Supporting information

Gold-catalysed glycosylation reaction using an easily accessible leaving group

Srinivasa Rao Koppolu[a] Ramana Niddana[a] and Rengarajan Balamurugan[a]*

[a]School of Chemistry, University of Hyderabad, Prof. C. R. Rao road, Hyderabad-500046. INDIA.

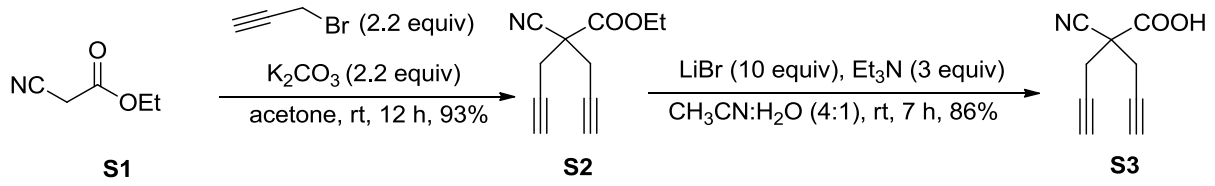
E-mail: rbsc@uohyd.ernet.in

General information

All reagents were obtained commercially and used without further purification unless otherwise mentioned. Dichloromethane was freshly distilled over anhydrous CaH_2. Thin-layer chromatography was performed by using Merck silica gel F-254 coated aluminum plates and the visualization of spots were done using UV illumination and charring the TLC plates sprayed with Seebach solution or 5% H_2SO_4 solution in methanol. Column chromatography was performed over silica gel procured from Merck, using hexanes and ethyl acetate mixture as eluent. Solvents were removed under reduced pressure using rotovap. Dextrose, mannose and galactose were purchased from Merck Chemical Company, India. $AuCl_3$ and $AgSbF_6$ used in the reaction was purchased from Sigma-Aldrich. IR spectra were recorded using JASCO FT-IR spectrophotometer model 5300. The ^1H NMR spectra were recorded in a Bruker Avance 400 MHz NMR machine using solutions in $CDCl_3$ containing TMS as an internal standard. ^{13}C NMR spectra were recorded in $CDCl_3$ solvent with reference to central line of $CDCl_3$ peak. HRMS data was recorded in a Bruker Maxis machine using ESI-TOF technique. Optical rotations were measured using an AUTOPOL-II automatic polarimeter (readabllity ± 0.01°).

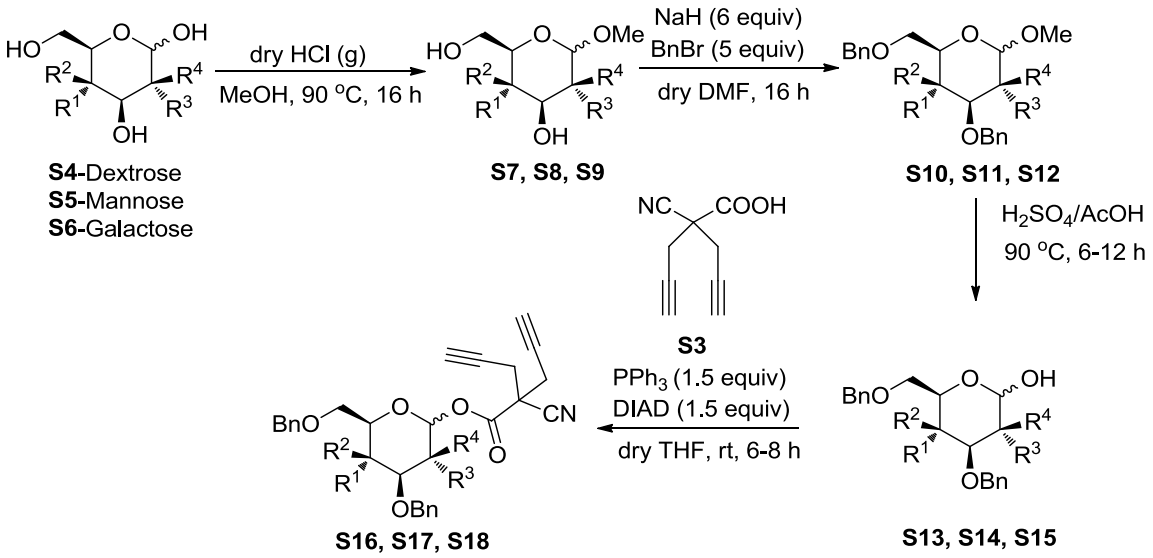
Preparation of starting materials

Dipropargyl ethyl ester **S2** was made by alkylating ethyl cyanoacetate **S1** with propargyl bromide using potassium carbonate as base. This ester **S2** was hydrolysed under basic conditions to get the acid fragment **S3** (Scheme 1).



Scheme 1. Synthesis of carboxylic acid fragment **S3**

Methyl glucoside **S7**, mannoside **S8** and galactoside **S9** were synthesized from commercially available dextrose **S4**, mannose **S5** and galactose **S6** respectively by treating them separately with methanolic HCl solution (dry HCl gas was produced by dropwise addition of 35 % HCl onto the $CaCl_2$ granules placed in a separate dry chamber). These methyl glycosides on benzylation using NaH/BnBr gave methyl tetra-*O*-benzylglucoside **S10**, mannoside **S11** and galactoside **S12** respectively. Lactols of gluco **S13**, manno **S14** and galacto **S15** derivatives were made by heating the corresponding methyl tetra-*O*-benzylglycosides with H_2SO_4/AcOH system. These lactols were coupled with dipropargylcyanoacetic acid **S3** to furnish respective glycosyl esters of gluco **S17**, manno **S18** and galacto **S19** derivatives (Scheme 2).

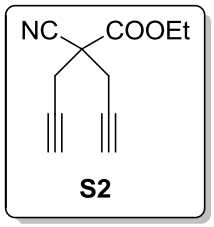


gluco series: $R^1 = R^3 =$ OBn; $R^2 = R^4 =$ H; **S7**, (commercially avialable); **S10**, 87%; **S13**, 61%; **S16**, 97%
manno series: $R^1 = R^4 =$ OBn; $R^2 = R^3 =$ H;(manno-): **S8**, 90%; **S11**, 55%; **S14**, 52%; **S17**, 78%
galacto series: $R^2 = R^3 =$ OBn; $R^1 = R^4 =$ H; (galacto-): **S9**, 85%; **S12**, 51%; **S15**, 60%; **S18**, 78%

Scheme 2. Synthesis of glycosyl esters starting from corresponding commercially available sugars

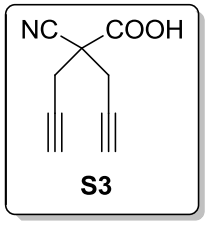
Synthesis of carboxylic acid fragment S3

Preparation of dipropargyl ethylcyanoacetate S2[1]



To a solution of ethyl cyanoacetate **S1** (3 g, 24.3 mmol) and distilled acetone (70 mL) in a 100 mL round bottom flask, K_2CO_3 (8.4 g, 60.9 mmol) was added. After stirring for 30 min, propargyl bromide (5.5 mL, 60.9 mmol) was added drop wise. The reaction mixture was stirred at room temperature. After 12 h, the resulting solution was concentrated, and diluted with ethyl acetate. The organic fraction was washed with saturated NH_4Cl solution several times to remove base. The organic layers were combined and washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography to get compound **S2 (**4.6 g**)** as clear liquid. Yield: 93%; IR (neat, cm^{-1}): 3294, 1747, 1242, 1217, 659; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.34 (q, *J* = 7.2 Hz, 2H, -C*H*$_2$-CH$_3$), 2.94 (d, *J* = 2.4 Hz, 4H, -C*H*$_2$-), 2.23 (t, *J* = 2.4 Hz, 2H, alkyne C*H*), 1.35 (t, *J* = 7.2 Hz, 3H, -CH$_2$-C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 117.0, 76.0, 73.6, 63.5, 47.1, 25.6, 13.8; HRMS (ESI) m/z calcd for $C_{11}H_{11}NO_2$ $[M+Na]^+$ = 212.0687, found = 212.0702.

Preparation of acid derivative S3[2]



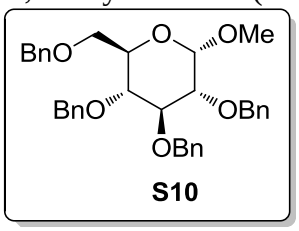
Dipropargyl cyanoester **S2** (1.57 g, 9.35 mmol) was dissolved in a mixture of CH_3CN and H_2O (4:1) solvent. To this solution, triethylamine (2.83 g, 28 mmol) was added followed by addition of LiBr (8.12 g, 93.5 mmol). The reaction mixture was stirred vigorously at room temperature for 7 h. The reaction progress was monitored by TLC, and the reaction mixture was quenched by adding AcOH carefully. The reaction mixture was washed with ethyl acetate to remove any unreacted ester. This ethyl acetate layer was drained off. After that the p^H of the reaction mixture (aqueous layer from ethyl acetate washing) was taken to 6 by adding 2N HCl carefully before doing work up. Now again the aqueous acidic solution was washed with ethyl acetate several times. The combined organic layer was washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The pasty acid **S3 (**1.3 g) was used for the next step without any further purification. Yield: 86%; IR (KBr, cm^{-1}): 3298, 1741, 1253, 663; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (br s, 1H, -COO*H*), 2.99-2.98 (m, 4H, -

CH_2-), 2.29 (t, *J* = 2.5 Hz, 2H, alkyne C*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 116.4, 75.7, 74.1, 47.5, 25.6; HRMS (ESI) m/z calcd for $C_9H_7NO_2$ $[M+Na]^+$ = 184.0374, found = 184.0377.

Synthesis of glucosyl ester S16

Preparation of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside S10[3]

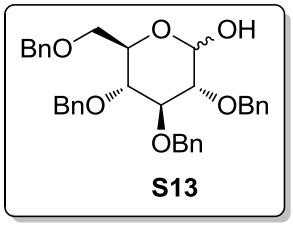
To a solution of methyl glucoside **S7** (2.0 g, 10.29 mmol) in dry DMF (75 mL) sodium hydride (3.52 g, 88.1 mmol) was added portion wise at 0 °C. After 30 min, benzyl bromide (8.3 mL , 70.8 mmol) was added drop wise. The reaction was monitored by TLC. After completion of the reaction, the brown colored reaction mixture was poured into water and extracted with ethyl acetate. The combined organic layer was washed with NH_4Cl solution and brine solution. The organic fraction was concentrated under reduced pressure and purified by column chromatography (silica gel, hexanes/EtOAc = 5/1) to get methyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside **S7** (4.9 g) as colourless oily liquid. Yield = 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.25 (m, 18H, Ar*H*), 7.13-7.11 (m, 2H, Ar*H*), 4.97 (d, *J* = 10.4 Hz, 1H, -OCH_2Ph), 4.83-4.78 (m, 3H, *H*-1, -OCH_2Ph), 4.65 (d, *J* = 12.0 Hz, 1H, -OCH_2Ph), 4.62-4.48 (m, 2H, -OCH_2Ph), 4.47-4.45 (m, 2H, -OCH_2Ph), 3.98 (t, *J* = 9.8 Hz, 1H, H-5), 3.75-3.70 (m, 2H, H-3, H-2), 3.64-3.60 (m, 2H, H-6, H-6'), 3.55 (dd, *J* = 9.6, 2.6 Hz, 1H, H-4), 3.37 (s, 3H, -OMe).



S10

Preparation of 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranose S13[3]

Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside **S10** (3 g, 5.5 mmol) was dissolved in a mixture of glacial acetic acid (60 mL) and aqueous H_2SO_4 (2M, 30 mL). The reaction mixture was heated to 90 °C for 12 h. After completion of the reaction, the reaction mixture was diluted with cold water (70 mL) and ethyl acetate (70 mL). The organic layer was washed several times with water to remove AcOH and then with aqueous $NaHCO_3$. The organic fraction was concentrated to give syrup. The syrup was purified by column chromatography (silica gel, hexanes/EtOAc = 3/1) to get 2,3,4,6-tetra-*O*-benzyl-glucopyranose **S13** (1.8 g) as a white solid. Yield = 61%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.26 (m, 18H, Ar*H*), 7.14-7.12 (m, 2H, Ar*H*), 5.22 (d, *J* = 3.5 Hz, 1H, H-1), 4.94 (d, *J* = 11.0 Hz, 1H, -OCH_2Ph), 4.83 (d, *J* = 11.2 Hz, 1H, -OCH_2Ph), 4.81 (d, *J* = 10.8 Hz, 1H, -OCH_2Ph), 4.74

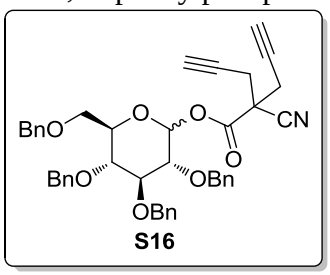


S13

(d, *J* = 11.2 Hz, 1H, -OC*H*$_2$Ph), 4.68 (d, *J* = 12.1 Hz, 1H, -OC*H*$_2$Ph), 4.59 (d, *J* = 12.1 Hz, 1H, -OC*H*$_2$Ph), 4.49 (d, *J* = 10.8 Hz, 1H, -OC*H*$_2$Ph), 4.48 (d, *J* = 12.2 Hz, 1H, -OC*H*$_2$Ph), 4.05-4.01 (m, 1H, H-5), 3.96 (t, *J* = 9.1 Hz, 1H, H-3), 3.70 (dd, *J* = 10.4, 3.4 Hz, 1H, H-6), 3.63 (dd, *J* = 7.7, 2.1 Hz, 2H, H-6', H-2), 3.59-3.52 (m, 1H, H-4).

Esterification reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranose S13 and 2-cyano-2-(prop-2-ynyl)pent-4-ynoic acid S3

2,3,4,6-Tetra-*O*-benzyl-glucopyranose **S13** (1.96 g, 3.6 mmol) was dissolved in dry THF (15 mL) in an oven dried 100 mL round bottom flask. A solution of cyano carboxylic acid derivative **S3** (0.878 g, 5.45 mmol) in dry THF was added. To this reaction mixture, triphenylphosphine (1.43 g, 5.45 mmol), diisopropyl azodicarboxylate (1.1 g, 5.45 mmol) were added successively. The reaction mixture was stirred at room temperature under N_2 atmosphere. After 6 h, the resulting solution was concentrated and diluted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$ solution several times to remove acid. It was washed with brine solution and dried over anhydrous Na_2SO_4. Solvents were evaporated under reduced pressure. The residue was purified by column chromatography to get glucosyl ester **S16** (2.3 g) as a mixture of anomers. Yield = 97%; $[\alpha]_D^{25}$ +39.2 (c, 2.5, $CHCl_3$); IR (KBr, cm^{-1}): 3290, 2920, 1759, 1093, 1070, 738, 698; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.24 (m, 37H, Ar*H*), 7.18-7.14 (m, 4H, Ar*H*), 6.38 (d, *J* = 3.0 Hz, 1H, H-1$^{\alpha}$), 5.66 (d, *J* = 7.0 Hz, 1H, H-1$^{\beta}$), 4.94-4.90 (m, 1.7H, -OC*H*$_2$Ph), 4.88-4.87 (m, 1H, -OC*H*$_2$Ph), 4.85-4.83 (m, 3H, -OC*H*$_2$Ph), 4.80-4.78 (m, 1.6H, -OC*H*$_2$Ph), 4.65 (m, 2H, -OC*H*$_2$Ph), 4.58 (d, *J* = 11.0 Hz, 1H, -OC*H*$_2$Ph), 4.57 (d, *J* = 11.8 Hz, 1H, -OC*H*$_2$Ph), 4.52 (d, *J* = 11.0 Hz, 1H, -OC*H*$_2$Ph), 4.45 (d, *J* = 11.1 Hz, 1H, -OC*H*$_2$Ph), 3.97-3.92 (m, 4H), 3.79-3.69 (m, 6H), 3.63 (d, *J* =11.4 Hz, 2H), 2.98-2.83 (m, 7H, -C*H*$_2$-), 2.17 (t, *J* = 2.3 Hz, 1.7H, alkyne C*H*), 2.10 (t, *J* = 2.1 Hz, 1H, alkyne C*H*), 2.04-2.03 (t, *J* = 2.1 Hz, 1H, alkyne C*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 164.6, 138.3, 138.2, 137.9, 137.8, 137.7, 137.5, 128.4, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 116.7, 96.5, 93.6, 84.4, 81.2, 80.3, 78.6, 76.0, 75.9, 75.7, 75.6, 75.2, 75.0, 74.9, 74.3, 74.0, 73.8, 73.7, 73.5, 73.4, 68.1, 67.9, 47.5, 26.0, 25.8, 25.5; HRMS (ESI) m/z calcd for $C_{43}H_{41}NO_7$ $[M+Na]^+$ = 706.2781, found = 706.2781.

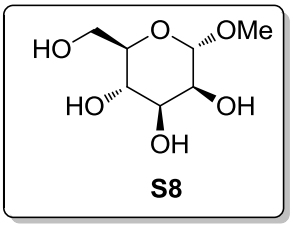


S16

Synthetic route for making 2,3,4,6-tetra-*O*-benzyl-D-mannosyl ester S17

Preparation of methyl-α-D-mannopyranoside S8

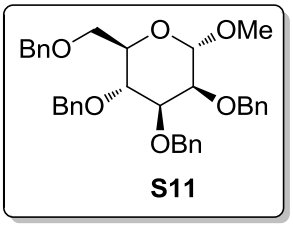
D-Mannose **S5** (3 g, 16.67 mmol) was dissolved in dry methanol (100 mL) and dry HCl gas was passed through the reaction mixture (dry HCl gas was produced by dropwise addition of 35% HCl onto the $CaCl_2$ granules in a separate dry chamber). After complete passage of dry HCl through the reaction mixture, it was refluxed at 90 °C. After 16 h, a light brown solution was formed which was cooled to room temperature. The resulting solution was neutralized with $PbCO_3$ (s). The resulting white slurry was filtered to remove inorganic salts. The solvent was removed under reduced pressure and thus yielded in a creamy solid of methyl α-D-mannopyranoside **S8** (2.9 g) which was used directly in the next step without any further purification. Yield = 90%.



S8

Preparation of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside S11[4]

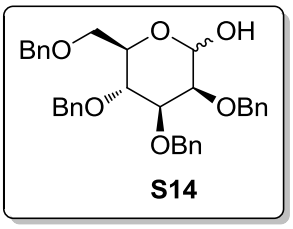
To a solution of methyl mannoside **S8** (2.8 g, 14.6 mmol) in dry DMF (75 mL), sodium hydride (3.52 g, 88.1 mmol) was added at 0 °C. After 30 min, benzyl bromide (8.3 mL, 70.8 mmol) was added dropwise at 0 °C. The reaction mixture was stirred overnight. After completion of the reaction, the white cloudy reaction mixture was poured into water and extracted with ethyl acetate and washed with NH_4Cl and brine solution. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, hexanes/EtOAc = 5/1) to get methyl 2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside **S11** (4.4 g) as colourless oily liquid. Yield = 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.25 (m, 18H, Ar*H*), 7.16–7.14 (m, 2H, Ar*H*), 4.88 (d, *J* = 11.1 Hz, 1H, -OC*H*$_2$Ph), 4.77-4.73 (m, 3H, -OC*H*$_2$Ph), 4.66 (d, *J* = 12.1 Hz, 1H, -OC*H*$_2$Ph), 4.60 (m, 2H, -OC*H*$_2$Ph), 4.55 (d, *J* = 12.0 Hz, 1H, -OC*H*$_2$Ph), 4.49 (d, *J* = 10.8 Hz, 1H, -OC*H*$_2$Ph), 3.97 (t, *J* = 9.6 Hz, 1H, H-6), 3.88 (dd , *J* = 9.3, 3.1 Hz, 1H, H-6'), 3.80–3.72 (m, 4H, *H*-5, *H*-3, *H*-2, *H*-4), 3.32 (s, 3H, -OMe).



S11

Preparation of 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranose S14[5]

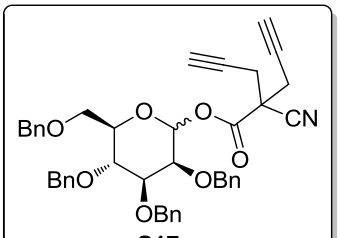
Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside **S11** (2 g, 3.6 mmol) was dissolved in a mixture of glacial acetic acid (55 mL) and aqueous H_2SO_4 (1M, 18 mL). The reaction mixture was heated to 90 °C with vigorous stirring for 3 h. After completion of the reaction, the reaction mixture was diluted with cold water (70 mL) and ethyl acetate (70 mL). The organic layer was separated and washed several times with water to remove excess AcOH, and then with aqueous $NaHCO_3$ followed by water. The solution was concentrated to get syrup. The syrup was purified by column chromatography to get 2,3,4,6-tetra-*O*-benzyl-mannopyranose **S14** (1.0 g) as dense liquid. Yield = 52%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.24 (m, 18H, Ar*H*), 7.16–7.14 (m, 2H, Ar*H*), 5.24 (m, 1H, H-1), 4.87 (d, *J* = 11.0 Hz, 1H, -OC*H*$_2$Ph), 4.74 (d, *J* = 12.3 Hz, 1H, -OC*H*$_2$Ph), 4.69 (d, *J* = 12.3 Hz, 1H, -OC*H*$_2$Ph), 4.60-4.59 (m, 2H, -OC*H*$_2$Ph), 4.57 (d, *J* = 12.0 Hz, 1H, -OC*H*$_2$Ph), 4.52 (d, *J* = 12.5 Hz, 1H, -OC*H*$_2$Ph), 4.48 (d, *J* = 11.2 Hz, 1H, -OC*H*$_2$Ph), 4.02 (m, 1H, H-5), 3.95 (dd, *J* = 9.3, 3.0 Hz, 1H, H-3), 3.87-3.82 (m, 1H, H-6), 3.81-3.78 (m, 1H, H-6'), 3.73-3.69 (m, 1H, H-2), 3.65 (dd, *J* = 10.2, 6.4 Hz, 1H, H-4).



S14

Esterification reaction between 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranose S14 with 2-cyano-2-(prop-2-ynyl)pent-4-ynoic acid S3

2,3,4,6-Tetra-*O*-benzyl-mannopyranose **S14** (1 g, 1.66 mmol) was dissolved in dry THF (15 mL) in an oven dried 100 mL round bottom flask. Cyano carboxylic acid derivative (0.402 g, 2.49 mmol) in dry THF was added. To this reaction mixture, triphenylphosphine (0.653 g, 2.49 mmol), diisopropyl azodicarboxylate (0.5037 g, 2.49 mmol) were added in tandem. The reaction mixture was stirred at room temperature under N_2 atmosphere. After 6 h, the resulting solution was concentrated and diluted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$ solution several times to remove acid. It was washed with brine solution and dried over anhydrous Na_2SO_4. Solvents were evaporated under reduced pressure. The residue was purified by column chromatography to get mannosyl ester **S17** (0.9 g) as α-anomer. Yield = 78%; $[\alpha]_D^{25}$ +10.24 (c, 1.3, $CHCl_3$); IR (KBr, cm^{-1}): 3288, 2870, 1759, 1319, 1028; ^{1}H NMR (400 MHz,



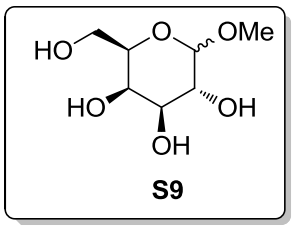
S17

$CDCl_3$): δ 7.39–7.36 (m, 2H, Ar-*H*), 7.33–7.24 (m, 16H, Ar*H*), 7.20–7.17 (m, 2H, Ar*H*), 6.25 (d, *J* = 2.0 Hz, $1H^{\alpha}$), 4.87 (d, *J* = 11.5 Hz, 1H, -OCH_2Ph), 4.74 (br s, 2H, -OCH_2Ph), 4.65 (d, *J* = 11.8 Hz, 1H, -OCH_2Ph), 4.63 (d, *J* = 11.6 Hz, 1H, -OCH_2Ph), 4.57 (d, *J* = 11.6 Hz, 1H, -OCH_2Ph), 4.54 (d, *J* = 11.6 Hz, 1H, -OCH_2Ph), 4.50 (d, *J* = 12.0 Hz, 1H, -OCH_2Ph) 4.13–4.08 (m, 1H, H-5), 4.03–3.98 (m, 1H, H-2), 3.91–3.85 (m, 1H, H-3), 3.79– 3.74 (m, 2H, H-6, H-6'), 3.68 (d, *J* = 11.2 Hz, 1H, H-4), 2.86–2.82 (m, 4H, -CH_2-), 2.16–2.13 (m, 1H, alkyne C*H*), 2.07 (t, *J* = 2.5 Hz, 1H, alkyne C*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 137.9, 137.8, 137.3, 128.4, 128.3, 128.3, 128.2, 127.9, 127.8, 127.7, 127.5, 116.4, 94.8, 78.6, 75.8, 75.7, 75.1, 75.0, 74.1, 73.9, 73.8, 73.4, 73.3, 73.1, 72.7, 72.4, 68.4, 47.5, 25.6; HRMS (ESI) m/z calcd for $C_{43}H_{41}NO_7$ $[M+Na]^+$ = 706.2781, found = 706.2781.

Synthesis of galactosyl ester S18

Preparation of methyl-α/β-D-galactopyranoside S9

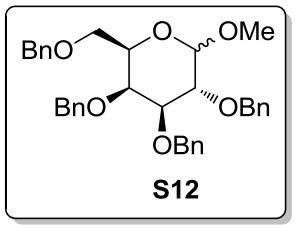
Galactose **S6** (5 g, 27.7 mmol) was dissolved in dry methanol (35 mL) and dry HCl gas was passed through the reaction mixture (dry HCl gas was produced by dropwise addition of 35 % HCl onto the $CaCl_2$ granules in a separate dry chamber). After complete passage of dry HCl through the reaction mixture, it was refluxed at 90 °C. After 14 h, a clear solution formed which was cooled to room temperature. The resulting solution was neutralized with $PbCO_3$ (s). The resulting white slurry was filtered to remove inorganic salts. Solvent was removed under reduced pressure. The resulting brown syrup was used directly for the next step without any further purification. Yield: 4.5 g, 85%.



S9

Preparation of methyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranoside S12[4]

Methyl α-D-galactopyranoside **S9** (4.49 g, 23.14 mmol) was dissolved in dry DMF (75 mL). Sodium hydride (60% dispersion in mineral oil) (5.2 g, 139 mmol) was added portion-wise to the solution at 0 °C under N_2 atmosphere. After 1 h, benzyl bromide (19.25 mL, 115.9 mmol) was added dropwise and the reaction mixture was stirred at room temperature overnight. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was quenched by adding methanol carefully. The solution was

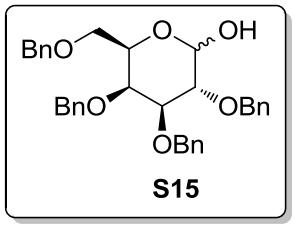


S12

diluted with ethyl acetate, the organic layer was washed with water several times to remove DMF. The organic layers were combined and washed with brine solution and dried over anhydrous Na_2SO_4. Solvents was evaporated under reduced pressure. The residue was purified by column chromatography to get methyl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside **S12** (6.5 g) as a clear liquid. Yield: 51%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.24 (m, 37H, Ar*H*), 4.93 (d, *J* = 11.5 Hz, 1H, -OC*H*$_2$Ph), 4.84 (d, *J* = 11.8 Hz, 1H, -OC*H*$_2$Ph), 4.83 (d, *J* = 12.0 Hz, 1H, -OC*H*$_2$Ph), 4.75 (d, *J* = 11.0 Hz, 1H, -OC*H*$_2$Ph), 4.72 (d, *J* = 10.7 Hz, 1H, -OC*H*$_2$Ph), 4.71-4.66 (m, 3H, -OC*H*$_2$Ph), 4.56 (d, *J* = 11.3 Hz, 1H, -OC*H*$_2$Ph), 4.52 (d, *J* = 10.7 Hz, 1H, -OC*H*$_2$Ph), 4.47 (d, *J* = 11.6 Hz, 1H, -OC*H*$_2$Ph), 4.38 (d, *J* = 11.9 Hz, 1H, -OC*H*$_2$Ph), 4.05-3.98 (m, 2H, H$^{\alpha}$-5, H$^{\beta}$-5), 3.94 (m, 2H, H-2$^{\alpha}$, H-2$^{\beta}$), 3.92-3.87 (m, 2H, H-3$^{\alpha}$, H-3$^{\beta}$), 3.82-3.76 (m, 2H, H-6$^{\alpha}$, H-6$^{\beta}$), 3.79-3.68 (m, 2H, H-6'$^{\alpha}$, H-6'$^{\beta}$), 3.61-3.58 (m, 1H, H-4$^{\alpha}$), 3.54-3.50 (m, 1H, H-4$^{\beta}$), 3.36 (s, 3H, -OMe).

