SUPPORTING INFORMATION

Stereoselective Synthesis of 2-deoxy-2-Bromo-hexopyrano-β-Nucleosides: Solvent-Free Lewis Acid Catalysis.

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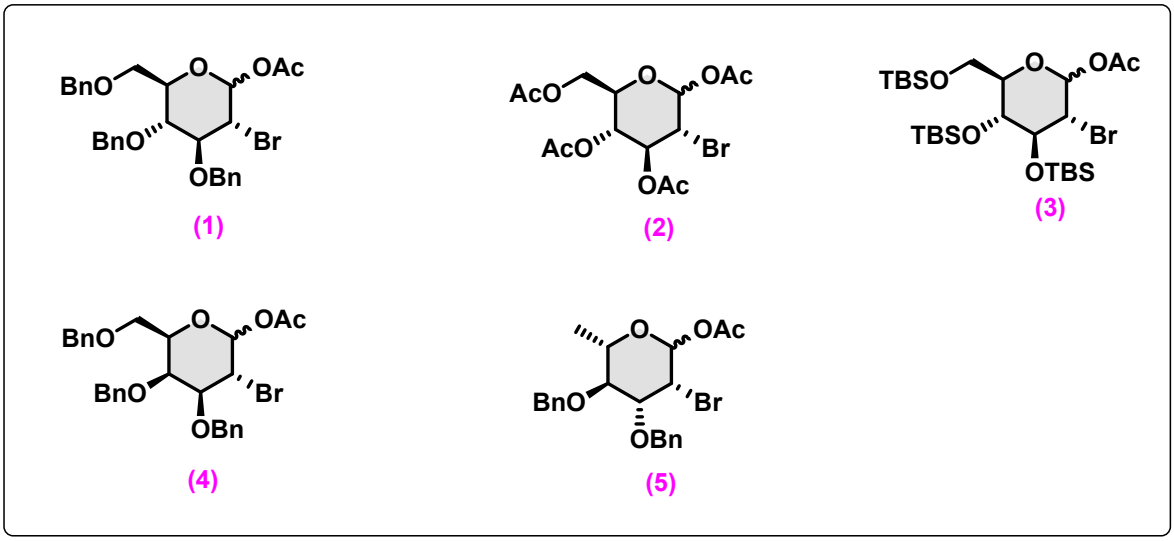
1. General information:

^{1}H and ^{13}C NMR spectra were recorded on 400, 101 and 126 MHz spectrometers with TMS as internal standard. Chemical shifts are expressed in parts per million (δ ppm). Silica gel coated aluminum plates were used for TLC. The products were purified by column chromatography on silica gel (60-120/100-200 mesh) using hexane–ethyl acetate and DCM-MeOH as the eluent to obtain the pure products. Mass spectra were obtained using Q-TOF-LC/MS spectrometer using electron spray ionization. Reagents used were mostly purchased from Sigma Aldrich, TCI and Alfa Aesar.

2. Starting materials:

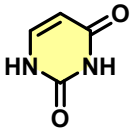
2.1 Different sugars chosen for study:

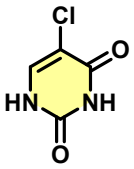


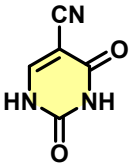
All are synthesized according to the general procedure **A**.

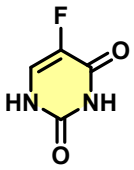
2.2 Different Nucleobases chosen for study:

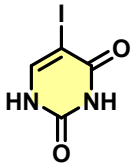
Uracils

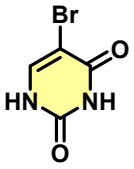

Uracil

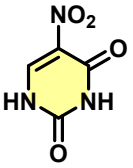

5-chloro-uracil

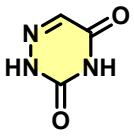

5-cyano-uracil


5-fluoro-uracil

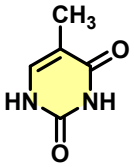

5-iodo-uracil


5-bromo-uracil

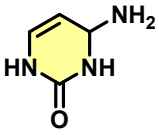

5-nitrol-uracil

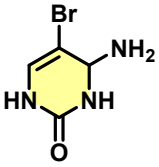

Aza-Uracil

Thymine

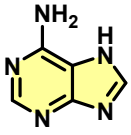


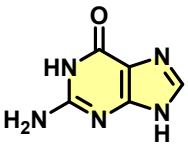
Cytosines

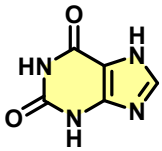

Cytosine


5-bromo cytosine

Purines


adenine

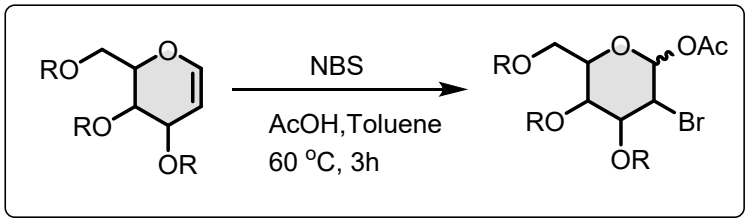

guanine


xanthine

All the nucleobases used are commericially available.

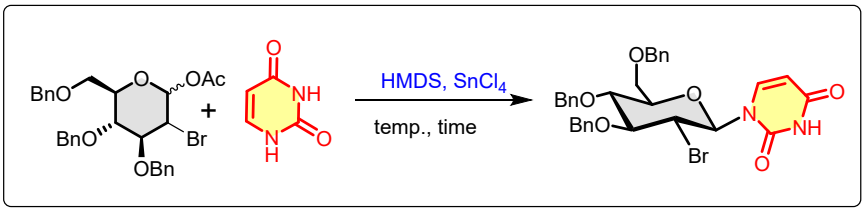
3. General Procedures:

A. General Procedure for the synthesis of Starting material



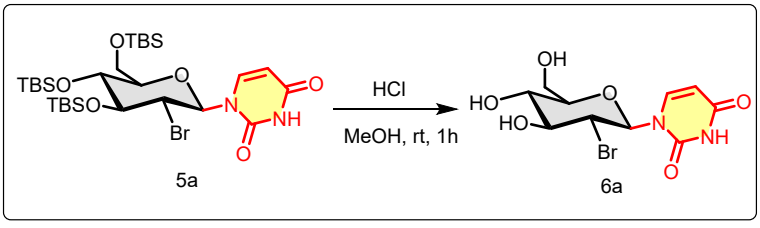
In a round-bottomed flask containing the solution of Glucal in toluene was added NBS (2.0 equiv.) and AcOH (1.5 equiv.) and allowed to stir for 3h at 60 °C. After the completion of the reaction, the reaction mixture was extracted with ethyl acetate and the residue was purified by column chromatography.

B. General Procedure for the synthesis of 2-bromo-nucleoside



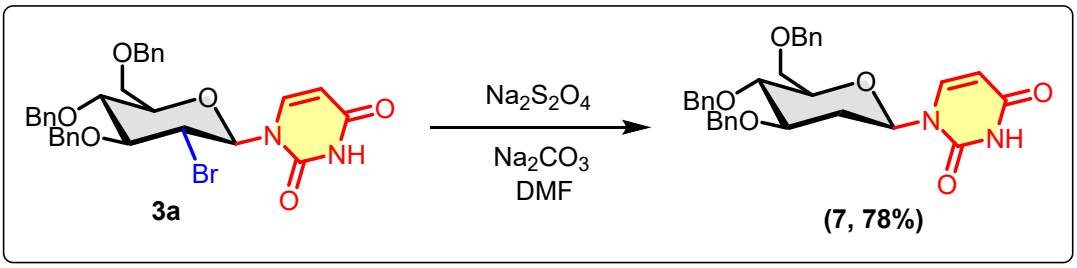
In a round-bottomed flask containing the solution of (1 equiv.) of nucleobase (NB) in in Hexamethyldisilazane (HMDS) (2.0 equiv.) and $SnCl_4$ (0.3 equiv.) at 80 °C and stirred the mixture for 1 h at the same temperature. The reaction mixture was cooled to 60 °C, then charged with 1-acetoxy-2-bromo-glycal (0.3 equiv.), and $SnCl_4$ (10 mol%) successively. After the completion of the reaction, the reaction mixture was extracted with ethyl acetate and the residue was purified by column chromatography.

C. General procedure for the synthesis of deportected nucleosides:



To the solution of **5a** in MeOH was added a drop of HCl at RT and allowed it to stir for 1h. Upon completion of the reaction, the reaction mixture was directly evaporated on rota vapour to give **6a** as gummy liquid.

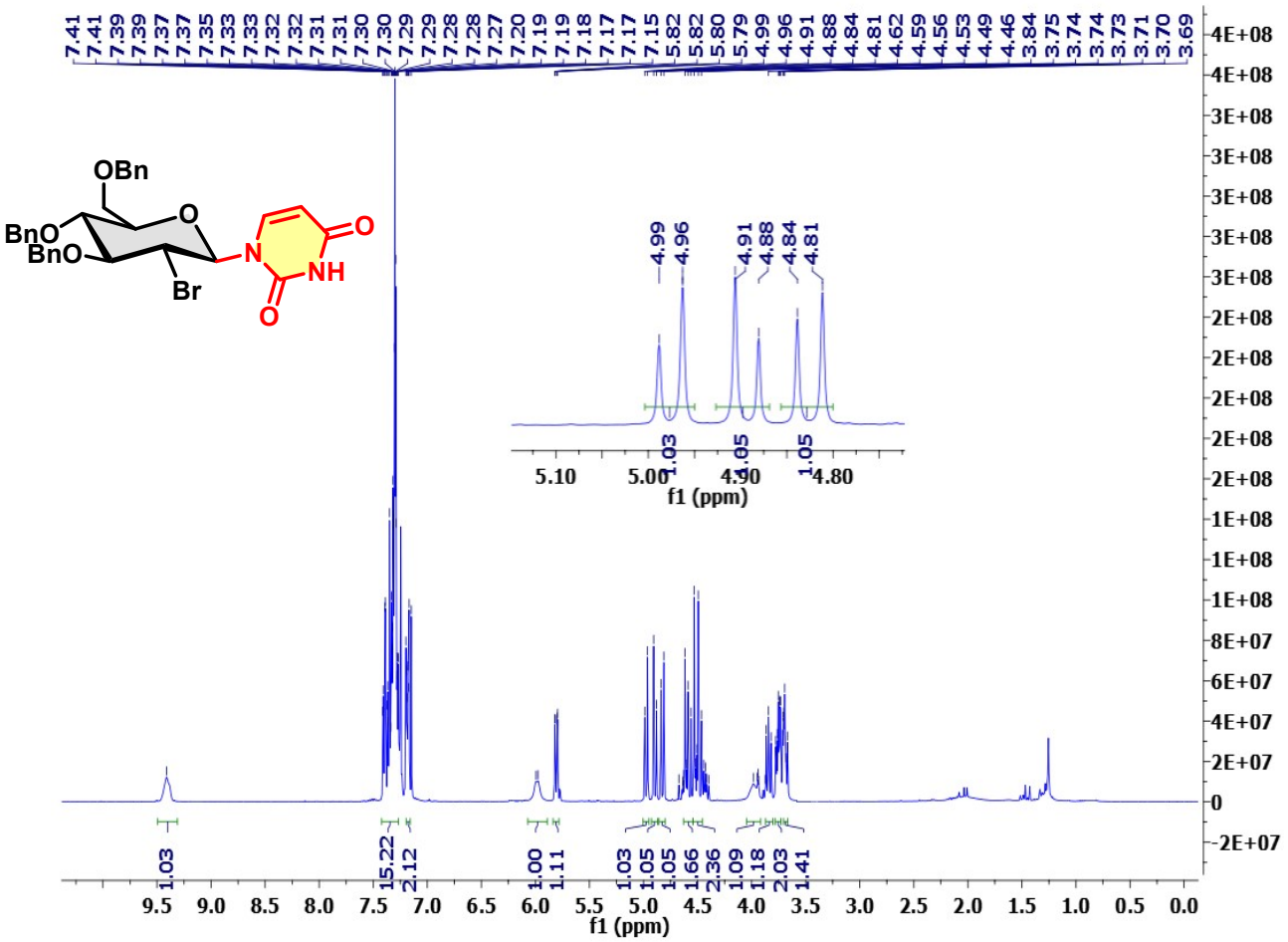
D. General procedure for the synthesis of 7 from 3a:



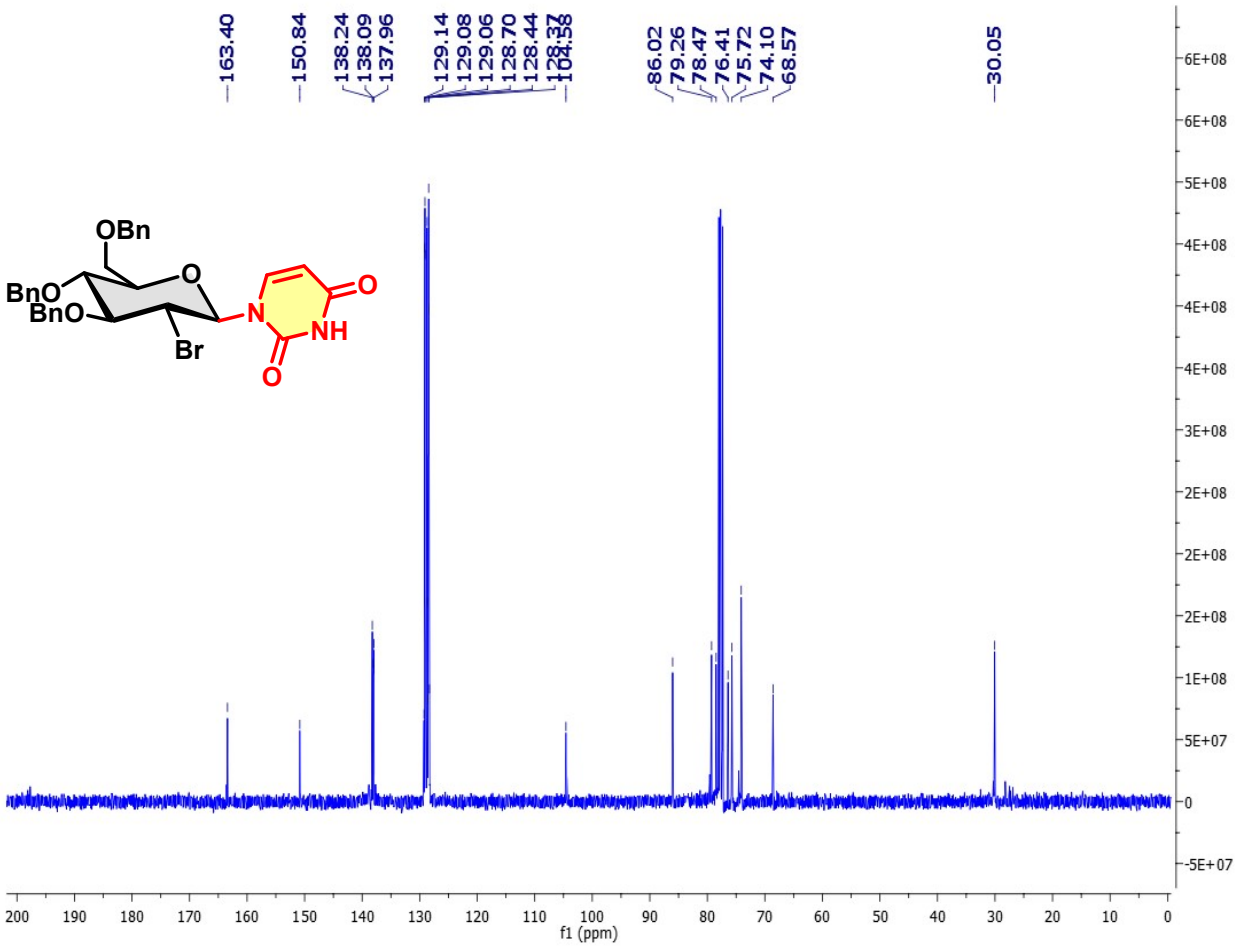
To the solution of **3a** in DMF at 80 °C, add 2.0 equiv. of $Na_2S_2O_4$ and 1.0 equiv. of Na_2CO_3 and allow it to stir for 1 hour. Upon consumption of starting material, filter the reaction mixture through celite and was extracted with ethyl acetate and the residue was purified by column chromatography.

4. NMR Spectrum

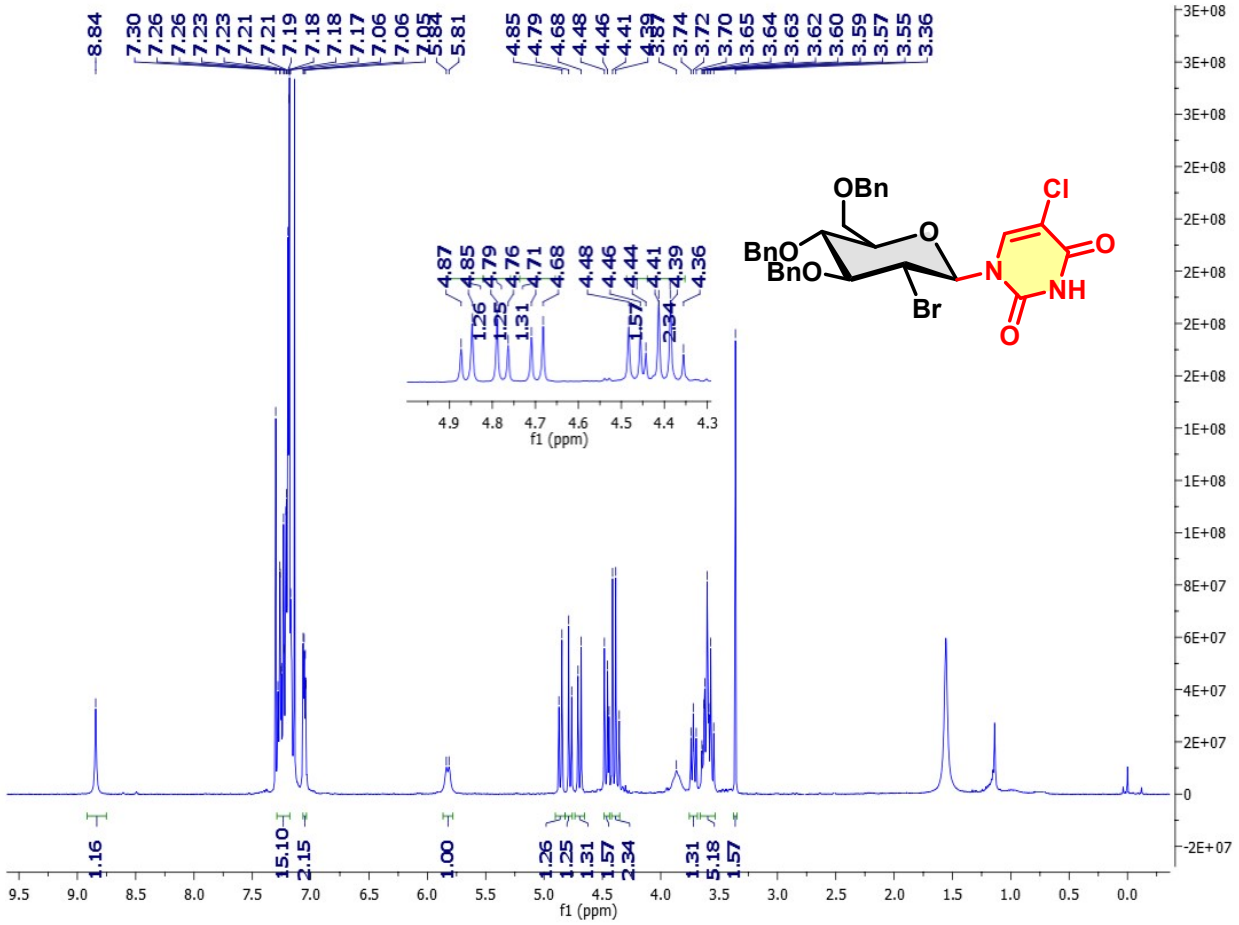
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3a



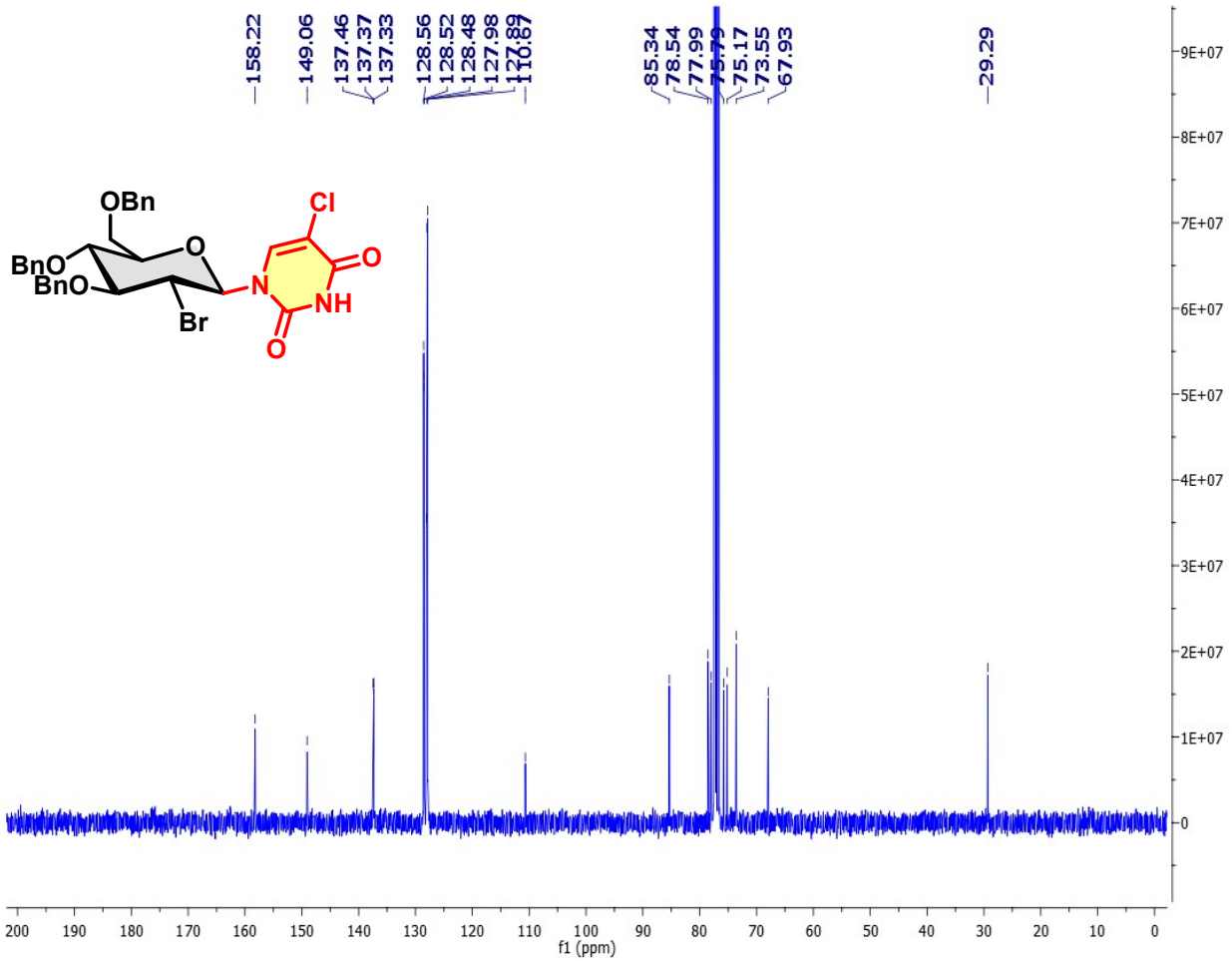
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3a



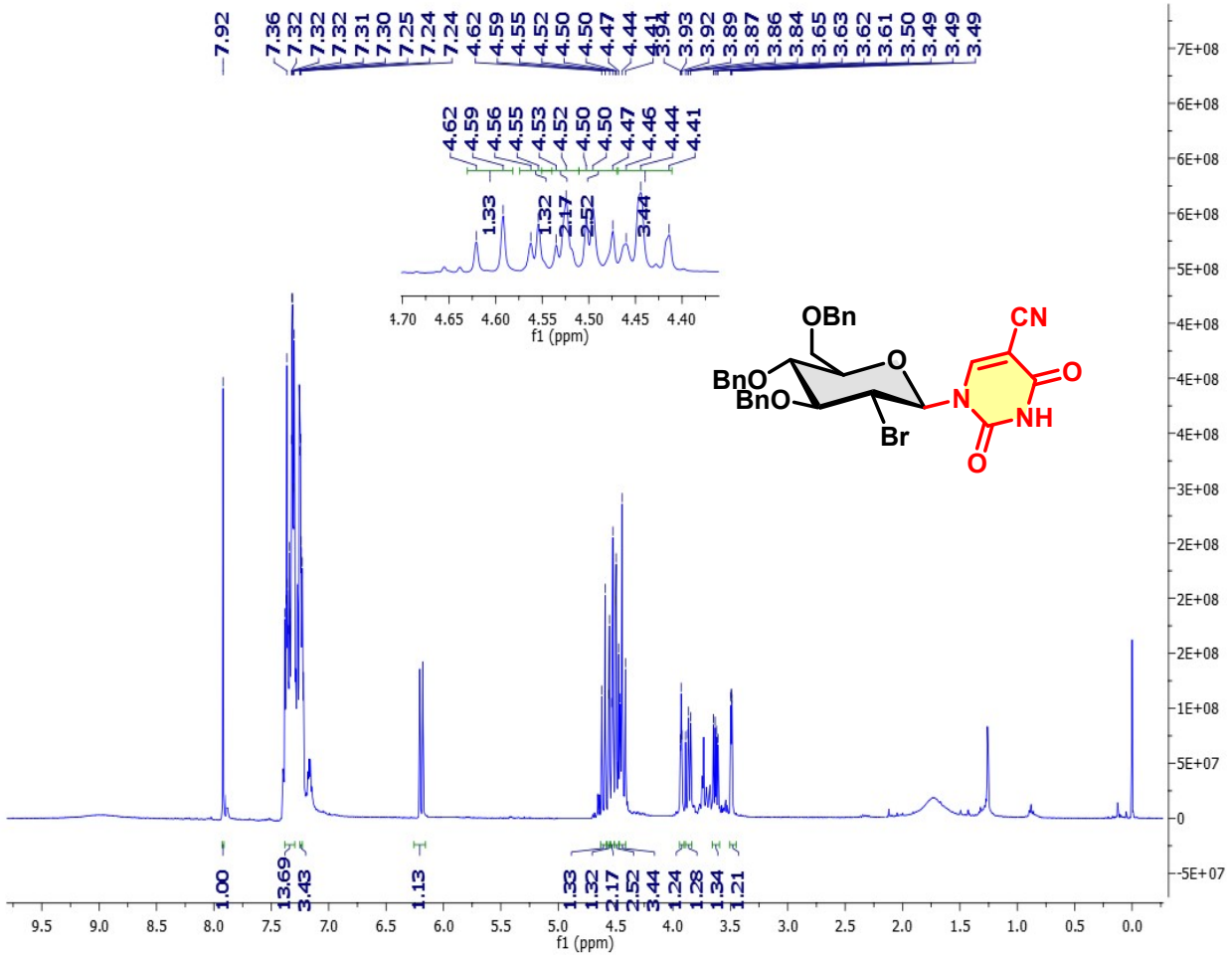
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3b



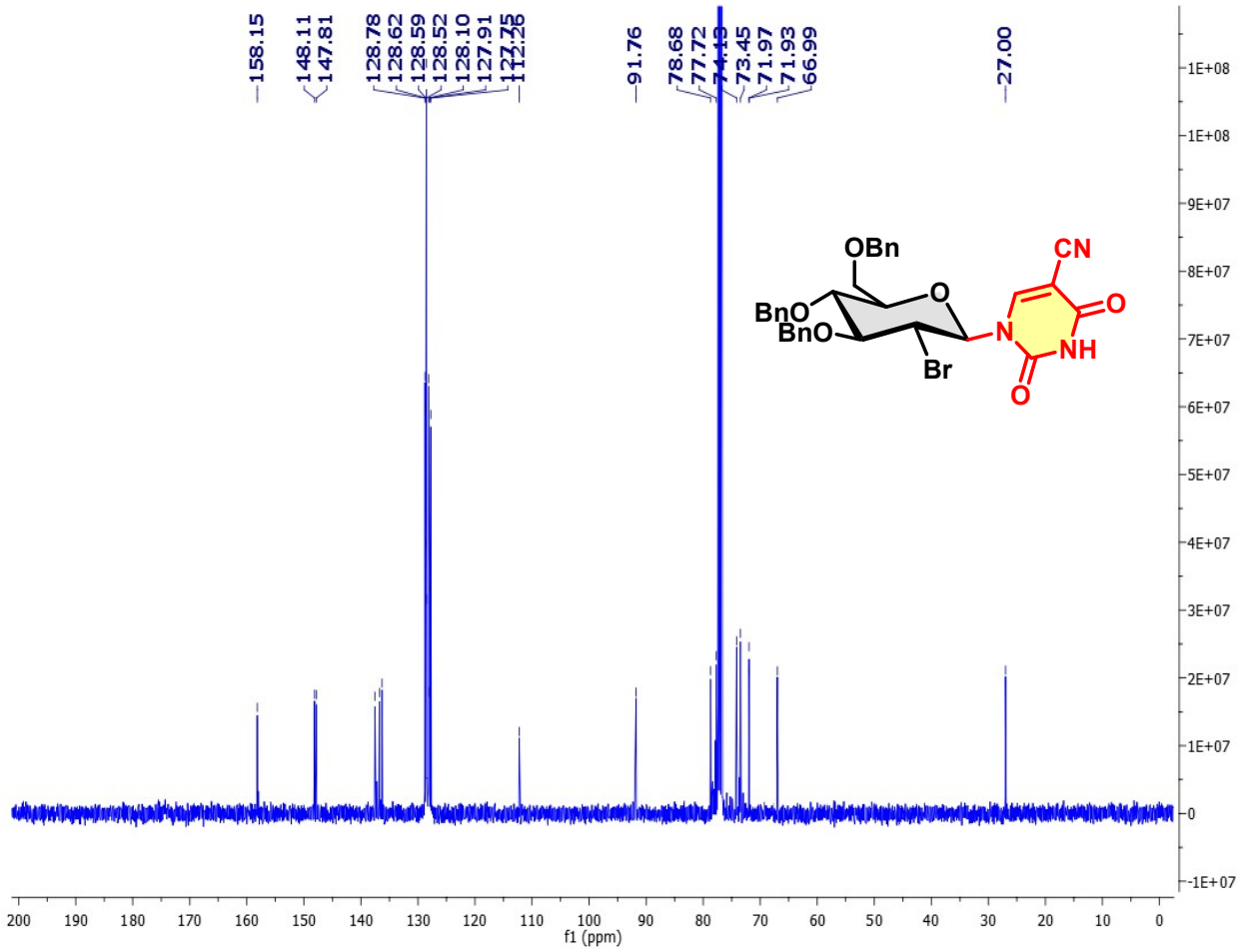
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3b



