Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Carbohydrate-Based *N*-Heterocyclic Carbenes for Asymmetric Catalysis

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Supporting Information

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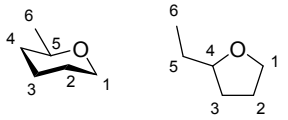
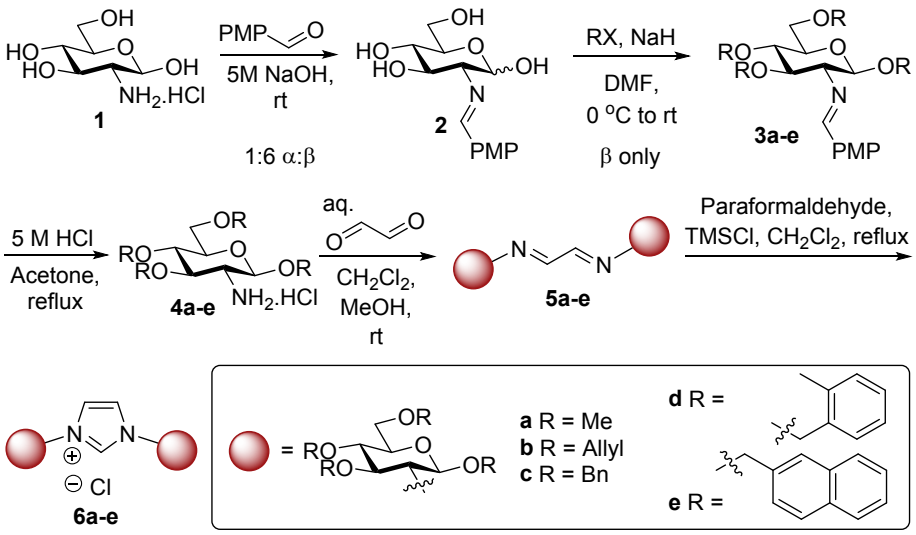
General Experiment Details:

Commercial starting materials were used without further purification unless stated. Carbohydrate substrates were left under high vacuum for (minimum) 1 h prior to initiating reactions. Dry solvents were obtained by distillation or by passage through a column of anhydrous alumina and transferred anhydrously. All reactions were performed under inert atmospheres – unless otherwise stated – of N_2 or Ar by employing Schlenk techniques in conjunction with oven / flame dried glassware. Commercially available Merck Kieselgel $60F_{254}$ aluminium backed plates were used for TLC analysis. TLC plates were stained with acid, ninhydrin, $KMnO_4$, vanillin, or a combination thereof, solutions and thermally developed. FCC was performed according to Still,[1] using Fluorochem 60 silica (40-63 μm particle size). Solvents for flash column chromatography (FCC) and thin layer chromatography (TLC) are listed in volume:volume percentages. Infra-red spectra were recorded in the range 4000-650 cm^{-1} on a Perkin Elmer Spectrum either as neat films or solids compressed onto a diamond window. NMR spectra were recorded on an ECS 400, Varian 400 MHz or Varian 500 MHz spectrometers at 25.0 °C unless otherwise stated. Chemical shifts are quoted in ppm with spectra referenced to the residual protium of the deuterated solvent. Coupling constants are quoted to the nearest 0.5 Hz. Other abbreviations used are: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and *app*. (apparent). Assignments of ^1H NMR and ^{13}C NMR signals were made where possible, using COSY, HSQC and HMBC experiments. Mass spectra were determined by the University of Bristol mass spectrometry service by either; chemical ionisation (CI), electrospray ionisation (ESI) or by matrix-assisted laser deposition/ionization (MALDI) modes. Single crystal analysis was performed on a Bruker-AXS Microstar or a Kappa Apex II diffractometer. Enantiomeric excess was determined by high performance liquid chromatography (HPLC) using an Agilent Infinity 1260 instrument in conjunction with Chiralpak IA, IB and IC columns. Petrol refers to petroleum ether 40-60. See below for carbohydrate numbering nomenclature in pyranoside and furanoside systems.

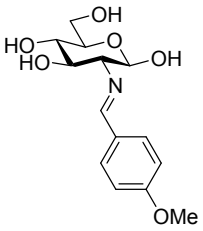


Experimental Procedures and Data:

Imidazolium Chloride 6a-e Synthesis Overview:



2-Amino- 2-deoxy-*N*-4-methoxybenzylidine-D-glucopyranose (2):



As reported by Feigel and co-workers.[2] To a solution of D-glucosamine hydrochloride (2.00 g, 9.26 mmol) in 5 M NaOH (2.04 mL, 10.2 mmol) at rt, was added *p*-anisaldehyde (1.13 mL, 9.26 mmol). The solution was shaken until a white solid precipitated (5 min) and then stored at 4 °C for 20 h. Buchner filtration yielded a cream residue which was washed with H_2O (2 x 5 mL) and 2:1 Et_2O:hexane (2 x 5 mL) to yield **2** (2.64 g, 95%, ~1:6 α:β) as an off white powder;

ν_{max} / cm^{-1} (film): 3484, 3320, 2932, 2895, 1639, 1604, 1515, 1452, 1429, 1371, 1314, 1250, 1172, 1151, 1104, 1061, 1028;

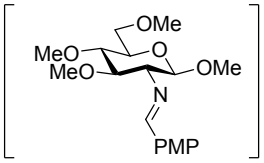
^{1}H NMR (400 MHz, $(CD_3)_2SO$) *data for the β-anomer* δ: 8.11 (1H, s, HC=N), 7.68 (2H, *app.* d, *J* = 9.0 Hz, ArCH), 6.98 (2H, *app.* d, *J* = 9.0 Hz, ArCH), 6.52 (1H, br, OH), 4.98 (1H, br, OH), 4.85 (1H, br, OH), 4.69 (1H, d, *J* = 8.0 Hz, H-1), 4.56 (1H, br, OH), 3.79 (3H, s, OCH_3), 3.72 (1H, *app.* d, *J* = 11.0 Hz, H-6a), 3.49 (1H, dd, *J* = 11.0 and 6.0 Hz, H-6b), 3.43 (1H, *app.* t, *J* = 9.0 Hz, H-3), 3.23 (1H, ddd, *J* = 9.0, 6.0 and 2.0 Hz, H-5), 3.15 (1H, *app.* t, *J* = 9.0 Hz, H-4), 2.79 (1H, dd, *J* = 9.0 and 8.0 Hz, H-2). *Characteristic data for the α-anomer* 4.91 (0.15H, d, *J* = 3.5 Hz, H-1);

^{13}C NMR (100 MHz, $(CD_3)_2SO$) *data for the β-anomer* δ: 161.2 (C=N), 161.0 (Ar*C*OCH$_3$), 129.6 (ArCH), 192.1 (Ar*C*(HC=N)), 113.9 (ArCH), 95.7 (C-1), 78.2 (C-2), 76.9 (C-5), 74.6 (C-3), 70.4 (C-4), 61.3 (C-6), 55.3 (OCH$_3$). *Spectroscopic data in agreement with literature*.[2]

General Procedure A: Alkylation of 2

Adapted from Schmidt and co-workers.[3] *Step 1:* To a solution of **2** (100 mol%) in anhydrous DMF (0.3 M) and electrophile (475 mol%) at 0 °C, was added NaH (60% dispersion in mineral oil, 475 mol%) in four portions over 2 h. The resulting mixture was allowed to warm to rt over 14 h. Excess NaH was quenched by addition of EtOAc and the solvent was removed *in vacuo*. The residue was suspended in EtOAc, washed with H_2O, then dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude material was further purified by FCC to yield **3a-e** and immediately used in the next step. *Step 2:* To a solution of the resulting imine (100 mol%) in solvent (0.5 M) at rt, was added 5 M HCl (110 mol%) and the resulting solution was refluxed (60 °C) for 0.3 h. The precipitate was collected by Büchner filtration and washed with chilled acetone to yield the crude material. Purification by recrystallization (EtOH) afforded the pure products **4a-e**.

Methyl 2-amino-2-deoxy-*N*-4-methoxybenzylidine-3,4,6-tri-*O*-methyl -β-D-glucopyranoside (3a):



Following General Procedure A – Step 1: Electrophile = MeI and FCC (80:20 to 60:40 petrol:EtOAc + 5% Et$_3$N) to yield **3a** (1.74 g, 73%) as a colourless oil with trace impurities (< 5 %) of *p*-anisaldehyde.

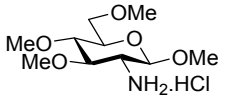
R_f = 0.1 (60:40 petrol:EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (1H, s, HC=N), 7.72 (2H, *app.* d, *J* = 8.5 Hz, ArCH), 6.92 (2H, *app.* d, *J* = 8.5 Hz, ArCH), 4.53 (1H, d, *J* = 8.0 Hz, H-1), 3.84 (3H, s, ArCO*C*H$_3$), 3.70 (1H, dd, *J* = 2.0 and 10.5 Hz, H-6a), 3.62 (1H, dd, *J* = 4.5 and 10.5 Hz, H-6b), 3.55 (3H, s, OCH$_3$), 3.47-3.42 (2H, m, H-3 and H-5) 3.46 (3H, s, OCH$_3$), 3.43 (3H, s, OCH$_3$), 3.41 (3H, s, OCH$_3$), 3.25 (1H, *app.* t, *J* = 9.5 Hz, H-4), 3.10 (1H, dd, *J* = 8.0 and 9.5 Hz, H-2);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.4 (HC=N), 161.9 (Ar*C*OCH$_3$), 130.1 (ArCH), 129.3 (ArC), 114.0 (ArCH), 102.7 (C-1), 85.2 (C-3), 79.5 (C-4), 76.7 (C-2), 74.9 (C-5), 71.5 (C-6), 60.7 (OCH$_3$), 60.4 (OCH$_3$), 59.4 (OCH$_3$), 57.0 (OCH$_3$), 55.4 (ArCO*C*H$_3$);

m/z HRMS (ESI): Found $[M+Na]^+$ 376.1727, $C_{18}H_{27}N_2O_6Na$ requires 376.1731.

Methyl 2-amino-2-deoxy-3,4,6-tri-*O*-methyl-β-D-glucopyanoside hydrochloride (4a):



Following General Procedure A – Step 2: Imine = **3a** (5.22 g, 14.77 mmol); solvent = Et_2O; the purification method was modified from the general procedure. After refluxing in Et_2O, a biphasic solution formed upon cooling to rt. The aqueous phase was separated and concentrated *in vacuo*. The resulting residue was triturated with hot Et_2O (2 x 40 mL) and the excess solvent decanted. The remaining material was dried under high vacuum to yield **4a** (3.75 g, 94%) as an amorphous solid;

ν_{max} / cm^{-1} (film): 2884, 1597, 1505, 1443, 1383, 1189, 1170, 1109, 1091, 1064, 1052;

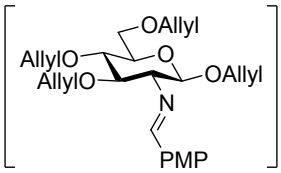
^{1}H NMR (400 MHz, CD_3OD) δ: 4.46 (1H, d, *J* = 8.5 Hz, H-1), 3.67-3.65 (2H, m, H-6a and H-6b), 3.66 (3H, s, CH_3), 3.56 (3H, s, CH_3), 3.55 (3H, s, CH_3), 3.44 (1H, ddd, *J* = 3.5, 6.0 and 9.5 Hz, H-5), 3.42 (3H, s, CH_3), 3.39 (1H, dd, *J* = 8.5 and 10.5 Hz, H-3), 3.29 (1H, dd, *J* = 8.5 and 9.5 Hz, H-4), 2.85 (1H, dd, *J* = 8.5 and 10.5 Hz, H-2);

^{13}C NMR (100 MHz, CD_3OD) δ: 109.0 (C-1), 90.2 (C-3), 89.2 (C-4), 83.6 (C-5), 79.9 (C-6), 69.3 (OCH_3), 69.1 (OCH_3), 68.0 (OCH_3), 66.0 (OCH_3), 63.9 (C-2);

m/z HRMS (ESI): Found $[M(-HCl)+Na]^+$ 258.1304, $C_{10}H_{21}N_1O_5Na$ requires 258.1311;

$[\alpha]^{21}_D$ = 14 (c = 1.0, MeOH).

Allyl 2-amino-2-deoxy-*N*-4-methoxybenzylidine-3,4,6-tri-*O*-allyl-β-D-glucopyanoside (3b):



Following General Procedure A – Step 1: Electrophile = allyl bromide and FCC (90:10 to 80:20 petrol:EtOAc + 5% Et_3N) yielded **3b** (984 mg, 64%, α:β 1:4) as a colourless oil with trace impurities (< 5 %) of *p*-anisaldehyde.

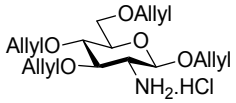
R_f = 0.6 (60:40 petrol:EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$) δ: *data for the β-anomer* 8.23 (1H, s, HC=N), 7.69 (2H, d, *J* = 8.5 Hz, ArCH), 6.93 (2H, d, *J* = 8.5 Hz, ArCH), 6.01-5.89 (3H, m, CH_2CHCH_2O), 5.86-5.70 (1H, m, CH_2CHCH_2O), 5.34-5.01 (8H, m, CH_2CHCH_2O), 4.66 (1H, d, *J* = 8.0 Hz, H-1), 4.35 (2H, m, CH_2CHCH_2O), 4.17-3.99 (6H, m, OCH_2CH), 3.85 (3H, s, $ArCOCH_3$) 3.77 (1H, dd, *J* = 2.0 and 11.0 Hz, H-6a), 3.69 (1H, dd, *J* = 4.5 and 11.0 Hz, H-6b), 3.66 (1H, *app.* d, *J* = 9.0 Hz, H-3), 3.52 (1H, ddd, *J* = 2.0, 4.5 and 9.5 Hz, H-5), 3.47 (1H, dd, *J* = 8.5 and 9.5 Hz, H-4), 3.20 (1H, dd, *J* = 8.0 and 9.5 Hz, H-2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.3 (HC=N), 161.7 ($ArCOCH_3$), 135.1 (CH_2CHCH_2O), 134.9 (CH_2CHCH_2O), 134.8 (CH_2CHCH_2O), 134.7 (CH_2CHCH_2O), 134.1 (ArC), 129.9 (ArCH), 117.44 (CH_2CHCH_2O), 117.40 (CH_2CHCH_2O), 117.0 (CH_2CHCH_2O), 116.8 (CH_2CHCH_2O), 113.9 (ArCH), 101.0 (C-1), 83.2 (C-3), 77.5 (C-4), 76.7 (C-2), 75.1 (C-5), 73.8 (CH_2CHCH_2O), 72.5 (CH_2CHCH_2O), 71.8 (CH_2CHCH_2O), 69.8 (CH_2CHCH_2O), 69.1 (C-6);

m/z HRMS (ESI): ∶ Found $[M+H]^+$ 457.2523, $C_{26}H_{36}NO_6$ requires 458.2537.

Allyl 2-amino-2-deoxy-3,4,6-tri-*O*-allyl-β-D-glucopyanoside hydrochloride (4b):



Following General Procedure A – Step 2: Imine = **3b** (750 mg, 1.65 mmol); solvent = Et_2O and the isolation method was modified from the general procedure. After refluxing for 0.3 h the solution was allowed to cool rt and then cooled to -20 °C for 16 h. The resulting precipitate was collected by Buchner filtration and washed with cold Et_2O (2 x 10 mL). The remaining material was dried under high vacuum to yield **4b** (316 mg, 51%) as a colourless amorphous solid;

ν_{max} / cm^{-1} (film): 3049, 2868, 1600, 1497, 1371, 1343, 1255, 1170, 1124, 1094, 1067, 1052, 1013;

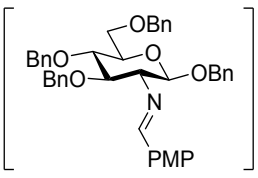
^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ: 8.45 (3H, s, NH_3), 6.04-5.85 (4H, m, CH_2CHCH_2O), 5.33 (1H, ddd, *J* = 17.5, 3.5 and 1.5 Hz, CH_2CHCH_2O), 5.28 (1H, ddd, *J* = 9.5, 3.5 and 1.5 Hz, CH_2CHCH_2O), 5.26-5.25 (1H, m, CH_2CHCH_2O), 5.23 (1H, ddd, *J* = 9.5, 3.5 and 1.5 Hz, CH_2CHCH_2O), 5.19 (1H, ddd, *J* = 10.0, 3.5, and 1.5 Hz, CH_2CHCH_2O), 5.17 (3H, m, CH_2CHCH_2O), 4.67 (1H, d, *J* = 8.5 Hz, H-1), 4.31-4.21 (3H, m, found *J* = 12.0, 5.5 and 1.5 Hz, CH_2CHCH_2O), 4.16-4.06 (3H, m, found *J* = 12.0, 5.5 and 1.5 Hz, CH_2CHCH_2O), 4.01 (1H, ddd, *J* = 13.5, 5.5 and 1.5 Hz, CH_2CHCH_2O), 3.96 (1H, ddd, *J* = 13.5, 5.5 and 1.5 Hz, CH_2CHCH_2O), 3.69 (1H, dd, *J* = 10.5 and 8.5 Hz, H-3), 3.60 (1H, dd, *J* = 11.5 and 2.0 Hz, H-6a), 3.55 (1H, dd, *J* = 11.5 and 4.5 Hz, H-6b), 3.42 (1H, ddd, *J* = 9.5, 4.5 and 2.0 Hz, H-5), 3.36 (1H, dd, *J* = 9.5 and 8.5 Hz, H-4), 2.85 (1H, dd, *J* = 10.5 and 8.5 Hz, H-2);

^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ: 135.2 (CH_2CHCH_2O), 135.0 (CH_2CHCH_2O), 134.9 (CH_2CHCH_2O), 134.1 (CH_2CHCH_2O), 117.6 (CH_2CHCH_2O), 116.8 (CH_2CHCH_2O), 116.6 (CH_2CHCH_2O), 116.5 (CH_2CHCH_2O), 97.9 (C-1), 78.8 (C-3), 77.8 (C-4), 74.2 (C-5), 73.2 (CH_2CHCH_2O), 72.8 (CH_2CHCH_2O), 71.3 (CH_2CHCH_2O), 69.8 (CH_2CHCH_2O), 68.1 (C-6), 54.6 (C-2);

m/z HRMS (ESI): found $[M-Cl]^+$ 340.2132, $C_{18}H_{30}N_1O_5$ requires 340.2118;

$[\alpha]^{23}_D$ = 16 (c 0.7, DMSO).

Benzyl 2-amino-2-deoxy-*N*-4-methoxybenzylidine-3,4,6-tri-*O*-benzyl-β-D-glucopyanoside (3c):



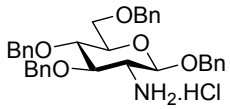
Following General Procedure A – Step 1: Electrophile = BnBr and FCC (90:10 to 80:20 petrol:EtOAc + 5% Et_3N) to yield **3c** (1.44 g, 65%) as a colourless oil with trace impurities (< 5 %) of *p*-anisaldehyde.

R_f = 0.2 (80:20 petrol:EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (1H, s, HC=N), 7.73 (2H, *app*. d, *J* = 9.0 Hz, ArCH), 7.42-7.11 (20H, m, ArCH), 6.98 (2H, *app.* d, *J* = 9.0 Hz, ArCH), 4.91 (1H, d, *J* = 12.5 Hz, PhC*H*H), 4.89 (1H, d, *J* = 11.0 Hz, PhC*H*H), 4.75 (1H, d, *J* = 8.0 Hz, H-1), 4.69 (1H, d, *J* = 12.5 Hz, PhCH*H*), 4.69 (1H, d, *J* = 12.0 Hz, PhC*H*H), 4.69 (1H, d, *J* = 10.5 Hz, PhC*H*H), 4.62 (1H, d, *J* = 12.0 Hz, PhCH*H*), 4.62 (1H, d, *J* = 11.0 Hz, PhCH*H*), 4.58 (1H, d, *J* = 10.5 Hz, PhCH*H*), 3.90 (1H, *app.* t, *J* = 9.5 Hz, H-3), 3.89 (3H, s, ArCO*C*H$_3$), 3.84 (1H, dd, *J* = 2.0 and 10.5 Hz, H-6a), 3.79 (1H, dd, *J* = 4.5 and 10.5 Hz, H-6b), 3.74 (1H, *app.* t, *J* = 9.5 Hz, H-4), 3,64 (1H, ddd, *J* = 2.0, 4.5 and 9.5 Hz, H-5), 3.40 (1H, dd, *J* = 8.0 and 9.5 Hz, H-2);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.6 (HC=N), 161.8 (Ar*C*OCH$_3$), 138.3 (ArCH), 138.2 (ArC), 138.1 (ArC), 137.8 (ArC), 130.0 (ArCH), 129.3 (ArC), 129.2 (ArC), 128.41 (ArCH), 128.36 (ArCH), 128.27 (ArCH), 128.26 (ArCH), 128.2 (ArCH), 127.9 (ArCH), 127.76 (ArCH), 127.73 (ArCH), 127.64 (ArCH), 127.57 (ArCH), 127.4 (ArCH), 114.0 (ArCH), 101.0 (C-1), 83.9 (C-3), 77.9 (C-4), 76.9 (C-2), 75.24 and 75.20 (PhCH$_2$ and C-5), 75.0 (PhCH$_2$), 73.5 (PhCH$_2$), 70.7 (PhCH$_2$), 69.2 (C-6), 55.4 (ArCO*C*H$_3$). *Spectroscopic data in agreement with literature*.[3]

Benzyl 2-amino-2-deoxy-3,4,6-tri-*O*-benzyl -β-D-glucopyranoside hydrochloride (4c):



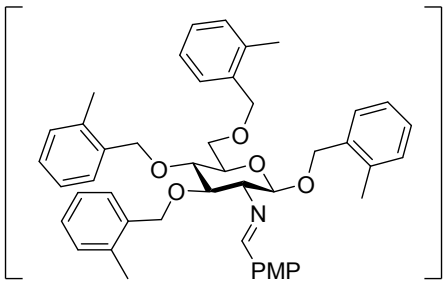
Following General Procedure A – Step 2: Imine = **3c** (630 mg, 0.95 mmol); solvent = acetone to yield **4c** (320 mg, 68%) as an amorphous solid;

ν_{max} / cm^{-1} (film): 2896, 1596, 1498, 1453, 1366, 1210, 1141, 1102, 1067, 1050, 1028;

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ: 8.55 (3H, s, NH_3), 7.48-7.45 (2H, m, ArCH), 7.42-7.27 (16H, m, ArCH), 7.16-7.14 (2H, m ArCH), 4.89 (1H, d, *J* = 11.0 Hz, PhC*H*H), 4.86 (1H, d, *J* = 8.5 Hz, H-1), 4.84 (1H, d, *J* = 12.0 Hz, PhC*H*H), 4.81 (1H, d, *J* = 11.0 Hz, PhCH*H*), 4.70 (1H, d, *J* = 11.5 Hz, PhC*H*H), 4.65 (1H, d, *J* = 11.0 Hz, PhC*H*H), 4.58 (1H, d, *J* = 11.5 Hz, PhCH*H*), 4.56 (1H, d, *J* = 11.0 Hz, PhCH*H*), 4.52 (1H, d, *J* = 12.0 Hz, PCH*H*), 3.95 (1H, dd, *J* = 10.5 and 8.5 Hz, H-3), 3.74-3.58 (4H, m, H-4 & H-5 & H-6a & H-6b), 3.05 (1H, dd, *J* = 10.5 and 8.5 Hz, H-2);

^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ: 138.1 (ArC), 138.0 (ArC), 137.7 (ArC), 137.0 (ArC), 128.30 (ArCH), 128.28 (ArCH), 128.26 (ArCH), 128.2 (ArCH), 128.1 (ArCH), 127.8 (ArCH), 127.71 (ArCH), 127.66 (ArCH), 127.64 (ArCH), 127.63 (ArCH), 127.50 (ArCH), 127.46 (ArCH), 98.2 (C-1), 79.3 (C-3), 78.3 (C-4 or C-5), 74.3 (C-4 or C-5), 73.9 (PhCH$_2$), 73.7 (PhCH$_2$), 72.4 (PhCH$_2$), 70.6 (PhCH$_2$), 68.2 (C-6), 54.6 (C-2). *Spectroscopic data in agreement with the literature*.[3]

2-Methylbenzyl 2-amino-2-deoxy-*N*-4-methoxybenzylidine-3,4,6-tri-*O*-(2-methylbenzyl)-β-D-glucopyanoside (3d):



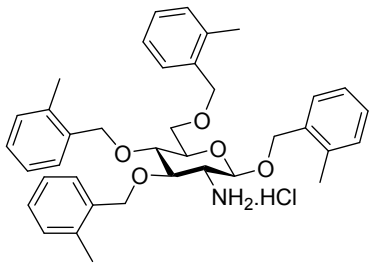
Following General Procedure A – Step 1: Electrophile = 1-(bromomethyl)-2-methylbenzene and FCC (80:20 to 60:40 petrol:EtOAc + 5% Et_3N) to yield **3d** (1.19 g, 66%) as a colourless oil with trace impurities (< 5 %) of *p*-anisaldehyde. R_f = 0.2 (80:20 petrol:EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (1H, s, HC=N), 7.61 (2H, d, *J* = 9.0 Hz, ArCH), 7.38-7.36 (1H, m, ArCH), 7.27 (1H, *app.* t, *J* = 7.0 Hz, ArCH), 7.21-7.03 (12H, m, ArCH), 7.00-6.93 (2H, m, ArCH), 6.91 (2H, d, *J* = 9.0 Hz, ArCH), 4.89 (1H, d, *J* = 12.0 Hz, ArC*H*H), 4.87 (1H, d, *J* = 12.0 Hz, ArCH*H*), 4.70 (1H, d, *J* = 8.0 Hz, H-1), 4.66 (1H, d, *J* = 12.0 Hz, ArC*H*H), 4.65-4.59 (4H, m, $ArCH_2$), 4.55 (1H, d, *J* = 12.0 Hz, ArCH*H*), 3.96 (1H, *app.* t, *J* = 8.5 Hz, H-3), 3.86 (3H, s, $ArCOCH_3$), 3.81 (1H, dd, *J* = 1.5 and 10.5 Hz, H-6a), 3.74 (1H, dd, *J* = 4.5 and 10.5 Hz, H-6b), 3.70 (1H, *app.* d, *J* = 9.5 Hz, H-4), 3.68-3.64 (1H, m, H-5), 3.37 (1H, dd, *J* = 8.0 and 8.5 Hz, H-2), 2.36 (3H, s, CH_3), 2.18 (3H, s, CH_3), 2.17 (3H, s, CH_3), 1.99 (3H, s, CH_3);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.6 (HC=N), 161.7 ($ArCOCH_3$), 137.1 (ArC), 136.6 (ArC), 136.5 (ArC), 136.4 (ArC), 136.3 (ArC), 136.1 (ArC), 135.6 (ArC), 135.2 (ArC), 132.0 (ArC), 130.14 (ArCH), 130.11 (ArCH), 130.0 (ArCH), 129.9 (ArCH), 129.0 (ArCH), 128.6 (ArCH), 128.4 (ArCH), 127.9 (ArCH), 127.8 (ArCH), 127.7 (ArCH), 127.5 (ArCH), 125.8 (ArCH), 125.7 (ArCH), 125.6 (ArCH), 114.3 (ArCH), 100.4 (C-1), 84.1 (C-3), 78.1 (C-4), 77.2 (C-2), 75.3 (C-5), 73.1 ($ArCH_2$), 72.6 ($ArCH_2$), 71.9 ($ArCH_2$), 69.6 (C-6), 69.3 ($ArCH_2$), 55.4 ($ArCOCH_3$), 18.9 (CH_3), 18.78 (CH_3), 18.79 (CH_3), 18.7(CH_3);

m/z HRMS (ESI): Found $[M+H]^+$ 714.3788, $C_{46}H_{52}N_1O_6$ requires 714.3789.

2-Methylbenzyl 2-amino-2-deoxy-3,4,6-tri-*O*-(2-methylbenzyl)-β-D-glucopyanoside hydrochloride (4d):



Following General Procedure A – Step 2: Imine = **3d** (1.14 g, 1.60 mmol); solvent = acetone to yield **4d** (589 mg, 58%) as a colourless amorphous solid;

ν_{max} / cm^{-1} (film): 2857, 1599, 1501, 1463, 1369, 1116, 1092, 1063;

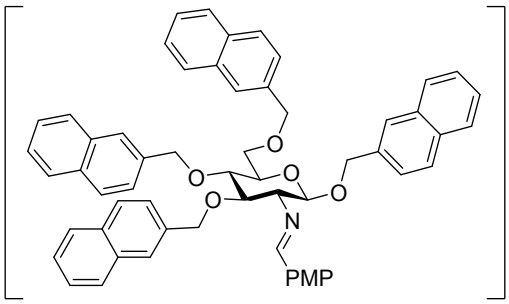
^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ: 8.51 (3H, s, NH_3), 7.51-7.49 (1H, m, ArCH), 7.43 (1H, *app.* d, *J* = 7.5 Hz, ArCH), 7.32 (1H, *app.* d, *J* = 7.5 Hz, ArCH), 7.25-7.04 (13H, m, ArCH), 4.88 (1H, d, *J* = 8.5 Hz, H-1), 4.88 (1H, d, *J* = 12.5 Hz, ArC*H*H), 4.86 (1H, d, *J* = 11.5 Hz, ArC*H*H), 4.76 (1H, d, *J* = 12.5 Hz, ArCH*H*), 4.67 (1H, d, *J* = 11.5 Hz, ArCH*H*), 4.59-4.52 (3H, m, found *J* = 12.0, 12.0 and 12.0 Hz, $ArCH_2$), 4.48 (1H, d, *J* = 12.0 Hz, ArCH*H*), 4.02 (1H, dd, *J* = 8.5 and 10.0 Hz, H-3), 3.74-3.62 (4H, m, H-4, H-5, H-6a and H-6b), 3.12 (1H, br t, *J* = 9.0 Hz, H-2), 2.32 (3H, s, CH_3), 2.27 (3H, s, CH_3), 2.04 (3H, s, CH_3), 2.02 (3H, s, CH_3);

^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ: 136.6 (ArC), 136.5 (ArC), 136.21 (ArC), 136.15 (ArC), 136.0 (ArC), 135.4 (ArC), 134.9 (ArC), 134.2 (ArC), 129.92 (ArCH), 129.88 (ArCH), 129.8 (ArCH), 129.4 (ArCH), 129.2 (ArCH), 128.1 (ArCH), 128.0 (ArCH), 127.6 (ArCH), 127.5 (ArCH), 127.4 (ArCH), 126.8 (ArCH), 126.4 (ArCH), 125.60 (ArCH), 125.55 (ArCH), 125.5 (ArCH), 98.1 (C-1), 79.7 (C-3), 78.1 (C-4), 74.4 (C-5), 71.7 ($ArCH_2$), 71.0 ($ArCH_2$), 70.9 ($ArCH_2$), 68.62 and 68.61 (C-6 and $ArCH_2$), 54.5 (C-2), 18.5 (CH_3), 18.4 (CH_3), 18.10 (CH_3), 18.09 (CH_3);

m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 596.3382, $C_{38}H_{46}N_1O_5$ requires 596.3371;

$[\alpha]^{22}_D$ = 2 (c = 1.0, DMSO).

Methyl-2-naphthyl 2-amino-2-deoxy-*N*-4-methoxybenzylidine-3,4,6-tri-*O*-(2-naphthyl-(methyl))-β-D-glucopyanoside (3e):



Following General Procedure A – Step 1: Electrophile = 2-(bromomethyl)naphthalene and FCC (80:20 to 60:40 petrol:EtOAc + 5% Et_3N) to yield **3e** (1.85 g, 64%) as a colourless oil with trace impurities (< 5 %) of *p*-anisaldehyde.

R_f = 0.5 (60:40 petrol:EtOAc);

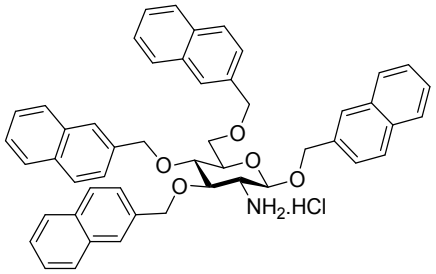
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (1H, s, HC=N), 7.84-7.36 (28H, m, ArCH), 7.27-7.24 (2H, m, ArCH), 6.96 (2H, *app.* d, *J* = 8.5 Hz, ArCH), 5.09 (1H, d, *J* = 12.5 Hz, $ArCH_2$), 5.06 (1H, d, *J* = 11.5 Hz, $ArCH_2$), 4.87 (2H, d, *J* = 12.5 Hz, $ArCH_2$), 4.86 (2H, d, *J* = 11.0 Hz, $ArCH_2$), 4.81-4.72 (3H, m, H-1 and $ArCH_2$), 4.01 (1H, *app.* d, *J* = 9.0 Hz, H-3), 3.94-3.89 (3H, m, H-4, H-6a and H-6b), 3.90 (3H, s, $ArCOCH_3$), 3.74-3.71 (1H, m, H-5), 3.49 (1H, dd, *J* = 8.0 and 9.0 Hz, H-2);

^{13}C NMR (100 MHz, $CDCl_3$) δ: *observed peaks* 163.7 ($ArCOCH_3$), 161.9 (HC=N), 135.8 (ArC), 135.7 (ArC), 135.6 (ArC), 135.3 (ArC), 133.3 (ArC), 133.2 (ArC), 133.0 (ArC), 132.9 (ArC), 130.09 (ArCH), 128.2 (ArCH), 128.01 (ArCH), 128.0 (ArCH), 127.94 (ArCH), 127.91 (ArCH), 127.7 (ArCH), 127.61 (ArCH), 127.56 (ArCH),

127.0 (ArCH), 126.6 (ArCH), 126.5 (ArCH), 126.3 (ArCH), 126.1 (ArCH), 126.0 (ArCH), 125.9 (ArCH), 125.8 (ArCH), 125.7 (ArCH), 114.03 (ArCH), 101.1 (H-1), 84.1 (C-3), 78.0 (C-4), 76.8 (C-2), 75.35 and 75.32 (C-5 and $ArCH_2$), 75.0 ($ArCH_2$), 73.7 ($ArCH_2$), 70.8 ($ArCH_2$), 69.2 (C-6), 55.4 ($ArCOCH_3$).

m/z HRMS (ESI): Found $[M+H]^+$ 858.3769, $C_{58}H_{52}N_1O_6$ requires 858.3789.

2-Naphthylmethyl 2-amino-2-deoxy-3,4,6-tri-*O*-(2-naphthylmethyl)-β-D-glucopyanoside hydrochloride (4e):



Following General Procedure A – Step 2: Imine = **3e** (1.82 g, 1.82 mmol); solvent = acetone to yield **4e** (1.17 g, 71%) as an amorphous solid which was sparingly soluble in common solvents;

ν_{max} / cm^{-1} (film): 2909, 2871, 1601, 1507, 1349, 1145, 1097, 1081, 1055;

^1H NMR (500 MHz, $(CD_3)_2SO$) δ: 8.63 (3H, s, NH_3), 7.99 (1H, s, ArCH), 7.93-7.80 (11H, m, ArCH), 7.78-7.76 (1H, m, ArCH), 7.69 (1H, *app.* d, *J* = 8.5 Hz, ArCH), 7.64 (1H, dd, *J* = 8.5 and 1.5 Hz, ArCH), 7.61 (1H, dd, *J* = 8.0 and 1.5 Hz, ArCH), 7.56 (1H, dd, *J* = 8.5 and 1.5 Hz, ArCH), 7.54-7.42 (10H, m, ArCH), 7.23 (1H, dd, *J* = 8.5 and 1.5 Hz, ArCH), 5.09 (1H, d, *J* = 11.5 Hz, ArC*H*H), 5.04 (1H, d, *J* = 12.0 Hz, ArC*H*H), 4.99 (1H, d, *J* = 11.5 Hz, ArCH*H*), 4.96 (1H, d, *J* = 8.0 Hz, H-1), 4.91 (1H, d, *J* = 12.0 Hz, ArCH*H*), 4.83 (1H, d, *J* = 11.5 Hz, ArC*H*H), 4.76 (1H, d, *J* = 12.5 Hz, ArC*H*H), 4.75 (1H, d, *J* = 11.5 Hz, ArCH*H*), 4.67 (1H, d, *J* = 12.5 Hz, ArCH*H*), 4.05 (1H, dd, *J* = 10.5 and 9.0 Hz, H-3), 3.86-3.78 (3H, m, H-4, H-6a and H-6b), 3.74-3.70 (1H, m, H-5), 3.19 (1H, *app.* t, *J* = 9.0 Hz, H-2);

^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ: *observed peaks* 135.7 (ArC), 135.3 (ArC), 134.6 (ArC), 132.76 (ArC), 132.73 (ArC), 132.68 (ArC), 132.60 (ArC), 132.56 (ArC), 132.5 (ArC), 132.4 (ArC), 127.9 (ArCH), 127.8 (ArCH), 127.7 (ArCH), 127.64 (ArCH), 127.56 (ArCH), 127.5 (ArCH), 126.7 (ArCH), 126.2 (ArCH), 126.14 (ArCH), 126.06 (ArCH), 126.0 (ArCH), 125.9 (ArCH), 125.7 (ArCH), 98.3 (C-1), 79.4 (C-3), 78.3 (C-4), 74.4 (C-5), 74.0 ($ArCH_2$), 73.7 ($ArCH_2$), 72.5 ($ArCH_2$), 70.7 ($ArCH_2$), 68.3 (C-6), 54.7 (C-2).

m/z HRMS (ESI): Found $[M-Cl]^+$ 740.3362, $C_{50}H_{46}NO_5$ requires 740.3371;

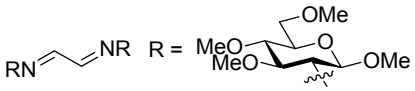
$[\alpha]^{23}_D$ = -38 (c 0.7, DMSO).

General Procedure B: Formation of the diimine

To a solution of NaOAc (700 mol%) in H_2O (3 M) at rt, was added a suspension of pyranoside hydrochloride **4a-e** (100 mol%) in CH_2Cl_2 (0.1 M). The biphasic mixture was shaken until no solid was visible and then the organic layer was separated, dried ($MgSO_4$) and concentrated *in vacuo* to give an oily residue. The oil was re-

dissolved in CH_2Cl_2 (0.5 M) to which was added MeOH (0.5 M) and a solution of glyoxal (50 mol%, 40% wt solution in H_2O) in MeOH (1 M) at rt. After 8 h the solvent was removed *in vacuo* and the dry residue was suspended in cold MeOH. Isolation by filtration yielded **5a-c**.

Bis(2-amino-1,3,4,6-tetra-*O*-methyl-2-deoxy-β-D-glucopyanoside)-*N,N'*-iminoethylidene (5a):



Following General Procedure B: Pyranoside hydrochloride = **4a** (1.67 g, 5.52 mmol) to yield **5a** (1.26 g, 93%) as a colourless amorphous solid;

R_f = 0.9 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 2938, 2911, 1628, 1444, 1381, 1193, 1133, 1111, 1091, 1064, 1049, 1015;

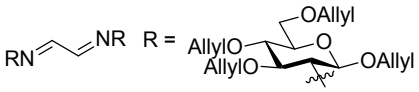
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (2H, s, HC=N), 4.49 (2H, d, *J* = 8.0 Hz, H-1), 3.67 (2H, dd, *J* = 10.5 and 2.0 Hz, H-6a), 3.60 (2H, dd, *J* = 10.5 and 4.5 Hz, H-6b), 3.54 (6H, s, CH_3), 3.47 (6H, s, CH_3), 3.41 (6H, s, CH_3), 3.41-3.38 (2H, m, H-5), 3.38 (6H, s, CH_3), 3.36 (2H, *app.* t, *J* = 9.5 Hz, H-3), 3.25 (2H, dd, *J* = 9.5 and 9.0 Hz, H-4), 3.09 (2H, dd, *J* = 9.5 and 8.0 Hz, H-2);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 164. 8 (HC=N), 102.6 (C-1), 84.5 (C-3), 79.5 (C-4), 76.3 (C-2), 75.1 (C-5), 71.4 (C-6), 60.7 (CH_3), 60.5 (CH_3), 59.5 (CH_3), 57 .1 (CH_3);

m/z HRMS (ESI): Found $[M+Na]^+$ 515.2571, $C_{22}H_{40}N_2O_{10}Na$ requires 515.2575;

$[\alpha]^{22}_D$ = 2 (c 0.9, $CHCl_3$).

Bis(2-amino-1,3,4,6-tetra-*O*-allyl-2-deoxy-β-D-glucopyanoside)-*N,N'*-iminoethylidene (5b):



Following General Procedure B: Pyranoside hydrochloride = **4b** (1.50 mg, 0.40 mmol) to yield **5b** (151 mg, 96%) as a colourless amorphous solid. In this instance, the isolation method was modified from the general procedure. Upon completion, the reaction was concentrated under reduced pressure, re-dissolved in CH_2Cl_2 (40 mL) and washed with sat. aq. $NaHCO_3$ (3 mL). The separated organic phase was dried (Na_2SO_4), concentrated *in vacuo* and dried under high vacuum to afford **5b**.

R_f = 0.9 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 2924, 2876, 1625, 1459, 1421, 1403, 1347, 1318, 1260, 1144, 1106, 1077, 1054;

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.93 (2H, s, HC=N), 5.96-5.72 (8H, m, CH_2CHCH_2O), 5.31-5.05 (16H, m, CH_2CHCH_2O), 4.61 (2H, d, *J* = 8.0 Hz, H-1), 4.32-4.25 (4H, m, CH_2CHCH_2O), 4.15-3.97 (12H, m,

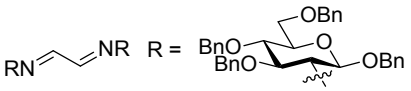
CH_2CHCH_2O), 3.74 (2H, dd, *J* = 11.0 and 1.5 Hz, H-6a), 3.67 (2H, dd, *J* = 11.0 and 4.0 Hz, H-6b), 3.64 (2H, br. t, *J* = 9.0-9.5 Hz, H-3), 3.51-3.45 (4H, m, H-4 & H-5), 3.21 (2H, dd, *J* = 9.5 and 8.0 Hz, H-2);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.8 (C=N), 134.9 (2 x CH_2CHCH_2O), 134.8 (CH_2CHCH_2O), 134.0 (CH_2CHCH_2O), 117.3 (CH_2CHCH_2O), 117.19 (CH_2CHCH_2O), 117.18 (CH_2CHCH_2O), 116.8 (CH_2CHCH_2O), 100.6 (C-1), 82.6 (C-3), 77.6 (C-4 or C-5), 76.6 (C-2), 75.3 (C4 or C-5), 73.94 (CH_2CHCH_2O), 73.88 (CH_2CHCH_2O), 72.7 (CH_2CHCH_2O), 70.2 (CH_2CHCH_2O), 69.1 (C-6);

m/z HRMS (ESI): Found $[M+Na]^+$ 723.3834, $C_{38}H_{56}N_2O_{10}Na$ requires 723.3827.

$[\alpha]^{22}_D$ = 5 (c 0.6, $CHCl_3$).

Bis(2-amino-1,3,4,6-tetra-*O*-benzyl-2-deoxy-β-D-glucopyanoside)-*N*,*N'*-iminoethylidene (5c):



Following General Procedure B: Pyranoside hydrochloride = **4c** (100 mg, 0.17 mmol) to yield **5c** (88.3 mg, 92%) as a colourless amorphous solid;

R_f = 0.9 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3029, 2874, 1629, 1496, 1453, 1397, 1357, 1309, 1209, 1073, 1059, 1026;

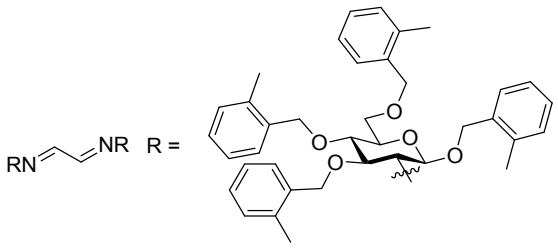
^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.07 (2H, s, HC=N), 7.37-6.99 (40H, m, ArCH), 4.86 (2H, d, *J* = 12.5 Hz, PhC*H*H), 4.72 (2H, d, *J* = 8.0 Hz, H-1), 4.70 (2H, d, *J* = 11.0 Hz, PhC*H*H), 4.65 (2H, d, *J* = 12.5, PhC*H*H), 4.62 (2H, d, *J* = 12.5 Hz, PhCH*H*), 4.58 (2H, d, *J* = 12.5 Hz, PhCH*H*), 4.51 (2H, d, *J* = 11.0 Hz, PhCH*H*), 4.46 (2H, d, *J* = 11.0 Hz, PhC*H*H), 4.33 (2H, d, *J* = 11.0 Hz, PhCH*H*), 3.81-3.74 (6H, m, H-2 & H-6a & H-6b), 3.70 (2H, dd, *J* = 10.0 and 9.0 Hz, H-4), 3.59 (2H, ddd, *J* = 10.0, 4.5 and 2.0 Hz, H-5), 3.42 (2H, dd, *J* = 9.5 and 8.0 Hz, H-2);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.9 (C=N), 138.3 (ArC), 138.13 (ArC), 138.08 (ArC), 137.5 (ArC), 128.52 (ArCH), 128.51 (ArCH), 128.4 (ArCH), 128.3 (ArCH), 128.1 (ArCH), 128.0 (ArCH), 127.92 (ArCH), 127.90 (ArCH), 127.8 (ArCH), 127.6 (ArCH), 127.4 (ArCH), 100.5 (C-1), 82.8 (C-3), 78.0 (C-4), 76.8 (C-2), 75.3 (C-5), 75.1 ($PhCH_2$), 74.9 ($PhCH_2$), 73.7 ($PhCH_2$), 71.0 ($PhCH_2$), 69.1 ($PhCH_2$);

m/z HRMS (ESI): Found $[M+Na]^+$ 1123.5079, $C_{70}H_{72}N_2O_{10}Na$ requires 1123.5069;

$[\alpha]^{22}_D$ = 12 (c 1.0, CHCl3).

Bis(2-amino-1,3,4,6-tetra-*O*-(2-methylbenzyl)-2-deoxy-β-D-glucopyanoside)-*N*,*N'*-iminoethylidene (5d):



Following General Procedure B: Pyranoside hydrochloride = **4d** (2.50 g, 3.96 mmol) to yield **5d** (2.30 g, 96%) as a colourless amorphous solid;

R_f = 0.9 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3026, 2867, 1622, 1493, 1460, 1353, 1292, 1184, 1121, 1079, 1059, 1039, 1018;

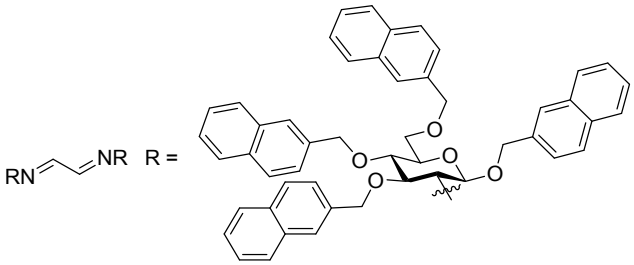
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (2H, s, HC=N), 7.35 (2H, dd, *J* = 7.0 and 2.0 Hz, ArCH), 7.23 (2H, dd, *J* = 7.5 and 1.5 Hz, ArCH), 7.20-7.02 (22H, m, ArCH), 6.98-6.95 (4H, m, ArCH), 6.76-6.73 (2H, m, ArCH), 4.84 (2H, d, *J* = 12.0 Hz, ArC*H*H), 4.67 (2H, d, *J* = 11.5 Hz, ArC*H*H), 4.65 (2H, d, *J* = 7.5, H-1), 4.62 (2H, d, *J* = 12.0 Hz, ArC*H*H), 4.59 (2H, d, *J* = 12.0 Hz, ArCH*H*), 4.52 (2H, d, *J* = 12.0 Hz, ArCH*H*), 4.51 (2H, d, *J* = 11.5 Hz, ArCH*H*), 4.42 (2H, d, *J* = 11.5, ArC*H*H), 4.31 (2H, d, *J* = 11.5 Hz, ArCH*H*), 3.87 (2H, dd, *J* = 9.5 and 8.5 Hz, H-3), 3.76 (2H, dd, *J* = 10.5 and 2.0 Hz, H-6a), 3.71 (2H, dd, *J* = 10.5 and 5.0 Hz, H-6b), 3.67 (2H, dd, *J* = 10.0 and 8.5 Hz, H-4), 3.61 (2H, ddd, *J* = 10.0, 5.0 and 2.0 Hz, H-5), 3.41 (2H, dd, *J* = 9.5 and 7.5 Hz, H-2), 2.34 (6H, s, CH_3), 2.17 (6H, s, CH_3), 2.07 (6H, s, CH_3), 1.78 (6H, s, CH_3);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.9 (C=N), 137.0 (ArC), 136.6 (ArC), 136.5 (ArC), 136.4 (ArC), 136.3 (ArC), 135.9 (ArC), 135.3 (ArC), 135.1 (ArC), 130.28 (ArCH), 130.24 (ArCH), 130.1 (ArCH), 129.8 (ArCH), 129.0 (ArCH), 128.5 (ArCH), 128.1 (ArCH), 128.0 (ArCH), 127.8 (ArCH), 127.7 (ArCH), 127.3 (ArCH), 127.2 (ArCH), 125.90 (ArCH), 125.84 (ArCH), 125.8 (ArCH), 125.7 (ArCH), 99.7 (C-1), 83.6 (C-3), 78.1 (C-4), *C-2 under $CDCl_3$ peak*, 75.3 (C-5), 72.82 ($ArCH_2$), 72.76 ($ArCH_2$), 72.1 ($ArCH_2$), 69.5 (C-6), 69.1 ($ArCH_2$), 19.0 (CH_3), 18.9 (CH_3), 18.7 (CH_3), 18.6 (CH_3);

m/z HRMS (ESI): Found $[M+Na]^+$ 1235.6375, $C_{78}H_{88}N_2O_{10}Na$ requires 1235.6331;

$[\alpha]^{23}_D$ = 23 (c 1.0, $CHCl_3$).

Bis(2-amino-1,3,4,6-tetra-*O*-(2-naphthylmethyl)-deoxy-β-D-glucopyanoside)-*N*,*N'*-iminoethylidene (5e):



Following General Procedure B: Pyranoside hydrochloride = **4e** (1.0 g, 1.29 mmol) to yield **5e** (749 mg, 82%) as a colourless amorphous solid which was sparingly soluble in common solvents;

ν_{max} / cm^{-1} (film): 3053, 2857, 1634, 1601, 1345, 1363, 1270, 1174, 1123, 1104, 1075, 1058;

^{1}H NMR (500 MHz, C_6D_6, 70 °C) δ: 8.50 (2H, s, HC=N), 7.74-7.40 (38H, m, ArCH), 7.25-7.17 (14H, m, ArCH), 7.12-7.10 (4H, m, ArCH), 4.98 (2H, d, *J* = 12.0 Hz, ArC*H*H), 4.88 (2H, d, *J* = 8.0 Hz, H-1), 4.87 (2H, d, *J* = 12.0 Hz, ArCH*H*), 4.77 (2H, d, *J* = 12.5 Hz, ArC*H*H), 4.70 (2H, d, *J* = 12.0 Hz, ArC*H*H), 4.67 (2H, d, *J* = 12.5 Hz, ArCH*H*), 4.66 (2H, d, *J* = 11.5 Hz, ArC*H*H), 4.65 (2H, d, *J* = 11.5 Hz, ArCH*H*), 4.59 (2H, d *J* = 12.0 Hz, ArCH*H*), 3.97 (2H, *app.* t, *J* = 9.0 Hz, H-3), 3.92 (2H, *app.* t, *J* = 9.5 Hz, H-4), 3.86-3.80 (4H, m, H-6a and H-6b), 3.74 (2H, *app.* t, *J* = 8.0 Hz, H-2), 3.56 (2H, *app.* d, *J* = 9.5 Hz, H-5);

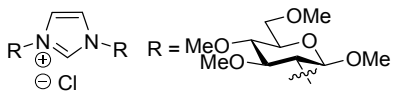
^{13}C NMR (125 MHz, C_6D_6, 70 °C) *observed peaks* δ: 164.8 (HC=N), 136.2 (ArC), 136.1 (ArC), 136.0 (ArC), 135.4 (ArC), 133.6 (ArC), 133.49 (ArC), 133.46 (ArC), 133.3 (ArC), 133.21 (ArC), 133.18 (ArC), 133.0 (ArC), 132.9 (ArC), 128.0 (ArCH), 127.93 (ArCH), 127.89 (ArCH), 127.88 (ArCH), 127.83 (ArCH), 127.81 (ArCH), 127.72 (ArCH), 127.68 (ArCH), 127.64 (ArCH), 127.62 (ArCH), 127.52 (ArCH), 127.49 (ArCH), 127.4 (ArCH), 126.5 (ArCH), 126.3 (ArCH), 126.0 (ArCH), 125.9 (ArCH), 125.81 (ArCH), 125.78 (ArCH), 125.7 (ArCH), 125.54 (ArCH), 125.52 (ArCH), 125.48 (ArCH), 125.45 (ArCH), 125.3 (ArCH), 100.5 (C-1), 83.3 (C-3), 78.1 (C-4), 77.2 (C-2), 75.58 (C-5), 74.57 ($ArCH_2$), 74.5 ($ArCH_2$), 73.4 ($ArCH_2$), 70.5 ($ArCH_2$), 69.3 (C-6);

m/z HRMS (ESI): Found $[M+Na]^+$ 1523.6266, $C_{102}H_{88}N_2O_{10}Na$ requires 1523.6331.

General Procedure C: Imidazolium chloride formation

Adapted from Hintermann and co-workers.[4] To a re-sealable pressure vessel containing a solution of diimine (100 mol%) in anhydrous solvent (0.11 M) under argon at rt, was added paraformaldehyde (300 mol%) and the resulting mixture was heated at 70 °C for 0.5 h. After cooling to rt, freshly distilled TMSCl (150 mol%) was added in solvent (1.5 M) and the solution heated at 70 °C for a further 24 h. Removal of volatiles *in vacuo* afforded a residue which was purified by FCC which yielded **6a-e**.

1,3-Bis(1,3,4,6-tetra-*O*-methyl-2-deoxy-β-D-glucopyanoside)imidazolium chloride (6a):



Following General Procedure C: Diimine = **5a** (50 mg, 0.11 mmol); solvent = CH_2Cl_2 and FCC (100:0 to 90:10 PhMe:MeOH) to yield **6a** (33.2, 60% mg) as a colourless solid;

R_f = 0.2 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 2941, 1557, 1450, 1385, 1187, 1060;

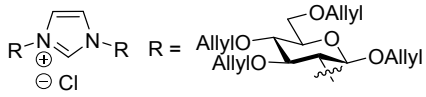
^{1}H NMR (500 MHz, $CDCl_3$) δ: 12.06 (1H, s, CH $_{Imidazolium}$), 7.17 (2H, d, *J* = 1.5 Hz, CH $_{Imidazolium}$), 5.55 (2H, d, *J* = 8.5 Hz, H-1), 4.25 (2H, dd, *J* = 10.5 and 9.0 Hz, H-3), 3.82 (2H, *app*. dt, *J* = 10.0 and 2.5 Hz, H-5), 3.79 (2H, dd, *J* =10.5 and 8.5 Hz, H-2), 3.65 (4H, *app.* d, *J* = 2.5 Hz, H-6a & H-6b), 3.52 (6H, s, OCH_3), 3.49 (6H, s, OCH_3), 3.43 (2H, dd, *J* = 10.0 and 9.0 Hz, H-4), 3.41 (6H, s, OCH_3), 3.36 (6H, s, OCH_3);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 136.3 (CH $_{Imidazolium}$), 122.0 (CH $_{Imidazolium}$), 100.2 (C-1), 83.7 (C-3), 80.1 (C-4), 74.3 (C-5), 70.3 (C-6), 67.2 (C-2), 61.2 (OCH_3), 60.1 (OCH_3), 59.4 (OCH_3), 57.4 (OCH_3);

m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 505.2745, $C_{23}H_{41}N_2O_{10}$ requires 505.2756;

$[\alpha]^{22}_D$ = 64 (c 0.9, $CHCl_3$).

