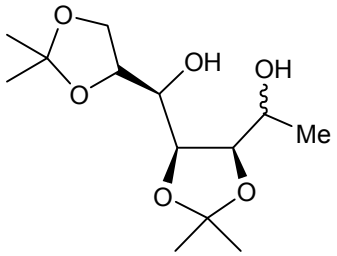
Supplementary Material (ESI) for Chemical Communications

Supplementary Data.

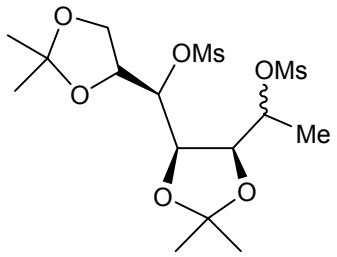
General: Optical rotations were measured at 25 ºC in a spectropolarimeter Perkin-Elmer 241-MC. ^{1}H- and ^{13}C-NMR spectra were registered in Bruker Advance 300 and 500 spectrometers, the spectra were obtained for solutions in CD_3OD or DMSO-d_6 and chemical shifts in spectra are reported in parts per million. ^{1}H- and ^{13}C-NMR assignments were confirmed by 2D COSY and HMQC, and also by NOE experiments when necessary. FAB-MS and CI-MS were measured with a Kratos MS-80-RFA instrument; for HR-MS a Micromass AutoSpeQ instrument was used.

1-Dideoxy-3,4:6,7-di-*O*-isopropylidene-D-*glycero*-D-*galacto*-heptitol and 1-deoxy-3,4:6,7-di-*O*-isopropylidene-D-*glycero*-D-*talo*-heptitol (12)



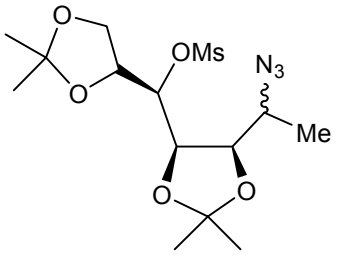
To a stirred solution of D-mannose diacetonide (6.15 g, 23.61 mmoles) in dry THF (30 ml) at -78 ºC, MeMgCl (3M in THF, 24 ml, 70.8 mmol) was added dropwise. The mixture was left at room temperature overnight. The excess of Grignard reagent was destroyed with NH_4Cl (5 ml). The mixture was washed with water and extracted with AcOEt. The organic phase was dried (Na_2SO_4) and the solvent evaporated to yield **12** (6.4 g, 95%, *R*/*S* = 1) as a yellow solid.

1,2,5-Trideoxy-3,4:6,7-di-*O*-isopropylidene-2,5-di-*O*-methanesulphonyl-D-*glycero*-D-*galacto*-heptitol and 1,2,5-trideoxy-3,4:6,7-di-*O*-isopropylidene-2,5-di-O-methanesulphonyl-D-*glycero*-D-*talo*-heptitol (13)



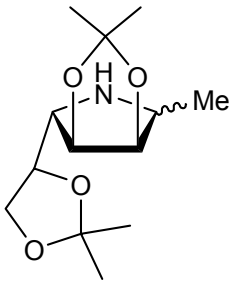
To a stirred solution of the mixture of epimers **12** (*R*/*S* = 1, 0.5 g, 1.81 mmoles) in pyridine (5 ml), methanesulphonyl chloride (1.12 ml, 14.5 mmoles) and catalytic dimethylaminopyridine were added. The mixture was stirred overnight, then cooled to 0 ºC, H_2O (1 ml) was added and the reaction was stirred for 15 min. The solvent was evaporated, the crude was diluted with dichloromethane, washed with HCl (1 M), saturated aqueous $NaHCO_3$ and brine. The resulting residue was purified by column chromatography (AcOEt:petroleum ether, 1:3→1:1) to obtain 13 (0.57 g, 74%, *R*/*S* = 1) as a yellow amorphous solid.

2-Azide-1,2,5-trideoxy-3,4:6,7-di-*O*-isopropylidene-5-*O*-methanesulphonyl-D-*glycero*-D-*galacto*-heptitol and 2-azide-1,2,5-trideoxy-3,4:6,7-di-*O*-isopropylidene-5-*O*-methanesulphonyl-D-*glycero*-D-*talo*-heptitol (14)



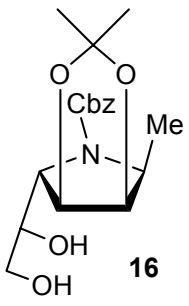
To a stirred solution of **13** (260 mg, 0.6 mmol, *R*/*S* = 1) in DMF (3 ml), trimethylsilyl azide (316 µl, 2.5 mmoles) and tetrabuylammonium fluoride (757 mg, 2.4 mmoles) were added, and the reaction mixture was stirred for 4.5 h at 90 ºC. Then, the solvent was evaporated and the resulting residue was directly purified by column chromatography (AcOEt:petroleum ether, 1:4) to give pure **14** (124 mg, 55%, *S*/*R* = 3).

1,2,5-Trideoxy-2,5-imino-3,4:6,7-di-*O*-isopropylidene-D-*glycero*-L-*altro*-heptitol and 1,2,5-trideoxy-2,5-imino-3,4:6,7-di-*O*-isopropylidene-D-*glycero*-L-*allo*-heptitol (15)

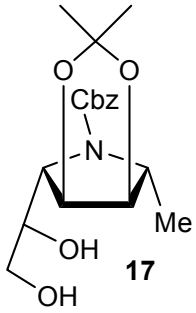


To a solution of azide derivatives **14** (400 mg, 1.06 mmol, *S*/*R* = 3) in methanol (5 ml), catalytic Pd/C (10 %) was added, and the mixture was hydrogenated under atmospheric pressure for 2 h. Then, the catalyst was filtered off, DBU (162 µl, 1.06 mmol) was added to the filtered solution, and the reaction mixture was stirred at r.t. for 12 h. The, the solvent was evaporated and the resulting residue was purified by column chromatography (CH_2Cl_2:MeOH, 30:1→15:1) to give pure **15** (265 mg, 99%, *S*/*R* = 3).

***N*-Benzyloxycarbonyl-1,2,5-trideoxy-2,5-imino-3,4-*O*-isopropylidene-D-*glycero*-L-*altro*-heptitol (16) and *N*-Benzyloxycarbonyl-1,2,5-trideoxy-2,5-imino-3,4-*O*-isopropylidene-D-*glycero*-L-*allo*-heptitol (17)**



16

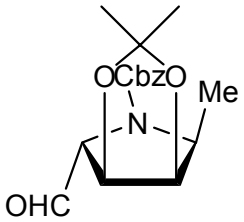


17

To a solution of **15** (1.63 g, 6.34 mmol) in 1:1 EtOH:H_2O (35 mL), $NaHCO_3$ (1.06 g, 12.68 mmol) and ClCbz (1.08 mL, 7.64 mmol) were added. After stirring for 2 h at r.t., the mixture was poured into sat. aq. soln. of $NaHCO_3$ (40 mL) and extracted with AcOEt (3x50 mL). The organic phases were dried (Na_2SO_4), filtered and concentrated. The crude product was then dissolved in CH_3CN (40 mL) and $Zn(NO_3)_2.6H_2O$ was added. After heating at 50 ºC for 12 h, the solvent was

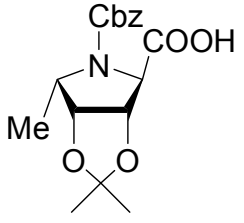
evaporated. The residue was diluted with CH_2Cl_2 and washed with water and brine. The organic phases were dried, filtered and concentrated. Column chromatography (toluene:acetone 5:1) afforded **17** (0.322 g) and **16** (0.966 g) (58% global yield, 2 steps).
Data for compound **16**: ^{1}H-NMR (300 MHz, DMSO-d_6, 363 K, *J* Hz, δ ppm) δ 7.37-7.09 (m, 5 H, H-aromat.), 5.1 (d, 1 H, $^2J_{H,H}$ = 12.6, C*H*HPh), 5.0 (d, 1 H, CH*H*Ph), 4.75 (d, 1 H, $J_{3,4}$ = 6.2, H-4), 4.68 (br. t, 1 H, OH), 4.59 (t, 1 H, $J_{2,3}$ = 6.1, H-3), 4.18 (br. m, 1 H, OH), 4.07 (d, 1 H, $J_{5,6}$ = 4.7, H-5), 3.85 (qui, 1 H, $J_{2,CH}$ = 6.3, H-2), 3.82 (br. m, 1 H, H-6), 3.39-3.23 (m, 2 H, H-7a and H-7b), 1.37 (s, 3 H, CH_3 of acetonide), 1.29 (d, 3 H, CH_3), 1.29 (s, 3 H, CH_3 of acetonide). ^{13}C-NMR (75.4 MHz, DMSO-d_6, 353 K, δ ppm) δ 155.0 (CO), 137.4, 128.8, 128.2, 128.1 (6 C aromat.), 110.5 ($C(OMe)_2$), 81.0 (C-3), 80.5 (C-4), 71.1 (C-6), 66.3 (C-5), 65.8 (CH_2Ph), 63.1 (C-7), 57.9 (C-2), 26.4, 25.4 (2 CH_3 of acetonide), 15.7 (br. s, CH_3). $[\alpha]_D$ = +52 (*c* 1.8, CH_2Cl_2). CIMS: 352 (10% $[M+H]^+$). HRCIMS found: 352.1752 (calcd. for $C_{18}H_{25}NO_6$+H: 352.1760).
Data for compound **17**: ^{1}H-NMR (500 MHz, DMSO-d_6, 373 K, *J* Hz, δ ppm) δ 7.37-7.22 (m, 5 H, H-aromat.), 5.14 (d, 1 H, $^2J_{H,H}$ = 12.6, C*H*HPh), 5.10 (d, 1 H, CH*H*Ph), 4.75 (br. s, 1 H, OH), 4.70 (d, 1 H, $J_{3,4}$ = 5.7, H-4), 4.37 (dd, 1 H, $J_{2,3}$ = 2.3, H-3), 4.25 (br. s, 1 H, OH), 4.15 (d, 1 H, $J_{5,6}$ = 3.9, H-5), 3.96 (qd, 1 H, $J_{2,CH}$ = 6.8, H-2), 3.67 (br. m, 1 H, H-6), 3.42 (dd, 1 H, $J_{7a,OH}$ = 5.0, $J_{7a,7b}$ = 11.4, H-7a), 3.28 (dd, 1 H, $J_{7b,OH}$ = 6.7, H-7b), 1.34 (s, 3 H, CH_3 of acetonide), 1.29 (d, 3 H, CH_3), 1.26 (s, 3 H, CH_3 of acetonide). ^{13}C-NMR (75.4 MHz, DMSO-d_6, 353 K, δ ppm) δ 136.6, 127.9, 127.2, 126.7 (6 C aromat.), 110.0 ($C(OMe)_2$), 85.2 (C-3), 81.9 (C-4), 71.4 (C-6), 65.8 (CH_2Ph), 65.7 (C-5), 62.6 (C-7), 61.5 (C-2), 26.9, 24.9 (2 CH_3 of acetonide), 18.1 (CH_3). $[\alpha]_D$ = +40 (*c* 1.3, CH_2Cl_2). HRCIMS found: 352.1736 (calcd. for $C_{18}H_{25}NO_6$+H: 352.1760).