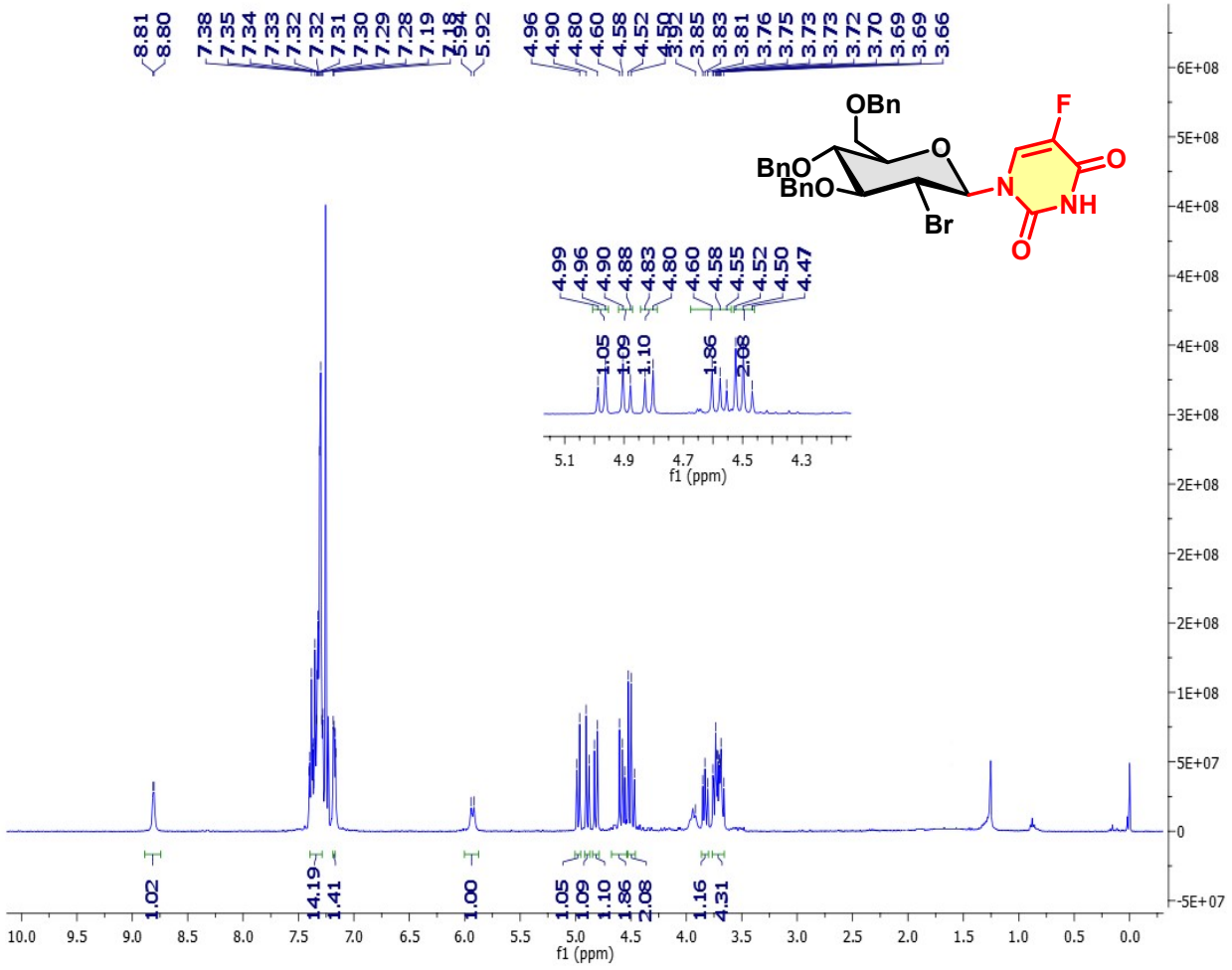
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3c



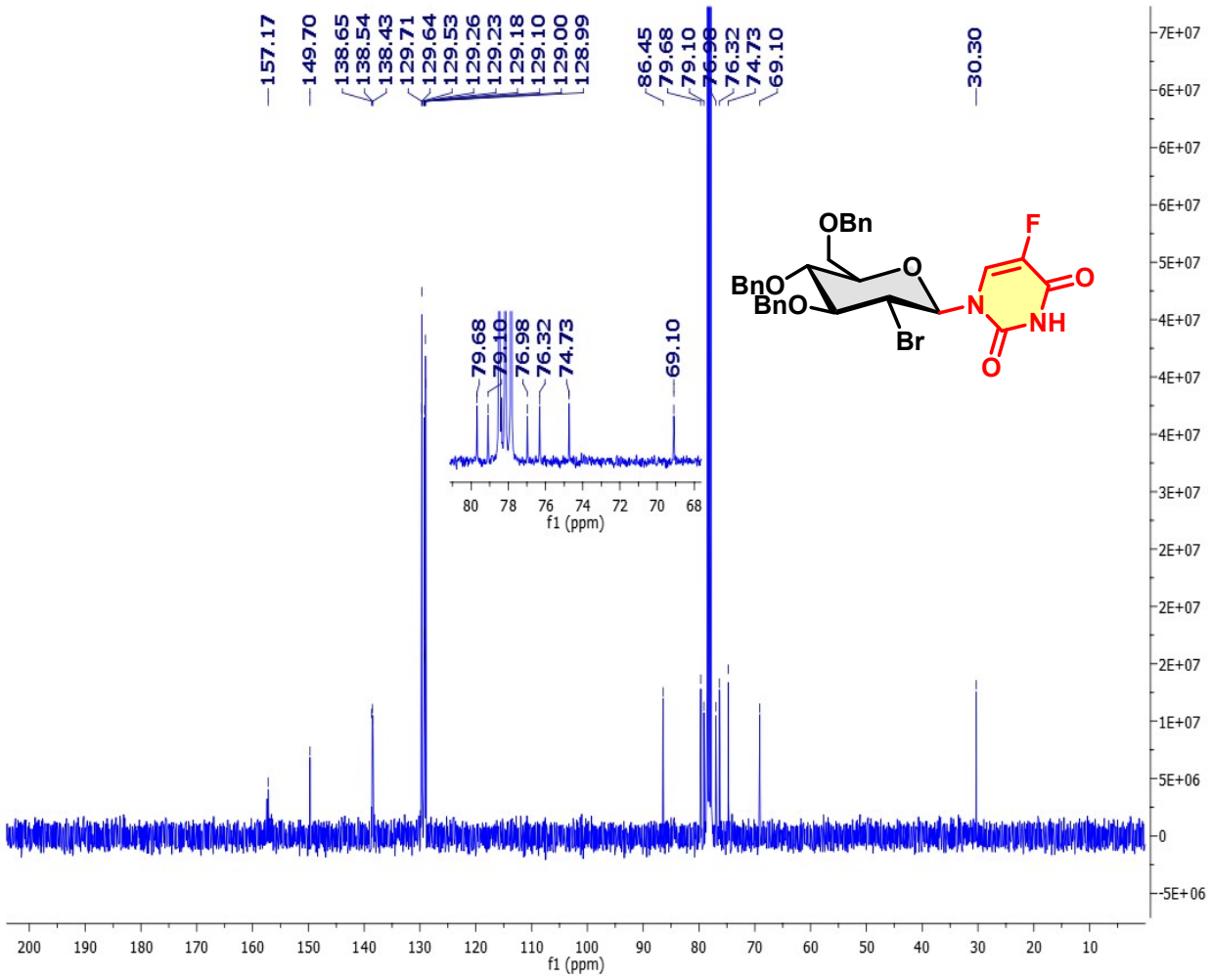
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3c



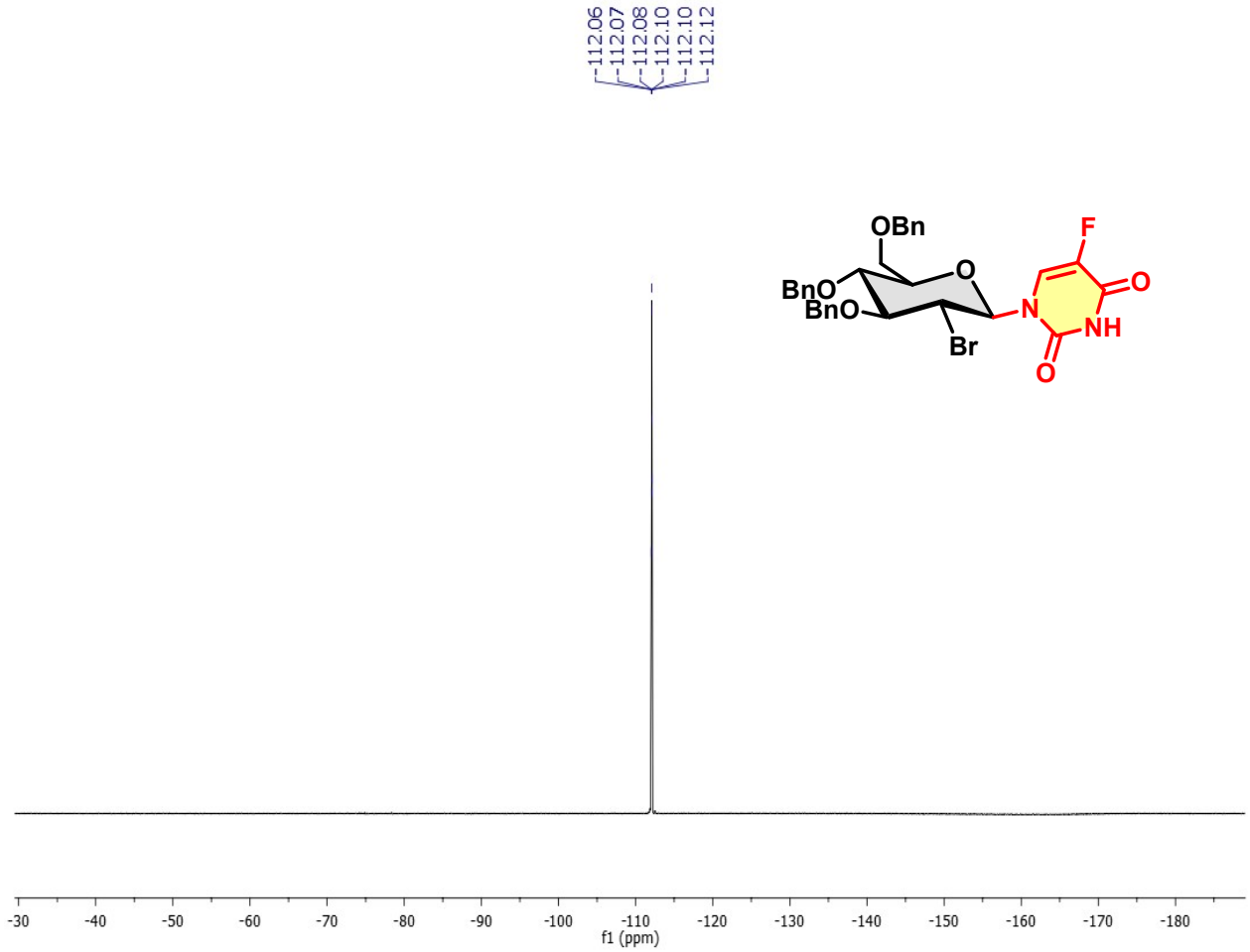
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3d



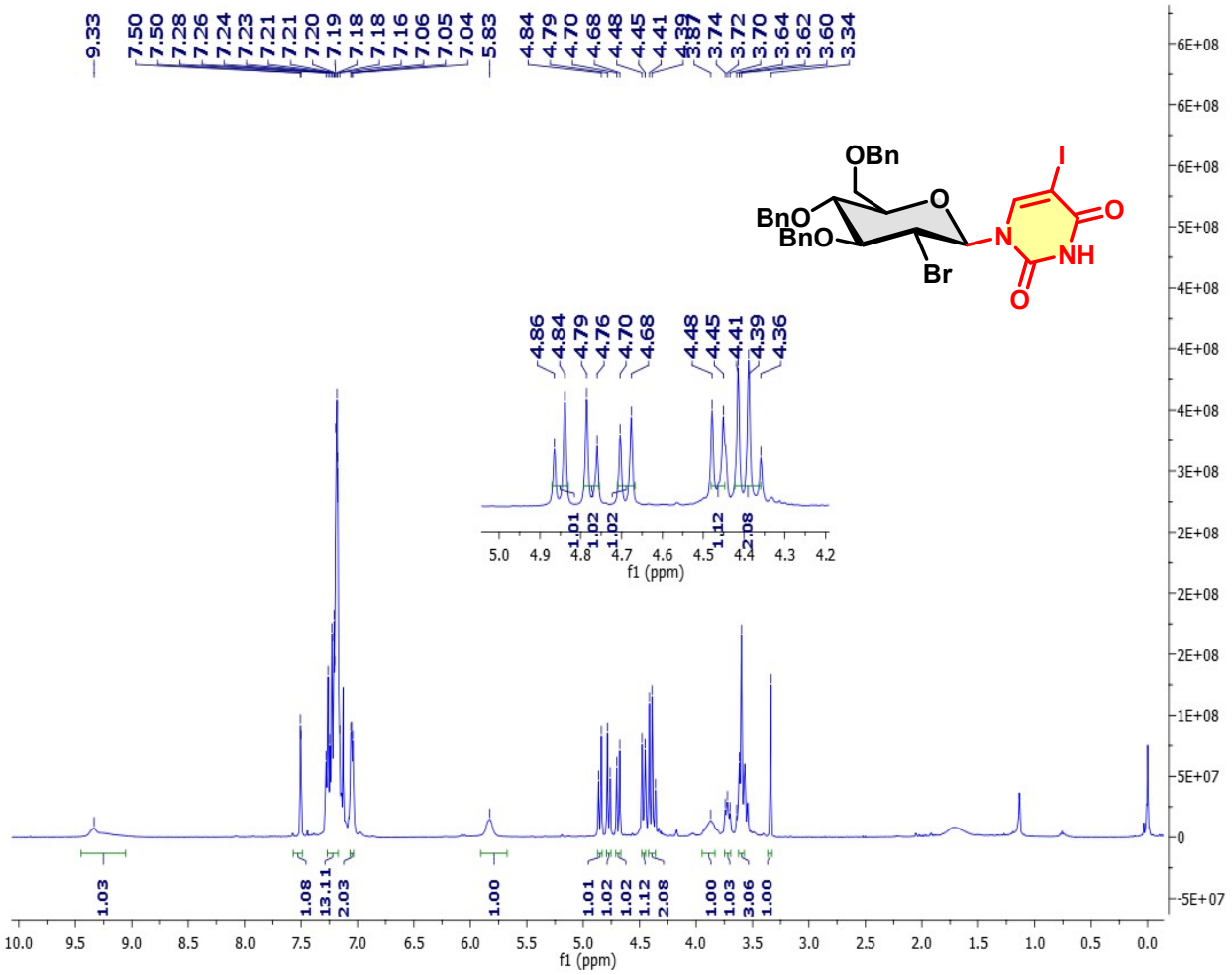
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3d



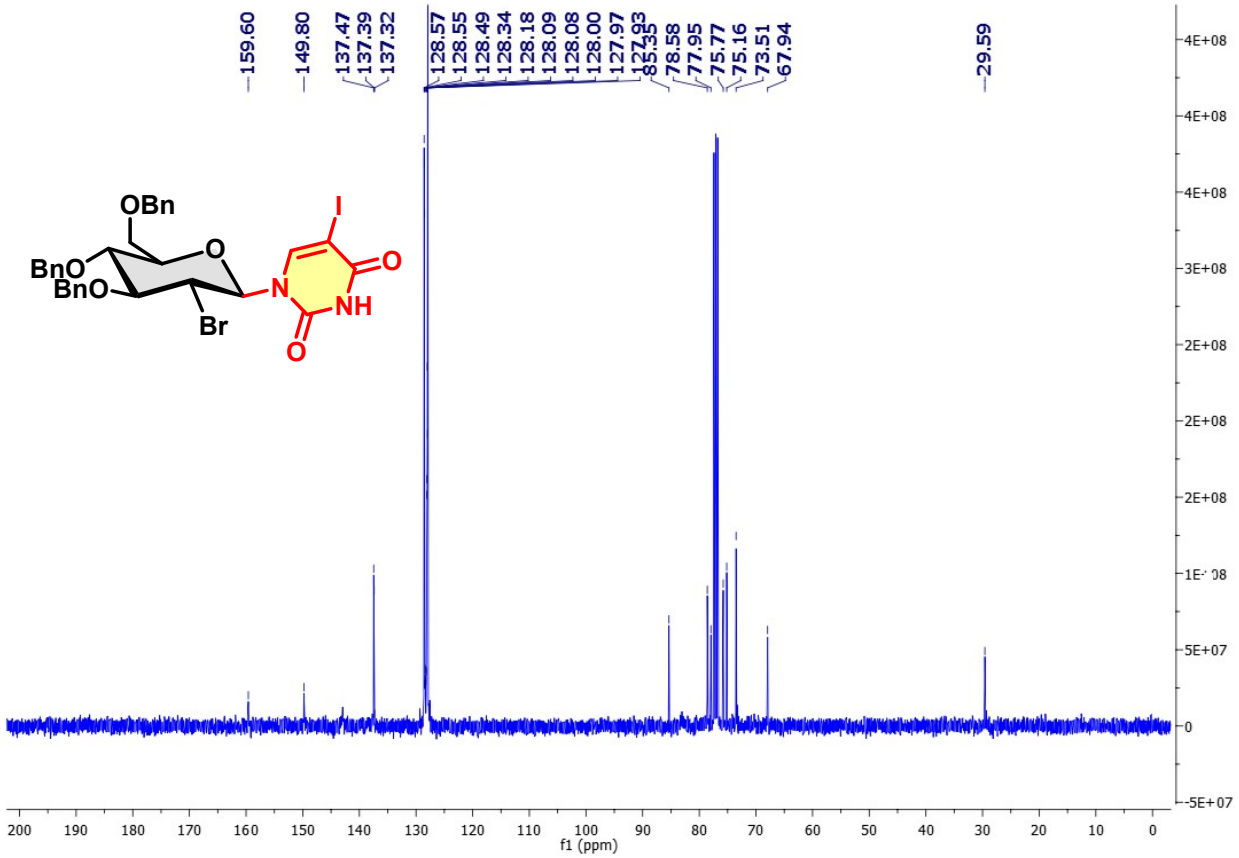
^{19}FNMR (377 MHz, $CDCl_3$) of 3d



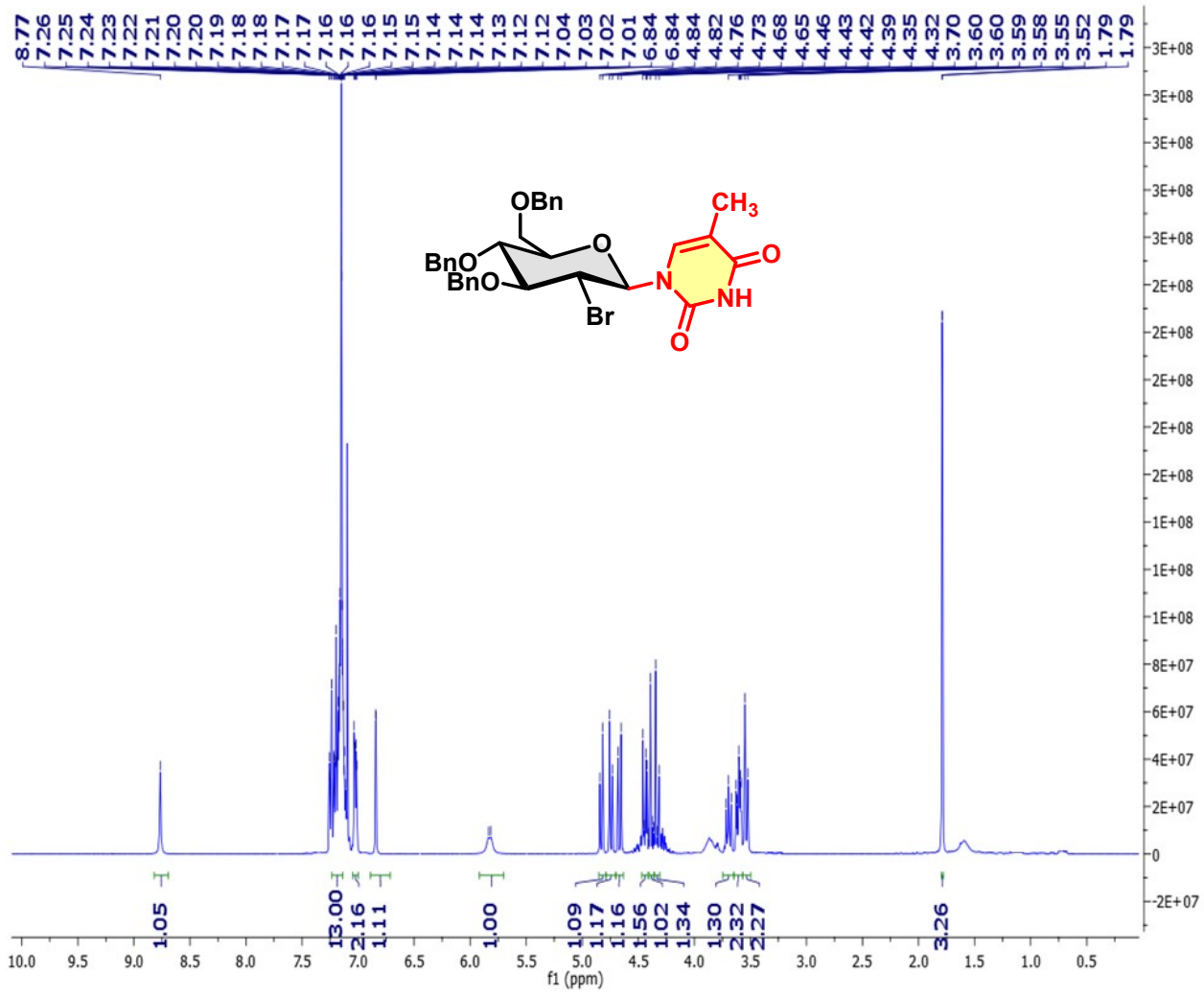
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3e



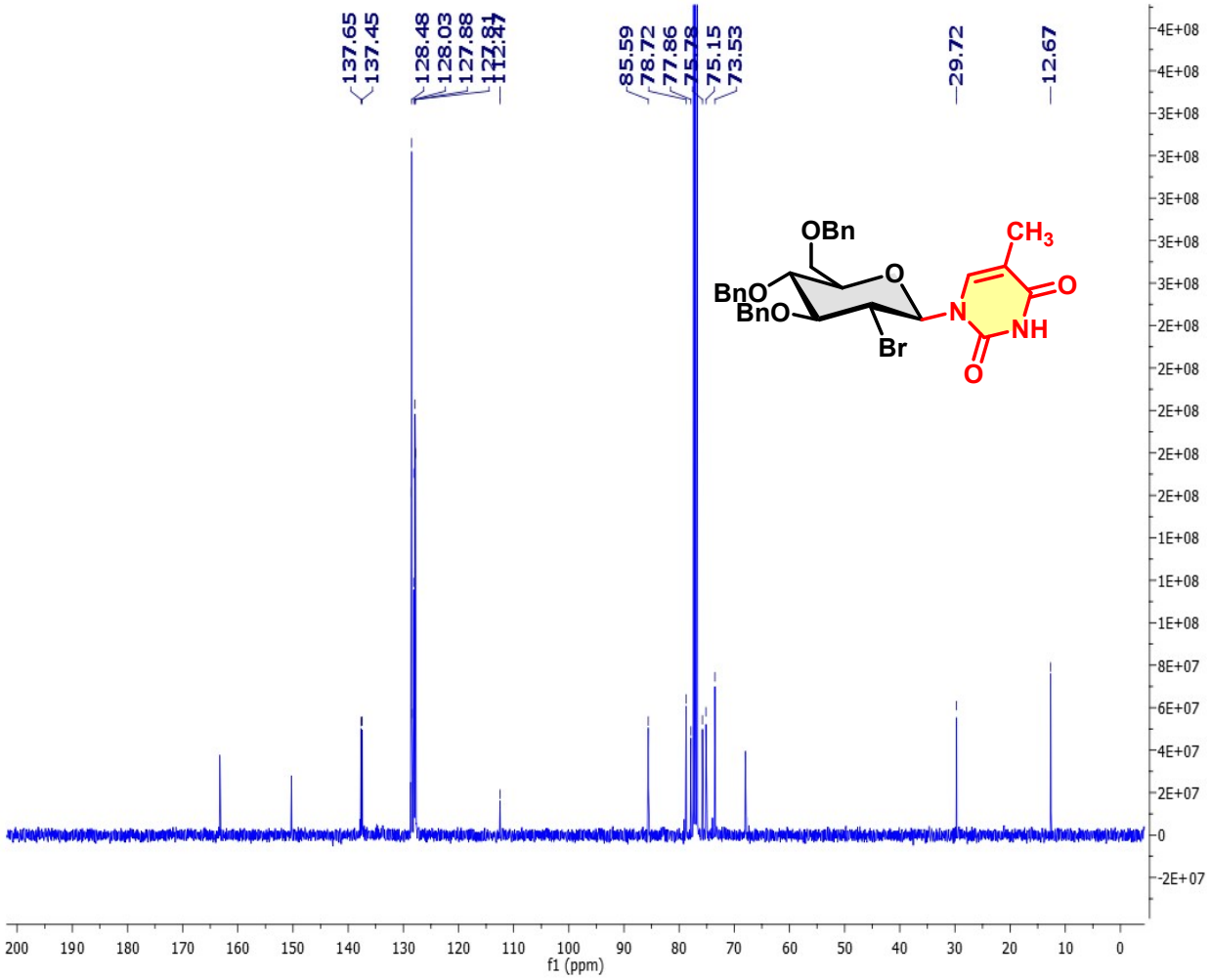
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3e



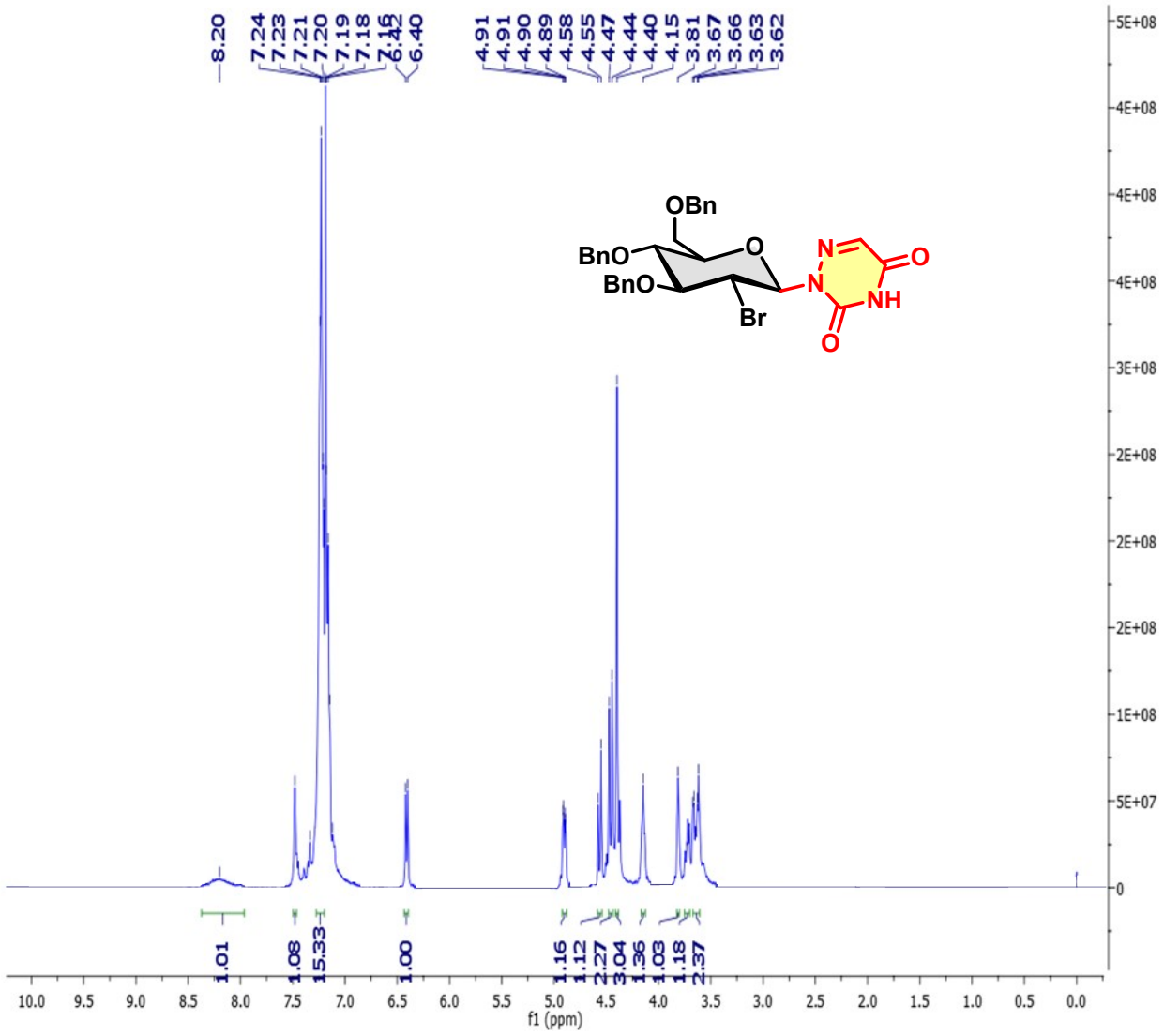
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3f