Preparation of 2,3,4,6-tetra-*O*-benzylgalactopyranose S15[6]

Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranoside **S12** (5.8 g, 10.46 mmol) was dissolved in a mixture of glacial acetic acid (60 mL) and aqueous sulfuric acid (3M, 9 mL). The reaction mixture was heated to 90 °C with good stirring. The mixture was diluted with cold water (70 mL) and ethyl acetate (70 mL) was added to it. The layers were separated and the organic layer was first washed with water to remove excess of AcOH, followed by aqueous $NaHCO_3$, dried over anhydrous sodium sulfate. The solution was concentrated to get a syrup. The crude syrup was purified by column chromatography to get 2,3,4,6-tetra-*O*-benzyl-galactopyranose **S15** (3.4 g) as a syrup. Yield: 60%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.27 (m, 20H, Ar*H*), 5.27 (d, *J* = 3.5 Hz, 1H, H-1), 4.95-4.90 (m, 1H, -OC*H*$_2$Ph), 4.83-4.68 (m, 4H, -OC*H*$_2$Ph), 4.57 (d, *J* = 11.5 Hz, 1H, -OC*H*$_2$Ph), 4.47 (d, *J* = 11.8 Hz, 1H, -OC*H*$_2$Ph), 4.39 (d, *J* = 12.0 Hz, 1H, -OC*H*$_2$Ph), 4.17-4.13 (m, 1H, H-5), 4.03 (dd, *J* = 10.0, 3.5 Hz, 1H, H-3), 3.95-3.87 (m, 2H, H-6, 6'), 3.55-3.44 (m, 2H, H-2, H-4).

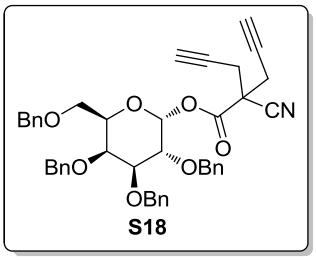


S15

Preparation of galactosyl ester S18

2,3,4,6-Tetra-*O*-benzyl-galactopyranose **S15** (2 g, 3.7 mmol) was dissolved in dry THF (20 mL) in a dry 100 mL round bottom flask. Cyanocarboxylic acid derivative **S3** (0.896 g, 5.56

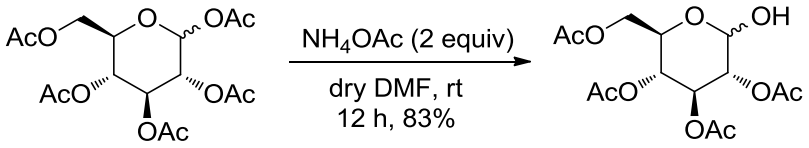
mmol) was added as a solution in dry THF. To this mixture triphenylphosphine (1.46 g, 5.56 mmol) and diisopropyl azodicarboxylate (1.12 g, 5.56 mmol) were added. The reaction mixture, was stirred at room temperature under N_2 atmosphere. The reaction was monitored by TLC. After 5 h, The resulting solution was concentrated and diluted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$ solution several times to remove acid then with brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography to get galactosyl ester **S18** (1.9 g) as pure α-anomer. Yield: 78%; $[\alpha]_D^{25}$ +39.8 (c, 0.7, $CHCl_3$); IR (KBr, cm^{-1}): 3290, 2924, 1759, 1211, 1105, 698; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.21 (m, 20H, Ar*H*), 6.39 (d, *J* = 3.3 Hz 1H, H-1$^{\alpha}$), 4.94 (d, *J* = 11.3 Hz, 1H, -OC*H*$_2$Ph), 4.80 (d, *J* = 11.7 Hz, 1H, -OC*H*$_2$Ph), 4.75 (d, *J* = 11.9 Hz 1H, -OC*H*$_2$Ph), 4.71 (d, *J* = 11.7 Hz, 1H, -OC*H*$_2$Ph), 4.64 (d, *J* = 10.9 Hz, 1H, -OC*H*$_2$Ph), 4.57 (d, *J* = 11.2 Hz, 1H, -OC*H*$_2$Ph), 4.44 (d, *J* = 11.8 Hz, 1H, -OC*H*$_2$Ph), 4.39 (d, *J* = 11.4 Hz, 1H, -OC*H*$_2$Ph), 4.19-4.09 (m, 2H, -OC*H*$_2$Ph), 4.03 (br s, 1H, H-5), 3.94 (dd, *J* = 10.0, 2.4 Hz, 1H, H-2), 3.52 (d, *J* = 5.6 Hz, 2H, H-6, 6'), 2.86 (qd, *J* = 17.0, 2.6 Hz, 2H, H-3, H-4), 2.80-2.71 (m, 2H, propargylC*H*$_2$-), 2.11 (t, *J* = 2.5 Hz, 1H, alkyne *H*), 2.03 (t, *J* = 2.5 Hz, 1H, alkyne *H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 138.1, 137.8, 137.6, 128.4, 128.2, 128.2, 127.9, 127.8, 127.8, 127.7, 127.6, 116.8, 94.3, 77.9, 76.0, 75.8, 75.0, 74.9, 74.1, 73.9, 73.8, 73.4, 73.3, 72.9, 72.6, 68.1, 47.6, 25.9, 25.5; HRMS (ESI) m/z calcd for $C_{43}H_{41}NO_7$ $[M+Na]^+$ = 706.2781, found = 706.2781.



S18

Preparation of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl ester S21

Preparation of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose S20

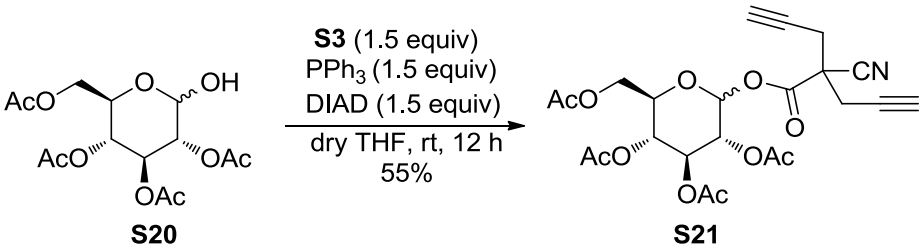


S19 **S20**

To a solution of glucose pentaacetate **S19** (2 g, 5.1 mmol) in dry DMF (20 mL), NH_4OAc (790 mg, 10.24 mmol, 2 equiv) was added portion wise. The resulting reaction mixture was stirred for 12 h at room temperature. After completion of the reaction as judged by TLC, the reaction

mixture was mixed with water and extracted with EtOAc several times. The organic layer was evaporated and crude reaction mixture was purified using silica gel chromatography to get the 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose **S20** (1.48 g, 83%) as a light brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.54 (t, *J* = 9.6 Hz, 1H, H-1), 5.46 (d, *J* = 3.2 Hz, 1H, H-3), 5.09 (t, *J* = 8.8 Hz, 1H, H-2), 4.92-4.87 (m, 1H, H-5), 4.30-4.22 (m, 2H, H-4, H-6), 4.17-4.09 (m, 1H, H-6'), 2.1 (s, 3H, -OAc), 2.09 (s, 3H, -OAc), 2.04 (s, 3H, -OAc), 2.02 (s, 3H, -OAc).

Preparation of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl ester S21



To a solution of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose **S20** (600 mg, 1.7 mmol) in dry THF (10 mL), dipropargyl cyanoaceticacid **S3** (417 mg, 2.6 mmol, 1.5 equiv) was added portion wise. To this solution, PPh_3 (678 mg, 2.6 mmol, 1.5 equiv) and diisopropyl azodicarboxylate (513 µL, 2.6 mmol, 1.5 equiv) were added in sequence. The reaction mixture was stirred for 12 h at room temperature. After complete consumption of starting sugar as judged by TLC, it was mixed with water and extracted with EtOAc several times. The combined organic layer was concentrated and crude reaction mixture was purified using silica gel chromatography to get the anomeric mixture of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl ester (465 mg) **S21** as a colorless dense liquid. Yield: 55%; $[\alpha]_D^{25}$ +37.896 (c, 1.8, $CHCl_3$); IR (KBr, cm^{-1}): 3280, 1746, 1367, 1210, 1069, 1036; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.41 (d, *J* = 4.0 Hz, 1H, H^{α}-1), 5.74 (d, *J* = 8.1 Hz, 1H, H^{β}-1), 5.51 (t, *J* = 10.0 Hz, 1H), 5.30-5.11 (m, 5H), 4.32-4.20 (m, 3H), 4.14-4.08 (m, 2H), 3.90-3.86 (m, 1H), 3.02-2.95 (m, 7H, propargylCH_2-), 2.36 (t, *J* = 2.8 Hz, 1H, alkyne C*H*), 2.31 (t, *J* = 2.8 Hz, 1H, alkyne C*H*), 2.26-2.23 (m, 2H, alkyne C*H*), 2.09 (s, 6H, -OAc), 2.09 (s, 3H, -OAc), 2.06 (s, 3H, -OAc), 2.06 (s, 3H, -OAc), 2.04 (s, 3H, -OAc), 2.03 (s, 6H, -OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.5, 170.0, 169.8, 169.6, 169.4, 169.3, 169.2, 164.4, 164.0, 116.3, 115.2, 93.5, 91.9, 75.7, 75.5, 74.6, 74.1, 74.0, 72.9, 72.1, 70.5, 69.6, 69.5, 69.1, 67.5, 67.2, 61.2, 61.0,

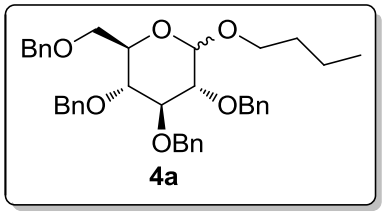
47.6, 47.4, 26.0, 25.4, 25.2, 20.6, 20.6, 20.3; HRMS (ESI) m/z calcd for $C_{23}H_{25}NO_{11}$ $[M+Na]^+$ = 514.1325, found = 514.1327.

General procedure for gold-catalysed glycosylation reaction

To a stirred solution of glycosyl ester (0.1 g, 0.146 mmol) in dry dichloromethane (2 mL), nucleophile (1.5 equiv) was added. To this reaction mixture $AuCl_3$ (5 mol%)/3$AgSbF_6$ (15 mol%) were added successively under inert atmosphere and the reaction mixture was stirred at room temperature. After completion of the reaction as revealed by TLC analysis, dichloromethane was evaporated. The concentrated reaction mixture was directly loaded on to the silica gel column and purified using EtOAc/hexanes as eluents.

Characterisation data for the glycosides

***n*-Butyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside 4a**[7]

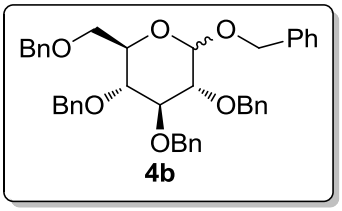


4a

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.24 (m, 18H, Ar*H*), 7.16-7.12 (m, 2H, Ar*H*), 4.92 (d, *J* = 10.8 Hz, 1H, -OC*H*$_2$Ph), 4.82 (d, *J* = 10.8 Hz, 1H, -OC*H*$_2$Ph), 4.81 (d. *J* = 11.3 Hz, 1H, -OC*H*$_2$Ph), 4.75 (t, *J* = 3.7 Hz, 1H, -OC*H*$_2$Ph), 4.71 (d, *J* = 11.0 Hz, 1H, -OC*H*$_2$Ph), 4.64 (d, *J* = 12.6 Hz, 1H, -OC*H*$_2$Ph), 4.61 (d, *J* = 12.1 Hz, 1H, -OC*H*$_2$Ph), 4.55 (d, *J* = 11.3 Hz, 1H, -OC*H*$_2$Ph), 4.46 (d, *J* = 11.0 Hz, 1H, -OC*H*$_2$Ph), 4.00-3.94 (m, 1H, H-5), 3.79-3.68 (m, 2H, H-2, H-3), 3.67-3.58 (m, 3H, H-6, H-6', H-4), 3.56-3.51 (m, 1H, -C*H*$_2$CH$_2$CH$_2$CH$_3$), 3.46-3.39 (m, 1H, -C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.71-1.58 (m, 2H, -CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.46-1.34 (m, 2H, -CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.92 (m, 3H, -CH$_2$CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 138.7, 138.5, 138.3, 138.2, 138.0, 129.6, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 103.7, 96.9, 84.8, 82.3, 82.2, 80.2, 78.0, 77.8, 77.3, 75.7, 75.1, 75.0, 74.9, 73.5, 73.2, 70.1, 69.8, 69.1, 68.6, 67.9, 31.9, 31.5, 29.7.

Benzyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside 4b[8]

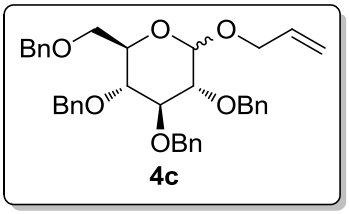
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.25 (m, 44H, Ar*H*), 7.18-7.11 (m, 4H, Ar*H*), 5.00 (d, *J* = 10.8 Hz, 1H, -OCH_2Ph), 4.98 (d, *J* = 11.8 Hz, 1H, -OCH_2Ph), 4.95 (d, *J* = 10.8 Hz, 1H, -OCH_2Ph), 4.92 (d, *J* = 10.9 Hz, 1H, -OCH_2Ph), 4.85-4.80 (m, 3H, PhCH_2), 4.78 (d, *J* = 10.9 Hz, 1H, PhCH_2), 4.72 (d, *J* = 11.1 Hz, 1H, -OCH_2Ph), 4.69-4.62 (m, 3H, -OCH_2Ph), 4.59-4.52 (m, 4H, -OCH_2Ph), 4.50-4.45 (m, 2H, -OCH_2Ph), 4.04 (t, *J* = 9.2 Hz, 2H, H-5), 3.80 (m, 1H, H-2), 3.76 (dd, *J* = 10.9, 1.9 Hz, 1H, H-3), 3.72-3.71 (m, 1H, H-6), 3.69-3.67 (m, 1H, H-6'), 3.65-3.61 (m, 2H), 3.59-3.57 (m, 1H), 3.56-3.54 (m, 1H), 3.49-3.45 (m, 1H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 138.6, 138.4, 138.2, 138.1, 138.1, 137.9, 137.4, 137.1, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 102.6, 95.6, 84.7, 82.3, 82.1, 79.9, 77.8, 77.3, 77.7, 75.7, 75.0, 75.0, 74.9, 74.9, 73.4, 73.0, 71.1, 70.3, 69.1, 68.9, 68.4.



4b

Allyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside 4c[5]

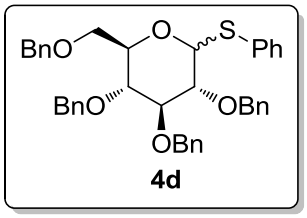
Mixture of anomers; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.25 (m, 18H, Ar*H*), 7.17-7.12 (m, 2H, Ar*H*), 6.02-5.87 (m, 1H, -OCH$_2$C*H*=CH$_2$), 5.36-5.27 (m, 1H, -OCH$_2$CH=CH_2), 5.20 (dd, *J* = 10.4, 1.4 Hz, 1H, -OCH$_2$CH=CH_2), 4.97 (t, *J* = 11.1 Hz, 1H, -OCH_2Ph), 4.92 (d, *J* = 11.1 Hz, 1H, -OCH_2Ph), 4.84-4.75 (m, 3H, -OCH_2Ph, H-1), 4.73-7.51 (m, 2H, -OCH_2Ph), 4.47-4.41 (m, 2H, -OCH_2Ph), 4.14 (ddd, *J* =12.6, 5.4, 1.1 Hz, 1H, -OCH_2Ph), 4.03-3.96 (m, 1H, H-5), 3.82-3.68 (m, 2H, -OCH_2CH=CH$_2$), 3.67-3.64 (m, 1H, H-2), 3.62-3.55 (m, 1H, H-3), 3.50-3.43 (m, 3H, H-6, H-6', H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 138.6, 138.4, 138.2, 138.1, 138.0, 137.9, 134.0, 133.7, 128.3, 128.2, 128.1, 127.9, 127.9, 127.7, 127.7, 127.6, 118.2, 117.2, 102.7, 95.7, 84.7, 82.3, 82.1, 79.9, 77.9, 77.7, 75.7, 75.0, 74.9, 73.5, 73.2, 70.3, 70.2, 69.0, 68.4, 68.2.



4c

Phenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-thio glucopyranoside 4d[9]

Mixture of anomers; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.14 (m, 38H, Ar*H*), 5.64 (d, *J* = 4.3 Hz, 1H, H-1), 4.99 (d, *J* = 10.9 Hz, 1H, -OCH_2Ph), 4.91-4.77 (m, 4H, -OCH_2Ph), 4.74-4.65 (m, 3H, -OCH_2Ph), 4.61-4.55 (m, 2H, -OCH_2Ph), 4.49 (d, *J* = 10.3 Hz, 1H, -OCH_2Ph), 4.40 (d, *J* = 11.1 Hz,

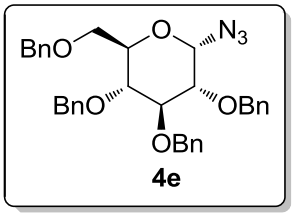


4d

1H, -OCH_2Ph), 4.34-4.31 (m, 1H, -OCH_2Ph), 3.90-3.88 (m, 2H, H-5, H-2), 3.80-3.72 (m, 1H, H-3), 3.70-3.65 (m, 2H, H-6, H-6'), 3.60 (dd, *J* = 10.5, 1.6 Hz, 1H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 138.4, 138.3, 138.2, 138.0, 137.9, 137.7, 134.5, 132.0, 131.6, 128.9, 128.5, 128.4, 128.2, 128.2, 128.0, 127.9, 127.8, 127.7, 127.7, 127.1, 87.4, 87.0, 82.6, 80.8, 79.8, 79.1, 77.8, 75.8, 75.4, 75.1, 73.4, 72.6, 71.2, 69.0, 68.5.

2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl azide 4e[10]

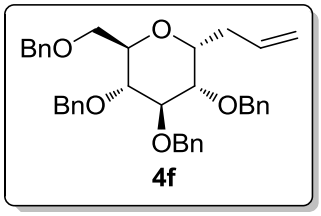
IR (KBr, cm^{-1}): 2916, 2866, 2112, 1093; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.21 (m, 18H, Ar*H*), 7.13-7.11 (m, 2H, Ar*H*), 5.21 (d, *J* = 4.2 Hz, 1H, H-1), 4.92 (d, *J* = 10.8 Hz, 1H-OCH_2Ph), 4.83-4.78 (m, 2H, -OCH_2Ph), 4.75 (d, *J* = 10.9 Hz, 1H, -OCH_2Ph), 4.74 (d, *J* = 10.8 Hz, 1H, -OCH_2Ph), 4.64 (d, *J* = 11.5 Hz, 1H, -OCH_2Ph), 4.58 (d, *J* = 11.8 Hz, 1H, -OCH_2Ph), 4.47 (d, *J* = 10.8 Hz, 1H, -OCH_2Ph), 4.46 (d, *J* = 11.8 Hz, 1H, -OCH_2Ph), 3.88-3.82 (m, 1H, H-5), 3.73-3.71 (m, 1H, H-2), 3.66-3.60 (m, 4H, H-3, H-6, H-6', H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 138.3, 137.6, 137.7, 128.7, 128.5, 128.2, 128.1, 128.0, 127.8, 127.8, 88.1, 81.7, 79.4, 77.3, 75.1, 73.8, 73.6, 73.5, 72.5, 68.1.



4e

Prop-1-en-3-yl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside 4f[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.24 (m, 18H, Ar*H*), 7.13-7.10 (m, 2H, Ar*H*), 5.86-5.76 (m, 1H, -CH_2-C*H*=CH_2), 5.12-5.05 (m, 2H, -CH_2-CH=CH_2), 4.93 (d, *J* = 10.9 Hz, 1H, -OCH_2Ph), 4.81 (d, *J* = 10.5 Hz, 2H, -OCH_2Ph), 4.69 (d, *J* = 11.6 Hz, 2H, -OCH_2Ph), 4.62 (d, *J* = 11.9 Hz, 1H, -OCH_2Ph), 4.46 (d. *J* = 11.9 Hz, 2H, -OCH_2Ph), 4.13 (m, 1H, H-5), 3.82-3.73 (m, 2H, H-1), 3.70 (m, 1H, H-3), 3.66-3.58 (m, 3H, H-6, H-6', H-4), 2.55-2.43 (m, 2H, -CH_2-CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 138.3, 138.2, 138.1, 134.8, 128.5, 128.4, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 117.0, 82.5, 80.1, 78.2, 75.5, 75.2, 73.8, 73.5, 73.2, 71.2, 69.0, 29.9.

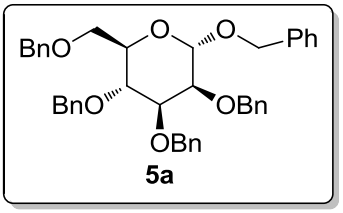


4f

Benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside 5a[11]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.25 (m, 22H, Ar*H*), 7.16-7.15 (m, 3H, Ar*H*), 4.97 (br s, 1H, H-1), 4.87 (d, *J* = 10.8 Hz, 1H, -OCH_2Ph), 4.72 (m, 3H, -OCH_2Ph), 4.70 (d, *J* = 11.3

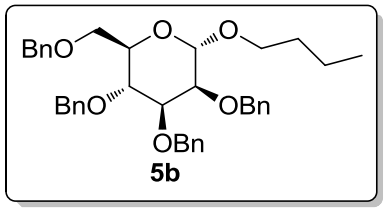
Hz, 1H, -OCH_2Ph), 4.60 (m, 2H, -OCH_2Ph), 4.55 (d, J = 12.2 Hz, 1H, -OCH_2Ph), 4.50 (d, J = 10.7 Hz, 1H, -OCH_2Ph), 4.45 (d, J = 10.6 Hz, 1H, -OCH_2Ph), 4.01 (t, J = 9.2 Hz, 1H, H-5), 3.95 (dd, J = 9.2, 3.0 Hz, 1H, H-2), 3.85-3.77 (m, 3H, H-3, H-6, H-6'), 3.70 (dd, J = 10.4 Hz, 1H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 138.4, 138.4, 138.2, 137.3, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 97.2, 80.2, 77.3, 75.2, 74.9, 74.6, 73.4, 72.5, 72.2, 72.0, 69.2, 68.9.



5a

_n_-Butyl 2,3,4,6-tetra-_O_-benzyl-α-D-mannopyranoside 5b[12]

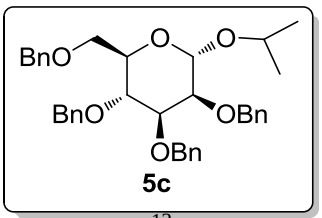
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.23 (m, 18H, ArH), 7.16-7.14 (m, 2H, ArH), 4.87 (d, J = 10.7 Hz, 2H, -OCH_2Ph), 4.75 (d, J = 12.4 Hz, 1H, -OCH_2Ph), 4.71 (d, J = 12.4 Hz, 1H, -OCH_2Ph), 4.66 (d, J = 12.1 Hz, 1H, -OCH_2Ph), 4.62 (m, 2H, -OCH_2Ph), 4.54 (d, J = 12.2 Hz, 1H, -OCH_2Ph), 4.49 (d, J = 10.5 Hz, 1H, H-1), 3.98 (t, J = 9.4 Hz, 1H, H-5), 3.90 (dd, J = 9.2, 3.2 Hz, 1H, H-6), 3.80-3.71 (m, 4H, H-6', H-2, H-3, H-4), 3.68-3.63 (m, 1H, -CH_2CH$_2$CH$_2$CH$_3$), 3.38-3.32 (m, 1H, -CH_2CH$_2$CH$_2$CH$_3$), 1.53-1.46 (m, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.35-1.23 (m, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 0.88 (t, J = 7.6 Hz, 3H, -CH$_2$CH$_2$CH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 138.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 97.7, 80.3, 75.2, 74.9, 74.7, 73.3, 72.5, 72.1, 71.7, 69.2, 67.3, 31.5, 19.3, 13.9.



5b

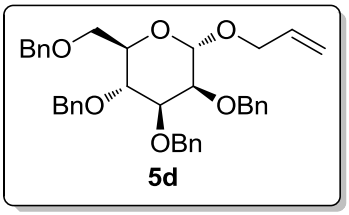
Isopropyl 2,3,4,6-tetra-_O_-benzyl-α-D-mannopyranoside 5c[11]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.23 (m, 18H, ArH), 7.16-7.14 (m, 2H, ArH), 4.96 (d, J = 1.8 Hz, 1H, H-1), 4.77 (d, J = 12.5 Hz, 1H, -OCH_2Ph), 4.70 (d, J = 12.6 Hz, 1H, -OCH_2Ph), 4.67 (d, J = 12.1 Hz, 1H, -OCH_2Ph), 4.63 (m, 2H, -OCH_2Ph), 4.53 (d, J = 12.1 Hz, 1H, -OCH_2Ph), 4.49 (d, J = 10.8 Hz, 1H, -OCH_2Ph), 3.99 (t, J = 9.3 Hz, 1H), 3.93-3.91 (m, 1H, -CH(CH$_3$)$_2$), 3.90-3.86 (m, 1H), 3.84-3.77 (m, 2H), 3.74-3.70 (m, 2H), 1.15 (d, J = 6.2 Hz, 3H, -CH(CH_3)$_2$), 1.05 (d, J = 6.1 Hz, 3H, -CH(CH_3)$_2$).^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 138.6, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 127.5, 127.5, 95.9, 80.5, 75.3, 75.2, 73.4, 72.7, 72.2, 71.8, 69.4, 68.9, 23.3, 21.3.



5c

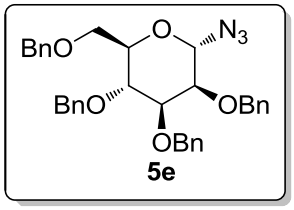
Allyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside 5d[5]



5d

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.24 (m, 18H, Ar*H*), 7.16-7.14 (m, 2H, Ar*H*), 5.88-5.79 (m, 1H, -CH_2CH=CH_2), 5.20 (dd, *J* = 17.2, 1.6 Hz, 1H, -CH_2CH=CH_2), 5.14 (dd, *J* = 10.3, 1.3 Hz, 1H, -CH_2CH=CH_2), 4.92 (d, *J* = 1.7 Hz, 1H, H-1), 4.88 (d, *J* = 10.7 Hz, 1H, -OCH_2Ph), 4.75 (d, *J* = 12.6 Hz, 1H, -OCH_2Ph), 4.71 (d, *J* = 12.4 Hz, 1H, -OCH_2Ph), 4.66 (d, *J* = 12.1 Hz, 1H, -OCH_2Ph), 4.62 (s, 2H, -CH_2CH=CH_2), 4.54 (d, *J* = 12.1 Hz, 1H, -OCH_2Ph), 4.50 (d, *J* = 10.7 Hz, 1H, -OCH_2Ph), 4.17 (ddt, *J* = 13.0, 4.9, 1.4 Hz, 1H, H-5), 4.02-3.91 (m, 3H, H-6, H-6', H-3), 3.81-3.71 (m, 4H, H-2, H-4, -OCH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 138.4, 138.4, 138.3, 133.7, 128.3, 128.0, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 117.2, 97.0, 80.2, 75.1, 74.9, 74.6, 73.3, 72.5, 72.1, 71.8, 69.2, 67.8.

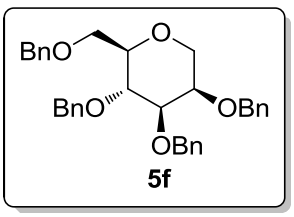
2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl azide 5e[13]



5e

IR (KBr, cm^{-1}): 3030, 2916, 2112; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.25 (m, 18H, Ar*H*), 7.17-7.15 (m, 2H, Ar*H*), 5.39 (d, *J* = 2.0 Hz, 1H, H-1), 4.86 (d, *J* = 10.9 Hz, 1H, -OCH_2Ph), 4.73 (d, *J* = 12.3 Hz, 1H, -OCH_2Ph), 4.70-4.65 (m, 2H, -OCH_2Ph), 4.62 (d, *J* = 11.4 Hz, 1H, -OCH_2Ph), 4.58-4.49 (m, 3H, -OCH_2Ph), 4.02 (t, *J* = 9.2 Hz, 1H, H-5), 3.89-3.86 (m, 1H, H-2), 3.82-3.77 (m, 2H, H-3, H-6), 3.73 (dd, *J* = 10.9, 1.7 Hz, 1H, H-6'), 3.62 (m, 1H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 138.2, 137.9, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 88.1, 79.1, 75.2, 74.6, 74.4, 74.0, 73.5, 72.8, 72.5, 68.9.

