

## EFFICIENT SYNTHESIS OF *O*-LINKED GLYCOCONJUGATES OF AMINO ACIDS FROM CARBOHYDRATE-DERIVED DONOR-ACCEPTOR-CYCLOPROPANES

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## General experimental details

All reactions were carried out in oven-dried apparatus using dry solvents under anhydrous conditions, unless otherwise noted. Reaction mixtures were stirred magnetically. All solvents for routine isolation of products and chromatography were reagent grade and redistilled. All the solvents used for the reaction were dried following the prescribed method over 4 Å molecular sieves or other appropriate drying agents.<sup>47</sup> Chromatography was performed using silica gel (230-400 mesh) with indicated solvents. All reactions were monitored by thin-layer chromatography on 0.25 mm silica plates (F-254) visualizing under UV light and developed using H<sub>2</sub>SO<sub>4</sub> or vanillin solution. <sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded on a 400 MHz NMR spectrometer “Bruker Avance 400” spectrometer and chemical shifts are cited with respect to SiMe<sub>4</sub> as internal (<sup>1</sup>H and <sup>13</sup>C). Chemical shifts, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd doublet of doublet), coupling constant in Hertz (Hz), and number of protons are presented in standard format. HRMS were recorded “MicroMass ESI-TOF” with electrospray ionization (ESI) and quadrupolar mass analyzer with time-of-flight (TOF) detector. Optical rotation of compounds was recorded on “JASCO digital polarimeter DIP-370”. Single crystal X-ray data collection was recorded on a BRUKER-SMART APEX CCD-single crystal diffractometer.

## Preparation of methyl diazoacetate

A solution of methyl glycerate hydrochloride (35 g, 1 mole) in water (75 mL) was mixed with CH<sub>2</sub>Cl<sub>2</sub> (180 mL) in a 2-l. four-necked round-bottomed flask fitted with dropping funnel, thermometer, and nitrogen inlet tube, and cooled to -5° C. The flask is flushed with nitrogen and an ice-cold solution of sodium nitrite (24.9 gm, 1.2 moles) in water (75 mL) is added with stirring. The temperature is lowered to -10° C, and 5% H<sub>2</sub>SO<sub>4</sub> (29 mL) is added from the dropping funnel during a period of about 3 minutes. The temperature

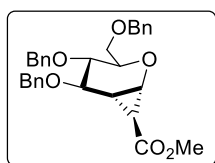
may rise to a maximum of +1° C with the cooling bath at -20° C. The reaction terminates within 10 minutes, when heat is no longer evolved. The reaction mixture is transferred to an ice-cold separatory funnel, and the yellow-green CH<sub>2</sub>Cl<sub>2</sub> layer is run into cold 5% NaHCO<sub>3</sub> (100 mL) solution. The aqueous layer is extracted once with CH<sub>2</sub>Cl<sub>2</sub> (10 X 3 mL). The CH<sub>2</sub>Cl<sub>2</sub> and NaHCO<sub>3</sub> solutions are returned to the separatory funnel and shaken until no trace of acid remains, as shown by indicator paper. The golden yellow organic layer is separated, transferred to a dry separatory funnel, and shaken for 5 minutes with anhydrous sodium sulphate (5 g). The dried methyl diazoacetate solution is filtered through a cotton plug inserted in the separatory funnel stem, and the bulk of the solvent is distilled and a maximum pot temperature of 35° C. This yellow oil product is used for cyclopropanation without further purification.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) : δ 3.75 (s, 3H), 5.31(s, 2H, DCM solvent)

### General procedure for the cyclopropanation of D-glycals (1a–1c)<sup>30</sup>

To a stirred suspension of D-glycal (10 mmol) and Rh<sub>2</sub>(OAc)<sub>4</sub> (0.1 mmol) in anhydrous DCM (10 mL), methyl diazoacetate (20.0 mmol) in DCM (75 mL) was added drop wise over a period of 2 h. After cessation of the nitrogen evolution (5 min), the reaction mixture was concentrated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (230–400 mesh) using EtOAc and petroleum ether of appropriate composition to obtain the cyclopropanecarboxylate

#### 1,5-anhydro-2-deoxy-1,2-C-(*exo*-carbmethoxymethylene)-3,4,6-tri-*O*-benzyl- $\alpha$ -D-glucitol (1a)

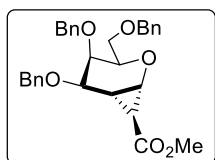


Yield 56%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.21–7.32 (m, 15H), 4.71 (s, 2H), 4.58 (s, 2H), 4.62 (s, 1H), 4.54 (s, 2H), 3.97 (dd, 1H, J = 2.4 Hz, J = 7.8 Hz), 3.77 (dd, 1H, J = 1.7 Hz, J = 6.3 Hz), 3.67 – 3.52 (m, 7H), 1.89 - 1.94 (m, 1H), 1.8 (m, 1H); <sup>13</sup>C NMR

(75 MHz, CDCl<sub>3</sub>): δ 172.4, 138.2, 137.9, 137.8, 128.3, 128.3, 128.2, 127.8, 127.6, 127.5, 75.4, 74.4, 73.4,

73.3, 71.9, 71.4, 68.9, 57.5, 51.8, 25.7, 24.2. HRMS (ESI-QTOF)  $m/z$ : Calcd for  $C_{30}H_{32}O_6$   $[M+Na]^+$  511.2198; Found 511.2195.

### 1,5-anhydro-2-deoxy-1,2-C-(*exo*-carbmethoxymethylene)-3,4,6-tri-*O*-benzyl- $\alpha$ -D-galactol (**1b**)



Yield 62%;  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.22–7.37 (m, 15H), 4.83 (s, 1H), 4.75 (s, 1H), 4.6 (s, 1H), 4.59 (s, 1H), 4.49 (s, 1H), 4.41 (s, 1H), 3.96 (dd, 1H,  $J = 2.4$  Hz,  $J = 7.8$  Hz), 3.63–3.67 (m, 8 H), 1.89–1.94 (m, 1H), 1.60 (dd, 1H,  $J = 2.4$  Hz,  $J = 6$  Hz);

$^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  172.4, 138.2, 137.9, 137.8, 128.3, 128.3, 128.2, 127.8, 127.6, 127.5, 75.4, 74.4, 73.4, 73.3, 71.9, 71.4, 68.9, 57.5, 51.8, 25.7, 24.2. HRMS (ESI-QTOF)  $m/z$ : Calcd for  $C_{30}H_{32}O_6$   $[M+Na]^+$  511.2198; Found 511.2188.

### General procedure for the synthesis of iodides (**2a–2k**)

To a solution of cyclopropanecarboxylate (1 mmol) and N-protected amino acid (1.2 mmol) in  $CH_2Cl_2$  (7 mL) under argon atmosphere was added N-iodosuccinimide (1.3 mmol) and 4 Å molecular sieves (250 mg). The reaction mixture was stirred for certain time (2 h for **2a–2h** and 12 h for **2i–2k**) at room temperature (25 °C). After complete the disappearance of the starting material, the reaction mixture was diluted with  $CH_2Cl_2$  (20 mL). The reaction mixture was treated with a saturated  $Na_2S_2O_3$  solution and then the organic layer was separated and dried over anhydrous  $Na_2SO_4$ . The crude product obtained after removal of solvent was purified by column chromatography on silica gel (230–400 mesh) using EtOAc and petroleum ether of appropriate composition to obtain the corresponding iodide derivatives.

### 3,4,6-tri-*O*-benzyl-2-(1-iodo-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranos-1-yl N-[(2-methyl-2-propanyl)oxy]carbonyl-L-phenylalaninate (**2b**)

Yield 50%; Colourless solid; m.p. 53–55 °C;  $R_f = 0.5$  (hexanes/EtOAc, 8:2);  $[\alpha]^{25}_D +9.2$  ( $c$  0.5,  $CHCl_3$ ); IR (KBr): 3434, 2927, 1748, 1718, 1497, 1366, 1160, 1089, 738,  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ ): 7.33–7.08 (m, 20H), 5.57 (d,  $J = 7.2$  Hz, 1H), 4.93 (d,  $J = 10.5$  Hz, 1H), 4.75–4.48 (m, 6H), 4.21 (s, 1H), 3.91

(t,  $J = 17.7, 8.7$  Hz, 1H), 3.83–3.69 (m, 3H), 3.63–3.56 (m, 1H), 3.32 (s, 3H), 3.18–3.04 (m, 2H), 2.09 (t,  $J = 8.4$  Hz, 1H), 1.40 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 170.3, 167.0, 154.8, 137.9, 137.7, 137.6, 135.5, 129.2, 128.7, 128.3, 128.3, 128.0, 127.9, 127.7, 127.7, 127.6, 127.6, 127.4, 126.9, 95.1, 81.3, 79.9, 79.0, 75.7, 74.8, 74.6, 73.5, 67.9, 54.4, 53.3, 48.4, 38.5, 28.2; HRMS (ESI–QTOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{44}\text{H}_{50}\text{INO}_{10}\text{Na}$  902.2377; Found 902.2432.

**3,4,6-Tri-*O*-benzyl-2-(1-iodo-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranos-1-yl N-[(2-methyl-2-propanyl)oxy]carbonyl}-L-prolinate (2c)**

Yield 72%; Gummy;  $R_f = 0.4$  (hexanes/EtOAc, 7:3);  $[\alpha]^{25}_{\text{D}} -5.54$  ( $c$  3,  $\text{CHCl}_3$ ); IR (Neat): 2951, 2927, 1764, 1748, 1701, 1396, 1365, 1161, 1087, 1074, 1168, 1051, 752, 736, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): (two diastereomers exists in 3:2 ratio. Stereo chemistry of minor isomer was not able to identified and its NMR peaks are represented with \* ) 7.33–7.10 (m, 15 H), 5.69–5.67 (d, 0.4H,  $J = 8.6$  Hz)\*, 5.60–5.58 (d, 0.6 H,  $J = 8.6$  Hz), 4.99–4.94 (m, 1H), 4.84 (m, 3H), 4.69–4.57 (m, 2H), 4.53–4.48 (m, 1H), 3.99–3.70 (m, 5H), 3.62–3.46 (m, 3H), 3.36 (s, 3H), 2.32–2.21 (m, 1H), 2.19–2.14 (m, 2H), 2.08–2.04 (m, 2H), 1.90–1.86 (m, 2H), 1.46 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 171.7\*, 170.9, 167.7\*, 167.2, 154.3\*, 153.7, 138.1\*, 137.9, 137.85\*, 137.82, 137.7\*, 137.6, 128.43, 128.41, 128.35, 128.1, 128.1, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 94.8, 94.5\*, 81.7\*, 81.2, 80.4, 80.1\*, 79.3, 79.2\*, 75.63\*, 74.83\*, 74.8, 73.45\*, 73.38, 68.1, 68.0\*, 58.8, 58.6\*, 53.5, 53.4, 49.2\*, 48.7, 46.6\*, 46.3, 30.7, 29.5\*, 28.4, 28.3, 27.5\*, 26.3, 24.5\*, 23.5; HRMS (ESI–QTOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{40}\text{H}_{48}\text{INO}_{10}\text{Na}$  852.2221; Found 852.2231.

**3,4,6-Tri-*O*-benzyl-2-(1-iodo-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-galactopyranos-1-yl N-[(2-methyl-2-propanyl)oxy]carbonyl}-L-alaninate (2d)**

Yield 85%; Colourless crystalline solid, m.p. 53–54 °C;  $R_f = 0.5$  (hexanes/EtOAc, 7:3);  $[\alpha]^{25}_{\text{D}} +15.4$  ( $c$  1,  $\text{CHCl}_3$ ); IR (Neat): 3349, 2926, 1764, 1740, 1678, 1516, 1172, 1082, 1063, 736  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.36–7.26 (m, 15H), 5.61 (d,  $J = 9$  Hz, 1H), 5.00–4.96 (m, 1H), 4.83 (d,  $J = 11.0$  Hz, 1H), 4.66 (d,  $J = 11.0$  Hz, 1H), 4.56–4.53 (m, 2H), 4.53–4.43 (m, 2H), 4.31–4.27 (m, 1H), 4.01 (s, 1H), 3.76–3.65 (m, 4H), 3.57 (dd,  $J = 5.0, 8.0$  Hz, 1H), 3.44 (s, 3H), 2.67–2.61 (m, 1H), 1.43 (s, 9H), 1.39 (d,  $J = 7.0$  Hz, 3H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 171.7, 167.5, 155.0, 138.5, 137.7, 136.9, 128.4, 128.4, 128.2, 128.1, 127.9, 127.8, 127.5, 95.3, 81.1, 80.0, 74.6, 74.2, 73.4, 72.3, 71.0, 67.8, 53.2, 49.2, 44.0, 28.2, 17.9; HRMS (ESI-QTOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{38}\text{H}_{46}\text{INO}_{10}\text{Na}$  826.2064; Found 826.2119.

**3,4,6-Tri-*O*-benzyl-2-(1-iodo-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranos-1-yl N<sup>6</sup>-[(benzyloxy)carbonyl]-N<sup>2</sup>-{[(2-methyl-2-propanyl)oxy]carbonyl}-L-lysinate (2e)**

Yield 61%; Colourless solid; m.p. 59–60 °C;  $R_f$  = 0.5 (hexanes/EtOAc, 5:5);  $[\alpha]_D^{25} +8.5$  (c 3,  $\text{CHCl}_3$ ); IR (KBr): 3394, 2925, 2111, 1747, 1716, 1153, 1077, 736, 697  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.36–7.08 (m, 20H), 5.66 (d,  $J$  = 8.7 Hz, 1H), 5.16–4.37 (m, 12H), 3.97–3.57 (m, 6H), 3.77 (s, 3H), 2.52–2.475 (m, 2H), 2.26–2.10 (m, 2H), 2.07–2.00 (m, 1H), 1.47–1.41 (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 172.4, 170.5, 167.4, 155.2, 137.9, 137.9, 137.6, 135.7, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 127.8, 127.7, 127.5, 95.0, 81.2, 80.3, 79.1, 75.8, 74.8, 74.7, 73.5, 68.1, 66.5, 53.4, 52.9, 48.8, 30.1, 28.3, 27.2; HRMS (ESI-QTOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{49}\text{H}_{59}\text{IN}_2\text{O}_{12}\text{Na}$  1017.3010; Found 1017.3039.

**3,4,6-Tri-*O*-benzyl-2-(1-iodo-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranos-1-yl N-{[(2-methyl-2-propanyl)oxy]carbonyl}-L-valinate (2f)**

Yield 74%; Gummy;  $R_f$  = 0.5 (hexanes/EtOAc, 7:3);  $[\alpha]_D^{25} +12.29$  (c 2.4,  $\text{CHCl}_3$ ); IR (Neat): 2954, 2928, 2875, 1745, 1722, 1714, 1495, 1455, 1366, 1154, 1086, 1076, 1046, 736, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.34–7.20 (m, 20H), 5.89 (s, 1H), 4.91 (d,  $J$  = 11.5 Hz, 1H), 4.81 (d,  $J$  = 10.9 Hz, 1H), 4.69–4.54 (m, 5H), 4.34 (d, 1H,  $J$  = 8.4 Hz), 3.89 (dd, 1H,  $J$  = 10.7, 3.4 Hz), 3.74–3.60 (m, 6H), 3.50 (s, 3H), 3.39–3.37 (m, 1H), 2.24–2.20 (m, 1H), 1.38 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 176.9, 155.5, 140.3, 138.3, 138.2, 138.1, 128.8, 128.6, 128.5, 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.8, 127.7, 127.2, 126.6, 126.6, 100.6, 80.0, 79.9, 79.2, 78.4, 75.1, 74.7, 74.6, 73.6, 73.3, 68.8, 52.0, 50.4, 49.9, 28.4, 28.4; HRMS (ESI-QTOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{40}\text{H}_{50}\text{INO}_{10}\text{Na}$  854.2377; Found 854.2383.

**3,4,6-Tri-*O*-(*tert*-butyldimethylsilyl)-2-(1-iodo-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranos-1-yl N-{[(benzyl)oxy]carbonyl}-L-valinate (2g)**

Yield 67%; Gummy;  $R_f = 0.4$  (hexanes/EtOAc, 9:1);  $[\alpha]^{25}_D +36.9$  ( $c$  2.2,  $\text{CHCl}_3$ ); IR (Neat): 2954, 1730, 1259, 1085, 735  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.38–7.32 (m, 5H), 6.11 (s, 1H), 5.29 (d,  $J = 9.1$  Hz, 1H), 5.12 (dd,  $J = 10.0, 12.3$  Hz, 2H, ), 4.93 (d,  $J = 9.1$  Hz, 1H), 4.37 (m, 2H), 4.27 (t,  $J = 9.1$  Hz, 1H), 4.03 (s, 1H), 3.83–3.79 (m, 1H), 3.76 (s, 3H), 3.56–3.52 (m, 1H), 2.32–2.29 (m, 2H), 1.66 (s, 1H), 1.00–0.84 (m, 32H), 0.20–0.14 (m, 12H), 0.03 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) 172.01, 171.40, 156.33, 136.31, 128.51, 128.42, 128.19, 128.02, 127.92, 92.07, 74.71, 72.98, 70.90, 68.84, 62.42, 60.00, 52.62, 50.12, 46.71, 31.53, 30.52, 25.97, 25.92, 25.88, 25.77, 25.74, 19.28, 19.14, 18.34, 18.28, 18.11, 18.08, 17.94, 17.86, 17.44,  $-2.77, -2.85, -3.40$ ; HRMS (ESI-QTOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{40}\text{H}_{72}\text{INO}_{10}\text{Si}_3\text{Na}$  960.3407; Found 960.3412.

**3,4,6-Tri-*O*-benzyl-2-(1-iodo-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranos-1-yl N-[(9H-fluoren-9-ylmethoxy)carbonyl]-L-valinate (2h)**

Yield 62%; Gummy;  $R_f = 0.5$  (hexanes/EtOAc, 7:3);  $[\alpha]^{25}_D +5.96$  ( $c$  1,  $\text{CHCl}_3$ ); IR (KBr): 3381, 2952, 1759, 1748, 1727, 1498, 1088, 740, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.77–7.75 (d,  $J = 7.8$  Hz, 2H), 7.61–7.59 (m, 2H), 7.42–7.12(m, 19H), 5.67 (d,  $J = 8.7$  Hz, 1H), 5.31 (d,  $J = 9.3$  Hz, 1H), 4.96 (d,  $J = 10.5$  Hz, 1H), 4.84–4.72 (m, 3H), 4.64–4.51 (m, 3H), 4.42–4.34 (m, 3H), 4.24 (t,  $J = 6.9$  Hz, 1H), 3.98–3.58 (m, 5H), 3.58 (s, 3H), 2.28–2.17 (m, 2H), 1.02 (d,  $J = 6.9$  Hz, 3H), 0.95 (d,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 170.5, 167.3, 156.2, 143.9, 143.7, 141.3, 138.0, 137.7, 128.4, 128.3, 128.1, 127.8, 127.6, 127.4, 127.0, 126.9, 126.5, 119.9, 94.91, 81.3, 79.2, 75.4, 74.8, 74.7, 73.5, 68.2, 67.1, 58.9, 53.4, 48.8, 47.2, 31.1, 18.8, 17.4; HRMS (ESI-QTOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{50}\text{H}_{52}\text{INO}_{10}\text{Na}$  976.2534; Found 976.2500.

**2-Carbomethoxy-2-([(2-methyl-2-propanyloxy)carbonyl]amino)ethyl 3,4,6-tri-*O*-benzyl-2-(1-iodo-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranoside (2i)**

Yield: 75%; Gummy;  $R_f = 0.5$  (hexanes/EtOAc, 7:3);  $[\alpha]^{25}_D +7.5$  ( $c$  0.8,  $\text{CHCl}_3$ ); IR (neat): 3418, 2924, 1746, 1722, 1102, 1061, 737, 698, 417  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.35–7.08 (m, 15H), 5.49 (d, 1H, 7.7Hz), 4.99–4.93 (m, 2H), 4.77–4.71 (m, 2H), 4.67–4.64 (m, 1H), 4.58–4.54 (m, 2H), 4.48–4.46 (m,

1H), 4.33–4.25 (m, 2H), 3.88–3.83 (m, 2H), 3.78–3.37 (m, 6H), 3.45–3.43 (m, 1H), 3.35 (s, 3H), 1.96–1.91 (m, 1H), 1.45 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 171.1, 168.1, 155.8, 138.6, 138.4, 138.1, 129.0, 128.9, 128.6, 128.4, 128.24, 128.19, 127.9, 103.8, 81.8, 80.5, 80.2, 75.6, 75.3, 74.0, 70.1, 68.8, 60.9, 54.5, 53.9, 53.1, 50.3, 28.9; HRMS (ESI–QTOF) *m/z*: [M+Na] Calcd for C<sub>39</sub>H<sub>48</sub>INO<sub>11</sub>Na 856.2170; Found 856.2156.

**2-Phenyl-2-([(2-methyl-2-propanyl)oxy]carbonyl)amino)ethyl 3,4,6-tri-*O*-benzyl-2-(1-iodo-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucofuranoside (2j)**

Yield: 68%; Gummy; *R<sub>f</sub>* = 0.5 (hexanes/EtOAc, 7:3); [ $\alpha$ ]<sup>25</sup><sub>D</sub> +18.6 (*c* 2, CHCl<sub>3</sub>); IR (Neat): 2926, 1744, 1715, 1497, 1365, 1164, 1104, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.36–7.23 (m, 20H), 5.53 (bs, 1H), 4.91 (d, *J* = 10.8 Hz, 2H), 4.74–4.65 (m, 4H), 4.57–4.55 (m, 2H), 4.27 (d, *J* = 8.1 Hz, 1H), 4.21 (dd, *J* = 10.1, 3.2 Hz, 1H), 3.85 (t, *J* = 9.0 Hz, 1H), 3.77–3.69 (m, 4H), 3.45 (dq, *J* = 9.1, 2.3 Hz, 1H), 3.32 (s, 3H), 1.91 (td, *J* = 9.2, 2.4 Hz, 1H), 1.43 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 167.6, 155.4, 138.2, 138.0, 137.7, 128.4, 128.1, 127.8, 127.74, 127.66, 127.4, 126.5, 103.6, 81.4, 79.8, 79.6, 75.2, 74.7, 73.6, 68.5, 53.3, 50.0, 28.4; HRMS (ESI–QTOF) *m/z*: [M+Na] Calcd for C<sub>43</sub>H<sub>50</sub>INO<sub>9</sub>Na 874.2428; Found 874.2432.

**3-Phenyl-2-(S)-([(2-methyl-2-propanyl)oxy]carbonyl)amino)propyl 3,4,6-tri-*O*-benzyl-2-(1-iodo-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucofuranoside (2k)**

Yield: 52%; Gummy; *R<sub>f</sub>* = 0.5 (hexanes/EtOAc, 7:3); [ $\alpha$ ]<sup>25</sup><sub>D</sub> +9.22 (*c* 1.8, CHCl<sub>3</sub>); IR (KBr): 3031, 2954, 2867, 1745, 1713, 1519, 1497, 1366, 1104, 1059, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.34–7.09 (m, 20H), 5.25 (d, *J* = 8.4 Hz, 1H), 5.05 (d, *J* = 1.5 Hz, 1H), 4.95 (d, *J* = 10.8 Hz, 1H, ), 4.80–4.53 (m, 6H), 4.31 (d, *J* = 8.1 Hz, 1H), 4.02–3.72 (m, 6H), 3.58–3.45 (m, 2H), 3.37 (s, 3H), 2.92–2.82 (m, 1H), 1.42 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 167.6, 155.3, 138.0, 137.97, 137.8, 137.6, 129.4, 128.4, 128.4, 128.0, 127.77, 127.75, 127.7, 127.6, 127.6, 127.3, 126.3, 103.2, 81.3, 79.7, 79.2, 75.0, 74.72, 74.68, 73.4, 70.5, 68.3, 53.4, 51.7, 50.1, 37.8, 28.3; HRMS (ESI–QTOF) *m/z*: [M+Na] Calcd for C<sub>44</sub>H<sub>52</sub>INO<sub>9</sub>Na 888.2585; Found 888.2568.

## General procedure for the synthesis of azides (3a–3g and 3i–3k)

To a stirred solution of iodo derivative of glycosyl ester of amino acid (1 mmol) in dry DMF (5 mL) was added NaN<sub>3</sub> (2 mmol) and the reaction mixture was stirred for 24 h at room temperature (25 °C). DMF was removed under vacuum and the crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The organic layer was washed with water (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated and the crude product was purified by column chromatography on silica gel (230–400 mesh) using EtOAc and petroleum ether of appropriate composition to furnish the pure azide derivatives.

### **3,4,6-Tri-*O*-benzyl-2-(1-azido-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranos-1-yl N-[(2-methyl-2-propanyl)oxy]carbonyl}-L-phenylalaninate (3b)**

Yield 76%; Gummy;  $R_f = 0.5$  (hexanes/EtOAc, 8:2);  $[\alpha]_D^{25} +71.1$  ( $c$  1, CHCl<sub>3</sub>); IR (neat): 3400, 3031, 2925, 2869, 2113, 1747, 1716, 1497, 1454, 1365, 1216, 1159, 1076, 1054, 1027, 737, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.38–7.20 (m, 20H), 5.58 (d,  $J = 8.7$  Hz, 1H), 4.99–4.35 (m, 8H), 3.84–3.51 (m, 9H), 3.18–3.15 (m, 1H), 2.99–2.86 (m, 1H), 2.59–2.52 (m, 1H), 1.35 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 170.4, 169.7, 154.6, 137.8, 137.6, 135.8, 129.6, 128.6, 128.4, 128.3, 128.3, 127.9, 127.8, 127.8, 127.7, 126.8, 92.6, 79.8, 79.1, 78.2, 75.8, 75.0, 74.7, 73.6, 67.9, 57.7, 54.2, 52.7, 46.8, 28.2; HRMS (ESI-QTOF)  $m/z$ :  $[M+Na]^+$  Calcd for C<sub>44</sub>H<sub>50</sub>N<sub>4</sub>O<sub>10</sub>Na 817.3425; Found 817.3455.

