A highly expeditious synthesis of bicyclic iminosugar using novel key step of $[NMM]^+[HSO_4]^-$ promoted conjugate addition and *Mitsunobu Reaction*

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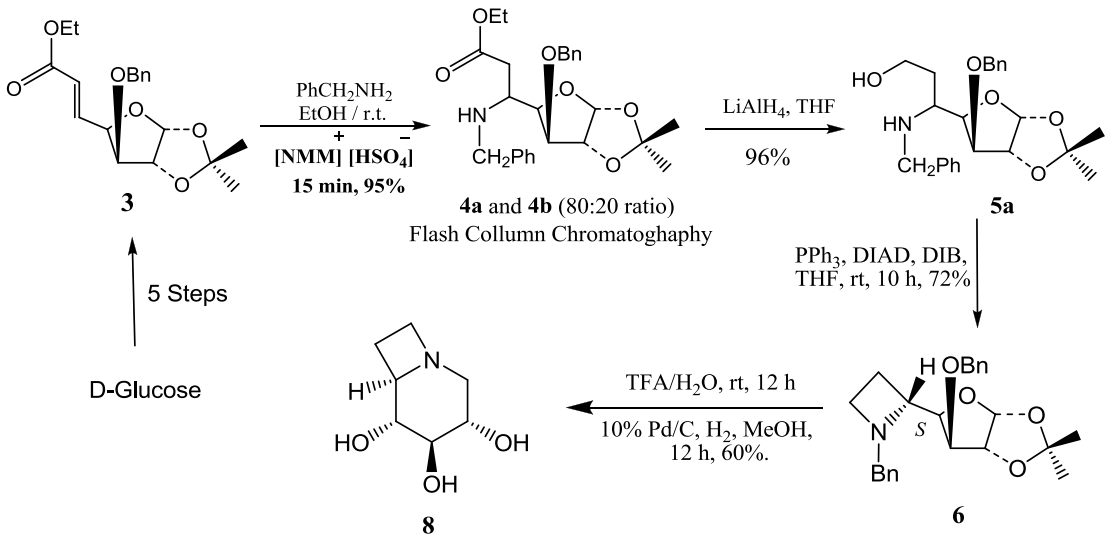
Abstract:



A simple and highly facile protocol has been developed for stereoselective synthesis of a novel bicyclic iminosugar analogue 1-deoxy-norcastanospermine from readily available D-glucose. *N*-methylmorpholinium hydrogen sulfate for the first time noticed as suitable catalyst for the facile conjugate addition of amine to glycosyl olefinic ester. Furthermore, the key step of the strategy is the internal reductive amination of glycosyl azetidine, obtained from glycosyl *β*-amino alcohol under *Mitsunobu* reaction condition.

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EXPERIMENTAL

1. General Experimental: All reagents and solvents were pure analytical grade materials purchased from Spectrochem/Aldrich and were used without further purification, if not stated otherwise. Glass wares were dried over an open flame before use in connection with an inert atmosphere (N_2) and solvents were evaporated under reduced pressure at temperature <50 °C. Thin layer chromatography (TLC) was performed using silica gel 60 F-254 plates with I_2 vapors as detecting agents followed by spraying with methanolic-H_2SO_4 solution and *Draggendorff* reagent. Column chromatography was carried out on silica gel (230-400 mesh, E Merck). Elemental analyses were performed on a Perkin-Elmer 2400 C, H, N analyzer and values were found to be within ± 0.5% of the calculated values. NMR spectra were recorded on JEOL AL300 FT-NMR Spectrometer (300 MHz ^{1}H NMR and 75 MHz ^{13}C NMR) and *TMS* (0.0 ppm) was used as an internal standard in ^{1}H NMR. Chemical shift

values are reported in ppm relative to TMS as internal reference, unless otherwise stated; s (singlet), d (doublet), t (triplet), m (multiplet), dd (double doublet); J values are in hertz. Infrared spectra were recorded as KBr pelletes by a Perkin-Elemer RX-1 (4000-450 cm^{-1}) spectrometer.

2. Typical experimental procedure for synthesis of ethyl-(3-*O*-benzyl-5,6-dideoxy-5-benzylamino-1,2-*O*-isopropylidene)-α-D-*gluco* & *β*-L-*ido*-heptofuran-nuronate (4): A solution of (1*R*, 2*R*, 3*S*, 4*R*)-ethyl-(3-*O*-benzyl-1,2-*O*-isopropylidene-1,4-pentofuranose-4-yl)-hept-5-enoate (3.60 g, 10.33 mmol) in EtOH (15 ml), was added benzyl amine (1.11 ml, 10.36 mmol) and $[NMM]^{+}[HSO_4]^{-}$ (in catalytic amount, 2 mmol %) and the reaction was magnetically stirred at room temperature (25 °C) for 20 min. The Solvent was evaporated under reduced pressure and the syrup thus obtained was dissolved in ethyl acetate (100 ml) and washed with H_2O (2 × 25 ml). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to get crude product, which was subjected to flash column chromatography (SiO_2) using 20% EtOAc in *n*-hexane as eluent and afforded compound **4** as major and minor isomers. Yield: 95% (diastereomeric ratio, 80:20).

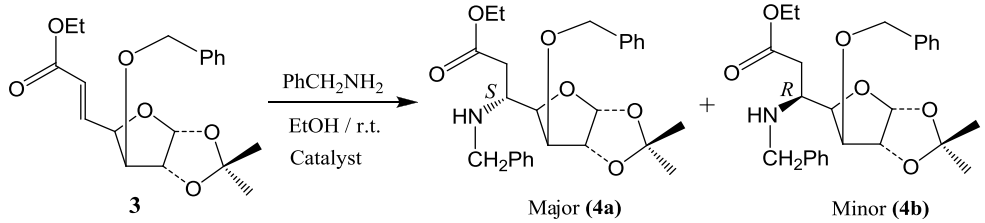
*Ethyl-3-O-benzyl-5,6-dideoxy-5-benzylamino-1,2-O-isopropylidene-β-L-ido-hepto-furannuronate (**4a**):* Major isomer, Yellow oil; IR (KBr): ν_{max} cm^{-1} 3350 (-NH), 3020, 2980, 2920 (CH_3 and CH_2 stretching), 1710 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32-7.20 (m, 10 H, Ar-*H*), 5.95 (d, *J* = 3.9 Hz, 1 H, H-1), 4.70 (d, *J* = 11.7 Hz, 1 H, -OCH_A*Ph*), 4.65 (d, *J* = 3.9 Hz, 1 H, H-2), 4.45 (d, *J* = 11.7 Hz, 1 H, -OCH_B*Ph*), 4.23 (dd, *J* = 8.7 Hz and 3.0 Hz, 1 H, H-4), 4.09 (q, *J* = 7.2 Hz, 2 H, -OC$H_2$$CH_3$), 3.94 (d, *J* = 3.0 Hz, 1 H, H-3), 3.85 and 3.82 (each d, each *J* = 12.0 Hz, each 1 H, NHCH_aPh and -NHCH_bPh), 3.52 (m, 1 H, H-5), 2.42 (dd, *J* = 14.8 and 4.4 Hz, 1 H, H-6_A), 2.31 (dd, *J* = 15.0 Hz and 6.6 Hz, 1 H, H-6_B), 1.79 (bs, 1 H, N*H*), 1.48 and 1.32 [each s, each 3 H, >C(CH_3)$_2$], 1.22 (t, *J* = 7.20 Hz, 3 H, -OCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.7 (*C*=O), 140.5, 137.0, 128.5,128.3, 128.2, 128.1, 127.9 & 126.8 (Ar–*C*), 111.6 [>*C*$(CH_3)_2$], 104.9 (C-1), 82.3 (C-2), 81.7 (C-4), 81.6 (C-3), 71.4 (-O*C*H_2Ph), 60.4 (O*C*$H_2$$CH_3$), 53.8 (C-5), 51.6 (-NH*C*H_2Ph), 36.4 (C-6), 26.7 & 26.3 [>C(*C*H_3)$_2$], 14.2 (OCH$_2$*C*H_3) ppm.

*Ethyl-3-O-benzyl-5,6-dideoxy-5-benzylamino-1,2-O-isopropylidene-α-D-glucohepto -furannuronate (**4b**):* Minor isomer **4b** was isolated as colourless oil; IR (KBr): ν_{max} cm^{-1} 3350 (NH), 3019, 2980, 2920 (CH_3 and CH_2 stretching), 1710 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37-7.24 (m, 10 H, Ar-*H*), 5.89 (d, *J* = 3.9 Hz, 1 H, H-1),

4.68 (d, J = 13.5 Hz, 1 H, -OCH_APh), 4.60 (d, J = 3.6 Hz, 1 H, H-2), 4.54 (d, J = 11.7 Hz, 1 H, -OCH_BPh), 4.18-4.09 (m, 4 H, H-4, -OCH_2CH$_3$, and H-3), 3.84 (d, J = 12.9 Hz, 1 H, -NHCH_APh), 3.73 (d, J = 12.6 Hz, 1 H, -NHCH_BPh), 3.52 (m, 1 H, H-5), 2.82 (dd, J = 15.6 and 3.9 Hz, 1 H, H-6$_A$), 2.59 (dd, J = 15.9 and 6.6 Hz, 1 H, H-6$_B$), 1.47 and 1.31 [each s, each 3 H, >C(CH_3)$_2$], 1.24 (t, J = 7.2 Hz, 3 H, -OCH$_2$CH_3); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 172.4 (C=O), 140.5, 137.5, 128.5, 128.3, 127.9, 127.8, 127.7 and 126.9 (Ar-C), 111.6 [>C(CH$_3$)$_2$], 104.7 (C-1), 82.1 (C-2), 81.7 (C-4), 81.6 (C-3), 72.0 (-OCH$_2$Ph), 60.3 (-OCH$_2$CH$_3$), 52.6 (C-5), 51.2 (-NHCH$_2$Ph), 35.7 (C-6), 26.7 and 26.3 [>C(CH$_3$)$_2$], 14.2 (-OCH$_2$$CH_3$) ppm.

