Supporting Information

Site-Selective and Stereoselective C–H Alkylations of Carbohydrates via Combined Diarylborinic Acid and Photoredox Catalysis

Victoria Dimakos, ‡ Hsin Y. Su, ‡ Graham E. Garrett and Mark S. Taylor

Department of Chemistry, University of Toronto

80 St George Street, Toronto ON, Canada, M5S 3H6

Table of Contents

General Information

Materials

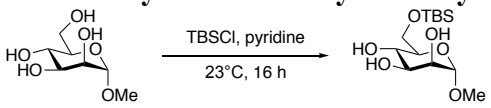
Stainless steel needles and syringes were used to transfer air and moisture-sensitive liquids. Schlenk flasks were dried at 140 °C for at least 24 hours prior to use. Toluene and acetonitrile were HPLC grade and purified using a solvent purification system equipped with columns of activated alumina under nitrogen. (Innovative Technology, Inc.). Anhydrous dimethylformamide and pyridine were purchased from Sigma Aldrich and used directly from the SureSeal bottle. 4 Å molecular sieves were stored for at least 24 hours at 140 °C prior to use. Other reagents and solvents were used without further purification. Flash column chromatography was carried out using neutral silica gel (60 Å, 230–400 mesh, Silicycle). Analytical thin layer chromatography was carried out using aluminum- backed silica gel 60 F_{254} plates (EMD), and compounds were visualized through the use of UV light and aqueous basic $KMnO_4$ or Hanessian's stain.

Instrumentation

^1H and ^{13}C NMR and 2D NMR spectra were recorded using a Varian Mercury 400 MHz, Bruker Avance III 400 MHz, Agilent DD2 600 (600 MHz), or Agilent DD2-500 (500 MHz) spectrometer equipped with a XSens cryoprobe. ^1H NMR are reported in parts per million (ppm) relative to tetramethylsilane and referenced to residual protium in the solvent. Spectral features are tabulated in the following order: chemical shift (δ, ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quartet, m-complex multiplet); number of protons; coupling constant(s) (*J*, Hz); assignment. Assignments were made on the basis of 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 single-bounce diamond/ZnSe ATR accessory as neat samples, or as thin film from CH_2Cl_2 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 approximately 5 inches from a Kessil® LED lamp (either : A160WE Tuna Blue (40 W) or H150-Blue (32 W).

Preparation of Substrates

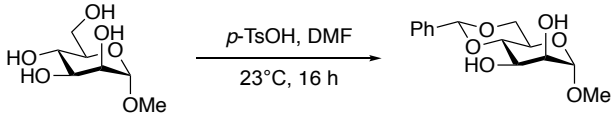
1b – Methyl 6-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranoside



Prepared from methyl α-D-mannopyranoside as previously reported.[1]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.72 (d, *J* = 1.7 Hz, 1H), 3.95–3.91 (m, 2H), 3.87–3.76 (m, 3H), 3.59 (ddd, *J* = 9.0, 6.5, 4.9 Hz, 1H), 3.38 (s, 3H), 3.28 (s, 1H), 2.65 (s, 1H), 2.37 (s, 1H), 0.91 (s, 9H), 0.11 (s, 3H), 0.11 (s, 3H).

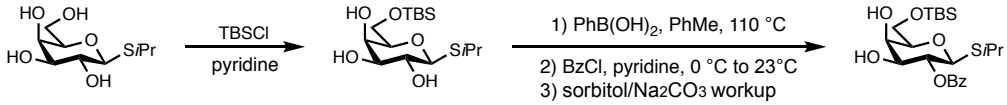
1c – Methyl 4,6-*O*-(phenylmethylene)-α-D-mannopyranoside



Prepared from methyl α-D-mannopyranoside from an adapted literature procedure using *p*-TsOH instead of camphorsulfonic acid.[2]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.51–7.46 (m, 2H), 7.41–7.35 (m, 3H), 5.58 (s, 1H), 4.78 (d, *J* = 1.2 Hz, 1H), 4.34–4.26 (m, 1H), 4.10–4.03 (m, 2H), 3.96–3.89 (m, 1H), 3.87–3.79 (m, 2H), 3.41 (s, 3H), 2.55 (d, *J* = 2.1 Hz, 1H), 2.51 (d, *J* = 3.1 Hz, 1H).

1f – Isopropyl 2-*O*-benzoyl-6-O-*tert*-butyldimethylsilyl-β-D-thiogalactopyranoside



S1

To a round-bottomed flask containing isopropyl-β-D-thiogalactoside (300 mg, 1.26 mmol, 1 equiv), and *tert*-butyldimethylsilyl chloride (208.7 mg, 1.38 mmol, 1.1 equiv.) was added 1.8 mL of pyridine. The reaction mixture was stirred at room temperature for 16 hours, and then concentrated under reduced pressure. Residual pyridine was removed azeotropically with toluene to afford a colourless oil. **S1** was obtained following flash chromatography on silica gel (10% to 20% acetone in dichloromethane) as a light yellow oil. Spectral features are in agreement with those previously reported.[1]

^{1}H NMR (500 MHz, CD_3OD): δ (ppm) = 4.51 (d, *J* = 9.3 Hz, 1H), 4.00 (dd, *J* = 3.2, 1.1 Hz, 1H), 3.90 (dd, *J* = 6.0, 1.1 Hz, 2H), 3.67–3.61 (m, 2H), 3.60 (dd, *J* = 9.3, 3.2 Hz, 1H), 3.33 (p, *J* = 6.8 Hz, 1H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.01 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H).

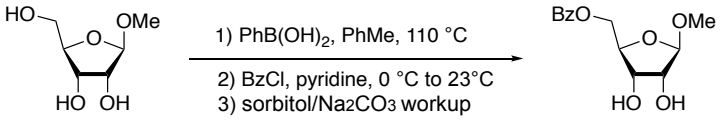
Prepared from an adapted literature procedure.[3] To a round-bottomed flask containing **S1** (703 mg, 1.99 mmol, 1 equiv.) was added phenylboronic acid (243 mg, 1.99 mmol,1 equiv.) and toluene (10 mL). The flask was equipped with a reflux condenser and the reaction mixture stirred

for 16 hours. The mixture was then concentrated under reduced pressure, and dried by azeotropic removal of water with toluene. To the resulting colourless oil was added pyridine (4 mL), and the solution was cooled to 0°C and benzoyl chloride (0.35 mL, 2.99 mmol, 1.5 equiv.). The reaction was stirred at room temperature for 45 minutes, after which it was quenched with methanol (1 mL) and then concentrated under reduced pressure. The crude material was then dissolved in ethyl acetate (80 mL) and transferred to a separatory funnel along with a sorbitol: sodium carbonate solution (1M:1M) and hand shaken vigorously for 5 minutes. The aqueous layer was back-extracted with EtOAc (40 mL × 2) and the combined organic extracts dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude material was purified by flash chromatography on silica gel (2% acetone in dichloromethane) to give the product as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.11–8.00 (m, 2H), 7.62–7.52 (m, 1H), 7.49 – 7.40 (m, 2H), 5.27 (dd, *J* = 9.6, 9.6 Hz, 1H), 4.64 (d, *J* = 10.0 Hz, 1H), 4.19–4.12 (m, 1H), 4.01–3.87 (m, 2H), 3.79 (ddd, *J* = 9.2, 8.1, 3.4 Hz, 1H), 3.60–3.53 (m, 1H), 3.23 (hept, *J* = 6.7 Hz, 1H), 3.07 (d, *J* = 2.0 Hz, 1H), 3.06 (d, *J* = 6.2 Hz, 1H), 1.31 (d, *J* = 6.7 Hz, 3H), 1.26 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 167.0, 133.4, 130.1, 129.9, 128.5, 83.1, 78.1, 74.3, 72.9, 69.8, 63.1, 34.9, 26.0, 24.6, 23.9, 18.4, -5.3, -5.3.

1h – Methyl 5-*O*-benzoyl β-D-ribofuranoside



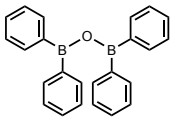
Prepared from an adapted literature procedure.[3] To a round-bottomed flask containing methyl β-D-ribofuranoside (328 mg, 2 mmol, 1 equiv.) and phenylboronic acid (244 mg, 2 mmol, 1 equiv.) was added toluene (10 mL). The reaction mixture was stirred at 110 °C for 16 hours, and then cooled to room temperature and concentrated under reduced pressure. The resulting boronic ester intermediate was dried through azeotropic removal of water with toluene to give a white solid, which was then dissolved in pyridine (4 mL). The solution was cooled to 0 °C, and benzoyl chloride (0.35 mL, 3 mmol, 1.5 equiv.) was added. The reaction mixture was warmed to room temperature, stirred vigorously for 45 minutes and then quenched with 4 mL of MeOH. The crude was then concentrated under reduced pressure, suspended in ethyl acetate (80 mL) and then transferred to a separatory funnel along with a sorbitol:sodium carbonate solution (1M:1M). The contents of the flask were hand shaken vigorously for 5 minutes. The aqueous layer was then back-extracted with ethyl acetate (40 mL × 2) and the combined organic layers were dried over $MgSO_4$. The titled compound was obtained following purification of the crude material by flash chromatography on silica gel (50% acetone in dichloromethane) as a white solid. Spectral features are in agreement with those previously reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.10–8.04 (m, 2H), 7.60–7.53 (m, 1H), 7.48–7.40 (m, 2H), 4.88 (s, 1H), 4.58 (dd, *J* = 11.8, 3.9 Hz, 1H), 4.48–4.38 (m, 2H), 4.30–4.22 (m, 1H), 4.09 (dd, *J* = 4.2 Hz, 1H), 3.33 (s, 3H), 2.62 (d, *J* = 3.6 Hz, 1H), 2.55 (d, *J* = 7.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 166.8, 133.3, 130.0, 129.9, 128.6, 108.2, 81.2, 75.3, 72.2, 65.2, 55.3.

Synthesis of Borinic Acids

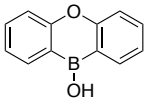
3a – Diphenylborinic anhydride



Prepared from 2-aminoethyl diphenylborinate as previously reported.[5]

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 7.71–7.66 (m, 2H), 7.50–7.44 (m, 1H), 7.44–7.38 (m, 2H).

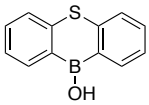
3b – 10*H*-Dibenzo[*b*,*e*][1,4]oxaborinin-10-ol



Prepared from diphenyl ether as previously reported.[6]

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 9.84 (s, 1H), 8.14 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.67 (ddd, *J* = 8.7, 7.0, 1.8 Hz, 2H), 7.43 (dd, *J* = 8.4, 1.0 Hz, 2H), 7.28 (ddd, *J* = 7.3, 1.0 Hz, 2H).

3c – 10*H*-Dibenzo[*b*,*e*][1,4]thiaborinin-10-ol



Prepared from diphenyl sulfide as previously reported.[6]

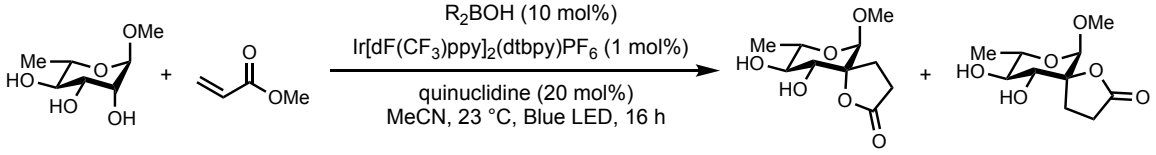
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 9.87 (s, 1H), 8.38 – 8.31 (m, 2H), 7.63 – 7.53 (m, 4H), 7.39 (ddd, *J* = 7.6, 6.0, 2.2 Hz, 2H).

Site-Selective *C*-Alkylation

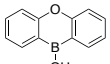
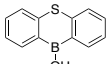
Optimization Procedure

Methyl α-L-rhamnopyranoside (35.6 mg, 0.2 mmol, 2 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%), borinic acid (0.01 mmol, 10 mol%) were combined in 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 (0.4 mL) was added under a balloon of argon. The balloon was removed and methyl acrylate (8.6 mg, 0.1 mmol, 1 equiv.) was added to the vial. The rubber septum was quickly replaced with the vial cap and sealed with Teflon tape. The vial was placed 5 inches from a blue LED Kessil lamp and stirred at 1050 rpm (the temperature under the light was monitored and remained at ~25 °C throughout the course of the reaction). After 16 hours, the crude reaction mixture was concentrated under reduced pressure, and analyzed by ^{1}H NMR spectroscopy.

Table S1: Optimization of stoichiometry and borinic acid catalyst

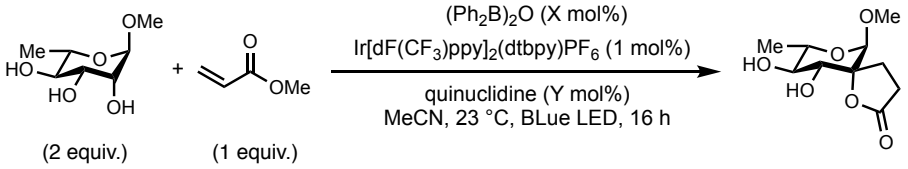


1a **S2** **2a** **S3**

Entry	1a (equiv.)	S2 (equiv.)	Borinic acid	NMR yield 2a[a]	Diastereoselectivity[b] (2a: S3)	Dialkylation[c]
1[d]	2	1		46%	7.2:1	9%
2[d]	2	1		55%	>20:1	5%
3	2	1		72%	>20:1	8%
4	1	2		37%	5.1:1	19%
5	1	1		53%	n.d.	n.d.

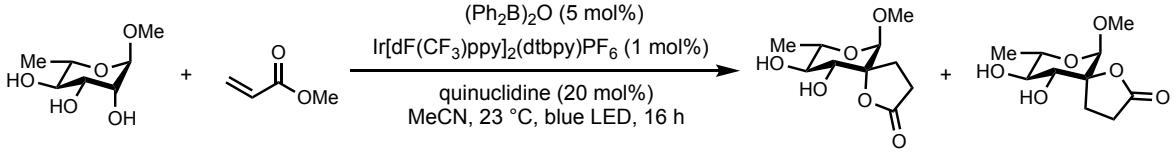
[a] Yields of 2a was determined from ^{1}H NMR spectra of the crude reaction mixture (integration of singlet at 4.51 ppm relative to 1,3,5-trimethoxybenzene.
[b]Ratios of diastereomers were determined by integration of the ^{1}H NMR spectrum of the crude reaction mixture in CD_3OD. 2a (s, 4.51 ppm, H-1): S3 (d, 3.95 ppm, H-3).
[c] Amounts of dialkylation were determined from ^{1}H NMR spectra of the crude reaction mixture (total integration of doublets at 4.71 ppm and 4.63 ppm relative to 1,3,5-trimethoxybenzene.
[d]Reaction was run for 18 hours instead of 16 hours.

Table S2: Effects of the ratio of borinic acid to quinuclidine



Quinuclidine (mol%)	(Ph$_2$B)$_2$O (mol%) 2.5	5	10
10	43%	<5%	<5%
20	54%	72%	20%
40	41%	43%	53%

Table S3: Control experiments



Entry	Changes to above reaction conditions	NMR yield 2a[a]	Diastereoselectivity[b] (2a: S3)	Dialkylation[c]
1	No Blue LED	<5%	N/A	N/A
2	No Ir cat.	<5%	N/A	N/A
3	No (Ph$_2$B)$_2$O	5%	1:4.1	17%
4	No quinuclidine	<5%	N/A	N/A
5	No quinuclidine, tetrabutylammonium benzoate (20 mol%)	<5%	N/A	N/A
6	No quinuclidine, Methyl thioglycolate (20 mol%)	<5%	N/A	N/A
7[d]	No (Ph$_2$B)$_2$O, 10 mol% quinuclidine, 25 mol% $Bu_4NPO_4H_2$, ACN (0.25 M)	<5%	N/A	N/A
8[e]	No (Ph$_2$B)$_2$O, 10 mol% quinuclidine, 25 mol% $Bu_4NPO_4H_2$ DMSO (0.5 M)	5%	1: 4.4	33%

[a] Yields of 2a was determined from ^{1}H NMR spectra of the crude reaction mixture (integration of singlet at 4.51 ppm relative to 1,3,5-trimethoxybenzene.
[b]Ratios of diastereomers were determined by integration of the ^{1}H NMR spectrum of the crude reaction mixture in CD_3OD. 2a (s, 4.51 ppm, H-1): S1 (d, 3.95 ppm, H-3).

[c] Amounts of dialkylation were determined from ^{1}H NMR spectra of the crude reaction mixture (total integration of doublets at 4.71 ppm and 4.63 ppm relative to 1,3,5-trimethoxybenzene.
[d] Reaction was set up and run according to the optimization procedure above, however using conditions reported by MacMillan and coworkers. The reaction was run more dilute to allow for solubility of 1a.[7]
[e]Reaction was set up and run according to the optimization procedure above, however using conditions reported by Minnaard and coworkers.[8]

General Procedure A for reactions run on 0.1 mmol scale

Carbohydrate/diol, (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (1 mg, 0.001 mmol, 1 mo l%), quinuclidine (2.2 mg, 0.02 mmol, 20 mol%), and $(Ph_2B)_2O$ borinic acid (1.7 mg, 0.005 mmol, 5 mol%) were combined in 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 (0.4 mL) was added under a balloon of argon. The balloon was removed and methyl acrylate was added to the vial using an airtight glass syringe. The rubber septum was quickly replaced with the vial cap and sealed with Teflon tape. The vial was placed 5 inches from a blue LED Kessil lamp and stirred at 1050 rpm (the temperature under the light was monitored and remained at ~25 °C throughout the course of the reaction). After 16 hours, the crude reaction mixture was concentrated under reduced pressure, and analyzed by ^{1}H NMR spectroscopy.

General Procedure B for reactions run on 0.2 mmol scale with 5 mol% $(Ph_2B)_2O$

Carbohydrate/diol, (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (2 mg, 0.002 mmol, 1 mol %), quinuclidine (4.4 mg, 0.04 mmol, 20 mol%), and $(Ph_2B)_2O$ (3.5 mg, 0.005 mmol, 5 mol%) were combined in 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 (0.8 mL) was added under a balloon of argon. The balloon was removed and methyl acrylate was added to the vial using an airtight glass syringe. The rubber septum was quickly replaced with the vial cap and sealed with Teflon tape. The vial was placed 5 inches from a Blue LED Kessil lamp and stirred at 1050 rpm (the temperature under the light was monitored and remained at ~25 °C throughout the course of the reaction). After 16 hours, the crude reaction mixture was concentrated under reduced pressure, and site- and/or diastereoselectivity was analyzed by ^{1}H NMR spectroscopy prior to column chromatography.

General Procedure C for reactions run on 0.2 mmol scale with 2.5 mol% $(Ph_2B)_2O$

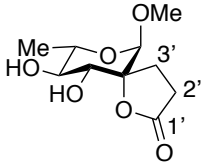
Carbohydrate/diol, Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (2 mg, 0.002 mmol, 1 mol%) and quinuclidine (4.4 mg, 0.04 mmol, 20 mol%) were combined in a 1 dram vial. A rubber septum was used to seal the vial, which was then evacuated and backfilled with argon three times on a Schlenk line. A solution of $(Ph_2B)_2O$ in dry, degassed acetonitrile was prepared (3.4 mg in 0.8 mL). The $(Ph_2B)_2O$ solution (0.4 mL, 0.005 mmol, 2.5 mol%), as well as 0.4 mL of dry, degassed acetonitrile was added to the 1 dram vial containing the diol, iridium catalyst and quinuclidine. The balloon was removed and methyl acrylate was added to the vial using an airtight glass syringe. The rubber septum was quickly replaced with the vial cap and sealed with Teflon tape. The vial was placed 5 inches from a blue LED Kessil lamp and stirred at 1050 rpm (the temperature under the light was monitored and remained at ~25 °C throughout the course of the

reaction). After 16 hours, the crude reaction mixture was concentrated under reduced pressure, and site- and/or diastereoselectivity was analyzed by ^{1}H NMR spectroscopy prior to column chromatography.

General Procedure D for reactions run in the absence of $(Ph_2B)_2O$

Carbohydrate/diol, $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (1 mg, 0.001 mmol, 1 mol%) and quinuclidine (2.2 mg, 0.01 mmol, 20 mol%) were combined in 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 (0.4 mL) was added under a balloon of argon. The balloon was removed and methyl acrylate was added to the vial using an airtight glass syringe. The rubber septum was quickly replaced with the vial cap and sealed with Teflon tape. The vial was placed 5 inches from a blue LED Kessil lamp and stirred at 1050 rpm (the temperature under the light was monitored and remained at ~25 °C throughout the course of the reaction). After 16 hours, ~40 mg of Amberlyst 15 resin was added to the vial and the mixture stirred at 50 °C for three hours. The resin was then removed by filtration over cotton and the crude reaction mixture was concentrated under reduced pressure. 1,3,5-Trimethoxybenzene was added and the reaction was analyzed by ^{1}H NMR spectroscopy.

2a – (5*R*,6*R*,8*S*,9*R*,10*R*)-9,10-Dihydroxy-6-methoxy-8-methyl-1,7-dioxaspiro[4.5]decan-2-one



Prepared according to General Procedure A from methyl α-L-rhamnopyranoside (**1a**) (71.8 mg, 0.4 mmol, 2 equiv.) and methyl acrylate (17 mg, 0.2 mmol, 1 equiv.). **2a** was obtained as a colourless oil (34.4 mg, 70%) after flash chromatography on silica gel (10% to 60% ethyl acetate in hexanes). In addition to the reported product, analysis of the crude reaction mixture indicated 7% of an overalkylation product and <5% of a diastereomer of the reported compound.

A reaction run according to General Procedure D afforded 5% of **2a** and 22% of **S3**. Two overalkylation products were also observed in a combined yield of 17%.

^{1}H NMR (500 MHz, CD_3OD): δ (ppm) = 4.51 (s, 1H, H-1), 3.65–3.60 (m, 2H, H-3, H-5), 3.39 (s, 3H, OCH_3), 3.28 (dd, *J* = 9.5, 9.5 Hz, 1H, H-4), 2.68 (ddd, *J* = 17.9, 10.8, 9.2 Hz, 1H, H-2'a), 2.48 (ddd, *J* = 17.9, 10.8, 4.0 Hz, 1H, H-2'b), 2.28 (ddd, *J* = 13.3, 10.8, 4.0 Hz, 1H, H-3'a), 2.16 (ddd, *J* = 13.6, 10.8, 9.2 Hz, 1H, H-3'b), 1.28 (d, *J* = 6.3 Hz, 3H, CH_3).

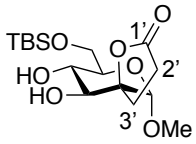
^{13}C NMR (126 MHz, CD_3OD): δ (ppm) = 179.6, 103.3, 88.4, 75.3, 74.9, 69.7, 55.6, 29.7, 28.0, 18.0.

IR (neat, cm^{-1}): 3416 (br, m), 2983 (w), 2937 (w), 2845 (w), 1760 (s), 1454 (m), 1416 (w), 1375 (w), 1192 (s), 1143 (s), 1105 (s), 1047 (s), 970 (s), 916 (s), 850 (m), 808 (m), 782 (m), 675 (m), 632 (m).

HRMS (DART$^+$, m/z): calculated for $C_{10}H_{20}NO_6$ $[M+NH_4]^+$: 250.12906, found 250.12849.

$[\alpha]_D^{20}$ = −57.2 (c= 0.325 g/100 mL^{-1}, $CHCl_3$)

2b – (5*S*,6*S*,8*R*,9*S*,10*S*)-8-(((*tert*-Butyldimethylsilyl)oxy)methyl)-9,10-dihydroxy-6-methoxy-1,7-dioxaspiro[4.5]decan-2-one



Prepared according to General Procedure A from methyl 6-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranoside (**1b**) (61.5 mg, 0.2 mmol, 2 equiv.), and methyl acrylate (8.4 mg, 0.1 mmol, 1 equiv.). **2b** was obtained as a colourless oil (28.4 mg, 68%) after flash chromatography on silica gel (10% to 50% ethyl acetate in hexanes). In addition to the mono-alkylated carbohydrate, a dialkylated product was isolated in 9% yield and compounds resulting from starting material decomposition were also observed.

A reaction run according to General Procedure D, but without subjecting the crude to Amberlyst 15 resin afforded 14% of **2b** along with compounds resulting from starting material decomposition.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) =4.49 (s, 1H, H-1), 3.93–3.83 (m, 2H, H-6a and H-6b), 3.81 (d, *J* = 9.2 Hz 1H, H-3), 3.78 (dd, *J* = 9.2, 9.2 Hz, 1H, H-4), 3.69 (br s, 1H, OH) 3.68–3.61 (m, 2H, H-5), 3.39 (s, 3H, OCH_3), 3.00 (br s, 1H, OH), 2.79 (ddd, *J* = 17.6, 10.4, 9.3 Hz, 1H, H-2a'), 2.47–2.34 (m, 2H, H-2b' and H-3a'), 2.10 (ddd, *J* = 13.6, 10.6, 9.3 Hz, 1H, H-3b'), 0.90 (s, 9H, $SiC(C\mathbf{H}_3)_3$), 0.11 (d, *J* = 4.9 Hz, 6H $Si(C\mathbf{H}_3)_2$).

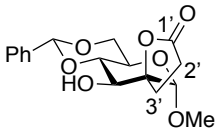
^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) =177.2, 102.0, 85.5, 74.5, 72.3, 70.6, 65.4, 55.5, 28.9, 27.2, 26.0, 18.3, -5.4, -5.4.

IR (neat, cm^{-1}): 3418 (br, w), 2958 (w), 2929 (w), 2899 (w), 2857 (w), 1768 (s), 1463 (w), 1418 (w), 1364 (w), 1252 (m), 1192 (m), 1148 (s), 1073 (s), 1048 (s), 973 (m), 919 (w), 833 (s), 775 (s), 666 (m), 635 (m).

HRMS ($DART^+$, m/z): calculated for $C_{16}H_{34}NO_7Si$ $[M+NH_4]^+$: 380.21045, found 380.21013.

$[\alpha]_D^{20}$ = +30.3 (c= 0.145 g/100 mL^{-1}, $CHCl_3$)

2c – (2*S*,2'*R*,4a'*R*,6'*S*,8'*S*,8a'*S*)-8'-Hydroxy-6'-methoxy-2'-phenylhexahydro-5*H*,6'*H*-spiro[furan-2,7'-pyrano[3,2-*d*][1,3]dioxin]-5-one



Prepared according to General Procedure A from methyl 4,6-*O*-benzylidine-α-D-mannopyranoside (**1c)** (56.5 mg, 0.2 mmol, 2 equiv.), and methyl acrylate (8.5 mg, 0.1 mmol, 1 equiv.). **2c** was obtained as a white solid (22.5 mg, 67%) after flash chromatography on silica gel (10% to 40% ethyl acetate in hexanes).

A reaction run according to General Procedure D, but without subjecting the crude to Amberlyst 15 resin afforded 12% of **2c** along with decomposition of methyl 4,6-O-benzylidine-α-D-mannopyranoside.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.51–7.46 (m, 2H, Ar-H), 7.42–7.35 (m, 3H, Ar-H), 5.56 (s, 1H, C**H**Ph), 4.56 (s, 1H, H-1), 4.30 (ddd, *J* = 6.0, 2.4, 2.4 Hz, 1H, H-6a'), 4.06 (dd, *J* = 9.7, 3.3 Hz, 1H, H-3), 3.97–3.90 (m, 1H, H-4), 3.90–3.81 (m, 2H, H-5, H-6b'), 3.43 (s, 3H, OCH_3), 2.87–2.79 (m, 1H, CH_2), 2.50–2.40 (m, 2H, CH_2), 2.36 (d, *J* = 3.3 Hz, 1H, OH), 2.19–2.10 (m, 1H, CH_2).

^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) = 176.8, 137.6, 129.5, 128.5, 126.4, 103.1, 102.3, 85.8, 79.5, 72.4, 68.9, 63.5, 55.7, 28.8, 27.9.

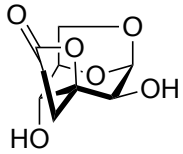
IR (neat, cm^{-1}): 3429 (br, w), 2949 (w), 2911 (w), 2841 (w), 1753 (s), 1466 (w), 1406 (w), 1375 (w), 1329 (w), 1215 (m), 1192 (m), 1158 (s), 1128 (m), 1108 (s), 987 (s), 966 (s), 918 (s), 815 (m), 783 (m), 767 (s), 739 (m), 704 (s), 657 (m), 612 (m),

HRMS ($DART^+$, m/z): calculated for $C_{17}H_{21}O_7$ $[M+H]^+$: 337.12873, found

337.12778.

$[\alpha]_D^{20}$ = +26.3 (c= 0.19g/100 mL^{-1}, $CHCl_3$)

2d – (1*R*,2*R*,3*S*,4*S*,5*R*)-2,4-Dihydroxydihydro-5'*H*-6,8-dioxaspiro[bicyclo[3.2.1]octane-3,2'-furan]-5'-one



Prepared according to General Procedure B from 1,6-β-D-anhydromannopyranoside (**1d)** (64.9 mg, 0.4 mmol, 2 equiv.), and methyl acrylate (17 mg, 0.2 mmol, 1 equiv.). **2d** was obtained as a white solid (28.4 mg, 68%) after flash chromatography on silica gel (30% to 90% ethyl acetate in hexanes) along with a compound resulting from 1,6-β-D-anhydromannopyranoside decomposition. Compound **2d** was diacetylated (**S4**) to obtain a NOSEY spectrum.

A reaction run according to General Procedure D afforded 9% of **2d** along with a 1,6-β-D-anhydromannopyranoside decomposition product.

^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 5.21 (d, *J* = 2.0 Hz, 1H, H-1), 4.47 (ddd, *J* = 5.9, 2.0, 1.1 Hz, 1H, H-5), 4.06 (dd, *J* = 7.6, 1.1 Hz, 1H, H-6a), 3.65 (dd, *J* = 7.6, 5.9 Hz, 1H, H-6b), 3.61

(dd, J = 8.0, 2.1 Hz, 1H, H-4), 3.53 (dd, J = 9.7, 2.0 Hz, 1H, H-2), 3.49 (d, J = 8.2 Hz, 1H, 4-OH), 3.23 (d, J = 9.7 Hz, 1H, 2-OH), 2.54–2.33 (m, 3H, CH_2), 2.19–2.10 (m, 1H, CH_2).

^{13}C NMR (126 MHz, CD_3CN): δ (ppm) = 178.2, 102.9, 86.8, 77.9, 73.1, 72.5, 65.7, 29.8, 28.3, 1.8, 1.7, 1.5, 1.3, 1.2, 1.0, 0.8.

IR (neat, cm^{-1}): 3349 (br, s), 3293 (br, s), 2977 (m), 2900 (w), 1724 (s), 1483 (w), 1464 (m), 1422 (m), 1350 (m), 1332 (s), 1313 (s), 1269 (s), 1257 (s), 1188 (m), 1157 (s), 1127 (s), 1021 (s), 1009 (s), 974(s), 982 (s), 954 (s), 933 (m), 896 (s), 866 (m), 821 (s), 808 (s), 773 (s), 708 (m), 615 (m).

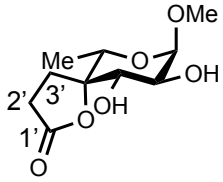
HRMS (DART$^+$, m/z): calculated for $C_9H_{16}NO_6$ $[M+NH_4]^+$: 234.09776, found 234.09728.

$[\alpha]_D^{20}$ = − 158.3 (c= 0.120 g/100 mL^{-1}, CH_3CN)

Compound **S4**:

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.46 (d, J = 1.8 Hz, 1H, H-1), 4.93 (d, J = 1.8 Hz, 1H, H-2), 4.90 (d, J = 1.9 Hz, 1H, H-4), 4.66–4.60 (m, 1H, H-5), 4.39 (dd, J = 7.8, 1.0 Hz, 1H, H-6a), 3.83 (dd, J = 7.9, 5.8 Hz, 1H, H-6b), 2.52–2.36 (m, 2H, CH_2), 2.20 (s, 3H, C(O)CH_3), 2.17 (s, 3H, C(O)CH_3), 2.18–2.09 (m, 2H, CH_2).

2e – (5*S*,6*S*,8*R*,9*S*,10*S*)-9,10-Dihydroxy-8-methoxy-6-methyl-1,7-dioxaspiro[4.5]decan-2-one



Prepared according to General Procedure C from methyl α-L-fucopyranoside (**1e**) (71.3 mg, 0.4 mmol, 2 equiv.) and methyl acrylate (16.8 mg, 0.195 mmol, 1 equiv.). Analysis of the crude ^{1}H NMR spectrum revealed a 5.3:1 ratio of regioisomers (H-1 **2e**: H-2 **S5**). Integration of **2e** (H-1) was determined through subtraction of the integrations of the doublet at 4.14 ppm and the singlet at 4.06 ppm due to overlap of anomeric protons of **2e**, **S5** and a dialkylated product. **2e** was obtained as an off-white solid (22.5 mg, 50%) after flash chromatography on silica gel (20% to 50% acetone in dichloromethane) along with a mixed fraction containing **S5** and **2e** (yellow oil, 6.4 mg, 87:13 **S5:2e**) to give a total combined yield of 51% of **2e**. A single dilactone derived from fucopyranoside was additionally isolated as a yellow oil (6.4 mg, 10%).

A reaction run according to General Procedure D, but with subjection of the crude reaction mixture to acetylation conditions (1 mL acetic anhydride, 1 mL pyridine, room temperature, overnight) prior to addition of the internal standard and analysis by ^{1}H NMR in $CDCl_3$ afforded a 20% combined yield of the two regioisomers in a 1:1.2 (H-1 **2e**:CH_2 **S5**) ratio.

^{1}H NMR (600 MHz, CD_3OD): δ (ppm) = 4.68 (d, J = 3.4 Hz, 1H, H-1), 3.90 (q, J = 6.4 Hz, 1H, H-5), 3.70 (d, J = 10.1 Hz, 1H, H-3), 3.67 (dd, J = 10.1, 3.4 Hz, 1H, H-2), 3.40 (s, 3H, OCH_3),

2.67 (ddd, *J* = 18.5, 11.6, 7.0 Hz, 1H, H-2a'), 2.53 (ddd, *J* = 18.4, 11.4, 5.6 Hz, 1H, H-2b'), 2.29 (ddd, *J* = 13.4, 11.6, 5.6 Hz, 1H, H-3a'), 2.00 (ddd, *J* = 13.4, 11.4, 7.0 Hz, 1H, H-3b'), 1.17 (d, *J* = 6.4 Hz, 3H, CH_3).

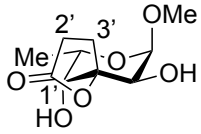
^{13}C NMR (126 MHz, CD_3OD): δ (ppm) = 180.3, 101.3, 90.1, 74.0, 70.9, 69.4, 55.9, 29.3, 26.5, 13.6.

IR (neat, cm^{-1}): 3408 (br, m), 2991 (w), 2953 (w), 2931 (w), 2849 (w), 1761 (s), 1449 (w), 1439 (w), 1422 (w), 1388 (w), 1366 (w), 1280 (w), 1252 (w), 1209 (s), 1154 (s), 1099 (s), 1040 (s), 1019 (s), 1005 (s), 980 (s), 950 (s), 919 (s), 890 (s), 844 (m),818 (w), 743 (m), 684 (m), 627 (w).

HRMS (DART$^+$, m/z): calculated for $C_{10}H_{20}NO_6$ $[M+NH_4]^+$: 250.12906, found 250.12934.

$[\alpha]_D^{20}$ = −160.8 (c= 0.265 g/100 mL^{-1}, $CHCl_3$)

S5 – (5*R*,6*S*,7*R*,9*S*,10*R*)-6,10-Dihydroxy-7-methoxy-9-methyl-1,8-dioxaspiro[4.5]decan-2-one



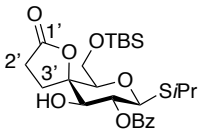
^{1}H NMR (600 MHz, CD_3OD): δ (ppm) = 4.69 (d, *J* = 4.4 Hz, 1H, H-1), 4.14 (d, *J* = 4.4 Hz, 1H, H-2), 4.00 (dq, *J* = 6.6, 1.0 Hz, 1H, H-5), 3.59 (d, *J* = 1.0 Hz, 1H, H-4), 3.38 (s, 3H, OCH_3), 2.86 (ddd, *J* = 13.3, 10.7, 5.5 Hz, 1H, H-3a'), 2.67 (ddd, *J* = 18.1, 10.7, 7.5 Hz, 1H, H-2 a'), 2.54 (ddd, *J* = 18.0, 10.7, 5.5 Hz, 1H, H-2b'), 1.86 (ddd, *J* = 13.4, 10.6, 7.5 Hz, 1H, H-3b'), 1.25 (d, *J* = 6.5 Hz, 3H, CH_3).

^{13}C NMR (151 MHz, CD_3OD): δ (ppm) = 179.7, 101.7, 90.4, 76.2, 69.1, 65.5, 55.9, 30.5, 26.7, 16.7.

IR (thin film, cm^{-1}): 3424 (s), 2999 (w), 2933 (m), 2854 (w), 1760 (s), 1643 (w), 1464 (w), 1368 (w), 1218 (m), 1197 (m), 1168 (s), 1110 (m), 1053 (s), 1002 (s), 935 (w), 898 (w), 818 (w), 785 (w).

HRMS (DART$^+$, m/z): calculated for $C_{10}H_{20}NO_6$ $[M+NH_4]^+$: 250.12906, found 250.12925.

2f – (5*R*,6*R*,8*S*,9*R*,10*R*)-6-(((*tert*-Butyldimethylsilyl)oxy)methyl)-10-hydroxy-2-oxo-8-1,7-dioxaspiro[4.5]decan-9-yl benzoate



Isopropyl-2-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-β-D-thiogalactopyranoside (**1f**) (45.7 mg, 0.1 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%), were combined in 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. A solution of $(Ph_2B)_2O$ in dry, degassed acetonitrile was prepared under inert atmosphere (2 mg in 0.92 mL). The $(Ph_2B)_2O$ solution (0.4 mL, 0.0025 mmol, 2.5 mol%), was added to the ½ dram vial containing the carbohydrate, iridium catalyst and quinuclidine. The balloon was removed and methyl acrylate (8.5 mg, 0.1 mmol, 1 equiv.) was added to the vial using an airtight glass syringe. The rubber septum was quickly replaced with the vial cap and sealed with Teflon tape. The vial was placed 5 inches from a Blue LED Kessil lamp and stirred at 1050 rpm (the temperature under the light was maintained at ~25 °C). After 16 hours, the crude reaction mixture was concentrated under reduced pressure. **2f** was obtained as an off-white solid (27.5 mg, 54%) after flash chromatography on silica gel (2% acetone in dichloromethane). Analysis of the crude reaction mixture revealed 6% of unreacted **1f** and a combined 15% of overalkylation products.

A reaction run according to General Procedure D, but without subjecting the crude to Amberlyst 15 resin afforded <5% of **2f** and 7% of an overalkylation product.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 8.07–8.02 (m, 2H, Ar-H), 7.62–7.55 (m, 1H, Ar-H), 7.48–7.42 (m, 2H, Ar-H), 5.17 (dd, *J* = 9.7, 9.7 Hz, 1H, H-2), 4.74 (d, *J* = 9.9 Hz, 1H, H-1), 3.86 (dd, *J* = 11.0, 6.4 Hz, 1H, H-6a), 3.81 (dd, *J* = 11.0, 4.7 Hz, 1H, H-6b), 3.76–3.70 (m, 1H, H-3), 3.60 (dd, *J* = 6.5, 4.7 Hz, 1H, H-5), 3.23 (hept, *J* = 6.8 Hz, 1H, SC**H**$(CH_3)_2$), 2.95 (s, 1H, 3-OH), 2.71 (ddd, *J* = 17.6, 11.3, 6.0 Hz, 1H, H-2a'), 2.58 (ddd, *J* = 17.7, 11.2, 6.0 Hz, 1H, H-2b'), 2.48 (ddd, *J* = 13.0, 11.2, 6.1 Hz, 1H, H-3a'), 2.34 (ddd, *J* = 12.9, 11.4, 6.2 Hz, 1H, H-3b'), 1.32 (d, *J* = 6.8, 3H, SCH(C**H**$_3)_2$), 1.25 (d, *J* = 6.8 Hz, 3H, SCH(C**H$_3$**$)_2$), 0.89 (s, 9H, SiC(C**H**$_3)_3$), 0.09 (s, 3H, Si(C**H**$_3$)), 0.08 (s, 3H, Si(C**H**$_3$)).

^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) = 177.2, 167.2, 133.7, 130.2, 129.5, 128.6, 82.7, 80.9, 77.7, 72.9, 62.0, 34.8, 28.4, 25.9, 24.7, 24.6, 23.9, 18.3, -5.36, -5.42.

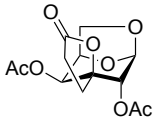
IR (neat, cm^{-1}): 3389 (br, w), 2966 (m), 2930 (m), 2859 (m), 1757 (s), 1716 (s), 1457 (m), 1301 (m), 1259 (s), 1227 (s), 1094 (s), 1052 (s), 1027 (s), 974 (m), 939 (m), 836 (s), 778 (s), 708 (s), 640 (m).

HRMS (DART$^+$, m/z): calculated for $C_{25}H_{42}NO_7SSi[M+NH_4]^+$: 528.24512, found

528.24492.

$[\alpha]_D^{20}$ = −36.5 (c= 0.17g/100 mL^{-1}, $CHCl_3$)

2g – (2*S*,3*S*,4*R*)-5'-Oxodihydro-3'*H*-6,8-dioxaspiro[bicyclo[3.2.1]octane-3,2'-furan]-2,4-diyl diacetate



Prepared according to General Procedure A from 1,6-b-D-anhydrogalactopyranoside (**1g**) (16.2 mg, 0.1 mmol, 1 equiv.), and methyl acrylate (17 mg, 0.2 mmol, 2 equiv.) The reaction was run for 18 hours instead of 16 hours. Prior to isolation the crude concentrated reaction mixture was subjected to acetic anhydride (1 mL) and pyridine (1 mL), stirred at room temperature overnight, and then concentrated under reduced pressure. Analysis of the crude ^{1}H NMR spectrum revealed a 6:1 ratio of diastereomers (H2 **2g**: H4 **S6**). The titled compound was obtained as a light yellow oil in 43% (13.6 mg total mass, 94:6 **2g: S6)** after flash chromatography on silica gel (10% to 60% ethyl acetate in hexanes), along with a minor diastereomer (light yellow oil, 2.9 mg, 86:14 **S6**: quinuclidine derived impurity, 8% **S6**). The total yield of **S6** from the two mixed fractions was 11%. Per-acetylated 1,6-b-D-anhydrogalactopyranoside was also recovered (9.1 mg, 31%).

A reaction run according to General Procedure D, for 18h instead of 16 hours and with the aforementioned acylation step prior to analysis of the crude ^{1}H NMR spectrum revealed a 0.6: 1 ratio of diastereomers (H2 **2g**: H4 **S6** in a combined yield of 18%, as well as per-acetylated **1g** (79%).

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 5.43 (d, *J* = 1.8 Hz, 1H, H-1), 5.14 (dd, *J* = 4.0, 1.0 Hz, 1H, H-4), 4.88 (d, *J* = 1.8 Hz, 1H, H-2), 4.50 (dd, *J* = 4.5, 4.5 Hz, 1H, H-5), 4.45 (d, *J* = 7.7 Hz, 1H, H-6a), 3.71–3.67 (m, 1H, H-6b), 2.46 (ddd, *J* = 18.0, 9.8, 5.8 Hz, 1H, CH_2), 2.37 (ddd, *J* = 18.2, 9.3, 9.3 Hz, 1H, CH_2), 2.16 (s, 3H, $C(O)CH_3$), 2.13 (s, 3H, $C(O)CH_3$), 2.15–2.07 (m, 2H, CH_2).

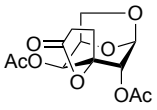
^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) = 175.7, 169.9, 169.7, 99.2, 83.0, 73.5, 72.1, 71.0, 64.5, 29.5, 27.3, 20.9, 20.8.

IR (thin film, cm^{-1}): 2970 (w), 2948 (w), 1783 (s), 1743 (s), 1439 (w), 1374 (m), 1222 (s), 1144 (s), 1087 (m), 1050 (s), 973 (w), 936 (m), 892 (w).

HRMS ($DART^+$, m/z): calculated for $C_{13}H_{20}NO_8$ $[M+NH_4]^+$: 318.11889, found

318.11884.

S6 – (2*S*,3*R*,4*R*)-5'-Oxodihydro-3'*H*-6,8-dioxaspiro[bicyclo[3.2.1]octane-3,2'-furan]-2,4-diyl diacetate



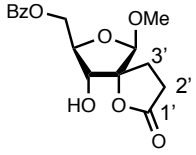
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.45 (d, *J* = 1.6 Hz, 1H, H-1), 5.02–4.97 (m, 1H, H-4), 4.81 (dd, *J* = 1.5, 1.5 Hz 1H, H-2), 4.40 (d, *J* = 7.9 Hz, 1H, H-6a), 4.27 (dd, *J* = 5.1, 1.1 Hz, 1H, H-5), 3.81 (dd, *J* = 7.9, 5.3 Hz, 1H, H-6b), 2.78 (ddd, *J* = 18.0, 11.0, 9.8 Hz, 1H, CH_2), 2.59 (ddd, *J* = 17.9, 9.5, 2.8 Hz, 1H, CH_2), 2.50 (ddd, *J* = 13.6, 9.8, 2.8 Hz, 1H, CH_2), 2.36 (ddd, *J* = 13.6, 11.0, 9.4 Hz, 1H, CH_2), 2.15 (s, 3H, $C(O)CH_3$), 2.14 (s, 3H, $C(O)CH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 175.1, 170.3, 169.2, 99.1, 79.1, 77.6, 71.5, 70.3, 65.5, 31.6, 27.7, 21.0, 20.9.

IR (thin film, cm^{-1}): 2962 (w), 2932 (w), 2858 (w), 1797 (s), 1744 (s), 1372 (m), 1225 (s), 1189 (m), 1145 (m), 1047 (s), 964 (w), 886 (w).

HRMS (DART$^+$, m/z): calculated for $C_{13}H_{20}NO_8$ $[M+NH_4]^+$: 318.11889, found 318.11861.

2h – ((5*R*,6*R*,8*R*,9*R*)-9-Hydroxy-6-methoxy-2-oxo-1,7-dioxaspiro[4.4]nonan-8-yl)methyl benzoate



Prepared according to General Procedure A from methyl β-D-ribofuranoside (**1h**) (26.8 mg, 0.1 mmol, 1 equiv.) and methyl acrylate (17 mg, 0.2 mmol, 2 equiv.). After 18 hours, ~80 mg of Amberlyst 15 resin was added to the vial and the mixture stirred at 50 °C for three hours. The resin was then removed through filtration and the crude reaction mixture was concentrated under reduced pressure. **2h** was isolated as a mixture with C-3 isomer and two di-alkylation products (confirmed by mass spectrometry) after flash chromatography on silica gel (colourless oil, 18.7 mg in total, 66% purity by mass, 12.3 mg of **2h**, 38% yield). The reaction was repeated and analyzed by crude NMR in the presence of 1,3,5-trimethoxybenzene, revealing 54% of the titled compound, 5% of the C-3 regioisomer, and a 9% combined yield of two overalkylation products. The relative configuration of the major product was determined through analysis of the NOE difference spectrum of the dibenzoyl derivative (**S7**).

A control reaction run according to General Procedure D for 18 hours, and treated with 80 mg of Amberlyst resin, and then acylated (BzCl (18 uL, 0.5 mL pyridine, 2 hours, room temperature) prior to analysis by crude ^{1}H NMR revealed 6% of the C2 alkylated product.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 8.08–8.05 (m, 2H, Ar-H), 7.60–7.55 (m, 1H, Ar-H), 7.46–7.43 (m, 2H, Ar-H), 4.80 (s, 1H, H-1), 4.61 (dd, *J* = 12.0, 3.3 Hz, 1H, H-5a), 4.44 (dd, *J* = 12.0, 4.5 Hz, 1H, H-5b), 4.26–4.18 (m, 2H, H-3 and H-4), 3.35 (s, 3H, -OCH_3), 2.75–2.68 (m, 1H, H-2a'), 2.60–2.53 (m, 1H, H-2b'), 2.52–2.46 (m, 1H, H-3a'), 2.42 (d, *J* = 10.6 Hz, 1H, OH), 2.32 (ddd, *J* = 13.6, 10.1, 6.5 Hz, 1H, H-3b').

^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) = 176.2, 166.6, 133.4, 129.9, 129.9, 128.6, 105.7, 90.8, 80.5, 75.4, 64.4, 55.4, 28.4, 24.4.

Select peaks for minor products:

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 4.91 (d, *J* = 3.8 Hz, 0.8H, H-1), 4.78 (s, 0.13H, H-1), 4.77 (s, 0.13H, H-1).

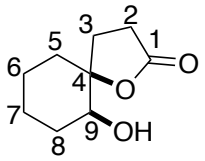
IR (thin film, cm^{-1}): 3448 (w), 2941 (w), 1783 (s), 1720 (s), 1608 (w), 1452 (m), 1321 (m), 1276 (s), 1195 (m), 1117 (s), 1059 (s), 1027 (m), 975 (s), 924 (w), 713 (s).

HRMS (DART$^+$, m/z): calculated for $C_{16}H_{22}NO_7$ $[M+NH_4]^+$: 340.13963, found 340.13907.

Compound **S7**:

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.02–7.99 (m, 4 H, Ar-H), 7.61–7.58 (m, 1 H, Ar-H), 7.54–7.50 (m, 1H, Ar-H), 7.46–7.43 (m, 1H, Ar-H), 5.80 (d, *J* = 7.8 Hz, 1H, H-3), 4.90 (s, 1H, H-1), 4.65 (dd, *J* = 11.6, 4.0 Hz, 1H, H-5), 4.56 (ddd, *J* = 7.9, 4.8, 4.0 Hz, 1H, H-4), 4.56 (dd, *J* = 11.8, 4.8 Hz, 1H, H-5), 3.40 (s, 3H, OCH_3), 2.56–2.39 (m, 4H, CH_2).

2i – 6-Hydroxy-1-oxaspiro[4.5]decan-2-one



Prepared according to General Procedure C from *cis*-1,2-cyclohexanediol (**1i**) (46.5 mg, 0.4 mmol, 2 equiv.) and methyl acrylate (17 mg, 0.2 mmol, 1 equiv.). After 16 hours the crude reaction mixture was concentrated under reduced pressure, dissolved in ethyl acetate, and then filtered through silica. The diastereoselectivity analyzed by crude ^{1}H NMR (11:1, OH **2i**:OH **S8** in DMSO-d_6). **2i** was obtained as a yellow oil (17.2 mg, 57%) after flash chromatography on silica gel (2% to 10% acetone in dichloromethane). The isolated material was contaminated with a small amount (<5% by mass) of a quinuclidine-derived impurity, as judged by ^{1}H NMR spectroscopy. In addition to the reported product two products resulting from overalkylation of the above lactone were isolated in a combined yield of 9%.

A reaction run according to General Procedure D afforded a 68% combined isolated yield of diastereomeric mixture (1.7:1 **2i**:**S8** in DMSO-d_6).

^{1}H NMR (600 MHz, CD_3CN): δ (ppm) = 3.43 (ddd, *J* = 10.6, 6.1, 4.1 Hz, 1H, H-9), 3.01 (d, *J* = 6.1 Hz, 1H, OH), 2.57 (ddd, *J* = 17.8, 10.7, 7.9 Hz, 1H, H-2a), 2.44 (ddd, *J* = 17.8, 10.7, 5.0 Hz, 1H, H-2b), 2.29 (ddd, *J* = 12.8, 10.7, 5.0 Hz, 1H, H-3a), 1.90–1.86 (m, 1H, CH_2), 1.83 (ddd, *J* = 12.8, 10.7, 8.0 Hz, 1H, H-3b), 1.75–1.66 (m, 2H, CH_2), 1.56–1.43 (m, 4H, CH_2), 1.38–1.25 (m, 1H, CH_2).

^{13}C NMR (151 MHz, CD_3CN): δ (ppm) = 178.5, 88.3, 75.0, 37.0, 31.7, 31.5, 29.9, 24.5, 22.7.

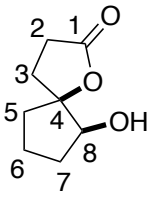
Select peaks for minor diastereomer **S8**:

^{1}H NMR (600 MHz, CD_3CN): δ (ppm) = 3.64–3.59 (m, 0.2H), 3.19 (d, *J* = 4.6 Hz, 0.1H, OH).

IR (neat, cm^{-1}): 3427 (br, m), 2938 (s), 2864 (m), 1752 (s), 1451 (w), 1422 (w), 1351 (w), 1271 (m), 1210 (s), 1133 (m), 1080 (m), 1072 (m), 1006 (w), 967 (s), 931 (w), 852 (w), 823 (w), 664 (w).

HRMS (DART$^+$, m/z): calculated for $C_9H_{18}NO_3$ $[M+NH_4]^+$: 188.12867, found 188.12826.

2j – 6-Hydroxy-1-oxaspiro[4.4]nonan-2-one



$Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (2 mg, 0.002 mmol, 1 mol%) and quinuclidine (4.4 mg, 0.04 mmol, 20 mol%) were combined in 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 solution of $(Ph_2B)_2O$ in dry, degassed acetonitrile was prepared under inert atmosphere (3.4 mg in 0.8 mL). A second solution of *cis*-cyclopentanediol (**1i**) was prepared in dry, degassed acetonitrile under inert atmosphere (81.7 mg in 0.8 mL). 0.4 mL of each solution was added to the 1 dram vial containing the iridium catalyst and quinuclidine. The balloon was removed and methyl acrylate (16.8 mg, 0.195 mmol, 1 equiv.) was added to the vial using an airtight glass syringe. The rubber septum was quickly replaced with the vial cap and sealed with Teflon tape. The vial was placed 5 inches from a Blue LED Kessil lamp and stirred at 1050 rpm for 16 hours (the temperature under the light was maintained at ~25 °C). After 16 hours, ~80 mg of Amberlyst 15 resin was added to the vial and the mixture stirred at 50 °C for three hours. The resin was then removed by filtration over cotton and the crude reaction mixture was concentrated under reduced pressure. **2j** was obtained as a colourless oil (19.6 mg, 63%, >20:1) after flash chromatography on silica gel (2% to 10% acetone in dichloromethane). The isolated material was contaminated with a small amount (<5% by mass) of a quinuclidine-derived impurity, as judged by ^{1}H NMR spectroscopy. In addition to the reported lactone an overalkylation product was obtained in 9% yield. A reaction run according to the procedure above, in the absence of borinic acid catalyst (adding 0.4 mL of dry, degassed acetonitrile in replacement of the borinic acid solution) afforded 35% of **2j**.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.83 (ddd, *J* = 8.0 Hz, 7.9 Hz, 7.9 Hz 1H, H-8), 2.70 (ddd, *J* = 18.7, 10.0, 7.7 Hz, 1H, H-2a), 2.57–2.43 (m, 2H, H-2b, OH), 2.26 (ddd, *J* = 12.9, 10.0, 6.0 Hz, 1H, H-3a), 2.16–1.96 (m, 3H, H-3b, CH_2), 1.90–1.78 (m, 1H, CH_2), 1.79–1.69 (m, 1H, CH_2), 1.71–1.53 (m, 2H, CH_2).

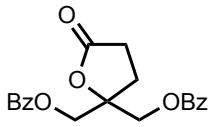
^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 177.4, 93.0, 78.5, 34.4, 31.2, 29.5, 29.4, 18.6.