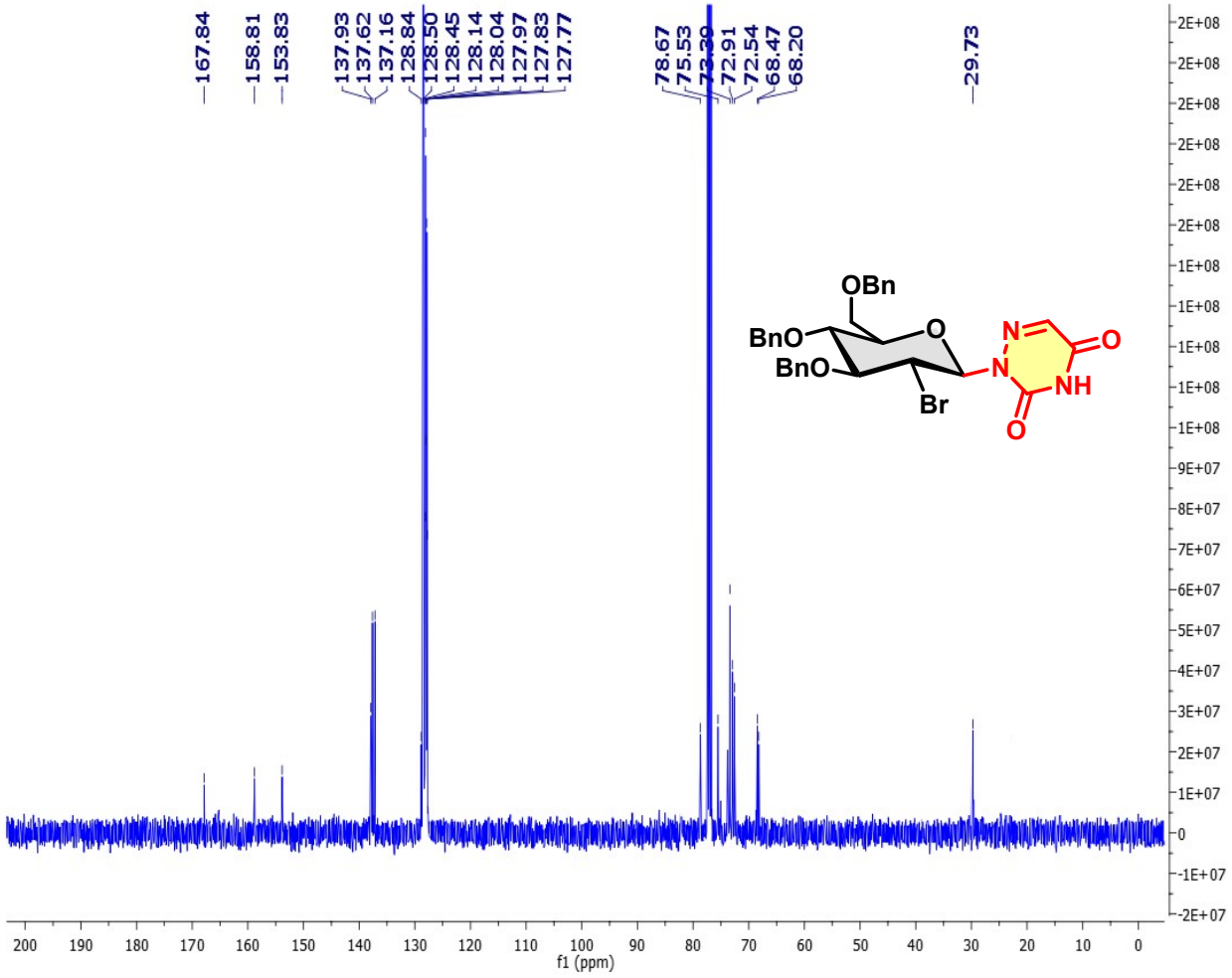
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3f



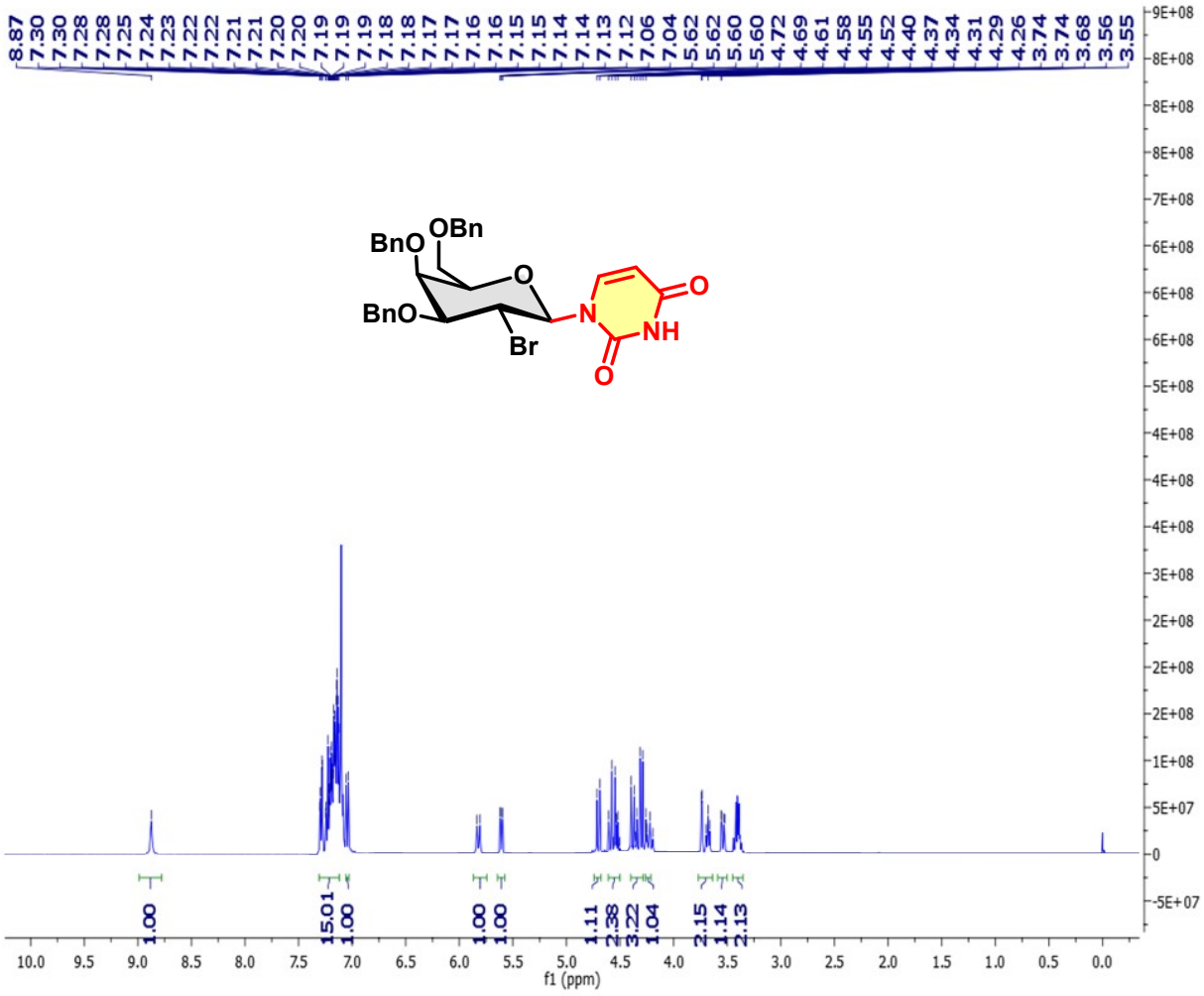
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3g



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3g



^{1}H NMR (400 MHz, $CDCl_3$) of compound 3h



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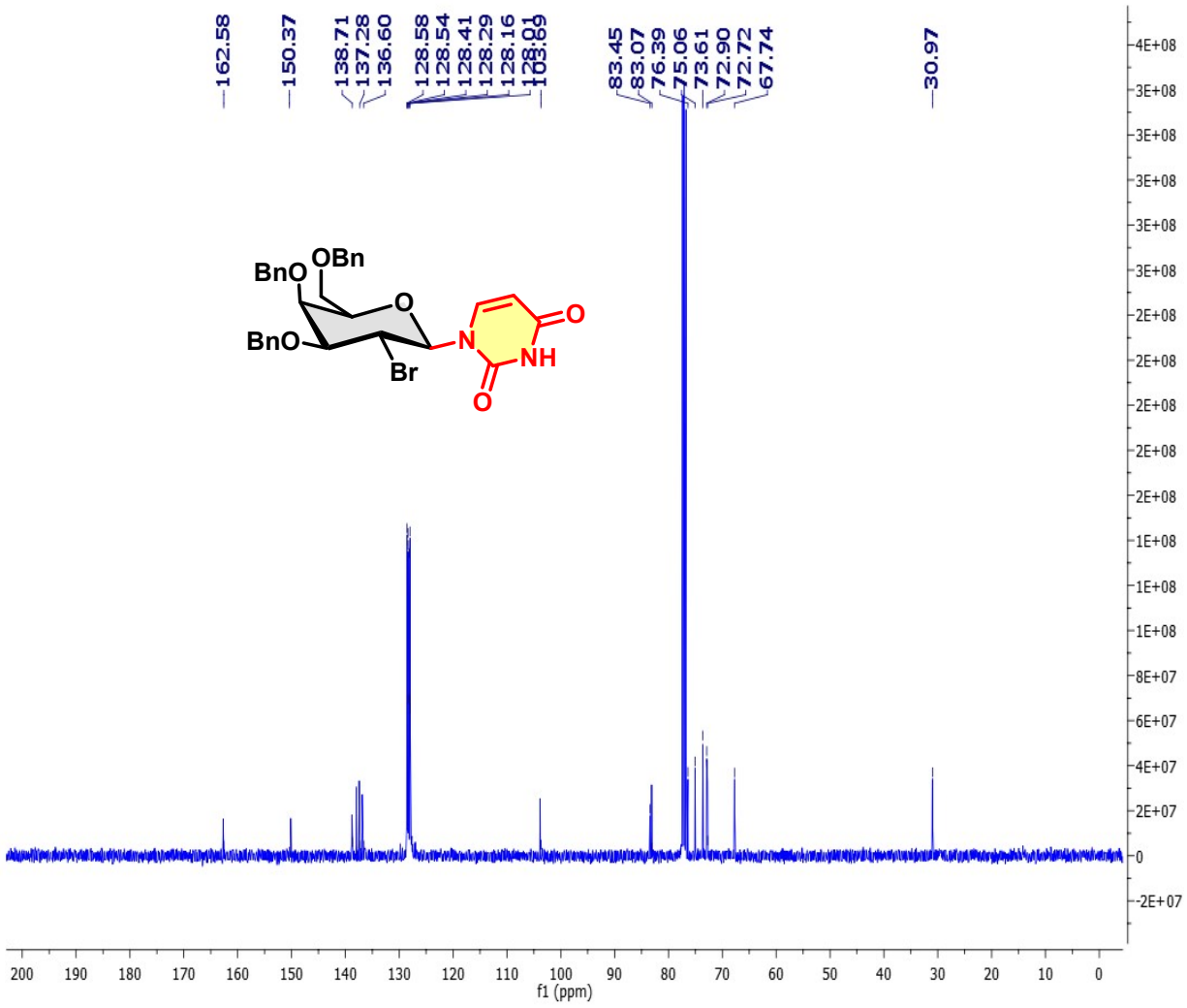
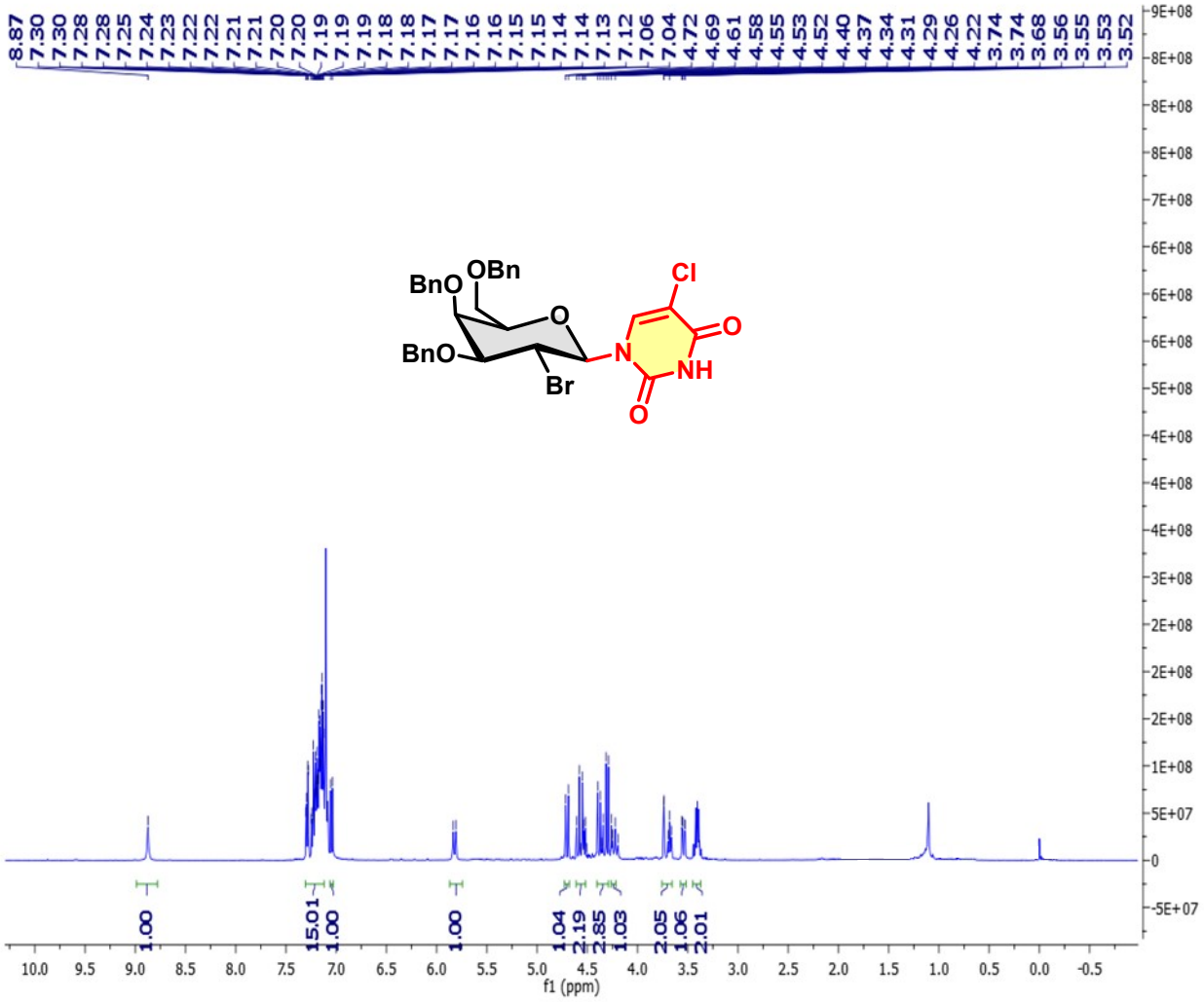


^{1}H NMR (400 MHz, $CDCl_3$) of compound 3i



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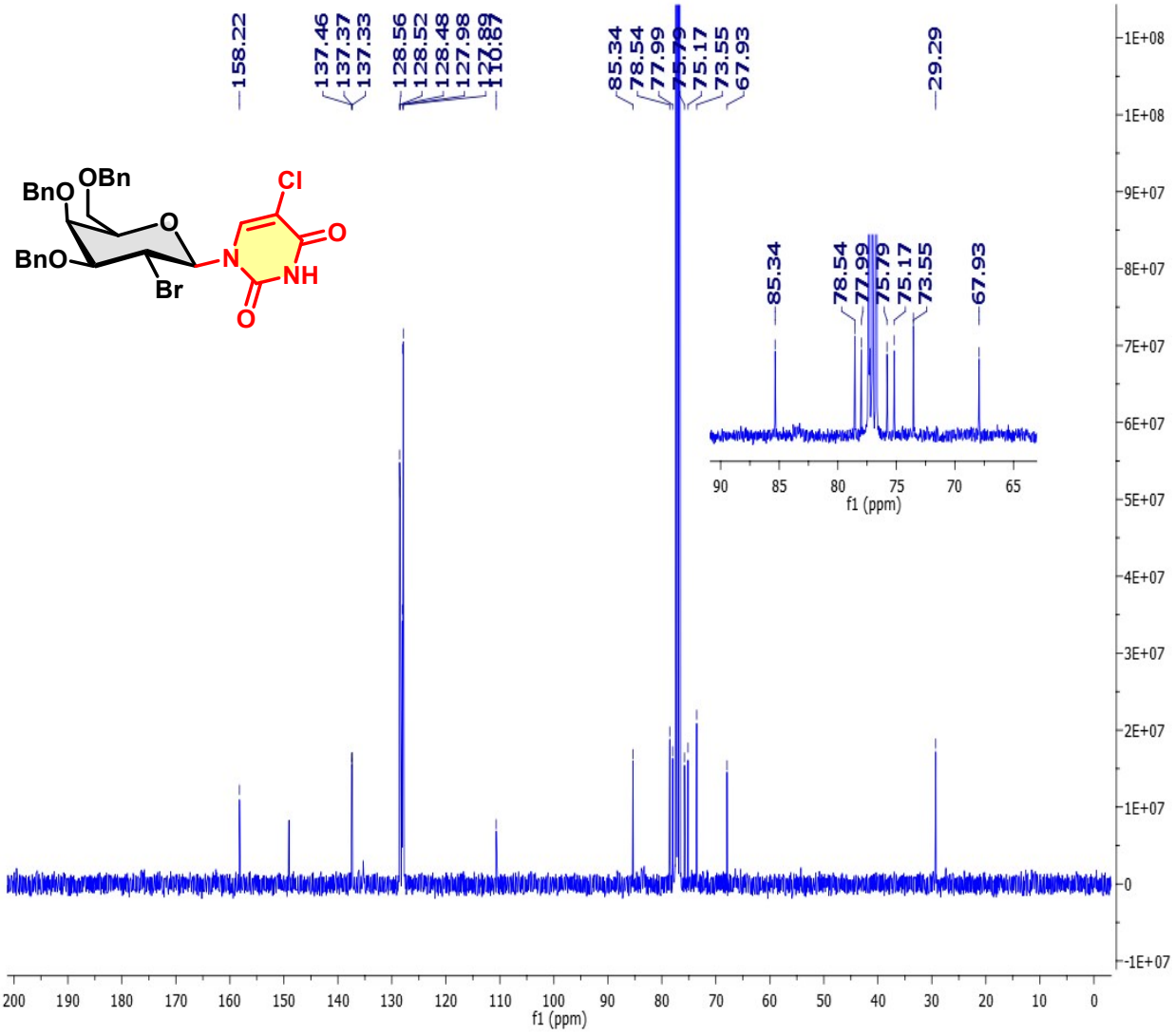
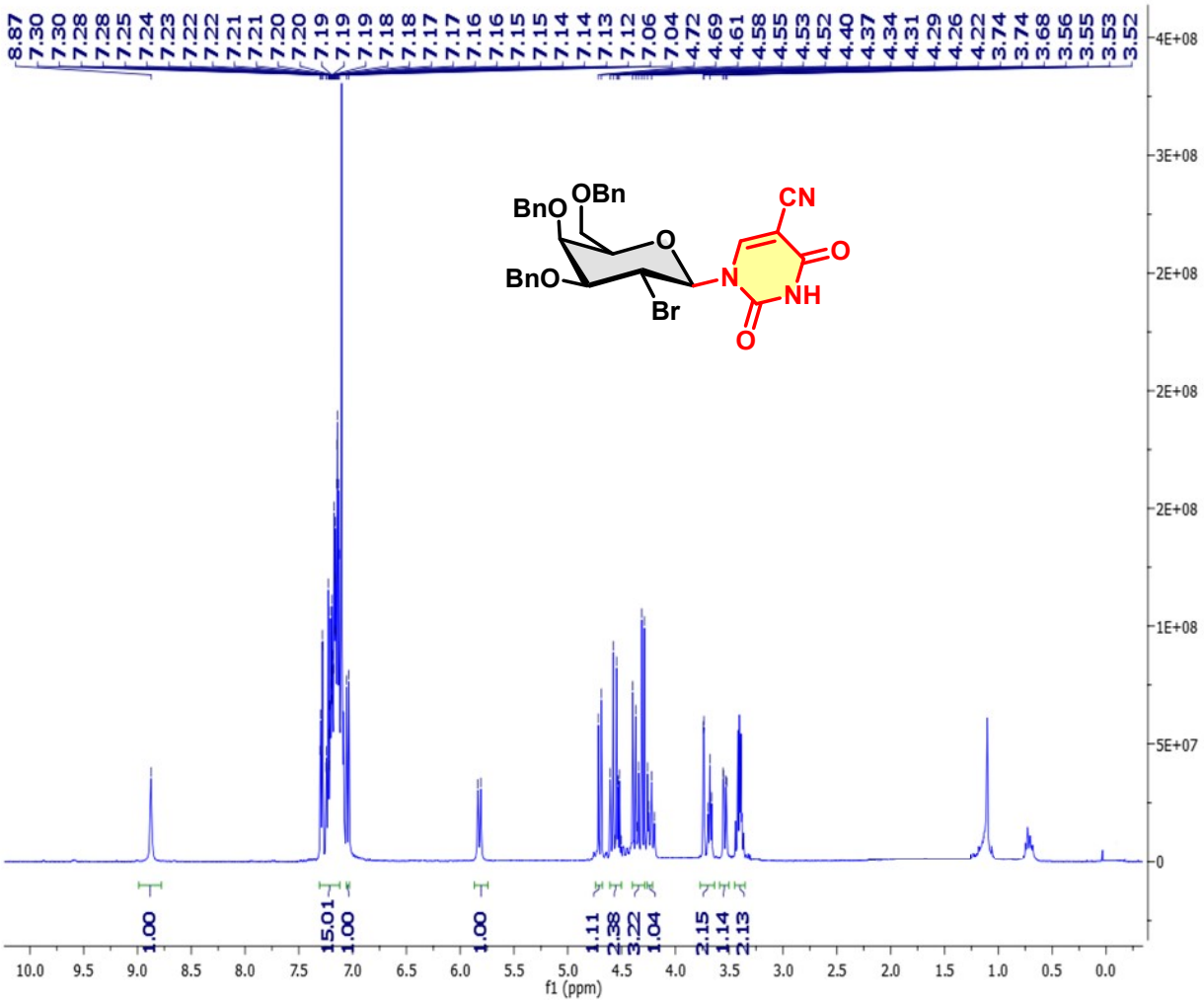
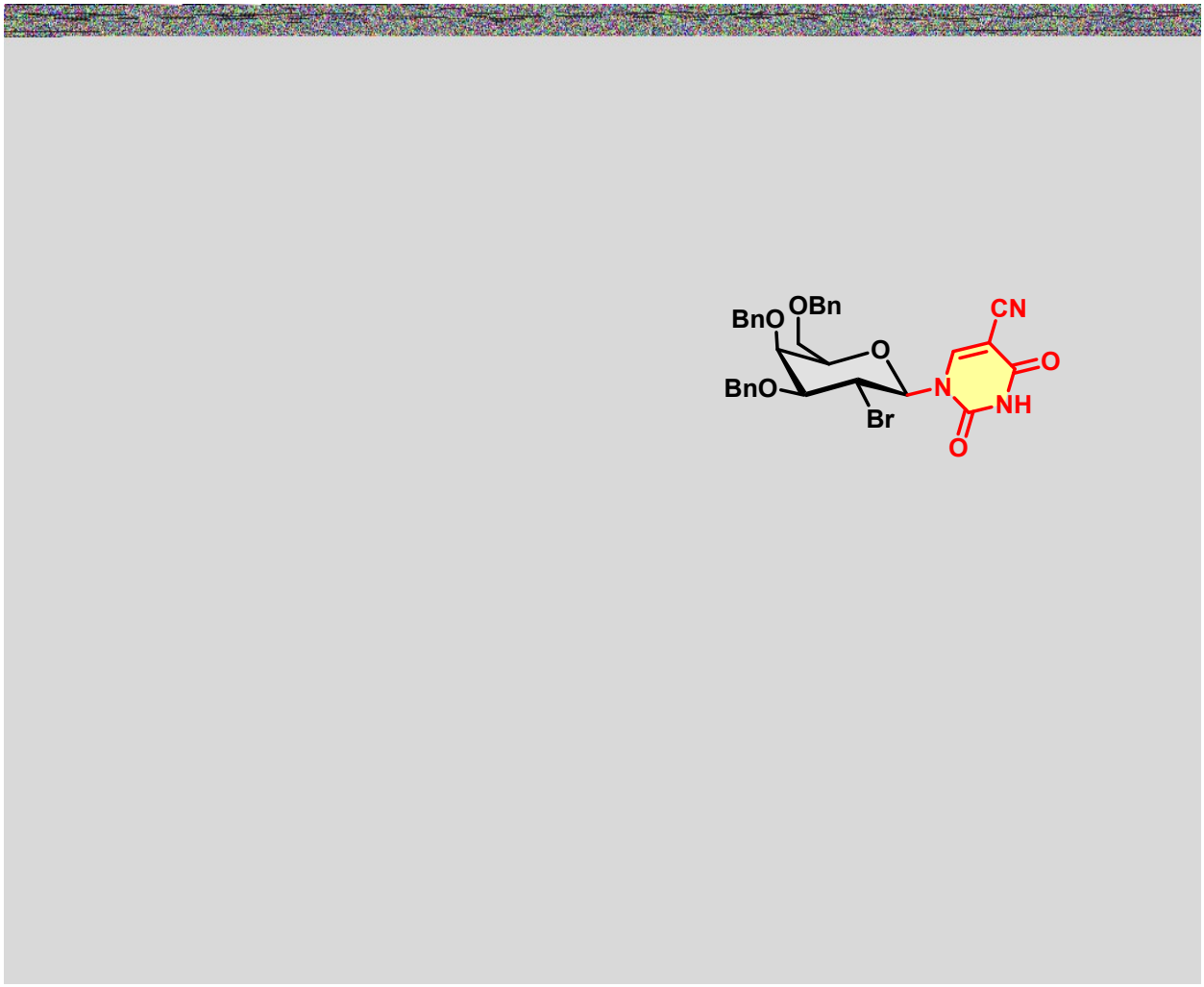


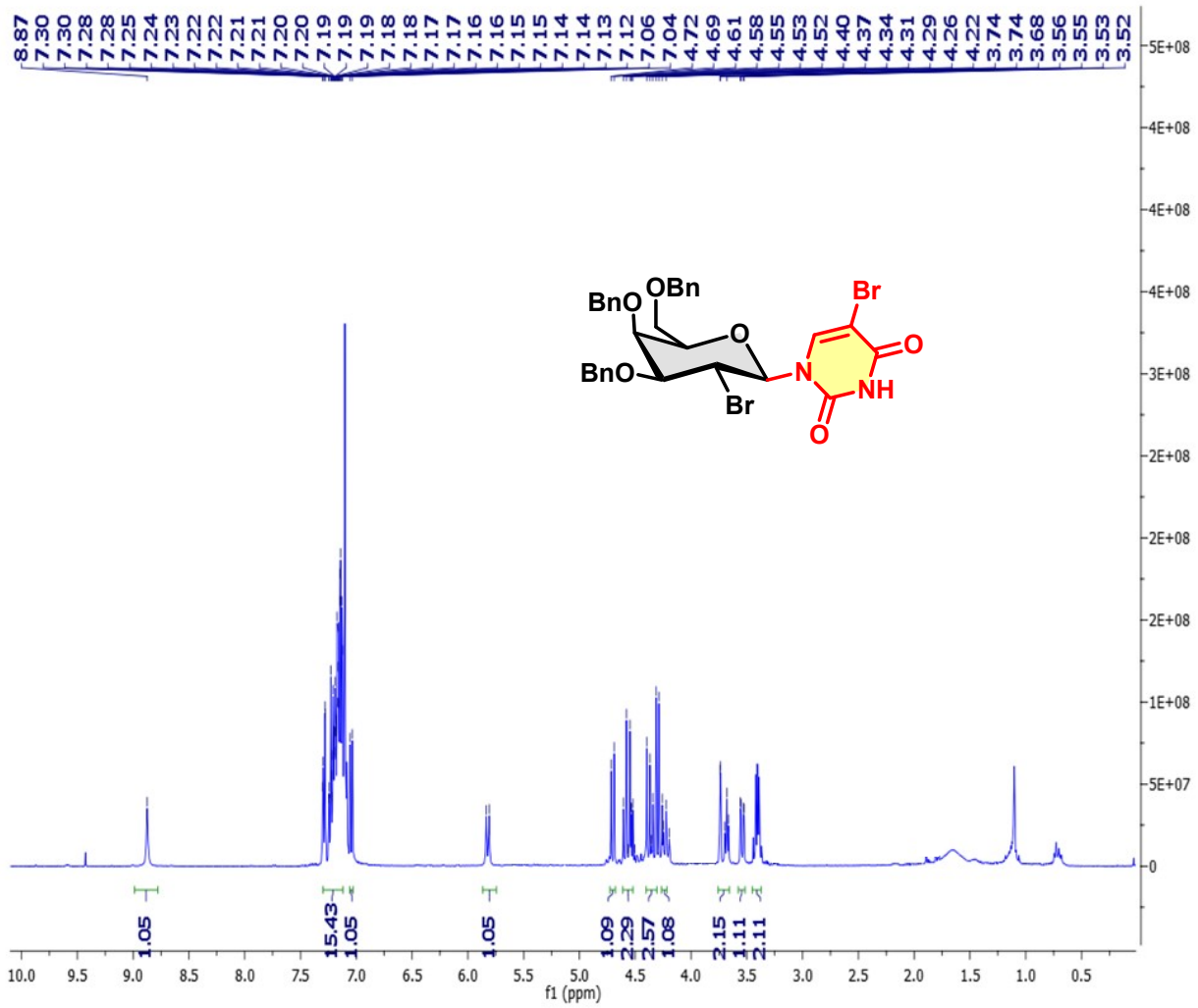
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3j