A variety of known promising catalysts such as InCl$_3$, DBU, DABCO, starch, Y(NO$_3$)$_3$·6H$_2$O and ionic liquids e.g. *N*-methylmorpholinium hydrogen sulfate [NMM]$^+$[HSO$_4$]$^-$ and *N*-methylmorpholinium methyl sulfonate [NMM]$^+$[CH$_3$SO$_3$]$^-$ were screened to identify a suitable activator for high diastereoselective addition, where no significant improvement in diastereoselectivity was noticed (Table 1). The predominant diastereoselectivity observed in this addition was mainly due to the presence of well-known alkene-arene π stacking effect shown on the basis of Felkin-Anh like transition state model.[1-3]

Table 1. Optimization of 1,4-conjugate addition of benzyl amine to olefinic ester **3**



3 Major **(4a)** Minor **(4b)**

Entry	**Catalyst used**	**time**[a]	**Yield**[b]**(%)**	**dr** (major/minor)[c]
1	--	40 h	85	78:22
2	InCl$_3$ (5 mmol %)	12 h	90	75:25
3	DBU	20 h	85	74:26
4	DABCO	20 h	85	77:23
5	starch	30 h	70	76:24
6	Y(NO$_3$)$_3$·6H$_2$O	18 h	91	80:20
7	Y(NO$_3$)$_3$·6H$_2$O, solvent free	25 h	85	77:23
8	[NMM]$^+$[CH$_3$SO$_3$]$^-$	20 min	95	80:20
9	**[NMM]$^+$[HSO$_4$]$^-$**	**15 min**	**95**	80:20

[a] Time required. [b] isolated yield. [c] determined by ^{1}HNMR signal

3. Synthesis of ionic liquids:

3.1 ***Synthesis of N-methylmorpholinium methyl sulfonate*** *$[NMM]^+[CH_3SO_3]^-$: N*-Methylmorpholine (10.1 g, 0.1 mol) was added to a 100 ml flask with a magnetic stirrer. Then, methanesulfonic acid (9.6 g, 0.1mol) was dropped slowly into the flask over a period of 0.5 h in an ice bath. The reaction was allowed to run for another 5 h at room temperature and mixture was washed three times with ethyl acetate and dried at 90 °C under vacuum for 4 h. *N*-Methylmorpholinium methyl sulfonate[4] was obtained in quantitative yield.^{1}H NMR (300 MHz, DMSO): δ = 2.42 (s, 3 H), 2.79 (s, 3 H), 3.05 (d, J = 10.5 Hz, 2 H), 3.34 (d, J = 12.3 Hz, 2 H), 3.63 (t, J = 12.6 Hz, 2 H), 3.94 (d, J = 12.3 Hz, 2 H), 9.87 (s, 1 H); ^{13}C NMR (75 MHz, DMSO): δ = 38.6, 42.7, 52.6, 63.5 ppm.

3.2 ***Synthesis of N-methylmorpholinium hydrogen sulfate*** *$[NMM]^+[HSO_4]^-$:* $[NMM]^+[HSO_4]^-$ is prepared by mixing *N*-methylmorpholine with concentrated H_2SO_4 (98%) at 0 °C and stirring for 2 h at room temperature. After that the liquid is washed with EtOAc three times and dried at 80 °C in vacuum. *N*-Methylmorpholinium hydrogen sulfate[4] was obtained in quantitative yield. ^{1}H NMR (300 MHz, DMSO): δ = 2.79 (s, 3 H), 3.05 (s, 2 H), 3.32 (s, 2 H), 3.61 (s, 2 H), 3.92 (s, 2 H), 6.40 (s, 1 H) 9.67 (s, 1 H); ^{13}C NMR (75 MHz, DMSO): δ = 42.6, 52.6, 63.4 ppm.

4. Synthesis of 5-benzylamino-5,6-dideoxy-6-hydroxymethyl-1,2-*O*-isopropylidene-3-*O*-benzyl-*α*-D-*gluco* & *β*-L-*ido*-furanose

*4.1 Synthesis of 5-benzylamino-5,6-dideoxy-6-hydroxymethyl-1,2-O-isopropylidene-3-O-benzyl-β-L-ido-furanose (**5a**):* A solution of ethyl-3-*O*-benzyl-5,6-dideoxy-5-benzylamino-1,2-*O*-isopropylidene-*β*-L-*ido*-heptofurannuronate (**4a**) in anhydrous THF (2.90 g, 6.37 mmol) was added drop wise to a stirring slurry of $LiAlH_4$ (0.242 g, 6.37 mmol, in 2 ml THF) under nitrogen atmosphere at 0 °C. After the complete addition, the stirring of the reaction mixture was continued for 30 min at same temperature and then at ambient temperature for an additional 2.5 h. The excess of reducing agent ($LiAlH_4$) was quenched with saturated aqueous solution of Na_2SO_4 and reaction mixture was filtered over a celite pad and solid cake was washed with tetrahydrofuran. The filtrate was evaporated under reduced pressure and residue thus obtained was dissolved in ethyl acetate, washed with water, dried (over anhyd. Na_2SO_4) and evaporated under reduced pressure to give a residual mass which on flash column chromatography over SiO_2 (230–400 mesh) using

chloroform-methanol (97:2) as eluent gave amino alcohol **5a** in 96% yield as a colorless oil. IR (KBr): ν_{max} cm^{-1} 3346, 2927 and 2856; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36-7.25 (m, 10 H, Ar-*H*), 5.96 (d, *J* = 3.6 Hz, 1 H, H-1), 4.70 (d, *J* = 12.0 Hz, 1 H, -OCH_APh), 4.66 (d, *J* = 3.9 Hz, 1 H, H-2), 4.41 (d, *J* = 12.0 Hz, 1 H, -OCH_BPh), 4.25 (dd, *J* = 9.60 and 3.0 Hz, 1 H, H-4), 3.93 (d, *J* = 12.0 Hz, 1 H, -NHCH_2Ph), 3.85 (d, *J* = 3.0 Hz, 1 H, H-3), 3.84 (d, *J* = 12.3, 1 H, -NHCH_2Ph), 3.78-3.75 (m, 2 H, CH_2OH), 3.36 (m, 1 H, H-5), 1.62-1.55 (m, 2 H, H-6), 1.50 and 1.34 (each s, each 3 H, >C(CH_3)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.5, 136.8, 128.5, 128.5, 128.2, 128.0, and 127.1 (Ar–*C*), 111.6 [>*C*(CH_3)$_2$], 104.7 (C-1), 81.8 (C-2), 81.6 (C-4), 81.2 (C-3), 71.7 (–O*C*H_2Ph), 62.3 (C-7), 56.8 (-NH*C*H_2Ph), 50.7 (C-5), 29.2 (C-6), 26.7 and 26.2 [>C(*C*H_3)$_2$] ppm; Anal. Calc. for $C_{24}H_{31}NO_5$: C, 69.70; H, 7.56; N, 3.39. Found: C, 69.35; H, 7.62; N, 3.27.