(2*S*,3*S*,4*R*,5*S*)-1-Benzyloxycarbonyl-2-formyl-5-methylpyrrolidine-3,4-diol (18)



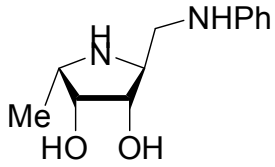
A solution of $NaIO_4$ (246 mg, 1.18 mmol) in water (5 mL) was added dropwise to a solution of **16** (207 mg, 0.59 mmol) in THF (6 mL) cooled to 0 ºC. After stirring for 1 h at r.t., THF was evaporated and the residue dissolved in CH_2Cl_2 (30 mL) and washed successively with water, sat. aq. soln. of $NaHCO_3$ and brine. The organic phase was dried, filtered and concentrated to give crude aldehyde **18** (173 mg, 92%) which was used for the next step without further purification.
^{1}H-NMR (300 MHz, DMSO-d_6, 363 K, *J* Hz, δ ppm) δ 9.52 (d, 1 H, $J_{2,CHO}$ = 1.41, C*H*O), 7.36-7.32 (m, 5 H, H-aromat.), 5.07 (br. s, 2 H, CH_2Ph), 4.84 (d, 1 H, $J_{3,4}$ = 6.3, H-3), 4.59 (t, 1 H, $J_{4,5}$ = 6.2, H-4), 4.39 (br. s, 1 H, H-2), 3.87 (qui, 1 H, $J_{2,CH}$ = 6.6, H-5), 1.47-1.24 (m, 9 H, 2 CH_3 of acetonide and CH_3). ^{13}C-NMR (75.4 MHz, DMSO-d_6, 353 K, δ ppm) δ 198.4 (CHO), 136.3, 128.1, 127.7, 127.4 (6 C aromat.), 111.2 (*C*$(OMe)_2$), 80.2 (C-4), 77.2 (C-3), 71.4 (C-2), 66.3 (CH_2Ph), 57.3 (C-5), 26.0, 24.8 (2 CH_3 of acetonide), 14.4 (br. s, CH_3). IR ν 2986, 2938, 1694, 1412, 1032 cm^{-1}. HRCIMS found: 320.1496 (calcd. for $C_{17}H_{21}NO_5$+H: 320.1498).

(2*S*,3*S*,4*R*,5*S*)-1-Benzyloxycarbonyl-2-carboxi-5-methylpyrrolidine-3,4-diol (23)



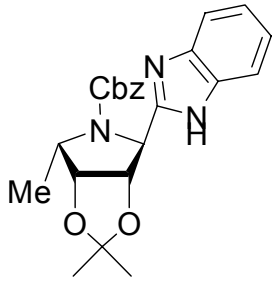
To a stirred solution of aldehyde **18** (271 mg, 0.86 mmol) and 2-methyl-2-butene (0.9 ml) in tert-butanol (10 ml), a solution of $NaClO_2$ (0.82 g, 9 mmoles) and KH_2PO_4 (1.23 g, 9 mmoles) in water (8 ml) was added. The reaction mixture was stirred overnight at r.t. Then, the solvent was evaporated, the resulting residue was dissolved in CH_2Cl_2, washed with water, the organic phase dried (Na_2SO_4) and the solvent evaporated to give pure **23** (235 mg, 82%) which was used in the next step without further purification.

(2*S*,3*S*,4*R*,5*S*)-5-Methyl-2-phenylaminomethyl-pyrrolidine-3,4-diol (24)



To a solution of **18** (115 mg, 0.36 mmol) in 1,2-dichloroethane (3 mL), aniline (0.1 mL, 1.08 mmol) and $NaBH(OAc)_3$ (120 mg, 0.54 mmol) were added. The reaction mixture was stirred at r.t. for 4 h under argon. Then, sat. aq. soln. of $NaHCO_3$ (10 mL) was added and the mixture extracted with AcOEt (3x15 mL). The organic phases were dried (Na_2SO_4), filtered and concentrated. Column chromatography (AcOEt:petroleum ether 1:5) afforded **22** (105 mg, 74%). To a solution of **22** (90 mg, 0.227 mmol) in THF (2 mL), 1 N HCl (2 mL) was added. After stirring at r.t for 6 h, THF was evaporated, the mixture neutralized with sat. aq. soln. of $NaHCO_3$ and extracted with AcOEt. The organic phases were dried, filtered and concentrated. The crude intermediate was then dissolved in MeOH (6 mL) and hydrogenated over Pd/C for 4 h. The mixture was filtered through celite and evaporated. Chromatography on silica gel (CH_2Cl_2:MeOH:NH_4OH 6:1:0.1) yielded **24** (50 mg, 100%).
^{1}H-NMR (300 MHz, CD_3OD, δ ppm, *J* Hz) δ 6.99 (t, 2 H, *J* = 7.5, H-aromat.), 6.52 (m, 3 H, H-aromat.), 3.82 (dd, 1 H, $J_{2,3}$ = 7.1, $J_{3,4}$ = 4.3, H-3), 3.72 (t, 1 H, $J_{4,5}$ = 3.2, H-4), 3.24-3.16 (m, 2 H, H-2 and R-C*H*H-NHR'), 3.07 (qd, 1 H, $J_{5,CH}$ = 6.7, H-5), 3.01 (dd, 1 H, $^2J_{H,H}$ = 13.6, $J_{CH,H}$ = 8.9, R-CH*H*-NHR') 1.07 (d, 3 H, CH_3). ^{13}C-NMR (75.4 MHz, CD_3OD, δ ppm) δ 128.6, 116.8, 112.7 (6 C-aromat.), 76.8, 74.0 (C-3, C-4), 60.7 (C-2), 55.0 (C-5), 47.0 (R-*C*H_2-NHR'), 13.2 (CH_3). $[\alpha]_D$ = -67 (*c* 0.8, MeOH). CIMS: 223 (50% $[M+H]^+$). HRCIMS found: 223.1439 (calcd. for $C_{12}H_{18}N_2O_2$+H: 223.1446).

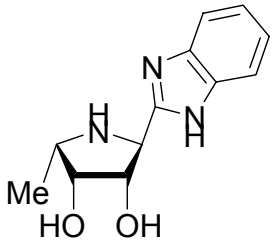
(2*S*,3*S*,4*R*,5*S*)-2-(1*H*-Benzoimidazol-2-yl)-1-benzyloxycarbonyl-3,4-isopropylidenedioxy-5-methylpyrrolidine (26)



To a solution of acid **23** (54 mg, 0.161 mmol) and *o*-phenylenediamine (19 mg, 0.177 mmol), PyBOP (92 mg, 0.177 mmol) and diisopropylethylamine (55 µl, 0.322 mmol) were added, and the mixture was stirred at r.t. for 1 h. Then, the solvent was evaporated, the resulting residue was dissolved in CH_2Cl_2 and washed with saturated aqueous solution of citric acid and brine. The organic phase was dried (Na_2SO_4) and concentrated, the resulting crude was purified by column

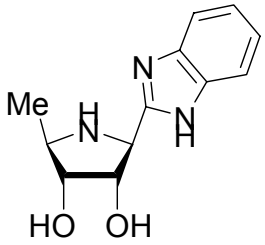
chromatography (CH_2Cl_2:MeOH, 30:1) to give **25** (45 mg, 65%). Compound **25** (45 mg, 0.104 mmol) was dissolved in glacial AcOH (2 ml) and the mixture was stirred for 30 min. at 45 ºC. Then, the solvent was evaporated and the resulting residue was purified by column chromatography (ether:petroleum ether, 3:1) to give pure **26** (43 mg, 100%).

(2*S*,3*S*,4*R*,5*S*)-2-(1*H*-Benzoimidazol-2-yl)-5-methylpyrrolidine-3,4-diol (27)



A solution of **26** (43 mg, 0.104 mmol) in THF-(1M)HCl (1:1, 2 ml) was stirred for 12 h, then the solvent was evaporated. The resulting residue was dissolved in MeOH (3 ml), catalytic Pd-C (10%) was added and the mixture was hydrogenated under atmospheric pressure for 3 h. The catalyst was filtered off, the filtered solution was concentrated and the resulting residue was purified by column chromatography (CH_2Cl_2:MeOH:NH_4OH, 6:1:0.1) to give **27** (21 mg, 87%).
^{1}H-NMR (500 MHz, CD_3OD, δ ppm, *J* Hz) δ 7.52 (dd, 2 H, *J* = 3.2, 6.0, H-aromat.), 7.20 (dd, 2 H, H-aromat.), 4.47 (dd, 1 H, $J_{2,3}$ = 7.7, $J_{3,4}$ = 4.1, H-3), 4.35 (d, 1 H, H-2), 3.96 (t, 1 H, $J_{4,5}$ = 3.2, H-4), 3.49 (qd, 1 H, $J_{5,CH}$ = 6.7, H-5), 1.22 (d, 3 H, CH_3). ^{13}C-NMR (75.4 MHz, CD_3OD, δ ppm) δ 158.3, 123.9 (7 C-aromat.), 80.9 (C-3), 76.2 (C-4), 62.0 (C-2), 57.6 (C-5), 15.4 (CH_3). $[\alpha]_D$ = -28 (*c* 0.5, MeOH). FABMS: 234 (60% $[M+H]^+$), 256 (16%, $[M+Na]^+$). HRFABMS found: 234.1242 (calcd. for $C_{12}H_{15}N_3O_2$+H: 234.1243).

(2*S*,3*S*,4*R*,5*R*)-2-(1*H*-Benzoimidazol-2-yl)-5-methylpyrrolidine-3,4-diol (28)



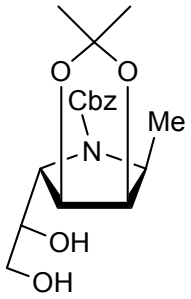
^{1}H-NMR (300 MHz, CD_3OD, δ ppm, *J* Hz) δ 7.53 (dd, 2 H, *J* = 3.2, 6.0, H-aromat.), 7.20 (dd, 2 H, H-aromat.), 4.27 (d, 1 H, $J_{2,3}$ = 5.2, H-2), 4.17 (t, 1 H, $J_{3,4}$ = 5.6, H-3), 3.65 (t, 1 H, $J_{4,5}$ = 6.2, H-4), 3.19 (qui, 1 H, $J_{5,CH}$ = 6.5, H-5), 1.30 (d, 3 H, CH_3). ^{13}C-NMR (75.4 MHz, CD_3OD, δ ppm) δ 157.0, 123.8 (7 C-aromat.), 78.8 (C-3), 78.1 (C-4), 63.7 (C-2), 60.3 (C-5), 19.3 (CH_3). $[\alpha]_D$ = -12 (*c* 1.3, MeOH). CIMS: 234 (70%, $[M+H]^+$). HRCIMS found: 234.1235 (calcd. for $C_{12}H_{15}N_3O_2$+H: 234.1243).

Supplementary Data.

General: Optical rotations were measured at 25 ºC in a spectropolarimeter Perkin-Elmer 241-MC. ^{1}H- and ^{13}C-NMR spectra were registered in Bruker Advance 300 and 500 spectrometers, the

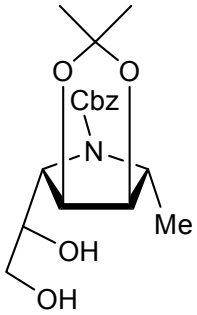
spectra were obtained for solutions in CD_3OD or DMSO-d_6 and chemical shifts in spectra are reported in parts per million. ^{1}H- and ^{13}C-NMR assignments were confirmed by 2D COSY and HMQC, and also by NOE experiments when necessary. FAB-MS and CI-MS were measured with a Kratos MS-80-RFA instrument; for HR-MS a Micromass AutoSpeQ instrument was used.

(2*S*,3*S*,4*R*,5*R*,1'*R*)-1-Benzyloxycarbonyl-2-(1',2'-dihydroxyethyl)-3,4-isopropylide-nedioxy-5-methylpyrrolidine (16)



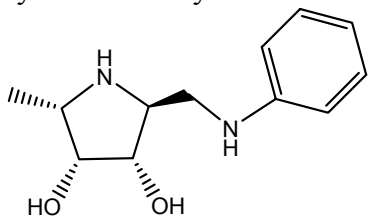
^{1}H-NMR (300 MHz, DMSO-d_6, 363 K, *J* Hz, δ ppm) δ 7.37-7.09 (m, 5 H, H-aromat.), 5.1 (d, 1 H, $^2J_{H,H}$ = 12.6, C*H*HPh), 5.0 (d, 1 H, CH*H*Ph), 4.75 (d, 1 H, $J_{3,4}$ = 6.2, H-3), 4.68 (br. t, 1 H, OH), 4.59 (t, 1 H, $J_{4,5}$ = 6.1, H-4), 4.18 (br. m, 1 H, OH), 4.07 (d, 1 H, $J_{2,1'}$ = 4.7, H-2), 3.85 (qui, 1 H, $J_{5,CH}$ = 6.3, H-5), 3.82 (br. m, 1 H, H-1'), 3.39-3.23 (m, 2 H, H-2'a and H-2'b), 1.37 (s, 3 H, CH_3 of acetonide), 1.29 (d, 3 H, CH_3), 1.29 (s, 3 H, CH_3 of acetonide). ^{13}C-NMR (75.4 MHz, DMSO-d_6, 353 K, δ ppm) δ 155.0 (CO), 137.4, 128.8, 128.2, 128.1 (6 C aromat.), 110.5 ($C(OMe)_2$), 81.0 (C-4), 80.5 (C-3), 71.1 (C-1'), 66.3 (C-2), 65.8 (CH_2Ph), 63.1 (C-2'), 57.9 (C-5), 26.4, 25.4 (2 CH_3 of acetonide), 15.7 (br. s, CH_3). $[\alpha]_D$ = +52 (*c* 1.8, CH_2Cl_2). CIMS: 352 (10% $[M+H]^+$). HRCIMS found: 352.1752 (calcd. for $C_{18}H_{26}NO_6$+H: 352.1760).

(2*S*,3*S*,4*R*,5*S*,1'*R*)-1-Benzyloxycarbonyl-2-(1',2'-dihydroxyethyl)-3,4-isopropylide-nedioxy-5-methylpyrrolidine (17)



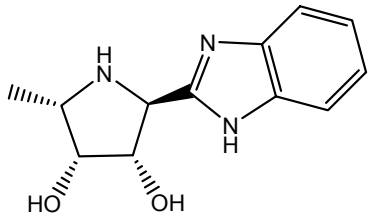
^{1}H-NMR (500 MHz, DMSO-d_6, 373 K, *J* Hz, δ ppm) δ 7.37-7.22 (m, 5 H, H-aromat.), 5.14 (d, 1 H, $^2J_{H,H}$ = 12.6, C*H*HPh), 5.10 (d, 1 H, CH*H*Ph), 4.75 (br. s, 1 H, OH), 4.70 (d, 1 H, $J_{3,4}$ = 5.7, H-3), 4.36 (dd, 1 H, $J_{4,5}$ = 2.3, H-4), 4.25 (br. s, 1 H, OH), 4.15 (d, 1 H, $J_{2,1'}$ = 3.9, H-2), 3.93 (qd, 1 H, $J_{5,CH}$ = 6.8, H-5), 3.67 (br. m, 1 H, H-1'), 3.42 (dd, 1 H, $J_{2'a,OH}$ = 5.0, $J_{2'a,2'b}$ = 11.4, H-2'a), 3.28 (dd, 1 H, $J_{2'b,\ OH}$ = 6.7, H-2'b), 1.34 (s, 3 H, CH_3 of acetonide), 1.29 (d, 3 H, CH_3), 1.26 (s, 3 H, CH_3 of acetonide). ^{13}C-NMR (75.4 MHz, DMSO-d_6, 353 K, δ ppm) δ 136.6, 127.9, 127.2, 126.7 (6 C aromat.), 110.0 ($C(OMe)_2$), 85.2 (C-4), 81.9 (C-3), 71.4 (C-1'), 65.8 (CH_2Ph), 65.7 (C-2), 62.6 (C-2'), 61.5 (C-5), 26.9, 24.9 (2 CH_3 of acetonide), 18.1 (CH_3). $[\alpha]_D$ = +40 (*c* 1.3, CH_2Cl_2). HRCIMS found: 352.1736 (calcd. for $C_{18}H_{25}NO_6$+H: 352.1760).

(2*S*,3*R*,4*S*,5*S*)-2-Methyl-5-phenylaminomethyl-pyrrolidine-3,4-diol (24)



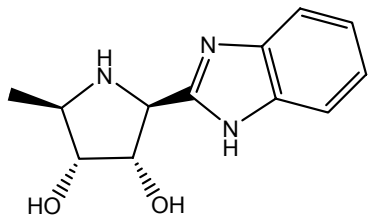
^{1}H-NMR (300 MHz, CD_3OD, δ ppm, *J* Hz) δ 6.99 (t, 2 H, *J* = 7.5, H-aromat.), 6.52 (m, 3 H, H-aromat.), 3.82 (dd, 1 H, $J_{4,5}$ = 7.1, $J_{3,4}$ = 4.3, H-4), 3.72 (t, 1 H, $J_{2,3}$ = 3.2, H-3), 3.24-3.16 (m, 2 H, H-5 and R-C*H*H-NHR'), 3.07 (qd, 1 H, $J_{2,CH}$ = 6.7, H-2), 3.01 (dd, 1 H, $^2J_{H,H}$ = 13.6, $J_{CH,H}$ = 8.9, R-CHH-NHR') 1.07 (d, 3 H, CH_3). ^{13}C-NMR (75.4 MHz, CD_3OD, δ ppm) δ 128.6, 116.8, 112.7 (6 C-aromat.), 76.8, 74.0 (C-3, C-4), 60.7 (C-5), 55.0 (C-2), 47.0 (R-CH_2-NHR'), 13.2 (CH_3). $[\alpha]_D$ = -67 (*c* 0.8, MeOH). CIMS: 223 (50% $[M+H]^+$). HRCIMS found: 223.1439 (calcd. for $C_{12}H_{18}N_2O_2$+H: 223.1446).

(2*S*,3*S*,4*R*,5*S*)-2-(1*H*-Benzoimidazol-2-yl)-5-methylpyrrolidine-3,4-diol (27)

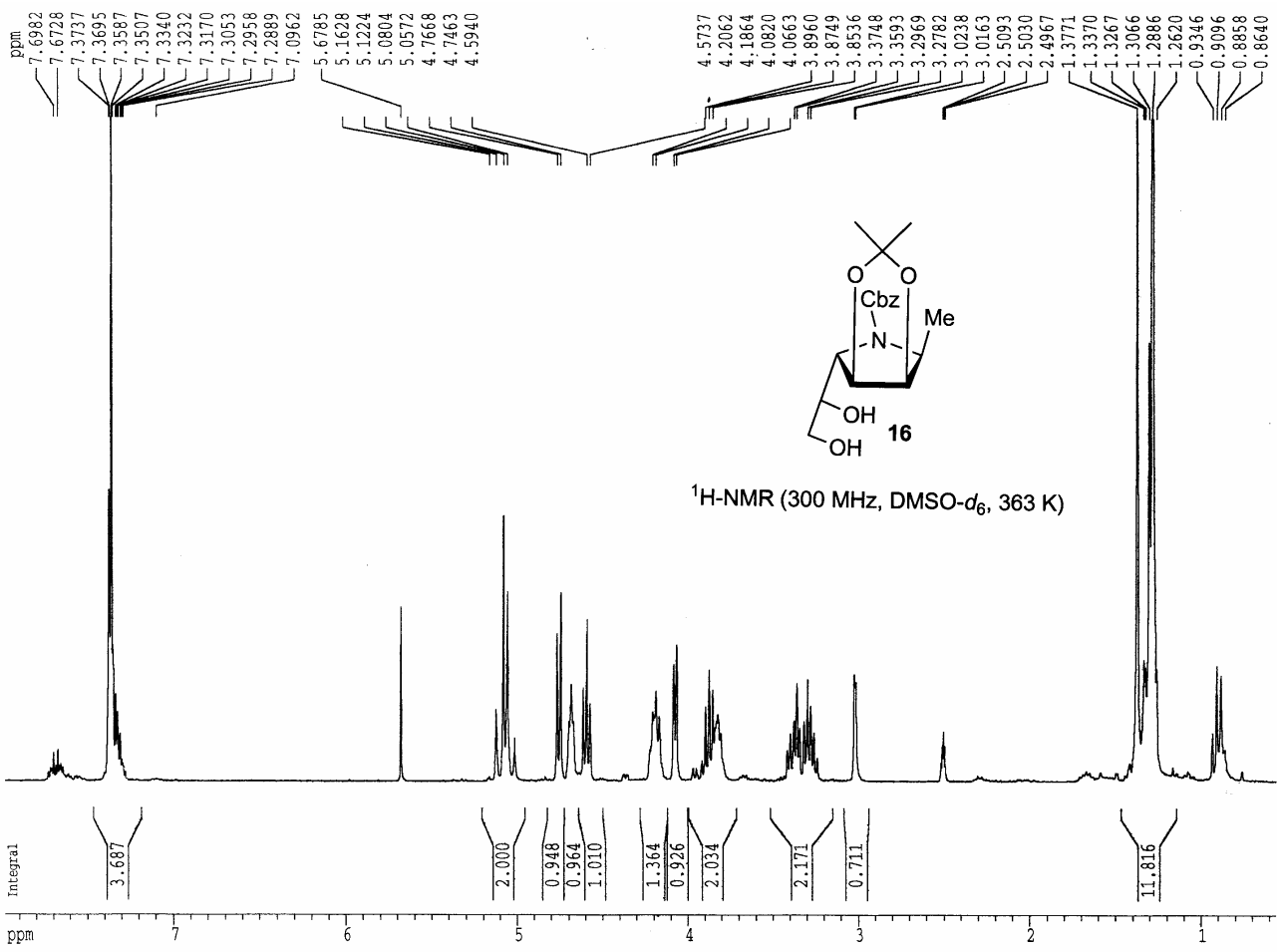


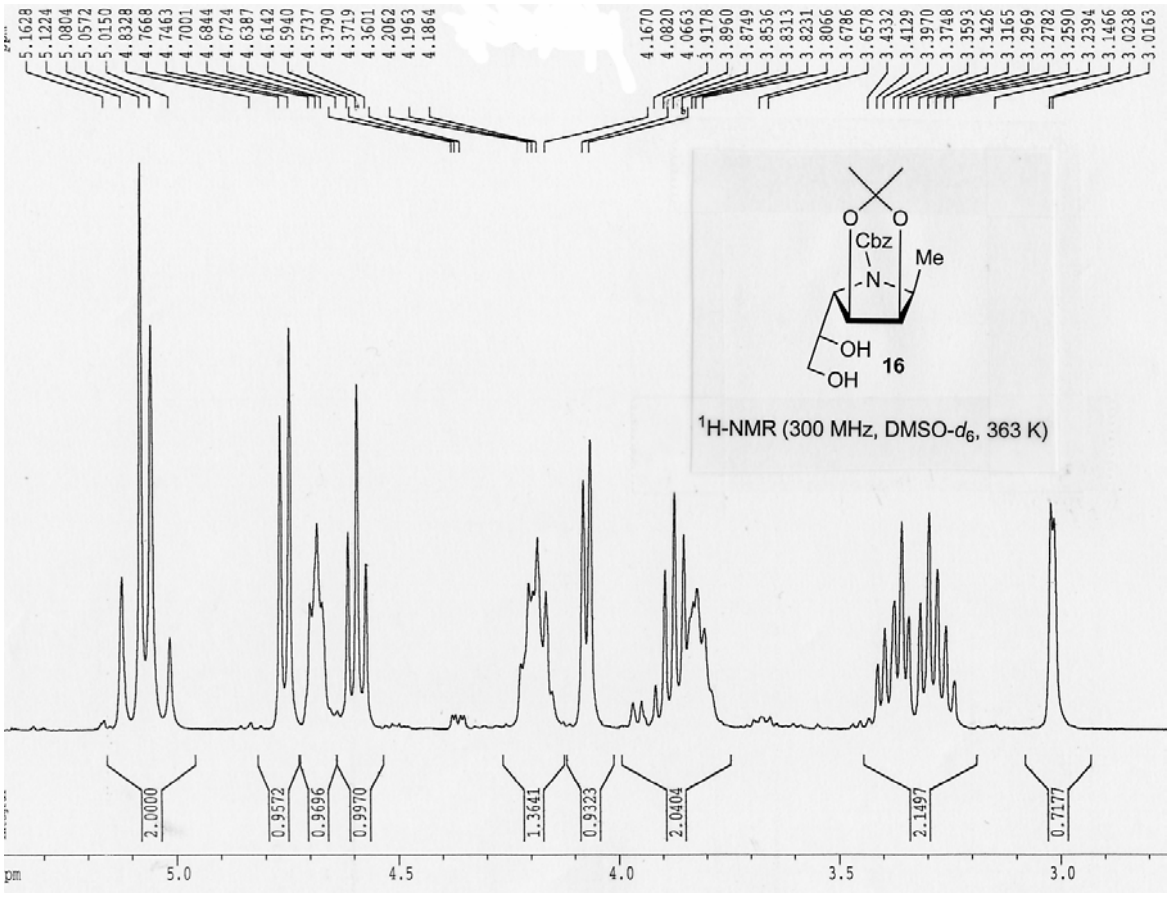
^{1}H-NMR (500 MHz, CD_3OD, δ ppm, *J* Hz) δ 7.52 (dd, 2 H, *J* = 3.2, 6.0, H-aromat.), 7.20 (dd, 2 H, H-aromat.), 4.47 (dd, 1 H, $J_{2,3}$ = 7.7, $J_{3,4}$ = 4.1, H-3), 4.35 (d, 1 H, H-2), 3.96 (t, 1 H, $J_{4,5}$ = 3.2, H-4), 3.49 (qd, 1 H, $J_{5,CH}$ = 6.7, H-5), 1.22 (d, 3 H, CH_3). ^{13}C-NMR (75.4 MHz, CD_3OD, δ ppm) δ 158.3, 123.9 (7 C-aromat.), 80.9 (C-3), 76.2 (C-4), 62.0 (C-2), 57.6 (C-5), 15.4 (CH_3). $[\alpha]_D$ = -28 (*c* 0.5, MeOH). FABMS: 234 (60% $[M+H]^+$), 256 (16%, $[M+Na]^+$). HRFABMS found: 234.1242 (calcd. for $C_{12}H_{15}N_3O_2$+H: 234.1243).

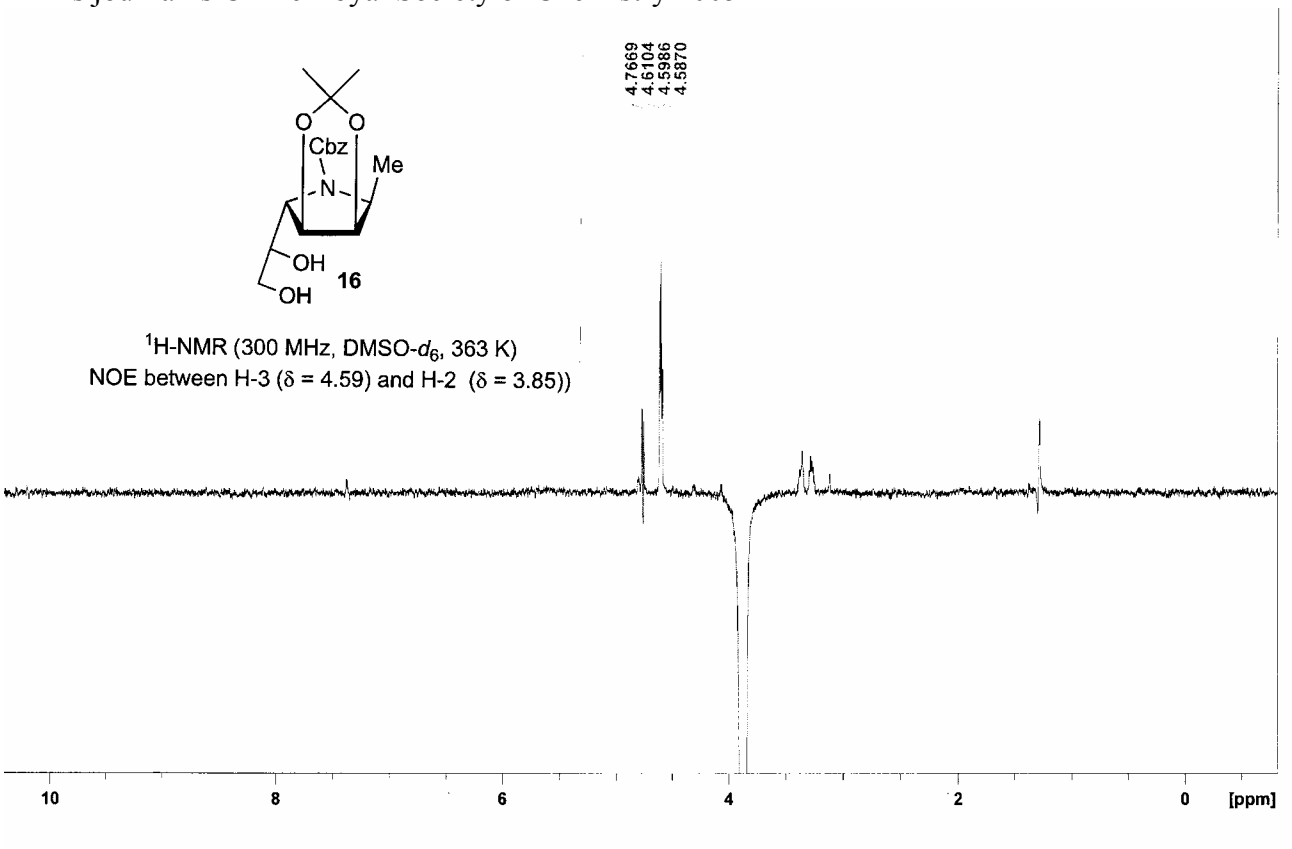
(2*S*,3*S*,4*R*,5*R*)-2-(1*H*-Benzoimidazol-2-yl)-5-methylpyrrolidine-3,4-diol (28)



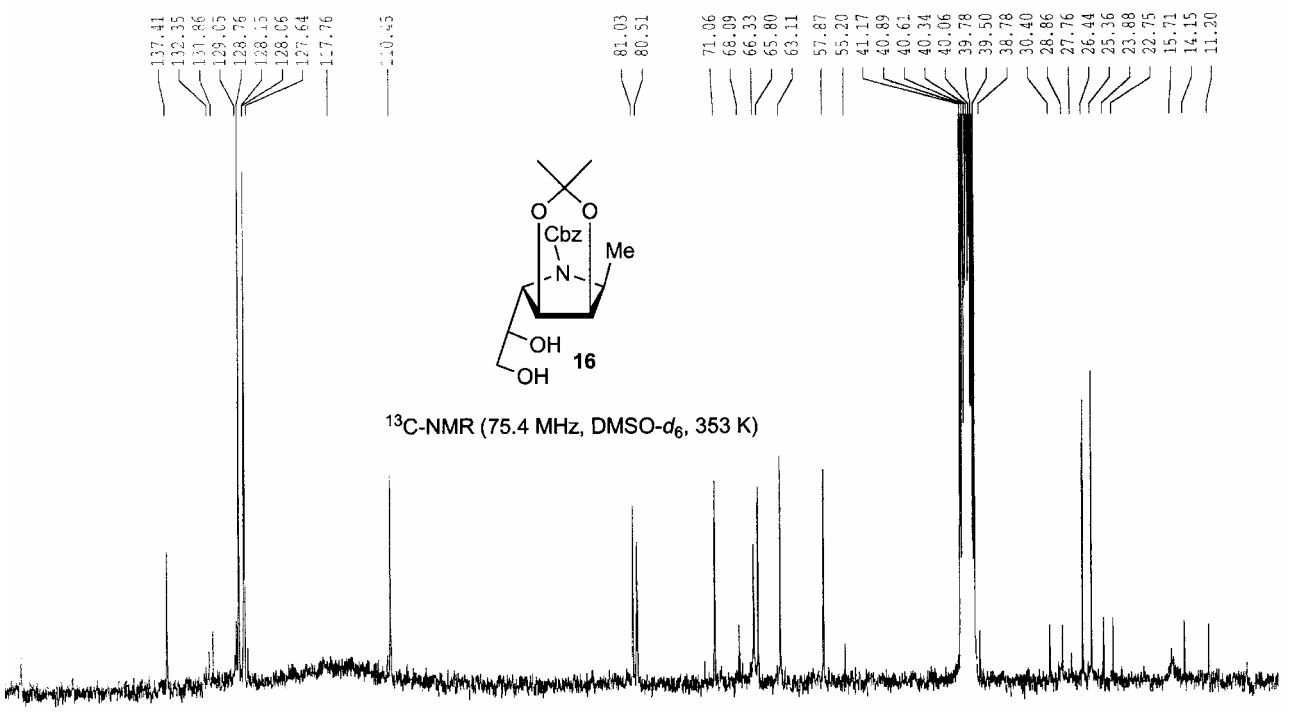
^{1}H-NMR (300 MHz, CD_3OD, δ ppm, *J* Hz) δ 7.53 (dd, 2 H, *J* = 3.2, 6.0, H-aromat.), 7.20 (dd, 2 H, H-aromat.), 4.27 (d, 1 H, $J_{2,3}$ = 5.2, H-2), 4.17 (t, 1 H, $J_{3,4}$ = 5.6, H-3), 3.65 (t, 1 H, $J_{4,5}$ = 6.2, H-4), 3.19 (qui, 1 H, $J_{5,CH}$ = 6.5, H-5), 1.30 (d, 3 H, CH_3). ^{13}C-NMR (75.4 MHz, CD_3OD, δ ppm) δ 157.0, 123.8 (7 C-aromat.), 78.8 (C-3), 78.1 (C-4), 63.7 (C-2), 60.3 (C-5), 19.3 (CH_3). $[\alpha]_D$ = -12 (*c* 1.3, MeOH). CIMS: 234 (70%, $[M+H]^+$). HRCIMS found: 234.1235 (calcd. for $C_{12}H_{15}N_3O_2$+H: 234.1243).



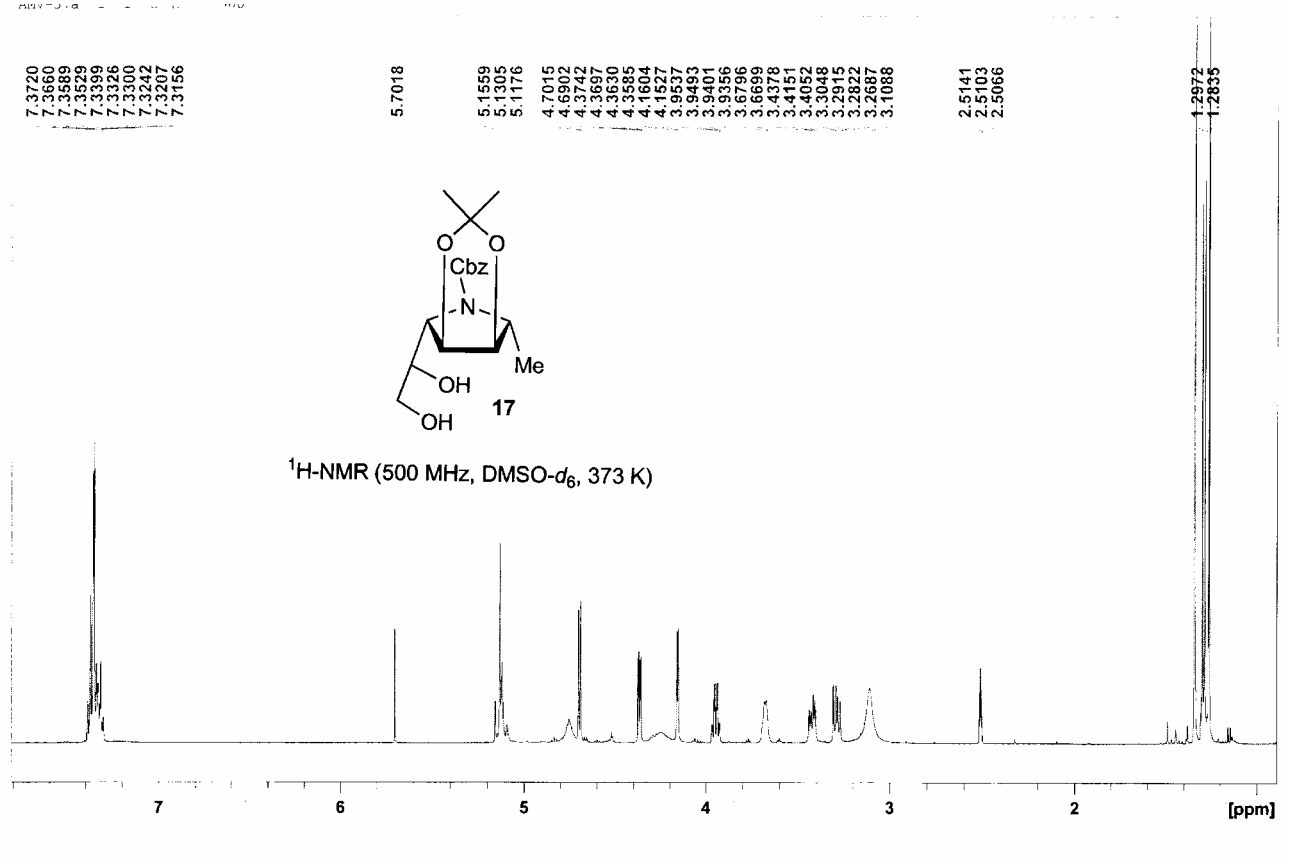


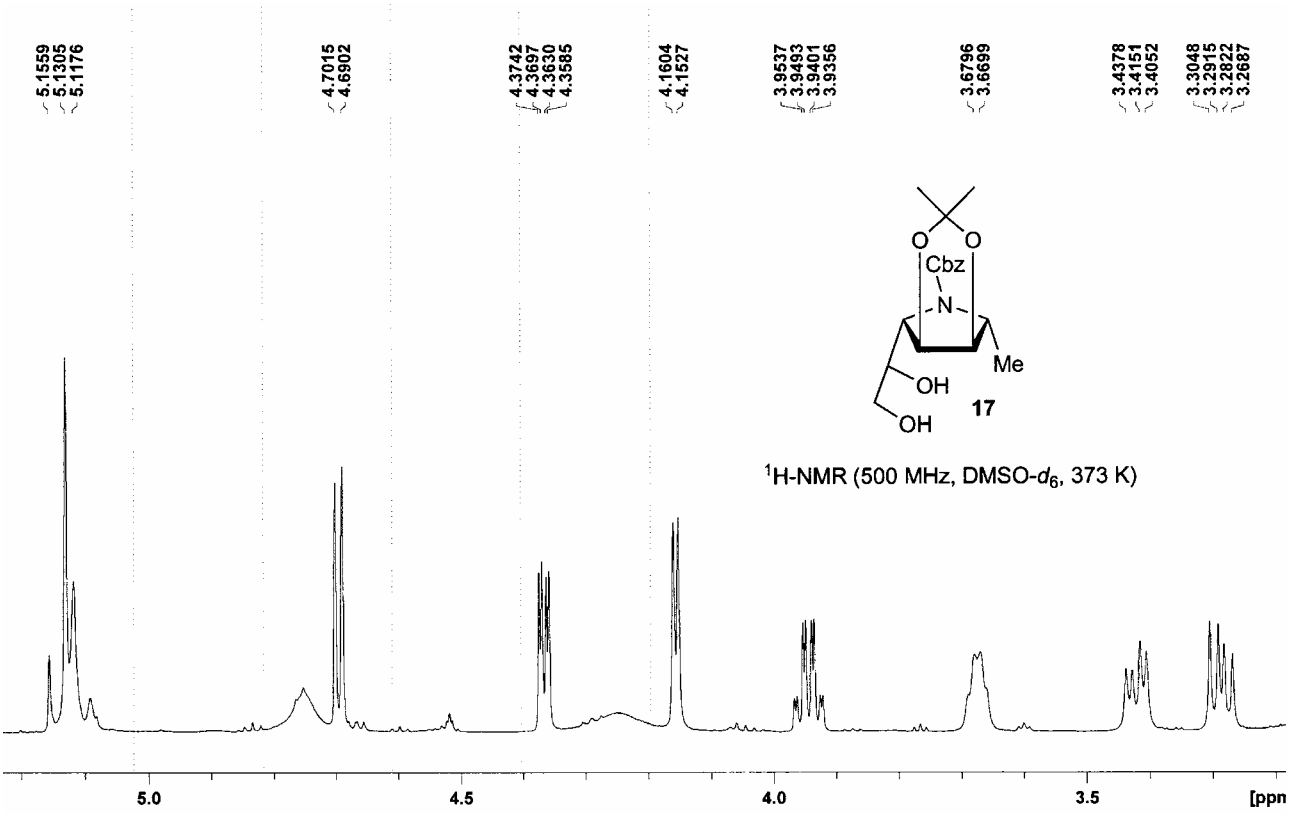


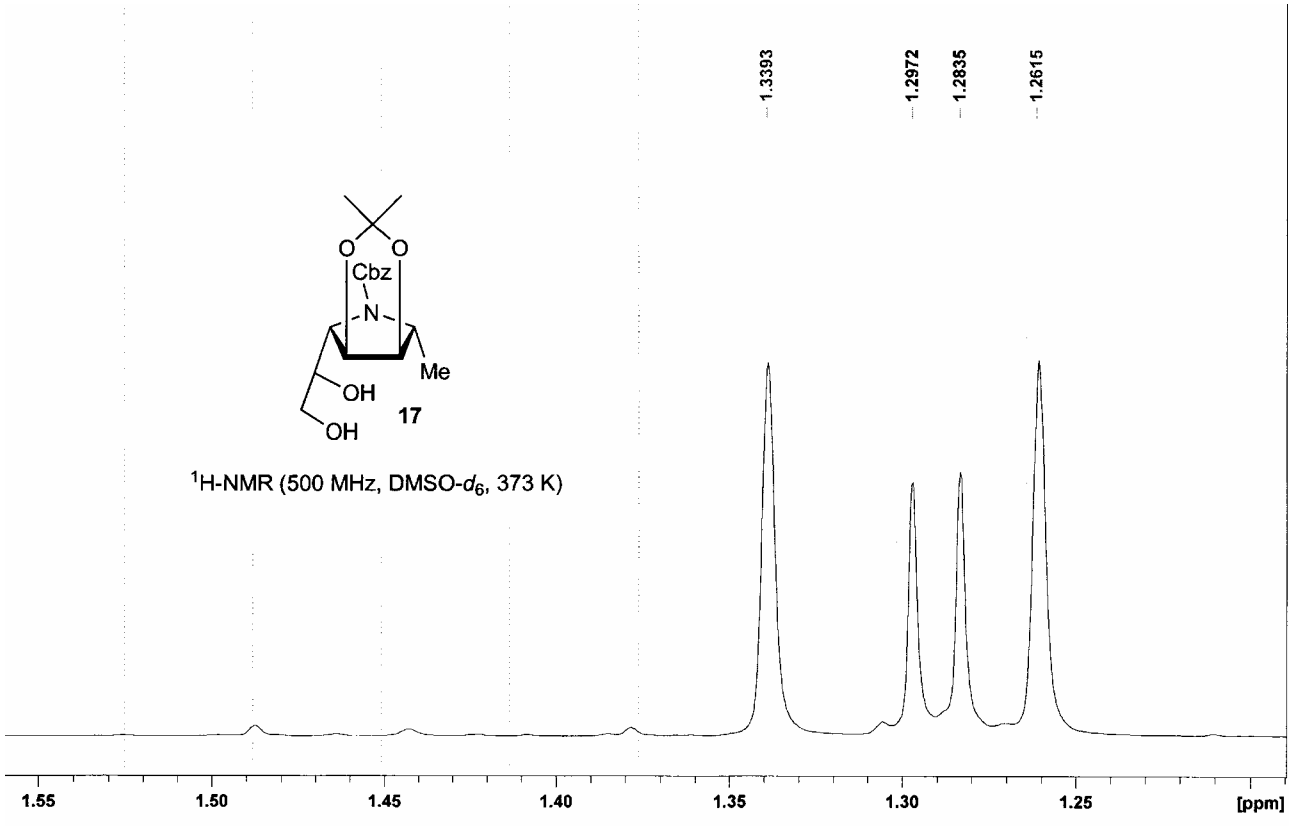
^{1}H-NMR (300 MHz, DMSO-d_6, 363 K)
NOE between H-3 (δ = 4.59) and H-2 (δ = 3.85))



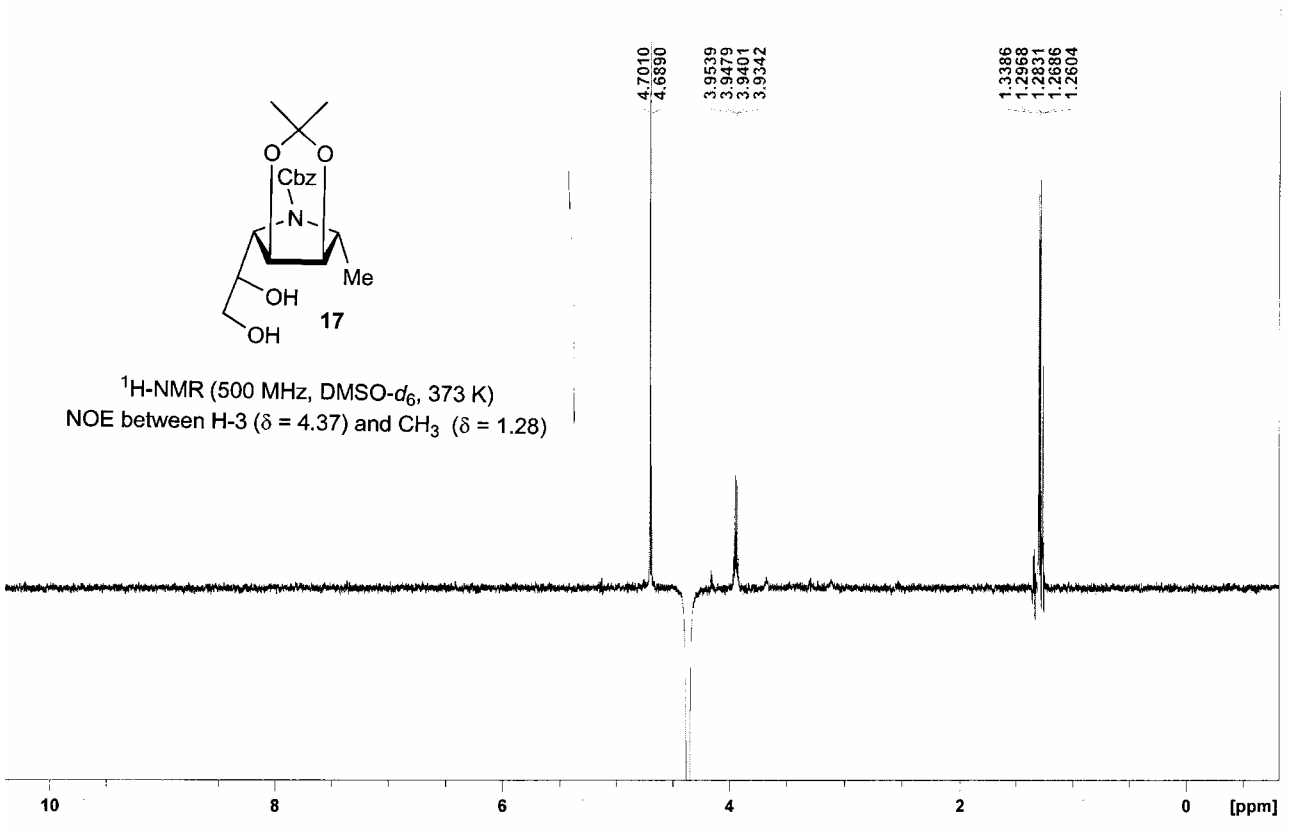
^{13}C-NMR (75.4 MHz, DMSO-d_6, 353 K)



