Supporting Information

Synthesis of ketodeoxysugars from acylated pyranosides using photoredox catalysis and hydrogen atom transfer

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General Information

Materials

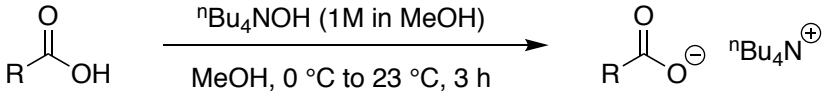
Stainless steel needles and syringes were used to transfer air and moisture sensitive liquids. Schlenk flasks and 4 Å molecular sieves were stored at 140 ℃ for at least 24 hours before use. Acetonitrile was HPLC grade and purified using a solvent purification system equipped with columns of activated alumina under nitrogen (Innovative Technology, Inc.). Other solvents and reagents were used without further purification. Flash column chromatography was performed using neutral silica gel (60 Å, 230 – 400 mesh, Silicycle). Thin-layer chromatography (TLC) was performed using aluminum backed silica gel plates (details), and compounds were visualized by UV irradiation at 254 nm and by staining with $KMnO_4$ solution.

Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C) spectra were recorded on a 400 MHz Varian Mercury Spectrometer or a 400 MHz Bruker Spectrometer. Chemical shifts for protons are recorded in parts per million (ppm) relative to tetramethylsilane and are referenced to residual protium in the solvent ($CDCl_3$: δ 7.26, DMSO-d_6: δ 2.50). Chemical shifts for carbons are recorded in parts per million (ppm) relative to tetramethylsilane and are referenced to residual carbon in the solvent ($CDCl_3$: δ 77.16, DMSO-d_6: δ 39.52). Data are represented in the following order: chemical shift (δ, ppm); multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br s, broad singlet); coupling constant (J, Hz); number of protons; assignment. Proton assignments were made based on coupling constants and 2D NMR spectra. High-resolution mass spectra (HRMS) were obtained on a JEOL AccuTOF JMS- T1000LC mass spectrometer equipped with a DART (direct analysis in real time) ion source. Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum 100 instrument equipped with a singlebounce diamond/ZnSe ATR accessory as neat samples, or as thin film from CH2Cl2 as indicated. Spectral features are tabulated as follows: wavenumber (cm–1); intensity (s-strong, m-medium, w-weak). Specific rotations were measured with a Rudolph Autopol IV digital polarimeter equipped with a sodium lamp source (589 nm) and concentration (c) is reported in g/100 mL. Alkylation reactions were all run in ½ dram or 1 dram vials and placed 5 inches from a Kessil® LED lamp (either: A160WE Tuna Blue (40 W) or H150-Blue (32 W).

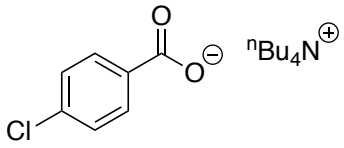
Preparation of Hydrogen Bond Acceptors

General Procedure A for preparation of hydrogen bond acceptor catalysts



Synthesized according to adapted literature procedures.[1] To an oven-dried round bottom flask equipped with a magnetic stir bar was added the carboxylic acid (5 mmol, 1 equiv.). A rubber septum was used to seal the flask, which was then evacuated and backfilled with argon three times under Schlenk line. Dry methanol (3 mL) was added to the flask under a balloon of argon. Reaction cooled to 0 ℃, and tetrabutylammonium hydroxide (1 M in methanol) (5 mL, 5 mmol) was added dropwise. Reaction was warmed to room temperature and stirred for 3 hours under a balloon argon. Solvent was removed under reduced pressure and reaction mixture was transferred to a vacuum desiccator until dry.

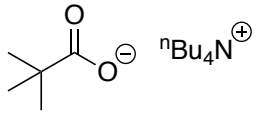
Tetrabutylammonium 4-chlorobenzoate



Prepared according to General Procedure A using 4-chlorobenzoic acid (782.8 mg, 5.00 mmol, 1 equiv.). The product was isolated as a white solid in quantitative yield. NMR data were consistent with previous literature reports.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.03 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 3.41–3.34 (m, 8H), 1.70–1.59 (m, 8H), 1.47–1.36 (m, 8H), 0.97 (t, *J* = 7.3 Hz, 12H).

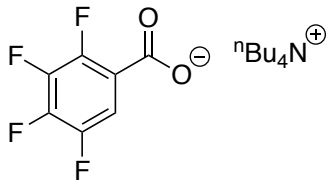
Tetrabutylammonium trimethylacetate



Prepared according to General Procedure A using trimethylacetic acid (510.0 mg, 5.00 mmol, 1 equiv.). The product was isolated as a pale-yellow oil in quantitative yield.
Spectral data were in agreement with those previously reported.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.27–3.20 (m, 8H, -CH_2), 1.64–1.54 (m, 8H, -CH_2), 1.38–1.27 (m, 8H, -CH_2), 0.97 (s, 9H, -C(CH_3)), 0.93 (t, *J* = 7.3 Hz, 12H, -CH_3).

Tetrabutylammonium 2,3,4,5-tetrafluorobenzoate

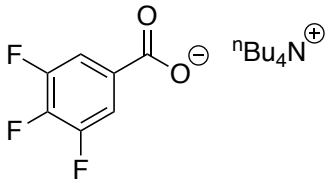


Prepared according to General Procedure A using 2,3,4,5-tetrafluorobenzoic acid (5.00 mmol, 1 equiv.). The product was isolated as a white solid in quantitative yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.48–7.41 (m, 1H, Ar-H), 3.37–3.33 (m, 8H, -CH_2), 1.70–1.62 (m, 8H, -CH_2), 1.46–1.37 (m, 8H, -CH_2), 0.97 (t, *J* = 7.3 Hz, 12H, -CH_3)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 59.0, 24.2, 19.9, 13.7.

Tetrabutylammonium 3,4,5-trifluorobenzoate

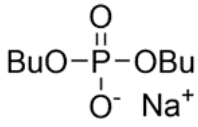


Prepared according to General Procedure A using 3,4,5-triflurobenzoic acid (5.00 mmol, 1 equiv.). The product was isolated at as white solid in quantitative yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.74–7.67 (m, 2H, Ar-H), 3.37–3.33 (m, 8H, -CH_2), 1.69–1.61 (m, 8H, -CH_2), 1.47–1.37 (m, 8H, -CH_2), 0.98 (t, *J* = 7.3 Hz, 12H, -CH_3)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 59.0, 24.2, 19.9, 13.8.

Sodium dibutylphosphate



Synthesized according to previous literature procedures.[3]

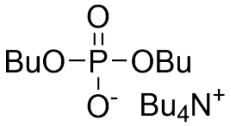
Spectral data were in agreement with those previously reported.[3]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.79 (q, J=6.5 Hz, 2H), 1.59 (dq, J=12.4, 7.0 Hz, 2H), 1.44-1.30 (m, 2H), 0.94 (t, J=7.3 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 33.0, 32.9, 19.1, 13.9

^{31}P NMR (121 MHz, $CDCl_3$): δ (ppm) = 1.50

Tetrabutylammonium dibutylphosphate

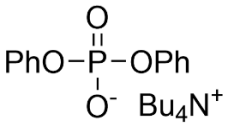


Prepared according to General Procedure A using dibutylphosphate (5.00 mmol, 1 equiv.). The product was isolated as a clear liquid in quantitative yield and stored under vacuum.

Spectral data were in agreement with those previously reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.85-3.80 (m, 4.2H), 3.42-3.35 (m, 8H), 1.70-1.60 (m, 12.4H), 1.49-1.35 (m, 12.4 H), 0.99 (t, J=7.4 Hz, 12H), 0.89 (t, J = 7.4 Hz, 6.5H)

Tetrabutylammonium diphenylphosphate



Prepared according to General Procedure A using dibutylphosphate (5.00 mmol, 1 equiv.). The product was isolated as a white solid in quantitative yield and stored under vacuum.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.28=7.17 (m, 4H), 7.05 (m, 1H), 3.21-3.12 (m, 2H), 1.54 (p, J=8.1, 7.6 Hz, 2H), 1.32 (h, J=7.3 Hz, 2H), 0.90 (t, J=7.3 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 152.3, 152.2, 129.2, 123.6 (2C), 120.4 (2C), 58.63, 23.8, 19.6, 13.6

^{31}P NMR (121 MHz, $CDCl_3$): δ (ppm) = -12.9

Preparation of Substrates

General Procedure B for monoacylation of carbohydrates

Monoacylation was adapted from previous literature procedures.[5]

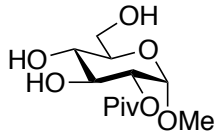
Methyl-α-L-rhamnopyranoside (1 equiv.) and phenyl boronic acid (1 equiv.) were dissolved in toluene (5 mL/mmol) and heated at 110 ℃ for 13 h. Toluene was removed under reduced pressure and the resulting residue was azeotroped with toluene three times. The boronic ester was dissolved in pyridine (2 mL/mmol) and cooled to 0 ℃ with stirring. Trimethyl acetyl chloride (2 equiv.) was added and the reaction was warmed to 23 ℃ and allowed to stir until TLC revealed full consumption of the starting material (ca. 13 h). Reaction was dilute with toluene and filtered through a pad of Celite® followed by removal of the solvent under vacuum. The resulting residue was dissolved in ethyl acetate, added to a solution of 1.0 M sorbitol:1 M sodium carbonate aqueous solution and shaken for five minutes. The aqueous phase was extracted with ethyl acetate several times. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum.

General Procedure C for monoacylation of carbohydrates

Monoacylation was adapted from previous literature procedures.[6]

To round bottom flask equipped with a magnetic stir bar was added the pyranoside derivative (1.00 mmol, 1 equiv.) and copper (II) trifluoroacetic acid (1.30 mmol, 1.3 equiv.), and dissolved in acetonitrile (8 mL). The anhydride (1.30 mmol, 1.3 equiv.) was added then 2,4,6-collidine (1.30 mmol, 1.3 equiv.) was added dropwise. The reaction was allowed to stir at 25 ℃ for 6 hours. The reaction was diluted with dichloromethane and washed with 1 M hydrochloric acid, saturated sodium bicarbonate, then water. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude material was then purified by flash column chromatography on silica gel.

2a – Methyl 2-*O*-trimethylacetyl-*α*-D-glucopyranoside

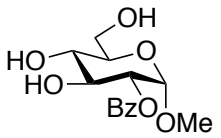


Prepared according to previous literature procedures from methyl *α*-D-glucopyranoside and trimethylacetyl chloride.[5]

Spectral data were in agreement with those previously reported.[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.90 (d, *J* = 3.7 Hz, 1H, H-1), 4.60 (dd, *J* = 10.0, 3.7 Hz, 1H, H-2), 4.03–3.95 (m, 1H, H-3), 3.90–3.83 (m, 2H, H-6, H-6), 3.71–3.62 (m, 2H, H-4, H-5), 3.37 (s, 3H, -OCH_3), 1.24 (s, 9H, $(CH_3)_3CCO$).

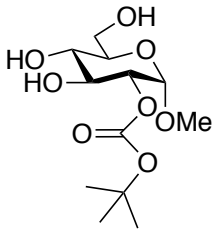
3a – Methyl 2-*O*-benzoyl-*α*-D-glucopyranoside



Prepared according to a modified literature procedure from methyl α-D-glucopyranoside and benzoyl chloride using dibutyltin chloride.[7]
Spectral data were in agreement with those previous reported.[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.09 (d, *J* = 6.9 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 5.04 (d, *J* = 3.6 Hz, 1H), 4.91 (dd, *J* = 3.6, 9.9 Hz, 1H), 4.16 (t, *J* = 3.6 Hz, 1H), 3.92-3.89 (m, 2H), 3.75-3.72 (m, 2H), 3.40 (s, 3H), 2.62 (br s, 1H), 2.50 (br s, 1H), 2.00 (br s, 1H).

3b – Methyl 2-*O*-(*tert*-butyloxycarbonyl)*α*-D-glucopyranoside



Prepared according to General Procedure B from methyl α-D-glucopyranoside and di-*tert*-butyl decarbonate with the following changes: di-*tert*-butyl decarbonate was used as the acylating agent in place of trimethylacetyl chloride, and DMAP (10 mol%) was added. Product **3b** was obtained as an off-white solid (30%) after flash column chromatography on silica (20% to 50% acetone in DCM).

R_f = 0.22 (Acetone:DCM 1:1)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.95 (d, *J* = 3.6 Hz, 1H), 4.47 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.96 (t, *J* = 8.8 Hz, 1H), 3.86 (s, 2H), 3.69-3.59 (m, 2H), 3.58 (s, 1H), 3.39 (s, 3H), 3.31 (s, 1H), 1.49 (s, 9H).

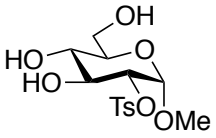
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 153.2, 97.1, 83.2, 75.7, 71.7, 70.8, 70.5, 61.9, 55.3, 27.7

IR (neat, cm-1): 3422 (w), 2989 (w), 2940 (w), 1739 (s), 1278 (s), 1154 (s), 1038 (s), 820 (s)

HRMS (DART$^+$, m/z): calculated for $C_{12}H_{24}O_8$ $[M+NH_4]^+$: 312.16584; found: 312.16529

$[\alpha]_D^{20}$ = +32.0 (c = 13.3 mg/mL, $CHCl_3$)

3c – Methyl 2-*O*-tosyl-*α*-D-glucopyranoside



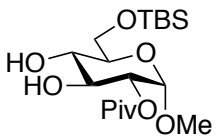
Prepared according to a modified literature procedure from methyl α-D-glucopyranoside and tosyl chloride using dibutyltin chloride.[7]

Methyl α-D-glucopyranoside (1 mmol, 1 equiv.), Bu_2SnCl_2 (0.05 mmol, 0.05 equiv.), and DIPEA (2 mmol, 2 equiv.) were added to a round bottom flask equipped with a magnetic stir bar and dissolved in THF (4 mL). 4-toluenesulfonyl chloride (1.1 mmol, 1.1 equiv.) was added and the reaction was stirred at 23 ℃ for 2.5 hours. 3 % aqueous hydrochloric acid solution (40 mL) was added to the reaction and extracted with ethyl acetate (3 × 40 mL). Combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Crude material was purified by flash column chromatography on silica (10 % methanol in dichloromethane) to afford the product as a clear solid (50 mg, 14%).

Spectral data agreed with those previously reported.[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.84 (d, *J* = 8.3 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 4.65 (d, *J* = 3.7 Hz, 1H), 4.36 (dd, *J* = 9.7, 3.7 Hz, 1H), 4.14 (br s, 1H), 3.96-3.87 (m, 1H), 3.81 (dd, *J* = 13.9, 2.9 Hz, 1H), 3.66-3.51 (m, 1H), 3.25 (s, 1H), 2.94 (br s, 1H), 2.43 (s, 3H)

2b – Methyl 2-*O*-trimethylacetyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-glucopyranoside



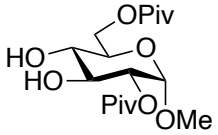
Prepared according to adapted literature procedures.[9]

Methyl 2-*O*-trimethylacetyl-α-D-glucopyranoside (278.2 mg, 1 mmol, 1 equiv.) and *tert*-bityldimethylsilyl chloride (180.9 mg, 1.2 mmol, 1.2 equiv.) were dissolved in pyridine (0.7 M) and stirred at 23 °C for 13 hours. Reaction mixture was diluted with dichloromethane and washed with water, then aqueous layer was extracted several times with dichloromethane. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under vacuum. The resulting residue was purified by flash column chromatography on silica (30% to 50% ethyl acetate in hexanes) to afford **2b** as a white solid (311.3mg, 79%).

Spectral data were in agreement with those previously reported.[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.87 (d, *J* = 3.7 Hz, 1H), 4.61 (dd, *J* = 10.0, 3.7 Hz, 1H), 4.03–3.96 (m, 1H), 3.90 (dd, *J* = 10.5, 4.6 Hz, 1H), 3.82 (dd, 10.5, 5.0 Hz, 1H), 3.63 (m, 2H), 3.36 (s, 3H), 1.24 (s, 9H), 0.91 (s, 9H), 0.10 (s, 3H), 0.10 (s, 3H).

2c – Methyl 2,6-di-*O*-trimethylacetyl-α-D-glucopyranoside

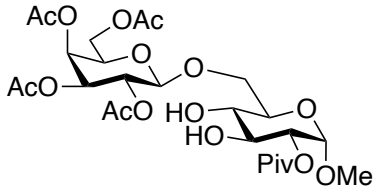


Prepared according to previous literature procedures.[11]

Spectral data were in agreement with those previously reported.[11]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.89 (d, *J* = 3.7 Hz, 1H), 4.60 (dd, *J* = 10.0, 3.7 Hz, 1H), 4.50 (dd, *J* = 12.2, 4.5 Hz, 1H), 4.26 (dd, *J* = 12.2, 2.2 Hz, 1H), 3.98 (dd, *J* = 9.4, 9.4 Hz, 1H), 3.79 – 3.74 (m, 1H), 3.37 (s, 3H), 3.35 (dd, *J* = 9.5, 9.5 Hz, 1H), 1.23 (s, 18H).

2d – Methyl 2-O-Trimethylacetyl-6-O-(2′,3′,4′,6′-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyranoside



Synthesized according to adapted literature procedures.[12]

Methyl-α-D-glucopyranoside (485.4 mg, 2.5 mmol, 1 equiv.) and 4-(trifluoromethyl)phenylboronic acid (474.8 mg, 2.5 mmol, 1 equiv.) were dissolved in toluene (12 mL) and stirred at 110 °C overnight. After reaction solvent was removed under vacuum and the

crude residue was azeotroped with toluene three times. The crude boronic ester was dissolved in anhydrous pyridine (5 mL) and cooled to 0 °C with stirring. Trimethylacetyl chloride (0.37 mL, 3 mmol, 1.2 equiv.) was added then the reaction was warmed to 23 °C and stirred for 30 minutes. Reaction mixture was dilute with toluene, filtered through a tightly packed pad of Celite ®, and concentrated under vacuum. Crude material was dissolved in dry dichloromethane (12.5 mL) and transferred to an oven dried flask equipped with a magnetic stir bar and 4 Å molecular sieves under argon. 2,3,4,6-tetra-*O*-acteyl-α-D-galactosyl bromide (1.54 g, 3.75 mmol, 1.5 equiv.), silver(I) oxide (868.9 mg, 3.75 mmol, 1.5 equiv.), and triethylamine (2.1 mL, 15 mmol, 6 equiv.) were added under argon and the mixture was stirred vigorously (> 800 rpm) overnight. Reaction was quenched with methanol, filtered through a tightly packed pad of Celite ®, and concentrated under vacuum. The crude residue was purified by flash column chromatography on silica (10% to 40% acetone in dichloromethane) to afford (**2d**) as a white solid (710 mg, 47%).

R_f = 0.29 (20% acetone in dichloromethane)

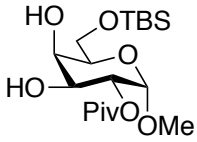
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.39 (dd, *J* = 3.4, 1.2 Hz, 1H, H-4'), 5.25 (dd, *J* = 10.5, 8.1 Hz, 1H, H-2'), 5.03 (dd, *J* = 10.4, 3.4 Hz, 1H, H-3'), 4.87 (d, *J* = 3.7 Hz 1H, H-1), 4.60 (dd, *J* = 9.9, 3.7 Hz, 1H, H-2), 4.58 (d, *J* = 8.0 Hz, 1H, H-1'), 4.20 (dd, *J* = 11.2, 6.6 Hz, 1H, H-6'), 4.15–4.10 (m, 2H, H-6, H-6'), 3.97–3.92 (m, 2H, H-3), 3.80 (dd, *J* = 10.6, 5.4 Hz, 1H, H-6), 3.77–3.73 (m, 1H, H-5, H-5'), 3.52 (apt t, *J* = 9.3 Hz, 1H, H-4), 3.35 (s, 3H, -OCH_3), 2.75 (br s, 1H, -OH), 2.45 (br s, 1H, -OH), 2.15 (s, 3H, -CO(C**H**$_3$), 2.06 (s, 3H, -CO(C**H**$_3$), 2.06 (s, 3H, -CO(C**H**$_3$), 1.99 (s, 3H, -CO(C**H**$_3$), 1.23 (s, 9H, -C(C**H**$_3$)$_3$).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 178.6, 170.7, 170.4, 170.3, 169.8, 101.6, 97.2, 73.3, 71.9, 71.5, 71.1, 70.9, 69.7, 69.0, 68.8, 67.2, 61.5, 55.6, 39.0, 27.2, 20.9, 20.8, 20.8, 20.7.

IR (neat, cm^{-1}): 3474 (w), 2945 (w), 1737 (s), 1369 (s), 1220 (s), 1158 (s), 1037 (s), 910 (s).

HRMS (DART$^+$, m/z): calculated for $C_{26}H_{44}NO_{16}$ $[M+NH_4]^+$: 626.26546, found: 626.26517.

2e – Methyl 2-*O*-trimethylacetyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-galactopyranoside



Synthesized according to General Procedure B from methyl 6-*O*-(*tert*-butyldimethylsilyl)-α-D-galactopyranoside. The crude material was purified by flash column chromatography on silica (20% to 50% ethyl acetate in hexanes to afford **2e** as a white solid (30%).

R_f = 0.42 (30% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.96 (dd, *J* = 10.0, 3.8 Hz, 1H, H-2), 4.89 (d, *J* = 3.8 Hz, 1H, H-1), 4.13–4.12 (m, 1H, H-5), 3.99–3.87 (m, 3H, H-3, H-6a, H-6b), 3.78 (dd, *J* = 5.1, 5.1 Hz,

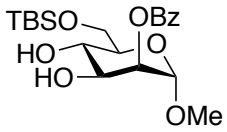
1H, H-4), 3.36 (s, 3H, -OCH_3), 3.25 (d, *J* = 2.8 Hz, 1H, -OH), 2.50 (d, *J* = 7.9 Hz, 1H, -OH), 1.24 (s, 9H, -$C(CH_3)_3$), 0.90 (s, 3H, -$C(CH_3)_3$), 0.10 (s, 3H, -$Si(CH_3)_2$), 0.10 (s, 3H, -$Si(CH_3)_2$).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 179.1, 97.7, 71.9, 70.5, 69.1, 68.9, 63.7, 55.6, 39.1, 27.2, 26.0, 18.4, -5.3.

IR (neat, cm-1): 3519 (w), 2930 (w), 2856 (w), 1711 (s), 1358 (s), 1294 (s), 1254 (s), 1182 (s), 1143 (s), 1084 (s), 1031 (s), 837 (s), 775 (s), 695 (s).

HRMS ($DART^+$, m/z): calculated for $C_{18}H_{37}O_7Si$ $[M+H]^+$: 393.23031; found: 393.23113.

2f – Methyl 2-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-mannopyranoside

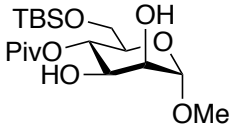


Prepared according to General Procedure C from methyl 6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-mannopyranoside and benzoic anhydride. Product **2f** was isolated as a white solid (58%) after flash column chromatography on silica (30% to 50% ethyl acetate in hexanes).

Spectral data were in agreement with those previously reported.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.07–8.03 (m, 2H), 7.61 – 7.55 (m, 1H), 7.47 – 7.41 (m, 2H), 5.33 (dd, *J* = 3.4, 1.7 Hz, 1H), 4.82 (d, *J* = 1.5 Hz, 1H), 4.12 (dd, *J* = 9.5, 3.5 Hz, 1H), 4.00 (t, *J* = 9.4 Hz, 1H), 3.98 (dd, *J* = 5.6, 4.6 Hz, 1H), 3.89 (dd, *J* = 10.6, 5.2 Hz, 1H), 3.66 (dt, *J* = 9.4, 4.7 Hz, 1H), 3.40 (s, 3H), 0.93 (s, 9H), 0.12 (s, 6H).

2g – Methyl 4-*O*-trimethylacetyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-mannopyranoside



Synthesized according to General Procedure B from methyl 6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-mannopyranoside.

The crude material was purified by flash column chromatography on silica (30% to 50% ethyl acetate in hexanes to afford **2g** as a yellow solid (78%).

***R*$_f$** = 0.47 (40% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.93 (tt, *J* = 9.5, 2.0 HZ, 1H, H-4), 4.77 (d, *J* = 1.5 Hz, 1H, H-1), 3.92–8.85 (m, 2H, H-2, H-3), 3.7–3.67 (m, 3H, H-5, H-6a, H-6b), 3.39 (s, 3H, -OC**H**$_3$), 1.22 (s, 9H, -C(C**H**$_3$)$_3$), 0.88 (s, 9H, -C(C**H**$_3$)$_3$), 0.06 (s, 3H, -Si(C**H**$_3$)$_2$), 0.05 (s, 3H, -Si(C**H**$_3$)$_2$).

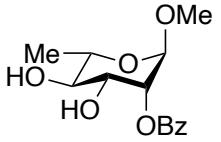
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 179.8, 100.4, 71.0, 70.8, 70.8, 70.6, 62.6, 55.1, 39.1, 27.2, 26.0, 18.4, -5.2, -5.2.

IR (neat, cm-1): 3444 (w), 2934 (w), 1731 (s), 1249 (s), 1150 (s), 1110 (s), 1038 (s), 972 (s), 836 (s), 776 (s), 569 (s).

HRMS ($DART^+$, m/z): calculated for $C_{18}H_{37}O_7Si$ $[M+H]^+$: 393.23031; found: 393.23089

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = + 63.6 (c = 8.75 mg/mL, $CHCl_3$)

2h – Methyl 2-*O*-benzoyl-*α*-L-rhamnopyranoside

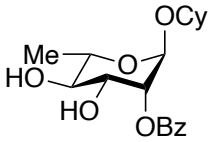


Prepared according to previous literature procedures.[6]

Spectral data were in agreement with those previously reported.[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.06–8.01 (m, 2H, Ar-H), 7.61–7.55 (m, 1H, Ar-H), 7.47–7.41 (m, 2H, Ar-H), 5.32 (dd, *J* = 3.5, 1.6 Hz, 1H, H-2), 4.76 (d, *J* = 1.5 Hz, 1H, H-1), 4.04 (dd, *J* = 9.4, 3.5 Hz, 1H, H-3), 3.73 (dd, *J* = 9.3, 6.2 Hz, 1H, H-5), 3.60 (app t, *J* = 9.4 Hz, 1H, H-4), 3.39 (s, 3H, -OCH_3), 1.37 (d, 3H, -CH_3).

2i – Cyclohexyl 2-*O*-benzoyl-*α*-L-rhamnopyranoside



Prepared according to adapted literature procedure.[14]

To an oven-dried Schlenk flask was added 2.0 g of 4 Å sieves and a magnetic stir bar. The flask was sealed with a rubber septum, evacuated and the sieves were activated using a heat gun. After 30 minutes, the flask was filled with argon and a solution of 2,3,4-tri-O-benzoyl-α-L-rhamnopyranosyl bromide (4 mmol, 1 equiv.) and cyclohexanol (4 mmol, 1 equiv.) in 35 mL of a 1:1 mixture of dichloromethane and toluene was added to the flask. The reaction mixture for stirred

for 10 minutes and then cooled to -20 °C. A solution of silver trifluoromethanesulfonate (4 mmol, 1 equiv.) in 15 mL of a 1:1 mixture of dichloromethane and toluene was added to the flask dropwise. The reaction mixture was then stirred at -20 °C. After 2 hours, the reaction was quenched by addition of 5 mL of pyridine, diluted with dichloromethane and filtered through a pad of celite. The solution was then washed with a 1:1 mixture of sat. aq. $NaHCO_3$ and 1M $Na_2S_2O_3$ and H_2O afterwards. The organic phase was then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was then purified by flash chromatography (10 to 30% ethyl acetate in hexane). The product was transferred to an oven-dried, round-bottom flask, along with NaOMe (0.5 equiv.) and a magnetic stir bar. The flask was then evacuated and backfilled with argon three times on a Schlenk line. Under a balloon of argon, methanol ([sugar]=0.2M) was added and the mixture was stirred at room temperature. After 18 hours, the reaction was quenched with H^+ resin, filtered and concentrated. The crude material was then purified by flash chromatography (10% methanol in dichloromethane), giving cyclohexyl α-L-rhamnopyranoside as a white solid

Cyclohexyl α-L-rhamnopyranoside (246.15 mg, 1 mmol) was then subjected to General Procedure C and acylated with benzoic anhydride. Product **2i** was obtained as a white solid (222.0 mg, 63%) after flash column chromatography on silica (20% to 40% acetone in hexanes).

$\boldsymbol{R_f}$ = 0.36 (30% acetone in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.06–8.03 (m, 2H, Ar-**H**), 7.61–7.56 (m, 1H, Ar-**H**), 7.48–7.43 (m, 2H, Ar-**H**), 5.28 (dd, *J* = 3.4, 1.7 Hz, 1H, H-2), 5.03 (d, *J* = 1.6 Hz, 1H, H-1), 4.12–4.09 (m, 1H, H-3), 3.88–3.82 (m, 1H, H-5), 3.65–3.58 (m, 1H, H-4), 1.90–1.83 (m, 2H, -Cy), 1.78–1.70 (m, 2H, -Cy), 1.56–1.48 (m, 1H, -Cy), 1.46–1.21 (m, 5H, -Cy), 1.36 (d, *J* = 6.2 Hz, 3H, -C**H**$_3$).

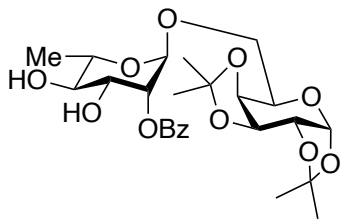
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 166.7, 133.6, 130.0, 129.7, 128.6, 95.7, 75.8, 74.1, 73.9, 70.9, 68.1, 33.4, 31.6, 25.7, 24.2, 23.9, 17.8.

IR (neat, cm-1): 3408 (w), 2931 (w), 2858 (w), 1715 (s), 1451 (s), 1290 (s), 1112 (s), 1048 (s), 1025 (s), 977 (s), 840 (s), 709 (s), 685 (s).

HRMS ($DART^+$, m/z):): calculated for $C_{19}H_{27}O_6$ $[M+H]^+$: 351.18022; found: 351.18022.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = − 30.0 (c = 7.00 mg/mL, $CHCl_3$)

2j – 1,2,3,4-di-O-isopropylidene-6-O-(2-*O*-benzoyl-α-L-rhamnopyranosyl)-α-D-galactopyranoside



Prepared according to adapted literature procedures.[14]

To an oven-dried Schlenk flask was added 2.0 g of 4 Å sieves and a magnetic stir bar. The flask was sealed with a rubber septum, evacuated and the sieves were activated using a heat gun. After 30 minutes, the flask was filled with argon and a solution of 2,3,4-tri-O-benzoyl-α-L-rhamnopyranosyl bromide (4 mmol, 1 equiv.) and 1,2:3,4-Di-O-isopropylidene-α-D-galactopyranose (4 mmol, 1 equiv.) in 35 mL of a 1:1 mixture of dichloromethane and toluene was added to the flask. The reaction mixture for stirred for 10 minutes and then cooled to -20 °C. A solution of silver trifluoromethanesulfonate (4 mmol, 1 equiv.) in 15 mL of a 1:1 mixture of dichloromethane and toluene was added to the flask dropwise. The reaction mixture was then stirred at -20 °C. After 45 minutes, the reaction was quenched by addition of 5 mL of pyridine, diluted with dichloromethane and filtered through a pad of celite. The solution was then washed with a 1:1 mixture of sat. aq. $NaHCO_3$ and 1M $Na_2S_2O_3$ and H_2O afterwards. The organic phase was then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was then purified by flash chromatography (10 to 40% ethyl acetate in hexane). The product was transferred to an oven-dried, round-bottom flask, along with NaOMe (0.5 equiv.) and a magnetic stir bar. The flask was then evacuated and backfilled with argon three times on a Schlenk line. Under a balloon of argon, a 1:1 mixture of methanol and tetrahydrofuran ([sugar]=0.2M) was added and the mixture was stirred at room temperature. After 18 hours, the reaction was quenched with H^+ resin, filtered and concentrated. The crude material was then purified by flash chromatography (10% methanol in dichloromethane), giving 1,2:3,4-di-O-isopropylidene-6-O-α-L-rhamnopyranosyl-α-D-galactopyranose as a white solid.

1,2:3,4-di-O-isopropylidene-6-O-α-L-rhamnopyranosyl-α-D-galactopyranose (243.8 mg, 0.6 mmol) was then subjected to General Procedure C and acylated with benzoic anhydride. Product **2j** was obtained as a white solid (105 mg, 34 %) after flash column chromatography on silica (20 to 40% acetone in hexanes).

$\boldsymbol{R_f}$ = 0.28 (30% acetone in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.06 – 8.03 (m, 2H, Ar-H), 7.60 – 7.57 (m, 1H, Ar-H), 7.47 – 7.44 (m, 2H, Ar-H), 5.53 (d, *J* = 5.0 Hz, 1H), 5.39 (dd, *J* = 3.4, 1.6 Hz, 1H), 4.94 (d, *J* = 1.7 Hz, 1H), 4.63 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.33 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.27 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.07 (dd, *J* = 9.4, 3.6 Hz, 1H), 3.99 (td, *J* = 6.4, 1.5 Hz, 1H), 3.91 – 3.83 (m, 2H), 3.64 – 3.58 (m, 2H), 1.56 (s, 3H), 1.45 (s, 3H), 1.37 (d, *J* = 6.2 Hz, 3H), 1.35 (s, 3H), 1.34 (s, 3H).

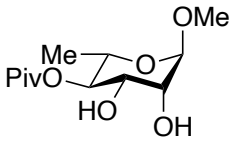
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 166.6, 133.6, 130.3, 130.0, 129.6, 109.5, 108.8, 97.8, 96.4, 73.8, 73.0, 71.1, 71.0, 70.8, 70.7, 68.3, 66.7, 65.9, 31.7, 26.3, 26.1, 25.1, 24.6, 17.7.

IR (neat, cm-1): 3435 (w), 2989 (w), 2937 (w), 1718 (s), 1453 (s), 1377 (s), 1262 (s), 1211 (s), 1113 (s), 1060 (s), 1001 (s), 918 (s), 890 (s), 711 (s).

HRMS (DART$^+$, m/z): calculated for $C_{25}H_{38}NO_{11}$ $[M+NH_4]^+$: 528.24394; found: 528.24441.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}} = -59.2$ (c = 3.33 mg/mL, $CHCl_3$)

2k – Methyl 4-*O*-benzoyl-α-L-rhamnopyranoside



Prepared according to General Procedure B from methyl-α-L-rhamnopyranoside.

The crude material was purified by flash column chromatography on silica (10% to 30% acetone in dichloromethane to afford **2k** as a white solid (68%).

R_f = 0.38 (20% acetone in dichloromethane)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.74 (t, *J* = 9.7 Hz, 1H, H-4), 4.72 (d, *J* =1.7 Hz, 1H, H-1), 3.93 (td, *J* = 3.8, 1.7 Hz, 1H, H-3), 3.87–3.77 (m, 2H, H-2, H-5), 3.38 (s, 3H, -CH_3), 3.11 (d, *J* = 6.4 Hz, 1H, -OH), 2.72 (d, *J* = 4.2 Hz, 1H, -OH), 1.23 (s, 9H, -$C(CH_3)_3$) 1.22 (d, *J* = 7.0 Hz, 3H, -CH_3).

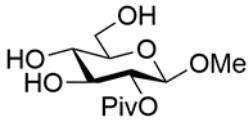
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 180.0, 100.5, 75.7, 70.9, 70.6, 65.5, 55.2, 39.1, 27.2, 17.6.

IR (neat, cm-1): 3452 (w), 2955 (w), 1735 (s), 1481 (s), 1396 (s), 1280 (s), 1153 (s), 1066 (s)1036 (s), 972 (s), 805 (s), 791 (s), 681 (s).

HRMS ($DART^+$, m/z): calculated for $C_{12}H_{23}O_6$ $[M+H]^+$: 263.14957; found: 263.14891.

$[\alpha]_D^{20} = -90.8$ (c = 6.07 mg/mL, $CHCl_3$)

2l – Methyl 2-O-trimethylacteyl-β-D-glucopyranoside



To a vigorously stirred, cooled (ice bath) biphasic solution of 3,4,6-tri-O-benzyl-D-glucal (3.00 mmol) in DCM (12 mL), acetone (1.2 mL) and sat. aq, $NaHCO_3$ (20 mL), a solution of Oxone (3.59 g) in H_2O (14 mL) was added dropwise over 15 min. The mixture was vigorously stirred at 0°C for 30 min and then at 23°C for an additional 2 h. The reaction was then extracted with DCM. The combined organic phases were dried and concentrated to afford 3,4,6-tri-O-benzyl-D-glucal epoxide (90%) as a white solid.[15]

3,4,6-tri-O-benzyl-D-glucal epoxide (1.4 mmol) was dissolved in DCM (1.2 mL), and dry methanol (1 mL) was added. Reaction was stirred until TLC revealed full consumption of the

starting material (ca. 2 hours). Reaction was concentrated under reduced pressure and the crude material was used without purification.[16]

Methyl 3,4,6-tri-O-benzyl-β-D-glucopyranoside (0.5 mmol) and DMAP (5 mol%) were dissolved in pyridine (5 mL) and cooled to 0°C. Trimethylacetyl chloride (3 equiv.) was added dropwise and the reaction mixture was heated to 40°C for several days until TLC revealed consumption of the starting material (ca. 4 days). The reaction was then extracted with DCM, washed with sat. aq. $NaHCO_3$, dried and concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (5% to 20% ethyl acetate in hexane) to give methyl 3,4,6-tri-O-benzyl-2-O-pivaloyl-β-D-glucopyranoside as an off-white solid (85%).

The benzylated glycoside was dissolved in EtOH, and Pd/C (10 % w/w) was added. The reaction mixture was purged with nitrogen, then the flask was purged with hydrogen three times. The reaction mixture was stirred at 23°C under hydrogen until TLC revealed consumption of the starting material (ca. 16 h). The solution was filtered through Celite®, and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel (10% to 50% acetone in dichloromethane) to afford **2l** as a white solid (81%).

R_f = 0.28 (Acetone:DCM 1:1)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.70 (dd, *J* = 9.5, 7.9 Hz, 1H), 4.38 (d, *J* = 7.9 Hz, 1H), 3.95-3.84 (m, 2H), 3.72-3.57 (m, 3H), 3.50 (s, 3H), 3.43-3.34 (m, 2H), 2.72 (br s, 1H), 1.22 (s, 9H)

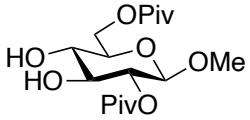
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 178.7, 102.1, 75.5, 75.3, 73.9, 70.7, 61.9, 57.2, 38.9, 27.0

IR (neat, cm^{-1}): 3412 (b), 2985 (s), 1738 (s), 1405 (s), 1485 (s), 1289 (s), 1161 (s), 1060 (s)

HRMS ($DART^+$, m/z): calculated for $C_{12}H_{22}O_7$ $[M+NH_4]^+$: 296.17093; found: 296.17038

$[\alpha]_D^{20}$ = -19.4 (c = 5 mg/mL, $CHCl_3$)

2m – Methyl 2,6-di-O-trimethylacteyl-β-D-glucopyranoside



Synthesized according to adapted literature procedures.[11]

Methyl 2-O-pivaloyl-β-D-glucopyranoside (**2l**) was dissolved in pyridine, and cooled to 0 °C, followed by addition of trimethylacetyl chloride (2 equiv.). Reaction was warmed to 23 °C and stirred until TLC revealed consumption of the starting material (ca. 2 hours). The reaction was then diluted with ethyl acetate and the organic layer was washed with 1M HCl, sat. aq. $NaHCO_3$,

and brine, then dried and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (10% to 30% acetone in dichloromethane) to afford **2m** as a white solid (55%).

R_f = 0.45 (20% acetone in dichloromethane)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.69 (dd, *J* = 9.4, 7.8 Hz, 1H, H-2), 4.47 (dd, *J* = 12.2, 4.8 Hz, 1H, H-6a), 4.37 (d, *J* = 7.8 Hz, 1H, H-1), 4.34 (dd, *J* = 12.1, 2.3 Hz, 1H, H-6b), 3.62 (dd, *J* = 8.8, 8.8 Hz, 1H, H-3), 3.48 (s, 3H, -OCH_3), 3.47 (dd, *J* = 4.8, 2.4 Hz, 1H, H-5), 3.41 (d, *J* = 8.8 Hz, 1H, H-4), 1.23 (s, 9H, -$C(CH_3)_3$), 1.23 (s, 9H, -$C(CH_3)_3$).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 179.6, 178.8, 102.0, 99.1, 75.5, 74.0, 71.0, 63.1, 57.0, 39.1, 27.3, 27.2.

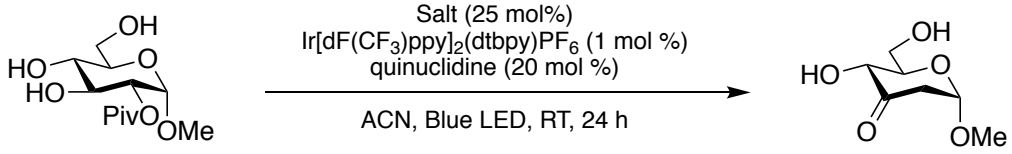
IR (neat, cm^{-1}): 3471 (w), 2979 (w), 1730 (s), 1291 (s), 1175 (s), 1157 (s), 1087 (s), 1041 (s), 992 (s), 815 (s).

HRMS (DART$^+$, m/z): calculated for $C_{17}H_{34}NO_8$ $[M+NH_4]^+$: 380.22805; found: 380.22789.

$[\alpha]_D^{20} = -22.6$ (c = 3.25 mg/mL, $CHCl_3$)

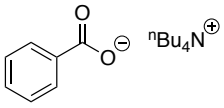
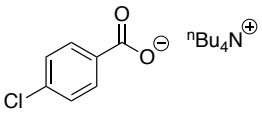
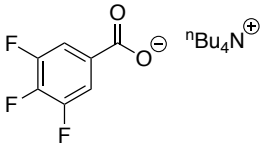
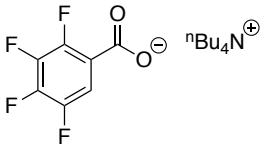
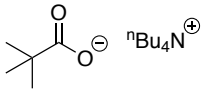
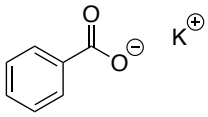
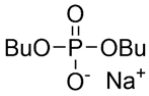
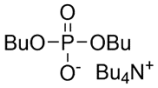
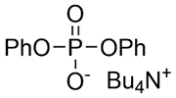
Reaction Optimization

Optimization Procedure



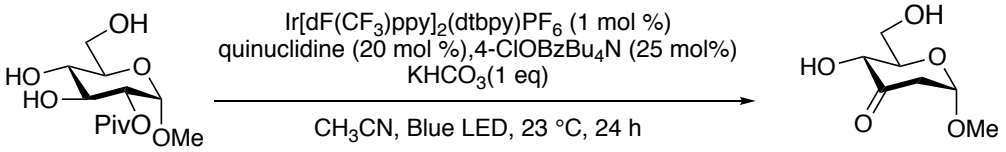
Methyl 2-*O*-trimethylacetylglucopyranoside (27.8 mg, 0.10 mmol, 1 equiv.), ($Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (1 mg, 0.001 mmol, 1 mol %), quinuclidine (2.2 mg, 0.02 mmol, 20 mol %), salt additive (0.025 mmol, 25 mol%) and a small magnetic stir bar were added to a ½ dram vial. A rubber septum was used to seal the vial, which was then evacuated and backfilled with argon three times on a Schlenk line. Dry, degassed acetonitrile (0.8 mL) was added to the vial under a balloon of argon. The rubber septum was removed and quickly replaced with the vial cap which was sealed with Teflon tape and parafilm. The vial was placed 5 inches away from a blue LED Kessil lamp and stirred at 1050 rpm for 24 hours at 25 ℃. After 24 hours the crude reaction was concentrated under reduced pressure and analyzed by ^{1}H NMR Spectroscopy.

Table S1. Evaluation of the hydrogen bond acceptor catalyst.

Entry	Salt	NMR yield[a]	NMR yield[a] with 1 eq K_2CO_3
1	TBAP	—	67%
2		35%	40%
3		70%	71%
4		70%	64%
5		70%	64%
6		69%	—
7		45%	56%
8		37%	56%
9		57%	76%
10		22%	—

[a] Yields of **4a** were determined via ^{1}H NMR spectra of the crude mixture (integration of the ddd at 2.82 ppm relative to internal standard 1,3,5-trimethoxybenzene).

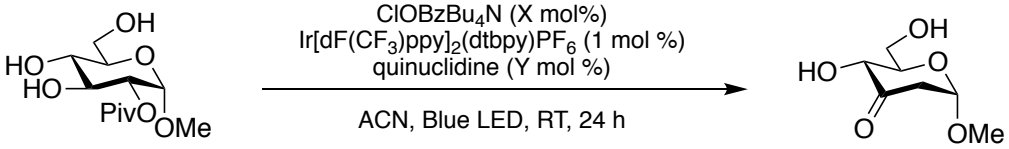
Table S2. Control Reactions



Entry	Changes to Above	NMR Yield 4a[a]	Remaining Starting Material[a]
1	No Ir. cat	<5%	91%
2	No quinuclidine	<5%	92%
3	No blue LED light	<5%	83%
4	No 4-ClOBzBu4N	30%	56%

[a] Yields of **4a** were determined via ^{1}H NMR spectra of the crude mixture (integration of the ddd at 2.82 ppm relative to internal standard 1,3,5-trimethoxybenzene).

Table S3. Effects on the ratio of HBA catalyst to quinuclidine on the yield of **4a**.



quinuclidine (mol %) \ ClOBzBu4N (mol %)	25	50	100
10	62%	61%	45%
20	70%	59%	
30	15%		53%

Characterization of Products

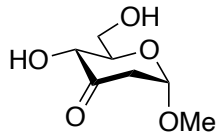
General Procedure D for reactions run with solid acylated sugar

Pyranoside derivative (1 equiv.), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (1 mol%), quinuclidine (20 mol%), tetrabutylammonium 4-chlorobenzoate (25 mol%), potassium bicarbonate (1 equiv.) and a small magnetic stir bar were added to a 1 dram vial. A rubber septum was used to seal the vial, which was then evacuated and backfilled with argon three times on a Schlenk line. Dry, degassed acetonitrile (0.125 M) was added to the vial under a balloon of argon. The rubber septum was removed and quickly replaced with the vial cap which was sealed with Teflon tape and parafilm. The vial was placed 5 inches from a blue LED Kessil lamp and stirred at 1050 rpm for 24 hours at 25 ℃. After 24 hours the crude reaction was concentrated under reduced pressure and analyzed by ^{1}H NMR spectroscopy. The crude material was then subjected to flash column chromatography on silica.

General Procedure E for reactions run with non-solid acylated sugar

$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (1 mol%), quinuclidine (20 mol%), tetrabutylammonium 4-chlorobenzoate (25 mol%), potassium bicarbonate (1 equiv.) and a small magnetic stir bar were added to a 1 dram vial. A rubber septum was used to seal the vial, which was then evacuated and backfilled with argon three times on a Schlenk line. A 0.125M solution of the pyranoside derivative was prepared under argon in dry degassed acetonitrile. 1.6 mL of the solution (1 equiv.) was added to the vial under a balloon of argon. The rubber septum was removed and quickly replaced with the vial cap which was sealed with Teflon tape and parafilm. The vial was placed 5 inches from a blue LED Kessil lamp and stirred at 1050 rpm for 24 hours at 25 ℃. After 24 hours the crude reaction was concentrated under reduced pressure and analyzed by ^{1}H NMR spectroscopy. The crude material was then subjected to flash column chromatography on silica.

4a – Methyl 2-deoxy-α-D-*erythro*-hexopyranoside-3-ulose



Prepared according to General Procedure D from methyl 2-*O*-trimethylacetyl-α-D-glucopyranoside (**2a**) (55.6 mg, 0.2 mmol). **4a** was obtained as a pale yellow oil (23.5 mg, 67%) after flash column chromatography on silica (20 to 40% acetone in dichloromethane).

The amount of remaining starting material in the reaction was found to be 25% by analysis of the crude ^{1}H NMR spectra relative to internal standard 1,3,5-trimethoxybenzene.

R_f = 0.33 (40% acetone in dichloromethane)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.17 (d, *J* = 4.4 Hz, 1H, H-1), 4.23 (dd, *J* = 9.8, 2.2 Hz, 1H, H-4), 3.98 (dd, *J* = 11.9, 2.8 Hz, 1H, H-6), 3.92 (dd, *J* = 12.0, 3.7 Hz, 1H, H-6), 3.76–3.72 (m, 1H, H-5), 3.35 (s, 3H, -OCH_3), 2.82 (ddd, *J* = 14.0, 4.6, 1.4 Hz, 1H, H-2), 2.70 (dd, *J* = 14.0, 1.1 Hz, 1H, H-2).

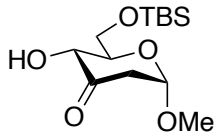
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 205.4, 100.1, 74.8, 73.3, 62.6, 55.1, 45.2.

IR (neat, cm^{-1}): 3438 (w), 2930 (w), 1724 (s), 1365 (s), 1290 (s), 1194 (s), 1116(s), 1099 (s), 1034 (s), 1002 (s), 955 (s), 878 (s), 840 (s).

HRMS (DART$^+$, m/z): calculated for $C_7H_{16}NO_5$ $[M+NH_4]^+$: 194.10230, found: 19410223.

$[\alpha]_D^{20}$ = + 117.1 (c = 11.75 mg/mL, $CHCl_3$)

4b – Methyl 2-deoxy-6-*O*-(*tert*-butyldimethylsilyl)-α-D-*erythro*-hexopyranoside-3-ulose



Prepared according to General Procedure D from methyl 2-*O*-trimethylacetyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-glucopyranoside (**2b**) (78.5 mg, 0.2 mmol). Product (**4b**) was obtained as an off white solid (47.4 mg, 66%) after flash column chromatography on silica (10 to 20% ethyl acetate in hexanes).

The amount of remaining starting material in the reaction was found to be 0% by analysis of the crude ^{1}H NMR spectra relative to internal standard 1,3,5-trimethoxybenzene.

R_f = 0.45 (20% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.16 (d, *J* = 4.4 Hz, 1H, H-1), 4.18 (dd, *J* = 9.8, 1.3 Hz, 1H, H-4), 3.98 (dd, *J* = 11.4, 2.1 Hz, 1H, H-6), 3.93 (dd, *J* = 11.4, 4.5 Hz, 1H, H-6), 3.69–3.65 (m, 1H, H-5), 3.34 (s, 3H, -OCH_3), 2.80 (ddd, *J* = 14.0, 4.6, 1.4 Hz, 1H, H-2), 2.68 (dd, *J* = 14.0, 1.0 Hz, 1H, H-2), 0.92 (s, 9H, -C(CH_3)$_3$), 0.11 (s, 6H, -Si(CH_3)).

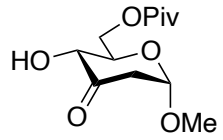
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 206.1, 99.9, 75.6, 73.2, 73.1, 63.0, 54.9, 45.3, 27.2, 26.1, 18.6, −5.1, −5.2.

IR (neat, cm^{-1}): 3410 (w), 2935 (w), 2857 (s), 1730 (s), 1472 (s), 1412 (s), 1368 (s),1291 (s), 1251 (s), 1098 (s), 1033 (s), 942 (s), 885 (s), 835 (s), 775 (s).

HRMS (DART$^+$, m/z): calculated for $C_{13}H_{27}O_5Si$ $[M+H]^+$: 291.16223, found: 261.16262.

$[\alpha]_D^{20}$ = +89.5 (9.55 mg/mL, $CHCl_3$).

4c – Methyl 2-deoxy-6-*O*-trimethylacetyl-α-D-*erythro*-hexopyranoside-3-ulose



Prepared according to General Procedure D from methyl 2,6-di-*O*-trimethylacetyl-α-D-glucopyranoside (**2c**) (72.5 mg, 0.2 mmol). Product (**4c**) was obtained as a pale yellow oil (45.3mg, 87%) after flash column chromatography on silica (0 to 5% acetone in dichloromethane).

$\boldsymbol{R_f}$ = 0.56 (5% acetone in dichloromethane)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.15 (d, *J* = 4.3 Hz, 1H, H-1), 4.49 (dd, *J* = 12.0, 2.2 Hz, 1H, H-6a), 4.36 (dd, *J* = 12.0, 6.0 Hz, 1H, H-6b), 4.09 (d, *J* = 8.8 Hz, 1H, H-4), 3.91–3.88 (m, 1H, H-5), 3.36 (s, 3H, -OCH_3), 2.83 (ddd, *J* = 14.0, 4.6, 1.4 Hz, 1H, H-2a), 2.71 (dd, *J* = 14.0, 1.1 Hz, 1H, H-2b), 1.24 (s, 9H, -$C(CH_3)_3$).

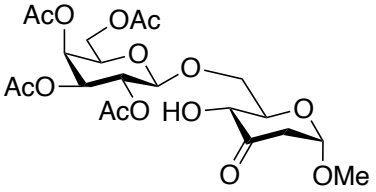
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 204.7, 178.3, 99.7, 73.5, 73.0, 63.6, 55.0, 45.2, 39.1 27.4, 27.2.

IR (neat, cm^{-1}): 3469 (w), 2982 (w), 1726 (s), 1482 (s), 1366 (s), 1285 (s), 1150 (s), 1119 (s), 1102 (s), 1036 (s). 950 (s), 770 (s).

HRMS ($DART^+$, m/z): calculated for $C_{12}H_{21}O_6$ $[M+H]^+$: 261.13383, found: 261.13326.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = + 112.2 (c = 4.87 mg/mL, $CHCl_3$)

4d – Methyl 6-O-(2′,3′,4′,6′-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-*erythro*-hexopyranoside-3-ulose



Prepared according to General Procedure D from methyl 2-O-Trimethylacetyl-6-O-(2′,3′,4′,6′-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyranoside (**2d**). Product (**4d**) was obtained as a yellow amorphous solid (41.9 mg, 83%) after flash column chromatography on silica (0 to 10% acetone in dichloromethane).

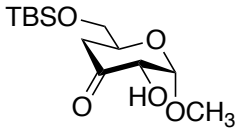
$\mathbf{R}_f$ = 0.33 (5% acetone in dichloromethane)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.40 (dd, *J* = 3.4, 1.2 Hz, 1H, H-4'), 5.28 (dd, *J* = 10.9, 8.3 Hz, 1H, H-2'), 5.14 (d, *J* = 4.0 Hz, 1H, H-1), 5.04 (dd, *J* = 10.5, 3.4 Hz, 1H, H-3'), 4.55 (d, *J* = 8.0 Hz, 1H, H-1'), 4.26 (dd, *J* = 10.6, 1.2 Hz, 1H), 4.24–4.12 (m, 3H, H-6', H-6', H-6), 3.94 (td, *J* = 6.8, 1.2 Hz, 1H, H-6), 3.85–3.79 (m, 2H, H-5, H-5'), 3.53 (d, *J* = 4.0 Hz, 1H, -OH), 3.33 (s, 3H, -OCH_3), 2.83 (ddd, *J* = 14.1, 4.6, 1.3 Hz, 1H, H-2a), 2.68 (dd, *J* = 14.1, 1.1 Hz, 1H, H-2b), 2.13 (s, 3H, -CO(C**H**$_3$), 2.05 (s, 3H, -CO(C**H**$_3$), 2.04 (s, 3H, -CO(C**H**$_3$), 1.98 (s, 3H, -CO(C**H**$_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 205.5, 170.6, 170.4, 170.3, 169.8, 102.2, 99.9, 73.6, 72.9, 70.9, 70.9, 69.6, 69.0, 67.1, 61.4, 55.1, 45.2, 31.1, 20.8, 20.8, 20.8, 20.7.

IR (neat, cm^{-1}): 3490 (w), 2937 (w), 1738 (s), 1427 (w), 1368 (s), 1218 (s), 1176 (s), 1103 (s), 1042 (s), 952 (s), 908 (s), 878 (s), 736 (s).

4e – Methyl 4-deoxy-6-*O*-(*tert*-butyldimethylsilyl)-α-D-*erythro*-hexopyranoside-3-ulose



Prepared according to General Procedure E from methyl 4-*O*-trimethylacetyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside (**2g**) (78.5 mg, 0.2 mmol). Product (**4e**) was obtained as yellow solid (33.1 mg, 57%) after flash column chromatography on silica (20 to 40% ethyl acetate in hexanes).

The amount of remaining starting material in the reaction was found to be 0% by analysis of the crude ^{1}H NMR spectra relative to internal standard 1,3,5-trimethoxybenzene.

R_f = 0.66 (30% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.16 (d, *J* = 4.3, 1H, H-1), 4.18 (ddd, *J* = 9.8, 3.8, 1.3 Hz, 1H, H-2), 3.98 (dd, *J* = 11.4, 2.1 Hz, 1H, H-6), 3.94 (dd, *J* = 11.3, 4.5 Hz, 1H, H-6), 3.67 (m, 1H, H-5), 3.54 (d, *J* = 3.9, 1H, -O**H**) 3.34 (s, 3H, -OC**H**$_3$), 2.80 (ddd, *J* = 14.0, 4.6, 1.4 Hz, 1H, H-4), 2.68 (dd, *J* = 14.0, 1.1 Hz, 1H, H-4), 0.92 (s, 9H, -C(C**H**$_3$)$_3$), 0.11 (s, 6H, -Si(C**H**$_3$)$_2$).

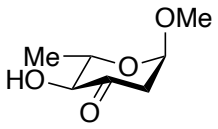
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 206.1, 99.9, 75.6, 73.1, 63.0, 54.9, 45.3, 26.1, 18.6, −5.1, −5.2.

IR (neat, cm^{-1}): 3410 (w), 2935 (w), 2857 (w), 1730 (s), 1466 (s), 1369 (s), 1291 (s), 1251 (s), 1193 (s), 1135 (s), 1098 (s), 1032 (s), 834 (s), 776 (s), 571 (s).

HRMS (DART$^+$, m/z): calculated for $C_{13}H_{27}O_5Si$ $[M+H]^+$: 291.16223, found: 261.16115.

$[\alpha]_D^{20}$ = +58.5 (6.85 g/mL, $CHCl_3$)

4f – Methyl 2,6-dideoxy-α-D-*erythro*-hexopyranoside-3-ulose



Prepared according to General Procedure E from methyl 2-*O*-benzoyl-α-L-rhamnopyranoside (**2h**) (56.5 mg, 0.2 mmol). Product (**4f**) was obtained as a yellow oil (23.0 mg, 72%) after flash column chromatography on silica (0 to 5% acetone in dichloromethane).

The amount of remaining starting material in the reaction was found to be 0% by analysis of the crude ^{1}H NMR spectra relative to internal standard 1,3,5-trimethoxybenzene.

$\mathbf{R_f}$ = 0.57 (5% acetone in dichloromethane)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.08 (d, *J* = 4.5 Hz, 1H, H-1), 3.83 (dd, *J* = 9.5, 2.4 Hz, 1H, H-5), 3.55 (d, *J* = 3.5 Hz, 1H, H-4), 3.33 (s, 3H, -OCH_3), 2.81 (ddd, *J* = 14.0, 4.6, 1.3 Hz, 1H, H-2), 2.67 (dd, *J* = 14.0, 1.0 Hz, 1H, H-2), 1.44 (d, *J* = 5.9 Hz, 3H, -CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 205.4, 99.7, 78.6, 71.0, 54.9, 45.3, 18.9.

IR (neat, cm^{-1}): 3448 (w), 2918 (w), 1723 (s), 1236 (s), 1193 (s), 1118 (s), 1065 (s), 1038 (s), 958 (s), 878 (s), 610 (s), 569 (s).

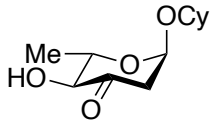
HRMS (DART$^+$, m/z): calculated for $C_7H_{16}NO_4$ $[M+NH_4]^+$: 178.10738, found: 178.10710.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$ = − 148.6 (6.40 mg/mL, $CHCl_3$)

<u>2.5 mmol Scale Reaction</u>

Methyl 2-*O*-benozyl-α-L-rhamnopyranoside (705.7 mg, 2.5 mmol, 1 equiv.), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (28.0 mg, 0.25 mmol, 1 mol%), quinuclidine (55.6 mg, 0.5 mmol, 20 mol%), tetrabutylammonium 4-chlorobenzoate (248.8 mg, 0.625 mmol, 25 mol%), potassium bicarbonate (250.0 mg, 2.5 mmol, 1 equiv.) and a magnetic stir bar were added to a 9.5 dram vial. A rubber septum was used to seal the vial, which was then evacuated and backfilled with argon three times on a Schlenk line. Dry, degassed acetonitrile (0.125 M) was added to the vial under a balloon of argon. The rubber septum was removed and quickly replaced with the vial cap which was sealed with Teflon tape and parafilm. The vial was placed 5 inches from three blue LED Kessil lamps and stirred at 1050 rpm for 24 hours at 25 ℃. After 24 hours the crude reaction was washed with saturated aqueous sodium bicarbonate. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica (0 to 5% acetone in dichloromethane) to afford (**4f**) as a yellow oil (271.9 mg, 68%).

4g – Cyclohexyl 2,6-dideoxy-α-D-*erythro*-hexopyranoside-3-ulose



Prepared according to General Procedure D from cyclohexyl 2-*O*-benzoyl-α-L-rhamnopyranoside (**2i**) (70.1 mg, 0.2 mmol). Product (**4g**) was obtained as a pale yellow solid (28.5mg, 63%) after flash column chromatography on silica (0 to 5% acetone in dichloromethane).

$\mathbf{R_f}$ = 0.68 (5% acetone in dichloromethane)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.35 (d, *J* = 4.7 Hz, 1H, H-1), 3.90–3.84 (m, 1H, H-5), 3.81 (ddd, *J* = 9.5, 3.8, 1.4 Hz, 1H, H-4), 3.59–3.53 (m, 1H, -O**H**), 2.81 (ddd, *J* = 13.9, 4.8, 1.4 Hz, 1H, H-2), 2.63 (dd, *J* = 13.9, 1.0 Hz, 1H, H-2), 1.87–1.76 (m, 2H, -Cy), 1.75–1.67 (m, 2H, -Cy), 1.54–1.48 (m, 1H, -OC**H**-), 1.42 (d, *J* = 6.0 Hz, 3H, -C**H**$_3$), 1.39–1.15 (m, 5H, -Cy).