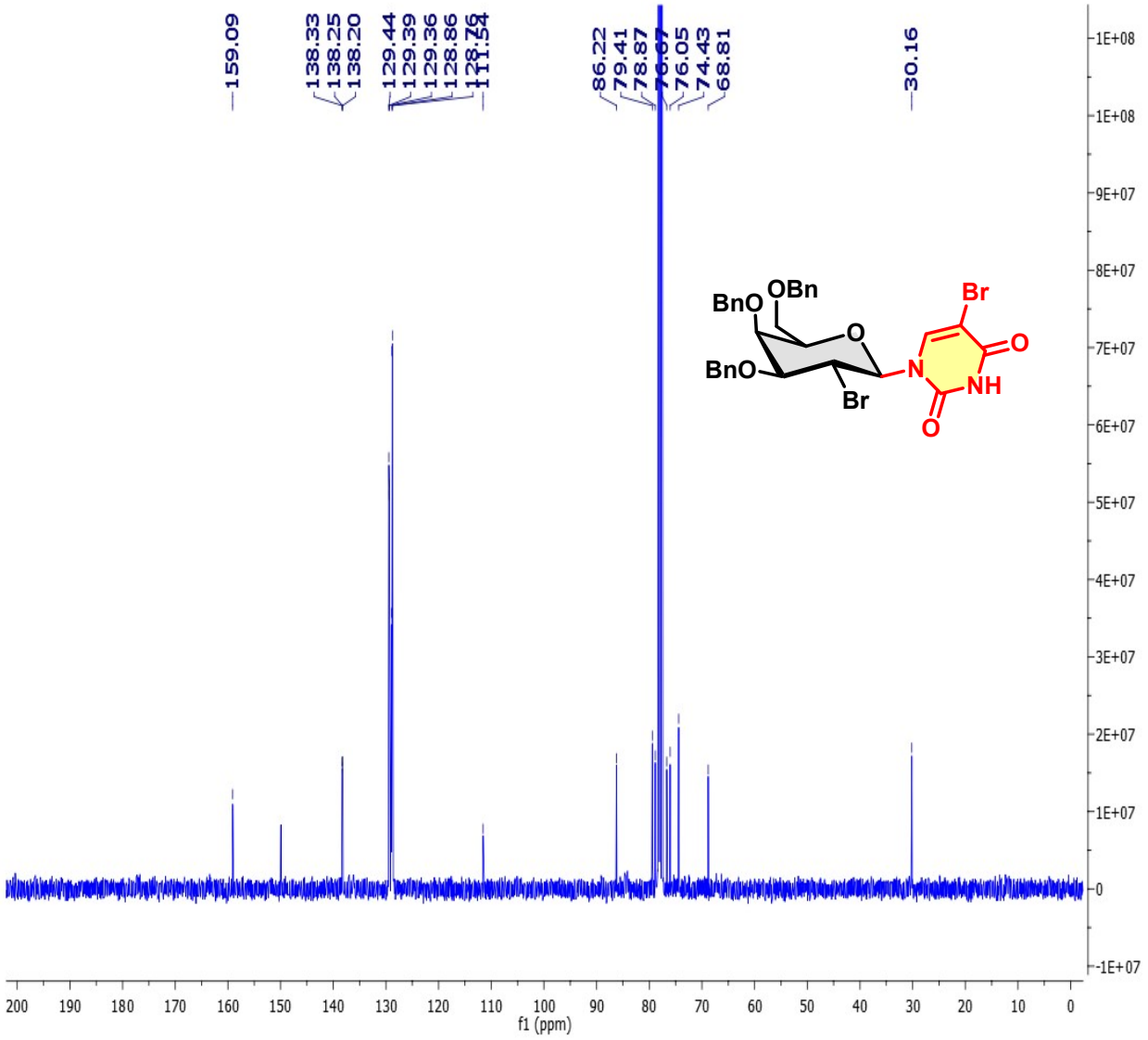
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3j



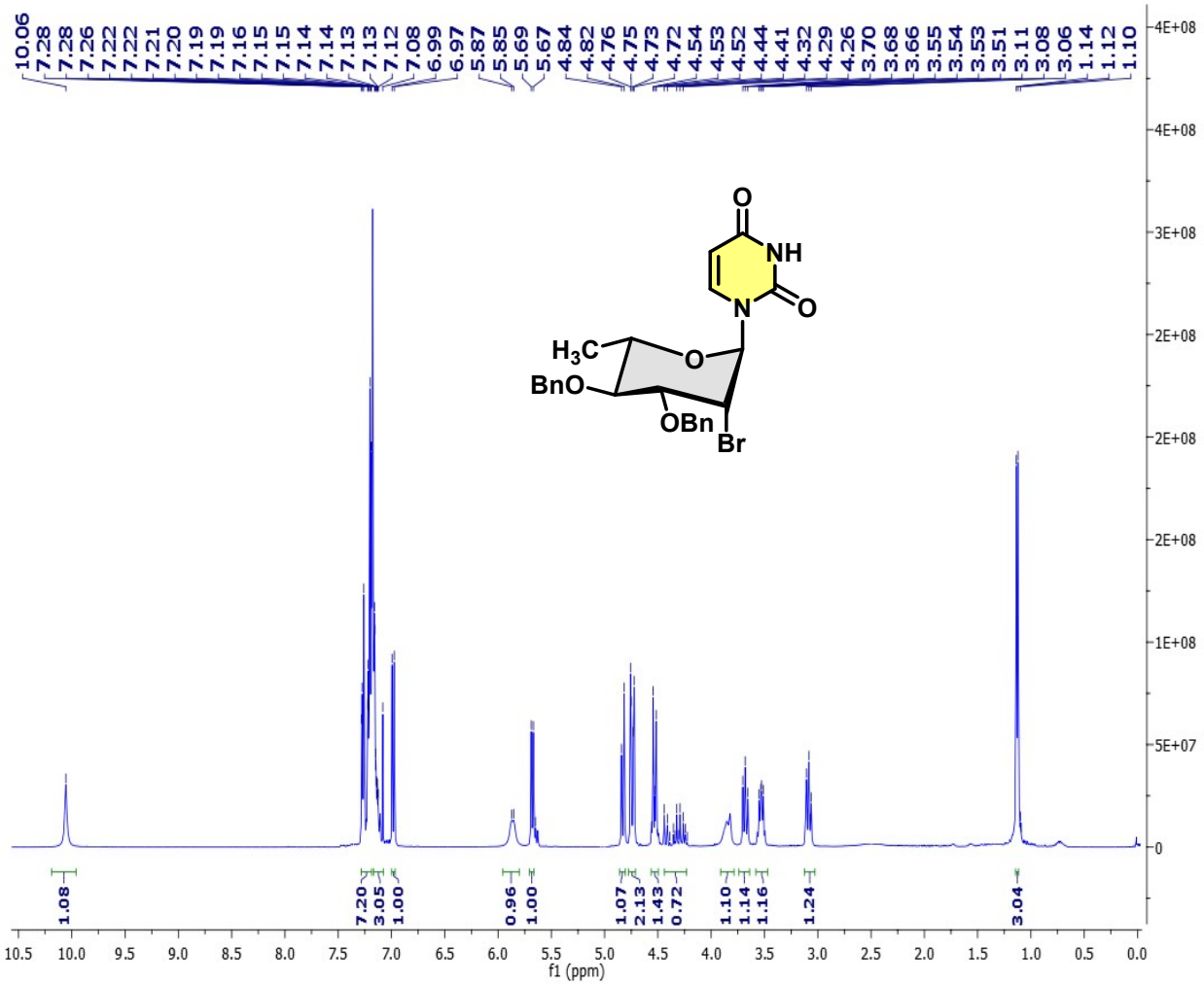
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3k



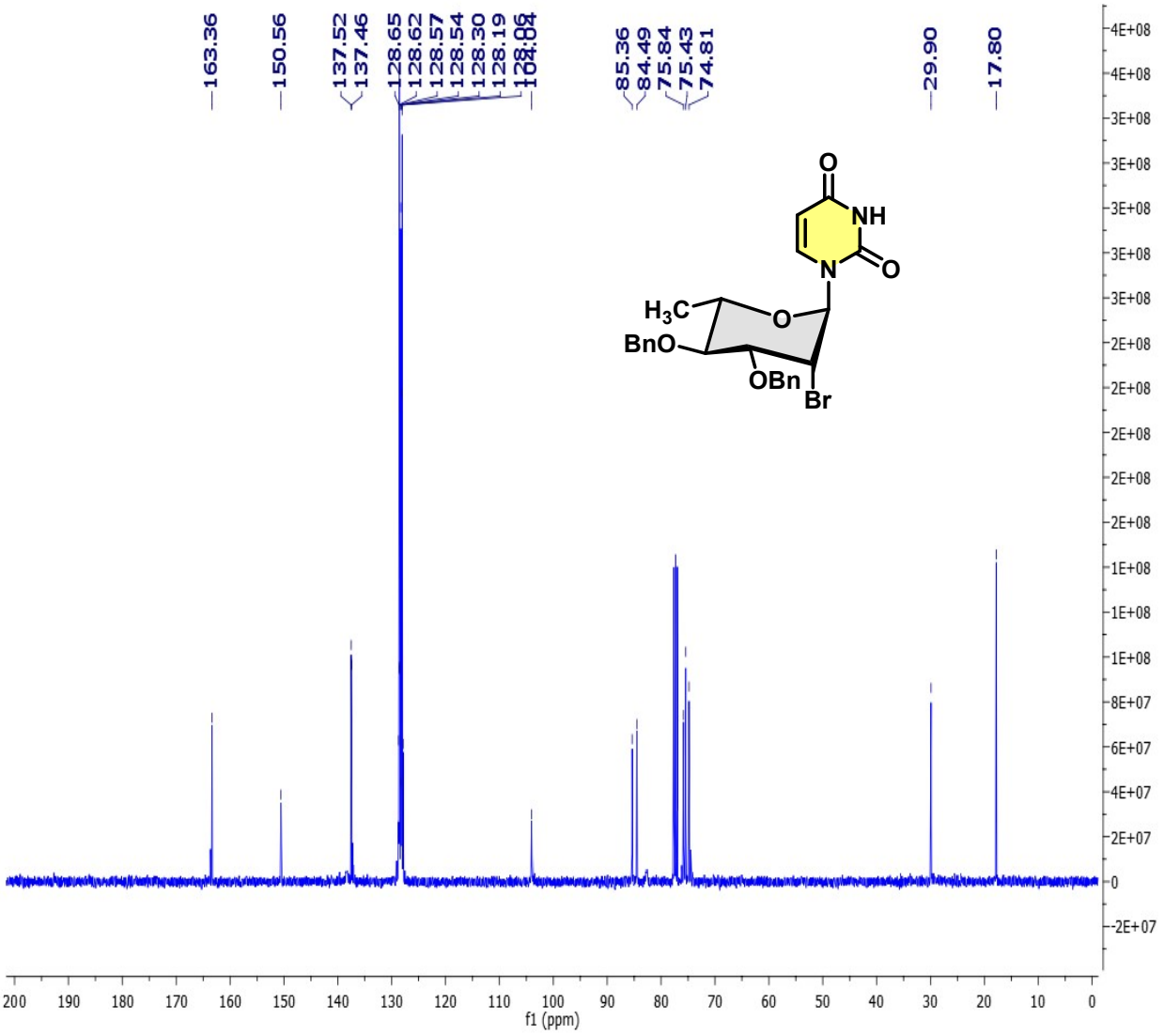
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3k



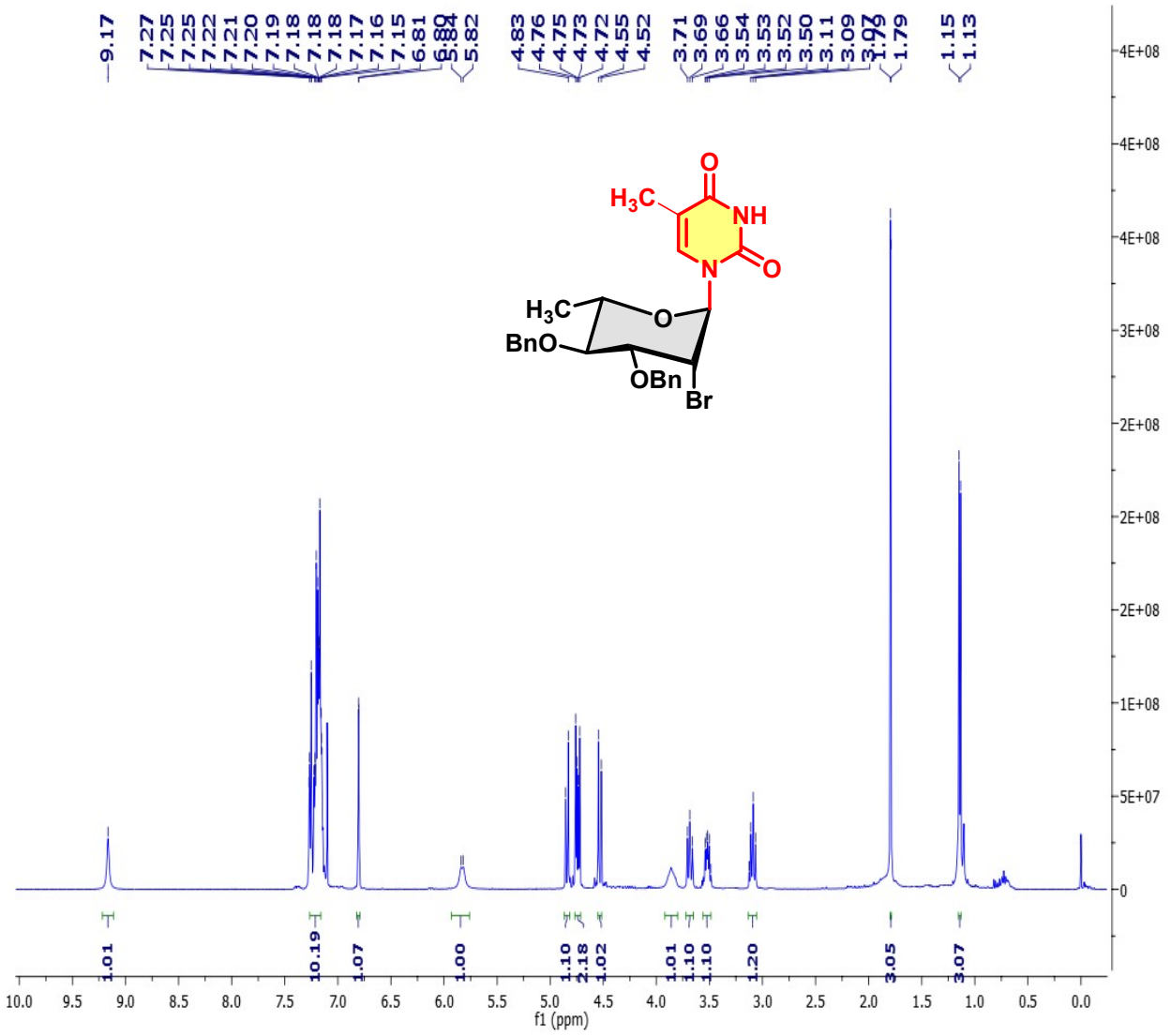
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3l



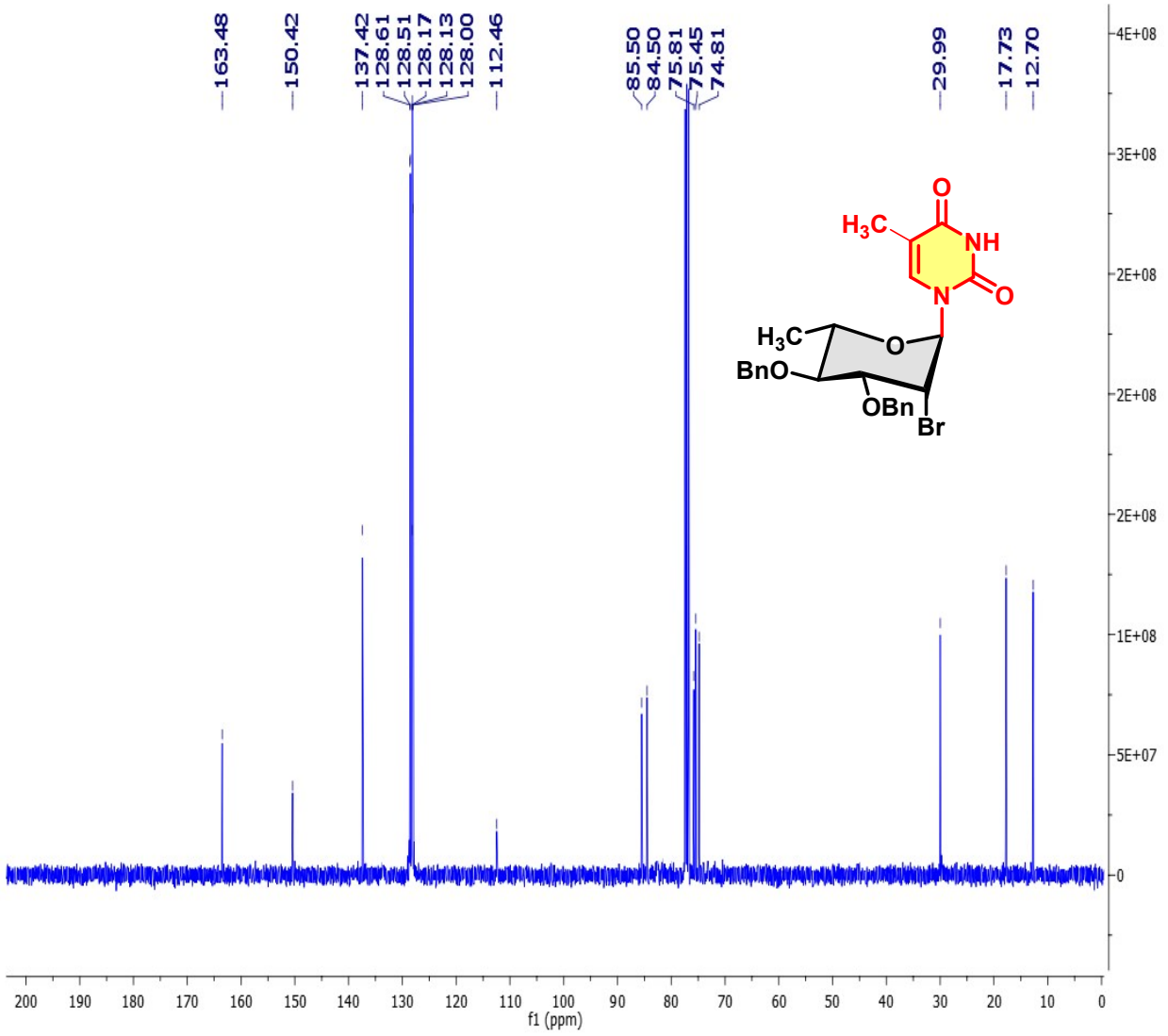
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3l



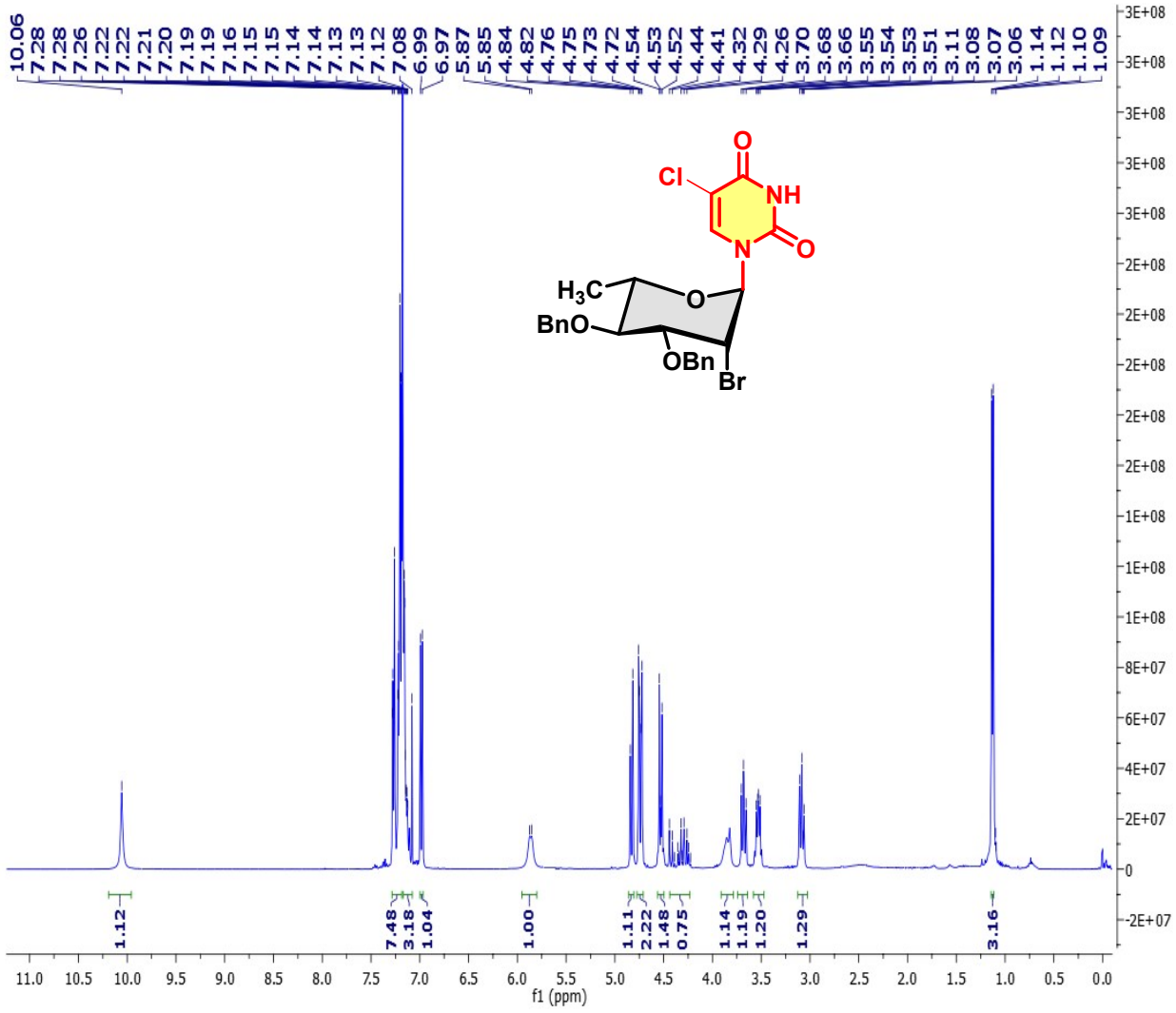
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3m



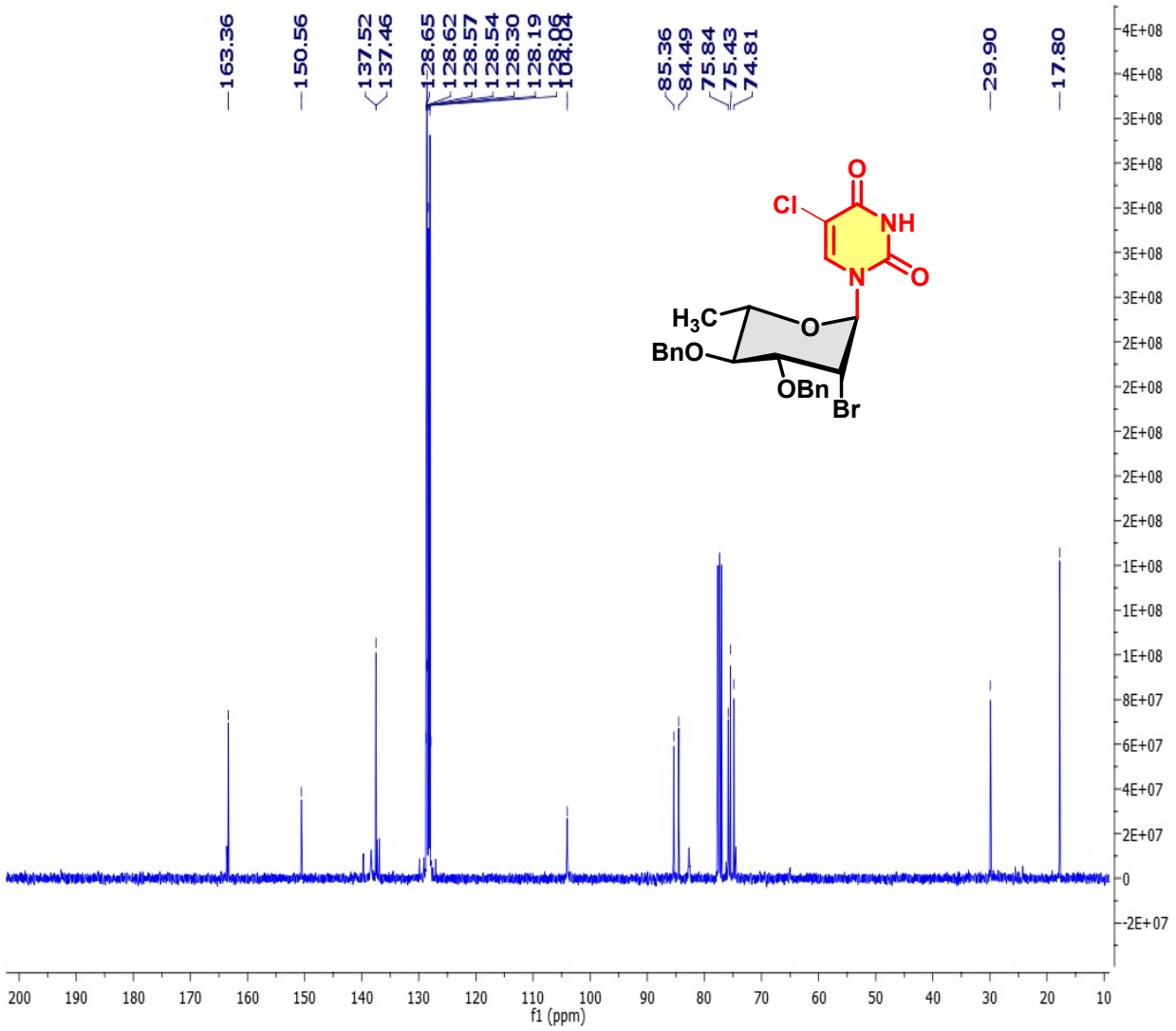
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3m



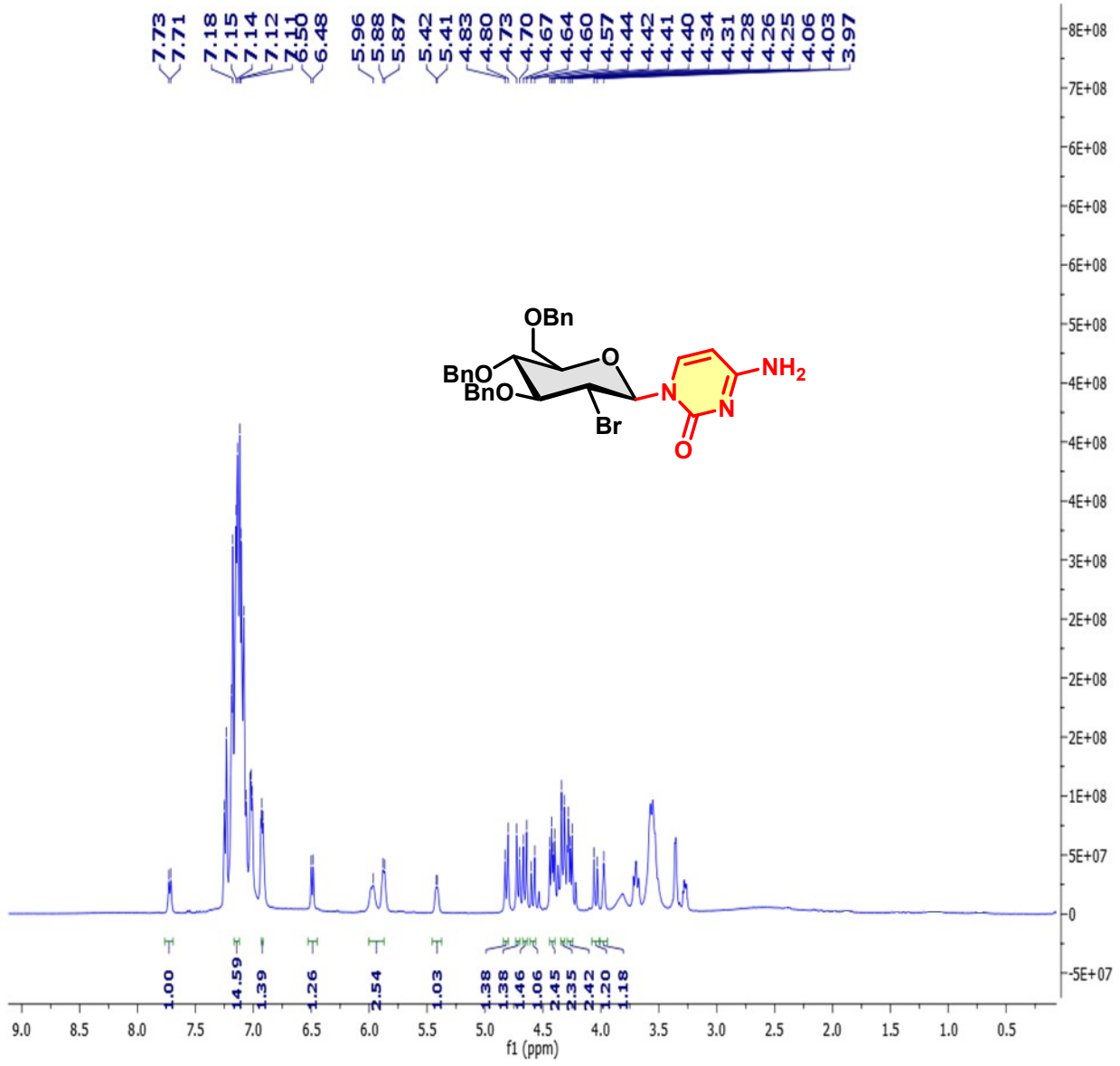
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3n



