Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A new way to do an old reaction: highly efficient reduction of organic azides by sodium iodide in the presence of acidic ion exchange resin

Kajitha Suthagar,[a] and Antony J. Fairbanks*[a,b]

a Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand.
b Biomolecular Interaction Centre, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand.

* E-mail: antony.fairbanks@canterbury.ac.nz

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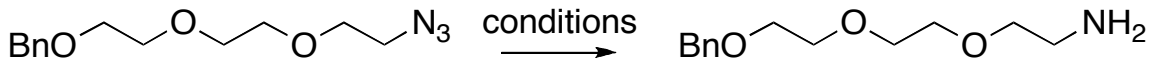
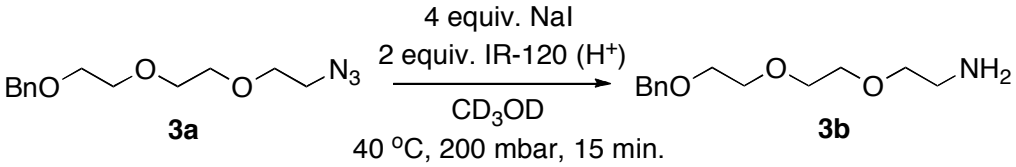
Table S1: Study of the effect of iodide concentration on reaction efficiency



3a **3b**

Entry	Iodide concentration	NaI/ equiv.	Acid/ equiv.	Solvent	Temp/ °C	Time	Conversion/ %
1	1 M	8	2	CD_3OD	rt	0.25 h	15
						0.5 h	38
						1 h	59
2	2 M	8	2	CD_3OD	rt	0.25 h	50
						0.5 h	90
						1 h	96
3	4 M	8	2	CD_3OD	rt	0.25 h	100

Table S2: Study of the effect on reaction efficiency of ion exchange resin re-cycling



3a **3b**

Recycle number	NaI/ Equiv.	Acid/ equiv.	Solvent	Temp/ °C	Time	Conversion/ %
1	4	2	CH_3OH	40	0.25 h	100
2	4	2	CH_3OH	40	0.25 h	80
3	4	2	CH_3OH	40	0.25 h	80

General methods

All reactions were carried out in oven-dried, nitrogen-purged glassware under an atmosphere of nitrogen. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer Polarimeter 341 with a path length of 1 dm. Concentrations are given in g / 100 mL. Infrared spectra were recorded on a Perkin-Elmer Spectrum One. Proton and carbon nuclear magnetic resonance (δ_H, δ_C) spectra were recorded on Agilent Technologies 400 MR (400 MHz) or Varian VNMR500 (500 MHz) spectrometers. All chemical shifts are quoted on the δ-scale in ppm using residual solvent as an internal standard. High-resolution mass spectra were recorded with a Bruker maXis 3G UHR-TOF mass spectrometer. Thin Layer Chromatography (t.l.c.) was carried out on Merck silica gel $60F_{254}$ aluminium-backed plates. Visualisation of the plates was achieved using a UV lamp (λ_{max} = 254 or 365 nm), and/or 5% w/v ammonium molybdate in 2 M sulfuric acid. Flash column chromatography was carried out using Sorbsil C60 40/60 silica. Reverse phase high performance liquid chromatography (RP-HPLC) was performed on a Dionex P680 HPLC instrument fitted with a Dionex Corona ultra RS Charged Aerosol Detector (CAD), using a Phenomenex Luna C 18(2) 100 A column (5 μm, 10 x 250 mm) at 15 °C. The column was eluted with a gradient of MeCN/H_2O at a flow rate of 1 $mLmin^{-1}$. Unless preparative details are provided, all reagents were commercially available or made following literature procedures. "Petrol" refers to the fraction of light petroleum ether boiling in the range of 40-60 °C.

General Procedure A: Reduction of polar azides and purification by ion exchange

Azide (1 equiv.) was dissolved in MeOH (1 mL), and the resulting solution was added to a stirred solution of NaI (4 equiv.) and Amberlite IR 120 (1.8 meq/mL by wetted bed volume of exchangeable H^+ ions, 2 equiv.) in MeOH (1 mL). The reaction mixture was then concentrated on a rotary evaporator at 40 °C and 200 mbar until dryness (approx. 15 min.). MeOH (5 mL), aqueous 1M HCl in MeOH (5 mL) and an excess of Amberlite IR 120 (H^+ form) were then added, and the material placed on a chromatography column. The column was then eluted with MeOH (100 mL), with H_2O (500 mL), before elution of the amine product with 2.5 M NH_3 in MeOH.

General Procedure B: Reduction of non-polar azides and purification by ion exchange

Azide (1 equiv.) was dissolved in $CHCl_3$ (1.5 mL), and the resulting solution was added to a stirred solution of NaI (4 equiv.) and Amberlite IR 120 (1.8 meq/mL by wetted bed volume

of exchangeable H^+ ions, 2 equiv.) in MeOH (1 mL). The reaction mixture was then concentrated on a rotary evaporator at 40 °C and 200 mbar until dryness (approx. 15 min.). MeOH (5 mL), aqueous 1M HCl in MeOH (5 mL) and an excess of Amberlite IR 120 (H^+ form) were then added, and the material placed on a chromatography column. The column was then eluted with MeOH (100 mL), with H_2O (500 mL), before elution of the amine product with 2.5 M NH_3 in MeOH.

General Procedure C: mesylation and azide displacement

Methanesulfonylchloride (1.5 equiv.) was added drop-wise to a stirred solution of the alcohol (1 equiv.) and Et_3N (1.5 equiv.) in anhydrous DCM (30 mL) at 0 ˚C under nitrogen. The reaction mixture was then allowed to warm to room temperature, and stirred for 2 hours. The reaction mixture was then poured into water (10 mL), and extracted with diethyl ether (3 x 20 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was dissolved in DMF (25 mL), sodium azide (3 equiv.) was added, and the mixture was stirred at 60 ˚C for 16 hours. The reaction mixture was concentrated *in vacuo*, and the residue was extracted with diethyl ether (3 x 50 mL). The combined organic extracts were washed with distilled water (2 x 30 mL) and brine (30 mL), dried over anhydrous $MgSO_4$, filtered, concentrated *in vacuo,* and the residue was purified by column chromatography.

General Procedure D: azide displacement

Sodium azide (3 equiv.) was added to a solution of the halide (1 equiv.) in DMF (10 mL). The solution was then stirred at 50 ˚C for 16 hours. The reaction mixture was cooled, and diluted with diethyl ether (50 mL). The organic layer was separated and washed with water (2 x 30 mL) and brine (30 mL), dried over anhydrous $MgSO_4$, filtered, concentrated *in vacuo,* and the residue was purified by column chromatography.

General Procedure E: Appel reaction

Glycoside (1 equiv.) was dissolved in dry THF (25 mL) and triphenylphosphine (2 equiv.), iodine (1.5 equiv.) and imidazole (1.5 equiv.) were then added sequentially. The reaction mixture was then heated to 50 °C, and stirred at for 16 h under nitrogen. The reaction mixture was then cooled to room temperature and the solvent was removed *in vacuo*. The residue was then dissolved in ethyl acetate (30 mL), and the resulting solution was washed with 10% w/v aqueous $Na_2S_2O_3$ (20 mL), and water (2 x 20 mL). The organic extracts were dried over

anhydrous $MgSO_4$, filtered, and concentrated *in vacuo,* to give a residue that was purified by column chromatography

6-Amino-6-deoxy-D-mannopyranose 2: D-Mannose **1** (0.5 g, 2.7 mmol, 1 equiv.) was dissolved in dry DMF (5 mL) and triphenylphosphine (1.45 g, 5.5 mmol, 2 equiv.), iodine (1.05 g, 4.2 mmol 1.5 equiv.) and imidazole (280 mg, 4.1 mmol, 1.5 equiv.) were added sequentially. The reaction mixture was then stirred at 50 °C for 3 h under nitrogen. After this time, t.l.c. (EtOAc: MeOH: H_2O, 7: 2: 1) indicated the formation of a single product (R_f 0.6). The solvent was removed *in vacuo* and the residue was dissolved in H_2O (30 mL). This solution was then washed with DCM (3 x 20 mL). The aqueous extracts were concentrated *in vacuo* to afford crude 6-deoxy-6-iodo-D-mannopyranose, as a yellow oil. This crude material was dissolved in DMF (25 mL), sodium azide (3 equiv.) was added, and the mixture was stirred at 60 ˚C for 16 h. After this time, t.l.c. (EtOAc: MeOH: H_2O, 7: 2: 1) indicated the formation of a single product (R_f 0.5). The mixture was cooled, the solvent was removed *in vacuo*, and the residue was dissolved in H_2O (5 mL). This solution was then filtered through a column of Amberlite IR 120 (H^+ form), and then concentrated *in vacuo* to give a residue, which was purified by RP-HPLC [Luna C-18 column (Phenomenex); eluent: A (0.05 % TFA in H_2O) and B MeCN; gradient: the sample was run at 1 mL/min with a gradient of 0-100 % B; column oven: 40 °C; detection: CAD], to afford 6-amino-6-deoxy-D-mannopyranose **2** as pale yellow waxy solid (0.28 g, 56 %). υ_{max} (neat) 3330 (O-H); δ_H (400 MHz, D_2O) 2.97-3.12 (2H, m, H-6α, H-6β), 3.30 - 3.38 (2H, m, H-6'α, H-6'β), 3.42 - 3.58 (3H, m, H-4α, H-4β, H-3α/β), 3.73 (1H, dd, $J_{2,3}$ 2.3 Hz, $J_{3,4}$ 9.4 Hz, H-3α/β), 3.81 - 3.92 (4H, m, H-2α, H-2β, H-5α, H-5β), 4.81 (1H, s, H-1β), 5.08 (1H, s, H-1α); δ_C (100 MHz, D_2O) 40.4, 40.5 (t, C-6α, C-6β), 68.1, 68.1 (d, C-5α, C-5β), 68.4 (d, C-3α/β or C-4α/β), 69.8 (d, C-3α/β), 70.5, 71.0 (d, C-2α, C-2β), 71.7 (d, C-3α/β or C-4α/β), 72.6 (d, C-4α/β), 93.7 (d, C-1β), 94.0 (d, C-1α). HRMS (ESI) calculated for $C_6H_{14}NO_5$ ($M+H^+$): 180.0866. Found 180.0857.

2',5'-Deoxy-5'-iodo-β-D-thymidine[1]

General procedure **E**, using thymidine (1 g, 4.1 mmol) and purification by flash chromatography (gradient elution, 100 % DCM to DCM: MeOH, 97:3) afforded 2',5'-deoxy-5'-iodo-β-D-thymidine (0.59 g, 41 %) as a white solid. m.p 168-170 °C (DCM/Petrol) [lit 170-173 °C][1]; $[\alpha]_D^{20}$ +22.8 (*c*, 1.0 in CH_3OH); δ_H (500 MHz, CD_3OD) 1.90 (3H, s, 5-CH_3), 2.26-2.34 (2H, m, H-2a', H-2b'), 3.43-3.53 (2H, m, H-5a', H-5b'), 3.83-3.86 (1H, m, H-4'), 4.29-4.32 (1H, m, H-3'), 6.28 (1H, t, $J_{1,2}$ 7.0 Hz, H-1'), 7.61 (1H, s, H-6).

Methyl 6-deoxy-6-iodo-α-D-mannopyrannoside[2]: General procedure **E**, using methyl α-D-mannopyrannoside (2 g, 10.3 mmol) and purification by flash chromatography (ethyl acetate: methanol: water, 7:2:1, R_f 0.5) afforded methyl 6-deoxy-6-iodo-α-D-mannopyrannoside (2.3 g, 74 %) as a white solid. m.p 120-123 °C (EtOH/Et_2O) [lit 118-120 °C][2]; $[\alpha]_D^{20}$ +76.2 (*c*, 0.5 in CH_3OH) [lit. $[\alpha]_D^{22}$ +67.5 (*c*, 1.0 in CH_3OH)][2]; δ_H (400 MHz, D_2O) 3.25 (1H, dd, $J_{6,6'}$ 10.6 Hz, $J_{5,6}$ 7.0 Hz, H-6), 3.32 (3H, s, OCH_3), 3.35-3.49 (1H, m, H-5), 3.45 (1H, t, $J_{3,4}$ 9.4 Hz, H-4), 3.52 (1H, t, $J_{6,6'}$ 11.0 Hz, H-6'), 3.64 (1H, dd, $J_{3,4}$ 9.4 Hz, $J_{2,3}$ 3.1 Hz, H-3), 3.80 - 3.83 (1H, m, H-2), 4.61 (1H, s, H-1).

((2-(2-(2-Azidoethoxy)ethoxy)ethoxy)methyl)benzene 3a[3]: General procedure **C**, using 2-(2-(2-(benzyloxy)ethoxy)ethoxy)ethanol (1 g, 4.2 mmol) and purification by flash chromatography (petrol: ethyl acetate, 1:1, R_f 0.4) afforded ((2-(2-(2-azidoethoxy)ethoxy)ethoxy)methyl)benzene **3a** (0.92 g, 83 %) as a clear oil. δ_H (400 MHz, $CDCl_3$) 3.36 (2H, t, *J* 4.0 Hz, CH_2N_3), 3.63-3.68 (10H, m, 5 x CH_2), 4.56 (2H, s, $PhCH_2$), 7.26-7.34 (5H, m, Ar-H).

5'-Azido-2',5'-dideoxy-β-D-thymidine 4a[4]: General procedure **D**, using 2',5'-dideoxy-5'-iodo-β-D-thymidine (0.5 g, 1.4 mmol) and purification by flash chromatography (ethyl acetate 100%, R_f 0.1) to afford 5'-azido-2',5'-dideoxy-β-D-thymidine **4a** (0.27 g, 70 %) as a white solid. m.p 157-159 °C (EtOH/Et_2O) [lit 161-163 °C][5]; $[\alpha]_D^{20}$ +66.4 (*c*, 0.5 in CH_3OH) [lit. $[\alpha]_D^{22}$ +89.5 (*c*, 0.94 in CH_3OH)][4] ; δ_H (500 MHz, CD_3OD) 1.89 (3H, s, 5-CH_3), 2.24-2.31 (2H, m, H-2a', H-2b'), 3.50-3.64 (2H, m, H-5a', H-5b'), 3.96 (1H, aq, *J* 3.9 Hz, H-4'), 4.33-4.37 (1H, m, H-3'), 6.26 (1H, t, $J_{1,2}$ 6.8 Hz, H-1'), 7.54 (1H, s, H-6).

Methyl 6-azido-6-deoxy-α-D-mannopyrannoside 5a[6]: General procedure **D**, using methyl 6-deoxy-6-iodo-α-D-mannopyrannoside (1 g, 3.3 mmol**)**, and purification by flash chromatography (ethyl acetate: methanol: water, 7:2:1, R_f 0.5) afforded methyl 6-azido-6-deoxy-α-D-mannopyrannoside **5a** (530 mg, 74 %) as a yellow oil. $[\alpha]_D^{20}$ +43 (*c*, 0.5 in CH_3OH) [lit. $[\alpha]_D^{24.3}$ +41 (*c*, 0.066 in CH_3OH)][6]; δ_H (400 MHz, CD_3CN) 3.37 (3H, s, OCH_3), 3.44 (1H, dd, $J_{5,6}$ 6.3 Hz, $J_{6,6'}$ 12.9 Hz, H-6), 3.48-3.62 (4H, m, H-3, H-4, H-5, H-6'), 3.76 (1H, dd, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 3.1 Hz, H-2), 4.64 (1H, s, H-1).

1-Azido-3,7-dimethyloctane 6a[3]: General procedure **C**, using 3,7-dimethyl-1-octanol (1 g, 6.3 mmol), and purification by flash chromatography (petrol: ethyl acetate, 2:1, R_f 0.9) afforded 1-azido-3,7-dimethyloctane **6a** (1.08 g, 94 %) as a clear oil. δ_H (500 MHz, $CDCl_3$) 0.85-0.89 (9H, m, 3 x CH_3), 1.11-1.42 (7H, m, 3 x CH_2, CH), 1.48-1.63 (3H, m, CH_2, CH), 3.27 (2H, m, CH_2N_3).

Toluenesulfonylazide 7a[7]: Sodium azide (511 mg, 7.9 mmol, 1.5 equiv.) was added to a solution of the toluenesulfonylchloride (1 g, 5.2 mmol, 1 equiv.) in DMF (5 mL). The solution was then stirred at room temperature for 30 minutes. The reaction mixture was diluted with ethyl acetate (20 mL), and then the organic layer was separated and washed with water (2 x 30 mL) and brine (30 mL), dried over anhydrous $MgSO_4$, filtered, concentrated *in vacuo,* and the residue was purified by column chromatography (Petrol 100 %, R_f 0.1) afforded toluenesulfonylazide **7a** (0.7 g, 68 %) as a clear oil. δ_H (400 MHz, $CDCl_3$) 2.48 (3H, s, CH_3), 7.41, 7.84 (4H, 2 x d, *J* 8.2 Hz, 4 x Ar(C)H).

Methyl 6-azido-6-deoxy-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 8a[8]: General procedure **C**, using methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (1 g, 2.2 mmol), and purification by flash chromatography (petrol: ethyl acetate, 2:1, R_f 0.7) afforded methyl 6-azido-6-deoxy-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **8a** (1 g, 95 %) as a pale yellow oil. $[\alpha]_D^{20}$ +51.3 (*c*, 1.0 in $CHCl_3$) [lit. $[\alpha]_D^{20}$ +53.1 (*c*, 2.4 in $CHCl_3$)][8]; δ_H (400 MHz, $CDCl_3$) 3.33 (1H, dd, $J_{6,6'}$ 12.9 Hz, $J_{5,6}$ 5.5 Hz, H-6), 3.40 (3H, s, OCH_3), 3.42 - 3.46 (2H, m, H-6', H-4), 3.54 (1H, dd, $J_{1,2}$ 3.5 Hz, $J_{2,3}$ 9.4 Hz, H-2), 3.78 (1H, td, $J_{4,5}$ 9.8 Hz, $J_{5,6}$ 5.9 Hz, $J_{5,6'}$ 2.3 Hz, H-5), 3.98 (1H, t, $J_{2,3}$ 9.2 Hz, H-3), 4.57 (1H, d, *J* 11.0 Hz, CH_2Ph), 4.61 (1H, d, $J_{1,2}$ 3.5 Hz, H-1), 4.67 (1H, d, *J* 12.1 Hz, CH_2Ph), 4.77-4.84 (2H, m, CH_2Ph), 4.90 (1H, d, *J* 11.0 Hz, CH_2Ph), 5.0 (1H, d, *J* 11.0 Hz, CH_2Ph), 7.23 - 7.40 (15H, m, Ar-H).

