Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supplementary Information

Novel 5'-deoxy nucleosyl amino acid scaffolds for the synthesis of muraymycin analogues

Anatol P. Spork and Christian Ducho*

Georg-August-University Göttingen, Department of Chemistry, Institute of Organic and Biomolecular Chemistry, Tammannstr. 2, 37077 Göttingen, Germany. Fax: +49 (0)551 39 9660; Tel: +49 (0)551 39 3285; E-mail: cducho@gwdg.de

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Syntheses

General methods. Chemicals were purchased from Sigma-Aldrich, Alfa Aesar, ABCR and VWR. Reactions involving oxygen and/or moisture sensitive reagents were carried out under an atmosphere of argon using anhydrous solvents. Anhydrous solvents were obtained in the following manner: THF was dried over sodium/benzophenone and distilled, MeOH was dried over activated molecular sieves (3 Å) and thoroughly degassed prior to its use in hydrogenation reactions, DMF and EtOAc were dried over activated molecular sieves (4 Å) and degassed. All other solvents were of technical quality and distilled prior to their use, and deionised water was used throughout. Column chromatography was carried out on silica gel 60 (0.040-0.063 mm, 230-400 mesh ASTM, VWR) under flash conditions. TLC was performed on aluminium plates precoated with silica gel 60 F_{254} (VWR). Visualisation of the spots was carried out using UV light (254 nm) and/or staining under heating (staining solution: 4 g vanillin, 25 mL conc. H_2SO_4, 80 mL HOAc and 680 mL MeOH). 300 MHz- and 600 MHz-^{1}H as well as 75 MHz-, 126 MHz- and 151 MHz-^{13}C NMR spectra were recorded on Varian UNITY 300, MERCURY 300, INOVA 500 and INOVA 600 spectrometers. All ^{13}C NMR spectra are ^{1}H-decoupled. All spectra were recorded at room temperature, except of the spectra of compound **S1**, which were recorded at 100 °C to avoid rotamer formation. All NMR spectra were referenced internally to solvent reference frequencies. Chemical shifts (δ) are quoted in ppm, and coupling constants (*J*) are reported in Hz. Assignment of signals was carried out using ^{1}H,^{1}H-COSY, HSQC and HMBC spectra obtained on the spectrometers mentioned above. Low resolution ESI mass spectrometry was performed on a Varian MAT 311 A spectrometer operating in positive ionisation mode. High resolution (HR) ESI mass spectrometry was carried out on a Bruker microTOF spectrometer or a Bruker 7 T FTICR APEX IV spectrometer. Melting points (mp) were measured on a Büchi instrument and are not corrected. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter with a Na source using a 10 cm cell. Infrared spectroscopy (IR) was performed on a Perkin-Elmer Spectrum BX spectrometer with solids being measured as KBr pills. Wavenumbers (ν) are quoted in cm^{-1}. UV spectroscopy was carried out on a Perkin-Elmer Lambda-2 spectrometer. Wavelengths of maximum absorption (λ_{max}) are reported in nm with the corresponding logarithmic molar extinction coefficient (log ε, ε/dm^3 mol^{-1} cm^{-1}) given in brackets.

(6'*S*)-nucleosyl amino acid 8 (*via* the *N*-Boc strategy). To a solution of the *N*-Boc protected (6'*S*)-nucleosyl amino acid **15** (400 mg, 0.496 mmol) in EtOAc (3 mL), a saturated solution of HCl in EtOAc[1] (2 mL) was carefully added dropwise at rt, and the reaction mixture was stirred at rt for 20 h. Due to unsatisfactory conversion, more saturated solution of HCl in EtOAc (2 mL) was added at rt, and the mixture was further stirred for 2 d. After addition of EtOAc (200 mL), the organic layer was washed with saturated $NaHCO_3$ solution (1 x 200 mL), and the aqueous layer was reextracted with EtOAc (4 x 100 mL). The combined organics were dried over Na_2SO_4 and evaporated under reduced pressure. The resultant crude product was purified by column chromatography (petroleum ether-CH_2Cl_2-EtOAc-NEt_3, 40 : 40 : 19 : 1) to give **8** (120 mg, 34 %) and recovered starting material **15** (102 mg, 27 %) as colourless solids; **8**: mp 69 °C; $[\alpha]_D^{25}$ +44.6 (*c* 1.2 in MeOH); λ_{max} (MeCN)/nm 194 (4.72), 223 (4.16) and 263 (3.99); ν_{max} (KBr)/cm^{-1} 2931, 1670, 1513, 1456, 1391, 1250, 1159, 839 and 777; δ_H (300 MHz; CD_3OD) -0.01 (3 H, s, $SiCH_3$), 0.06 (3 H, s, $SiCH_3$), 0.10 (3 H, s, $SiCH_3$), 0.12 (3 H, s, $SiCH_3$), 0.85 (9 H, s, $SiC(CH_3)_3$), 0.93 (9 H, s, $SiC(CH_3)_3$), 1.47 (9 H, s, $OC(CH_3)_3$), 1.86 (1 H, ddd, *J* 5.3, 11.3 and 14.1, 5'-H_a), 2.13 (1 H, ddd, *J* 2.5, 8.0 and 14.1, 5'-H_b), 3.55 (1 H, dd, *J* 5.3 and 8.0, 6'-H), 3.75 (3 H, s, OCH_3), 3.85 (1 H, dd, *J* 5.0 and 5.0, 3'-H), 4.14 (1 H, ddd, *J* 2.5, 5.0 and 11.3, 4'-H), 4.27 (1 H, dd, *J* 4.2 and 5.0, 2'-H), 4.96 (1 H, d, *J* 13.7, PMB-CH_2-H_a), 5.06 (1 H, d, *J* 13.7, PMB-CH_2-H_b), 5.80 (1 H, d, *J* 4.2, 1'-H), 5.84 (1 H, d, *J* 8.1, 5-H), 6.82 (2 H, d, *J* 8.8, PMB-3-H, PMB-5-H), 7.35 (2 H, d, *J* 8.8, PMB-2-H, PMB-6-H) and 7.64 (1 H, d, *J* 8.1, 6-H); δ_C (75 MHz; CD_3OD) -4.5, -4.5, -4.3, -4.0, 18.8, 19.0, 26.4, 26.5, 28.3, 39.1, 44.5, 53.6, 55.7, 76.0, 76.6, 82.8, 83.0, 92.7, 102.5, 114.7, 130.3, 131.4, 140.8, 152.2, 160.7, 164.7 and 174.6; *m/z* (HR-ESI^+) 706.3915 ($M+H^+$. $C_{35}H_{60}N_3O_8Si_2$ requires 706.3913).

(6'*R*)-nucleosyl amino acid 9 (*via* the *N*-Boc strategy). The synthesis of **9** was performed as the synthesis of **8** (*vide supra*) with the *N*-Boc protected (6'*R*)-nucleosyl amino acid **16** (145 mg, 0.180 mmol), a saturated solution of HCl in EtOAc (2 x 1 mL) and EtOAc (1.5 mL). Purification by column chromatography (petroleum ether-CH_2Cl_2-EtOAc-NEt_3, 40 : 40 : 19 : 1) gave **9** (35 mg, 28 %) and recovered starting material **16** (23 mg, 16 %) as colourless solids; **9**: mp 52 °C; $[\alpha]_D^{25}$ +30.1 (*c* 0.9 in MeOH); λ_{max} (MeCN)/nm 223 (4.14) and 263

[1] For the preparation of this solution, HCl gas was generated from the reaction of conc. H_2SO_4 with NaCl. The evolving HCl gas (1 mol) was passed through conc. H_2SO_4 to remove trace water and was bubbled through dry EtOAc (15 mL).

(3.96); ν_{max} (KBr)/cm^{-1} 2931, 1670, 1514, 1456, 1391, 1250, 1160, 839 and 777; δ_H (300 MHz; CD_3OD) -0.02 (3 H, s, $SiCH_3$), 0.06 (3 H, s, $SiCH_3$), 0.10 (3 H, s, $SiCH_3$), 0.13 (3 H, s, $SiCH_3$), 0.84 (9 H, s, $SiC(CH_3)_3$), 0.94 (9 H, s, $SiC(CH_3)_3$), 1.48 (9 H, s, $OC(CH_3)_3$), 2.07 (2 H, dd, *J* 5.7 and 6.8, 5'-H), 3.65 (1 H, dd, *J* 5.7 and 5.7, 6'-H), 3.75 (3 H, s, OCH_3), 3.89 (1 H, dd, *J* 4.5 and 4.5, 3'-H), 4.13 (1 H, dd, *J* 4.5 and 6.8, 4'-H), 4.32 (1 H, dd, *J* 4.5 and 4.5, 2'-H), 4.97 (1 H, d, *J* 13.7, PMB-CH_2-H_a), 5.05 (1 H, d, *J* 13.7, PMB-CH_2-H_b), 5.77 (1 H, d, *J* 4.5, 1'-H), 5.83 (1 H, d, *J* 8.1, 5-H), 6.82 (2 H, d, *J* 8.8, PMB-3-H, PMB-5-H), 7.35 (2 H, d, *J* 8.8, PMB-2-H, PMB-6-H) and 7.61 (1 H, d, *J* 8.1, 6-H); δ_C (75 MHz; CD_3OD) -4.5, -4.5, -4.3, -4.0, 18.8, 19.0, 26.4, 26.5, 28.3, 37.4, 44.5, 53.8, 55.7, 75.5, 76.6, 82.6, 83.1, 93.0, 102.4, 114.7, 130.3, 131.4, 141.0, 152.2, 160.7, 164.7 and 174.3; *m/z* (HR-ESI^+) 706.3909 ($M+H^+$. $C_{35}H_{60}N_3O_8Si_2$ requires 706.3913).

(6'*S*)-nucleosyl amino acid 8 (*via* the *N*-Cbz strategy). Under strictly anaerobic conditions, (*S*,*S*)-Me-DUPHOS-Rh (12 mg, 20 μmol) was added to a solution of **(*Z*)-18** (1.00 g, 1.19 mmol) in MeOH (25 mL). The reaction mixture was stirred under an atmosphere of H_2 (1 bar) at rt for 3 d. Pd/C (10 %, 136 mg, 128 μmol) was then added portionwise to the reaction mixture, and the reaction was stirred under an atmosphere of H_2 (1 bar) at rt for 5 h. After filtration through celite™ and washing the celite™ with hot MeOH (100 mL), the solvent of the filtrate was evaporated under reduced pressure. The resultant crude product was purified by column chromatography (petroleum ether-CH_2Cl_2-EtOAc-NEt_3, 40 : 40 : 19 : 1) to give **8** (723 mg, 86 %) as a colourless solid; analytical data were found to be identical with the product obtained *via* the *N*-Boc strategy (*vide supra*).

(6'*R*)-nucleosyl amino acid 9 (*via* the *N*-Cbz strategy). The synthesis of **9** was performed as the synthesis of **8** (*vide supra*) with **(*Z*)-18** (1.00 g, 1.19 mmol), (*R*,*R*)-Me-DUPHOS-Rh (24 mg, 40 μmol, added portionwise), Pd/C (10 %, 120 mg, 113 μmol), MeOH (25 mL) and a reaction period of 14 d for the homogenous hydrogenation step. Purification by column chromatography (petroleum ether-CH_2Cl_2-EtOAc-NEt_3, 40 : 40 : 19 : 1) gave **9** (675 mg, 80 %) as a colourless solid; analytical data were found to be identical with the product obtained *via* the *N*-Boc strategy (*vide supra*).

(6'*S*)-configured 5'-deoxy muraymycin analogue 10. To a solution of **22** (44 mg, 0.044 mmol) in MeOH (5 mL), Pd/C (10 %, 20 mg, 19 μmol) was added. The reaction mixture was stirred under an atmosphere of H_2 (1 bar) at rt for 3 h. After filtration through

celite™ and washing the celite™ with hot MeOH (3 x 25 mL), the solvent of the filtrate was evaporated under reduced pressure to give **10** (38 mg, 99 %) as a colourless solid; mp 56 °C; $[\alpha]_D^{25}$ +31.0 (*c* 1.1 in $CHCl_3$); λ_{max} (MeOH)/nm 201 (4.51), 222 (4.16) and 264 (3.99); ν_{max} (KBr)/cm^{-1} 2956, 1670, 1514, 1457, 1391, 1250, 1158, 839 and 777; δ_H (600 MHz; C_6D_6) 0.06 (3 H, s, $SiCH_3$), 0.08 (3 H, s, $SiCH_3$), 0.10 (3 H, s, $SiCH_3$), 0.11 (3 H, s, $SiCH_3$), 0.85 (3 H, d, *J* 6.6, Leu-5-H_a), 0.90 (3 H, d, *J* 6.6, Leu-5-H_b), 0.96 (9 H, s, $SiC(CH_3)_3$), 0.97 (9 H, s, $SiC(CH_3)_3$), 1.23-1.30 (1 H, m, Leu-3-H_a), 1.42 (9 H, s, $OC(CH_3)_3$), 1.46-1.52 (2 H, m, propylene-2-H), 1.55-1.62 (1 H, m, Leu-4-H), 1.77-1.84 (1 H, m, Leu-3-H_b), 2.08 (1 H, ddd, *J* 5.3, 9.7 and 14.0, 1 H, 5'-H_a), 2.15 (1 H, ddd, *J* 3.6, 8.3 and 14.0, 5'-H_b), 2.51 (1 H, ddd, *J* 5.9, 5.9 and 11.5, propylene-1-H_a), 2.69 (1 H, ddd, *J* 5.6, 5.6 and 11.5, propylene-1-H_b), 3.21-3.26 (1 H, m, Leu-2-H), 3.27 (3 H, s, OCH_3), 3.27-3.30 (1 H, m, propylene-3-H_a), 3.32-3.37 (1 H, m, propylene-3-H_b), 3.54 (1 H, dd, *J* 5.3 and 8.3, 6'-H), 3.87 (1 H, dd, *J* 4.4 and 4.7, 3'-H), 4.36 (1 H, ddd, *J* 3.6, 4.7 and 9.7, 4'-H), 4.37 (1 H, dd, *J* 4.1 and 4.4, 2'-H), 5.06 (1 H, d, *J* 13.5, PMB-CH_2-H_a), 5.09 (1 H, d, *J* 13.5, PMB-CH_2-H_b), 5.69 (1 H, d, *J* 7.7, 5-H), 5.91 (1 H, d, *J* 4.1, 1'-H), 6.73 (2 H, d, *J* 8.6, PMB-3-H, PMB-5-H), 7.16 (1 H, d, *J* 7.7, 6-H), 7.39 (1 H, s, NH) and 7.63 (2 H, d, *J* 8.6, PMB-2-H, PMB-6-H); δ_C (126 MHz; C_6D_6) -4.7, -4.4, -4.1, 18.2, 18.3, 21.7, 23.5, 25.0, 26.1, 26.1, 28.1, 30.4, 37.2, 37.9, 43.6, 44.6, 45.8, 53.7, 54.7, 59.9, 75.2, 75.9, 81.0, 81.6, 92.2, 102.2, 114.0, 129.8, 131.3, 138.4, 151.2, 159.7, 162.2, 174.1 and 174.7; *m/z* (HR-ESI^+) 876.5330 ($M+H^+$. $C_{44}H_{78}N_5O_9Si_2$ requires 876.5333).