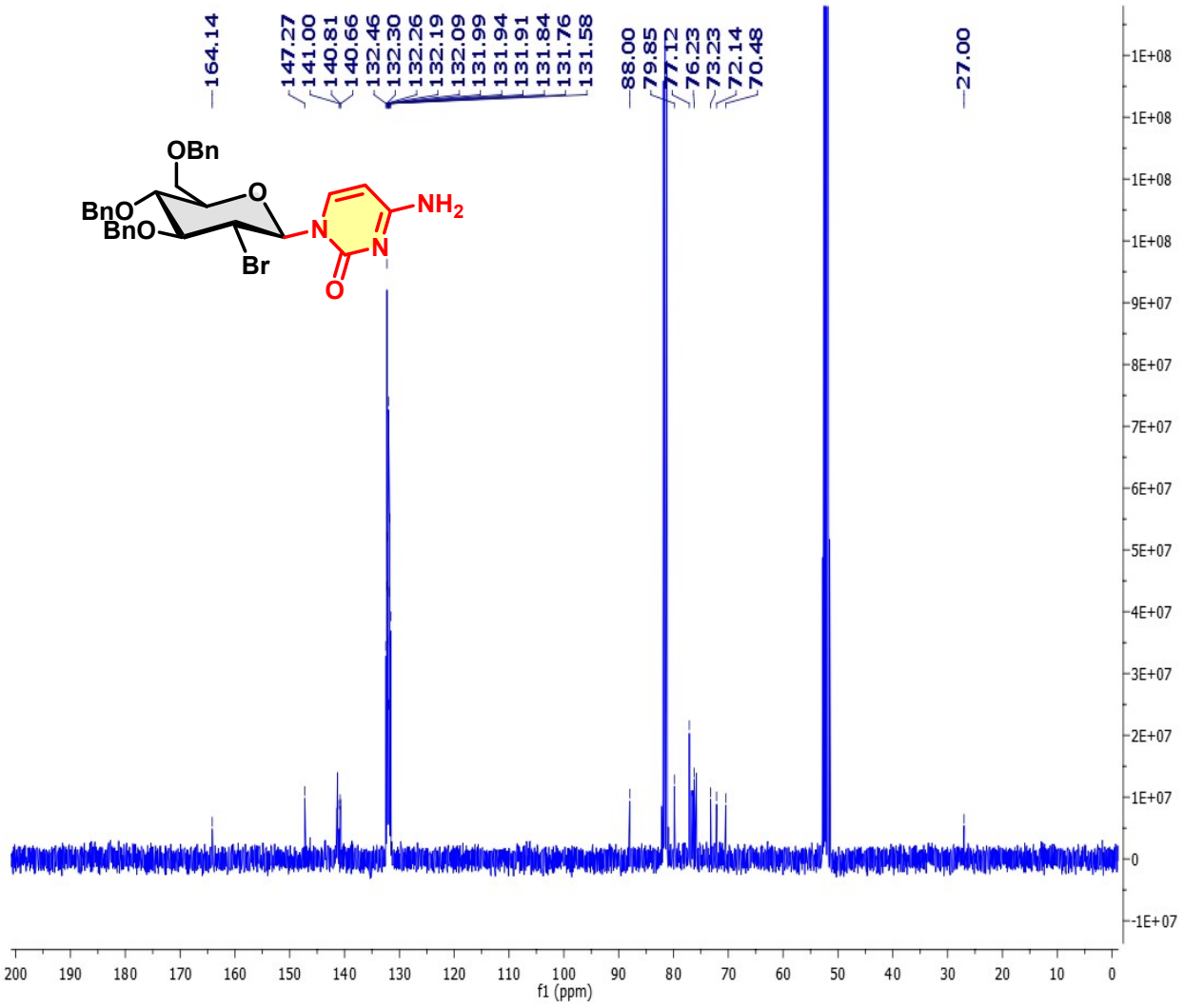
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3n



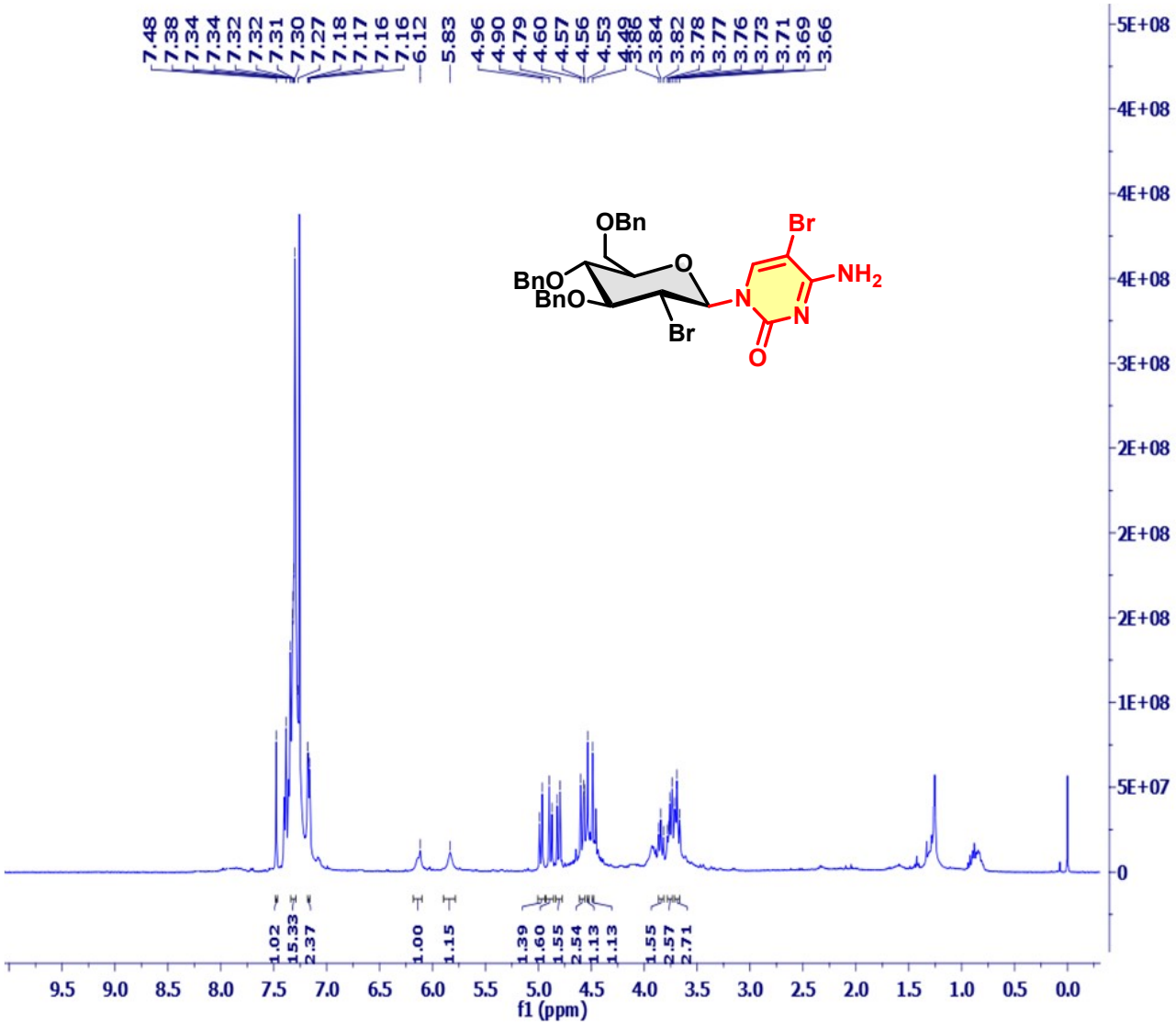
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4a



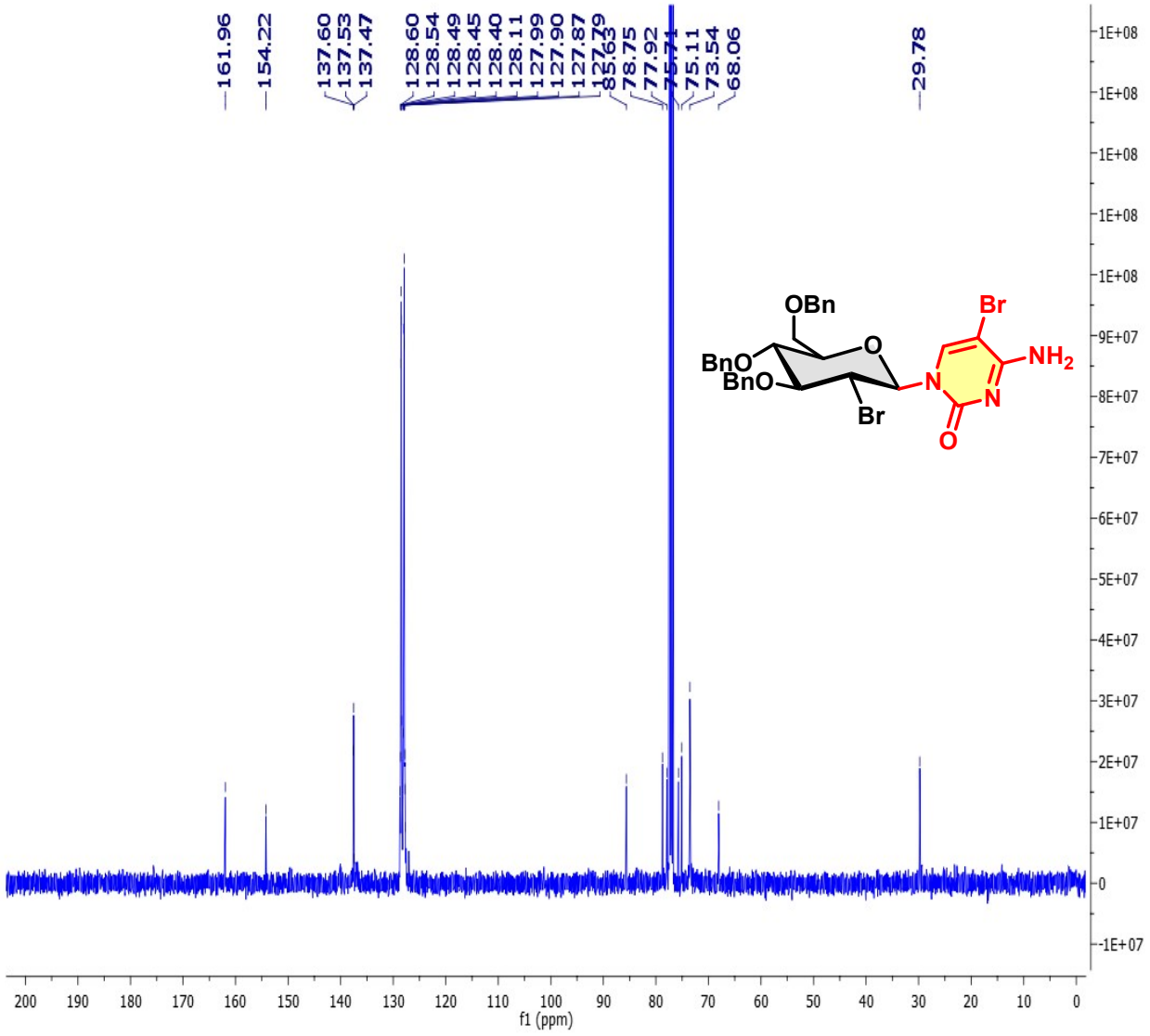
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 4a



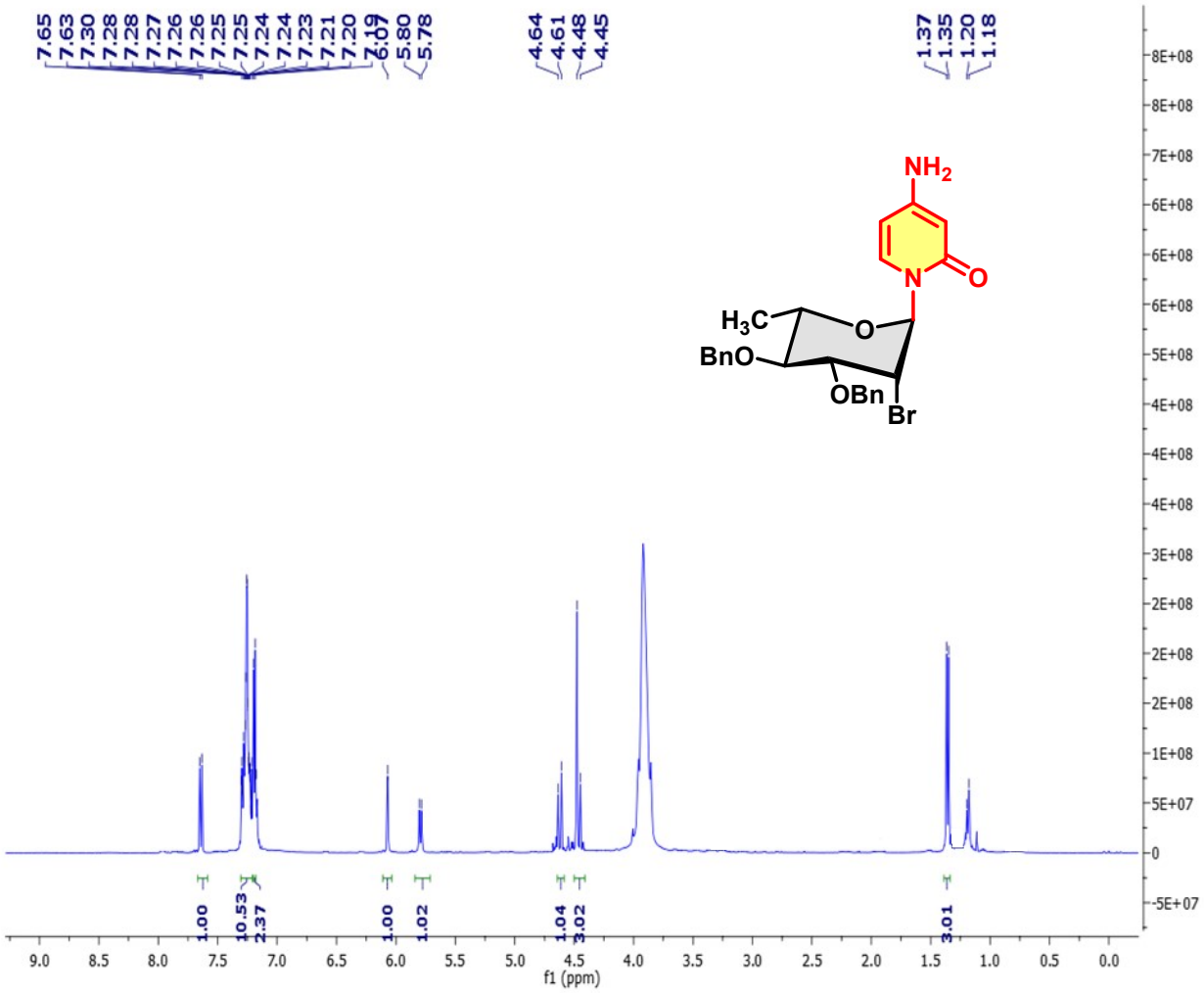
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4b



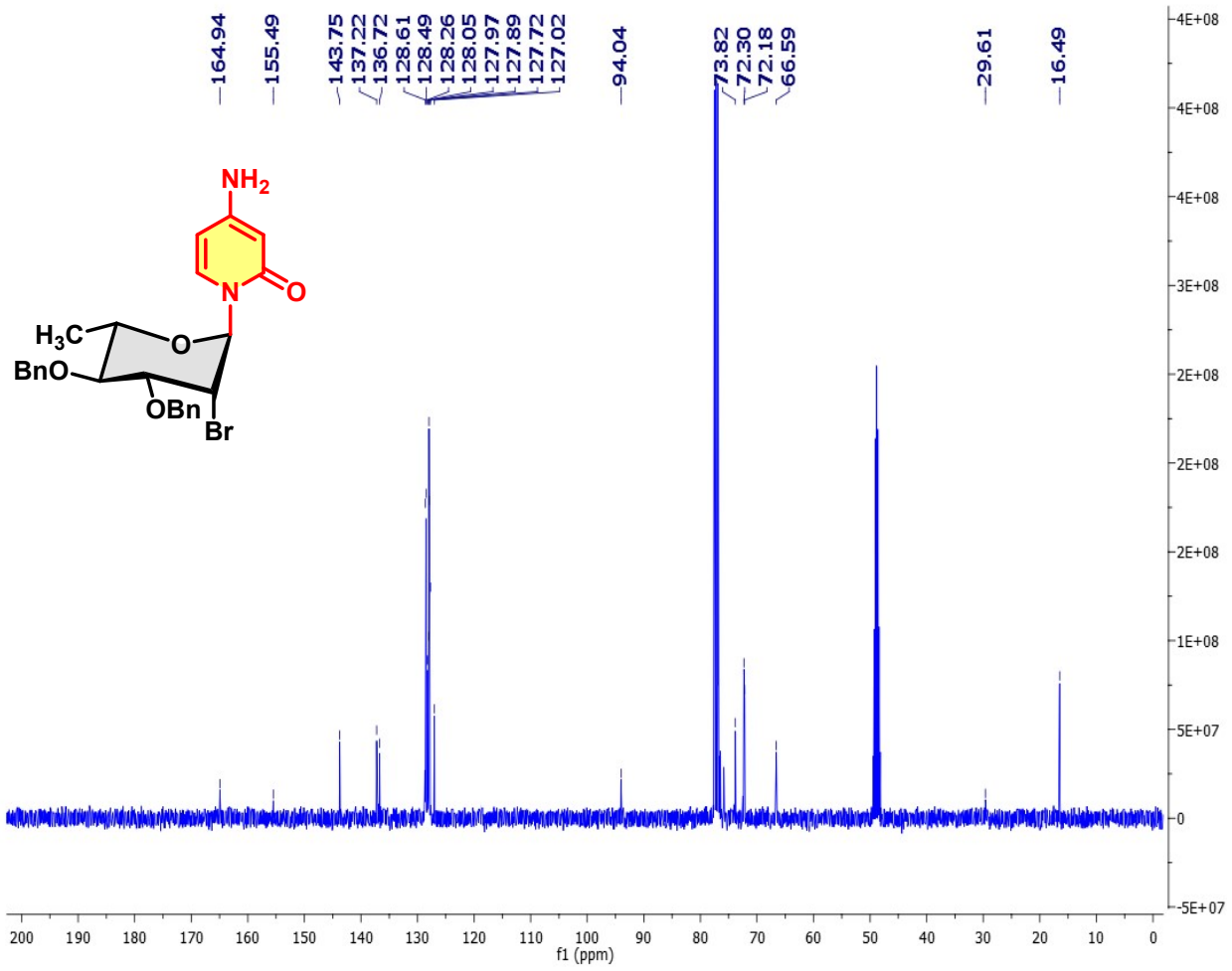
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 4b



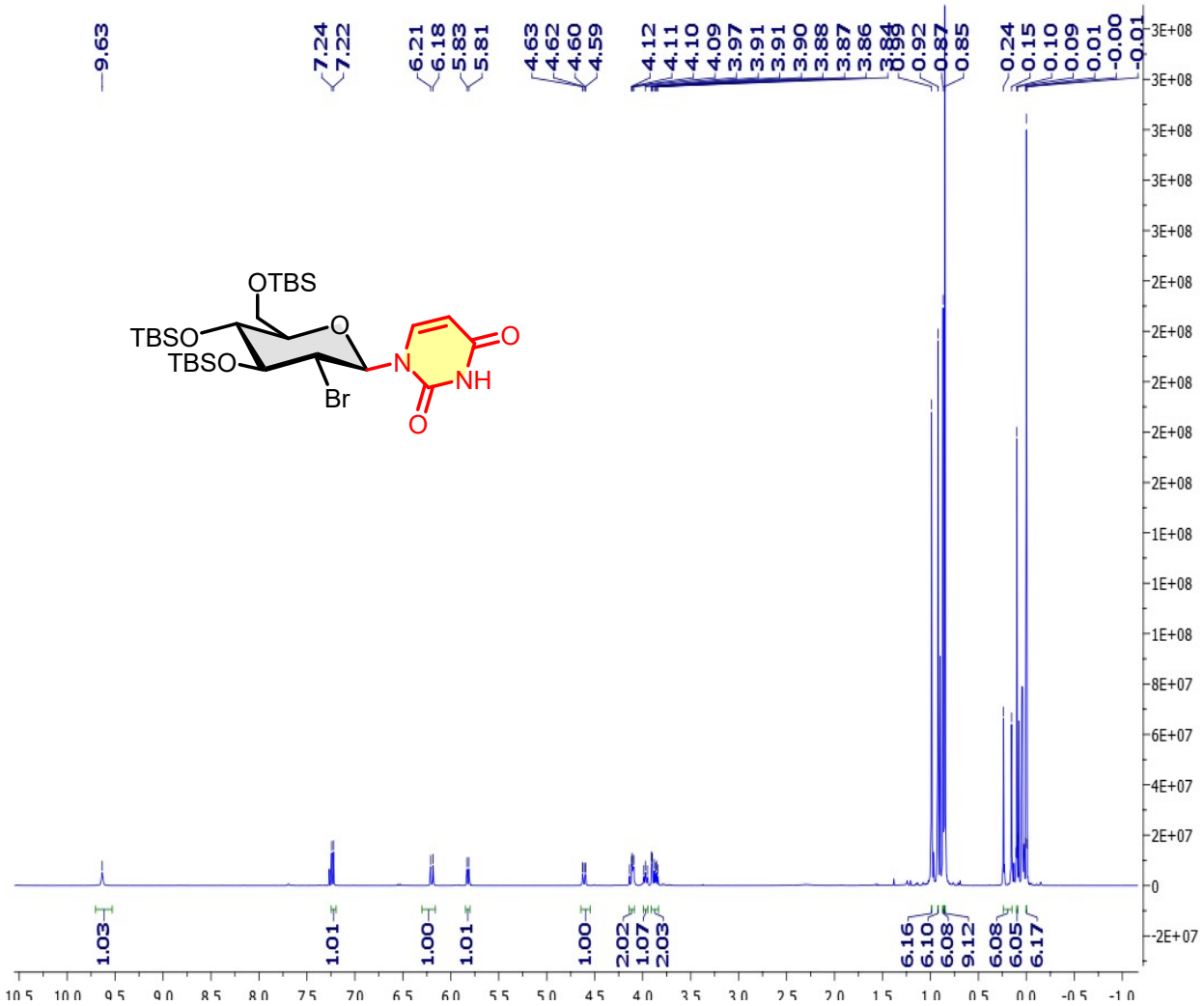
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4c



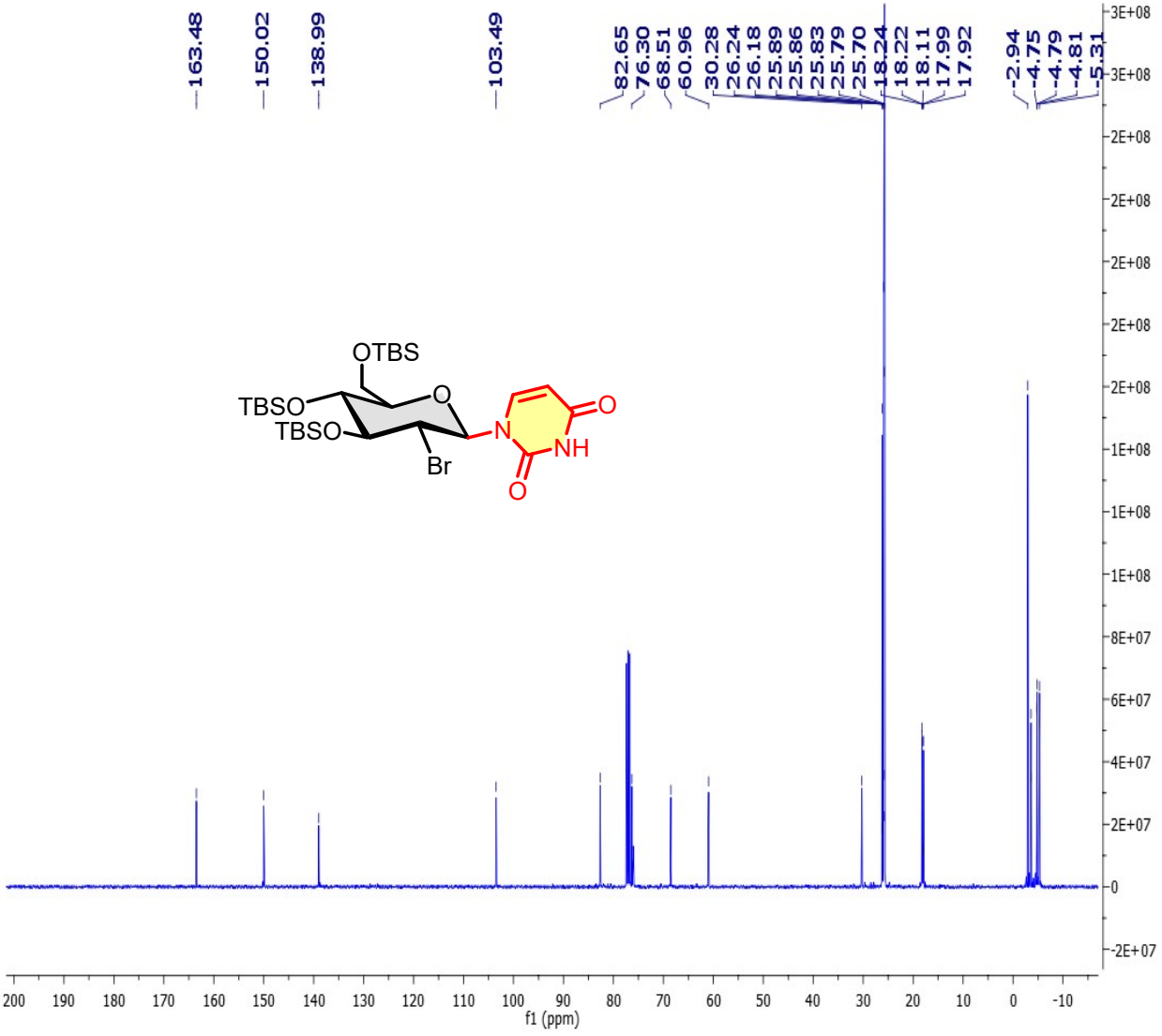
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 4c



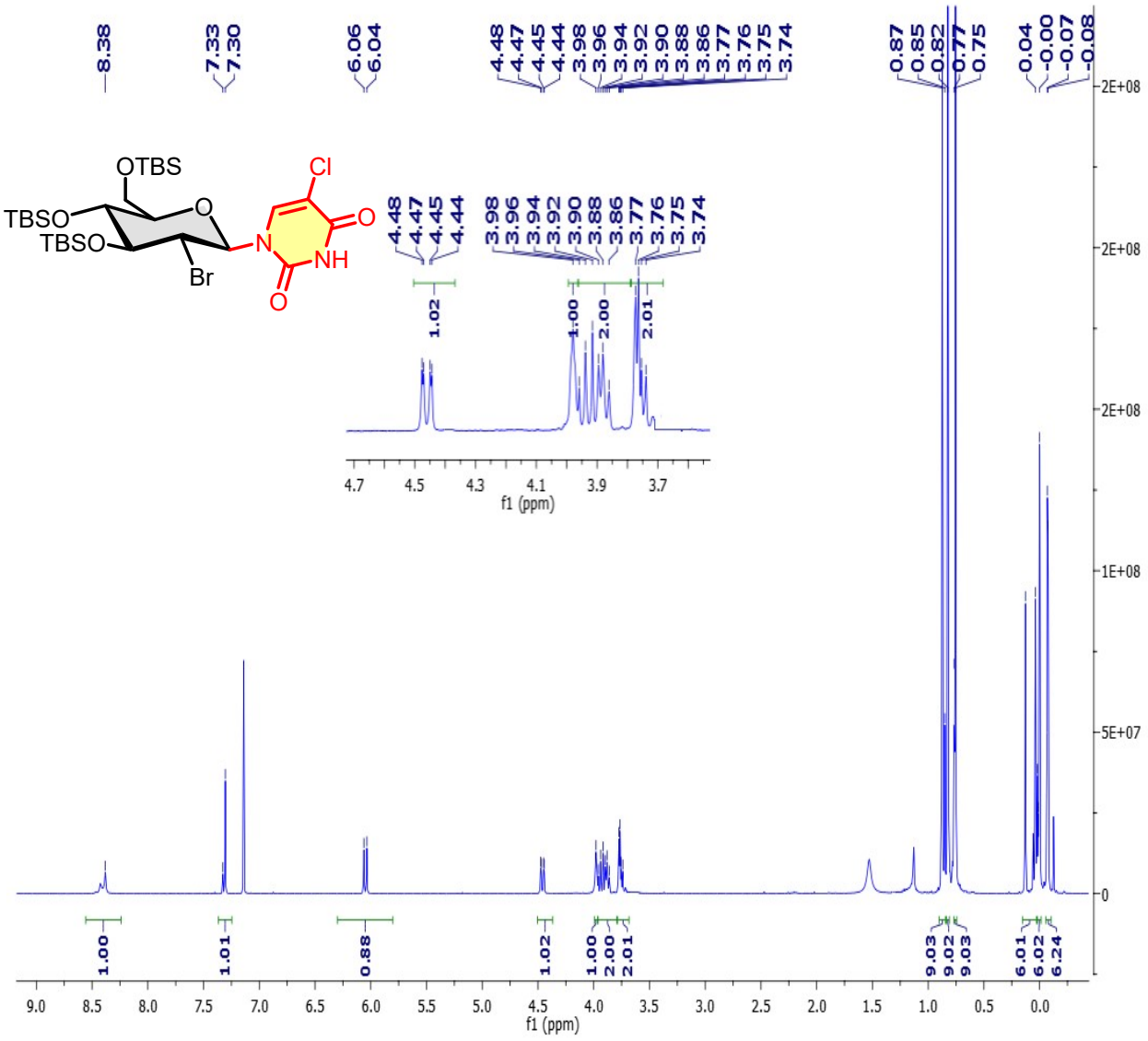
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5a