1,5-Anhydro-2,3,4,6-tetra-*O*-benzyl-α-D-manno-hexitol 5f[14]

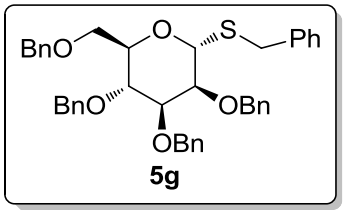


5f

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.39 (d, *J* = 7.1 Hz, 2H, Ar*H*), 7.35-7.24 (m, 16H, Ar*H*), 7.17-7.16 (m, 2H, Ar*H*), 4.91 (d, *J* = 10.8 Hz, 1H, -OCH_2Ph), 4.78 (d, *J* = 12.6 Hz, 1H, -OCH_2Ph), 4.69-4.52 (m, 6H, -OCH_2Ph), 4.13 (dd, *J* = 12.8, 2.1 Hz, 1H, H-5), 3.88 (t, *J* = 9.4 Hz, 1H, H-3), 3.75-3.73 (m, 2H, H-1, H-1'), 3.68 (dd, *J* = 10.4,

5.7 Hz, 1H, H-6), 3.56 (dd, *J* = 9.1, 3.2 Hz, 1H, H-6'), 3.41 (m, 1H, H-2), 3.28 (d, *J* = 12.6 Hz, 1H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 138.3, 138.2, 128.3, 128.0, 128.0, 127.9, 127.7, 127.6, 127.5, 82.8, 79.8, 75.3, 73.5, 72.4, 71.5, 71.0, 69.7, 66.8.

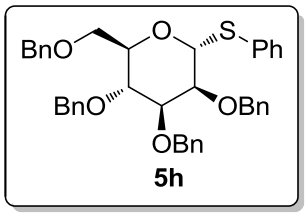
Benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-manno-thiopyranoside 5g[15]



5g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.16 (m, 25H, Ar*H*), 5.28 (s, 1H, H-1), 4.87 (d, *J* = 11.0 Hz, 1H, -OCH_2Ph), 4.67 (d, *J* = 12.1 Hz, 1H, -OCH_2Ph), 4.62 (d, *J* = 12.4 Hz, 1H, -OCH_2Ph), 4.55-4.47 (m, 5H, -OCH_2Ph), 4.11 (dd, *J* = 9.9, 4.7 Hz, 1H, PhCH_2S-), 4.02 (t, *J* = 9.4 Hz, 1H, H-5), 3.90-3.78 (m, 2H, PhCH_2S-), 3.77-3.72 (m, 2H, H-2, H-3), 3.69 (m, 1H, H-6, H-6'), 3.64 (m, 1H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 138.4, 138.2, 137.8, 129.0, 128.5, 128.3, 127.9, 127.8, 127.6, 127.5, 127.1, 80.8, 80.4, 75.7, 75.1, 75.0, 73.3, 72.3, 71.9, 71.7, 69.1, 34.7.

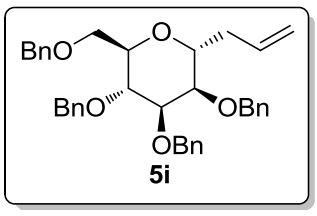
Phenyl 2,3,4,6-tetra-*O*-benzyl-α-D-manno-thiopyranoside 5h[16]



5h

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.43 (m, 2H, Ar*H*), 7.35-7.18 (m, 23H, Ar*H*), 5.61 (s, 1H, H-1), 4.90 (d, *J* = 10.1 Hz, 1H, -OCH_2Ph), 4.73 (d, *J* = 12.0 Hz, 1H, -OCH_2Ph), 4.66-4.56 (m, 4H, -OCH_2Ph), 4.52 (d, *J* = 11.1 Hz, 1H, -OCH_2Ph), 4.48 (d, *J* = 12.0 Hz, 1H, -OCH_2Ph), 4.28 (m, 1H, H-5), 4.07 (t, *J* = 9.8 Hz, 1H, H-2), 3.99 (m, 1H, H-3), 3.87-3.82 (m, 2H, H-6, H-6'), 3.76-3.73 (m, 1H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 138.4, 138.2, 137.9, 134.4, 131.7, 129.1, 128.5, 128.4, 128.3, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 127.5, 127.4, 85.7, 80.2, 76.2, 75.3, 75.0, 73.3, 72.8, 72.1, 71.9, 69.2.

3-C-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)-1-propene 5i[16]

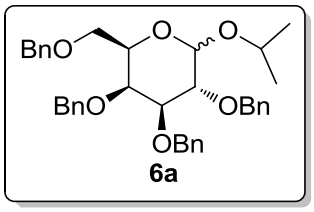


5i

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.24 (m, 18H, Ar*H*), 7.23-7.19 (m, 2H, Ar*H*), 5.82-5.66 (m, 1H, -CH_2-C*H*=CH_2), 5.05-4.99 (m, 2H, -CH_2-CH=CH_2), 4.75-4.68 (m, 2H, -OCH_2Ph), 4.63-4.52 (m, 6H, -OCH_2Ph), 4.05 (q, *J* = 7.0 Hz, 1H, H-5), 3.90-3.83 (m, 2H, H-1, H-6), 3.81-3.77 (m, 2H, H-4, H-6'), 3.74-3.69 (m, 1H, H-2), 3.65-3.63 (m, 1H, H-3), 2.42-2.47 (m, 2H, -CH_2-CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 138.3, 138.2,

138.1, 134.3, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.4, 117.2, 77.2, 76.9, 75.1, 74.9, 73.8, 73.7, 72.3, 73.3, 72.0, 71.5, 69.1, 34.6.

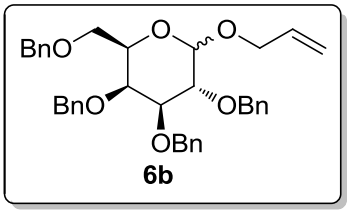
Isopropyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranoside 6a[6]



6a

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.24 (m, 30H, Ar*H*), 4.96-4.91 (m, 3H, PhCH_2, H-1), 4.84 (d, *J* = 11.4 Hz, 1H, -OCH_2Ph), 4.80 (d, *J* = 12.0 Hz, 1H, -OCH_2Ph), 4.74-4.71 (m, 2H, -OCH_2Ph), 4.66 (dd, *J* = 11.8 Hz, 1H, -OCH_2Ph), 4.61 (d, *J* = 11.6 Hz, 1H, -OCH_2Ph), 4.56 (d, *J* = 11.4 Hz, 1H, -OCH_2Ph), 4.47 (d, *J* = 11.8 Hz, 1H, -OCH_2Ph), 4.42-4.38 (m, 2H, -OCH_2Ph), 4.03-4.00 (m, 2H, -OCH_2Ph), 3.98-3.95 (m, 1H, H-5), 3.93-3.86 (m, 1H, H-2), 3.87-3.85 (m, 1H, H-3), 3.81-3.76 (m, 1H, H-6), 3.58-3.55 (m, 1H, H-6'), 3.54-3.48 (m, 2H, H-4, -C*H*$(CH_3)_2$), 1.26 (d, *J* = 6.3 Hz, 3H, -CH(CH_3)$_2$), 1.23 (d, *J* = 4.8 Hz, 3H, -CH(CH_3)$_2$), 1.21 (d, *J* = 4.8 Hz, 3H, -CH(CH_3)$_2$), 1.17 (d, *J* = 6.1 Hz, 3H, -CH(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 138.8, 138.7, 138.6, 138.6, 138.0, 137.9, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1. 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 102.4, 95.4, 82.4, 79.6, 79.2, 77.2, 76.4, 75.2, 75.1, 74.7, 74.4, 73.5, 73.4, 73.3, 73.2, 73.1, 73.1, 72.1, 69.1, 69.0, 23.6, 23.2, 22.1, 21.2.

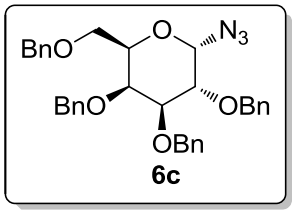
Allyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranoside 6b[5]



6b

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.24 (m, 20H, Ar*H*), 5.98-5.87 (m, 1H, -OCH_2CH=CH_2), 5.34-5.26 (m, 1H, -OCH_2CH=CH_2), 5.19-5.15 (m, 1H, -OCH_2CH=CH_2), 4.94 (d, *J* = 11.4 Hz, 1H, -OCH_2Ph), 4.88-4.79 (m, 2H, H-1, -OCH_2Ph), 4.77-4.72 (m, 1H, -OCH_2Ph), 4.66 (d, *J* = 12.1 Hz, 1H, -OCH_2Ph), 4.56 (d, *J* = 11.4 Hz, 1H, -OCH_2Ph), 4.46 (d, *J* = 11.8 Hz, 1H, -OCH_2Ph), 4.43-4.38 (m, 2H, -OCH_2Ph), 4.15 (dd, *J* = 11.1 Hz, 4.8 Hz, 1H, -OCH_2Ph), 4.06-3.94 (m, 5H, H-5, H-2, H-3, H-6, H-6'), 3.88-3.82 (m, 1H, H-4), 3.52-3.51 (m, 2H, -OCH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 138.7, 138.6, 138.0, 137.9, 134.2, 134.0, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 118.0, 117.1, 103.0, 96.3, 82.2, 79.6, 79.2, 76.5, 75.3, 75.2, 74.8, 74.5, 73.5, 73.4, 73.3, 73.1, 70.2, 69.4, 69.0, 68.9, 68.3.

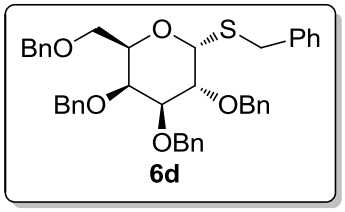
2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl azide 6c[10]



6c

IR (KBr, cm^{-1}): 3030, 2914, 2114, 1452, 1095; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.26 (m, 20H, Ar*H*), 5.31 (d, *J* = 4.2 Hz, 1H, H-1), 4.94 (d, *J* = 11.5 Hz. 1H, -OC*H*$_2$Ph), 4.86 (d, *J* = 11.6 Hz, 1H, -OC*H*$_2$Ph), 4.82 (d, *J* = 11.6 Hz, 1H, -OC*H*$_2$Ph), 4.74 (d, *J* = 12.0 Hz, 1H, -OC*H*$_2$Ph), 4.70 (d, *J* = 12.0 Hz, 1H, -OC*H*$_2$Ph), 4.57 (d, *J* = 11.5 Hz, 1H, -OC*H*$_2$Ph), 4.50 (d, *J* = 11.8 Hz, 1H, -OC*H*$_2$Ph), 4.41 (d, *J* = 12.1 Hz, 1H, -OC*H*$_2$Ph), 4.13 (dd, *J* = 10.0, 4.7 Hz, 1H, H-5), 4.03 (t, *J* = 6.5 Hz, 1H, H-2), 3.97 (m, 1H, H-3), 3.81 (dd, *J* = 9.7, 2.6 Hz, 1H, H-6), 3.56-3.51 (m, 2H, H-6', H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 138.4, 138.0, 137.8, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 88.9, 78.9, 76.0, 74.9, 74.6, 74.0, 73.6, 73.2, 71.7, 60.5.

Benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-galacto-thiopyranoside 6d[14]



6d

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.23 (m, 25H, Ar*H*), 5.26 (d, *J* = 5.3 Hz, 1H, H-1), 4.92 (d, *J* = 11.1 Hz, 1H, -OC*H*$_2$Ph), 4.82 (d, *J* = 11.6 Hz, 1H, -OC*H*$_2$Ph), 4.68 (d, *J* = 12.2 Hz, 1H, -OC*H*$_2$Ph), 4.56 (d, *J* = 11.4 Hz, 1H, -OC*H*$_2$Ph), 4.53-4.38 (m, 4H, -OC*H*$_2$Ph), 4.31 (m, 1H, H-5), 4.27-4.19 (m, 1H, H-2), 3.92 (m, 1H, H-3), 3.84-3.70 (m, 2H, H-6, H-6'), 3.63 (d, *J* = 11.8 Hz, 1H, PhC*H*$_A$H$_B$S-), 3.51-3.49 (m, 2H, PhCH$_A$*H*$_B$S-, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 138.6, 138.2, 138.1, 129.2, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.5, 126.9, 83.2, 82.2, 798, 76.2, 75.9, 75.0, 74.8, 73.5, 72.0, 69.9, 69.2, 33.0.

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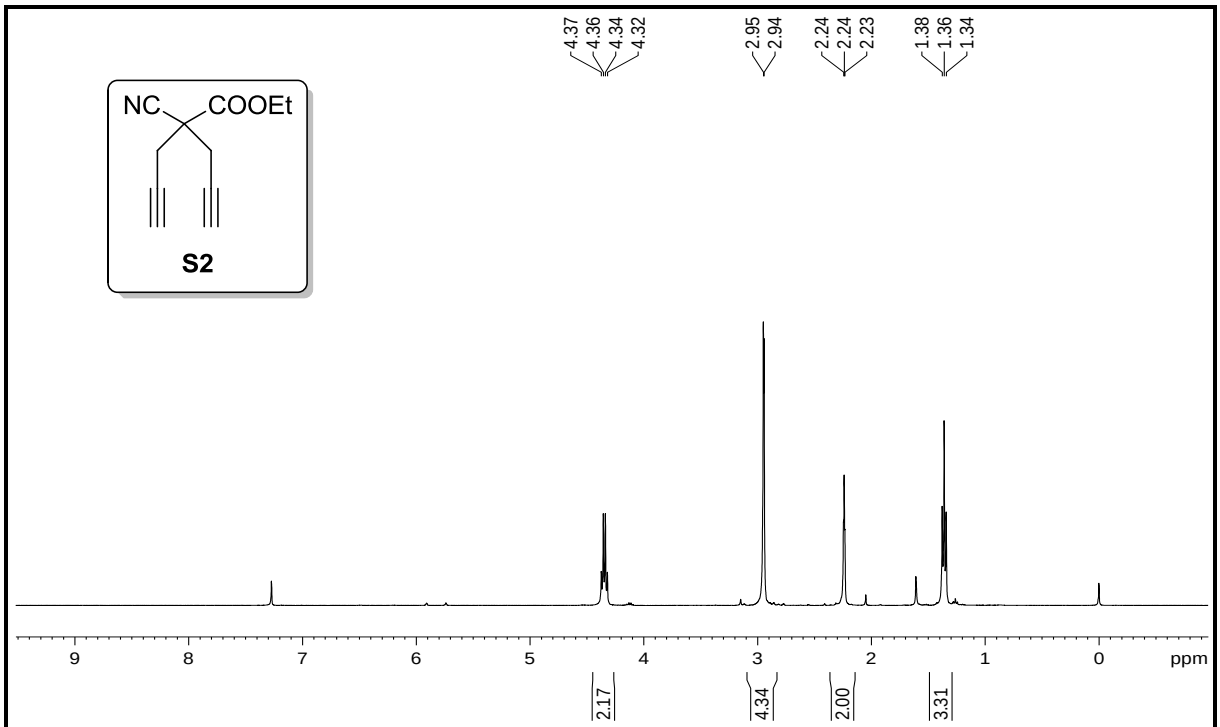
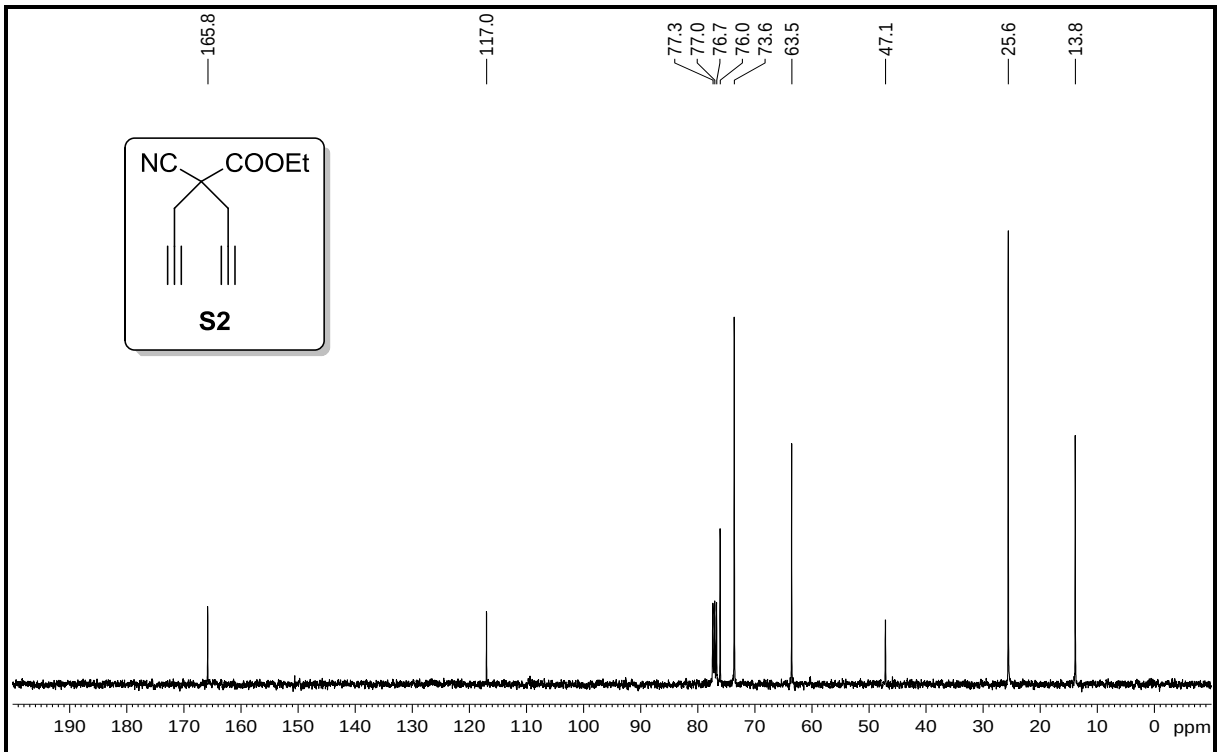
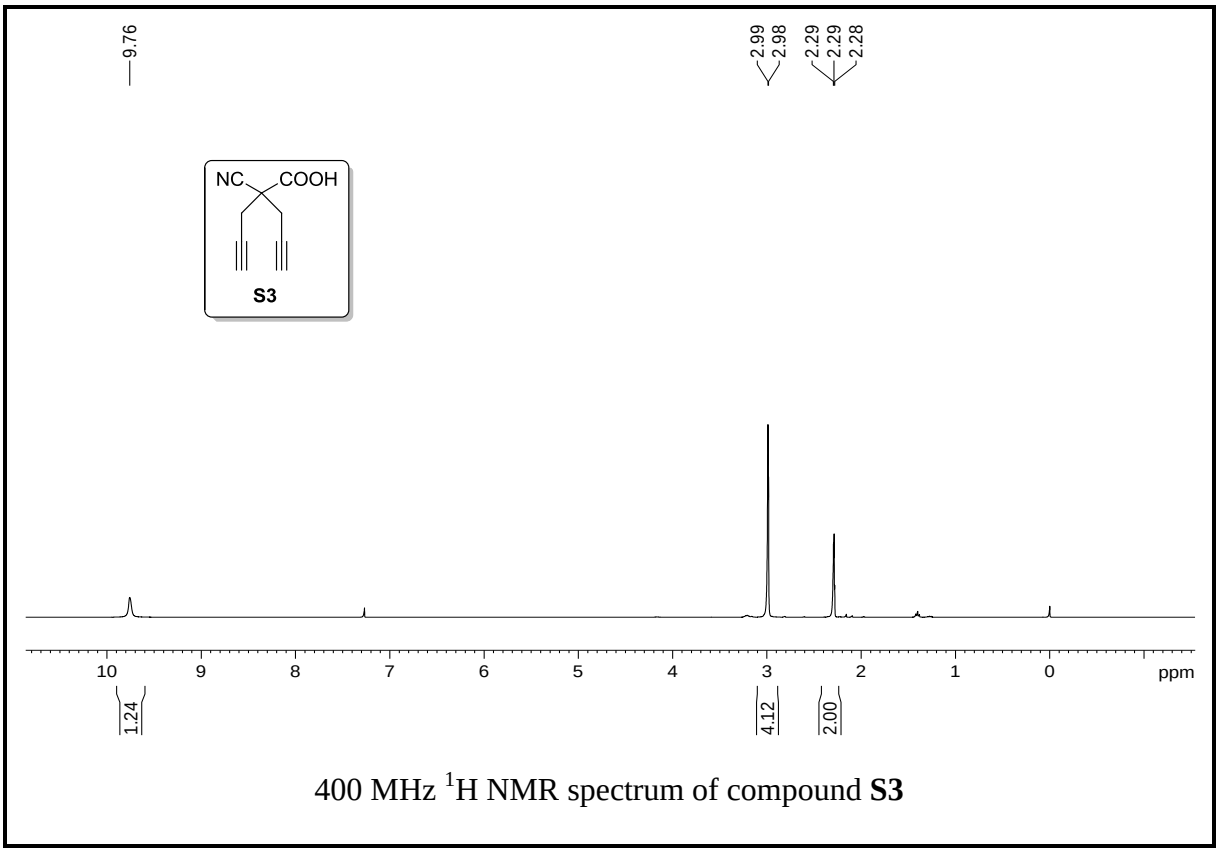


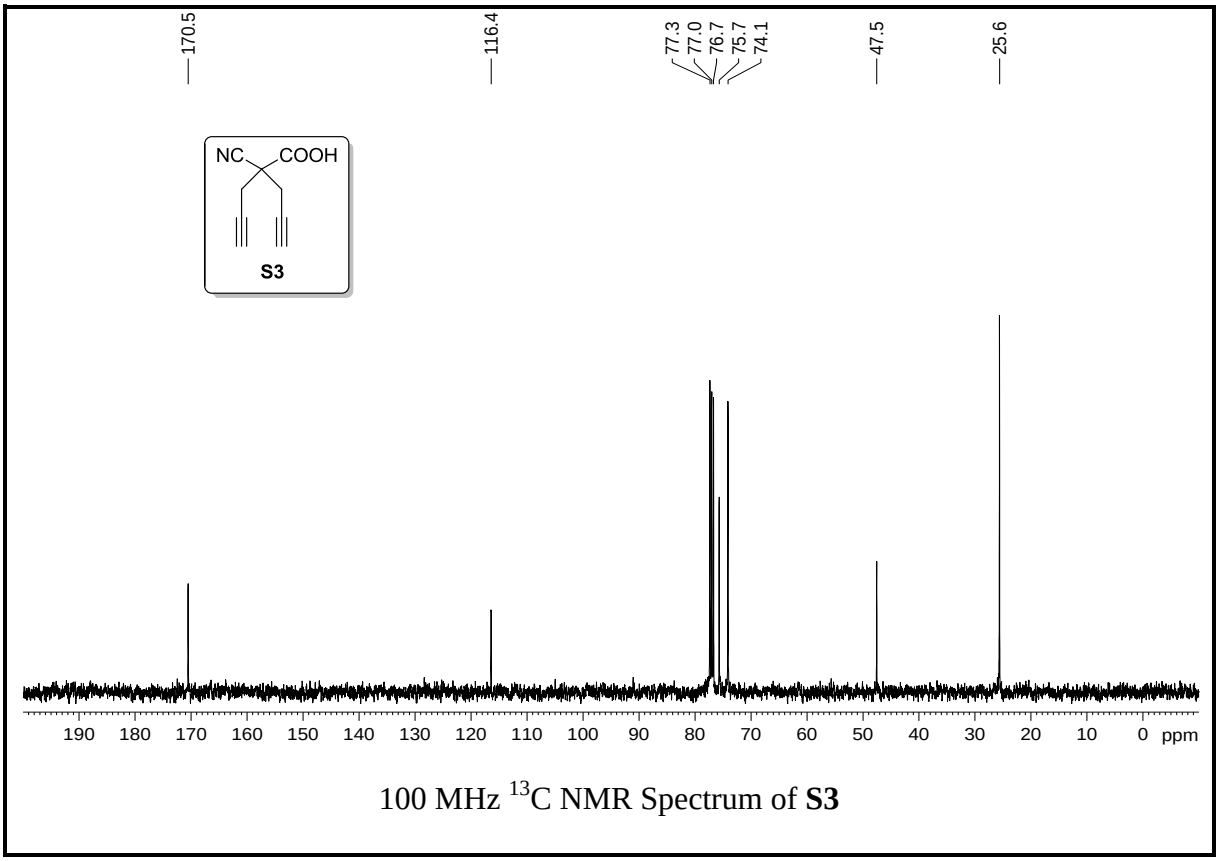
400 MHz ^{1}H NMR spectrum of compound **S2**



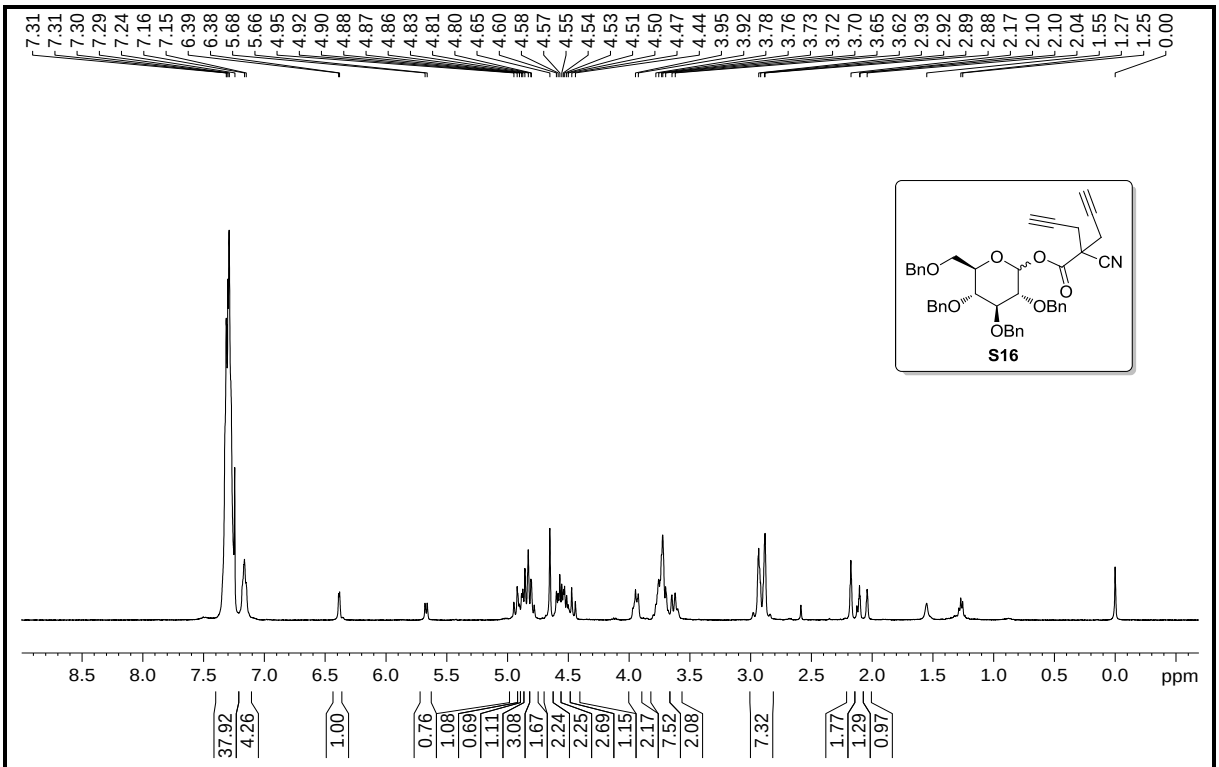
100 MHz ^{13}C NMR Spectrum of **S2**



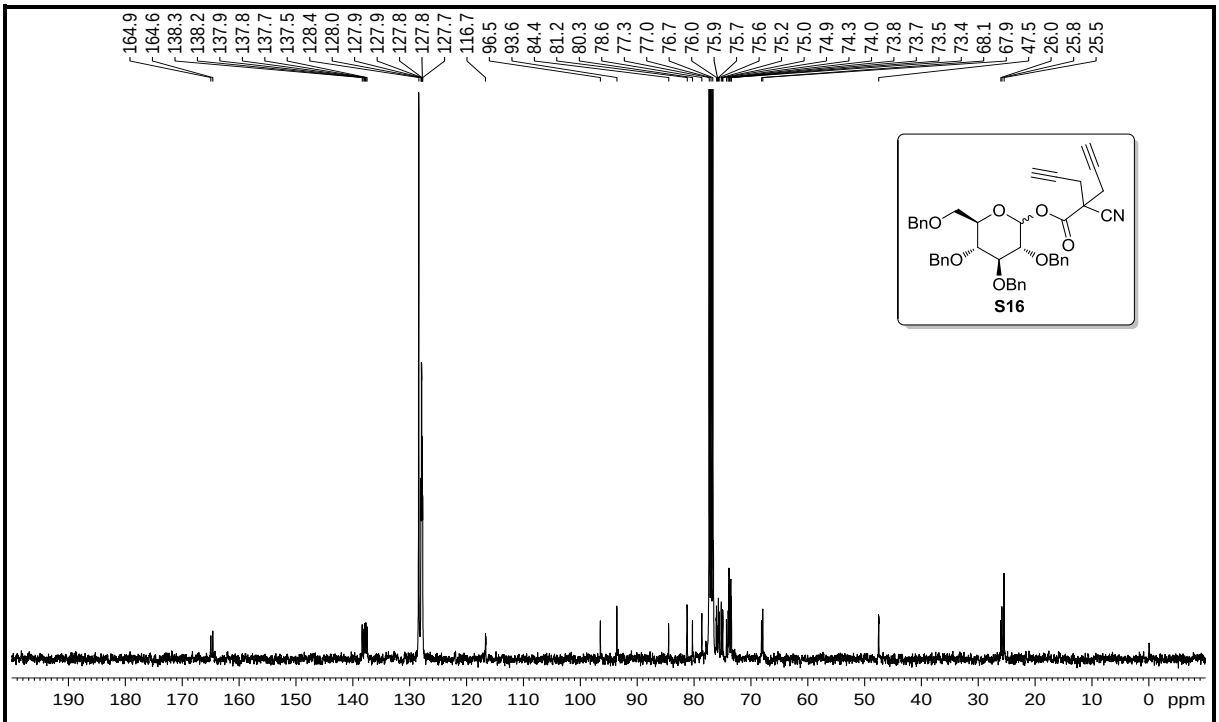
400 MHz ^{1}H NMR spectrum of compound **S3**



