Supporting Information

A stereoselective Route Towards Polyhydroxylated Piperidines. A Total Synthesis of Deoxymannojirimycin.

Cécile Boglio, Sebastian Stahlke, Serge Thorimbert* and Max Malacria*

Institut de chimie moléculaire (FR 2769). Laboratoire de Chimie Organique (UMR CNRS 7611). Université Pierre et Marie Curie, 4 place Jussieu, 75005 Paris, France

Max.malacria@upmc.fr

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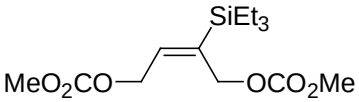
General Experimental Methods : Reagents and chemicals were purchased from commercial sources and used as received. All reactions requiring anhydrous conditions were performed under a positive pressure of argon in oven-dried glassware. All solvents were purified and distilled by standard methods. Thin layer chromatography (TLC) was performed on 0.25 mm E. Merck silica gel (60F-254) plates using UV light, *p*-anisaldehyde or ninhydrine. Column chromatography was carried out on Merck silica gel 60 (40-63 μm). ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR at 100 MHz with the sample solvent being $CDCl_3$ unless otherwise noted (Bruker ARX 400). Chemical shifts are given in ppm, referenced to the residual proton resonances of the solvents. Coupling constants (*J*) are given in Hertz (Hz). The letters m, s, d, t, q mean respectively multiplet, singulet, doublet, triplet, quartet. The letters br mean the signal is broad. IR spectra were recorded on a Bruker Tensor 27 using ATR method. Elemental analysis were carried out by the "Service de microanalyse", ICSN - CNRS, 91198 Gif sur Yvette, France or by the "Service de microanalyse", SIARE, 4 place Jussieu 75252 Paris cedex 05, France.

Compounds **7a**[1] and **8a**[2] have been all ready described by us ([1] Commander, C.; Thorimbert, S.; Malacria, M. *J. Org. Chem.* **2003**, *68*, 5588-5595; [2] Branchadell, V.; Moreno-Manas, M.; Pleixtats, R.; Thorimbert, S.; Commander, C.; Boglio, C.; Malacria, M. *J. Organomet. Chem.* **2003**, *687*, 337-345)

(*E*)-1,4-dimethyloxycarbonyloxy-2-(dimethylphenyl)silyl-but-2-ene (7b)

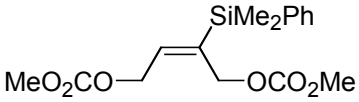


Triethylsilane (1.6 mL, 9.89 mmol, 1 equiv.) was added to a solution of 1,4-dimethyloxycarbonyloxybut-2-yne (2.005 g, 9.89 mmol) in dry THF (25 mL) at room temperature. Then $H_2PtCl_6.6H_20$ (1.98 μmol, 0.2 mL of a 0.01 M solution in THF, 0.02 mol %) was added dropwise and the resulting mixture was refluxing for 24 h. After evaporation of the solvent under vacuum, the crude was purified by flash chromatography (PE/EA = 95/5) or by distillation (bp = 140°C, $7.5.10^{-3}$ mmHg) to afford the silane **7b** (2.82 g, 18.1 mmol, 90% yield) as a colorless oil.

R_f = 0.25 (PE/EA = 9/1) ; IR : 2950, 2900, 1740, 1610, 1430, 1220, 1150, 1020, 730 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.60 (q, *J*= 8.1 Hz, 6H), 0.87 (t, *J*= 8.1 Hz, 9H), 3.73 (s, 3H), 3.74 (s, 3H), 4.73 (s, 2H), 4.79 (d, *J*= 5.8 Hz, 2H), 5.93 (t, *J*= 5.8 Hz, 1H) ; ^{13}C-NMR (100

MHz, $CDCl_3$): □ = 2.7 (CH_2), 7.2 (CH_3), 54.8 (CH_3), 54.9 (CH_3), 64.7 (CH_2), 66.1 (CH_2), 137.3 (C_q), 138.3 (CH), 155.6 (2*C_q). Anal. Calcd. for $C_{14}H_{26}O_6Si$ (318.44) : C 52.81 , H 8.23 ; Found: C 52.87, H 8.31.

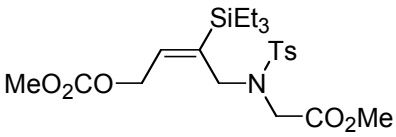
(*E*)-1,4-dimethyloxycarbonyloxy-2-(dimethylphenyl)silyl-but-2-ene (7c)



Dimethylphenylsilane (10 mL, 65 mmol, 1.1 equiv.) was added to a solution of 1,4-dimethyloxycarbonyloxybut-2-yne (12 g, 59 mmol) in dry THF (30 mL) at room temperature. Then $H_2PtCl_6.6H_20$ (1.2 □mol, 1.2 mL of a 0.001 M solution in THF, 0.001 mol %) was added dropwise and the resulting mixture was stirred at 50°C for 5 h. After evaporation of the solvent under vacuum, the crude was purified by flash chromatography (PE/EA = 9/1) to afford the silane **7c** (20.9 g, 61.8 mmol, 95% yield) as a colorless oil.

R_f = 0.25 (PE/EA = 9/1) ; IR : 2957, 1746, 1442, 1244, 1111, 957, 818, 790, 777, 733, 701 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$): □ = 0.43 (s, 6H), 3.61 (s, 3H), 3.72 (s, 3H), 4.79 (s, 2H), 4.82 (d, *J* = 5.8 Hz, 2H), 6.05 (t, *J* = 5.8 Hz, 1H), 7.31-7.33 (m, 3H), 7.49-7.51 (m, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): □ = -3.00 (2*CH_3), 54.5 (CH_3), 54.7 (CH_3), 64.6 (CH_2), 66.0 (CH_2), 127.8 (2*CH), 129.3 (CH), 134.0 (2*CH), 136.7 (C_q), 138.2 (CH), 139.1 (C_q), 155.3 (C_q), 155.5 (C_q) ; Anal. Calcd. for $C_{16}H_{22}O_6Si$ (338.12) : C 56.78 , H 6.55 ; Found: C 56.73, H 6.67.

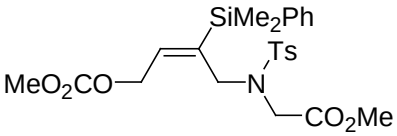
(*E*)-[(4-Methoxycarbonyloxy-2-triethylsilanyl-but-2-enyl)-(toluene-4-sulfonyl)-amino]-acetic acid methyl ester (8b)



Palladium acetate (3.53 mg, 0.016 mmol, 0.05 equiv.) and diphenylphosphinoethane (12.4 mg, 0.032 mmol, 0.10 equiv.) were diluted in *i*-PrOH (1 mL) and heated at 50°C for 30 min. The catalyst was then transfered with a cannula to a solution of N-tosylglycinemethylester (150.7 mg, 0.62 mmol, 2 equiv.), the dicarbonate **7b** (100 mg, 0.314 mmol) and triethylamine (0.09 mL, 0.62 mmol, 2 equiv.) in *i*-PrOH (1 mL) at the same temperature. The resulting reaction mixture was stirred for 1 h at 50°C, then hydrolysed with a solution of aqueous NH_4Cl (10 mL). After extraction with diethyl ether the organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. After purification by

flash chromatography (PE/EA = 8/2) **8b** (114 mg, 0.24 mmol, 75% yield) was obtained as a colorless oil. R_f = 0.25 (PE/EA = 8/2) ; IR : 2950, 2875, 1740, 1440, 1340, 1260, 1160, 1090, 720 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.69 (q, *J*= 7.8 Hz, 6H), 0.92 (t, *J*= 7.8 Hz, 9H), 2.44 (s, 3H), 3.48 (s, 3H), 3.78 (s, 3H), 3.99 (s, 2H), 4.18 (s, 2H), 4.71 (d, *J*= 6.1 Hz, 2H), 6.08 (t, *J*= 6.1 Hz, 1H), 7.32 (d, *J*= 8.3 Hz , 2H), 7.69 (d, *J*= 8.3 Hz, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 2.6 (3*CH_2), 7.4 (3*CH_3), 21.7 (CH_3), 45.7 (CH_2), 45.75 (CH_2), 52.0 (CH_3), 55.0 (CH_3), 64.3 (CH_2), 127.6 (2*CH), 129.6 (2*CH), 136.3 (C_q), 137.1 (C_q), 141.1 (CH), 143.6 (C_q), 155.6 (C_q), 169.3 (C_q) ; $C_{22}H_{35}NO_7SSi$ (485.67) : C 54.41, H 7.26, N 2.88 ; Found : C 54.30, H 7.44, N 3.00.

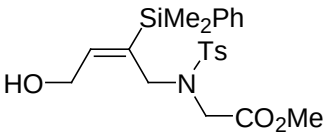
(*E*)-[[2-(Dimethyl-phenyl-silanyl)-4-methoxycarbonyloxy-but-2-enyl]-(toluene-4-sulfonyl)-amino]-acetic acid methyl ester (8c)



Palladium acetate (300 mg, 1.3 mmol, 0.025 equiv.) and diphenylphosphinoethane (1.050 g, 2.6 mmol, 0.05 equiv.) were diluted in *i*-PrOH (110 mL) and heated at 55°C for 30 min. The catalyst was then transfered with a cannula to a solution of N-tosylglycinemethylester (15.5 g, 63.4 mmol, 1.2 equiv.), the dicarbonate **7c** (17.92 g, 53 mmol) and triethylamine (8.9 mL, 64 mmol, 1.2 equiv.) in *i*-PrOH (140 mL) at the same temperature. The resulting solution was stirred for 1 h at 55°C, then cooled with an ice bath and aqueous NH_4Cl (50 mL) was added. After extraction with diethyl ether the organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. After purification by flash chromatography (PE/EA = 85/15) **8c** (19.06 g, 37.7 mmol) was obtained in 71% yield as a 95/5 mixture of *E/Z* stereoisomers.

white solid, mp : 92-94°C ; R_f = 0.25 (PE/EA = 8/2) ; IR: 2954, 1745, 1598, 1440, 1340, 1262, 1158, 1092, 911.0, 815, 734, 701 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.48 (s, 6H), 2.44 (s, 3H), 3.41 (s, 3H), 3.63 (s, 2H), 3.77 (s, 3H), 4.21 (s, 2H), 4.69 (d, *J* = 6.0 Hz, 1H), 6.12 (t, *J* = 6.0 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.37-7.39 (m, 3H), 7.52-7.54 (m, 2H), 7.63 (d, *J* = 8.6 Hz, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = -3.3 (2*CH_3), 21.6 (CH_3), 45.6 (CH_2), 45.7 (CH_2), 51.7 (CH_3), 54.9 (CH_3), 64.2 (CH_2), 127.5 (2*CH), 127.9 (2*CH), 129.4 (3*CH), 134.1 (2*CH), 136.1 (C_q), 136.6 (C_q) 138.8 (C_q), 141.1 (CH), 143.5 (C_q), 155.5 (C_q), 168.7 (C_q) ; Anal. Calcd. for $C_{24}H_{31}NO_7SSi$ (505.66) : C 57.01, H 6.18, N 2.77 ; Found : C 57.00, H 6.22, N 2.71.

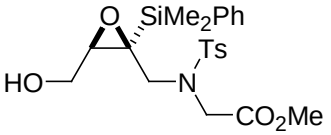
(*E*)-**[[2-(Dimethyl-phenyl-silanyl)-4-hydroxy-but-2-enyl]-(toluene-4-sulfonyl)-amino]-acetic acid methyl ester (6)**



Potassium carbonate (800 mg, 5.8 mmol, 0.2 equiv.) was added to a solution of aminosilane **7c** (15 g, 29 mmol) in MeOH (120 mL). The resulting suspension was stirred at room temperature. After 2 h, the methanol was removed under reduced pressure and AcOEt was added. The organic phase was washed with water. After extraction with AcOEt, the organic layers were washed with brine, dried over $MgSO_4$ and concentrated to afford **6** (12.98 g, 29 mmol, quantitative yield). The conversion was quantitative by NMR.

R_f = 0.2 (PE/EA = 7/3) ; IR: 3539, 2953, 1739, 1598, 1338, 1248, 1212, 1109, 815, 736, 701 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.44 (s, 6H), 2.43 (s, 3H), 3.43 (s, 3H), 3.59 (s, 2H), 4.10 (s, 2H), 4.19 (d, *J* = 6.1 Hz, 2H), 6.25 (t, *J* = 6.1 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.35-7.37 (m, 3H), 7.49-7.51 (m, 2H), 7.63 (d, *J* = 8.3 Hz, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = -3.4 (2*CH_3), 21.3 (CH_3), 45.7 (2*CH_2), 51.5 (CH_3), 58.6 (CH_2), 127.3 (2*CH), 127.7 (2*CH), 129.1 (CH), 129.4 (2*CH), 133.9 (2*CH), 134.3 (C_q), 136.0 (C_q), 137.1 (CH), 143.4 (C_q), 148.2 (C_q), 169.1 (C_q).

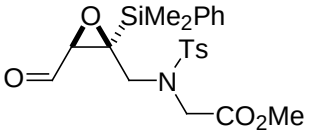
(2*R, 3*R**)-[[2-(Dimethyl-phenyl-silanyl)-3-hydroxymethyl-oxiranylmethyl]-(toluene-4-sulfonyl)-amino]-acetic acid methyl ester (10)**



A solution of the allylic alcohol **6** (10.1 g, 22.6 mmol) in CH_2Cl_2 (100 mL) was cooled to 0°C. Then *m*-CPBA (12 g, 50 mmol, 70% *m*-CPBA in H_2O, 2.2 equiv.) was added by portion. The resulting suspension was stirred at room temperature for 3 h. The reaction mixture was filtered over celite and then treated with aqueous NaOH (50 mL of a 1M solution). The organic layer was seperated and the aqueous phase was extracted with CH_2Cl_2 (3*100 mL). The combined organic layers were neutralized with aqueous NH_4Cl washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The product could be purified on a silica gel column in order to afford **10** (7.86 g, 16.95 mmol, 75% yield) as a colorless oil.

R_f = 0.25 (PE/EA = 7/3) ; IR: 3538, 2953, 1746, 1598, 1428, 1338, 1250, 1213, 1156, 1097, 837, 735, 701 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.48 (s, 3H), 0.54 (s, 3H), 2.42 (s, 3H), 2.97 (t, *J* = 5.5 Hz, 1H), 3.38 (s, 3H), 3.41 (d, *J* = 15 Hz, 1H), 3.66 (d, *J* = 18.5 Hz, 1H), 3.71 (d, *J* = 5.5 Hz, 2H), 3.92 (d, *J* = 16 Hz, 1H), 3.93 (d, *J* = 17 Hz, 1H), 7.26 (d, *J* = 8 Hz, 2H), 7.34 to 7.41 (m, 3H), 7.54 to 7.62 (m, 4H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = -5.0 (CH_3), -4.9 (CH_3), 21.5 (CH_3), 47.2 (CH_2), 47.6 (CH_2), 51.7 (CH_3), 55.8 (C_q), 58.9 (CH), 60.2 (CH_2), 127.4 (2*CH), 127.9 (2*CH), 129.5 (2*CH), 129.7 (CH), 134.4 (2*CH), 135.1 (C_q), 136.0 (C_q), 143.6 (C_q), 168.9 (C_q) ; HRMS calcd. for $C_{22}H_{29}NO_6SSiNa$ 486.1383, found 486.1373

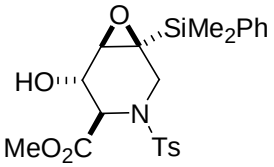
(2*R, 3*R**)-[[2-(Dimethyl-phenyl-silanyl)-3-formyl-oxiranylmethyl]-(toluene-4-sulfonyl)-amino]-acetic acid methyl ester (5)**



A solution of IBX (15.4 mmol, 4.3 g, 1.1 equiv.) in DMSO (50 mL) was transfered by a cannula to a solution of the epoxy alcohol **10** (14 mmol, 6.6 g) in DMSO. The resulting mixture was stirred for 3 h at room temperature, then cooled to 0°C and aqueous $NaHCO_3$ (10 mL) was added dropwise. Further $NaHCO_3$ (40 mL) was added. The solution was filtered off the white precipitate and extracted with ether (200 mL). The organic layer was then washed with brine (30 mL) and dried over $MgSO_4$.

R_f = 0.3 (PE/EA = 5/5) ; IR: 2953, 1746, 1718, 1597, 1428, 1341, 1253, 1213, 1159, 1041, 917, 838, 815, 736, 700 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.52 (s, 3H), 0.59 (s, 3H), 2.39 (s, 3H), 3.12 (d, *J* = 4.5 Hz, 1H), 3.38 (s, 3H), 3.56 (d, *J* = 14.6 Hz, 1H), 3.72 (d, *J* = 18.9 Hz, 1H), 3.94 (d, *J* = 18.9 Hz, 1H), 3.96 (d, *J* = 14.6 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.39 to 7.41 (m, 3H), 7.55 to 7.61 (m, 4H), 9.44 (d, *J* = 4.5 Hz, 1H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = -5.2 (CH_3), -4.9 (CH_3), 21.6 (CH_3), 47.0 (CH_2), 47.3 (CH_2), 51.8 (CH_3), 59.8 (C_q), 61.0 (CH), 127.4 (2*CH), 128.1 (2*CH), 129.6 (2*CH), 130.2 (CH), 133.8 (C_q), 134.4 (2*CH), 135.7 (C_q), 143.8 (C_q), 168.5 (C_q), 198.8 (CHO) ; Anal. Calcd. for $C_{22}H_{27}NO_6SSi$ (461.13) : C 57.24, H 5.90, N 3.03 ; Found: C 57.15, H 6.02, N 3.05.

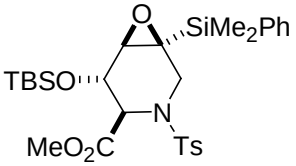
(1*R, 4*R**, 5*S**, 6*R**)-1-(Dimethyl-phenyl-silanyl)-5-hydroxy-3-(toluene-4-sulfonyl)-7-oxa-3-aza-bicyclo[4.1.0]heptane-4-carboxylic acid methyl ester (4)**



Diazabicycloundecene (1.21 mL, 8.06 mmol, 1.2 equiv.) was added to a solution of epoxyaldehyde **5** (3.10 g, 6.72 mmol) in dry THF (100 mL). The solution was stirred for 18 h at room temperature. Then aqueous NH_4Cl (200 mL) was added and the aqueous layer was extracted with EtOAc (3*100 mL). The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The crude was purified by flash chromatography on silica gel (Pentane/EA = 7/3) to afford **4** (2.42 g, 5.24 mmol, 78% yield) as a colorless sticky oil at room temperature.

R_f = 0.5 (PE/EA = 6/4) ; IR: 3491, 2954, 1736, 1597, 1428, 1329, 1251, 1213, 1158, 1100, 1030, 813, 783, 702 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.31 (s, 3H), 0.36 (s, 3H), 2.42 (3H), 3.10 (d, *J* = 2.6 Hz, 1H), 3.56 (d, *J* = 14 Hz, 1H), 3.57 (s, 3H), 3.87 (d, *J* = 14 Hz, 1H), 4.59 (d, *J* = 2.6 Hz, 1H), 4.80 (s, 1H), 7.22 to 7.49 (m, 7H), 7.64 (d, *J* = 8.3 Hz, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = -5.9 (CH_3), -5.8 (CH_3), 21.6 (CH_3), 40.8 (CH_2), 52.1 (CH_3), 52.6 (C_q), 58.2 (CH), 60.5 (CH), 66.7 (CH), 127.5 (2*CH), 128.1 (2*CH), 129.5 (2*CH), 130.0 (CH), 133.8 (C_q), 134.1 (2*CH), 135.7 (C_q), 143.6 (C_q), 168.0 (C_q) ; Anal. Calcd. for $C_{22}H_{27}NO_6SSi$ (461.13) : C 57.24, H 5.90, N 3.03 ; Found: C 56.84, H 5.85, N 3.22.

(1*R, 4*R**, 5*S**, 6*R**)-5-(tert-Butyl-dimethyl-silanyloxy)-1-(dimethyl-phenyl-silanyl)-3-(toluene-4-sulfonyl)-7-oxa-3-aza-bicyclo[4.1.0]heptane-4-carboxylic acid methyl ester (12)**

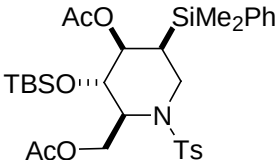


Imidazole (0.6 g, 8.2 mmol, 2.0 equiv.) was added to a solution of alcohol **4** (2.0 g, 4 mmol) in DMF (7 mL). The solution was cooled to 0°C and dimethyltertbutylsilylchloride (1.0 g, 6.5 mmol, 1.6 equiv.) was added, the resulting reaction mixture was stirred for 16 h at room temperature. Then aqueous NH_4Cl (30 mL) was added. The aqueous layer was extracted with ether (3*100 mL), dried over Na_2SO_4 and concentrated under reduce pressure. The crude

purified by column chromatography on silica gel (PE/EA = 9/1 to 8/2) affords **12** as a white cristallin solid (3.59 g, 6.24 mmol, 96% yield).

white solid, mp 74-75°C ; R_f = 0.7 (PE/EA = 8/2) ; IR : 2953, 2922, 2857, 1754, 1735, 1598, 1429, 1336, 1253, 1199, 1162, 1100, 1035, 835, 813, 779, 732, 701 ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 3H), 0.20 (s, 3H), 0.21 (s, 3H), 0.33 (s, 3H), 0.97 (s, 9H), 2.41 (s, 3H), 2.99 (dd, *J* = 2.5, 0.7 Hz, 1H), 3.58 to 3.64 (m, 2H), 3.69 (s, 3H), 4.65 (d, *J* = 2.5 Hz, 1H), 4.93 (t, *J* = 2.5 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.28 to 7.37 (m, 5H), 7.70 (d, *J* = 8.3 Hz, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = -5.9 (2*CH_3), -4.8 (2*CH_3), 18.2 (C_q), 21.5 (CH_3), 25.7 (3*CH_3), 40.7 (CH_2), 52.0 (C_q), 52.3 (CH_3), 55.6 (CH), 58.2 (CH), 67.6 (CH), 127.5 (2*CH), 128.1 (2*CH), 129.3 (2*CH), 129.8 (CH), 133.9 (2*CH), 134.0 (C_q), 136.6 (C_q), 143.0 (C_q), 168.8 (C_q) ; Anal. Calcd. for $C_{28}H_{41}NO_6SSi_2$ (575.22) : C 58.40, H 7.18, N 2.43 ; Found: C 58.37, H 7.36, N 2.27.

(2*S, 3*S**, 4*R**, 5*S**)-Acetic acid 2-acetoxymethyl-3-(tert-butyl-dimethyl-silanyloxy)-5-(dimethyl-phenyl-silanyl)-1-(toluene-4-sulfonyl)-piperidin-4-yl ester (13)**

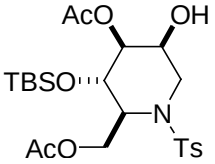


A solution of **12** (2.1 g, 3.6 mmol) in dry diethylether (75 mL) was cooled to 0°C. Then $LiAlH_4$ (0.6 g, 15 mmol, 4.2 equiv.) was added by portion. The resulting reaction mixture was stirred at room temperature for 10 h. Then aqueous Na_2SO_4 (5 mL) was added dropwise. The suspension was filtered off, and the white precipitate was washed with diethylether and ethylacetate. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The product was not purified but directly acetylated. The crude (1.98 g, 3.6 mmol) was solubilized in dry CH_2Cl_2 (4 mL). Then DMAP (0.03 g, 0.24 mmol, 0.1 equiv.) and NEt_3 (2.0 mL, 14 mmol, 5.8 equiv.) were added. The solution was cooled to 0°C and acetic anhydride (1.1 mL, 12 mmol, 5.0 equiv.) was added dropwise. The solution was stirred at room temperature for 24 h and aqueous NH_4Cl (10 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3*50 mL) and the combined organic layers were washed with brine and dried over Na_2SO_4. The crude was purified by column chromatography on silica gel (PE/EA = 9/1 to 0/10) to afford **13** (1.25 g, 1.98 mmol, 54% yield, two steps, 6% yield of **14**).

white solid, mp 116-118°C ; R_f = 0.5 (PE/EA = 8/2) ; IR : 2953, 2922, 2856, 1742, 1598, 1325, 1224, 1160, 1099, 1037, 835, 812, 776, 734, 700 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ

= 0.13 (s, 3H), 0.18 (s, 3H), 0.23 (s, 3H), 0.27 (s, 3H), 0.95 (s, 9H), 1.63 (ddd, *J* = 7.2 Hz, 7.0 Hz and 1.6 Hz, 1H), 1.96 (s, 3H), 2.10 (s, 3H), 2.44 (s, 3H), 3.36 to 3.38 (m, 2H), 3.82 (dd, *J* = 3.3 Hz, 1.6 Hz, 1H), 4.22 (dd, *J* = 11 Hz, 7 Hz, 1H), 4.35 (dd, *J* = 11 Hz, 8 Hz, 1H), 4.43 (dd, *J* = 8 Hz, 7 Hz, 1H), 4.80 (m, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.30 to 7.38 (m, 5H), 7.77 (d, *J* = 8.1 Hz, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = -5.2 (CH_3), -5.15 (CH_3), -4.7 (CH_3), -4.5 (CH_3), 18.0 (C_q), 20.6 (CH_3), 20.7 (CH_3), 21.3 (CH_3), 22.0 (CH), 25.6 (3*CH_3), 37.2 (CH_2), 57.0 (CH), 60.6 (CH_2), 64.2 (CH), 71.1 (CH), 127.5 (2*CH), 127.9 (2*CH), 129.2 (2*CH), 129.3 (CH), 133.2 (2*CH), 135.7 (C_q), 137.8 (C_q), 142.8 (C_q), 169.3 (C_q), 170.4 (C_q) ; Anal. Calcd. for $C_{31}H_{47}NO_7SSi_2$ (633.26) : C 58.73, H 7.47, N 2.21 ; Found: C 58.62, H 7.39, N 2.15.

(2*S, 3*S**, 4*R**, 5*S**)-Acetic acid 4-acetoxy-3-(tert-butyl-dimethyl-silanyloxy)-5-hydroxy-1-(toluene-4-sulfonyl)-piperidin-2-ylmethyl ester (15)**

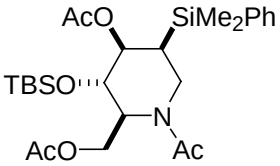


Peracetic acid (7.5 mL of a 33% solution in HOAc, 65 mmol, #50 equiv.) was introduced to a solution of **13** (0.8 g, 1.26 mmol) in acetic acid (11.5 mL). Then mercury acetate (0.63 g, 2.0 mmol, 1.6 equiv.) was added and the resulting suspension was stirred at room temperature for 18 h. The solution was cooled to 0°C and ethyl acetate was added, then the reaction mixture was slowly quenched with a satured aqueous solution of $Na_2S_2O_3$. The layers were separated and the aquous phase was extracted with ethyl acetate. The organic layers were washed with a satured solution of $NaHCO_3$, then with brine and dryed over $MgSO_4$. After concentration in vacuo, the crude was purified by flash chromatography on silica gel (PE/EA = 7/3) to afford **15** as white cristals (422 mg, 0.82 mmol, 65% yield).

white solid, mp 137-140°C ; IR : 3492, 2953, 2932, 2860, 1753, 1729, 1594, 1332, 1266, 1240, 1224, 1165, 1100, 1036, 936, 843, 818, 780, 734, 710, 691 cm^{-1}; R_f = 0.4 (PE/EA = 6/4) ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.14 (s, 3H), 0.16 (s, 3H), 0.92 (s, 9H), 2.07 (s, 3H), 2.10 (s, 3H), 2.41 (s, 3H), 3.08 (dd, *J* = 13.5 Hz, 11.4 Hz, 1H), 3.48 (dd, *J* = 5.4 Hz, 3.55 Hz, 1H), 3.97 (ddd, *J* = 11.4 Hz, 5.4 Hz, 3 Hz, 1H), 4.03 (d, *J* = 3.5 Hz, 1H), 4.20 (dd, *J* = 10.1 Hz, 5.5 Hz, 1H), 4.30 (dd, *J* = 10.1 Hz, 8.4 Hz, 1H), 4.33 (d, *J* = 8.4 Hz, 1H), 4.93 (dd, *J* = 3.3 Hz, 3.1 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = -5.2 (CH_3), -5.0 (CH_3), 18.2 (C_q), 20.8 (CH_3), 20.9 (CH_3), 21.5 (CH_3), 25.8 (3*CH_3), 41.4

(CH_2), 56.7 (CH), 60.5 (CH_2), 62.8 (CH), 67.4 (CH) , 72.7 (CH), 127.5 (2*CH), 129.6 (2*CH), 137.6 (C_q), 143.5 (C_q), 170.4 (C_q), 170.8 (C_q) ; Anal. Calcd. for $C_{23}H_{37}NO_8SSi$ (515.20) : C 53.57, H 7.23, N 2.72 ; Found: C 53.81, H 7.14, N 2.61. HRMS calcd. for $C_{23}H_{37}NO_8SSiNa$ 538.1907, found 538.1884.

(2*S, 3*S**, 4*R**, 5*S**)-Acetic acid 4-acetoxy-1-acetyl-3-(tert-butyl-dimethyl-silanyloxy)-5-(dimethyl-phenyl-silanyl)-piperidin-2-ylmethyl ester (14)**

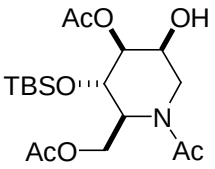


A solution of **12** (450 mg, 0.708 mmol) in dry diethylether (15 mL) was cooled to 0°C. Then $LiAlH_4$ (152 mg, 3.91 mmol, 5 equiv.) was added by portion. The resulting reaction mixture was stirred at room temperature for 48 h. Then few drops of aqueous Na_2SO_4 were added. The suspension was filtered off, and the white precipitate was washed with ethylacetate. The organic layer was dried over $MgSO_4$ and concentrated under reduce pressure. The crude was solubilized in dry CH_2Cl_2 (2 mL). Then, DMAP (8.6 mg, 0.07 mmol, 0.1 equiv.) and NEt_3 (0.60 mL, 4.25 mmol, 6 equiv.) were added. The solution was cooled to 0°C and acetic anhydride (0.67 mL, 7.08 mmol, 10 equiv.) was added dropwise. The solution was stirred at room temperature for 16 h and aqueous NH_4Cl (5 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3*5 mL) and the combined organic layers were washed with brine and dried over Na_2SO_4. After evaporation of the solvant, the crude was purified by column chromatography on silica gel (pentane/EA = 85/15) and **14** (289 mg, 0.55 mmol, 78% yield, two steps) was obtained as white cristals.

white solid, mp 48-50°C ; R_f = 0.2 (PE/EA = 7/3) ; IR : 2953, 2930, 2856, 1742, 1632, 1429, 1365, 1252, 1221, 1084, 1030, 834, 776, 739, 703 cm^{-1}; 2 rotamers were observed by NMR : 1) major ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.02 (s, 3H), 0.05 (s, 3H), 0.32 (s, 3H), 0.34 (s, 3H), 0.85 (s, 9H), 1.71 (ddd, *J* = 13.6 Hz, 4.0 Hz, 2.3 Hz, 1H), 1.88 (s, 3H), 2.02 (s, 3H), 2.09 (s, 3H), 2.86 (t, *J* = 13.6 Hz, 1H), 3.69 (m, 1H), 3.98 to 4.17 (m, 2H), 4.33 to 4.39 (m, 1H), 4.62 to 4.67 (m, 2H), 7.33 to 7.36 (m, 5H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = -5.3 (CH_3), -5.0 (CH_3), -4.2 (CH_3), -4.1 (CH_3), 17.9 (C_q), 20.7 (CH_3), 20.9 (CH_3), 21.2 (CH_3), 23.4 (CH_3), 25.6 (3*CH_3), 33.2 (CH_2), 59.1 (CH), 61.0 (CH_2), 65.3 (CH), 71.7 (CH), 128.0 (2*CH), 129.5 (CH), 133.6 (2*CH), 136.2 (C_q), 169.6 (C_q), 170.4 (C_q), 170.5 (C_q) 2) minor ^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 0.06 (s, 3H), 0.07 (s, 3H), 0.31 (s, 3H), 0.34 (s, 3H), 0.85 (s, 9H),

1.80 (m, 1H), 1.92 (s, 3H), 1.96 (s, 3H), 1.99 (s, 3H), 3.38 to 3.51 (m, 2H), 3.98 to 4.17 (m, 2H), 4.79 (m, 1H), 4.91 (t, *J* = 7.6 Hz, 1H), 7.33 to 7.36 (m, 5H) ; ^{13}C-NMR (400 MHz, CDCl3): δ = -5.25 (CH_3), -5.2 (CH_3), -4.6 (CH_3), -4.3 (CH_3), 17.9 (C_q), 20.8 (CH_3), 21.0 (CH_3), 21.5 (CH_3), 24.2 (CH_3), 25.6 (3*CH_3), 39.0 (CH_2), 53.0 (CH), 60.5 (CH_2), 64.7 (CH), 77.4 (CH), 128.2 (2*CH), 129.7 (CH), 133.5 (2*CH), 136.2 (C_q), 169.7 (C_q), 170.3 (C_q), 170.9 (C_q) ; Anal. Calcd. for $C_{26}H_{43}NO_6Si_2$ (521.26) : C 59.85, H 8.31, N 2.68 ; Found: C 60.06, H 8.48, N 2.76.

(2*S, 3*S**, 4*R**, 5*S**)-Acetic acid 2-acetoxymethyl-3-(tert-butyl-dimethyl-silanyloxy)-5-hydroxy-piperidin-4-yl ester (16)**

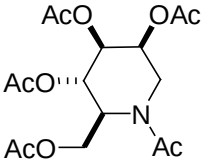


Peracetic acid (1.93 mL of a 33% solution in HOAc, 17 mmol, 50 equiv.) and mercury acetate (165 mg, 0.52 mmol, 1.5 equiv.) were added to a solution of **14** (180 mg, 0.34 mmol) in acetic acid (3 mL). Using the procedure previously described (synthesis of **15**), **16** was obtained as a white cristallin solid (107 mg, 0.26 mmol, 78%).

white solid, mp 86-87°C ; R_f = 0.2 (PE/EA = 1/9) ; IR : 3392, 2954, 2930, 2857, 1753, 1729, 1332, 1428, 1367, 1221, 1093, 1036, 837, 777 cm^{-1}; 2 rotamers were observed by NMR spectroscopy : 1) major ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 3H), 0.13 (s, 3H), 0.85 (9H), 2.00 (s, 3H), 2.10 (s, 3H), 2.12 (s, 3H), 2.77 (dd, *J* = 14 Hz, 5 Hz, 1H), 3.94 to 4.05 (m, 1H), 4.10 (dd, *J* = 11.7 Hz, 5.3 Hz, 1H), 4.43 (dd, *J* = 11 Hz, 9.5 Hz, 1H), 4.65 (dd, *J* = 13 Hz, 5 Hz, 1H), 4.98 (br s, 1H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = -5.3 (CH_3), -5.0 (CH_3), 17.9 (C_q), 20.8 (CH_3), 21.1 (CH_3), 21.3 (CH_3), 25.6 (3*CH_3), 37.9 (CH_2), 58.9 (CH), 60.9 (CH_2), 62.9 (CH), 67.9 (CH), 71.7 (CH), 170.3 (C_q), 170.6 (C_q), 170.9 (C_q)

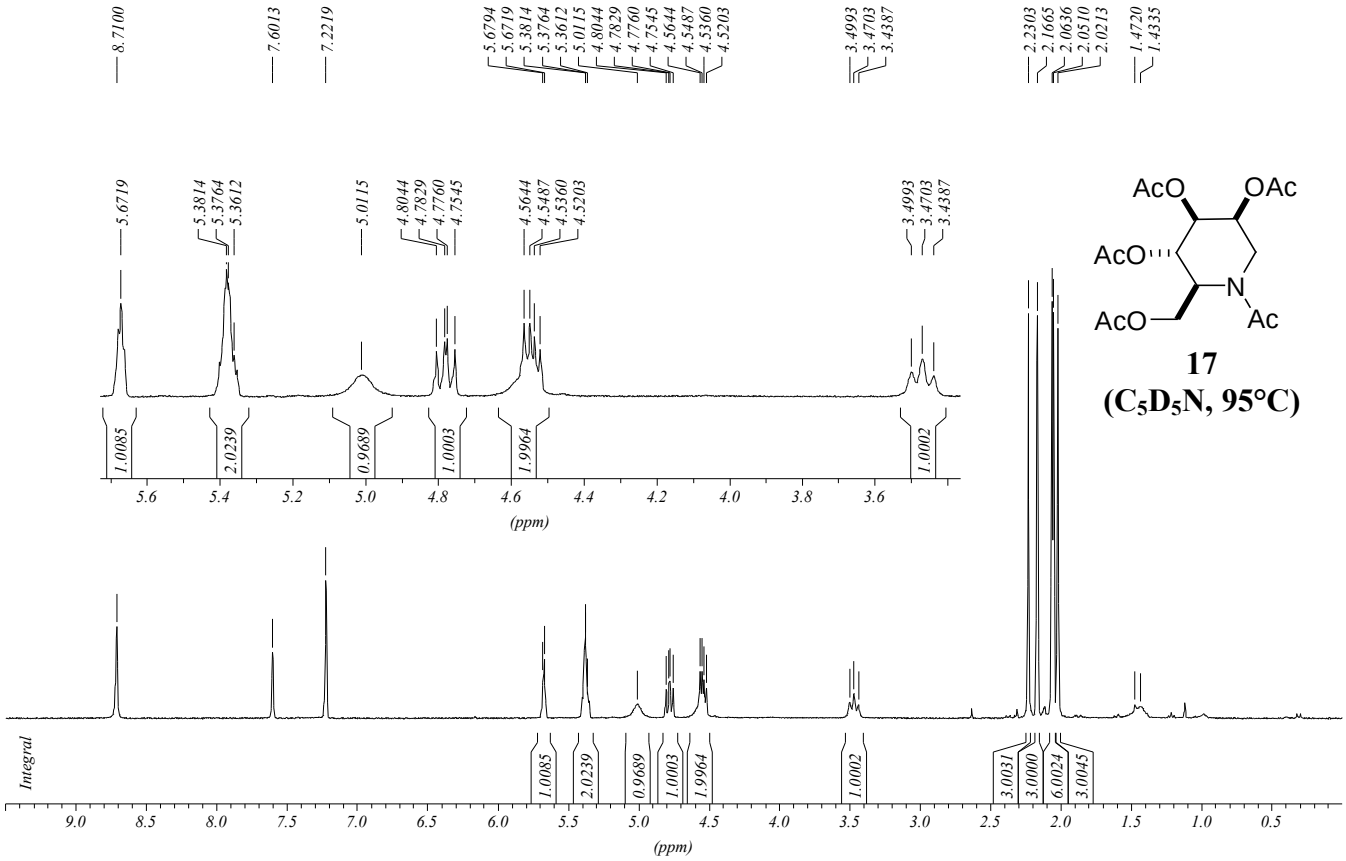
2) minor ^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 0.04 (s, 3H), 0.08 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H), 2.12 (s, 3H), 3.27 (t, *J* = 12 Hz, 1H), 3.68 (dd, *J* = 13 Hz, 5 Hz, 1H), 3.94 to 4.05 (m, 1H), 4.08 to 4.13 (m, 1H), 4.08 to 4.13 (m, 1H), 4.89 (t, *J* = 7.5 Hz, 1H), 4.98 (br s, 1H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = -5.2 (CH_3), -5.1 (CH_3), 17.9 (C_q), 20.8 (CH_3), 21.1 (CH_3), 21.8 (CH_3), 25.6 (3*CH_3), 43.5 (CH_2), 52.6 (CH), 60.3 (CH_2), 63.7 (CH), 73.0 (CH), 170.4 (C_q), 170.6 (C_q), 170.9 (C_q); Anal. Calcd. for $C_{18}H_{33}NO_7Si$ (403.20) : C 53.57, H 8.24, N 3.47 ; Found: C 53.48, H 8.25, N 3.35.

(2*S, 3*S**, 4*R**, 5*S**)-Acetic acid 4,5-diacetoxy-2-acetoxymethyl-1-acetyl-piperidin-3-yl ester (17)**



16 (23 mg, 0.057 mmol) was solubilized in dry THF (1 mL) and TBAF (0.1 mL, 0.1 mmol, 1 M solution in THF, 2 equiv.) was added. The solution was stirred at room temperature for 9 h. The reaction mixture was then concentrated under vacuo. The crude was solubilized in dry CH_2Cl_2 (1 mL). Then DMAP (1 mg, 0.0082 mmol, 0.14 equiv.) and NEt_3 (0.16 mL, 1.14 mmol, 20 equiv.) were added. The solution was cooled to 0°C and acetic anhydride (0.11 mL, 1.14 mmol, 20 equiv.) was added. The mixture was stirred at room temperature for 20 h. Then CH_2Cl_2 and aqueous NH_4Cl (5 mL) were added. The aqueous layer was extracted with CH_2Cl_2 (3*10 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The crude was purified by flash chromatography on silica gel (pentane/EA = 3/7) to afford **17** (21.3 mg, 0.057 mmol, 99% yield, two steps) as a colorless oil.

R_f = 0.25 (pentane/EA = 3/7) ; IR : 2929, 2856, 1739, 1655, 1422, 1368, 1210, 1207 cm^{-1}; ^{1}H-NMR (400 MHz, C_5D_5N, 95°C) : δ = 2.02 (s, 3H), 2.05 (s, 3H), 2.06 (s, 3H), 2.17 (s, 3H), 2.23 (s, 3H), 3.47 (br t, *J* = 12.1 Hz, 1H), 4.54 (dd, *J* = 11.3 Hz, 6.3 Hz, 2H), 4.78 (br dd, *J* = 11.3 Hz, 8.6 Hz, 1H), 5.01 (br s, 1H), 5.36-5.38 (m, 2H), 5.67-5.68 (m, 1H).



Spectral data from literature :

1) Hardick, D. J.; Hutchinson, D. W.; Trew, S. J.; Wellington, E. M. H. *Tetrahedron* **1992**, *48*(30), 6285 :

"^{1}H-NMR (400 MHz, C_5D_5N, 90°C): δ = 1.96 (s, 3H), 2.01 (s, 3H), 2.03 (s, 3H), 2.13 (s, 3H), 2.22 (s, 3H), 3.46 (br s, 1H), 3.85 (br s, 2H), 4.50 (dd, *J* = 11.4 Hz, 6.1 Hz, 1H), 4.81 (br dd, 1H), 5.36 (m, 2H), 5.70 (t, *J* = 3.3 Hz, 1H)."

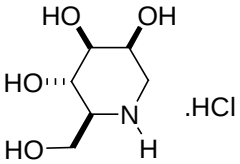
2) Haukass, M. H.; O'Doherty, G. A. *Org. Lett.* **2001**, *3*, 401-404 :

"^{1}H-NMR (300 MHz, C_5D_5N, 95°C) : 2.05 (s, 6H), 2.16 (s, 6H), 2.26 (s, 3H), 3.62 (br m, 1H), 4.18 (br m, 2H), 4.66 (dd, *J* = 11.7 Hz, 7.5 Hz, 1H), 5.56 (dd, *J* = 5.7 Hz, 3.0 Hz, 1H), 5.62 (dd, *J* = 3.6 Hz, 3.6 Hz, 1H), 5.70 (dd, *J* = 3.0, 3.0 Hz, 1H)."

Spectra could be also recordered at 293K in $(CD_3)_2CO$:

2 rotamers were observed by NMR (ratio = 60/40) : 1) major ^{1}H-NMR (400 MHz, $(CD_3)_2CO$): δ = 1.91 (s, 3H), 1.93 (s, 3H), 2.00 (s, 3H), 2.01 (s, 3H), 2.02 (s, 3H), 2.86 (br t, *J* = 12.4 Hz, 1H), 4.16 to 4.24 (m, 2H), 4.47 (dd, *J* = 13 Hz, 5.3 Hz, 1H), 4.63 (dd, *J* = 10.3 Hz, 8.1 Hz, 1H), 4.77 (ddd, *J* = 11.6 Hz, 5.3 Hz, 3.3 Hz, 1H), 4.88 to 4.93 (m, 1H), 5.13-5.19 (m, 1H) ; 2) minor ^{1}H-NMR (400 MHz, $(CD_3)_2CO$) : δ = 1.84 (s, 3H), 1.85 (s, 3H), 1.86 (s, 3H), 1.90 (s, 3H), 1.92 (s, 3H), 3.43 (dd, *J* = 13.6 Hz, 12.4 Hz, 1H), 3.79 (dd, *J* = 13.6 Hz, 5 Hz, 1H), 4.16 to 4.24 (m, 1H), 4.33 (dd, *J* = 11.4 Hz, 8.8 Hz, 1H), 4.88 to 4.93 (m, 3H), 5.14 to 5.19 (m, 1H) ; ^{13}C-NMR (100 MHz, $(CD_3)_2CO$) 2 rotamers : δ = 20.6 (CH_3), 20.65 (CH_3), 20.7 (CH_3), 20.75 (CH_3), 21.4 (CH_3), 21.7 (CH_3), 34.9 (CH_2), 40.9 (CH_2), 50.8 (CH), 56.7 (CH), 60.4 (CH_2), 60.9 (CH_2), 65.9 (CH), 66.7 (CH), 67.5 (CH), 67.8 (CH), 68.8 (CH), 69.3 (CH), 169.7 (C_q), 169.9 (C_q), 170.1 (C_q), 170.3 (C_q), 170.7 (C_q), 170.8 (C_q), 170.85 (C_q).

(±)-Deoxymannojirimycin hydrochloride (1.HCl)



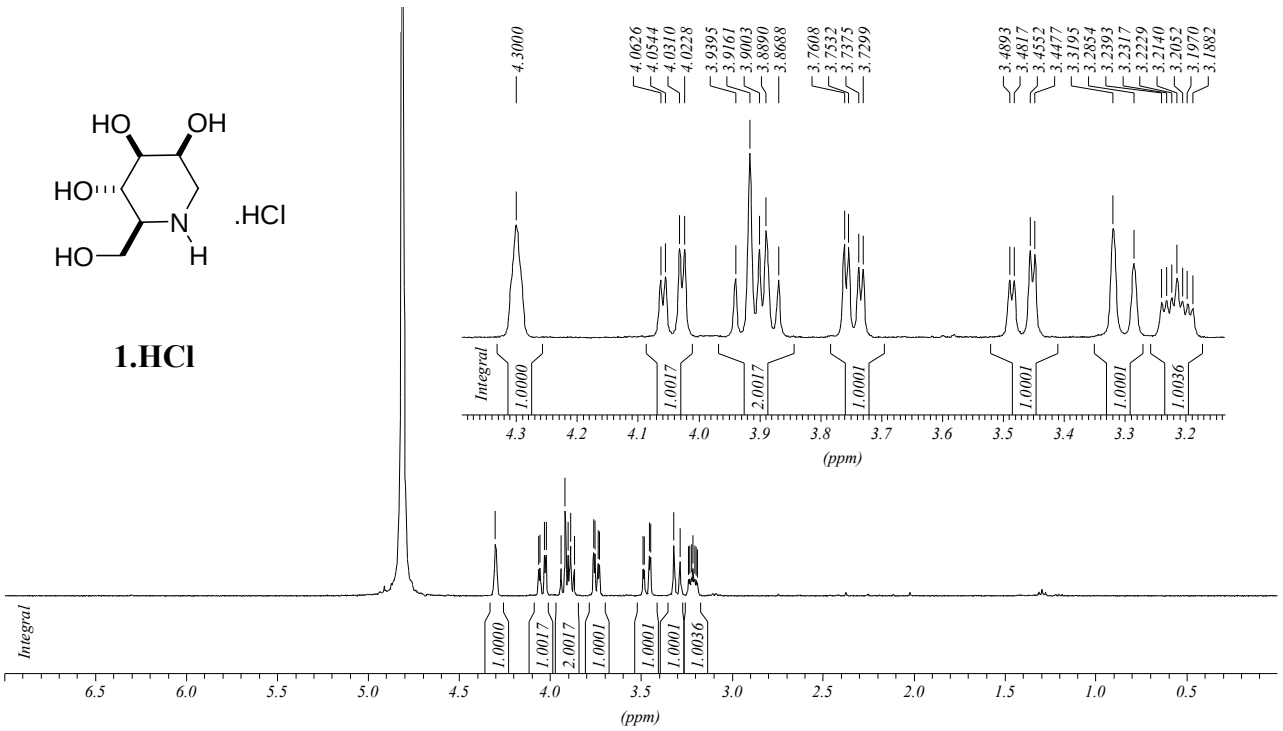
The peracetylated compound **17** (13.7 mg, 0.0367 mmol) was refluxing in 6N HCl for 16h. Then the reaction mixture was concentrated under reduce pressure, and **1** was obtained as a white cristallin product (7.3 mg, 0.0366 mmol, 99% yield).

white solid, IR : 3545 (br), 3053 (br), 2854, 2789, 2729, 2317 (br), 2216, 2136, 1608, 1560, 1410, 1339, 1258, 1176, 1114, 1070 cm^{-1}; ^{1}H-NMR (400 MHz, D_2O): δ = 3.21 (ddd, *J* = 10.2 Hz, 6.6 Hz, 3.1 Hz, 1H), 3.30 (br d, *J* = 13.6 Hz, 1H), 3.47 (dd, *J* = 13.6 Hz, 3.1 Hz, 1H), 3.74 (dd, *J* = 9.3 Hz, 3.0 Hz, 1H), 3.87 to 3.94 (m, 2H), 4.04 (dd, *J* = 12.4 Hz, 3.3 Hz, 1H), 4.30 (br s, 1H). ^{13}C-NMR (100 MHz, D_2O): δ = 47.4 (CH_2), 57.95 (CH_2), 60.2 (CH), 65.6 (CH) , 65.7 (CH), 72.3 (CH).

This values are in accordance with the litterature :

Singh, O. V.; Han, H. *Tetrahedron Letters* **2003**, *44*, 2387–2391 :

"^{1}H NMR (500 MHz, D_2O): 3.13 to 3.24 (m, 1H), 3.30 (dd, *J* = 13.5 Hz, 1.0 Hz, 1H), 3.47 (dd, *J* = 13.7 Hz, 2.5 Hz, 1H), 3.75 (dd, *J* = 9.5 Hz, 3.5 Hz, 1H), 3.87 to 3.93 (m, 2H), 4.04 (dd, *J* = 12.5 Hz, 3.0 Hz, 1H), 4.30 (m, 1H) ; ^{13}C NMR (75 MHz, D_2O): 47.40, 57.95, 60.18, 65.57, 65.73, 72.24."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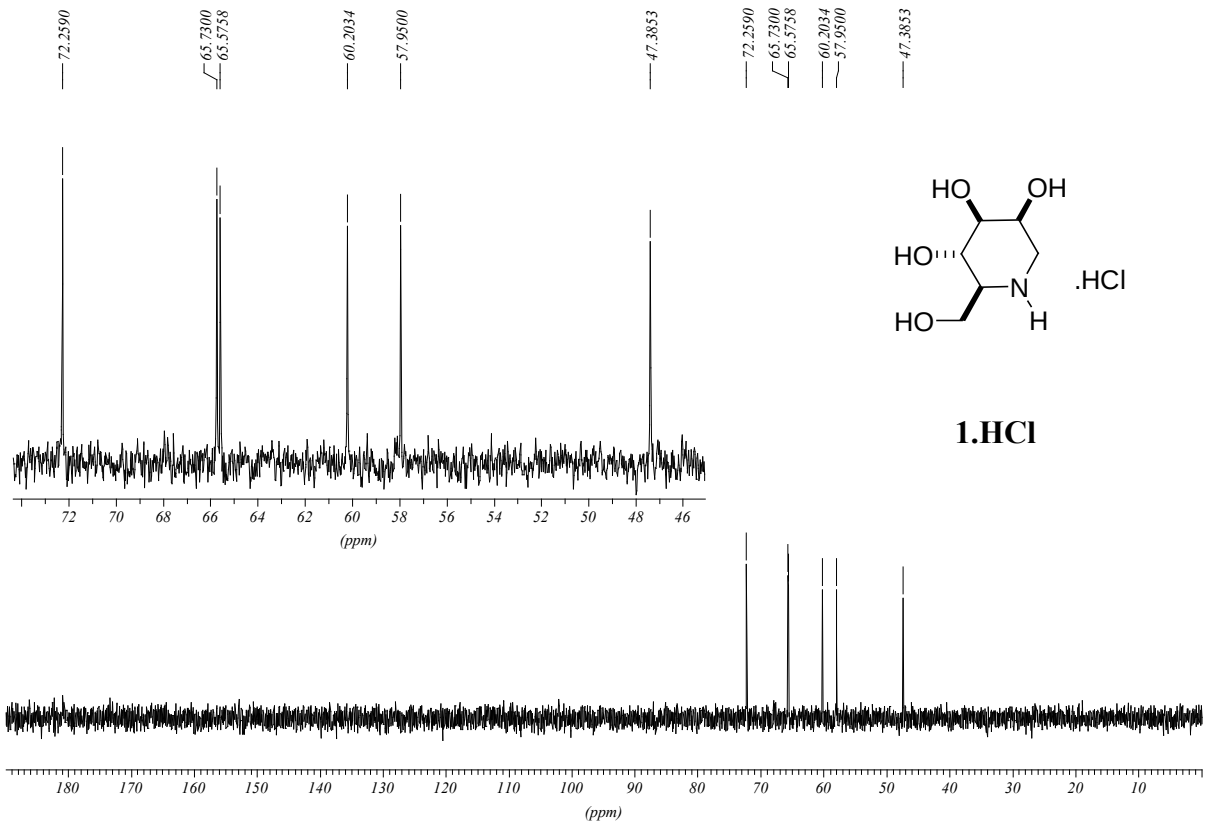
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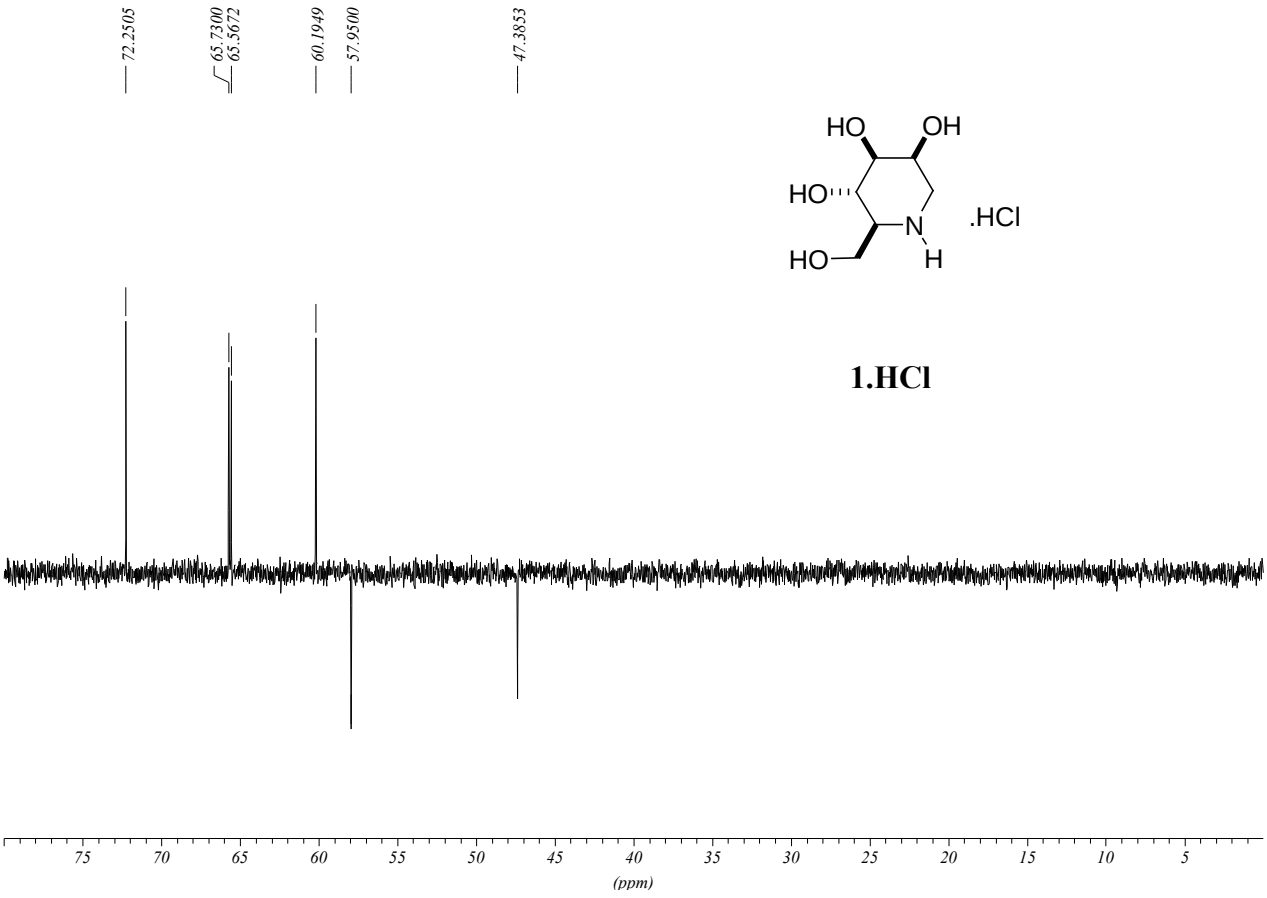
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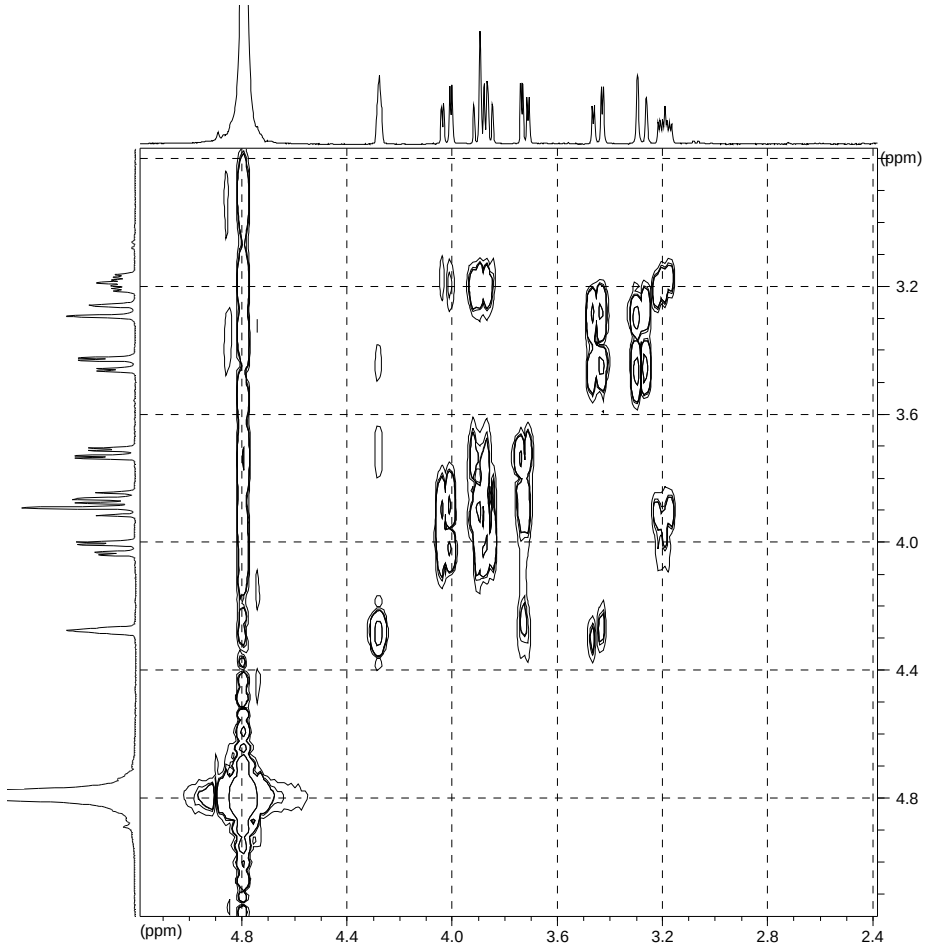
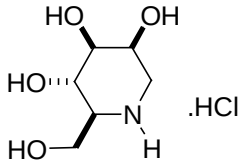
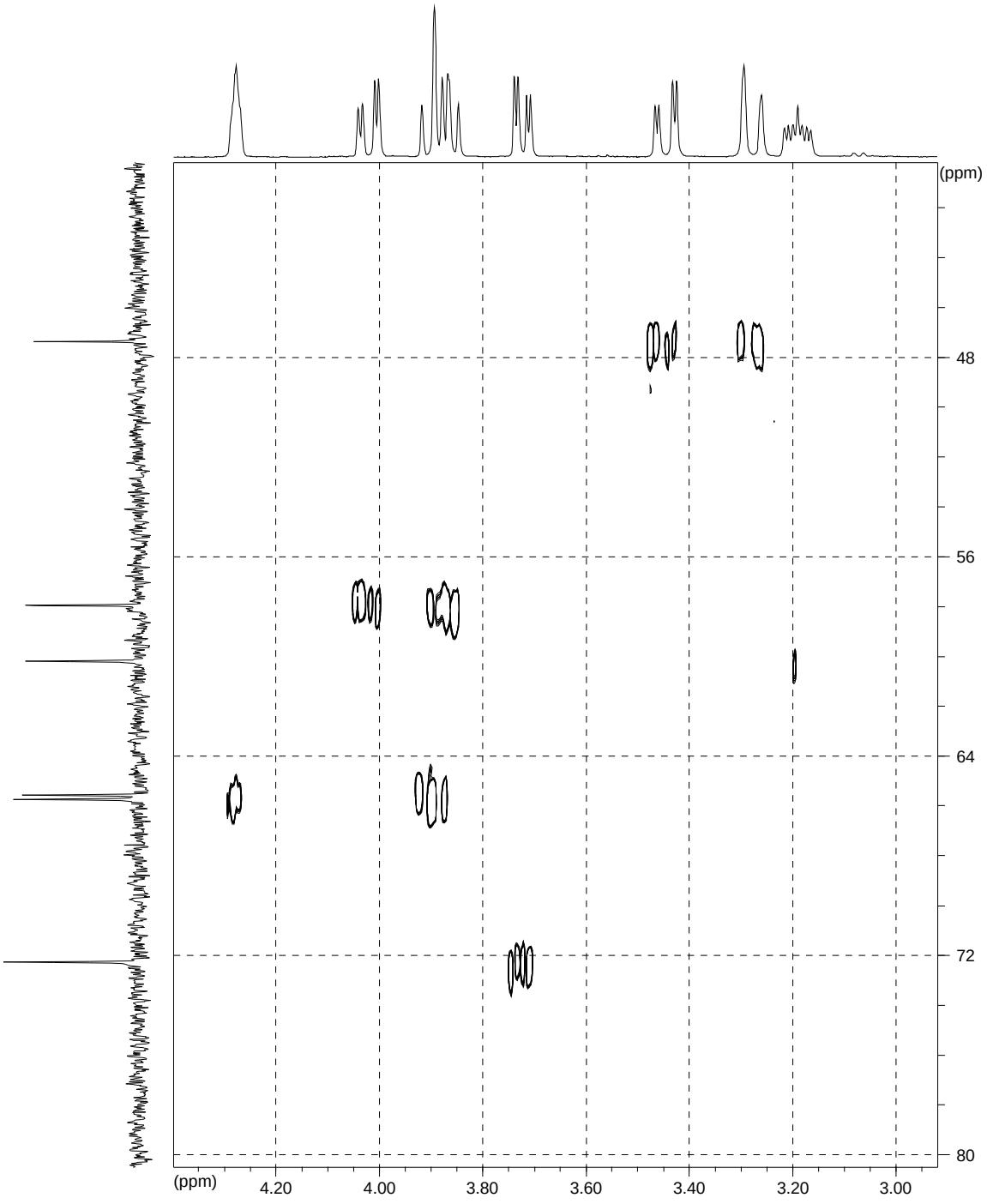
(ppm)

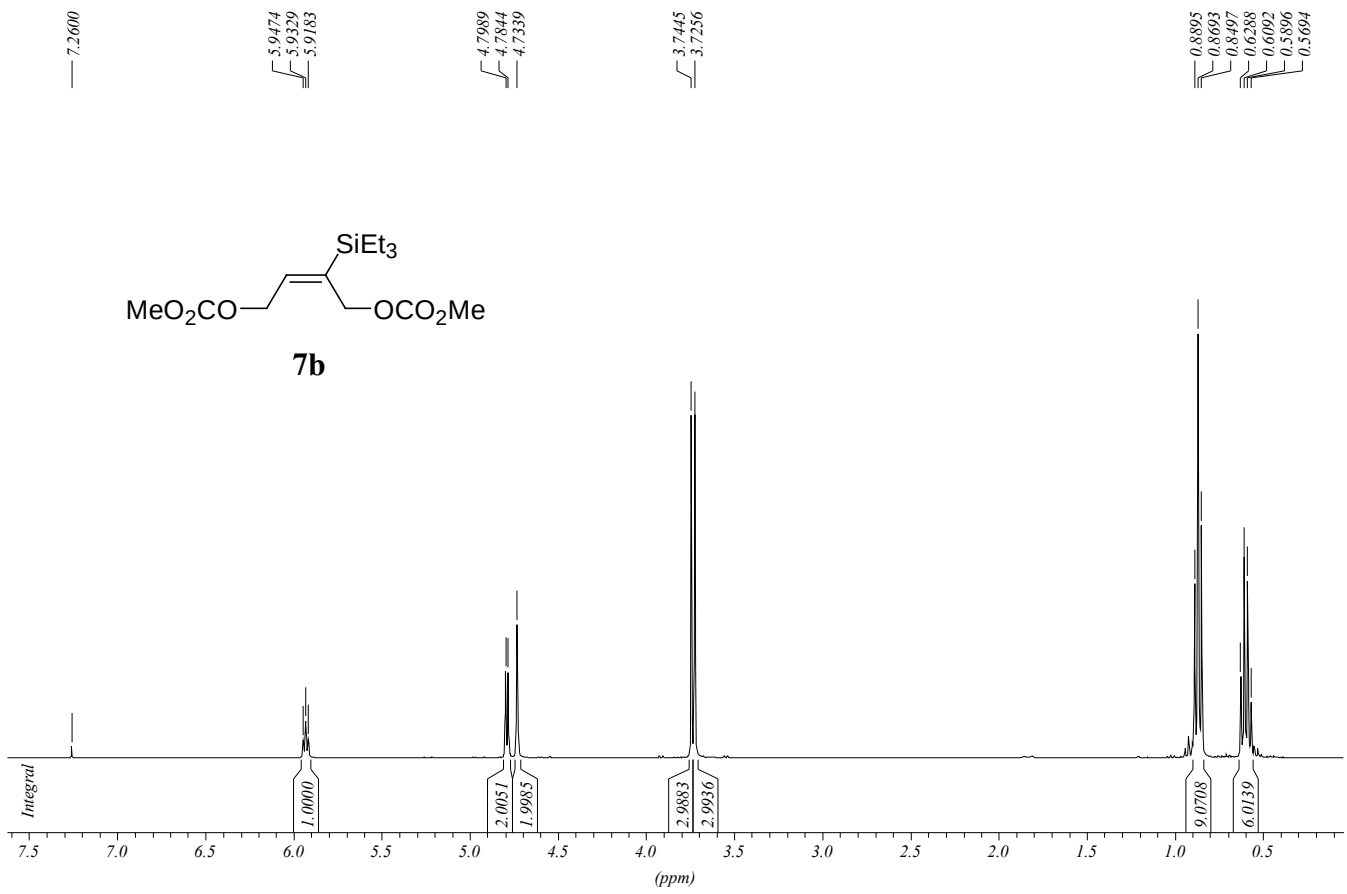
1.HCl


(ppm)
3.2
3.6
4.0
4.4
4.8
(ppm)
4.8
4.4
4.0
3.6
3.2
2.8
2.4

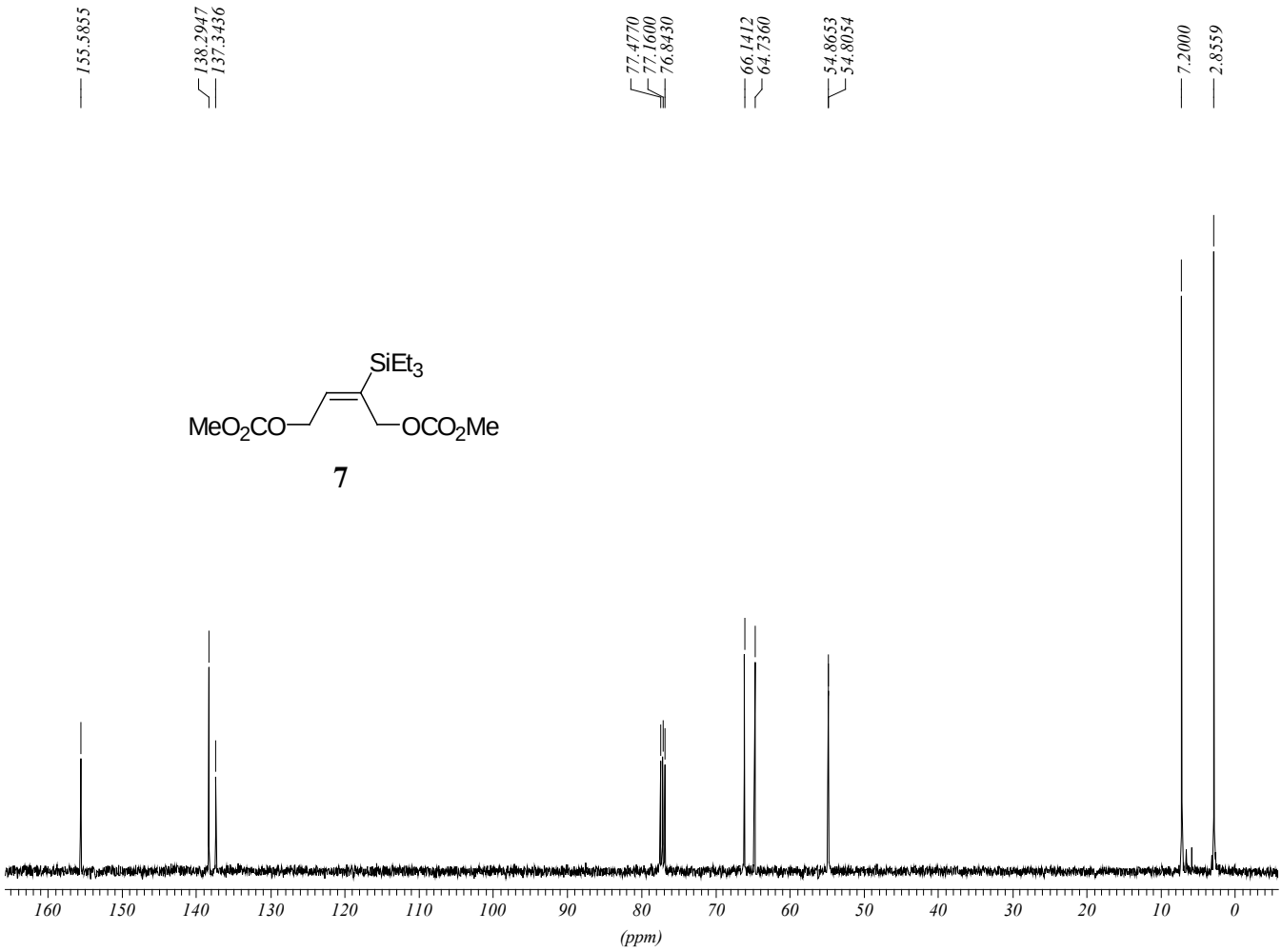

HO
OH
HO
N
H
HO
.HCl

1.HCl

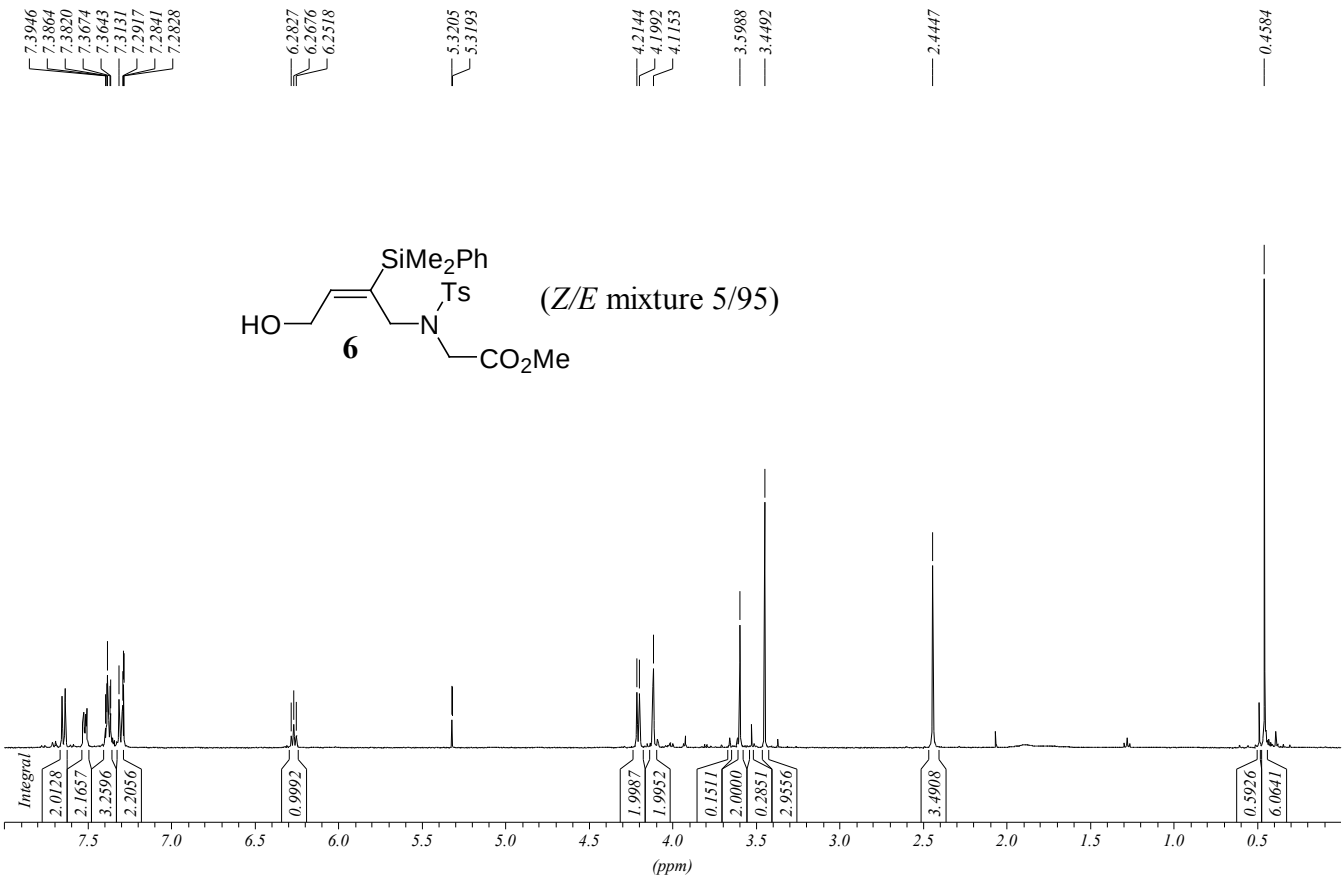

(ppm)
48
56
64
72
80
(ppm)
4.20
4.00
3.80
3.60
3.40
3.20
3.00

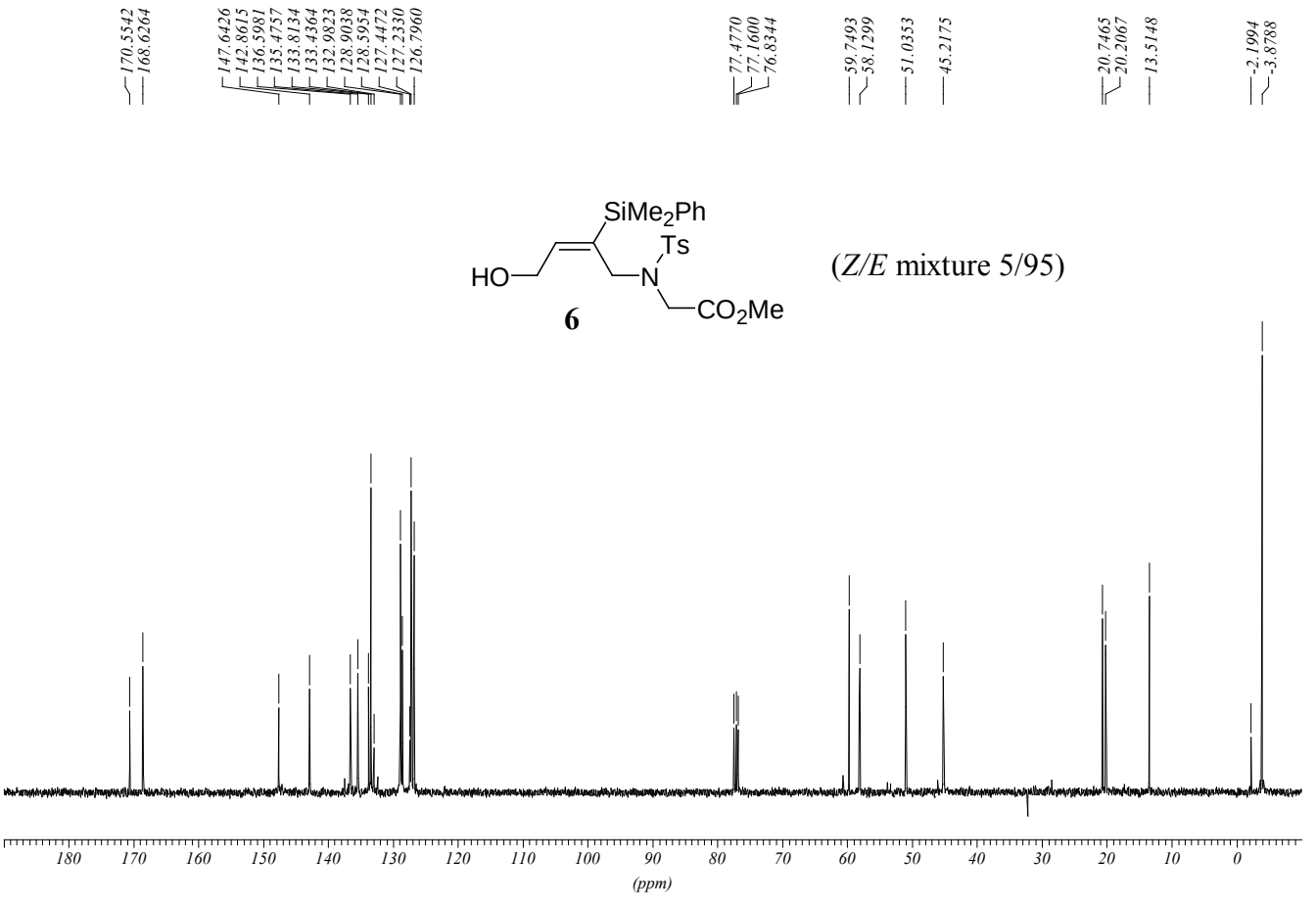

7.2600
5.9474
5.9329
5.9183
4.7989
4.7844
4.7339
3.7445
3.7256
0.8895
0.8693
0.8497
0.6288
0.6092
0.5896
0.5694
SiEt3
MeO2CO
OCO2Me
Integral
1.0000
2.0051
1.9985
2.9883
2.9936
9.0708
6.0139
(ppm)

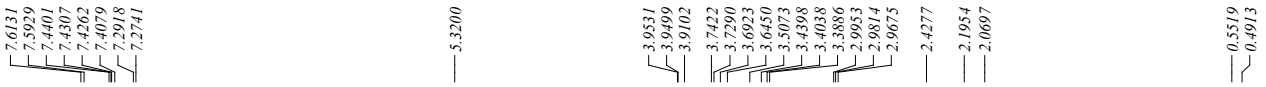
7b

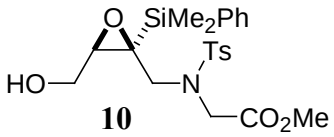

155.5855
138.2947
137.3436
77.4770
77.1600
76.8430
66.1412
64.7360
54.8653
54.8054
7.2000
2.8559
SiEt3
MeO2CO
OCO2Me
(ppm)

7

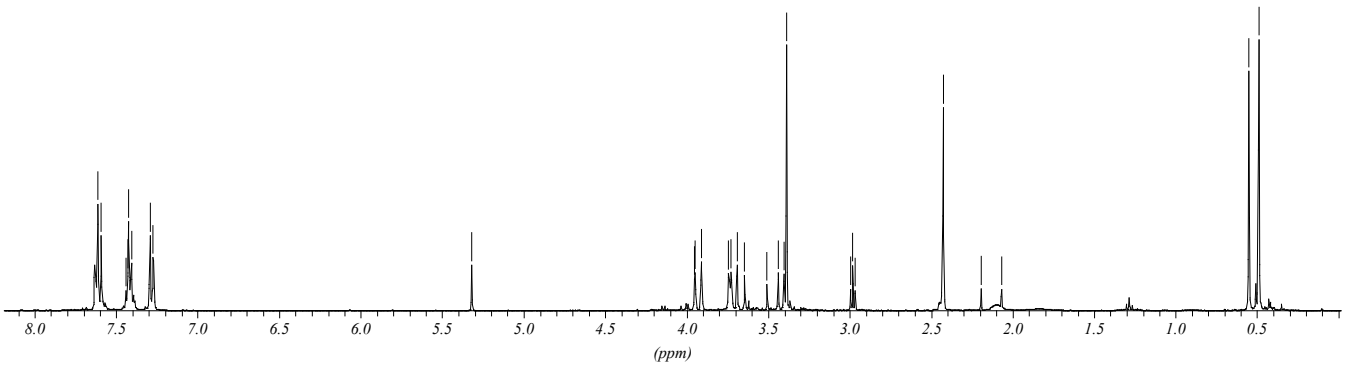

7.3946
7.3864
7.3820
7.3674
7.3643
7.3131
7.2917
7.2841
7.2828
6.2827
6.2676
6.2518
5.3205
5.3193
4.2144
4.1992
4.1153
3.5988
3.4492
2.4447
0.4584
SiMe2Ph
Ts
HO
N
CO2Me
6
(Z/E mixture 5/95)
Integral
2.0128
2.1657
3.2596
2.2056
0.9992
1.9987
1.9952
0.1511
2.0000
0.2851
2.9556
3.4908
0.5926
6.0641
(ppm)

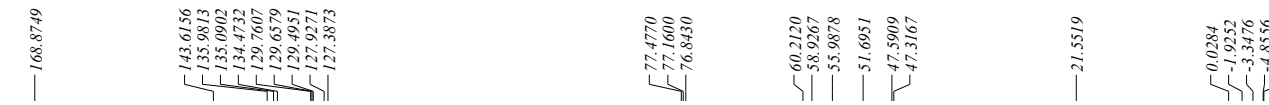

170.5542
168.6264
147.6426
142.8615
136.5981
135.4757
133.8134
133.4364
132.9823
128.9038
128.5954
127.4472
127.2330
126.7960
77.4770
77.1600
76.8344
59.7493
58.1299
51.0353
45.2175
20.7465
20.2067
13.5148
-2.1994
-3.8788
SiMe2Ph
Ts
HO
N
CO2Me
6
(Z/E mixture 5/95)
(ppm)

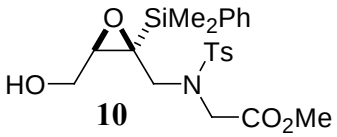

7.6131
7.5929
7.4401
7.4307
7.4262
7.4079
7.2918
7.2741
5.3200
3.9531
3.9499
3.9102
3.7422
3.7290
3.6923
3.6450
3.5073
3.4398
3.4038
3.3886
2.9953
2.9814
2.9675
2.4277
2.1954
2.0697
0.5519
0.4913


O
SiMe2Ph
Ts
HO
N
CO2Me

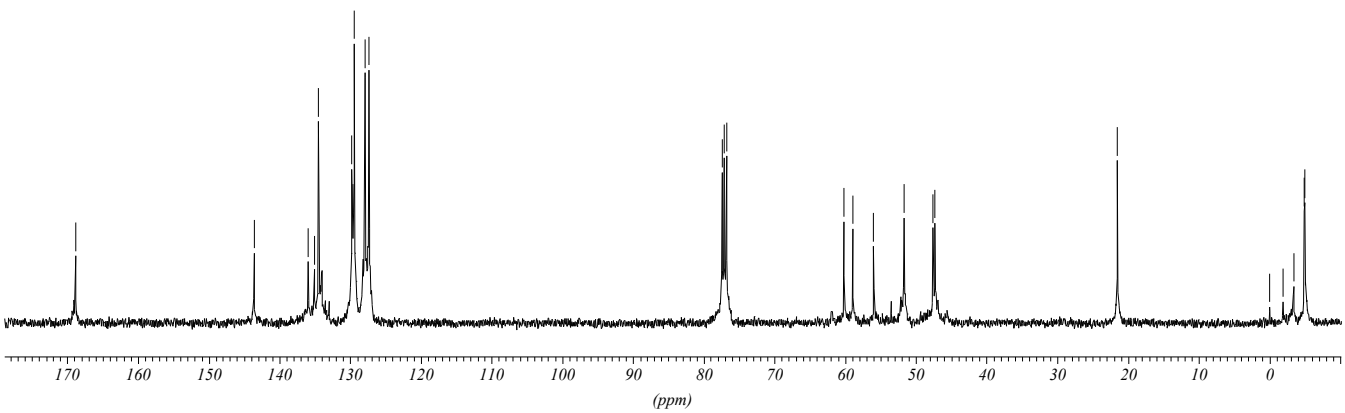
10

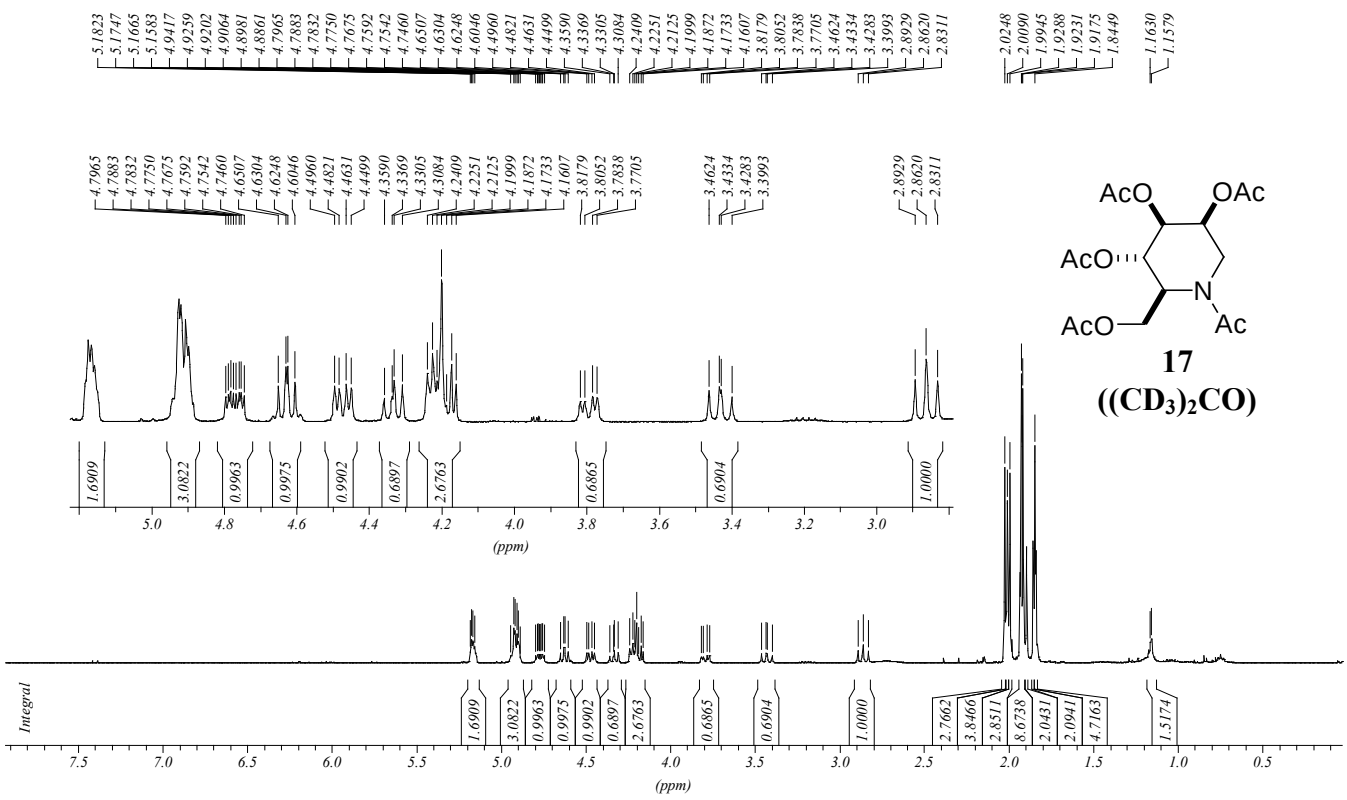

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

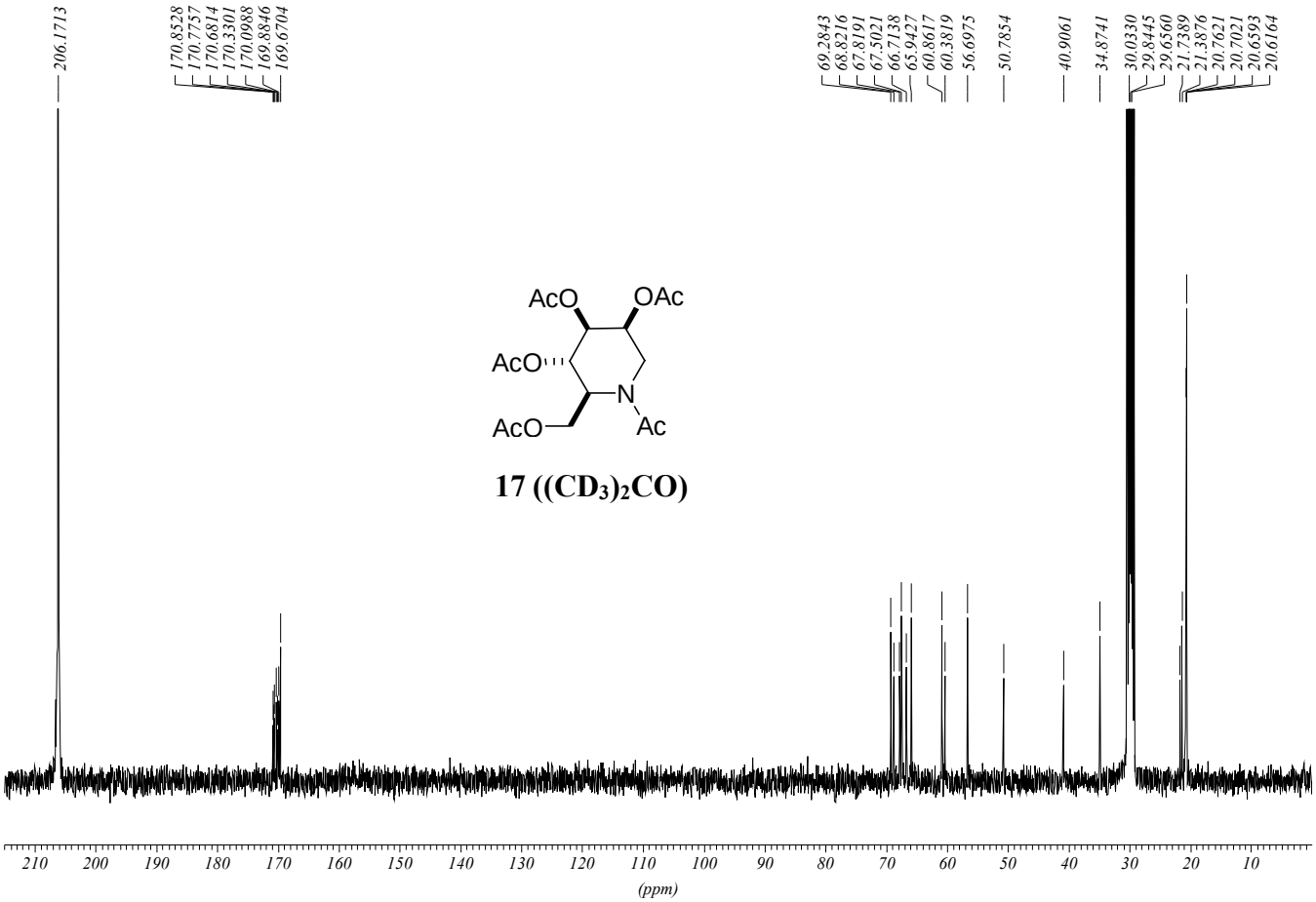

168.8749
143.6156
135.9813
135.0902
134.4732
129.7607
129.6579
129.4951
127.9271
127.3873
77.4770
77.1600
76.8430
60.2120
58.9267
55.9878
51.6951
47.5909
47.3167
21.5519
0.0284
-1.9252
-3.3476
-4.8556
-4.9841

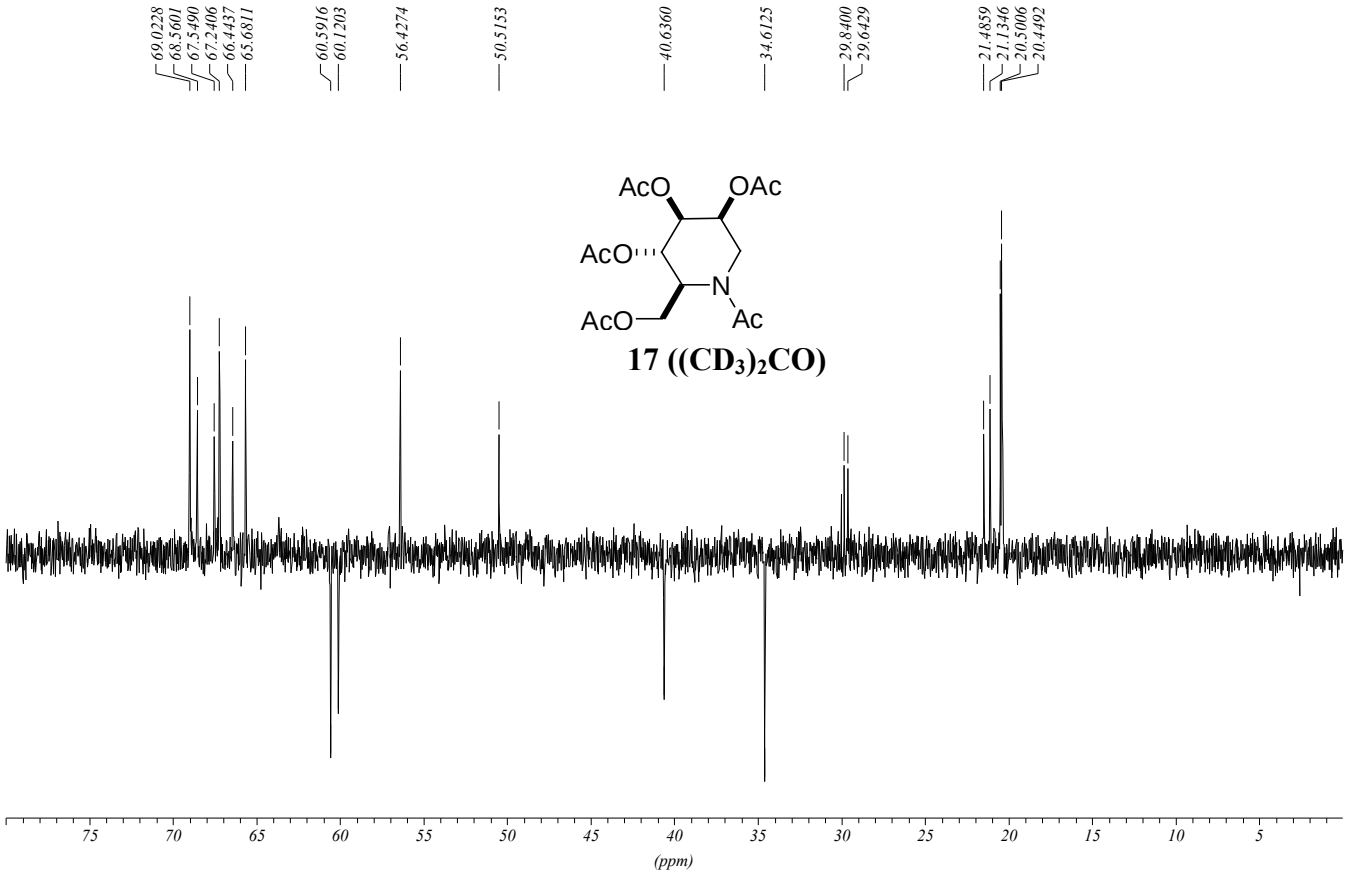

O
SiMe2Ph
Ts
HO
N
CO2Me

10


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


AcO
OAc
AcO
N
Ac
AcO
17
((CD3)2CO)
(ppm)
Integral
(ppm)


AcO
OAc
AcO
N
Ac
AcO
17 ((CD3)2CO)
(ppm)


69.0228
68.3601
67.5490
67.2406
66.4437
65.6811
60.5916
60.1203
56.4274
50.5153
40.6360
34.6125
29.8400
29.6429
21.4859
21.1346
20.5006
20.4492
AcO
OAc
AcO
N
AcO
Ac
17 ((CD3)2CO)
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
(ppm)