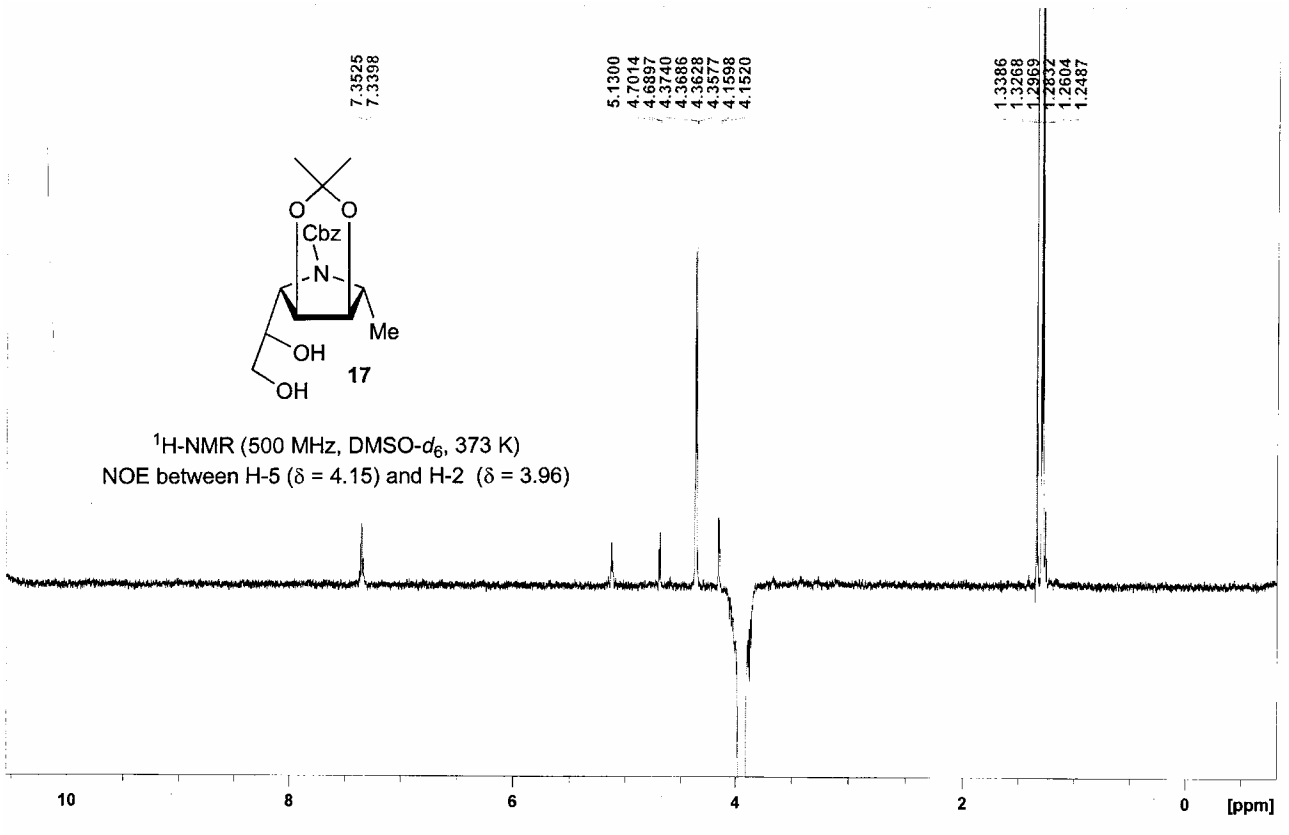


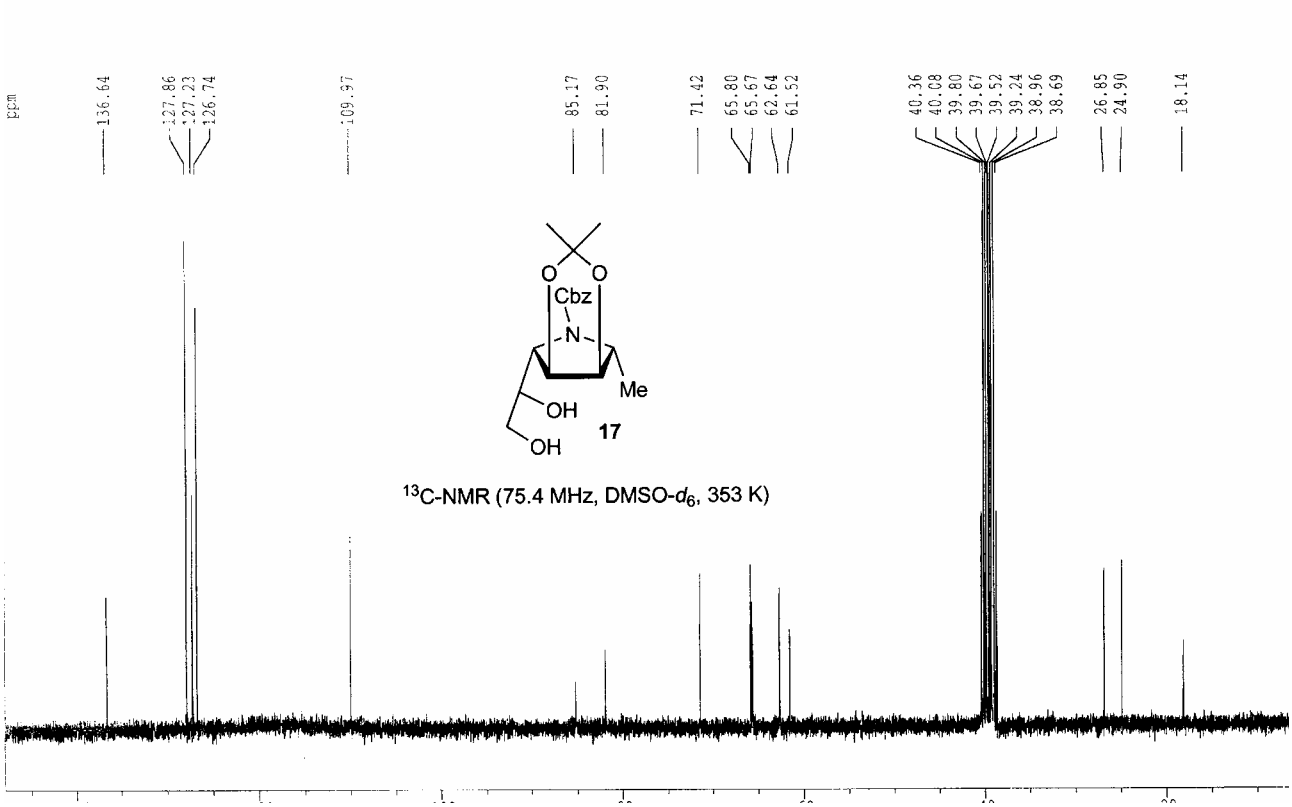


^{1}H-NMR (500 MHz, DMSO-d_6, 373 K)

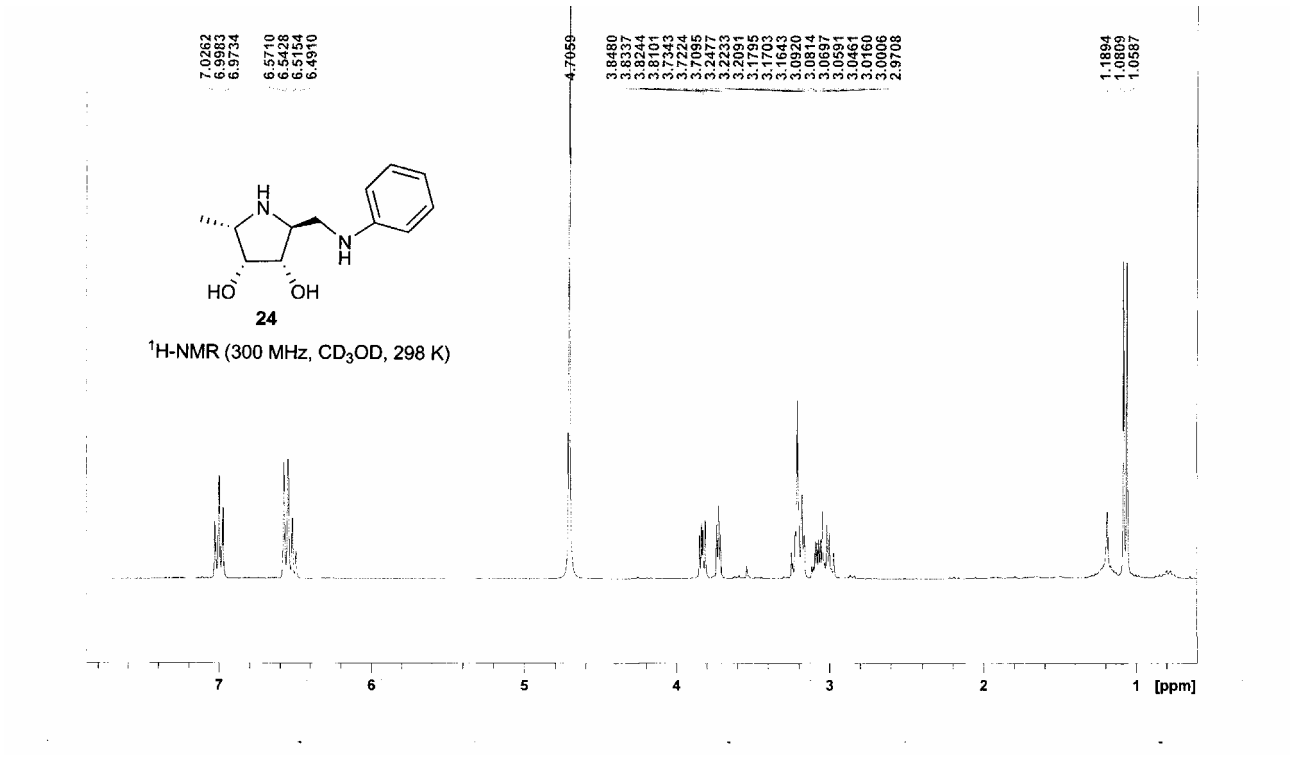


^{1}H-NMR (500 MHz, DMSO-d_6, 373 K)
NOE between H-3 (δ = 4.37) and CH_3 (δ = 1.28)