11-Azidoundecene 9a[9]: General procedure **D**, using 11-bromoundecene (1 g, 4.3 mmol), and purification by flash chromatography (petrol: ethyl acetate, 2:1, R_f 0.9) afforded 11-azidoundecene **9a** (0.6 g, 71 %) as a pale yellow oil. δ_H (400 MHz, $CDCl_3$) 1.23-1.45 (12H, m, 6 x CH_2), 1.53-1.65 (2H, m, CH_2), 2.04 (2H, q, *J* 7.0 Hz, CH_2), 3.26 (2H, t, *J* 7.0 Hz, NCH_2), 4.90-5.03 (2H, m, $=CH_2$), 5.77-5.87 (1H, m, =CH).

Methyl 4-azidobutyrate 10a[10]: General procedure **D**, using methyl 4-chlorobutyrate (1 g, 1.1 mmol), and purification by flash chromatography (petrol 100 %, R_f 0.4) afforded methyl

4-azidobutyrate **10a** (0.73 g, 70 %) as a clear oil. δ_H (400 MHz, $CDCl_3$) 1.87-1.95 (2H, m, CH_2), 2.41 (2H, t, *J* 7.4 Hz, $COCH_2$), 3.35 (2H, t, *J* 6.3 Hz, NCH_2), 3.69 (3H, s, OCH_3).

1,10-Diazidodecane 11a[11]: General procedure **D**, using 1,10-dibromodecane (1 g, 3.4 mmol), and purification by flash chromatography (petrol 100 %, R_f 0.4) afforded 1,10-diazidodecane **11a** (0.6 g, 80 %) as a clear oil. δ_H (400 MHz, $CDCl_3$) 1.23-1.41 (12H, m, 6 x CH_2), 1.53-1.63 (4H, m, 2 x CH_2), 3.25 (4H, t, *J* 7.0 Hz, 2 x NCH_2).

1-Azidomethyl-4-nitrobenzene 12a[12]: General procedure **D**, using 1-chloromethyl-4-nitrobenzene **12a** (1 g, 5.8 mmol), and purification by flash chromatography (petrol: ethyl acetate, 5:1, R_f 0.4) afforded 1-azidomethyl-4-nitrobenzene (0.7 g, 67 %) as a pale yellow oil. δ_H (400 MHz, $CDCl_3$) 4.50 (2H, s, $PhCH_2$), 7.50, 8.25 (4H, 2 x d, *J* 8.6 Hz, 4 x Ar(C)H).

2-(2-(2-(Benzyloxy)ethoxy)ethoxy)ethanamine 3b[3]: General procedure **A**, using ((2-(2-(2-azidoethoxy)ethoxy)ethoxy)methyl)benzene **3a** (100 mg, 0.4 mmol), afforded 2-(2-(2-(benzyloxy)ethoxy)ethoxy)ethanamine **3b** (80 mg, 89 %) as a pale yellow waxy solid. υ_{max} (neat) 3408 (w, NH) cm^{-1} ; δ_H (500 MHz, CD_3OD) 3.09 (2H, t, *J* 5.5 Hz, CH_2NH_2), 3.62-3.73 (10H, m, CH_2), 4.55 (2H, s, Ph-CH_2), 7.25-7.38 (5H, m, Ar-H); δ_C (100 MHz, CD_3OD) 39.3 (t, CH_2NH_2), 66.4 (t, $PhCH_2$), 69.0, 69.8, 70.0, 70.1, 72.7 (5 x t, 5 x CH_2), 127.4, 127.6, 128.0 (3 x d, 5 x Ar(C)H), 138.0 (s, Ar(C)C); HRMS (ESI) calculated for $C_{13}H_{21}NNaO_3$ ($M+Na^+$) 262.1419. Found 262.1414.

5'-Amino-2',5'-dideoxy-β-D-thymidine 4b: General procedure **A**, using 5'-azido-2',5'-dideoxy-β-D-thymidine **4a** (50 mg, 0.2 mmol) afforded 5'amino-5'-deoxy-β-D-thymidine **4b** (42 mg, 93 %) as a white solid. m.p 165-167 °C ($EtOH/Et_2O$); $[\alpha]_D^{20}$ +23.2 (*c*, 0.5 in CH_3OH); υ_{max} (neat) 3339 (w, NH), 1655 (s, C=O) cm^{-1}; δ_H (400 MHz, CD_3OD) 1.89 (3H, s, 5-CH_3), 2.20-2.31, 2.49-2.60 (2H, 2 x m, H-2a', H-2b'), 3.17-3.27 (2H, m, H-5a', H-5b'), 3.95-4.03 (1H, m, H-4'), 4.32-4.41 (1H, m, H-3'), 6.13 (1H, t, $J_{1,2}$ 6.8 Hz, H-1'), 7.45 (1H, s, H-6); δ_C (100 MHz, CD_3OD) 10.8 (q, 5-CH_3), 37.9 (t, C-2'), 41.4 (t, C-5'), 71.6 (d, C-3'), 82.7 (d, C-4'), 87.6 (d, C-1'), 110.3 (s, C-5), 138.2 (d, C-6), 150.8, 164.9 (2 x s, C-2, C-3); HRMS (ESI) calculated for $C_{10}H_{16}N_3O_4$ ($M+H^+$) 242.1135. Found 242.1140.

Methyl 6-amino-6-deoxy-α-D-mannopyrannoside 5b[13]: General procedure **A** using methyl 6-azido-6-deoxy-α-D-mannopyrannoside **5a** (50 mg, 0.3 mmol), afforded methyl 6-amino-6-

deoxy-α-D-mannopyrannoside **5b** (40 mg, 91 %) as a white foam. $[\alpha]_D^{20}$ +81 (*c*, 1.0 in CH_3OH) [lit. $[\alpha]_D^{23}$ +76 (*c*, 1.0 in CH_3OH)][13] ; υ_{max} (neat) 3340 (w, NH and OH) cm^{-1}; δ_H (400 MHz, CD_3OD) 2.96-3.03 (1H, m, H-6), 3.23 (1H, dd, $J_{6,6'}$ 13.1 Hz, $J_{5,6'}$ 2.9 Hz, H-6'), 3.39 (3H, s, OCH_3), 3.51 (1H, at, *J* 9.4 Hz, H-4), 3.56-3.62 (1H, m, H-5), 3.66 (1H, dd, $J_{3,4}$ 9.2 Hz, $J_{2,3}$ 3.3 Hz, H-3), 3.79 - 3.81 (1H, m, H-2), 4.66 (1H, d, $J_{1,2}$ 1.6 Hz, H-1); δ_C (100 MHz, CD_3OD) 41.2 (t, C-6), 54.2 (q, OCH_3), 68.4 (d, C-4), 70.1 (d, C-5), 70.5 (d, C-2), 70.7 (d, C-3), 101.6 (d, C-1); HRMS (ESI) calculated for $C_7H_{16}NO_5$ ($M+H^+$) 194.1023. Found 194.1023.

1-Amino-3,7-dimethyloctane 6b[3]: General procedure **B**, using 1-azido-3,7-dimethyloctane **6a** (100 mg, 0.5 mmol), afforded 1-amino-3,7-dimethyloctane **6b** (78 mg, 85 %) as a clear oil; υ_{max} (neat) 3260 (w, NH) cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.81-0.83 (9H, m, CH_3), 1.07-1.32 (6H, m, CH_2), 1.46-1.64, 1.73-1.82 (4H, m, 2 x CH, CH_2), 2.95-3.07 (2H, m, CH_2NH_2); δ_C (125 MHz, $CDCl_3$) 19.1, 22.6, 22.7 (3 x q, 3 x CH_3), 24.6 (t, CH_2), 27.9, 30.7 (2 x d, 2 x CH), 34.7, 36.8, 38.4 (3 x t, 3 x CH_2), 39.1 (t, CH_2NH_2); (ESI) calculated for $C_{10}H_{24}N$ ($M+H^+$) 158.1909. Found 158.1906.

Toluenesulfonamide 7b[14]: General procedure **B**, using toluenesulfonylazide **7a** (100 mg, 0.5 mmol), toluenesulfonamide **7b** (82 mg, 95 %) as a pale yellow solid; m.p 118-120 °C (Ethanol/Et_2O) [lit 125-126 °C][15]; υ_{max} (neat) 3258, 3355 (w, NH), 1385, 1154 (s, S=O) cm^{-1}; δ_H (400 MHz, CD_3OD) 2.41 (3H, s, CH_3), 7.34 (2H, d *J* 7.8 Hz, Ar(C)H), 7.77 (2H, d *J* 8.2 Hz, Ar(C)H) ; δ_C (100 MHz, CD_3OD) 20.0 (q, CH_3), 125.7, 129.1 (2 x d, 2 x Ar(C)H), 140.7, 142.7 (2 x s, Ar(C)SO_2, Ar(C)CH_3); HRMS (ESI) calculated for $C_7H_9NNaO_2S$ ($M+Na^+$) 194.0246. Found 194.0245.

Methyl 6-amino-6-deoxy-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 8b[16]: General procedure **B**, using methyl 6-azido-6-deoxy-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **8a** (100 mg, 0.2 mmol), afforded methyl 6-amino-6-deoxy-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **8b** (88 mg, 93 %) as white solid. m.p 89-91 °C (Et_2O) [lit 86-89 °C][16]; $[\alpha]_D^{20}$ +41.2 (*c*, 0.25 in CH_3OH) [lit. $[\alpha]_D^{20}$ +54.8 (*c*, 1.0 in $CHCl_3$)][17]; υ_{max} (neat) 3392 (w, NH) cm^{-1}; δ_H (400 MHz, CD_3OD) 2.83 (1H, dd, $J_{6,6'}$ 13.1 Hz, $J_{5,6}$ 9.2 Hz, H-6), 3.15 (1H, dd, $J_{6,6'}$ 13.1 Hz, $J_{5,6'}$ 2.5 Hz, H-6'), 3.32-3.36 (1H, m, H-4), 3.41 (3H, s, OCH_3), 3.57 (1H, dd, $J_{1,2}$ 3.5 Hz, $J_{2,3}$ 9.4 Hz, H-2), 3.74 (1H, td, $J_{4,5}$ 9.4 Hz, $J_{5.6}$ 9.4 Hz, $J_{5,6'}$ 2.7 Hz, H-5), 3.89 (1H, at, *J* 9.2 Hz, H-3), 4.62 (1H, d, *J* 11.0 Hz, CH_2Ph), 4.70 (1H, d, *J* 11.0 Hz, CH_2Ph), 4.75 (2H, d, *J* 11.0 Hz, CH_2Ph),

4.77 (1H, d, $J_{1,2}$ 3.5 Hz, H-1), 4.87-4.95 (2H, m, CH_2Ph), 7.20 - 7.46 (15H, m, Ar-H); δ_C (100 MHz, CD_3OD) 40.9 (t, C-6), 54.7 (q, OCH_3), 67.8 (d, C-5), 72.7 (t, CH_2Ph), 74.5 (t, CH_2Ph), 75.1 (t, CH_2Ph), 78.8 (d, C-4), 79.9 (d, C-2), 81.2 (d, C-3), 97.8 (d, C-1), 127.3, 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.4, 128.6, 128.7 (10 x d, 15 x Ar(C)H), 138.0, 138.1, 138.5 (3 x s, 3 x Ar(C)CH_2); HRMS (ESI) calculated for $C_{28}H_{34}NO_5$ ($M+H^+$) 464.2437. Found 464.2432.

10-Undeceneamine 9b[18]: General procedure **B**, using 11-azidoundecene **9a** (100 mg, 0.5 mmol), afforded 10-undeceneamine **9b** (81 mg, 87 %) as a pale yellow oil. υ_{max} (neat) 3418 (w, NH), 3010 (m, =CH), 1640 (m, C=C) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.20-1.48 (12H, m, CH_2), 1.75-1.85 (2H, m, CH_2), 2.04 (2H, q, *J* 6.9 Hz, CH_2), 3.03-3.14 (2H, m, NCH_2), 4.90-5.03 (2H, m, $=CH_2$), 5.75-5.87 (1H, m, =CH), 7.40 (br s, 1H, NH); δ_C (100 MHz, $CDCl_3$) 26.6, 27.5, 28.9, 29.1, 29.1, 29.4, 33.8, (7 x t, 8 x CH_2), 40.6 (t, CH_2N), 114.2 (t, $=CH_2$), 139.1 (d, =CH); HRMS (ESI) calculated for $C_{11}H_{24}N$ ($M+H^+$) 170.1903. Found 170.1905.

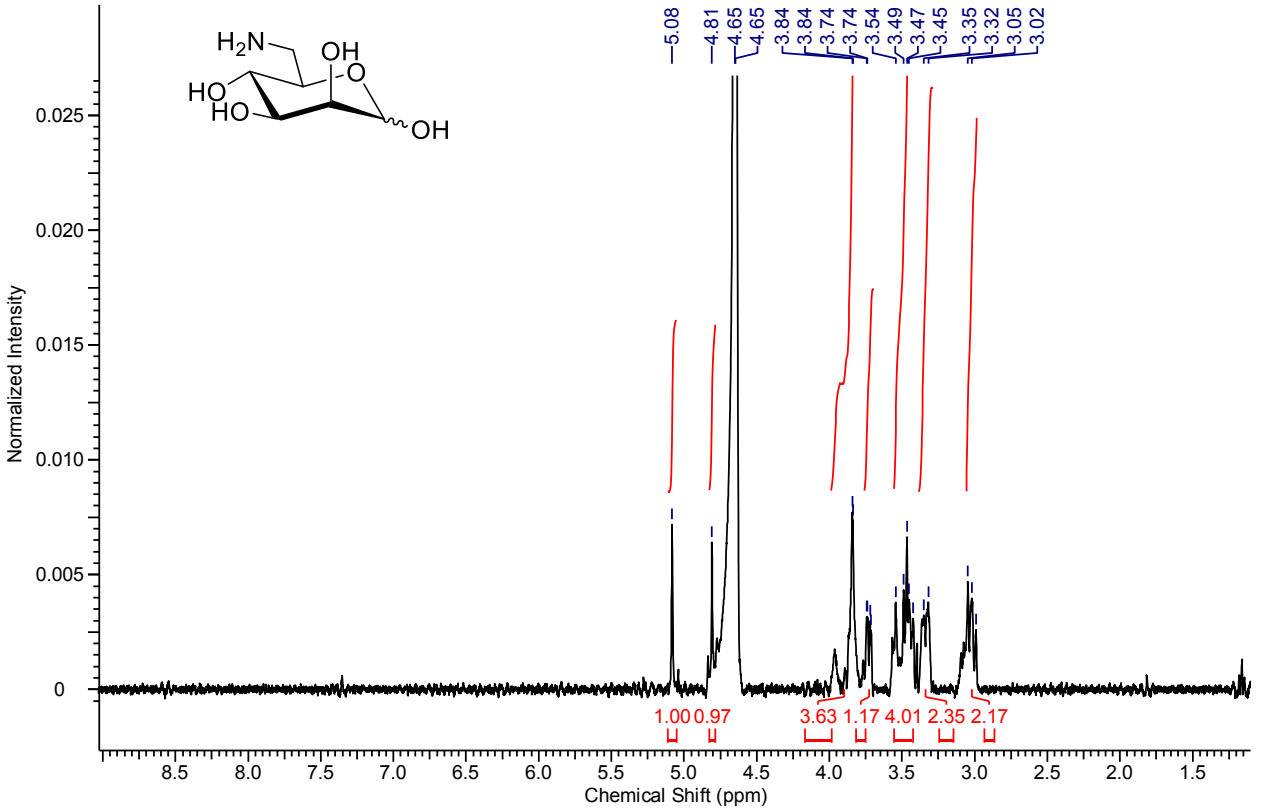
2-Pyrrolidinone 10b[19]: General procedure **B**, using methyl 4-azidobutyrate **10a** (100 mg, 0.7 mmol), afforded methyl 4-aminobutyrate **10b** (59 mg, quantitative yield) as a white waxy solid.; υ_{max} (neat) 1654 (s, C=O) cm^{-1}; δ_H (400 MHz, CD_3OD) 2.13-2.24 (2H, m, CH_2), 2.48 (2H, t, *J* 8.2 Hz, $COCH_2$), 3.50 (2H, t, *J* 7.0 Hz, NCH_2); δ_C (100 MHz, CD_3OD) 20.0 (t, CH_2), 29.8 (t, $COCH_2$), 43.3 (t, NCH_2), 180.9 (s, C=O); HRMS (ESI) calculated for C_4H_8NO ($M+H^+$) 86.0600. Found 86.0603.