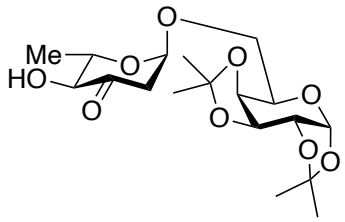
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 205.8, 96.5, 78.7, 76.9, 71.2, 45.9, 33.4, 31.4, 25.7, 24.2, 24.0, 18.8.

IR (neat, cm^{-1}): 3442 (w), 2933 (w), 2859 (w), 1719 (s), 1451 (s), 1380 (s), 1282 (s), 1143 (s), 1087 (s), 1062 (s), 1013 (s), 980 (s), 958 (s), 924 (s), 846 (s), 824 (s), 607 (s).

HRMS (DART$^+$, m/z): calculated for $C_{12}H_{24}NO_4$ $[M+NH_4]^+$: 246.17037, found: 246.16998.

$[\alpha]_D^{20} = -126.6$ (c = 3.50 mg/mL, $CHCl_3$)

4h – 1,2,3,4-di-O-isopropylidene-6-O-(2,6-dideoxy-α-D-*erythro*-hexopyranoside-3-ulosyl)-α-D-galactopyranoside



Prepared according to General Procedure D from 1,2,3,4-di-O-isopropylidene-6-O-(2-*O*-benzoyl-α-L-rhamnopyranosyl)-α-D-galactopyranoside (**2j**) (51.0 mg, 0.1 mmol). Product (**4h**) was obtained as a light yellow oil (29.2 mg, 75%) after flash column chromatography on silica (5–20% acetone in dichloromethane).

$\mathbf{R_f}$ = 0.21 (5% acetone in dichloromethane)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.50 (d, *J* = 5.0 Hz, 1H, gal-H1), 5.30 (d, *J* = 3.8 Hz, 1H, rham-H1), 4.58 (dd, *J* = 7.9, 2.4 Hz, 1H, gal-H3), 4.29 (dd, *J* = 5.0, 2.4 Hz, 1H, gal-H2), 4.17 (dd, *J* = 8.0, 1.9 Hz, 1H, gal-H4), 3.94 (ddd, *J* = 6.3, 6.3, 1.8 Hz, 1H, gal-H5), 3.92 – 3.87 (m, 1H, rham-H5), 3.83 (dd, *J* = 3.8, 1.3 Hz, 1H, rham-H4), 3.82 – 3.78 (m, 1H, gal-H6a), 3.58 (dd, *J* = 10.2, 6.7 Hz, 1H, gal-H6b), 3.53 (d, *J* = 3.8 Hz, 1H, -OH), 2.80 (ddd, *J* = 14.1, 4.7, 1.3 Hz, 1H, rham-H2a), 2.71 (dd, *J* = 14.1, 1.0 Hz, 1H, rham-H2b), 1.52 (s, 3H, -CH_3), 1.43 (s, 3H, -CH_3), 1.42 (d, *J* = 6.1 Hz, 3H, rham-CH_3), 1.32 (s, 3H, -CH_3), 1.31 (s, 3H, -CH_3).

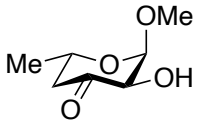
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 205.7, 109.4, 108.8, 98.6, 96.3, 78.6, 71.2, 71.0, 70.7, 70.7, 67.0, 65.6, 45.3, 26.2, 26.1, 25.1, 24.5, 18.7.

IR (neat, cm^{-1}): 3464 (w), 2985 (w), 2929 (w), 1725 (s), 1378 (s), 1252 (s), 1211 (s), 1121 (s), 1063 (s), 1003 (s), 961 (s), 891 (s), 764 (s), 610 (s).

HRMS (DART$^+$, m/z): calculated for $C_{18}H_{32}NO_9$ $[M+NH_4]^+$: 406.20716, found: 406.20805.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}} = -$ 101.9 (c = 3.42 mg/mL, $CHCl_3$)

4i – Methyl 4,6-dideoxy-*α*-D-*erythro*-hexopyranoside-3-ulose



Prepared according to General Procedure D from methyl 4-*O*-trimethylacetyl-*α*-L-rhamnopyranoside (**2k**) (56.5 mg, 0.2 mmol). Product (**4i**) was obtained as a yellow solid (20.7 mg, 65%) after flash column chromatography on silica (5 to 10% acetone in dichloromethane).

The amount of remaining starting material in the reaction was found to be 0% by analysis of the crude ^{1}H NMR spectra relative to internal standard 1,3,5-trimethoxybenzene.

$\mathbf{R}_f$ = 0.62 (10% acetone in dichloromethane)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.08 (d, *J* = 4.2 Hz, 1H, H-1), 4.29 (ddd, *J* = 7.1, 4.3, 1.3 Hz, 1H, H-2), 4.17–4.13 (m, 1H, H-5), 3.41 (s, 3H, -OC**H**$_3$), 3.26 (d, *J* = 7.1 Hz, 1H, -O**H**), 2.56 (dd, *J* = 13.7, 2.8 Hz, 1H, H-4), 2.41 (ddd, *J* = 13.7, 11.0, 1.3 Hz, 1H, H-4), 1.35 (d, *J* = 6.2 Hz, 3H, -C**H**$_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 204.8, 102.3, 75.7, 66.4, 55.7, 47.9, 21.5.

IR (neat, cm^{-1}): 3446 (w), 2932 (w), 1724 (s), 1384 (s), 1359 (s), 1263 (s), 1111 (s). 1097 (s), 1025 (s), 977 (s), 901 (s), 786 (s), 643 (s).

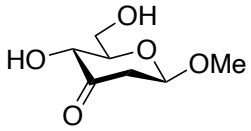
HRMS (DART$^+$, m/z): calculated for $C_7H_{16}NO_4$ $[M+NH_4]^+$: 178.10738, found: 178.10648.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}} = -$ 153.0 (5.65 mg/mL, $CHCl_3$)

2.5 mmol Scale Reaction

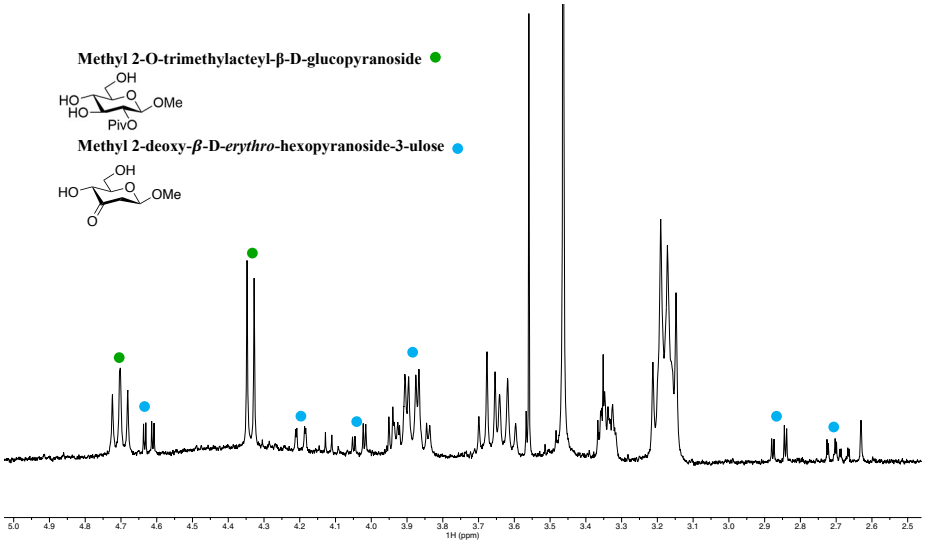
Methyl 4-*O*-trimethylacetyl-α-L-rhamnopyranoside (655.8 mg, 2.5 mmol, 1 equiv.), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (28.0 mg, 0.25 mmol, 1 mol%), quinuclidine (55.6 mg, 0.5 mmol, 20 mol%), tetrabutylammonium 4-chlorobenzoate (248.8 mg, 0.625 mmol, 25 mol%), potassium bicarbonate (250.0 mg, 2.5 mmol, 1 equiv.) and a magnetic stir bar were added to a 9.5 dram vial. A rubber septum was used to seal the vial, which was then evacuated and backfilled with argon three times on a Schlenk line. Dry, degassed acetonitrile (0.125 M) was added to the vial under a balloon of argon. The rubber septum was removed and quickly replaced with the vial cap which was sealed with Teflon tape and parafilm. The vial was placed 5 inches from three blue LED Kessil lamps and stirred at 1050 rpm for 24 hours at 25 °C. After 24 hours the crude reaction was washed with saturated aqueous sodium bicarbonate. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica (5% to 10% acetone in dichloromethane) to afford **4i** as a yellow solid (240.8 mg, 60%).

4j – Methyl 2-deoxy-β-D-*erythro*-hexopyranoside-3-ulose



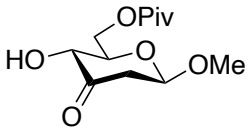
Prepared according to General Procedure D from methyl 2,6-di-*O*-trimethylacetyl-β-D-glucopyranoside (**2l**) (72.5 mg, 0.2 mmol). The yield of **4j** was determined by ^{1}H NMR spectroscopic analysis with a quantitative internal standard from the crude material. The yield determined via ^{1}H NMR spectra of the crude mixture to be 27% (integration of the dd at 2.86 ppm relative to internal standard 1,3,5-trimethoxybenzene).

The amount of remaining starting material in the reaction was found to be 67% by analysis of the crude ^{1}H NMR spectra relative to internal standard 1,3,5-trimethoxybenzene.



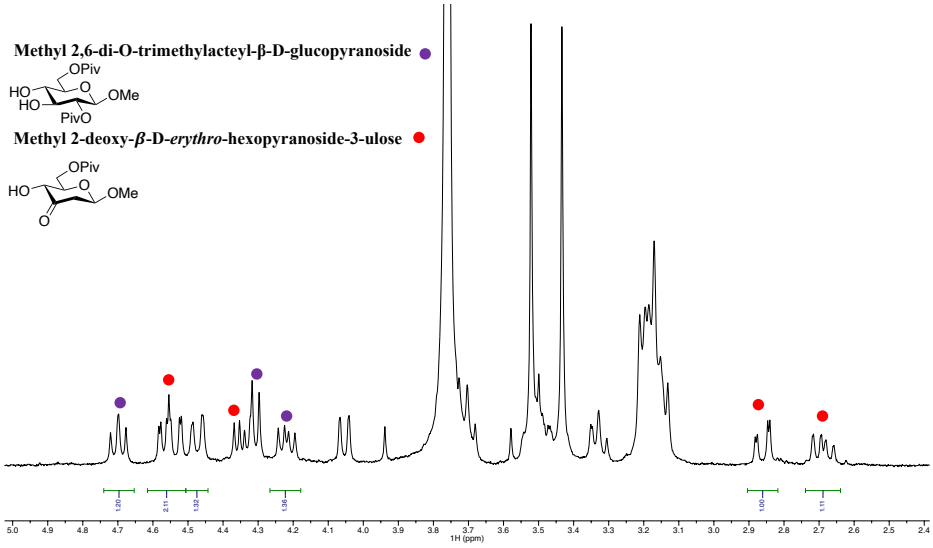
Crude ^{1}H NMR spectra showing select peaks of 4j.

4k – Methyl 2-deoxy-6-*O*-trimethylacetyl-*β*-D-*erythro*-hexopyranoside-3-ulose



Prepared according to General Procedure D from methyl 2,6-di-*O*-trimethylacetyl-*β*-D-glucopyranoside (**2m**) (72.5 mg, 0.2 mmol). The yield of **4k** was determined by ^{1}H NMR spectroscopic analysis with a quantitative internal standard from the crude material. The yield determined via ^{1}H NMR spectra of the crude mixture to be 36% (integration of the dd at 2.86 ppm relative to internal standard 1,3,5-trimethoxybenzene).

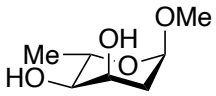
The amount of remaining starting material in the reaction was found to be 42% by analysis of the crude ^{1}H NMR spectra relative to internal standard 1,3,5-trimethoxybenzene.



Crude ^{1}H NMR spectra showing select peaks of 4k.

Derivatizations

5a – Methyl-α-L-digitoxose

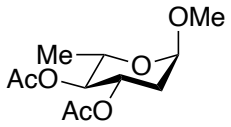


Product **4f** (32.0 mg, 0.2 mmol, 1 equiv.) was added to a 2 dram vial equipped with a magnetic stir bar, dissolved in methanol (2 mL) after which $CeCl_3 \cdot 7H_2O$ (37.2 mg, 0.2 mmol, 1 equiv.) was added. Sodium borohydride (7.6 mg, 0.1 mmol, 0.5 equiv.) was added to a separate 2 dram vial and dissolved in methanol (2 mL). The solution of sodium borohydride was added dropwise to the reaction vial and the reaction was allowed to stir at 23 °C until TLC revealed full consumption of starting material. Reaction mixture was concentrated under vacuum, dissolved in a 15% methanol in dichloromethane solution and filtered through a pad of silica to afford **5a** as a white solid (25.3 mg, 78%).

Spectral data were in agreement with those previously reported.[17]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.77 (d, *J* = 2.6 Hz, 1H), 3.96 – 3.92 (m, 1H), 3.73 – 3.68 (m, 1H), 3.42 (d, 10.0 Hz, 1H), 3.37 9s, 3H), 3.14 (ddd, *J* = 10.3, 10.3, 3.3 Hz, 1H), 2.52 (d, *J* = 10.5 Hz, 1H), 2.17 (ddd, *J* = 14.7, 3.2, 1.2 Hz, 1H), 1.90 (ddd, *J* = 14.7, 3.3, 3.3 Hz, 1H), 1.33 (d, = 6.2 Hz, 3H).

5b – Methyl 3,4-di-*O*-acteyl-α-L-olivose



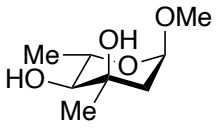
Synthesized according to adapted literature procedures.[18]

Product **4f** (48.0 mg, 0.3 mmol, 1 equiv.) was added to a 2 dram vial equipped with a magnetic stir bar and dissolved in anhydrous tetrahydrofuran (2.2 mL) under an atmosphere of argon gas and cooled to –10 °C. Catecholborane (0.1 mL, 0.9 mmol, 3 equiv.) was added and the reaction mixture was stirred overnight. Reaction was quenched by addition of methanol (1 mL) and saturated aqueous sodium potassium tartrate (1 mL) and stirred at 23 °C for 2 hours, followed by removal of solvent under vacuum. The resulting residue was dissolved in pyridine (6 mL), acetic anhydride (1.2 mL) was added to the vial and the mixture was stirred overnight. Reaction was quenched with methanol and concentrated under vacuum. The crude material was dissolved in ethyl acetate and washed with 1 M aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by flash column chromatography on silica (5% to 10% acetone in dichloromethane) to afford **5b** (30.3 mg, 41%) as a white solid.

Spectral data were in agreement with those previously reported.[19]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =5.26 (q, *J* = 3.5 Hz, 1H), 4.68 (d, *J* = 2.6 Hz, 1H), 4.64 (dd, *J* = 9.5, 3.2 Hz, 1H), 4.24–4.15 (m, 1H), 3.35 (s, 3H), 2.11 (ddd, *J* = 15.1, 3.7, 1.7 Hz, 1H), 2.08 (s, 3H), 2.03 (s, 3H), 2.00 (dt, *J* = 15.1, 3.9 Hz, 1H), 1.18 (d, *J* = 6.5 Hz, 3H).

5c – Methyl-*α*-L-mycaroside



Prepared according to adapted literature procedures.[20]

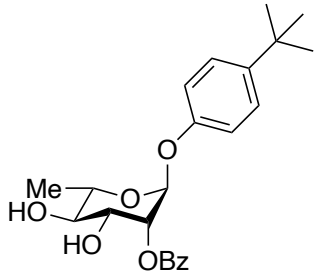
Product **4f** (48.0 mg, 0.3 mmol, 1 equiv.) was added to a 2 dram vial equipped with a magnetic stir bar. The vial was capped with a rubber septa and evacuated and backfilled with argon three times under Schlenk line. Anhydrous tetrahydrofuran (6 mL) was added and the reaction was cooled to –78 °C, followed by dropwise addition of methylmagnesium bromide (0.58 mL, 1.74 mmol, 5.8 equiv.). The reaction was stirred at –78 °C for 30 minutes, then at 0 °C for 10 minutes, then quenched by addition of saturated aqueous ammonium chloride. The mixture was extracted with ethyl acetate three times, then the combined organic layers were dried over sodium sulfate, filtered, and concentrated under vacuum. The crude material was purified by flash column chromatography on silica (20% ethyl acetate in hexanes) to afford **5c** (27.3 mg, 52%) as a yellow oil.

Spectral data were in agreement with those previously reported.[21]

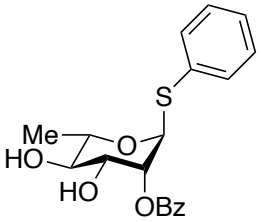
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.76 (d, *J* = 2.9, 1H), 3.85 (s, 1H), 3.63–3.56 (m, 1H), 3.37 (s, 3H), 2.97 (dd, *J* = 11.0, 9.6 Hz, 1H), 2.24 (d, *J* = 11.1 Hz, 1H), 2.04 (dd, *J* = 14.6, 1.4 Hz, 1H), 1.81 (dd, *J* = 14.6, 3.6 Hz, 1H), 1.33 (d, *J* = 6.2, 3H), 1.23 (s, 3H).

Substrate Limitations

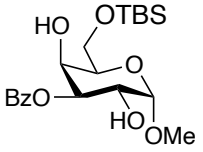
Following substrates exhibited low conversion or trace product formation when subjected to General Procedure D/E.



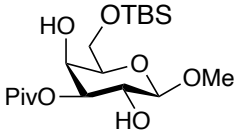
2n
trace product
<5% conversion



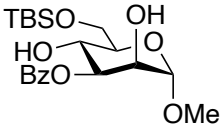
2o
trace product
50% conversion



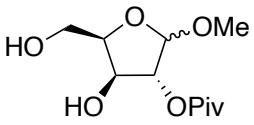
2p
trace product
43% conversion



2p'
trace product
40% conversion



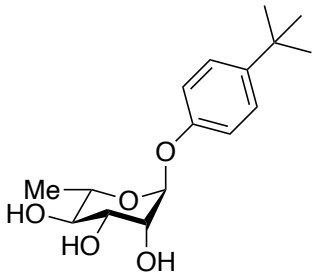
2q
5% product
81% conversion



2r
trace product
<5% conversion

Preparation of Substrates 2n – 2r

4-tert-butylphenyl-α-L-rhamnopyranoside

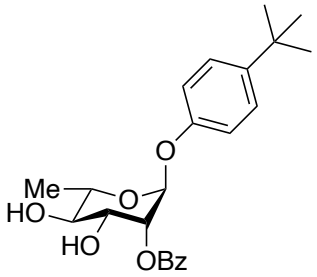


Prepared according to previous literature procedures.[22]

Spectral data were in agreement with those previously reported.[22]

^{1}H NMR (400 MHz, CD_3OD): δ (ppm) = 7.37 – 7.32 (m, 2H), 7.03 – 6.98 (m, 2H), 5.41 (d, *J* = 1.8 Hz, 1H), 4.01 (dd, *J* = 3.4, 1.8 Hz, 1H), 3.97 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.73 – 3.65 (m, 1H), 3.48 (t, *J* = 9.5 Hz, 1H), 1.32 (s, 9H), 1.26 (d, *J* = 6.2 Hz, 3H).

2n – 4-tert-butylphenyl-2-*O*-benzoyl-α-L-rhamnopyranoside



Prepared according General Procedure C from 4-tert-butylphenyl-α-L-rhamnopyranoside and benzoic anhydride. **2n** was isolated as a clear, colourless oil (102.6 mg, 18%) after flash column chromatography on silica (40 to 50% ethyl acetate in hexanes).

$\boldsymbol{R_f}$ = 0.18 (40% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.12 – 8.06 (m, 2H, Ar-H), 7.65 – 7.57 (m, 1H, Ar-H), 7.51 – 7.44 (m, 2H, Ar-H), 7.34 – 7.28 (m, 2H, Ar-H), 7.04 – 6.98 (m, 2H, Ar-H), 5.58 (d, *J* = 1.7 Hz, 1H, H-1), 5.52 (dd, *J* = 3.4, 1.7 Hz, 1H, H-2), 4.30 (dd, *J* = 9.5, 3.5 Hz, 1H, H-3), 3.97 – 3.89 (m, 1H, H-5), 3.71 (t, *J* = 9.5 Hz, 1H, H-4), 1.37 (d, *J* = 6.2 Hz, 3H, -CH_3), 1.30 (s, 9H, -$C(CH_3)_3$).

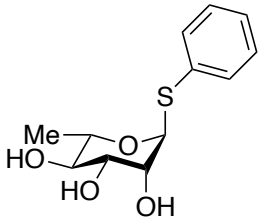
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.6, 155.3, 146.5, 134.6, 134.0, 131.1, 130.8, 130.7, 129.6, 129.5, 127.4, 117.2, 97.3, 74.4, 74.4, 70.7, 70.6, 35.0, 31.9, 18.2.

IR (neat, cm-1): 3409 (w), 2947 (w), 1709 (s), 1511 (s), 1267 (s), 1230 (s), 1112 (s), 1018 (s), 981 (s), 830 (s), 708 (s), 615 (s), 567 (s).

HRMS ($DART^+$, m/z): calculated for $C_{23}H_{28}O_6$ $[M+H]^+$: 401.19587; found: 401.19627.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = –16.2 (16.80 mg/mL, $CHCl_3$)

Phenyl 1-thio-α-L-rhamnopyranoside

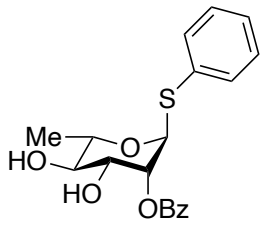


Prepared according to previous literature procedures.[23]

Spectral data were in agreement with those previously reported.[23]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =7.48–7.44 (m, 2H), 7.33–7.27 (m, 3H), 5.49 (d, *J* = 1.0 Hz, 1H), 4.21–4.13 (m, 1H), 3.80 (dd, *J* = 9.4, 3.4 Hz, 1H), 3.55 (t, *J* = 9.3 Hz, 1H), 1.33 (d, *J* = 6.2 Hz, 3H).

2o – Phenyl 2-*O*-benzoyl-1-thio-*α*-L-rhamnopyranoside

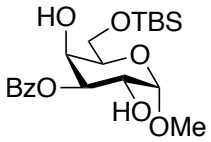


Prepared according to General Procedure C from phenyl 1-thio-*α*-L-rhamnopyranoside and benzoic anhydride.

Spectral data were in agreement with those previously reported.[24]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.05–8.02 (m, 2H), 7.60–7.56 (m, 1H), 7.51–7.48 (m, 2H), 7.47–7.43 (m, 2H), 7.34–7.28 (m, 3H), 5.62 (dd, *J* = 3.4, 1.5 Hz, 1H), 5.58 (d, *J* = 1.0 Hz, 1H), 4.29–4.22 (m, 1H), 4.08 (dd, *J* = 9.4, 3.4 Hz, 1H), 3.71 (t, *J* = 9.4 Hz, 1H), 1.40 (d, 6.2 Hz, 3H).

2p – Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-galactopyranoside

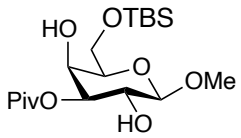


Synthesized according to previous literature procedures.[9]

Spectral data were in agreement with those previously reported.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.14–8.09 (m, 2H), 7.60–7.54 (m, 1H), 7.48–7.42 (m, 2H), 5.28 (dd, *J* = 10.3, 3.0 Hz, 1H), 4.91 (d, *J* = 3.9 Hz, 1H), 4.33 (d, *J* = 7.2 Hz, 1H), 4.29–4.21 (m, 1H), 3.98–3.83 (m, 3H), 3.47 (s, 3H), 0.91 (s, 9H), 0.10 (s, 3H), 0.10 (s, 3H).

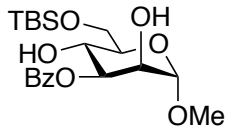
2p' – Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside



Synthesized according to previous literature procedures from methyl 6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (1 equiv.) and trimethylacetyl chloride (1.2 equiv.).[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.80 (dd, *J* = 10.1, 3.2 Hz, 1H, H3), 4.24 (d, *J* = 7.7 Hz, 1H, H1), 4.12 – 4.08 (m, 1H, H4), 3.92 (dd, *J* = 10.6, 5.8 Hz, 1H, H6a), 3.89 – 3.83 (m, 2H, H2, H6b), 3.55 (s, 3H, CH_3), 3.52 (ddd, *J* = 5.8, 4.9, 1.0 Hz, 1H, H5), 1.25 (s, 9H, CH_3), 0.89 (s, 9H, CH_3), 0.09 – 0.07 (m, 6H, CH_3).

2q – Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-mannopyranoside

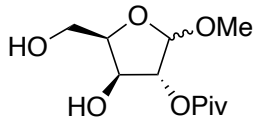


Synthesized according to previous literature procedures.[9]

Spectral data were in agreement with those previously reported.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.12–8.08 (m, 2H), 7.60–7.55 (m, 1H), 7.48–7.42 (m, 2H), 5.35 (dd, *J* = 9.7, 3.2 Hz, 1H), 4.75 (d, *J* = 1.8 Hz, 1H), 4.17–4.08 (m, 2H), 3.99–3.89 (m, 2H), 3.77–3.71 (m, 1H), 3.43 (s, 3H), 0.91 (s, 9H), 0.11 (s, 3H), 0.11 (s, 3H).

2r – Methyl 2-*O*-trimethylacetyl-D-xylofuranoside



Prepared according to adapted literature procedures.[25,5]

Acetyl chloride (6.5 mmol, 1.3 equiv.) and methanol (0.5 mL) were added to a 2 dram vial equipped with a magnetic stir bar and stirred at 0 °C for 3o minutes. A solution of D-xylose (5 mmol, 1 equiv.) in methanol (0.5 mL) was added dropwise at 0 °C, the reaction was then warmed to 23 °C and stirred for 7 hours. The reaction was quenched with pyrdine (1.5 mL) and concentrated under vacuum. The crude material was purified by flash column chromatography on silica (15% to 20% methanol in dichloromethane to afford methyl D-xylofuranoside as a white solid (587 mg, 72%).

Methyl D-xylofuranoside (3.6 mmol, 1 equiv.) and phenyl boronic acid (3.6 mmol, 1 equiv.) were dissolved in toluene (18 mL) and heated at 110 °C for 13 h. Toluene was removed under reduced pressure and the resulting residue was azeotroped with toluene three times. The boronic ester was dissolved in pyridine (7.2 mL) and cooled to 0 °C with stirring. Trimethyl acetyl chloride (4.32 mmol, 1.2 equiv.) was added, and the reaction was warmed to 23 °C and allowed to stir until TLC revealed full consumption of the starting material (ca. 2 h). Reaction was dilute with toluene and filtered through a pad of Celite® followed by removal of the solvent under vacuum. The resulting residue was dissolved in ethyl acetate, added to a solution of 1.0 M sorbitol:1 M sodium carbonate aqueous solution and shaken for five minutes. The aqueous phase was extracted with ethyl acetate several times. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude material was purified by flash column chromatography on silica (10% to 30% acetone in dichloromethane) to afford methyl 2-*O*-trimethylacetyl-D-xylofuranoside (mixture of 2.5:1 α:β) as a white solid (361 mg, 40%).

Isolated as a 2.5:1 mixture of α and β anomers.

Select peaks for methyl 2-*O*-trimethylacetyl-α-D-xylofuranoside (major isomer)
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.10 (d, *J* = 4.5 Hz, 1H), 4.73 (dd, *J* = 6.1 Hz, 4.4 Hz, 1H), 4.55 (dd, *J* = 7.2, 7.2 Hz, 1H), 4.24–4.21 (m, 1H), 3.36 (s, 3H), 1.22 (s, 9H).

Select peaks for methyl 2-*O*-trimethylacetyl-β-D-xylofuranoside (minor isomer)
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.96 (d, *J* = 2.2 Hz, 1H), 4.36 (ddd, *J* = 10.6, 10.6, 4.9, 1H), 3.44 (s, 3H), 1.20 (s, 9H).

Computational Data

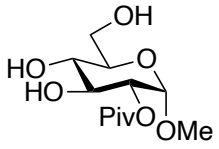
DFT calculations were carried out using the Gaussian 16 suite of programs[26] at the B97-D3/Def2-TZVP level of theory.[27, 28] Vibrational frequency calculations were carried out for each stationary point to ensure they were either an energy minimum (no imaginary frequencies) or a transition state (one imaginary frequency) on the potential energy surface. The imaginary frequency for each saddle point was visualized to verify that it corresponded to a transition state for H-atom transfer. The Intrinsic Reaction Coordinate (IRC) method was used to verify all transition states. Frequency calculations were carried out at 1 atm and 298.15 K. Structures were visualized using Avogadro 1.2.0. Geometry optimizations and frequency calculations were carried out in the gas phase for calculated energies of all species except for proposed reaction intermediated and transition states depicted in Table S5 and Figure S1.

Geometry optimizations and frequency calculations were carried out in acetonitrile using the polarizable continuum model (PCM) for calculated energies of all proposed reaction intermediates and transition states. The calculated energies of these species (depicted in Figure S1) are listed in Table S12.

Single point energy calculations were carried out using the Gaussian 16 suite of programs[26] at the M06-2X/aug-cc-pVTZ level of theory[27,28] in acetonitrile using the polarizable continuum model (PCM) for calculated energies of all proposed reaction intermediates and transition states. The calculated energies of these species (depicted in Figure S2) are listed in Table S13.

Single point energy calculations were carried out using the ORCA 4.2.1 suite of programs at the ωB97M-V/ma-def2-TZVP level of theory[29.30] in acetonitrile using the conductor-like polarizable continuum model (CPCM) for calculated energies of all proposed reaction intermediates and transition states. The calculated energies of these species (depicted in Figure S3) are listed in Table S14.

Calculated free energies of transition states of HAT

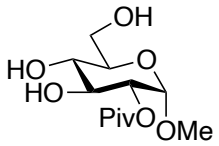


2-OPiv-α-Glc

Table S4. Calculated gas-phase free energies of transition states for hydrogen atom transfer from 2-OPiv-α-Glc to the quinuclidine radical cation.[a]

Reaction	Gibbs free energy of transition state for HAT
2-OPiv-α-Glc (H1) + quinuclidine	−3.8
2-OPiv-α-Glc (H2) + quinuclidine	−1.9
2-OPiv-α-Glc (H3) + quinuclidine	−8.0
2-OPiv-α-Glc (H4) + quinuclidine	−6.8
2-OPiv-α-Glc (H5) + quinuclidine	−2.5

[a]Gibbs free energies in kcal/mol, calculated in gas phase.

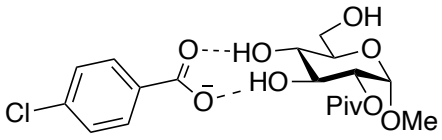


2-OPiv-α-Glc

Table S5. Calculated free energies of transition states for hydrogen atom transfer from 2-OPiv-α-Glc to the quinuclidine radical cation (PCM(acetonitrile)).[a]

Reaction	Gibbs free energy of transition state for HAT
2-OPiv-α-Glc (H1) + quinuclidine	–
2-OPiv-α-Glc (H2) + quinuclidine	8.0
2-OPiv-α-Glc (H3) + quinuclidine	0.0
2-OPiv-α-Glc (H4) + quinuclidine	1.1
2-OPiv-α-Glc (H5) + quinuclidine	3.2

[a]Gibbs free energies in kcal/mol (PCM(acetonitrile)).

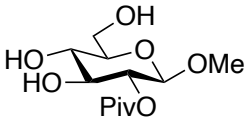


[2-OPiv-α-Glc•4-ClOBz]$^-$

Table S6. Calculated gas-phase free energies of transition states for hydrogen atom transfer from 2-OPiv-α-Glc•4-ClOBz]$^-$ to the quinuclidine radical cation.[a]

Reaction	Gibbs free energy of transition state for HAT
[2OPiv-αGlc•4-ClOBz]$^-$ (H1) + quinuclidine	−63.2
[2OPiv-αGlc•4-ClOBz]$^-$ (H2) + quinuclidine	–
[2OPiv-αGlc•4-ClOBz]$^-$ (H3) + quinuclidine	−78.5
[2OPiv-αGlc•4-ClOBz]$^-$ (H4) + quinuclidine	−73.9
[2OPiv-αGlc•4-ClOBz]$^-$ (H5) + quinuclidine	−68.5

[a]Gibbs free energies in kcal/mol, calculated in gas phase.

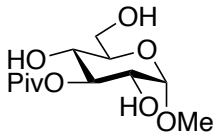


2-OPiv-β-Glc

Table S7. Calculated gas-phase free energies of transition states for hydrogen atom transfer from 2-OPiv-β-Glc to the quinuclidine radical cation.[a]

Reaction	Gibbs free energy of transition state for HAT
2-OPiv-β-Glc (H1) + quinuclidine	−4.9
2-OPiv-β-Glc (H2) + quinuclidine	−0.1
2-OPiv-β-Glc (H3) + quinuclidine	−5.2
2-OPiv-β-Glc (H4) + quinuclidine	−7.2
2-OPiv-β-Glc (H5) + quinuclidine	–

[a]Gibbs free energies in kcal/mol, calculated in gas phase.

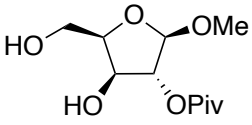


3-OPiv-α-Glc

Table S8. Calculated gas-phase free energies of transition states for hydrogen atom transfer from 3-OPiv-Glc to the quinuclidine radical cation.[a]

Reaction	Gibbs free energy of transition state for HAT
3-OPiv-α-Glc (H1) + quinuclidine	−6.2
3-OPiv-α-Glc (H2) + quinuclidine	−3.0
3-OPiv-α-Glc (H3) + quinuclidine	−3.4
3-OPiv-α-Glc (H4) + quinuclidine	−4.8
3-OPiv-α-Glc (H5) + quinuclidine	−5.6

[a]Gibbs free energies in kcal/mol, calculated in gas phase.

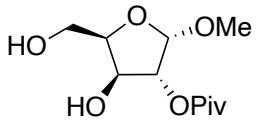


2-OPiv-β-xyl

Table S9. Calculated gas-phase free energies of transition states for hydrogen atom transfer from 2-OPiv-β-xyl to the quinuclidine radical cation.[a]

Reaction	Gibbs free energy of transition state for HAT
2-OPiv-β-xyl (H1) + quinuclidine	–
2- OPiv--β-xyl (H2) + quinuclidine	−3.3
2- OPiv--β-xyl (H3) + quinuclidine	−5.4
2- OPiv--β-xyl (H4) + quinuclidine	−7.1
2- OPiv--β-xyl (H5) + quinuclidine	−4.8

[a]Gibbs free energies in kcal/mol, calculated in gas phase.



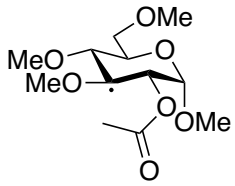
2-OPiv-α-xyl

Table S10. Calculated gas-phase free energies of transition states for hydrogen atom transfer from 2-OPiv-β-xyl to the quinuclidine radical cation.[a]

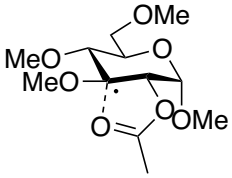
Reaction	Gibbs free energy of transition state for HAT
2- OPiv-α-xyl (H1) + quinuclidine	–
2- OPiv-α-xyl (H2) + quinuclidine	−0.2
2- OPiv-α-xyl (H3) + quinuclidine	−4.4
2- OPiv-α-xyl (H4) + quinuclidine	−8.2
2- OPiv-α-xyl (H5) + quinuclidine	−3.5

[a]Gibbs free energies in kcal/mol, calculated in gas phase.

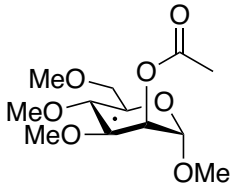
Effect of coordination of the carbonyl to the radical at C-3.



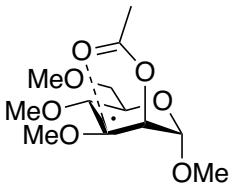
per-Me-α-Glc_C3$^{\bullet}$



per-Me-α-Glc_C3$^{\bullet}$_coord



per-Me-α-Man_C3$^{\bullet}$



per-Me-α-Man_C3$^{\bullet}$_coord

Table S11. Calculated energies of per-methylated 2-*O*-acylated-α-gluco- and manno-pyranosides with a radical at C-3.[a]

Species	Sum of electronic and zero-point energies	Sum of electronic and thermal energies	Sum of electronic and thermal enthalpies	Sum of electronic and thermal free energies
per-Me-α-Glc_C3$^{\bullet}$	-995.861089	-995.838376	-995.837432	-995.916630
per-Me-α-Glc_C3$^{\bullet}$_coord	-995.854743	-995.832377	-995.831433	-995.908236
per-Me-α-Man_C3$^{\bullet}$	-995.857846	-995.835214	-995.834270	-995.912713
per-Me-α-Man_C3$^{\bullet}$_coord	-995.859704	-995.837086	-995.836141	-995.913602

[a]Energies, enthalpies and free energies in kcal/mol, calculated in the gas phase

Proposed Reaction Pathway

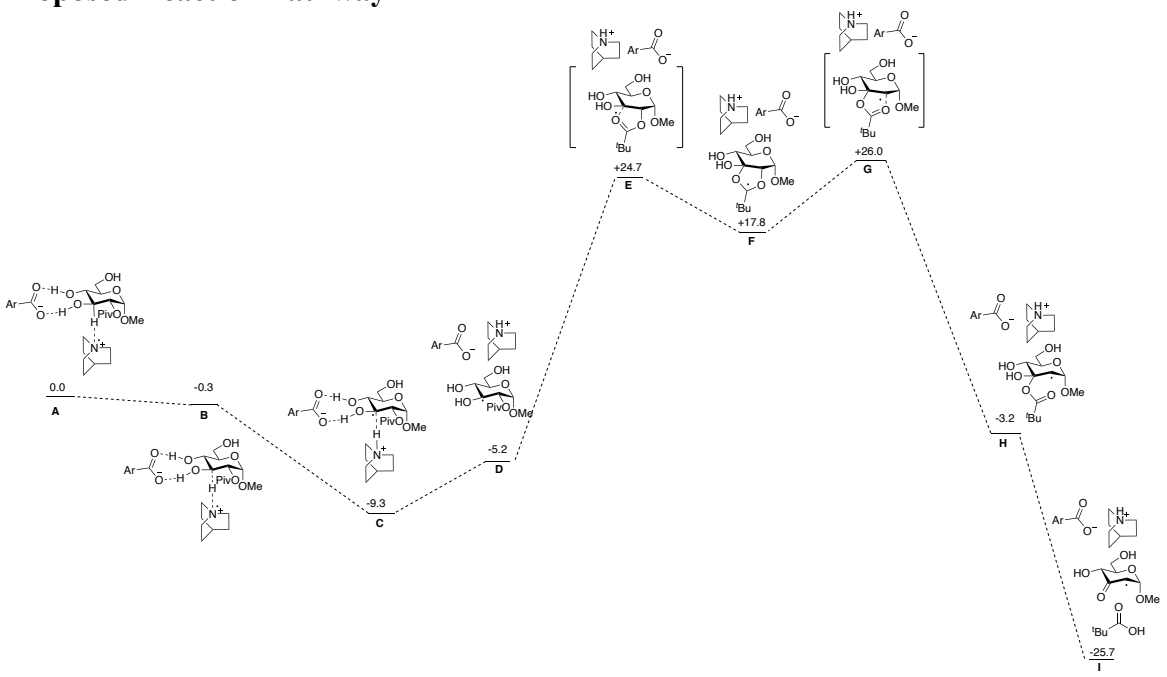


Figure S1. Calculated free energy profile of proposed intermediates and transition states for HAT and 1,2-acyloxy migration from a 2-O-pivoylated glucopyranoside (B97-D3/def2-TZVP, PCM (acetonitrile)).

Table S12. Calculated energies of reaction intermediates in Figure S1.[a]

Species	Sum of electronic and zero-point energies	Sum of electronic and thermal energies	Sum of electronic and thermal enthalpies	Sum of electronic and thermal free energies
HAT_PRC	-2205.2633	-2205.223258	-2205.222313	-2205.342957
HAT_TS	-2205.266069	-2205.226849	-2205.225904	-2205.343399
HAT_PostRC	2205.279863	-2205.240062	-2205.239118	-2205.359
OPiv-C2_rad-C3	-995.923298	-995.901628	-995.900684	-995.975
quin-H+_ArCO2-	-1209.327160	-1209.310287	-1209.309343	-1209.375589
1,2-mig_TS1	-995.880132	-995.859569	-995.858624	-995.9288
1,2-mig_int	-995.890123	-995.869653	-995.868709	-995.9383
1,2-mig_TS2	-995.876692	-995.856191	-995.855247	-995.9248
OPiv-C3_rad-C2	-995.922464	-995.900743	-995.899799	-995.9731
C3-keto C2-rad	-649.111462	-649.09902	-649.098076	-649.151
PivOH	-346.82486	-346.816438	-346.815494	-346.8574

[a]Energies, enthalpies and free energies in kcal/mol (PCM (acetonitrile)).

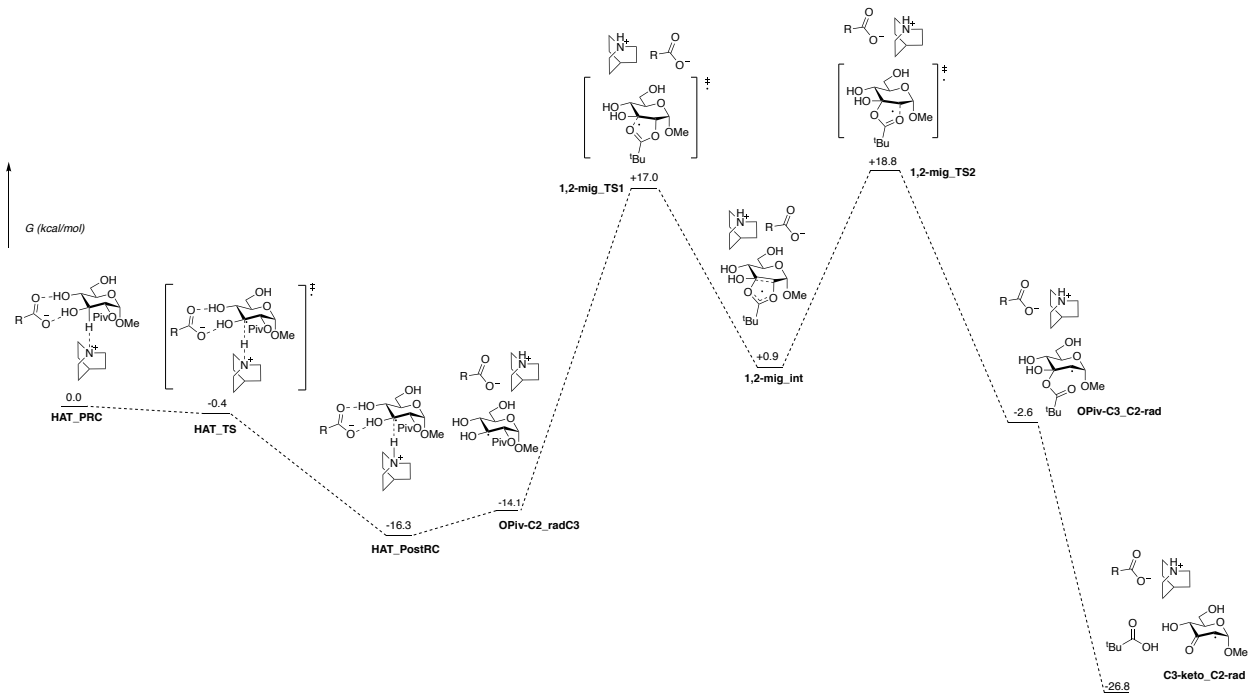


Figure S2. Calculated free energy profile of proposed intermediates and transition states for HAT and 1,2-acyloxy migration from a 2-O-pivoylated glucopyranoside (M06-2X/aug-cc-pVTZ, PCM (acetonitrile) single point energies, using the geometries and frequencies calculated at the B97-D3/def2-TZVP, PCM(acetonitrile) level of theory).

Table S13. Calculated energies of reaction intermediates in Figure S2.[a]

Species	Single point energies (M06-2X)	Free energy correction (data from Table S12)	M06-2X free energies
HAT_PRC	-2206.183262	0.542038	-2205.641224
HAT_TS	-2206.182836	0.54092	-2205.641916
HAT_PostRC	-2206.212416	0.545269	-2205.667147
OPiv-C2_rad-C3	-996.4449682	0.274265	-996.1707032
quin-H^+_$ArCO_2^-$	-1209.740848	0.24779	-1209.493058
1,2-mig_TS1	-996.3972467	0.27611	-996.1211367
1,2-mig_int	-996.425824	0.279161	-996.146663
1,2-mig_TS2	-996.3945701	0.276299	-996.1182711
OPiv-C3_rad-C2	-996.425824	0.273535	-996.152289
C3-keto_C2-rad	-649.4199971	0.139371	-649.2806261
PivOH	-347.0208234	0.110516	-346.9103074

[a]Energies, enthalpies and free energies in kcal/mol (PCM (acetonitrile)).

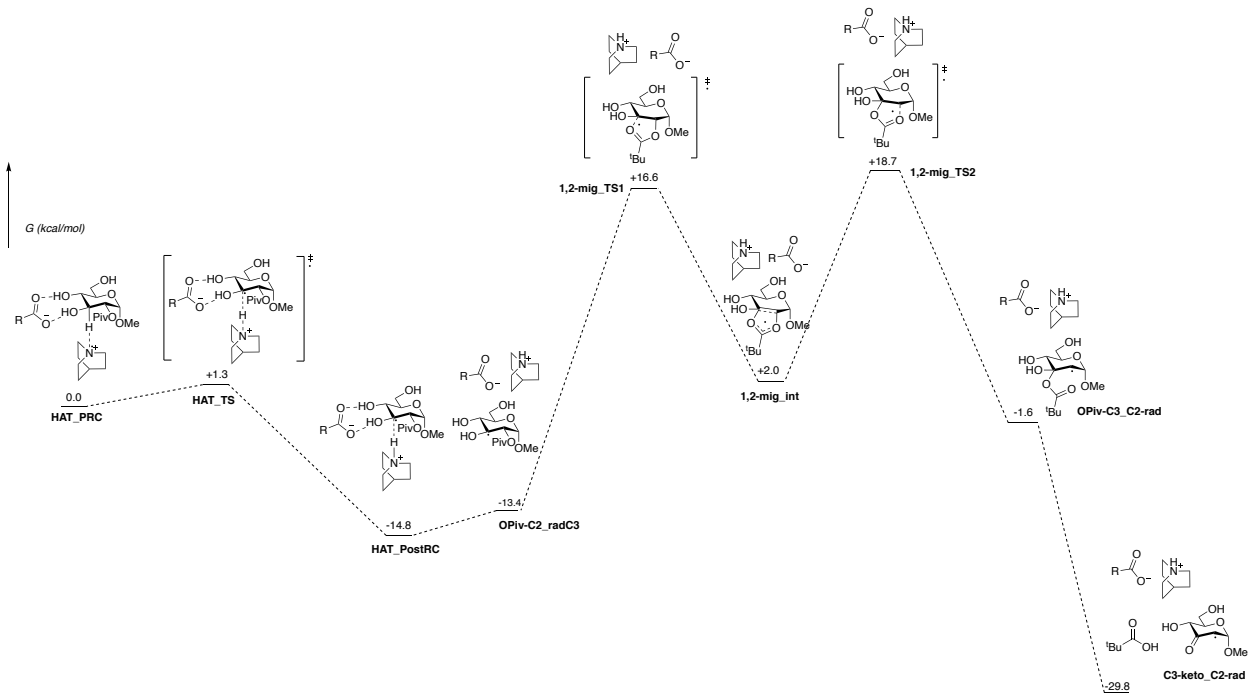


Figure S3. Calculated free energy profile of proposed intermediates and transition states for HAT and 1,2-acyloxy migration from a 2-O-pivoylated glucopyranoside (*ω*B97M-V/ma-def2-TZVP, CPCM (acetonitrile) single point energies, using the geometries and frequencies calculated at the B97-D3/def2-TZVP, PCM(acetonitrile) level of theory).

Table S14. Calculated energies of reaction intermediates in Figure S3.[a]

Species	Single point energies (*ω*B97M-V)	Free energy correction(data from Table S12)	*ω*B97M-V free energies
HAT_PRC	-2206.258338	0.542038	-2205.7163
HAT_TS	-2206.255118	0.54092	-2205.714198
HAT_PostRC	-2206.285143	0.545269	-2205.739874
OPiv-C2_rad-C3	-996.5004876	0.274265	-996.2262226
quin-H^+_$ArCO_2^-$	-1209.759282	0.24779	-1209.511492
1,2-mig_TS1	-996.4544627	0.27611	-996.1783527
1,2-mig_int	-996.4808604	0.279161	-996.2016994
1,2-mig_TS2	-996.4512958	0.276299	-996.1749968
OPiv-C3_rad-C2	-996.4808604	0.273535	-996.2073254
C3-keto_C2-rad	-649.4702592	0.139371	-649.3308882
PivOH	-347.0319577	0.110516	-346.9214417

[a]Energies, enthalpies and free energies in kcal/mol (CPCM (acetonitrile)).

Calculated energies and geometries.

Calculated free energies and geometries for HAT transition states.

[quinuclidine]$^{\bullet+}$

Energy (Hartree/particle): -328.948761853

Zero-point correction= 0.190863 (Hartree/Particle)
Thermal correction to Energy= 0.197729
Thermal correction to Enthalpy= 0.198674
Thermal correction to Gibbs Free Energy= 0.158914
Sum of electronic and zero-point Energies= -328.757904
Sum of electronic and thermal Energies= -328.751037
Sum of electronic and thermal Enthalpies= -328.750093
Sum of electronic and thermal Free Energies= -328.789853

Number of imaginary frequencies: 0

Geometry:

N	1.17345	0.00428	-0.00794
C	0.81955	0.25548	-1.38432
C	0.83823	-1.31711	0.46515
C	0.83226	1.07095	0.90222
C	-0.76904	1.09146	0.94874
H	1.22419	2.01557	0.52214
H	1.24867	0.85885	1.88818
C	-0.78234	0.26723	-1.41406
C	-0.76292	-1.36717	0.48093
H	1.24353	-1.46043	1.46793
H	1.24539	-2.06496	-0.21708
C	-1.27828	-0.00488	0.00884
H	-1.11198	2.08129	0.63809
H	-1.08909	0.91988	1.97929
H	-1.12132	-0.50051	-2.11375
H	-1.11624	1.24182	-1.77812
H	-1.09227	-1.59335	1.49791
H	-1.09201	-2.17353	-0.17888
H	-2.37662	-0.00911	0.01648
H	1.22266	1.22017	-1.69635
H	1.21619	-0.54136	-2.01527

[2-OPiv-α-Glc]

Energy (Hartree/particle): -996.892644643

Zero-point correction= 0.339655 (Hartree/Particle)
Thermal correction to Energy= 0.361296
Thermal correction to Enthalpy= 0.362240
Thermal correction to Gibbs Free Energy= 0.288371
Sum of electronic and zero-point Energies= -996.552989
Sum of electronic and thermal Energies= -996.531348
Sum of electronic and thermal Enthalpies= -996.530404
Sum of electronic and thermal Free Energies= -996.604274

Number of imaginary frequencies: 0

Geometry:

C	-0.48786	1.12969	0.39560
C	0.03709	-0.31627	0.42709
C	-0.86247	-1.25160	-0.36270
O	-0.40742	-2.58825	-0.16928
C	-2.30671	-1.09537	0.11147
C	-2.74175	0.37504	0.08119
C	-4.11650	0.60479	0.71193
O	-5.16018	-0.11652	0.03526
O	-1.83556	1.17293	0.85769
O	-3.10350	-1.91798	-0.74270
O	1.35766	-0.39799	-0.14084
O	-0.34503	1.62932	-0.90889
H	-2.75027	0.71856	-0.96597
H	0.06428	1.74886	1.11321
H	0.07944	-0.63150	1.47413
H	-0.81756	-0.97974	-1.42854
H	-2.36509	-1.45209	1.15462
C	-0.51425	3.04359	-0.99616
C	2.39848	-0.02072	0.64703
H	-4.11381	0.23154	1.74090
H	-4.33118	1.68174	0.73997
H	-4.03023	-1.74270	-0.50654
H	-1.08092	-3.15940	-0.56692
H	-5.29400	0.29645	-0.82909
O	2.26432	0.38941	1.77975
C	3.72839	-0.17447	-0.10062
C	4.87815	0.21502	0.83653
C	3.70827	0.76048	-1.32885
C	3.88962	-1.63880	-0.55756
H	-0.32713	3.31671	-2.03731
H	0.20604	3.56301	-0.34653
H	-1.53123	3.34558	-0.71308

H	4.84832	-1.75364	-1.07614
H	3.08578	-1.93511	-1.23545
H	3.88304	-2.31956	0.30070
H	5.83134	0.11132	0.30649
H	4.90090	-0.42686	1.72197
H	4.77923	1.24983	1.17678
H	4.66337	0.68247	-1.86054
H	3.57313	1.80457	-1.02430
H	2.90139	0.49445	-2.01609

[2-OPiv-α-Glc(H1)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.86493782

Zero-point correction= 0.527471 (Hartree/Particle)
Thermal correction to Energy= 0.557560
Thermal correction to Enthalpy= 0.558504
Thermal correction to Gibbs Free Energy= 0.464732
Sum of electronic and zero-point Energies= -1325.337467
Sum of electronic and thermal Energies= -1325.307378
Sum of electronic and thermal Enthalpies= -1325.306434
Sum of electronic and thermal Free Energies= -1325.400206

Number of imaginary frequencies: 1, -1020.7599

Geometry:

C	-0.75147	-0.29663	0.60245
C	-0.83873	0.94438	-0.29851
C	-2.28743	1.44580	-0.33124
O	-2.34732	2.48395	-1.28807
C	-3.24291	0.30468	-0.69174
C	-3.04849	-0.90045	0.23522
C	-3.79013	-2.15356	-0.21945
O	-5.18437	-1.84058	-0.23612
O	-1.63457	-1.29117	0.23106
O	-4.54706	0.85160	-0.58073
O	-0.02163	2.00150	0.19519
O	-0.75062	0.06728	1.92682
H	-3.35127	-0.62900	1.25491
H	0.37471	-0.88127	0.33574
H	-0.52525	0.66802	-1.30895
H	-2.54988	1.81571	0.67309
H	-3.02938	-0.01183	-1.72822
C	-0.88983	-0.95771	2.92950
C	1.19600	2.20283	-0.39045

H	-3.42905	-2.43493	-1.22022
H	-3.57473	-2.97767	0.47619
H	-5.18141	0.12193	-0.68580
H	-3.28487	2.69493	-1.41813
H	-5.67203	-2.59054	-0.60053
O	1.64437	1.45115	-1.23211
C	1.87652	3.45126	0.16043
C	2.01538	3.31366	1.69225
C	1.00075	4.67730	-0.18317
C	3.26157	3.59401	-0.48411
H	4.23012	-3.85057	-0.89346
C	3.39133	-3.20241	-0.62490
H	1.85814	-4.74294	-0.61547
H	3.51279	-1.87389	-2.34137
H	4.19287	-2.51629	1.27585
H	2.54413	-3.32091	-2.63065
H	2.70981	-4.58291	0.92163
H	4.71750	-1.55177	-0.10624
C	2.29649	-4.02024	0.07955
C	2.79204	-2.55940	-1.88560
C	3.86669	-2.08872	0.32253
C	1.20548	-3.03953	0.59649
C	1.50377	-1.78590	-1.48251
C	2.69095	-1.09409	0.54767
N	1.45091	-1.70216	0.00095
H	0.19622	-3.35010	0.31833
H	1.49698	-0.76674	-1.86898
H	2.52378	-0.88421	1.60743
H	0.59517	-2.30065	-1.80393
H	1.24557	-2.92438	1.68208
H	2.84204	-0.15159	0.02175
H	-1.34633	-0.47336	3.79380
H	0.10467	-1.32699	3.20557
H	-1.51327	-1.78234	2.57796
H	1.04047	3.23670	2.17909
H	2.53107	4.19572	2.08453
H	2.61088	2.43197	1.95785
H	3.18819	3.67613	-1.57171
H	3.90169	2.73697	-0.25142
H	3.74647	4.49671	-0.10039
H	0.87157	4.77683	-1.26569
H	1.49493	5.58154	0.18621
H	0.01299	4.60520	0.27769

[2-OPiv-α-Glc(H2)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.86274115

Zero-point correction= 0.527491 (Hartree/Particle)
Thermal correction to Energy= 0.557432
Thermal correction to Enthalpy= 0.558376
Thermal correction to Gibbs Free Energy= 0.465583
Sum of electronic and zero-point Energies= -1325.335251
Sum of electronic and thermal Energies= -1325.305310
Sum of electronic and thermal Enthalpies= -1325.304365
Sum of electronic and thermal Free Energies= -1325.397158

Number of imaginary frequencies: 1, -1236.1025

Geometry:

C	-0.68747	-1.13524	-1.08888
C	-0.14956	-0.59879	0.25215
C	-1.12926	-0.66059	1.40836
O	-0.65165	0.18105	2.45563
C	-2.56062	-0.30142	1.00803
C	-2.94786	-1.00891	-0.29516
C	-4.30726	-0.57844	-0.83594
O	-5.28652	-0.91475	0.15451
O	-1.99633	-0.63610	-1.31190
O	-3.35887	-0.66382	2.12210
O	1.06658	-1.11698	0.68602
O	-0.60555	-2.52851	-1.02495
H	-2.93892	-2.09560	-0.14204
H	-0.10646	-0.74891	-1.93222
H	0.05087	0.67118	0.02831
H	-1.14358	-1.71239	1.74463
H	-2.61946	0.78553	0.82720
C	-0.72954	-3.17328	-2.30557
C	2.15212	-1.23617	-0.17799
H	-4.29366	0.50522	-1.03040
H	-4.50086	-1.10059	-1.78255
H	-4.28430	-0.68936	1.81810
H	-1.26951	0.07721	3.19500
H	-6.15776	-0.63295	-0.15201
O	2.19280	-0.63773	-1.22529
C	3.21696	-2.14372	0.41468
C	4.39376	-2.23395	-0.56590
C	2.60450	-3.54311	0.64767
C	3.68673	-1.54239	1.75983
H	1.36090	5.45359	-0.51708

C	1.06490	4.40682	-0.40332
H	-0.53064	4.89971	0.99661
H	3.02263	3.83533	0.36604
H	0.62474	4.19998	-2.52787
H	1.81987	4.15308	1.61847
H	-1.06669	4.72907	-0.67670
H	2.23234	3.63563	-2.06705
C	-0.39029	4.31999	0.07986
C	1.96787	3.71256	0.62791
C	1.18609	3.67548	-1.74941
C	-0.73507	2.82679	0.35595
C	1.61628	2.19687	0.65728
C	0.62499	2.23066	-1.58924
N	0.38185	1.98657	-0.14424
H	-0.85136	2.60637	1.41763
H	2.39797	1.58913	0.20062
H	-0.33084	2.09867	-2.10155
H	1.42078	1.82668	1.66490
H	-1.64037	2.51471	-0.16849
H	1.32339	1.47151	-1.94025
H	-0.61196	-4.24199	-2.11992
H	0.05892	-2.82489	-2.98603
H	-1.71247	-2.97915	-2.74913
H	4.10789	-0.54058	1.61913
H	4.47274	-2.18076	2.17466
H	2.86996	-1.48393	2.48309
H	4.07965	-2.64892	-1.52773
H	5.16358	-2.88640	-0.14359
H	4.83752	-1.25128	-0.74961
H	2.23473	-3.97229	-0.28885
H	1.77964	-3.50773	1.36325
H	3.38039	-4.20507	1.04439

[2-OPiv-α-Glc(H3)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.87383911

Zero-point correction= 0.528489 (Hartree/Particle)
Thermal correction to Energy= 0.558062
Thermal correction to Enthalpy= 0.559006
Thermal correction to Gibbs Free Energy= 0.467040
Sum of electronic and zero-point Energies= -1325.345350
Sum of electronic and thermal Energies= -1325.315777
Sum of electronic and thermal Enthalpies= -1325.314833
Sum of electronic and thermal Free Energies= -1325.406799

Number of imaginary frequencies: 1, -951.0240

Geometry:

C	0.28094	-1.93604	0.95105
C	0.72645	-1.41304	-0.42736
C	-0.42777	-0.79202	-1.17804
O	-0.06526	-0.37046	-2.44518
C	-1.68659	-1.64565	-1.16006
C	-1.99734	-2.17122	0.24979
C	-3.08186	-3.24426	0.23490
O	-4.26032	-2.65163	-0.33704
O	-0.83717	-2.80247	0.80083
O	-2.72695	-0.84828	-1.71833
O	1.78312	-0.45122	-0.32497
O	0.01394	-0.84138	1.78842
H	-2.32068	-1.33591	0.88384
H	1.06644	-2.57217	1.37541
H	1.09185	-2.28239	-0.99016
H	-0.74834	0.29041	-0.56678
H	-1.48443	-2.52138	-1.80527
C	-0.09344	-1.19727	3.17686
C	3.05932	-0.97765	-0.28645
H	-2.73631	-4.09897	-0.36345
H	-3.26828	-3.58542	1.26126
H	-3.55075	-1.36051	-1.60603
H	-0.88040	-0.29574	-2.97304
H	-4.93983	-3.33209	-0.42784
O	3.25720	-2.16802	-0.31182
C	4.11696	0.12104	-0.19306
C	3.94538	1.10513	-1.36833
C	5.50820	-0.52588	-0.24888
C	3.93509	0.85938	1.15120
H	-1.94532	4.99324	0.80348
C	-1.68737	3.96990	0.51585
H	0.45113	4.34195	0.71031
H	-2.65053	4.16315	-1.43012
H	-2.78370	3.10795	2.18871
H	-0.91215	4.46727	-1.45267
H	-0.28558	3.60732	2.13573
H	-3.70005	3.16606	0.68140
C	-0.28985	3.60844	1.04129
C	-1.69241	3.83748	-1.01501
C	-2.70757	2.98364	1.10459
C	0.09566	2.19912	0.50276
C	-1.44787	2.34317	-1.38587

C	-2.24564	1.53204	0.77654
N	-1.09357	1.60477	-0.15226
H	0.88523	2.24505	-0.24841
H	-2.33731	1.86698	-1.80241
H	-1.90633	0.99411	1.66277
H	-0.62211	2.22686	-2.09130
H	0.41220	1.51505	1.28915
H	-3.02715	0.95052	0.28513
H	-0.25565	-0.26677	3.72507
H	0.83509	-1.66845	3.52399
H	-0.93396	-1.87954	3.34672
H	4.04002	0.59106	-2.33031
H	4.72742	1.86926	-1.31400
H	2.97255	1.60322	-1.34014
H	2.96107	1.35180	1.21100
H	4.71483	1.62133	1.25050
H	4.02855	0.16861	1.99597
H	5.65499	-1.06902	-1.18641
H	5.65173	-1.23067	0.57426
H	6.27248	0.25416	-0.17643

[2-OPiv-α-Glc(H4)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.87027726

Zero-point correction= 0.528114 (Hartree/Particle)
Thermal correction to Energy= 0.557996
Thermal correction to Enthalpy= 0.558940
Thermal correction to Gibbs Free Energy= 0.465294
Sum of electronic and zero-point Energies= -1325.342163
Sum of electronic and thermal Energies= -1325.312282
Sum of electronic and thermal Enthalpies= -1325.311338
Sum of electronic and thermal Free Energies= -1325.404983

Number of imaginary frequencies: 1, -1067.6370

Geometry:

C	-1.21390	1.86868	-0.92327
C	-1.17480	0.55997	-0.13662
C	-0.41770	0.71372	1.18506
O	-0.27263	-0.53831	1.84739
C	0.96514	1.29828	0.91501
C	0.91855	2.50849	-0.03995
C	2.28686	2.97695	-0.54527

O	3.23722	3.05867	0.53826
O	0.15492	2.23863	-1.20623
O	1.66434	1.52027	2.07594
O	-2.49668	0.09487	0.15192
O	-1.89656	2.83110	-0.19344
H	0.45086	3.32085	0.54226
H	-1.65574	1.71979	-1.91795
H	-0.67826	-0.18363	-0.76117
H	-0.95192	1.42885	1.82914
H	1.59732	0.32880	0.31803
C	-2.27809	3.98928	-0.95430
C	-2.84621	-1.14619	-0.34770
H	2.66969	2.25959	-1.27631
H	2.17325	3.94169	-1.04826
H	2.40089	2.13484	1.84407
H	-1.13519	-0.78026	2.21127
H	3.46549	3.98250	0.70014
O	-2.09602	-1.81103	-1.02271
C	-4.25872	-1.52714	0.08993
C	-5.25120	-0.44233	-0.37983
C	-4.27843	-1.62644	1.63207
C	-4.62484	-2.88303	-0.52790
H	4.36001	-3.73978	-0.79335
C	3.75632	-2.85608	-0.56748
H	3.03614	-3.54519	1.36228
H	2.44532	-3.03053	-2.29211
H	5.39833	-1.43341	-0.62804
H	1.87915	-3.91689	-0.87583
H	4.57299	-2.68137	1.44471
H	4.63674	-1.70720	-2.19652
C	3.59664	-2.69974	0.95198
C	2.36408	-2.99244	-1.20158
C	4.43826	-1.59808	-1.12642
C	2.83943	-1.37084	1.24073
C	1.49538	-1.77368	-0.77199
C	3.49922	-0.37718	-0.89340
N	2.35953	-0.80628	-0.04780
H	1.96897	-1.51033	1.88074
H	1.06628	-1.25923	-1.63427
H	4.01160	0.43950	-0.37982
H	0.68491	-2.05324	-0.09946
H	3.48656	-0.62036	1.69951
H	3.08432	-0.00025	-1.83125
H	-2.83313	4.63505	-0.27230
H	-2.92281	3.69884	-1.79423
H	-1.39781	4.52022	-1.33590

H	-4.60244	-2.83940	-1.62034
H	-5.63518	-3.16254	-0.21361
H	-3.93296	-3.66701	-0.20760
H	-5.23319	-0.34043	-1.47033
H	-5.02583	0.52916	0.06674
H	-6.26485	-0.73306	-0.08603
H	-4.06002	-0.66147	2.09824
H	-3.55630	-2.37093	1.98822
H	-5.27247	-1.94594	1.96044

[2-OPiv-α-Glc(H5)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.86348671

Zero-point correction= 0.527881 (Hartree/Particle)
Thermal correction to Energy= 0.557801
Thermal correction to Enthalpy= 0.558745
Thermal correction to Gibbs Free Energy= 0.465368
Sum of electronic and zero-point Energies= -1325.335605
Sum of electronic and thermal Energies= -1325.305686
Sum of electronic and thermal Enthalpies= -1325.304742
Sum of electronic and thermal Free Energies= -1325.398119

Number of imaginary frequencies: 1, -1058.8104

Geometry:

C	-0.90086	0.19008	1.25647
C	-1.63202	0.92820	0.12655
C	-0.69242	1.27781	-1.01440
O	-1.41850	2.02782	-1.97151
C	0.47119	2.10485	-0.47121
C	1.10171	1.51862	0.80923
C	2.00852	2.47489	1.57704
O	2.96394	3.03990	0.67391
O	0.23860	0.97049	1.73127
O	1.41892	2.23872	-1.52089
O	-2.67582	0.10646	-0.39717
O	-0.48207	-1.06852	0.83540
H	1.89234	0.59584	0.34670
H	-1.54325	0.12835	2.13754
H	-2.06377	1.84305	0.54870
H	-0.30096	0.35085	-1.45857
H	0.06729	3.09595	-0.19332
C	-0.62337	-2.10479	1.82406

C	-3.83258	0.03868	0.34710
H	1.37065	3.25539	2.01951
H	2.50176	1.93640	2.39910
H	2.08880	2.87191	-1.21464
H	-0.79781	2.29250	-2.66621
H	3.37008	3.80821	1.09608
O	-3.93114	0.57607	1.42601
C	-4.89915	-0.78758	-0.36722
C	-6.16080	-0.83196	0.50467
C	-4.35663	-2.21688	-0.58684
C	-5.21507	-0.12885	-1.72774
H	5.10559	-3.03771	-0.97249
C	4.41049	-2.23995	-0.69612
H	3.76020	-3.28959	1.10005
H	3.27272	-2.45496	-2.54205
H	6.00116	-0.75807	-0.56328
H	2.58839	-3.32551	-1.16872
H	5.02809	-2.09557	1.38260
H	5.15505	-0.77032	-2.11146
C	4.11698	-2.29674	0.81103
C	3.08966	-2.39879	-1.46520
C	5.01835	-0.86941	-1.03035
C	3.02862	-1.23519	1.14238
C	2.18075	-1.17370	-1.15626
C	4.06372	0.24424	-0.50951
N	2.79962	-0.39089	-0.05549
H	2.07280	-1.69016	1.40013
H	2.08962	-0.49843	-2.00863
H	4.48103	0.78706	0.33990
H	1.18267	-1.46824	-0.83051
H	3.33167	-0.57886	1.96189
H	3.80675	0.96636	-1.28387
H	-0.26789	-3.02617	1.35806
H	-1.67628	-2.22433	2.10288
H	-0.02726	-1.88471	2.71876
H	-5.12798	-2.82198	-1.07399
H	-4.10886	-2.69531	0.36784
H	-3.46644	-2.21469	-1.22118
H	-5.99995	-0.70411	-2.22958
H	-4.33474	-0.10028	-2.37438
H	-5.57941	0.89489	-1.59234
H	-6.92974	-1.42294	-0.00274
H	-6.55587	0.17212	0.68108
H	-5.95780	-1.28916	1.47737

[2-OPiv-α-Glc] (PCM(acetonitrile)

Energy (Hartree/particle): -996.907000108

Zero-point correction= 0.339041 (Hartree/Particle)
Thermal correction to Energy= 0.360730
Thermal correction to Enthalpy= 0.361674
Thermal correction to Gibbs Free Energy= 0.287985
Sum of electronic and zero-point Energies= -996.567959
Sum of electronic and thermal Energies= -996.546270
Sum of electronic and thermal Enthalpies= -996.545326
Sum of electronic and thermal Free Energies= -996.619015

Number of imaginary frequencies: 0

Geometry:

C	-0.49481	1.13692	0.39823
C	0.03829	-0.30609	0.41226
C	-0.85560	-1.23307	-0.39313
O	-0.38242	-2.57278	-0.22834
C	-2.29857	-1.09803	0.09239
C	-2.74626	0.36977	0.09579
C	-4.11688	0.57025	0.74615
O	-5.15157	-0.16260	0.06605
O	-1.83429	1.15797	0.88215
O	-3.10215	-1.90496	-0.77255
O	1.36542	-0.36373	-0.15311
O	-0.37252	1.64497	-0.90287
H	-2.76981	0.73955	-0.93985
H	0.06223	1.75770	1.11190
H	0.08039	-0.63762	1.45331
H	-0.81757	-0.94574	-1.45423
H	-2.34953	-1.47783	1.12719
C	-0.59454	3.05852	-0.98666
C	2.41167	-0.08226	0.66337
H	-4.09474	0.18369	1.77012
H	-4.35175	1.64115	0.78259
H	-4.02786	-1.67558	-0.56898
H	-1.03269	-3.14531	-0.66178
H	-5.35443	0.30218	-0.75865
O	2.28271	0.19796	1.83874
C	3.73833	-0.15109	-0.10022
C	4.89651	0.09892	0.87393
C	3.72622	0.94085	-1.19254
C	3.88868	-1.54230	-0.75010
H	-0.40174	3.34188	-2.02332

H	0.09593	3.59740	-0.32276
H	-1.62692	3.31520	-0.72083
H	4.85145	-1.59352	-1.26996
H	3.09236	-1.73231	-1.47383
H	3.86704	-2.33356	0.00726
H	5.84393	0.05691	0.32658
H	4.92029	-0.65828	1.66360
H	4.81283	1.08227	1.34583
H	4.68474	0.92938	-1.72243
H	3.59032	1.93500	-0.75259
H	2.92592	0.76846	-1.91660

[2-OPiv-α-Glc(H2)•quinuclidine]$^{\bullet+}$ (transition state for HAT) (PCM(acetonitrile)

Energy (Hartree/particle): -1325.92462258

Zero-point correction= 0.527226 (Hartree/Particle)
Thermal correction to Energy= 0.557133
Thermal correction to Enthalpy= 0.558077
Thermal correction to Gibbs Free Energy= 0.466412
Sum of electronic and zero-point Energies= -1325.397397
Sum of electronic and thermal Energies= -1325.367490
Sum of electronic and thermal Enthalpies= -1325.366546
Sum of electronic and thermal Free Energies= -1325.458211

Number of imaginary frequencies: 1, -1449.5690

Geometry:

C	-0.49481	1.13692	0.39823
C	0.03829	-0.30609	0.41226
C	-0.85560	-1.23307	-0.39313
O	-0.38242	-2.57278	-0.22834
C	-2.29857	-1.09803	0.09239
C	-2.74626	0.36977	0.09579
C	-4.11688	0.57025	0.74615
O	-5.15157	-0.16260	0.06605
O	-1.83429	1.15797	0.88215
O	-3.10215	-1.90496	-0.77255
O	1.36542	-0.36373	-0.15311
O	-0.37252	1.64497	-0.90287
H	-2.76981	0.73955	-0.93985
H	0.06223	1.75770	1.11190
H	0.08039	-0.63762	1.45331
H	-0.81757	-0.94574	-1.45423
H	-2.34953	-1.47783	1.12719

C	-0.59454	3.05852	-0.98666
C	2.41167	-0.08226	0.66337
H	-4.09474	0.18369	1.77012
H	-4.35175	1.64115	0.78259
H	-4.02786	-1.67558	-0.56898
H	-1.03269	-3.14531	-0.66178
H	-5.35443	0.30218	-0.75865
O	2.28271	0.19796	1.83874
C	3.73833	-0.15109	-0.10022
C	4.89651	0.09892	0.87393
C	3.72622	0.94085	-1.19254
C	3.88868	-1.54230	-0.75010
H	-0.40174	3.34188	-2.02332
H	0.09593	3.59740	-0.32276
H	-1.62692	3.31520	-0.72083
H	4.85145	-1.59352	-1.26996
H	3.09236	-1.73231	-1.47383
H	3.86704	-2.33356	0.00726
H	5.84393	0.05691	0.32658
H	4.92029	-0.65828	1.66360
H	4.81283	1.08227	1.34583
H	4.68474	0.92938	-1.72243
H	3.59032	1.93500	-0.75259
H	2.92592	0.76846	-1.91660

[2-OPiv-α-Glc(H3)•quinuclidine]$^{\bullet+}$ (transition state for HAT) (PCM(acetonitrile)

Energy (Hartree/particle): -1325.93811216

Zero-point correction= 0.528083 (Hartree/Particle)
Thermal correction to Energy= 0.557670
Thermal correction to Enthalpy= 0.558614
Thermal correction to Gibbs Free Energy= 0.467202
Sum of electronic and zero-point Energies= -1325.410029
Sum of electronic and thermal Energies= -1325.380442
Sum of electronic and thermal Enthalpies= -1325.379498
Sum of electronic and thermal Free Energies= -1325.470910

Number of imaginary frequencies: 1, -1168.8932

Geometry:

C	-0.71174	-1.15007	-1.09666
C	-0.15996	-0.61172	0.23499
C	-1.12361	-0.69737	1.40309
O	-0.61972	0.10309	2.46995

C	-2.54821	-0.30322	1.01872
C	-2.96676	-0.98708	-0.28755
C	-4.31406	-0.49805	-0.80760
O	-5.31414	-0.84286	0.16786
O	-2.01931	-0.65029	-1.31691
O	-3.37084	-0.67354	2.12249
O	1.06848	-1.12541	0.65364
O	-0.63872	-2.54830	-1.02417
H	-2.99739	-2.07464	-0.13865
H	-0.13517	-0.77582	-1.94694
H	0.03864	0.67953	0.02327
H	-1.14824	-1.75925	1.70667
H	-2.58986	0.78548	0.86277
C	-0.79056	-3.19473	-2.30032
C	2.14126	-1.25571	-0.21269
H	-4.27134	0.58928	-0.95581
H	-4.52761	-0.97839	-1.77148
H	-4.28970	-0.64390	1.79214
H	-1.26521	0.04619	3.19025
H	-6.10844	-0.32490	-0.01898
O	2.16086	-0.72439	-1.29688
C	3.23896	-2.09942	0.42040
C	4.41112	-2.20861	-0.56316
C	2.67044	-3.50182	0.73100
C	3.70470	-1.41532	1.72584
H	1.39999	5.42164	-0.52841
C	1.09048	4.37948	-0.40919
H	-0.44305	4.89130	1.04965
H	3.06386	3.77100	0.28709
H	0.57066	4.19256	-2.51613
H	1.90413	4.09468	1.58391
H	-1.04378	4.72957	-0.60680
H	2.18505	3.59173	-2.11223
C	-0.34615	4.31441	0.12599
C	2.01719	3.66502	0.58446
C	1.15087	3.65457	-1.76172
C	-0.70531	2.82706	0.41504
C	1.64769	2.15417	0.61086
C	0.56285	2.22233	-1.59219
N	0.37630	1.97133	-0.13895
H	-0.77353	2.60974	1.48095
H	2.40306	1.54725	0.11279
H	-0.41552	2.12023	-2.06433
H	1.49299	1.77873	1.62271
H	-1.63843	2.53987	-0.07038
H	1.23084	1.45355	-1.97875

H	-0.65009	-4.26181	-2.12002
H	-0.02932	-2.83360	-3.00401
H	-1.78965	-3.01582	-2.71312
H	4.09128	-0.41018	1.52693
H	4.51155	-2.01072	2.16480
H	2.89163	-1.34199	2.45189
H	4.10103	-2.68543	-1.49761
H	5.20193	-2.81474	-0.11084
H	4.82277	-1.22304	-0.79963
H	2.30177	-3.98644	-0.17886
H	1.85325	-3.44999	1.45469
H	3.46962	-4.12066	1.15144

[2-OPiv-α-Glc(H4)•quinuclidine]$^{\bullet+}$ (transition state for HAT) (PCM(acetonitrile)

Energy (Hartree/particle): -1325.93610966

Zero-point correction= 0.528083 (Hartree/Particle)
Zero-point correction= 0.528444 (Hartree/Particle)
Thermal correction to Energy= 0.557937
Thermal correction to Enthalpy= 0.558881
Thermal correction to Gibbs Free Energy= 0.466893
Sum of electronic and zero-point Energies= -1325.407665
Sum of electronic and thermal Energies= -1325.378173
Sum of electronic and thermal Enthalpies= -1325.377229
Sum of electronic and thermal Free Energies= -1325.469217

Number of imaginary frequencies: 1, -1174.6756

Geometry:

C	0.30883	-1.93159	0.95587
C	0.75016	-1.42521	-0.42879
C	-0.40298	-0.80040	-1.18155
O	-0.02585	-0.38815	-2.44707
C	-1.65513	-1.66518	-1.16146
C	-1.96636	-2.17858	0.25290
C	-3.05358	-3.24744	0.24681
O	-4.25237	-2.64417	-0.27374
O	-0.80344	-2.80860	0.81029
O	-2.70900	-0.89214	-1.72549
O	1.81395	-0.46470	-0.32505
O	0.03531	-0.82469	1.76609
H	-2.28448	-1.34104	0.88447
H	1.09587	-2.55609	1.39591
H	1.11032	-2.29396	-0.99216

H	-0.74078	0.29494	-0.57215
H	-1.44152	-2.54468	-1.79681
C	-0.11365	-1.14528	3.15887
C	3.08765	-0.95827	-0.30546
H	-2.73403	-4.08868	-0.38210
H	-3.21171	-3.60959	1.27077
H	-3.52917	-1.39628	-1.55405
H	-0.83203	-0.28878	-2.98393
H	-4.86376	-3.35089	-0.52065
O	3.33015	-2.14401	-0.37826
C	4.11496	0.16629	-0.16656
C	3.93073	1.17746	-1.31713
C	5.52637	-0.43351	-0.22063
C	3.89383	0.86328	1.19391
H	-2.03916	4.95030	0.78807
C	-1.75813	3.93280	0.50124
H	0.36972	4.34866	0.71270
H	-2.70942	4.10899	-1.45105
H	-2.84669	3.04517	2.16435
H	-0.97196	4.44168	-1.45828
H	-0.36458	3.58838	2.13107
H	-3.75203	3.08351	0.64494
C	-0.35842	3.59993	1.03710
C	-1.74838	3.80203	-1.02901
C	-2.76122	2.92541	1.08076
C	0.06374	2.20405	0.49398
C	-1.47823	2.31333	-1.40095
C	-2.26536	1.48425	0.75981
N	-1.11020	1.58261	-0.16527
H	0.85054	2.27958	-0.25691
H	-2.36052	1.82333	-1.81419
H	-1.92080	0.96051	1.65123
H	-0.65193	2.21479	-2.10713
H	0.39268	1.52961	1.28268
H	-3.03222	0.88826	0.26467
H	-0.24290	-0.19531	3.68044
H	0.78597	-1.65225	3.53084
H	-0.98976	-1.78185	3.32472
H	4.05552	0.69124	-2.29054
H	4.68851	1.96269	-1.22690
H	2.94388	1.64478	-1.28790
H	2.90907	1.33203	1.24755
H	4.65514	1.63928	1.32487
H	3.98563	0.15017	2.02024
H	5.70317	-0.94514	-1.17144
H	5.68381	-1.15107	0.58972

H	6.26199	0.37072	-0.11872

[2-OPiv-α-Glc(H5)•quinuclidine]$^{\bullet+}$ (transition state for HAT) (PCM(acetonitrile)

Energy (Hartree/particle): -1325.93216460

Zero-point correction= 0.527796 (Hartree/Particle)
Thermal correction to Energy= 0.557601
Thermal correction to Enthalpy= 0.558545
Thermal correction to Gibbs Free Energy= 0.466376
Sum of electronic and zero-point Energies= -1325.404369
Sum of electronic and thermal Energies= -1325.374563
Sum of electronic and thermal Enthalpies= -1325.373619
Sum of electronic and thermal Free Energies= -1325.465788

Number of imaginary frequencies: 1, -1212.0009

Geometry:

C	-1.24303	1.53439	-0.90879
C	-1.12101	0.29800	-0.00951
C	-0.33115	0.57844	1.27088
O	-0.06917	-0.61643	1.99931
C	0.99164	1.25186	0.92394
C	0.80628	2.41526	-0.06175
C	2.11055	3.04332	-0.55862
O	2.94936	3.43685	0.54631
O	0.08053	1.99856	-1.21543
O	1.71745	1.56966	2.04665
O	-2.41181	-0.18403	0.40877
O	-2.02381	2.49100	-0.26127
H	0.23499	3.18623	0.48153
H	-1.66529	1.26648	-1.88530
H	-0.62825	-0.48072	-0.59260
H	-0.89996	1.28710	1.89348
H	1.67860	0.30765	0.32481
C	-2.41963	3.58370	-1.10637
C	-3.05714	-1.05173	-0.42597
H	2.68368	2.32220	-1.14309
H	1.87548	3.89826	-1.20005
H	2.36250	2.27096	1.77312
H	-0.92276	-0.98479	2.26982
H	2.67695	4.31890	0.83839
O	-2.58430	-1.42108	-1.47959
C	-4.42225	-1.44552	0.13987
C	-5.31564	-0.18430	0.14745

C	-4.25881	-1.98337	1.57626
C	-5.04669	-2.52311	-0.75620
H	4.75505	-3.50534	-0.82849
C	4.07878	-2.67816	-0.59483
H	4.25645	-3.00482	1.55112
H	2.43017	-3.58058	-1.69430
H	5.36079	-1.21815	-1.58011
H	2.40030	-3.89768	0.04544
H	5.33244	-1.75239	0.91770
H	4.03654	-1.81772	-2.58798
C	4.32898	-2.18035	0.83630
C	2.61925	-3.13916	-0.71184
C	4.30893	-1.51683	-1.57210
C	3.25940	-1.10533	1.18389
C	1.68855	-1.90796	-0.51346
C	3.43510	-0.30914	-1.12420
N	2.51286	-0.76043	-0.05233
H	2.52712	-1.46401	1.90759
H	1.21101	-1.60782	-1.44796
H	4.04444	0.49611	-0.71068
H	0.92401	-2.08850	0.24154
H	3.71024	-0.18957	1.56935
H	2.83127	0.08093	-1.94521
H	-3.07744	4.21410	-0.50569
H	-2.96324	3.21043	-1.98442
H	-1.54960	4.16393	-1.43436
H	-5.17786	-2.16093	-1.77979
H	-6.02853	-2.79797	-0.35757
H	-4.42301	-3.42182	-0.78774
H	-5.42533	0.22498	-0.86268
H	-4.90081	0.59188	0.79573
H	-6.31045	-0.45343	0.51778
H	-3.87134	-1.21498	2.24984
H	-3.58128	-2.84396	1.59954
H	-5.23555	-2.30828	1.94977

[2OPiv-*α*Glc•4-ClOBz]$^-$ (with 4-ClOBz bound at C-3 and C-4)

Energy (Hartree/particle): -1876.76253539

Zero-point correction= 0.430302 (Hartree/Particle)
Thermal correction to Energy= 0.461722
Thermal correction to Enthalpy= 0.462666
Thermal correction to Gibbs Free Energy= 0.361587
Sum of electronic and zero-point Energies= -1876.332233

Sum of electronic and thermal Energies= -1876.300813
Sum of electronic and thermal Enthalpies= -1876.299869
Sum of electronic and thermal Free Energies= -1876.400949

Number of imaginary frequencies: 0

Geometry:

C	3.74713	-1.04800	-0.10080
C	2.68084	-0.03678	-0.52810
C	1.26683	-0.41625	-0.10171
O	0.39423	0.47954	-0.74553
C	0.97042	-1.89321	-0.46799
C	2.13123	-2.80688	-0.04647
C	1.95483	-4.23446	-0.53669
O	2.79826	-5.18487	0.14020
O	3.39644	-2.33505	-0.55716
O	-0.17271	-2.38001	0.19290
O	2.96591	1.27401	0.02759
O	3.90979	-0.98355	1.30574
H	2.16072	-2.80897	1.05509
H	4.70534	-0.82625	-0.59330
H	2.72099	0.03755	-1.61888
H	1.19158	-0.33986	0.99561
H	0.85814	-1.93720	-1.56753
C	4.98300	-1.79228	1.76866
C	3.82121	2.07667	-0.62585
H	0.89599	-4.50071	-0.43219
H	2.23542	-4.28958	-1.59387
H	-1.00911	-1.94780	-0.16272
H	-0.50553	0.46451	-0.30077
H	2.52668	-5.17651	1.06787
O	4.45433	1.75776	-1.61367
C	3.86471	3.46404	0.03894
C	4.94590	4.31623	-0.63619
C	4.17515	3.31047	1.54055
C	2.47967	4.11999	-0.14564
Cl	-8.77260	0.94022	0.23835
C	-6.12882	1.54679	0.54105
C	-4.76817	1.25216	0.45859
C	-2.82788	-0.29697	-0.10289
C	-4.32293	0.01398	-0.01757
C	-7.05097	0.58188	0.13921
C	-5.27331	-0.93358	-0.41375
C	-6.63898	-0.66068	-0.33950
O	-2.51918	-1.42705	-0.57310
O	-2.04542	0.60497	0.30465

H	-6.47506	2.50793	0.91004
H	-4.02140	1.97985	0.76263
H	-4.91595	-1.89095	-0.78166
H	-7.37723	-1.39589	-0.64657
H	5.04805	-1.63973	2.85007
H	5.93551	-1.49053	1.30121
H	4.81093	-2.85554	1.55361
H	4.74920	4.42613	-1.70638
H	5.93533	3.86074	-0.52470
H	4.96707	5.31260	-0.17849
H	2.24493	4.23977	-1.20912
H	2.47837	5.11318	0.32062
H	1.69247	3.51219	0.30678
H	5.13952	2.81156	1.69263
H	3.40438	2.72312	2.04425
H	4.22558	4.30185	2.00770

[2OPiv-*α*Glc•4-ClOBz]$^-$ (with 4-ClOBz bound at C-4 and C-6)

Energy (Hartree/particle): -1876.76622074

Zero-point correction= 0.430967 (Hartree/Particle)
Thermal correction to Energy= 0.462109
Thermal correction to Enthalpy= 0.463053
Thermal correction to Gibbs Free Energy= 0.363361
Sum of electronic and zero-point Energies= -1876.335253
Sum of electronic and thermal Energies= -1876.304112
Sum of electronic and thermal Enthalpies= -1876.303168
Sum of electronic and thermal Free Energies= -1876.402860

Number of imaginary frequencies: 0

Geometry:

C	3.08261	1.22751	0.80846
C	2.91676	-0.20899	0.28241
C	1.93464	-0.25770	-0.86724
O	1.69372	-1.61294	-1.24150
C	0.61628	0.41464	-0.45827
C	0.88321	1.84934	0.01529
C	-0.34189	2.59832	0.56220
O	-1.10858	3.19782	-0.45394
O	1.83607	1.79303	1.12178
O	-0.23858	0.32058	-1.57380
O	4.18497	-0.74236	-0.18792
O	3.80965	1.96738	-0.16040

H	1.30773	2.43857	-0.80850
H	3.63715	1.22263	1.75820
H	2.56471	-0.83324	1.10843
H	2.35181	0.30134	-1.72028
H	0.19652	-0.14361	0.39732
C	4.13561	3.27833	0.28021
C	5.05970	-1.20485	0.72257
H	-0.94684	1.90888	1.17234
H	0.04478	3.38199	1.23438
H	-1.17903	0.16261	-1.23667
H	0.83588	-1.55836	-1.70138
H	-1.92231	2.64187	-0.58550
O	4.87233	-1.20519	1.92294
C	6.33064	-1.72578	0.02804
C	7.29802	-2.26928	1.08600
C	6.98685	-0.55700	-0.73558
C	5.94301	-2.84535	-0.95895
Cl	-9.05616	-1.68083	0.65802
C	-6.39050	-1.91762	0.12435
C	-5.12365	-1.39632	-0.13727
C	-3.51478	0.54873	-0.48502
C	-4.90752	-0.01506	-0.19702
C	-7.45120	-1.03650	0.32756
C	-5.99243	0.84366	0.01199
C	-7.26767	0.34432	0.27459
O	-3.41688	1.80137	-0.52771
O	-2.59765	-0.30782	-0.65025
H	-6.55884	-2.98963	0.17108
H	-4.27499	-2.05394	-0.30067
H	-5.81235	1.91365	-0.03654
H	-8.11021	1.01035	0.43669
H	4.75013	3.72957	-0.50426
H	4.71057	3.24765	1.22116
H	3.23660	3.88803	0.43870
H	5.45896	-3.67705	-0.43471
H	6.84514	-3.22966	-1.45089
H	5.25277	-2.47806	-1.72187
H	7.25272	0.25647	-0.05074
H	6.31210	-0.15531	-1.49513
H	7.90441	-0.90673	-1.22457
H	7.57728	-1.49133	1.80289
H	8.20749	-2.63792	0.59670
H	6.84594	-3.09200	1.64805

[2OPiv-αGlc•4-ClOBz]$^-$ (H1)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -2205.83005982

Zero-point correction= 0.617756 (Hartree/Particle)
Thermal correction to Energy= 0.657431
Thermal correction to Enthalpy= 0.658375
Thermal correction to Gibbs Free Energy= 0.538520
Sum of electronic and zero-point Energies= -2205.212304
Sum of electronic and thermal Energies= -2205.172629
Sum of electronic and thermal Enthalpies= -2205.171685
Sum of electronic and thermal Free Energies= -2205.291539

Number of imaginary frequencies: 1, -1389.4384

Geometry:

C	1.87935	-0.78159	0.47675
C	1.13111	0.01086	-0.57590
C	-0.15976	-0.74844	-1.03050
O	-0.69938	-0.06946	-2.10118
C	0.17809	-2.20758	-1.39146
C	0.97251	-2.87331	-0.26305
C	1.48548	-4.25481	-0.61451
O	2.03651	-4.95412	0.50875
O	2.16664	-2.05825	0.06530
O	-0.98496	-2.96381	-1.61640
O	0.70811	1.28222	-0.07468
O	1.30753	-0.64938	1.73108
H	0.33239	-2.92559	0.62867
H	3.17710	-0.25507	0.49256
H	1.77090	0.14651	-1.45057
H	-0.84391	-0.75908	-0.16758
H	0.79568	-2.19588	-2.30697
C	1.79544	-1.51574	2.76496
C	1.34072	2.39981	-0.49641
H	0.66115	-4.81080	-1.07715
H	2.29560	-4.16154	-1.34666
H	-1.79746	-2.43362	-1.35869
H	-1.68277	0.19207	-1.83260
H	1.29740	-5.31970	1.01237
O	2.38832	2.38395	-1.11692
C	0.55774	3.65141	-0.09928
C	1.39013	4.89597	-0.43172
C	0.23892	3.61284	1.40911
C	-0.75762	3.65438	-0.91305
Cl	-9.20895	0.47940	1.26612
C	-6.87876	1.23971	0.08198

C	-5.59591	0.99769	-0.40465
C	-3.62897	-0.53988	-0.85578
C	-5.02674	-0.27921	-0.33121
C	-7.59642	0.18649	0.64861
C	-5.77010	-1.31880	0.23961
C	-7.05391	-1.09590	0.73201
O	-3.18248	-1.71173	-0.76218
O	-3.01757	0.46962	-1.34063
H	-7.32276	2.22874	0.02469
H	-5.01730	1.79934	-0.85267
H	-5.32297	-2.30684	0.28847
H	-7.63246	-1.90114	1.17409
H	1.03453	-1.50669	3.54726
H	2.73658	-1.11993	3.17185
H	1.95807	-2.53283	2.39847
H	7.98413	0.78699	0.13829
C	6.91713	0.55945	0.21937
H	7.12666	-1.60222	0.20498
H	6.31210	1.55760	-1.61224
H	6.60389	1.57329	2.11478
H	6.80701	-0.12004	-1.84566
H	7.25487	-0.88835	1.81269
H	6.41774	2.62178	0.70767
C	6.71916	-0.82530	0.86016
C	6.26721	0.55514	-1.17430
C	6.21652	1.61672	1.09108
C	5.20296	-1.05146	1.08832
C	4.79282	0.09842	-1.03287
C	4.68997	1.34287	1.07234
N	4.43796	0.03251	0.41438
H	4.84643	-2.00209	0.68639
H	4.09472	0.79381	-1.50010
H	4.26298	1.29272	2.07797
H	4.62360	-0.90075	-1.44126
H	4.94076	-1.01524	2.14891
H	4.13956	2.09124	0.50049
H	-0.55203	3.65889	-1.98851
H	-1.32489	4.55947	-0.66851
H	-1.37390	2.78094	-0.68853
H	1.63217	4.93791	-1.49703
H	2.33099	4.90846	0.12921
H	0.82144	5.79386	-0.16811
H	-0.38017	2.75003	1.66336
H	-0.30313	4.52381	1.68494
H	1.15742	3.57181	2.00721

[2OPiv-αGlc•4-ClOBz]$^-$ (H3)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -2205.85659541

Zero-point correction= 0.617767 (Hartree/Particle)
Thermal correction to Energy= 0.656963
Thermal correction to Enthalpy= 0.657907
Thermal correction to Gibbs Free Energy= 0.540723
Sum of electronic and zero-point Energies= -2205.238828
Sum of electronic and thermal Energies= -2205.199632
Sum of electronic and thermal Enthalpies= -2205.198688
Sum of electronic and thermal Free Energies= -2205.315872

Number of imaginary frequencies: 1, -709.0604

Geometry:

C	1.87935	-0.78159	0.47675
C	1.13111	0.01086	-0.57590
C	-0.15976	-0.74844	-1.03050
O	-0.69938	-0.06946	-2.10118
C	0.17809	-2.20758	-1.39146
C	0.97251	-2.87331	-0.26305
C	1.48548	-4.25481	-0.61451
O	2.03651	-4.95412	0.50875
O	2.16664	-2.05825	0.06530
O	-0.98496	-2.96381	-1.61640
O	0.70811	1.28222	-0.07468
O	1.30753	-0.64938	1.73108
H	0.33239	-2.92559	0.62867
H	3.17710	-0.25507	0.49256
H	1.77090	0.14651	-1.45057
H	-0.84391	-0.75908	-0.16758
H	0.79568	-2.19588	-2.30697
C	1.79544	-1.51574	2.76496
C	1.34072	2.39981	-0.49641
H	0.66115	-4.81080	-1.07715
H	2.29560	-4.16154	-1.34666
H	-1.79746	-2.43362	-1.35869
H	-1.68277	0.19207	-1.83260
H	1.29740	-5.31970	1.01237
O	2.38832	2.38395	-1.11692
C	0.55774	3.65141	-0.09928
C	1.39013	4.89597	-0.43172
C	0.23892	3.61284	1.40911

C	-0.75762	3.65438	-0.91305
Cl	-9.20895	0.47940	1.26612
C	-6.87876	1.23971	0.08198
C	-5.59591	0.99769	-0.40465
C	-3.62897	-0.53988	-0.85578
C	-5.02674	-0.27921	-0.33121
C	-7.59642	0.18649	0.64861
C	-5.77010	-1.31880	0.23961
C	-7.05391	-1.09590	0.73201
O	-3.18248	-1.71173	-0.76218
O	-3.01757	0.46962	-1.34063
H	-7.32276	2.22874	0.02469
H	-5.01730	1.79934	-0.85267
H	-5.32297	-2.30684	0.28847
H	-7.63246	-1.90114	1.17409
H	1.03453	-1.50669	3.54726
H	2.73658	-1.11993	3.17185
H	1.95807	-2.53283	2.39847
H	7.98413	0.78699	0.13829
C	6.91713	0.55945	0.21937
H	7.12666	-1.60222	0.20498
H	6.31210	1.55760	-1.61224
H	6.60389	1.57329	2.11478
H	6.80701	-0.12004	-1.84566
H	7.25487	-0.88835	1.81269
H	6.41774	2.62178	0.70767
C	6.71916	-0.82530	0.86016
C	6.26721	0.55514	-1.17430
C	6.21652	1.61672	1.09108
C	5.20296	-1.05146	1.08832
C	4.79282	0.09842	-1.03287
C	4.68997	1.34287	1.07234
N	4.43796	0.03251	0.41438
H	4.84643	-2.00209	0.68639
H	4.09472	0.79381	-1.50010
H	4.26298	1.29272	2.07797
H	4.62360	-0.90075	-1.44126
H	4.94076	-1.01524	2.14891
H	4.13956	2.09124	0.50049
H	-0.55203	3.65889	-1.98851
H	-1.32489	4.55947	-0.66851
H	-1.37390	2.78094	-0.68853
H	1.63217	4.93791	-1.49703
H	2.33099	4.90846	0.12921
H	0.82144	5.79386	-0.16811
H	-0.38017	2.75003	1.66336

H	-0.30313	4.52381	1.68494
H	1.15742	3.57181	2.00721

[2OPiv-αGlc•4-ClOBz]$^-$ (H4)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -2205.85386592

Zero-point correction= 0.618953 (Hartree/Particle)
Thermal correction to Energy= 0.657726
Thermal correction to Enthalpy= 0.658670
Thermal correction to Gibbs Free Energy= 0.543321
Sum of electronic and zero-point Energies= -2205.234913
Sum of electronic and thermal Energies= -2205.196140
Sum of electronic and thermal Enthalpies= -2205.195195
Sum of electronic and thermal Free Energies= -2205.310545

Number of imaginary frequencies: 1, -924.1700

Geometry:

C	3.23480	1.47511	1.06115
C	3.08311	0.26969	0.13019
C	2.26232	0.61921	-1.09853
O	2.02918	-0.56725	-1.85115
C	0.93533	1.29102	-0.69667
C	1.18658	2.45891	0.27923
C	-0.00951	3.22902	0.84012
O	-0.59805	4.03360	-0.15182
O	1.93992	1.96227	1.40437
O	0.19157	1.47870	-1.79990
O	4.37579	-0.21855	-0.26920
O	4.04081	2.43504	0.43921
H	1.79757	3.18417	-0.28221
H	2.58839	-0.51956	0.69303
H	2.82285	1.34833	-1.70703
H	0.31979	0.37106	0.01323
C	4.40808	3.51745	1.29797
C	4.67195	-1.51724	0.02378
H	-0.73897	2.54049	1.28384
H	0.38564	3.85295	1.65841
H	-0.86977	1.67623	-1.68261
H	1.40830	-0.30428	-2.54896
H	-1.52402	3.69962	-0.26876
O	3.94507	-2.24532	0.66457
C	6.03012	-1.90682	-0.56829

C	5.93981	-1.79756	-2.10571
C	6.35966	-3.34898	-0.16290
C	7.11398	-0.94636	-0.03667
Cl	-7.75026	-1.92598	0.00404
C	-5.57770	-1.03500	-1.36623
C	-4.51815	-0.15602	-1.57824
C	-3.10088	1.83611	-0.88974
C	-4.31053	0.93923	-0.73092
C	-6.43575	-0.81412	-0.28774
C	-5.19946	1.15218	0.32952
C	-6.25954	0.27932	0.56168
O	-3.00026	2.83098	-0.14082
O	-2.23808	1.44273	-1.75245
H	-5.74203	-1.88297	-2.02377
H	-3.83568	-0.31236	-2.40752
H	-5.03613	2.00797	0.97728
H	-6.94338	0.43723	1.38967
H	-2.59128	-3.34890	1.84027
C	-1.94850	-2.54794	1.46185
H	-0.50389	-2.63402	3.08118
H	-3.46075	-0.98824	1.46856
H	-1.49507	-3.51617	-0.42856
H	-2.60467	-1.15730	3.00487
H	-0.13188	-3.71900	1.73967
H	-2.93871	-2.49411	-0.46995
C	-0.51554	-2.72494	1.98980
C	-2.48181	-1.18146	1.91719
C	-1.92183	-2.57179	-0.07364
C	0.39530	-1.63779	1.34946
C	-1.47342	-0.08669	1.47745
C	-1.07312	-1.37268	-0.57667
N	-0.44893	-0.68745	0.58623
H	0.93959	-1.06744	2.10563
H	-1.96489	0.72176	0.94039
H	-0.25604	-1.68840	-1.22695
H	-0.93825	0.34504	2.32666
H	1.11830	-2.07007	0.65631
H	-1.67180	-0.62951	-1.10495
H	5.08096	4.15508	0.72086
H	4.93148	3.14348	2.19080
H	3.53031	4.09525	1.61197
H	3.67313	1.16427	2.02224
H	6.41280	-3.45287	0.92492
H	7.32856	-3.63371	-0.58713
H	5.60083	-4.04600	-0.52945
H	7.17976	-0.99503	1.05625

H	6.90666	0.08661	-0.32628
H	8.08758	-1.23619	-0.44729
H	5.14743	-2.44327	-2.49883
H	6.89154	-2.11403	-2.54696
H	5.73328	-0.77113	-2.41825

[2OPiv-*α*Glc•4-ClOBz]$^{-}$ (H5)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -2205.84292215

Zero-point correction= 0.618918 (Hartree/Particle)
Thermal correction to Energy= 0.657978
Thermal correction to Enthalpy= 0.658922
Thermal correction to Gibbs Free Energy= 0.541072
Sum of electronic and zero-point Energies= -2205.224004
Sum of electronic and thermal Energies= -2205.184944
Sum of electronic and thermal Enthalpies= -2205.184000
Sum of electronic and thermal Free Energies= -2205.301850

Number of imaginary frequencies: 1, -1043.9537

Geometry:

C	3.23480	1.47511	1.06115
C	3.08311	0.26969	0.13019
C	2.26232	0.61921	-1.09853
O	2.02918	-0.56725	-1.85115
C	0.93533	1.29102	-0.69667
C	1.18658	2.45891	0.27923
C	-0.00951	3.22902	0.84012
O	-0.59805	4.03360	-0.15182
O	1.93992	1.96227	1.40437
O	0.19157	1.47870	-1.79990
O	4.37579	-0.21855	-0.26920
O	4.04081	2.43504	0.43921
H	1.79757	3.18417	-0.28221
H	2.58839	-0.51956	0.69303
H	2.82285	1.34833	-1.70703
H	0.31979	0.37106	0.01323
C	4.40808	3.51745	1.29797
C	4.67195	-1.51724	0.02378
H	-0.73897	2.54049	1.28384
H	0.38564	3.85295	1.65841
H	-0.86977	1.67623	-1.68261
H	1.40830	-0.30428	-2.54896

H	-1.52402	3.69962	-0.26876
O	3.94507	-2.24532	0.66457
C	6.03012	-1.90682	-0.56829
C	5.93981	-1.79756	-2.10571
C	6.35966	-3.34898	-0.16290
C	7.11398	-0.94636	-0.03667
Cl	-7.75026	-1.92598	0.00404
C	-5.57770	-1.03500	-1.36623
C	-4.51815	-0.15602	-1.57824
C	-3.10088	1.83611	-0.88974
C	-4.31053	0.93923	-0.73092
C	-6.43575	-0.81412	-0.28774
C	-5.19946	1.15218	0.32952
C	-6.25954	0.27932	0.56168
O	-3.00026	2.83098	-0.14082
O	-2.23808	1.44273	-1.75245
H	-5.74203	-1.88297	-2.02377
H	-3.83568	-0.31236	-2.40752
H	-5.03613	2.00797	0.97728
H	-6.94338	0.43723	1.38967
H	-2.59128	-3.34890	1.84027
C	-1.94850	-2.54794	1.46185
H	-0.50389	-2.63402	3.08118
H	-3.46075	-0.98824	1.46856
H	-1.49507	-3.51617	-0.42856
H	-2.60467	-1.15730	3.00487
H	-0.13188	-3.71900	1.73967
H	-2.93871	-2.49411	-0.46995
C	-0.51554	-2.72494	1.98980
C	-2.48181	-1.18146	1.91719
C	-1.92183	-2.57179	-0.07364
C	0.39530	-1.63779	1.34946
C	-1.47342	-0.08669	1.47745
C	-1.07312	-1.37268	-0.57667
N	-0.44893	-0.68745	0.58623
H	0.93959	-1.06744	2.10563
H	-1.96489	0.72176	0.94039
H	-0.25604	-1.68840	-1.22695
H	-0.93825	0.34504	2.32666
H	1.11830	-2.07007	0.65631
H	-1.67180	-0.62951	-1.10495
H	5.08096	4.15508	0.72086
H	4.93148	3.14348	2.19080
H	3.53031	4.09525	1.61197
H	3.67313	1.16427	2.02224
H	6.41280	-3.45287	0.92492

H	7.32856	-3.63371	-0.58713
H	5.60083	-4.04600	-0.52945
H	7.17976	-0.99503	1.05625
H	6.90666	0.08661	-0.32628
H	8.08758	-1.23619	-0.44729
H	5.14743	-2.44327	-2.49883
H	6.89154	-2.11403	-2.54696
H	5.73328	-0.77113	-2.41825

[2-OPiv-*β*-glu]

Energy (Hartree/particle): -996.889258613

Zero-point correction= 0.339043 (Hartree/Particle)
Thermal correction to Energy= 0.360783
Thermal correction to Enthalpy= 0.361727
Thermal correction to Gibbs Free Energy= 0.287535
Sum of electronic and zero-point Energies= -996.550216
Sum of electronic and thermal Energies= -996.528476
Sum of electronic and thermal Enthalpies= -996.527532
Sum of electronic and thermal Free Energies= -996.601724

Number of imaginary frequencies: 0

Geometry:

C	-0.63604	1.21838	-0.17913
C	-0.01548	-0.09795	0.29777
C	-0.85055	-1.27869	-0.17706
O	-0.31325	-2.47030	0.38207
C	-2.31586	-1.09212	0.21162
C	-2.82904	0.27851	-0.25625
C	-4.23999	0.59297	0.24831
O	-5.21296	-0.36945	-0.19076
O	-1.99667	1.31066	0.26846
O	-3.03041	-2.17760	-0.38135
O	1.29474	-0.20655	-0.28462
H	-2.81870	0.29773	-1.36326
H	0.06836	-0.08711	1.38767
H	-0.80111	-1.32112	-1.28001
H	-2.39139	-1.13086	1.31154
C	2.37236	-0.20793	0.55789
H	-4.24871	0.55144	1.34193
H	-4.52008	1.61001	-0.05748
H	-3.97346	-2.00761	-0.21710
H	-0.93514	-3.17794	0.15746

H	-5.35715	-0.23698	-1.13782
O	2.28786	-0.14354	1.76014
C	3.67600	-0.30061	-0.24561
C	4.86043	-0.31326	0.72883
C	3.77554	0.92447	-1.17814
C	3.66582	-1.59896	-1.07908
H	-0.63065	1.26093	-1.28814
O	0.08336	2.26905	0.35809
C	-0.20271	3.53729	-0.23448
H	0.49180	4.25049	0.21468
H	-1.23415	3.84852	-0.03010
H	-0.03934	3.50378	-1.32262
H	5.79692	-0.37902	0.16386
H	4.80259	-1.16790	1.40882
H	4.88227	0.59581	1.33664
H	4.61187	-1.68745	-1.62540
H	2.84461	-1.60251	-1.80005
H	3.55940	-2.47722	-0.43344
H	4.72551	0.89081	-1.72365
H	3.74408	1.85712	-0.60405
H	2.95826	0.93814	-1.90390

[2-OPiv-*β*-glu(H1)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.86434685

Zero-point correction= 0.527758 (Hartree/Particle)
Thermal correction to Energy= 0.557665
Thermal correction to Enthalpy= 0.558609
Thermal correction to Gibbs Free Energy= 0.464899
Sum of electronic and zero-point Energies= -1325.336589
Sum of electronic and thermal Energies= -1325.306682
Sum of electronic and thermal Enthalpies= -1325.305738
Sum of electronic and thermal Free Energies= -1325.399448

Number of imaginary frequencies: 1, -342.3873

Geometry:

C	-0.65755	-0.48863	1.11970
C	0.11262	-1.47424	0.21610
C	-0.65839	-1.74394	-1.06618
O	0.01693	-2.77520	-1.75701
C	-2.10633	-2.12517	-0.75529
C	-2.77273	-1.05723	0.12466
C	-4.14280	-1.46960	0.66081

O	-4.99257	-1.69558	-0.46614
O	-1.98491	-0.80540	1.31589
O	-2.75069	-2.23702	-2.01357
O	1.38958	-0.92380	-0.10420
H	-2.86189	-0.12713	-0.45491
H	0.25481	-2.40054	0.78632
H	-0.68630	-0.82556	-1.67696
H	-2.11006	-3.08638	-0.21341
C	2.49531	-1.58913	0.42283
H	-4.02427	-2.38024	1.26591
H	-4.53697	-0.67025	1.30428
H	-3.70006	-2.36916	-1.84764
H	-0.55539	-3.05027	-2.48968
H	-5.83166	-2.06142	-0.15720
O	2.38385	-2.47937	1.22340
C	3.79605	-1.08211	-0.19584
C	3.84143	0.45617	-0.23693
C	3.85479	-1.64777	-1.63498
C	4.97607	-1.61747	0.62819
H	-0.60303	0.63048	0.52045
O	0.01338	-0.30108	2.29264
C	-0.73391	0.09139	3.46226
H	0.01771	0.33758	4.21208
H	-1.36092	-0.73518	3.80699
H	-1.36555	0.96169	3.25053
H	0.20685	5.37905	-1.15020
C	0.02179	4.35890	-0.80242
H	-0.20787	3.59549	-2.83112
H	-1.73141	4.95306	0.34682
H	1.96196	4.21475	0.17564
H	-2.10173	4.34714	-1.26808
H	1.41178	3.39001	-2.16175
H	0.65067	4.70602	1.24900
C	0.34535	3.35389	-1.91898
C	-1.45348	4.20230	-0.39853
C	0.90747	4.04730	0.41374
C	-0.04394	1.92822	-1.43097
C	-1.65931	2.77428	0.19039
C	0.69153	2.55917	0.81348
N	-0.41468	1.99416	0.00320
H	-0.90877	1.53689	-1.97280
H	-1.87388	2.80033	1.26181
H	1.57244	1.94560	0.62551
H	-2.47199	2.24180	-0.30989
H	0.77613	1.21535	-1.52890
H	0.42231	2.45308	1.86630

H	4.79154	-1.33102	-2.10522
H	3.01832	-1.28810	-2.24068
H	3.82790	-2.74146	-1.62572
H	3.06195	0.86543	-0.88572
H	4.80987	0.77600	-0.63419
H	3.73499	0.88333	0.76682
H	5.91519	-1.29392	0.16860
H	4.96584	-2.70886	0.66886
H	4.94580	-1.24106	1.65542

[2-OPiv-β-glu(H2)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.85789593

Zero-point correction= 0.527206 (Hartree/Particle)
Thermal correction to Energy= 0.557055
Thermal correction to Enthalpy= 0.557999
Thermal correction to Gibbs Free Energy= 0.466231
Sum of electronic and zero-point Energies= -1325.330690
Sum of electronic and thermal Energies= -1325.300841
Sum of electronic and thermal Enthalpies= -1325.299897
Sum of electronic and thermal Free Energies= -1325.391665

Number of imaginary frequencies: 1, -1547.5565

Geometry:

C	-0.65755	-0.48863	1.11970
C	0.11262	-1.47424	0.21610
C	-0.65839	-1.74394	-1.06618
O	0.01693	-2.77520	-1.75701
C	-2.10633	-2.12517	-0.75529
C	-2.77273	-1.05723	0.12466
C	-4.14280	-1.46960	0.66081
O	-4.99257	-1.69558	-0.46614
O	-1.98491	-0.80540	1.31589
O	-2.75069	-2.23702	-2.01357
O	1.38958	-0.92380	-0.10420
H	-2.86189	-0.12713	-0.45491
H	0.25481	-2.40054	0.78632
H	-0.68630	-0.82556	-1.67696
H	-2.11006	-3.08638	-0.21341
C	2.49531	-1.58913	0.42283
H	-4.02427	-2.38024	1.26591
H	-4.53697	-0.67025	1.30428
H	-3.70006	-2.36916	-1.84764

H	-0.55539	-3.05027	-2.48968
H	-5.83166	-2.06142	-0.15720
O	2.38385	-2.47937	1.22340
C	3.79605	-1.08211	-0.19584
C	3.84143	0.45617	-0.23693
C	3.85479	-1.64777	-1.63498
C	4.97607	-1.61747	0.62819
H	-0.60303	0.63048	0.52045
O	0.01338	-0.30108	2.29264
C	-0.73391	0.09139	3.46226
H	0.01771	0.33758	4.21208
H	-1.36092	-0.73518	3.80699
H	-1.36555	0.96169	3.25053
H	0.20685	5.37905	-1.15020
C	0.02179	4.35890	-0.80242
H	-0.20787	3.59549	-2.83112
H	-1.73141	4.95306	0.34682
H	1.96196	4.21475	0.17564
H	-2.10173	4.34714	-1.26808
H	1.41178	3.39001	-2.16175
H	0.65067	4.70602	1.24900
C	0.34535	3.35389	-1.91898
C	-1.45348	4.20230	-0.39853
C	0.90747	4.04730	0.41374
C	-0.04394	1.92822	-1.43097
C	-1.65931	2.77428	0.19039
C	0.69153	2.55917	0.81348
N	-0.41468	1.99416	0.00320
H	-0.90877	1.53689	-1.97280
H	-1.87388	2.80033	1.26181
H	1.57244	1.94560	0.62551
H	-2.47199	2.24180	-0.30989
H	0.77613	1.21535	-1.52890
H	0.42231	2.45308	1.86630
H	4.79154	-1.33102	-2.10522
H	3.01832	-1.28810	-2.24068
H	3.82790	-2.74146	-1.62572
H	3.06195	0.86543	-0.88572
H	4.80987	0.77600	-0.63419
H	3.73499	0.88333	0.76682
H	5.91519	-1.29392	0.16860
H	4.96584	-2.70886	0.66886
H	4.94580	-1.24106	1.65542

[2-OPiv-β-glu(H3)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.86558253

Zero-point correction= 0.527663 (Hartree/Particle)
Thermal correction to Energy= 0.557319
Thermal correction to Enthalpy= 0.558263
Thermal correction to Gibbs Free Energy= 0.465776
Sum of electronic and zero-point Energies= -1325.337919
Sum of electronic and thermal Energies= -1325.308263
Sum of electronic and thermal Enthalpies= -1325.307319
Sum of electronic and thermal Free Energies= -1325.399806

Number of imaginary frequencies: 1, -921.1548

Geometry:

C	0.12066	-1.37116	1.03761
C	-0.17473	-0.71683	-0.32430
C	0.74374	-1.21286	-1.43230
O	0.66982	-0.29838	-2.52290
C	2.19573	-1.45626	-1.00261
C	2.26761	-2.12248	0.37867
C	3.68393	-2.19271	0.94151
O	4.47530	-2.94532	0.01651
O	1.51465	-1.32330	1.30593
O	2.75673	-2.23830	-2.04482
O	-1.48764	-0.90098	-0.74262
H	1.84639	-3.13913	0.31844
H	0.09144	0.58549	-0.14228
H	0.34465	-2.19540	-1.74154
H	2.71132	-0.48634	-0.92936
C	-2.59203	-0.24869	-0.18145
H	4.07329	-1.16947	1.05939
H	3.65732	-2.67222	1.92927
H	3.61814	-2.56356	-1.72876
H	1.16706	-0.69499	-3.25376
H	5.38282	-2.99610	0.34241
O	-2.49438	0.83624	0.32524
C	-3.85521	-1.07443	-0.37077
C	-3.68085	-2.40379	0.39785
C	-4.06569	-1.35679	-1.87505
C	-5.04713	-0.28955	0.19331
H	-0.18936	-2.43662	0.96308
O	-0.57473	-0.72491	2.03474
C	-0.64703	-1.45831	3.27227

H	-1.29959	-0.88013	3.92785
H	0.34467	-1.55949	3.72445
H	-1.08119	-2.45262	3.10149
H	1.33268	5.38982	0.20387
C	1.06128	4.33267	0.13282
H	0.76491	4.18384	2.28888
H	2.98656	3.80802	-0.74717
H	-0.63357	4.76789	-1.16749
H	2.88525	3.52217	0.99234
H	-0.72450	4.40662	1.36769
H	0.82003	4.25063	-2.02512
C	0.24881	3.90634	1.36499
C	2.32538	3.46456	0.05368
C	0.21795	4.08265	-1.12658
C	0.05550	2.36332	1.33136
C	1.89932	1.99559	-0.22814
C	-0.30669	2.61962	-1.09242
N	0.43079	1.88167	-0.02706
H	0.70409	1.84569	2.03987
H	2.10364	1.69478	-1.25656
H	-1.36324	2.56480	-0.83635
H	2.37962	1.29156	0.45340
H	-0.97298	2.06364	1.51693
H	-0.14003	2.08919	-2.03068
H	-4.16128	-0.42460	-2.44133
H	-4.99238	-1.92536	-2.00013
H	-3.24317	-1.93924	-2.29674
H	-5.17819	0.66240	-0.32863
H	-4.91679	-0.07762	1.25826
H	-5.95920	-0.88031	0.06697
H	-4.60291	-2.98693	0.31346
H	-3.49041	-2.22317	1.46116
H	-2.86182	-3.00064	-0.01345

[2-OPiv-*β*-glu(H4)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.86841195

Zero-point correction= 0.527620 (Hartree/Particle)
Thermal correction to Energy= 0.557439
Thermal correction to Enthalpy= 0.558383
Thermal correction to Gibbs Free Energy= 0.465399
Sum of electronic and zero-point Energies= -1325.340792
Sum of electronic and thermal Energies= -1325.310973

Sum of electronic and thermal Enthalpies= -1325.310029
Sum of electronic and thermal Free Energies= -1325.403013

Number of imaginary frequencies: 1, -1066.5780

Geometry:

C	0.83827	1.87223	0.80206
C	1.02575	0.67419	-0.13641
C	0.32942	0.90248	-1.47601
O	0.46455	-0.25574	-2.27415
C	-1.13311	1.27598	-1.21453
C	-1.25397	2.45189	-0.23652
C	-2.69531	2.80828	0.14493
O	-3.51928	2.97322	-1.02601
O	-0.58293	2.13357	0.96765
O	-1.84826	1.37378	-2.38233
O	2.41594	0.46191	-0.35104
H	-0.78968	3.33076	-0.72734
H	0.61265	-0.20804	0.35563
H	0.79648	1.76962	-1.97809
H	-1.57849	0.23036	-0.58129
C	2.89425	-0.80143	-0.05924
H	-3.13167	1.99268	0.72855
H	-2.70012	3.70714	0.76905
H	-2.63170	1.94703	-2.19478
H	0.22026	-0.02723	-3.18155
H	-3.58933	3.91226	-1.24272
O	2.17824	-1.69091	0.33720
C	4.39884	-0.88396	-0.29892
C	4.69513	-0.54018	-1.77439
C	4.87546	-2.30865	0.01507
C	5.10386	0.12714	0.63207
H	1.30614	2.78373	0.38325
O	1.35904	1.54239	2.02696
C	1.58342	2.65698	2.90787
H	2.06987	2.24878	3.79476
H	0.63684	3.13176	3.18846
H	2.24459	3.39324	2.43149
H	-3.73749	-3.90169	1.32685
C	-3.25200	-3.00987	0.92051
H	-1.43190	-4.09716	0.41983
H	-3.38173	-1.95555	2.82520
H	-4.80136	-2.73571	-0.58819
H	-1.82642	-2.73948	2.53638
H	-2.56059	-3.92221	-0.92604
H	-5.03423	-1.76516	0.86724

C	-2.13712	-3.41023	-0.05635
C	-2.63568	-2.18053	2.05739
C	-4.28020	-2.14719	0.17206
C	-1.37900	-2.12723	-0.50492
C	-2.08423	-0.85121	1.46516
C	-3.53211	-0.96398	-0.50869
N	-2.13216	-0.93797	-0.01692
H	-0.37188	-2.07872	-0.08852
H	-2.68505	0.00959	1.76401
H	-3.48935	-1.07021	-1.59487
H	-1.05248	-0.66146	1.76306
H	-1.29712	-2.04423	-1.58815
H	-3.99418	-0.00168	-0.27654
H	6.18697	0.04170	0.49757
H	4.87447	-0.07923	1.68294
H	4.80711	1.15429	0.40520
H	4.38102	-3.04305	-0.62709
H	4.66991	-2.57636	1.05517
H	5.95504	-2.37309	-0.15279
H	4.16698	-1.22059	-2.45085
H	5.76939	-0.64589	-1.95681
H	4.40374	0.48561	-2.01362

[3-*O*-Piv-*α*-glu]

Energy (Hartree/particle): -996.888776867

Zero-point correction= 0.339275 (Hartree/Particle)
Thermal correction to Energy= 0.360993
Thermal correction to Enthalpy= 0.361937
Thermal correction to Gibbs Free Energy= 0.288163
Sum of electronic and zero-point Energies= -996.549502
Sum of electronic and thermal Energies= -996.527784
Sum of electronic and thermal Enthalpies= -996.526840
Sum of electronic and thermal Free Energies= -996.600614

Number of imaginary frequencies: 0

Geometry:

C	-2.21718	-1.44769	-0.55237
C	-0.71465	-1.36870	-0.84328
C	-0.08723	-0.25504	-0.00881
O	1.29952	-0.14626	-0.41561
C	-0.78865	1.07004	-0.27890