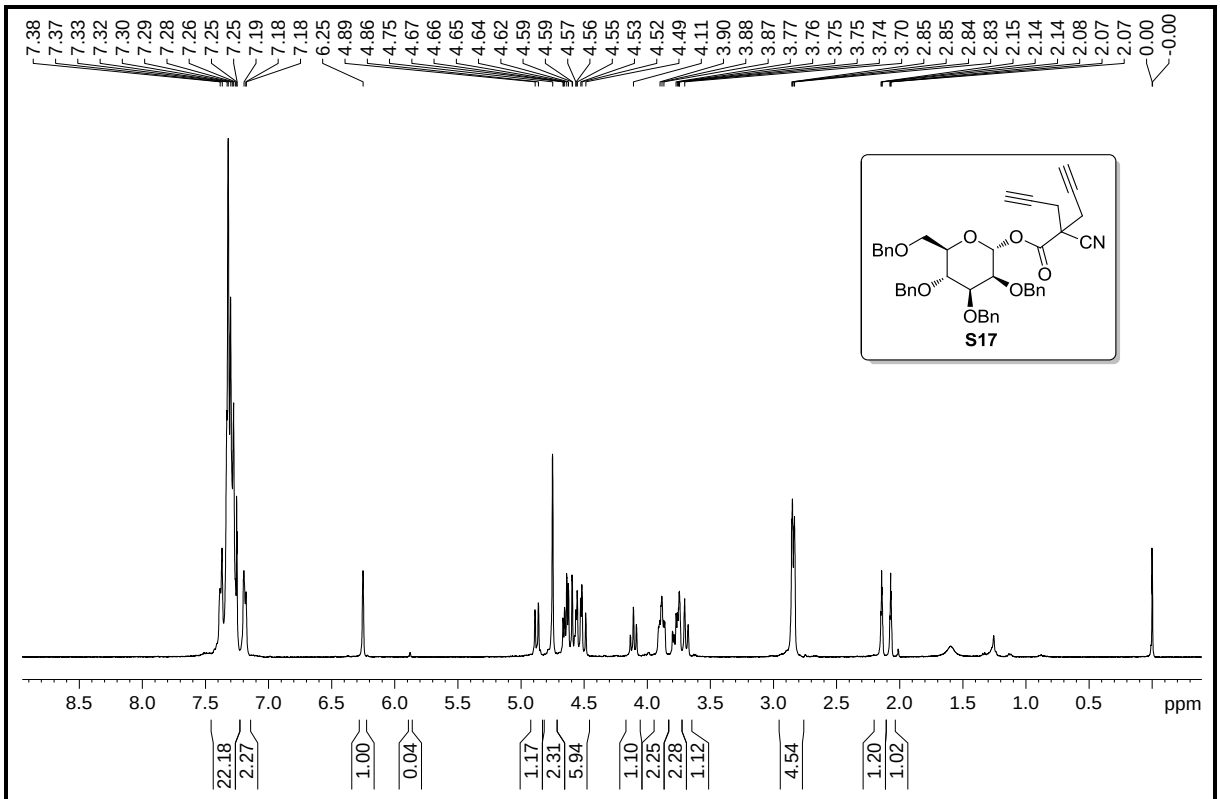
100 MHz ^{13}C NMR Spectrum of **S3**



400 MHz ^{1}H NMR spectrum of compound **S16**



100 MHz ^{13}C NMR Spectrum of **S16**



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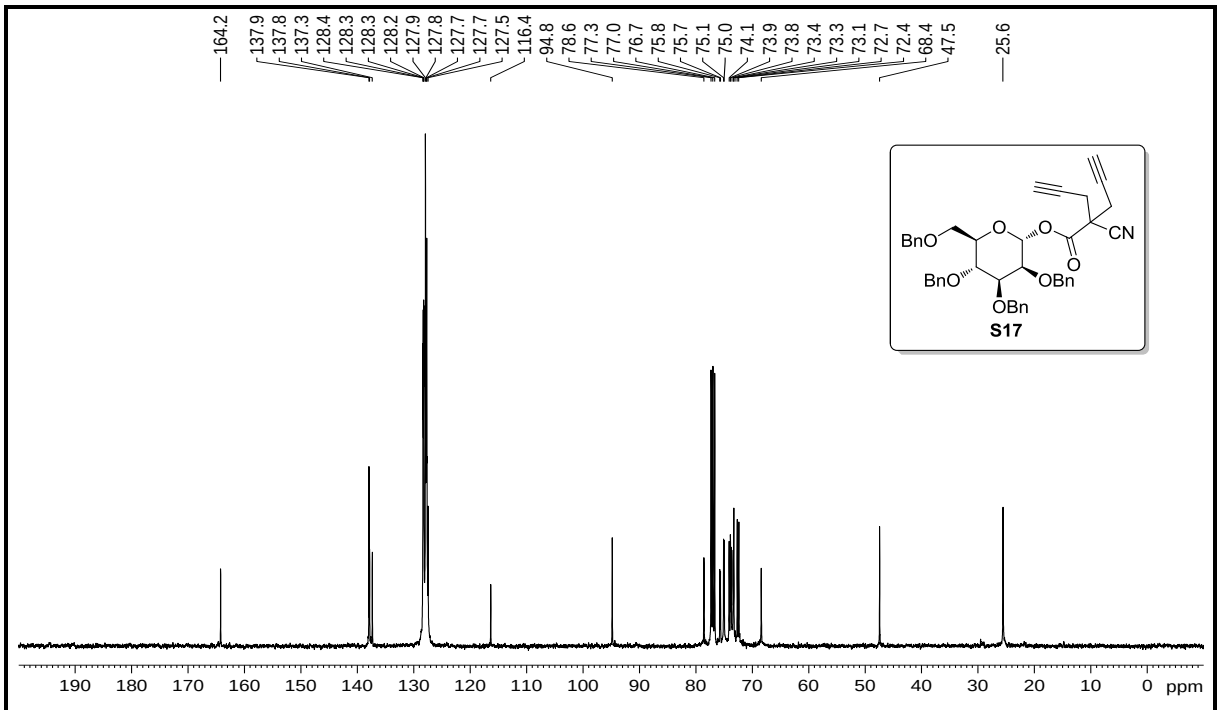
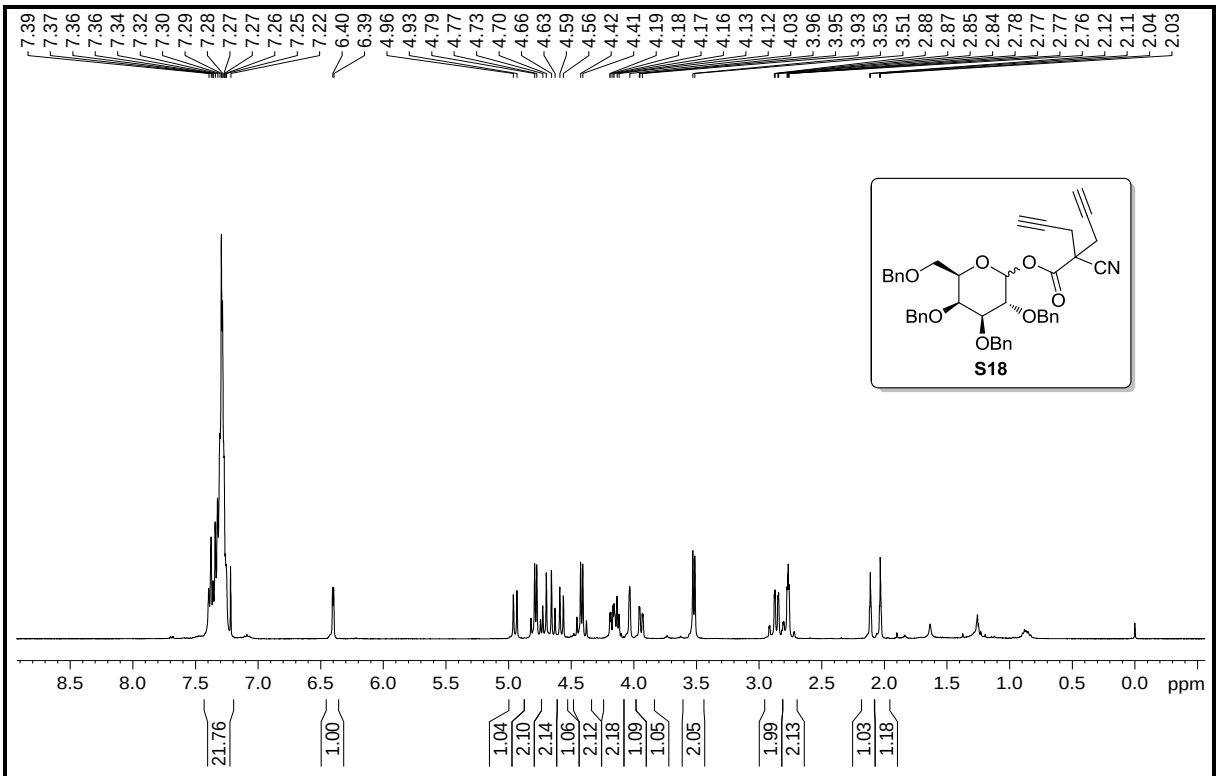


100 MHz ^{13}C NMR Spectrum of **S17**



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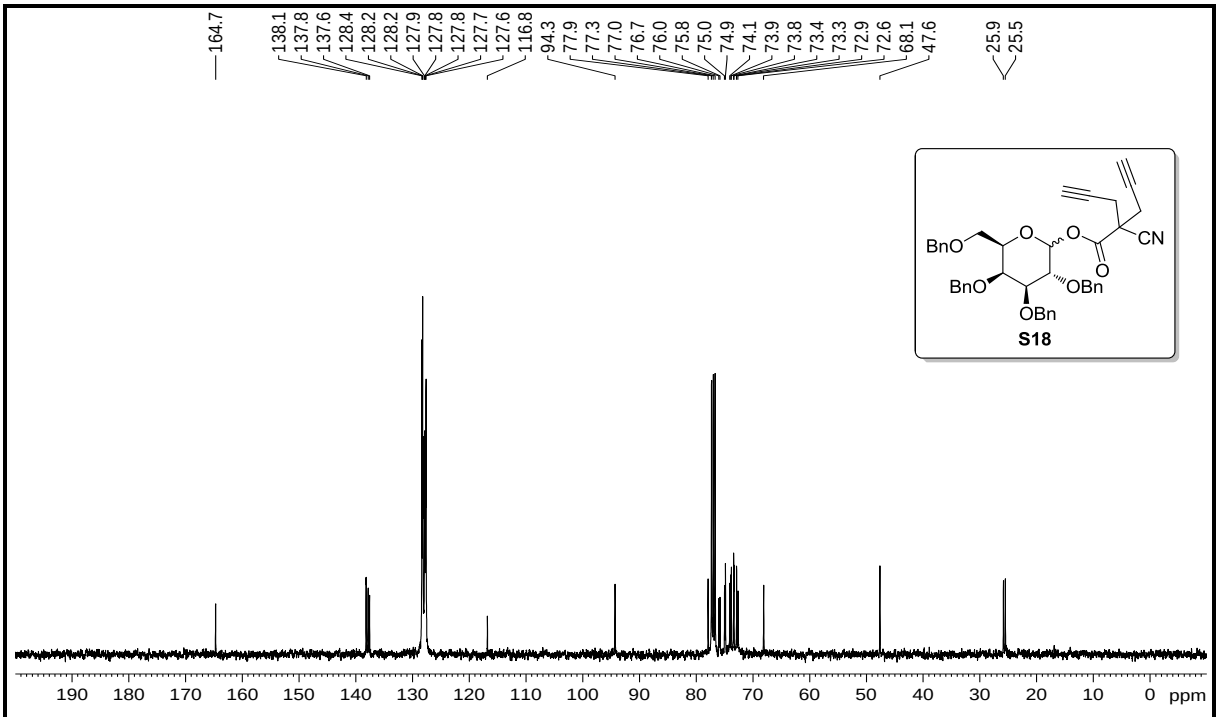
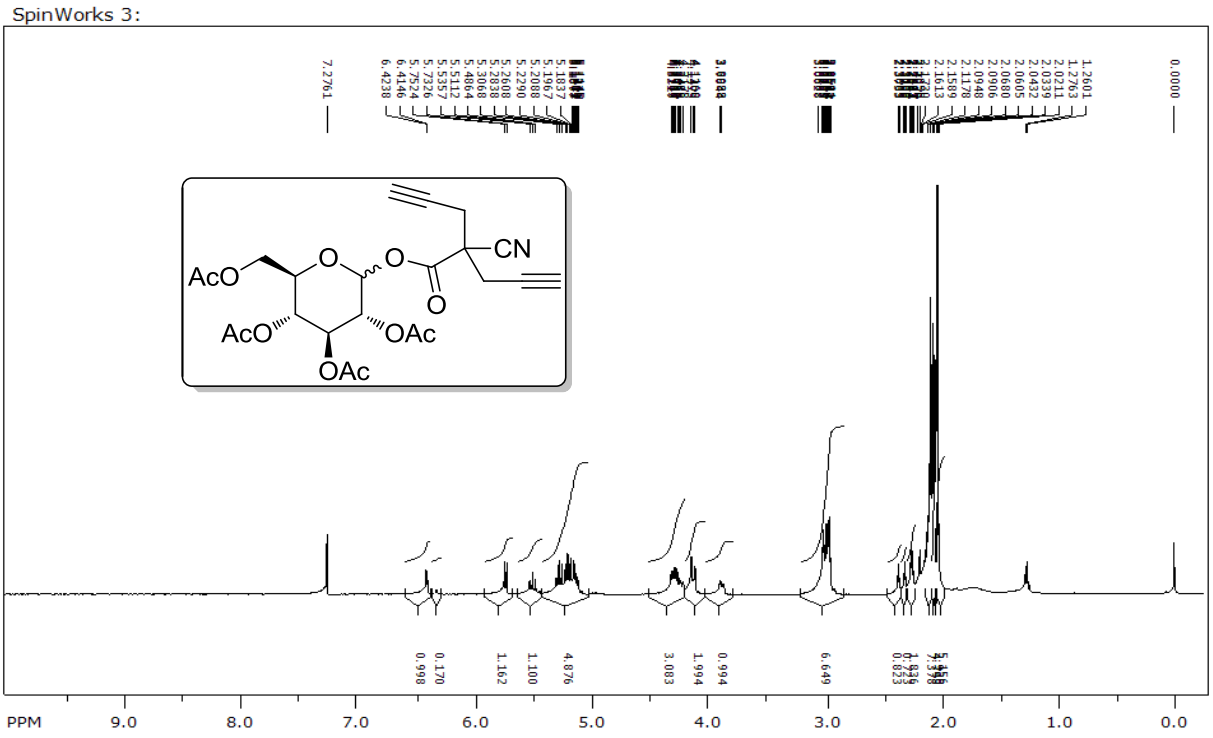
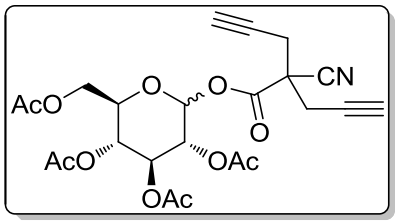
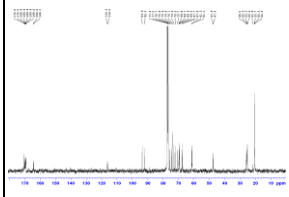