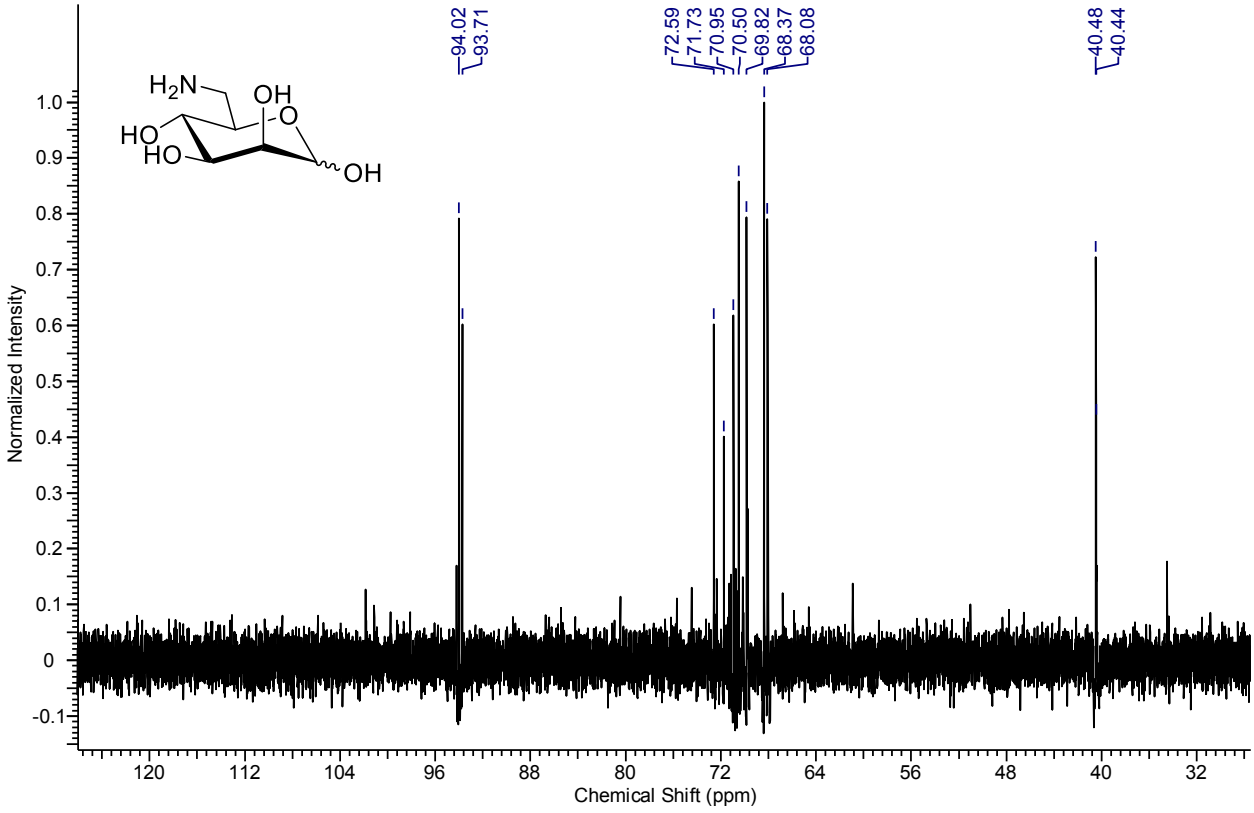
1,10-Diaminodecane 11b[20]: General procedure **B** using 1,10-diazidodecane **11a** (100 mg, 0.4 mmol) and 8. equiv. of NaI and 4 equiv. of acid, afforded 1,10-diaminodecane **11b** (70 mg, 92 %) as a white solid. m.p 66-68 °C ($MeOH/Et_2O$) [lit 62-64 °C][20]; υ_{max} (neat) 3420 (w, NH) cm^{-1}; δ_H (400 MHz, CD_3OD) 1.32-1.43 (12H, m, 6 x CH_2), 1.60-1.70 (4H, m, 2 x CH_2), 2.91 (4H, t, *J* 7.4 Hz, 2 x NCH_2); δ_C (100 MHz, CD_3OD) 26.0, 27.2, 28.8, 29.0 (4 x t, 8 x CH_2), 39.4 (t, 2 x NCH_2); HRMS (ESI) calculated for $C_{10}H_{25}N_2$ ($M+H^+$) 173.2012. Found 173.2010.

(4-Nitrophenyl)methanamine 12b[21]: General procedure **B**, using 1-azidomethyl-4-nitrobenzene **12a** (100 mg, 0.6 mmol), afforded (4-nitrophenyl)methanamine **12b** (85 mg, quantitative yield) as a pale yellow waxy solid. υ_{max} (neat) 3308 (w, NH), 1541, 1350 (s, NO_2) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 4.16 (2H, s, $PhCH_2$), 7.74 (2H, d, *J* 8.6 Hz, 2 x

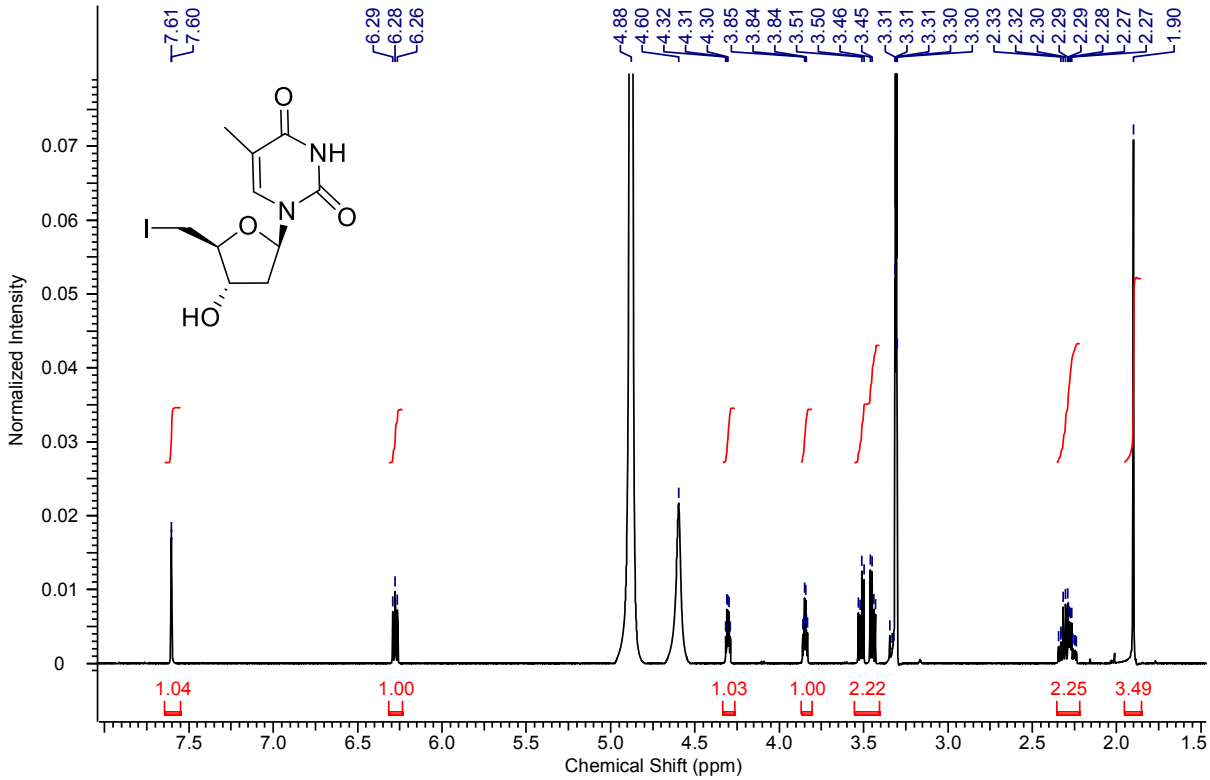
Ar(C)H), 8.27 (2H, d, *J* 8.2 Hz, 2 x Ar(C)H); δ_C (100 MHz, DMSO-d_6) 42.0 (t, $PhCH_2$), 124.0, 130.5 (2 x d, 4 x Ar(C)H), 142.5, 147.8 (2 x s, 2 x Ar(C)CH_2); HRMS (ESI) calculated for $C_7H_9N_2O_2$ ($M+H^+$) 153.0659. Found 153.0659.

6-Amino-6-deoxy-D-mannopyranose 2

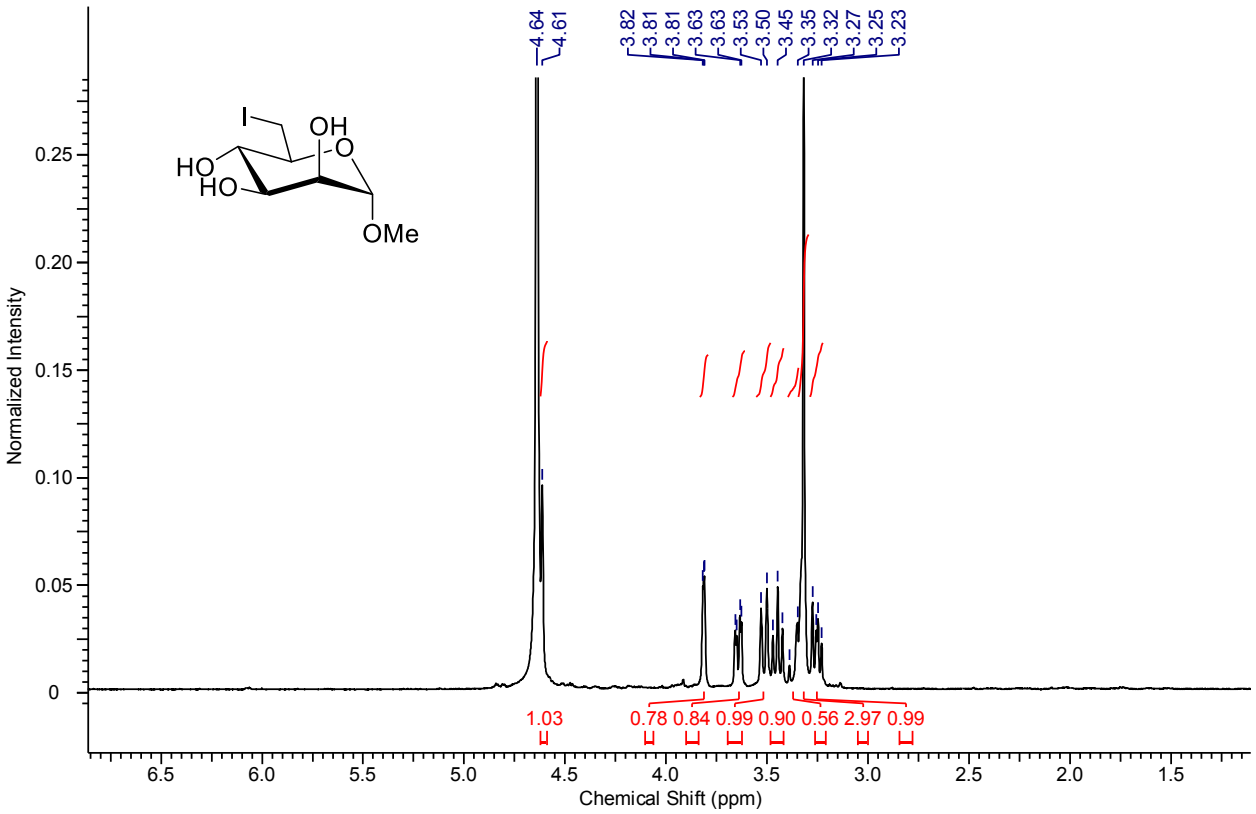




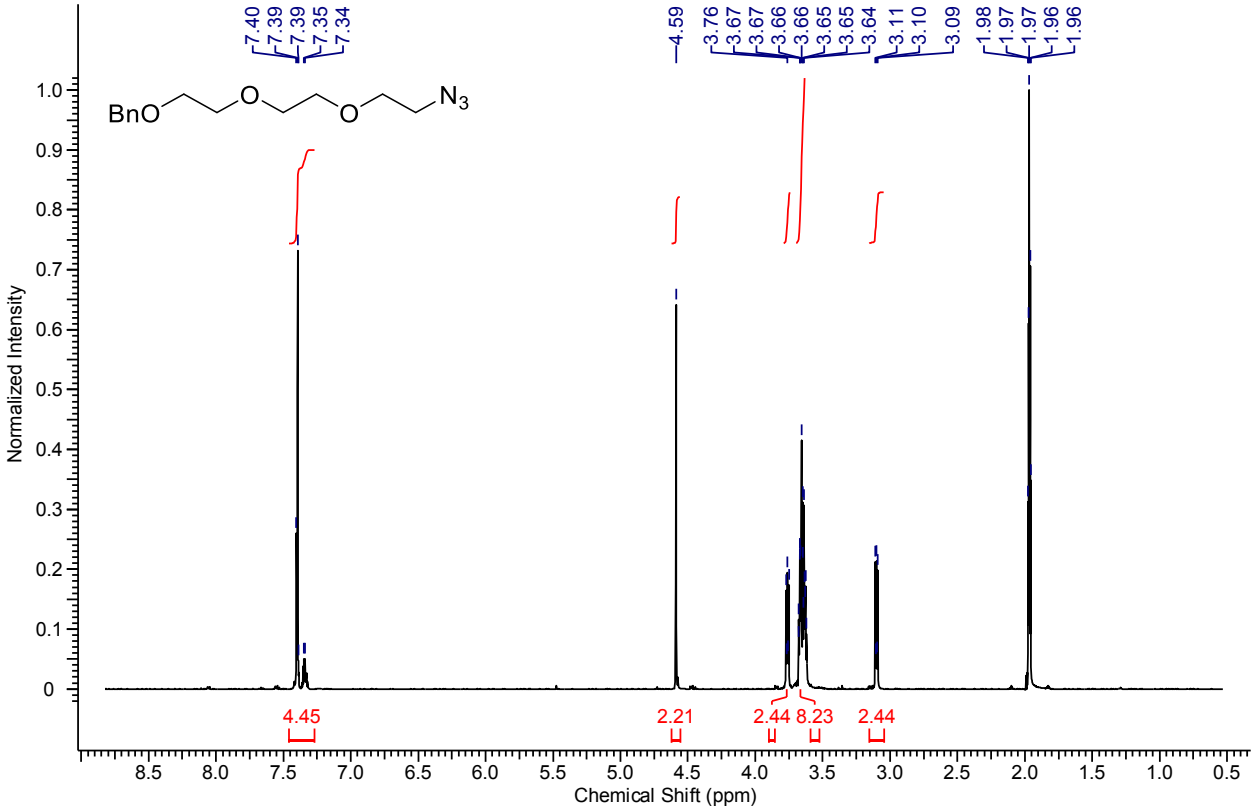
2',5'-Deoxy-5'-iodo-β-D-thymidine



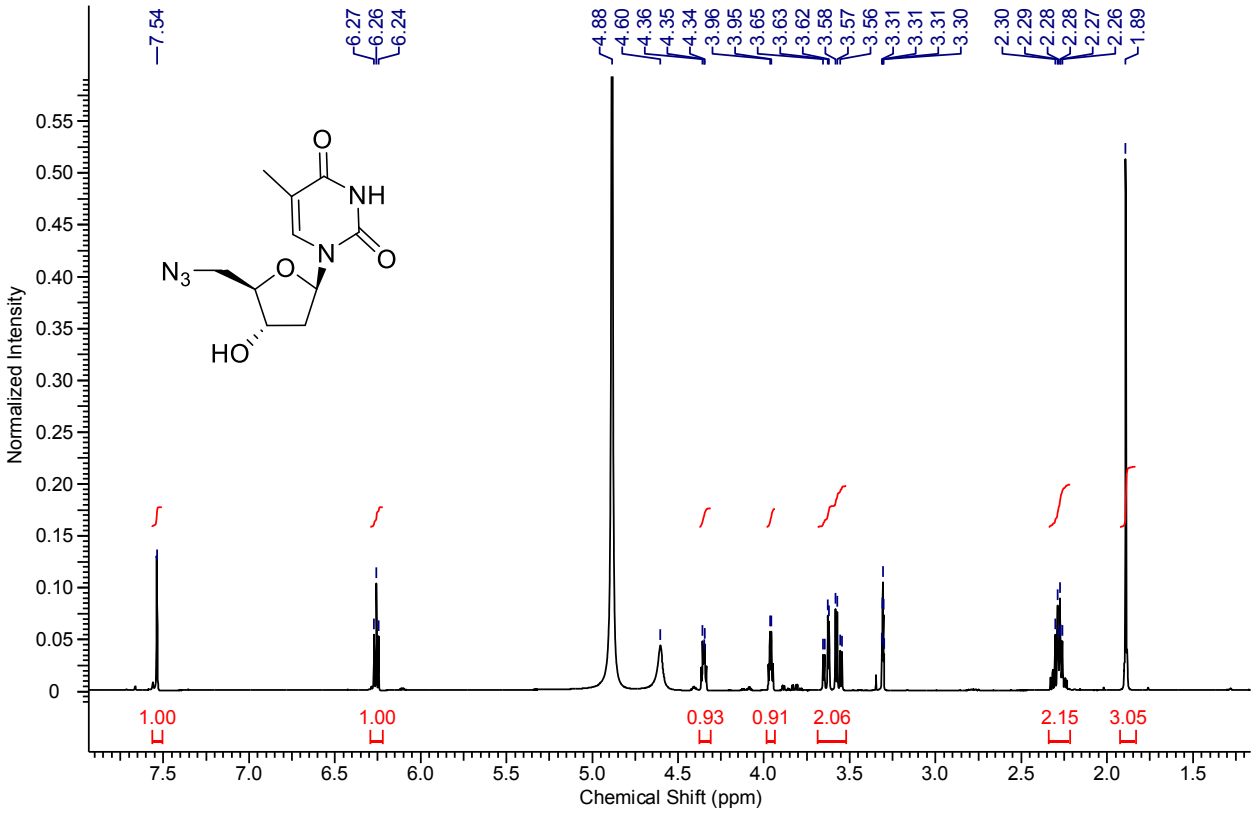
Methyl 6-deoxy-6-iodo-α-D-mannopyrannoside



