SUPPORTING INFORMATION

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Title: Synthesis of Eight 1-Deoxynojirimycin Isomers from a Single Chiral Cyanohydrin
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General Remarks

Unless noted otherwise, all reactions were performed under an argon atmosphere. All general chemicals (Fluka, Fischer, Merck, Sigma-Aldrich) were used as received. \((R)-(+)\)-tert-butanesulfinamide and \((S)-(+)\)-tert-butanesulfinamide were purchased from Advanced Asymmetrics, Inc. (Millstadt, IL, USA). Column chromatography was performed on silica gel ( Screening Devices b.v.) with a particle size of 40-63 μm and a pore size of 60 Å. The eluents ethyl acetate (EtOAc) and petroleum ether (40-60 °C boiling range) (PE) were distilled prior to use. TLC analysis was conducted on Merck aluminum sheets (Silica gel 60 F254). Compounds were visualized by UV absorption (254 nm), by spraying with a solution of \((NH_4)_6Mo_7O_{24}\cdot4H_2O (25 \text{ g/L})\) and \((NH_4)_4Ce(SO_4)_4\cdot2H_2O (10 \text{ g/L})\) in 10% sulfuric acid, a solution of KMnO₄ (20 g/L) and K₂CO₃ (10 g/L) in water, or ninhydrin (0.75 g/L) and acetic acid (12.5 mL/L) in ethanol, where appropriate, followed by charring at circa 150 °C. Tetrahydrofuran (THF), dichloromethane (DCM), methanol (MeOH), were of peptide synthesis grade, purchased at Biosolve, and used as received. Toluene and diethyl ether were of Anhydrous grade. Solvents that were used in reactions were stored over 4Å molecular sieves, except for methanol which was stored over 3Å molecular sieves. Diethyl ether was dried over sodium wire. Molecular sieves were flame dried in vacuo before use. Infrared (IR) spectra were recorded on a Shimadzu FT-IR 8300. ¹H-NMR spectra were recorded on a Bruker AV-400 (400 MHz) spectrometer. Chemical shifts are given in ppm (δ) relative to the following internal standards: CDCl₃ (TMS, 0 ppm), MeOD-d₄ (MeOH, 3.31 ppm), DMSO-d₆ (DMSO, 2.50 ppm) D₂O (H₂O, 4.79 ppm). ¹³C-NMR ispectra were recorded on a Bruker AV-400 (101 MHz) spectrometer. Chemical shifts are given in ppm (δ) relative to the following internal standards: CDCl₃ (CDCl₃, 77.0 ppm), MeOD-d₄ (MeOD-d₄, 49.0 ppm), DMSO-d₆ (DMSO-d₆, 39.52 ppm). High resolution mass spectra were recorded by direct injection (2 μL of a 2 μM solution in water/acetonitrile; 50/50; v/v and 0.1% formic acid) on a mass spectrometer (Thermo Finnigan LTQ Orbitrap) equipped with an electrospray ion source in positive mode (source voltage 3.5 kV, sheath gas flow 10, capillary temperature 250 °C) with resolution \(R = 60000\) at \(m/z\) 400 (mass range \(m/z\) = 150-2000) and dioctylphthalate \((m/z = 391.28428)\) as a “lock mass”. The high resolution mass spectrometer was calibrated prior to measurements with a calibration mixture (Thermo Finnigan). Optical rotations were recorded on a Propol automatic polarimeter at ambient temperature. LC-MS analysis was performed on a Finnigan Surveyor HPLC system with a Gemini C18 50 × 4.60 mm column (detection at 200-600 nm), coupled to a Finnigan LCQ Advantage Max mass spectrometer with ESI. Chiral HPLC analysis was performed on a Spectroflow 757 system (ABI Analytical Kratos Division, detection at 254 nm) equipped with a Chiralcel OD column (150 × 4.6 mm).
compound 14 in CDCl₃
compound 16 in D$_2$O
compound 17 in CDCl₃
N-Boc-6-Cl-β-L-α-threo-1-DNJ
in MeCO$_2$-$d_4$
compound 20
L-α-fro-1-DNJ.HCl
in D$_2$O
compound 24 in CDCl₃
compound 23 in MeOD
(-)-L-galacto-1-DNJ hydrochloride compound 28 in D$_2$O