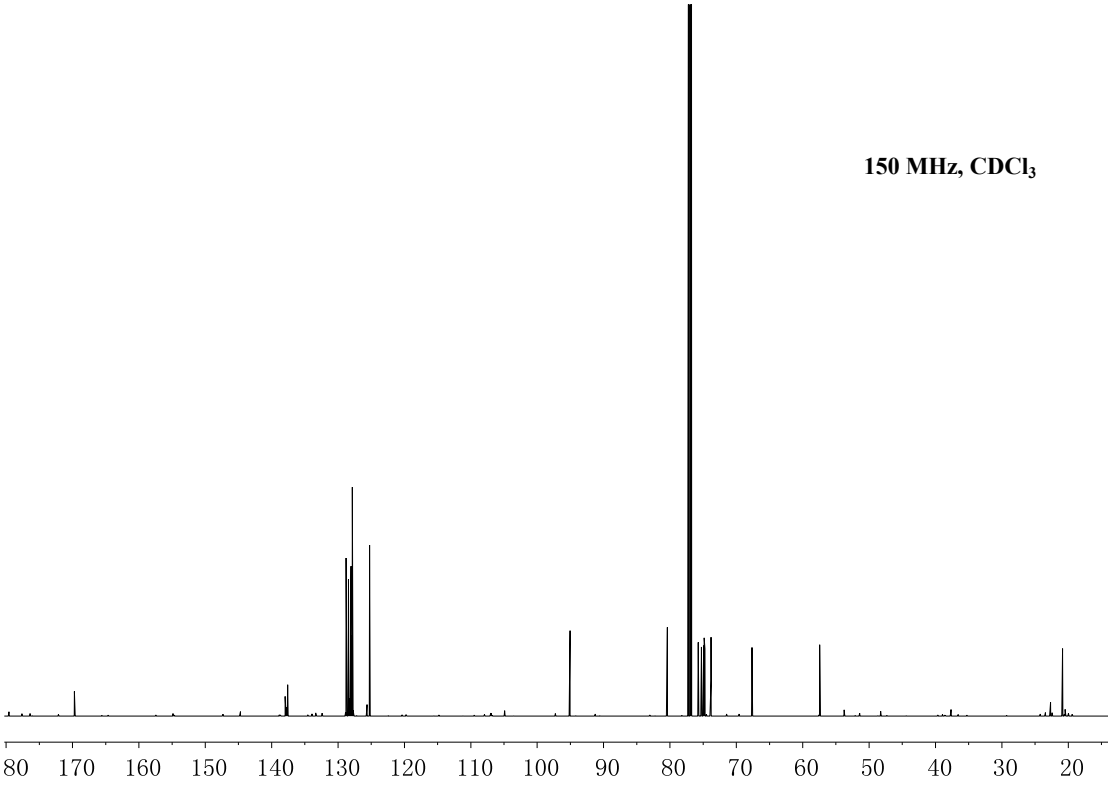


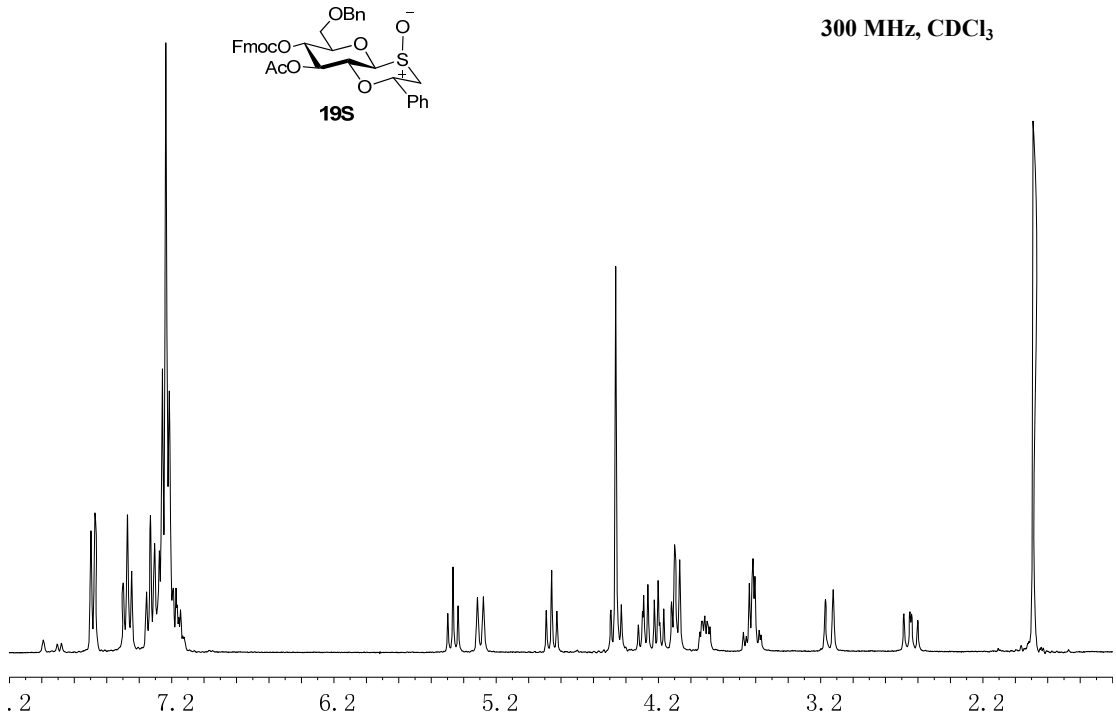
18R

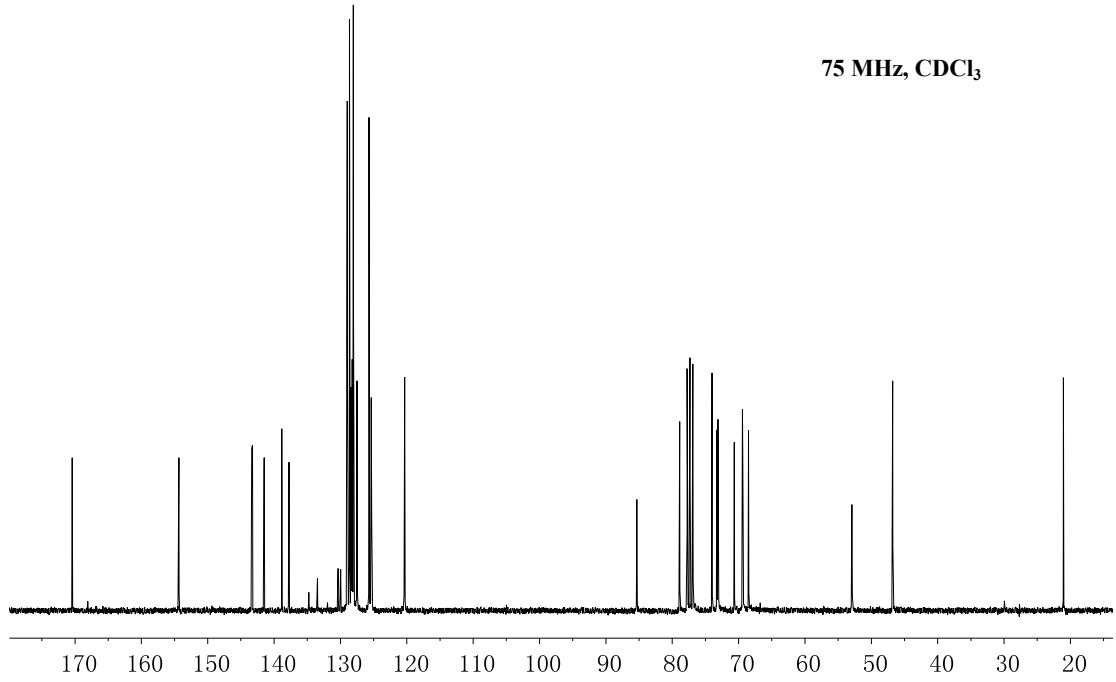
600 MHz, $CDCl_3$

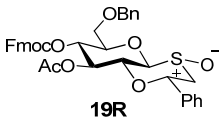


150 MHz, $CDCl_3$



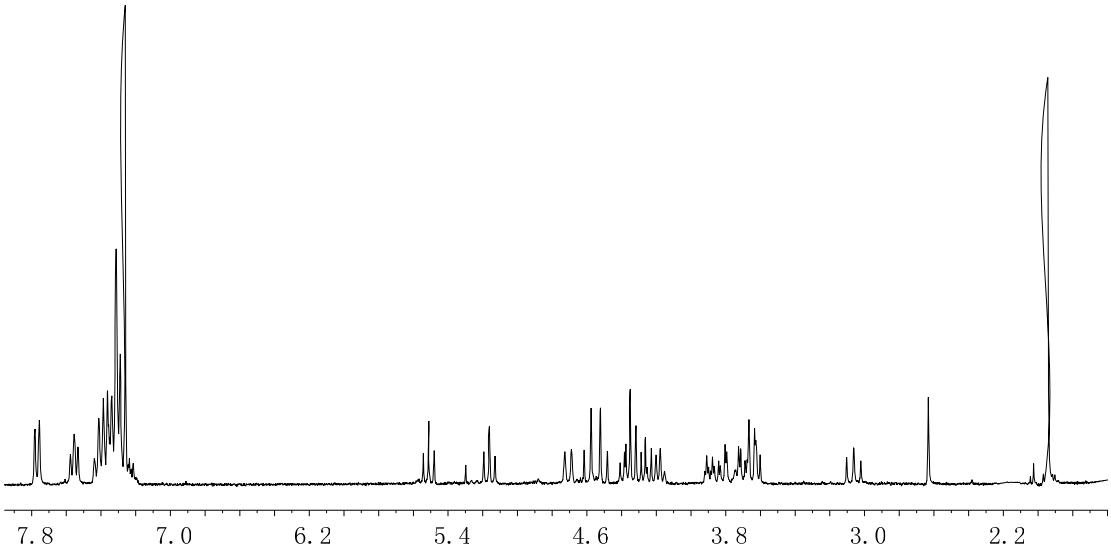

OBn
FmocO
AcO
O
O
S
+
O
Ph
19S
300 MHz, CDCl3
. 2
7. 2
6. 2
5. 2
4. 2
3. 2
2. 2


75 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

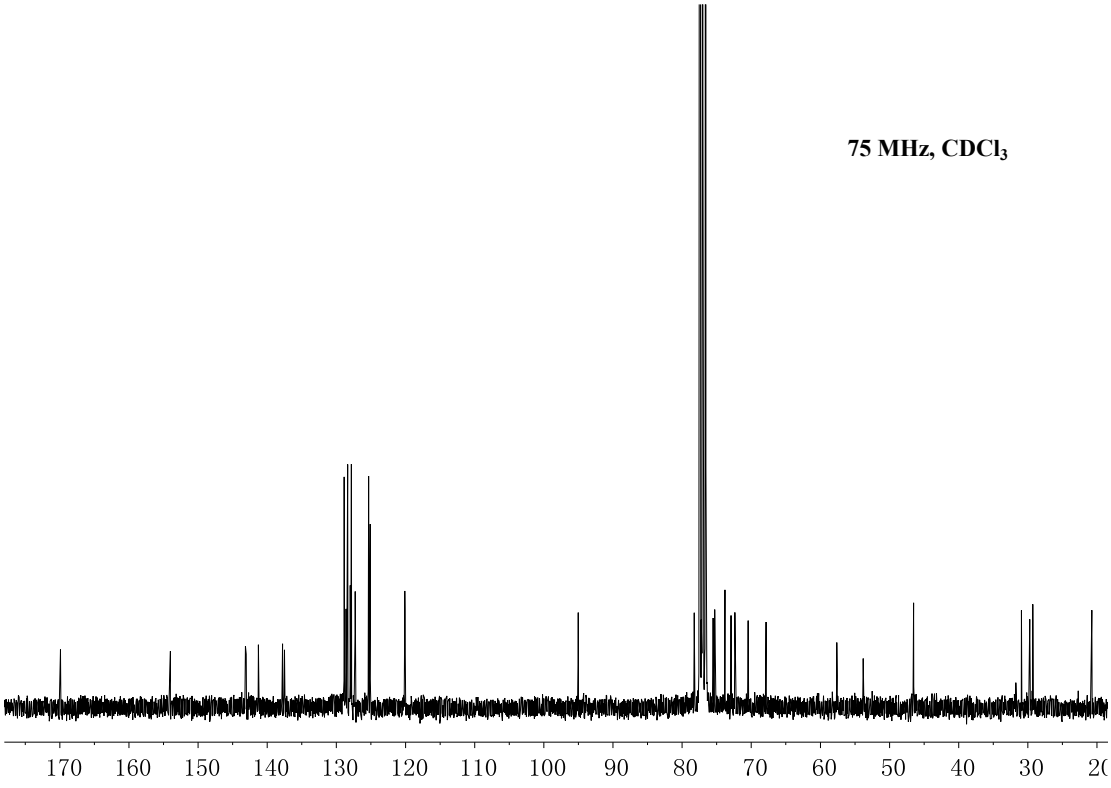


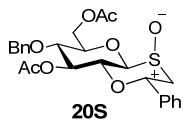
19R

300 MHz, $CDCl_3$



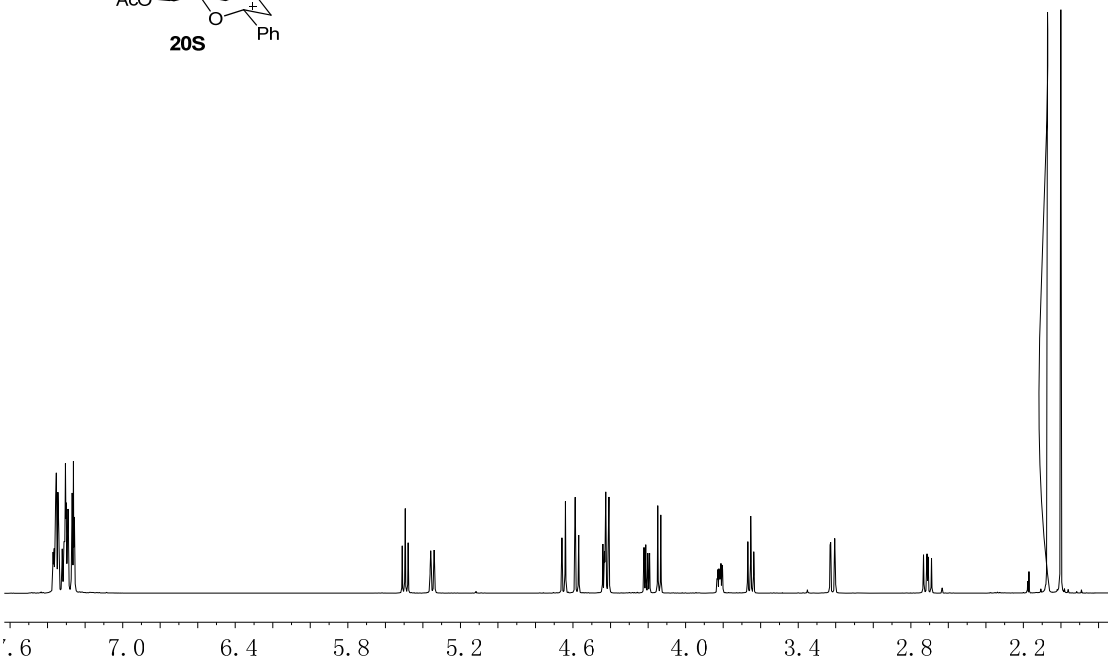
75 MHz, $CDCl_3$



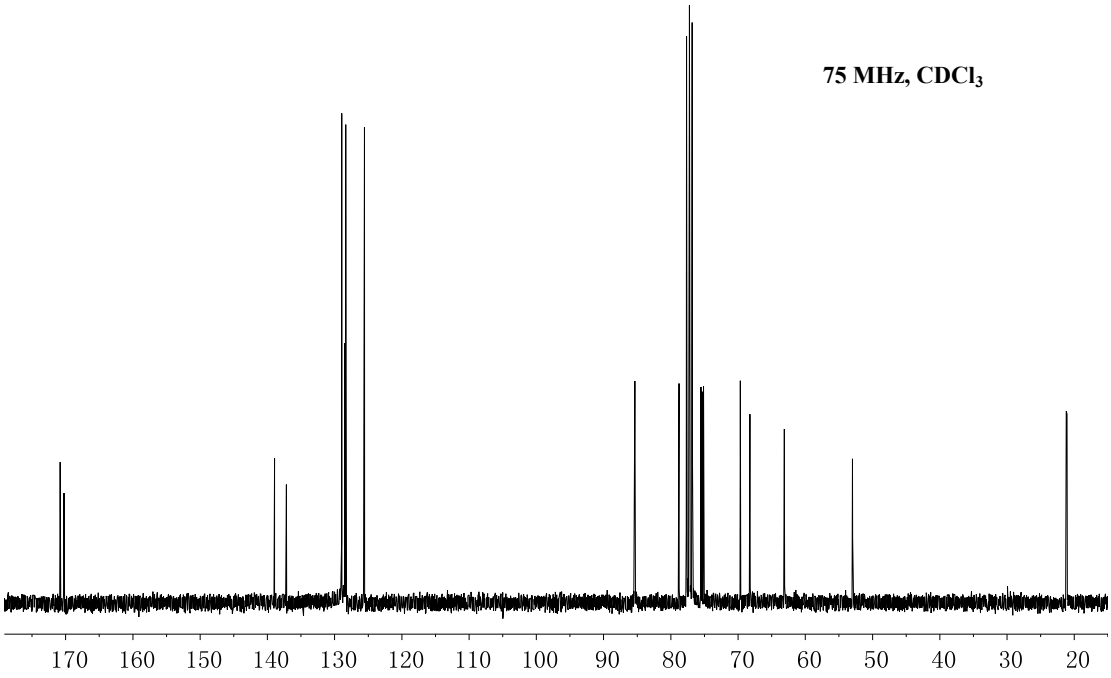


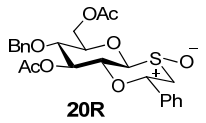
20S

600 MHz, $CDCl_3$



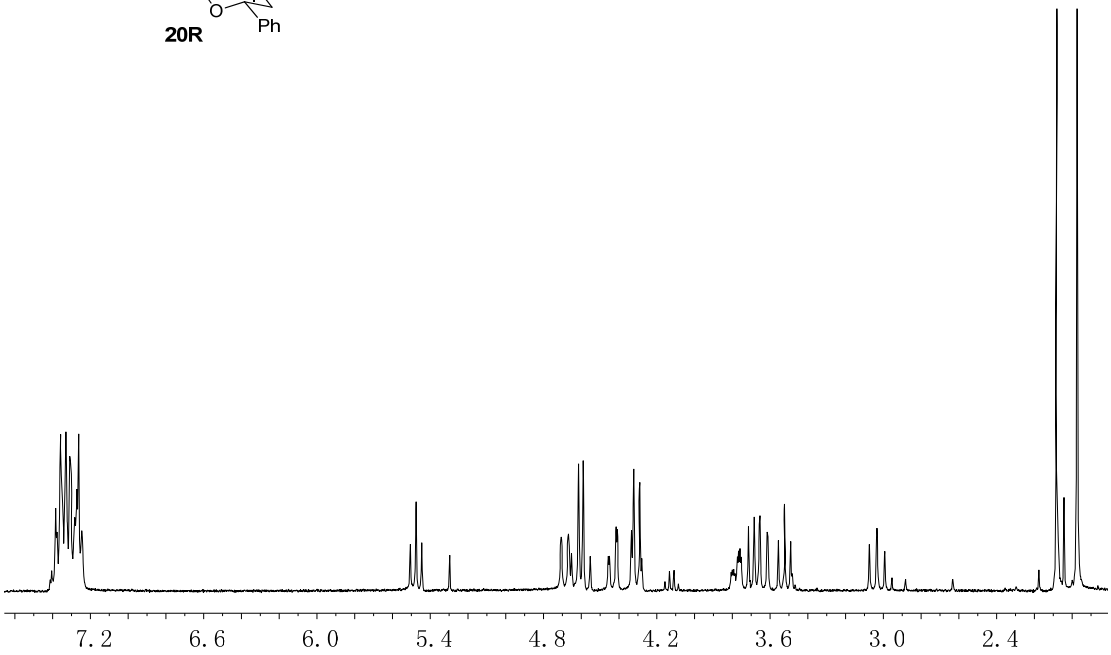
75 MHz, $CDCl_3$



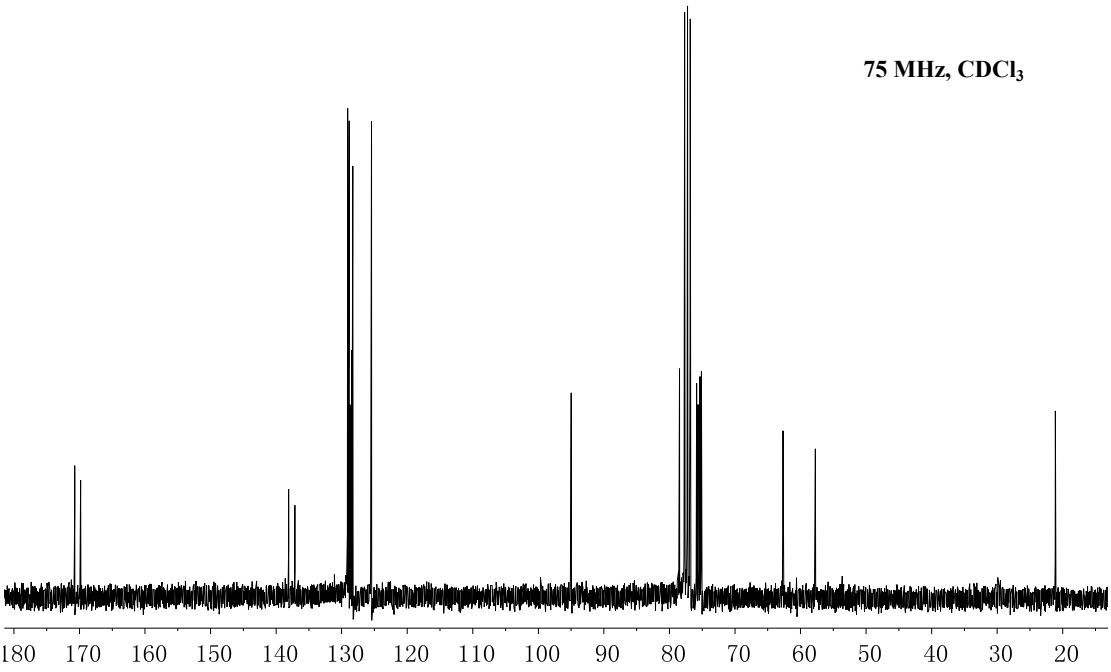


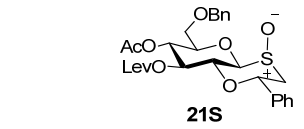
20R

300 MHz, $CDCl_3$



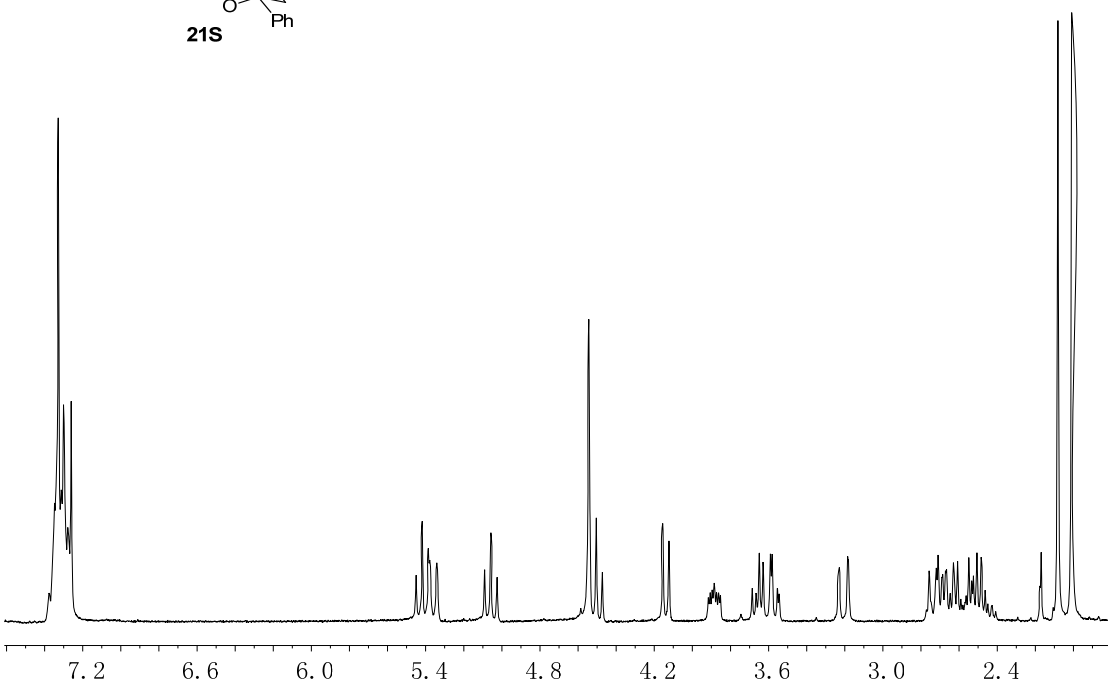
75 MHz, $CDCl_3$



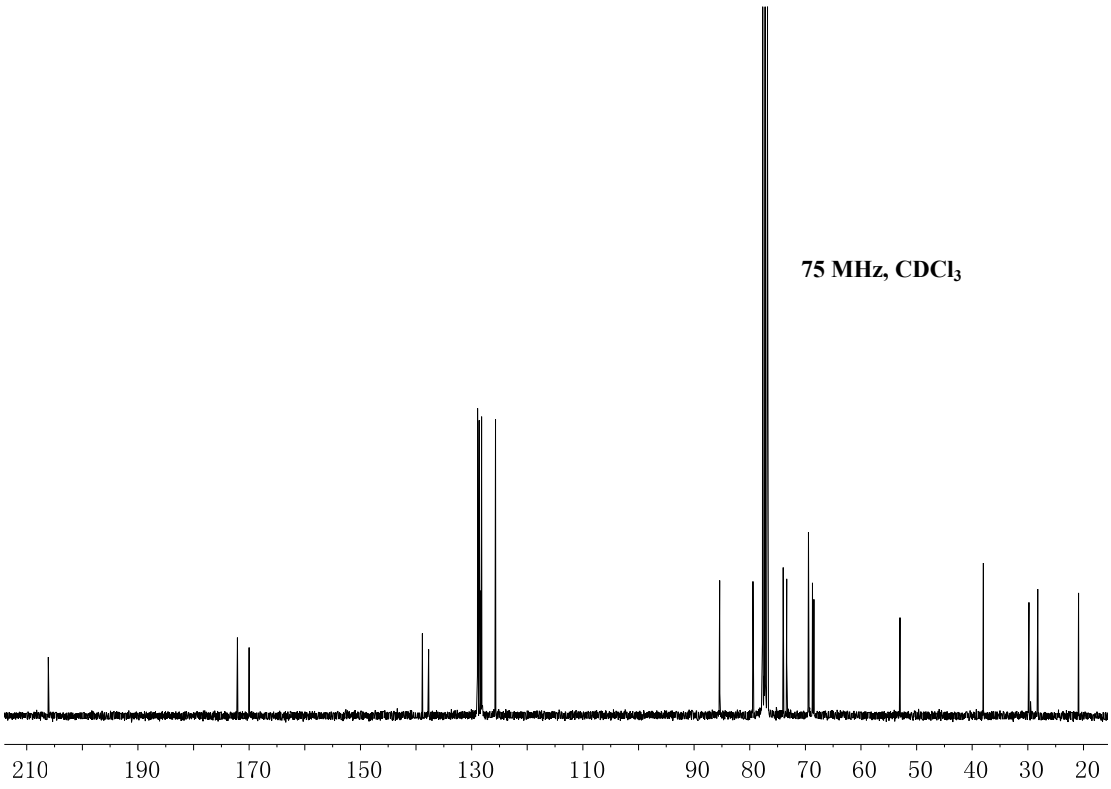


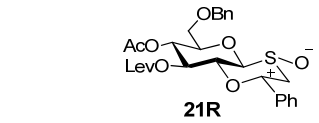
21S

300 MHz, $CDCl_3$



75 MHz, $CDCl_3$

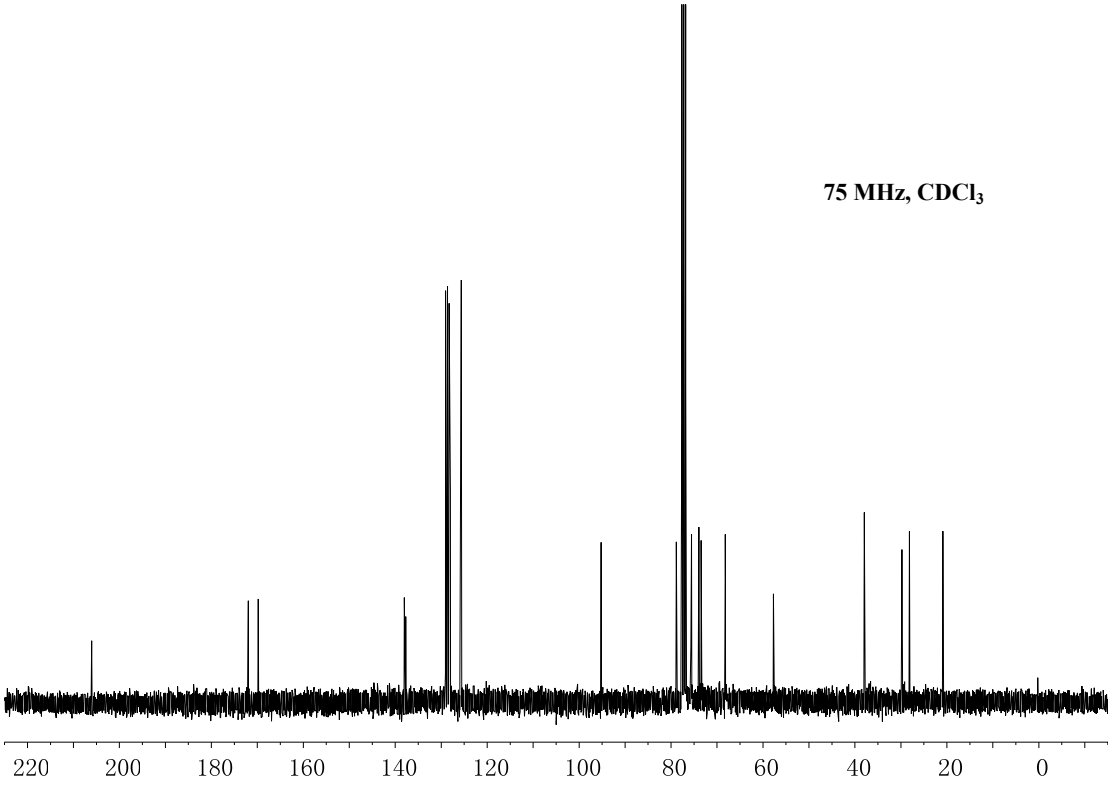


