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

Pseudo-Enantiomeric Carbohydrate-Based N-Heterocyclic Carbenes as Promising Chiral Ligands for Enantiotopic Discrimination

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Supporting Information

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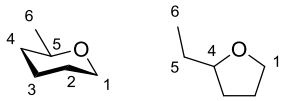
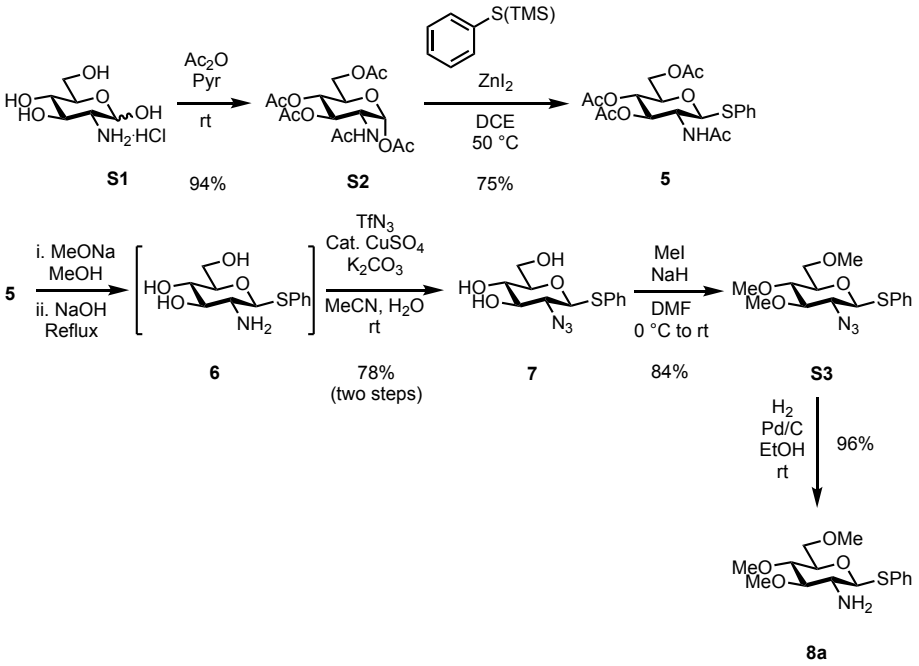
General Experiment Details:

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, DEPT, HMQC, 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:

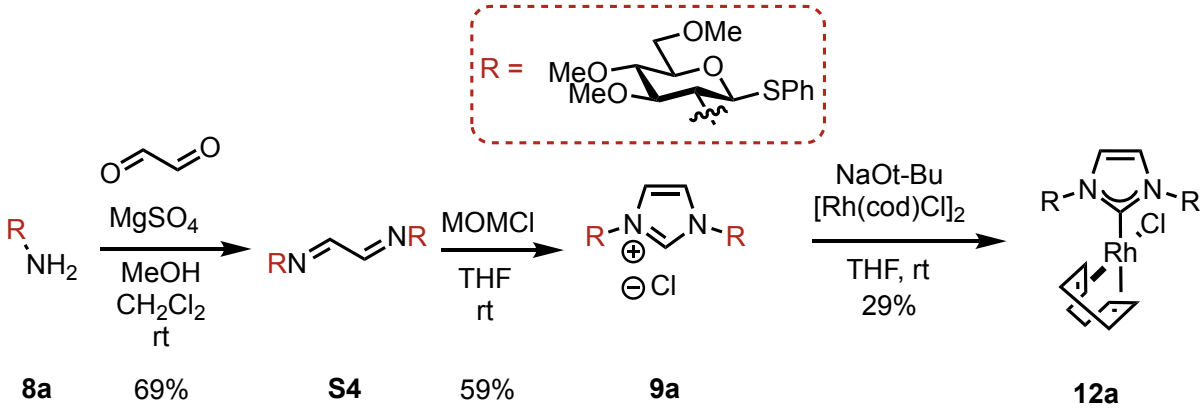
Synthesis of a building block 8a with steric bulk at C1



Phenyl 2-amino-3,4,6-tri-*O*-methyl-2,1-dideoxy-1-thio-β-D-glucopyranoside (8a):

To a solution of azide **7**[2] (317 mg, 0.93 mmol) in EtOH (5% wt 12 M HCl, 0.2 M) under Ar at rt, was added Pd (5% wt on C, 10 mol%). H2 (1 atm, balloon) was bubbled through the solvent until the Ar atmosphere was replaced. After 4 h, the H2 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 to afford a colourless solution. Concentration *in vacuo* and subsequent trituration with MeOH (3 x washes) yielded **8a** (280 mg, 96%) as a colourless solid. *Rf* = 0.8 (90:10 CH2Cl2:MeOH); νmax / cm^{-1} (film): 3403, 2902, 1599, 1504, 1388, 1063; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53-7.51 (2H, m, ArCH), 7.29-7.25 (3H, m, ArCH), 4.41 (1H, d, *J* = 10.0 Hz, H-1), 3.64 (1H, dd, *J* = 11.0 and 2.0 Hz, H-6a), 3.63 (3H, s, OCH_3), 3.59 (1H, dd, *J* = 11.0 and 4.5 Hz, H-6b), 3.51 (3H, s, OCH_3), 3.40 (3H, s, OCH_3), 3.34 (1H, ddd, *J* = 9.0, 4.5 and 2.0 Hz, H-5), 3.21 (1H, *app*. t, *J* = 10.0, H- 4), 3.06 (1H, *app*. t, *J* = 9.0 Hz, H-3), 2.75 (1H, *app*. t, *J* = 9.5 Hz, H-2), 1.70 (2H, br s, NH2); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 132.9 (ArC), 132.4 (ArCH), 132.4 (ArCH), 128.8 (ArCH), 127.7 (ArCH), 89.3 (C-1), 88.2 (C- 3), 79.8 (C-4), 79.2 (C-5), 71.4 (C-6), 60.9 (OCH_3), 60.2 (OCH_3), 59.4 (OCH_3), 55.6 (C-2); *m/z* HRMS (ESI): Found $[M+Na]^+$ 336.1240, $C_{15}H_{23}NO_4SNa$ requires 336.1240; $[\alpha]^{24}_D$ = -4 (*c* 1.2, $CHCl_3$).

Synthesis of a carbohydrate-based imidazolium salt with steric bulk at C1



Bis(phenyl 2-amino-3,4,6-tri-*O*-methyl-2,1-dideoxy-1-thio-β-D-glucopyranoside)-*N,N'*-iminoethylidene (S4):

To a solution of amine **8a** ((761 mg, 2.18 mmol) and glyoxal (aq. 40%, 1.14 mmol) in anhydrous MeOH (0.5 M) at rt, was added MgSO4 (0.5 g per mmol). After 18 h, the reaction was diluted with CHCl3 (10 mL), filtered and then concentrated. Purification by trituration with cool Et_2O (2 x 5 mL) yielded bis(imine) **S4** as a colourless solid. Note: bis(imine)s were generally insoluble in MeOH and soluble in CHCl3. *Rf* = 0.9 (90:10 CH2Cl2:MeOH); νmax / cm-1 (film): 2932, 2834, 1721, 2629, 1583, 1479, 1375, 1139, 1104; ^{1}H NMR (500 MHz, CDCl3) δ: 7.75 (2H, s, HC=N), 7.51-5.49 (4H, m, ArCH), 7.29-7.25 (6H, m, ArCH), 4.91 (2H, d, *J* = 10.0 Hz, H-1), 3.70 (2H, dd, *J* = 11.0 and 2.0 Hz, H-6a), 3.64 (2H, dd, *J* = 11.0 and 4.5 Hz, H-6b), 3.54 (6H, s, OCH3), 3.47 (2H, ddd, *J* = 10.0, 4.5 and 2.0 Hz, H-5), 3.43 (6H, s, OCH3), 3.364 (6H, s, OCH3), 3.361 (2H, *app*. t, *J* = 9.0 Hz, H-3), 3.27 (2H, dd, *J* = 10.0 and 9.0 Hz, H- 4), 3.18 (2H, dd, *J* = 10.0 and 9.0 Hz, H-2); 13C NMR (125 MHz, CDCl3) δ: 164.5 (C=N), 132.71 (ArC), 132.65 (ArCH), 129.0 (ArCH), 127.9 (ArCH), 86.0 & 85.9 (C-1 & C-3), 79.6 (C-5), 79.3 (C-4), 75.0 (C-2), 71.6 (C-6), 60.9 (OCH3), 60.6 (OCH3), 59.6 (OCH3); *m/z* HRMS (ESI): Found [M+Na]+ 671.2424, C32H44N2O8S2Na requires 671.2431; [α]21D = -32 (*c* 0.4, CHCl3).

1,3-Bis(phenyl 2-amino-3,4,6-tri-*O*-methyl-2,1-dideoxy-1-thio-β-D-glucopyranoside)imidazolium chloride (9a):

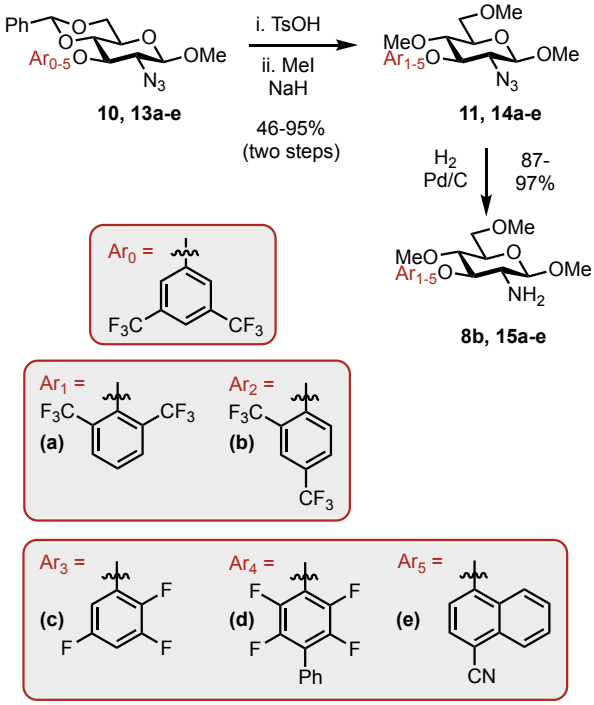
Adapted from Huynh and co-workers.[3] To a solution of bis(imine) **S4** (490 mg, 0.75 mmol) in CH(OEt)3 (2000 mol%) at rt, was added NH_4Cl (120 mol%) and the suspension was heated to 100 °C under an Ar atmosphere. After 14 h the reaction was allowed to cool to 60 °C and then placed under vacuum for 0.5 h to afford a residue. Purification by FCC (95:5 to 90:10 EtOAc:MeOH) yielded the imidazolinium chloride **9a** (308 mg, 59%) as a hydroscopic beige solid. *Rf* = 0.4 (90:10 CH2Cl2:MeOH); νmax / cm^{-1} (film): 3318, 2927, 1735, 1474, 1444, 1258, 1105, 1051; ^{1}H NMR (400 MHz, CDCl3) δ: 12.45 (1H, br s, $CH_{Imidazolium}$), 7.43-7.40 (4H, m, ArCH), 7.32-7.27 (6H, m, ArCH), 6.93 (2H, s, $CH_{Imidazolium}$), 5.97 (2H, d, *J* = 10.5 Hz, H-1), 4.33 (2H, dd, *J* = 10.5 and 9.0 Hz, H-3), 3.95 (2H, *app* dt, *J* = 10.0 and 2.5 Hz, H-5), 3.82 (2H, *app*. t, *J* = 10.5 Hz, H-2), 3.70-3.62 (4H, m, H-6a &

H-6b), 3.51 (6H, s, OCH_3), 3.42 (6H, s, OCH_3), 3.37 (2H, dd, J = 10.0 and 9.0 Hz, H-4), 3.34 (6H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.6 ($CH_{Imidazolium}$), 133.0 (ArCH), 132.1 (ArC), 129.2 (ArCH), 128.5 (ArCH), 122.3 ($CH_{Imidazolium}$), 85.2 (C-3), 83.0 (C-1), 79.7 (C-4), 78.6 (C-5), 70.4 (C-6), 65.0 (C-2), 61.5 (OCH_3), 59.9 (OCH_3), 59.3 (OCH_3); *m/z* HRMS (ESI): Found $[M\text{-}Cl]^+$ 661.2605, $C_{33}H_{45}N_2O_5S_2$ requires 661.2612; $[\alpha]^{21}_D$ = 20 (*c* 0.9, $CHCl_3$).

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

Following General Procedure D. NHC·HCl **285a** (43.0 mg, 65.0 μmol); in a modification of the general procedure, NaO*t*-Bu (6.2 mg, 65.0 μmol) was used instead of KO*t*-Bu; FCC (100:0 to 98:2 CH_2Cl_2:MeOH) yielded **291a** (17.0 mg, 29%) as an orange oil; R_f = 0.7 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 2925, 1723, 1582, 1533, 1462, 1365, 1246, 1192, 1098; ^1H NMR (500 MHz, $CDCl_3$) *observed peaks* δ: 7.57-7.13 (12H, m, ArCH & $CH_{Imidazolylidene}$), 6.04-3.98 (8H, m, $H\text{-}_{Carbohydrate}$ & CH_{COD}), 3.68-2.87 (28H, m, $H\text{-}_{Carbohydrate}$ & CH_{COD}), 2.55-1.65 (8H, m, $CH_{2\ COD}$); ^{13}C NMR (125 MHz, $CDCl_3$) *observed peaks* δ: 137.4, 132.9, 132.7, 132.0, 131.2, 129.8, 129.4, 129.2, 128.8, 128.5, 128.3, 128.2, 122.4, 97.8, 85.0, 83.0, 79.7, 78.5, 78.1, 77.4, 77.3, 77.0, 76.7, 70.5, 65.0, 61.5, 61.3, 59.9, 59.9, 59.4, 59.3, 59.2, 29.7; *m/z* HRMS (ESI): Found $[M]^+$ 871.2537, $C_{41}H_{56}N_2O_{10}RhS_2$ requires 871.2528; $[\alpha]^{22}_D$ = 102 (*c* 0.1, $CHCl_3$).

Synthesis of a carbohydrate-based imidazolium salt with steric bulk at C3



General Hydrogenation Procedure: Pd/C Catalysed Azide Hydrogenation

To solution of azides **11**[4] and **14a-e**[4] (100 mol%) in EtOH (5% wt 12 M HCl, 0.2 M) under Ar at rt, was added Pd (5% wt on C, 10 mol%). H_2 (1 atm, balloon) was bubbled through the solvent until the Ar atmosphere was 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 to afford a colourless solution. Concentration *in vacuo* and subsequent trituration with MeOH (3 x washes) yielded the amines **15a-e.**

Methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(3',5'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside (8b): Following General Hydrogenation Procedure with some modifications. Azide **11**[4] (1.15 g, 2.49 mmol); trituration with $CHCl_3$ (3 x 5 mL) yielded **8b** (932 mg, 86%) as colourless oil; *Rf* = 0.8 (90:10 CH_2Cl_2:MeOH); vmax / cm^{-1} (film): 3662, 2933, 1612, 1468, 1377, 1278, 1173, 1130, 1057, 1010; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.57 (2H, br s, ArCH), 7.47 (1H, br s, ArCH), 4.24 (1H, dd, *J* = 9.5 and 8.5 Hz, H-3), 4.17 (1H, d, *J* = 8.0 Hz, H-1), 3.69 (1H, dd, *J* = 10.5 and 2.0 Hz, H-6a), 3.64 (1H, dd, *J* = 10.5 and 3.5 Hz, H-6b), 3.55 (3H, s, OCH^3), 3.49 (1H, dd, *J* = 9.5 and 8.5 Hz, H-4), 3.44 (1H, ddd, *J* = 9.5, 3.5 and 2.0 Hz, H-5), 3.43 (3H, s, OCH^3), 3.29 (3H, s, OCH^3), 3.05 (1H, dd, *J* = 9.5 and 8.0 Hz, H-2); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.4 (ArCOR), 133.0 (q, *J* = 33.5 Hz, Ar*C*CF_3), 123.3 (q, *J* = 273.0 Hz, ArC*C*F^3), 116.8 (d, *J* = 4.0 Hz, ArCH), 115.2 (t, *J* = 4.0 Hz, ArCH), 104.5 (C- 1), 85.7 (C-3), 79.3 (C-4), 74.9 (C-5), 71.0 (C-6), 60.4 (OCH_3), 59.5 (OCH_3), 57.4 (OCH_3), 57.0 (C-2); ^{19}F NMR (470 MHz, $CDCl_3$) δ: -63.0 (CF_3); *m/z* HRMS (ESI): Found $[M+H]^+$ 434.1392, $C_{17}H_{22}NF_6O_5$ requires 434.1397; $[\alpha]^{23}_D$ = 45 (*c* 0.9, $CHCl_3$).

Methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',6'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside (15a): Following General Hydrogenation Procedure with some modifications. Azide **14a**[4] (600 mg, 1.31 mmol); trituration with $CHCl_3$ (3 x 5 mL) yielded **15a** (543 mg, 96%) as colourless solid; *Rf* = 0.8 (90:10 CH_2Cl_2:MeOH); νmax / cm^{-1} (film): 3392, 2941, 1602, 1521, 1461, 1389, 1344, 1300, 1243, 1211, 1166, 1127, 1088, 1066; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.78 (2H, d, *J* = 8.0 Hz, ArCH), 7.25 (br t, *J* = 8.0 Hz, ArCH), 4.72 (1H, *app.* t, *J* = 9.5 Hz, H-3), 4.68 (1H, d, *J* = 8.0 Hz, H-1), 3.65 (1H, br t, *J* = 9.0 Hz, H-4), 3.602 (1H, dd, *J* = 11.0 and 2.0 Hz, H-6a), 3.298 (3H, s, OCH_3), 3.51 (1H, dd, *J* = 11.0 and 4.0 Hz, H-6b), 3.36 (3H, s, OCH_3), 3.30 (1H, ddd, *J* = 9.5, 4.0 and 2.0 Hz, H-5), 3.22 (1H, dd, *J* = 10.0 and 8.0 Hz, H-2), 2.73 (3H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.3 (ArCOR), 131.4 (d, *J* = 5.0 Hz, ArCH), 124.6 (q, *J* = 31.0 Hz, Ar*C*CF3), 123.2 (q, *J* = 273.0 Hz, ArC*C*F_3), 123.1 (ArCH), 101.9 (C-1), 84.4 (C-3), 78.3 (C-4), 74.7 (C-5), 70.5 (C-6), 59.3 (OCH_3), 58.6 (OCH_3), 57.4 (OCH_3), 56.6 (C-2); ^{19}F NMR (470 MHz, $CDCl_3$) δ: -62.9 (CF_3); *m/z* HRMS (ESI): Found $[M+H]^+$ 434.1395, $C_{17}H_{22}F_6NO5$ requires 434.1397; $[\alpha]^{21}_D$ = -9 (*c* 0.8, $CHCl_3$).

Methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',4'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside (15b): Following General Hydrogenation Procedure with some modifications. Azide **14b**[4] (463 mg, 1.01 mmol); trituration with $CHCl_3$ (3 x 5 mL) yielded **15b** (425 mg, 97%) as colourless solid; *Rf* = 0.7 (90:10 CH_2Cl_2:MeOH); νmax / cm^{-1} (film): 2939, 2841, 1628, 1594, 1508, 1348, 1315, 1287, 1262, 1124, 1083, 1055; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (1H, d, *J* = 2.0 Hz, ArCH), 7.72 (1H, dd, *J* = 9.0 and 2.5 Hz, ArCH), 7.51 (1H, d, *J* = 9.0 Hz, ArCH), 4.42 (1H, t, *J* = 9.5 Hz, H-3), 4.16 (1H, d, *J* = 8.0 Hz, H-1), 3.70 (1H, dd, *J* = 10.5 and 2.0 Hz, H-6a), 3.64 (1H, dd, *J* = 10.5 and 4.0 Hz, H-6b), 3.54 (3H, s, OCH_3), 3.53 (1H, dd, *J* = 10.0 and 9.0 Hz, H-4), 3.45 (1H, ddd, *J* = 10, 4.0 and 2.0 Hz, H-5), 3.43 (3H, s, OCH_3), 3.27 (3H, s, OCH_3), 3.11 (1H, dd, *J* = 9.5 and 8.0 Hz, H-2), 1.48 (2H, br s, NH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.8 (ArCOR), 130.5 (q, *J* = 4.0 Hz, ArCH), 124.9-124.7 (m, ArCH), 123.6 (q, *J* = 271.5 Hz, ArC*C*F_3), 123.1 (q, *J* = 270.0 Hz, ArC*C*F_3), 123.0 (q, *J* = 34.0 Hz, Ar*C*CF_3), 119.5 (q, *J* = 31.5 Hz, Ar*C*CF_3), 115.2 (ArCH), 104.4 (C-1), 85.2 (C-3), 79.1 (C-4), 75.0 (C-5), 71.1 (C-6), 60.4 (OCH_3), 59.5 (OCH_3), 57.4 (OCH_3), 56.7 (C-2); 19F NMR (470 MHz, $CDCl_3$) δ: -62.0 (s, CF_3), -62.6 (s, CF_3); *m/z* HRMS (ESI): Found $[M+H]^+$ 434.1383, $C_{17}H_{22}F_6NO_5$ requires 434.1397; $[\alpha]^{23}_D$ = 59 (*c* 0.6, $CHCl_3$).

Methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',3',5'-trifluoro)benzene-2-deoxy-β-D-glucopyranoside (15c): According to General Hydrogenation Procedure. Azide **14c**[4] (715 mg, 1.89 mmol); trituration yielded **15c** (581 mg, 87%) as a colourless solid which was contaminated by an unknown impurity (~10%); *Rf* = 0.7 (90:10 CH_2Cl_2:MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.94 (1H, ddt, *J* = 10.5, 5.5 and 2.5 Hz, ArCH), 6.55 (1H, dddd, *J* = 10.0, 8.5, 5.5 and 2.5 Hz, ArCH), 4.15 (1H, d, *J* = 8.0 Hz, H-1), 4.09 (1H, *app*. t, *J* = ~9.0-9.5 Hz, H-3), 3.68 (1H, dd, *J* = 10.5 and 2.0 Hz, H-6a), 3.63 (1H, dd, *J* = 10.5 and 4.0 Hz, H-6b), 3.54 (3H, s, OCH_3), 3.50 (1H, dd, *J* = 9.5 and 9.0 Hz, H-4), 3.43 (3H, s, OCH_3), 3.41-3.38 (1H, m, H-5), 3.38 (3H, s, OCH_3), 3.09 (1H, dd, *J* = 9.5 and 8.0 Hz, H-2), 1.73 (2H, br s, NH2); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.4 (ddd, *J* = 244.0, 13.5 and 4.0 Hz, ArCF), 151.0 (ddd, *J* = 248.5, 15.5 and 12.0 Hz, ArCF), 149.5 (dd, *J* = 8.5 and 4.5 Hz, ArC), 138.4 (ddd, *J* = 243.0, 13.5 and 5.0 Hz, ArCF), 104.2 (C-1), 101.1 (dd, *J* = 27.5 and 3.5 Hz, ArCH), 98.1 (dd, *J* = 28.0 and 21.5 Hz, ArCH), 87.6 (C-3), 78.9 (C-4), 74.9 (C-5), 70.9 (C-6), 60.4 (OCH_3), 59.4 (OCH_3), 57.2 (OCH_3), 56.7 (C-2);

^{19}F NMR (377 MHz, $CDCl_3$) δ: -114.3 – -114.4 (m, ArCF), -134.1 – -134.2 (m, ArCF), -163.6 – -163.7 (m, ArCF); *m/z* HRMS (ESI): Found $[M+H]^+$ 352.1363, $C_{15}H_{21}F_3NO_5$ requires 352.1366.

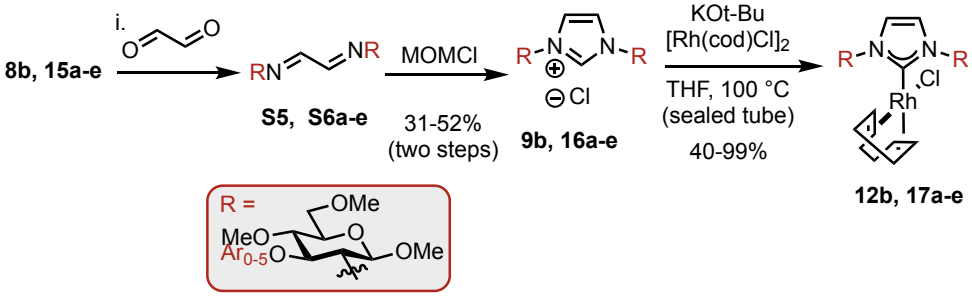
Methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(4'-phenyl-2',3',5',6'-tetrafluoro)benzene-2-deoxy-β-D-glucopyranoside (15d):

Following General Hydrogenation Procedure with some modifications. Azide **14d**[4] (963 mg, 2.04 mmol); trituration with $CHCl_3$ (3 x 5 mL) yielded **15d** (883 mg, 97%) as colourless oil; *Rf* = 0.7 (90:10 CH_2Cl_2:MeOH); νmax / cm^{-1} (film): 2931, 1725, 1511, 1495, 1488, 1441, 1196, 1083; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49-7.41 (5H, m, ArCH), 4.30 (1H, dd, *J* = 10.0 and 9.0 Hz, H-3), 4.15 (1H, d, *J* = 8.0 Hz, H-1), 3.68 (1H, dd, *J* = 11.0 and 2.0 Hz, H-6a), 3.66-3.59 (2H, m, H-4 & H-6b), 3.56 (OCH_3), 3.43 (OCH_3), 3.36 (OCH_3), 3.32 (1H, ddd, *J* = 9.5, 3.5 and 2.0 Hz, H-5), 3.11 (1H, *app*. t, *J* = 9.0 Hz, H-2); ^{13}C NMR (125 MHz, CDCl3) δ: 144.3 (dddd, *J* = 246.0, 16.5, 8.0 and 4.0 Hz, ArCF), 141.1 (ddt, *J* = 246.0, 15.5 and 4.5 Hz, ArCF), 137.2 (ArC), 130.4 (t, *J* = 2.0 Hz, ArCH), 129.0 (ArCH), 128.7 (ArCH), 127.4 (ArC), 114.3 (t, *J* = 17.0 Hz, ArC), 104.9 (C-1), 88.2 (t, *J* = 2.5 Hz, C-3), 80.0 (C-4), 74.8 (C-5), 71.0 (C-6), 60.1 (OCH3), 59.4 (OCH3), 57.5 (OCH3), 57.1 (C-2); ^{19}F NMR (470 MHz, $CDCl_3$) δ: -145.3 (dd, *J* = 22.5 and 8.5 Hz, ArCF), -156.0 (dd, *J* = 22.0 and 8.5 Hz, ArCF); *m/z* HRMS (ESI): Found $[M+H]^+$ 446.1585, $C_{21}H_{24}F_4NO_5$ requires 446.1585; $[\alpha]^{22}_D$ = -32 (*c* 0.3, $CHCl_3$).

Methyl 2-amino-4,6-di-*O*-methyl-3-*O*-1'-(4'-cyano)naphthlene-2-deoxy-β-D-glucopyranoside (15e):

Following General Hydrogenation Procedure with some modifications. Azide **14e**[4] (963 mg, 2.04 mmol); trituration with CHCl3 (3 x 5 mL) yielded **15e** (896 mg, 90%) as colourless oil; *Rf* = 0.7 (90:10 CH_2Cl_2:MeOH); νmax / cm^{-1} (film): 2930, 2218, 1577, 1509, 1391, 1324, 1228, 1057; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (1H, ddd, *J* = 8.5, 1.5 and 0.5 Hz, ArCH), 8.20 (1H, dt, *J* = 8.5 and 1.5 Hz, ArCH), 7.85 (1H, d, *J* = 8.0 Hz, ArCH), 7.71 (1H, ddd, *J* = 8.5, 7.0 and 1.5 Hz, ArCH), 7.61 (1H, ddd, *J* = 8.0, 7.0 and 1.5 Hz, ArCH), 7.31 (1H, d, *J* = 8.5 Hz, ArCH), 4.56 (1H, br t, *J* = 9.5 Hz, H-3), 4.22 (1H, d, *J* = 8.0 Hz, H-1), 3.72 (1H, dd, *J* = 11.0 and 2.0 Hz, H-6a), 3.67 (1H, dd, *J* = 11.0 and 3.5 Hz, H-6b), 3.63 (1H, br t, *J* = 9.5 Hz, H-4), 3.57 (3H, s, OCH3), 3.49 (1H, ddd, *J* = 9.5, 3.5 and 2.0 Hz, H-5), 3.45 (3H, s, OCH3), 3.24 (3H, s, OCH_3), 3.22 (1H, dd, *J* = 9.5 and 8.0 Hz, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.2 (ArCOR), 134.1 (ArCH), 134.0 (ArC), 129.1 (ArCH), 127.1 (ArCH), 125.6 (ArC), 125.3 (ArCH), 122.6 (ArCH), 118.4 (ArC*C*N), 107.1 (ArCH), 104.6 (C-1), 102.6 (Ar*C*CN), 85.3 (C-3), 79.2 (C- 4), 75.0 (C-5), 71.1 (C-6), 60.6 (OCH_3), 59.5 (OCH_3), 57.5 (OCH_3), 57.2 (C-2); *m/z* HRMS (ESI): Found $[M+H]^+$ 373.1760, $C_{20}H_{25}N_2O_5$ requires 373.1758; $[\alpha]^{22}_D$ = 8 (*c* 0.2, $CHCl_3$).

Synthesis of complexes 12b and 17a-e



General Procedure A. Bis(imine) Synthesis 1.

Adapted from Kündig and co-workers.[5] To a solution of **amine** (100 mol%) in CH_2Cl_2 (0.4 M) at rt, was added Na_2SO_4 (1 g per mmol of amine), formic acid (7 mol%) and glyoxal (40% by wt in H_2O, 50 mol%). After stirring for 16 h the solution was filtered and then concentrated. Purification by trituration with **solvent** (3 x washes) yielded the **bis(imine)** as a colourless solid. Note: the bis(imine)s were generally insoluble in MeOH and soluble in $CHCl_3$.

General Procedure B. Bis(imine) Synthesis 2

To a solution of **amine** (100 mol%) and glyoxal (aq. 40%, 50 mol%) in anhydrous MeOH (0.5 M) at rt, was added $MgSO_4$ (0.5 g per mmol). After 18 h, the reaction was diluted with $CHCl_3$ (10 mL), filtered and then concentrated. Purification by trituration with cool **solvent** (3 x 5 mL) yielded **bis(imine)** as a colourless solid. Note: bis(imine)s were generally insoluble in MeOH and soluble in $CHCl_3$.

General Procedure C. Imidazolium Chloride Synthesis with MOMCl

To a solution of **bis(imine)** (100 mol%) in anhydrous THF (0.2 M) at rt, was added MOMCl (2000 mol%). After 16 h, the reaction was concentrated and the resulting residue was further purified by FCC to yield the **imidazolium chloride.**

General Procedure D. NHC.HCl Ligation to [Rh(COD)Cl]$_2$

Adapted from Ekkehardt and co-workers.[6] To a solution of **imidazol(in)ium 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 through Celite®. The filtrate was concentrated to afford a residue. Purification by FCC yielded the **[RhNHC(COD)Cl]** complex.

Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(3',5'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)-*N,N'*-iminoethylidene (S5):

Following General Procedure A. Amine **8b** (913 mg, 2.11 mmol); trituration with MeOH yielded **S5** (742 mg, 79%) as a colourless solid; R_f = 0.9 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 3661, 2987, 2901, 1623, 1611, 1468, 1405, 1393, 1369, 1276, 1169, 1126, 1065, 1056, 1038; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.83 (2H, s, HC=N), 7.29 (4H, d, *J* = 1.5 Hz, ArCH), 7.25 (2H, t, *J* = 1.5 Hz, ArCH), 4.49 (2H, d, *J* = 7.5 Hz, H-1), 4.47 (2H, *app*. t, *J* = 9.5

Hz, H-3), 3.70 (2H, dd, *J* = 10.5 and 2.0 Hz, H-6a), 3.65 (2H, dd, *J* = 10.5 and 3.5 Hz, H- 6b), 3.56 (2H, dd, *J* = 10.0 and 9.0 Hz, H-4), 3.48 (6H, s, OCH_3), 3.48 (2H, ddd, *J* = 10.0, 3.5 and 2.0 Hz, H-5), 3.44 (6H, s, OCH_3), 3.36 (2H, m, found *J* = 7.5 Hz, H-2), 3.35 (6H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.3 (HC=N), 160.2 (ArCOR), 132.4 (q, *J* = 33.5 Hz, Ar*C*CF_3), 123.1 (q, *J* = 272.5 Hz, ArC*C*F_3), 117.5 (br s, ArCH), 115.1 (br s, ArCH), 102.0 (C-1), 84.7 (C-3), 78.9 (C-4), 75.4 (C-2), 74.8 (C-5), 70.9 (C-6), 60.5 (OCH_3), 59.5 (OCH_3), 57.3 (OCH_3); ^{19}F NMR (377 MHz, $CDCl_3$) δ: -63.1 (CF_3); *m/z* HRMS (ESI): Found $[M+H]^+$ 889.2562, $C_{36}H_{41}N_2F_{12}O_{10}$ requires 889.2564; $[\alpha]^{20}_D$ = -59 (*c* 0.7, $CHCl_3$).

Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',6'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)-*N*,*N*'-iminoethylidene (S6a):

Following General Procedure A with some modifications. Amine **15a** (660 mg, 1.52 mmol); after filtration to remove the desiccant, concentration afforded the crude product, contaminated with the starting material. Dissolution of the residue in a small quantity of Et_2O and then the addition of hexane precipitated unreacted starting material. Decanting the solvent and its subsequent concentration yielded **S6a** (257 mg, 39%) as a colourless solid; R_f = 0.9 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 2935, 2888, 2842, 1635, 1602, 1460, 1380, 1343, 1300, 1286, 1246, 1210, 1165, 1130, 1088, 1065; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.60 (2H, s, HC=N), 7.55 (4H, d, *J* = 8.0 Hz, ArCH), 6.89 (2H, t, *J* = 8.0 Hz, ArCH), 4.73 (2H, *app.* t, *J* = 9.0 Hz, H-3), 4.49 (2H, d, *J* = 7.5 Hz, H-1), 3.65 (2H, *app.* t, *J* = 9.5 Hz, H-4), 3.64 (2H, dd, *J* = 11.0 and 2.0 Hz, H-6a), 3.56 (2H, dd, *J* = 11.0 and 4.0 Hz, H-6b), 3.44 (6H, s, OCH_3), 3.42-3.40 (2H, m, H-2), 3.39 (6H, s, OCH_3), 3.34 (2H, ddd, *J* = 9.5, 4.0 and 2.0 Hz, H-5), 2.94 (6H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.4 (HC=N), 154.8 (ArCOR), 131.0 (ArCH), 124.2 (br q, *J* = 31.0 Hz, Ar*C*CF_3), 123.7 (q, *J* = 274.0 Hz, ArC*C*F_3), 122.3 (ArCH), 102.2 (C-1), 84.6 (C-3), 78.2 (C-4), 74.8 (C-5), 74.6 (C-2), 70.9 (C-6), 59.4 (OCH_3), 59.1 (OCH_3), 57.2 (OCH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ: -59.4 (CF_3); *m/z* HRMS (ESI): Found $[M+H]^+$ 889.2577, $C_{36}H_{41}F_{12}N_2O_{10}$ requires 889.2564; $[\alpha]^{22}_D$ = 25 (*c* 0.6, $CHCl_3$).

Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',4'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)-*N*,*N*'-iminoethylidene (S6b):

Following General Procedure A. Amine **15b** (172 mg, 0.40 mmol); trituration with MeOH yielded **S6b** (89.4 mg, 52%) as a colourless solid; R_f = 0.9 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 2929, 2888, 1631, 1594, 1514, 1450, 1386, 1352, 1319, 1292, 1264, 1218, 1178, 1135, 1085, 1055, 1024; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.70 (2H, s, HC=N), 7.66 (2H, dd, *J* = 9.0 and 2.5 Hz, ArCH), 7.52 (2H, d, *J* = 2.5 Hz, ArCH), 7.38 (2H, d, *J* = 9.0 Hz, ArCH), 4.82 (2H, *app*. ddd, *J* = 10.0, 9.0 and 6.0 Hz, H-3), 4.54 (2H, d, *J* = 7.5 Hz, H-1), 3.70 (2H, dd, *J* = 10.5 and 1.5 Hz, H-6a), 3.64 (2H, dd, *J* = 10.5 and 2.5 Hz, H-6b), 3.55-3.52 (4H, m, H-4 & H-5), 3.48 (6H, s, OCH_3), 3.43 (6H, s, OCH_3), 3.33 (2H, dd, *J* = 9.5 and 7.5 Hz, H-2), 3.15 (6H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.6 (HC=N), 158.8 (ArCOR), 130.3 (ArCH), 124.3 (br s, ArCH), 123.8 (q, *J* = 273.0 Hz, ArC*C*F_3), 122.56 (q, *J* = 32.5 Hz, Ar*C*CF_3), 122.54 (q, *J* = 272.0 Hz, ArC*C*F_3), 118.7 (q, *J* = 31.5 Hz, Ar*C*CF_3), 114.4 (ArCH), 102.2 (C-1), 80.6 (C-2), 79.3 (C-4 or C-5), 75.3 (C-2), 74.8 (C-4 or C-5), 70.9 (C-6), 60.4 (OCH_3), 59.5 (OCH_3), 57.3 (OCH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ: -62.1 (s, CF_3), -63.5 (s, CF_3); *m/z* HRMS (ESI): Found $[M+Na]^+$ 911.2381, $C_{36}H_{40}F_{12}N_2O_{10}Na$ requires 911.2384; $[\alpha]^{20}_D$ = 8 (*c* 0.8, $CHCl_3$).

Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',3',5'-trifluoro)benzene-2-deoxy-β-D-glucopyranoside)-*N*,*N*'-iminoethylidene (S6c):

Following General Procedure B. Amine **15c** (546 mg, 1.55 mmol); trituration solvent: MeOH (2 x 5 mL) yielded **S6c** (546 mg, 97%) as a colourless solid which was contaminated by an unknown impurity (~10%); R_f = 0.9 (90:10 CH_2Cl_2:MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (2H, s, HC=N), 6.68 (2H, ddt, *J* = 10.5, 5.5 and 2.5 Hz, ArCH), 6.40 (2H, dddd, *J* = 10.0, 8.5, 5.5 and 3.0 Hz, ArCH), 4.50 (2H, d, *J* = 7.5 Hz, H-1), 4.37 (2H, *app*. t, *J* = 9.5 Hz, H-3), 3.70 (2H, dd, *J* = 10.5 and 2.0 Hz, H-6a), 3.64 (2H, dd, *J* = 10.5 and 4.0 Hz, H- 6b), 3.57 (1H, dd, *J* = 9.5 and 9.0 Hz, H-4), 3.47 (6H, s, OCH_3), 3.47-3.44 (2H, m, H-5), 3.44 (6H, s, OCH_3), 3.40 (6H, s, OCH_3), 3.37 (2H, dd, *J* = 9.5 and 7.5 Hz, H-2); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.2 (C=N), 157.1 (ddd, *J* = 244.0, 14.0 and 3.5 Hz, ArCF), 150.7 (ddd, *J* = 248.5, 15.5 and 12.0 Hz, ArCF), 149.2-149.0 (m, ArC), 138.5 (ddd, *J* = 244.0, 14.0 and 5.0 Hz, ArCF), 102.0 (C-1), 101.0 (dd, *J* = 27.5 and 3.0 Hz, ArCH), 97.9 (dd, *J* = 27.5 and 22.0 Hz, ArCH), 85.3 (C-3), 78.6 (C-4), 75.3 (C-2), 74.8 (C-5), 70.8 (C-6), 60.5 (OCH_3), 59.4 (OCH_3), 57.1 (OCH_3); ^{19}F NMR (470 MHz, $CDCl_3$) *major compound* δ: -115.0 (q, *J* = 10.0 Hz, ArCF), -134.7 (dd, *J* = 19.0 and 10.0 Hz, ArCF), -164.0 (td, *J* = 11.5 and 5.5 Hz, ArCF). *Impurity δ:-120.1 (t,* J *= 11.0 Hz, ArCF), 139.0 (d,* J *= 20.0 Hz, ArCF)*. *m/z* HRMS (ESI): Found $[M+H]^+$ 725.2507, $C_{32}H_{39}N_2O_{10}$ requires 725.2503.

Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(4'-phenyl-2',3',5',6'-tetrafluoro)benzene-2-deoxy-β-D-glucopyranoside)-*N*,*N*'-iminoethylidene (S6d):

Following General Procedure A. Amine **15d** (905 mg, 2.03 mmol); trituration with MeOH yielded **S6d** (577 mg, 62%) as a colourless solid; R_f = 0.9 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 2937, 2879, 2843, 1632, 1512, 1488, 1438, 1382, 1197, 1138, 1116, 1080, 1054, 1020; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.92 (2H, s, HC=N), 7.37-7.35 (6H, m, ArCH), 7.26-7.23 (4H, m, ArcH), 4.58 (2H, *app.* t, *J* = 9.0 Hz, H-3), 4.52 (2H, d, *J* = 8.0 Hz, H-1), 3.71 (2H, dd, *J* = 11.0 and 2.0 Hz, H-6a), 3.70 (2H, *app.* t, *J* = 9.0 Hz, H-4), 3.64 (2H, dd, *J* = 11.0 and 3.5 Hz, H-6b), 3.48 (6H, s, OCH_3), 3.45 (2H, dd, *J* = 9.5 and 8.0 Hz, H-2), 3.44 (6H, s, OCH_3), 3.42 (2H, ddd, *J* = 9.5, 3.5 and 2.0 Hz, H-5), 3.38 (6H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.5 (HC=N), 144.1 (dddd, *J* = 246.0, 12.0, 8.0 and 4.0 Hz, ArCF), 141.0 (ddt, *J* = 247.5, 16.0 and 3.5 Hz, ArCF), 136.8 (t, *J* = 12.0 Hz, ArC), 130.2 (ArCH), 128.8 (ArCH), 128.5 (ArCH), 127.3 (ArC), 114.4 (t, *J* = 17.0 Hz, ArC), 102.2 (C-1), 85.8 (C-3), 79.5 (C-4), 75.1 (C-2), 74.7 (C-5), 71.0 (C-6), 60.3 (OCH_3), 59.5 (OCH_3), 57.4 (OCH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ: -146.1 (dd, *J* = 22.0 and 8.5 Hz, ArCF), -156.0 (dd, *J* = 22.0 and 8.5 Hz, ArCF); *m/z* HRMS (ESI): Found $[M+Na]^+$ 935.2755, $C_{44}H_{44}F_8N_2O_{10}Na$ requires 935.2760; $[\alpha]^{21}_D$ = -104 (*c* 0.6, $CHCl_3$).

Bis(methyl 2-amino-4,6-di-*O*-methyl-3-*O*-1'-(4'-cyano)naphthlene-2-deoxy-β-D-glucopyranoside)-*N*,*N*'-iminoethylidene (S6e):

Following General Procedure A. Amine **15e** (651 mg, 1.75 mmol); trituration with MeOH yielded **S6e** (449 mg, 67%) as a colourless solid; R_f = 0.9 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 2934, 2838, 2217, 1632, 1577, 1509, 1462, 1428, 1388, 1322, 1277, 1244, 1277, 1135, 1119, 1112, 1105, 1016, 1014; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93-7.90 (4H, m, ArCH), 7.73 (2H, s, N=CH), 7.54 (2H, d, *J* = 8.5 Hz, ArCH), 7.38 (2H, ddd, *J* = 8.5, 7.0 and 1.0 Hz, ArCH), 7.17 (2H, ddd, *J* = 8.5, 7.0 and 1.0 Hz, ArCH), 6.98 (2H, d, *J* = 8.5 Hz, ArCH), 4.78 (2H, t, *J* = 9.0 Hz, H-3), 4.50 (2H, d, *J* = 7.5 Hz, H-1), 3.69 (2H, dd, *J* = 10.5 and 2.0 Hz, H-6a), 3.62 (2H, dd, *J* = 10.5 and 3.5 Hz, H-6b), 3.60 (2H, t, *J* = 9.5 Hz, H-4), 3.49 (2H, ddd, *J* = 9.5, 3.5 and 2.0 Hz, H-5), 3.47 (6H, s, OCH_3),

3.42 (6H, s, OCH_3), 3.41 (2H, dd, *J* = 9.5 and 7.5 Hz, H-2), 3.10 (6H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.0 (C=N), 158.7 (ArCOR), 133.5 (ArCH), 133.4 (ArC), 128.9 (ArCH), 126.6 (ArCH), 125.04 (ArC), 124.95 (ArCH), 122.1 (ArCH), 118.3 (ArC*C*N), 107.2 (ArCH), 102.3 (Ar*C*CN), 102.0 (C-1), 83.0 (C-3), 79.1 (C-4), 75.4 (C-2), 74.9 (C-5), 70.9 (C-6), 60.5 (OCH_3), 59.5 (OCH_3), 57.3 (OCH_3); *m/z* HRMS (ESI): Found $[M+H]^+$ 767.3286, $C_{42}H_{47}N_4O_{10}$ requires 767.3287; $[\alpha]^{21}_D$ = 10 (*c* 0.8, $CHCl_3$).