1,3-Bis(1,3,4,6-tetra-*O*-allyl-2-deoxy-β-D-glucopyanoside)imidazolium chloride (6b):



Following General Procedure C: Diimine = **5b** (140 mg, 0.20 mmol); solvent = PhMe and FCC (95:5 to 90:10 PhMe:MeOH) to yield **6b** (87.0 mg, 60%) as a colourless oil;

R_f = 0.5 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3393, 3079, 3015, 2925, 2869, 1727, 1646, 1558, 1460, 1421, 1349, 1272, 1118, 1071;

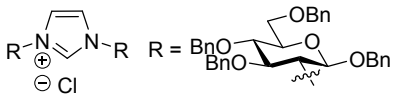
^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.10 (1H, s, CH $_{Imidazolium}$), 7.20 (2H, s, CH $_{Imidazolium}$), 5.96 (4H, m, found *J* = 17.0, 11.0 and 5.5 Hz, CH_2CHCH_2O), 5.81-5.71 (2H, m, CH_2CHCH_2O), 5.79 (2H, d, *J* = 8.5 Hz, H-1), 5.64-5.54 (2H, m, found *J* = 17.0, 11.0 and 5.5 Hz, CH_2CHCH_2O), 5.32-5.02 (16H, m, found *J* = 17.0, 11.0 and 1.5 Hz, CH_2CHCH_2O), 4.40 (2H, *app.* dd, *J* = 12.5 and 5.5 Hz, CH_2CHCH_2O), 4.26 (2H, *app.* t, *J* = 10.0 Hz, H-3), 4.22-4.14 (8H, m, CH_2CHCH_2O), 4.10 (4H, *app.* dd, *J* = 13.0 and 5.5 Hz, CH_2CHCH_2O), 4.00 (4H, *app.* dd, *J* = 13.0 and 5.5 Hz, CH_2CHCH_2O), 3.90 (2H, dd, *J* = 10.5 and 8.5 Hz, H-2), 3.89-3.86 (2H, m, H-5), 3.73-3.67 (4H, m, found *J* = 11.0, 5.0 and 3.0 Hz, H-6a and H-6b), 3.63 (2H, *app.* t, *J* = 10.0 Hz, H-4), 3.60 (2H, *app.* dd, *J* = 11.0 and 5.5 Hz, CH_2CHCH_2O);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.4 (CH $_{Imidazolium}$), 134.71 (CH_2CHCH_2O), 134.70 (CH_2CHCH_2O), 133.7 (CH_2CHCH_2O), 133.6 (CH_2CHCH_2O), 122.8 (CH $_{Imidazolium}$), 117.62 (CH_2CHCH_2O), 117.55 (CH_2CHCH_2O), 117.4 (CH_2CHCH_2O), 116.9 (CH_2CHCH_2O), 98.7 (C-1), 82.4 (C-3), 78.1 (C-4), 74.64 and 74.56 (C-5 and CH_2CHCH_2O), 73.5 (CH_2CHCH_2O), 72.6 (CH_2CHCH_2O), 70.6 (CH_2CHCH_2O), 67.9 (C-6), 67.4 (C-2);

m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 713.4006, $C_{39}H_{57}N_2O_{10}$ requires 713.4008;

$[\alpha]^{24}_D$ = 63 (*c* 0.4, $CHCl_3$).

1,3-Bis-(1,3,4,6-tetra-*O*-benzyl-2-deoxy-β-D-glucopyanoside)imidazolium chloride (6c):



Following General Procedure C: Diimine = **5c** (100 mg, 90.8 μmol); solvent = CH_2Cl_2 and FCC (94:6 CH_2Cl_2:MeOH) to yield **6c** (74.1 mg, 74%) as a colourless amorphous solid;

R_f = 0.4 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3030, 2869, 1556, 1496, 1454, 1363, 1260, 1209, 1116, 1071, 1028;

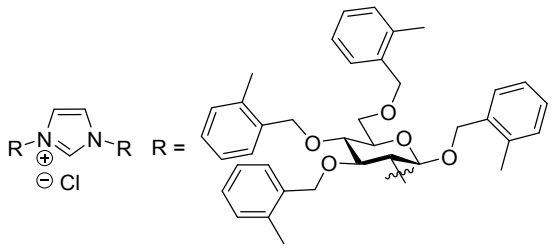
^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.14 (1H, br s, CH $_{Imidazolium}$), 7.38-6.96 (36H, m, ArCH), 6.88 (1H, s, CH $_{Imidazolium}$), 6.87 (1H, s, CH $_{Imidazolium}$), 6.72-6.69 (4H, m, ArCH), 6.27 (2H, d, *J* = 8.5 Hz, H-1), 4.98 (2H, d, *J* = 11.0 Hz, PhC*H*H), 4.90 (2H, d, *J* = 11.0 Hz, PhCH*H*), 4.73 (2H, d, *J* = 11.0 Hz, PhC*H*H), 4.67 (2H, d, *J* = 12.0 Hz, PhC*H*H), 4.66 (2H, d, *J* = 11.0 Hz, PhCH*H*), 4.53 (2H, d, *J* = 12.0 Hz, PhCH*H*), 4.43 (2H, d, *J* = 11.0 Hz, PhC*H*H), 4.19 (2H, dd, *J* = 10.5 and 8.5 Hz, H-3), 4.06 (2H, dt, *J* = 9.5 and 2.5 Hz, H-5), 3.97 (2H, dd, *J* = 10.5 and 8.5 Hz, H-2), 3.91-3.86 (4H, m, H-4 & H-6a), 3.79 (2H, dd, *J* = 11.0 and 2.0 Hz, H-6b), 3.49 (2H, d, *J* = 11.0 Hz, PhCH*H*);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.0 (ArC), 137.9 (ArC), 137.10 (ArC), 137.05 (ArC), 136.2 (CH $_{Imidazolium}$), 128.6 (ArCH), 128.4 (ArCH), 128.29 (ArCH), 128.25 (ArCH), 127.8 (ArCH), 127.73 (ArCH), 127.66 (ArCH), 127.6 (ArCH), 127.5 (ArCH), 122.4 (CH $_{Imidazolium}$), 98.8 (C-1), 83.8 (C-3), 78.4 (C-4), 75.8 ($PhCH_2$), 74.7 (C-5), 74.6 ($PhCH_2$), 73.5 ($PhCH_2$), 71.9 ($PhCH_2$), 68.0 (C-6), 67.0 (C-2);

m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 1113.5260, $C_{71}H_{73}N_2O_{10}$ requires 1113.5268;

$[\alpha]^{21}_D$ = 22 (c 1.1, $CHCl_3$).

1,3-Bis(1,3,4,6-tetra-*O*-(methyl)-*o*-tol-2-deoxy-β-D-glucopyanoside)imidazolium chloride (6d):



Following General Procedure C: Diimine = **5d** (420 mg, 0.34 mmol); solvent = CH_2Cl_2 and FCC (100:0 to 90:10 CH_2Cl_2:MeOH) yielded **6d** (312 mg, 72%) as a colourless amorphous solid;

R_f = 0.7 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3022, 2899, 1562, 1460, 1362, 1189, 1121, 1075, 1060, 1048, 1019, 1001;

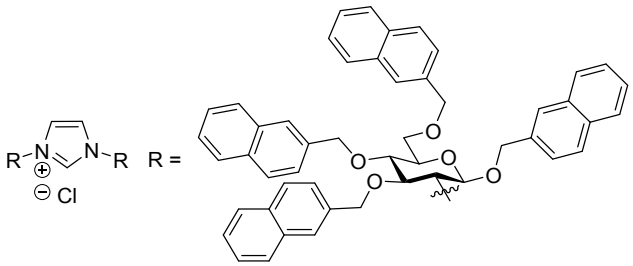
^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.09 (1H, s, C2H), 7.35-7.30 (6H, m, ArCH), 7.20-7.09 (12H, m, ArCH), 7.07-7.02 (2H, m, ArCH), 6.93-6.83 (10H, m, ArCH), 6.81 (2H, s, C4H and C5H), 6.66 (2H, *app.* d, *J* = 8.0 Hz, ArCH), 6.23 (2H, d, *J* = 8.5 Hz, H-1), 5.04 (2H, d, *J* = 11.0 Hz, ArC*H*H), 4.87 (2H, d, *J* = 11.0 Hz, ArCH*H*), 4.72 (2H, d, *J* = 12.0 Hz, ArC*H*H), 4.67 (2H, d, *J* = 12.5 Hz, ArC*H*H), 4.62 (2H, d, *J* = 12.5 Hz, ArCH*H*), 4.50 (2H, d, *J* = 12.0 Hz, ArCH*H*), 4.47 (2H, d, *J* = 12.5 Hz, ArC*H*H), 4.26 (2H, dd, *J* = 10.5 and 9.0 Hz, H-3), 4.08 (2H, br d, *J* = 9.5 Hz, H-5), 3.97 (2H, dd, *J* = 10.5 and 8.5 Hz, H-2), 3.91 (2H, *app*. t, *J* = 9.0 Hz, H-4), 3.87 (2H, dd, *J* = 11.0 and 3.0 Hz, H-6a), 3.77 (2H, dd, *J* = 11.0 and 2.0 Hz, H-6b), 3.61 (2H, d, *J* = 12.5 Hz, ArCH*H*), 2.32 (CH_3), 2.21 (CH_3), 2.14 (CH_3), 1.71 (CH_3);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.8 (ArC), 136.6 (ArC), 136.4 (ArC), 136.3 (ArC), 135.9 (ArC), 135.6 (ArC), 135.5 (ArC), 135.3 (ArC), 130.3 (ArCH), 130.01 (ArCH), 129.97 (ArCH), 129.6 ($CH_{Imidazolium}$), 128.4 (ArCH), 128.1 (ArCH), 128.0 (ArCH), 127.8 (ArCH), 127.62 (ArCH), 127.55 (ArCH), 126.0 (ArCH), 125.9 (ArCH), 125.84 (ArCH), 125.80 (ArCH), 122.5 (2 x $CH_{Imidazolium}$), 98.8 (C-1), 83.8 (C-3), 79.0 (C-4), 74.9 (C-5), 73.9 ($ArCH_2$), 72.6 ($ArCH_2$), 72.0 ($ArCH_2$), 69.9 ($ArCH_2$), 68.5 (C-6), 67.2 (C-2), 19.02 (CH_3), 18.99 (CH_3), 18.8 (CH_3), 18.4 (CH_3);

m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 1225.6520, $C_{79}H_{89}N_2O_{10}$ requires 1225.6512;

$[\alpha]^{23}_D$ = 20 (c 1.1, $CHCl_3$).

1,3-Bis(1,3,4,6-tetra-*O*-(2-naphthylmethyl)-2-deoxy-β-D-glucopyanoside)imidazolium chloride (6e):



Following General Procedure C: Diimine = **5e** (500 mg, 0.33 mmol); solvent = PhMe. In this instance, the isolation method was modified from the general procedure. The crude material was collected by Büchner filtration and washed with cold Et_2O (2 x 10 mL). The remaining solid was dried under high vacuum to yield **6e** (31.7 mg, 61%) as a colourless amorphous solid which was sparingly soluble in common solvents;

ν_{max} / cm^{-1} (film): 3051, 2921, 1509, 1368, 1343, 1271, 1237, 1172, 1089, 1016;

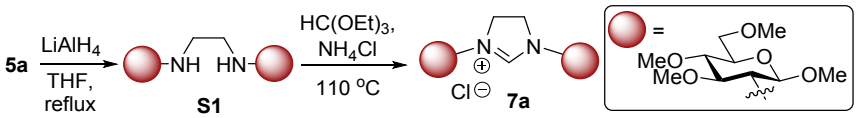
^{1}H NMR (500 MHz, C_6D_6, 70 °C) δ: 12.31 (1H, br s, C2H), 8.02 (2H, s, ArCH), 7.71-7.67 (6H, m, ArCH), 7.63-7.30 (28H, m, ArCH), 7.24-7.18 (10H, m, ArCH), 7.06-6.99 (4H, m, ArCH), 6.96 (2H, s, C4H and C5H), 6.93-6.90 (4H, m, ArCH), 6.68 (2H, *app.* d, *J* = 9.5 Hz, ArCH), 6.40 (2H, br s, H-1), 5.55 (2H, d, *J* = 11.5 Hz, ArC*H*H), 5.40 (2H, *app.* d, *J* = 10.5 Hz, H-6a), 5.15 (2H, m, H-3), 5.00 (2H, d, *J* = 11.5 Hz, ArC*H*H), 4.97 (2H, d, *J* = 11.5 Hz, ArCH*H*), 4.75 (2H, m, H-5), 4.67 (2H, d, *J* = 11.5 Hz, ArCH*H*), 4.59 (2H, d, *J* = 12.0 Hz, ArC*H*H), 4.41 (2H, d, *J* = 12.0 Hz, ArCH*H*), 4.23 (2H, *app.* t, *J* = 9.5 Hz, H-4), 3.91 (2H, *app.* d, *J* = 10.5 Hz,

H-6b), 3.86 (2H, *app.* d, *J* = 8.5 Hz, H-2), 3.82 (2H, d, *J* = 11.5 Hz, ArC*H*H), 3.76 (2H, d, *J* = 11.5 Hz, ArCH*H*);

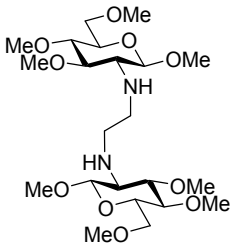
^{13}C NMR (125 MHz, $(CD_3)_2SO$) *observed peaks* δ: 137.4 (CH $_{Imidazolium}$), 135.7 (ArC), 135.4 (ArC), 134.6 (ArC), 134.0 (ArC), 132.8 (ArC), 132.6 (ArC), 132.48 (ArC), 132.46 (ArC), 132.44 (ArC), 132.40 (ArC), 132.35 (ArC), 132.3 (ArC), 127.9 (ArCH), 127.8 (ArCH), 127.71 (ArCH), 127.69 (ArCH), 127.62 (ArCH), 127.57 (ArCH), 127.55 (ArCH), 127.53 (ArCH), 127.50 (ArCH), 127.38 (ArCH), 127.36 (ArCH), 126.3 (ArCH), 126.2 (ArCH), 126.14 (ArCH), 126.12 (ArCH), 126.04 (ArCH), 126.01 (ArCH), 125.98 (ArCH), 125.97 (ArCH), 125.95 (ArCH), 125.92 (ArCH), 125.90 (ArCH), 125.87 (ArCH), 125.8 (ArCH), 125.6 (ArCH), 125.3 (ArCH), 122.2 (CH $_{Imidazolium}$), 97.9 (C-1), 80.7 (C-3), 77.9 (C-$_{carbhydrate}$), 74.4 (C-$_{carbhydrate}$), 73.9 ($ArCH_2$), 73.8 ($ArCH_2$), 72.5 ($ArCH_2$), 70.1 ($ArCH_2$), 68.3 (C-6), 64.2 (C-2).

m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 1513.6529, $C_{103}H_{89}N_2O_{10}Rh$ requires 1513.6512;

Imidazolinium Chloride 7a Synthesis Overview:



***N*,*N*'-Di(1,3,4,6-tetra-*O*-methyl-2-deoxy-β-D-glucopyranoside)ethyldiamine (S1):**



To a suspension of **5a** (776 mg, 1.57 mmol) in anhydrous THF (7.9 mL) at rt, was added $LiAlH_4$ (1 M THF, 6.30 mL) and the mixture was heated to 70 °C. After 14 h the reaction was allowed to cool to rt and then quenched by the careful addition of: H_2O (0.4 mL), followed by aq. NaOH (15% by wt, 0.4 mL) and then H_2O (1.2 mL), which formed a precipitate. Filtration through Celite®, and further washing of the filter pad with Et_2O (3 x 25 mL), gave a colourless solution. The solution was concentrated under reduced pressure to yield **S1** (781 mg, 100%) as a colourless solid;

R_f = 0.5 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 2932, 2833, 1447, 1381, 1319, 1186, 1101, 1050;

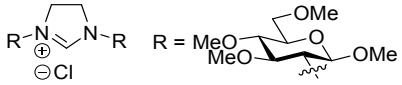
^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.10 (2H, d, *J* = 8.0 Hz, H-1), 3.63 (2H, dd, *J* = 11.0 and 2.0 Hz, H-6a), 3.60 (6H, s, CH_3), 3.57 (2H, dd, *J* = 11.0 and 4.5 Hz, H-6b), 3.52 (6H, s, CH_3), 3.48 (6H, s, CH_3), 3.41 (6H, s, CH_3), 3.29 (2H, ddd, *J* = 9.5, 4.5 and 2.0 Hz, H-5), 3.24 (2H, *app.* t, *J* = 9.5 Hz, H-4), 3.11 (2H, dd, *J* = 10.0 and 8.5 Hz, H-3), 2.95 (2H, m, found *J* = 13.0, 5.5 and 5.0 Hz, C*H*H), 2.77 (2H, m, found *J* = 13.0, 5.5 and 5.0 Hz, CH*H*), 2.48 (2H, dd, *J* = 10.0 and 8.0 Hz, H-2), 1.82 (2H, br s, NH);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 105.3 (C-1), 85.5 (C-3), 80.1 (C-4), 74.8 (C-5), 71.3 (C-6), 62.7 (C-2), 60.14 (CH_3), 60.06 (CH_3), 59.3 (CH_3), 56.8 (CH_3), 49.0 (CH_2);

m/z HRMS (ESI): Found $[M+H]^+$ 497.3090, $C_{22}H_{45}N_2O_{10}$ requires 497.3069;

$[\alpha]^{21}_D$ = -6 (*c* 1.0, $CHCl_3$).

1,3-Bis(1,3,4,6-tetra-*O*-methyl-2-deoxy-β-D-glucopyranoside)imidazolinium chloride (7a):



Adapted from Huynh and co-workers.[5] To a solution of **S1** (781 mg, 1.57 mmol) in $CH(OEt)_3$ (5.3 mL) at rt, was added NH_4Cl (92.6 mg, 1.73 mmol) and the suspension was heated to 100 °C under a balloon of Ar. After 14 h the reaction was allowed to cool to 60 °C and then placed under vacuum for 0.5 h to give a residue. Purification by FCC (98:2-90:10 CH_2Cl_2:MeOH) yielded **7a** (638 mg, 74%) as a colourless solid;

R_f = 0.1 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3426, 2941, 1642, 1452, 1382, 1319, 1254, 1223, 1193, 1123, 1066;

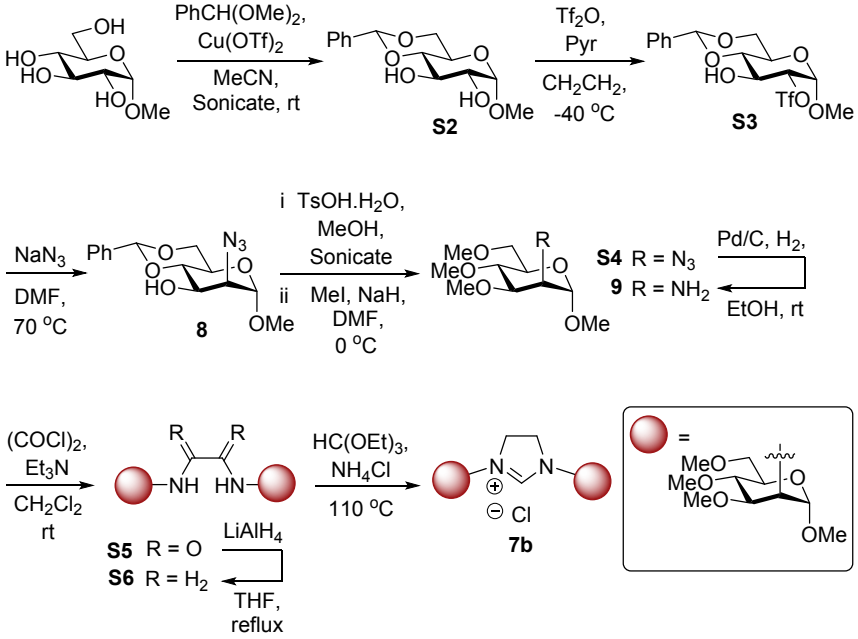
^{1}H NMR (500 MHz, $CDCl_3$) δ: 10.86 (1H, s, $CH_{Imidazolinium}$), 5.16 (2H, d, *J* = 8.5 Hz, H-1), 4.12 (2H, dd, *J* = 11.0 and 9.0 Hz, H-3), 4.07 (4H, s, $CH_{2\ Imidazolinium}$), 3.66 (2H, *app*. dt, *J* = 10.0 and 2.5 Hz, H-5), 3.63 (6H, s, CH_3), 3.60- 3.59 (4H, m, H-6a and H-6b), 3.52 (6H, s, CH_3), 3.49 (6H, s, CH_3), 3.38 (6H, s, CH_3), 3.31 (2H, dd, *J* = 10.0 and 9.0 Hz, H-4), 3.04 (2H, dd, *J* = 11.0 and 8.5 Hz, H-2);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.0 ($CH_{Imidazolinium}$), 100.8 (C-1), 82.9 (C-3), 80.5 (C-4), 74.1 (C-5), 70.3 (C-6), 64.3 (C-2), 61.1 (CH_3), 59.9 (CH_3), 59.3 (CH_3), 57.1 (CH_3), 51.3 ($CH_{2\ Imidazolinium}$).

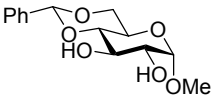
m/z HRMS (ESI): Found $[M-Cl]^+$ 507.2902, $C_{23}H_{43}N_2O_{10}$ requires 507.2912;

$[\alpha]^{20}_D$ = 37 (*c* 0.9, $CHCl_3$).

Imidazolinim Chloride 7b Synthesis Overview:



4,6-*O*-Benzylidene-1-*O*-methyl-α-D-glucopyranoside (S2):



As reported by Galan and co-workers.[6] To suspension of methyl-α-D-glucopyranoside (10.0 g, 51.5 mmol) in anhydrous MeCN (260 mL) at rt, was added distilled $PhCH(OMe)_2$ (9.3 mL, 61.8 mmol) and $Cu(OTf)_2$ (0.93 g, 2.58 mmol). The resulting mixture was sonicated at rt for 3 h, by which time the medium was transparent, and the reaction was quenched by addition of Et_3N (3 mL), causing a green precipitate to form. The solvent was removed *in vacuo* and the residue was purified by FCC (dry loaded, 98:2-90:10 CH_2Cl_2:MeOH) to yield **S2** (13.1 g, 90%) as a colourless solid;

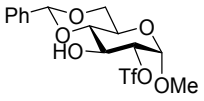
R_f = 0.5 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3395, 2937, 2864, 1454, 1423, 1411, 1374, 1350, 1336, 1294, 1226, 1209, 1189, 1162, 1142, 1125, 1084, 1067, 1039, 1023;

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.48 (2H, m, ArCH), 7.38-7.35 (3H, m, ArCH), 5.53 (1H, s, PhCH), 4.78 (1H, d, *J* = 4.0 Hz, H-1), 4.28 (1H, dd, *J* = 9.5 and 4.5 Hz, H-6a), 3.92 (1H, td, *J* = 9.5 and 2.0 Hz, H-3), 3.86-3.75 (1H, m, H-5), 3.74 (1H, dd, *J* = 10.5 and 9.5 Hz, H-6b), 3.62 (1H, td, *J* = 9.5 and 4.0 Hz, H-2), 9.23 (1H, *app*. t, *J* = 9.5 Hz, H-4), 3.45 (3H, s, OCH_3), 2.83 (1H, d, *J* = 2.0 Hz, OH), 2.35 (1H, d, *J* = 9.5 Hz, OH),

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.1 (ArC), 129.4 (ArCH), 128.5 (ArCH), 126.4 (ArCH), 102.0 (PhCH), 99.8 (C-1), 81.0 (C-4), 73.0 (C-2), 71.9 (C-3), 69.1 (C-6), 62.5 (C-5), 55.7 (OCH_3). *Spectroscopic data in agreement with the literature*.[7]

4,6-*O*-Benzylidene-1-*O*-methyl-2-*O*-trifluoromethylsulfonate-α-D-glucopyranoside (S3):



Adapted from Fairbanks and co-workers.[8] To a solution of freshly distilled pyridine (9.4 mL, 116 mmol) and anhydrous CH_2Cl_2 (165 mL) at -50 °C (achieved by careful monitoring of an acetone – dry ice bath), was added anhydrous Tf_2O (5.4 mL, 32.0 mmol) dropwise. Another solution, consisting of **S2** (8.2 g, 29.1 mmol) dissolved in anhydrous CH_2Cl_2 (390 mL) at -78 °C (acetone – dry ice bath), was added *via* cannula. The dry ice bath was allowed to warm to -30 °C and then maintained at this temperature. After 3 h the reaction was quenched by the addition of H_2O (10 mL) and then allowed to warm to rt. The organic phase was washed with H_2O (2 x 200 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Further purification of the residue by FCC (99:1-90:10 PhMe:EtOAc) afforded some di-triflated material (not isolated, R_f = 0.3 (80:20 PhMe:EtOAc)) and **S3** (8.8 g, 73%, R_f = 0.2 (80:20 PhMe:EtOAc)) as a colourless oil that crystallised upon standing;

R_f = 0.3 (80:20 hexane:EtOAc);

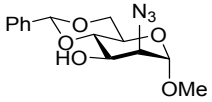
ν_{max} / cm^{-1} (film): 3499, 2936, 1461, 1412, 1381, 1274, 1247, 1213, 1143, 1088, 1036, 1025;

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49-7.47 (2H, m, ArCH), 7.40-7.37 (3H, m, ArCH), 5.54 (1H, s, PhCH), 4.97 (1H, d, *J* = 4.0 Hz, H-1), 4.69 (1H, dd, *J* = 9.5 and 4.0 Hz, H-2), 4.32 (1H, dd, *J* = 10.5 and 5.0 Hz, H-6a), 4.26 (1H, td, *J* = 9.5 and 3.5 Hz, H-3), 3.90-3.83 (1H, m, H-5), 3.75 (1H, *app*. t, *J* = 10.5 Hz, H-6b), 3.54 (1H, *app*. t, *J* = 9.5 Hz, H-4), 3.48 (3H, s, OCH_3), 2.72 (1H, d, *J* = 3.5 Hz, OH);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 136.7 (ArC), 129.6 (ArCH), 128.6 (ArCH), 126.4 (ArCH), 118.6 (q, *J* = 319.5 Hz, CF_3) 102.3 (PhCH), 97.7 (C-1), 84.2 (C-2), 81.2 (C-4), 68.8 (C-6), 68.4 (C-3), 62.1 (C-5), 56.1 (OCH_3);

^{19}F NMR (470 MHz, $CDCl_3$) δ: -74.5 (s, CF_3). *Spectroscopic data in agreement with the literature*.[8]

2-Azido-4,6-*O*-benzylidene-1-*O*-methyl-2-deoxy-α-D-mannopyranoside (8):



As reported by Moravcová and co-workers.[9] To a solution of **S3** (3.32 g, 8.01 mmol) in anhydrous DMF (80 mL) at rt, was added NaN_3 (2.60, 40.1 mmol). The suspension was heated to 70 °C for 16 h and then concentrated *in vacuo*. The residue was suspended in CH_2Cl_2 (50 mL) and washed with H_2O (10 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by FCC (90:10 Petrol:EtOAc) yielded **8** (2.32 g, 94%) as a colourless oil;

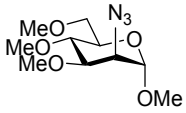
R_f = 0.3 (80:20 hexane:EtOAc);

ν_{max} / cm^{-1} (film): 3462, 2916, 2104, 1456, 1379, 1309, 1270, 1212, 1200, 1128, 1094, 1058, 1020;

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.45 (2H, m, ArCH), 7.42-7.34 (3H, m ArCH), 5.58 (1H, s, PhCH), 4.70 (1H, d, *J* = 1.5 Hz, H-1), 4.33-4.22 (2H, m, H-6a & H-3), 3.99 (1H, dd, *J* = 4.0 and 1.5 Hz, H-2), 3.90 (1H, m, found *J* = 9.5 Hz, H-5), 3.85-3.79 (1H, m, H-6a), 3.79-3.72 (1H, m, H-4), 3.39 (3H, s, OCH_3), 2.58 (1H, s, OH);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.0 (ArC), 129.3 (ArCH), 128.4 (ArCH), 126.2 (ArCH), 102.3 (PhCH), 100.0 (C-1), 79.0 (H-5), 68.9 (C-3), 68.7 (C-6), 63.6 (C-2), 63.3 (C-4), 55.2 (OCH_3). *Spectroscopic data in agreement with the literature*.[9]

2-Azido-1,3,4,6-tetra-*O*-methyl-2-deoxy-α-D-mannopyranoside (S4):



Adapted from Chang and co-workers.[10] To a solution of **8** (950 mg, 3.10 mmol) in MeOH (15.5 mL) at rt, was added TsOH.H_2O (59 mg, 0.31 mmol). The reaction was sonicated for 1 h and then quenched with Et_3N (0.5 mL). The solution was concentrated *in vacuo*, dissolved in DMF (15.5 mL) and cooled to 0 °C. MeI (0.7 mL, 11.2 mmol) and NaH (60% dispersion in mineral oil, 450 mg, 11.2 mmol) were added and the suspension was allowed to warm to rt over 15 h. The reaction was quenched with MeOH (3 mL) and concentrated *in vacuo* to afford a residue which was taken up in EtOAc (25 mL). The organic phase was washed with H_2O (2 x 5 mL), dried (Na_2SO_4), and concentrated. Purification by FCC (90:10-80:20 hexane:EtOAc) yielded **S4** (730 mg, 90%) as a colourless oil;

R_f = 0.5 (60:40 hexane:EtOAc);

ν_{max} / cm^{-1} (film): 2912, 233, 2013, 1449, 1377, 1312, 1270, 1195, 1136, 1104, 1067;

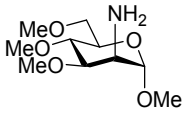
^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.69 (1H, d, *J* = 2.0 Hz, H-1), 3.96 (1H, dd, *J* = 4.0 and 2.0 Hz, H-2), 3.65 (1H, dd, *J* = 9.0 and 4.0 Hz, H-3), 3.60 (1H, dd, *J* = 10.5 and 4.5 Hz, H-6a), 3.58 (1H, dd, *J* = 10.5 and 1.0 Hz, H-6b), 3.57-3.54 (1H, m, H-5), 3.54 (3H, s, CH_3), 3.51 (3H, s, CH_3), 3.44 (1H, *app*. t, *J* = 9.5 Hz, H-4), 3.41 (3H, s, CH_3), 3.35 (3H, s, CH_3);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 99.2 (C-1), 81.5 (C-3), 76.3 (C-4), 71.5 (C-6), 71.3 (C-5), 60.9 (CH_3), 60.5 (C-2), 59.5 (CH_3), 58.0 (CH_3), 55.1 (CH_3);

m/z HRMS (ESI): Found $[M+Na]^+$ 284.1220, $C_{10}H_{19}N_3O_5Na$ requires 284.1217.

$[\alpha]^{21}_D$ = 63 (*c* 1.2, $CHCl_3$).

2-Amino-1,3,4,6-tetra-*O*-methyl-2-deoxy-α-D-mannopyranoside (9):



To solution of **S4** (730 mg, 2.80 mmol) in EtOH (5% wt 12 M HCl, 14.0 mL) under Ar at rt, was added Pd (5% wt on C, 0.28 mmol). H_2 (1 atm, balloon) was bubbled through the solvent until the Ar atmosphere was gradually replaced. After 4 h, the H_2 was displaced by a stream of N_2 and the suspension was neutralised with sat. aq. $NaHCO_3$. The reaction mixture was filtered through Celite® using EtOH as eluent (2 x 15 mL) to afford a colourless solution. Concentration *in vacuo* and subsequent trituration with MeOH (3 x 5 mL) yielded **9** (650 mg, 99%) as a colourless oil which was used without further purification;

R_f = 0.4 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 2903, 1588, 1523, 1458, 1404, 1298, 1206, 1171, 1148, 1092, 1039;

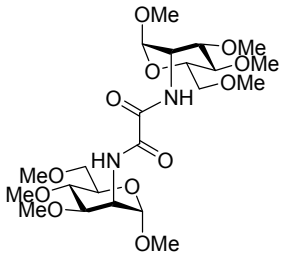
^{1}H NMR (500 MHz, CD_3OD) δ: 4.79 (1H, *app.* s, H-1), 3.68-3.60 (5H, m), 3.52 (3H, s, CH_3), 3.49 (3H, s, CH_3), 3.43 (3H, s, CH_3), 3.40 (3H, s, CH_3), 3.31 (1H, *signal under residual solvent peak*);

^{13}C NMR (125 MHz, CD_3OD) δ: 102.1 (C-1), 82.5 (CH), 79.1 (C-6), 74.9 (CH), 74.3 (CH), 63.5 (CH_3), 62.0 (CH_3), 61.0 (CH_3), 58.3 (CH_3), 54.7 (CH);

m/z HRMS (ESI): Found $[M+Na]^+$ 236.1317, $C_{10}H_{21}NO_5Na$ requires 236.1312;

$[\alpha]^{21}_D$ = 30 (*c* 1.1, $CHCl_3$).

***N*,*N*'-Bis(1,3,4,6-tetra-*O*-methyl-2-deoxy-α-D-mannopyranoside)oxalamide (S5):**



Adapted from Grubbs and co-workers.[11] To a solution of **9** (650 mg, 2.78 mmol) in CH_2Cl_2 (13.6 mL) and distilled Et_3N (381 µL, 2.78 mmol) at rt, was added freshly distilled $(COCl)_2$ (112 µL, 1.38 mmol) dropwise. After 14 h the mixture was concentrated *in vacuo* to afford a residue. Purification by FCC (95:5 CH_2Cl_2:MeOH) yielded **S5** (720 mg, 98%) as a colourless oil;

R_f = 0.8 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3394, 2917, 2831, 1686, 1503, 1370, 1281, 1196, 1129, 1110, 1065;

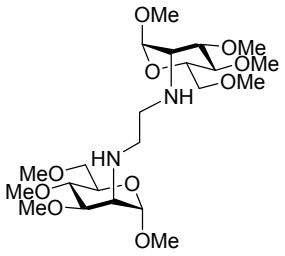
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53 (2H, d, *J* = 8.5 Hz, NH), 4.73 (2H, d, *J* = 1.5 Hz, H-1), 4.41 (2H, ddd, *J* = 8.5, 4.5 and 1.5 Hz, H-2), 3.69 (2H, dd, *J* = 9.5 and 4.5 Hz, H-3), 3.65-3.62 (2H, m, H-5), 3.60 (2H, dd, *J* = 10.0 and 5.5 Hz, H-6a), 3.58 (2H, dd, *J* = 10.0 and 2.0 Hz, H-6b), 3.51 (6H, s, CH_3), 3.42 (12H, s, CH_3), 3.36 (6H, s, CH_3), 3.24 (2H, *app*. t, *J* = 9.5 Hz, H-4);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.8 (C=O), 99.4 (C-1), 79.3 (C-3), 76.0 (C-4), 71.5 (-C6), 70.7 (C-5), 61.0 (CH_3), 59.5 (CH_3), 57.3 (CH_3), 55.3 (CH_3), 49.9 (C-2);

m/z HRMS (ESI): Found $[M+Na]^+$ 547.2483, $C_{22}H_{40}N_2O_{12}Na$ 547.2473;

$[\alpha]^{22}_D = 10$ (*c* 1.7, $CHCl_3$).

_N_,_N_'-Bis(1,3,4,6-tetra-_O_-methyl-2-deoxy-α-D-mannopyranoside)ethyldiamine (S6):



To a suspension of **S5** (648 mg, 1.24 mmol) in anhydrous THF (6.2 mL) at rt, was added $LiAlH_4$ (1 M THF, 4.95 mL) and the mixture was heated to 70 °C. After 14 h the reaction was allowed to cool to rt and then quenched by the careful addition of: H_2O (0.33 mL), followed by aq. NaOH (15% by wt, 0.33 mL) and then H_2O (0.33 mL), which formed a precipitate. Filtration through Celite®, and further washing of the filter pad with Et_2O (3 x 25 mL), gave a colourless solution which was concentrated *in vacuo*. Purification by FCC (95:5 CH_2Cl_2:MeOH) yielded **S6** (497 mg, 75%) as a colourless oil;

R_f = 0.5 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 2908, 2827, 1456, 1107, 1058

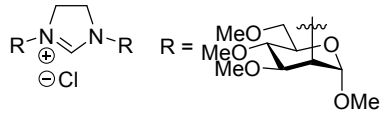
^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.68 (2H, br s, H-1), 3.60 (8H, m, C3H, C5H, H-6a and H-6b), 3.49 (6H, s, CH_3), 3.43 (6H, s, CH_3), 3.40 (6H, s, CH_3), 3.35 (6H, s, CH_3), 3.33 (2H, br *app*. t, *J* = 9.5 Hz, H-4), 3.04 (2H, *app.* d, *J* = 3.0 Hz, H-2), 2.87 (2H, br s, C*H*H and C*H*H), 2.71 (2H, br s, CH*H* and CH*H*);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 99.6 (C-1), 80.6 (C-3 or C-5), 76.1 (C-4), 71.8 (C-6), 70.6 (C-3 or C-5), 60.4 (CH_3), 59.2 (CH_3), 57.9 (C-2), 57.2 (CH_3), 54.9 (CH_3), 48.3 (CH_2);

m/z HRMS (ESI): Found $[M+H]^+$ 497.3061, $C_{22}H_{45}N_2O_{10}$ requires 497.3069;

$[\alpha]^{22}_D = 20$ (*c* 1.0, $CHCl_3$).

1,3-Bis(1,3,4,6-tetra-_O_-methyl-2-deoxy-α-D-mannopyranoside)imidazolinium chloride (7b):



Adapted from Huynh and co-workers.[5] To a solution of **S6** (450 mg, 0.91 mmol) in $CH(OEt)_3$ (3.0 mL) at rt, was added NH_4Cl (53.3 mg, 1.00 mmol) and the suspension was heated to 100 °C under an Ar atmosphere. After 14 h the reaction was allowed to cool to 60 °C and then placed under vacuum for 0.5 h to give a residue. Purification by FCC (90:10 CH_2Cl_2:MeOH) yielded **7b** (430 mg, 87%) as a colourless solid;

R_f = 0.2 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3382, 2934, 2830, 1634, 1512, 1449, 1378, 1298, 1256, 1195, 1099, 1064, 1026;

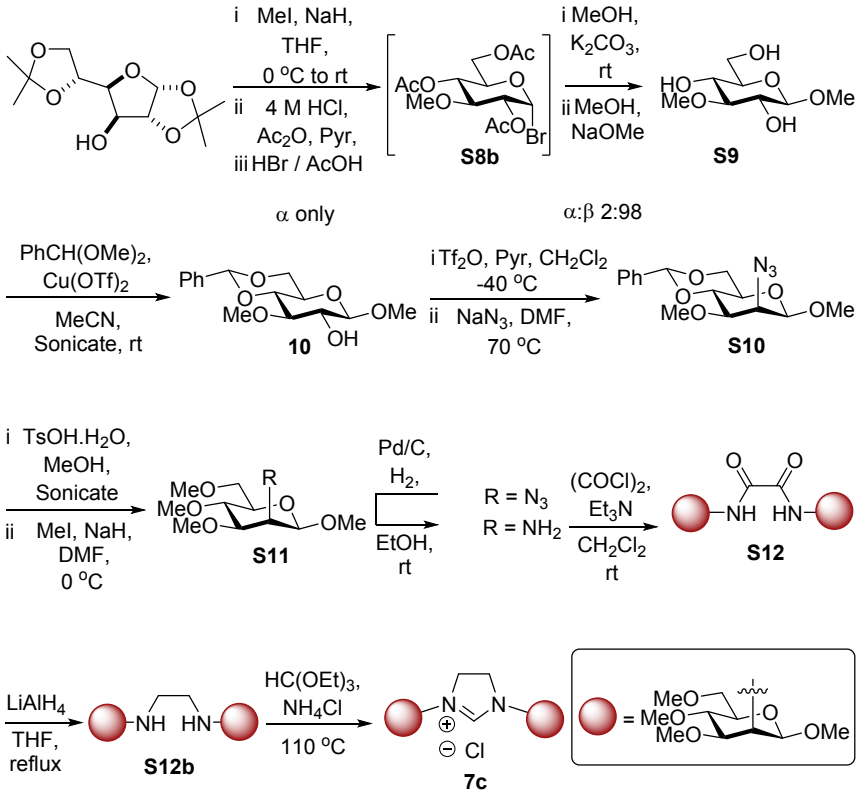
^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.69 (1H, s, CH), 5.12 (2H, d, *J* = 1.5 Hz, H-1), 4.52 (2H, dd, *J* = 5.0 and 1.5 Hz, H-2), 4.22-4.14 (2H, m, C*H*H and C*H*H), 4.10-4.01 (2H, m, CH*H* and CH*H*), 3.74 (2H, dd, *J* = 9.5 and 5.0 Hz, H-3), 3.63 (2H, dd, *J* = 10.5 and 3.0 Hz, H-6a), 3.59 (2H, ddd, *J* = 10.5, 3.0 and 2.0 Hz, H-5), 3.56 (6H, s, CH_3), 3.54 (2H, dd, *J* = 10.5 and 2.0 Hz, H-6b), 3.51 (6H, s, CH_3), 3.38 (6H, s, CH_3), 3.37 (6H, s, CH_3), 3.36 (2H, *app*. t, *J* = 10.5-9.5 Hz, H-4);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.4 (CH), 99.0 (C-1), 79.4 (C-3), 75.7 (C-4), 70.9 (C-6), 70.6 (C-5), 60.7 (CH_3), 59.4 (CH_3), 58.9 (CH_3), 57.9 (C-2), 55.5 (CH_3), 50.1 (CH_2).

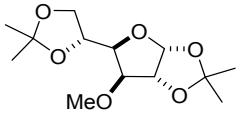
m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 507.2920, $C_{23}H_{43}N_2O_{10}$ requires 507.2912;

$[\alpha]^{21}_D$ = -12 (*c* 1.1, $CHCl_3$).

Imidazolinium Chloride 7c Synthesis Overview:



1,2:5,6-Di-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranoside (S7):



To a solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranoside (20.0 g, 76.8 mmol) and MeI (7.18 mL, 115 mmol) in anhydrous THF (250 mL) at 0 °C, was added NaH (60% dispersion in mineral oil, 4.61 g, 115 mmol)

in 2 portions, 0.5 h apart. After 8 h the reaction was quenched with MeOH (10 mL) and concentrated *in vacuo*. The residue was suspended in EtOAc (150 mL) and was washed with H_2O (50 mL) and brine (50 mL). The organic phase was dried (Na_2SO_4) and concentrated *in vacuo.* Purification by FCC (70:30 hexane:EtOAc) yielded **S7** (20.6 g, 98%) as a colourless oil;

R_f = 0.6 (60:40 hexane:EtOAc);

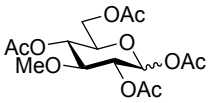
ν_{max} / cm^{-1} (film): 2986, 2936, 2832, 1456, 1371, 1253, 1213, 1164, 1122, 1069, 1013;

^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.86 (1H, d, *J* = 4.0 Hz, H-1), 4.56 (1H, d, *J* = 4.0 Hz, H-2), 4.29 (1H, ddd, *J* = 8.0, 6.0 and 5.5 Hz, H-5), 4.10 (1H, dd, *J* = 8.0 and 3.0 Hz, H-4), 4.08 (1H, dd, *J* = 8.5 and 6.0 Hz, H-6a), 4.00 (1H, dd, *J* = 8.5 and 5.5 Hz, H-6b), 3.77 (1H, br d, *J* = 3.0, H-3), 3.45 (3H, s, OCH_3), 1.50 (3H, s, CH_3), 1.43 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.32 (3H, s, CH_3);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.9 (C4°), 109.2 (C4°), 105.3 (C-1), 83.8 (C-3), 82.0 (C-2), 81.2 (C-4), 72.5 (C-5), 67.4 (C-6), 58.3 (CH_3), 27.02 (CH_3), 26.97 (CH_3), 26.4 (CH_3), 25.6 (CH_3);

Spectroscopic data in agreement with the literature.[12]

1,2,4,6-Tetra-*O*-acetate-2-*O*-methyl-α,β-D-glucopyranoside (S8):



To **S7** (20.6 g, 75.1 mmol) at rt, was added aq. HCl (4 M, 188 mL, 751 mmol). After 0.75 h the reaction was quenched with pyridine (67 mL, 827 mmol) and concentrated *in vacuo*. The residue was suspended in pyridine (245 mL) and Ac_2O (123 mL) was added. After 18 h, the reaction was concentrated *in vacuo* and the residue redissolved in CH_2Cl_2 (250 mL) and washed with: aq. HCl (1 M, 100 mL), H_2O (100 mL), sat. aq. $NaHCO_3$ (100 mL) and brine (100 mL). The organic phase was dried (Na_2SO_4), concentrated, and azeotroped with PhMe (2 x 50 mL) to yield **S8** (26.5 g, 97%, 0.5:1 α:β) as a colourless oil;

R_f = 0.9 (90:10 EtOAc:MeOH);

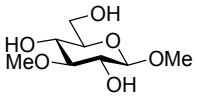
ν_{max} / cm^{-1} (film): 2941, 1741, 1433, 1369, 1208, 1152, 1086, 1058, 1033;

^{1}H NMR (400 MHz, $CDCl_3$) *data for the β anomer* δ: 5.63 (1H, d, *J* = 8.0 Hz, H-1), 5.09 (1H, dd, *J* = 9.5 and 8.0 Hz, H-2), 5.07 (1H, dd, *J* = 10.0 and 9.5 Hz, H-4), 4.21 (1H, dd, *J* = 12.5 and 5.0 Hz, H-6a), 4.08 (1H, dd, *J* = 12.5 and 2.5 Hz, H-6b), 3.71 (1H, ddd, *J* = 10.0, 5.0 and 2.5 Hz, H-5), 3.52 (1H, *app*. t, *J* = 9.5 Hz, H-3), 3.41 (3H, s, OCH_3), 2.089 (3H, s, CH_3), 2.086 (3H, s, CH_3), 2.08 (3H, s, CH_3), 2.07 (3H, s, CH_3). *Data for the α anomer* δ: 6.28 (1H, d, *J* = 3.5 Hz, H-1), 5.07 (1H, *app*. t, *J* = 10.0 Hz, H-4), 4.99 (1H, dd, *J* = 10.0 and 3.5 Hz, H-2), 4.19 (1H, dd, *J* = 12.5 and 4.5 Hz, H-6a), 4.05 (1H, dd, *J* = 12.5 and 2.5 Hz, H-6b), 3.99 (1H, ddd, *J* = 12.5, 4.5 and 2.5 Hz, H-5), 3.70 (1H, *app*. t, *J* = 10.0 Hz, H-3), 3.45 (3H, s, OCH_3), 2.15 (3H, s, CH_3), 2.10 (3H, s, CH_3), 2.07 (3H, s, CH_3), 2.05 (3H, s, CH_3);

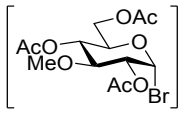
^{13}C NMR (100 MHz, $CDCl_3$) *data for the β anomer* δ: 170.8 (C=O), 169.42 (C=O), 169.35 (C=O), 169.3 (C=O), 92.1 (C-1), 81.5 (C-3), 73.1 (C-5), 71.2 (C-2), 68.6 (C-4), 61.9 (C-6), 59.4 (OCH_3), 21.0 (CH_3), 20.92 (CH_3), 20.89 (CH_3), 20.88 (CH_3). *Data for the α anomer* δ: 170.9 (C=O), 169.7 (C=O), 169.4 (C=O), 168.9 (C=O), 89.6 (C-1), 78.3 (-C3), 71.2 (C-2), 70.3 (C-5), 69.0 (C-4), 61.9 (C-6), 60.2 (OCH_3), 21.02 (CH_3), 20.92 (CH_3), 20.87 (CH_3), 20.8 (CH_3);

m/z HRMS (ESI): Found $[M+Na]^+$ 385.1104, $C_{15}H_{22}O_{10}Na$ requires 385.1105.

1,3-Di-*O*-methyl-β-D-glucopyranoside (S9):



To **S8** (26.4 g, 72.9 mmol) at rt, was added anhydrous HBr (33% by wt in AcOH, 21.1 mL, 87.4 mmol). After 18 h the reaction was quenched by addition of NaOAc (~20 g). The residue was suspended in EtOAc 200 mL and filtered. The filtrate was washed with sat. aq. $NaHCO_3$ (2 x 100 mL) and then brine (100 mL). The organic phase was dried (Na_2SO_4) and concentrated *in vacuo* to yield crude 2,4,6-tri-*O*-acetate-3-*O*-methyl-α-D-glucopyranosyl bromide **S8b** (27.6 g, 99%) as an oil, which was used in the next step without further purification.



S8b

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.62 (1H, d, *J* = 4.0 Hz, H-1), 5.10 (1H, dd, *J* = 10.5 and 9.5 Hz, H-4), 4.70 (1H, dd, *J* = 9.5 and 4.0 Hz, H-2), 4.26 (1H, dd, *J* = 12.5 and 4.5 Hz, H-6a), 4.17 (1H, ddd, *J* = 10.5, 4.5 and 2.0 Hz, H-5), 4.10 (1H, dd, *J* = 12.5 and 2.0 Hz, H-6b), 3.79 (1H, *app*. t, *J* = 9.5 Hz, H-3), 3.50 (3H, s, OCH_3), 2.15 (3H, s, CH_3), 2.12 (3H, s, CH_3), 2.09 (3H, s, CH_3);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.8 (C=O), 169.9 (C=O), 169.4 (C=O), 88.2 (C-1), 78.9 (C-3), 72.9 (C-2), 72.7 (C-5), 68.4 (C-4), 61.3 (C-6), 60.9 (OCH_3), 21.0 (3H, s, CH_3), 20.9 (3H, s, CH_3), 20.8 (3H, s, CH_3);

m/z HRMS (ESI): Found $[M+Na]^+$ 405.0153, $BrC_{13}H_{19}O_8Na$ requires 405.0156

To a solution of **S8b** (9.7 g, 25.4 mmol) in anhydrous MeOH (254 mL) at rt, was added activated powdered 4Å MS (~2 g) and K_2CO_3 (1.75 g, 12.7 mmol). After 48 h the reaction was filtered through Celite® and concentrated to ~100 mL volume. To this solution at rt, was added 2 M NaOMe (2.54 mL, 5.08 mmol). After 0.5 h, H_2O (5.0 mL) was added and the reaction was concentrated *in vacuo*. Purification of the residue by FCC (dry loaded, 95:5 EtOAc:MeOH) yielded **S9** (2.15 g, 41%);

R_f = 0.4 (90:10 EtOAc:MeOH);

ν_{max} / cm^{-1} (film): 3357, 2942, 1644, 1451, 1383, 1219, 1189, 1108, 1074, 1034;

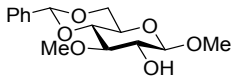
^{1}H NMR (400 MHz, CD_3OD) δ: 4.17 (1H, d, *J* = 8.0 Hz, H-1), 3.86 (1H, dd, *J* = 12.0 and 2.5 Hz, H-6a), 3.66 (1H, dd, *J* = 12.0 and 5.5 Hz, H-6b), 3.63 (3H, s, OCH_3), 3.52 (3H, s, OCH_3), 3.35 (1H, dd, *J* = 10.0 and 8.5 Hz, H-4), 3.26 (1H, ddd, *J* = 10.0, 5.5 and 2.5 Hz, H-5), 3.21 (1H, dd, *J* = 9.0 and 8.0 Hz, H-2), 3.07 (1H, dd, *J* = 9.0 and 8.5 Hz, H-3);

^{13}C NMR (125 MHz, CD_3OD) δ: 105.3 (C-1), 87.7 (C-3), 77.7 (C-5), 74.8 (C-2), 71.1 (C-4), 62.5 (C-6), 61.1 (OCH_3), 57.4 (OCH_3);

m/z HRMS (ESI): Found $[M+Na]^+$ 231.0838, $C_8H_{16}O_6Na$ requires 231.0839.

$[\alpha]^{23}_D$ = -26 (*c* 1.2, MeOH).

4,6-*O*-Benzylidene-1,3-di-*O*-methyl-β-D-glucopyranoside (10):



As reported by Galan and co-workers.[6] To solution of **S9** (3.50 g, 16.8 mmol) in anhydrous MeCN (85 mL) at rt, was added distilled $PhCH(OMe)_2$ (3.0 mL, 20.2 mmol) and $Cu(OTf)_2$ (608 mg, 1.68 mmol). The resulting solution was sonicated at rt for 3 h and the reaction was quenched by addition of Et_3N (2.0 mL), causing a green precipitate to form. The solvent was removed *in vacuo* and the residue was purified by FCC (dry loaded, 60:40 to 40:60 hexane:EtOAc) to yield **10** (3.19 g, 64%) as a colourless solid;

R_f = 0.5 (80:20 EtOAc:hexane);

ν_{max} / cm^{-1} (film): 3407, 2983, 2933, 2879, 2845, 1470, 1453, 1409, 1378, 1329, 1304, 1272, 1235, 1215, 1190, 1170, 1093, 1080, 1070, 1013;

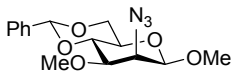
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.47 (2H, m, ArCH), 7.40-7.35 (3H, m, ArCH), 5.56 (1H, s, PhCH), 4.36 (1H, dd, *J* = 10.5 and 5.0 Hz, H-6a), 4.34 (1H, d *J* = 7.5 Hz, H-1), 3.79 (1H, *app*. t, *J* = 10.5 Hz, H-6b), 3.68 (3H, s, OCH_3), 3.63 (1H, *app*. t, *J* = 9.0 Hz, H-4), 3.58 (3H, s, OCH_3), 3.51-3.41 (3H, m, H-2 & H-3 & H-5), 2.64 (1H, br. s, OH);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.3 (ArC), 129.1 (ArCH), 128.4 (ArCH), 126.1 (ArCH), 104.3 (C-1), 101.4 (PhC), 82.4 (C-3), 81.7 (C-4), 74.2 (C-2), 68.8 (C-6), 66.5 (C-5), 61.1 (OCH_3), 57.6 (OCH_3).

Spectroscopic data in agreement with the literature.[13]

Continued elution (90:10 EtOAc:MeOH) yielded **S9** (0.99 g, 28%) as a colourless oil.

Methyl 2-azido-4,6-*O*-benzylidene-3-*O*-methyl-2-deoxy-β-D-mannopyranoside (S10):



To a solution of **10** (2.03 g, 6.85 mmol) and pyridine (1.44 mL, 17.8 mmol) in anhydrous CH_2Cl_2 (140 mL) at 0 °C, was added Tf_2O (1.50 mL, 8.91 mmol) dropwise. The solution was maintained at 0 °C for 2 h and then

quenched with H_2O (50 mL) and allowed to warm to rt. The mixture was washed with H_2O (2 x 50 mL), brine (50 mL), and the organic phase dried over anhydrous Na_2SO_4. Concentration *in vacuo* afforded crude 4,6-*O*-benzylidene-1,3-di-*O*-methyl-2-trifluoromethanesulfonate-β-D-glucopyranoside (2.93 g, 100%) as an orange oil which was immediately used without further purification (see below). To a solution of methyl 4,6-*O*-benzylidene-3-*O*-methyl-2-trifluoromethanesulfonate-β-D-glucopyranoside (2.93 g, 6.85 mmol) in anhydrous DMF (70 mL) at rt, was added NaN_3 (2.28 g, 35.0 mmol). The suspension was heated at 70 °C for 14 h and then allowed to cool to rt. The mixture was concentrated *in vacuo* and the subsequent residue was suspended in CH_2Cl_2 (100 mL). The organic phase was washed with H_2O (40 mL) and brine (40 mL), and then dried over anhydrous Na_2SO_4. Concentration *in vacuo*, followed by purification by FCC (80:20 hexane:EtOAc) yielded **S10** (1.85 g, 87%) as a colourless oil;

R_f = 0.6 (80:20 hexane:EtOAc);

ν_{max} / cm^{-1} (film): 2888, 2106, 1451, 1378, 1284, 1218, 1166, 1093, 1044;

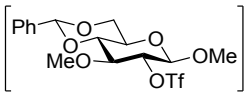
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49-7.47 (2H, m, ArCH), 7.39-7.34 (3H, m, ArCH), 5.58 (1H, s, PhCH), 4.54 (1H, d, *J* = 1.5 Hz, H-1), 4.33 (1H, dd, *J* = 10.5 and 5.0 Hz, H-6a), 4.13 (1H, dd, *J* = 4.0 and 1.5 Hz, H-2), 3.96 (1H, *app*. t, *J* = 9.5 Hz, H-4), 3.88 (1H, *app*. t, *J* = 10.5 Hz, H-6b), 3.581 (3H, s, OCH_3), 3.580 (3H, s, OCH_3), 3.56 (1H, dd, *J* = 9.5 and 4.0 Hz, H-3), 3.36 (1H, ddd, *J* = 10.0, 9.5 and 5.0 Hz, H-5);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.3 (ArC), 129.2 (ArCH), 128.4 (ArCH), 126.2 (ArCH), 101.9 (PhCH), 101.5 (C-1), 79.2 (C-3), 78.7 (C-4), 68.6 (C-6), 67.4 (C-5), 62.6 (C-2), 59.2 (OCH_3), 57.6 (OCH_3);

m/z HRMS (ESI): Found $[M+Na]^+$ 344.1223, $C_{15}H_{19}O_5Na$ requires 344.1222.