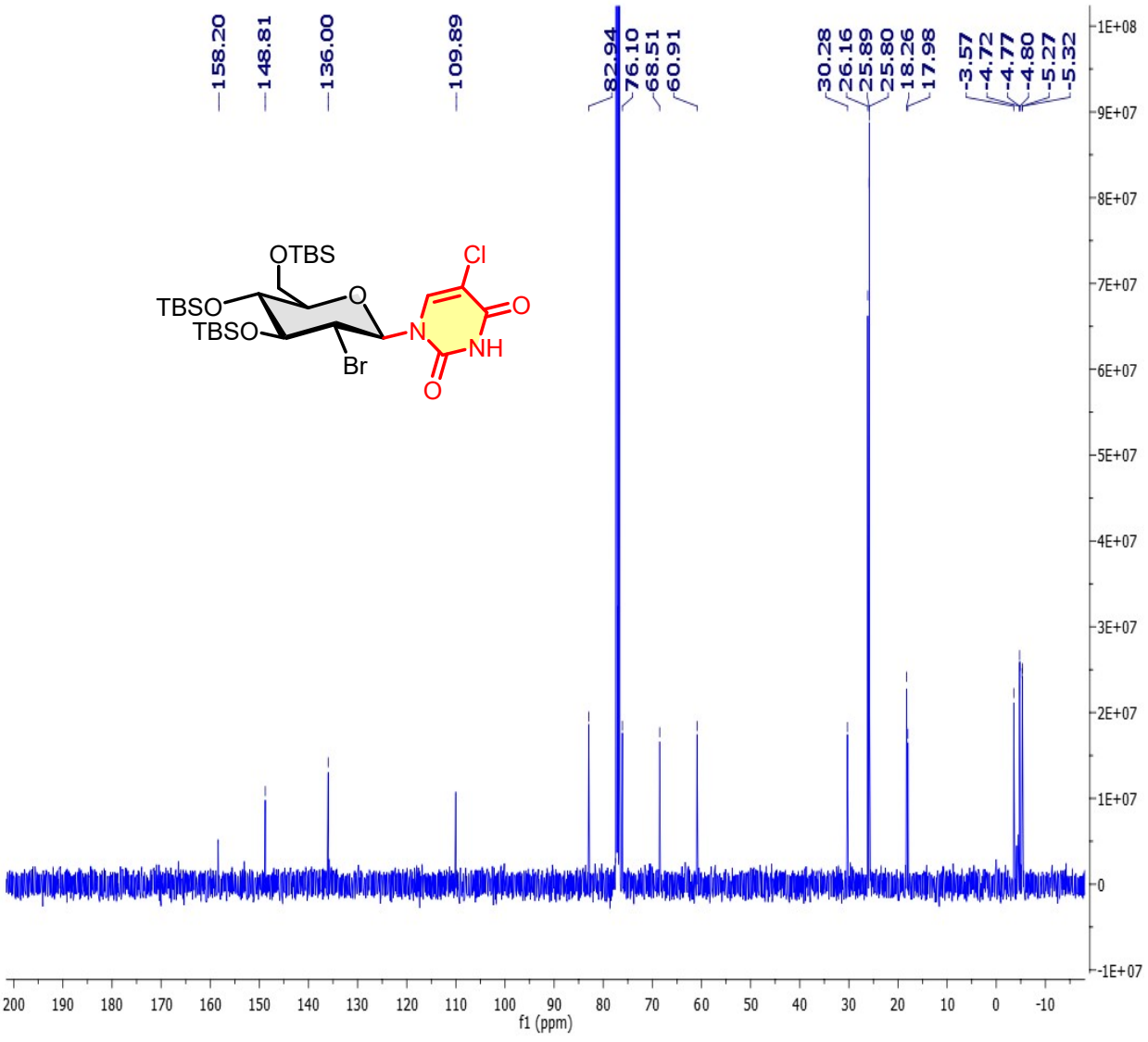
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5a



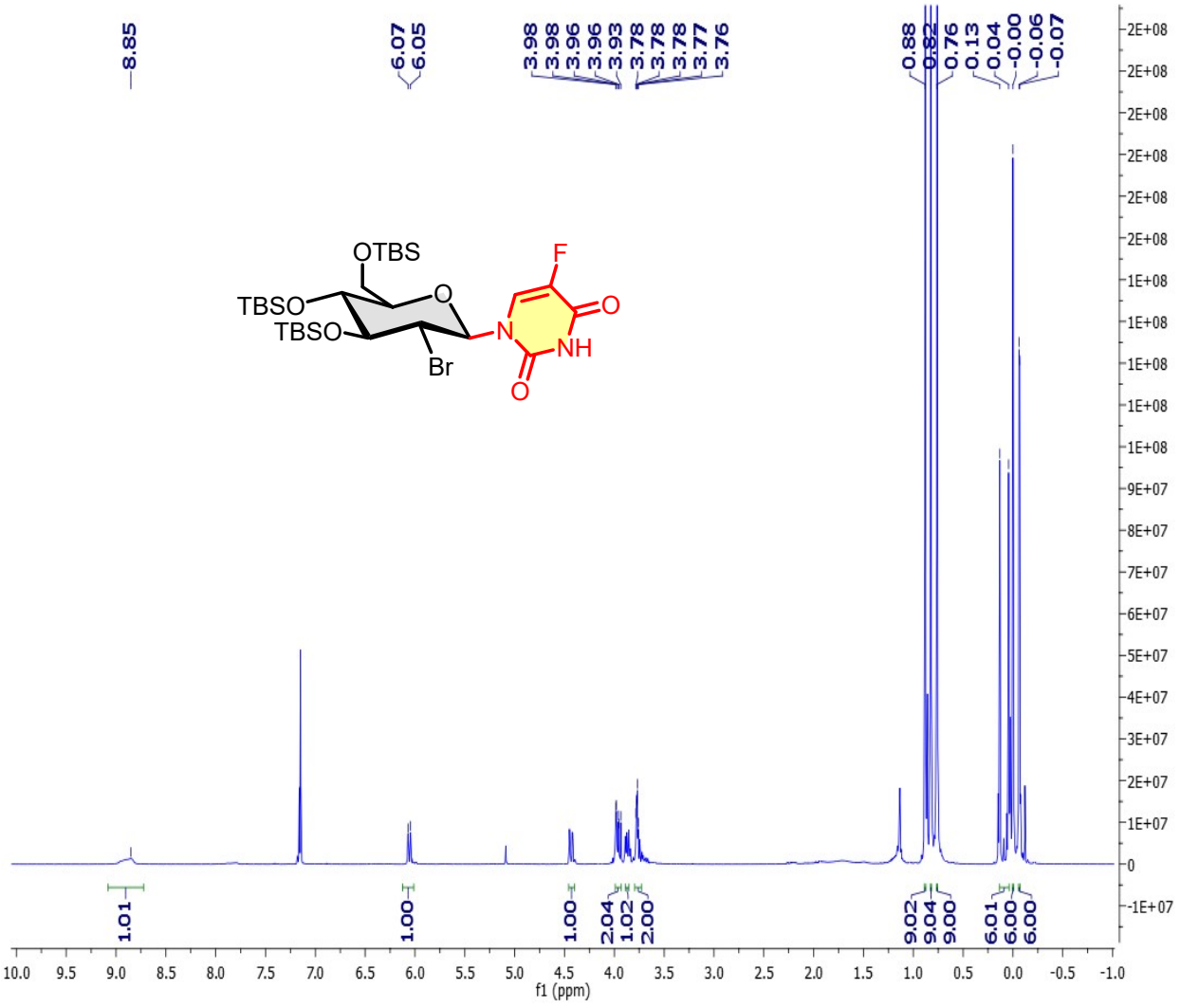
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5b



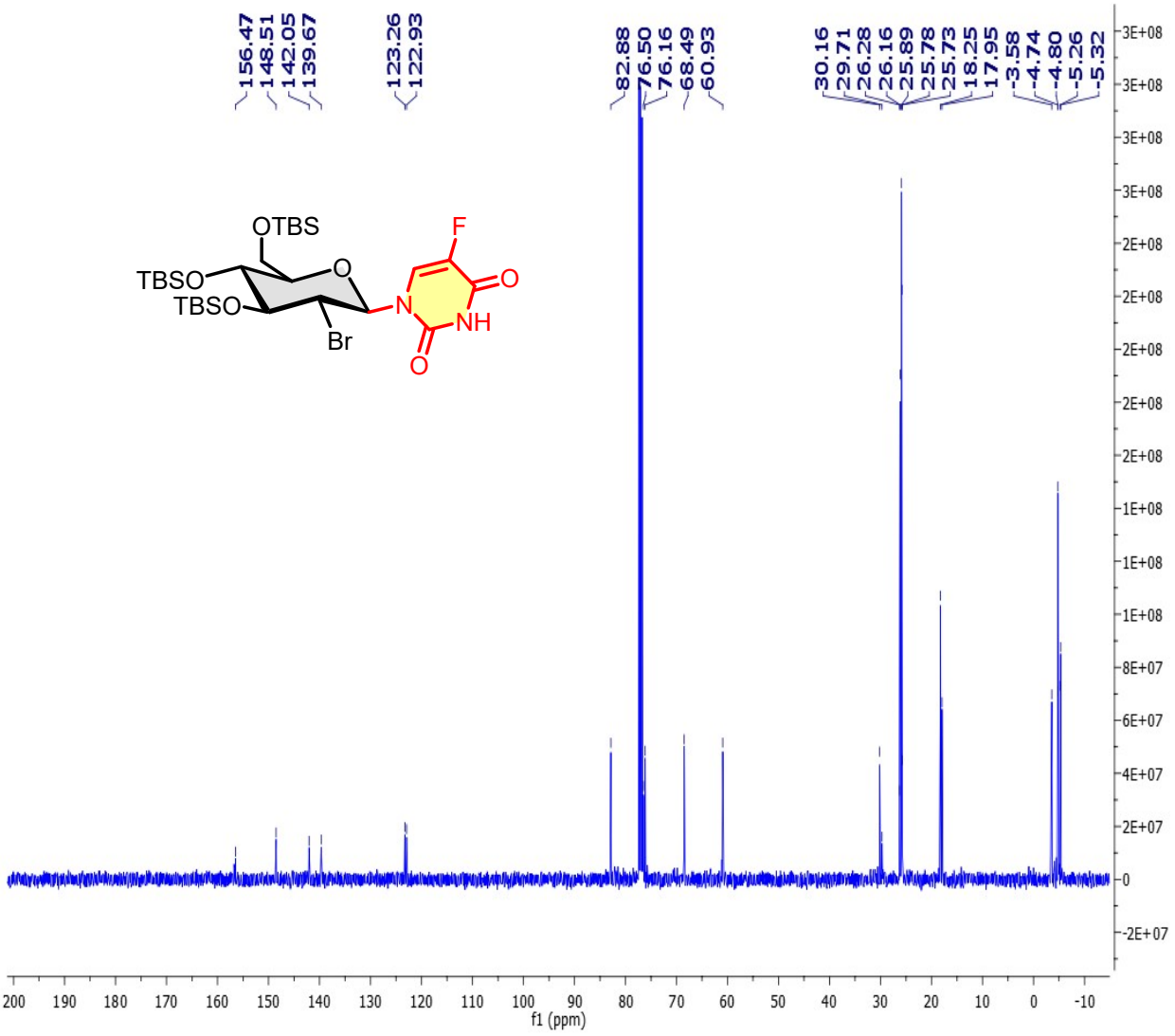
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5b



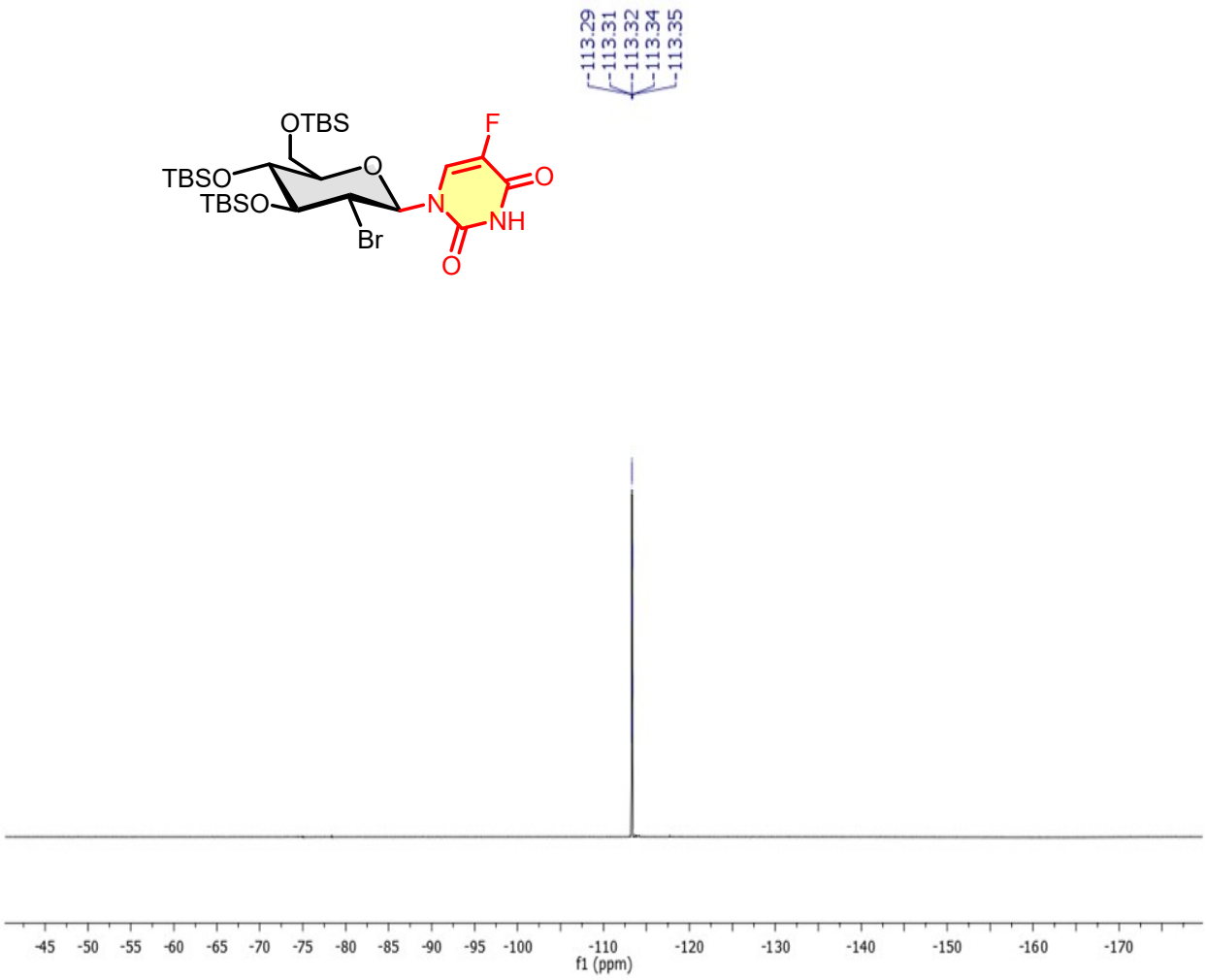
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5c



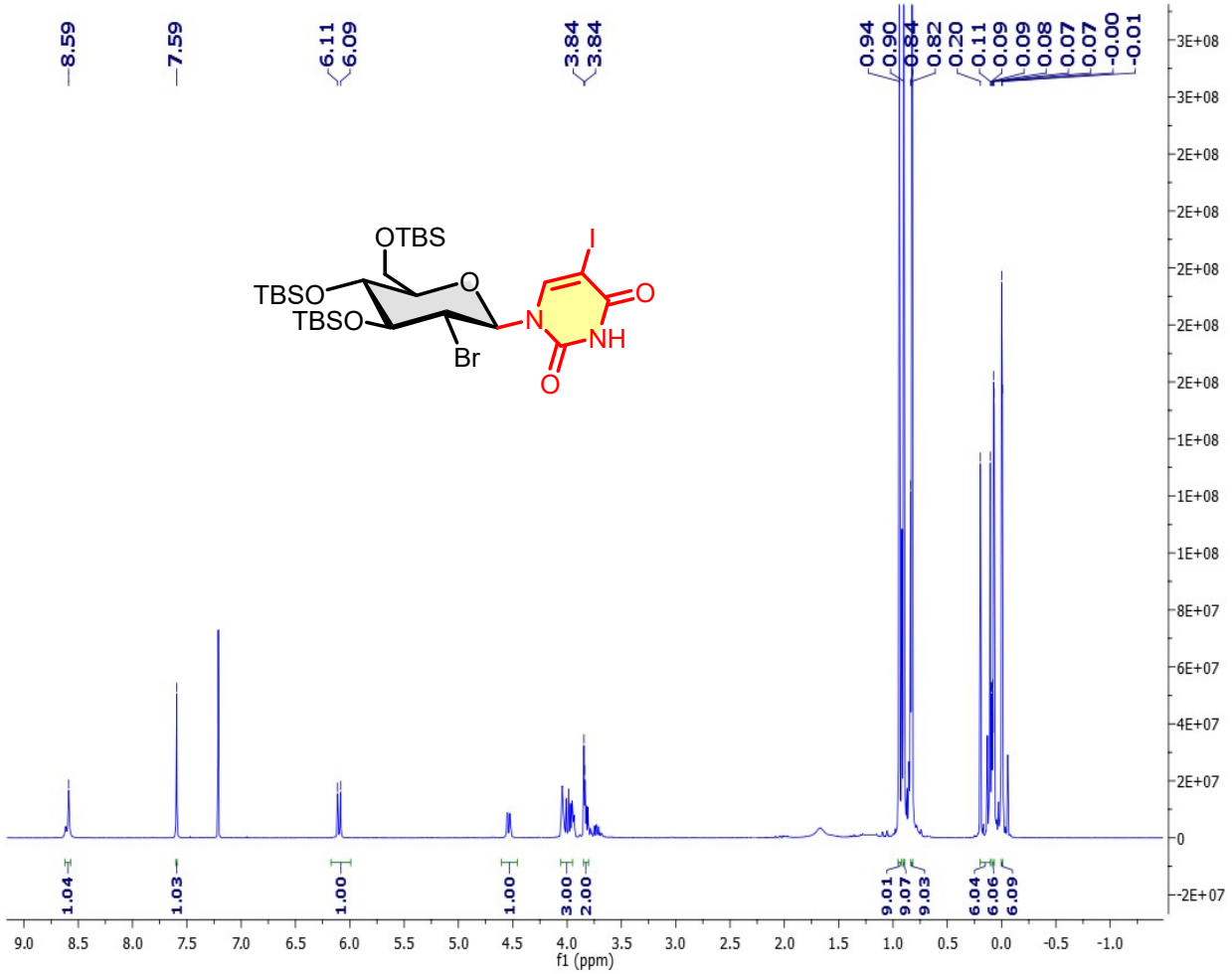
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5c



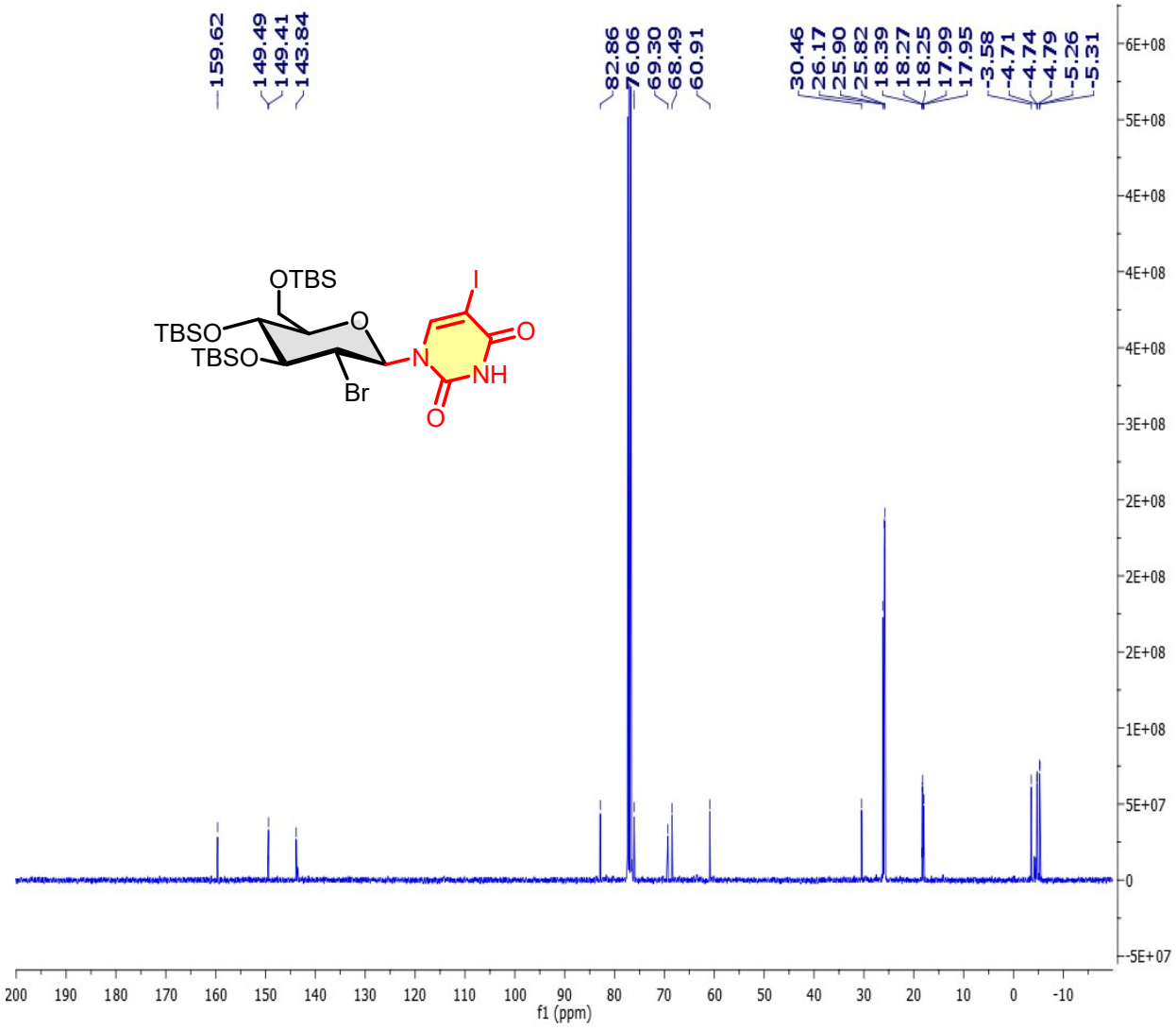
^{19}FNMR (377 MHz, $CDCl_3$) of compound 5c



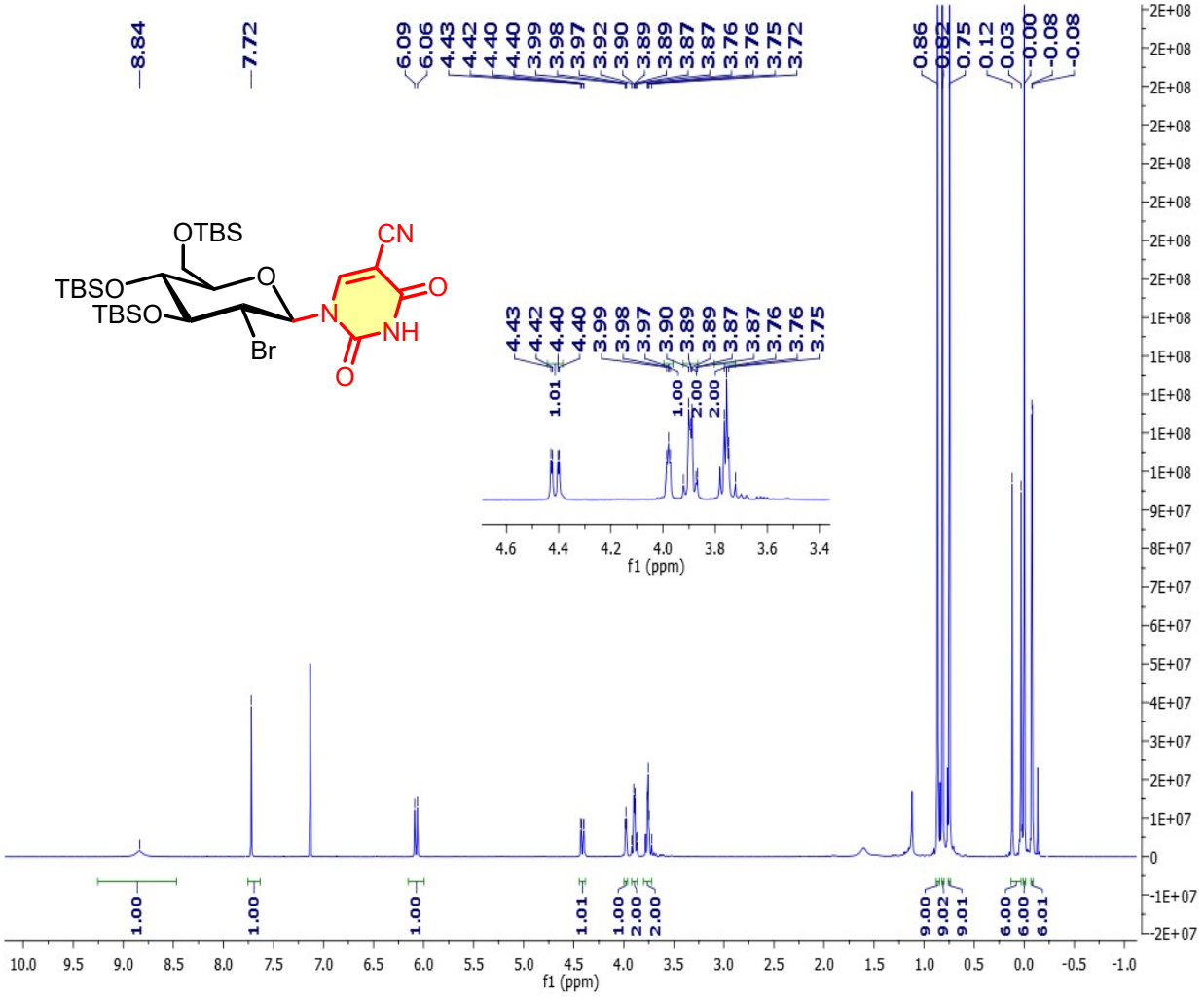
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5d



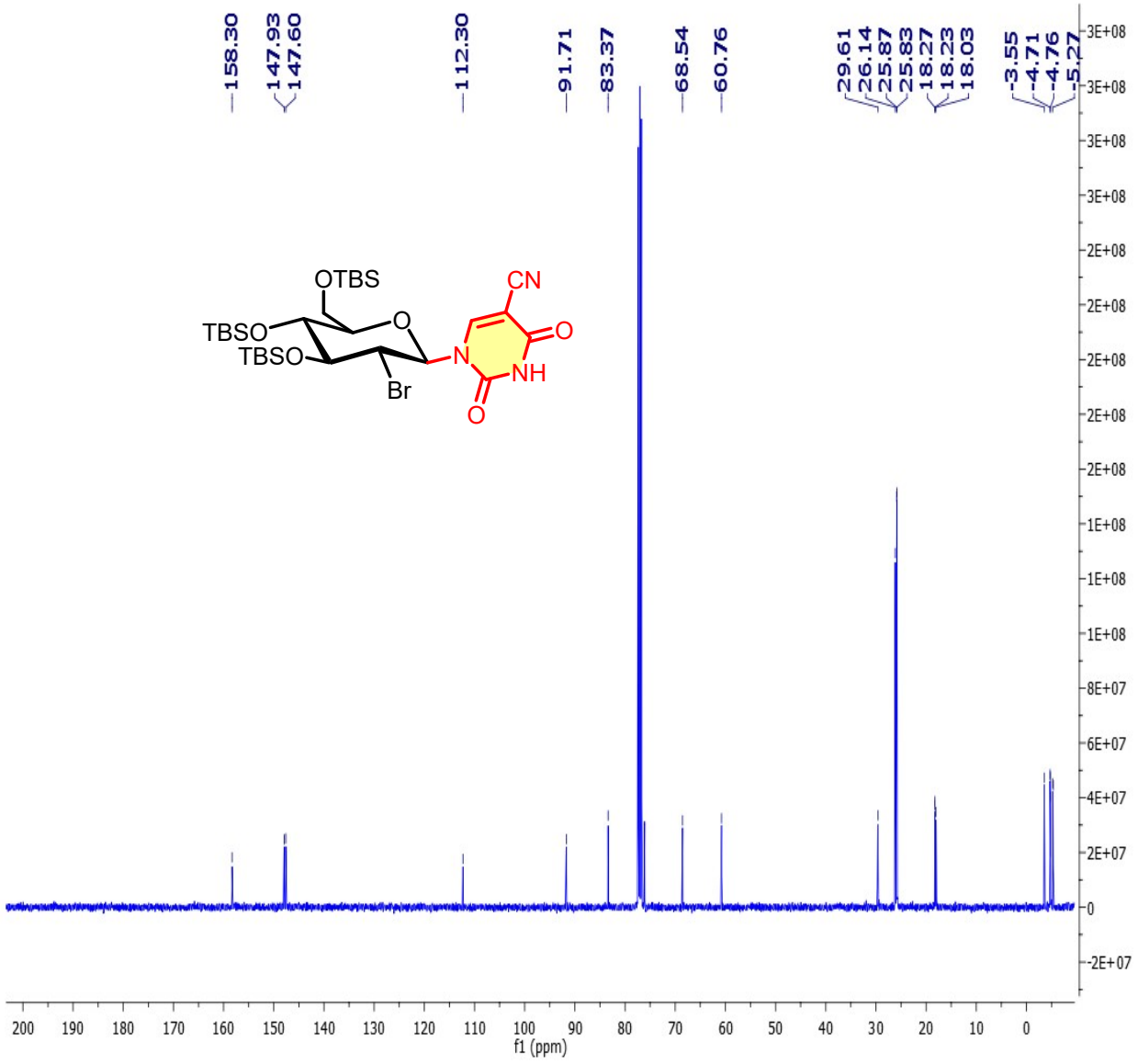
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5d



