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

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

![Reaction conditions]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Iodide concentration</th>
<th>NaI/ equiv.</th>
<th>Acid/ equiv.</th>
<th>Solvent</th>
<th>Temp/ °C</th>
<th>Time</th>
<th>Conversion/ %</th>
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<td>2</td>
<td>CD&lt;sub&gt;3&lt;/sub&gt;OD</td>
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Table S2: Study of the effect on reaction efficiency of ion exchange resin re-cycling

![Reaction conditions]

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<th>Acid/ equiv.</th>
<th>Solvent</th>
<th>Temp/ °C</th>
<th>Time</th>
<th>Conversion/ %</th>
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<td>4</td>
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<td>3</td>
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<td>CH&lt;sub&gt;3&lt;/sub&gt;OH</td>
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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 ($\delta_H$, $\delta_C$) spectra were recorded on Agilent Technologies 400 MR (400 MHz) or Varian VNMR500 (500 MHz) spectrometers. All chemical shifts are quoted on the $\delta$-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 ($\lambda_{\text{max}}$ = 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 $\mu$m, 10 x 250 mm) at 15 °C. The column was eluted with a gradient of MeCN/H$_2$O 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$_2$O (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 H₂O (500 mL), before elution of the amine product with 2.5 M NH₃ 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 Et₃N (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 MgSO₄, 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 MgSO₄, 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 MgSO₄, 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 Na₂S₂O₃ (20 mL), and water (2 x 20 mL). The organic extracts were dried over
anhydrous MgSO₄, 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: H₂O, 7: 2: 1) indicated the formation of a single product (Rf 0.6). The solvent was removed in vacuo and the residue was dissolved in H₂O (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 50 °C for 16 h. After this time, t.l.c. (EtOAc: MeOH: H₂O, 7: 2: 1) indicated the formation of a single product (Rf 0.5). The mixture was cooled, the solvent was removed in vacuo, and the residue was dissolved in H₂O (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 H₂O) 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 %). ν_max (neat) 3330 (O-H); δ_H (400 MHz, D₂O) 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, J₂,3 2.3 Hz, J₃,₄ 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, D₂O) 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 C₆H₄NO₅ (M+H⁺): 180.0866. Found 180.0857.

**2’,5’-Deoxy-5’-iodo-β-D-thymidine**: 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]; [α]_D ^20 +22.8 (c, 1.0 in CH₃OH); δ_H (500 MHz, CD₃OD) 1.90 (3H, s, 5-CH₃), 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, J₁,₂ 7.0 Hz, H-1’), 7.61 (1H, s, H-6).
Methyl 6-deoxy-6-iodo-α-D-mannopyrannoside: 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, Rf 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/Et₂O) [lit 118-120 °C]; [α]D<sup>20</sup> +76.2 (c, 0.5 in CH₃OH) [lit. [α]D<sup>22</sup> +67.5 (c, 1.0 in CH₃OH)]; δH (400 MHz, D₂O) 3.25 (1H, dd, J<sub>6,6</sub> 10.6 Hz, J<sub>5,6</sub> 7.0 Hz, H-6), 3.32 (3H, s, OCH₃), 3.35-3.49 (1H, m, H-5), 3.45 (1H, t, J<sub>3,4</sub> 9.4 Hz, H-4), 3.52 (1H, t, J<sub>6,6</sub> 11.0 Hz, H-6’), 3.64 (1H, dd, J<sub>5,4</sub> 9.4 Hz, J<sub>2,3</sub> 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 3α: 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, Rf 0.4) afforded ((2-(2-(2-azidoethoxy)ethoxy)ethoxy)methyl)benzene 3a (0.92 g, 83 %) as a clear oil. δH (400 MHz, CDCl₃) 3.36 (2H, t, J 4.0 Hz, CH₃N₃), 3.63-3.68 (10H, m, 5 x CH₂), 4.56 (2H, s, PhCH₂), 7.26-7.34 (5H, m, Ar-H).

5’-Azido-2’‘,5’‘-dideoxy-β-D-thymidine 4α: 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%, Rf 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/Et₂O) [lit 161-163 °C]; [α]D<sup>20</sup> +66.4 (c, 0.5 in CH₃OH) [lit. [α]D<sup>22</sup> +89.5 (c, 0.94 in CH₃OH)]; δH (500 MHz, CD₃OD) 1.89 (3H, s, 5-CH₃), 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<sub>1,2</sub> 6.8 Hz, H-1’), 7.54 (1H, s, H-6).