(6'*R*)-configured 5'-deoxy muraymycin analogue 11. The synthesis of **11** was performed as the synthesis of **10** (*vide supra*) with **23** (43 mg, 0.043 mmol), Pd/C (10 %, 20 mg, 19 μmol) and MeOH (5 mL). The solvent of the filtrate was evaporated under reduced pressure to give **11** (37 mg, 98 %) as a colourless solid; mp 47 °C; $[\alpha]_D^{25}$ +27.3 (*c* 1.2 in $CHCl_3$); λ_{max} (MeOH)/nm 222 (4.17) and 263 (3.99); ν_{max} (KBr)/cm^{-1} 2956, 1670, 1514, 1457, 1391, 1250, 1158, 839 and 777; δ_H (600 MHz; C_6D_6) 0.05 (3 H, s, $SiCH_3$), 0.06 (3 H, s, $SiCH_3$), 0.07 (3 H, s, $SiCH_3$), 0.09 (3 H, s, $SiCH_3$), 0.83 (3 H, d, *J* 6.6, 3 H, Leu-5-H_a), 0.89 (3 H, d, *J* 6.6, Leu-5-H_b), 0.94 (9 H, s, $SiC(CH_3)_3$), 0.95 (9 H, s, $SiC(CH_3)_3$), 1.21-1.28 (1 H, m, Leu-3-H_a), 1.40 (9 H, s, $OC(CH_3)_3$), 1.45-1.52 (2 H, m, propylene-2-H), 1.53-1.61 (1 H, m, Leu-4-H), 1.74-1.80 (1 H, m, Leu-3-H_b), 1.99 (1 H, ddd, *J* 3.3, 8.0 and 14.0, 5'-H_a), 2.08 (1 H, ddd, *J* 4.3, 10.1 and 14.0, 5'-H_b), 2.41 (1 H, ddd, *J* 6.6, 6.6 and 11.5, propylene-1-H_a), 2.75 (1 H, ddd, *J* 5.7, 5.7 and 11.5, propylene-1-H_b), 3.21-3.26 (1 H, m, Leu-2-H), 3.27 (3 H, s, OCH_3), 3.28-3.36 (2 H, m, propylene-3-H), 3.36 (1 H, dd, *J* 4.3 and 8.0, 6'-H), 3.84 (1 H, dd, *J* 4.4 and 4.4,

3'-H), 4.38 (1 H, dd, *J* 4.4 and 4.4, 2'-H), 4.49 (1 H, ddd, *J* 3.3, 4.4 and 10.1, 4'-H), 5.07 (1 H, d, *J* 13.5, PMB-CH_2-H_a), 5.09 (1 H, d, *J* 13.5, PMB-CH_2-H_b), 5.70 (1 H, d, *J* 8.1, 5-H), 5.86 (1 H, d, *J* 4.4, 1'-H), 6.73 (2 H, d, *J* 8.7, PMB-3-H, PMB-5-H), 7.18 (1 H, d, *J* 8.1, 6-H), 7.27 (1 H, s, NH) and 7.65 (2 H, d, *J* 8.7, PMB-2-H, PMB-6-H); δ_C (126 MHz; C_6D_6) -4.7, -4.6, -4.4, -4.3, 18.2, 18.3, 21.7, 23.5, 25.0, 26.0, 26.0, 28.1, 30.42, 37.0, 37.7, 43.6, 44.5, 45.8, 53.7, 54.7, 60.1, 75.0, 76.1, 80.9, 81.7, 92.4, 102.1, 114.0, 129.9, 131.4, 138.5, 151.1, 159.7, 162.2, 174.3 and 174.7; *m/z* (HR-ESI$^+$) 876.5332 ($M+H^+$. $C_{44}H_{78}N_5O_9Si_2$ requires 876.5333).

***N*-Boc protected didehydro nucleosyl amino acid 14.** To a solution of KO*t*-Bu (188 mg, 1.67 mmol) in THF (15 mL), a solution of phosphonate **13**[2] (683 mg, 1.86 mmol) in THF (15 mL) was added at -78 °C. After 5 min, a solution of protected uridine aldehyde **12**[3] (1.10 g, 1.86 mmol) in THF (7.5 mL) was added at -78 °C. The reaction mixture was stirred for 16 h and slowly warmed to rt during this period. The reaction was quenched by addition of MeOH (5 mL) at 0 °C. After the addition of EtOAc (350 mL), the organic layer was washed with water (1 x 350 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The resultant crude product was purified by column chromatography (petroleum ether-EtOAc, 4 : 1) to give **(*Z*)-14** (884 mg, 66 %) and **(*E*)-14** (22 mg, 2 %) as colourless solids; **(*Z*)-14**: mp 89 °C; $[\alpha]_D^{25}$ +48.0 (*c* 1.2 in $CHCl_3$); λ_{max} (MeCN)/nm 194 (4.79), 224 (4.33) and 266 (4.16); ν_{max} (KBr)/cm^{-1} 2932, 1671, 1455, 1368, 1251, 1159, 1060, 839 and 777; δ_H (300 MHz; $CDCl_3$) 0.03 (12 H, s, $SiCH_3$), 0.85 (9 H, s, $SiC(CH_3)_3$), 0.86 (9 H, s, $SiC(CH_3)_3$), 1.42 (9 H, s, $OC(CH_3)_3$), 1.48 (9 H, s, $OC(CH_3)_3$), 3.74 (3 H, s, OCH_3), 3.81 (1 H, dd, *J* 3.6 and 6.1, 3'-H), 4.17 (1 H, dd, *J* 3.6 and 3.6, 2'-H), 4.87 (1 H, dd, *J* 6.1 and 8.0, 4'-H), 4.98 (1 H, d, *J* 13.5, PMB-CH_2-H_a), 5.04 (1 H, d, *J* 13.5, PMB-CH_2-H_b), 5.67 (1 H, d, *J* 3.6, 1'-H), 5.75 (1 H, d, *J* 8.1, 5-H), 6.12 (1 H, d, *J* 8.0, 5'-H), 6.54 (1 H, s, NH), 6.78 (2 H, d, *J* 8.7, PMB-3-H, PMB-5-H), 7.20 (1 H, d, *J* 8.1, 6-H) and 7.41 (2 H, d, *J* 8.7, PMB-2-H, PMB-6-H); δ_C (75 MHz; $CDCl_3$) -5.0, -4.9, -4.6, -4.5, 17.9, 18.0, 25.7, 25.8, 27.8, 28.1, 43.4, 55.1, 74.9, 76.2, 79.0, 80.8, 82.3, 92.2, 102.0, 113.6, 123.3, 128.9, 130.7, 131.9, 137.6, 150.5, 152.5, 159.0, 162.4 and 163.1; *m/z* (HR-ESI$^+$) 826.4096 ($M+Na^+$. $C_{40}H_{65}N_3NaO_{10}Si_2$ requires 826.4101); **(*E*)-14**: mp 92 °C; $[\alpha]_D^{25}$ +40.8 (*c* 0.8 in MeOH); λ_{max} (MeCN)/nm 194 (4.81), 226 (4.29) and 258 (4.18); ν_{max} (KBr)/cm^{-1} 2931, 1667, 1512, 1456, 1369, 1249, 1158, 839 and 777; δ_H

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[3] A. P. Spork, S. Koppermann and C. Ducho, *Synlett*, 2009, 2503.

(300 MHz; $CDCl_3$) 0.02 (6 H, s, $SiCH_3$), 0.03 (3 H, s, $SiCH_3$), 0.04 (3 H, s, $SiCH_3$), 0.84 (9 H, s, $SiC(CH_3)_3$), 0.86 (9 H, s, $SiC(CH_3)_3$), 1.45 (9 H, s, $OC(CH_3)_3$), 1.51 (9 H, s, $OC(CH_3)_3$), 3.75 (3 H, s, OCH_3), 3.76 (1 H, dd, *J* 3.5 and 6.2, 3'-H), 4.05 (1 H, dd, *J* 3.5 and 3.5, 2'-H), 5.02 (2 H, s, PMB-CH_2), 5.38 (1 H, dd, *J* 6.2 and 9.9, 4'-H), 5.79 (1 H, d, *J* 8.2, 5-H), 5.80 (1 H, d, *J* 3.5, 1'-H), 6.71 (1 H, d, *J* 9.9, 5'-H), 6.79 (2 H, d, *J* 8.7, PMB-3-H, PMB-5-H), 6.93 (1 H, s, NH), 7.36 (1 H, d, *J* 8.2, 6-H) and 7.43 (2 H, d, *J* 8.7, PMB-2-H, PMB-6-H); δ_C (126 MHz; $CDCl_3$) -4.8, -4.8, -4.7, -4.3, 18.0, 18.1, 25.8, 25.8, 28.0, 28.2, 43.5, 55.2, 76.3, 76.8, 79.3, 80.8, 84.3, 91.0, 102.0, 113.6, 117.3, 129.1, 130.8, 131.4, 137.4, 150.8, 152.4, 159.0, 162.6 and 162.6; *m/z* (HR-ESI$^+$) 826.4102 ($M+Na^+$. $C_{40}H_{65}N_3NaO_{10}Si_2$ requires 826.4101).

***N*-Boc protected (6'*S*)-nucleosyl amino acid 15.** Under strictly anaerobic conditions, (*S*,*S*)-Me-DUPHOS-Rh (8 mg, 13 μmol) was added to a solution of **(*Z*)-14** (500 mg, 0.622 mmol) in MeOH (20 mL). The reaction mixture was stirred under an atmosphere of H_2 (1 bar) at rt for 2 d. The solvent was evaporated under reduced pressure. The resultant crude product was purified by column chromatography (petroleum ether-EtOAc, 4 : 1) to give **15** (459 mg, 92 %) as a colourless solid; mp 81 °C; $[\alpha]_D^{25}$ +35.5 (*c* 1.2 in MeOH); λ_{max} (MeOH)/nm 223 (4.18) and 263 (4.02); ν_{max} (KBr)/cm^{-1} 2932, 1670, 1513, 1455, 1367, 1250, 1159, 839 and 777; δ_H (300 MHz; C_6D_6) -0.02 (3 H, s, $SiCH_3$), 0.01 (3 H, s, $SiCH_3$), 0.09 (3 H, s, $SiCH_3$), 0.10 (3 H, s, $SiCH_3$), 0.93 (9 H, s, $SiC(CH_3)_3$), 0.95 (9 H, s, $SiC(CH_3)_3$), 1.29 (9 H, s, $OC(CH_3)_3$), 1.38 (9 H, s, $OC(CH_3)_3$), 2.09 (1 H, ddd, *J* 4.7, 10.4 and 14.3, 5'-H_a), 2.27 (1 H, ddd, *J* 2.7, 7.1 and 14.3, 5'-H_b), 3.25 (3 H, s, OCH_3), 3.71 (1 H, dd, *J* 4.3 and 5.3, 3'-H), 4.31 (1 H, dd, *J* 3.7 and 4.3, 2'-H), 4.39 (1 H, ddd, *J* 2.7, 5.3 and 10.4, 4'-H), 4.58 (1 H, ddd, *J* 4.7, 6.4 and 7.1, 6'-H), 5.06 (1 H, d, *J* 13.4, PMB-CH_2-H_a), 5.11 (1 H, d, *J* 13.4, PMB-CH_2-H_b), 5.47 (1 H, d, *J* 6.4, NH), 5.73 (1 H, d, *J* 8.1, 5-H), 5.80 (1 H, d, *J* 3.7, 1'-H), 6.73 (2 H, d, *J* 8.7, PMB-3-H, PMB-5-H), 7.30 (1 H, d, *J* 8.1, 6-H) and 7.66 (2 H, d, *J* 8.7, 2 H, PMB-2-H, PMB-6-H); δ_C (126 MHz; C_6D_6) -4.8, -4.8, 4.4, 4.2, 18.2, 26.0, 26.1, 27.8, 28.3, 36.7, 43.6, 52.3, 54.6, 75.3, 75.9, 79.6, 80.9, 82.0, 92.3, 102.2, 114.0, 129.9, 131.4, 138.4, 151.2, 155.3, 159.7, 162.1 and 171.1; *m/z* (HR-ESI$^+$) 806.4441 ($M+H^+$. $C_{40}H_{68}N_3O_{10}Si_2$ requires 806.4438).

***N*-Boc protected (6'*R*)-nucleosyl amino acid 16.** To a solution of **(*Z*)-14** (500 mg, 0.622 mmol) in MeOH (10 mL), Pd/C (10 %, 100 mg, 94.0 μmol) was added. The reaction mixture was stirred under an atmosphere of H_2 (1 bar) at rt for 2 d. The solvent was

evaporated under reduced pressure. The resultant crude product was purified by column chromatography (petroleum ether-EtOAc, 4 : 1) to give **16** (477 mg, 95 %) as a colourless solid; mp 56 °C; $[\alpha]_D^{25}$ +33.8 (*c* 1.2 in MeOH); λ_{max} (MeCN)/nm 194 (4.72), 223 (4.14) and 262 (3.98); ν_{max} (KBr)/cm^{-1} 2932, 1671, 1513, 1455, 1367, 1250, 1159, 840 and 777; δ_H (300 MHz; C_6D_6) -0.05 (3 H, s, $SiCH_3$), -0.03 (3 H, s, $SiCH_3$), 0.11 (3 H, s, $SiCH_3$), 0.16 (3 H, s, $SiCH_3$), 0.91 (9 H, s, $SiC(CH_3)_3$), 0.95 (9 H, s, $SiC(CH_3)_3$), 1.38 (9 H, s, $OC(CH_3)_3$), 1.42 (9 H, s, $OC(CH_3)_3$), 1.91 (1 H, ddd, *J* 4.7, 11.0 and 14.7, 5'-H_a), 2.25 (1 H, ddd, *J* 2.1, 4.7 and 14.7, 5'-H_b), 3.25 (3 H, s, OCH_3), 3.60 (1 H, dd, *J* 3.8 and 6.5, 3'-H), 4.23 (1 H, dd, *J* 2.7 and 3.8, 2'-H), 4.26 (1 H, ddd, *J* 2.1, 6.5 and 11.0, 4'-H), 4.65 (1 H, ddd, *J* 4.7, 4.7 and 8.7, 6'-H), 5.02 (1 H, d, *J* 13.4, PMB-CH_2-H_a), 5.07 (1 H, d, *J* 13.4, PMB-CH_2-H_b), 5.40 (1 H, d, *J* 2.7, 1'-H), 5.54 (1 H, d, *J* 8.1, 5-H), 5.67 (1 H, d, *J* 8.7, NH), 6.74 (2 H, d, *J* 8.8, PMB-3-H, PMB-5-H), 6.81 (1 H, d, *J* 8.1, 6-H) and 7.66 (2 H, d, *J* 8.8, PMB-2-H, PMB-6-H); δ_C (75 MHz; C_6D_6) -4.9, -4.9, -4.2, 18.2, 26.0, 26.0, 27.9, 28.4, 34.9, 43.5, 53.1, 54.7, 74.9, 75.5, 79.5, 80.8, 81.6, 92.9, 101.9, 114.0, 129.8, 131.4, 137.3, 150.8, 155.7, 159.7, 161.9 and 170.8; *m/z* (HR-ESI^+) 806.4436 ($M+H^+$. $C_{40}H_{68}N_3O_{10}Si_2$ requires 806.4438).