1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(3',5'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)imidazolium chloride (9b):

Following General Procedure C. Bis(imine) **S5** (340 mg, 0.39 mmol); FCC (100:0 to 96:4 CH_2Cl_2:MeOH) yielded **9b** (201 mg, 56%) as a tan amorphous solid; R_f = 0.6 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 3276, 2929, 1659, 1560, 1591, 1469, 1372, 1283, 1230, 1178, 1136, 1120, 1102, 1058, 1008; ^1H NMR (500 MHz, CD_3OD) δ: 7.97 (2H, br s, CH $_{Imidazolium}$), 7.55 (2H, br s, ArCH), 7.54 (4H, br s, ArCH), 5.31 (2H, dd, *J* = 10.5 and 8.5 Hz, H-3), 4.83 (2H, d, *J* = 8.5 Hz, H-1), 4.57 (2H, dd, *J* = 10.5 and 8.5 Hz, H-2), 3.77-3.70 (6H, m, H-5 & H-6a & H-6b), 3.67 (2H, dd, *J* = 9.5 and 8.5 Hz, H-4), 3.44 (6H, s, OCH_3), 3.29 (6H, s, OCH_3), 3.20 (6H, s, OCH_3), *CH $_{Imidazolium}$ undergoes exchange in CD_3OD and was not observed*; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.4 (ArCOR), 139.6 (t, *J* = 33.0 Hz, CD $_{Imidazolium}$), 134.0 (q, *J* = 33.5 Hz, Ar*C*CF_3), 124.4 (q, *J* = 272.0 Hz, ArC*C*F_3), 122.3 (CH $_{Imidazolium}$), 117.5 (ArCH), 116.6 (ArCH), 100.7 (C-1), 81.0 (C-3 & C-4), 75.9 (C-5), 71.5 (C-6), 65.5 (C-2), 60.9 (OCH_3), 59.6 (OCH_3), 57.2 (OCH_3); ^{19}F NMR (283 MHz, $CDCl_3$) δ: -60.4 (CF_3); *m/z* HRMS (ESI): Found $[M-Cl]^+$ 901.2566, $C_{37}H_{41}N_2O_{10}$ requires 901.2564; $[\alpha]^{21}_D$ = 45 (*c* 0.6, CH_3OH).

1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',6'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)imidazolium chloride (16a):

Following General Procedure C. Bis(imine) **15a** (70 mg, 0.08 mmol); FCC (100:0 to 95:5 CH_2Cl_2:MeOH) yielded **16a** (59.2 mg) as a tan amorphous solid; R_f = 0.5 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 2982, 1603, 1462, 1344, 1300, 1243, 1212, 1134, 1090; ^1H NMR (500 MHz, $CDCl_3$) δ: 12.19 (1H, s, CH $_{Imidazolium}$), 7.76 (4H, d, *J* = 8.0 Hz, ArCH), 7.26 (2H, t, *J* = 8.0 Hz, ArCH), 7.05 (2H, s, CH $_{Imidazolium}$), 6.16 (2H, d, *J* = 8.0 Hz, H-1), 5.12 (2H, *app.* t, *J* = 9.5 Hz, H-3), 4.19 (2H, *app.* t, *J* = ~9.0 Hz, H-2), 3.89-3.80 (4H, m, H-4 & H-5), 3.69 (6H, s, OCH_3), 3.65 (2H, dd, *J* = 11.0 and 2.0 Hz, H-6a), 3.51 (2H, dd, *J* = 11.0 and 4.0 Hz, H-6b), 3.35 (6H, s, OCH_3), 2.66 (6H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 153.3 (ArCOR), 136.7 (CH $_{Imidazolium}$), 131.3 (ArCH), 124.1 (br, Ar*C*CF_3), 123.4 (ArCH), 123.1 (q, *J* = 272.5 Hz, ArC*C*F_3), 122.9 (CH $_{Imidazolium}$), 99.1 (C-1), 84.6 (C-3), 78.0 & 73.6 (C-4 & C-5), 70.0 (C-6), 66.9 (C-2), 59.2 (OCH_3), 58.1 (OCH_3), 57.3 (OCH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ: -59.2 (CF_3); *m/z* HRMS (ESI): Found $[M-Cl]^+$ 901.2571, $C_{37}H_{41}F_{12}N_2O_{10}$ requires 901.2564; $[\alpha]^{22}_D$ = 58 (*c* 0.7, $CHCl_3$).

1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',4'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)imidazolium chloride (16b):

Following General Procedure C. Bis(imine) **15b** (90 mg, 0.10 mmol); FCC (100:0 to 96:4 CH_2Cl_2:MeOH) yielded **16b** (80.0 mg) as a tan amorphous solid; R_f = 0.5 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 2939, 1627, 1597, 1509, 1384, 1347, 1286, 1260, 1220, 1180, 1122, 1100, 1084, 1053, 1003; ^1H NMR (500 MHz, $CDCl_3$) δ: 12.31 (1H, s, CH $_{Imidazolium}$), 7.95 (2H, d, *J* = 9.0 Hz, ArCH), 7.80 (2H, dd, *J* = 9.0 and 2.5 Hz, ArCH), 7.67 (2H, d, *J* =

2.5 Hz, ArCH), 7.05 (2H, s, CH $_{Imidazolium}$), 6.04 (2H, dd, J = 10.5 and 8.5 Hz, H-3), 4.86 (2H, d, J = 8.0 Hz, H-1), 4.05 (2H, dd, J = 10.5 and 8.0 Hz, H-2), 3.92 (2H, dt, J = 10.0 and 2.5 Hz, H-5), 3.67-3.63 (6H, m, H-4 & H-6a & H-6b), 3.39 (6H, s, OCH_3), 3.21 (6H, s, OCH_3), 2.77 (6H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.0 (ArCOR), 135.6 (CH $_{Imidazolium}$), 131.4 (d, J = 4.0 Hz, ArCH), 124.4-124.1 (m, ArCH), 123.50 (q, J = 33.5 Hz, Ar*C*CF_3), 123.46 (q, J = 271.5 Hz, ArC*C*F_3), 123.0 (CH $_{Imidazolium}$), 121.8 (q, J = 273.0 Hz, ArC*C*F_3), 118.8 (q, J = 31.5 Hz, Ar*C*CF_3), 115.4 (ArCH), 100.8 (C-1), 79.4 (C-4), 79.3 (C-3), 74.2 (C-5), 69.9 (C-6), 66.1 (C-2), 60.4 (OCH_3), 59.4 (OCH_3), 56.9 (OCH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ: -62.2 (CF_3), -62.9 (CF_3); *m/z* HRMS (ESI): Found $[M\text{-}Cl]^+$ 901.2563, $C_{37}H_{41}F_{12}N_2O_{10}$ requires 901.2564. $[\alpha]^{22}_D$ = 75 (*c* 2.5, $CHCl_3$).

1,3-Bis(methyl 2-amino-4-6-bis-*O*-methyl-3-*O*-(2',3',5'-trifluoro)benzene-2-deoxy-β-D-glucopyranoside)imidazolium chloride (16c):

Following General Procedure C. Bis(imine) **S5c** (520 mg, 0.72 mmol); FCC (99:1 to 90:10 CH_2Cl_2:MeOH) yielded **16c** (345 mg, 62%) as a hydroscopic beige solid which was contaminated by an unknown impurity (~10%); R_f = 0.6 (90:10 CH_2Cl_2:MeOH); ^1H NMR (400 MHz, $CDCl_3$) δ: 12.16 (1H, s, CH $_{Imidazolium}$), 7.24 (2H, CH $_{Imidazolium}$), 7.06 (2H, m, ArCH), 6.49 (2H, dddd, J = 11.0, 8.5, 5.5 and 3.0 Hz, ArCH), 5.49 (2H, d, J = 8.0 Hz, H-1), 5.31 (2H, *app*. t, J = 9.5 Hz, H-3), 4.09 (2H, dd, J = 10.5 and 8.0 Hz, H-2), 3.92 (2H, *app.* dt, J = 10.0 and 2.5 Hz, H-5), 3.71-3.66 (6H, m, H-4 & H-6a & H-6b), 3.42 (6H, s, OCH_3), 3.33 (6H, s, OCH_3), 3.24 (6H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.6 (ddd, J = 245.5, 14.0 and 3.65 Hz, ArCF), 150.8 (ddd, J = 249.0, 15.5 and 12.5 Hz, ArCF), 148.1-147.8 (m, ArC), 134.4 (ddd, J = 243.0, 14.5 and 5.5 Hz, ArCF), 136.4 (CH $_{Imidazolium}$), 123.0 (CH $_{Imidazolium}$), 101.1 (dd, J = 27.5 and 3.5, ArCH), 99.9 (C-1), 98.8 (dd, J = 27.5 and 21.5 Hz, ArCH), 83.0 (C-3), 79.4 (C-4), 74.1 (C-5), 70.0 (C-6), 66.4 (C-2), 60.3 (OCH_3), 59.4 (OCH_3), 57.2 (OCH_3); $_{19}F$ NMR (377 MHz, $CDCl_3$) δ: -112.7 (q, J = 9.5 Hz, ArCF), -133.6 (dd, J = 20.5 and 10.0 Hz, ArCF), 163.7 (ddt, J = 22.0, 11.5 and 6.0 Hz, ArCF); *m/z* HRMS (ESI): Found $[M]^+$ 737.2522, $C_{33}H_{39}F_6N_2O_{10}$ requires 737.2503.

1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(4'-phenyl-2',3',5',6'-tetrafluoro)benzene-2-deoxy-β-D-glucopyranoside)imidazolium chloride (16d):

Following General Procedure C. Bis(imine) **15d** (310 mg, 0.34 mmol); FCC (98:2 to 95:5 CH_2Cl_2:MeOH) yielded **16d** (169 mg, 52%) as a tan amorphous solid; R_f = 0.4 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 2935, 2850, 1512, 1488, 1441, 1196, 1136, 1084, 1071; ^1H NMR (500 MHz, $CDCl_3$) δ: 12.51 (1H, s, CH $_{Imidazolium}$), 7.48-7.36 (10H, m, ArCH), 7.21 (2H, d, J = 1.5 Hz, CH $_{Imidazolium}$), 6.02 (2H, d, J = 8.5 Hz, H-1), 5.06 (2H, dd, J = 10.5 and 8.5 Hz, H-3), 4.25 (2H, dd, J = 10.5 and 8.5 Hz, H-2), 3.95 (2H, *app*. dt, J = 10.0 and 2.0 Hz, H-5), 3.89 (2H, br t, J = 9.0 Hz, H-4), 3.74 (2H, dd, J = 11.0 and 2.0 Hz, H-6a), 3.66 (6H, s, OCH_3), 3.62 (2H, dd, J = 11.0 and 2.5 Hz, H-6b), 3.44 (6H, s, OCH_3), 3.36 (6H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.2 (ddd, J = 247.5, 6.5 and 2.5 Hz, ArCF), 141.1 (ddt, J = 246.5, 15.5 and 4.5 Hz, ArCF), 137.6 (CH $_{Imidazolium}$), 136.0 (tt, J = 12.0 and 3.0 Hz, ArC), 130.2 (ArCH), 129.2 (ArCH), 128.7 (ArCH), 127.0 (ArC), 123.0 (CH $_{Imidazolium}$), 115.5 (t, J = 17.0 Hz, ArC), 99.7 (C-1), 85.8 (C-3), 80.0 (C-4), 73.6 (C-5), 70.2 (C-6), 66.8 (C-2), 59.7 (OCH_3), 59.3 (OCH_3), 57.5 (OCH_3); ^{19}F NMR (470 MHz, $CDCl_3$) δ: -144.4 (dd, J = 22.5 and 8.5 Hz, ArCF), -157.0 (dd, J = 23.0 and 8.5 Hz, ArCF); *m/z* HRMS (ESI): Found $[M\text{-}Cl]^+$ 925.2944, $C_{45}H_{45}N_2F_8O_{10}$ requires 925.2941; $[\alpha]^{21}_D$ = 32 (*c* 0.6, $CHCl_3$).

1,3-Bis(methyl 2-amino-4,6-di-*O*-methyl-3-*O*-1'-(4'-cyano)naphthlene-2-deoxy-β-D-glucopyranoside)imidazolium chloride (16e):

Following General Procedure C. Bis(imine) **15e** (200 mg, 0.26 mmol); FCC (95:5 PhMe:MeOH) yielded **16e**(164 mg, 77%) as a tan amorphous solid; R_f = 0.3 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 2939, 2219, 1577, 1509, 1463, 1388, 1324, 1246, 1084; ^1H NMR (500 MHz, $CDCl_3$) δ: 12.35 (1H, s, CH $_{Imidazolium}$), 8.12 (2H, dt, *J* = 8.5 and 1.0 Hz, ArCH), 8.10 (2H, dt, *J* = 8.5 and 1.0 Hz, ArCH), 7.86 (2H, d, *J* = 8.5 Hz, ArCH), 7.67-7.63 (4H, m, ArCH), 7.53 (2H, ddd, *J* = 8.5, 7.0 and 1.0 Hz, ArCH), 6.93 (2H, d, *J* = 1.5 Hz, CH $_{Imidazolium}$), 6.08 (2H, dd, *J* = 10.5 and 8.5 Hz, H-3), 5.12 (2H, d, *J* = 8.0 Hz, H-1), 4.11 (2H, dd, *J* = 10.5 and 8.0 Hz, H-2), 3.99 (2H, dt, *J* = 10.0 and 2.5 Hz, H-5), 3.74 (2H, dd, *J* = 10.0 and 8.5 Hz, H-4), 3.69-3.67 (4H, m, H-6a & H-6b), 3.40 (6H, s, OCH_3), 3.14 (6H, s, OCH_3), 2.78 (6H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.0 (ArCOR), 136.1 (CH $_{Imidazolium}$), 134.3 (ArCH), 133.5 (ArC), 129.0 (ArCH), 127.0 (ArCH), 125.2 (ArCH), 124.7 (ArC), 122.8 (CH $_{Imidazolium}$), 121.8 (ArCH), 117.8 (ArC*C*N), 107.0 (ArCH), 102.9 (Ar*C*CN), 100.2 (C-1), 79.5 (C-3), 79.4 (C- 4), 74.1 (C-5), 69.8 (C-6), 66.4 (C-2), 60.3 (OCH_3), 59.3 (OCH_3), 56.7 (OCH_3); *m/z* HRMS (ESI): Found $[M-Cl]^+$ 779.3292, $C_{43}H_{47}N_4O_{10}$ requires 779.3287; $[\alpha]^{21}_D$ = 91 (*c* 0.7, $CHCl_3$).

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

Following General Procedure D with some modifications. NHC.HCl **9b** (40 mg, 43 μmol); sealed tube and heated at 100 °C for 16 h; FCC (100:0 to 99:1 CH_2Cl_2:MeOH) yielded **12b** (35.1 mg, 72%) as an orange oil; R_f = 0.8 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 2934, 1610, 1468, 1386, 1276, 1171, 1132, 1032, 1010; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.88 (2H, s, ArCH), 7.41 (1H, s, ArCH), 7.38 (1H, s, ArCH), 7.22 (2H, s, ArCH), 6.95 (1H, d, *J* = 2.0 Hz, CH $_{Imidazolylidene}$), 6.80 (1H, s, CH $_{Imidazolylidene}$), 6.35 (1H, br s, H-$_{Carbohydrate}$), 5.50 (1H, br s, H-$_{Carbohydrate}$), 5.17-5.11 (1H, m, CH $_{COD}$), 4.94(1H, br s, CH $_{COD}$), 4.66 (1H, br s, H-$_{Carbohydrate}$), 4.55 (1H, *app*. d, *J* = 9.0 Hz, H-$_{Carbohydrate}$), 4.47 (1H, d, *J* = 8.0 Hz, H-$_{Carbohydrate}$), 4.06-3.99 (1H, m, H-$_{Carbohydrate}$), 3.99-3.94 (1H, m, CH $_{COD}$), 3.85-3.72 (3H, m, H-$_{Carbohydrate}$ & H-$_{Carbohydrate}$ & H-6a & H-6b), 3.70-3.61 (H-$_{Carbohydrate}$ & H-6a & H- 6b), 3.49 (3H, s, OCH_3), 3.46 (3H, s, OCH_3), 3.45 (3H, s, OCH_3), 3.41 (3H, s, OCH_3), 3.35 (3H, s, OCH_3), 3.28 (3H, s, OCH_3), 3.17 (1H, br s, CH $_{COD}$), 2.43-2.32 (4H, m, C*H*H $_{COD}$), 1.97-1.76 (4H, m, CH*H* $_{COD}$). *Only observed 13 carbohydrate protons*. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 189.2 (*app*. br s, C $_{Carbene}$), 160.1 (ArC), 159.5 (ArC), 132.9 (q, *J* = 33.5 Hz, Ar*C*CF_3), 132.4 (q, *J* = 33.5 Hz, Ar*C*CF_3), 123.2 (q, *J* = 272.5 Hz, ArC*C*F_3), 123.1 (q, *J* = 272.5 Hz, ArC*C*F_3), 118.8 (br s, CH $_{Imidazolylidene}$), 117.7 (CH $_{Imidazolylidene}$ & ArCH), 116.3 (br, ArCH), 115.5 (m, ArCH), 103.2 (C-$_{Carbohydrate}$), 101.8 (C-$_{Carbohydrate}$), 99.2 (d, *J* = 5.5 Hz, CH $_{COD}$), 98.3 (d, *J* = 7.0 Hz, CH $_{COD}$), 83.0 (C-$_{Carbohydrate}$ & C-$_{Carbohydrate}$), 78.8 (C-$_{Carbohydrate}$), 78.2 (C-$_{Carbohydrate}$), 75.9 (C-$_{Carbohydrate}$), 75.8 (C-$_{Carbohydrate}$), 73.5 (C-6), 71.3 (C-6), 69.9-69.5 (m, CH $_{COD}$ & CH $_{COD}$), 67.4, 64.3 (C-$_{Carbohydrate}$), 60.6 (OCH_3), 60.2 (OCH_3), 59.6 (OCH_3), 59.4 (OCH_3), 57.1 (OCH_3), 56.8 (OCH_3), 33.1 (CH_2 $_{COD}$), 32.5 (CH_2 $_{COD}$), 29.1 (CH_2 $_{COD}$) 28.9 (CH_2 $_{COD}$); ^{19}F NMR (283 MHz, $CDCl_3$) δ: -62.6 (CF_3), -63.0 (CF_3); *m/z* HRMS (ESI): Found $[M-Cl]^+$ 1111.2472, $C_{45}H_{52}F_{12}N_2O_{10}Rh$ requires 1111.2480; $[\alpha]^{21}_D$ = -47 (*c* 1.2, $CHCl_3$).

[1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',6'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (17a):

Following General Procedure D with some modifications. NHC.HCl **16a**(45 mg, 0.046 mmol); sealed tube and heated at 100 °C for 16 h; FCC (100:0 to 98:2 CH_2Cl_2:MeOH) yielded **291c** (21.8 mg, 40%) as an orange oil; R_f = 0.5 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 2937, 2835, 1602, 1459, 1343, 1300, 1242, 1210, 1165, 1128, 1088; ^{1}H NMR (500 MHz, $CDCl_3$) *observed peaks* δ: 7.84 (4H, m, ArCH), 7.23-7.17 (2H, m, ArCH), 7.11 (1H, d, *J* = 2.0 Hz, CH Imidazolylidene), 7.05 (1H, d, *J* = 2.0 Hz, CH Imidazolylidene), 6.44 (1H, d, *J* = 5.0 Hz, H-Carbohydrate), 5.19 (1H, br s, H- Carbohydrate), 5.04 (1H, s, H-Carbohydrate), 4.95 (1H, q, *J* = 7.5 Hz, CH COD), 4.89-4.84 (3H, m, H-Carbohydrate & H-Carbohydrate & CH COD), 4.39 (1H, t, *J* = 9.5 Hz, H-Carbohydrate), 3.89 (1H, t, *J* = 9.5 Hz, H-Carbohydrate), 3.85 (1H, m, CH COD), 3.78-3.74 (1H, m, CH COD), 3.74-3.69 (2H, m, H-Carbohydrate & H-6a), 3.68-3.63 (2H, m, H-Carbohydrate & H-6b), 3.59-3.53 (H-6a & H-6b), 3.52 (3H, s, OCH_3), 3.49 (3H, s, OCH_3), 3.44 (3H, s, OCH_3), 3.39 (3H, s, OCH_3), 2.86 (6H, s, OCH_3), 2.59-2.51 (1H, m, C*H*H COD), 2.46 (1H, ddt, *J* = 15.0, 10.0 and 7.5 Hz, C*H*H COD), 2.37-2.21 (2H, m, C*H*H COD & C*H*H COD), 2.01 (1H, dd, *J* = 16.0 and 7.0 Hz, CH*H* COD), 1.91-1.84 (1H, m, CH*H* COD), 1.81-1.70 (2H, m, CH*H* COD & CH*H* COD); ^{13}C NMR (125 MHz, $CDCl_3$) *observed peaks* δ: 185.8 (d, *J* = 47.5 Hz, C Carbene), 155.4 (ArC), 154.1 (ArC), 132.0 (ArCH), 131.4 (ArCH), 130.9 (ArCH), 122.9 (ArCH), 122.6 (ArCH), 121.5(CH Imidazolylidene), 118.5 (CH Imidazolylidene), 102.8 (C-1), 102.6 (C-1), 98.5 (d, *J* = 6.5 Hz, CH COD), 97.0 (d, *J* = 5.0 Hz, CH COD), 86.1 (C-Carbohydrate), 85.1 (C-Carbohydrate), 78.6 (C-Carbohydrate), 77.9 (C-Carbohydrate), 76.6 (C-Carbohydrate), 75.8 (C-Carbohydrate), 74.7 (C-6), 71.4 (C-6), 70.6 (d, *J* = 14.0 Hz, CH COD), 67.5 (C-Carbohydrate), 66.8 (d, *J* = 13.0 Hz, CH COD), 65.0 (C-Carbohydrate), 59.4 (OCH_3), 59.3 (OCH_3), 58.6 (OCH_3), 58.3 (OCH_3), 57.6 (OCH_3), 56.6 (OCH_3), 33.7 (CH_2 COD), 31.8 (CH_2 COD), 29.9 (CH_2 COD), 27.9 (CH_2 COD); ^{19}F NMR (470 MHz, $CDCl_3$) δ: -58.8 (CF_3), -59.0 (CF_3); *m/z* HRMS (ESI): Found $[M-Cl]^+$ 1111.2495, $C_{45}H_{52}N_2O_{10}Rh$ requires 1111.2480; $[\alpha]^{23}_D$ = 31 (*c* 0.6, $CHCl_3$).

[1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',4'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside](chloro)(1,5-cyclooctadiene)rhodium(I) (17b):

Following General Procedure D with some modifications. NHC.HCl **16b** (50 mg, 53 μmol); sealed tube and heated at 100 °C for 16 h; FCC (100:0 to 95:5 CH_2Cl_2:MeOH) yielded **17b** (60.8 mg, 99%) as an orange oil; R_f = 0.7 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 2937, 1627, 1595, 1509, 1347, 1315, 1284, 1262, 1220, 1178, 1125, 1084, 1054; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.93 (1H, br s, ArCH), 7.85 (1H, d, *J* = 2.5 Hz, ArCH), 7.77 (1H, dd, *J* = 9.0 and 2.5 Hz, ArCH), 7.69 (1H, d, *J* = 2.5 Hz, ArCH), 7.57 (1H, dd, *J* = 9.0 and 2.5 Hz, ArCH), 7.22 (1H, d, *J* = 2.0 Hz, CH Imidazolylidene), 7.16 (1H, d, *J* = 9.0 Hz, ArCH), 6.78 (1H, d, *J* = 2.0 Hz, CH Imidazolylidene), 6.33 (1H, br s, H-carbohydrate), 6.17 (1H, br s, H-carbohydrate), 4.99 (1H, tt, *J* = 9.0 and 2.5 Hz, CH COD), 4.95 (1H, br s, H-carbohydrate), 4.79 (1H, br s, H-carbohydrate), 4.66 (1H, q, *J* = 7.5 Hz, CH COD), 4.28 (1H, br s, H-carbohydrate), 4.07 (1H, *app*. dt, *J* = 7.0 and 1.5 Hz, H-carbohydrate), 3.93 (1H, ddd, 10.0, 4.0 and 2.0 Hz, H-5), 3.78 (1H, dd, *J* = 11.0 and 2.0 Hz, H-6a), 3.73 (1H, dd, *J* = 10.0 and 6.5 Hz, H-6a), 3.72 (1H, dd, *J* = 11.0 and 4.0 Hz, H-6b), 3.66-3.61 (1H, m, H-carbohydrate), 3.61 (3H, s, OCH_3), 3.56 (1H, dd, *J* = 10.0 and 7.0 Hz, H-6b), 3.50 (3H, s, OCH_3), 3.48 (3H, s, OCH_3), 4.43 (1H, br s, H-carbohydrate), 3.36 (2H, br s, CH COD), 3.28 (3H, s, OCH_3), 3.15 (3H, s, OCH_3), 2.71 (3H, s, OCH_3), 2.61 (1H, br s, CH_2 COD), 2.55-2.46 (1H, m, CH_2 COD), 2.24-2.11 (2H, m, CH_2 COD), 2.06-1.93 (2H, m, CH_2 COD), 1.77-1.69 (1H, m, CH_2 COD), 1.63-1.57 (1H, m, CH_2 COD). *Only observed 13 carbohydrate protons.* ^{13}C NMR (125 MHz, $CDCl_3$) *observed peaks* δ: 183.7 (br d, *J* = 50.0 Hz, C Imidazolylidene), 158.5 (ArCOR), 157.0 (ArCOR), 130.8 (d, *J* = 4.0 Hz, ArCH), 130.0 (d, *J* = 4.0 Hz, ArCH), 125.1 (br s, ArCH), 123.9 (br s, ArCH), 123.8 (q, *J* = 271.0 Hz, ArC*C*F_3), 123.7 (q, *J* = 271.0 Hz, ArC*C*F_3), 123.0 (q, *J* = 32.0 Hz, ArC*C*F_3), 122.3 (q, *J* = 33.0 Hz, ArC*C*F_3),

119.5 (br s, CH Imidazolylidene), 119.5 (br s, CH Imidazolylidene), 119.2 (q, *J* = 32.0 Hz, ArC*C*F$_3$), 118.0 (q, *J* = 32.0 Hz, ArC*C*F$_3$), 116.5 (br s, ArCH), 113.8 (s, ArCH), 100.3 (C carbohydrate), 98.8 (d, *J* = 7.0 Hz, CH COD), 98.0 (d, *J* = 7.0 Hz, CH COD), 81.7 (C carbohydrate), 80.0 (C carbohydrate), 75.7 (C carbohydrate), 74.5 (C carbohydrate), 74.2 (C carbohydrate), 73.4 (C carbohydrate), 72.4 (C carbohydrate), 71.0 (C carbohydrate), 67.9 (d, *J* = 16.0 Hz, CH COD), 67.6 (C carbohydrate), 62.5 (C carbohydrate), 56.0 (OCH$_3$), 59.52 (OCH$_3$), 59.47 (C carbohydrate), 59.0 (OCH$_3$), 56.8 (OCH$_3$), 56.5 (OCH$_3$), 54.8 (OCH$_3$), 33.7 (CH$_2$ COD), 31.5 (CH$_2$ COD), 31.0 (CH$_2$ COD), 27.1 (CH$_2$ COD); ^{19}F NMR (470 MHz, CDCl$_3$) δ: -61.89 (CF$_3$), -61.92 (CF$_3$), -62.1 (CF$_3$), -62.3 (CF$_3$); *m/z* HRMS (ESI): Found [M-Cl]$^+$ 1111.2456, $C_{45}H_{52}F_{12}N_2O_{10}Rh$ requires 1111.2480; $[\alpha]^{21}_D$ = 81 (*c* 1.9, CHCl$_3$).

[1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',3',5'-trifluoro)benzene-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (17c):

Following General Procedure D. NHC.HCl **16c** (20.0 mg, 26.0 μmol), FCC (100:0 to 98:2 CH$_2$Cl$_2$:MeOH) yielded **17c** (15.5 mg, 69%) as an orange oil which was contaminated by an unknown impurity (~10%); R_f = 0.7 (90:10 CH$_2$Cl$_2$:MeOH); ν_{max} / cm^{-1} (film): 2924, 1632, 1515, 1453, 1124, 1087; ^{1}H NMR (500 MHz, CDCl$_3$) *observed peaks* δ: 7.10 (1H, d, *J* = 2.0 Hz, CH Imidazolylidene), 6.92 (1H, d, *J* = 2.0 Hz, CH Imidazolylidene), 6.85-6.68 (2H, m, ArCH), 6.52-6.41 (2H, m, ArCH), 5.05-4.97 (2H, m), 4.90-4.84 (2H, m), 4.83-4.68 (1H, br s), 3.97-3.92 (1H, m), 3.89-3.85 (1H, br s), 3.81-3.62 (8H, m), 3.59-3.53 (3H, m), 3.51-3.45 (8H, m), 3.43-3.36 (7H, m), 3.30-3.20 (3H, br s), 2.59-2.46 (1H, br s), 2.46 (3H, m), 2.03-1.80 (4H, m); ^{13}C NMR (125 MHz, CDCl$_3$) *observed peaks* δ: 171.12, 137.85, 129.02, 128.20, 125.28, 122.90 (br, CH Imidazolylidene), 99.75, 79.33, 79.25, 77.27, 77.01, 76.76, 76.08, 73.89, 72.07, 70.11, 69.89, 66.73, 66.28, 64.17, 60.38, 60.28, 60.14, 59.35, 59.34, 59.26, 59.18, 57.07, 57.00, 32.54, 31.92, 29.69, 29.65, 29.35, 22.68, 21.44, 21.03, 14.19, 14.10; ^{19}F NMR (377 MHz, CDCl$_3$) δ: -114.3 (q, *J* = 11.0 Hz, ArCF), -119.5 (q, *J* = 11.0 Hz, ArCF), -138.4 (br s, ArCF), -163.7 (br, s, ArCF); *m/z* HRMS (ESI): Found [M]$^+$ 947.2419, $C_{41}H_{50}F_6N_2O_{10}Rh$ requires 947.2410; $[\alpha]^{22}_D$ = 5 (*c* 0.2, CHCl$_3$).

[1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(4'-phenyl-2',3',5',6'-tetrafluoro)benzene-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (17d):

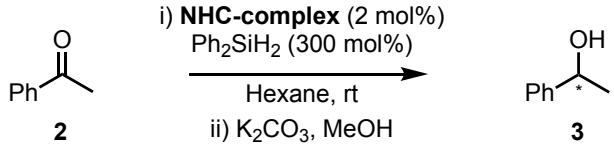
Following General Procedure D with some modifications. NHC.HCl **16d** (52 mg, 54 μmol); sealed tube and heated at 100 °C for 16 h; FCC (100:0 to 98:2 CH$_2$Cl$_2$:MeOH) yielded **17d** (40.6 mg, 64%) as an orange oil; R_f = 0.5 (90:10 CH$_2$Cl$_2$:MeOH); ν_{max} / cm^{-1} (film): 2932, 2834, 1650, 1486, 1440, 1196, 1079; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.41-7.28 (10H, m, ArCH), 7.11-7.08 (2H, m, CH Imidazolylidene), 6.48 (1H, br s, H-Carbohydrate), 5.09-5.04 (2H, m, H-Carbohydrate & CH COD), 4.95-4.82 (3H, m, H-Carbohydrate & H-Carbohydrate & CH COD), 4.18 (1H, *app*. t, *J* = 9.5 Hz, H-Carbohydrate), 3.88 (1H, *app*. t, *J* = 7.0 Hz, H-Carbohydrate), 3.85-3.73 (5H, m, H-Carbohydrate & H-Carbohydrate & CH COD & H-6a & H-6b), 3.69-3.61 (3H, m CH COD & H-6a & H-6b), 3.56 (OCH$_3$), 3.50 (OCH$_3$), 3.48 (OCH$_3$), 3.46 (OCH$_3$), 3,43 (OCH$_3$), 3.36 (OCH$_3$), 2.64-2.32 (4H, m, C*H*H COD), 2.05-1.79 (4H, m, CH*H* COD). *Only observed 13 carbohydrate protons*; ^{13}C NMR (125 MHz, CDCl$_3$) δ: 185.8 (*app*. br s, C Carbene), 144.1 (br d, *J* = 245.0 Hz, ArCF & ArCF), 141.2 (dd, *J* = 246.0 and 15.0 Hz, ArCF), 140.8 (dd, *J* = 247.0 and 16.0 Hz, ArCF), 136.5 (br s, ArC), 135.8 (br s, ArC), 130.2 (ArCH), 130.1 (ArCH), 128.8 (ArCH), 128.7 (ArCH), 128.5 (ArCH), 128.4 (ArCH), 127.3 (ArC), 127.1 (ArC), 117.5 (CH Imidazolylidene & CH Imidazolylidene), 114.5 (t, *J* = 17.0 Hz, ArC), 114.1 (t, *J* = 17.0 Hz, ArC), 103.5 (C-Carbohydrate), 101.9 (C-Carbohydrate), 98.8 (d, *J* = 6.5 Hz, CH COD), 97.1 (br s, CH COD), 84.5 (C-Carbohydrate), 79.4 (C-Carbohydrate), 79.3 (C-Carbohydrate), 77.3 (C-Carbohydrate) ,76.5 (C-Carbohydrate), 75.1 (C-Carbohydrate), 73.8

(C-6), 71.4 (C-6), 70.5 (br s, CH COD), 67.9 (br s, CH COD), 64.87, 60.5 (OCH_3), 59.3 (OCH_3), 59.2 (OCH_3), 57.4 (OCH_3) 56.9 (OCH_3), 33.3 (CH_2 COD), 32.0 (CH_2 COD), 29.7 (CH_2 COD), 28.2 (CH_2 COD); ^{19}F NMR (470 MHz, $CDCl_3$) δ: -145.5 (CF), -145.8 (CF), -156.3 (CF), -157.3 (CF); *m/z* HRMS (ESI): Found $[M\text{-}Cl]^+$ 1135.2867, $C_{53}H_{56}F_8N_2O_{10}Rh$ requires 1135.2857; $[\alpha]^{21}_D$ = -1 (*c* 0.7, $CHCl_3$).

[1,3-Bis(methyl 2-amino-4,6-di-*O*-methyl-3-*O*-1'-(4'-cyano)naphthlene-2-deoxy-β-D-glucopyranoside) imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (17e):

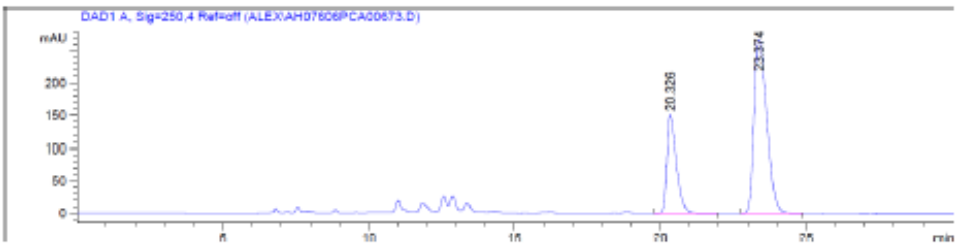
Following General Procedure D with some modifications. NHC.HCl **16e** (28.0 mg, 54.0 μmol); sealed tube and heated at 100 °C for 16 h; FCC (100:0 to 98:2 CH_2Cl_2:MeOH) yielded **17e** (29.3 mg, 82%) as an orange oil; R_f = 0.9 (90:10 CH_2Cl_2:MeOH); ν_{max} / cm^{-1} (film): 3074, 2929, 2834, 2217, 1575, 1462, 1427, 1387, 1323, 1278, 1244, 1228, 1100, 1082, 1061, 1015; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.55 (1H, d *J* = 8.5 Hz, ArCH), 8.30 (1H, d, *J* = 8.5 Hz, ArCH), 8.16 (1H, d, *J* = 8.5 Hz, ArCH), 8.13 (1H, d, *J* = 8.5 Hz, ArCH), 7.84 (1H, d, *J* = 8.0 Hz, ArCH), 7.69-7.56 (5H, m, ArCH), 8.17 (1H, br s, CH Imidazolylidene), 7.05 (1H, br s, CH Imidazolylidene) 6.92 (2H, br s, ArCH), 6.21 (1H, br s, H-Carbohydrate), 5.77 (1H, br s, H-Carbohydrate), 5.11 (1H, br s, H-Carbohydrate), 4.96 (1H, d, *J* = 6.0 Hz, H-Carbohydrate), 4.81 (1H, td, *J* = 8.0 and 4.0 Hz, CH COD), 4.37 (1H, d, *J* = 8.0 Hz, CH COD), 4.00 (1H, td, *J* = 6.0 and 3.0 Hz, H-Carbohydrate), 3.93 (1H, ddd, 9.5, 4.5 and 2.5 Hz, H-Carbohydrate), 3.86 (1H, br s, H-Carbohydrate), 3.77-3.61 (4H, m, H-Carbohydrate), 3.56 (3H, s, OCH_3), 3.54-3.49 (1H, m, H-Carbohydrate), 3.47 (3H, s, OCH_3), 3.45 (3H, s, OCH_3), 3.45-3.28 (4H, m, H-Carbohydrate & H-Carbohydrate & CH COD & CH COD), 3.16 (3H, s, OCH_3), 3.15 (3H, s, OCH_3), 2.79 (3H, s, OCH_3), 2.47-2.29 (2H, m, CHH COD), 2.16-2.09 (1H, m, CHH COD), 1.93-1.80 (3H, m, CHH COD), 1.66-1.56 (2H, m, CHH COD); ^{13}C NMR (125 MHz, $CDCl_3$) *observed peaks* δ: 185.7 (br s, C Carbene), 157.5, 156.7, 134.0, 133.9, 133.8, 133.6, 129.0, 128.9, 126.9, 126.8, 125.5, 125.2, 125.2, 125.1, 123.4, 122.7, 119.6, 118.5, 118.3, 107.48, 106.2, 102.6, 102.1, 100.7, 98.7, 97.7, 81.3, 79.1, 76.8, 76.2, 75.7, 75.5, 75.3, 74.7, 73.5, 73.0, 72.5, 71.9, 70.7, 68.6, 68.1, 67.4, 63.9, 60.2, 59.5, 59.1, 57.6, 57.2, 55.7, 33.2, 32.3, 29.7, 28.1; *m/z* HRMS (ESI): Found $[M\text{-}Cl]^+$ 989.3193, $C_{51}H_{58}N_4O_{10}Rh$ requires 989.3202; $[\alpha]^{21}_D$ = 111 (*c* 0.9, $CHCl_3$).

Asymmetric Catalysis:



General Procedure F. 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** (0.5 mmol, 100 mol%) and the solution was stirred for 18 h. Desilylation was mediated by 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 which yielded the product **alcohol**.

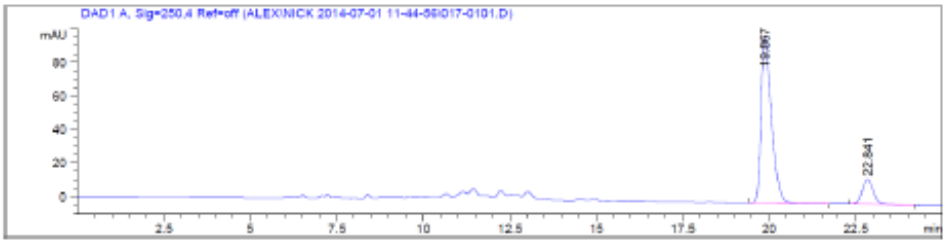
Following General Procedure E. Complex **12a** (9.1 mg); ketone **2** (58.3 μL); FCC (hexane:Et_2O 85:15) yielded **3** (45.8 mg, 75%) as a colourless oil; the enantiomeric excess of **3** was determined by chiral HPLC (Chiralpak IB, hexane:I-PrOH 97:3, 0.5 mL min^{-1}, 20.0 °C); t_R (major) = 18.5 min and t_R (minor) = 20.1 min.



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.326	BB	0.3456	3469.70337	151.28224	29.9830
2	23.374	BB	0.4780	8102.51660	268.55630	70.0170

Following General Procedure E. Complex **17c** (9.8 mg); ketone **2** (58.3 µL); FCC (hexane:Et_2O 85:15) yielded **3** (54.4 mg, 89%) as a colourless oil; the enantiomeric excess of **3** was determined by chiral HPLC (Chiralpak IB, hexane:*i*-PrOH 97:3, 0.5 mL min^{-1}, 20.0 °C); t_R (major) = 18.5 min and t_R (minor) = 20.1 min.