IR (neat, cm^{-1}): 3421 (br, m), 2953 (m), 2924 (w), 2874 (w), 2858 (w), 1751 (s), 1459 (w), 1418 (w), 1227 (s), 1185 (s), 1158 (s), 1111 (s), 1060 (s), 1012 (s), 997 (m), 928 (s), 857 (w), 802 (m), 730 (m), 646 (w).

HRMS ($DART^+$, m/z): calculated for $C_8H_{16}NO_3$ $[M+NH_4]^+$: 174.11302, found

174.11274.

2k – (5-oxotetrahydrofuran-2,2-diyl)bis(methylene) dibenzoate



(Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (2 mg, 0.002 mmol, 1 mol%), quinuclidine (22.2 mg, 0.2 mmol, 1 equiv.), and $(Ph_2B)_2O$ (3.5 mg, 0.005 mmol, 5 mol%) were combined in 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 (0.8 mL) was added under a balloon of argon. The balloon was removed and glycerol (**1k**) (36.8 mg, 0.4 mmol, 2 equiv.) and methyl acrylate (17.2 mg, 0.2 mmol, 1 equiv.) were added to the vial using airtight glass syringes. The rubber septum was quickly replaced with the vial cap and sealed with Teflon tape. The vial was placed 5 inches from a Blue LED Kessil lamp and stirred at 1050 rpm (the temperature under the light was maintained at ~25 °C). After 16 hours, the crude reaction mixture was concentrated under reduced pressure and dissolved in pyridine (2 mL). Benzoyl chloride was then added (0.17 mL, 7 equiv.) and the reaction was stirred overnight. **2k** (40.4 mg, 57%) was obtained after flash chromatography on silica gel (5% acetone in dichloromethane).

A reaction run according to General Procedure D, but with 1 equiv. of quinuclidine afforded **2k** in 23%.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.03–8.01 (m, 4H, Ar*H*), 7.61–7.58 (m, 2H, Ar*H*), 7.48–7.45 (m, 4H, Ar*H*), 4.58 (m, 4H, BzOC*H*2), 2.76 (t, *J* = 8.33 Hz, 2H, C(O)C*H*2CH2), 2.34 (t, *J* = 8.43 Hz, 2H, C(O)CH2C*H*2).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 175.7, 166.0, 133.8, 129.9, 129.2, 128.8, 84.1, 66.3, 28.6, 26.6.

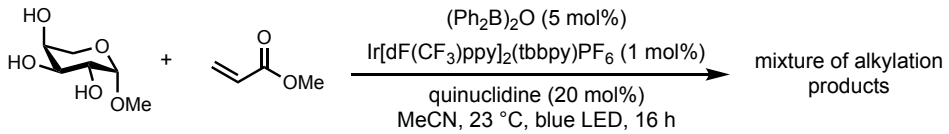
IR (neat, cm $^{-1}$): 1783 (m), 1724 (s), 1452 (w), 1316 (w), 1265 (s), 1204 (w), 1177 (w), 1107 (m), 1099

(m), 1027 (w), 710 (m).

HRMS (DART, *m/z*): calculated for $C_{20}H_{19}O_6$ [$(M + H)^+$]: 355.1180. Found: 355.1182.

Additional investigations into substrate scope

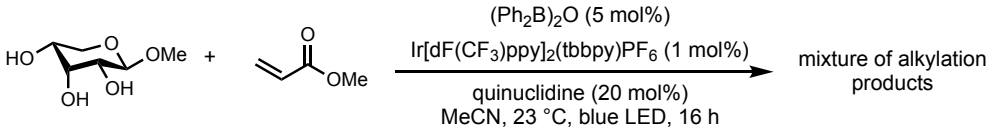
Carbohydrates



(1 equiv.) (2 equiv.)

S9 **S2**

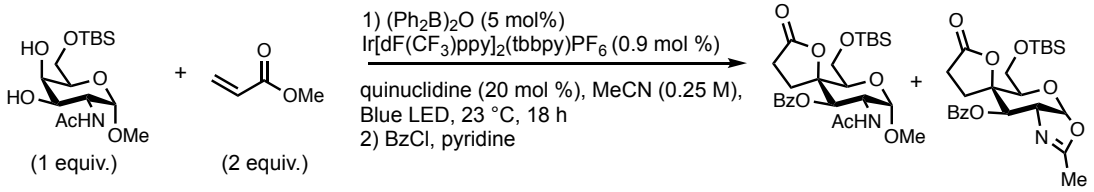
Methyl β-L-arabinopyranoside (**S9**) (0.1 mmol, 16.4 mg) and methyl acrylate (**S2**) (0.2 mmol, 17 mg) were subject to optimized reaction conditions according to General Procedure A. Following flash chromatography on silica gel (5% methanol in dichloromethane), a mixture of two mono-alkylated lactone products were obtained in 37% yield (8.2 mg, ~1:1), along with 33% (10 mg) of a dialkylated product.



(1 equiv.) (2 equiv.)

S10 **S2**

Methyl β-D-ribopyranoside (**S10**) (0.1 mmol, 16.4 mg) and methyl acrylate (**S2**) (0.2 mmol, 17 mg) were subject to optimized reaction conditions according to General Procedure A. The crude reaction mixture was analyzed by ^{1}H and ^{13}C NMR spectroscopy in $CDCl_3$. A mixture of three alkylation products were observed in 25%, 6% and 6% yield (determined by integration of H-1 signals relative to 1,3,5-trimethoxybenzene).



(1 equiv.) (2 equiv.)

S11 **S2** **S12** **S13**

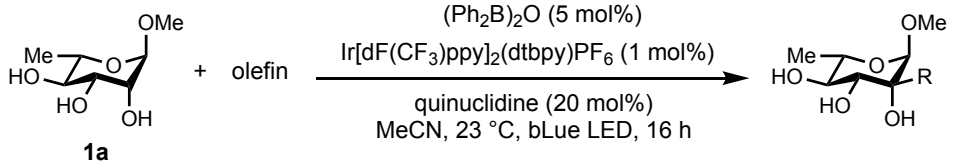
61% isolated (3:1 mixture)

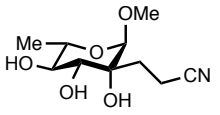
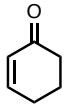
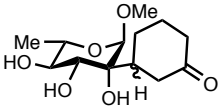
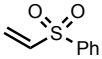
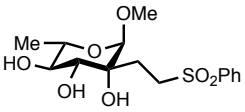
Methyl-2-acetamido-2-deoxy-α-D-galactopyranoside was prepared according to an adapted literature procedure from N-acetyl-D-galactosamine (reaction was stirred at 70 °C for 16 h)[9], and then subsequently TBS protected using TBSCl/pyridine (same procedure used to prepare S1) to give methyl 2-(acetylamino)-2-deoxy-6-O-*tert*-butyldimethylsilyl-α-D-galactopyranoside (**S11**). **S11** (0.1 mmol, 35 mg) and methyl acrylate (**S2**) (0.2 mmol, 17 mg) were subject to optimized reaction conditions according to General Procedure A. Following concentration of the reaction mixture, the crude material was dissolved in 1 mL of pyridine and benzoyl chloride (3 equiv.) was added. The mixture was stirred at room temperature for 16 hours, quenched with methanol and then subject to flash chromatography on silica gel (20% to 80% ethyl acetate in hexane).

Olefins

1a was subjected to optimized reaction conditions according to General Procedure A, replacing methyl acrylate (**S2**) with olefins **S14-S16** to give products **S17-19**. The best results obtained for each olefin are illustrated in Table S4.

Table S4. C-H alkylation reactions of 1a with olefins S14-S16

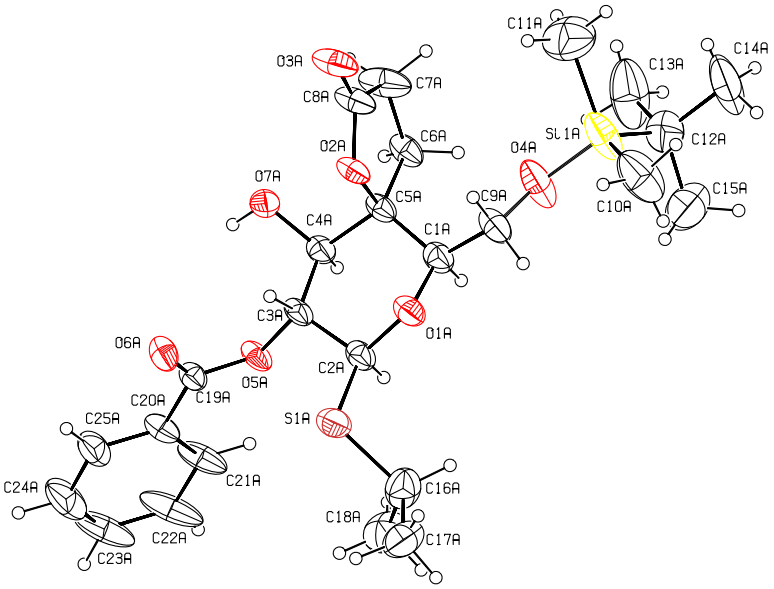


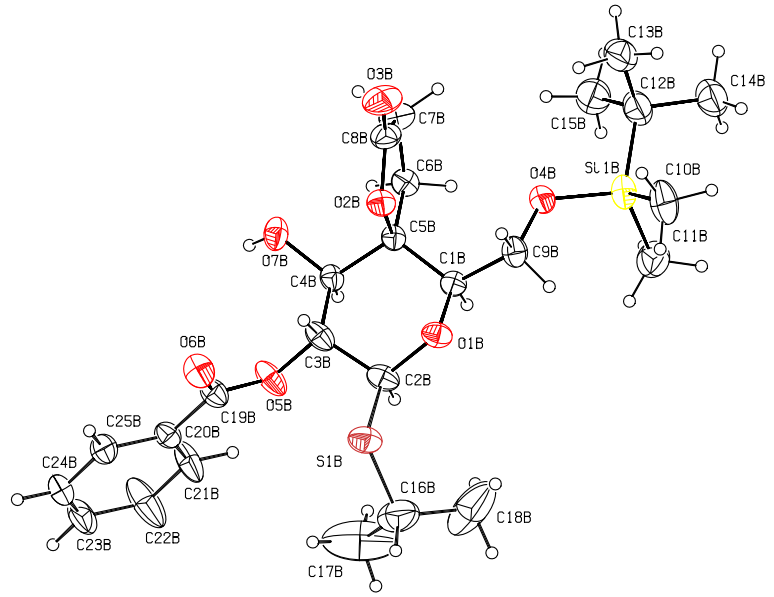
Olefin	1a: olefin	Major Product(s)	Yield
 **S14**	1:1	 **S17**	33%[a]
 **S15**	2:1	 **S18**	~40% (2.9:1 mixture of diastereomers)[b]
 **S16**	1:1	 **S19**	43%[a]

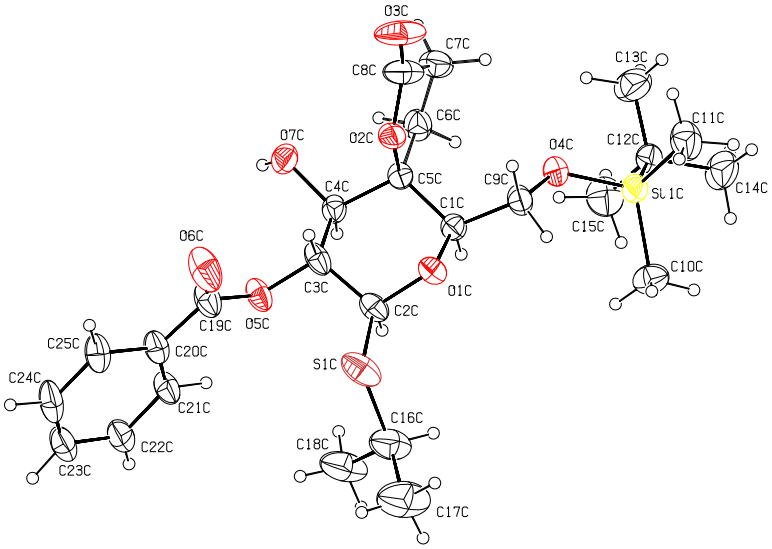
[a] Yields were determined through analysis of crude ^{1}H NMR spectra through integration of H-1 (~4.4 ppm) relative to 1,3,5-trimethoxybenzene in CD_3OD.
[b]Yield obtained following flash chromatography on silica gel. Diastereomer ratio was determined by analysis of the crude ^{1}H NMR spectrum in CD_3OD and integration of the H-1 signals (major 4.52 ppm: minor 4.41 ppm)

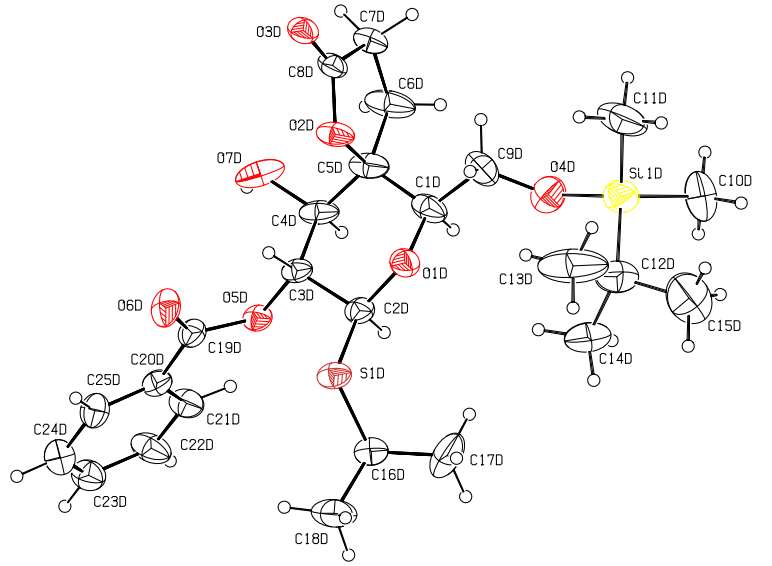
X-Ray Crystallographic Data for 2f

Compound 2f was crystallized from 3:1 diethyl ether: dichloromethane by liquid-liquid diffusion (dissolved 2f in dichloromethane and slowly added ether) over 8 days (melting point: 57-61°C). Four independent molecules were found in the asymmetric unit of the crystal structure due to the flexibility of the side chains on the molecule.






O3C
C7C
C8C
C6C
O7C
O2C
C4C
C5C
C1C
C9C
O4C
C13C
C11C
C12C
Si1C
C14C
C15C
C10C
O6C
C3C
O1C
C19C
O5C
C2C
C25C
C20C
S1C
C24C
C21C
C16C
C18C
C22C
C23C
C17C


C7D
O3D
C8D
C6D
C11D
O2D
C9D
O7D
C5D
C1D
O4D
Si1D
C10D
C4D
C13D
C12D
O1D
C3D
O5D
O6D
C2D
C19D
C15D
C20D
S1D
C25D
C21D
C14D
C24D
C22D
C16D
C17D
C23D
C18D

Computational Data

DFT calculations were carried out using the Gaussian 16 suite of programs[10] at the B97-D3/Def2-TZVP level of theory.[11,12] 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. Frequency calculations were carried out at 1 atm and 298.15 K. Structures were visualized using GaussView 5.0 and Avogadro 1.2.0.

Bond dissociation enthalpy calculations:

Geometry optimizations and frequency calculations were carried out for rhamnopyranoside **1a** and borinic ester [**1a**•BPh_2]$^-$, and for the radical species resulting from H-atom abstraction from each site ([**1a**–H1]$^\bullet$, [**1a**–H2]$^\bullet$, [**1a**•BPh_2–H1]$^{\bullet-}$, [**1a**•BPh_2–H2]$^{\bullet-}$, etc. The calculated energies of these species, along with that of the hydrogen atom, are listed in Table S5. The calculated BDEs, as well as the changes in Gibbs free energy and electronic energy upon bond dissociation, are summarized in Table S5.

Table S5. Calculated quantities used to determine the bond dissociation energies of 1a and [1a•BPh2]$^-$.[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
H	–0.502454	–0.501038	–0.500093	–0.513108
1a	–650.934556	–650.921505	–650.920561	–650.972833
[**1a**–H1]$^\bullet$	-650.292534	-650.279234	-650.278289	-650.332003
[**1a**–H2]$^\bullet$	-650.291968	-650.278562	-650.277618	-650.331717
[**1a**–H3]$^\bullet$	–650.291039	–650.277718	–650.276774	–650.330644
[**1a**–H4]$^\bullet$	-650.294828	-650.282087	-650.281142	-650.333564
[**1a**–H5]$^\bullet$	-650.288697	-650.275269	-650.274325	-650.328486
[**1a**•BPh_2]$^-$	–1137.708575	–1137.685367	–1137.684423	–1137.764037
[**1a**•BPh_2–H1]$^{\bullet-}$	-1137.063132	-1137.039928	-1137.038984	-1137.119204
[**1a**•BPh_2–H2]$^{\bullet-}$	-1137.07301	-1137.049607	-1137.048663	-1137.130056
[**1a**•BPh_2–H3]$^{\bullet-}$	-1137.071813	-1137.048195	-1137.04725	-1137.12933
[**1a**•BPh_2–H4]$^{\bullet-}$	-1137.071553	-1137.048634	-1137.04769	-1137.126622
[**1a**•BPh_2–H5]$^{\bullet-}$	-1137.062485	-1137.038983	-1137.038039	-1137.119637

[a] Energies in Hartree, calculated in the gas phase.

Table S6. Bond dissociation energies, enthalpies and free energies calculated from the data in Table S5.[a]

Species(position)	Bond dissociation energy	Bond dissociation enthalpy	Bond dissociation free energy
1a(H1)	88.6	89.2	80.1
1a(H2)	89.0	89.6	80.3
1a(H3)	89.6	90.2	81.0
1a(H4)	86.8	87.4	79.2
1a(H5)	91.1	91.7	82.4
[**1a**•BPh_2]$^-$(H1)	90.6	91.2	82.7
[**1a**•BPh_2]$^-$(H2)	84.5	85.1	75.8
[**1a**•BPh_2]$^-$(H3)	85.4	86.0	76.3
[**1a**•BPh_2]$^-$(H4)	85.1	85.7	78.0
[**1a**•BPh_2]$^-$(H5)	91.2	91.8	82.4

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

Calculation of ΔΔG‡ for HAT with the quinuclidine radical cation

Geometry optimizations were carried out to identify pre-reactive complexes arising from the interaction of **1a** or [**1a**•BPh_2]$^-$ with quinuclidine radical cation at each C–H bond. Transition states were then identified for hydrogen atom transfer (HAT) from these pre-reactive complexes. The calculated, gas-phase Gibbs free energies of the pre-reactive complexes and transition states for HAT from each position (relative to the sum of the energies of the isolated starting materials) are summarized in Table S7.

Table S7. Calculated gas-phase free energies of pre-reactive complexes and transition states for hydrogen atom transfer from 1a or [1a•BPh2]$^-$ to the quinuclidine radical cation.[a]

Reaction	Gibbs free energy of pre-reactive complex	Gibbs free energy of transition state for HAT
1a(H1) + quinuclidine$^{•+}$	–5.61	–4.92
1a(H2) + quinuclidine$^{•+}$	–8.72	–8.71
1a(H3) + quinuclidine$^{•+}$	–5.13	–4.73
1a(H4) + quinuclidine$^{•+}$	–4.50	–2.18
1a(H5) + quinuclidine$^{•+}$	–3.65	–3.32
[**1a**•BPh_2]$^-$(H1) + quinuclidine$^{•+}$	–87.45	–72.95
[**1a**•BPh_2]$^-$(H2) + quinuclidine$^{•+}$	–88.24	–88.30
[**1a**•BPh_2]$^-$(H3) + quinuclidine$^{•+}$	–89.39	–82.63
[**1a**•BPh_2]$^-$(H4) + quinuclidine$^{•+}$	ND	ND
[**1a**•BPh_2]$^-$(H5) + quinuclidine$^{•+}$	–86.47	–66.33

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

Calculated energies and geometries.

H

Energies (Hartree/particle): -0.502453925715

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.010654
Sum of electronic and zero-point Energies= -0.502454
Sum of electronic and thermal Energies= -0.501038
Sum of electronic and thermal Enthalpies= -0.500093
Sum of electronic and thermal Free Energies= -0.513108

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
1	0.000000	0.000000	0.000000

1a

Energies (Hartree/particle): -651.149575568

Zero-point correction= 0.215019 (Hartree/Particle)
Thermal correction to Energy= 0.228071
Thermal correction to Enthalpy= 0.229015
Thermal correction to Gibbs Free Energy= 0.176743
Sum of electronic and zero-point Energies= -650.934556
Sum of electronic and thermal Energies= -650.921505
Sum of electronic and thermal Enthalpies= -650.920561
Sum of electronic and thermal Free Energies= -650.972833

Number of imaginary frequencies: 0

Geometry:

	Coordinates

Atomic Number	X	Y	Z
6	0.000646	1.390798	0.047722
6	1.013228	-0.803913	-0.598179
6	1.300230	0.574713	-0.019633
1	-0.395752	1.492274	-0.973912
1	0.646984	-0.679372	-1.628577
1	1.697256	0.459436	0.998987
8	-0.949918	0.686722	0.869658
6	-1.285076	-0.610195	0.406997
1	-1.929823	-1.016057	1.200115
8	-1.963840	-0.591694	-0.831739
6	-3.232946	0.055898	-0.772957
1	-3.131821	1.119257	-0.520924
1	-3.681209	-0.045494	-1.764331
1	-3.883690	-0.424997	-0.026322
6	0.185437	2.763652	0.669145
1	0.852561	3.377424	0.054819
1	-0.777169	3.279049	0.739354
1	0.602825	2.675690	1.678795
8	2.285445	1.176648	-0.879632
1	2.710556	1.894176	-0.393791
8	2.180710	-1.633506	-0.585671
1	2.906378	-1.077475	-0.905867
6	-0.060997	-1.517067	0.224318
1	-0.383677	-2.419676	-0.315828
8	0.420912	-1.855403	1.521080
1	1.314705	-2.204446	1.380710

[**1a**•BPh_2]$^-$

Energies (Hartree/particle): -1138.08169025

Zero-point correction= 0.373115 (Hartree/Particle)
Thermal correction to Energy= 0.396323
Thermal correction to Enthalpy= 0.397267
Thermal correction to Gibbs Free Energy= 0.317653
Sum of electronic and zero-point Energies= -1137.708575
Sum of electronic and thermal Energies= -1137.685367
Sum of electronic and thermal Enthalpies= -1137.684423
Sum of electronic and thermal Free Energies= -1137.764037

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	3.316268	0.605965	0.459302
6	1.159288	-0.467260	1.158312
6	1.924942	0.852084	1.027342
1	3.846593	-0.124110	1.092181
1	1.617084	-1.051786	1.973437
1	1.385548	1.498646	0.321076
8	3.155905	0.059851	-0.870000
6	2.485275	-1.185996	-0.925861
1	2.314591	-1.349136	-2.001117
8	3.297390	-2.241674	-0.402384
6	4.516592	-2.405326	-1.103662
1	5.168525	-1.525375	-1.007240
1	5.017888	-3.278366	-0.672446
1	4.338280	-2.585934	-2.178222
6	4.148729	1.867675	0.317951
1	4.290369	2.329092	1.299446
1	5.128221	1.637418	-0.117712
1	3.635228	2.583729	-0.333648
8	2.014766	1.499009	2.308015
1	1.108377	1.446297	2.651458
8	-0.198430	-0.223884	1.435963
6	1.151105	-1.235166	-0.172004
1	0.928883	-2.301047	0.023792
8	0.125447	-0.621566	-0.904708
6	-2.195159	-1.200854	0.115852
6	-2.989654	-1.378110	-1.031006
6	-2.547045	-1.952006	1.248205
6	-4.068802	-2.262498	-1.056152
1	-2.751094	-0.803343	-1.925823
6	-3.630560	-2.837145	1.242357
1	-1.946220	-1.835387	2.148419
6	-4.397163	-2.998713	0.086922
1	-4.660439	-2.378791	-1.964479
1	-3.877475	-3.404640	2.140240
1	-5.241212	-3.687261	0.075561
6	-1.409850	1.345847	-0.259376

6	-0.923123	2.060444	-1.365536
6	-2.339164	2.007863	0.561989
6	-1.333870	3.369026	-1.638972
1	-0.196079	1.573432	-2.012815
6	-2.752092	3.316815	0.308281
1	-2.748699	1.477341	1.421652
6	-2.250108	4.006329	-0.799867
1	-0.936288	3.895885	-2.506844
1	-3.469077	3.802774	0.970298
1	-2.571108	5.026572	-1.006034
5	-0.920960	-0.173247	0.092877

[**1a**–H1]$^{\bullet}$

Energies (Hartree/particle): -1137.42019490

Zero-point correction= 0.359781 (Hartree/Particle)
Thermal correction to Energy= 0.383189
Thermal correction to Enthalpy= 0.384133
Thermal correction to Gibbs Free Energy= 0.303180
Sum of electronic and zero-point Energies= -1137.060414
Sum of electronic and thermal Energies= -1137.037006
Sum of electronic and thermal Enthalpies= -1137.036062
Sum of electronic and thermal Free Energies= -1137.117015

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	0.436021	1.452417	-0.203948
6	1.134256	-0.933875	-0.56473
6	1.478631	0.383875	0.137912
1	0.432717	1.599747	-1.294864
1	1.178174	-0.765181	-1.647707
1	1.462406	0.219918	1.228106
8	-0.877018	0.975172	0.190709
6	-1.226684	-0.243297	-0.343258
8	-2.524109	-0.590136	-0.101946
6	-3.507218	0.438433	-0.308843
1	-3.390733	0.880575	-1.306294
1	-4.477053	-0.057116	-0.229661
1	-3.421844	1.22169	0.450657
6	0.665456	2.7694	0.508854
1	1.645268	3.167658	0.233454
1	-0.105514	3.49468	0.230637
1	0.637515	2.624371	1.59415
8	2.756596	0.8518	-0.283343
1	3.332746	0.071707	-0.281741
8	2.113281	-1.932288	-0.276465
1	1.856338	-2.31449	0.5785
6	-0.277364	-1.387653	-0.193563
1	-0.597731	-2.208709	-0.848814
8	-0.181406	-1.885941	1.178172

1	-1.069623	-2.159505	1.44202
6	0.436021	1.452417	-0.203948
6	1.134256	-0.933875	-0.56473
6	1.478631	0.383875	0.137912
1	0.432717	1.599747	-1.294864
1	1.178174	-0.765181	-1.647707
1	1.462406	0.219918	1.228106
8	-0.877018	0.975172	0.190709
6	-1.226684	-0.243297	-0.343258
8	-2.524109	-0.590136	-0.101946
6	-3.507218	0.438433	-0.308843
1	-3.390733	0.880575	-1.306294
1	-4.477053	-0.057116	-0.229661
1	-3.421844	1.22169	0.450657
6	0.665456	2.7694	0.508854
1	1.645268	3.167658	0.233454
1	-0.105514	3.49468	0.230637
1	0.637515	2.624371	1.59415
8	2.756596	0.8518	-0.283343
1	3.332746	0.071707	-0.281741
8	2.113281	-1.932288	-0.276465
1	1.856338	-2.31449	0.5785

[**1a**–H2]$^{\bullet}$

Energies (Hartree/particle): -650.492447925

Zero-point correction= 0.201933 (Hartree/Particle)
Thermal correction to Energy= 0.215028
Thermal correction to Enthalpy= 0.215972
Thermal correction to Gibbs Free Energy= 0.162782
Sum of electronic and zero-point Energies= -650.290514
Sum of electronic and thermal Energies= -650.277420
Sum of electronic and thermal Enthalpies= -650.276476
Sum of electronic and thermal Free Energies= -650.329666

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	-0.305262	1.415008	0.012516
6	-1.039821	-0.964259	0.316725
6	-1.487066	0.435311	-0.093858
1	0.055644	1.414694	1.051706
1	-0.90753	-0.959457	1.419105
1	-1.821392	0.396151	-1.141522
8	0.748729	0.968007	-0.862434
6	1.302619	-0.294218	-0.500519
1	1.99017	-0.544406	-1.323599
8	2.03939	-0.221372	0.719908
6	3.239115	0.544341	0.610959
1	3.026795	1.598687	0.389347
1	3.748326	0.46847	1.575145
1	3.893151	0.13991	-0.17752
6	-0.661576	2.82858	-0.412003
1	-1.42118	3.250309	0.25439
1	0.223192	3.470378	-0.364296
1	-1.039022	2.838592	-1.441225
8	-2.574449	0.784942	0.775541
1	-3.071129	1.501843	0.362031
8	-2.00859	-1.975214	-0.020202
1	-2.782662	-1.81092	0.535906
6	0.23269	-1.314049	-0.366066
8	0.621278	-2.621518	-0.39596

1	-0.189427	-3.147301	-0.280818

[**1a**–H3]$^{\bullet}$

Energies (Hartree/particle): -650.492551150

Zero-point correction= 0.201513 (Hartree/Particle)
Thermal correction to Energy= 0.214833
Thermal correction to Enthalpy= 0.215777
Thermal correction to Gibbs Free Energy= 0.161908
Sum of electronic and zero-point Energies= -650.291039
Sum of electronic and thermal Energies= -650.277718
Sum of electronic and thermal Enthalpies= -650.276774
Sum of electronic and thermal Free Energies= -650.330644

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	0.020655	1.385104	0.074816
6	1.075873	-0.807986	-0.354103
6	1.345302	0.602000	0.034152
1	-0.358008	1.439675	-0.955510
1	1.810251	0.650935	1.040062
8	-0.916101	0.673328	0.902271
6	-1.265761	-0.617216	0.420955
1	-1.927396	-1.018887	1.201536
8	-1.923681	-0.577079	-0.824799
6	-3.182703	0.090977	-0.777432
1	-3.067979	1.152290	-0.522009
1	-3.621293	-0.000910	-1.773996
1	-3.849652	-0.380466	-0.038917
6	0.165701	2.777437	0.659478
1	0.856748	3.374356	0.054600
1	-0.802210	3.287454	0.670682
1	0.541129	2.726121	1.687797
8	2.274060	1.144317	-0.934347
1	2.784064	1.837318	-0.495852
8	2.135406	-1.570721	-0.773894
1	2.798616	-0.940811	-1.108249
6	-0.050248	-1.541801	0.257979
1	-0.341853	-2.392193	-0.373778
8	0.263721	-2.026544	1.600328

1	1.074884	-2.546180	1.515438

[**1a**–H4]•

Energies (Hartree/particle): -650.488255149

Zero-point correction= 0.201314 (Hartree/Particle)
Thermal correction to Energy= 0.214590
Thermal correction to Enthalpy= 0.215534
Thermal correction to Gibbs Free Energy= 0.161736
Sum of electronic and zero-point Energies= -650.286941
Sum of electronic and thermal Energies= -650.273665
Sum of electronic and thermal Enthalpies= -650.272721
Sum of electronic and thermal Free Energies= -650.326519

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	-0.185518	1.413342	-0.275563
6	1.0042	-0.754919	-0.846614
6	1.093506	0.728892	-0.584752
1	-0.840113	1.332334	-1.153117
1	0.498011	-0.941641	-1.801888
8	-0.888187	0.695206	0.830328
6	-1.134262	-0.664402	0.528837
1	-1.623062	-1.060944	1.433091
8	-1.95284	-0.858007	-0.603703
6	-3.28208	-0.364094	-0.435085
1	-3.290612	0.723033	-0.286627
1	-3.826172	-0.615311	-1.348553
1	-3.770662	-0.844455	0.426291
6	-0.065517	2.858781	0.165917
1	0.412774	3.448915	-0.621818
1	-1.058271	3.272045	0.365835
1	0.540838	2.937922	1.07168
8	2.208494	1.150867	0.098926
1	2.894061	0.490576	-0.121816
8	2.311796	-1.339684	-0.901445
1	2.442937	-1.750886	-0.029217
6	0.175847	-1.428196	0.278633
1	-0.046292	-2.467347	0.014138
8	0.948755	-1.484119	1.481476

1	1.005355	-0.574768	1.819103

[**1a**–H5]$^{\bullet}$

Energies (Hartree/particle): -650.489833851

Zero-point correction= 0.201139 (Hartree/Particle)
Thermal correction to Energy= 0.214565
Thermal correction to Enthalpy= 0.215509
Thermal correction to Gibbs Free Energy= 0.161353
Sum of electronic and zero-point Energies= -650.288695
Sum of electronic and thermal Energies= -650.275269
Sum of electronic and thermal Enthalpies= -650.274325
Sum of electronic and thermal Free Energies= -650.328481

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	0.017617	1.364336	0.238068
6	1.030757	-0.750864	-0.605021
6	1.301044	0.613985	0.022805
1	0.637575	-0.591784	-1.619128
1	1.79913	0.438562	0.997634
8	-0.988248	0.663052	0.878278
6	-1.266742	-0.658689	0.39155
1	-1.909378	-1.085907	1.174346
8	-1.918461	-0.63384	-0.849124
6	-3.197555	-0.001243	-0.818426
1	-3.108027	1.069771	-0.600508
1	-3.634396	-0.139446	-1.810085
1	-3.847275	-0.468876	-0.062776
6	0.00672	2.817	0.546409
1	0.643179	3.363849	-0.156311
1	-1.01013	3.217258	0.472085
1	0.366992	3.032512	1.57086
8	2.21703	1.294213	-0.85691
1	2.684085	1.964115	-0.342588
8	2.214794	-1.553024	-0.642665
1	2.917735	-0.975397	-0.975402
6	-0.007887	-1.510624	0.216357
1	-0.295855	-2.423642	-0.32576
8	0.483432	-1.830766	1.514344

1	1.384261	-2.1615	1.375802

[**1a**•BPh_2–H1]$^{\bullet-}$

Energies (Hartree/particle): -1137.42019490

Zero-point correction= 0.359781 (Hartree/Particle)
Thermal correction to Energy= 0.383189
Thermal correction to Enthalpy= 0.384133
Thermal correction to Gibbs Free Energy= 0.303180
Sum of electronic and zero-point Energies= -1137.060414
Sum of electronic and thermal Energies= -1137.037006
Sum of electronic and thermal Enthalpies= -1137.036062
Sum of electronic and thermal Free Energies= -1137.117015

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	-3.611035	-0.077836	-0.679438
6	-1.229089	-0.497848	-1.332251
6	-2.296439	0.57282	-1.095154
1	-3.905017	-0.820666	-1.441371
1	-1.522017	-1.086193	-2.219043
1	-1.961328	1.215139	-0.267334
8	-3.393769	-0.765551	0.571894
6	-2.397858	-1.718996	0.535107
8	-2.462813	-2.411581	1.721216
6	-1.343272	-3.24312	2.02424
1	-0.416552	-2.659231	2.060583
1	-1.554066	-3.680205	3.004691
1	-1.23871	-4.051447	1.284241
6	-4.737781	0.912774	-0.450954
1	-4.940207	1.457161	-1.37765
1	-5.647751	0.394052	-0.128859
1	-4.45235	1.634273	0.322757
8	-2.481545	1.356935	-2.282064
1	-1.573054	1.545676	-2.569469
8	0.028533	0.092736	-1.53095
6	-1.072682	-1.380572	-0.084242
1	-0.571752	-2.320972	-0.38234
8	-0.20981	-0.61166	0.746681
6	2.147324	-0.770827	-0.318043

6	2.914887	-1.060366	0.824628
6	2.631056	-1.259571	-1.541754
6	4.094507	-1.802826	0.757374
1	2.571086	-0.6915	1.790966
6	3.815134	-2.000088	-1.627844
1	2.052644	-1.054431	-2.440978
6	4.553352	-2.277416	-0.475946
1	4.662381	-2.012324	1.664132
1	4.162723	-2.364713	-2.594968
1	5.474977	-2.854878	-0.536046
6	1.037157	1.601394	0.33729
6	0.354405	2.158817	1.430304
6	1.963241	2.429502	-0.320354
6	0.575734	3.475589	1.845283
1	-0.368308	1.537832	1.956418
6	2.187923	3.749335	0.075352
1	2.523716	2.023421	-1.162365
6	1.492934	4.280323	1.166061
1	0.030151	3.87763	2.699287
1	2.909139	4.366246	-0.460969
1	1.667352	5.307576	1.48347
5	0.755041	0.080797	-0.183464

[**1a**•BPh_2–H2]$^{\bullet-}$

Energies (Hartree/particle): -1137.43296367

Zero-point correction= 0.359954 (Hartree/Particle)
Thermal correction to Energy= 0.383356
Thermal correction to Enthalpy= 0.384301
Thermal correction to Gibbs Free Energy= 0.302908
Sum of electronic and zero-point Energies= -1137.073010
Sum of electronic and thermal Energies= -1137.049607
Sum of electronic and thermal Enthalpies= -1137.048663
Sum of electronic and thermal Free Energies= -1137.130056

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	3.278125	0.603283	0.616107
6	1.109919	-0.539701	1.155018
6	1.863910	0.803849	1.166661
1	3.782830	-0.177650	1.209384
1	1.569133	-1.179105	1.930321
1	1.332785	1.498840	0.498795
8	3.189062	0.178206	-0.759048
6	2.476557	-1.070664	-0.955502
1	2.322646	-1.112699	-2.043651
8	3.301296	-2.167891	-0.537132
6	4.528308	-2.244787	-1.243737
1	5.181479	-1.385625	-1.033810
1	5.023497	-3.167189	-0.921251
1	4.359575	-2.289706	-2.334373
6	4.111206	1.874266	0.628562
1	4.208389	2.246628	1.652415
1	5.109173	1.682062	0.217442
1	3.625430	2.645647	0.020048
8	1.924487	1.349009	2.495528
1	1.016633	1.255936	2.824037
8	-0.264064	-0.371384	1.421594
6	1.188448	-1.127048	-0.224606
8	0.040807	-0.895569	-0.894119
6	-2.336037	-1.199015	0.119484

6	-3.331285	-1.059297	-0.862326
6	-2.547533	-2.180581	1.101174
6	-4.472985	-1.863656	-0.878018
1	-3.209061	-0.295074	-1.629117
6	-3.688968	-2.986659	1.104695
1	-1.792945	-2.303016	1.875781
6	-4.658468	-2.833447	0.110650
1	-5.224005	-1.731524	-1.656835
1	-3.825022	-3.737615	1.883223
1	-5.549854	-3.459500	0.108170
6	-1.285540	1.251588	-0.328903
6	-0.961101	1.780517	-1.588038
6	-1.903128	2.124730	0.583673
6	-1.230396	3.111492	-1.922347
1	-0.469838	1.133115	-2.311989
6	-2.175737	3.456078	0.266722
1	-2.168632	1.745706	1.570305
6	-1.839639	3.957897	-0.994370
1	-0.960013	3.491798	-2.907496
1	-2.649650	4.107519	1.001022
1	-2.047720	4.996458	-1.247622
5	-0.979449	-0.295628	0.100473

[**1a**•BPh_2–H3]$^{\bullet-}$

Energies (Hartree/particle): -1137.43107368

Zero-point correction= 0.359261 (Hartree/Particle)
Thermal correction to Energy= 0.382879
Thermal correction to Enthalpy= 0.383823
Thermal correction to Gibbs Free Energy= 0.301744
Sum of electronic and zero-point Energies= -1137.071813
Sum of electronic and thermal Energies= -1137.048195
Sum of electronic and thermal Enthalpies= -1137.047250
Sum of electronic and thermal Free Energies= -1137.129330

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	3.445589	-0.244333	1.115110
6	1.015222	-0.021429	0.964901
6	2.178895	0.273198	1.818841
1	3.412315	-1.345220	1.112905
1	2.277444	1.356865	1.996208
8	3.449397	0.238123	-0.244538
6	2.485242	-0.388913	-1.078186
1	2.288336	0.333513	-1.882470
8	2.999695	-1.597927	-1.633194
6	4.098021	-1.388335	-2.503787
1	4.959876	-0.954636	-1.976734
1	4.375484	-2.366706	-2.910898
1	3.824262	-0.717612	-3.336620
6	4.728514	0.226554	1.773364
1	4.726590	-0.064392	2.828129
1	5.605089	-0.209989	1.280412
1	4.801650	1.318947	1.710521
8	2.089154	-0.329455	3.160546
1	1.360245	-0.965072	3.073753
8	-0.097305	0.723574	1.016219
6	1.146443	-0.725476	-0.365646
1	1.125020	-1.827854	-0.250827
8	0.051674	-0.281742	-1.130212
6	-2.049217	-0.818597	0.292914

6	-2.700990	-1.632426	-0.650038
6	-2.396490	-1.010281	1.640054
6	-3.647222	-2.587428	-0.275198
1	-2.448577	-1.513544	-1.703209
6	-3.343844	-1.961848	2.031803
1	-1.903111	-0.400871	2.395570
6	-3.975932	-2.756144	1.073451
1	-4.131454	-3.204292	-1.032358
1	-3.588325	-2.086751	3.086847
1	-4.713944	-3.499352	1.372125
6	-1.676079	1.610259	-0.836967
6	-1.210921	2.197325	-2.024511
6	-2.778153	2.221879	-0.215517
6	-1.808154	3.338989	-2.565934
1	-0.361262	1.738898	-2.526651
6	-3.377126	3.370181	-0.737180
1	-3.178057	1.781449	0.697085
6	-2.894425	3.934713	-1.920997
1	-1.425846	3.768012	-3.492339
1	-4.226422	3.823586	-0.226309
1	-3.362165	4.826022	-2.337138
5	-0.960500	0.299831	-0.195769

[**1a**•BPh_2–H4]$^{\bullet-}$

Energies (Hartree/particle): -1137.43194810

Zero-point correction= 0.360397 (Hartree/Particle)
Thermal correction to Energy= 0.383315
Thermal correction to Enthalpy= 0.384259
Thermal correction to Gibbs Free Energy= 0.305333
Sum of electronic and zero-point Energies= -1137.071552
Sum of electronic and thermal Energies= -1137.048633
Sum of electronic and thermal Enthalpies= -1137.047689
Sum of electronic and thermal Free Energies= -1137.126615

Number of imaginary frequencies: 0

Geometry:

Atomic Number	X	Y	Z
6	3.448075	0.587319	0.694402
6	1.163007	-0.397577	1.235629
6	2.137587	0.753586	1.358622
1	3.964634	-0.274907	1.14188
1	1.403688	-1.189399	1.966474
8	3.252124	0.248757	-0.744301
6	2.521955	-0.937362	-0.931445
1	2.347203	-0.987195	-2.01831
8	3.265534	-2.095369	-0.51734
6	4.482681	-2.251098	-1.222259
1	5.181976	-1.425247	-1.026732
1	4.929082	-3.193171	-0.885742
1	4.310103	-2.303303	-2.31178
6	4.346951	1.81061	0.710089
1	4.574029	2.094081	1.74347
1	5.283908	1.600991	0.182113
1	3.844335	2.651568	0.224819
8	1.562203	1.993102	1.327756
1	0.597831	1.772283	1.406791
8	-0.151324	0.087447	1.4199
6	1.167684	-1.002699	-0.209213
1	0.87896	-2.068265	-0.148257
8	0.210811	-0.254073	-0.901735
6	-1.938673	-1.277064	0.117182
6	-2.468674	-1.802585	-1.074265

6	-2.365348	-1.874036	1.31398
6	-3.372107	-2.866712	-1.077614
1	-2.15459	-1.363988	-2.020964
6	-3.273448	-2.937873	1.328915
1	-1.963071	-1.493093	2.251327
6	-3.782358	-3.44042	0.129862
1	-3.760296	-3.252542	-2.020446
1	-3.583043	-3.379336	2.276569
1	-4.488019	-4.270138	0.134225
6	-1.648107	1.394577	-0.243764
6	-1.001114	2.412532	-0.965906
6	-2.941101	1.674691	0.228614
6	-1.609517	3.647634	-1.202603
1	0.002194	2.221339	-1.340069
6	-3.55893	2.907944	0.006057
1	-3.477955	0.902211	0.777917
6	-2.893804	3.90244	-0.715041
1	-1.081599	4.415927	-1.767498
1	-4.562247	3.093615	0.389412
1	-3.371495	4.864561	-0.896007
5	-0.895793	-0.015671	0.075824

[**1a**•BPh_2–H5]$^{\bullet-}$

Energies (Hartree/particle): -1137.42191302

Zero-point correction= 0.359428 (Hartree/Particle)
Thermal correction to Energy= 0.382930
Thermal correction to Enthalpy= 0.383874
Thermal correction to Gibbs Free Energy= 0.302276
Sum of electronic and zero-point Energies= -1137.062485
Sum of electronic and thermal Energies= -1137.038983
Sum of electronic and thermal Enthalpies= -1137.038039
Sum of electronic and thermal Free Energies= -1137.119637

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	3.246552	0.641639	0.358097
6	1.139770	-0.470264	1.135674
6	1.917261	0.850849	1.000302
1	1.603019	-1.062363	1.939219
1	1.316184	1.504598	0.338477
8	3.175937	0.023952	-0.884106
6	2.444961	-1.208468	-0.953053
1	2.280932	-1.348094	-2.032165
8	3.220277	-2.277390	-0.432199
6	4.448710	-2.471350	-1.111575
1	5.133575	-1.624599	-0.967645
1	4.899318	-3.378870	-0.696810
1	4.287971	-2.609969	-2.194884
6	4.342961	1.639203	0.448619
1	4.404309	2.029535	1.467886
1	5.307277	1.191462	0.173269
1	4.176949	2.499468	-0.229818
8	2.053495	1.486425	2.281053
1	1.148493	1.481169	2.630425
8	-0.213220	-0.216249	1.422174
6	1.110613	-1.215154	-0.205374
1	0.855951	-2.276705	-0.025890
8	0.105402	-0.559526	-0.929306
6	-2.225932	-1.123615	0.078055

6	-3.016681	-1.265373	-1.076218
6	-2.597325	-1.888895	1.194622
6	-4.111126	-2.129835	-1.123476
1	-2.762957	-0.678667	-1.959021
6	-3.696321	-2.754210	1.166453
1	-1.999272	-1.800136	2.099783
6	-4.458974	-2.880858	0.004058
1	-4.699504	-2.218891	-2.036957
1	-3.958211	-3.333821	2.052230
1	-5.314933	-3.553998	-0.024568
6	-1.400800	1.414897	-0.234161
6	-0.980791	2.115370	-1.376176
6	-2.252892	2.099482	0.650085
6	-1.382501	3.431582	-1.625125
1	-0.311226	1.612704	-2.071703
6	-2.655260	3.416087	0.420763
1	-2.607880	1.581065	1.540733
6	-2.221313	4.091005	-0.724522
1	-1.037383	3.947348	-2.521579
1	-3.310671	3.919849	1.131455
1	-2.534279	5.117416	-0.911233
5	-0.934635	-0.117754	0.082573

Quinuclidine radical cation

[**1a**(H1)•quinuclidine]$^{\bullet+}$ (pre-reactive complex)

Energies (Hartree/particle): -328.948766751

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:

	Coordinates		
Atomic Number	X	Y	Z
6	0.829160	-0.120147	-1.397629
6	-1.276807	-0.003251	0.002396
6	-0.772333	-0.127102	-1.437840
1	1.229950	0.730784	-1.950630
1	1.233869	-1.052474	-1.794467
1	-1.107751	0.709034	-2.056133
1	-1.103894	-1.058634	-1.902828
6	0.829508	1.272279	0.590635
1	1.235226	1.326794	1.602044
1	1.229416	2.082854	-0.020542
6	-0.772026	1.307073	0.612576
1	-1.102668	1.423905	1.647449
1	-1.108299	2.174810	0.039966
1	-2.375303	-0.005998	0.004478
6	-0.765469	-1.185815	0.829420
1	-1.096763	-1.124637	1.868839
1	-1.095978	-2.141075	0.414533
6	0.835775	-1.145889	0.802501
1	1.240268	-1.020950	1.808112
1	1.241161	-2.048165	0.342009
7	1.175284	0.002856	-0.002116

[**1a**(H1)•quinuclidine]$^{\bullet+}$ (pre-reactive complex)

Energies (Hartree/particle): -980.124929776

Zero-point correction= 0.406331 (Hartree/Particle)
Thermal correction to Energy= 0.428285
Thermal correction to Enthalpy= 0.429229
Thermal correction to Gibbs Free Energy= 0.353311
Sum of electronic and zero-point Energies= -979.718598
Sum of electronic and thermal Energies= -979.696645
Sum of electronic and thermal Enthalpies= -979.695701
Sum of electronic and thermal Free Energies= -979.771619

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	2.504421	1.059731	0.697951
6	2.841018	-1.047771	-0.628127
6	3.029950	-0.384857	0.735455
1	3.066792	1.615936	-0.064474
1	3.457430	-0.509235	-1.364317
1	2.461238	-0.948194	1.489568
8	1.096109	1.020750	0.319238
6	0.839872	0.445460	-0.928954
8	1.325016	1.176076	-2.020471
6	0.996753	2.570861	-2.027600
1	1.448095	3.096823	-1.180315
1	1.384611	2.967501	-2.966454
1	-0.094167	2.703370	-1.991646
6	2.582540	1.773833	2.031188
1	3.626519	1.887572	2.337525
1	2.147422	2.774638	1.955619
1	2.043017	1.214948	2.804122
8	4.431684	-0.436011	1.008084
1	4.572900	-0.385591	1.962242
6	1.379102	-0.987120	-1.075837
1	1.308842	-1.268994	-2.135193
7	-2.127014	0.106898	-0.197750
6	-2.946988	1.282810	-0.443791
6	-4.328369	-0.404315	0.825163

6	-4.389702	0.956755	0.119337
1	-2.499088	2.134945	0.071047
1	-2.977945	1.480193	-1.517508
1	-4.689398	1.749198	0.810507
1	-5.106716	0.937248	-0.706053
6	-1.852409	-0.117044	1.214801
1	-1.192209	-0.979646	1.297576
1	-1.343596	0.760786	1.616144
6	-3.249301	-0.358095	1.914675
1	-3.208876	-1.298365	2.471446
1	-3.448445	0.448640	2.625732
1	-5.301795	-0.629708	1.275976
6	-3.967127	-1.490168	-0.197008
1	-3.849690	-2.461158	0.291873
1	-4.740563	-1.587292	-0.963820
6	-2.603871	-1.082326	-0.888537
1	-1.847910	-1.863158	-0.795450
1	-2.751576	-0.837152	-1.942453
1	-0.280449	0.403432	-0.972341
8	0.564272	-1.847195	-0.278949
1	1.098169	-2.647698	-0.141376
8	3.191258	-2.427592	-0.591616
1	4.040044	-2.492384	-0.127410

[**1a**(H1)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energies (Hartree/particle): -980.123391030

Zero-point correction= 0.403622 (Hartree/Particle)
Thermal correction to Energy= 0.424883
Thermal correction to Enthalpy= 0.425827
Thermal correction to Gibbs Free Energy= 0.352862
Sum of electronic and zero-point Energies= -979.719769
Sum of electronic and thermal Energies= -979.698508
Sum of electronic and thermal Enthalpies= -979.697564
Sum of electronic and thermal Free Energies= -979.770529

Number of imaginary frequencies: 1

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	2.546807	1.065714	0.740736
6	2.758196	-0.968331	-0.715973
6	3.102774	-0.360817	0.642559
1	3.004141	1.671695	-0.053598
1	3.230210	-0.360322	-1.504168
1	2.655364	-0.976359	1.435542
8	1.090135	1.024683	0.507022
6	0.678815	0.426601	-0.657659
8	0.767988	1.187547	-1.809852
6	0.682161	2.620722	-1.677521
1	1.582266	3.024003	-1.205351
1	0.590679	3.000546	-2.695167
1	-0.191832	2.905730	-1.083901
6	2.746748	1.721208	2.088764
1	3.815555	1.845635	2.286981
1	2.287267	2.713458	2.106367
1	2.303599	1.113961	2.885263
8	4.528921	-0.368998	0.726097
1	4.794624	-0.364716	1.654770
6	1.239782	-0.973607	-0.940857
1	1.026832	-1.224052	-1.988903
7	-1.936598	0.015742	-0.073581
6	-2.666171	1.279420	-0.311290
6	-4.347996	-0.374417	0.555666

6	-4.181932	1.035163	-0.033195
1	-2.244178	2.032892	0.358030
1	-2.485632	1.584478	-1.344896
1	-4.553353	1.793039	0.662445
1	-4.753311	1.129987	-0.961339
6	-1.963121	-0.363973	1.356882
1	-1.405593	-1.295942	1.450594
1	-1.435354	0.411659	1.916047
6	-3.452607	-0.504624	1.798209
1	-3.600232	-1.475096	2.280590
1	-3.704375	0.269153	2.529794
1	-5.393754	-0.543270	0.828518
6	-3.904559	-1.407811	-0.491603
1	-3.942646	-2.416465	-0.069574
1	-4.568255	-1.388161	-1.360760
6	-2.447324	-1.072745	-0.937041
1	-1.771241	-1.921606	-0.828957
1	-2.406418	-0.717281	-1.969836
1	-0.532683	0.232297	-0.436733
8	0.602741	-1.892822	-0.061095
1	1.182236	-2.672996	-0.038617
8	3.172236	-2.324252	-0.807966
1	4.082080	-2.368151	-0.475138

[**1a**(H2)•quinuclidine]$^{\bullet+}$ (pre-reactive complex)

Energies (Hartree/particle): -980.130040541

Zero-point correction=	0.406010 (Hartree/Particle)
Thermal correction to Energy=	0.427671
Thermal correction to Enthalpy=	0.428615
Thermal correction to Gibbs Free Energy=	0.353464
Sum of electronic and zero-point Energies=	-979.724031
Sum of electronic and thermal Energies=	-979.702369
Sum of electronic and thermal Enthalpies=	-979.701425
Sum of electronic and thermal Free Energies=	-979.776576

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	3.348334	0.370502	-0.31892
6	1.362561	-1.15614	-0.27461
6	2.895617	-1.09509	-0.18803
1	2.985156	0.769073	-1.27603
1	1.070427	-0.80598	-1.2751
1	3.213486	-1.47515	0.794236
8	2.751942	1.108717	0.773242
6	1.345893	1.165234	0.774619
1	1.090433	1.68611	1.70799
8	0.797327	1.817636	-0.34726
6	1.169669	3.203836	-0.44197
1	2.24902	3.315308	-0.58704
1	0.638851	3.6056	-1.30683
1	0.869003	3.745846	0.465172
6	4.850795	0.543597	-0.20947
1	5.348461	0.0311	-1.03815
1	5.11434	1.603336	-0.26111
1	5.220572	0.140943	0.739529
8	3.372546	-1.92628	-1.24122
1	4.24351	-2.27305	-1.00684
8	0.865856	-2.4712	-0.03385
1	1.431941	-3.08108	-0.53268
8	0.751646	-0.79707	2.053525
1	0.776129	-1.76666	1.941128

6	0.74127	-0.24995	0.778589
1	-0.38015	-0.09958	0.462872
7	-1.9588	-0.07931	0.104161
6	-2.54105	-1.26736	0.743416
6	-2.07973	-0.1231	-1.35935
6	-2.48949	1.169936	0.666337
6	-4.06719	-1.30613	0.387935
1	-2.0097	-2.14626	0.372528
1	-2.37446	-1.18509	1.820097
1	-1.50817	0.711519	-1.77029
1	-1.63558	-1.05989	-1.70318
6	-3.60215	-0.03516	-1.72026
6	-4.03576	1.196414	0.414434
1	-1.97627	1.998693	0.175223
1	-2.25152	1.191005	1.732711
6	-4.41184	-0.04157	-0.41417
1	-4.28771	-2.20377	-0.19708
1	-4.65784	-1.35492	1.30703
1	-3.79762	0.879501	-2.28758
1	-3.87849	-0.88379	-2.35244
1	-4.30518	2.114604	-0.11527
1	-4.56847	1.195089	1.369796
1	-5.48253	-0.02603	-0.64063

[**1a**(H2)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energies (Hartree/particle): -980.129849656