***N*-Cbz protected didehydro nucleosyl amino acid 18.** The synthesis of **18** was performed as the synthesis of **14** (*vide supra*) with protected uridine aldehyde **12**[4] (1.99 g, 3.37 mmol), phosphonate **17**[5] (1.21 g, 3.24 mmol), KHMDS (0.5 M in toluene, 6.48 mL, 3.24 mmol) as base and THF (12 mL (**12**), 25 mL (**17**), 20 mL (KHMDS)). Purification by column chromatography (petroleum ether-EtOAc, 4 : 1) gave **(*Z*)-18** (1.82 g, 67 %) and **(*E*)-18** (159 mg, 6 %) as colourless solids; **(*Z*)-18**: mp 72 °C; $[\alpha]_D^{25}$ +39.1 (*c* 1.1 in $CHCl_3$); λ_{max} (MeCN)/nm 225 (4.31) and 257 (4.14); ν_{max} (KBr)/cm^{-1} 2957, 1715, 1666, 1514, 1456, 1251, 1157, 1055 and 839; δ_H (300 MHz; $CDCl_3$) -0.01 (3 H, s, $SiCH_3$), 0.01 (3 H, s, $SiCH_3$), 0.04 (3 H, s, $SiCH_3$), 0.05 (3 H, s, $SiCH_3$), 0.83 (9 H, s, $SiC(CH_3)_3$), 0.86 (9 H, s, $SiC(CH_3)_3$), 1.46 (9 H, s, $OC(CH_3)_3$), 3.75 (3 H, s, OCH_3), 3.91 (1 H, dd, *J* 4.1 and 5.5, 3'-H), 4.28 (1 H, dd, *J* 3.9 and 4.1, 2'-H), 4.82 (1 H, dd, *J* 5.5 and 7.4, 4'-H), 4.97 (1 H, d, *J* 13.5, PMB-CH_2-H_a), 5.04 (1 H, d, *J* 13.5, PMB-CH_2-H_b), 5.11 (2 H, s, Cbz-CH_2), 5.62 (1 H, d, *J* 3.9, 1'-H), 5.74

[4] (see footnote 3)

[5] (*a*) U. Schmidt, A. Lieberknecht, U. Schanbacher, T. Beuttler and J. Wild, *Angew. Chem.*, 1982, **94**, 797; *Angew. Chem. Int. Ed.*, 1982, **21**, 776. (*b*) U. Schmidt, A. Lieberknecht and J. Wild, *Synthesis*, 1984, 53. (*c*) U. Schmidt and J. Wild, *Liebigs Ann. Chem.*, 1985, 1882. (*d*) R. Hamzavi, F. Dolle, B. Tavitian, O. Dahl and P. E. Nielsen, *Bioconjugate Chem.*, 2003, **14**, 941.

(1 H, d, *J* 8.1, 5-H), 6.28 (1 H, d, *J* 7.4, 5'-H), 6.70 (1 H, s, NH), 6.79 (2 H, d, *J* 8.8, 2 H, PMB-3-H, PMB-5-H), 7.15 (1 H, d, *J* 8.1, 6-H), 7.28-7.35 (5 H, m, Cbz-Aryl-H) and 7.41 (2 H, d, *J* 8.8, PMB-2-H, PMB-6-H); δ_C (126 MHz; $CDCl_3$) -4.7, -4.5, -4.3, 18.1, 18.2, 25.8, 25.9, 27.9, 43.5, 55.3, 67.5, 74.6, 76.2, 79.6, 82.6, 92.9, 102.1, 113.6, 124.8, 128.1, 128.2, 128.4, 128.9, 130.7, 130.8, 135.7, 138.2, 150.5, 153.5, 159.0, 162.3 and 162.7; *m/z* (HR-ESI$^+$) 860.3952 (M+Na$^+$. $C_{43}H_{63}N_3NaO_{10}Si_2$ requires 860.3944); **(*E*)-18**: mp 69 °C; $[\alpha]_D^{25}$ -21.9 (*c* 1.1 in $CHCl_3$); λ_{max} (MeCN)/nm 224 (4.28) and 257 (4.09); ν_{max} (KBr)/cm^{-1} 2959, 2935, 1673, 1391, 1339, 1251, 1161, 1051 and 839; δ_H (300 MHz; $CDCl_3$) -0.25 (3 H, s, $SiCH_3$), -0.05 (3 H, s, $SiCH_3$), 0.04 (3 H, s, $SiCH_3$), 0.10 (3 H, s, $SiCH_3$), 0.77 (9 H, s, $SiC(CH_3)_3$), 0.93 (9 H, s, $SiC(CH_3)_3$), 1.46 (9 H, s, $OC(CH_3)_3$), 3.75 (3 H, s, OCH_3), 4.44 (1 H, dd, *J* 2.5 and 3.2, 3'-H), 4.51 (1 H, dd, *J* 3.2 and 6.9, 2'-H), 4.98 (1 H, d, *J* 13.9, PMB-CH_2-H_a), 4.99 (1 H, dd, *J* 2.5 and 8.6, 4'-H), 5.04 (1 H, d, *J* 13.9, PMB-CH_2-H_b), 5.09 (1 H, d, *J* 12.2, 1 H, Cbz-CH_2-H_a), 5.18 (1 H, d, *J* 12.2, Cbz-CH_2-H_b), 5.76 (1 H, d, *J* 6.9, 1'-H), 5.77 (1 H, d, *J* 8.0, 5-H), 6.43 (1 H, d, *J* 8.6, 5'-H), 6.68 (1 H, s, NH), 6.78 (2 H, d, *J* 8.7, 2 H, PMB-3-H, PMB-5-H), 7.09 (1 H, d, *J* 8.0, 6-H), 7.30-7.36 (5 H, m, 5 H, Cbz-Aryl-H) and 7.37 (2 H, d, *J* 8.7, PMB-2-H, PMB-6-H); δ_C (126 MHz; $CDCl_3$) -5.1, -4.2, 18.0, 18.2, 25.9, 26.0, 28.0, 43.6, 55.3, 67.5, 74.5, 75.4, 79.1, 82.8, 92.6, 102.2, 113.6, 126.0, 127.9, 128.0, 128.2, 128.5, 128.8, 130.4, 135.8, 139.6, 150.6, 154.1, 158.9, 162.5 and 163.0; *m/z* (HR-ESI$^+$) 860.3948 (M+Na$^+$. $C_{43}H_{63}N_3NaO_{10}Si_2$ requires 860.3944).

***N*-Cbz protected (6'*S*)-configured 5'-deoxy muraymycin analogue 22.** To a solution of (6'*S*)-nucleosyl amino acid **8** (50 mg, 0.071 mmol) in THF (3 mL), activated molecular sieves (4 Å) were added, and the mixture was stirred at rt for 5 min to remove traces of water. A solution of aldehyde **21**[6] (23 mg, 0.071 mmol) in THF (1.5 mL) was then added dropwise at rt, and the reaction mixture was stirred at rt for 22 h. Amberlyst-15^{TM} (3.2 mg, 0.015 mmol) and $NaBH(OAc)_3$ (30 mg, 0.14 mmol) were added, and the reaction mixture was further stirred at rt for 18 h. After filtration and dilution of the filtrate with EtOAc (50 mL), the organic layer was washed with saturated $NaHCO_3$ solution (1 x 50 mL), and the aqueous layer was reextracted with EtOAc (1 x 50 mL). The combined organics were dried over Na_2SO_4 and evaporated under reduced pressure. The resultant crude product was purified by column

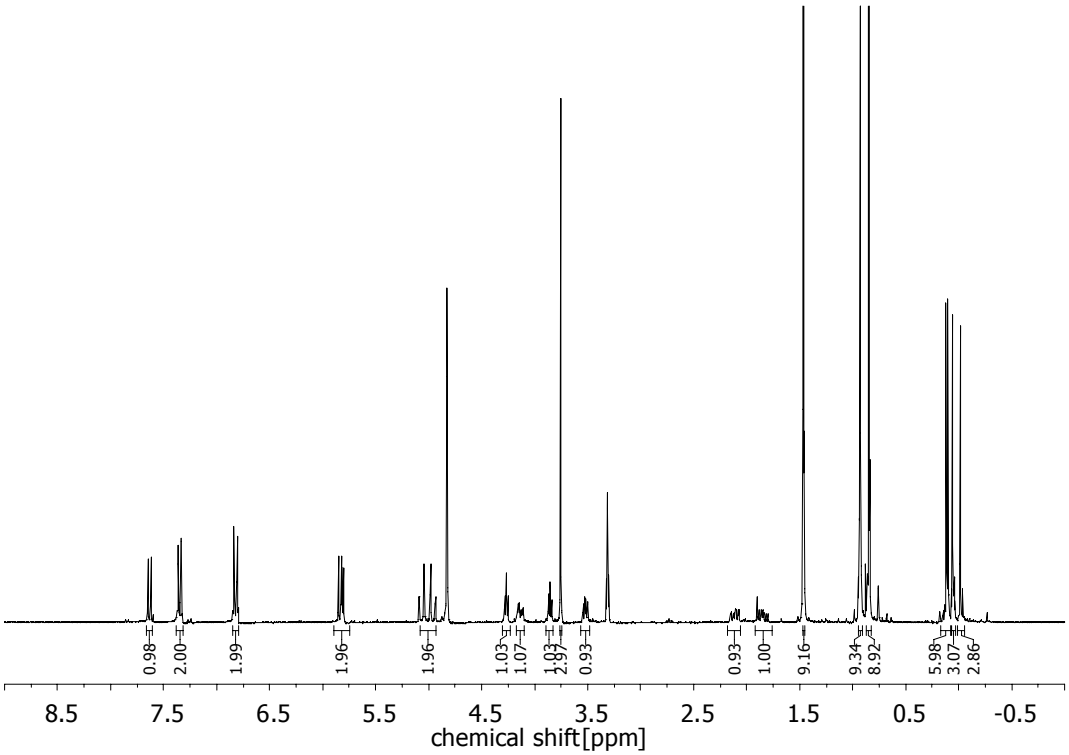
[6] (*a*) A. Yamashita, E. Norton, P. J. Petersen, B. A. Rasmussen, G. Singh, Y. Yang, T. S. Mansour and D. M. Ho, *Bioorg. Med. Chem. Lett.*, 2003, **13**, 3345. (*b*) M. Y. H. Lai, M. A. Brimble, D. J. Callis, P. W. R. Harris, M. S. Levi and F. Sieg, *Bioorg. Med. Chem.*, 2005, **13**, 533.

chromatography (petroleum ether-CH_2Cl_2-EtOAc-NEt_3, 40 : 40 : 19 : 1 → 30 : 30 : 39 : 1) to give **22** (54 mg, 75 %) as a colourless solid; mp 48 °C; $[\alpha]_D^{25}$ +22.3 (*c* 1.8 in MeOH); λ_{max} (MeCN)/nm 263 (3.99); ν_{max} (KBr)/cm^{-1} 2956, 1669, 1514, 1456, 1391, 1250, 1159, 839 and 777; δ_H (300 MHz; CD_3OD) -0.05 (3 H, s, $SiCH_3$), 0.04 (3 H, s, $SiCH_3$), 0.10 (3 H, s, $SiCH_3$), 0.11 (3 H, s, $SiCH_3$), 0.83 (9 H, s, $SiC(CH_3)_3$), 0.91 (3 H, d, *J* 6.7, Leu-5-H_a), 0.93 (9 H, s, $SiC(CH_3)_3$), 0.93 (3 H, d, *J* 6.8, Leu-5-H_b), 1.48 (9 H, s, $OC(CH_3)_3$), 1.52 (2 H, dd, *J* 7.4 and 7.4, Leu-3-H), 1.60-1.71 (3 H, m, propylene-2-H, Leu-4-H), 1.87-1.97 (1 H, m, 5'-H_a), 1.99-2.09 (1 H, m, 5'-H_b), 2.50-2.69 (2 H, m, propylene-1-H), 3.20-3.28 (2 H, m, propylene-3-H), 3.36 (1 H, dd, *J* 4.6 and 9.2, 6'-H), 3.74 (3 H, s, OCH_3), 3.86 (1 H, dd, *J* 4.5 and 4.5, 3'-H), 4.02-4.12 (2 H, m, 2 H, 4'-H, Leu-2-H), 4.28 (1 H, dd, *J* 4.5 and 4.6, 2'-H), 4.93 (1 H, d, *J* 14.1, PMB-CH_2-H_a), 5.03 (1 H, d, *J* 14.1, PMB-CH_2-H_b), 5.07 (2 H, s, Cbz-CH_2), 5.81 (1 H, d, *J* 4.6, 1'-H), 5.83 (1 H, d, *J* 8.1, 5-H), 6.81 (2 H, d, *J* 8.8, PMB-3-H, PMB-5-H), 7.23-7.33 (5 H, m, 5 H, Cbz-Aryl-H), 7.34 (2 H, d, *J* 8.8, PMB-2-H, PMB-6-H) and 7.62 (1 H, d, *J* 8.1, 6-H); δ_C (75 MHz; CD_3OD) -4.5, -4.5, -4.4, -4.0, 18.8, 19.0, 22.0, 23.5, 25.9, 26.4, 26.5, 28.4, 30.2, 37.9, 38.1, 42.2, 44.5, 46.0, 55.2, 55.7, 60.6, 67.7, 75.9, 76.5, 82.7, 83.1, 92.3, 102.6, 114.7, 128.9, 129.02, 129.5, 130.3, 131.4, 138.1, 140.8, 152.2, 158.4, 160.6, 164.7, 174.4 and 175.6; *m/z* (HR-ESI^+) 1010.5722 ($M+H^+$. $C_{52}H_{84}N_5O_{11}Si_2$ requires 1010.5700).