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.867	BB	0.3197	2100.09668	99.72891	86.4289
2	22.841	BBA	0.3418	329.75827	14.92120	13.5711

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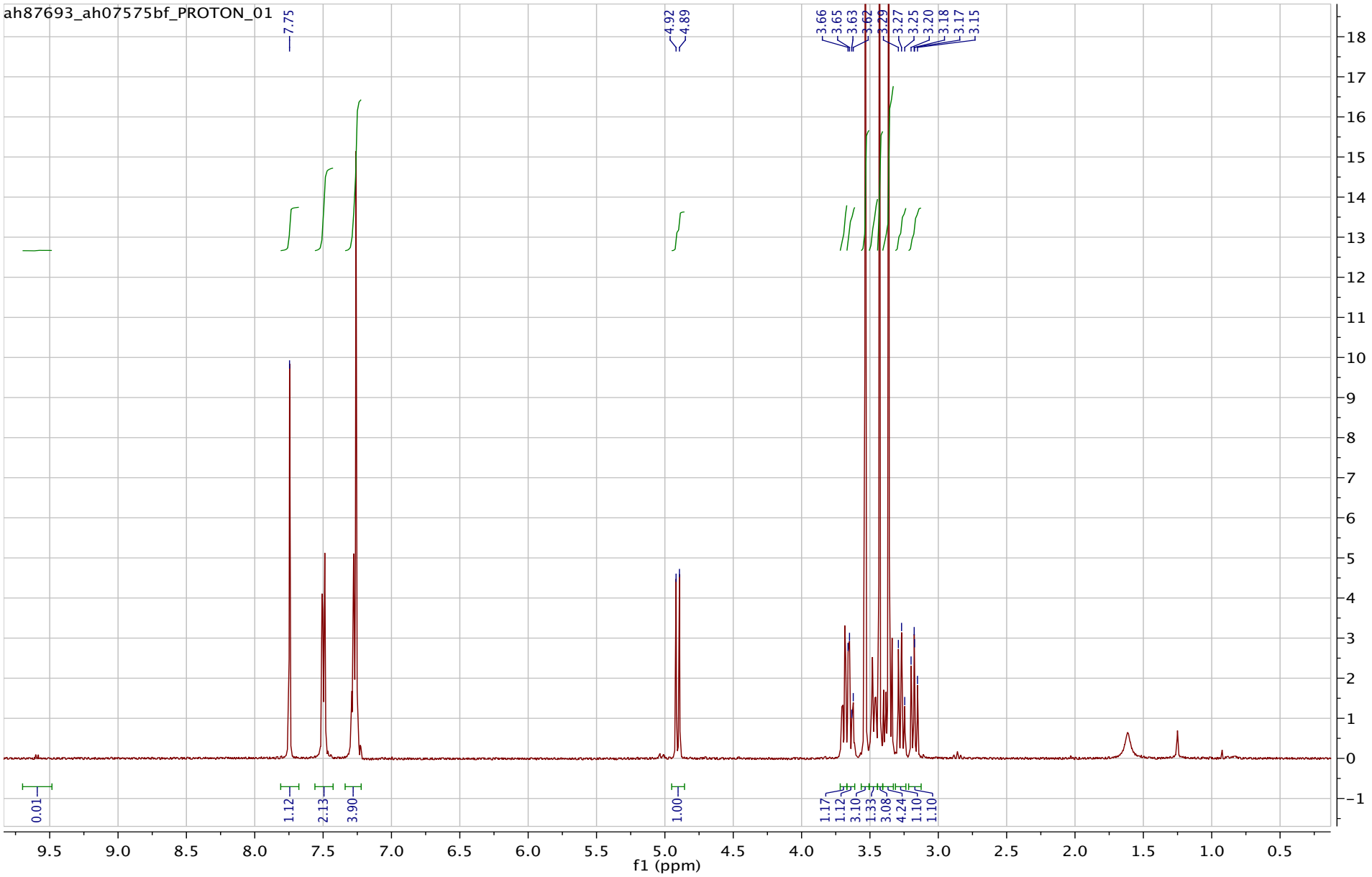
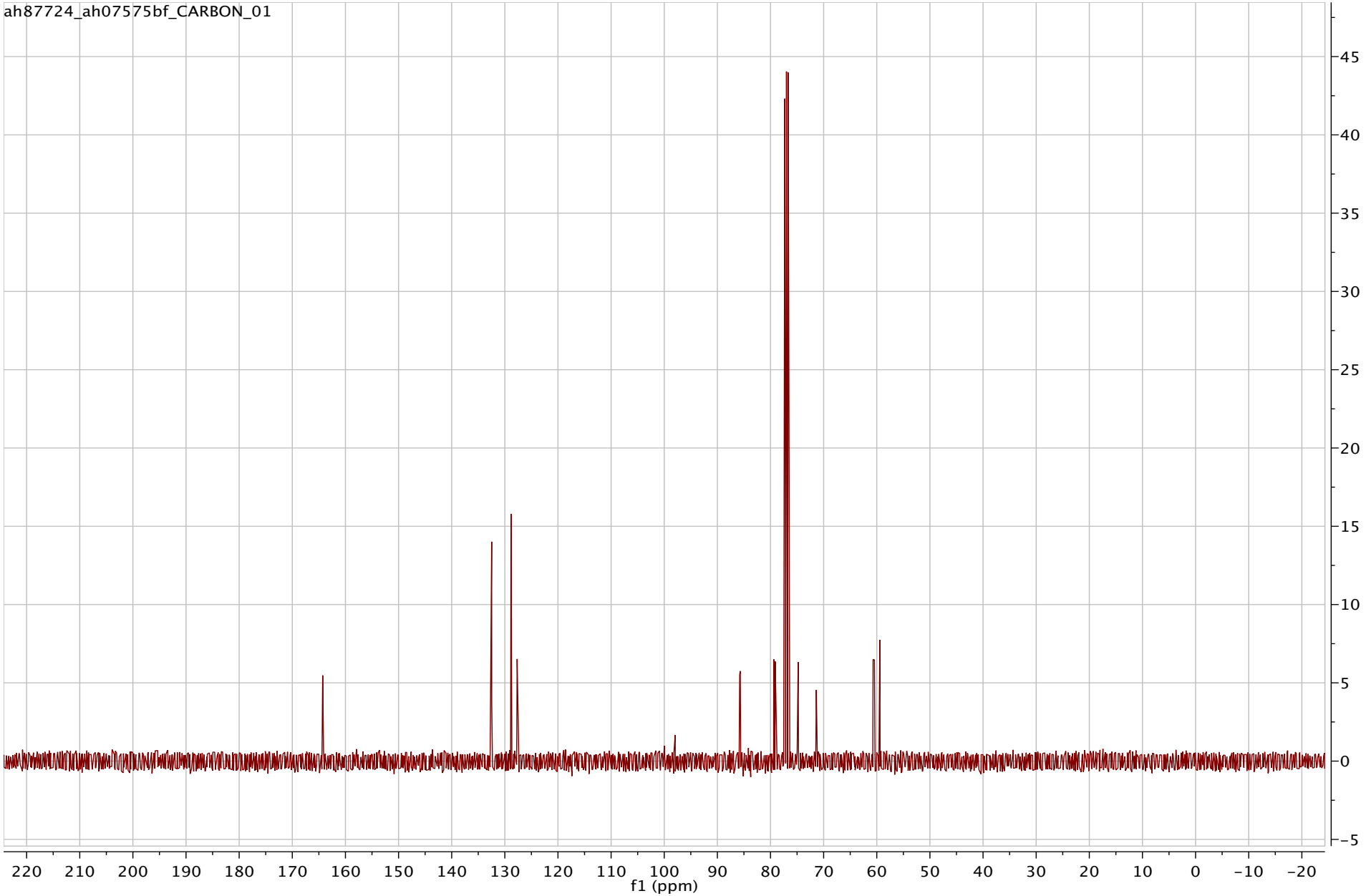
NMR data

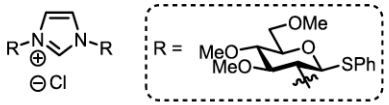
^{1}H NMR (500 MHz, $CDCl_3$) Bis(phenyl 2-amino-3,4,6-tri-*O*-methyl-2,1-dideoxy-1-thio-β-D-glucopyranoside)-*N*,*N*'-iminoethylidene (S4):

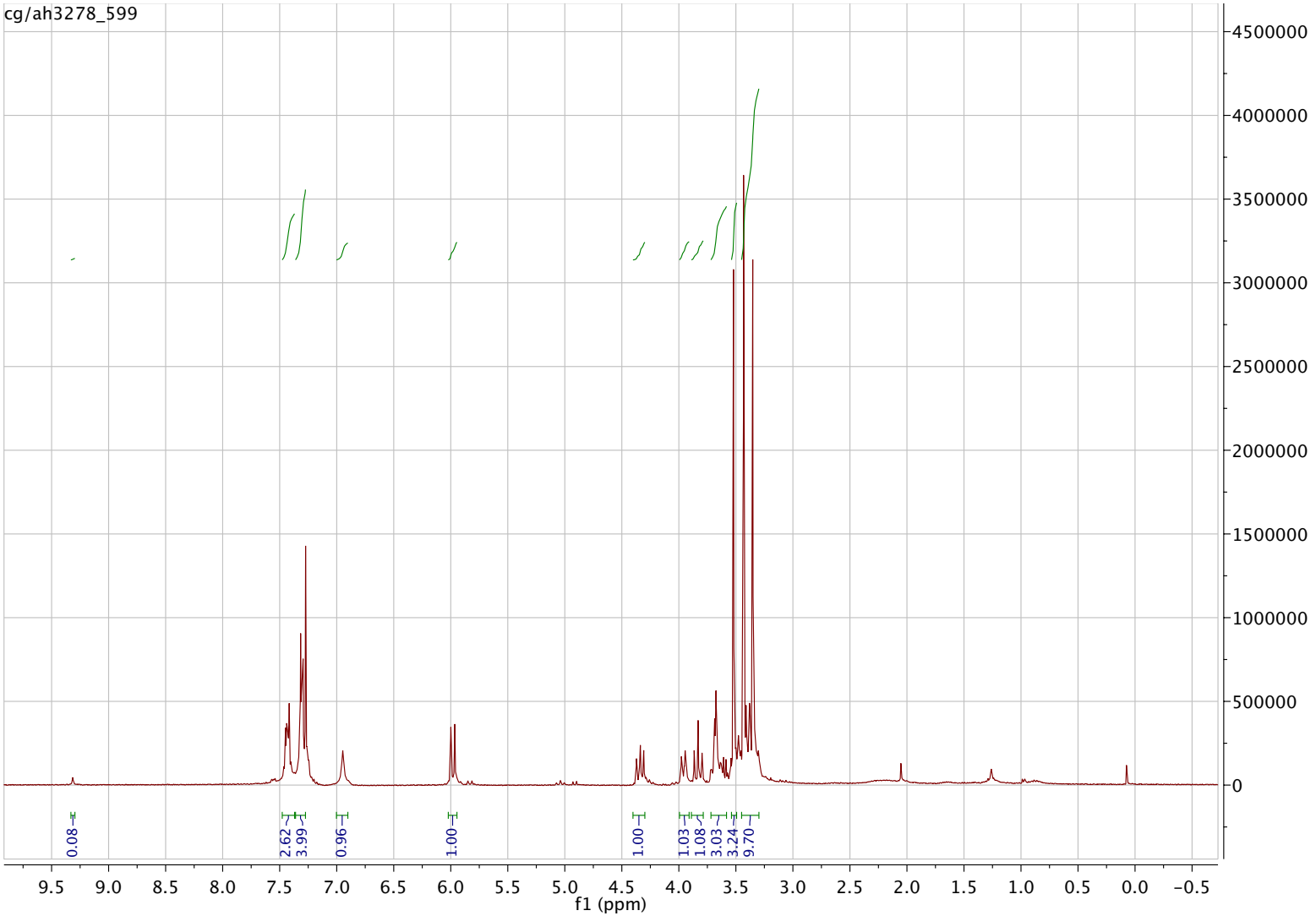


^{13}C NMR (125 MHz, $CDCl_3$)

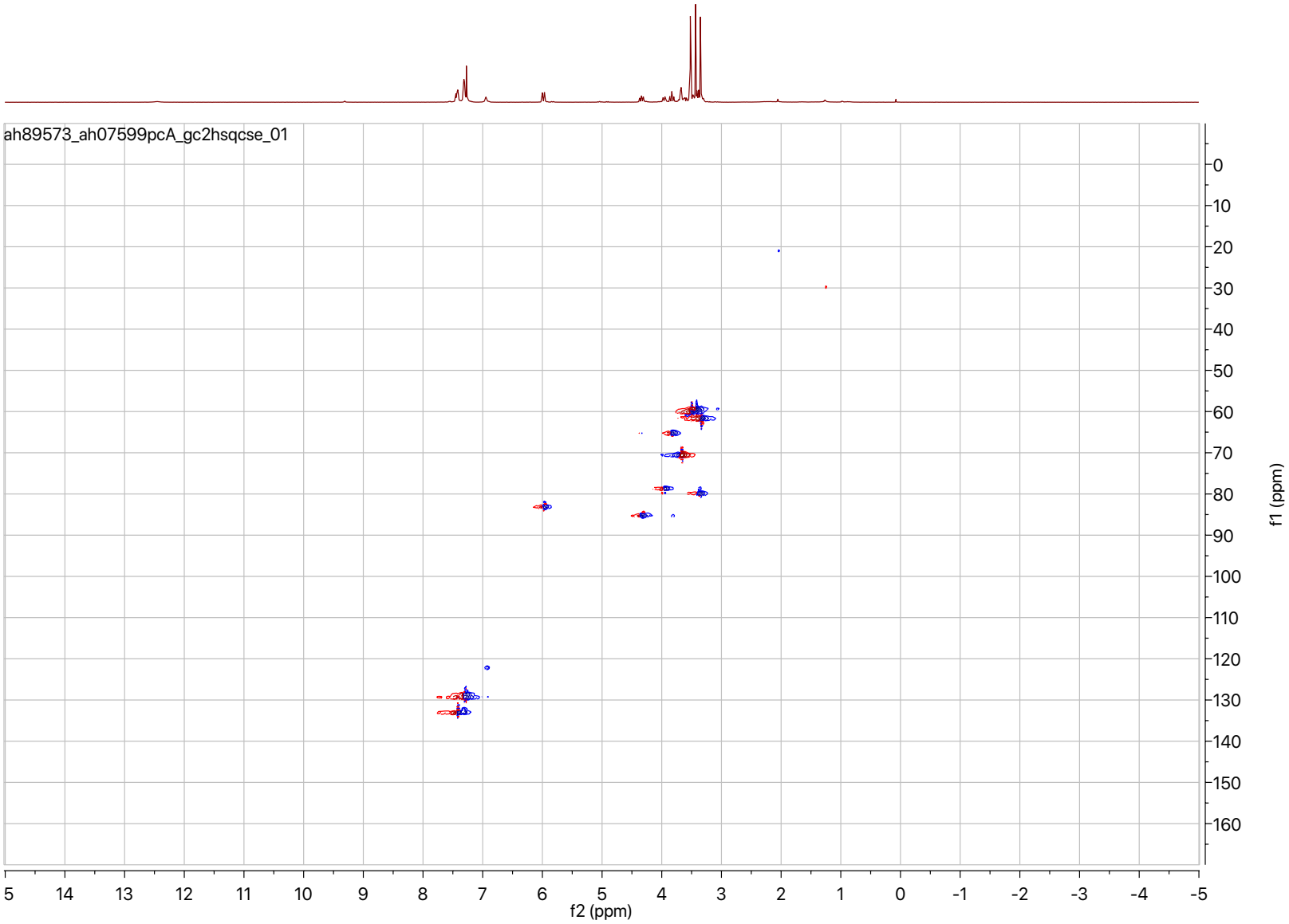


^{1}H NMR (500 MHz, $CDCl_3$) 1,3-Bis(phenyl 2-amino-3,4,6-tri-*O*-methyl-2,1-dideoxy-1-thio-β-D-glucopyranoside)imidazolium chloride (9a).

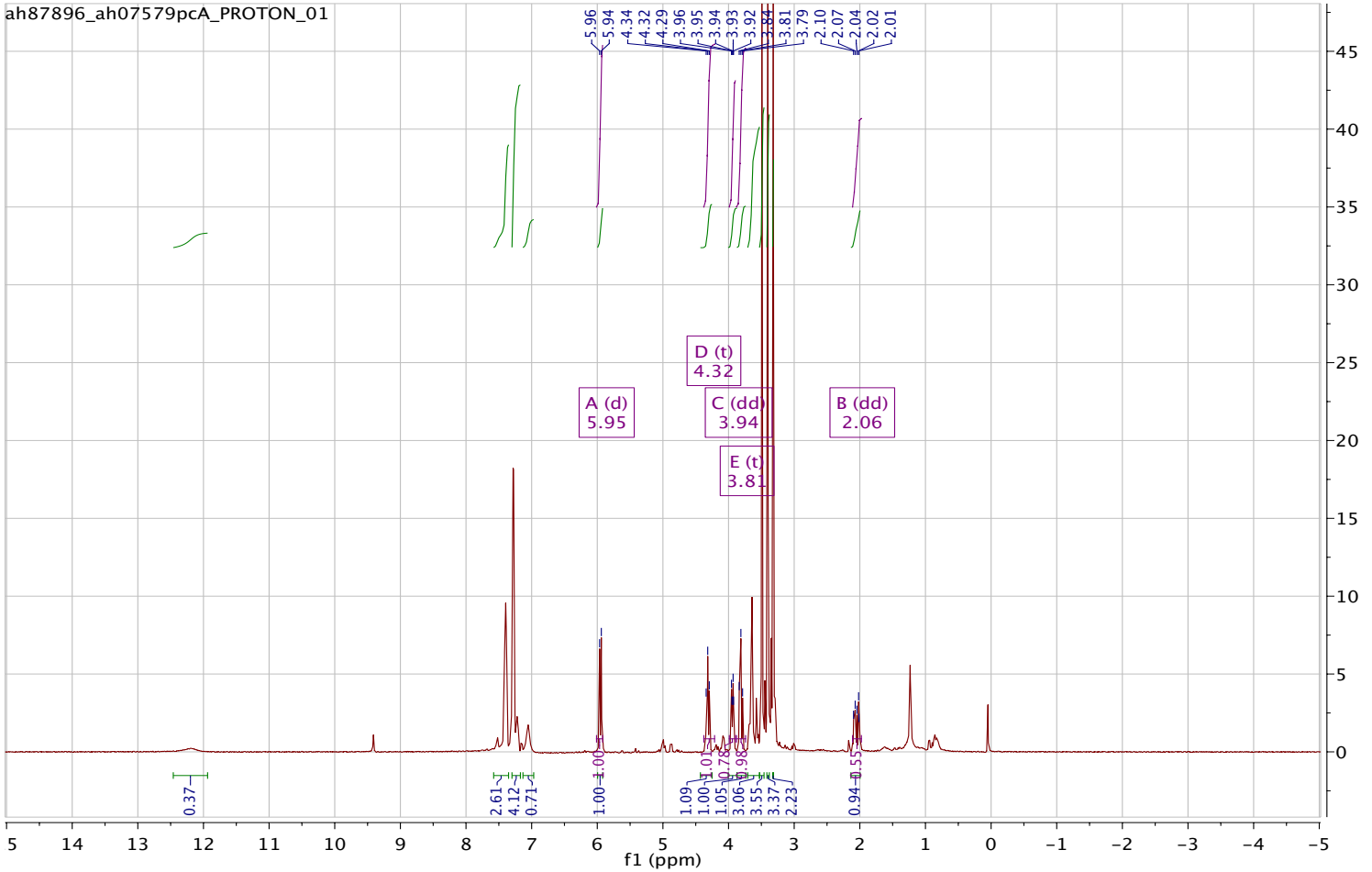




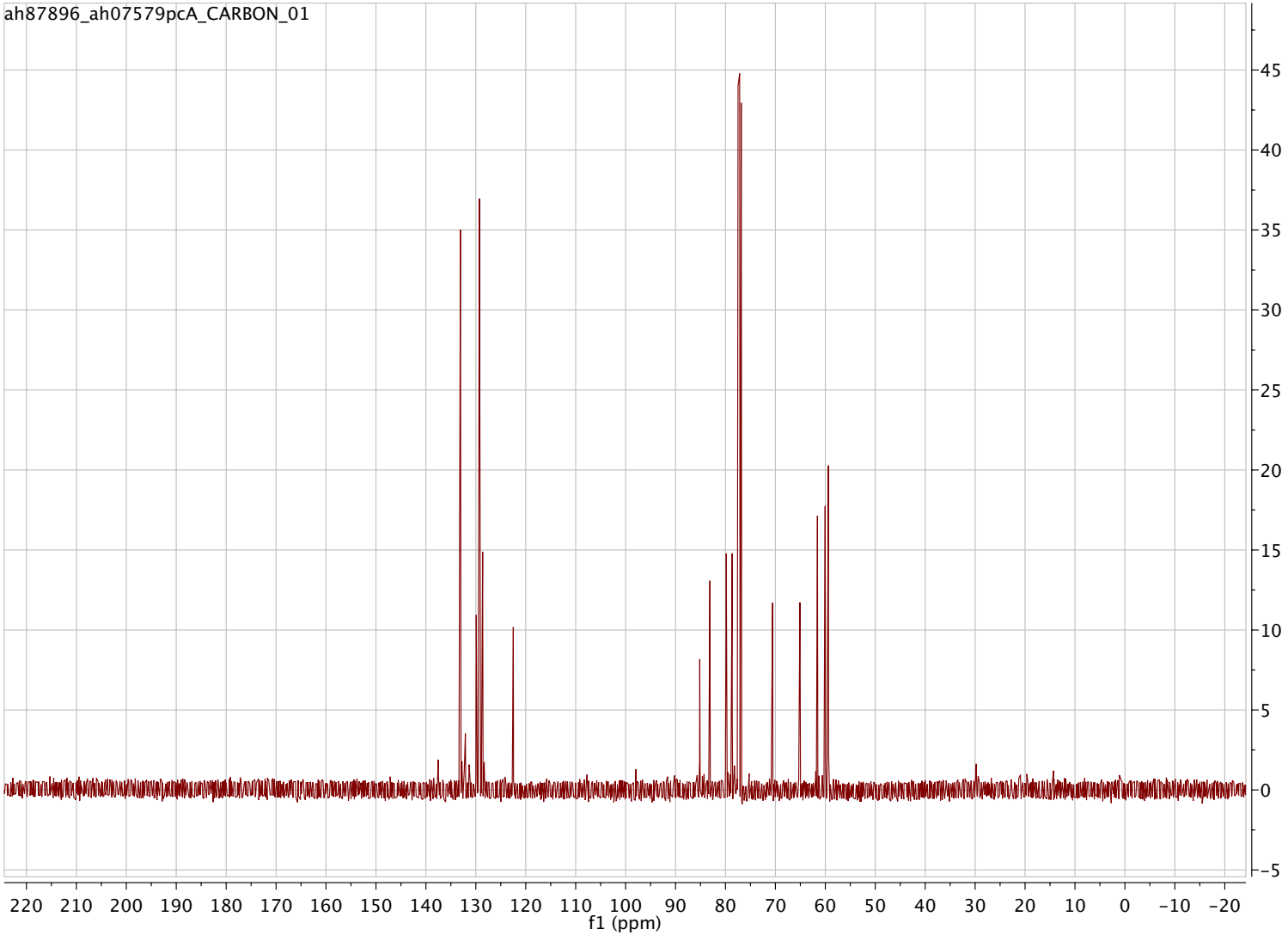
HSQC (CDCl3)



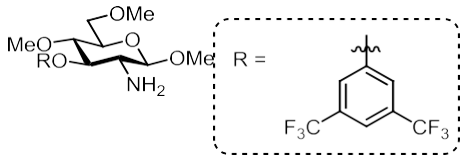
^{1}H NMR (500 MHz, $CDCl_3$) [1,3-Bis(phenyl 2-amino-3,4,6-tri-*O*-methyl-2,1-dideoxy-1-thio-β-D-glucopyranoside)imidazol-2- ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (12a):

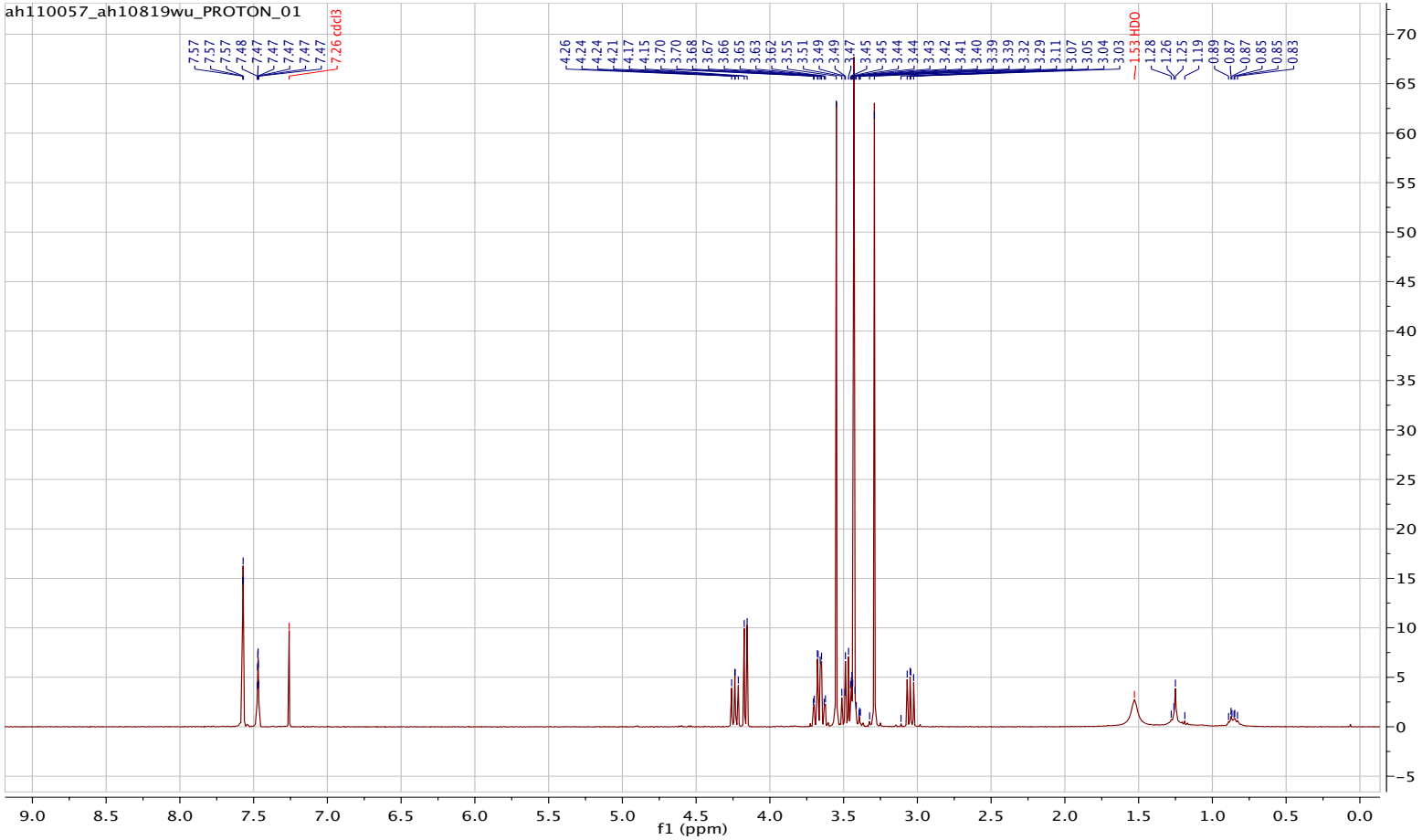


^{13}C NMR (125 MHz, $CDCl_3$)

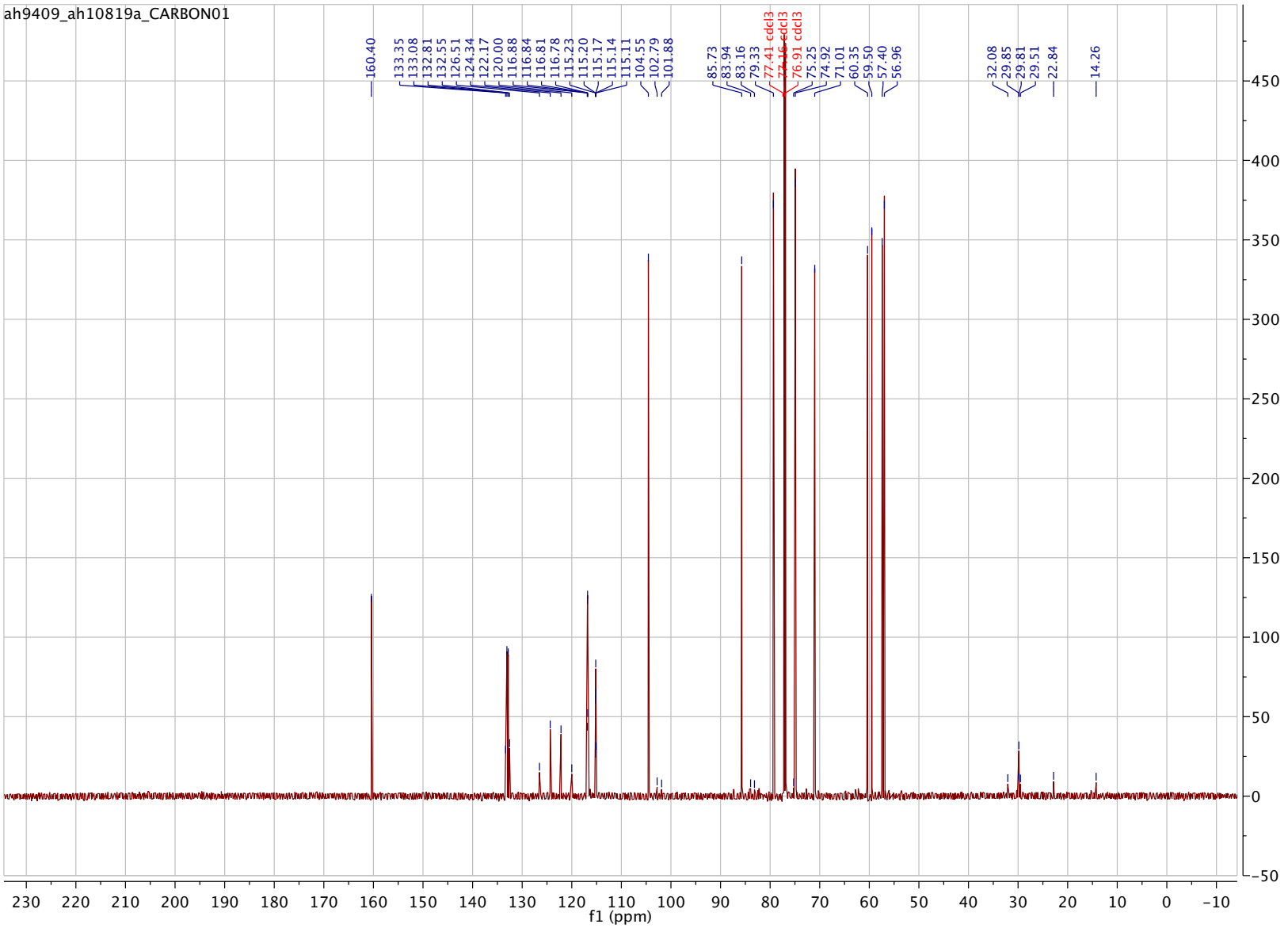


^{1}H NMR (500 MHz, $CDCl_3$) Methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(3',5'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside (8b):

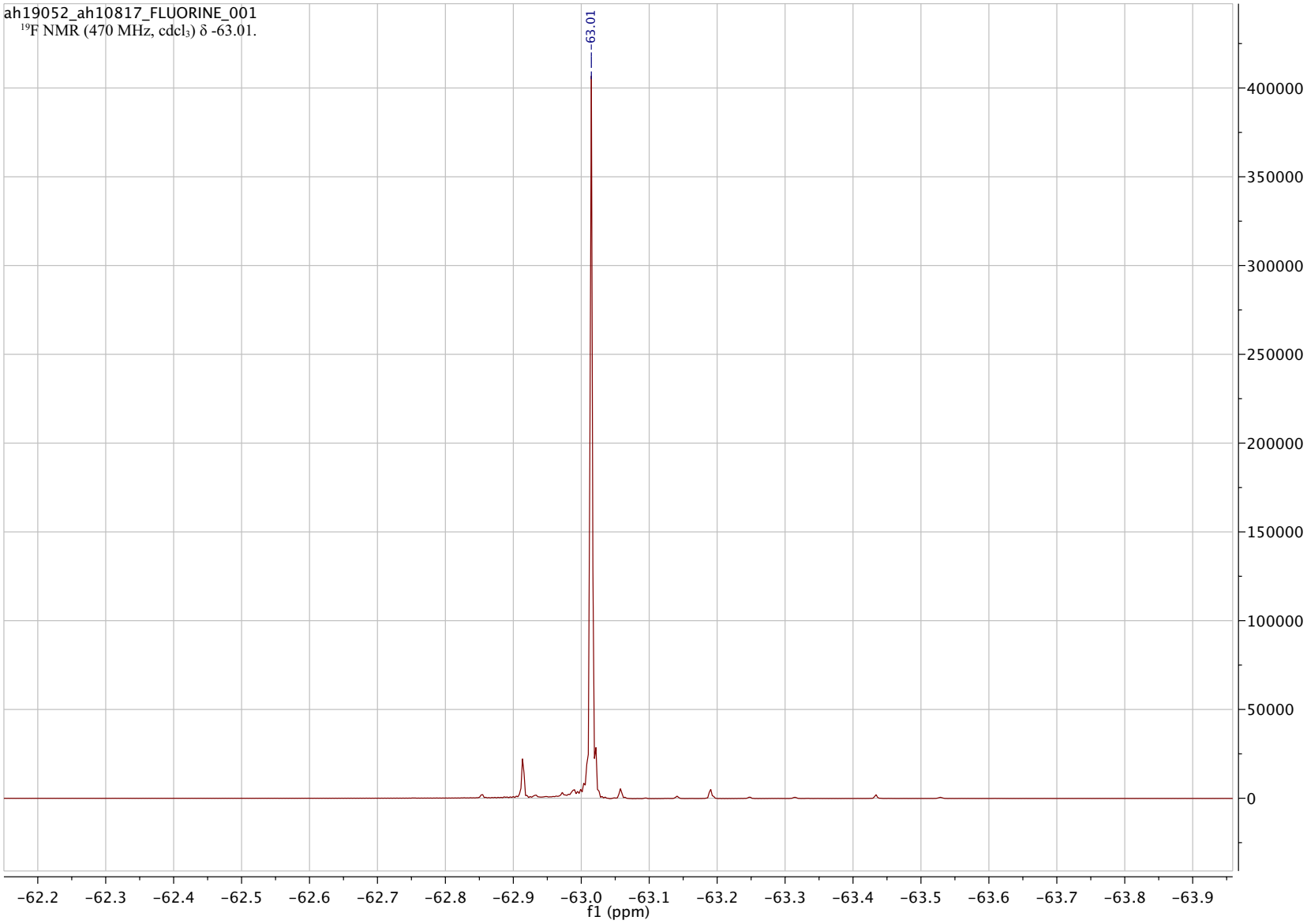




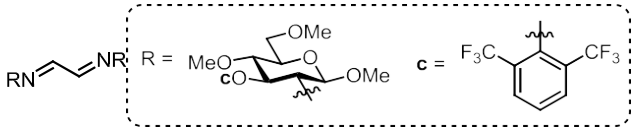
^{13}C NMR (125 MHz, $CDCl_3$)



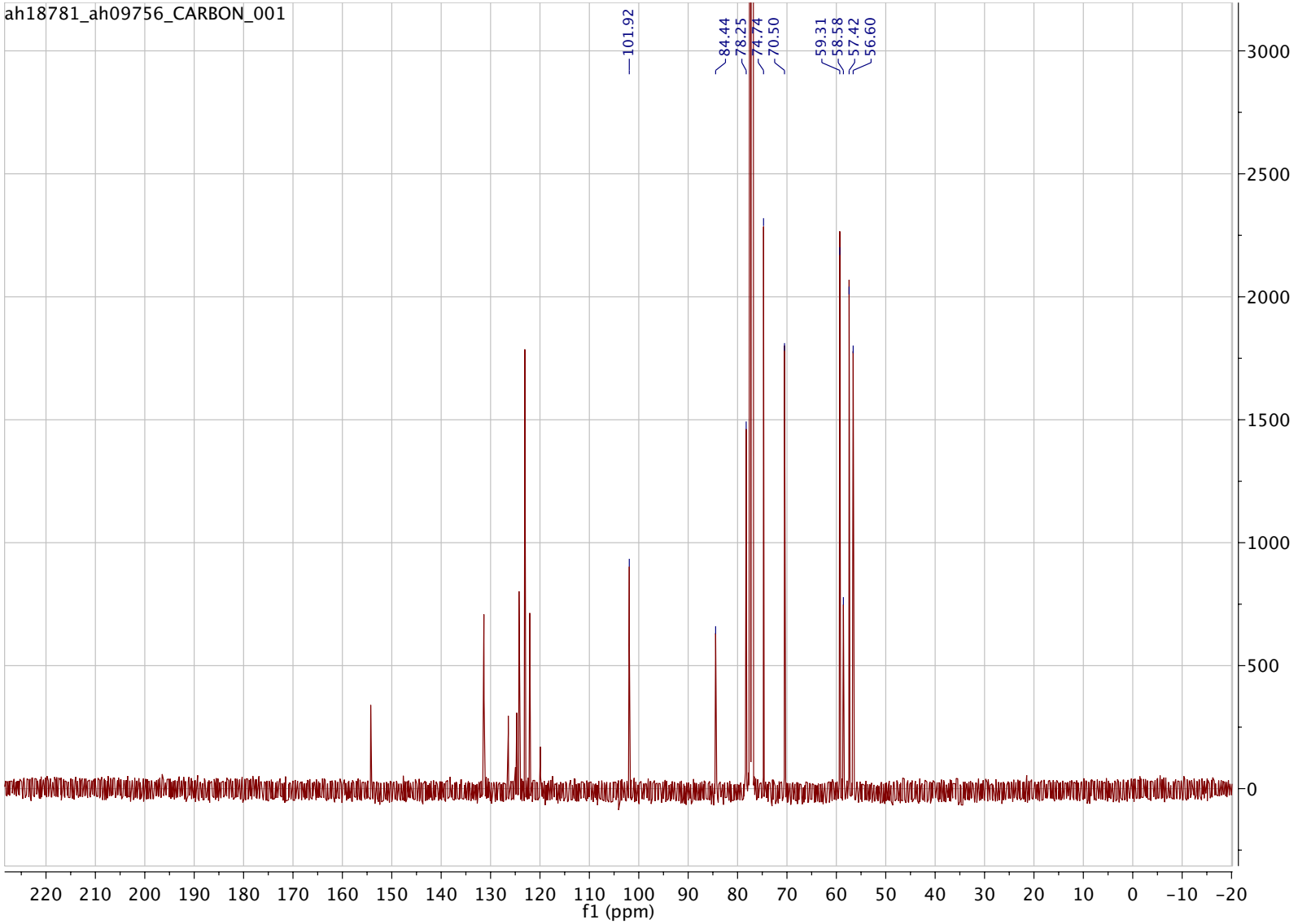
^{19}F NMR (470 MHz, $CDCl_3$)



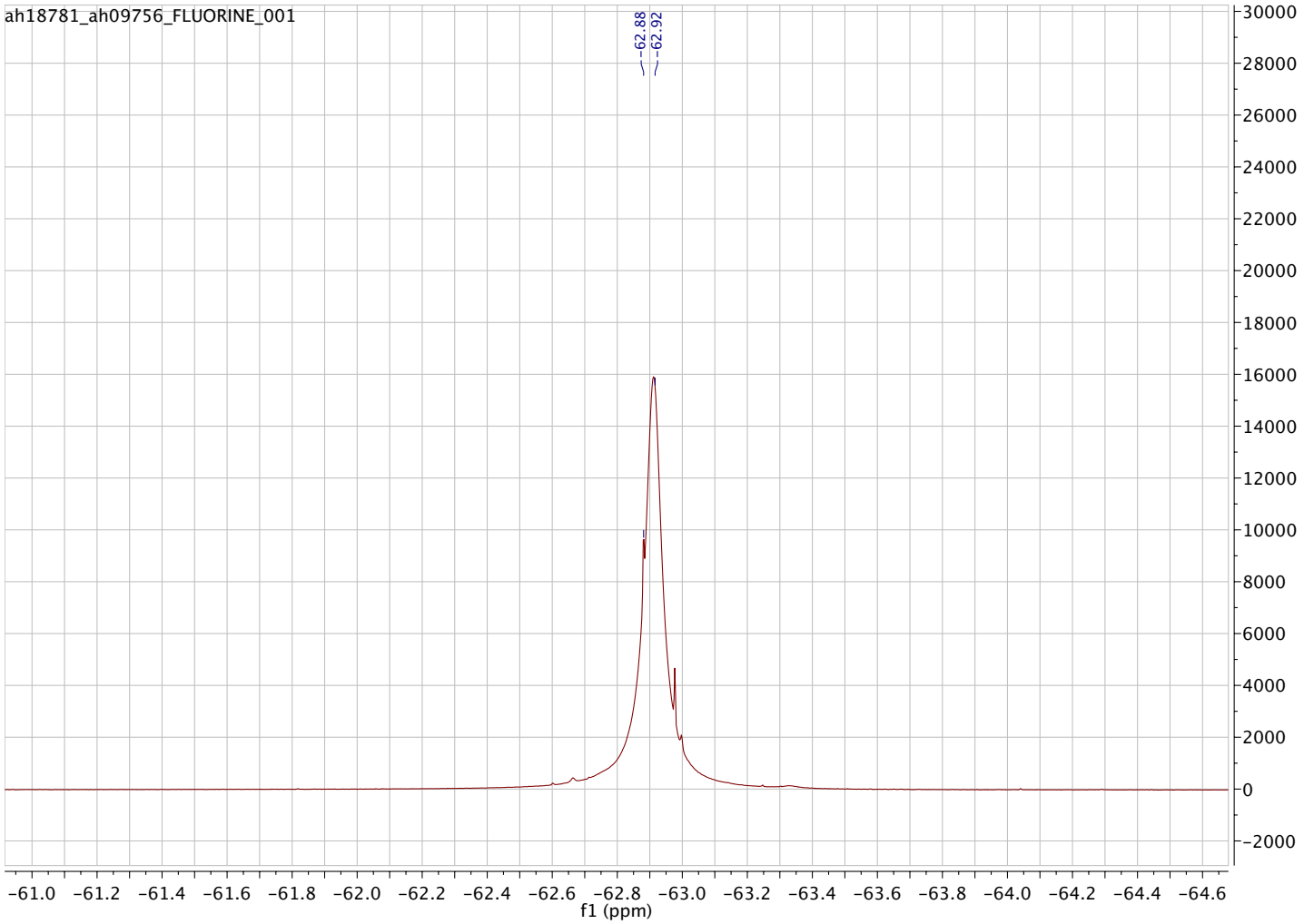
^{1}H NMR (500 MHz, $CDCl_3$) Methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',6'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside (15a):



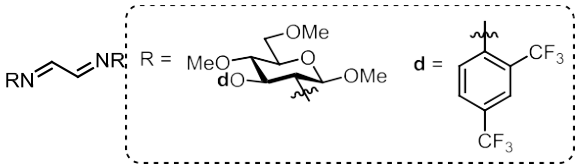
^{13}C NMR (125 MHz, $CDCl_3$)

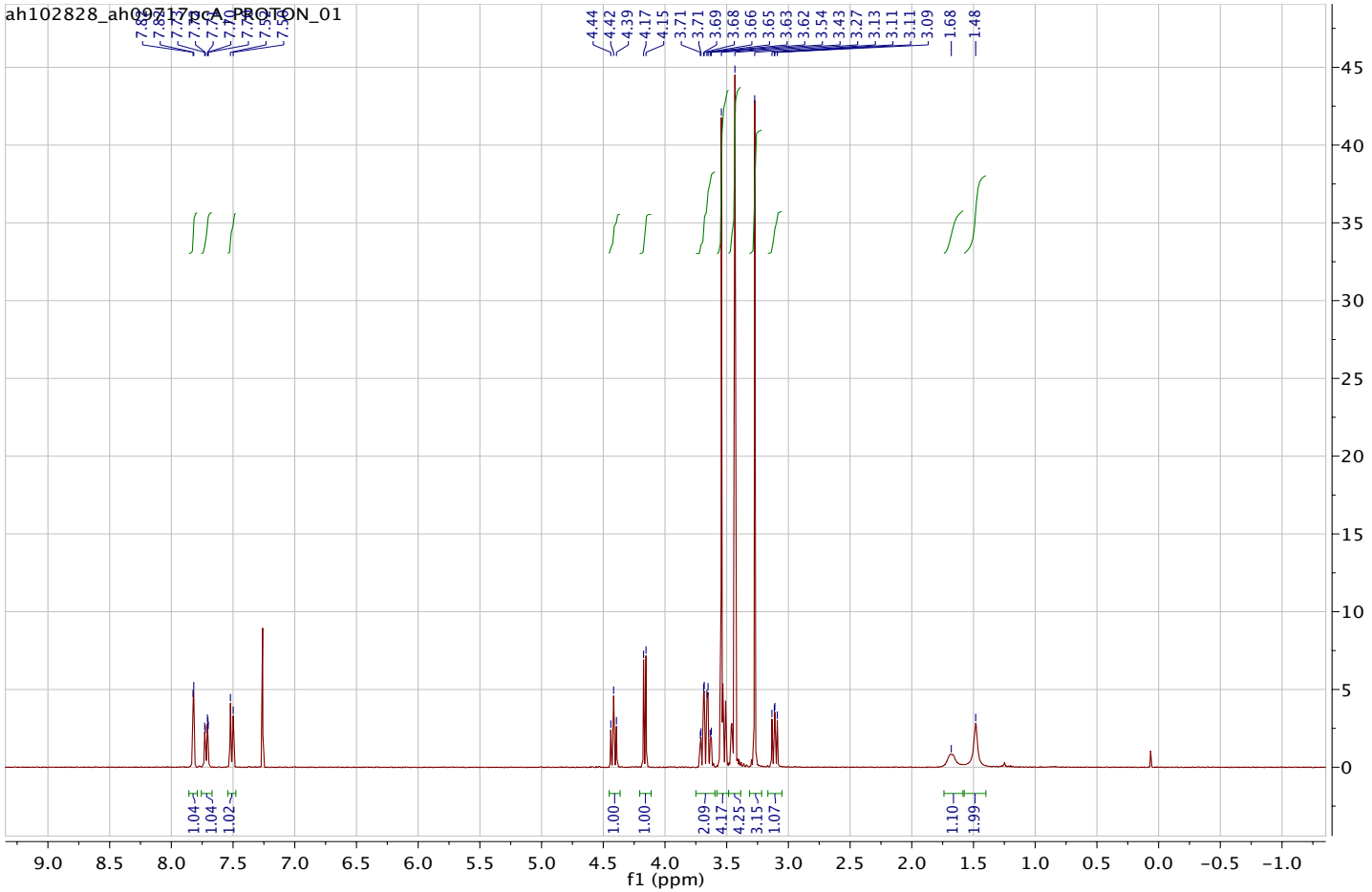


^{19}F NMR (470 MHz, $CDCl_3$)

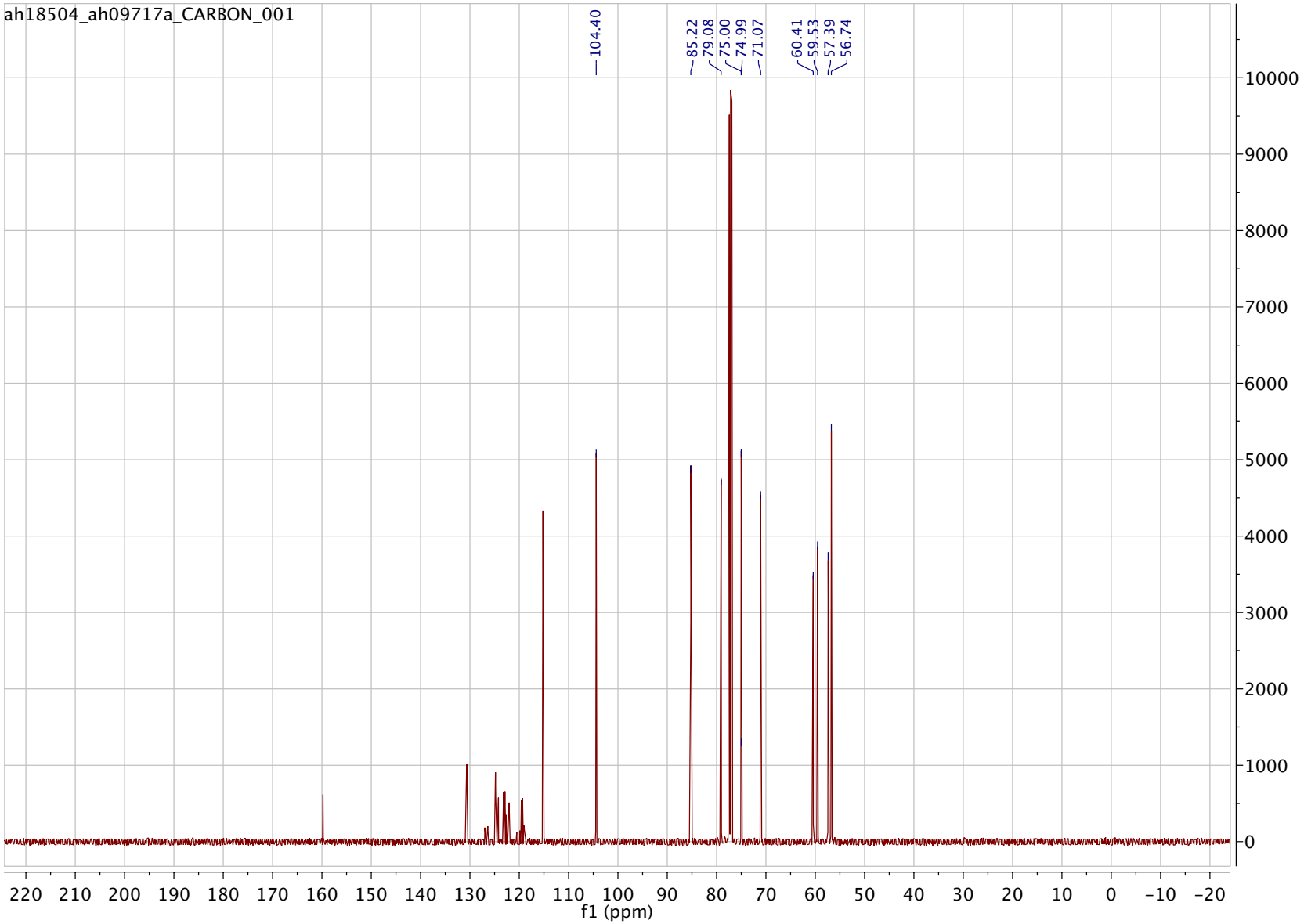


^{1}H NMR (500 MHz, $CDCl_3$) Methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',4'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside (15b):