100 MHz ^{13}C NMR Spectrum of **S18**

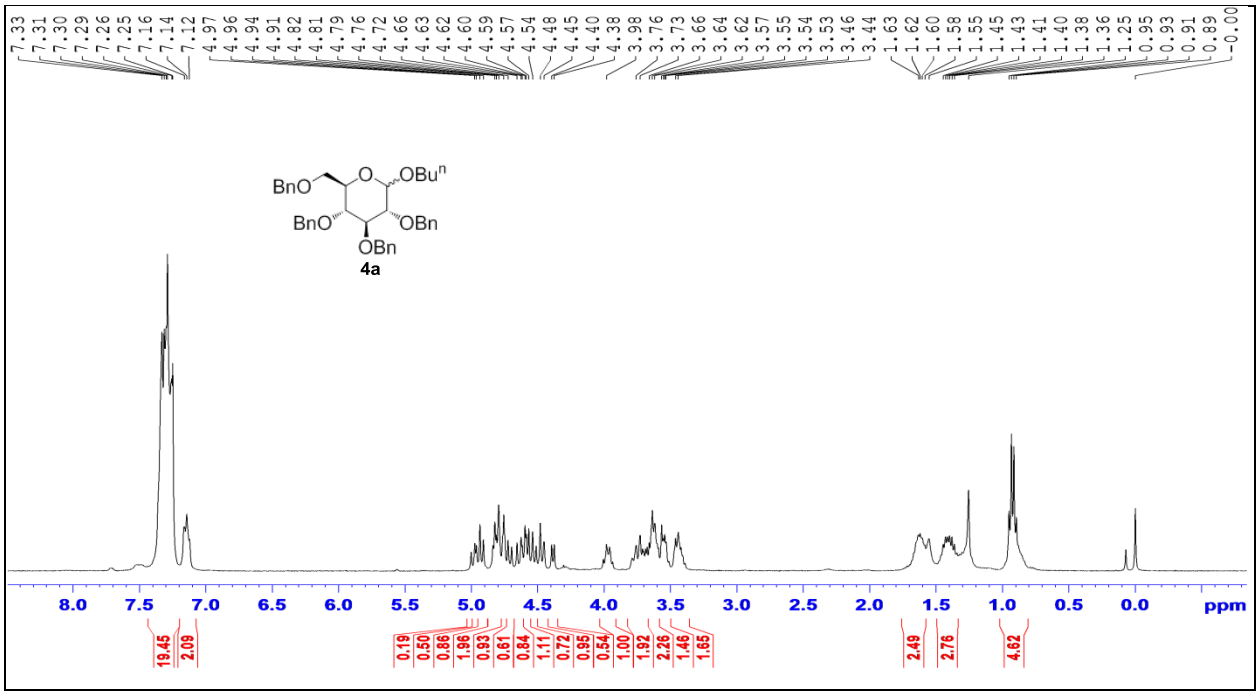


400 MHz ^{1}H NMR spectrum of compound **S21**





100 MHz ^{13}C NMR Spectrum of **S21**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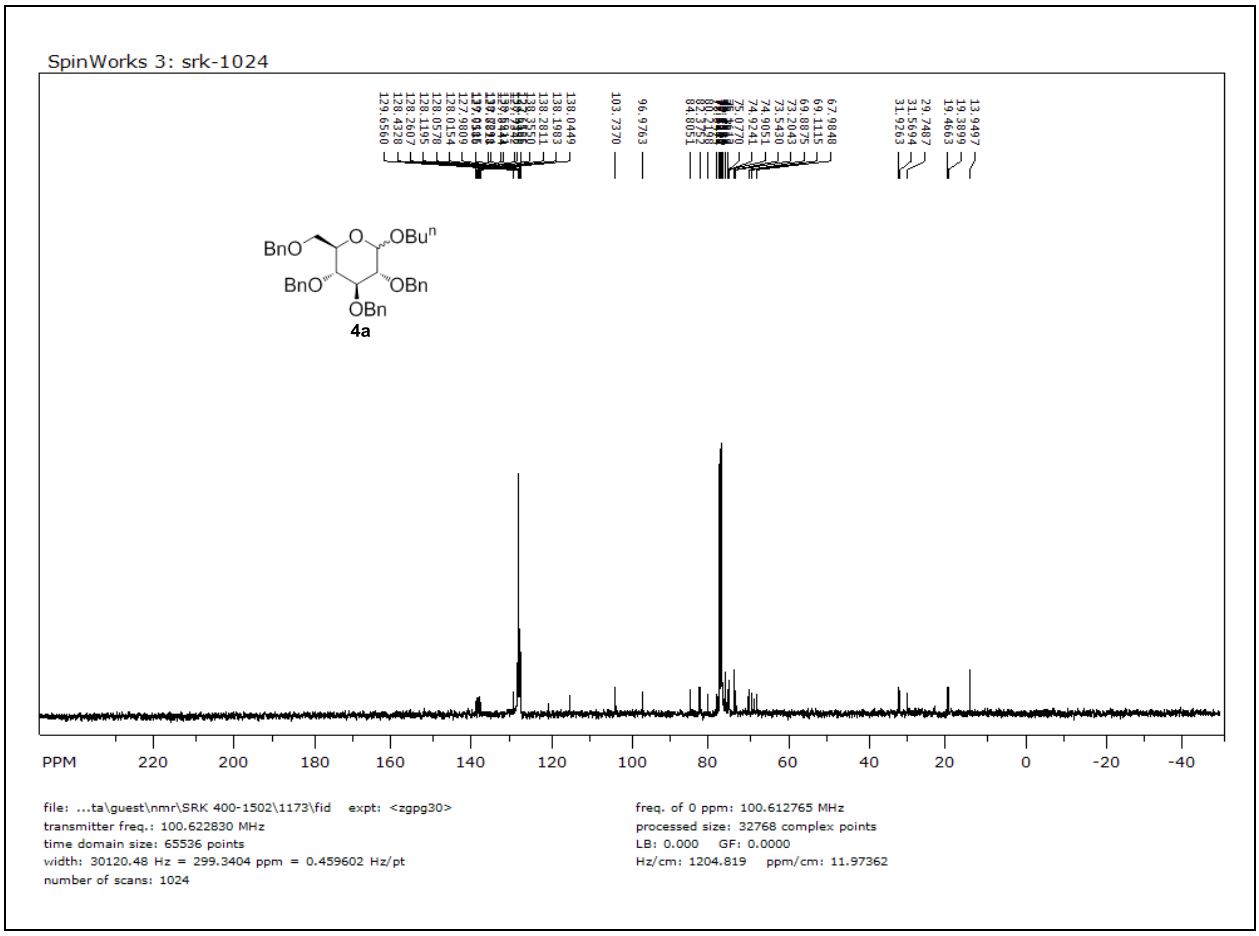
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width: 30120.48 Hz = 299.3404 ppm = 0.459602 Hz/pt
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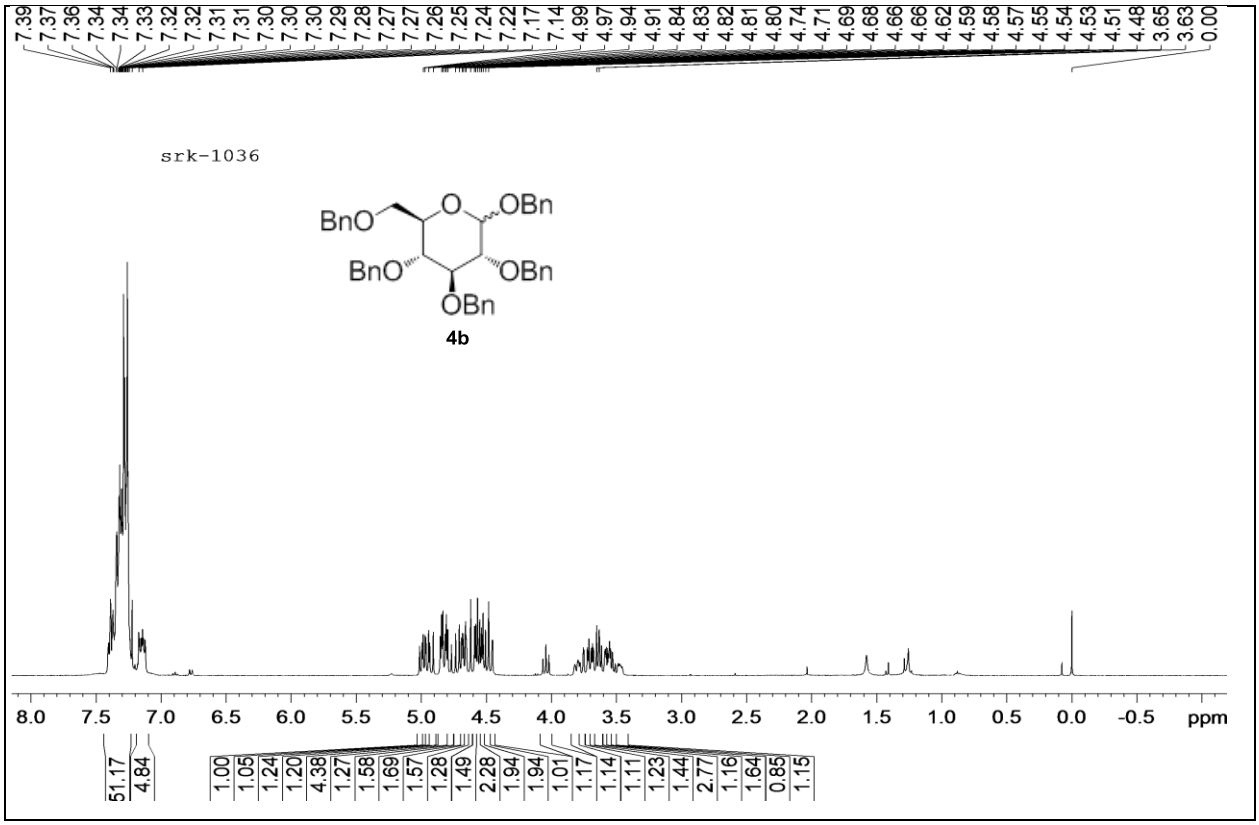
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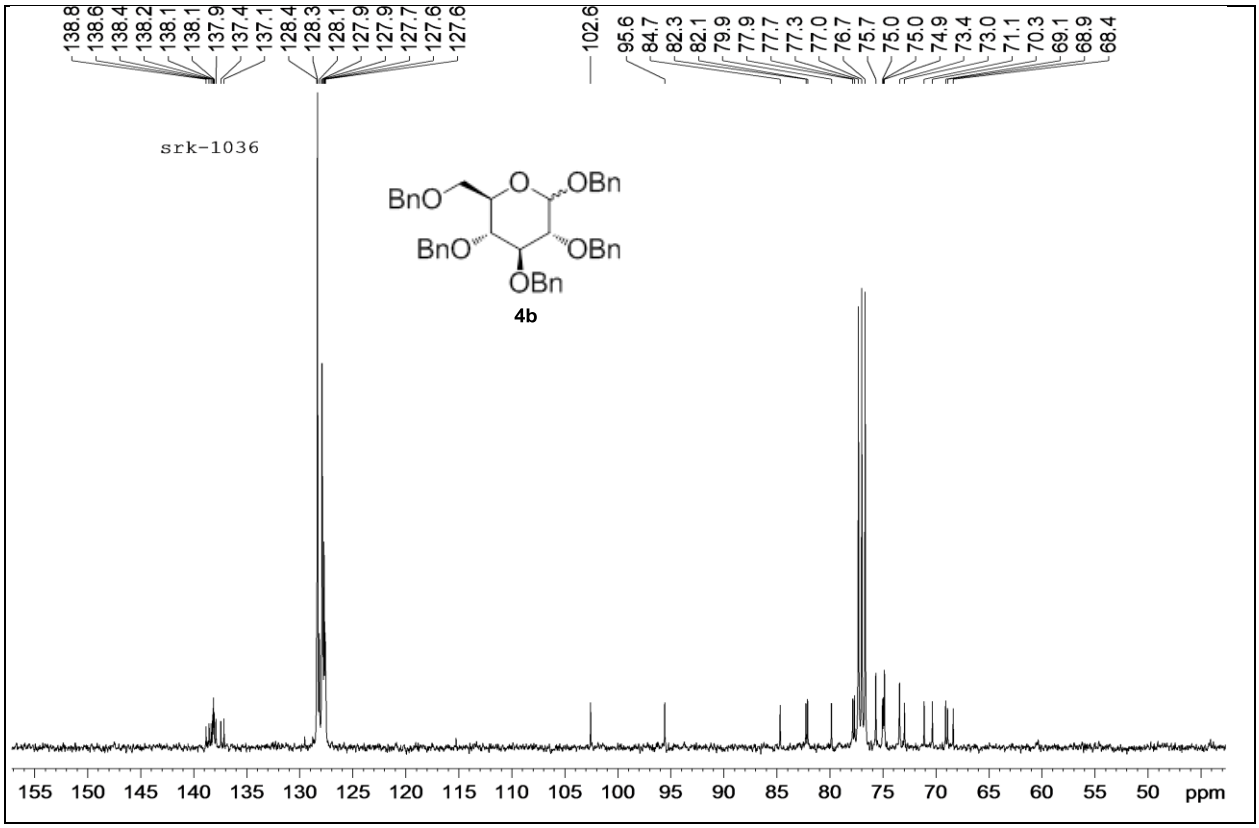
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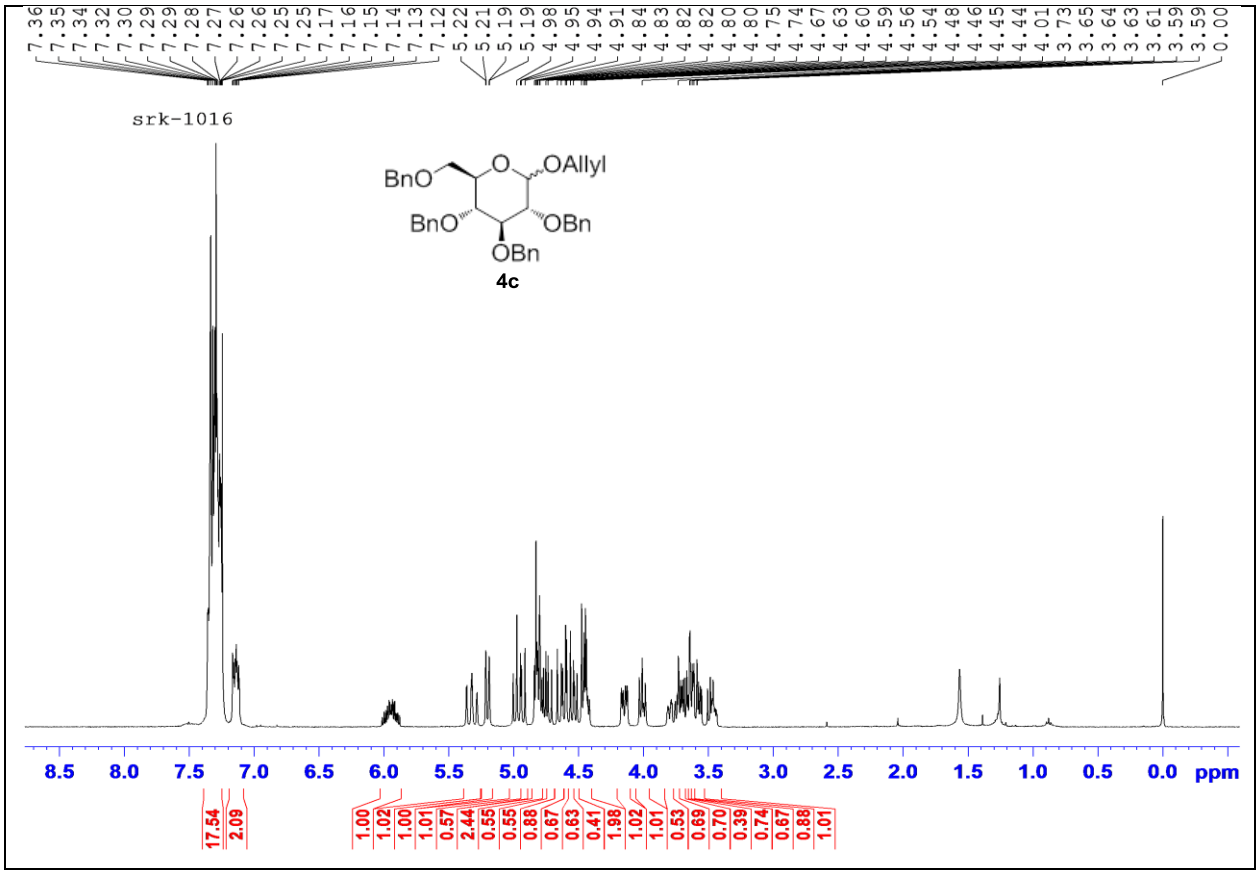
ppm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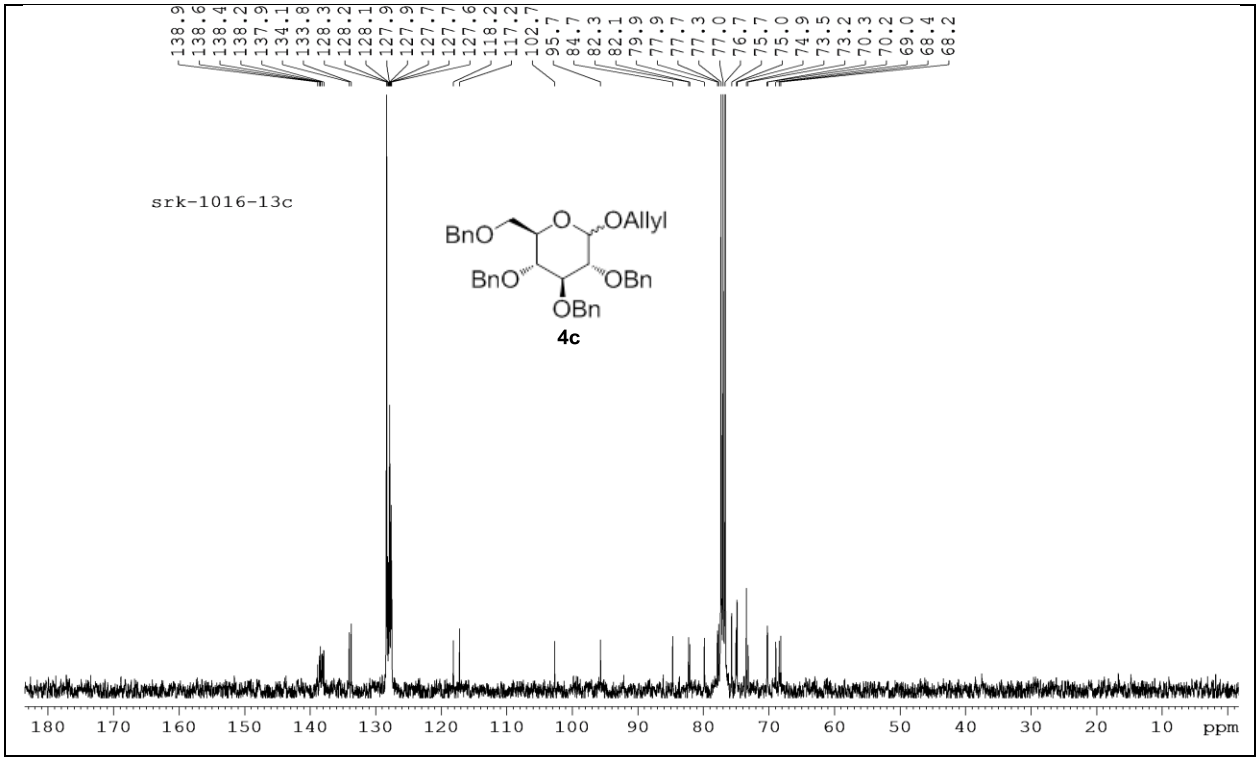
ppm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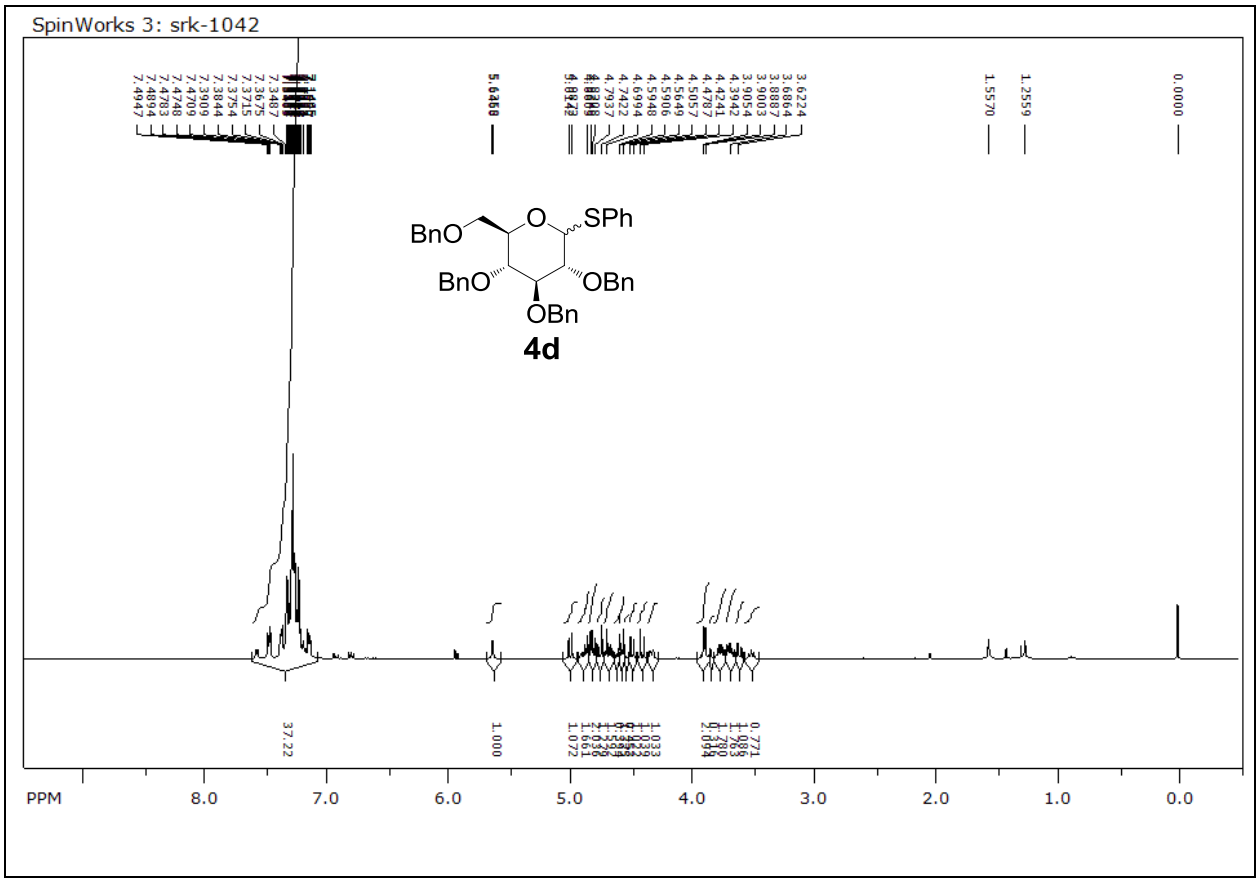
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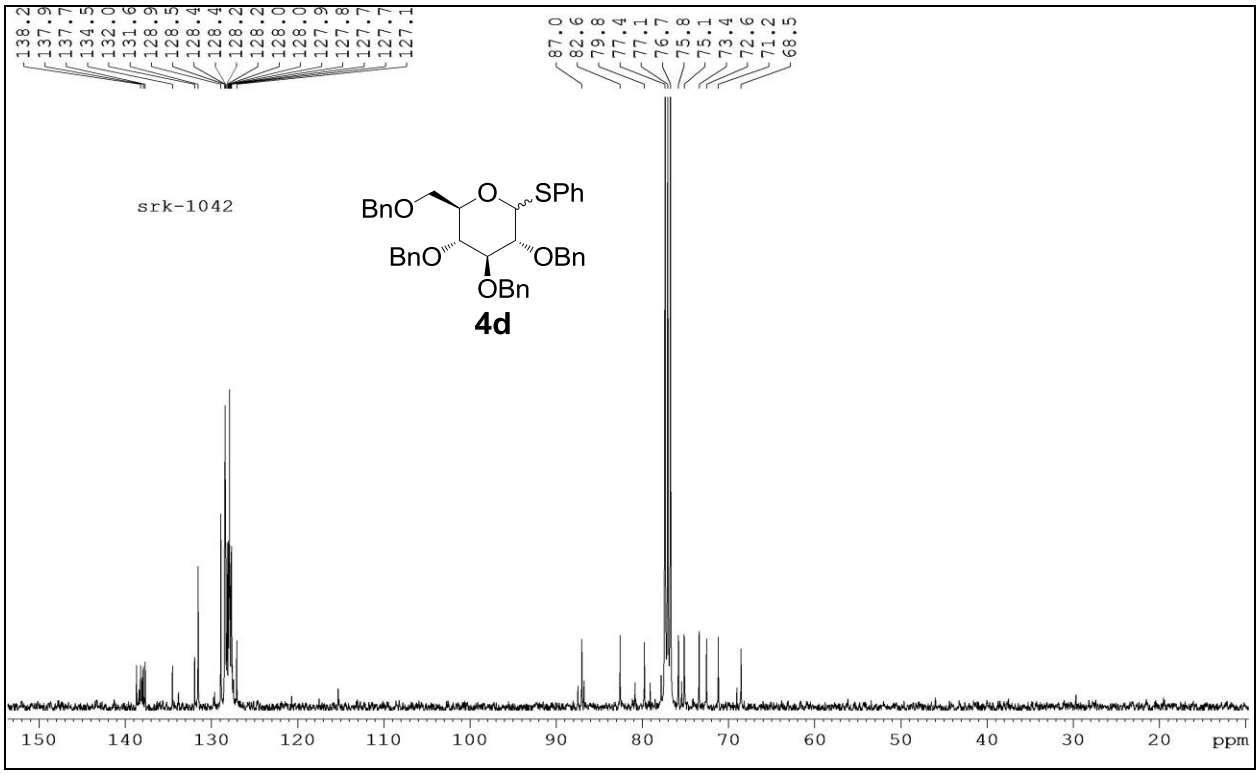
0.0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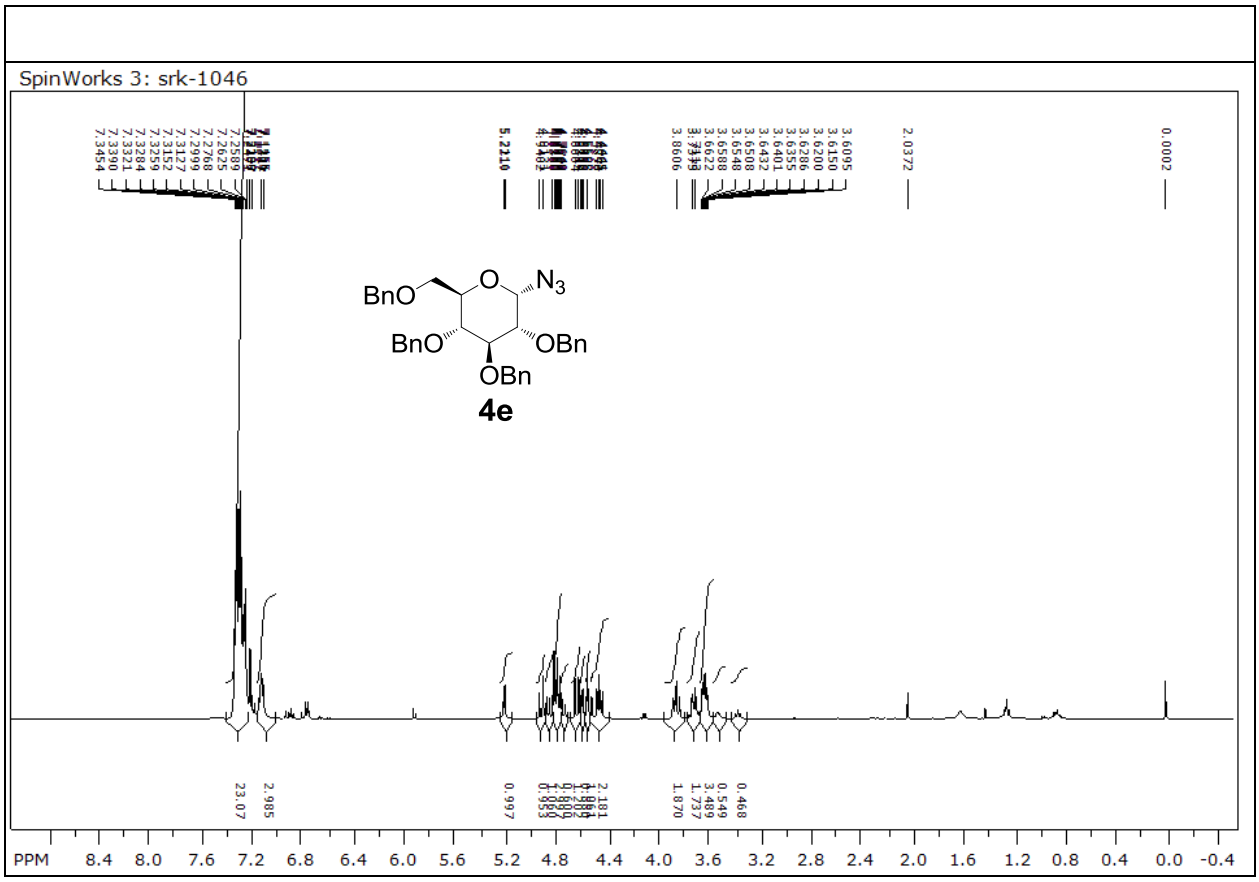
ppm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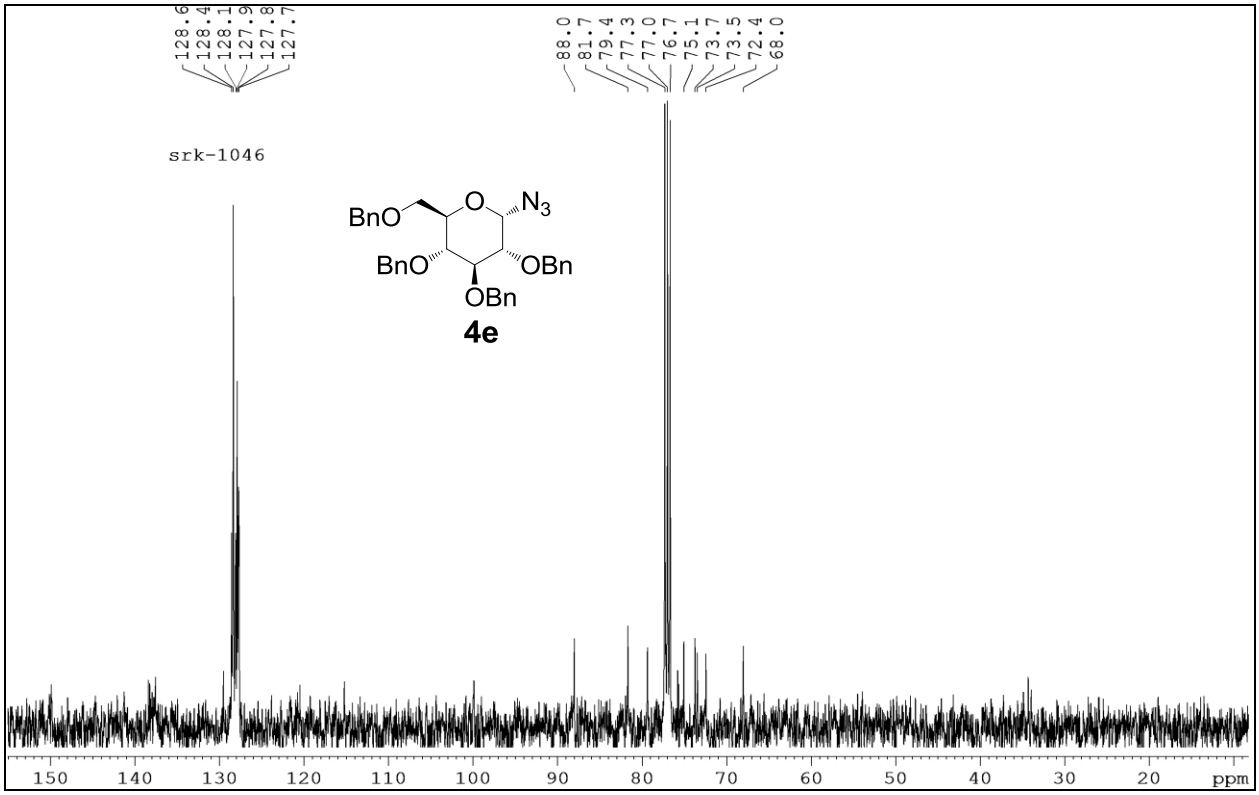
4e
PPM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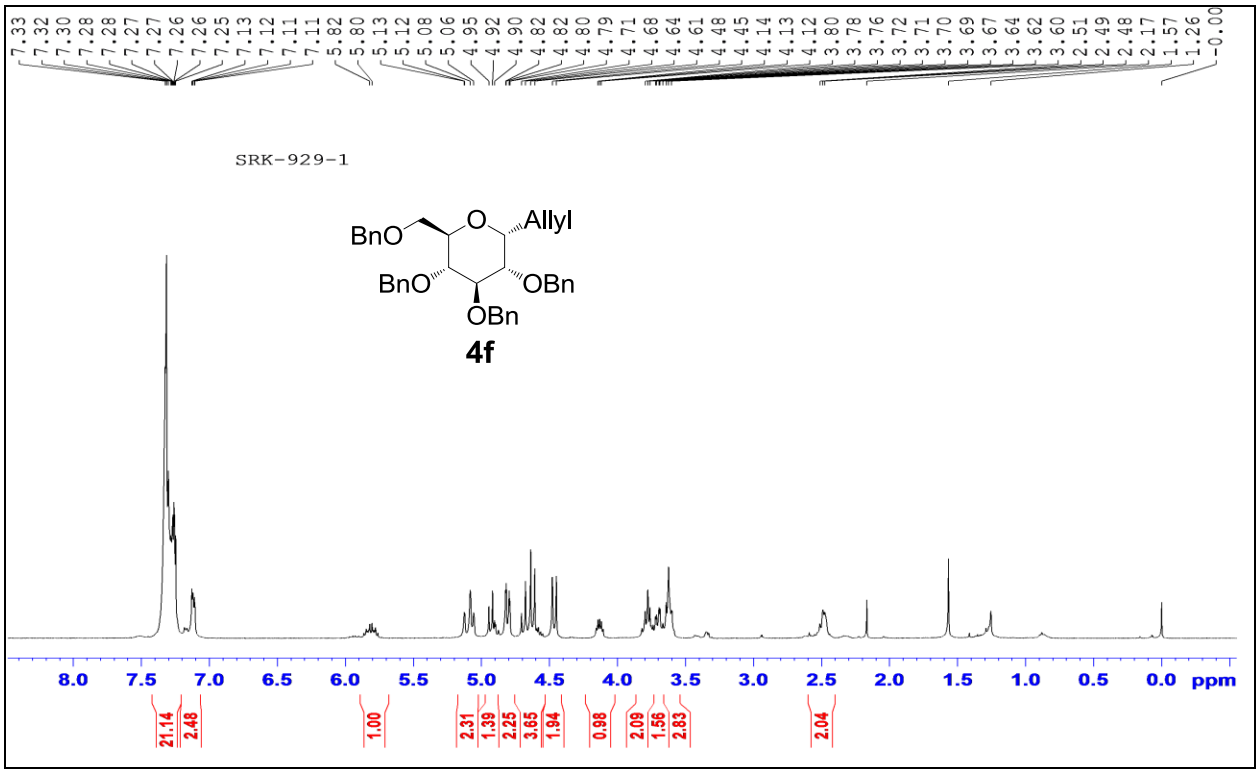
4e
ppm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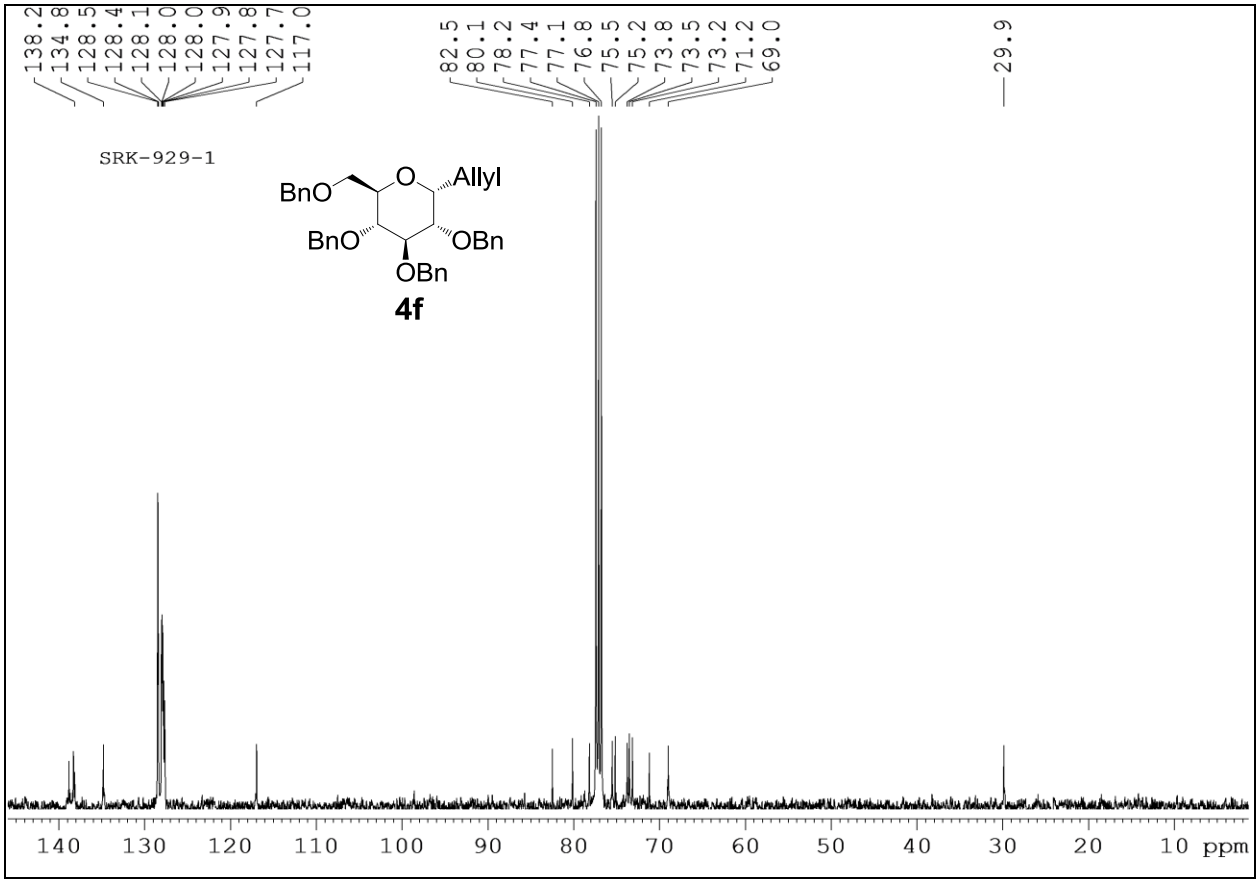
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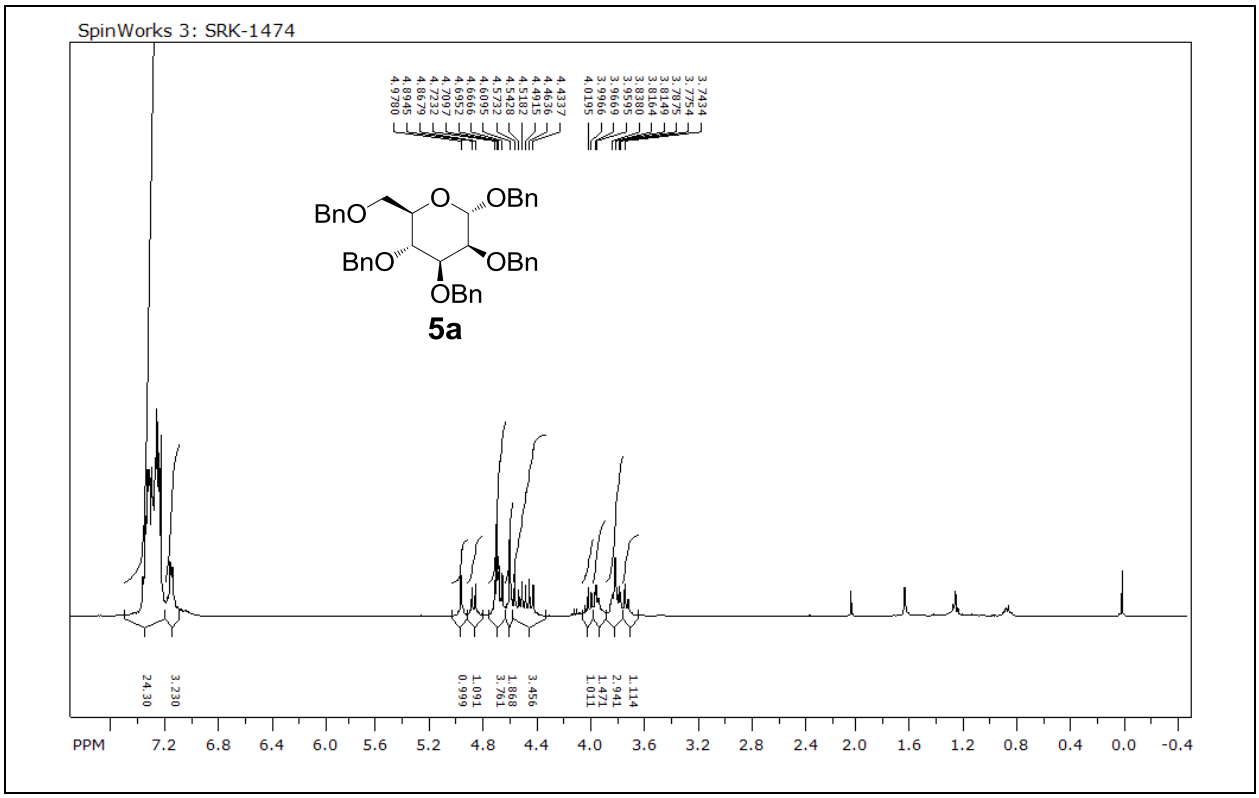
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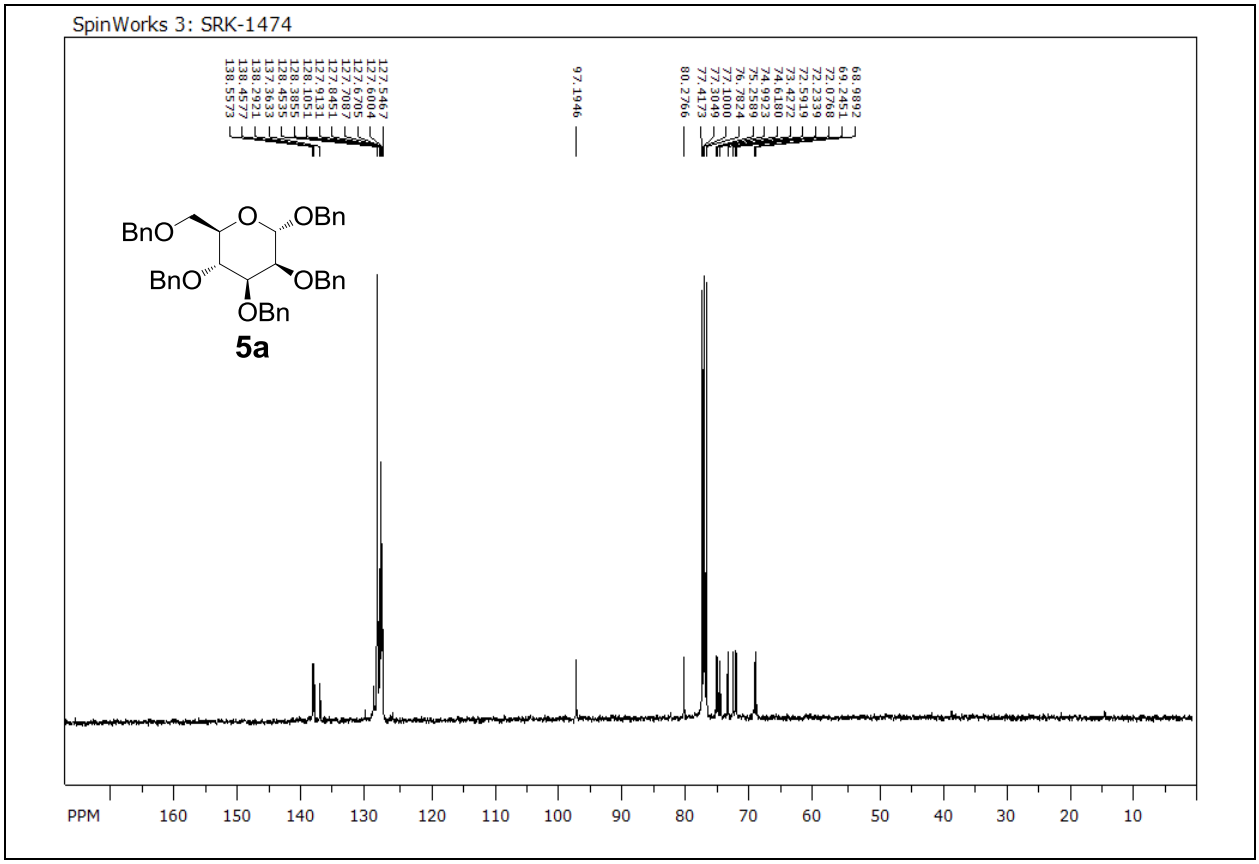
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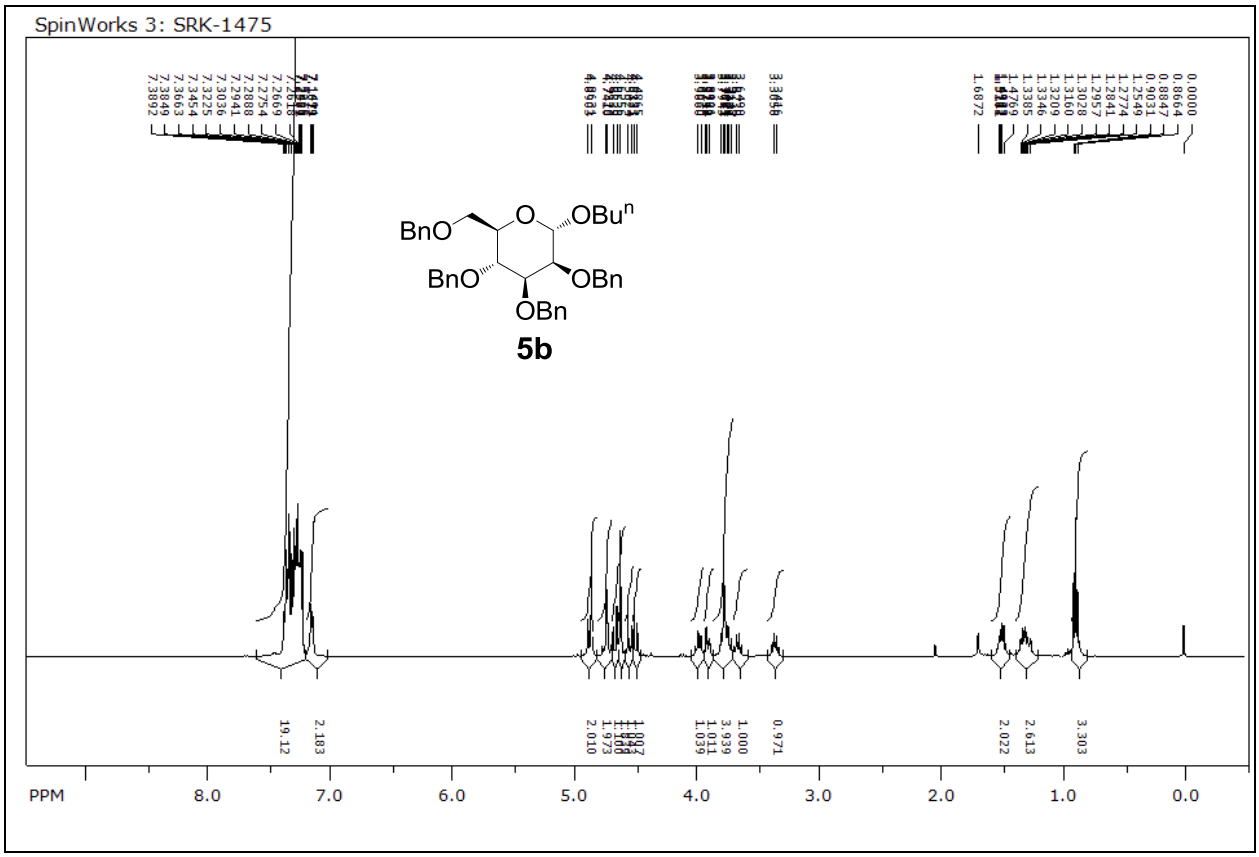
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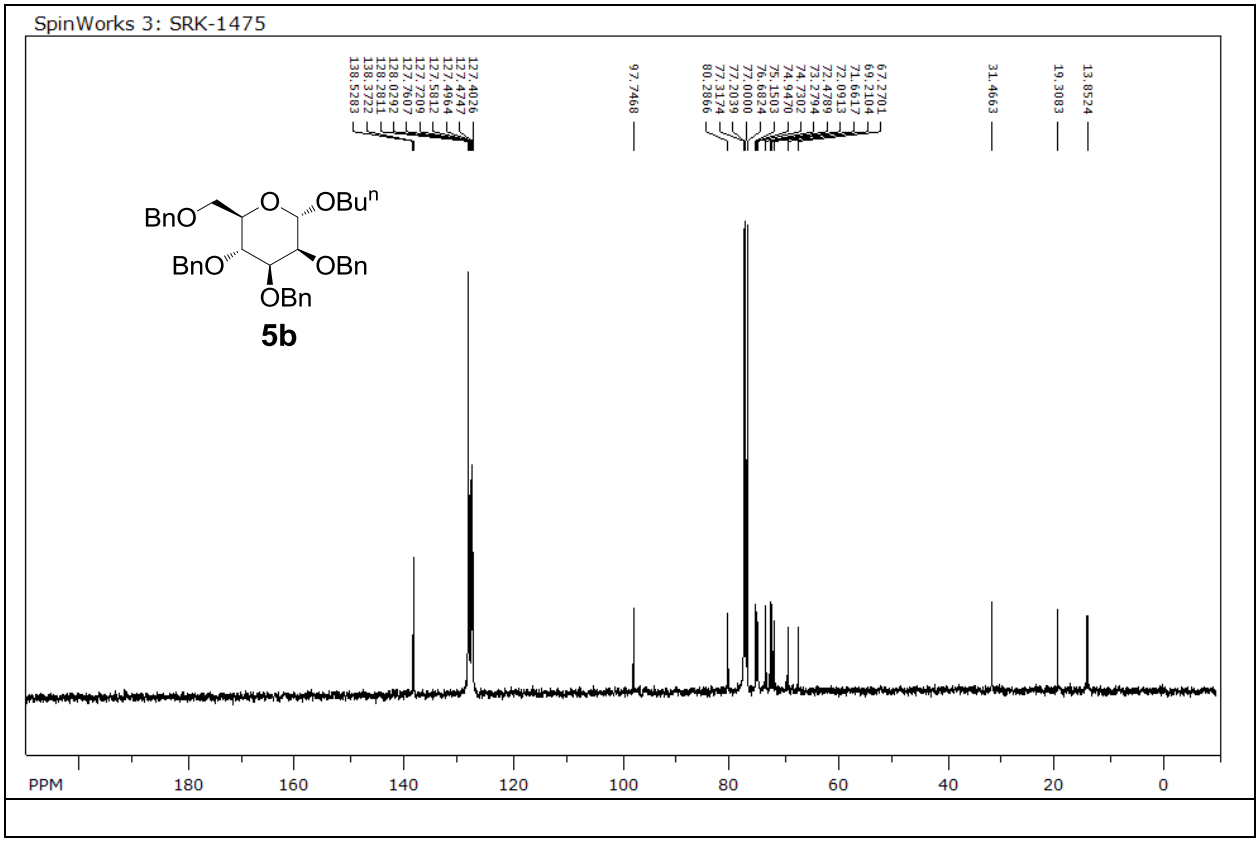
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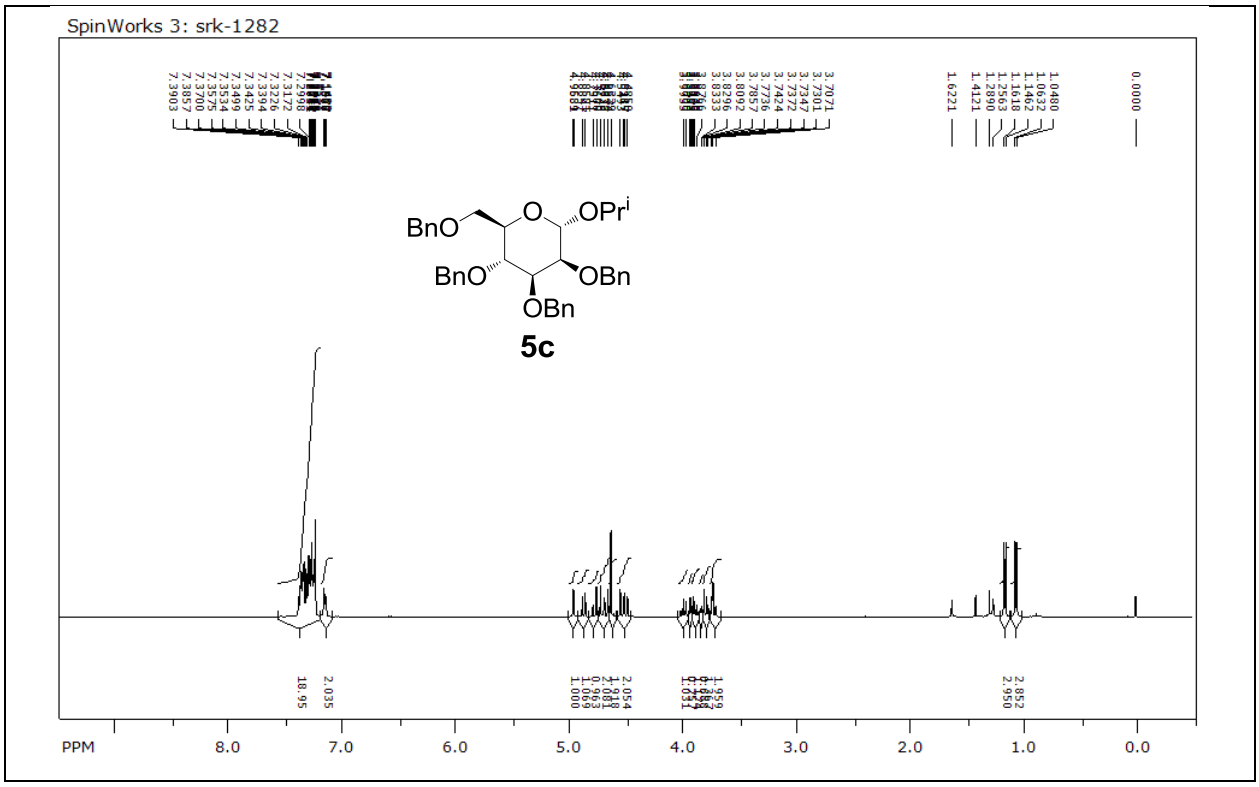
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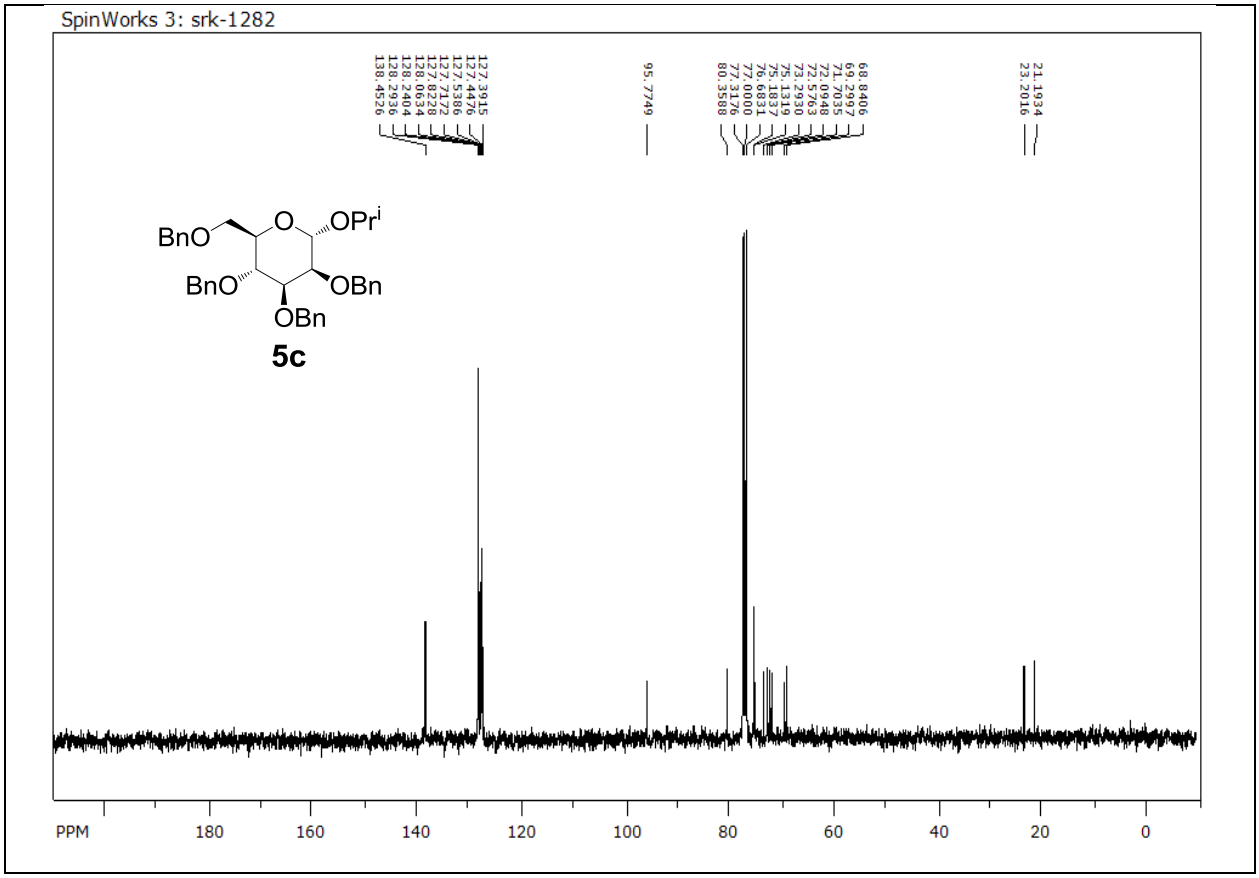
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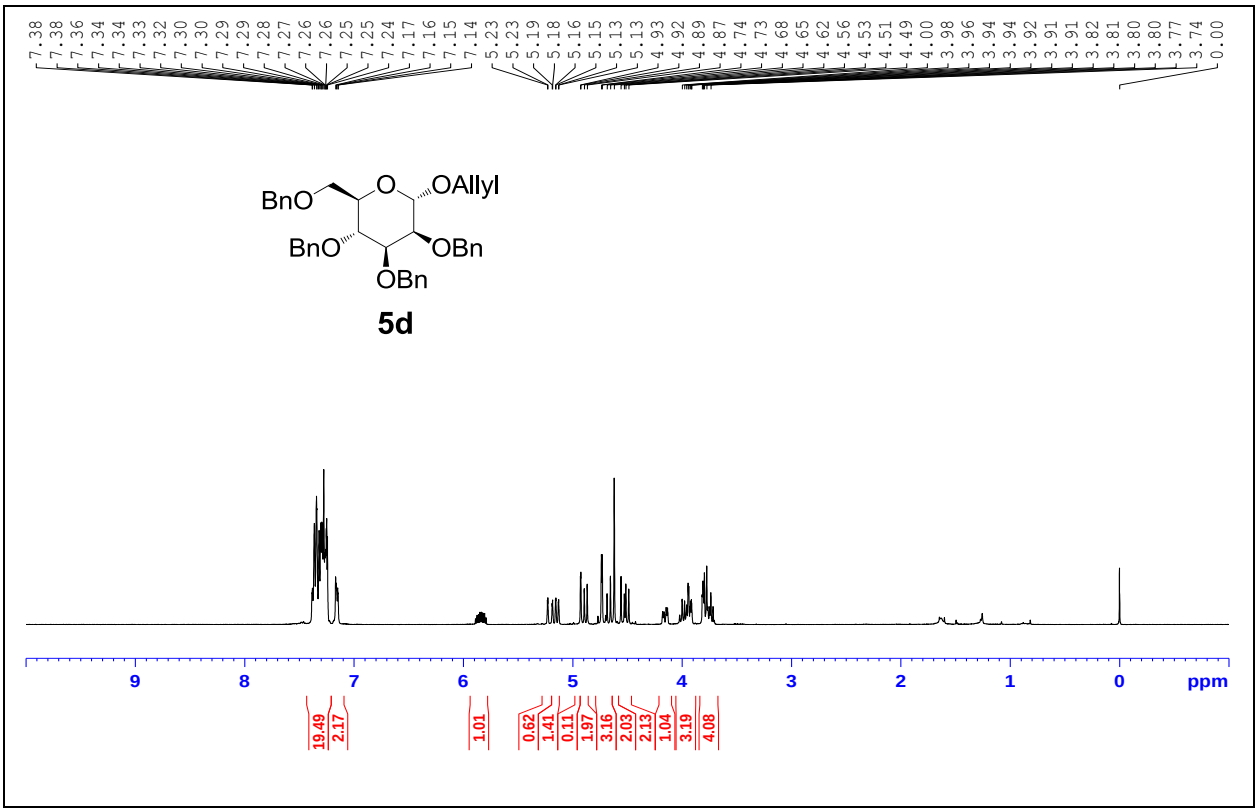
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5.23 5.23 5.19 5.18 5.16 5.15 5.13 5.13 4.93 4.92 4.89 4.87 4.74 4.73 4.68 4.65 4.62 4.56 4.53 4.51 4.49 4.00 3.98 3.96 3.94 3.94 3.92 3.91 3.91 3.82 3.81 3.80 3.80 3.77 3.74 0.00
BnO
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OAllyl
BnO
OBn
OBn
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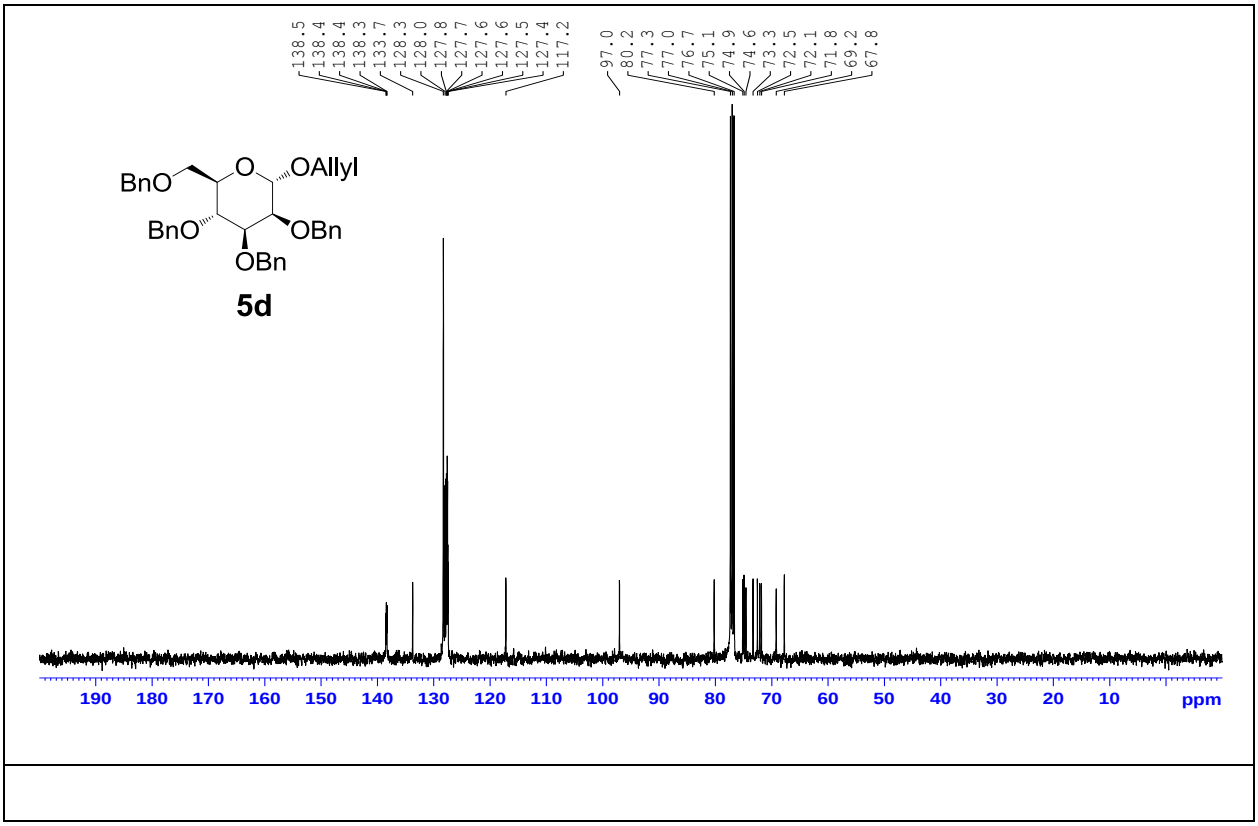
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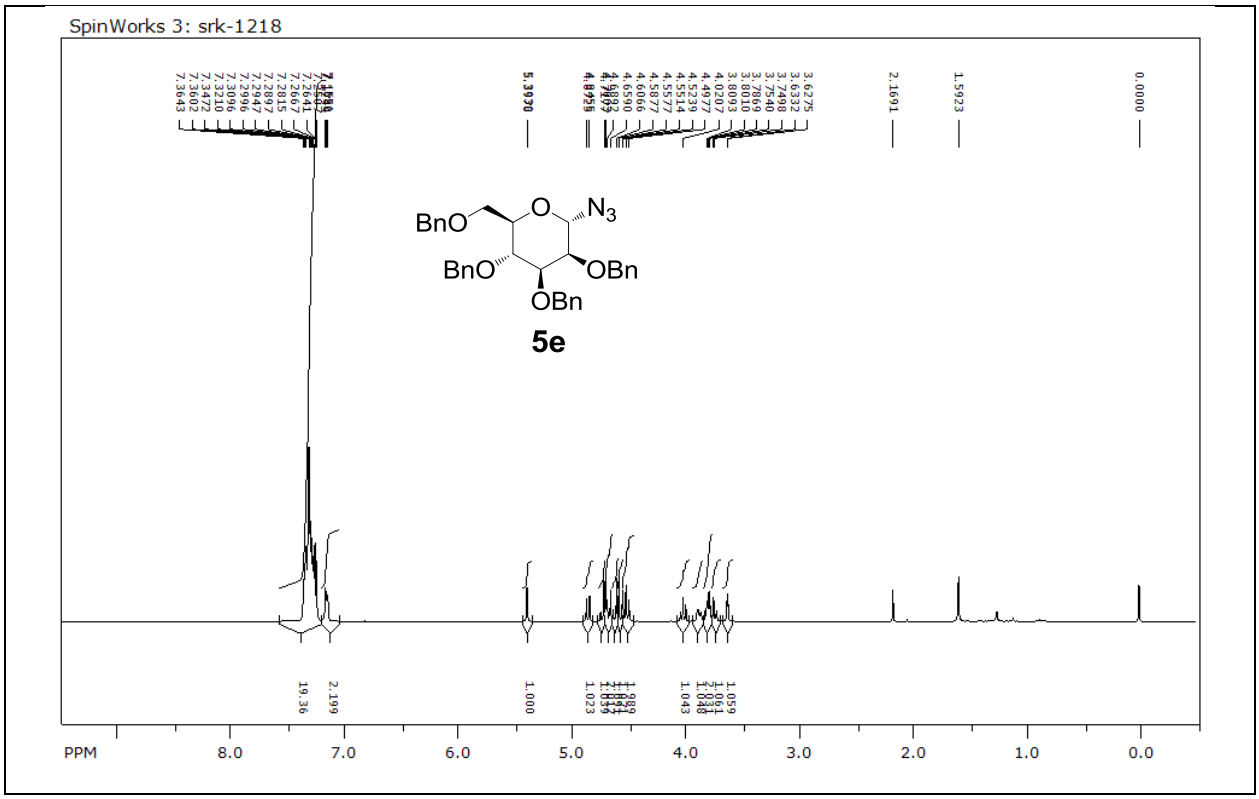
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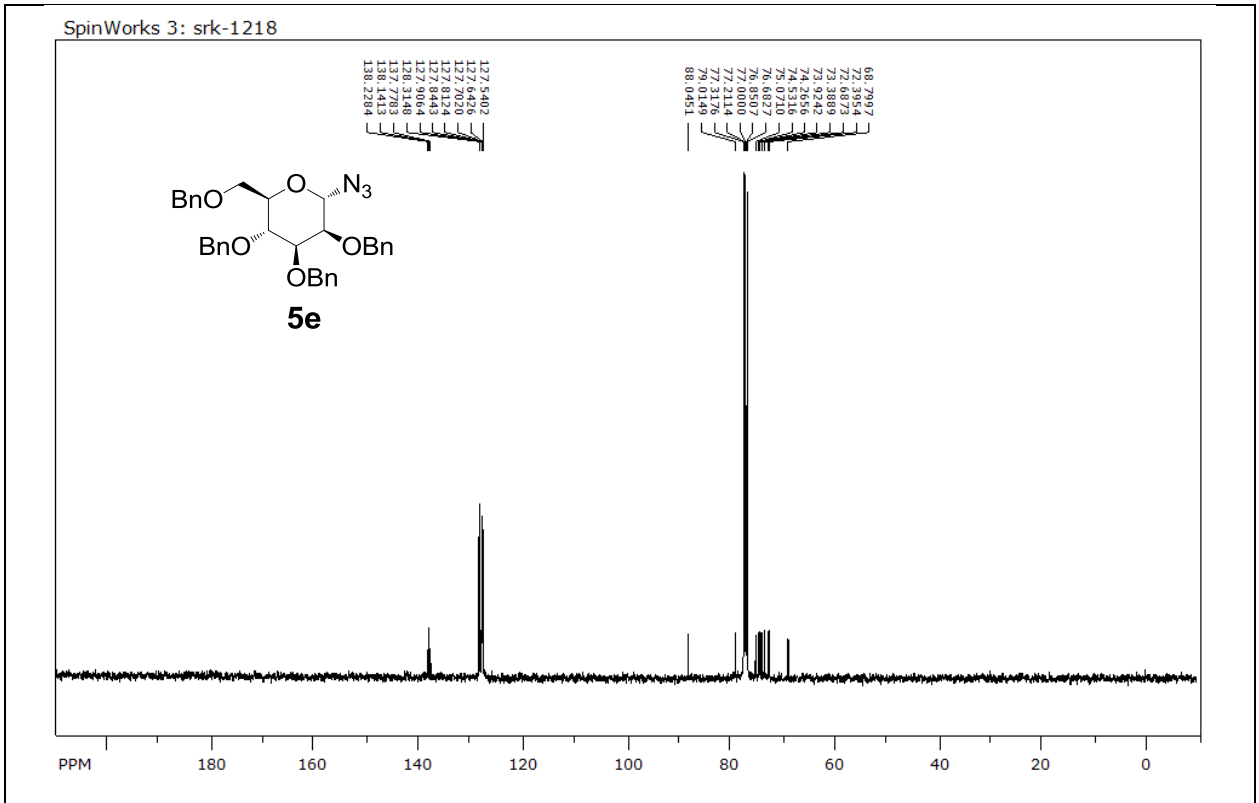
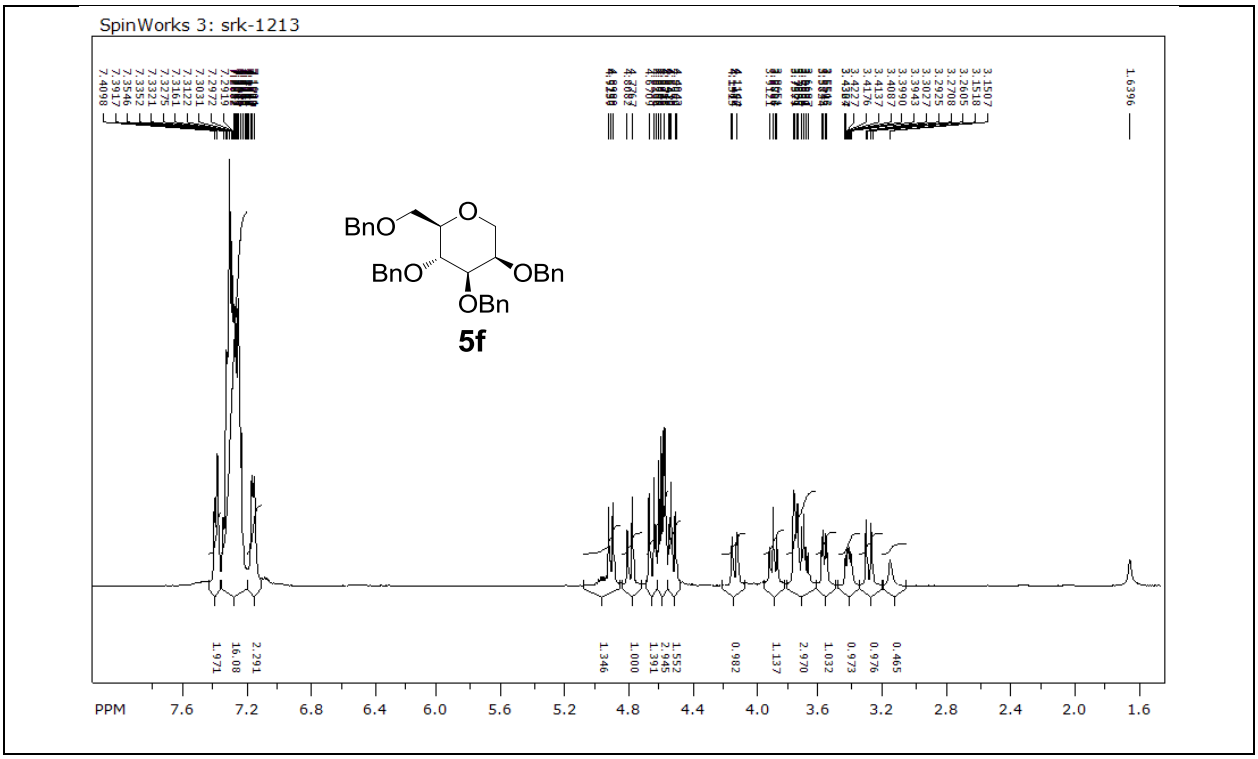
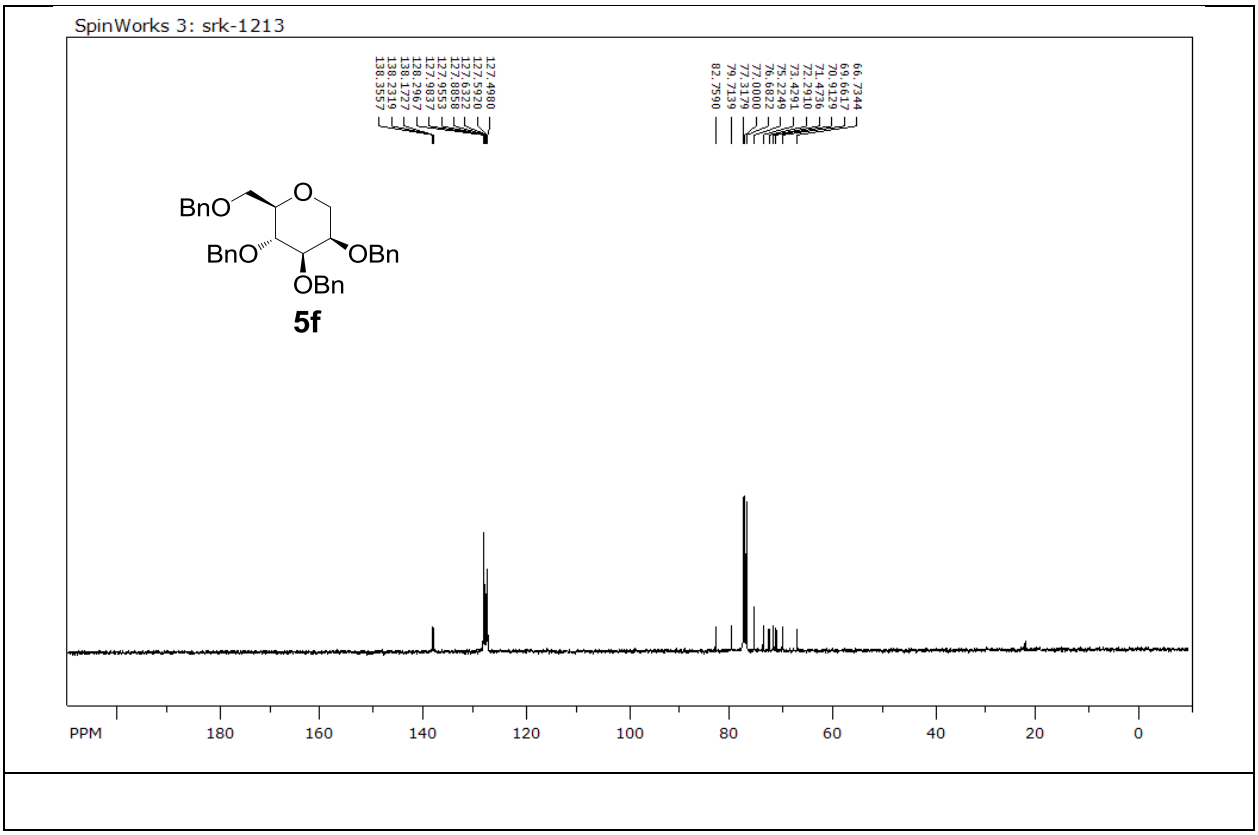
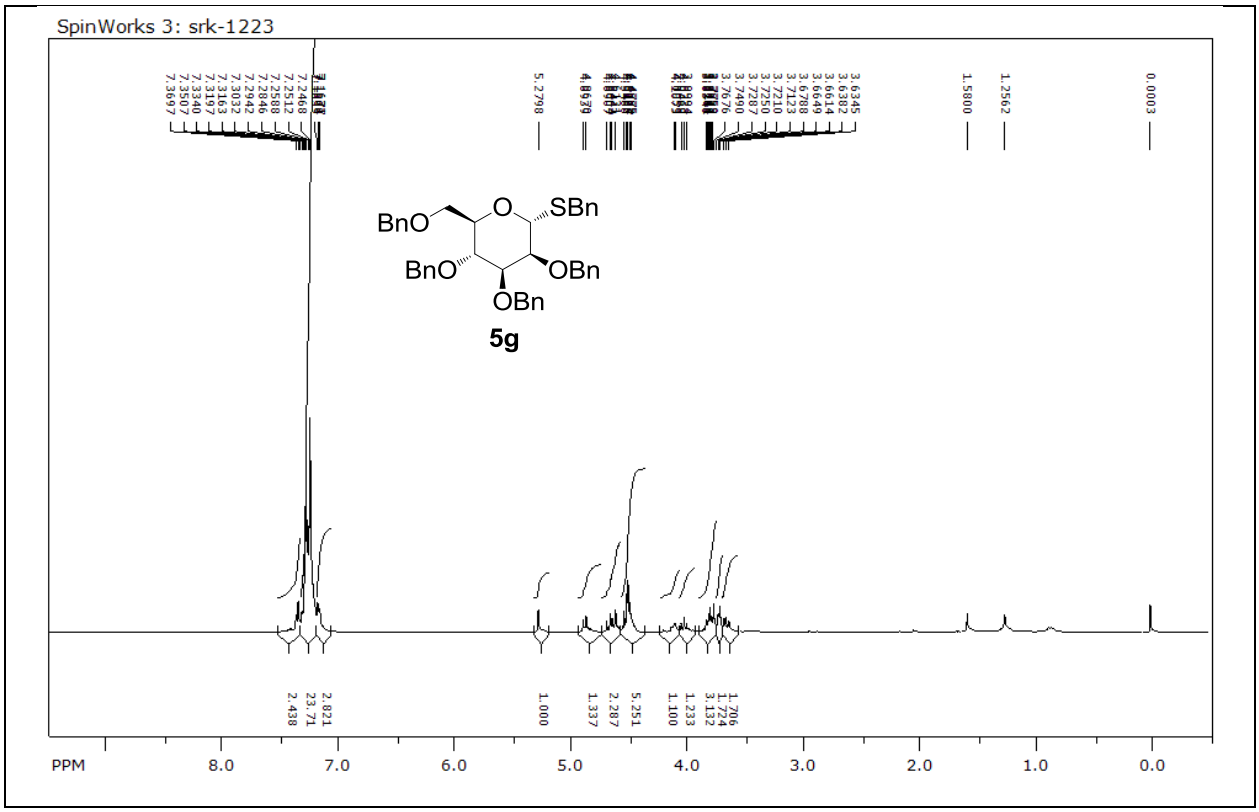
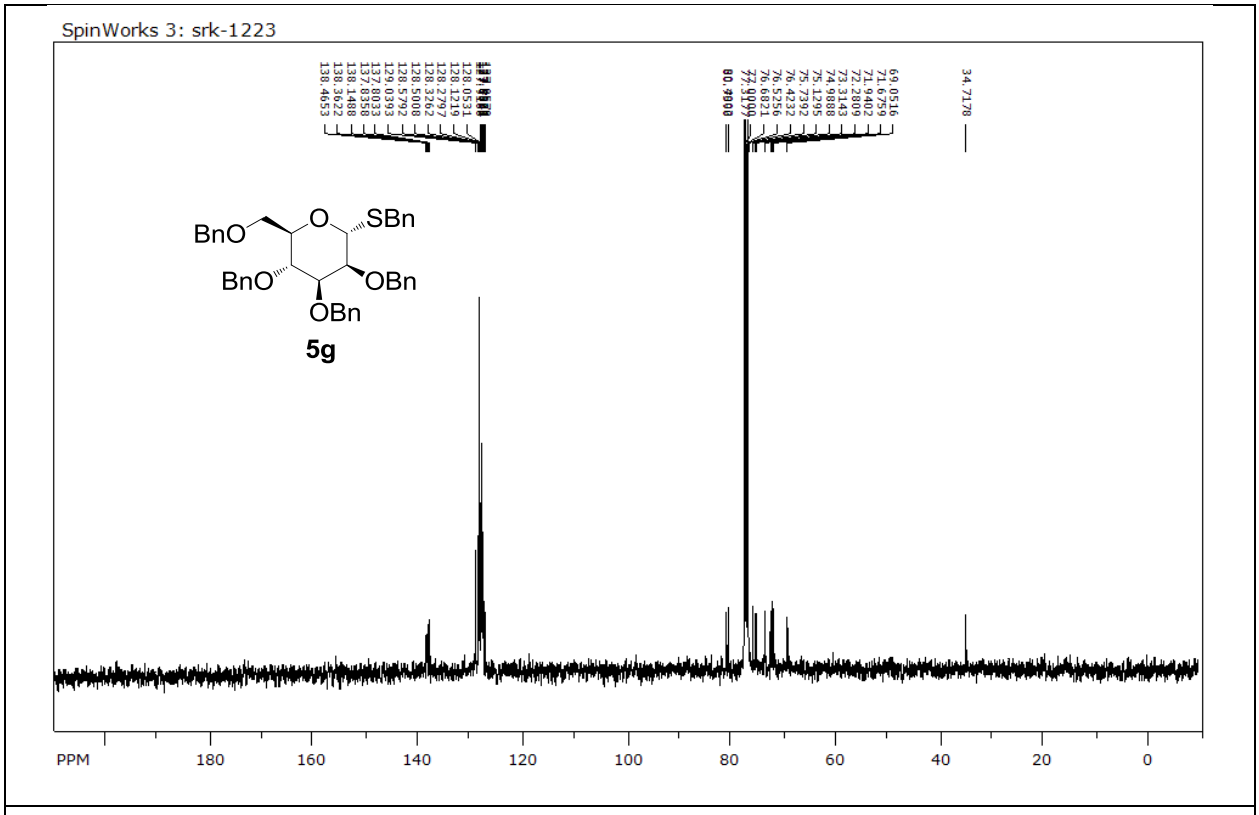
N3
BnO
OBn
OBn
5e
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