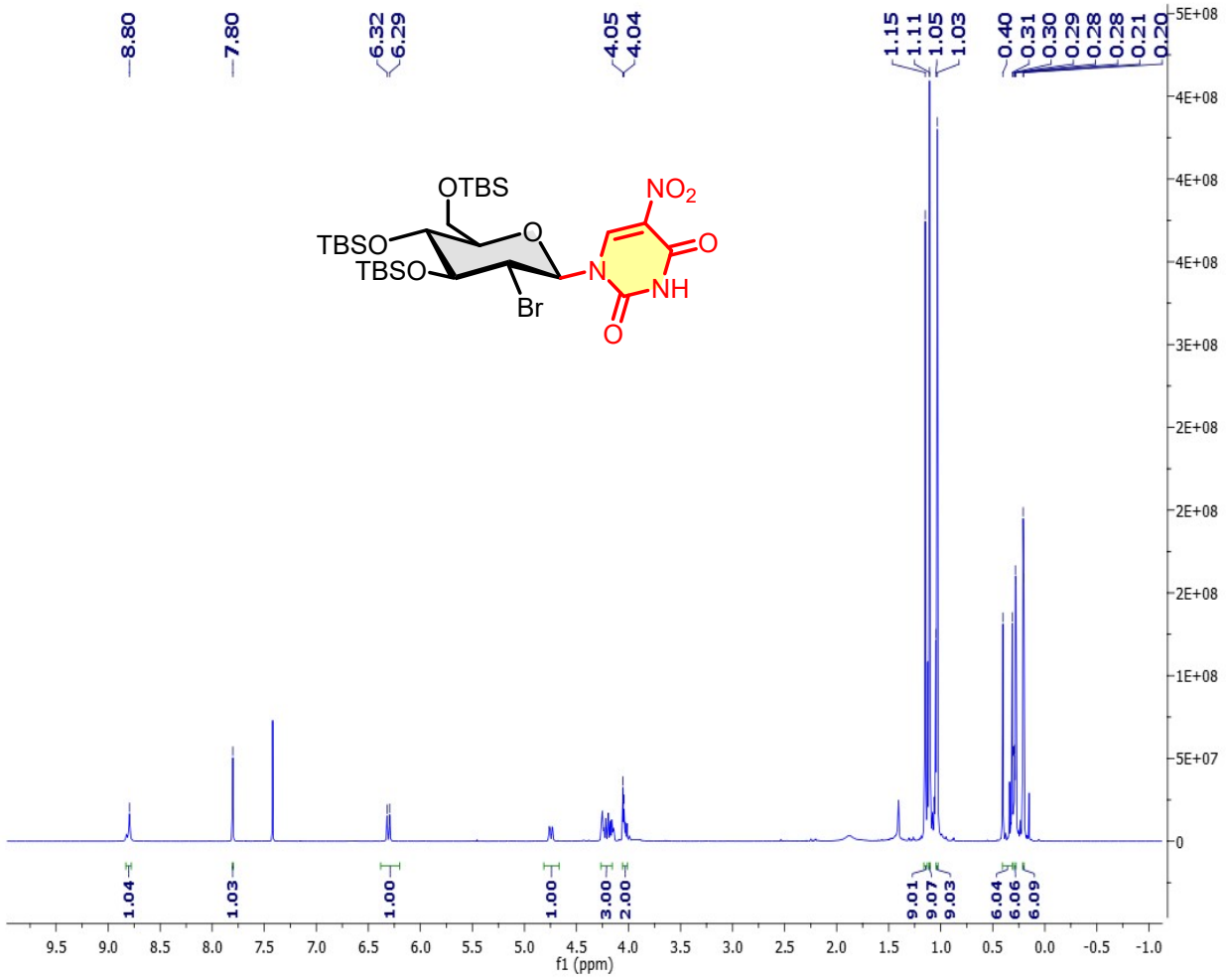
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5e



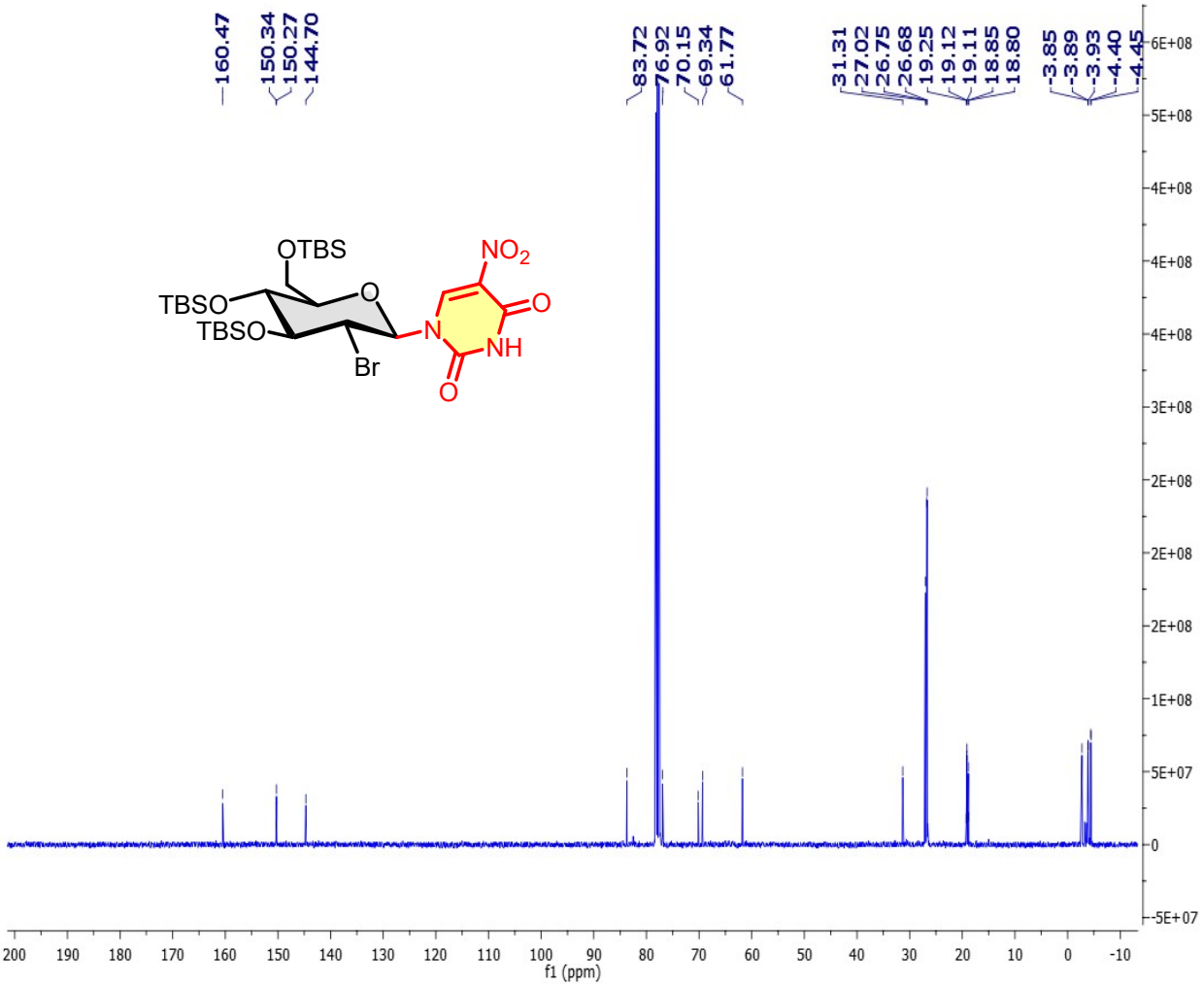
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5e



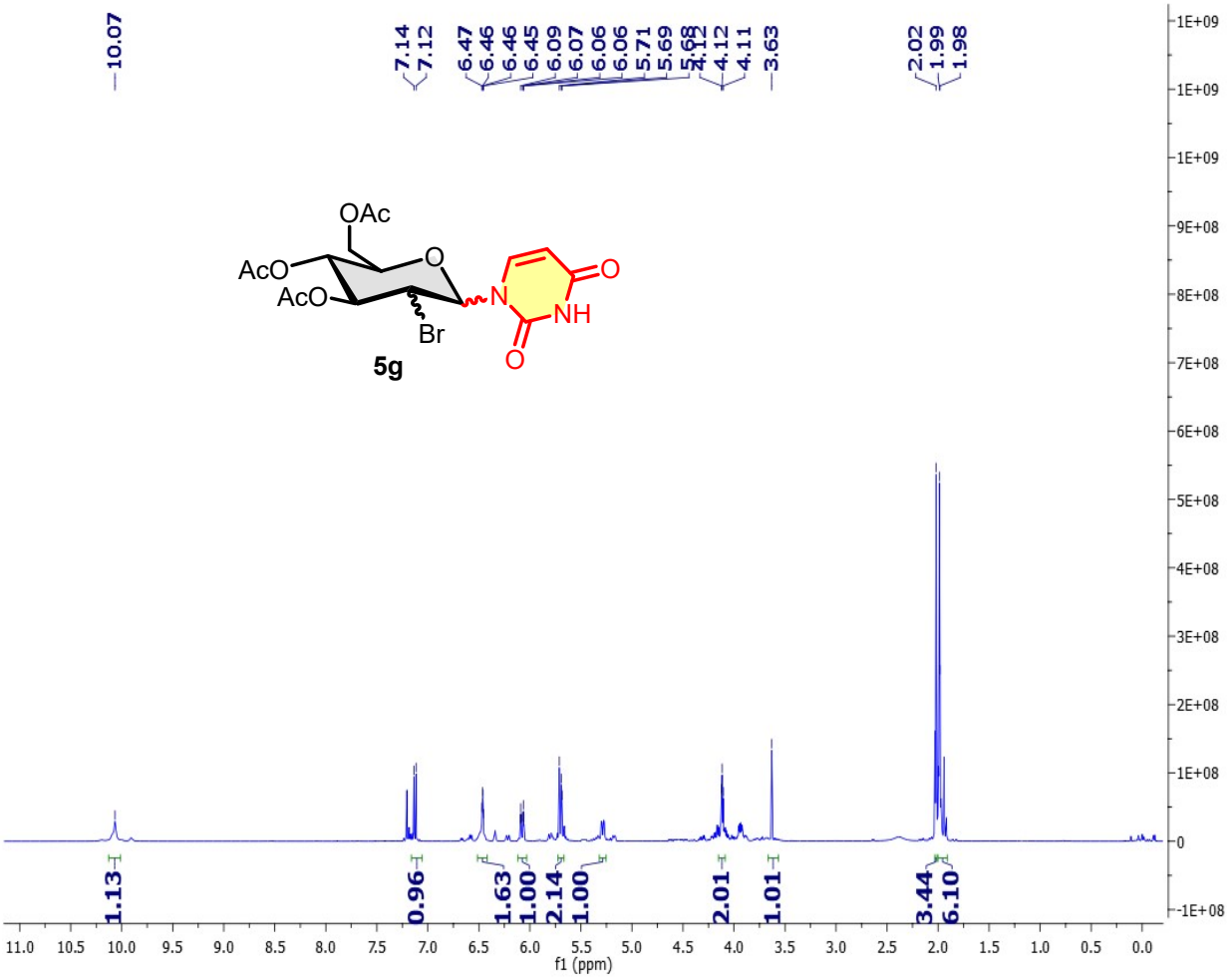
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5f



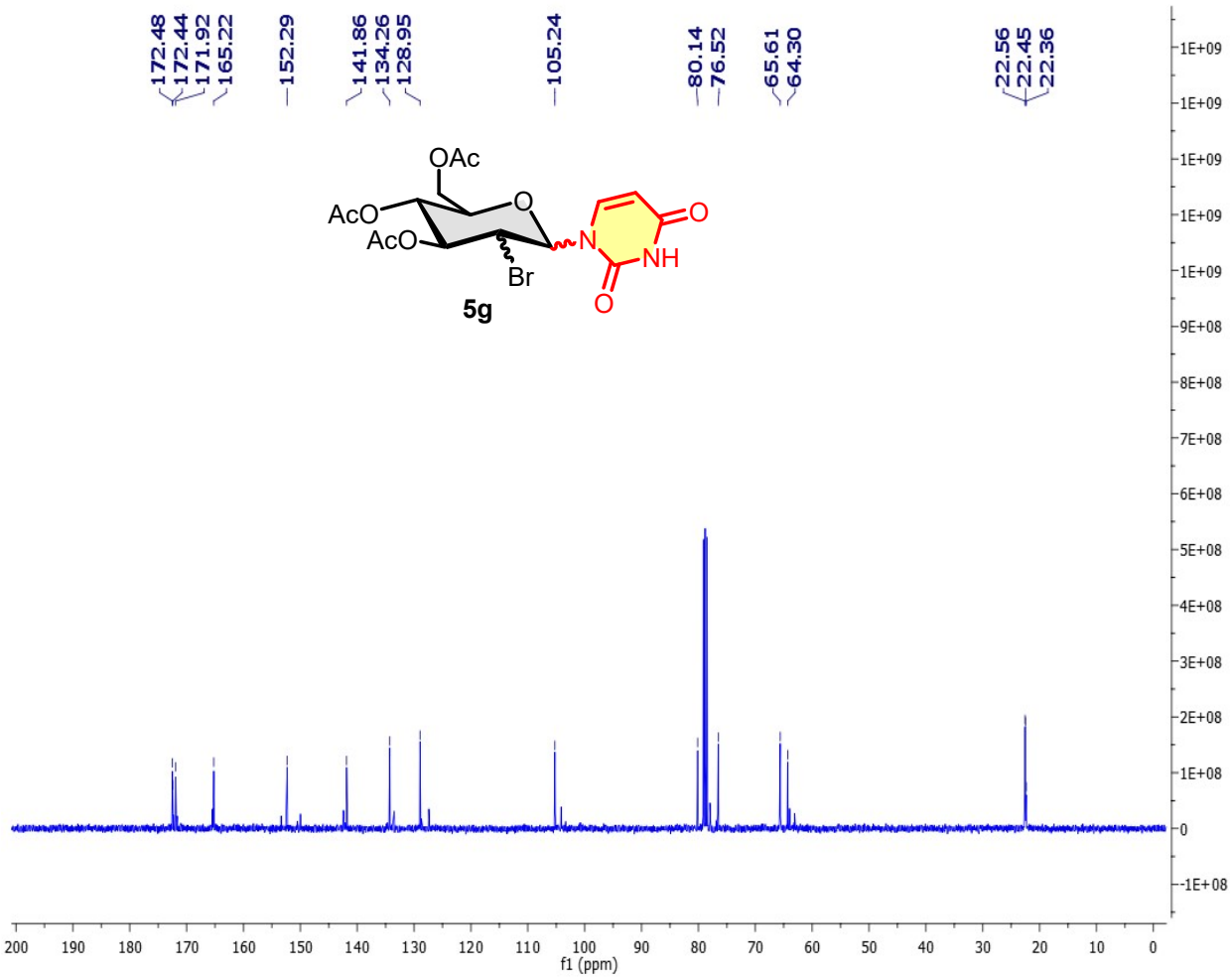
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5f



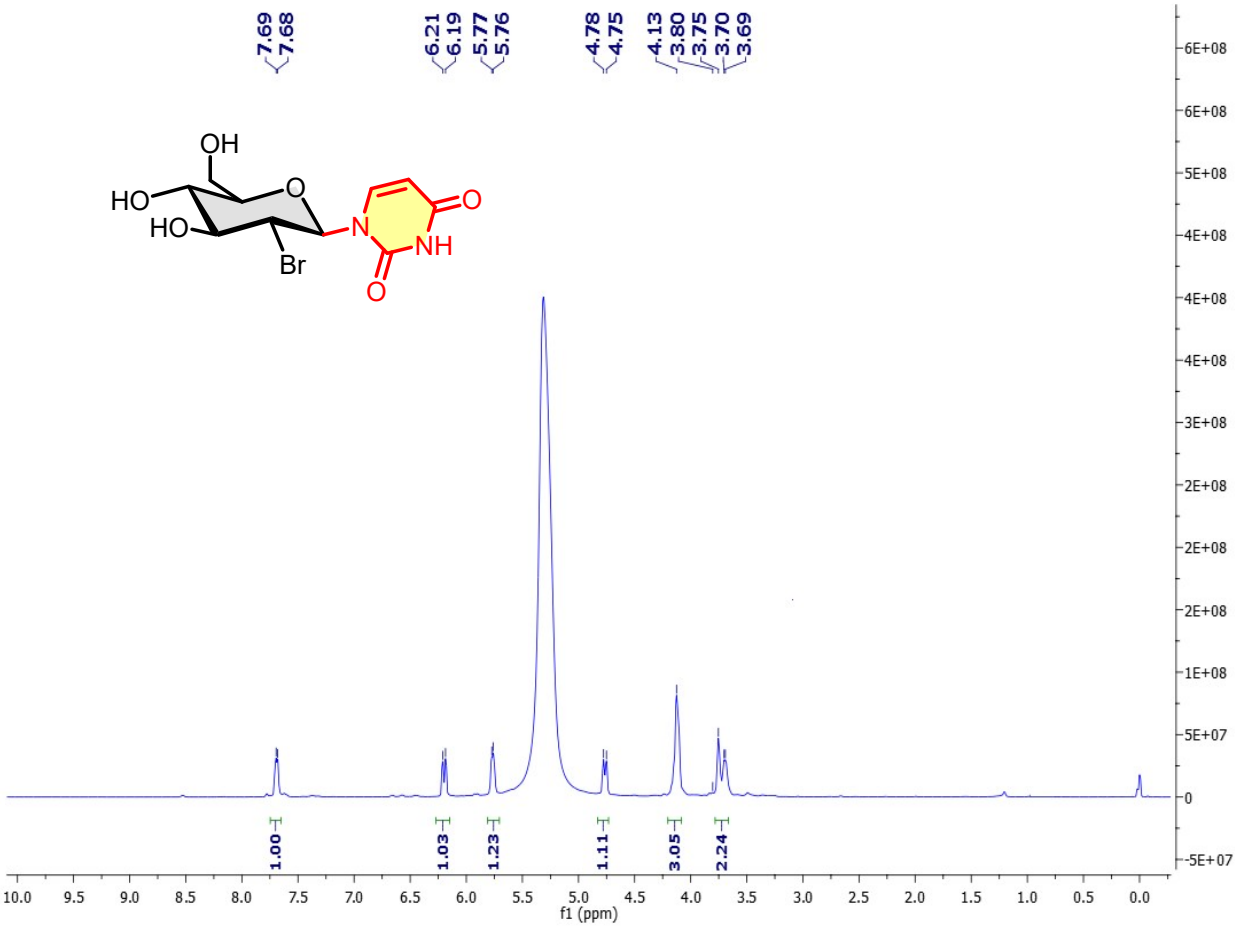
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5g



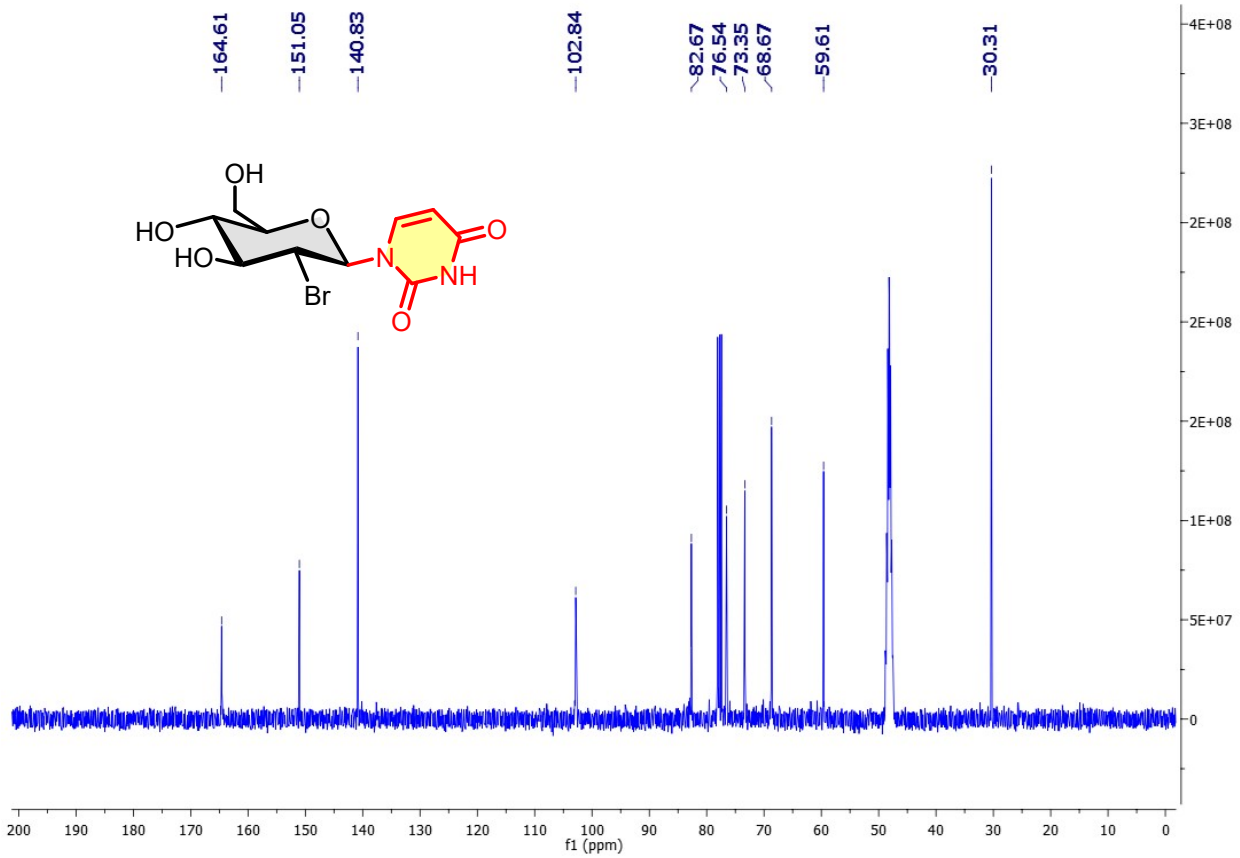
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5f



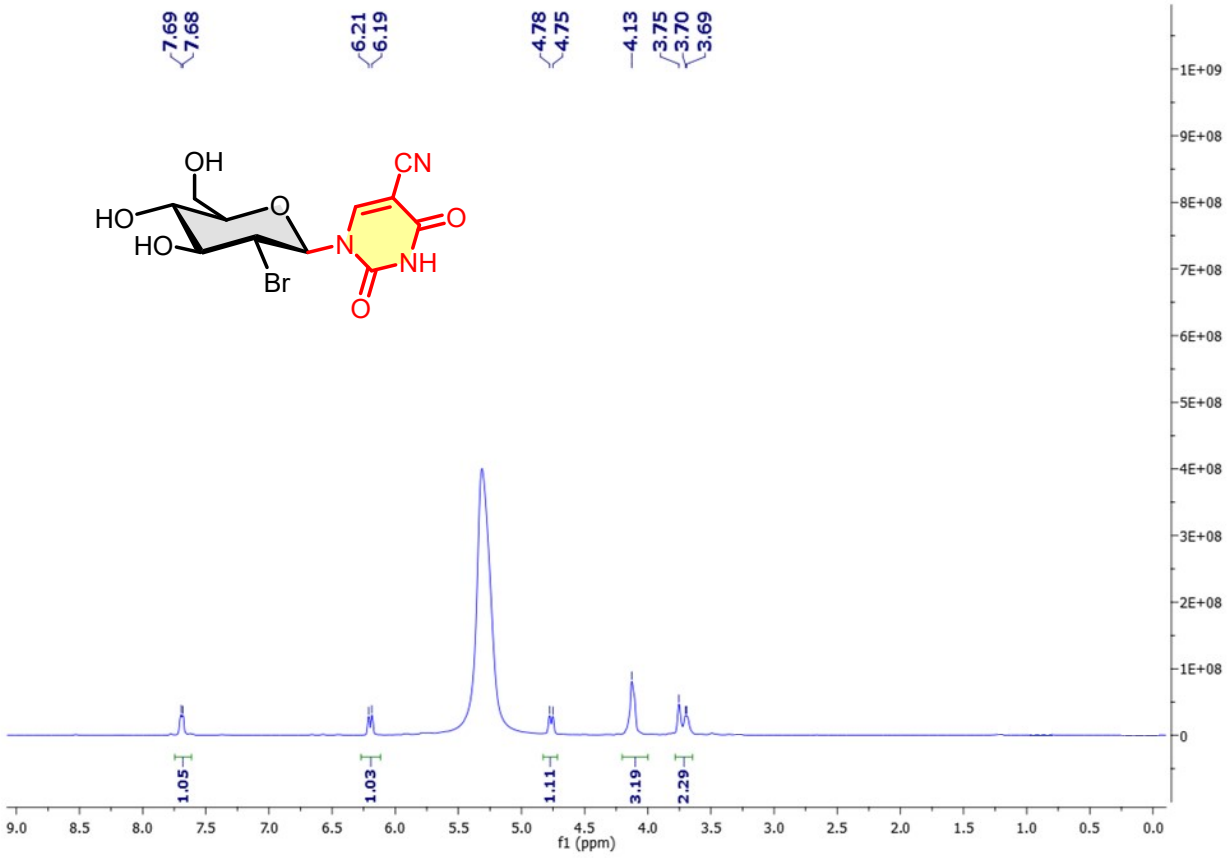
^{1}H NMR (400 MHz, MeOD) of compound 6a



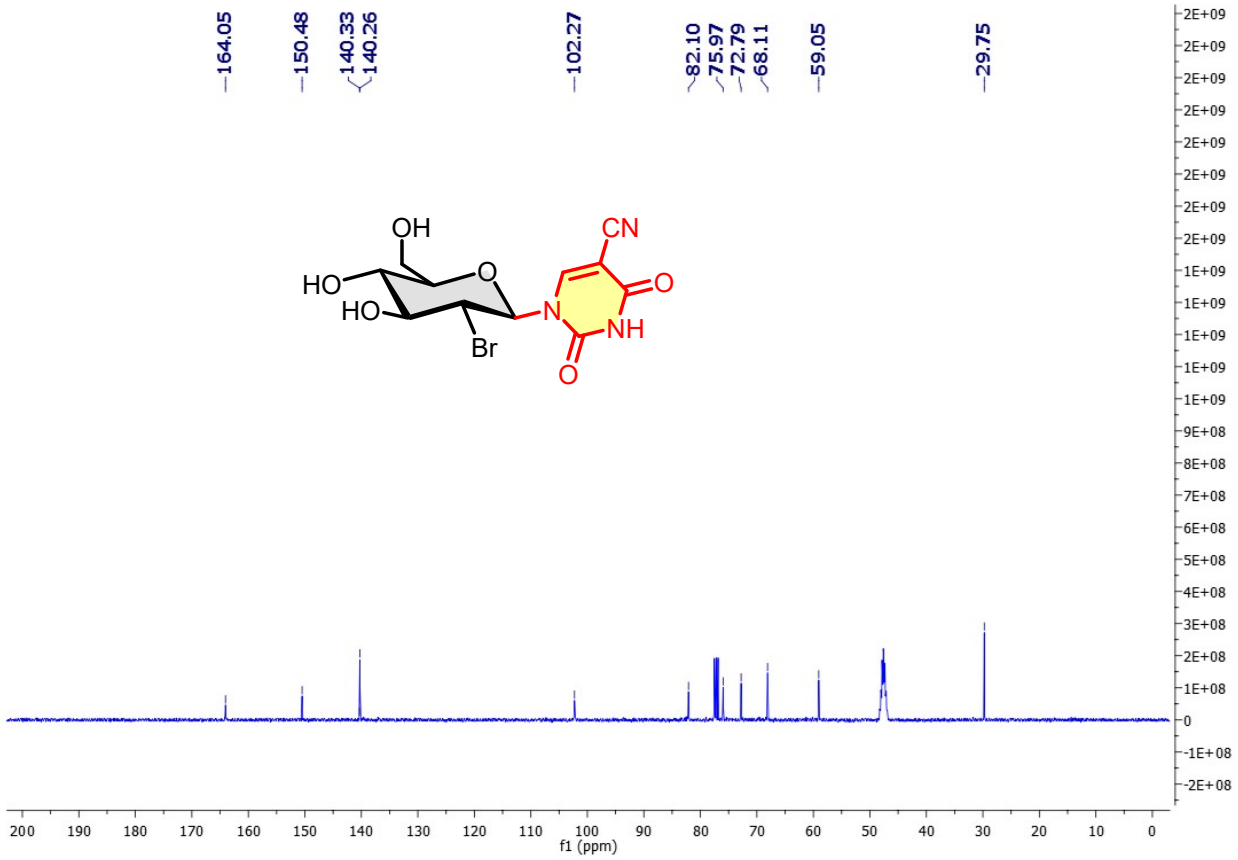
^{13}C {^{1}H} NMR (101 MHz, MeOD) of compound 6a



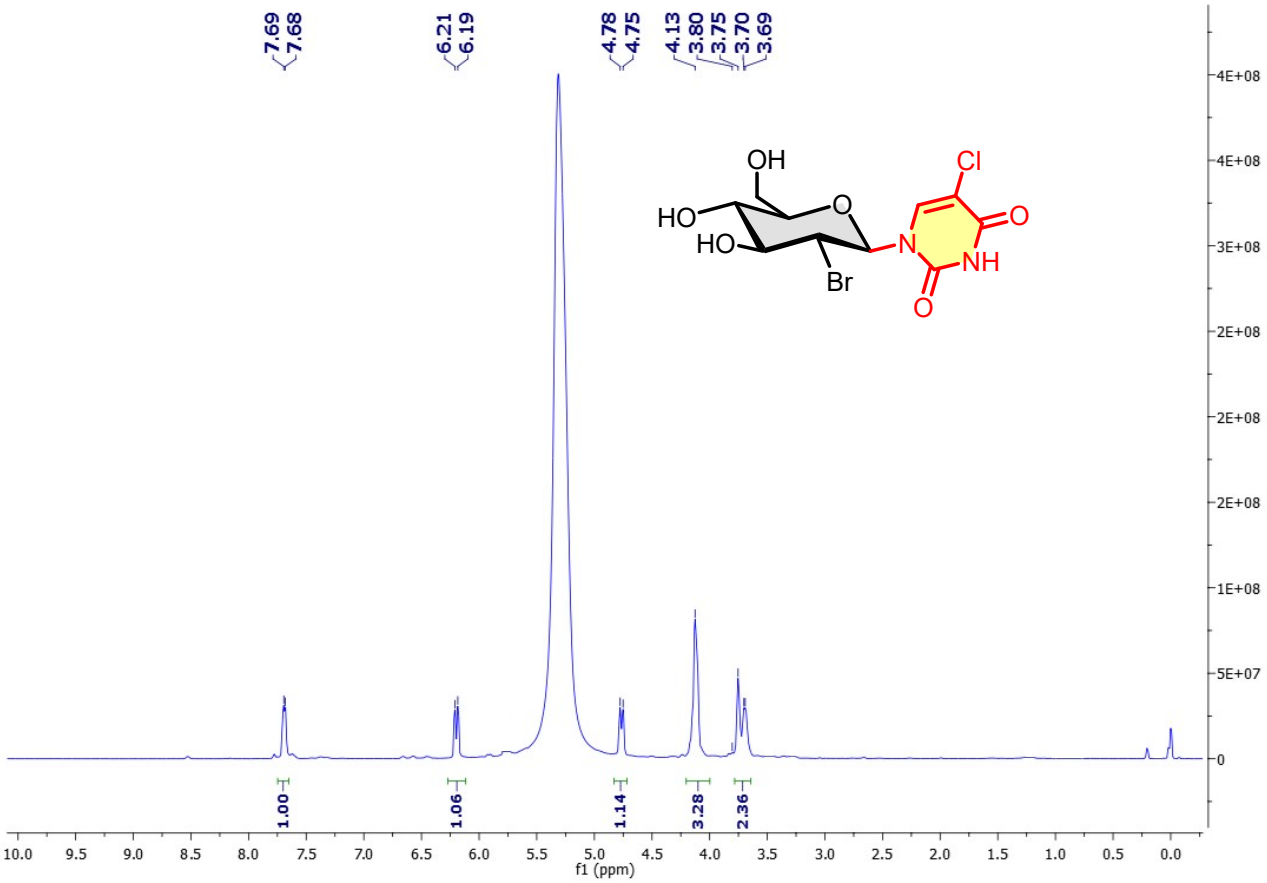
^{1}H NMR (400 MHz, MeOD) of compound 6b