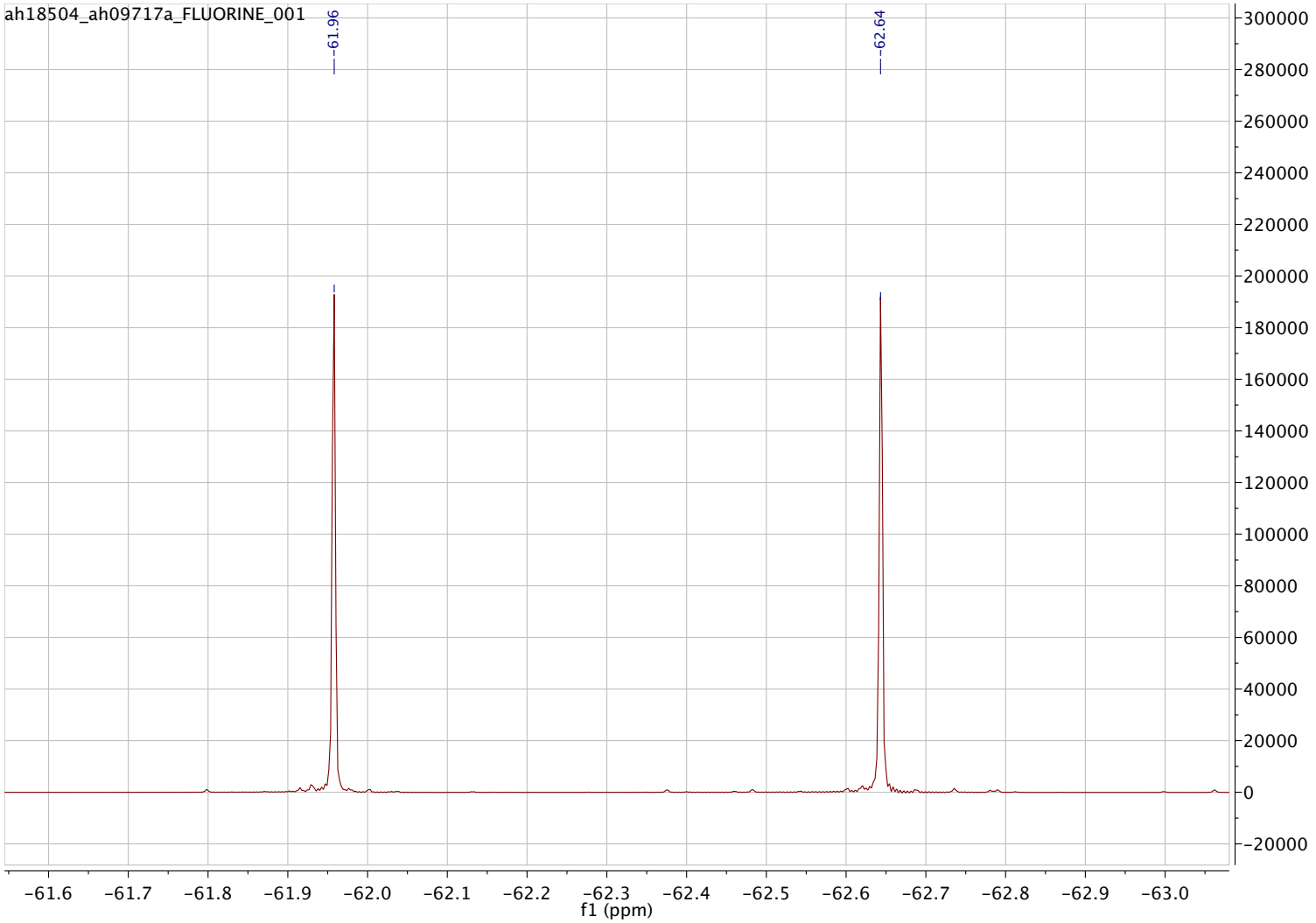




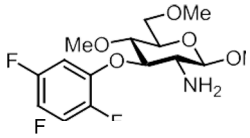
^{13}C NMR (125 MHz, $CDCl_3$)

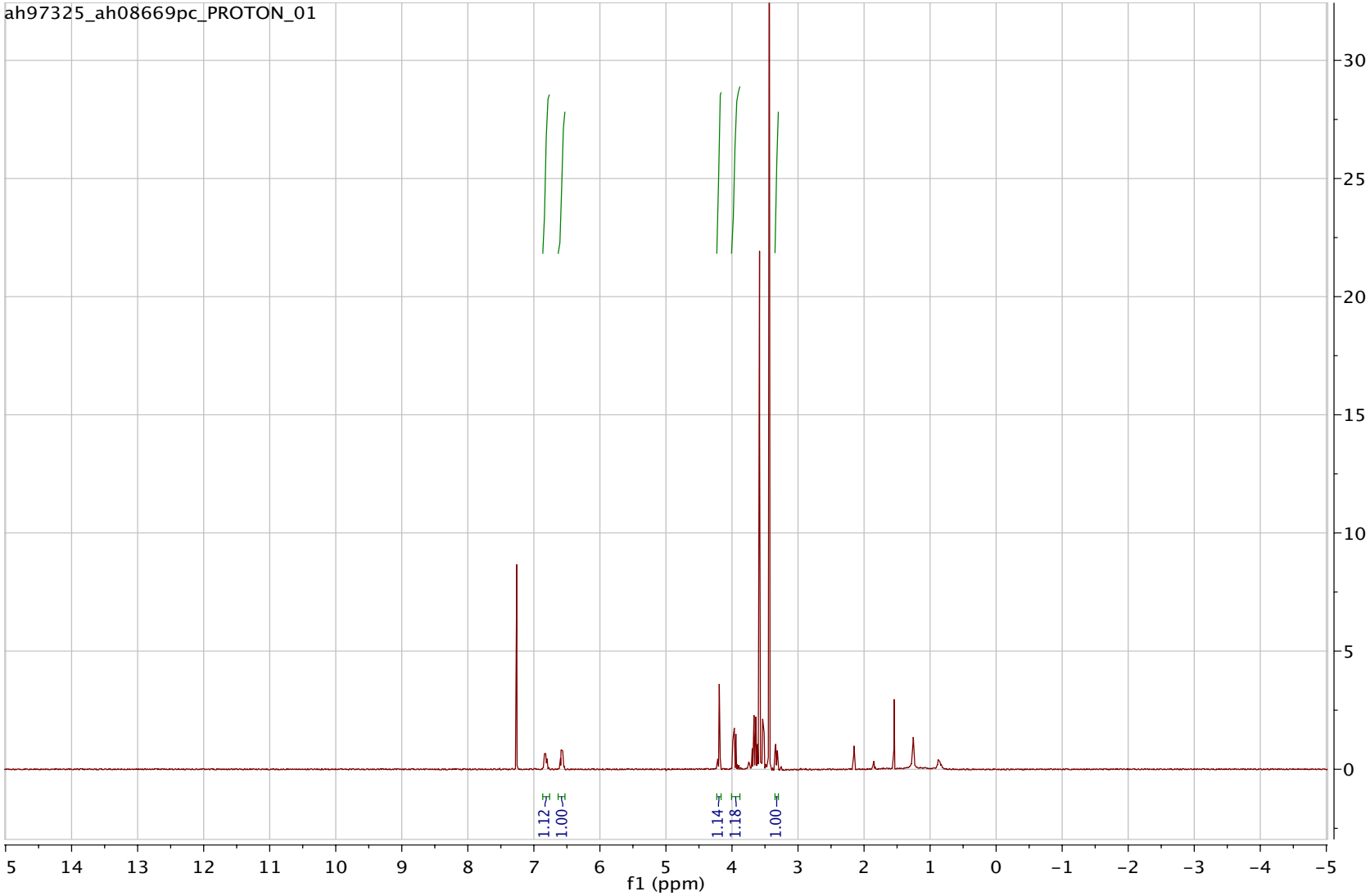


^{19}F NMR (470 MHz, $CDCl_3$)

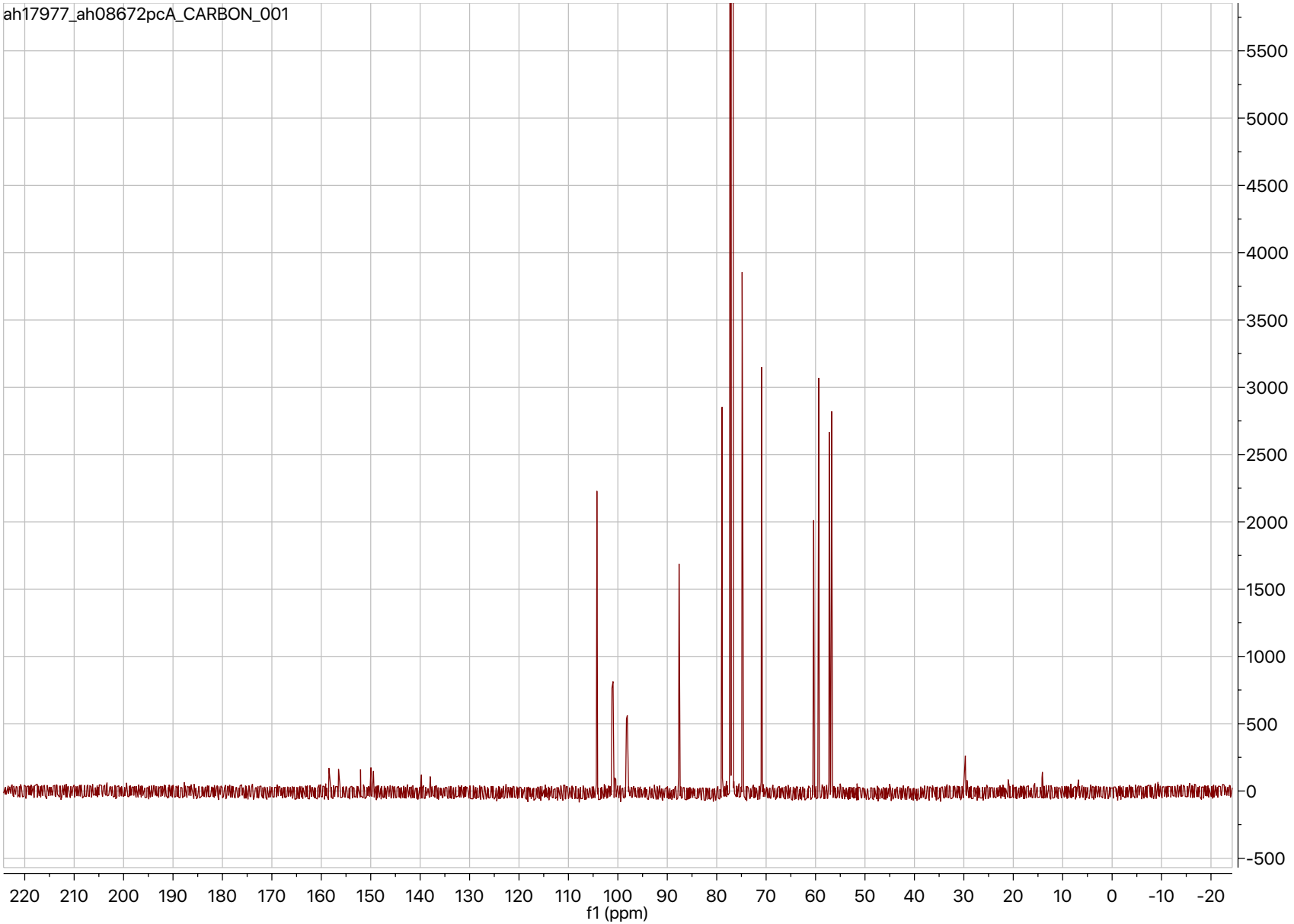


^{1}H NMR (500 MHz, $CDCl_3$) Methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',3',5'-trifluoro)benzene-2-deoxy-β-D-glucopyranoside (15c):

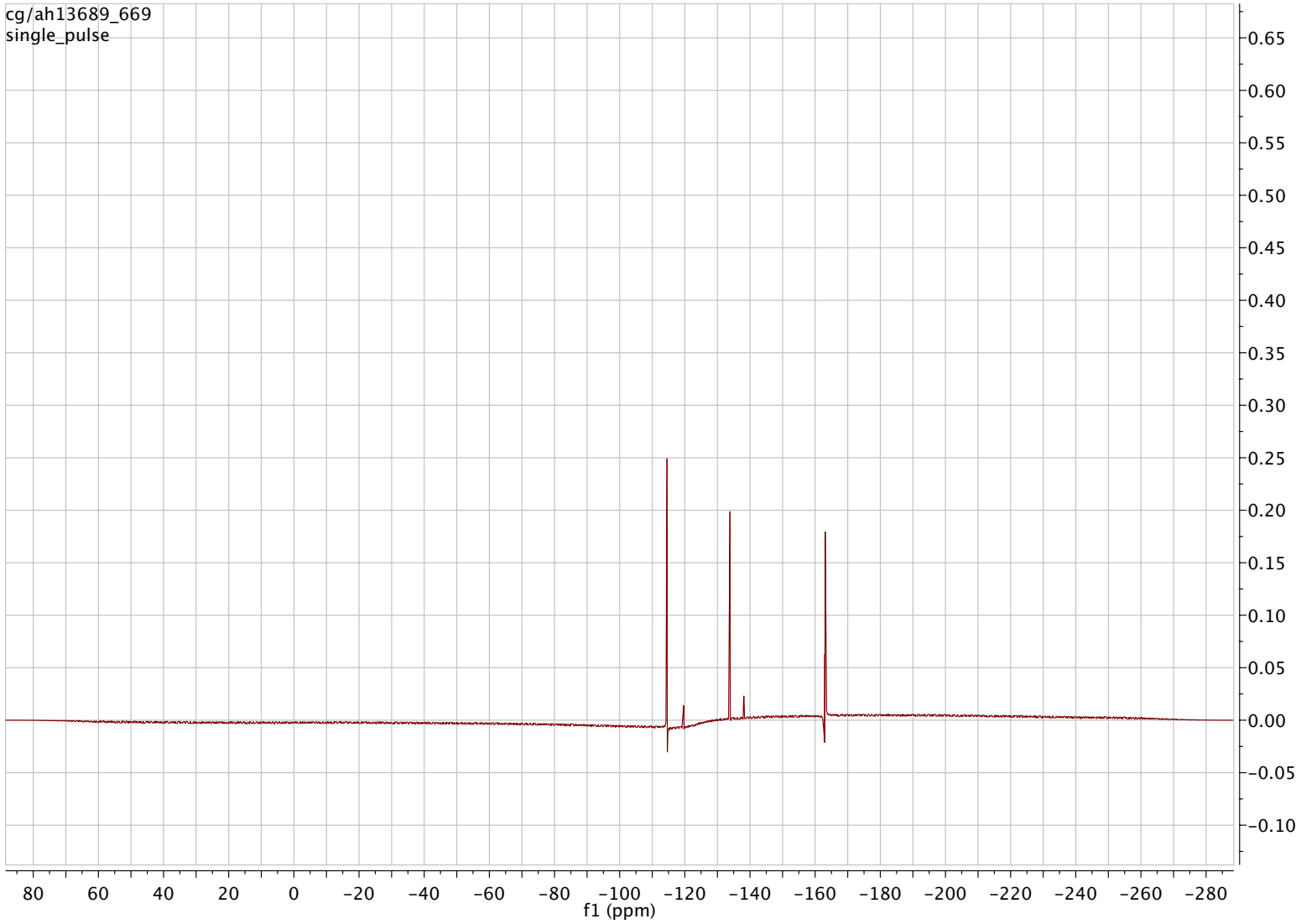




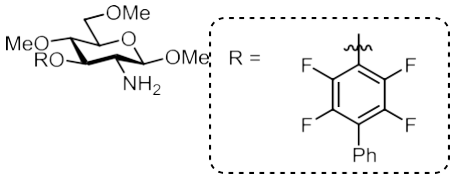
^{13}C NMR (125 MHz, $CDCl_3$)

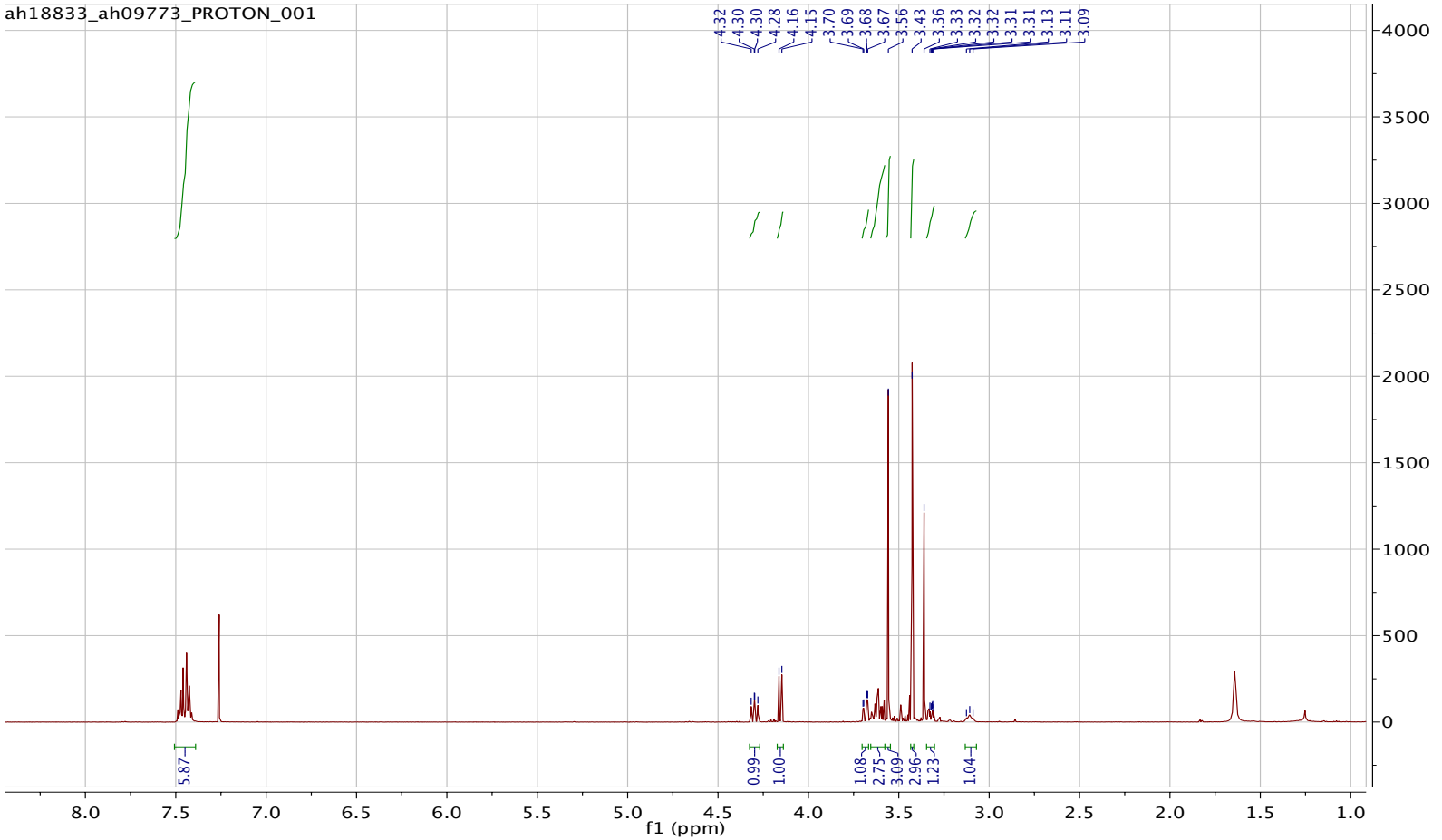


^{19}F NMR (377 MHz, $CDCl_3$)

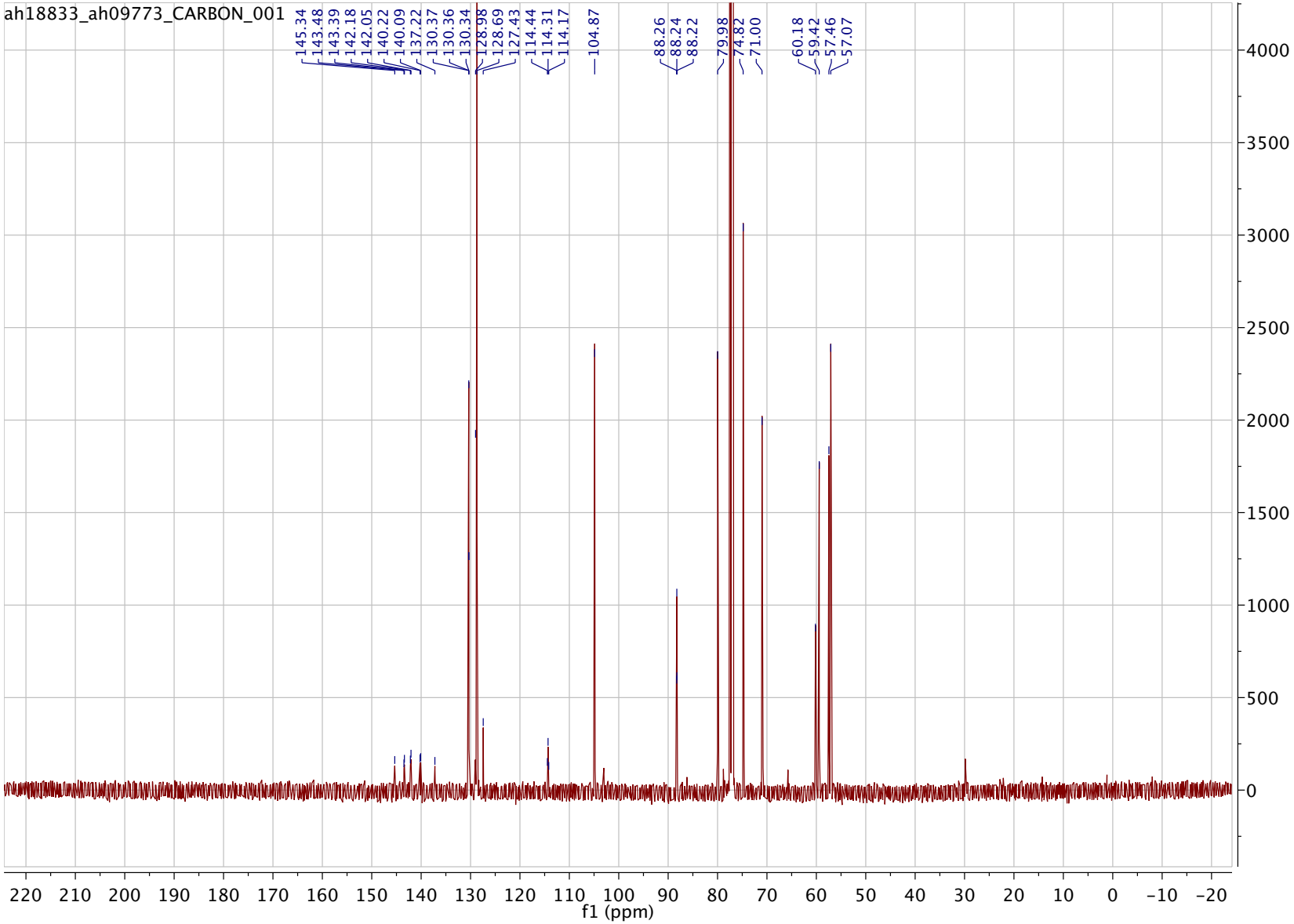


^{1}H NMR (500 MHz, $CDCl_3$) Methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(4'-phenyl-2',3',5',6'-tetrafluoro)benzene-2-deoxy-β-D-glucopyranoside (15d):

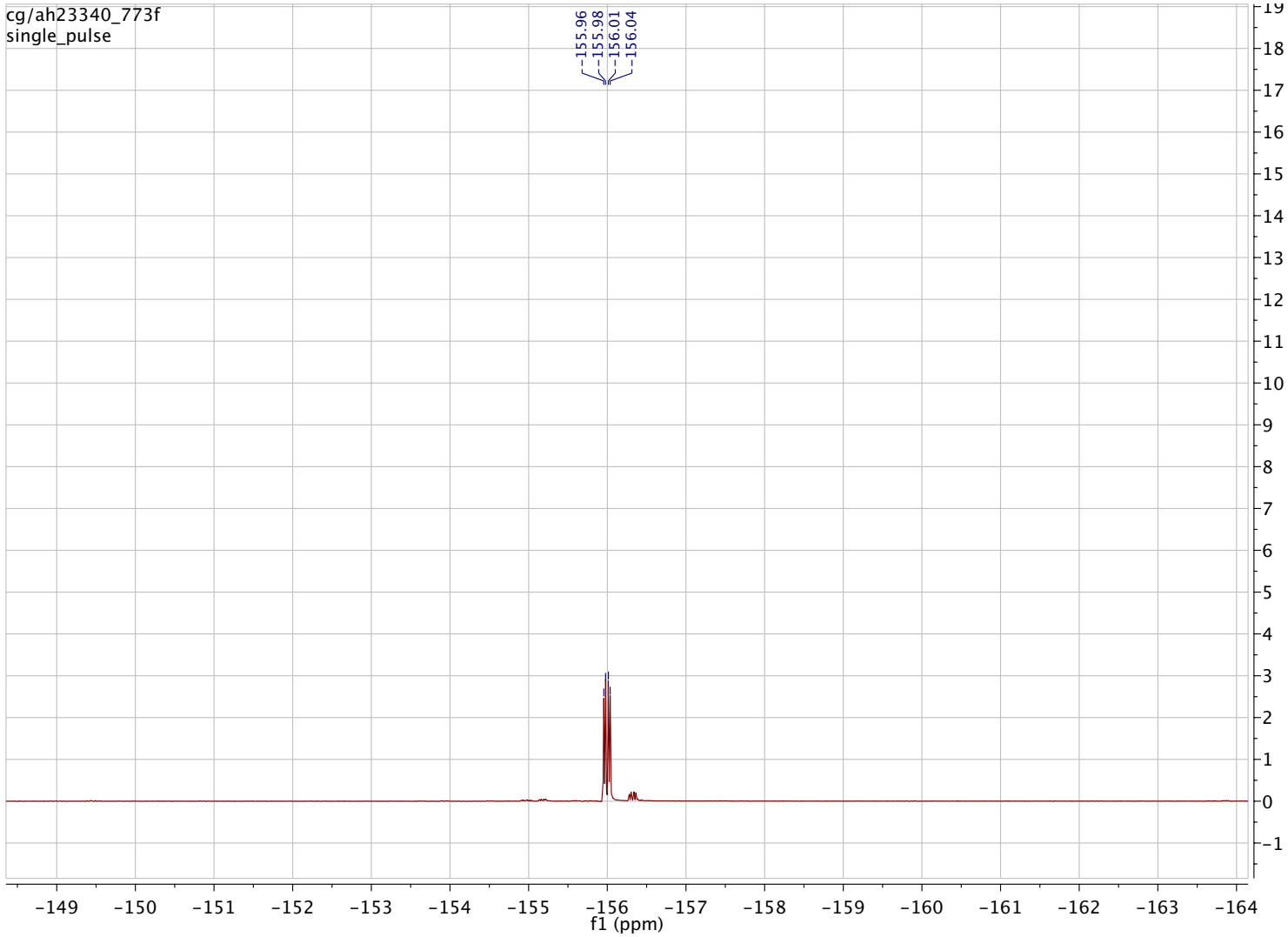




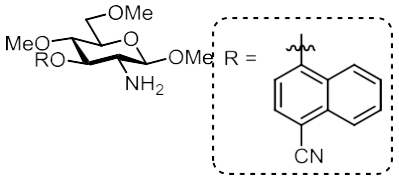
^{13}C NMR (125 MHz, $CDCl_3$)

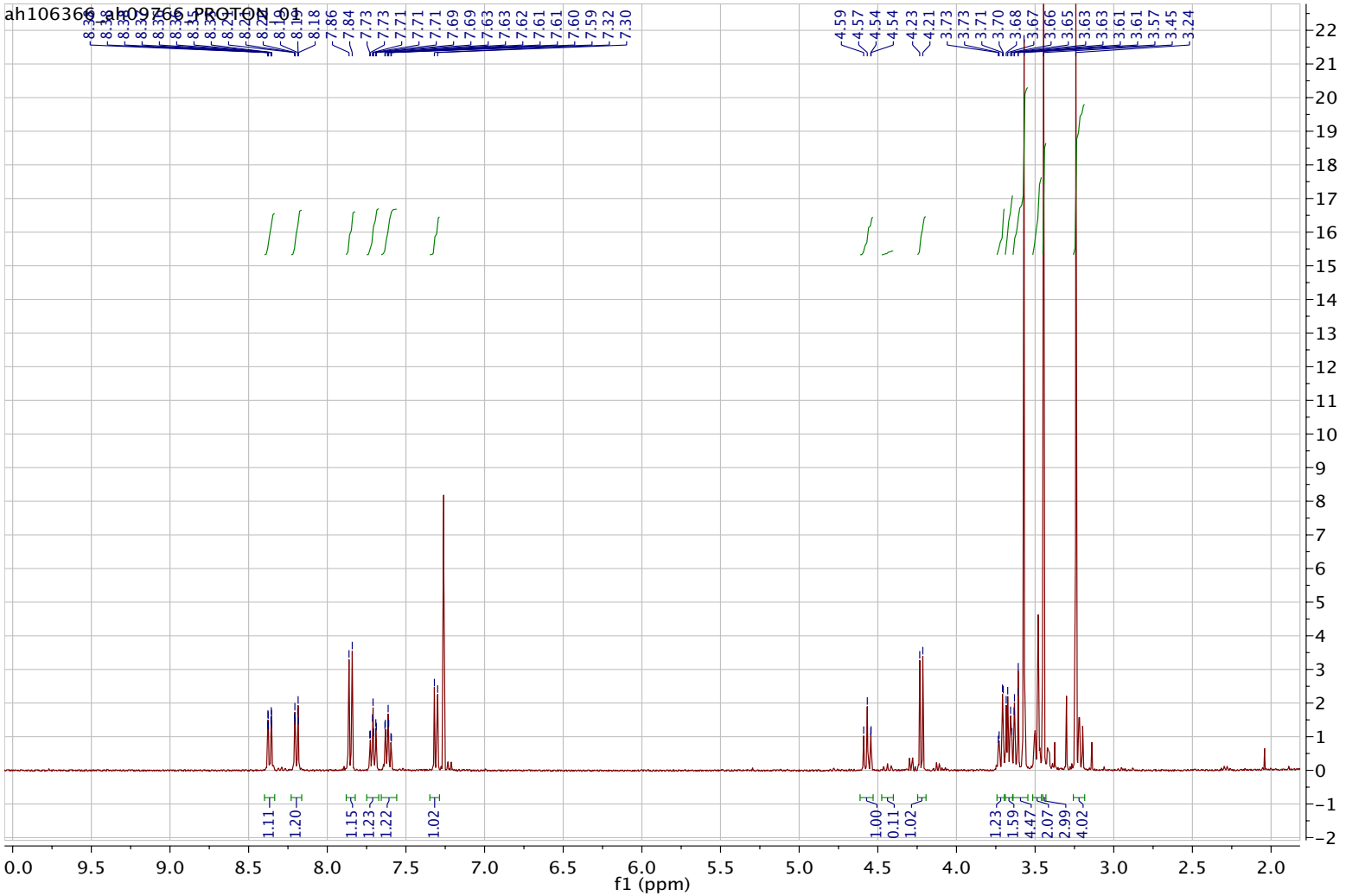


^{19}F NMR (470 MHz, $CDCl_3$)

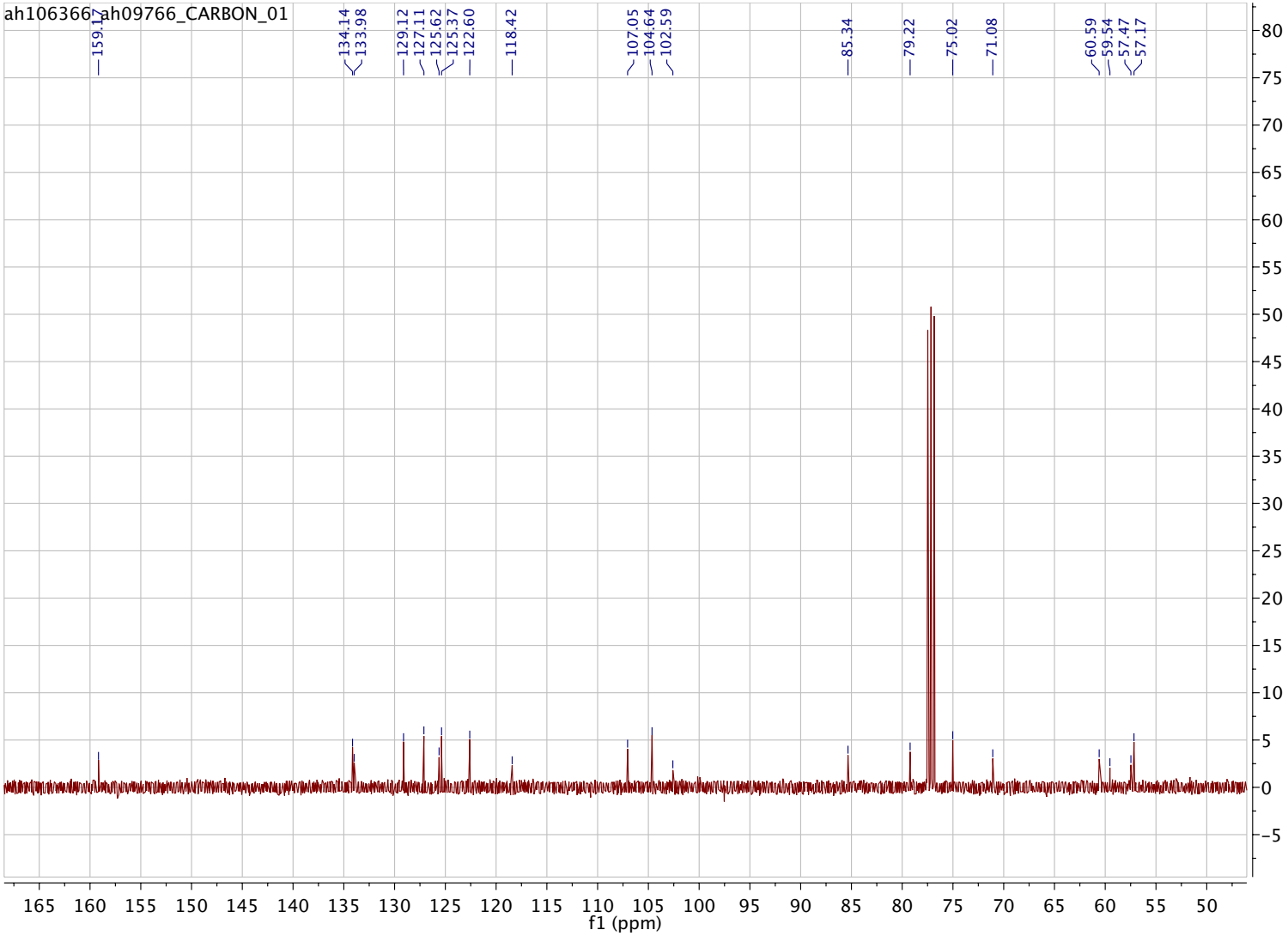


^{1}H NMR (500 MHz, $CDCl_3$) Methyl 2-amino-4,6-di-*O*-methyl-3-*O*-1'-(4'-cyano)naphthlene-2-deoxy-β-D-glucopyranoside (15e):

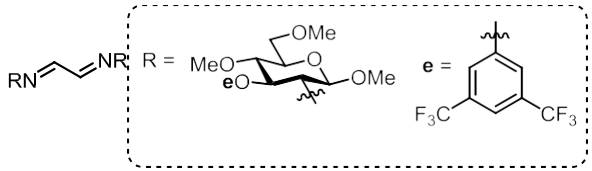


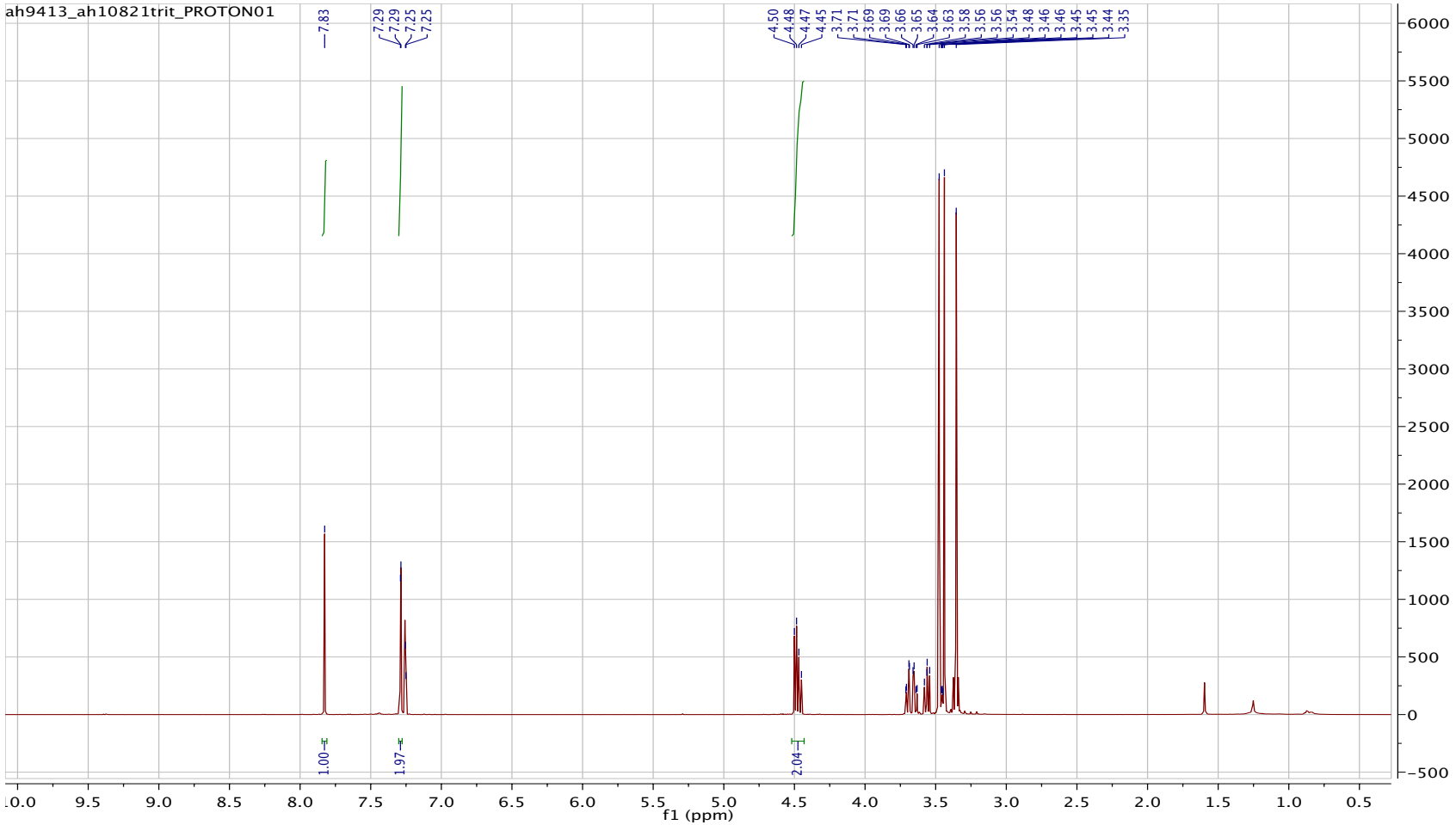


^{13}C NMR (125 MHz, $CDCl_3$)

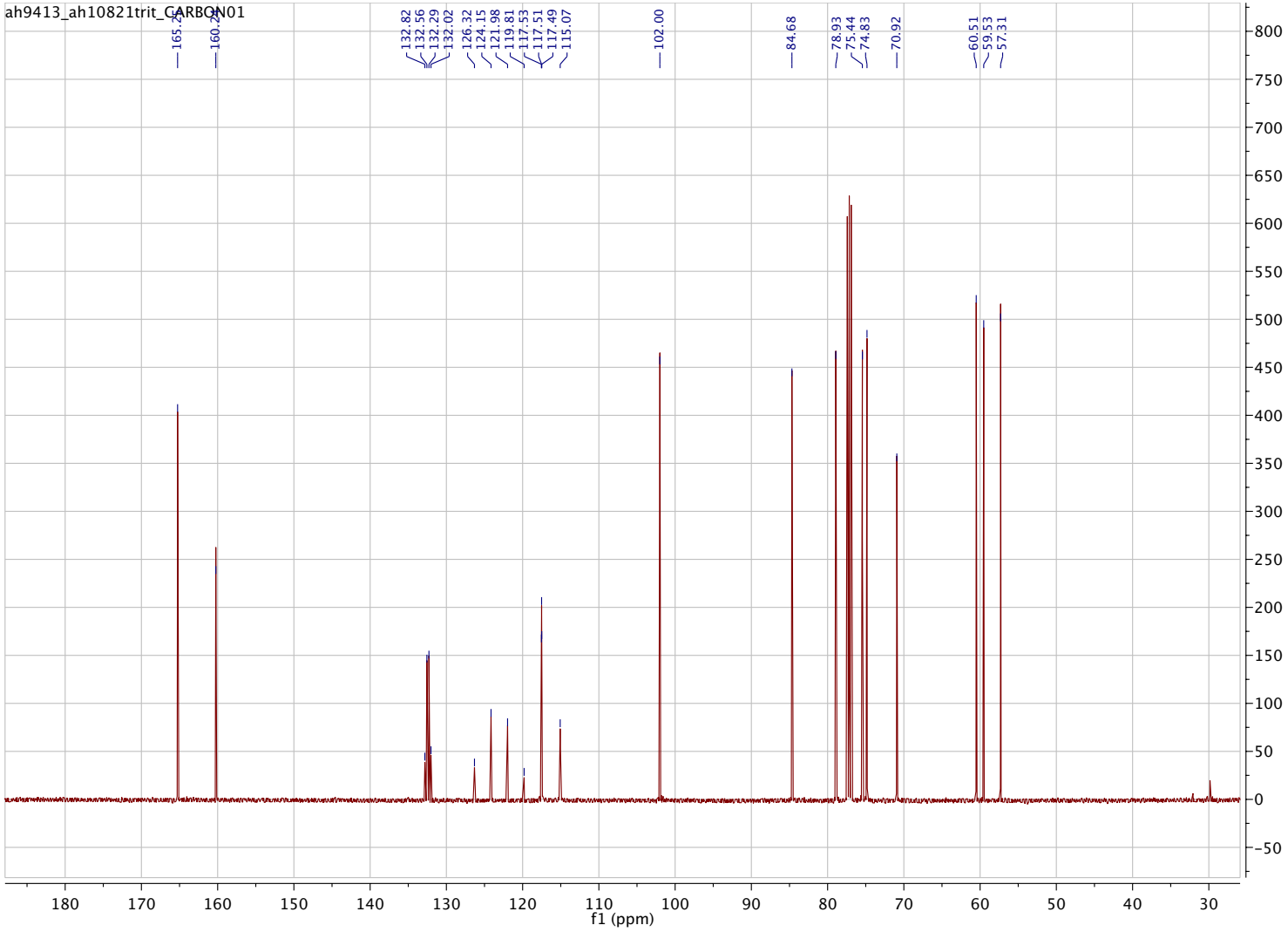


^{1}H NMR (500 MHz, $CDCl_3$) Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(3',5'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)- *N*,*N*'-iminoethylidene (S5):

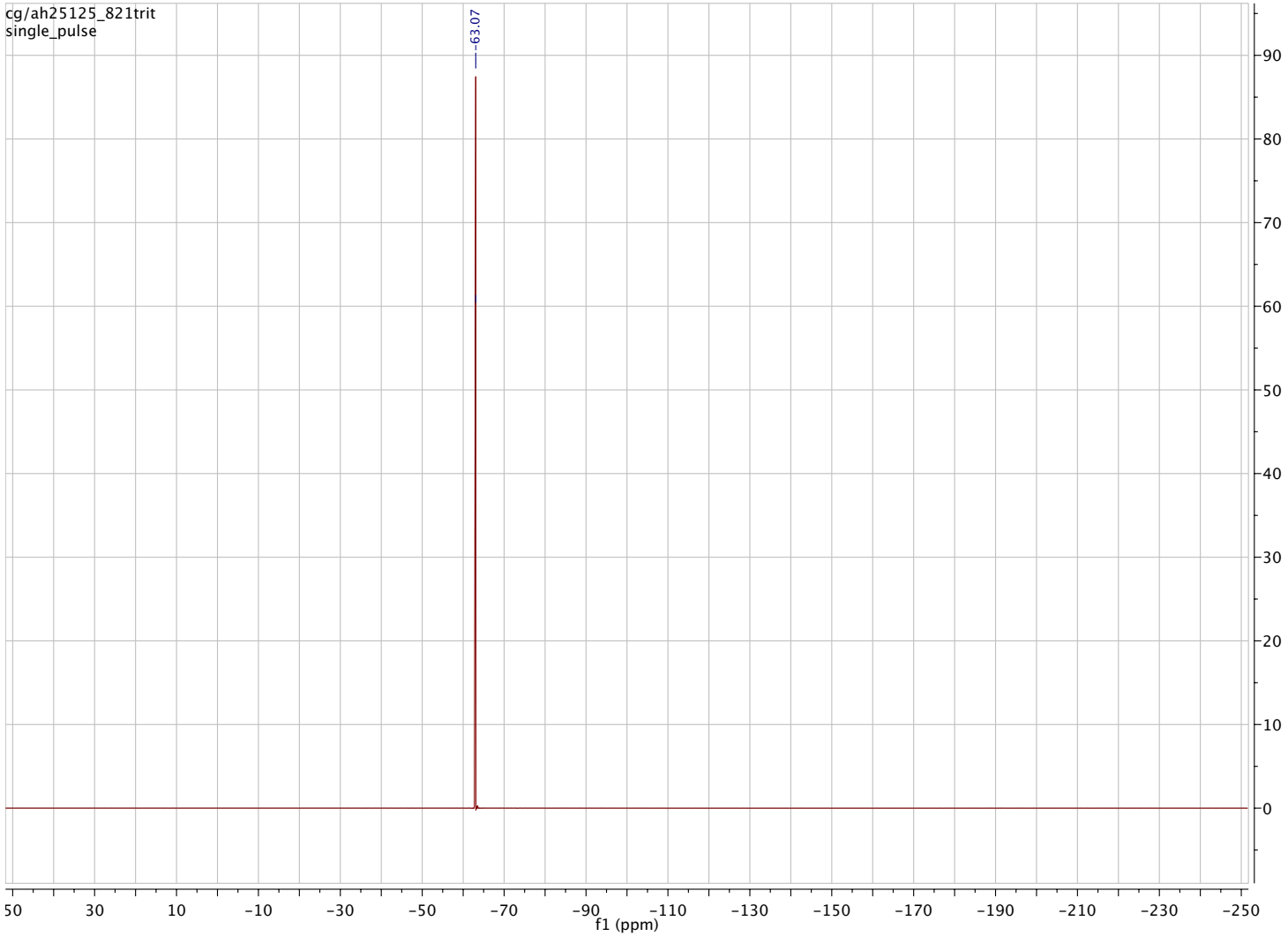




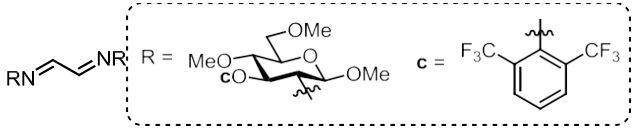
^{13}C NMR (125 MHz, CDCl3)