C	-2.30703	0.89923	-0.07187
C	-3.10838	2.12287	-0.52143
O	-2.76379	3.31156	0.20889
O	-2.82182	-0.18838	-0.85529
O	-0.24218	2.05183	0.59153
O	-0.12548	-2.63687	-0.60413
O	-2.40624	-1.83186	0.77883
H	-2.48494	0.71242	0.99931
H	-2.70557	-2.15606	-1.23728
H	-0.62395	-1.09733	-1.90815
H	-0.12422	-0.49936	1.05478
H	-0.61574	1.34521	-1.33496
C	-3.74878	-2.20645	1.08231
H	0.82769	-2.53139	-0.73242
H	-2.88607	2.34258	-1.57059
H	-4.18136	1.90216	-0.43879
H	-0.79540	2.84479	0.48772
C	2.26153	-0.13942	0.56100
H	-3.08037	3.20433	1.11669
H	-3.75352	-2.52743	2.12639
H	-4.07466	-3.04038	0.44266
H	-4.44180	-1.36453	0.95198
C	3.64208	0.12942	-0.05260
C	3.94812	-0.94459	-1.11658
C	4.69836	0.08019	1.05846
C	3.62795	1.52758	-0.70541
O	2.03466	-0.32750	1.73090
H	2.90279	1.57679	-1.52157
H	4.62303	1.75106	-1.10664
H	3.37138	2.29857	0.02850
H	5.68757	0.27587	0.63011
H	4.71641	-0.89952	1.54479
H	4.49584	0.83060	1.82751
H	3.22644	-0.91046	-1.93712
H	3.93410	-1.94883	-0.67678
H	4.94827	-0.77379	-1.53039

[3-*O*-Piv-*α*-glu(H1)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.86528099

Zero-point correction= 0.527851 (Hartree/Particle)
Thermal correction to Energy= 0.557649
Thermal correction to Enthalpy= 0.558593

Thermal correction to Gibbs Free Energy= 0.464959
Sum of electronic and zero-point Energies= -1325.337430
Sum of electronic and thermal Energies= -1325.307632
Sum of electronic and thermal Enthalpies= -1325.306688
Sum of electronic and thermal Free Energies= -1325.400322

Number of imaginary frequencies: 1, -837.4736

Geometry:

C	-2.21718	-1.44769	-0.55237
C	-0.71465	-1.36870	-0.84328
C	-0.08723	-0.25504	-0.00881
O	1.29952	-0.14626	-0.41561
C	-0.78865	1.07004	-0.27890
C	-2.30703	0.89923	-0.07187
C	-3.10838	2.12287	-0.52143
O	-2.76379	3.31156	0.20889
O	-2.82182	-0.18838	-0.85529
O	-0.24218	2.05183	0.59153
O	-0.12548	-2.63687	-0.60413
O	-2.40624	-1.83186	0.77883
H	-2.48494	0.71242	0.99931
H	-2.70557	-2.15606	-1.23728
H	-0.62395	-1.09733	-1.90815
H	-0.12422	-0.49936	1.05478
H	-0.61574	1.34521	-1.33496
C	-3.74878	-2.20645	1.08231
H	0.82769	-2.53139	-0.73242
H	-2.88607	2.34258	-1.57059
H	-4.18136	1.90216	-0.43879
H	-0.79540	2.84479	0.48772
C	2.26153	-0.13942	0.56100
H	-3.08037	3.20433	1.11669
H	-3.75352	-2.52743	2.12639
H	-4.07466	-3.04038	0.44266
H	-4.44180	-1.36453	0.95198
C	3.64208	0.12942	-0.05260
C	3.94812	-0.94459	-1.11658
C	4.69836	0.08019	1.05846
C	3.62795	1.52758	-0.70541
O	2.03466	-0.32750	1.73090
H	2.90279	1.57679	-1.52157
H	4.62303	1.75106	-1.10664
H	3.37138	2.29857	0.02850
H	5.68757	0.27587	0.63011
H	4.71641	-0.89952	1.54479

H	4.49584	0.83060	1.82751
H	3.22644	-0.91046	-1.93712
H	3.93410	-1.94883	-0.67678
H	4.94827	-0.77379	-1.53039

[3-*O*-Piv-*α*-glu(H2)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.86047667

Zero-point correction= 0.527438 (Hartree/Particle)
Thermal correction to Energy= 0.557226
Thermal correction to Enthalpy= 0.558170
Thermal correction to Gibbs Free Energy= 0.465213
Sum of electronic and zero-point Energies= -1325.333039
Sum of electronic and thermal Energies= -1325.303251
Sum of electronic and thermal Enthalpies= -1325.302307
Sum of electronic and thermal Free Energies= -1325.395264

Number of imaginary frequencies: 1, -1072.5672

Geometry:

C	-0.82400	0.82851	0.52937
C	0.19350	-0.20299	0.00495
C	1.59258	0.40970	0.20094
O	2.60475	-0.41938	-0.39899
C	1.68324	1.77250	-0.48459
C	0.53031	2.69997	-0.04943
C	0.39221	3.93632	-0.94344
O	1.60399	4.69252	-0.99291
O	-0.77049	2.02623	-0.14565
O	2.92609	2.34333	-0.12119
O	0.00461	-1.45492	0.60557
O	-0.81519	0.88822	1.90181
H	0.70865	2.99552	0.99377
H	-1.94308	0.29381	0.19587
H	0.01335	-0.28691	-1.07711
H	1.80265	0.51329	1.27098
H	1.61856	1.61382	-1.57472
C	-1.56523	1.94931	2.52359
H	0.80355	-1.66171	1.14027
H	0.18582	3.61071	-1.96860
H	-0.45393	4.54568	-0.60159
H	2.95783	3.22395	-0.53459

C	3.12639	-1.42542	0.36260
H	1.62107	5.31171	-0.25070
H	-1.11644	2.92579	2.32201
H	-1.54051	1.73760	3.59253
H	-2.60005	1.94959	2.16278
C	4.41966	-1.97461	-0.22409
C	4.22958	-2.29076	-1.72218
C	4.82083	-3.24356	0.53966
C	5.50173	-0.88177	-0.04930
O	2.59780	-1.79280	1.39667
H	-6.23711	0.01082	0.07346
H	-4.27425	1.26638	0.33608
H	-3.86518	1.07445	-1.37567
C	-5.50765	-0.25102	-0.69896
H	-5.94163	0.01906	-1.66590
C	-4.18585	0.54202	-0.47706
H	-5.46495	-1.96722	1.50486
C	-5.19353	-1.75510	-0.64607
N	-3.11182	-0.41564	-0.12167
H	-6.09464	-2.33196	-0.87226
H	-3.69360	-0.48475	1.88393
C	-4.67915	-2.11187	0.75784
C	-3.46266	-1.19966	1.09061
H	-2.41128	-0.69541	-2.07500
C	-2.79839	-1.31470	-1.26199
C	-4.09541	-2.07110	-1.67346
H	-4.41223	-1.76194	-2.67413
H	-4.37969	-3.16348	0.79503
H	-2.57510	-1.76355	1.38144
H	-2.00942	-1.99111	-0.92905
H	-3.89722	-3.14609	-1.70811
H	5.15890	-2.71576	-2.11407
H	3.99266	-1.39280	-2.29750
H	3.43203	-3.02647	-1.87332
H	6.44908	-1.25527	-0.45104
H	5.65150	-0.64322	1.00884
H	5.23236	0.03497	-0.57999
H	5.76205	-3.62534	0.13241
H	4.06079	-4.02453	0.44005
H	4.96062	-3.04050	1.60436

[3-*O*-Piv-*α*-glu(H3)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.86366853

Zero-point correction= 0.528024 (Hartree/Particle)
Thermal correction to Energy= 0.557436
Thermal correction to Enthalpy= 0.558380
Thermal correction to Gibbs Free Energy= 0.467841
Sum of electronic and zero-point Energies= -1325.335645
Sum of electronic and thermal Energies= -1325.306233
Sum of electronic and thermal Enthalpies= -1325.305288
Sum of electronic and thermal Free Energies= -1325.395828

Number of imaginary frequencies: 1, -1482.0103

Geometry:

C	-1.90631	1.41999	-1.74823
C	-0.37108	1.32232	-1.66410
C	0.07753	0.96170	-0.24029
O	1.44170	1.17460	0.07806
C	-0.69537	1.66011	0.87476
C	-2.19895	1.79712	0.57581
C	-2.87417	2.80188	1.50470
O	-2.71186	2.32013	2.84910
O	-2.40909	2.29187	-0.74718
O	-0.45324	0.95483	2.08659
O	0.05566	0.47926	-2.69776
O	-2.44993	0.13039	-1.66683
H	-2.67736	0.81807	0.70153
H	-2.17706	1.89589	-2.69979
H	0.00023	2.35656	-1.81333
H	-0.13112	-0.34081	-0.09625
H	-0.27499	2.68113	0.93446
C	-3.81831	0.05684	-2.09904
H	0.97616	0.21137	-2.51200
H	-2.40604	3.78825	1.37709
H	-3.93594	2.87875	1.23742
H	-1.03808	1.36672	2.75144
C	2.51139	0.59040	-0.54939
H	-3.04417	2.98704	3.46355
H	-4.11677	-0.98992	-2.01041
H	-3.90426	0.37238	-3.14655
H	-4.46671	0.68129	-1.47351
C	3.82229	1.02917	0.08862
C	3.91791	2.57056	0.02644
C	4.98973	0.39450	-0.67861
C	3.83412	0.56198	1.56292
O	2.38985	-0.18779	-1.47408

H	-2.12121	-3.57360	2.03940
H	-1.55122	-1.31192	1.75253
H	-2.32480	-1.41447	0.15714
C	-1.79805	-3.38721	1.01107
H	-2.58982	-3.74478	0.34562
C	-1.57640	-1.86108	0.81123
H	0.36514	-3.50415	2.61427
C	-0.48198	-4.11726	0.70906
N	-0.25420	-1.65662	0.16117
H	-0.57710	-5.18087	0.94596
H	0.84970	-1.30527	1.90478
C	0.63608	-3.48712	1.55421
C	0.85520	-2.02048	1.08146
H	-1.01070	-2.11242	-1.72870
C	-0.15996	-2.41313	-1.11745
C	-0.15067	-3.93336	-0.77930
H	-0.88521	-4.44816	-1.40524
H	1.56980	-4.04577	1.44285
H	1.78300	-1.91358	0.51838
H	0.75373	-2.09923	-1.61915
H	0.83137	-4.36005	-1.00535
H	4.99734	0.70923	-1.72579
H	4.93865	-0.69763	-0.65360
H	5.93185	0.70588	-0.21818
H	3.86475	2.92908	-1.00696
H	4.88204	2.87980	0.44126
H	3.12459	3.04747	0.60728
H	3.78328	-0.53024	1.63145
H	3.00412	0.99159	2.12902
H	4.77343	0.88081	2.02476

[3-*O*-Piv-*α*-glu(H4)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.86349319

Zero-point correction= 0.527476 (Hartree/Particle)
Thermal correction to Energy= 0.557287
Thermal correction to Enthalpy= 0.558232
Thermal correction to Gibbs Free Energy= 0.465298
Sum of electronic and zero-point Energies= -1325.336018
Sum of electronic and thermal Energies= -1325.306206
Sum of electronic and thermal Enthalpies= -1325.305262
Sum of electronic and thermal Free Energies= -1325.398195

Number of imaginary frequencies: 1, -869.1794

Geometry:

C	-0.05674	-2.79909	-1.26436
C	0.67090	-1.45458	-1.42936
C	1.07553	-0.91322	-0.05582
O	1.66895	0.38513	-0.22404
C	-0.13281	-0.84553	0.86694
C	-0.87588	-2.19222	0.89938
C	-2.17219	-2.18517	1.71258
O	-1.95388	-1.65070	3.03374
O	-1.21893	-2.59361	-0.41965
O	0.16403	-0.28938	2.08542
O	1.77738	-1.64120	-2.28187
O	0.82081	-3.72875	-0.73802
H	-0.17721	-2.91810	1.35042
H	-0.48217	-3.12866	-2.22122
H	-0.05835	-0.76259	-1.88390
H	1.82129	-1.57522	0.40362
H	-0.95029	-0.01879	0.29376
C	0.41053	-5.09613	-0.90272
H	2.24387	-0.79672	-2.35829
H	-2.91611	-1.54288	1.23328
H	-2.58359	-3.19861	1.75239
H	-0.51503	-0.61921	2.72406
C	2.89099	0.58609	0.41078
H	-1.79934	-2.37705	3.65247
H	1.20457	-5.70690	-0.47091
H	0.30124	-5.33455	-1.96849
H	-0.53517	-5.29189	-0.38260
C	3.39092	2.01926	0.22740
C	3.15472	2.52089	-1.20887
C	4.89074	2.06192	0.55863
C	2.61299	2.89846	1.23410
O	3.43654	-0.28059	1.04195
H	-4.28475	2.72600	1.15468
H	-3.07594	0.75511	1.50378
H	-1.65244	1.76867	1.78591
C	-3.28835	2.80520	0.71066
H	-2.81725	3.70424	1.11935
C	-2.45390	1.54527	1.07801
H	-4.85613	1.30998	-0.90252
C	-3.37731	2.90051	-0.82069
N	-1.82698	1.00508	-0.15480
H	-4.04726	3.71546	-1.10805
H	-3.29016	-0.42805	-0.62831

C	-3.90165	1.56524	-1.37327
C	-2.84741	0.45827	-1.08442
H	-0.31790	2.44180	-0.08600
C	-1.01591	2.05173	-0.82722
C	-1.96858	3.14856	-1.38125
H	-1.60085	4.13556	-1.08612
H	-4.07529	1.63229	-2.45105
H	-2.32372	0.14150	-1.98880
H	-0.43317	1.57223	-1.61475
H	-1.98554	3.11795	-2.47507
H	3.66158	1.88166	-1.94023
H	3.56721	3.52981	-1.30907
H	2.09185	2.56098	-1.46006
H	5.46432	1.43211	-0.12805
H	5.08214	1.71350	1.57591
H	5.25233	3.09079	0.46635
H	1.53833	2.89091	1.02688
H	2.96962	3.93091	1.16073
H	2.76940	2.55216	2.26019

[3-*O*-Piv-*α*-glu(H5)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1325.86556838

Zero-point correction= 0.527904 (Hartree/Particle)
Thermal correction to Energy= 0.557785
Thermal correction to Enthalpy= 0.558730
Thermal correction to Gibbs Free Energy= 0.466190
Sum of electronic and zero-point Energies= -1325.337665
Sum of electronic and thermal Energies= -1325.307783
Sum of electronic and thermal Enthalpies= -1325.306839
Sum of electronic and thermal Free Energies= -1325.399378

Number of imaginary frequencies: 1, -1191.1980

Geometry:

C	-0.23910	2.71709	-0.21958
C	1.21236	2.24443	-0.06916
C	1.21894	0.74227	0.19171
O	2.57995	0.30399	0.27729
C	0.49449	0.45194	1.49843
C	-0.89915	1.12231	1.49980

C	-1.60192	1.17781	2.85159
O	-1.58615	-0.12240	3.44834
O	-0.98916	2.39535	0.96993
O	0.40250	-0.94603	1.68125
O	1.88478	2.59559	-1.26167
O	-0.88138	2.12937	-1.31425
H	-1.59038	0.28643	0.76793
H	-0.28401	3.81028	-0.27881
H	1.64795	2.76936	0.79796
H	0.73940	0.22238	-0.63771
H	1.06945	0.91341	2.32364
C	-1.06488	2.99405	-2.45254
H	2.79533	2.27479	-1.19105
H	-1.06357	1.90650	3.47731
H	-2.62919	1.54459	2.71394
H	-0.02901	-1.08623	2.54054
C	2.90410	-0.85096	-0.41822
H	-1.81261	-0.03574	4.38352
H	-1.64213	2.41833	-3.17900
H	-0.09991	3.27261	-2.88487
H	-1.62750	3.89228	-2.16659
C	4.37241	-1.21519	-0.20998
C	4.69917	-2.45761	-1.04910
C	4.59774	-1.51391	1.28863
C	5.25944	-0.03120	-0.65177
O	2.10059	-1.45038	-1.08912
H	-3.67467	-3.58235	0.18231
H	-1.96333	-2.28939	1.13685
H	-3.24147	-1.27236	1.81278
C	-3.90953	-2.51686	0.10546
H	-4.90171	-2.36627	0.54255
C	-2.84482	-1.69691	0.88975
H	-2.05607	-3.14087	-1.75771
C	-3.90032	-2.06111	-1.36212
N	-2.38345	-0.57980	0.02518
H	-4.55648	-2.70047	-1.95949
H	-0.67933	-1.54825	-0.71898
C	-2.46088	-2.13339	-1.89285
C	-1.58938	-1.10112	-1.11982
H	-4.10188	0.52685	0.44816
C	-3.52969	0.24257	-0.43883
C	-4.37937	-0.60249	-1.43007
H	-5.43726	-0.52532	-1.16268
H	-2.42897	-1.90740	-2.96258
H	-1.31839	-0.24414	-1.73637
H	-3.12237	1.14449	-0.89641

H	-4.26789	-0.21512	-2.44763
H	4.53738	-2.27162	-2.11466
H	4.07701	-3.30779	-0.75672
H	5.74908	-2.72836	-0.90012
H	3.95079	-2.32983	1.62747
H	4.40214	-0.63359	1.90636
H	5.63815	-1.81903	1.44006
H	5.08091	0.22541	-1.70232
H	6.31234	-0.31341	-0.55200
H	5.08574	0.85420	-0.03396

[2-*O*-Piv-*β*-xylo]

Energy (Hartree/particle): -882.370128376

Zero-point correction= 0.306885 (Hartree/Particle)
Thermal correction to Energy= 0.326225
Thermal correction to Enthalpy= 0.327169
Thermal correction to Gibbs Free Energy= 0.258062
Sum of electronic and zero-point Energies= -882.063243
Sum of electronic and thermal Energies= -882.043903
Sum of electronic and thermal Enthalpies= -882.042959
Sum of electronic and thermal Free Energies= -882.112066

Number of imaginary frequencies: 0

Geometry:

O	-4.20641	-1.73565	0.11348
C	-3.61725	-0.65629	-0.64518
C	-2.11595	-0.92291	-0.70458
O	-1.48093	0.09884	-1.49963
C	-1.40806	-0.91498	0.68709
H	-0.91955	-1.88333	0.86066
C	-0.33849	0.17215	0.53900
C	-0.82178	1.00868	-0.66052
H	-4.01491	-0.63413	-1.66833
H	-3.79866	0.31280	-0.16652
H	-1.94083	-1.87597	-1.21670
O	0.90899	-0.48191	0.20709
O	-2.24665	-0.57442	1.78232
H	-5.15867	-1.58340	0.16071
H	-3.04877	-1.11650	1.69022
H	0.00756	1.45335	-1.22930
O	-1.73622	2.01583	-0.26266
H	-0.22169	0.75589	1.45177

C	-1.09929	3.19402	0.22698
H	-1.89617	3.90873	0.44556
H	-0.42255	3.61933	-0.53036
H	-0.52001	3.00275	1.14017
C	2.03981	0.26519	0.34071
C	3.27610	-0.52097	-0.11248
C	3.34838	-1.86502	0.63902
C	4.53130	0.31173	0.17747
C	3.15057	-0.77432	-1.63067
O	2.03573	1.40532	0.75012
H	3.08307	0.17044	-2.18156
H	2.26591	-1.37376	-1.86124
H	4.03804	-1.31085	-1.98456
H	4.49851	1.27210	-0.34419
H	5.41821	-0.23775	-0.15643
H	4.63165	0.51590	1.24763
H	4.25141	-2.40442	0.33187
H	2.47977	-2.49138	0.42172
H	3.39964	-1.70749	1.72206

[2-*O*-Piv-*β*-xylo(H2)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1211.34285612

Zero-point correction= 0.495186 (Hartree/Particle)
Thermal correction to Energy= 0.522616
Thermal correction to Enthalpy= 0.523560
Thermal correction to Gibbs Free Energy= 0.435686
Sum of electronic and zero-point Energies= -1210.847670
Sum of electronic and thermal Energies= -1210.820240
Sum of electronic and thermal Enthalpies= -1210.819296
Sum of electronic and thermal Free Energies= -1210.907170

Number of imaginary frequencies: 1, -1373.6248

Geometry:

O	-2.70112	3.52939	-1.58035
C	-2.14395	3.32429	-0.26978
C	-0.65311	3.07641	-0.49188
O	0.06441	2.98750	0.75707
C	-0.31772	1.76469	-1.25850
H	0.46049	1.97149	-2.00492
C	0.31441	0.87285	-0.17547
C	0.18096	1.63358	1.15480
H	-2.26231	4.21581	0.35895
H	-2.60986	2.46693	0.23267

H	-0.23717	3.93919	-1.02019
O	1.59458	0.50025	-0.57037
O	-1.42324	1.12271	-1.87628
H	-3.62184	3.80958	-1.49719
H	-2.02551	1.82766	-2.18440
H	1.06408	1.57398	1.79805
O	-0.95646	1.14119	1.81859
H	-0.41061	-0.21749	-0.04988
C	-1.13815	1.70989	3.12754
H	-2.02496	1.23453	3.55071
H	-1.29213	2.79255	3.06727
H	-0.26704	1.49663	3.76122
C	2.42060	-0.23001	0.29741
C	3.81834	-0.37337	-0.28269
C	3.72070	-1.15816	-1.61194
C	4.69133	-1.13960	0.72019
C	4.40667	1.03187	-0.54042
O	1.99775	-0.67213	1.33395
H	-1.88746	-3.68140	-2.23926
H	-3.81683	-2.37278	-1.18508
H	-2.76679	-0.31471	-0.68678
H	-1.16237	-1.44322	-2.11547
C	-3.34098	-2.40003	-0.19972
C	-1.37863	-3.49255	-1.28966
C	-2.55176	-1.08401	0.05268
C	-0.76204	-2.06465	-1.31360
C	-2.36320	-3.58100	-0.11243
H	-0.59117	-4.24491	-1.18198
H	-4.13435	-2.49410	0.54755
H	-2.90751	-4.52899	-0.14758
N	-1.09795	-1.38944	-0.03322
H	-2.72593	-0.67602	1.04862
H	0.32662	-2.08905	-1.40282
C	-1.57767	-3.46592	1.20280
C	-0.66644	-2.20623	1.13127
H	-0.95371	-4.34936	1.36647
H	-2.26734	-3.38880	2.04907
H	-0.73650	-1.57872	2.02002
H	0.38042	-2.46475	0.98010
H	5.42886	0.92312	-0.91552
H	4.44701	1.61889	0.38317
H	3.82529	1.58443	-1.28269
H	5.69823	-1.25113	0.30755
H	4.28831	-2.13615	0.92139
H	4.76572	-0.60597	1.67178
H	4.72815	-1.29128	-2.01775

H	3.11928	-0.62580	-2.35314
H	3.29095	-2.15359	-1.45186

[2-*O*-Piv-*β*-xylo(H3)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1211.34758322

Zero-point correction= 0.496082 (Hartree/Particle)
Thermal correction to Energy= 0.523065
Thermal correction to Enthalpy= 0.524009
Thermal correction to Gibbs Free Energy= 0.437036
Sum of electronic and zero-point Energies= -1210.851501
Sum of electronic and thermal Energies= -1210.824518
Sum of electronic and thermal Enthalpies= -1210.823574
Sum of electronic and thermal Free Energies= -1210.910547

Number of imaginary frequencies: 1, -394.3320

Geometry:

O	-0.81239	-4.15117	0.04834
C	0.43756	-3.79023	0.68607
C	0.35945	-2.27844	0.93254
O	1.55921	-1.78805	1.52111
C	0.17632	-1.45304	-0.37031
H	-0.82192	-0.73566	-0.17941
C	1.39705	-0.54634	-0.47185
C	2.38483	-1.22733	0.51458
H	0.55133	-4.30476	1.64638
H	1.29300	-4.02114	0.04269
H	-0.45248	-2.08494	1.64431
O	1.06276	0.78080	-0.00320
O	-0.07430	-2.14079	-1.53551
H	-0.82166	-5.10554	-0.10751
H	-0.51116	-2.99278	-1.28482
H	3.04658	-0.50005	1.00113
O	3.11053	-2.24612	-0.11100
H	1.78359	-0.50147	-1.48984
C	4.34710	-1.80882	-0.70297
H	4.81274	-2.70082	-1.12384
H	5.00324	-1.37343	0.06211
H	4.17390	-1.06881	-1.49288
C	2.00910	1.73751	-0.31155
C	1.67484	3.13399	0.21786
C	1.26812	3.98082	-1.01032
C	2.96378	3.70993	0.83981

C	0.54910	3.14652	1.26040
O	2.99028	1.46918	-0.96291
H	-3.48921	2.69094	-1.11815
H	-3.37604	2.34595	1.40288
H	-1.42298	1.02800	1.53303
H	-1.37248	1.72448	-0.80193
C	-3.61413	1.28269	1.29888
C	-3.55175	1.60059	-1.17997
C	-2.30394	0.44055	1.27297
C	-2.11962	0.99258	-1.10852
C	-4.37676	1.03411	-0.01308
H	-4.02339	1.35135	-2.13531
H	-4.21840	0.99418	2.16357
H	-5.35664	1.51835	0.02448
N	-2.11730	-0.08759	-0.09632
H	-2.36176	-0.41728	1.94758
H	-1.80526	0.55778	-2.06063
C	-4.54629	-0.48120	-0.21444
C	-3.13425	-1.11282	-0.41539
H	-5.16882	-0.69064	-1.08878
H	-5.03822	-0.92741	0.65522
H	-2.96996	-1.97349	0.23786
H	-2.96872	-1.42657	-1.44864
H	2.07102	4.00269	-1.75154
H	1.06081	5.00664	-0.68931
H	0.36457	3.58474	-1.48860
H	3.78341	3.70166	0.11855
H	3.26892	3.13265	1.71932
H	2.78275	4.74184	1.15604
H	-0.41137	2.85947	0.82266
H	0.43843	4.16136	1.65495
H	0.76536	2.47858	2.09979

[2-*O*-Piv-*β*-xylo(H4)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1211.34843325

Zero-point correction= 0.495176 (Hartree/Particle)
Thermal correction to Energy= 0.522836
Thermal correction to Enthalpy= 0.523780
Thermal correction to Gibbs Free Energy= 0.435130
Sum of electronic and zero-point Energies= -1210.853257
Sum of electronic and thermal Energies= -1210.825598
Sum of electronic and thermal Enthalpies= -1210.824653
Sum of electronic and thermal Free Energies= -1210.913303

Number of imaginary frequencies: 1, -309.5824

Geometry:

O	-0.81239	-4.15117	0.04834
C	0.43756	-3.79023	0.68607
C	0.35945	-2.27844	0.93254
O	1.55921	-1.78805	1.52111
C	0.17632	-1.45304	-0.37031
H	-0.82192	-0.73566	-0.17941
C	1.39705	-0.54634	-0.47185
C	2.38483	-1.22733	0.51458
H	0.55133	-4.30476	1.64638
H	1.29300	-4.02114	0.04269
H	-0.45248	-2.08494	1.64431
O	1.06276	0.78080	-0.00320
O	-0.07430	-2.14079	-1.53551
H	-0.82166	-5.10554	-0.10751
H	-0.51116	-2.99278	-1.28482
H	3.04658	-0.50005	1.00113
O	3.11053	-2.24612	-0.11100
H	1.78359	-0.50147	-1.48984
C	4.34710	-1.80882	-0.70297
H	4.81274	-2.70082	-1.12384
H	5.00324	-1.37343	0.06211
H	4.17390	-1.06881	-1.49288
C	2.00910	1.73751	-0.31155
C	1.67484	3.13399	0.21786
C	1.26812	3.98082	-1.01032
C	2.96378	3.70993	0.83981
C	0.54910	3.14652	1.26040
O	2.99028	1.46918	-0.96291
H	-3.48921	2.69094	-1.11815
H	-3.37604	2.34595	1.40288
H	-1.42298	1.02800	1.53303
H	-1.37248	1.72448	-0.80193
C	-3.61413	1.28269	1.29888
C	-3.55175	1.60059	-1.17997
C	-2.30394	0.44055	1.27297
C	-2.11962	0.99258	-1.10852
C	-4.37676	1.03411	-0.01308
H	-4.02339	1.35135	-2.13531
H	-4.21840	0.99418	2.16357
H	-5.35664	1.51835	0.02448
N	-2.11730	-0.08759	-0.09632
H	-2.36176	-0.41728	1.94758

H	-1.80526	0.55778	-2.06063
C	-4.54629	-0.48120	-0.21444
C	-3.13425	-1.11282	-0.41539
H	-5.16882	-0.69064	-1.08878
H	-5.03822	-0.92741	0.65522
H	-2.96996	-1.97349	0.23786
H	-2.96872	-1.42657	-1.44864
H	2.07102	4.00269	-1.75154
H	1.06081	5.00664	-0.68931
H	0.36457	3.58474	-1.48860
H	3.78341	3.70166	0.11855
H	3.26892	3.13265	1.71932
H	2.78275	4.74184	1.15604
H	-0.41137	2.85947	0.82266
H	0.43843	4.16136	1.65495
H	0.76536	2.47858	2.09979

[2-*O*-Piv-*β*-xylo(H5)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1211.34225793

Zero-point correction= 0.494849 (Hartree/Particle)
Thermal correction to Energy= 0.522637
Thermal correction to Enthalpy= 0.523582
Thermal correction to Gibbs Free Energy= 0.432759
Sum of electronic and zero-point Energies= -1210.847409
Sum of electronic and thermal Energies= -1210.819620
Sum of electronic and thermal Enthalpies= -1210.818676
Sum of electronic and thermal Free Energies= -1210.909499

Number of imaginary frequencies: 1, -809.0701

Geometry:

O	-2.10751	-2.89671	-1.60742
C	-1.38743	-3.15616	-0.39854
C	-0.47366	-1.96425	-0.18129
O	0.19770	-2.03130	1.01683
C	0.50835	-1.58799	-1.31512
H	0.07712	-0.84933	-1.99822
C	1.68420	-0.97822	-0.54138
C	1.62325	-1.61109	0.85495
H	-2.05929	-3.27422	0.46365
H	-0.76522	-4.05906	-0.47825
H	-1.26243	-0.99534	-0.09699
O	1.47539	0.44745	-0.48590

O	0.96484	-2.73169	-2.01288
H	-2.64443	-3.67212	-1.81816
H	0.26861	-2.99762	-2.63148
H	1.80488	-0.90450	1.67262
O	2.42816	-2.71325	0.90537
H	2.63833	-1.20685	-1.01660
C	2.68203	-3.22582	2.22776
H	3.41637	-4.02244	2.10506
H	1.76521	-3.62967	2.67113
H	3.09446	-2.43445	2.86677
C	2.59585	1.17596	-0.10446
C	2.40376	2.67983	-0.30531
C	3.61988	3.41036	0.28246
C	1.11793	3.16787	0.38819
C	2.31227	2.94547	-1.82521
O	3.59138	0.62890	0.29561
H	-4.29778	2.95984	0.80149
C	-3.65383	2.09923	0.59907
H	-3.70997	2.38451	-1.55815
H	-5.01615	0.68103	1.53158
H	-1.97335	2.89510	1.72931
H	-5.25071	0.86336	-0.20759
H	-2.34079	3.16672	-0.76565
H	-3.04104	1.85281	2.67223
C	-2.96602	2.26877	-0.76470
C	-4.49301	0.81120	0.57981
C	-2.57707	1.98355	1.69026
C	-2.09062	1.00967	-1.03856
C	-3.54464	-0.40097	0.32554
C	-1.66664	0.76265	1.36260
N	-2.16929	0.10967	0.13432
H	-2.44019	0.44376	-1.90522
H	-3.52538	-1.08668	1.17631
H	-0.63313	1.05592	1.17620
H	-3.81460	-0.96522	-0.56900
H	-1.03964	1.26281	-1.18855
H	-1.67424	0.01463	2.15892
H	2.21931	4.02265	-1.99733
H	1.44481	2.44779	-2.26903
H	3.21366	2.59752	-2.33953
H	1.11947	2.92011	1.45573
H	0.22530	2.74000	-0.07428
H	1.05283	4.25677	0.29825
H	3.70946	3.23066	1.35782
H	3.50915	4.48679	0.11879
H	4.54684	3.07958	-0.19149

[2-*O*-Piv-*α*-xylo]

Energy (Hartree/particle): -882.367488820

Zero-point correction= 0.306327 (Hartree/Particle)
Thermal correction to Energy= 0.325954
Thermal correction to Enthalpy= 0.326898
Thermal correction to Gibbs Free Energy= 0.256532
Sum of electronic and zero-point Energies= -882.061162
Sum of electronic and thermal Energies= -882.041535
Sum of electronic and thermal Enthalpies= -882.040591
Sum of electronic and thermal Free Energies= -882.110957

Number of imaginary frequencies: 0

Geometry:

O	3.40709	-2.39998	0.72321
C	3.41073	-0.97255	0.91174
C	1.97957	-0.48389	0.72642
O	2.00123	0.95161	0.66923
C	1.31385	-0.97023	-0.58244
H	0.73414	-1.88679	-0.42226
C	0.39507	0.20797	-0.91011
C	1.22650	1.41221	-0.45702
H	3.76743	-0.70593	1.91589
H	4.04953	-0.47552	0.16893
H	1.35901	-0.80122	1.57734
O	-0.77729	0.13706	-0.08258
O	2.22773	-1.11983	-1.66410
H	4.27941	-2.73753	0.96136
H	2.81029	-1.85577	-1.42184
H	0.12034	0.23772	-1.96510
C	-1.88191	-0.45992	-0.61346
C	-3.04590	-0.41373	0.38405
C	-2.61276	-1.07871	1.70663
C	-4.24530	-1.16094	-0.21201
C	-3.41274	1.06441	0.63663
O	-1.91357	-0.93984	-1.72325
H	-3.71713	1.55540	-0.29430
H	-2.56751	1.61529	1.05648
H	-4.25278	1.11530	1.33876
H	-4.56019	-0.71172	-1.15794
H	-5.08508	-1.12169	0.49046
H	-4.00221	-2.21008	-0.40522

H	-3.45738	-1.08277	2.40476
H	-1.78268	-0.53923	2.16944
H	-2.30485	-2.11767	1.54220
O	0.42420	2.49274	-0.11763
H	1.93216	1.69858	-1.25667
C	1.15940	3.69245	0.12593
H	0.42145	4.48477	0.27259
H	1.79831	3.94351	-0.73522
H	1.78350	3.59876	1.02326

[2-*O*-Piv-*α*-xylo(H2)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1211.33656009

Zero-point correction= 0.494992 (Hartree/Particle)
Thermal correction to Energy= 0.522614
Thermal correction to Enthalpy= 0.523559
Thermal correction to Gibbs Free Energy= 0.435421
Sum of electronic and zero-point Energies= -1210.841568
Sum of electronic and thermal Energies= -1210.813946
Sum of electronic and thermal Enthalpies= -1210.813002
Sum of electronic and thermal Free Energies= -1210.901139

Number of imaginary frequencies: 1, -1305.5759

Geometry:

O	3.40709	-2.39998	0.72321
C	3.41073	-0.97255	0.91174
C	1.97957	-0.48389	0.72642
O	2.00123	0.95161	0.66923
C	1.31385	-0.97023	-0.58244
H	0.73414	-1.88679	-0.42226
C	0.39507	0.20797	-0.91011
C	1.22650	1.41221	-0.45702
H	3.76743	-0.70593	1.91589
H	4.04953	-0.47552	0.16893
H	1.35901	-0.80122	1.57734
O	-0.77729	0.13706	-0.08258
O	2.22773	-1.11983	-1.66410
H	4.27941	-2.73753	0.96136
H	2.81029	-1.85577	-1.42184
H	0.12034	0.23772	-1.96510
C	-1.88191	-0.45992	-0.61346
C	-3.04590	-0.41373	0.38405
C	-2.61276	-1.07871	1.70663

C	-4.24530	-1.16094	-0.21201
C	-3.41274	1.06441	0.63663
O	-1.91357	-0.93984	-1.72325
H	-3.71713	1.55540	-0.29430
H	-2.56751	1.61529	1.05648
H	-4.25278	1.11530	1.33876
H	-4.56019	-0.71172	-1.15794
H	-5.08508	-1.12169	0.49046
H	-4.00221	-2.21008	-0.40522
H	-3.45738	-1.08277	2.40476
H	-1.78268	-0.53923	2.16944
H	-2.30485	-2.11767	1.54220
O	0.42420	2.49274	-0.11763
H	1.93216	1.69858	-1.25667
C	1.15940	3.69245	0.12593
H	0.42145	4.48477	0.27259
H	1.79831	3.94351	-0.73522
H	1.78350	3.59876	1.02326

[2-*O*-Piv-*α*-xylo(H3)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1211.34308069

Zero-point correction= 0.495588 (Hartree/Particle)
Thermal correction to Energy= 0.522788
Thermal correction to Enthalpy= 0.523732
Thermal correction to Gibbs Free Energy= 0.435237
Sum of electronic and zero-point Energies= -1210.847493
Sum of electronic and thermal Energies= -1210.820293
Sum of electronic and thermal Enthalpies= -1210.819349
Sum of electronic and thermal Free Energies= -1210.907844

Number of imaginary frequencies: 1, -440.5216

Geometry:

H	1.98548	4.30675	-1.44730
O	1.49313	1.77869	-1.94205
H	1.45193	-0.43450	-1.85882
O	-0.30204	-2.20313	-1.69280
C	1.37603	4.22317	-0.54524
H	-0.80141	-3.00494	-1.40417
H	0.32286	4.28275	-0.84238
C	1.43773	1.73806	-0.73830
C	1.31587	-0.65280	-0.79856
H	3.80158	2.91238	-0.30258

C	0.10785	-1.55074	-0.55213
H	2.73669	-2.29390	-0.91605
H	1.59501	5.07496	0.10603
H	-0.83802	-0.81239	-0.21888
C	1.67039	2.91697	0.20723
C	2.44806	-1.50376	-0.19849
C	3.17081	2.85071	0.58915
O	1.19771	0.56226	-0.04739
H	4.98485	-2.13434	-0.38446
O	3.51998	-0.74474	0.17358
H	3.40891	3.69852	1.23984
O	-1.09985	-4.09500	0.01976
C	4.71367	-1.49538	0.46676
H	0.96905	-4.27583	-0.31791
C	0.47454	-2.42176	0.68749
H	3.40127	1.92250	1.11831
C	0.27025	-3.92205	0.45165
H	-1.28955	-5.03965	-0.06288
O	1.83748	-2.14380	0.96672
C	0.81601	2.83710	1.48299
H	5.49974	-0.75834	0.63631
H	-0.25422	2.89962	1.25146
H	4.57486	-2.10675	1.36471
H	1.05608	3.68870	2.12714
H	-0.11762	-2.11524	1.55980
H	1.00889	1.92036	2.04521
H	0.46023	-4.46572	1.38321
H	-5.17108	1.71344	0.43566
C	-4.22998	1.17325	0.29955
H	-4.97559	-0.80135	0.82825
H	-3.06156	2.27604	1.76574
H	-3.95079	1.63878	-1.80655
H	-3.96811	0.92666	2.45354
H	-5.19826	-0.39095	-0.87428
H	-3.30183	2.86685	-0.71805
C	-4.51143	-0.30249	-0.02801
C	-3.38723	1.24706	1.58410
C	-3.42730	1.78934	-0.85765
C	-3.15860	-0.99260	-0.38291
C	-2.14897	0.31589	1.41536
C	-2.02668	1.10993	-0.89782
N	-2.06040	-0.07438	-0.00897
H	-3.01752	-1.93112	0.15884
H	-1.21590	0.80838	1.69097
H	-1.74973	0.77694	-1.90060
H	-2.24872	-0.60215	1.99962

H	-3.06735	-1.19059	-1.45331
H	-1.24470	1.77113	-0.52740

[2-*O*-Piv-*α*-xylo(H4)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1211.35011305

Zero-point correction= 0.495510 (Hartree/Particle)
Thermal correction to Energy= 0.523110
Thermal correction to Enthalpy= 0.524054
Thermal correction to Gibbs Free Energy= 0.436171
Sum of electronic and zero-point Energies= -1210.854603
Sum of electronic and thermal Energies= -1210.827003
Sum of electronic and thermal Enthalpies= -1210.826059
Sum of electronic and thermal Free Energies= -1210.913942

Number of imaginary frequencies: 1, -357.4163

Geometry:

O	2.94044	2.26505	-1.61508
C	2.45678	2.70629	-0.34362
C	1.16526	1.95131	-0.09610
O	0.61833	2.26152	1.12431
C	0.05904	2.01928	-1.16984
H	0.21044	1.28836	-1.96870
C	-1.20509	1.70135	-0.36528
C	-0.85553	2.03751	1.10711
H	3.17266	2.49835	0.46458
H	2.24019	3.78413	-0.33940
H	1.51345	0.74682	-0.07198
O	-1.53147	0.31955	-0.54388
O	-0.06139	3.33744	-1.68361
H	3.72918	2.77677	-1.83851
H	0.63143	3.46393	-2.34818
O	-1.19557	1.02682	1.96296
H	-2.03732	2.32339	-0.69698
C	-2.87083	0.00777	-0.33317
C	-3.15721	-1.46936	-0.60594
C	-4.63105	-1.74834	-0.27759
C	-2.25189	-2.35570	0.27220
C	-2.88843	-1.75729	-2.09920
O	-3.67108	0.84388	-0.00557
H	2.90886	-4.10429	0.39578
C	2.61836	-3.05509	0.28957
H	2.46735	-3.16289	-1.87880

H	4.44485	-2.30313	1.20335
H	0.81358	-3.26354	1.48571
H	4.52365	-2.43193	-0.55480
H	0.94531	-3.46355	-1.03723
H	2.23440	-2.77548	2.41249
C	1.85372	-2.85374	-1.02767
C	3.87169	-2.16463	0.28203
C	1.71296	-2.64111	1.46025
C	1.48208	-1.34699	-1.16122
C	3.42768	-0.67397	0.15278
C	1.31280	-1.14626	1.27773
N	1.95303	-0.63177	0.04696
H	1.96278	-0.87837	-2.02310
H	3.71243	-0.08885	1.03077
H	0.23671	-1.00853	1.17508
H	3.83683	-0.19057	-0.73625
H	0.40507	-1.19144	-1.23325
H	1.65472	-0.52368	2.10779
H	-3.12811	-2.80391	-2.31346
H	-1.84115	-1.58282	-2.36344
H	-3.51550	-1.12914	-2.73992
H	-2.35385	-2.10287	1.33270
H	-1.20118	-2.25794	-0.01037
H	-2.54039	-3.40373	0.14283
H	-4.84629	-1.54977	0.77609
H	-4.85606	-2.79881	-0.48686
H	-5.29536	-1.12339	-0.87927
C	-1.30235	1.41468	3.34717
H	-1.64983	0.53026	3.88296
H	-2.03390	2.22378	3.45950
H	-0.32899	1.73110	3.73884
H	-1.26929	3.00571	1.41495

[2-*O*-Piv-*α*-xylo(H5)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energy (Hartree/particle): -1211.33914000

Zero-point correction= 0.494697 (Hartree/Particle)
Thermal correction to Energy= 0.522458
Thermal correction to Enthalpy= 0.523402
Thermal correction to Gibbs Free Energy= 0.432709
Sum of electronic and zero-point Energies= -1210.844443
Sum of electronic and thermal Energies= -1210.816682
Sum of electronic and thermal Enthalpies= -1210.815738
Sum of electronic and thermal Free Energies= -1210.906431

Number of imaginary frequencies: 1, -654.4317

Geometry:

H	-6.50114	-0.04815	-0.84191
O	-4.37373	1.15216	0.36527
H	-2.71830	0.73967	2.03600
O	-0.96281	2.66193	1.73483
C	-5.80282	-0.11000	-1.68056
H	-1.78307	3.08875	2.01898
H	-5.68139	0.89640	-2.09193
C	-3.85934	0.18858	-0.15108
C	-1.98254	0.47860	1.27106
H	-5.33673	-2.08994	0.20442
C	-1.28602	1.73339	0.70916
H	-0.63201	-0.07293	2.89481
H	-6.24257	-0.74918	-2.45268
H	-1.87268	2.19371	-0.09260
C	-4.45626	-0.69920	-1.24055
C	-0.81788	-0.34664	1.84558
C	-4.65939	-2.11490	-0.65574
O	-2.60306	-0.25159	0.21343
H	-0.17139	-2.21377	3.55067
O	-1.03697	-1.70092	1.71501
H	-5.10756	-2.75769	-1.42059
O	1.08192	2.83805	-1.08418
C	-0.15573	-2.51660	2.49423
H	1.40708	2.60171	0.97137
C	0.01195	1.10145	0.17155
H	-3.71018	-2.55561	-0.34001
C	1.17505	2.05605	0.05055
H	1.50876	3.69502	-0.93659
O	0.37208	0.08349	1.10816
C	-3.48652	-0.76114	-2.43963
H	-0.52096	-3.54096	2.40287
H	-3.29176	0.23950	-2.84240
H	0.87392	-2.46112	2.11500
H	-3.93845	-1.36114	-3.23609
H	-0.20960	0.66549	-0.81536
H	-2.53467	-1.22068	-2.16005
H	2.15316	1.27500	-0.09073
H	5.89641	-2.00175	-0.95352
C	5.08507	-1.29335	-0.76343
H	3.82968	-2.13400	-2.33394
H	6.34300	0.43389	-1.19612
H	4.82695	-1.96183	1.29371

H	5.38660	-0.12262	-2.57105
H	3.49513	-2.77581	-0.72426
H	5.87740	-0.55445	1.12202
C	3.75476	-1.86736	-1.27594
C	5.36865	0.03228	-1.48833
C	4.96445	-1.02541	0.74555
C	2.64192	-0.79228	-1.08312
C	4.24961	1.05221	-1.11272
C	3.73920	-0.09288	0.99045
N	3.21806	0.34342	-0.32517
H	2.28317	-0.39822	-2.03720
H	4.63249	1.86887	-0.49519
H	2.92063	-0.59469	1.50771
H	3.76571	1.47776	-1.99545
H	1.79088	-1.16822	-0.51336
H	4.01062	0.80114	1.55733

Effect of coordination of the carbonyl to the radical at C-3.

[per-Me-*α*-Glc_C3•]

Energy (Hartree/particle): -996.185532513

Zero-point correction= 0.324443 (Hartree/Particle)
Thermal correction to Energy= 0.347157
Thermal correction to Enthalpy= 0.348101
Thermal correction to Gibbs Free Energy= 0.268903
Sum of electronic and zero-point Energies= -995.861089
Sum of electronic and thermal Energies= -995.838376
Sum of electronic and thermal Enthalpies= -995.837432
Sum of electronic and thermal Free Energies= -995.916630

Number of imaginary frequencies: 0

Geometry:

O	3.54410	-1.44044	-0.14184
C	2.86674	-1.09691	0.80353
H	0.37395	-1.51899	-2.10123
H	-0.26162	-3.72664	-1.60409
C	0.16036	-1.18928	-1.07279
H	2.07643	-0.22924	-1.32307
C	-0.54412	-3.39189	-0.59372
O	1.72478	-0.36928	0.71084
O	-1.14922	-0.65640	-1.15922

C	1.21672	-0.11357	-0.66206
H	-1.61155	-3.14433	-0.57801
O	0.24878	-2.27310	-0.19004
H	3.31375	1.67600	-0.68717
H	-5.37030	0.09445	1.07738
H	-0.33654	-4.18970	0.12327
H	-5.42262	-1.66607	0.76107
C	-5.02511	-0.71091	0.40684
O	-3.61322	-0.81893	0.40851
C	2.71580	2.20582	-1.43718
H	2.77429	1.67261	-2.39465
H	-3.22080	1.20931	0.65505
C	-1.48460	0.17475	-0.04198
C	-2.98341	0.37564	-0.02672
C	0.63197	1.23563	-0.71365
H	-1.26658	2.19639	-0.84276
C	-0.72539	1.50863	-0.16778
H	3.09554	3.22139	-1.56377
O	1.35594	2.35302	-1.01276
H	-1.17849	-0.30987	0.89386
H	-5.41407	-0.51119	-0.60591
H	-3.32574	0.64683	-1.04114
O	-0.72393	2.08495	1.15812
H	-1.30677	3.99772	0.54895
C	-0.56273	3.49617	1.18995
H	0.44065	3.80245	0.86657
H	-0.71990	3.80392	2.22810
C	3.16610	-1.41713	2.24819
H	4.20080	-1.74900	2.34554
H	2.49564	-2.22317	2.56780
H	2.97224	-0.55311	2.88945

[per-Me-α-Glc_C3'_coord]

Energy (Hartree/particle): -996.179373191

Zero-point correction= 0.324630 (Hartree/Particle)
Thermal correction to Energy= 0.346996
Thermal correction to Enthalpy= 0.347940
Thermal correction to Gibbs Free Energy= 0.271137
Sum of electronic and zero-point Energies= -995.854743
Sum of electronic and thermal Energies= -995.832377
Sum of electronic and thermal Enthalpies= -995.831433
Sum of electronic and thermal Free Energies= -995.908236

Number of imaginary frequencies: 0

Geometry:

O	-2.28037	0.01084	1.42156
C	-2.73814	0.81971	0.64824
H	0.03037	2.13356	-1.78037
H	0.70375	3.89435	-0.37418
C	0.06045	1.40771	-0.95322
H	-1.29122	0.32132	-2.20234
C	0.82867	3.15722	0.43426
O	-2.34956	0.98782	-0.64246
O	1.30697	0.75962	-1.09981
C	-1.08747	0.37722	-1.12404
H	1.86740	2.80634	0.44185
O	-0.08748	2.07173	0.27153
H	-3.32716	-1.78766	-0.45689
H	5.48958	-0.79543	0.71797
H	0.58705	3.62159	1.39295
H	5.83494	0.92511	0.36760
C	5.23668	0.05990	0.06850
O	3.87546	0.42678	0.19869
C	-2.79443	-1.98082	-1.39521
H	-3.04049	-1.19695	-2.12126
H	3.14254	-1.49385	0.51774
C	1.56661	-0.15997	-0.02478
C	2.99798	-0.63165	-0.15440
C	-0.73458	-0.97403	-0.64284
H	0.98219	-2.17621	-0.63046
C	0.57555	-1.33723	-0.03199
H	-3.08821	-2.95228	-1.79871
O	-1.38523	-2.06817	-1.15810
H	1.44710	0.35538	0.93357
H	5.48527	-0.20807	-0.97233
H	3.18738	-0.96245	-1.19094
O	0.52703	-1.76368	1.34355
H	0.02675	-3.74950	0.91467
C	-0.25858	-2.92132	1.58356
H	-1.32877	-2.71406	1.45798
H	-0.06860	-3.21154	2.62121
C	-3.84862	1.79279	0.97703
H	-4.33849	1.48949	1.90326
H	-4.57248	1.85635	0.15970
H	-3.40818	2.78776	1.10866

[per-Me-α-Man_C3•]

Energy (Hartree/particle): -996.182308693

Zero-point correction= 0.324463 (Hartree/Particle)
Thermal correction to Energy= 0.347095
Thermal correction to Enthalpy= 0.348039
Thermal correction to Gibbs Free Energy= 0.269596
Sum of electronic and zero-point Energies= -995.857846
Sum of electronic and thermal Energies= -995.835214
Sum of electronic and thermal Enthalpies= -995.834270
Sum of electronic and thermal Free Energies= -995.912713

Number of imaginary frequencies: 0

Geometry:

H	-0.95469	-4.26609	1.05507
C	-0.23956	-3.45854	0.88101
H	0.21218	-3.58483	-0.11003
H	0.54471	-3.47078	1.64275
O	-1.00994	-2.25553	0.95275
O	1.86058	-1.54997	0.81036
H	0.88298	-1.29387	-1.00415
C	-0.47185	-1.03981	0.64780
C	0.87485	-0.86621	0.01947
O	-2.22689	-0.28606	-0.80420
C	-1.52581	-0.02268	0.49196
H	-2.27924	-0.09096	1.27943
C	1.24835	0.64187	-0.06933
C	2.35054	0.97229	-1.07538
H	1.58831	0.93641	0.93107
C	-0.96347	1.39453	0.42322
O	0.13662	1.45501	-0.47249
O	-0.63639	1.77954	1.73303
H	-1.70503	2.07797	-0.01076
C	-3.52114	0.10834	-0.88165
O	-4.11305	0.70075	-0.00481
C	-0.29493	3.16114	1.84946
H	-0.12379	3.34971	2.91167
H	-1.11822	3.79771	1.49168
H	0.61417	3.40006	1.28244
O	3.62424	0.79519	-0.47312
H	2.21914	2.02142	-1.38474
H	2.25841	0.34399	-1.97896
C	4.68095	1.09979	-1.36736
H	5.61681	0.95510	-0.82094
H	4.62245	2.14349	-1.71786

H	4.66901	0.43618	-2.24854
C	2.85742	-2.24401	0.06924
H	3.51416	-1.55454	-0.47336
H	2.40740	-2.95803	-0.63976
H	3.45127	-2.79992	0.80058
C	-4.11758	-0.30089	-2.21008
H	-4.13570	-1.39363	-2.28355
H	-3.50039	0.07270	-3.03323
H	-5.13189	0.09150	-2.29097

[per-Me-α-Man_C3'_coord]

Energy (Hartree/particle): -996.184130182

Zero-point correction= 0.324426 (Hartree/Particle)
Thermal correction to Energy= 0.347045
Thermal correction to Enthalpy= 0.347989
Thermal correction to Gibbs Free Energy= 0.270528
Sum of electronic and zero-point Energies= -995.859704
Sum of electronic and thermal Energies= -995.837086
Sum of electronic and thermal Enthalpies= -995.836141
Sum of electronic and thermal Free Energies= -995.913602

Number of imaginary frequencies: 0

Geometry:

H	0.79372	-1.47238	-4.01060
C	0.23441	-1.23052	-3.10467
H	0.05164	-2.14734	-2.53107
H	-0.71507	-0.75274	-3.36741
O	1.07022	-0.33445	-2.36460
O	-1.58492	0.88151	-1.64063
H	-1.15308	-0.99570	-0.89357
C	0.61696	0.15028	-1.17568
C	-0.79756	0.03761	-0.75675
O	2.68305	-0.13057	0.24681
C	1.65389	0.79200	-0.37979
H	2.30405	1.42069	-0.99624
C	-1.04109	0.41009	0.73852
C	-1.56712	-0.76140	1.56248
H	-1.78825	1.21501	0.73058
C	1.05646	1.61164	0.76227
O	0.10873	0.85733	1.48079
O	0.53886	2.78987	0.19526
H	1.83279	1.84350	1.50678
C	2.39326	-1.41485	0.52564
O	1.33655	-1.97734	0.31920

C	0.09133	3.73621	1.16408
H	-0.24275	4.61469	0.60745
H	0.91016	4.02145	1.84316
H	-0.74114	3.34042	1.75964
O	-2.85327	-1.12062	1.07582
H	-1.62609	-0.45568	2.61978
H	-0.86587	-1.60486	1.48307
C	-3.36424	-2.27802	1.71383
H	-4.34549	-2.48174	1.27583
H	-3.47883	-2.12206	2.79944
H	-2.70663	-3.14795	1.55393
C	-2.94313	0.47243	-1.76227
H	-3.48797	0.54204	-0.81130
H	-3.01823	-0.56860	-2.11840
H	-3.40131	1.13999	-2.49772
C	3.59945	-2.08917	1.14947
H	3.81343	-1.63050	2.12098
H	4.48283	-1.95009	0.51887
H	3.39272	-3.15174	1.28290

Calculated free energies and geometries for Reaction Pathway.