Zero-point correction= 0.403985 (Hartree/Particle)
Thermal correction to Energy= 0.425064
Thermal correction to Enthalpy= 0.426008
Thermal correction to Gibbs Free Energy= 0.353289
Sum of electronic and zero-point Energies= -979.725864
Sum of electronic and thermal Energies= -979.704786
Sum of electronic and thermal Enthalpies= -979.703842
Sum of electronic and thermal Free Energies= -979.776561

Number of imaginary frequencies: 1

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	3.30997	0.36358	-0.31956
6	1.33158	-1.1758	-0.26193
6	2.865547	-1.10208	-0.17098
1	2.950578	0.747048	-1.28425
1	1.041842	-0.84572	-1.26983
1	3.179602	-1.46637	0.818829
8	2.703751	1.116347	0.758839
6	1.295497	1.163651	0.750142
1	1.030903	1.698326	1.673062
8	0.75275	1.793869	-0.38664
6	1.109606	3.183456	-0.49621
1	2.189619	3.305478	-0.62609
1	0.587327	3.565631	-1.37495
1	0.788033	3.734548	0.39814
6	4.810721	0.547415	-0.20404
1	5.31651	0.027131	-1.02296
1	5.068162	1.607896	-0.26874
1	5.177678	0.159987	0.752362
8	3.349028	-1.94779	-1.20909
1	4.228879	-2.27199	-0.97527
8	0.842418	-2.48836	0.003172
1	1.417479	-3.10537	-0.47641
8	0.688049	-0.77991	2.048494
1	0.712329	-1.75226	1.951171

6	0.711801	-0.25448	0.773777
1	-0.47721	-0.11426	0.424956
7	-1.89039	-0.0807	0.110198
6	-2.50209	-1.27148	0.740562
6	-2.03547	-0.11368	-1.36142
6	-2.43217	1.172027	0.680101
6	-4.0129	-1.31208	0.354511
1	-1.95904	-2.1507	0.387547
1	-2.35516	-1.18207	1.81961
1	-1.43392	0.699857	-1.77138
1	-1.62299	-1.06429	-1.70762
6	-3.5488	0.026337	-1.71078
6	-3.97629	1.187202	0.464248
1	-1.93249	1.999537	0.173589
1	-2.1651	1.199696	1.739605
6	-4.35909	-0.02114	-0.4052
1	-4.2157	-2.18699	-0.27039
1	-4.62244	-1.40378	1.257888
1	-3.72773	0.970543	-2.23385
1	-3.84837	-0.78392	-2.38156
1	-4.27052	2.121976	-0.02149
1	-4.49167	1.139963	1.42815
1	-5.42941	0.004089	-0.62904

[**1a**(H3)•quinuclidine]$^{\bullet+}$ (pre-reactive complex)

Energies (Hartree/particle): -980.125738171

Zero-point correction= 0.406447 (Hartree/Particle)
Thermal correction to Energy= 0.428159
Thermal correction to Enthalpy= 0.429104
Thermal correction to Gibbs Free Energy= 0.354880
Sum of electronic and zero-point Energies= -979.719291
Sum of electronic and thermal Energies= -979.697579
Sum of electronic and thermal Enthalpies= -979.696635
Sum of electronic and thermal Free Energies= -979.770858

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	-2.155567	-0.227047	1.284323
6	-1.038301	-0.942262	-0.843931
6	-1.797010	-1.423403	0.386038
1	-1.217903	0.219631	1.647328
1	-2.723187	-1.915082	0.056850
8	-2.885114	0.746380	0.516126
6	-2.209935	1.255700	-0.613011
1	-2.940212	1.920778	-1.091605
8	-1.028471	1.962315	-0.280169
6	-1.285332	3.175407	0.444789
1	-1.756709	2.967147	1.411754
1	-0.317442	3.658141	0.599922
1	-1.934017	3.842707	-0.137628
6	-3.033916	-0.613746	2.459549
1	-2.511716	-1.313783	3.120053
1	-3.288698	0.273155	3.045926
1	-3.964121	-1.073444	2.109801
8	-0.925165	-2.365572	1.034786
1	-1.454356	-2.930110	1.613539
6	-1.803531	0.151529	-1.602596
1	-1.155775	0.587331	-2.375816
6	2.308592	-1.407920	-0.257540
6	4.062938	0.318635	0.289628
6	3.857055	-1.149819	-0.110338

1	1.930273	-2.080024	0.514513
1	2.058066	-1.813285	-1.240708
1	4.260793	-1.826140	0.648209
1	4.359662	-1.367035	-1.056911
6	1.735559	0.406593	1.255275
1	1.179556	1.344083	1.293356
1	1.277708	-0.313661	1.935947
6	3.266417	0.611476	1.569097
1	3.430219	1.638431	1.907215
1	3.568806	-0.061172	2.376716
1	5.127643	0.508667	0.463424
6	3.549090	1.224453	-0.838362
1	3.620216	2.277570	-0.551845
1	4.131621	1.084829	-1.753145
6	2.044574	0.852237	-1.119131
1	1.382766	1.716366	-1.047079
1	1.922173	0.386845	-2.099538
7	1.645289	-0.118545	-0.103386
1	-0.079421	-0.453651	-0.464570
8	-2.998109	-0.368220	-2.156755
1	-2.757965	-1.011469	-2.839127
8	-0.671465	-1.980200	-1.714107
1	-0.588950	-2.787201	-1.176870

[**1a**(H3)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energies (Hartree/particle): -980.123678326

Zero-point correction= 0.403861 (Hartree/Particle)
Thermal correction to Energy= 0.425024
Thermal correction to Enthalpy= 0.425969
Thermal correction to Gibbs Free Energy= 0.353449
Sum of electronic and zero-point Energies= -979.719817
Sum of electronic and thermal Energies= -979.698654
Sum of electronic and thermal Enthalpies= -979.697710
Sum of electronic and thermal Free Energies= -979.770229

Number of imaginary frequencies: 1

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	2.114620	-0.181847	-1.272465
6	0.963295	-0.972955	0.820239
6	1.724894	-1.401843	-0.420594
1	1.196788	0.291607	-1.646685
1	2.650001	-1.897006	-0.085275
8	2.835700	0.748395	-0.446490
6	2.122138	1.248083	0.664378
1	2.845841	1.883669	1.190209
8	0.974184	1.985584	0.297908
6	1.282697	3.209402	-0.390837
1	1.786706	3.011176	-1.343083
1	0.330629	3.713316	-0.571500
1	1.921338	3.849112	0.231690
6	3.020173	-0.544057	-2.434619
1	2.506421	-1.213455	-3.132510
1	3.303129	0.357866	-2.983765
1	3.933965	-1.028792	-2.075453
8	0.873860	-2.334017	-1.105067
1	1.415383	-2.876208	-1.693985
6	1.655541	0.132852	1.615892
1	0.965292	0.560341	2.355379
6	-2.247163	-1.453439	0.178213
6	-3.937683	0.341606	-0.323492
6	-3.764293	-1.155639	-0.026992

1	-1.841951	-2.105257	-0.597938
1	-2.048033	-1.902388	1.153520
1	-4.147263	-1.759258	-0.854859
1	-4.324827	-1.433272	0.870308
6	-1.594494	0.429661	-1.236593
1	-0.994171	1.339471	-1.221899
1	-1.150881	-0.276101	-1.941420
6	-3.094853	0.709536	-1.553623
1	-3.227138	1.765380	-1.806954
1	-3.408910	0.120716	-2.420496
1	-4.991806	0.563871	-0.512947
6	-3.439089	1.151528	0.882599
1	-3.511731	2.223577	0.676756
1	-4.050355	0.943734	1.765434
6	-1.956208	0.765469	1.165784
1	-1.285924	1.625097	1.144804
1	-1.843218	0.254127	2.124915
7	-1.500711	-0.175115	0.112998
1	-0.151460	-0.475845	0.398401
8	2.825042	-0.383553	2.235393
1	2.555048	-1.011235	2.920786
8	0.566247	-2.018729	1.636125
1	0.480818	-2.810781	1.074719

[**1a**(H4)•quinuclidine]$^{\bullet+}$ (pre-reactive complex)

Energies (Hartree/particle): -980.122796166

Zero-point correction= 0.405647 (Hartree/Particle)
Thermal correction to Energy= 0.427817
Thermal correction to Enthalpy= 0.428762
Thermal correction to Gibbs Free Energy= 0.352939
Sum of electronic and zero-point Energies= -979.717149
Sum of electronic and thermal Energies= -979.694979
Sum of electronic and thermal Enthalpies= -979.694035
Sum of electronic and thermal Free Energies= -979.769857

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	1.750947	1.261735	0.637111
6	1.643170	-1.225831	1.073667
6	0.940792	0.126497	1.286099
1	2.748738	1.264963	1.103860
1	2.588687	-1.178311	1.635244
8	1.874727	0.975029	-0.759392
6	2.623019	-0.215114	-1.030711
1	2.599679	-0.296021	-2.125863
8	3.930709	-0.155413	-0.539836
6	4.771180	0.784048	-1.228091
1	4.395645	1.808073	-1.117458
1	5.759786	0.700270	-0.774253
1	4.832027	0.532276	-2.295531
6	1.127077	2.641044	0.763494
1	1.039143	2.957851	1.809463
1	1.758631	3.376697	0.258880
1	0.136310	2.667837	0.300344
8	0.710375	0.273982	2.668674
1	0.631774	1.213468	2.889044
8	0.854280	-2.325222	1.511757
1	0.856342	-2.333738	2.478423
6	1.973439	-1.455270	-0.404255
1	2.689765	-2.283976	-0.473152
8	0.801909	-1.764672	-1.165157

1	0.510101	-2.635633	-0.860701
1	-0.053928	0.081453	0.750097
7	-1.827286	0.133939	0.072934
6	-1.684100	0.460516	-1.341280
6	-2.579131	1.133180	0.820385
6	-2.317258	-1.221319	0.299091
6	-3.118846	0.341490	-1.986925
1	-1.289660	1.474553	-1.423080
1	-0.969851	-0.235750	-1.783007
1	-2.607150	0.833873	1.870466
1	-2.075228	2.097451	0.733807
6	-4.025964	1.188658	0.190079
6	-3.810222	-1.269186	-0.205451
1	-2.241221	-1.449051	1.363682
1	-1.678751	-1.906039	-0.256740
6	-4.132298	0.078303	-0.864460
1	-3.349283	1.268980	-2.518622
1	-3.127355	-0.474985	-2.714419
1	-4.768059	1.053579	0.981692
1	-4.188927	2.171194	-0.261755
1	-4.478138	-1.459135	0.639590
1	-3.923018	-2.092586	-0.916026
1	-5.147125	0.057547	-1.277183

[**1a**(H4)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energies (Hartree/particle): -980.119509658

Zero-point correction= 0.403019 (Hartree/Particle)
Thermal correction to Energy= 0.424376
Thermal correction to Enthalpy= 0.425320
Thermal correction to Gibbs Free Energy= 0.353346
Sum of electronic and zero-point Energies= -979.716491
Sum of electronic and thermal Energies= -979.695134
Sum of electronic and thermal Enthalpies= -979.694190
Sum of electronic and thermal Free Energies= -979.766163

Number of imaginary frequencies: 1

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	1.628521	1.290863	0.459306
6	1.481051	-1.152790	1.134320
6	0.811848	0.226057	1.199719
1	2.606364	1.332630	0.970911
1	2.405215	-1.055526	1.729067
8	1.816988	0.865005	-0.889037
6	2.584629	-0.343475	-0.997758
1	2.625934	-0.529417	-2.078933
8	3.856113	-0.224656	-0.434739
6	4.745107	0.635027	-1.168156
1	4.369124	1.664360	-1.194963
1	5.701885	0.603004	-0.644993
1	4.872227	0.266171	-2.194503
6	1.034634	2.689976	0.427243
1	0.862823	3.089992	1.433878
1	1.735951	3.366250	-0.067608
1	0.094235	2.712790	-0.128318
8	0.469527	0.512578	2.512420
1	0.398139	1.471808	2.636903
8	0.668842	-2.200299	1.642824
1	0.673879	-2.154507	2.608183
6	1.891524	-1.519872	-0.296595
1	2.608432	-2.348246	-0.243874
8	0.765574	-1.894699	-1.091393

1	0.517584	-2.787908	-0.816870
1	-0.325126	0.123175	0.562092
7	-1.630449	0.113309	0.077614
6	-1.598328	0.366816	-1.387121
6	-2.375679	1.177996	0.793191
6	-2.216711	-1.218972	0.378480
6	-3.062400	0.509078	-1.894779
1	-1.009754	1.268836	-1.559890
1	-1.067758	-0.470455	-1.839359
1	-2.224185	1.029078	1.865108
1	-1.937708	2.135900	0.506878
6	-3.878833	1.092514	0.397156
6	-3.629001	-1.299788	-0.268154
1	-2.250154	-1.317338	1.465173
1	-1.533444	-1.970483	-0.010048
6	-4.021282	0.098913	-0.766180
1	-3.258470	1.541522	-2.200770
1	-3.206037	-0.126328	-2.773303
1	-4.476639	0.763576	1.252435
1	-4.235873	2.085115	0.108036
1	-4.348507	-1.666691	0.469535
1	-3.621157	-2.008992	-1.101480
1	-5.052423	0.095379	-1.130435

[**1a**(H5)•quinuclidine]$^{\bullet+}$ (pre-reactive complex)

Energies (Hartree/particle): -980.121916320

Zero-point correction= 0.405930 (Hartree/Particle)
Thermal correction to Energy= 0.427903
Thermal correction to Enthalpy= 0.428847
Thermal correction to Gibbs Free Energy= 0.353410
Sum of electronic and zero-point Energies= -979.715986
Sum of electronic and thermal Energies= -979.694013
Sum of electronic and thermal Enthalpies= -979.693069
Sum of electronic and thermal Free Energies= -979.768506

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	-0.976857	-0.784480	1.108718
6	-2.165844	-0.488404	-1.104160
6	-1.777385	-1.483208	-0.019989
1	-1.251383	-0.121952	-1.595366
1	-2.692905	-1.898290	0.423666
8	-1.585368	0.388007	1.582869
6	-2.039717	1.334587	0.620981
1	-2.645470	2.038821	1.202457
8	-0.906773	1.980491	0.062380
6	-1.058835	3.401495	-0.074120
1	-1.234547	3.869531	0.903288
1	-0.123044	3.775787	-0.495223
1	-1.882816	3.652379	-0.754195
6	-0.673429	-1.672439	2.298262
1	-0.118636	-2.560203	1.983000
1	-0.078624	-1.131620	3.040044
1	-1.605385	-1.989179	2.779414
8	-0.990968	-2.511722	-0.629585
1	-1.183320	-3.352849	-0.195832
6	-2.896839	0.697959	-0.474749
1	-3.073971	1.457043	-1.252481
6	2.450137	-1.506360	0.272379
6	4.075964	0.255141	-0.507950
6	3.922380	-1.245104	-0.216375

1	2.423274	-1.804926	1.322383
1	1.947800	-2.266604	-0.328259
1	4.623860	-1.567596	0.558108
1	4.122180	-1.834705	-1.115760
6	2.181344	0.779756	1.065223
1	1.559467	1.664487	0.924793
1	2.046100	0.412261	2.085000
6	3.696710	1.054456	0.747259
1	3.844662	2.126411	0.588903
1	4.314657	0.753600	1.598148
1	5.111193	0.474559	-0.789677
6	3.129719	0.644962	-1.652639
1	3.167795	1.723189	-1.833147
1	3.407189	0.139978	-2.582167
6	1.669856	0.222200	-1.249066
1	0.971107	1.058973	-1.301538
1	1.300577	-0.595988	-1.870474
7	1.715481	-0.248664	0.134810
1	0.020934	-0.508288	0.618048
8	-3.049233	-1.063637	-2.057071
1	-2.654799	-1.893229	-2.363127
8	-4.114208	0.299311	0.135242
1	-4.628394	-0.171702	-0.538370

[**1a**(H5)•quinuclidine]$^{\bullet+}$ (transition state for HAT)

Energies (Hartree/particle): -980.121983833

Zero-point correction= 0.403515 (Hartree/Particle)
Thermal correction to Energy= 0.424764
Thermal correction to Enthalpy= 0.425709
Thermal correction to Gibbs Free Energy= 0.354005
Sum of electronic and zero-point Energies= -979.718468
Sum of electronic and thermal Energies= -979.697219
Sum of electronic and thermal Enthalpies= -979.696275
Sum of electronic and thermal Free Energies= -979.767979

Number of imaginary frequencies: 1

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	-0.926879	-0.666507	1.087364
6	-2.116987	-0.676665	-1.159187
6	-1.624621	-1.519888	0.009999
1	-1.254067	-0.260503	-1.699298
1	-2.501701	-1.983740	0.484360
8	-1.552405	0.519883	1.413066
6	-2.164226	1.320343	0.358921
1	-2.839139	1.977333	0.917825
8	-1.187736	2.038096	-0.331383
6	-0.851859	3.301450	0.271468
1	-0.475597	3.166223	1.292887
1	-0.077200	3.747138	-0.355892
1	-1.726923	3.961979	0.287522
6	-0.562671	-1.403771	2.357697
1	0.025468	-2.296484	2.133369
1	0.007545	-0.761019	3.034184
1	-1.478994	-1.707826	2.878967
8	-0.735558	-2.523566	-0.495981
1	-0.934730	-3.365229	-0.067280
6	-2.967341	0.473631	-0.624107
1	-3.260743	1.124320	-1.459948
6	2.359439	-1.376428	0.381015
6	3.936121	0.319747	-0.590667
6	3.785936	-1.159835	-0.203020

1	2.383536	-1.531378	1.462022
1	1.839396	-2.215814	-0.081958
1	4.534248	-1.444652	0.542058
1	3.935049	-1.797656	-1.079628
6	2.053912	0.985009	0.930591
1	1.458786	1.855979	0.656988
1	1.875600	0.761978	1.985215
6	3.566107	1.189093	0.621826
1	3.757449	2.246227	0.416269
1	4.171722	0.908148	1.488829
1	4.964430	0.525592	-0.900422
6	2.964036	0.631375	-1.739467
1	2.970363	1.703220	-1.960785
1	3.259443	0.106061	-2.652135
6	1.536159	0.177166	-1.317406
1	0.789923	0.959025	-1.467796
1	1.217885	-0.722444	-1.847886
7	1.553288	-0.155769	0.128250
1	0.206775	-0.397002	0.558556
8	-2.940434	-1.432387	-2.034905
1	-2.441610	-2.213841	-2.313358
8	-4.102293	-0.000694	0.085279
1	-4.606376	-0.558808	-0.525745

[**1a**•BPh_2(H1)•quinuclidine]$^{\bullet}$ (pre-reactive complex)

Energies (Hartree/particle): -1467.18969862

Zero-point correction= 0.565704 (Hartree/Particle)
Thermal correction to Energy= 0.598135
Thermal correction to Enthalpy= 0.599079
Thermal correction to Gibbs Free Energy= 0.496453
Sum of electronic and zero-point Energies= -1466.623995
Sum of electronic and thermal Energies= -1466.591563
Sum of electronic and thermal Enthalpies= -1466.590619
Sum of electronic and thermal Free Energies= -1466.693245

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	1.964269	3.441512	-0.097334
6	1.709992	1.338632	-1.444342
6	2.611495	2.106288	-0.470782
1	1.782192	4.023237	-1.013105
1	1.804561	1.778543	-2.443121
1	2.712213	1.518299	0.454266
8	0.704523	3.156448	0.549136
6	-0.257510	2.539034	-0.282869
8	-0.702740	3.389118	-1.326874
6	-1.442236	4.510425	-0.849114
1	-0.823062	5.162131	-0.218952
1	-1.776681	5.064621	-1.730013
1	-2.316839	4.178185	-0.269106
6	2.794010	4.252290	0.879865
1	3.766189	4.488111	0.439732
1	2.277898	5.184767	1.129809
1	2.954211	3.683916	1.802698
8	3.896224	2.345038	-1.050067
1	4.239800	1.480643	-1.316567
8	2.113373	-0.038375	-1.490812
6	0.258168	1.271195	-0.965204
1	-0.411959	1.047002	-1.807412
8	0.261486	0.162373	-0.063329
6	0.754096	-2.224734	-0.993448

6	-0.402799	-2.762913	-0.421039
6	1.415536	-2.919541	-2.011061
6	-0.949519	-3.941492	-0.927641
1	-0.891375	-2.248218	0.399861
6	0.865977	-4.098740	-2.516298
1	2.329590	-2.517830	-2.438039
6	-0.314887	-4.613249	-1.975203
1	-1.866189	-4.339314	-0.497874
1	1.362386	-4.616468	-3.333969
1	-0.732049	-5.540181	-2.360615
6	2.208486	-1.359073	0.772849
6	1.653035	-1.405995	2.055599
6	3.521376	-1.792465	0.564838
6	2.441175	-1.796555	3.138750
1	0.626553	-1.091402	2.215617
6	4.306285	-2.183209	1.649747
1	3.939148	-1.795249	-0.437762
6	3.766825	-2.188780	2.938368
1	2.017821	-1.794092	4.140662
1	5.337354	-2.488980	1.487684
1	4.374332	-2.506545	3.781998
5	1.314132	-0.720980	-0.499237
7	-3.224692	0.879025	0.472651
6	-4.606208	1.343198	0.649401
6	-4.774865	-1.158829	0.718963
6	-5.582545	0.143229	0.863451
1	-4.628615	2.026901	1.505630
1	-4.881191	1.919766	-0.241075
1	-6.043582	0.188497	1.857597
1	-6.395059	0.165844	0.127493
6	-2.808607	0.093112	1.643736
1	-1.751896	-0.154438	1.512711
1	-2.893007	0.738742	2.525173
6	-3.684072	-1.188851	1.803470
1	-3.074342	-2.094120	1.692257
1	-4.142139	-1.228262	2.799032
1	-5.436850	-2.025397	0.825163
6	-4.100239	-1.171662	-0.663029
1	-3.551603	-2.108907	-0.810638
1	-4.862021	-1.113294	-1.449903
6	-3.128861	0.046480	-0.735847

1	-2.093018	-0.291808	-0.820045
1	-3.349360	0.680682	-1.601453
1	-1.094416	2.283671	0.380519

[**1a**•BPh_2(H1)•quinuclidine]$^{\bullet}$ (transition state for HAT)

Energies (Hartree/particle): -1467.16675731

Zero-point correction= 0.562216 (Hartree/Particle)
Thermal correction to Energy= 0.593658
Thermal correction to Enthalpy= 0.594602
Thermal correction to Gibbs Free Energy= 0.496610
Sum of electronic and zero-point Energies= -1466.604541
Sum of electronic and thermal Energies= -1466.573100
Sum of electronic and thermal Enthalpies= -1466.572155
Sum of electronic and thermal Free Energies= -1466.670148

Number of imaginary frequencies: 1

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	-0.518221	3.595404	-0.326536
6	0.871828	1.848497	-1.505377
6	0.858762	2.950337	-0.432239
1	-0.800837	4.007563	-1.307238
1	0.797204	2.317635	-2.498117
1	1.107379	2.499025	0.536663
8	-1.509797	2.555615	0.026915
6	-1.579630	1.491159	-0.832509
8	-2.412412	1.665103	-1.939555
6	-3.521252	2.555748	-1.772453
1	-3.188878	3.588100	-1.623820
1	-4.102149	2.479935	-2.693722
1	-4.139822	2.259807	-0.915385
6	-0.616529	4.655991	0.747321
1	0.094036	5.457370	0.528787
1	-1.627389	5.074549	0.790213
1	-0.367531	4.227850	1.724012
8	1.801440	3.971901	-0.764170
1	2.637441	3.509409	-0.927940
8	2.013198	1.050737	-1.421367
6	-0.272740	0.837634	-1.223662
1	-0.444314	0.215144	-2.119264
8	0.244703	0.101374	-0.150626
6	1.851298	-1.536985	-1.238188

6	1.644168	-2.727128	-0.517351
6	2.028560	-1.654178	-2.624388
6	1.593094	-3.971480	-1.146388
1	1.528339	-2.672506	0.565415
6	1.987490	-2.895966	-3.267374
1	2.203287	-0.752023	-3.206952
6	1.762991	-4.059810	-2.531261
1	1.435006	-4.875435	-0.559710
1	2.130447	-2.955880	-4.345160
1	1.731772	-5.027351	-3.027841
6	2.595527	-0.028221	0.898487
6	2.060758	0.422588	2.115579
6	3.950429	-0.398285	0.895686
6	2.835155	0.504226	3.276307
1	1.014454	0.720737	2.151470
6	4.738752	-0.311348	2.043973
1	4.393201	-0.768941	-0.027542
6	4.181573	0.139329	3.243295
1	2.390014	0.854737	4.206411
1	5.787466	-0.600815	2.008081
1	4.790703	0.202866	4.142426
5	1.716683	-0.109926	-0.461792
7	-2.561338	-0.619224	0.519937
6	-4.035485	-0.542915	0.638109
6	-3.372423	-2.722592	1.692609
6	-4.572115	-1.865377	1.252266
1	-4.267261	0.324065	1.263530
1	-4.439108	-0.361700	-0.361843
1	-5.220785	-1.646435	2.106763
1	-5.172707	-2.410520	0.516271
6	-1.924420	-0.679579	1.863591
1	-0.852287	-0.749807	1.687375
1	-2.125014	0.272578	2.361870
6	-2.495752	-1.891749	2.644643
1	-1.673458	-2.500343	3.033646
1	-3.089211	-1.556163	3.502476
1	-3.725687	-3.627081	2.197520
6	-2.544216	-3.094965	0.451718
1	-1.637445	-3.631451	0.749053
1	-3.115803	-3.758586	-0.205256
6	-2.161810	-1.795603	-0.302614

1	-1.087775	-1.714781	-0.474507
1	-2.681613	-1.704812	-1.260340
1	-2.107526	0.481215	-0.116982

[**1a**•$BPh_2(H2)$•quinuclidine]˙ (pre-reactive complex)

Energies (Hartree/particle): -1467.19488793

Zero-point correction= 0.565371 (Hartree/Particle)
Thermal correction to Energy= 0.596977
Thermal correction to Enthalpy= 0.597921
Thermal correction to Gibbs Free Energy= 0.500376
Sum of electronic and zero-point Energies= -1466.629517
Sum of electronic and thermal Energies= -1466.597911
Sum of electronic and thermal Enthalpies= -1466.596967
Sum of electronic and thermal Free Energies= -1466.694512

Number of imaginary frequencies:

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	-2.244422	2.984756	0.447831
6	-0.771297	1.034484	1.058014
6	-2.211695	1.593750	1.076459
1	-1.528462	3.640970	0.965098
1	-0.176108	1.608799	1.781430
1	-2.842687	0.931172	0.467323
8	-1.845177	2.844844	-0.940299
6	-0.523458	2.405204	-1.146087
1	-0.455436	2.224374	-2.228854
8	0.444385	3.363279	-0.739699
6	0.350764	4.596364	-1.451022
1	-0.597864	5.108009	-1.248859
1	1.182435	5.217936	-1.109256
1	0.439030	4.430844	-2.536050
6	-3.624726	3.613168	0.445882
1	-3.976255	3.733486	1.473709
1	-3.597570	4.593513	-0.040594
1	-4.330678	2.972519	-0.092978
8	-2.693630	1.652435	2.414290
1	-2.674147	0.740105	2.740237
8	-0.720417	-0.334203	1.359500
6	-0.209303	1.123885	-0.367428
8	-0.565705	-0.024513	-0.999210
6	0.133781	-2.325866	-0.036321

6	0.396459	-2.944823	-1.268961
6	0.852924	-2.780473	1.079412
6	1.369771	-3.936832	-1.396212
1	-0.158434	-2.629253	-2.150473
6	1.824440	-3.779504	0.966275
1	0.653411	-2.334008	2.051209
6	2.095820	-4.353202	-0.276831
1	1.563436	-4.388495	-2.367278
1	2.366815	-4.113513	1.849261
1	2.854171	-5.127185	-0.371321
6	-2.448879	-1.566242	-0.164561
6	-3.070661	-1.552880	-1.421869
6	-3.199347	-2.035574	0.925136
6	-4.389709	-1.982902	-1.586239
1	-2.521759	-1.182248	-2.284856
6	-4.517649	-2.467709	0.771519
1	-2.738730	-2.063529	1.911622
6	-5.119400	-2.441351	-0.488546
1	-4.851594	-1.953894	-2.571422
1	-5.076112	-2.828354	1.633403
1	-6.147368	-2.774241	-0.612608
5	-0.913016	-1.094255	0.079067
6	2.847254	-0.274615	-0.965713
6	4.944826	0.074698	0.357834
6	4.356526	-0.641927	-0.868759
1	2.210522	-1.124478	-0.723032
1	2.572259	0.078584	-1.963664
1	4.463106	-1.726653	-0.771780
1	4.890401	-0.334691	-1.775317
6	2.671300	0.319404	1.384911
1	2.495671	1.175761	2.042386
1	1.882704	-0.413340	1.559661
6	4.091505	-0.280872	1.587796
1	4.544050	0.118518	2.501792
1	4.026064	-1.368884	1.695706
1	5.983457	-0.234126	0.514881
6	4.875063	1.595029	0.124122
1	5.198918	2.128386	1.024920
1	5.546053	1.889843	-0.689873
6	3.403584	1.972024	-0.230989
1	3.027050	2.795898	0.379766

1	3.298479	2.260591	-1.280148
7	2.543808	0.801352	-0.003373
1	0.977134	1.106705	-0.236372

[**1a**•$BPh_2(H2)$•quinuclidine]$^{\bullet}$ (transition state for HAT)

Energies (Hartree/particle): -1467.19427828

Zero-point correction= 0.563496 (Hartree/Particle)
Thermal correction to Energy= 0.594707
Thermal correction to Enthalpy= 0.595651
Thermal correction to Gibbs Free Energy= 0.499680
Sum of electronic and zero-point Energies= -1466.630782
Sum of electronic and thermal Energies= -1466.599572
Sum of electronic and thermal Enthalpies= -1466.598627
Sum of electronic and thermal Free Energies= -1466.694598

Number of imaginary frequencies: 1

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	2.211340	-2.978734	0.459176
6	0.746002	-1.019979	1.062260
6	2.186193	-1.584778	1.083437
1	1.495958	-3.630027	0.983940
1	0.154183	-1.595320	1.788911
1	2.818559	-0.926468	0.471498
8	1.807301	-2.849243	-0.928658
6	0.487171	-2.394341	-1.132728
1	0.419076	-2.218085	-2.216133
8	-0.485899	-3.348556	-0.722711
6	-0.399040	-4.583799	-1.431288
1	0.546621	-5.099882	-1.227358
1	-1.234326	-5.200321	-1.088777
1	-0.485560	-4.420299	-2.516775
6	3.589875	-3.611269	0.455964
1	3.945196	-3.725591	1.483145
1	3.558209	-4.594725	-0.023983
1	4.295257	-2.975979	-0.089935
8	2.670233	-1.643835	2.420890
1	2.649409	-0.731747	2.747048
8	0.697554	0.348376	1.365592
6	0.197660	-1.112670	-0.360876
8	0.509971	0.032056	-0.995370
6	-0.152937	2.347431	-0.017465

6	-0.419036	2.966505	-1.250396
6	-0.862657	2.814001	1.099909
6	-1.384057	3.966735	-1.375605
1	0.128938	2.644064	-2.133926
6	-1.825424	3.821700	0.990025
1	-0.661032	2.370397	2.072857
6	-2.099605	4.393746	-0.253360
1	-1.578281	4.418141	-2.346746
1	-2.359459	4.163747	1.875048
1	-2.850944	5.174830	-0.345709
6	2.422416	1.560171	-0.173594
6	3.040588	1.504773	-1.432263
6	3.186323	2.051422	0.898115
6	4.364383	1.911985	-1.614629
1	2.482757	1.117970	-2.282559
6	4.509419	2.460856	0.727924
1	2.731771	2.111843	1.886226
6	5.105395	2.391070	-0.533401
1	4.821036	1.850746	-2.600842
1	5.077530	2.835902	1.577311
1	6.137165	2.706560	-0.671102
5	0.887626	1.113376	0.086531
6	-2.786129	0.254369	-0.992648
6	-4.875157	-0.106676	0.334984
6	-4.301733	0.568728	-0.921574
1	-2.177995	1.124077	-0.748339
1	-2.477121	-0.104164	-1.978063
1	-4.447028	1.652332	-0.878936
1	-4.819925	0.199838	-1.814196
6	-2.607777	-0.294404	1.381344
1	-2.446760	-1.143966	2.050852
1	-1.813470	0.431747	1.554191
6	-4.022624	0.312686	1.545445
1	-4.476474	-0.037420	2.478549
1	-3.957566	1.404838	1.596228
1	-5.918452	0.188817	0.483172
6	-4.775252	-1.633201	0.160918
1	-5.069504	-2.135497	1.089274
1	-5.456852	-1.975489	-0.624957
6	-3.310904	-1.995594	-0.210736
1	-2.909544	-2.806844	0.399513

1	-3.211631	-2.289719	-1.258431
7	-2.452269	-0.806535	-0.005782
1	-1.121861	-1.080221	-0.194738

[**1a**•$BPh_2(H3)$•quinuclidine]$^{\bullet}$ (pre-reactive complex)

Energies (Hartree/particle): -1467.19457622

Zero-point correction= 0.566006 (Hartree/Particle)
Thermal correction to Energy= 0.598162
Thermal correction to Enthalpy= 0.599106
Thermal correction to Gibbs Free Energy= 0.498234
Sum of electronic and zero-point Energies= -1466.628570
Sum of electronic and thermal Energies= -1466.596414
Sum of electronic and thermal Enthalpies= -1466.595470
Sum of electronic and thermal Free Energies= -1466.696343

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	2.974711	2.549148	-0.502876
6	1.012254	1.085214	-1.052979
6	2.530731	1.243896	-1.158536
1	2.452751	3.393856	-0.976514
1	3.011630	0.421711	-0.608476
8	2.602335	2.478749	0.895211
6	1.212859	2.444574	1.134028
1	1.126289	2.269895	2.217178
8	0.566246	3.655635	0.774797
6	1.041116	4.784808	1.502619
1	2.096191	4.993386	1.285025
1	0.427860	5.635402	1.194040
1	0.929558	4.628066	2.587314
6	4.474301	2.767336	-0.552102
1	4.808920	2.817545	-1.591391
1	4.739502	3.700646	-0.044837
1	4.992930	1.939719	-0.056080
8	2.944170	1.229134	-2.528144
1	2.605548	0.401816	-2.899337
8	0.637349	-0.271459	-1.315630
6	0.482164	1.337438	0.365332
1	-0.589623	1.620826	0.318646
8	0.588036	0.081332	1.009886
6	-0.531412	-2.093173	0.123062

6	-0.973679	-2.525105	1.380001
6	-1.122781	-2.638205	-1.023979
6	-2.031336	-3.428065	1.491171
1	-0.500791	-2.135522	2.277914
6	-2.180037	-3.544361	-0.915546
1	-0.775415	-2.327735	-2.005730
6	-2.638190	-3.941221	0.341971
1	-2.378217	-3.737078	2.474840
1	-2.644079	-3.942328	-1.815692
1	-3.455825	-4.652888	0.426748
6	2.005214	-1.925199	0.187229
6	2.633312	-2.029153	1.430754
6	2.513551	-2.634669	-0.904198
6	3.798149	-2.788887	1.564677
1	2.238484	-1.486709	2.284773
6	3.679193	-3.391654	-0.770061
1	2.009649	-2.581491	-1.865768
6	4.323314	-3.471645	0.465998
1	4.298618	-2.840447	2.529431
1	4.079037	-3.924095	-1.630480
1	5.226450	-4.067388	0.573732
5	0.646127	-0.952099	-0.022384
6	-2.683859	0.690871	-1.318945
6	-4.957474	0.312269	-0.335466
6	-4.044374	-0.048352	-1.518626
1	-2.498576	1.406637	-2.126592
1	-1.848191	-0.012602	-1.298593
1	-4.509279	0.250808	-2.465235
1	-3.884171	-1.131171	-1.552772
6	-3.712627	2.487157	-0.090643
1	-3.651806	3.051981	0.845142
1	-3.476318	3.170901	-0.912174
6	-5.127614	1.841323	-0.275909
1	-5.786118	2.115896	0.556182
1	-5.596407	2.204528	-1.197734
1	-5.935208	-0.167724	-0.455445
6	-4.288824	-0.171367	0.961503
1	-4.922505	0.060069	1.825665
1	-4.146787	-1.256382	0.934103
6	-2.908411	0.547886	1.085316
1	-2.854317	1.155221	1.994909

1	-2.092923	-0.177131	1.115452
7	-2.692687	1.438112	-0.058470
1	0.534714	1.743195	-1.788767

[**1a**•BPh_2(H3)•quinuclidine]$^{\bullet}$ (transition state for HAT)

Energies (Hartree/particle): -1467.18459593

Zero-point correction= 0.563416 (Hartree/Particle)
Thermal correction to Energy= 0.594700
Thermal correction to Enthalpy= 0.595644
Thermal correction to Gibbs Free Energy= 0.499028
Sum of electronic and zero-point Energies= -1466.621180
Sum of electronic and thermal Energies= -1466.589896
Sum of electronic and thermal Enthalpies= -1466.588952
Sum of electronic and thermal Free Energies= -1466.685568

Number of imaginary frequencies: 1

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	-1.012702	3.269125	-0.471877
6	-0.012509	0.967075	-0.447436
6	-0.281439	2.209810	-1.293374
1	-1.990728	2.878624	-0.153323
1	0.699586	2.625360	-1.572660
8	-0.203656	3.538557	0.688106
6	-0.188935	2.491167	1.642379
1	0.560642	2.803548	2.381883
8	-1.461626	2.327374	2.258458
6	-1.891227	3.478875	2.981763
1	-2.052464	4.337929	2.318187
1	-2.831908	3.209807	3.469650
1	-1.150894	3.758185	3.746842
6	-1.196475	4.578980	-1.215084
1	-1.781447	4.417479	-2.124352
1	-1.714392	5.304548	-0.580075
1	-0.222211	4.994828	-1.493879
8	-1.032184	1.911756	-2.484511
1	-0.449971	1.377947	-3.042616
8	0.958470	0.180176	-0.938627
6	0.198166	1.114579	1.074982
1	-0.444349	0.385737	1.596227
8	1.547264	0.796685	1.272644
6	1.317391	-1.740738	0.732912

6	1.001772	-2.036954	2.068190
6	1.074780	-2.748917	-0.216980
6	0.440856	-3.262445	2.438054
1	1.188793	-1.279635	2.827060
6	0.516174	-3.979110	0.137250
1	1.327376	-2.561314	-1.259623
6	0.186459	-4.237169	1.470656
1	0.199723	-3.458510	3.481202
1	0.341000	-4.739139	-0.622551
1	-0.250931	-5.192032	1.753710
6	3.411553	-0.197274	-0.179285
6	3.984383	1.059927	-0.443621
6	4.221216	-1.326190	-0.373498
6	5.301772	1.186587	-0.882924
1	3.382708	1.952886	-0.285626
6	5.542900	-1.212390	-0.812173
1	3.815739	-2.314359	-0.166331
6	6.086964	0.046260	-1.071374
1	5.720678	2.172431	-1.076812
1	6.150666	-2.105239	-0.946939
1	7.115857	0.139258	-1.412624
5	1.878491	-0.276672	0.302493
6	-1.954162	-1.428381	-1.788219
6	-4.144548	-2.207120	-0.850793
6	-3.051846	-2.517855	-1.887704
1	-1.945350	-0.769079	-2.658959
1	-0.956311	-1.851115	-1.663037
1	-3.474652	-2.536500	-2.897744
1	-2.622957	-3.506103	-1.690759
6	-3.461446	0.211975	-0.793398
1	-3.609723	0.796674	0.118683
1	-3.290669	0.903514	-1.620889
6	-4.639326	-0.764568	-1.061107
1	-5.471661	-0.546113	-0.384011
1	-5.010578	-0.641831	-2.084523
1	-4.977537	-2.908846	-0.958899
6	-3.530719	-2.322676	0.553378
1	-4.271548	-2.044008	1.310838
1	-3.224893	-3.354043	0.754956
6	-2.293859	-1.389456	0.630988
1	-2.352558	-0.699551	1.475337

1	-1.362201	-1.948706	0.710407
7	-2.215494	-0.568683	-0.606698
1	-1.144135	0.266432	-0.533124

[**1a**•BPh_2(H4)•quinuclidine]$^{\bullet}$ (pre-reactive complex)

Geometry optimization of the complex resulting from an interaction between H-4 of [**1a**•BPh_2]$^{-}$ and the quinuclidine radical cation was unsuccessful.

[**1a**•BPh_2(H4)•quinuclidine]$^{\bullet}$ (transition state for HAT)

The search for a transition state for HAT between H-4 of [**1a**•BPh_2]$^{-}$ and the quinuclidine radical cation was unsuccessful.

[**1a**•$BPh_2(H5)$•quinuclidine]$^{\bullet}$ (pre-reactive complex)

Energies (Hartree/particle): -1467.18750005

Zero-point correction= 0.565629 (Hartree/Particle)
Thermal correction to Energy= 0.598096
Thermal correction to Enthalpy= 0.599040
Thermal correction to Gibbs Free Energy= 0.495807
Sum of electronic and zero-point Energies= -1466.621871
Sum of electronic and thermal Energies= -1466.589404
Sum of electronic and thermal Enthalpies= -1466.588460
Sum of electronic and thermal Free Energies= -1466.691693

Number of imaginary frequencies: 0

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	-1.326737	1.412925	0.756697
6	0.122305	-0.399977	-0.234560
6	-0.313658	1.066760	-0.333658
1	-0.652837	-1.036175	-0.672863
1	0.570204	1.704273	-0.182442
8	-0.698367	1.153859	2.036416
6	-0.401860	-0.202181	2.273239
1	0.123186	-0.201328	3.240846
8	-1.556407	-1.024084	2.335516
6	-2.494542	-0.613236	3.325779
1	-2.969186	0.339136	3.061232
1	-3.255442	-1.396284	3.376135
1	-2.009647	-0.510880	4.309139
6	-1.726770	2.875465	0.752149
1	-2.186621	3.133242	-0.205097
1	-2.446278	3.070116	1.553964
1	-0.849668	3.514287	0.905213
8	-0.893231	1.330690	-1.618762
1	-0.225109	1.082068	-2.272878
8	1.348666	-0.578463	-0.959664
6	0.483354	-0.828013	1.192524
1	0.417789	-1.922020	1.292133
8	1.846877	-0.431813	1.330299
6	3.734958	-1.370065	-0.229756

6	4.533200	-1.744142	0.858000
6	4.034019	-1.853122	-1.509630
6	5.564016	-2.666292	0.681287
1	4.323265	-1.343713	1.845234
6	5.063791	-2.777195	-1.682398
1	3.437444	-1.539351	-2.361026
6	5.833946	-3.182031	-0.588987
1	6.159891	-2.979600	1.535473
1	5.268788	-3.177510	-2.672671
1	6.648282	-3.888676	-0.728327
6	3.316236	1.019644	-0.261938
6	3.881792	1.690501	0.825031
6	3.430867	1.545343	-1.551072
6	4.476403	2.938225	0.631799
1	3.815807	1.265552	1.821660
6	4.027699	2.792480	-1.739585
1	3.024029	1.002156	-2.398763
6	4.553211	3.489731	-0.649243
1	4.881511	3.478281	1.484533
1	4.085515	3.216749	-2.739407
1	5.030153	4.455066	-0.798874
5	2.406778	-0.393026	0.004260
6	-4.745160	1.037475	-0.958980
6	-6.127001	-0.953471	-1.605819
6	-5.801531	0.504329	-1.976269
1	-5.146369	1.873693	-0.374991
1	-3.845557	1.392392	-1.471341
1	-6.714386	1.111558	-1.947837
1	-5.413088	0.550619	-3.000853
6	-5.494859	-0.459230	0.768489
1	-5.150000	-1.237743	1.457817
1	-5.841117	0.386254	1.374102
6	-6.634571	-0.994009	-0.153866
1	-6.910054	-2.019569	0.120179
1	-7.537393	-0.378692	-0.057006
1	-6.889717	-1.353843	-2.282727
6	-4.839396	-1.790623	-1.702374
1	-5.046581	-2.827001	-1.408754
1	-4.481721	-1.812731	-2.738796
6	-3.774209	-1.146977	-0.762336
1	-3.387198	-1.870158	-0.036459

1	-2.923960	-0.767076	-1.337571
7	-4.335876	-0.012417	-0.014203
1	-2.220009	0.783572	0.651561

[**1a**•$BPh_2(H5)$•quinuclidine]$^{\bullet}$ (transition state for HAT)

Energies (Hartree/particle): -1467.15436501

Zero-point correction= 0.561601 (Hartree/Particle)
Thermal correction to Energy= 0.593127
Thermal correction to Enthalpy= 0.594072
Thermal correction to Gibbs Free Energy= 0.494770
Sum of electronic and zero-point Energies= -1466.592764
Sum of electronic and thermal Energies= -1466.561238
Sum of electronic and thermal Enthalpies= -1466.560293
Sum of electronic and thermal Free Energies= -1466.659595

Number of imaginary frequencies: 1

Geometry:

	Coordinates		
Atomic Number	X	Y	Z
6	-1.390581	1.050137	0.894788
6	0.143077	-0.470002	-0.496349
6	-0.364381	0.945590	-0.216195
1	-0.591613	-1.016235	-1.104204
1	0.504275	1.534674	0.134150
8	-1.072823	0.336941	2.040607
6	-0.552778	-1.010676	1.918138
1	-0.085729	-1.182816	2.895326
8	-1.621318	-1.911906	1.708776
6	-2.361707	-2.199243	2.894649
1	-2.824140	-1.294491	3.312374
1	-3.139943	-2.916332	2.617594
1	-1.713988	-2.653446	3.657621
6	-1.807706	2.448824	1.281534
1	-2.093335	3.017459	0.393995
1	-2.640618	2.432668	1.993416
1	-0.964763	2.966107	1.761420
8	-0.887574	1.545610	-1.411492
1	-0.152837	1.496823	-2.043163
8	1.369448	-0.392497	-1.171506
6	0.480641	-1.186742	0.813488
1	0.570271	-2.271874	0.621754
8	1.702718	-0.622248	1.188625
6	3.692996	-1.235458	-0.389160

6	4.650190	-1.487538	0.607041
6	3.888447	-1.838948	-1.640224
6	5.745005	-2.320769	0.375134
1	4.531518	-1.022753	1.584649
6	4.985815	-2.669373	-1.886230
1	3.159342	-1.663466	-2.428340
6	5.918690	-2.914890	-0.877722
1	6.468219	-2.504251	1.168189
1	5.111822	-3.128551	-2.865769
1	6.774460	-3.560189	-1.065545
6	2.946900	1.297197	0.009620
6	2.972530	2.011262	1.220316
6	3.354736	1.981599	-1.149420
6	3.354588	3.354390	1.269551
1	2.667333	1.504280	2.133294
6	3.730893	3.323748	-1.113278
1	3.370262	1.446621	-2.097862
6	3.732331	4.017956	0.100872
1	3.361360	3.884419	2.220923
1	4.031102	3.831678	-2.028393
1	4.033140	5.062972	0.134855
5	2.434936	-0.247976	-0.091096
6	-4.158585	1.255879	-1.133092
6	-5.851917	-0.576090	-1.385545
6	-5.386695	0.778501	-1.947584
1	-4.410035	2.079578	-0.460029
1	-3.320164	1.569577	-1.756386
1	-6.190676	1.518587	-1.882185
1	-5.126111	0.673371	-3.006149
6	-4.662165	-0.175293	0.782744
1	-4.286269	-1.046912	1.318991
1	-4.679823	0.668881	1.476951
6	-6.045301	-0.438472	0.134903
1	-6.484566	-1.350714	0.551076
1	-6.735607	0.384018	0.351387
1	-6.789645	-0.881572	-1.858974
6	-4.754469	-1.621331	-1.649418
1	-5.009242	-2.564637	-1.154049
1	-4.671574	-1.828981	-2.720806
6	-3.409470	-1.071277	-1.113233
1	-2.875598	-1.787366	-0.485977

1	-2.741431	-0.752615	-1.915500
7	-3.670462	0.135556	-0.279471
1	-2.566967	0.505405	0.285106

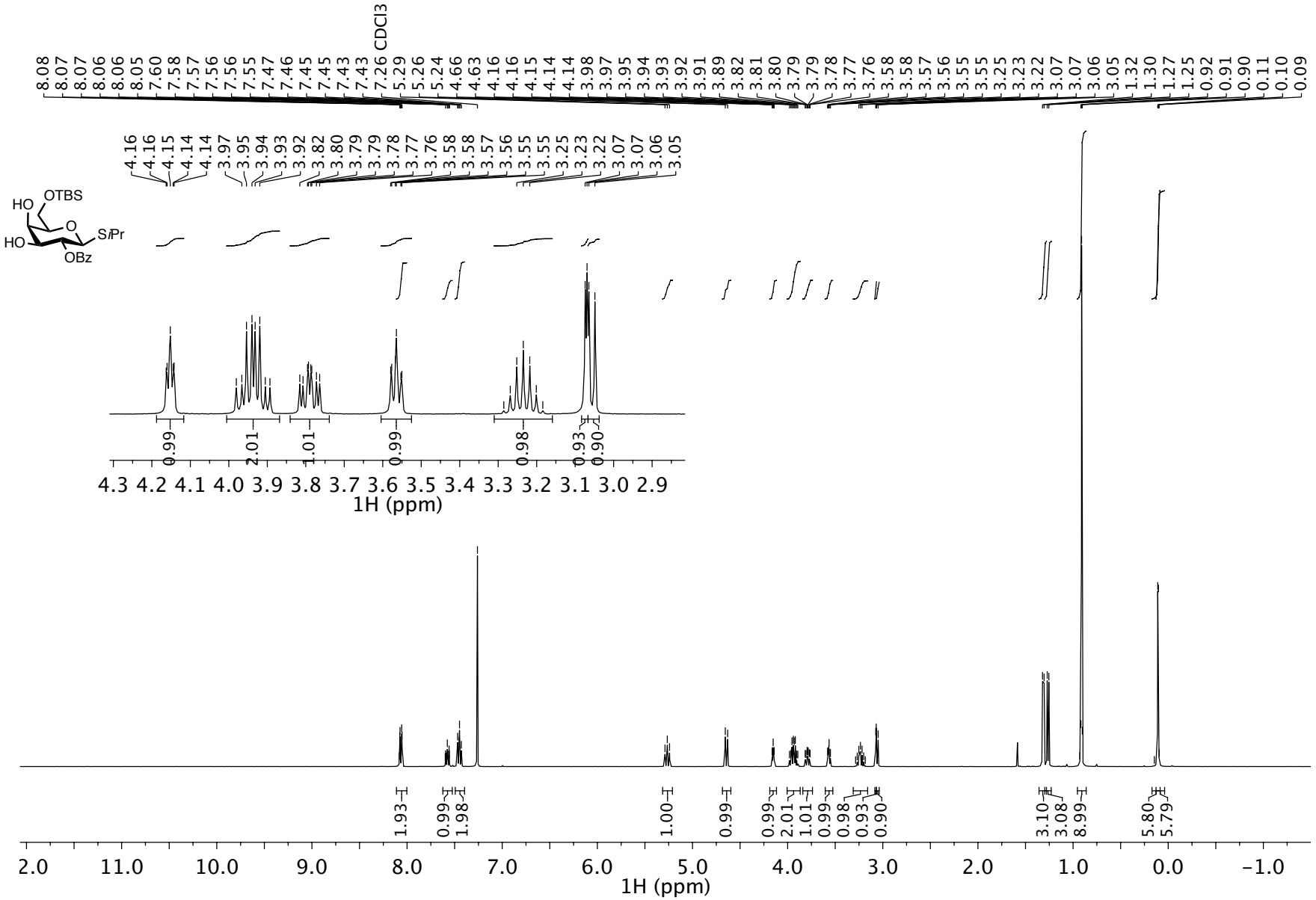
References

[1] Lee, D.; Taylor, M. S. *J. Am. Chem. Soc*. **2011**, *133***,** 3724–3727.
[2] Kumar, V.; Gauniyal, H. M.; Shaw, A. K. *Tetrahedron: Asymmetry.* **2007**, *18*, 2069–2073.
[3] Mancini, R. S.; Lee, J. B.; Taylor, M. S. *Org. Biomol. Chem.* **2017**, *15*, 132–143.
[4] Kim, M. J.; Jeong, L. S.; Kim, J. H.; Shin, J. H.; Chung, S. Y.; Lee, S. K.; Chun, M. W. *Nucleosides, Nucleotides Nucleic Acids.* **2004**, *23*, 715–724.
[5] Garrett, G. E.; Tanveer, K.; Taylor, M. S. *J. Org. Chem.* **2017**, *82*, 1085–1095.
[6] Dimitrijević, E.; Taylor, M. S. *Chem. Sci.* **2013**, *4*, 3298–3303.
[7] Jeffrey, J. L.; Terrett, J. A.; MacMillan, D. W. *Science* **2015**, *349*, 1532–1536.
[8] Wang, I. C.; Witte, M. D.; Minnaard, A. J. *Chem. Commun.* **2017**, *53*, 4926–4929.
[9] Liang, H.; Grindley, T. B. *J. Carbohydr. Chem.* **2004**, *23*, 71–82.
[10] Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A. ; Cheeseman, J. R. Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F. ; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox D. J. Gaussian, Inc., Wallingford CT, 2016.
[11]. Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456–1465.
[12]. Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