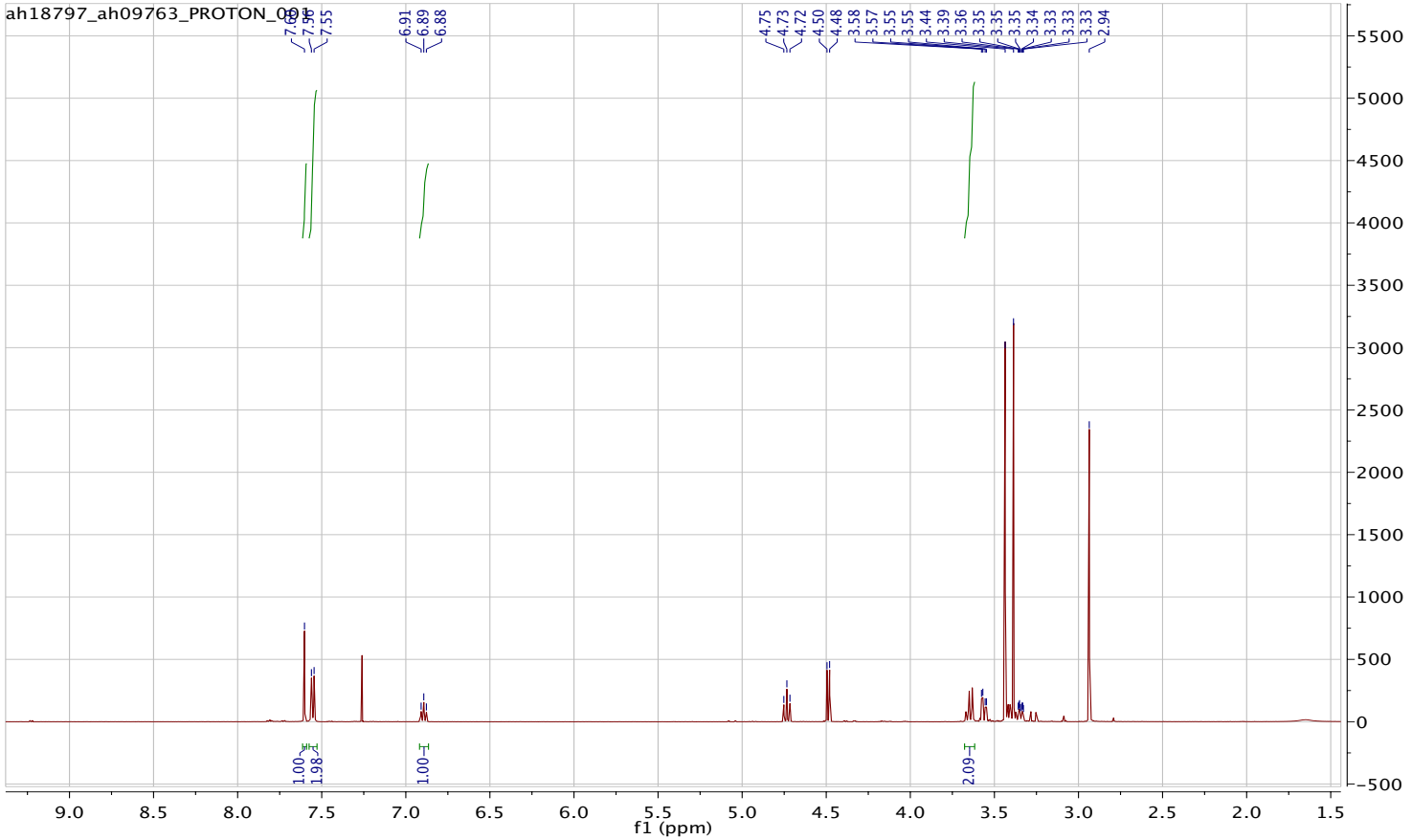


^{19}F NMR (377 MHz, $CDCl_3$)

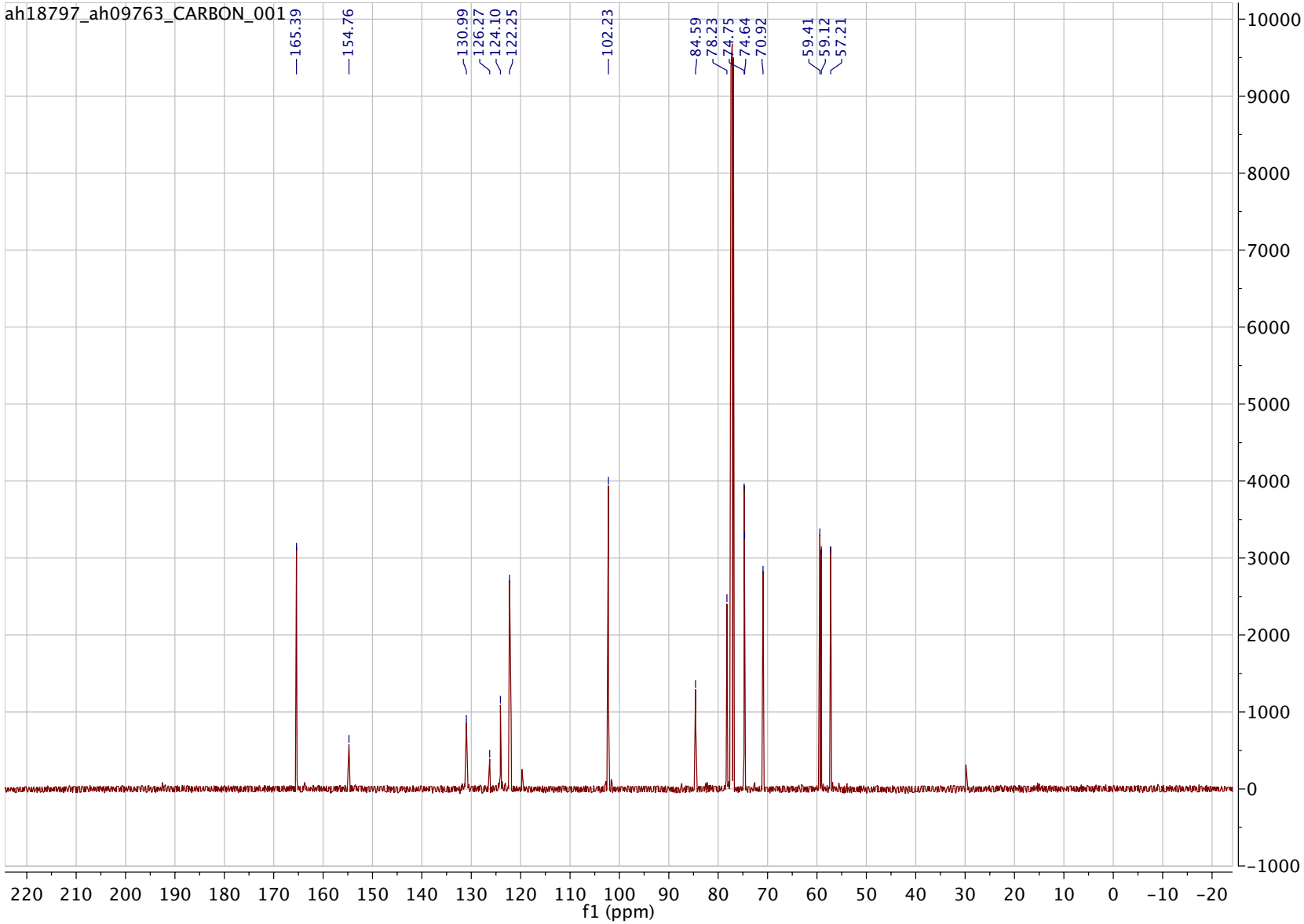


^{1}H NMR (500 MHz, $CDCl_3$) Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',6'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)- *N*,*N'*-iminoethylidene (S6a):

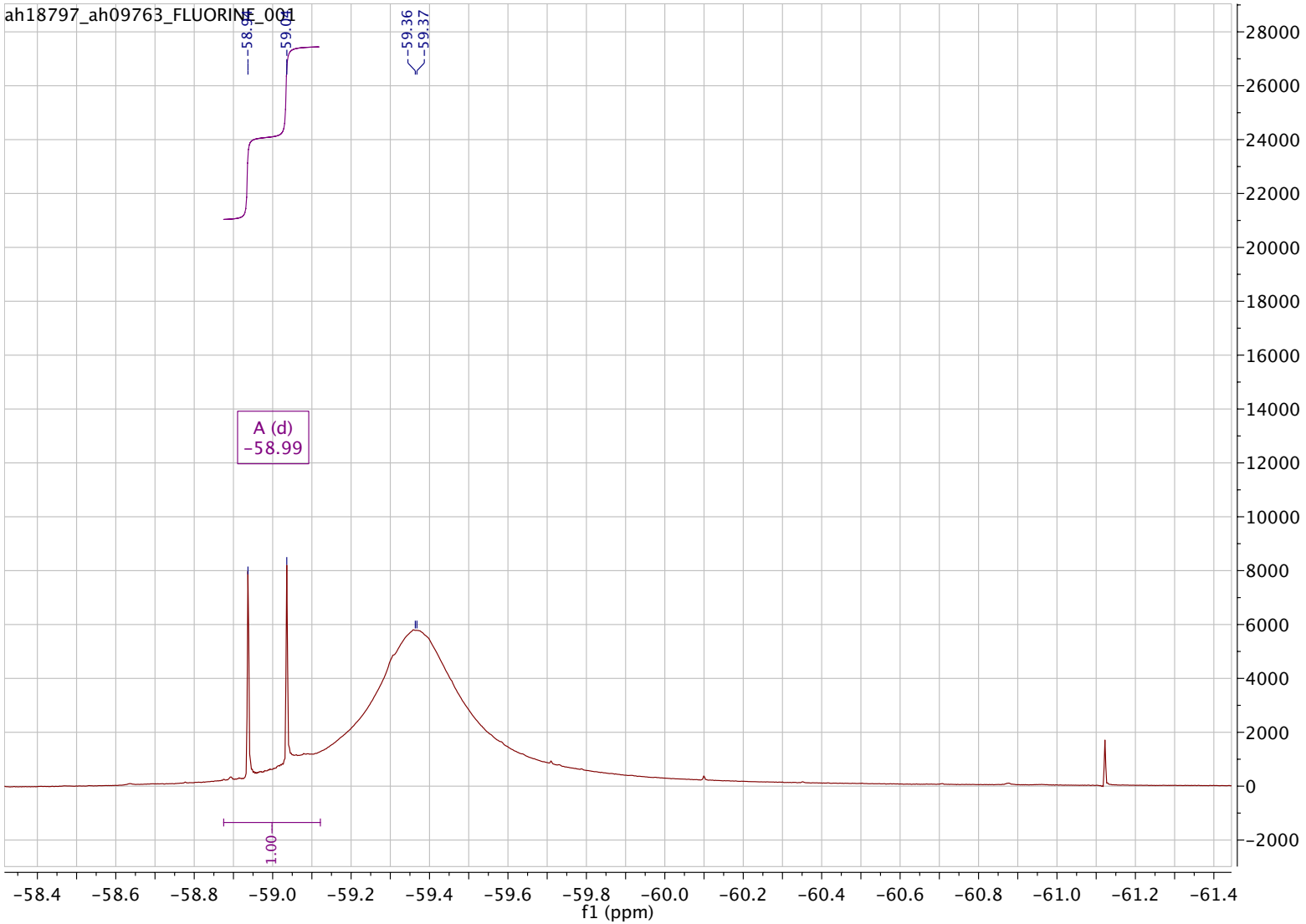




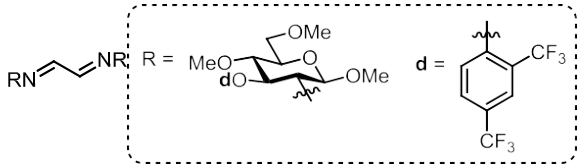
^{13}C NMR (125 MHz, CDCl3)

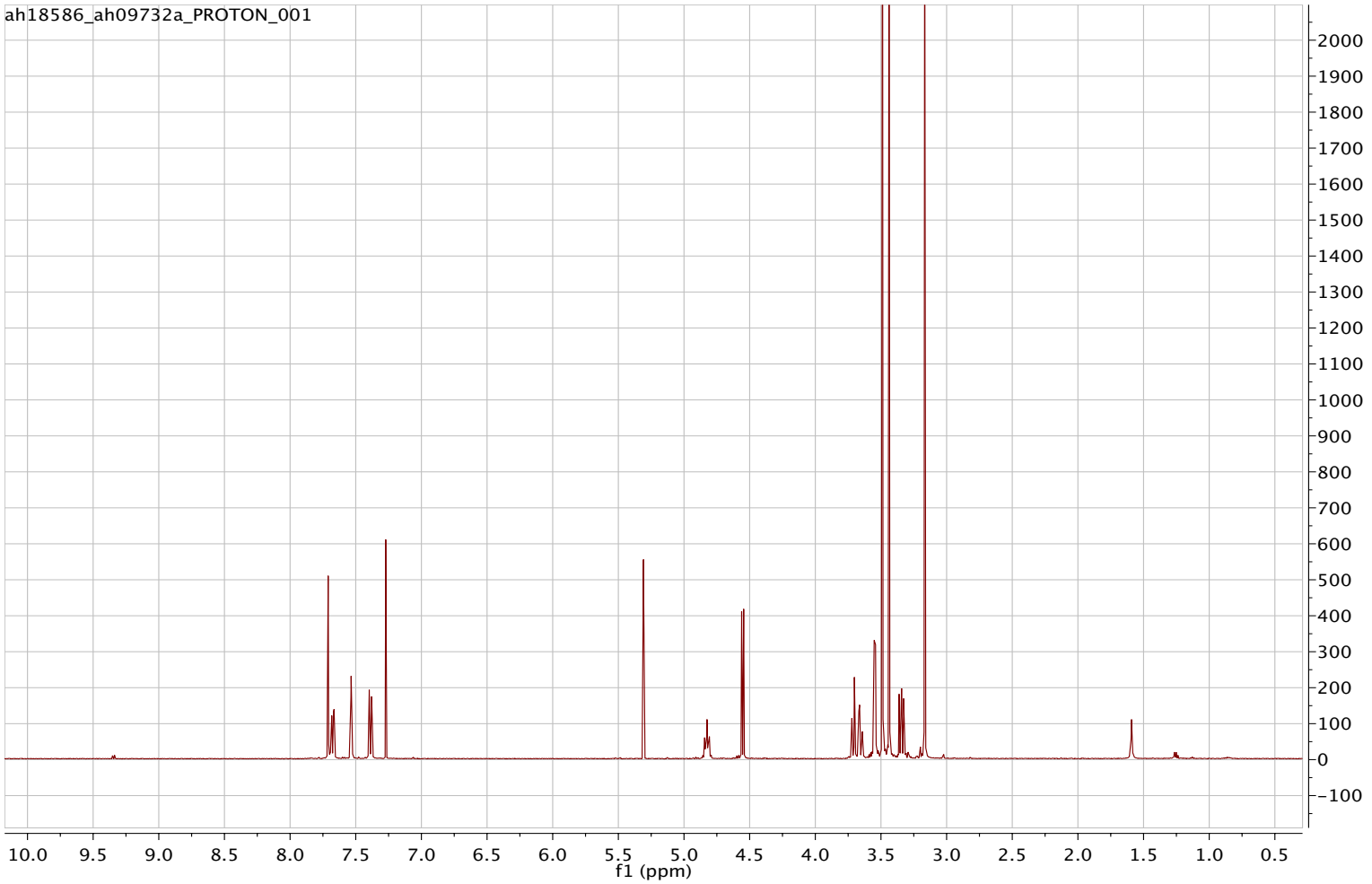


^{19}F NMR (470 MHz, $CDCl_3$)

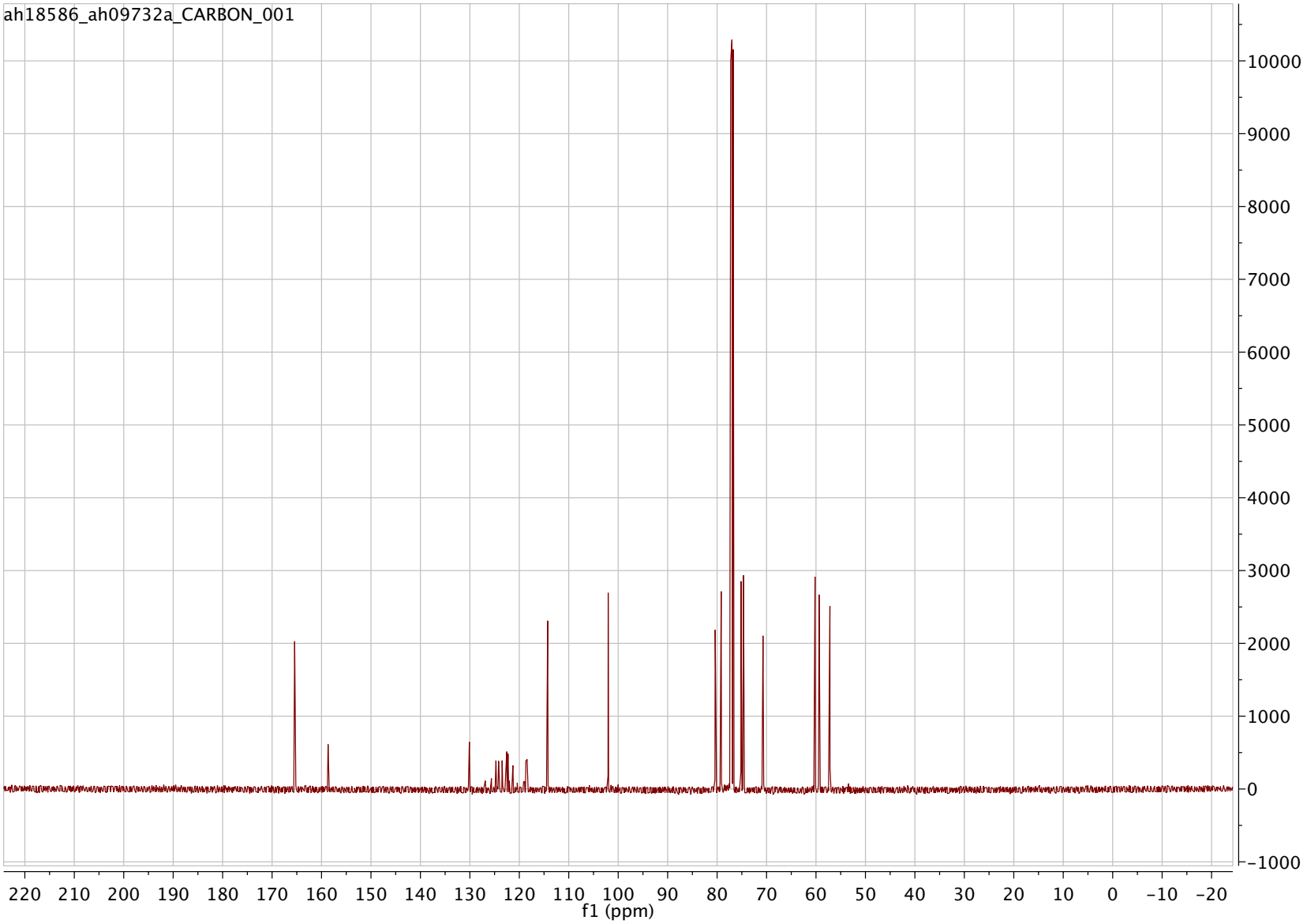


^{1}H NMR (500 MHz, $CDCl_3$) Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',4'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)- *N*,*N*'-iminoethylidene (S6b):

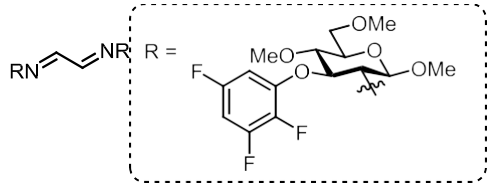


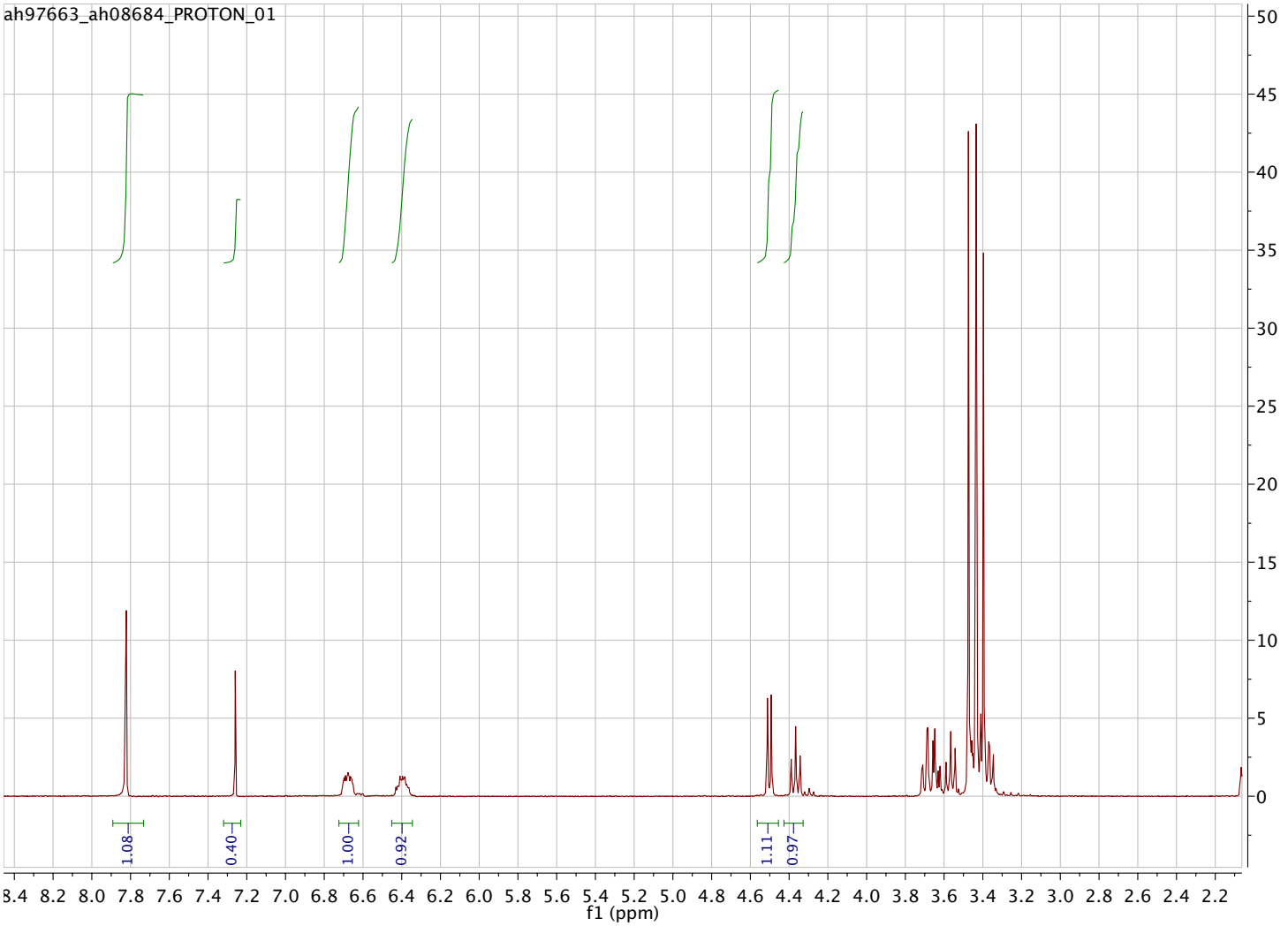


^{13}C NMR (125 MHz, CDCl3)

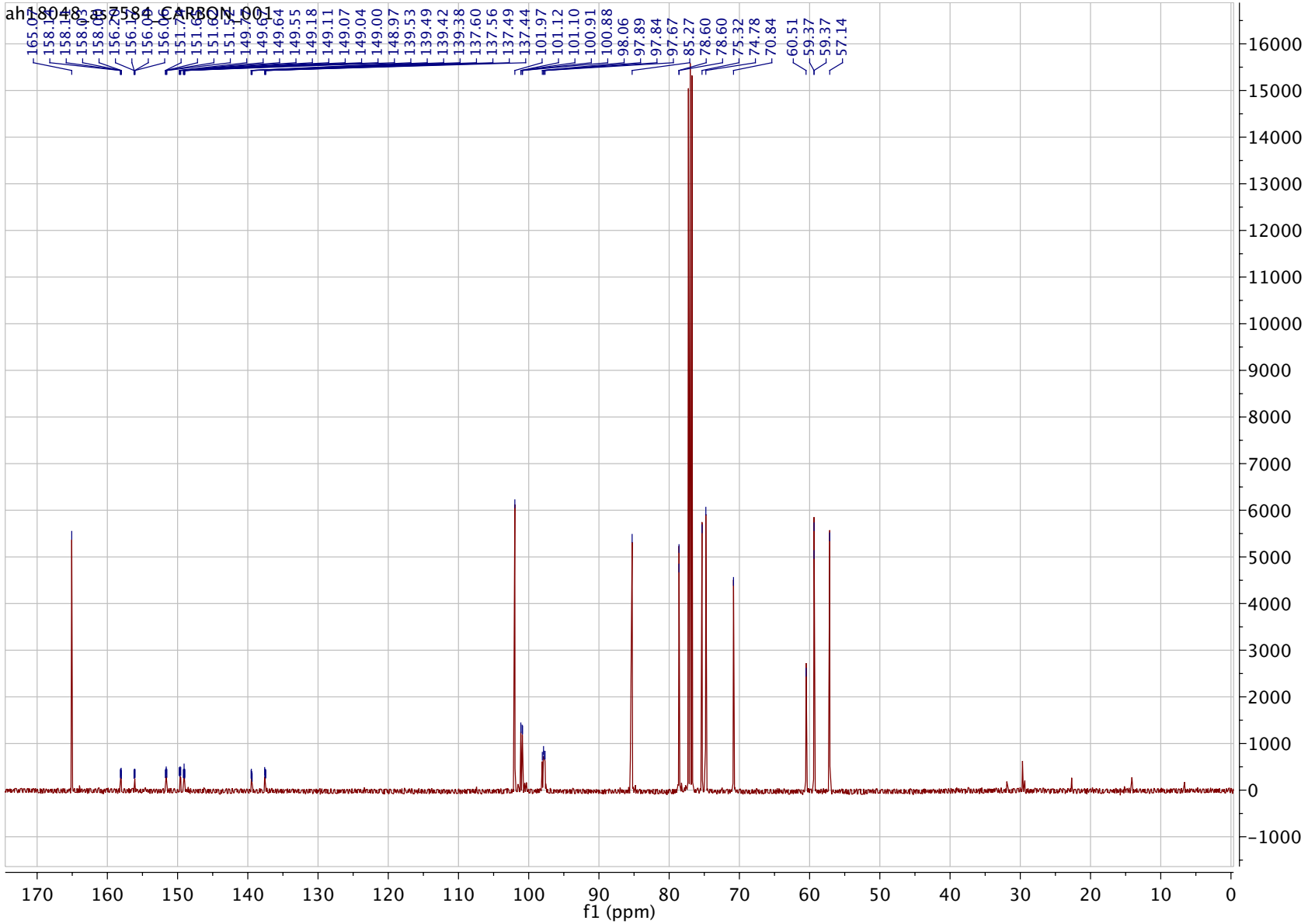


^{1}H NMR (500 MHz, $CDCl_3$) Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',3',5'-trifluoro)benzene-2-deoxy-β-D-glucopyranoside)-*N*,*N*'- iminoethylidene (S6c):

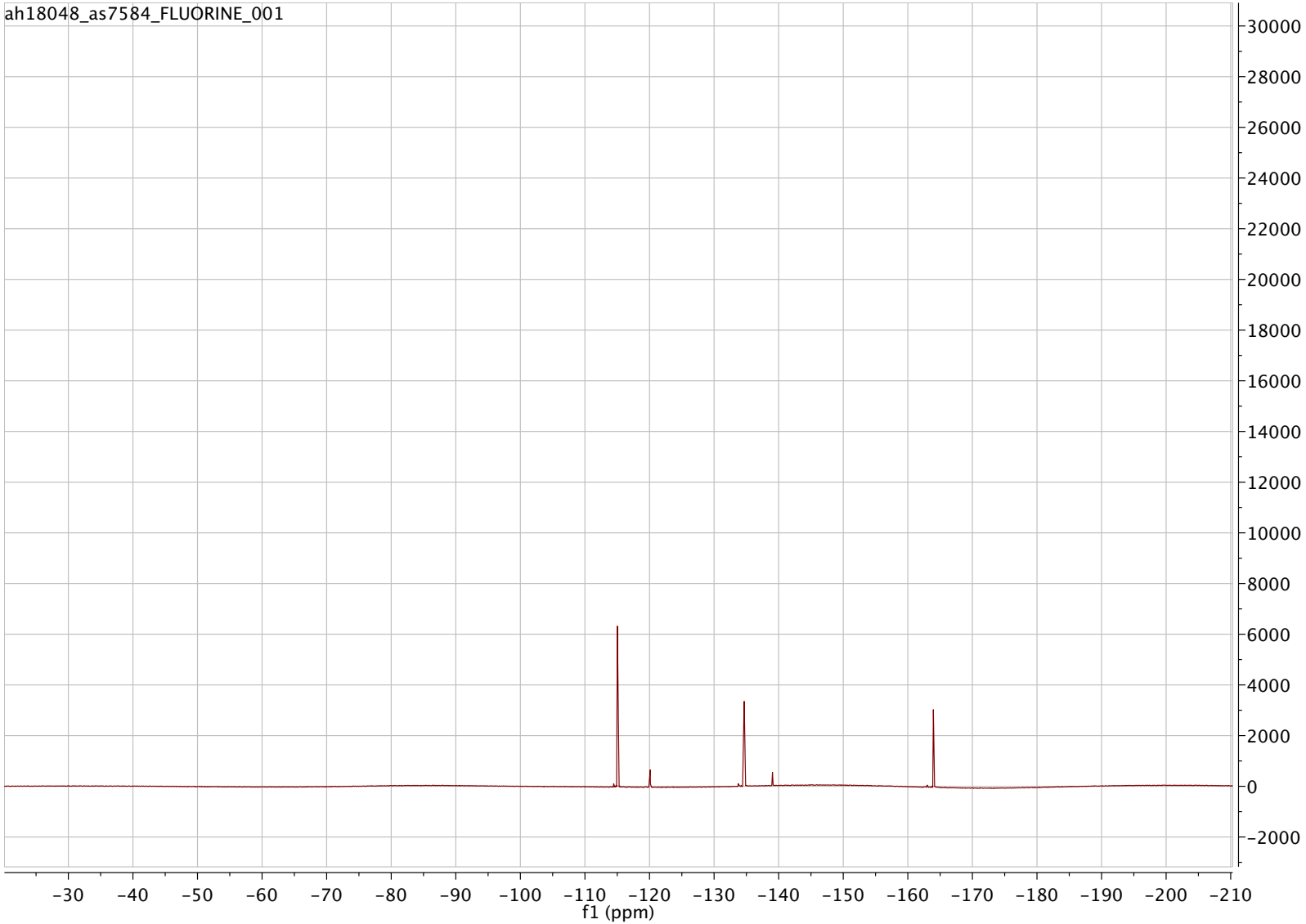




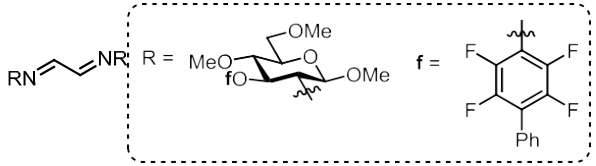
^{13}C NMR (125 MHz, CDCl3)

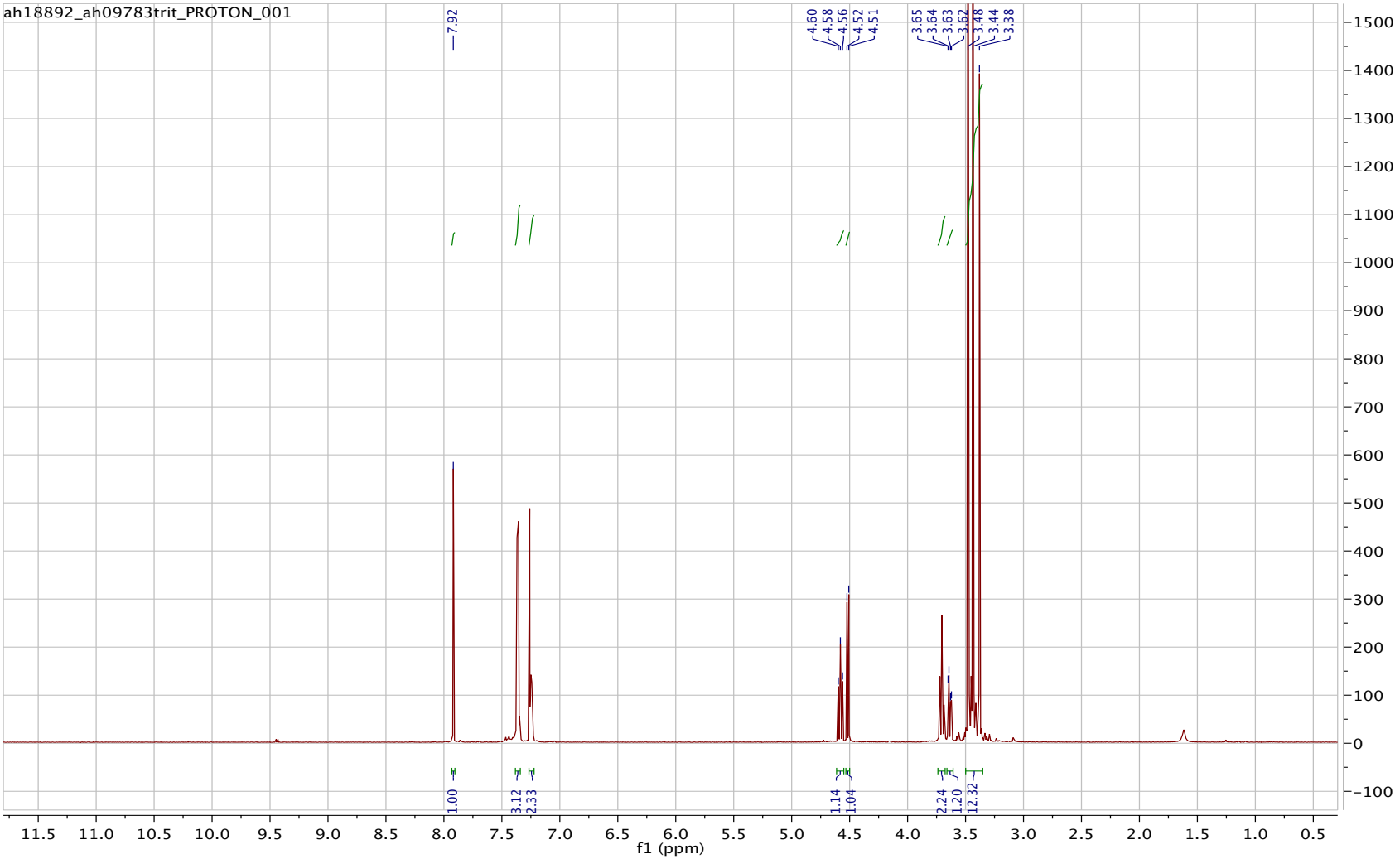


^{19}F NMR (470 MHz, $CDCl_3$)

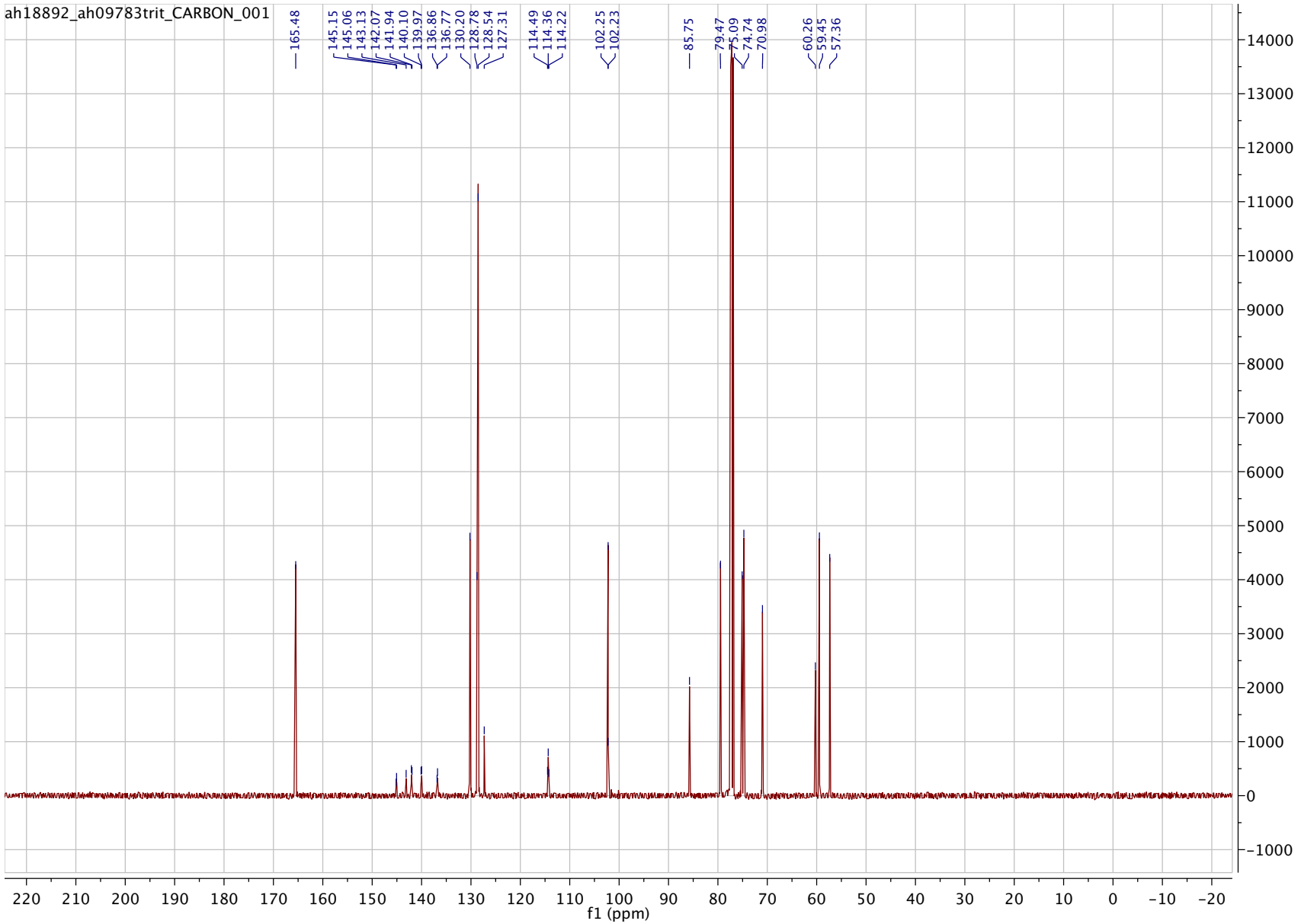


^{1}H NMR (500 MHz, $CDCl_3$) Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(4'-phenyl-2',3',5',6'-tetrafluoro)benzene-2-deoxy-β-D-glucopyranoside)-*N*,*N*'-iminoethylidene (S6d):

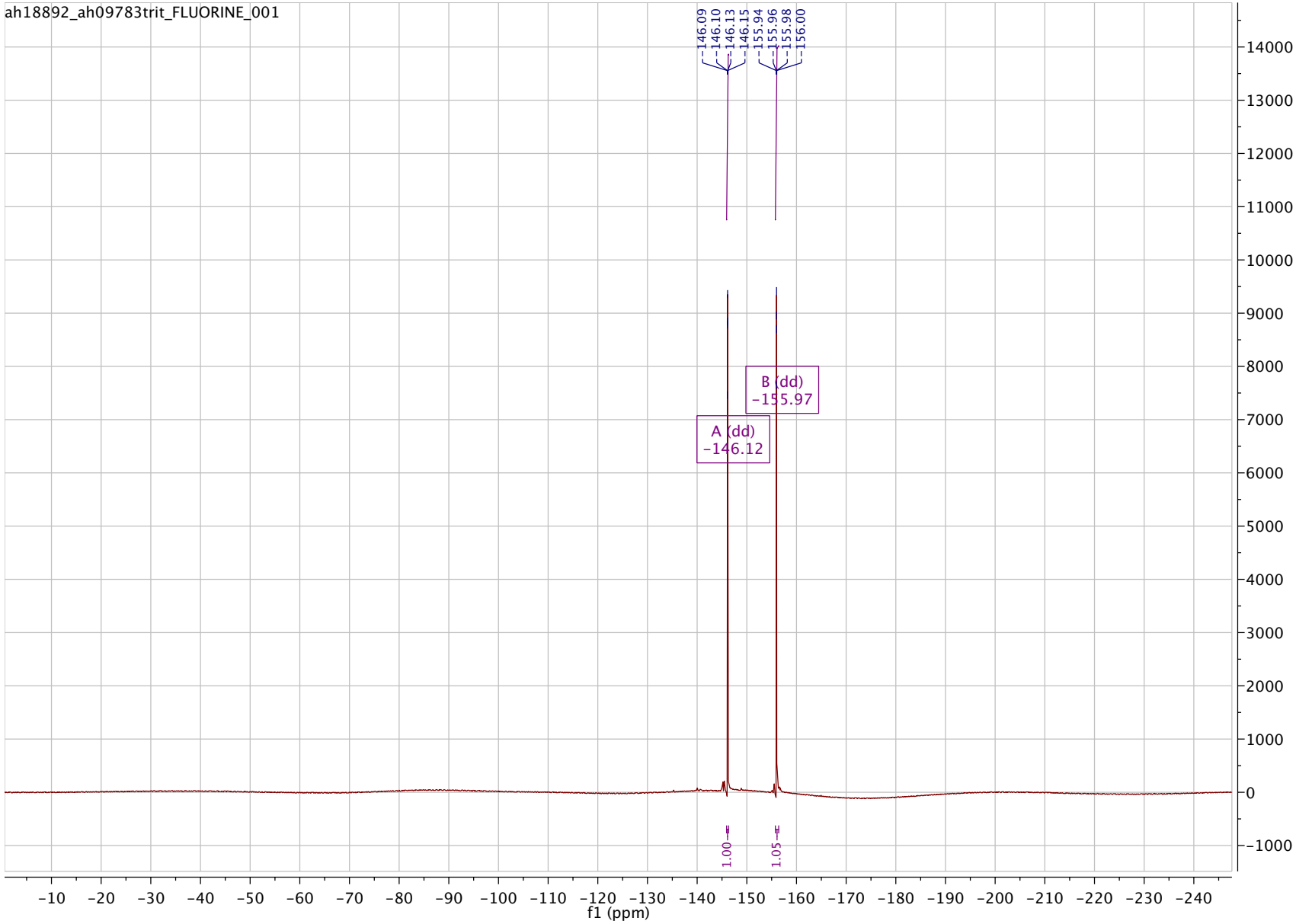




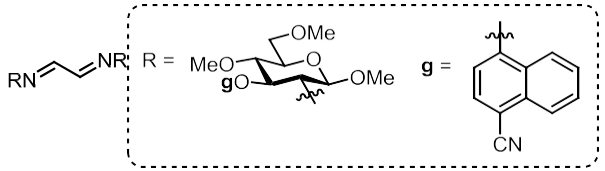
^{13}C NMR (125 MHz, $CDCl_3$)