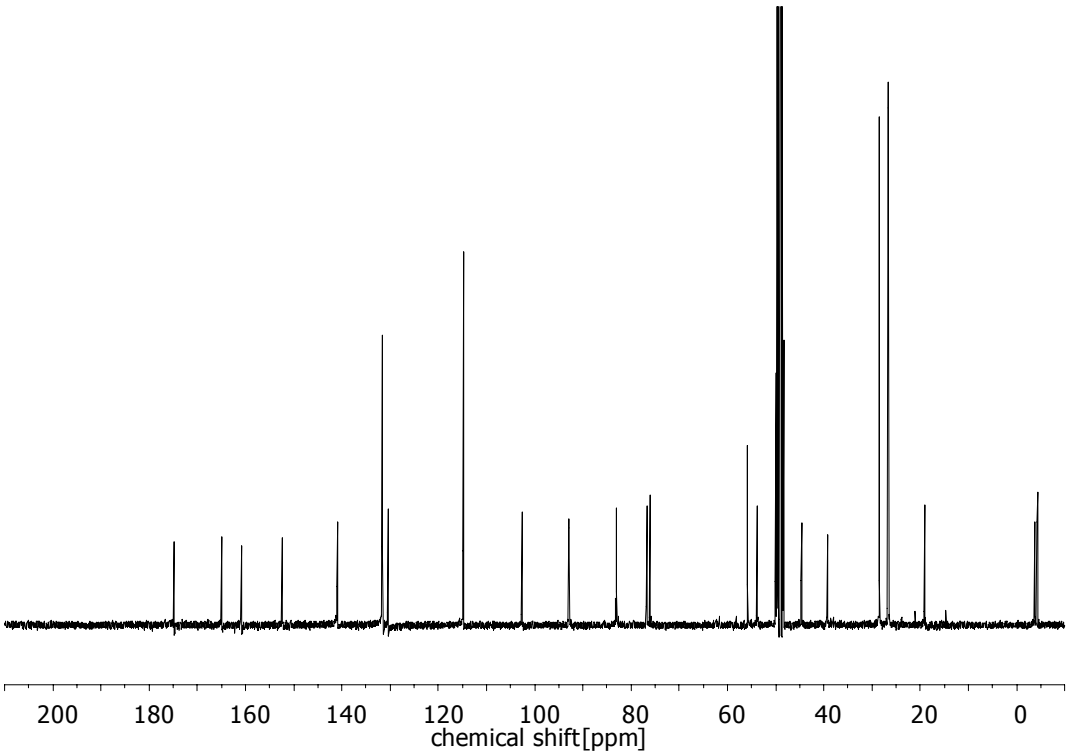
***N*-Cbz protected (6'*R*)-configured 5'-deoxy muraymycin analogue 23.** The synthesis of **23** was performed as the synthesis of **22** (*vide supra*) with the (6'*R*)-nucleosyl amino acid **9** (50 mg, 0.071 mmol), aldehyde **21**[7] (23 mg, 0.071 mmol), $NaBH(OAc)_3$ (30 mg, 0.14 mmol), Amberlyst-15^{TM} (3.2 mg, 0.015 mmol) and THF (3 mL (**9**), 1.5 mL (**21**)). Purification by column chromatography (petroleum ether-CH_2Cl_2-EtOAc-NEt_3, 40 : 40 : 19 : 1 → 35 : 35 : 29 : 1) gave **23** (60 mg, 84 %) as a colourless solid; mp 45 °C; $[\alpha]_D^{25}$ +18.8 (*c* 1.5 in MeOH); λ_{max} (MeCN)/nm 263 (3.97); ν_{max} (KBr)/cm^{-1} 2956, 1715, 1669, 1514, 1455, 1250, 1158, 839 and 777; δ_H (600 MHz; CD_3OD) -0.06 (3 H, s, $SiCH_3$), 0.04 (3 H, s, $SiCH_3$), 0.10 (3 H, s, $SiCH_3$), 0.12 (3 H, s, $SiCH_3$), 0.82 (9 H, s, $SiC(CH_3)_3$), 0.91-0.92 (6 H, m, Leu-5-H), 0.93 (9 H, s, $SiC(CH_3)_3$), 1.45 (9 H, s, $OC(CH_3)_3$), 1.53 (2 H, dd, *J* 7.5 and 7.5, Leu-3-H), 1.59-1.70 (3 H, m, propylene-2-H, Leu-4-H), 1.95 (1 H, ddd, *J* 3.7, 7.0 and 14.7, 5'-H_a), 2.00 (1 H, ddd, *J* 5.5, 10.3 and 14.7, 5'-H_b), 2.46 (1 H, ddd, *J* 7.1, 7.1 and 11.4, 1 H, propylene-1-H_a), 2.64 (1 H, ddd, *J* 6.9, 6.9 and 11.4, propylene-1-H_b), 3.23 (1 H, dd, *J* 6.5 and 6.5,

[7] (see footnote 6)

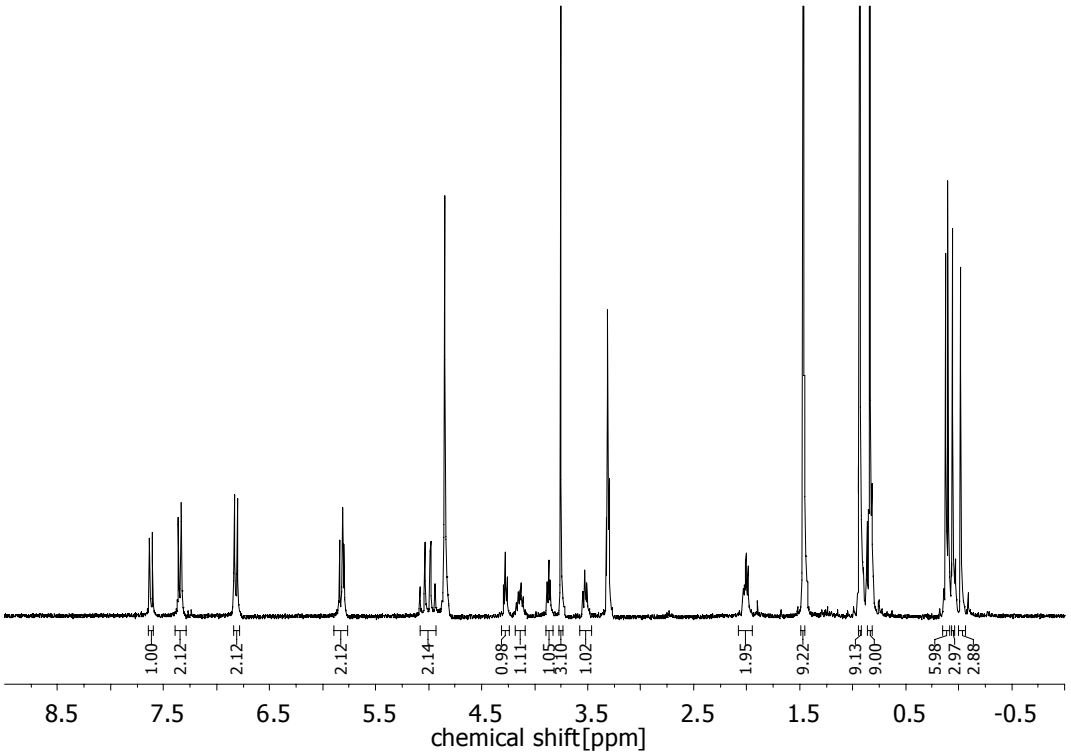
propylene-3-H_a), 3.24 (1 H, dd, *J* 6.4 and 6.4, propylene-3-H_b), 3.29 (1 H, dd, *J* 5.5 and 7.0, 6'-H), 3.74 (3 H, s, OCH_3), 3.89 (1 H, dd, *J* 4.1 and 4.5, 3'-H), 4.10 (1 H, dd, *J* 7.5 and 7.5, Leu-2-H), 4.17 (1 H, ddd, *J* 3.7, 4.1 and 10.3, 4'-H), 4.27 (1 H, dd, *J* 4.5 and 4.8, 2'-H), 4.94 (1 H, d, *J* 13.8, PMB-CH_2-H_a), 5.02 (1 H, d, *J* 13.8, PMB-CH_2-H_b), 5.05 (2 H, s, Cbz-CH_2), 5.80 (1 H, d, *J* 8.2, 5-H), 5.86 (1 H, d, *J* 4.8, 1'-H), 6.80 (2 H, d, *J* 8.8, PMB-3-H, PMB-5-H), 7.25-7.33 (5 H, m, Cbz-Aryl-H), 7.34 (2 H, d, *J* 8.8, PMB-2-H, PMB-6-H) and 7.61 (1 H, d, *J* 8.2, 6-H); δ_C (126 MHz; CD_3OD) -4.4, -4.4, -4.0, 18.8, 19.0, 22.0, 23.5, 24.9, 26.4, 26.5, 28.4, 30.3, 37.5, 38.2, 42.3, 44.5, 46.0, 55.1, 55.7, 60.9, 67.6, 75.8, 76.7, 82.7, 83.1, 92.0, 102.6, 114.7, 128.8, 129.0, 129.5, 130.2, 131.4, 138.1, 140.8, 152.3, 158.3, 160.6, 164.5, 175.1 and 175.3; *m/z* (HR-ESI^+) 1010.5697 ($M+H^+$. $C_{52}H_{84}N_5O_{11}Si_2$ requires 1010.5700).



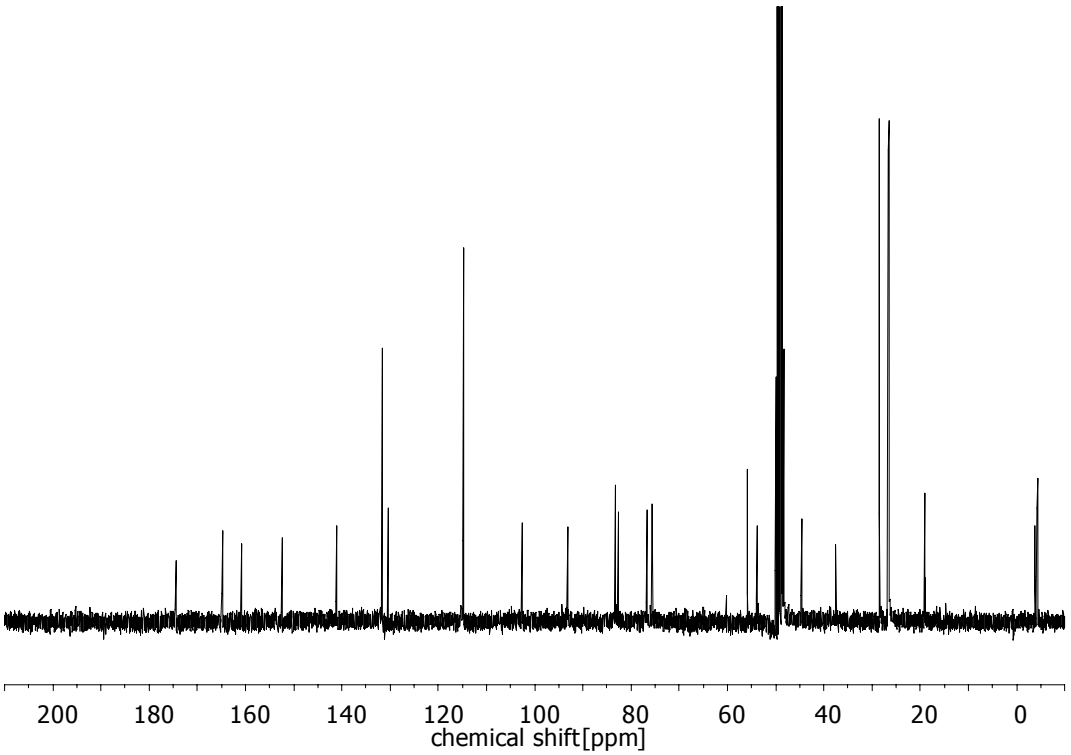
^{1}H NMR spectrum of **8** (300 MHz; CD_3OD)



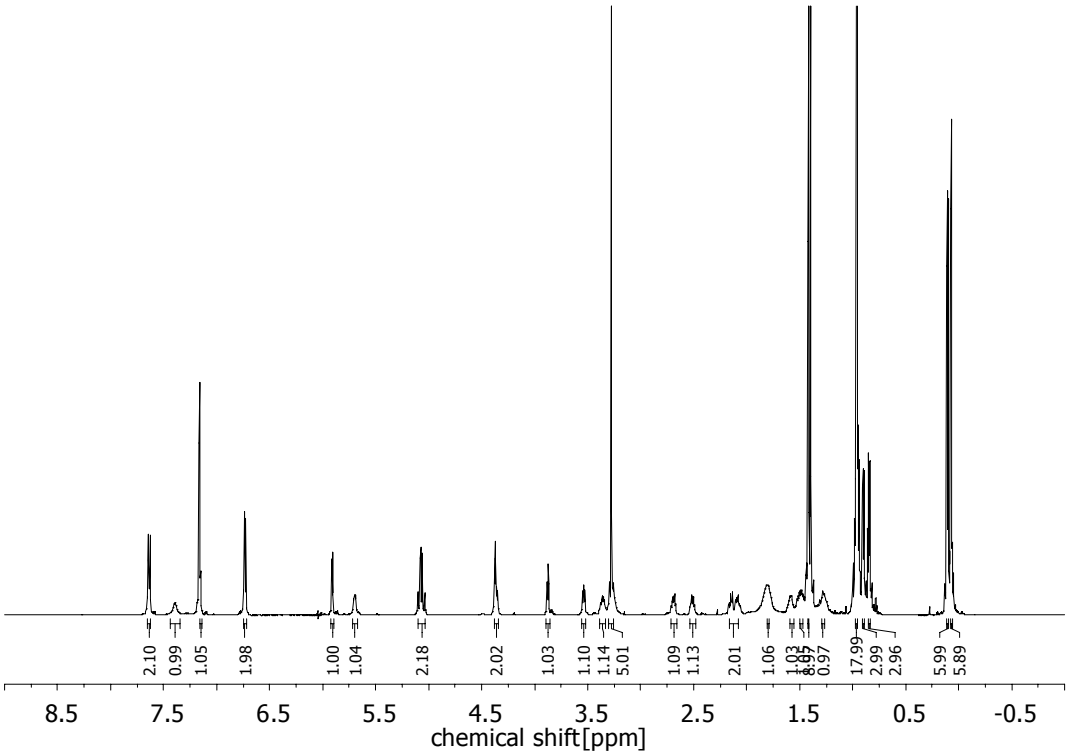
^{13}C NMR spectrum of **8** (75 MHz; CD_3OD)