$[\alpha]^{21}_D$ = -101 (*c* 0.7, $CHCl_3$).

Methyl 4,6-*O*-Benzylidene-3-*O*-methyl-2-trifluoromethanesulfonate-β-D-glucopyranoside:



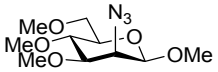
R_f = 0.8 (80:20 hexane:EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.47 (2H, m, ArCH), 7.40-7.37 (3H, m, ArCH), 5.57 (1H, s, PhCH), 4.55-4.49 (2H, m, H-1 & H-2), 4.39 (1H, dd, *J* = 10.5 and 5.0 Hz, H-6a), 3.80 (1H, *app*. t, *J* = 10.5 Hz, H-6b), 3.66 (1H, *app*. t, *J* = 9.0 Hz, H-4), 3.63 (3H, s, OCH_3), 3.60 (1H, *app*. t, *J* = 9.0 Hz, H-3), 3.58 (3H, s, OCH_3), 3.46 (1H, *app*. dt, *J* = 10.0 and 5.0 Hz, H-5);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.9 (ArC), 129.3 (ArCH), 128.5 (ArCH), 126.1 (ArCH), 118.6 (q, *J* = 319.5 Hz, SCF_3), 101.46 & 101.44 (C-1 & PhC), 84.8 (C-2), 81.6 (C-4), 80.1 (C-3), 68.5 (C-6), 66.3 (C-5), 61.2 (OCH_3), 57.9 (OCH_3); ^{19}F NMR (377 MHz, $CDCl_3$) δ: -74.2 (SCF_3);

m/z HRMS (ESI): Found $[M+H]^+$ 429.0825, $C_{16}H_{20}F_3O_8S$ requires 429.0825.

Methyl 2-azido-2-deoxy-3,4,6-tri-*O*-methyl-β-D-mannopyranoside (S11):



Adapted from Chang and co-workers.[10] To a solution of **S10** (1.88 g, 5.85 mmol) in MeOH (30.0 mL mL) at rt, was added TsOH.H_2O (111 mg, 0.59 mmol). The reaction was sonicated for 1.5 h and then quenched with Et_3N (0.5 mL). The solution was concentrated *in vacuo*, dissolved in DMF (30.0 mL) and cooled to 0 °C. MeI (0.91 mL, 14.6 mmol) and NaH (60% dispersion in mineral oil, 585 mg, 11.2 mmol) were added and the suspension was allowed to warm to rt over 3 h. The reaction was quenched with MeOH (5 mL) and concentrated *in vacuo* to afford a residue which was redissolved in EtOAc (50 mL). The organic phase was washed with H_2O (10 mL) and brine (10 mL), and then dried over anhydrous Na_2SO_4. Concentration *in vacuo*, followed by purification by FCC (80:20 hexane:EtOAc) yielded **S11** (1.26 g, 82%) as a colourless oil;

R_f = 0.3 (80:20 hexane:EtOAc);

ν_{max} / cm^{-1} (film): 2934, 2105, 1449, 1374, 1319, 1283, 1216, 1112, 1076, 1057, 1006;

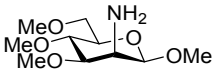
^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.38 (1H, d, *J* = 1.0 Hz, H-1), 4.03 (1H, dd, *J* = 3.5 and 1.0 Hz, H-2), 3.66 (1H, dd, *J* = 11.0 and 2.0 Hz, H-6a), 3.59 (1H, dd, *J* = 11.0 and 5.0 Hz, H-6b), 3.53 (3H, s, OCH_3), 3.52 (3H, s, OCH_3), 3.50 (3H, s, OCH_3), 3.41 (3H, s, OCH_3), 3.35 (1H, dd, *J* = 9.5 and 8.5 Hz, H-4), 3.30 (1H, dd, *J* = 8.5 and 3.5 Hz, H-3), 3.26 (1H, ddd, *J* = 9.5, 5.0 and 2.0 Hz, H-5);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 100.7 (C-1), 83.3 (C-3), 76.1 (C-4), 75.7 (C-5), 71.6 (C-6), 61.0 (C-2 & OCH_3), 59.6 (OCH_3), 57.8 (OCH_3), 57.2 (OCH_3);

m/z HRMS (ESI): Found $[M+Na]^+$ 284.1218, $C_{10}H_{19}N_3O_5Na$ requires 284.1217;

$[\alpha]^{22}_D$ = -113 (*c* 1.9, $CHCl_3$).

Methyl 2-amino-2-deoxy-3,4,6-tri-*O*-methyl-β-D-mannopyranoside (11):



To solution of **S11** (1.0 g, 3.83 mmol) in EtOH (5% wt 12 M HCl, 19.0 mL) under Ar at rt, was added Pd (5% wt on C, 0.38 mmol). H_2 (1 atm, balloon) was bubbled through the solvent and the Ar atmosphere was gradually replaced. After 2 h the H_2 was blown off by a stream of N_2 and the suspension was neutralised with sat. aq. $NaHCO_3$. The reaction mixture was filtered through Celite® using EtOH as eluent (2 x 15 mL) to afford a colourless solution. Concentration *in vacuo* and subsequent trituration with MeOH (3 x 5 mL) yielded **11** (580 mg, 64%) as a colourless oil, which solidified upon standing and which was used without further purification;

R_f = 0.3 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3378, 2931, 1449, 1380, 1318, 1179, 1103, 1055, 1007;

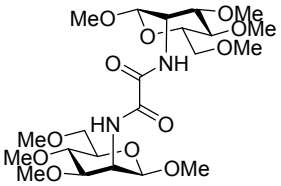
^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.28 (1H, d, *J* = 1.5 Hz, H-1), 3.66 (1H, dd, *J* = 10.5 and 2.0 Hz, H-6a), 3.59 (1H, dd, *J* = 10.5 and 5.0 Hz, H-6b), 3.50 (6H, s, OCH_3), 3.44 (3H, s, OCH_3), 3.41 (3H, s, OCH_3), 3.41-3.39 (1H, m, H-2), 3.37 (1H, *app*. t, *J* = 9.5-9.0 Hz, H-4), 3.25 (1H, ddd, *J* = 9.5, 5.0 and 2.0 Hz, H-5), 3.20 (1H, dd, *J* = 9.0 and 4.0 Hz, H-3), 1.57 (2H, br s, NH_2);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 102.0 (C-1), 84.0 (C-3), 75.8 (C-4), 75.4 (C-5), 71.8 (C-6), 60.7 (OCH_3), 59.5 (OCH_3), 57.0 (2 x OCH_3), 51.4 (C-2);

m/z HRMS (ESI): Found $[M+H]^+$ 236.1503, $C_{10}H_{22}NO_5$ requires 236.1492.

$[\alpha]^{22}_D$ = -79 (*c* 1.0, $CHCl_3$).

Bis(1,3,4,6-tetra-*O*-methyl-2-deoxy-β-D-mannopyranoside)oxalamide (S12):



Adapted from Grubbs and co-workers.[11] To a solution of **11** (530 mg, 2.25 mmol) in CH_2Cl_2 (11.3 mL) and distilled Et_3N (314 μL, 2.25 mmol) at rt, was added freshly distilled $(COCl)_2$ (95.3 μL, 1.13 mmol) dropwise. After 17 h the mixture was concentrated *in vacuo* to afford a residue. Purification by FCC (98:2 CH_2Cl_2:MeOH) yielded **S12** (540 mg, 91%) as a colourless solid;

R_f = 0.7 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3399, 2934, 1696, 1505, 1384, 1115, 1063, 1007;

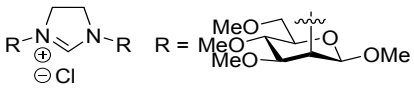
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (2H, d, *J* = 10.0 Hz, NH), 4.57 (2H, ddd, *J* = 10.0, 4.0 and 1.5 Hz, H-2), 4.41 (2H, d, *J* = 1.5 Hz, H-1), 3.67 (2H, dd, *J* = 10.5 and 2.5 Hz, H-6a), 3.60 (2H, dd, *J* = 10.5 and 5.5 Hz, H-6b), 3.50 (6H, s, OCH_3), 3.46 (6H, s, OCH_3), 3.44 (6H, s, OCH_3), 3.41 (6H, s, OCH_3), 3.41-3.38 (2H, m, H-5), 3.36 (2H, dd, *J* = 8.5 and 4.0 Hz, H-3), 3.21 (2H, *app*. t, *J* = 8.5-9.0 Hz, H-4);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2 (C=O), 100.1 (C-1), 82.5 (C-3), 75.8 (C-4), 75.6 (C-5), 71.7 (C-6), 60.7 (OCH_3), 59.5 (OCH_3), 57.6 (OCH_3), 56.8 (OCH_3), 49.7 (C-2);

m/z HRMS (ESI): Found $[M+Na]^+$ 547.2461, $C_{22}H_{40}N_2O_{12}Na$ requires 547.2473;

$[\alpha]^{22}_D$ = -88 (*c* 0.8, $CHCl_3$).

1,3-Bis(1,3,4,6-tetra-*O*-methyl-2-deoxy-β-D-mannopyranoside)imidazolinium chloride (7c):



To a suspension of **S12** (482 mg, 0.92 mmol) in anhydrous THF (4.6 mL) at rt, was added $LiAlH_4$ (1 M THF, 7.4 mL) and the mixture was heated to 70 °C. After 14 h the reaction was allowed to cool to rt and then quenched by the careful addition of: H_2O (0.51 mL), followed by aq. NaOH (15% by wt, 0.51 mL) and then H_2O (1.53 mL), which formed a precipitate. Filtration through Celite®, and further washing of the filter pad with Et_2O (3 x 20 mL), gave a colourless solution. The solution was concentrated *in vacuo* to afford crude *N*,*N*'-di-(2-amido-1,3,4,6-tetra-*O*-methyl-2-deoxy-β-D-mannopyranoside)ethyldiamine **S12b** (151 mg, 33%) which was used immediately without further purification (see below). Adapted from Huynh and co-workers.[5] To a solution of *N*,*N*'-di-(2-amido-1,3,4,6-tetra-*O*-methyl-2-deoxy-β-D-mannopyranoside)ethyldiamine (62.8 mg, 0.13 mmol) in $CH(OEt)_3$ (421 μL) at rt, was added NH_4Cl (7.4 mg, 0.14 mmol) and the suspension was heated to 100 °C under an Ar atmosphere. After 15 h the reaction was allowed to cool to 60 °C and then placed under vacuum for 0.5 h to give a residue. Purification by FCC (95:5-90:10 CH_2Cl_2:MeOH) yielded **7c** (57.0 mg, 83%) as a colourless solid;

R_f = 0.1 (80:20 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3391, 2940, 2835, 1637, 1512, 1451, 1376, 1259, 1195, 1110, 1067;

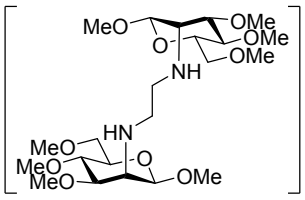
^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.96 (1H, s, CH $_{Imidazolinium}$), 4.87 (2H, dd, *J* = 5.5 and 2.0 Hz, H-2), 4.47 (2H, d, *J* = 2.0 Hz, H-1), 4.19-4.09 (2H, m, C*H*H and C*H*H $_{Imidazolinium}$), 4.01-3.92 (2H, m, CH*H* and CH*H* $_{Imidazolinium}$), 3.62-3.59 (4H, m, H-6a and H-6b), 3.56 (6H, s, OCH_3), 3.50 (6H, s, OCH_3), 3.49 (6H, s, OCH_3), 3.47 (2H, dd, *J* = 9.5 and 5.5 Hz, H-3), 3.37 (6H, s, OCH_3), 3.36 (2H, *app*. t, *J* = 9.5 Hz, H-4), 3.24 (2H, ddd, *J* = 9.5, 3.0 and 2.0 Hz, H-5),

^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3 (CH $_{Imidazolinium}$), 100.0 (C-1), 81.5 (C-3), 75.6 (C-4), 75.0 (C-5), 70.8 (C-6), 60.8 (OCH_3), 59.5 (OCH_3), 58.6 (OCH_3), 57.6 (OCH_3), 57.1 (C-2), 49.92 (CH_2 $_{Imidazolinium}$);

m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 507.2913, $C_{23}H_{43}N_2O_{10}$ requires 507.2912;

$[\alpha]^{22}_D$ = -100 (*c* 0.9, $CHCl_3$).

_N_,_N_'-Bis(1,3,4,6-tetra-_O_-methyl-2-deoxy-β-D-mannopyranoside)ethyldiamine (S12b):



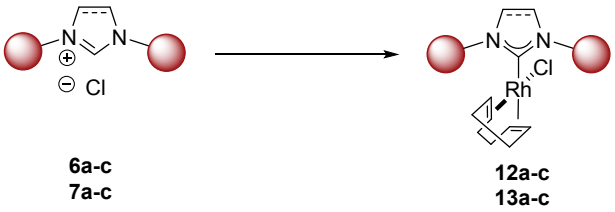
R_f = 0.3 (90:10 CH_2Cl_2:MeOH);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (2H, d, *J* = 10.0 Hz, NH), 4.58 (2H, ddd, *J* = 10.0, 4.0 and 2.0 Hz, H-2), 4.43 (2H, d, *J* = 2.0, H-1), 3.68 (2H, dd, *J* = 10.5 and 2.5 Hz, H-6a), 3.61 (2H, dd, *J* = 10.5 and 5.5 Hz, H-6b), 3.51 (6H, s, OCH_3), 3.47 (6H, s, OCH_3), 3.45 (6H, s, OCH_3), 3.42 (6H, s, OCH_3), 3.37 (2H, dd, *J* = 9.0 and 4.0 Hz, H-3), 3.42-3.39 (2H, m, C-5) 3.22 (2H, *app*. t, *J* = 9.0 Hz, H-4), 1.58 (2H, br s, C*H*H), 1.25 (2H, br s, CH*H*);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3 (C=O), 100.2 (C-1), 82.6 (C-3), 75.9 (C-4), 75.7 (C-5), 71.8 (C-6), 60.7 (OCH_3), 59.6 (OCH_3), 57.7 (OCH_3), 56.9 (OCH_3), 49.8 (C-2), 29.8 (CH_2), 29.6 (CH_2);

m/z HRMS (ESI): Found $[M+H]^+$ 497.3063, $C_{22}H_{45}N_2O_{10}$ requires 497.3068;

Complexation:



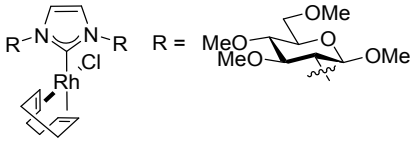
6a-c
7a-c

12a-c
13a-c

General Procedure D: Ligation to $[Rh(COD)Cl]_2$

Adapted from Ekkehardt and co-workers.[14] To a solution of imidazolium chloride (100 mol%) and KO^{t}Bu (100 mol%) in N_2 sat. anhydrous THF (0.01 M) at rt, was added $[Rh(COD)Cl]_2$ (50 mol%). After 14 h, the reaction was concentrated *in vacuo*, suspended in CH_2Cl_2 and filtered. The filtrate was concentrated to afford a residue. Purification by FCC yielded complexes **12a-e**.

[1,3-Bis(1,3,4,6-*O*-methyl-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (12a):



Following procedure D: Imidazolium salt = **6a** (40.0 mg, 74 μmol); $[Rh(COD)Cl]_2$ (18.3 mg, 37.0 μmol); KO^{t}Bu (8.3 mg, 74.0 μmol) and FCC (100:0 to 98:2 CH_2Cl_2:MeOH) to yield **12a** (35.6 mg, 64%) as a orange oil;

R_f = 0.7 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3087, 2932, 2880, 2831, 1448, 1423, 1379, 1320, 1244, 1226, 1188, 1107, 1059;

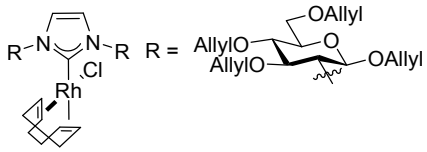
^{1}H NMR (500 MHz, $CDCl_3$) *observed peaks, rotameric* δ: 7.05 (1H, app. d, *J* = 2.0 Hz, CH $_{Imidazolylidene}$), 7.01 (1H, d, *J* = 2.0 Hz, CH $_{Imidazolylidene}$), 5.32 (1H, br s, H-$_{carbohydrate}$), 5.05 (1H, dd, *J* = 7.5 and 4.0 Hz, CH $_{COD}$), 5.00 (1H, d, *J* = 7.5 and 4.0 Hz, CH $_{COD}$), 4.71 (1H, br s, H-$_{carbohydrate}$), 3.87-3.44 (14), 3.56 (3H, s, OCH_3), 3.50 (3H, s, OCH_3), 3.49 (3H, s, OCH_3), 3.46 (3H, s, OCH_3), 3.45 (3H, s, OCH_3), 3.39 (3H, s, OCH_3), 3.35 (3H, s, OCH_3), 3.33 (3H, s, OCH_3), 2.49 (4H, m, CH_2 $_{COD}$), 1.95-1.85 (4H, m, CH_2 $_{COD}$);

^{13}C NMR (125 MHz, $CDCl_3$) *observed peaks, rotameric* δ: 118.2 (CH $_{Imidazolylidene}$), 102.0 (C-1), 100.0 (d, *J* = 7.0 Hz, CH $_{COD}$), 97.4 (d, *J* = 7.0 Hz, CH $_{COD}$), 89.3, 83.1, 79.3, 78.0, 75.8, 75.3, 72.8 (C-6), 72.2 (C-6), 69.4, 69.8, 67.4, 64.5 (C-1), 60.2, 60.0, 59.9, 59.7, 59.34, 59.27, 57.1, 56.2, 32.74 (CH_2 $_{COD}$), 32.67 (CH_2 $_{COD}$), 29.1 (CH_2 $_{COD}$), 28.8 (CH_2 $_{COD}$);

m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 715.2650, $C_{31}H_{52}N_2O_{10}Rh$ requires 715.2672.

$[\alpha]^{22}_D = 24$ (*c* 0.5, $CHCl_3$).

[1,3-Bis(1,3,4,6-*O*-allyl-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (12b):



Following procedure D: Imidazolium salt = **6b** (40.0 mg, 74 μmol); $[Rh(COD)Cl]_2$ (18.3 mg, 37.0 μmol); KO^{t}Bu (8.3 mg, 74.0 μmol) and FCC (100:0 to 98:2 CH_2Cl_2:MeOH) to yield **12b** (48.0 mg, 72%) as a orange oil;

R_f = 0.5 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3014, 2918, 2873, 1458, 1421, 1348, 1239, 1215, 1058;

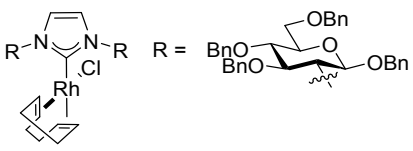
^{1}H NMR (500 MHz, $CDCl_3$) *observed peaks, rotameric* δ: 7.04 (1H, d, *J* = 2.0 Hz, CH $_{Imidazolylidene}$), 6.97 (1H, d, *J* = 2.0 Hz, CH $_{Imidazolylidene}$), 5.99-5.50 (8H, m, CH_2CHCH_2O), 5.32-4.92 (19H, m, CH_2CHCH_2O & CH $_{COD}$ & H-$_{carbohydrate}$), 4.77 (1H, br s, H-$_{carbohydrate}$), 4.35-3.66 (30H, m, CH_2CHCH_2O, CH $_{COD}$ & H-$_{carbohydrate}$), 2.47-2.31 (4H, m, CH_2 $_{COD}$), 1.91-1.79 (4H, m ,CH_2 $_{COD}$);

^{13}C NMR (125 MHz, $CDCl_3$) *observed peaks, rotameric* δ: 135.8 (CH_2CHCH_2O), 134.9 (CH_2CHCH_2O), 134.8 (CH_2CHCH_2O), 134.73 (CH_2CHCH_2O), 134.69 (CH_2CHCH_2O), 134.6 (CH_2CHCH_2O), 133.6 (CH_2CHCH_2O), 128.8 (CH $_{Imidazolylidene}$), 126.3 (CH $_{Imidazolylidene}$), 117.29 (CH_2CHCH_2O), 117.24 (CH_2CHCH_2O), 117.17 (CH_2CHCH_2O), 117.1 (CH_2CHCH_2O), 117.0 (CH_2CHCH_2O), 116.9 (CH_2CHCH_2O), 116.8 (CH_2CHCH_2O), 101.1 (C-$_{carbohydrate}$), 99.9 (C-$_{carbohydrate}$), 98.1 (d, *J* = 6.5 Hz, CH $_{COD}$), 97.2 (d, *J* = 6.5 Hz, CH $_{COD}$), 81.6, 80.1, 76.4, 76.3, 76.2, 73.9, 73.7, 73.0, 72.59, 72.55, 70.7, 69.94, 69.87, 67.6, 64.8, 32.9 (CH_2 $_{COD}$), 29.2 (CH_2 $_{COD}$), 28.9 (CH_2 $_{COD}$), 28.2 (CH_2 $_{COD}$);

m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 923.3884, $C_{47}H_{68}N_2O_{10}Rh$ requires 923.3926.

$[\alpha]^{22}_D = 6$ (*c* 1.4, $CHCl_3$).

[1,3-Bis(1,3,4,6-*O*-benzyl-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (12c):



Following procedure D: Imidazolium salt = **6c** (100 mg, 88.0 μmol); $[Rh(COD)Cl]_2$ (21.5 mg, 44.0 μmol); KO^{t}Bu (9.9 mg, 88.0 μmol) and FCC (100:0 to 95:5 CH_2Cl_2:MeOH) to yield **12c** (72.2 mg, 61%) as a orange solid;

R_f = 0.6 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3029, 1496, 1453, 1419, 1361, 1307, 1239, 1214, 1059, 1027;

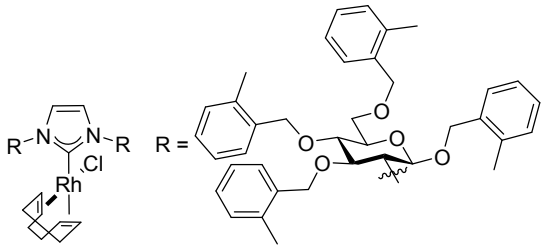
^{1}H NMR (500 MHz, $CDCl_3$) *observed peaks, rotameric* δ: 7.39-6.95 (40H, m, ArCH), 6.92 (1H, d, *J* = 2.0 Hz, CH $_{Imidazolylidene}$), 6.75 (1H, d, *J* = 2.0 Hz, CH $_{Imidazolylidene}$), 5.72 (2H, br s, H-$_{carbohydrate}$), 5.26 (1H, d, *J* = 11.5 Hz, $PhCH_2$), 5.12-5.07 (1H, m, CH $_{COD}$), 5.01-4.97 (1H, m, CH $_{COD}$), 4.79-4.25 (15H, m, $PhCH_2$), 4.04-3.63 (14H, m, H-$_{carbohydrate}$ & CH $_{COD}$), 2.39-2.08 (4H, m, CH $_{COD}$), 1.89-1.67 (4H, m, CH $_{COD}$);

^{13}C NMR (125 MHz, $CDCl_3$) *observed peaks* δ: 138.7 (ArC), 138.29 (ArC), 138.27 (ArC), 138.0 (ArC), 137.9 (ArC), 137.8 (ArC), 137.1 (ArC), 128.6 (ArCH), 128.50 (ArCH), 128.45 (ArCH), 128.43 (ArCH), 128.36 (ArCH), 128.29 (ArCH), 128.27, 128.2 (ArCH), 128.1 (ArCH), 128.0 (ArCH), 127.93 (ArCH), 127.91 (ArCH), 127.86 (ArCH), 127.83 (ArCH), 127.80 (ArCH), 127.79 (ArCH), 127.76 (ArCH), 127.7 (ArCH), 127.6 (ArCH), 127.4 (ArCH), 120.32 (CH $_{Imidazolylidene}$), 120.29 (CH $_{Imidazolylidene}$), 101.4, 99.0, 98.4, 97.9, 97.8, 82.0, 79.2, 76.9, 76.3, 75.3, 74.9, 74.8, 73.6, 73.5, 73.0, 70.8, 70.41, 70.3, 69.6, 67.9, 64.0, 33.1 (CH_2 $_{COD}$), 32.7 (CH_2 $_{COD}$), 29.2 (CH_2 $_{COD}$), 28.7 (CH_2 $_{COD}$);

m/z HRMS (ESI): Found $[M-Cl]^+$ 1323.5135, $C_{79}H_{84}N_2O_{10}Rh$ requires 1323.5176.

$[\alpha]^{22}_D$ = -12 (*c* 1.1, $CHCl_3$).

[1,3-Bis(1,3,4,6-*O*-(methyl-*o*-tol)-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (12d):



Following procedure D: Imidazolium salt = **6d** (50.0 mg, 40.0 μmol); $[Rh(COD)Cl]_2$ (9.8 mg, 20.0 μmol); KO^{t}Bu (4.5 mg, 40.0 μmol) and FCC (100:0 to 98:2 CH_2Cl_2:MeOH) to yield **12d** (40.7 mg, 70%) as a orange solid;

R_f = 0.7 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3020, 2872, 1493, 1461, 1359, 1287, 1240, 1218, 1187, 1119, 1064;

^{1}H NMR (500 MHz, $CDCl_3$) *observed peaks, rotameric* δ: 7.52-7.00 (32H, m, ArCH), 6.98 (1H, d, *J* = 7.5 Hz, CH $_{Imidazolylidene}$), 6.92 (1H, d, *J* = 7.5 Hz, CH $_{Imidazolylidene}$), 5.92-3.58 (34H, m, PhCHH & H-$_{carbohydrate}$ & CH

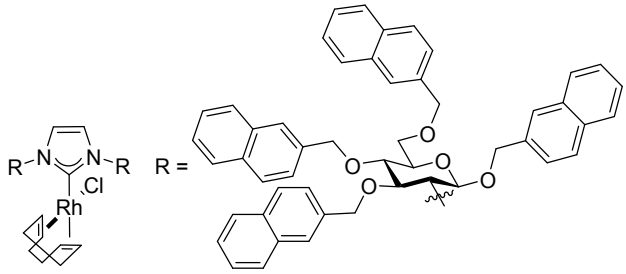
$_{COD}$), 2.40-2.19 (4H, m $CH_{2\ COD}$), 2.35 (3H, s, CH_3), 2.32 (3H, s, CH_3), 2.28 (3H, s, CH_3), 2.24 (3H, s, CH_3), 2.14 (3H, s, CH_3), 2.10 (3H, s, CH_3), 2.02 (3H, s, CH_3), 1.89-1.70 (4H, m, $CH_{2\ COD}$), 1.86 (3H, s, CH_3);

^{13}C NMR (125 MHz, $CDCl_3$) *observed peaks, rotameric* δ: 136.92, 136.87, 136.7, 136.42, 136.41, 136.16, 136.14, 136.10, 136.0, 135.91, 135.87, 135.6, 135.2, 134.9, 130.2, 130.10, 130.05, 130.0, 129.9, 129.8, 128.7, 128.6, 128.46, 128.42, 128.34, 128.28, 127.9, 127.81, 127.79, 127.68, 127.5, 127.3, 127.2, 127.1, 125.8, 125.73, 125.70, 125.67, 125.63, 125.60, 125.5, 101.2, 98.6, 98.1, 97.9, 81.8, 78.3, 76.2, 74.7, 72.4, 72.2, 71.8, 71.6, 71.1, 70.6, 69.4, 68.8, 68.5, 67.5, 63.3, 32.8, 32.7, 29.0, 28.7, 19.3, 19.1, 18.9, 18.80, 18.79, 18.7, 18.5, 18.3;

m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 1435.6456, $C_{87}H_{100}N_2O_{10}Rh$ requires 1435.6428.

$[\alpha]^{24}_D$ = -8 (*c* 1.5, $CHCl_3$).

[1,3-Bis(1,3,4,6-*O*-(methyl-2-naphthyl)-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cycooctadiene)rodium(I) (12e):



Following procedure D: Imidazolium salt = **6e** (50.0 mg, 32.0 μmol); $[Rh(COD)Cl]_2$ (8.0 mg, 16.0 μmol); KO^{t}Bu (3.6 mg, 32.0 μmol) and purification by FCC (100:0 to 98:2 CH_2Cl_2:MeOH) to yield **12e** (33.8 mg, 60%) as an orange solid;

R_f = 0.7 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 3054, 2870, 1601, 1508, 1366, 1271, 1064;

^{1}H NMR (500 MHz, $CDCl_3$) *observed peaks, rotameric* δ:7.85-6.99 (56H, m, ArCH), 6.94 (1H, d, *J* = 2.0 Hz, $CH_{\ Imidazolylidene}$), 6.78 (1H, d, *J* = 2.0 Hz, $CH_{\ Imidazolylidene}$), 5.44-4.46 (20H, m, ArCHH & H-1 & $CH_{\ COD}$), 4.20-3.78 (14H, m, $H\text{-}_{carbohydrate}$ & $CH_{\ COD}$), 2.55-2.19 (4H, m, $CH_{2\ COD}$), 1.97-1.76 (4H, m, $CH_{2\ COD}$);

^{13}C NMR (125 MHz, $CDCl_3$) *observed peaks, rotameric* δ: 136.2, 136.0, 135.78, 135.75, 135.7, 135.6, 135.4, 135.3, 135.2, 135.0, 134.5, 133.4, 133.4, 133.4, 133.4, 133.32, 133.25, 133.23, 133.17, 133.14, 133.11, 133.06, 133.02, 132.99, 132.98, 132.95, 132.9, 128.44, 128.40, 128.37, 128.35, 128.30, 128.26, 128.23, 128.17, 128.11, 128.10, 128.07, 128.05, 128.03, 128.00, 127.98, 127.95, 127.91, 127.89, 127.86, 127.82, 127.78, 127.75, 127.72, 127.68, 127.66, 127.1, 126.89, 126.87, 126.79, 126.75, 126.70, 126.67, 126.63, 126.61, 126.56, 126.53, 126.46, 126.4, 126.3, 126.20, 126.17, 126.12, 126.08, 126.03, 126.01, 125.99, 125.97, 125.91, 125.89, 125.87, 125.82, 125.79, 125.74, 125.68, 125.6, 125.5, 101.2, 99.3, 98.4, 97.9, 85.4, 82.2, 79.4, 78.9, 76.7, 76.3, 75.6, 75.5, 75.0, 74.9, 73.84, 73.76, 73.7, 73.2, 71.4, 70.8, 70.7, 70.2, 69.1, 67.6, 64.3, 57.3, 33.2, 32.8, 29.3, 28.7;

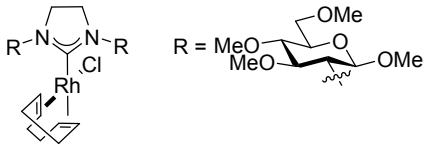
m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 1723.6468, $C_{111}H_{100}N_2O_{10}Rh$ requires 1723.6428.

$[\alpha]^{20}_D$ = -20 (*c* 1.0, $CHCl_3$).

General Procedure E: Ligation to $[Rh(COD)Cl]_2$

Adapted from Ekkehardt and co-workers.[14] To a solution of imidazolium chloride (100 mol%) and base (100 mol%) in N_2 sat. anhydrous THF (0.01 M) at rt, was added $[Rh(COD)Cl]_2$ (50 mol%). After 14 h, the reaction was concentrated *in vacuo*, suspended in CH_2Cl_2 and filtered. The filtrate was concentrated to afford a residue. Purification by FCC yielded complexes **13a-c**.

[1,3-Bis(1,3,4,6-tetra-*O*-methyl-2-deoxy-β-D-glucopyranoside)imidazolin-2-ylidene]chloro(1,5-cyclooctadiene)rhodium(I) (13a):



Following procedure E: Imidazolium salt = **7a** (16.0 mg, 29.0 μmol); base = KO^{t}Bu (3.3 mg, 29.0 μmol) and $[Rh(COD)Cl]_2$ (7.2 mg, 14.5 μmol). The procedure was slightly modified as follows: the reaction was stirred at 58 °C for 2.5 h and then allowed to cool to rt. Concentration *in vacuo* afforded a residue which was purified by FCC (100:0 to 95:5 CH_2Cl_2:MeOH) to yield **13a** (13.2 mg, 60%) as an orange oil;

R_f = 0.4 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 2926, 2830, 1256, 1134, 1107, 1071, 1052;

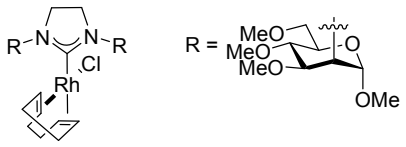
^{1}H NMR (500 MHz, $CDCl_3$) *observed peaks, rotameric* δ: 5.03-4.98 (1H, m, CH $_{COD}$), 4.96-4.89 (2H, m, H-$_{carbohydrate}$ & CH $_{COD}$), 4.51 (1H, d, *J* = 8.0 Hz, H-$_{carbohydrate}$), 3.86-3.80 (2H, m, H-$_{carbohydrate}$ & CH $_{COD}$), 3.73-3.31 (16H, m, H-$_{carbohydrate}$ & CH $_{COD}$ & CH_2 $_{Imidazolinylidene}$), 3.58 (3H, s, OCH_3), 3.57 (3H, s, OCH_3), 3.56 (3H, s, OCH_3), 3.55 (3H, s, OCH_3), 3.51 (3H, s, OCH_3), 3.45 (3H, s, OCH_3), 3.44 (3H, s, OCH_3), 3.43 (3H, s, OCH_3), 2.50-2.26 (4H, m CH_2 $_{COD}$), 1.94-1.79 (4H, m, CH_2 $_{COD}$);

^{13}C NMR (125 MHz, $CDCl_3$) *observed peaks, rotameric* δ: 102.8, 100.6, 99.1 (d, *J* = 6.5, CH $_{COD}$), 98.1 (d, *J* = 6.5, CH $_{COD}$), 81.7, 81.3, 79.0, 78.3, 75.7, 75.5, 73.9 (C-6), 72.1 (C-6), 70.5 (CH $_{COD}$), 69.0 (CH $_{COD}$), 66.4, 63.7, 60.23 (OCH_3), 60.19 (OCH_3), 60.0 (OCH_3), 59.7 (OCH_3), 59.3 (OCH_3), 59.3 (OCH_3), 56.8 (OCH_3), 56.2 (OCH_3), 45.7 (CH $_{Imidazolinylidene}$), 32.8 (CH_2 $_{COD}$), 32.3 (CH_2 $_{COD}$), 28.9 (CH_2 $_{COD}$), 28.5 (CH_2 $_{COD}$).

m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 717.2821, $C_{31}H_{54}N_2O_{10}Rh$ requires 717.2828;

$[\alpha]^{22}_D$ = 5 (*c* 0.4, $CHCl_3$).

[1,3-Bis(1,3,4,6-tetra-*O*-methyl-2-deoxy-α-D-mannopyranoside)imidazolin-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (13b):



Following procedure E: Imidazolium salt = **7a** (50.0 mg, 92.0 μmol); base = NaO^{t}Bu (8.8 mg, 92.0 μmol); $[Rh(COD)Cl]_2$ (22.7 mg, 46.0 μmol) and purification by FCC (100:0 to 98:2 CH_2Cl_2:MeOH) to yield **13b** (51.8 mg, 75%) as an orange oil;

R_f = 0.8 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} (film): 2932, 2828, 1486, 1454, 1321, 1263, 1192, 1105, 1062;

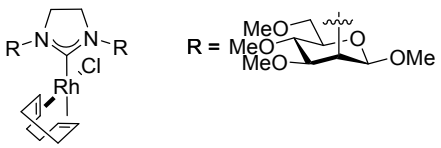
^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.88 (1H, dd, *J* = 6.0 and 1.5 Hz, H-2), 5.70 (1H, dd, *J* = 6.5 and 3.5 Hz, H-2'), 5.28 (1H, d, *J* = 1.5 Hz, H-1), 5.00 (1H, ddd, *J* = 8.0, 4.5 and 3.5 Hz, CH $_{COD}$), 4.89 (1H, d, *J* = 6.5 Hz, H-1'), 4.81 (1H, *app.* q, *J* = 7.5 Hz, CH $_{COD}$), 4.40 (1H, dd, *J* = 3.5 and 2.5 Hz, H-3'), 3.95-3.84 (3H, m, C*H*H $_{2H\text{-IMID}}$, C*H*H $_{2H\text{-IMID}}$ and H-5'), 3.80 (1H, dd, *J* = 9.5 and 6.0 Hz, H-3), 3.66-3.55 (9H, m, CH*H* $_{2H\text{-IMID}}$, CH*H* $_{2H\text{-IMID}}$, H-6a and H-6b, H-6'a and H-6'b, CH $_{COD}$, H-4' and H-5), 3.65 (3H, s, CH_3), 3.54 (3H, s, CH_3), 3.53 (3H, s, CH_3), 3.44 (3H, s, CH_3), 3.414 (3H, s, CH_3), 3.412 (3H, s, CH_3), 3.411 (3H, s, CH_3), 3.40 (3H, s, CH_3), 3.39-3.36 (1H, br s, CH $_{COD}$), 3.33 (1H, dd, *J* = 8.0 and 2.5 Hz, H-4'), 2.53-2.42 (2H, m, CH_2 $_{COD}$), 2.30-2.15 (2H, m, CH_2 $_{COD}$), 2.08-1.96 (2H, m, CH_2 $_{COD}$), 1.80-1.72 (2H, m, CH_2 $_{COD}$);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 217.2 (d, *J* = 47.5, C), 102.7 (C-1), 100.3 (d, *J* = 6.5 Hz, CH $_{COD}$), 98.4 (C-1'), 97.9 (d, *J* = 6.5 Hz, CH $_{COD}$), 80.21 and 80.16 (C-3 and C-3'), 78.0 (C-4), 77.1 (C-4'), 73.1 (C-6 or C-6'), 71.5 (C-5'), 71.3 (C-6 or C-6'), 70.3 (C-5), 69.4 (d, *J* = 14.5 Hz, CH $_{COD}$), 68.5 (d, *J* = 14.5 Hz, CH $_{COD}$), 61.0 (C-2), 60.72 (CH_3), 60.71 (CH_3), 59.5 (CH_3), 59.4 (CH_3), 59.3 (C-2'), 57.8 (CH_3), 57.6 (CH_3), 55.5 (CH_3), 55.4 (CH_3), 48.7 (CH_2 $_{2H\text{-IMID}}$), 48.3 (CH_2 $_{2H\text{-IMID}}$), 34.3 (CH_2 $_{COD}$), 31.5 (CH_2 $_{COD}$), 29.9 (CH_2 $_{COD}$), 27.7 (CH_2 $_{COD}$);

m/z HRMS (ESI): Found $[M\text{-Cl}]^+$ 717.2825, $C_{31}H_{54}N_2O_{10}Rh$ requires 717.2828;

$[\alpha]^{22}_D$ = 59 (*c* 1.0, $CHCl_3$).

[1,3-Bis(1,3,4,6-tetra-*O*-methyl-2-deoxy-β-D-mannopyranoside)imidazolin-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (13c):



Following procedure E: Imidazolium salt = **7c** (31.0 mg, 58.0 μmol); base = KO^{t}Bu (6.5 mg, 58.0 μmol); $[Rh(COD)Cl]_2$ (14.2 mg, 29.0 μmol) and purification by FCC (100:0 to 98:2 CH_2Cl_2:MeOH) to yield **13c** (19.2 mg, 44%) as an orange oil;

R_f = 0.5 (90:10 CH_2Cl_2:MeOH);

ν_{max} / cm^{-1} ($CHCl_3$): 2928, 2875, 1483, 1448, 1326, 1254, 1197, 1109, 1076, 1037;

^1H NMR (500 MHz, $CDCl_3$) δ: 6.15 (1H, dd, *J* = 3.5 and 4.5 Hz, H-2), 5.93 (1H, *app*. t, *J* = 4.0 Hz, H-2), 5.23 (1H, d, *J* = 4.0 Hz, H-1), 5.00-4.92 (2H, m, CH $_{COD}$), 4.76 (1H, d, *J* = 3.5 Hz, H-1), 4.22 (1H, *app*. t, *J* = 4.5 Hz, H-3), 4.04-4.00 (1H, m, H-5), 3.98 (1H, dd, *J* = 10.0 and 8.5 Hz, C*H*H $_{NHC}$), 3.95-3.90 (2H, m, H-6a & H-4), 3.84-3.76 (3H, m, C*H*H $_{NHC}$ & CH*H* $_{NHC}$ & H-6a), 3.73 (1H, dd, *J* = 9.5 and 6.5 Hz, H-6b), 3.69-3.66 (2H, H-5 & H-6b), 3.64-3.61 (2H, m, CH*H* $_{NHC}$ & H-3), 3.60 (3H, s, OCH_3), 3.58 (1H, *app*. t, *J* = 4.5 Hz, H-4), 3.50 (3H, s, OCH_3), 3.49 (3H, s, OCH_3), 3.48 (3H, s, OCH_3), 3.46 (3H, s, OCH_3), 3.45 (3H, s, OCH_3), 3.40 (6H, s, OCH_3), 3.38-3.34 (1H, br m, CH $_{COD}$), 3.29-3.24 (1H, br m, CH $_{COD}$), 2.46-2.38 (1H, m, CH_2 $_{COD}$), 2.39-2.29 (3H, m, CH_2 $_{COD}$), 1.94-1.83 (4H, m, CH_2 $_{COD}$);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 216.8 (d, *J* = 47.5 Hz, C $_{carbene}$), 101.3 (C-1), 100.9 (C-1), 99.7 (d, *J* = 6.5 Hz, CH $_{COD}$), 99.4 (d, *J* = 6.0 Hz, CH $_{COD}$), 81.5 (C-3), 79.6 (C-3), 75.6 (C-4), 74.9 (C-4), 74.8 (C-5), 73.1 (C-6), 72.9 (C-6), 71.5 (C-5), 68.6 (d, *J* = 14.5 Hz, CH $_{COD}$), 67.9 (d, *J* = 14.5 Hz, CH $_{COD}$), 59.12 (OCH_3), 59.09 (OCH_3), 58.99 (OCH_3), 58.97 (OCH_3), 58.3 (OCH_3), 57.7 (OCH_3), 56.8 (C-1), 56.70 (OCH_3), 56.67 (C-1), 56.4 (OCH_3), 49.8 (CH_2 $_{NHC}$), 49.5 (CH_2 $_{NHC}$), 32.7 (2 x CH_2 $_{COD}$), 28.9 (CH_2 $_{COD}$), 28.4 (CH_2 $_{COD}$);

m/z HRMS (ESI): Found $[M\text{-}Cl]^+$ 717.2834, $C_{31}H_{54}N_2O_{10}Rh$ requires 717.2828;

$[\alpha]^{22}_D$ = -5 (*c* = 0.4, $CHCl_3$).

Preparation of Racemates:

General Procedure F: Racemic reduction of ketones

Adapted from Woodard and co-workers.[15] To a solution of ketone (100 mol%) in EtOH (0.6 M, dried over 4 Å MS) was added $NaBH_4$ (125 mol%) at rt and the resulting suspension was stirred for 16 h. The reaction was quenched by addition of aq. NaCl (10% by wt) and the resulting solution was extracted with Et_2O (3 washes). The combined extracts were dried (Na_2SO_4) and concentration *in vacuo* afforded the pure product alcohol.

1-Phenylethanol (15a):

Following procedure F: Ketone = **14a** (2.00 g, 16.65 mmol) and alcohol **15a** (1.95 g, 96%) as a colourless oil;

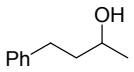
R_f = 0.1 (90:10 petrol:EtOAc);

ν_{max} / cm^{-1} (film): 3339, 3028, 2972, 2876, 1603, 1493, 1450, 1368, 1283, 1203, 1075, 1028, 1009;

^1H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.35 (4H, m, ArCH), 7.31-7.27 (1H, m, ArCH), 4.92 (1H, q, *J* = 6.5 Hz, CH), 1.76 (1H, s, OH), 1.51 (3H, d, *J* = 6.5 Hz, CH_3);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.9 (ArC), 128.7 (ArCH), 127.6 (ArCH), 125.5 (ArCH), 70.6 (CH), 25.3 (CH_3). *Spectroscopic data in agreement with the literature*.[15]

4-Phenylbutan-2-ol (15b):



Following procedure F: Ketone = **14b** (0.40 mL, 2.70 mmol) and alcohol **15b** (406 mg, 99%) as a colourless oil;

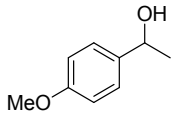
R_f = 0.2 (80:20 petrol:EtOAc);

ν_{max} / cm^{-1} (film): 3344, 3026, 2965, 2926, 1603, 1495, 1453, 1373, 1309, 1179, 1127, 1081, 1053, 1030;

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31-7.27 (2H, m, ArCH), 7.22-7.17 (3H, m, ArCH), 3.83 (1H, dt, *J* = 6.0 and 6.5 Hz, CH), 2.80-2.64 (1H, m, CH_2CHOH), 1.83-1.72 (2H, ArCCH_2), 1.45 (1H, br s, OH), 1.24 (3H, d, *J* = 6.5 Hz, CH_3);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.1 (ArC), 128.5 (ArCH), 128.3 (ArCH), 125.8 (ArCH), 67.6 (CH), 40.9 (ArCCH_2), 32.1 (CH_2CH), 23.7 (CH_3). *Spectroscopic data in agreement with the literature*.[16]

1-(4-Methoxyphenyl)ethanol (15c):



Following procedure F: Ketone = **14c** (1.00 g, 6.66 mmol) and alcohol **15c** (1.00 g, 99%) as a colourless oil;

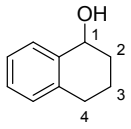
R_f = 0.25 (90:10 petrol:EtOAc);

ν_{max} / cm^{-1} (film): 3366, 2969, 2931, 1611, 1585, 1501, 1455, 1442, 1368, 1301, 1240, 1204, 1174, 1115, 1085, 1069, 1032, 1004;

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (2H, *app.* d, *J* = 8.5 Hz, ArCH), 6.88 (2H, *app.* d, *J* = 8.5 Hz, ArCH), 4.85 (1H, q, *J* = 6.5 Hz, CH), 3.80 (3H, s, ArCOCH_3), 1.85 (1H, s, OH), 1.48 (3H, d, *J* = 6.5 Hz);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.9 (ArCOCH_3), 138.0 (ArC), 126.7 (ArCH), 113.8 (ArCH), 70.0 (CH), 55.5 (ArCOCH_3), 25.0 (CH_3). *Spectroscopic data in agreement with the literature*.[16]

1,2,3,4-Tetrahydronaphthalen-1-ol (15d):



Following procedure F: Ketone = **14d** (1.00 g, 6.84 mmol) and alcohol **15d** (0.99 g, 99%) as a colourless oil;

R_f = 0.4 (80:20 petrol:EtOAc);

ν_{max} / cm^{-1} (film): 3275, 3046, 2946, 2923, 2892, 2855, 2835, 1492, 1453, 1431, 13831285, 1267, 1202, 1166, 1151, 1117, 1067, 1035, 1001;

^1H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.41 (1H, m, ArCH), 7.21-7.17 (2H, m, ArCH), 7.11-7.08 (1H, m, ArCH), 4.78 (1H, br s, C_1H), 2.84-2.72 (2H, m, C_2H_2), 2.03-1.87 (3H, m, C_4H_2 & C_3HH), 1.84-1.75 (2H, m, C_3HH & OH);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.9 (ArC), 137.2 (ArC), 129.1 (ArCH), 128.8 (ArCH), 127.7 (ArCH), 126.3 (ArCH), 68.3 (C1), 32.4 (C4), 29.3 (C2), 18.9 (C3). *Spectroscopic data in agreement with the literature*.[17]

Catalysis Data:

General Procedure G: Asymmetric Rh catalysed hydrosilylation

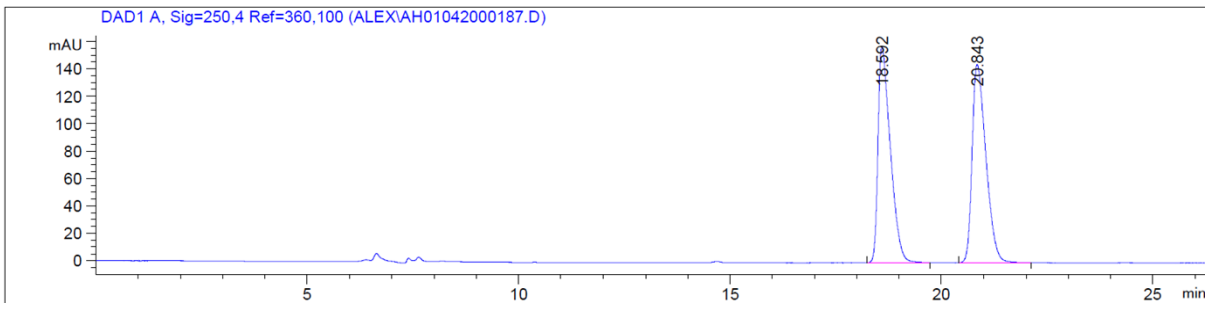
To a solution of **complex** (2 mol%) in anhydrous hexane (1 mL, 0.5 M) at rt, was added Ph_2SiH_2 (0.28 mL, 300 mol%) and ketone **14** (0.5 mmol, 100 mol%) and the solution was stirred for 18 h. Desilylation was mediated by removal of hexanes *in vacuo* and then the addition of MeOH (3.0 mL) and K_2CO_3 (30.0 mg). The solution was stirred for 2 h and then concentrated *in vacuo*. Purification of the title compound was accomplished by FCC (dry loaded) which yielded alcohol **15**.

1-Phenylethanol (15a):

Following General Procedure G. Complex = **12a** (7.5 mg); ketone = **14a** (58.3 µL) and purification by FCC (hexane:Et_2O 85:15) to yield **15a** (54.4 mg, 89%) as a colourless oil.

The enantiomeric excess of **15a** was determined by chiral HPLC (Chiralpak IB, hexane:^{i}PrOH 97:3, 0.5 mL min^{-1}, 20.0 °C); t_R (major) = 19.5 min and t_R (minor) = 22.3 min.

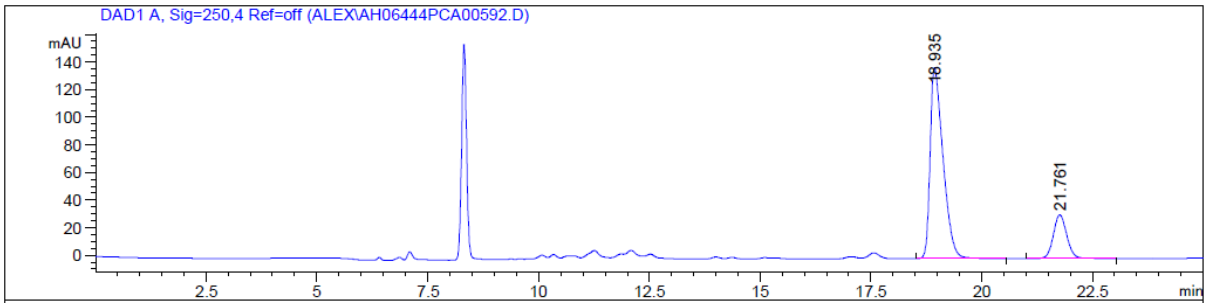
Racemate:



Signal 1: DAD1 A, Sig=250,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.592	BB	0.2955	3182.78687	157.69487	49.2688
2	20.843	BB	0.3339	3277.26367	144.63470	50.7312

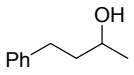
Asymmetric Catalysis:



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.935	BB	0.3038	2790.10522	138.01961	80.7857
2	21.761	BB	0.3269	663.60736	31.61288	19.2143

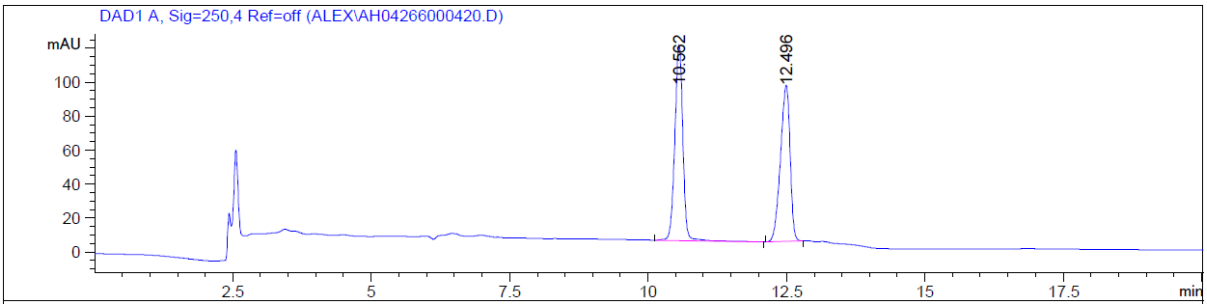
4-Phenylbutan-2-ol (15b):



Following General Procedure G. Complex = **12a** (7.5 mg); ketone = **14b** (74.9 μL) and purification by FCC (hexane:Et_2O 85:15) to yield **15b** (72.1 mg, 96%) as a colourless oil.

The enantiomeric excess of **14b** was determined by chiral HPLC (Chiralpak IB, hexane:^{i}PrOH 90:10, 0.5 mL min^{-1}, 20.0 °C); t_R (major) = 10.5 min and t_R (minor) = 12.5 min.

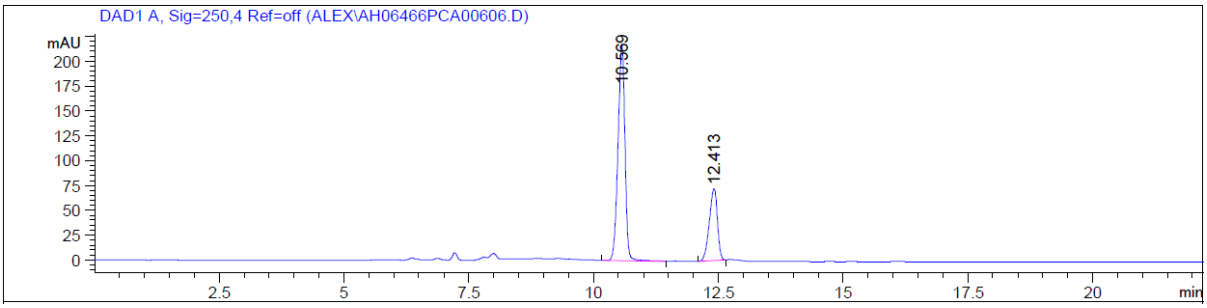
Racemate:



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.562	BB	0.1561	1163.81726	114.94138	51.1020
2	12.496	BB	0.1875	1113.62122	91.83420	48.8980

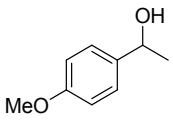
Asymmetric Catalysis:



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.569	BB	0.1500	2126.10449	217.49188	72.3626
2	12.413	BB	0.1770	812.02246	72.31108	27.6374

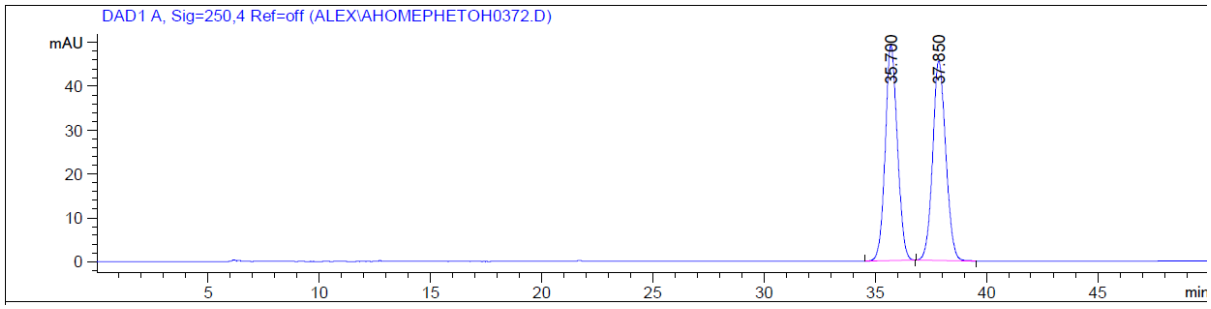
1-(4-Methoxyphenyl)ethanol (15c):



Following General Procedure G. Complex = **12a** (7.5 mg); ketone = **14c** (75.1 mg) and purification by FCC (hexane:Et_2O 70:30) to yield **15c** (72.3 mg, 95%) as a colourless oil.