Methyl 6-azido-6-deoxy-α-D-mannopyrannoside 5α: 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, Rf 0.5) afforded methyl 6-azido-6-deoxy-α-D-mannopyrannoside 5a (530 mg, 74 %) as a yellow oil. [α]D<sup>20</sup> +43 (c, 0.5 in CH₃OH) [lit. [α]D<sup>24.3</sup> +41 (c, 0.066 in CH₃OH)]; δH (400 MHz, CD₃CN) 3.37 (3H, s, OCH₃), 3.44 (1H, dd, J<sub>5,6</sub> 6.3 Hz, J<sub>6,6</sub> 12.9 Hz, H-6), 3.48-3.62 (4H, m, H-3, H-4, H-5, H-6’), 3.76 (1H, dd, J<sub>1,2</sub> 1.6 Hz, J<sub>2,3</sub> 3.1 Hz, H-2), 4.64 (1H, s, H-1).
1-Azido-3,7-dimethyloctane 6a³: General procedure C, using 3,7-dimethyl-1-octanol (1 g, 6.3 mmol), and purification by flash chromatography (petrol: ethyl acetate, 2:1, Rf 0.9) afforded 1-azido-3,7-dimethyloctane 6a (1.08 g, 94 %) as a clear oil. δH (500 MHz, CDCl₃) 0.85-0.89 (9H, m, 3 x CH₃), 1.11-1.42 (7H, m, 3 x CH₂, CH), 1.48-1.63 (3H, m, CH₂, CH), 3.27 (2H, m, CH₂N₃).

Toluenesulfonylazide 7a⁷: 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 MgSO₄, filtered, concentrated in vacuo, and the residue was purified by column chromatography (Petrol 100 %, Rf 0.1) afforded toluenesulfonylazide 7a (0.7 g, 68 %) as a clear oil. δH (400 MHz, CDCl₃) 2.48 (3H, s, CH₃), 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 8a⁸: 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, Rf 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. [α]D²⁰ +51.3 (c, 1.0 in CHCl₃) [lit. [α]D²⁰ +53.1 (c, 2.4 in CHCl₃)]⁸; δH (400 MHz, CDCl₃) 3.33 (1H, dd, J₆,₆' 12.9 Hz, J₅,₅' 5.5 Hz, H-6), 3.40 (3H, s, OCH₃), 3.42 - 3.46 (2H, m, H-6', H-4), 3.54 (1H, dd, J₁,₂ 3.5 Hz, J₂,₃ 9.4 Hz, H-2), 3.78 (1H, td, J₄,₅ 9.8 Hz, J₅,₆ 5.9 Hz, J₅,₆' 2.3 Hz, H-5), 3.98 (1H, t, J₂,₃ 9.2 Hz, H-3), 4.57 (1H, d, J 11.0 Hz, CH₂Ph), 4.61 (1H, d, J₁,₂ 3.5 Hz, H-1), 4.67 (1H, d, J 12.1 Hz, CH₂Ph), 4.77-4.84 (2H, m, CH₂Ph), 4.90 (1H, d, J 11.0 Hz, CH₂Ph), 5.0 (1H, d, J 11.0 Hz, CH₂Ph), 7.23 - 7.40 (15H, m, Ar-H).

11-Azidoundecene 9a⁹: General procedure D, using 11-bromoundecene (1 g, 4.3 mmol), and purification by flash chromatography (petrol: ethyl acetate, 2:1, Rf 0.9) afforded 11-azidoundecene 9a (0.6 g, 71 %) as a pale yellow oil. δH (400 MHz, CDCl₃) 1.23-1.45 (12H, m, 6 x CH₂), 1.53-1.65 (2H, m, CH₂), 2.04 (2H, q, J 7.0 Hz, CH₂), 3.26 (2H, t, J 7.0 Hz, NCH₂), 4.90-5.03 (2H, m, =CH₂), 5.77-5.87 (1H, m, =CH).

Methyl 4-azidobutyrate 10a¹⁰: General procedure D, using methyl 4-chlorobutyrate (1 g, 1.1 mmol), and purification by flash chromatography (petrol 100 %, Rf 0.4) afforded methyl
4-azidobutyrate 10a (0.73 g, 70 %) as a clear oil. δH (400 MHz, CDCl₃) 1.87-1.95 (2H, m, CH₂), 2.41 (2H, t, J 7.4 Hz, COCH₂), 3.35 (2H, t, J 6.3 Hz, NCH₂), 3.69 (3H, s, OCH₃).