[HAT_PRC]•

Energy (Hartree/particle): -2205.88499462

Zero-point correction= 0.621694 (Hartree/Particle)
Thermal correction to Energy= 0.661737
Thermal correction to Enthalpy= 0.662681
Thermal correction to Gibbs Free Energy= 0.542038
Sum of electronic and zero-point Energies= -2205.263300
Sum of electronic and thermal Energies= -2205.223258
Sum of electronic and thermal Enthalpies= -2205.222313
Sum of electronic and thermal Free Energies= -2205.342957

Number of imaginary frequencies: 0

Geometry:

O	-2.42771	5.20735	1.37696
H	-2.09168	5.01060	-0.61447
C	-1.70471	4.57695	0.31404
H	-2.02913	4.92272	2.21147
O	-3.26903	2.81764	-0.06282
H	-4.69593	1.43126	-0.28237
H	-0.63152	4.79209	0.38010

H	-5.36863	1.24188	1.95862
H	-4.13617	2.44727	2.44099
C	-1.89285	3.06507	0.27659
C	-3.63175	1.44769	-0.01212
C	-4.32014	1.38212	2.25714
O	-4.89174	-0.56265	-2.24965
H	-1.11372	2.83561	-1.73186
H	-3.10694	1.00839	-2.03505
C	-0.95446	2.39172	-0.73381
C	-2.80402	0.66780	-1.04052
H	-1.67776	2.64923	1.27215
O	-3.43805	0.86855	1.25287
H	-4.11940	0.81248	3.16696
C	-4.13887	-1.24886	-1.58705
H	-6.42830	-2.79302	-1.62825
O	0.36400	2.58837	-0.28804
C	-1.30446	0.87334	-0.86840
O	-3.05993	-0.75238	-0.93501
H	-5.52683	-3.06048	-3.13099
C	-5.54000	-3.26694	-2.05695
O	-0.65004	0.25852	-1.93041
H	1.02430	2.31955	-0.98696
H	-5.15996	-2.55335	0.60667
C	-4.25988	-2.76290	-1.37812
H	-0.97547	0.42501	0.10509
C	-4.31600	-3.06693	0.13339
O	2.41320	1.86775	-1.82290
H	-5.62247	-4.34931	-1.91347
H	-2.96861	-3.23073	-3.08293
H	0.34922	0.15181	-1.73383
C	-3.02827	-3.44634	-2.01063
H	-3.39866	-2.75743	0.63911
H	-1.12185	0.19534	3.10816
H	-2.02927	-1.07302	2.25811
H	-2.10018	-3.11323	-1.54006
H	-4.44529	-4.14463	0.27940
C	-1.04818	-0.78369	2.63317
C	2.68001	0.67082	-1.52070
N	-0.12498	-0.68641	1.51352
H	0.98633	0.89538	2.28595
H	-3.11326	-4.53098	-1.88390
O	1.82358	-0.26747	-1.44497
H	4.89696	2.22521	-1.77683
C	1.15791	-0.10109	1.87772
H	-0.98919	-2.27798	0.50561
C	0.00873	-1.92976	0.77168

H	1.76410	-0.03129	0.97616
H	0.59012	-1.73568	-0.13065
C	5.13925	1.24753	-1.37263
C	4.11067	0.31510	-1.18707
C	-0.45523	-1.86467	3.61893
H	-0.37129	-1.42813	4.61796
H	-1.13521	-2.71953	3.67258
C	1.81498	-1.06088	2.94359
H	1.91041	-0.53662	3.89861
C	0.74638	-2.95586	1.71572
C	0.91891	-2.29730	3.09038
C	6.45705	0.93632	-1.04568
C	4.42568	-0.94315	-0.65657
H	7.25387	1.65772	-1.19535
H	0.14736	-3.86794	1.78743
H	3.63095	-1.66676	-0.50724
H	2.81566	-1.33938	2.60129
H	1.71812	-3.21421	1.28582
C	6.74053	-0.32271	-0.51491
H	1.37692	-3.00826	3.78731
C	5.73557	-1.26920	-0.31267
H	5.97658	-2.24119	0.10559
Cl	8.39149	-0.72200	-0.09100

[HAT_TS]•

Energy (Hartree/particle): -2205.88431862

Zero-point correction= 0.618250 (Hartree/Particle)
Thermal correction to Energy= 0.657470
Thermal correction to Enthalpy= 0.658414
Thermal correction to Gibbs Free Energy= 0.540920
Sum of electronic and zero-point Energies= -2205.266069
Sum of electronic and thermal Energies= -2205.226849
Sum of electronic and thermal Enthalpies= -2205.225904
Sum of electronic and thermal Free Energies= -2205.343399

Number of imaginary frequencies: 1, -489.9654

Geometry:

C	-3.24434	0.97139	-1.49707
C	-2.21591	-0.16298	-1.48112
C	-0.93168	0.22515	-0.76360
O	-0.03124	-0.79112	-0.82002

C	-0.40201	1.62330	-1.17781
C	-1.54580	2.64555	-1.29259
C	-1.08021	3.92116	-1.98263
O	-2.03675	4.98375	-1.91064
O	-2.64768	2.12632	-2.06059
O	0.54733	2.11146	-0.26215
O	-2.75421	-1.34831	-0.85833
O	-3.71953	1.17005	-0.18979
H	-1.89126	2.89194	-0.27980
H	-4.07369	0.72427	-2.17327
H	-1.97675	-0.39477	-2.52472
H	-1.20250	0.38427	0.45186
H	0.04960	1.48698	-2.17687
C	-4.84046	2.06071	-0.11539
C	-3.41176	-2.22841	-1.65863
H	-0.11922	4.21980	-1.54631
H	-0.93168	3.71760	-3.04870
H	1.46794	1.82469	-0.56543
H	0.95500	-0.54745	-0.55395
H	-2.08232	5.27512	-0.98925
O	-3.56438	-2.05401	-2.85066
C	-3.92121	-3.43010	-0.85702
C	-4.91805	-2.92685	0.20919
C	-2.72588	-4.12920	-0.17626
C	-4.62570	-4.40846	-1.80585
Cl	9.09938	-1.18454	-0.15323
C	6.44157	-1.72956	0.05224
C	5.09374	-1.39149	-0.04586
C	3.23336	0.24721	-0.56730
C	4.69837	-0.11401	-0.46419
C	7.40231	-0.77166	-0.27319
C	5.68566	0.82701	-0.78465
C	7.03854	0.50846	-0.69219
O	2.93978	1.40133	-0.99125
O	2.39601	-0.64179	-0.21304
H	6.74550	-2.71995	0.37556
H	4.33288	-2.12399	0.20306
H	5.38358	1.81770	-1.10849
H	7.80139	1.23937	-0.94030
H	-5.15332	2.07650	0.93061
H	-5.66516	1.69425	-0.74185
H	-4.56391	3.07247	-0.43383
H	-1.31739	0.37103	5.53740
H	-2.31607	2.30880	4.34292
H	-0.55291	2.41189	4.24398
C	-1.42391	1.82764	3.93120

H	-3.43171	0.03231	4.17706
C	-1.30541	0.38400	4.44339
C	-2.48325	-0.43342	3.89196
H	-2.47282	-1.44898	4.29878
H	0.86916	0.29184	4.35647
C	0.00688	-0.22387	3.92354
C	-1.51590	1.79975	2.37609
H	0.07114	-1.27910	4.20612
H	-2.50408	2.09101	2.01831
C	-2.36281	-0.49167	2.34066
H	-0.76423	2.43481	1.90713
H	-3.27400	-0.17009	1.83760
N	-1.27489	0.41487	1.91714
C	0.04144	-0.07912	2.37306
H	-2.10413	-1.49145	1.99001
H	0.78918	0.63911	2.03636
H	0.23080	-1.03245	1.87642
H	-2.21774	-3.46226	0.52394
H	-1.99697	-4.47104	-0.91898
H	-3.08756	-5.00307	0.37599
H	-4.43581	-2.25370	0.92100
H	-5.31826	-3.78524	0.75911
H	-5.75660	-2.39753	-0.25640
H	-5.47845	-3.93532	-2.30165
H	-4.99135	-5.26625	-1.23202
H	-3.94160	-4.77482	-2.57711

[HAT_PostRC]•

Energy (Hartree/particle): -2205.90418673

Zero-point correction= 0.624324 (Hartree/Particle)
Thermal correction to Energy= 0.664124
Thermal correction to Enthalpy= 0.665069
Thermal correction to Gibbs Free Energy= 0.545269
Sum of electronic and zero-point Energies= -2205.279863
Sum of electronic and thermal Energies= -2205.240062
Sum of electronic and thermal Enthalpies= -2205.239118
Sum of electronic and thermal Free Energies= -2205.358918

Number of imaginary frequencies: 0

Geometry:

C	-3.41515	1.85332	-0.80295
C	-2.46623	0.85438	-1.49867

C	-1.05784	0.95705	-1.05033
O	-0.20140	0.20333	-1.77862
C	-0.52462	2.11862	-0.27817
C	-1.64292	3.00562	0.28946
C	-1.14599	4.41696	0.56377
O	-2.06464	5.21163	1.32064
O	-2.75169	3.09575	-0.61960
O	0.29880	1.70763	0.83804
O	-2.91036	-0.53857	-1.28175
O	-3.87091	1.28679	0.39835
H	-1.98128	2.54998	1.22982
H	-4.26367	2.08880	-1.45609
H	-2.54136	1.02817	-2.58122
H	-0.06502	0.21035	1.38517
H	0.11585	2.72206	-0.94730
C	-4.93381	2.02710	1.00828
C	-4.00327	-0.95087	-1.95703
H	-0.17258	4.34684	1.06825
H	-1.00507	4.94041	-0.38831
H	1.28319	1.71019	0.54707
H	0.76150	0.23768	-1.44049
H	-2.12349	4.82747	2.20676
O	-4.60622	-0.25155	-2.75055
C	-4.40556	-2.37841	-1.56021
C	-5.03616	-2.29608	-0.15181
C	-3.17719	-3.30630	-1.53261
C	-5.43986	-2.91228	-2.56023
Cl	8.96716	-0.75591	-0.82981
C	6.34455	-1.07940	-1.47887
C	4.99549	-0.74138	-1.40003
C	3.09413	0.67616	-0.51467
C	4.56268	0.32093	-0.59555
C	7.26879	-0.34050	-0.73965
C	5.51384	1.04513	0.13513
C	6.86747	0.72246	0.07001
O	2.77573	1.66627	0.21222
O	2.28688	-0.04364	-1.17333
H	6.67733	-1.90238	-2.10315
H	4.26187	-1.30445	-1.96770
H	5.18354	1.86877	0.75964
H	7.60229	1.28478	0.63713
H	-5.25281	1.44990	1.87876
H	-5.77620	2.13839	0.31097
H	-4.59602	3.02047	1.32750
H	-0.88181	-3.92934	3.45732
H	-0.17378	-1.88241	4.77769

H	1.19327	-2.70909	4.02549
C	0.28565	-2.13567	3.81734
H	-2.51381	-2.09972	3.78468
C	-0.69262	-2.96843	2.97186
C	-2.00866	-2.18768	2.81872
H	-2.68173	-2.72454	2.14381
H	0.90564	-3.65736	1.67657
C	-0.07991	-3.19175	1.57917
C	0.64710	-0.85174	3.04097
H	-0.70699	-3.86850	0.99170
H	0.51084	0.05505	3.63290
C	-1.69688	-0.78197	2.26336
H	1.66945	-0.86478	2.65793
H	-1.82809	0.00235	3.01154
N	-0.25362	-0.73125	1.84269
C	0.03700	-1.83248	0.85936
H	-2.29074	-0.52213	1.38610
H	1.03119	-1.64126	0.45326
H	-0.68577	-1.71383	0.05200
H	-2.44515	-2.97884	-0.79259
H	-2.68639	-3.33969	-2.51124
H	-3.49690	-4.32178	-1.27507
H	-4.32310	-1.90557	0.57776
H	-5.34746	-3.29758	0.16444
H	-5.91752	-1.64590	-0.15447
H	-5.74111	-3.92259	-2.26393
H	-5.02333	-2.95966	-3.57156
H	-6.33065	-2.27893	-2.58617

[Piv-C2_rad-C3]•

Energy (Hartree/particle): -996.249258477

Zero-point correction= 0.325961 (Hartree/Particle)
Thermal correction to Energy= 0.347631
Thermal correction to Enthalpy= 0.348575
Thermal correction to Gibbs Free Energy= 0.274265
Sum of electronic and zero-point Energies= -995.923298
Sum of electronic and thermal Energies= -995.901628
Sum of electronic and thermal Enthalpies= -995.900684
Sum of electronic and thermal Free Energies= -995.974994

Number of imaginary frequencies: 0

Geometry:

C	-0.50208	1.11973	0.47570
C	0.04165	-0.32213	0.58550
C	-0.88395	-1.29132	-0.05167
O	-0.42728	-2.58401	-0.11726
C	-2.35162	-1.10926	0.13456
C	-2.74073	0.37436	0.06051
C	-4.15204	0.63784	0.58674
O	-5.14296	-0.12840	-0.11838
O	-1.86473	1.15358	0.89319
O	-3.01813	-1.90084	-0.86453
O	1.34335	-0.44109	-0.05320
O	-0.31799	1.56718	-0.83782
H	-2.65986	0.70183	-0.98501
H	0.01565	1.77579	1.18597
H	0.18222	-0.53509	1.65689
H	-2.64197	-1.48691	1.13816
C	-0.53557	2.97548	-0.99441
C	2.42147	-0.00651	0.64228
H	-4.21305	0.32281	1.63362
H	-4.36995	1.71179	0.53308
H	-3.96973	-1.76749	-0.70826
H	-1.16448	-3.12544	-0.44883
H	-5.27770	0.28314	-0.98414
O	2.35047	0.46257	1.76181
C	3.70800	-0.17329	-0.17539
C	4.90883	0.26123	0.67449
C	3.60451	0.71937	-1.43172
C	3.86581	-1.65034	-0.59150
H	-0.28868	3.21356	-2.03097
H	0.11897	3.54440	-0.31941
H	-1.58050	3.24150	-0.79453
H	4.80078	-1.76873	-1.14984
H	3.03847	-1.97614	-1.22660
H	3.90844	-2.30321	0.28734
H	5.82625	0.14641	0.08785
H	4.99790	-0.35054	1.57747
H	4.82212	1.30855	0.97845
H	4.53297	0.63869	-2.00726
H	3.46317	1.77028	-1.15609
H	2.77145	0.41214	-2.06894

[quin-H^+_$ArCO_2^-$]

Energy (Hartree/particle): -1209.62337854

Zero-point correction= 0.296219 (Hartree/Particle)
Thermal correction to Energy= 0.313092
Thermal correction to Enthalpy= 0.314036
Thermal correction to Gibbs Free Energy= 0.247790
Sum of electronic and zero-point Energies= -1209.327160
Sum of electronic and thermal Energies= -1209.310287
Sum of electronic and thermal Enthalpies= -1209.309343
Sum of electronic and thermal Free Energies= -1209.375589

Number of imaginary frequencies: 0

Geometry:

C	0.37501	1.05914	0.37820
C	0.86264	-0.40625	0.42248
C	-0.14623	-1.32308	-0.16385
O	0.24721	-2.63246	-0.28332
C	-1.58836	-1.08281	0.12704
C	-1.91671	0.41692	0.10531
C	-3.27717	0.72979	0.72907
O	-4.34503	0.02590	0.07307
O	-0.95288	1.13974	0.89040
O	-2.35505	-1.82671	-0.83622
O	2.11311	-0.56686	-0.30922
O	0.48726	1.52792	-0.93606
H	-1.89213	0.76231	-0.93733
H	0.96760	1.67754	1.06365
H	1.07012	-0.64714	1.47681
H	-1.82532	-1.46713	1.14206
C	0.30005	2.94492	-1.05097
C	3.25455	-0.21239	0.33026
H	-3.28588	0.39225	1.77061
H	-3.44839	1.81343	0.71253
H	-3.28719	-1.65767	-0.61225
H	-0.53472	-3.13463	-0.57151
H	-4.50772	0.45783	-0.77793
O	3.29036	0.22964	1.46228
C	4.44938	-0.43276	-0.56063
H	5.36613	-0.23865	-0.00353
H	4.39081	0.24458	-1.41955
H	4.45110	-1.45575	-0.94846
H	0.48862	3.19835	-2.09609
H	1.01059	3.48171	-0.40698
H	-0.72247	3.23461	-0.78083

[1,2-mig_TS1]˙

Energy (Hartree/particle): -996.204949728

Zero-point correction= 0.324818 (Hartree/Particle)
Thermal correction to Energy= 0.345381
Thermal correction to Enthalpy= 0.346325
Thermal correction to Gibbs Free Energy= 0.276110
Sum of electronic and zero-point Energies= -995.880132
Sum of electronic and thermal Energies= -995.859569
Sum of electronic and thermal Enthalpies= -995.858624
Sum of electronic and thermal Free Energies= -995.928840

Number of imaginary frequencies: 1, -668.1175

Geometry:

C	-0.94984	1.62000	0.86075
C	0.10241	0.56034	1.31549
C	-0.17725	-0.83922	0.83150
O	0.49930	-1.77893	1.55793
C	-1.57705	-1.22883	0.44606
C	-2.33400	-0.04474	-0.15703
C	-3.82687	-0.32525	-0.33445
O	-4.07018	-1.46206	-1.18092
O	-2.25127	1.04463	0.77838
O	-1.51294	-2.38000	-0.39888
O	1.43347	0.90813	0.86377
O	-0.54615	2.21005	-0.33931
H	-1.88149	0.23683	-1.11619
H	-2.09399	-1.48995	1.38952
C	-1.31429	3.36909	-0.68437
C	1.72847	0.18481	-0.28138
H	-4.26811	-0.57219	0.63680
H	-4.32341	0.57167	-0.72471
H	-2.42771	-2.52947	-0.70248
H	-3.88426	-1.20038	-2.09427
O	0.72909	-0.53917	-0.69818
C	3.19385	-0.19650	-0.45445
C	3.38391	-0.78068	-1.86406
C	3.61355	-1.24627	0.59998
C	4.06495	1.06394	-0.29798
H	0.24382	-2.65425	1.22202
H	-0.85338	3.78938	-1.58058
H	-1.28437	4.10984	0.12765
H	-2.35813	3.10790	-0.89546

H	-1.05475	2.38507	1.64279
H	0.14827	0.57330	2.40730
H	2.77590	-1.67976	-2.00257
H	4.43580	-1.04764	-2.01557
H	3.09856	-0.05191	-2.63125
H	3.97063	1.48914	0.70570
H	3.77514	1.83084	-1.02540
H	5.11766	0.80987	-0.46573
H	3.46184	-0.86217	1.61337
H	4.67565	-1.49372	0.47834
H	3.02873	-2.16378	0.48818

[1,2-mig_int]•

Energy (Hartree/particle): -996.217482496

Zero-point correction= 0.327360 (Hartree/Particle)
Thermal correction to Energy= 0.347829
Thermal correction to Enthalpy= 0.348773
Thermal correction to Gibbs Free Energy= 0.279161
Sum of electronic and zero-point Energies= -995.890123
Sum of electronic and thermal Energies= -995.869653
Sum of electronic and thermal Enthalpies= -995.868709
Sum of electronic and thermal Free Energies= -995.938322

Number of imaginary frequencies: 0

Geometry:

C	-0.66232	1.50684	1.09300
C	0.09869	0.24309	1.59090
C	-0.28447	-1.06608	0.87426
O	-0.04597	-2.13568	1.77140
C	-1.71561	-1.13198	0.33747
C	-2.16975	0.21181	-0.23237
C	-3.65278	0.22303	-0.60724
O	-3.96374	-0.75870	-1.61226
O	-2.02438	1.19500	0.80729
O	-1.79442	-2.21223	-0.58627
O	1.50998	0.34143	1.34697
O	0.00159	2.04842	-0.00707
H	-1.55931	0.48077	-1.10481
H	-2.34956	-1.32859	1.21826
C	-0.48943	3.33544	-0.39736
C	1.84094	-0.55926	0.33189

H	-4.25385	-0.04107	0.26896
H	-3.93873	1.22942	-0.93628
H	-2.64511	-2.09909	-1.05134
H	-3.62359	-0.43808	-2.46012
O	0.66965	-1.09085	-0.19782
C	2.94618	-0.20939	-0.63426
C	3.31842	-1.48627	-1.41420
C	4.16681	0.27113	0.17256
C	2.52239	0.89444	-1.63257
H	-0.31109	-2.94977	1.31476
H	0.16920	3.68636	-1.19452
H	-0.45197	4.03689	0.44820
H	-1.51875	3.27473	-0.77019
H	-0.72760	2.24385	1.90604
H	-0.06534	0.14711	2.66660
H	3.62049	-2.28705	-0.73001
H	4.15356	-1.27431	-2.09096
H	2.47471	-1.84430	-2.01239
H	2.27815	1.81980	-1.10686
H	1.64320	0.58417	-2.20561
H	3.34226	1.09029	-2.33411
H	3.93907	1.18652	0.72718
H	4.99786	0.48077	-0.50974
H	4.49039	-0.49447	0.88660

[1,2-mig_TS2]•

Energy (Hartree/particle): -996.201092601
Zero-point correction= 0.324401 (Hartree/Particle)
Thermal correction to Energy= 0.344902
Thermal correction to Enthalpy= 0.345846
Thermal correction to Gibbs Free Energy= 0.276299
Sum of electronic and zero-point Energies= -995.876692
Sum of electronic and thermal Energies= -995.856191
Sum of electronic and thermal Enthalpies= -995.855247
Sum of electronic and thermal Free Energies= -995.924794

Number of imaginary frequencies: 1, -786.4869

Geometry:

C	0.52509	1.44539	-1.28392
C	0.01317	0.10049	-1.77960
C	0.41898	-1.14146	-1.01882
O	0.38429	-2.24453	-1.89409

C	1.78710	-1.02506	-0.33407
C	1.96726	0.35791	0.29871
C	3.36278	0.55939	0.89456
O	3.64914	-0.38444	1.94246
O	1.85235	1.33571	-0.74657
O	1.92910	-2.10785	0.57836
O	-1.67454	-0.12158	-1.51550
O	-0.36581	1.98688	-0.34393
H	1.20291	0.52419	1.07009
H	2.53392	-1.10365	-1.14191
C	-0.05155	3.33010	0.03776
C	-1.74209	-0.66187	-0.33168
H	4.11864	0.38995	0.12092
H	3.45846	1.59046	1.25574
H	2.66801	-1.86465	1.16871
H	3.13608	-0.13118	2.72359
O	-0.60180	-1.32996	0.02064
C	-2.66924	-0.24112	0.79836
C	-1.87677	0.26703	2.02395
C	-3.49093	-1.48315	1.21965
C	-3.61946	0.85571	0.29661
H	0.72715	-3.00664	-1.40091
H	-0.87541	3.67042	0.66870
H	0.02513	3.97680	-0.84807
H	0.88774	3.37729	0.60090
H	0.64773	2.13572	-2.12968
H	0.07762	-0.00502	-2.85677
H	-3.06242	1.75192	0.01176
H	-4.32419	1.11641	1.09366
H	-4.19409	0.51568	-0.57132
H	-4.08874	-1.85728	0.38123
H	-4.16870	-1.22052	2.04053
H	-2.83324	-2.28926	1.56173
H	-1.27640	1.14033	1.76173
H	-1.21066	-0.51016	2.40932
H	-2.57729	0.54524	2.82007

[Piv-C3_rad-C2]•

Energy (Hartree/particle): -996.246654150

Zero-point correction= 0.324191 (Hartree/Particle)
Thermal correction to Energy= 0.345911
Thermal correction to Enthalpy= 0.346855

Thermal correction to Gibbs Free Energy= 0.273535
Sum of electronic and zero-point Energies= -995.922464
Sum of electronic and thermal Energies= -995.900743
Sum of electronic and thermal Enthalpies= -995.899799
Sum of electronic and thermal Free Energies= -995.973119

Number of imaginary frequencies: 0

Geometry:

C	-1.14392	1.80198	0.88851
C	-0.51519	0.81147	1.80505
C	-0.33684	-0.58034	1.33691
O	0.01385	-1.42518	2.39296
C	-1.63105	-1.04670	0.63841
C	-2.07109	-0.01047	-0.40901
C	-3.40218	-0.37752	-1.07087
O	-3.32495	-1.62613	-1.78327
O	-2.30371	1.24549	0.24435
O	-1.42633	-2.34989	0.11224
O	2.22269	0.49890	1.46840
O	-0.18658	2.24889	-0.05455
H	-1.29048	0.09359	-1.17491
H	-2.40309	-1.06412	1.42596
C	-0.63425	3.35985	-0.84181
C	1.90502	-0.10350	0.46217
H	-4.17030	-0.51415	-0.30303
H	-3.71425	0.43636	-1.73624
H	-2.11056	-2.47855	-0.57383
H	-2.81807	-1.47795	-2.59480
O	0.69878	-0.67610	0.26561
C	2.82365	-0.34122	-0.74823
C	2.12530	0.14410	-2.03370
C	3.11009	-1.85551	-0.84597
C	4.13640	0.42640	-0.54656
H	-0.10563	-2.33565	2.07710
H	0.21404	3.66267	-1.45955
H	-0.93677	4.19762	-0.19700
H	-1.47574	3.07803	-1.48575
H	-1.54660	2.65925	1.44543
H	-0.23796	1.08723	2.81290
H	1.86677	1.20537	-1.96236
H	1.21019	-0.42124	-2.22610
H	2.80295	0.00960	-2.88403
H	3.58266	-2.22629	0.07042
H	3.79362	-2.04113	-1.68179
H	2.18991	-2.42055	-1.01696

H	3.95512	1.50237	-0.46151
H	4.79237	0.25341	-1.40632
H	4.65603	0.09511	0.35714

[C3-keto C2-rad]$^{\bullet}$

Energy (Hartree/particle): -649.290357350

Zero-point correction= 0.178895 (Hartree/Particle)
Thermal correction to Energy= 0.191337
Thermal correction to Enthalpy= 0.192282
Thermal correction to Gibbs Free Energy= 0.139371
Sum of electronic and zero-point Energies= -649.111462
Sum of electronic and thermal Energies= -649.099020
Sum of electronic and thermal Enthalpies= -649.098076
Sum of electronic and thermal Free Energies= -649.150986

Number of imaginary frequencies: 0

Geometry:

C	-1.66657	0.22789	0.51461
C	-1.09400	1.59286	0.31609
C	0.30320	1.82577	0.09007
O	0.72920	2.94187	-0.24458
C	1.23946	0.62881	0.27248
C	0.48380	-0.69657	0.04191
C	1.30653	-1.92609	0.43500
O	2.53813	-2.01358	-0.30184
O	-0.67287	-0.71546	0.89182
O	2.36636	0.77331	-0.57256
O	-2.33486	-0.12412	-0.68034
H	0.18523	-0.76835	-1.01373
H	1.53752	0.63979	1.33958
C	-3.19731	-1.26535	-0.53494
H	1.58785	-1.85115	1.49051
H	0.69951	-2.82930	0.29812
H	2.81445	-0.09448	-0.55336
H	2.33302	-2.32768	-1.19430
H	-3.68734	-1.40509	-1.50044
H	-3.95409	-1.08204	0.24017
H	-2.62211	-2.16271	-0.27952
H	-2.37695	0.22361	1.35704
H	-1.77537	2.43734	0.26464

[PivOH]

Energy (Hartree/particle): -346.967917559

Zero-point correction= 0.143058 (Hartree/Particle)
Thermal correction to Energy= 0.151479
Thermal correction to Enthalpy= 0.152424
Thermal correction to Gibbs Free Energy= 0.110516
Sum of electronic and zero-point Energies= -346.824860
Sum of electronic and thermal Energies= -346.816438
Sum of electronic and thermal Enthalpies= -346.815494
Sum of electronic and thermal Free Energies= -346.857402

Number of imaginary frequencies: 0

Geometry:

C	-0.94719	0.18811	-0.00003
C	0.56957	-0.01215	-0.00000
C	0.97057	-0.80393	1.26345
C	1.26245	1.35633	-0.00022
C	0.97061	-0.80436	-1.26319
O	-1.52580	1.25692	-0.00003
O	-1.62433	-0.99099	-0.00001
H	-2.57403	-0.77455	0.00002
H	0.66997	-0.27216	2.17275
H	2.05937	-0.92156	1.28117
H	0.51476	-1.79733	1.27323
H	0.99149	1.93786	0.88600
H	0.99152	1.93758	-0.88663
H	2.34770	1.21138	-0.00017
H	0.51477	-1.79775	-1.27264
H	2.05940	-0.92202	-1.28082
H	0.67005	-0.27288	-2.17267

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^{1}H, ^{13}C and 2D NMR Spectra

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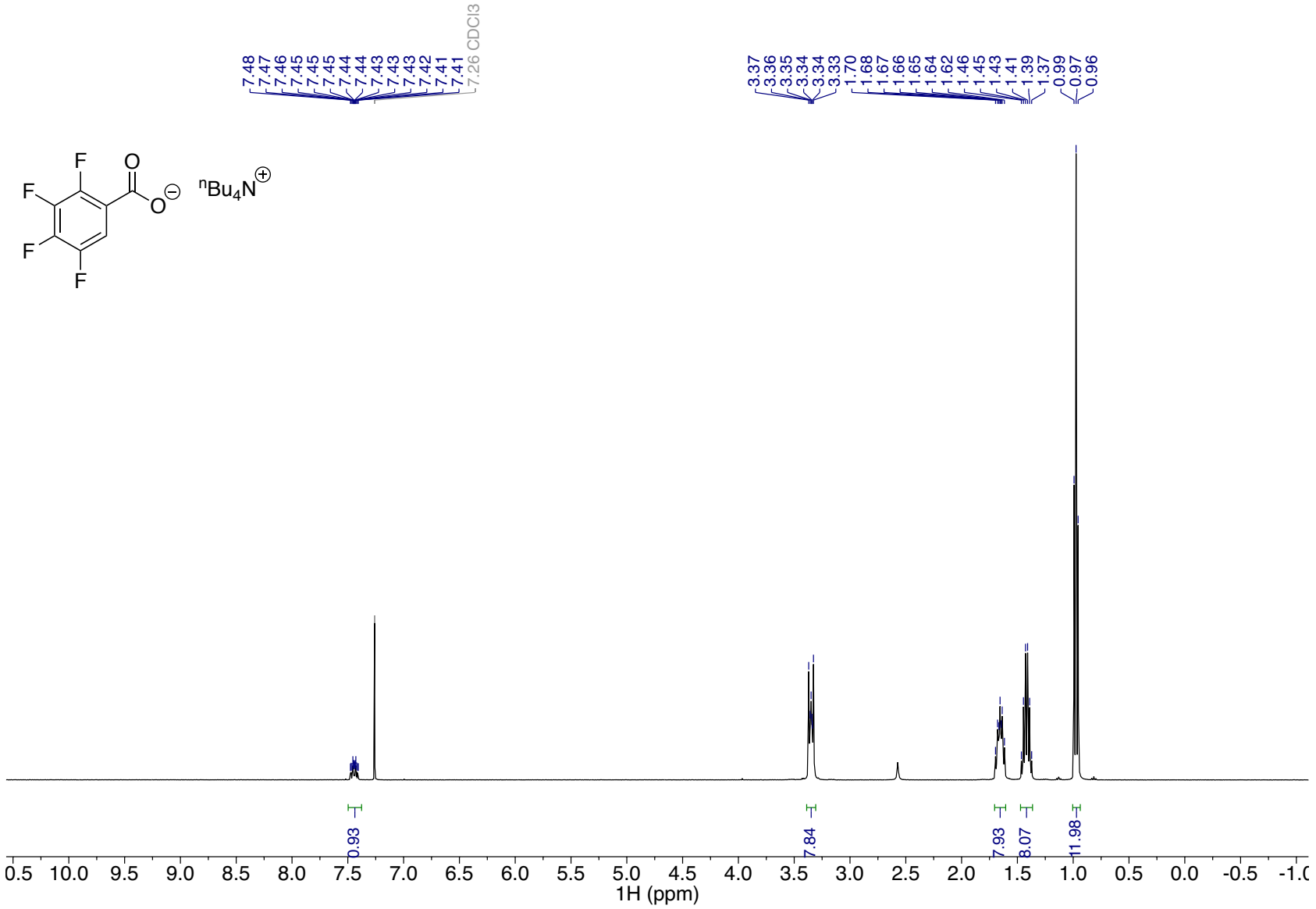
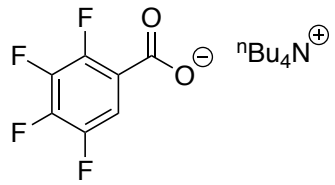
Tetrabutylammonium 2,3,4,5-tetrafluorobenzoate

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



Tetrabutylammonium 3,4,5-trifluorobenzoate

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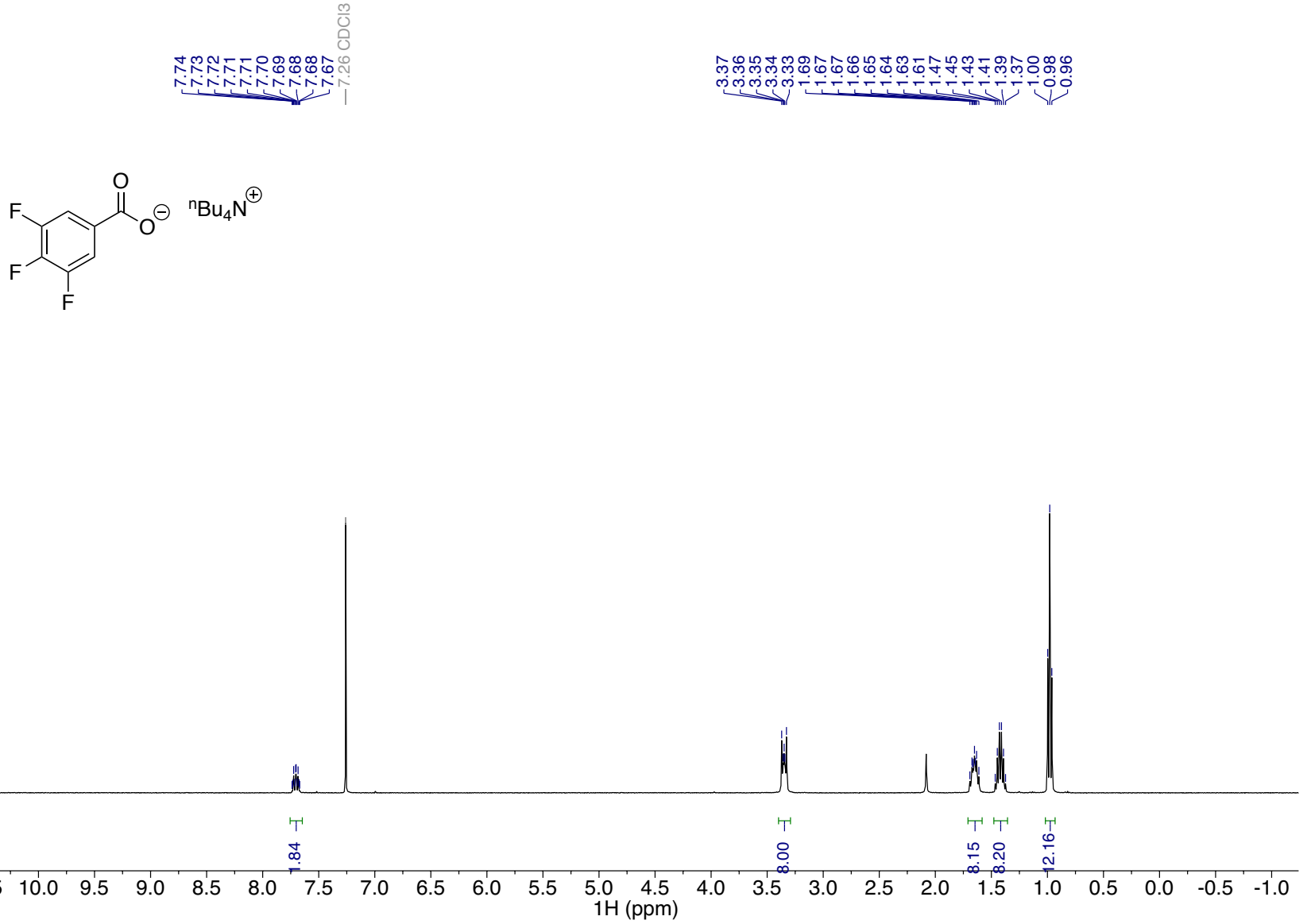

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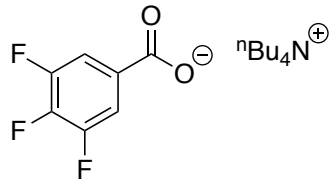
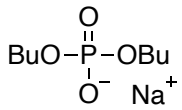


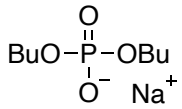
$^{n}Bu_4N^{\oplus}$

Sodium dibutylphosphate

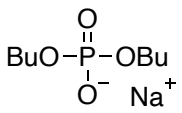
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

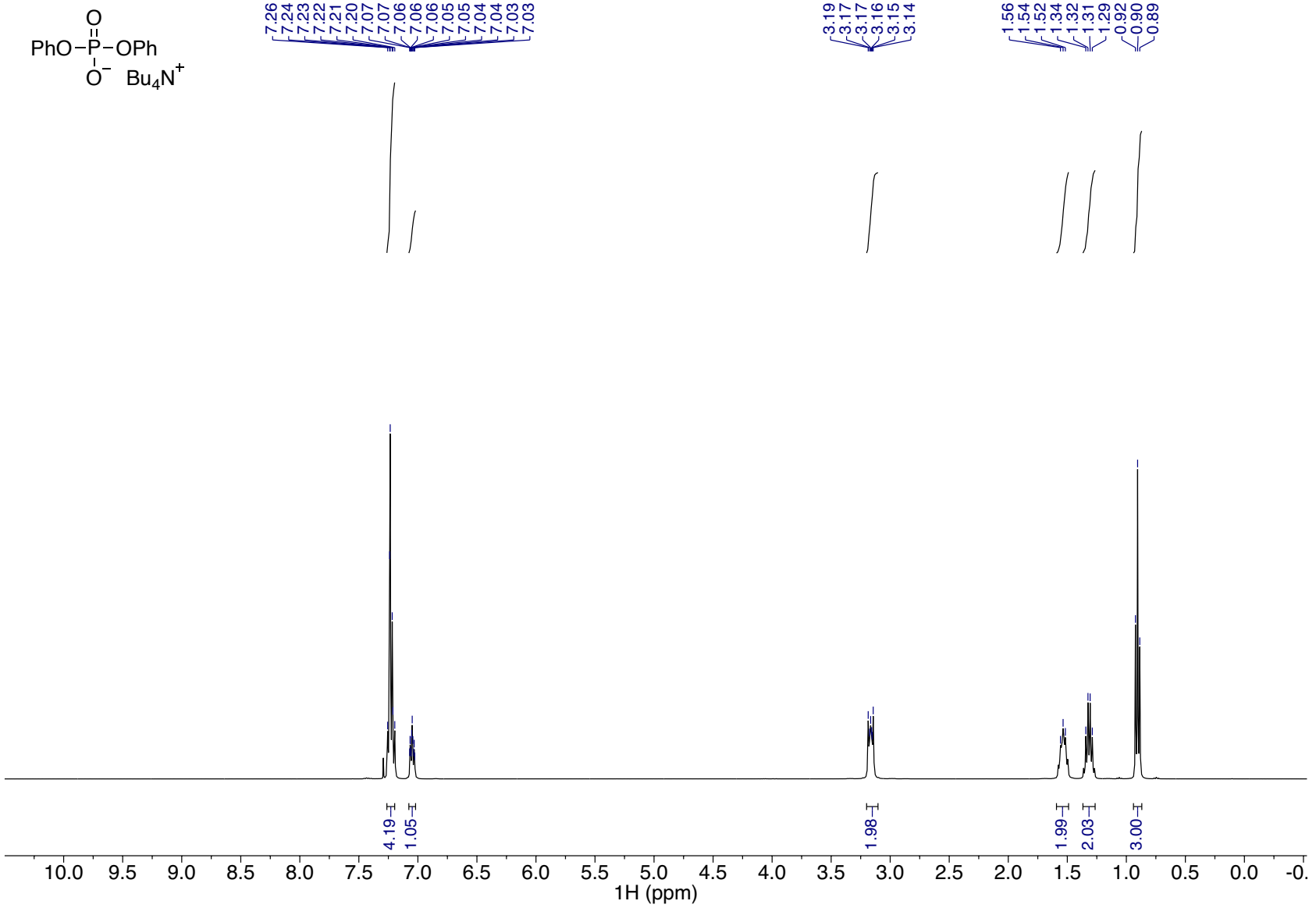


^{31}P NMR (121 MHz, $CDCl_3$)

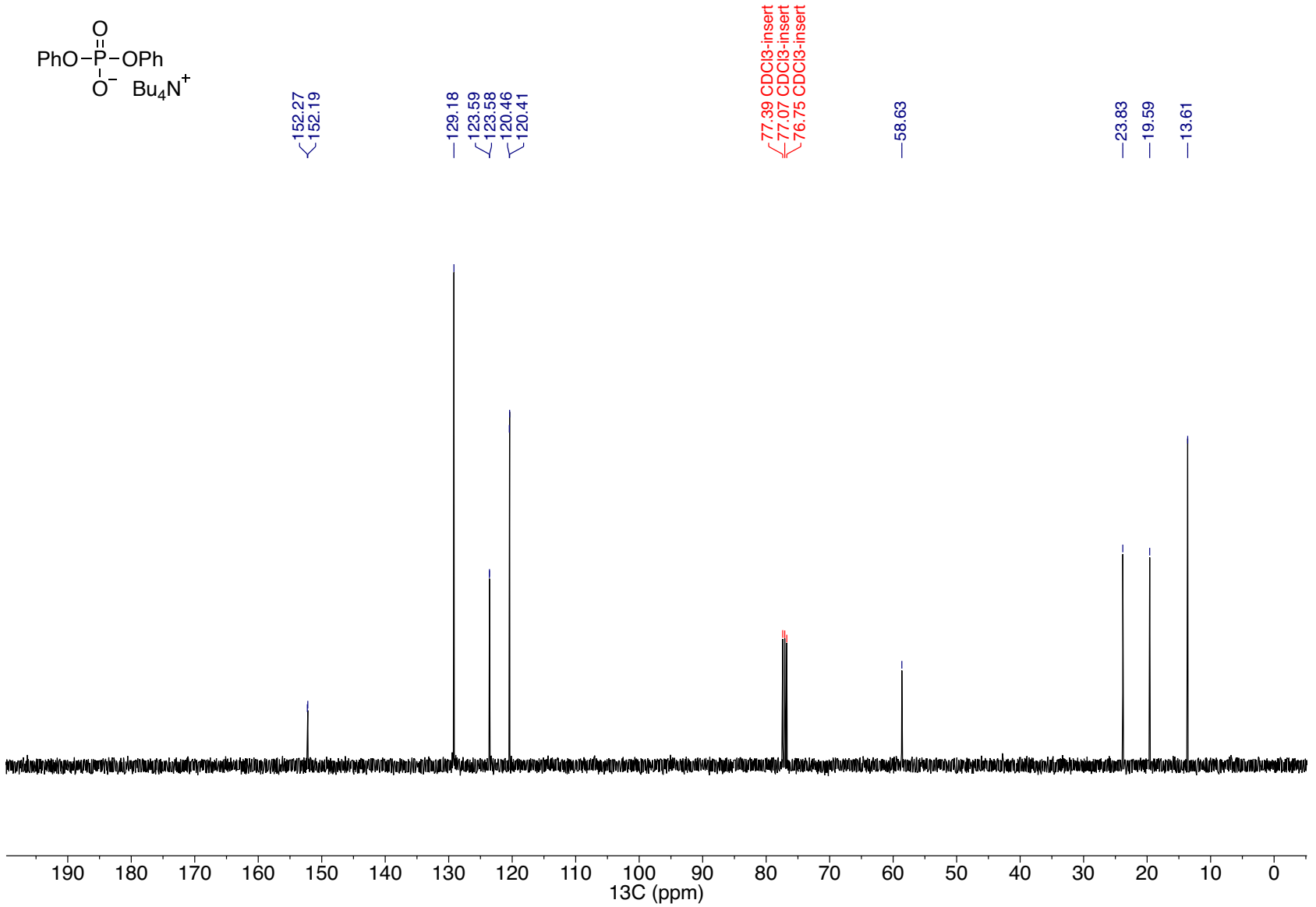


Tetrabutylammonium diphenylphosphate

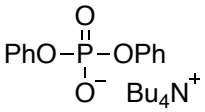
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

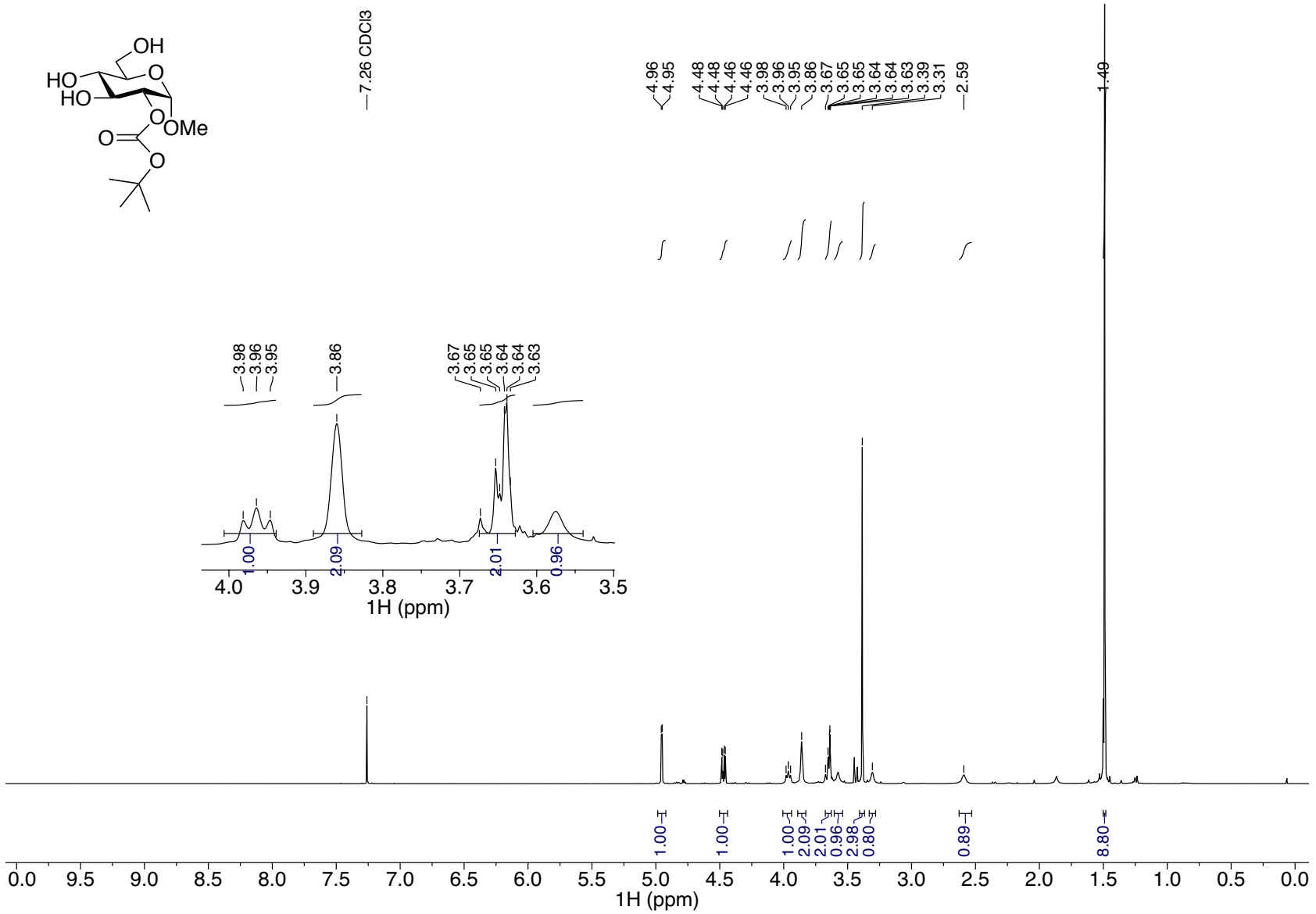


^{31}P NMR (121 MHz, $CDCl_3$)

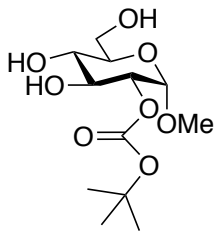


3b – Methyl 2-*O*-(*tert*-butyloxycarbonyl)*α*-D-glucopyranoside

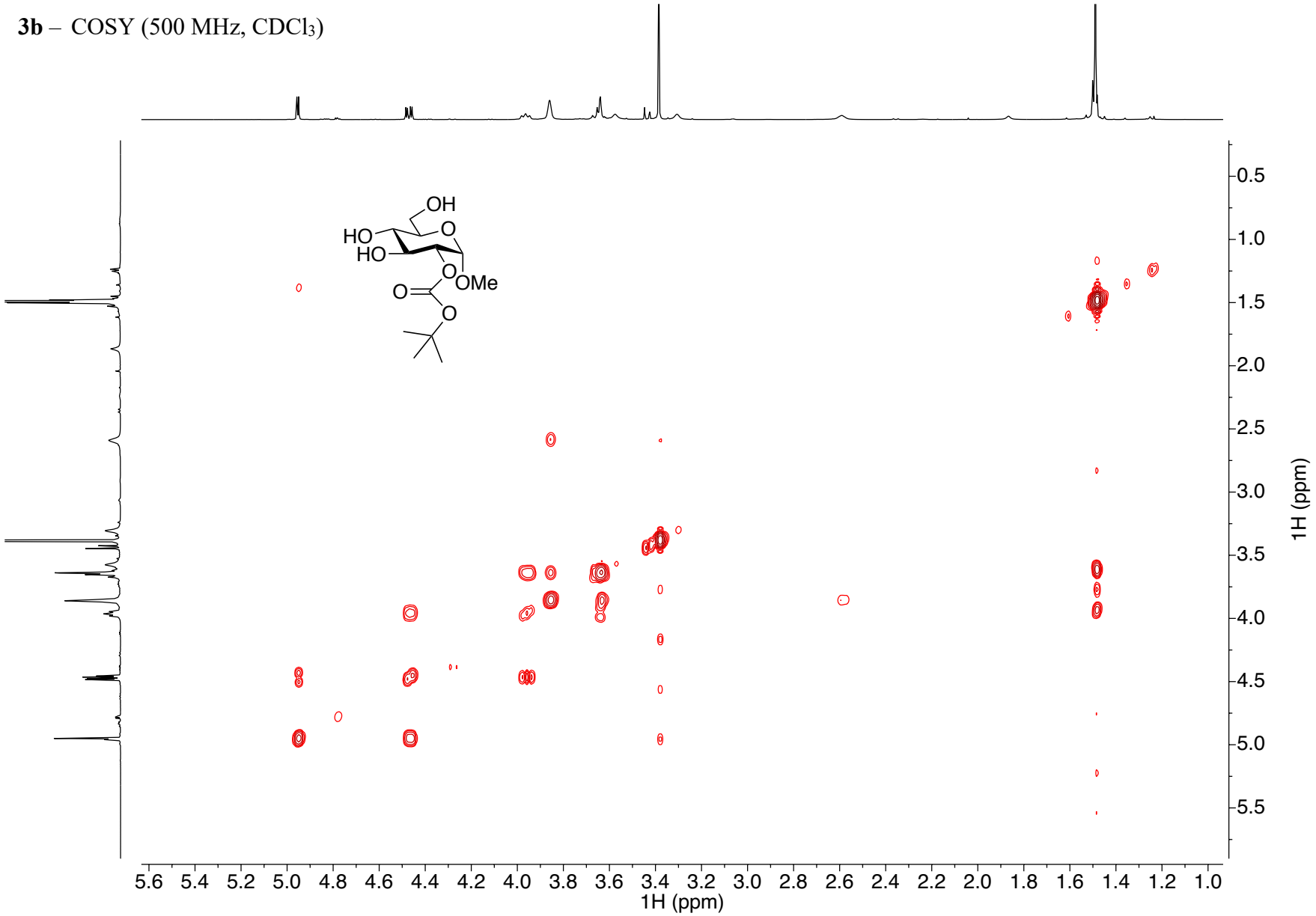
^{1}H NMR (500 MHz, $CDCl_3$)



3b – ^{13}C NMR (125 MHz, $CDCl_3$)

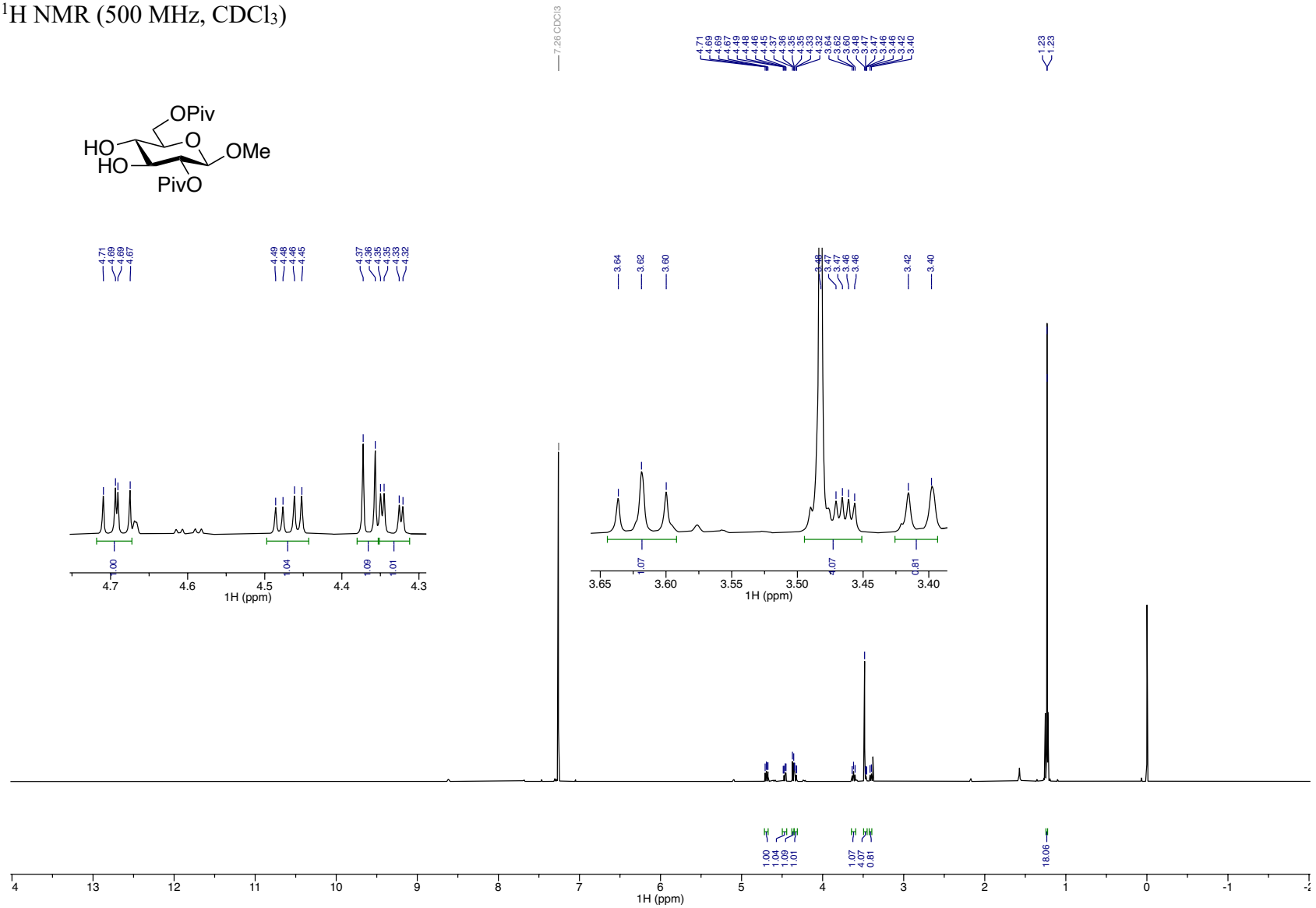


3b – COSY (500 MHz, $CDCl_3$)

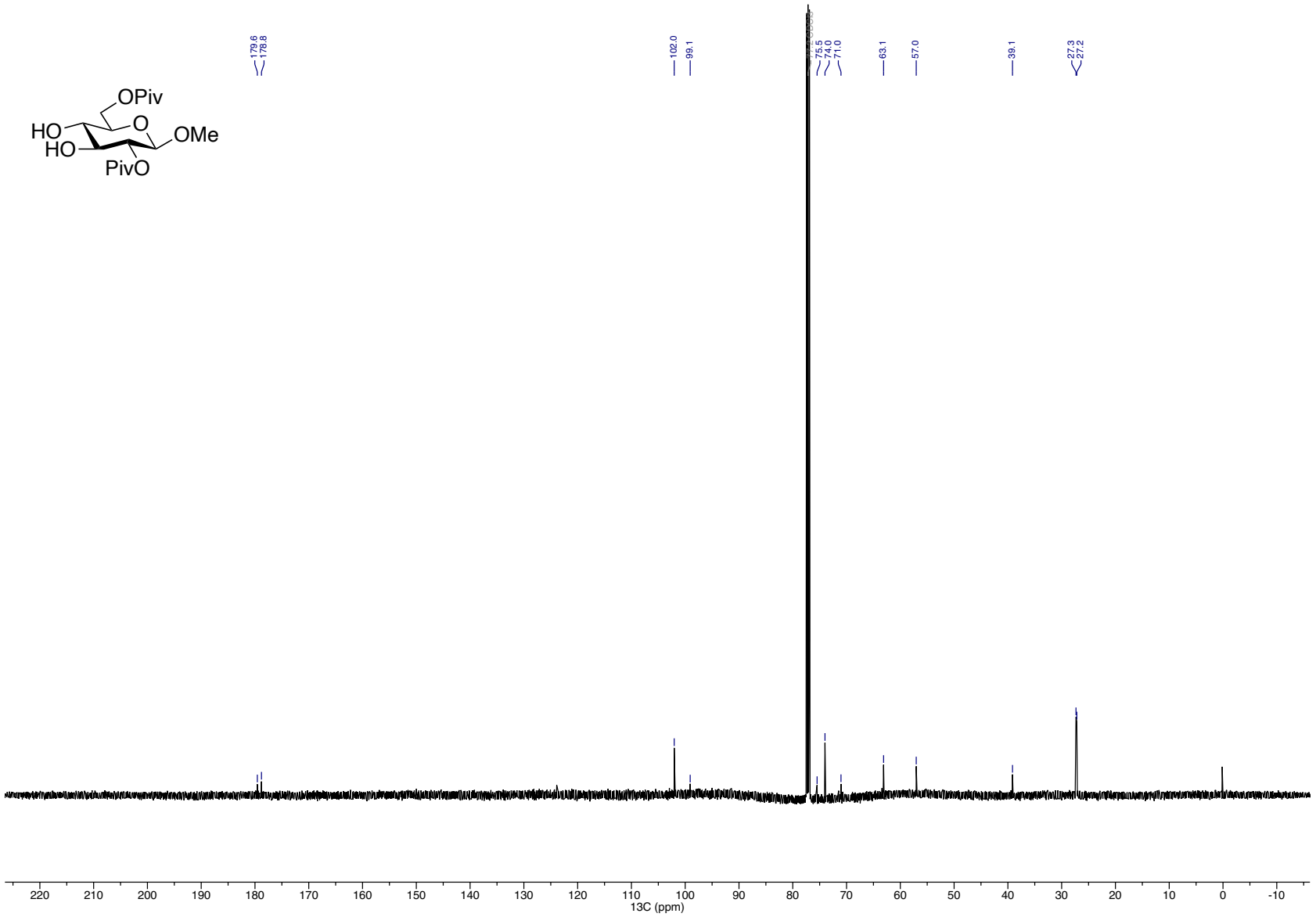


2c – Methyl 2,6-O-trimethylacteyl-β-D-glucopyranoside

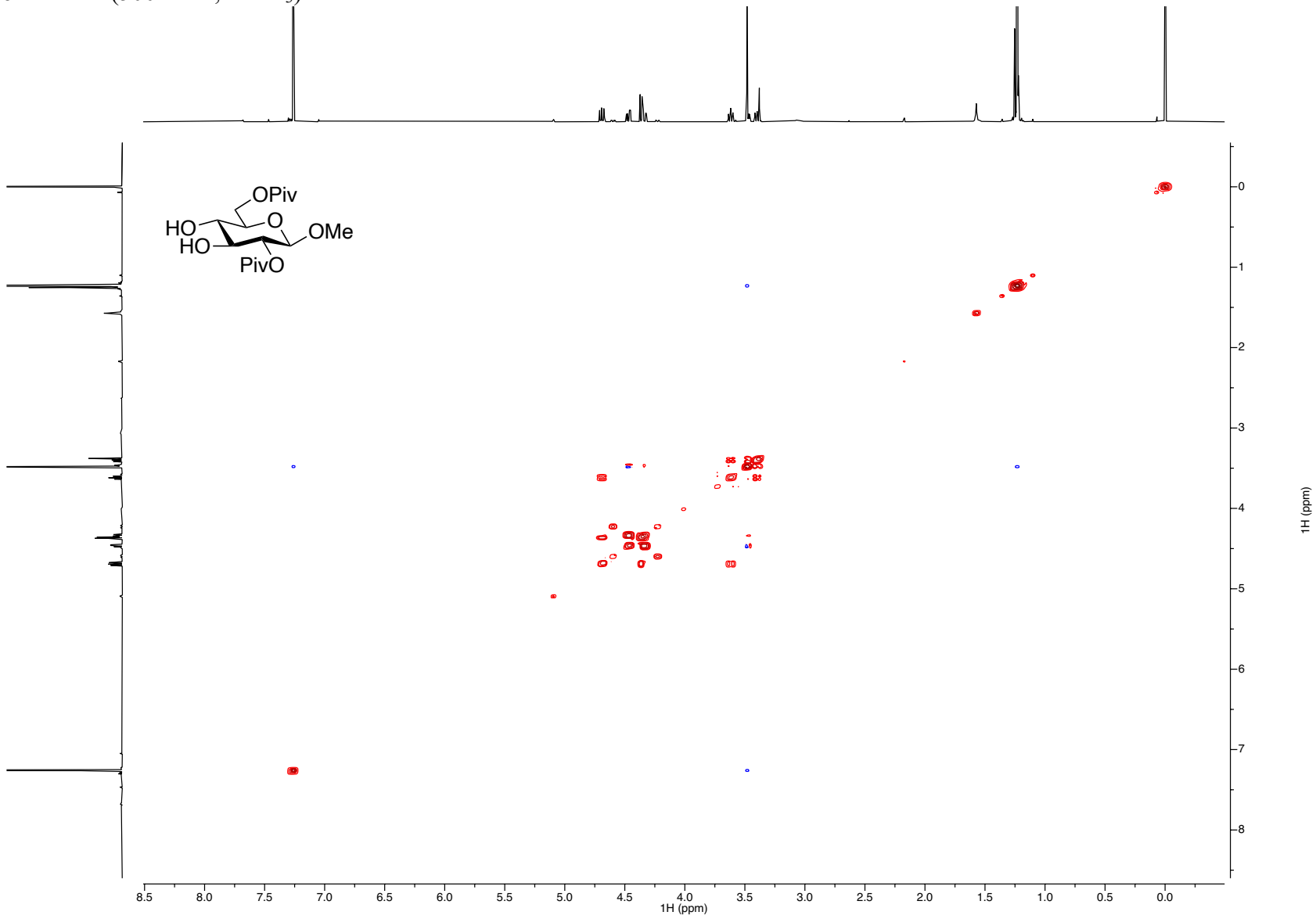
^{1}H NMR (500 MHz, $CDCl_3$)



2c – ^{13}C NMR (125 MHz, $CDCl_3$)

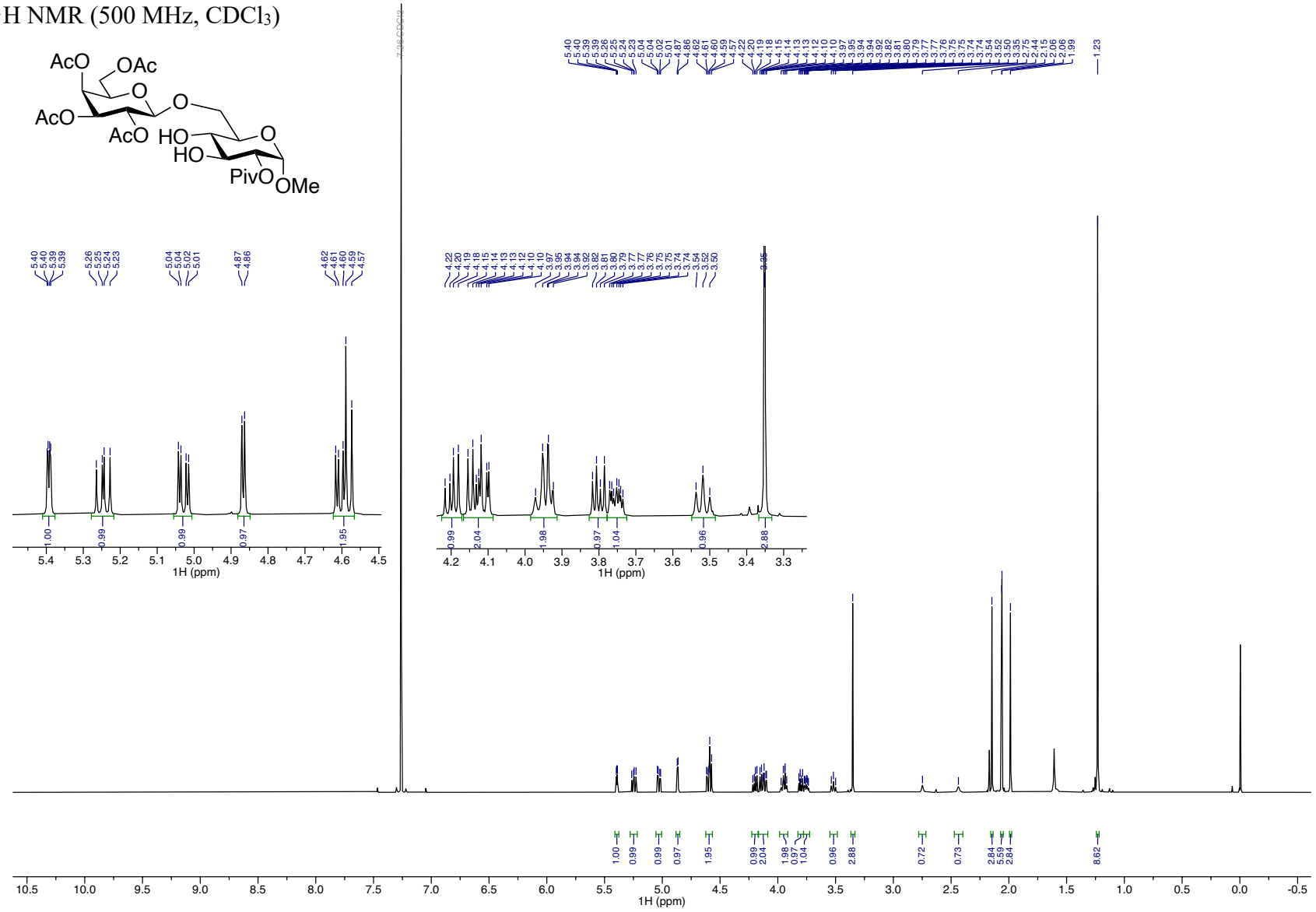


2c – COSY (500 MHz, $CDCl_3$)