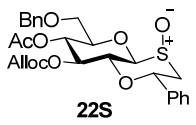


21R

600 MHz, $CDCl_3$

75 MHz, $CDCl_3$

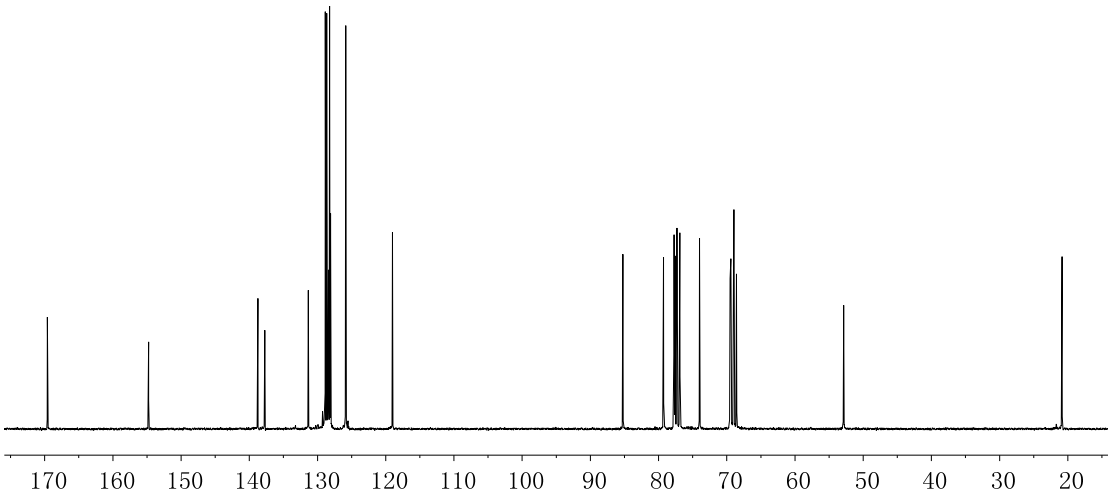


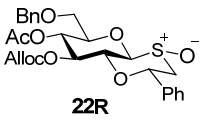


22S

300 MHz, $CDCl_3$

75 MHz, $CDCl_3$

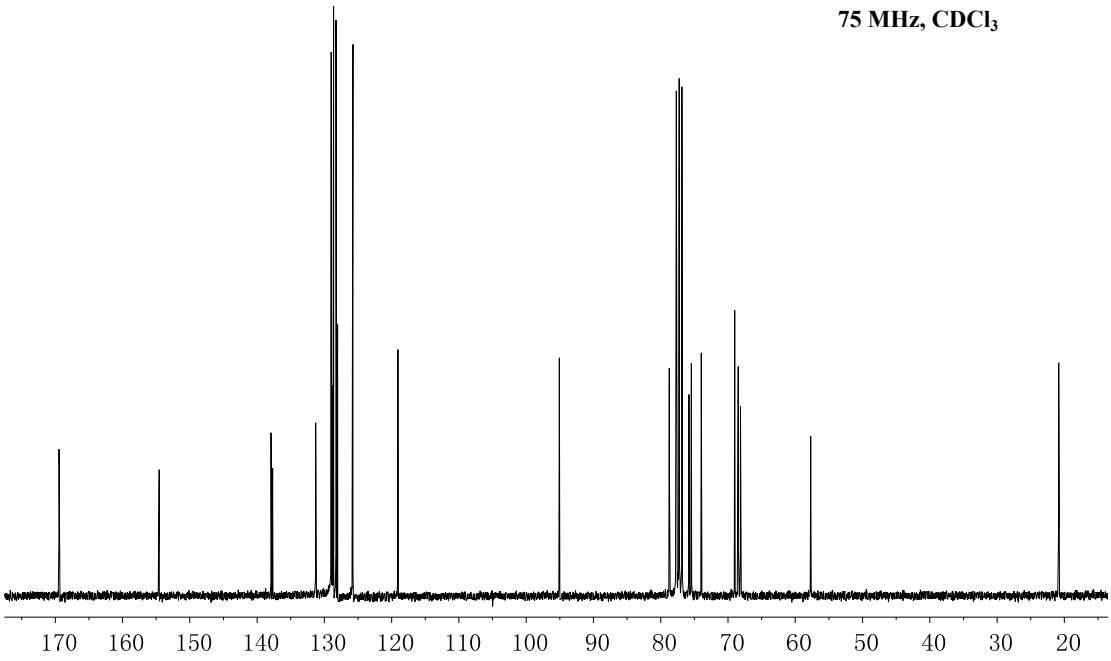


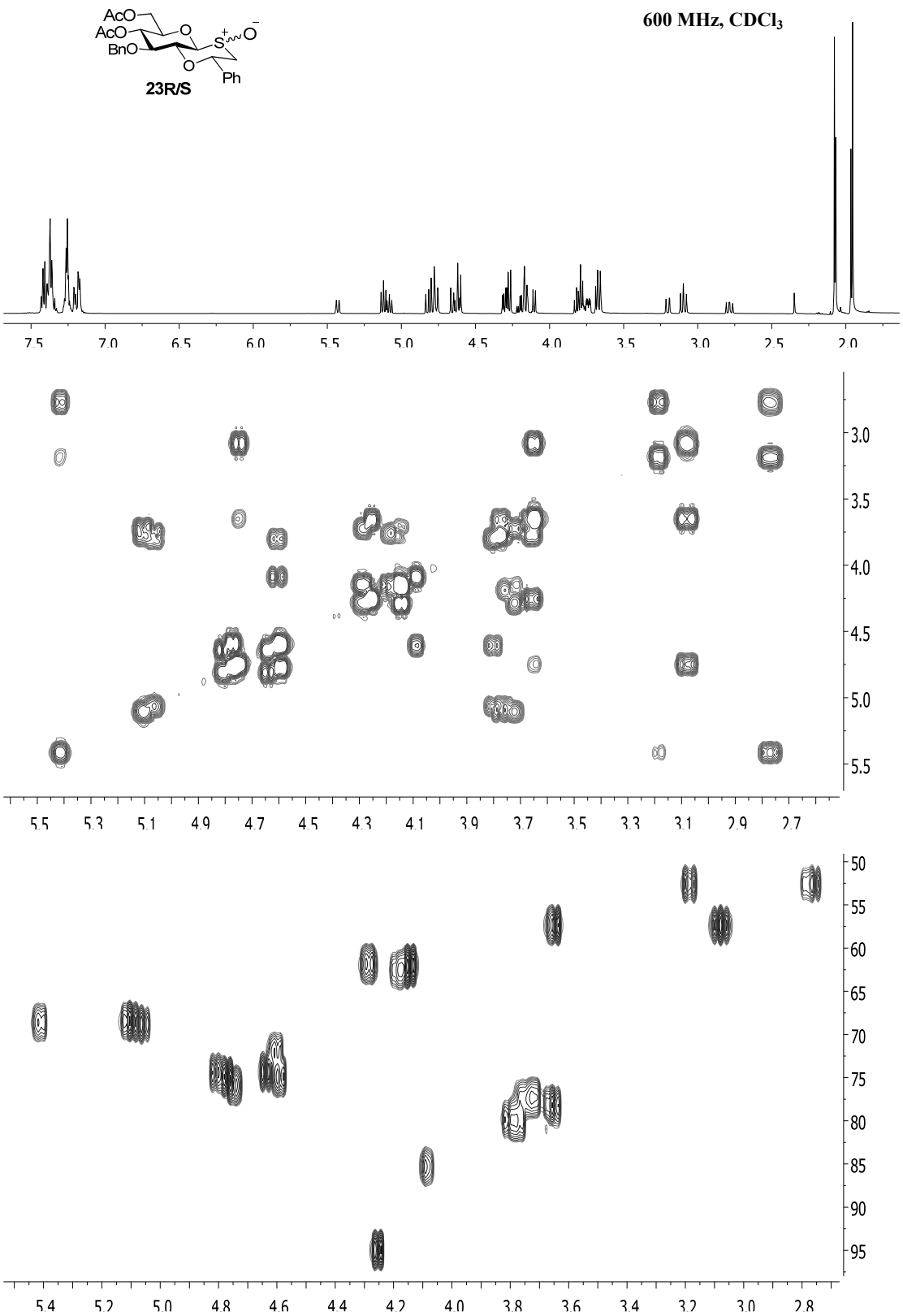


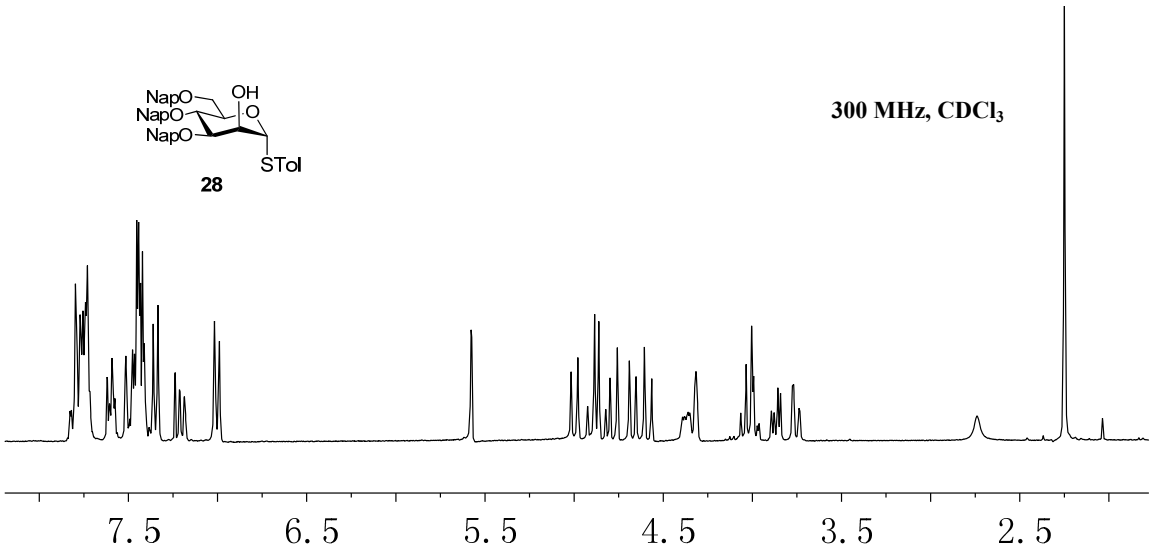
22R

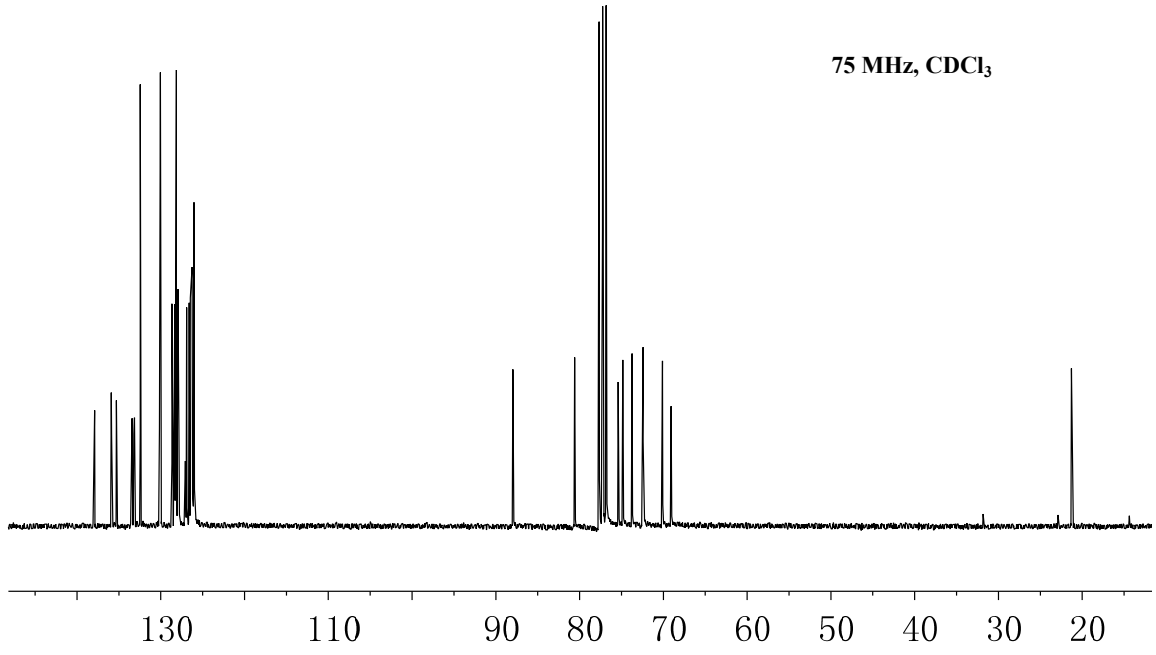
300 MHz, $CDCl_3$

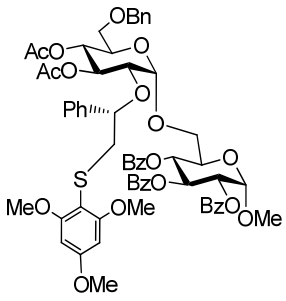
75 MHz, $CDCl_3$




AcO
AcO
BnO
O
S
O
O
Ph
23R/S
600 MHz, CDCl3


NapO
NapO
NapO
OH
O
STol
28
300 MHz, CDCl3
7.5
6.5
5.5
4.5
3.5
2.5

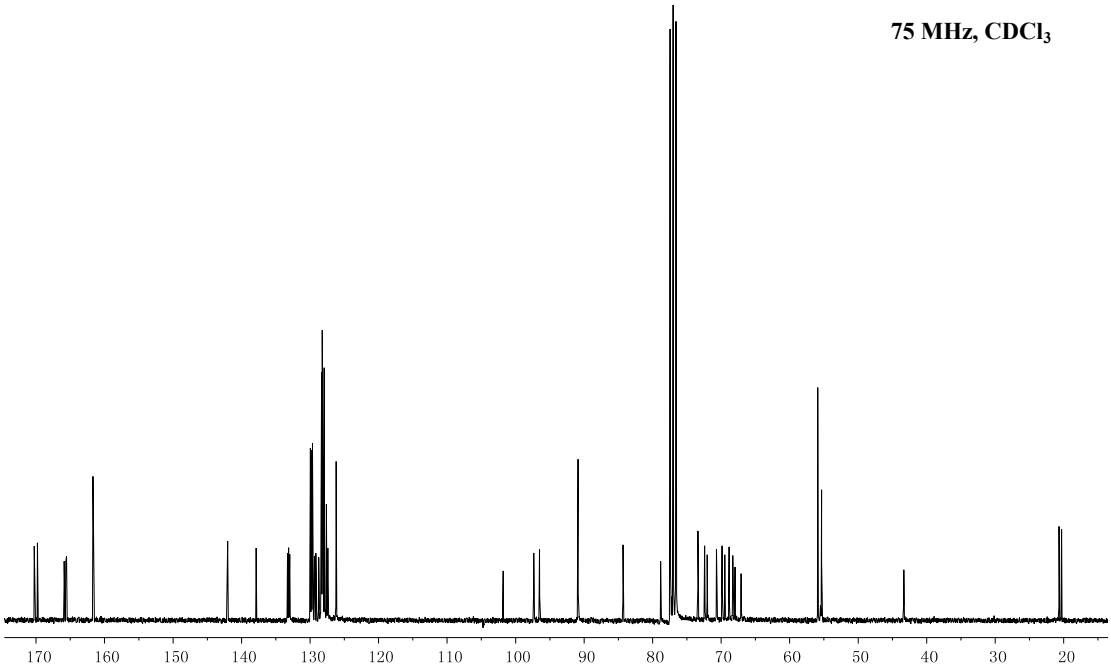

75 MHz, CDCl3
130
110
90
80
70
60
50
40
30
20

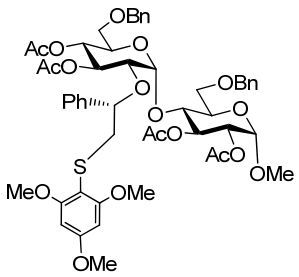


29

300 MHz, $CDCl_3$

75 MHz, $CDCl_3$

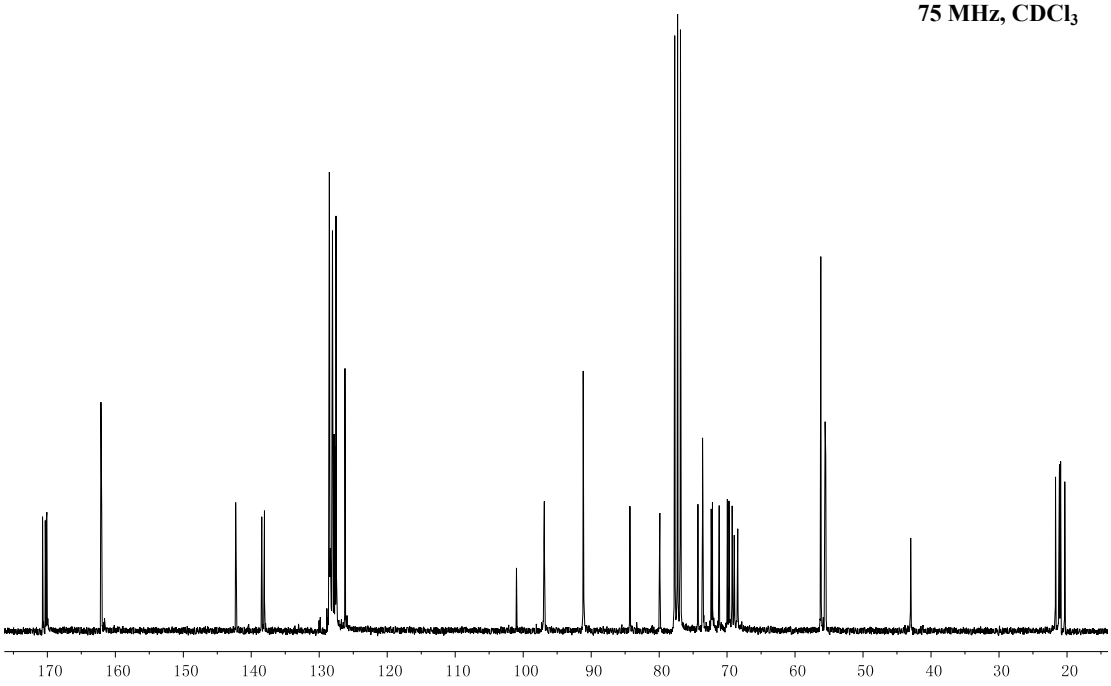


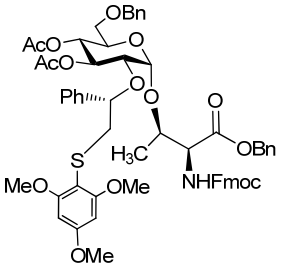


30

300 MHz, $CDCl_3$

75 MHz, $CDCl_3$

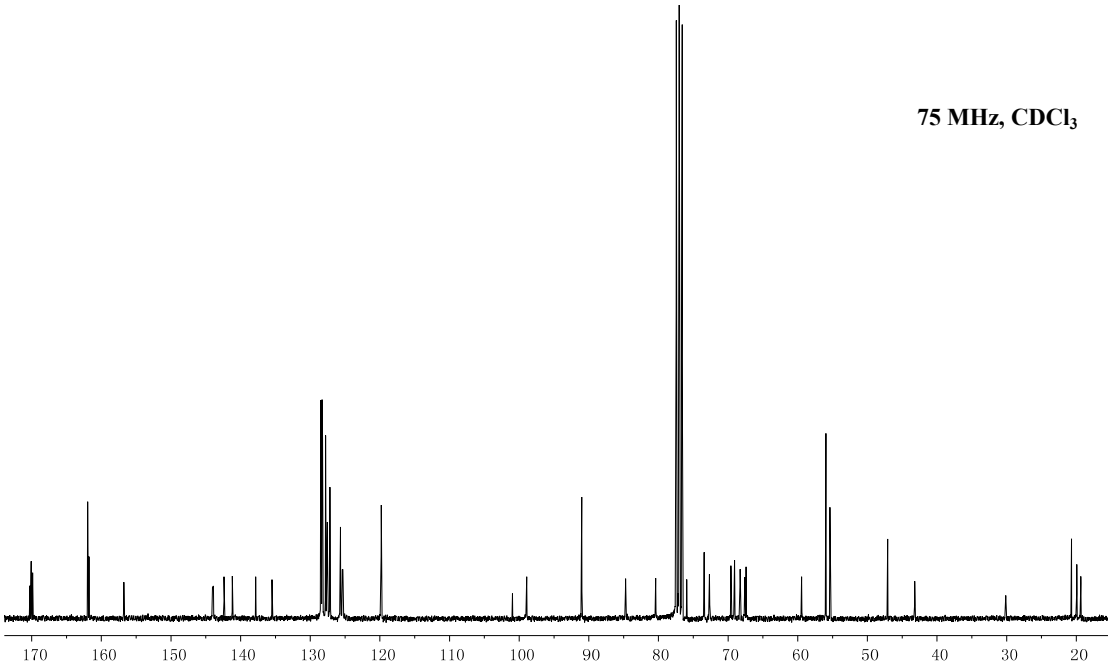


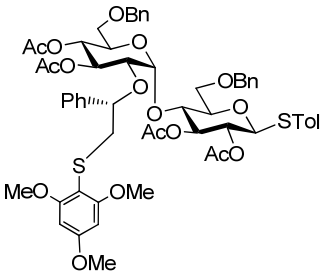


31

300 MHz, $CDCl_3$

75 MHz, $CDCl_3$

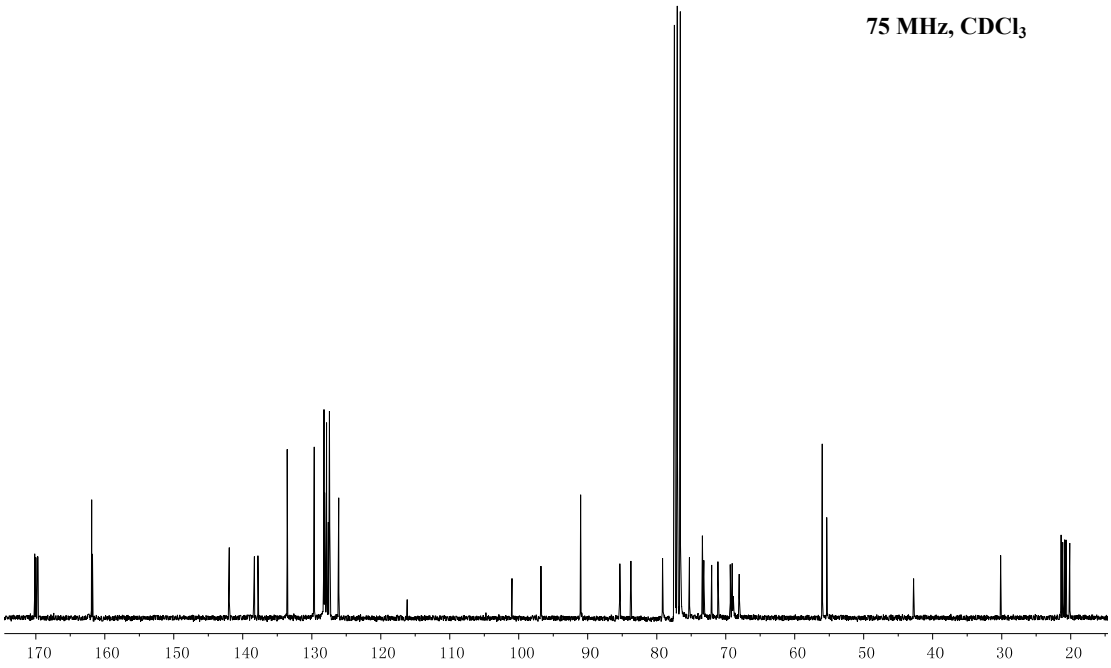


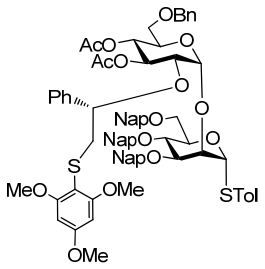