Similarly, the 5-benzylamino-5,6-dideoxy-6-hydroxymethyl-1,2-*O*-isopropylidene-3-*O*-benzyl-α-D-gluco-furanose was obtained by LAH reduction of compound ethyl-3-*O*-benzyl-5,6-dideoxy-5-benzylamino-1,2-*O*-isopropylidene-α-D-glucoheptofurannuronate (0.2 g) in anhydrous THF (10 mL). The physical data of developed compound is closely matched with reported earlier.[5]

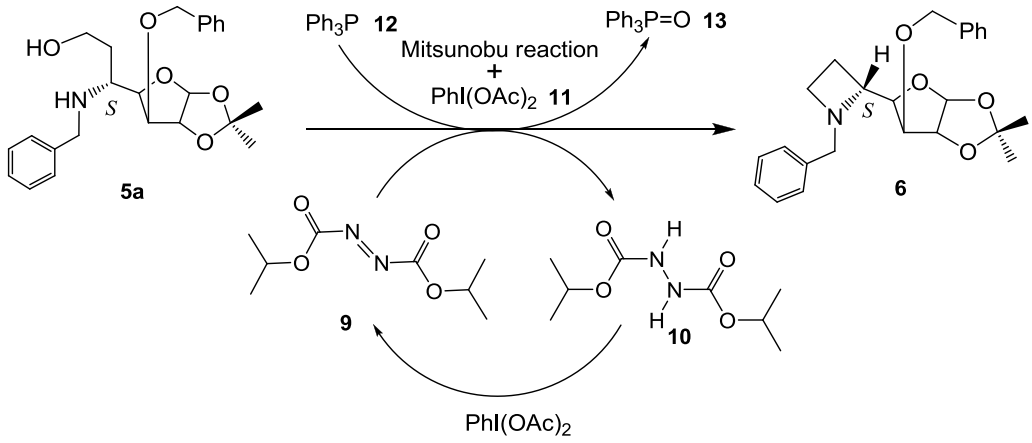
5. Typical experimental procedure for intramolecular cyclization of glycosyl *β*-amino alcohol under Mitsunobu reaction condition

5.1 ***Synthesis of 2-(3-O-benzyl-1,2-O-isopropylidene-β-L-ido-furanose)-1-benzyl azetidine*** (**6**): A solution of 5-benzylamino-5,6-dideoxy-6-hydroxymethyl-1,2-*O*-isopropylidene-3-*O*-benzyl-*β*-L-*ido*-furanose (**5a**, 0.5 g, 1.21 mmol), diisopropyl azodicarboxylate (DIAD) (0.05 g, 0.24 mmol, 0.2 eq.), triphenylphosphine (Ph_3P) (0.4 g, 1.52 mmol) and diacetoxyiodobenzene (DIB) (0.59 g, 1.8 mmol) in dry THF was added slowly and stirred magnetically at 0 °C under inert atmosphere for 30 min. Reaction mixture was stirred magnetically at room temperature for next 10 h. The reaction mass was concentrated under reduced pressure and obtained crude mass was chromatographed over SiO_2 column using chloroform-methanol (96:4) as eluent to give the glycosyl azetidine as colourless oil in 72% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36-7.26 (m, 10 H, Ar-*H*), 5.93 (d, *J* = 3.6 Hz, 1 H, H-1), 5.01-4.93 (d, 3 H, -OCH_2Ph, H-2), 4.68 (d, *J* = 11.7 Hz, 1 H, -NCH_APh), 4.65 (d, *J* = 3.9 Hz, 1 H, H-4), 4.45 (d, *J* = 11.7 Hz, 1 H, -NCH_BPh), 4.19 (d, *J* = 8.1 Hz, 1 H, >NC*H*<), 3.89 (s, 1 H, H-3), 3.73 (q, *J* = 11.7 Hz, 12 Hz, 2 H, >N-CH_2-), 2.02 (s, 2 H, >CH_2), 1.48 and 1.41 (each s, each 3 H, >C(CH_3)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$):

δ = 136.8, 133.1, 132.9, 132.2, 128.5 128.4, 128.3, 128.1, 128.0 and 127.9 (each Ar-*C*), 111.64 [>*C*(CH_3)$_2$], 104.6 (C-1), 81.8 (C-2), 81.3 (C-4), 71.6 (C-3), 69.8 (-O*C*H_2Ph), 62.7 (-N*C*H_2Ph), 54.2 (>N*C*H<), 40.4 (>N*C*H_2-), 26.7 and 26.2 [>C(*C*H_3)$_2$], 14.1 (>*C*H_2) ppm.

Following the *Mitsunobu* reaction condition, DEAD/PPh_3 induced intramolecular cyclization of glycosyl *β*-amino alcohol was carried out in anhydrous THF to afford 2-(3-*O*-benzyl-1,2-*O*-isopropylidene-*β*-L-*ido*-furanose)-1-benzyl azetidine **6**.[7] DEAD is known to be toxic, shock sensitive and thermally unstable, thus the diisopropyl azodicarboxylate (DIAD) was used because it is less expensive, reportedly easier to handle and has previously been proved to allow use of a wider range of nucleophiles. DIAD/PPh_3 mediated intramolecular cyclization of compound **5** was effective and fetched the product in high yield (72%), but required excess amount of reagent.

Table 2. Cycle of catalytic intramolecular cyclization of glycosyl *β*-amino alcohol **5a**



entry	amino alcohol (eq.)	Ph_3P (eq.)	DEAD (eq.)	DIAD (eq.)	DIB	yield (%)
1	1.0	1.2	1.2	-	-	68
2	1.0	1.5	1.5	-	-	70
3	1.0	1.5	0.1	-	2.0	72
4	1.0	1.2	-	1.2	-	70
5	1.0	1.5	-	1.5	-	73
6	1.0	1.2	-	0.2	1.5	72

Developing a strategy which could reduce the quantity of DIAD in the reaction would be of vital importance to expedite synthetic protocol for scale-up synthesis. Employing diacetoxyiodobenzene (DIB) to oxidize the 1,2-dicarbisopropoxyhydrazine back to DIAD during intramolecular cyclization of **5a**

was visualized.[6] The desired azetidine was formed in good yield using the initial conditions of 0.2 equiv of DIAD in combination with 1.5 equiv of each, DIB and PPh_3. Eventually, optimal conditions were determined to be 0.2 equiv of **9** and 1.2 and 1.5 equiv of both **11** and **12** respectively (Table 2, entry 6).

2-(3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-ido-furanose)-1-benzyl azetidine (**6**) could also be obtained from amino alcohol **5a** by reacting with DIAD (1.5 eq) and PPh_3 (1.5 eq.) in dry THF for 12 hours.[7] The progress of reaction was monitored on TLC, which after completion was concentrated under reduced pressure followed by extraction with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford a crude mass, which on silica-gel column chromatography and elution with $CHCl_3$–CH_3OH (98:2) afforded glycosyl azetidine **6** as a colorless oil in 70 % yield.

6. **Deprotection (and *in situ* cyclization) of glycosyl azetidine (6): *Synthesis of 1-deoxy-norcastanospermine (8):*** A solution of 2-(3-*O*-benzyl-1,2-*O*-isopropylidene-*β*-L-*ido*-furanose)-1-benzyl azetidine (**6**, 0.25 g, 0.6 mmol) in TFA-H_2O (3:2, 2 ml) was stirred at 25 °C for 2 h. Trifluroacetic acid was co-evaporated with benzene to furnish a thick liquid, which was directly used in the next reaction. To a solution of the above product in methanol, added 10% Pd-C (0.05 g) and solution was hydrogenated under the atmosphere of H_2 at 80 psi pressure for 20 h. The catalyst was filtered through celite, washed with methanol and the filtrate concentrated to get crude compound. The crude compound was washed with chloroform (which was discarded) and thick oil thus obtained was dissolved in methanol and stirred with basic ion exchange resin IRA 400 for 10 min. Filtration through celite and concentration of the methanol under reduced pressure afforded 1-deoxy-norcastanospermine in 60% yield as colourless oil. ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 4.72 (m, 1 H), 3.29 (q, J = 9.0 Hz, 1 H), 4.07 (d, J = 3.9 Hz, 1 H), 3.98 (dd, J = 9.0 Hz and 4.5 Hz, 1 H), 3.91 (d, J = 9.3 Hz, 1 H), 3.78 (t, J = 4.8 Hz, 1 H), 3.45 (d, J = 11.5 Hz and 4.5 Hz, 1 H), 3.30 (d, J = 10.8 Hz, 1 H), 2.75 (s, 1 H), 2.64 (d, J = 8.4 Hz, 1 H), 2.59 (d, J = 10.8 Hz, 1 H); ^{13}C NMR (75 MHz, CD_3COCD_3): δ = 74.6, 70.1, 69.3, 61.5, 55.1, 50.0, 19.3 ppm; Anal. Calc. for $C_7H_{13}NO_3$: C, 52.82; H, 8.23; N, 8.80. Found: C, 52.95; H, 8.15; N, 8.71.