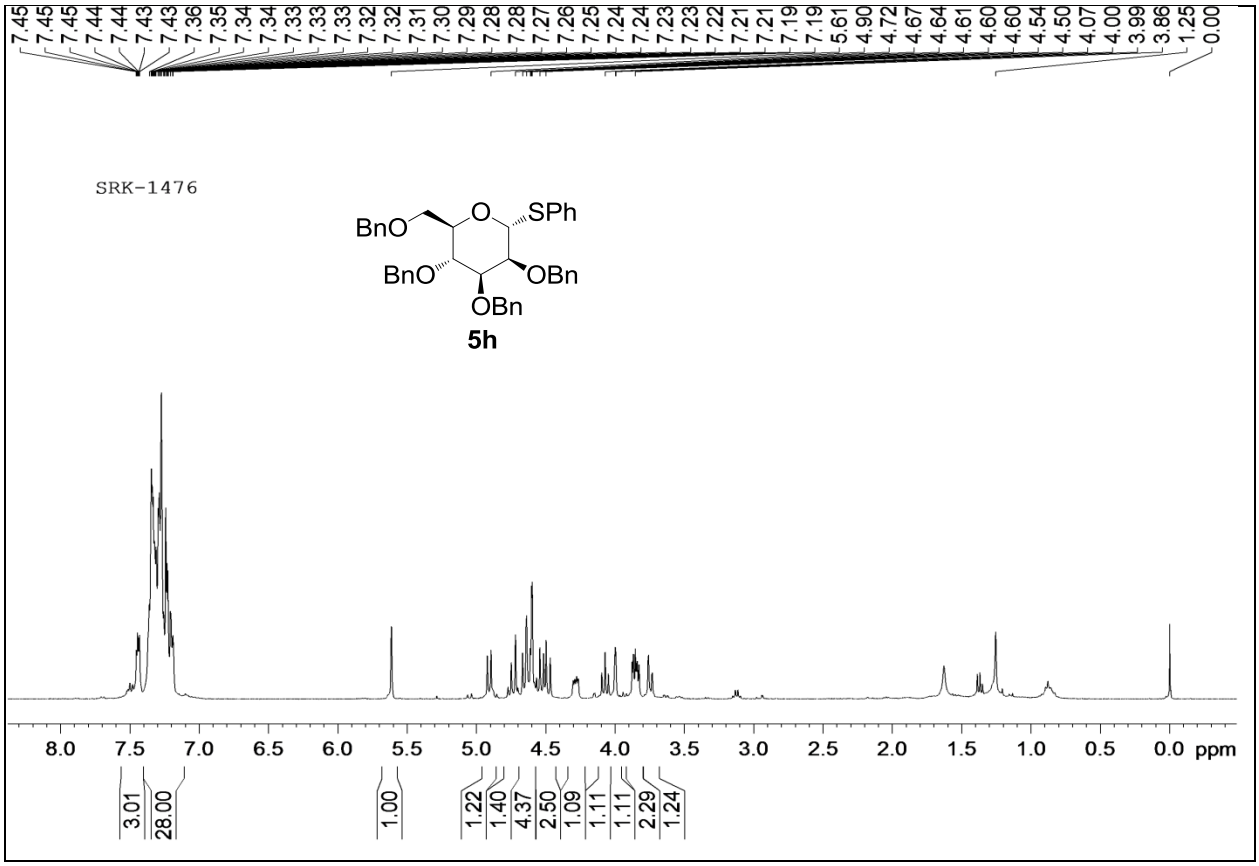

SpinWorks 3: srk-1218
BnO
O
N3
BnO
OBn
OBn
5e
PPM
180
160
140
120
100
80
60
40
20
0

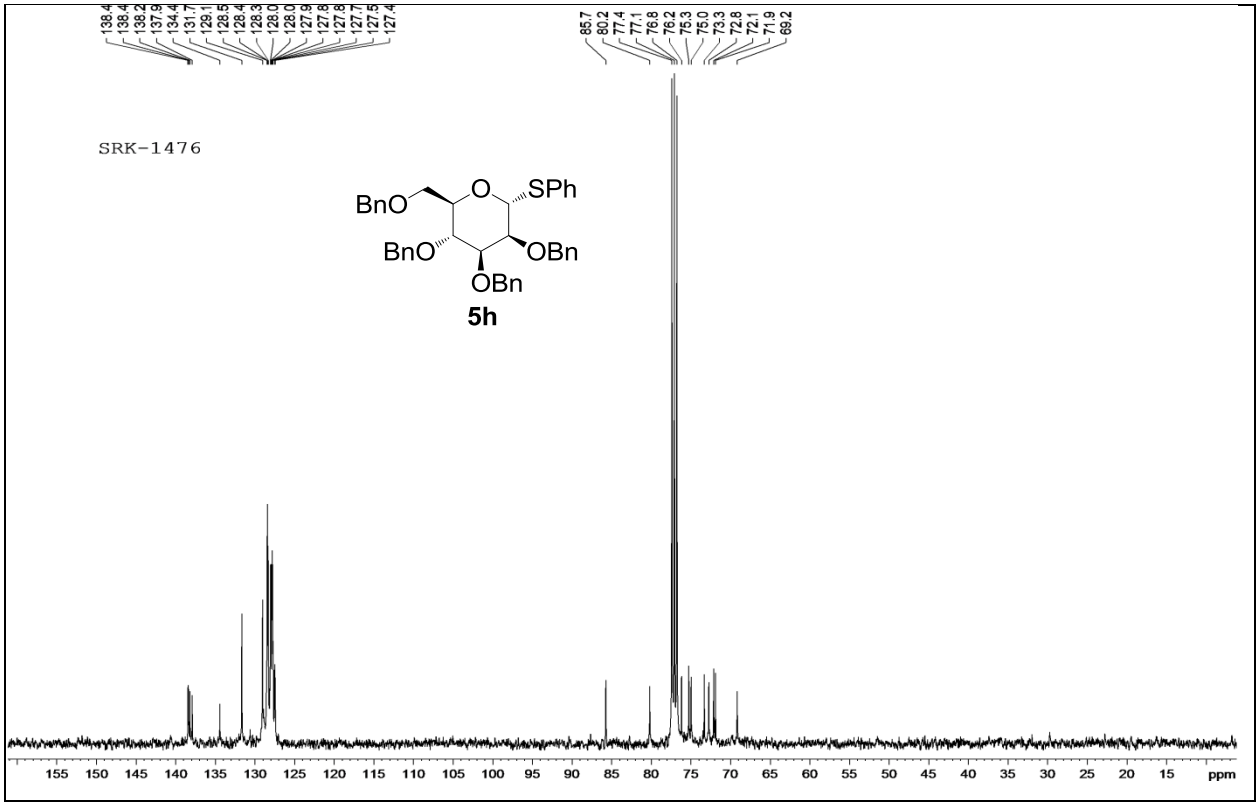

SpinWorks 3: srk-1213
BnO
BnO
OBn
OBn
5f
PPM
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6

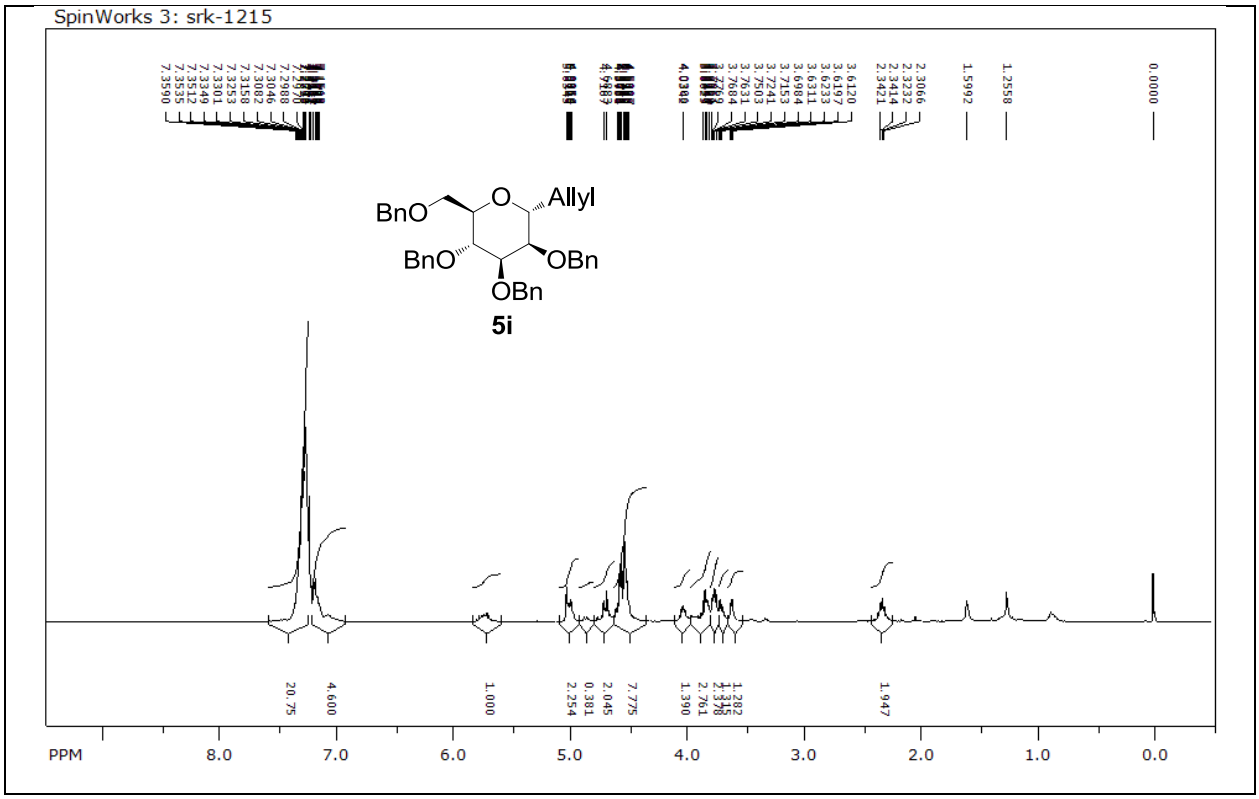

SpinWorks 3: srk-1213
BnO
BnO
OBn
OBn
5f
PPM
180
160
140
120
100
80
60
40
20
0

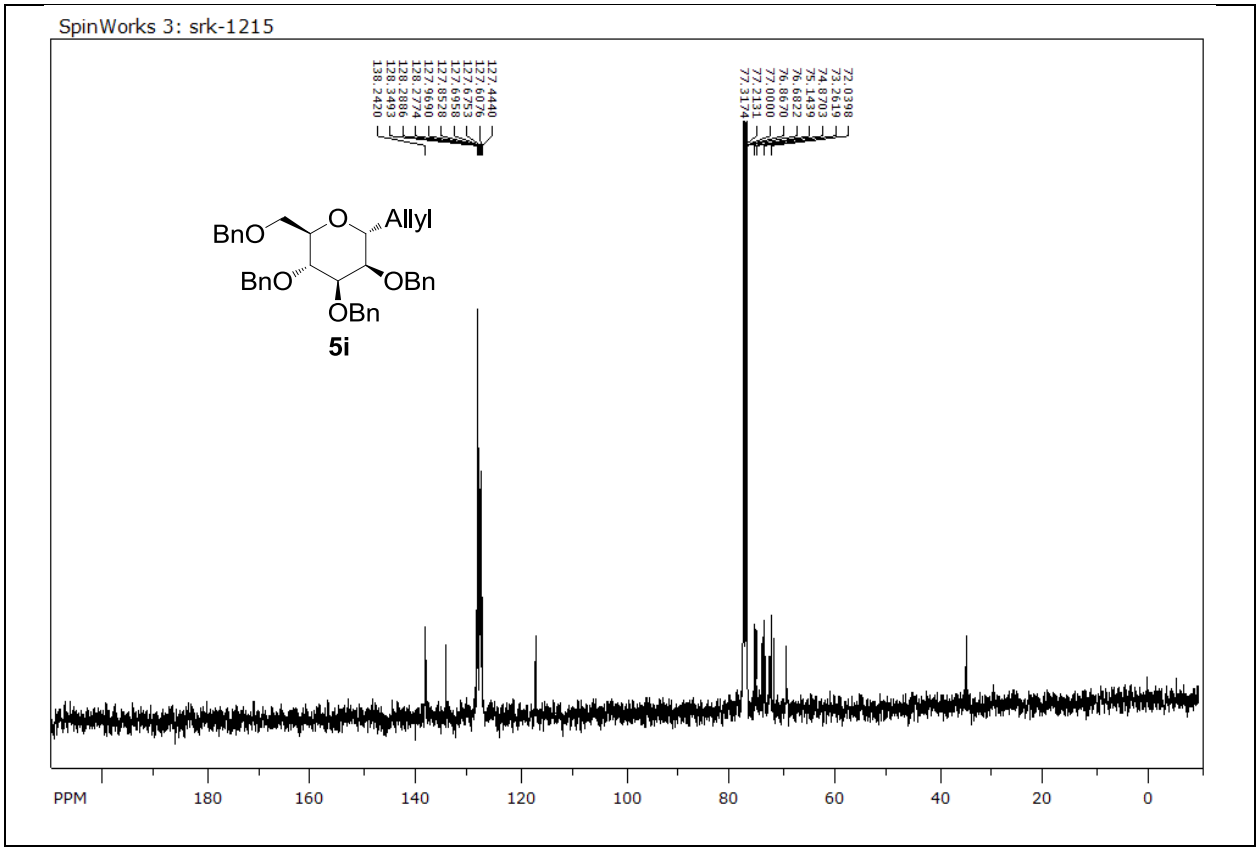

SpinWorks 3: srk-1223
BnO
O
SBn
BnO
OBn
OBn
5g
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