The enantiomeric excess of **15c** was determined by chiral HPLC (Chiralpak IA, hexane:^{i}PrOH 97:3, 0.5 mL min^{-1}, 20.0 °C); t_R (major) = 36.9 min and t_R (minor) = 39.1 min.

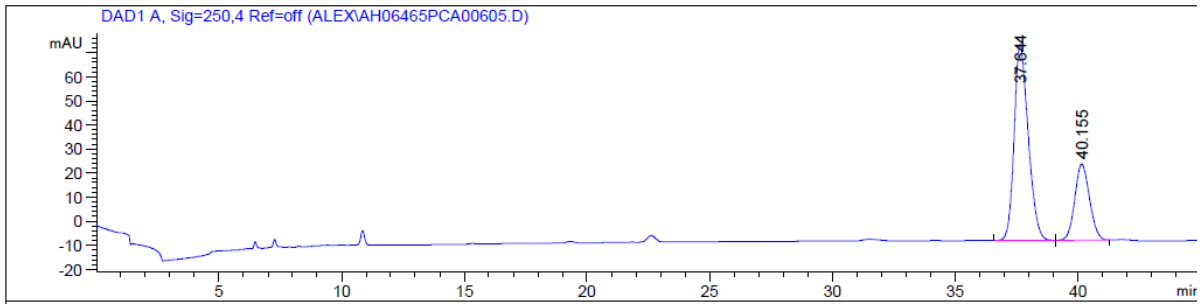
Racemate:



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.700	BB	0.5770	1858.81494	49.17525	49.8892
2	37.850	BB	0.6279	1867.07019	45.58044	50.1108

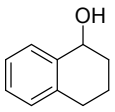
Asymmetric Catalysis:



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.644	BB	0.6061	3250.65503	81.37322	71.1312
2	40.155	BB	0.6380	1319.28796	31.67227	28.8688

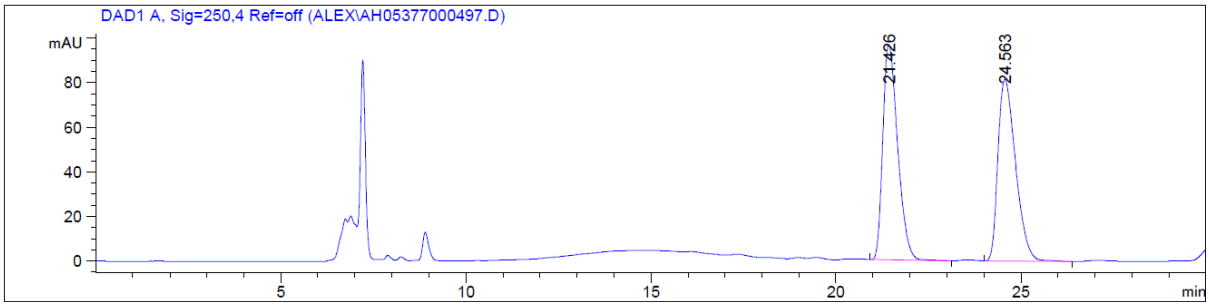
1,2,3,4-Tetrahydronaphthalen-1-ol (15d):



Following General Procedure G. Complex = **12a** (7.5 mg); ketone = **14d** (75.1 mg) and purification by FCC (hexane:Et_2O 80:20) to yield **15d** (61.7 mg, 84%) as a colourless oil.

The enantiomeric excess of **15d** was determined by chiral HPLC (Chiralpak IC, hexane:^{i}PrOH 97:3, 0.5 mL min^{-1}, 20.0 °C); t_R (major) = 21.4 min and t_R (minor) = 24.6 min.

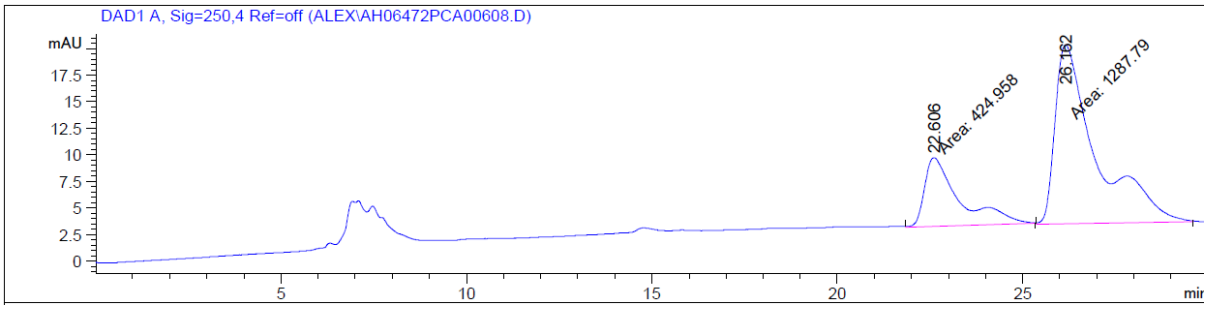
Racemate:



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.426	BB	0.4312	2690.58350	96.52808	49.9486
2	24.563	BB	0.5137	2696.11914	81.55587	50.0514

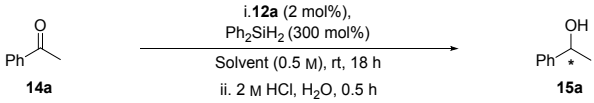
Asymmetric Catalysis:



Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.606	MM	1.0931	424.95816	6.47936	24.8114
2	26.162	MM	1.2745	1287.79285	16.84056	75.1886

Solvent Screen Data:



Entry	Solvent	Yield (%)[a]	e.r. (*R*:*S*)[b]
1	Hexane	62	80:20
2	Hexane	89[c]	81:19
3	PhMe	51	71:29
4	THF	64	67:33
5	CH_2Cl_2	51	65:35
6	MeCN	-	-
7	-	87	76:24
8	Cyclohexane	70	75:25
9	Heptane	43	76:24

[a] Isolated yields; [b] *R*:*S* ratio from HPLC; [c] Optimized Si ether cleavage conditions: K_2CO_3, MeOH, 2 h.

X-ray Structure Data:

Suitable crystals for X-ray diffraction were grown by vapour diffusion of hexane into a concentrated solution of **12c** in CH_2Cl_2.

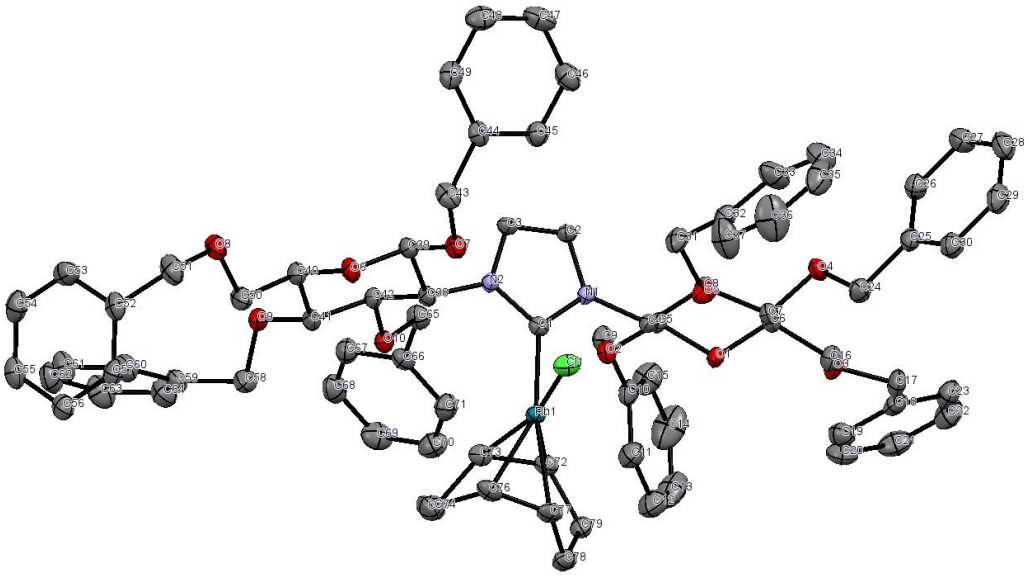


Table 1: Crystal data and structure refinement for 12c.

Empirical formula	$C_{79}H_{84}ClN_2O_{10}Rh$
Formula weight	1359.84
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	15.0756(2)
b/Å	15.9328(3)

c/Å	28.2582(6)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	6787.5(2)
Z	4
ρ_{calc}mg/mm^3	1.331
m/mm^{-1}	0.353
F(000)	2856.0
Crystal size/mm^3	0.29 × 0.22 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	3.86 to 55.04°
Index ranges	-19 ≤ h ≤ 17, -20 ≤ k ≤ 20, -28 ≤ l ≤ 36
Reflections collected	57669
Independent reflections	15480 [R_{int} = 0.0421, R_{sigma} = 0.0535]
Data/restraints/parameters	15480/0/839
Goodness-of-fit on F^2	1.013
Final R indexes [I>=2σ (I)]	R_1 = 0.0334, wR_2 = 0.0611
Final R indexes [all data]	R_1 = 0.0462, wR_2 = 0.0653
Largest diff. peak/hole / e Å^{-3}	0.42/-0.45
Flack parameter	-0.022(12)

Table 2: Selected bond Angles for 12c.

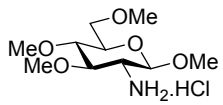
Atom	Atom	Atom	Angle/°
N1	C1	N2	103.16(18)

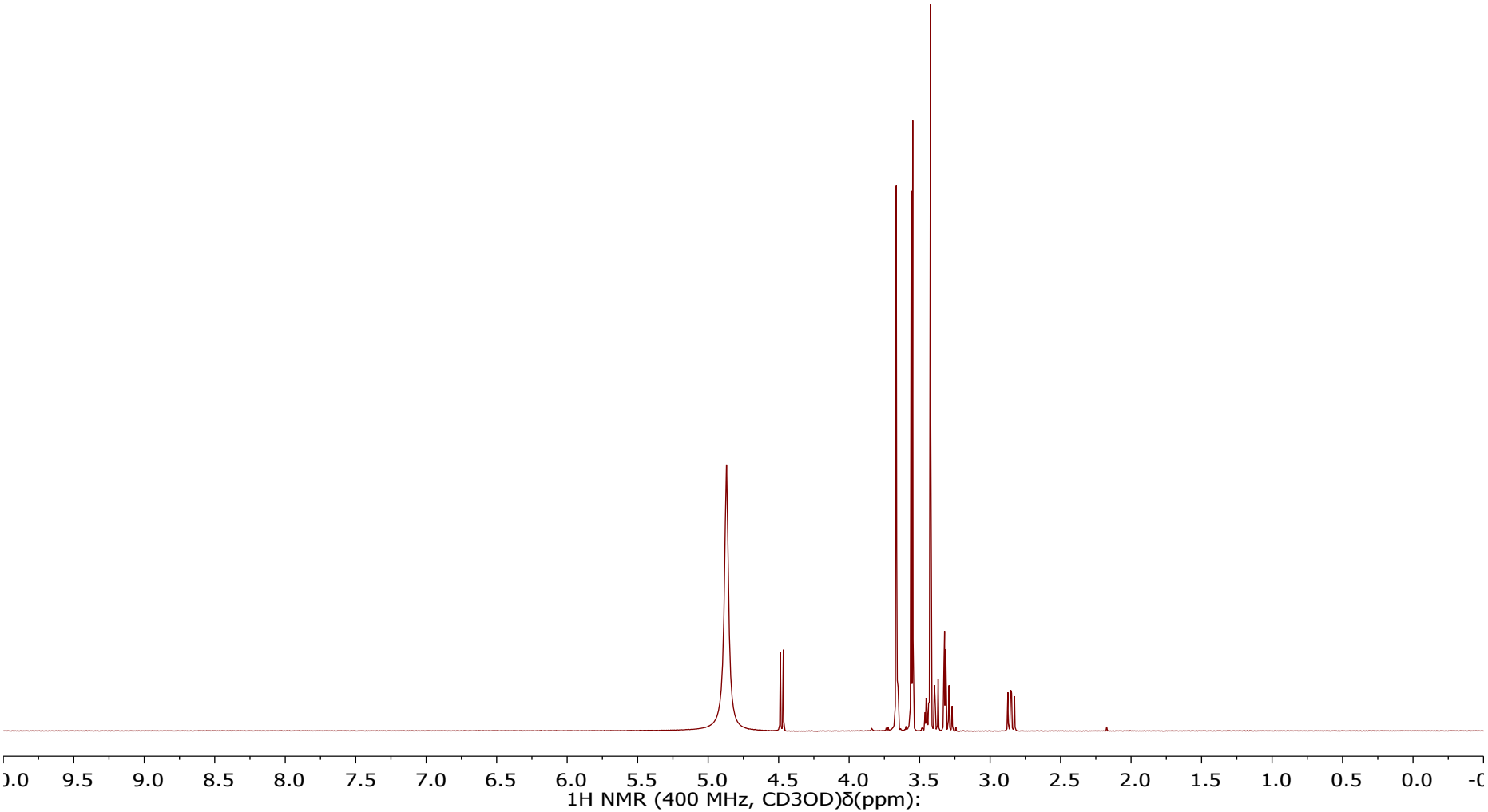
Table 3: Selected bond Lengths for 12c.

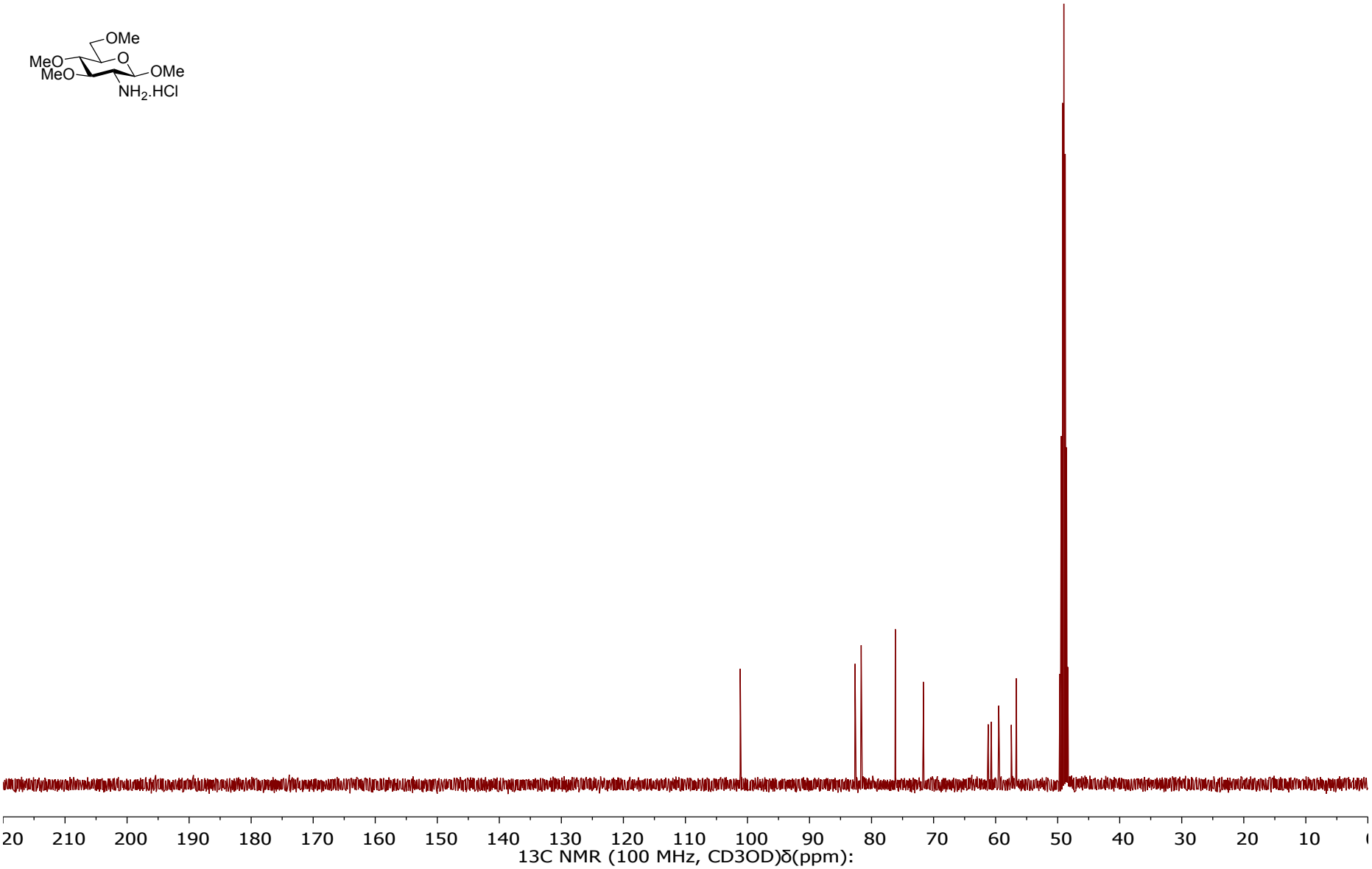
Atom	Atom	Length/Å
Rh1	C1	2.034(2)

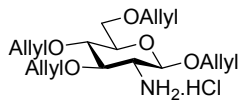
"CCDC 1017544 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif."

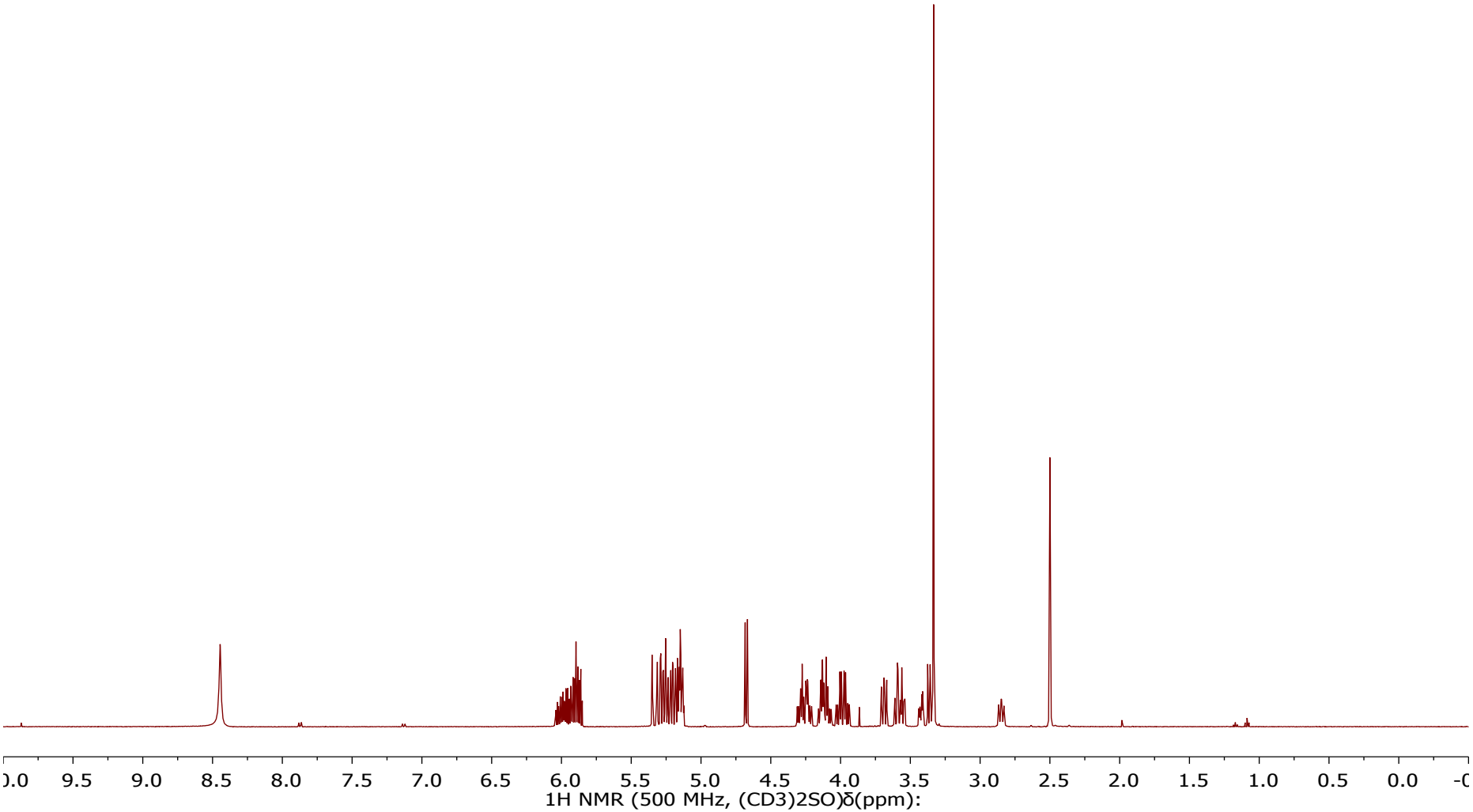
NMR Spectra of Novel Compounds:


OMe
MeO
O
MeO
OMe
NH2.HCl


9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (400 MHz, CD3OD)δ(ppm):


OMe
MeO
MeO
O
OMe
NH2.HCl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (100 MHz, CD3OD)δ(ppm):


OAllyl
AllylO
O
AllylO
OAllyl
NH2.HCl


9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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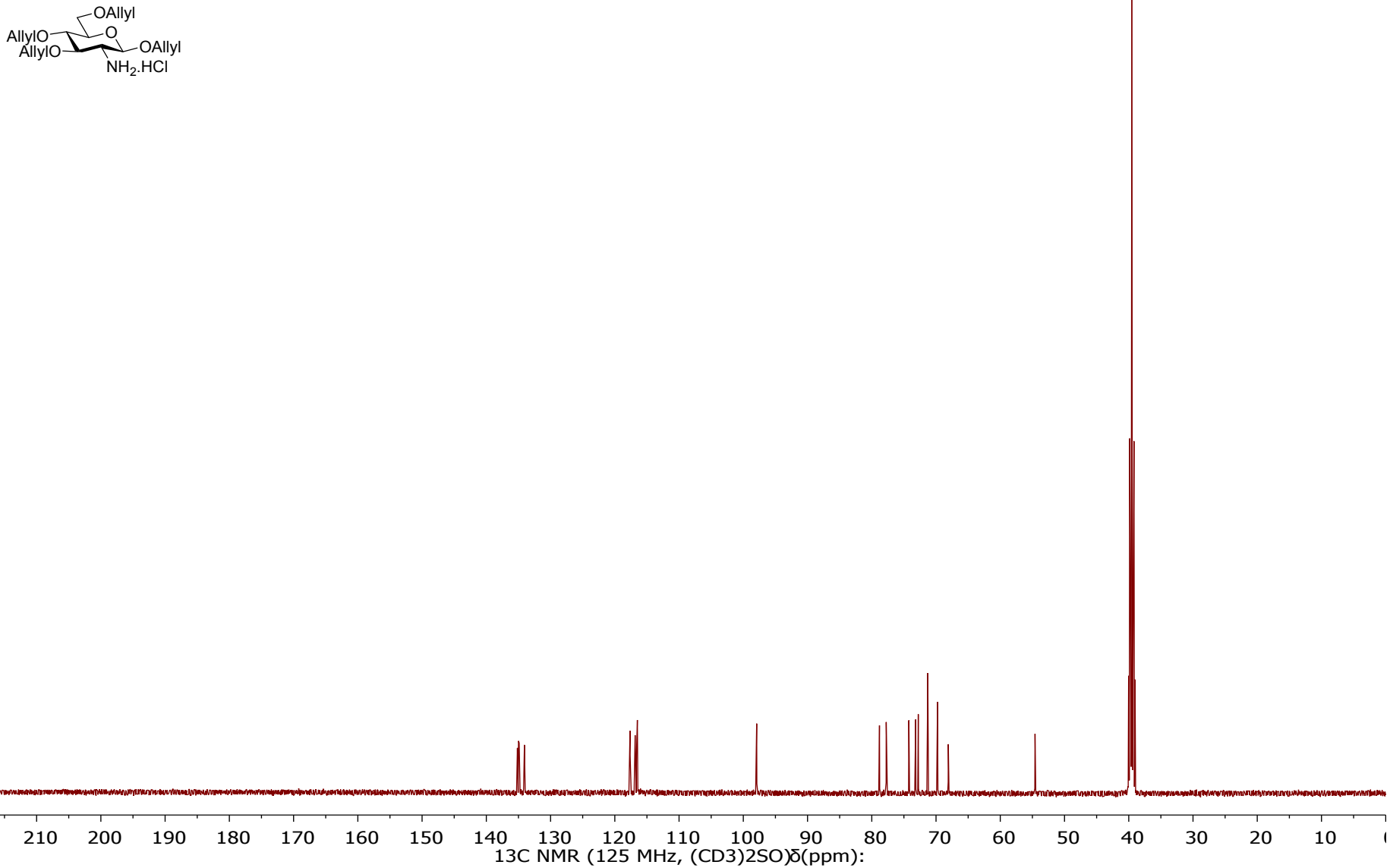
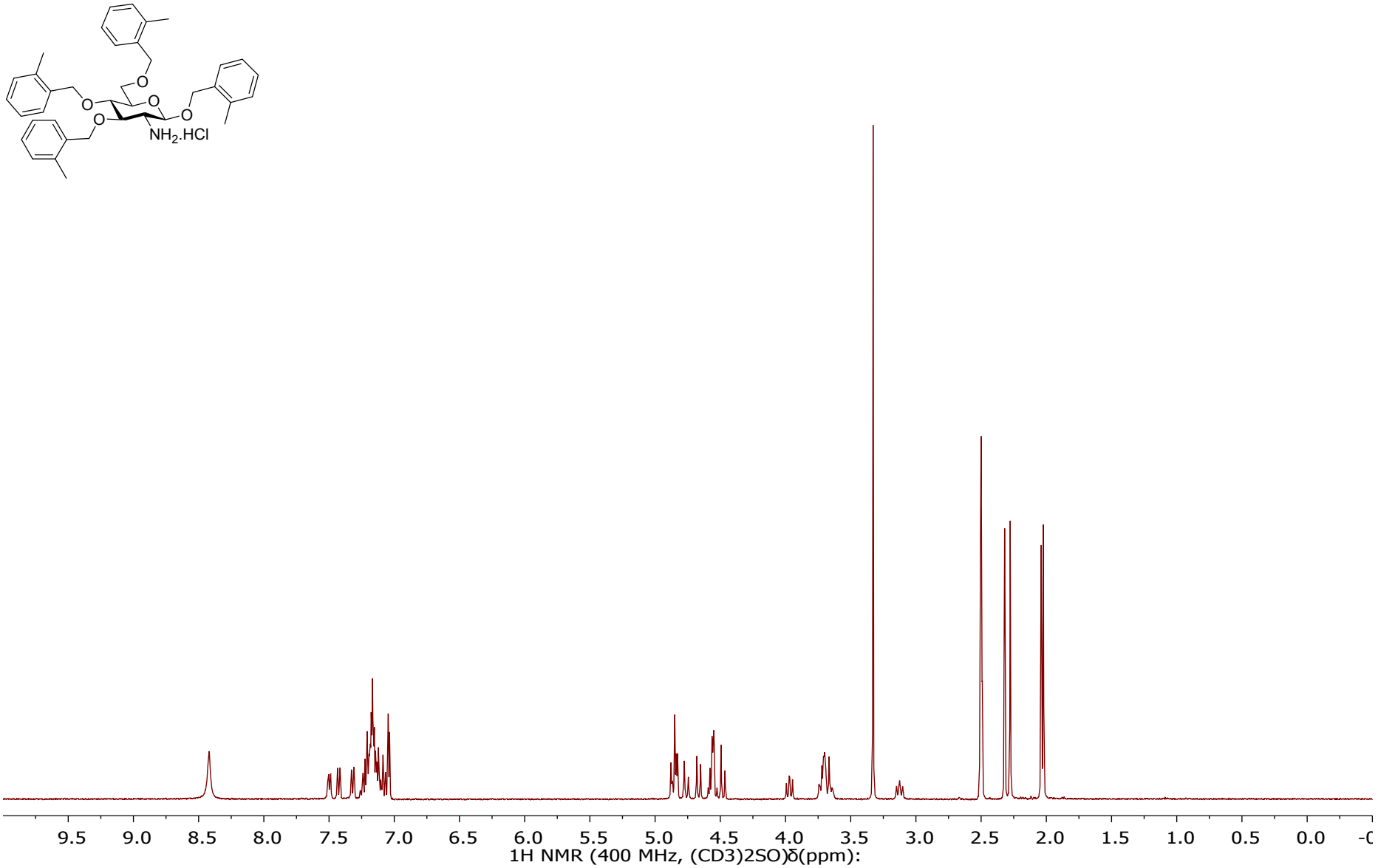

OAllyl
AllylO
O
OAllyl
AllylO
NH2.HCl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, (CD3)2SO) δ(ppm):


O
O
O
O
O
NH2.HCl
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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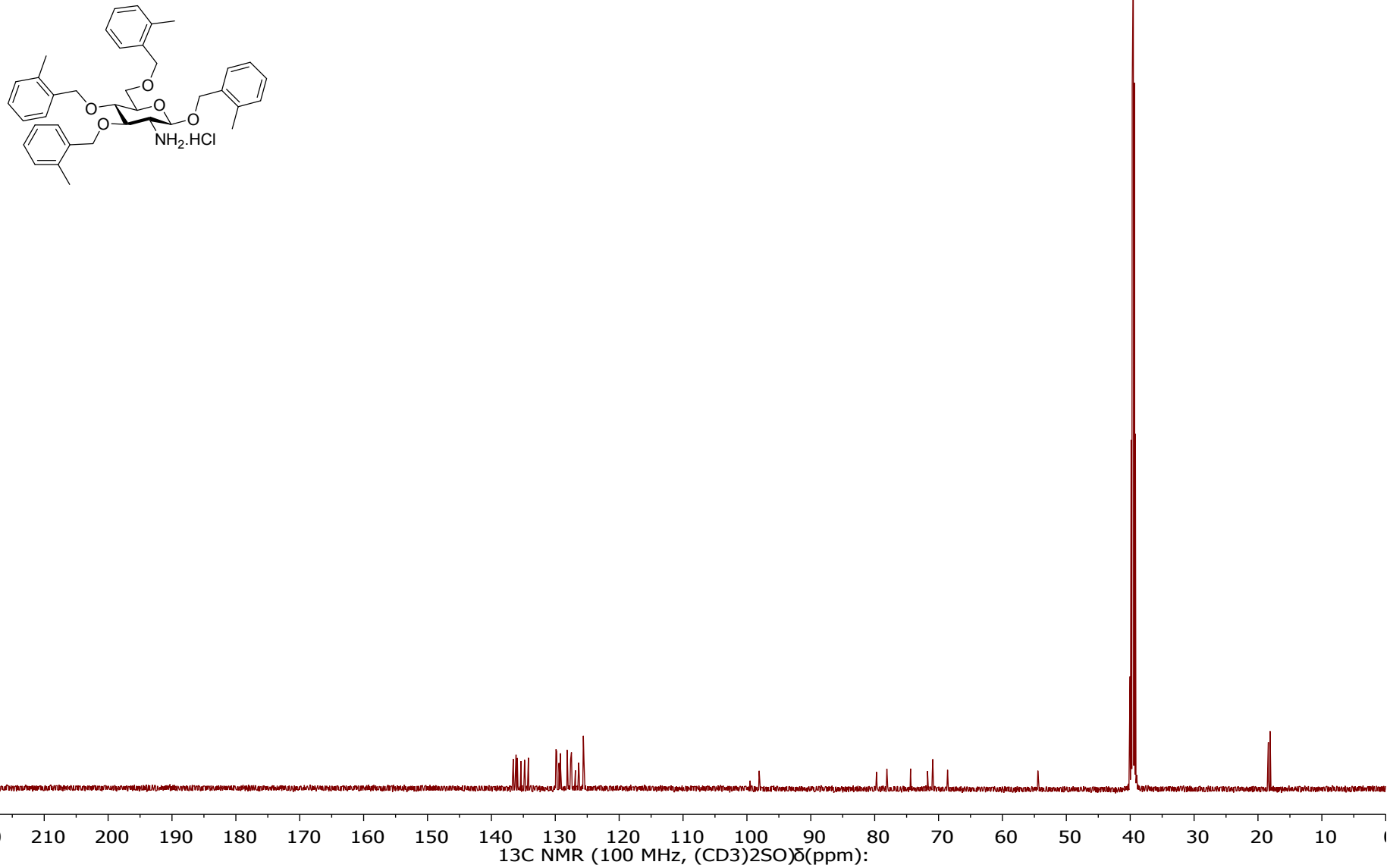
O
O
O
O
O
NH2.HCl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
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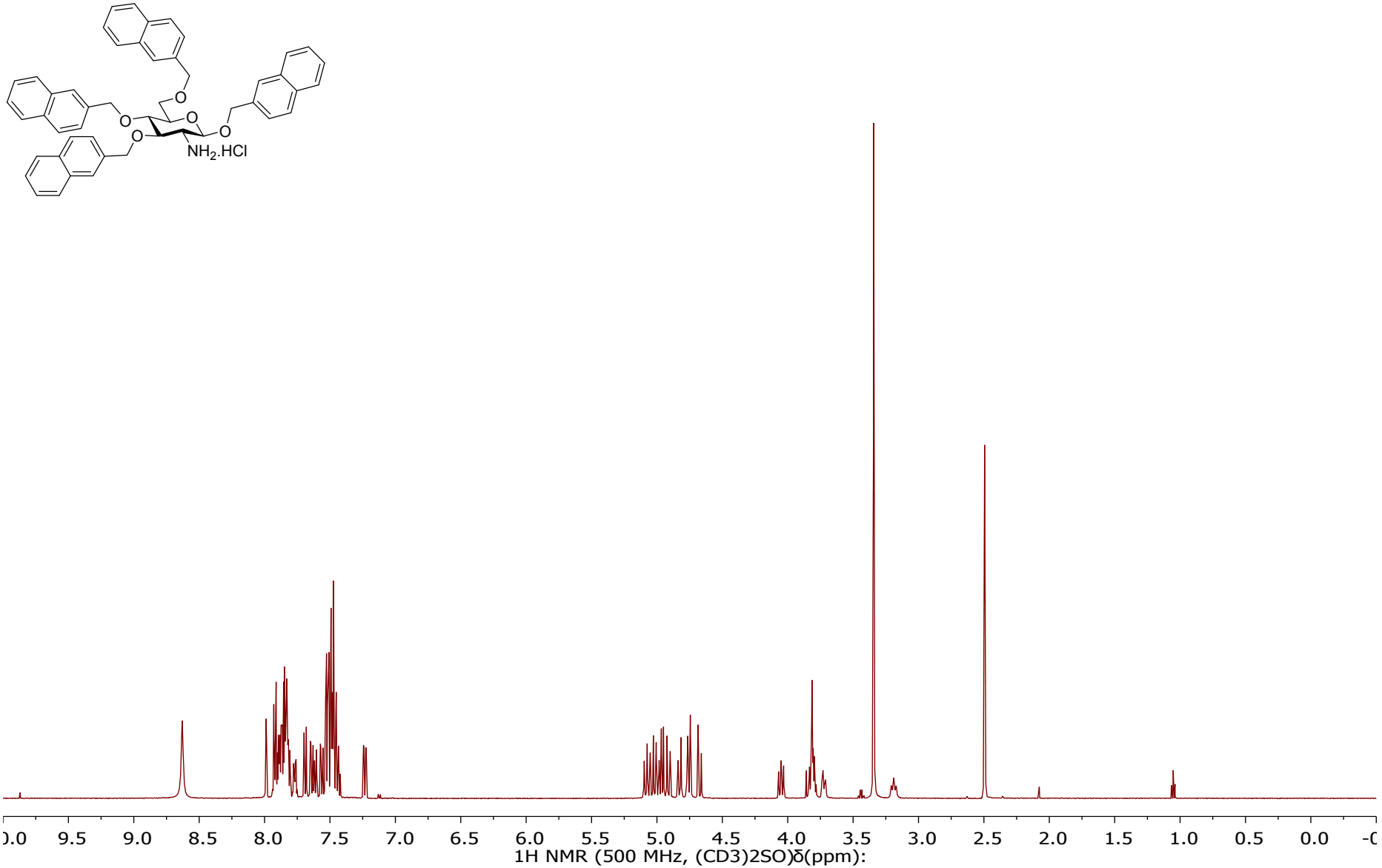
O
O
O
O
O
NH2.HCl
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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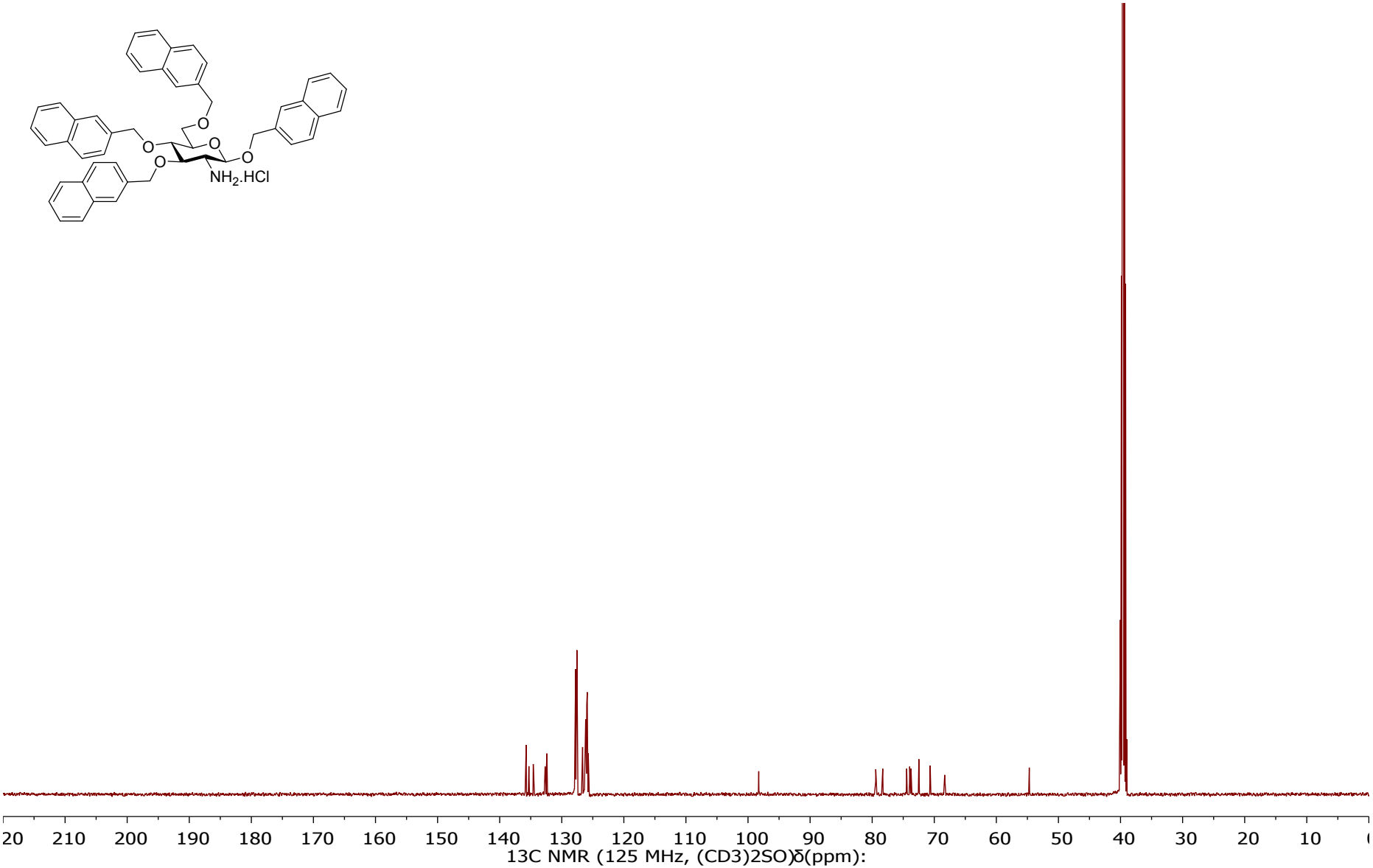
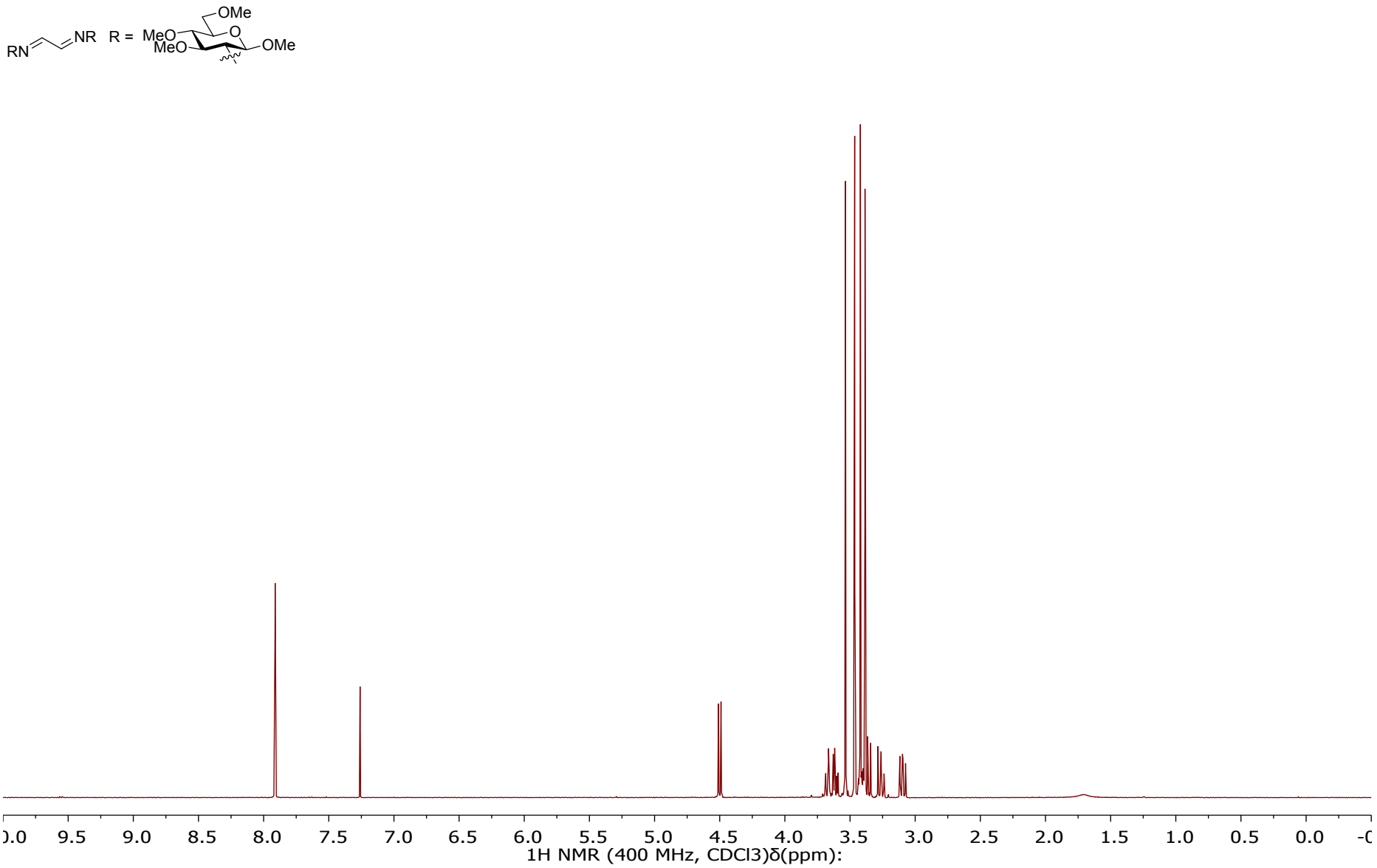

O
O
O
O
O
NH2.HCl
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
13C NMR (125 MHz, (CD3)2SO)δ(ppm):


RN
NR
R =
MeO
MeO
O
OMe
OMe
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
2.0
1.5
1.0
0.5
0.0
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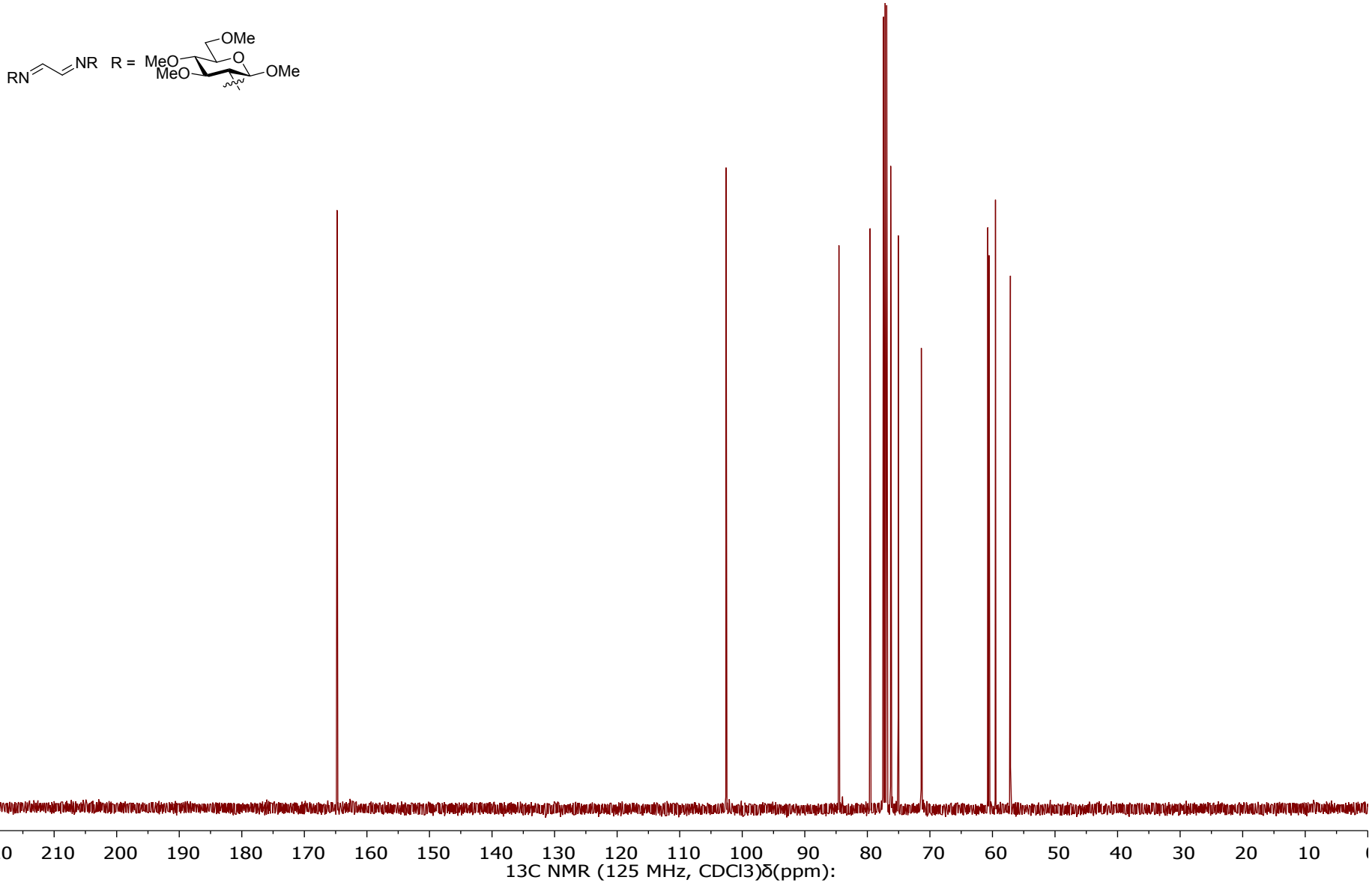
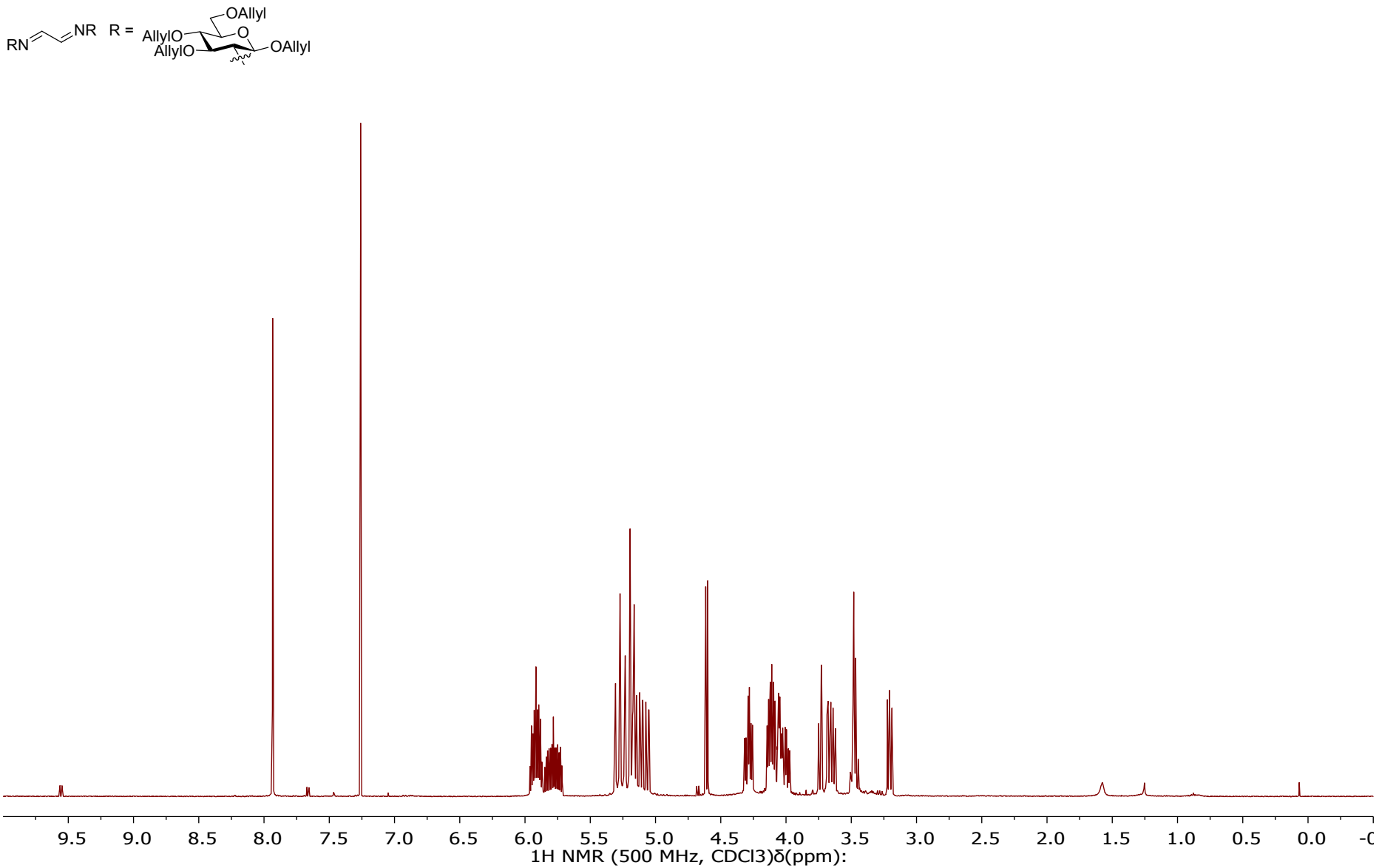

RN
NR
R =
MeO
MeO
O
OMe
OMe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CDCl3)δ(ppm):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NR
R =
AllylO
AllylO
O
OAllyl
OAllyl
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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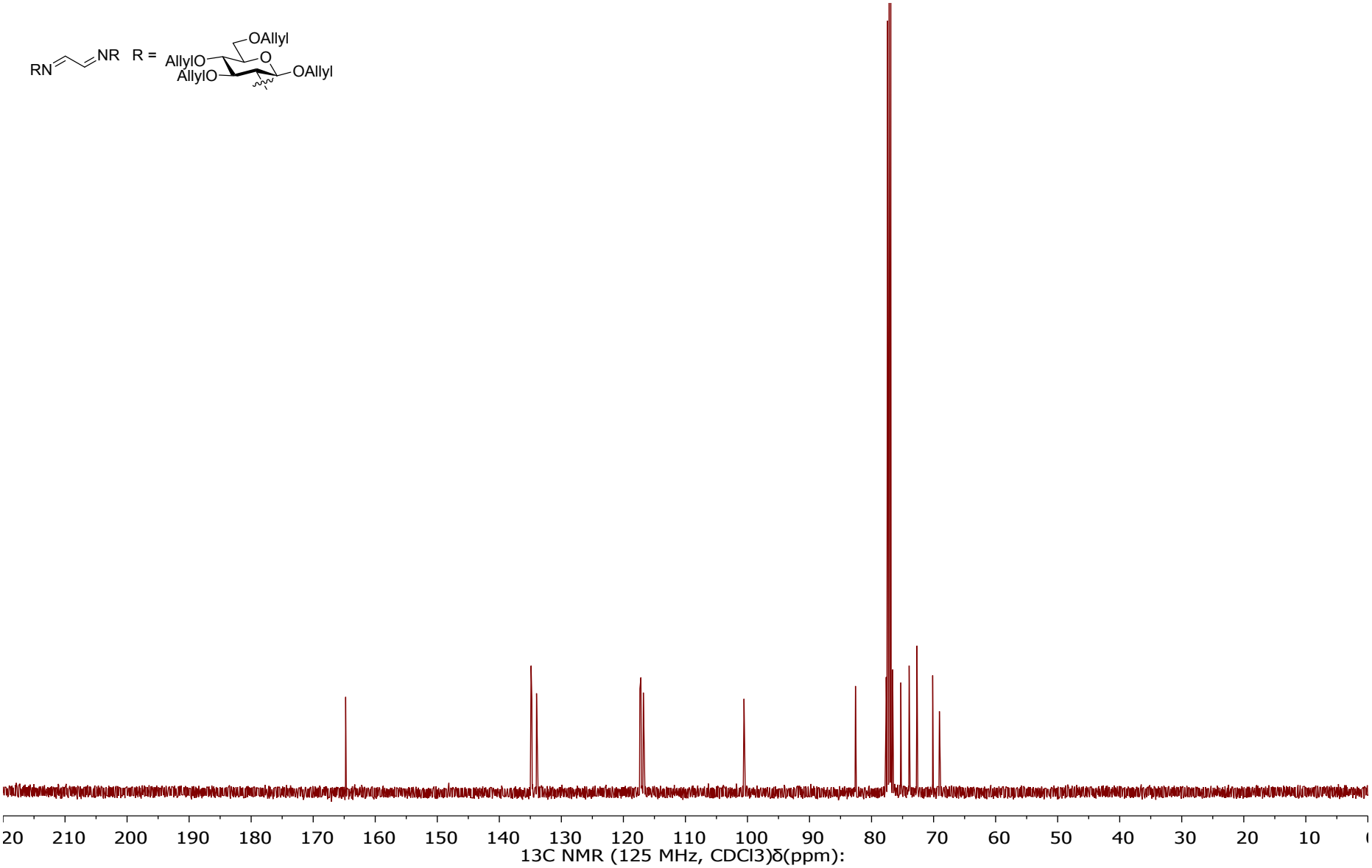
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NR
R =
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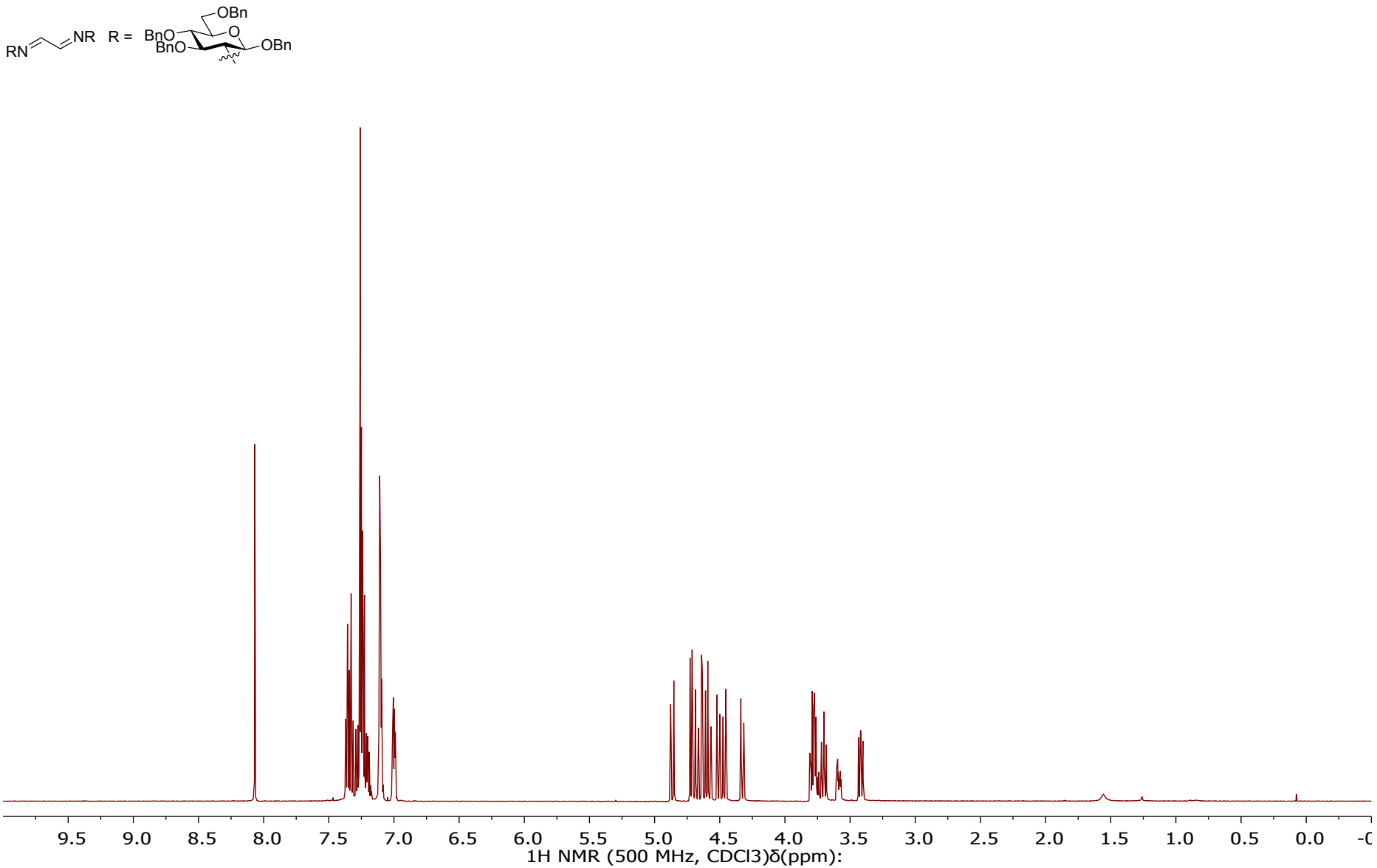
AllylO
O
OAllyl
OAllyl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CDCl3)δ(ppm):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NR
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BnO
O
OBn
OBn
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8.5
8.0
7.5
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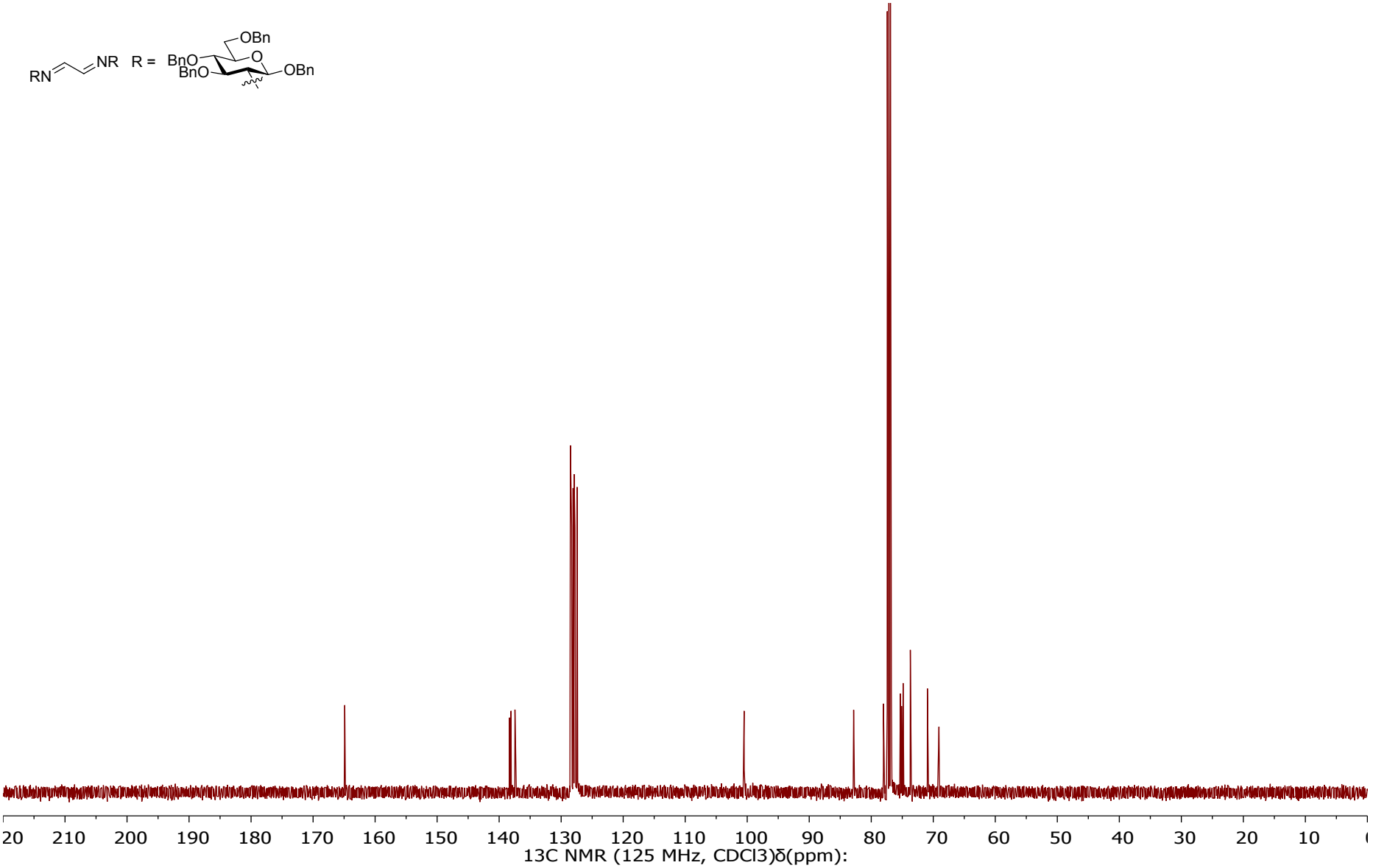
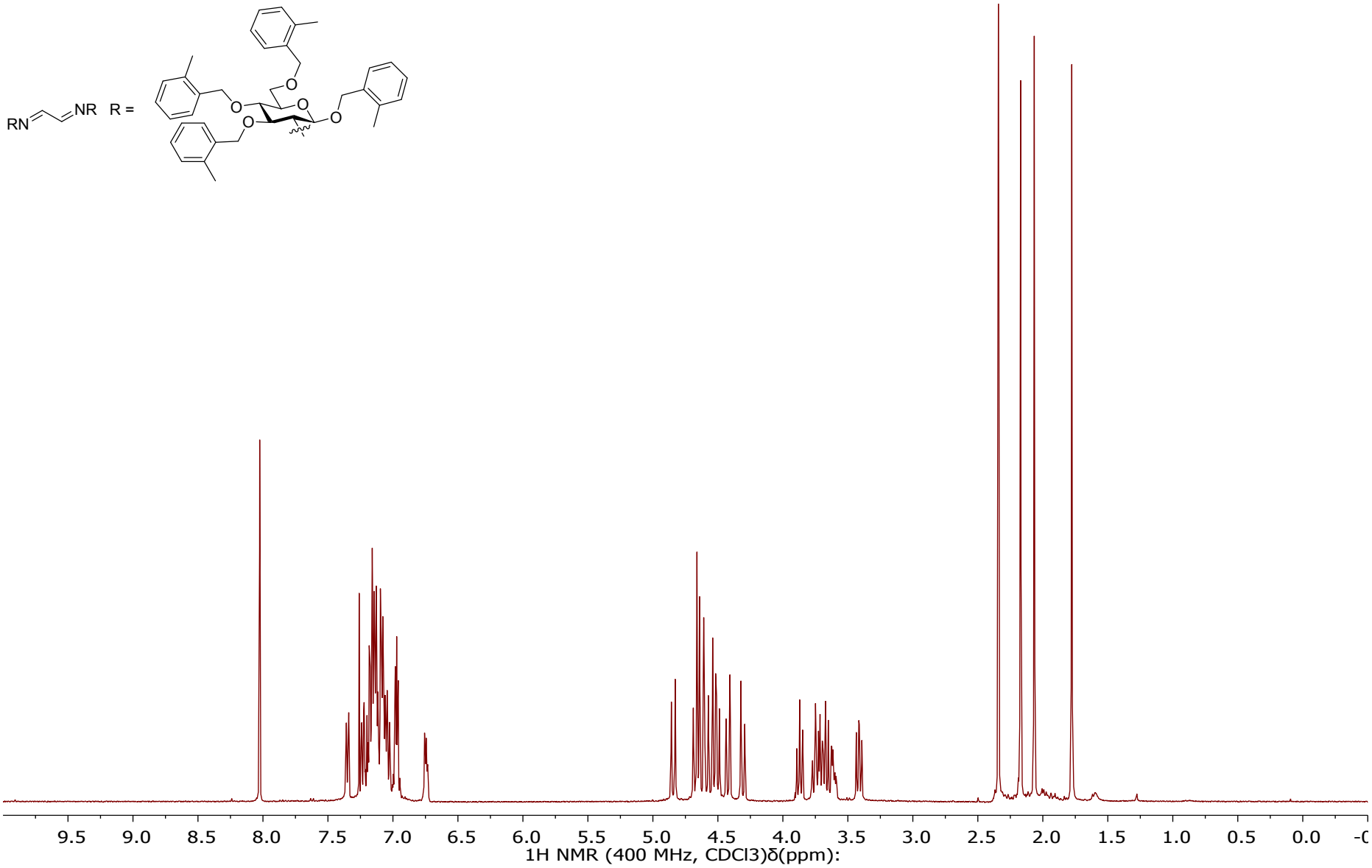
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (500 MHz, CDCl3)δ(ppm):


RN
NR
R =
BnO
BnO
O
OBn
OBn
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CDCl3)δ(ppm):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NR
R =
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O
O
O
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8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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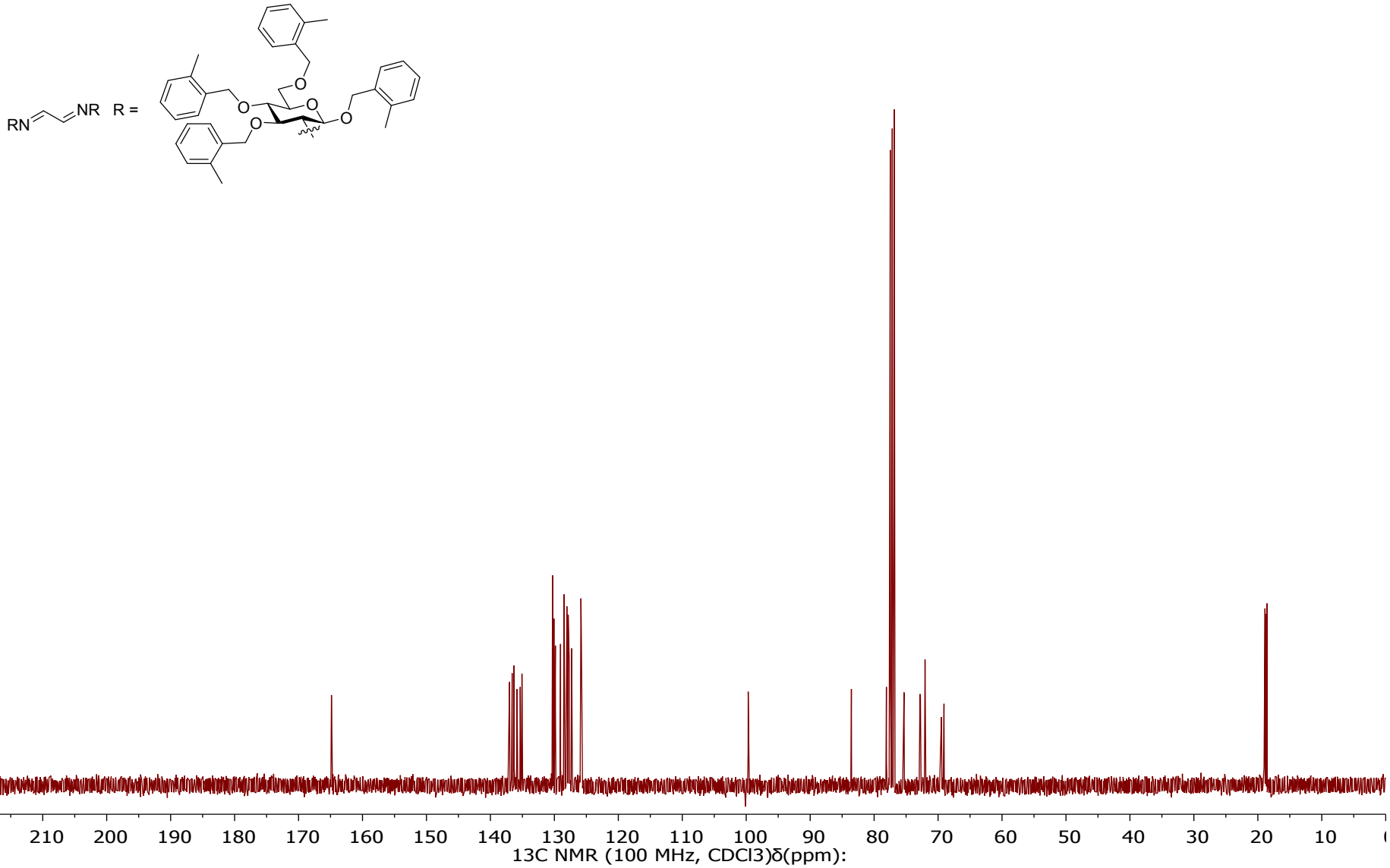
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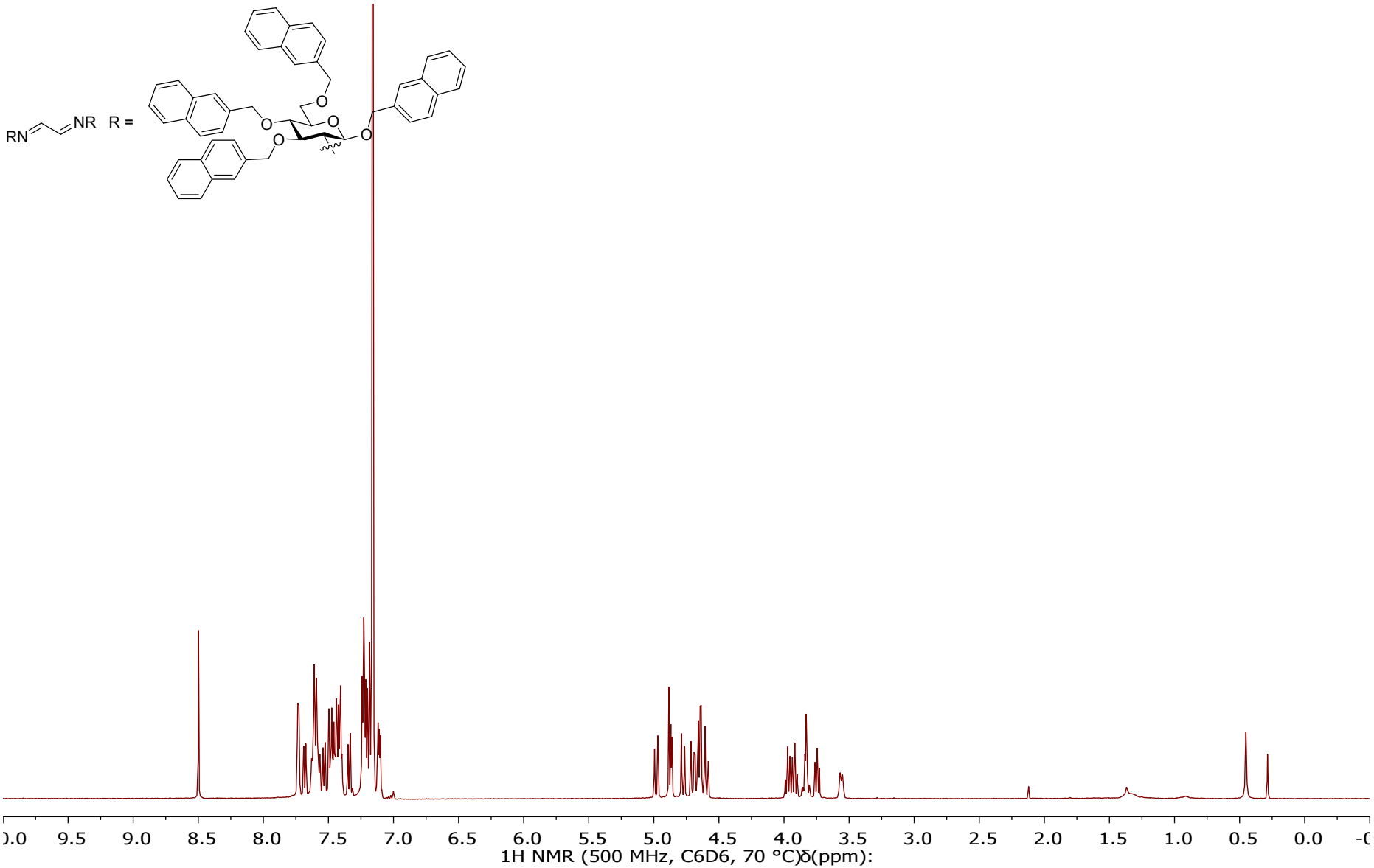
O
O
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
13C NMR (100 MHz, CDCl3)δ(ppm):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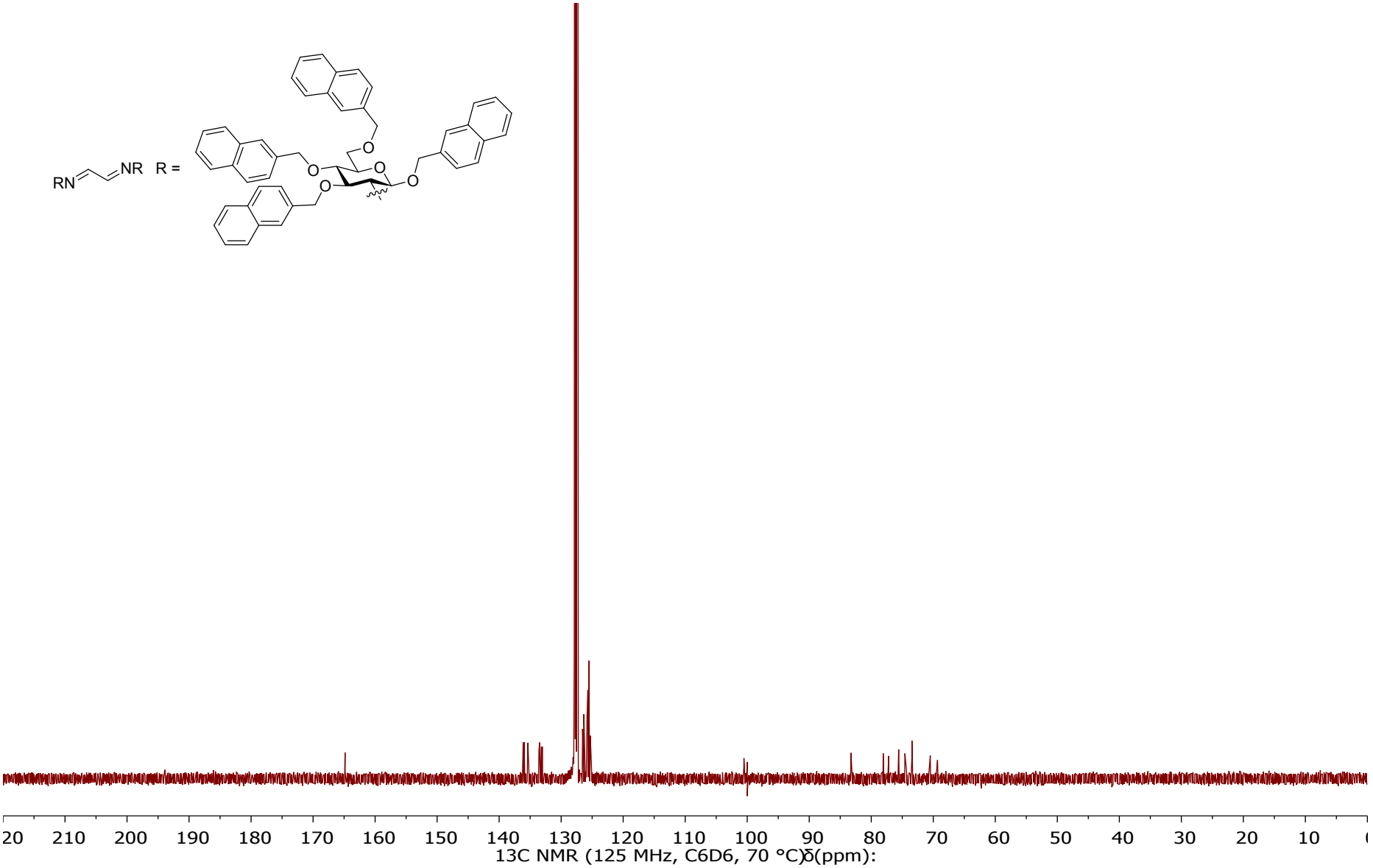
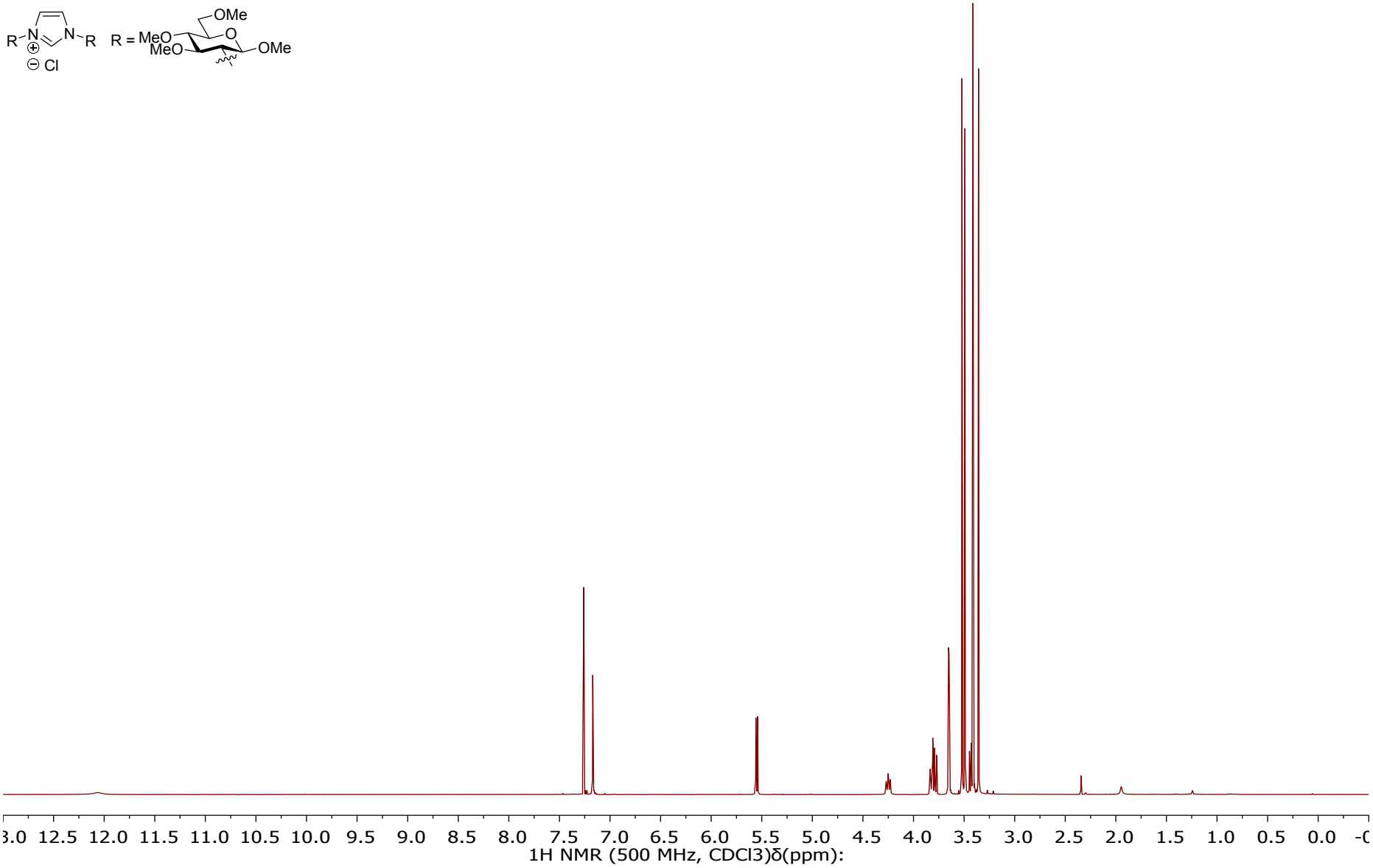
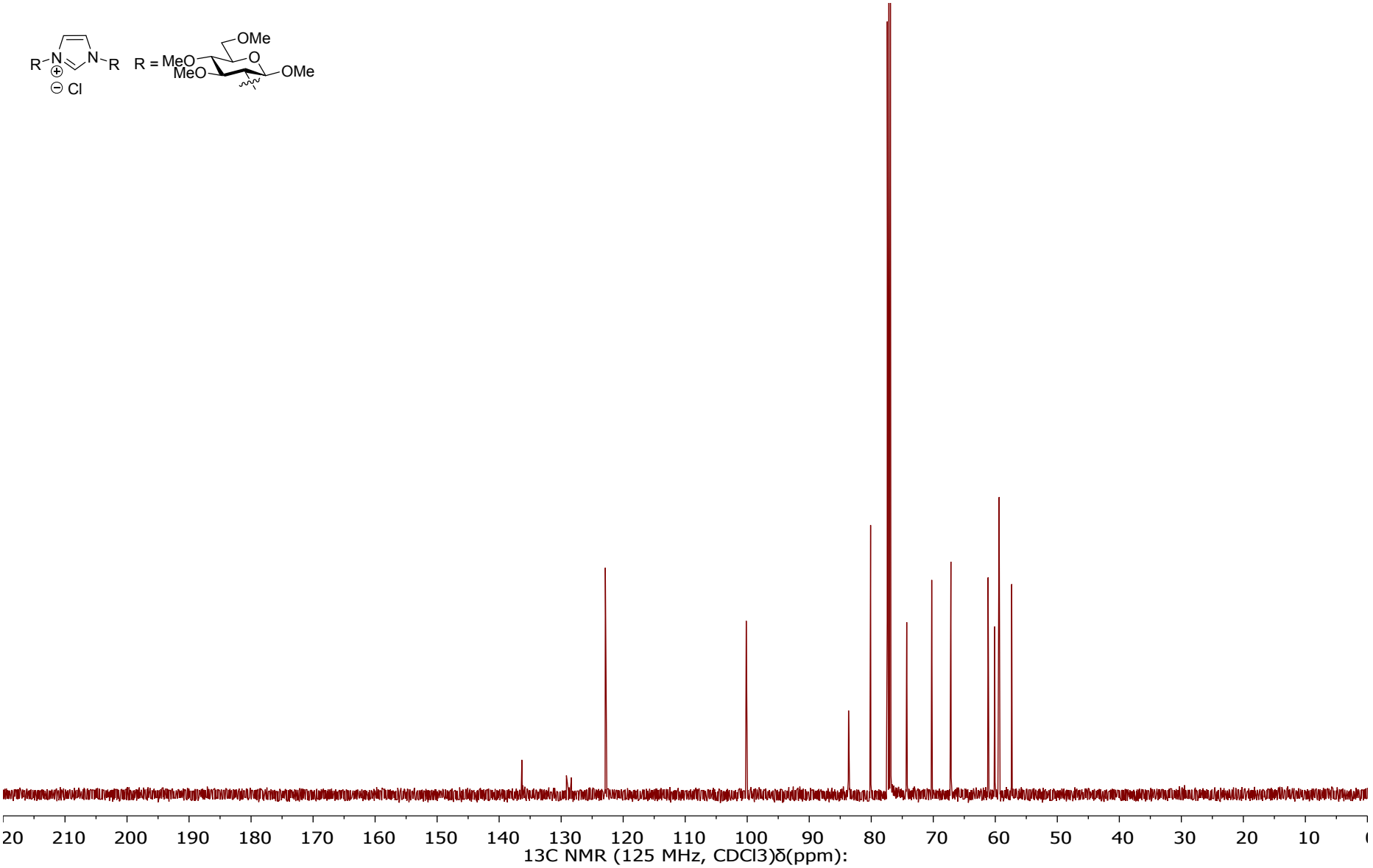
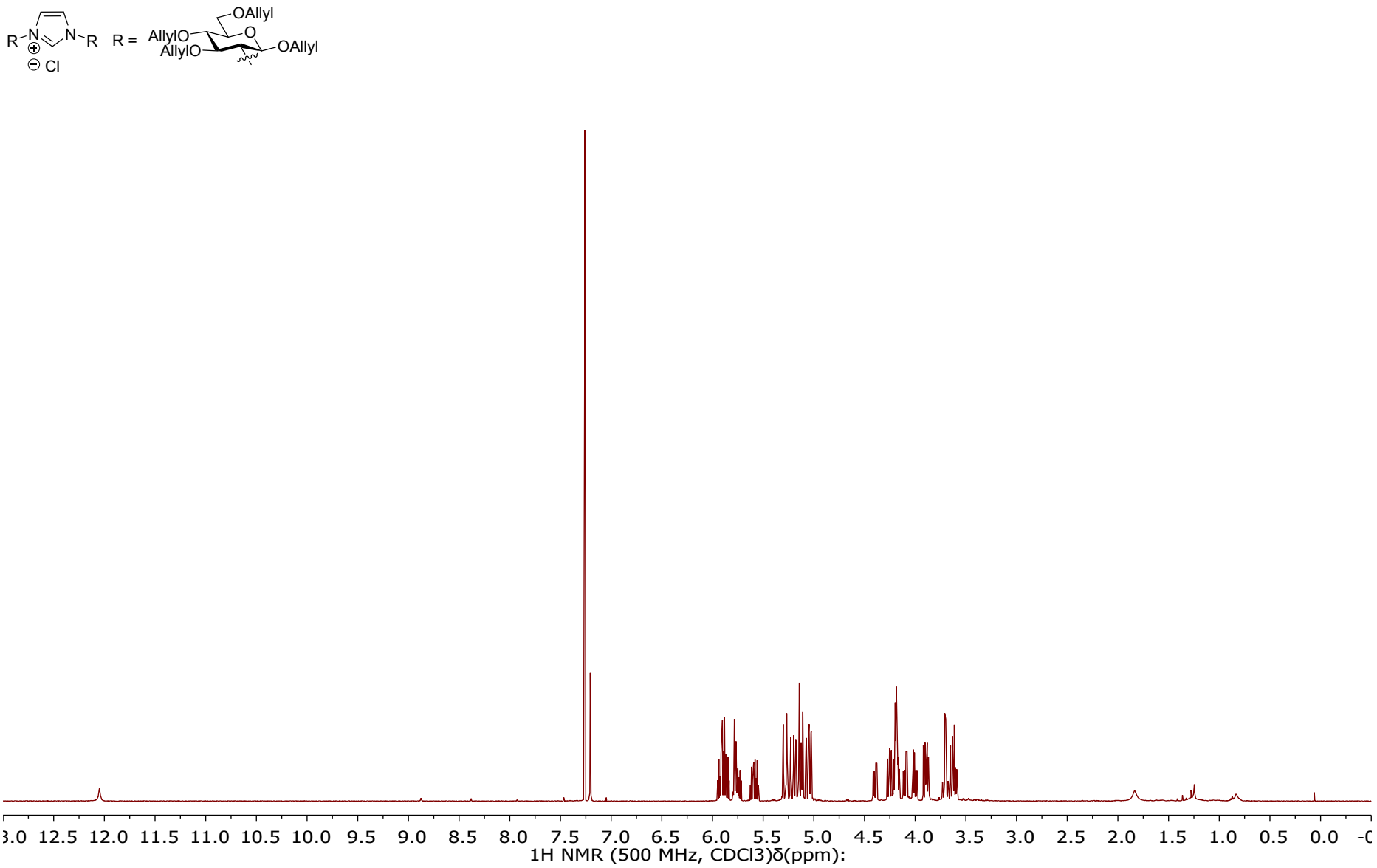
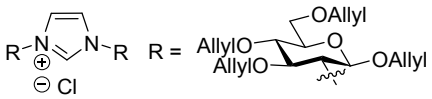
NR
R =
O
O
O
O
O
1H NMR (500 MHz, C6D6, 70 °C)δ(ppm):

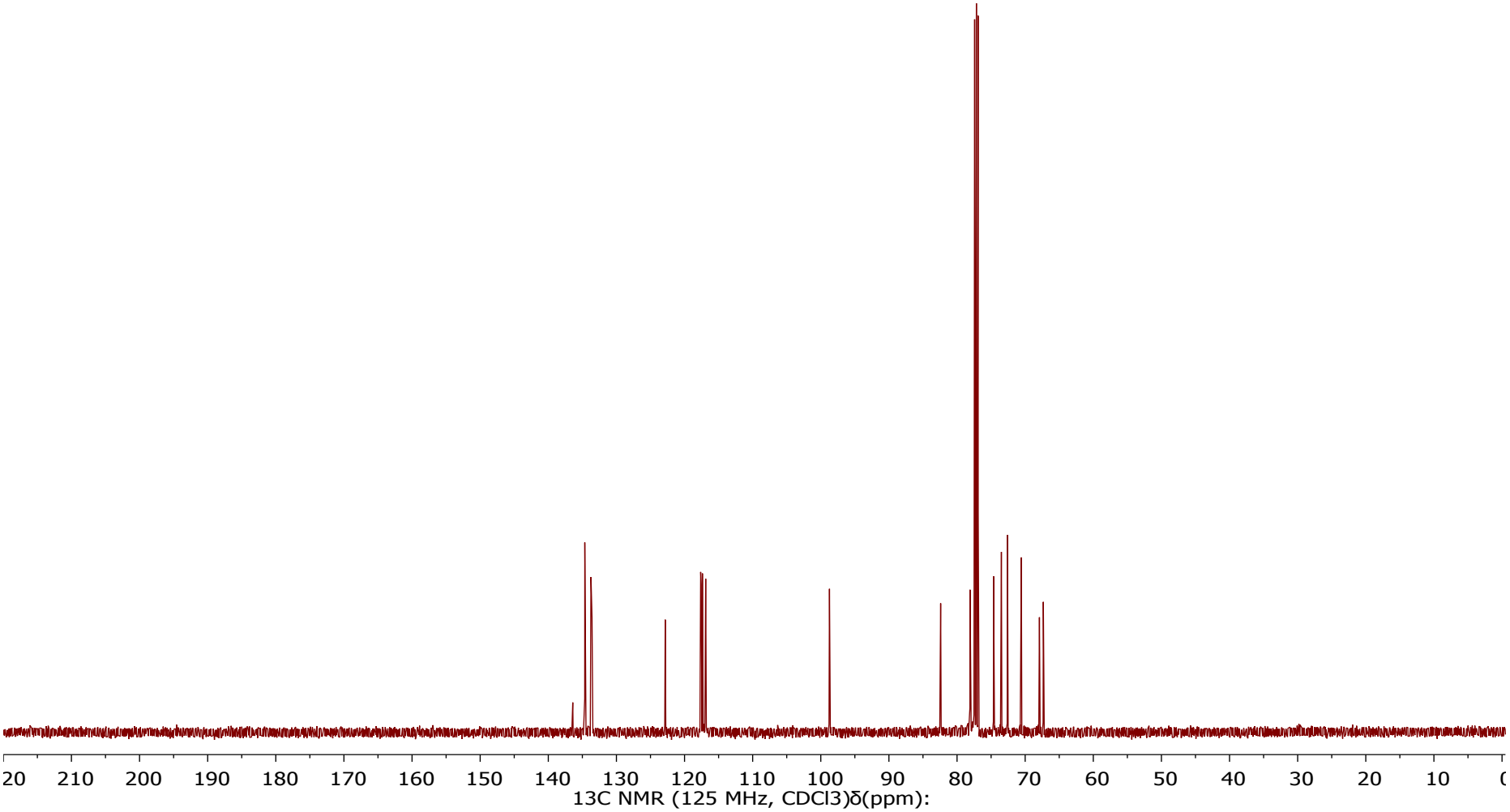

RN
NR
R =
O
O
O
O
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
13C NMR (125 MHz, C6D6, 70 °C) δ (ppm):

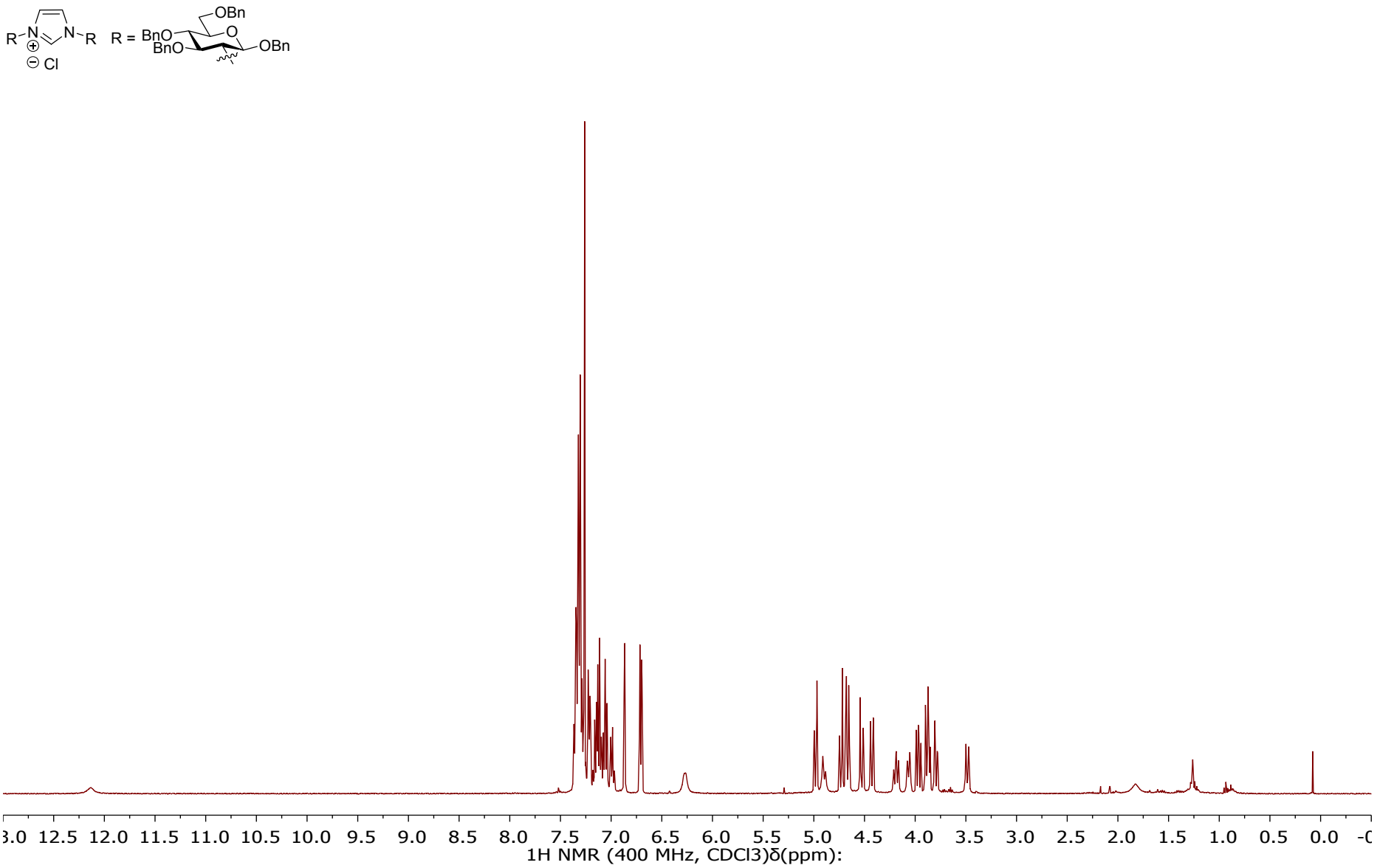

R = MeO
MeO
OMe
O
OMe
R
N
N
R
Cl
1H NMR (500 MHz, CDCl3)δ(ppm):

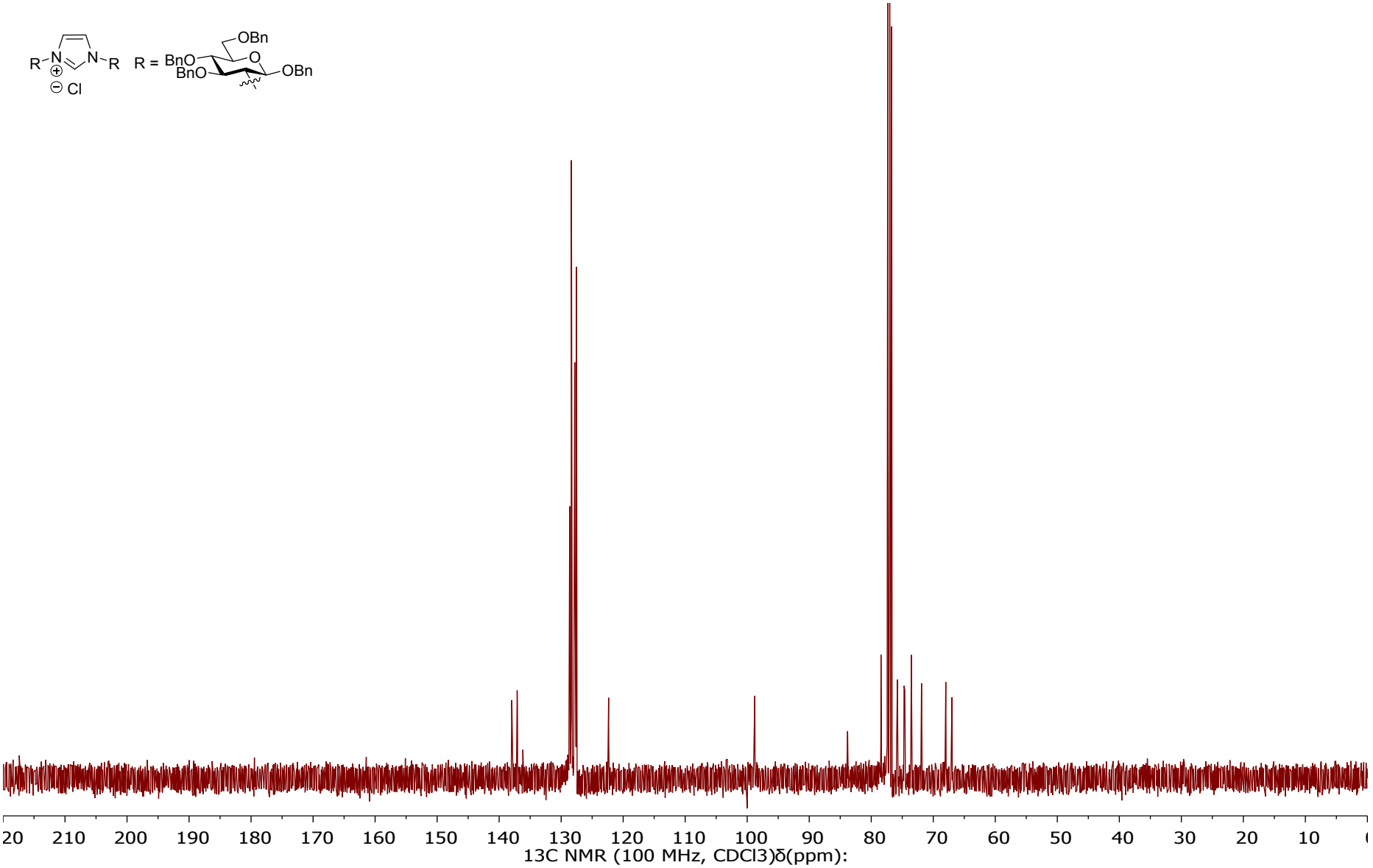

R = MeO
MeO
OMe
OMe
Cl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CDCl3)δ(ppm):

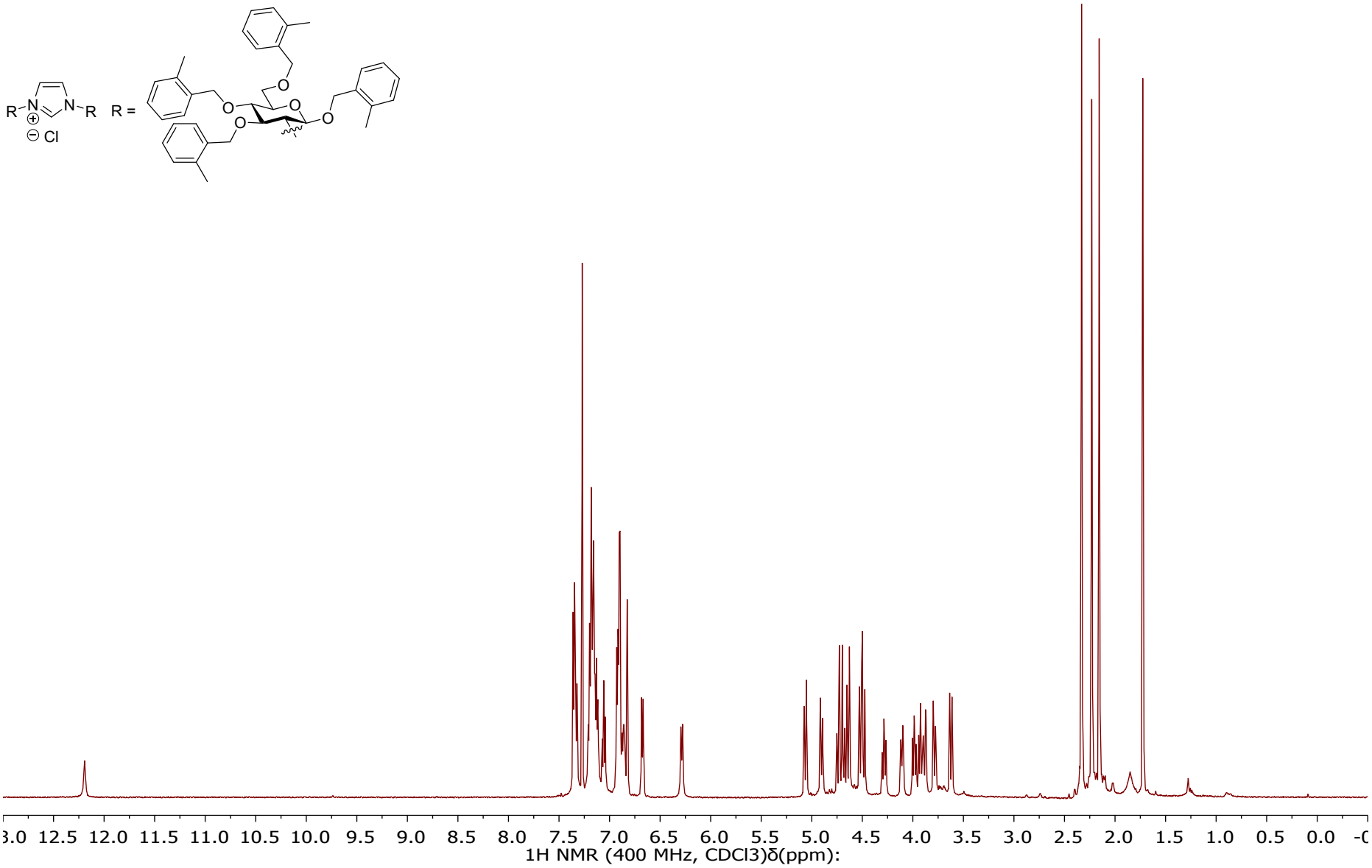

R
N
N
R
Cl
R =
AllylO
AllylO
O
OAllyl
OAllyl
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
1H NMR (500 MHz, CDCl3)δ(ppm):

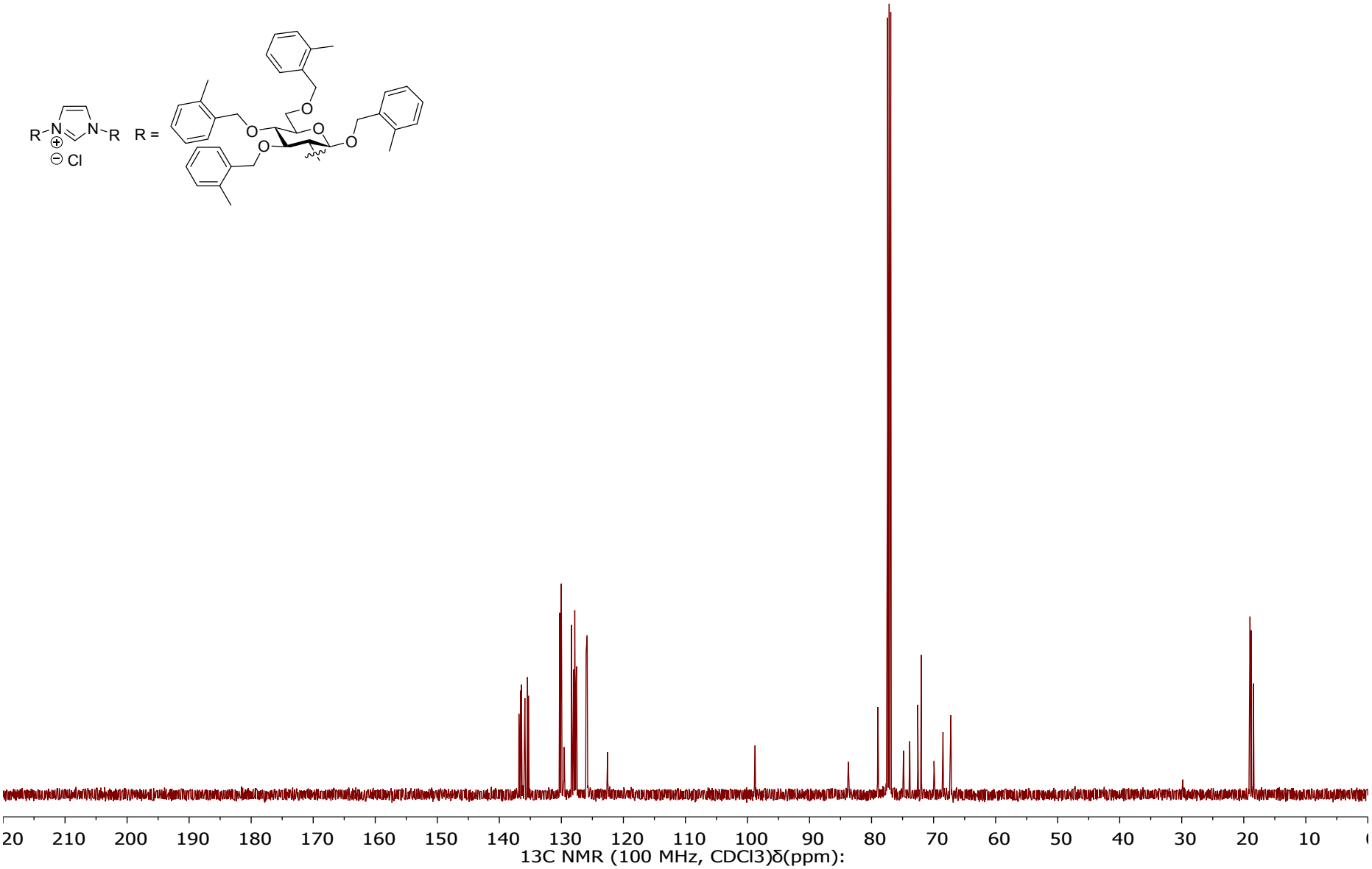

R
N
N
R
Cl
R =
AllylO
AllylO
O
OAllyl
OAllyl

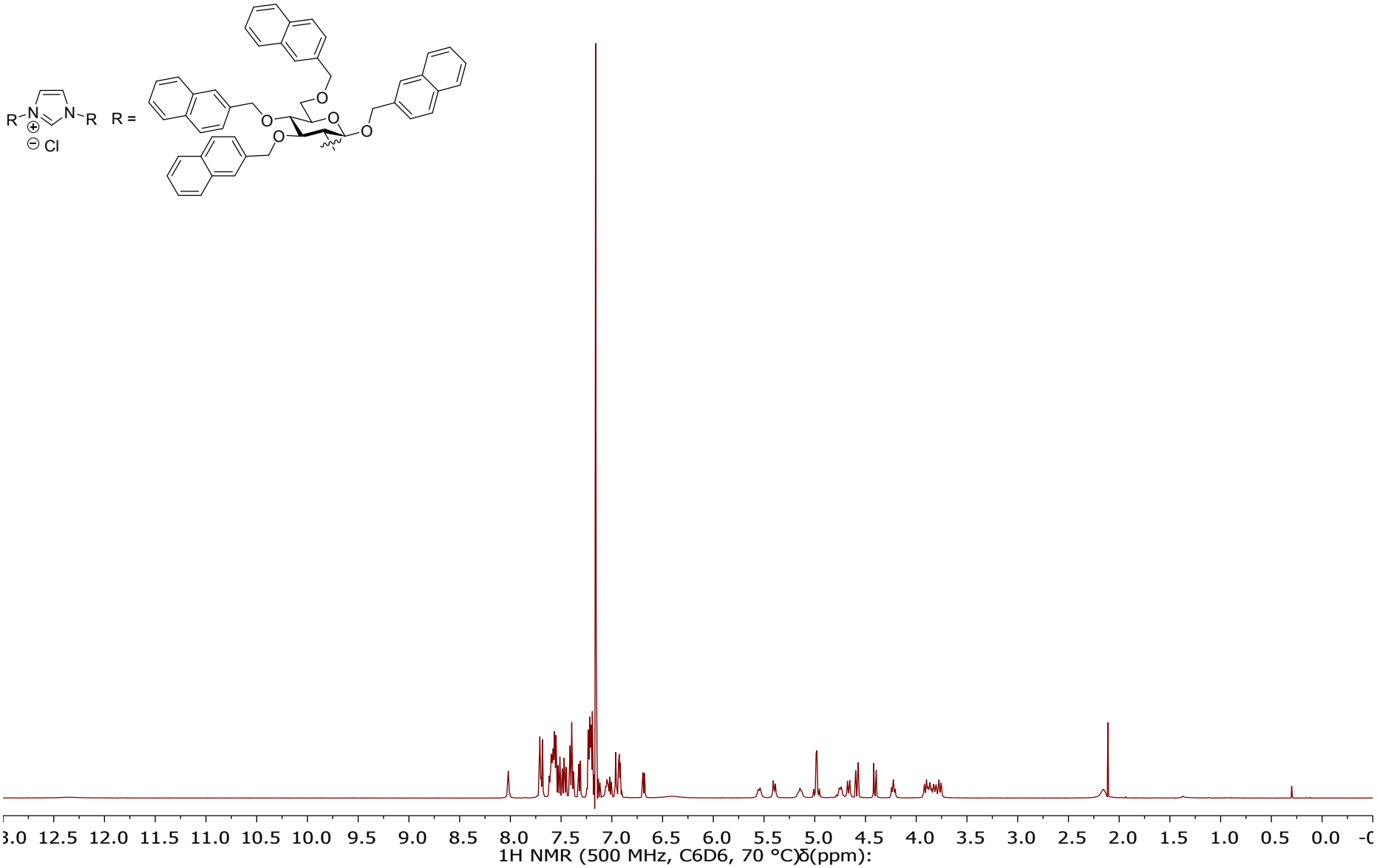

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CDCl3)δ(ppm):