### **3,4,6-Tri-*O*-benzyl-2-(1-azido-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranos-1-yl N-[(2-methyl-2-propanyl)oxy]carbonyl}-L-prolinate (3c)**

Yield 82%; Gummy;  $R_f = 0.4$  (hexanes/EtOAc, 6:4);  $[\alpha]_D^{25} +27.04$  ( $c$  3, CHCl<sub>3</sub>); IR (Neat): 3394, 2926, 2114, 17747, 1750, 1699, 1396, 1216, 1161, 1073, 1019, 753, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.40–7.20 (m, 15 H), 5.69–5.47 (d,  $J = 8.95$  Hz, 1H), 4.96 (d,  $J = 11.6$  Hz, 1H), 4.81 (d,  $J = 10.9$  Hz, 1H), 4.67–4.58 (m, 3H), 4.49–4.46 (m, 1H), 4.32 (d,  $J = 1.3$  Hz, 1H), 4.18 (dd,  $J = 11.6, 4.9$  Hz, 1H), 3.84–3.74 (m, 5H), 3.709–3.60 (m, 2H), 3.54–3.40 (m, 3H), 2.51–2.45 (m, 1H), 2.23–2.14 (m, 1H), 2.11–2.04 (m, 1H), 1.90–1.77 (m, 2H), 1.44 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 170.2, 170.1, 154.0, 137.9, 137.7,

128.7, 128.5, 128.4, 128.3, 127.9, 127.8, 127.8, 127.7, 92.4, 80.3, 79.4, 78.3, 75.7, 75.1, 74.8, 73.4, 68.1, 58.6, 57.7, 52.5, 47.0, 46.3, 30.4, 28.1, 23.5; HRMS (ESI-QTOF)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{40}H_{48}N_4O_{10}Na$  767.3268; Found 767.3268.

**3,4,6-Tri-*O*-benzyl-2-(1-azido-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-galactopyranos-1-yl N-[[2-methyl-2-propanyl]oxy]carbonyl]-L-alaninate (3d)**

Yield 73%; Gummy;  $R_f = 0.5$  (hexanes/EtOAc, 7:3);  $[\alpha]^{25}_D +48.1$  ( $c$  2,  $CHCl_3$ ); IR (Neat): 3839, 3751, 2923, 2112, 1733, 1716, 1522, 1095, 1059, 1028, 748  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 7.40–7.26 (m, 15H), 5.55 (d, 1H,  $J = 8.7$  Hz), 5.10–5.09 (m, 1H), 4.90 (d, 1H,  $J = 11.5$  Hz), 4.71 (d, 1H,  $J = 11.7$  Hz), 4.64 (d, 1H,  $J = 11.9$  Hz), 4.6 (s, 1H), 4.45 (d,  $J = 2.8$  Hz, 2H), 4.39 (d,  $J = 11.8$ , 1H), 4.26–4.22 (m, 1H), 4.03 (d, 1H,  $J = 2.1$  Hz), 3.82 (s, 3H), 3.69–3.63 (m, 2H), 3.58–3.51 (m, 2H), 2.94–2.89 (m, 1H), 1.43 (s, 9H), 1.36 (d,  $J = 7.0$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ): 170.8, 154.6, 138.3, 137.7, 137.0, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 92.3, 76.6, 74.7, 74.3, 73.5, 71.5, 70.2, 67.8, 58.0, 53.4, 52.7, 42.7, 29.7, 28.3; HRMS (ESI-QTOF)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{38}H_{46}N_4O_{10}Na$  741.3112; Found 741.3112.

**3,4,6-Tri-*O*-benzyl-2-(1-azido-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranos-1-yl N<sup>6</sup>-[(benzyloxy)carbonyl]-N<sup>2</sup>-[[2-methyl-2-propanyl]oxy]carbonyl]-L-lysinate (3e)**

Yield 70%; Gummy;  $R_f = 0.5$  (hexanes/EtOAc, 5:5);  $[\alpha]^{25}_D +354$  ( $c$  0.1,  $CHCl_3$ ); IR (Neat): 3394, 2930, 2113, 1748, 1716, 1247, 1047, 737, 698  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ ): 7.39–7.18 (m, 20 H), 5.59 (d,  $J = 8.8$  Hz, 1H), 5.12–5.04 (m, 3H), 4.95 (d, 1H,  $J = 11.6$  Hz), 4.8–4.73 (m, 1H), 4.66–4.56 (m, 4H), 4.47–4.44 (m, 1H), 4.33–4.27 (m, 2H), 3.81–3.6 (m, 8H), 3.52–3.50 (m, 1H), 3.16–3.06 (m, 2H), 2.50–2.45 (m, 1H), 1.81–1.67 (m, 2H), 1.49–1.26 (m, 12H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ): 170.5, 170.3, 156.4, 154.9, 137.73, 137.61, 136.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 92.1, 79.9, 79.2, 78.1, 75.6, 75.1, 74.7, 73.4, 67.9, 66.4, 57.8, 52.8, 47.1, 40.7, 32.3, 29.0, 28.3, 21.8; HRMS (ESI-QTOF)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{49}H_{59}N_5O_{12}Na$  932.4058; Found 932.403??.

**3,4,6-Tri-*O*-benzyl-2-(1-azido-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranos-1-yl N-{[(2-methyl-2-propanyl)oxy]carbonyl}-L-valinate (3f)**

Yield 84%; Gummy;  $R_f = 0.5$  (hexanes/EtOAc, 7:3);  $[\alpha]^{25}_D +34.4$  ( $c$  3,  $\text{CHCl}_3$ ); IR (Neat): 2852, 2113, 1750, 1736, 1718, 1510, 1074  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.38–7.21 (m, 15H), 5.60 (d, 1H), 4.96 (d,  $J = 11.2$  Hz, 1H), 4.80 (d, , 1H), 4.66–4.48 (m, 5H), 4.34 (s, 1H), 4.24 (dd,  $J = 9.3, 3.8$  Hz, 1H), 3.82–3.65 (m, 8H), 3.50 (d,  $J = 9.11$  Hz, 1H), 2.48 (t,  $J = 10$  Hz, 1H), 2.22–2.18 (m, 1H), 1.44 (s, 9H), 0.95 (d,  $J = 7.1$  Hz, 3H), 0.87 (d,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 170.4, 170.2, 155.3, 137.9, 137.8, 137.6, 128.6, 128.5, 128.4, 127.3, 127.8, 127.8, 127.7, 91.9, 79.7, 79.2, 78.1, 75.8, 75.1, 74.8, 73.5, 67.9, 57.8, 47.1, 33.8, 28.3, 22.7, 18.72; HRMS (ESI-QTOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{40}\text{H}_{50}\text{N}_4\text{O}_{10}$  769.3425; Found 769.3427.

**3,4,6-Tri-*O*-(*tert*-butyldimethylsilyl)-2-(1-azido-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranos-1-yl N-[(benzyloxy)carbonyl]-L-valinate (3g)**

Yield 74%; Gummy;  $R_f = 0.4$  (hexanes/EtOAc, 9:1);  $[\alpha]^{25}_D +30.1$  ( $c$  1.2,  $\text{CHCl}_3$ ); IR (Neat): 3674, 2957, 2109, 1748, 1735, 1259, 1089, 836, 778  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.37–7.32 (m, 5H), 6.30 (d,  $J = 2.6$  Hz, 1H), 5.32 (d,  $J = 9.1$  Hz, 1H), 5.15–5.08 (m, 2H, ), 4.48 (d,  $J = 10.2$  Hz, 1H), 4.37–4.33 (m, 2H), 4.21–4.17 (m, 1H), 3.97–3.85 (m, 6H), 3.64–3.60 (m, 1H), 2.27–2.25 (m, 2H), 1.00–0.99 (m, 3H), 0.91–0.89 (m, 29H); 0.13–0.09 (m, 12H), 0.04–0.03 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) 170.6, 169.10 156.1, 136.2, 128.4, 128.0, 91.3, 79.2, 69.2, 68.2, 66.9, 63.4, 60.7, 58.5, 52.5, 44.1, 30.8, 25.8, 25.7, 19.2, 18.2, 18.0, 17.9, 16.6, –4.4, –4.57, –4.67, –4.74, –5.4, –5.5; HRMS (ESI-QTOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{40}\text{H}_{72}\text{N}_4\text{O}_{10}\text{Si}_3\text{Na}$  875.4454; Found 875.4453.

**(*S*)-2-Carbmethoxy-2-({[(2-methyl-2-propanyl)oxy]carbonyl}amino)ethyl 3,4,6-tri-*O*-benzyl-2-(1-azido-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranoside (3i)**

Yield: 84%; Gummy;  $R_f = 0.5$  (hexanes/EtOAc, 7:3);  $[\alpha]^{25}_D +152.3$  ( $c$  1,  $\text{CHCl}_3$ ); IR (neat): 3389, 2927, 2112, 1746, 1715, 1065, 738, 699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.40–7.19 (m, 15H), 5.95 (d,  $J = 9.0$  Hz, 1H), 4.99–4.93 (m, 1H), 4.89–4.82 (m, 1H), 4.78–4.62 (m, 4H), 4.58–4.23 (m, 3H), 3.78–3.71 (m,

10H), 3.63–3.46 (m, 2H), 3.35–3.33 (m, 1H), 2.34–2.17 (m, 1H), 1.45 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 171.4, 170.4, 155.9, 137.9, 137.8, 128.6, 128.4, 128.3, 128.1, 127.8, 127.7, 100.65, 79.65, 78.4, 77.2, 75.1, 75.0, 74.7, 73.6, 70.3, 68.3, 58.2, 53.5, 52.8, 52.7, 48.6, 28.3; HRMS (ESI–QTOF) *m/z*: [M+Na] Calcd for C<sub>39</sub>H<sub>48</sub>N<sub>4</sub>O<sub>11</sub>Na 771.3217; Found 771.3219.

**(S)-2-Phenyl-2-([(2-methyl-2-propanyl)oxy]carbonyl)amino)ethyl 3,4,6-tri-O-benzyl-2-(1-azido-2-methoxy-2-oxoethyl)-1,2-dideoxy-β-D-glucopyranoside (3j)**

Yield: 76%; Gummy; *R<sub>f</sub>* = 0.4 (hexanes/EtOAc, 8:2); [α]<sup>25</sup><sub>D</sub> +101.5 (*c* 0.3, CHCl<sub>3</sub>); IR (Neat): 3367, 2928, 2111, 1743, 1717, 1676, 1497, 1365, 1165, 1101, 1062, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.36–7.19 (m, 20H), 5.83 (bs, 1H), 4.94 (d, *J* = 11.5 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.69–4.54 (m, 5H), 4.31 (d, *J* = 8.5 Hz, 1H), 4.26 (d, *J* = 1.5 Hz, 1H), 3.86 (dd, *J* = 10.7 Hz, 3.3 Hz, 1H), 3.79–3.70 (m, 4H), 3.59–3.55 (m, 1H), 3.46 (s, 3H), 3.36–3.34 (m, 1H), 2.33–2.28 (m, 1H), 1.38 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 170.8, 155.3, 138.0, 137.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.87, 127.86, 127.8, 127.7, 127.1, 126.6, 100.2, 79.6, 79.2, 78.5, 75.1, 75.0, 74.8, 73.6, 68.6, 58.3, 52.3, 48.9, 28.4; HRMS (ESI–QTOF) *m/z*: [M+Na] Calcd for C<sub>43</sub>H<sub>50</sub>N<sub>4</sub>O<sub>9</sub>Na 789.3475; Found 789.3479.

**3-Phenyl-2-(S)-([(2-methyl-2-propanyl)oxy]carbonyl)amino)propyl 3,4,6-tri-O-benzyl-2-(1-azido-2-methoxy-2-oxoethyl)-1,2-dideoxy-β-D-glucopyranoside (3k)**

Yield: 82%; Gummy; *R<sub>f</sub>* = 0.5 (hexanes/EtOAc, 7:3); [α]<sup>25</sup><sub>D</sub> +45.8 (*c* 1, CHCl<sub>3</sub>); IR (Neat): 2930, 2113, 1734, 1719, 1057, 737, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.39–7.19 (m, 20 H), 5.28 (d, *J* = 8.7 Hz, 1H), 4.97 (d, *J* = 11.4 Hz, 1H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.72–4.50 (m, 4H), 4.36–4.32 (m, 2H), 3.80–3.57 (m, 11H), 3.47–3.34 (m, 2H), 2.87–2.76 (m, 2H), 2.43–2.37 (m, 1H), 1.39 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 170.8, 155.4, 138.5, 137.9, 137.8, 129.4, 128.6, 128.5, 128.4, 128.2, 127.8, 127.7, 126.2, 100.7, 79.7, 79.0, 78.6, 75.1, 75.0, 74.8, 73.6, 70.5, 68.4, 58.3, 52.5, 52.0, 48.8, 28.4; HRMS (ESI–QTOF) *m/z*: [M+Na] Calcd for C<sub>44</sub>H<sub>52</sub>N<sub>4</sub>O<sub>9</sub>Na 803.3632; Found 803.3622.

## **General General procedure for the synthesis of glycosyl esters of amino acids (4a–4g, 4i–4k and 8)**

To a stirred solution of azide (1 mmol) in 10 mL of AcOH:THF (1:1), Zn dust (2 mmol) was added and the reaction mixture was stirred for 12 h at room temperature (25 °C). After disappearance of starting material, Zn was removed by filtration. The solvent was then removed under vacuum followed by dilution with 20 mL of EtOAc. The organic layer was thoroughly washed with water. To the organic layer, 20 mL of sat. NaHCO<sub>3</sub> solution was added left for stirring for 3 h. The organic layer was then separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The filtrate was concentrated and the crude product was purified by column chromatography on amine pre-treated silica gel (0.5 ml of Et<sub>3</sub>N for 50 g of silica gel) using EtOAc and petroleum ether of appropriate composition to furnish glycosyl esters.

### **3,4,6-Tri-O-benzyl-2-(1-amino-2-methoxy-2-oxoethyl)-1,2-dideoxy-β-D-glucopyranos-1-yl N-[(2-methyl-2-propanyl)oxy]carbonyl}-L-phenylalaninate (4b)**

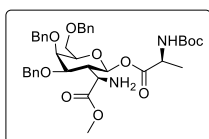
Yield 71 %; Gummy;  $R_f = 0.5$  (hexanes/EtOAc, 5:5);  $[\alpha]_D^{25} +37.5$  (*c* 3.3, CHCl<sub>3</sub>) IR (neat): 3367, 2927, 1674, 1496, 1053, 1027, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.33–7.191 (m, 20H), 5.21–5.09 (m, 2H), 4.86 (d, *J* = 11.3 Hz, 1H), 4.69–4.64 (m, 1H), 4.57–4.50 (m, 2H), 4.45–4.40 (m, 3H), 4.23 (s, 1H), 3.97–3.95 (m, 1H), 3.79 (t, *J* = 9.5 Hz, 1H), 3.67–3.54 (m, 6H), 3.22–3.20 (m, 1H), 3.04–2.98 (m, 1H), 2.46 (d, *J* = 10.3 Hz, 1H), 1.40 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 172.3, 171.8, 155.3, 138.3, 138.2, 137.9, 137.7, 136.7, 129.2, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 127.3, 126.8, 92.6, 80.0, 79.8, 76.2, 75.5, 74.5, 73.4, 70.9, 68.6, 52.5, 49.1, 45.8, 28.3; HRMS (ESI-QTOF) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>44</sub>H<sub>52</sub>N<sub>2</sub>O<sub>10</sub>Na 791.3520; Found 791.3516.

### **3,4,6-Tri-O-benzyl-2-(1-amino-2-methoxy-2-oxoethyl)-1,2-dideoxy-β-D-glucopyranos-1-yl N-[(2-methyl-2-propanyl)oxy]carbonyl}-L-prolinate (4c)**

Yield 78%; Gummy colourless;  $R_f = 0.6$  (hexanes/EtOAc, 3:7);  $[\alpha]_D^{25} -4.1$  (*c* 3, CHCl<sub>3</sub>); IR (Neat): 3358, 2927, 1709, 1163, 1104, 1054, 751, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.38–7.20 (m, 15 H), 5.26–

5.21 (m, 2H), 4.92 (d,  $J = 11.5$  Hz, 1H), 4.76 (d,  $J = 9.63$  Hz, 1H), 4.61–4.43 (m, 5H), 4.37 (d,  $J = 6.2$  Hz, 1H), 3.99–3.86 (m, 2H), 3.77–3.48 (m, 9H), 2.55–2.53 (m, 1 H), 2.26–2.04 (m, 3 H), 1.9 (bs, 1H), 1.47 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 172.8, 171.9, 154.9, 138.5, 137.8, 128.9, 128.5, 128.4, 128.3, 127.9, 127.7, 127.4, 127.0, 92.8, 81.0, 79.6, 75.8, 74.5, 73.4, 71.0, 68.5, 61.6, 52.3, 48.7, 46.9, 45.7, 31.4, 28.5, 22.9, 23.5; HRMS (ESI–QTOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd. for  $\text{C}_{40}\text{H}_{50}\text{N}_2\text{O}_{10}\text{Na}$  741.3363; Found 741.3403.

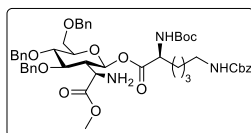
**3,4,6-tri-*O*-benzyl-2-(1-amino-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-galactopyranos-1-yl N-[[2-methyl-2-propanyl]oxy]carbonyl-L-alaninate (4d)**



Yield 72%; Gummy;  $R_f = 0.6$  (hexanes/EtOAc, 5:5);  $[\alpha]_D^{25} +48.1$  ( $c$  2,  $\text{CHCl}_3$ ); IR (Neat): 3839, 3751, 2923, 2112, 1733, 1716, 1522, 1095, 1059, 1028, 748  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR

(400 MHz,  $\text{CDCl}_3$ ): 7.40–7.26 (m, 15H), 5.55 (d, 1H,  $J = 8.7$  Hz), 4.6 (s, 1H), 4.45 (d, 1H,  $J = 2.8$  Hz), 4.64 (d, 1H,  $J = 11.9$  Hz), 4.26–4.22 (m, 1H), 4.03(d, 1H,  $J = 2.1$  Hz), 3.82 (s, 3H), 3.69–3.63 (m, 2H), 3.58–3.51(m, 2H), 2.94–2.89 (m, 1H), 1.43 (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 170.8, 154.6, 138.3, 137.7, 137.0, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 92.3, 76.6, 74.7, 74.3, 73.5, 71.5, 70.2, 67.8, 58.0, 53.4, 52.7, 42.7, 29.7, 28.3; HRMS (ESI–QTOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{38}\text{H}_{48}\text{N}_2\text{O}_{10}\text{Na}$  715.3207; Found 715.3217.

**3,4,6-tri-*O*-benzyl-2-(1-amino-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranos-1-yl N<sup>6</sup>-[(benzyloxy)carbonyl]-N<sup>2</sup>-[[2-methyl-2-propanyl]oxy]carbonyl-L-lysinate (4e)**



Yield 69%; Gummy;  $R_f = 0.4$  (EtOAc);  $[\alpha]_D^{25} +23.2$  ( $c$  3.5,  $\text{CHCl}_3$ ); IR (Neat): 3359, 2931, 1713, 1519, 1366, 1252, 1165, 1134, 1066, 738, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.36–7.19 (m, 20 H), 5.29–5.03 (m, 6H), 4.89 (d,  $J = 11.4$  Hz, 1H),

4.76 (d,  $J = 11.4$  Hz, 1H), 4.58–4.43 (m, 4H), 4.11–4.1 (m, 1H), 4.01–3.99 (m, 1H), 3.91–3.87 (m, 1H), 3.70–3.57 (m, 6H), 3.18–3.13 (m, 2H), 2.51–2.47 (m, 1H), 2.02–2.00 (m, 1H), 1.85 (bs, 1H), 1.74–1.72 (m, 1H), 1.49–1.26 (m, 11H), 1.29–1.2 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 172.4492, 172.1, 156.7, 155.6, 138.3, 138.0, 137.7, 137.6, 136.5, 128.7, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.5, 127.3, 92.7, 79.9, 79.8, 77.2, 76.4, 75.6, 74.9, 74.6, 73.4, 71.1, 68.7, 68.5, 66.6, 55.0, 52.5,

48.9, 45.9, 40.3, 31.8, 31.6, 29.5, 28.4, 28.3, 22.3; HRMS (ESI-QTOF)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{49}H_{61}N_3O_{12}Na$  906.4153; Found 906.4157.

**3,4,6-Tri-*O*-benzyl-2-(1-amino-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-galactopyranos-1-yl N-[[2-methyl-2-propanyl]oxy]carbonyl]-L-valinate (4f)**

Yield 73 %; Gummy;  $R_f$  = 0.5 (EtOAc);  $[\alpha]^{25}_D$  +13.4 ( $c$  1.3,  $CHCl_3$ ); IR (Neat): 2929, 1738, 1366, 1161, 1089, 738, 751  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 7.37–7.19 (m, 15H), 5.23 (s, 2H), 4.96–4.88 (m, 2H), 4.77 (d,  $J$  = 9.7 Hz, 1H), 4.6–4.47 (m, 5H), 4.06–3.99 (m, 2H), 3.92–3.87 (m, 1H), 3.74–3.63 (m, 8H), 2.56–2.53 (m, 1H), 2.367–2.35 (m, 1H), 1.47 (s, 9H), 1.01 (d,  $J$  = 6.73 Hz, 3H), 0.95 (d,  $J$  = 6.8 Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ): 172.1, 172.1, 155.8, 138.2, 138.0, 137.8, 137.7, 128.6, 128.4, 128.4, 128.3, 127.9, 127.9, 127.7, 127.6, 127.4, 92.9, 79.9, 76.4, 75.6, 74.7, 73.5, 71.2, 68.8, 60.3, 52.4, 49.0, 45.9, 30.2, 29.7, 28.4, 19.5; HRMS (ESI-QTOF)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{40}H_{52}N_2O_{10}Na$  743.3520; Found 743.3524.

**3,4,6-Tri-*O*-benzyl-2-(1-amino-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-galactopyranos-1-yl N-[(benzyloxy)carbonyl]-L-valinate (4g)**

Yield 68%; Gummy;  $R_f$  = 0.4 (hexanes/EtOAc, 9:1);  $[\alpha]^{25}_D$  –7.70 ( $c$  1.2,  $CHCl_3$ ); IR (Neat): 3374, 2932, 1733, 1253, 1065, 838  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 7.34–7.26 (m, 5H), 5.49 (d,  $J$  = 8.6 Hz, 1H), 5.13–5.00 (m, 5H), 4.36–4.34 (m, 1H, ), 4.19–4.01(m, 4H), 4.01–3.71 (m, 9H), 2.39–2.36 (m, 1H), 2.19–1.99 (m, 2H), 0.93–0.90 (m, 27H), 0.17–0.07 (m, 18H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ): 172.0, 171.4, 156.3, 136.3, 128.4, 127.9, 92.1, 74.7, 72.9, 70.9, 66.8, 62.4, 60.0, 52.6, 50.1, 46.7, 31.5, 25.9, 25.8, 25.8, 19.1, 18.3, 18.1, 18.1, –2.8, –2.9, –3.4, –5.3, –5.4; HRMS (ESI-QTOF)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{40}H_{74}N_2O_{10}Si_3Na$  849.4549; Found 849.4551.

**(S)-2-Carbmethoxy-2-([[(2-methyl-2-propanyl)oxy]carbonyl]amino)ethyl 3,4,6-tri-*O*-benzyl-2-(1-amino-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranoside (4i)**

Yield: 74%; Gummy;  $R_f$  = 0.5 (hexanes/EtOAc, 5:5);  $[\alpha]^{25}_D$  +11.02 ( $c$  2.5,  $CHCl_3$ ); IR (neat): 3374, 2931, 1757, 1728, 1715, 1514, 1366, 1165, 1056, 751, 738, 699  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 7.34–7.21 (m, 15H), 6.09 (d,  $J$  = 9 Hz, 1H), 4.92 (d,  $J$  = 11.6 Hz, 1H), 4.82 (d,  $J$  = 10.9 Hz, 1H), 4.69–4.53 (m, 4H),

4.39–4.32 (m, 2H), 3.74–3.63 (m, 11H), 3.48 (dd,  $J = 3.4, 9.6$  Hz, 1H), 3.39–3.37 (m, 1H), 2.24–2.20 (m, 1H), 1.46 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 177.5, 170.4, 155.5, 138.1, 138.0, 128.5, 128.4, 127.8, 127.6, 100.7, 79.8, 79.5, 78.2, 75.0, 74.6, 74.4, 73.5, 69.9, 68.4, 53.6, 52.3, 50.1, 49.8, 28.34; HRMS (ESI-QTOF)  $m/z$ :  $[\text{M}+\text{Na}]$  Calcd for  $\text{C}_{39}\text{H}_{50}\text{N}_2\text{O}_{11}\text{Na}$  745.3312; Found 745.3322.