1,10-Diazidodecane 11a: General procedure D, using 1,10-dibromodecane (1 g, 3.4 mmol), and purification by flash chromatography (petrol 100 %, R₇ 0.4) afforded 1,10-diazidodecane 11a (0.6 g, 80 %) as a clear oil. δH (400 MHz, CDCl₃) 1.23-1.41 (12H, m, 6 x CH₂), 1.53-1.63 (4H, m, 2 x CH₂), 3.25 (4H, t, J 7.0 Hz, 2 x NCH₂).

1-Azidomethyl-4-nitrobenzene 12a: General procedure D, using 1-chloromethyl-4-nitrobenzene 12a (1 g, 5.8 mmol), and purification by flash chromatography (petrol: ethyl acetate, 5:1, R₇ 0.4) afforded 1-azidomethyl-4-nitrobenzene (0.7 g, 67 %) as a pale yellow oil. δH (400 MHz, CDCl₃) 4.50 (2H, s, PhCH₂), 7.50, 8.25 (4H, 2 x d, J 8.6 Hz, 4 x ArH).

2-(2-(2-(Benzyloxy)ethoxy)ethoxy)ethanamine 3b: General procedure A, using (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. vₘₐₓ (neat) 3408 (w, NH) cm⁻¹; δH (500 MHz, CD₂OD) 3.09 (2H, t, J 5.5 Hz, CH₂NH₂), 3.62-3.73 (10H, m, CH₂), 4.55 (2H, s, Ph-CH₂), 7.25-7.38 (5H, m, Ar-H); δC (100 MHz, CD₂OD) 39.3 (t, CH₂NH₂), 66.4 (t, PhCH₂), 69.0, 69.8, 70.0, 70.1, 72.7 (5 x t, 5 x CH₂), 127.4, 127.6, 128.0 (3 x d, 5 x Ar(C)H), 138.0 (s, Ar(C)C); HRMS (ESI) calculated for C₁₃H₂₁NNaO₃ (M+Na⁺) 262.1414. 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'-dideoxy-β-D-thymidine 4b (42 mg, 93 %) as a white solid. m.p 165-167 ºC (EtOH/Et₂O); [α]D [20] +23.2 (c, 0.5 in CH₃OH); vₘₐₓ (neat) 3339 (w, NH), 1655 (s, C=O) cm⁻¹; δH (400 MHz, CD₂OD) 1.89 (3H, s, 5-CH₃), 2.20-2.21, 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, J₁,₂ 6.8 Hz, H-1'), 7.45 (1H, s, H-6); δC (100 MHz, CD₂OD) 10.8 (q, 5-CH₃), 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 C₁₀H₁₆N₃O₄ (M+H⁺) 242.1135. Found 242.1140.

Methyl 6-amino-6-deoxy-α-D-mannopyranoside 5b: General procedure A using methyl 6-azido-6-deoxy-α-D-mannopyranoside 5a (50 mg, 0.3 mmol), afforded methyl 6-amino-6-
deoxy-α-D-mannopyranoside 5b (40 mg, 91 %) as a white foam. [α]D20 +81 (c, 1.0 in CH3OH) [lit. [α]D23 +76 (c, 1.0 in CH3OH)]13; νmax (neat) 3340 (w, NH and OH) cm⁻1; δH (400 MHz, CD3OD) 2.96-3.03 (1H, m, H-6), 3.23 (1H, dd, J6,6' 13.1 Hz, J5,6' 2.9 Hz, H-6'), 3.39 (3H, s, OCH3), 3.51 (1H, at, J 9.4 Hz, H-4), 3.56-3.62 (1H, m, H-5), 3.66 (1H, dd, J3,4 9.2 Hz, J2,3 3.3 Hz, H-3), 3.79 - 3.81 (1H, m, H-2), 4.66 (1H, d, J1,2 1.6 Hz, H-1); δC (100 MHz, CD3OD) 41.2 (t, C-6), 54.2 (q, OCH3), 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 C7H16NO5 (M+H⁺) 194.1023. Found 194.1023.

1-Amino-3,7-dimethyloctane 6b3: 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; νmax (neat) 3260 (w, NH) cm⁻1; δH (500 MHz, CDCl3) 0.81-0.83 (9H, m, CH3), 1.07-1.32 (6H, m, CH2), 1.46-1.64, 1.73-1.82 (4H, m, 2 x CH, CH2), 2.95-3.07 (2H, m, CH2NH2); δC (125 MHz, CDCl3) 19.1, 22.6, 22.7 (3 x q, 3 x CH3), 24.6 (t, CH2), 27.9, 30.7 (2 x d, 2 x CH), 34.7, 36.8, 38.4 (3 x t, 3 x CH2), 39.1 (t, CH2NH2); (ESI) calculated for C10H24N (M+H⁺) 158.1909. Found 158.1906.