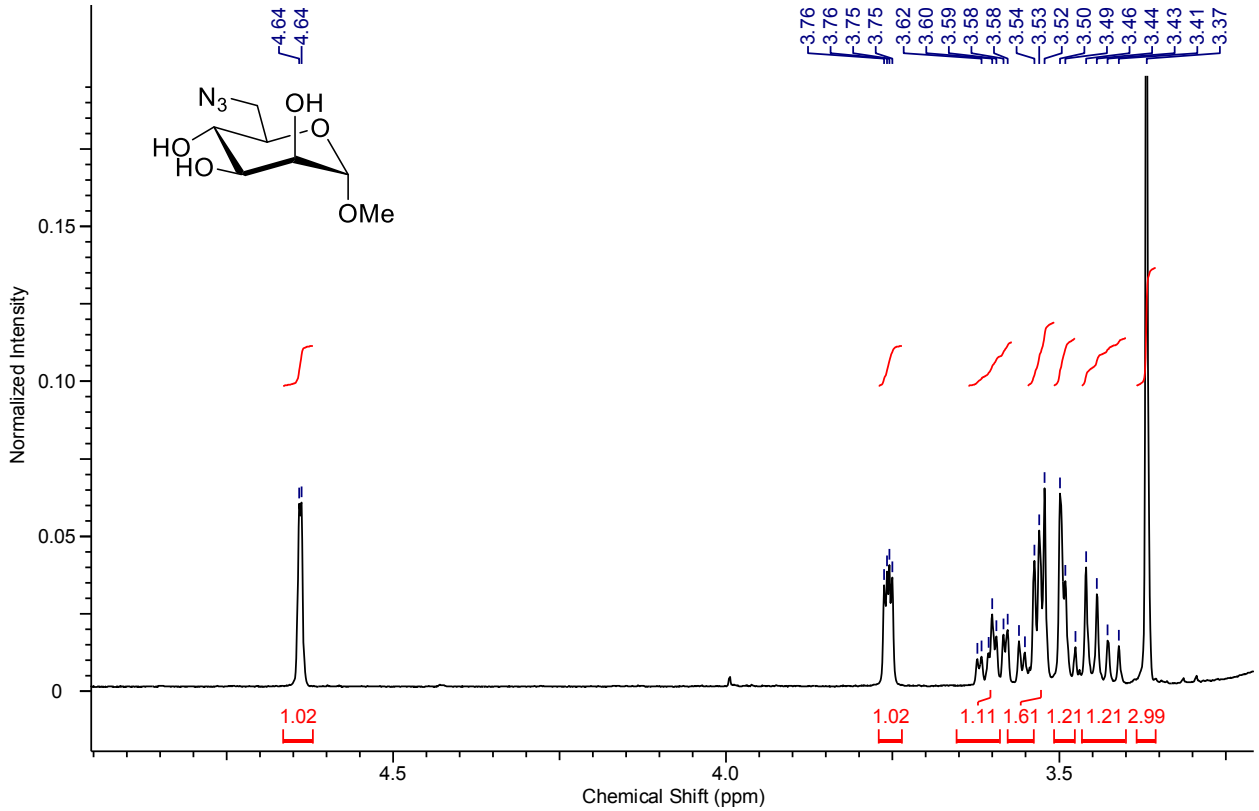
((2-(2-(2-Azidoethoxy) ethoxy)ethoxy)methyl)benzene 3a



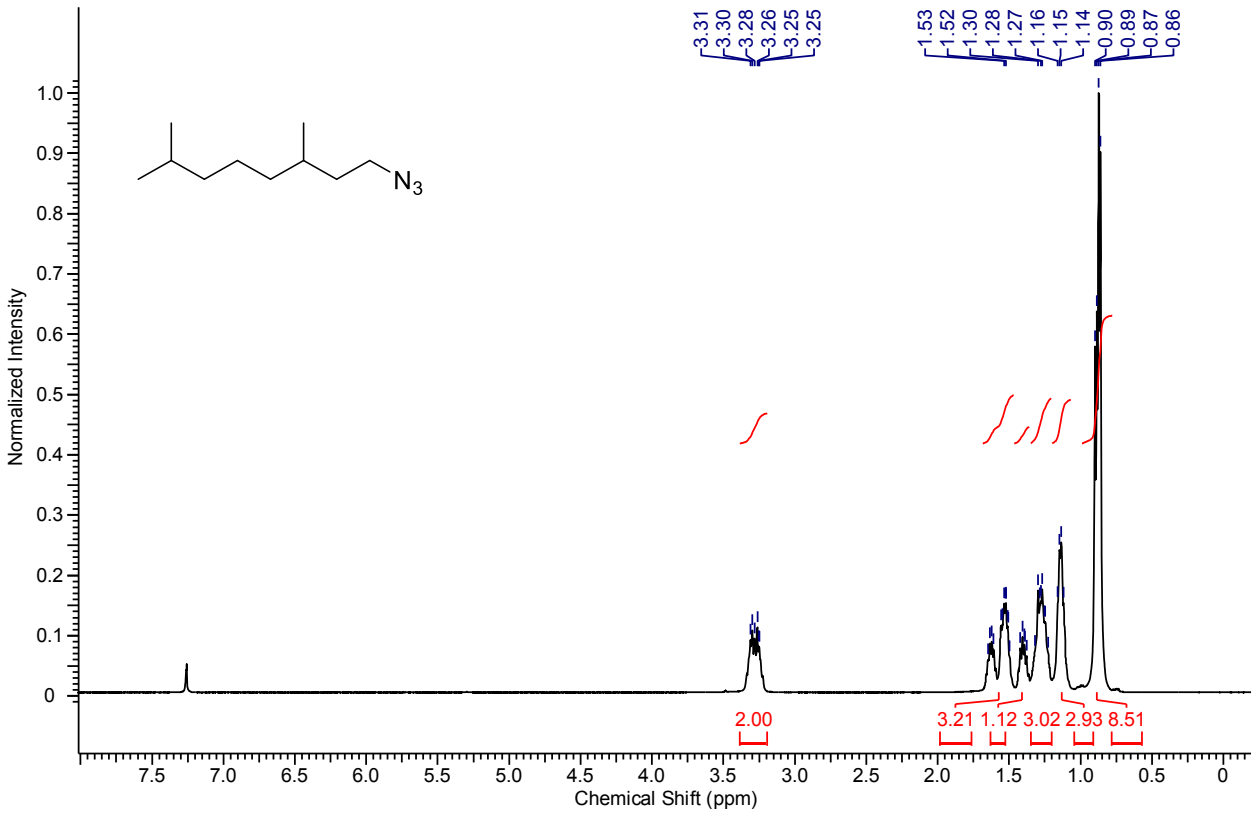
5’-Azido-2’,5’-dideoxy-β-D-thymidine 4a



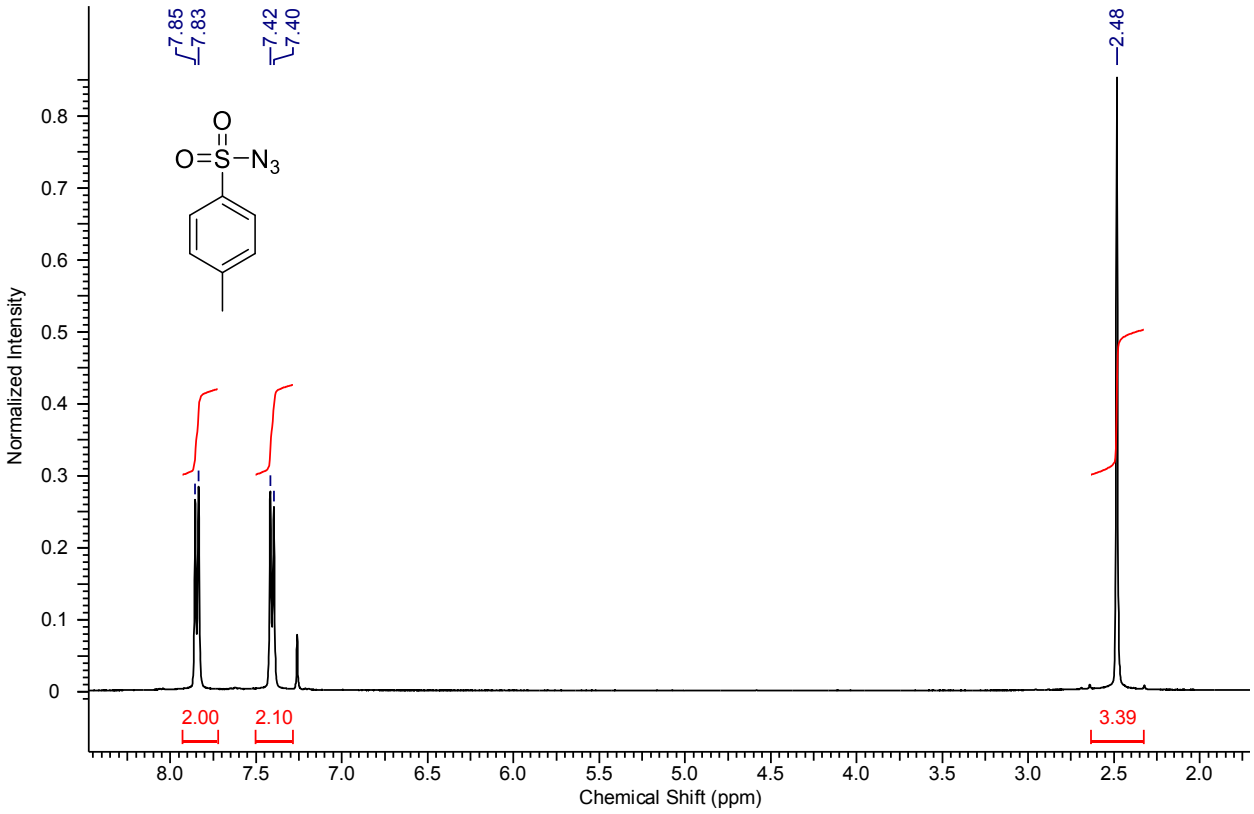
Methyl-6-azido-6-deoxy-α-D-mannopyrannoside 5a



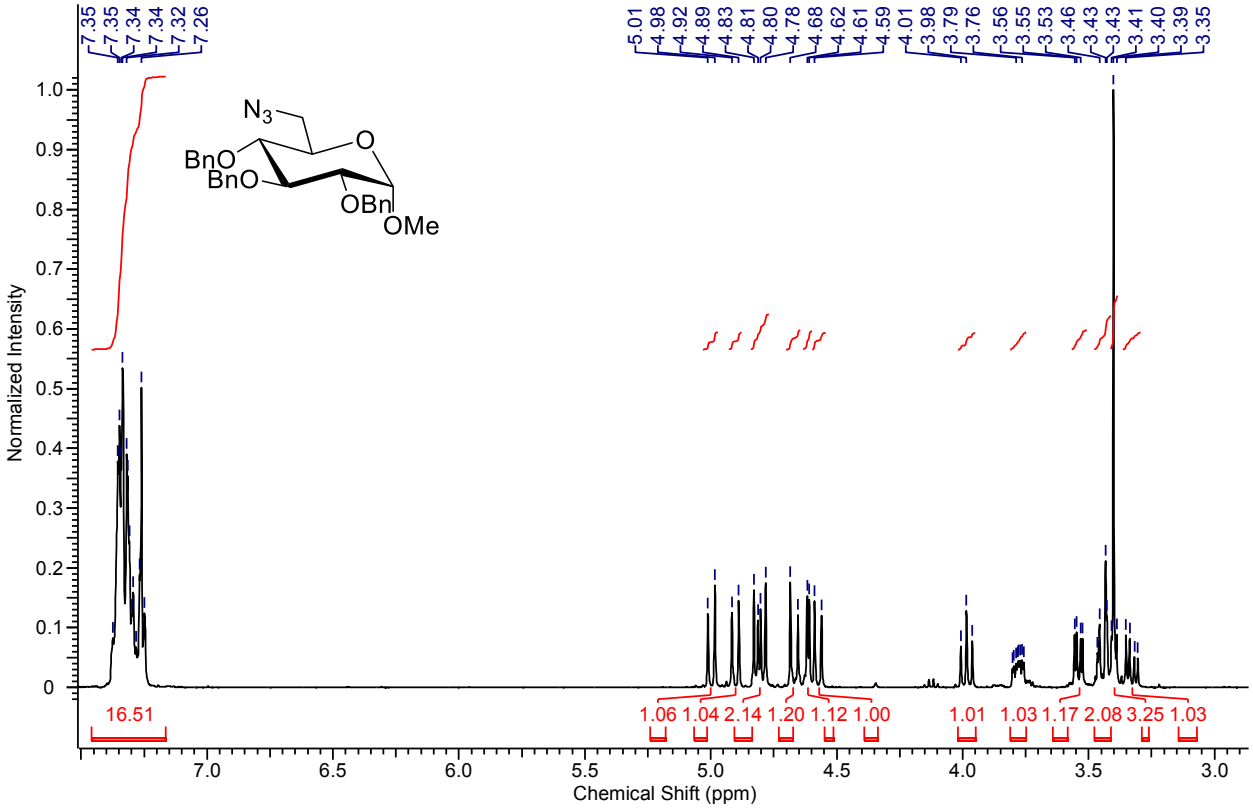
1-Azido-3,7-dimethyloctane 6a



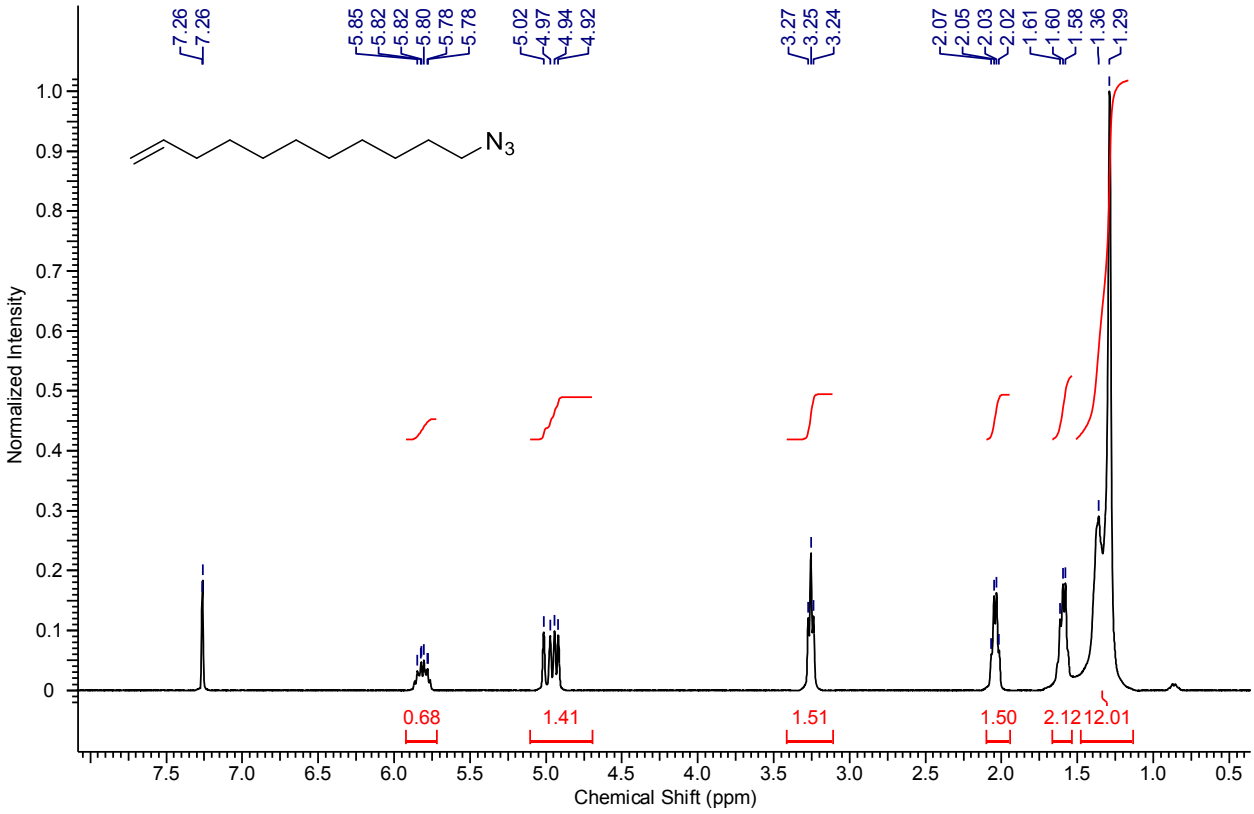
Toluenesulfonylazide 7a



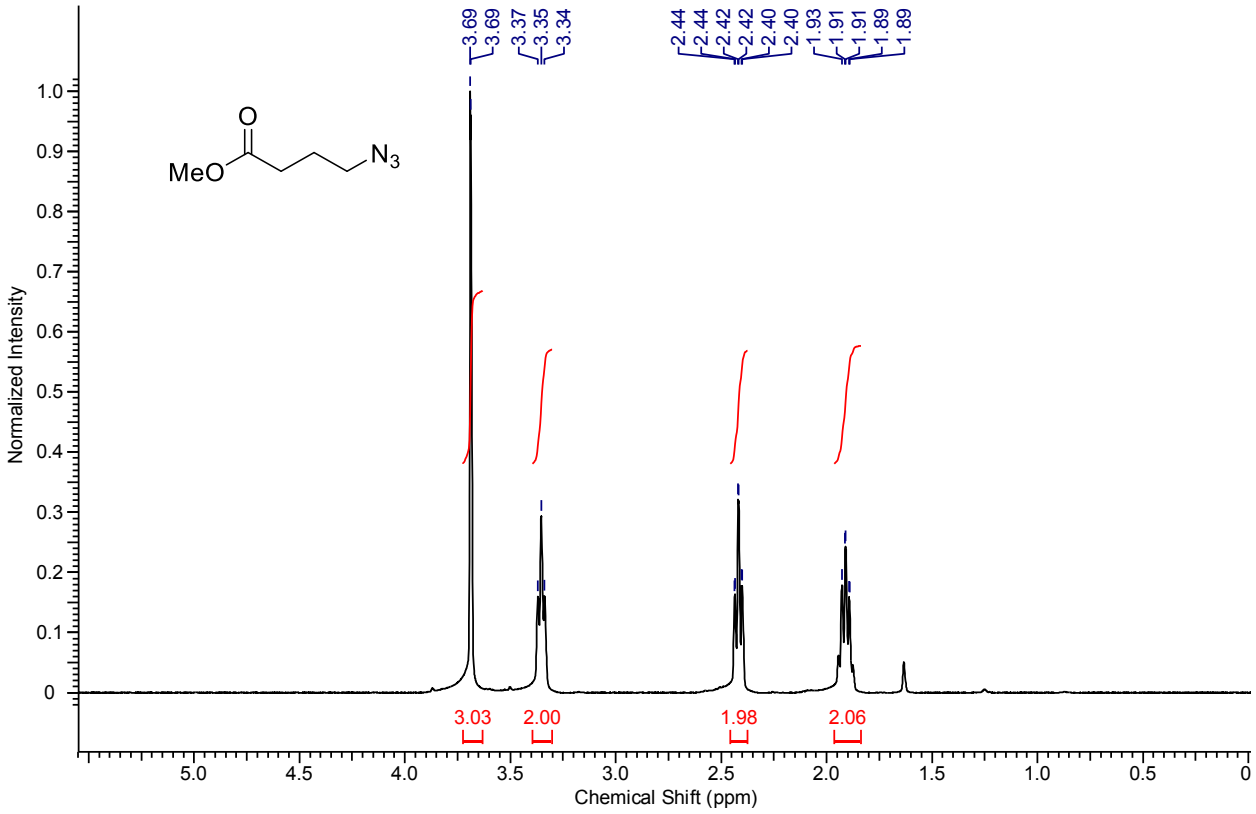
Methyl-6-azido-6-deoxy-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 8a