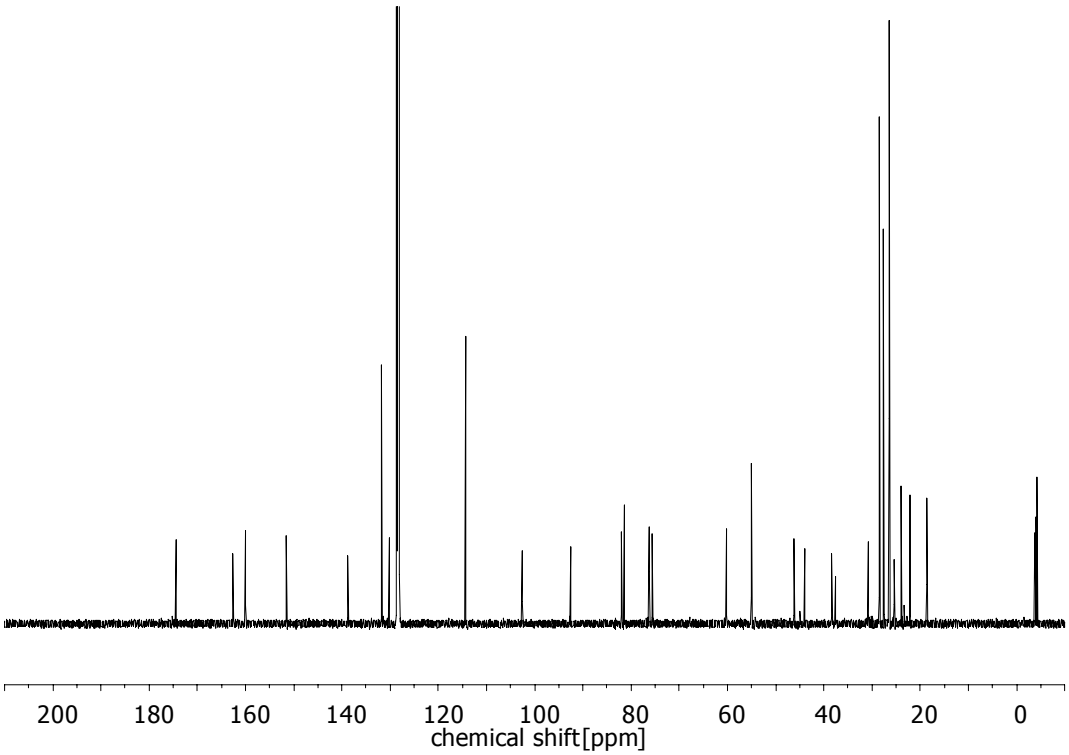
^{1}H NMR spectrum of **9** (75 MHz; CD_3OD)



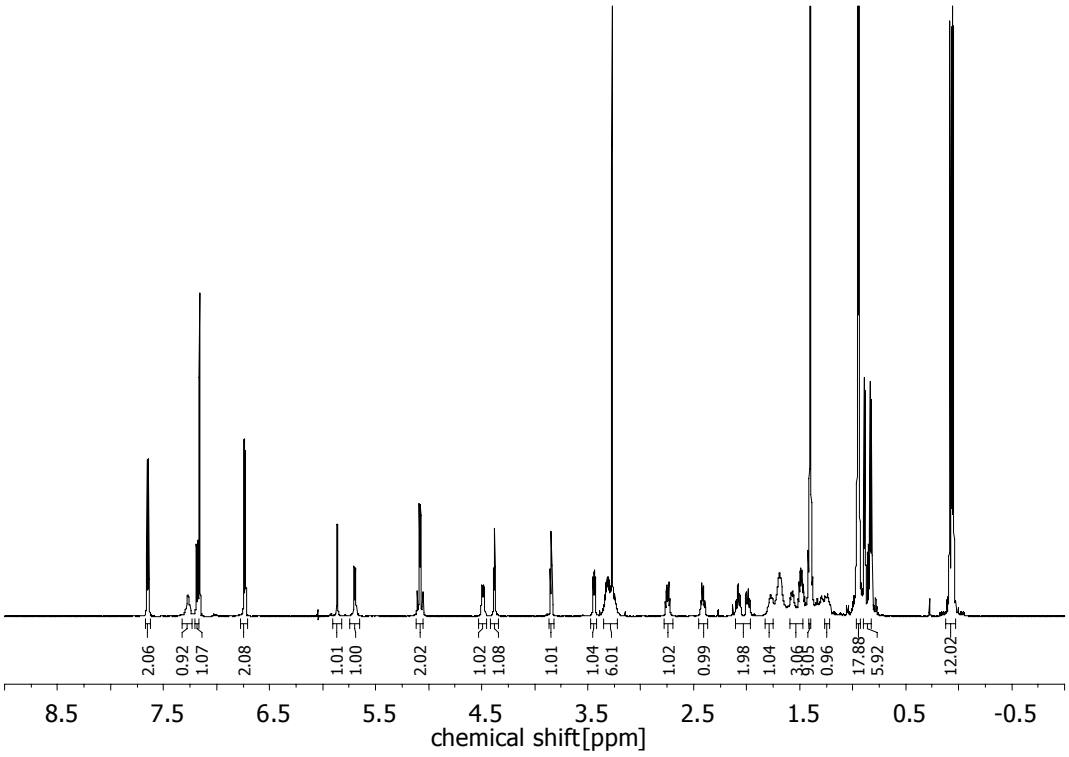
^{13}C NMR spectrum of **9** (75 MHz; CD_3OD)



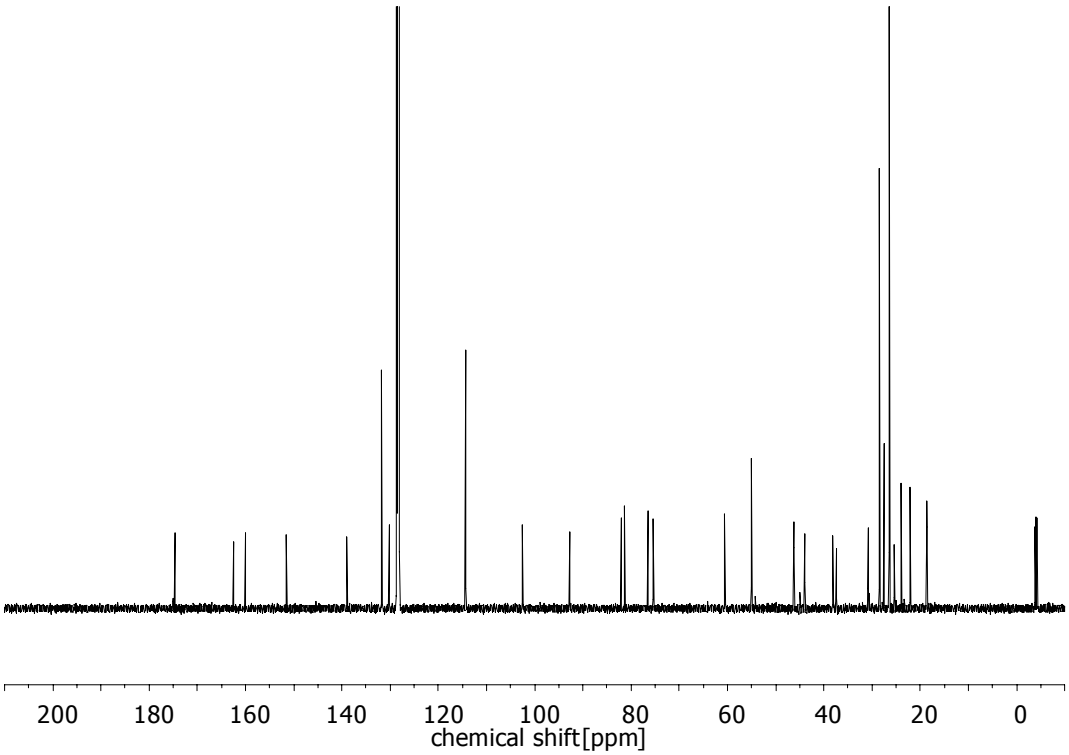
^{1}H NMR spectrum of **10** (600 MHz; C_6D_6)



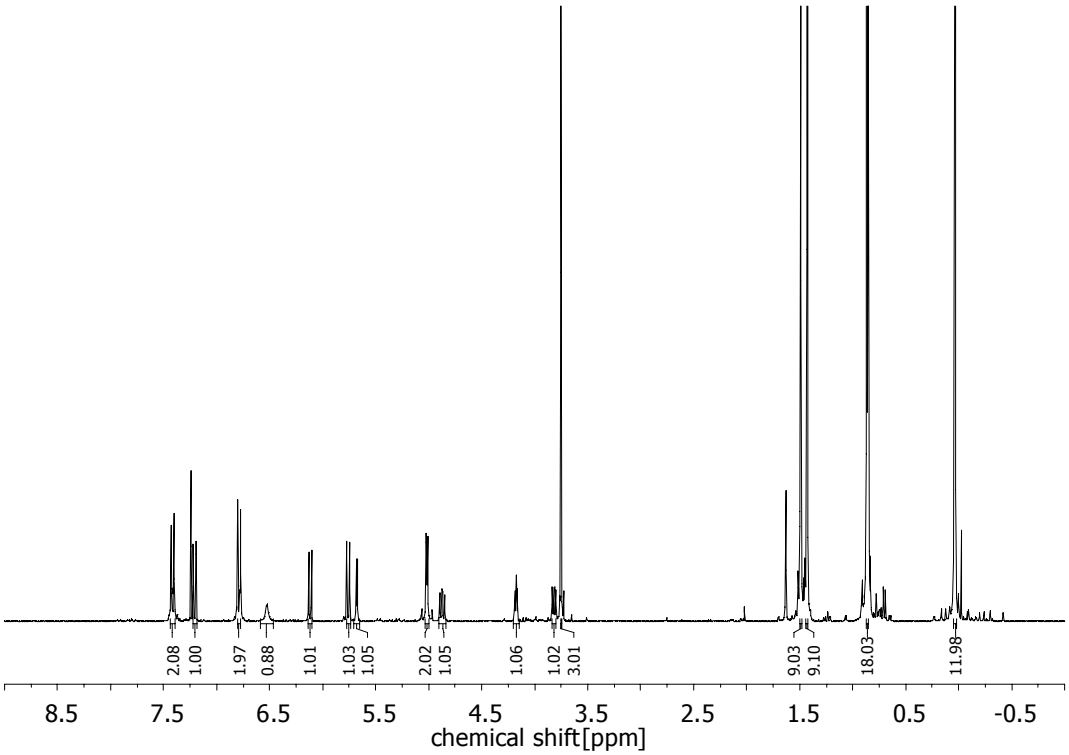
^{13}C NMR spectrum of **10** (126 MHz; C_6D_6)



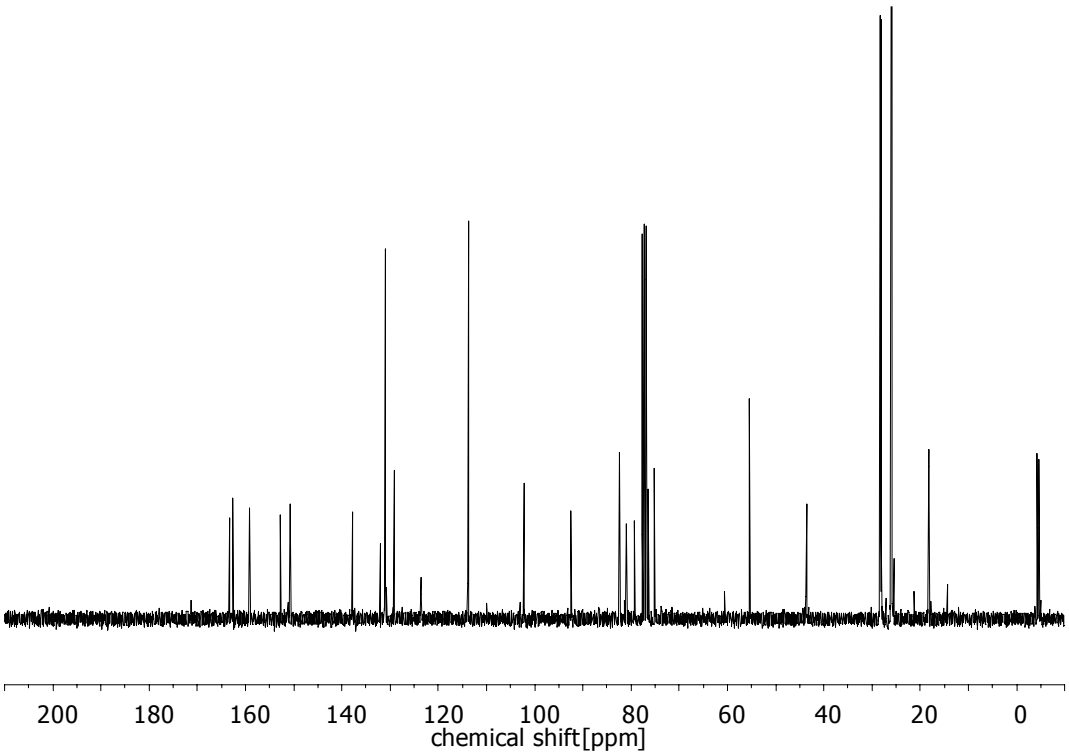
^{1}H NMR spectrum of **11** (600 MHz; C_6D_6)



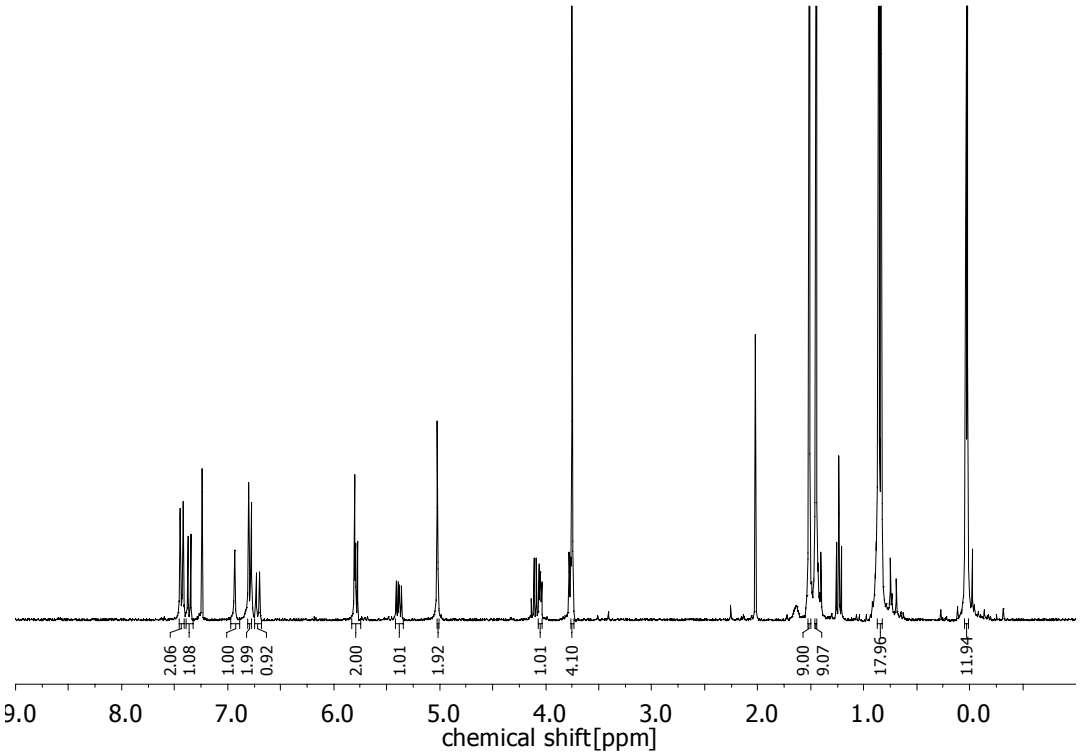
^{13}C NMR spectrum of **11** (126 MHz; C_6D_6)