Toluenesulfonamide 7b14: General procedure B, using toluenesulfonylazide 7a (100 mg, 0.5 mmol), toluenesulfonamide 7b (82 mg, 95 %) as a pale yellow solid; mp 118-120 °C (Ethanol/Et2O) [lit 125-126 °C]15; νmax (neat) 3258, 3355 (w, NH), 1385, 1154 (s, S=O) cm⁻1; δH (400 MHz, CD2OD) 2.41 (3H, s, CH3), 7.34 (2H, d J 7.8 Hz, Ar(C)H), 7.77 (2H, d J 8.2 Hz, Ar(C)H); δC (100 MHz, CD2OD) 20.0 (q, CH3), 125.7, 129.1 (2 x d, 2 x Ar(C)H), 140.7, 142.7 (2 x s, Ar(C)SO2, Ar(C)CH3); HRMS (ESI) calculated for C7H9NNO2S (M+Na⁺) 194.0246. Found 194.0245.

Methyl 6-amino-6-deoxy-2,3,4-tri-O-benzyl-α-D-glucopyranoside 8b16: 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. mp 89-91 °C (Et2O) [lit 86-89 °C]16; [α]D20 +41.2 (c, 0.25 in CH3OH) [lit. [α]D20 +54.8 (c, 1.0 in CHCl3)]17; νmax (neat) 3392 (w, NH) cm⁻1; δH (400 MHz, CD2OD) 2.83 (1H, dd, J6,6' 13.1 Hz, J5,6 9.2 Hz, H-6), 3.15 (1H, dd, J6,6' 13.1 Hz, J5,6' 2.5 Hz, H-6'), 3.32-3.36 (1H, m, H-4), 3.41 (3H, s, OCH3)), 3.57 (1H, dd, J1,2 3.5 Hz, J2,3 9.4 Hz, H-2), 3.74 (1H, td, J4,5 9.4 Hz, J5,6 9.4 Hz, J5,6' 2.7 Hz, H-5), 3.89 (1H, at, J 9.2 Hz, H-3), 4.62 (1H, d, J 11.0 Hz, CH2Ph), 4.70 (1H, d, J 11.0 Hz, CH2Ph), 4.75 (2H, d, J 11.0 Hz, CH2Ph),
4.77 (1H, d, J_{1,2} 3.5 Hz, H-1), 4.87-4.95 (2H, m, CH₂Ph), 7.20 - 7.46 (15H, m, Ar-H); δ_C (100 MHz, CD₃OD) 40.9 (t, C-6), 54.7 (q, OCH₃), 67.8 (d, C-5), 72.7 (t, CH₂Ph), 74.5 (t, CH₂Ph), 75.1 (t, CH₂Ph), 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)CH₂); HRMS (ESI) calculated for C_{28}H_{34}NO₅ (M+H⁺) 464.2437. Found 464.2432.

10-Undeceneamine 9b\(^{18}\): General procedure B, using 1-azidoundecene 9a (100 mg, 0.5 mmol), afforded 10-undeceneamine 9b (81 mg, 87 %) as a pale yellow oil. v_max (neat) 3418 (w, NH), 3010 (m, =CH), 1640 (m, C=C) cm⁻¹; δ_H (400 MHz, CDCl₃) 1.20-1.48 (12H, m, CH₂), 1.75-1.85 (2H, m, CH₂), 2.04 (2H, q, J 6.9 Hz, CH₂), 3.03-3.14 (2H, m, NCH₂), 4.90-5.03 (2H, m, =CH₂), 5.75-5.87 (1H, m, =CH), 7.40 (br s, 1H, NH); δ_C (100 MHz, CDCl₃) 26.6, 27.5, 28.9, 29.1, 29.1, 29.4, 33.8, (7 x t, 8 x CH₂), 40.6 (t, CH₂N), 114.2 (t, =CH₂), 139.1 (d, =CH); HRMS (ESI) calculated for C_{11}H_{24}N (M+H⁺) 170.1903. Found 170.1905.

2-Pyrroolidinone 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.; v_max (neat) 1654 (s, C=O) cm⁻¹; δ_H (400 MHz, CDCl₃) 2.13-2.24 (2H, m, CH₂), 2.48 (2H, t, J 8.2 Hz, COCH₂), 3.50 (2H, t, J 7.0 Hz, NCH₂); δ_C (100 MHz, CDCl₃) 20.0 (t, CH₂), 29.8 (t, COCH₂), 43.3 (t, NCH₂), 180.9 (s, C=O); HRMS (ESI) calculated for C₄H₈NO (M+H⁺) 86.0600. Found 86.0603.