7. References:

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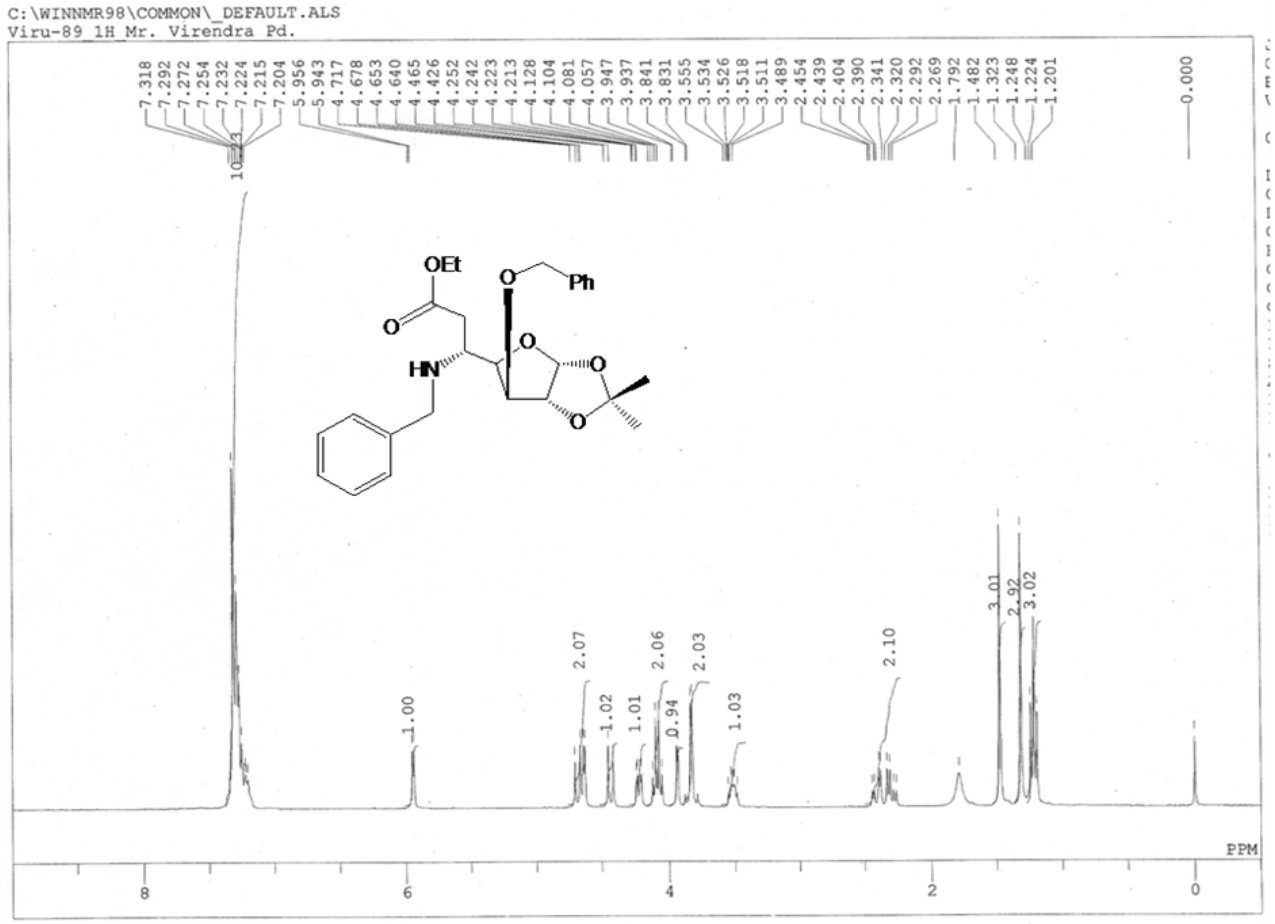

Figure 1: ^{1}H NMR of ethyl-3-*O*-benzyl-5,6-dideoxy-5-benzylamino-1,2-*O*-isopropylidene-*β*-L-*ido*-heptofurannuronate

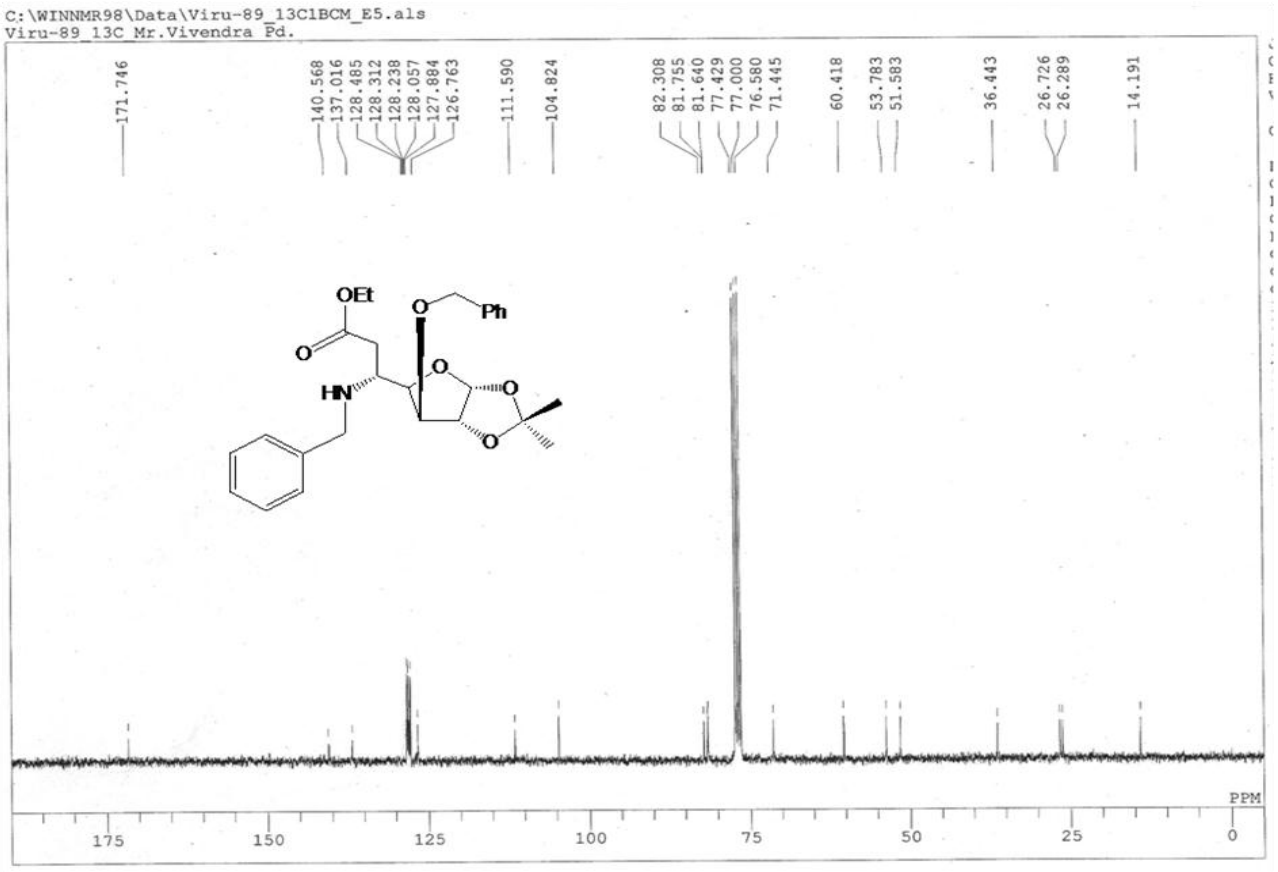

Figure 2: ^{13}C NMR of ethyl-3-*O*-benzyl-5,6-dideoxy-5-benzylamino-1,2-*O*-isopropylidene-*β*-L-*ido*-heptofurannuronate

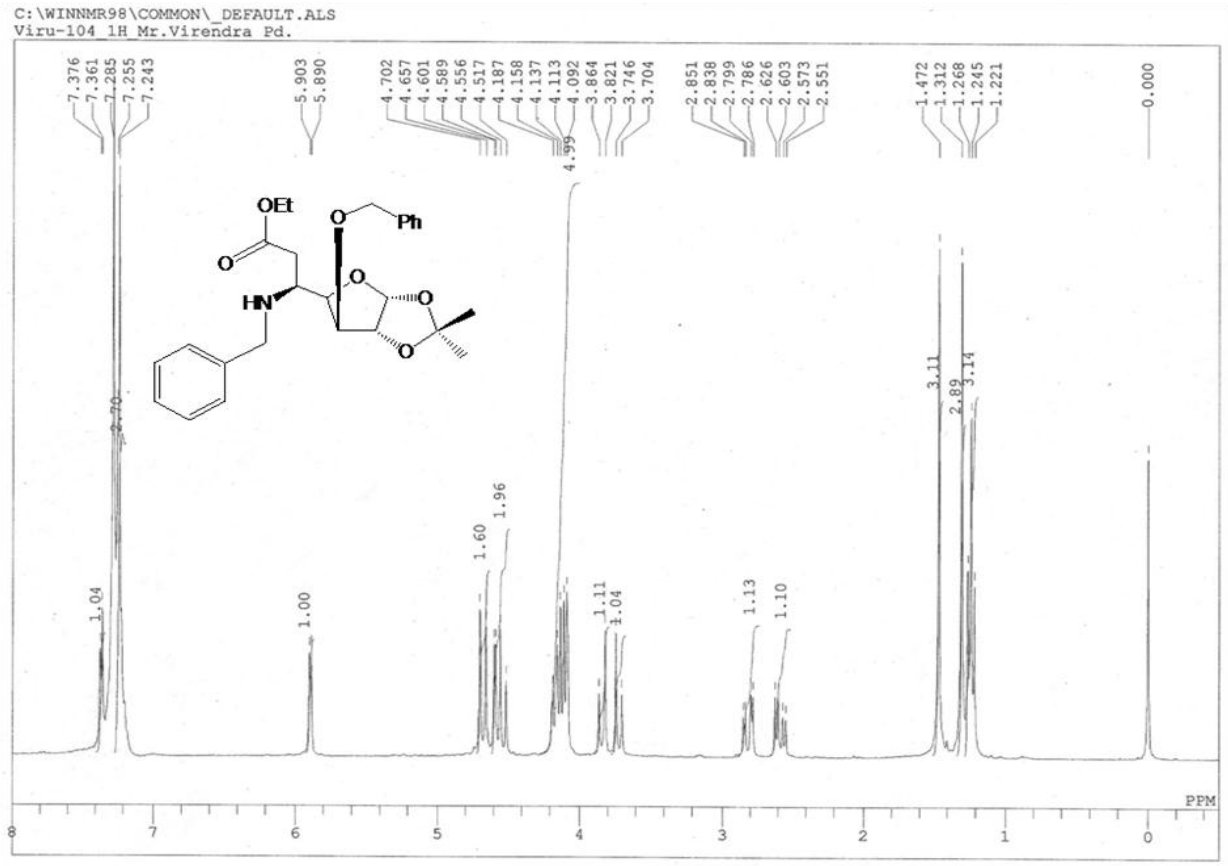

Figure 3: ^{1}H NMR of ethyl-3-*O*-benzyl-5,6-dideoxy-5-benzylamino-1,2-*O*-isopropylidene-*α*-D-*gluco*-heptofurannuronate

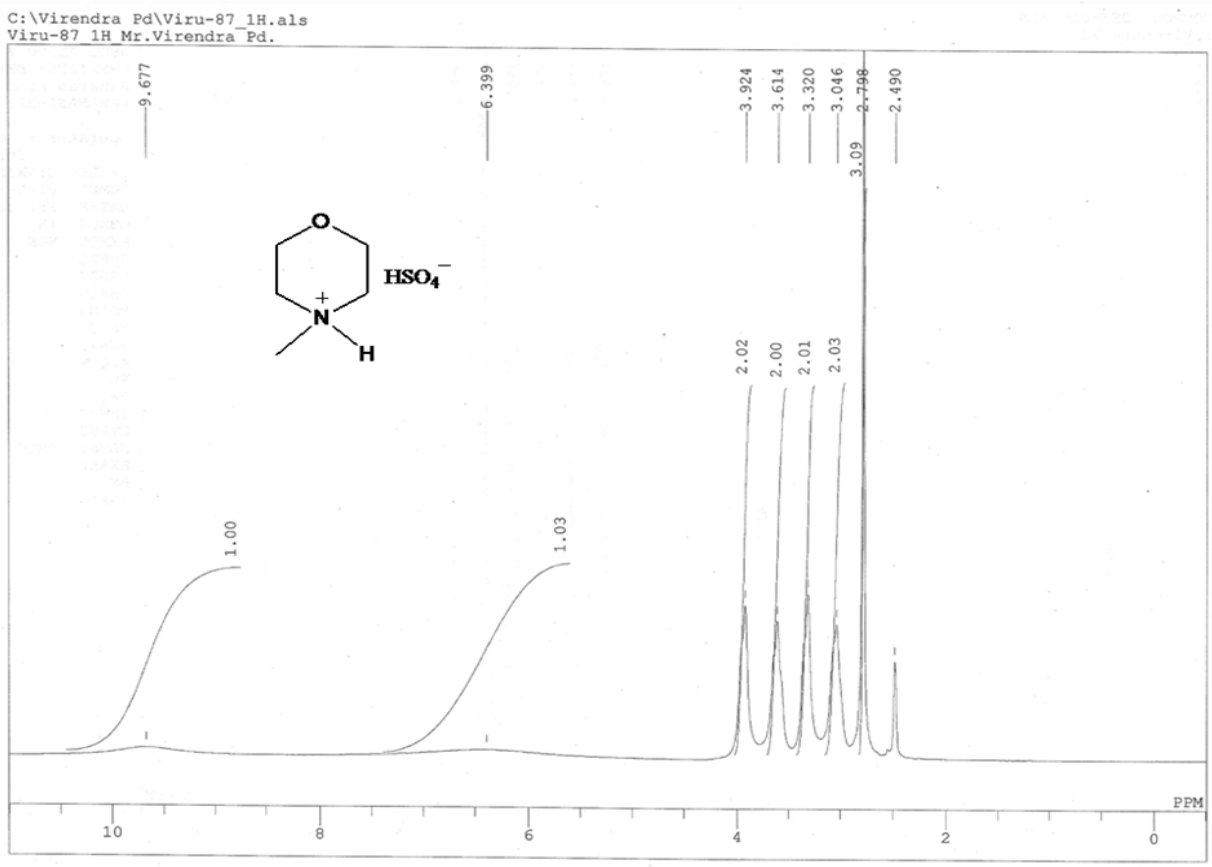

Figure 4: ^{1}H NMR of *N*-methylmorpholinium hydrogen sulphate

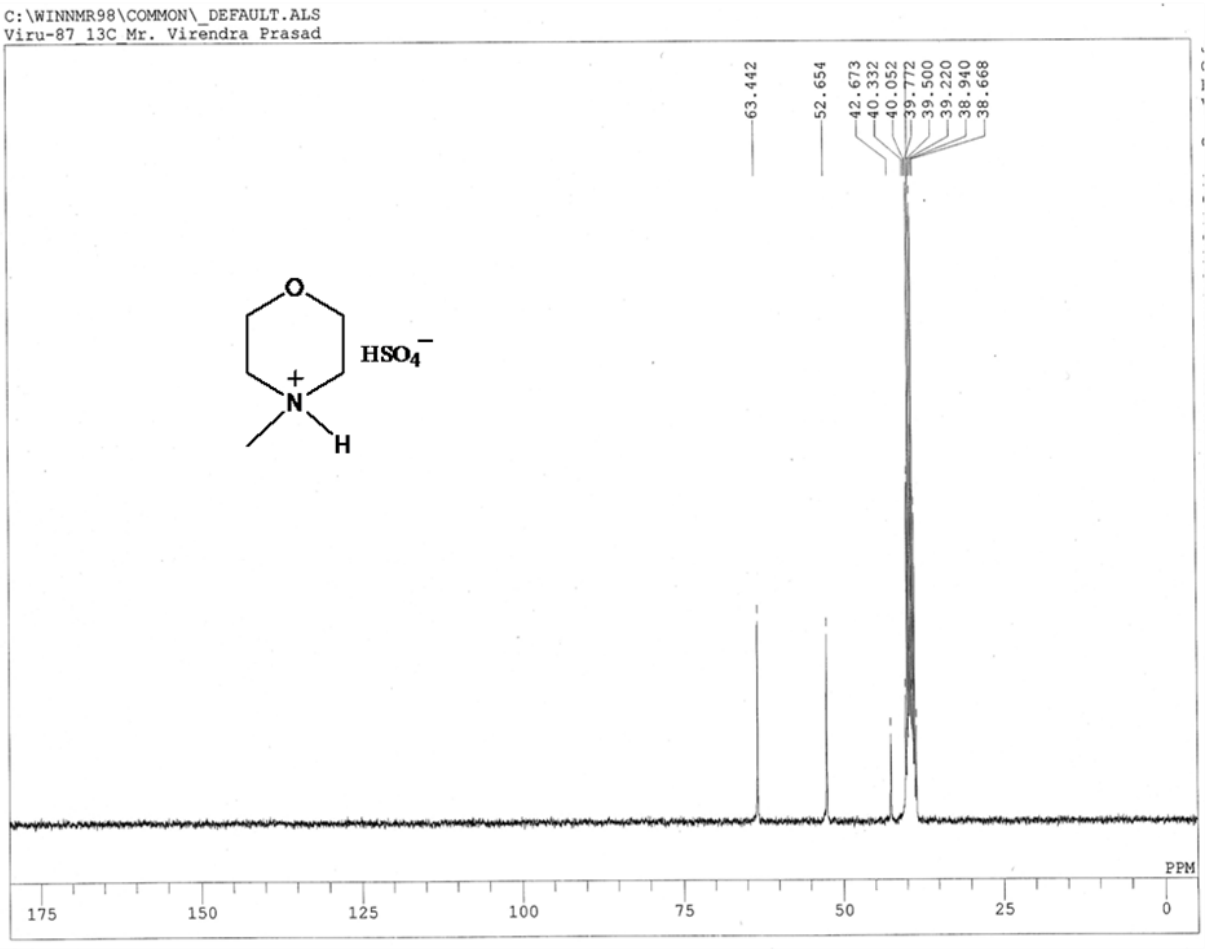

Figure 5: ^{13}C NMR of *N*-methylmorpholinium hydrogen sulphate

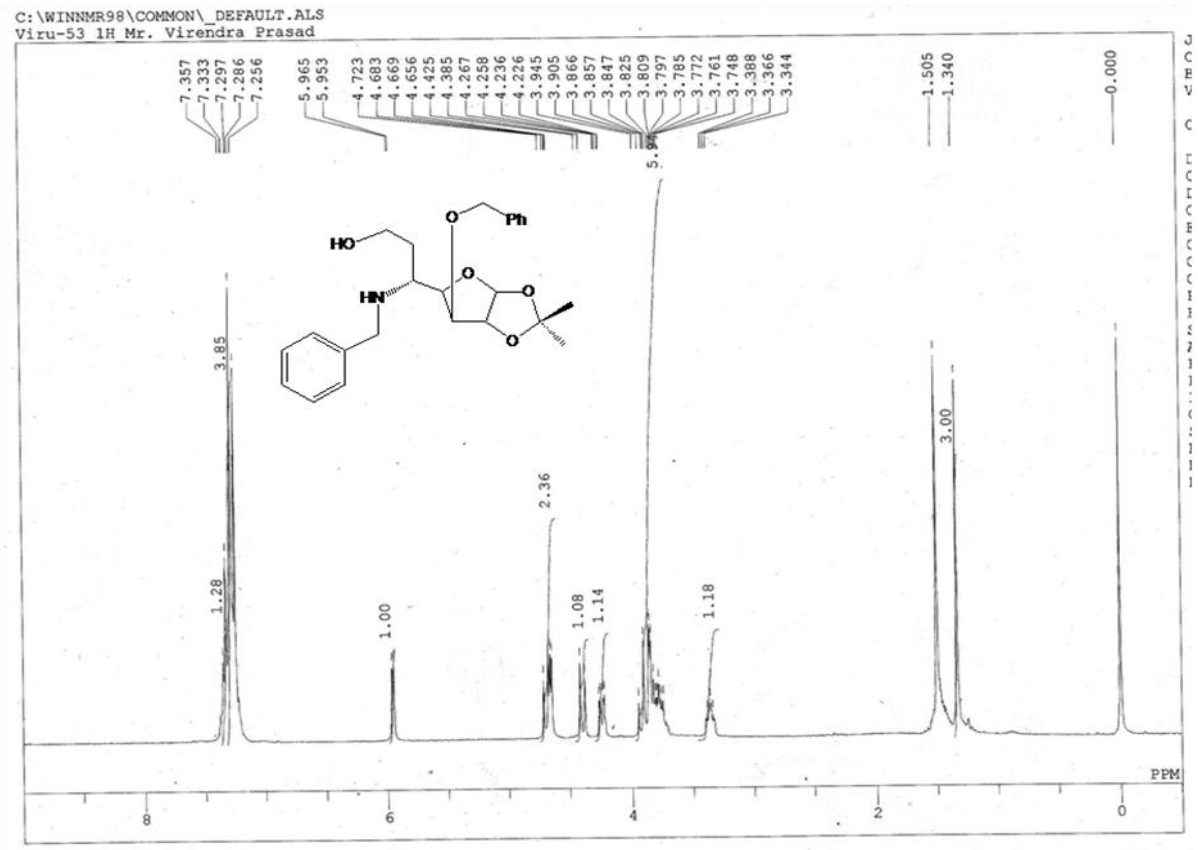

Figure 6: [1]H NMR of 5-benzylamino-5,6-dideoxy-6-hydroxymethyl-1,2-*O*-isopropylidene- 3-*O*-benzyl-*β*-L-*ido*-furanose

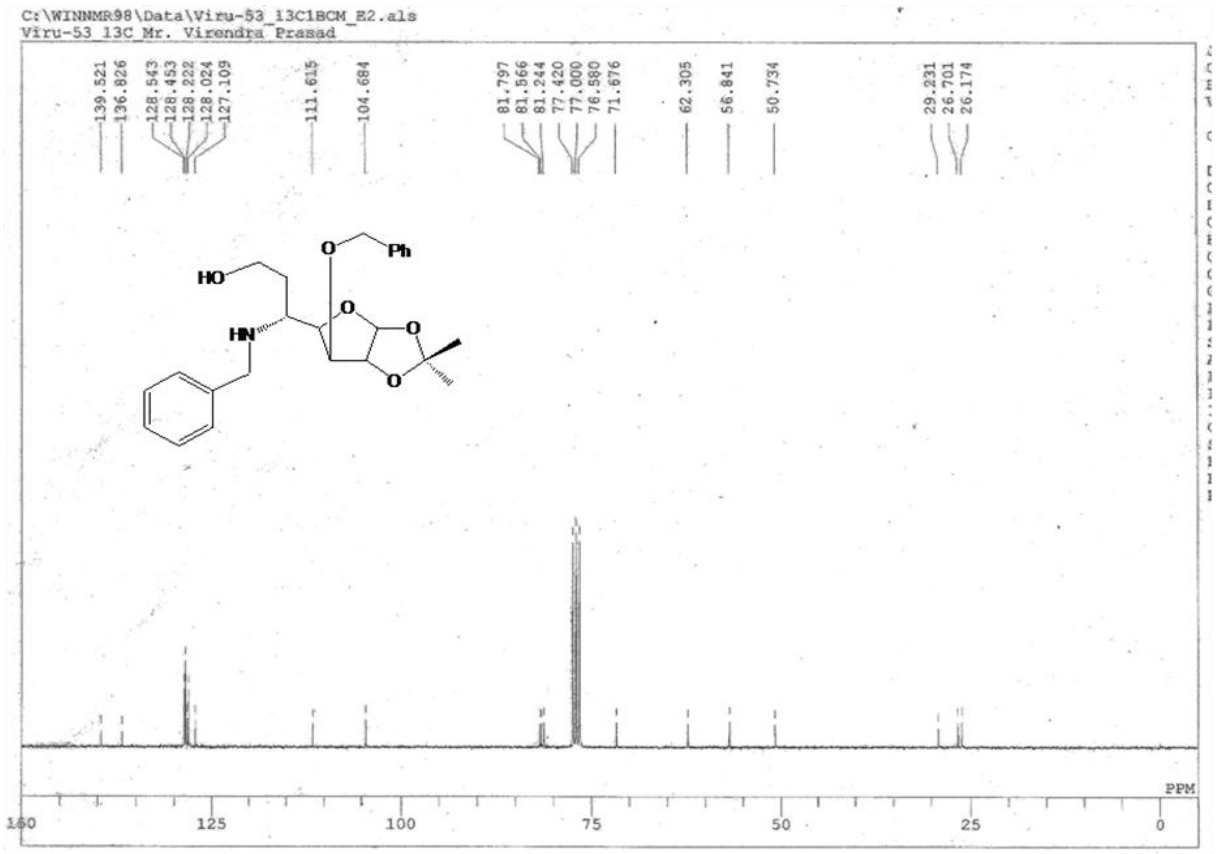

Figure 7: [13]C NMR of 5-benzylamino-5,6-dideoxy-6-hydroxymethyl-1,2-*O*-isopropylidene- 3-*O*-benzyl-*β*-L-*ido*-furanose

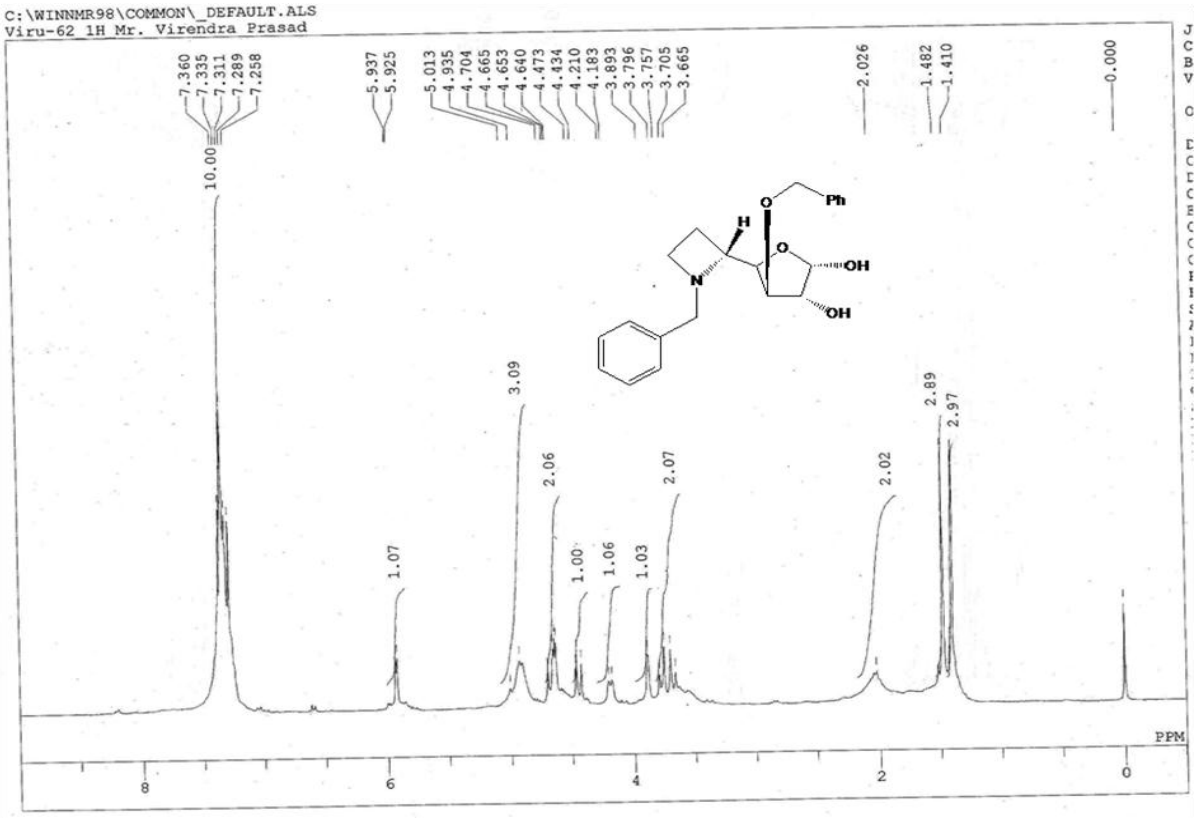

Figure 8: [1]H NMR 2-(3-*O*-benzyl-1,2-*O*-isopropylidene-*β*-L-*ido*-furanose)-1-benzyl azetidine