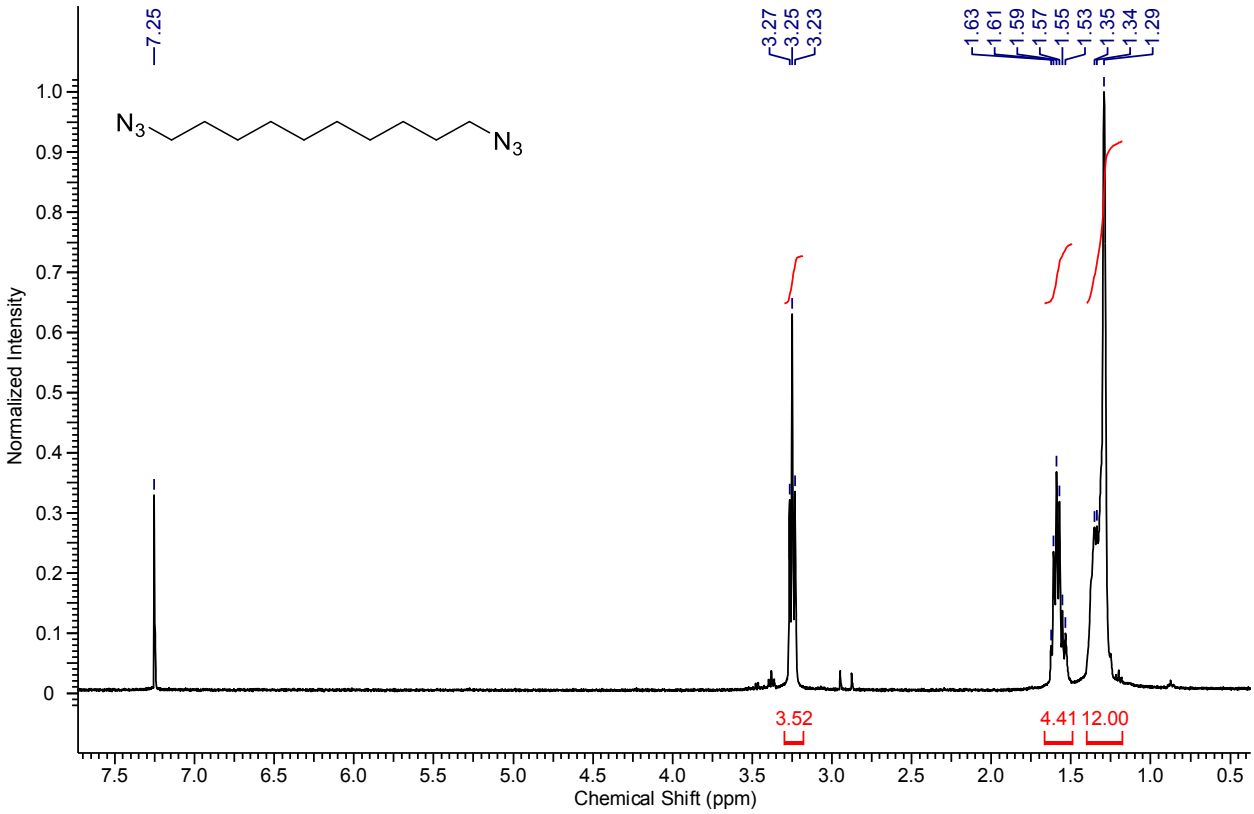
11-Azidoundecene 9a



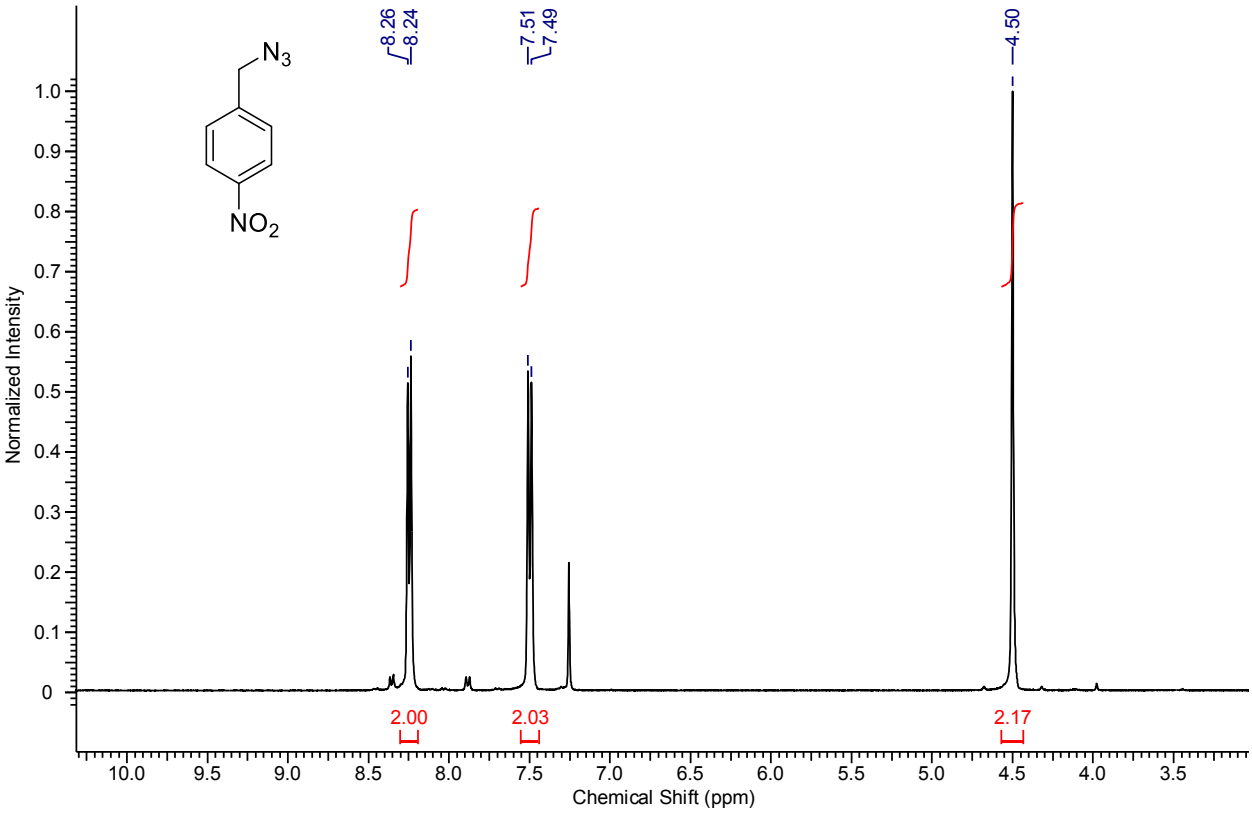
Methyl 4-azidobutyrate 10a



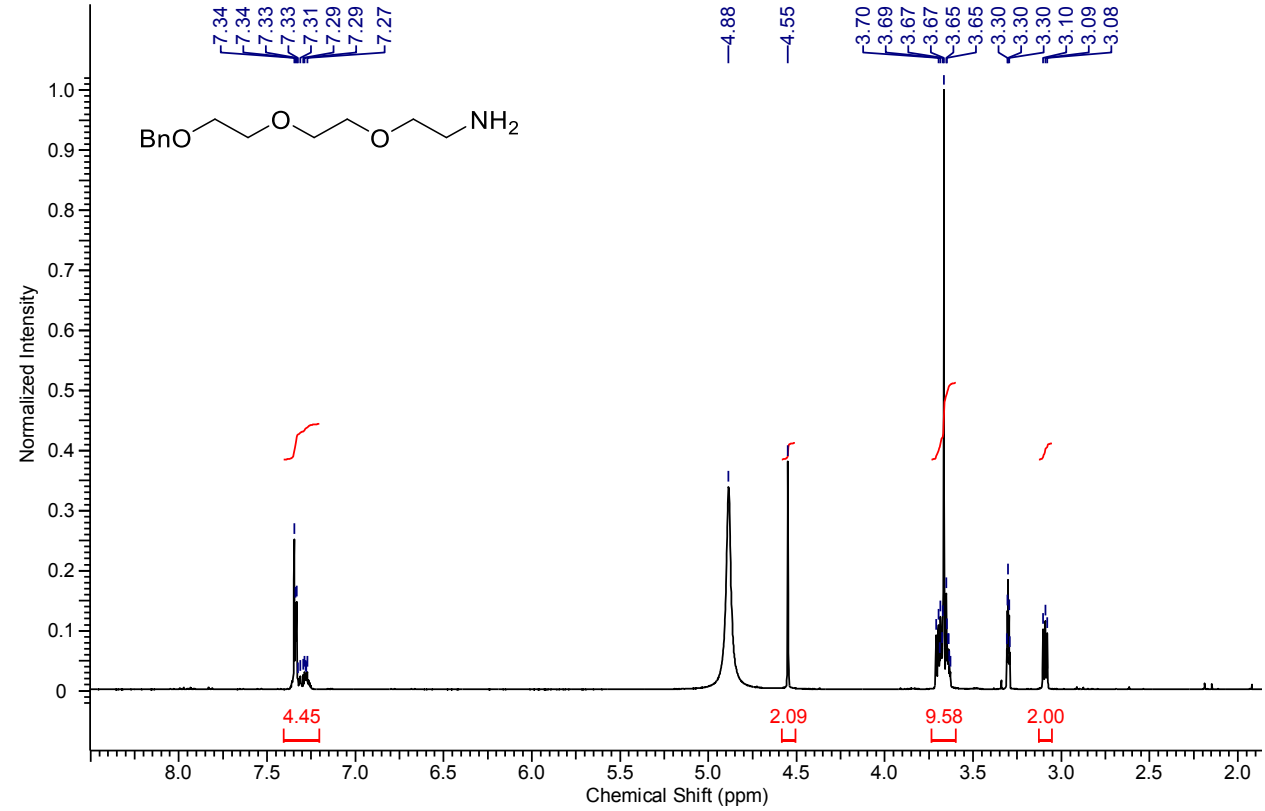
1,10-Diazidodecane 11a

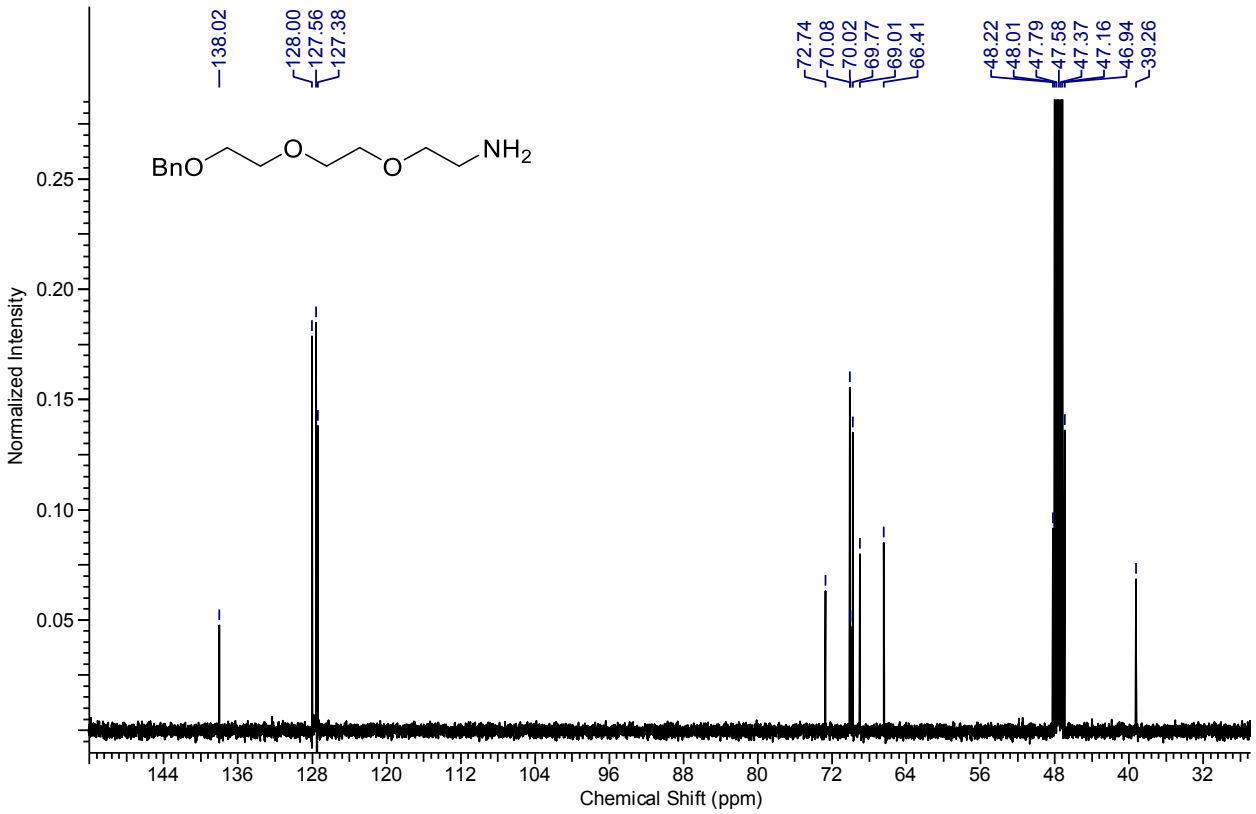


1-Azidomethyl-4-nitrobenzene 12a

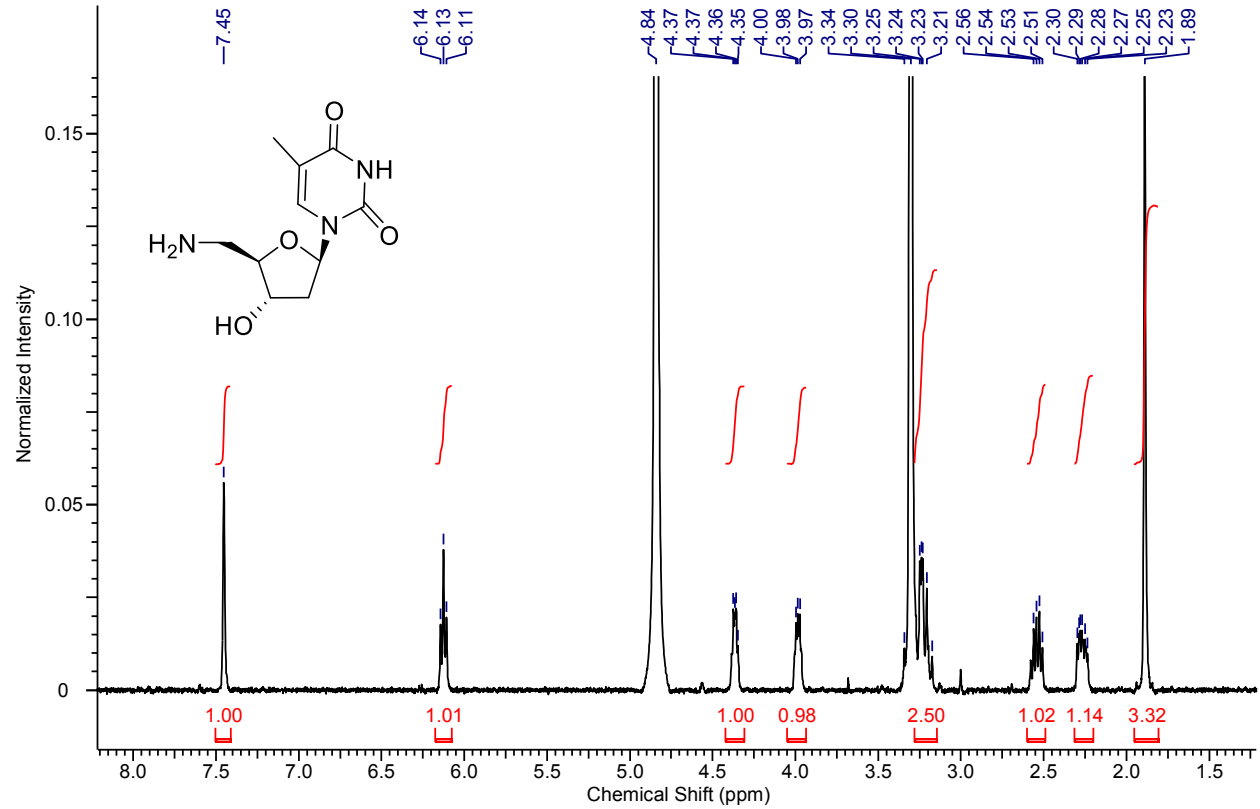


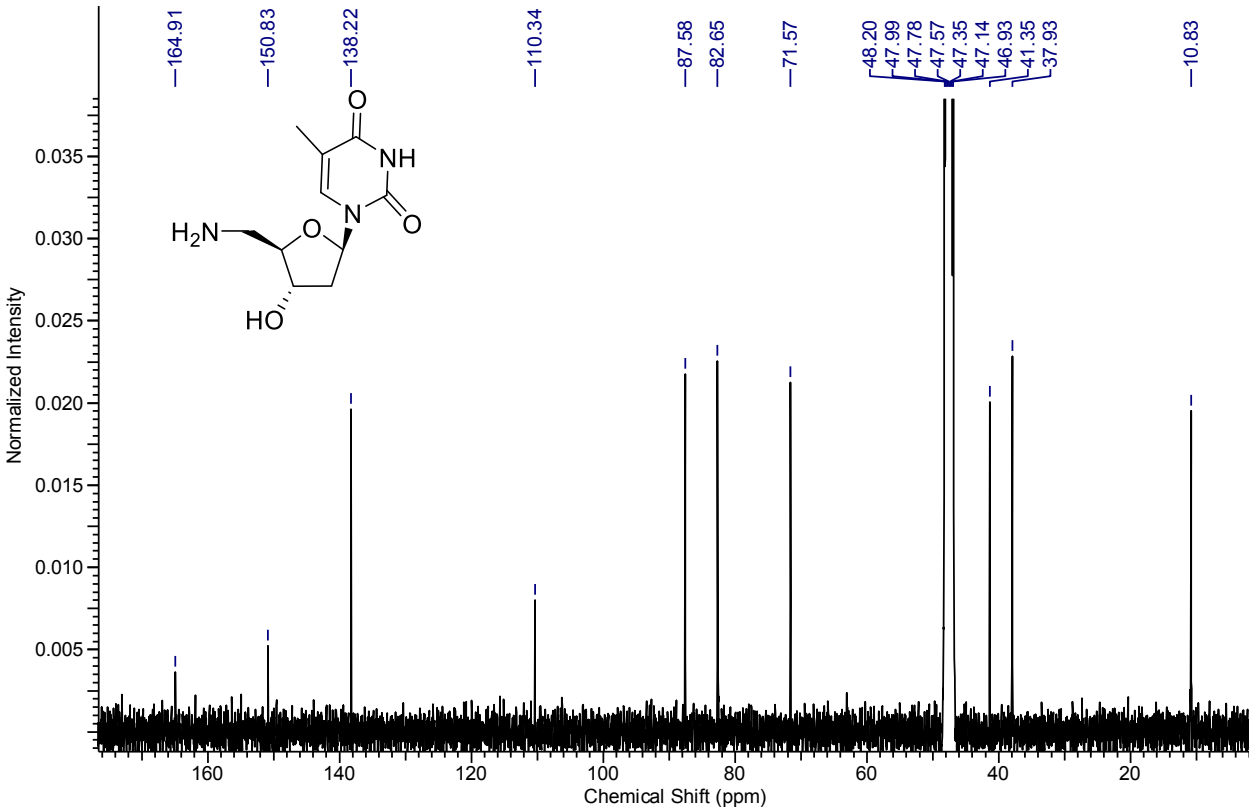
2-(2-(2-(Benzyloxy)ethoxy)ethoxy)ethanamine 3b