1,10-Diaminodecane 11b\(^{20}\): General procedure B using 1,10-diazipodecane 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/Et₂O) [lit 62-64 °C]\(^{20}\); v_max (neat) 3420 (w, NH) cm⁻¹; δ_H (400 MHz, CD₃OD) 1.32-1.43 (12H, m, 6 x CH₂), 1.60-1.70 (4H, m, 2 x CH₂), 2.91 (4H, t, J 7.4 Hz, 2 x NCH₂); δ_C (100 MHz, CD₃OD) 26.0, 27.2, 28.8, 29.0 (4 x t, 8 x CH₂), 39.4 (t, 2 x NCH₂); HRMS (ESI) calculated for C_{10}H_{25}N₂ (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. v_max (neat) 3308 (w, NH), 1541, 1350 (s, NO₂) cm⁻¹; δ_H (400 MHz, DMSO-d₆) 4.16 (2H, s, PhCH₂), 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); δc (100 MHz, DMSO-d6) 42.0 (t, PhCH2), 124.0, 130.5 (2 x d, 4 x Ar(C)H), 142.5, 147.8 (2 x s, 2 x Ar(C)CH2); HRMS (ESI) calculated for C7H9N2O2 (M+H+) 153.0659. Found 153.0659.
6-Amino-6-deoxy-D-mannopyranose 2

Chemical Shift (ppm)
$2',5'$-Deoxy-$5'$-iodo-$\beta$-D-thymidine

![Chemical Shift Graph](image-url)
Methyl 6-deoxy-6-iodo-α-D-mannopyranoside
((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-mannopyranoside 5a
1-Azido-3,7-dimethyloctane 6a
Toluenesulfonylazide 7a

Chemical Shift (ppm)

Normalized Intensity

O=S−N₃

S19
Methyl-6-azido-6-deoxy-2,3,4-tri-O-benzyl-\(\alpha\)-D-glucopyranoside 8a

![NMR spectrum of Methyl-6-azido-6-deoxy-2,3,4-tri-O-benzyl-\(\alpha\)-D-glucopyranoside 8a](image)

- **Chemical Shift (ppm):**
  - 16.51
  - 10.61
  - 7.35
  - 7.35
  - 7.34
  - 7.34
  - 7.32
  - 7.26
  - 5.01
  - 4.98
  - 4.92
  - 4.89
  - 4.83
  - 4.81
  - 4.80
  - 4.78
  - 4.68
  - 4.62
  - 4.61
  - 4.59
  - 4.01
  - 3.98
  - 3.79
  - 3.76
  - 3.56
  - 3.55
  - 3.53
  - 3.46
  - 3.43
  - 3.43
  - 3.41
  - 3.40
  - 3.39
  - 3.35
11-Azidoundecene 9a

![N3](image)

Chemical Shift (ppm)

Normalized Intensity

[Diagram showing chemical shifts and normalized intensities]
Methyl 4-azidobutyrate 10a
1,10-Diazidodecane 11a
1-Azidomethyl-4-nitrobenzene 12a

Chemical Shift (ppm)

Normalized Intensity

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

![NMR Spectrum](image)

**Chemical Shift (ppm)**

- 7.34
- 7.33
- 7.32
- 7.31
- 7.30
- 7.29
- 7.28
- 6.88
- 4.55
- 3.80
- 3.70
- 3.69
- 3.68
- 3.67
- 3.66
- 3.65
- 3.30

**Normalized Intensity**

- 144
- 136
- 128
- 120
- 112
- 104
- 96
- 88
- 80
- 72
- 64
- 56
- 48
- 40
- 32
5'-Amino-5'-deoxy-β-d-thymidine 4b
Methyl 6-amino-6-deoxy-α-D-mannopyranoside 5b
1-Amino-3,7-dimethyloctane 6b

Chemical Shift (ppm)

Normalized Intensity
10-Undeceneamine 9b

Chemical Shift (ppm)

Normalized Intensity

Normalized Intensity

Chemical Shift (ppm)
2-Pyrrolidinone 10b
1,10-Diaminodecane 11b

[Diagram of NMR spectrum with chemical shifts and normalized intensities]

Chemical Shift (ppm)

Normalized Intensity

48.21 48.00 47.86 47.79 47.57 47.36 47.15 46.94 39.40 28.98 28.78 27.18 26.05
(4-Nitrophenyl)methanamine 12b

Chemical Shift (ppm)

Normalized Intensity

0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09

220 200 180 160 140 120 100 80 60 40 20 0 -20

Chemical Shift (ppm)
References: