Supporting Information

Highly β-Selective O-Glucosidation Due to the Restricted Twist Boat Conformation

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1. General method

All commercially available reagents were used without further purification. All moisture and air sensitive reactions were performed in a glassware equipped with rubber septa under a positive pressure of argon or nitrogen. The glassware was dried under reduced pressure by heating with a heat-gun before use. When necessary, solvents and reagents were distilled prior to use and were transferred using a syringe or cannula. The reaction mixture was magnetically stirred.

Thin layer chromatography (TLC) was performed on Merck precoated silica gel 60 F-254 plates or Merck RP-19 F-254 plates. Column chromatography was performed on Merck silica gel 60 (0.063-0.200 mm, 70-230 mesh) or Merck silica gel 60 (0.040-0.063 mm, 230-400 mesh) for ordinary phase or Nacalai Tesque Cosmosil 140C18-PREP for reverse phase. Spots were detected by dipping in a solution of 2% anisaldehyde and 5% conc. H_2SO_4 in EtOH, a solution of 10% phosphomolybdic acid in EtOH, or an aqueous solution of 2% phosphomolybdic acid, 2% phosphoric acid, and 8% conc. H_2SO_4 aqueous solution followed by heating at ca. 200 °C.

The melting points were determined using a Yanagimoto micro melting point apparatus. Optical rotations were determined using a JASCO DIP-370 polarimeter with a 100 mm cell. Infrared spectra were recorded on a JASCO FT/IR-5300 instruments and the major absorbance bands are reported in wavenumber (cm^{-1}). The nuclear magnetic resonance (NMR) spectra were recorded on α-JEOL 400, JEOL JNM-ECA 400, and JNM-ECA 300 instruments. Chemical shifts of the NMR spectra were recorded in δ units downfield from tetramethylsilane. The ^1H NMR data are indicated by a chemical shift with the multiplicity, the coupling constants, the integration, and the assignment in parentheses in this order. The multiplicities are abbreviated as s, singlet; d, doublet; t, triplet; q, qualtet; m, multiplet; and br, broadend. The ^{13}C NMR data are reported as the chemical shift with the hydrogen multiplicity obtained from the DEPT spectra and the number of carbons in parentheses. When the number of carbons could not be analyzed due to heavy overlap, the number is not indicated. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100LC spectrometer for electrospray ionization (ESI), or a JEOL AX-500 spectrometer for fast atom bombardment ionization (FAB).

2. Preparation of 1-3.

2.1. Preparation of ethyl 2,3,4,6-tetrakis-*O*-triisopropylsilyl-1-thio-β-D-gluco-pyranoside (1).

A solution of ethyl 1-thio-β-D-glucopyranoside (**4**, 500 mg, 2.23 mmol) in 2,6-lutidine (22 mL) was heated to 130 °C, and TIPSOTf (3.41 g, 11.1 mmol) was added to the mixture in three portions at 5 min intervals. The mixture was stirred at 130 °C for 1 h. Then, further TIPSOTf (3.41 g, 11.1 mmol) was added, and the stirring was continued for 2 h. Again, further TIPSOTf (2.73 g, 8.88 mmol) was added, and the mixture was stirred for 1 h at 130 °C. After cooling to room temperature, the mixture was diluted with *n*-hexane (10 mL), and added saturated aqueous NH_4Cl (30 mL). The hexane layer was successively washed with saturated aqueous NH_4Cl (20 mL x 2) and brine (20 mL), dried over $MgSO_4$, filtered through a cotton pad, and evaporated. The resulting residue was successively purified by column successive chromatography using silica gel (silica-gel, 15 g, *n*-hexane) and ODS (ODS 45 g, 100% methanol → ethanol/water = 10/1 → 25/1 → 50/1) to afford **1** as colorless syrup (996 mg, 53% yield).

2.2. Preparation of ethyl 6-*O*-benzyl-2,3,4-tris-*O*-triisopropylsilyl-1-thio-β-D-gluco-pyranoside (2).

To a stirred solution of ethyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**5**, 208 mg, 0.524 mmol) and triethylsilane (306 mg, 2.62 mmol) in CH_2Cl_2, trifluoroacetic acid (296 mg, 2.62 mmol) was dropwise added at 0 °C. The mixture was stirred for 3 h. During the reaction period the reaction temperature gradually increased to room temperature. Then, EtOAc was added to dilute the mixture, and it was successively washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered through a cotton pad, and evaporated. The resulting residue was purified by column chromatography (silica gel 6.2 g, *n*-hexane/ethyl acetate = 4:1 → 3/1 → 2/1) to give ethyl 2,3-di-*O*-acetyl-6-*O*-benzyl-1- thio-β-D-glucopyranoside (**6**) as colorless syrup (181 mg, 87% yield).

To a solution of **6** (175 mg, 0.439 mmol) in 1/1 MeOH/THF (4 mL) was added sodium methoxide (4.7 mg, 0.088 mmol), and the mixture was stirred for 10 min at room

temperature. Then acidic ion-exchange resin (Amberlite IR120B) was added to neutralize the mixture, and it was filtered through a cotton pad. The filtrate was evaporated. Azeotropic drying of the resulting residue by several evaporation with benzene allowed direct use of the residue, whose main content was ethyl 6-*O*-benzyl-1-thio-β-D-glucopyranoside, as the starting material of the next step.

A solution of ethyl 6-*O*-benzyl-1-thio-β-D-glucopyranoside in DMF (4.5 mL), 2,6-lutidine (423 mg, 3.95 mmol) and TIPSOTf (403 mg, 1.32 mmol) was added, and the mixture was stirred for 12 h at 100 °C. Then, further TIPSOTf (403 mg, 1.32 mmol) was added to the mixture, and it was stirred for 8 h at the same temperature. The reaction was quenched by addition of water, and the mixture was extracted with *n*-hexane. The hexane layer was successively washed with 1 M hydrochloric acid, saturated aqueous $NaHCO_3$, and brine, then dried over $MgSO_4$ and filtered through a cotton pad. The filtrate was evaporated, and the resulting residue was purified by column chromatography (silica-gel 17.5 g, *n*-hexane/ethyl acetate = 500/1 → 300/1 → 100/1 → 80/1) to give **2** as colorless syrup (249 mg, 72% from **5**).

2.3. Preparation of ethyl 6-*O*-pivaloyl-2,3,4-tris-*O*-triisopropylsilyl-1-thio-β-D-glucopyranoside (3).

To a solution of ethyl 1-thio-β-D-glucopyranoside (**4**, 125 mg, 0.557 mmol) and DMAP (6.8 mg, 0.056 mmol) in pyridine (5.6 mL), pivaloyl chloride (73.9 mg, 0.613 mmol) was added and the mixture was stirred for 30 min at 0 °C. Then, further pivaloyl chloride (73.9 mg, 0.613 mmol) was added and the mixture was stirred for additional 30 min. The mixture was diluted with ethyl acetate, and it was successively washed with 1 M hydrochloric acid, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, filtered through a cotton pad, and then evaporated. The resulting residue was purified by column chromatography (silica-gel 4 g, *n*-hexane/ethyl acetate = 2/1 → 1/1 → 1/2 → 1/3) to give ethyl 6-*O*-pivaloyl-1-thio- β-D-glucopyranoside (**7**, 72.9 mg, 42% yield) as colorless syrup. Leaving the syrup of **7** slowly afforded colorless crystal.

A mixture of **7** (153 mg, 0.495 mmol), 2,6-lutidine (534 mg, 4.95 mmol), and TIPSOTf (329 mg, 1.07 mmol) in DMF (5 mL) was stirred for 1 h at 100 °C. Then, further TIPSOTf

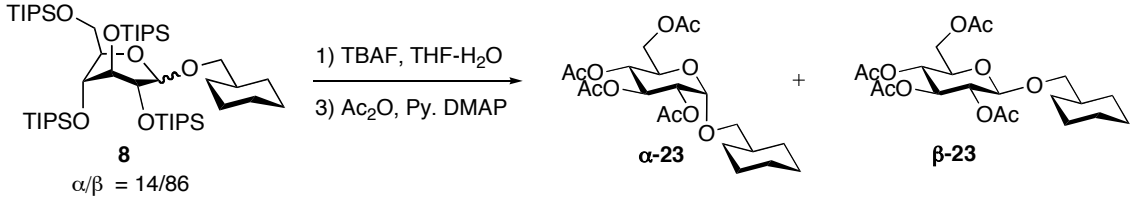
(each 329 mg, 1.07 mmol) was added twice at 1 h intervals, and the mixture was stirred for additional 38 h at 100 °C. After cooling, the mixture was added H_2O and extracted with *n*-hexane. The hexane layer was successively washed with 1 M hydrochloric acid, saturated aqueous $NaHCO_3$, and brine. It was dried over $MgSO_4$, filtered through a cotton pad, and evaporated. The resulting residue was purified by column chromatography (silica-gel 15 g, *n*-hexane/toluene = 5/1 → 4/1 → 3/1) to give **3** (169 mg, 44% yield) as a colorless syrup.

3. Typical procedure of the glucosidation (Table 1, entry 8).

A benzene solution of **4** (103 mg, 0.133 mmol) was evaporated to azeotropically remove trace water that was contained to the starting material. Then it was dissolved in CH_2Cl_2 (1.3 mL), and MS 4A (100 mg), cyclohexylmethanol (18.2 mg, 0.159 mmol), and MeOTf (87.3 mg, 0.532 mmol) was added, and the mixture was stirred for 1.5 at room temperature. After confirmation that the reaction was complete by monitoring TLC, the reaction mixture was diluted with hexane (15 mL), quenched with Et_3N (45 μL), and filtered through Celite. Then the filtrate was washed with H_2O, brine, dried over $MgSO_4$, and filtered. After evaporation, the resulting residue was purified by silica gel column chromatography (silica-gel, 6 g, hexane/ CH_2Cl_2 10/1 to 5/2 gradient) to afford anomeric mixture of glucoside **10** as colorless syrup (102 mg, 92% yield, α/β = 5/95). The anomeric ratio was determined by integral of the H-1 peaks in the ^1H NMR spectra.

4. Clarifications of the structures of of 8, 9, and 10.

4.1. Desilylation of 8 and acetylation of the desilylated compound.



To a solution of the glycosilated product **8** (28.7 mg, 0.032 mmol, α/β = 14/86) in THF (2 mL), a 1.0 M solution of TBAF (0.32 mL, 0.32 mmol) was added, and the mixture was

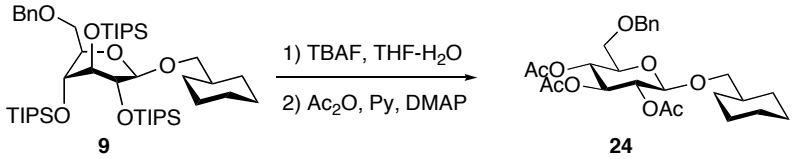
stirred for 18 h at rt. After confirmation that the reaction was complete by monitoring TLC, pyridine (1.5 mL), acetic anhydride (0.75 mL), and DMAP (10 mg, 82 μmol) was added to the mixture, and it was stirred for 1.5 h. Then, the solvents were almost evaporated under reduced pressure, and azeotropic removal of remaining trace pyridine was complete by evaporation with toluene. The resulting residue was purified by chromatography on silica-gel (2 g) eluting with 3/1 hexane/ethyl acetate to give an anomeric mixture of cyclohexylmethyl 2,3,4,6-tetra-O-acetyl-D-glucopyranoside (**23**) (18.8 mg, 100% yield). The mixture was further separated by HPLC (column: YMC-R-SIL-5, 250 × 4.6 mm; eluant: 4/1 hexane/ethyl acetate; flow rate: 2.0 mL/min) to give the α-**23** (Tr = 7.0 min) and the β-**23** (Tr = 9.1 min) as colorless syrup and white powder, respectively. The α/β-ratio due to the HPLC chromatogram was 7/93.

Data for α-**23**: $[\alpha]_D^{24}$ = +115° (c 1.60, $CHCl_3$); IR (film) 2926, 2855, 1752, 1370, 1227, 1038 cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ 5,46 (dd, *J* = 10.0, 9.6 Hz, 1H), 5.03 (dd, *J* = 9.3, 10.3 Hz, 1H), 5.02 (d, *J* = 3.6 Hz, 1H), 4.83 (dd, *J* = 10.1, 3.6 Hz, 1H), 4.24 (dd, *J* = 12.2, 4.5 Hz, 1H), 4.07 (dd, *J* = 12.2, 2.2 Hz, 1H), 3.99 (ddd, *J* = 10.3, 4.5, 2.2 Hz, 1H), 3.47 (dd, *J* = 9.6, 6.7 Hz, 1H), 3.18 (dd, *J* = 9.6, 6.4 Hz, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H) ; ^{13}C NMR (75 MHz in $CDCl_3$) δ 170.8 (s, 1C), 170.4 (s, 1C), 170.3 (s, 1C), 169.8 (s, 1C), 95.9 (d, 1C), 74.4 (t, 1C), 71.2 (d, 1C), 70.5 (d, 1C), 68.8 (d, 1C), 67.2 (d, 1C), 62.1 (t, 1C), 37.8 (d, 1C), 30.0 (t, 1C), 29.9 (t, 1C), 26.6 (t, 1C),25.9 (t, 1C), 20.9 (q, 2C), 20.8 (q, 2C); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{21}H_{32}O_{10}$ 467.1893, found 467.1879.

Data for β-**23**: mp 94-95 °C; $[\alpha]_D^{23}$ = –17.0° (c 0.67, $CHCl_3$); IR (film) 2926, 2855, 1757, 1370, 1225, 1042 cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ 5.19 (dd, *J* = 9.5, 9.5 Hz, 1H), 5.07 (dd, *J* = 9.8 9.3 Hz, 1H), 4.98(dd, *J* = 9.5, 7.9 Hz, 1H), 4.45 (d, *J* = 7.9 Hz, 1H), 4.25 (dd, *J* = 12.3, 4.6 Hz, 1H), 4.12 (dd, *J* = 12.2, 2.4 Hz, 1H), 3.69 (dd, *J* = 9.3, 6.3 Hz, 1H, overlapping with m, 1H), 3.23 (dd, *J* =9.5, 7.1 Hz, 1H), 2.08 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.81-1.49 (m, 6H), 1.30-1.05 (m, 3H), 0.94-0.84 (m, 2H); ^{13}C NMR (75 MHz in $CDCl_3$) δ 170.9 (s, 1C), 170.5 (s, 1C), 169.6 (s, 1C), 169.5 (s, 1C), 101.2 (d, 1C), 76.1 (t, 1C), 73.0 (d, 1C), 71.9 (d, 1C), 71.5 (d, 1C), 68.7 (d, 1C), 62.2 (t, 1C), 37.9 (d, 1C), 29.9 (t, 1C), 26.7 (t, 1C), 25.9 (t, 2C), 21.0 (q, 1C), 20.8 (q, 3C); HRMS-ESI (*m/z*):

$[M+Na]^+$ calcd for $C_{21}H_{32}O_{10}$ 467.1893, found 467.1902.

4.2. Desilylation of 9 and acetylation of the desilylated compound.

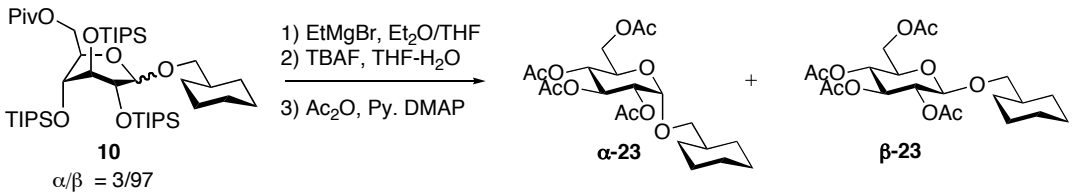


9 **24**

A 1 M solution of TBAF (1.6 mL, 1,6 mmol) was added to **9** (130 mg, 0.155 mmol), and the mixture was stirred for 15 h. After confirmation that the reaction was complete by monitoring TLC, pyridine (1.6 mL), THF was removed by evaporation. To the resulting residue, acetic anhydride (0.8 mL), and DMAP (10 mg, 82 μmol) was added, and it was stirred for 15 min. Then, the solvent, pyridine, was almost evaporated under reduced pressure, and azeotropic removal of remaining trace pyridine was complete by evaporation with toluene. The resulting residue was purified by chromatography on silica-gel (8 g) eluting with hexane/ethyl acetate (10/1→4/1→3/1) to give cyclohexylmethyl 2,3,4-tri-*O*-acetyl-6-*O*-benzyl-β-D-glucopyranoside (**24**) (67.5 mg, 88% yield) as white powder.

Data for **24**: mp 69-70 °C; $[\alpha]_D^{23}$ = –5.69° (c 0.6, $CHCl_3$); IR (film) 2926, 2855, 1757, 1246, 1221, 1051 cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ 7.59-7.25 (m, 5H), 5.19 (dd, J = 9.6, 9.5 Hz, 1H), 5.04 (dd, *J* = 9.6, 9.5 Hz, 1H), 4.98 (dd, *J* = 9.6, 7.9 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 7.9 Hz, 1H), 3.71 (dd, *J* = 9.5, 6.2 Hz, 1H), 3.66 (ddd, *J* = 9.6, 4.8, 3.8 Hz, 1H), 3.60-3.53 (m, 2H), 3.25(dd, *J* = 9.5, 6.9 Hz, 1H), 2.03 (s, 3H), 2.00 (s, 3H), 1.91(s, 3H), 1.78-1.52 (m, 6H), 1.30-0.83 (m, 5H); ^{13}C NMR (75 MHz in $CDCl_3$) δ 170.5 (s, 1C), 169.7 (s, 1C), 169.5 (s, 1C), 137.9 (s, 1C), 128.5 (d, 2C), 128.0 (d, 2C), 127.9 (d, 1C), 101.1 (d, 1C), 75.8 (t, 1C), 73.7 (t, 1C), 73.4 (d, 1C), 73.1 (d, 1C), 71.6 (d, 1C), 69.6 (d, 1C), 69.1 (t, 1C), 37.9 (d, 1C), 29.8 (t, 1C), 29.7 (t, 1C), 26.7 (t, 1C), 25.9 (t, 2C), 20.8 (q, 3C); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{26}H_{36}O_7$ 515.2257, found 515.2244.

4.3. Depivaloylation and desilylation of 10 and acetylation of the deprotected compound.



To a solution of **10** (94.0 mg, 0.113 mmol) in ether (1.2 mL) was added a 1.0 M THF solution of ethyl magnesium bromide (1.2 mL), and the mixture was stirred for 3.5 h at rt. After confirmation that the reaction was complete by monitoring TLC, saturated aqueous NH_4Cl was added to the mixture, and it was diluted to dissolve all salts. The mixture was extracted with hexane, and the hexane layer was washed with brine, dried over $MgSO_4$, filtered through a cotton pad, and evaporated. To the resulting residue was added 1.0 M solution of TBAF in THF (1.2 mL), and the mixture was stirred for 13 h at rt. Then, THF was evaporated, and pyridine (1.2 mL), acetic anhydride (0.6 mL), and DMAP (5 mg, 41 μmol) were added to the resulting residue, and the mixture was stirred for 10 min. After confirmation that the reaction was complete by monitoring TLC, the solvent, pyridine, was almost evaporated under reduced pressure, and azeotropic removal of remaining trace pyridine was complete by evaporation with toluene. The resulting residue was purified by chromatography on silica-gel (10 g) eluting with hexane/ethyl acetate (10/1→6/1→4/1→2/1) to give 2,3,4,6-tetra-*O*-acetyl-D- glucopyranoside (**23**) (44.1 mg, 88% yield). The mixture was separated by HPLC as described in 4.1.

5. Spectral data of the new compounds.

5.1. Ethyl 1-thio-2,3,4,6-tetrakis-*O*-TIPS-β-D-glucopyranoside (1)

$[\alpha]_D^{24}$ = –24.8° (*c* 1.49, $CHCl_3$); IR (film) 2944, 2893, 2868, 1464, 1109, 1067, 883, 681 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) δ 4.84 (d, *J* = 6.6 Hz, 1H), 4.13 (dd, *J* = 4.5, 1.0 Hz, 1H), 4.07 (dd, *J* = 4.5, 1.5 Hz, 1H), 4.00-3.87 (m, 3H), 3.87 (ddd, *J* = 6.6, 1.5, 1.0 Hz,

1H), 2.78-2.59 (m, 2H), 1.28 (t, *J* = 7.6 Hz, 3H), 1.30-1.03 (m, 84H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 84.1 (d, 1C), 83.9 (d, 1C), 77.7 (d, 1C), 76.5 (d, 1C), 71.4 (d, 1C), 65.9 (t, 1C), 25.6 (t, 1C), 18.7 (q, 6C), 18.6 (q, 9C), 18.5 (q, 3C), 18.2 (q, 6C), 15.0 (q, 1C), 13.1 (d, 6C), 12.8 (d, 3C), 12.3 (d, 3C); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{44}H_{96}O_5SSi_4$ 871.5953, found 871.5932.

5.2. Ethyl 6-*O*-benzyl-1-thio-2,3,4-tris-*O*-TIPS-β-D-glucopyranoside (2)

$[\alpha]_D^{24}$ = –29.7° (*c* 2.14, $CHCl_3$); IR (film) 2943, 2892, 2868, 1464, 1111, 1069, 883, 681 cm^{-1}; ^{1}H NMR (400 MHz in acetone-d_6) δ 7.35-7.28 (m, 5H), 4.89 (d, *J* = 6.6 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz), 4.21 (ddd, *J* = 2.9, 1.2, 0.5 Hz, 1H), 4.17 (ddd, *J* = 2.9, 1.7, 1.2 Hz, 1H), 4.06 (dddd, *J* = 6.8, 6.4, 1.7, 0.5 Hz, 1H), 3.95 (ddd, *J* = 6.6, 1.2, 1.2 Hz, 1H), 3.82 (dd, *J* = 9.5, 6.8 Hz, 1H), 3.73 (dd, *J* = 9.5, 6.4 Hz, 1H), 2.81-2.60 (m, 2H), 1.28 (t, *J* = 7.3 Hz, 3H), 1.30-1.06 (m, 63 H); ^{13}C NMR (75 MHz in acetone-d_6) δ 140.2 (s, 1C), 129.7 (d, 2C), 129.3 (d, 2C), 129.1 (d, 1C), 85.3 (d, 1C), 83.2 (d, 1C), 78.7 (d, 1C), 77.8 (d, 1C), 74.6 (t, 1C), 73.5 (t, 1C), 72.8 (d, 1C), 26.6 (t, 1C), 19.8 (q, 3C), 19.7 (q, 3C), 19.6 (q, 9C), 19.5 (q, 3C), 16.2 (q, 1C), 14.4 (d, 6C), 14.0 (d, 3C); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{42}H_{82}O_5SSi_3$ 805.5088, found 871.5083.

5.3. Ethyl 6-*O*-pivaloyl-1-thio-2,3,4-tris-*O*-TIPS-β-D-glucopyranoside (3)

$[\alpha]_D^{24}$ = –20.3° (*c* 1.97, $CHCl_3$); IR (film) 2946, 2893, 2868, 1736, 1464, 1123, 1069, 883, 681 cm^{-1}; ^{1}H NMR (400 MHz in $CDCl_3$) δ 4.88 (d, *J* = 5.9 Hz, 1H, H-1), 4.36 (dd, *J* = 11.5, 5.4, Hz, 1H, H-6a), 4.30 (dd, *J* = 11.2, 7.3 Hz, 1H, H-6b), 4.13 (dd, *J* = 2.7, 1.0 Hz, 1H, H-3), 4.03 (ddd, *J* = 7.3, 5.4, 2.0 Hz, 1H, H-5), 3.99 (ddd, *J* = 2.7, 2.0, 1.0 Hz, 1H, H-4), 3.93 (ddd, *J* = 5.9, 1.0, 1.0 Hz, 1H, H-2), 2.71-2.58 (m, 2H), 1.28 (t, *J* = 7.3 Hz, 3H), 1.19 (s, 9H), 1.09-1.06 (m, 63H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 178.4 (s, 1C), 84.0 (d, 1C), 80.2 (d, 1C), 76.8 (d, 1C), 76.0 (d, 1C), 71.6 (d, 1C), 66.4 (t, 1C), 38.9 (s, 1C), 27.3 (q, 3C), 25.8 (t, 1C), 18.6 (q, 6C), 18.5 (q, 9C), 18.4 (q, 3C), 15.1 (q, 1C), 13.0 (d, 6C), 12.7 (d, 3C); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{40}H_{84}O_6SSi_3$ 799.5194, found 799.5185.

5.4. Ethyl 2,3-di-*O*-acetyl-6-*O*-benzyl-1-thio-β-D-glucopyranoside (6)

$[\alpha]_D^{24}$ = –49.0° (*c* 1.21, $CHCl_3$); IR (film) 3476, 3088, 3063, 3030, 2965, 2930, 2870, 1752, 1373, 1240, 1074, 1049 cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ 7.41-7.20 (m, 5H), 5.07 (dd, *J* = 9.1, 9.3 Hz, 1H), 4.95 (dd, *J* = 9.8, 9.5 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.55 (12.0 Hz, 1H), 4.46 (d, *J* = 9.8 Hz, 1H), 3.81 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.74 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.77-3.72 (m, 1H), 3.54 (ddd, *J* = 9.4, 4.8, 4.8 Hz, 1H), 2.77-2.59 (m, 2H), 2.07 (s, 3H), 2.05 (s, 3H), 1.25 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz in $CDCl_3$) d 171.4 (s, 1C), 169.9 (s, 1C), 137.7 (s, 1C), 128.6 (d, 2C), 128.1 (d, 1C), 127.9 (d, 2C), 83.4 (d, 1C), 78.3 (d, 1C), 76.7 (d, 1C), 73.9 (t, 1C), 70.9 (d, 1C), 70.3 (t, 1C), 70.1 (d, 1C), 24.3 (t, 1C), 21.0 (q, 1C), 20.0 (q, 1C), 15.1 (q, 1C); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{19}H_{26}O_7S$ 421.1297, found 421.1286.

5.5. Ethyl 6-*O*-pivaloyl-1-thio- β-D-glucopyranoside (7)

mp 55.5-57.8 °C; $[\alpha]_D^{24}$ = –49.5° (*c* 1.64, $CHCl_3$); IR (film) 3420, 2973, 2930, 2874, 1730, 1289, 1169, 1080, 1036 cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ 4.42 (dd, *J* = 11.9, 6.7 Hz, 1H), 4.40 (d, *J* = 9,6 Hz, 1H), 4.20 (dd, *J* = 11.9, 6.7 Hz, 1H), 3.57 (dd, *J* = 8.8, 8.8 Hz, 1H), 3.51 (ddd, *J* = 9.8, 6.7, 1.7 Hz, 1H), 3.38 (dd, *J* = 9.6, 8.8 Hz, 1H), 3.37 (dd, *J* = 9.5, 8.9 Hz, 1H), 2.79-2.61 (2H, m), 1.29 (t, *J* = 7.4 Hz, 3H), 1.19 (s, 9H); ^{13}C NMR (75 MHz in $CDCl_3$) δ 179.2 (s, 1C), 85.5 (d, 1C), 78.0 (d, 1C), 77.9 (d, 1C), 72.8 (d, 1C), 70.5 (d, 1C), 64.2 (t, 1C), 39.0 (s, 1C), 27.4 (q, 3C), 24.7 (t, 1C), 15.6 (q, 1C); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{13}H_{24}O_6S$ 331.1191, found 331.1197.

5.6. Cylohexylmethyl 2,3,4,6-tetrakis-*O*-TIPS-β-D-glucopyranoside (8)

$[\alpha]_D^{22}$ = –7.45° (*c* 2.55, $CHCl_3$); IR (thin film) 2944, 2868, 1464, 1111, 1069, 883, 681 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.72 (d, *J* = 5.0 Hz, 1H), 4.05 (d, *J* = 3.0 Hz, 1H), 3.97 (dd, *J* = 3.0, 0.9 Hz, 1H), 3.96 (dd, *J* = 8.7, 5.7 Hz, 1H), 3.89 (dd, *J* = 5.7, 5.7 Hz, 1H), 3.84 (dd, *J* = 8.7, 5.7 Hz, 1H), 3.79 (d, *J* = 5.0 Hz, 1H), 3.65 (dd, *J* = 8.9, 6.9 Hz, 1H), 3.14 (dd, *J* = 8.9, 6.6 Hz, 1H), 1.77-1.52 (m, many H), 1.28-0.85 (m, many H, including TIPS groups); ^{13}C NMR (100 MHz, $CDCl_3$) δ 102.1 (d, 1C), 82.7 (d, 1C), 77.9 (d, 1C), 76.6 (d, 1C), 74.6 (t, 1C), 71.1 (d, 1C), 65.9 (t, 1C), 38.4 (d, 1C), 30.4 (t, 2C), 26.9 (t, 1C), 26.2 (t, 2C), 18.6 (q, many), 18.5 (q, many), 18.2 (q, many), 13.0 (d, 3C), 12.9 (d, 3C), 12.6 (d, 3C),

12.3 (d, 3C); HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{49}H_{104}O_6Si_4$ 923.6808, found 923.6821.

5.7. Cyclohexylmethyl 6-*O*-benzyl-2,3,4-tris-*O*-TIPS-β-D-glucopyranoside (9)

$[\alpha]_D^{24}$ = –12.1° (*c* 1.3, $CHCl_3$); IR (thin film) 3090, 3065, 3032, 2941, 2866, 2722, 1464, 1111, 1069, 1044, 1015, 999, 883, 681 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 7.37-7.26 (m, 5H), 4.80 (d, *J* = 5.4 Hz, 1H), 4.57 (d, *J* = 11.7 Hz, 1H), 4.52 (d, *J* = 11.7 Hz, 1H), 4.16 (ddd, *J* =2.9, 1.0, 0.5 Hz, 1H), 4.14 (ddd, *J* = 2.9, 1.0, 1.0 Hz, 1H), 4.08 (dddd, *J* = 7.3, 6.3, 1.0, 1.0 Hz, 1H), 3.87 (ddd, *J* = 5.4, 1.0, 0.5 Hz, 1H), 3.81 (dd, *J* = 9.3, 7.3 Hz, 1H), 3.70 (dd, *J* = 9.3, 6.3 Hz, 1H), 3.67 (dd, *J* = 9.0, 7.1 Hz, 1H), 3.23 (dd, *J* = 9.0, 6.1 Hz, 1H), 1.83-1.57 (m, 6H), 1.13-1.06 (m, 68H); ^{13}C NMR (75 MHz, acetone-d_6) δ 139.6 (s, 1C), 129.0 (d, 2C), 128.3 (d, 2C), 102.9 (d, 1C), 81.4 (d, 1C) 78.8 (d, 1C), 77.7 (d, 1C), 75.1 (t, 1C), 73.9 (t, 1C), 72.7 (d, 1C), 39.3 (d, 1C), 31.1 (t, 1C), 30.9 (t, 1C), 27.4 (t, 1C), 26.8 (t, 1C), 26.7 (t, 1C), 18.9 (q, many), 18.8 (q, many), 13.6 (d, 3C), 13.5 (d, 3C), 13.2 (d, 3C); HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{47}H_{90}O_6Si_3$ 857.5943, found 857.5956.

5.8. Cyclohexylmethyl 6-*O*-pivaloyl-2,3,4-tris-*O*-TIPS-β-D-glucopyranoside (10)

$[\alpha]_D^{22}$ = –3.82° (*c* 2.40, $CHCl_3$); IR (thin film) 2944, 2868, 1464, 1119, 883, 681 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.76 (d, *J* = 4.1 Hz, 1H), 4.33 (d, *J* = 6.6 Hz, 2H), 4.07 (ddd, *J* = 2.7, 0.7, 0.7 Hz, 1H), 4.03 (tdd, *J* = 6.6, 0.9, 0.7 Hz, 1H), 3.93 (ddd, *J* = 2.7, 0.9, 0.4 Hz, 1H), 3.65 (dd, *J* = 9.2, 6.6 Hz, 1H), 3.15 (dd, *J* = 9.2, 6.6 Hz, 1H), 1.76-1.51 (m, 8H), 1.20 (s, 9H), 1.08-1.03 (m, 63H), 0.98-0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4 (s, 1C), 102.1 (d, 1C), 78.3 (d, 1C), 76.5 (d, 1C), 75.4 (d, 1C), 74.7 (t, 1C), 70.8 (d, 1C), 66.4 (t, 1C), 38.9 (s, 1C), 38.3 (t, 2C), 27.4 (q, 3C), 26.9 (t, 1C), 26.1 (t, 2C), 18.5 (q, many), 18.4 (q, many), 12.8 (d, 6C), 12.5 (d, 3C); HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{45}H_{92}O_7Si_3$ 851.6049, found 851.6048.

5.9. 1,5-anhydro-6-*O*-pivaloyl-2,3,4-tris-*O*-TIPS-D-*arabino*-hex-1-enitol (11)

$[\alpha]_D^{24}$ = +4.7° (*c* 1.6, $CHCl_3$); IR (film) 2946, 2868, 1736, 1464, 1144, 1090, 1067, 883, 685 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) δ 6.11 (s, 1H), 4.39 (dd, J = 12.0, 8.1 Hz, 1H), 4.26 (dd, J =12.0, 3.9 Hz, 1H), 4.13 (ddd, J = 8.1, 3.9, 1.7 Hz, 1H), 4.10 (dd, J = 2.4, 1.7 Hz,

1H), 4.05 (dd, J = 2.4, 1.5 Hz, 1H), 1.21 (s, 9H), 1.15-1.00 (m, 63H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 178.6 (s, 1C), 134.5 (s, 1C), 127.3 (d, 1C), 75.9 (d, 1C), 71.0 (d, 1C), 70.0 (d, 1C), 63.3 (d, 1C), 38.9 (s, 1C), 27.4 (q, 3C), 18.5 (q, 3C), 18.3 (q, 12C), 18.2 (q, 3C), 13.3 (d, 3C), 12.9 (d, 3C), 12.6 (d, 3C); HRMS-FAB (*m*/*z*): M^+ calcd for $C_{38}H_{78}O_6Si_3$ 714.5106, found 714.5116.

5.10. Cyclohexyl 6-*O*-pivaloyl-2,3,4-tris-*O*-TIPS-β-D-glucopyranoside (16)

$[\alpha]_D^{23}$ = –8.58° (*c* 1.06, $CHCl_3$); IR (thin film) 2942, 2868, 1734, 1464, 1117, 1069, 1038, 1015, 997, 883, 681 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (d, *J* = 4.4 Hz, 1H), 4.36 (dd, *J* = 11.2, 5.7 Hz, 1H), 4.30 (dd, *J* = 11.2, 7.6 Hz, 1H), 4.07 (ddd, *J* = 3.0, 0.9, 0.7 Hz, 1H), 4.02 (dddd, *J* = 7.6, 5.7, 1.2, 0.7 Hz, 1H), 3.93 (ddd, *J* = 3.0, 1.2, 1.2 Hz, 1H), 3.83 (ddd, *J* = 4.4, 1.2, 0.9 Hz, 1H), 3.70-3.63 (m, 1H), 1.96-1.91 (m, 1H), 1.76-1.68 (m, 2H), 1.56-1.49 (m, 1H), 1.40-1.06 (m, many signals including TIPS groups) overlapping with 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5 (s, 1C), 98.9 (d, 1C), 78.2 (d, 1C), 76.6 (d, 1C), 75.8 (d, 1C), 75.6 (d, 1C), 71.0 (d, 1C), 66.5 (t, 1C), 38.9 (s, 1C), 33.8 (t, 1C), 31.5 (t, 1C), 27.4 (q, 3C), 26.0 (t, 1C), 24.7 (t, 1C), 24.6 (t, 1C), 18.5 (q, many), 18.4 (q, many) 12.9 (d, 6C), 12.5 (d, 3C); HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{44}H_{90}O_7Si_3$ 837.5892, found 837.5870.

5.11. (1*S*,2*R*,5*S*)-5-methyl-2-(1-methylethyl)cyclohexyl-6-*O*-pivaloyl-2,3,4-tris-*O*-TIPS-β-D-glucopyranoside (17)

$[\alpha]_D^{22}$ = –10.9° (*c* 1.48, $CHCl_3$); IR (thin film) 2948, 2868, 1736, 1464, 1117, 883, 683 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (d, *J* = 4.1 Hz, 1H), 4.31 (dd, *J* = 11.4, 5.0 Hz, 1H), 4.24 (dd, *J* = 11.4, 7.6 Hz, 1H), 4.05 (ddd, *J* = 2.8, 0.7, 0.4 Hz, 1H), 3.97 (dddd, *J* = 7.6, 5.0, 2.5, 0.4 Hz, 1H), 3.93 (ddd, *J* = 2.8, 2.5, 0.7 Hz, 1H), 3.86 (ddd, *J* = 4.1, 0.7, 0.7 Hz, 1H), 3.37 (td, *J* = 10.8, 4.3 Hz, 1H), 2.32-2.25 (m, 1H), 2.15-2.09 (m, 1H), 1.63-1.52 (m, 2H), 1.21 (s, 9H), 1.10-1.08 (m, 63H), 0.95-0.68 (m, 5H) overlapping with 0.88 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 7.1 Hz, 3H), and 0.73 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5 (s, 1C), 102.0 (d, 1C), 78.5 (d, 1C), 77.9 (d, 1C), 77.4 (d, 1C), 76.6 (d, 1C), 71.7 (d, 1C), 66.3 (t, 1C), 48.9 (d, 1C), 42.9 (t, 1C), 38.9 (s, 1C), 34.6 (t, 1C), 32.1 (d, 1C),

27.4 (q, 3C), 25.2 (d, 1C), 23.2 (t, 1C), 22.6 (q, 1C), 21.4 (q, 1C), 18.6 (q, many), 18.5 (q, many), 18.5 (q, many), 18.4 (q, many), 16.1 (q, 1C), 13.1 (d, 3C), 13.1 (d, 3C) 12.7 (d, 3C); HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{48}H_{98}O_7Si_3$ 893.6518, found 893.6544.

5.12. (1*R*,2*S*,5*R*)-5-methyl-2-(1-methylethyl)cyclohexyl-6-*O*-pivaloyl-2,3,4-tris-*O*-TIPS-β-D-glucopyranoside (18)

$[\alpha]_D^{25} = -27.2°$ (*c* 1.38, $CHCl_3$); IR (thin film) 2948, 2868, 1736, 1464, 1119, 1069, 1036, 1015, 883, 681 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.96 (d, *J* = 6.0 Hz, 1H), 4.23 (dd, *J* = 11.0, 7.6 Hz, 1H), 4.19 (dd, *J* = 11.0, 7.6 Hz, 1H), 4.08 (dd, *J* = 3.0, < 0.1Hz, 1H), 3.99 (ddd, *J* = 7.6, 5.5, 0.9 Hz, 1H), 3.92 (ddd, *J* = 3.0, 0.9, 0.9 Hz, 1H), 3.80 (ddd, *J* = 6.0, 0.9, < 0.1 Hz, 1H), 3.65 (td, *J* = 10.8, 3.9 Hz, 1H), 2.29 (dtd, *J* = 14.0, 7.1, 2.5 Hz, 1H), 2.09-2.03 (m, 1H), 1.67-1.58 (m, 2H), 1.19 (s, 9H), 1.10-1.03 (m, 63H), 0.98-0.71 (m, 5H) overlapping with 0.91 (d, *J* = 6.4 Hz, 3H), 0.83 (d, *J* = 7.1 Hz, 3H), 0.72 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5 (s, 1C), 96.6 (d, 1C), 79.7 (d, 1C), 78.5 (d, 1C), 78.0 (d, 1C), 73.3 (d, 1C), 71.7 (d, 1C), 66.6 (t, 1C), 48.3 (d, 1C), 39.5 (t, 1C), 38.9 (s, 1C), 34.9 (t, 1C), 31.7 (d, 1C), 27.3 (q, 3C), 25.4 (d, 1C), 22.7 (q, 1C), 21.2 (q, 1C), 18.6 (q, many), 18.5 (q, many), 18.4 (q, many), 13.1 (d, 3C), 12.9 (d. 3C), 12.5 (d. 3C); HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{48}H_{98}O_7Si_3$ 893.6518, found 893.6519.

5.13. Cholestanyl 6-*O*-pivaloyl-2,3,4-tris-*O*-TIPS-β-D-glucopyranoside (19)

$[\alpha]_D^{23} = -0.27°$ (*c* 1.48, $CHCl_3$); IR (thin film) 2944, 2868, 1734, 1466, 1155, 1117, 1069, 1038, 1015, 884, 681 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.99 (d, *J* = 4.8 Hz, 1H), 4.35 (dd, *J* = 11.2, 5.7 Hz, 1H), 4.28 (dd, *J* = 11.2, 7.3 Hz, 1H), 4.07 (d, *J* = 3.0 Hz, 1H), 4.02 (ddd, *J* = 7.3, 5.7, 0.9 Hz, 1H), 3.94 (ddd, *J* = 3.0, 0.9, < 0.1 Hz, 1H), 3.81 (dd, *J* = 4.8, < 0.1Hz, 1H), 3.68 (m, 1H), 1.99-1.93 (m, 1H), 1.89-1.76 (m, 2H), 1.70-1.43 (m, 7H), 1.38-0.84 (m, 20H) overlapping with 1.10-1.03 (m, 63H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.87 (d, *J* = 1.8 Hz, 3H), and 0.85 (d, *J* = 1.8 Hz, 3H), 0.77 (s, 3H), 0.65 (s, 3H), 0.63-0.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4 (s, 1C), 98.2 (d, 1C), 78.5 (d, 1C), 77.3 (d, 1C), 76.4 (d, 1C), 76.0 (d, 1C), 71.2 (d, 1C), 66.4 (t, 1C), 56.7 (d, 1C), 56.5 (d, 1C), 54.7 (d, 1C), 44.9 (d, 1C), 42.8 (s, 1C), 40.3 (t, 1C), 39.7 (t, 1C), 38.9 (s, 1C), 37.3 (t, 1C), 36.4 (t, 1C),

36.0 (d, 1C), 35.9 (s, 1C), 35.7 (d, 1C), 33.8 (t, 1C), 32.4 (t, 1C), 29.3 (t, 1C), 29.2 (t, 1C), 28.5 (t, 1C), 28.2 (d, 1C), 27.4 (q, 3C), 24.4 (t, 1C), 24.0 (t, 1C), 23.0 (q, 1C), 22.8 (q, 1C), 21.4 (t, 1C), 18.9 (q, 1C), 18.6 (q, many). 18.5 (q, many), 18.4 (q, many) 12.9 (d, 3C), 12.9 (d, 3C), 12.5 (d, 3C), 12.4 (q, 1C), 12.3 (q, 1C); HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{65}H_{126}O_7Si_3$ 1125.8709, found 1125.8693.

5.14. 1-adamantanyl 6-*O*-pivaloyl-2,3,4-tris-*O*-TIPS-β-D-glucopyranoside (20)

$[\alpha]_D^{22} = -5.98°$ (*c* 1.12, $CHCl_3$); IR (thin film) 2942, 2868, 1734, 1464, 1115, 883, 681 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.08 (d, *J* = 5.3 Hz, 1H), 4.28 (dd, *J* = 11.4, 5.3 Hz, 1H), 4.24 (dd, *J* = 2.8, 0.5 Hz, 1H), 4.05 (dd, *J* = 2.8, 0.5 Hz, 1H), 3.99 (ddd, *J* = 7.8, 5.3, 1.4 Hz, 1H), 3.90 (ddd, *J* = 2.8, 1.4, 0.9 Hz, 1H), 3.81 (ddd. *J* = 5.3, 0.9, 0.5 Hz, 1H), 2.10 (brs, 3H), 1.85 (brd, *J* = 2.7 Hz, 6H), 1.61 (brs, 6H), 1.20 (s, 9H), 1.15-1.06 (m, 63H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6 (s, 1C), 95.8 (d, 1C), 78.5 (d, 1C), 77.8 (d, 1C), 77.0 (d, 1C), 74.5 (s, 1C), 71.6 (d, 1C), 66.8 (t, 1C), 43.0 (t, 3C), 38.9 (s, 1C), 36.7 (t, 3C), 31.0 (d, 3C), 27.4 (q, 3C), 18.6 (q, many), 18.6 (q, many), 18.5 (q, many), 18.4 (q, many), 13.1 (d, 6C), 12.5 (d, 3C); HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{48}H_{94}O_7Si_3$ 889.6205, found 889.6205.

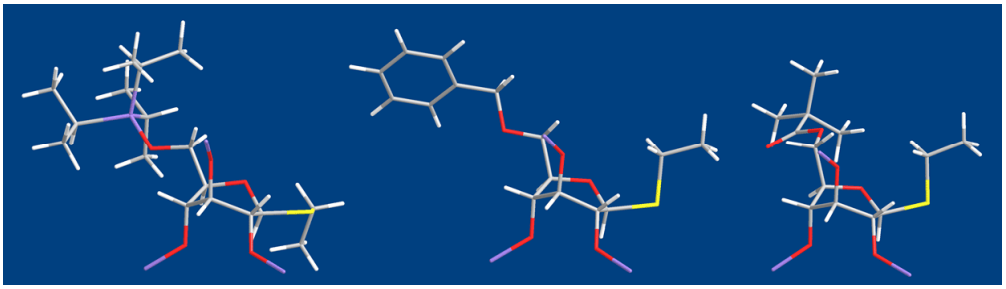
5.15. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(6-*O*-pivaloyl-2,3,4-tris-*O*-TIPS-β-D-glucopyranosyl)-α-D-glucopyranoside (21)

$[\alpha]_D^{24} = +13°$ (*c* 0.41, $CHCl_3$); IR (film) 3090, 3032, 2944, 2868, 1732, 1464, 1159, 1111, 1071, 1032, 883, 683 cm^{-1}; ^1H NMR (400 MHz in acetone-d_6) δ 7.41-7.23 (m, 15H), 4.96 (d, *J* = 11.2 Hz, 1H), 4.89 (d, *J* = 4.6 Hz, 1H), 4.88 (d, *J* = 11.4 Hz, 1H), 4.81 (d, *J* = 3.4 Hz, 1H), 4.78 (d, *J* = 11.2 Hz, 1H), 4.73 (s, 2H), 4.65 (d, *J* = 11.4 Hz, 1H), 4.41 (dd, *J* = 11.2, 6.6 Hz, 1H), 4.33 (dd, *J* = 11.2, 6.6 Hz, 1H), 4.18 (ddd, *J* = 2.9, 0.9, 0.9 Hz, 1H), 4.13 (dddd, *J* = 6.6, 6.6, 1.2, 0.9 Hz, 1H), 4.09 (ddd, *J* = 2.9, 1.2, 0.9 Hz, 1H), 4.04 (dd, *J* = 10.8, 2.1 Hz, 1H), 3.95-3.87 (m, 3H), 3.62 (dd, *J* = 10.8, 2.1 Hz, 1H), 3.55 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.39 (dd, *J* = 10.1, 8.7 Hz, 1H), 3.37 (s, 3H), 1.19 (s, 9H), 1.18-1.07 (m, 63H); ^{13}C NMR (100 MHz in acetone-d_6) δ 178.6 (s, 1C), 140.7 (s, 1C), 140.3 (s, 1C), 140.1 (s, 1C), 129.5 (d, 2C), 129.4 (d, 2C), 129.4 (d, 2C), 128.9 (d, 4C), 128.8 (d, 2C), 128.7 (d, 1C), 128.6 (d, 1C), 128.5 (d, 1C),

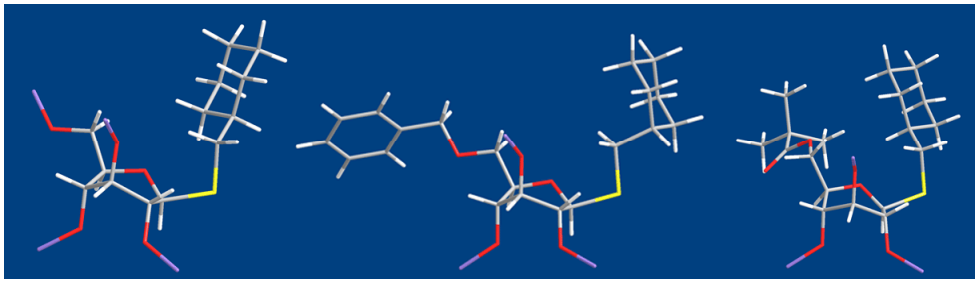
103.9 (d, 1C), 98.6 (d, 1C), 83.0 (d, 1C), 81.7 (d, 1C), 79.9 (d, 1C), 79.8 (d, 1C), 78.2 (d, 1C), 77.2 (d, 1C), 76.1 (t, 1C), 75.5 (t, 1C), 73.3 (t, 1C), 72.0 (d, 1C), 71.6 (d, 1C), 70.6 (t, 1C), 67.2 (t, 1C), 55.5 (q, 1C), 39.7 (s, 1C), 27.9 (q, 3C), 19.2 (q, many), 19.1 (q, many), 13.8 (d, 3C), 13.7 (d, 3C), 13.5 (d, 3C); HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{66}H_{110}O_{12}Si_3$ 1201.7203, found 1201.7189.

6. Assembled models of 1-3 and 8-10 based on the coupling constants.

The following models were constructed by Spartan ('04 Windows) to confirm the conformation of compounds **1**-**3** and **8-10**. Each model was optimized by a simple MMFF calculation after constraint of the dihedral angles (H-1–C-1–C-2–H-2, H-2–C-2–C-3–H-3, H-3–C-3–C-4–H-4, and H-4–C-4–C-5–H-5) to the calculated dihedral angles using the Karplus equation modified by Haasnoot and Altona ($J = 7.76 \cos^2 \omega - 1.1 \cos \omega + 1.4$, where J is the vicinal coupling constant and ω is the dihedral angle)[1] based on the observed coupling constants ($^3J_{H\text{-}H}$) in each ^{1}H NMR spectrum. Substituents on the silicon atoms are omitted for clarity.



1 **2** **3**

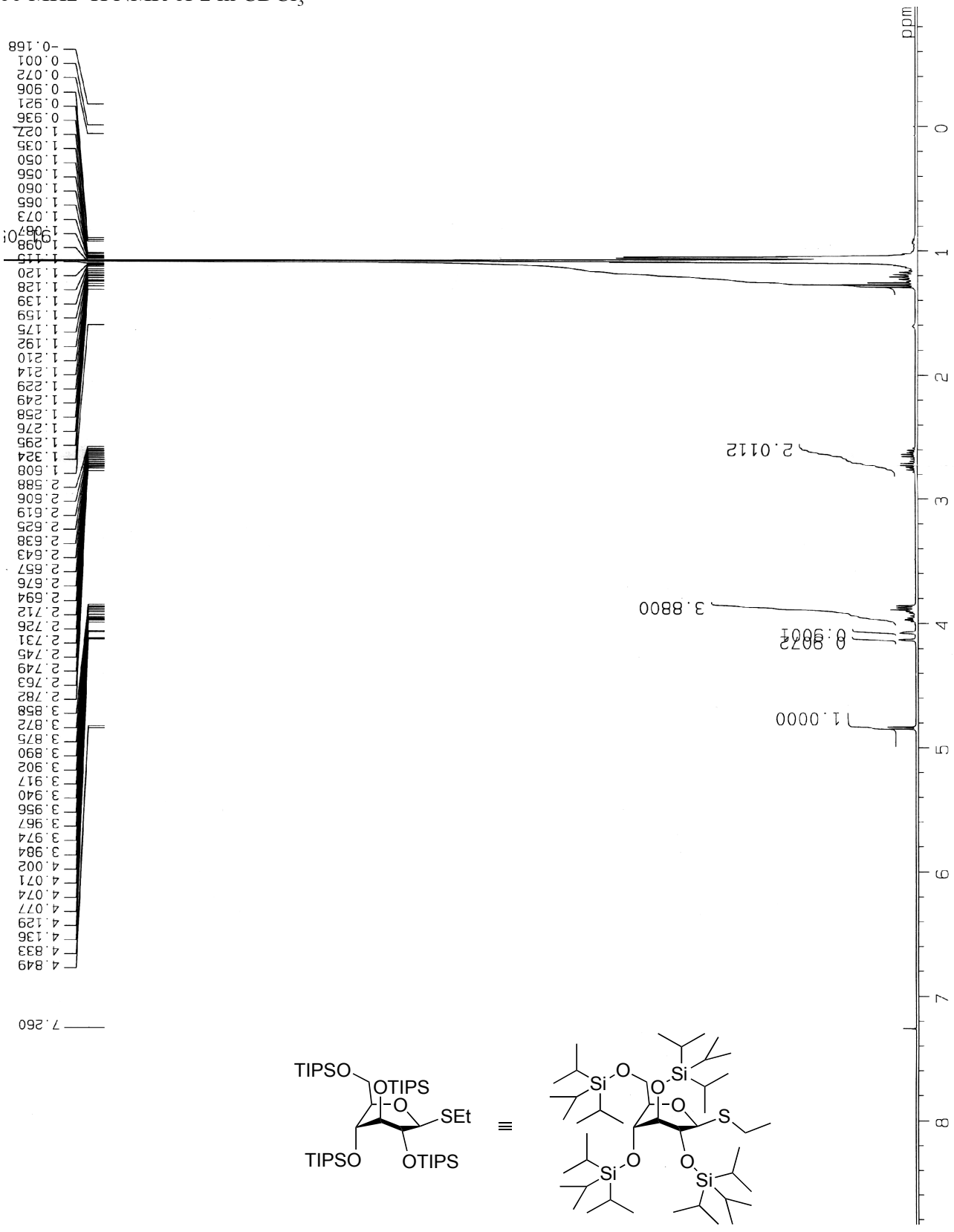


8 **9** **10**

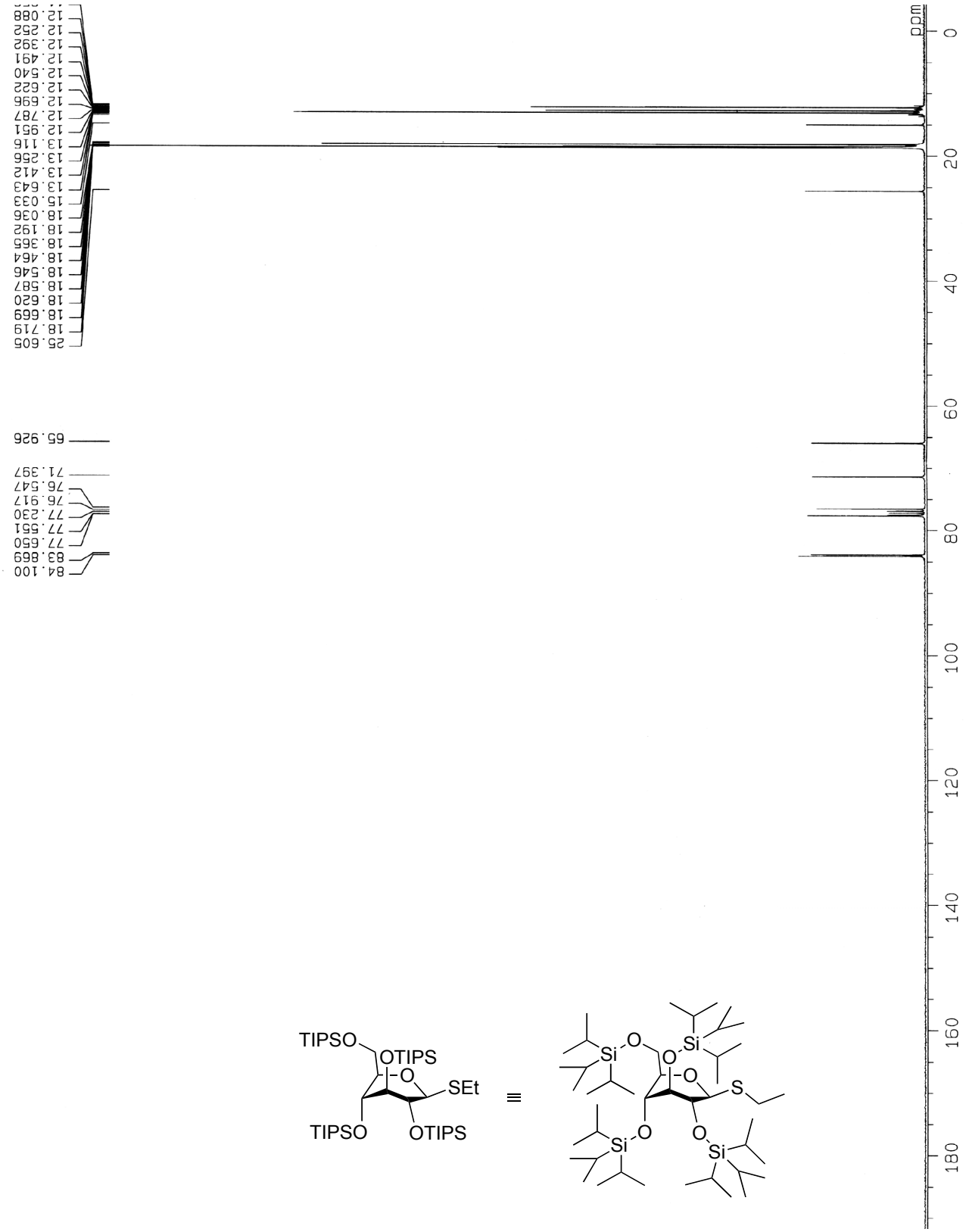
Reference

1 Haasnoot, C. A. G.; de Leeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783–2792.

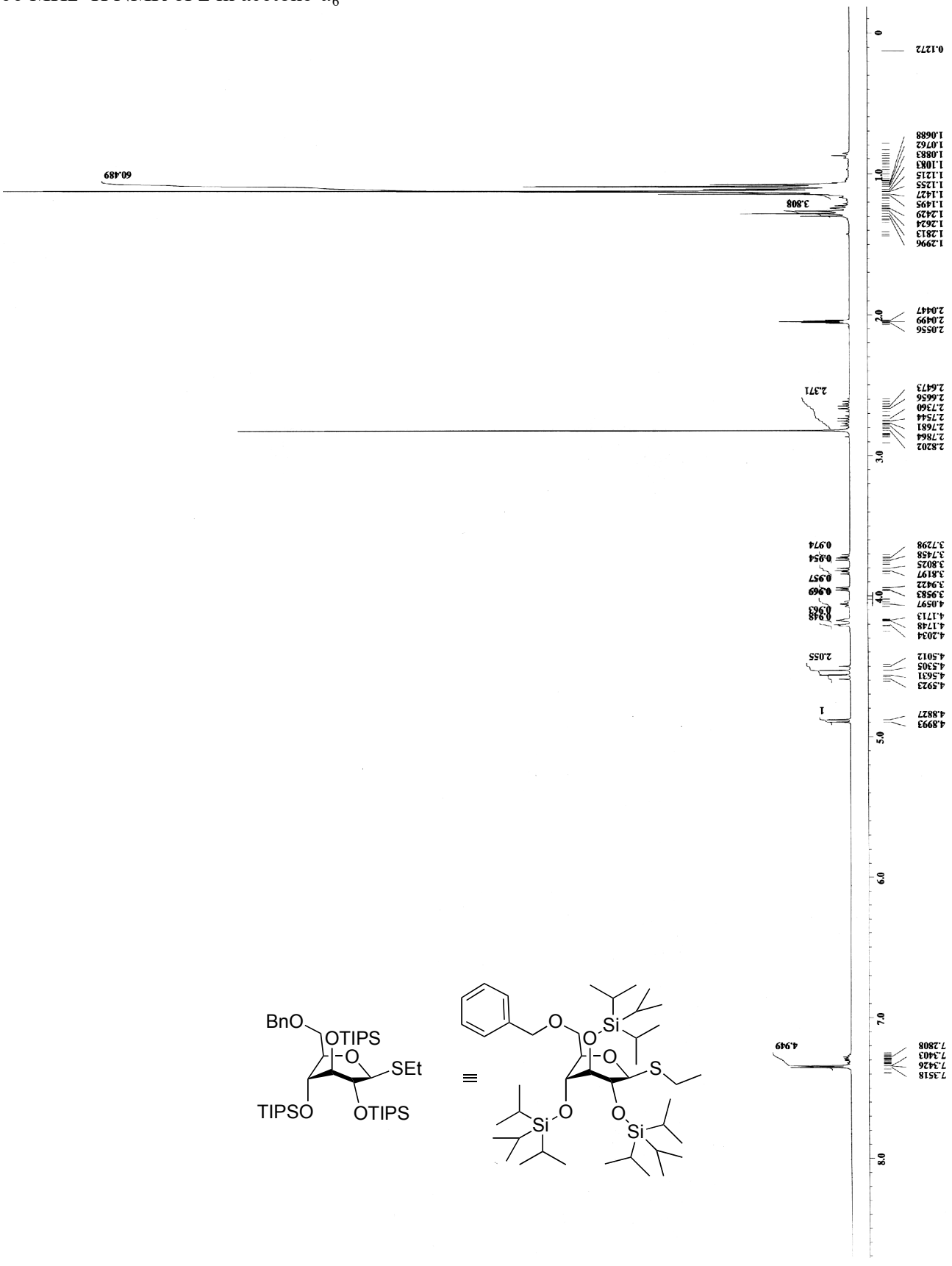
400 MHz ^{1}H NMR of **1** in $CDCl_3$



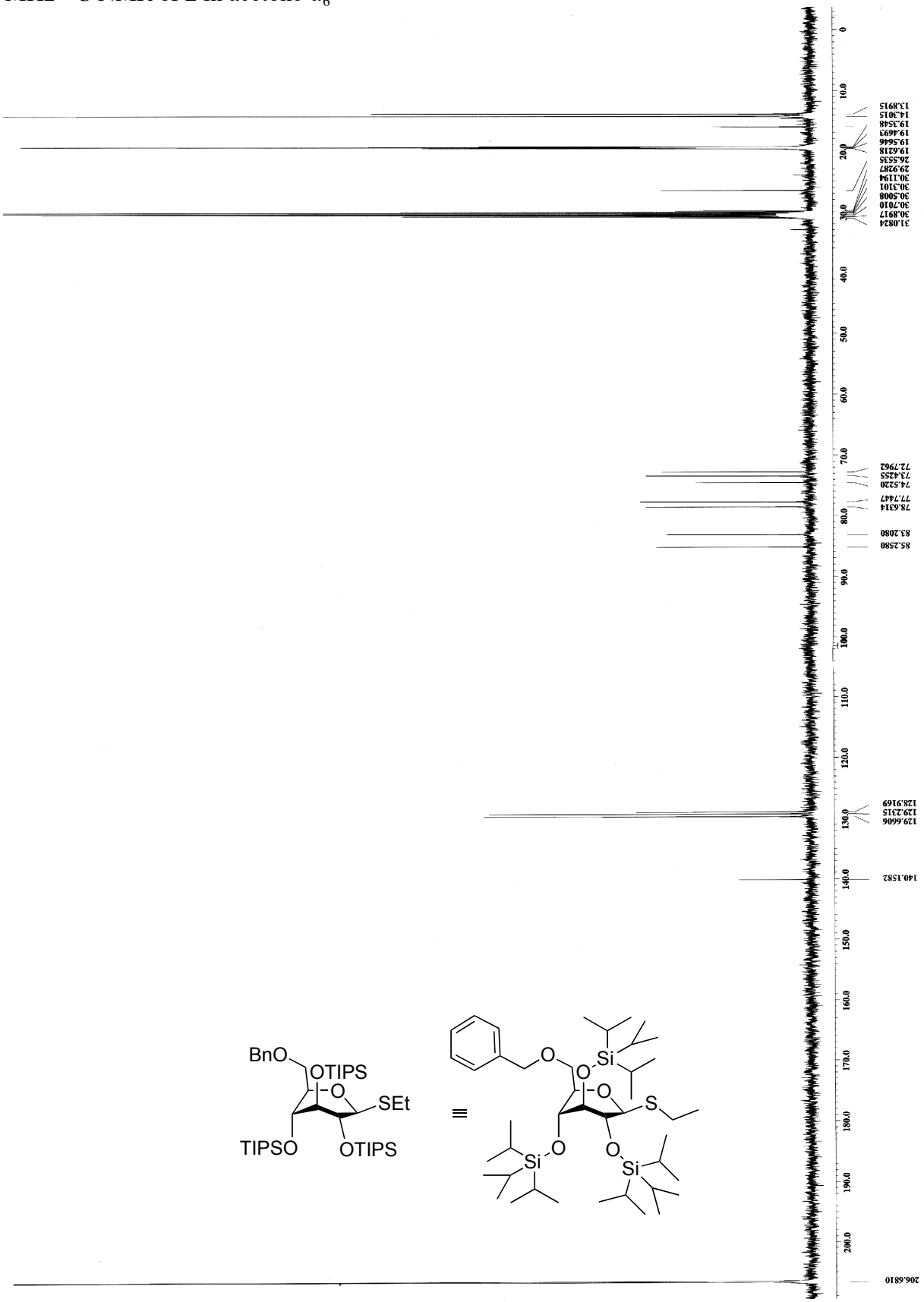
100 MHz ^{13}C NMR of **1** in $CDCl_3$



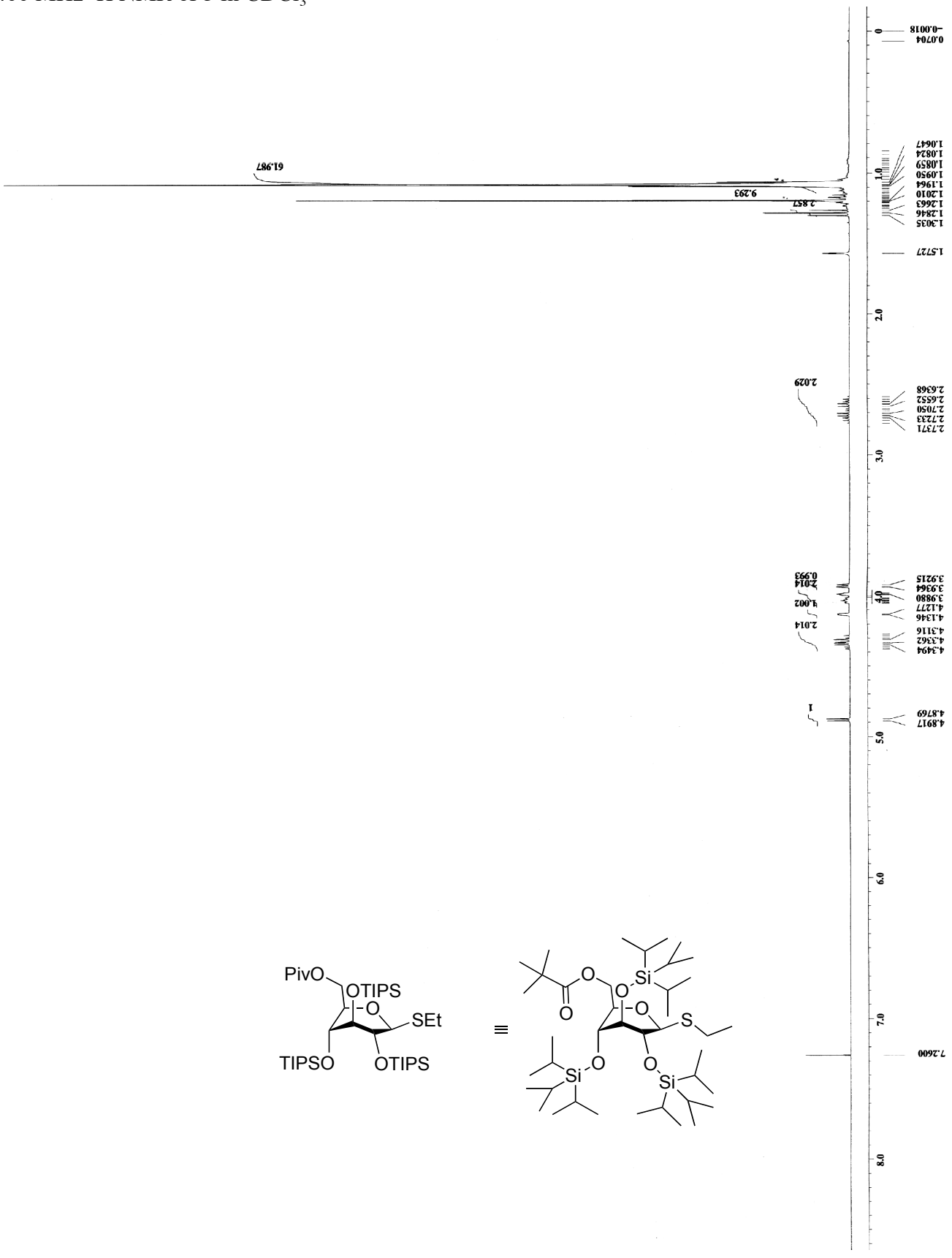
400 MHz ^{1}H NMR of **2** in acetone-d_6



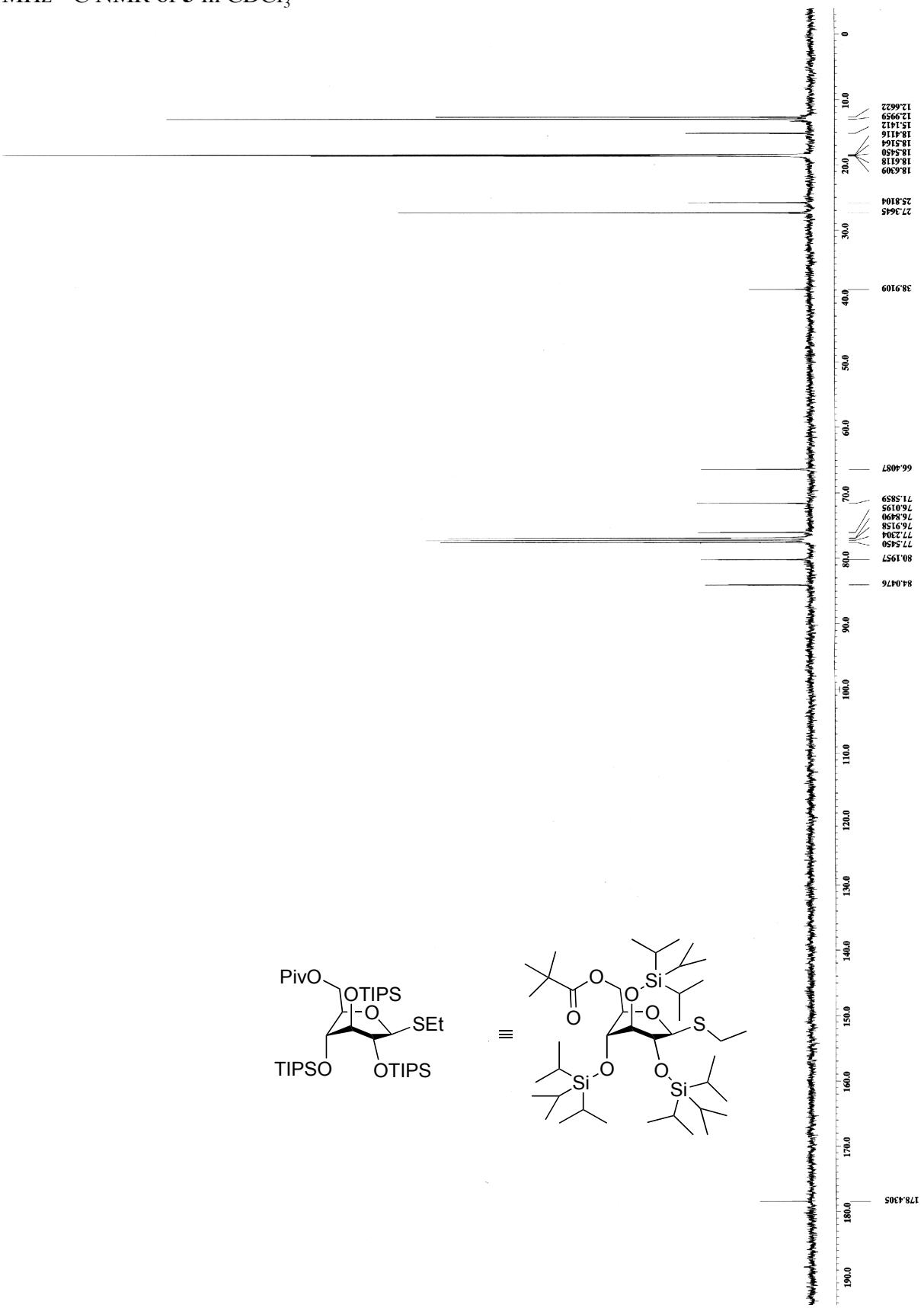
100 MHz ^{13}C NMR of **2** in acetone-d_6



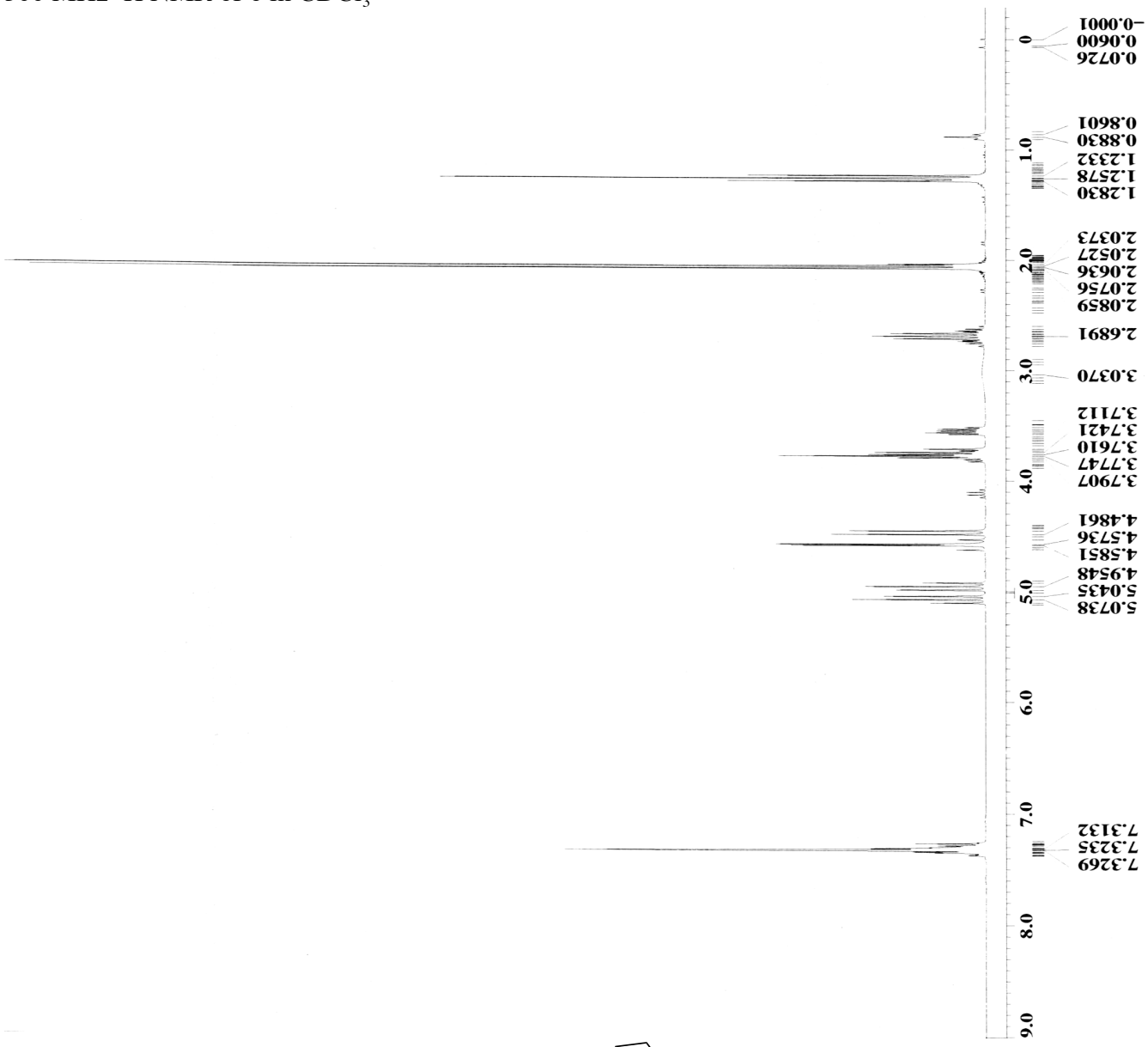
400 MHz ^{1}H NMR of **3** in $CDCl_3$

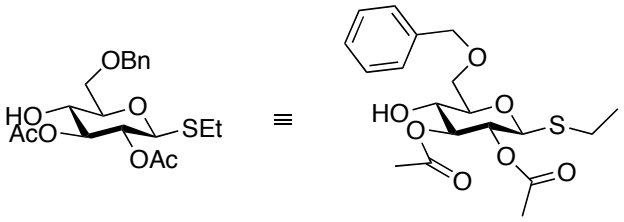


100 MHz ^{13}C NMR of **3** in $CDCl_3$

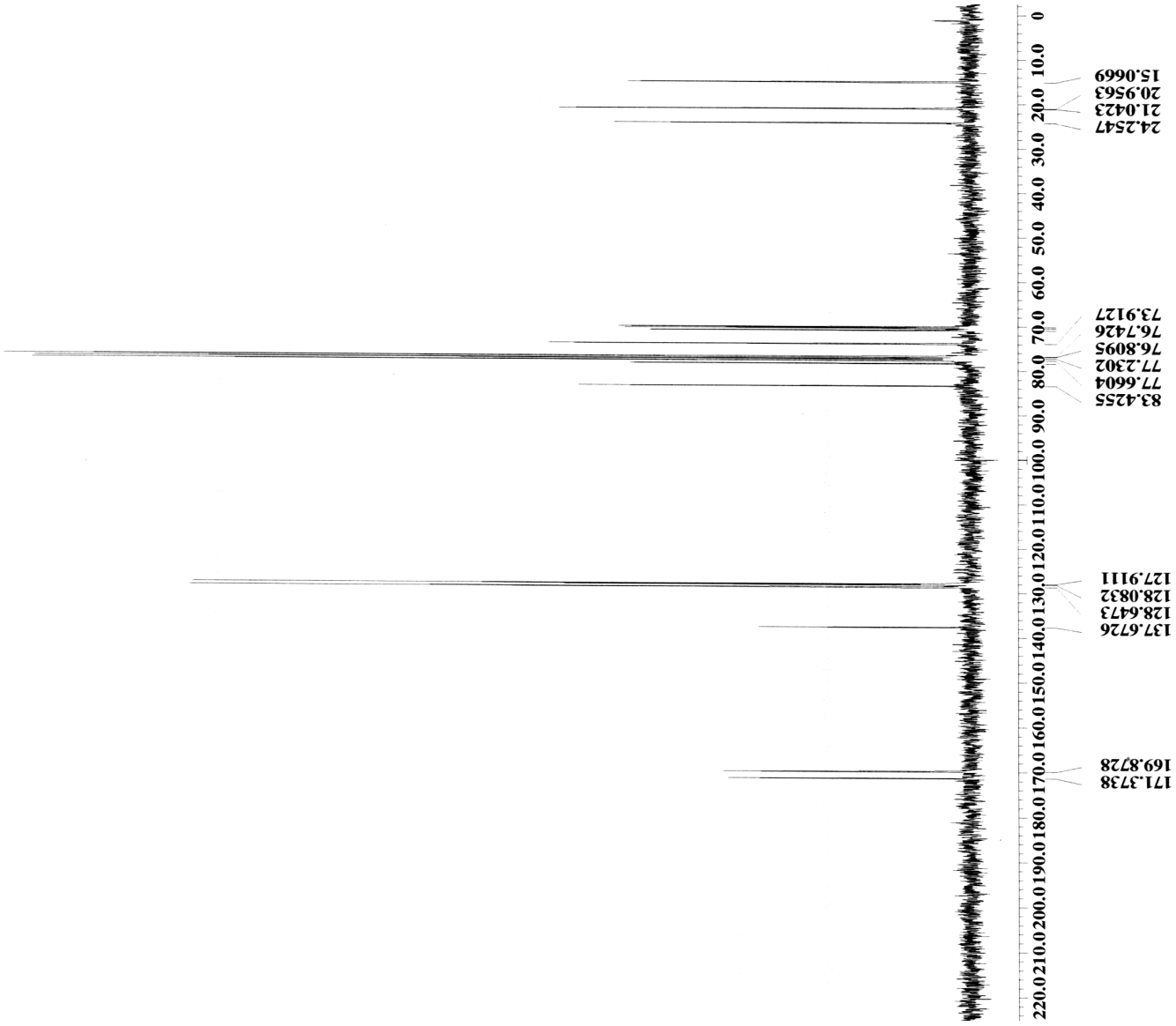


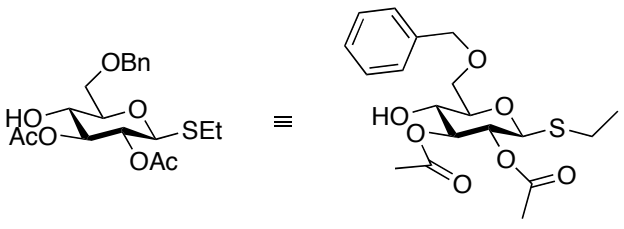
300 MHz ^{1}H NMR of **6** in $CDCl_3$



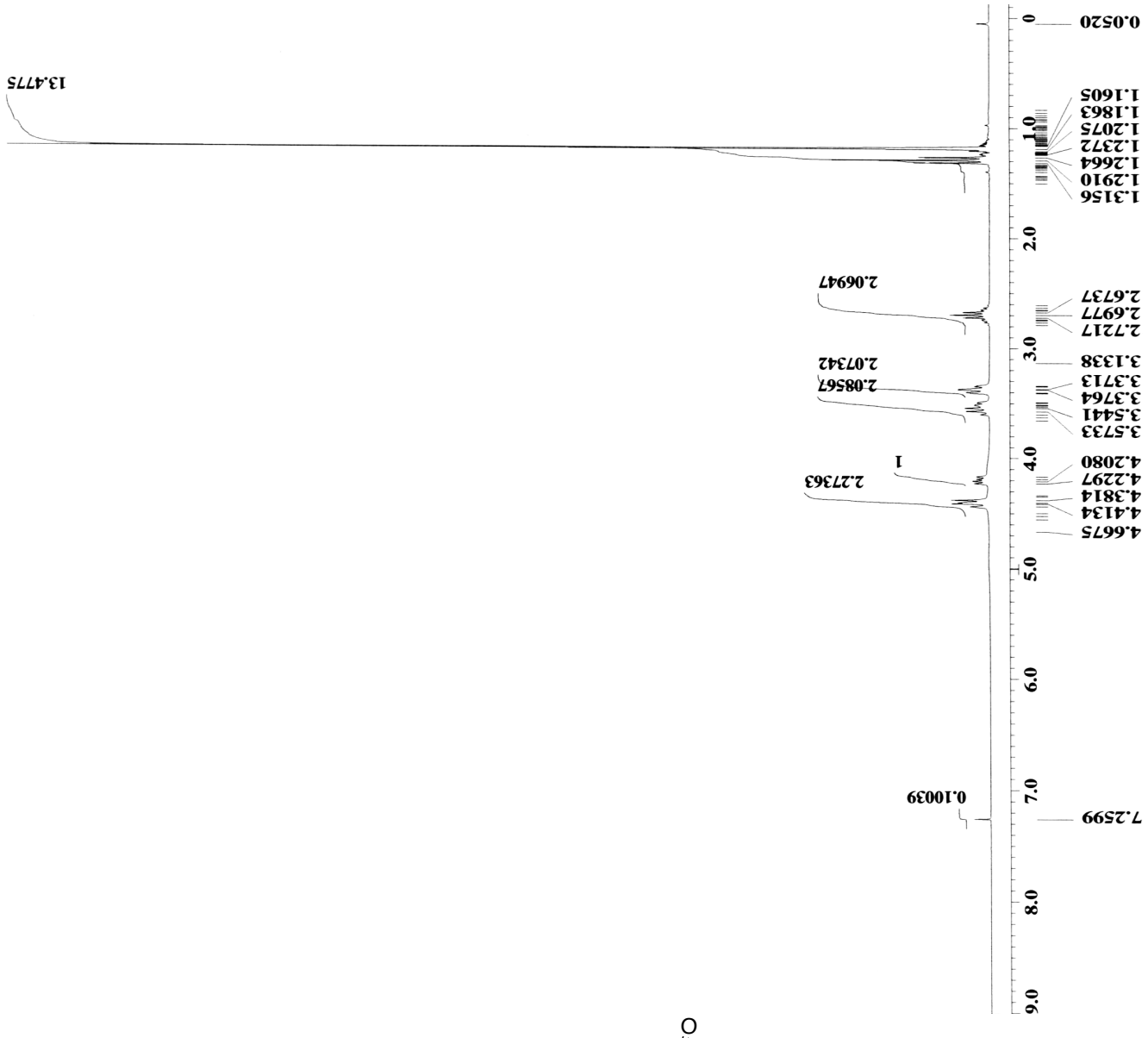


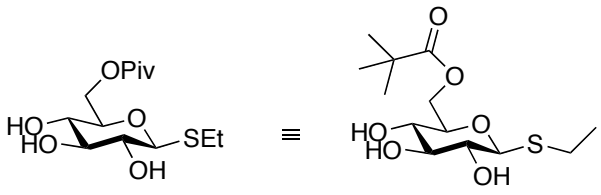
75 MHz ^{13}C NMR of **6** in $CDCl_3$



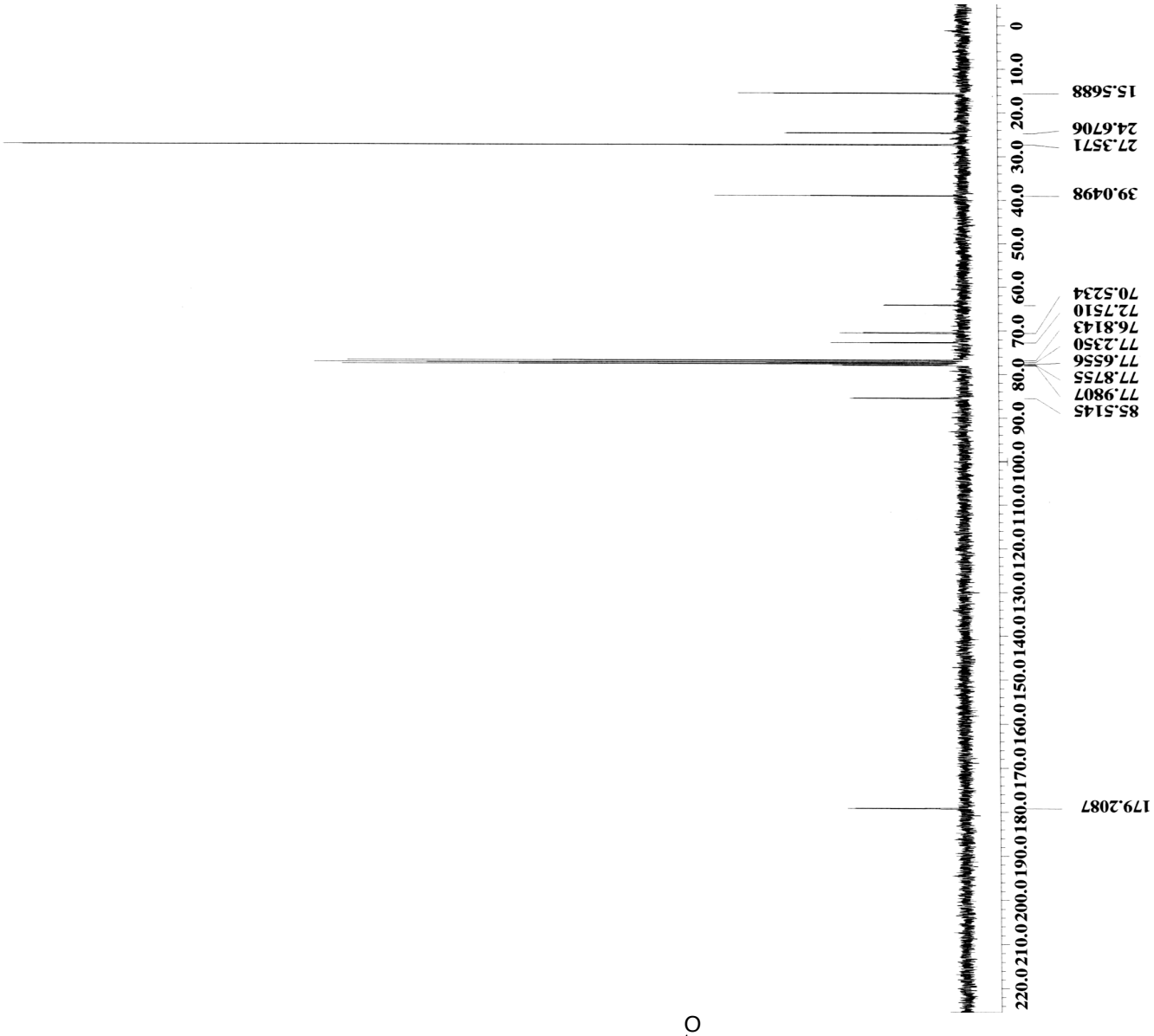


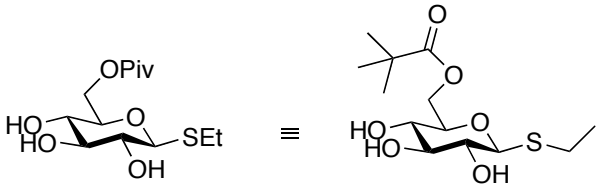
300 MHz ^{1}H NMR of **7** in $CDCl_3$



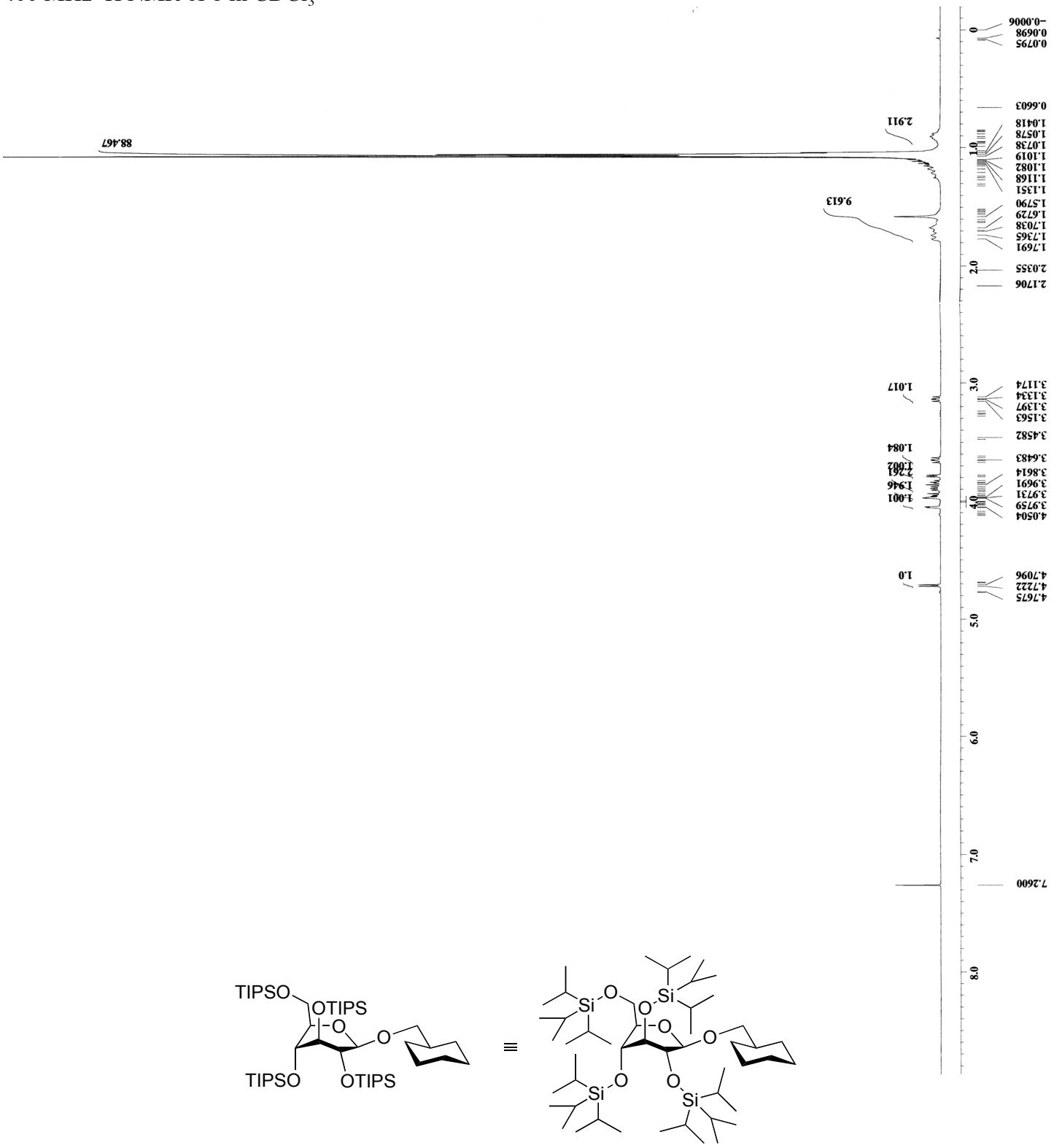


75 MHz ^{13}C NMR of **7** in $CDCl_3$

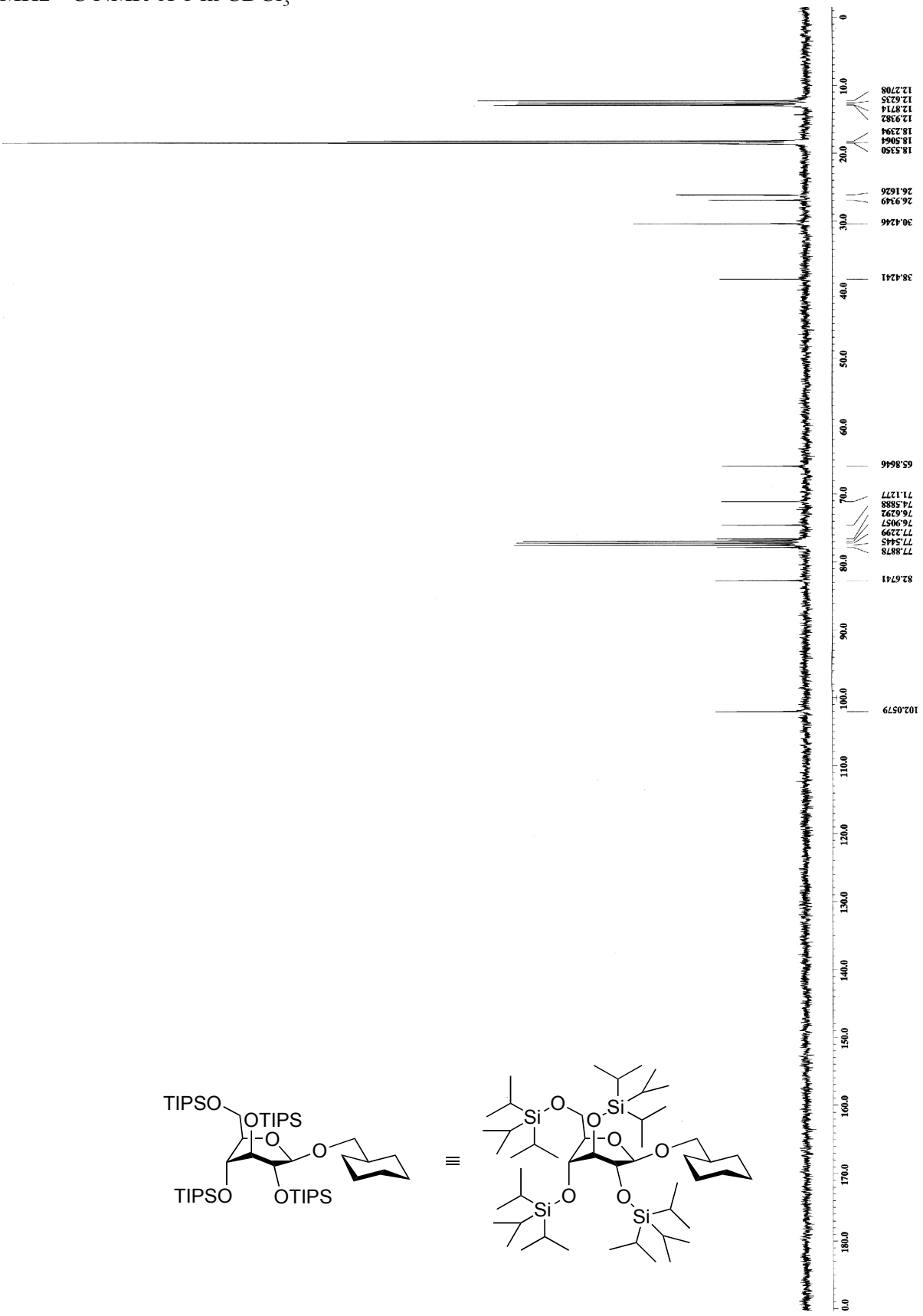




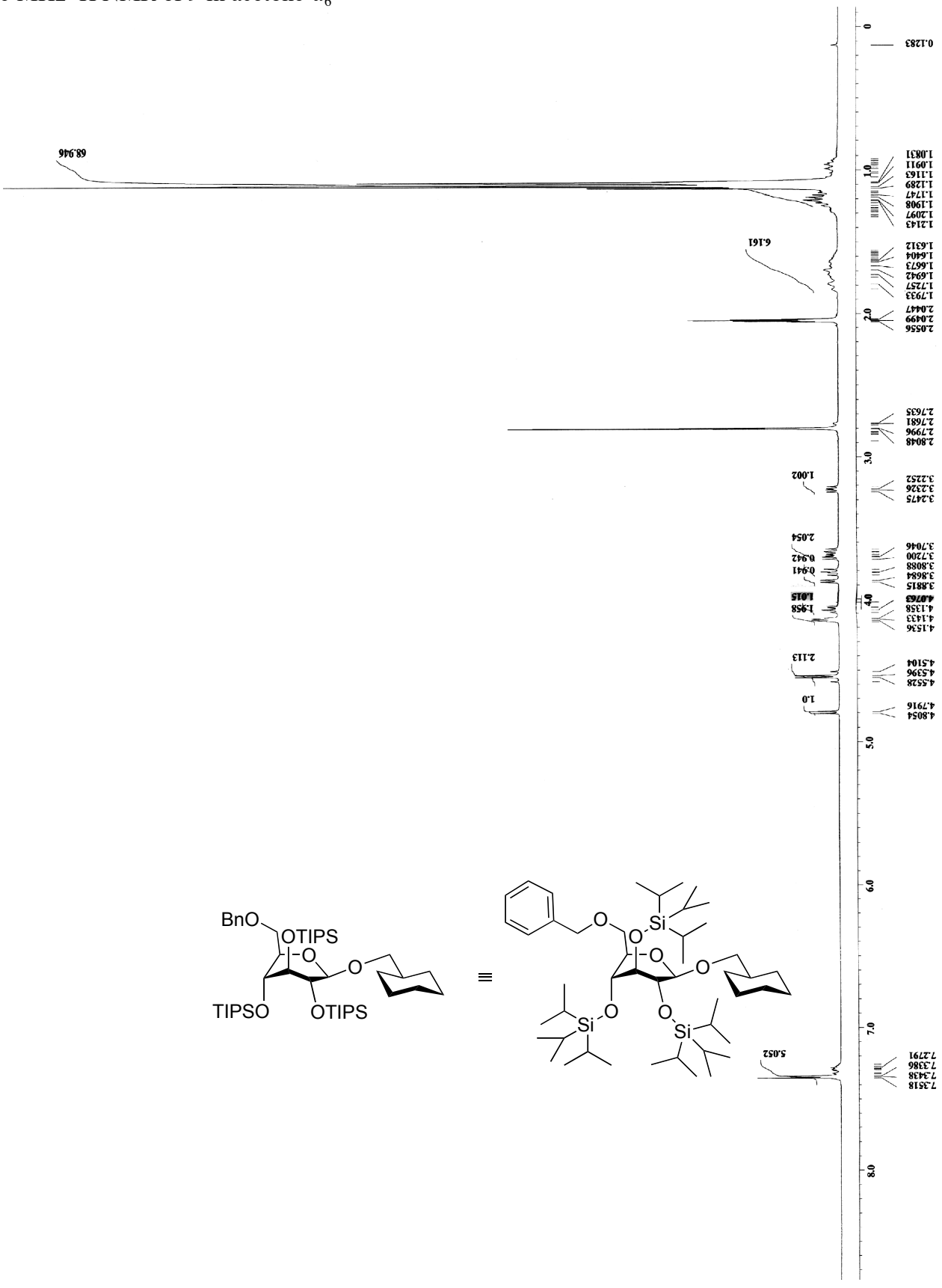
400 MHz ^{1}H NMR of **8** in $CDCl_3$



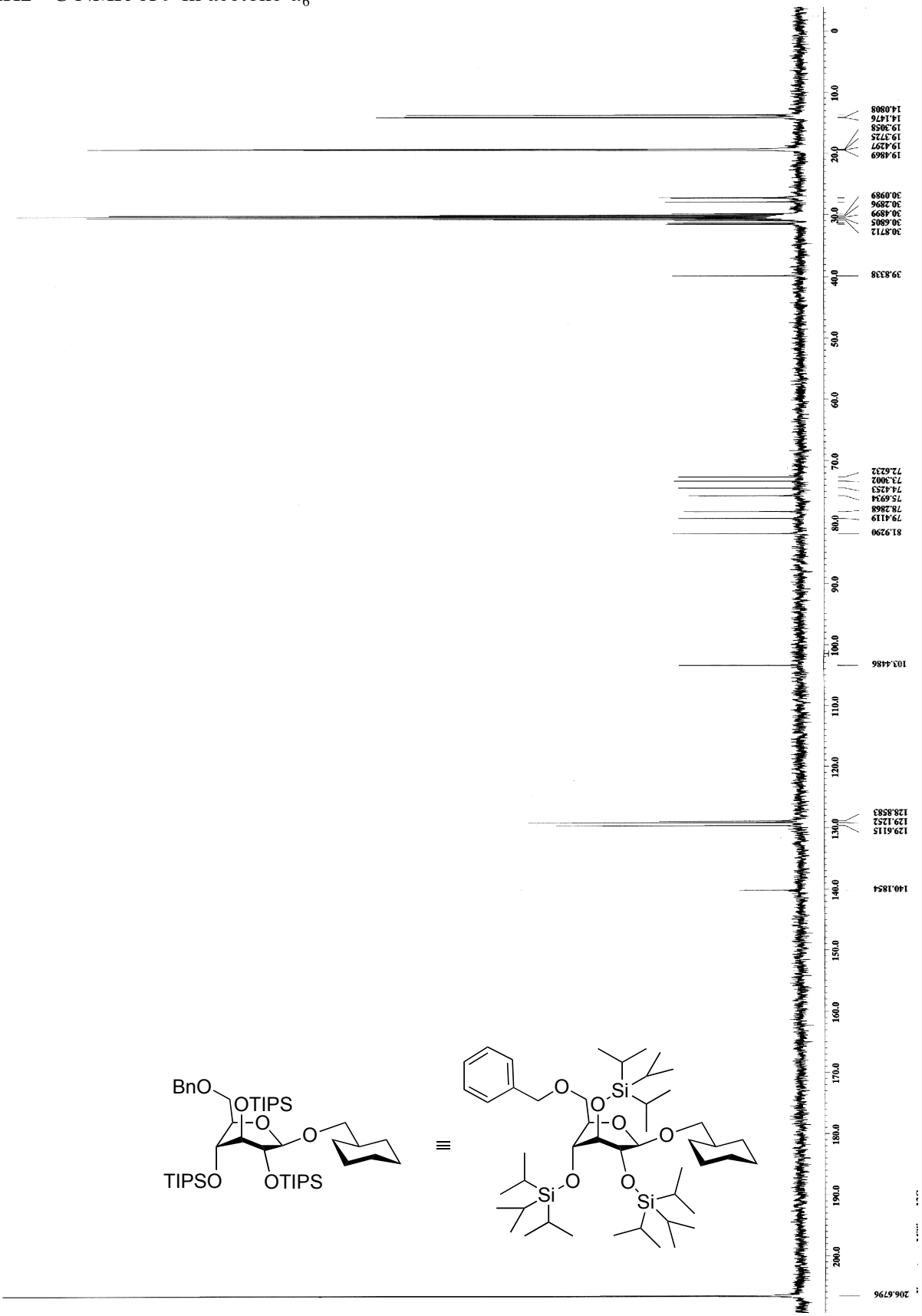
100 MHz ^{13}C NMR of **8** in $CDCl_3$



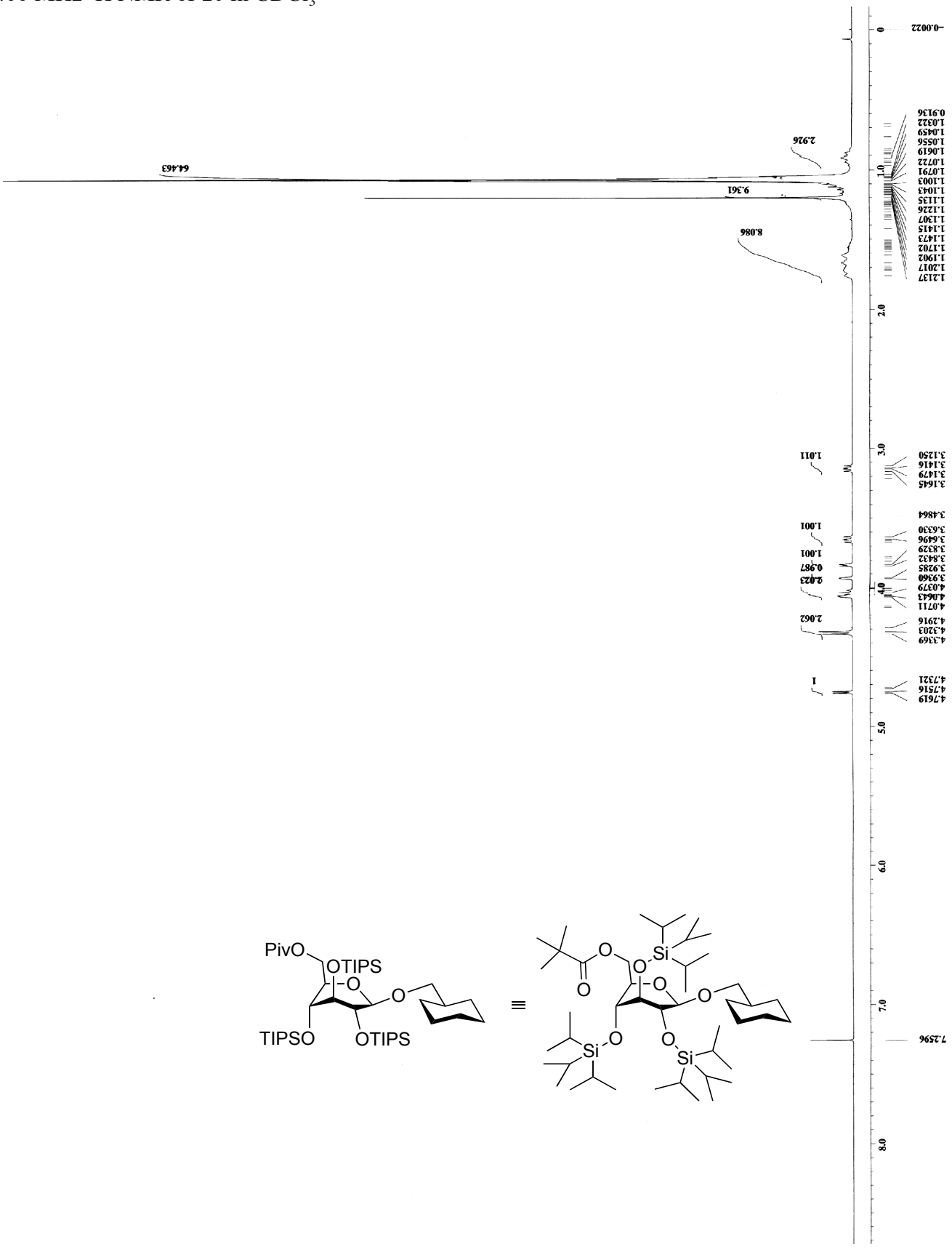
400 MHz ^{1}H NMR of **9** in acetone-d_6



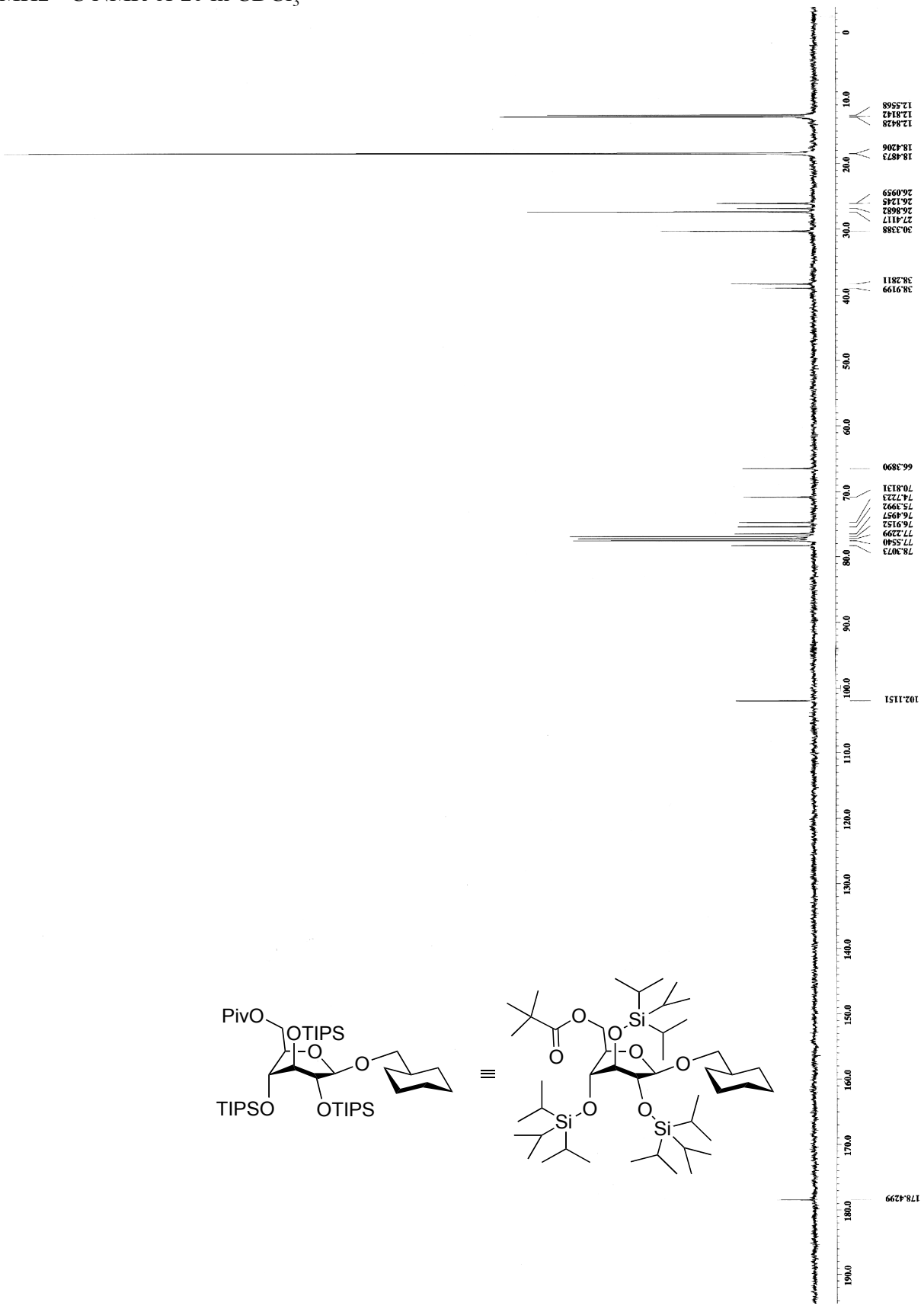
100 MHz ^{13}C NMR of **9** in acetone-d_6



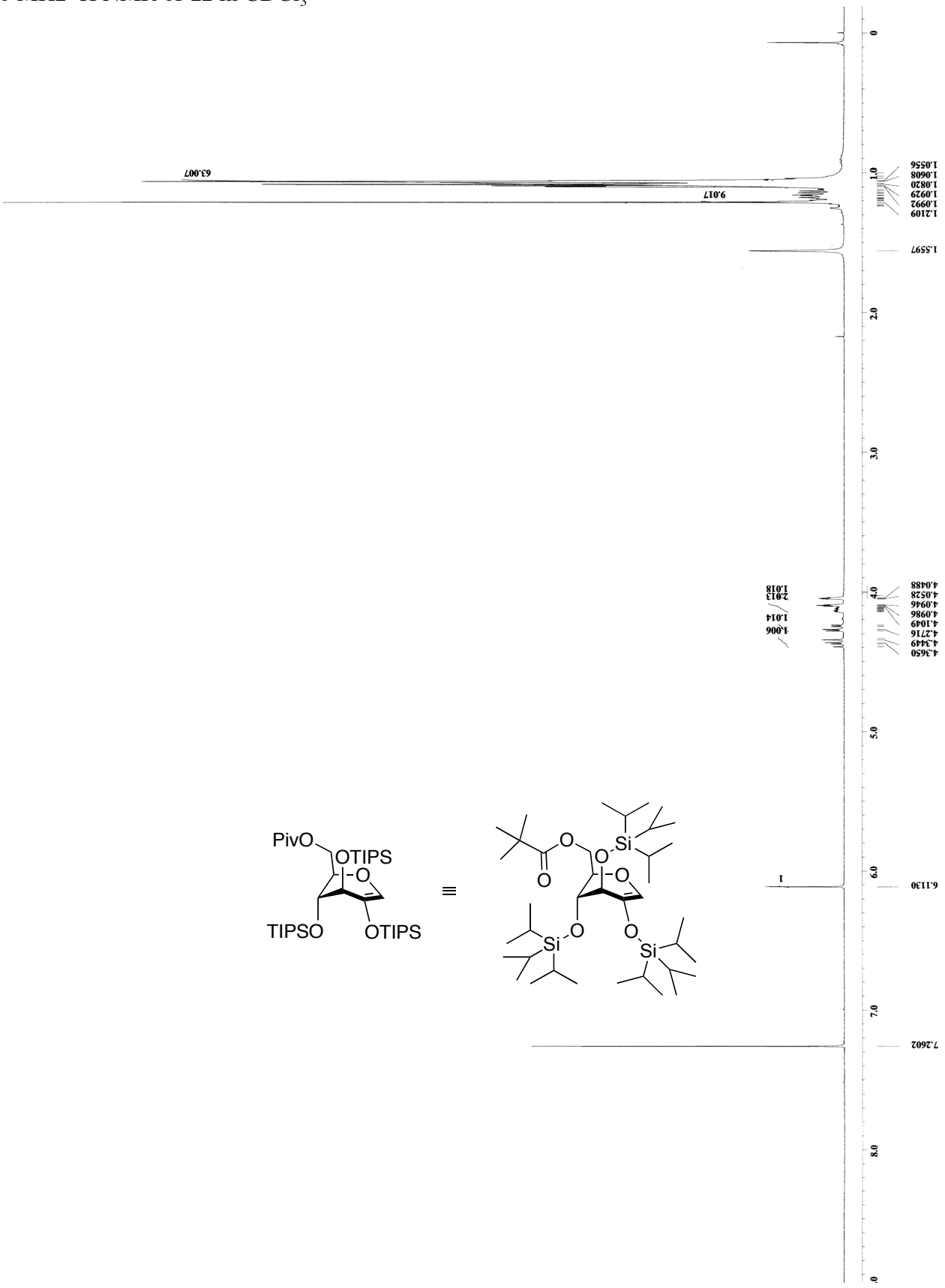
400 MHz ^{1}H NMR of **10** in $CDCl_3$



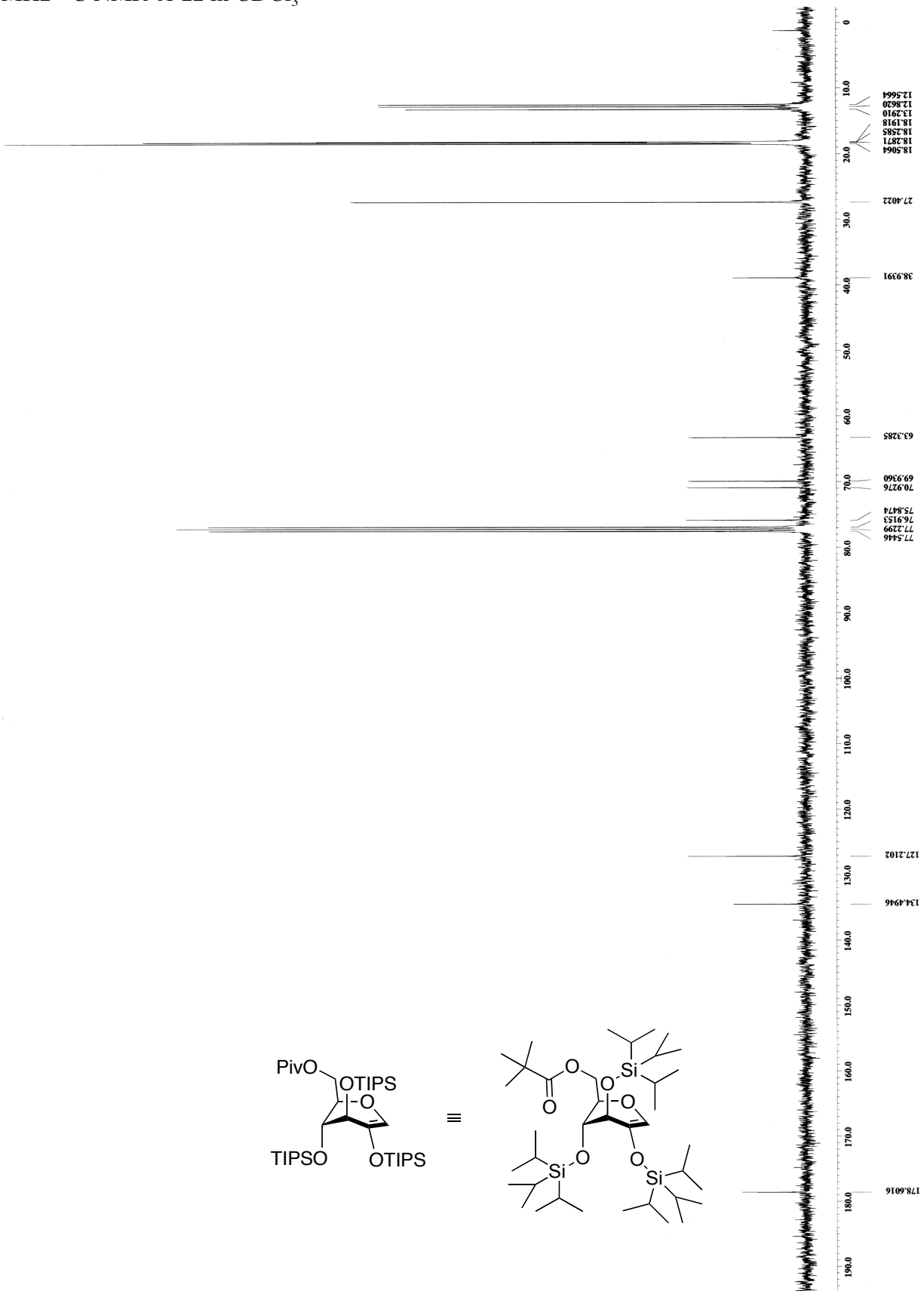
100 MHz ^{13}C NMR of **10** in $CDCl_3$



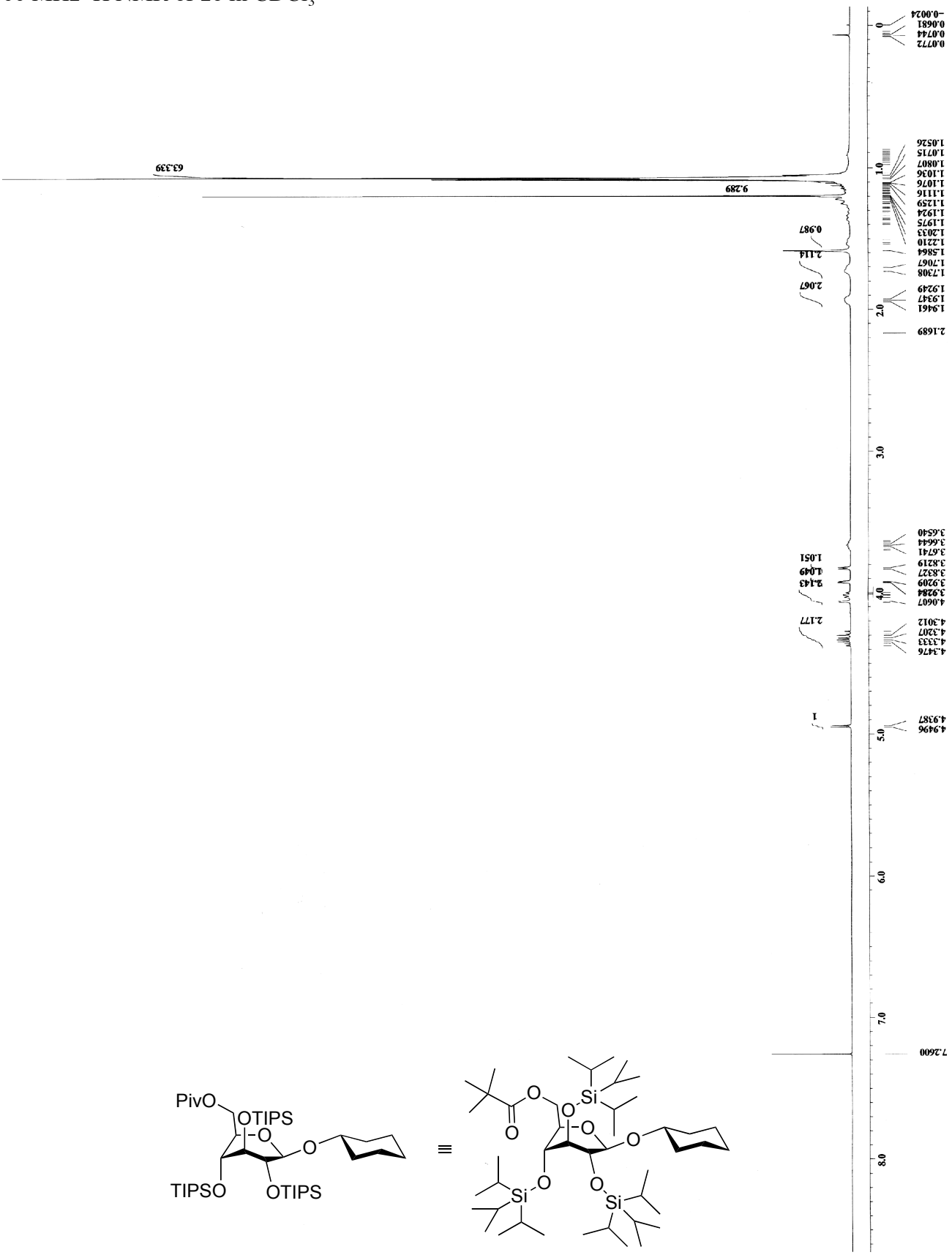
400 MHz ^{1}H NMR of **11** in $CDCl_3$



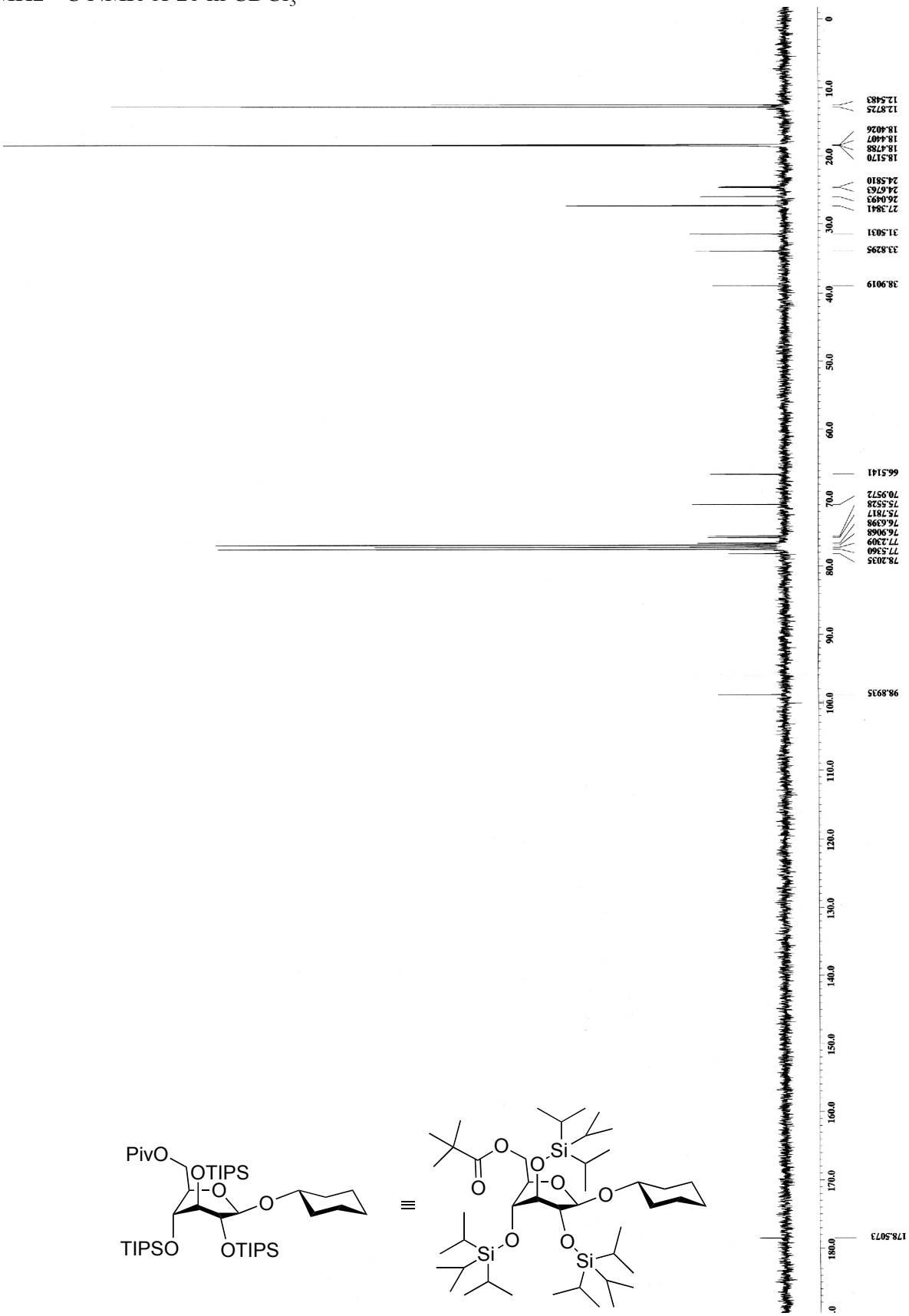
100 MHz ^{13}C NMR of **11** in $CDCl_3$



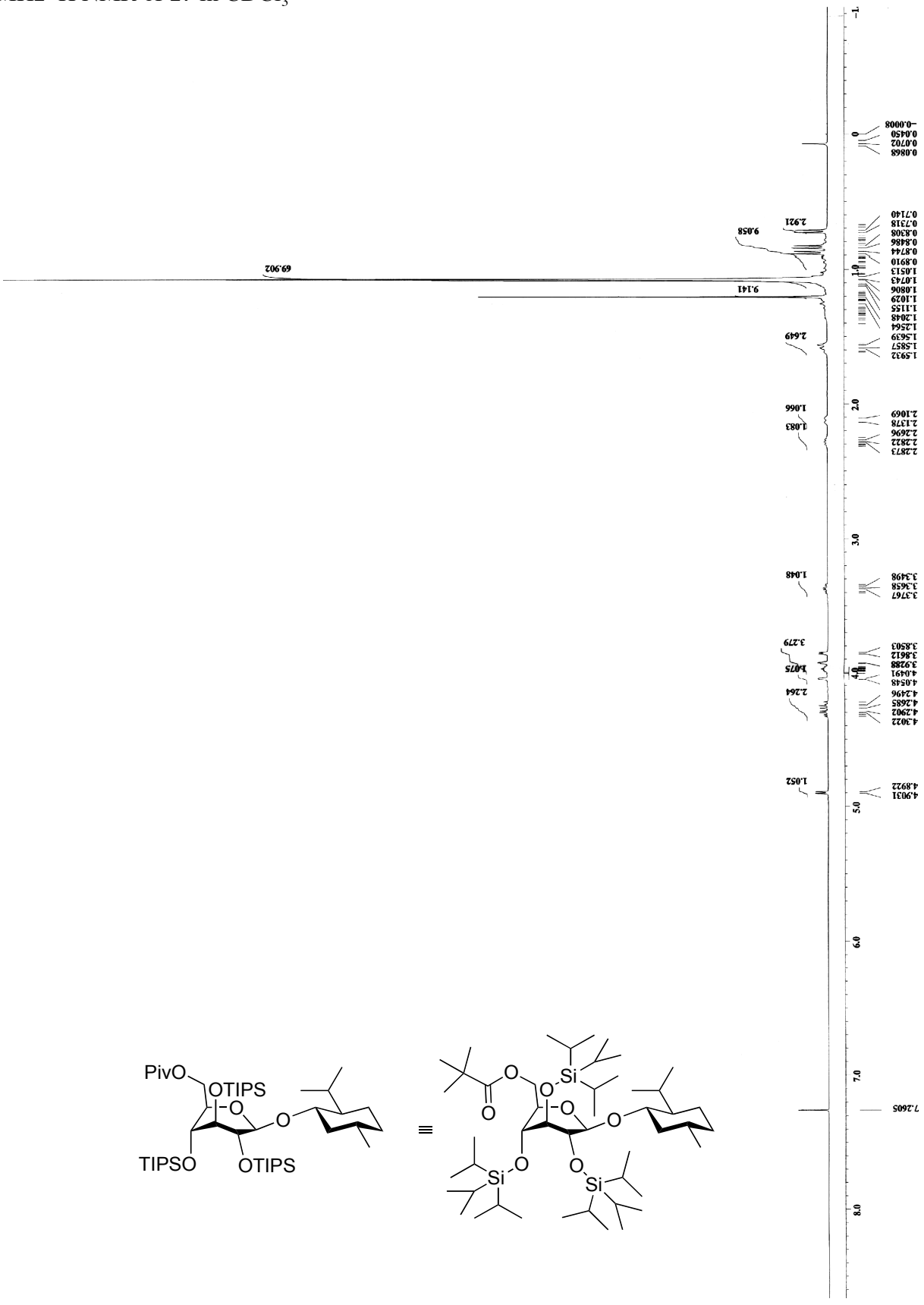
400 MHz ^{1}H NMR of **16** in $CDCl_3$



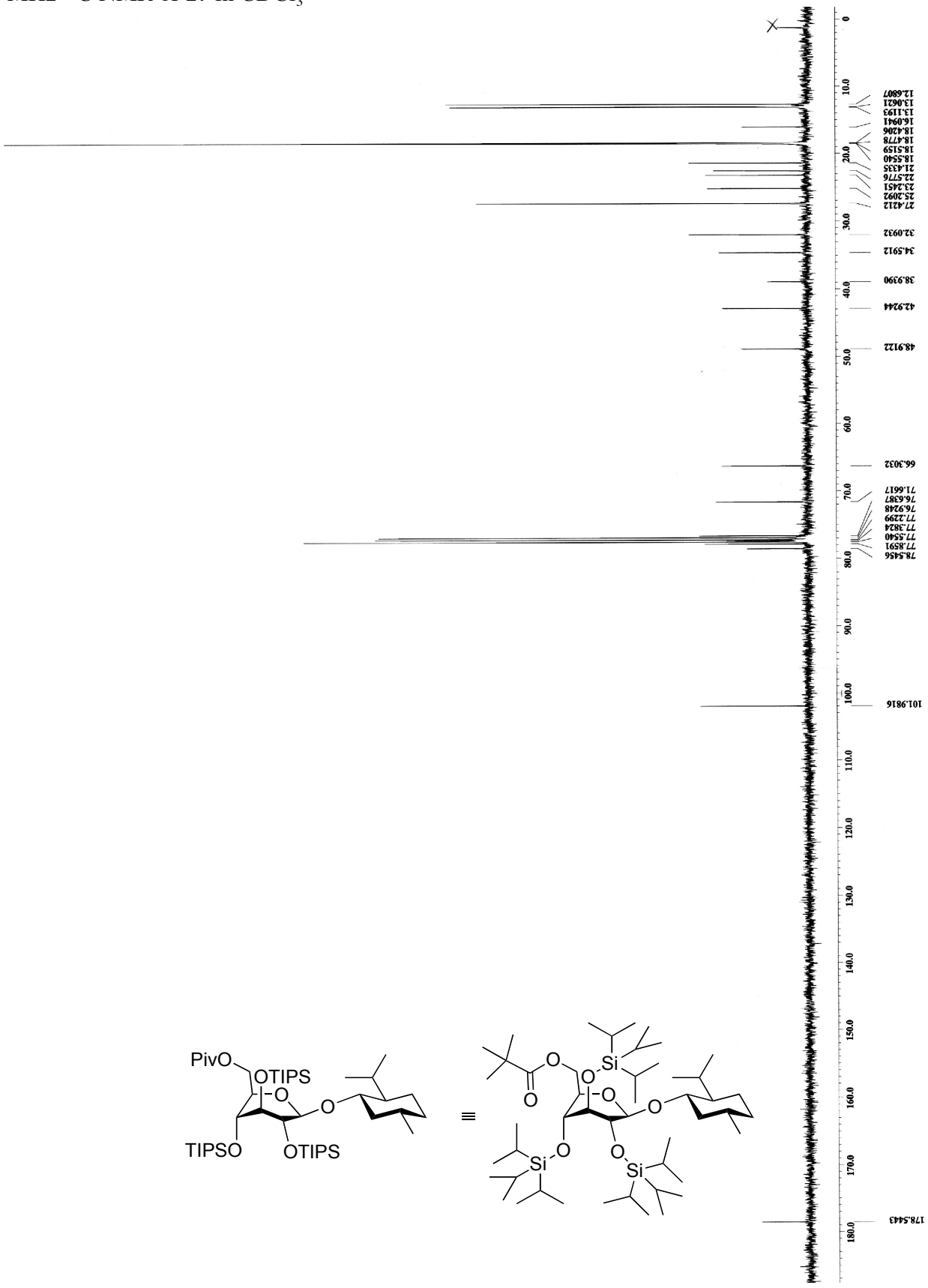
100 MHz ^{13}C NMR of **16** in $CDCl_3$



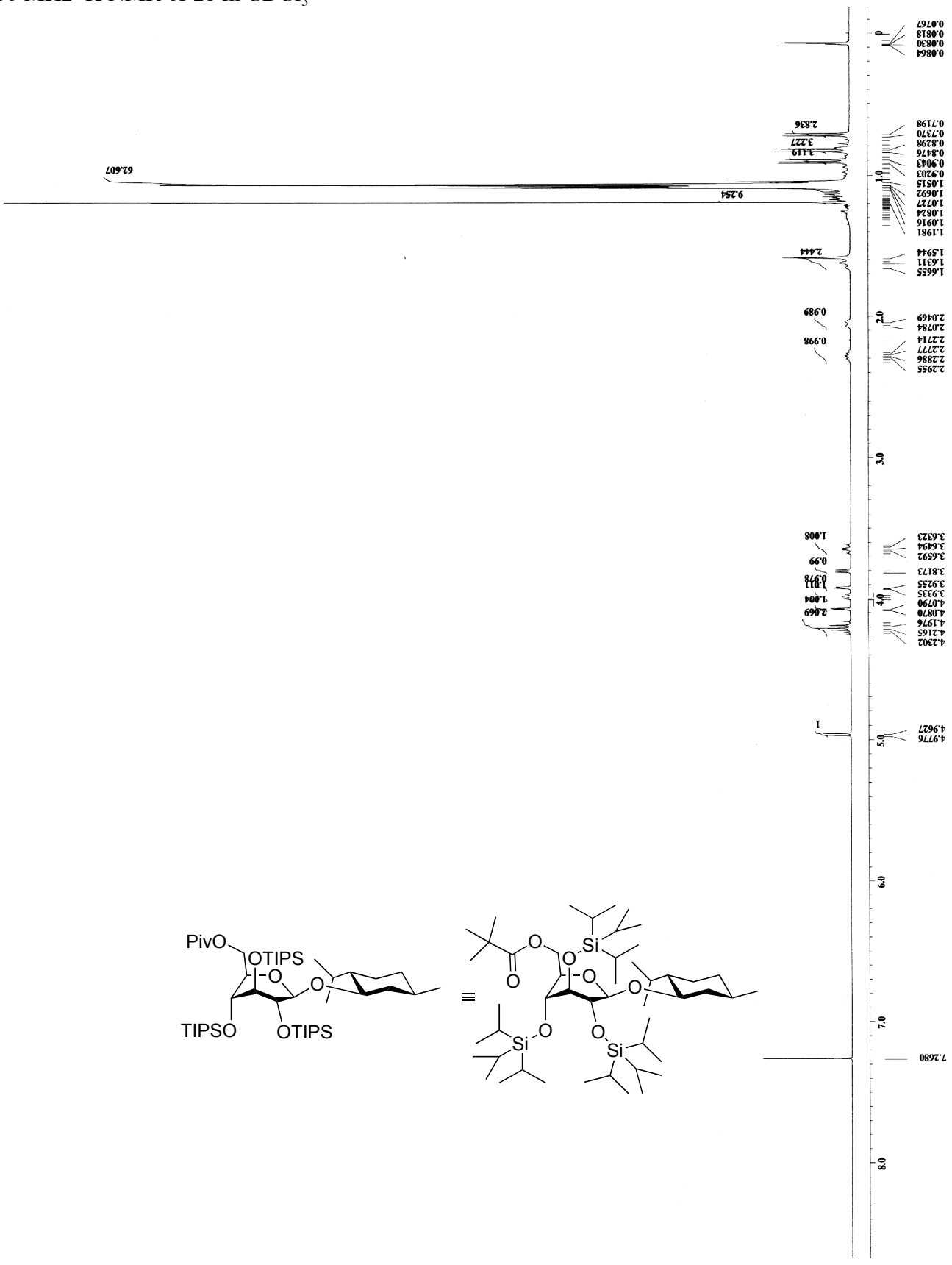
400 MHz ^{1}H NMR of **17** in $CDCl_3$



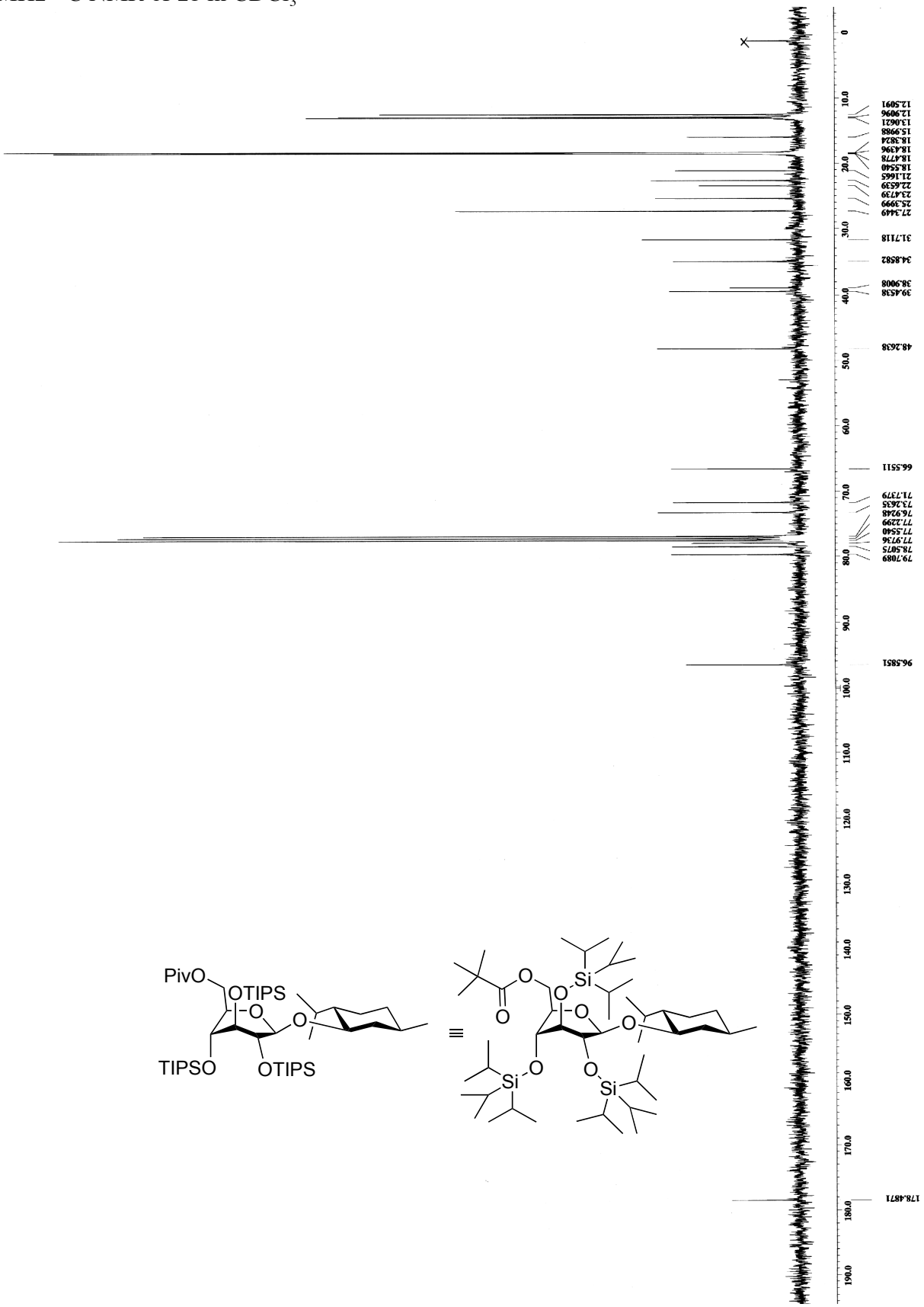
100 MHz ^{13}C NMR of **17** in $CDCl_3$



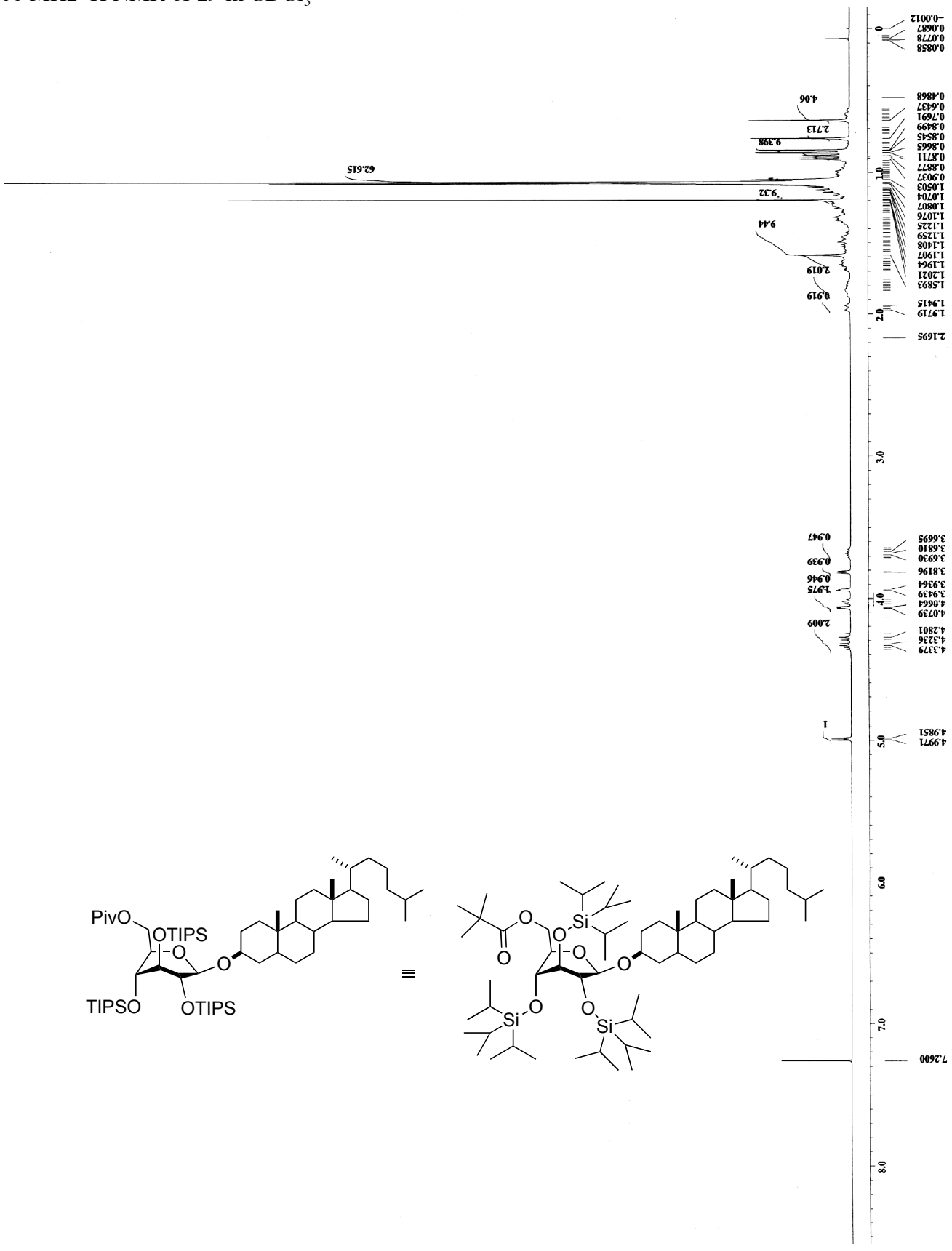
400 MHz ^{1}H NMR of **18** in $CDCl_3$



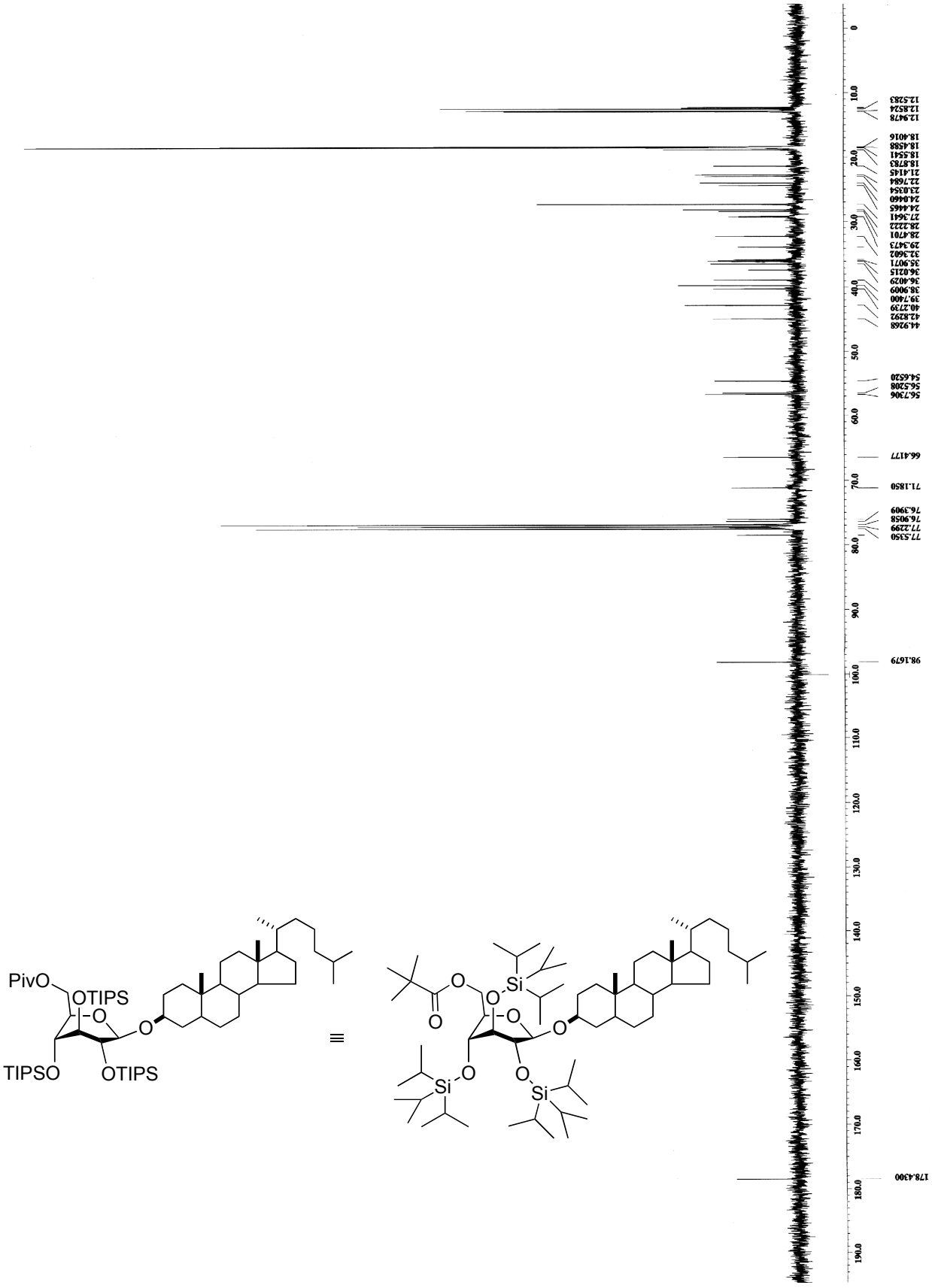
100 MHz ^{13}C NMR of **18** in $CDCl_3$



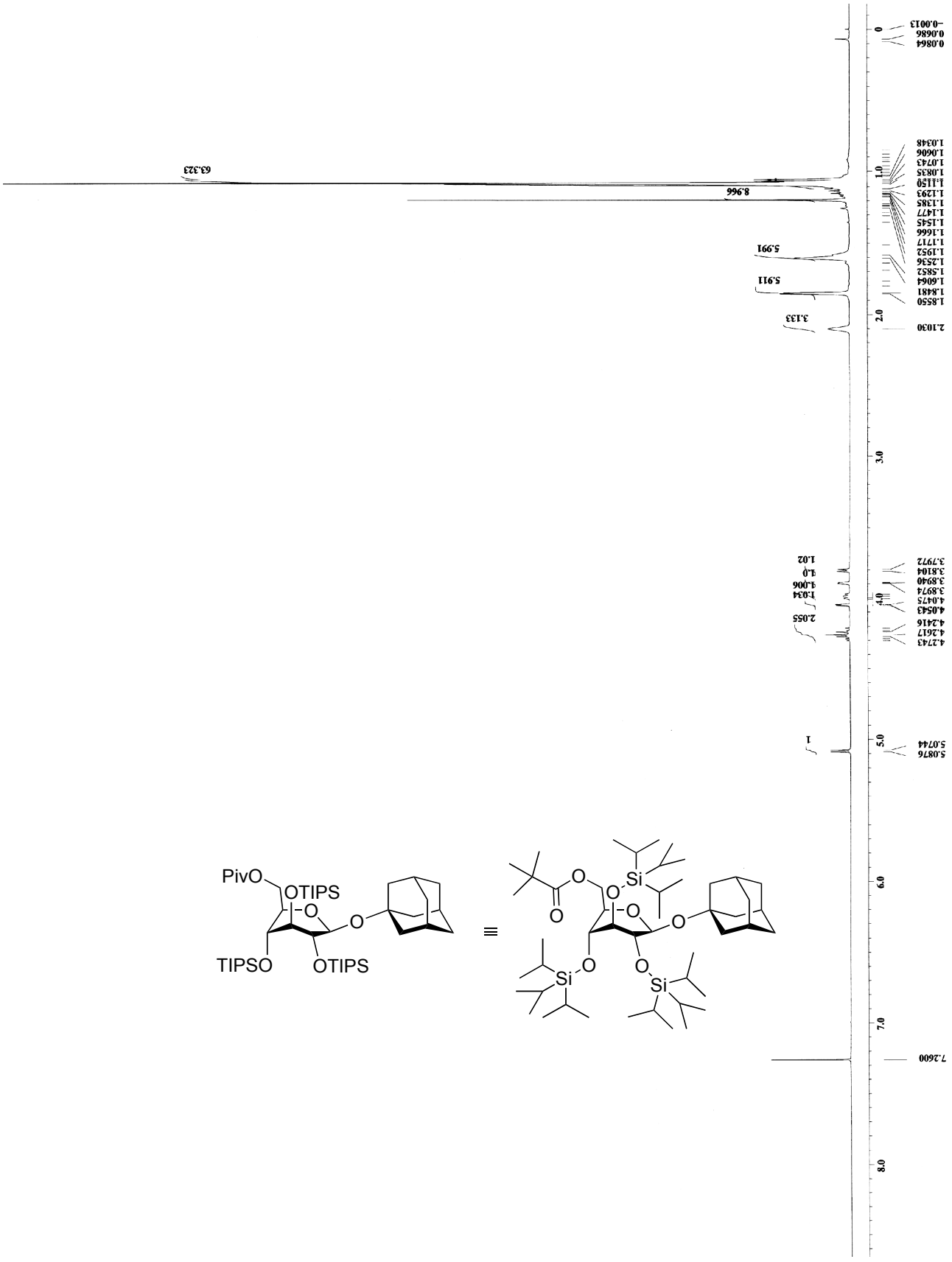
400 MHz ^{1}H NMR of **19** in $CDCl_3$



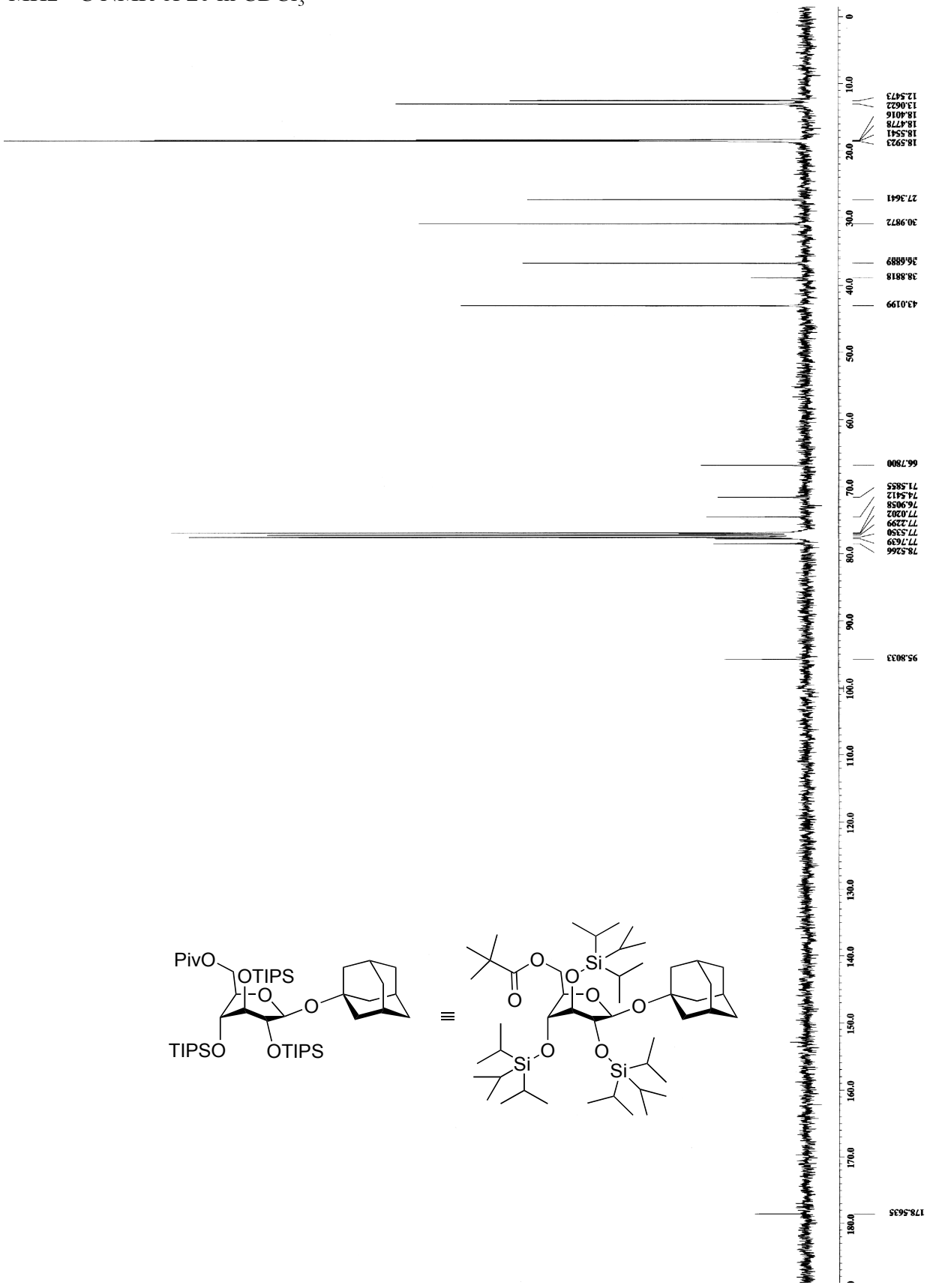
100 MHz ^{13}C NMR of **19** in $CDCl_3$



400 MHz ^{1}H NMR of **20** in $CDCl_3$



100 MHz ^{13}C NMR of **20** in $CDCl_3$



400 MHz ^{1}H NMR of **21** in acetone-d_6

100 MHz ^{13}C NMR of **21** in acetone-d_6