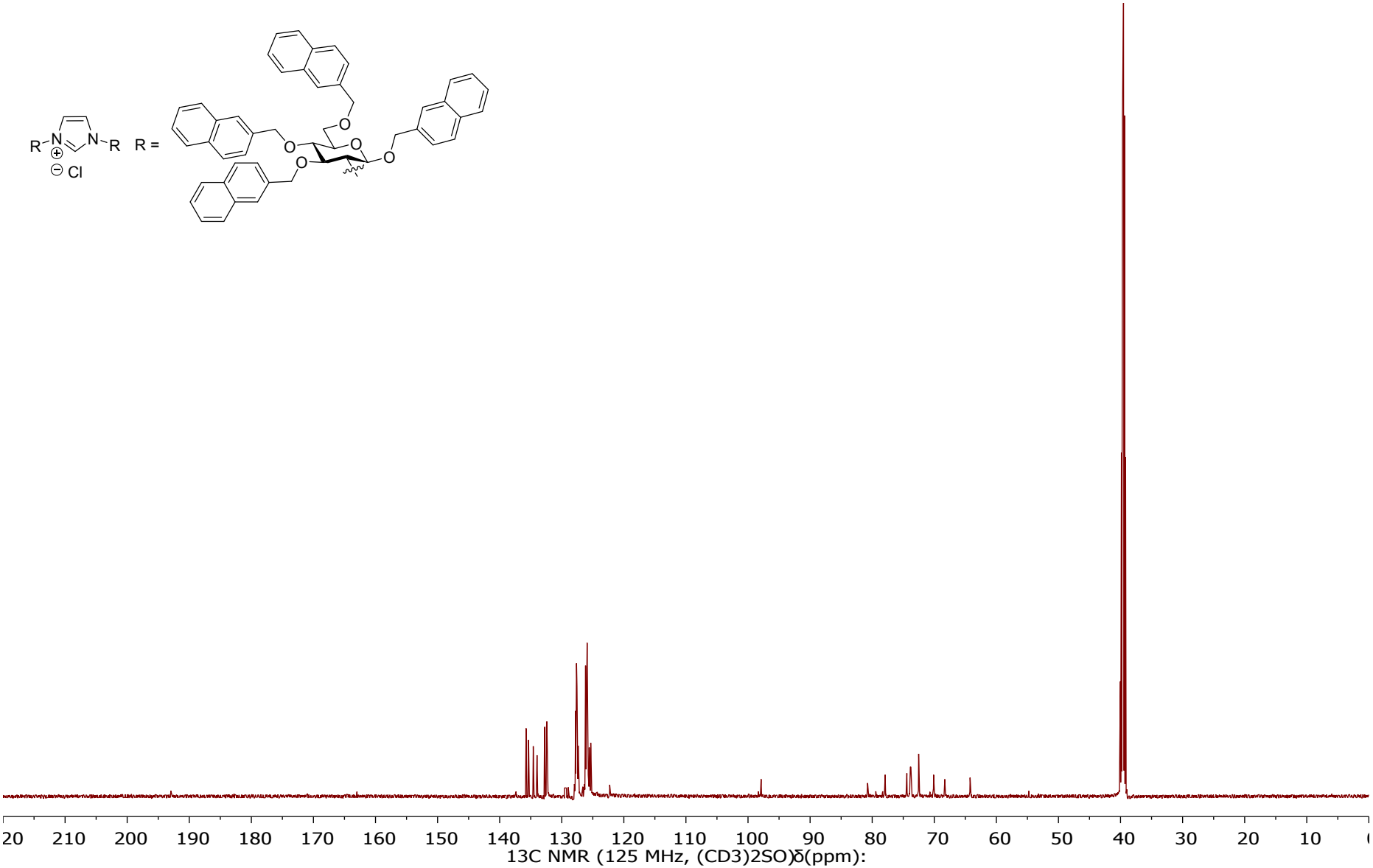

R
N
N
R
Cl
R = BnO
BnO
O
OBn
OBn
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
1H NMR (400 MHz, CDCl3)δ(ppm):

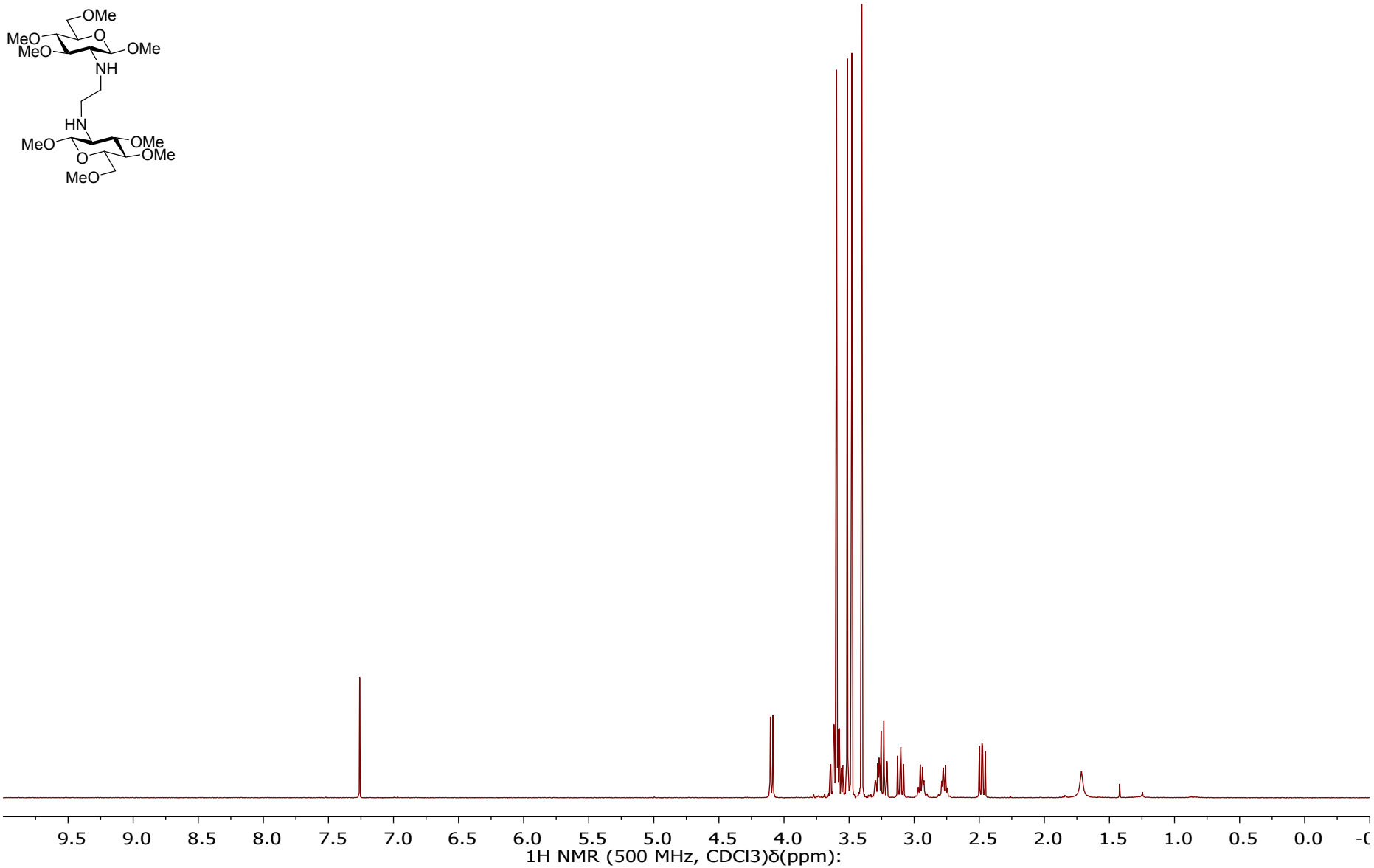

R = BnO
BnO
OBn
O
OBn
Cl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (100 MHz, CDCl3)δ(ppm):

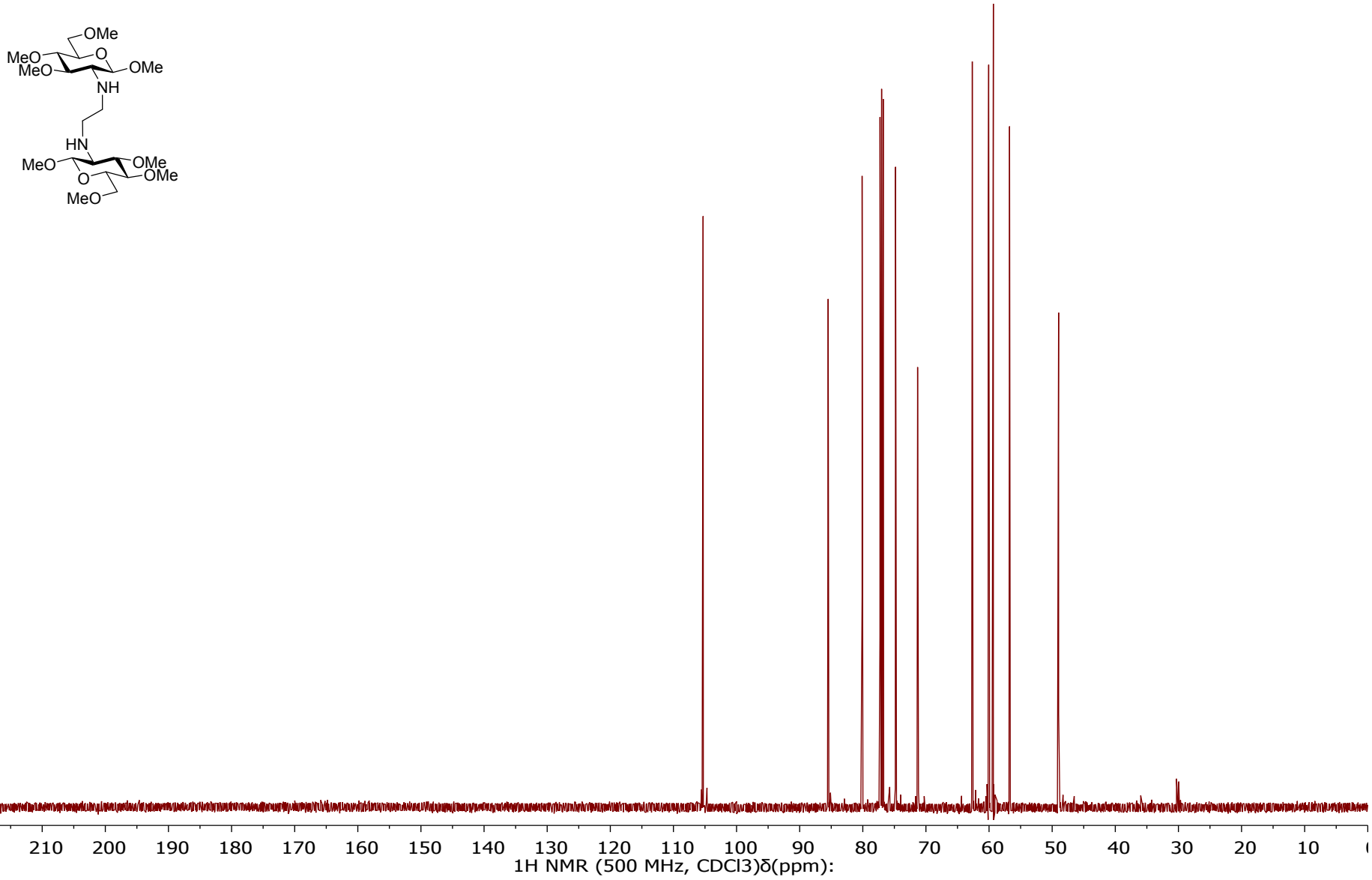

R
N
N
R
R =
Cl
O
O
O
O
O
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
1H NMR (400 MHz, CDCl3)δ(ppm):

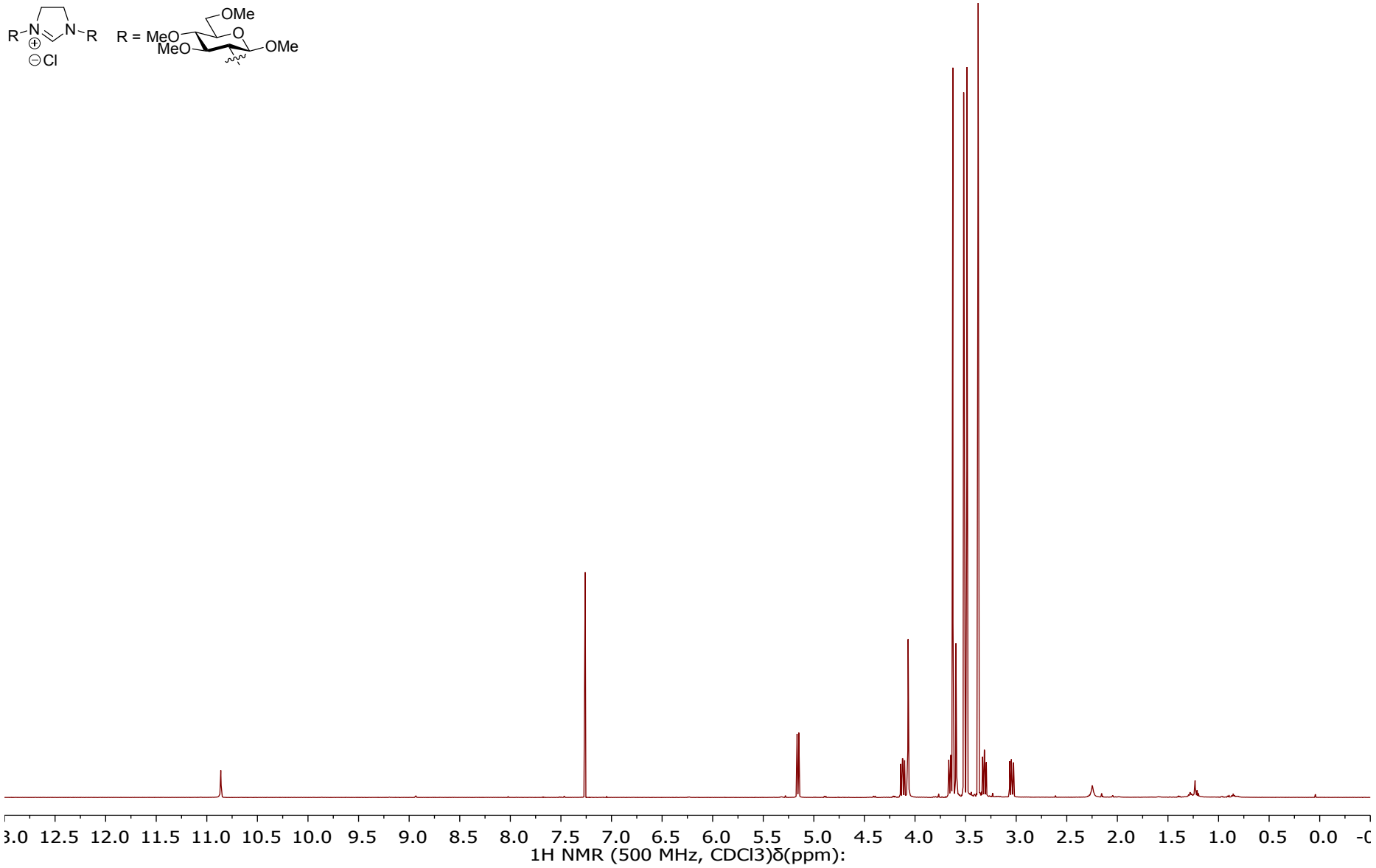

R
N
N
R
R =
Cl
O
O
O
O
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
13C NMR (100 MHz, CDCl3)δ(ppm):

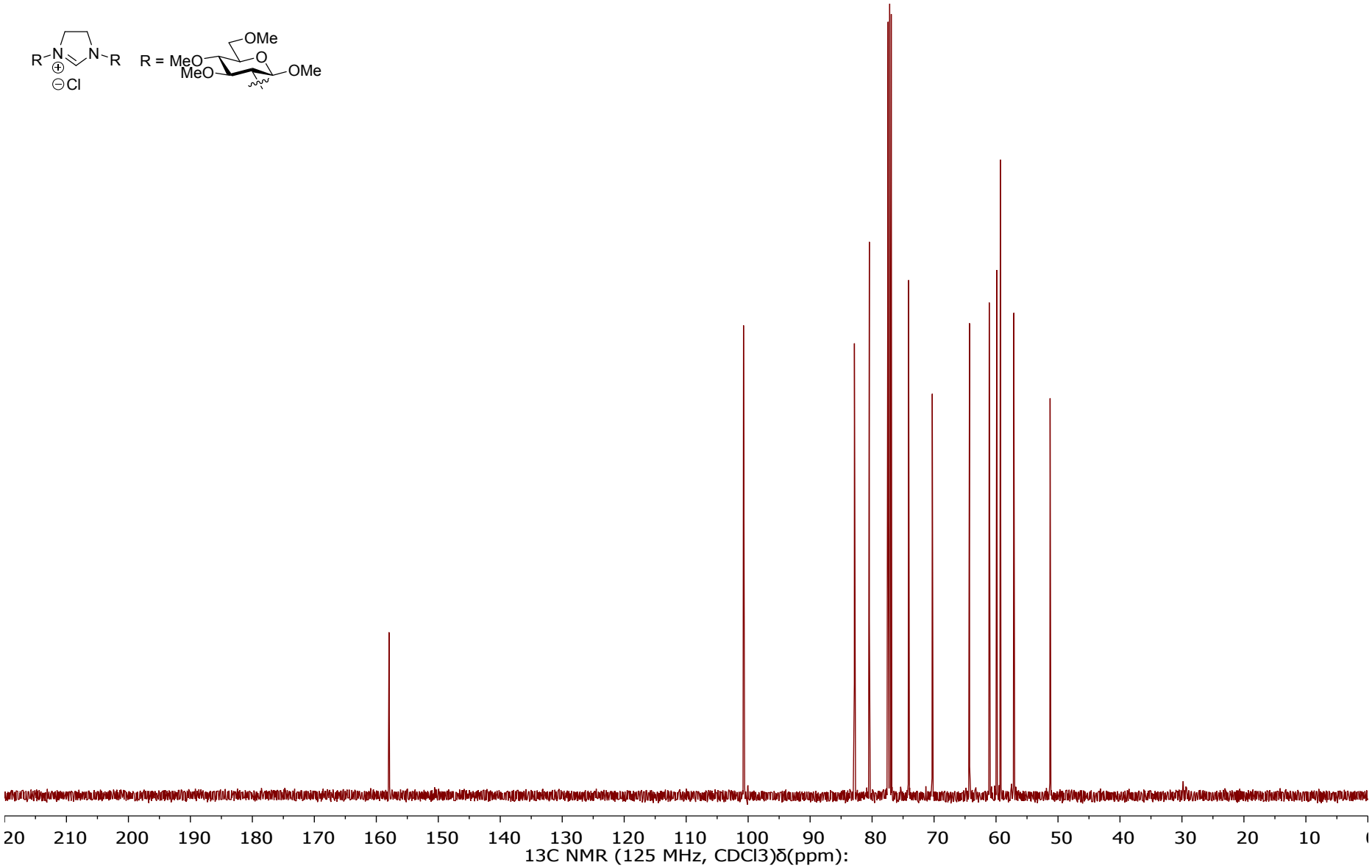

R
N
N
R
Cl
R =
O
O
O
O
O
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
1H NMR (500 MHz, C6D6, 70 °C) δ (ppm):

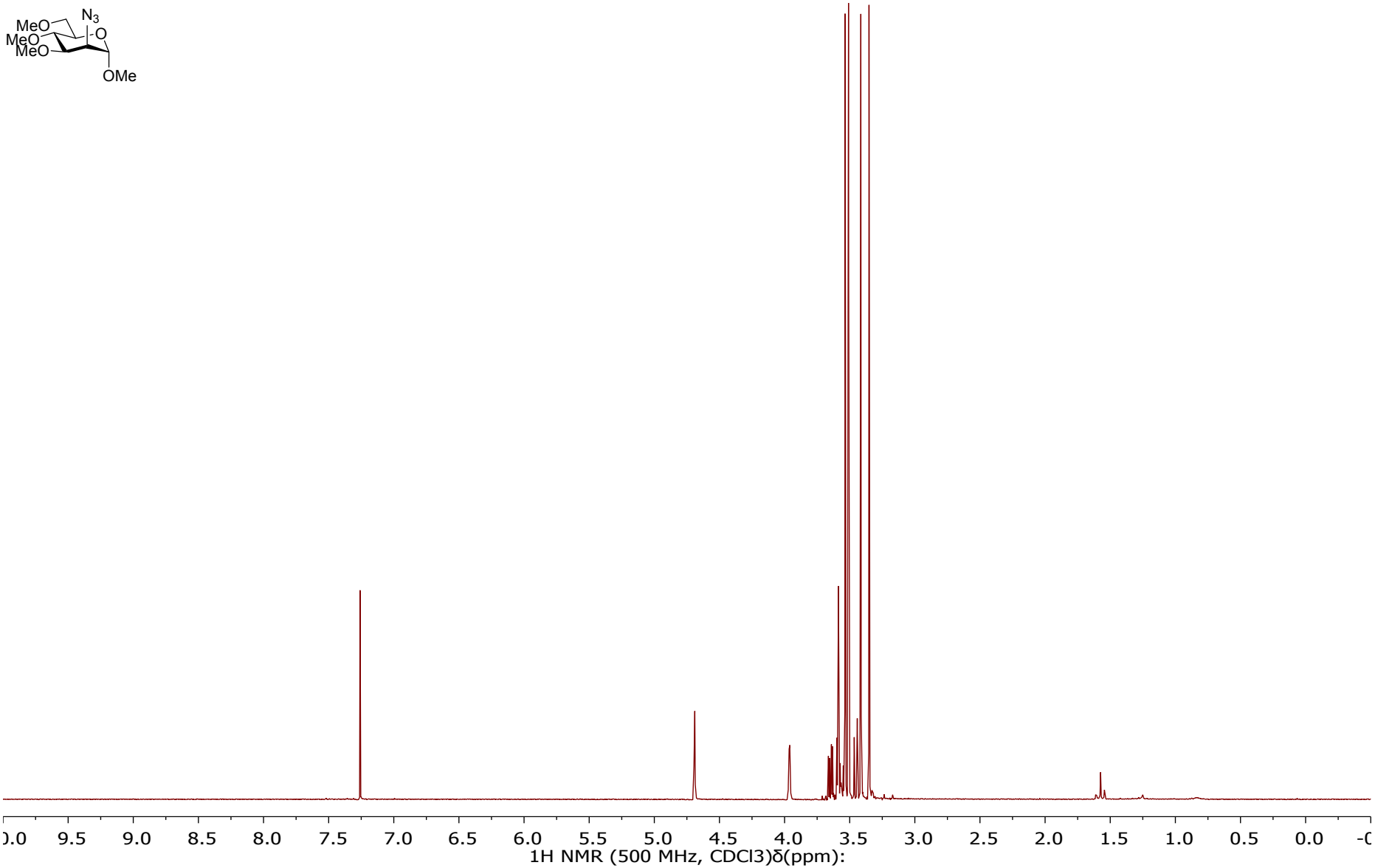

R
N
N
R
R =
Cl
O
O
O
O
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
13C NMR (125 MHz, (CD3)2SO)δ(ppm):

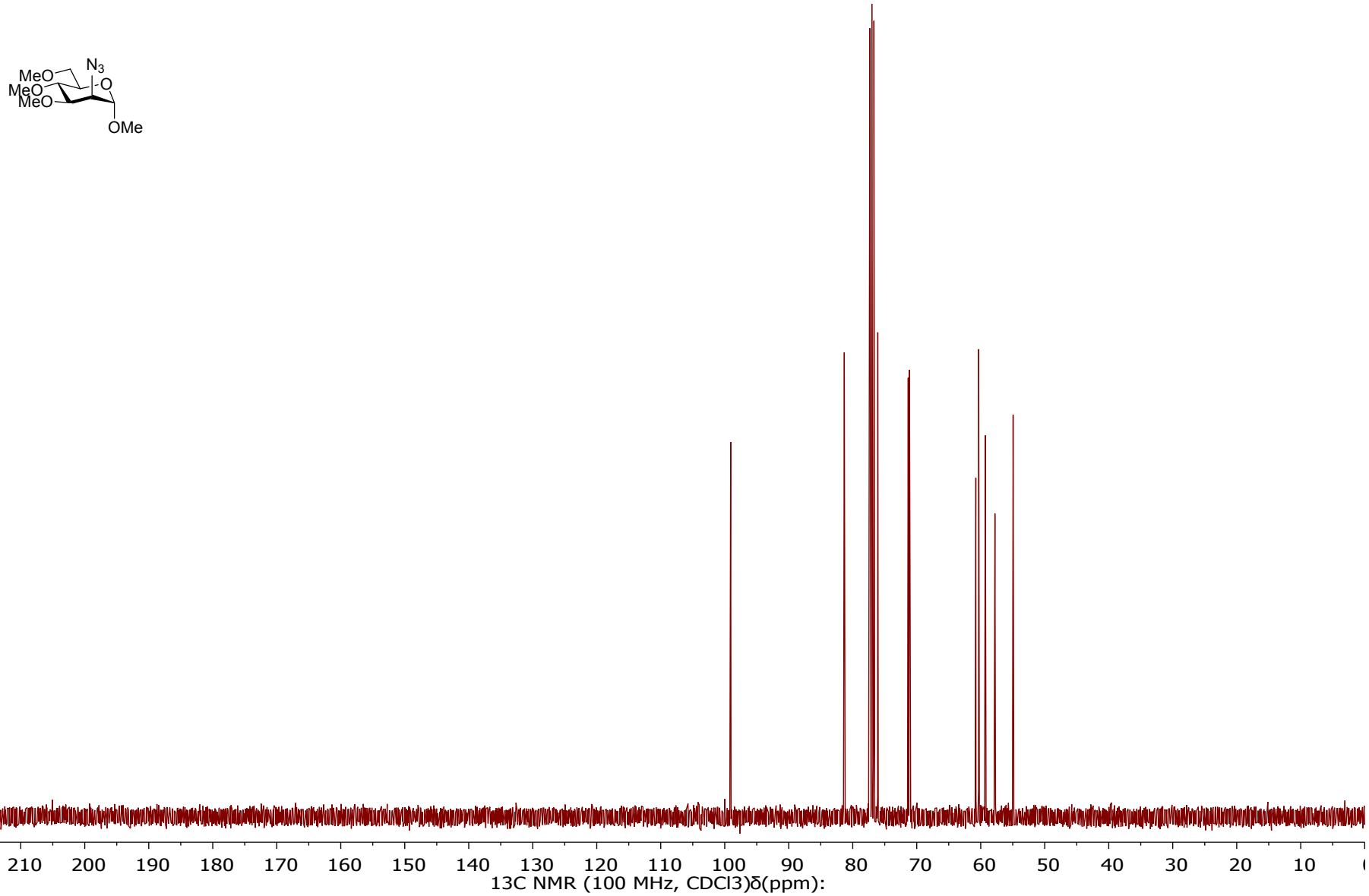

OMe
MeO
O
MeO
OMe
NH
HN
MeO
OMe
OMe
O
MeO
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (500 MHz, CDCl3)δ(ppm):

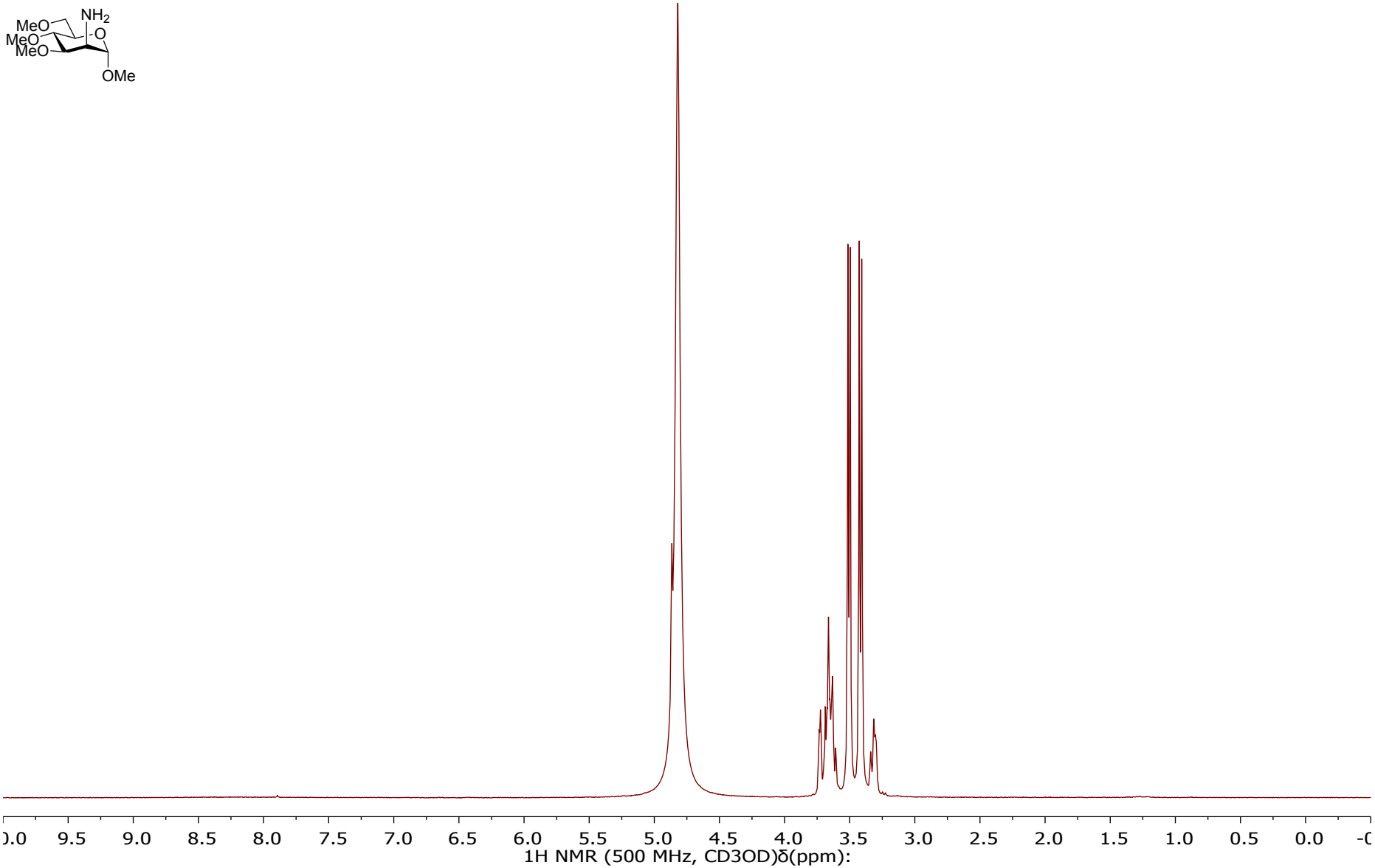

OMe
MeO
O
MeO
OMe
NH
HN
MeO
OMe
OMe
O
MeO
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
1H NMR (500 MHz, CDCl3)δ(ppm):

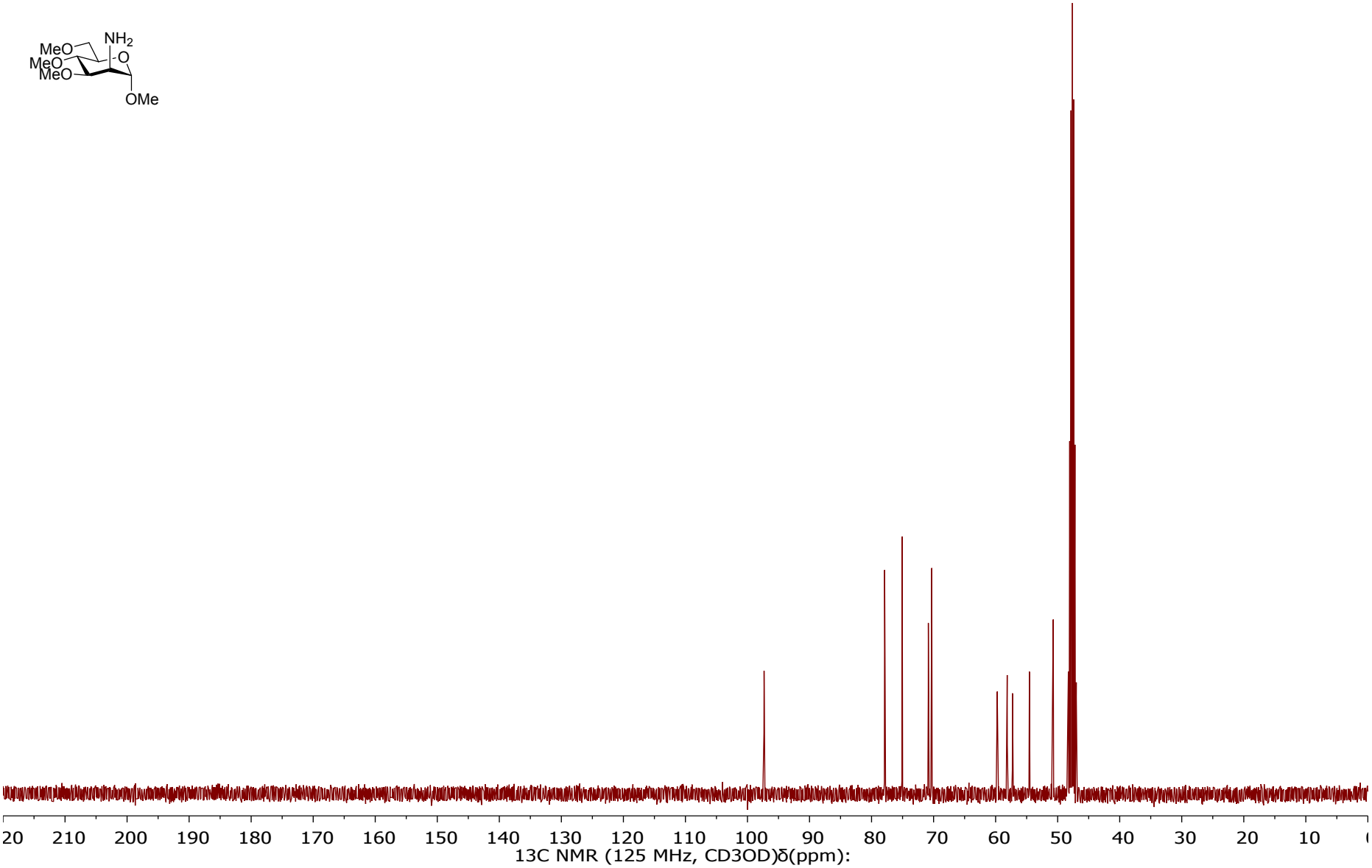

R = MeO
MeO
OMe
OMe
Cl
1H NMR (500 MHz, CDCl3)δ(ppm):

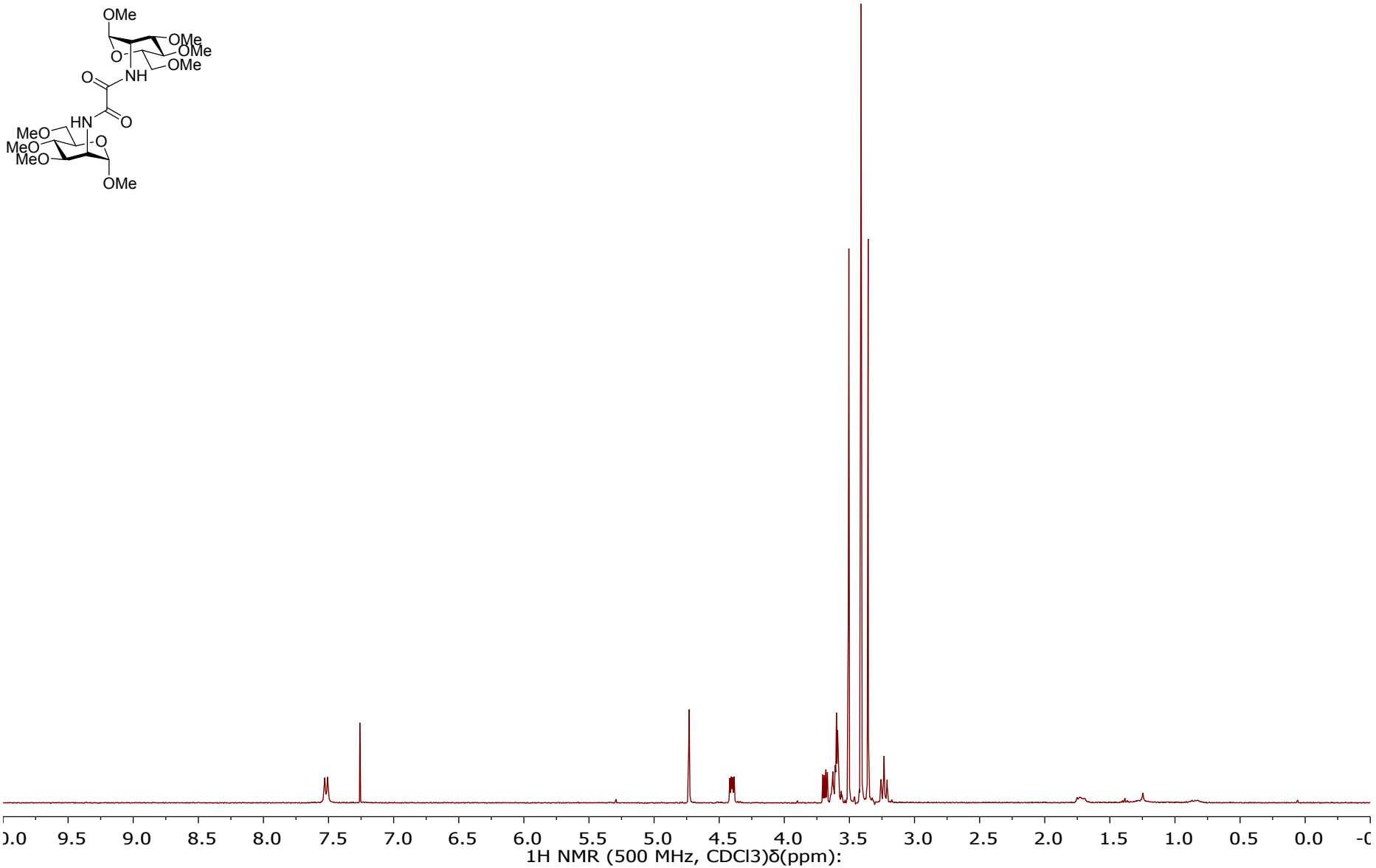

R = MeO
MeO
OMe
OMe
Cl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CDCl3)δ(ppm):

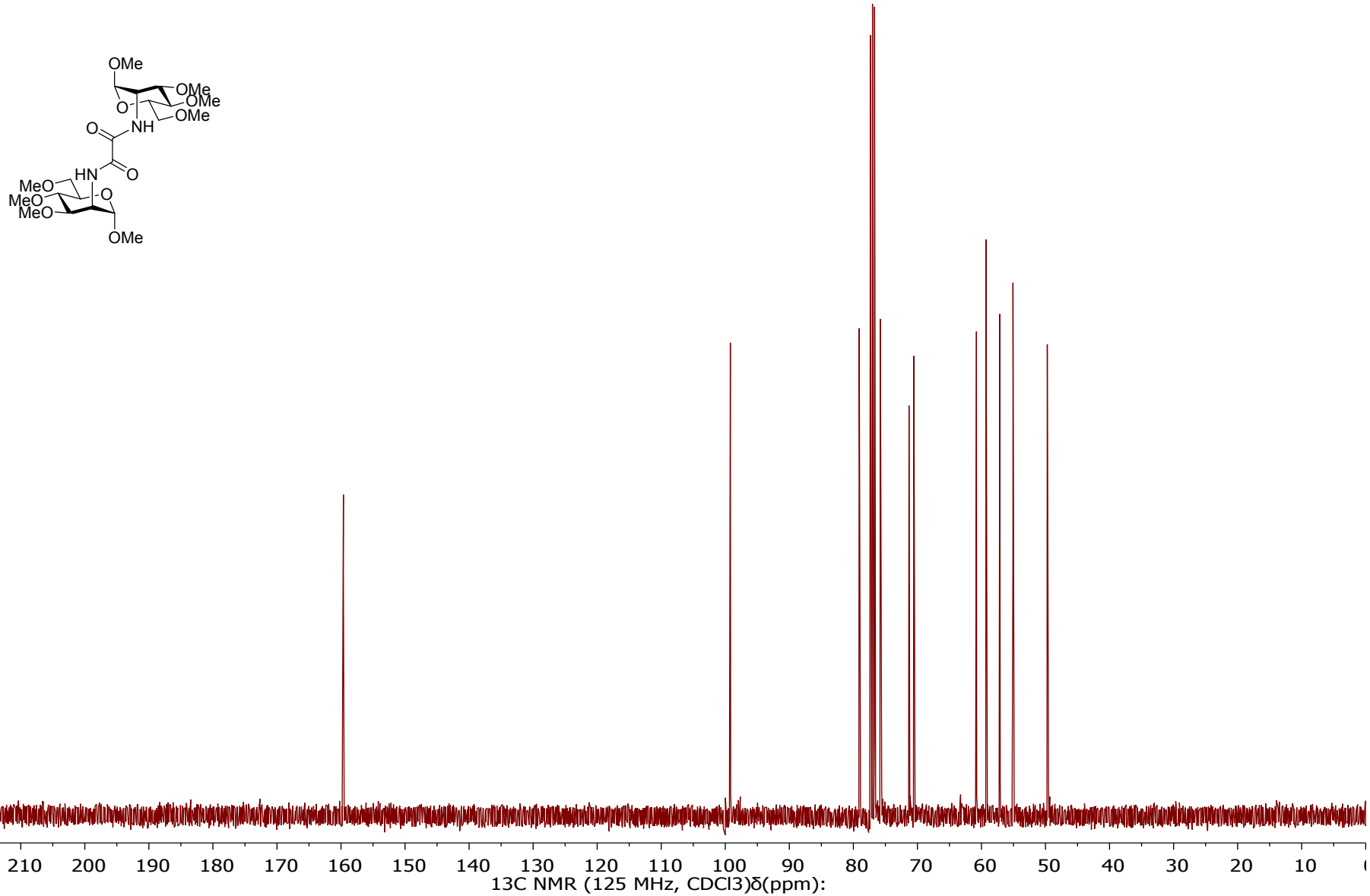

MeO
MeO
MeO
N3
O
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (500 MHz, CDCl3)δ(ppm):

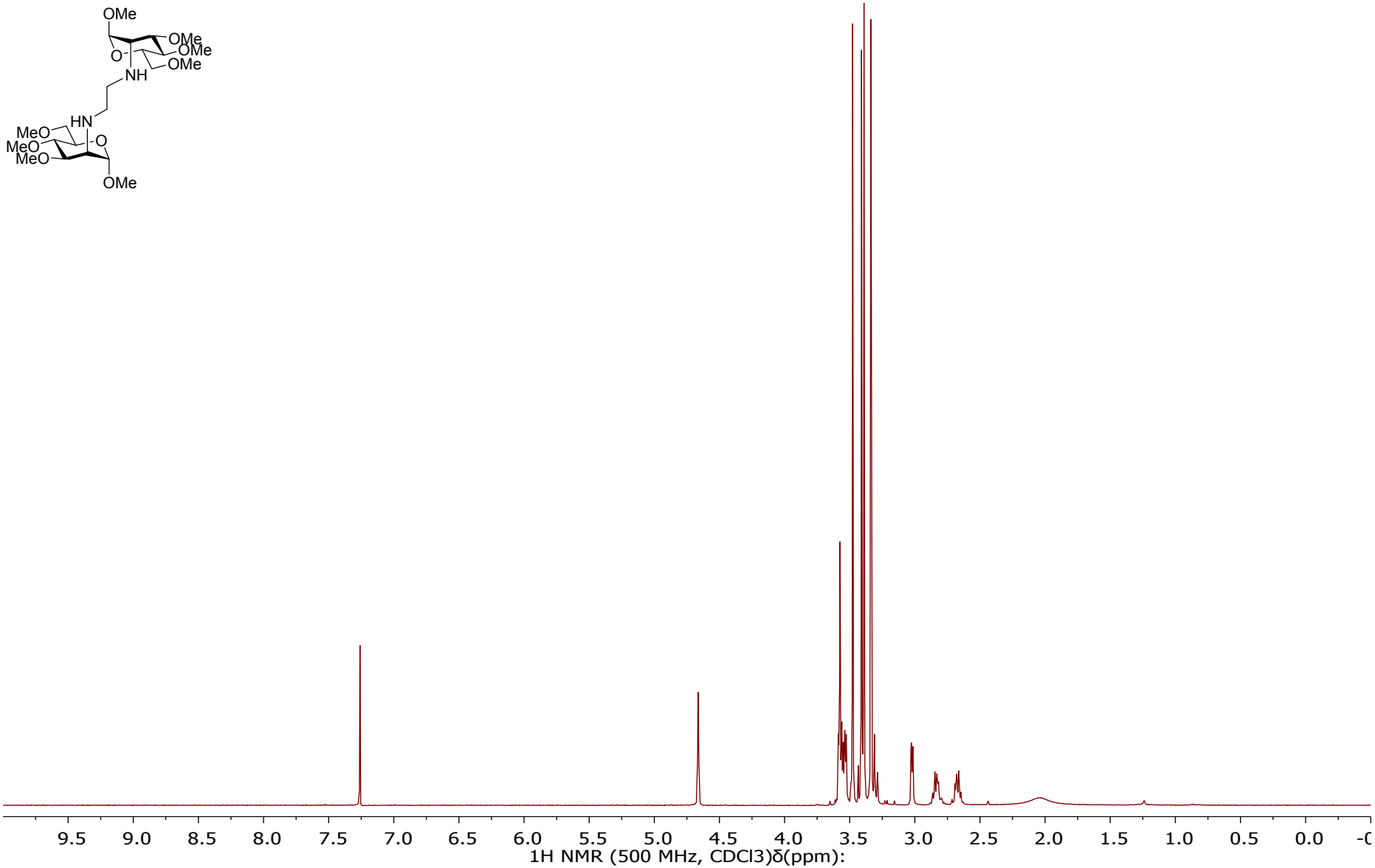

MeO
MeO
MeO
N3
O
OMe
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (100 MHz, CDCl3)δ(ppm):

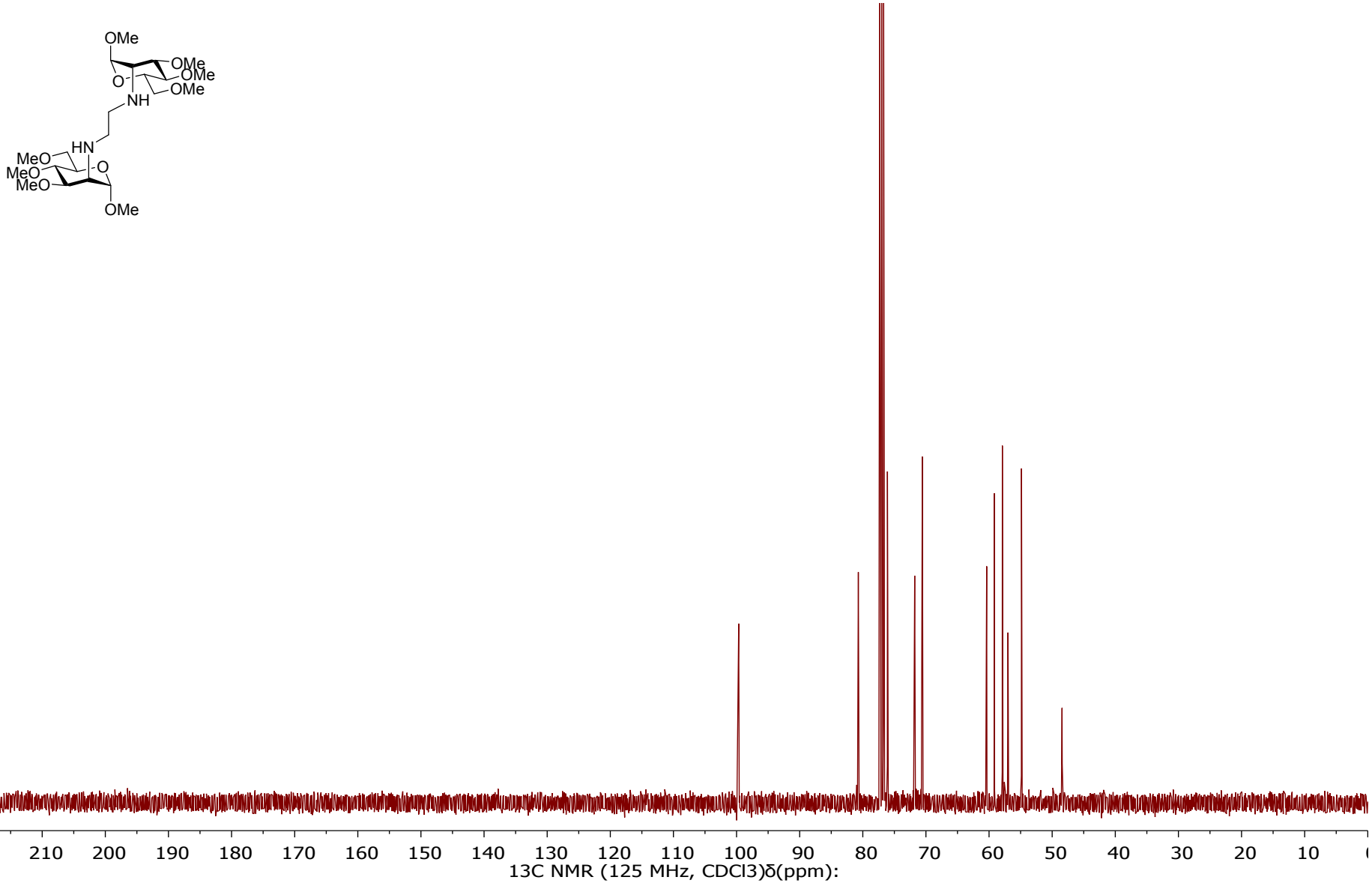

MeO
MeO
MeO
NH2
O
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (500 MHz, CD3OD)δ(ppm):

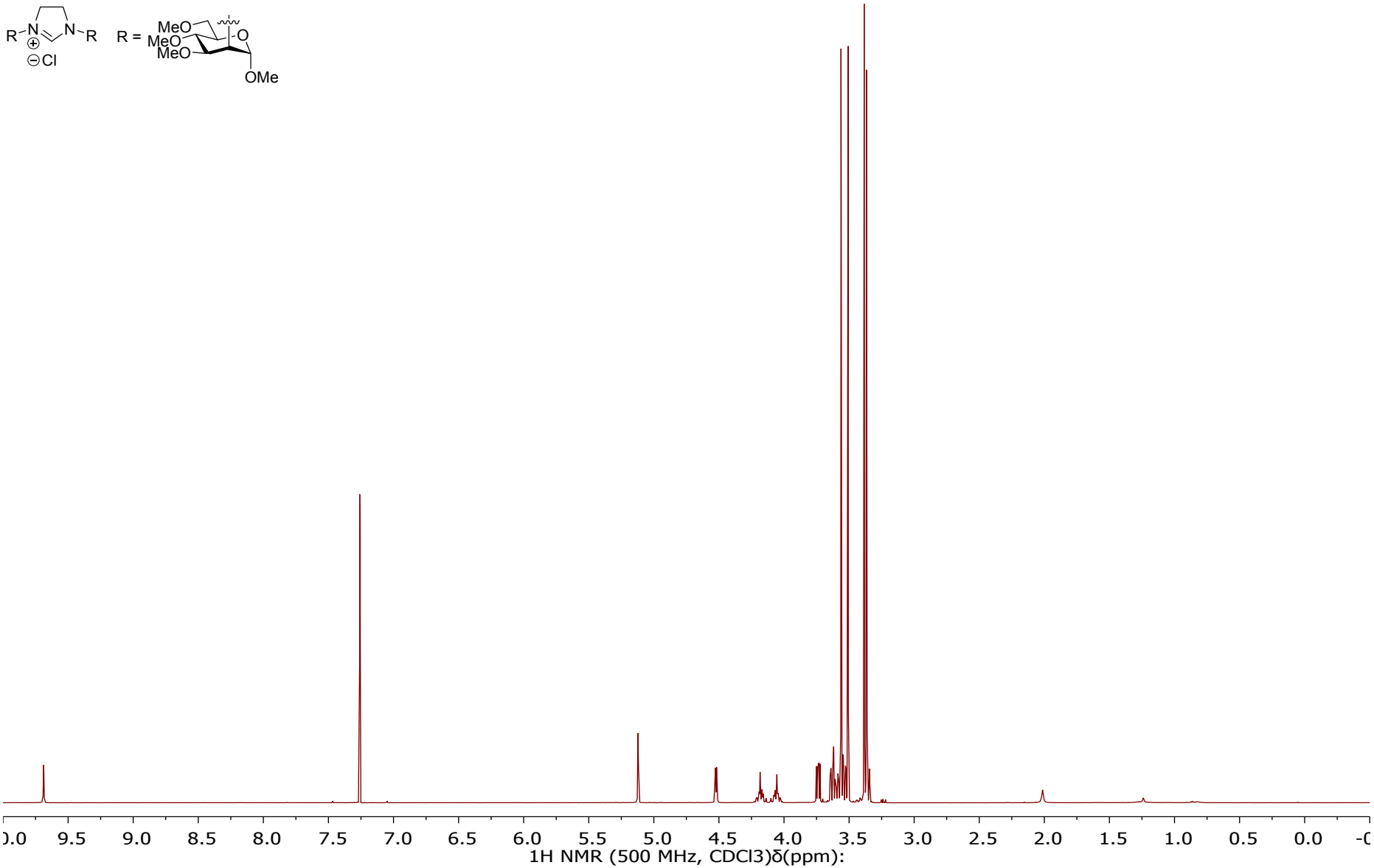

NH2
MeO
MeO
MeO
O
OMe
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CD3OD)δ(ppm):