32

300 MHz, $CDCl_3$

75 MHz, $CDCl_3$

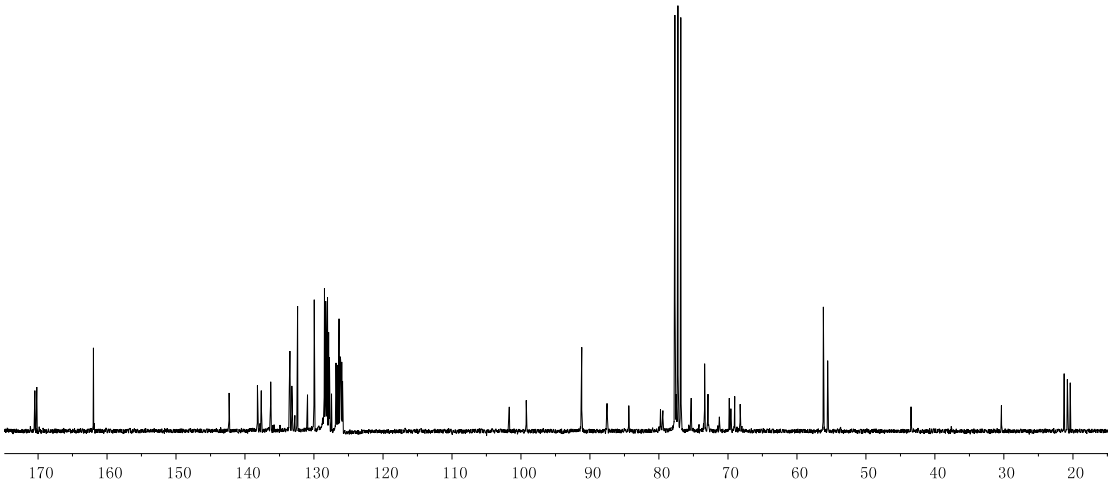


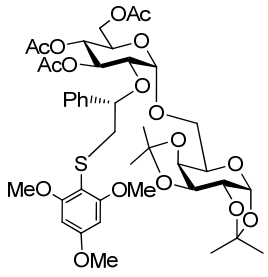


33

500 MHz, $CDCl_3$

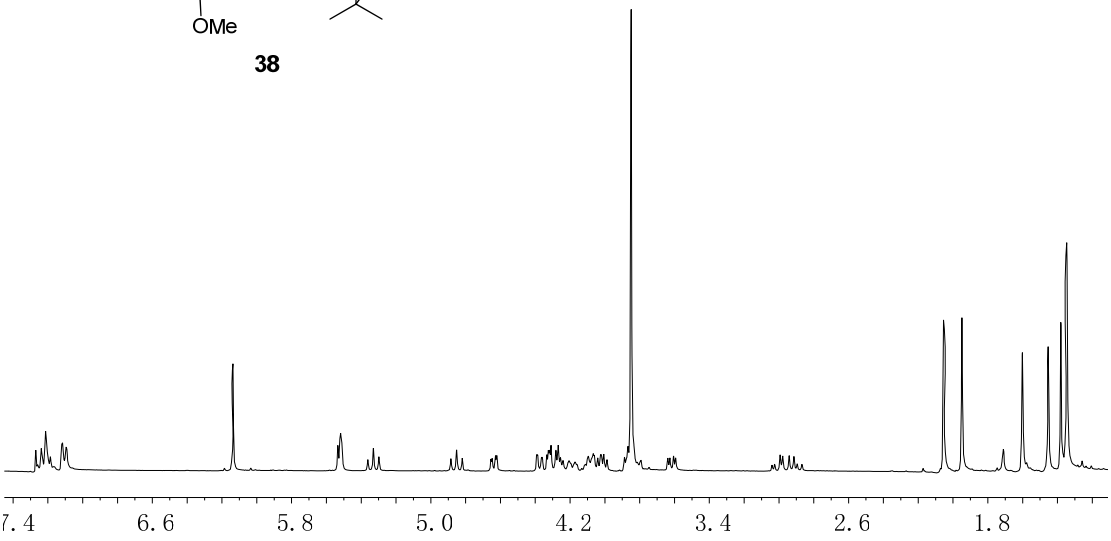
150 MHz, $CDCl_3$



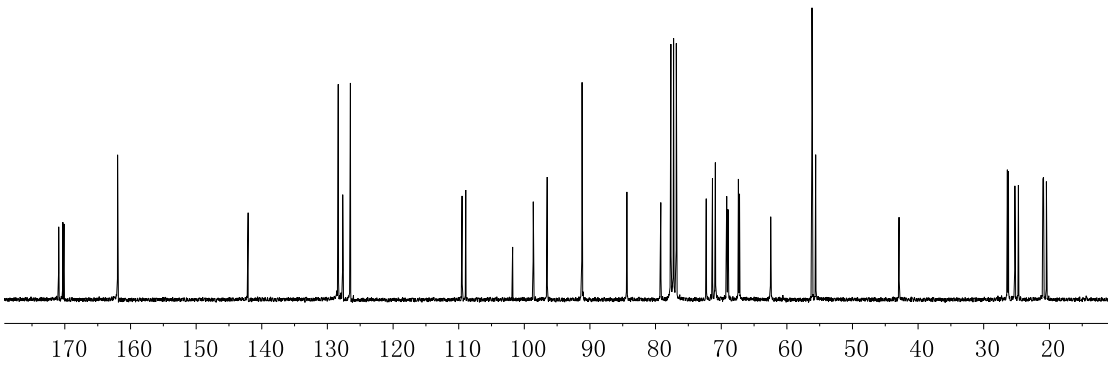


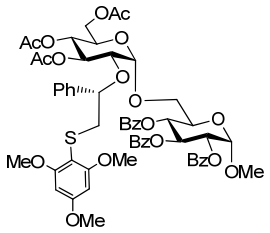
38

300 MHz, $CDCl_3$



75 MHz, $CDCl_3$

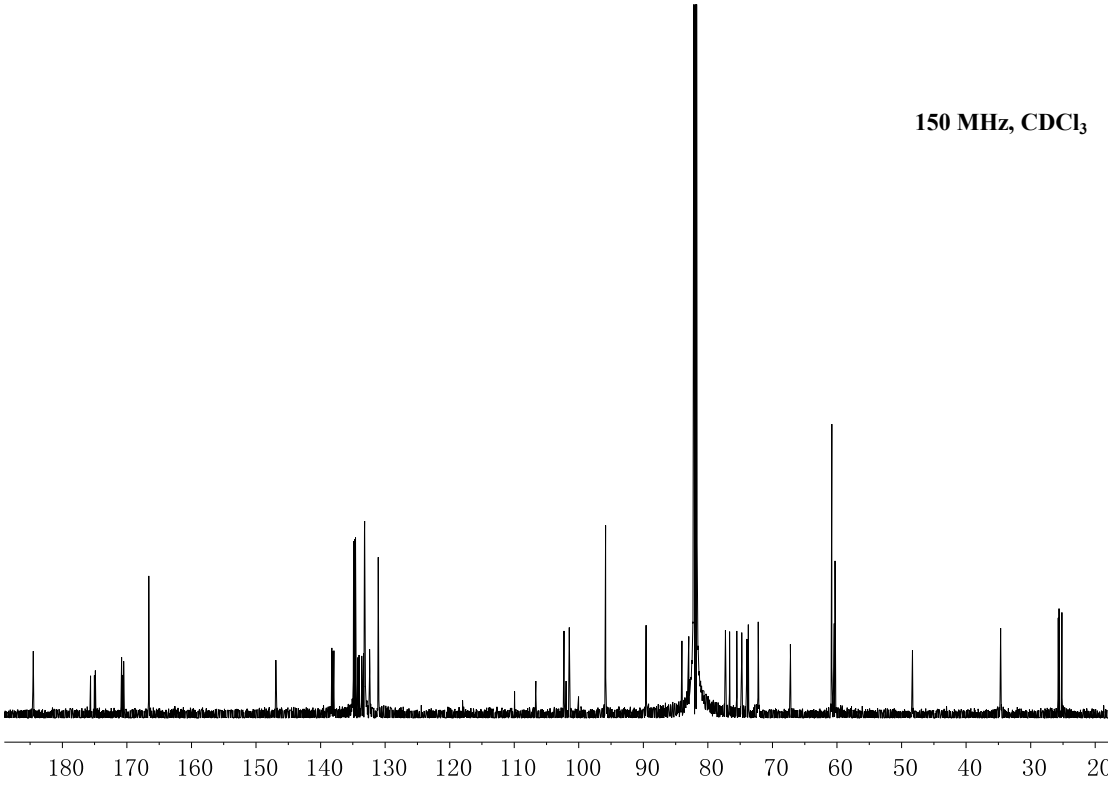


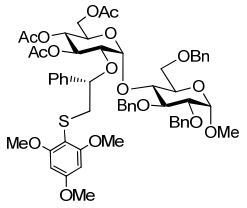


39

600 MHz, $CDCl_3$

150 MHz, $CDCl_3$

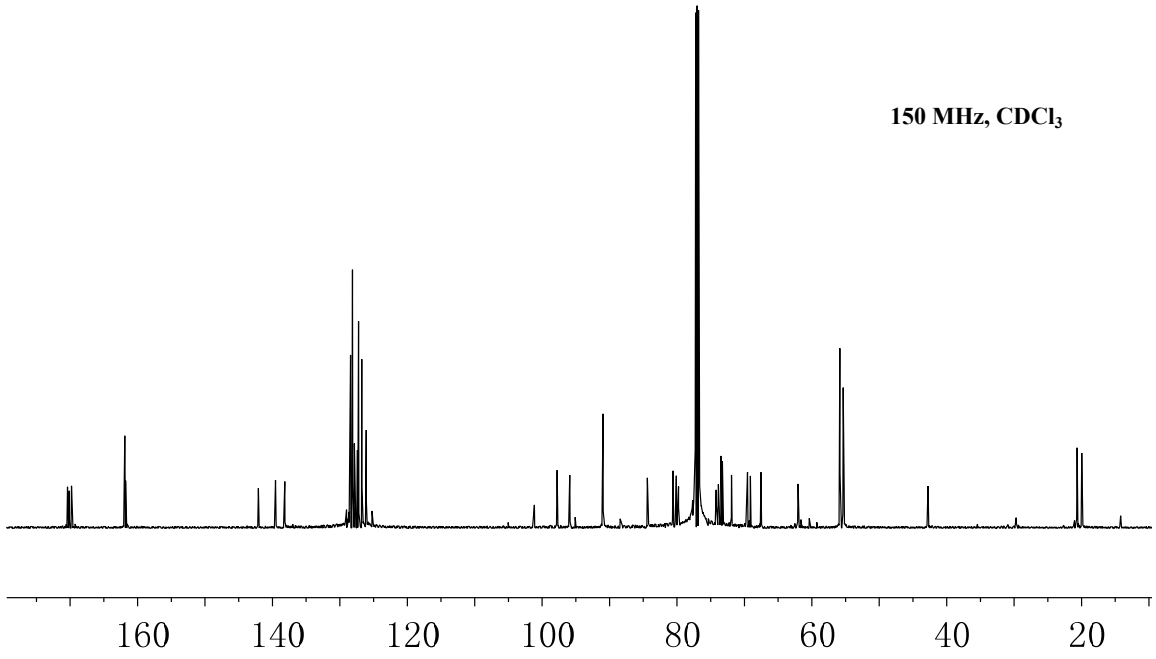


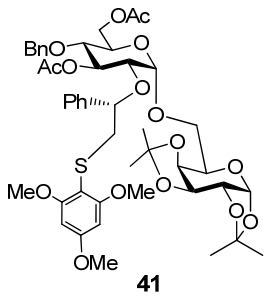


40

500 MHz, $CDCl_3$

150 MHz, $CDCl_3$

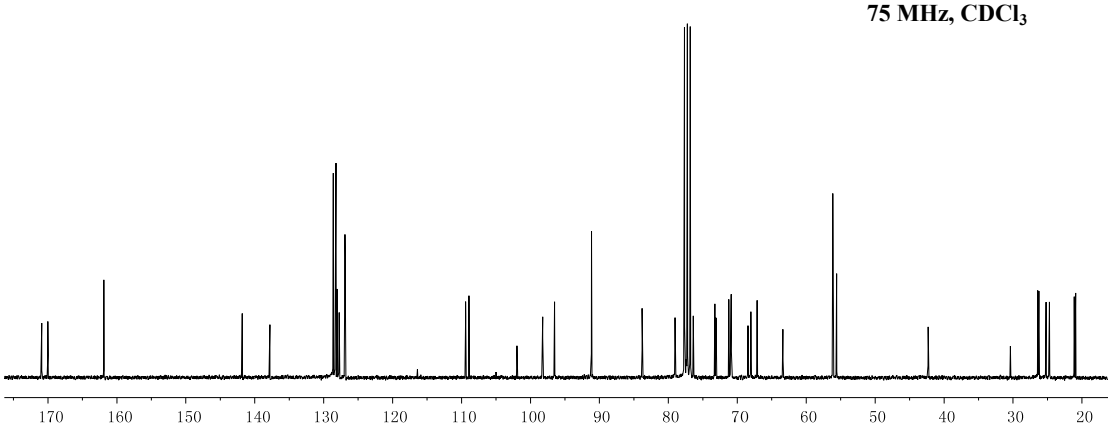




41

300 MHz, $CDCl_3$

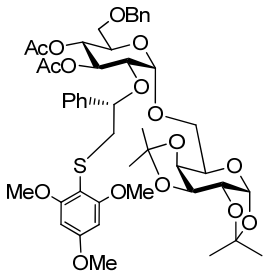
75 MHz, $CDCl_3$



42

600 MHz, $CDCl_3$

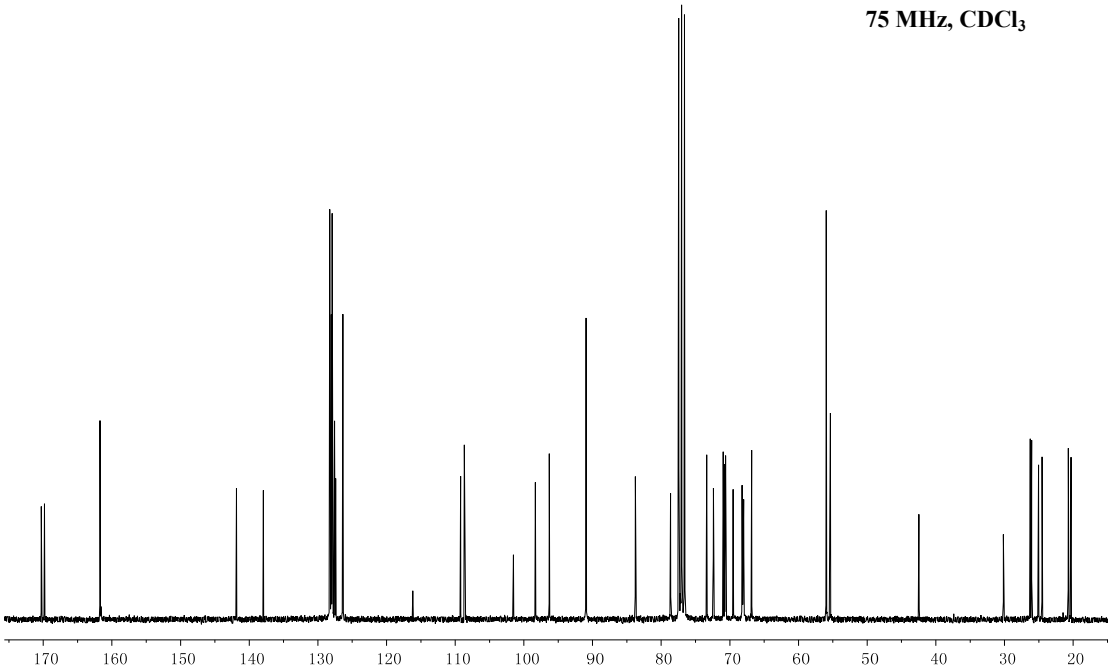
150 MHz, $CDCl_3$

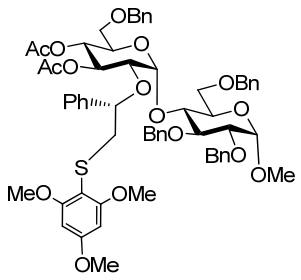


43

300 MHz, $CDCl_3$

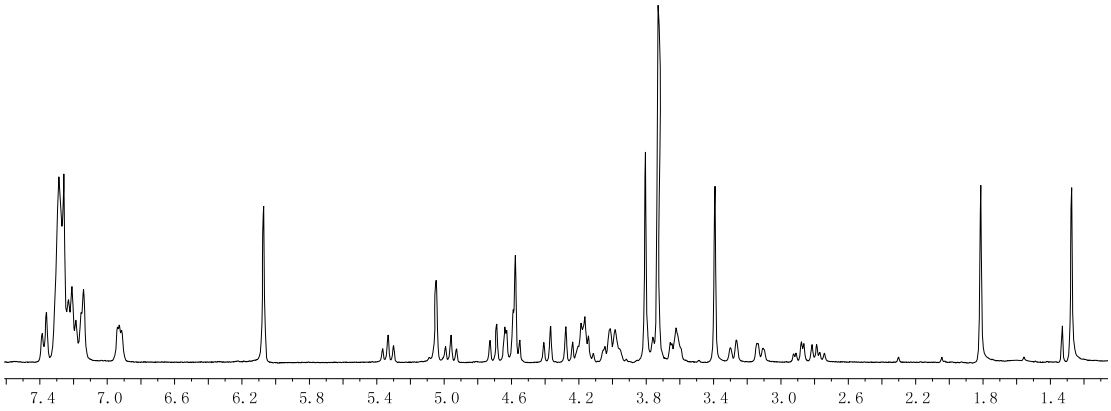
75 MHz, $CDCl_3$



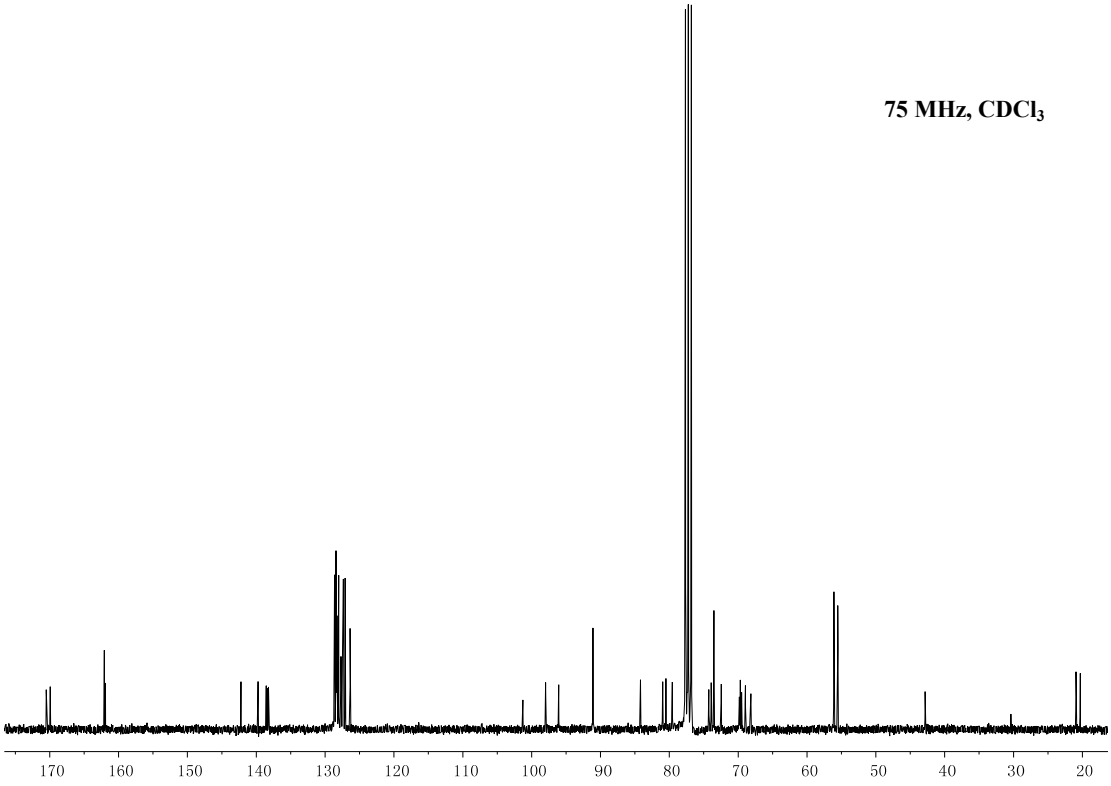


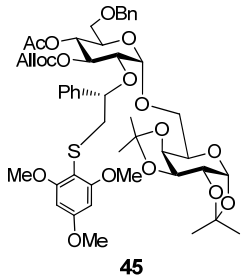
44

300 MHz, $CDCl_3$



75 MHz, $CDCl_3$