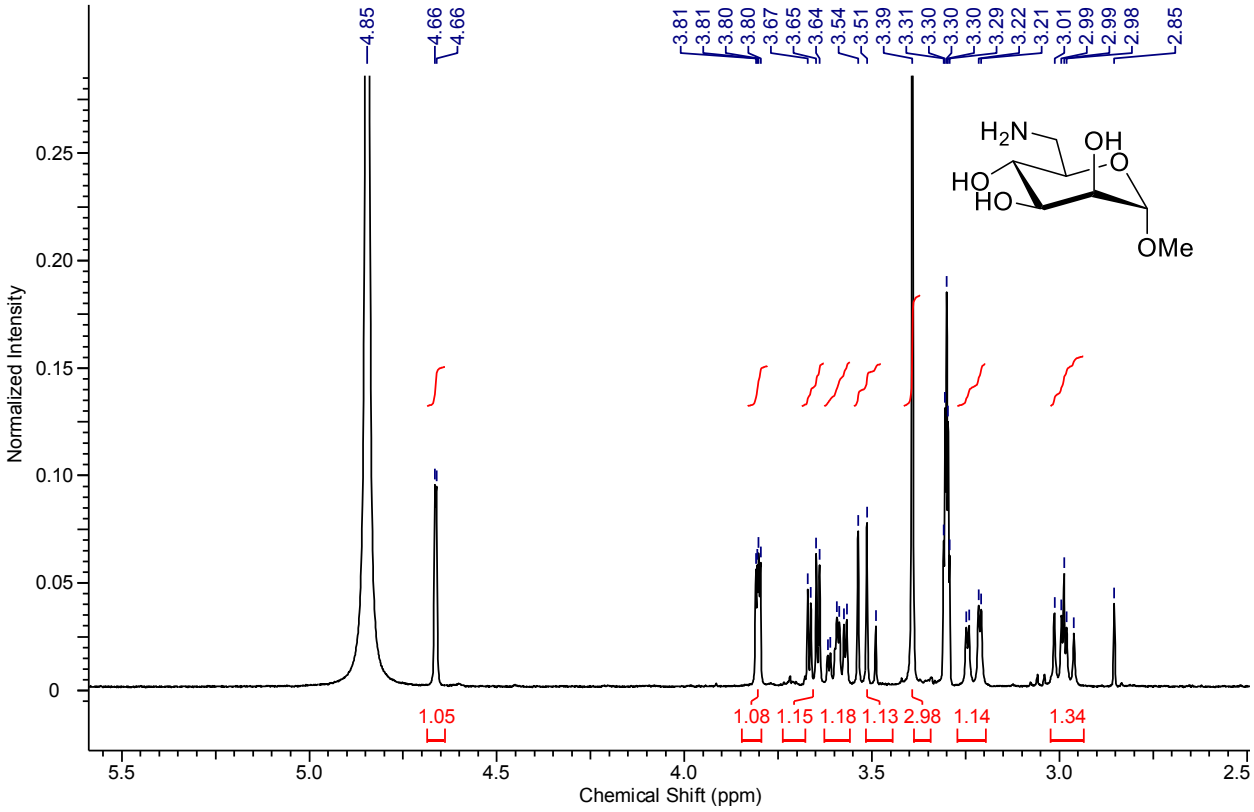


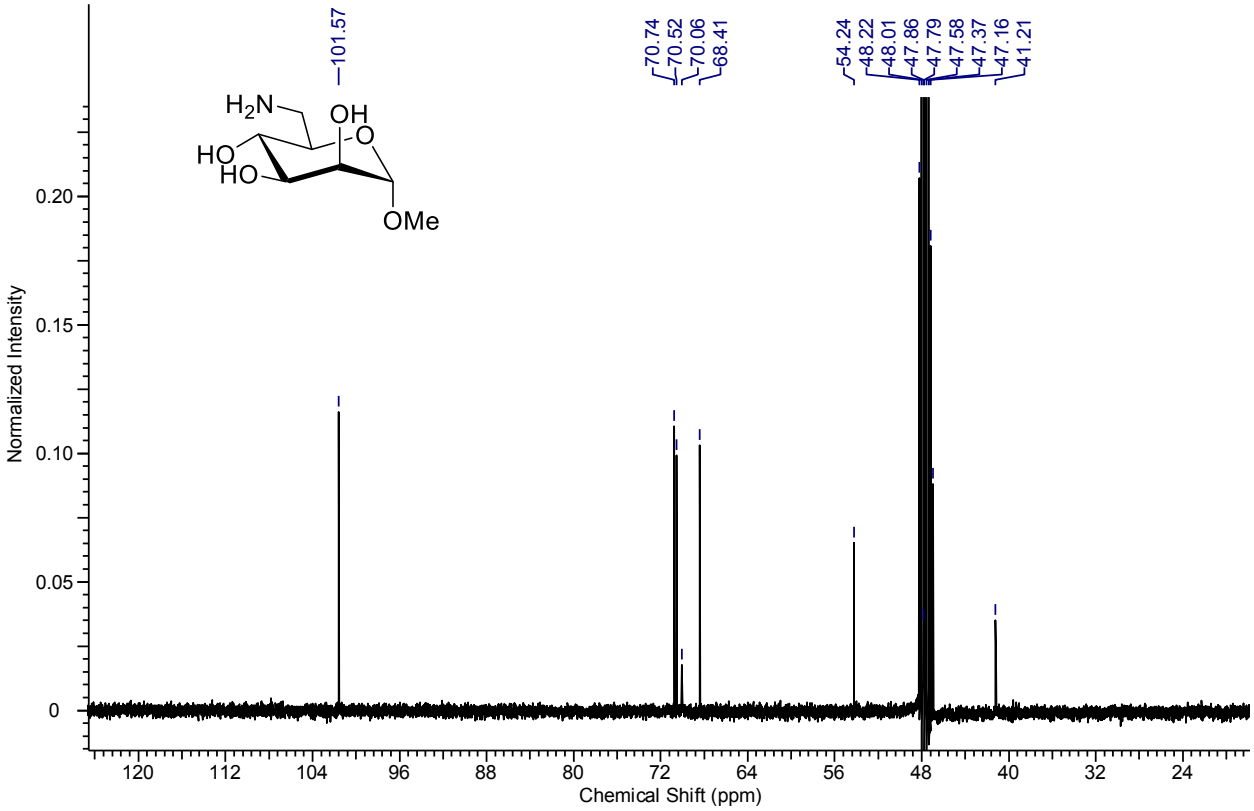
5’-Amino-5’-deoxy-β-D-thymidine 4b



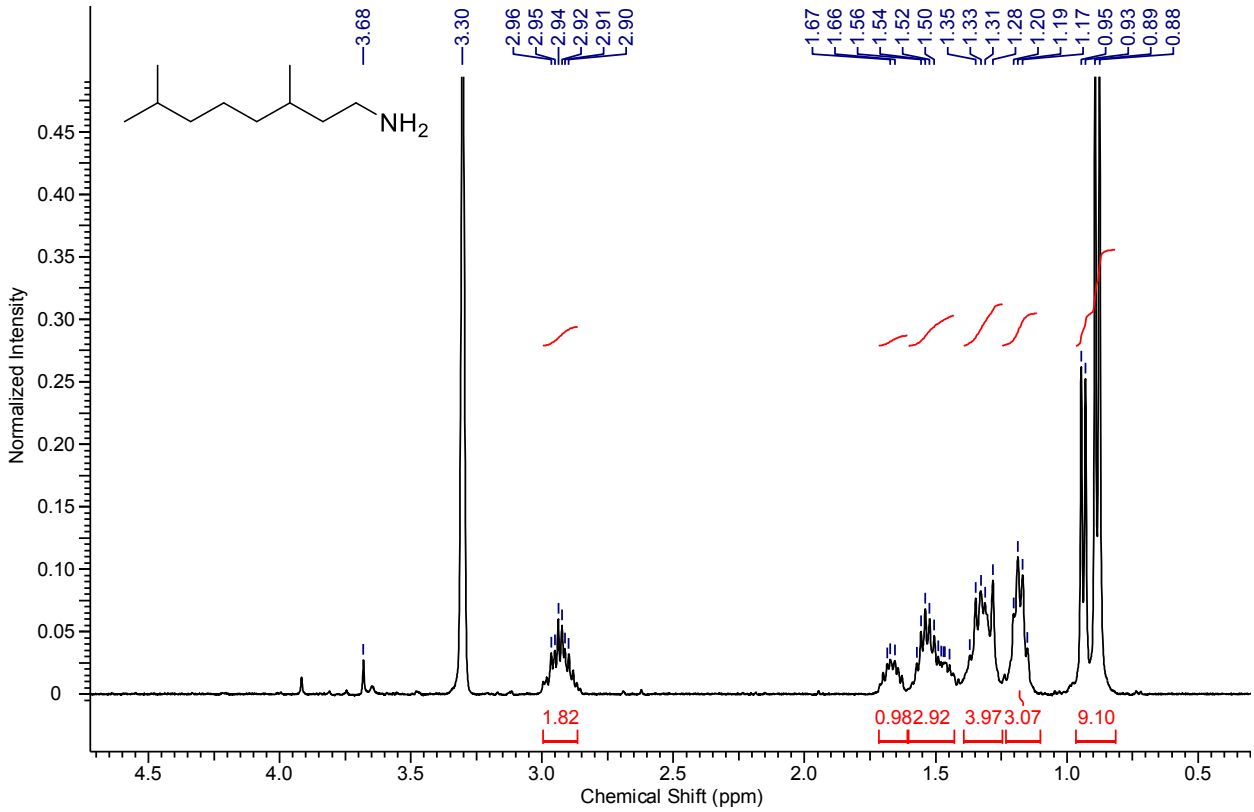


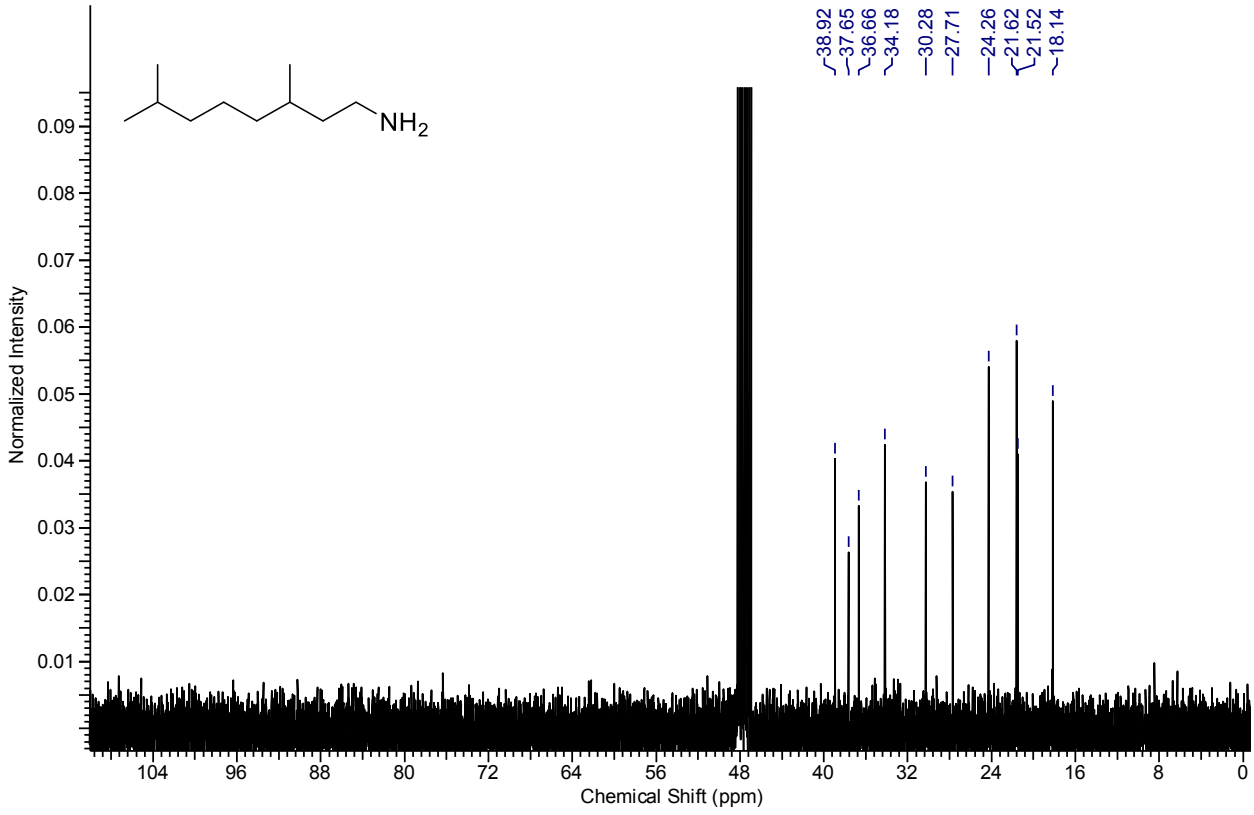
Methyl 6-amino-6-deoxy-α-D-mannopyrannoside 5b