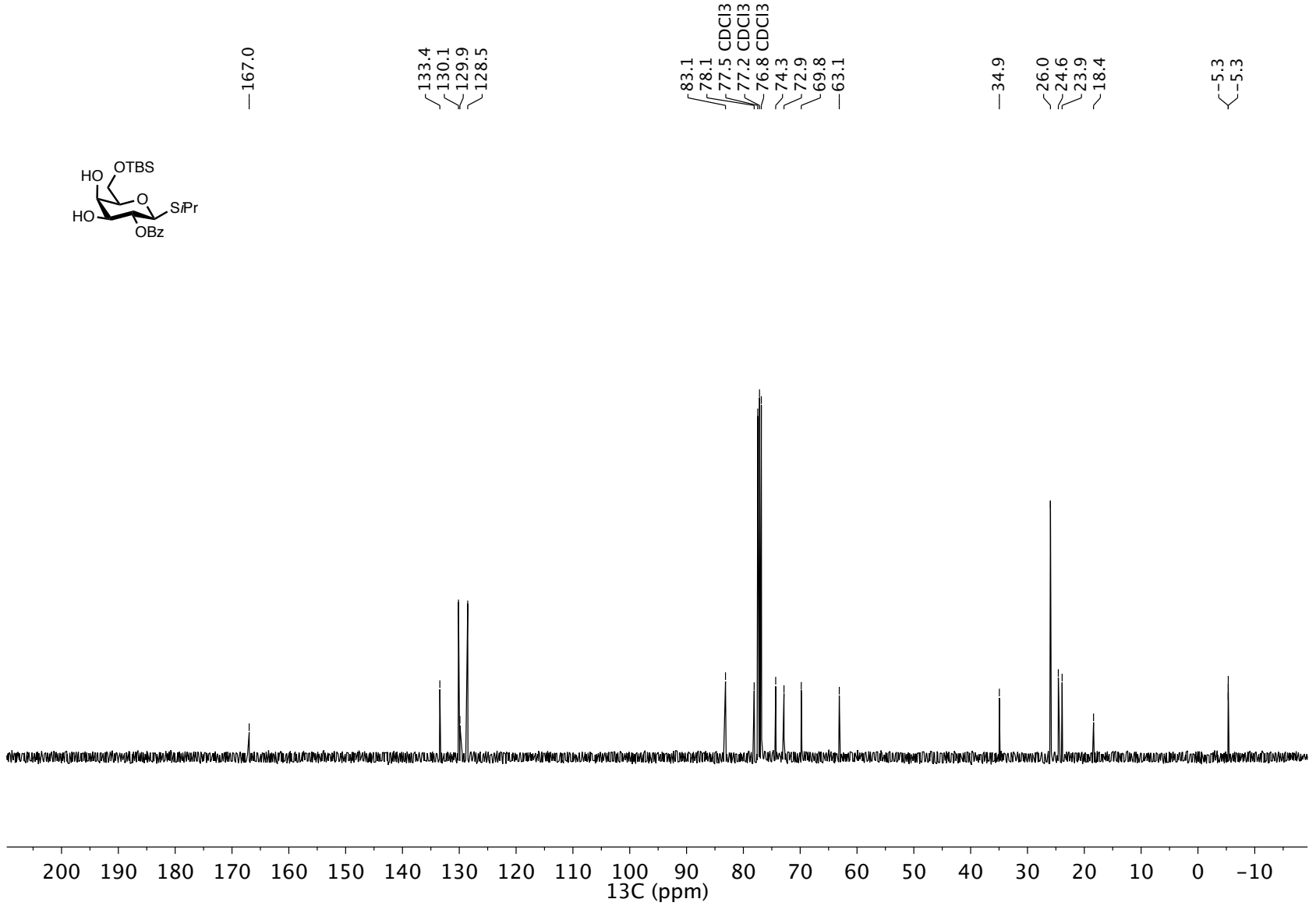
^{1}H, ^{13}C and 2D NMR Spectra

This page intentionally left blank

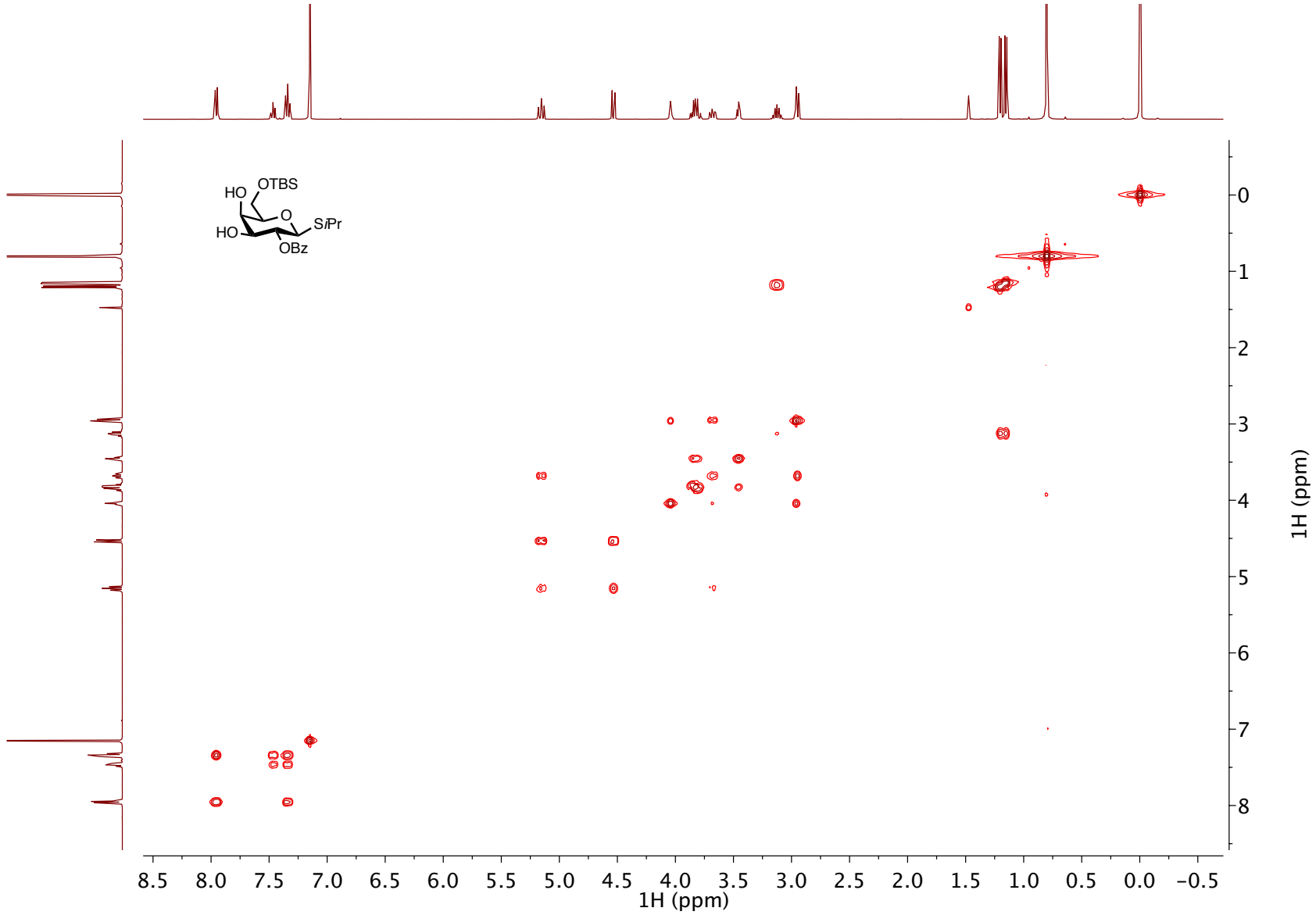
1f – ^{1}H NMR (400 MHz, $CDCl_3$)



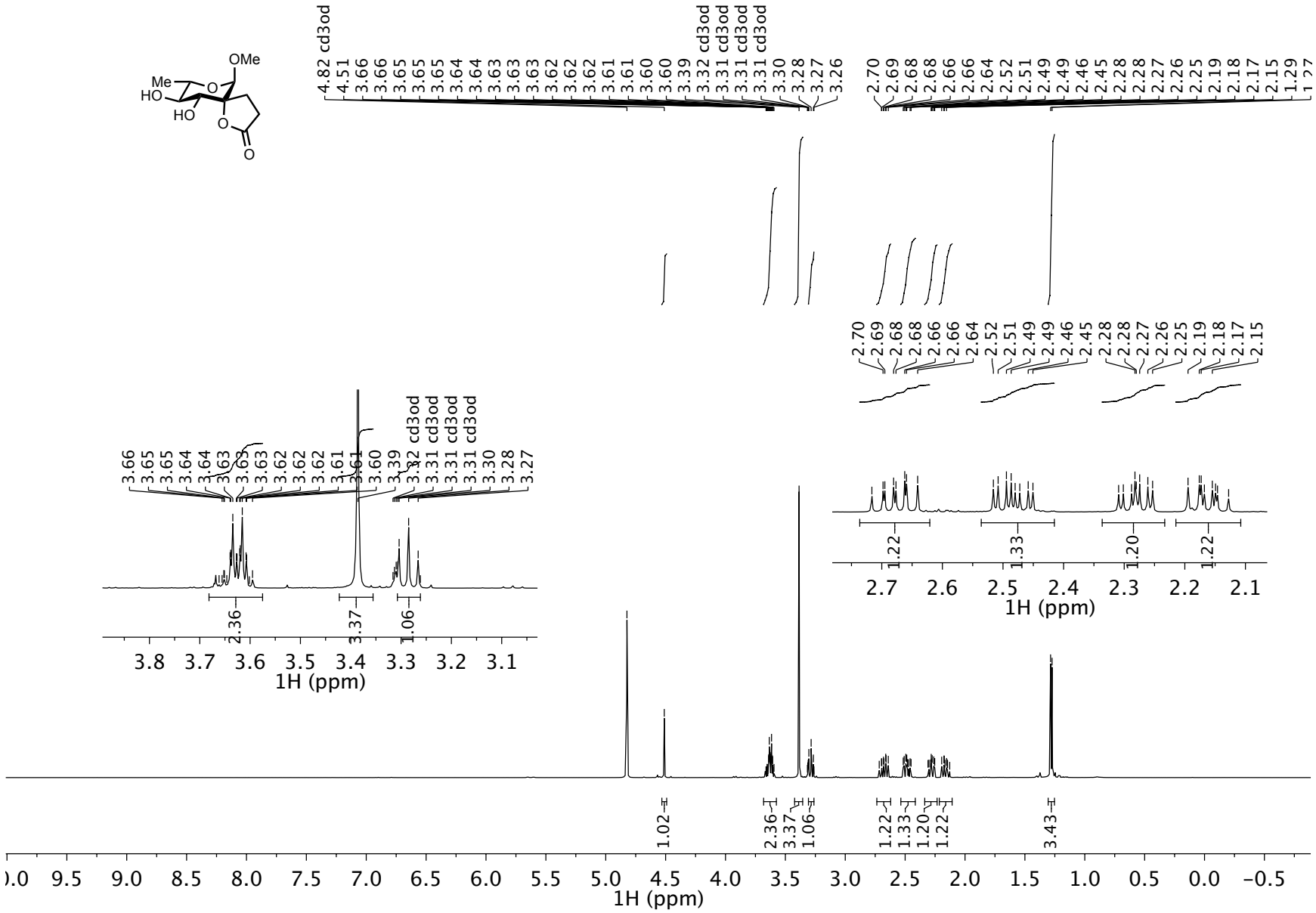
1f – ^{13}C NMR (101 MHz, $CDCl_3$)



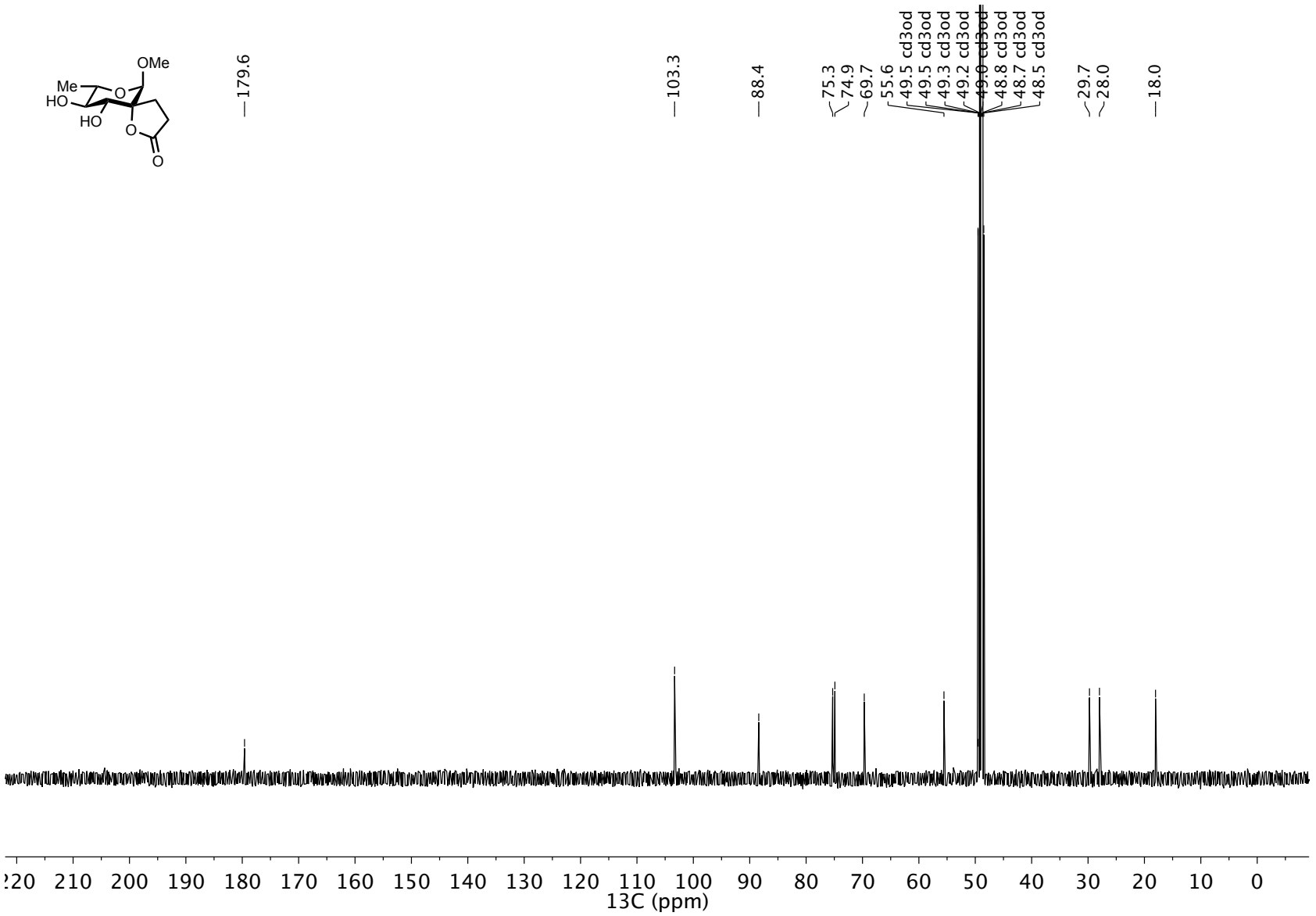
1f – COSY (400 MHz, $CDCl_3$)



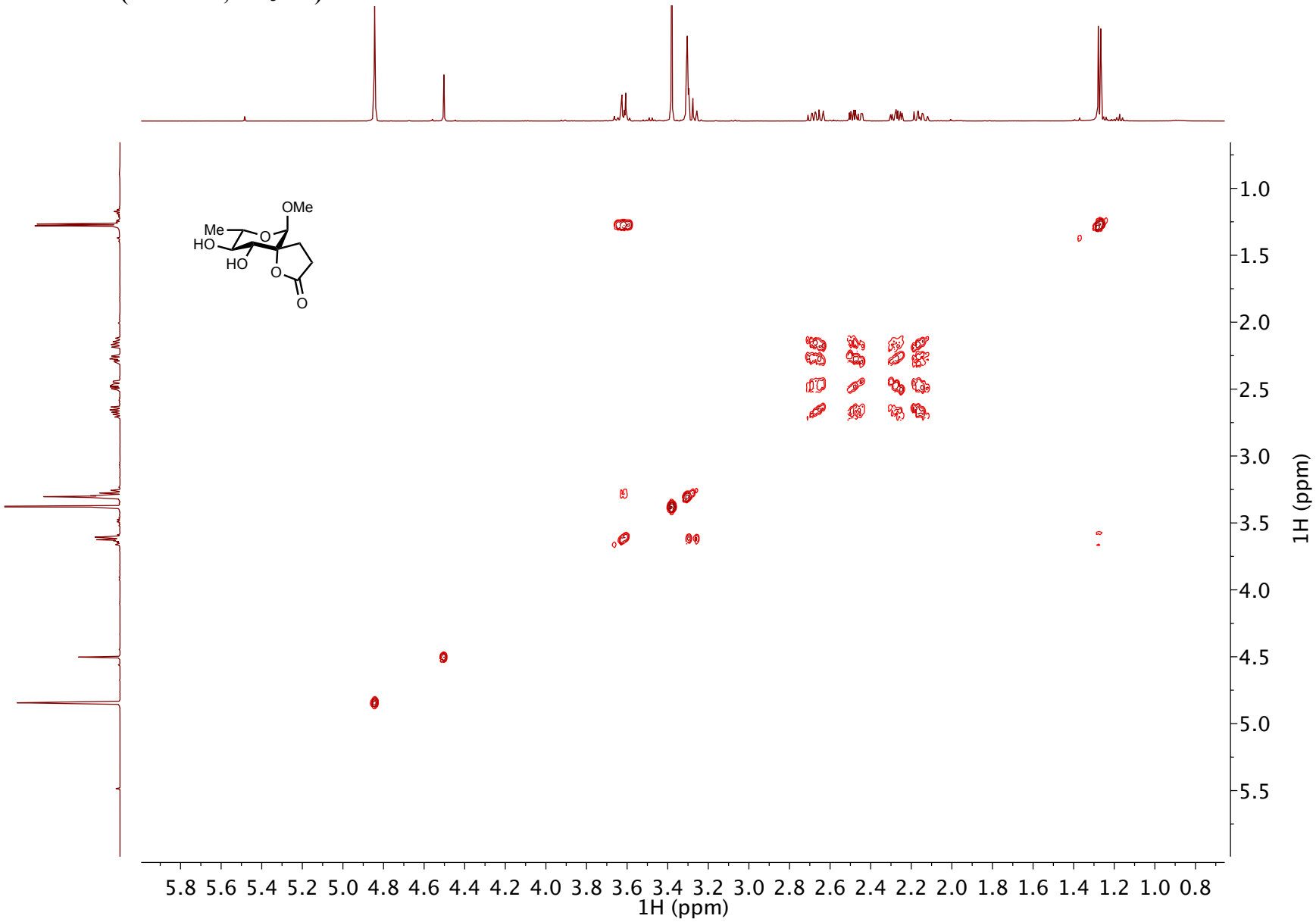
2a– ^{1}H NMR (500 MHz, CD_3OD)



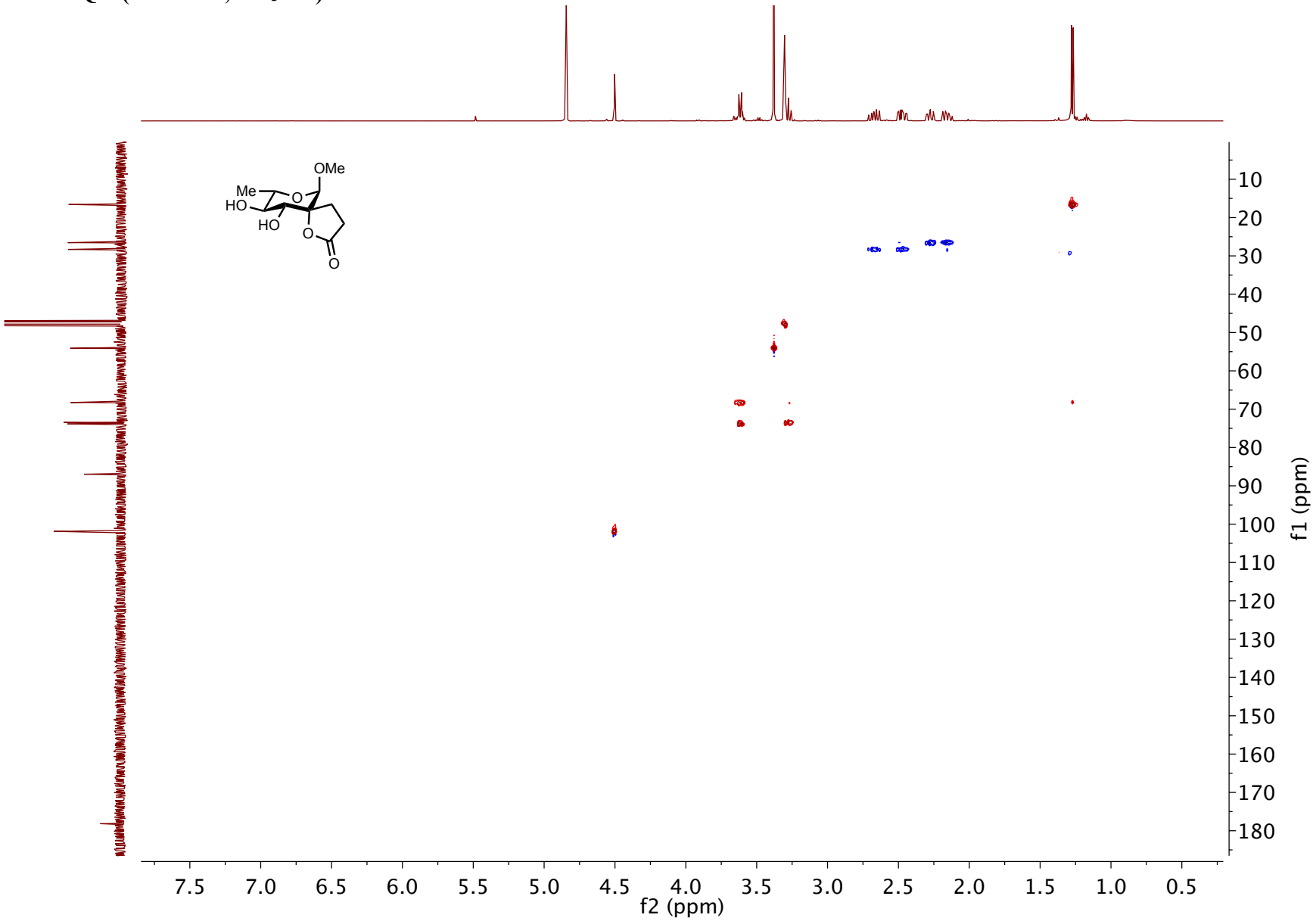
2a– ^{13}C NMR (126 MHz, CD_3OD)



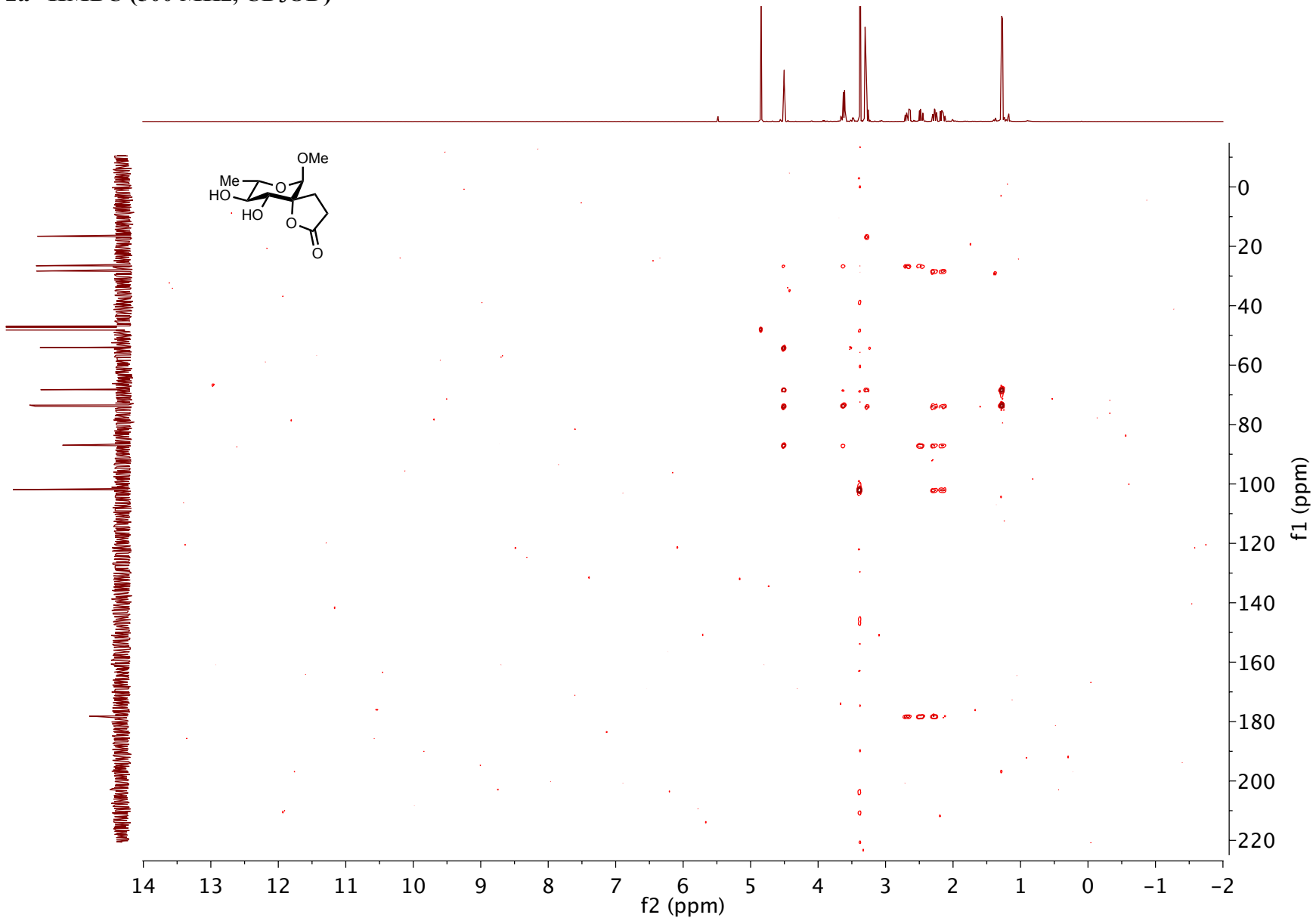
2a– COSY (500 MHz, CD_3OD)



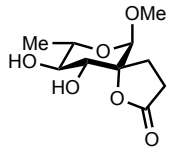
2a– HSQC (500 MHz, CD_3OD)

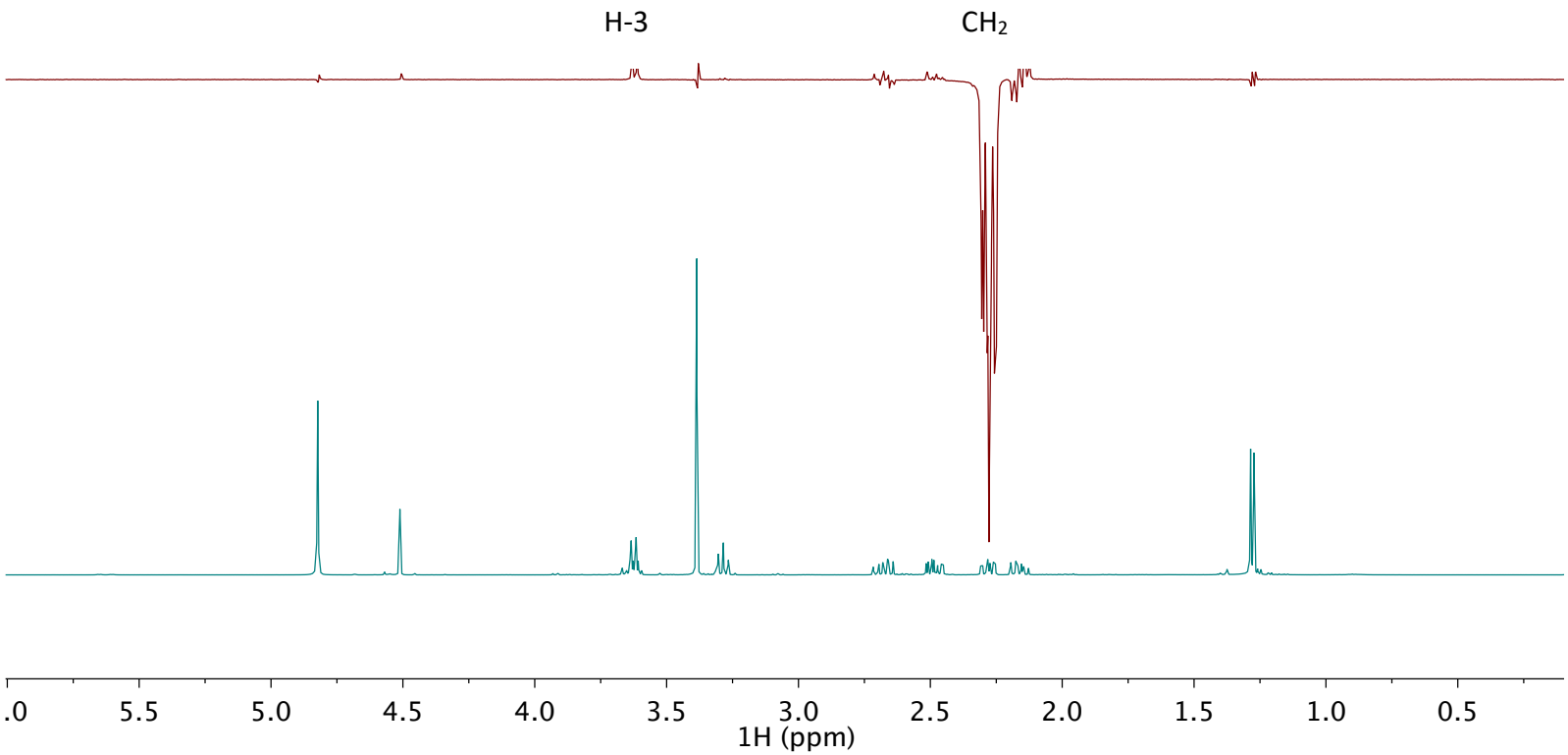


2a– HMBC (500 MHz, CD_3OD)

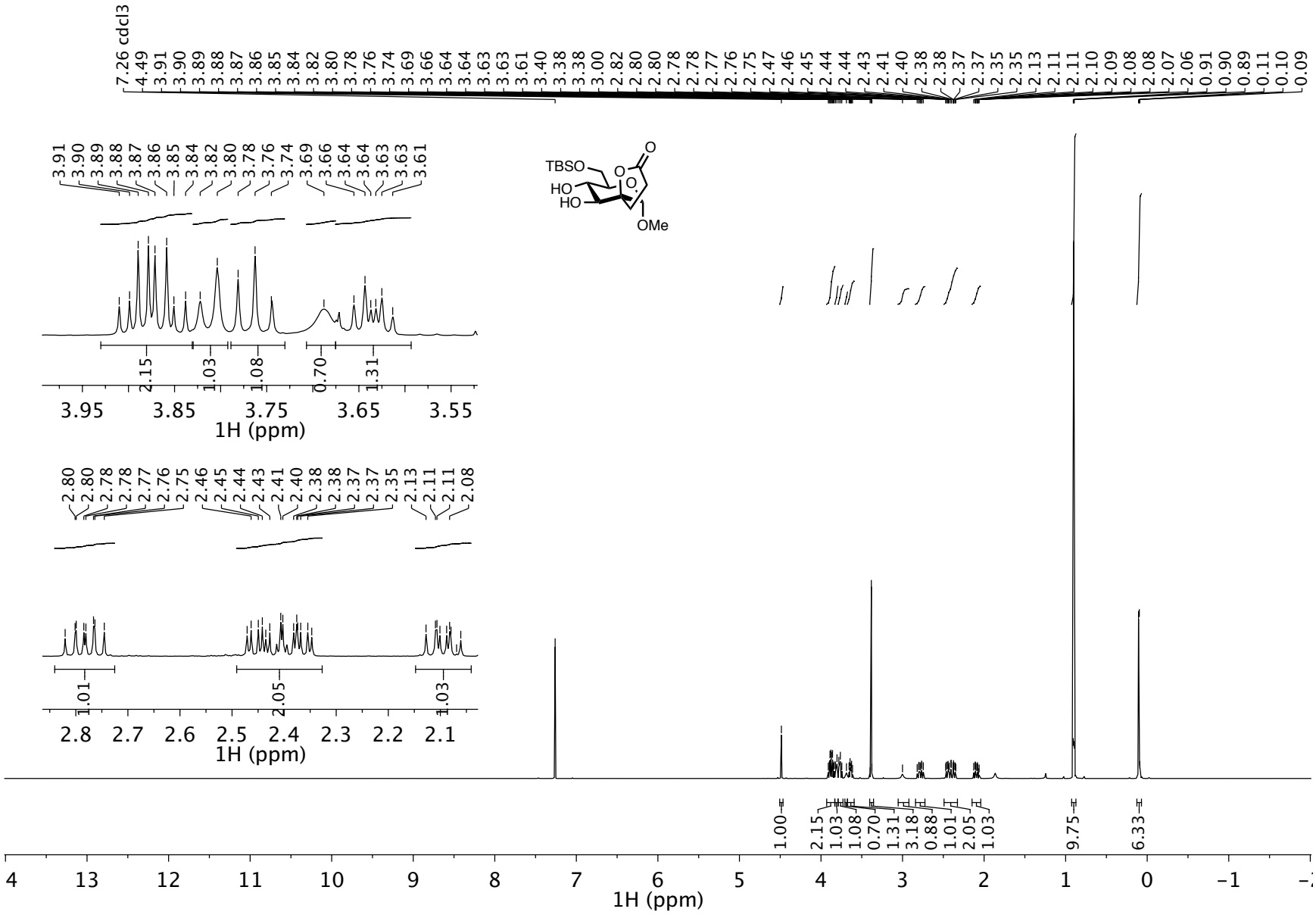


2a– 1D NOESY (500 MHz, CD_3OD)

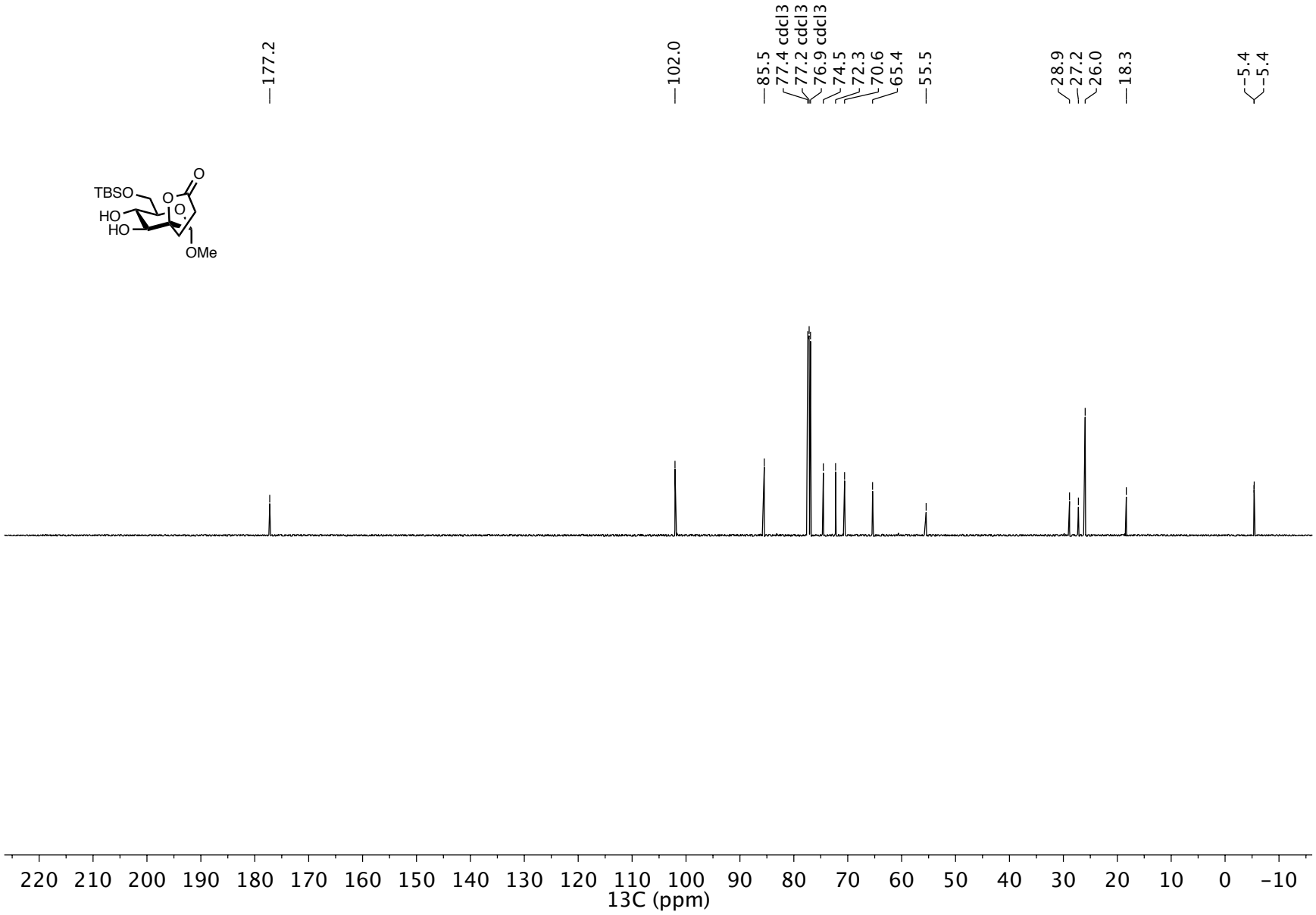




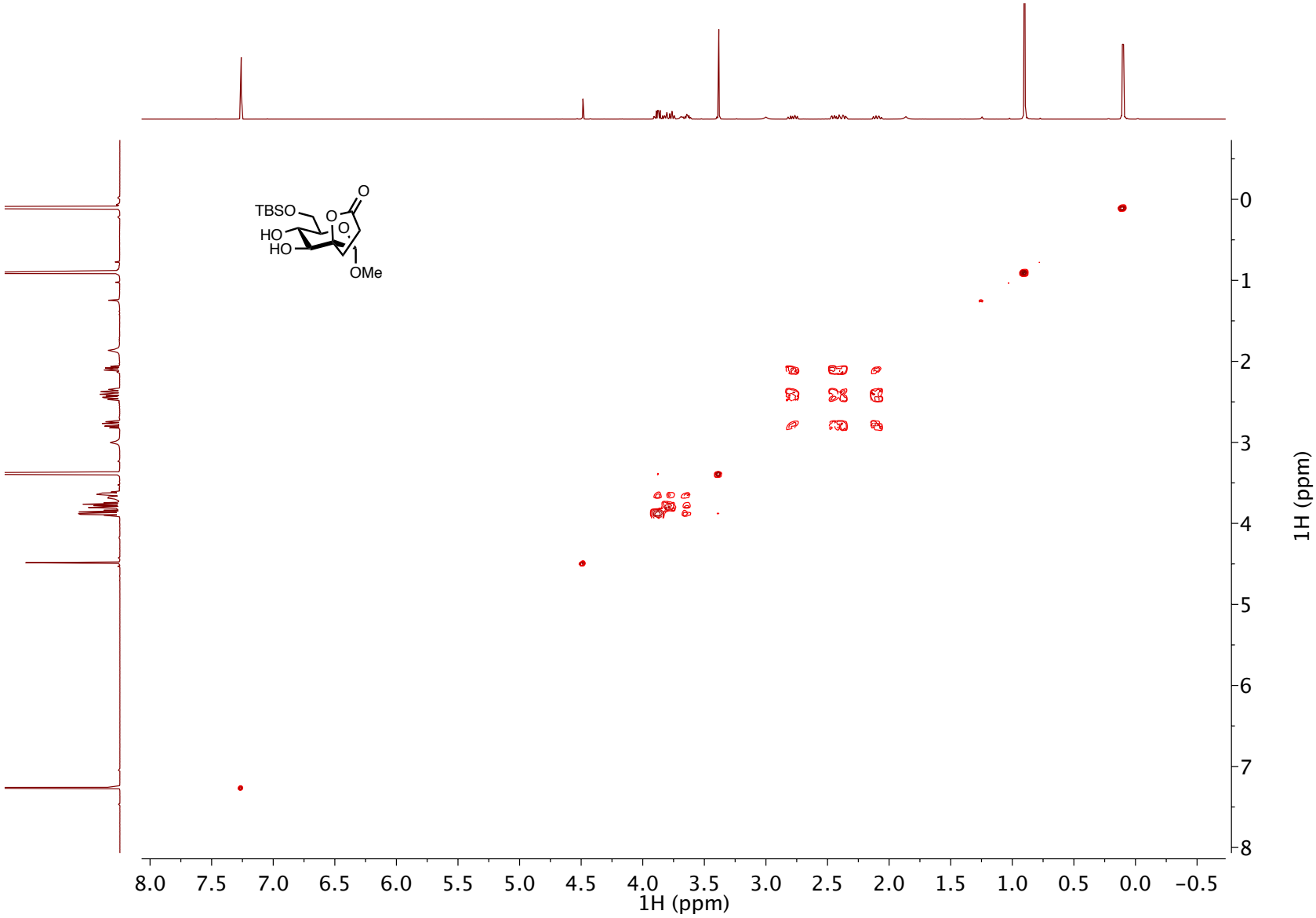
2b –^{1}H NMR (500 MHz, $CDCl_3$)



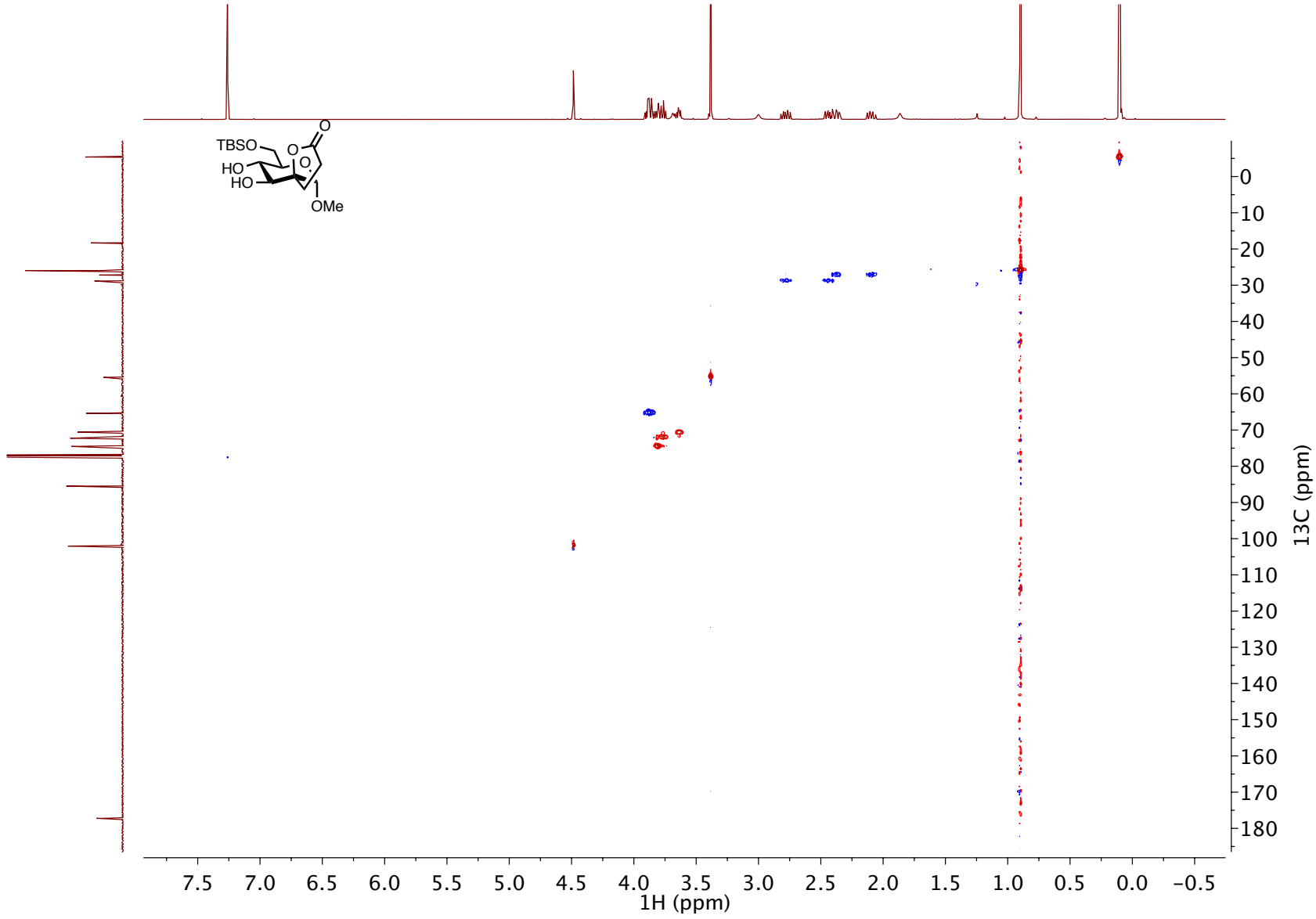
2b –^{13}C NMR (151 MHz, $CDCl_3$)



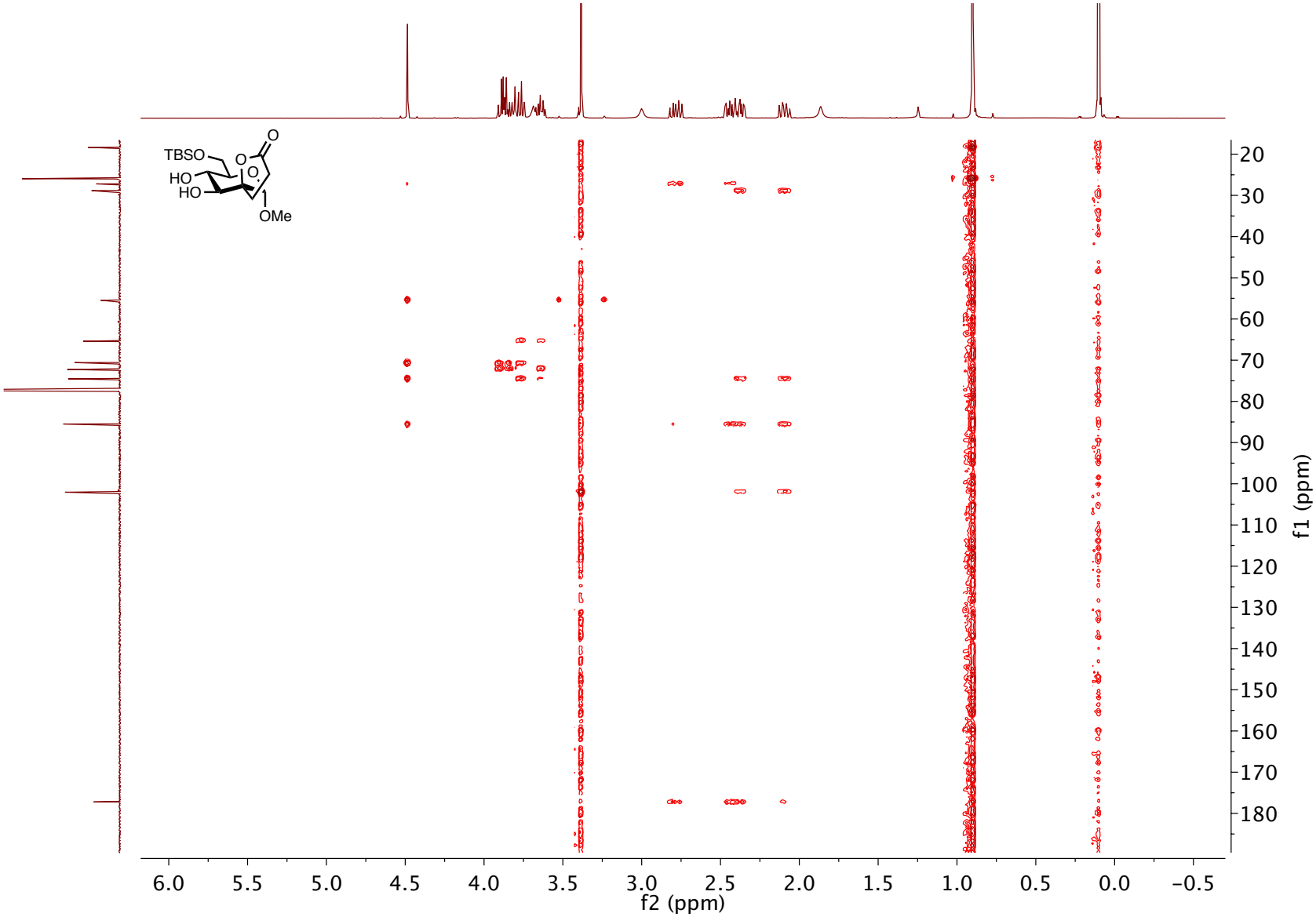
2b –COSY (500 MHz, $CDCl_3$)



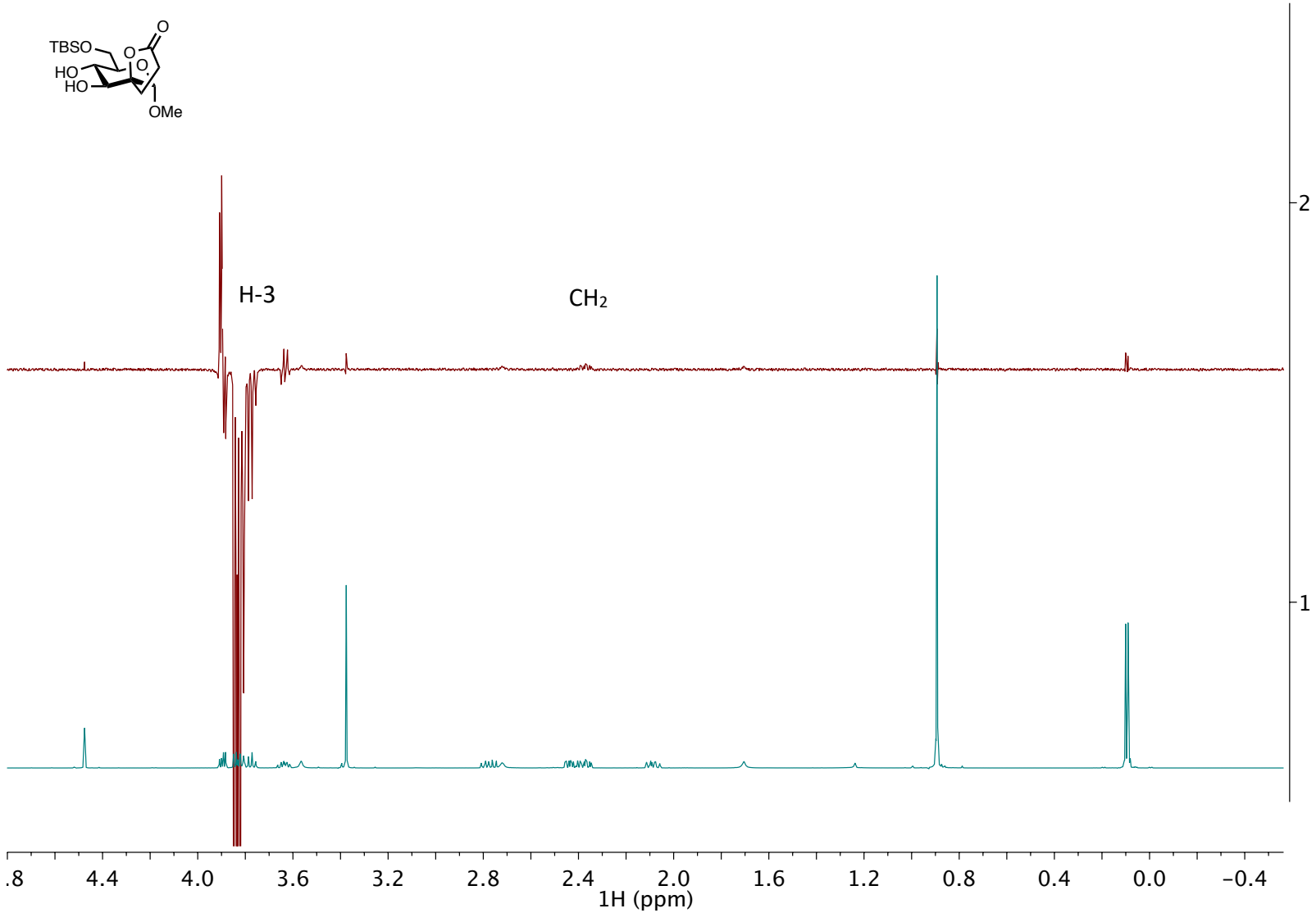
2b –HSQC (500 MHz, $CDCl_3$)



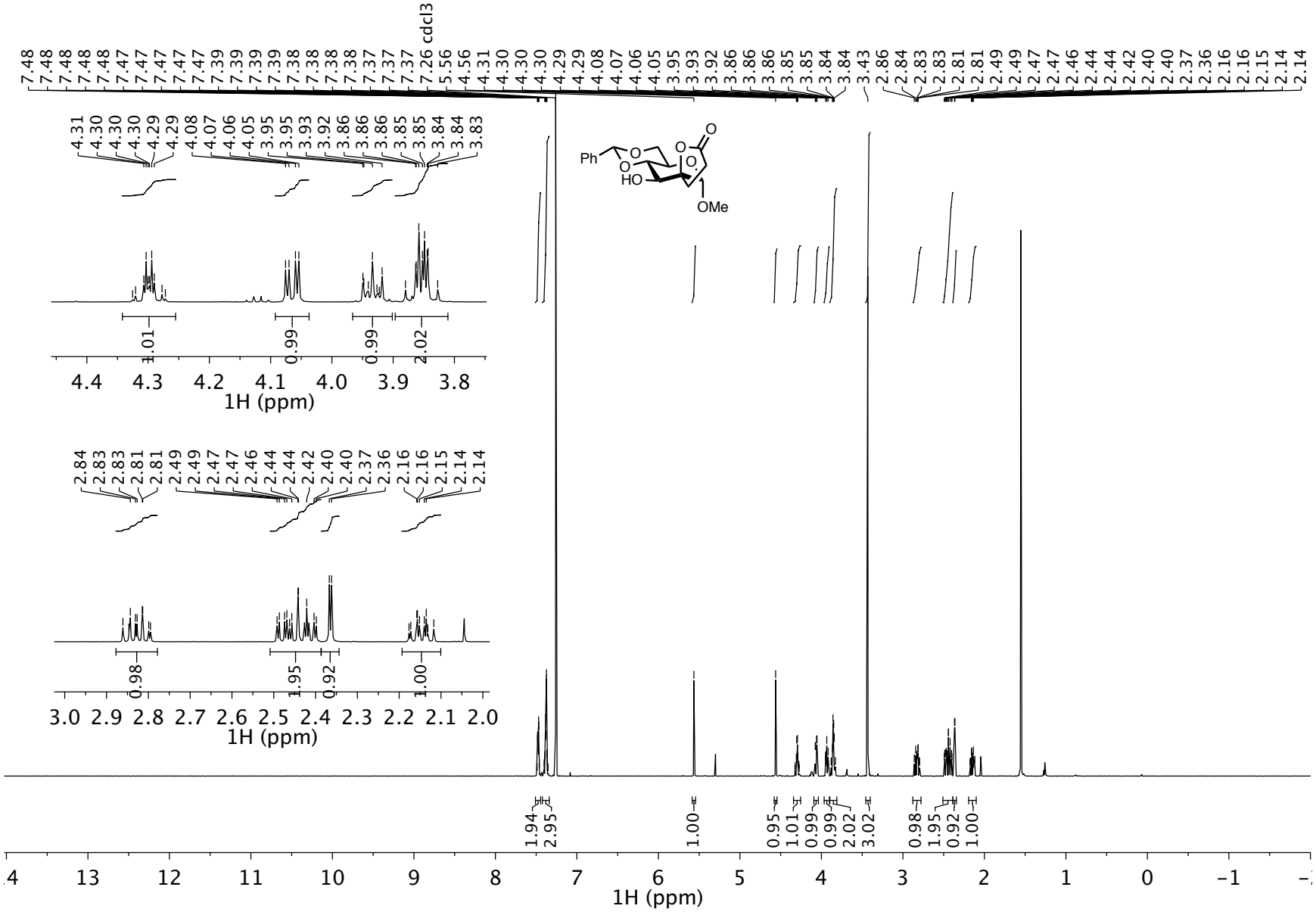
2b –HMBC (500 MHz, $CDCl_3$)