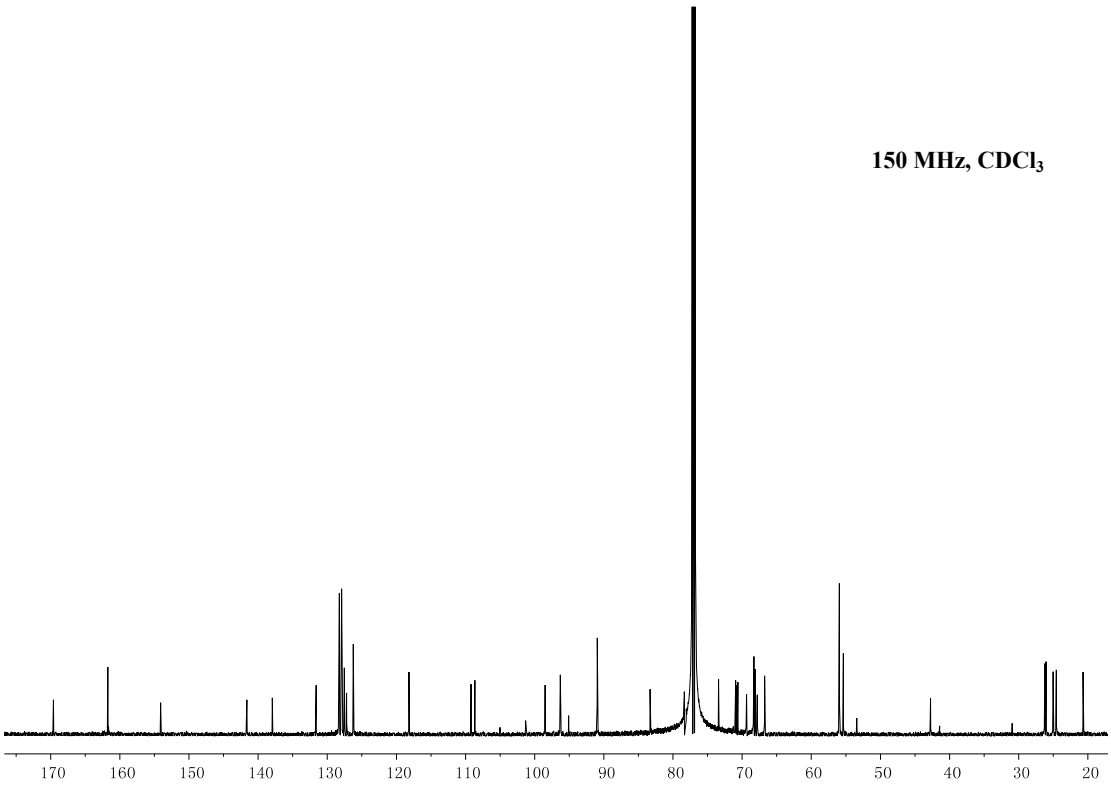


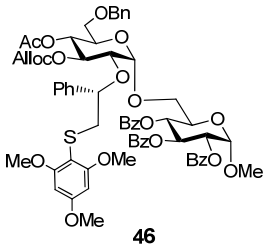


45

600 MHz, $CDCl_3$

150 MHz, $CDCl_3$

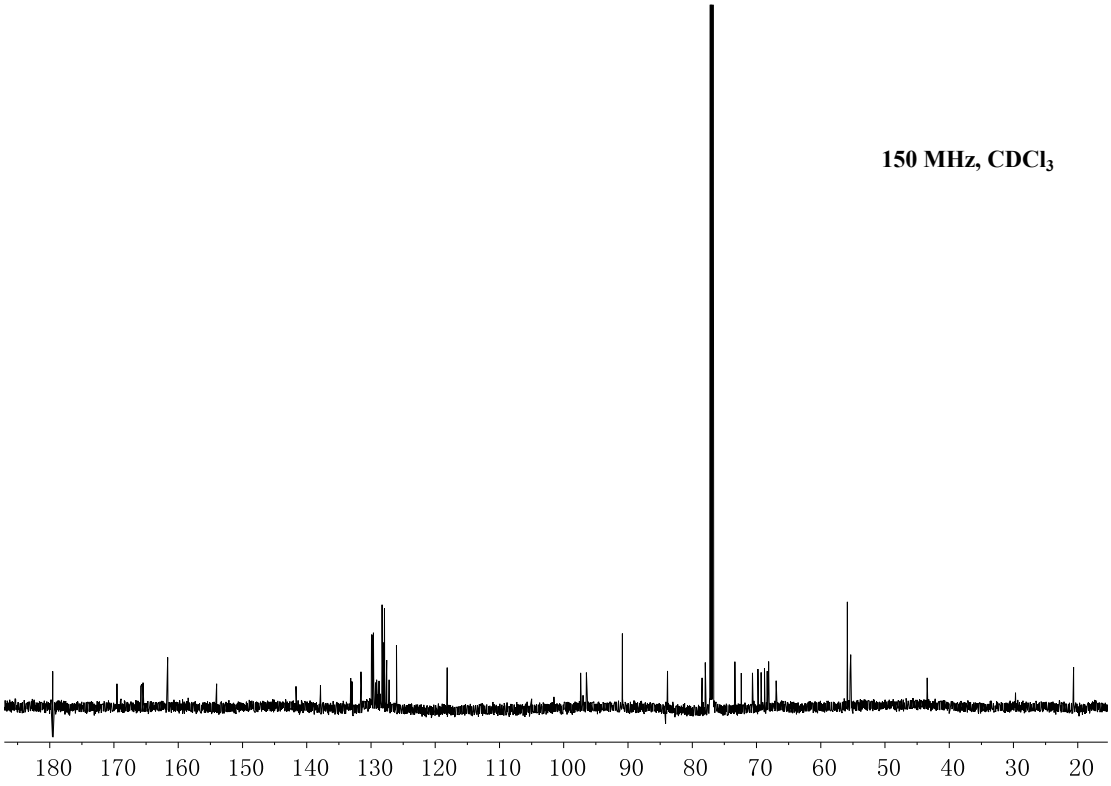


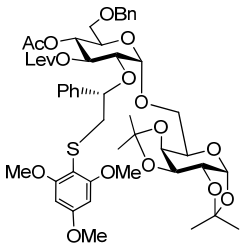


46

500 MHz, $CDCl_3$

150 MHz, $CDCl_3$

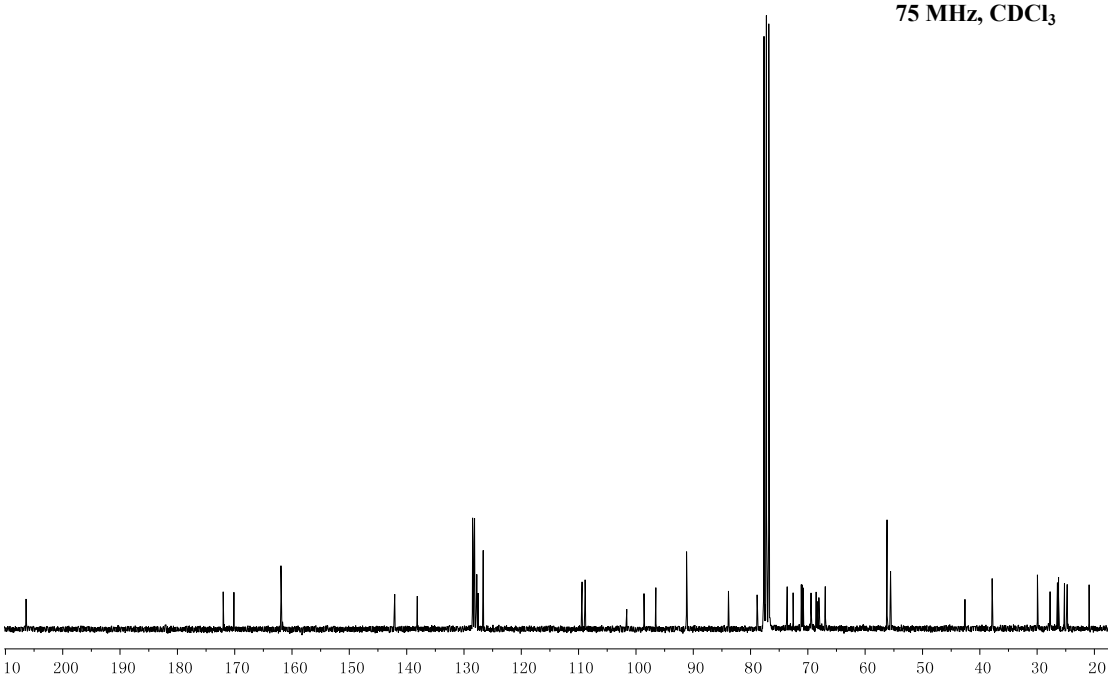


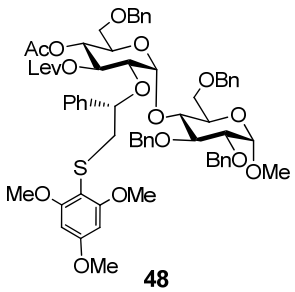


47

300 MHz, $CDCl_3$

75 MHz, $CDCl_3$

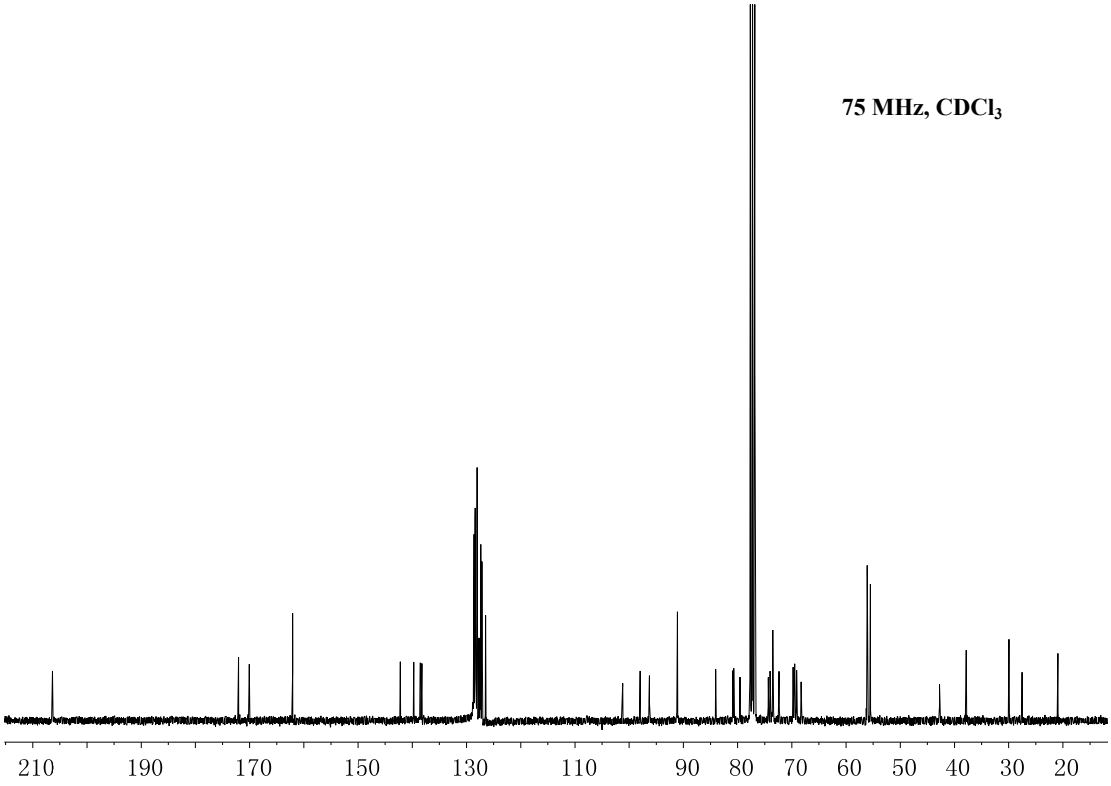


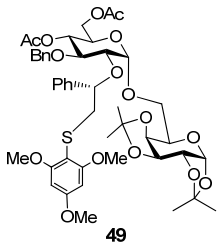


48

500 MHz, $CDCl_3$

75 MHz, $CDCl_3$

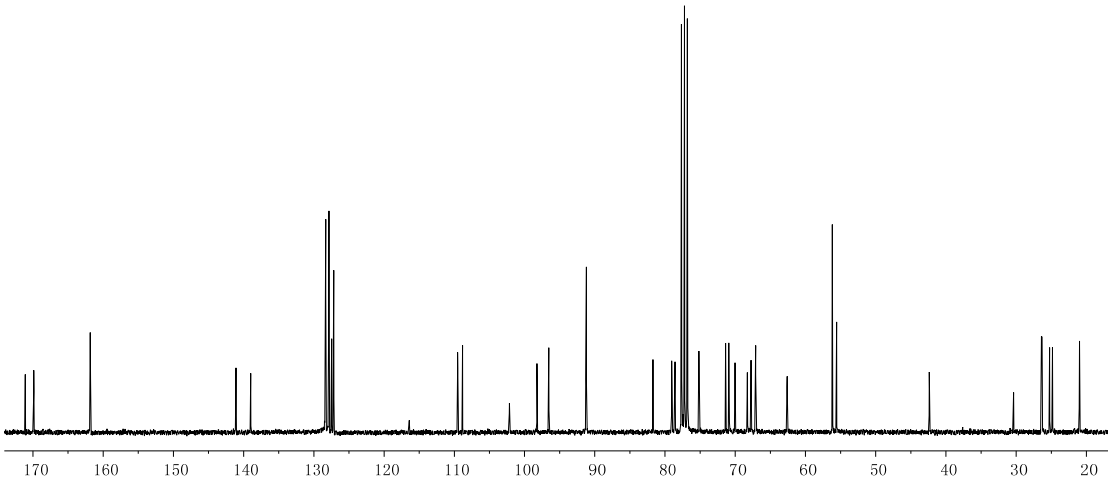


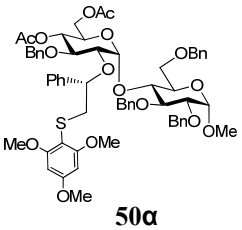


49

300 MHz, $CDCl_3$

75 MHz, $CDCl_3$

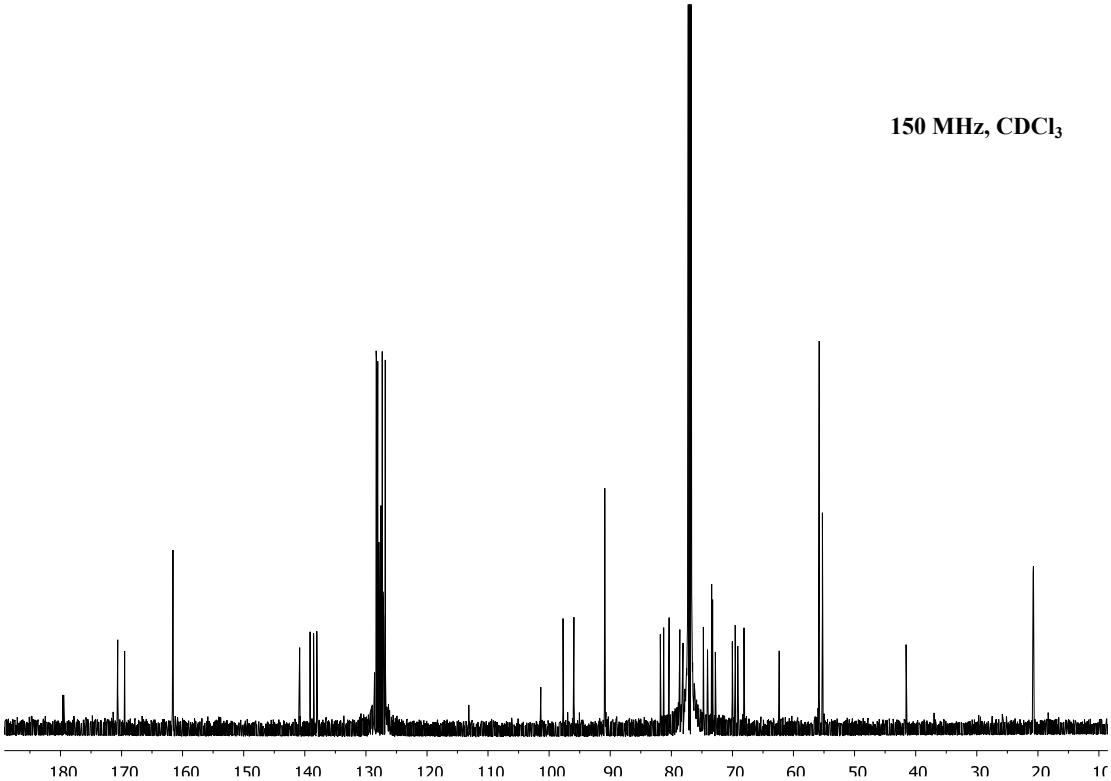


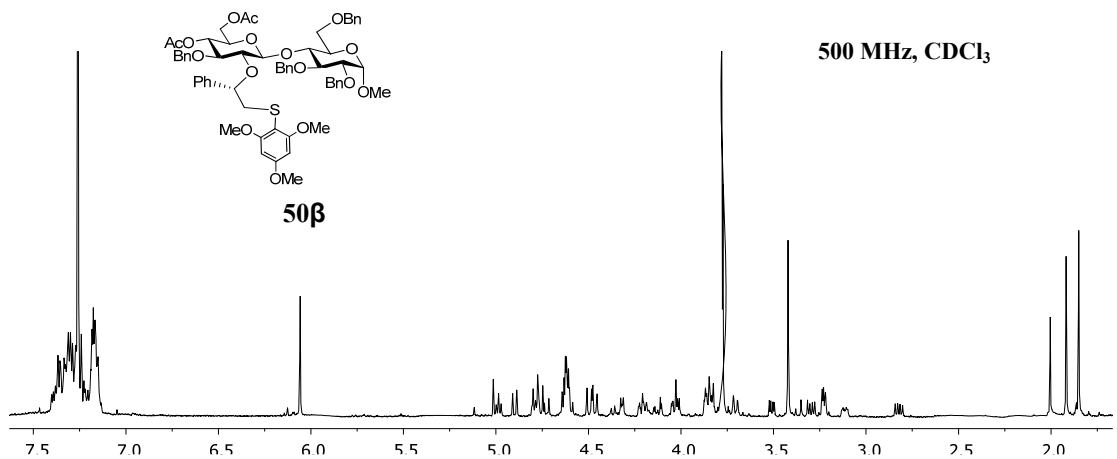


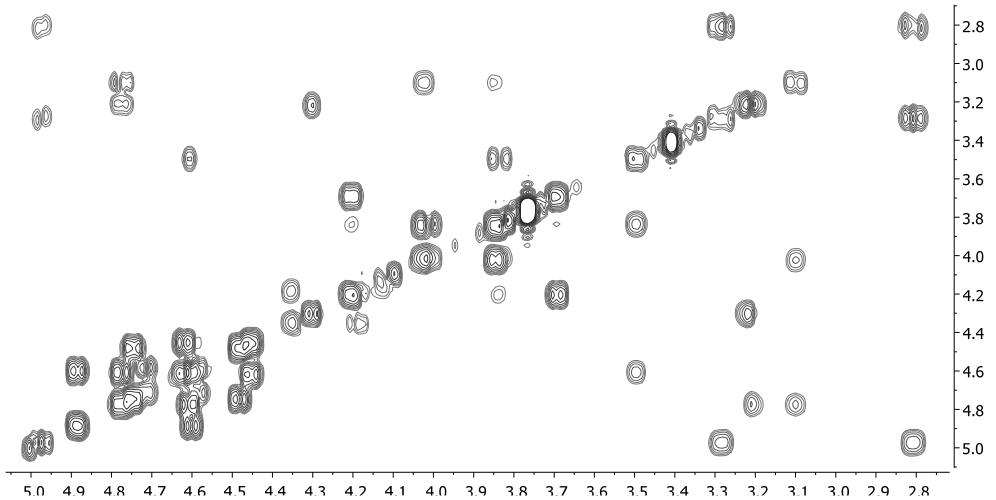
50α

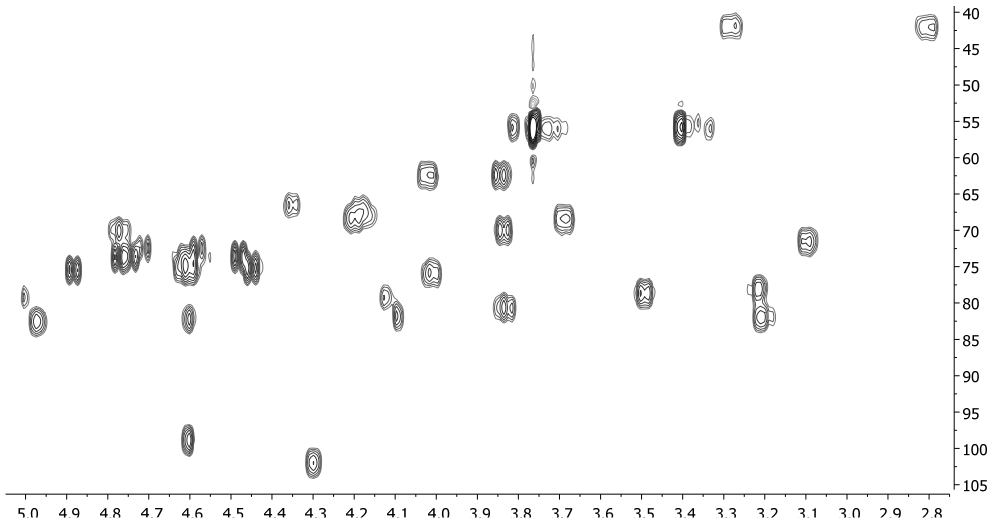
500 MHz, $CDCl_3$

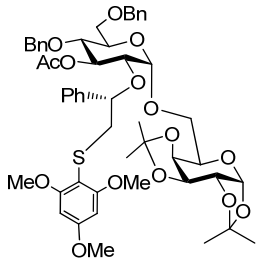
150 MHz, $CDCl_3$




OAc
OBn
AcO
BnO
O
BnO
BnO
OMe
Ph
S
MeO
OMe
OMe
500 MHz, CDCl3
50β



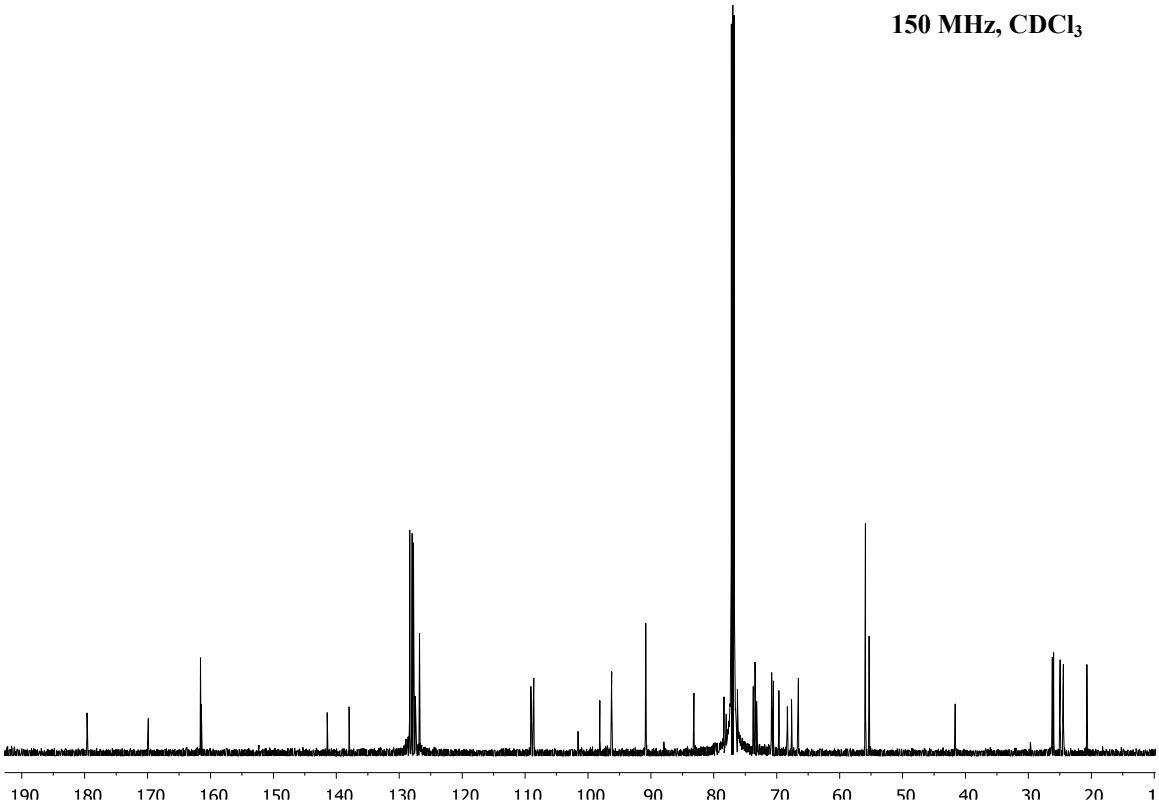


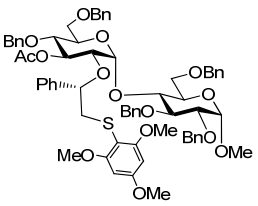


51

600 MHz, $CDCl_3$