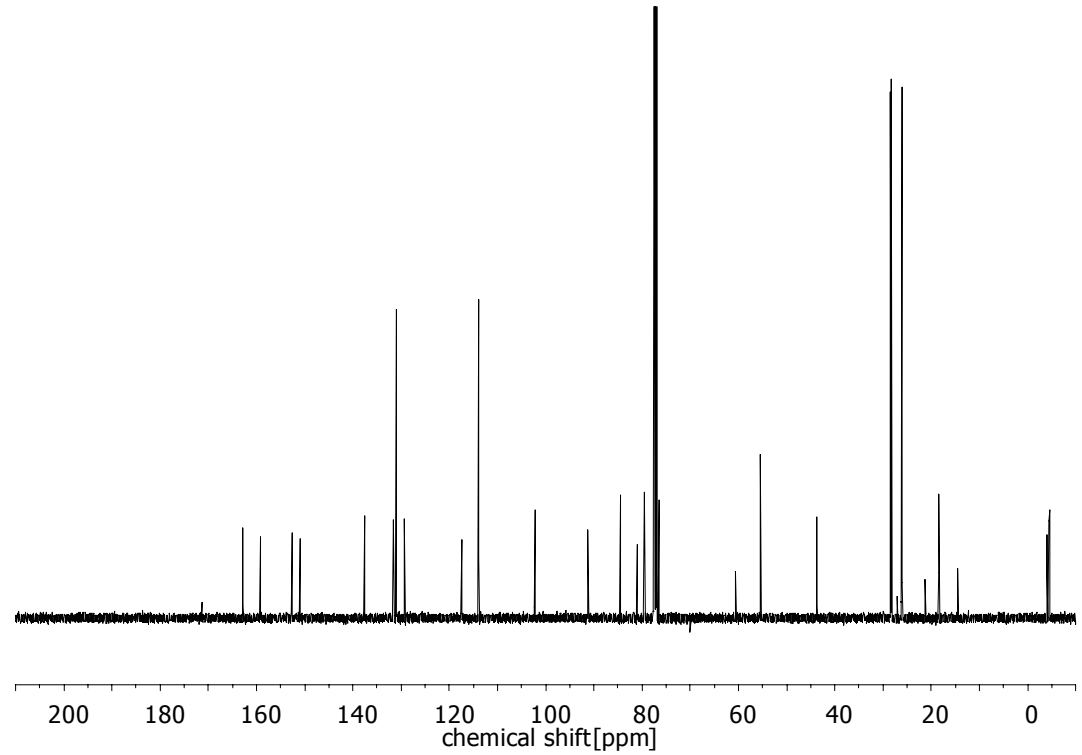
^{1}H NMR spectrum of **(*Z*)-14** (300 MHz; $CDCl_3$)



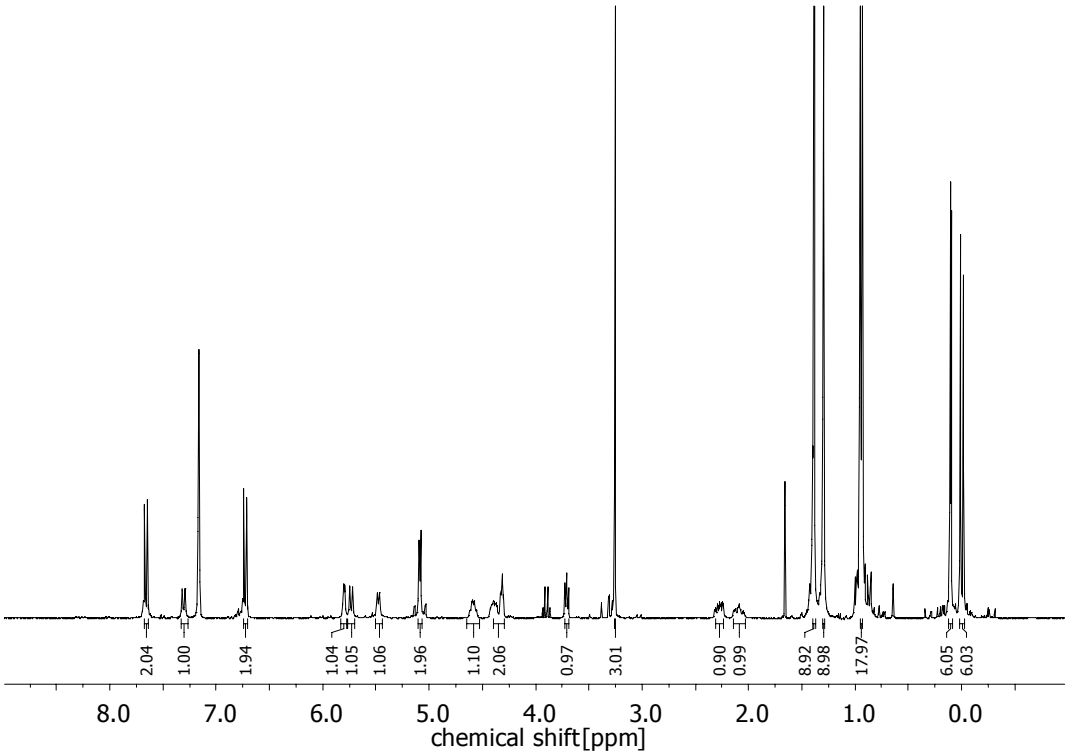
^{13}C NMR spectrum of **(*Z*)-14** (75 MHz; $CDCl_3$)



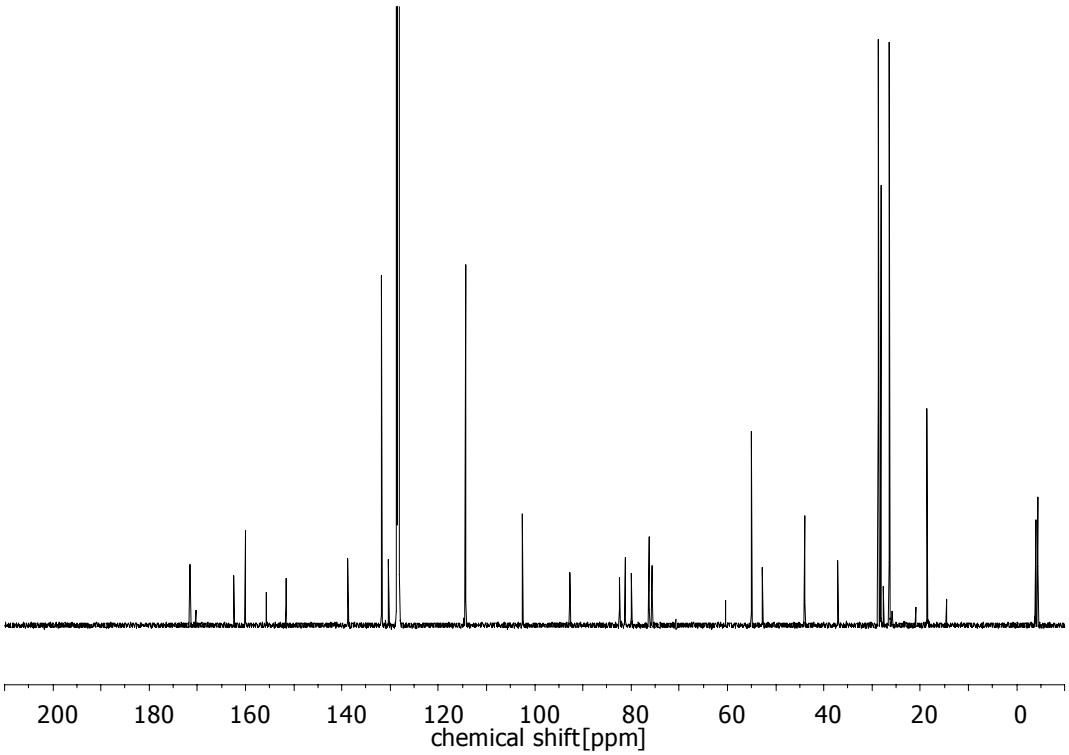
^{1}H NMR spectrum of **(*E*)-14** (300 MHz; $CDCl_3$)



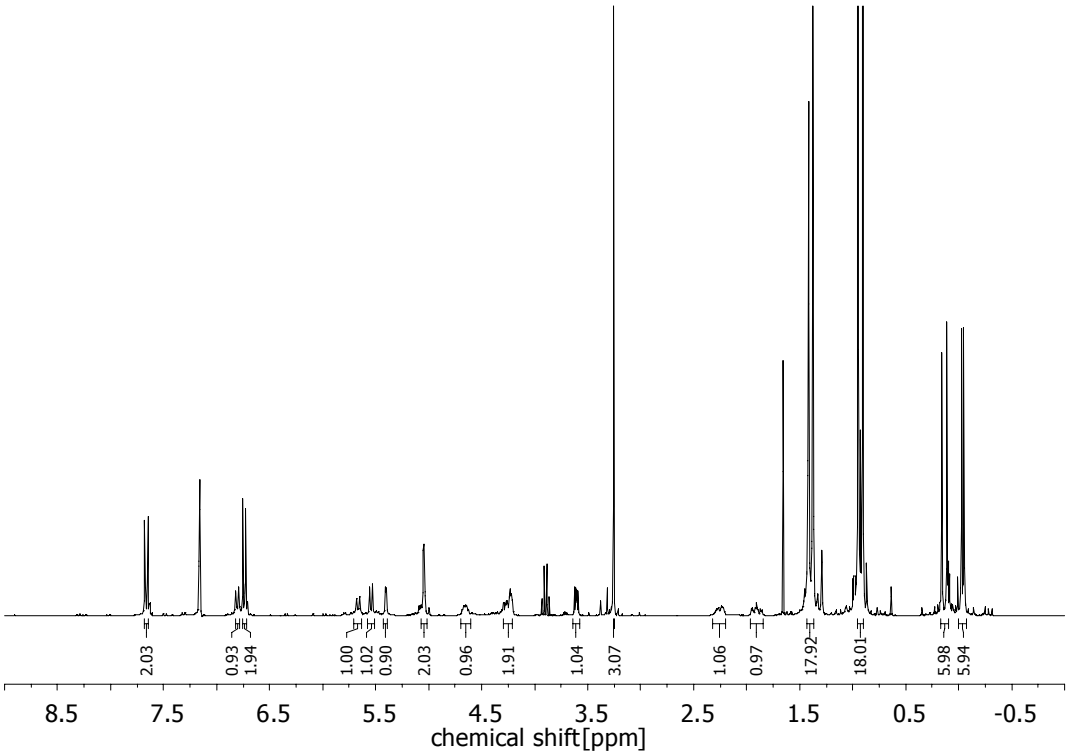
^{13}C NMR spectrum of **(*E*)-14** (126 MHz; $CDCl_3$)



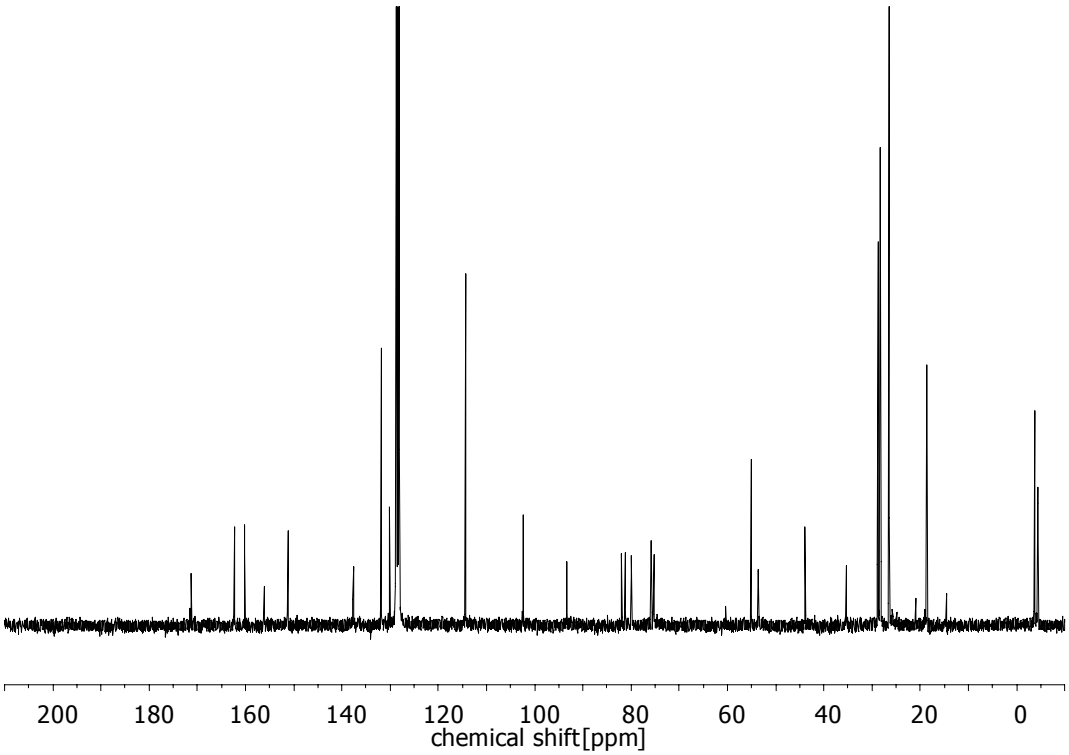
^{1}H NMR spectrum of **15** (300 MHz; C_6D_6)