**(S)-2-Phenyl-2-(((2-methyl-2-propanyl)oxy)carbonyl)amino)ethyl 3,4,6-tri-*O*-benzyl-2-(1-amino-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranoside (4j)**

Yield: 72%; Gummy;  $R_f = 0.5$  (hexanes/EtOAc, 5:5);  $[\alpha]^{25}_{\text{D}} +5.5$  ( $c$  2,  $\text{CHCl}_3$ ); IR (Neat): 3615, 3385, 2928, 1733, 1716, 1508, 1364, 1170, 1049, 752, 699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.34–7.20 (m, 20H), 5.89 (s, 1H), 4.91 (d,  $J = 11.5$  Hz, 1H), 4.81 (d,  $J = 10.9$  Hz, 1H), 4.69–4.54 (m, 5H), 4.34 (d,  $J = 8.4$  Hz, 1H), 3.89 (dd,  $J = 10.7, 3.4$  Hz, 1H), 3.74–3.60 (m, 6H), 3.50 (s, 3H), 3.39–3.37 (m, 1H), 2.24–2.20 (m, 1H), 1.38 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 176.9, 155.5, 140.3, 138.3, 138.2, 138.1, 128.8, 128.6, 128.5, 128.41, 128.36, 128.31, 128.0, 127.9, 127.83, 127.80, 127.7, 127.2, 126.6, 126.57, 100.6, 80.0, 79.9, 79.2, 78.4, 75.1, 74.7, 74.6, 73.6, 73.3, 68.8, 52.0, 50.4, 49.9, 28.4, 28.37; HRMS (ESI-QTOF)  $m/z$ :  $[\text{M}+\text{Na}]$  Calcd for  $\text{C}_{43}\text{H}_{52}\text{N}_2\text{O}_9\text{Na}$  763.3571; Found: 763.3589.

**3-Phenyl-2-(S)-(((2-methyl-2-propanyl)oxy)carbonyl)amino)propyl 3,4,6-tri-*O*-benzyl-2-(1-amino-2-methoxy-2-oxoethyl)-1,2-dideoxy- $\beta$ -D-glucopyranoside (4k)**

Yield: 69%; Gummy;  $R_f = 0.4$  (hexanes/EtOAc, 5:5);  $[\alpha]^{25}_{\text{D}} -6.43$  ( $c$  4,  $\text{CHCl}_3$ ); IR (Neat): 3390, 2929, 1737, 1711, 1497, 1365, 1168, 1051, 738, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.35–7.15 (m, 20H), 5.33 (s, 1H), 4.93 (d,  $J = 11.4$  Hz, 1H), 4.83 (d,  $J = 10.8$  Hz, 1H), 4.71–4.60 (m, 3H), 4.53 (d,  $J = 11.4$  Hz, 1H), 4.42 (d,  $J = 8.7$  Hz, 1H), 3.78–3.65 (m, 10H), 3.46–3.40 (m, 2H), 2.9–2.76 (m, 2H), 2.35–2.29 (m, 1H), 1.39 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 176.6, 155.3, 138.5, 138.2, 138.0, 129.4, 128.3, 128.5, 128.4, 128.0, 127.85, 127.8, 127.6, 126.2, 101.0, 79.9, 78.9, 78.4, 75.0, 74.7, 74.5, 73.5, 70.4, 68.6, 52.1, 50.4, 50.0, 28.4; HRMS (ESI-QTOF)  $m/z$ :  $[\text{M}+\text{Na}]$  Calcd for  $\text{C}_{44}\text{H}_{54}\text{N}_2\text{O}_9$  777.3727; Found 777.3721.

## Synthesis of glycosyl amino acid (5 & 6) by deprotection of NHBoc

### Method A: Use of trifluoroacetic acid

To a cold solution of N-Boc protected amine, **3a** (0.1 mmol) in 3 mL of 10% trifluoroacetic acid (TFA) in CH<sub>2</sub>Cl<sub>2</sub> was added at an ice-cold temperature and the reaction mixture was stirred for 3 h. After the disappearance of starting material, the solvent was removed under vacuum followed by dilution with 20 mL of EtOAc. The organic layer was thoroughly washed with water. To the organic layer, 20 mL of saturated NaHCO<sub>3</sub> solution was added and left for stirring for 3 h. The organic layer was then separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The filtrate was concentrated and the crude product was purified by column chromatography on amine pre-treated silica gel (0.5 ml of Et<sub>3</sub>N for 50 gr of silica gel) using EtOAc and petroleum ether of appropriate composition to furnish free amine derivative of glycosyl amino acids (**5** and **6**).

### Method B: Use of trimethylsilyl chloride

To an ice-cold solution of N-Boc protected amine, **3a**, (0.2 mmol) in 3 mL of in CH<sub>2</sub>Cl<sub>2</sub>, trimethylsilyl chloride (1 mmol) was added at ice-cold temperature and the reaction mixture was stirred for 8–12 h. After disappearance of starting material, the reaction mixture was diluted with 20 mL of EtOAc. The organic layer was thoroughly washed with water. To the organic layer, 20 mL of saturated NaHCO<sub>3</sub> solution was added and left for stirring for 3 h. The organic layer was then separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The filtrate was concentrated and the crude product was purified by column chromatography on amine pre-treated silica gel (0.5 ml of Et<sub>3</sub>N for 50 gr of silica gel) using EtOAc and petroleum ether of appropriate composition to furnish free amine derivative of glycosyl amino acid.

**(S)-2-Phenyl-2-aminoethyl 3,4,6-tri-O-benzyl-2-(1-azido-2-methoxy-2-oxoethyl)-1,2-dideoxy-β-D-glucopyranoside (6)**

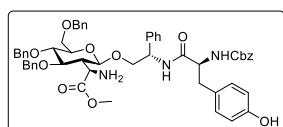
Yield: 66 %; Gummy;  $R_f = 0.4$  (hexanes/EtOAc, 5:5); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.4–7.2 (m, 15H), 4.97 (d,  $J = 11.6$  Hz, 1H, ), 4.81 (d,  $J = 11.0$  Hz, 1H), 4.66–4.58 (m, 4H), 4.46 (d,  $J = 8.4$  Hz, 1H), 4.3 (d,  $J =$

1.72 Hz, 1H), 4.12–4.1 (m, 1H), 3.94–3.6 (m, 13H), 3.38–3.30 (m, 1H), 2.42–2.38 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 171.2, 141.6, 137.9, 137.8, 137.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.8, 127.6, 127.4, 126.9, 100.5, 79.8, 78.6, 76.7, 75.2, 74.9, 74.7, 73.5, 68.4, 58.3, 55.5, 52.5, 48.9; HRMS (ESI–QTOF)  $m/z$ :  $[\text{M}+\text{Na}]$  Calcd for  $\text{C}_{38}\text{H}_{42}\text{N}_4\text{O}_7$  688.2873; Found 688.2890.

## Synthesis of glycopeptide

EDC·HCl (1.2 mmol) was added to an ice-cold solution of glycosyl amino acid derivative (0.1 mmol), amino acid (0.13 equiv.), N, N-diisopropylethylamine (2.5 mmol.) and HOBT (1.2 mmol.) in 2 mL of DMF. The reaction mixture was stirred for 10 h. After the disappearance of starting material, the solvent was removed under vacuum followed by dilution with 20 mL of EtOAc. The organic layer was thoroughly washed with 2N HCl solution, followed by water and then with a saturated  $\text{NaHCO}_3$  solution. It was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The filtrate was concentrated and the crude product was purified by column chromatography on silica gel (230–400 mesh) using EtOAc and petroleum ether of appropriate composition to furnish glycopeptides.

### Glycopeptide 8

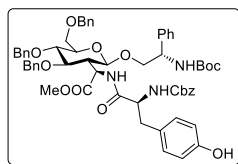


Yield: 65%; Gummy oil;  $R_f = 0.5$  ( $\text{CHCl}_3/\text{MeOH}$ , 8:2);  $[\alpha]_D^{25} +24.7$  ( $c$  0.8,  $\text{CHCl}_3$ );

IR (Neat): 3338, 2925, 1734, 1516, 1455, 1364, 1230, 1104, 752, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$

NMR (400 MHz,  $\text{CDCl}_3$ ): 7.32–7.10 (m, 26H), 6.77 (d,  $J = 7.7$  Hz, 2H), 6.66 (d,  $J = 8.3$  Hz, 1H), 5.60 (d,  $J = 8.1$  Hz, 1H), 5.09 (s, 2H), 4.90 (d,  $J = 12.0$  Hz, 1H), 4.79 (d,  $J = 11.0$  Hz, 1H), 4.78 (d,  $J = 10.9$  Hz, 1H), 4.68 (d,  $J = 12.0$  Hz, 1H), 4.63 (d,  $J = 11.6$  Hz, 1H), 4.53 (d,  $J = 12.0$  Hz, 1H), 4.47 (d,  $J = 11.3$  Hz, 1H), 4.41–4.37 (m, 1H), 3.92 (d,  $J = 8.1$  Hz, 1H), 3.73–3.47 (m, 10H), 3.24–3.11 (m, 2H), 2.89–2.83 (m, 1H), 2.09–2.03 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 170.5, 155.5, 155.3, 138.8, 138.1, 137.8, 137.1, 136.4, 130.5, 128.54, 128.51, 128.47, 128.3, 128.2, 128.0, 127.95, 127.88, 127.1, 126.6, 117.0, 100.7, 79.5, 78.6, 77.2, 74.7, 74.5, 74.1, 73.6, 72.8, 68.6, 66.8, 57.2, 52.4, 52.1, 49.9, 49.6; HRMS (ESI–QTOF)  $m/z$ :  $[\text{M}+\text{Na}]$  Calcd for  $\text{C}_{55}\text{H}_{59}\text{N}_3\text{O}_{11}\text{Na}$  960.4047; Found 960.4045.

## Glycopeptide 9



Yield: 67%; Gummy;  $R_f = 0.6$  ( $\text{CHCl}_3/\text{MeOH}$ , 8:2);  $[\alpha]_D^{25} +1.7$  ( $c$  1.7,  $\text{CHCl}_3$ ); IR

(Neat): 3391, 2928, 1687, 1515, 1498, 1455, 1052, 754, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400

MHz,  $\text{CDCl}_3$ ): 7.32–7.10 (m, 26H), 6.77 (d,  $J = 7.7$  Hz, 2H), 6.66 (d,  $J = 8.3$  Hz, 1H),

5.60 (d,  $J = 8.1$  Hz, 1H), 5.09 (s, 2H), 4.90 (d,  $J = 12.0$  Hz, 1H), 4.79 (d,  $J = 11.0$  Hz, 1H), 4.78 (d,  $J = 10.9$

Hz, 1H), 4.68 (d,  $J = 12.0$  Hz, 1H), 4.63 (d,  $J = 11.6$  Hz, 1H), 4.53 (d,  $J = 12.0$  Hz, 1H), 4.47 (d,  $J = 11.3$

Hz, 1H), 4.41–4.37 (m, 1H), 3.92 (d,  $J = 8.1$  Hz, 1H), 3.73–3.47 (m, 10H), 3.24–3.11 (m, 2H), 2.89–2.83

(m, 1H), 2.09–2.03 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 170.5, 155.5, 155.3, 138.8, 138.1, 137.8, 137.1,

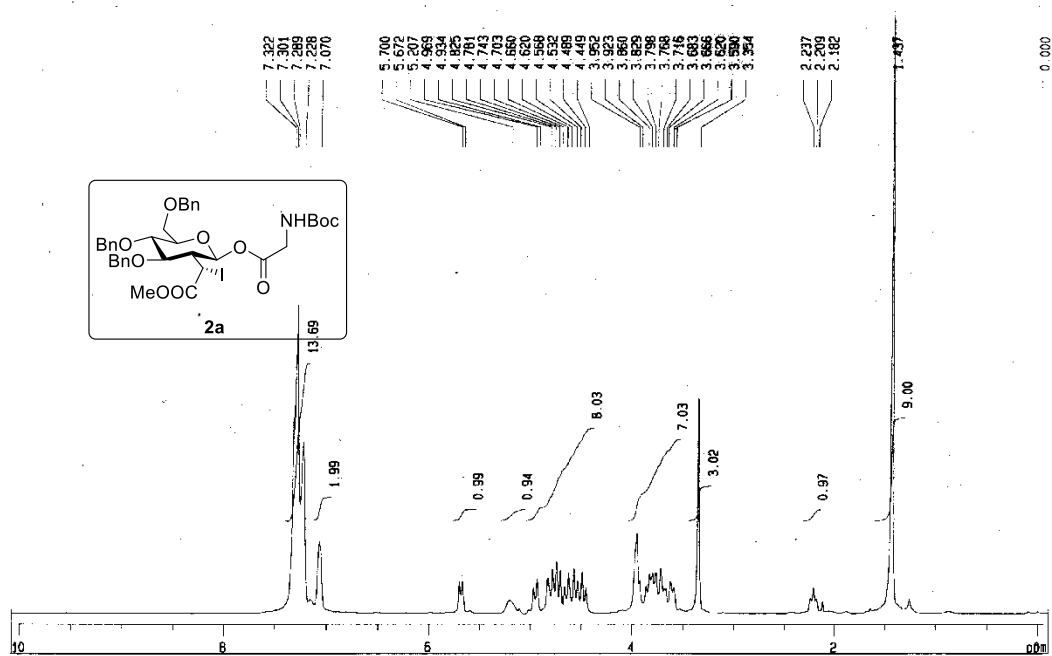
136.4, 130.5, 128.54, 128.51, 128.47, 128.3, 128.2, 128.0, 127.95, 127.88, 127.1, 126.6, 117.0, 100.7, 79.5,

78.6, 77.2, 74.7, 74.5, 74.1, 73.6, 72.8, 68.6, 66.8, 57.2, 52.4, 52.1, 49.9, 49.6; HRMS (ESI-QTOF)  $m/z$ :

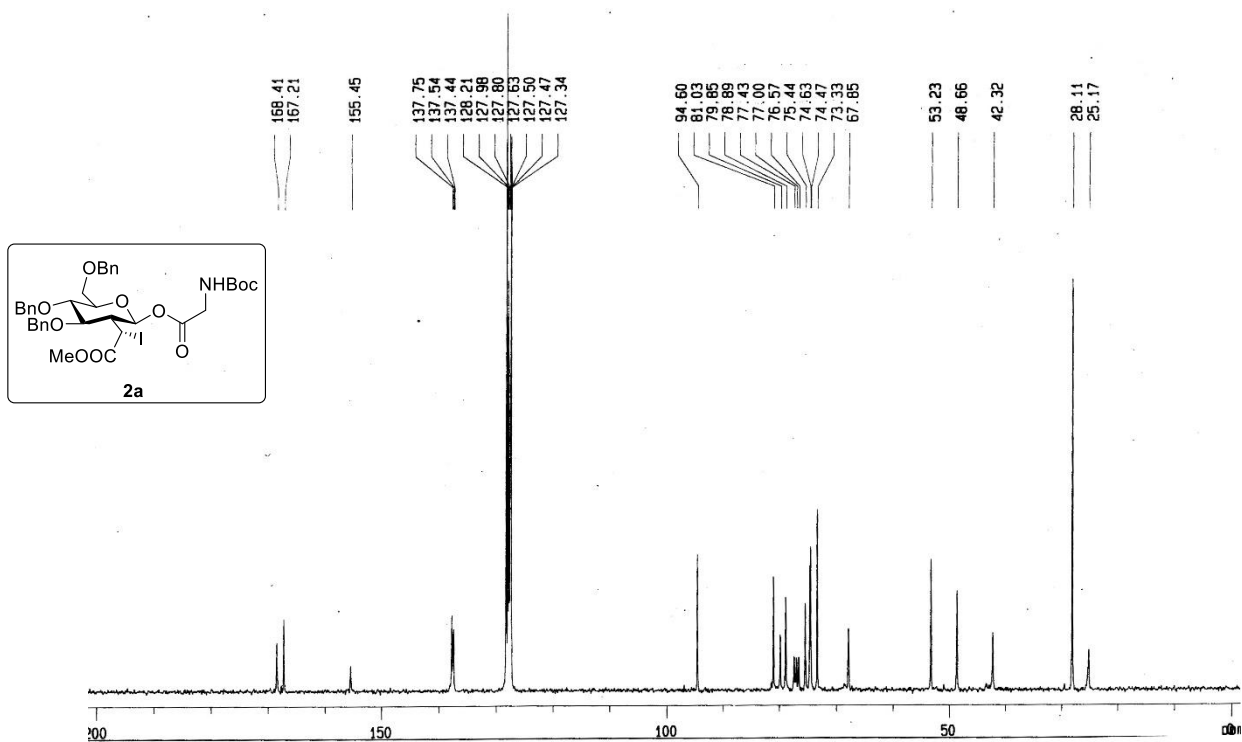
[M+Na] Calcd for  $\text{C}_{60}\text{H}_{67}\text{N}_3\text{O}_{13}\text{Na}$  1060.4572; Found 1060.4518.

# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Iodides 2a–2k

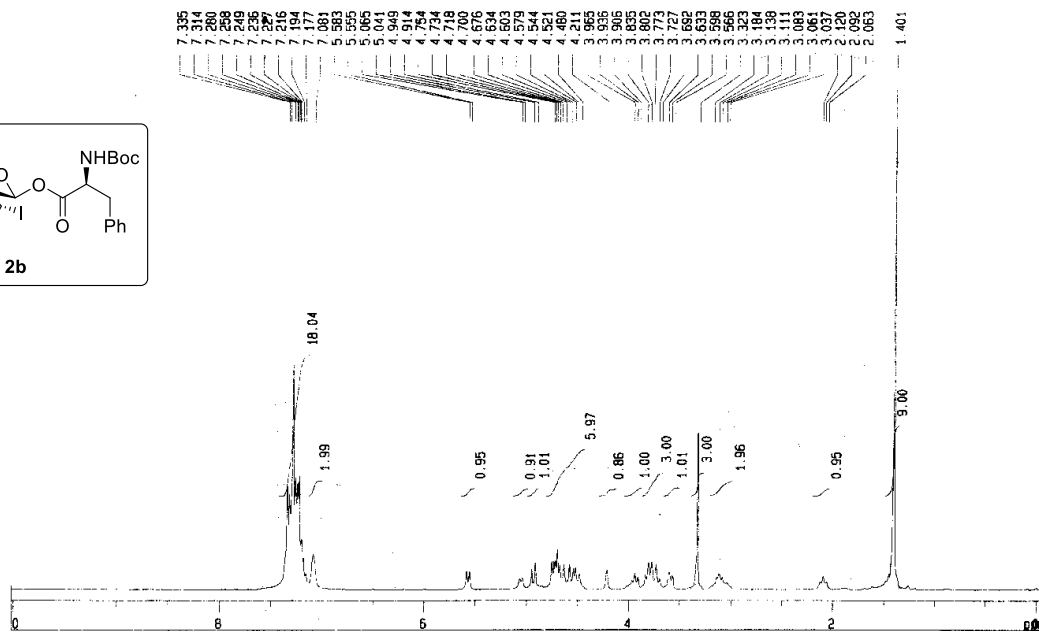
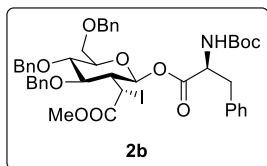
$^1\text{H}$ ,  $\text{CDCl}_3$ , 300 MHz



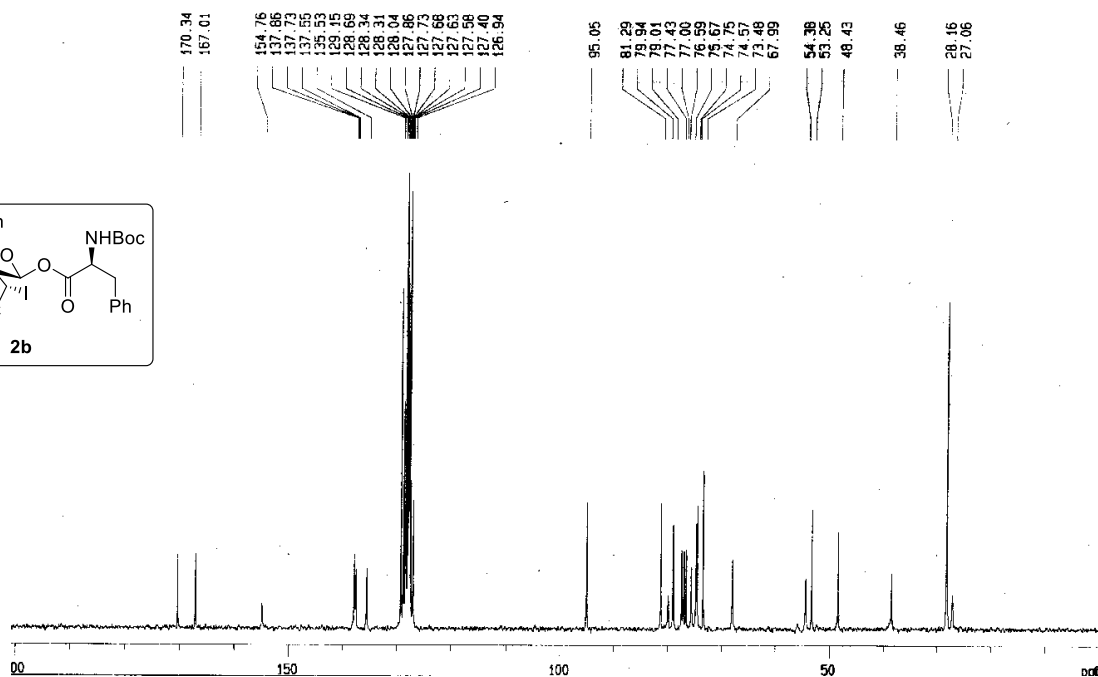
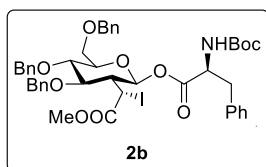
$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 75 MHz



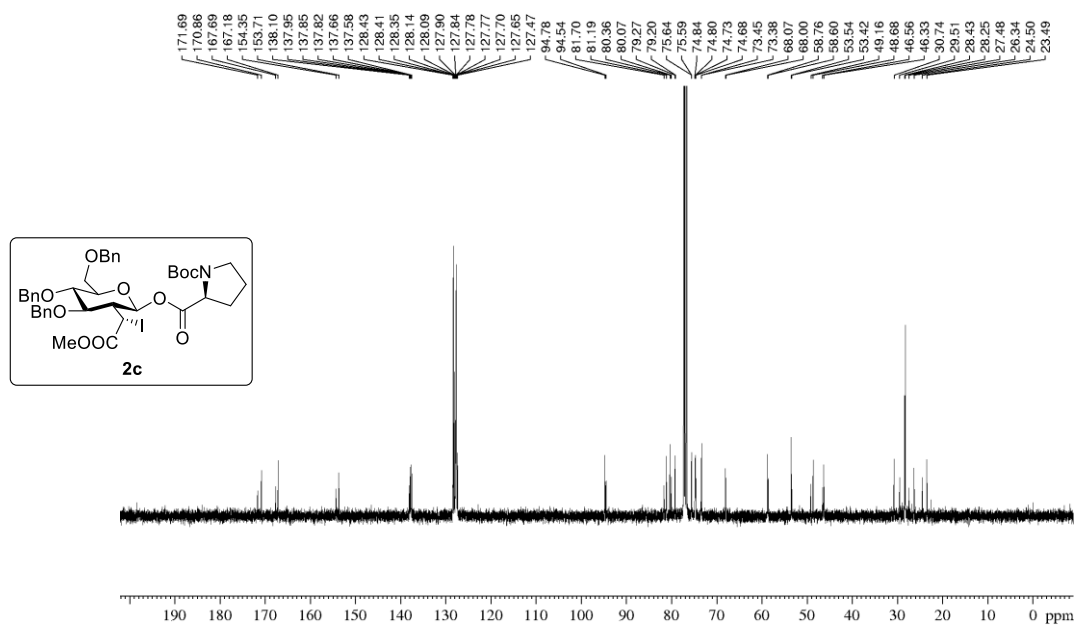
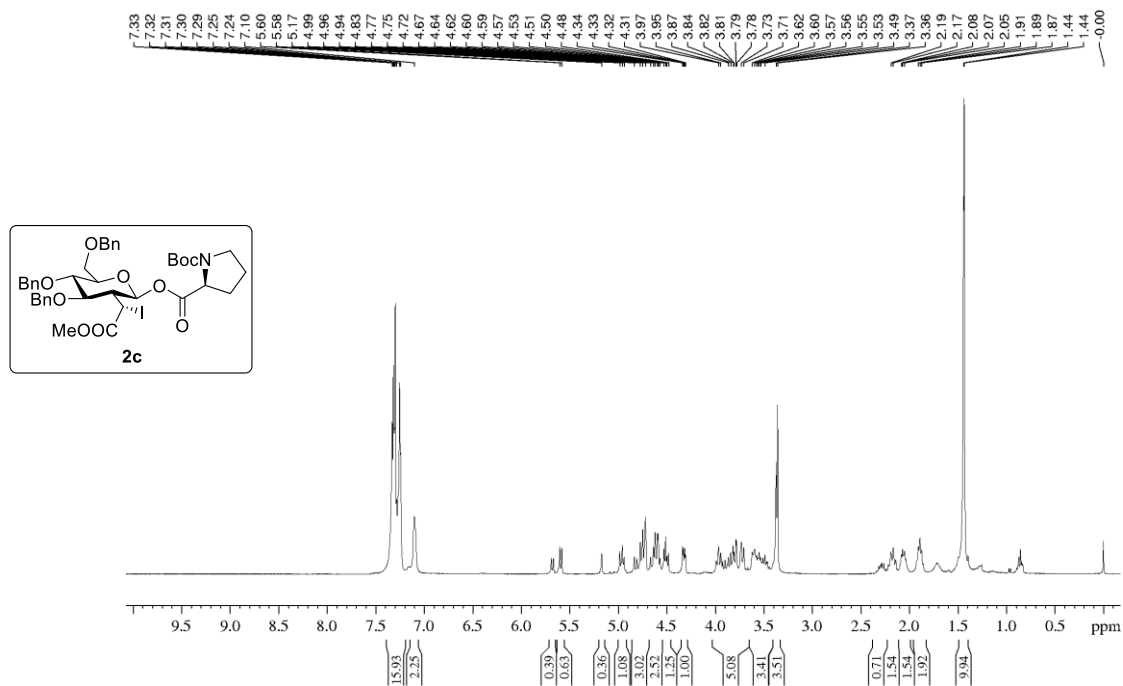
$^1\text{H}$ ,  $\text{CDCl}_3$ , 300 MHz