150 MHz, $CDCl_3$

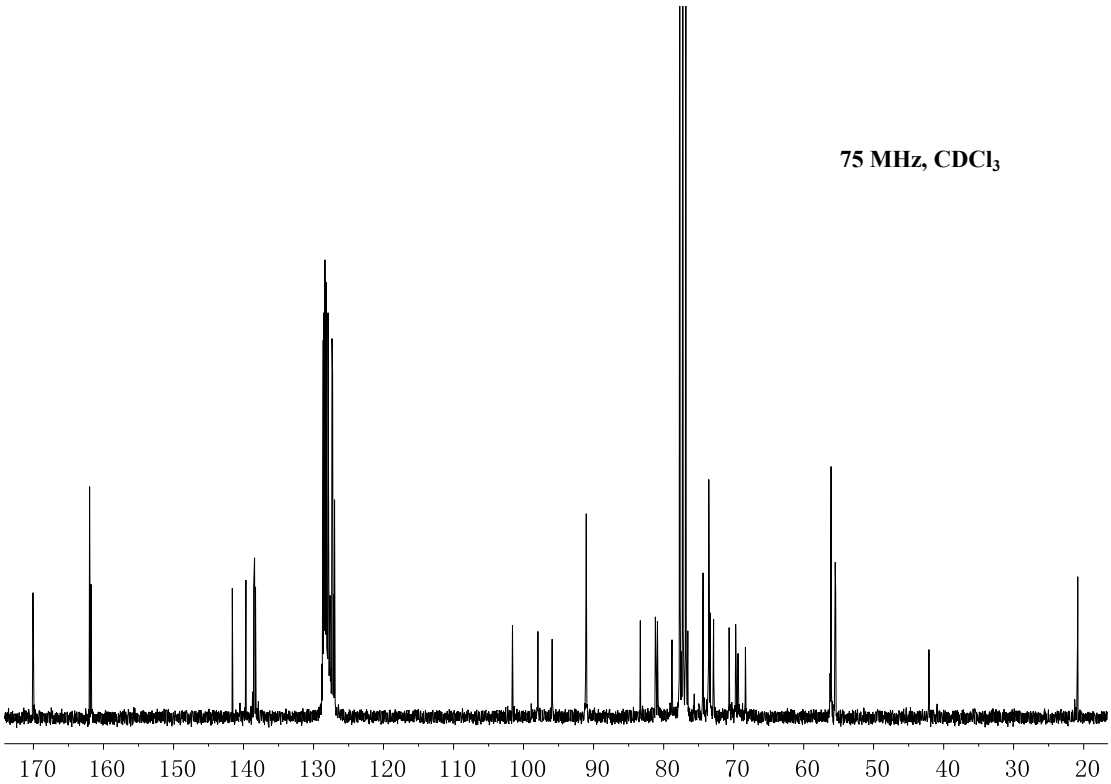


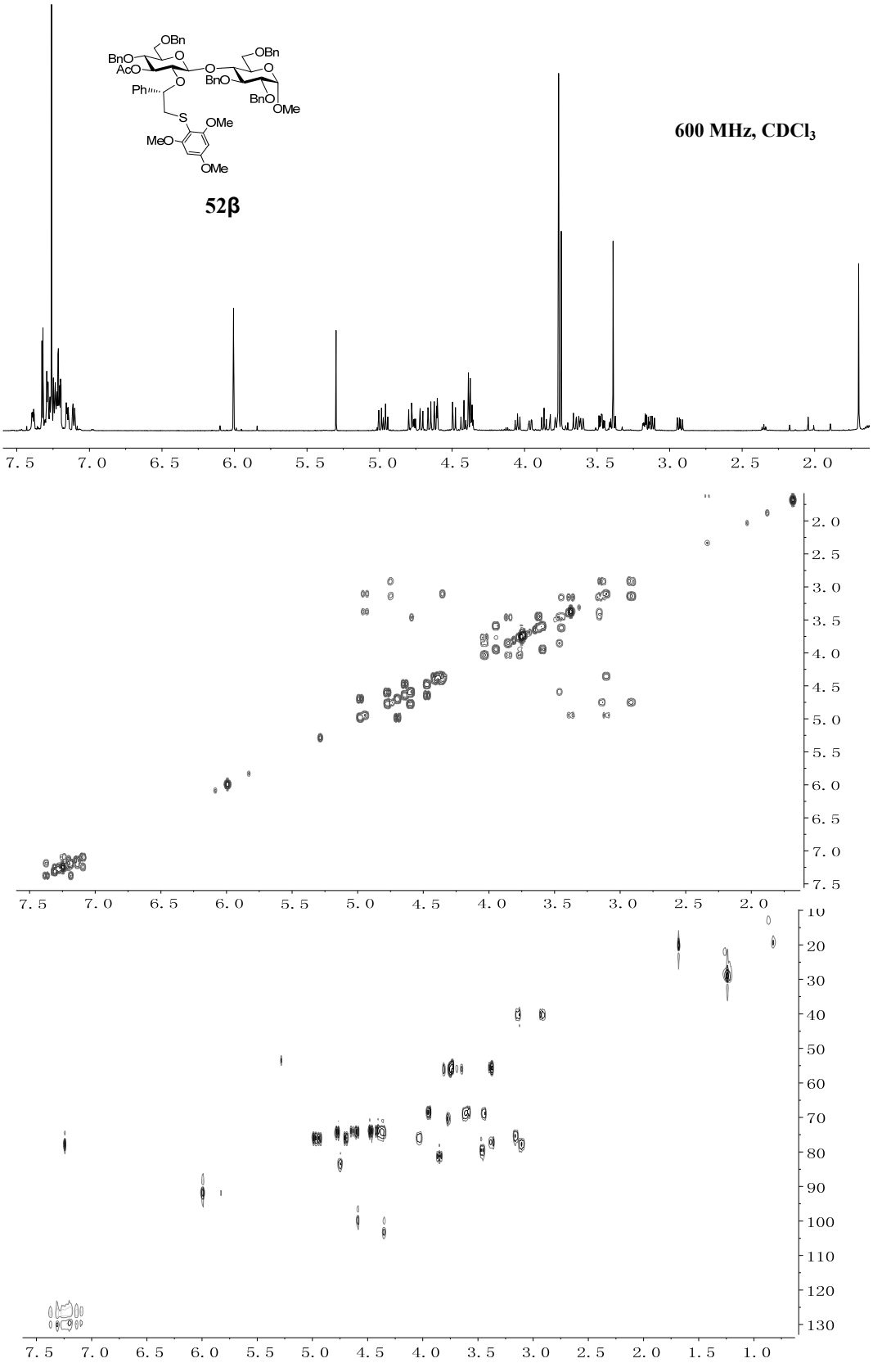


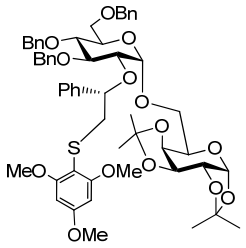
52α

600 MHz, $CDCl_3$

75 MHz, $CDCl_3$

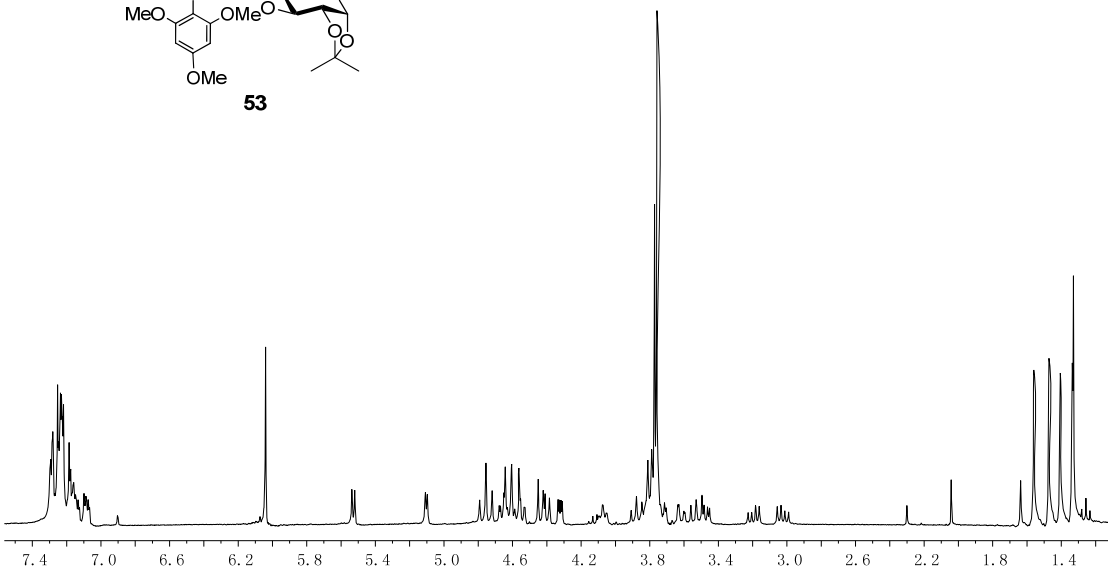



OBn
BnO
AcO
O
OBn
O
BnO
BnO
OMe
Ph
S
OMe
MeO
OMe
52β
600 MHz, CDCl3

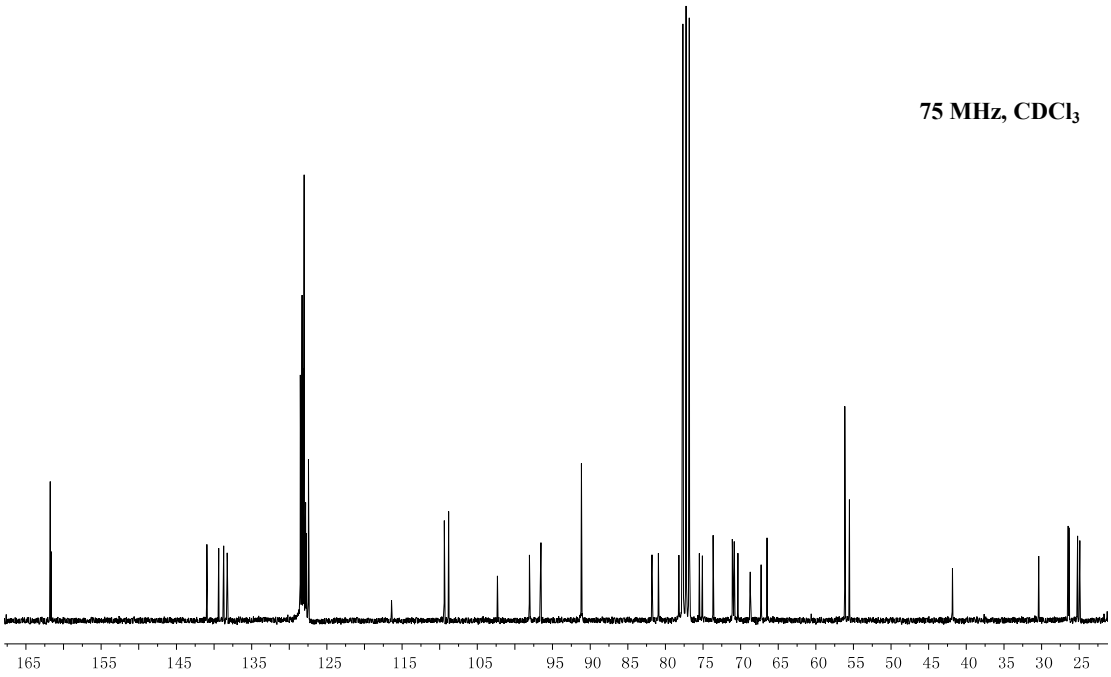


53

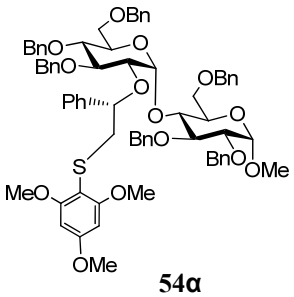
300 MHz, $CDCl_3$



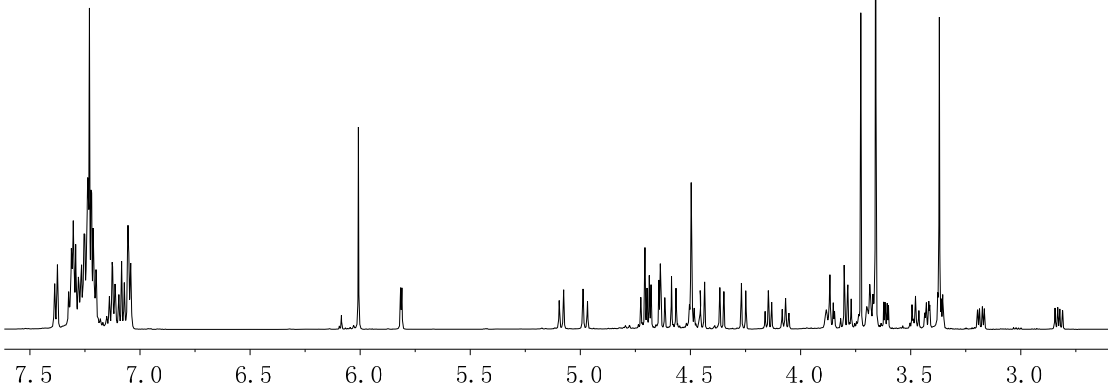
75 MHz, $CDCl_3$



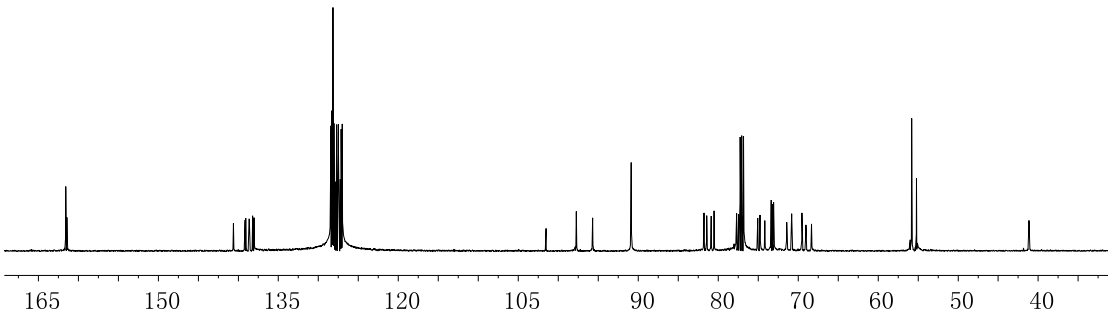
600 MHz, $CDCl_3$

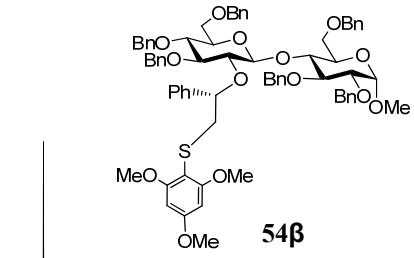


54α



150 MHz, $CDCl_3$

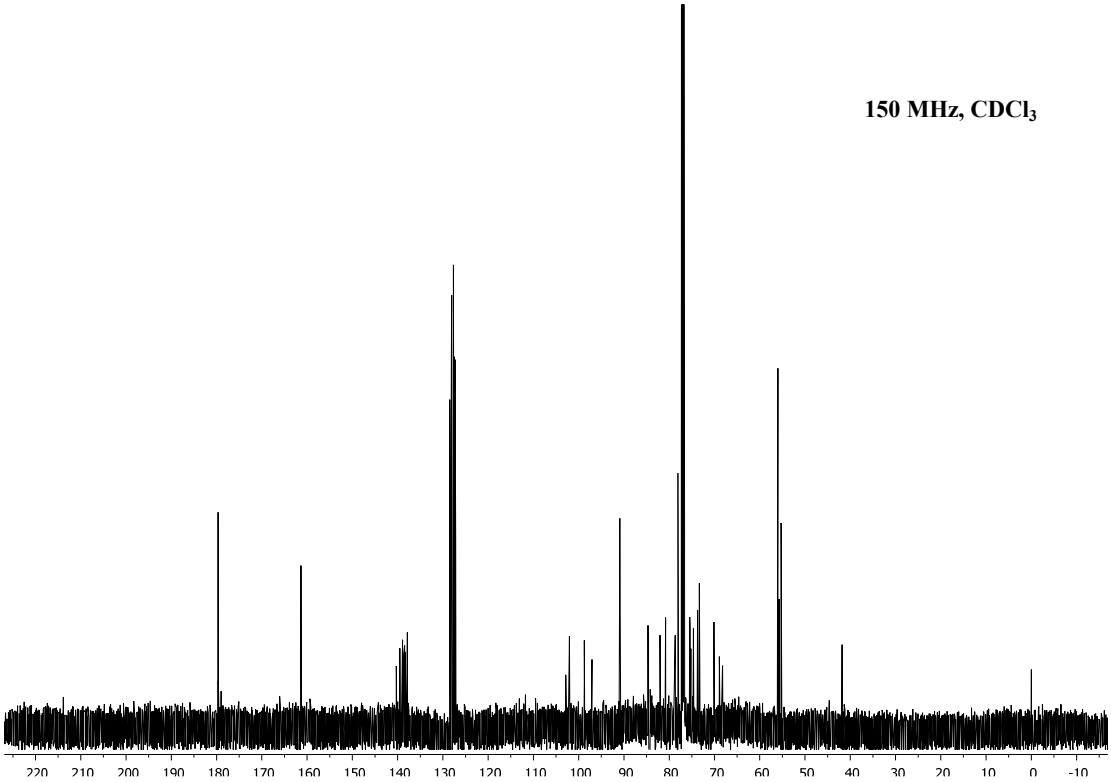


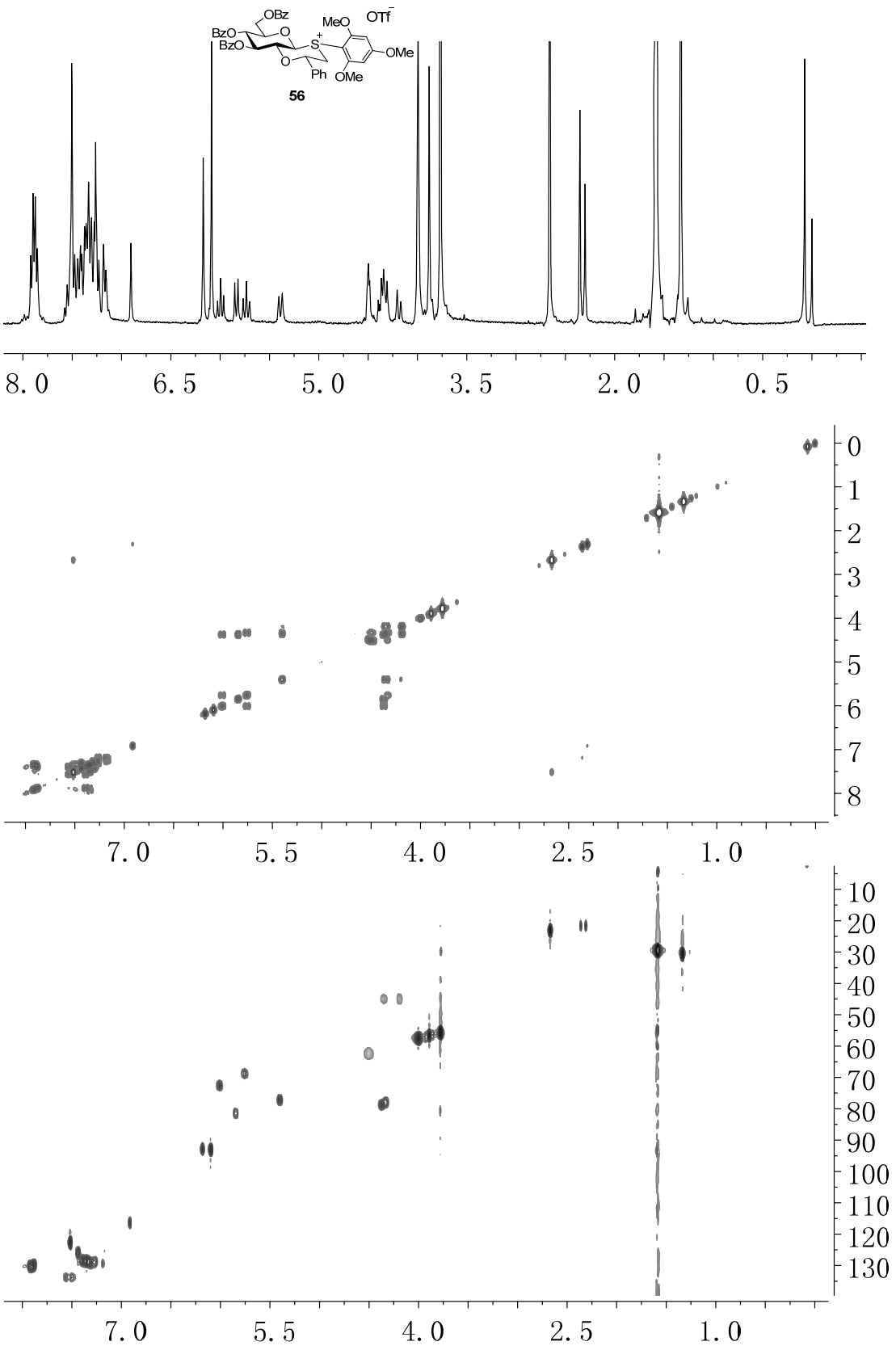


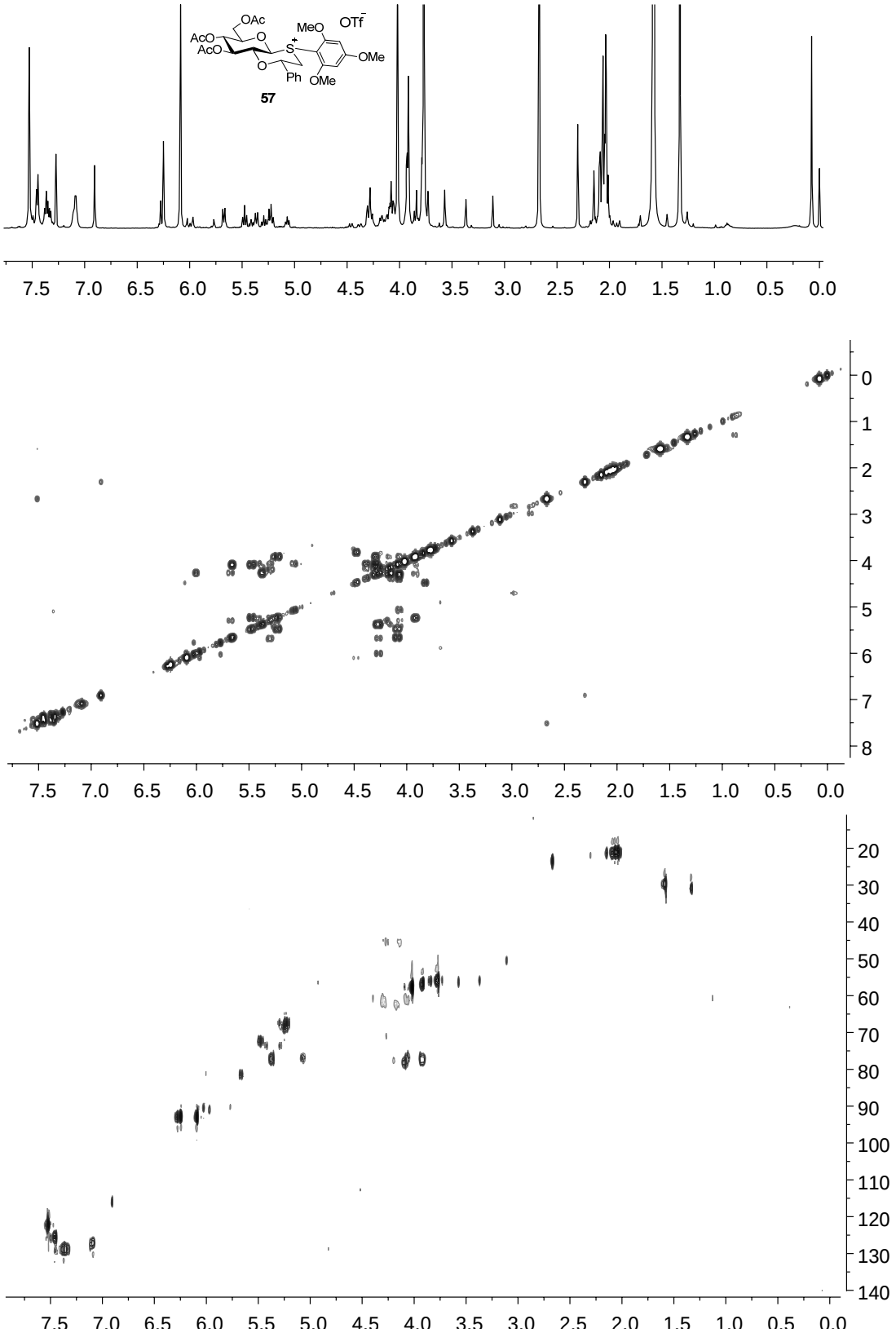
54β

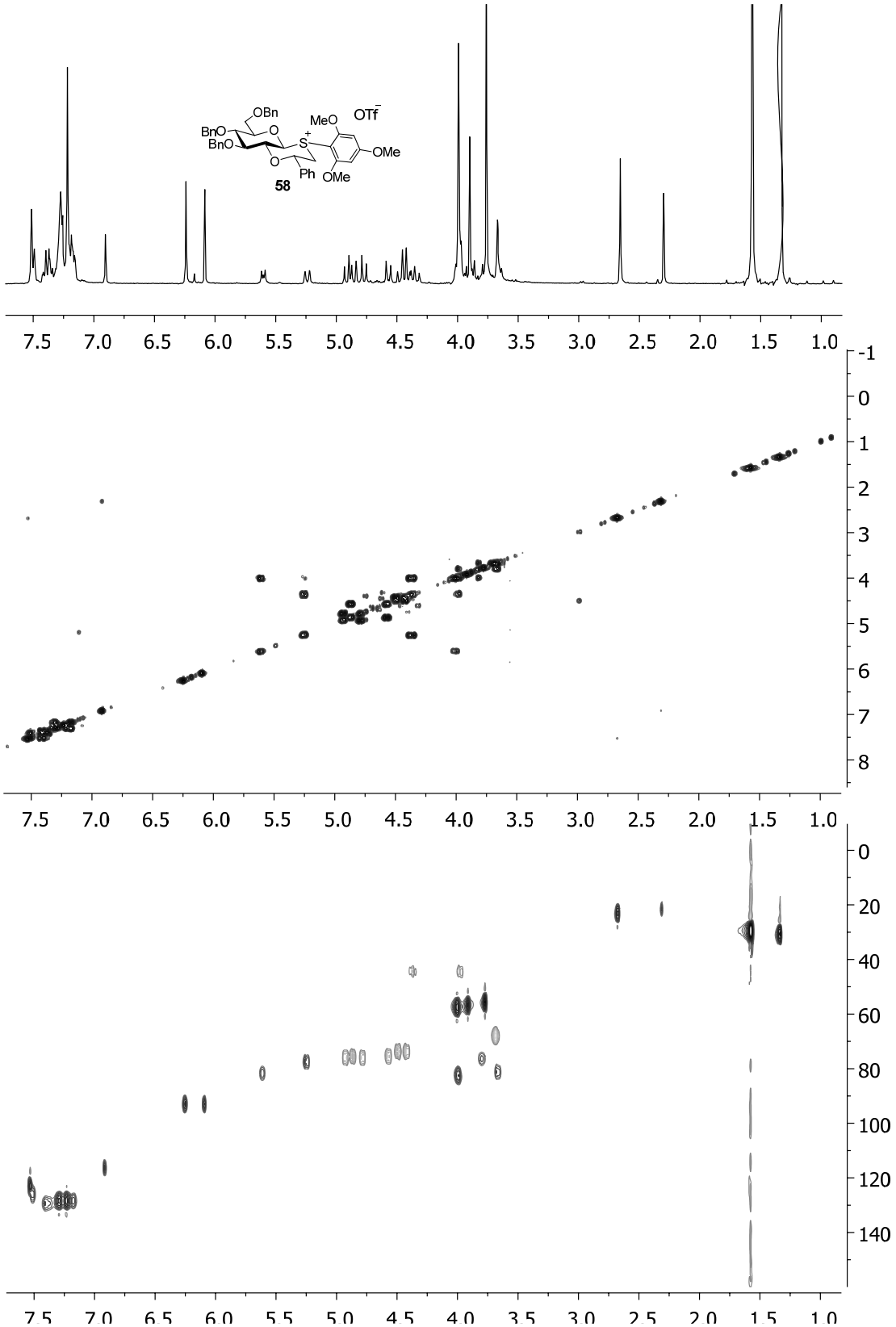
500 MHz, $CDCl_3$

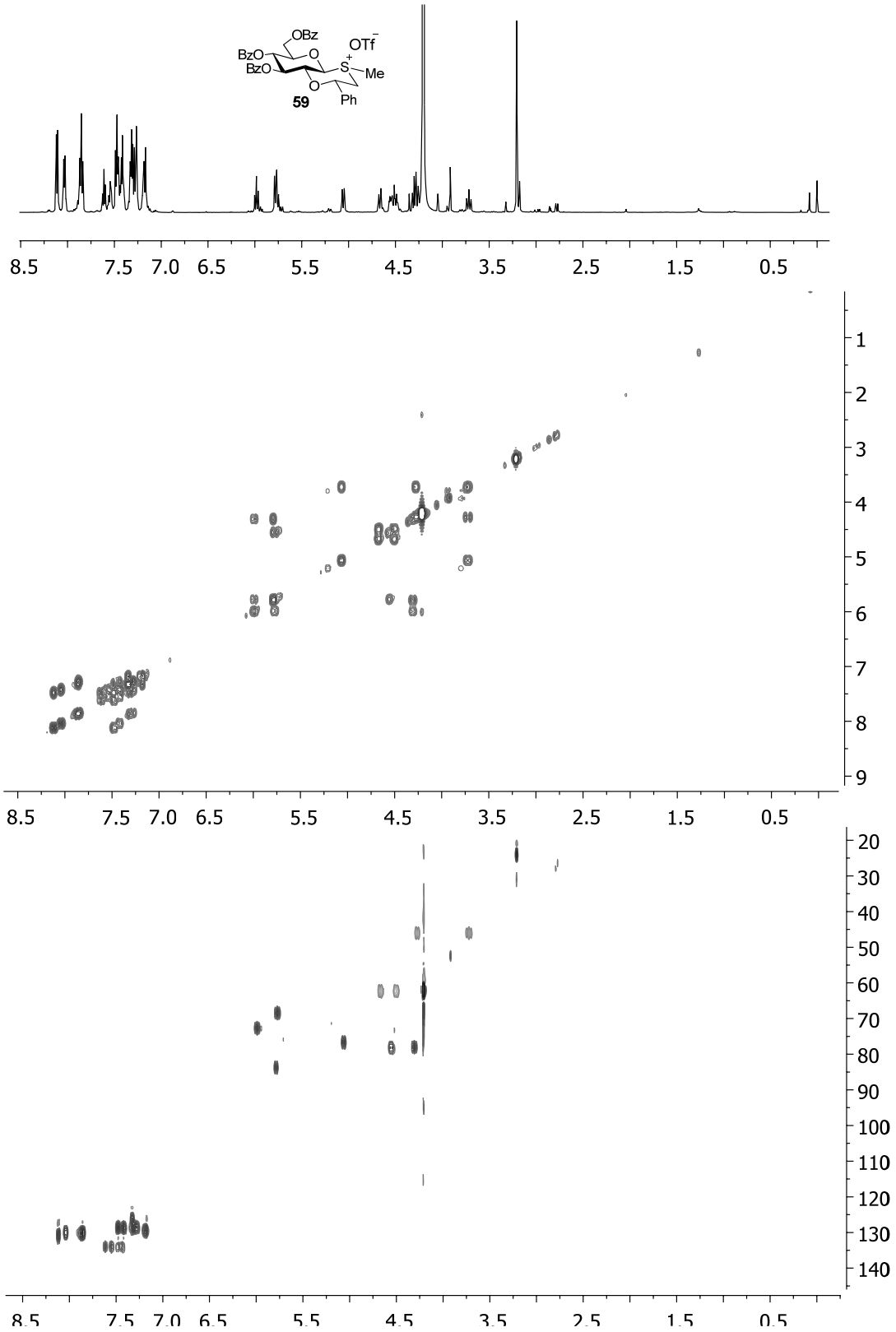
150 MHz, $CDCl_3$

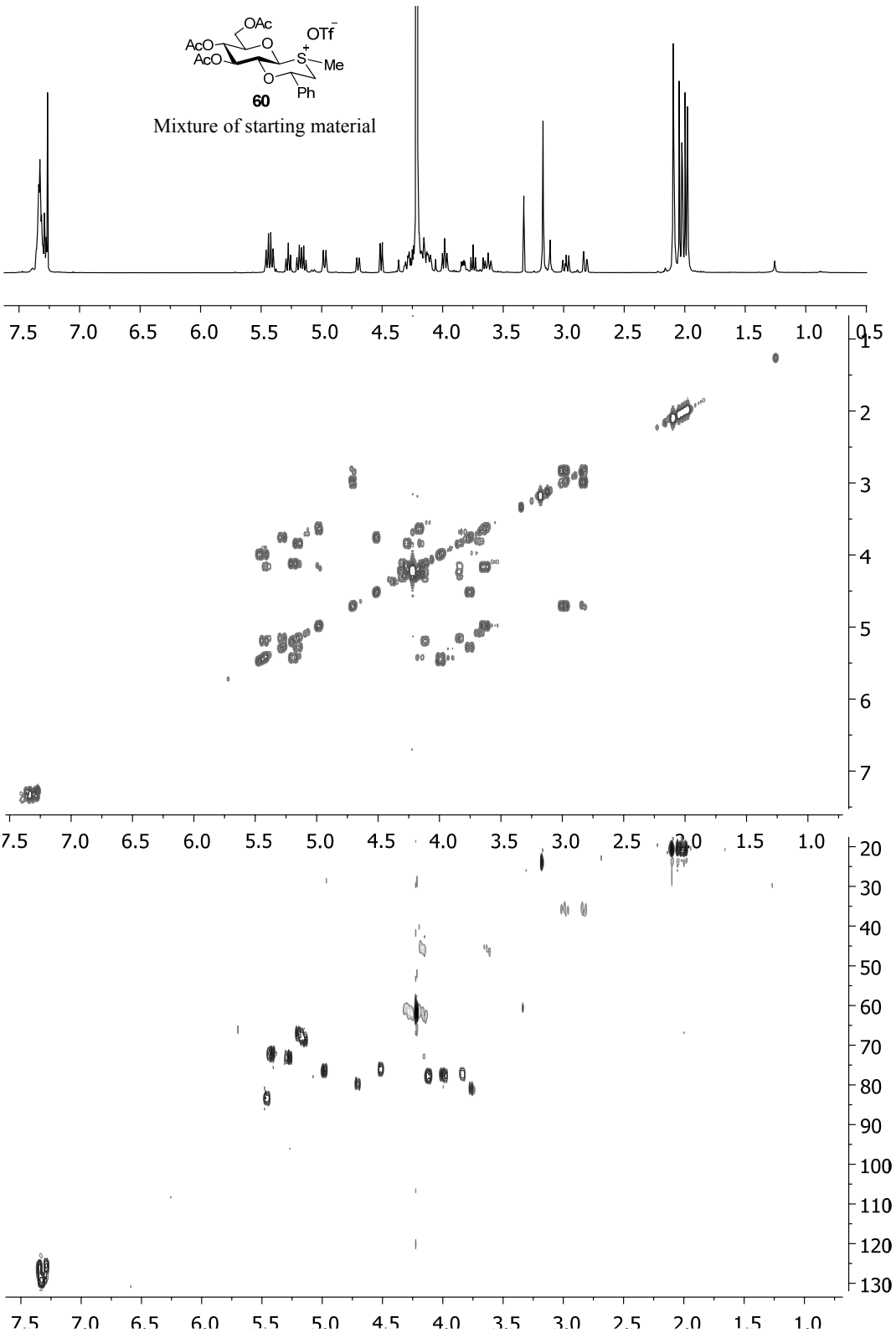


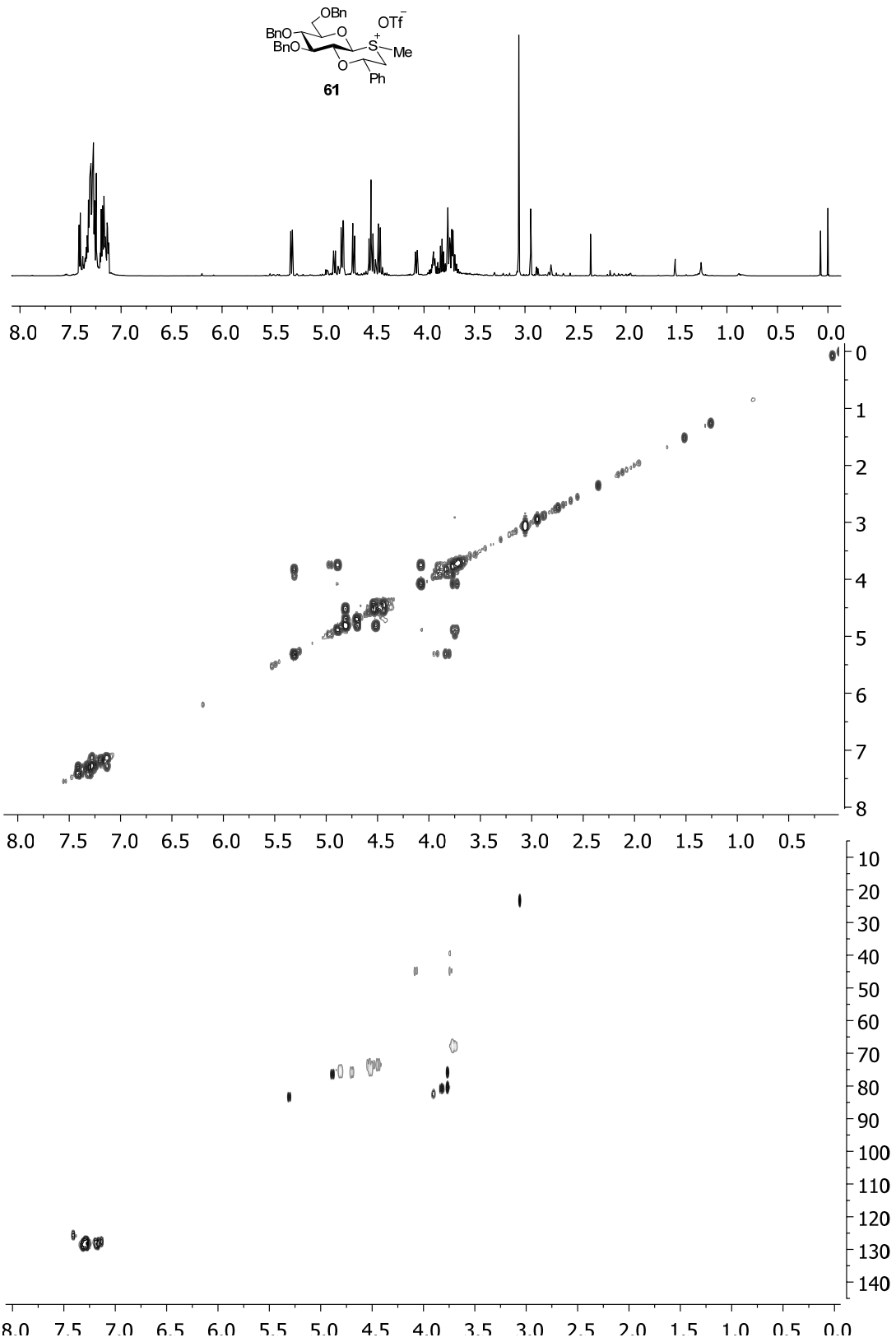

OBz
BzO
BzO
O
S
Ph
MeO
OTf
OMe
OMe
56
8.0
6.5
5.0
3.5
2.0
0.5
0
1
2
3
4
5
6
7
8
7.0
5.5
4.0
2.5
1.0
10
20
30
40
50
60
70
80
90
100
110
120
130
7.0
5.5