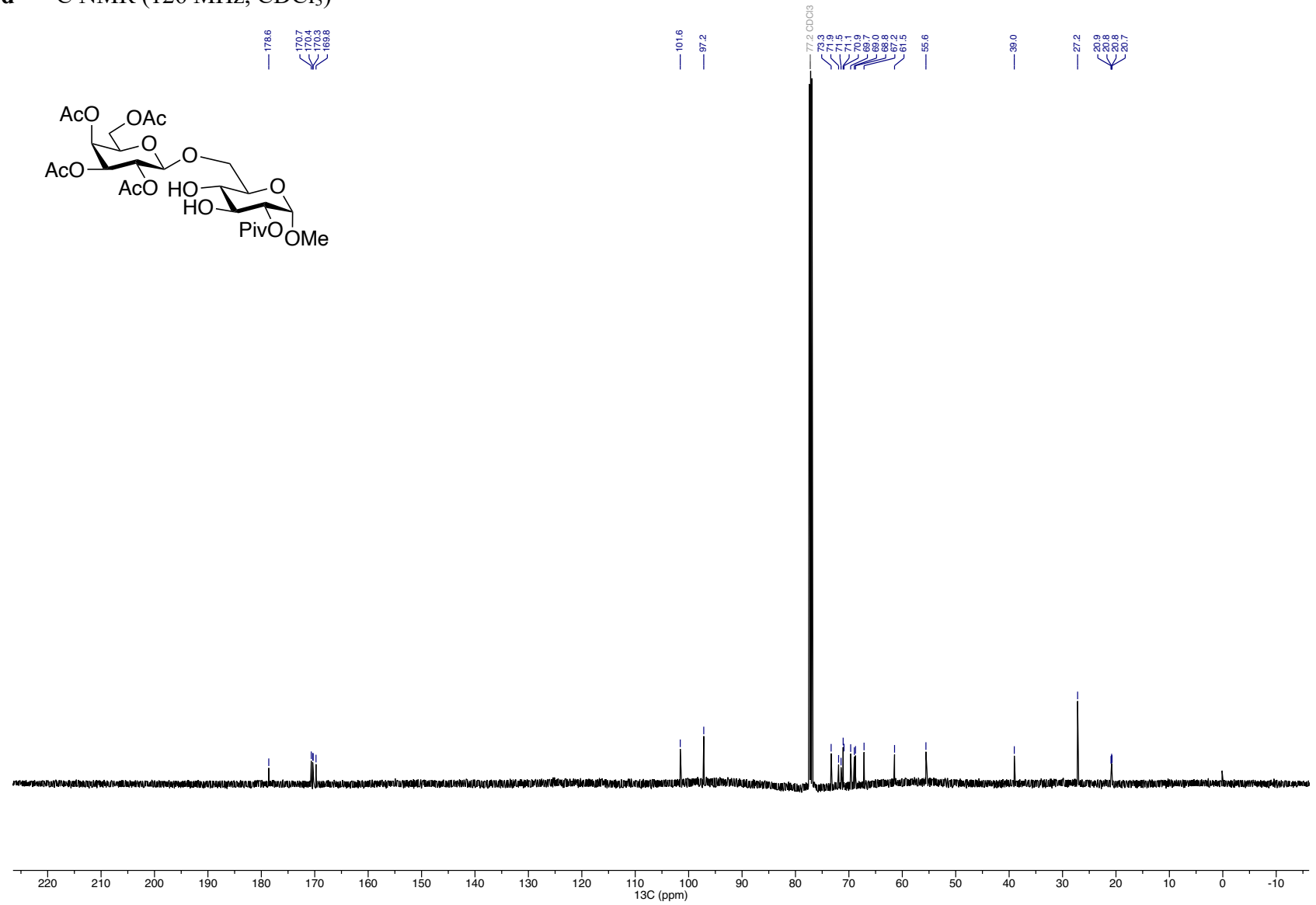


2d – Methyl 2-O-Trimethylacetyl-6-O-(2′,3′,4′,6′-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyranoside

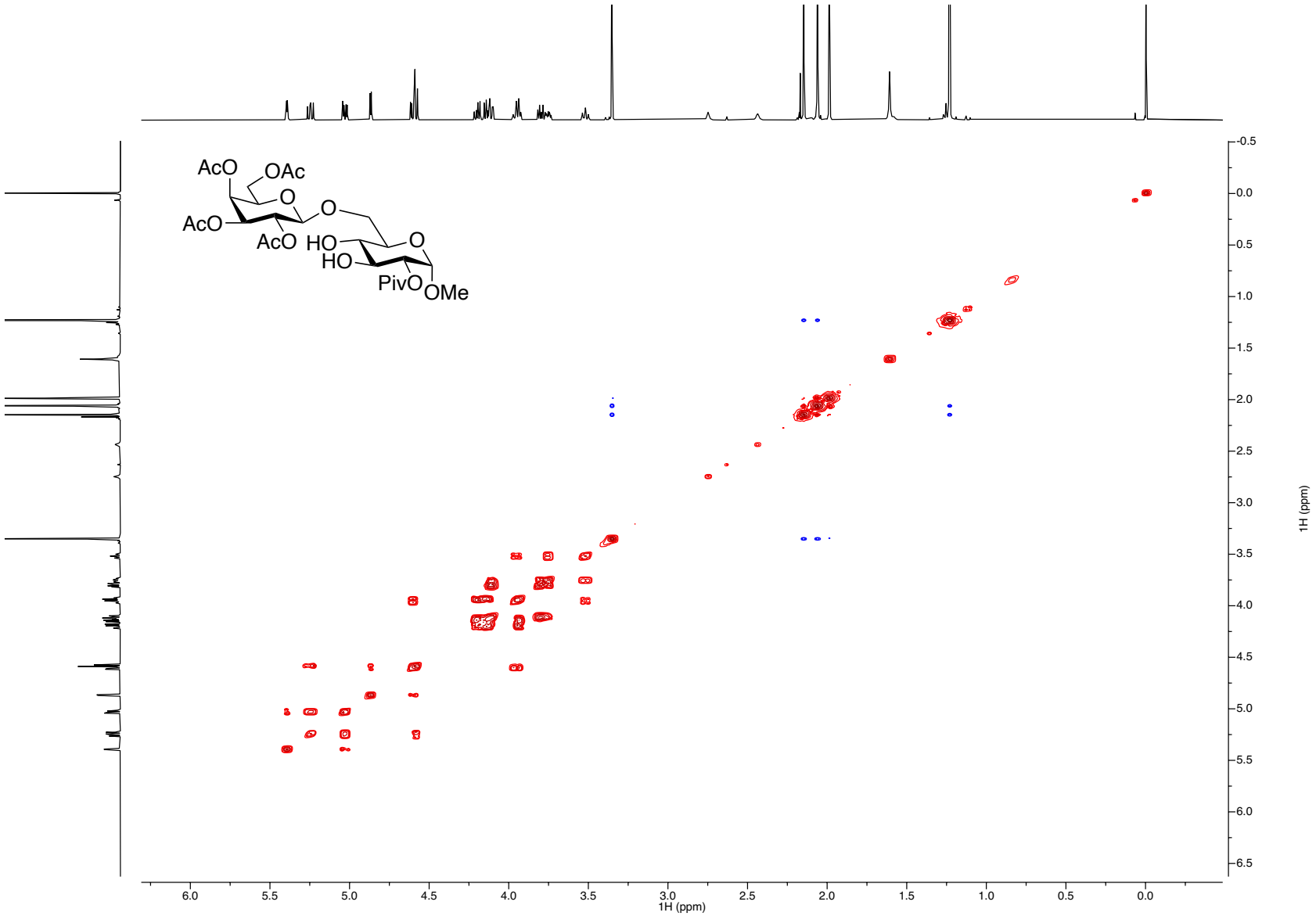
^{1}H NMR (500 MHz, $CDCl_3$)



2d – ^{13}C NMR (126 MHz, $CDCl_3$)

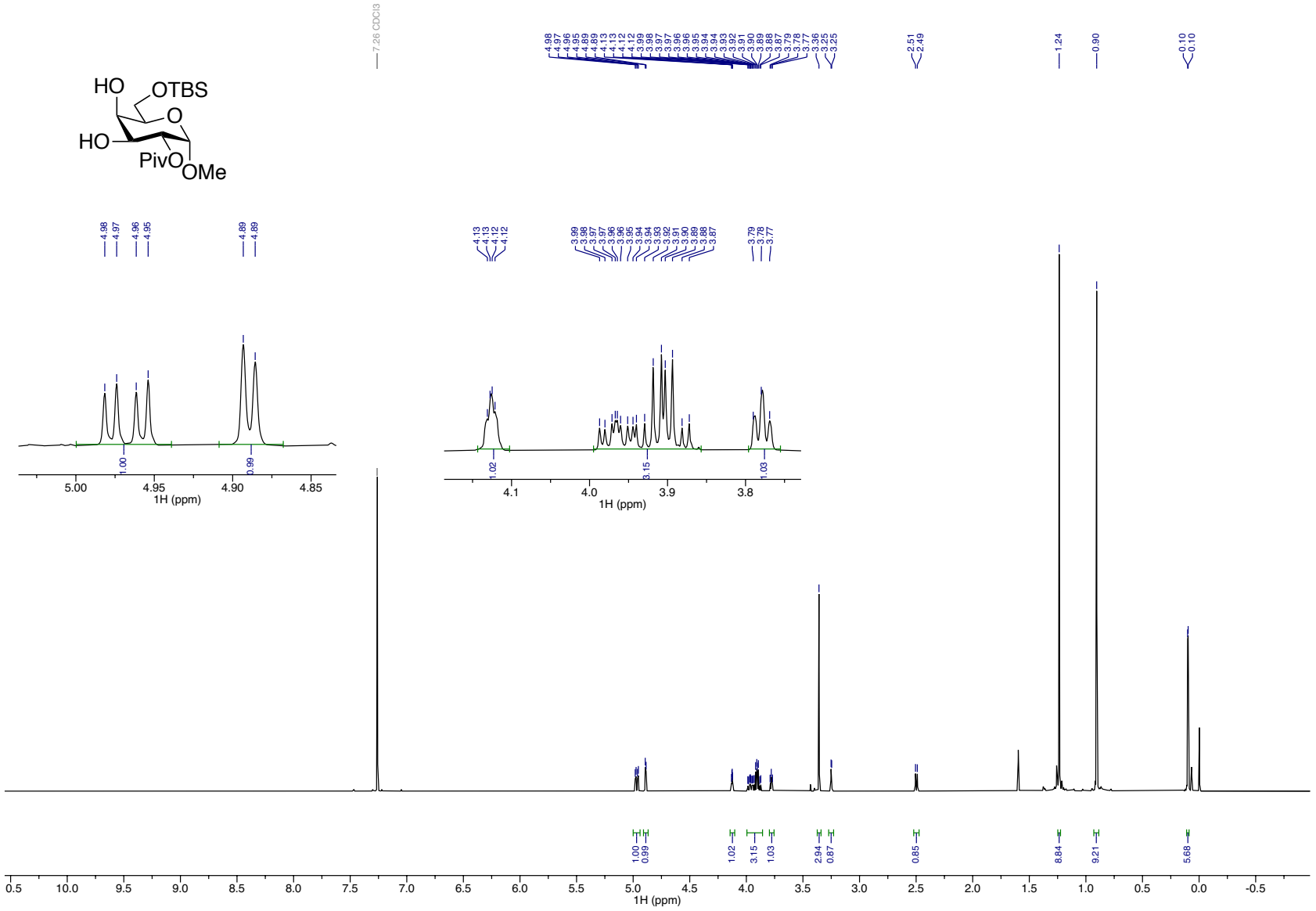


2d – COSY (500 MHz, $CDCl_3$)

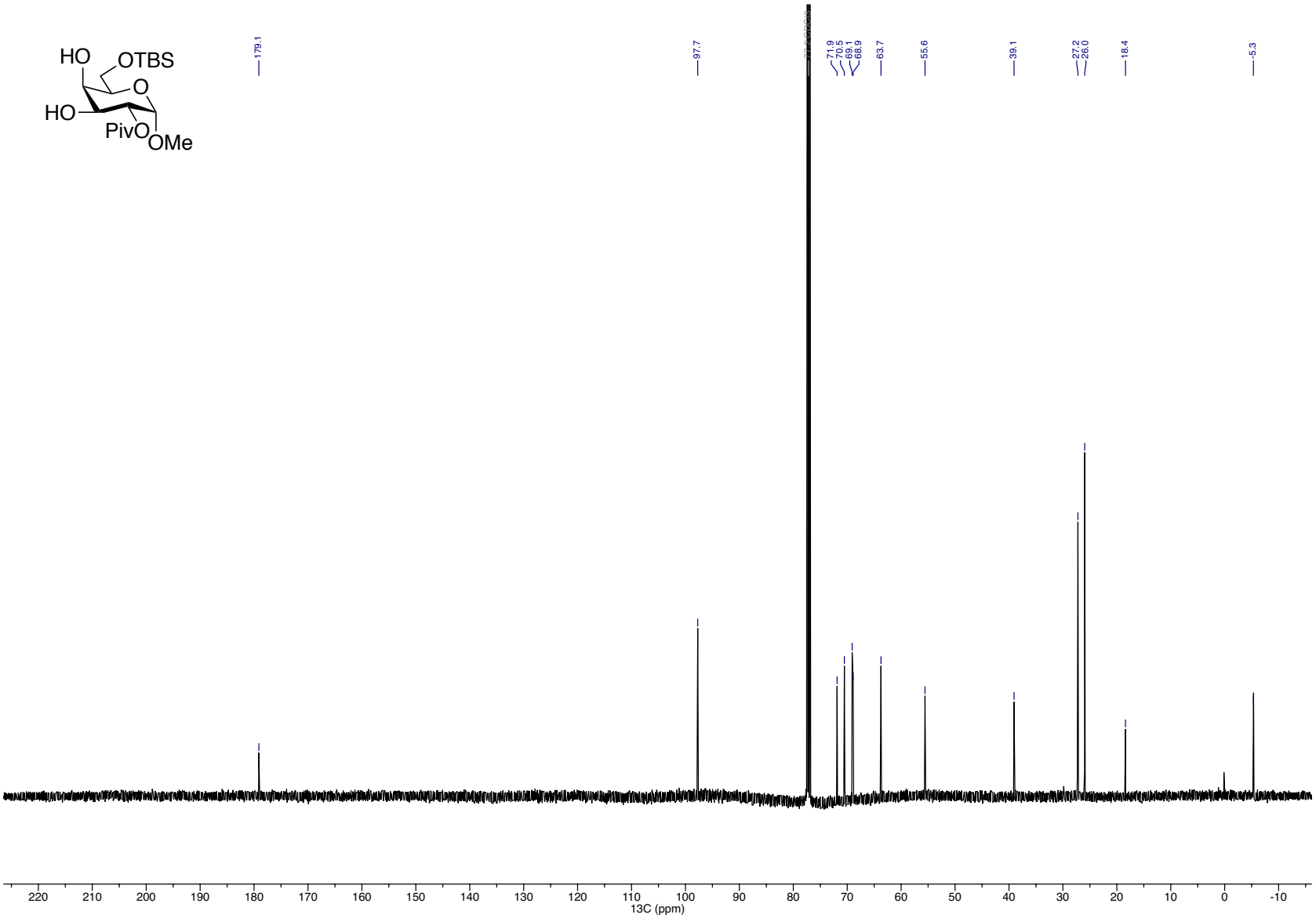


2e – Methyl 2-*O*-trimethylacetyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-galactopyranoside

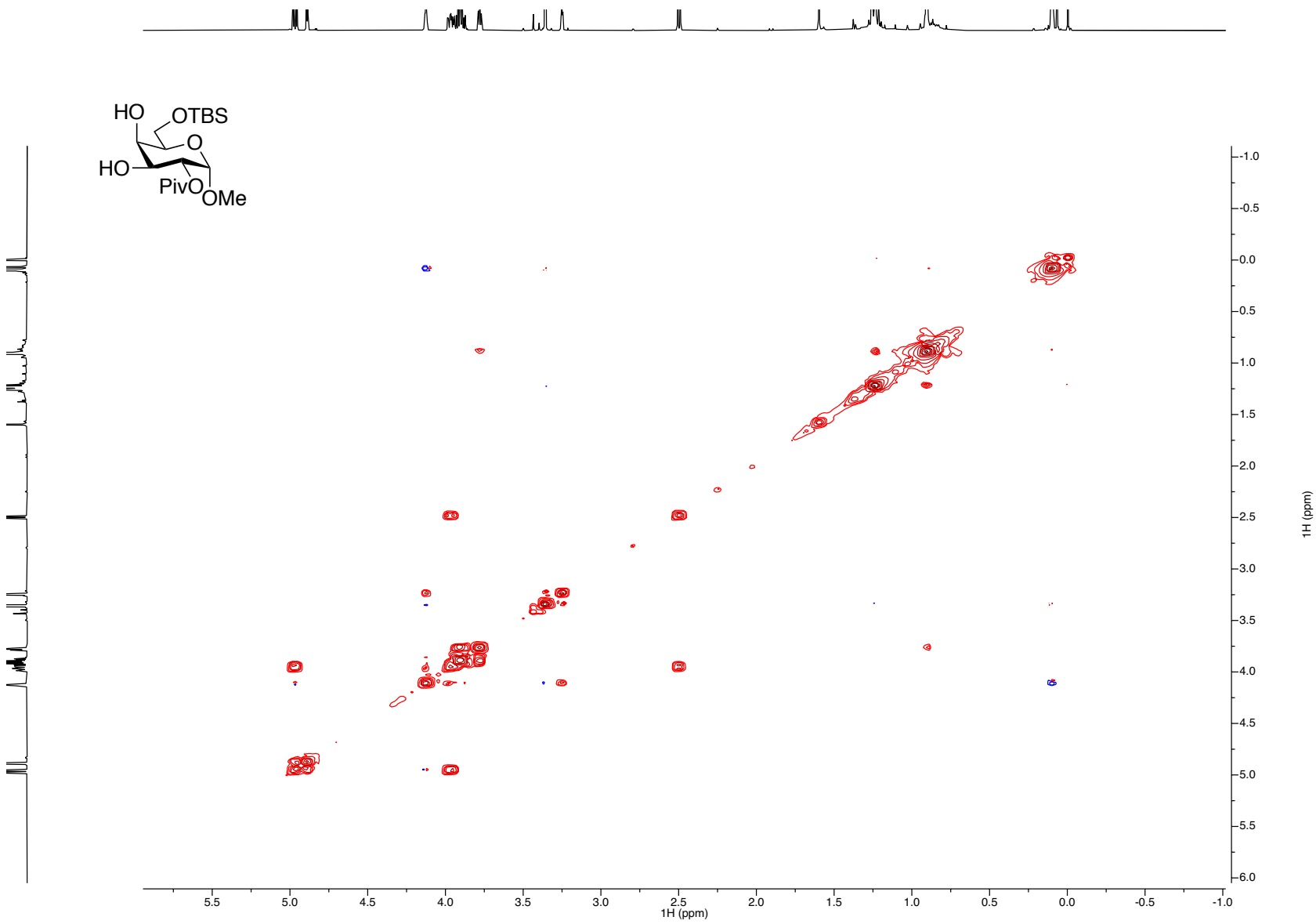
^{1}H NMR (500 MHz, $CDCl_3$)



2e – ^{13}C NMR (125 MHz, $CDCl_3$)

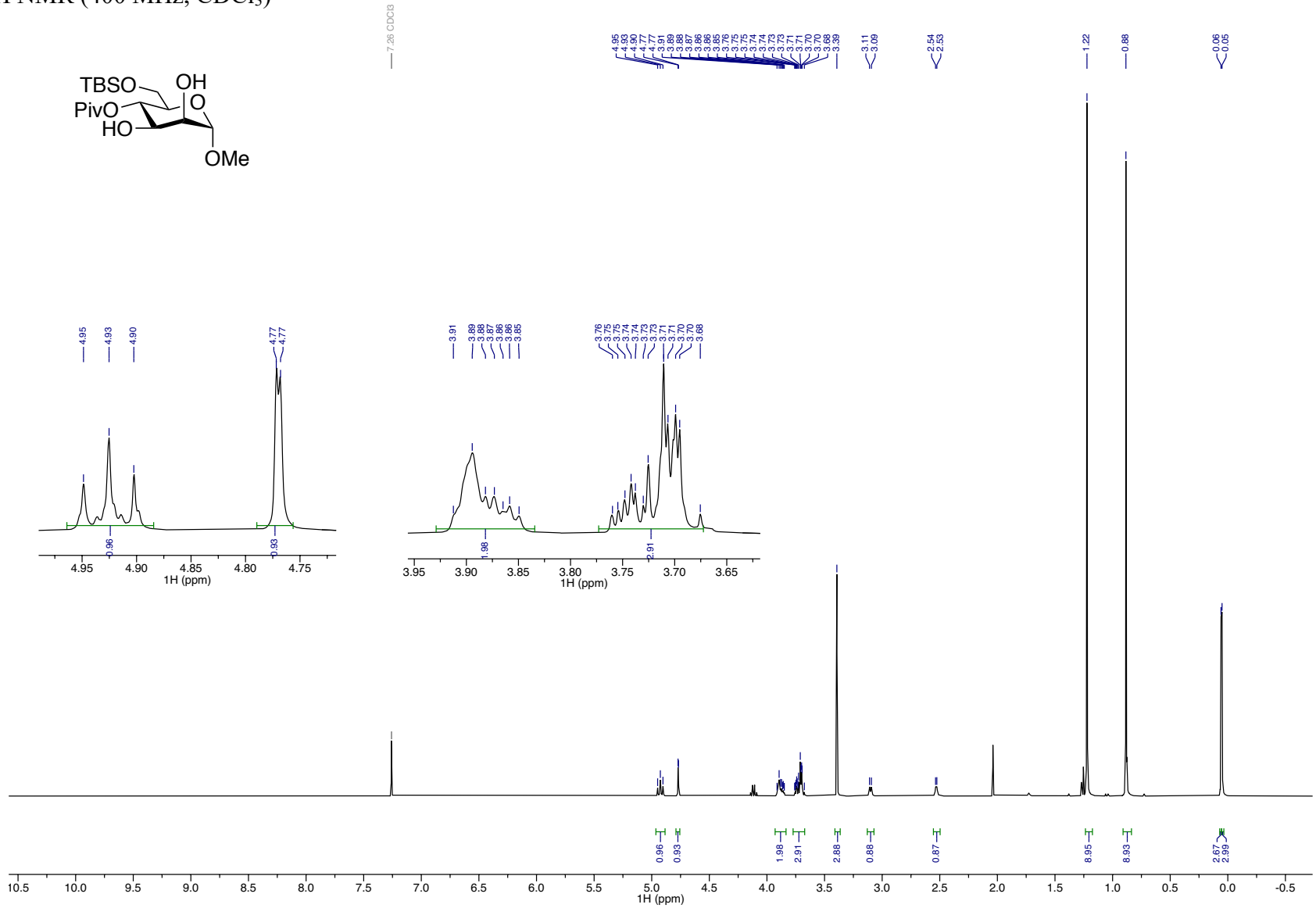


2e –COSY (500 MHz, $CDCl_3$)

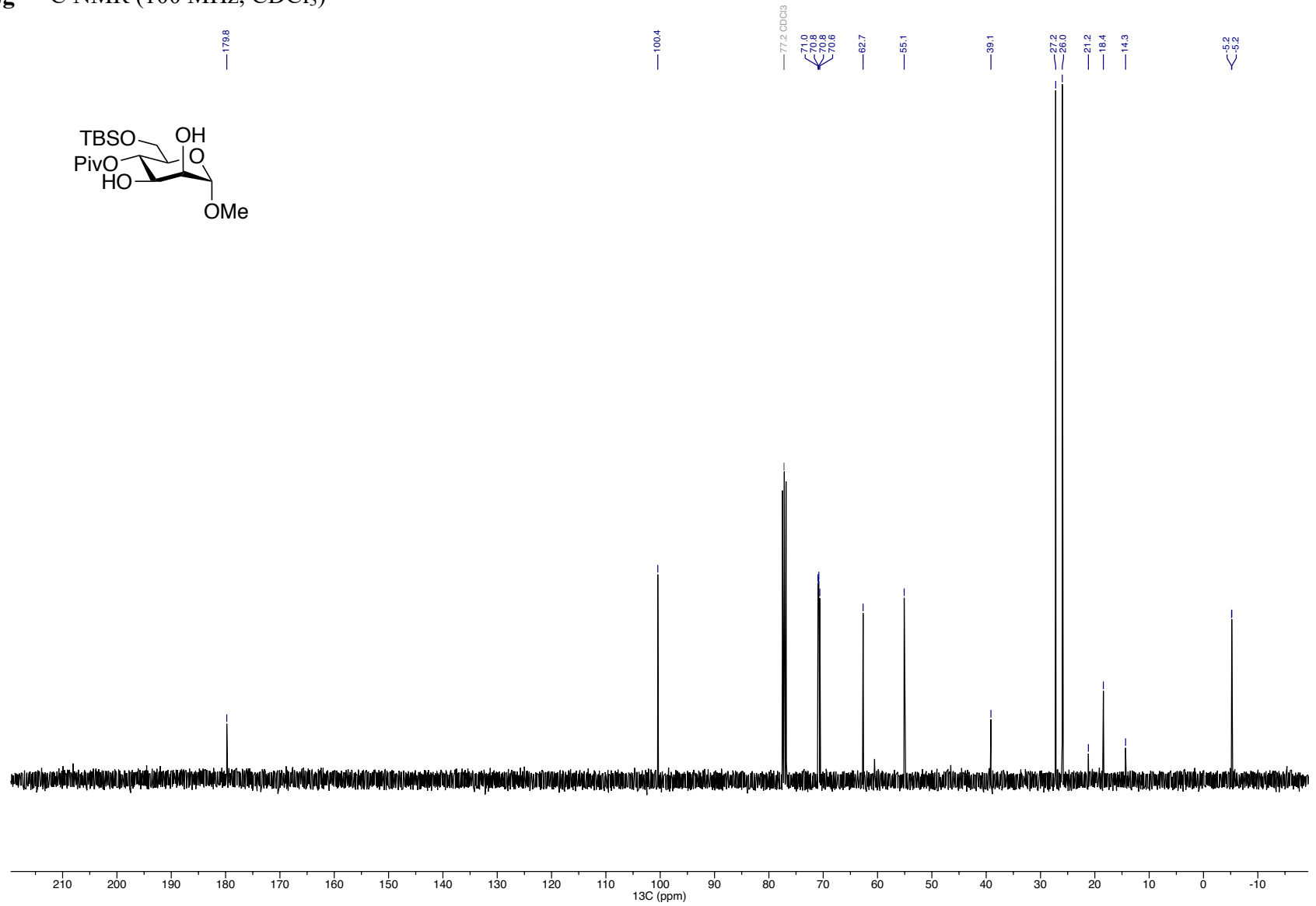


2g – Methyl 4-*O*-trimethylacetyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-mannopyranoside

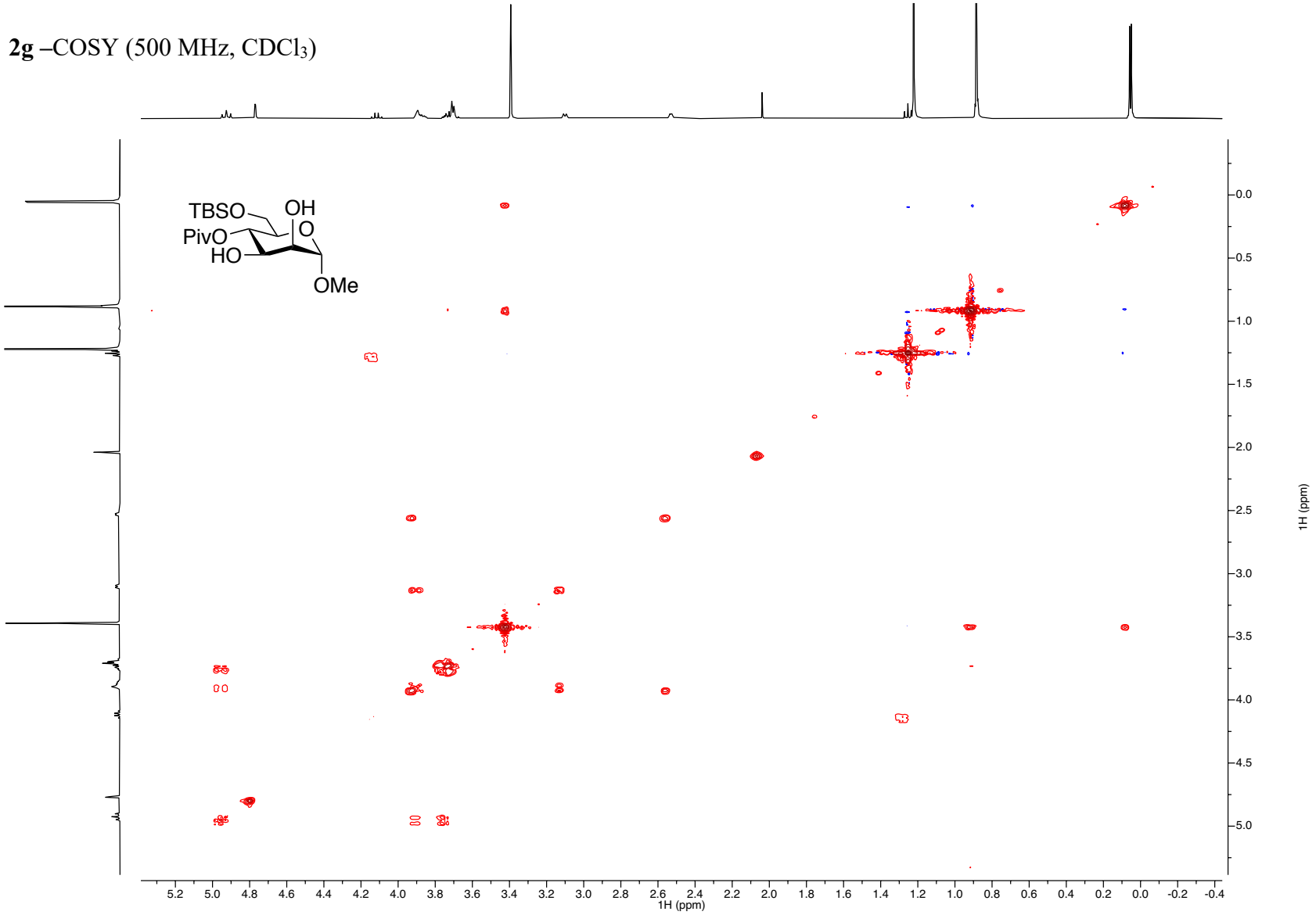
^{1}H NMR (400 MHz, $CDCl_3$)



2g – ^{13}C NMR (100 MHz, $CDCl_3$)

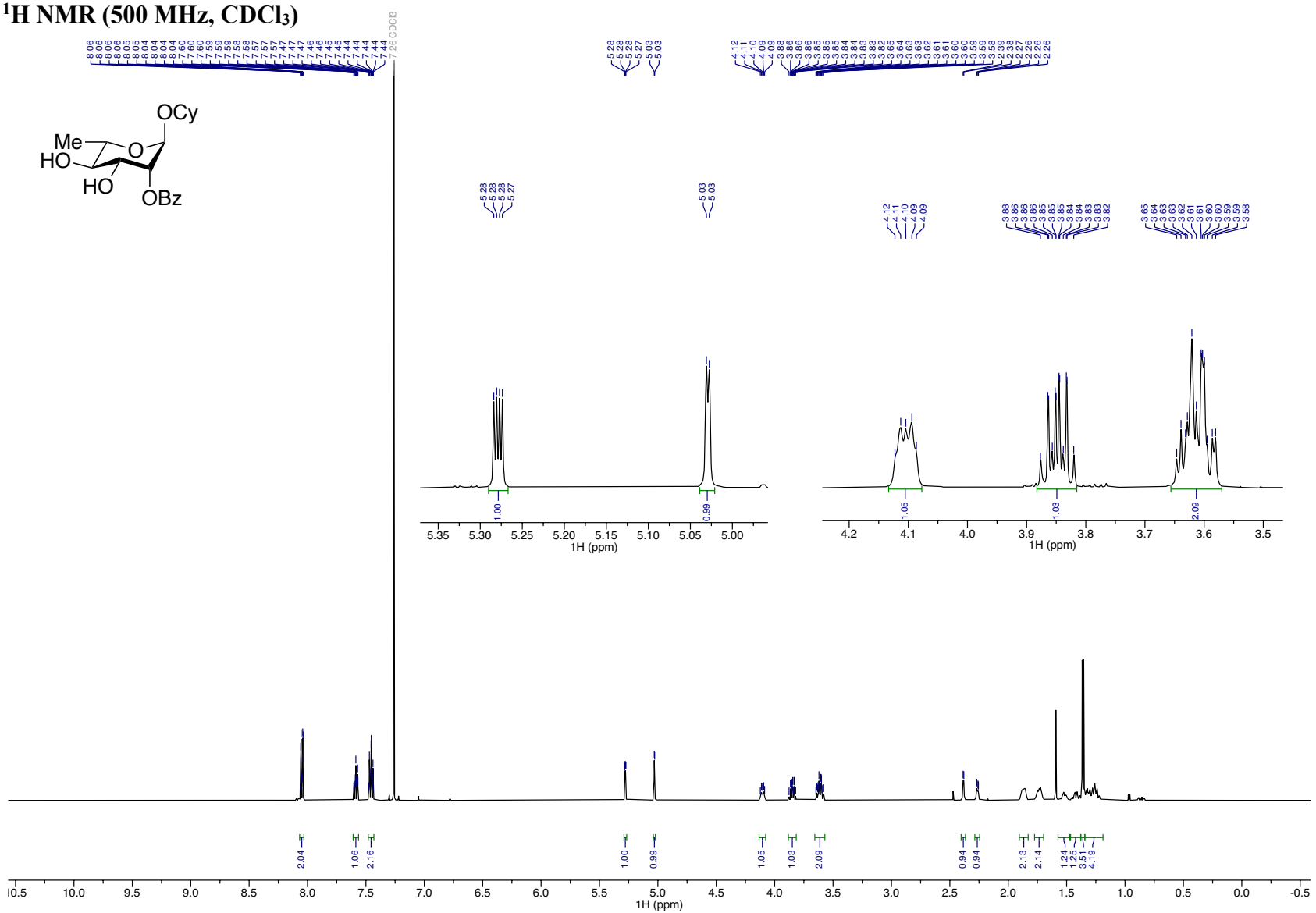


2g –COSY (500 MHz, $CDCl_3$)

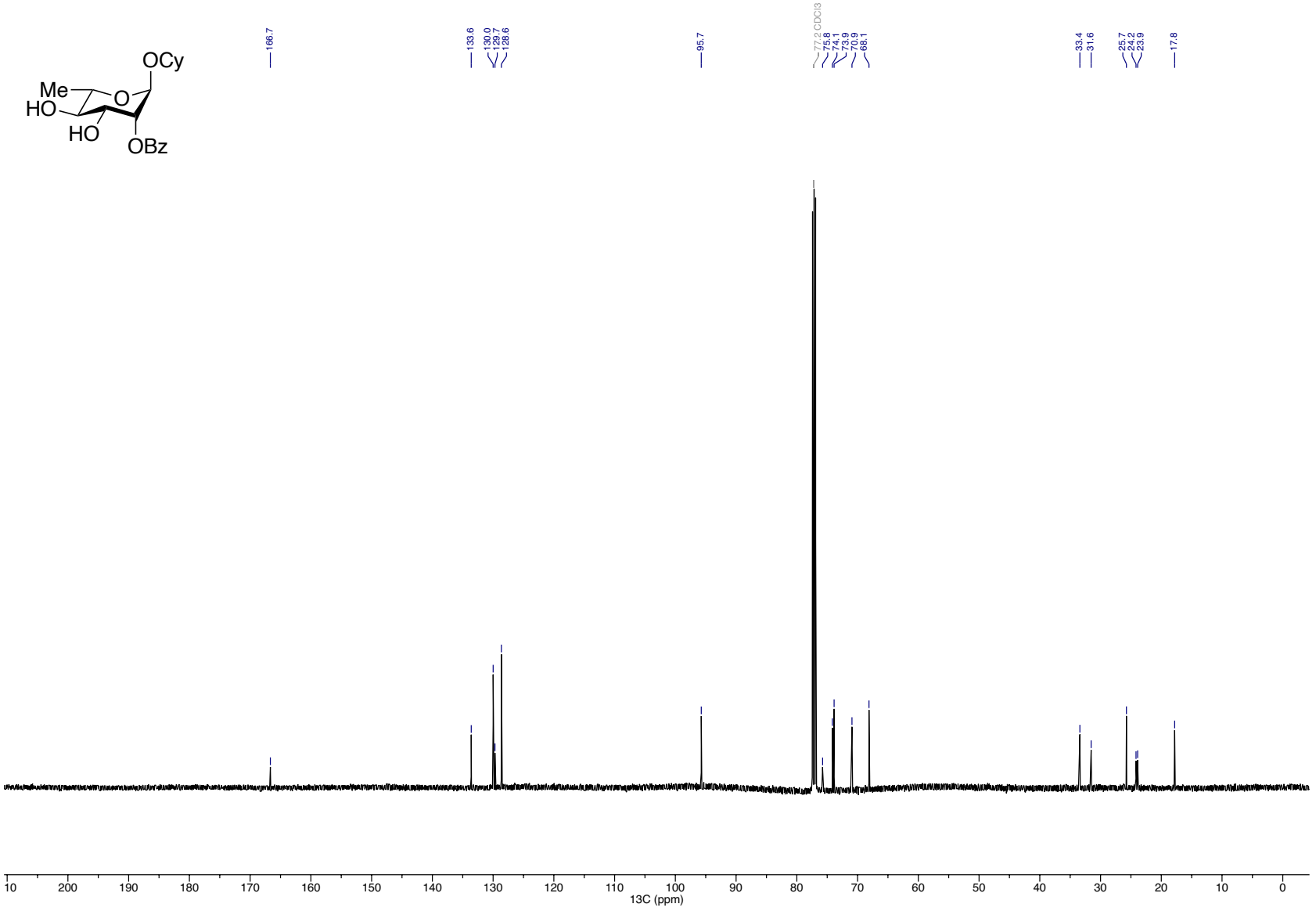


2i – Cyclohexyl 2-*O*-benzoyl-α-L-rhamnopyranoside

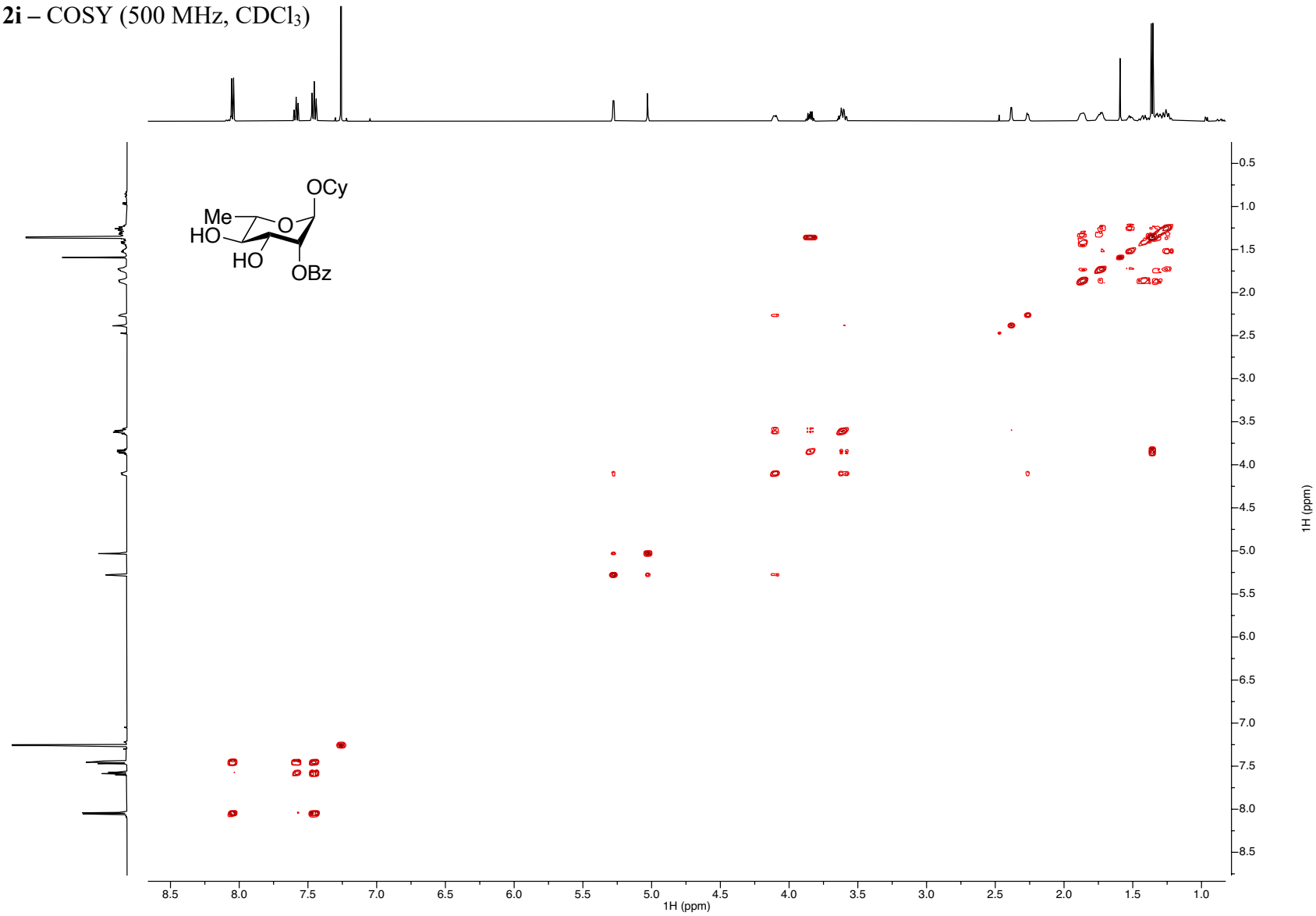
^{1}H NMR (500 MHz, $CDCl_3$)



2i – ^{13}C NMR (125 MHz, CDCl3)

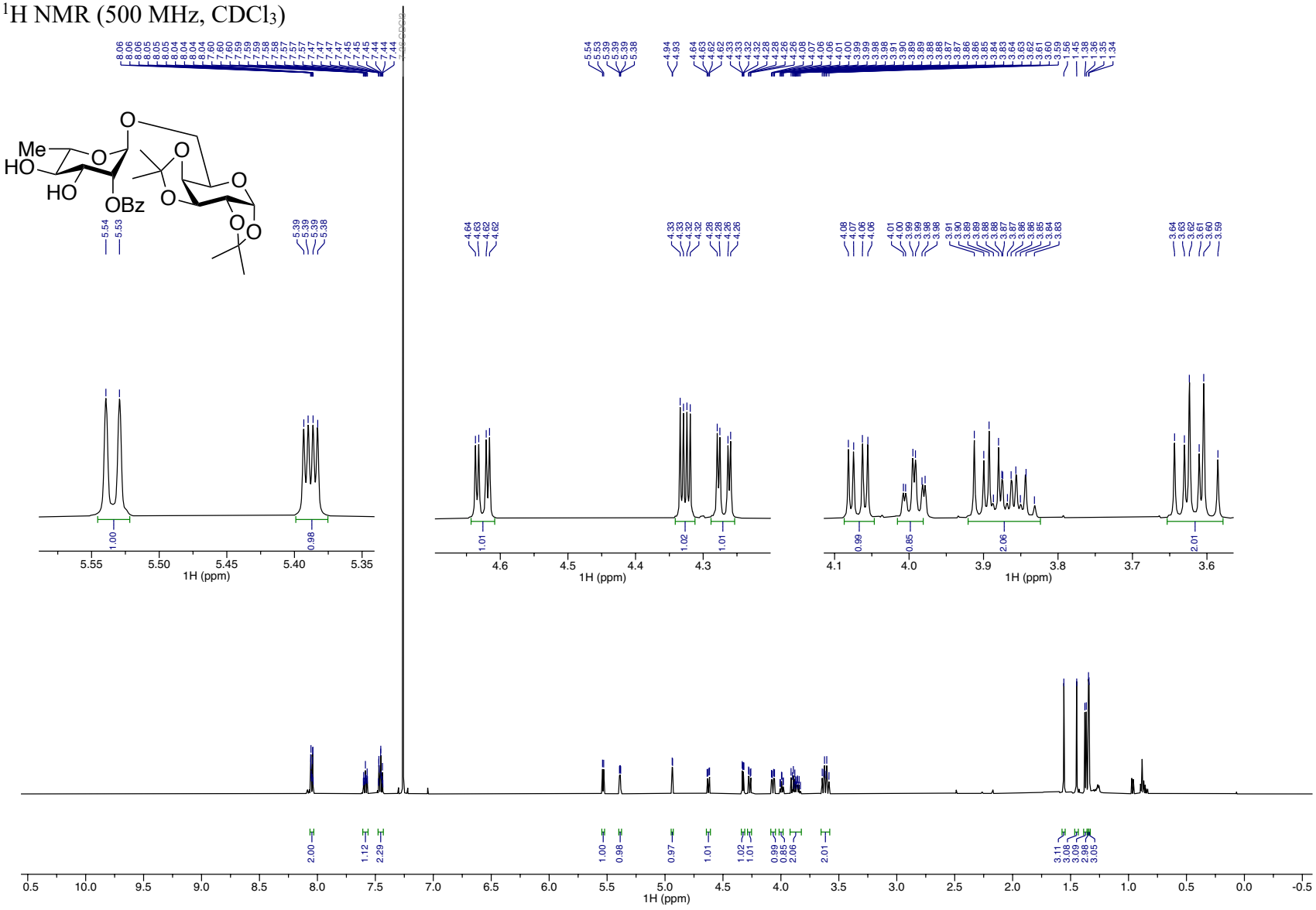


2i – COSY (500 MHz, $CDCl_3$)

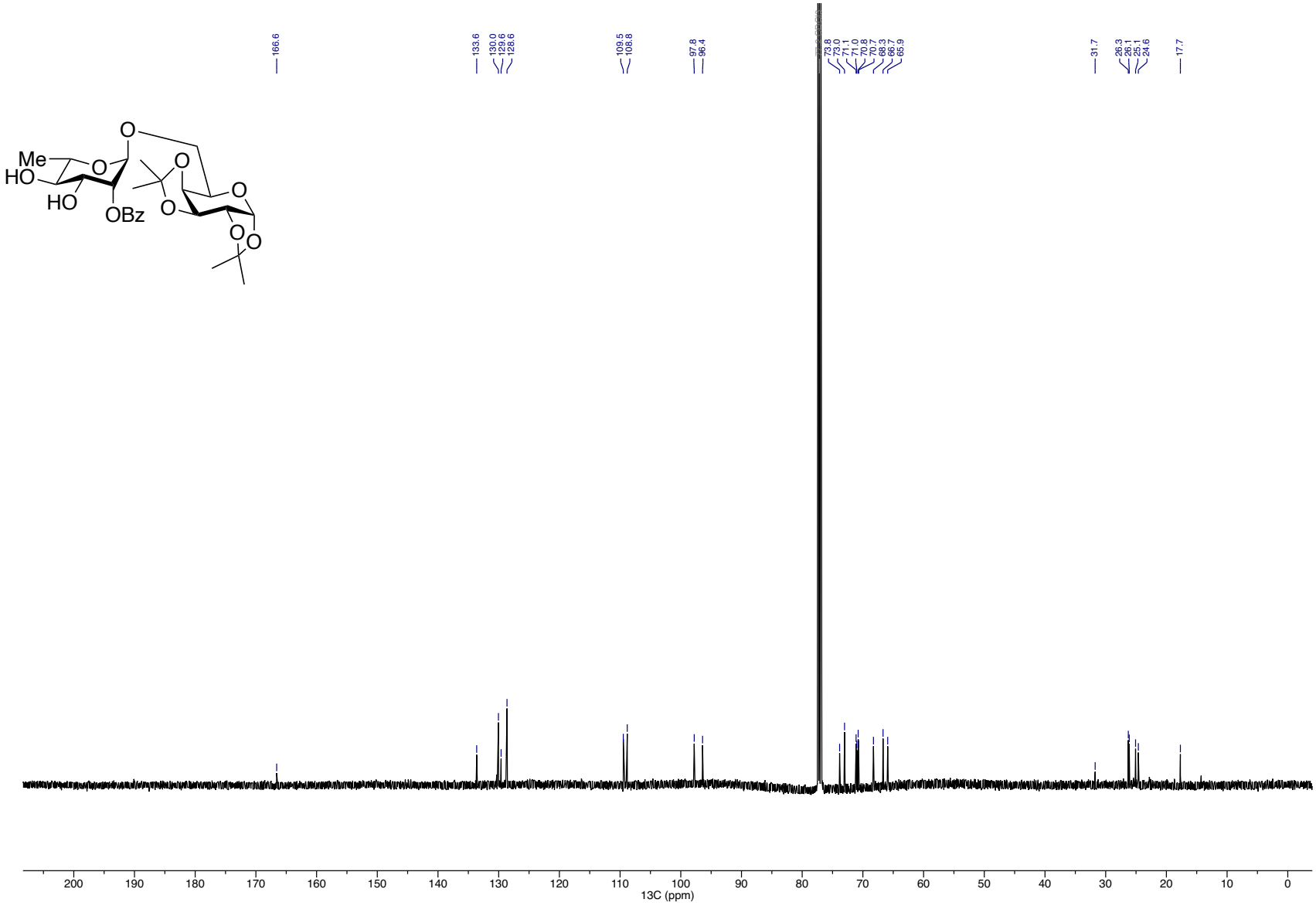


2j – 1,2,3,4-di-O-isopropylidene-6-O-(2-*O*-benzoyl-*α*-L-rhamnopyranosyl)-α-D-galactopyranoside

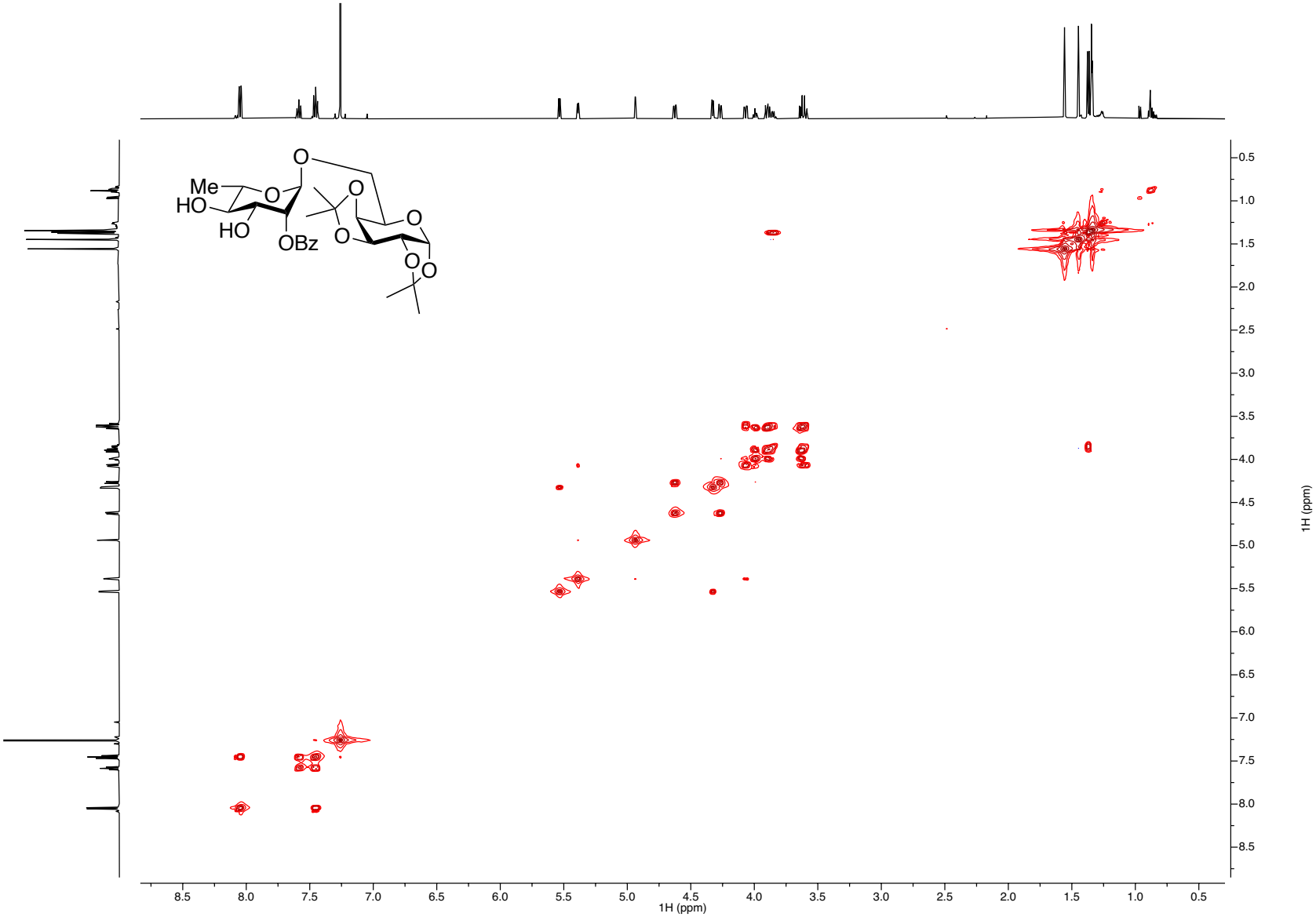
^{1}H NMR (500 MHz, $CDCl_3$)



2j – ^{13}C NMR (125 MHz, $CDCl_3$)

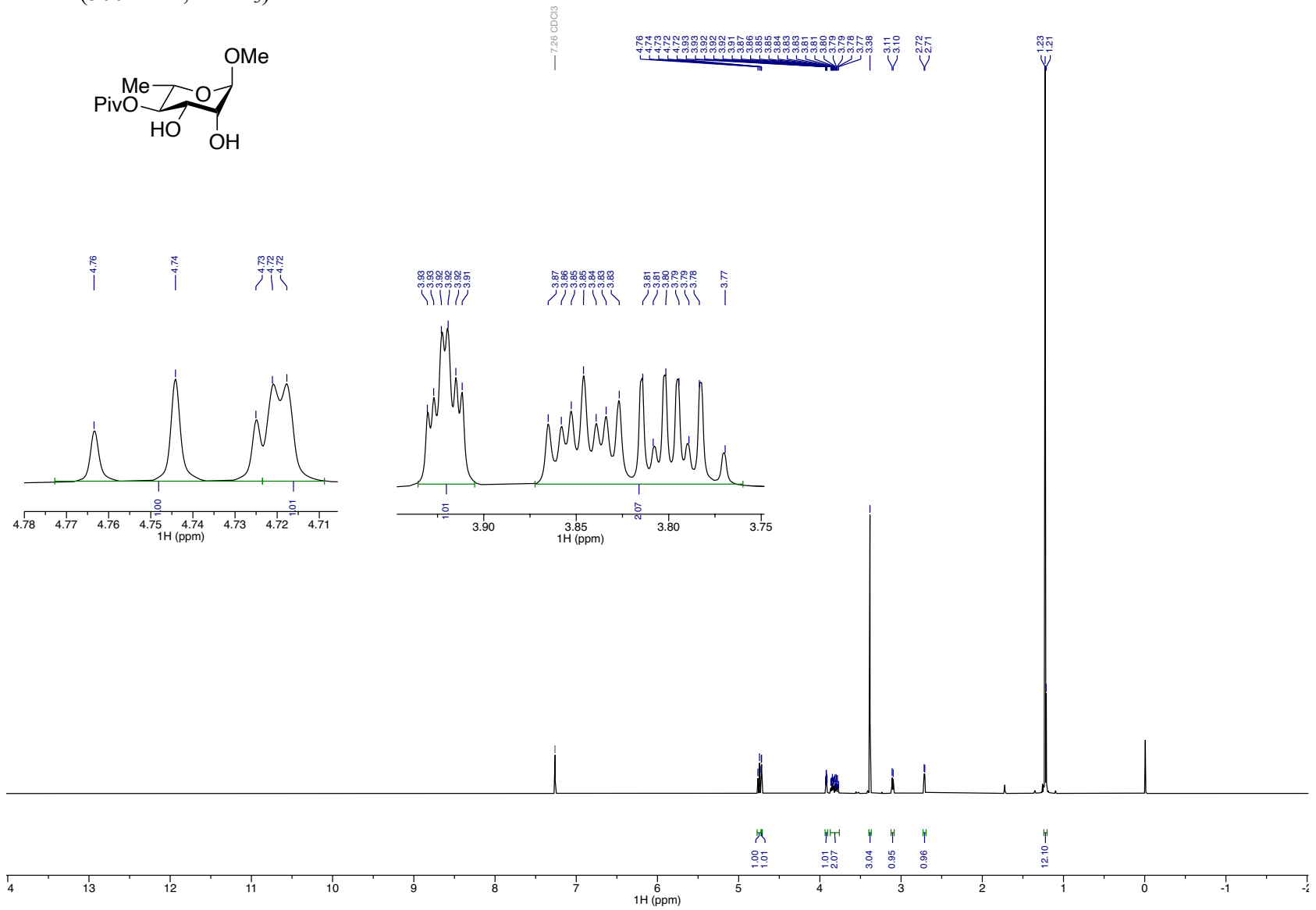


2j – COSY (500 MHz, $CDCl_3$)

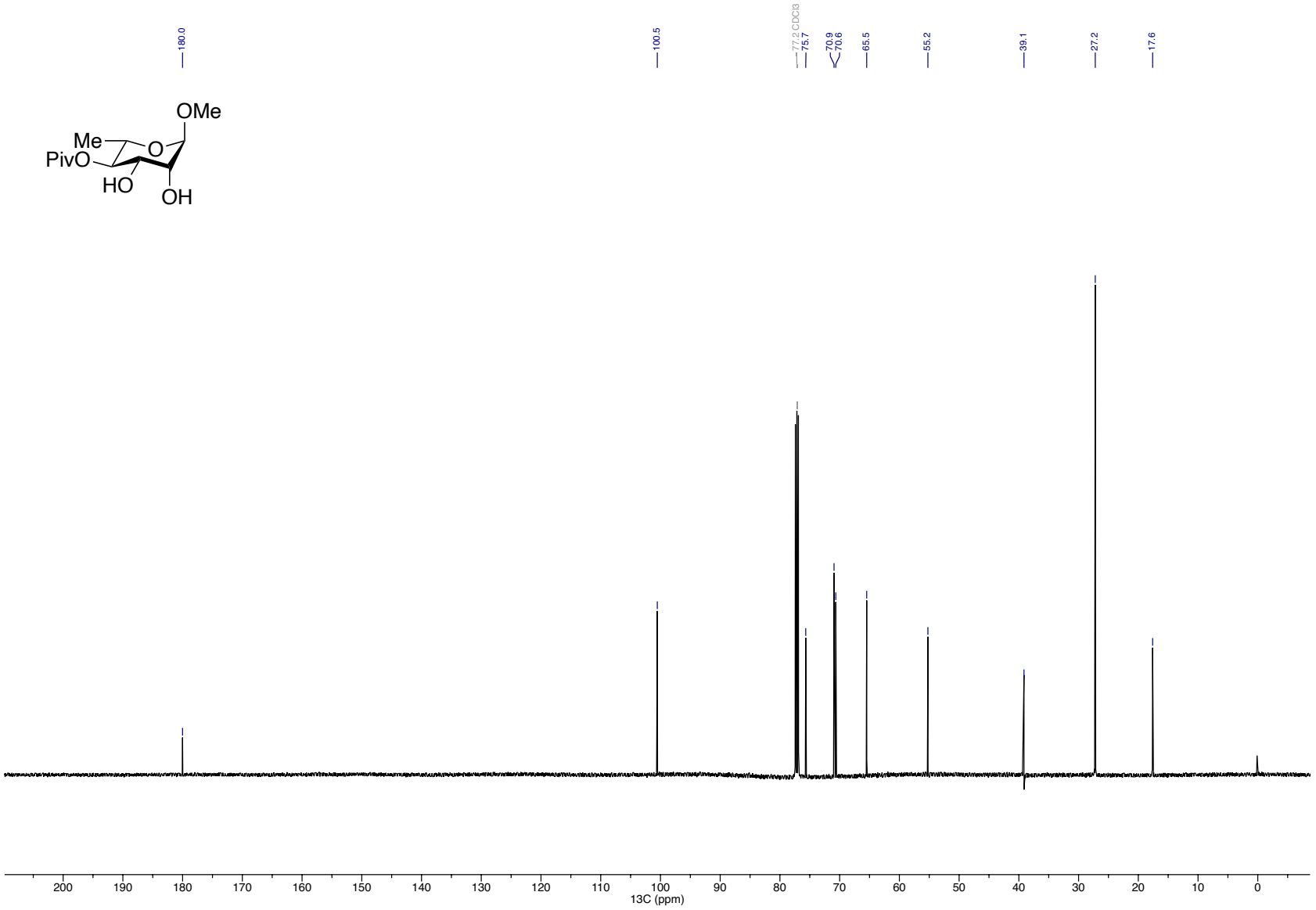


2k – Methyl 4-*O*-trimethylacetyl-*α*-L-rhamnopyranoside

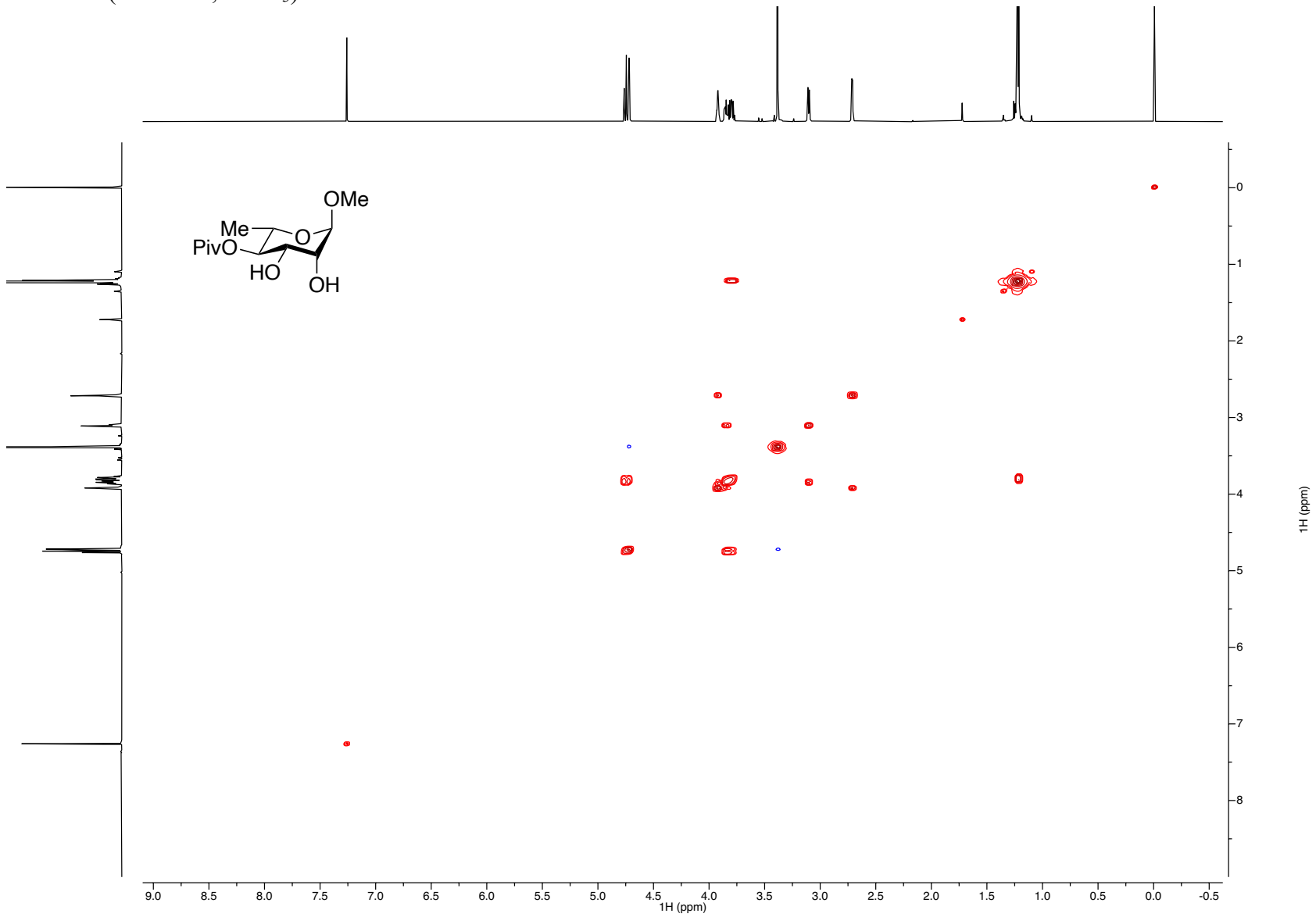
^{1}H NMR (500 MHz, $CDCl_3$)