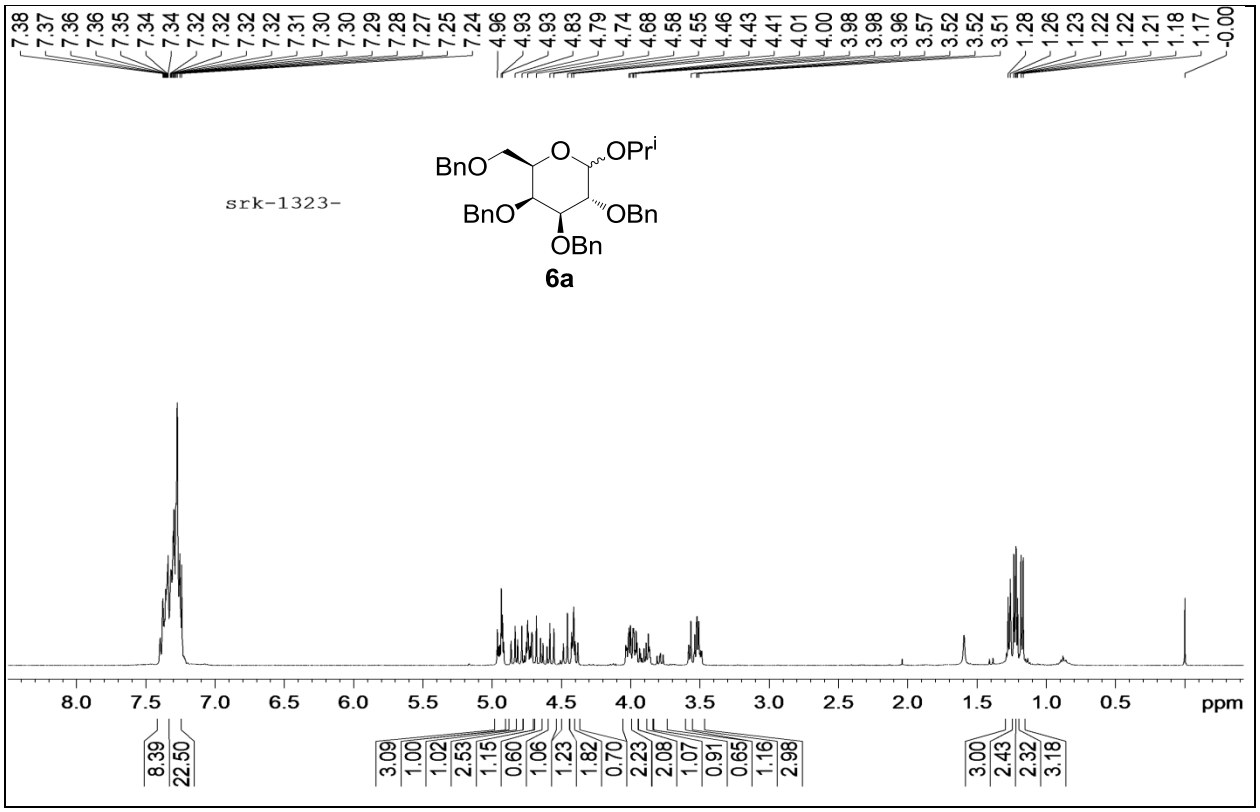

SpinWorks 3: srk-1223
BnO
O
SBn
BnO
OBn
OBn
5g
PPM
180
160
140
120
100
80
60
40
20
0

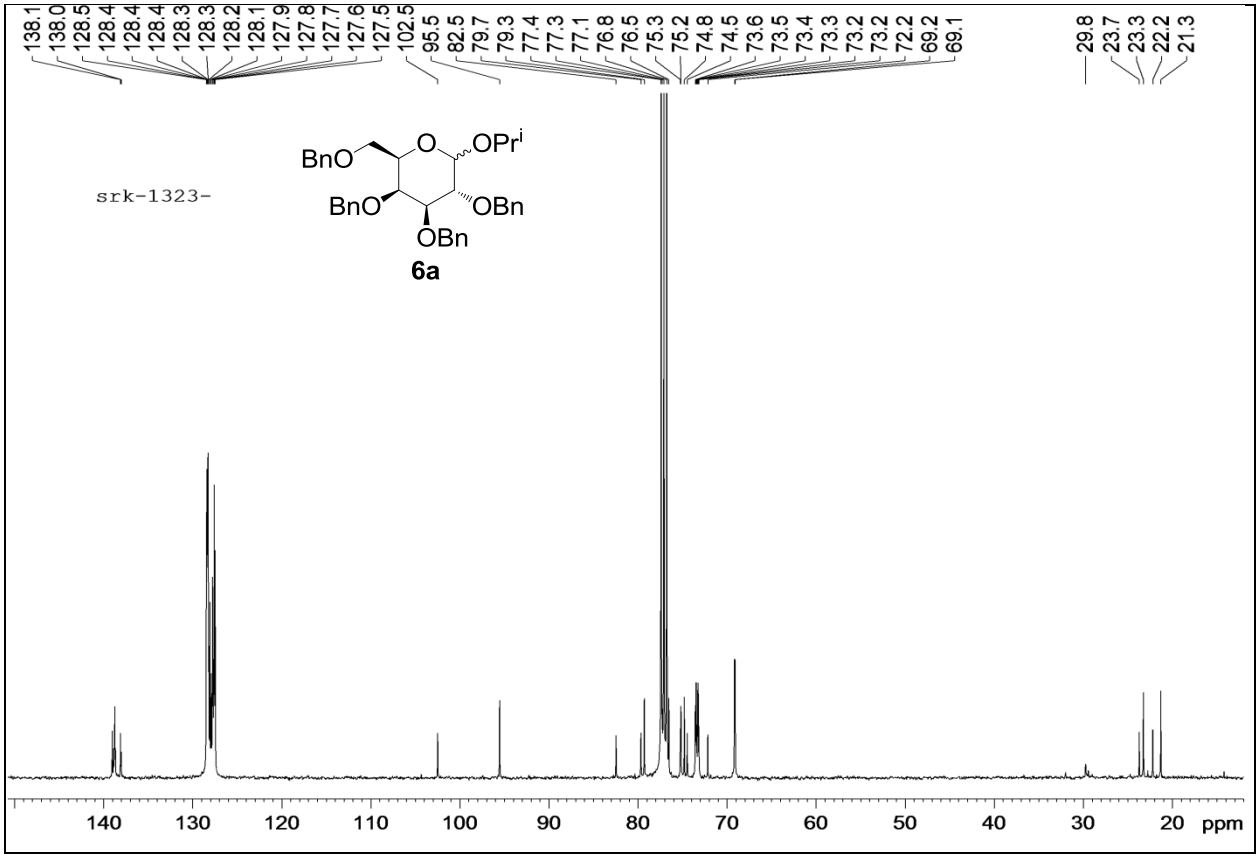

SRK-1476
BnO
O
SPh
BnO
OBn
OBn
5h
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.01
28.00
1.00
1.22
1.40
4.37
2.50
1.09
1.11
1.11
2.29
1.24

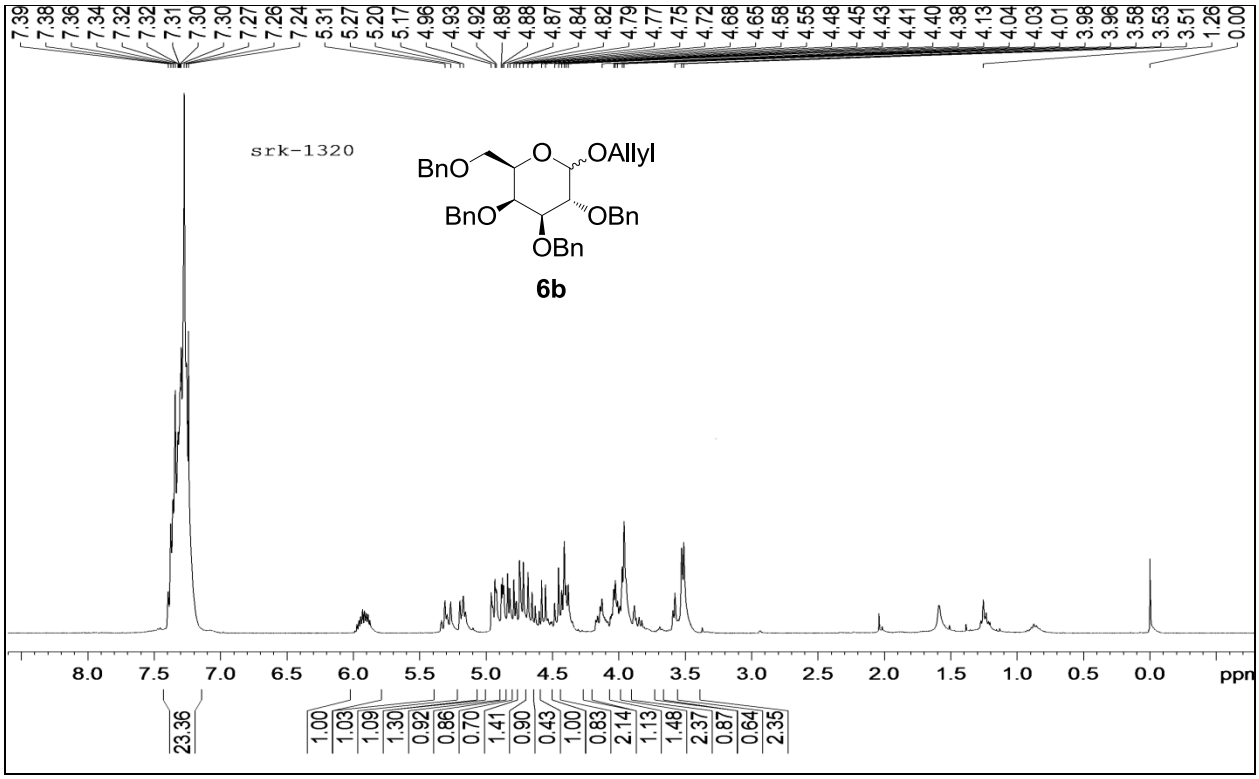

SRK-1476
BnO
O
SPh
BnO
OBn
OBn
5h
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 ppm

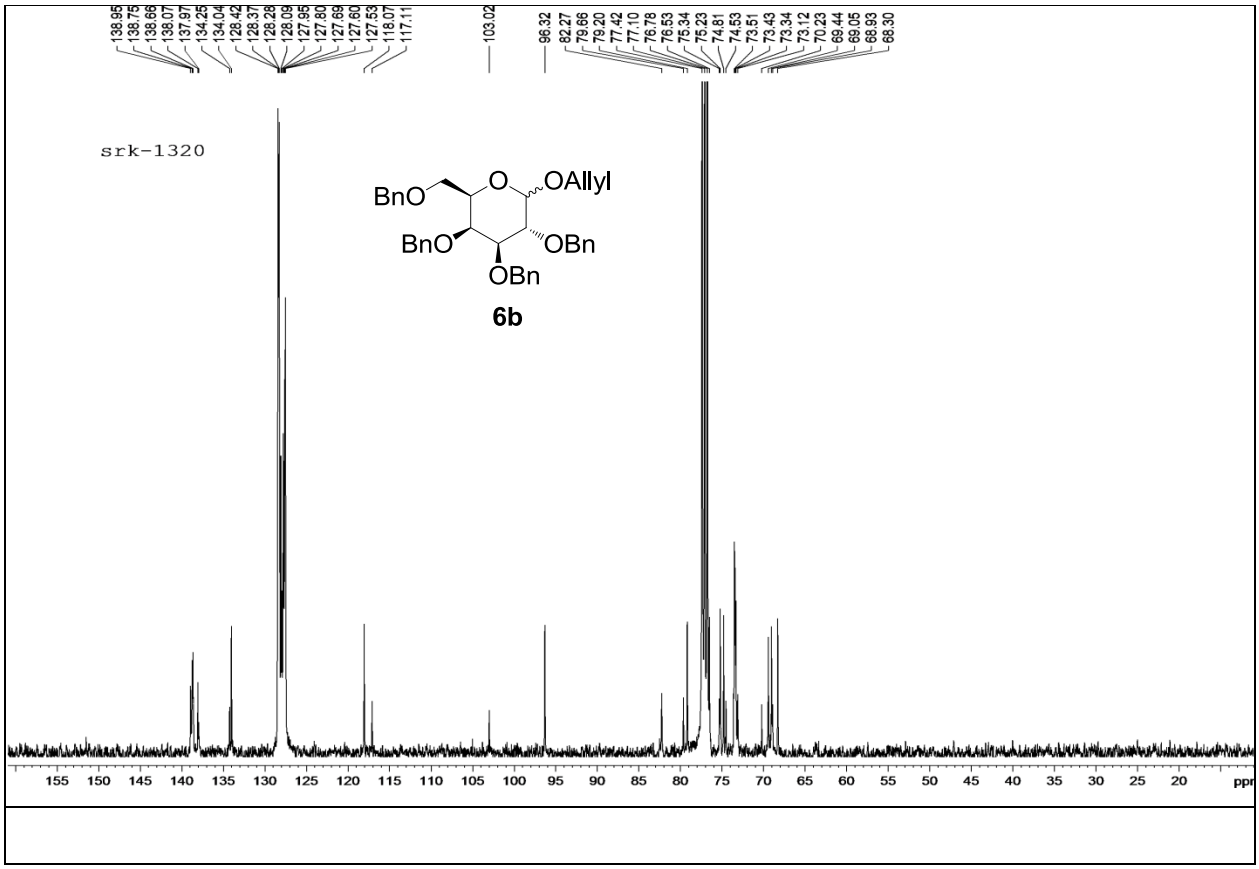

SpinWorks 3: srk-1215
BnO
O
Allyl
BnO
OBn
OBn
5i
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

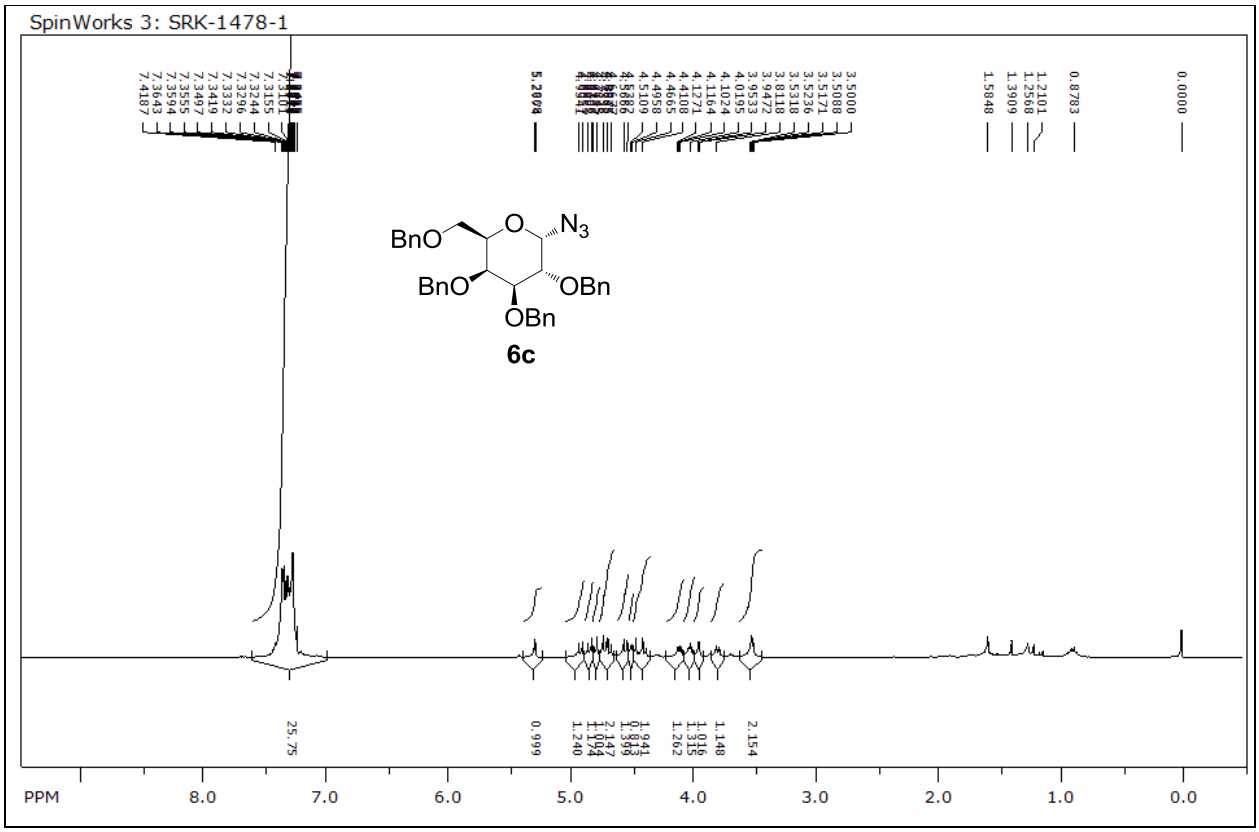

SpinWorks 3: srk-1215
BnO
O
Allyl
BnO
OBn
OBn
5i
PPM
180
160
140
120
100
80
60
40
20
0

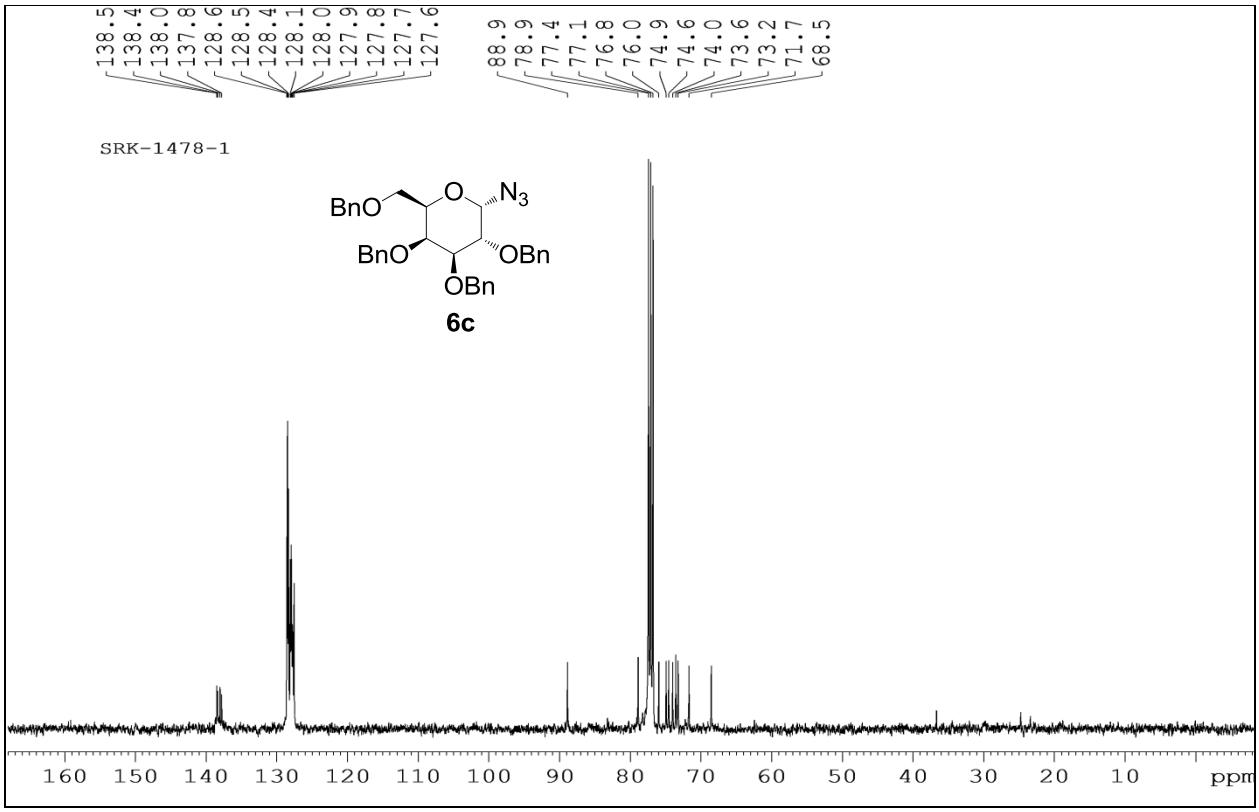

srk-1323-
BnO
BnO
OBn
OBn
OPr^i
6a
ppm

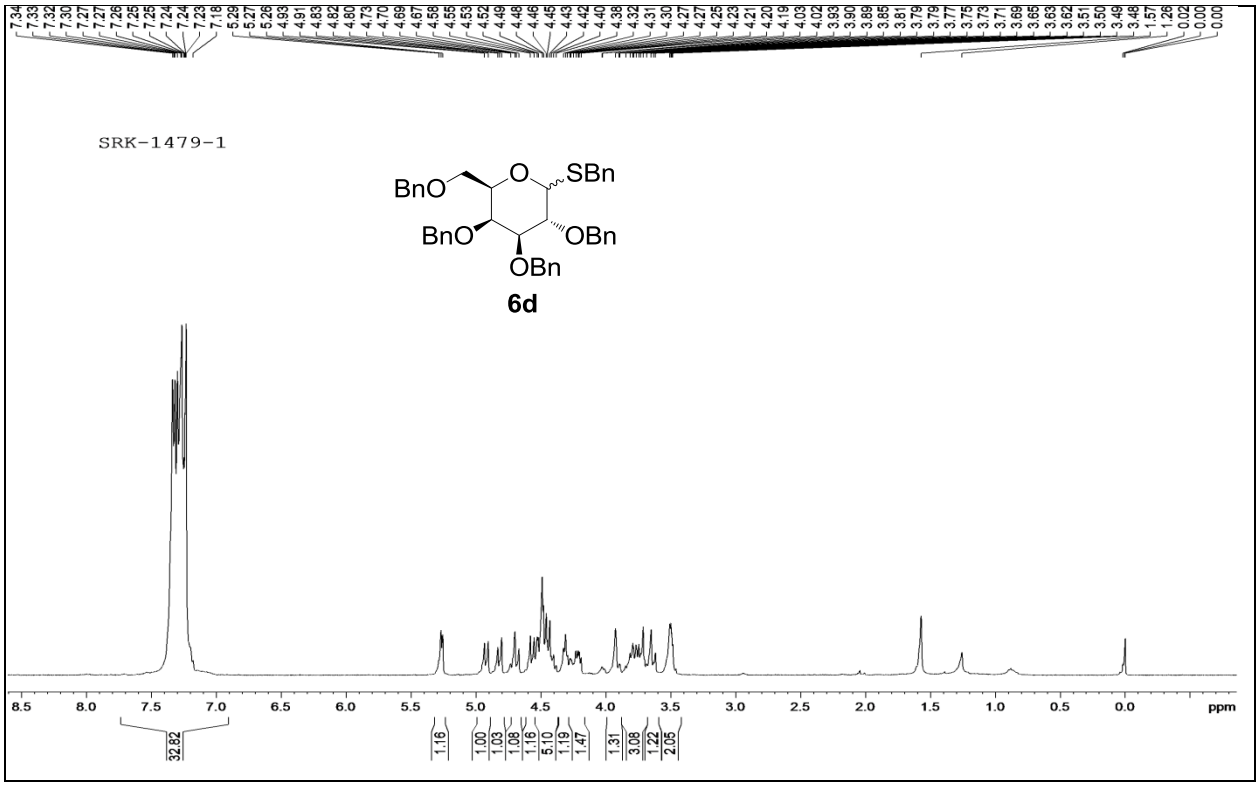

srk-1323-
BnO
BnO
OBn
OBn
OPr^i
6a
ppm

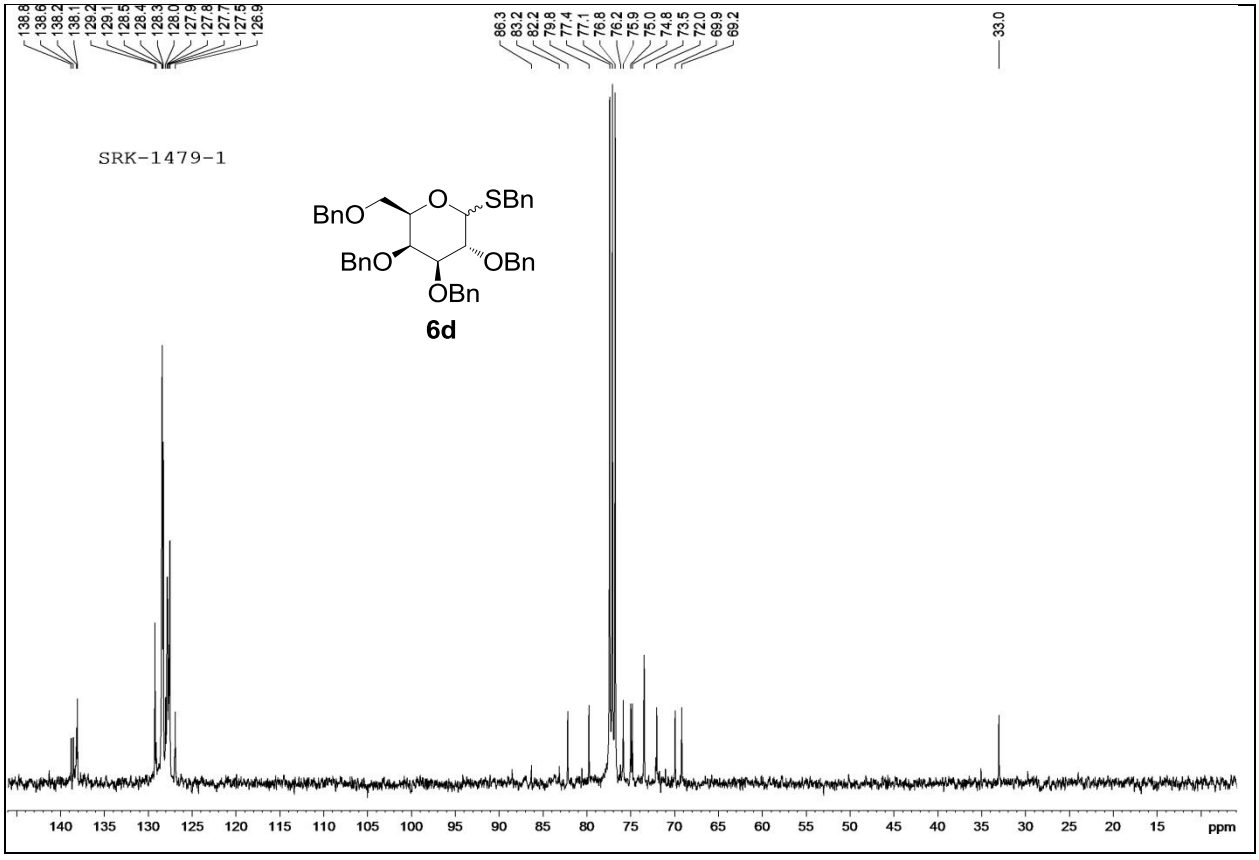

srk-1320
BnO
BnO
OBn
OBn
OAllyl
6b


srk-1320
BnO
BnO
OBn
OBn
OAllyl
6b


SpinWorks 3: SRK-1478-1
BnO
O
N3
BnO
OBn
OBn
6c
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


SRK-1478-1
BnO
O
N3
BnO
OBn
OBn
6c
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


SRK-1479-1
BnO
O
SBn
BnO
OBn
OBn
6d
ppm


SRK-1479-1
BnO
O
SBn
BnO
OBn
OBn
6d
ppm