4.0
2.5
1.0

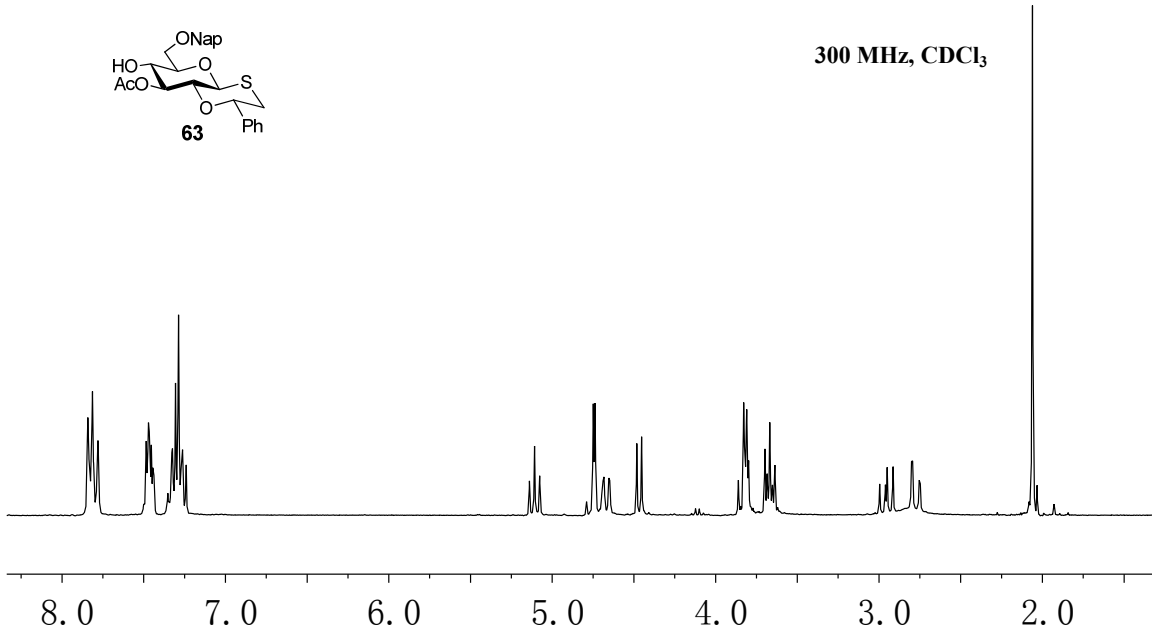

OAc
AcO
AcO
O
O
S+
Ph
MeO
OTf−
OMe
OMe
57
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
20 30 40 50 60 70 80 90 100 110 120 130 140
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

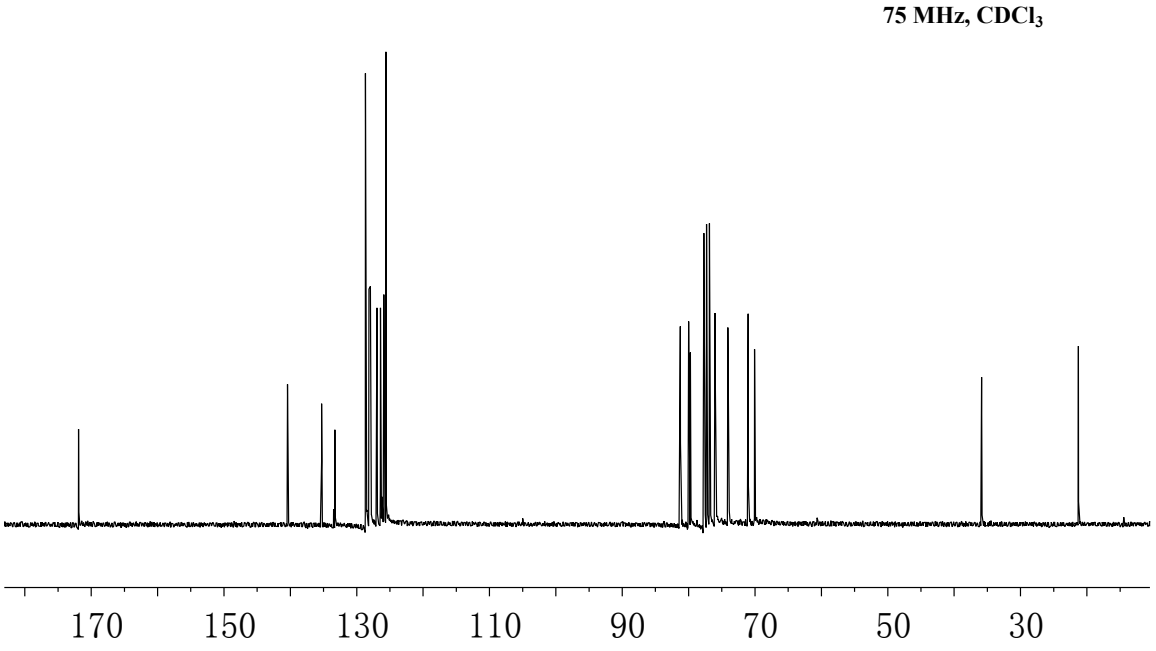

OBn
BnO
BnO
O
S
+
MeO
OTf
OMe
Ph
OMe
58
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
-1 0 1 2 3 4 5 6 7 8
0 20 40 60 80 100 120 140

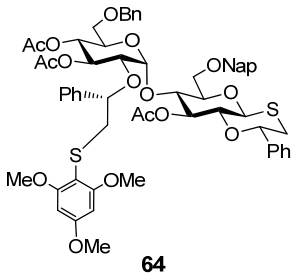

OBz
OTf
BzO
BzO
O
S
Me
O
59
Ph
8.5
7.5
7.0
6.5
5.5
4.5
3.5
2.5
1.5
0.5
1
2
3
4
5
6
7
8
9
20
30
40
50
60
70
80
90
100
110
120
130
140


OAc
AcO
AcO
O
OTf
S
Me
Ph
60
Mixture of starting material
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
1 2 3 4 5 6 7
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
20 30 40 50 60 70 80 90 100 110 120 130
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0


OBn
OTf
BnO
BnO
O
S+
Me
O
Ph
61
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
10 20 30 40 50 60 70 80 90 100 110 120 130 140
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