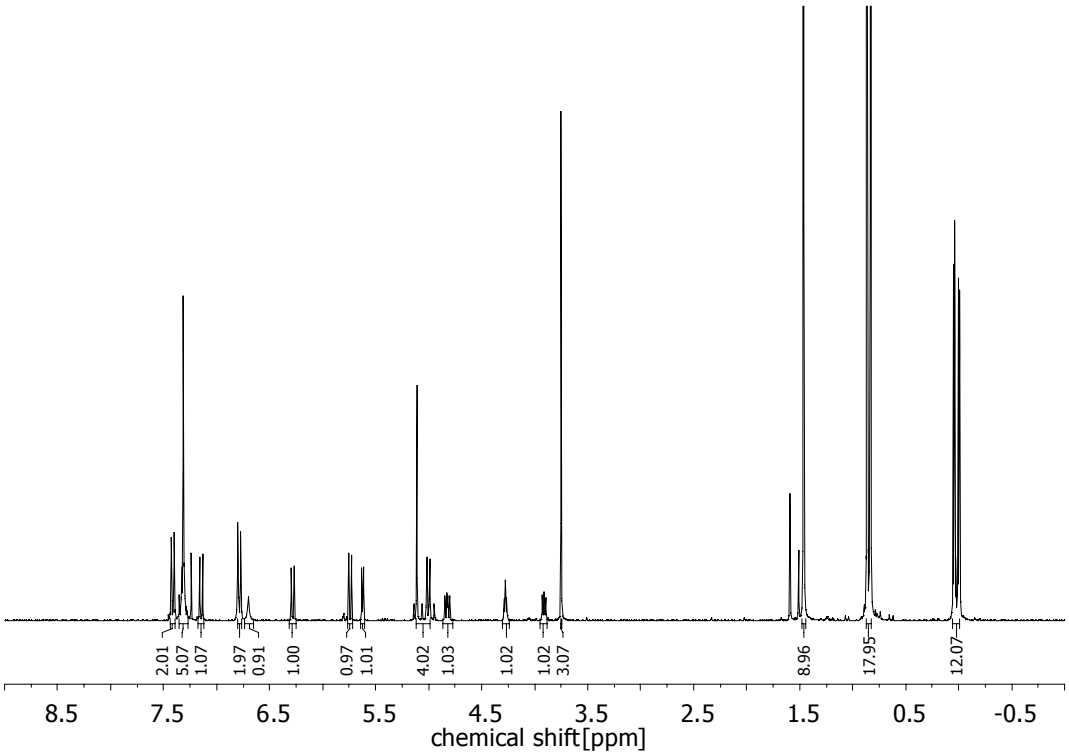
^{13}C NMR spectrum of **15** (126 MHz; C_6D_6)



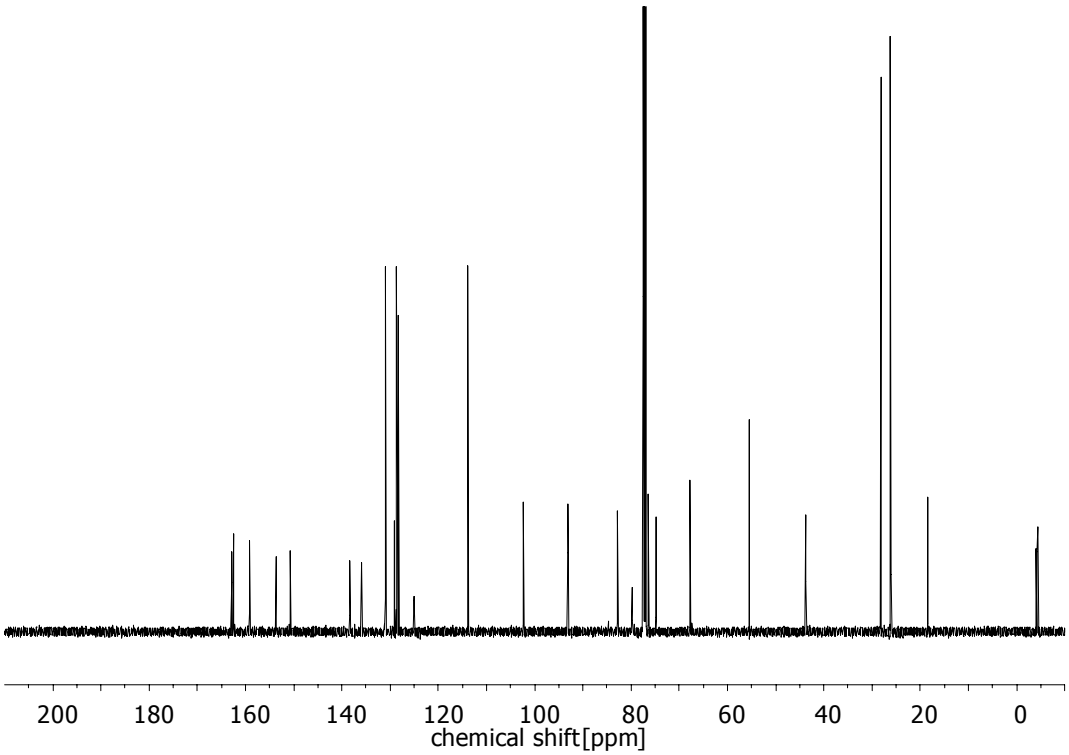
^{1}H NMR spectrum of **16** (300 MHz; C_6D_6)



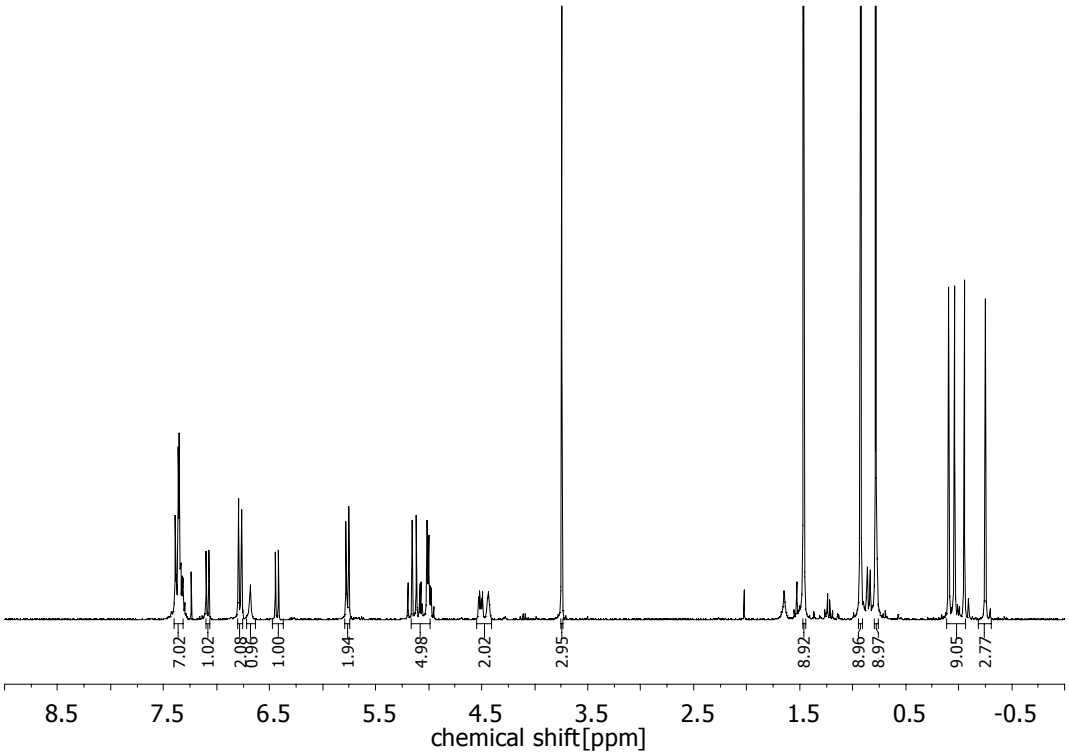
^{13}C NMR spectrum of **16** (75 MHz; C_6D_6)



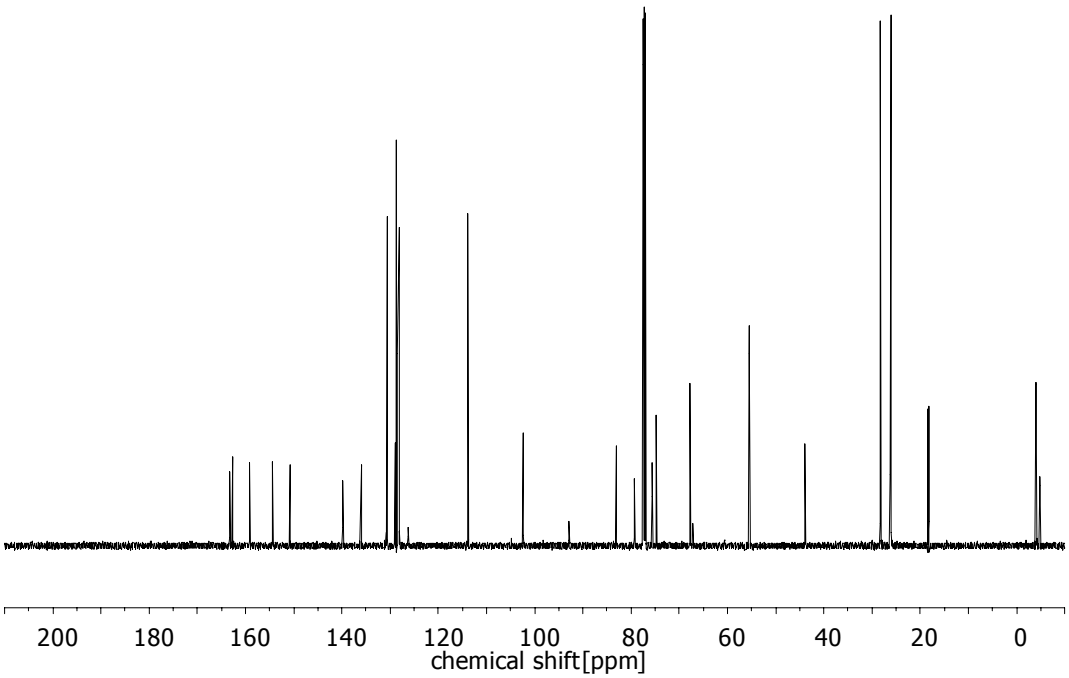
^{1}H NMR spectrum of **(*Z*)-18** (300 MHz; $CDCl_3$)



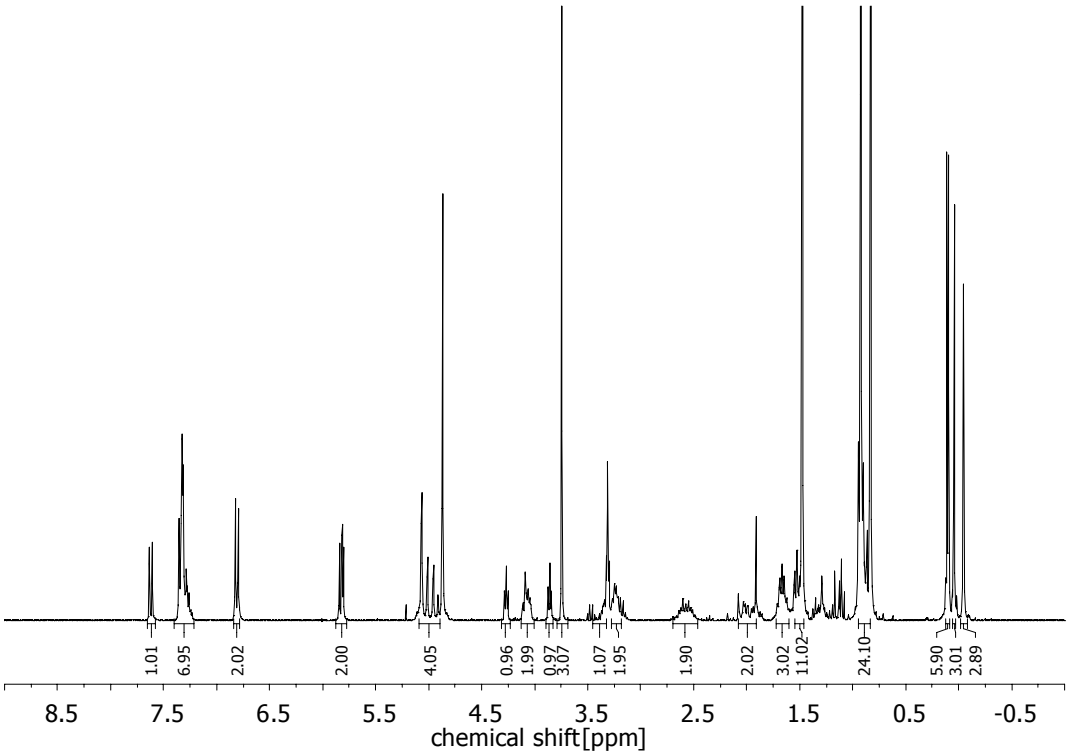
^{13}C NMR spectrum of **(*Z*)-18** (126 MHz; $CDCl_3$)



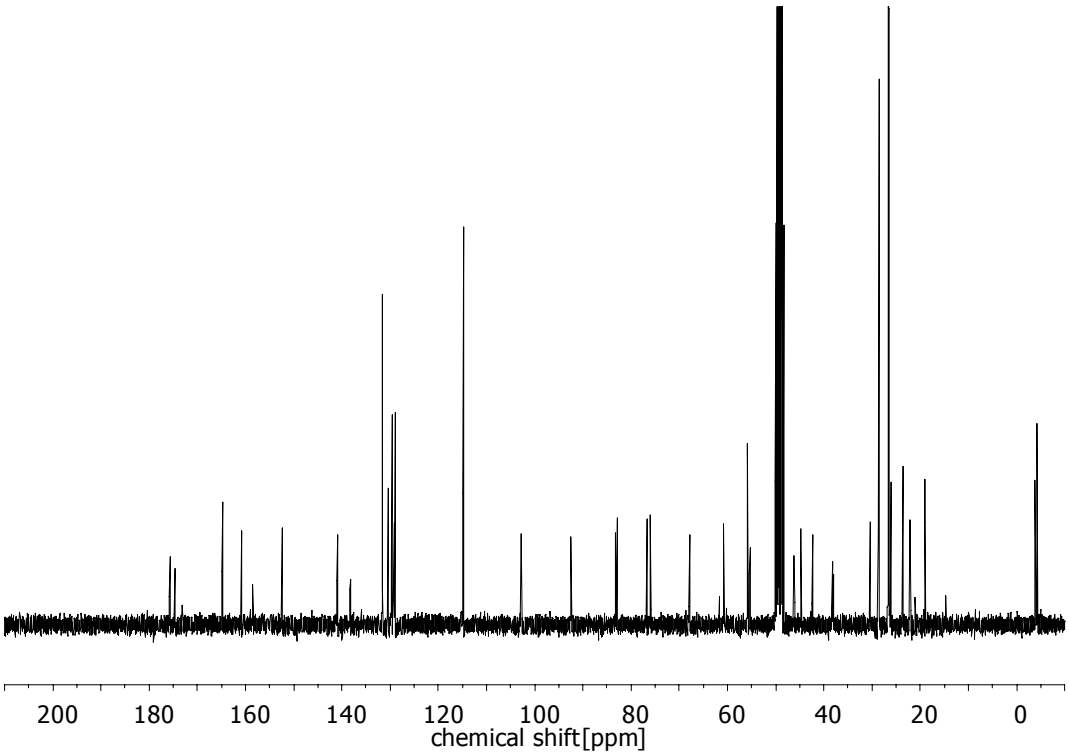
^{1}H NMR spectrum of **(*E*)-18** (300 MHz; $CDCl_3$)