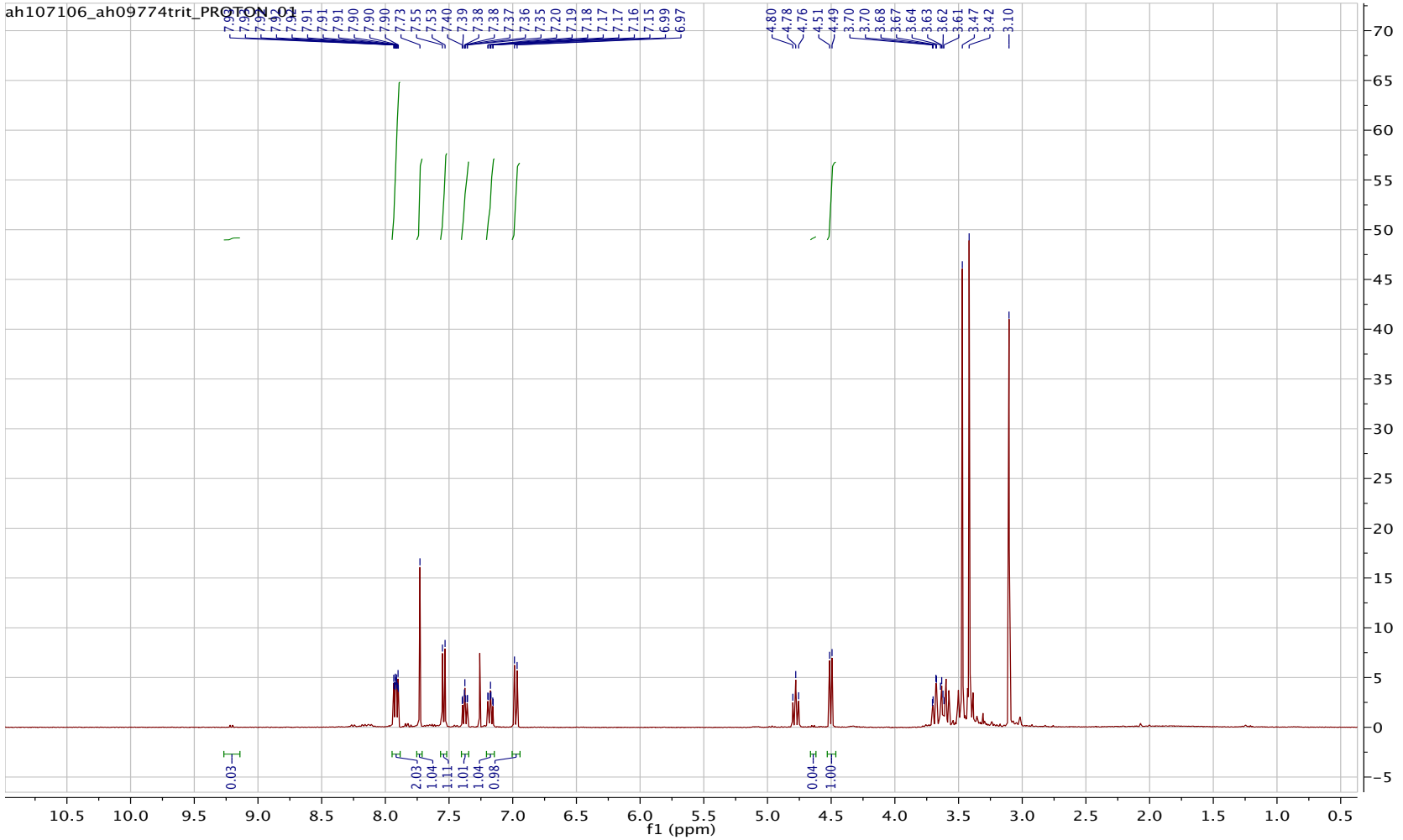


^{19}F NMR (470 MHz, $CDCl_3$)

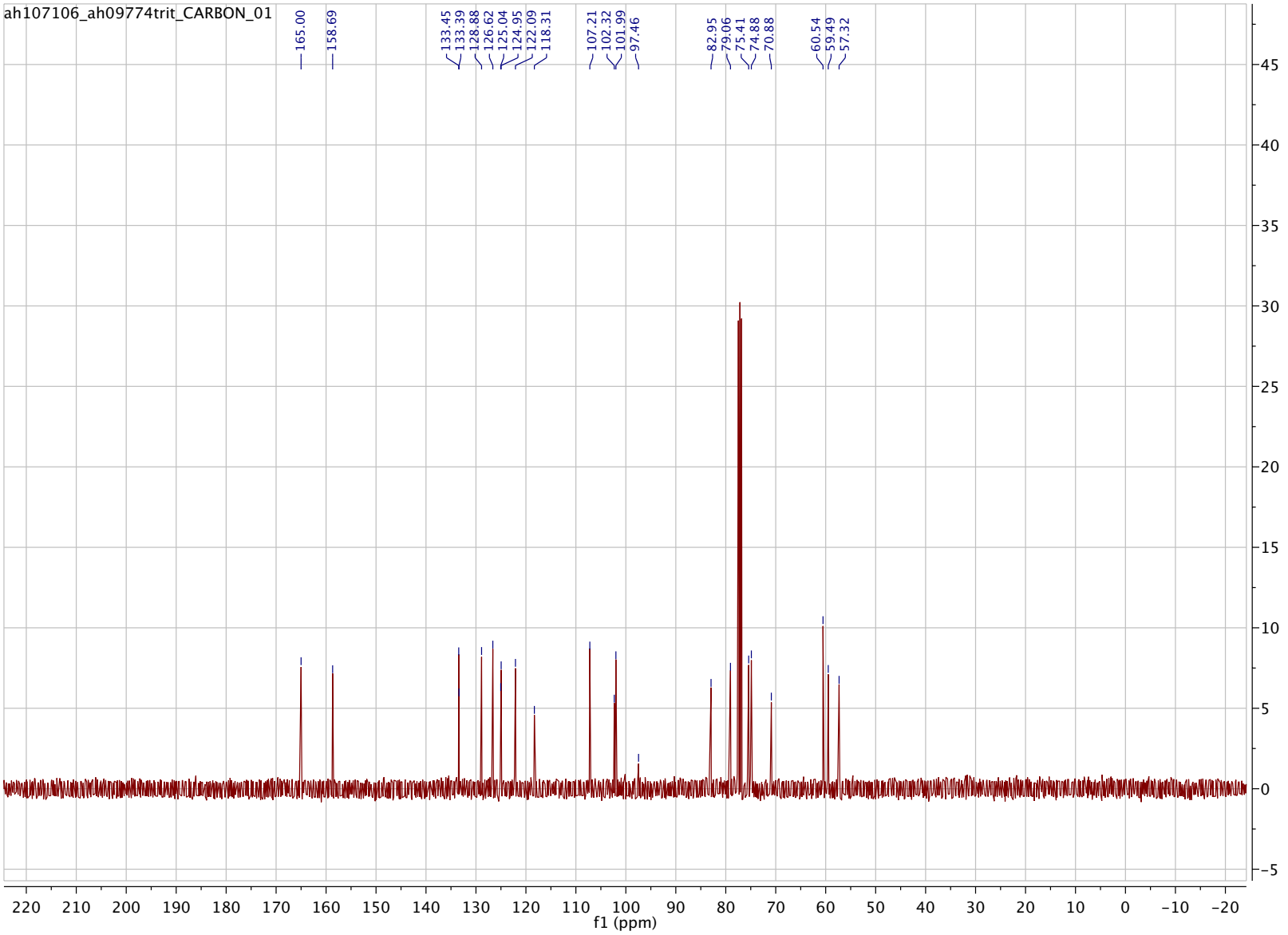


^{1}H NMR (500 MHz, $CDCl_3$) Bis(methyl 2-amino-4,6-di-*O*-methyl-3-*O*-1'-(4'-cyano)naphthlene-2-deoxy-β-D-glucopyranoside)-*N*,*N*'-iminoethylidene (S6e):

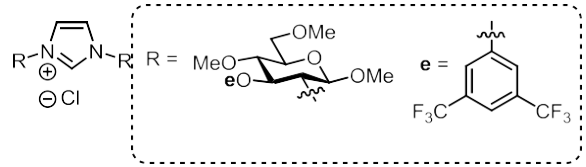


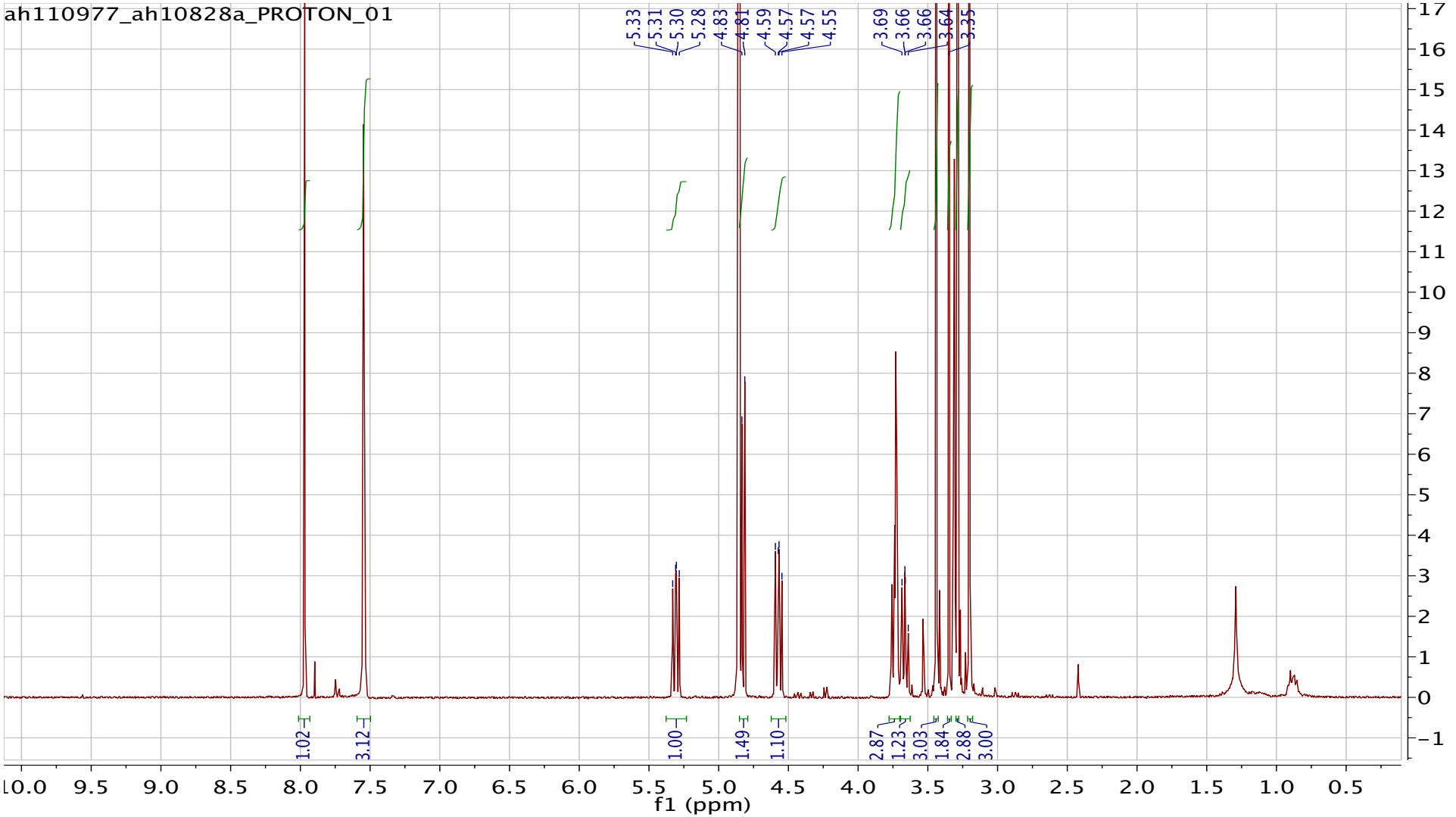


^{13}C NMR (125 MHz, $CDCl_3$)

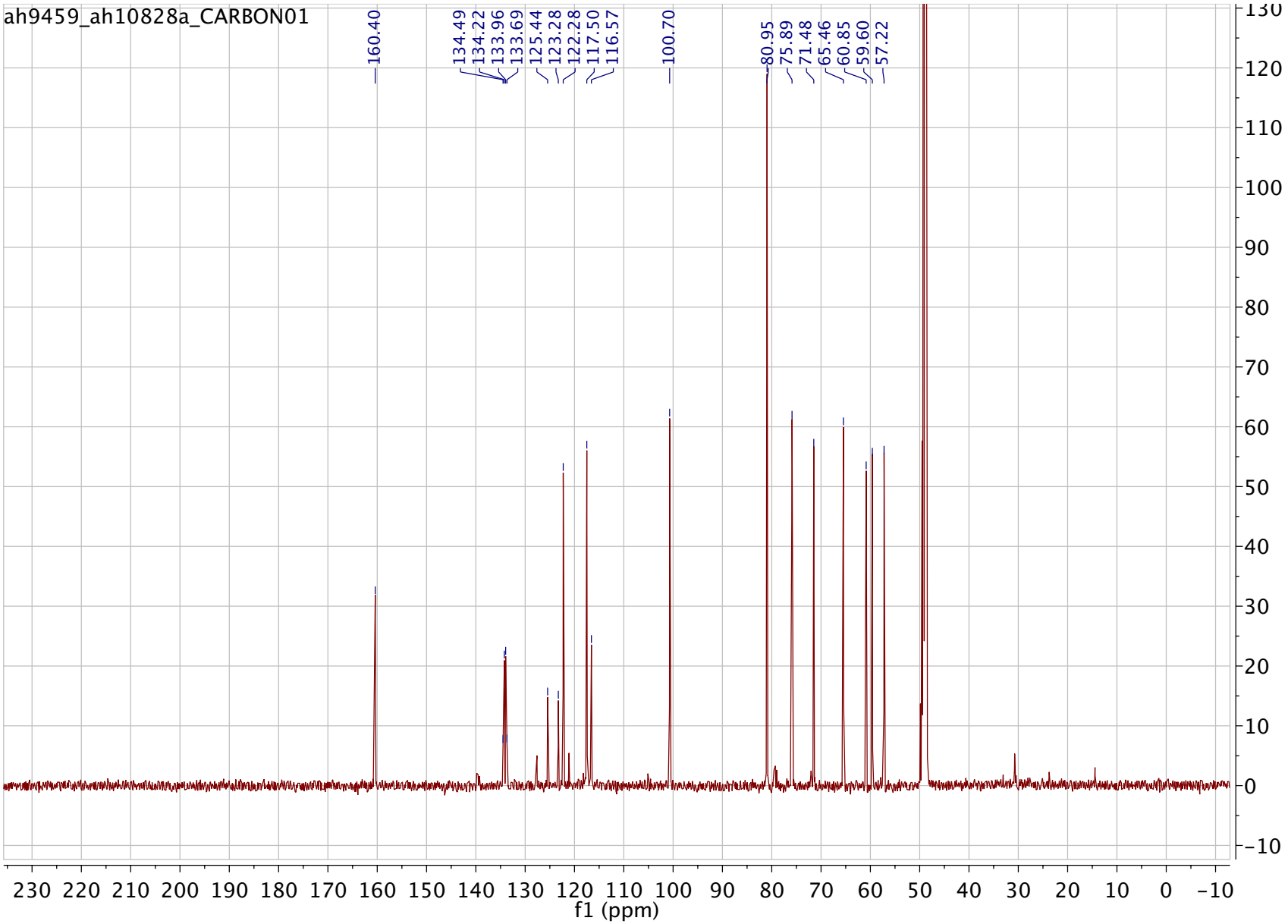


^{1}H NMR (500 MHz, $CDCl_3$) 1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(3',5'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)imidazolium chloride (9b):

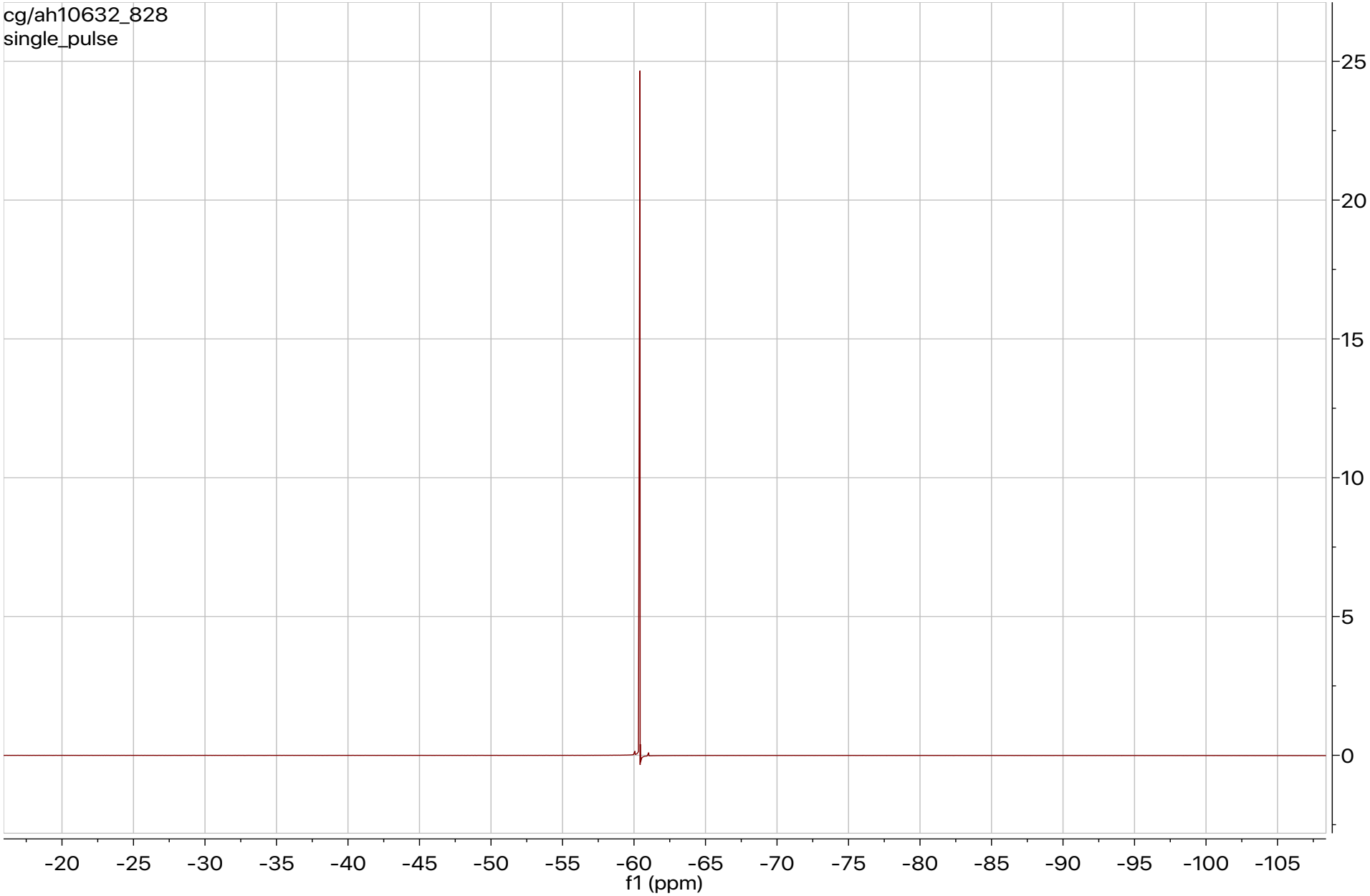




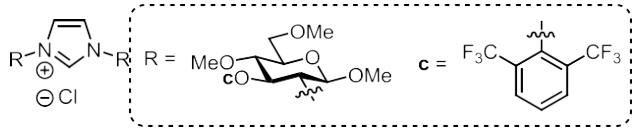
^{13}C NMR (125 MHz, $CDCl_3$)

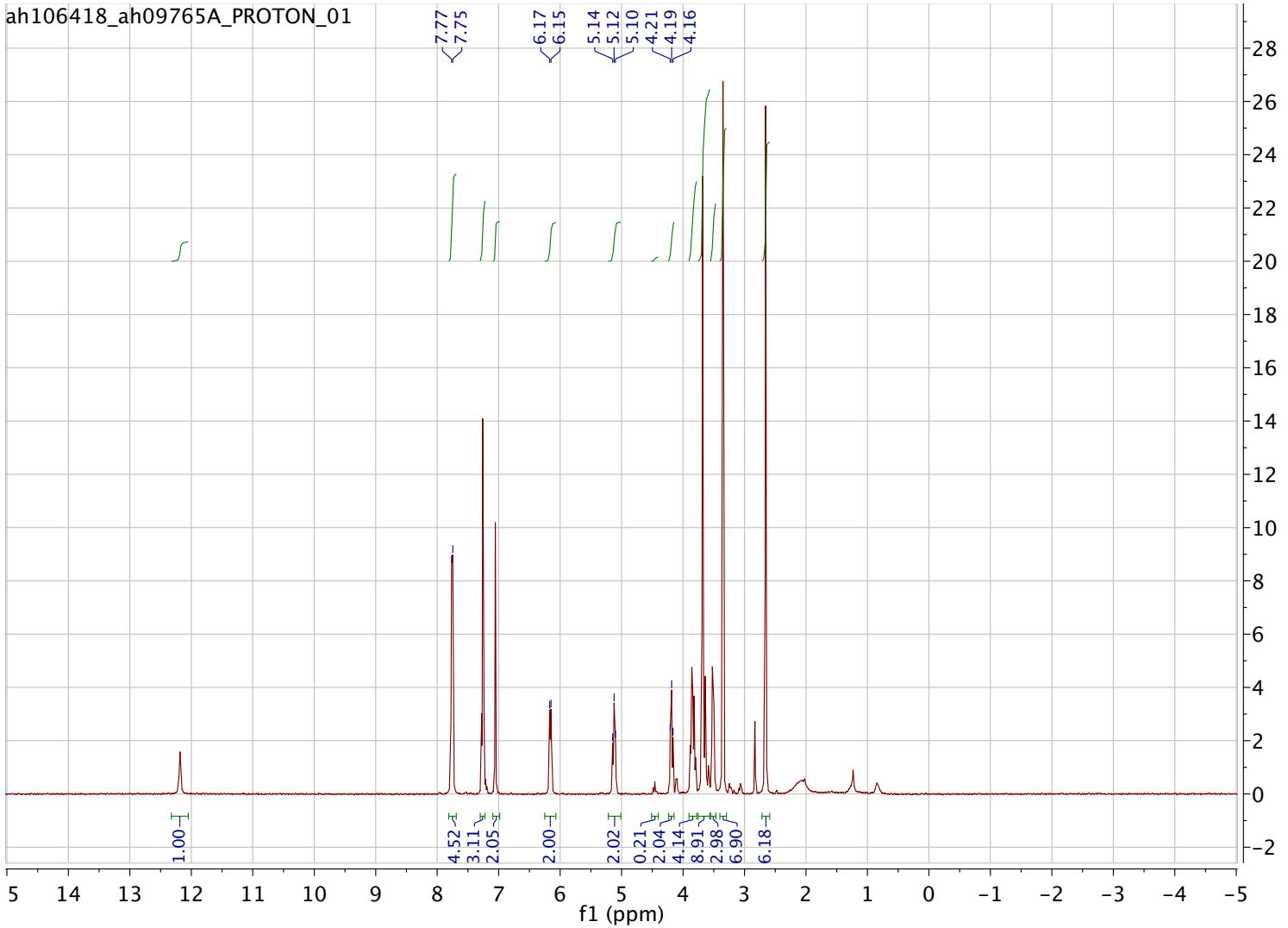


^{19}F NMR (283 MHz, $CDCl_3$)

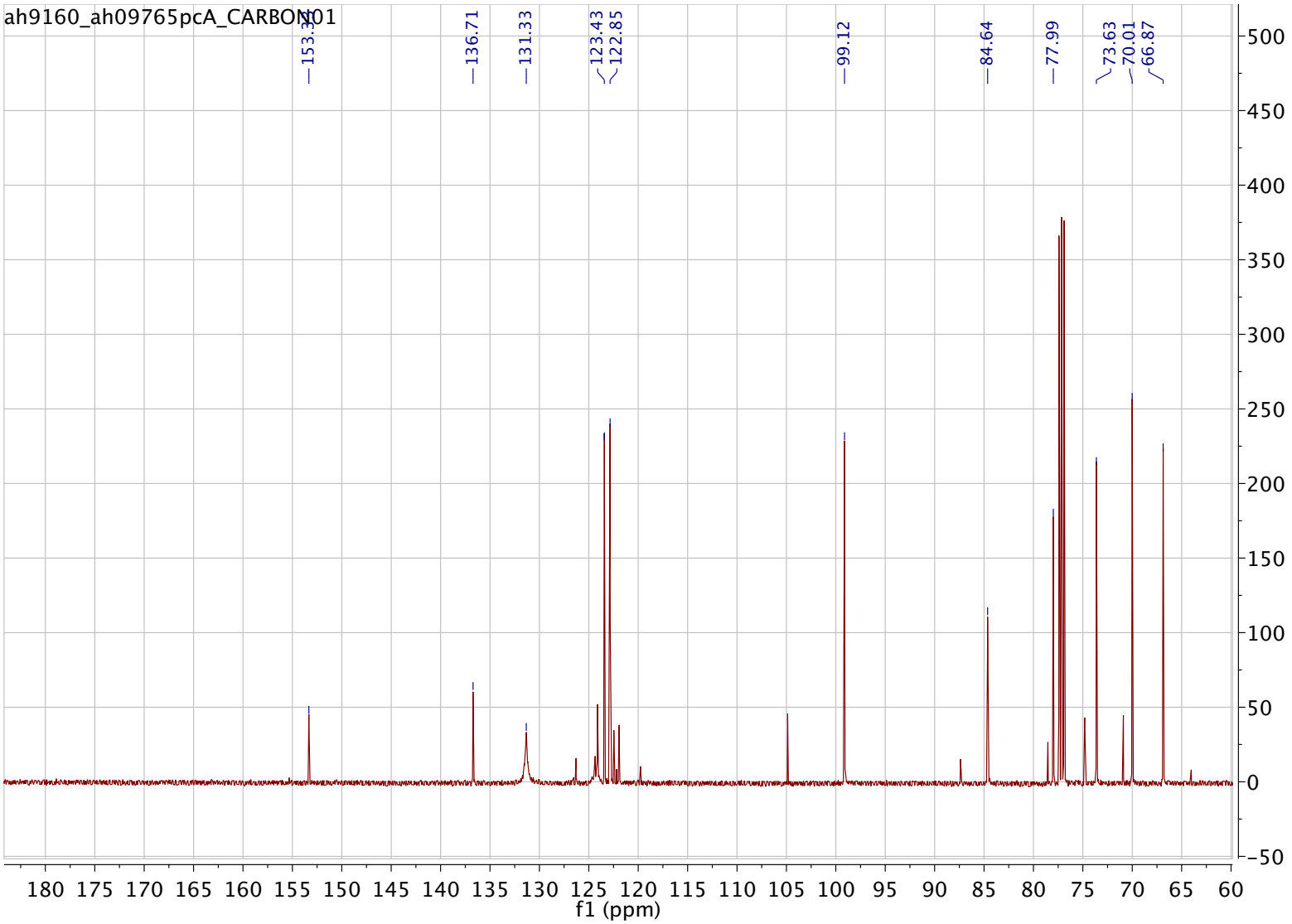


^{1}H NMR (500 MHz, $CDCl_3$) 1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',6'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)imidazolium chloride (16a):

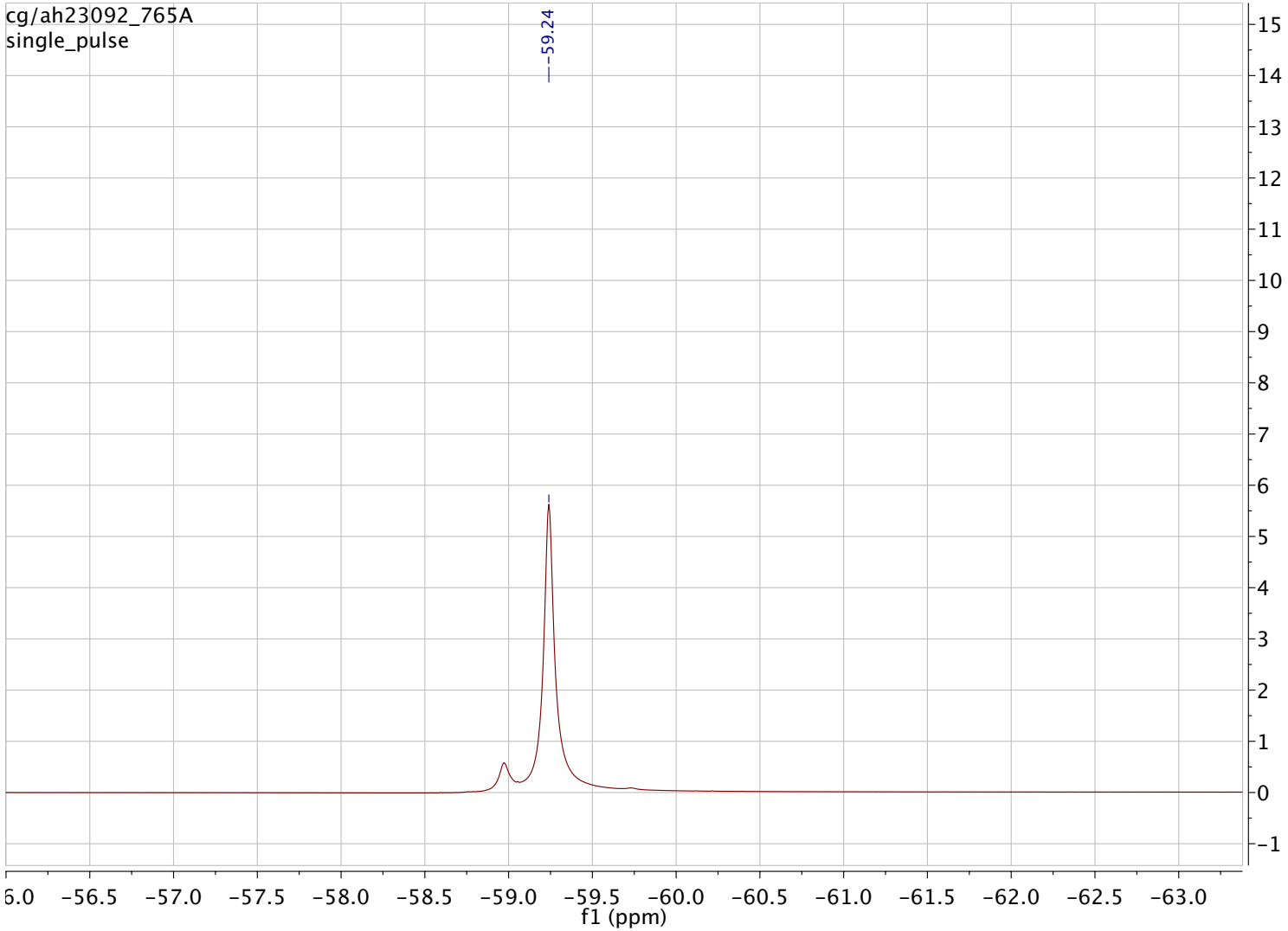




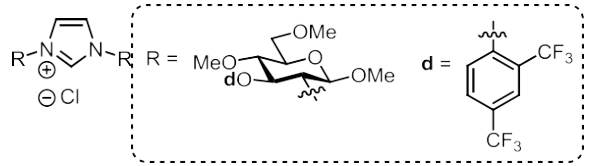
^{13}C NMR (125 MHz, $CDCl_3$)

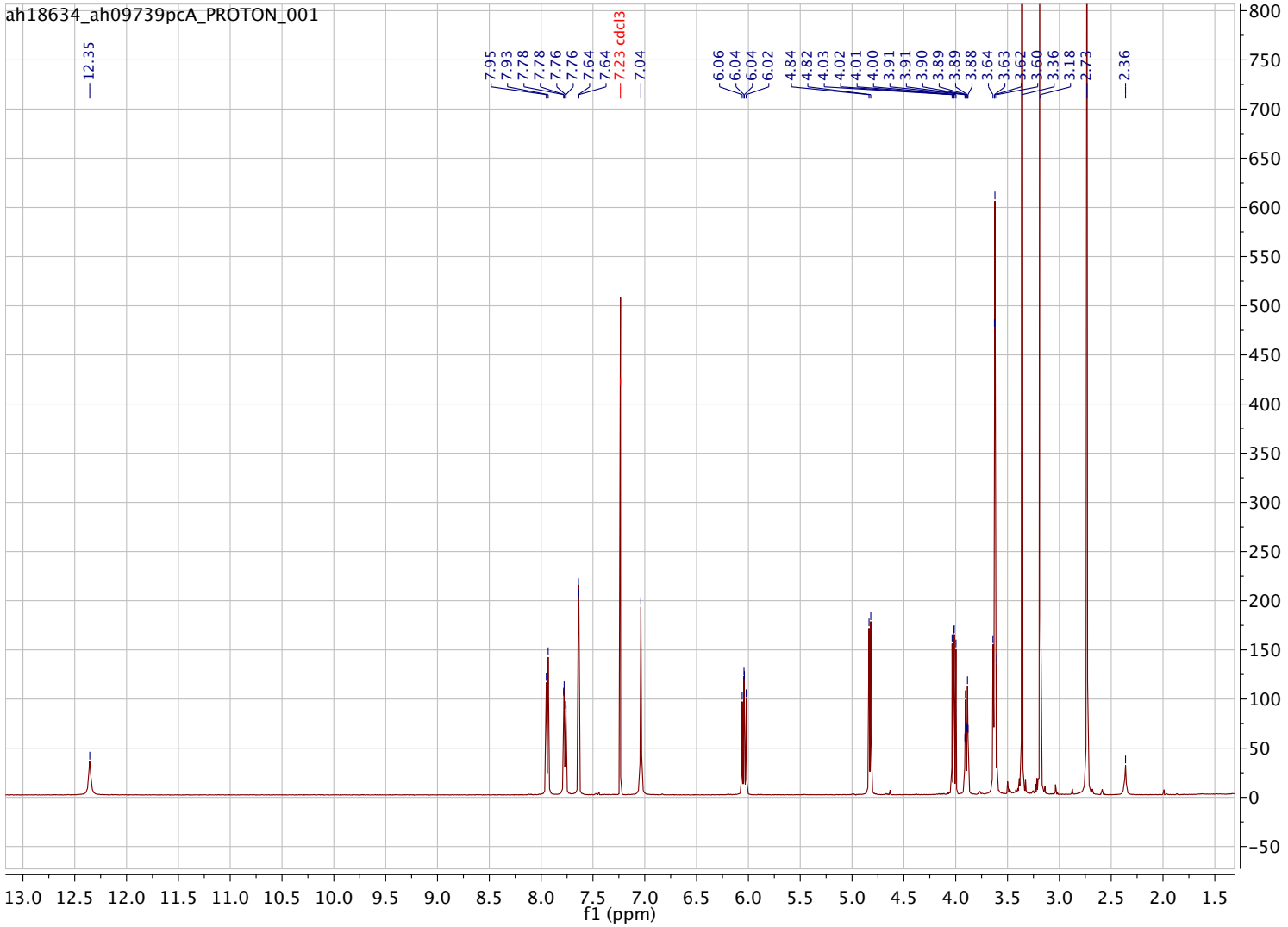


^{19}F NMR (470 MHz, $CDCl_3$)

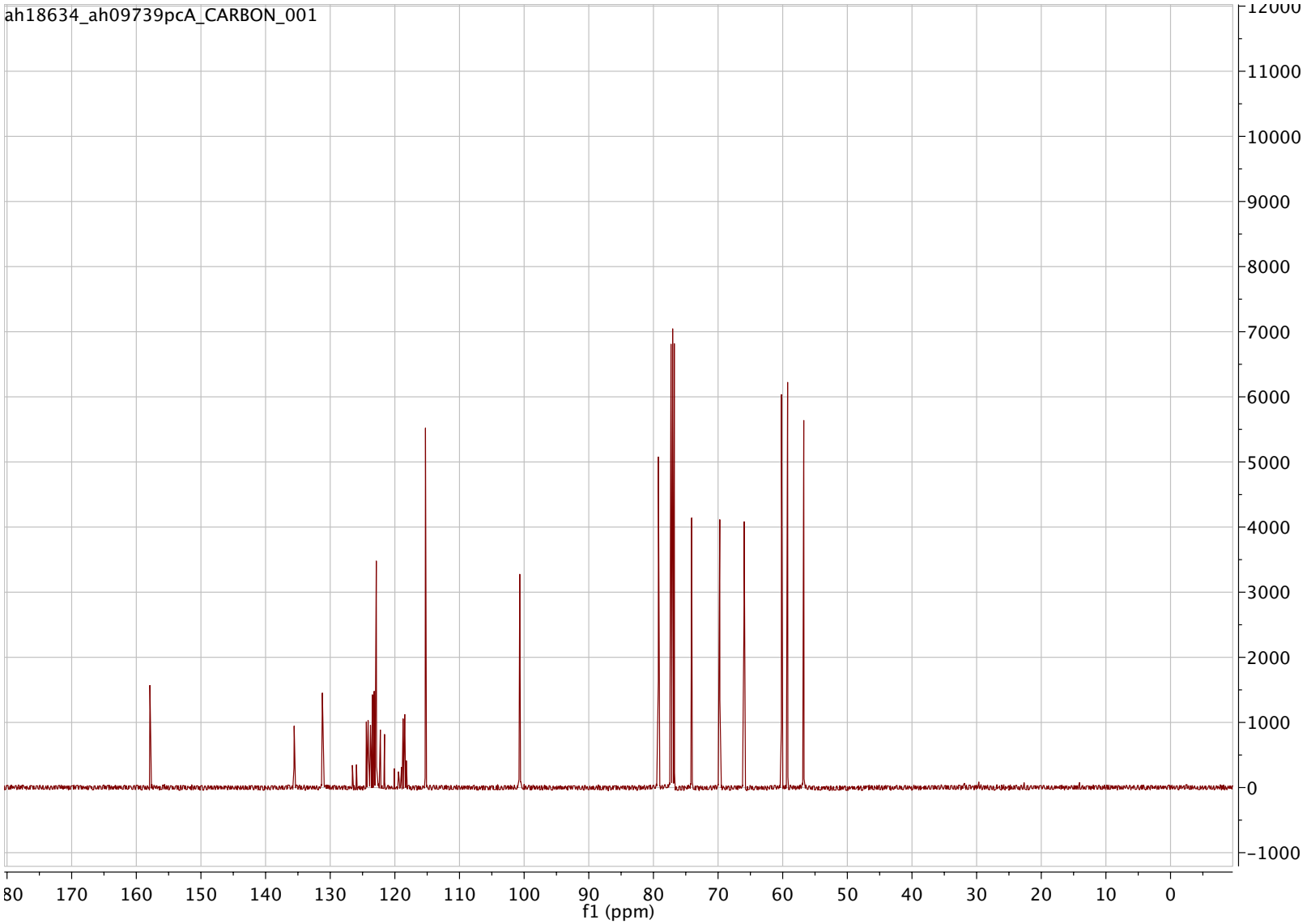


^{1}H NMR (500 MHz, $CDCl_3$) 1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',4'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)imidazolium chloride (16b):

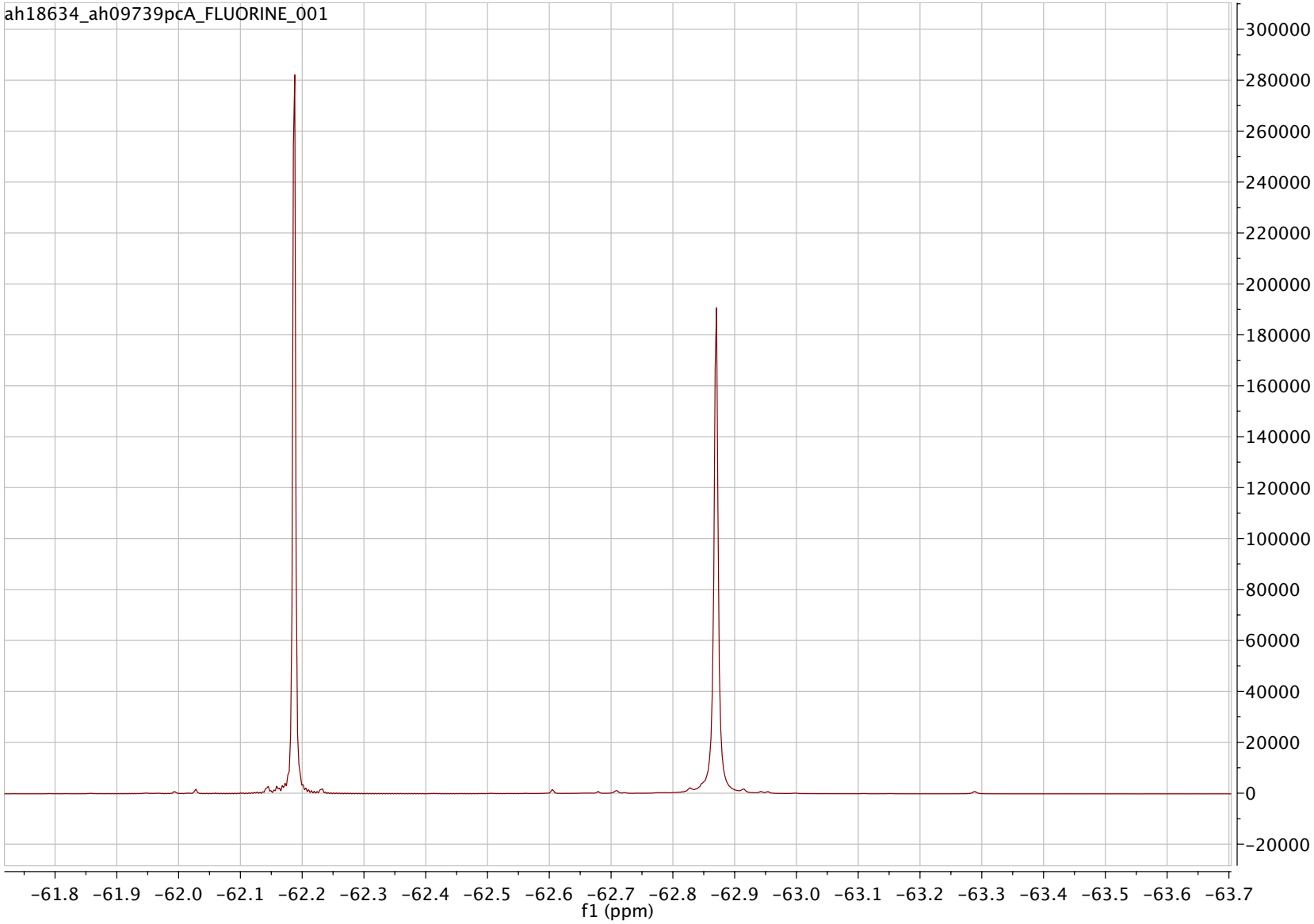




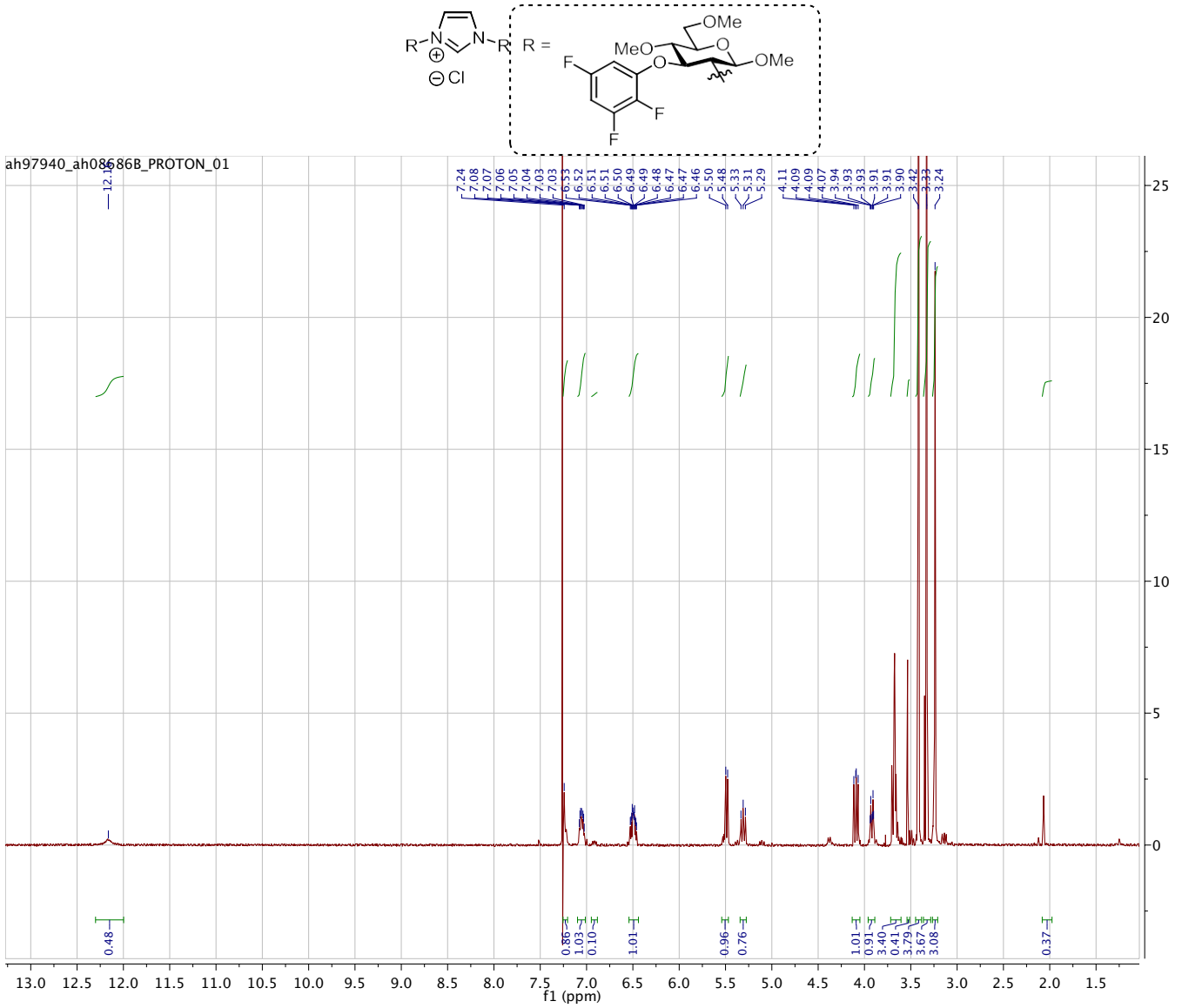
^{13}C NMR (125 MHz, $CDCl_3$)