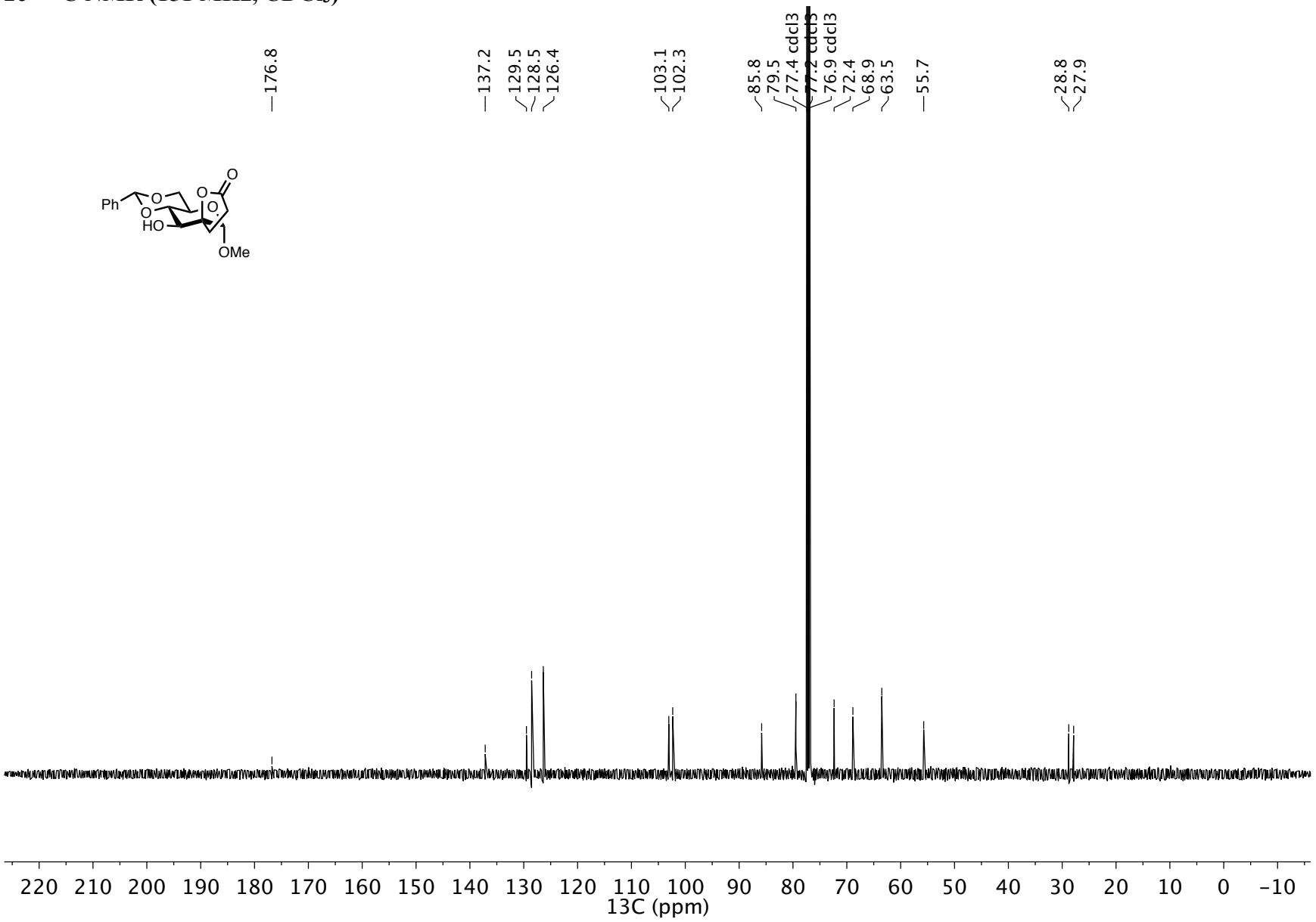
2b –1D NOESY (600 MHz, $CDCl_3$)



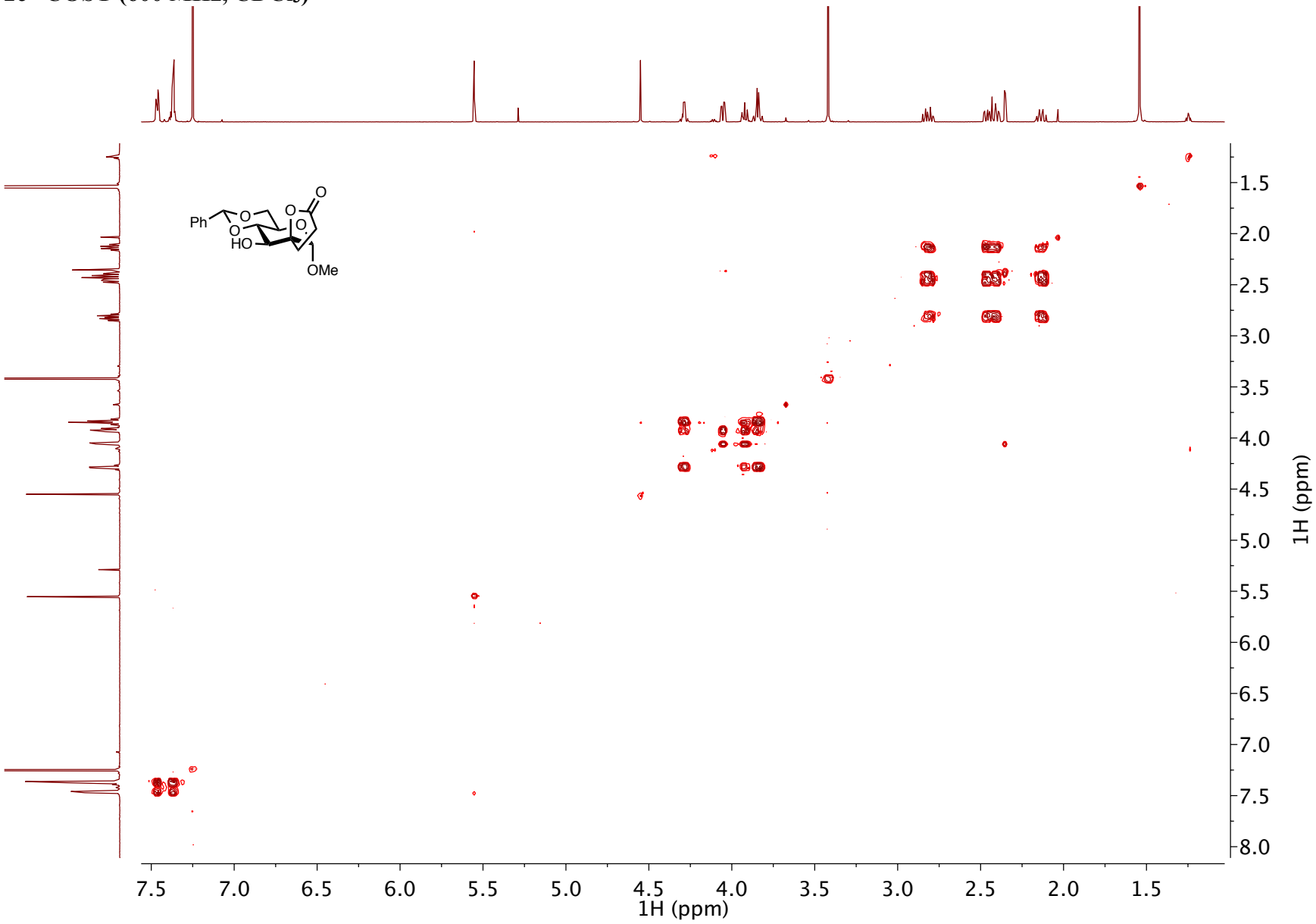
2c –^{1}H NMR (600 MHz, $CDCl_3$)



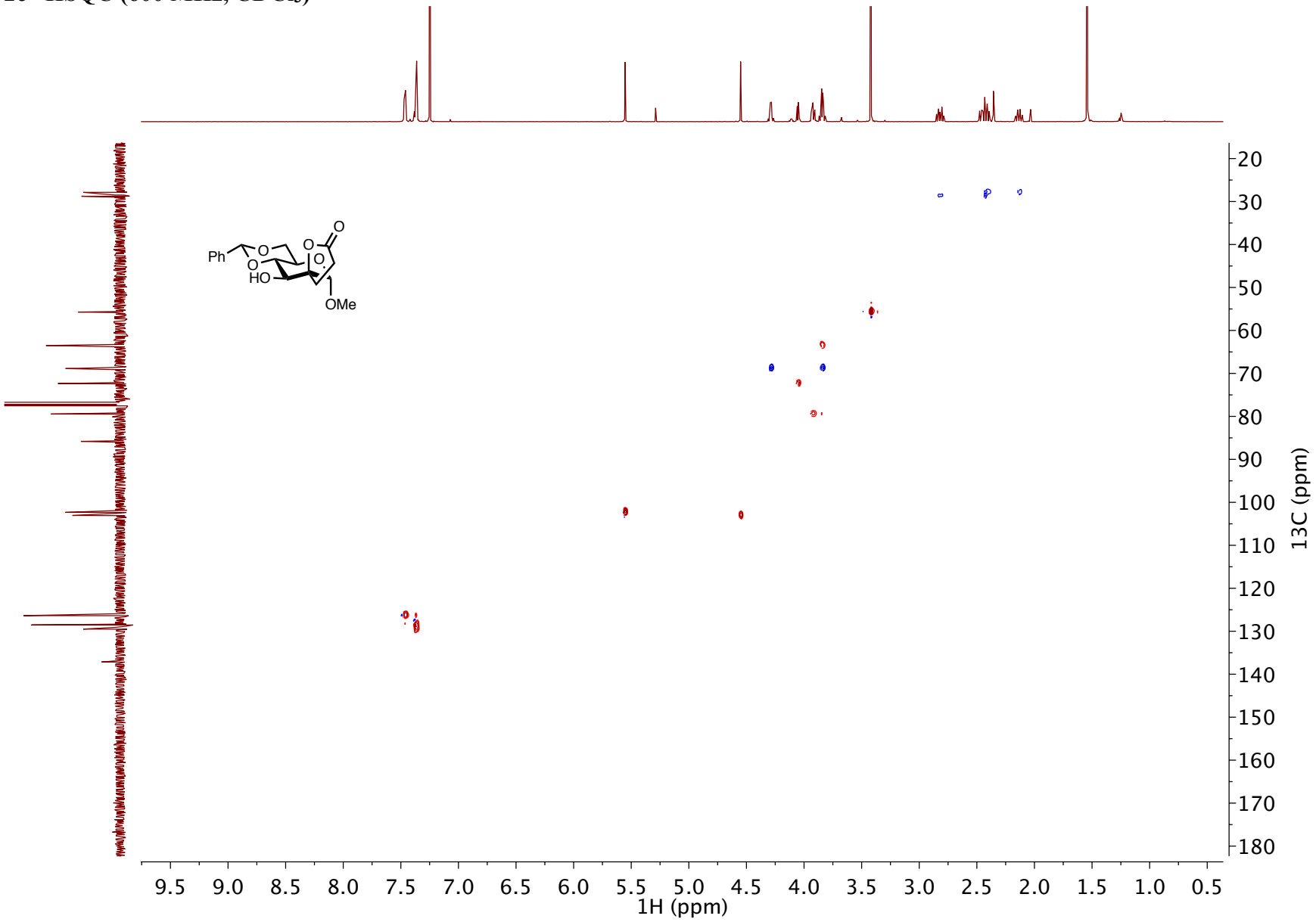
2c –^{13}C NMR (151 MHz, $CDCl_3$)



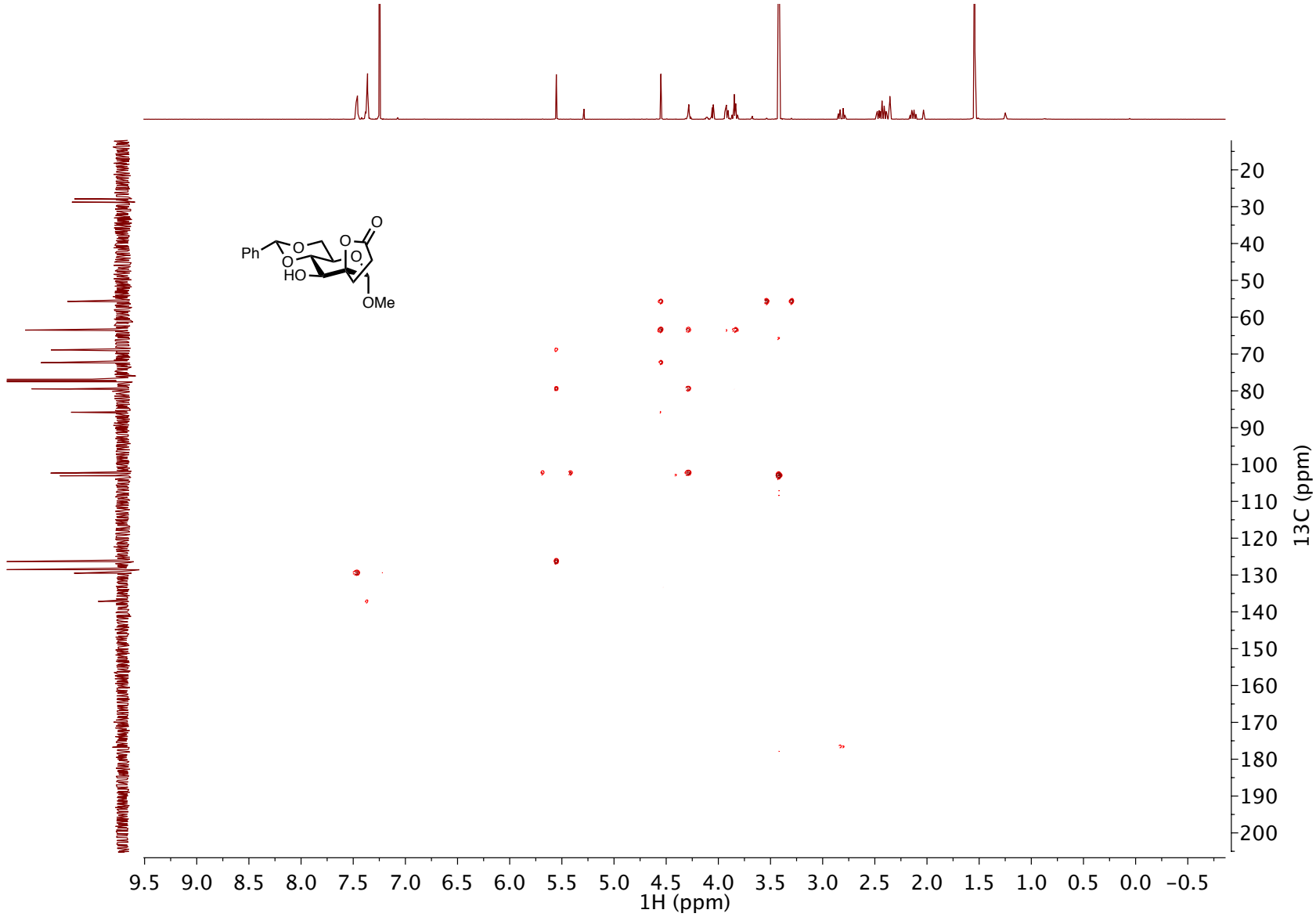
2c –COSY (600 MHz, $CDCl_3$)



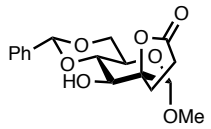
2c –HSQC (600 MHz, $CDCl_3$)

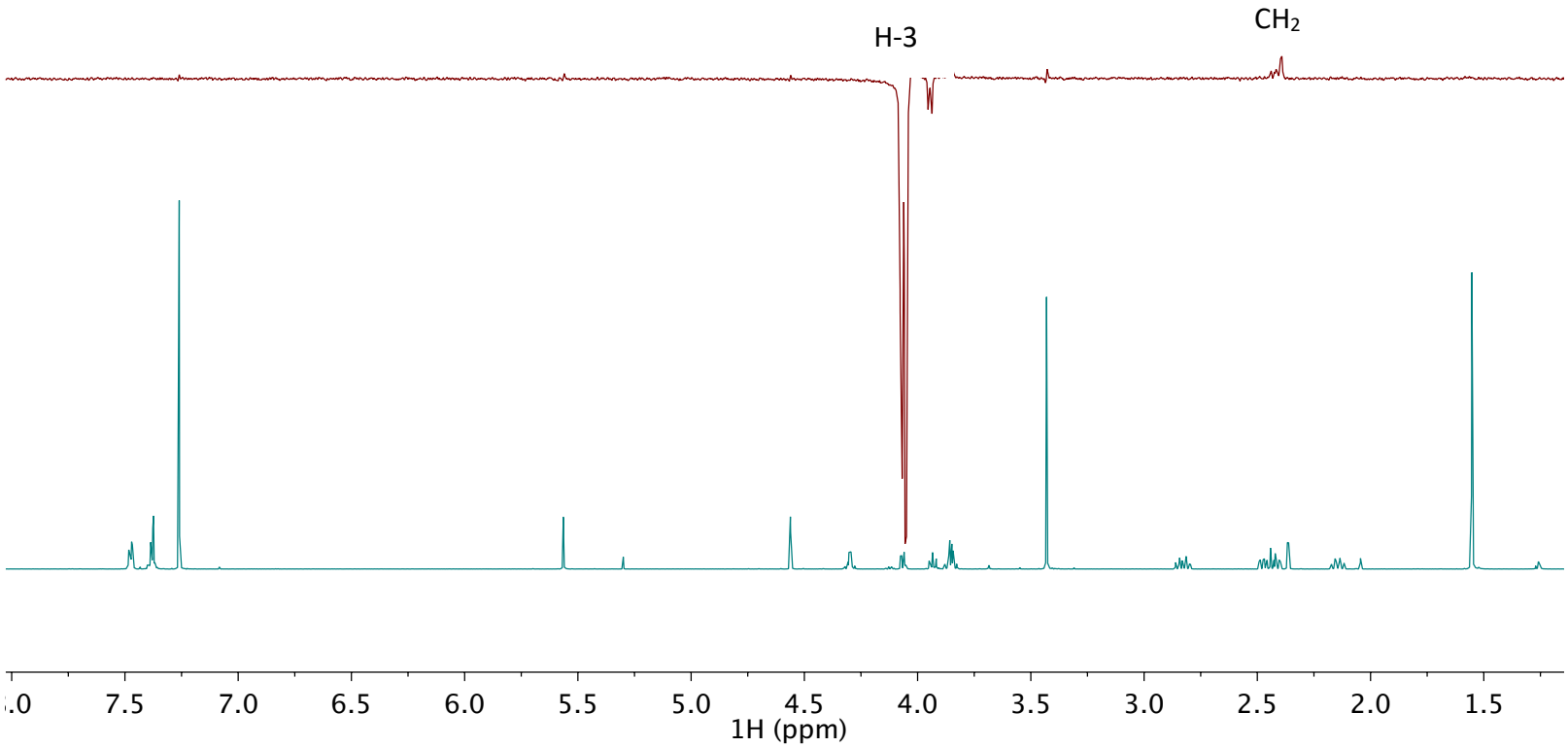


2c –HMBC (600 MHz, $CDCl_3$)

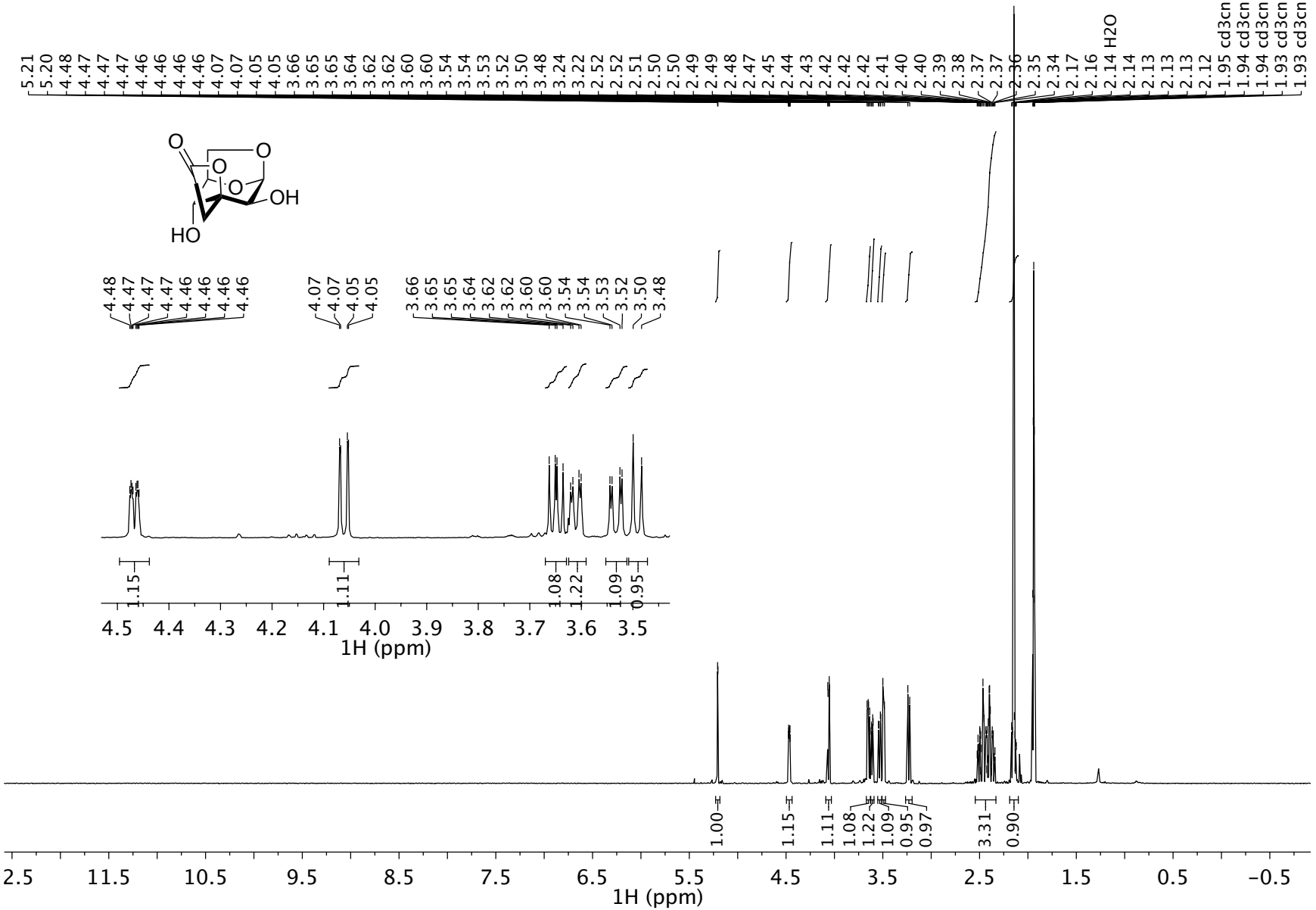


2c –1D NOESY (500 MHz, $CDCl_3$)

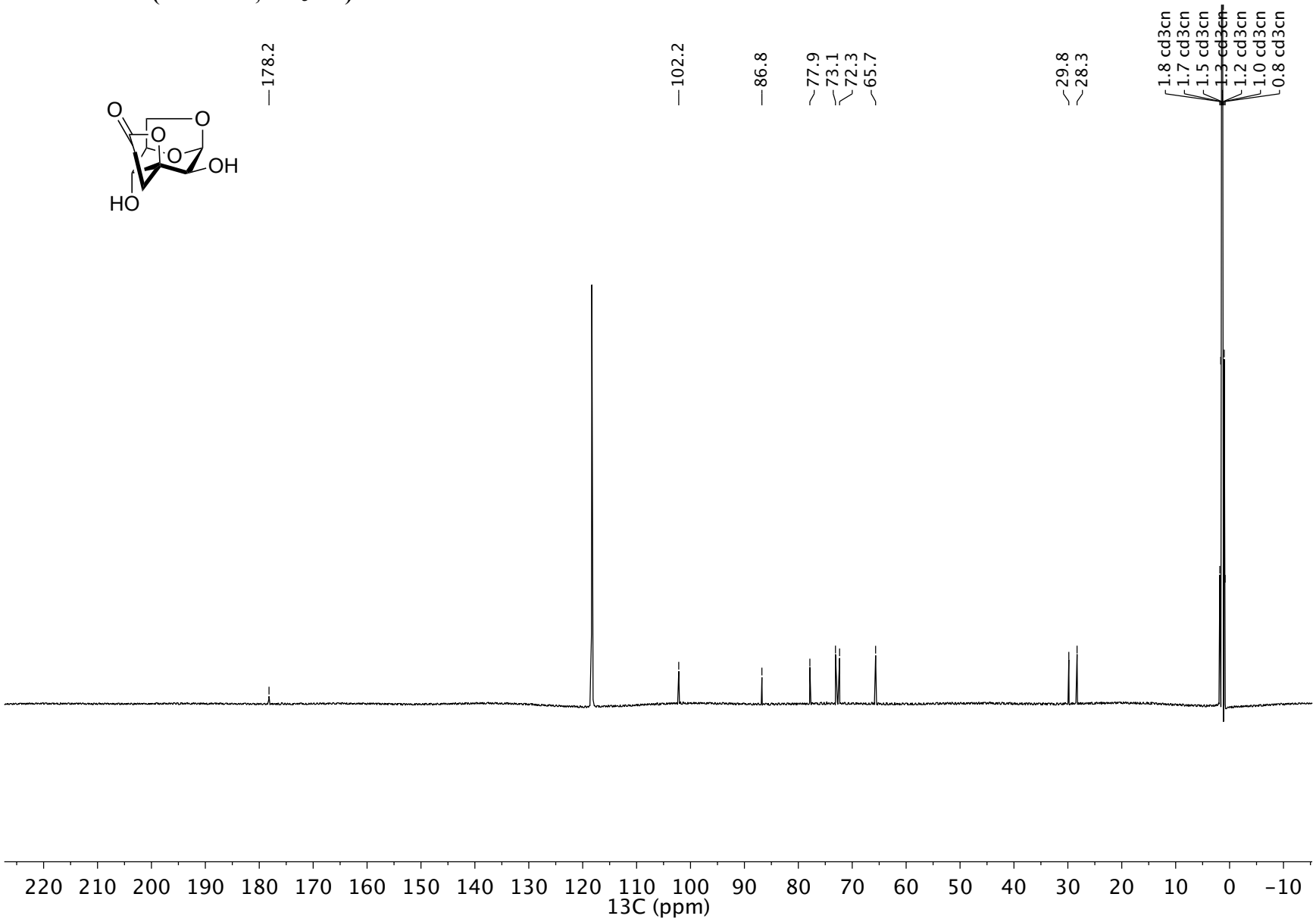




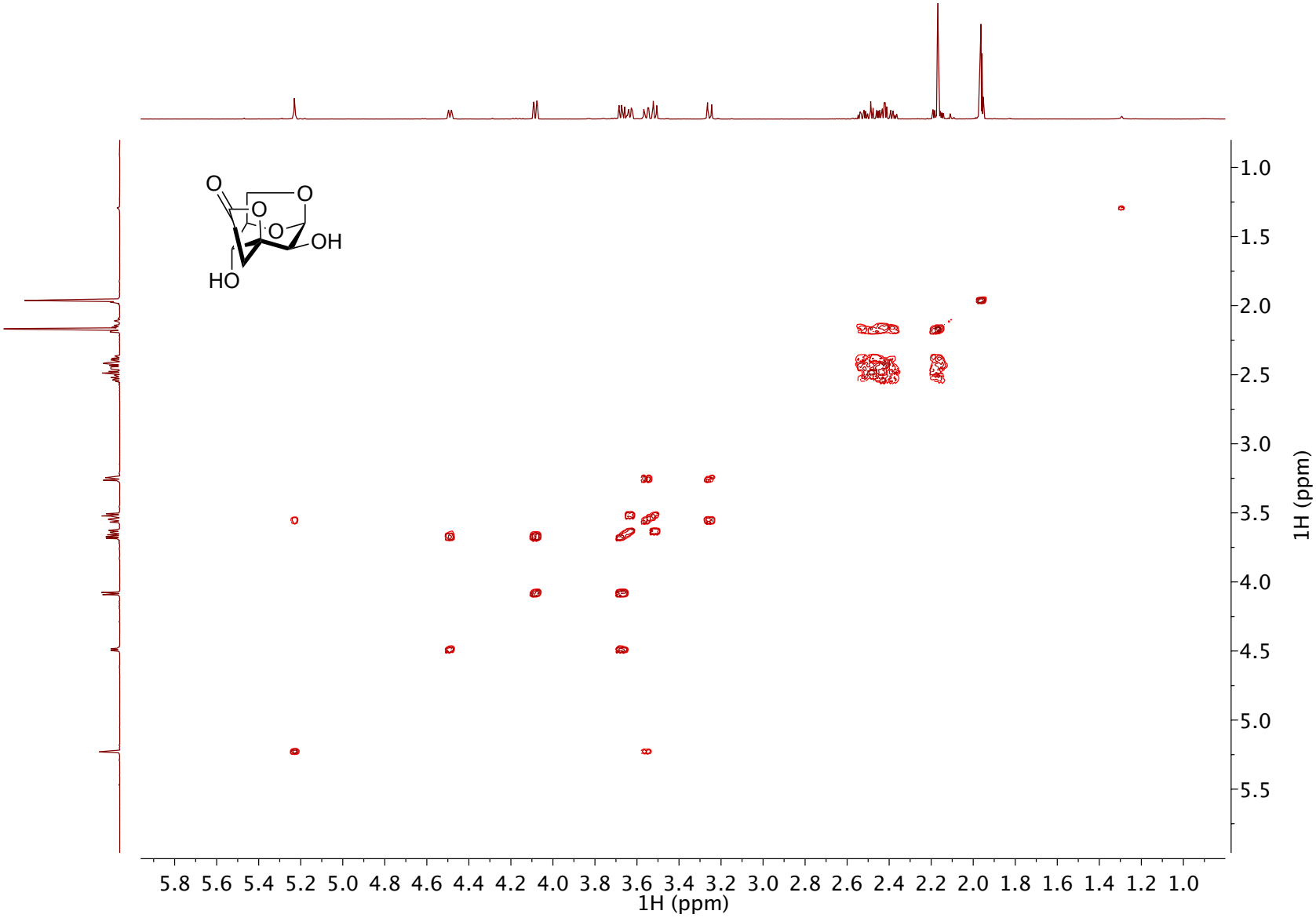
2d –^{1}H NMR (500 MHz, CD_3CN)



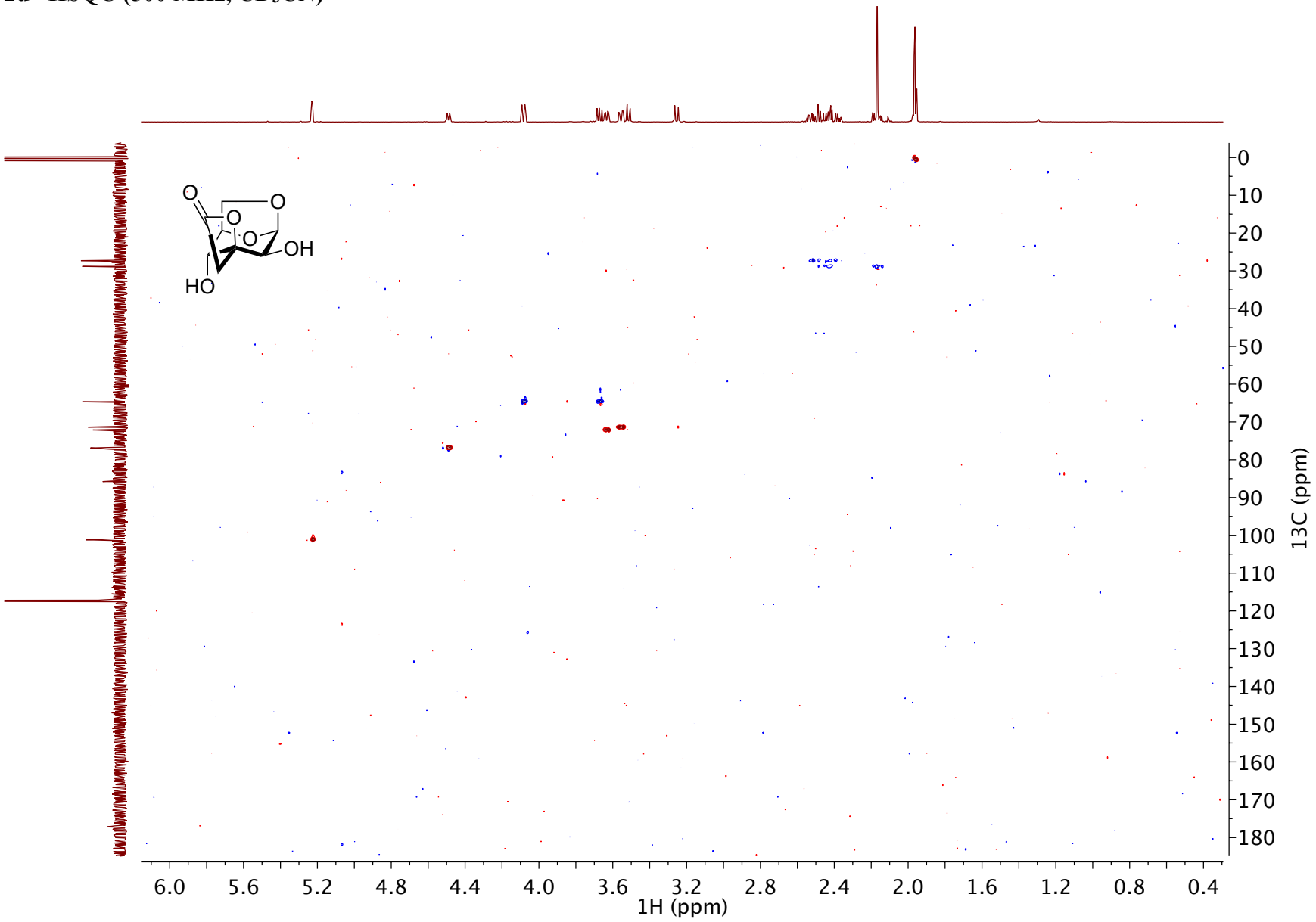
2d –^{13}C NMR (126 MHz, CD_3CN)



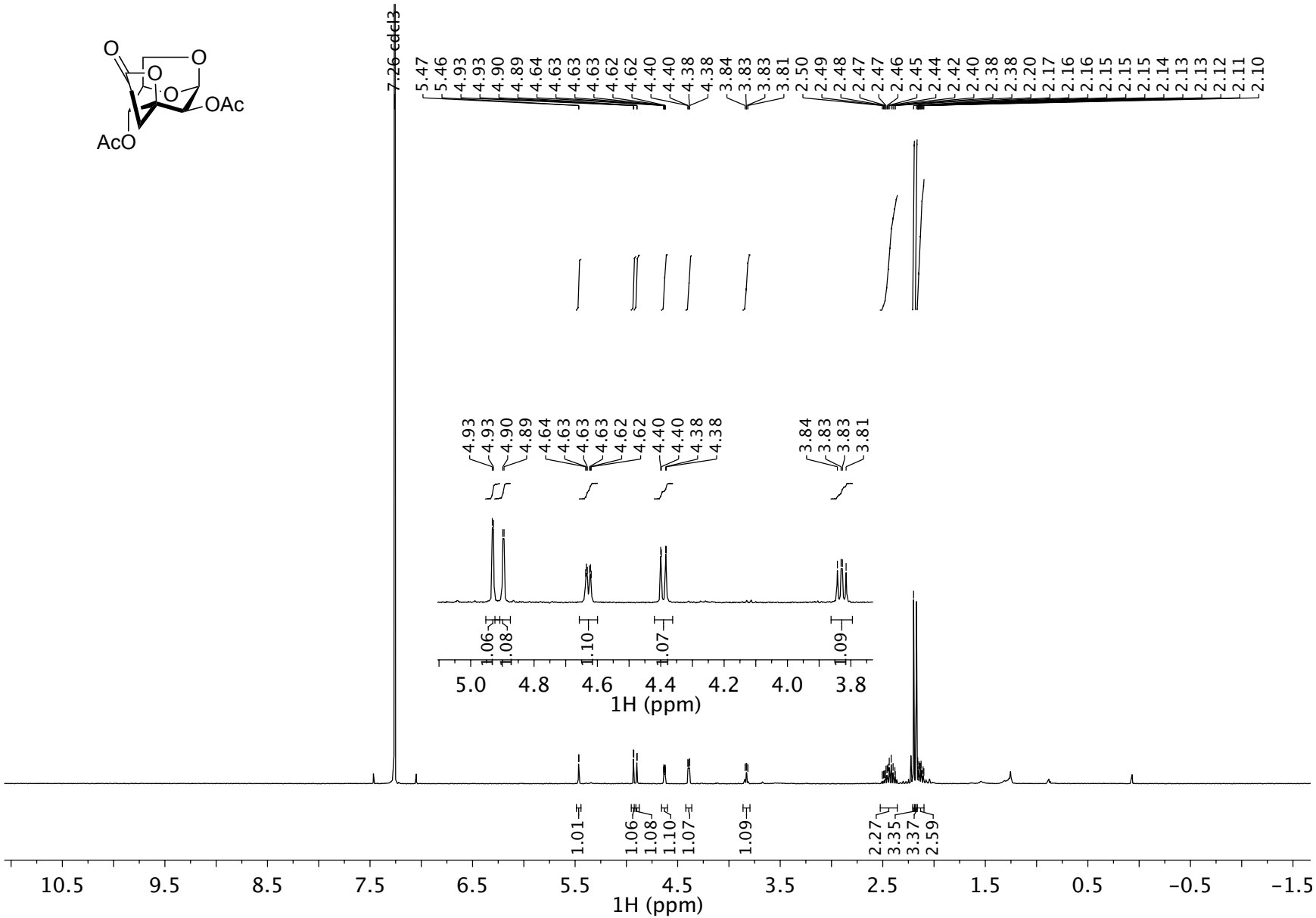
2d –COSY (500 MHz, CD_3CN)



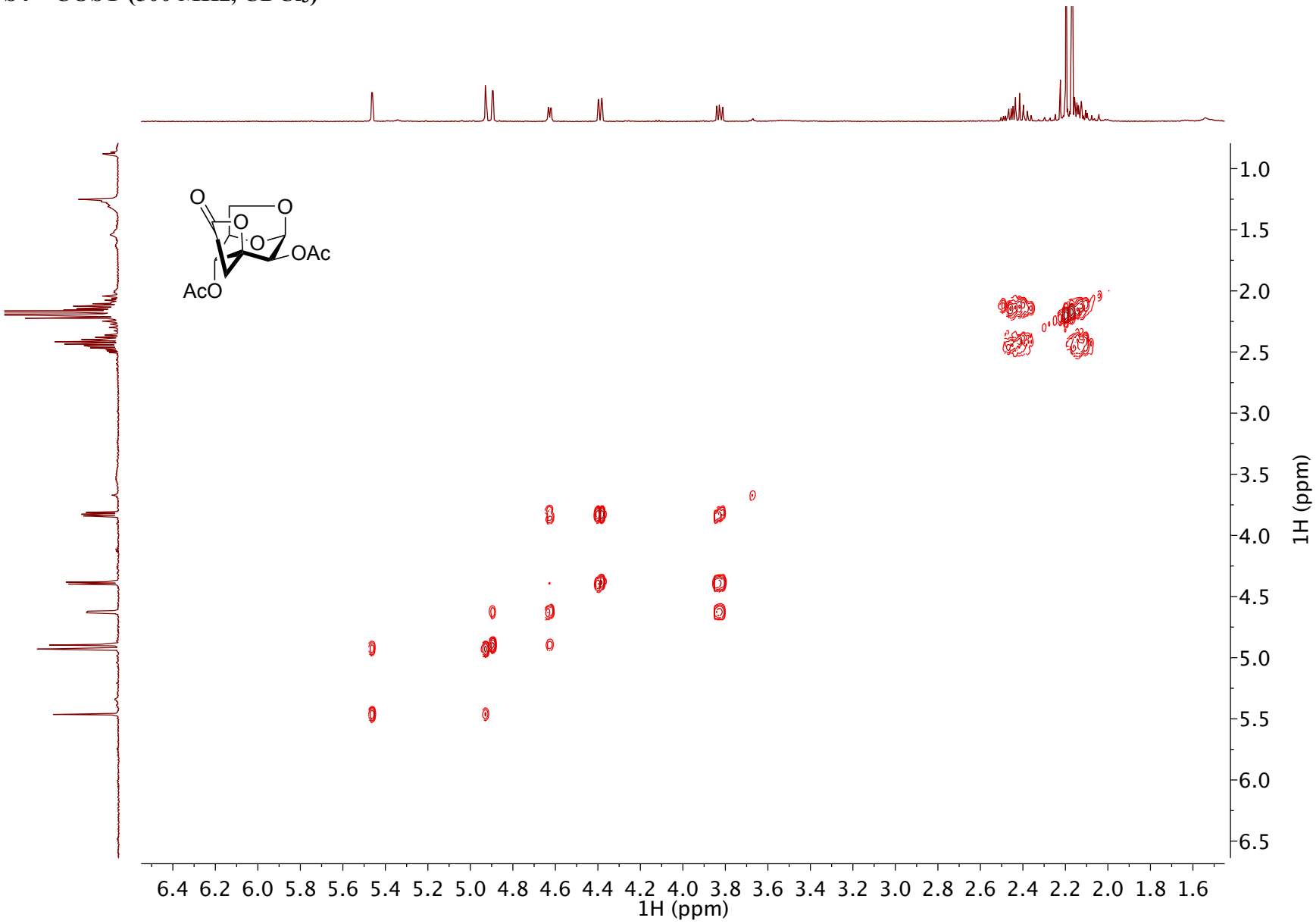
2d –HSQC (500 MHz, CD_3CN)



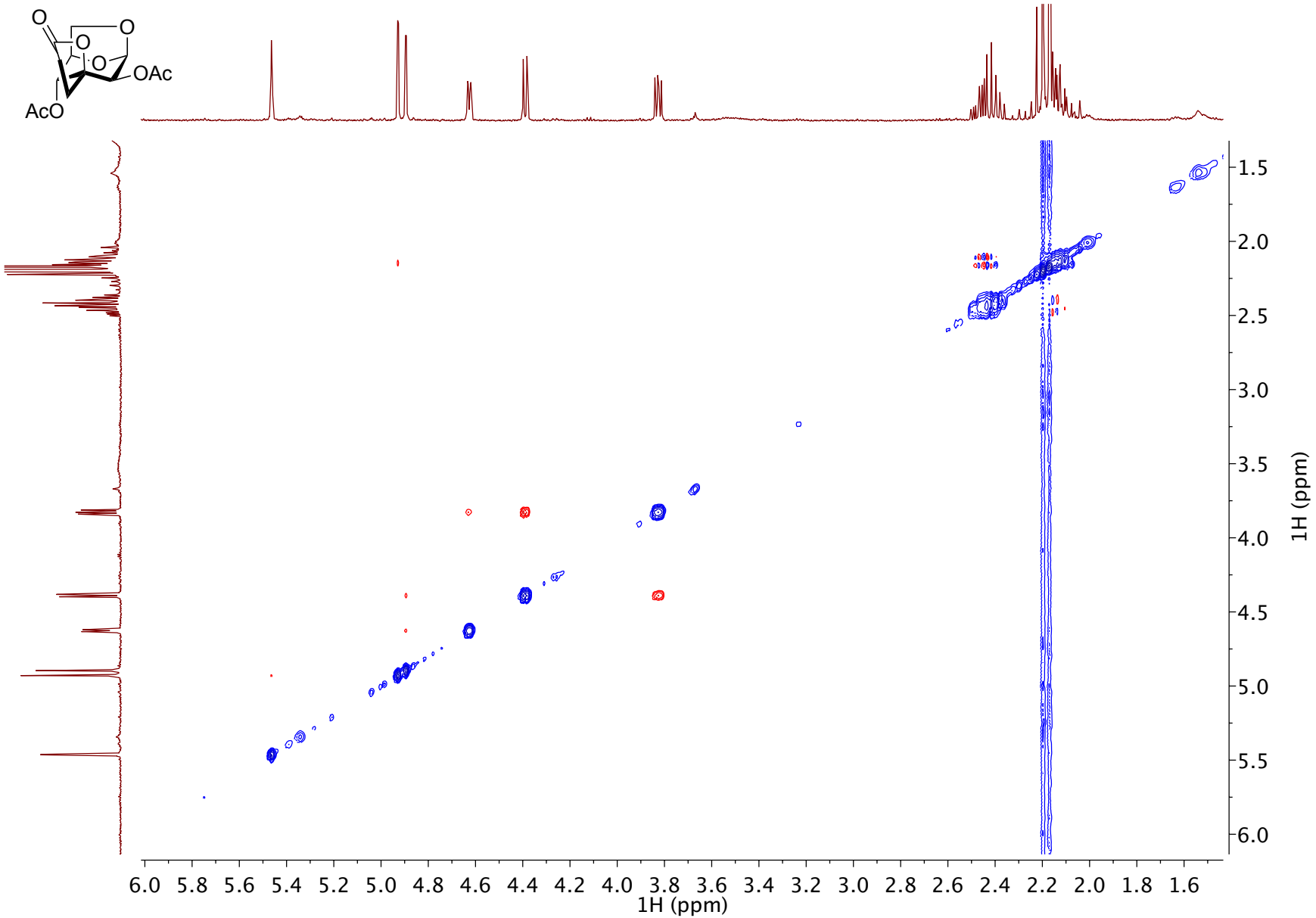
S4 –^{1}H NMR (500 MHz, $CDCl_3$)



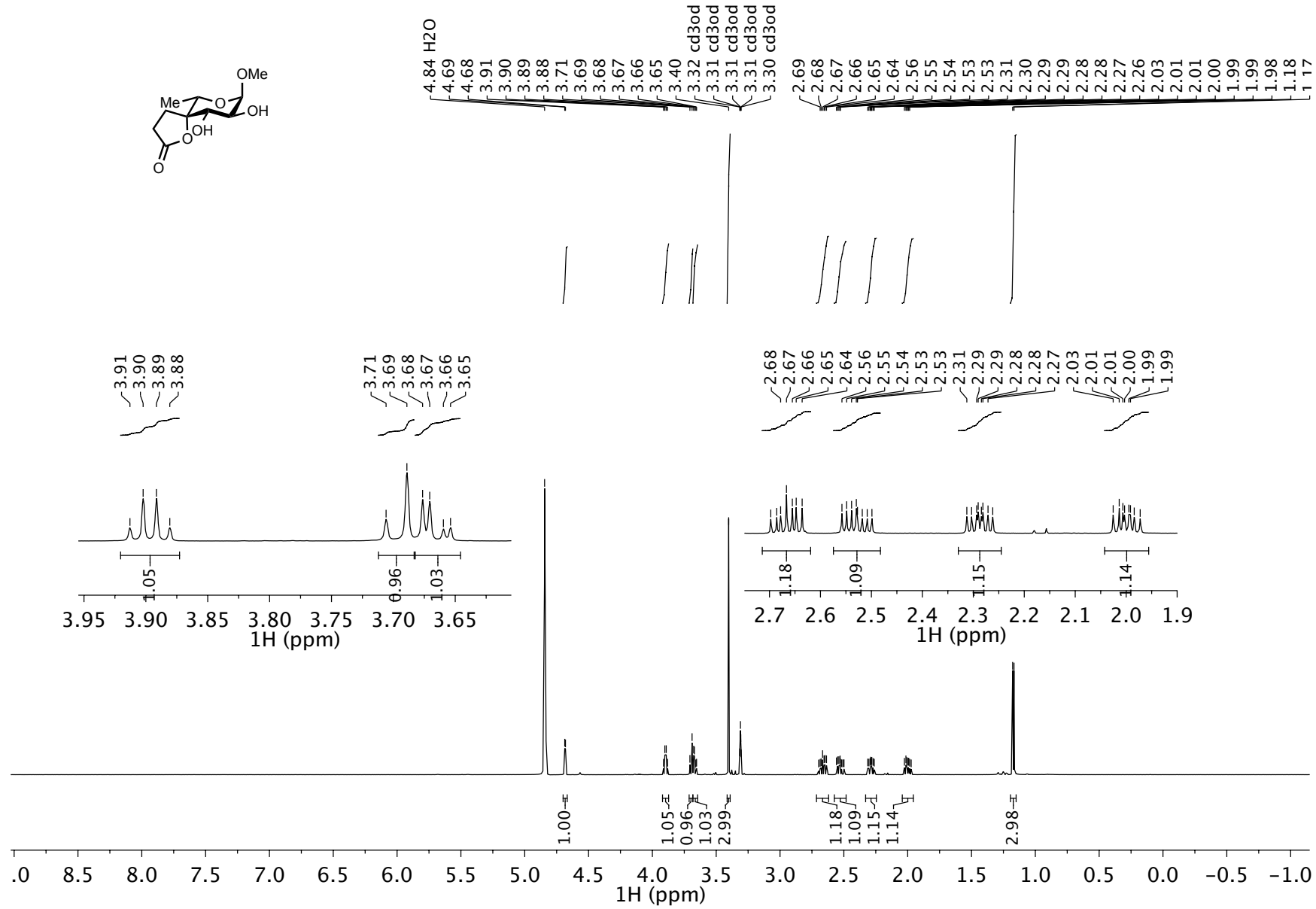
S4 – COSY (500 MHz, $CDCl_3$)



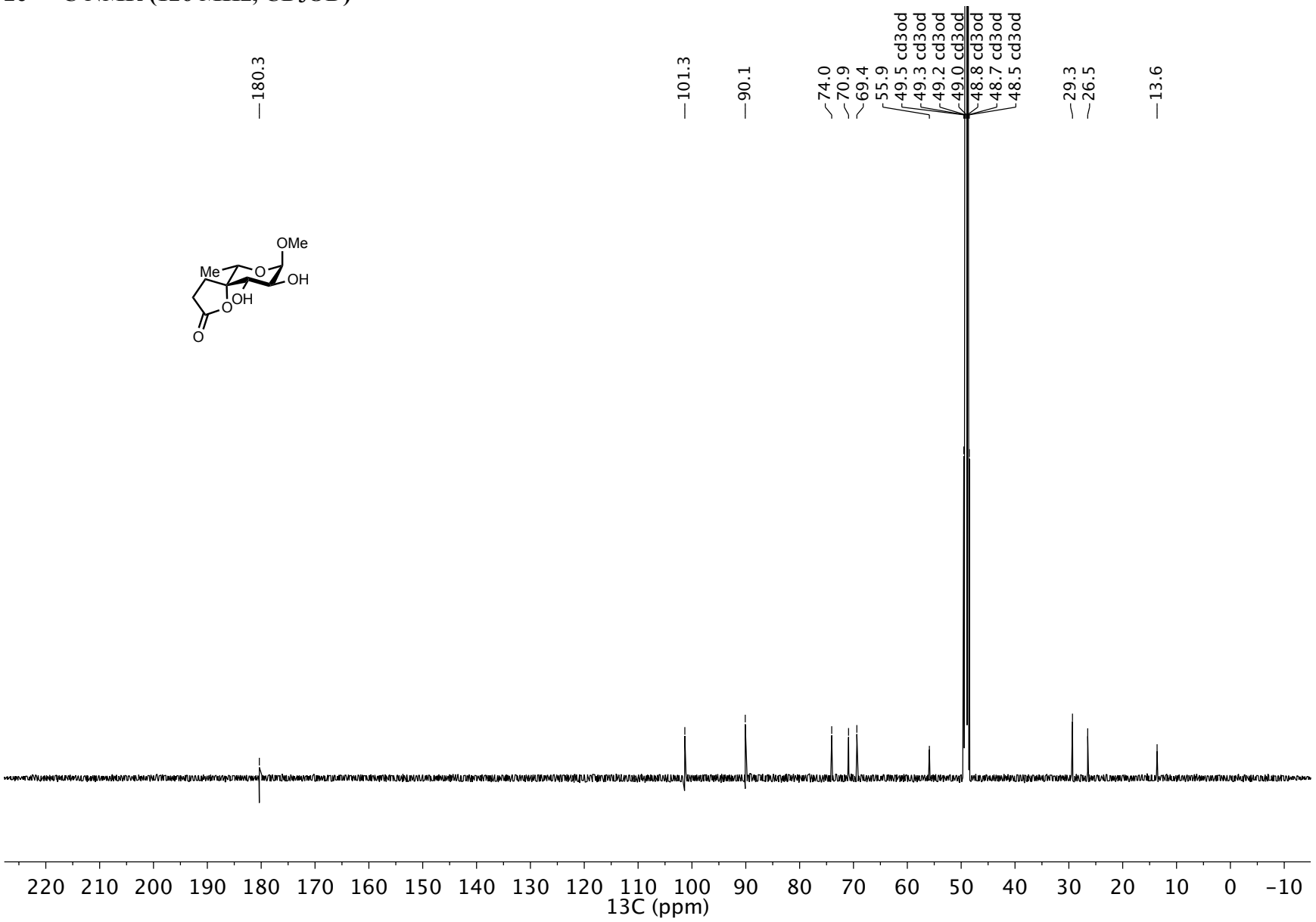
S4 –NOESY (500 MHz, $CDCl_3$)



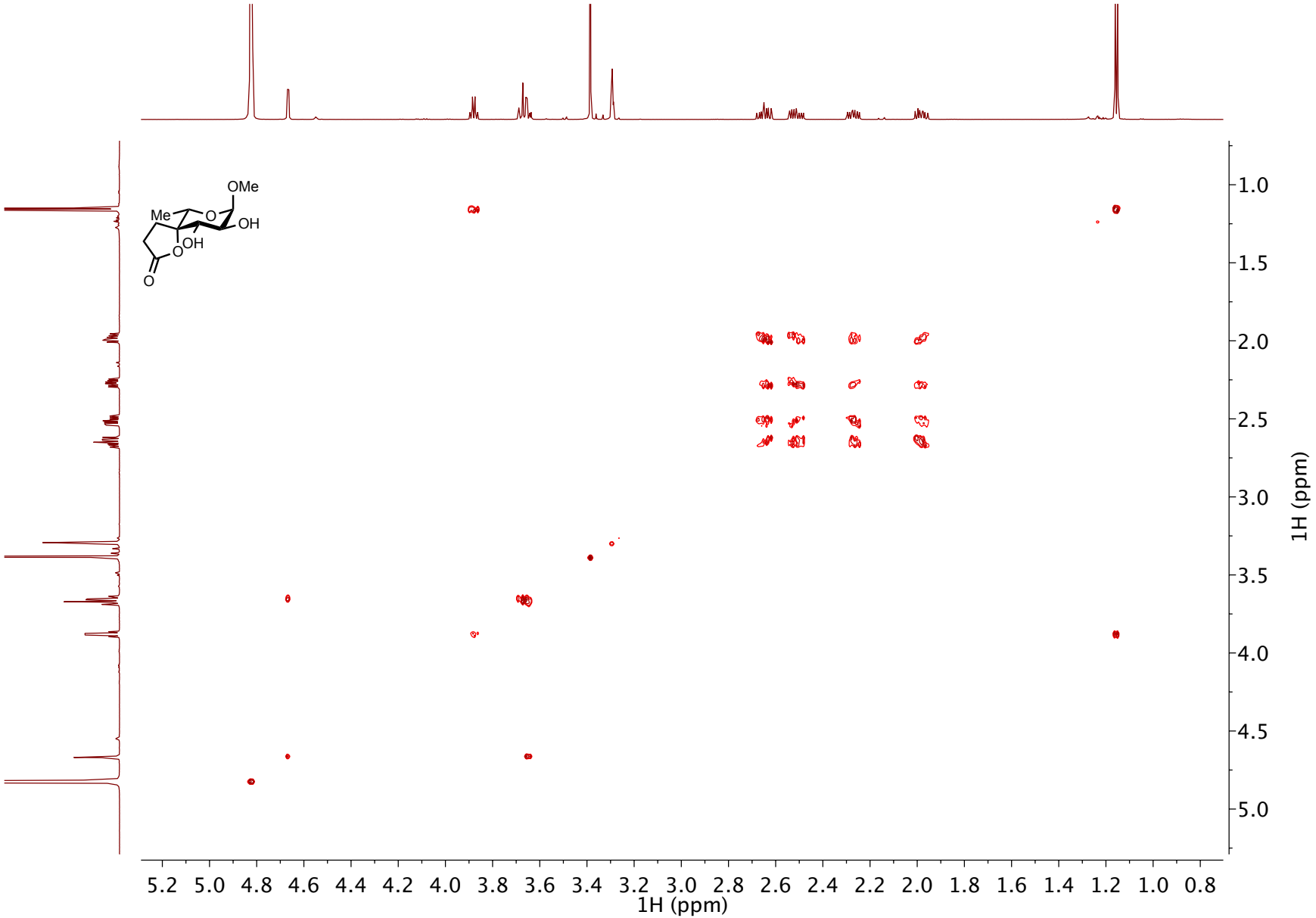
2e –^{1}H NMR (600 MHz, CD_3OD)