ONap
HO
AcO
O
S
O
Ph
63
300 MHz, CDCl3
8.0
7.0
6.0
5.0
4.0
3.0
2.0

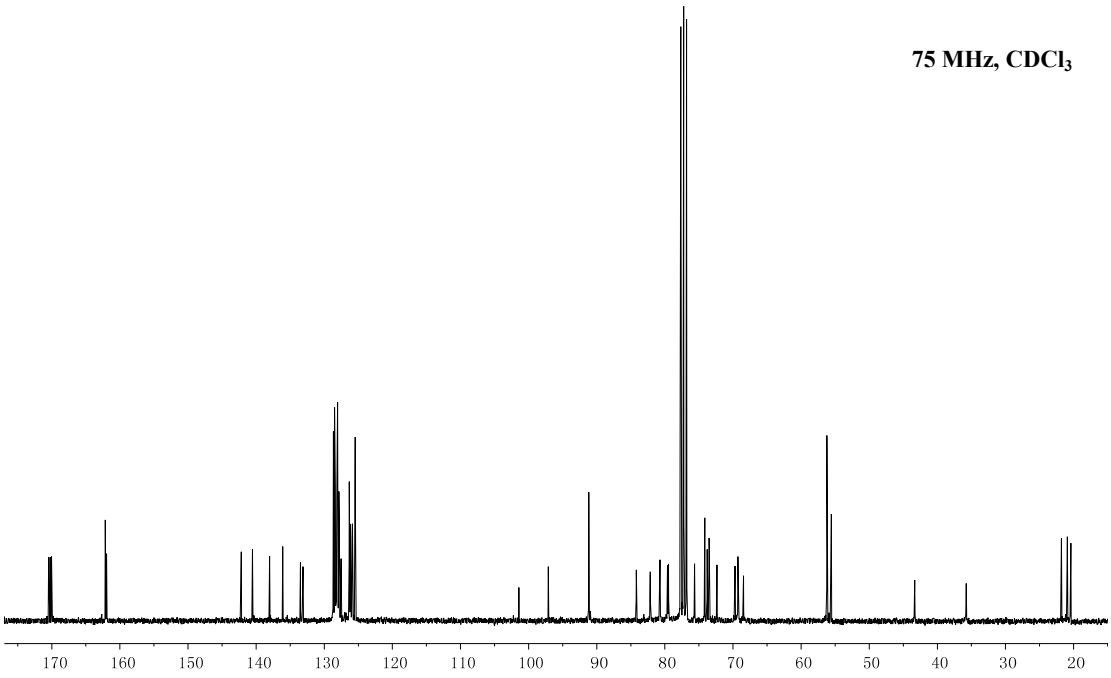

75 MHz, CDCl3
170
150
130
110
90
70
50
30

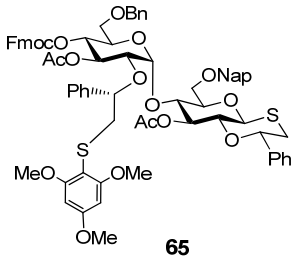


64

300 MHz, $CDCl_3$

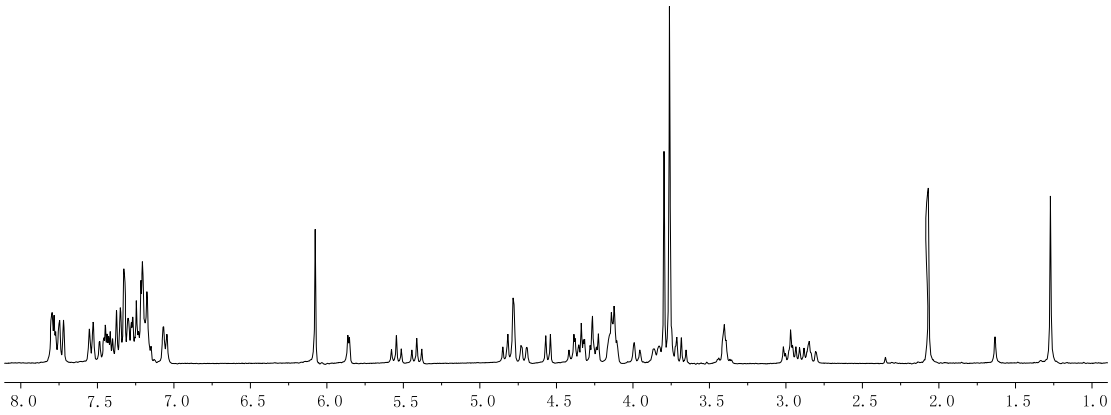
75 MHz, $CDCl_3$



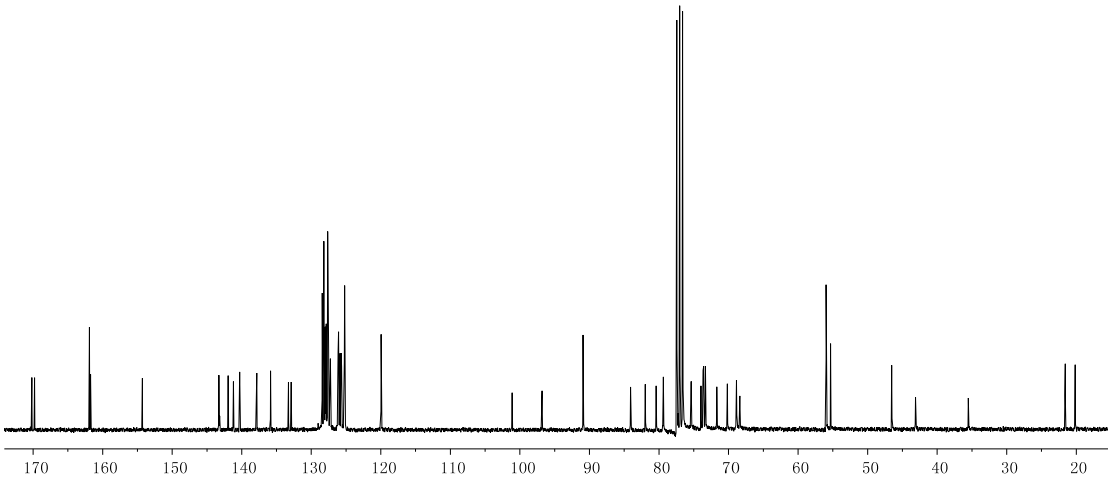


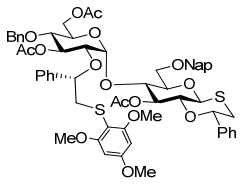
65

300 MHz, $CDCl_3$



75 MHz, $CDCl_3$

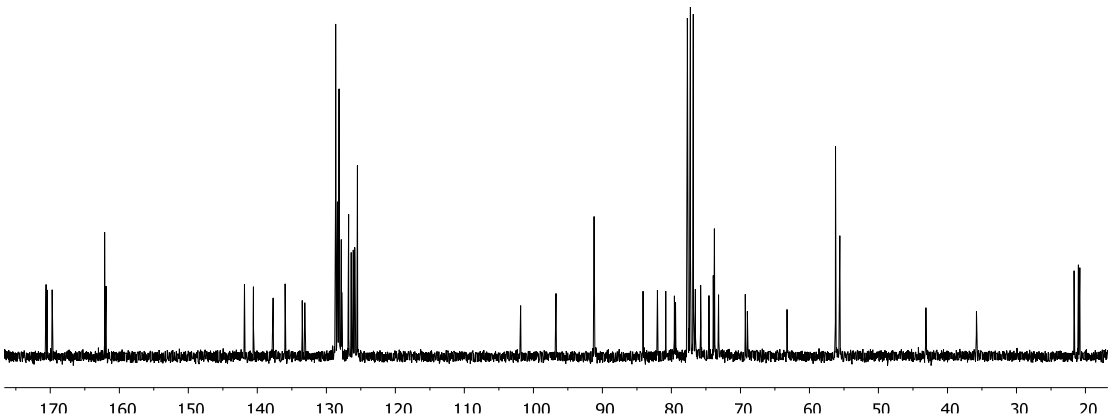


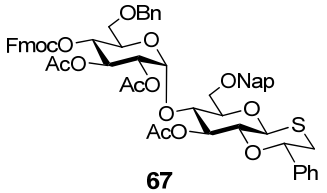


66

600 MHz, $CDCl_3$

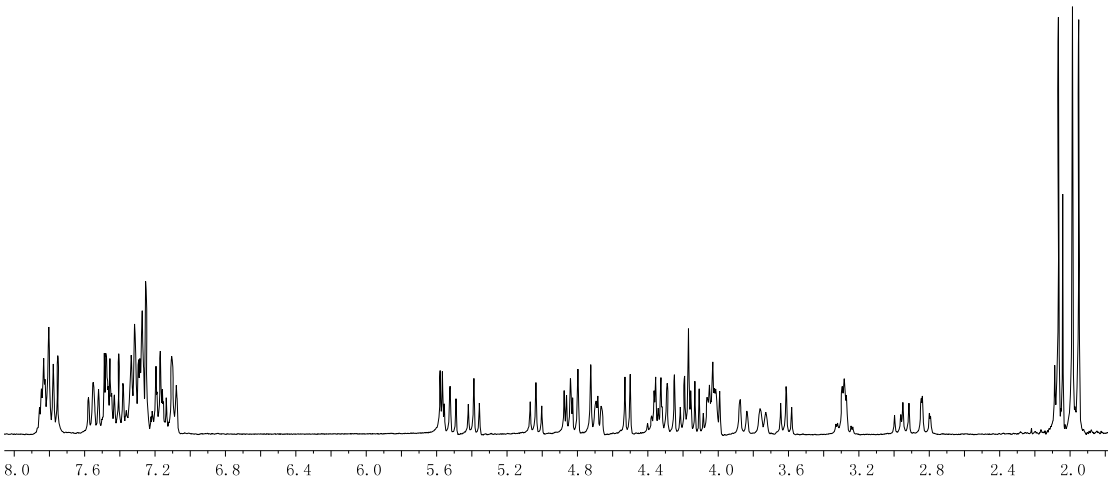
75 MHz, $CDCl_3$



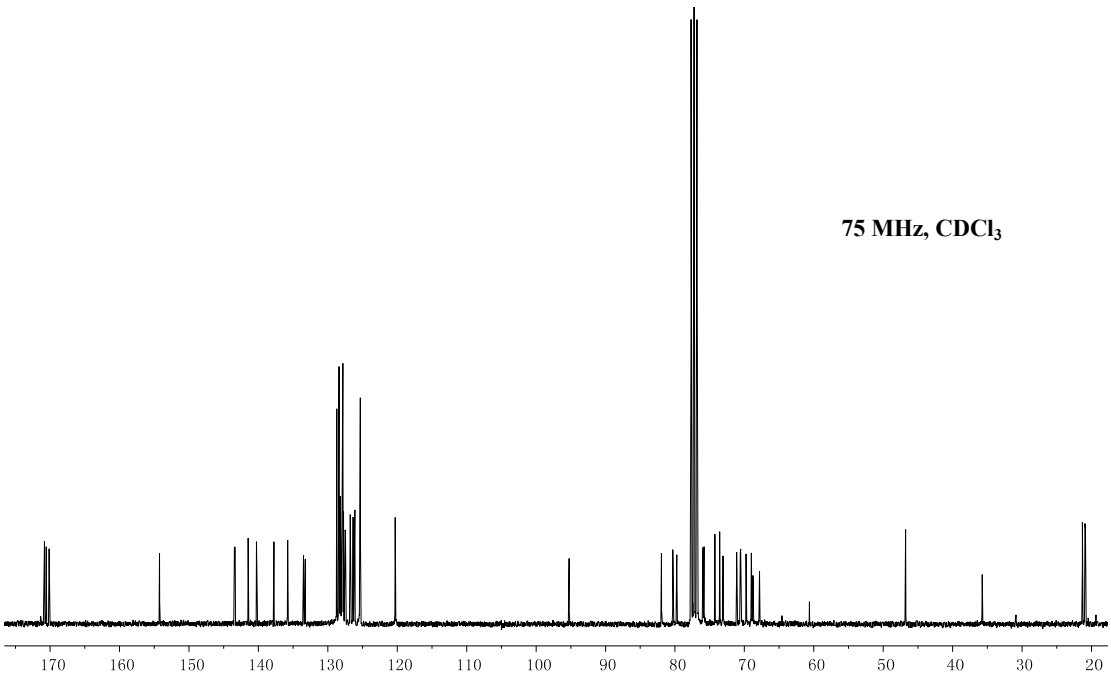


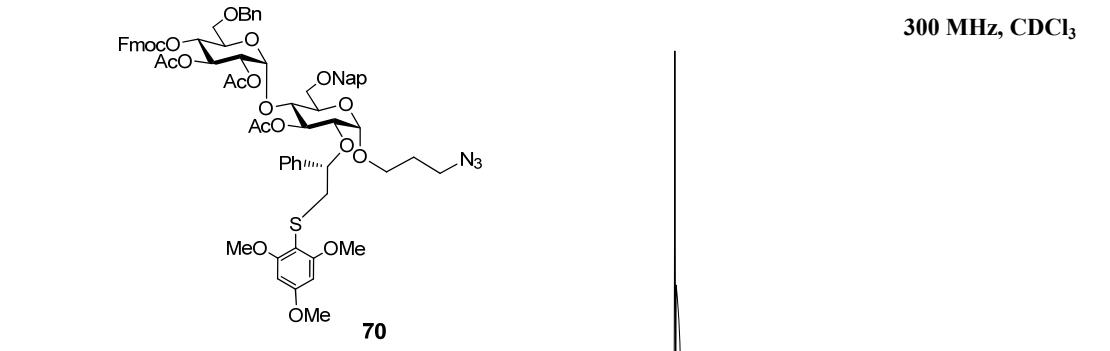
67

300 MHz, $CDCl_3$



75 MHz, $CDCl_3$

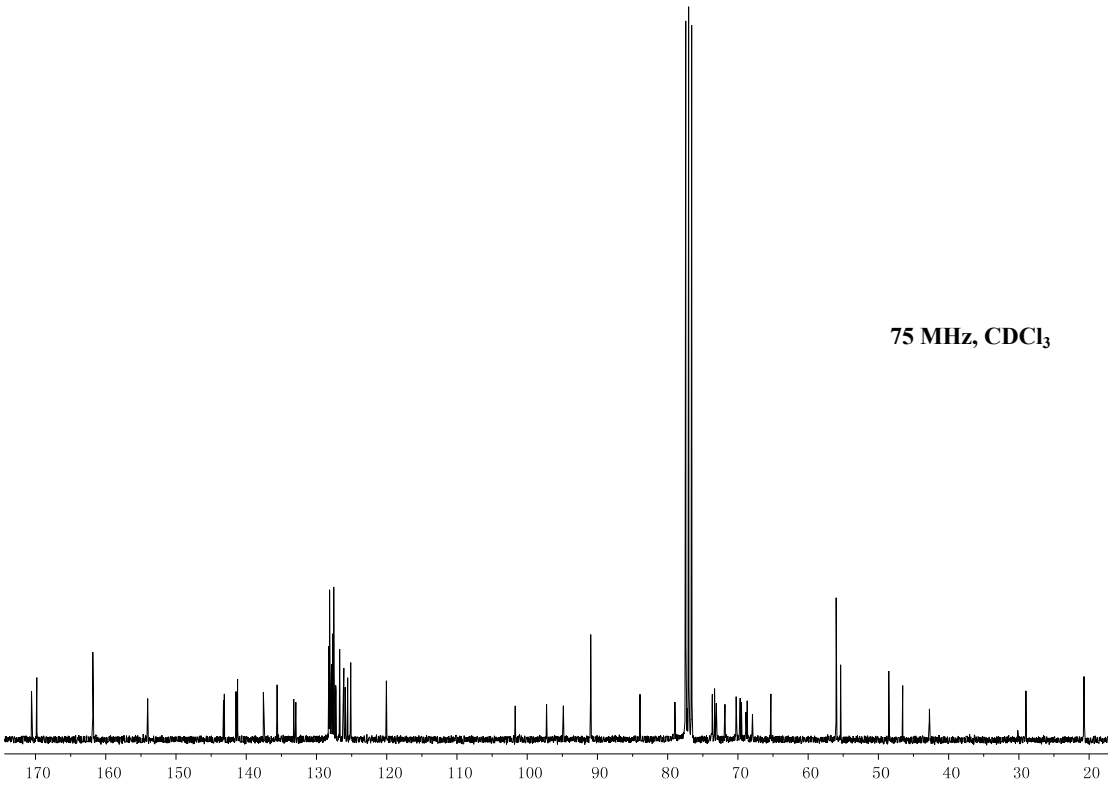


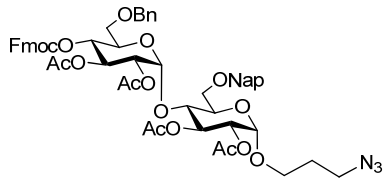


70

300 MHz, $CDCl_3$

75 MHz, $CDCl_3$

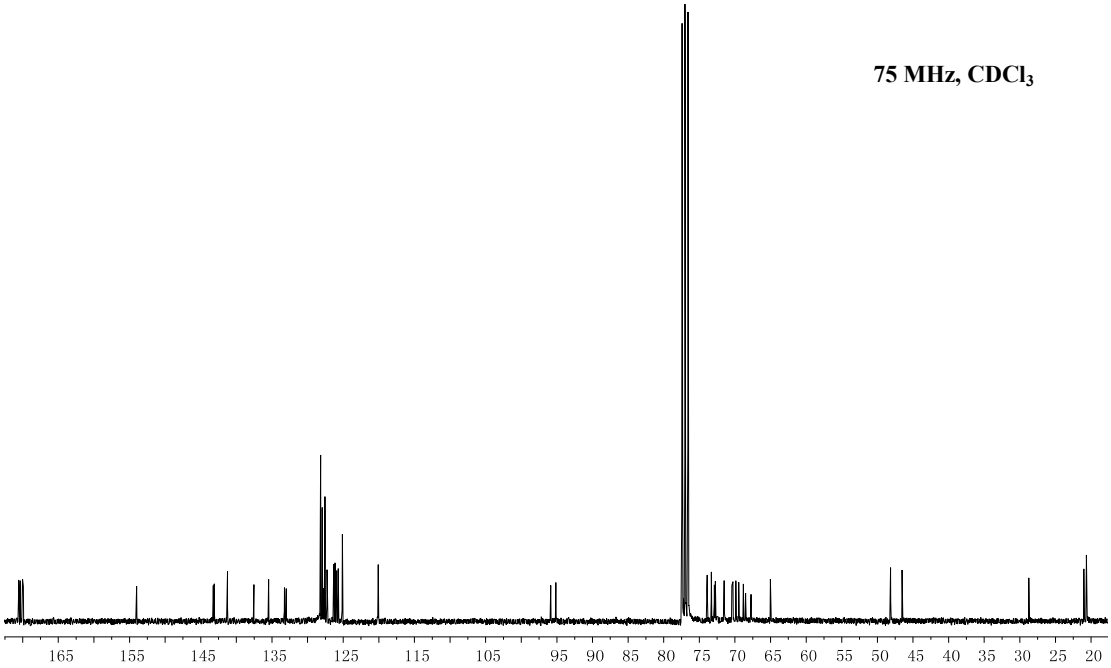


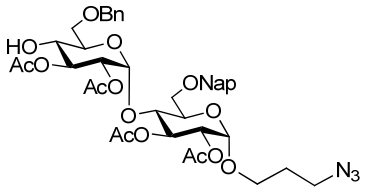


71

300 MHz, $CDCl_3$

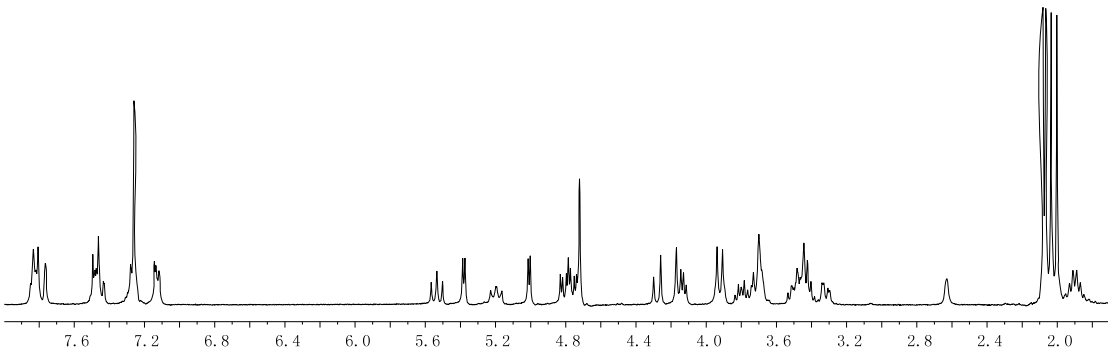
75 MHz, $CDCl_3$



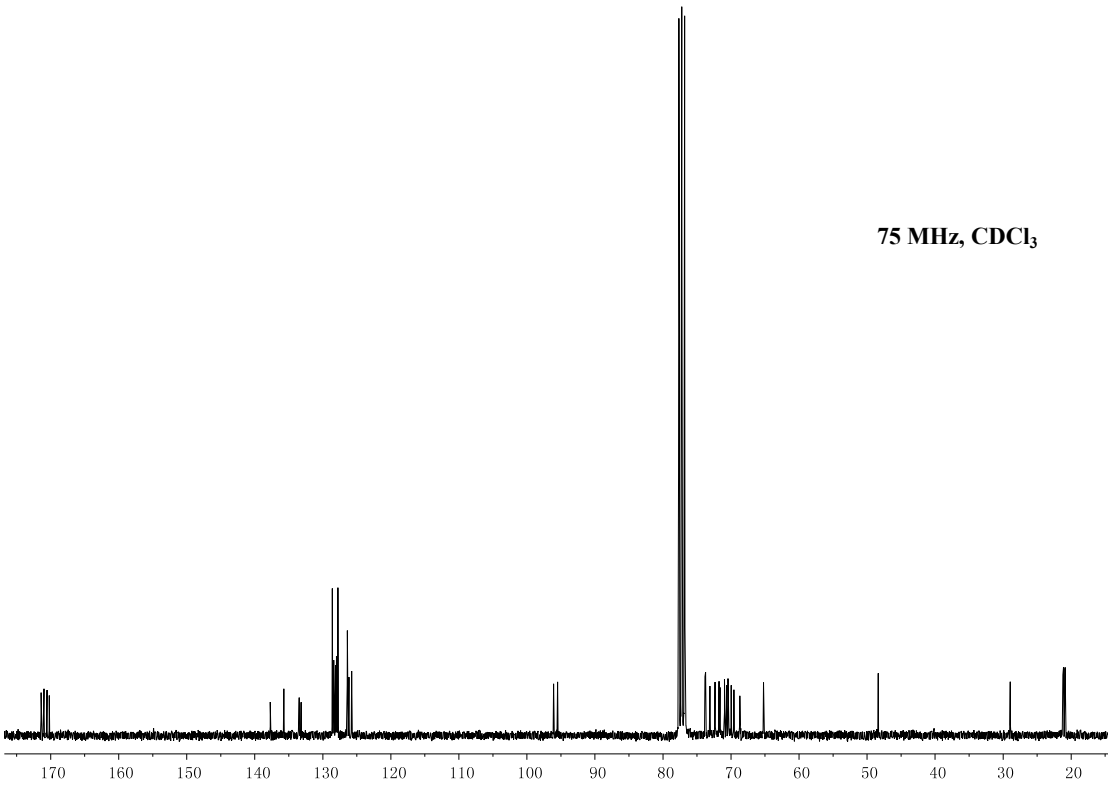


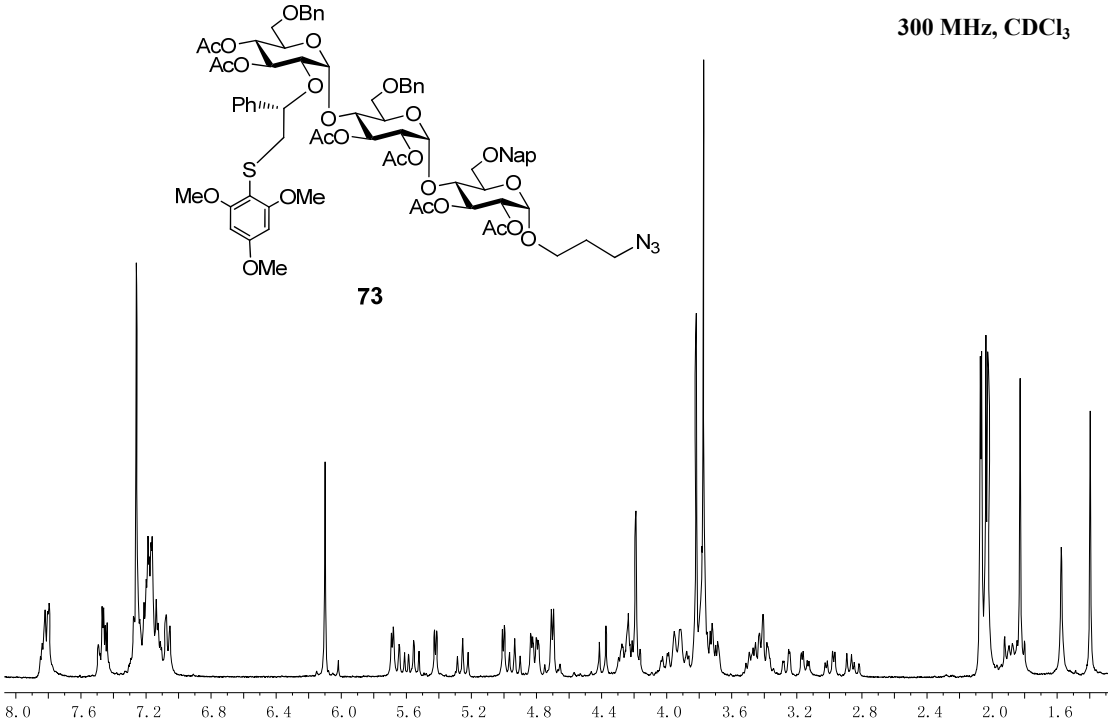
72

300 MHz, $CDCl_3$



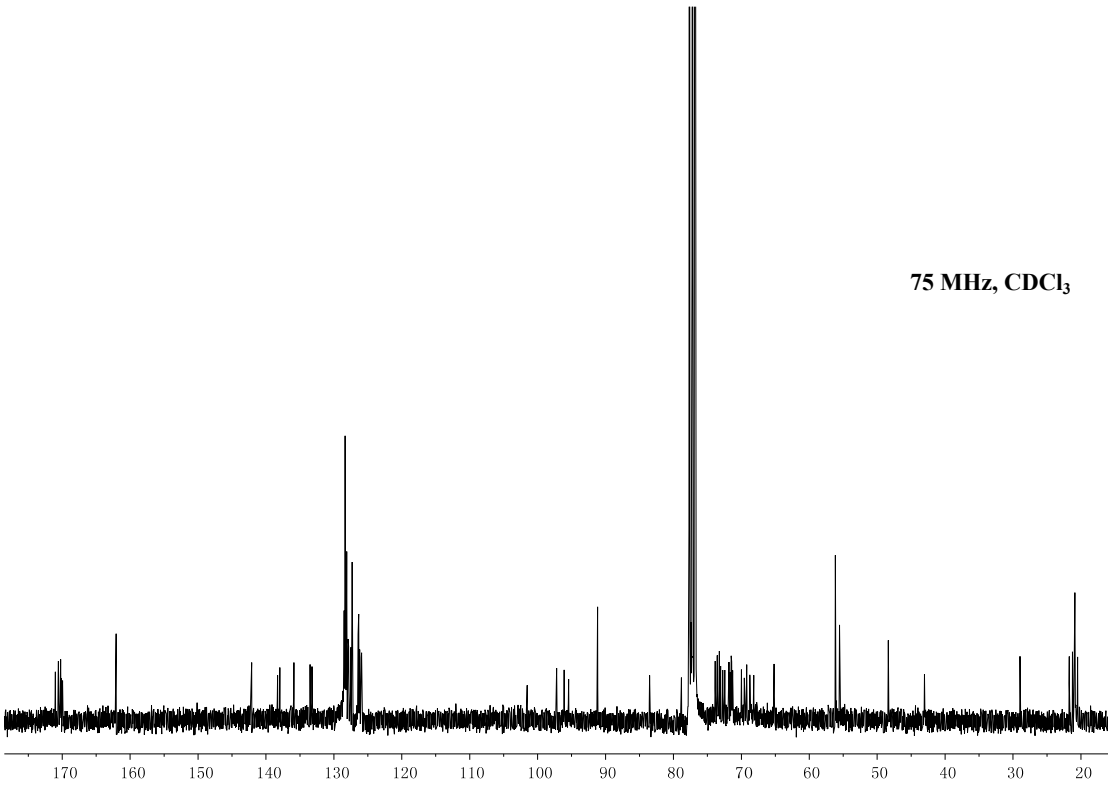
75 MHz, $CDCl_3$



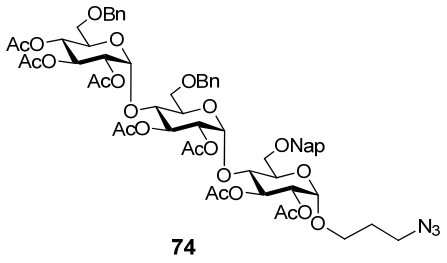