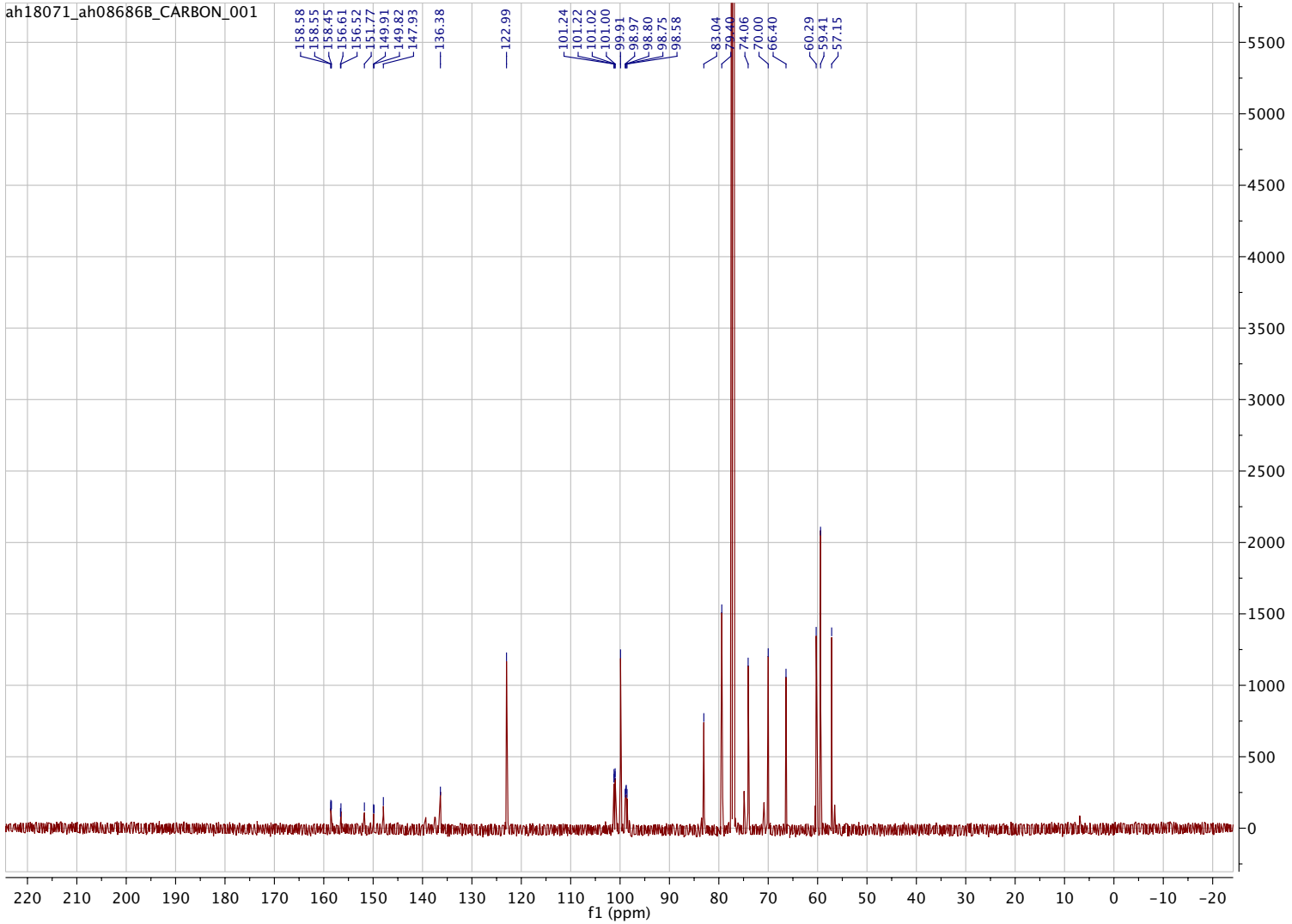
^{19}F NMR (470 MHz, $CDCl_3$)



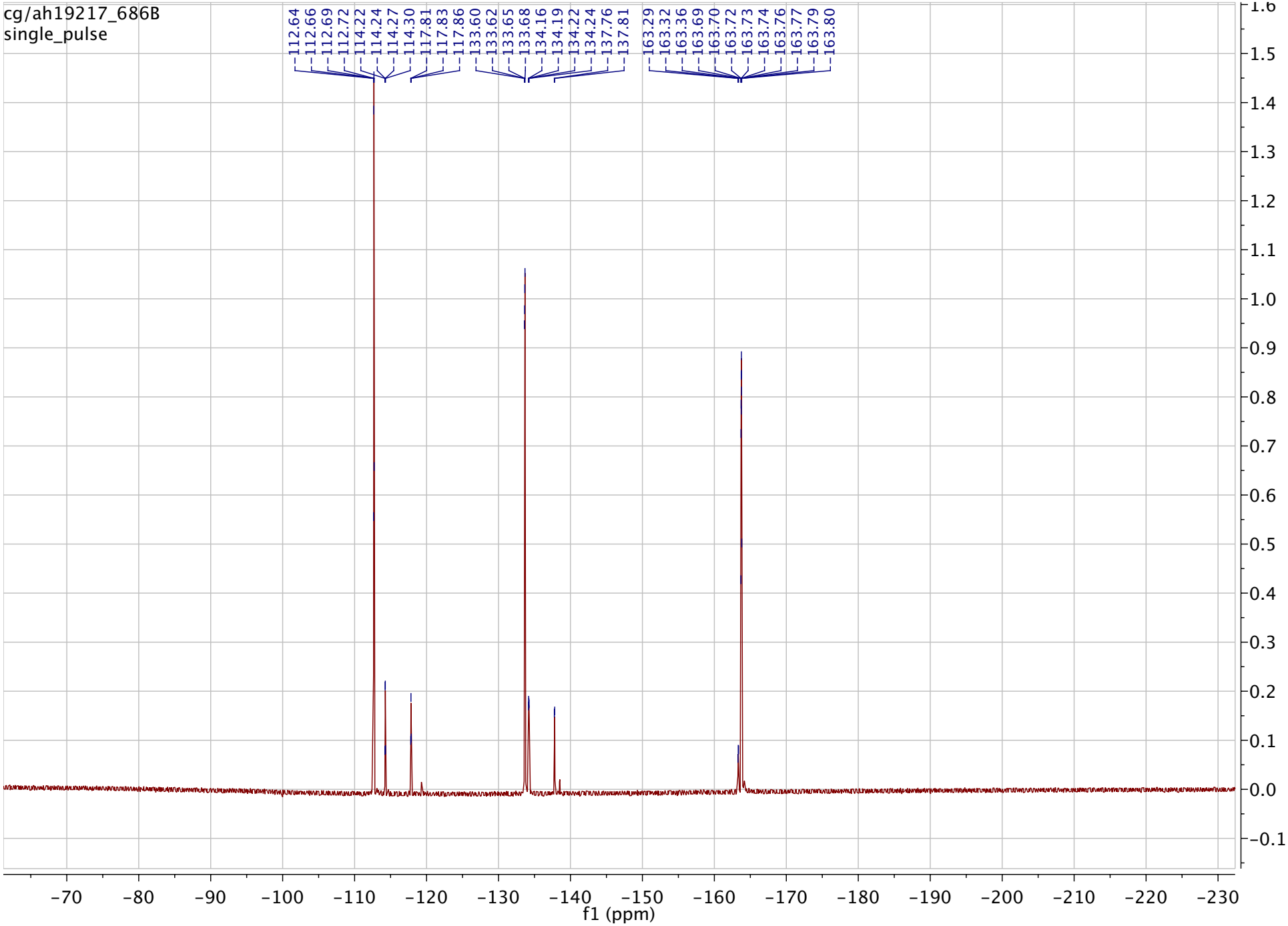
^{1}H NMR (500 MHz, $CDCl_3$) 1,3-Bis(methyl 2-amino-4-6-bis-*O*-methyl-3-*O*-(2',3',5'-trifluoro)benzene-2-deoxy-β-D-glucopyranoside)imidazolium chloride (16c):



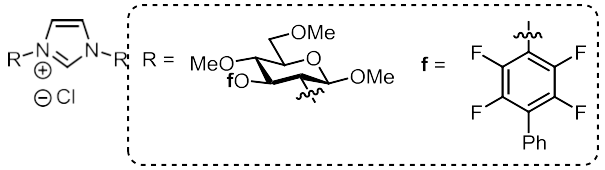
^{13}C NMR (125 MHz, $CDCl_3$)

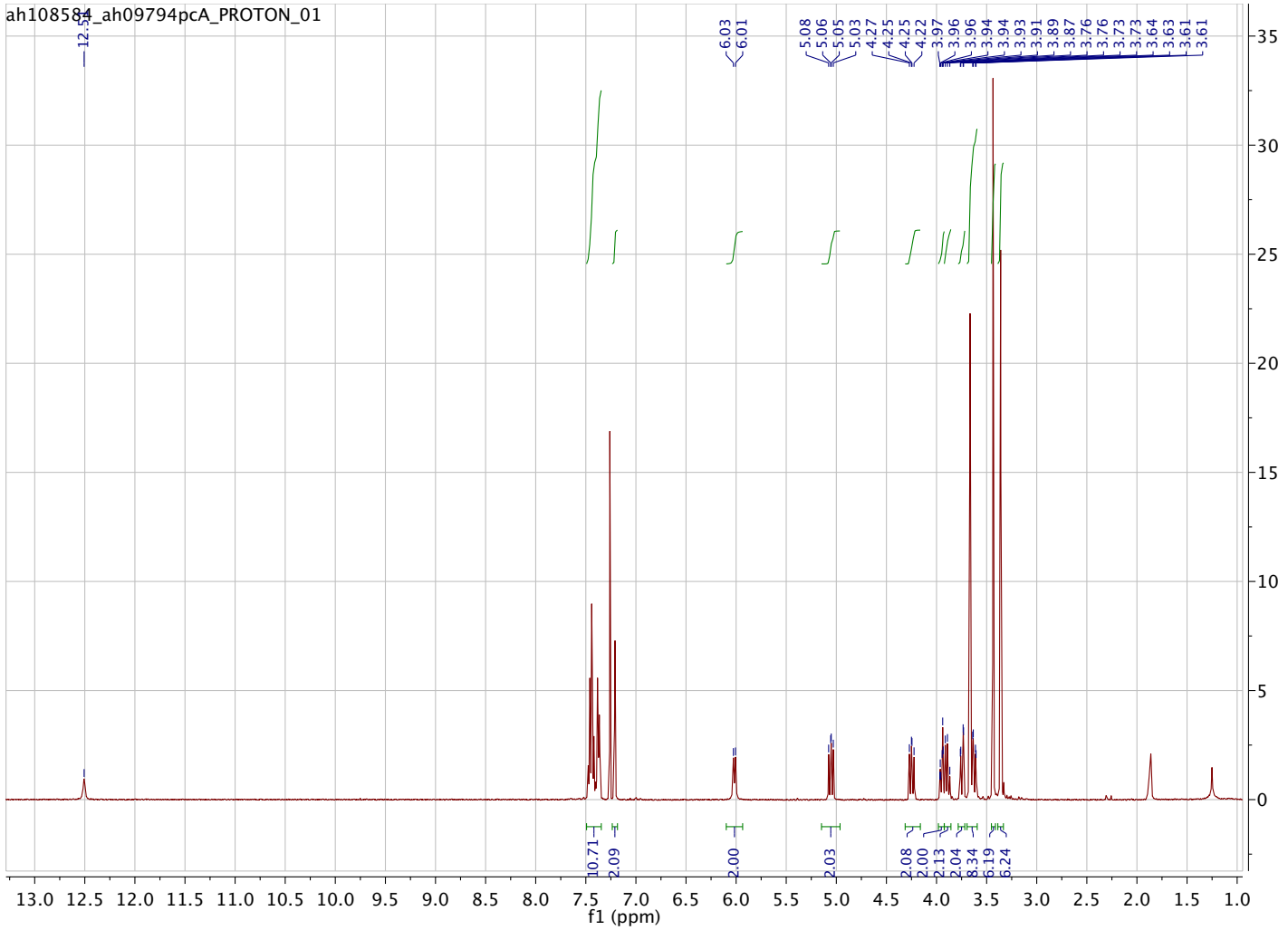


^{19}F NMR (377 MHz, $CDCl_3$)

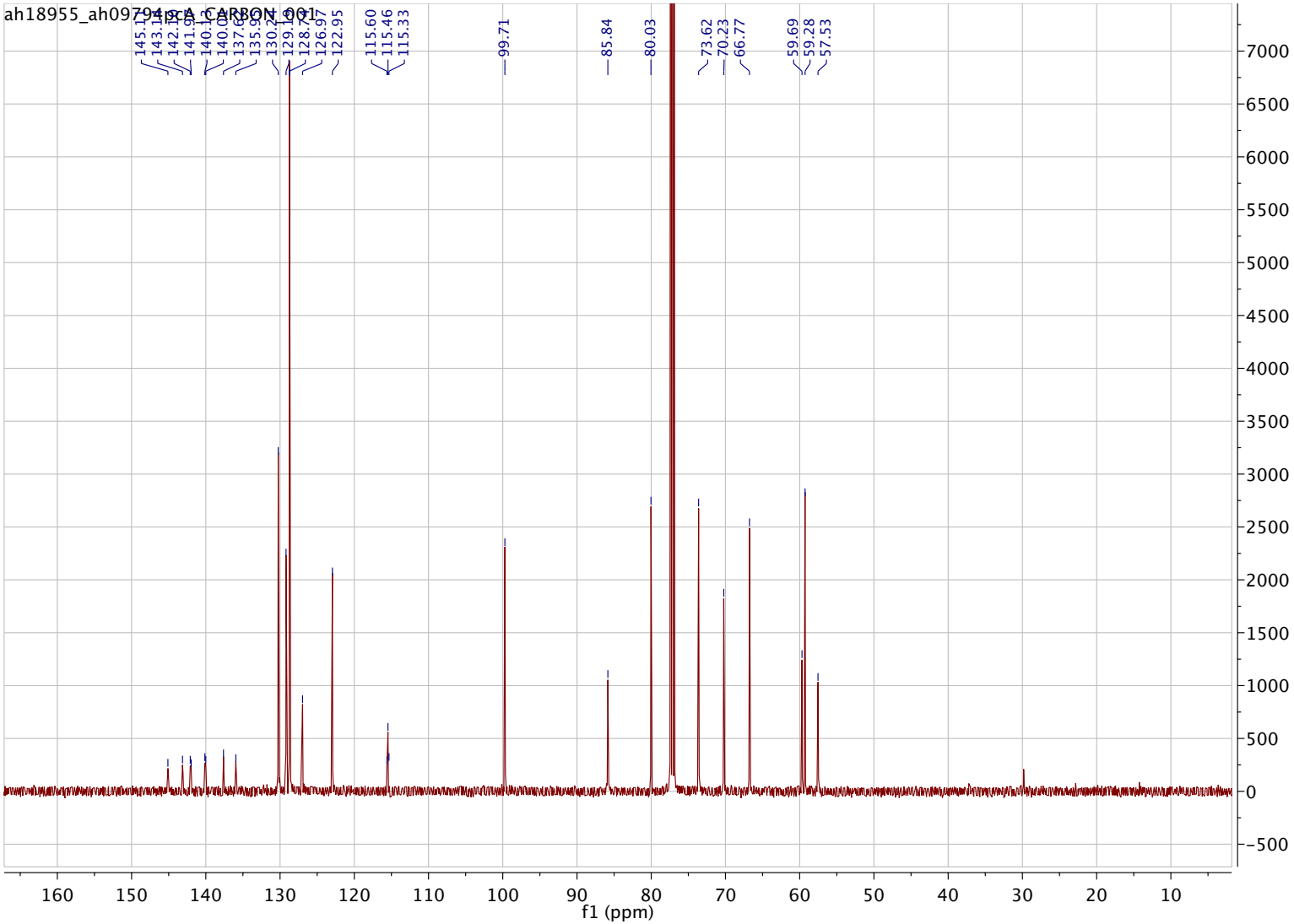


^{1}H NMR (500 MHz, $CDCl_3$) 1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(4'-phenyl-2',3',5',6'-tetrafluoro)benzene-2-deoxy-β-D-glucopyranoside)imidazolium chloride (16d):

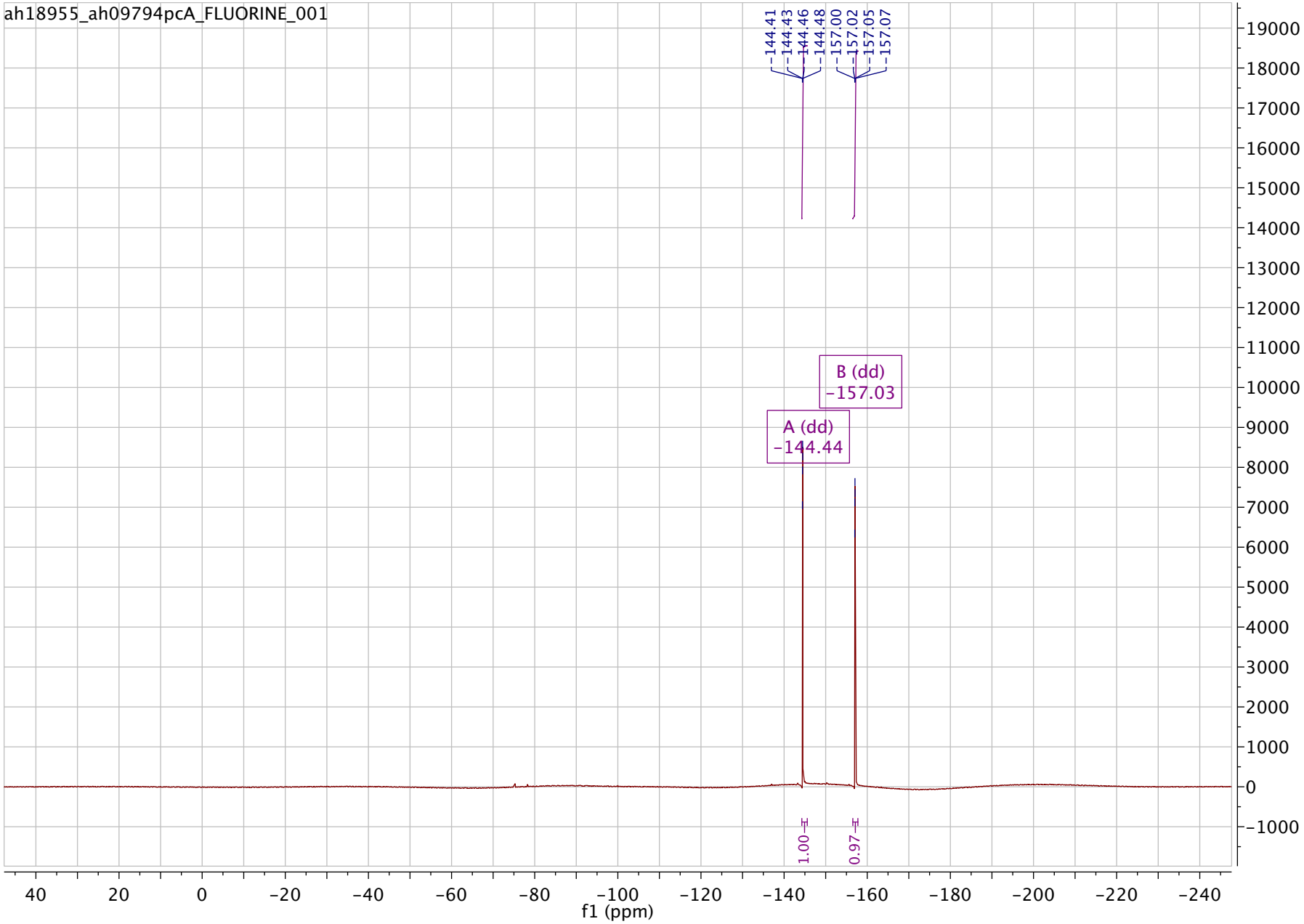




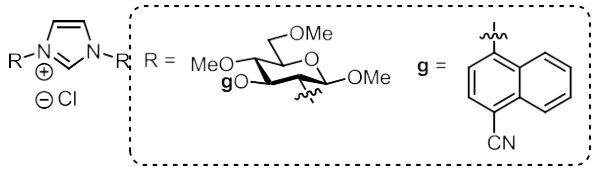
^{13}C NMR (125 MHz, $CDCl_3$)

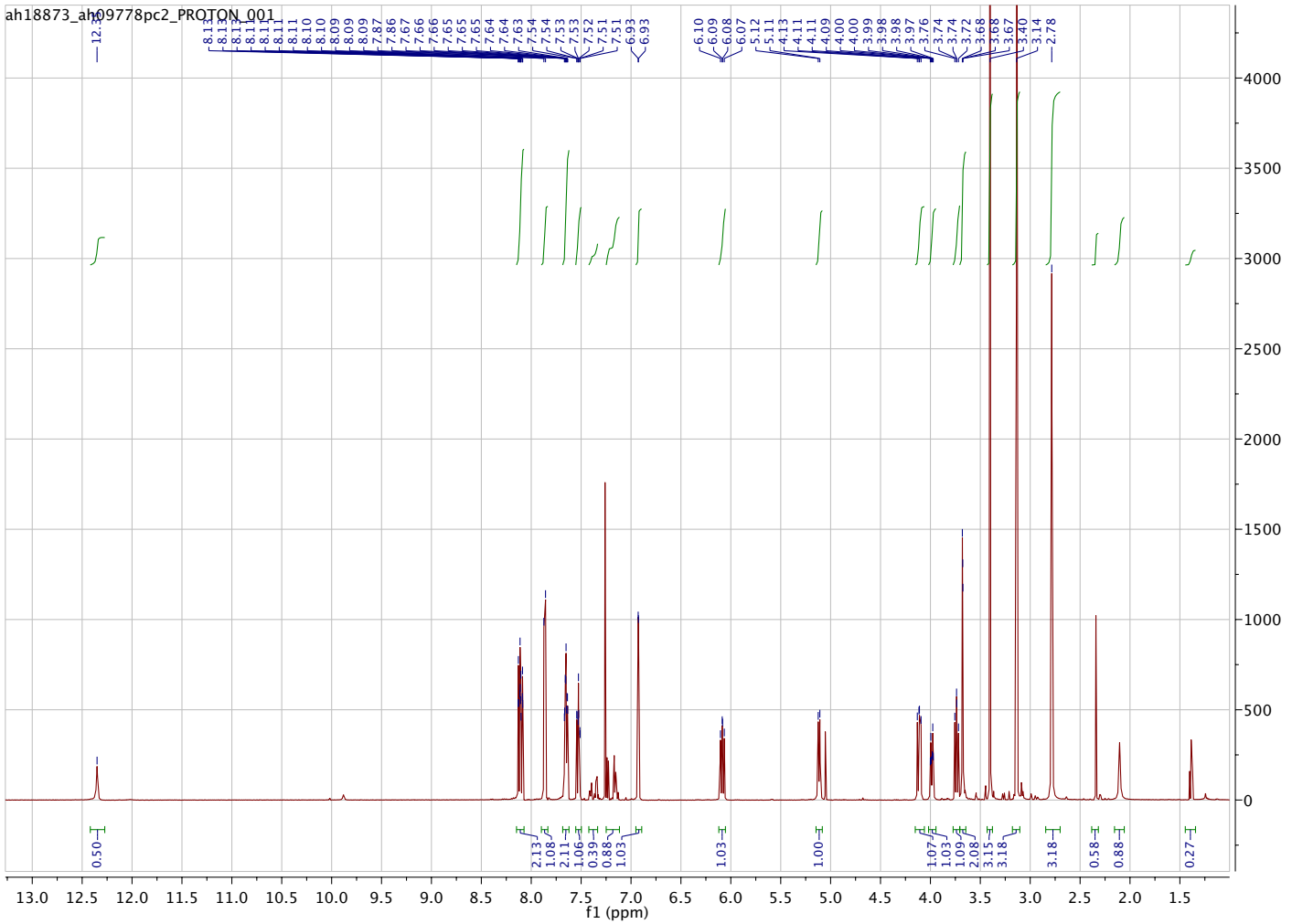


^{19}F NMR (470 MHz, $CDCl_3$)

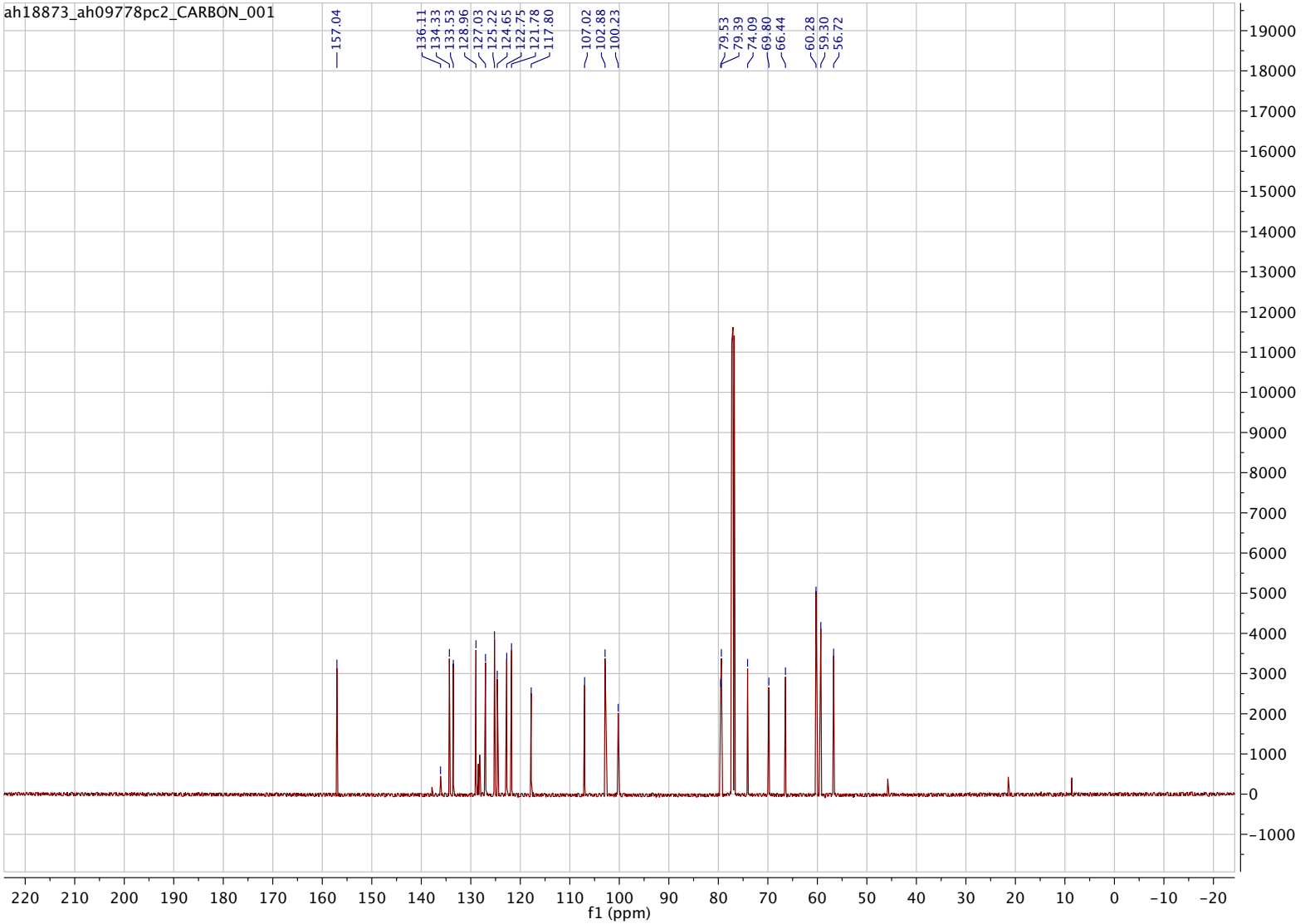


^{1}H NMR (500 MHz, $CDCl_3$) 1,3-Bis(methyl 2-amino-4,6-di-*O*-methyl-3-*O*-1'-(4'-cyano)naphthlene-2-deoxy-β-D-glucopyranoside)imidazolium chloride (16e):

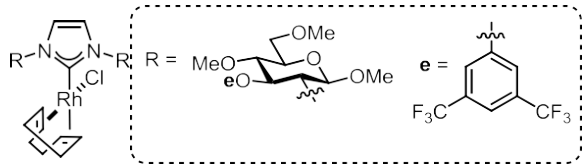


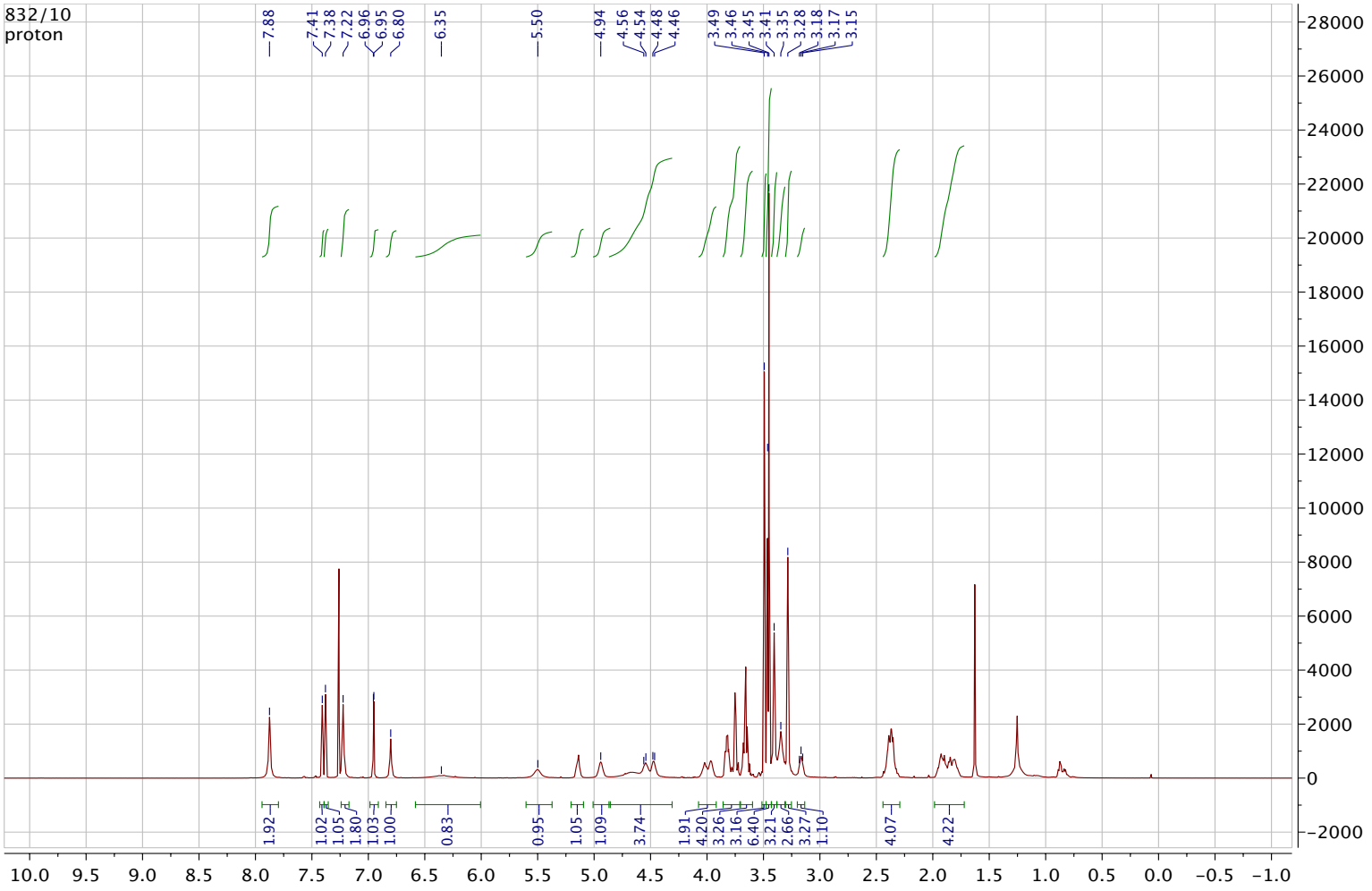


^{13}C NMR (125 MHz, $CDCl_3$)

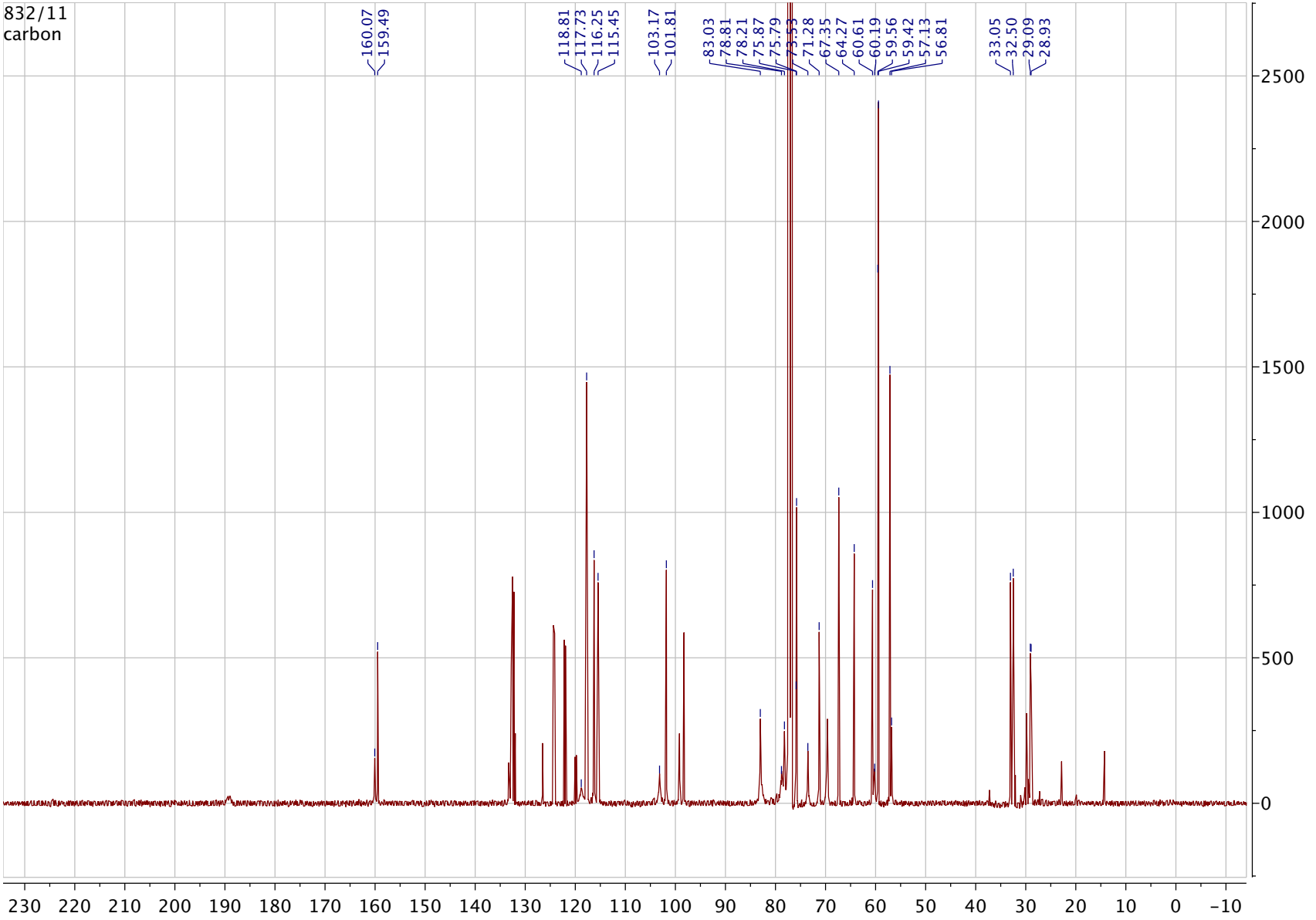


^{1}H NMR (500 MHz, $CDCl_3$) [1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(3',5'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (12b):

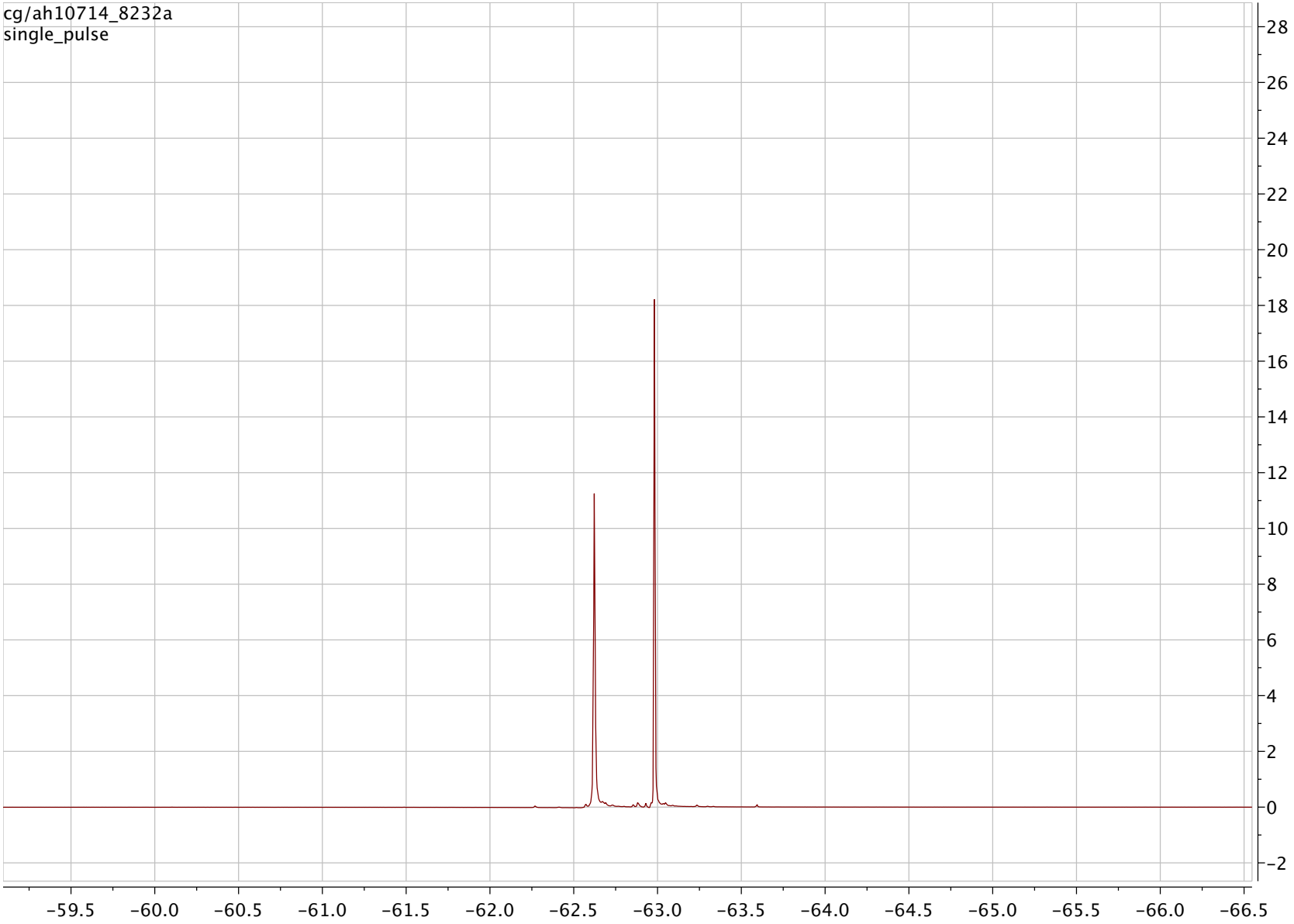




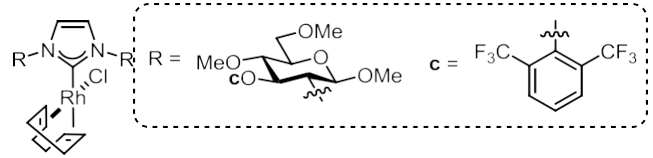
^{13}C NMR (125 MHz, $CDCl_3$)

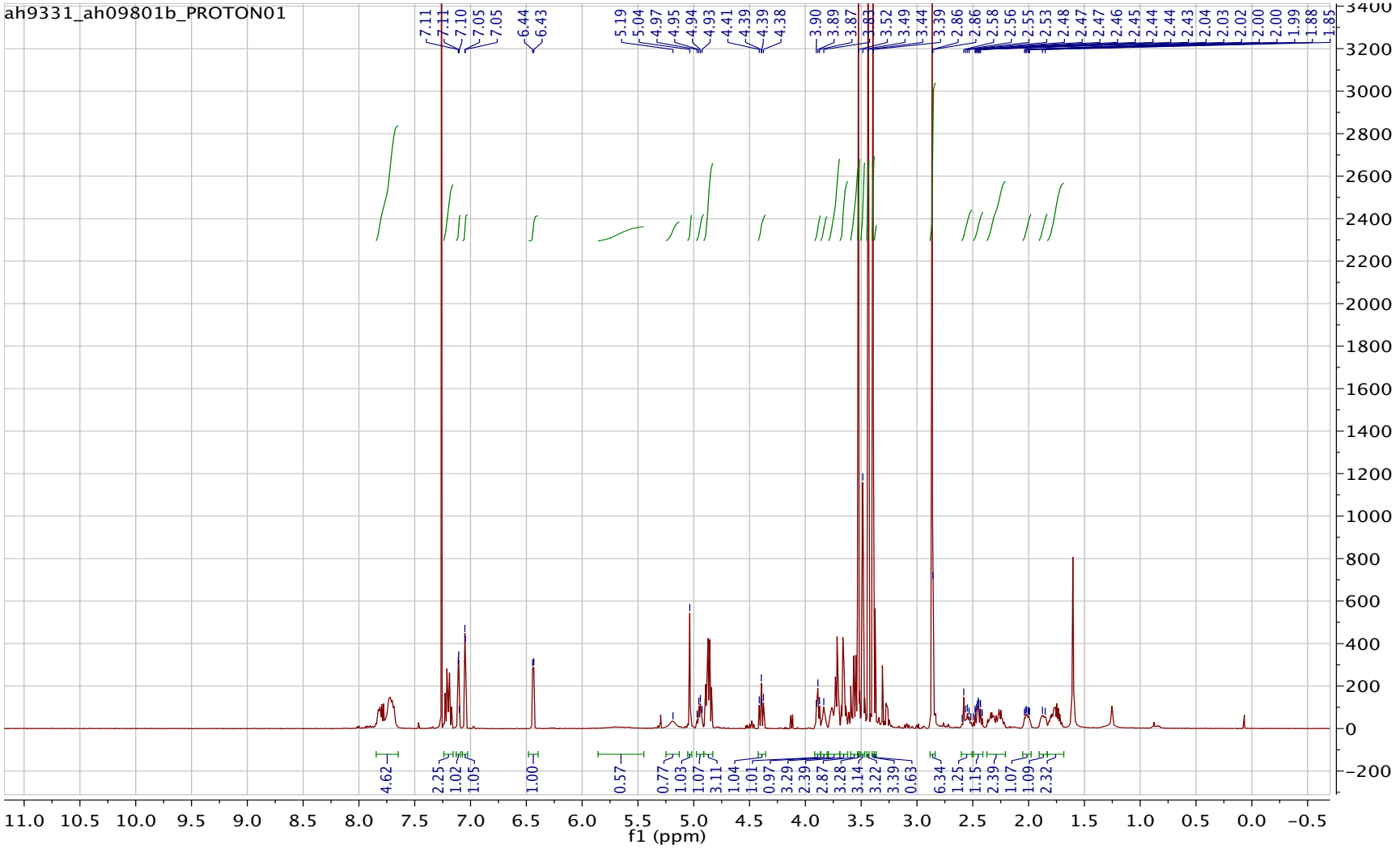


^{19}F NMR (283 MHz, $CDCl_3$)