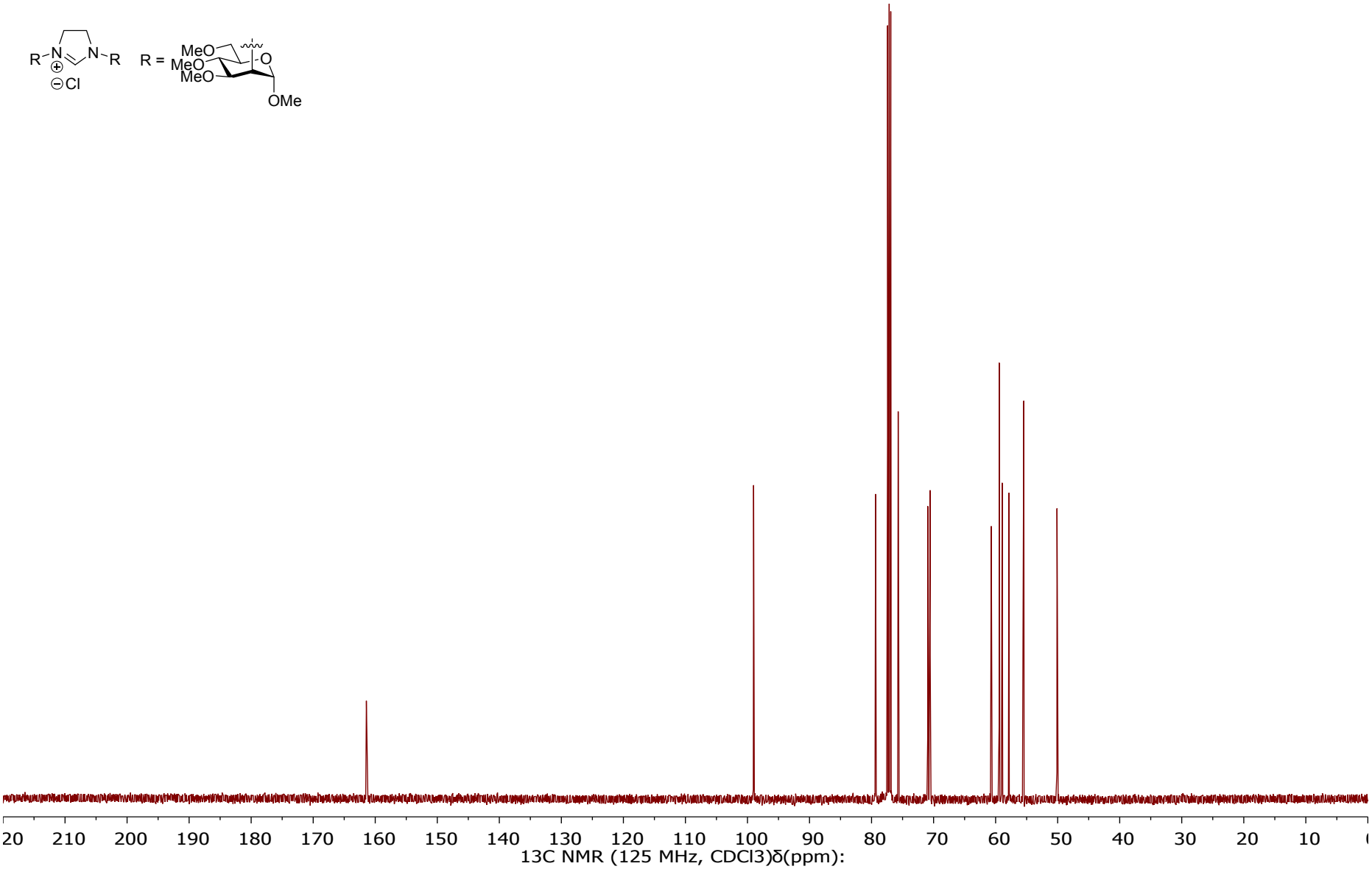

OMe
OMe
OMe
OMe
O
NH
O
HN
O
MeO
MeO
MeO
O
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (500 MHz, CDCl3)δ(ppm):

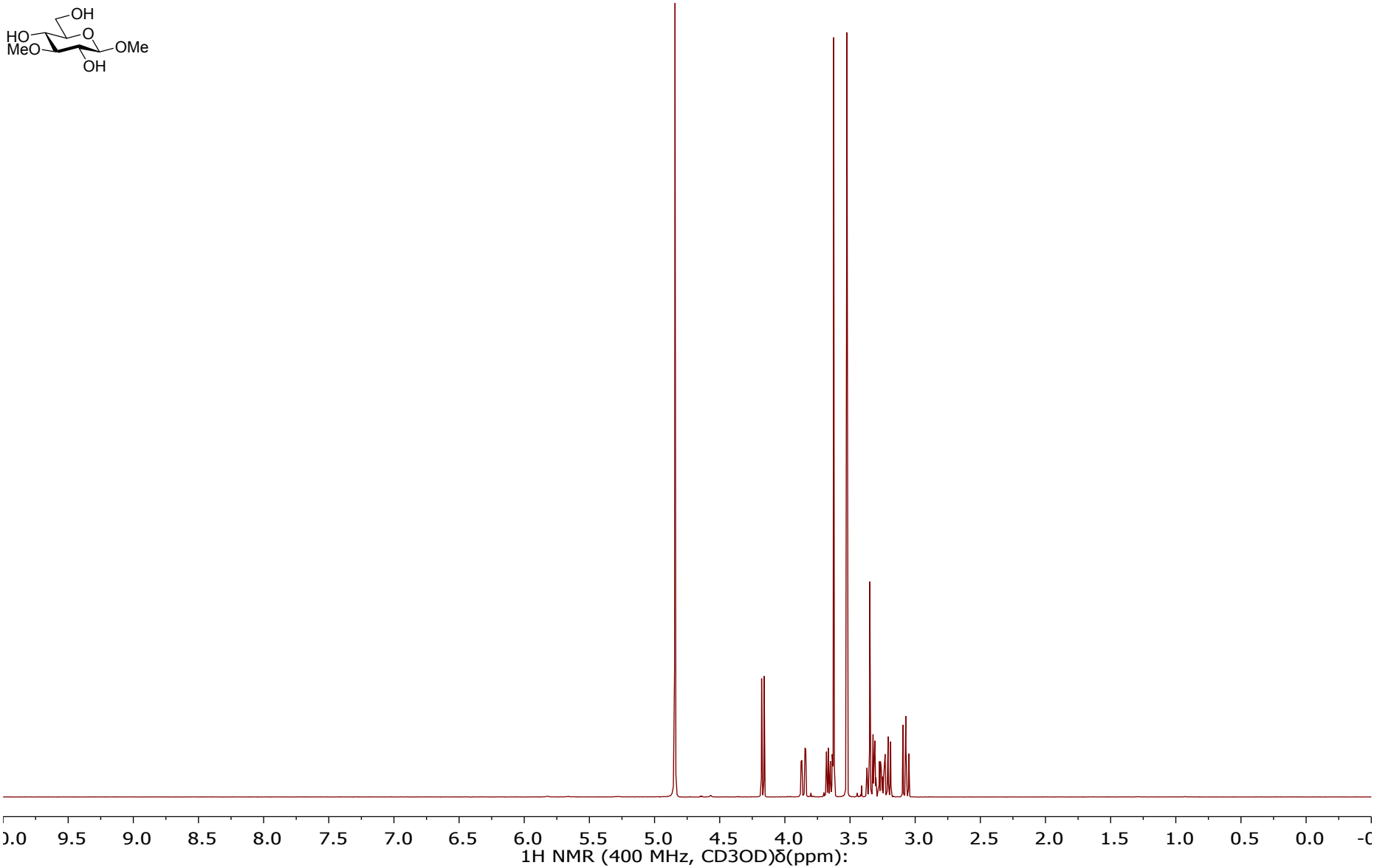

OMe
OMe
OMe
OMe
O
NH
O
HN
O
MeO
MeO
MeO
O
OMe
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CDCl3)δ(ppm):

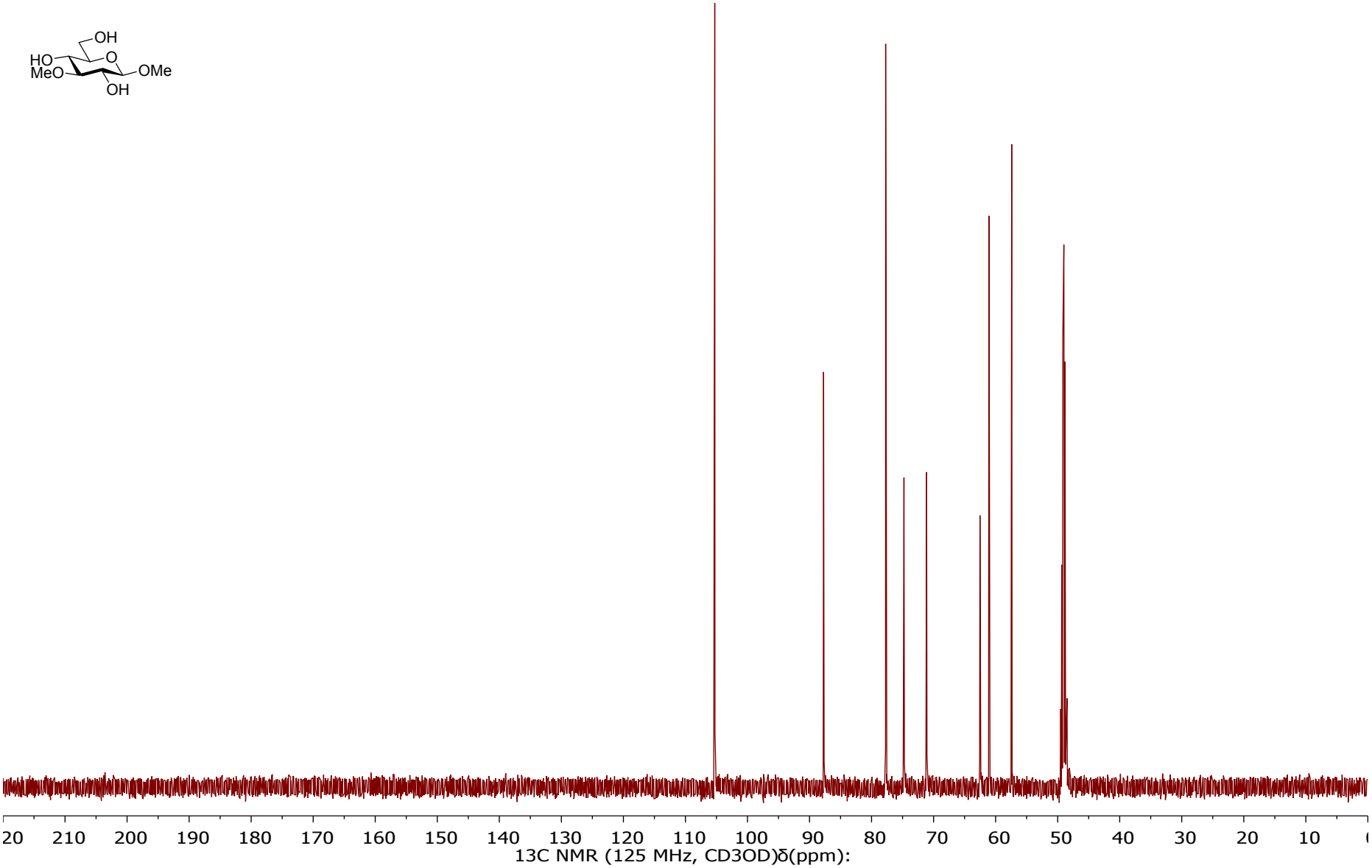

OMe
OMe
OMe
OMe
O
NH
HN
MeO
MeO
MeO
O
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (500 MHz, CDCl3)δ(ppm):

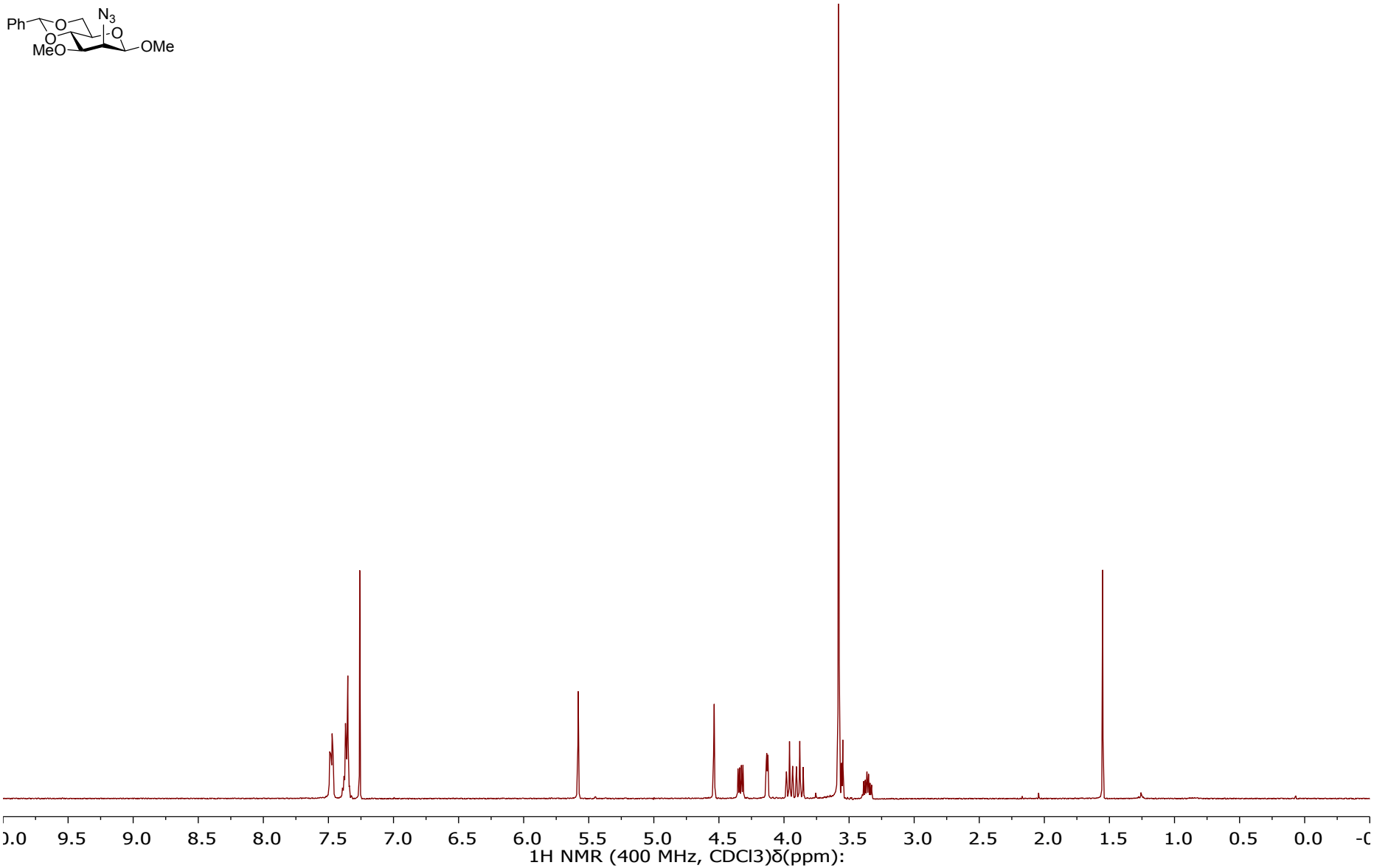

OMe
OMe
OMe
OMe
O
NH
HN
MeO
MeO
MeO
O
OMe
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CDCl3)δ(ppm):

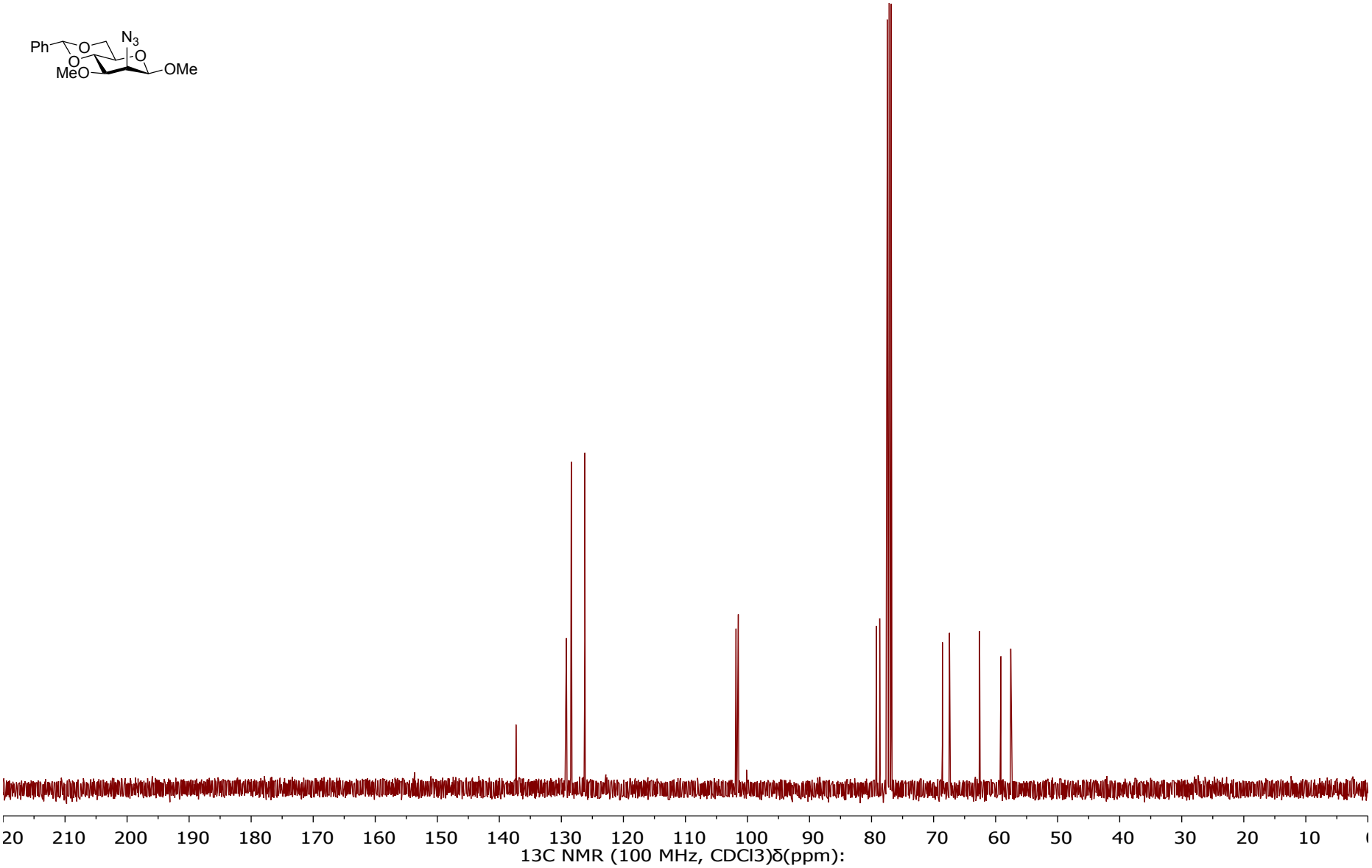

R
N
N
R
Cl
R =
MeO
MeO
MeO
O
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (500 MHz, CDCl3)δ(ppm):

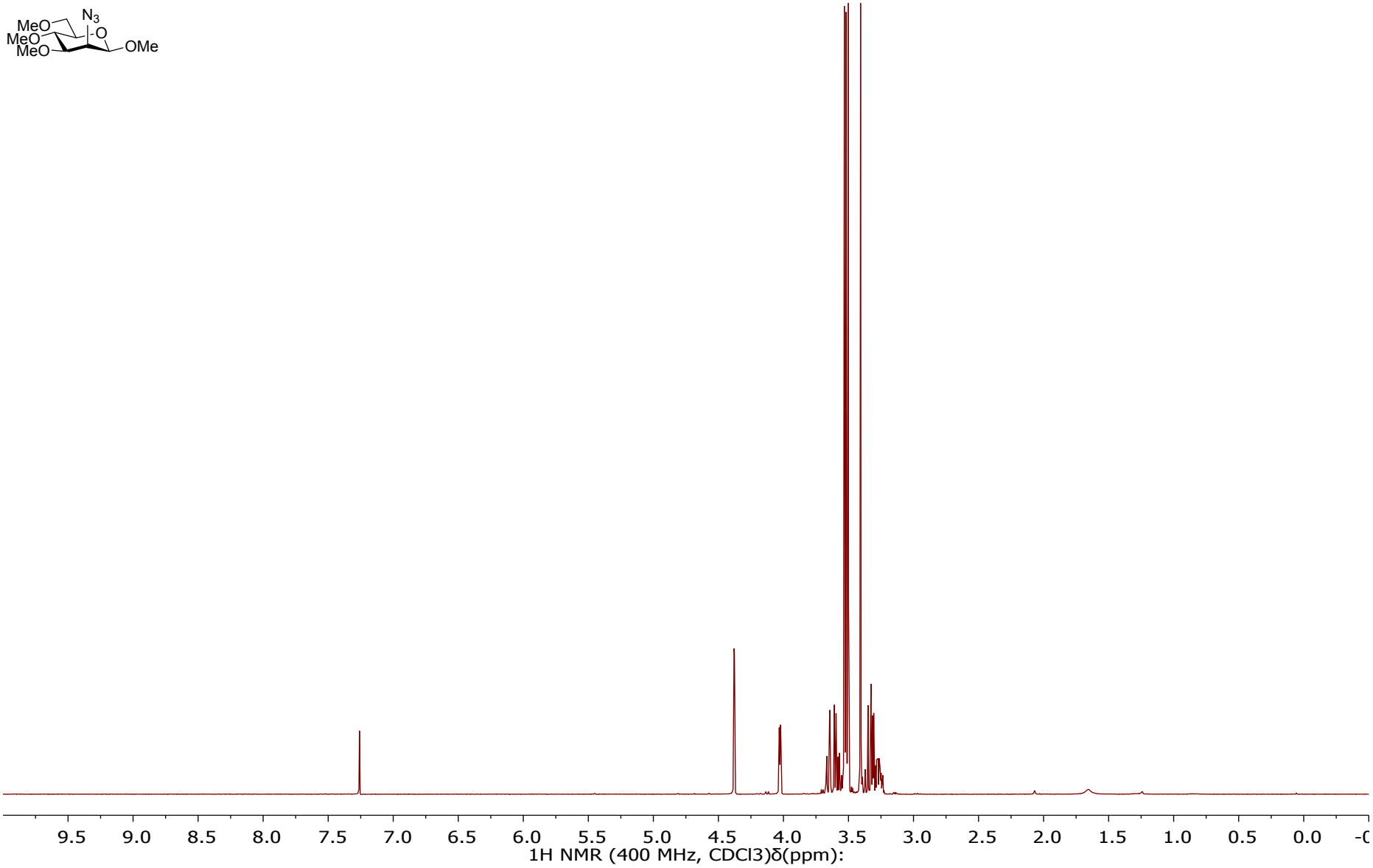

R
N
N
R
Cl
R =
MeO
MeO
MeO
O
OMe
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
13C NMR (125 MHz, CDCl3)δ(ppm):

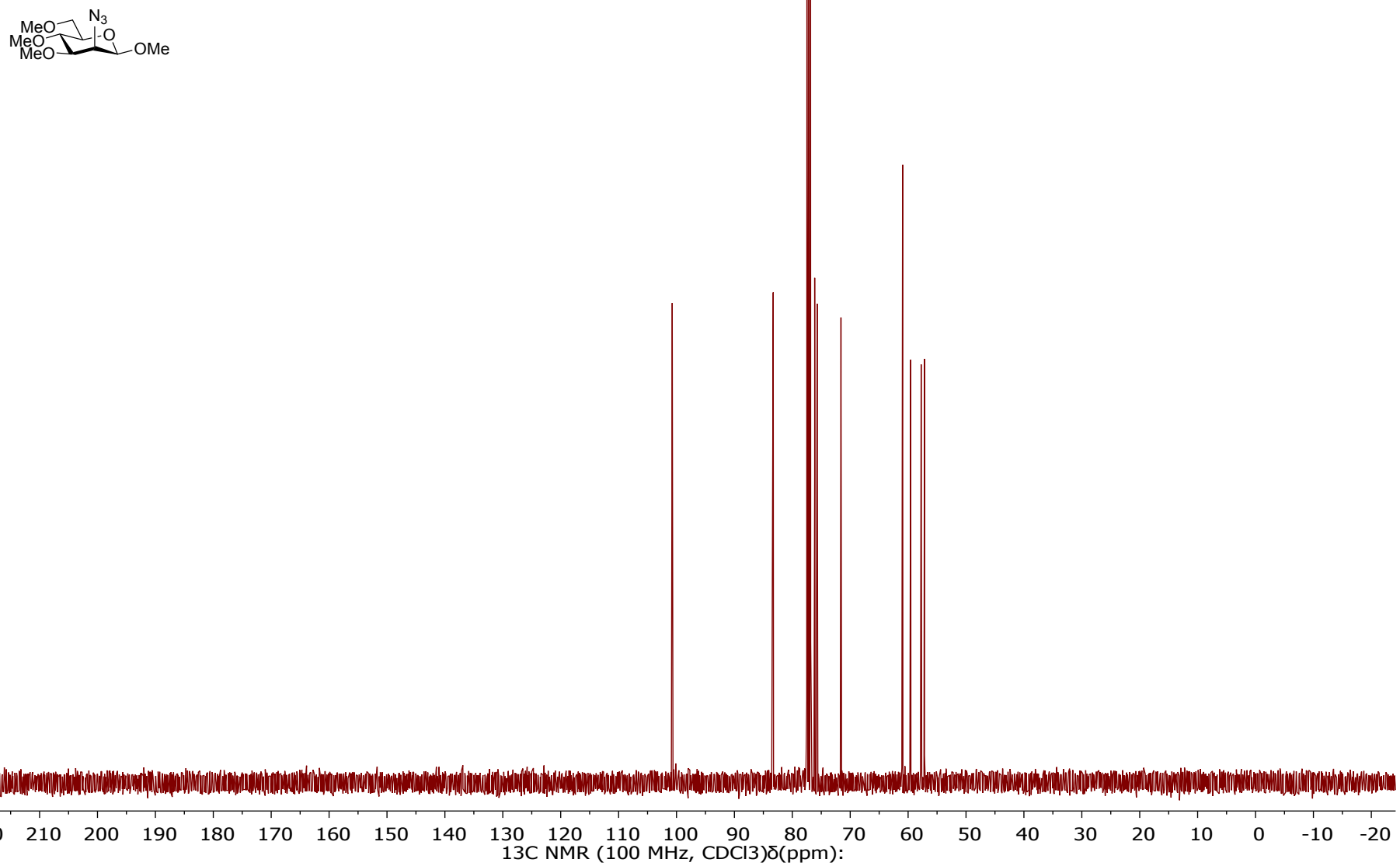

OH
HO
O
MeO
OMe
OH
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (400 MHz, CD3OD)δ(ppm):

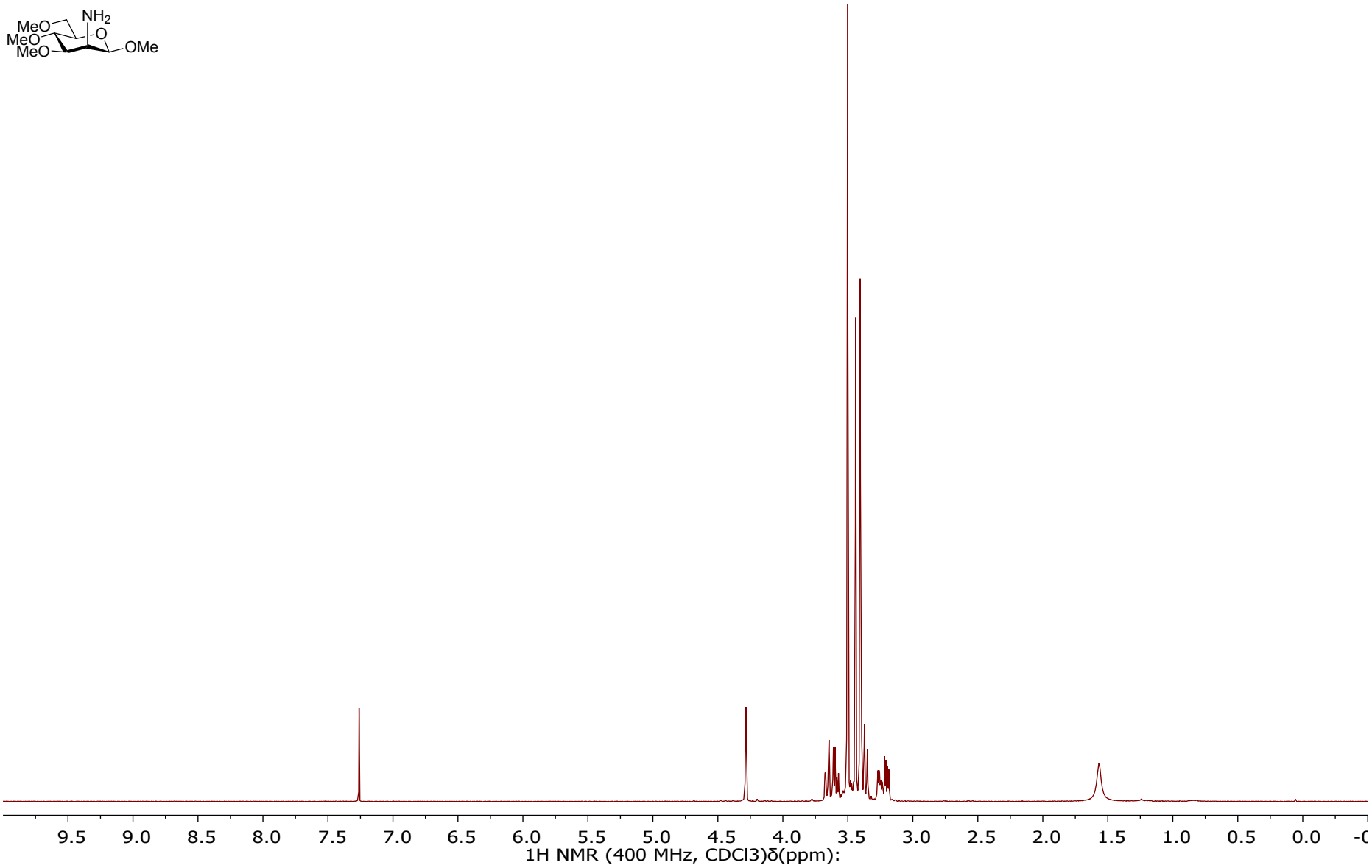

OH
HO
O
OMe
MeO
OH
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CD3OD)δ(ppm):

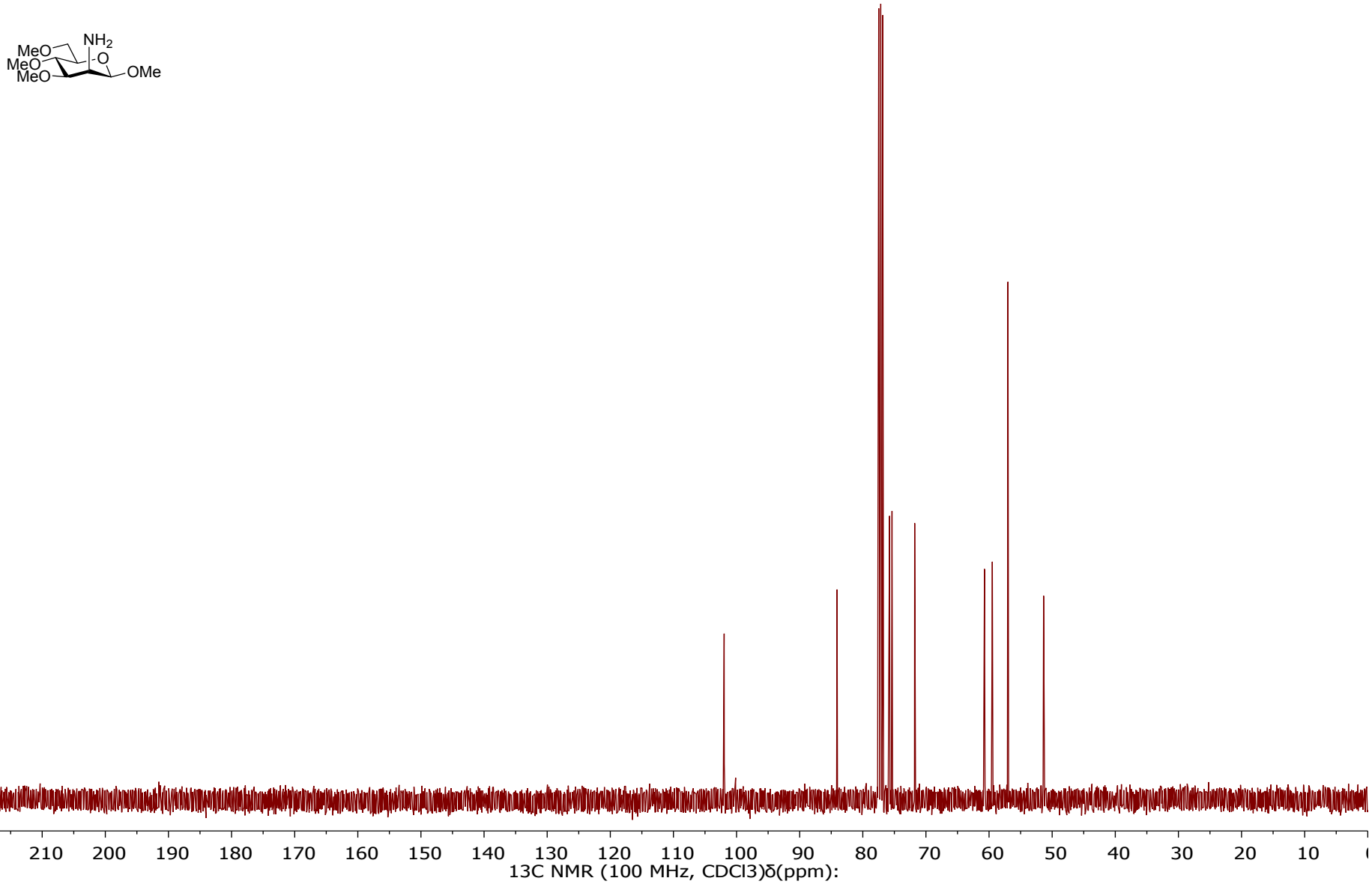

Ph
O
N3
O
O
MeO
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (400 MHz, CDCl3)δ(ppm):

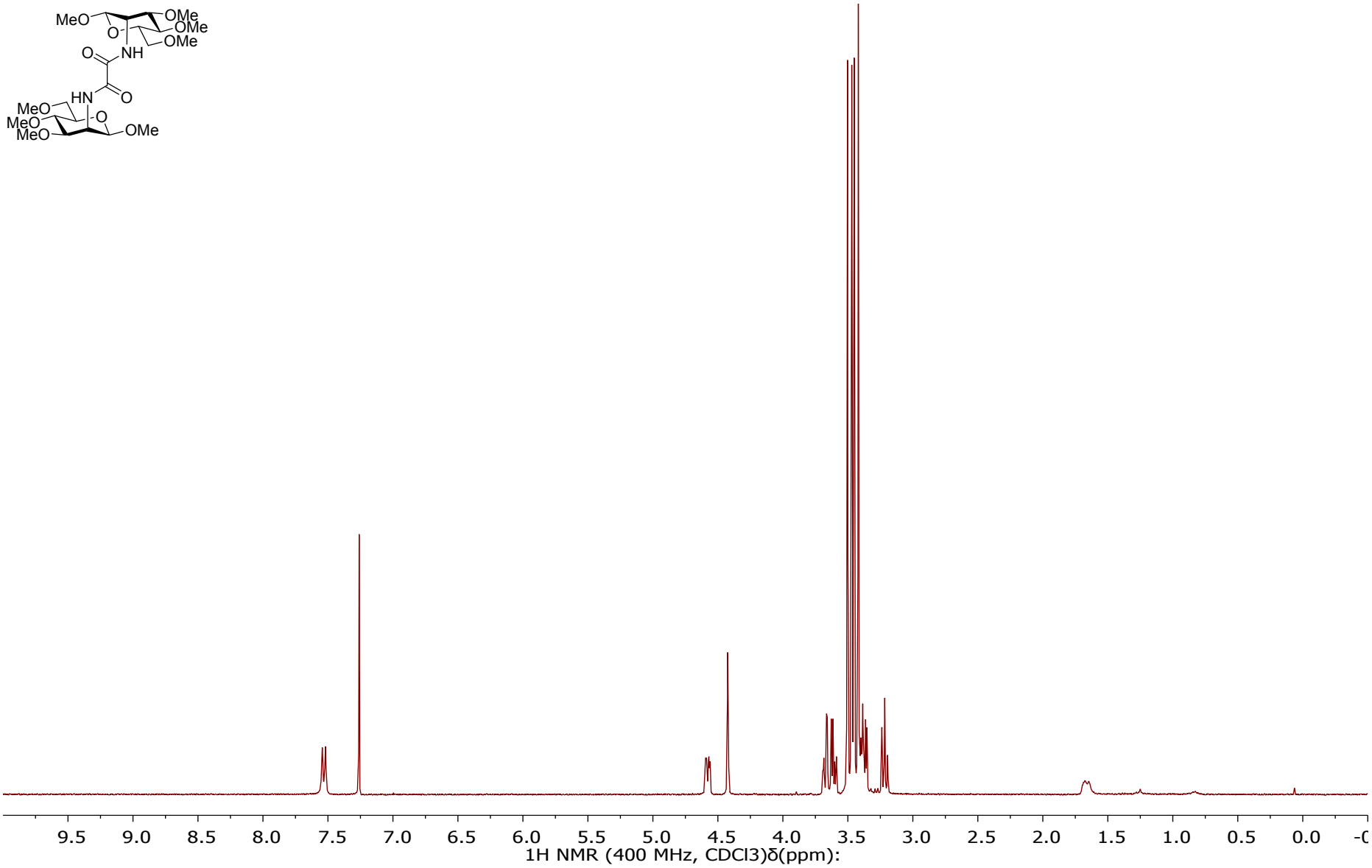

Ph
O
O
MeO
N3
O
OMe
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
13C NMR (100 MHz, CDCl3)δ(ppm):

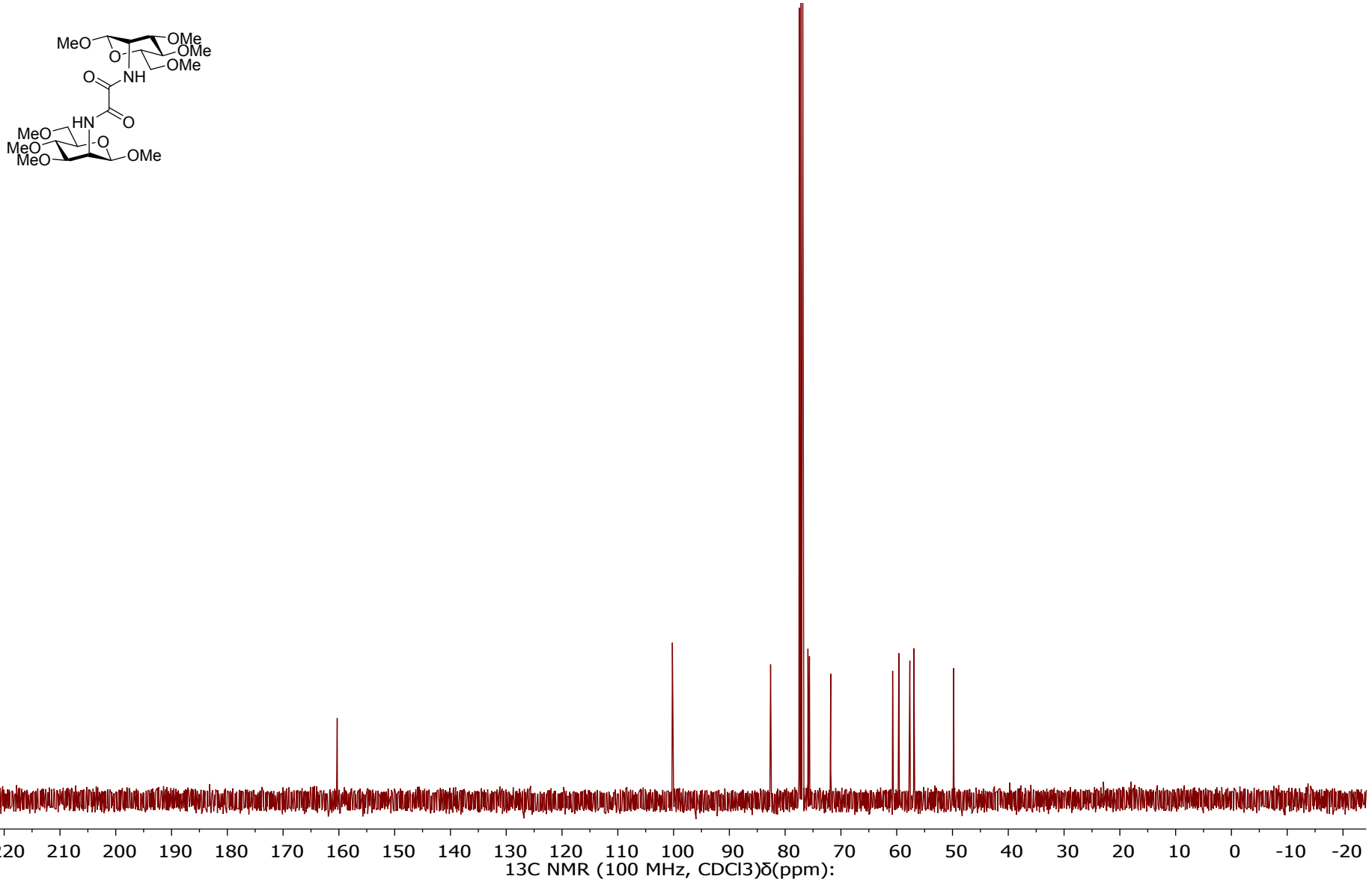

MeO
MeO
MeO
N3
O
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (400 MHz, CDCl3)δ(ppm):

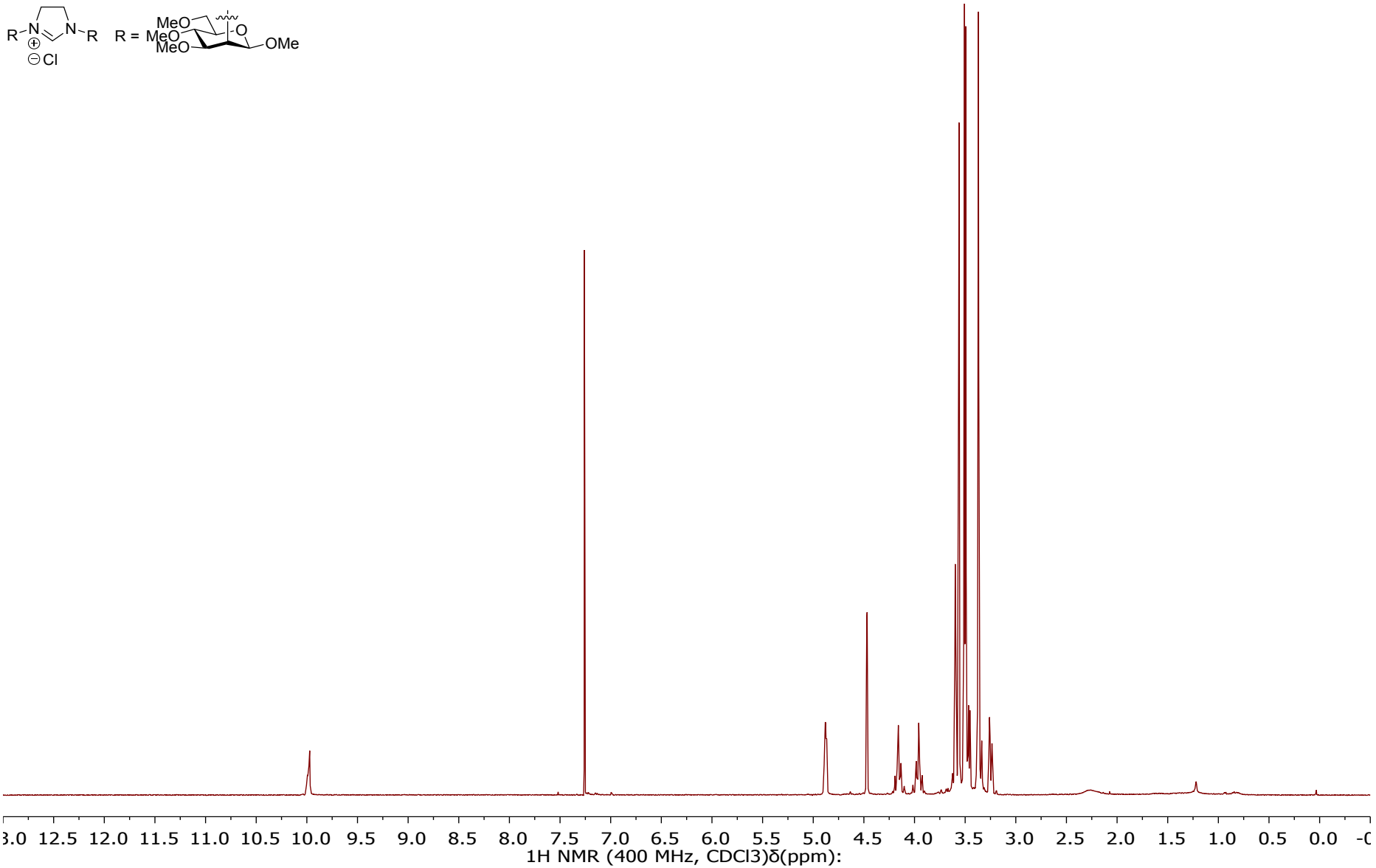

MeO
MeO
MeO
N3
O
OMe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
13C NMR (100 MHz, CDCl3)δ(ppm):

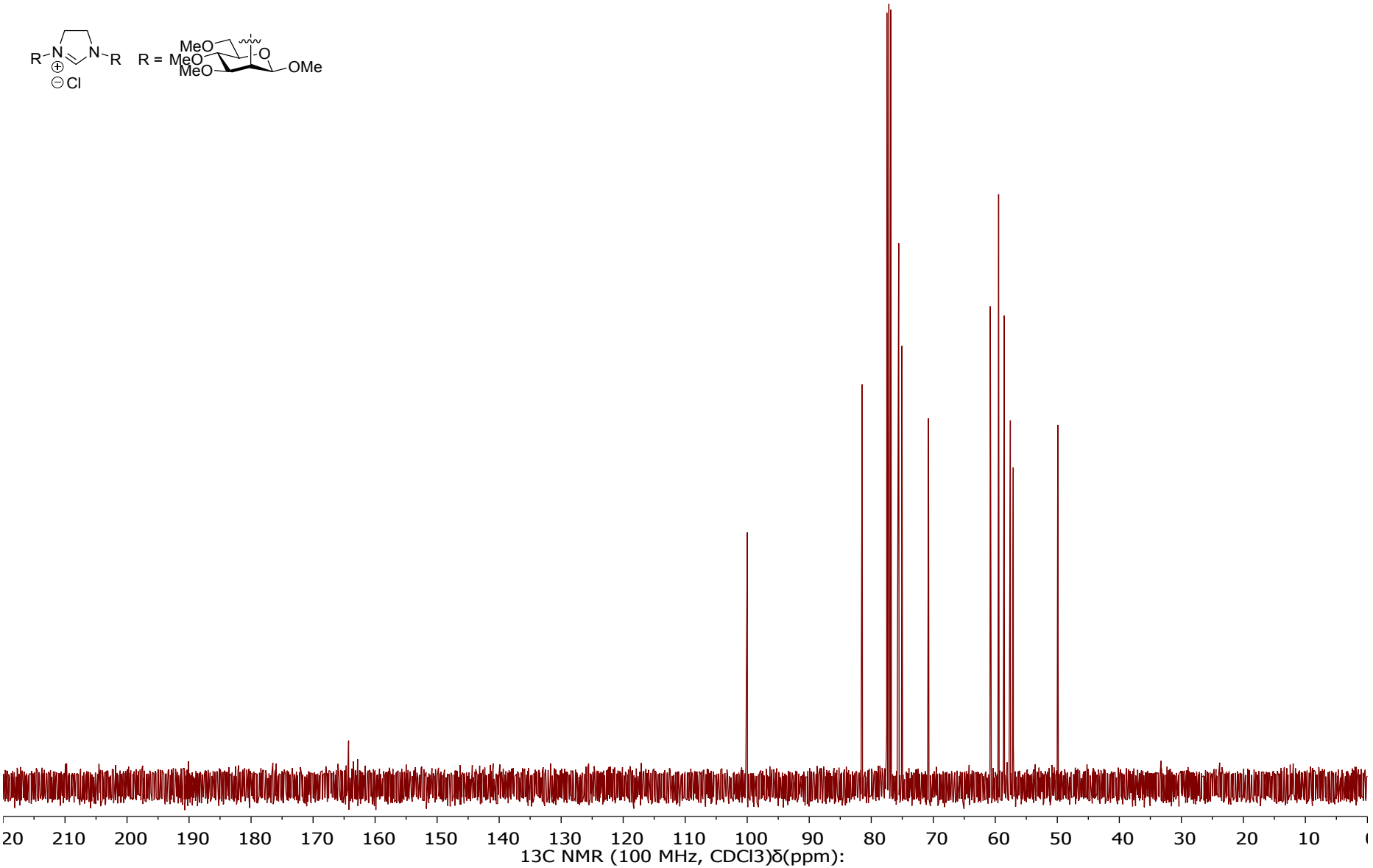

NH2
MeO
MeO
MeO
O
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (400 MHz, CDCl3)δ(ppm):

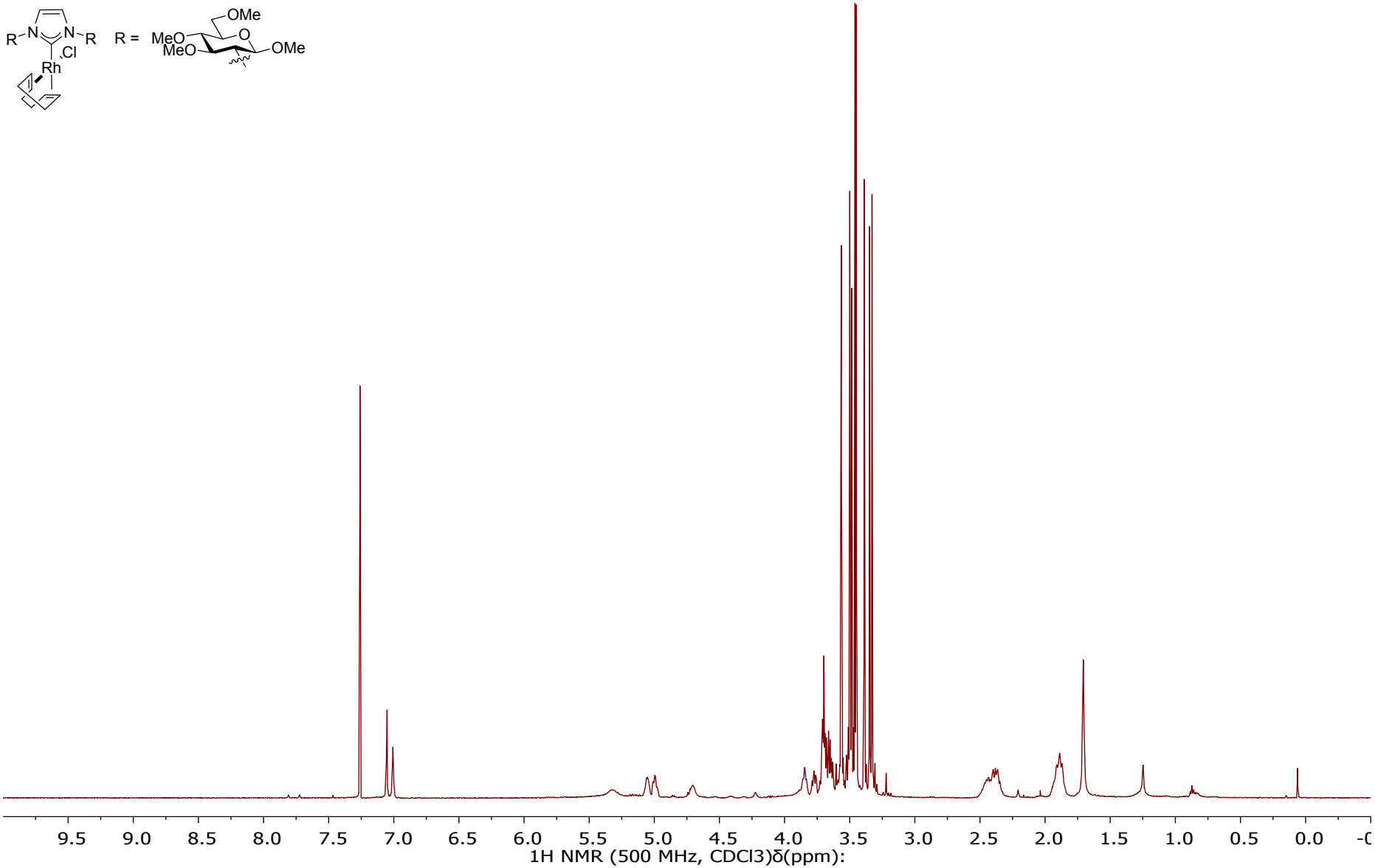

NH2
MeO
MeO
MeO
O
OMe
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (100 MHz, CDCl3)δ(ppm):

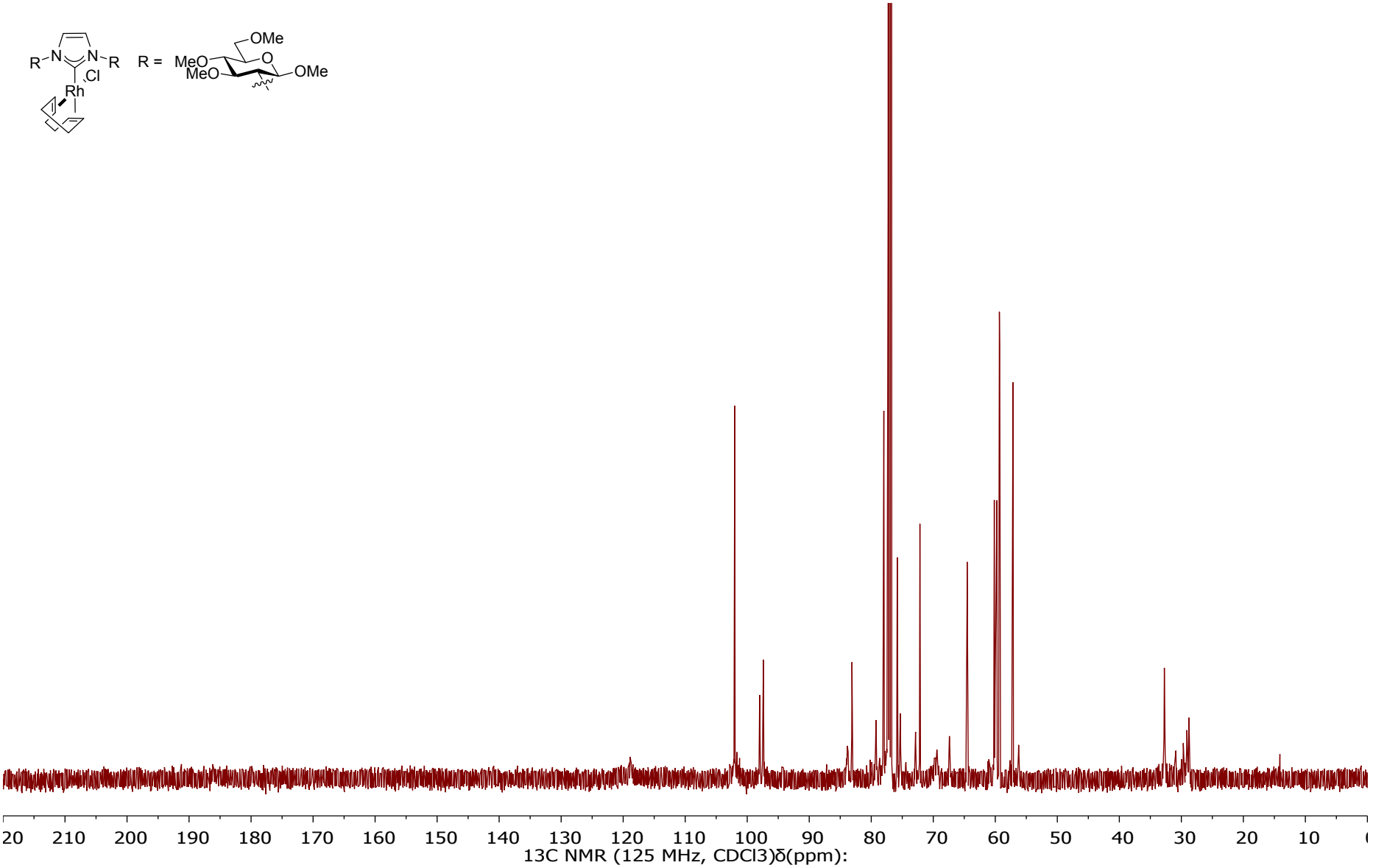

MeO
OMe
OMe
OMe
O
NH
O
HN
O
MeO
MeO
MeO
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (400 MHz, CDCl3)δ(ppm):