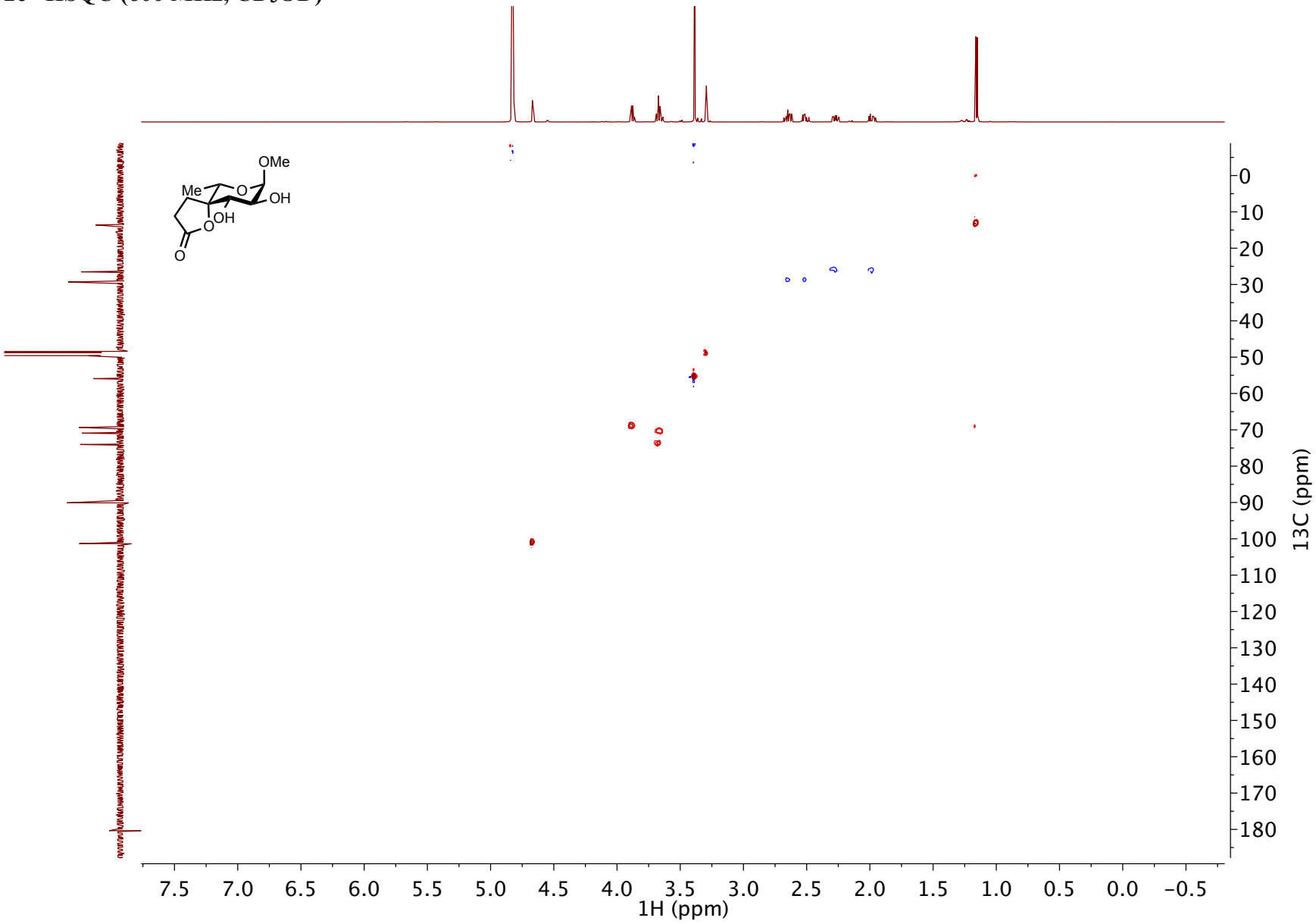
2e –^{13}C NMR (126 MHz, CD_3OD)



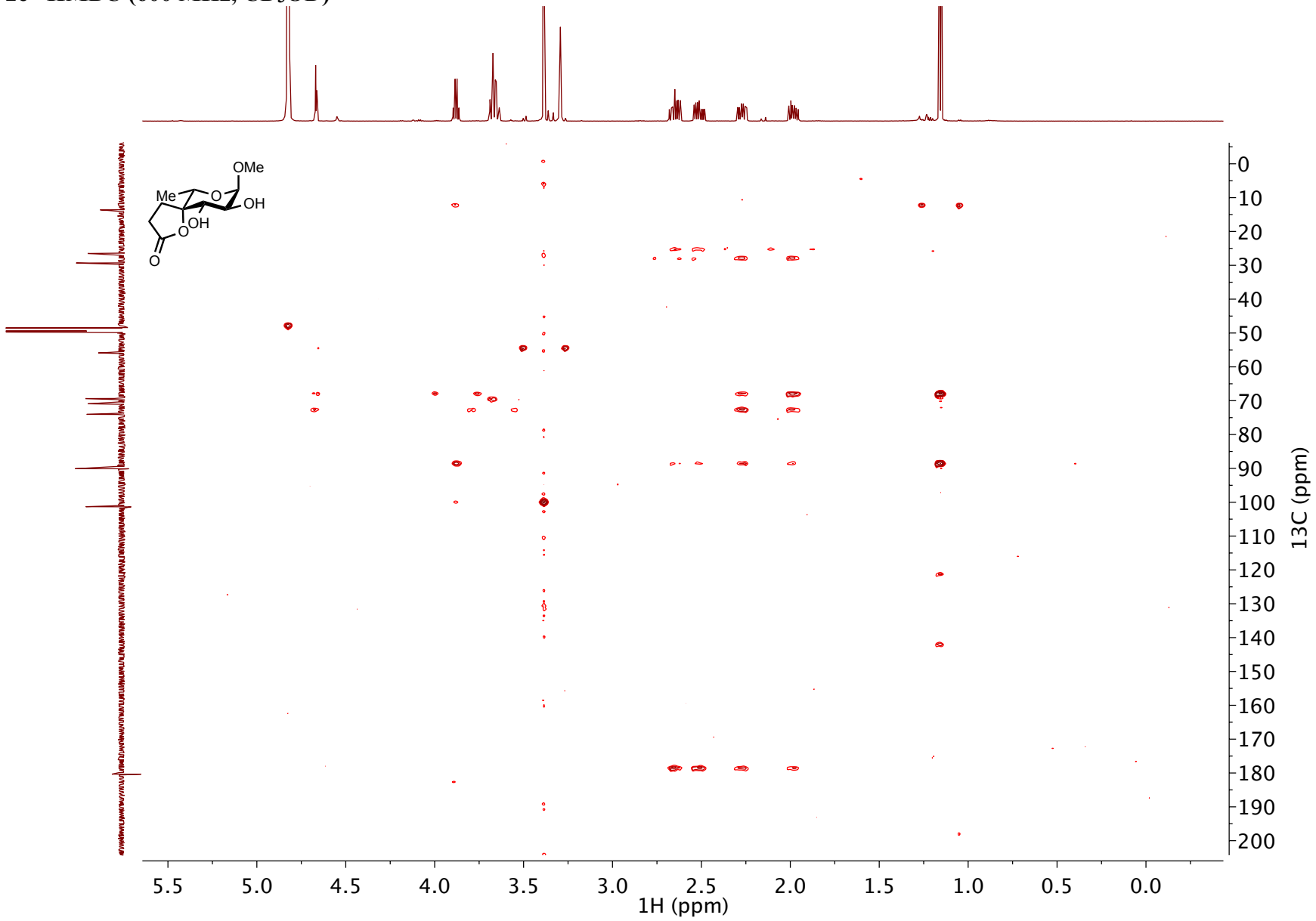
2e –COSY (600 MHz, CD_3OD)



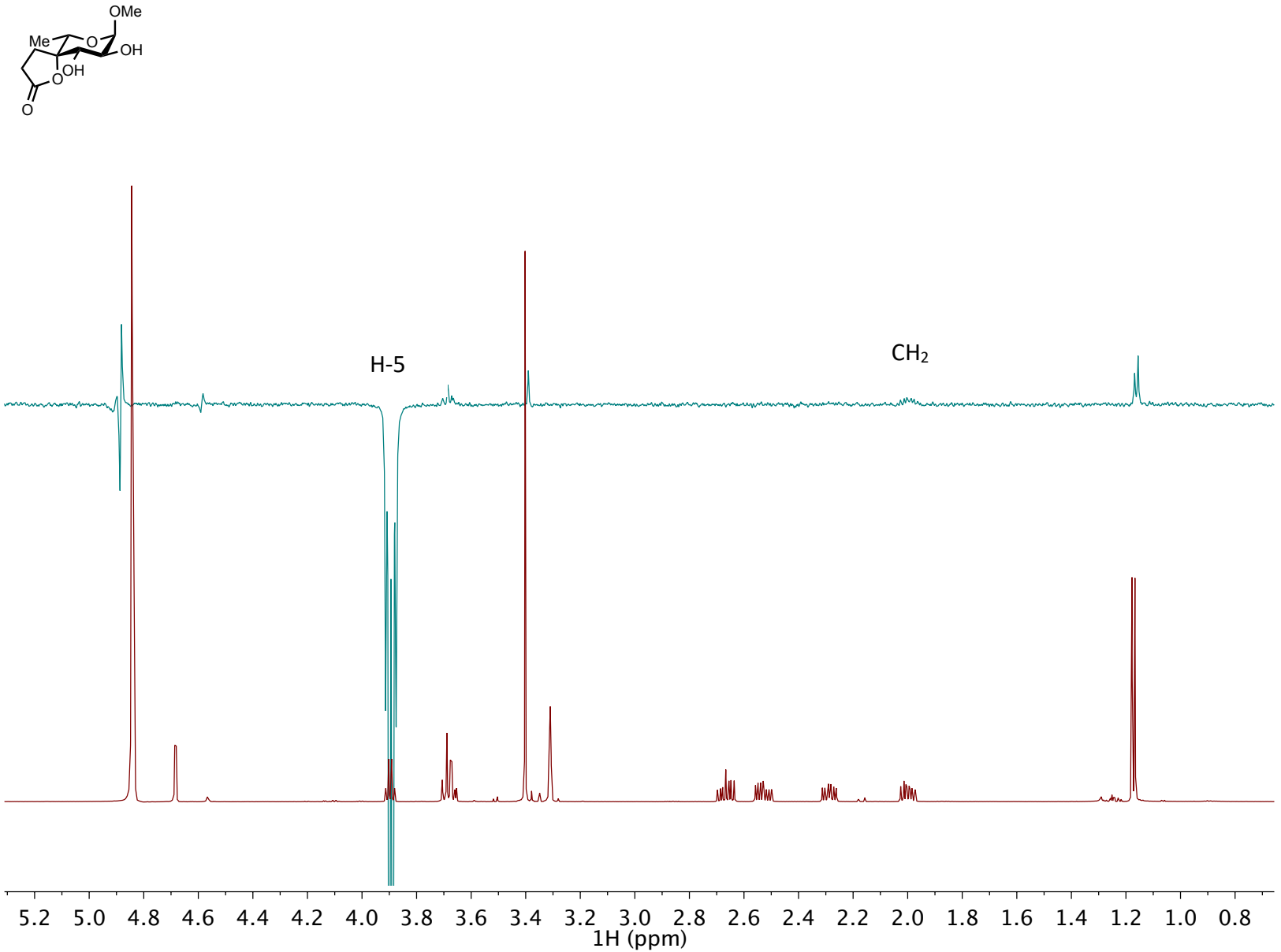
2e –HSQC (600 MHz, CD_3OD)



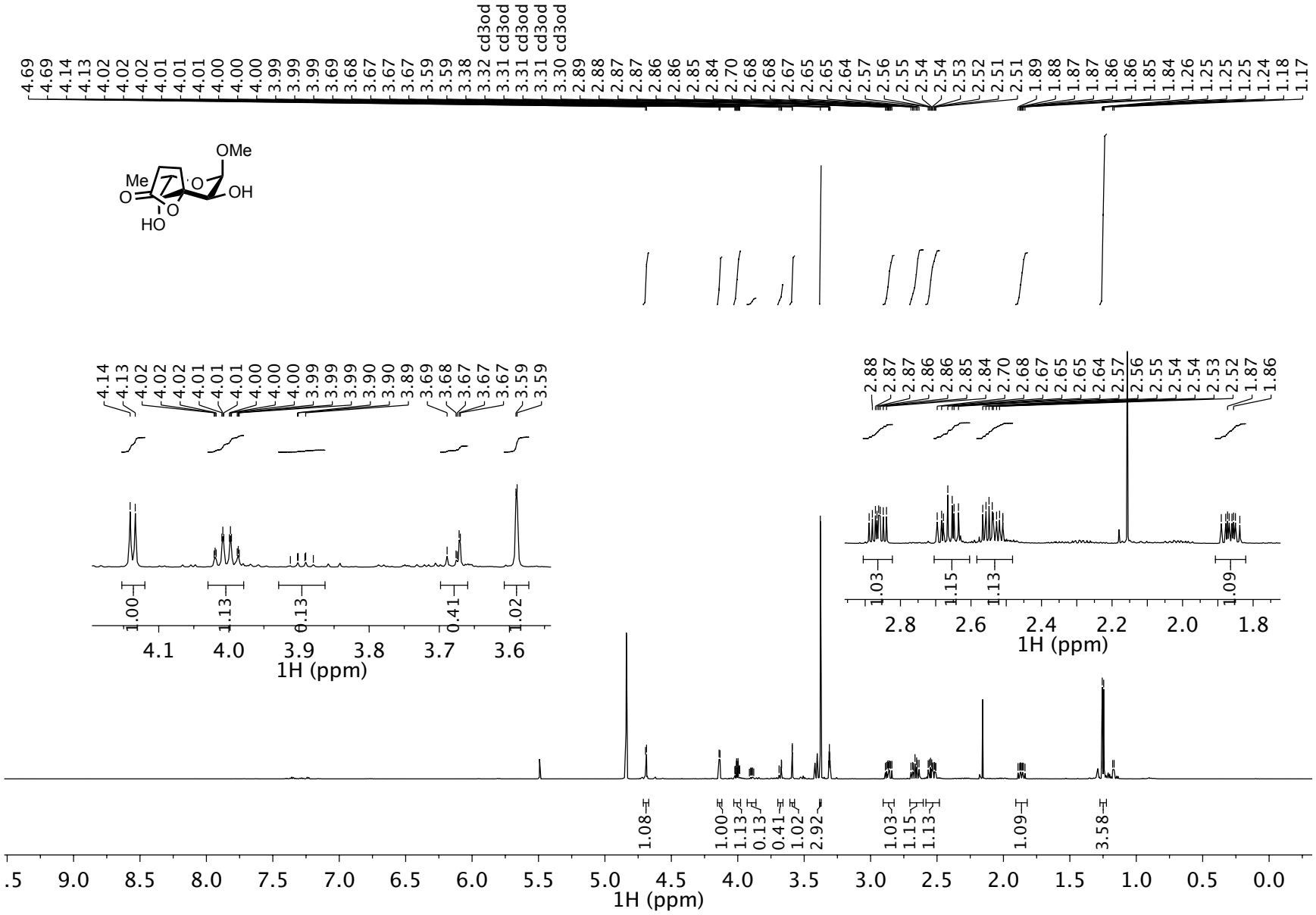
2e –HMBC (600 MHz, CD_3OD)



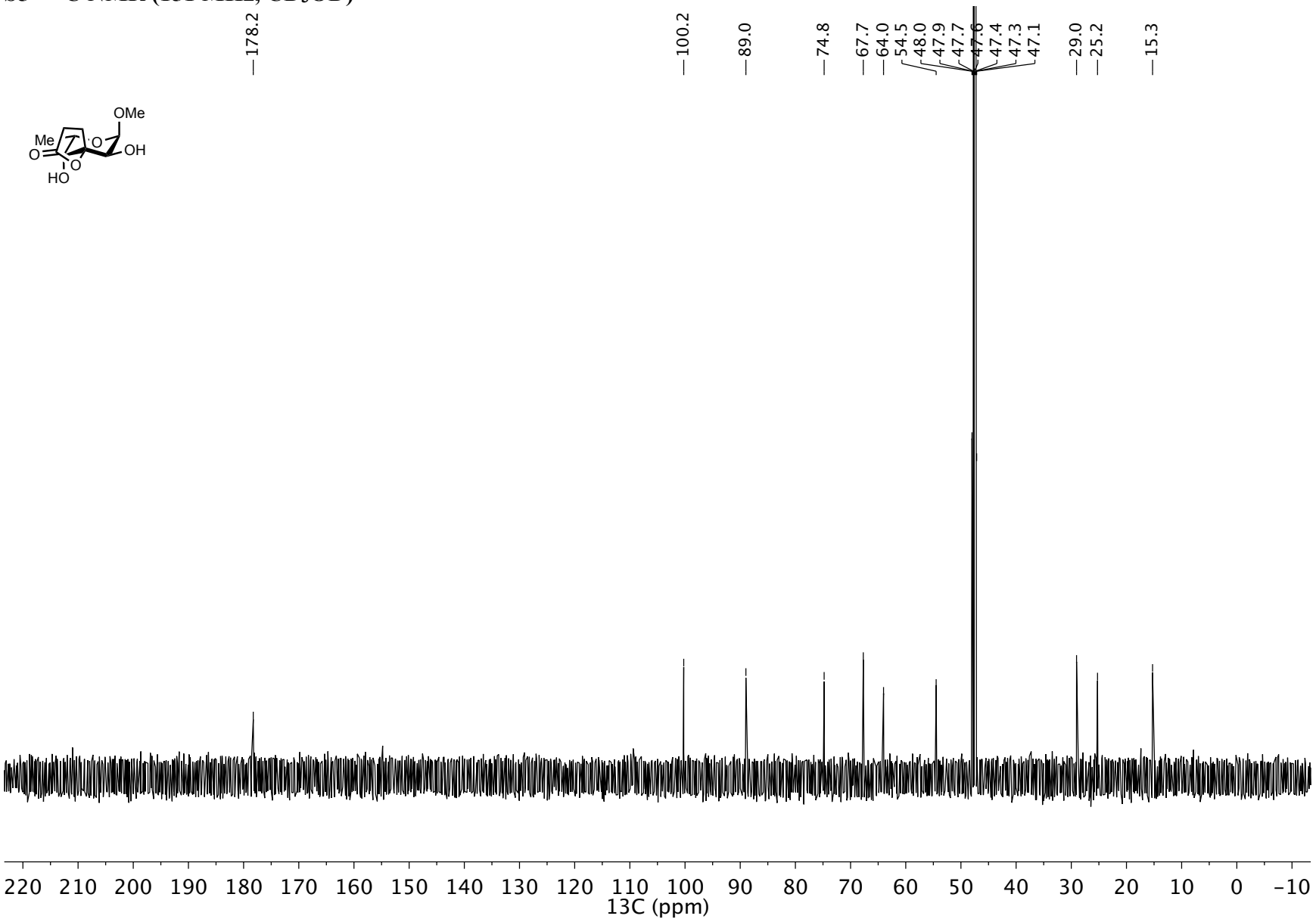
2e –1D NOESY (500 MHz, CD_3OD)



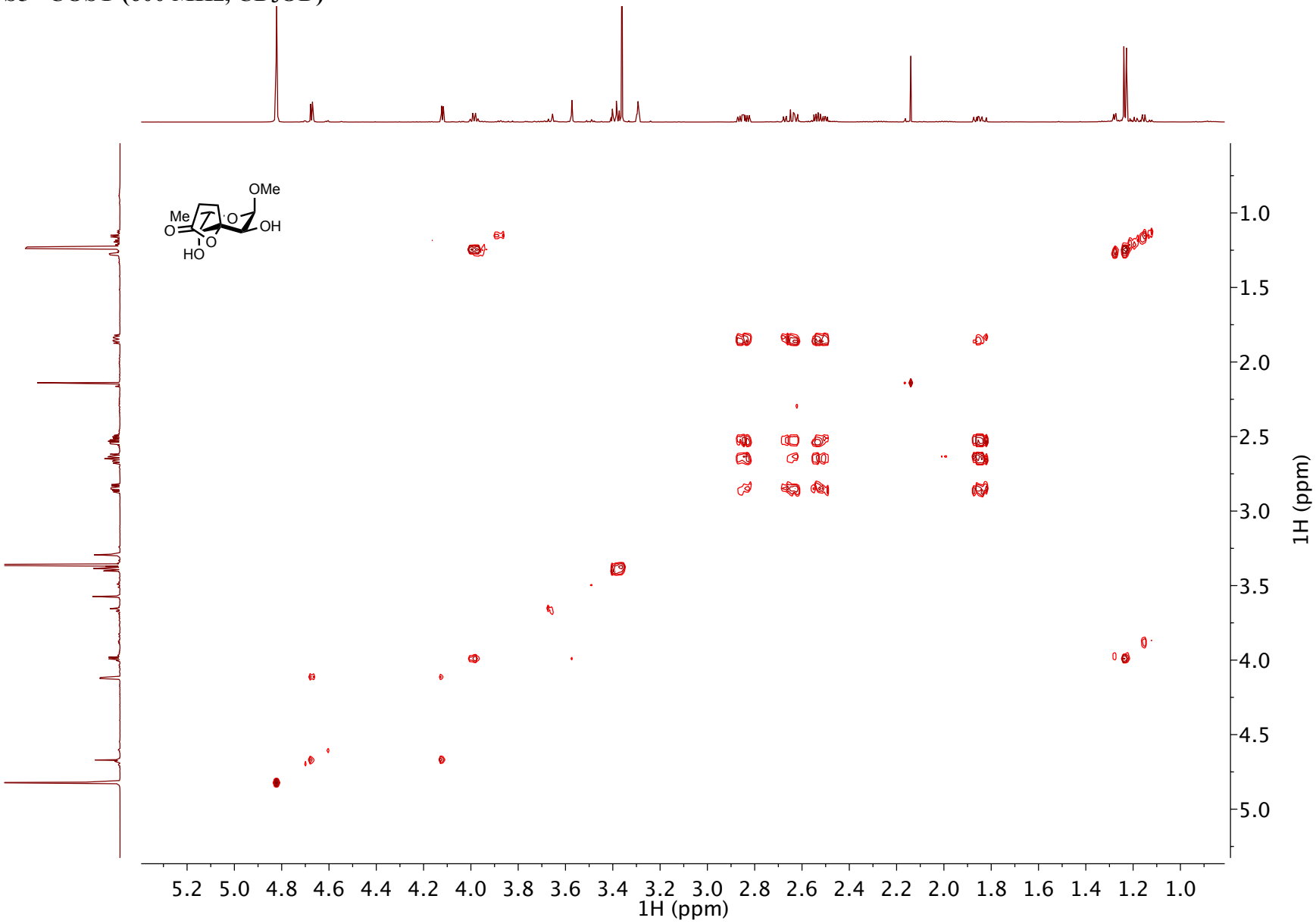
S5 –^{1}H NMR (600 MHz, CD_3OD)



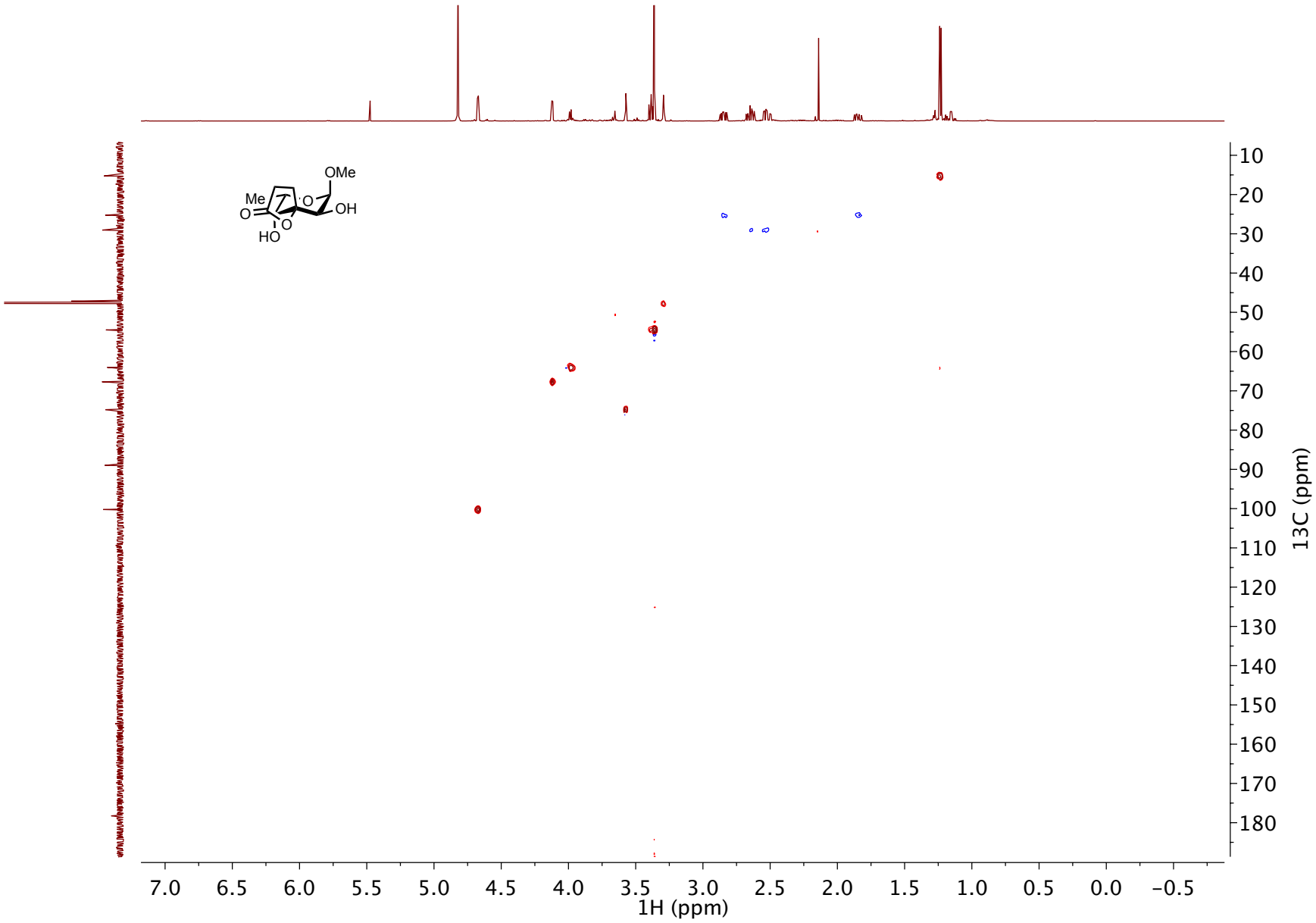
S5 –^{13}C NMR (151 MHz, CD_3OD)



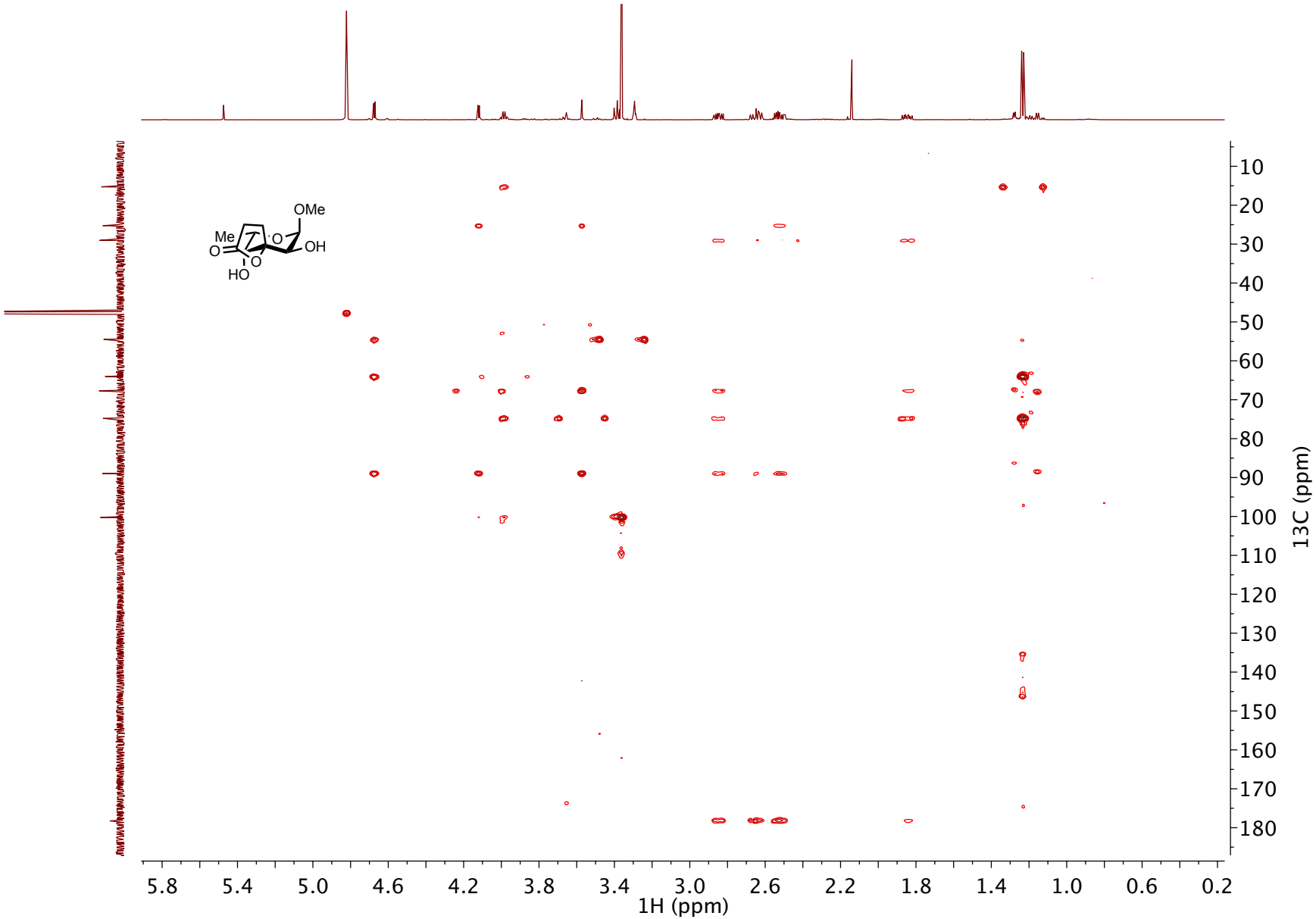
S5 –COSY (600 MHz, CD_3OD)



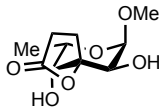
S5 –HSQC (600 MHz, CD_3OD)

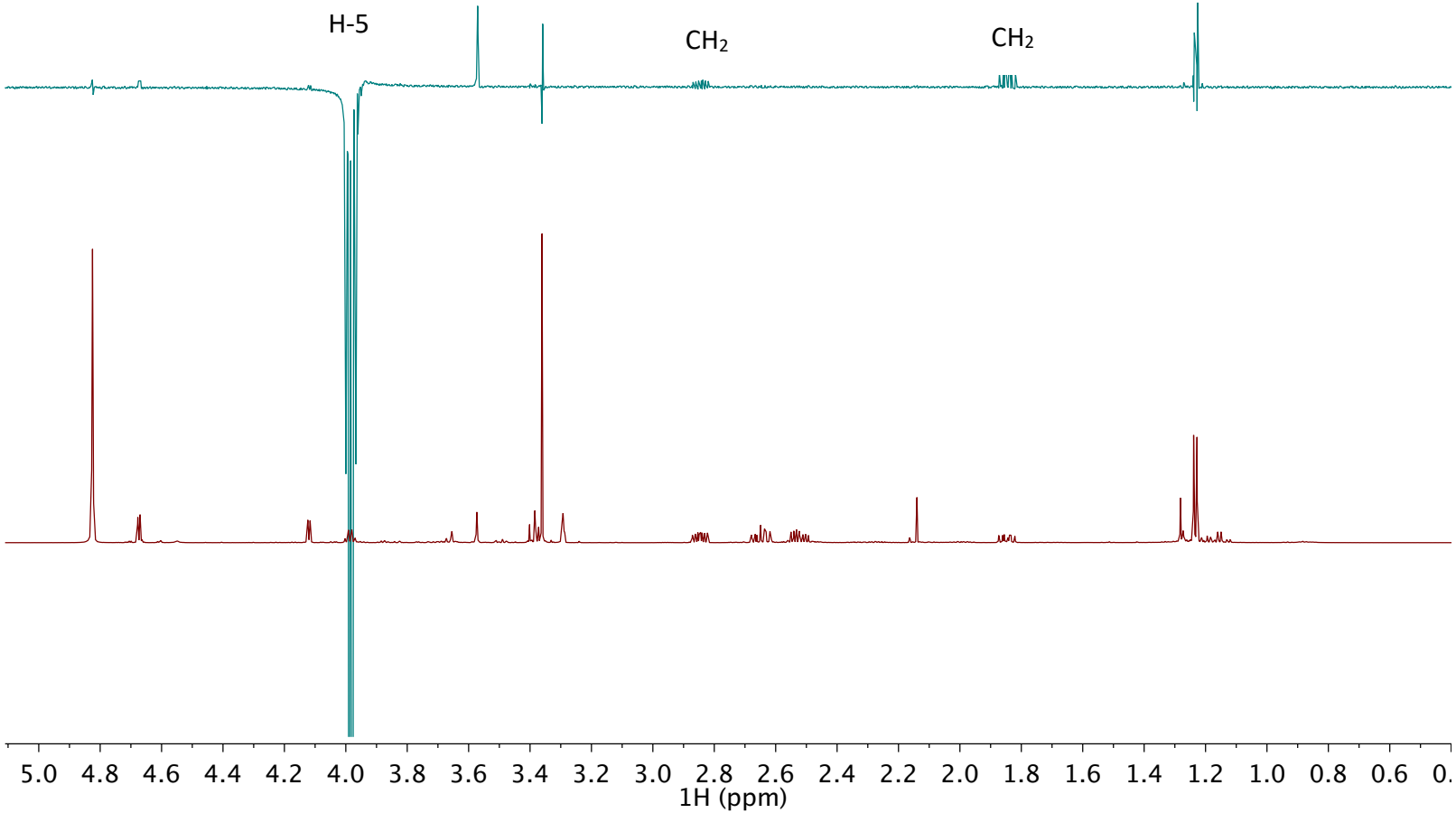


S5 –HMBC (600 MHz, CD_3OD)

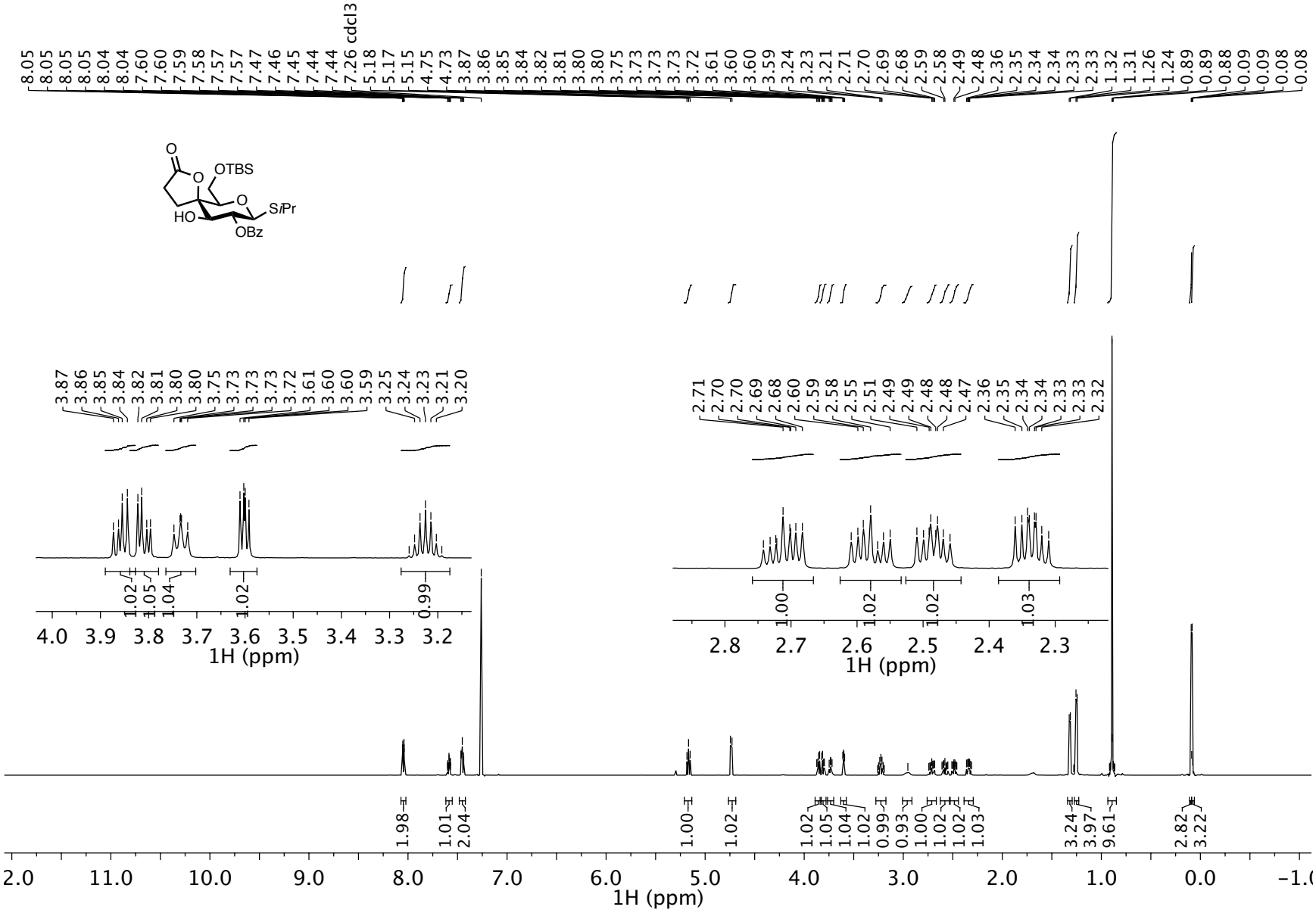


S5 –1D NOESY (600 MHz, CD_3OD)

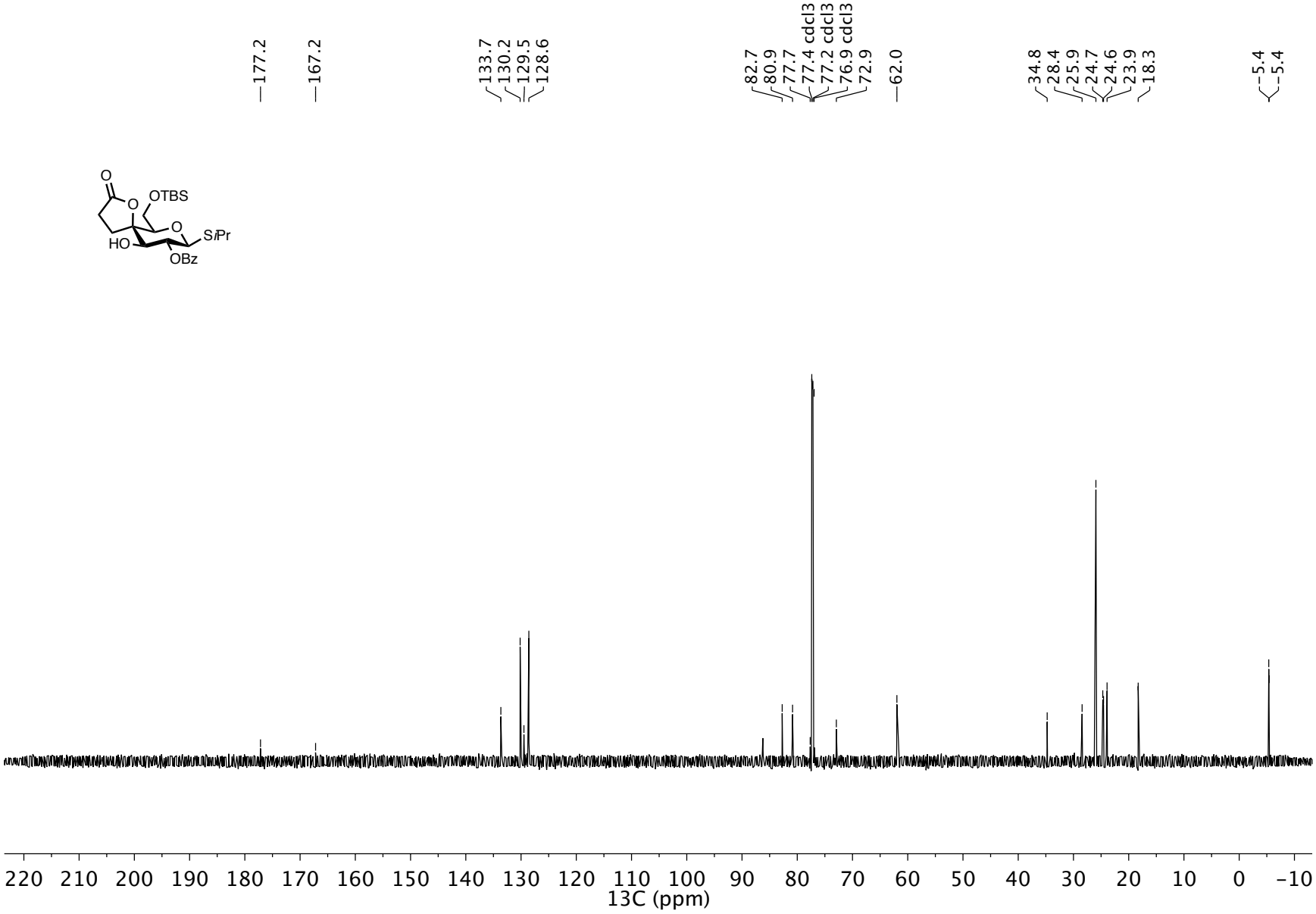




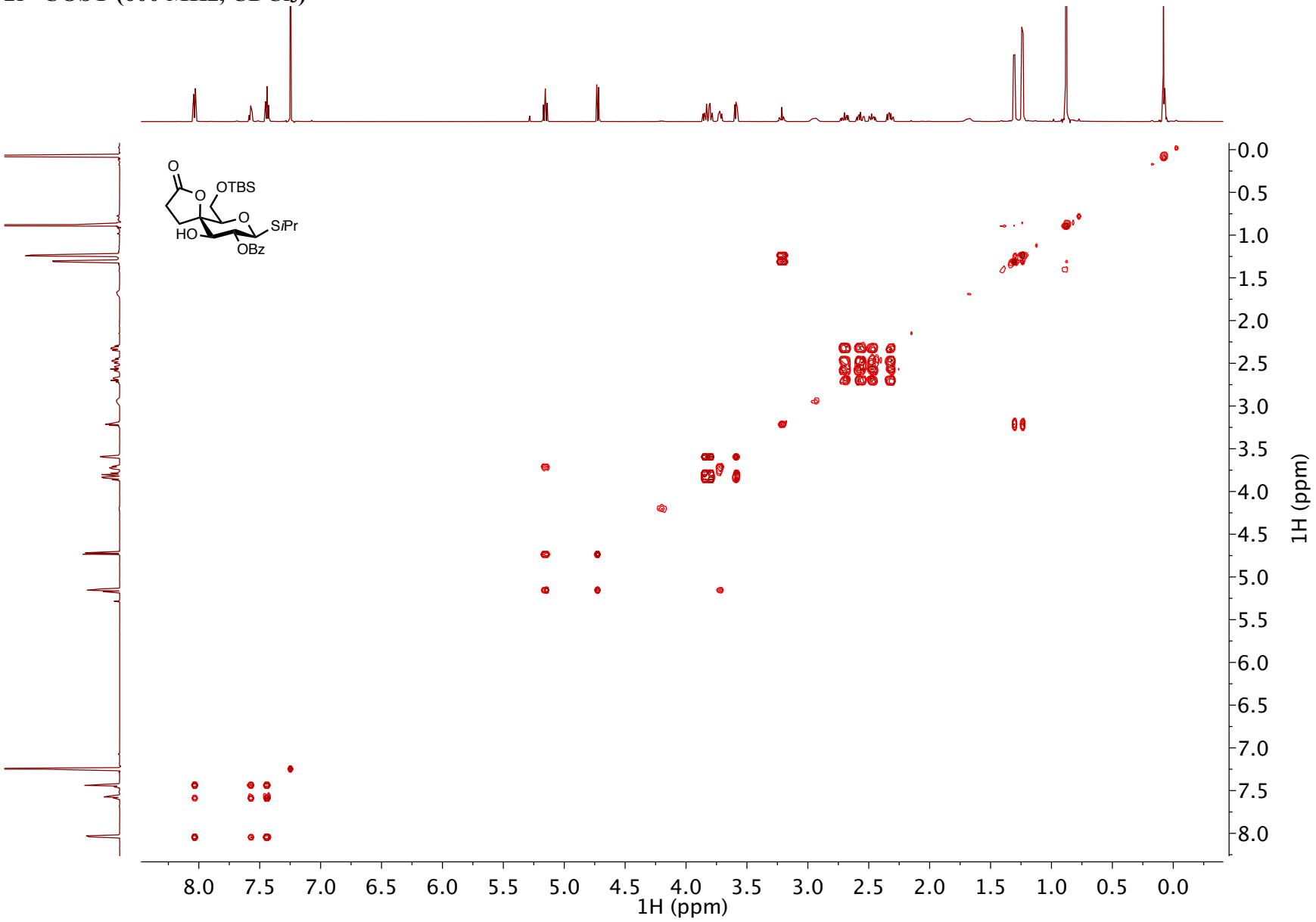
2f –^{1}H NMR (600 MHz, $CDCl_3$)



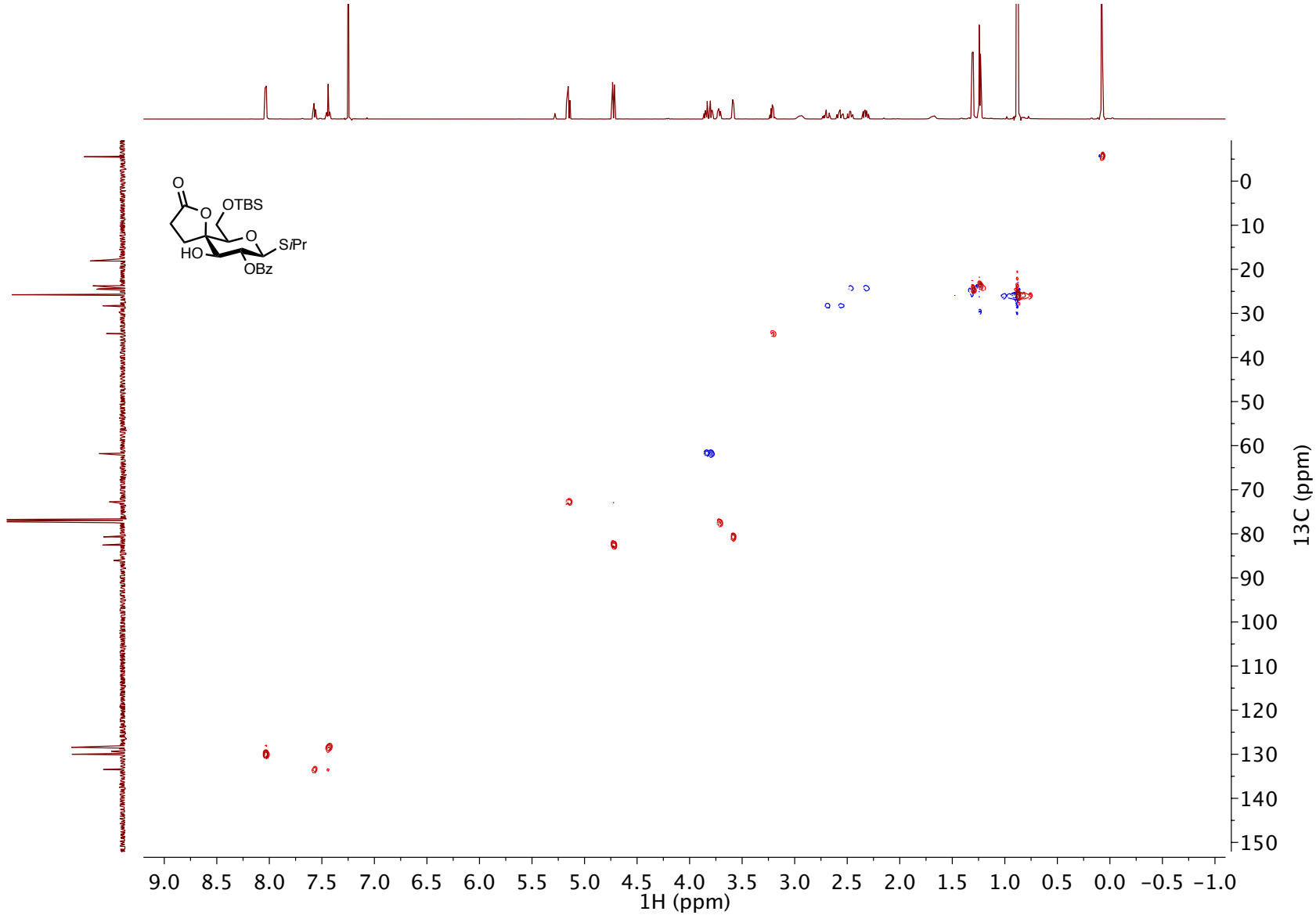
2f –^{13}C NMR (151 MHz, $CDCl_3$)



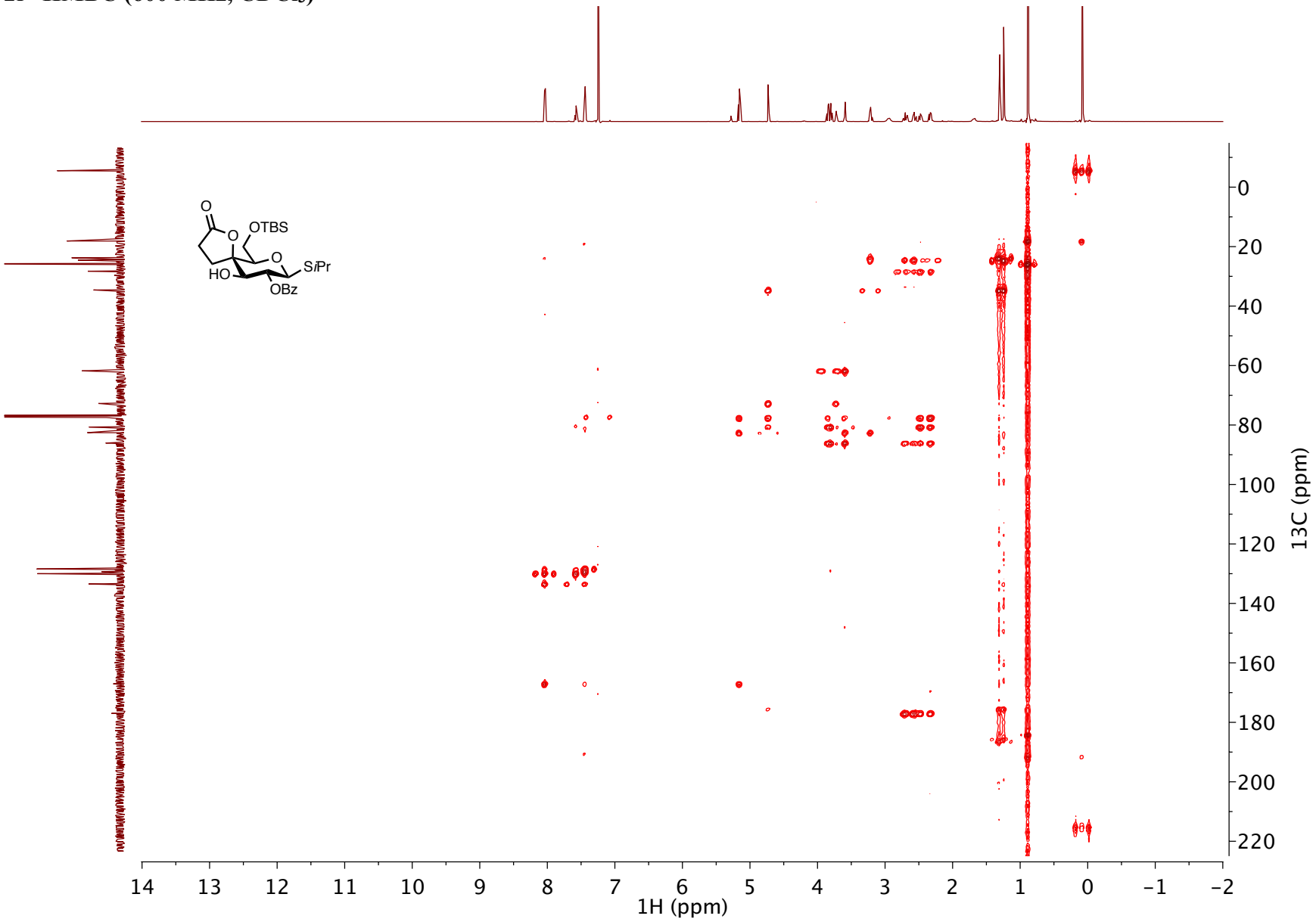
2f –COSY (600 MHz, $CDCl_3$)



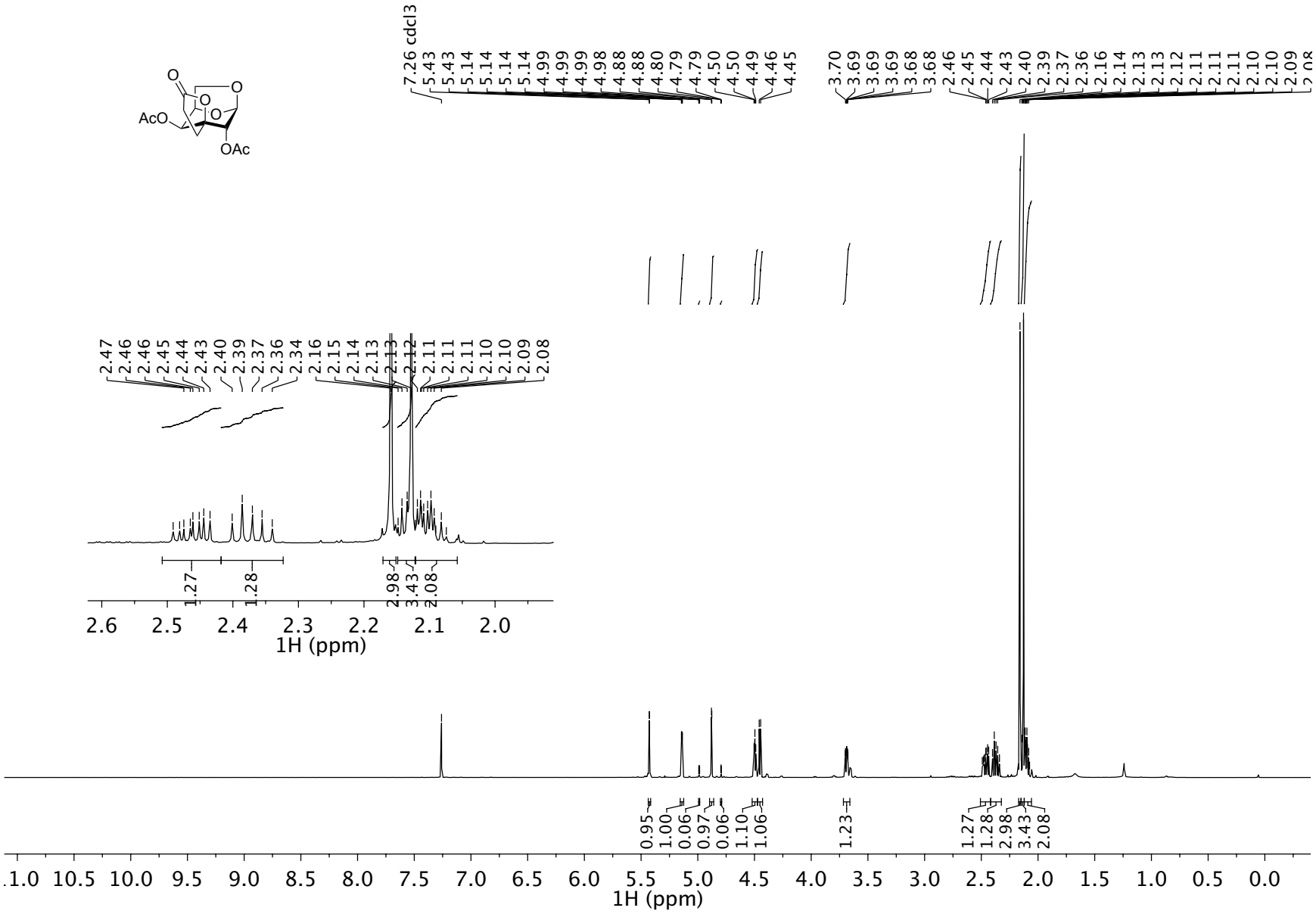
2f –HSQC (600 MHz, $CDCl_3$)