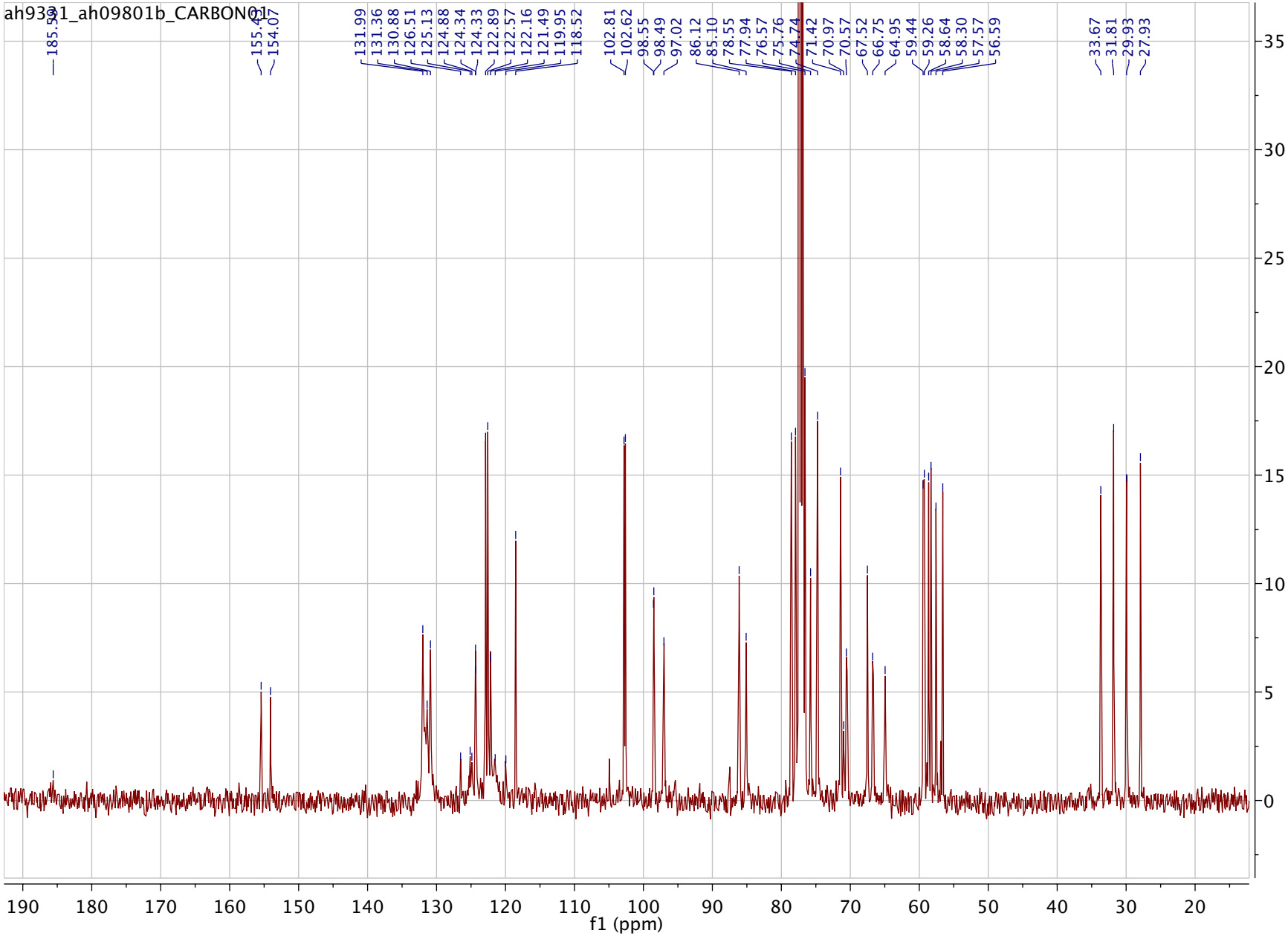


^{1}H NMR (500 MHz, $CDCl_3$) [1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',6'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (17a):

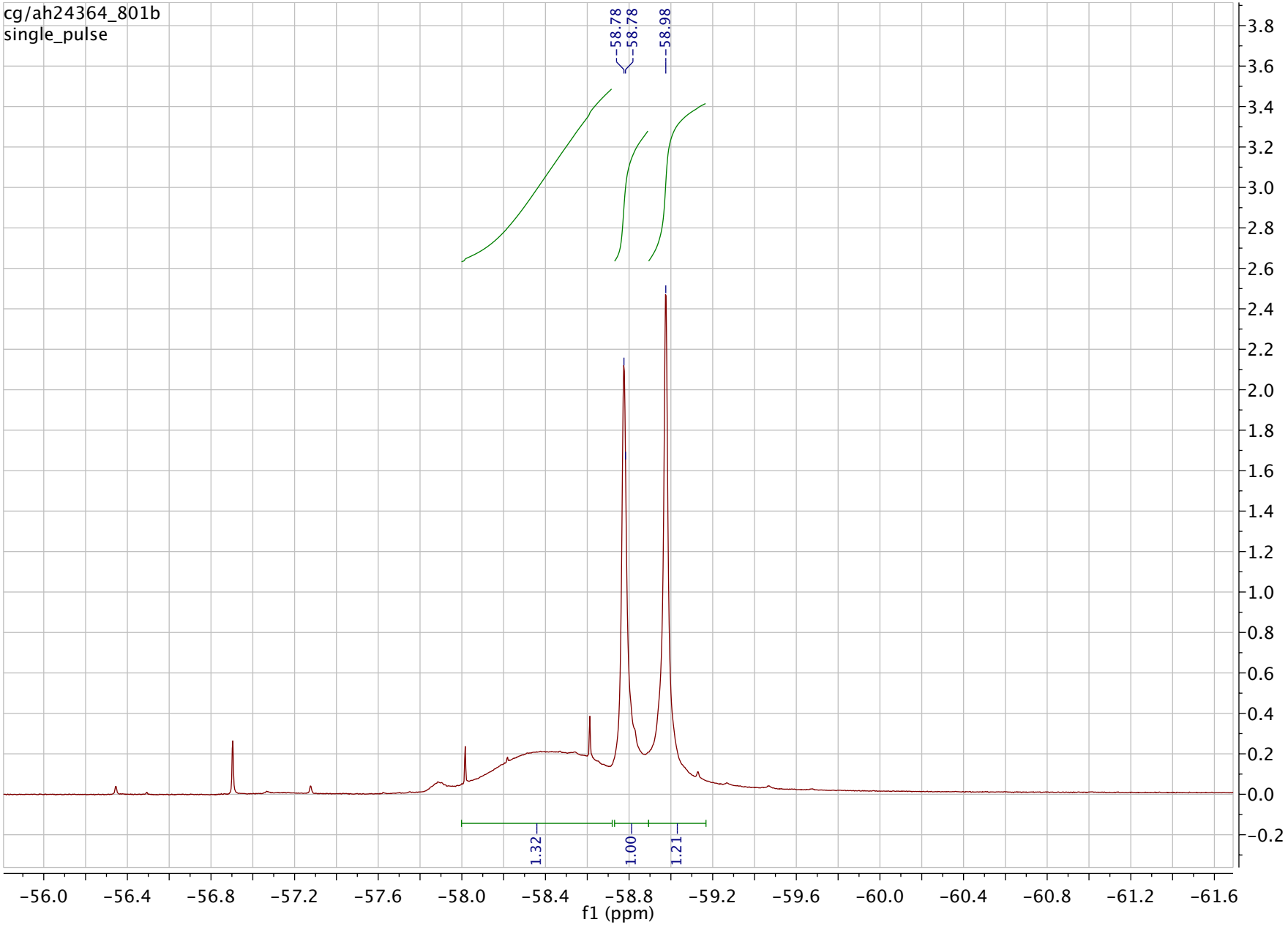




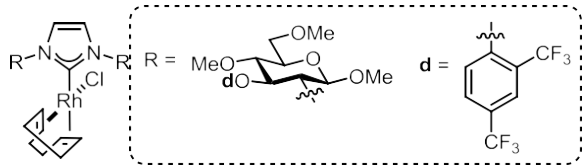
^{13}C NMR (125 MHz, $CDCl_3$)

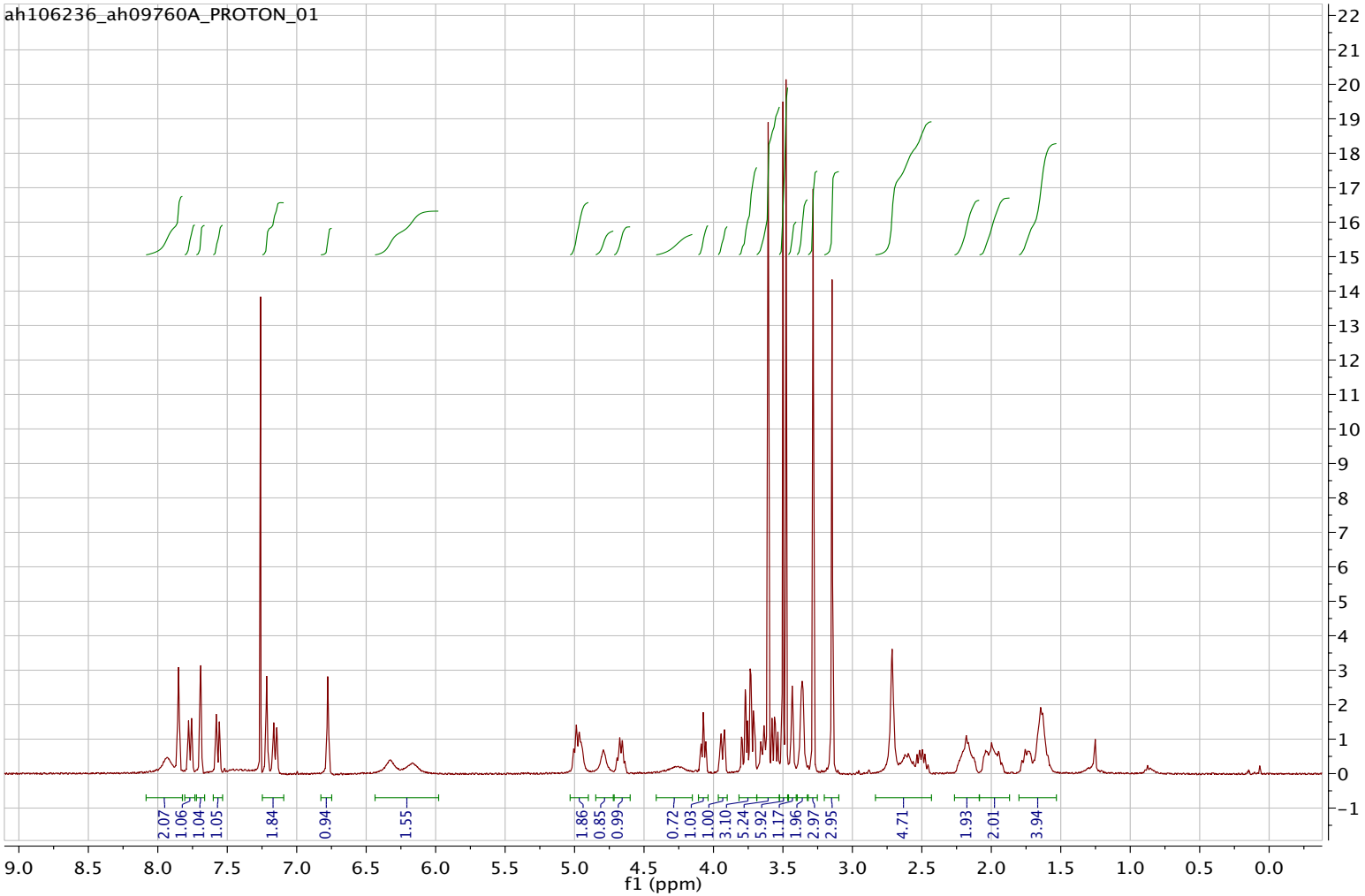


^{19}F NMR (470 MHz, $CDCl_3$)

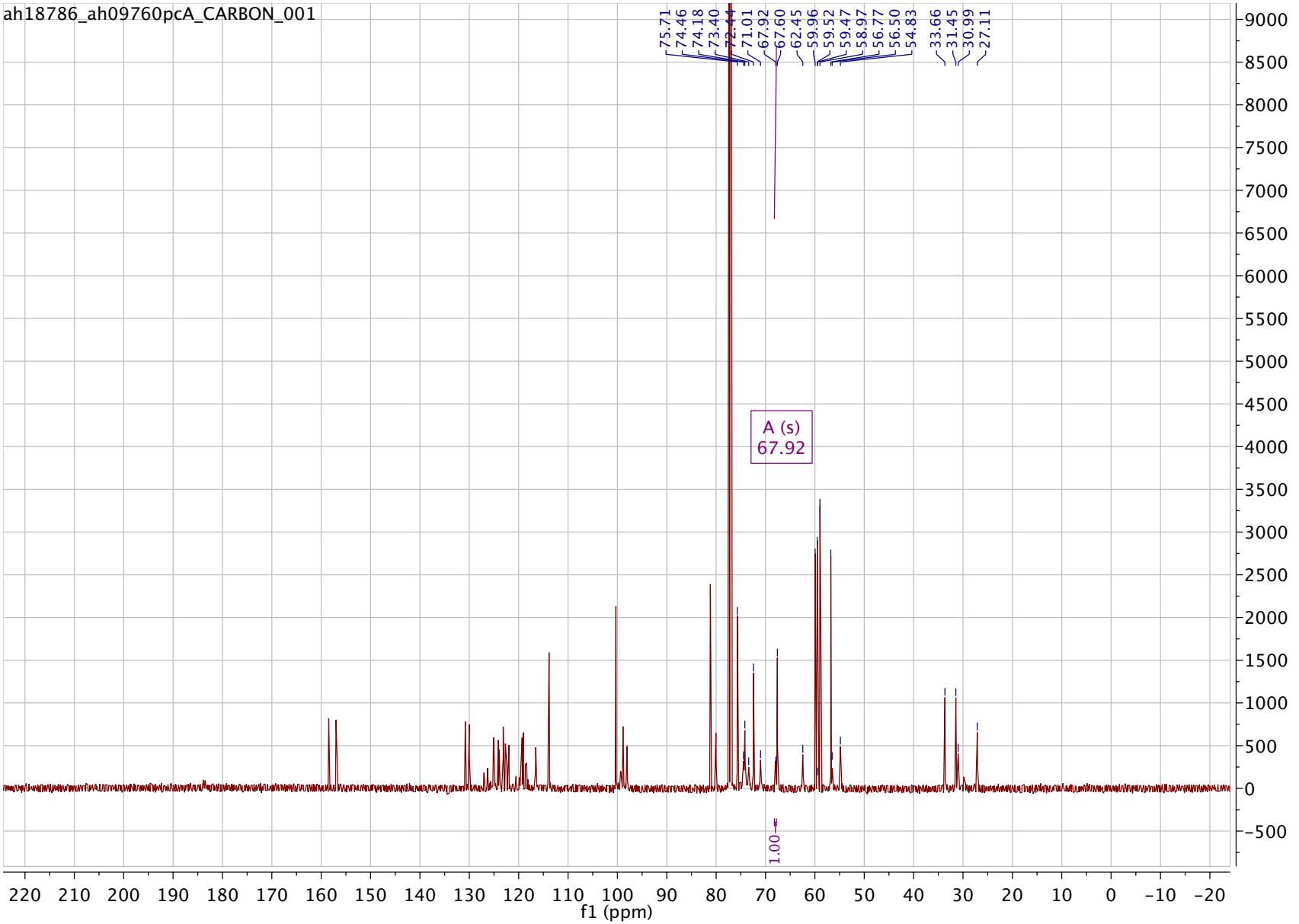


^{1}H NMR (500 MHz, $CDCl_3$) [1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',4'-trifluoromethyl)benzene-2-deoxy-β-D-glucopyranoside](chloro)(1,5-cyclooctadiene)rhodium(I) (17b):

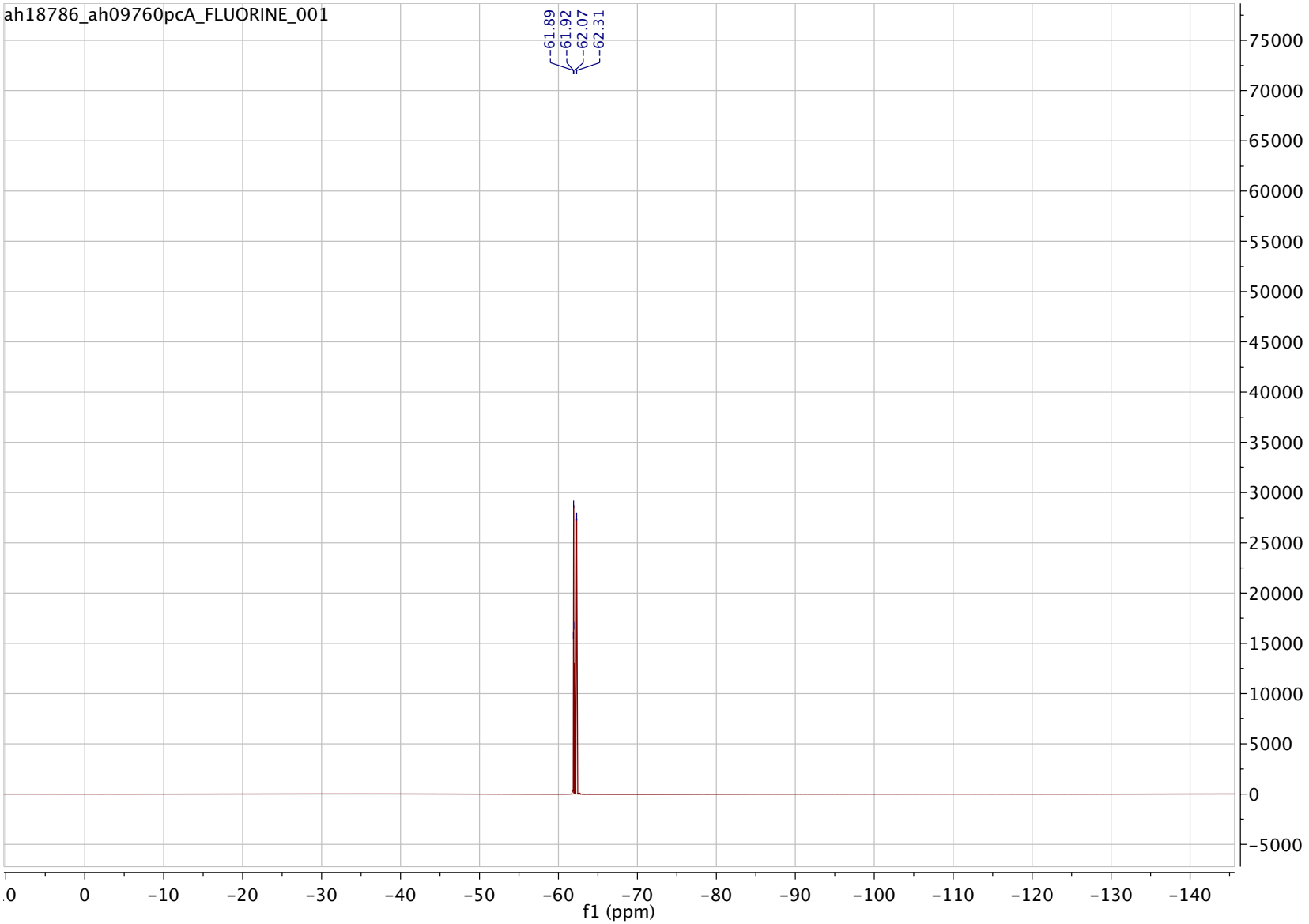




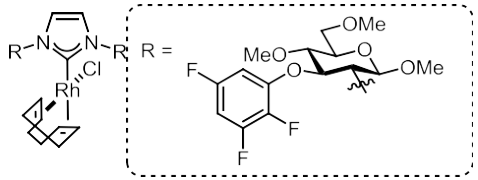
^{13}C NMR (125 MHz, $CDCl_3$)

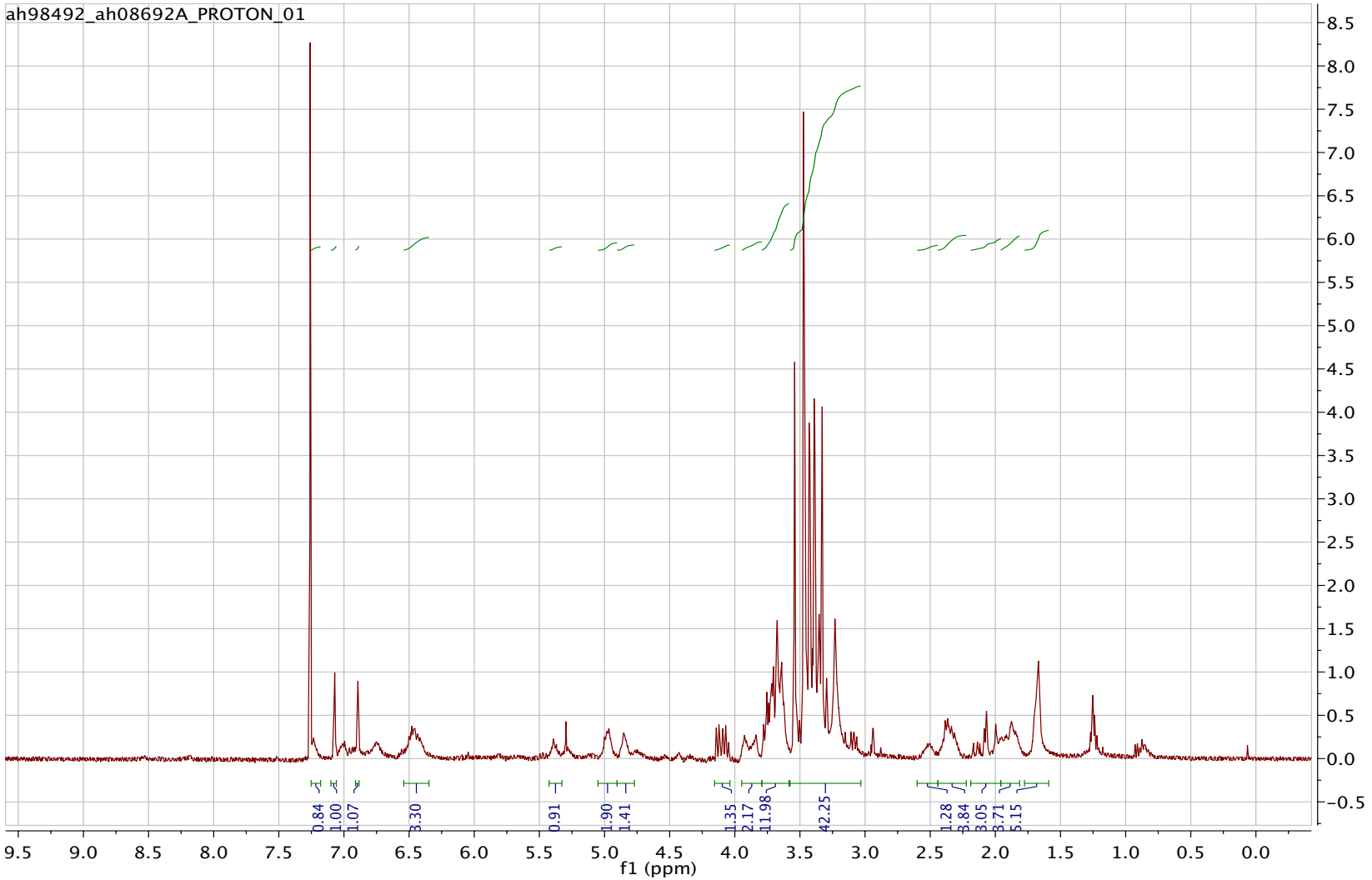


^{19}F NMR (470 MHz, $CDCl_3$)

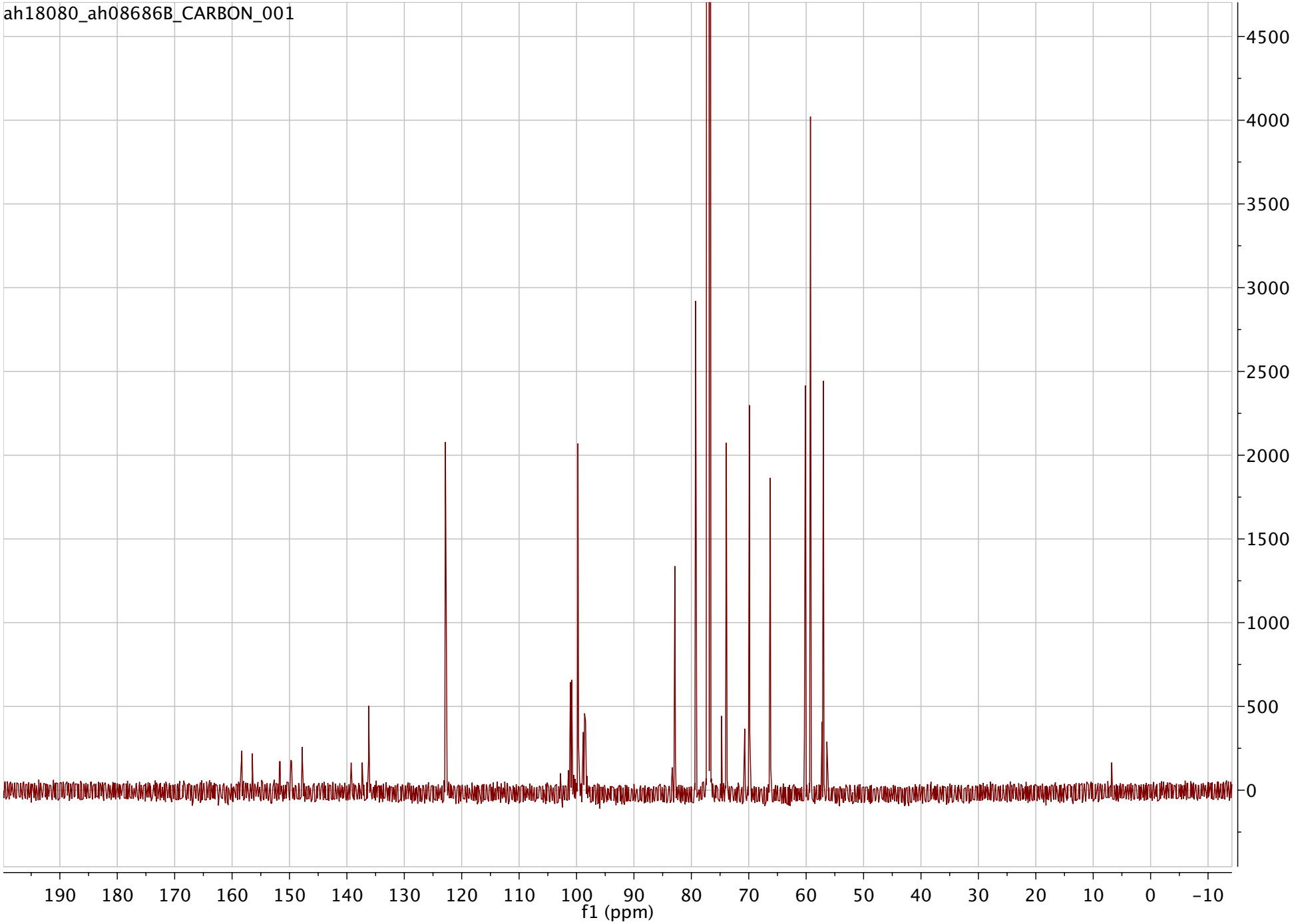


^{1}H NMR (500 MHz, $CDCl_3$) [1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(2',3',5'-trifluoro)benzene-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (17c):

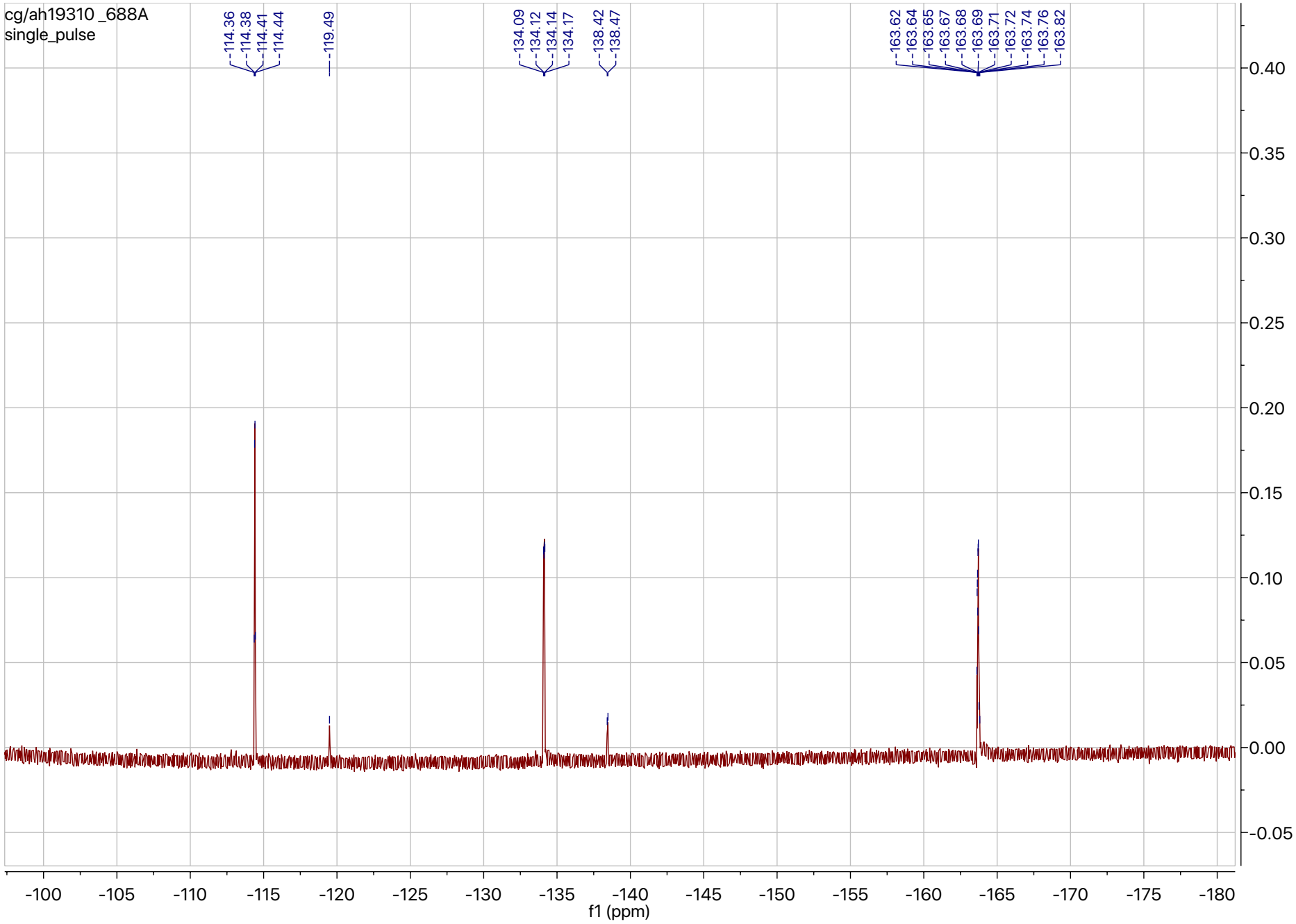




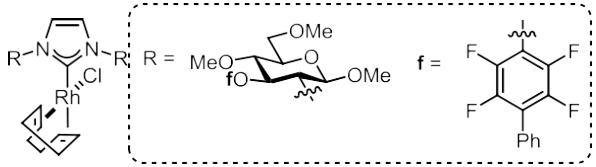
^{13}C NMR (125 MHz, $CDCl_3$)

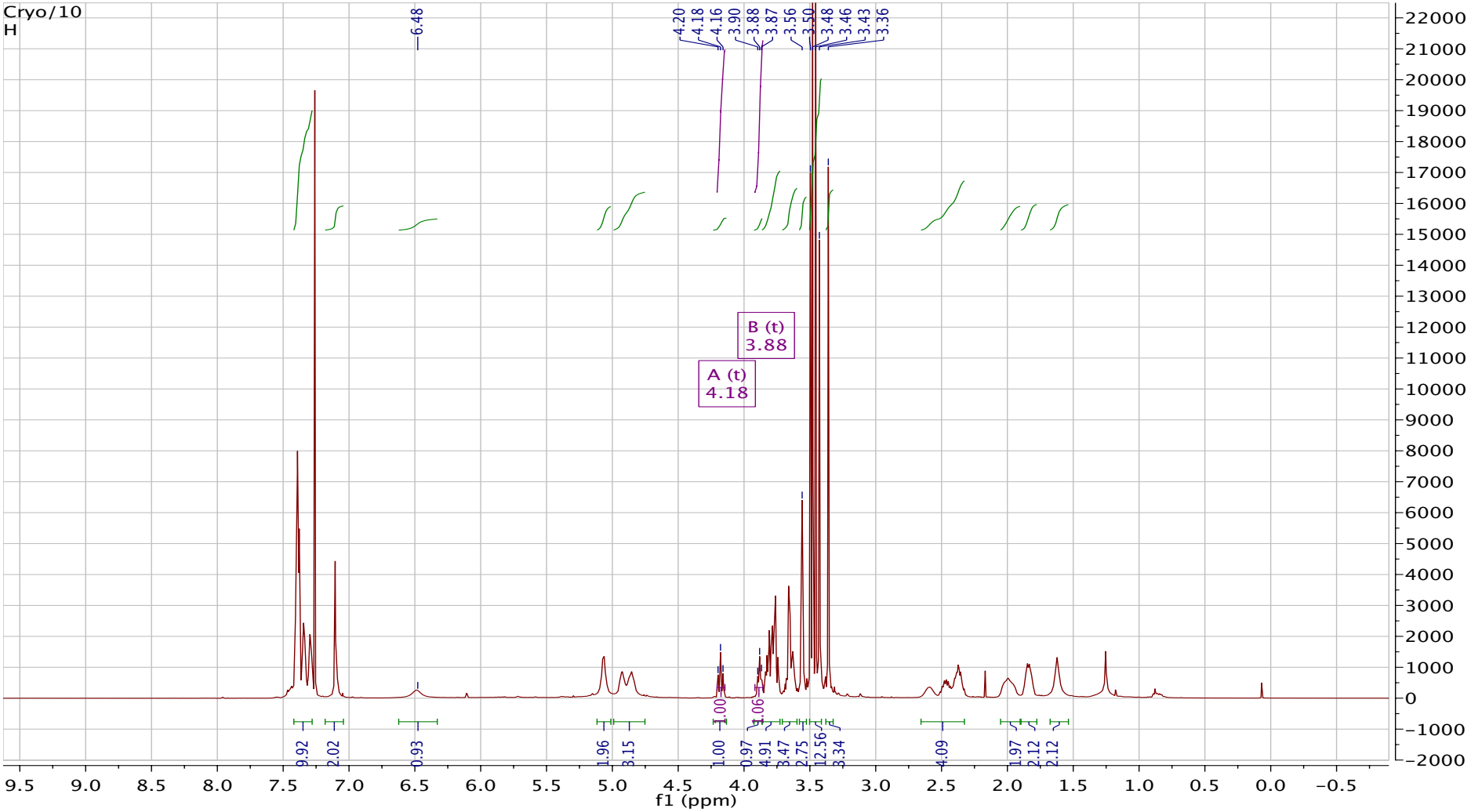


^{19}F NMR (377 MHz, $CDCl_3$)

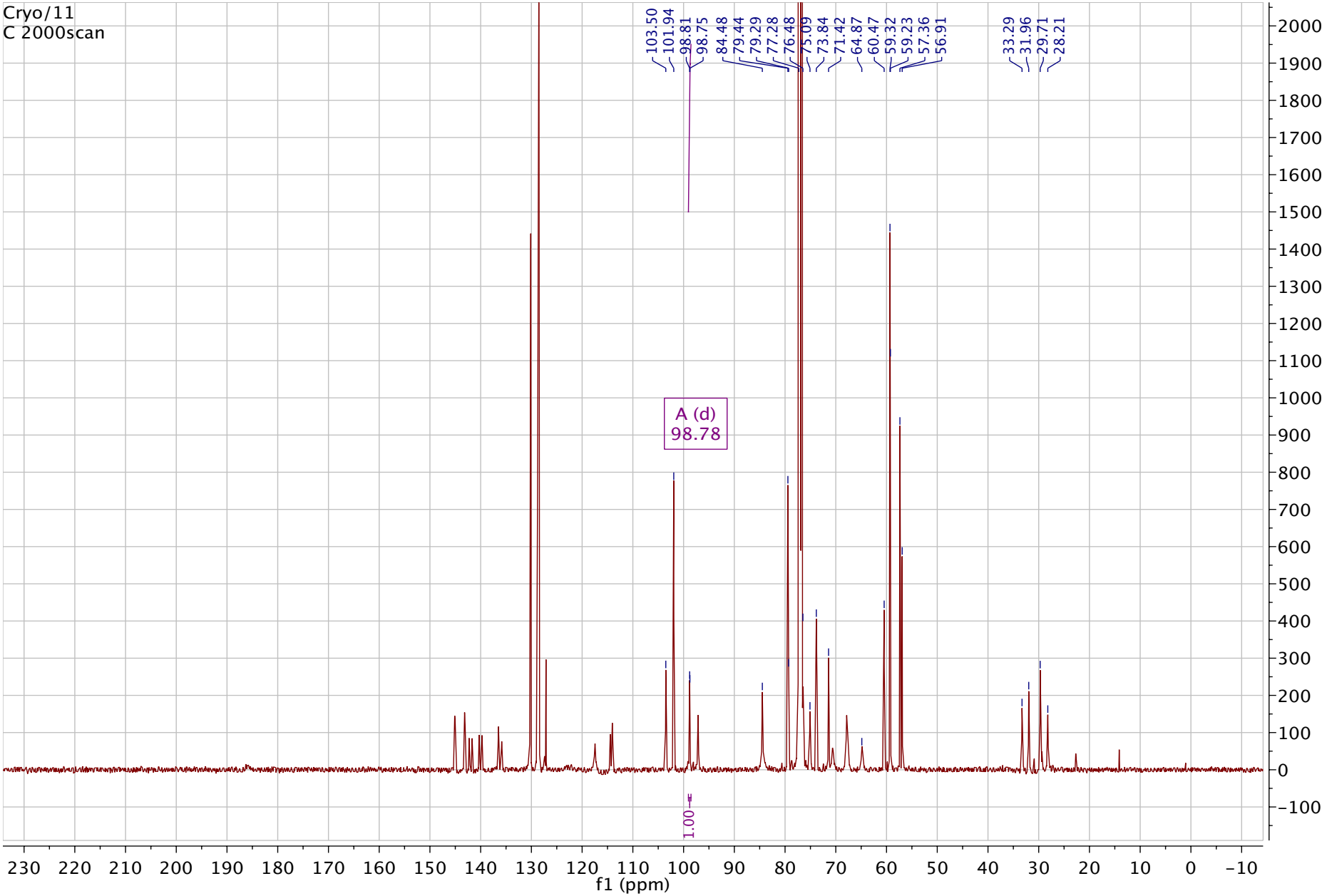


^{1}H NMR (500 MHz, $CDCl_3$) [1,3-Bis(methyl 2-amino-4,6-bis-*O*-methyl-3-*O*-(4'-phenyl-2',3',5',6'-tetrafluoro)benzene-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (17d):

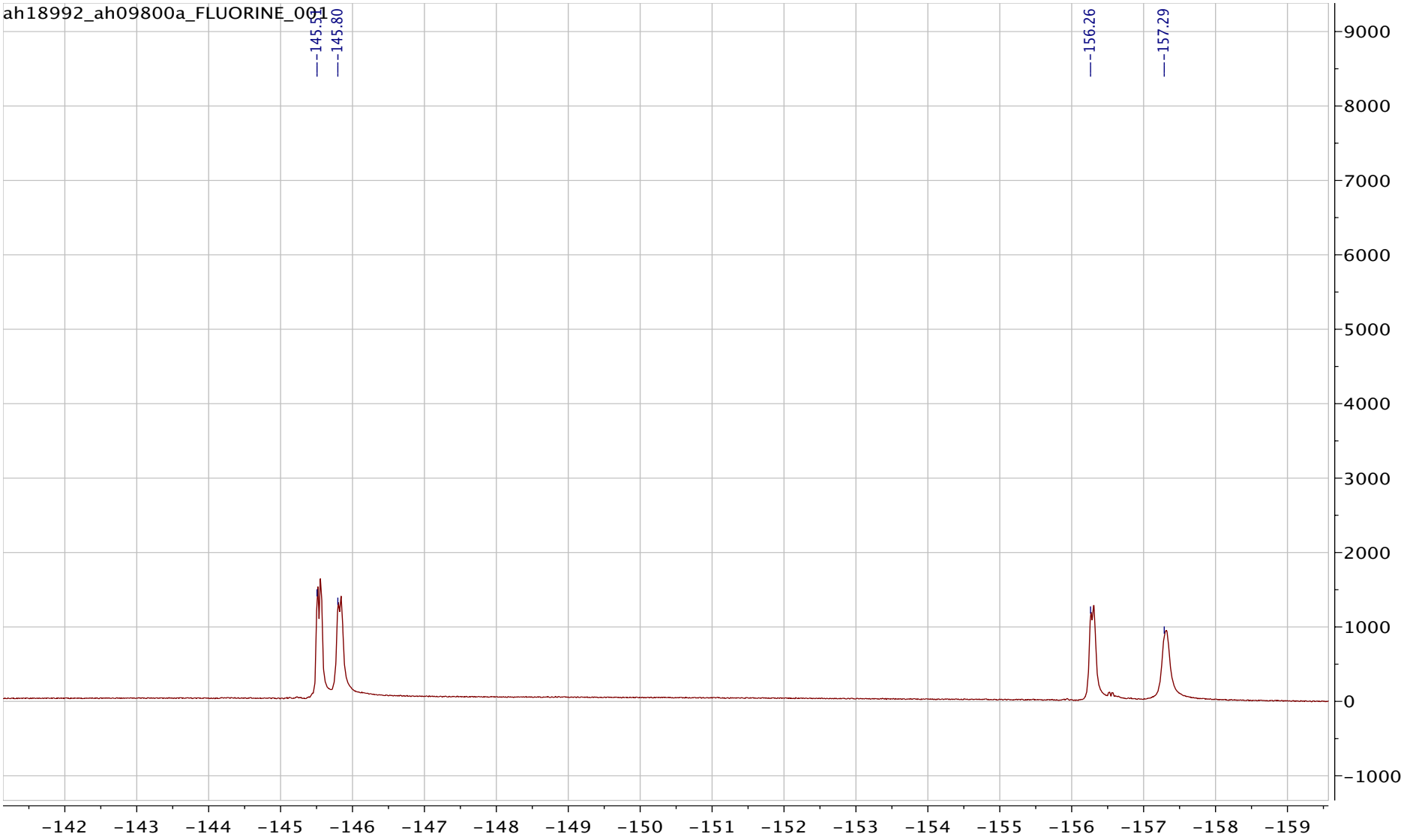




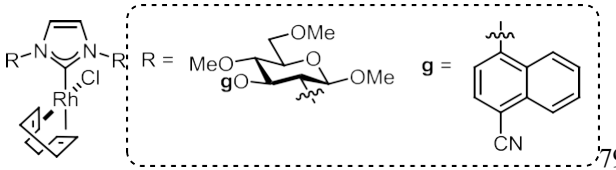
^{13}C NMR (125 MHz, $CDCl_3$)

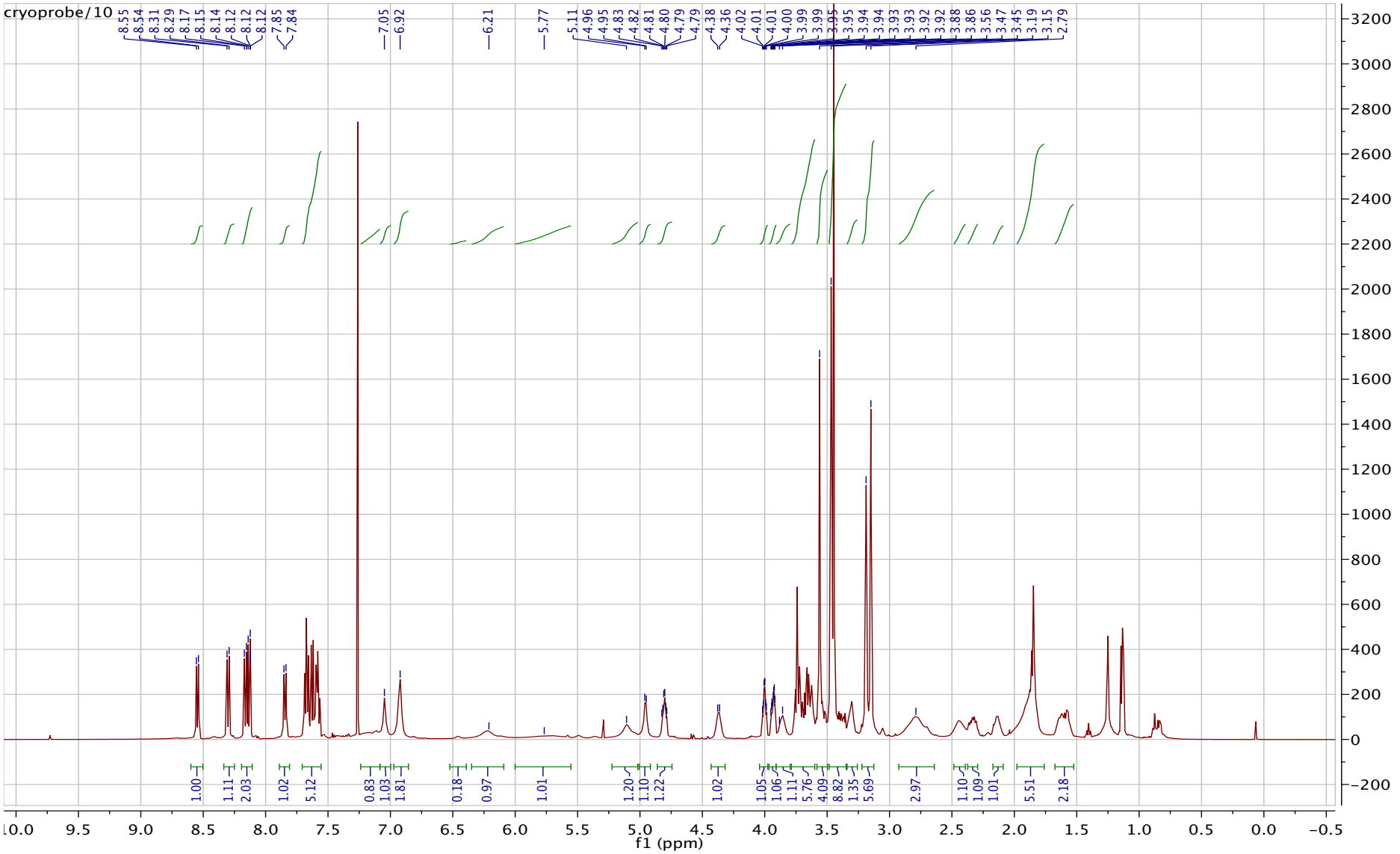


^{19}F NMR (470 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$) [1,3-Bis(methyl 2-amino-4,6-di-*O*-methyl-3-*O*-1'-(4'-cyano)naphthlene-2-deoxy-β-D-glucopyranoside)imidazol-2-ylidene](chloro)(1,5-cyclooctadiene)rhodium(I) (17e):





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