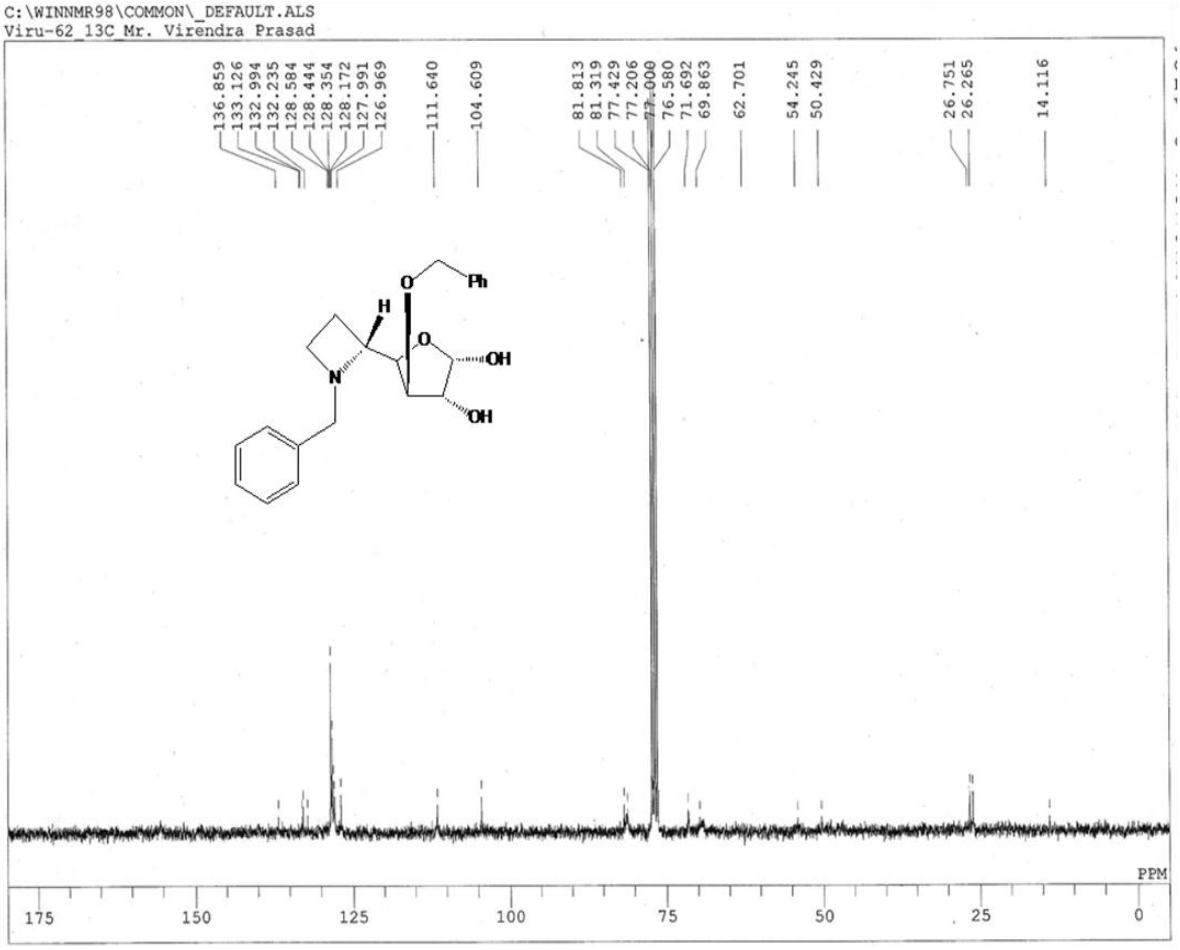

Figure 9: [13]C NMR 2-(3-*O*-benzyl-1,2-*O*-isopropylidene-*β*-L-*ido*-furanose)-1-benzyl azetidine

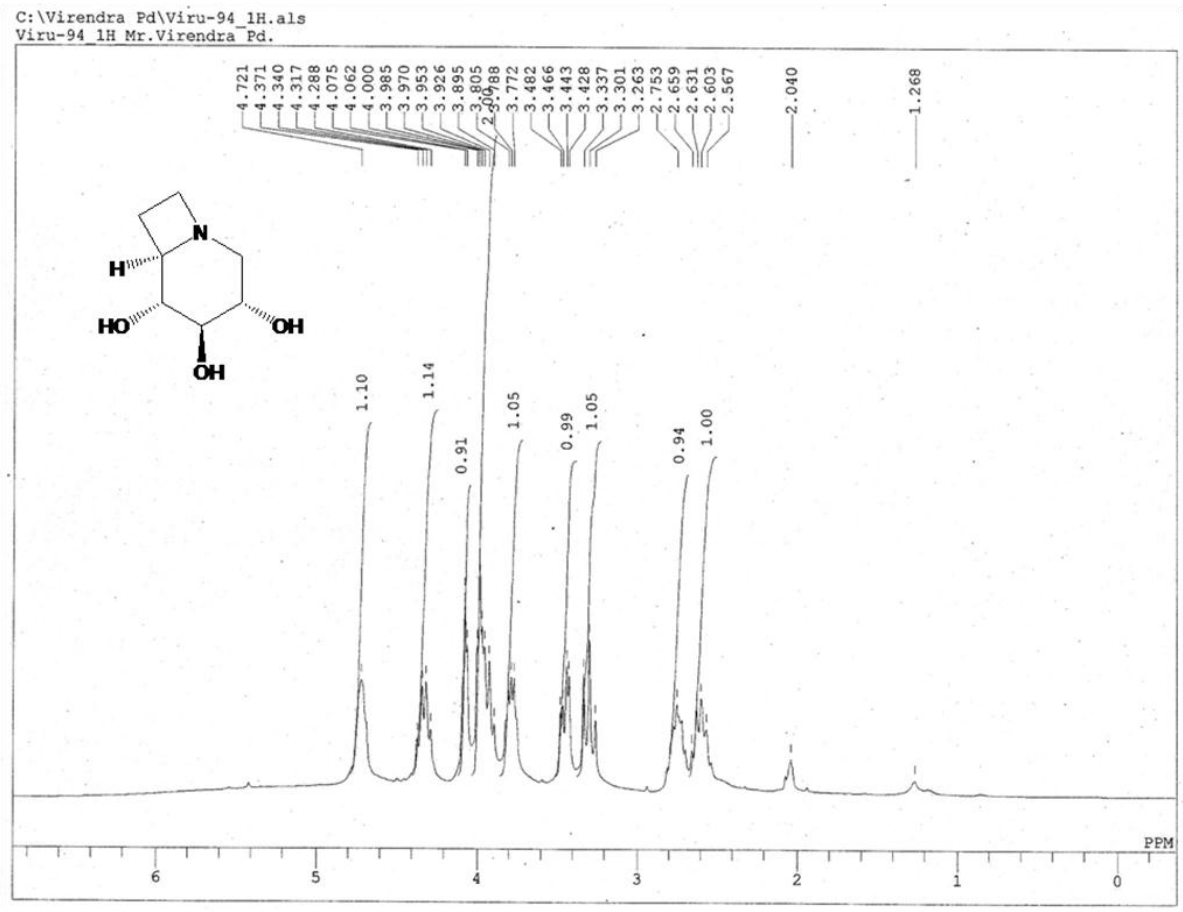

Figure 10: ^{1}H NMR of 1-deoxy-norcastanospermine (in deuterated acetone)