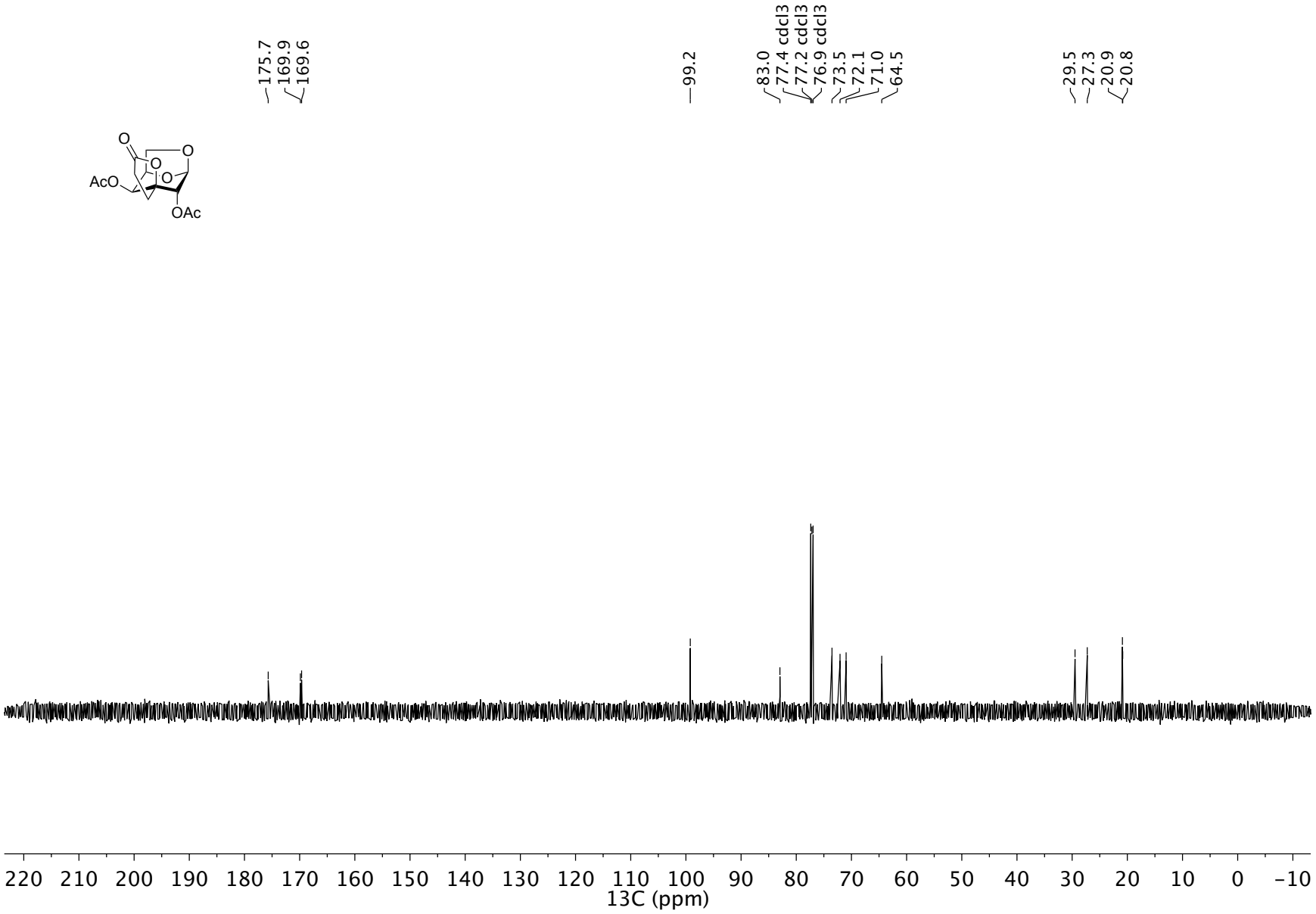
2f –HMBC (600 MHz, $CDCl_3$)



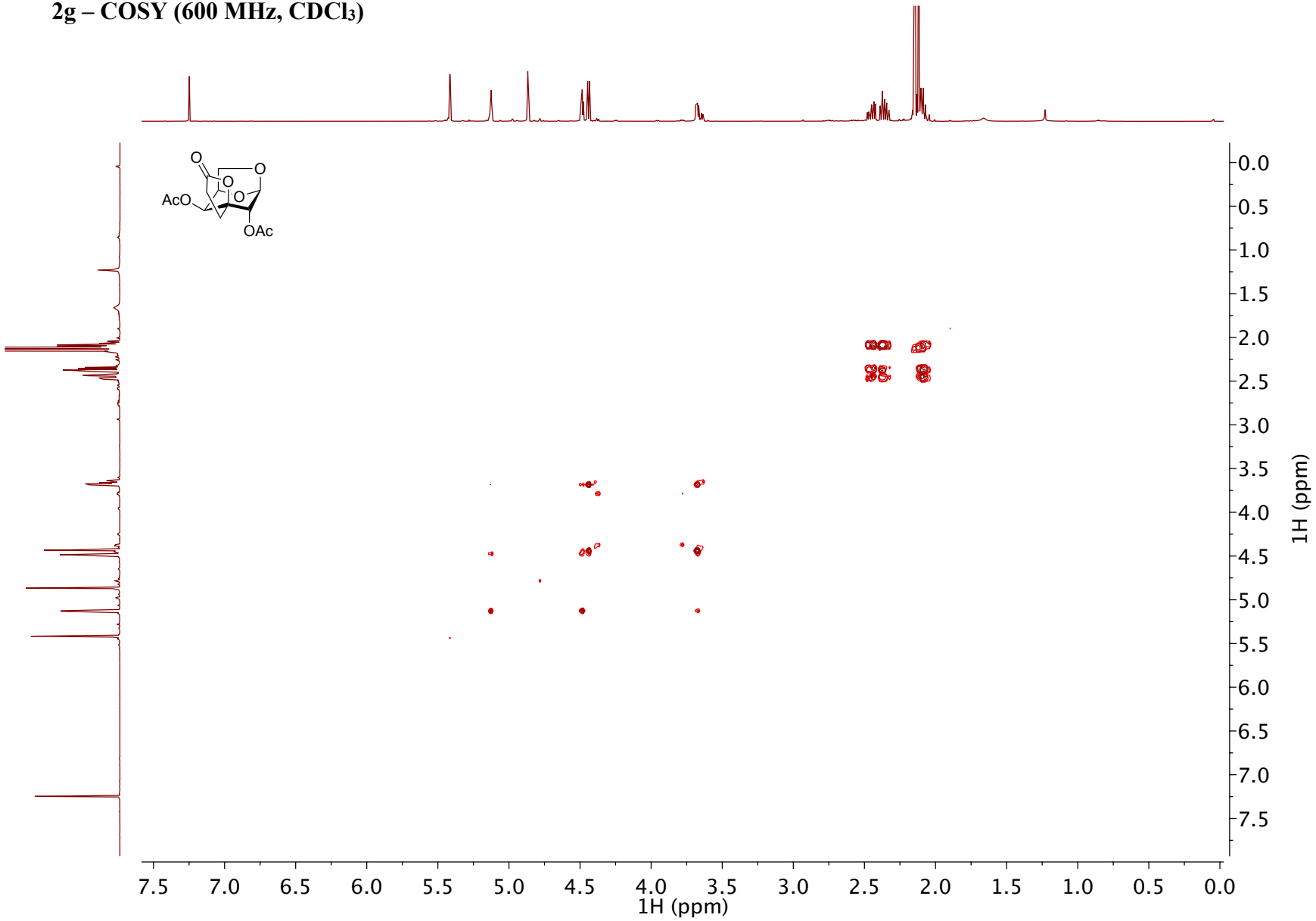
2g –^{1}H NMR (600 MHz, $CDCl_3$)



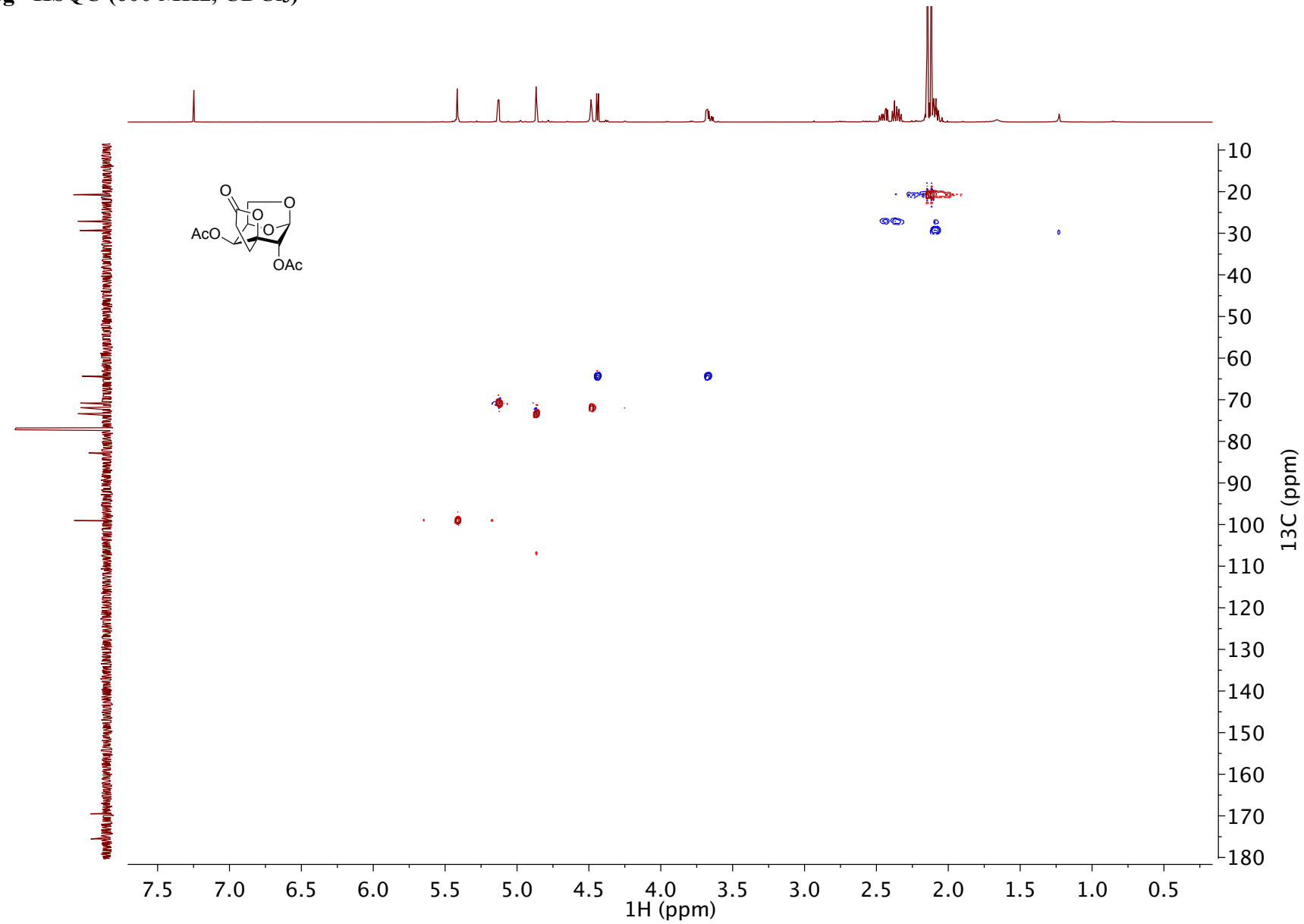
2g –^{13}C NMR (151 MHz, $CDCl_3$)



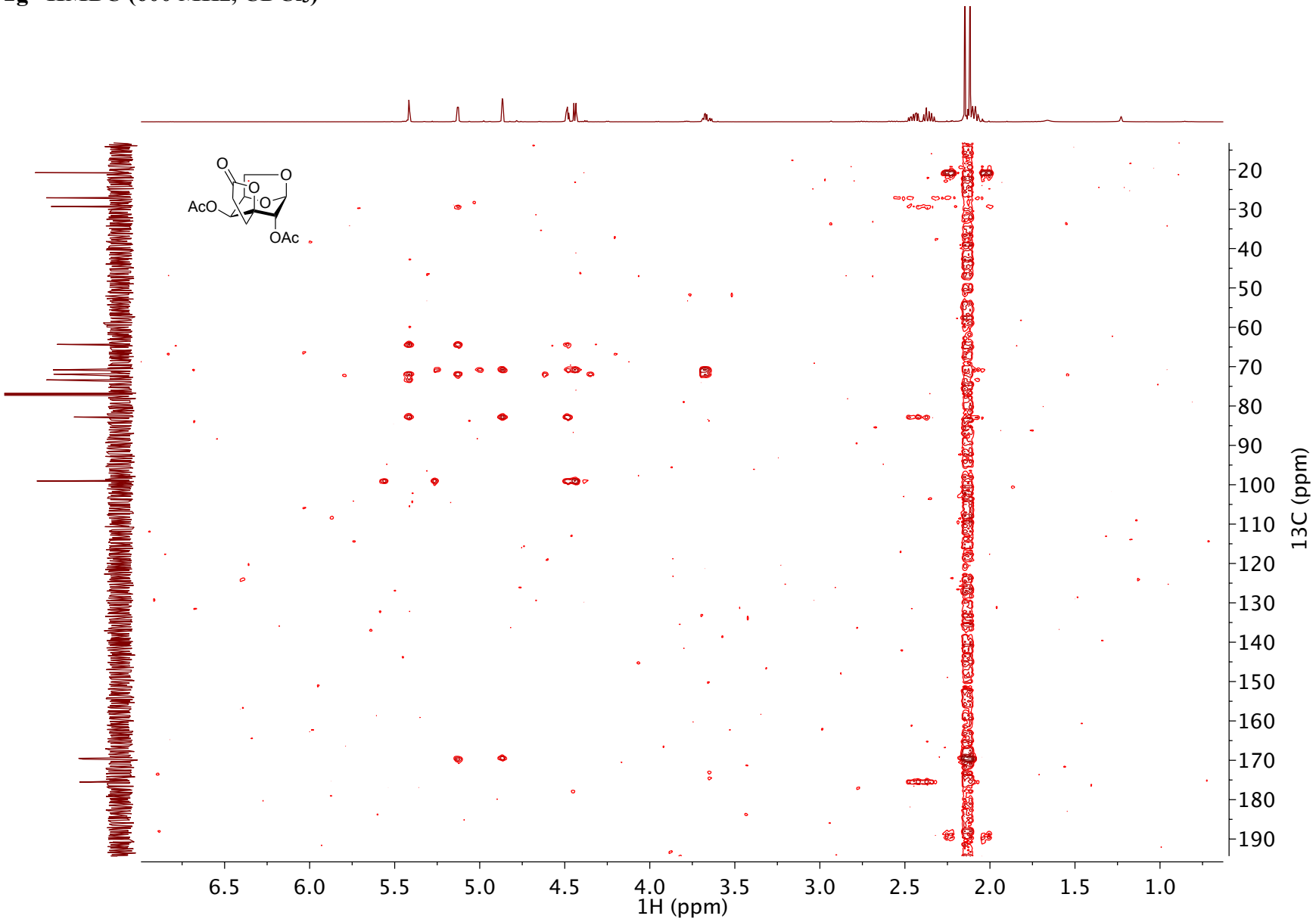
2g – COSY (600 MHz, $CDCl_3$)



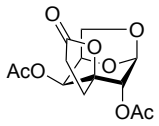
2g –HSQC (600 MHz, $CDCl_3$)

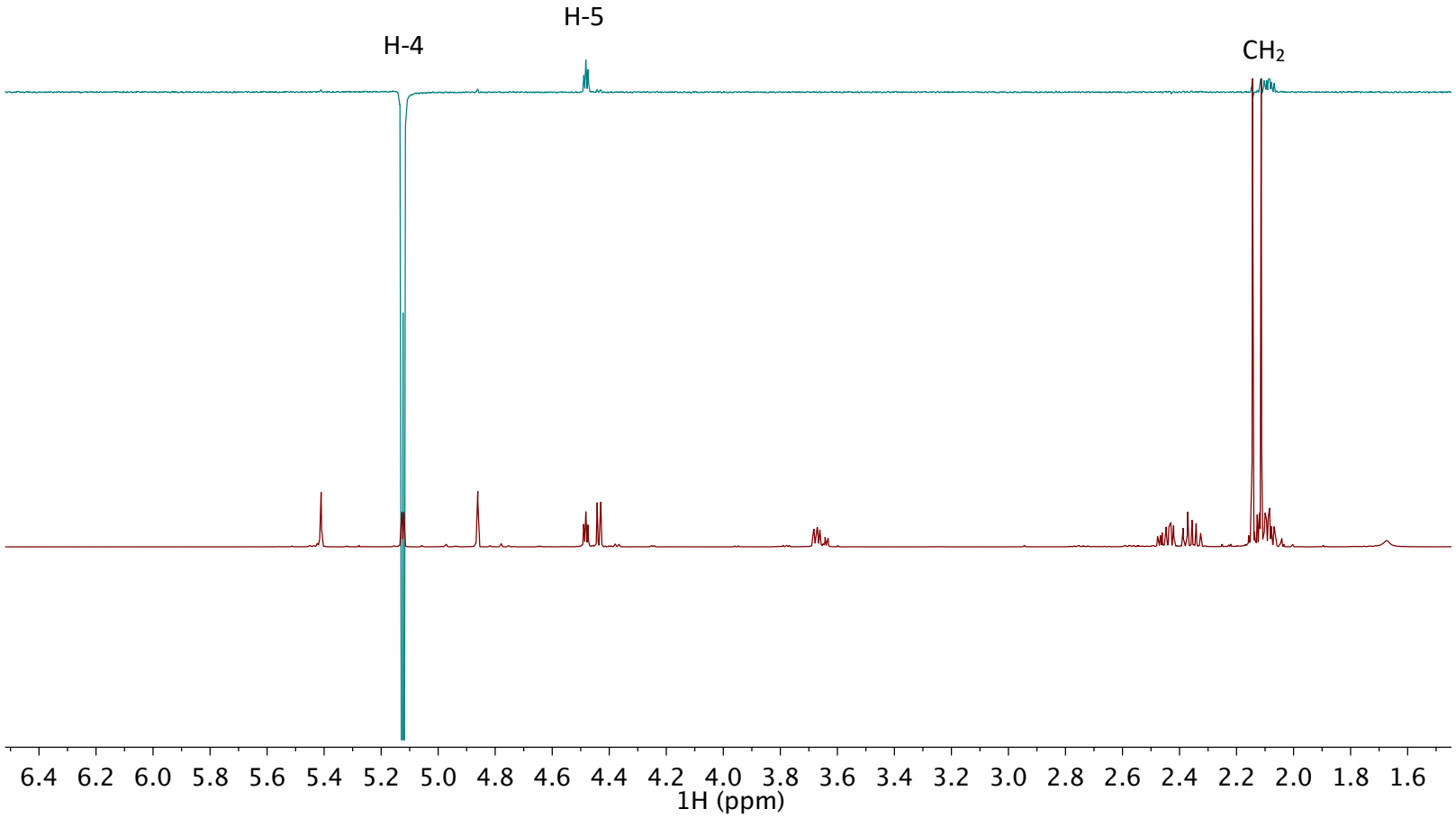


2g –HMBC (600 MHz, $CDCl_3$)

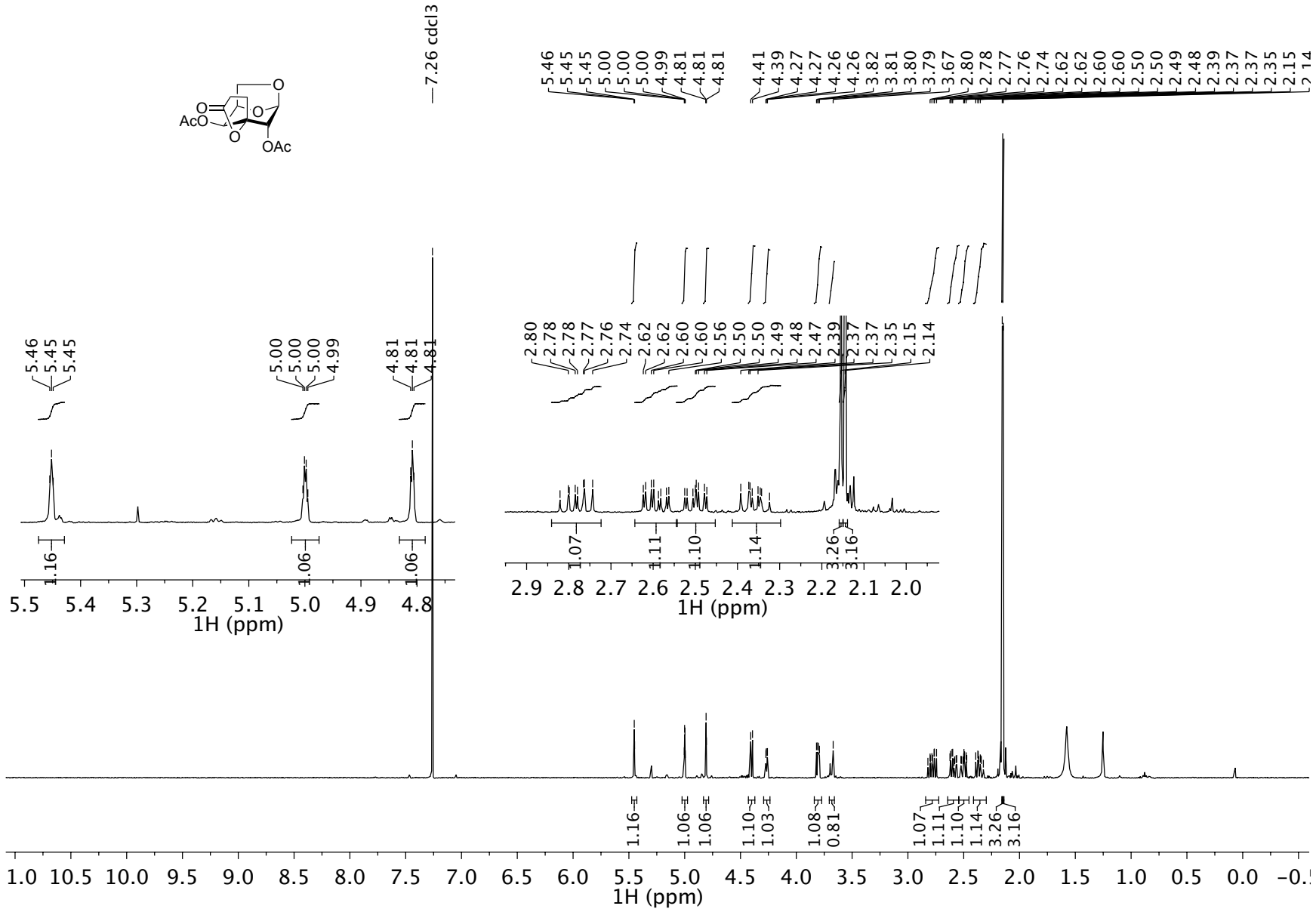


2g –1D NOESY (600 MHz, $CDCl_3$)

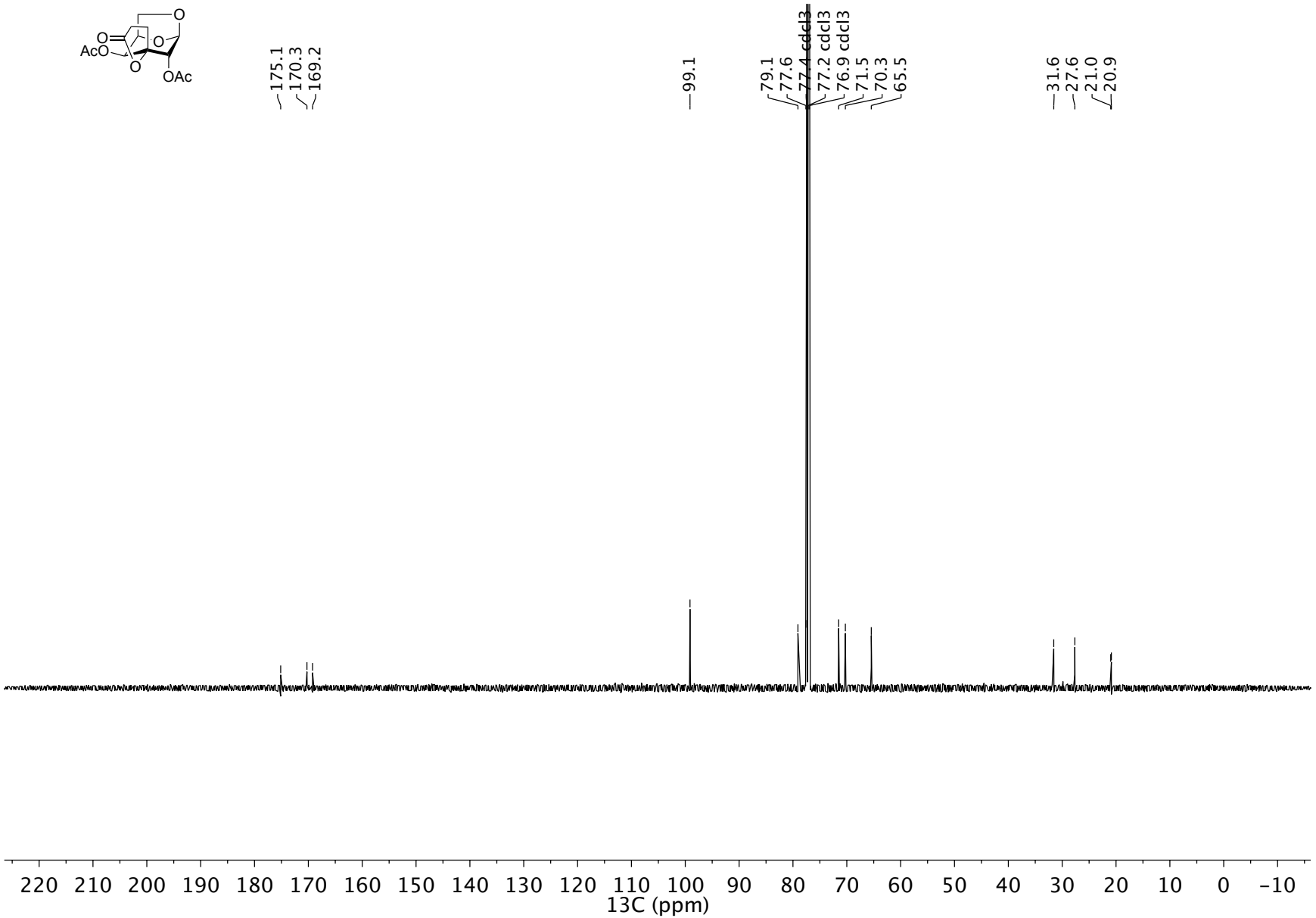




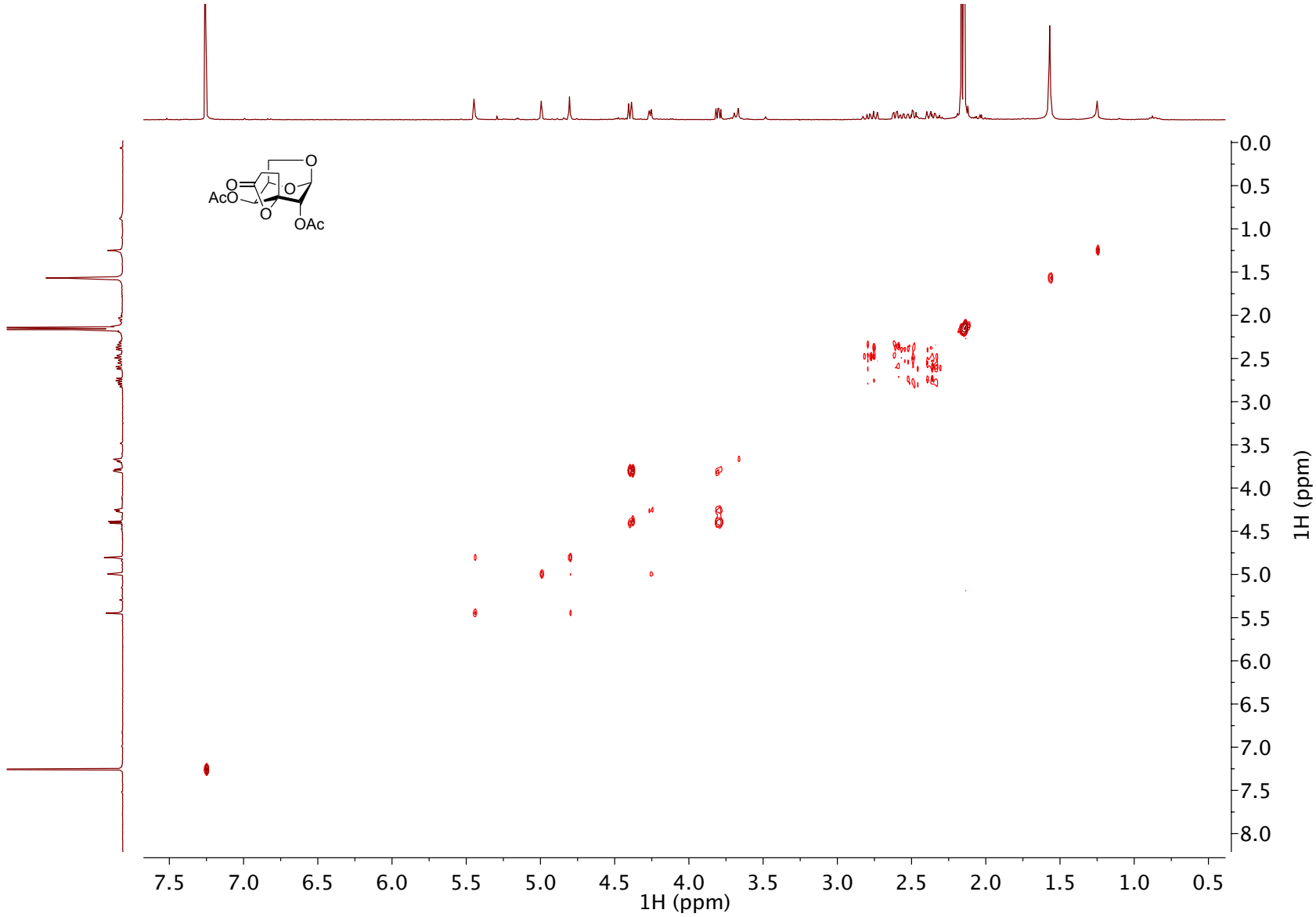
S6 –^{1}H NMR (500 MHz, $CDCl_3$)



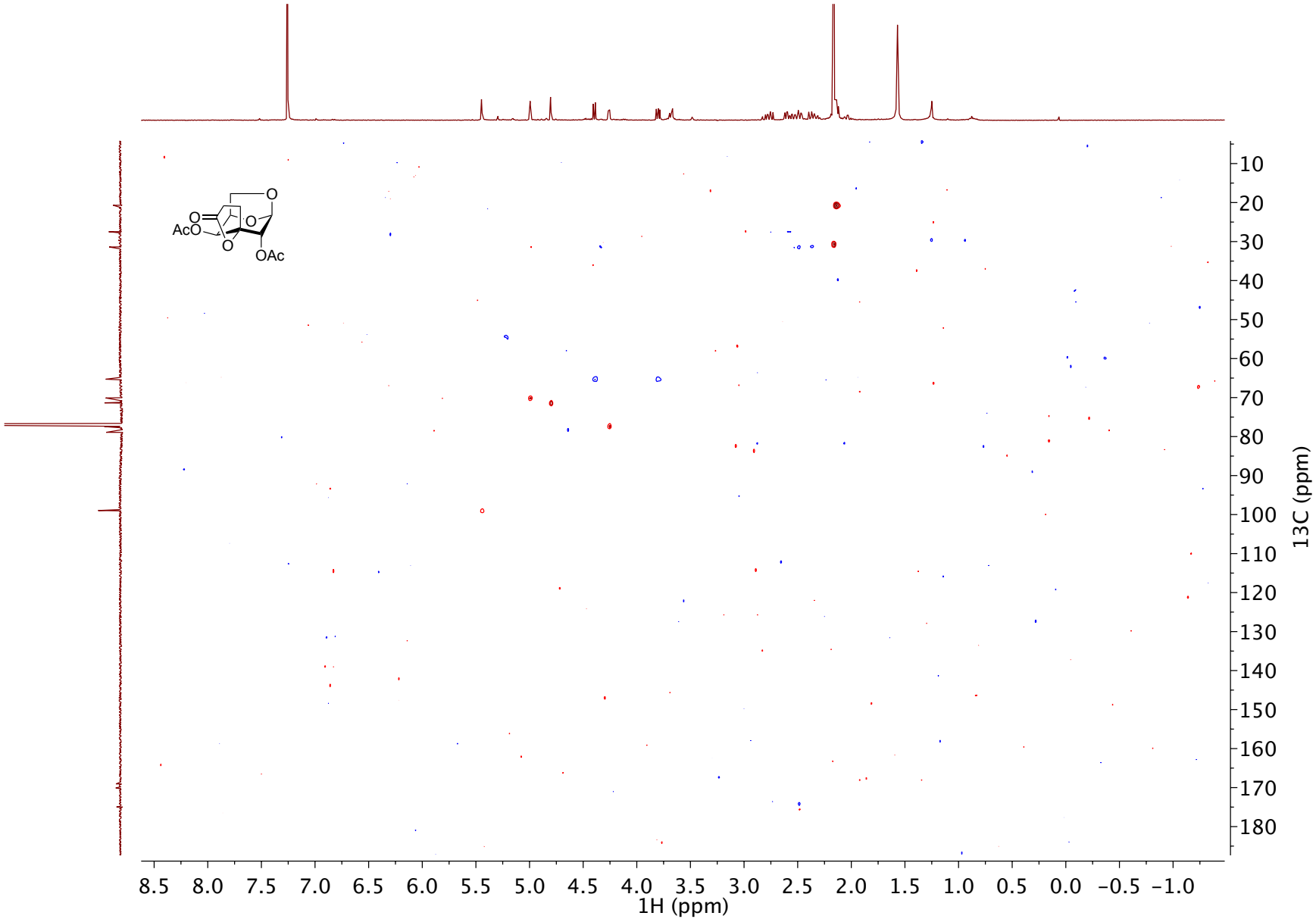
S6 –^{13}C NMR (126 MHz, $CDCl_3$)



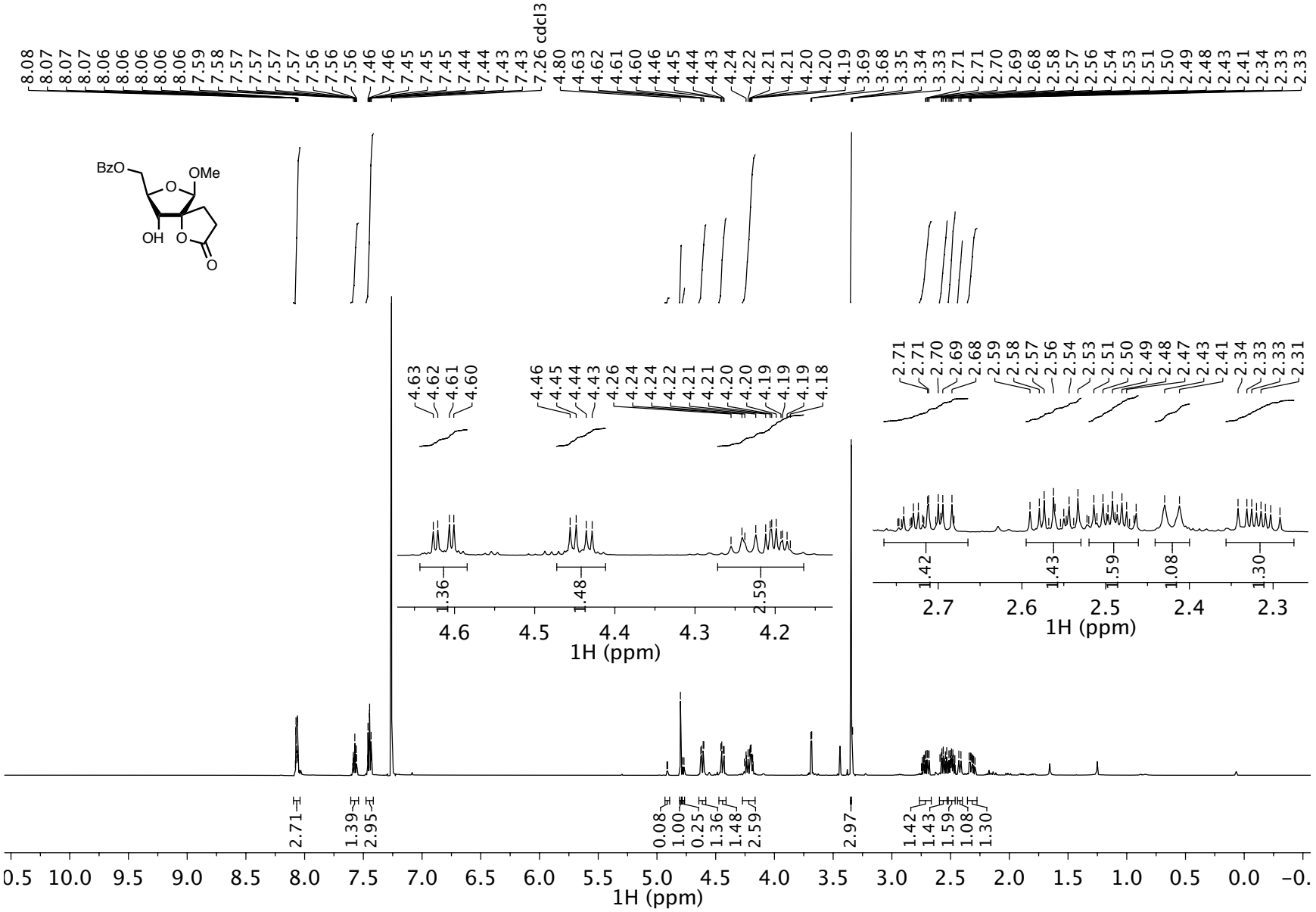
S6 –COSY (400 MHz, $CDCl_3$)



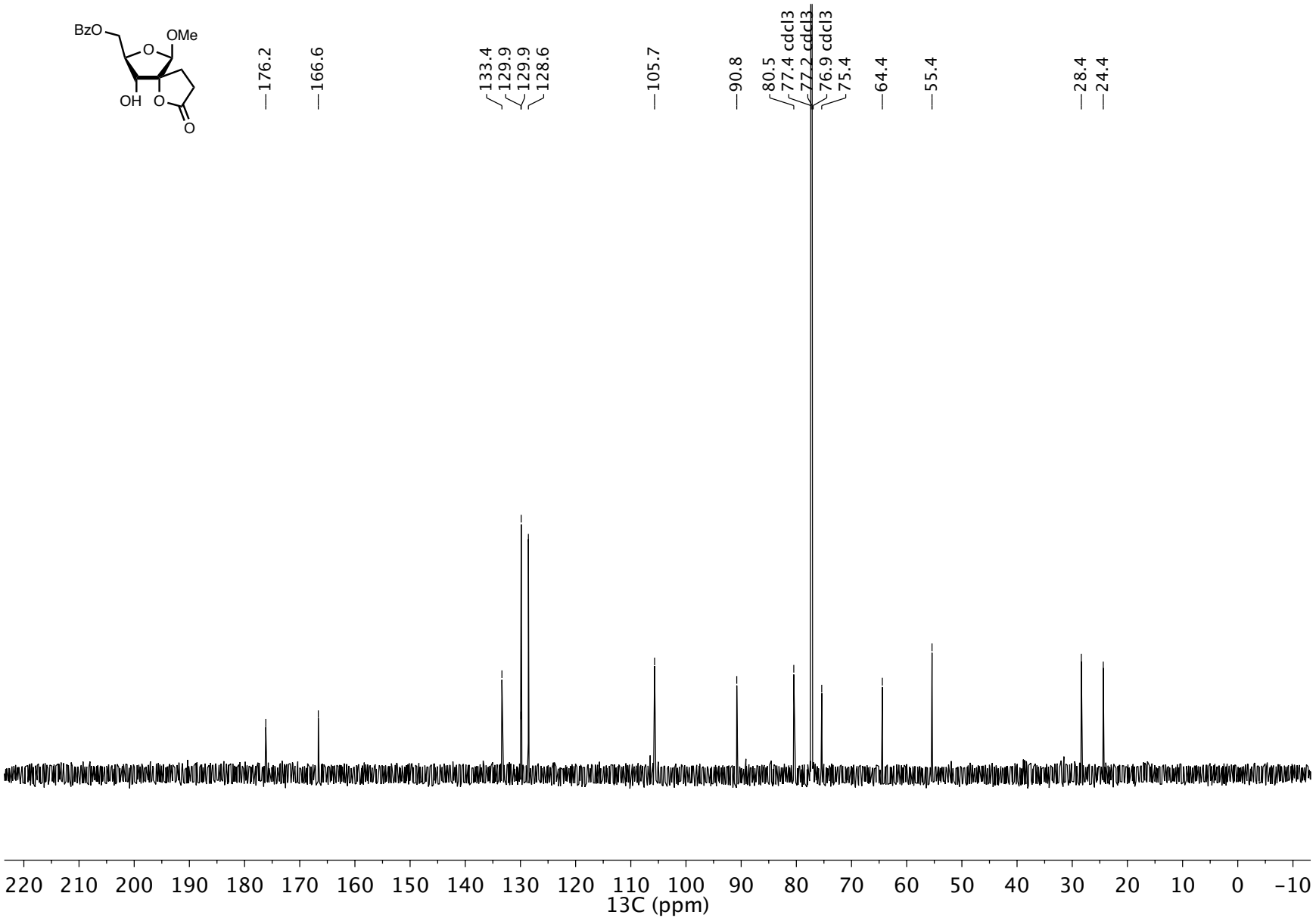
S6 –HSQC (400 MHz, $CDCl_3$)



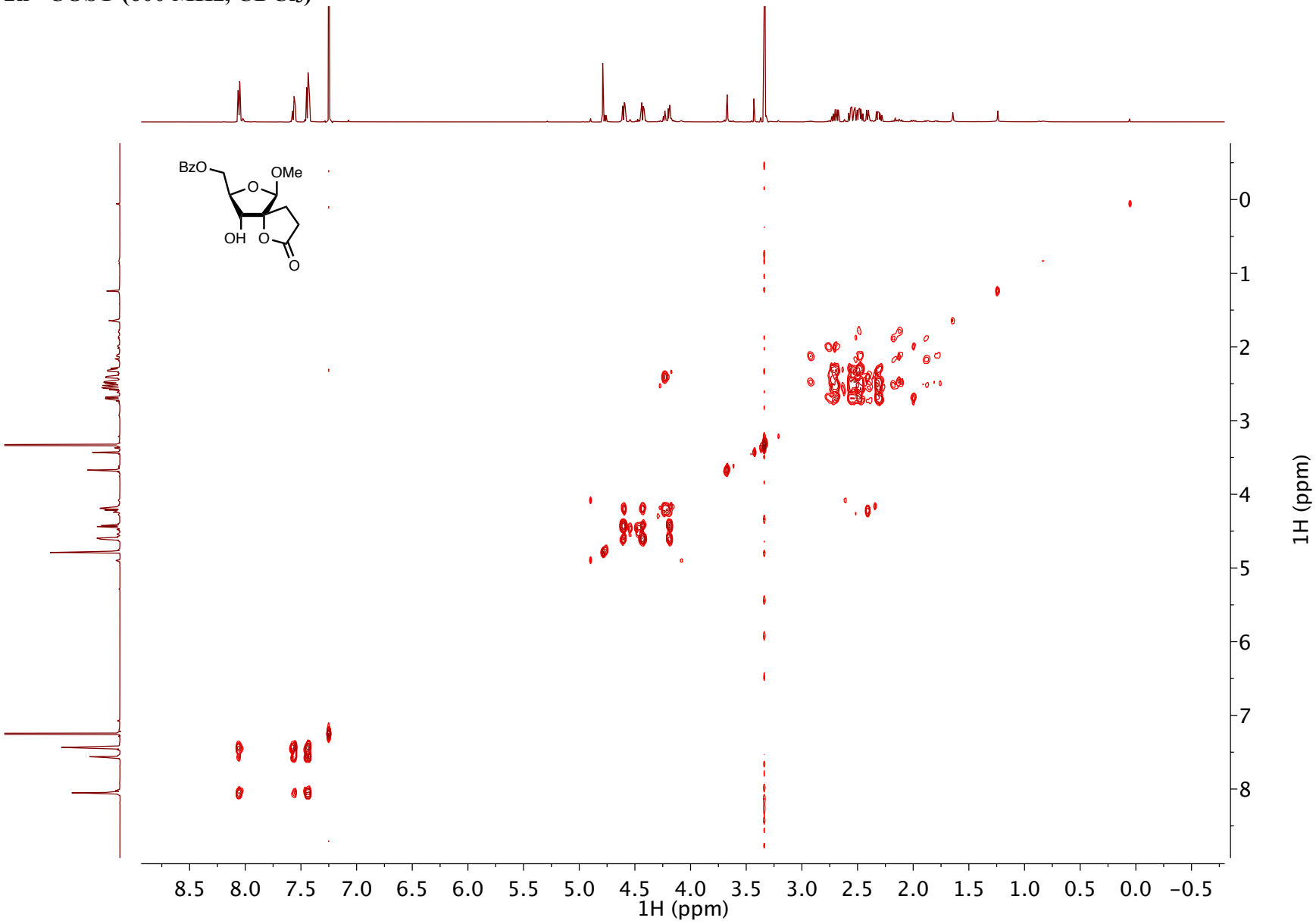
2h –^{1}H NMR (600 MHz, $CDCl_3$)



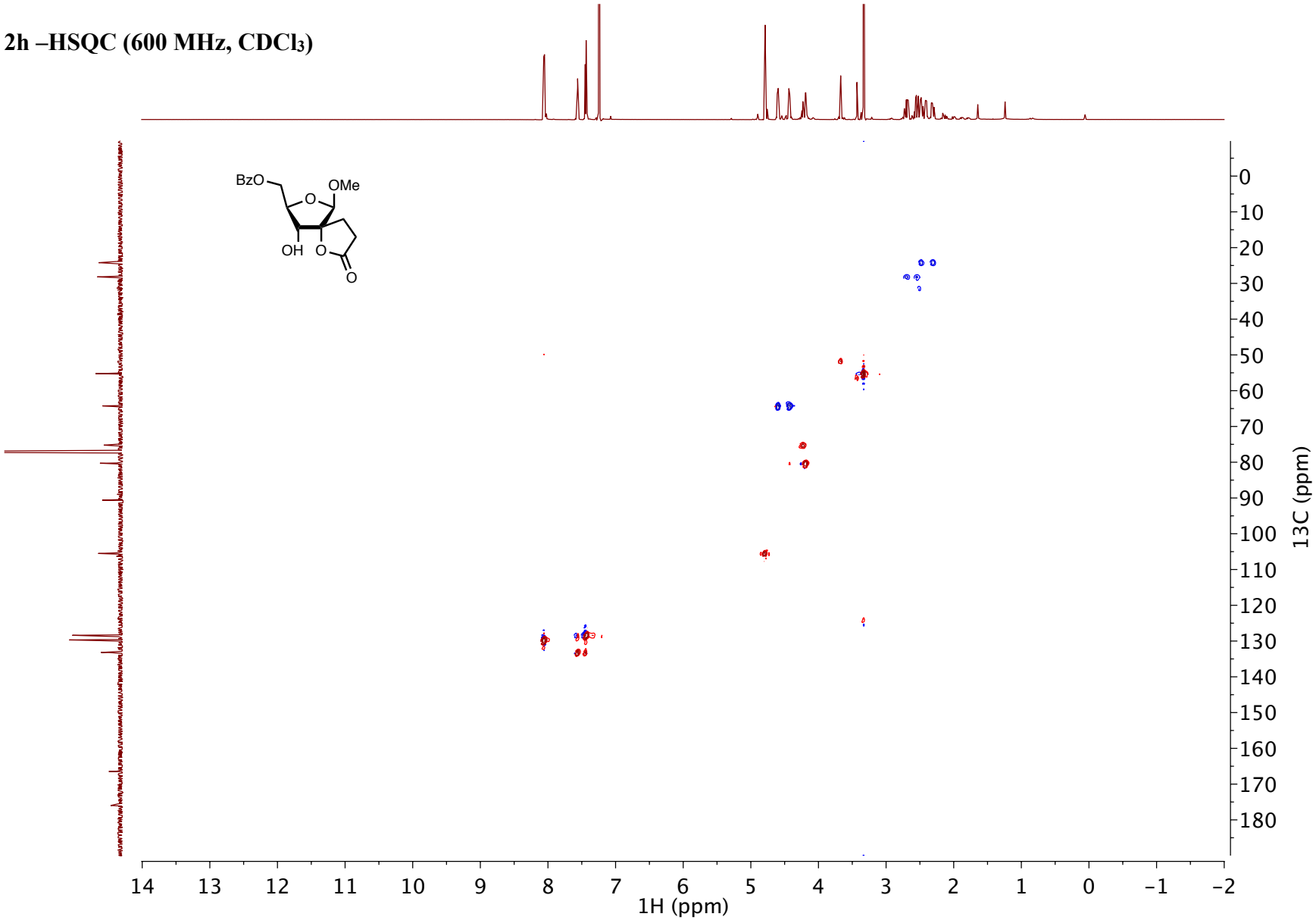
2h –^{13}C NMR (151 MHz, $CDCl_3$)



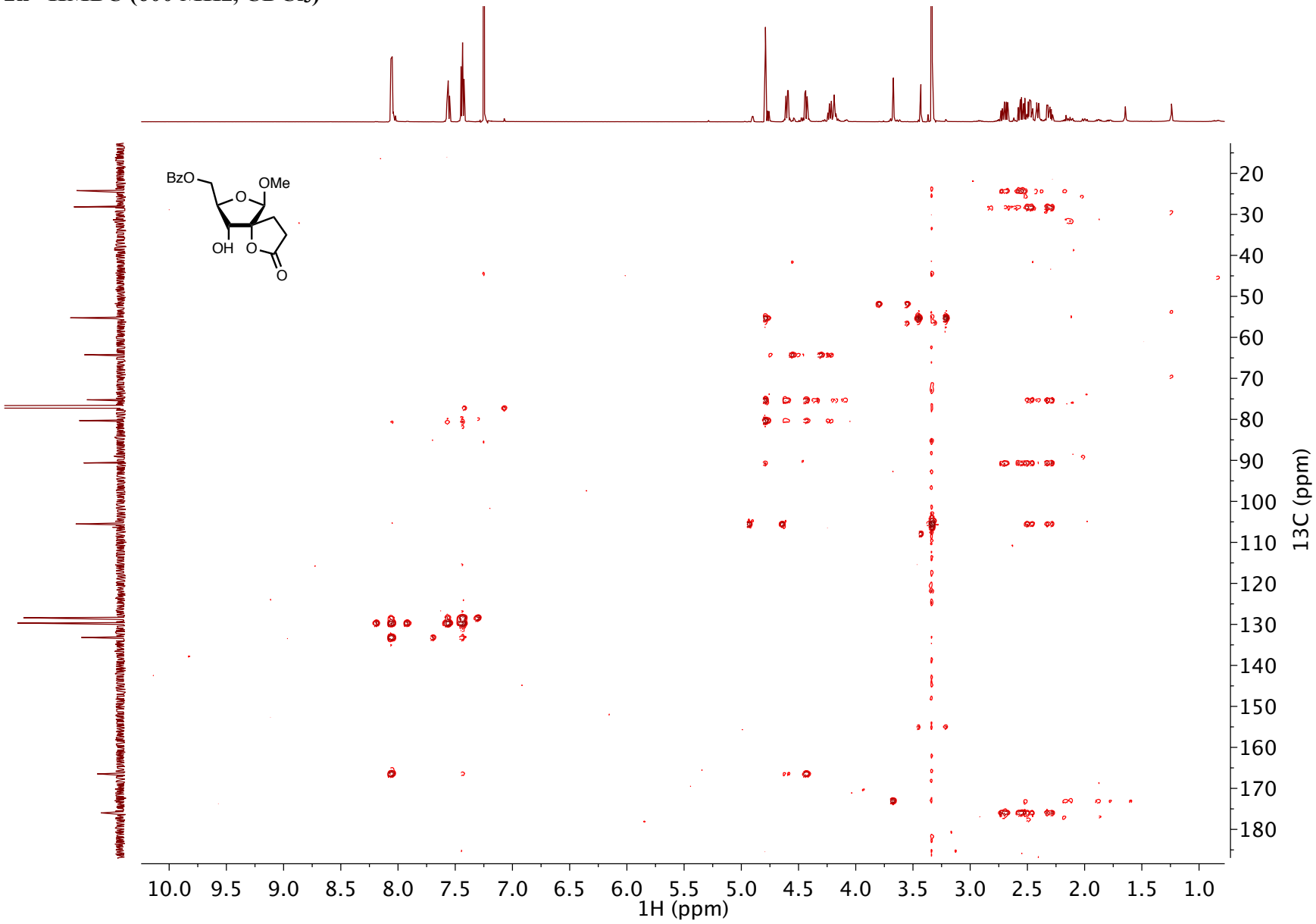
2h –COSY (600 MHz, $CDCl_3$)