$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 75 MHz

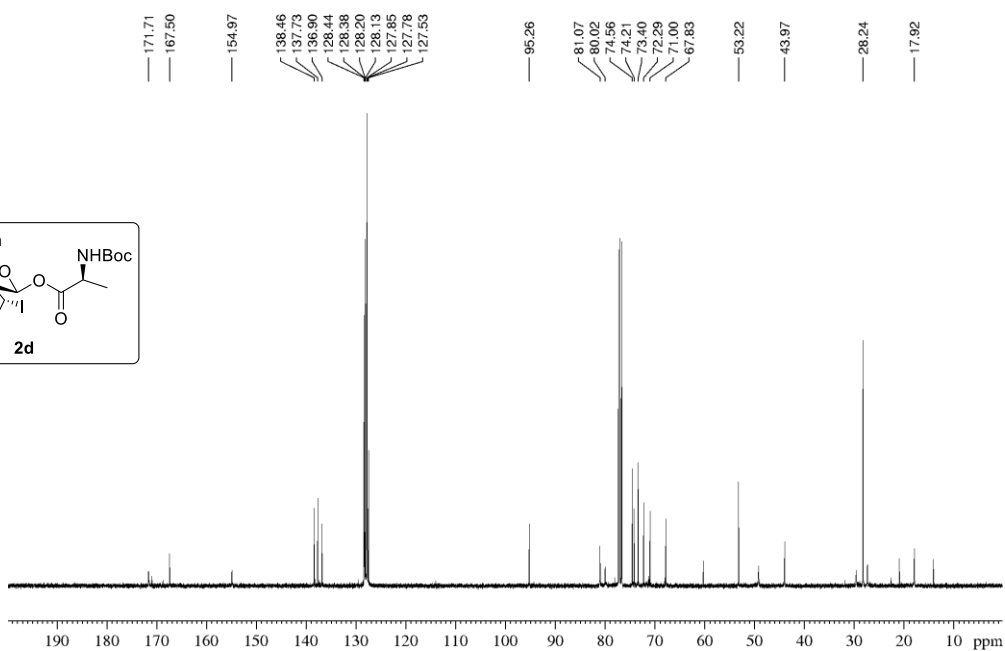
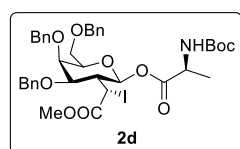
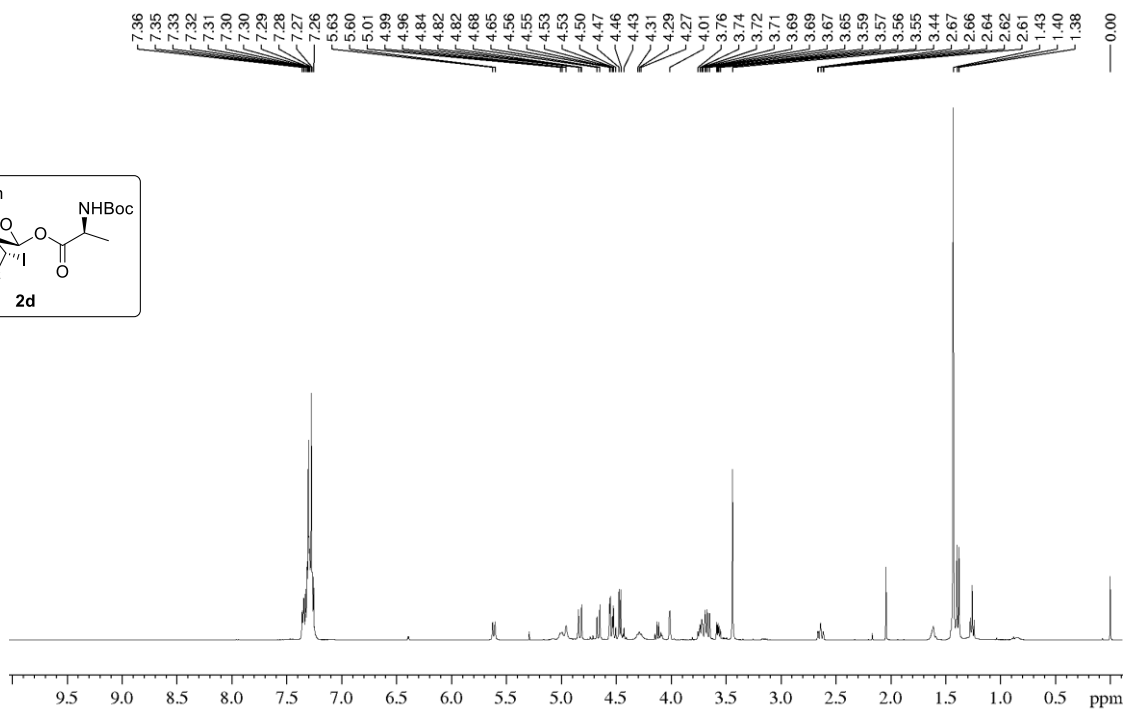
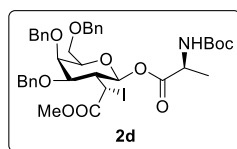


$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



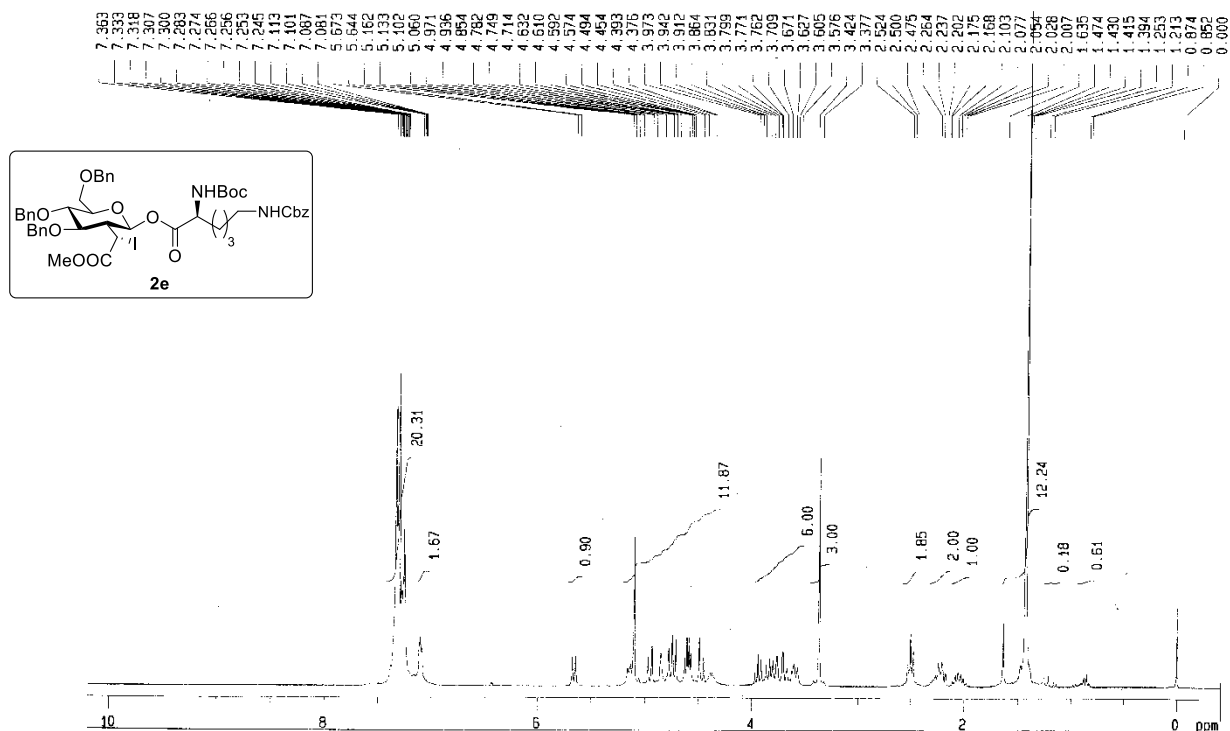
$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz

$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz

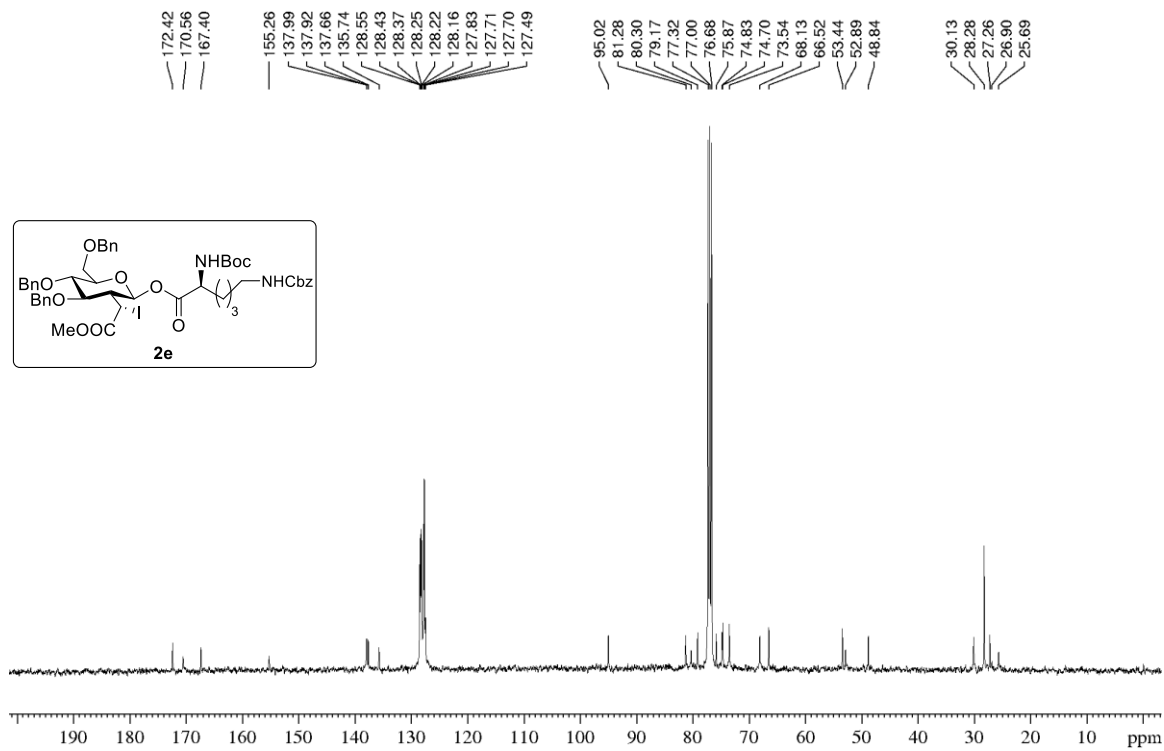


$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz

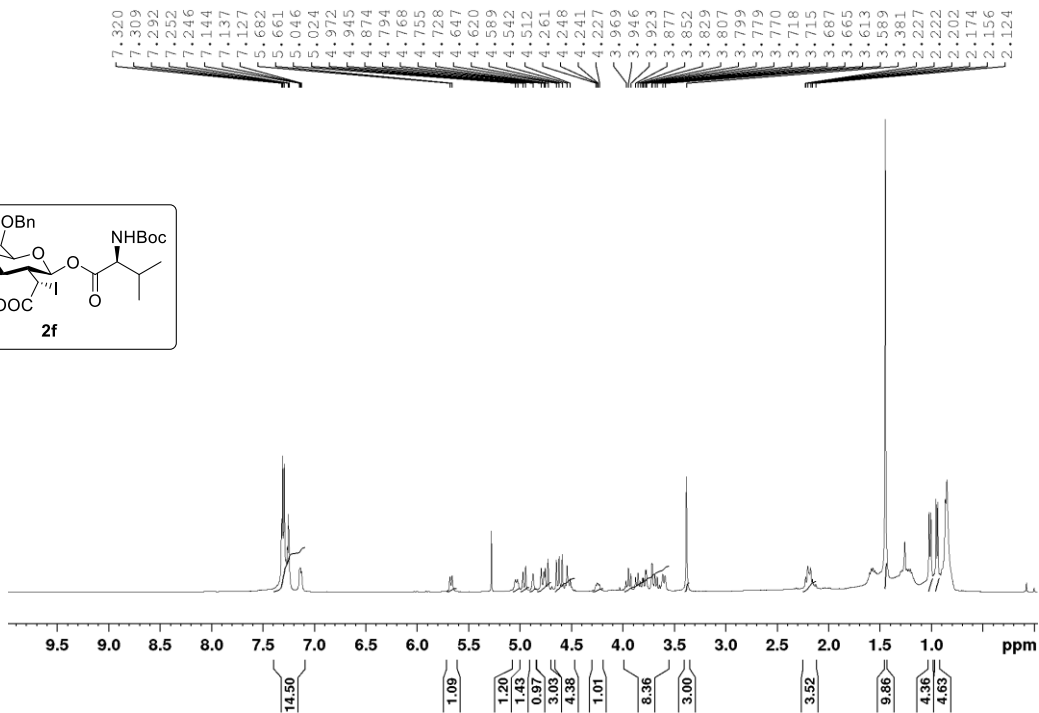
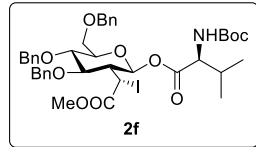
$^1\text{H}$ ,  $\text{CDCl}_3$ , 300 MHz



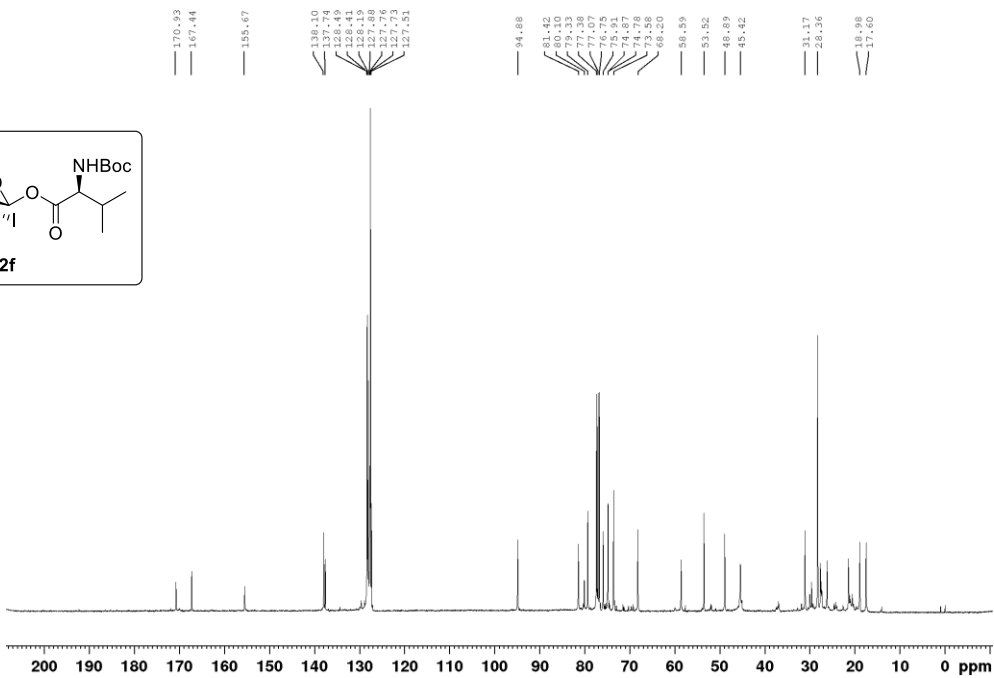
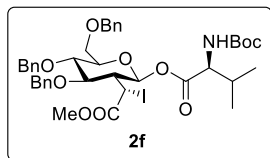
$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz



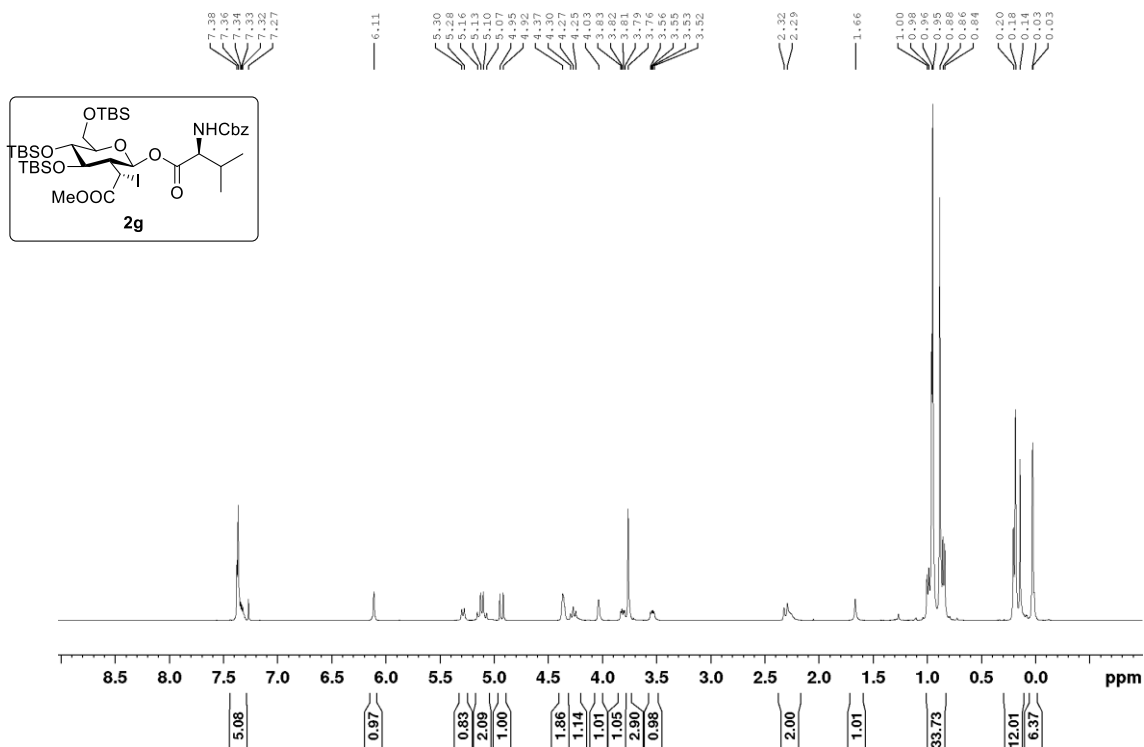
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



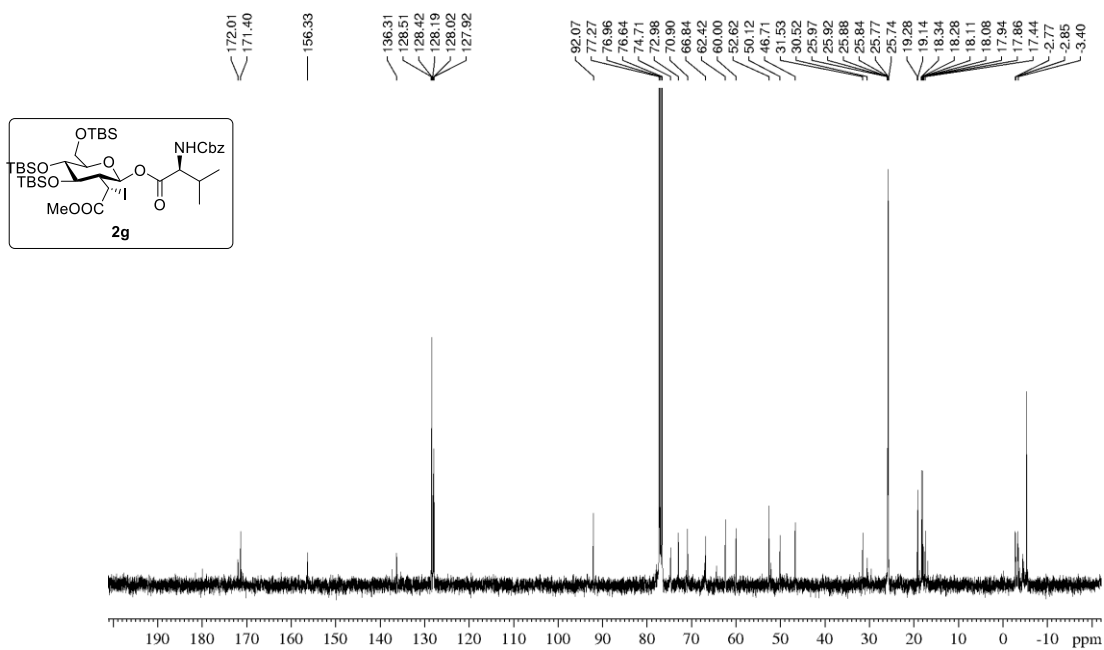
<sup>13</sup>C, CDCl<sub>3</sub>, 100 MHz



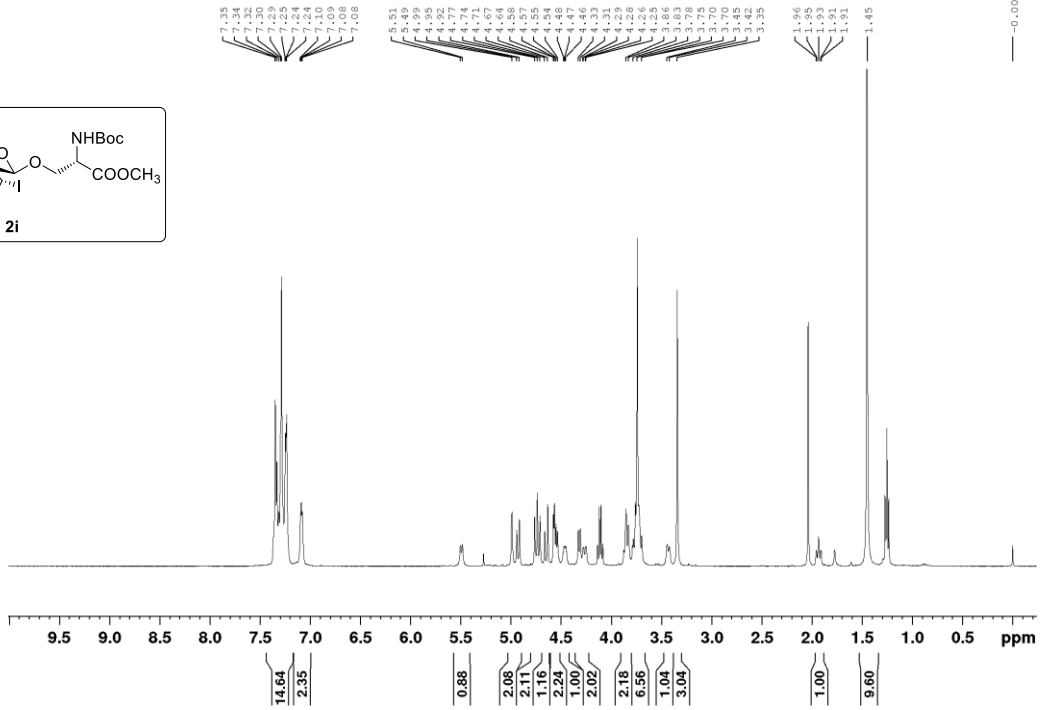
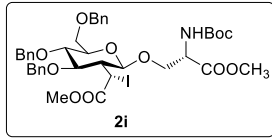
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



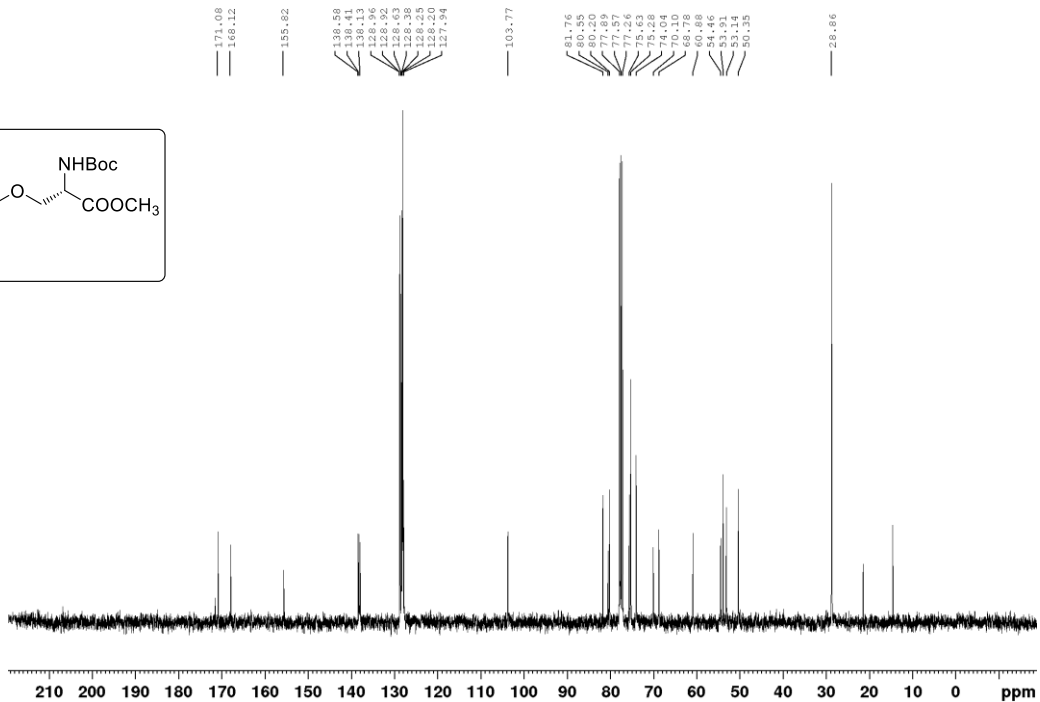
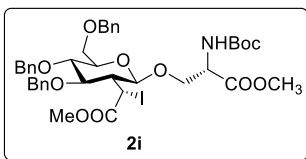
$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz



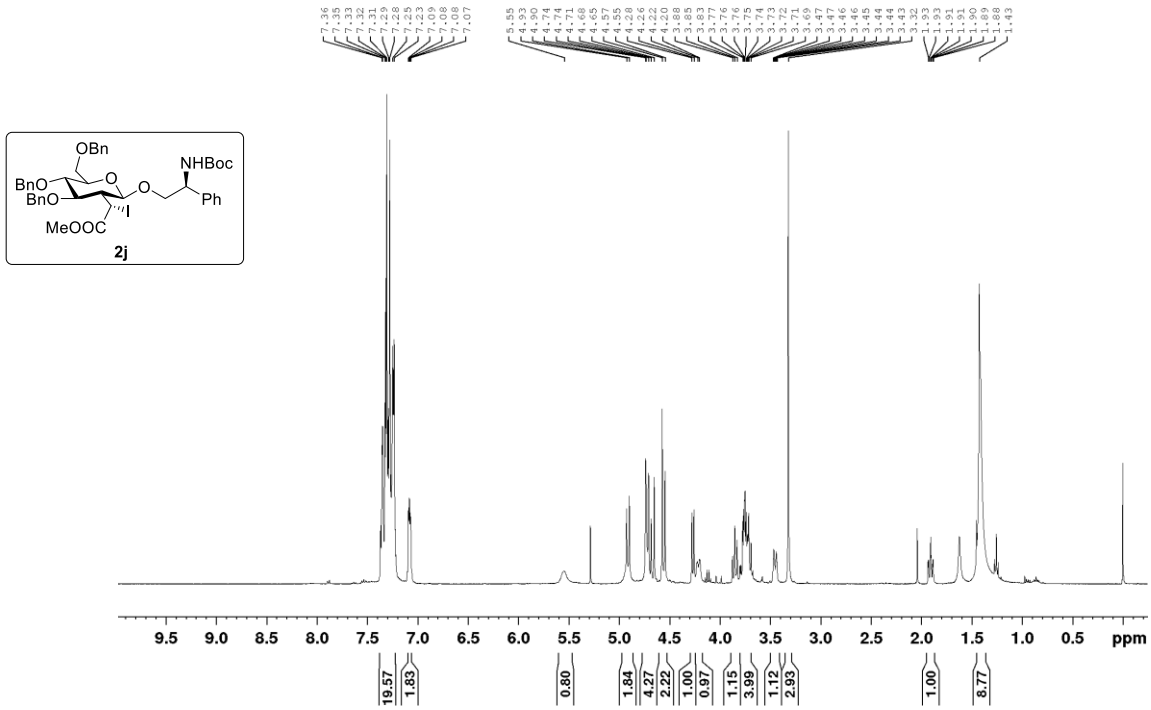
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



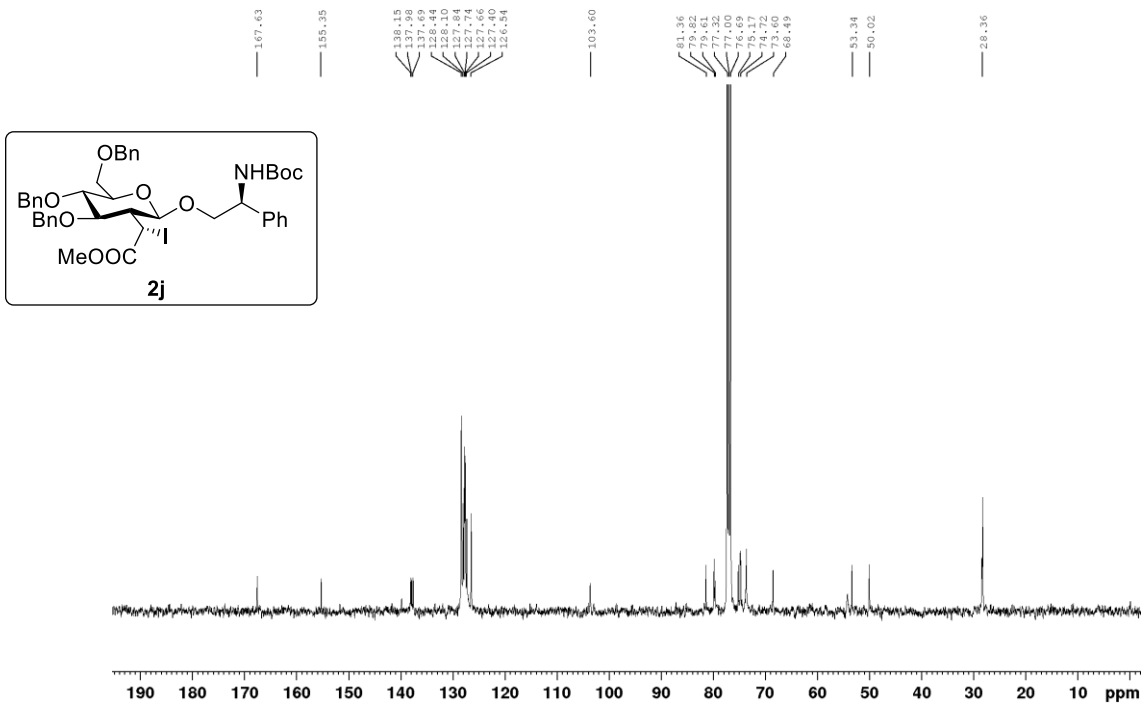
$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz



$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



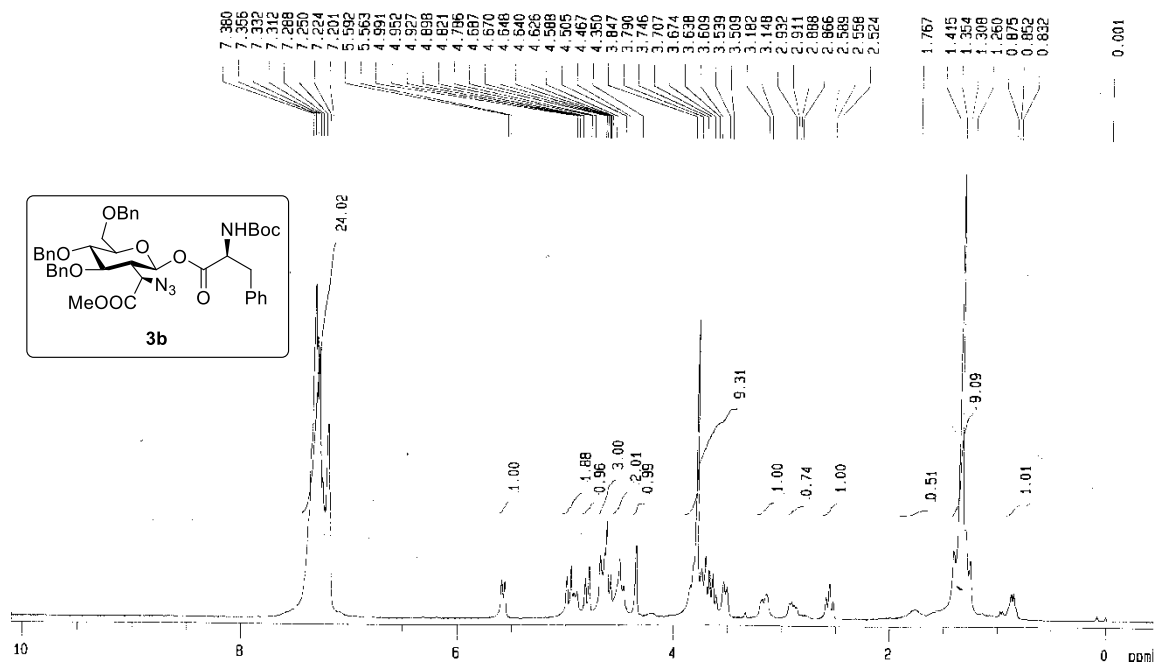
$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz



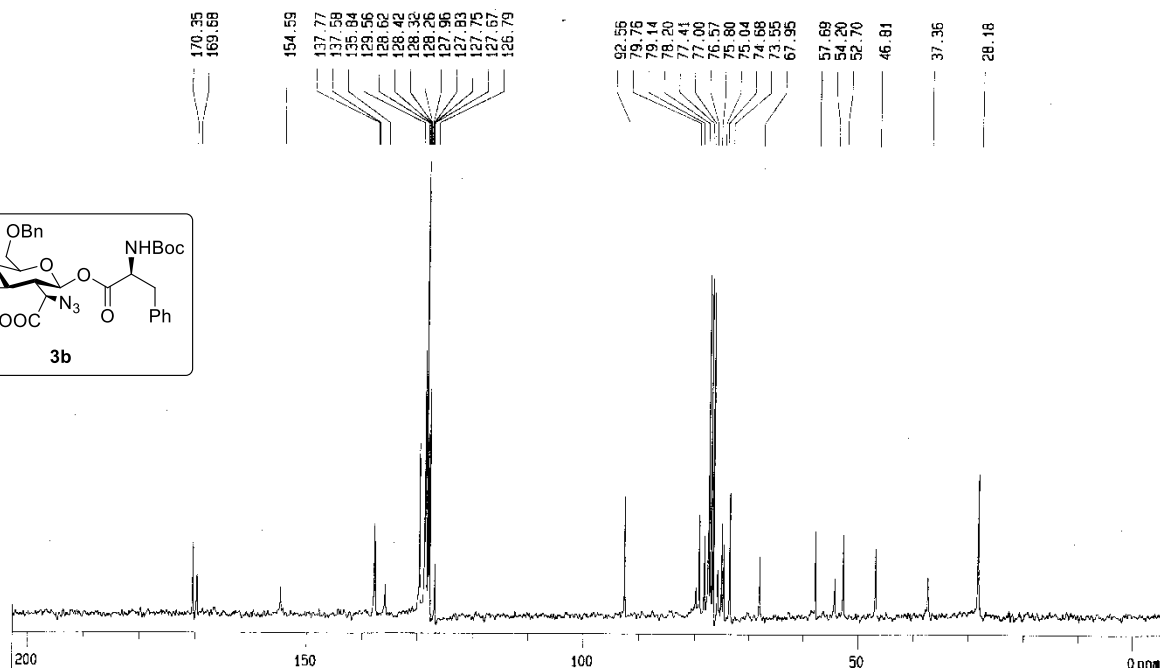




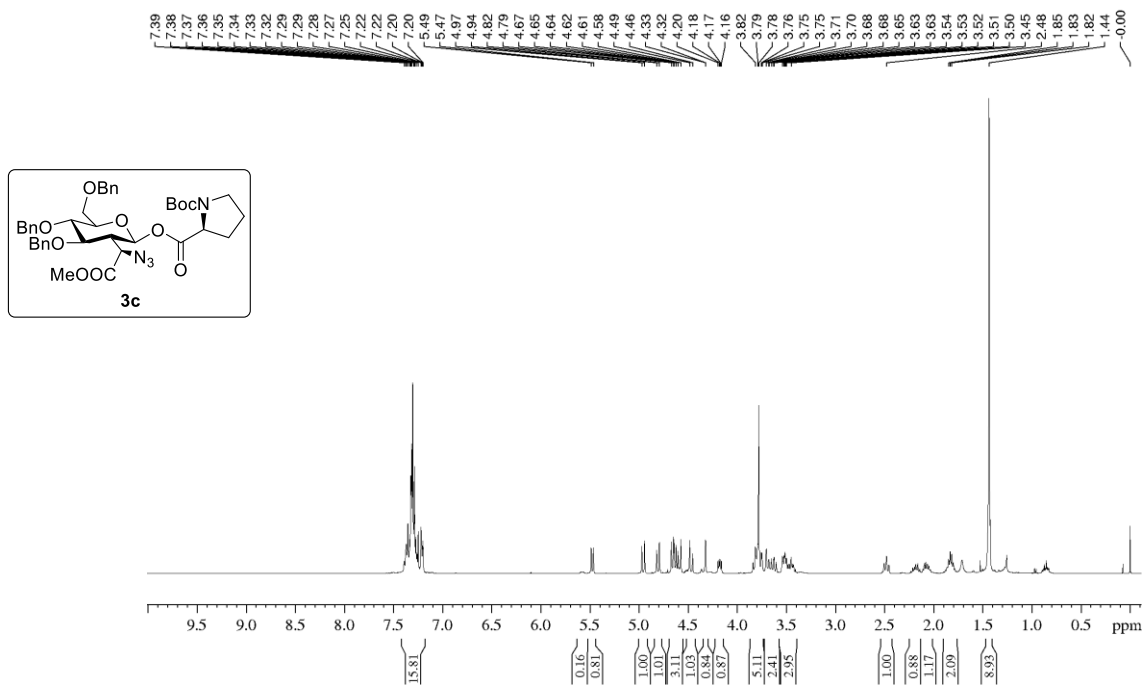
$^1\text{H}$ ,  $\text{CDCl}_3$ , 300 MHz



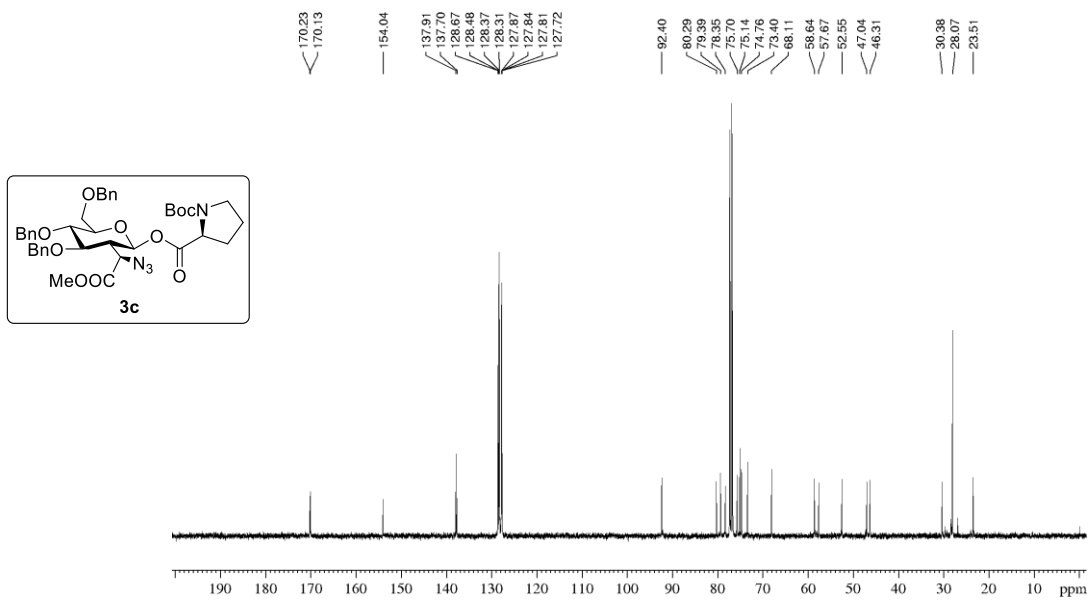
$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 75 MHz



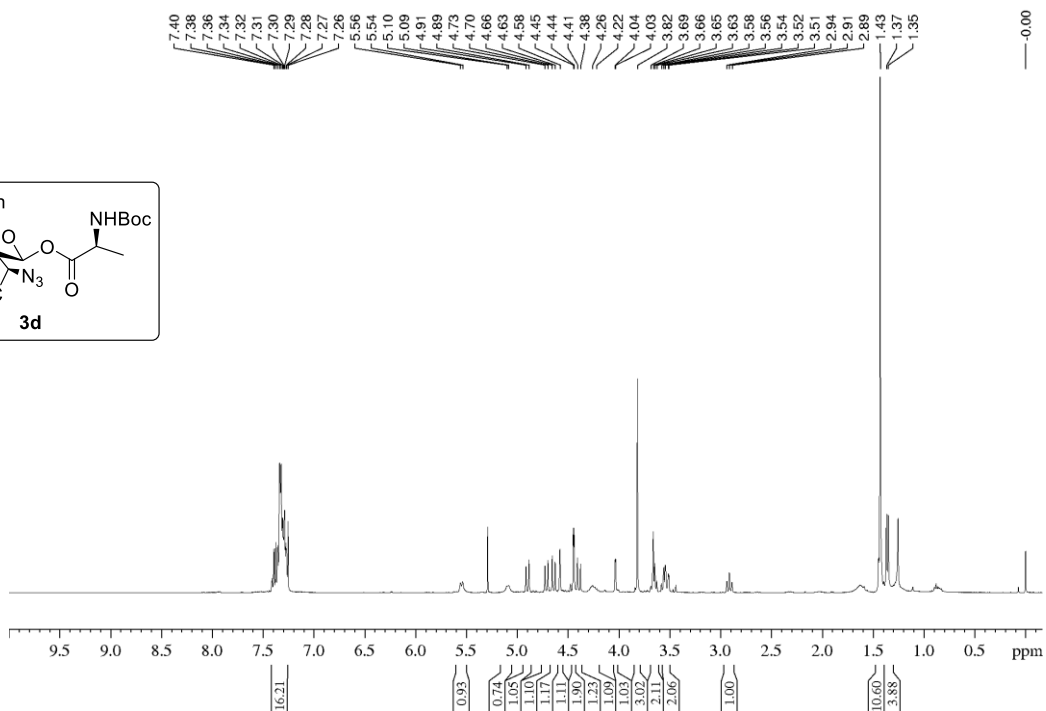
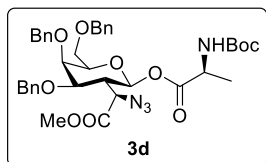
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



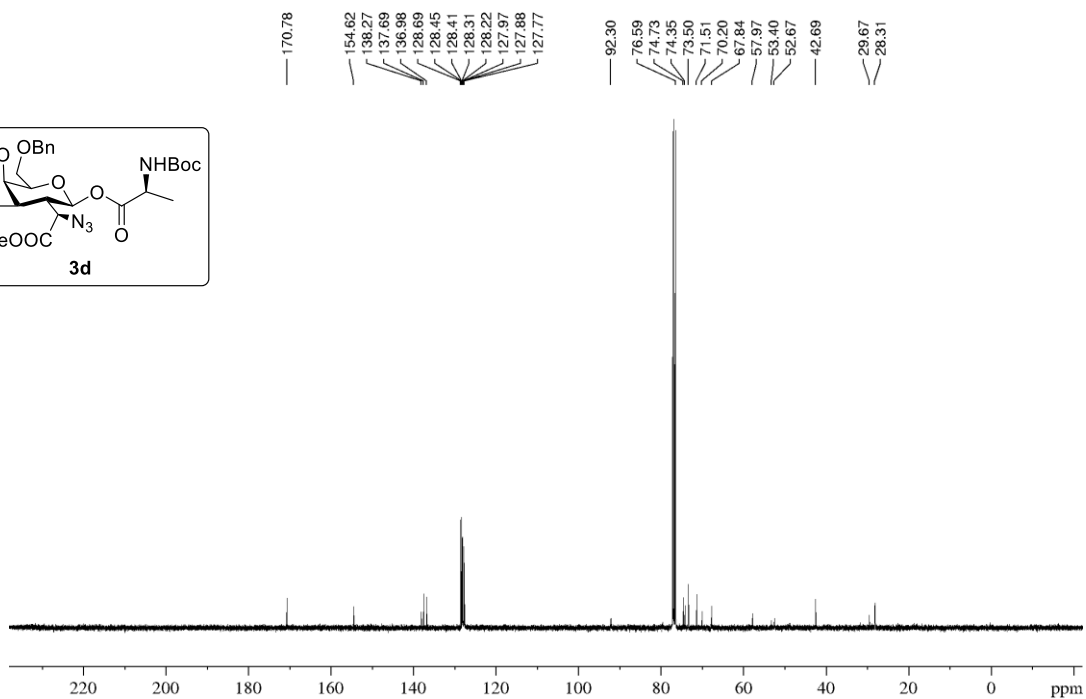
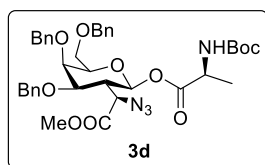
$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz



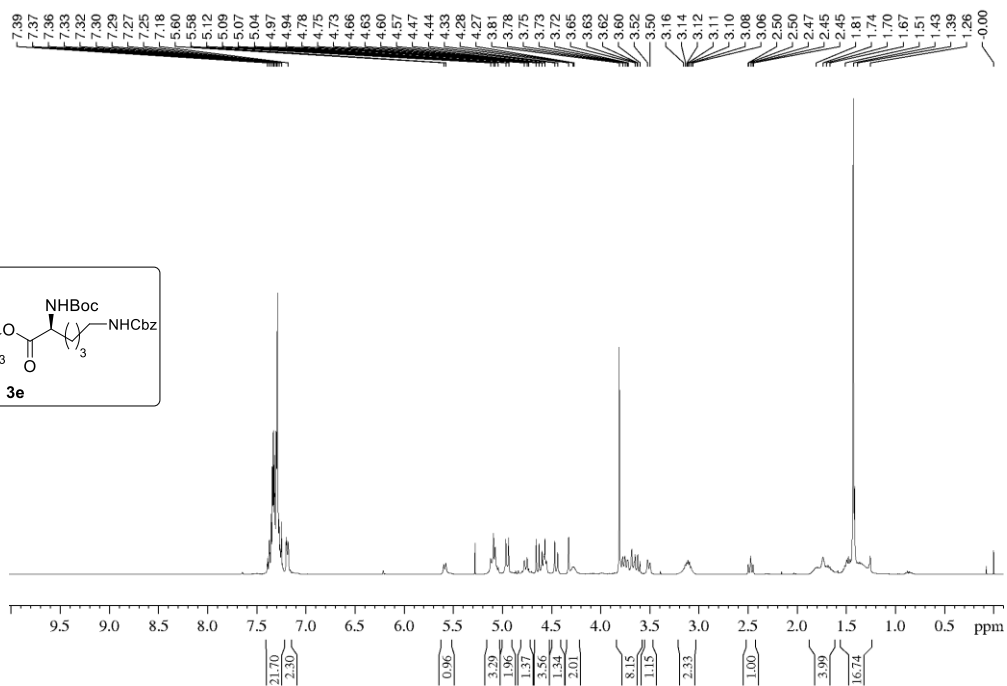
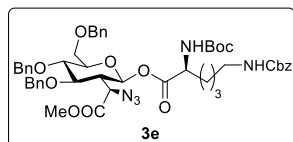
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



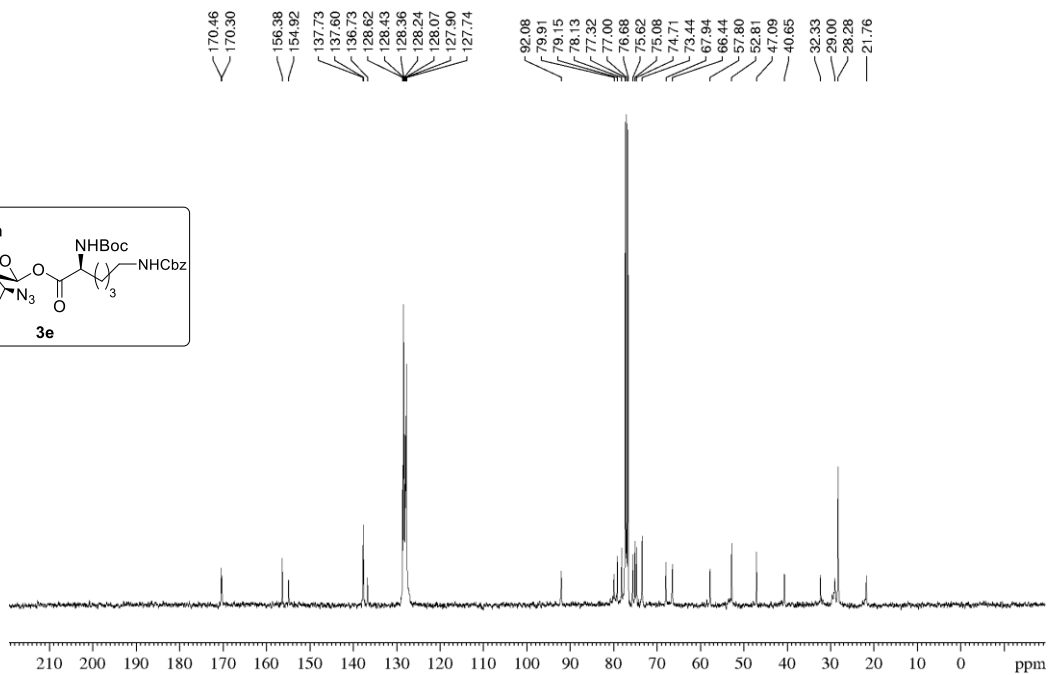
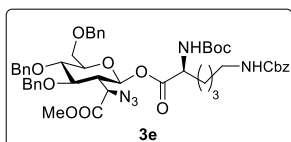
$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz



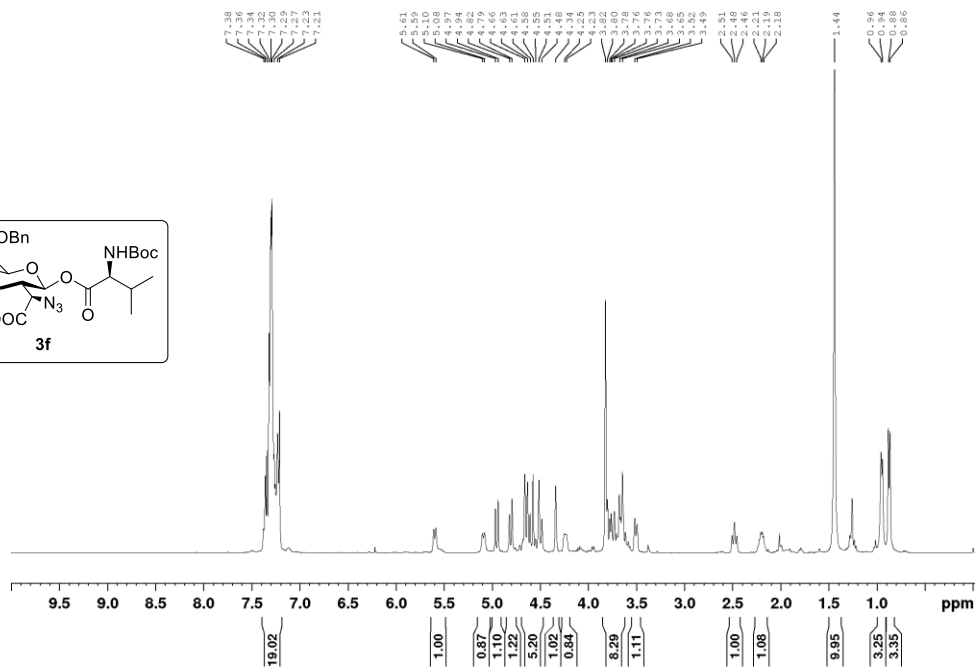
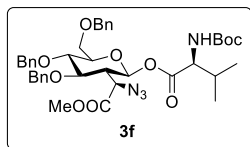
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



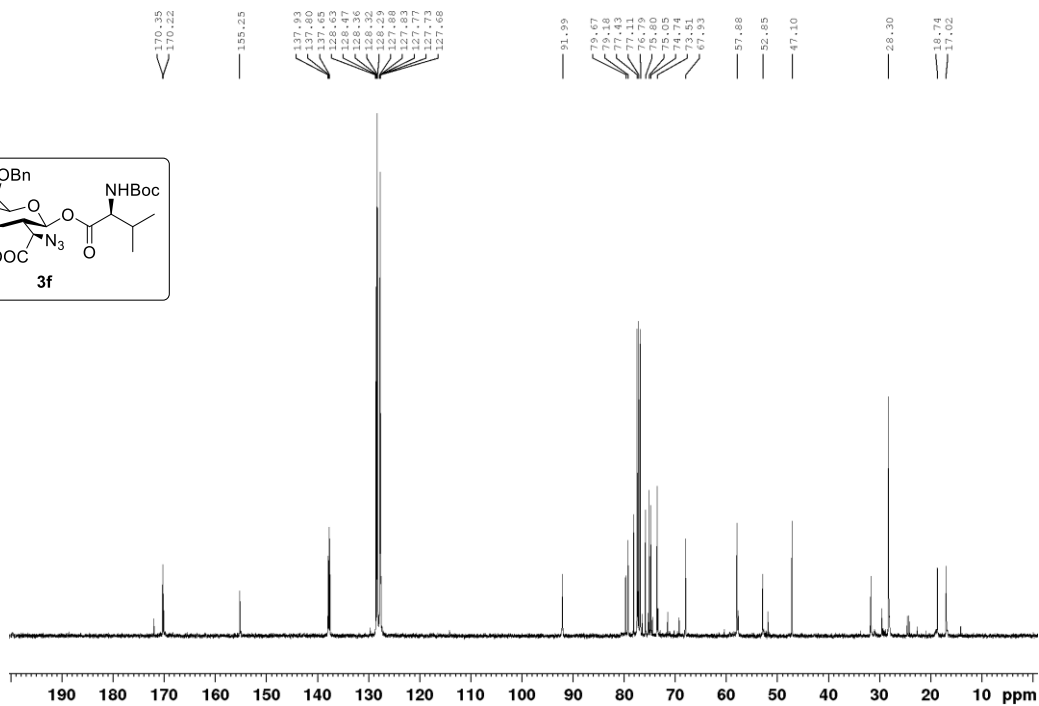
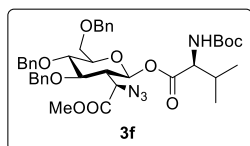
<sup>13</sup>C, CDCl<sub>3</sub>, 100 MHz



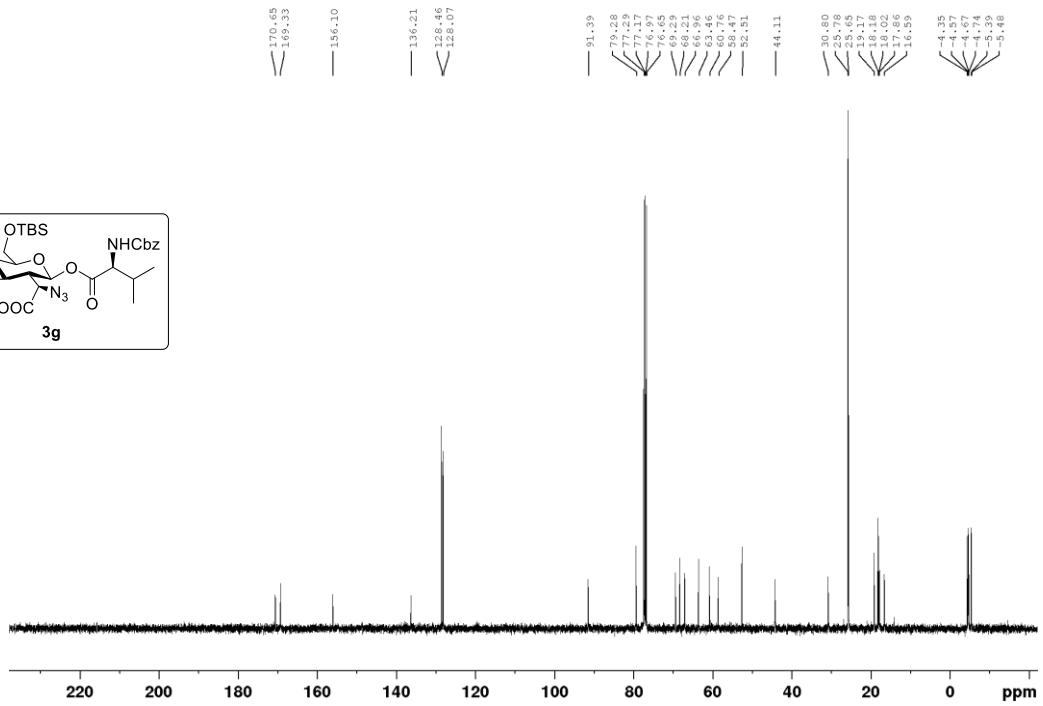
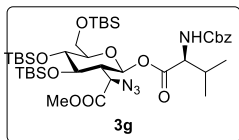
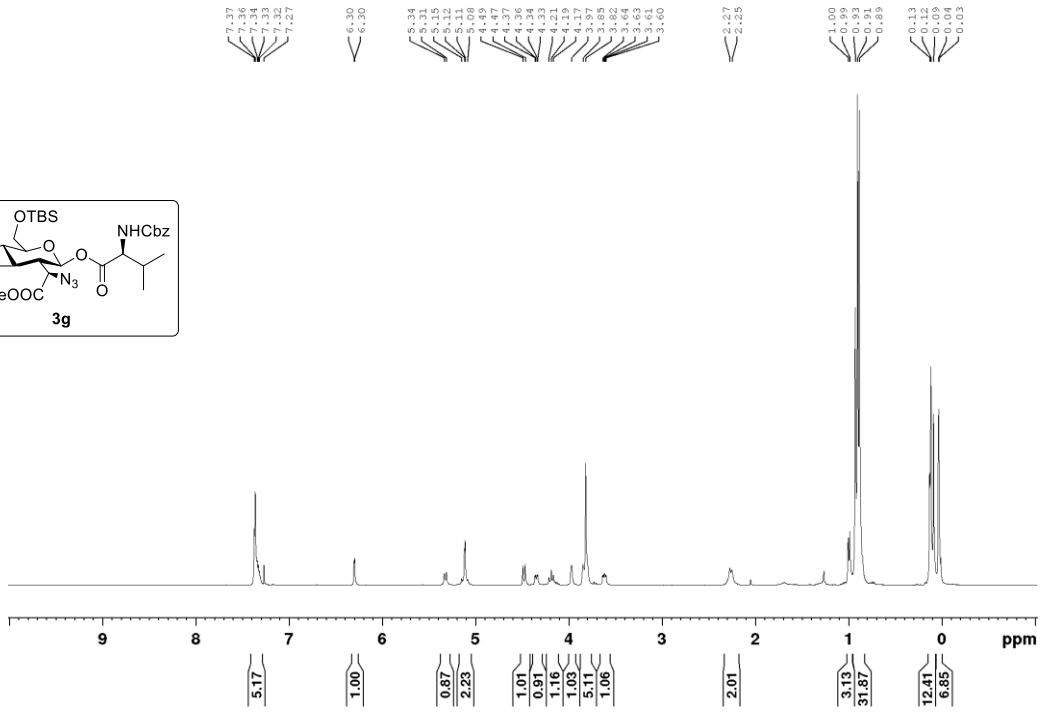
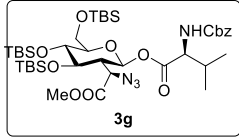
<sup>1</sup>H, CDCl<sub>3</sub>, 400 MHz



$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz



$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz

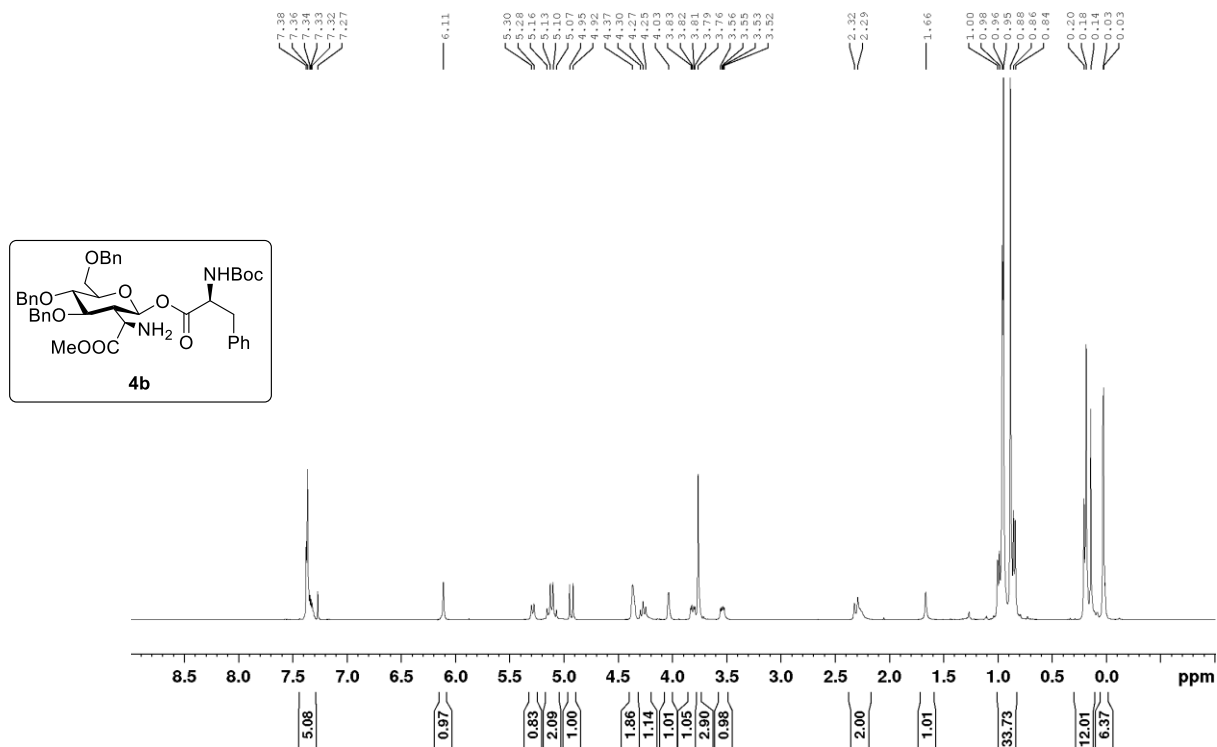




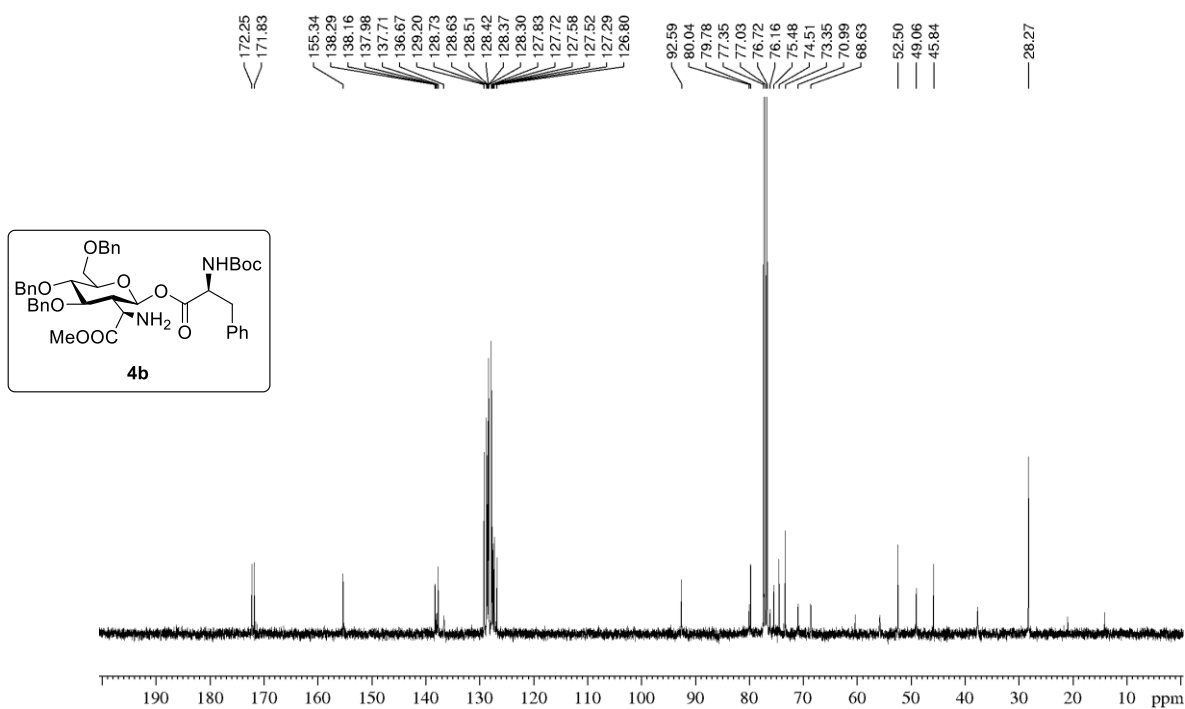


# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of amines 4a–4g, 4i–4k, 5 and 6

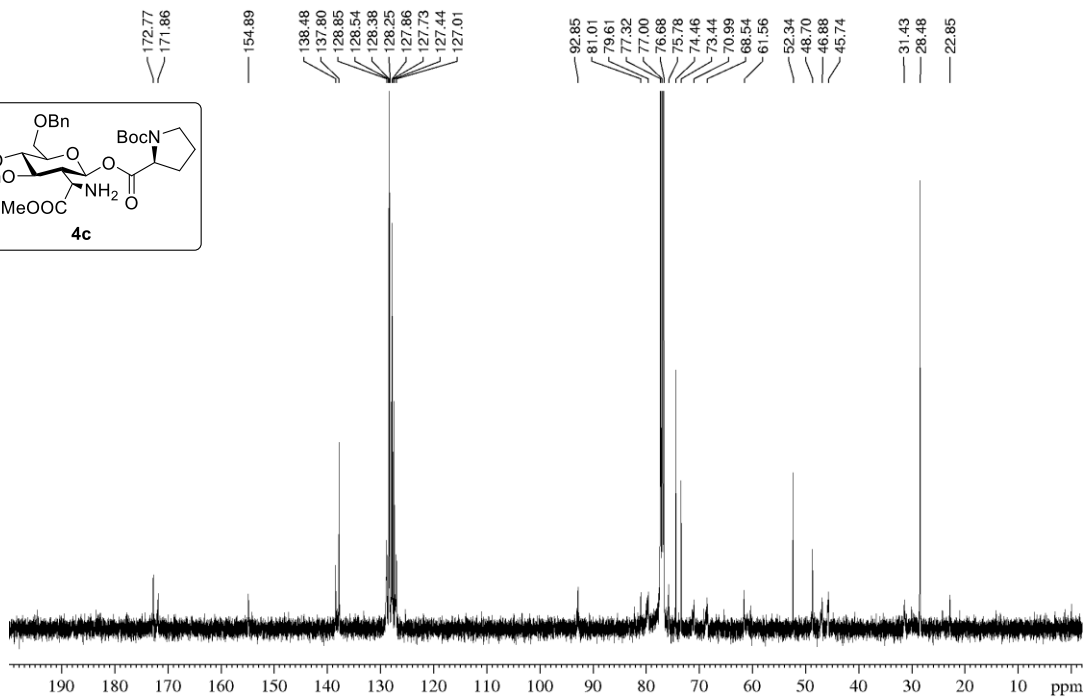
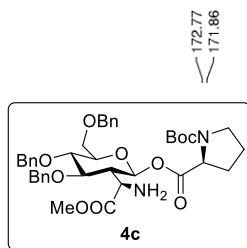
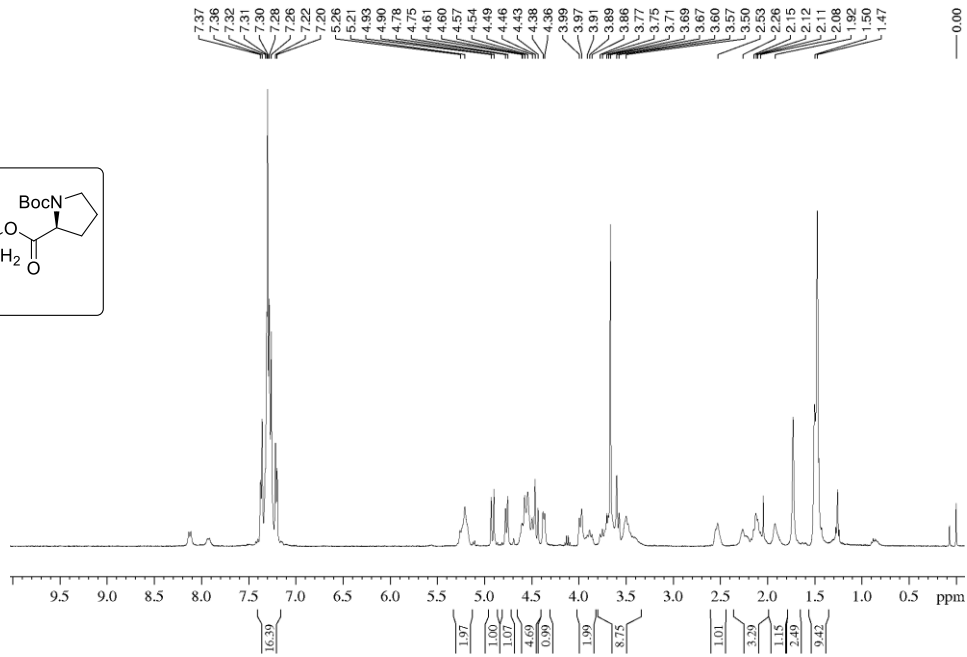
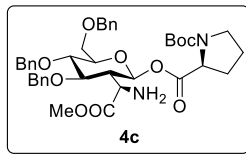
$^1\text{H}$ ,  $\text{CDCl}_3$ , 300 MHz