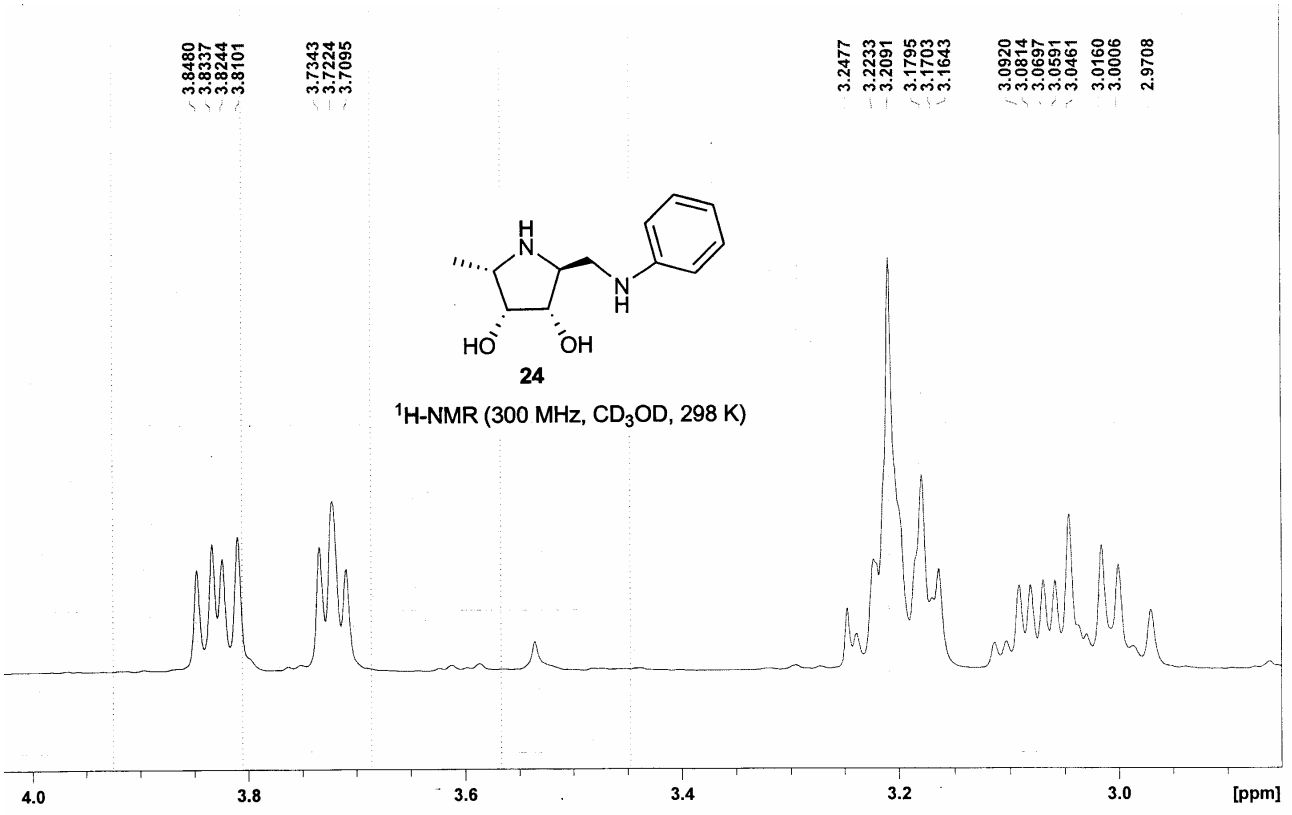


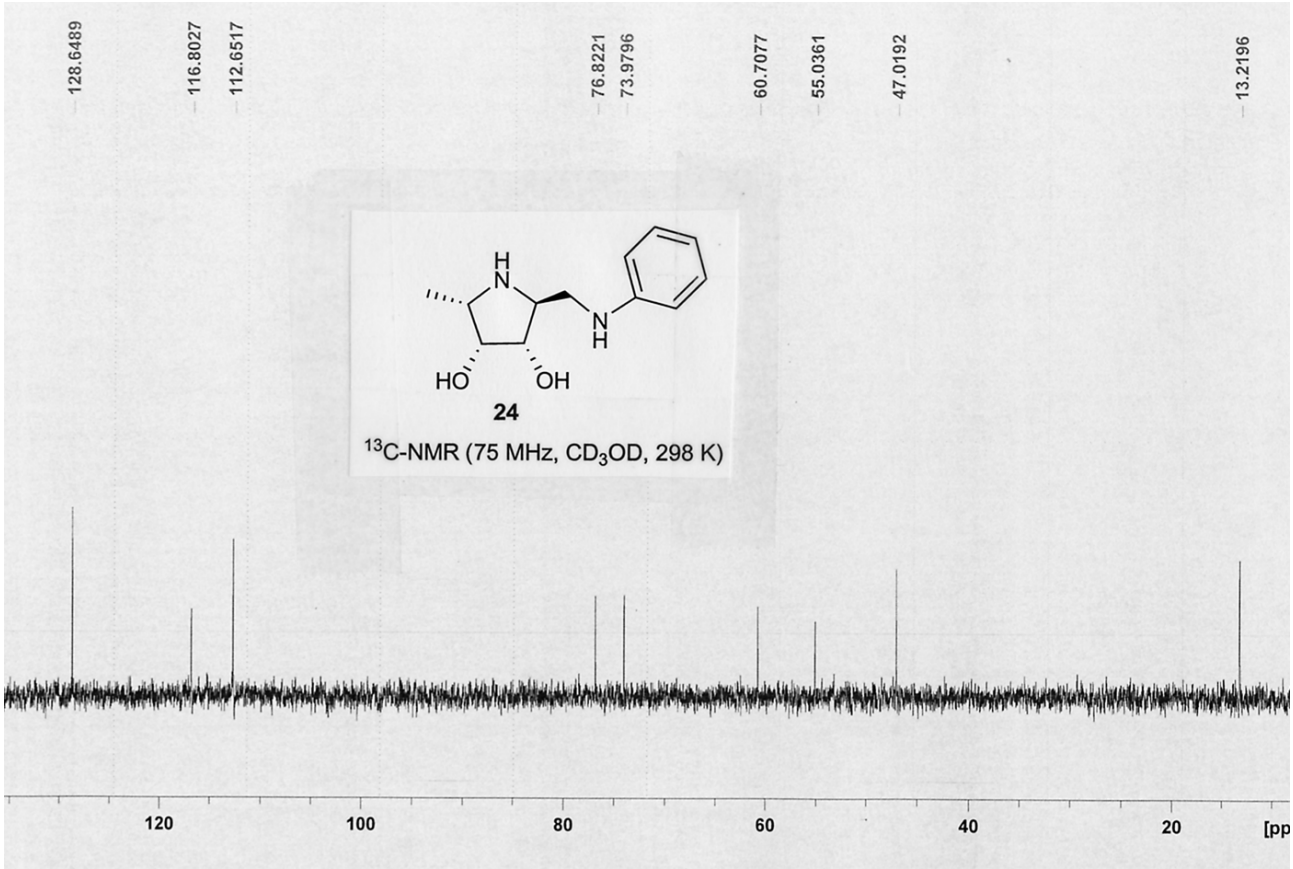


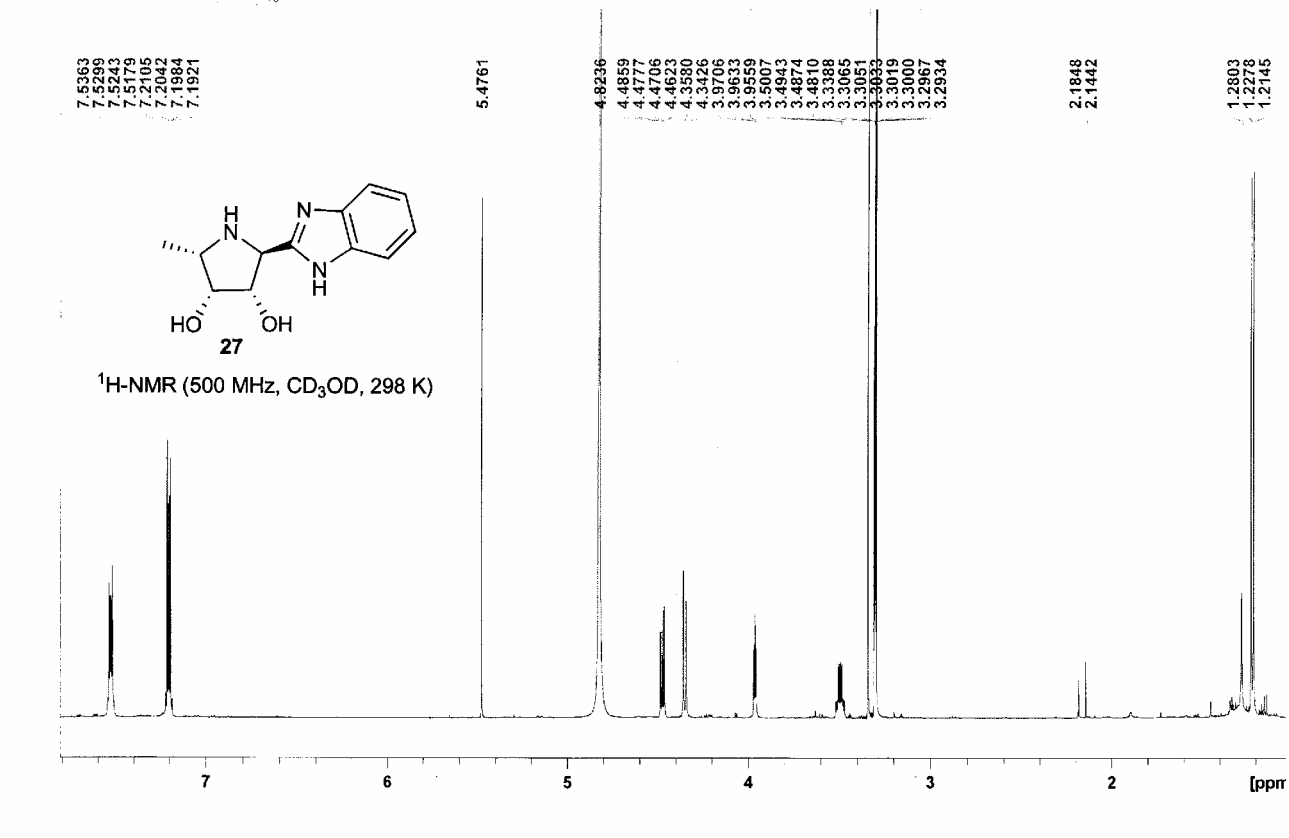
^{13}C-NMR (75.4 MHz, DMSO-d_6, 353 K)