2k – ^{13}C NMR (125 MHz, $CDCl_3$)

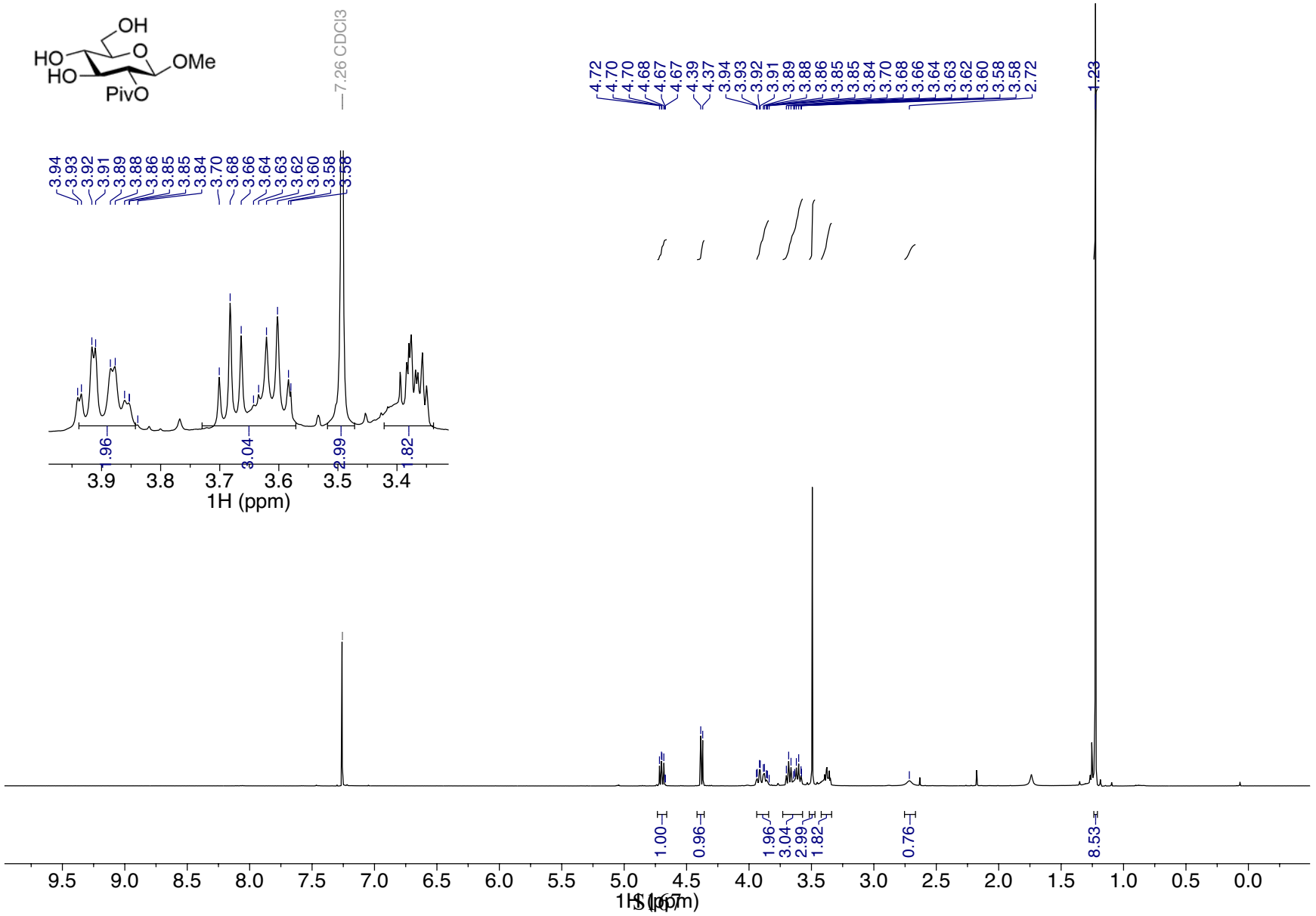


2k – COSY (400 MHz, $CDCl_3$)

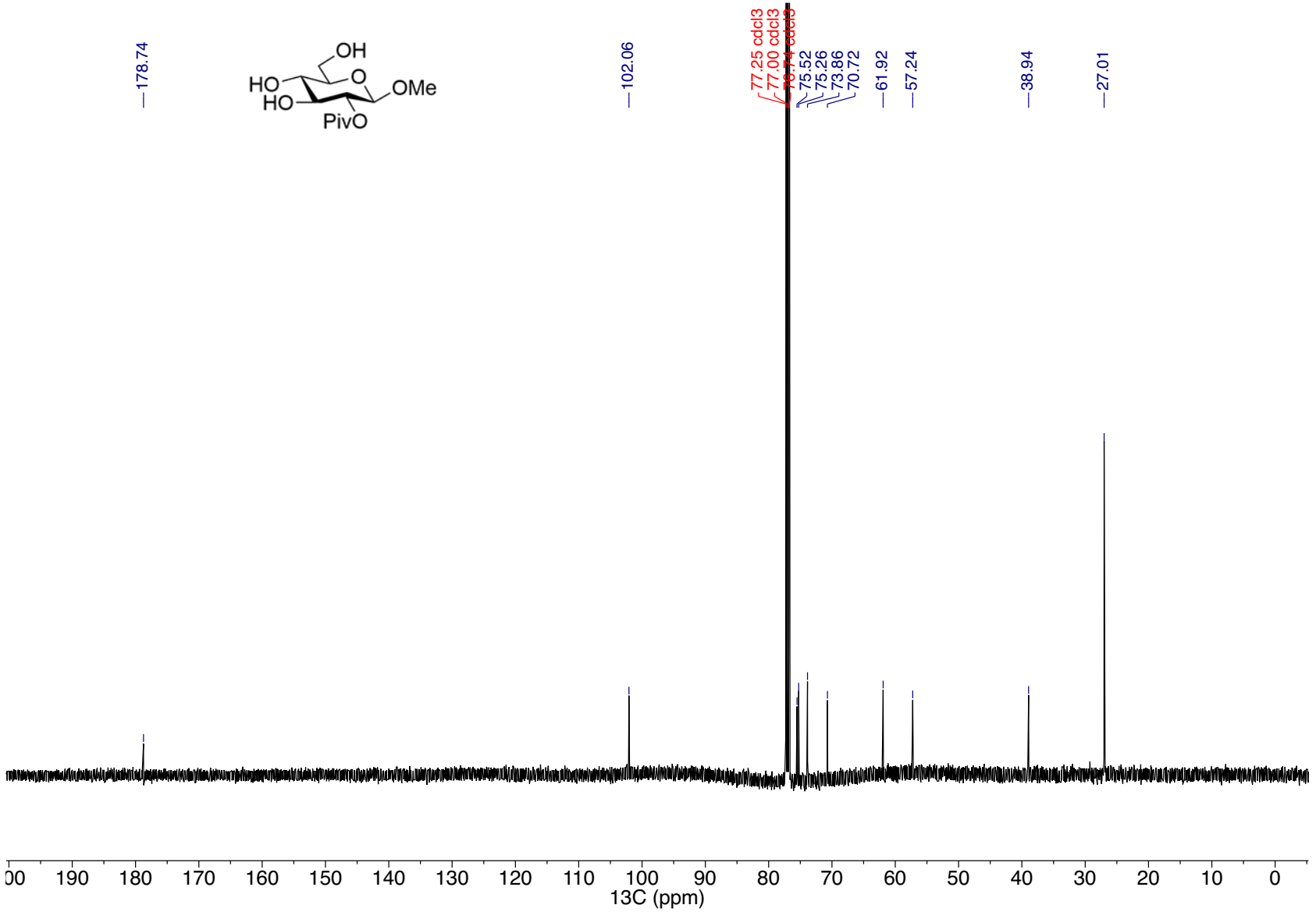


2l – Methyl 2-O-trimethylacteyl-β-D-glucopyranoside

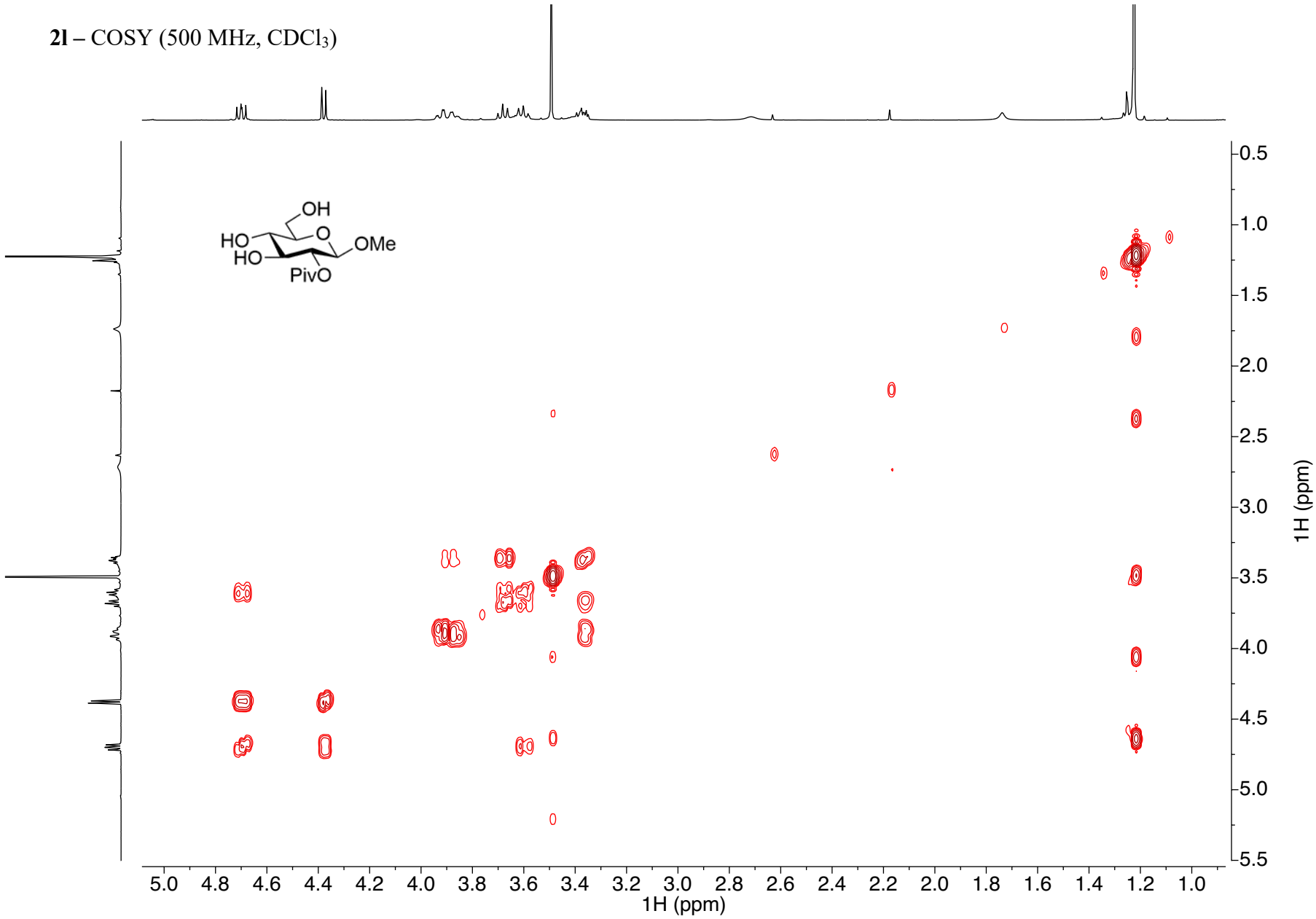
^{1}H NMR (500 MHz, $CDCl_3$)



2l – ^{13}C NMR (125 MHz, $CDCl_3$)

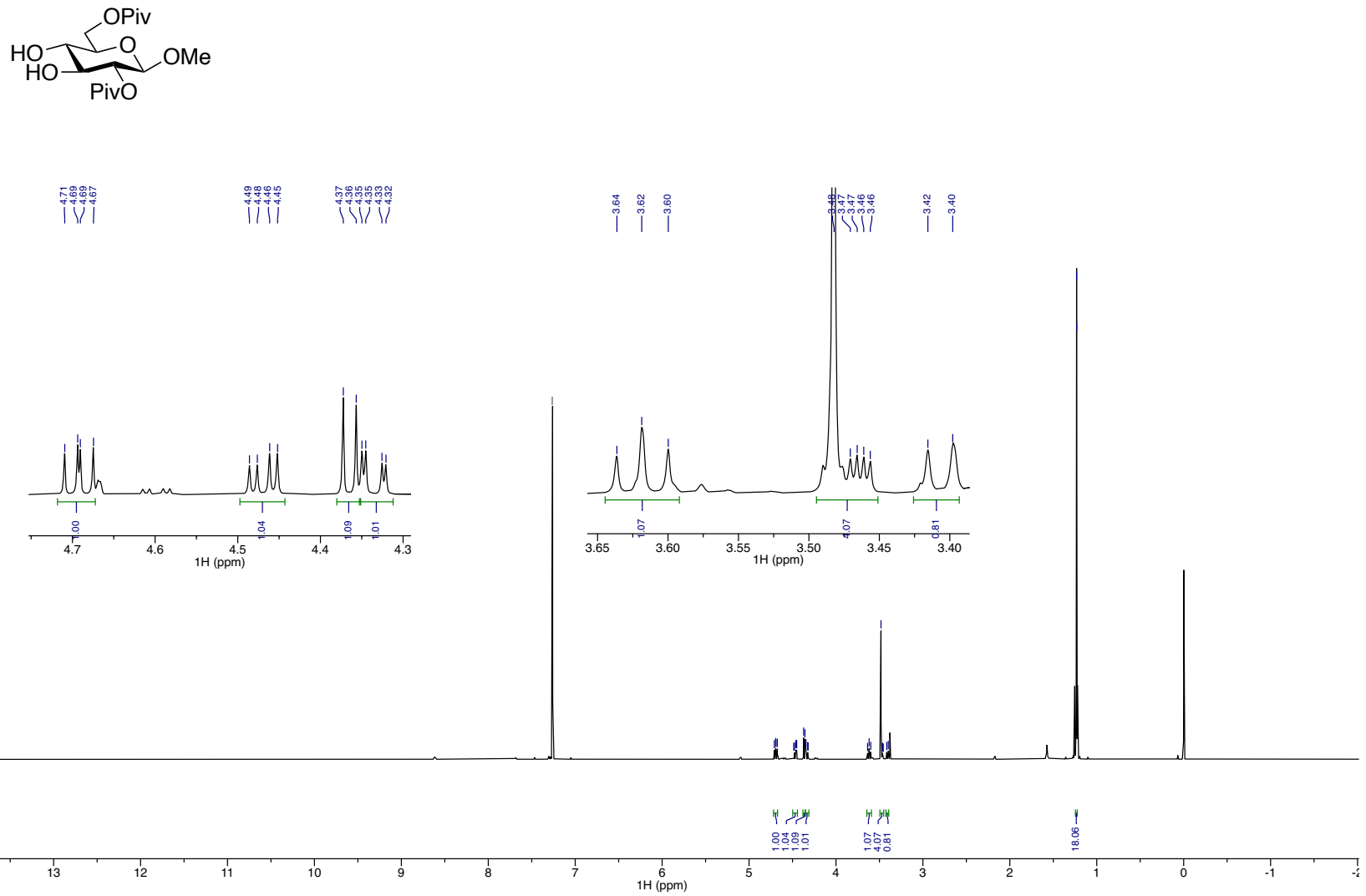


2l – COSY (500 MHz, $CDCl_3$)

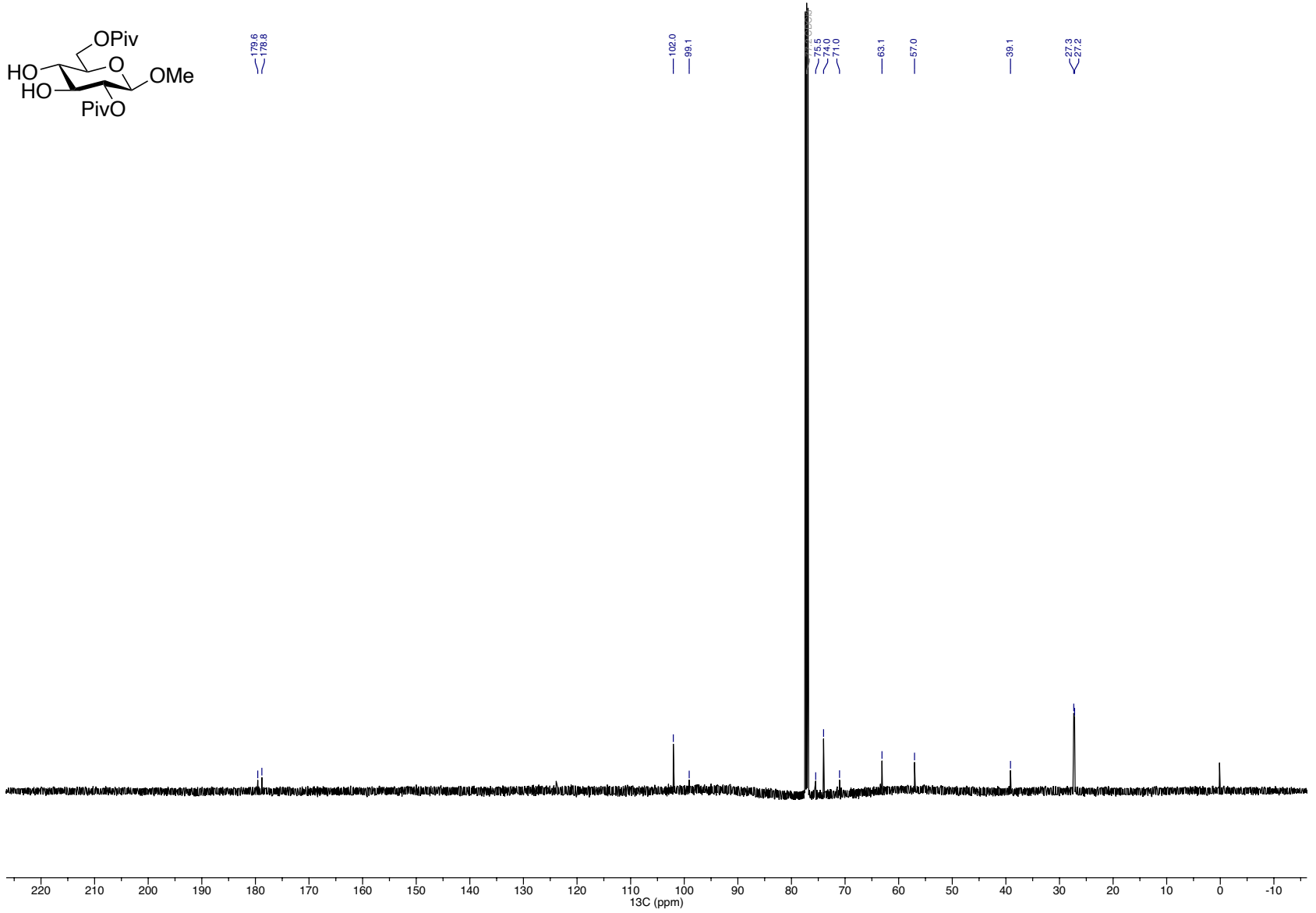


2m – Methyl 2-O-trimethylacteyl-β-D-glucopyranoside

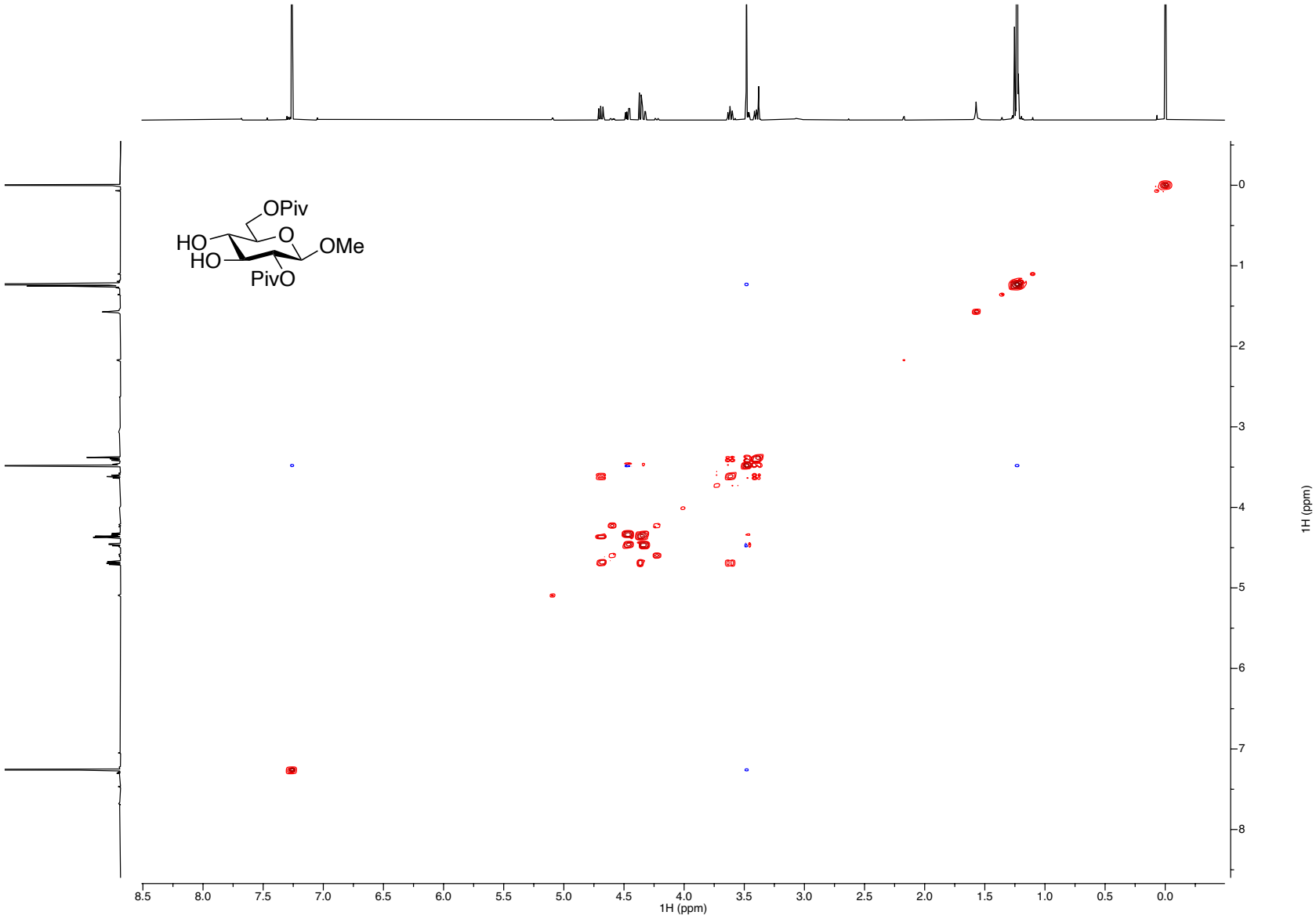
^{1}H NMR (500 MHz, $CDCl_3$)



2m – ^{13}C NMR (125 MHz, $CDCl_3$)

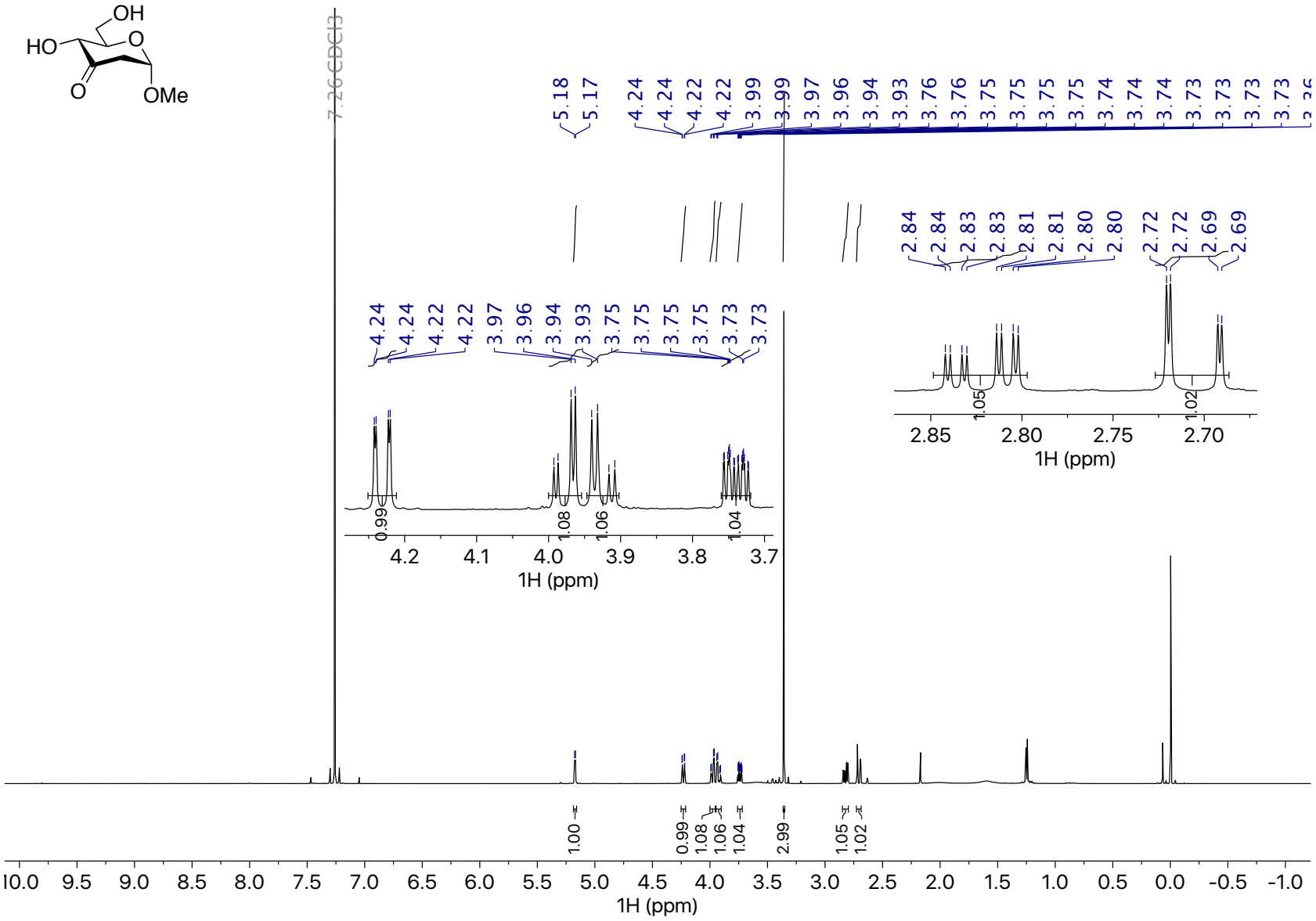


2m – COSY (500 MHz, $CDCl_3$)

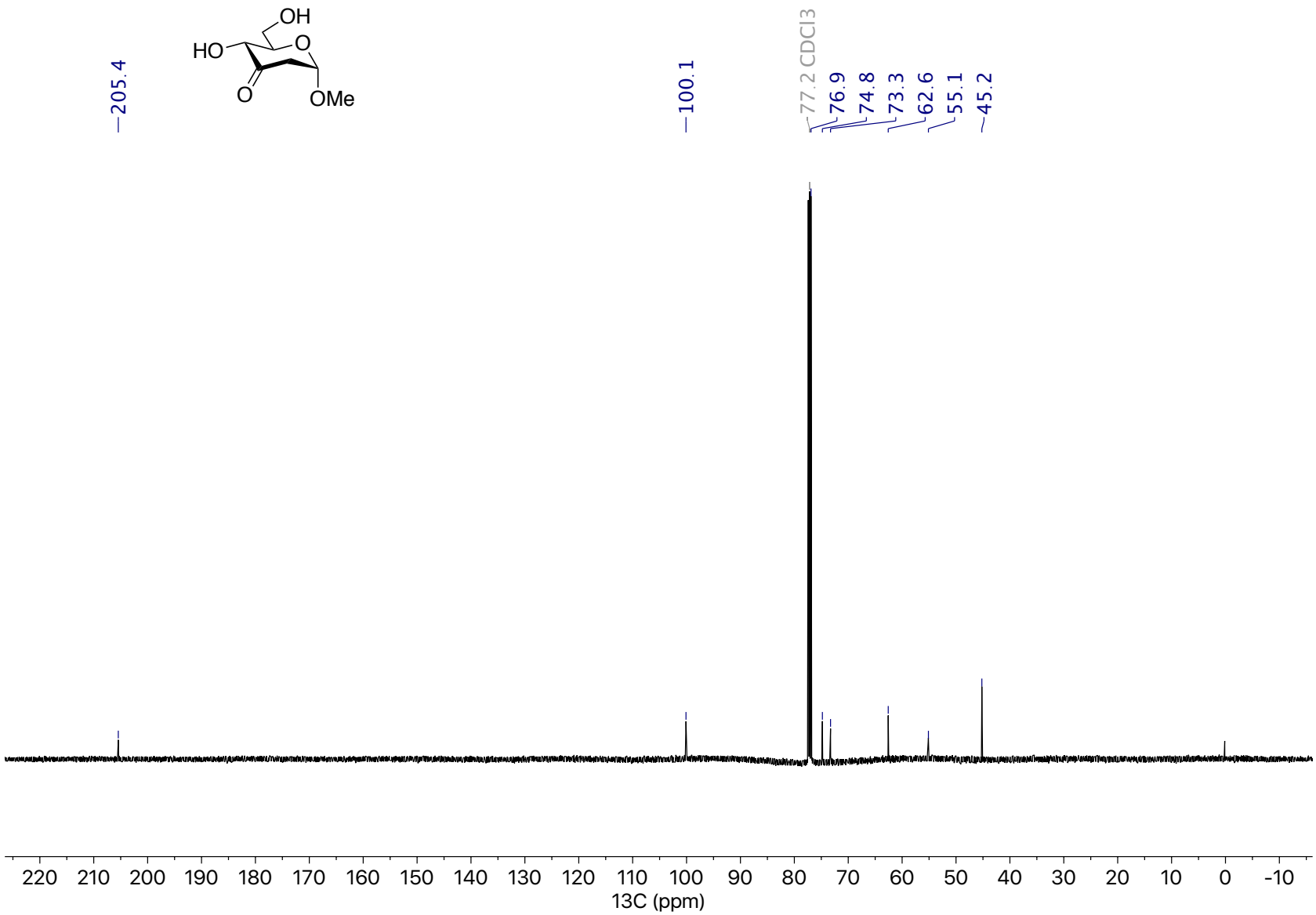


4a – Methyl 2-deoxy-*α*-D-*erythro*-hexopyranoside-3-ulose

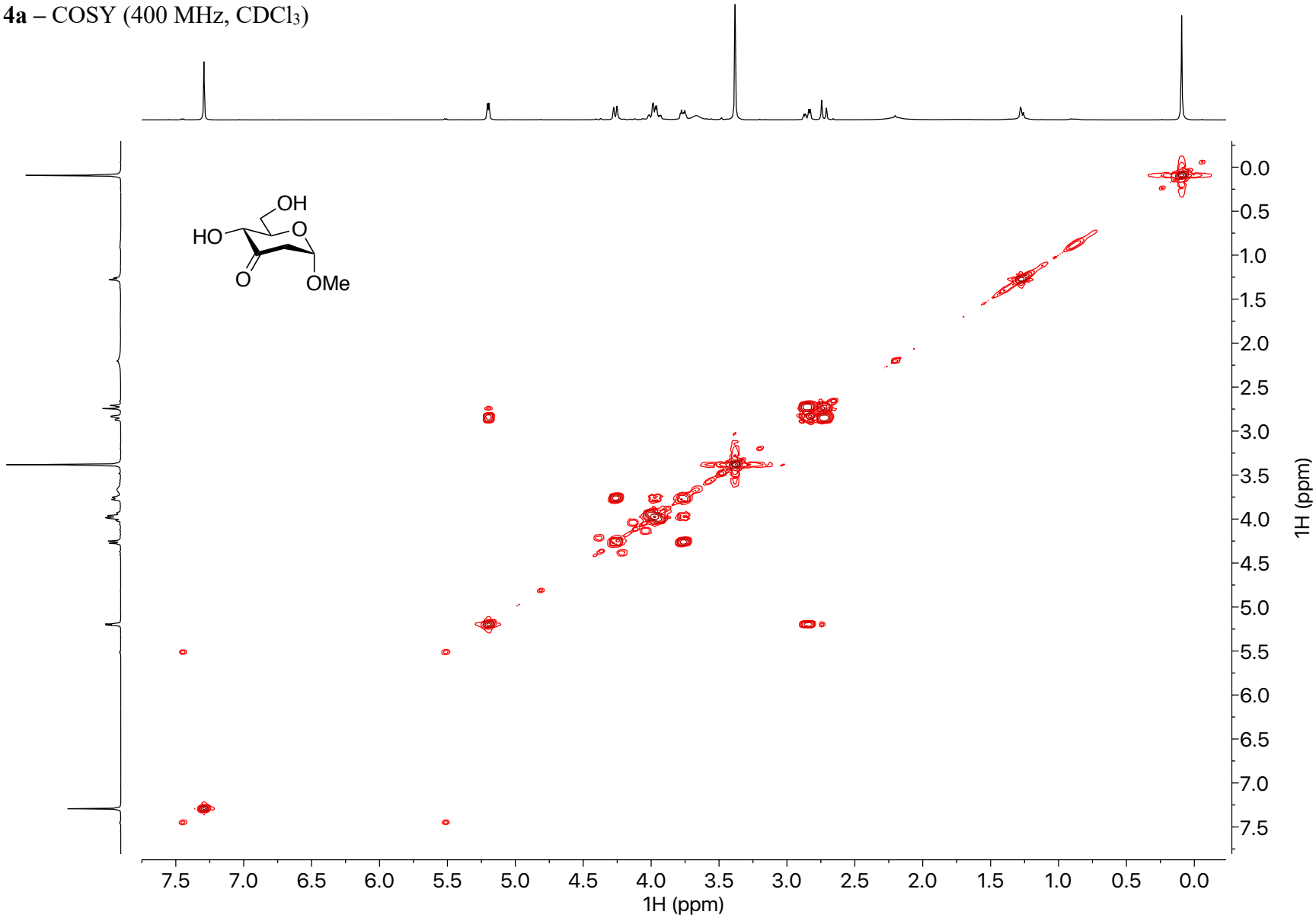
^{1}H NMR (500 MHz, $CDCl_3$)



4a – ^{13}C NMR (125 MHz, $CDCl_3$)

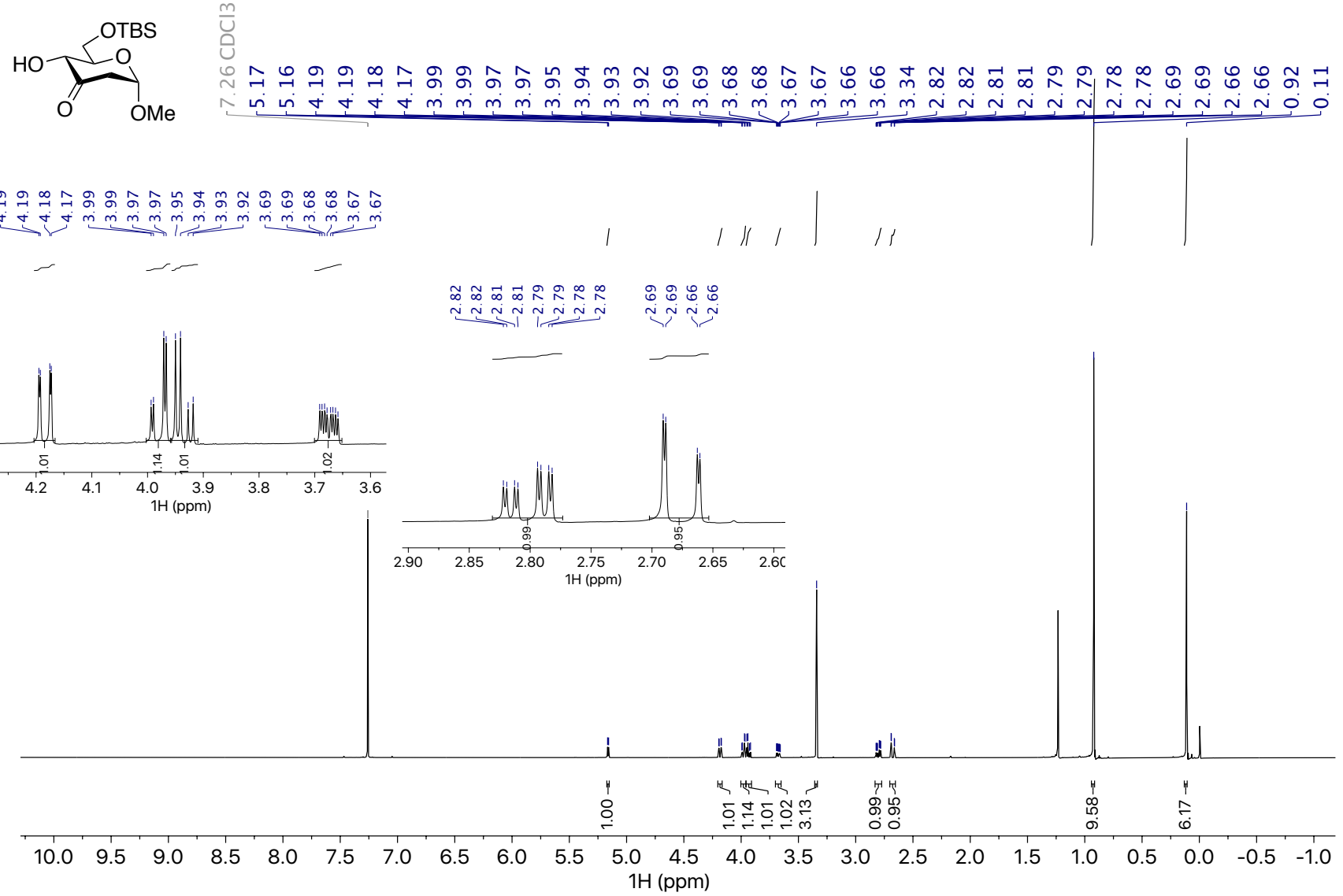


4a – COSY (400 MHz, $CDCl_3$)

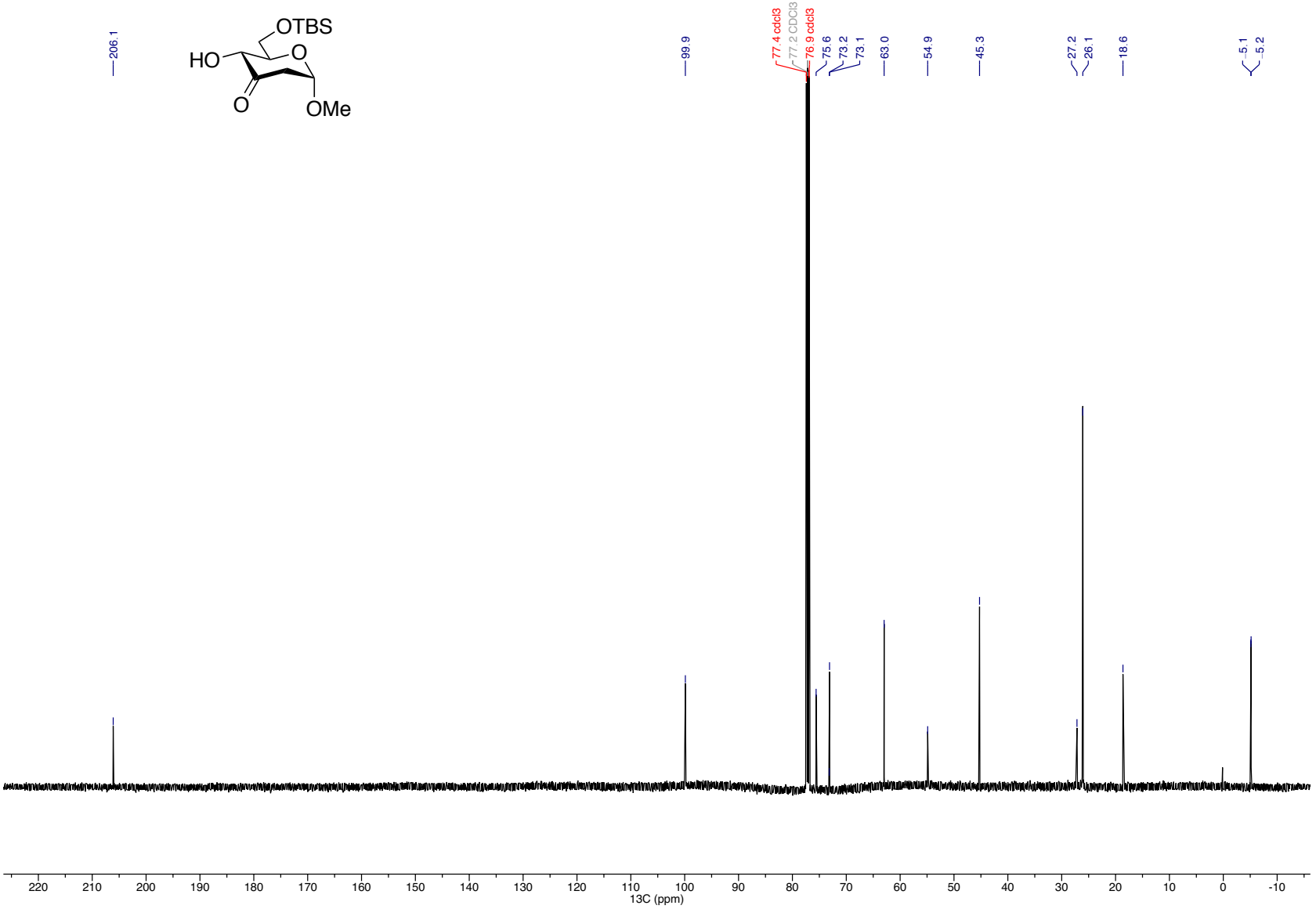


4b – Methyl 2-deoxy-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-*erythro*-hexopyranoside-3-ulose

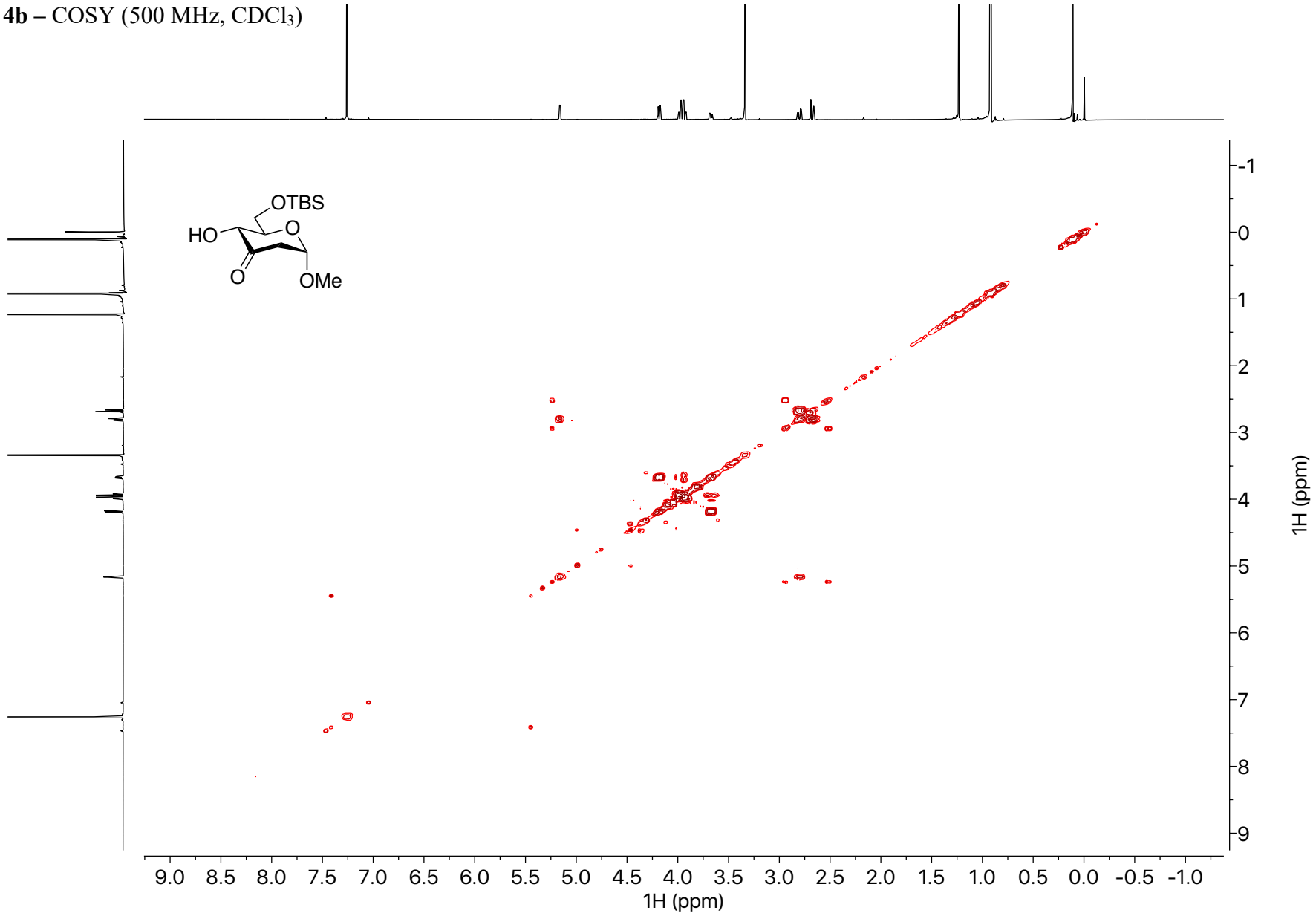
^{1}H NMR (500 MHz, $CDCl_3$)



4b – ^{13}C NMR (125 MHz, $CDCl_3$)

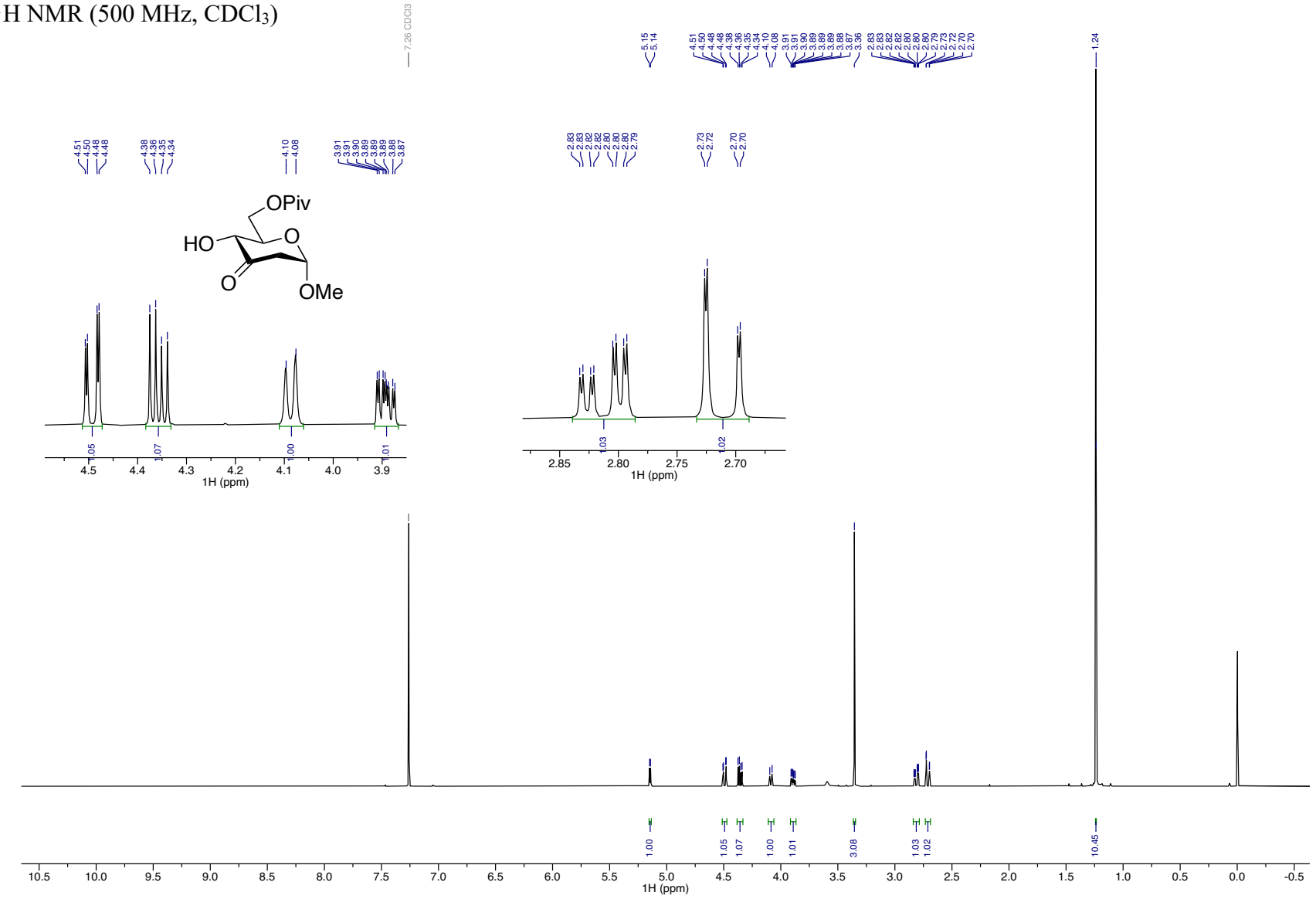


4b – COSY (500 MHz, $CDCl_3$)

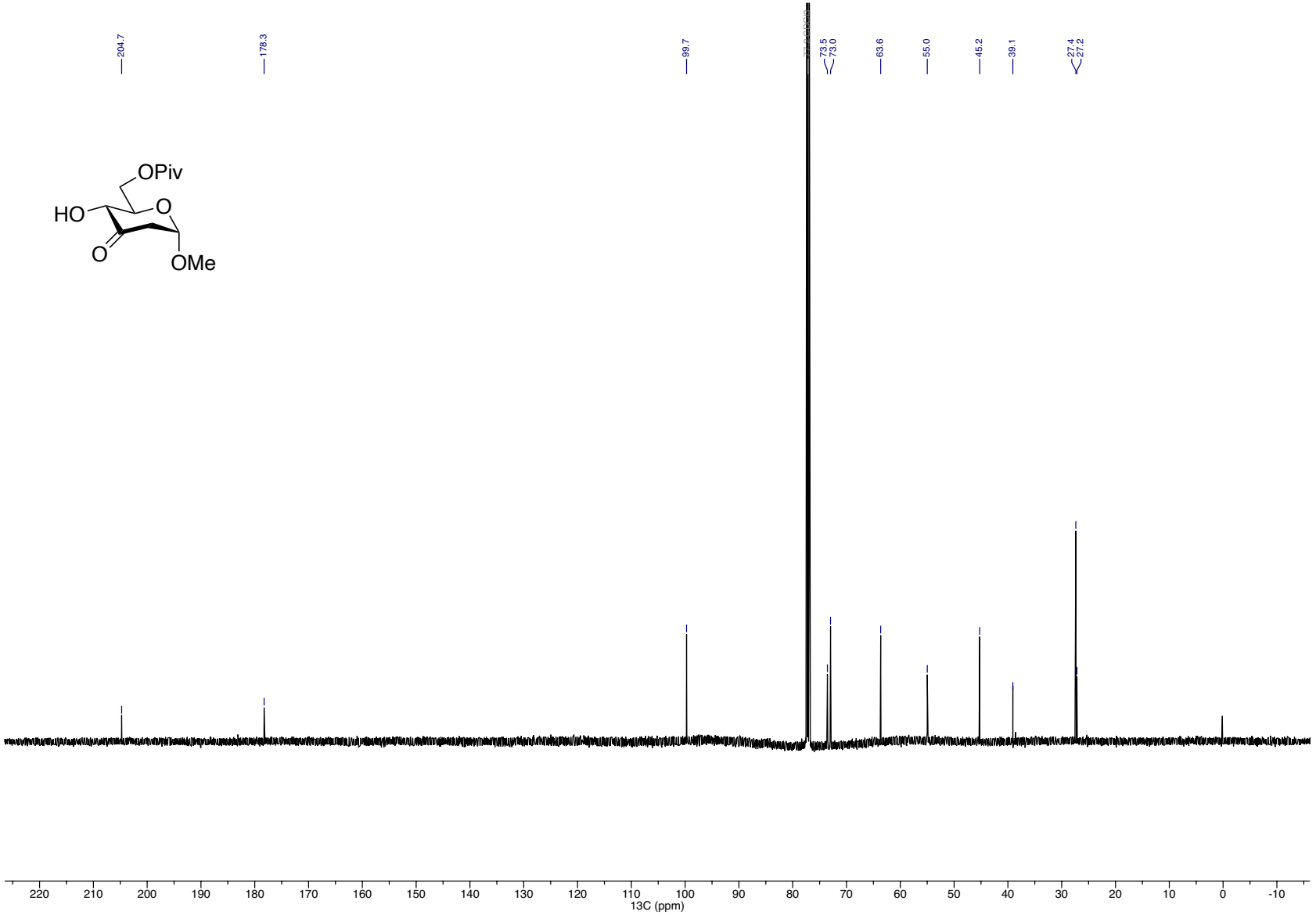


4c – Methyl 2-deoxy-6-*O*-trimethylacetyl-α-D-*erythro*-hexopyranoside-3-ulose

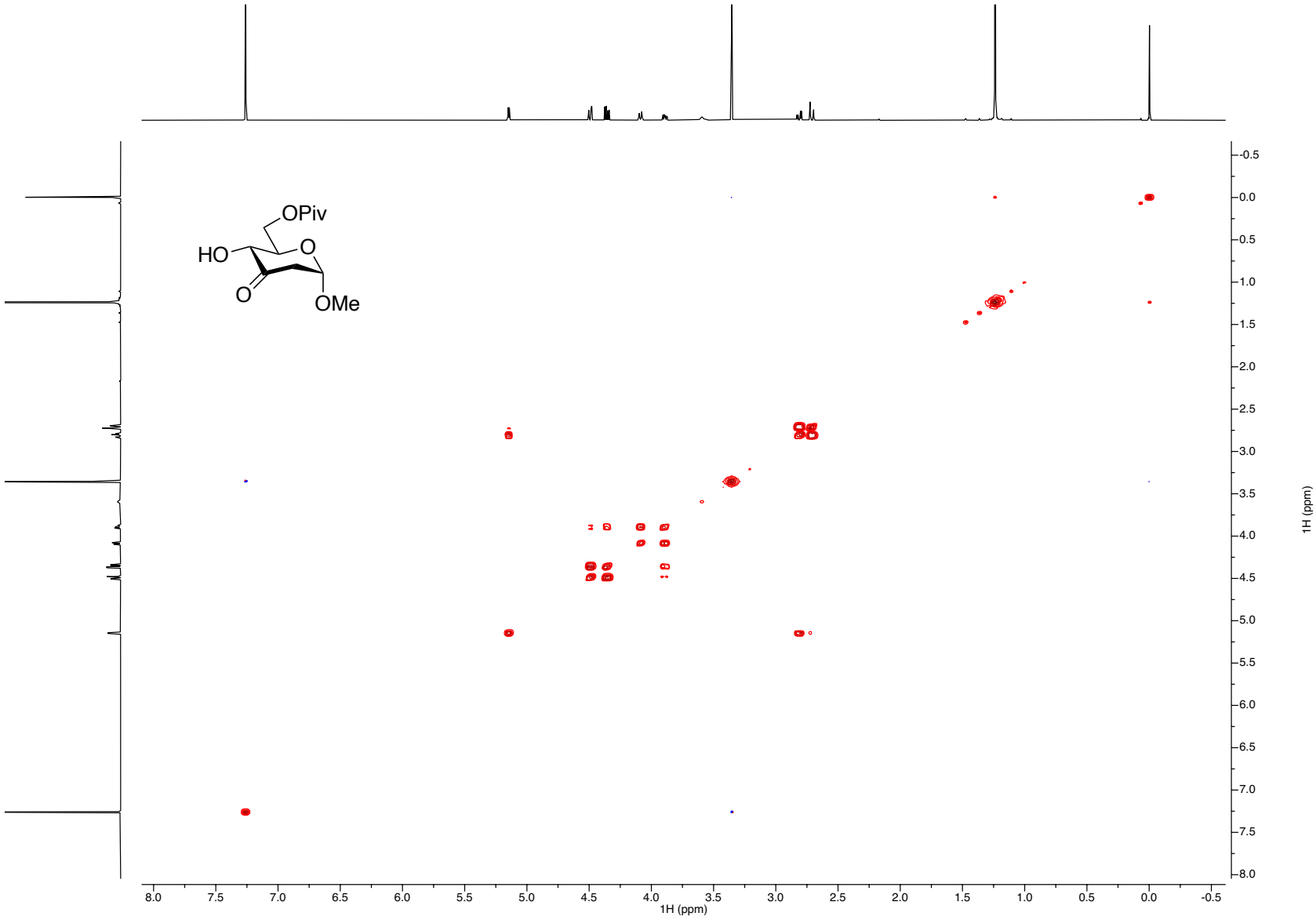
^{1}H NMR (500 MHz, $CDCl_3$)



4c – ^{13}C NMR (126 MHz, $CDCl_3$)

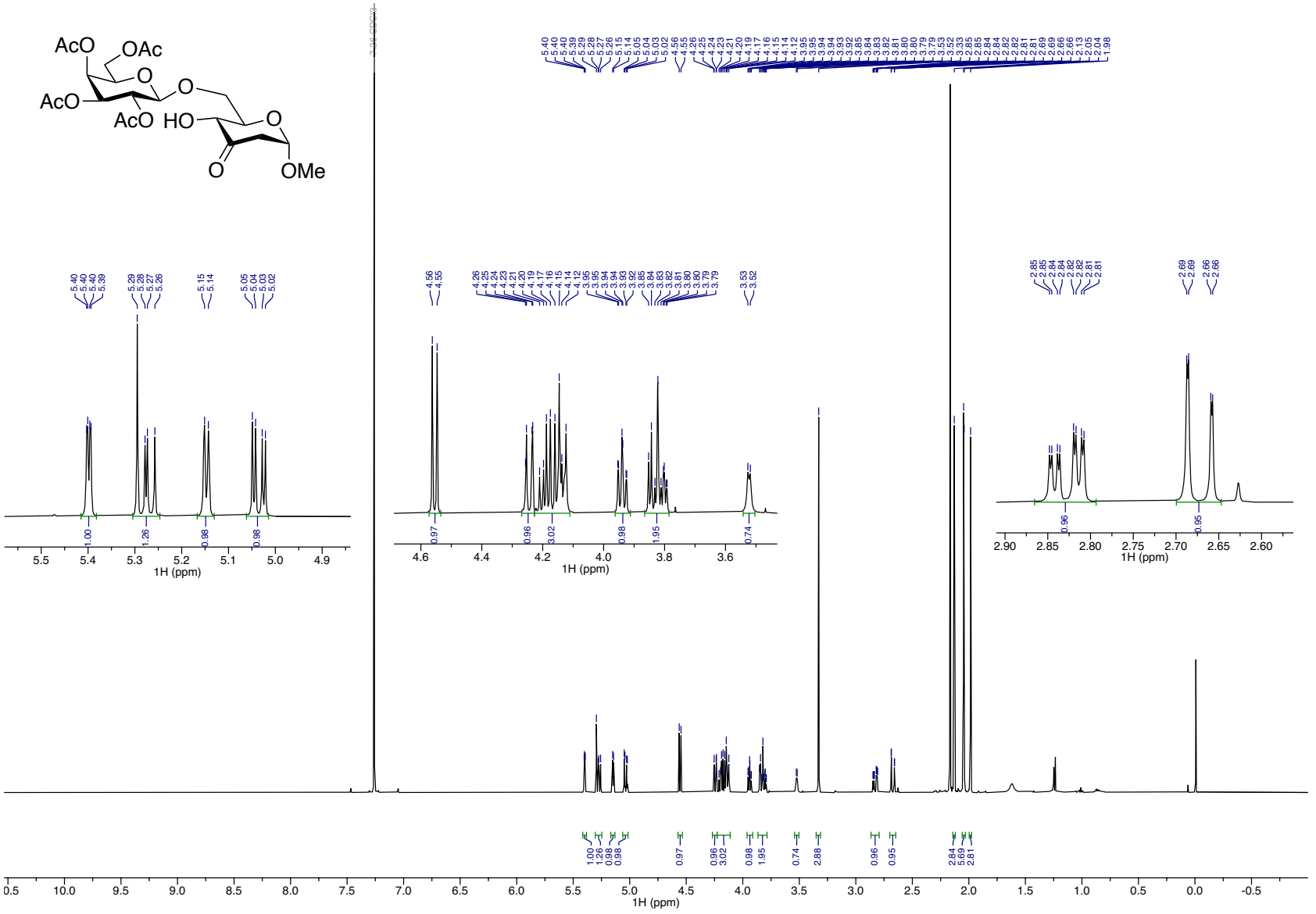


4c –COSY (500 MHz, $CDCl_3$)

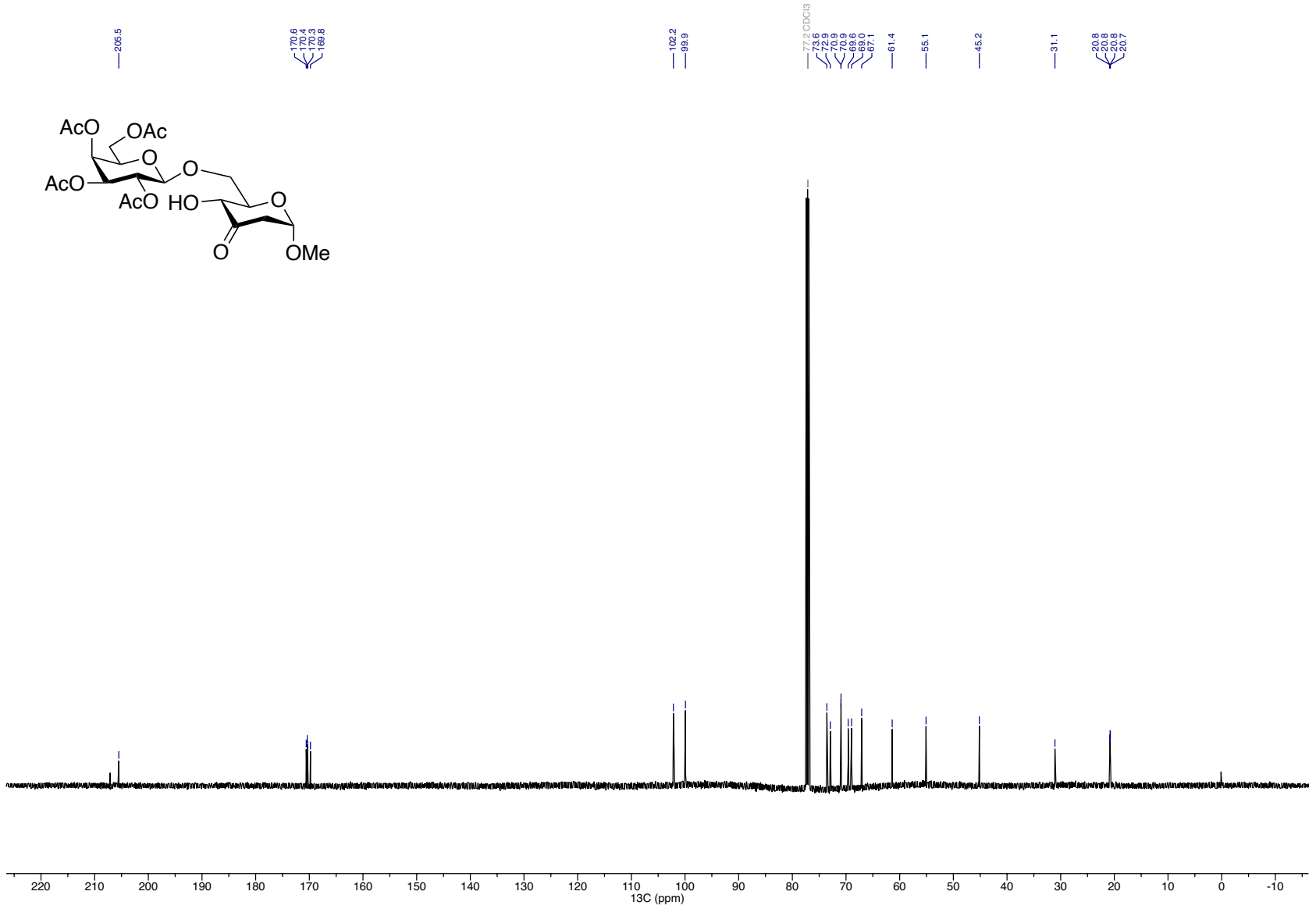


4d – Methyl 6-O-(2′,3′,4′,6′-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-*erythro*-hexopyranoside-3-ulose

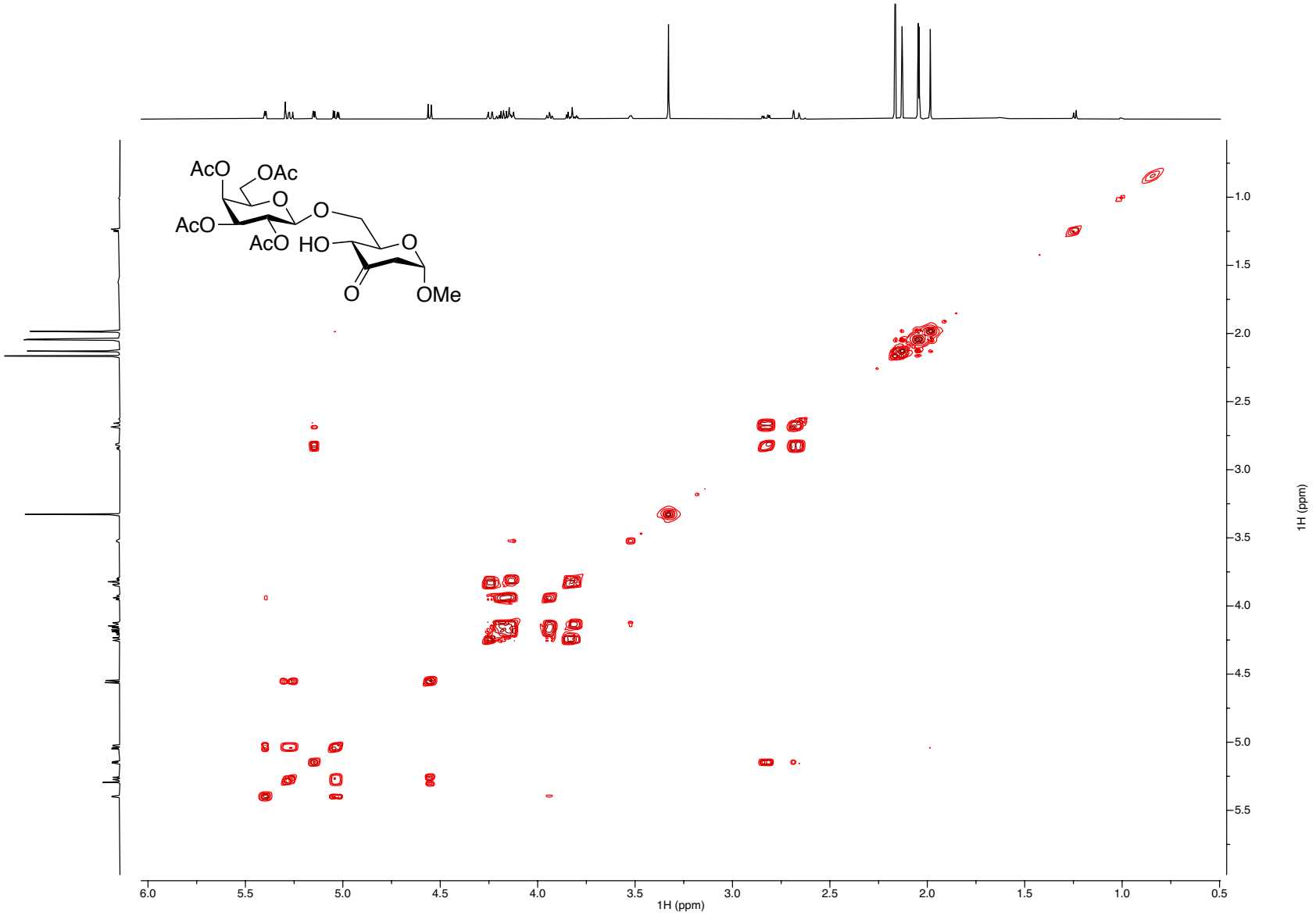
^{1}H NMR (500 MHz, $CDCl_3$)



4d – ^{13}C NMR (126 MHz, $CDCl_3$)

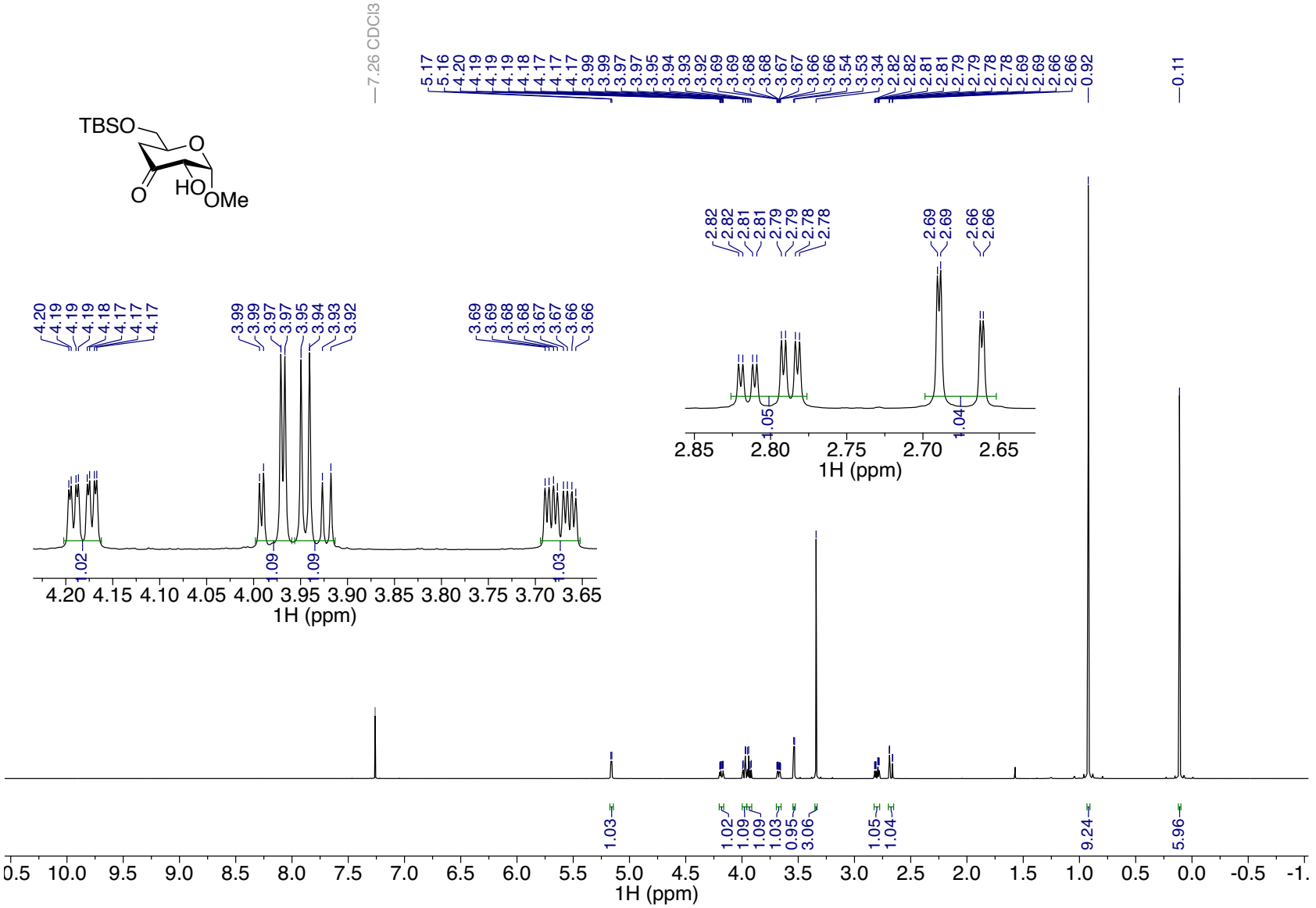


4d –COSY (500 MHz, $CDCl_3$)

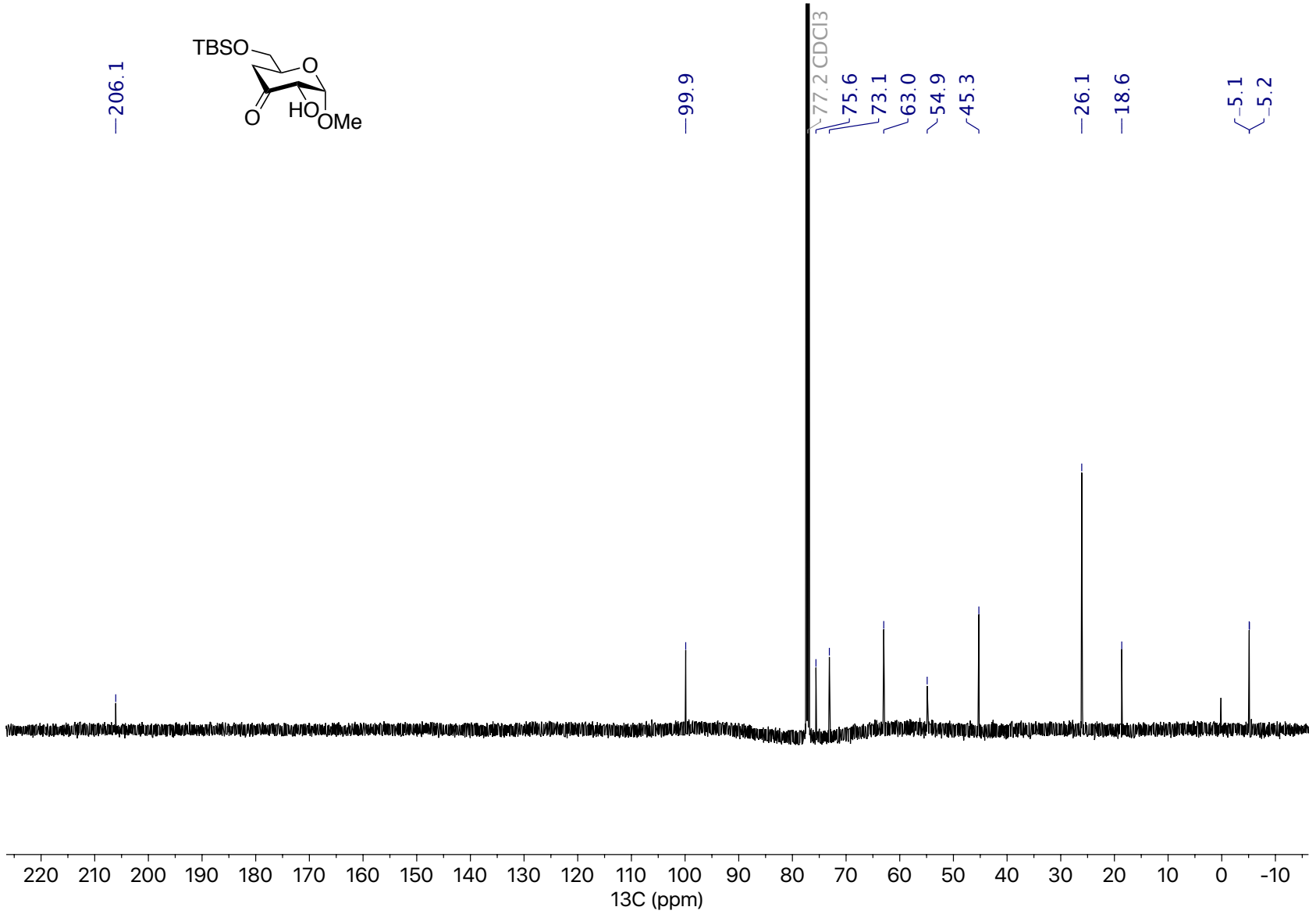


4e – Methyl 4-deoxy-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-*erythro*-hexopyranoside-3-ulose

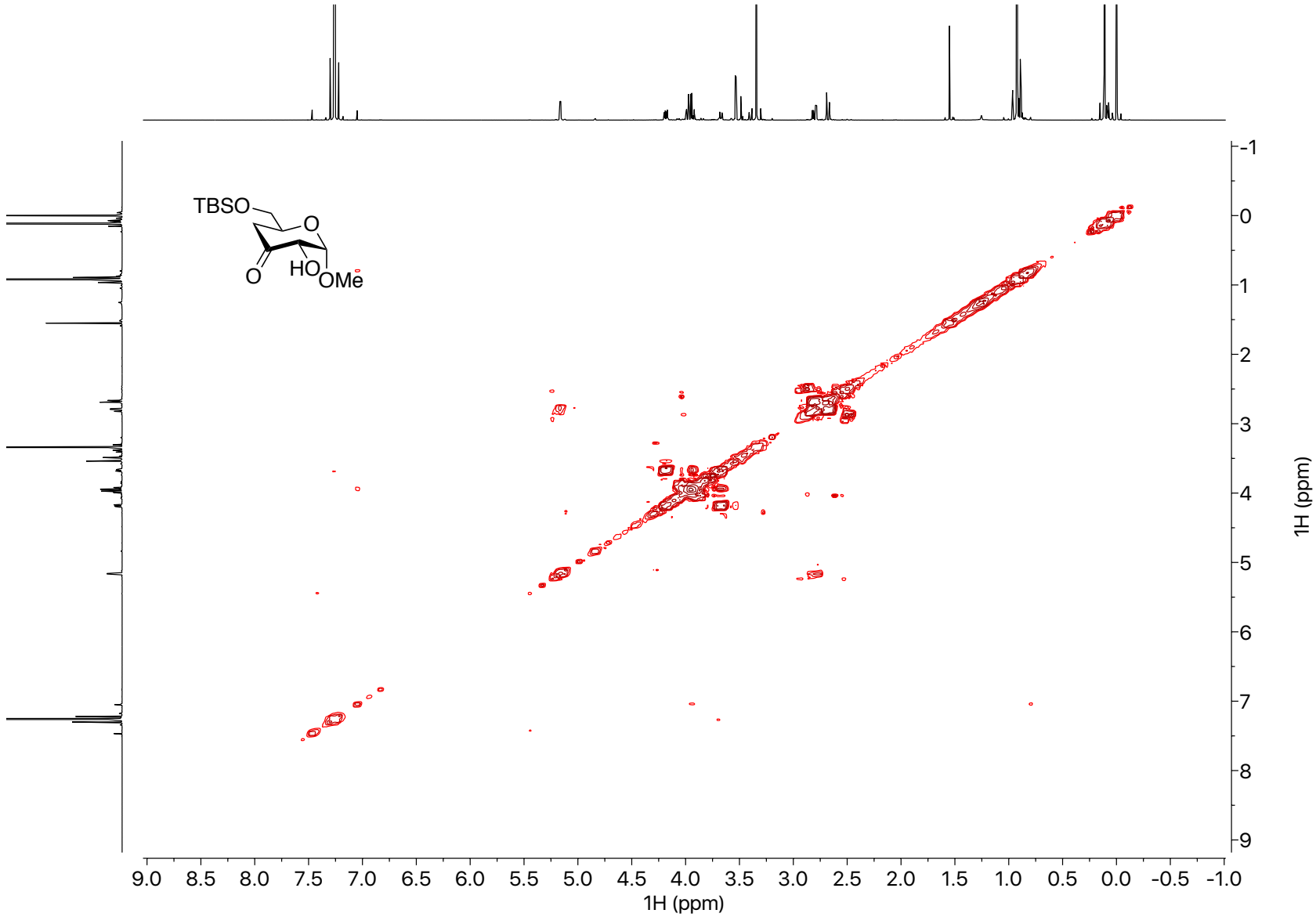
^{1}H NMR (500 MHz, $CDCl_3$)



4e – ^{13}C NMR (126 MHz, $CDCl_3$)

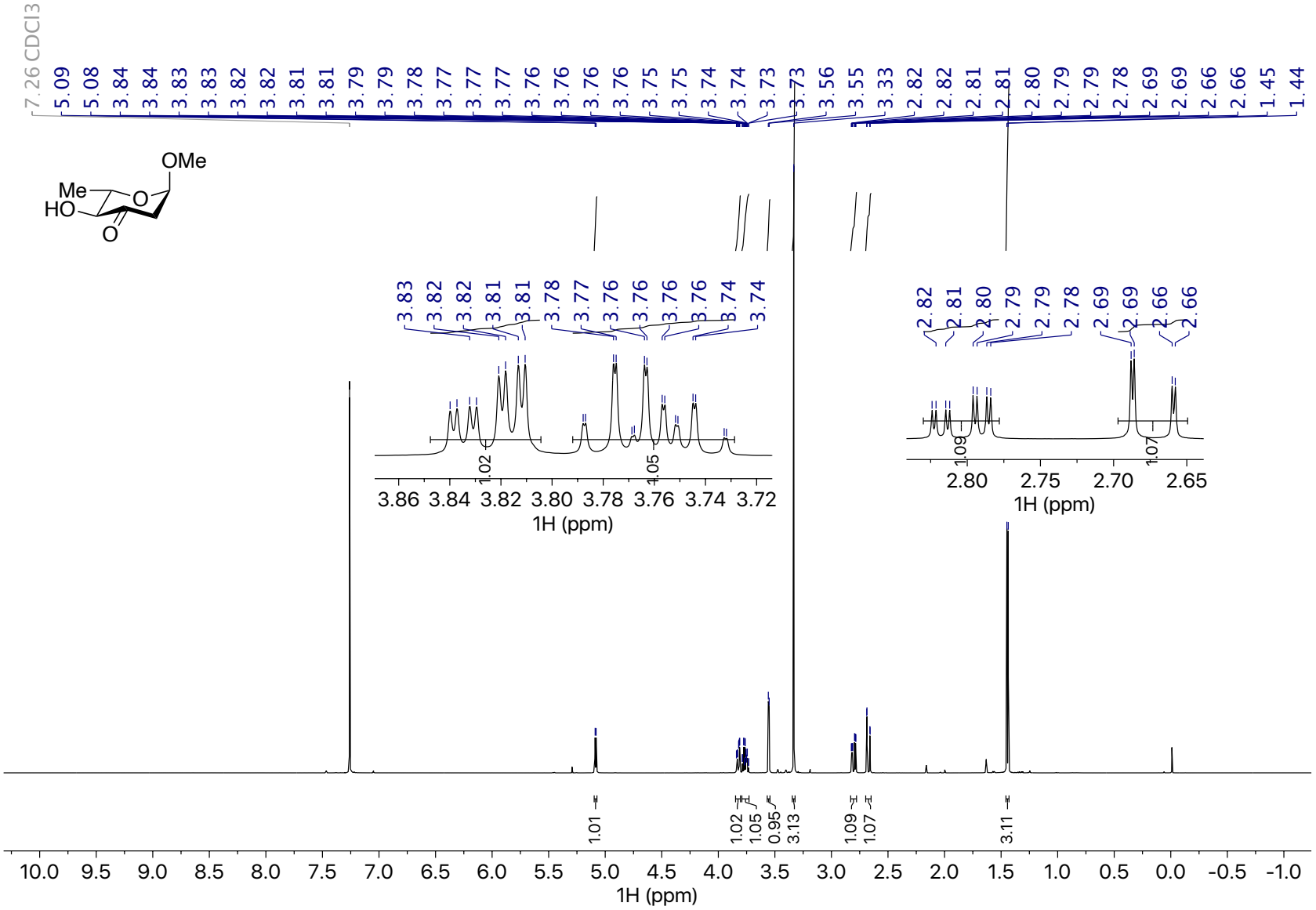


4e –COSY (500 MHz, $CDCl_3$)

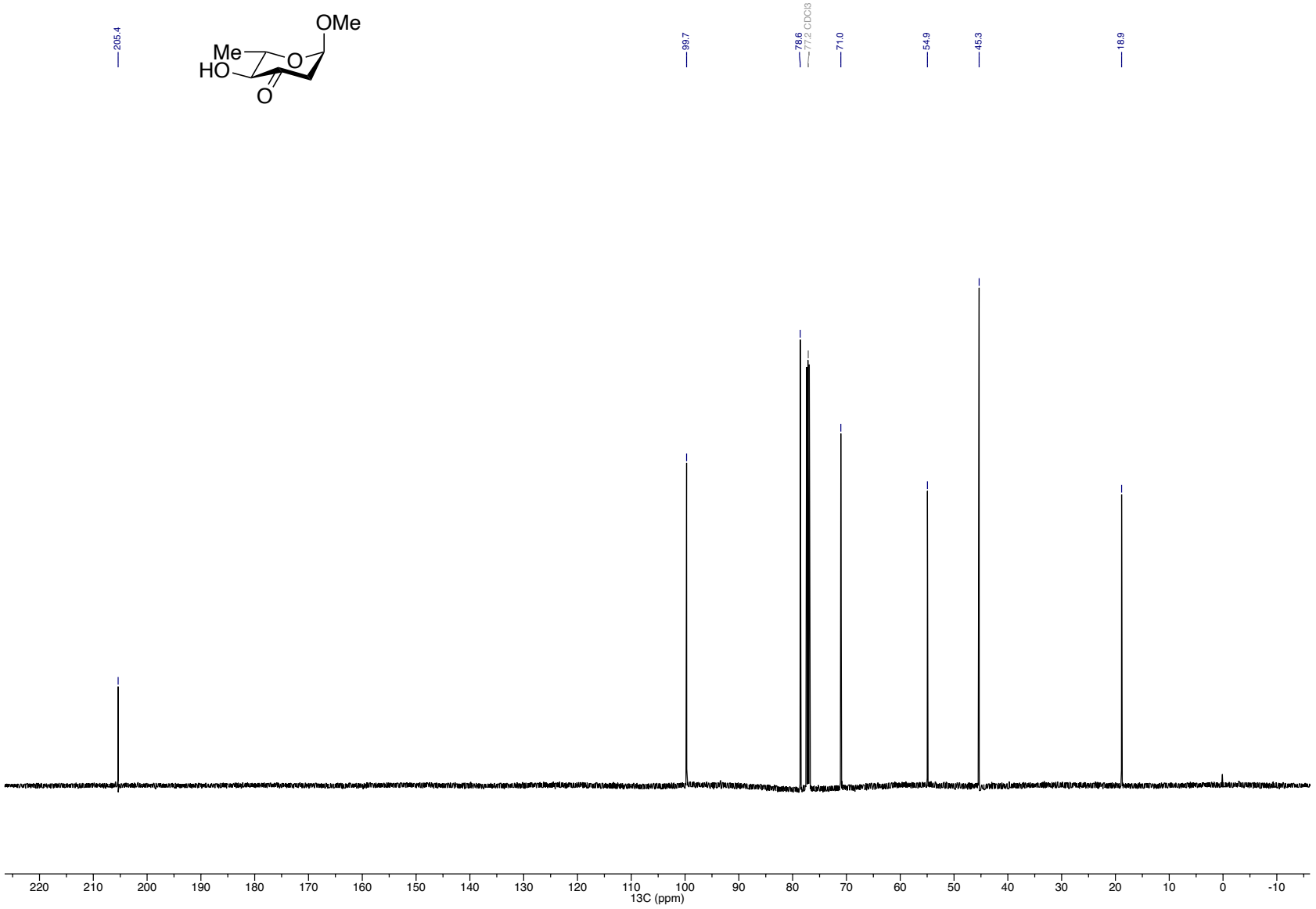


4f – Methyl 2,6-dideoxy-*α*-D-*erythro*-hexopyranoside-3-ulose

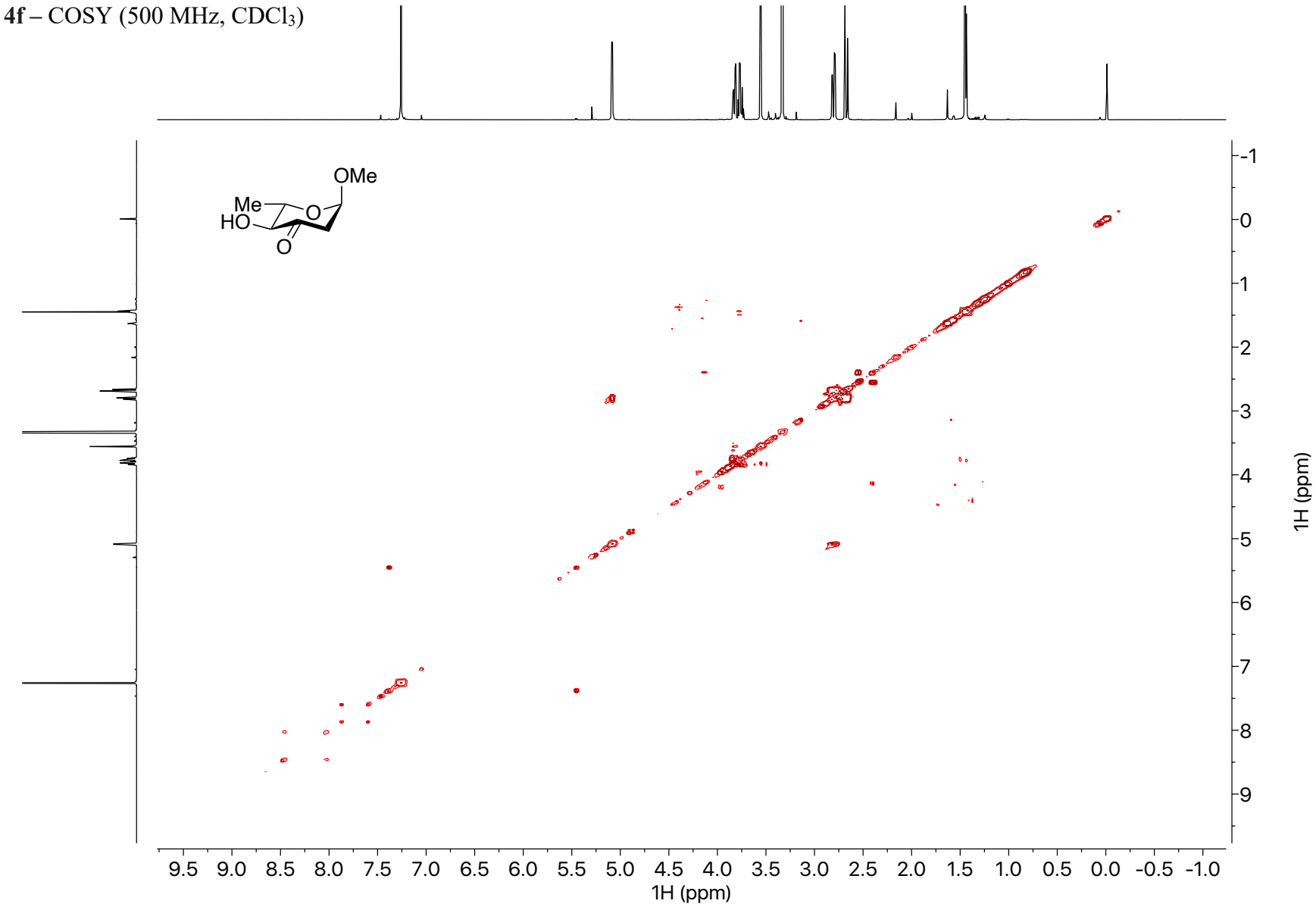
^{1}H NMR (500 MHz, $CDCl_3$)



4f – ^{13}C NMR (126 MHz, $CDCl_3$)

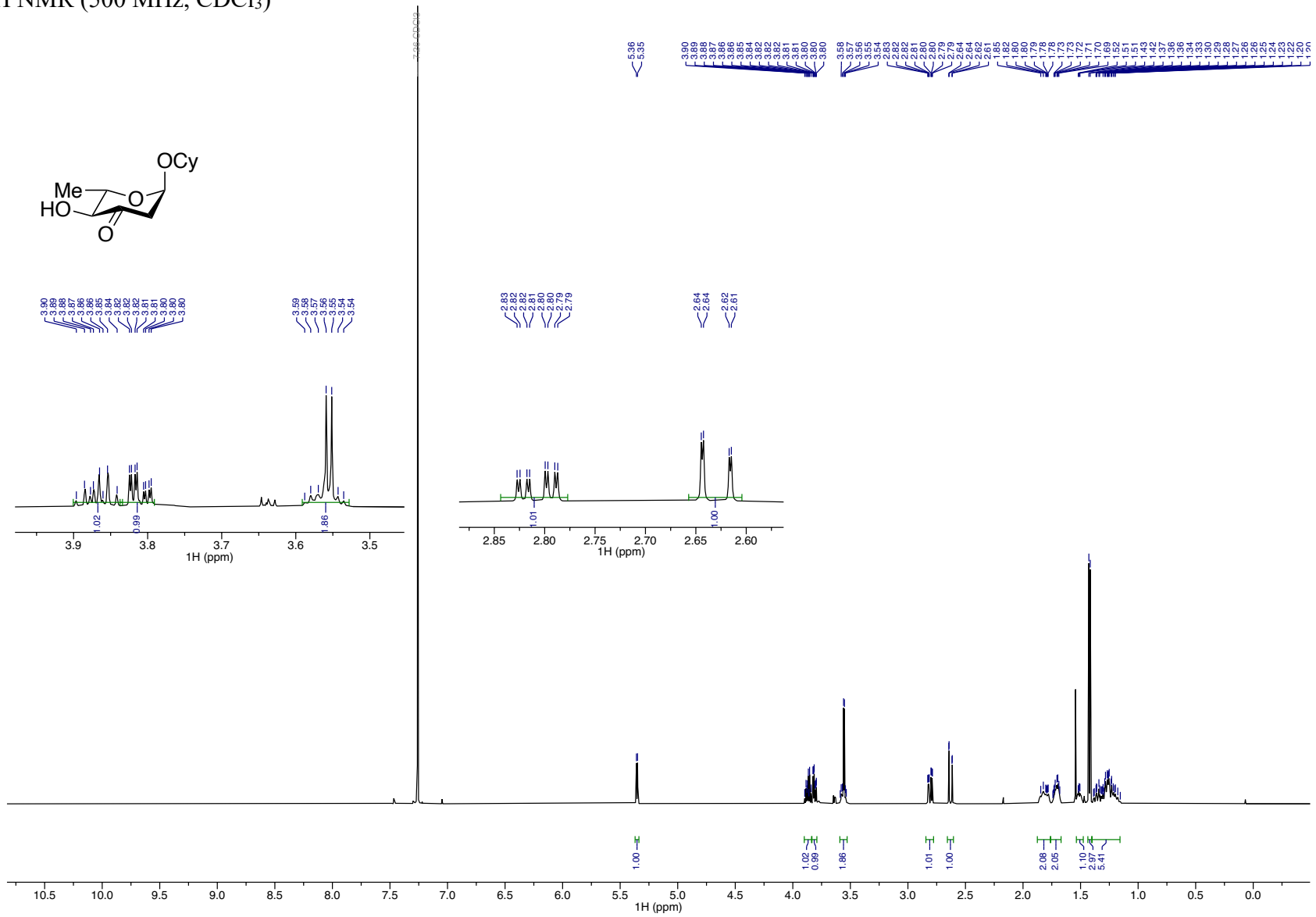


4f – COSY (500 MHz, $CDCl_3$)

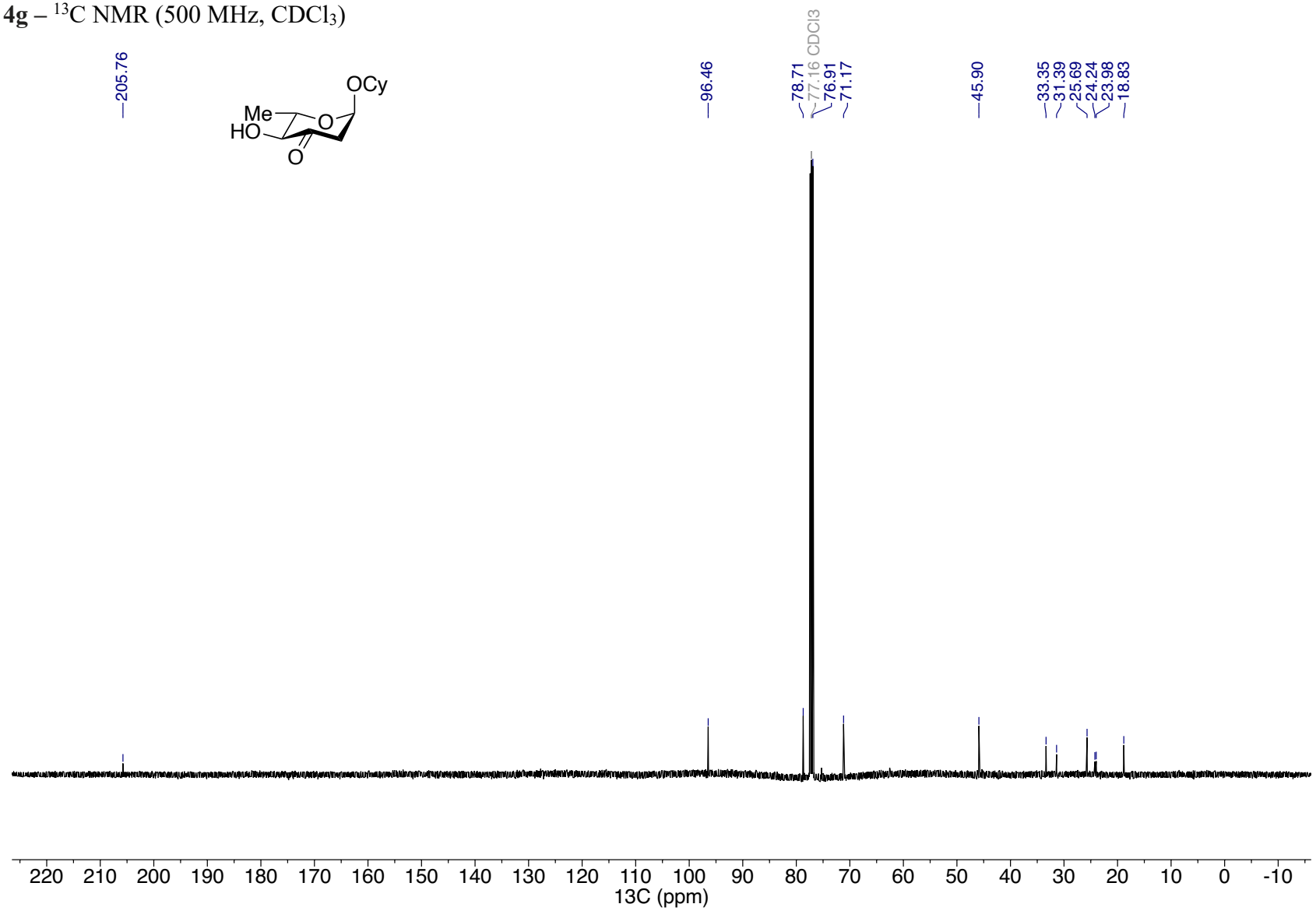


4g – Cyclohexyl 2,6-dideoxy-*α*-D-*erythro*-hexopyranoside-3-ulose

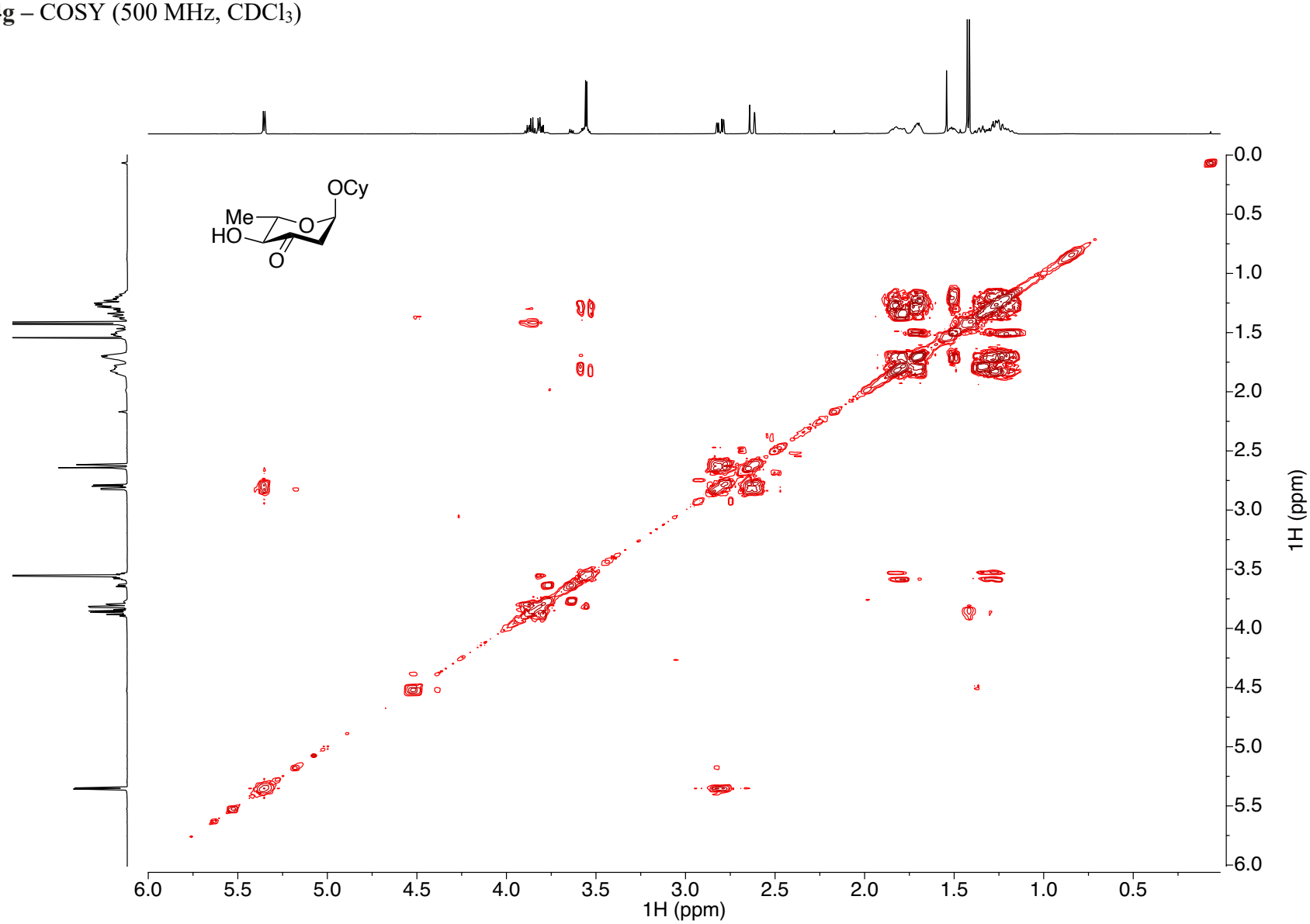
^{1}H NMR (500 MHz, $CDCl_3$)



4g – ^{13}C NMR (500 MHz, $CDCl_3$)

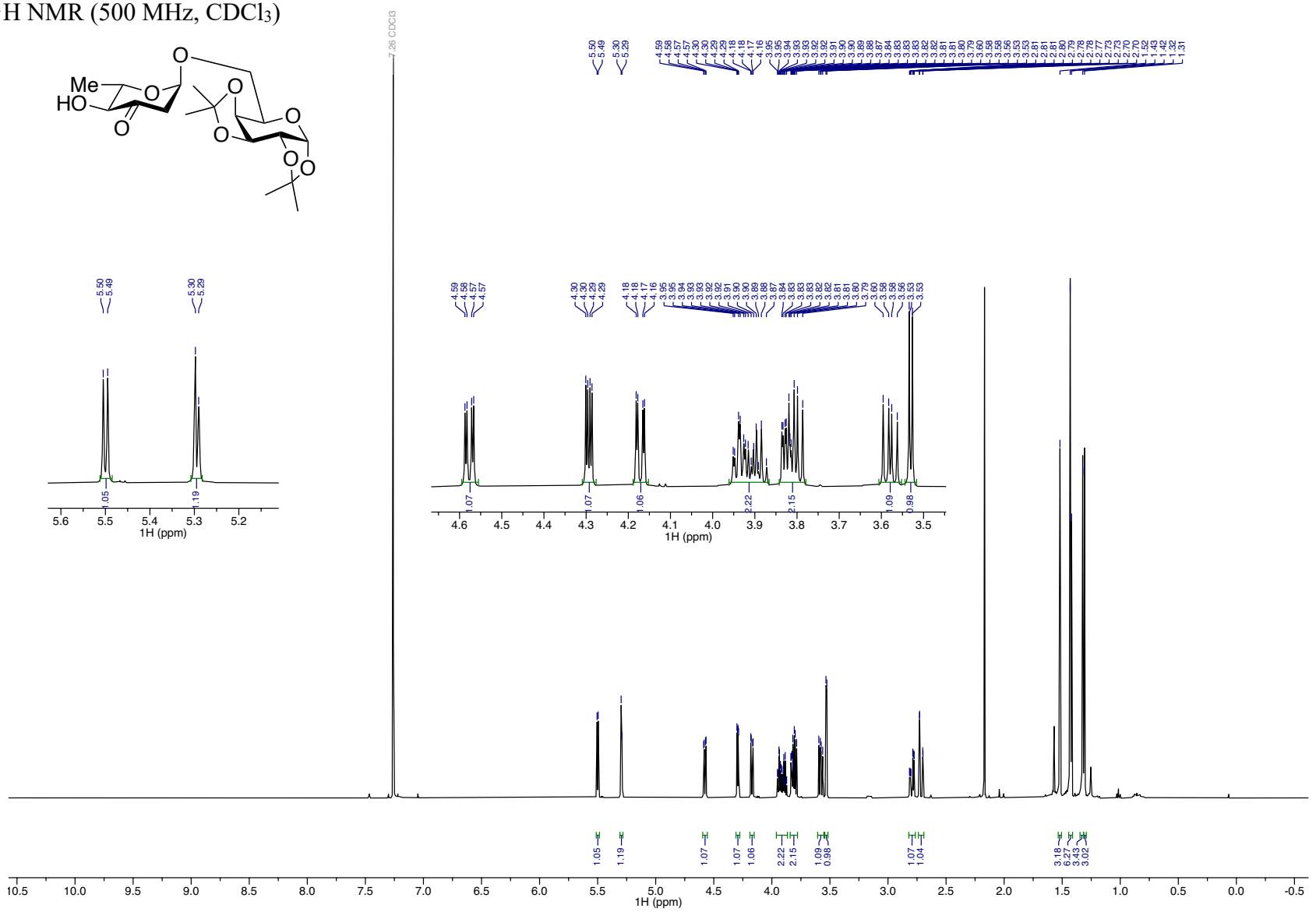


4g – COSY (500 MHz, $CDCl_3$)

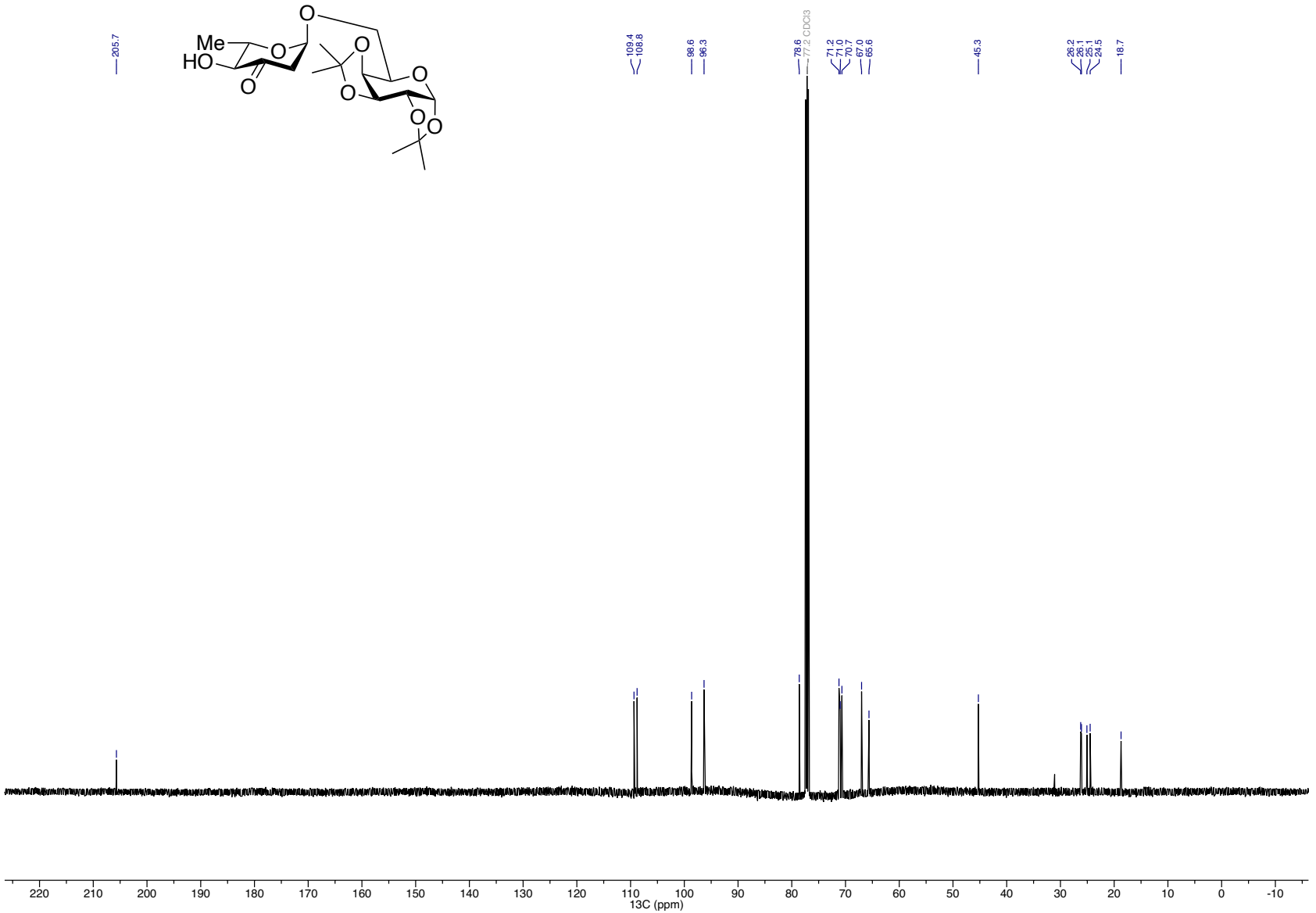


4h – 1,2,3,4-di-O-isopropylidene-6-O-(2,6-dideoxy-*α*-D-*erythro*-hexopyranoside-3-ulosyl)-α-D-galactopyranoside

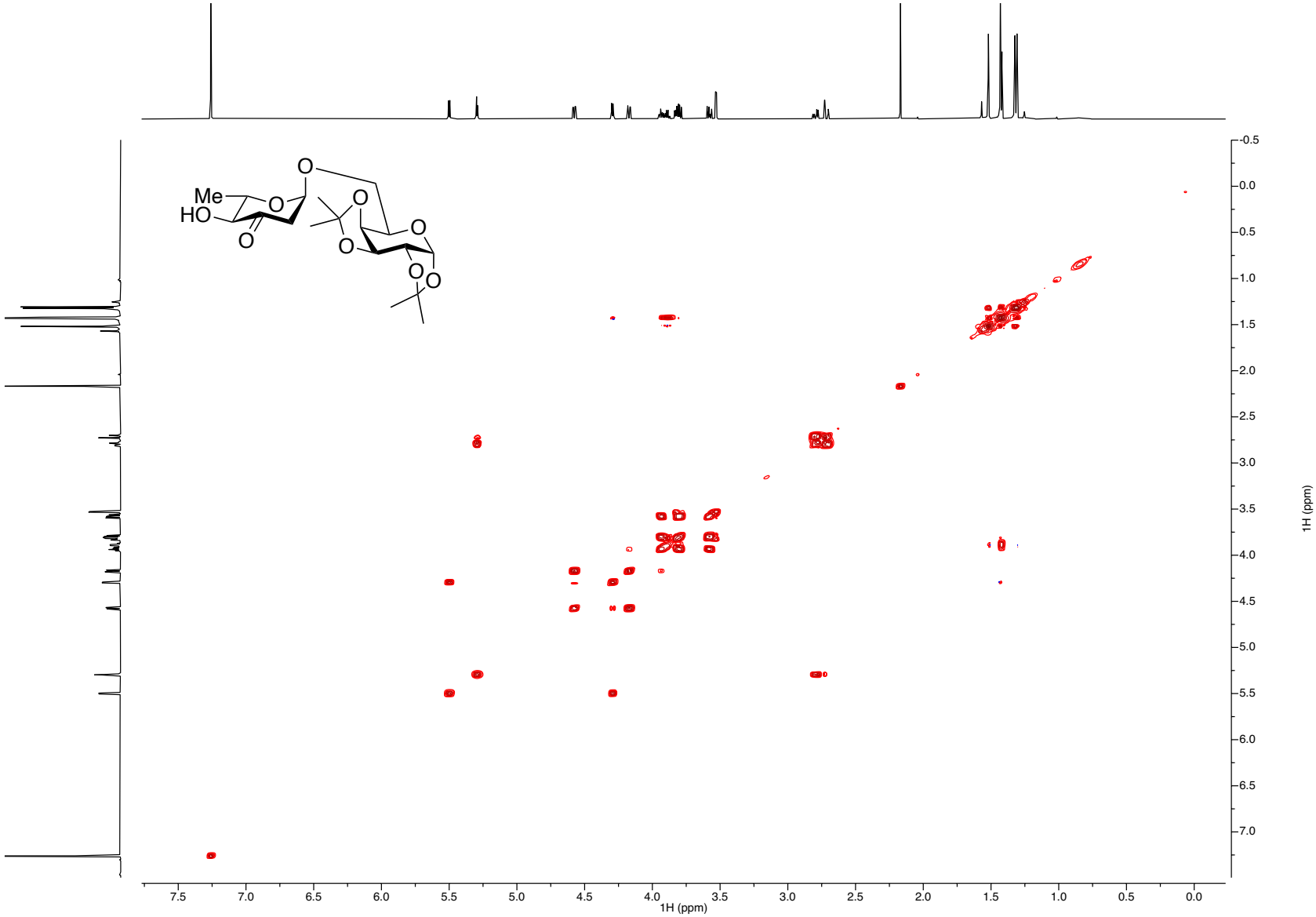
^{1}H NMR (500 MHz, $CDCl_3$)



4h – ^{13}C NMR (500 MHz, $CDCl_3$)

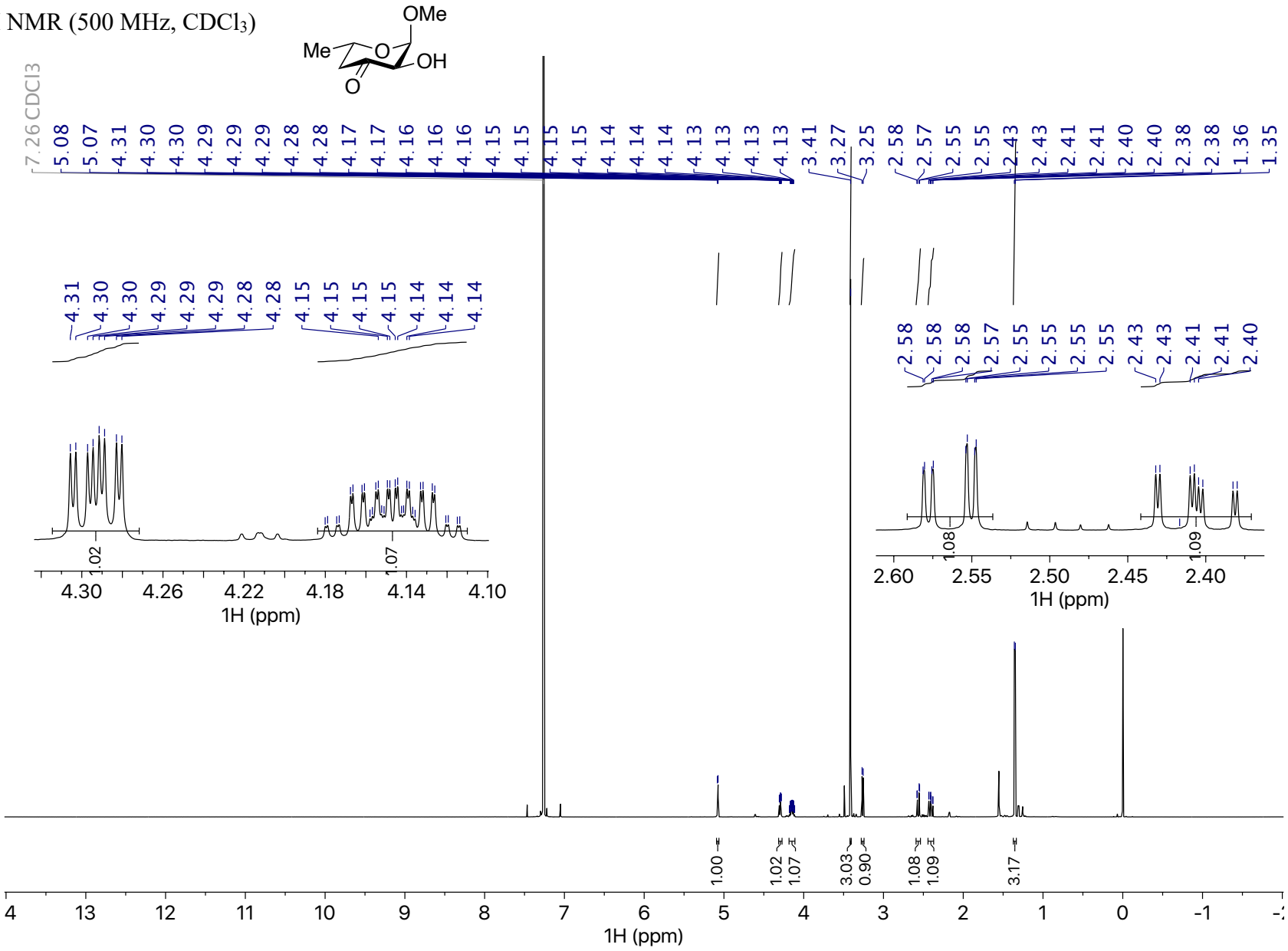


4h – COSY (500 MHz, $CDCl_3$)

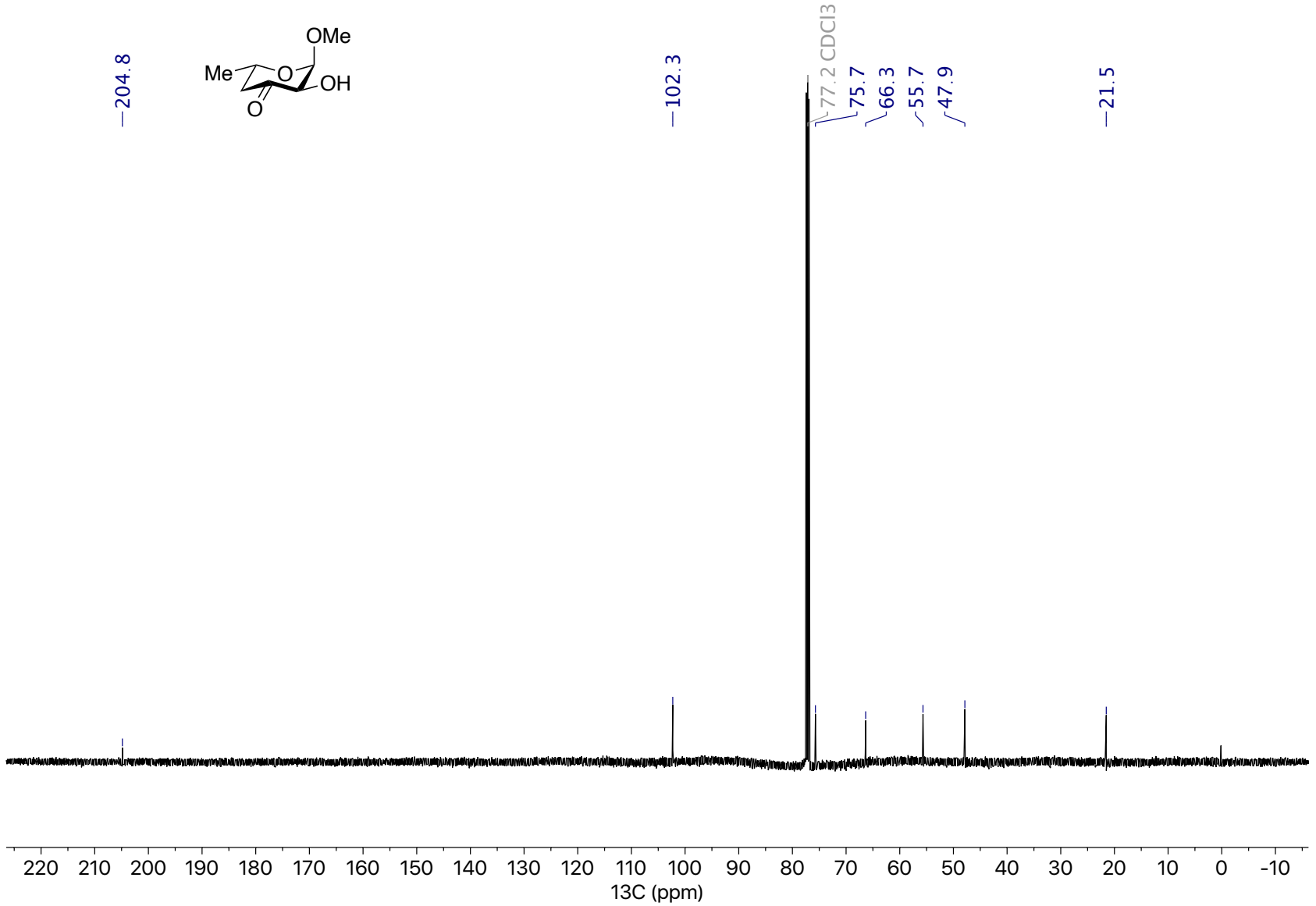


4i – Methyl 4,6-dideoxy-*α*-D-*erythro*-hexopyranoside-3-ulose

^{1}H NMR (500 MHz, $CDCl_3$)



4i – ^{13}C NMR (126 MHz, $CDCl_3$)



4i – COSY (500 MHz, $CDCl_3$)