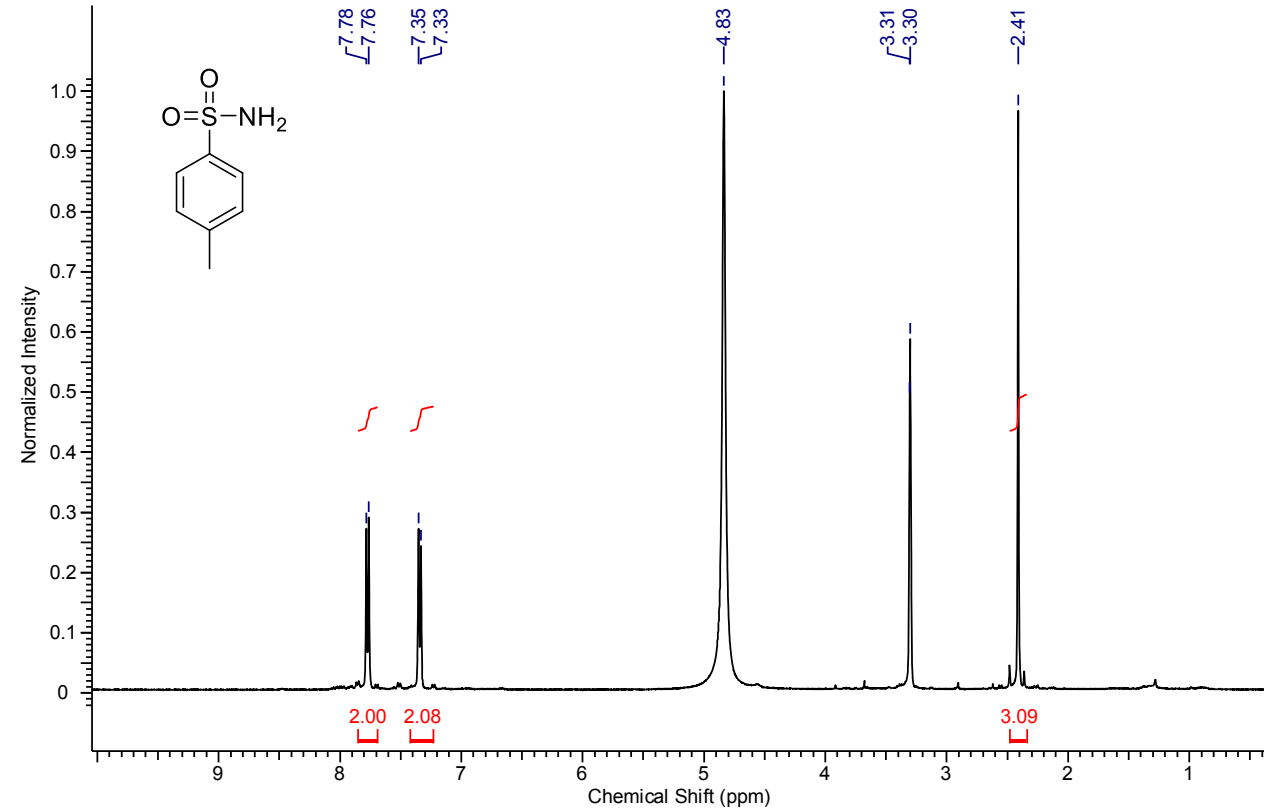


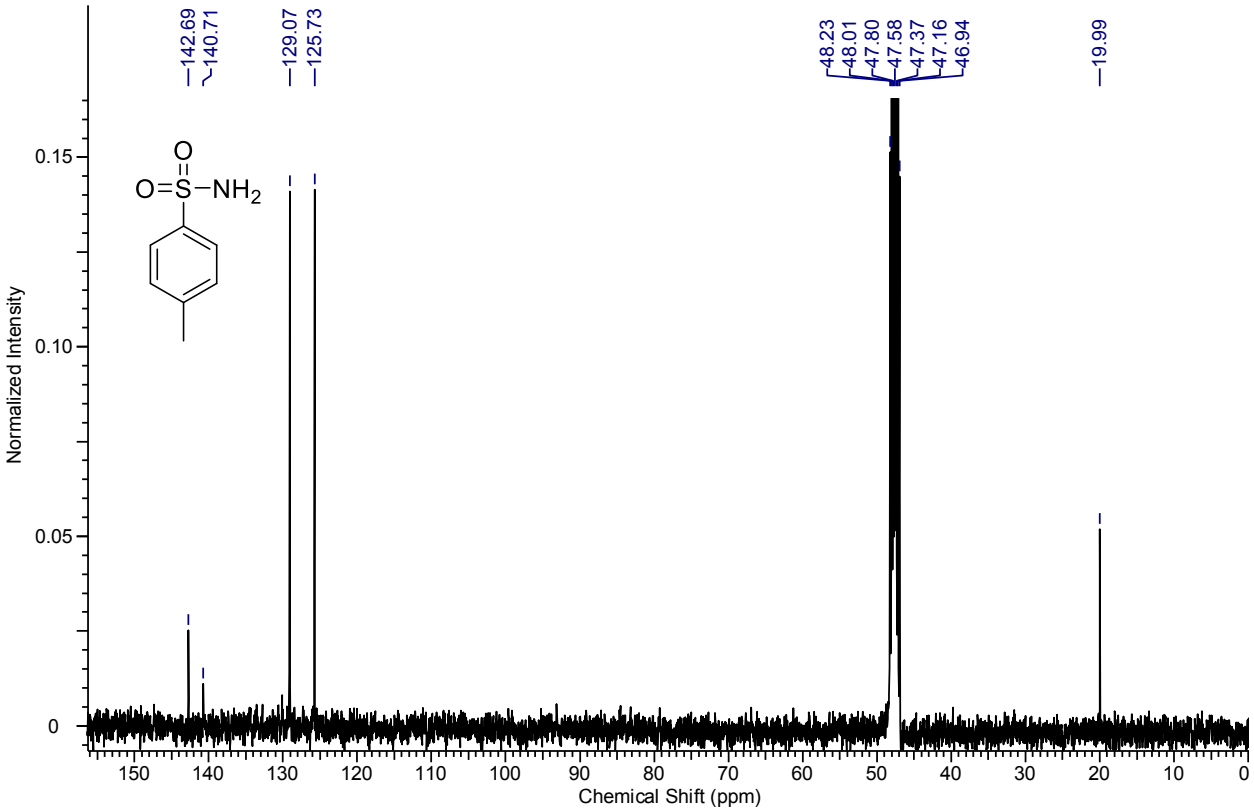
1-Amino-3,7-dimethyloctane 6b



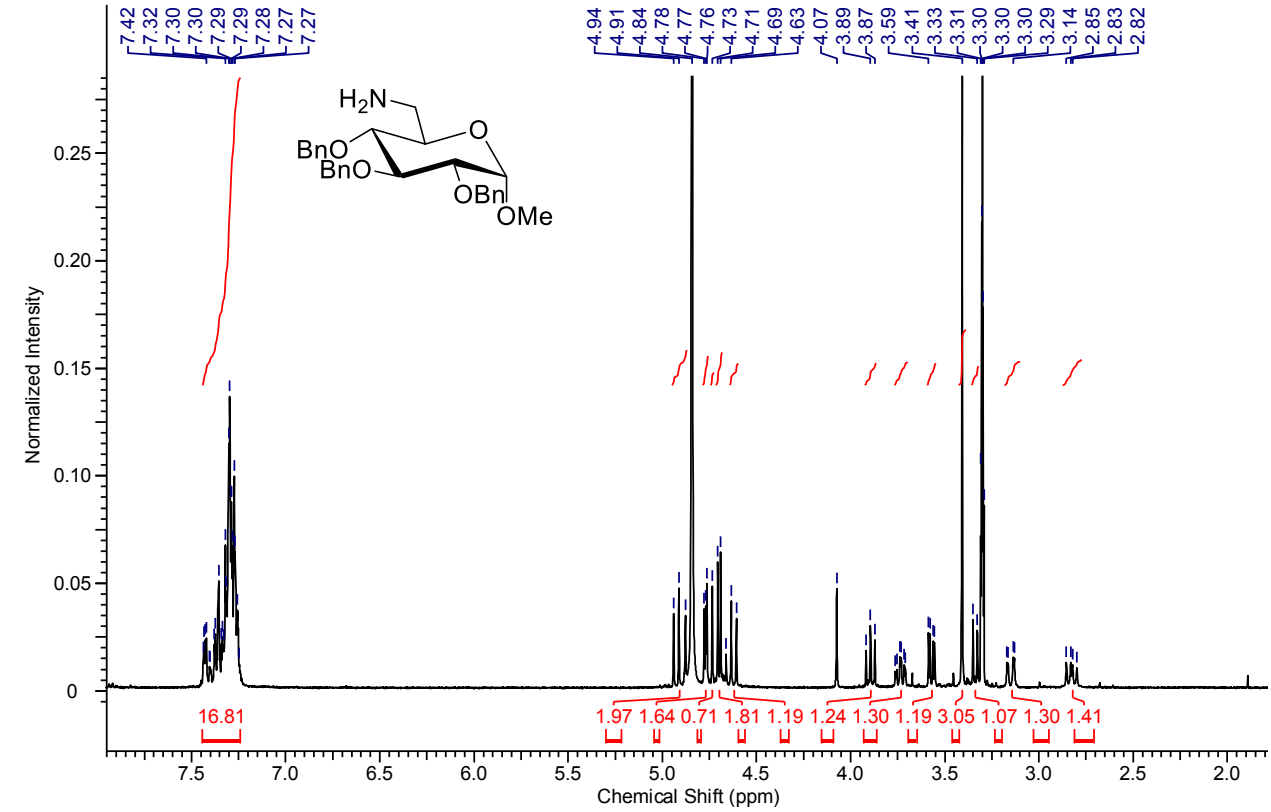


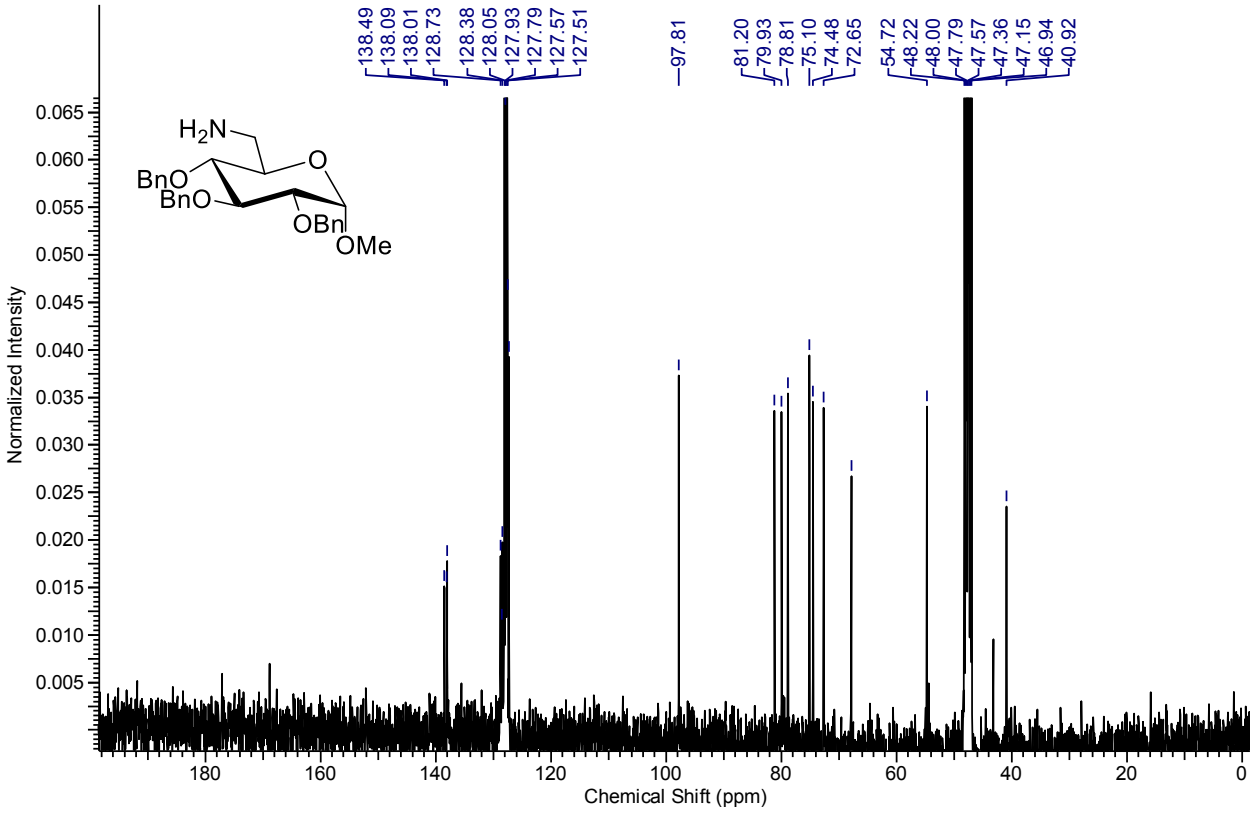
Toluenesulfonamide 7b



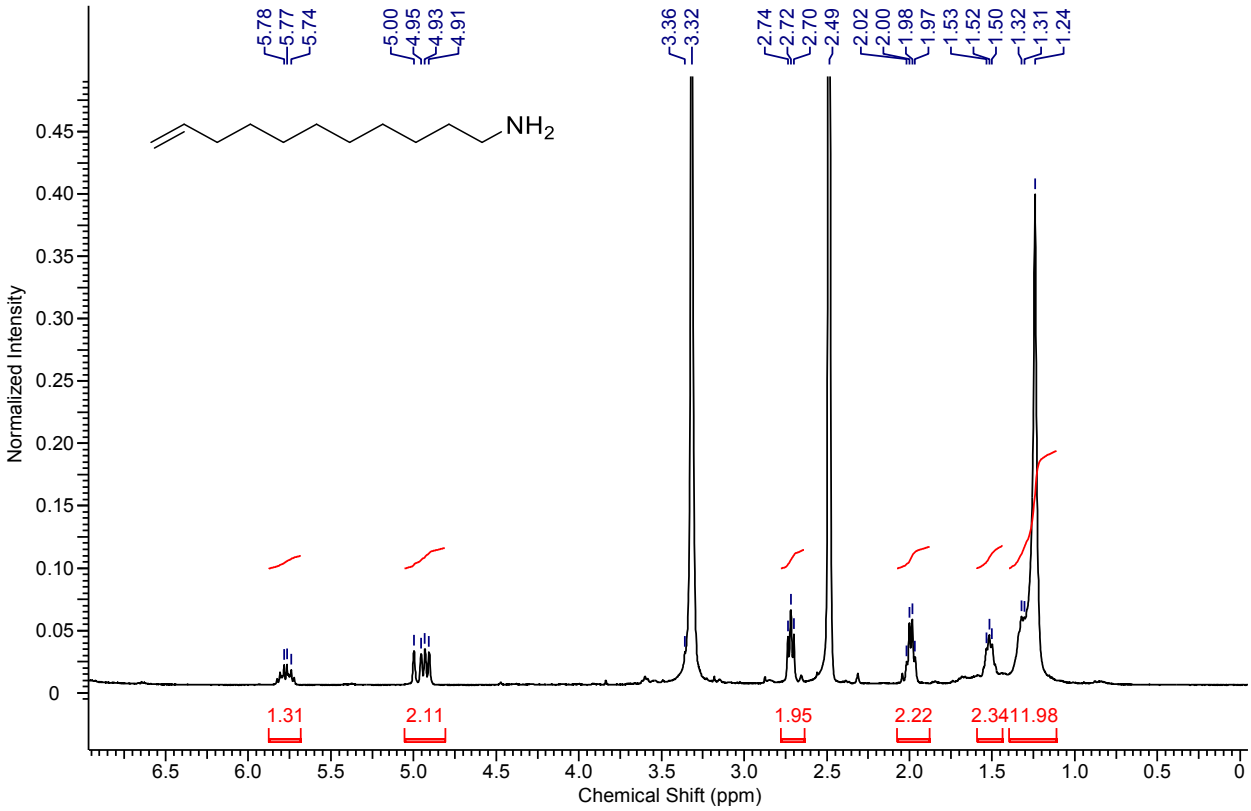


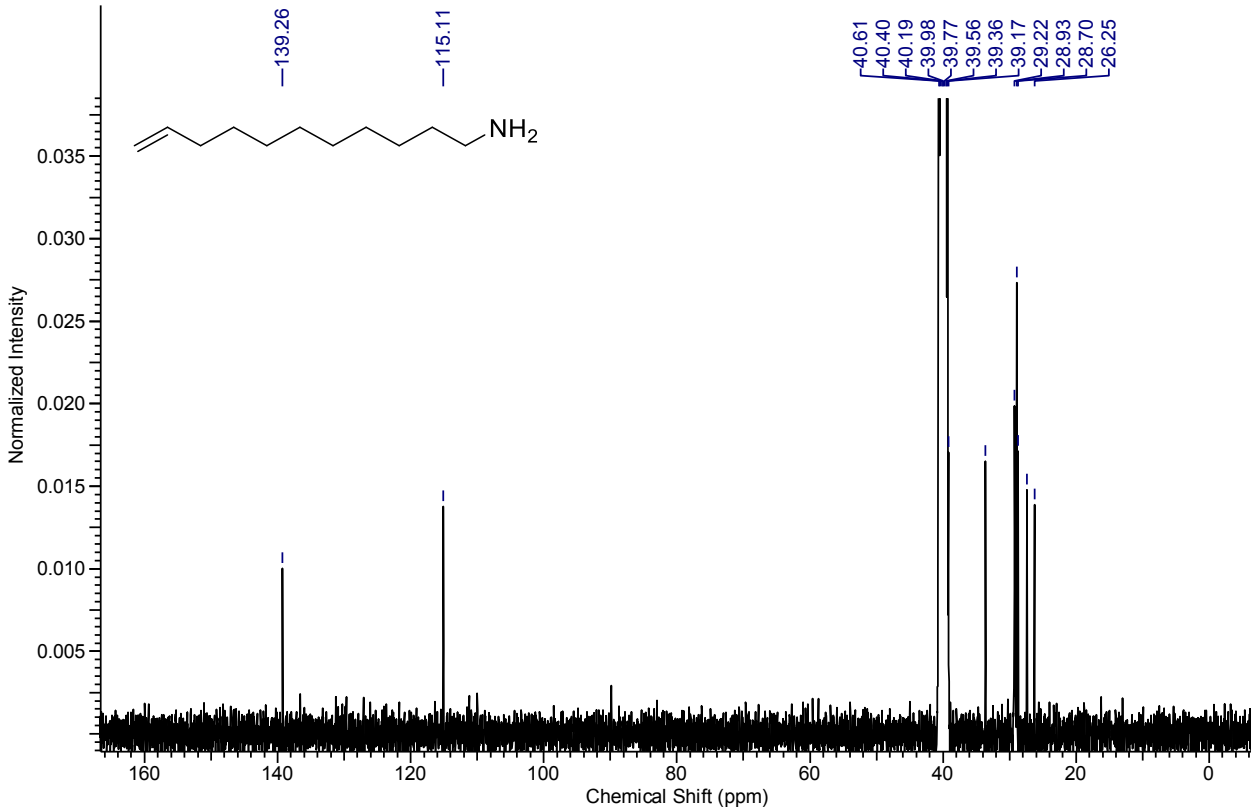
Methyl 6-amino-6-deoxy-2,3,4-tri-*O*-benzyl-α-D-gluc opyranoside 8b