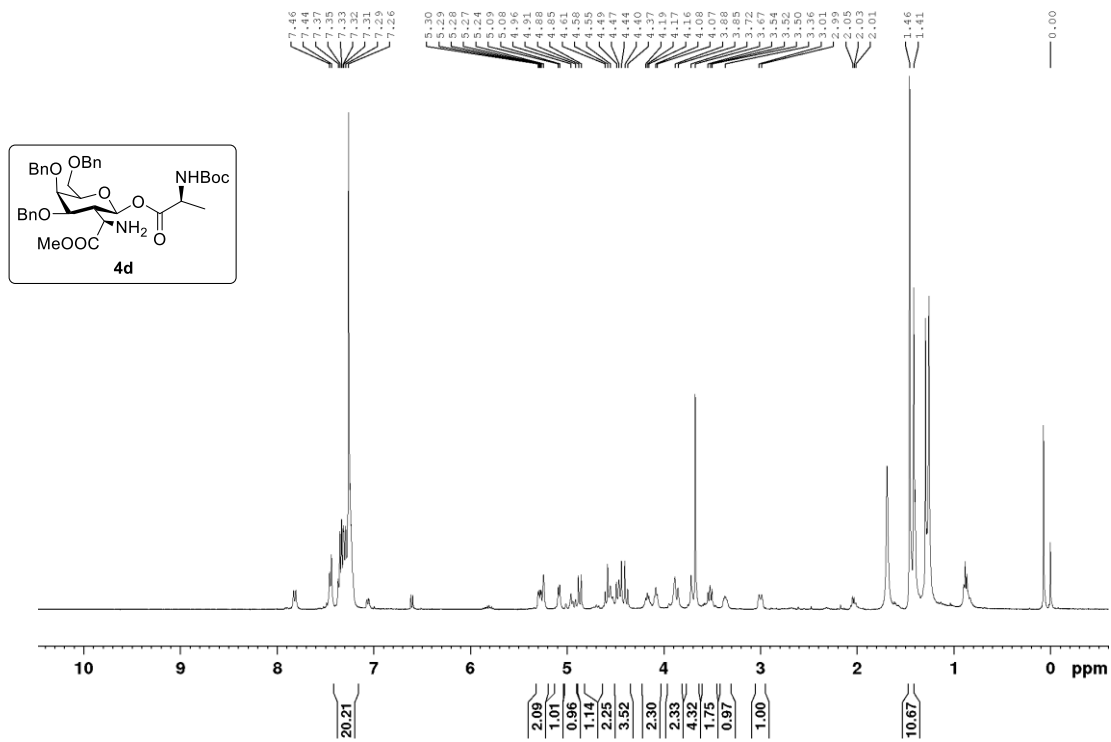


$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 75 MHz

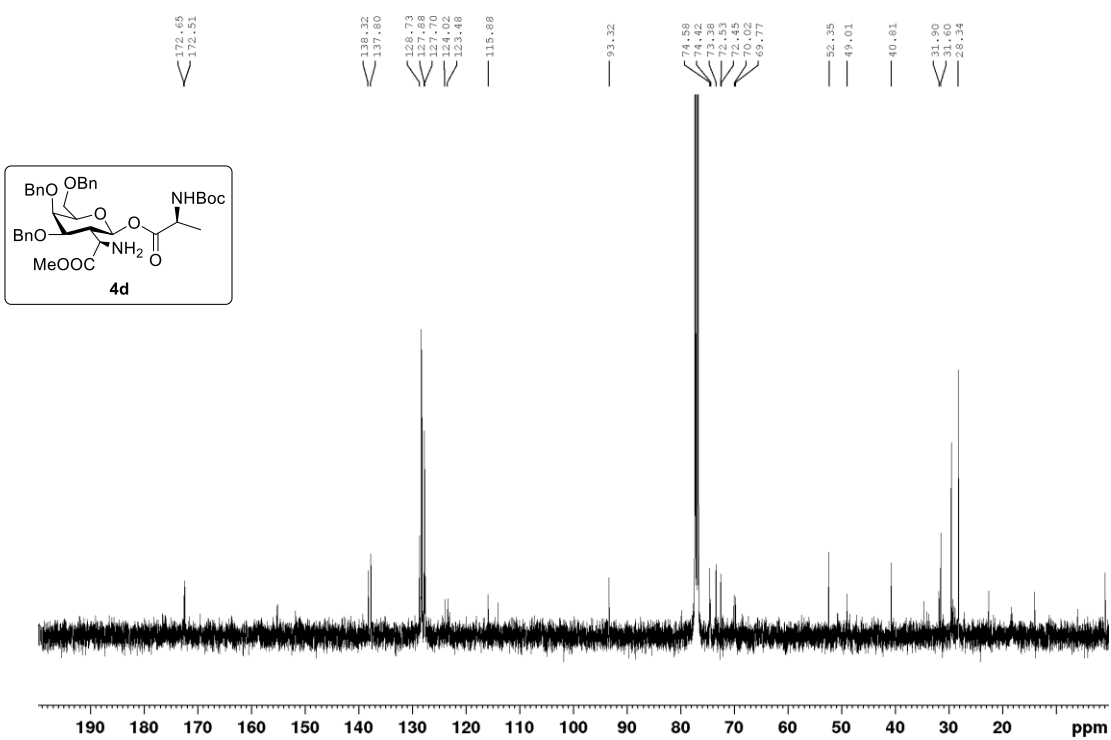


$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz

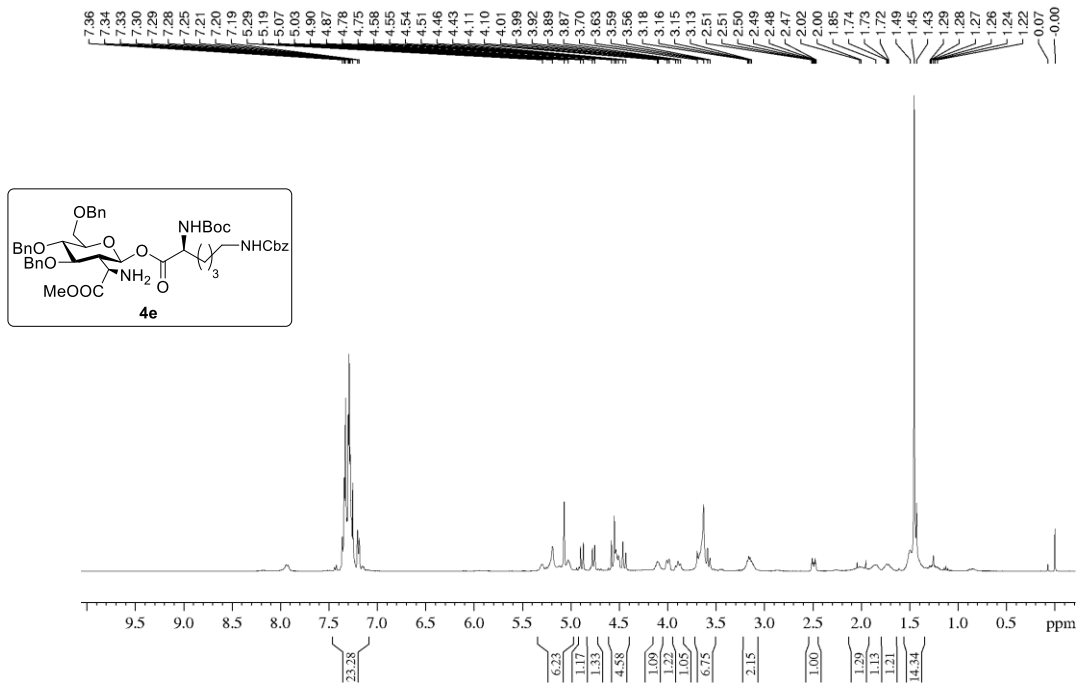




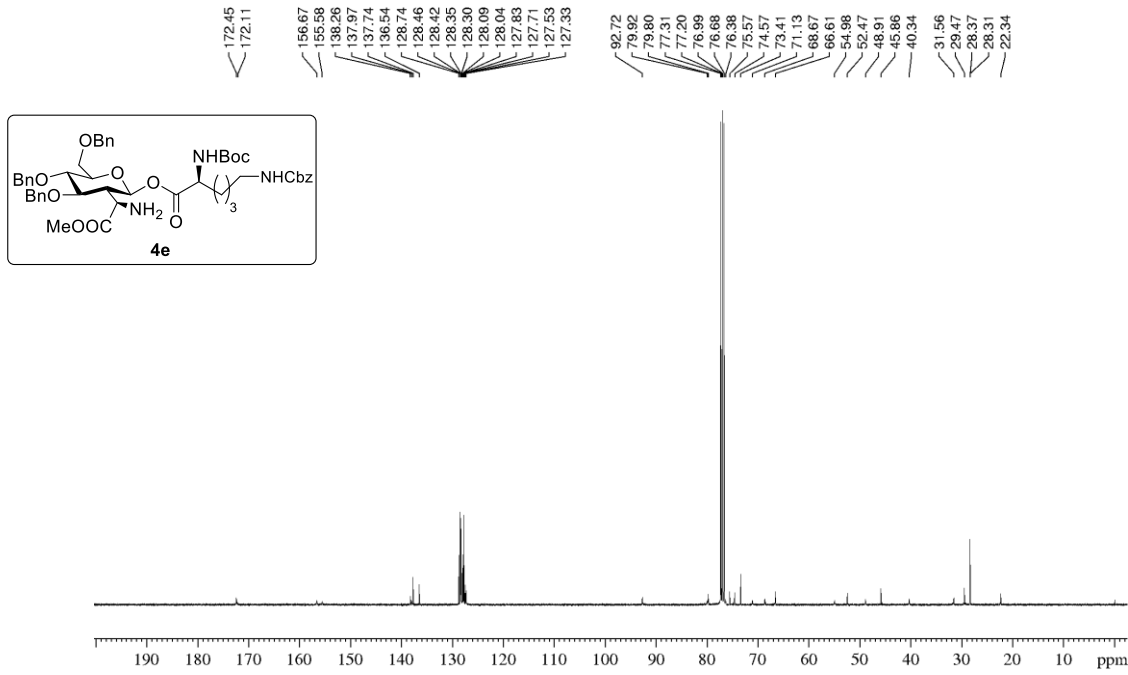
$^{13}\text{C}$   $\text{CDCl}_3$ , 100 MHz



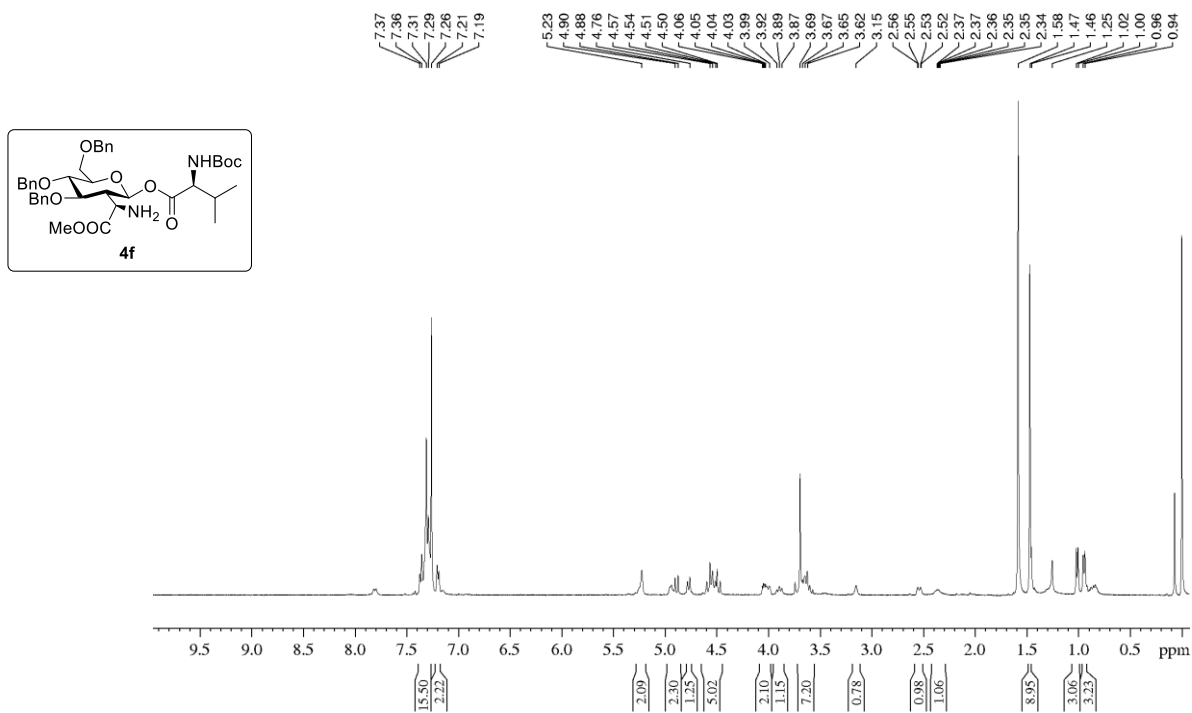
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



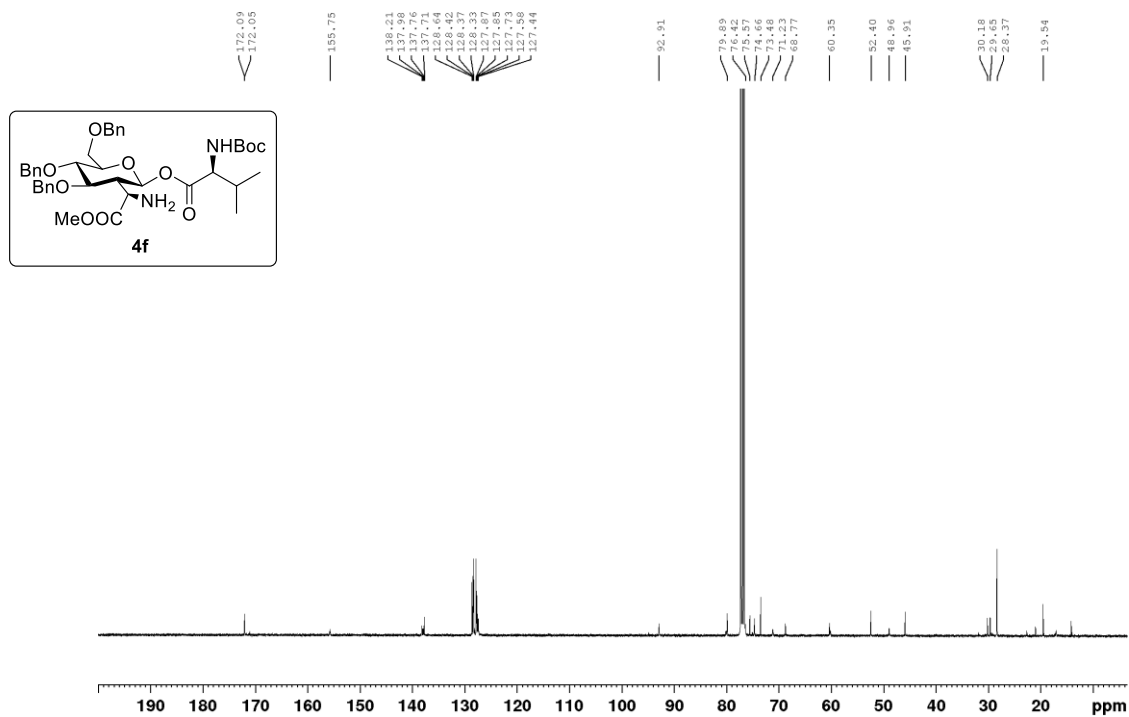
<sup>13</sup>C, CDCl<sub>3</sub>, 100 MHz



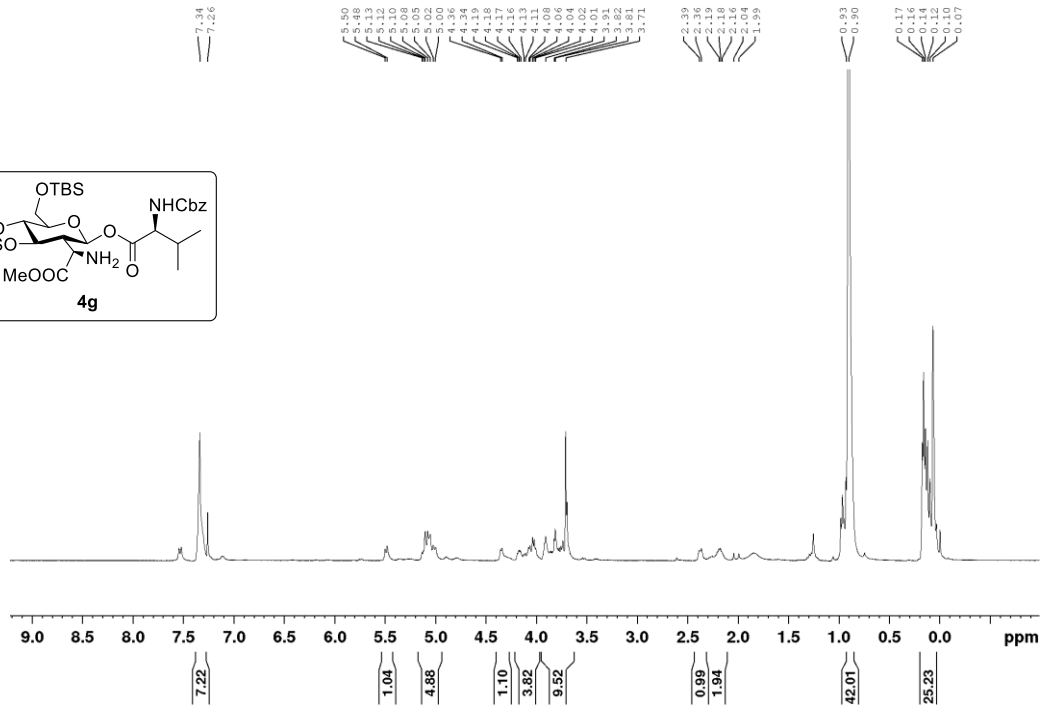
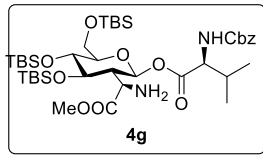
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



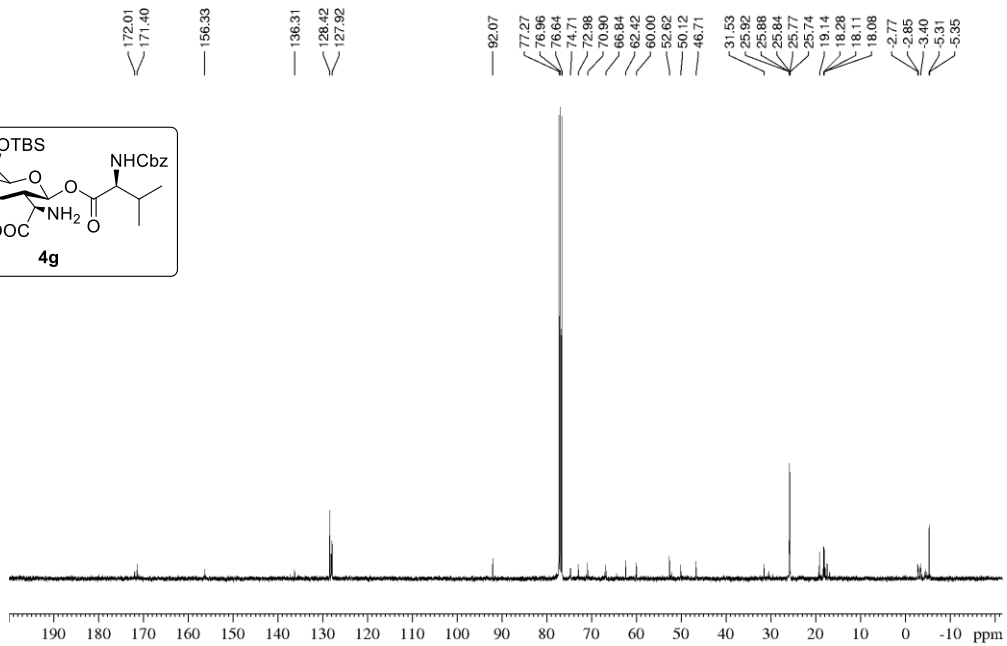
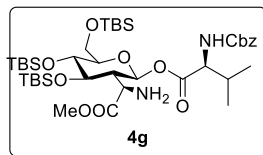
$^{13}\text{C}$   $\text{CDCl}_3$ , 100 MHz



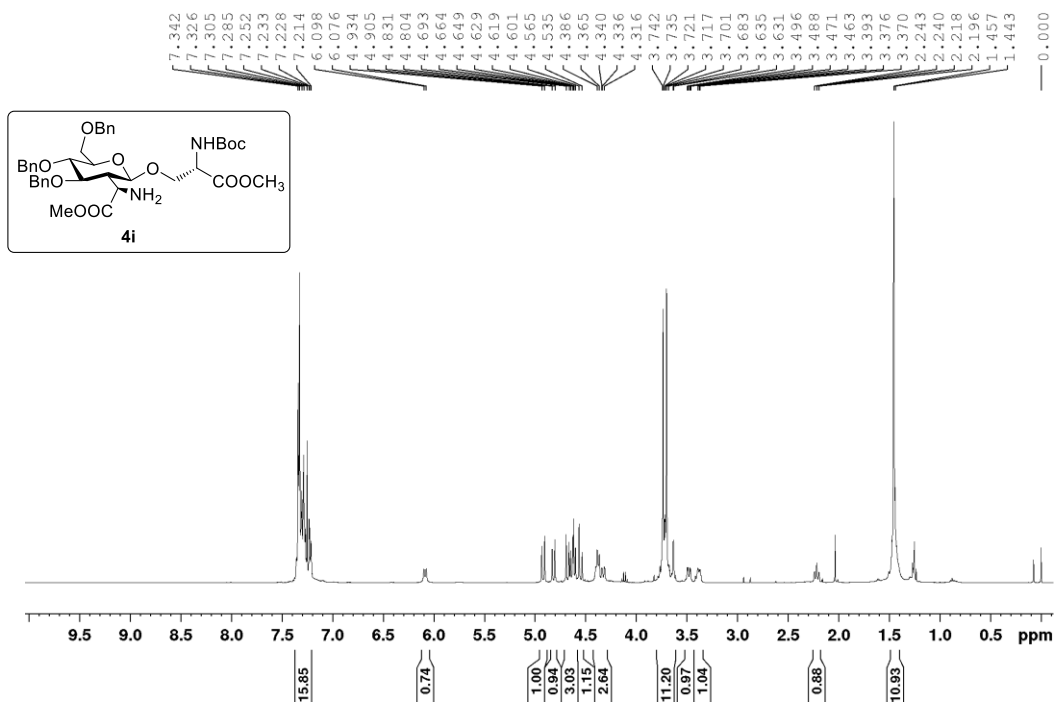
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



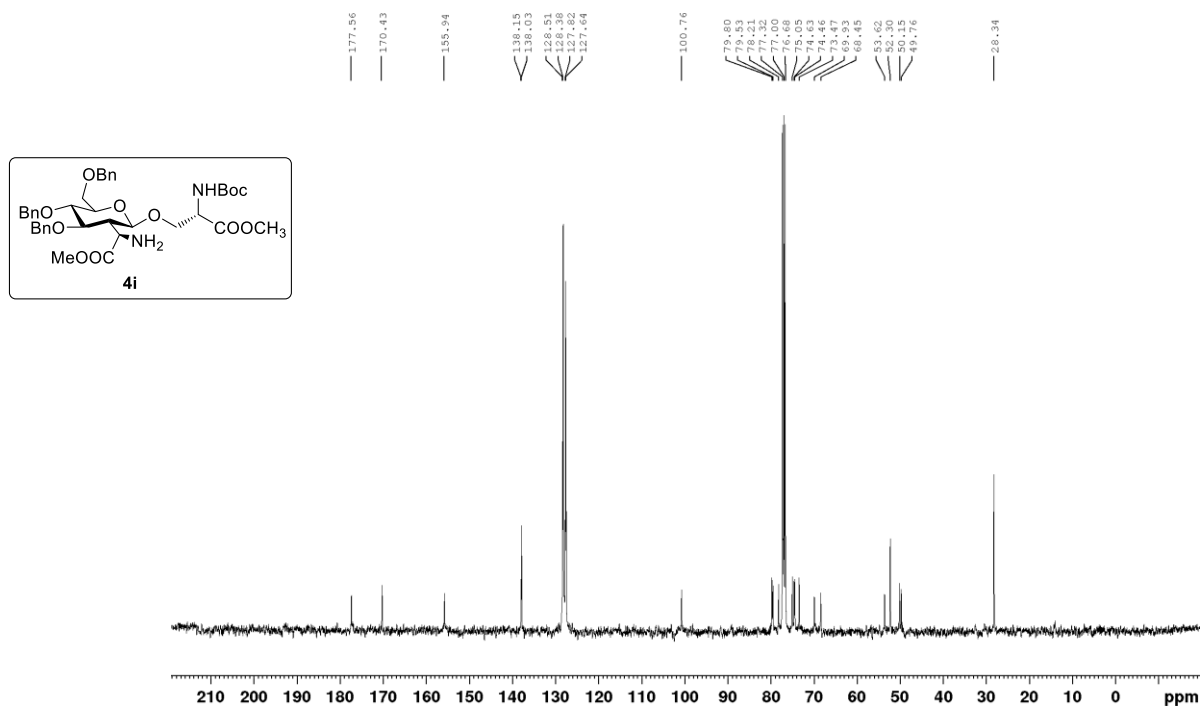
<sup>13</sup>C, CDCl<sub>3</sub>, 100 MHz



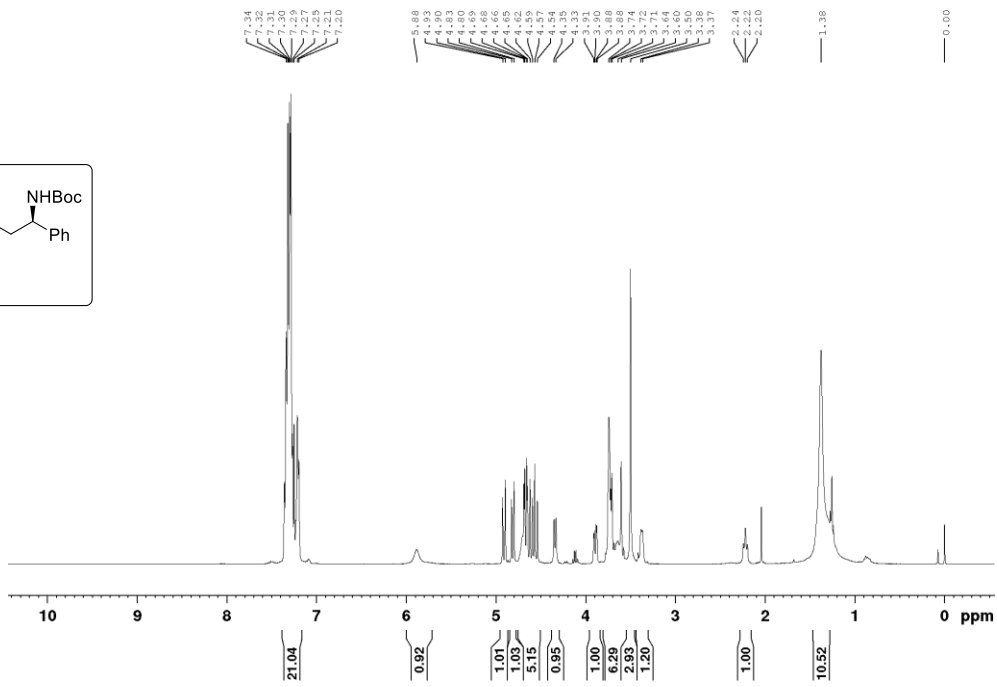
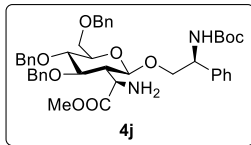
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



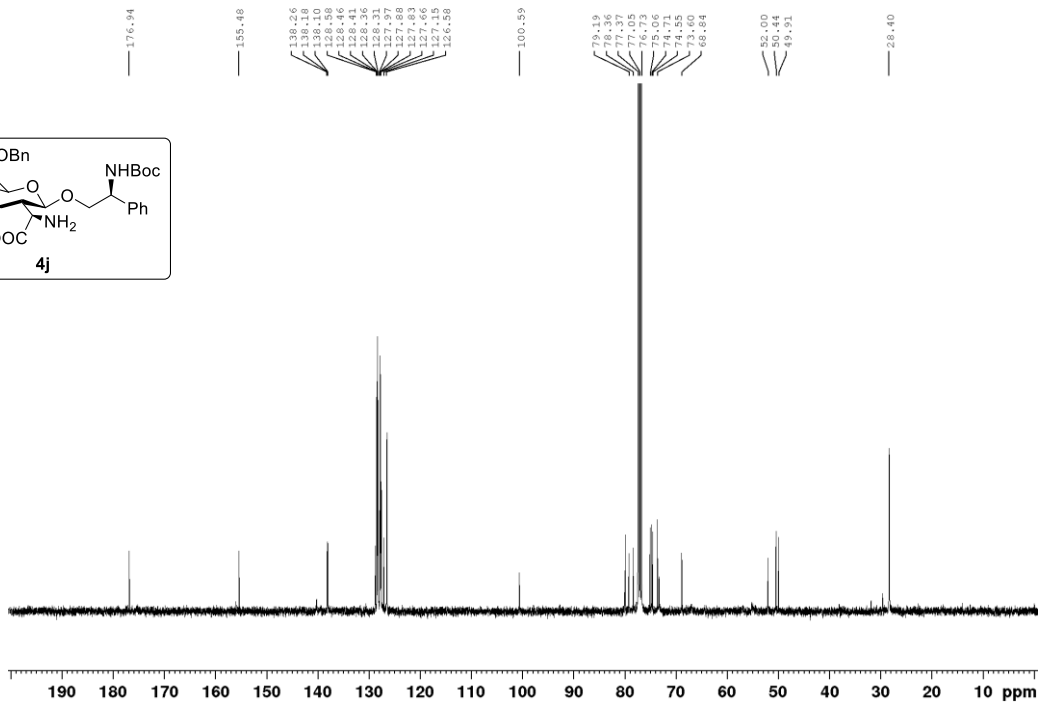
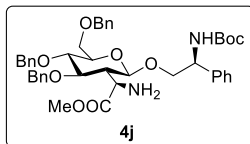
$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz



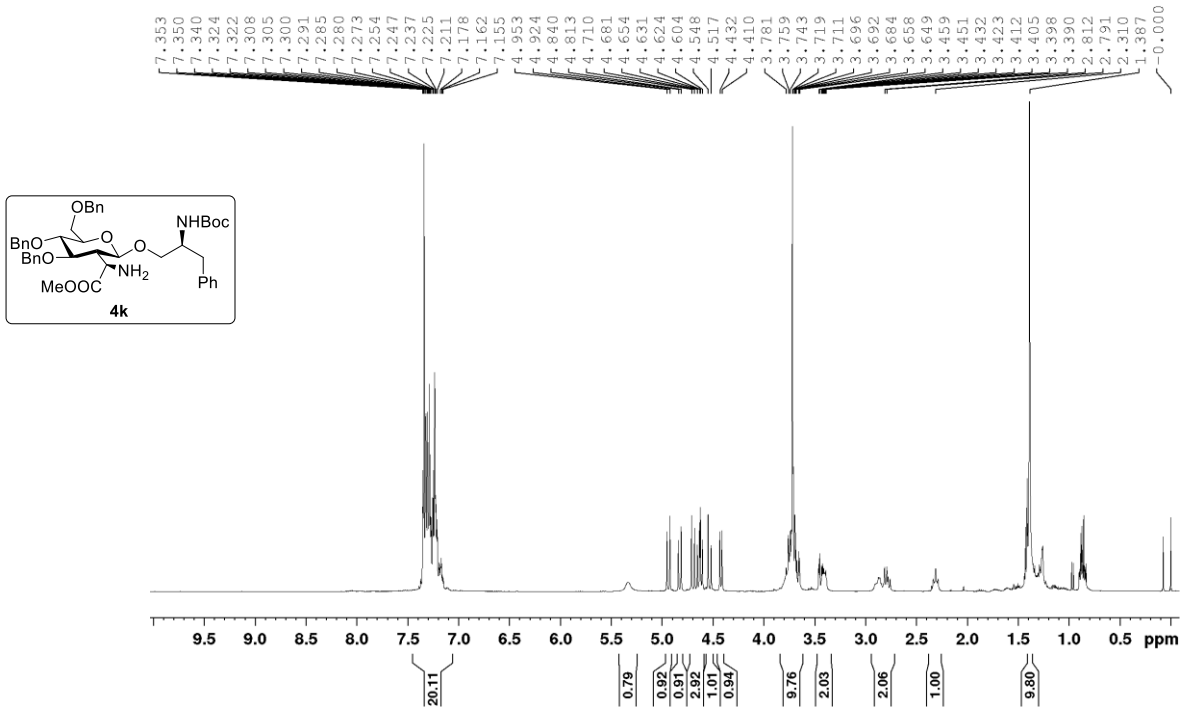
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



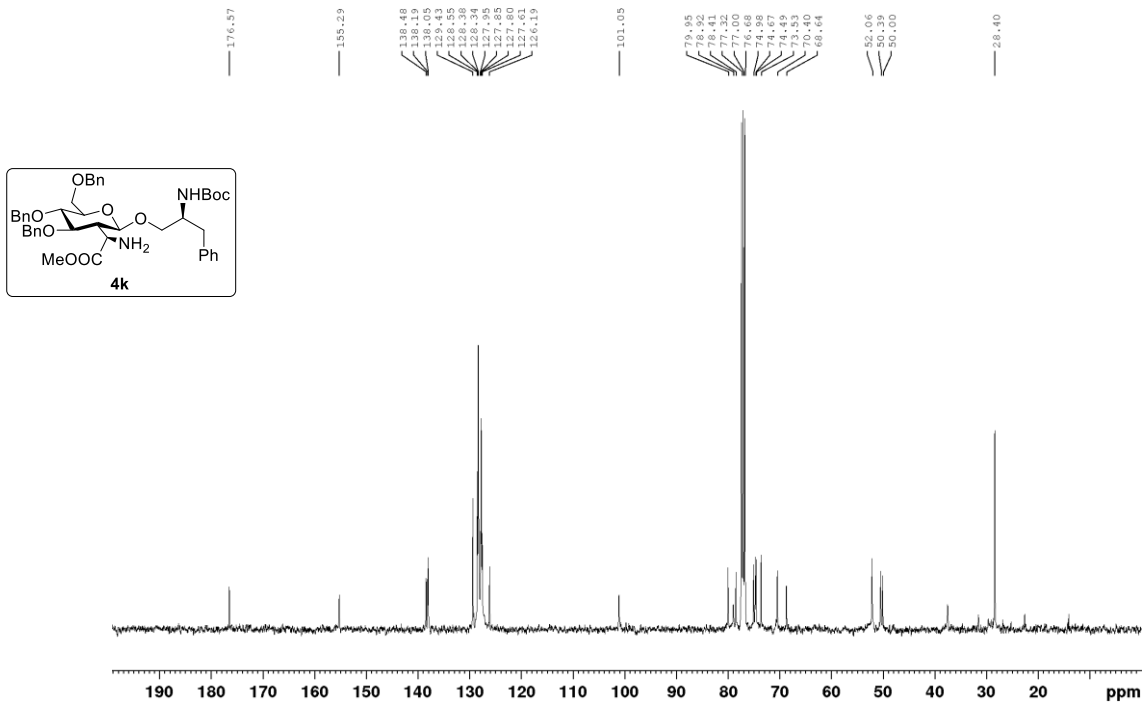
$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz



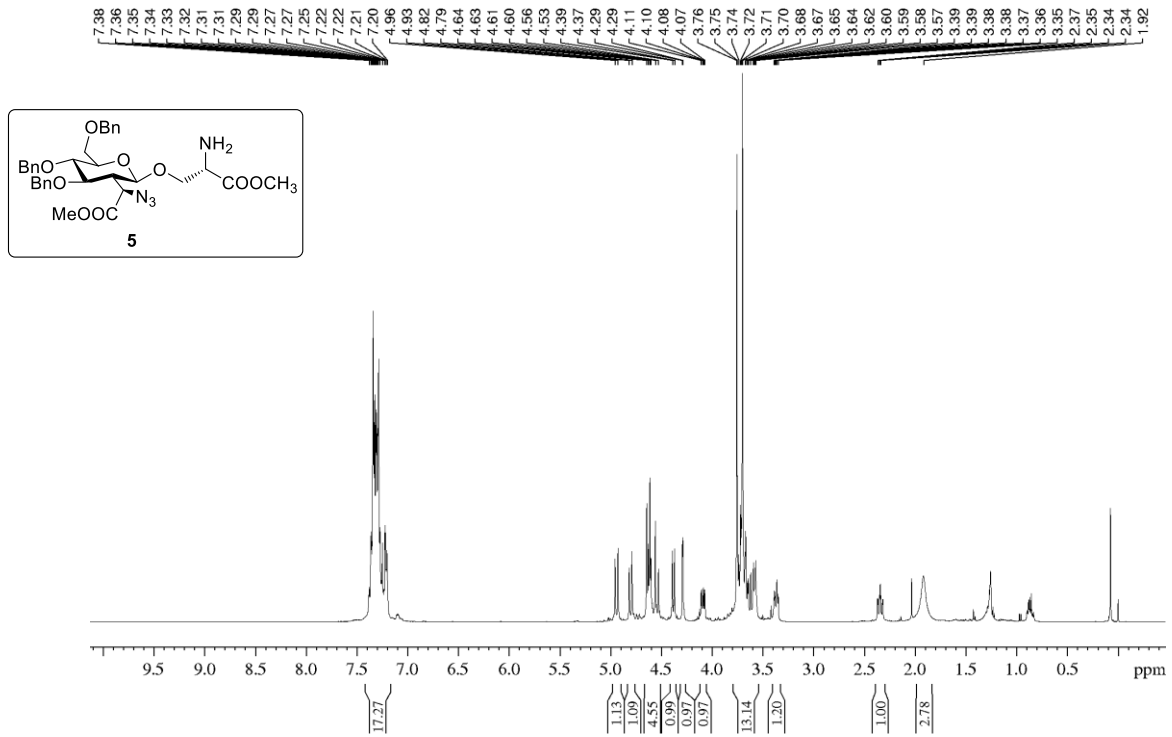
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



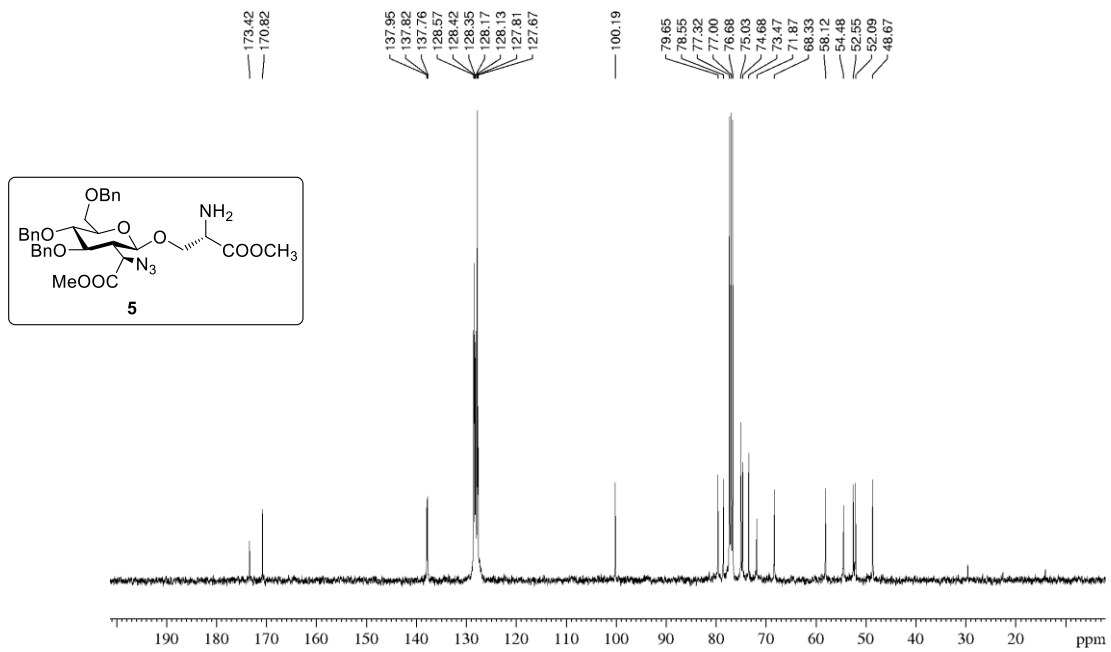
$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz



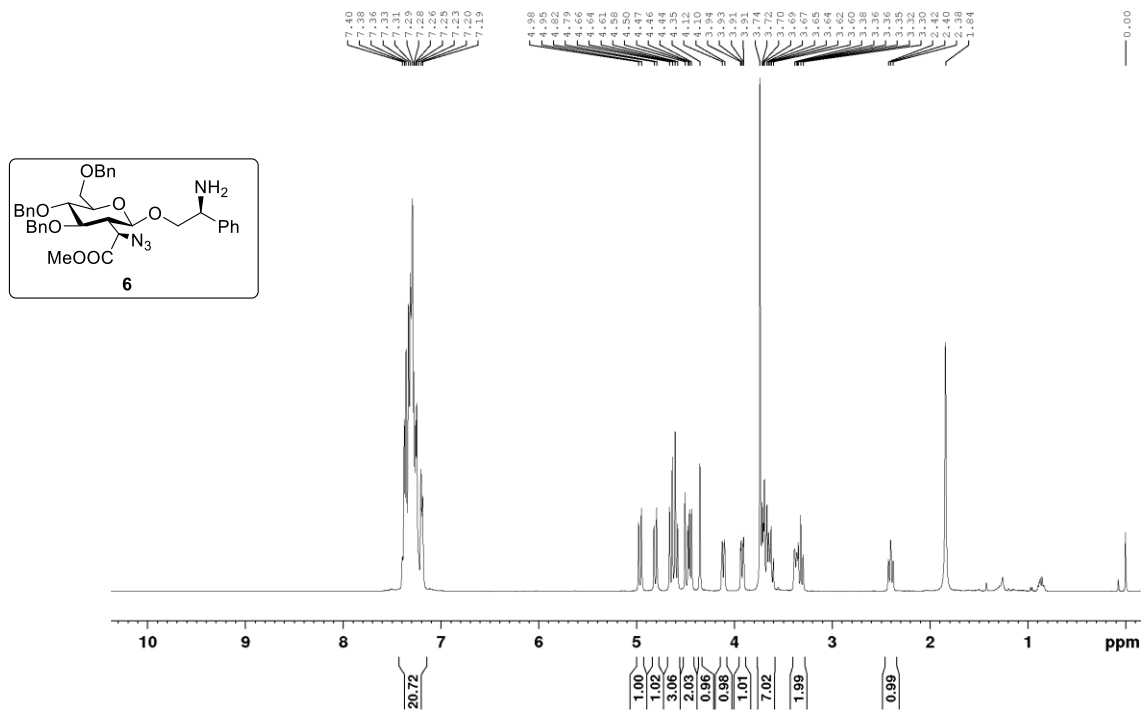
$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



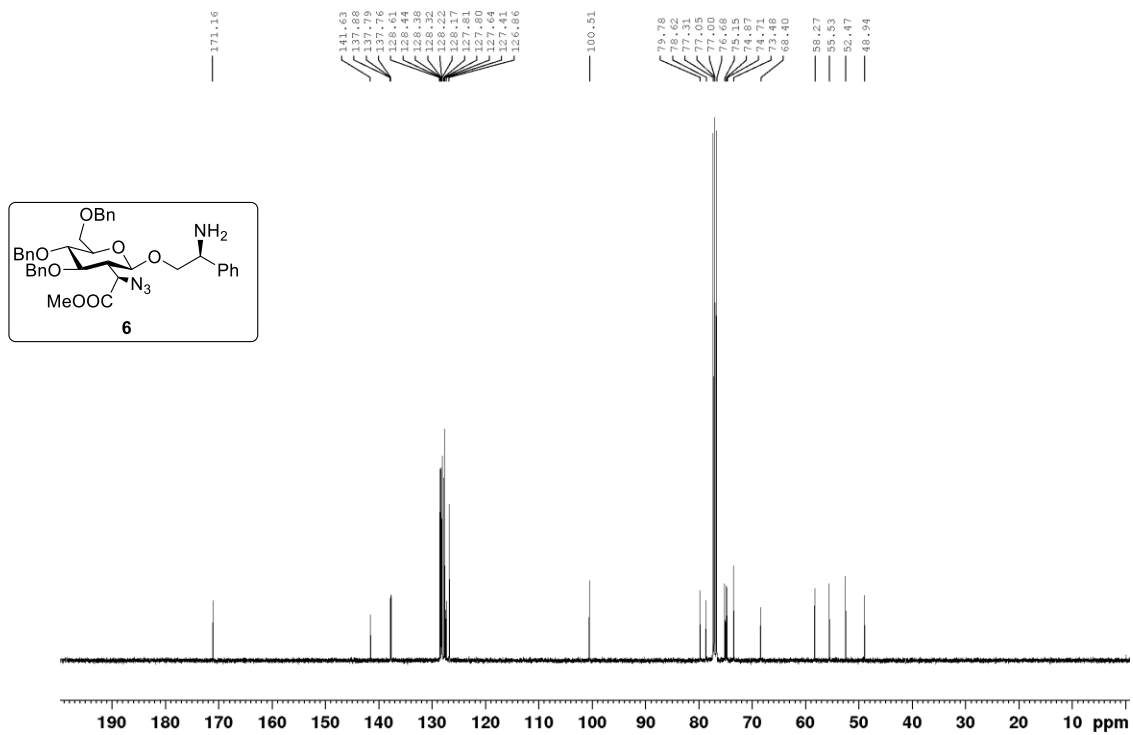
$^{13}\text{C}$   $\text{CDCl}_3$ , 100 MHz



$^1\text{H}$   $\text{CDCl}_3$ , 400 MHz

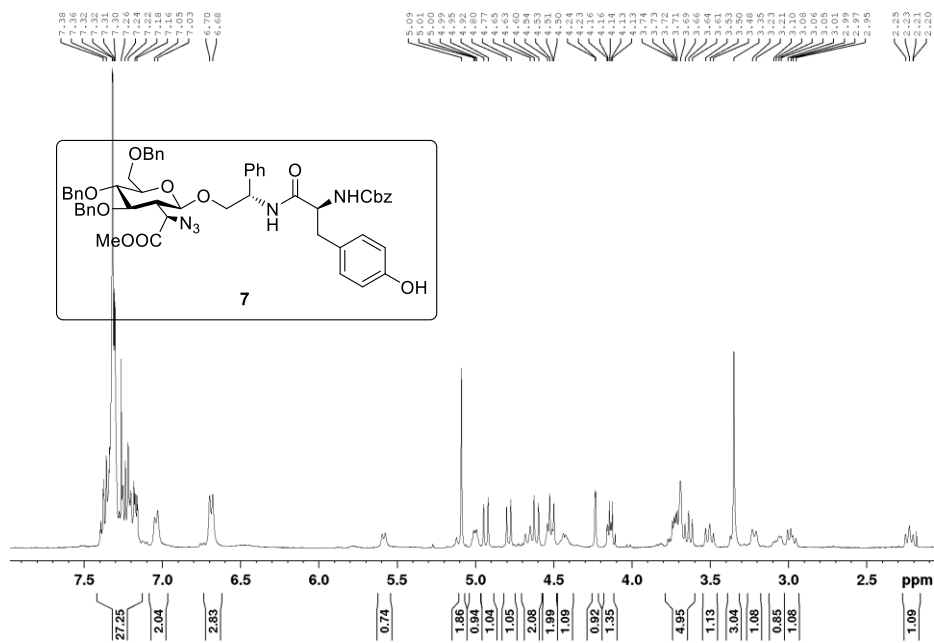


$^{13}\text{C}$   $\text{CDCl}_3$ , 100 MHz

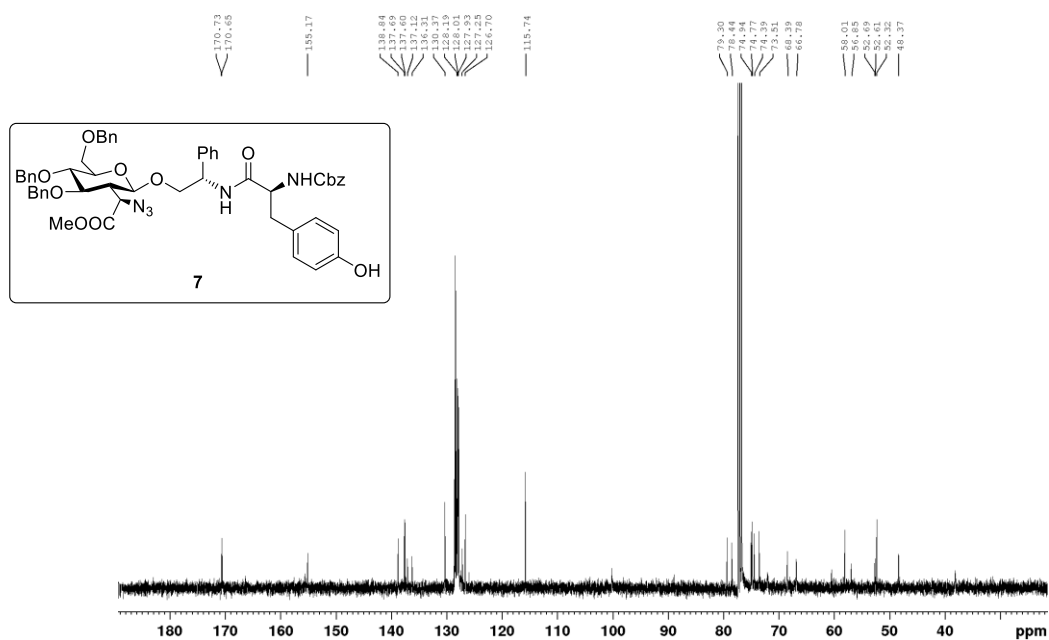


# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of glycopeptides 7-9

$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz

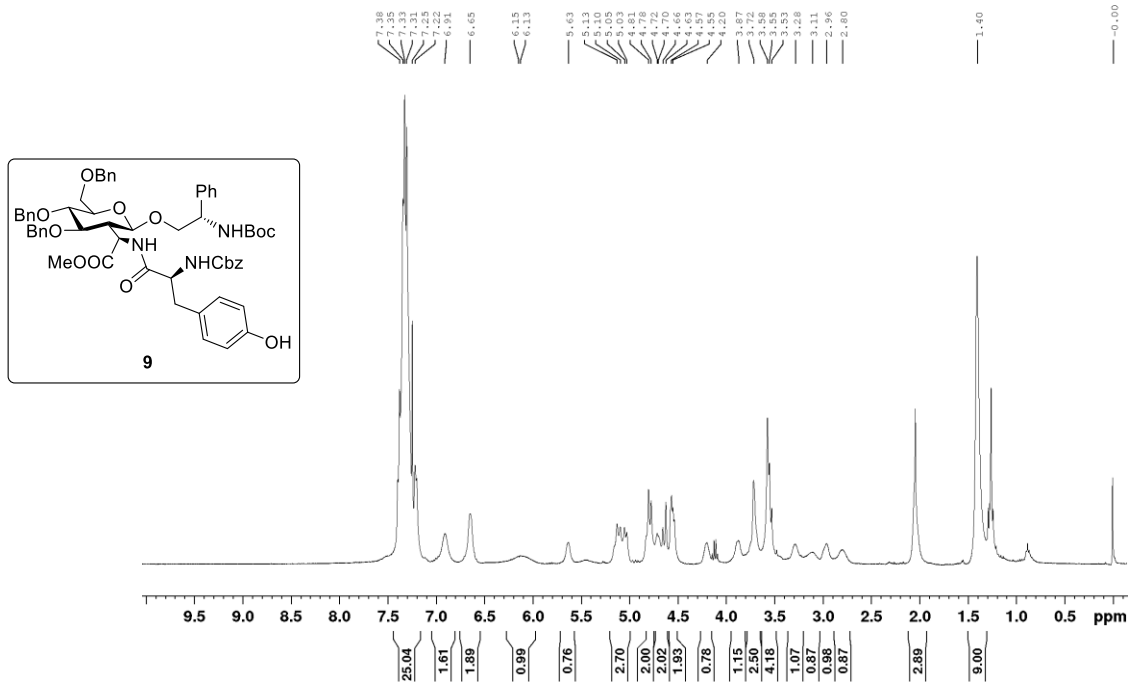


$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz

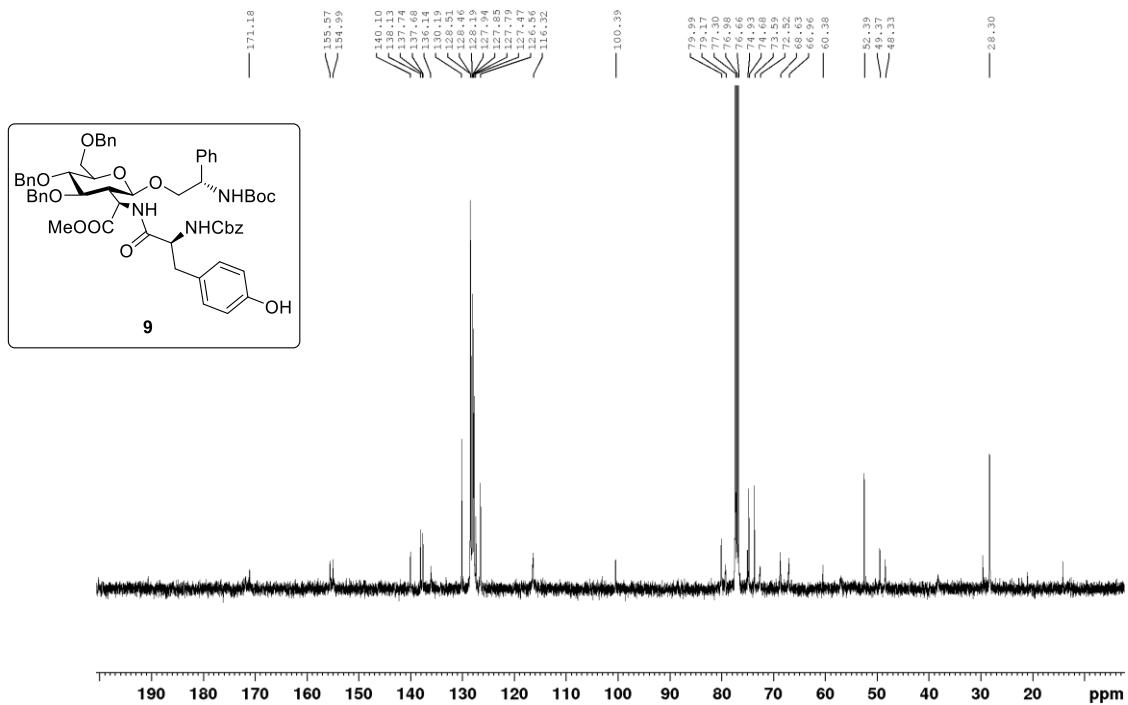




$^1\text{H}$ ,  $\text{CDCl}_3$ , 400 MHz



$^{13}\text{C}$ ,  $\text{CDCl}_3$ , 100 MHz



## Crystal data

**Table 1: Crystal data and structure refinement for iodide 2d (CCDC number: 995269).**

Identification code	<b>2d</b>	
Empirical formula	$C_{38}H_{45}INO_{10}$	
Formula weight	802.65	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	$a = 13.0510(3)$ Å	$\alpha = 90^\circ$
	$b = 9.74430(10)$ Å	$\beta = 91.155(2)^\circ$
	$c = 15.3151(2)$ Å	$\gamma = 90^\circ$ .
Volume	$1947.27(6)$ Å <sup>3</sup>	
Z	2	
Density (calculated)	$1.369$ Mg/m <sup>3</sup>	
Absorption coefficient	$0.877$ mm <sup>-1</sup>	
F(000)	826	
Crystal size	$0.30 \times 0.25 \times 0.20$ mm <sup>3</sup>	
Theta range for data collection	$2.48$ to $24.99^\circ$ .	
Index ranges	$-15 \leq h \leq 15$ , $-11 \leq k \leq 11$ , $-18 \leq l \leq 18$	
Reflections collected	19437	
Independent reflections	6724 [R(int) = 0.0268]	
Completeness to theta = $24.99^\circ$	99.9 %	
Max. and min. transmission	0.8441 and 0.7788	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	6724 / 1 / 456	
Goodness-of-fit on F <sup>2</sup>	0.926	

Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0289, wR2 = 0.0567
R indices (all data)	R1 = 0.0393, wR2 = 0.0589
Absolute structure parameter	-0.019(9)
Largest diff. peak and hole	0.307 and -0.276 e.Å <sup>-3</sup>