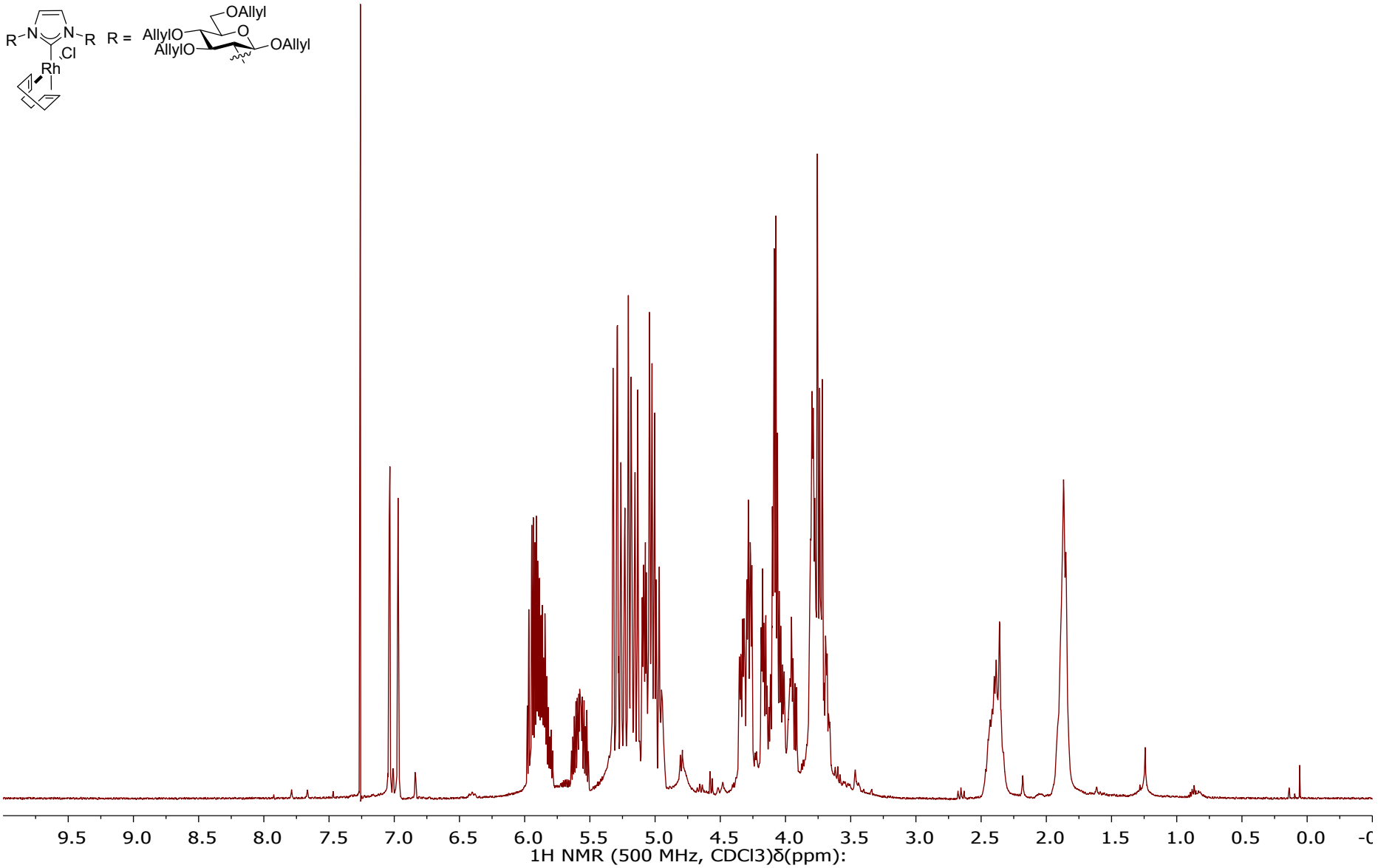

MeO
OMe
OMe
OMe
O
NH
O
HN
O
MeO
MeO
MeO
O
OMe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
13C NMR (100 MHz, CDCl3)δ(ppm):

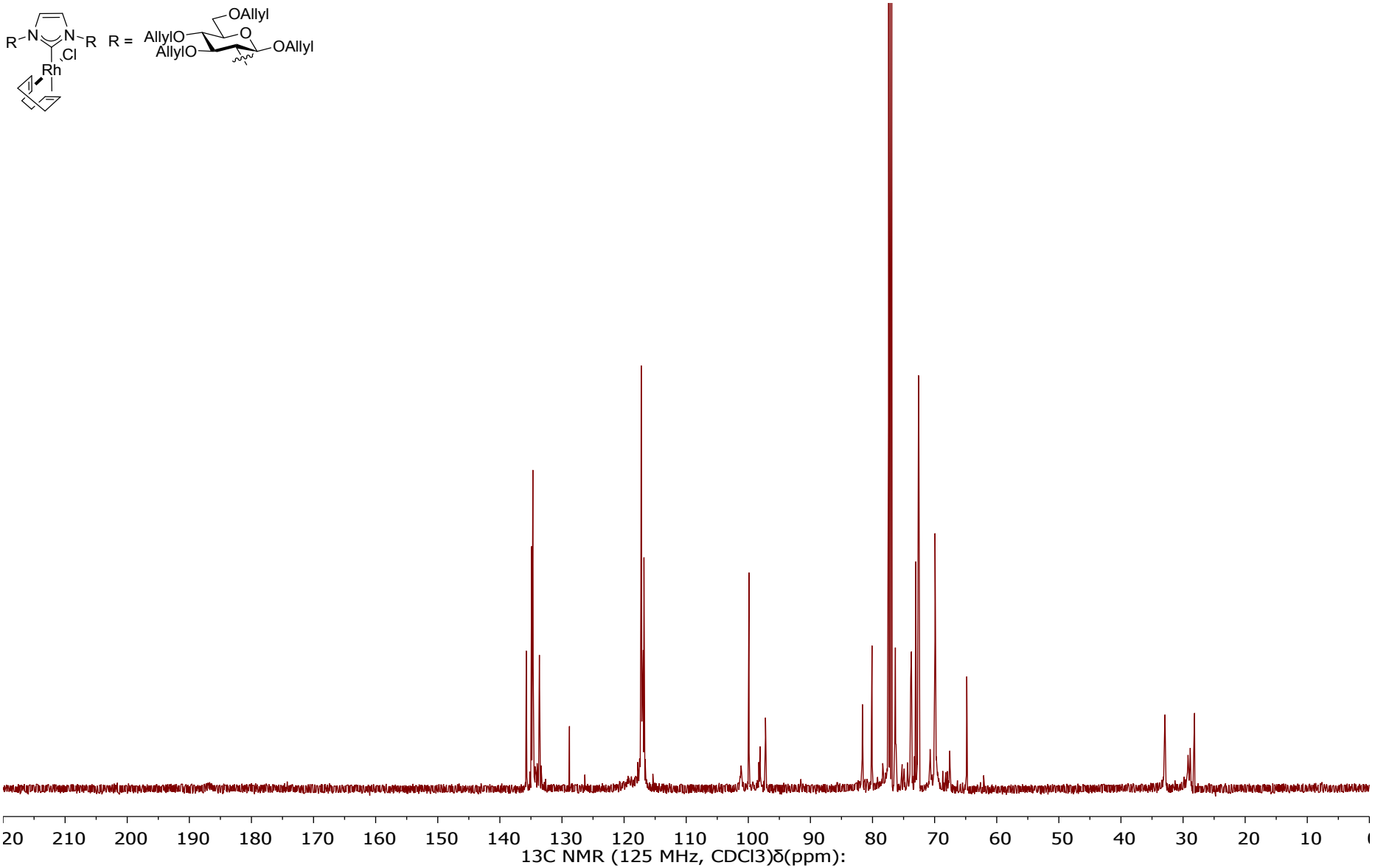

R = MeO MeO MeO OMe
Cl
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
1H NMR (400 MHz, CDCl3)δ(ppm):

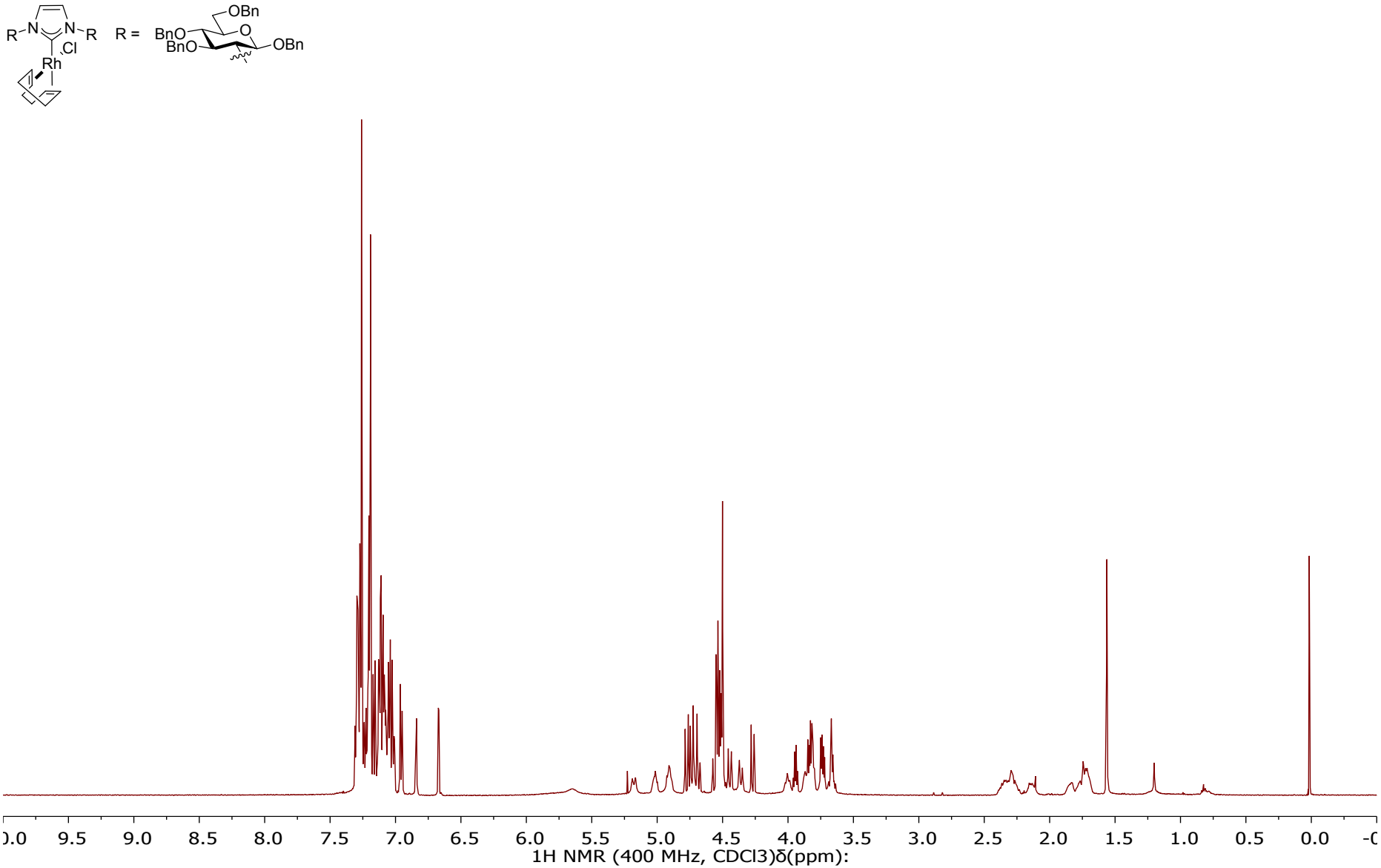

R = MeO MeO MeO OMe
Cl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (100 MHz, CDCl3)δ(ppm):

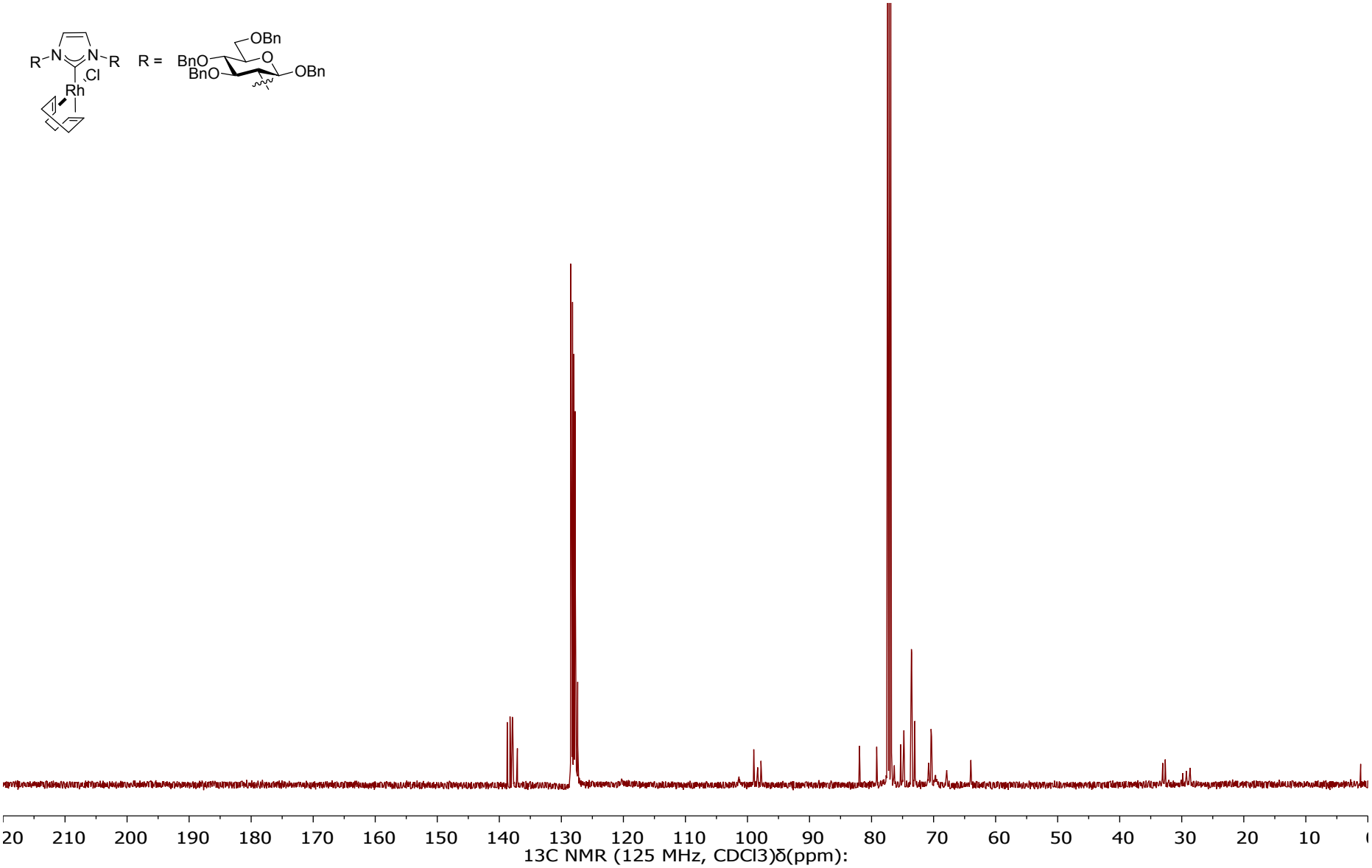

R
N
N
R
Cl
Rh
R =
OMe
MeO
O
MeO
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (500 MHz, CDCl3)δ(ppm):

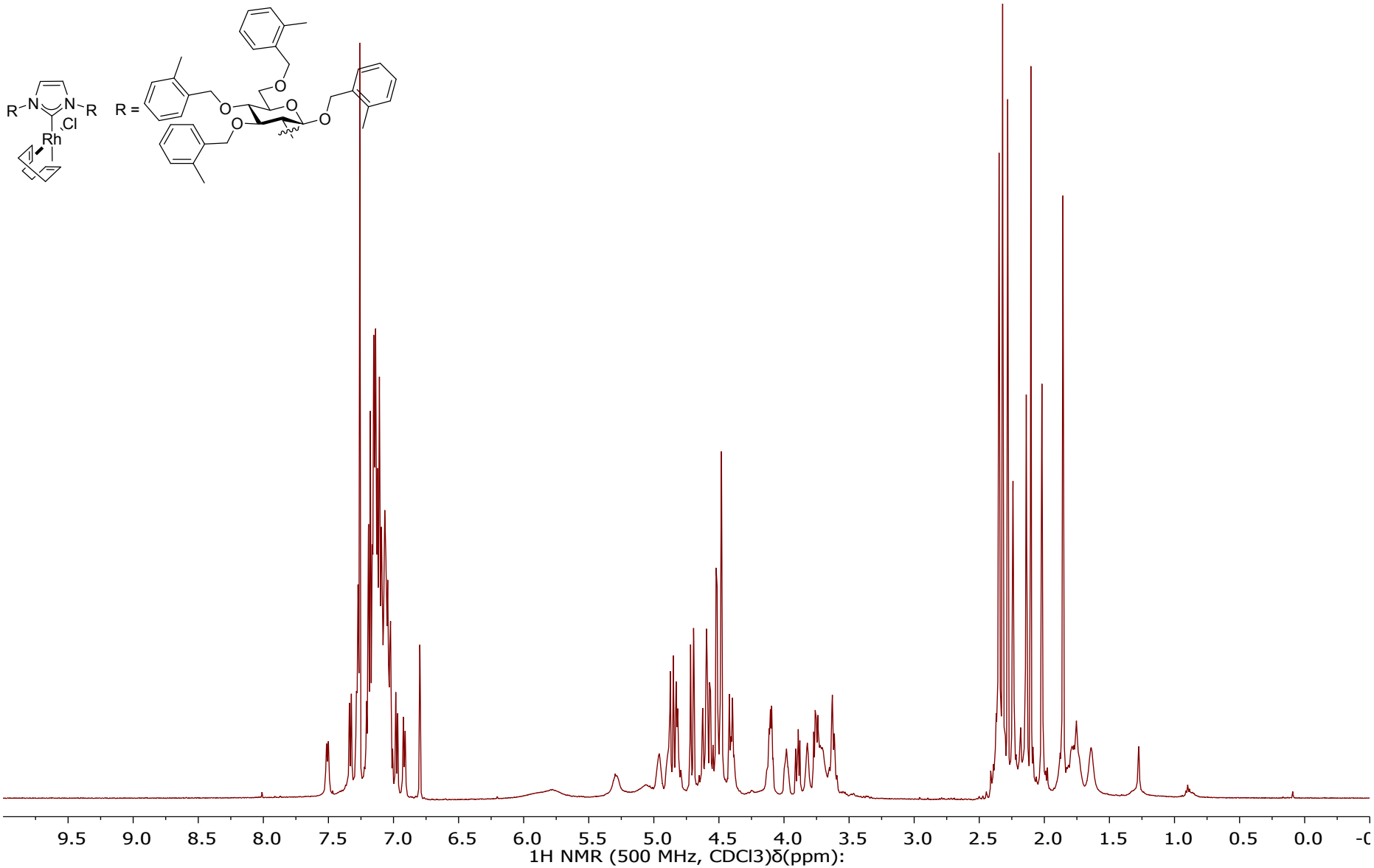

R
N
N
R
Cl
Rh
R =
OMe
O
MeO
MeO
OMe
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CDCl3)δ(ppm):

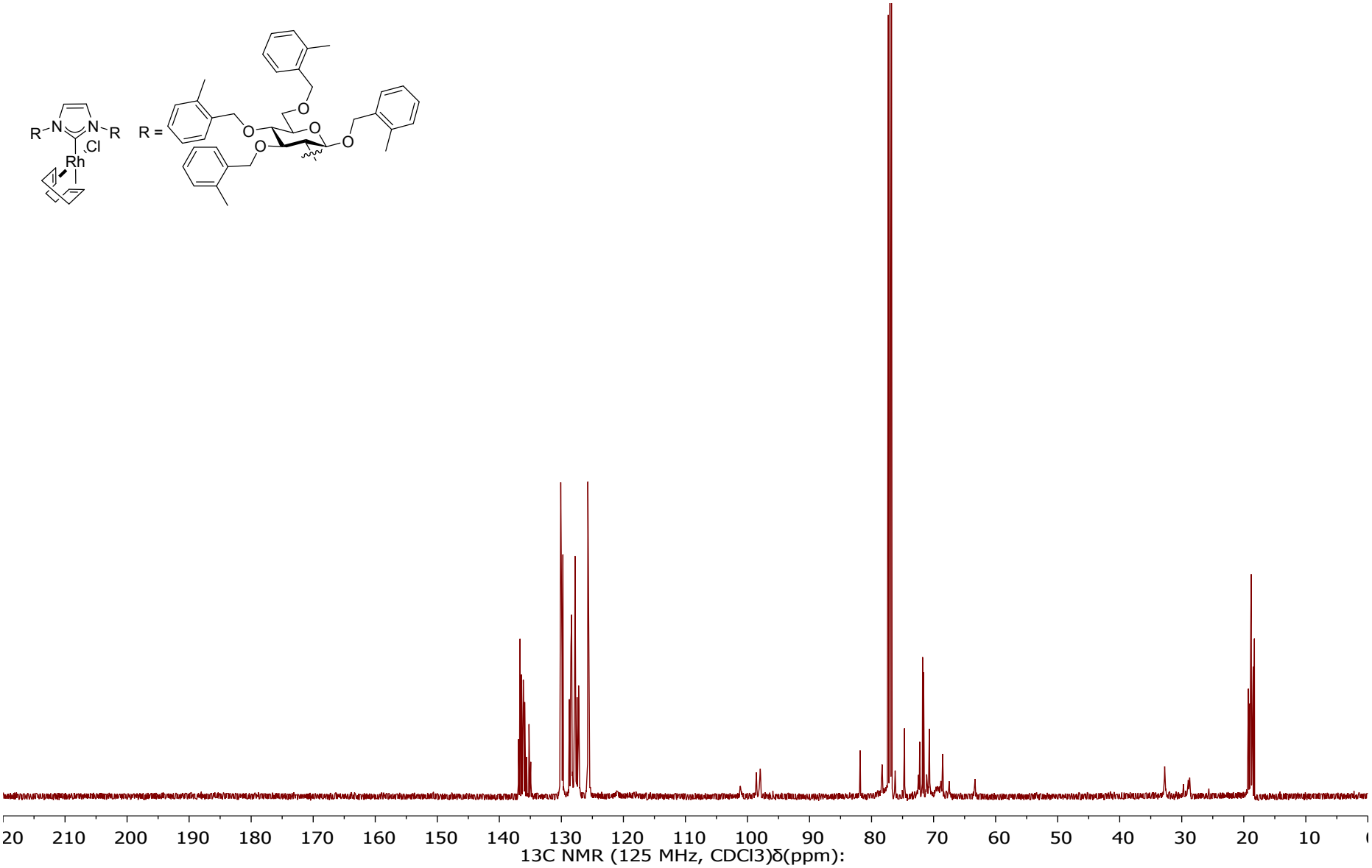

R
N
N
R
Cl
Rh
R =
AllylO
AllylO
O
OAllyl
OAllyl
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (500 MHz, CDCl3)δ(ppm):

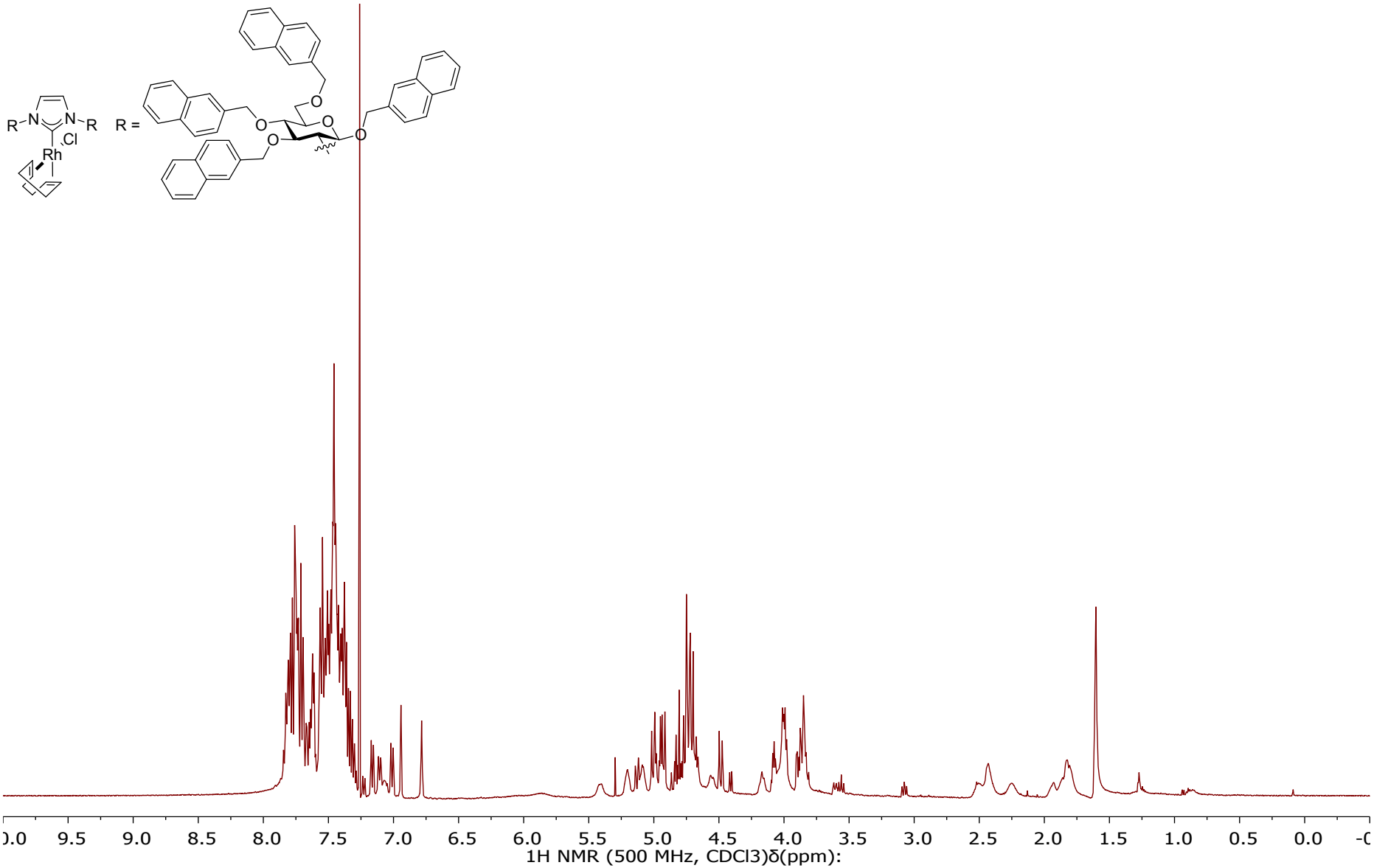

R
N
N
R
Cl
Rh
R =
OAllyl
AllylO
AllylO
O
OAllyl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CDCl3)δ(ppm):

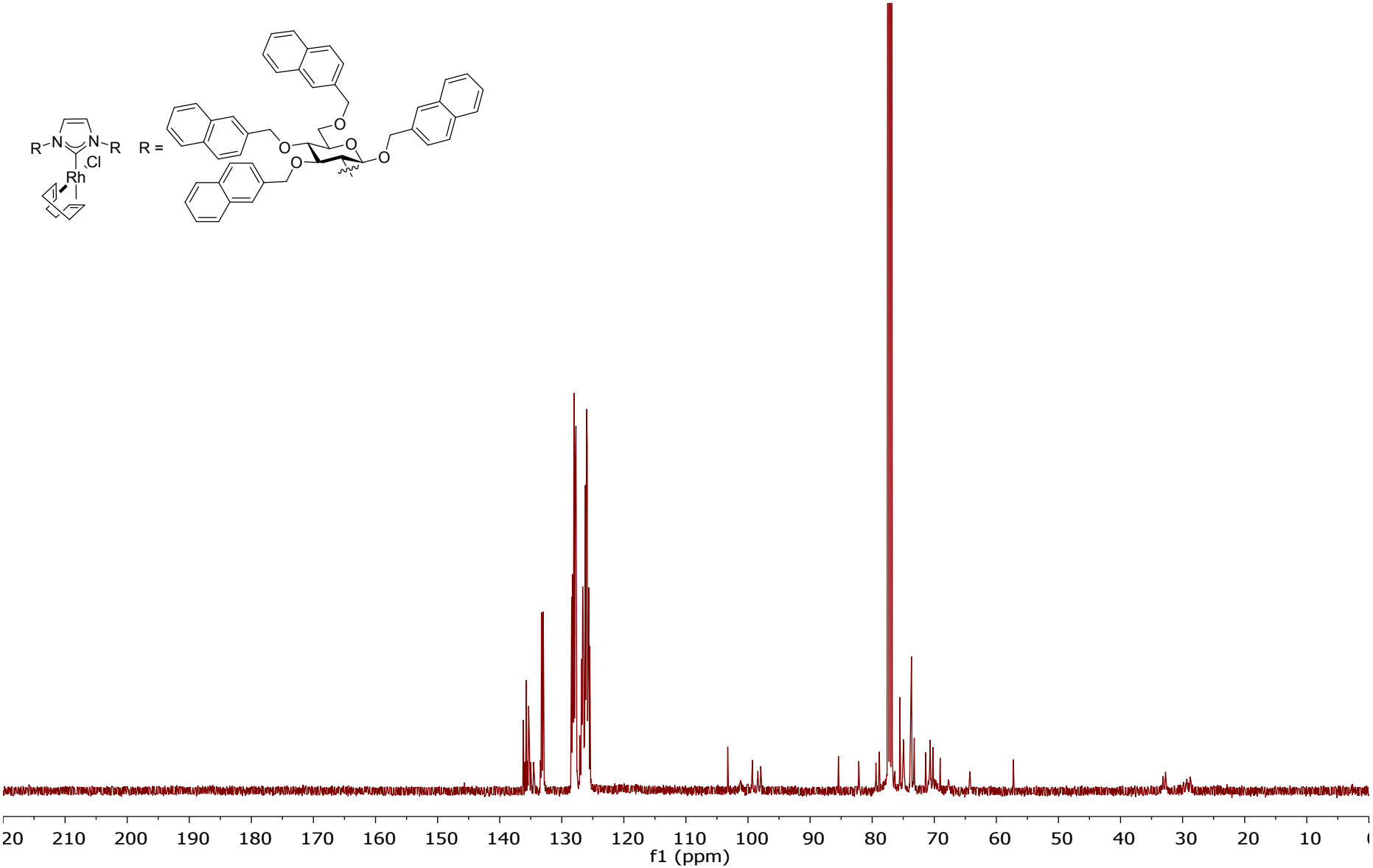

R
N
N
R
Cl
Rh
R =
BnO
BnO
O
OBn
OBn
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (400 MHz, CDCl3)δ(ppm):

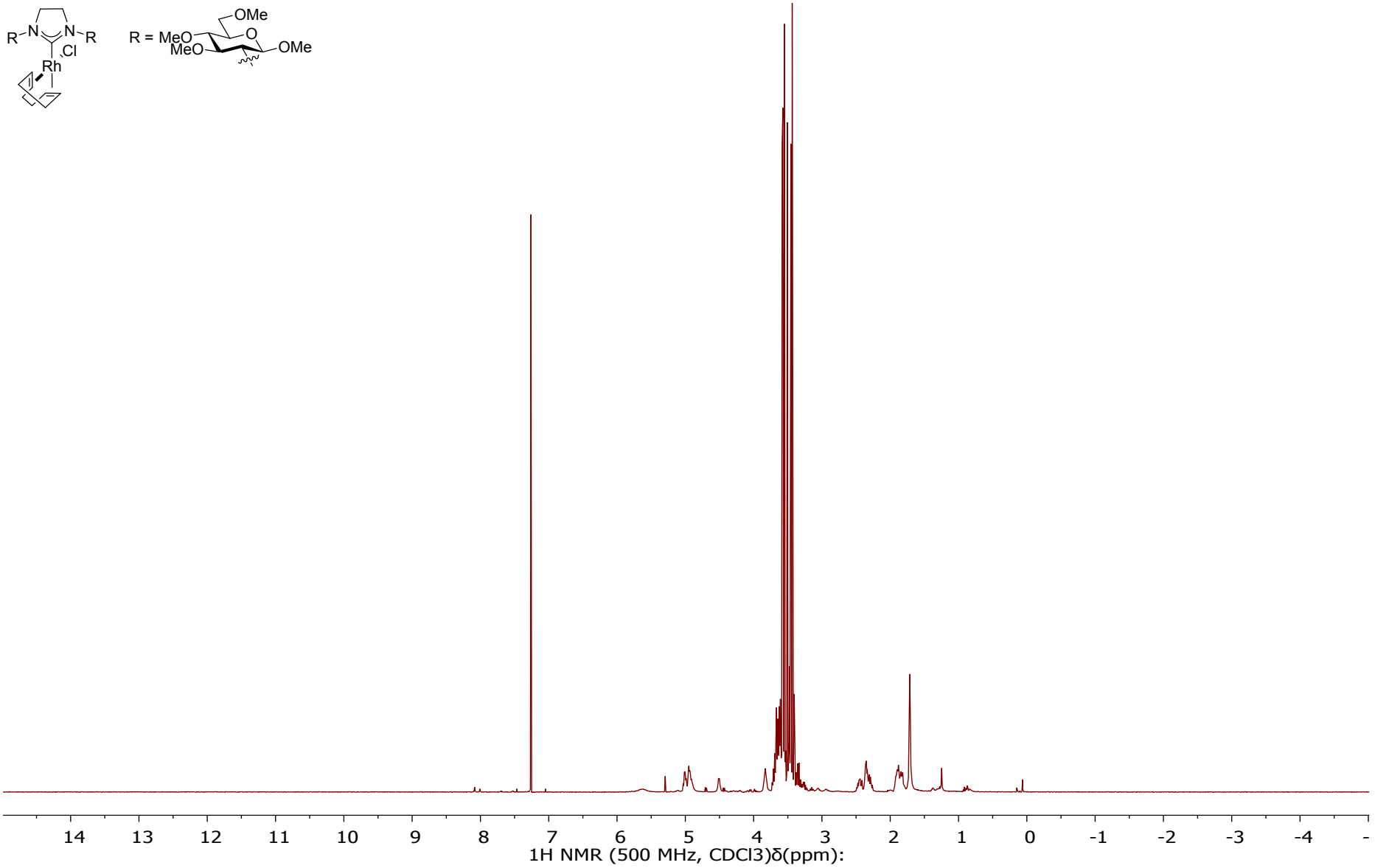

R
N
N
R
Cl
Rh
R =
OBn
BnO
BnO
O
OBn
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CDCl3)δ(ppm):

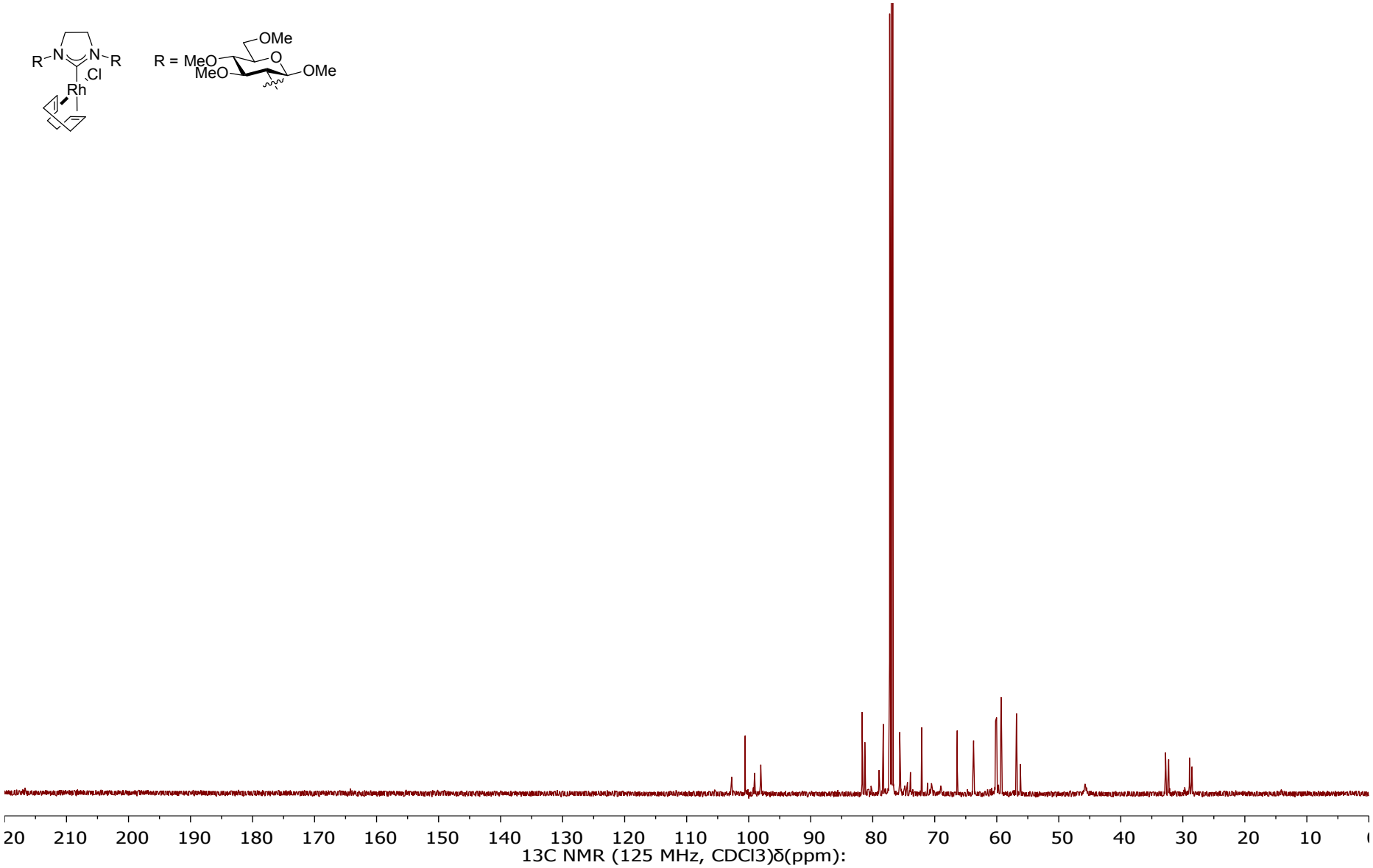

R
N
N
R
Cl
Rh
R =
O
O
O
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (500 MHz, CDCl3)δ(ppm):

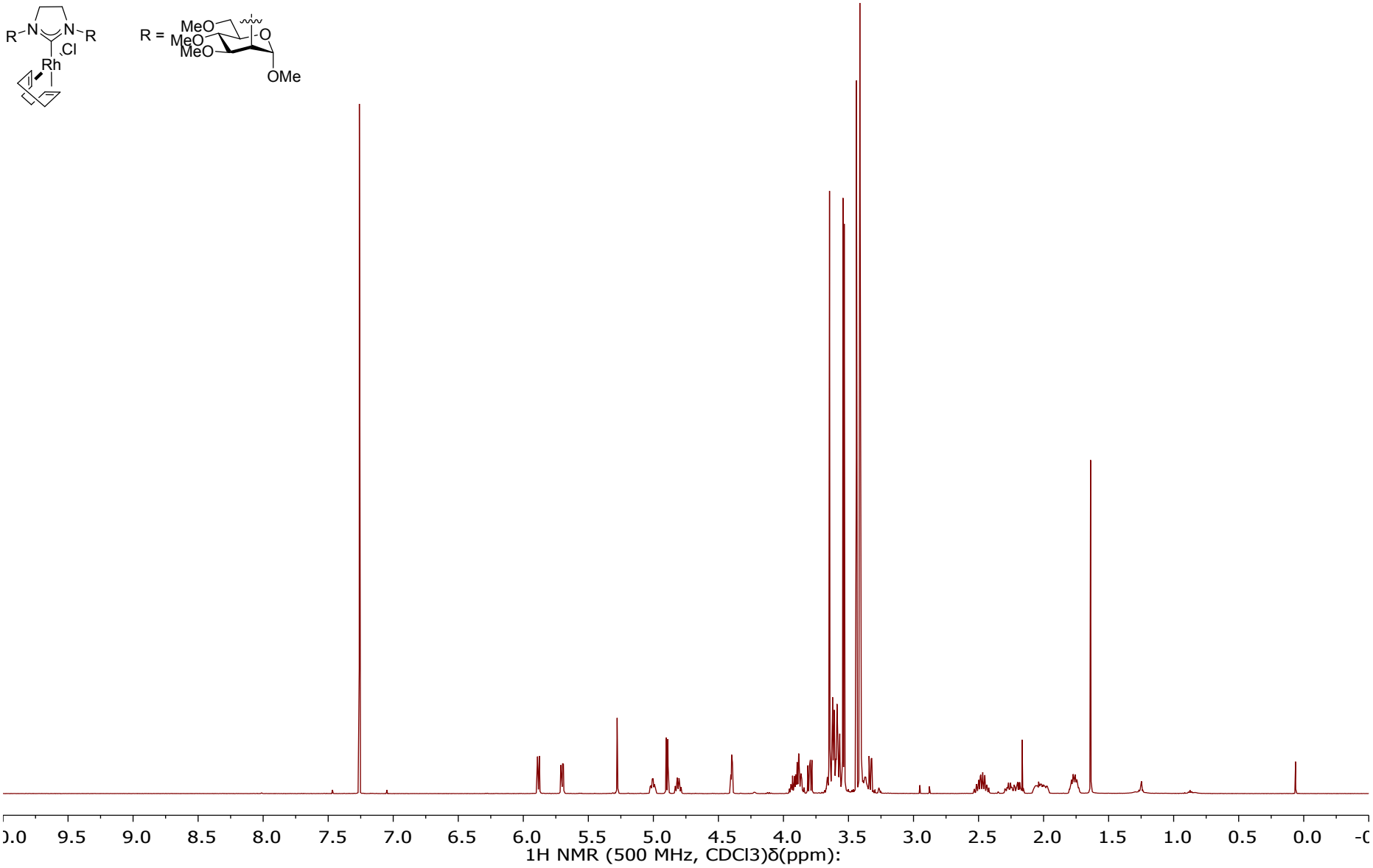

R
N
N
R
Cl
Rh
R =
O
O
O
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
13C NMR (125 MHz, CDCl3)δ(ppm):

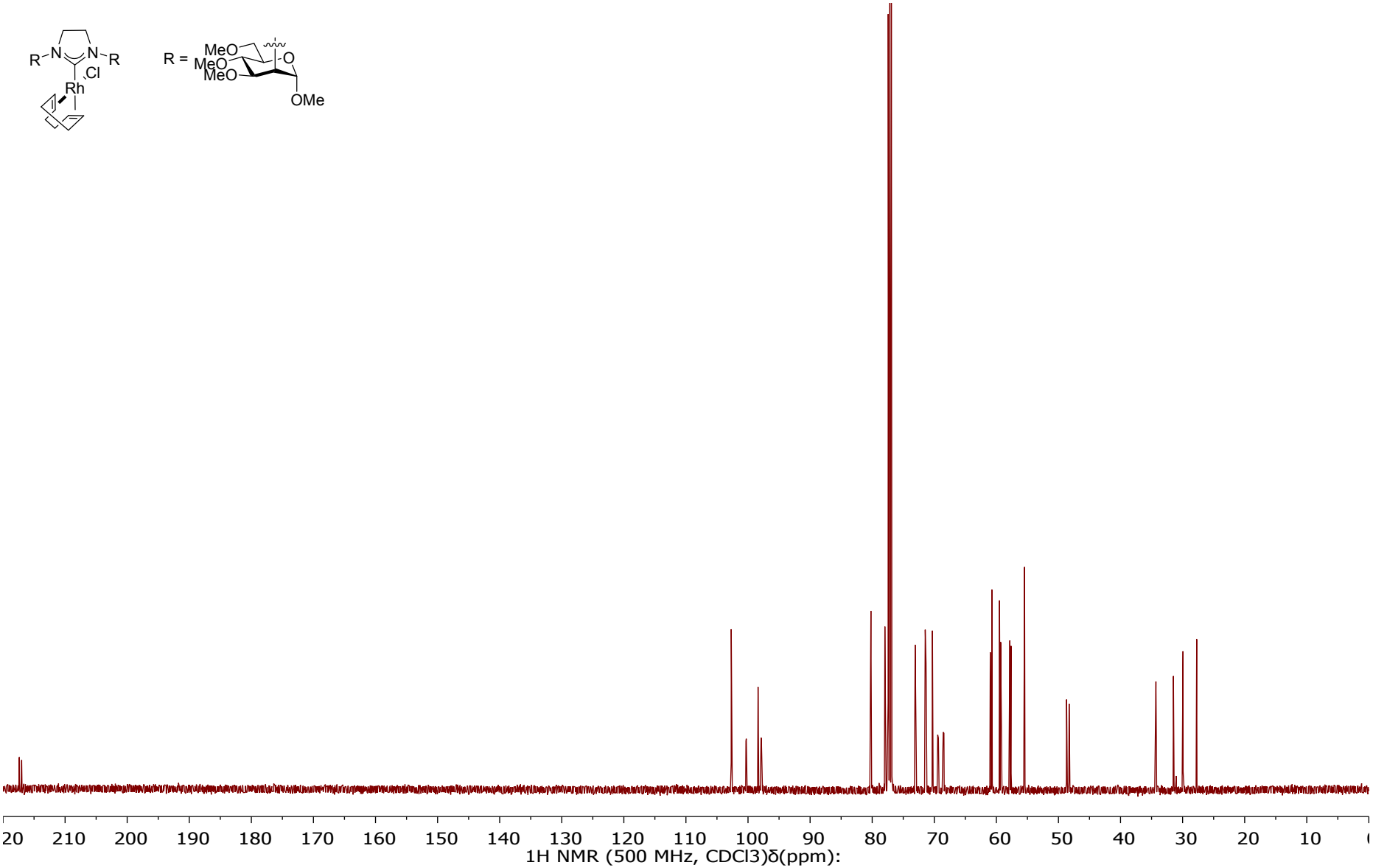

R
N
N
R
Cl
Rh
R =
O
O
O
O
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (500 MHz, CDCl3)δ(ppm):

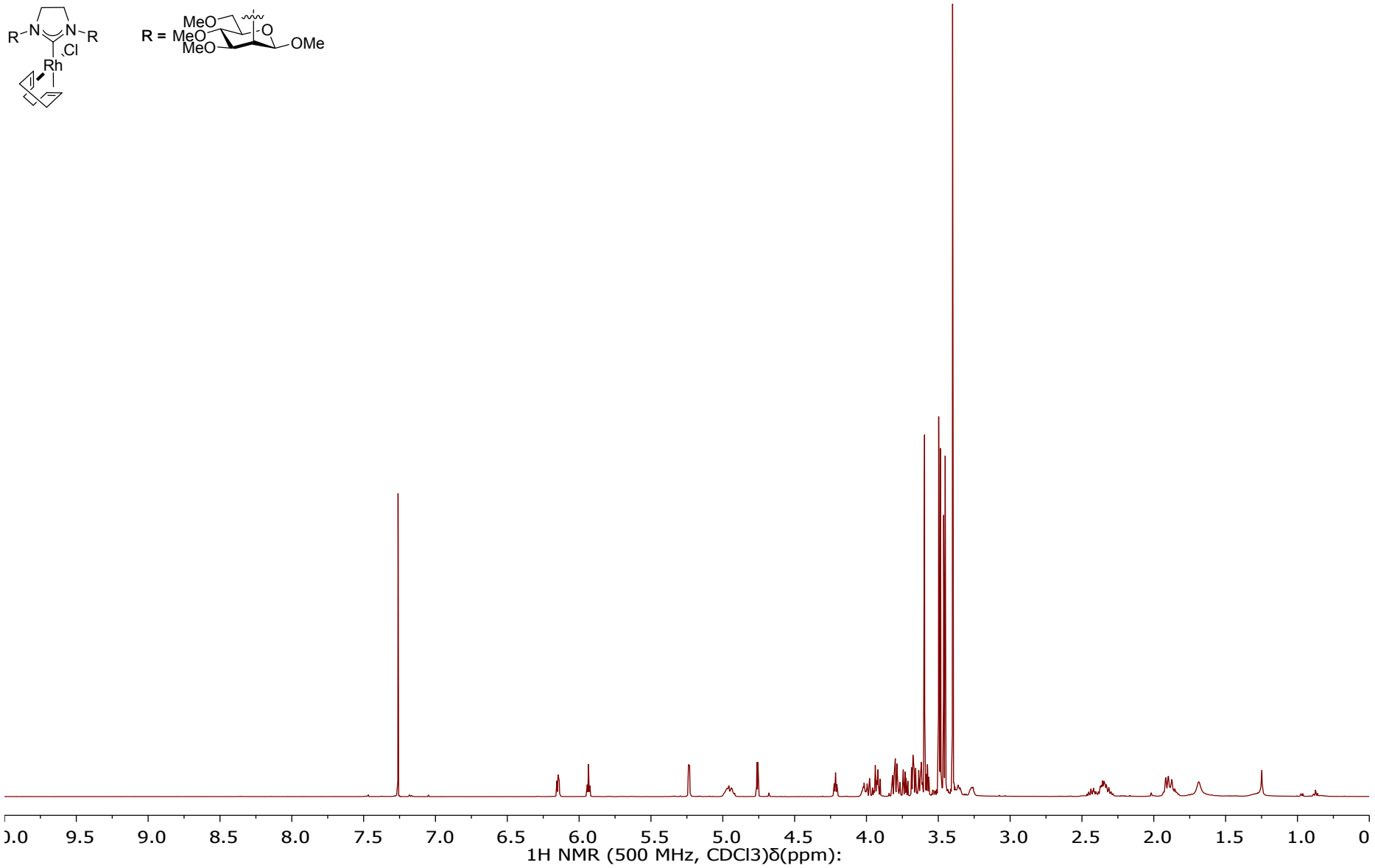

R
N
N
R
Cl
Rh
R =
O
O
O
O
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

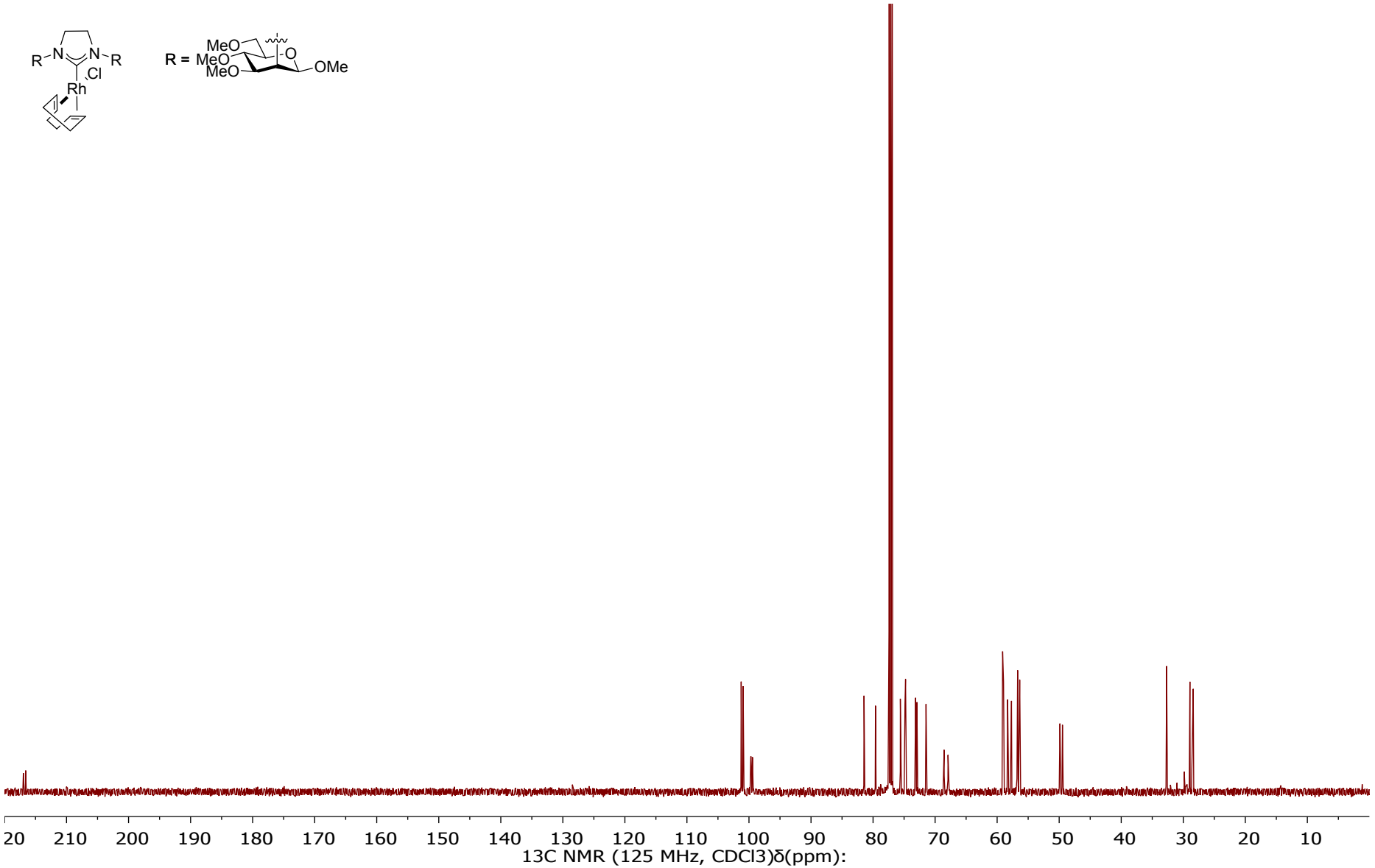

R
N
N
R
Cl
Rh
R = MeO
MeO
OMe
O
OMe
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-
1H NMR (500 MHz, CDCl3)δ(ppm):


R
N
N
R
Cl
Rh
R = MeO
MeO
O
OMe
OMe
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C NMR (125 MHz, CDCl3)δ(ppm):


R
N
N
R
Cl
Rh
R =
MeO
MeO
MeO
O
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H NMR (500 MHz, CDCl3)δ(ppm):


R
N
N
R
Cl
Rh
R =
MeO
MeO
MeO
O
OMe
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
1H NMR (500 MHz, CDCl3)δ(ppm):


R
N
N
R
Cl
Rh
R =
MeO
MeO
MeO
O
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
1H NMR (500 MHz, CDCl3)δ(ppm):


R
N
N
R
Cl
Rh
R =
MeO
MeO
MeO
O
OMe
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
13C NMR (125 MHz, CDCl3)δ(ppm):

References:

(1) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.
(2) Kyas, A.; Feigel, M. *Helv. Chim. Acta* **2005**, *88*, 2375-2396.
(3) Aly, M. R. E.; Schmidt, R. R. *Eur. J. Org. Chem.* **2005**, *2005*, 4382-4392.
(4) Hintermann, L. *Beilstein J. Org. Chem.* **2007**, *3*, 22.
(5) Huynh, H. V.; Han, Y.; Jothibasu, R.; Yang, J. A. *Organometallics* **2009**, *28*, 5395-5404.
(6) Tran, A.-T.; Jones, R. A.; Pastor, J.; Boisson, J.; Smith, N.; Galan, M. C. *Adv. Synth. Catal.* **2011**, *353*, 2593-2598.
(7) Elchert, B.; Li, J.; Wang, J. H.; Hui, Y.; Rai, R.; Ptak, R.; Ward, P.; Takemoto, J. Y.; Bensaci, M.; Chang, C. W. T. *J. Org. Chem.* **2004**, *69*, 1513-1523.
(8) Chambers, D. J.; Evans, G. R.; Fairbanks, A. J. *Tetrahedron: Asymmetry* **2003**, *14*, 1767-1769.
(9) Popelová, A.; Kefurt, K.; Hlaváčková, M.; Moravcová, J. *Carbohydrate Research* **2005**, *340*, 161-166.
(10) Deng, S.; Gangadharmath, U.; Chang, C.-W. T. *J. Org. Chem.* **2006**, *71*, 5179-5185.
(11) Dinger, M. B.; Nieczypor, P.; Mol, J. C. *Organometallics* **2003**, *22*, 5291-5296.
(12) Dang, H.-S.; Roberts, B. P.; Tocher, D. A. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2452-2461.
(13) Nycholat, C. M.; Bundle, D. R. *Carbohydrate Research* **2009**, *344*, 1397-1411.
(14) Paas, M.; Wibbeling, B.; Fröhlich, R.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2006**, *2006*, 158-162.
(15) Onami, T.; Ikeda, M.; Woodard, S. S. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3601-3605.
(16) Wei, Y.; Xue, D.; Lei, Q.; Wang, C.; Xiao, J. *Green Chem.* **2013**, *15*, 629-634.
(17) Zhao, Q.; Curran, D. P.; Malacria, M.; Fensterbank, L.; Goddard, J.-P.; Lacôte, E. *Synlett* **2012**, *2012*, 433-437.