300 MHz, $CDCl_3$

73



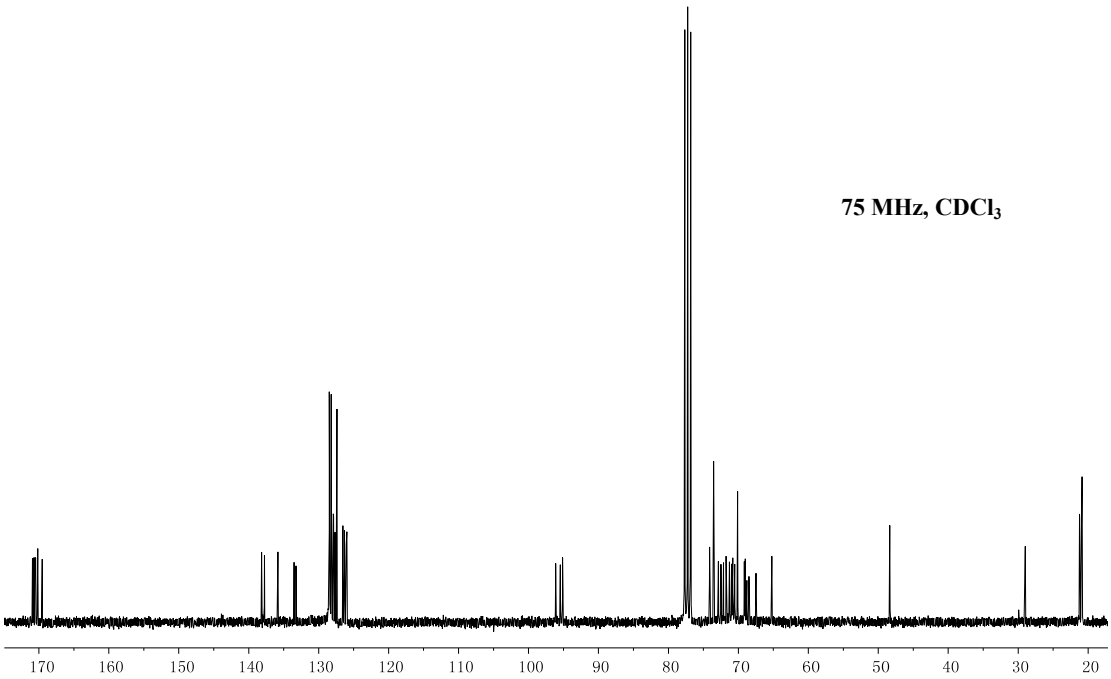
75 MHz, $CDCl_3$

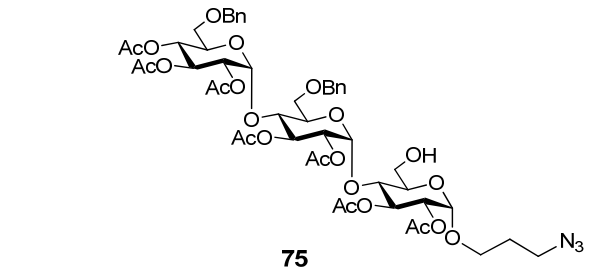


74

300 MHz, $CDCl_3$

75 MHz, $CDCl_3$

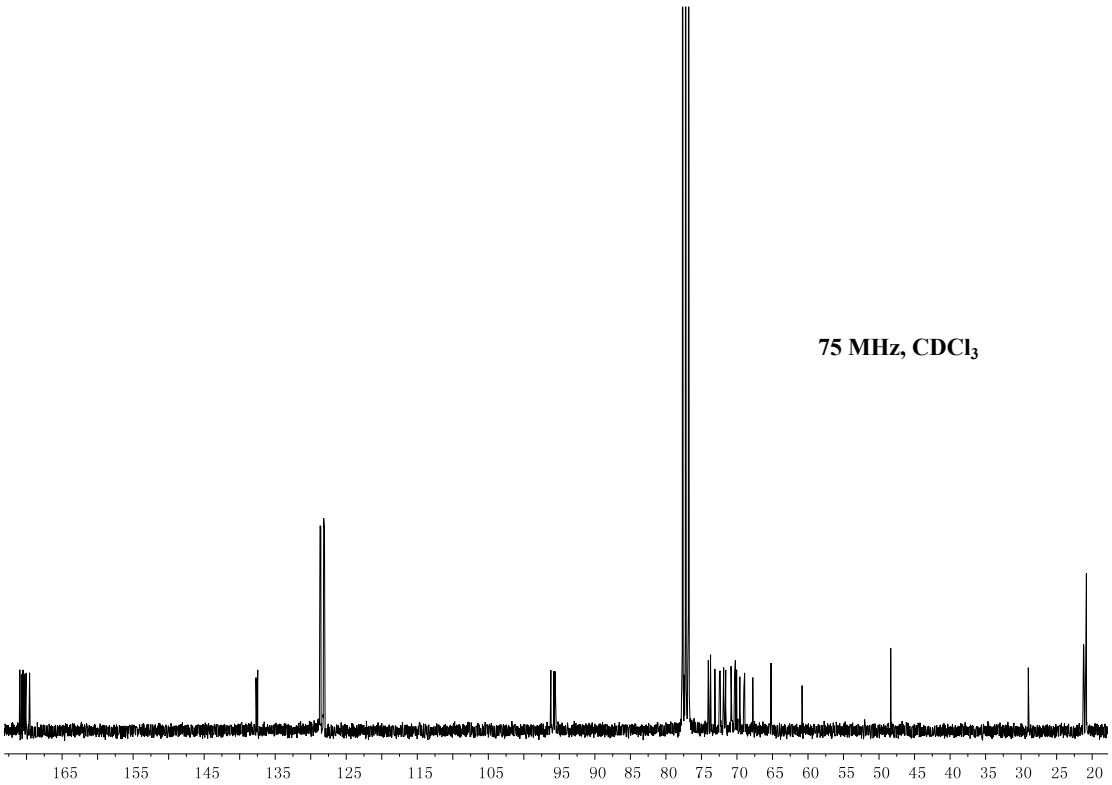


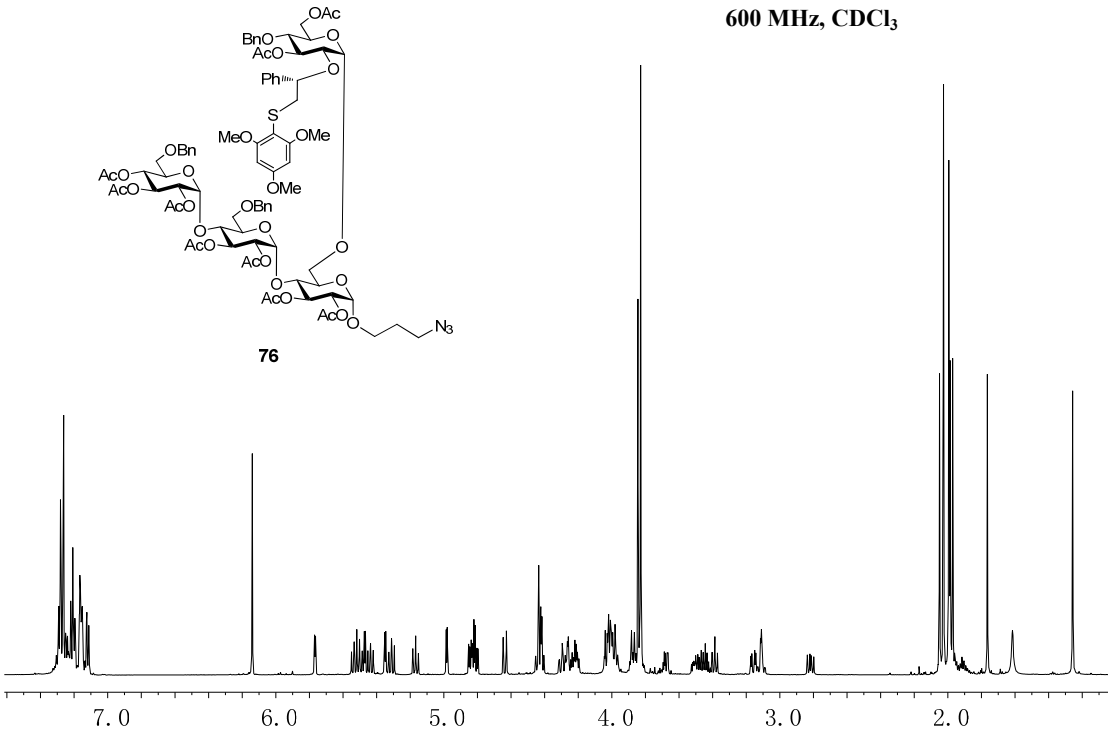


75

300 MHz, $CDCl_3$

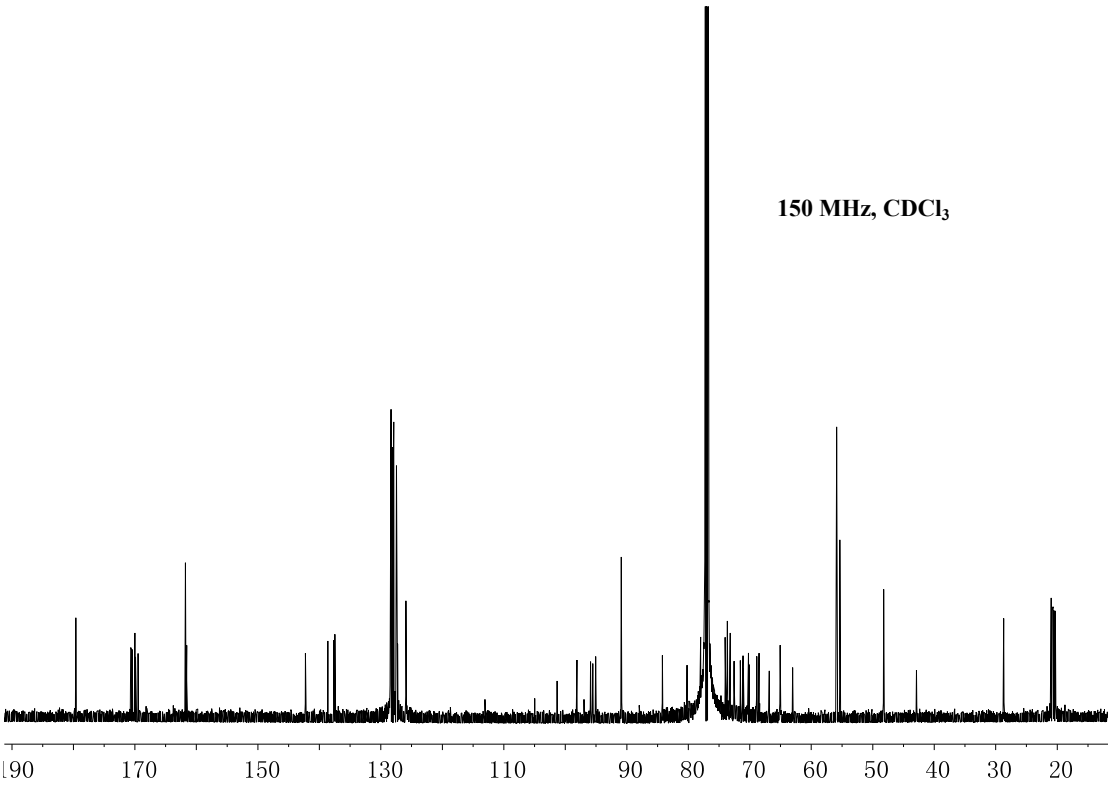
75 MHz, $CDCl_3$



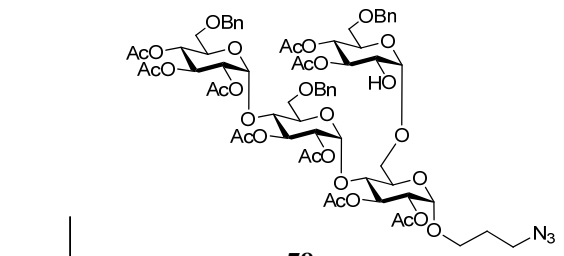


76

600 MHz, $CDCl_3$

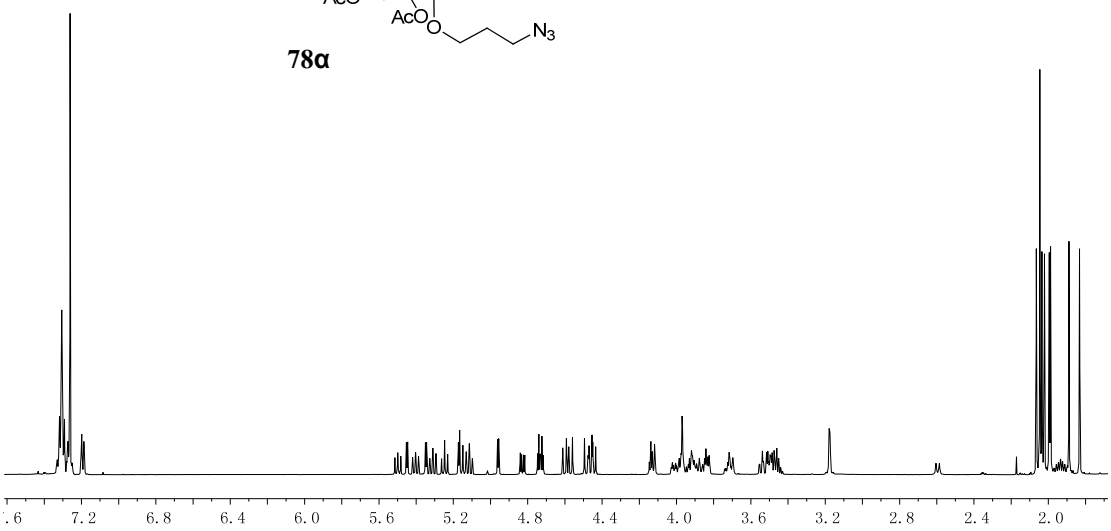


150 MHz, $CDCl_3$

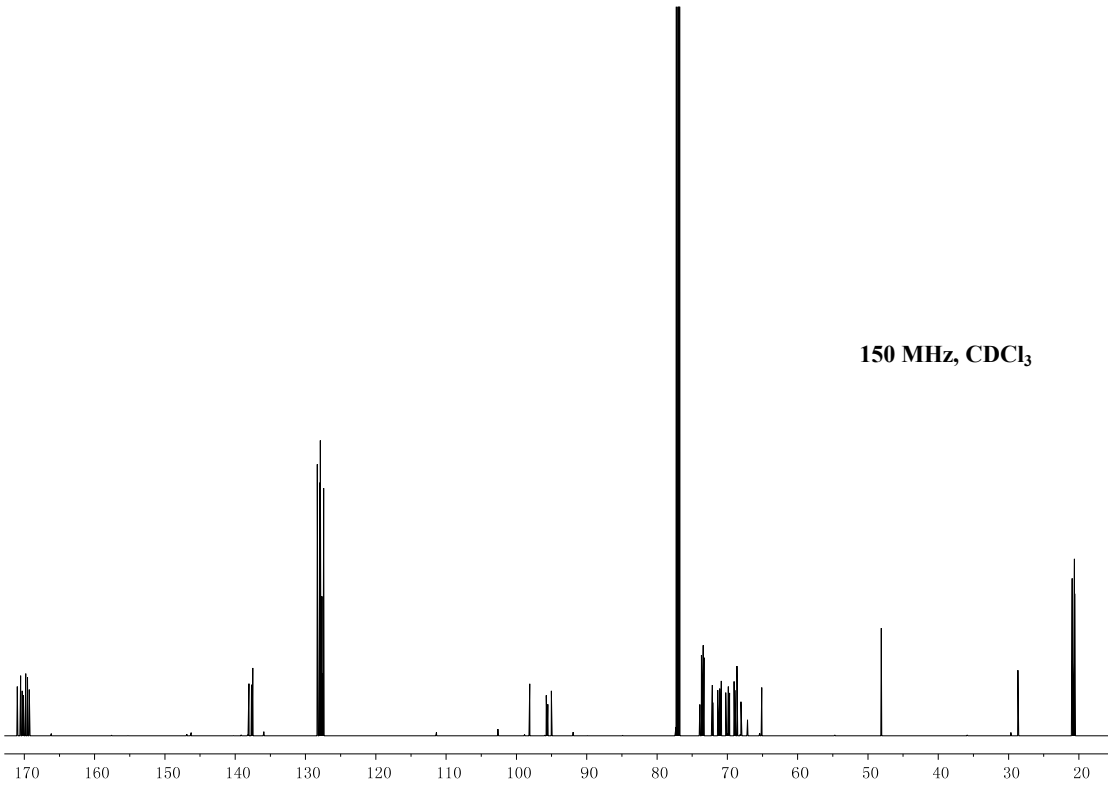


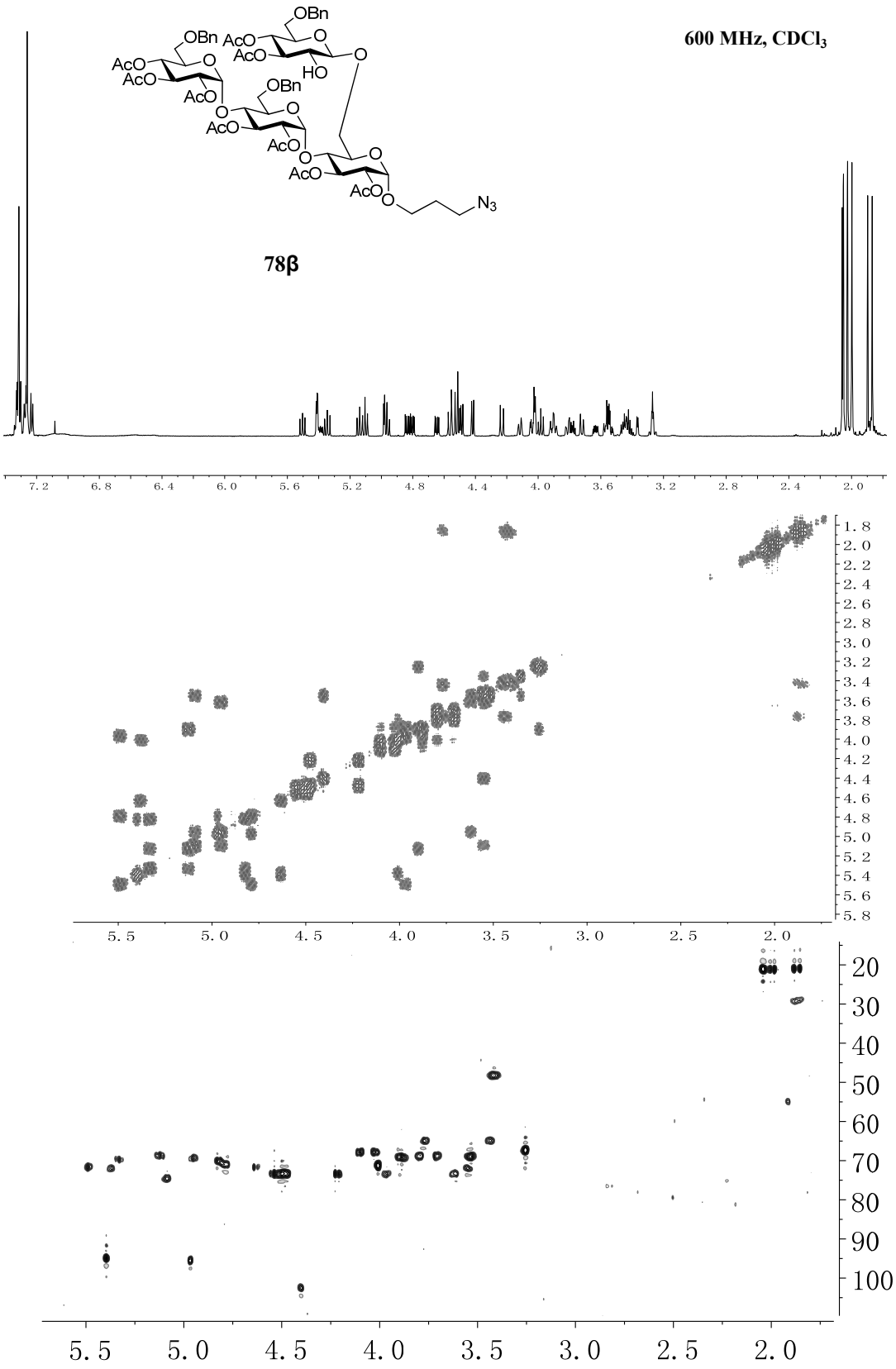
78α

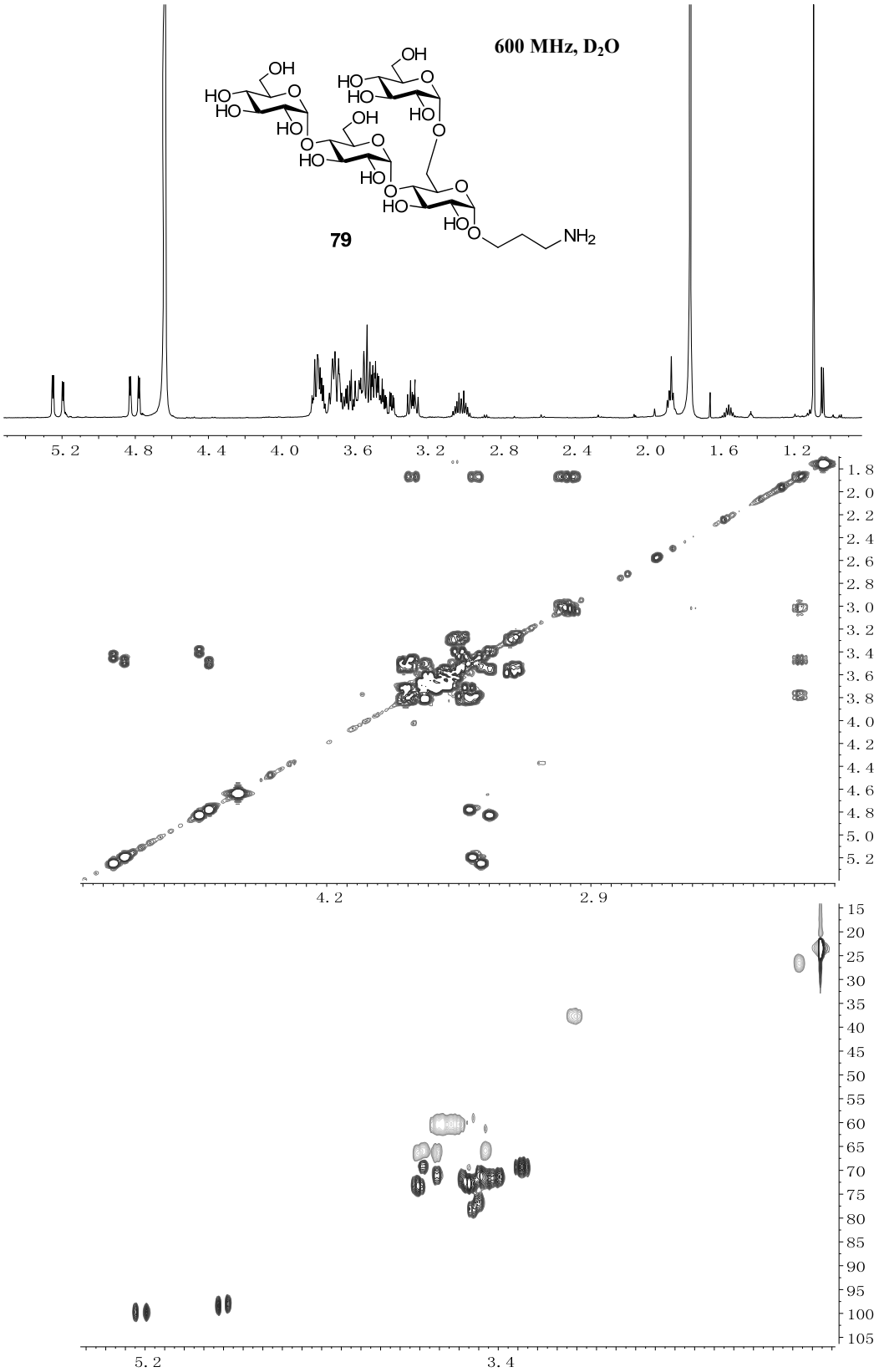
600 MHz, $CDCl_3$

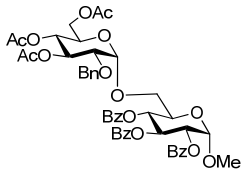


150 MHz, $CDCl_3$



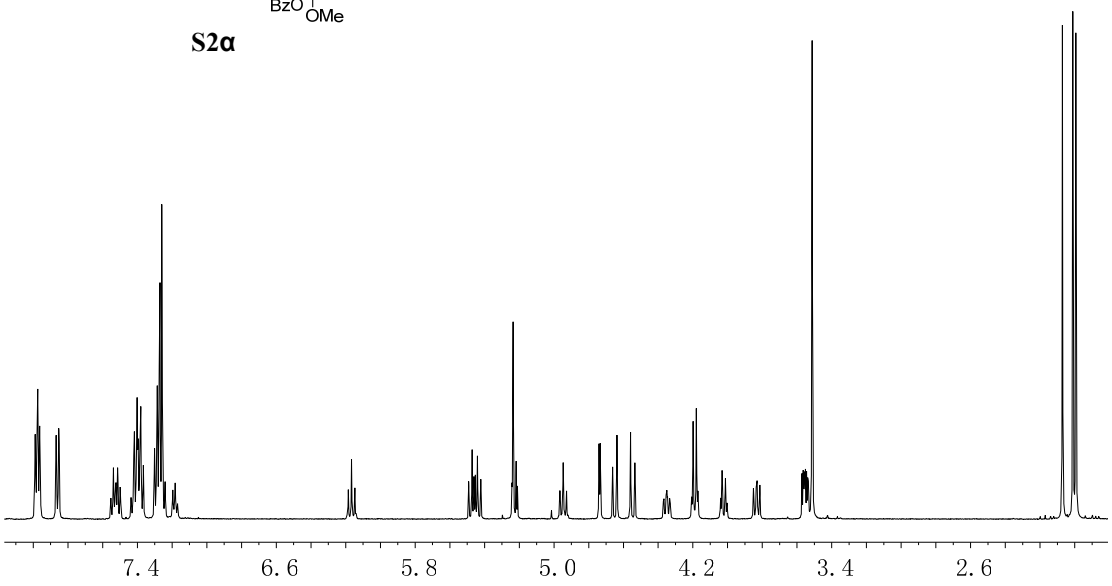

600 MHz, CDCl3
78β
OBn
AcO
HO
N3


600 MHz, D2O
79
NH2
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
4.2
2.9
5.2
3.4

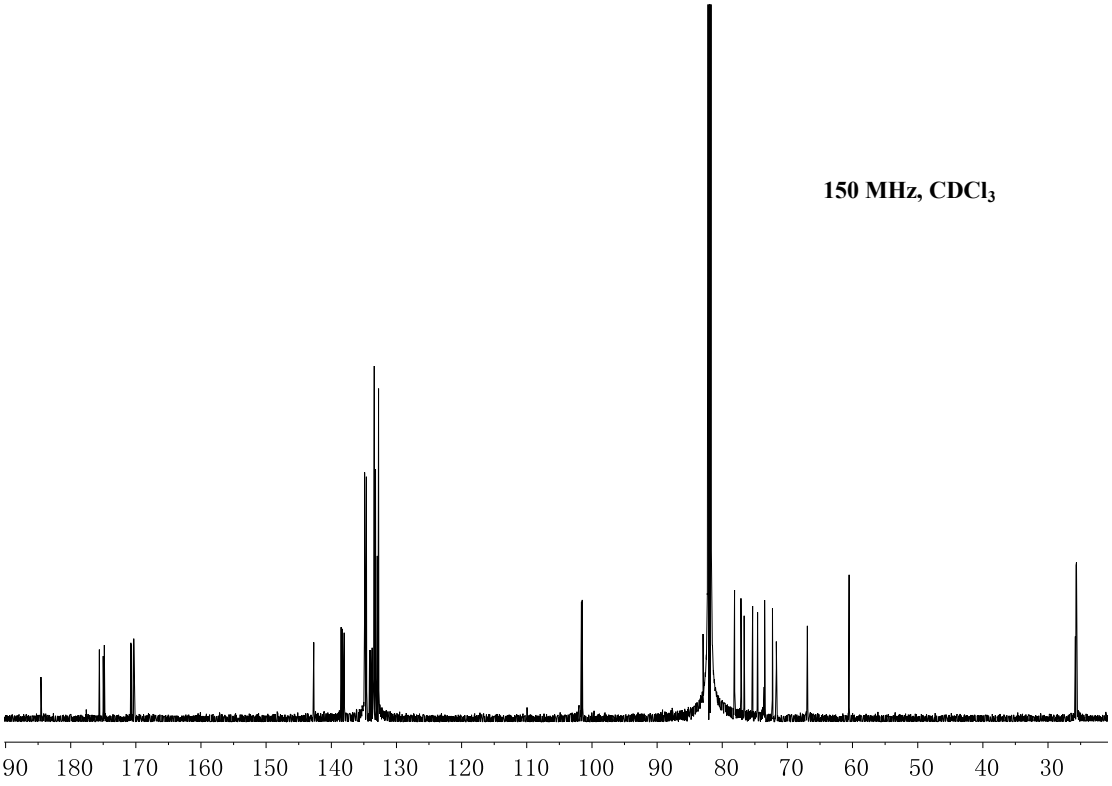


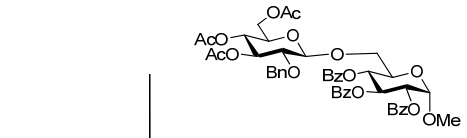
S2α

500 MHz, $CDCl_3$



150 MHz, $CDCl_3$

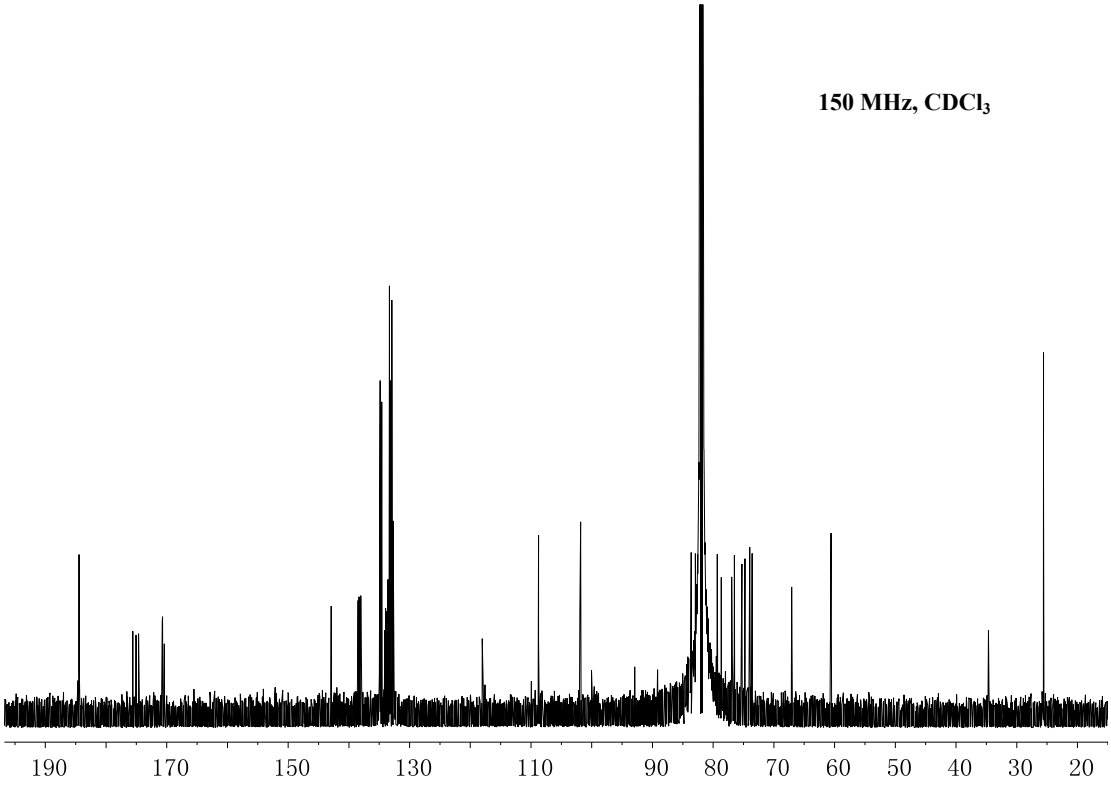


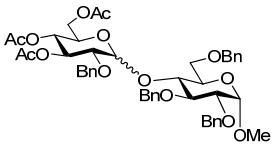


S2β

500 MHz, $CDCl_3$

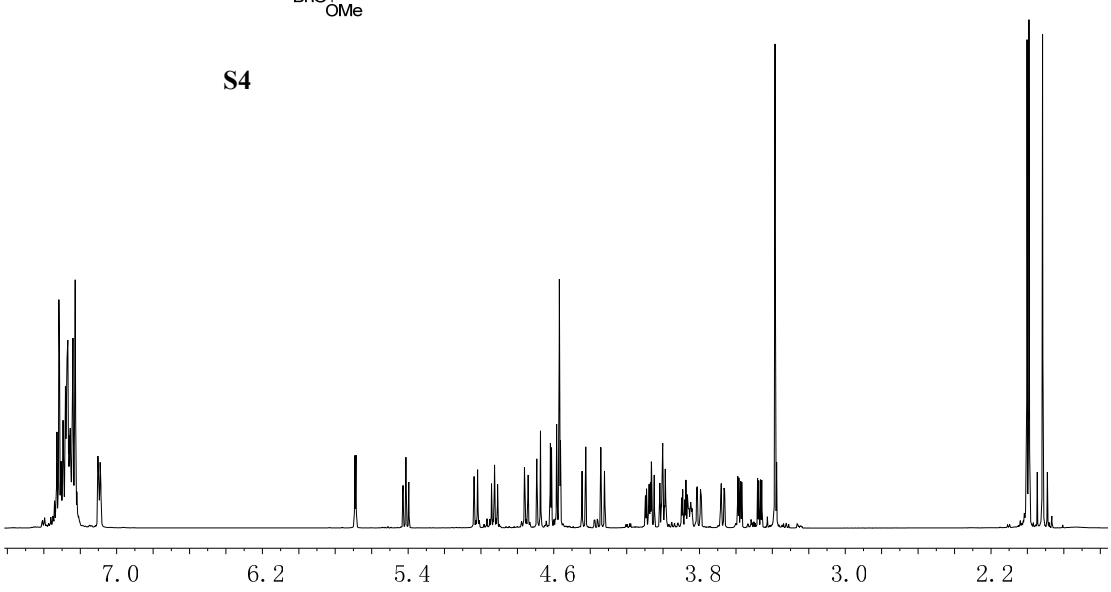
150 MHz, $CDCl_3$





S4

600 MHz, $CDCl_3$



150 MHz, $CDCl_3$