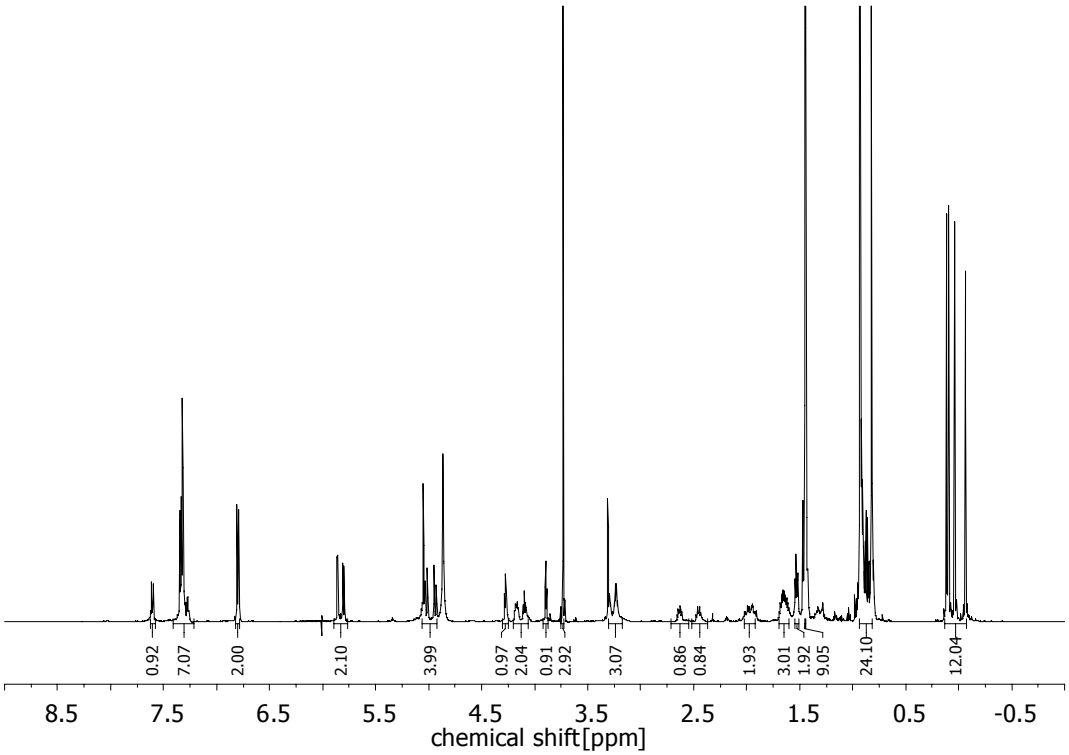
^{13}C NMR spectrum of **(*E*)-18** (126 MHz; $CDCl_3$)



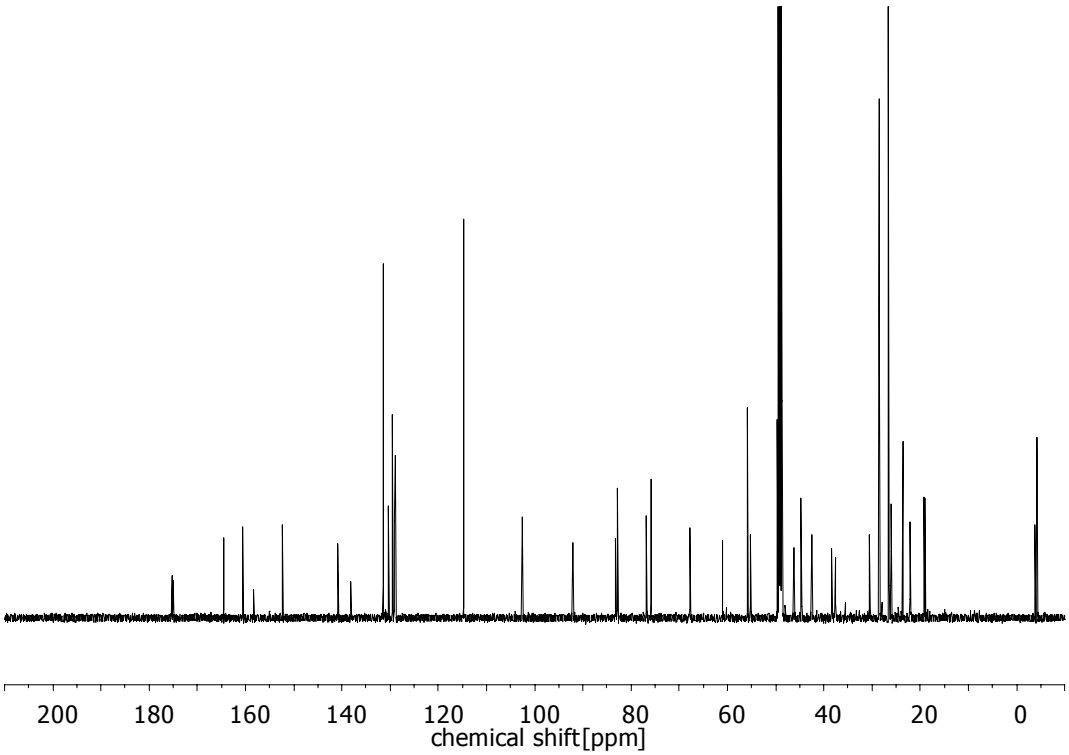
^{1}H NMR spectrum of **22** (300 MHz; CD_3OD)



^{13}C NMR spectrum of **22** (75 MHz; CD_3OD)

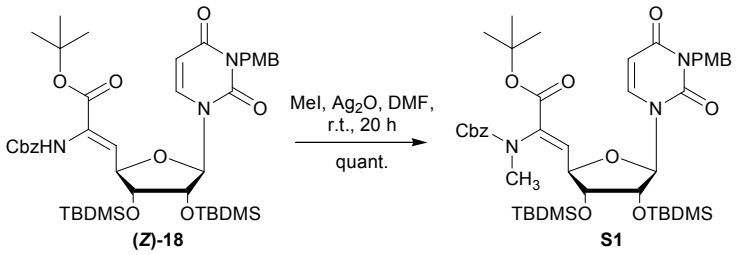


^{1}H NMR spectrum of **23** (600 MHz; CD_3OD)

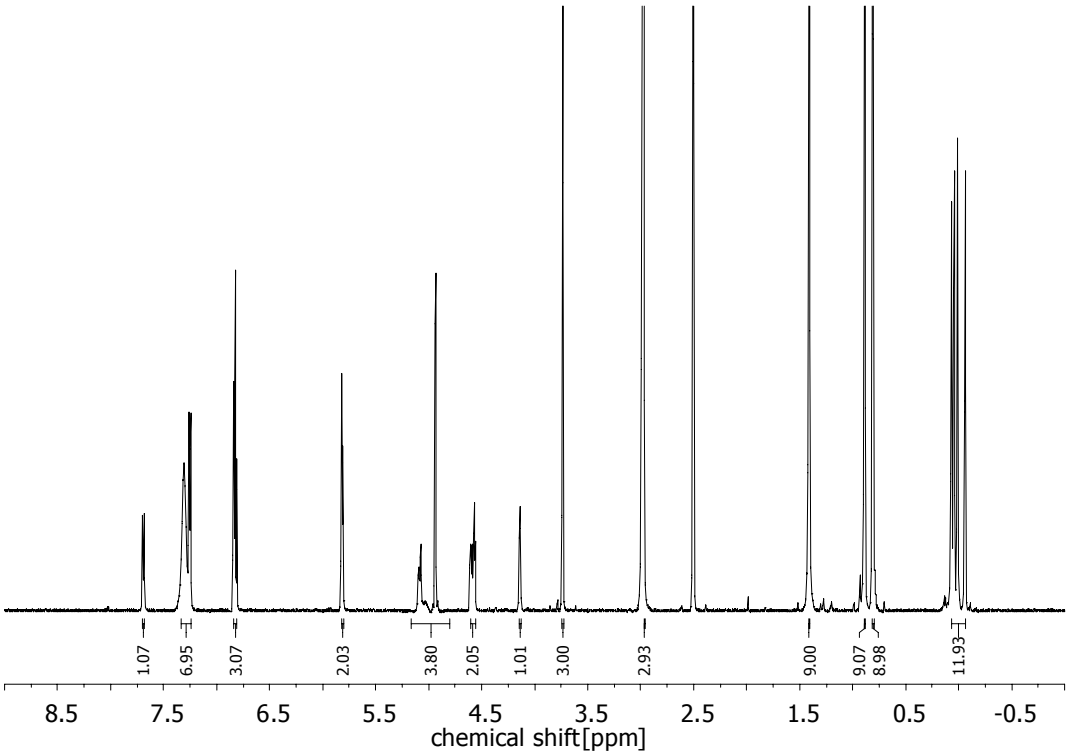


^{13}C NMR spectrum of **23** (126 MHz; CD_3OD)

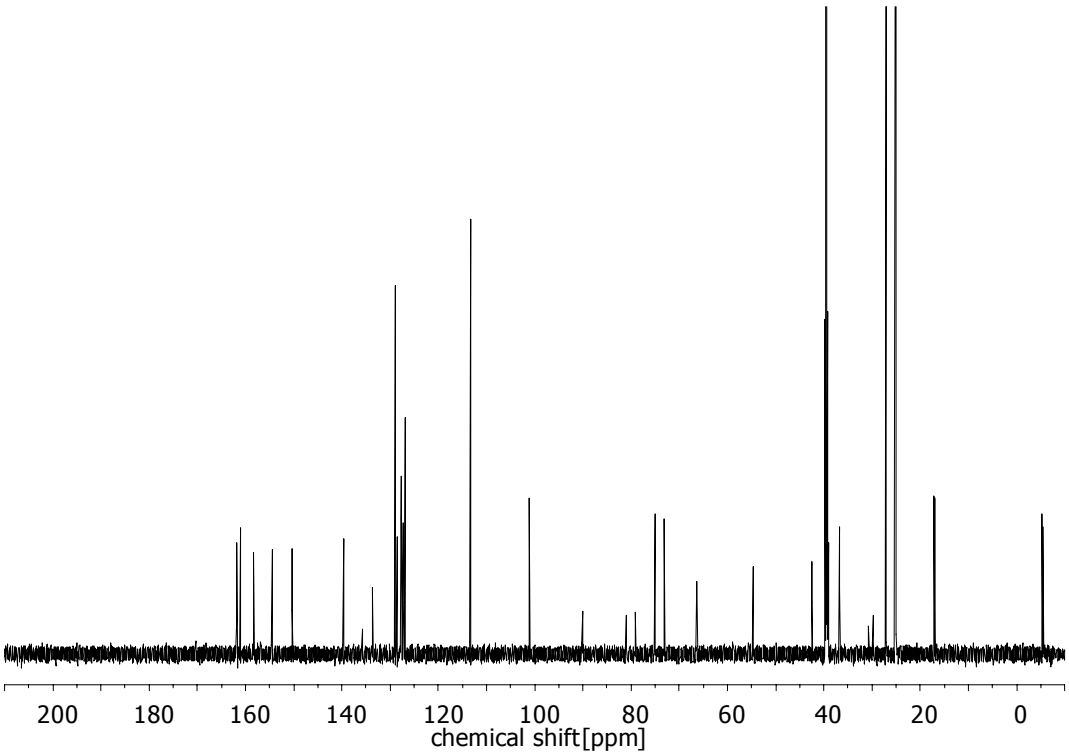
^{1}H-^{1}H NOESY NMR experiments



***N*-Cbz protected *N*-methyl (*Z*)-didehydro nucleosyl amino acid S1.** To a solution of **(*Z*)-18** (50 mg, 0.060 mmol) in DMF (2 mL), Ag_2O (118 mg, 0.510 mmol) and methyl iodide (38 mg, 0.27 mmol) were added at rt, and the reaction mixture was stirred at rt for 20 h. After filtration through celite^{TM} and washing the celite^{TM} with CH_2Cl_2 (3 x 20 mL), the solvent of the filtrate was evaporated under reduced pressure. The resultant crude product was purified by column chromatography (petroleum ether-EtOAc, 4 : 1) to give **S1** (51 mg, quant.) as a colourless solid; mp 54 °C; $[\alpha]_D^{25}$ +47.1 (*c* 0.7 in $CHCl_3$); λ_{max} (MeCN)/nm 260 (4.06); ν_{max} (KBr)/cm^{-1} 1725, 1673, 1455, 1391, 1339, 1251, 1161, 839, 776; δ_H (600 MHz; DMSO-d_6; 100 °C) -0.06 (3 H, s, $SiCH_3$), 0.01 (3 H, s, $SiCH_3$), 0.04 (3 H, s, $SiCH_3$), 0.07 (3 H, s, $SiCH_3$), 0.89 (9 H, s, $SiC(CH_3)_3$), 0.93 (9 H, s, $SiC(CH_3)_3$), 1.41 (9 H, s, $OC(CH_3)_3$), 2.97 (3 H, s, NCH_3), 3.73 (3 H, s, OCH_3), 4.14 (1 H, dd, *J* 2.3 and 4.1, 3'-H), 4.57 (1 H, dd, *J* 4.1 and 5.7, 2'-H), 4.60 (1 H, dd, *J* 2.3 and 9.0, 4'-H), 4.94 (2 H, s, PMB-CH_2), 5.03-5.11 (2 H, m, Cbz-CH_2), 5.81 (1 H, d, *J* 7.9, 5-H), 5.81 (1 H, d, *J* 5.7, 1'-H), 6.82 (1 H, d, *J* 9.0, 5'-H), 6.83 (2 H, d, *J* 8.7, 2 H, PMB-3-H, PMB-5-H), 7.25 (2 H, d, *J* 8.7, PMB-2-H, PMB-6-H), 7.27-7.37 (5 H, m, Cbz-Aryl-H) and 7.69 (1 H, d, *J* 7.9, 6-H); δ_C (151 MHz; DMSO-d_6; 100 °C) -5.6, -5.5, -5.3, -5.3, 17.0, 17.1, 25.0, 25.1, 27.1, 36.7, 42.5, 55.7, 66.4, 73.1, 75.0, 79.0, 81.0, 90.1, 101.1, 113.3, 126.9, 127.2, 127.6, 128.6, 129.0, 133.6, 135.7, 135.8, 139.7, 150.3, 154.5, 158.3, 161.1 and 161.8; *m/z* (HR-ESI$^+$) 874.4107 (M+Na$^+$. $C_{44}H_{65}N_3NaO_{10}Si_2$ requires 874.4101).



^{1}H NMR spectrum of **S1** (600 MHz; DMSO-d_6; 100 °C)



^{13}C NMR spectrum of **S1** (151 MHz; DMSO-d_6; 100 °C)

Compound **S1** was used in a standard ^{1}H-^{1}H NOESY NMR experiment (600 MHz; DMSO-d_6; 100 °C). No cross peak representing a nuclear Overhauser effect (nOe) of the *N*-methyl group and 5'-H was observed. In contrast, a cross peak of the *N*-methyl group with 4'-H was clearly detectable. These two findings are an excellent indication of the (*Z*)-configuration of the olefin moiety.