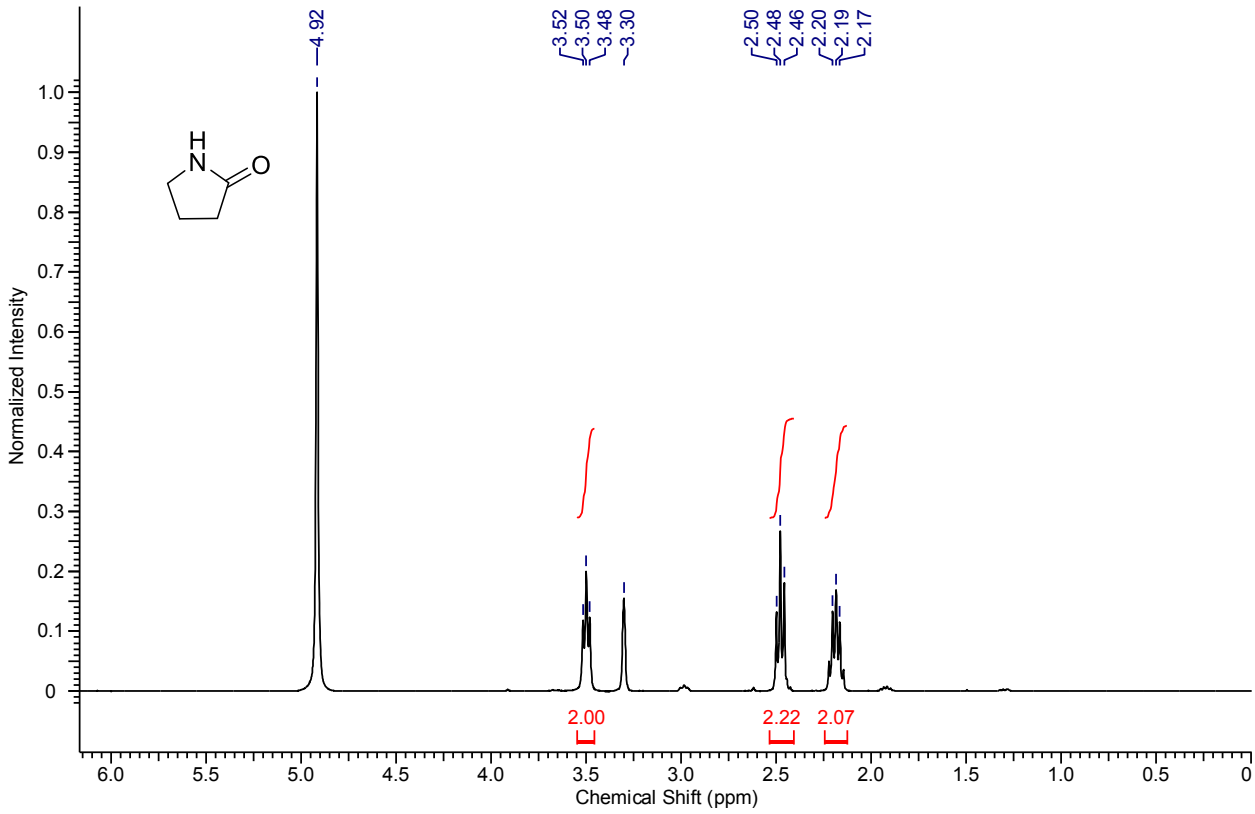


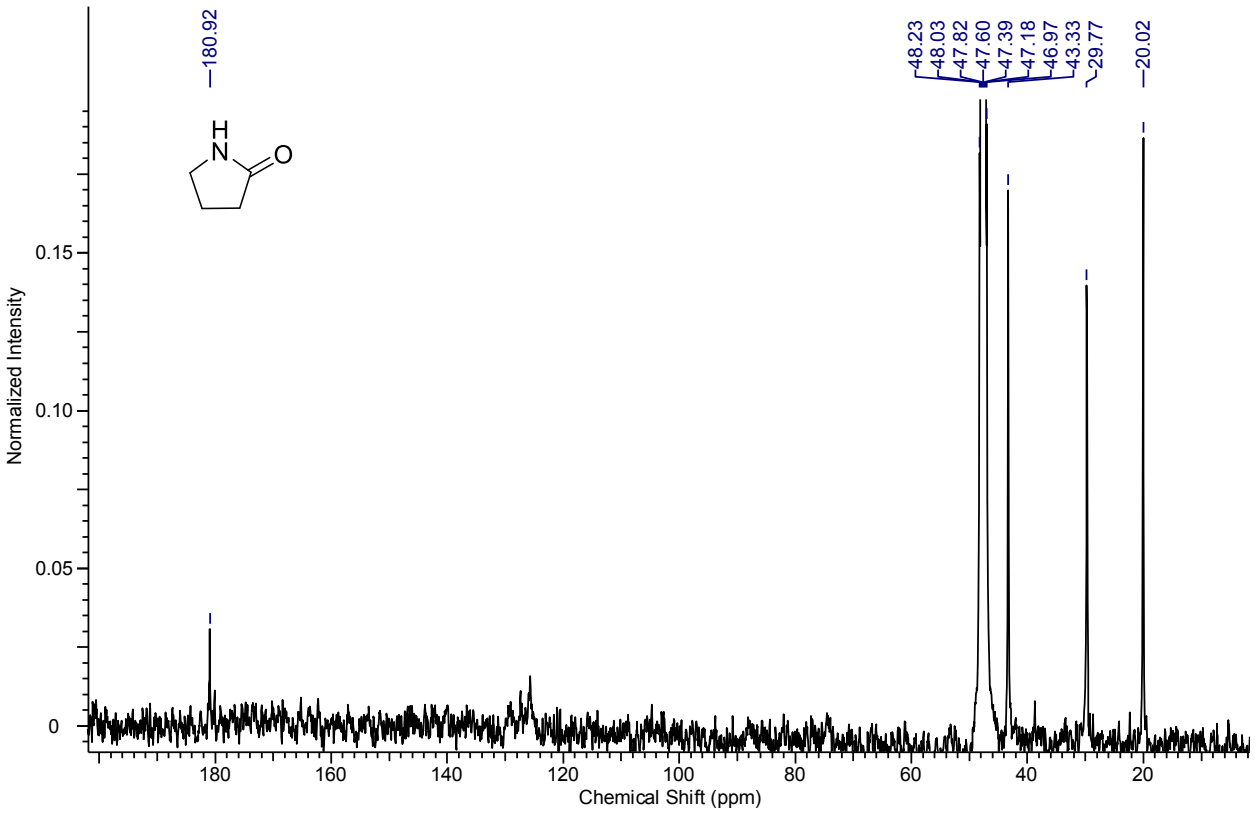
10-Undeceneamine 9b



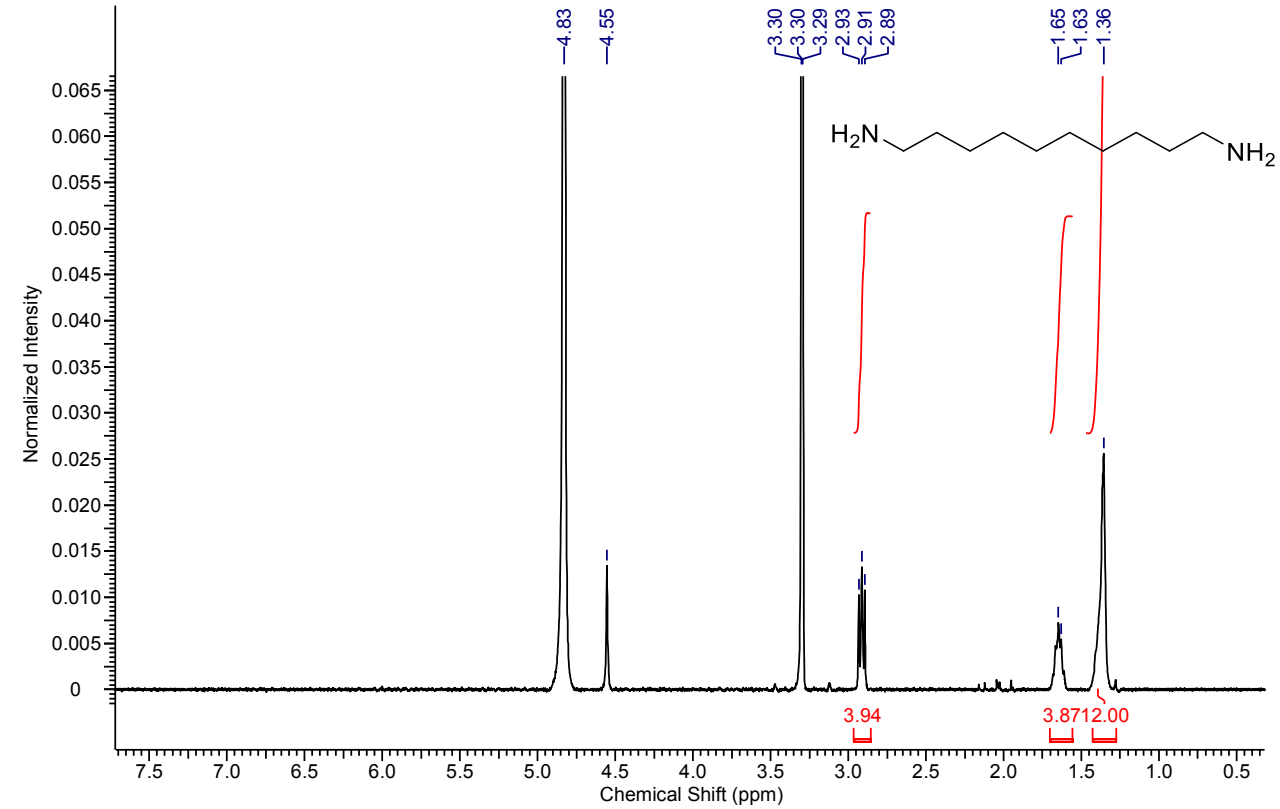


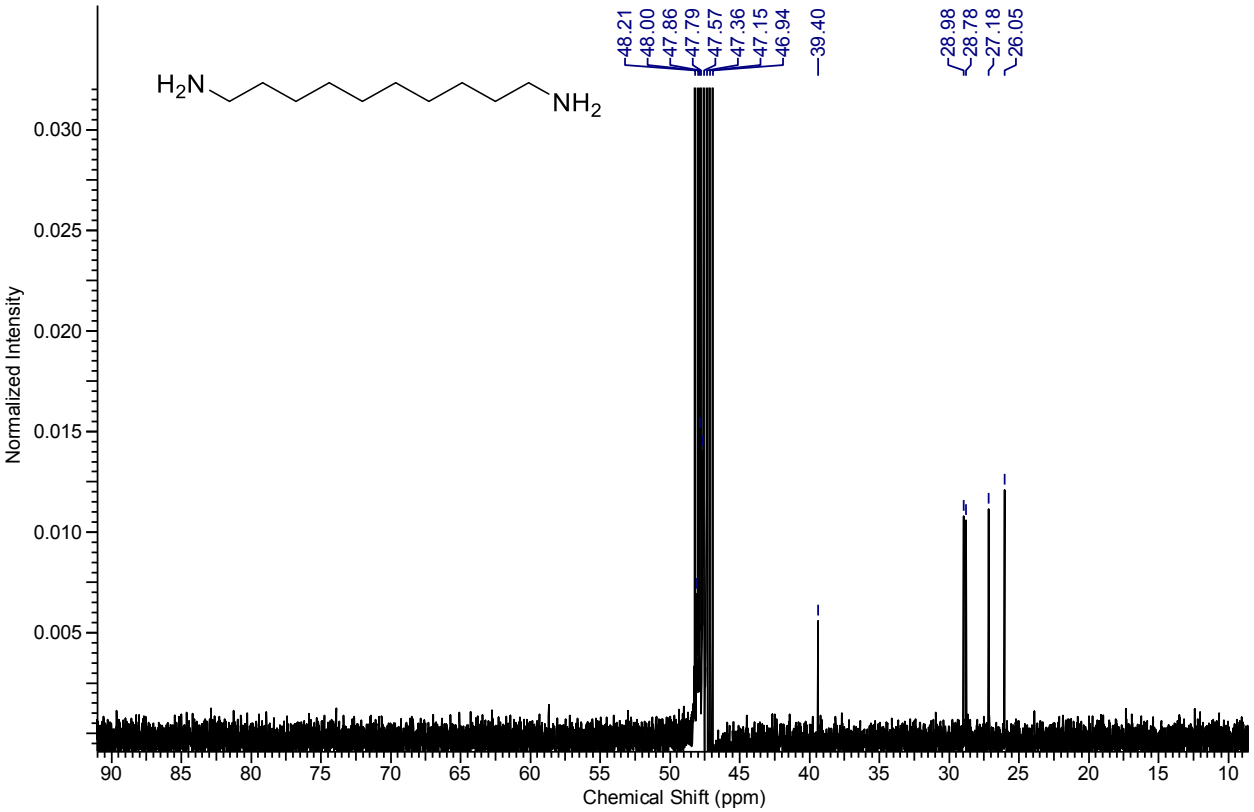
2-Pyrrolidinone 10b



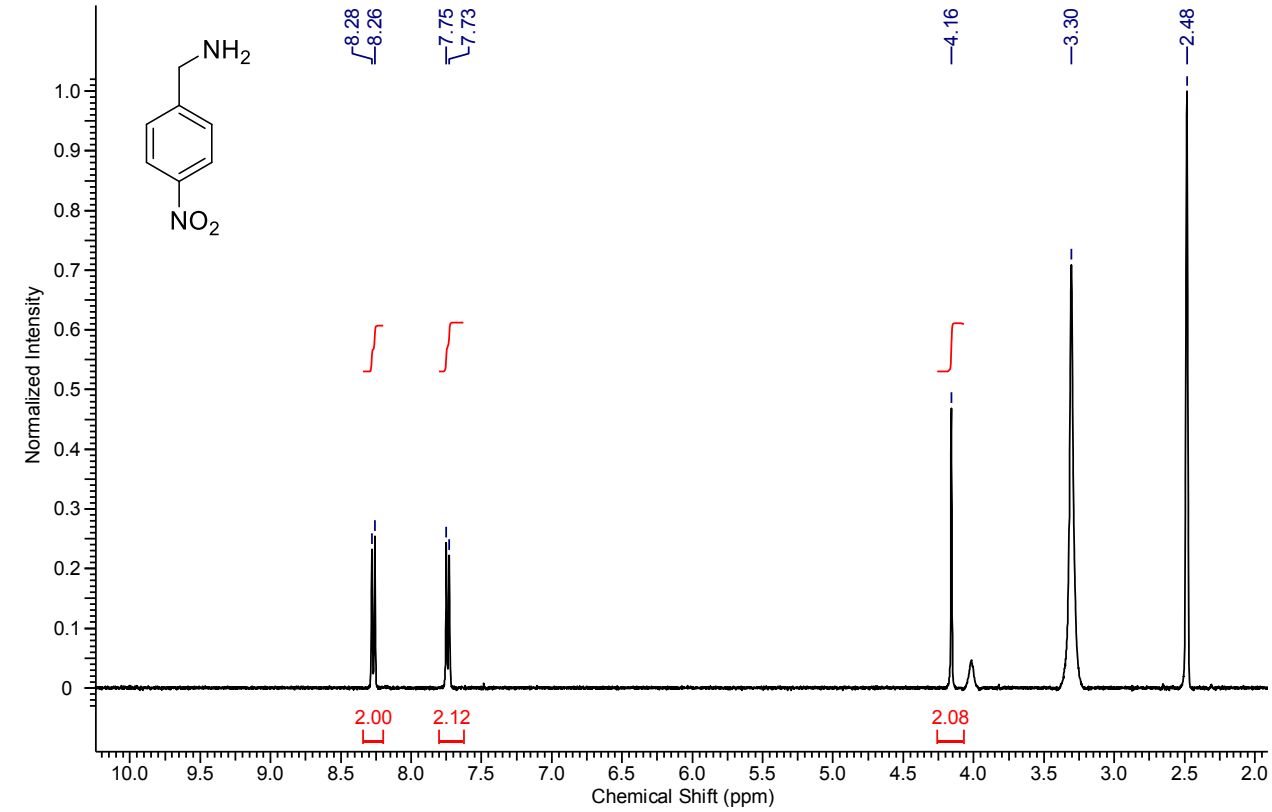


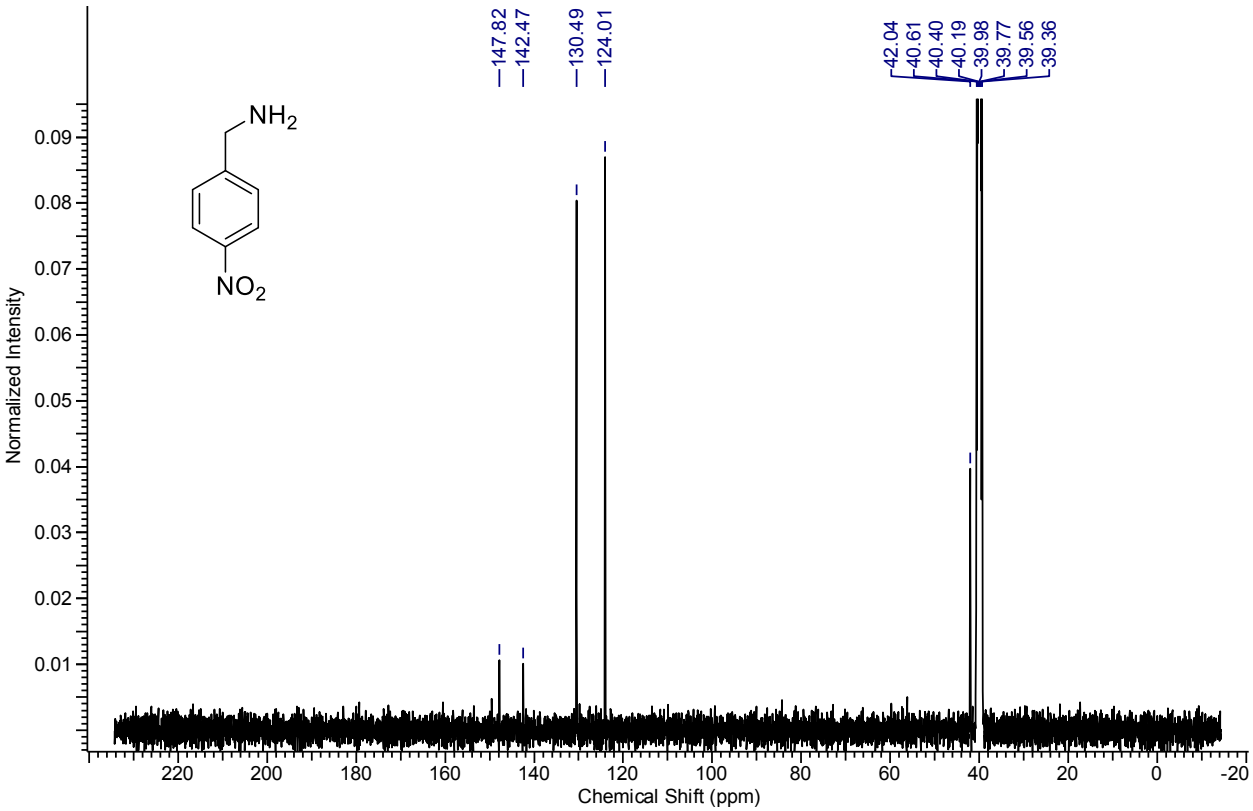
1,10-Diaminodecane 11b





(4-Nitrophenyl)methanamine 12b





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