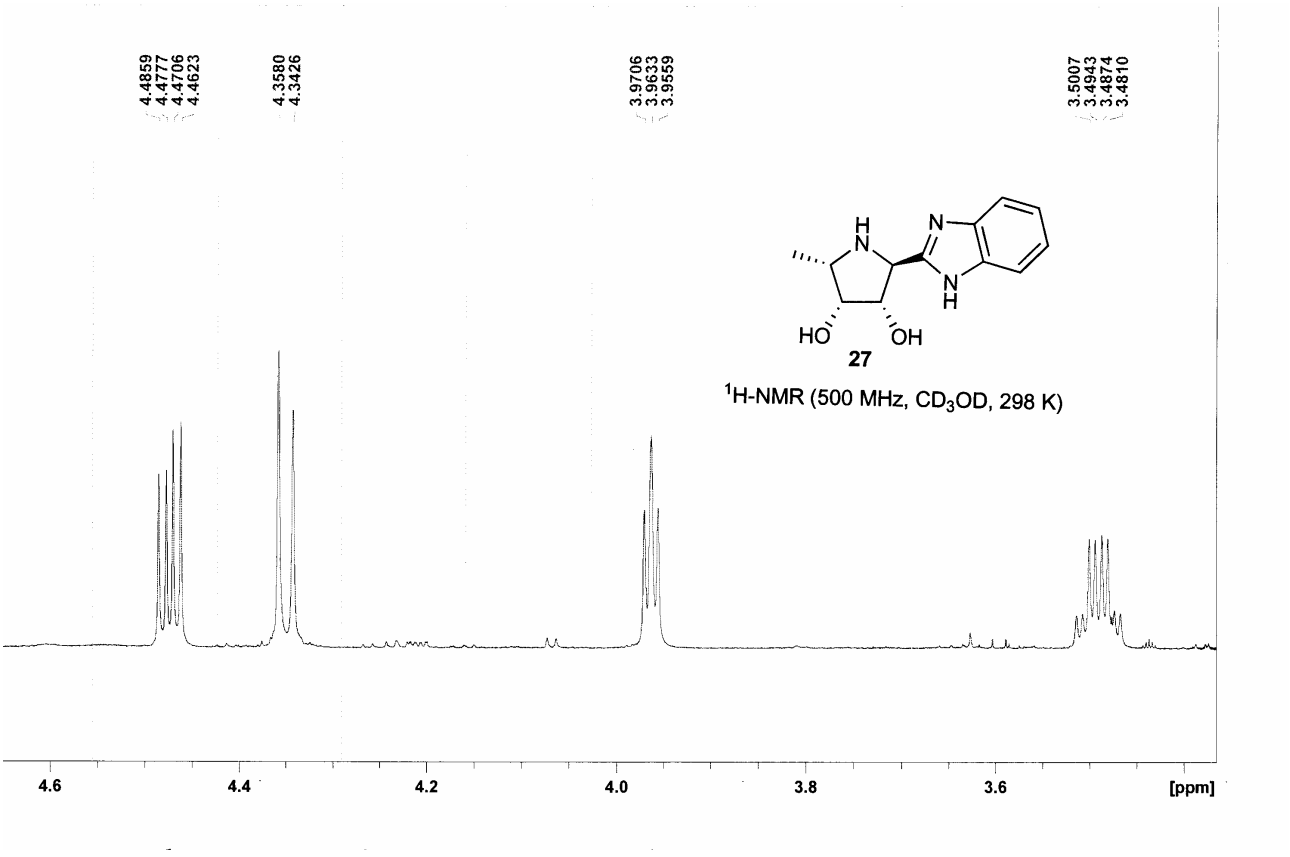


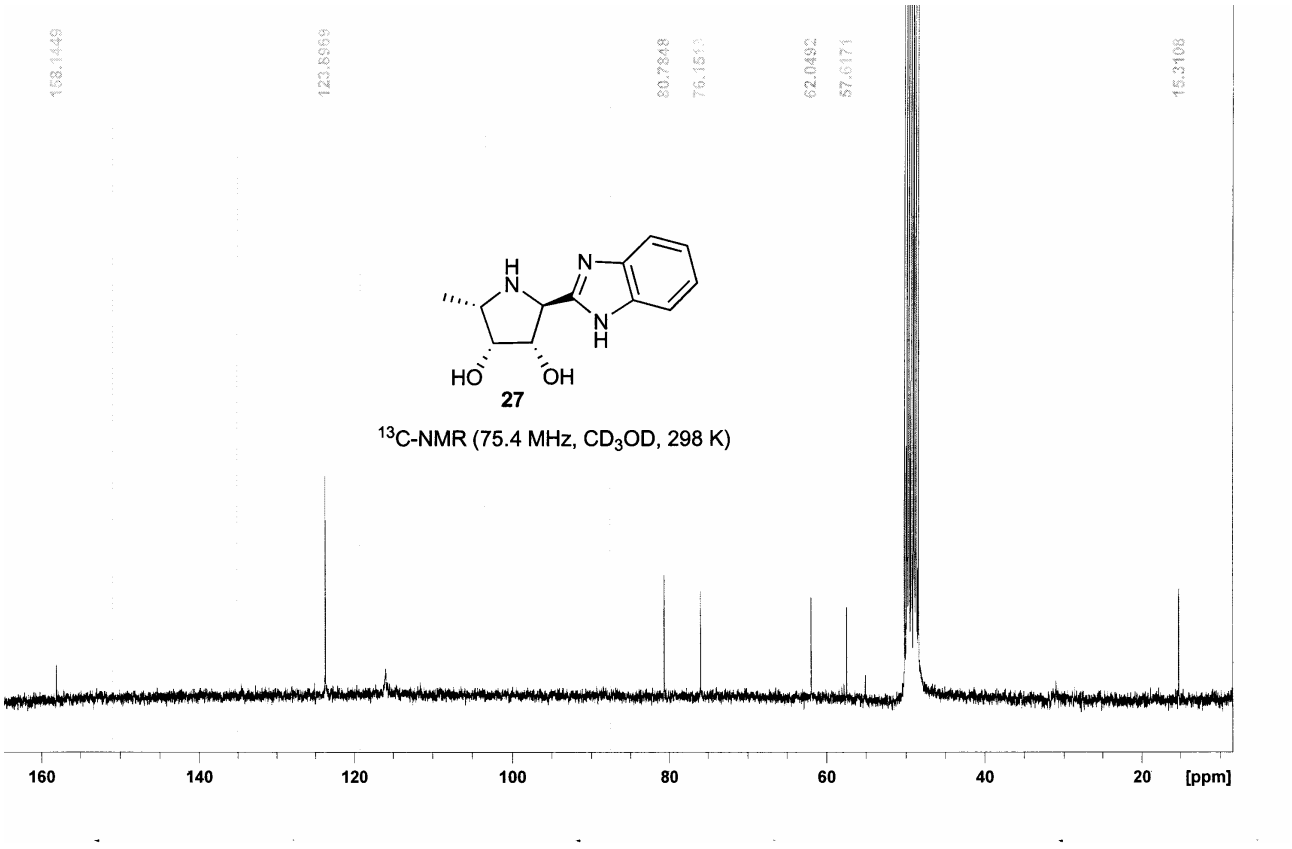
^{1}H-NMR (300 MHz, CD_3OD, 298 K)

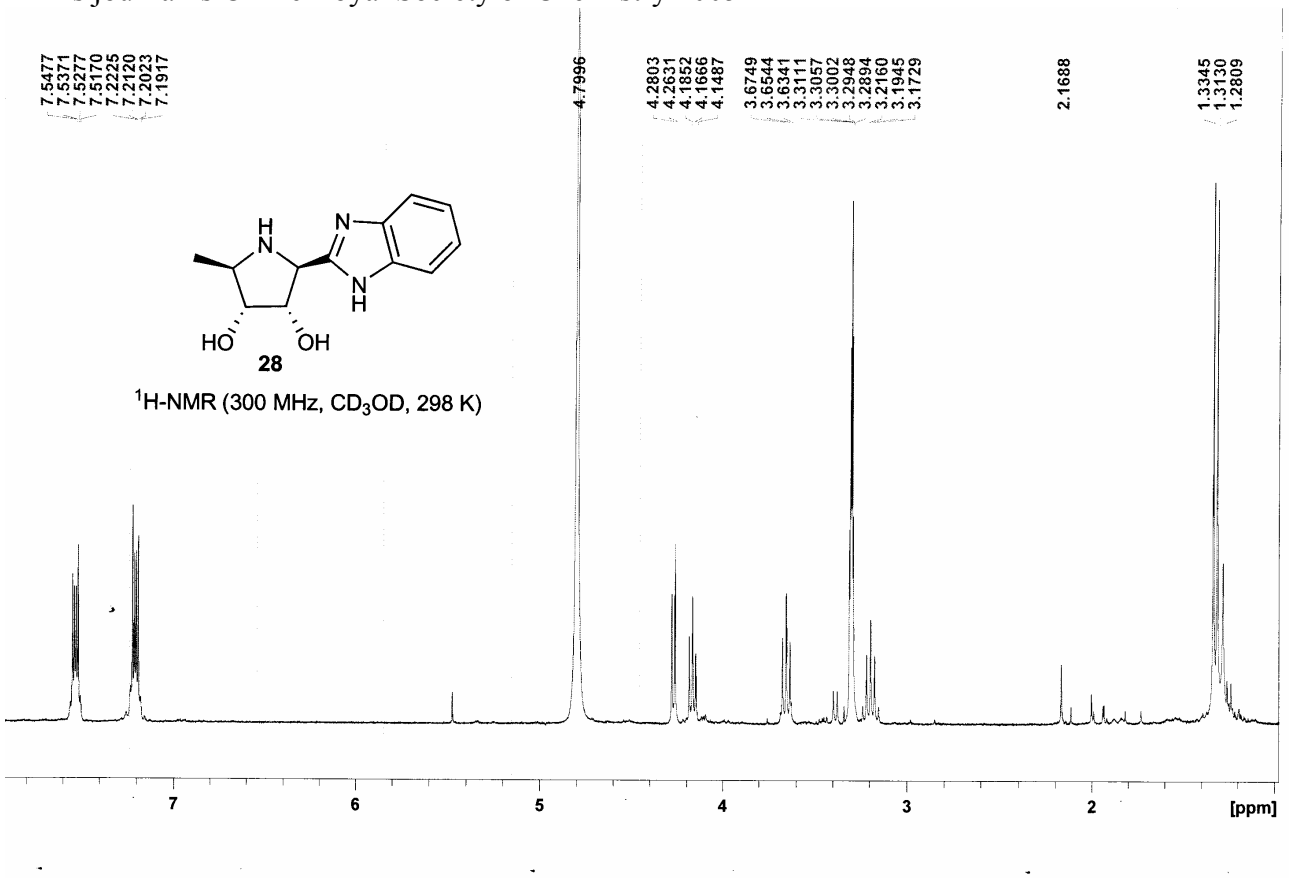




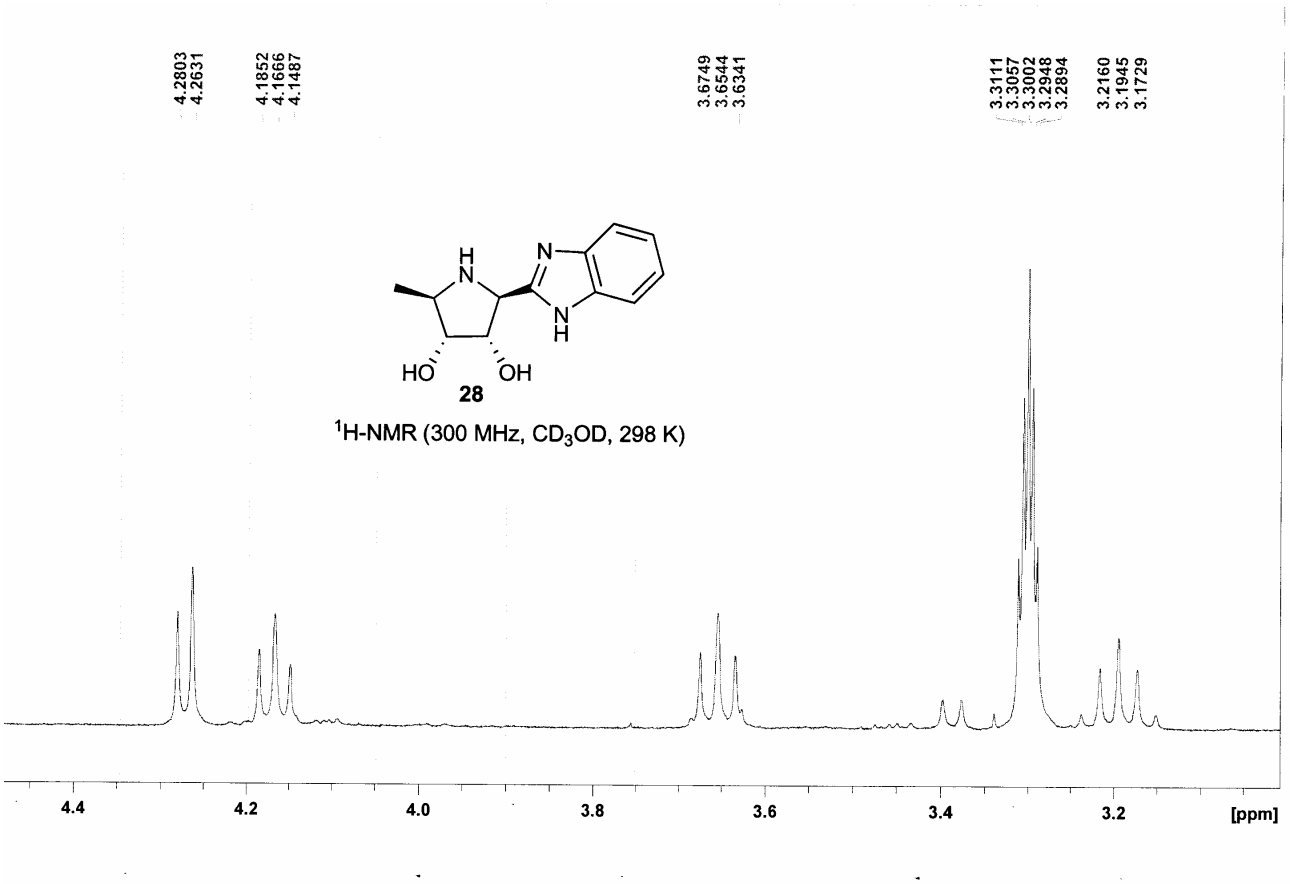








^{1}H-NMR (300 MHz, CD_3OD, 298 K)



^{1}H-NMR (300 MHz, CD_3OD, 298 K)