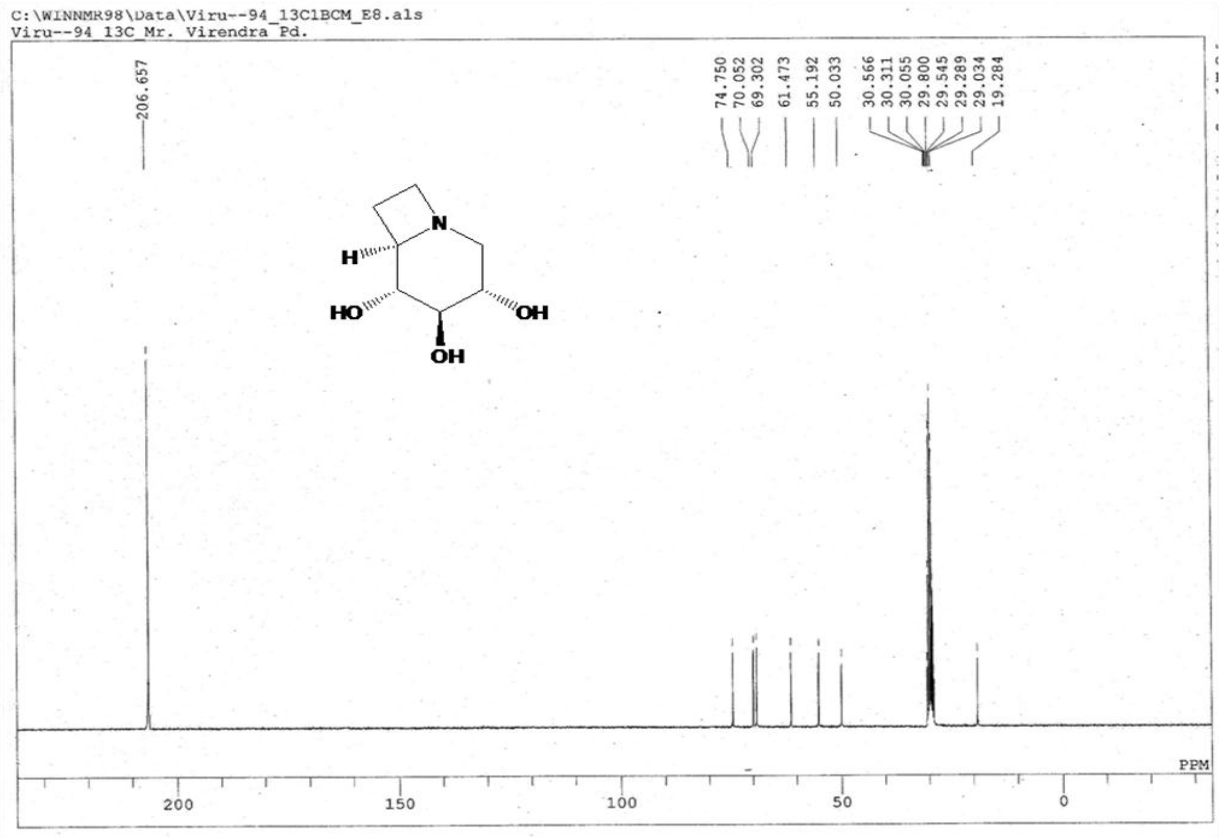

Figure 11: ^{13}C NMR of 1-deoxy-norcastanospermine (in deuterated acetone)

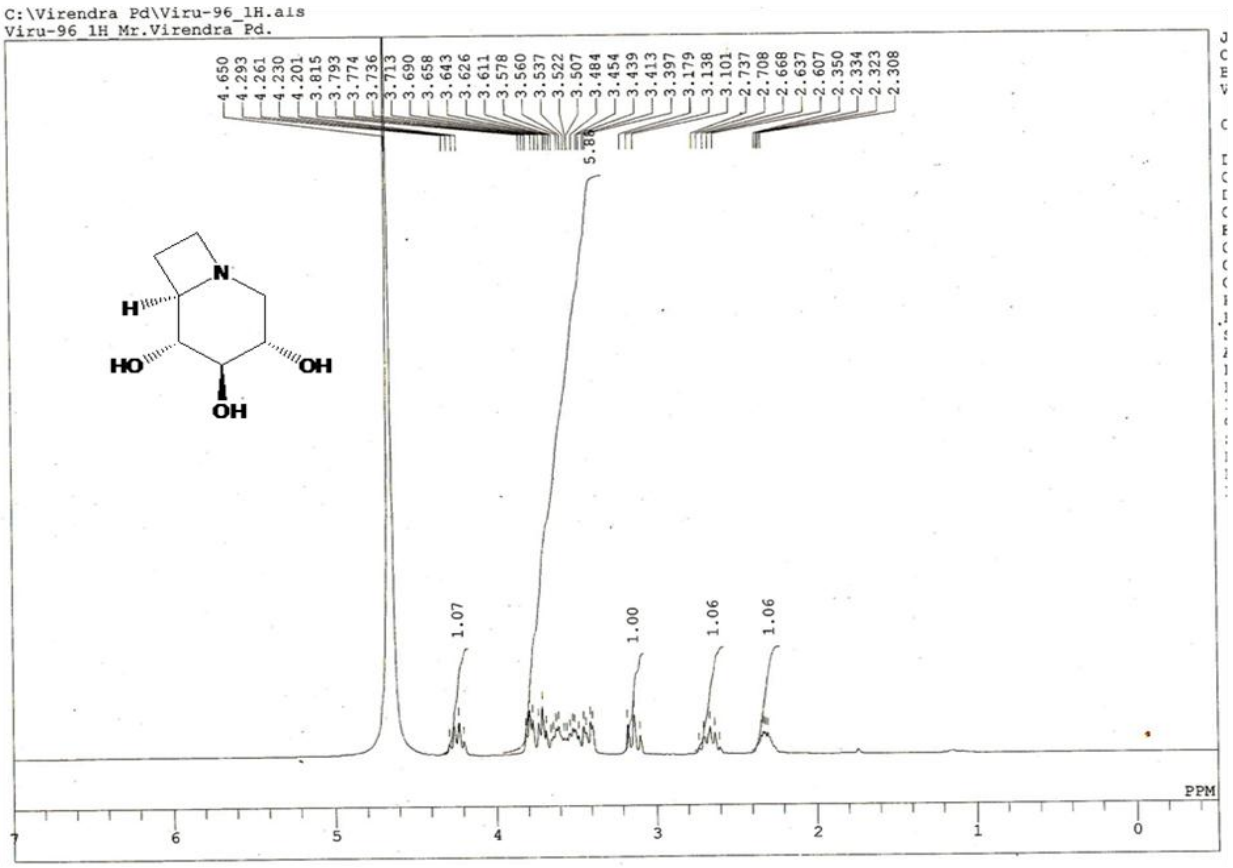

Figure 12: ^{13}C NMR of 1-deoxy-norcastanospermine (in D_2O)

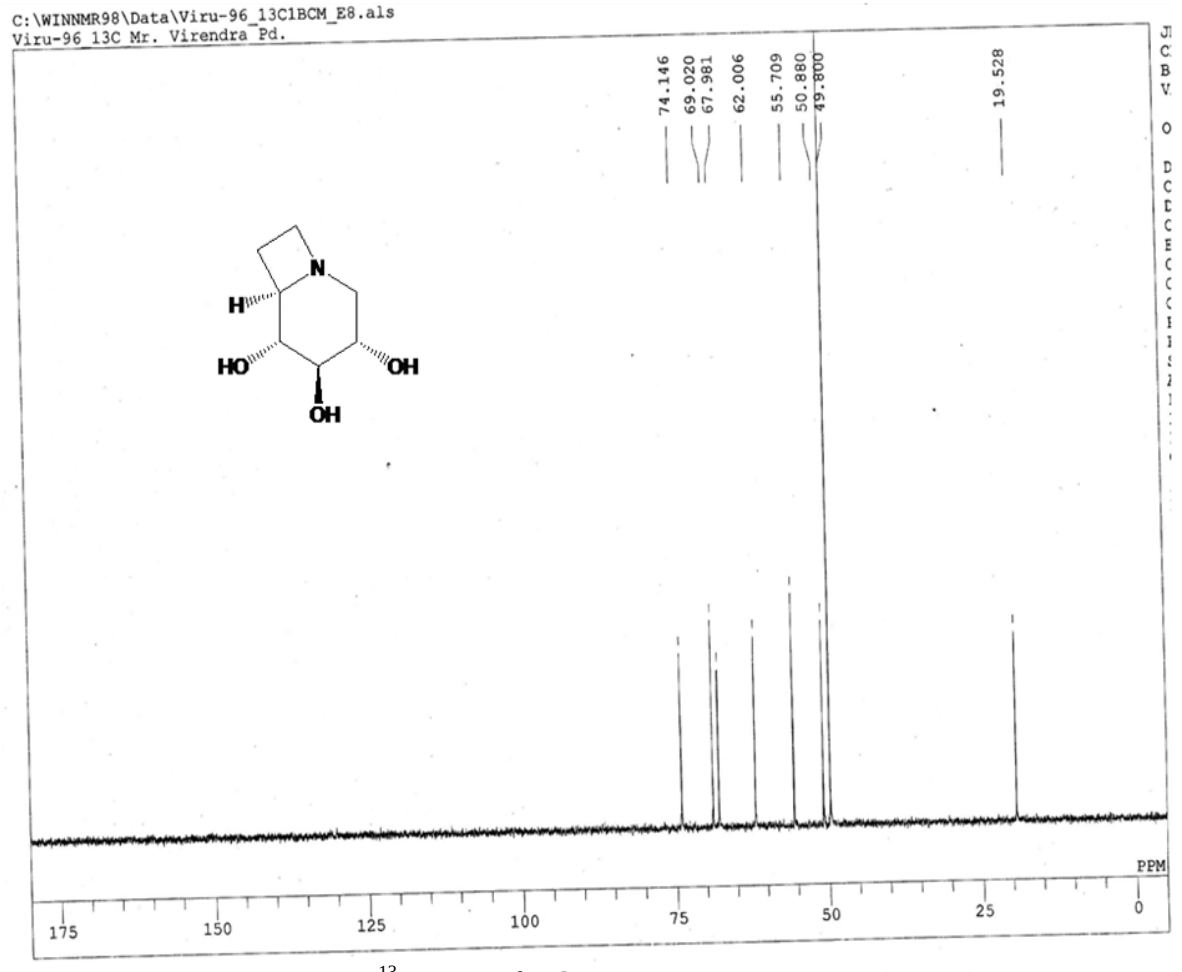

Figure 13: ^{13}C NMR of 1-deoxy-norcastanospermine (in D_2O)