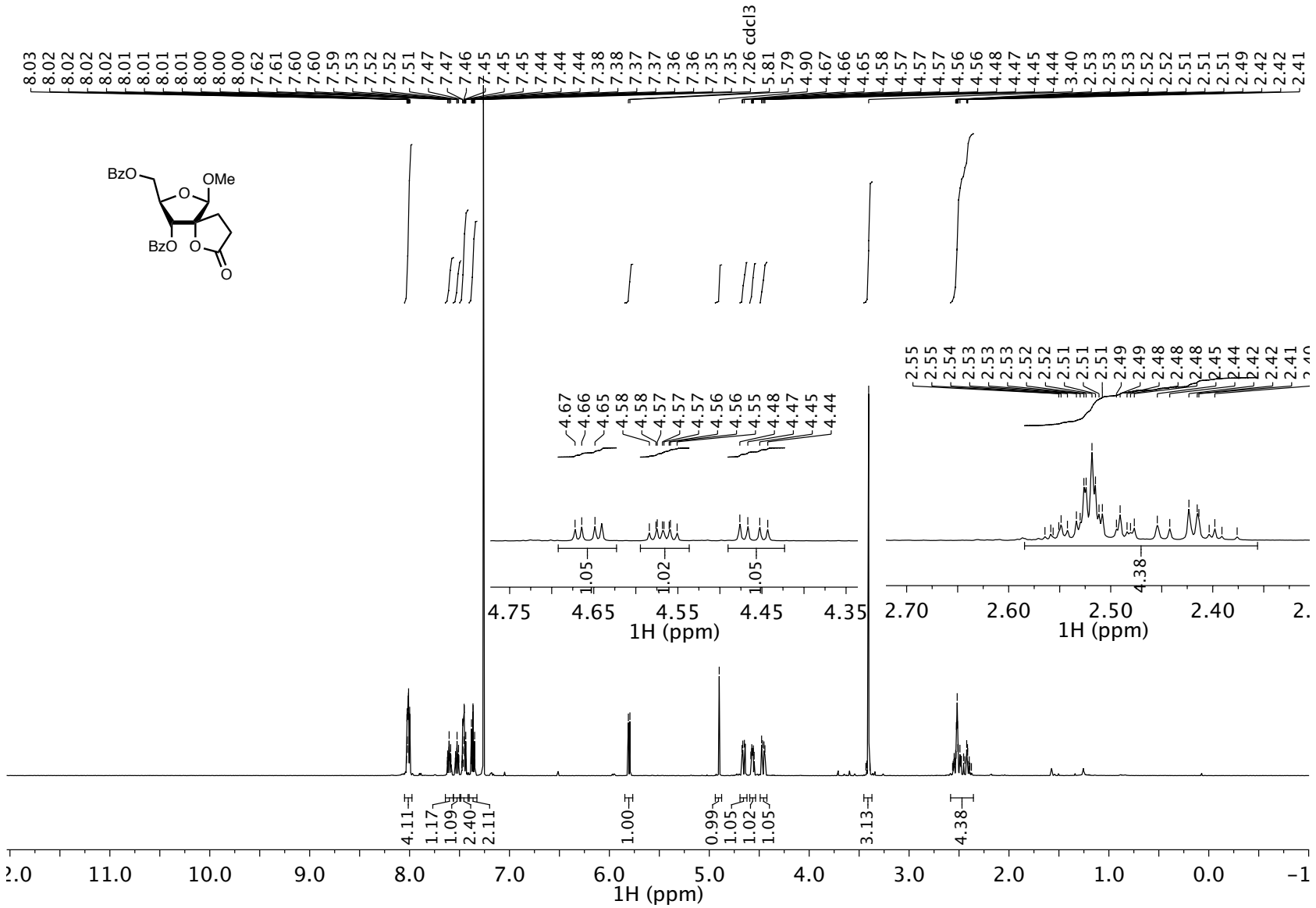
2h –HSQC (600 MHz, $CDCl_3$)



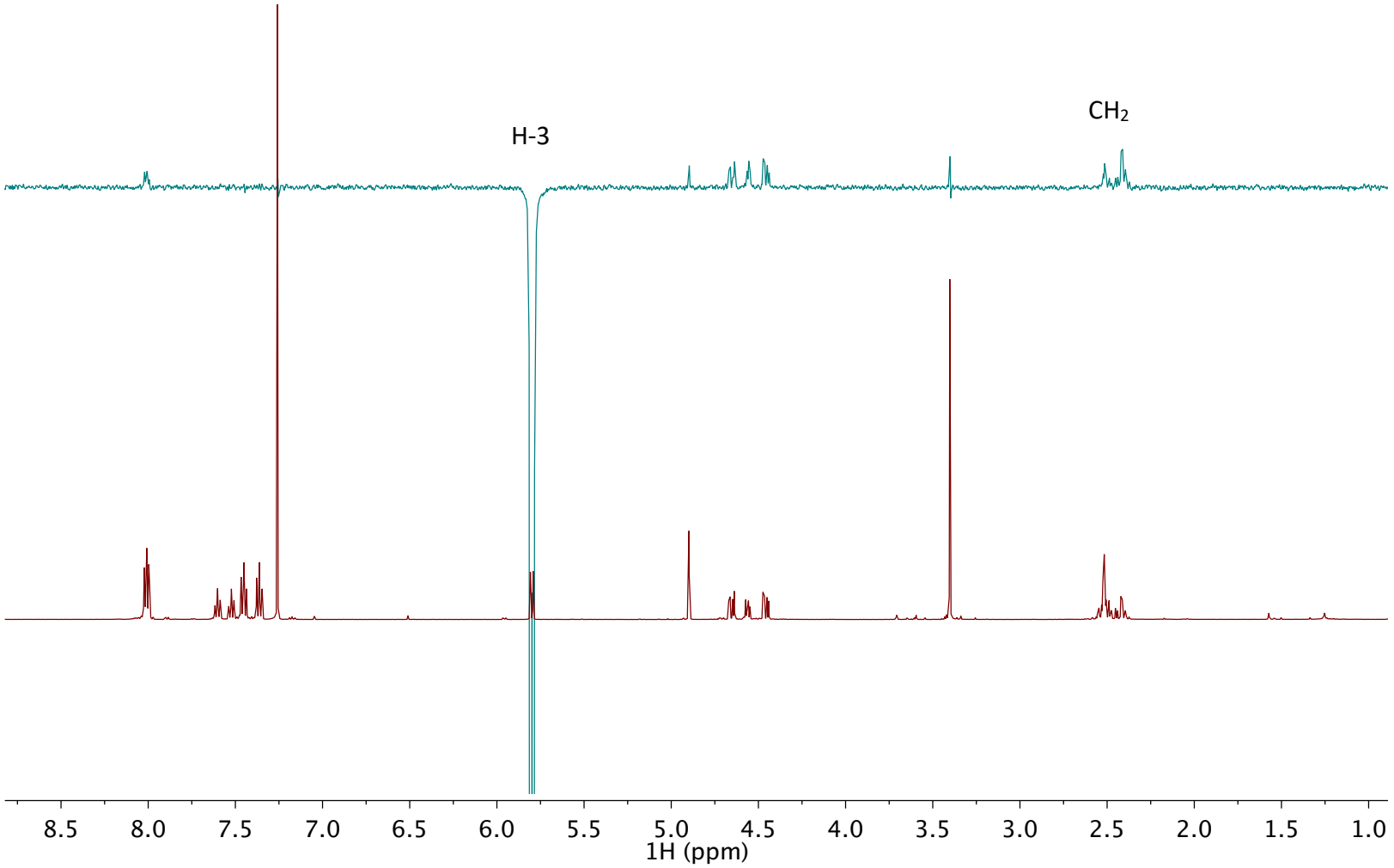
2h –HMBC (600 MHz, $CDCl_3$)



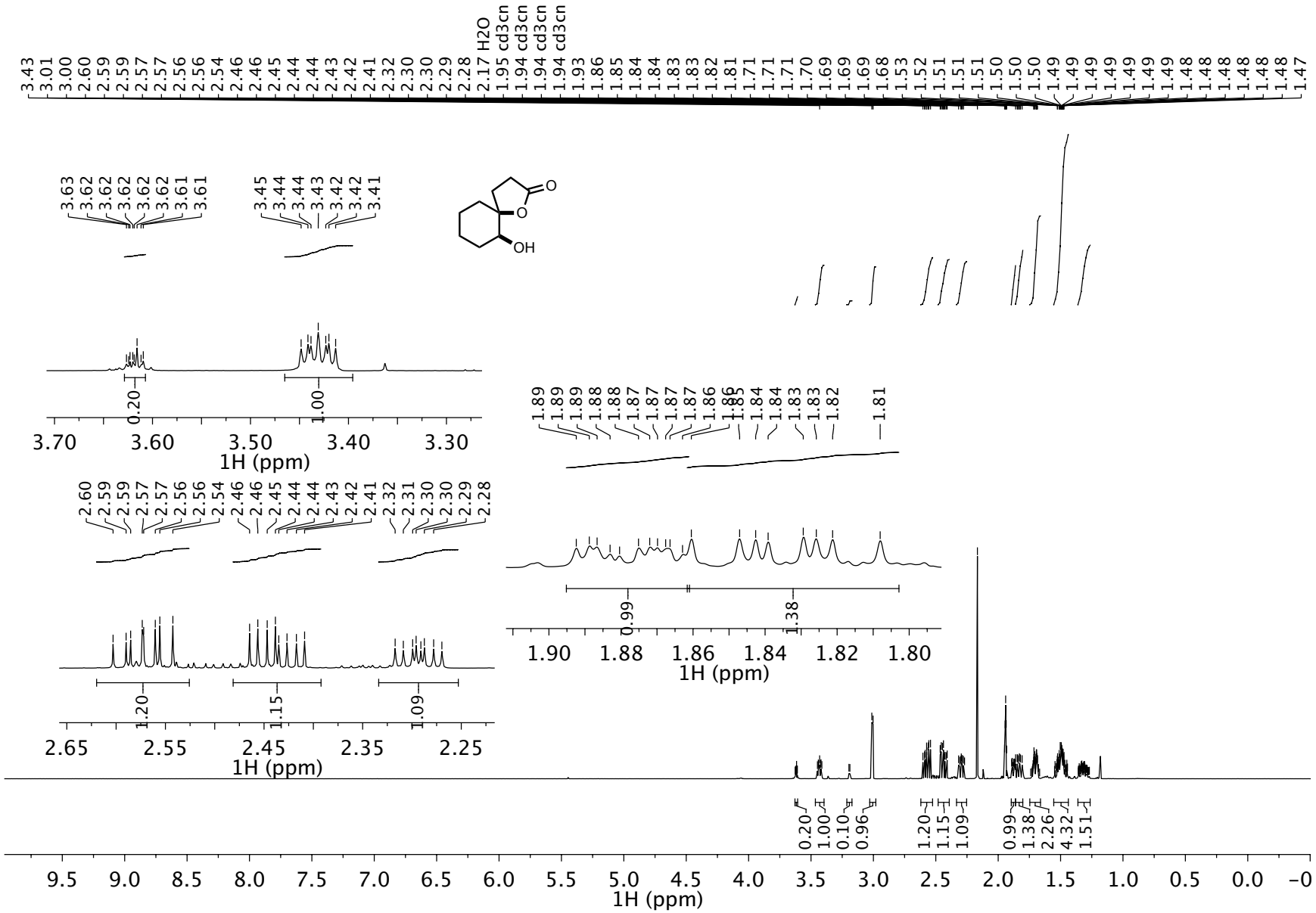
S7 –^{1}H NMR (500 MHz, $CDCl_3$)



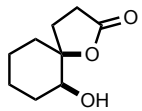
S7 –1D NOESY (500 MHz, $CDCl_3$)



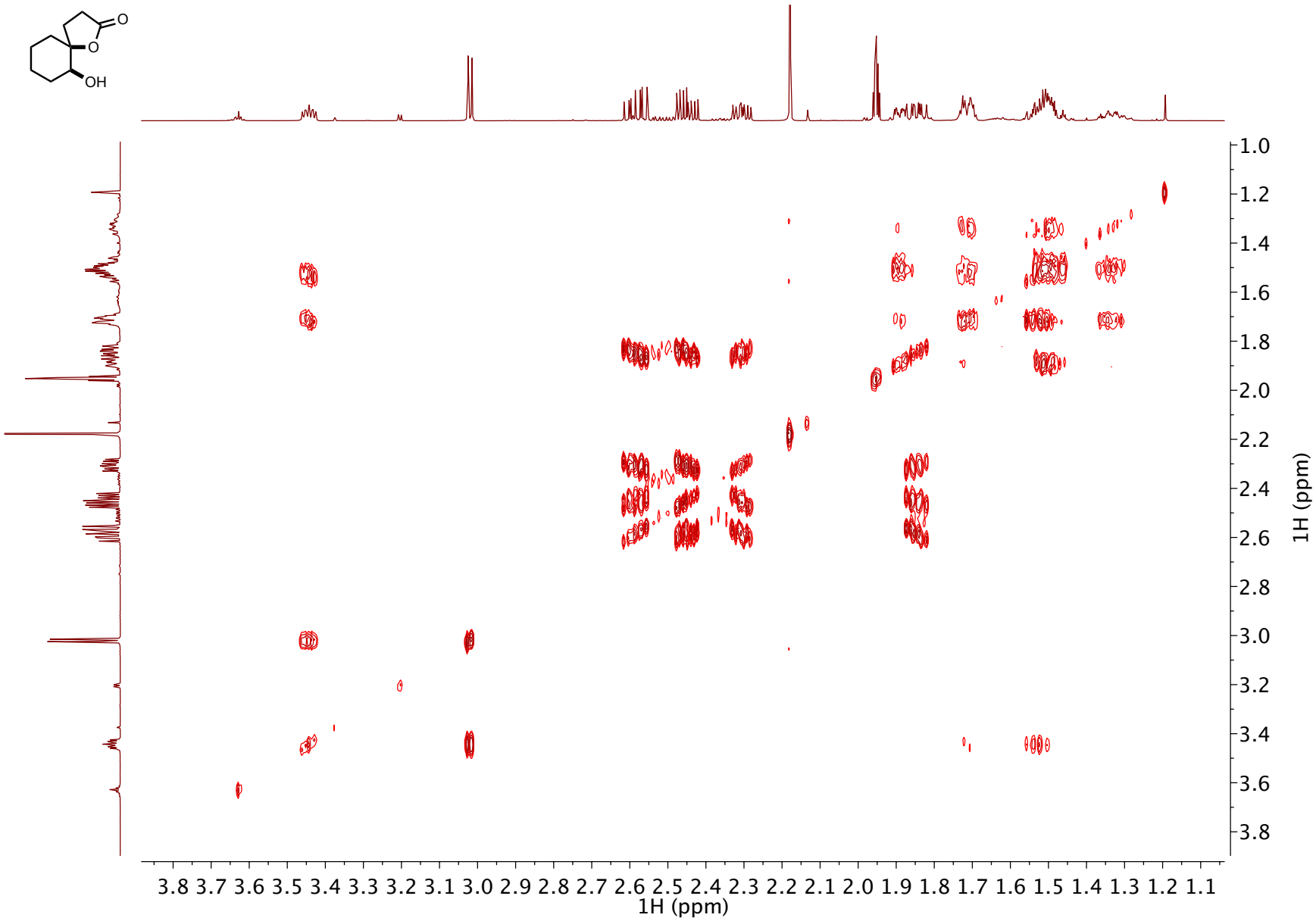
2i –^{1}H NMR (600 MHz, CD_3CN)



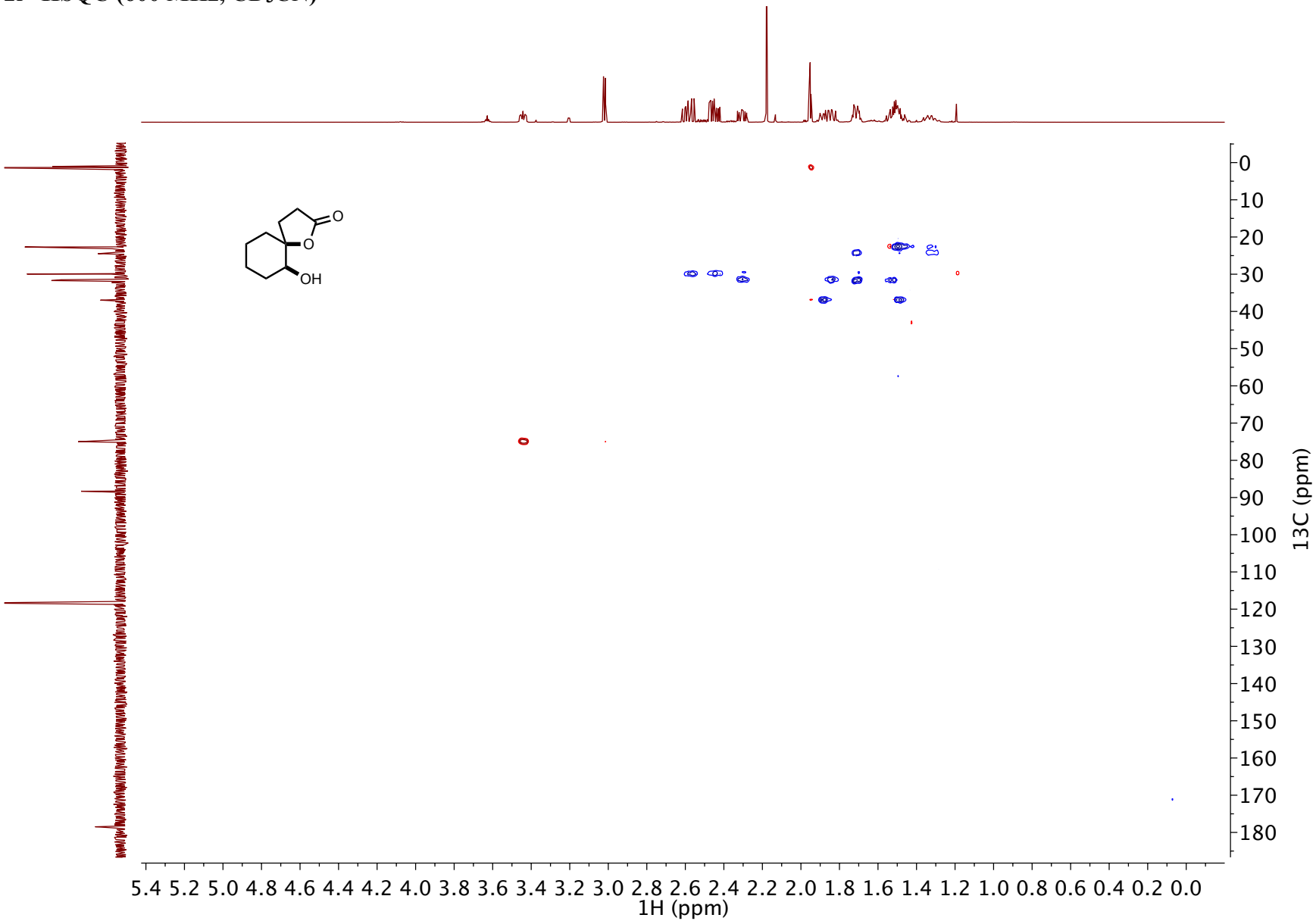
2i –^{13}C NMR (600 MHz, CD_3CN)



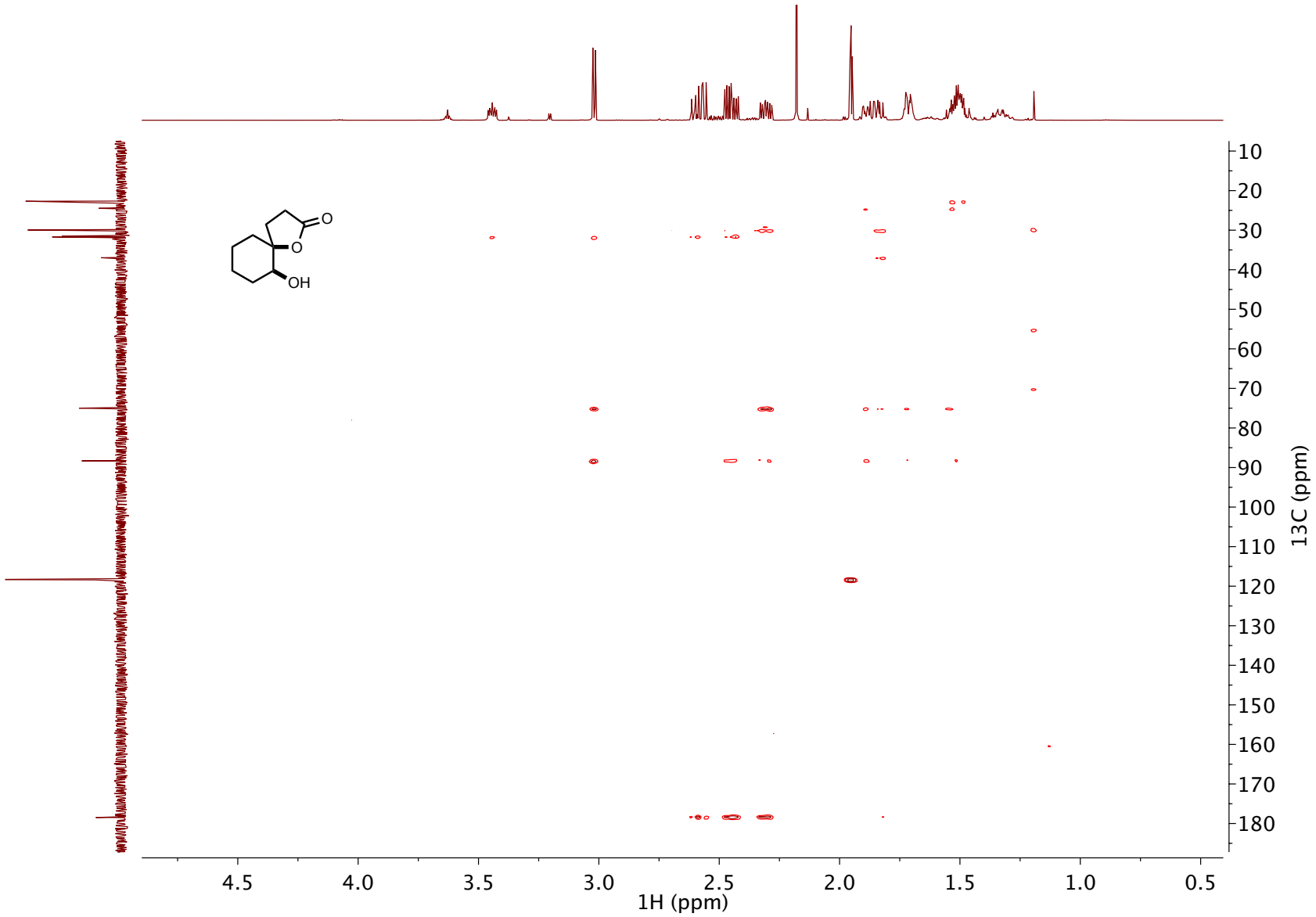
2i –COSY (600 MHz, CD_3CN)



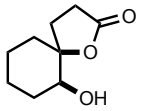
2i –HSQC (600 MHz, CD_3CN)

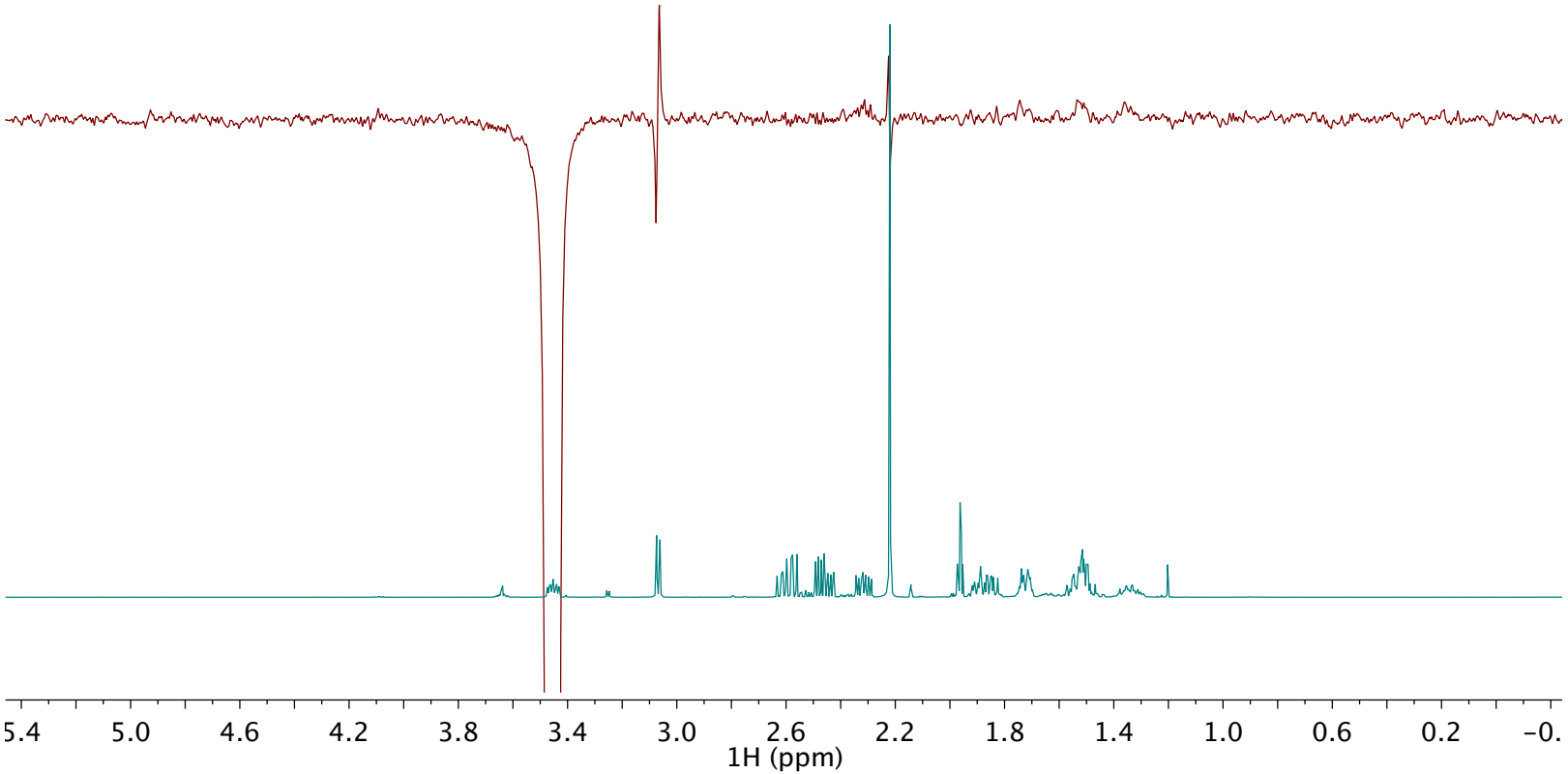


2i –HMBC (600 MHz, CD_3CN)

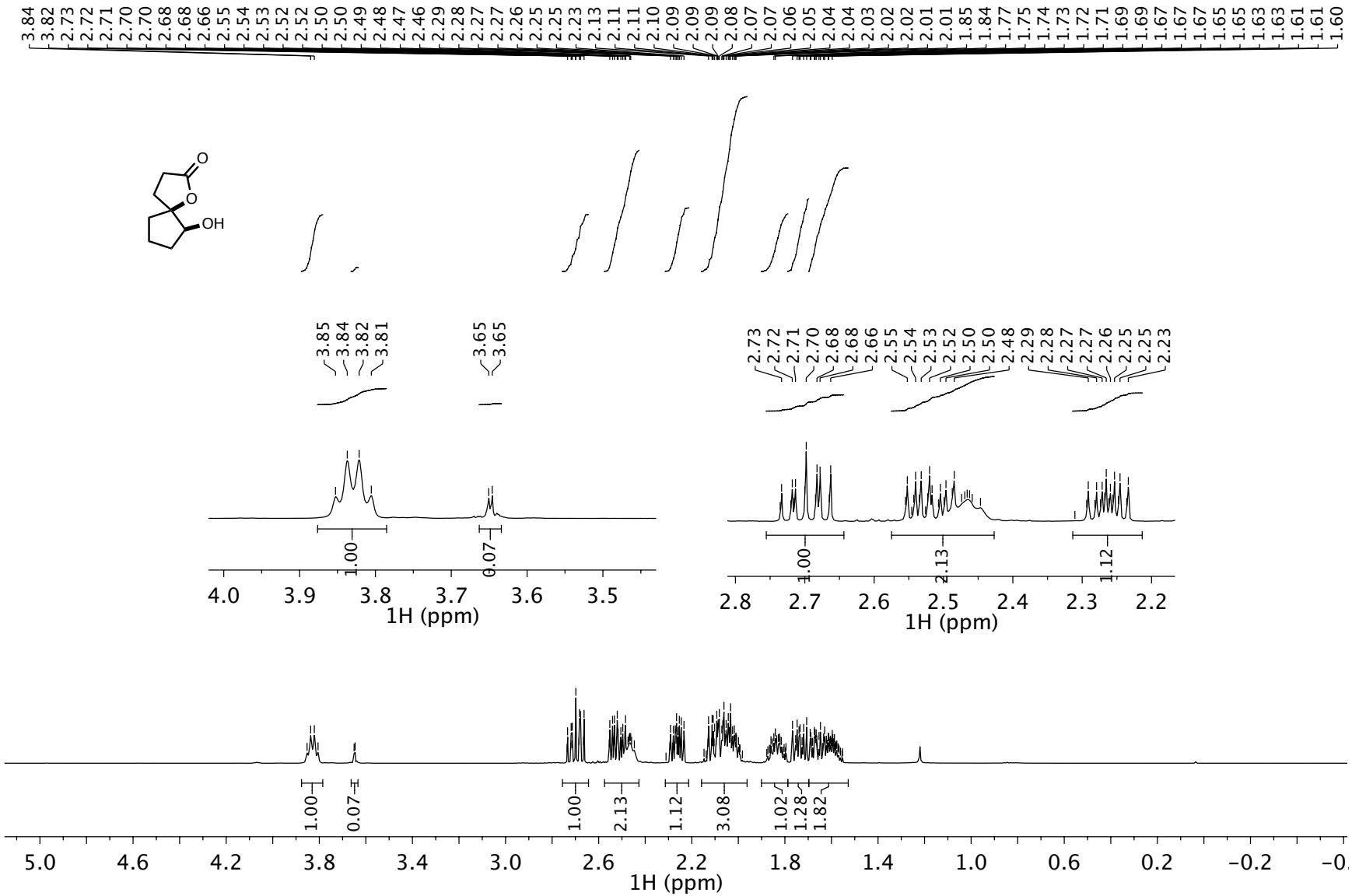


2i –1D NOESY (500 MHz, CD_3CN)

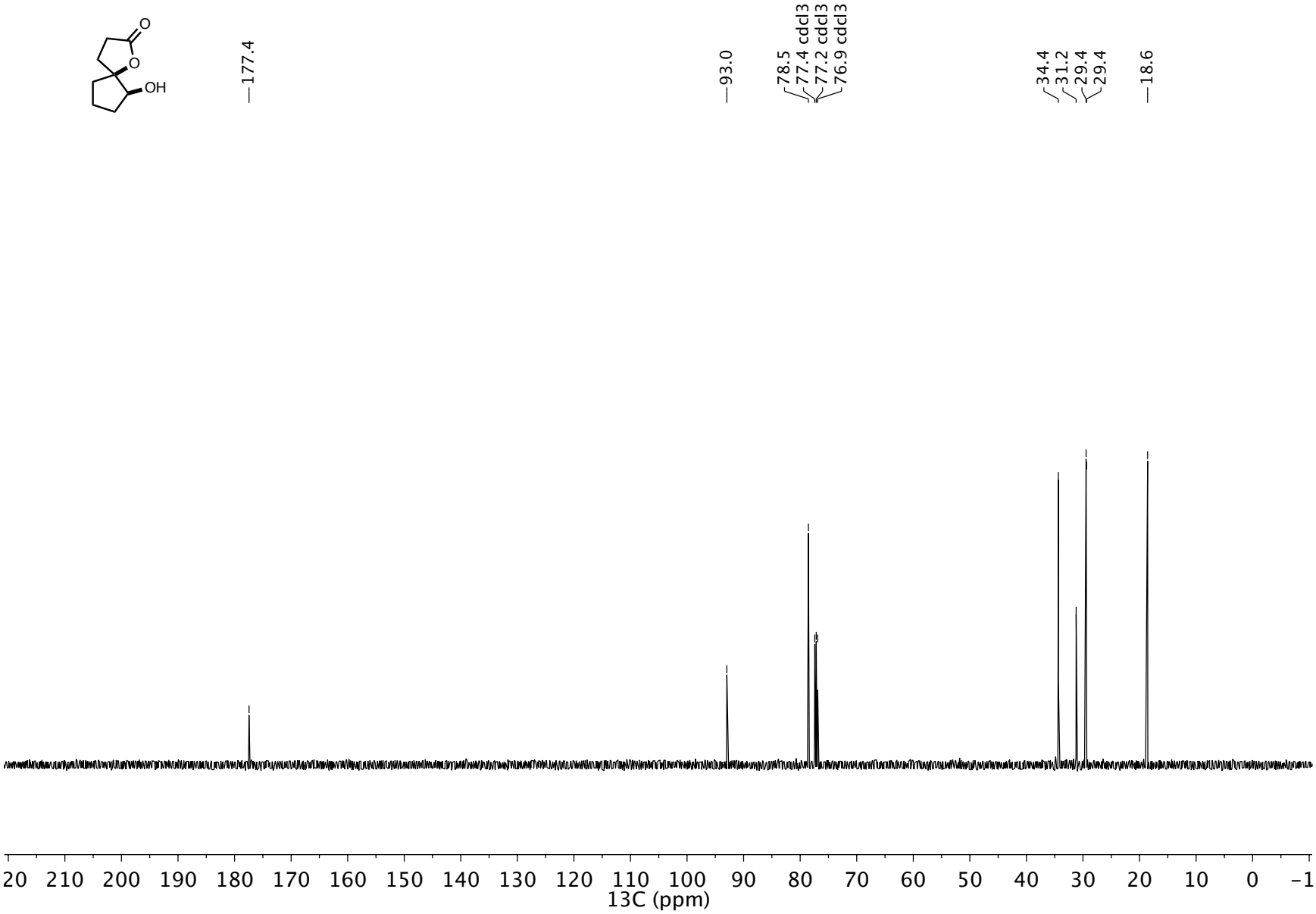




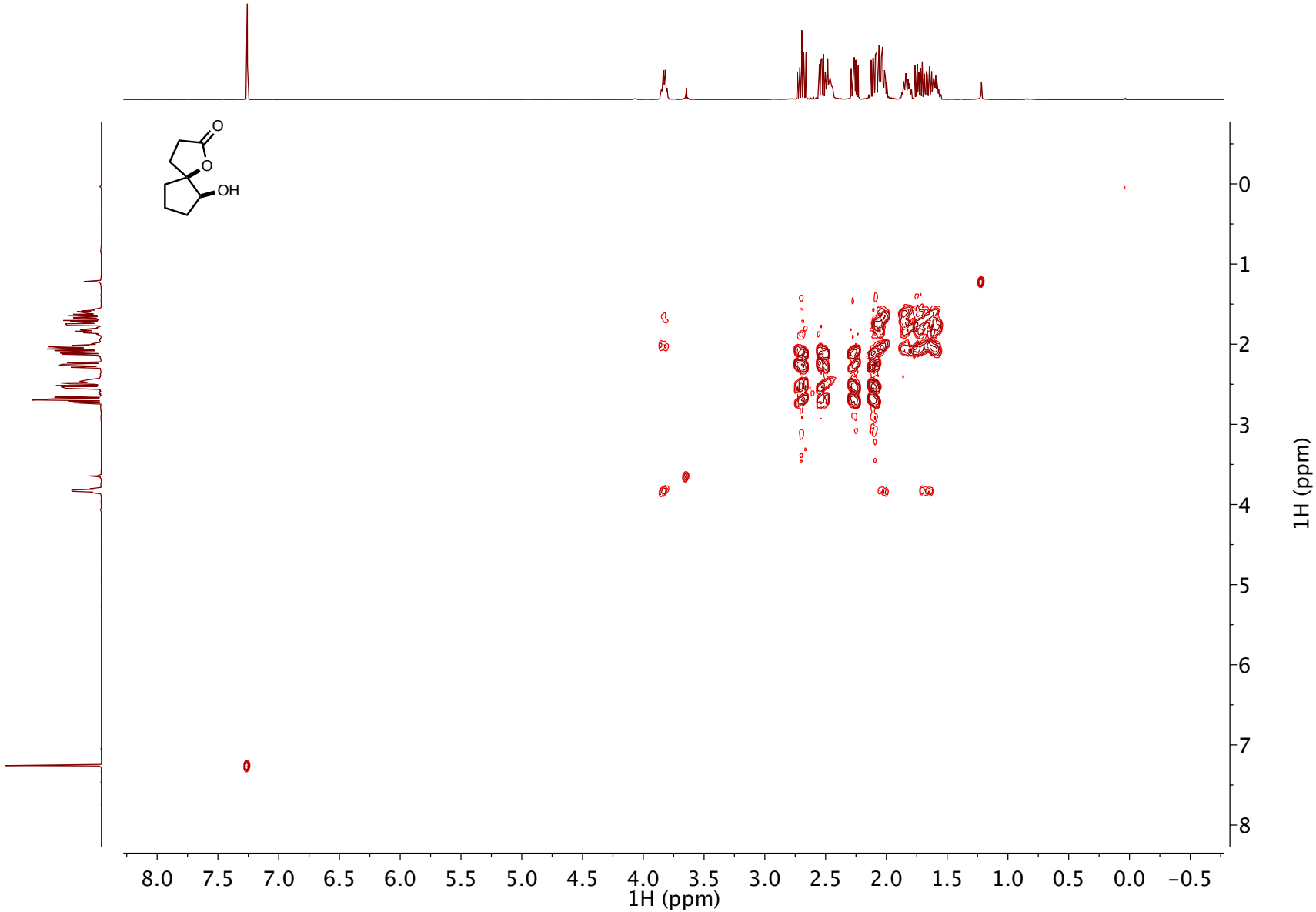
2j –^{1}H NMR (500 MHz, $CDCl_3$)



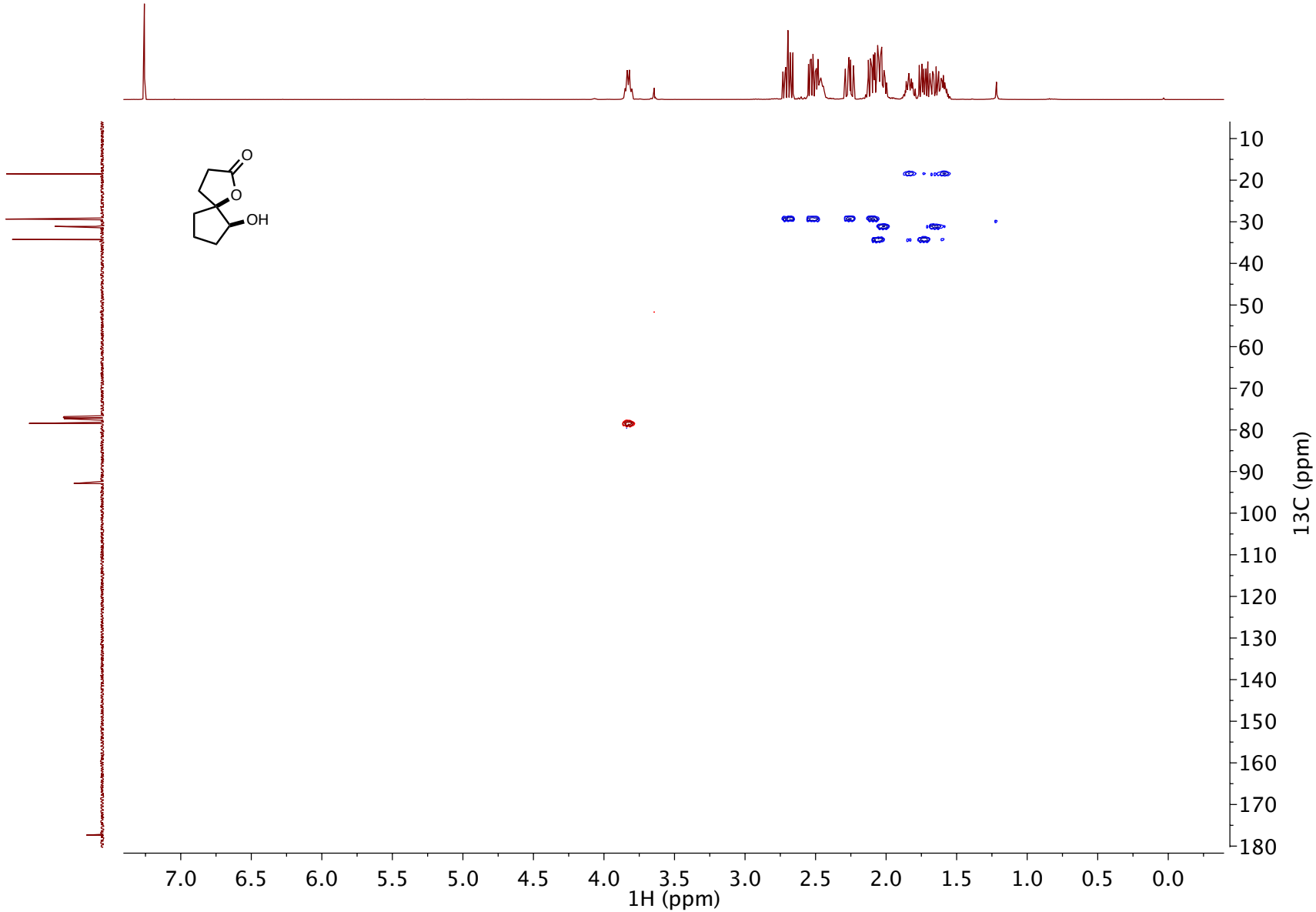
2j –^{13}C NMR (126 MHz, $CDCl_3$)



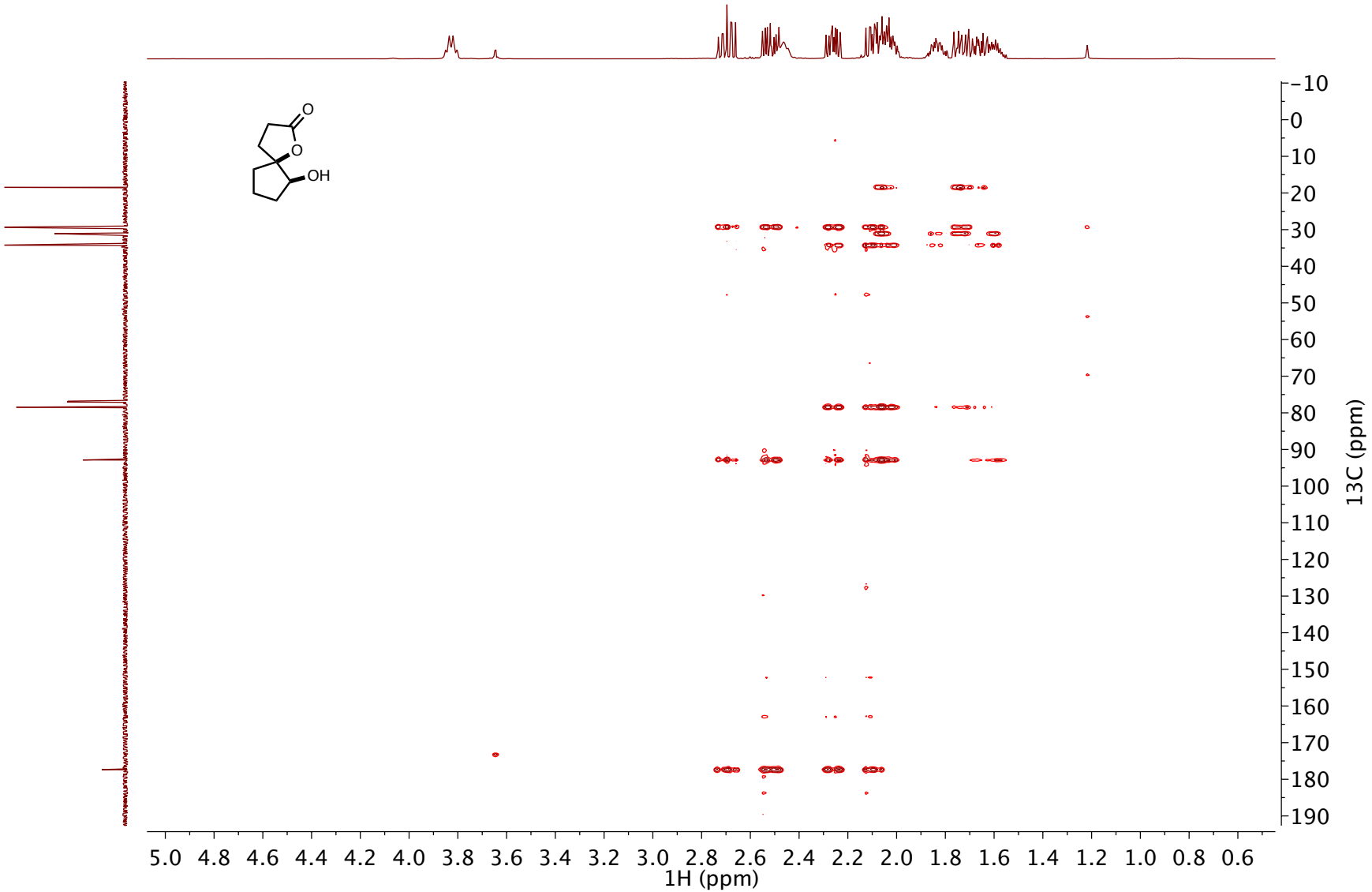
2j – COSY (500 MHz, $CDCl_3$)



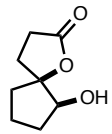
2j – HSQC (500 MHz, $CDCl_3$)

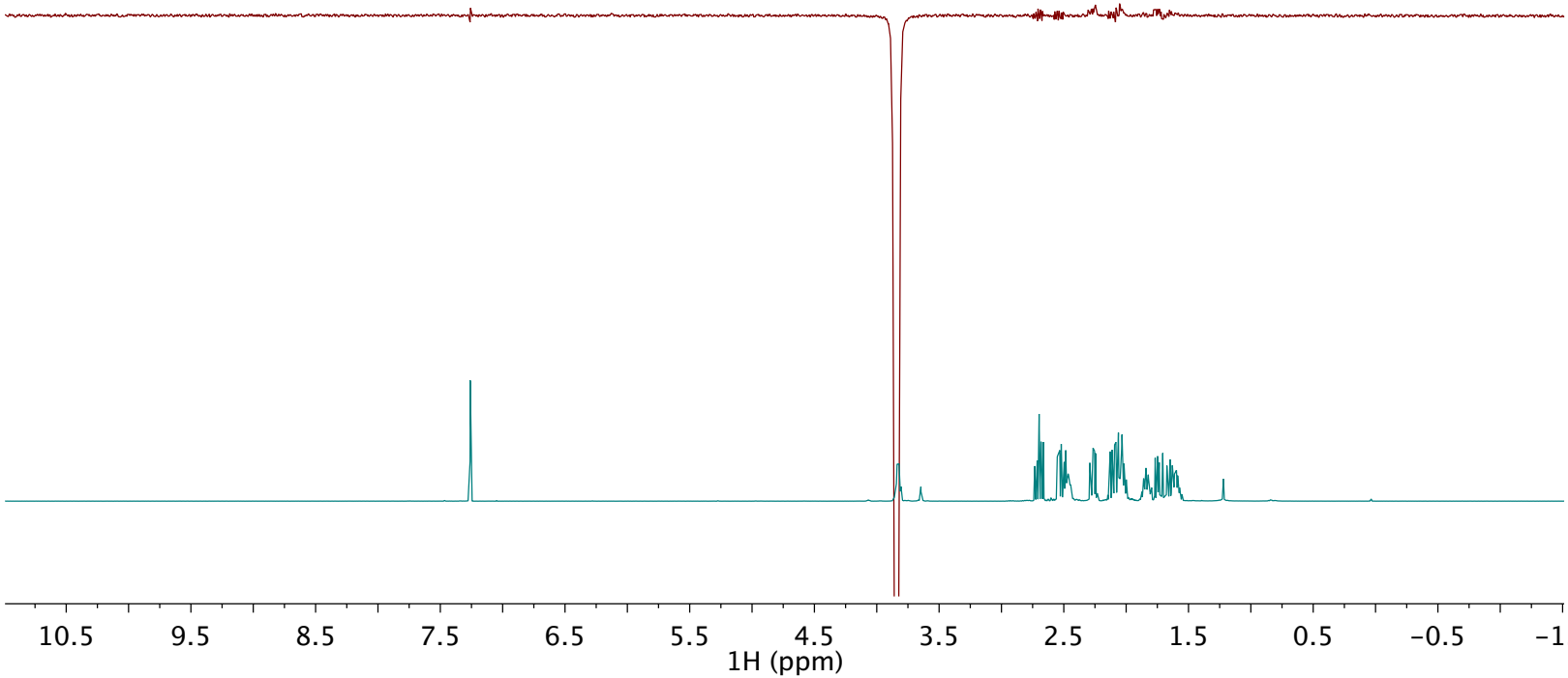


2j – HMBC (500 MHz, $CDCl_3$)

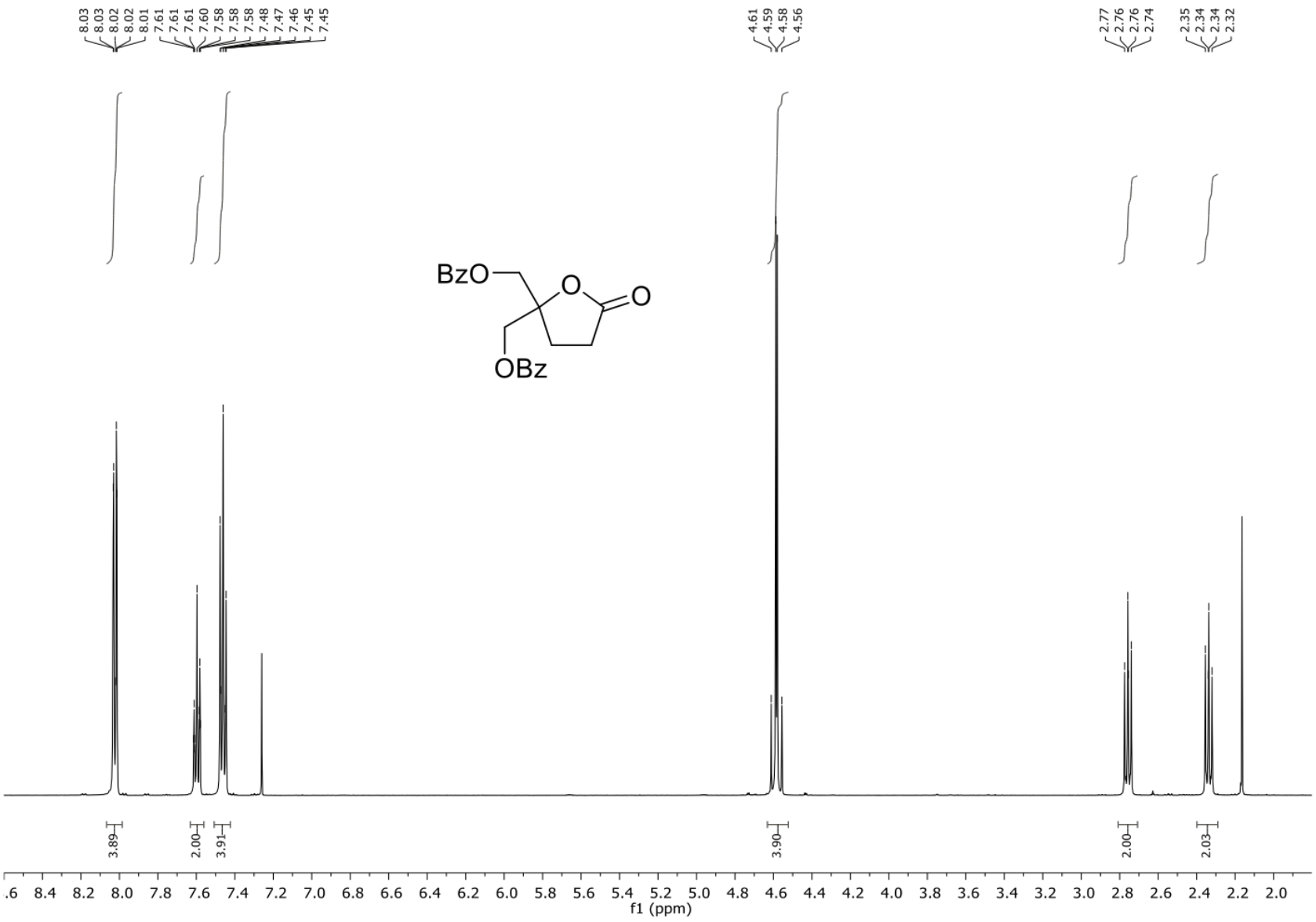


2j –1D NOESY (500 MHz, $CDCl_3$)

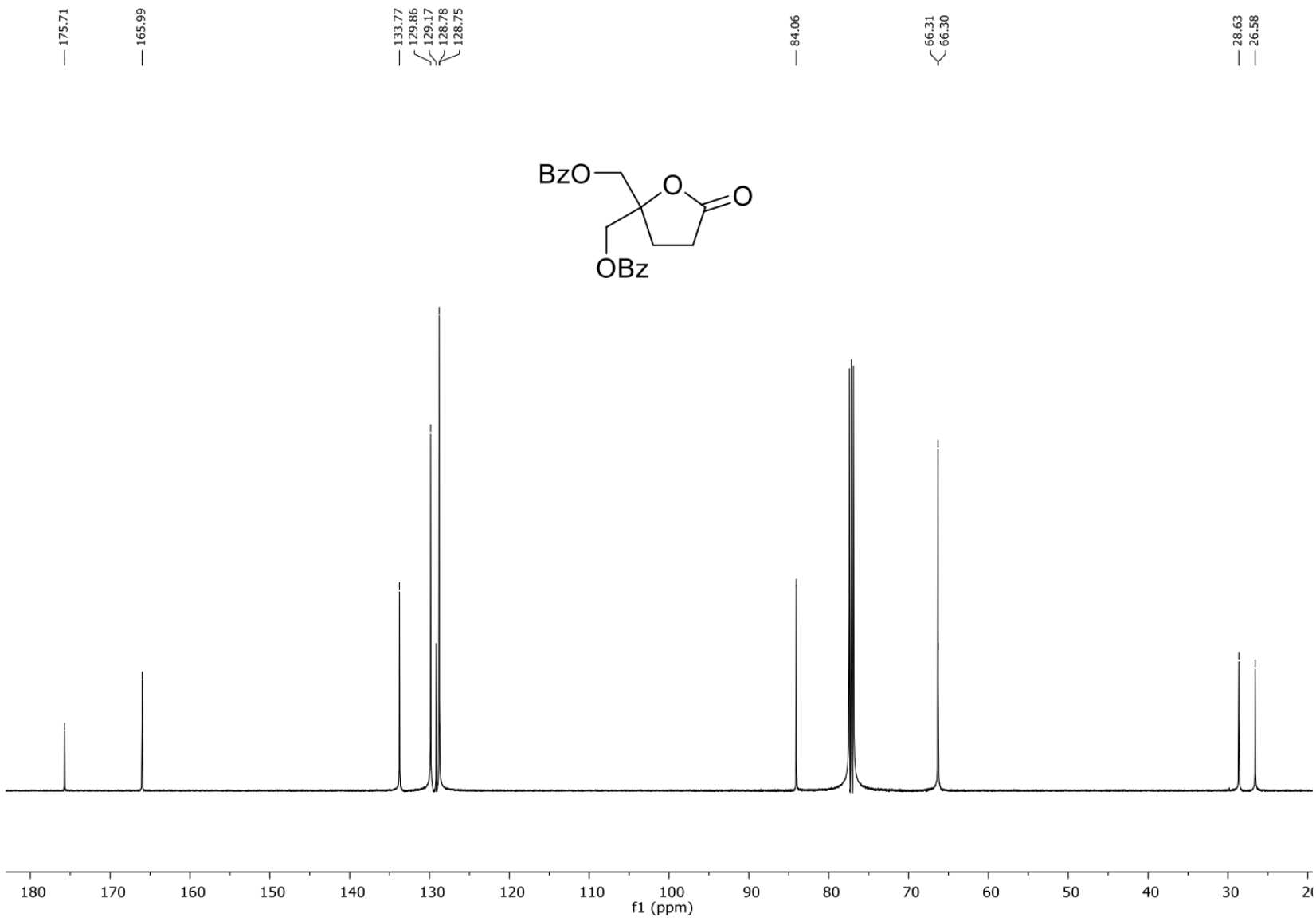




2k –^{1}H NMR (400 MHz, $CDCl_3$)



2k –^{13}C NMR (125 MHz, $CDCl_3$)



2k – COSY (400 MHz, $CDCl_3$)