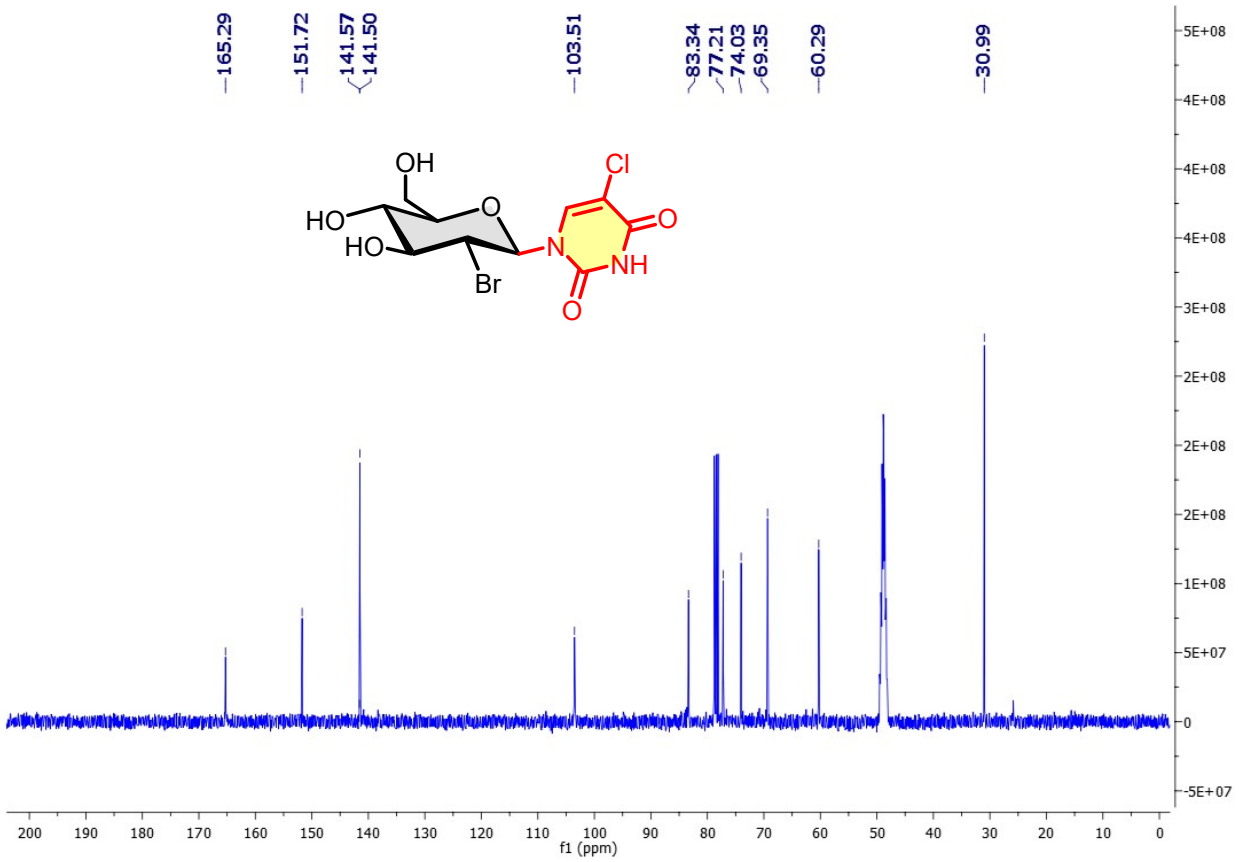
^{13}C {^{1}H} NMR (101 MHz, MeOD) of compound 6b



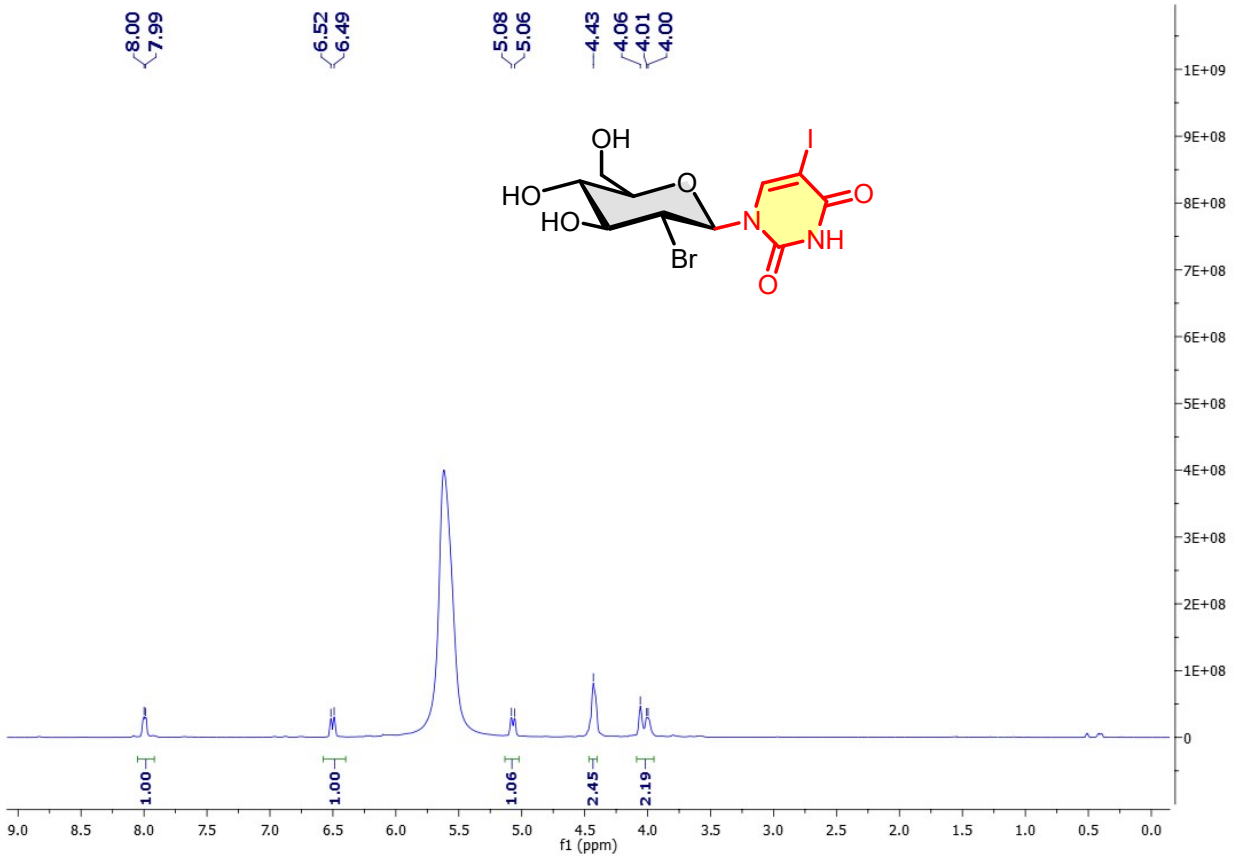
^{1}H NMR (400 MHz, MeOD) of compound 6c



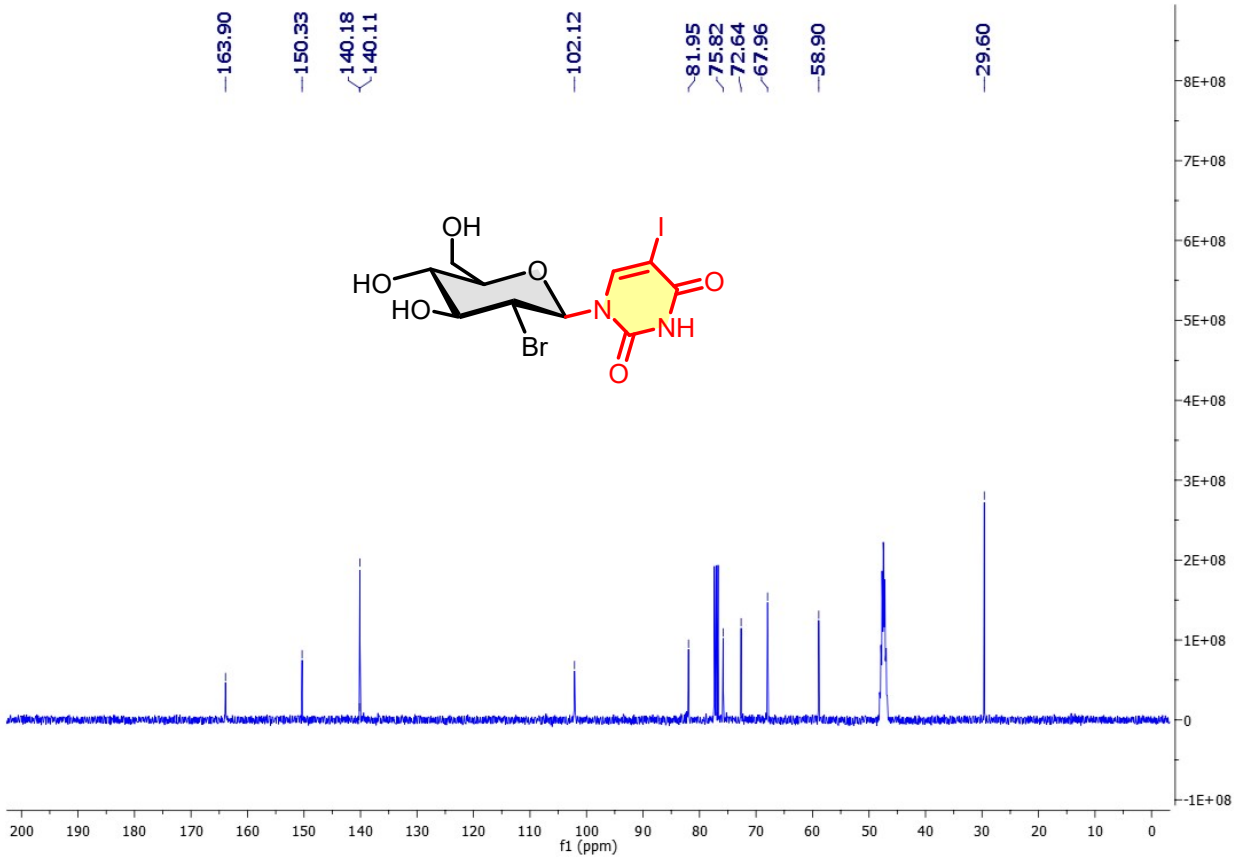
^{13}C {^{1}H} NMR (101 MHz, MeOD) of compound 6c



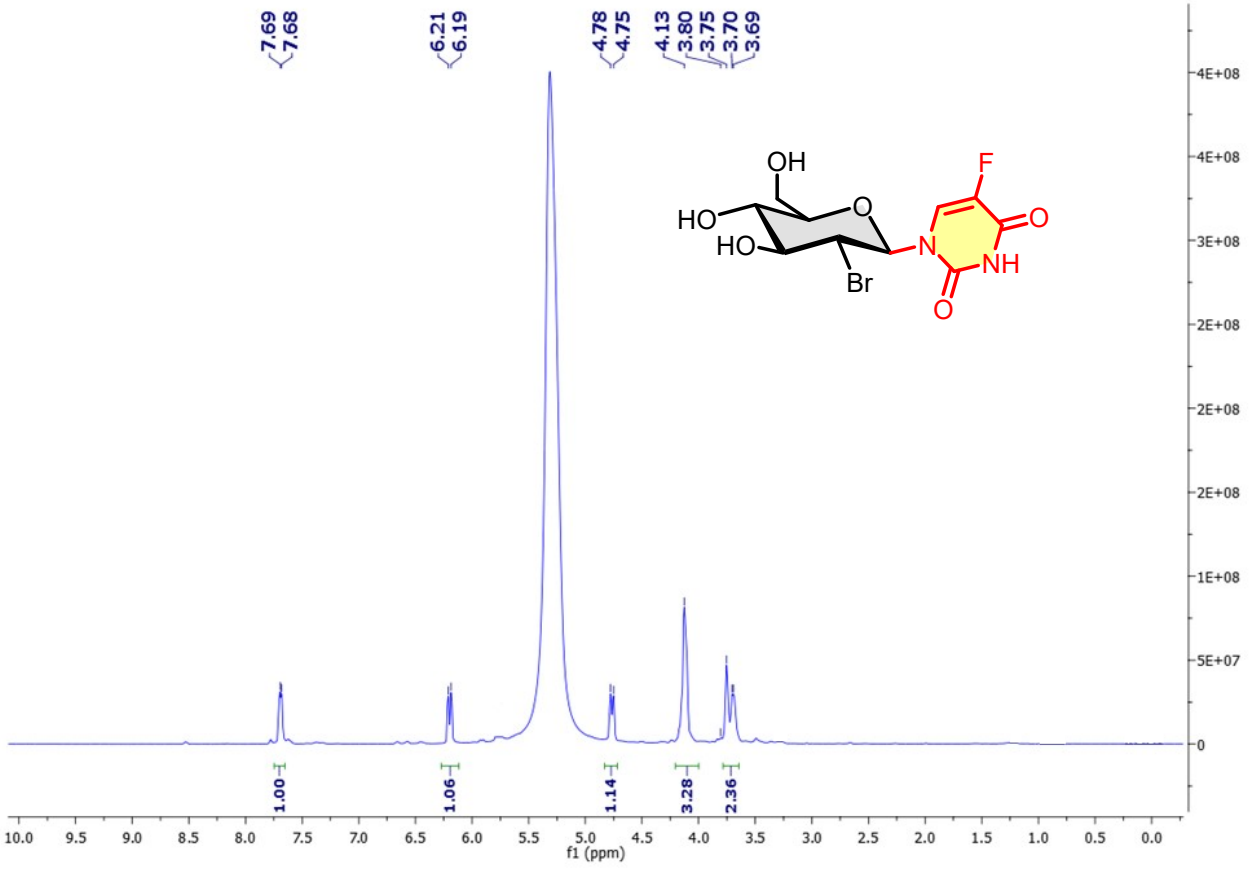
^{1}H NMR (400 MHz, MeOD) of compound 6d



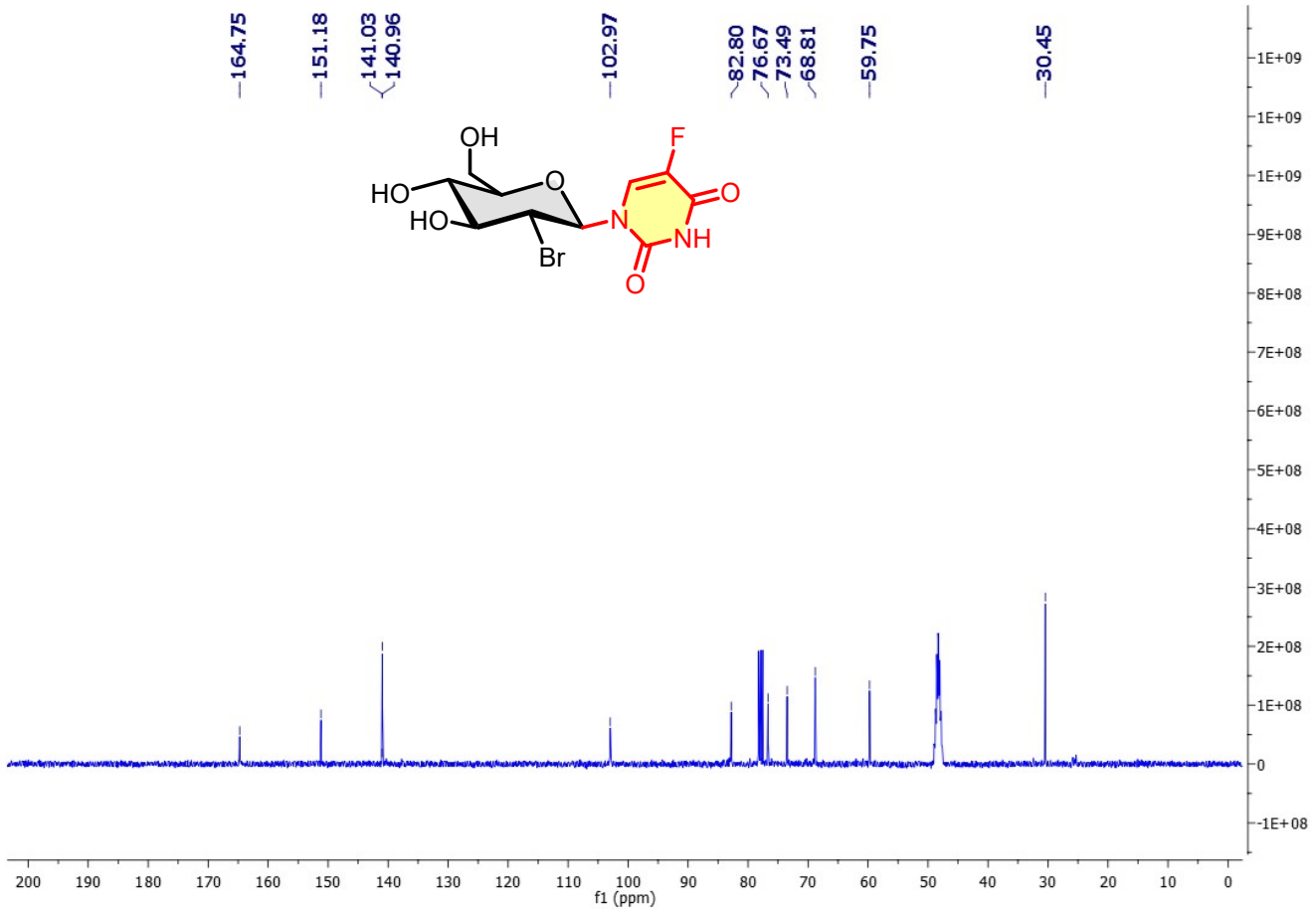
^{13}C {^{1}H} NMR (101 MHz, MeOD) of compound 6d



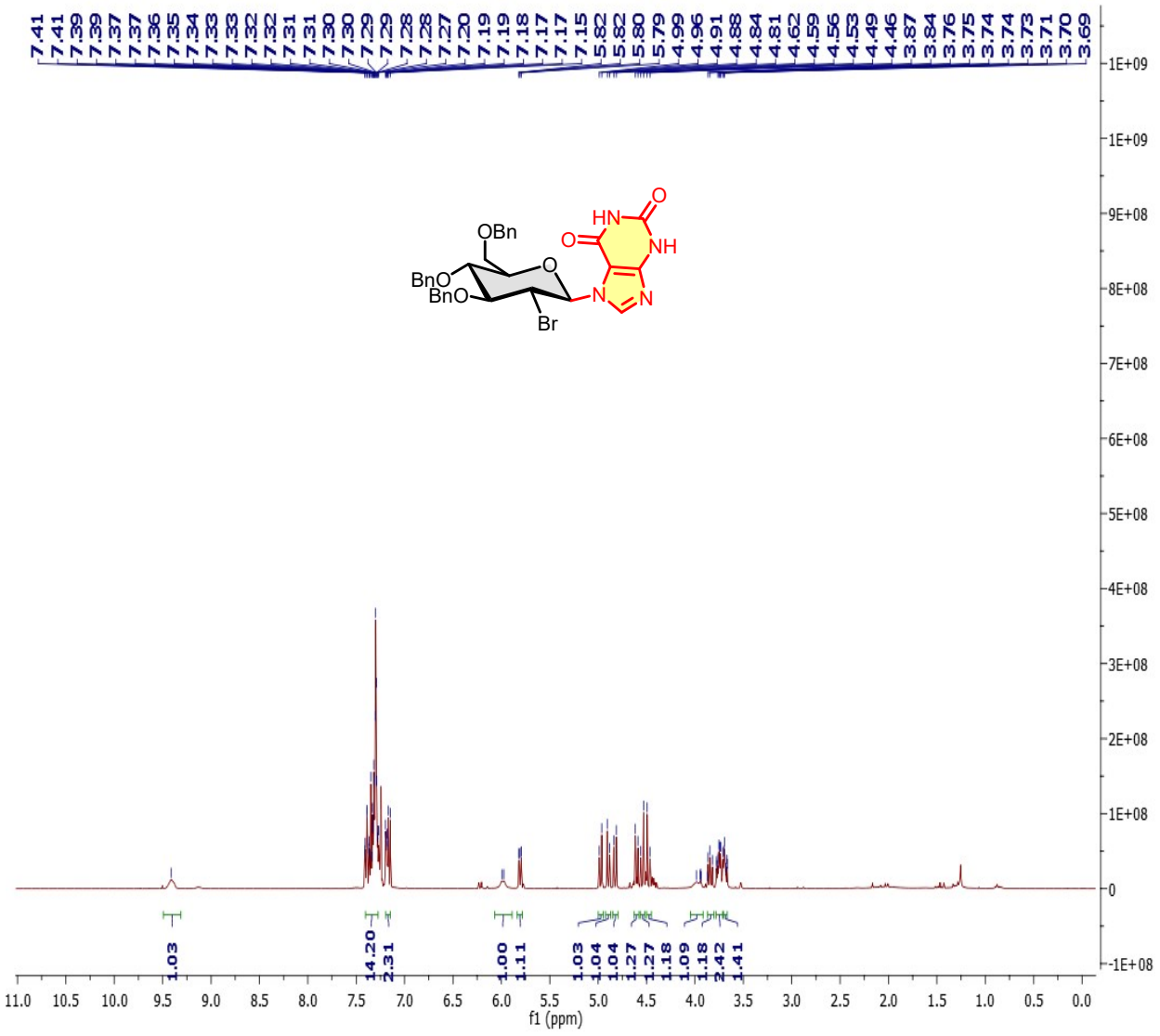
^{1}H NMR (400 MHz, MeOD) of compound 6e



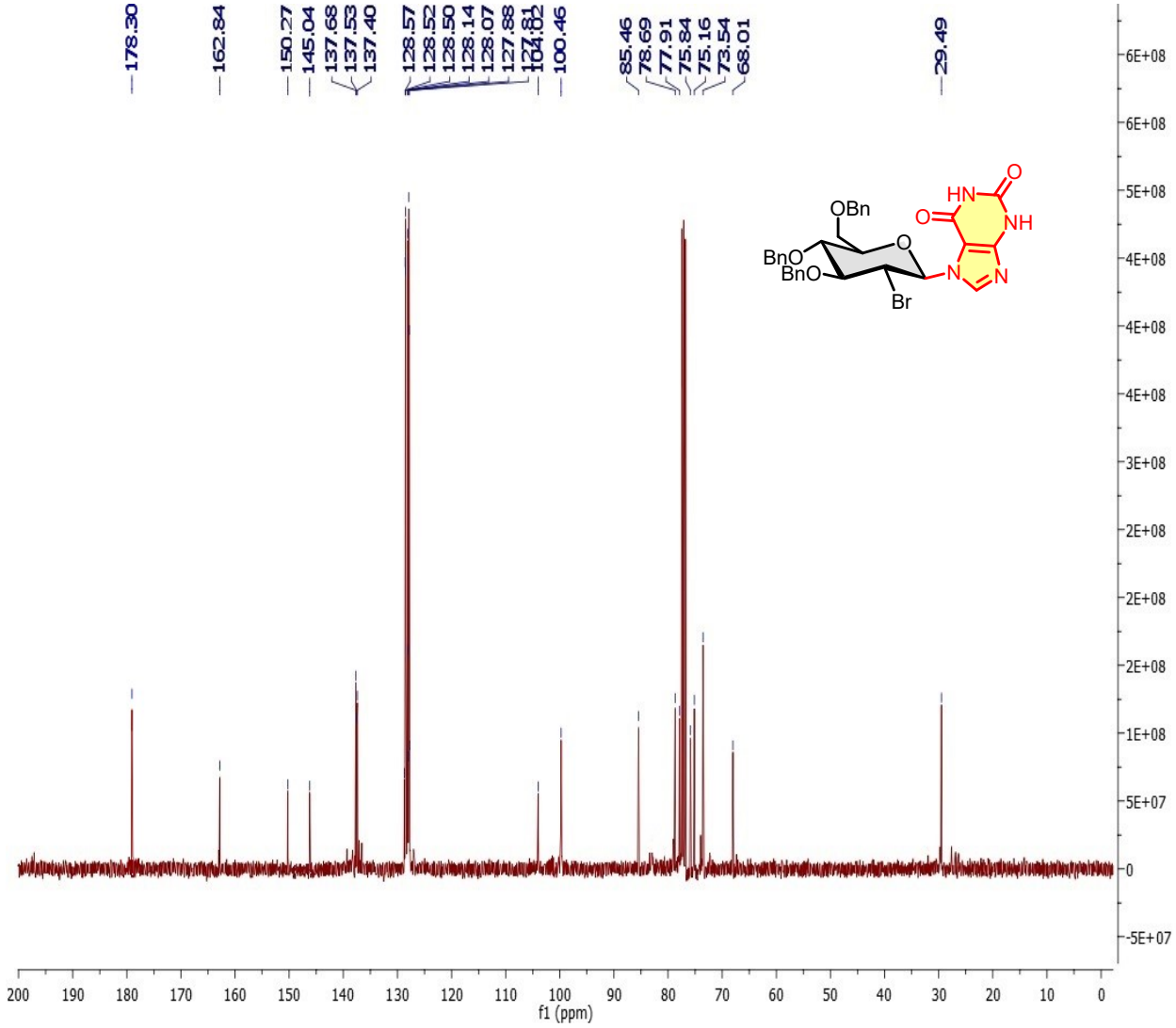
^{13}C {^{1}H} NMR (101 MHz, MeOD) of compound 6e



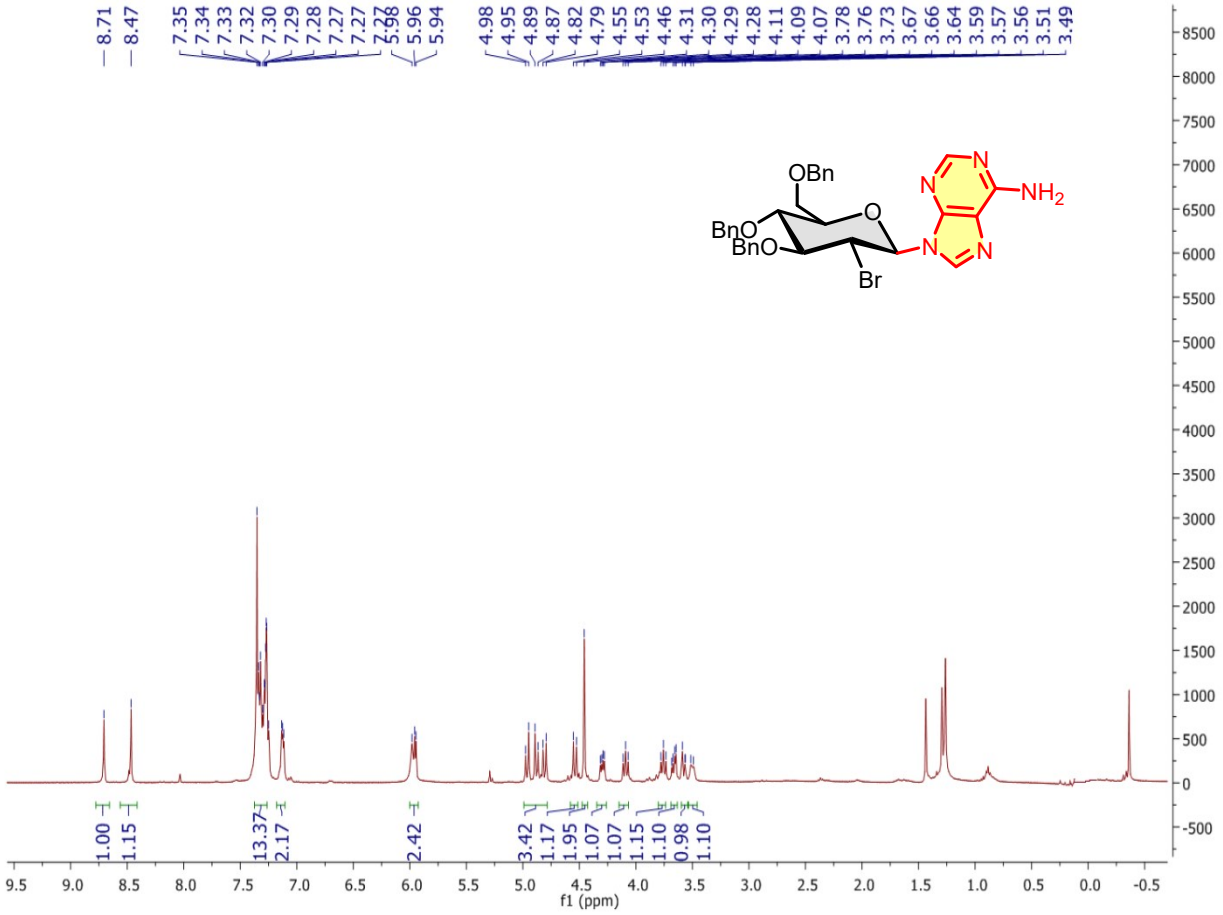
^{1}H NMR (400 MHz, $CDCl_3$) of compound 7a



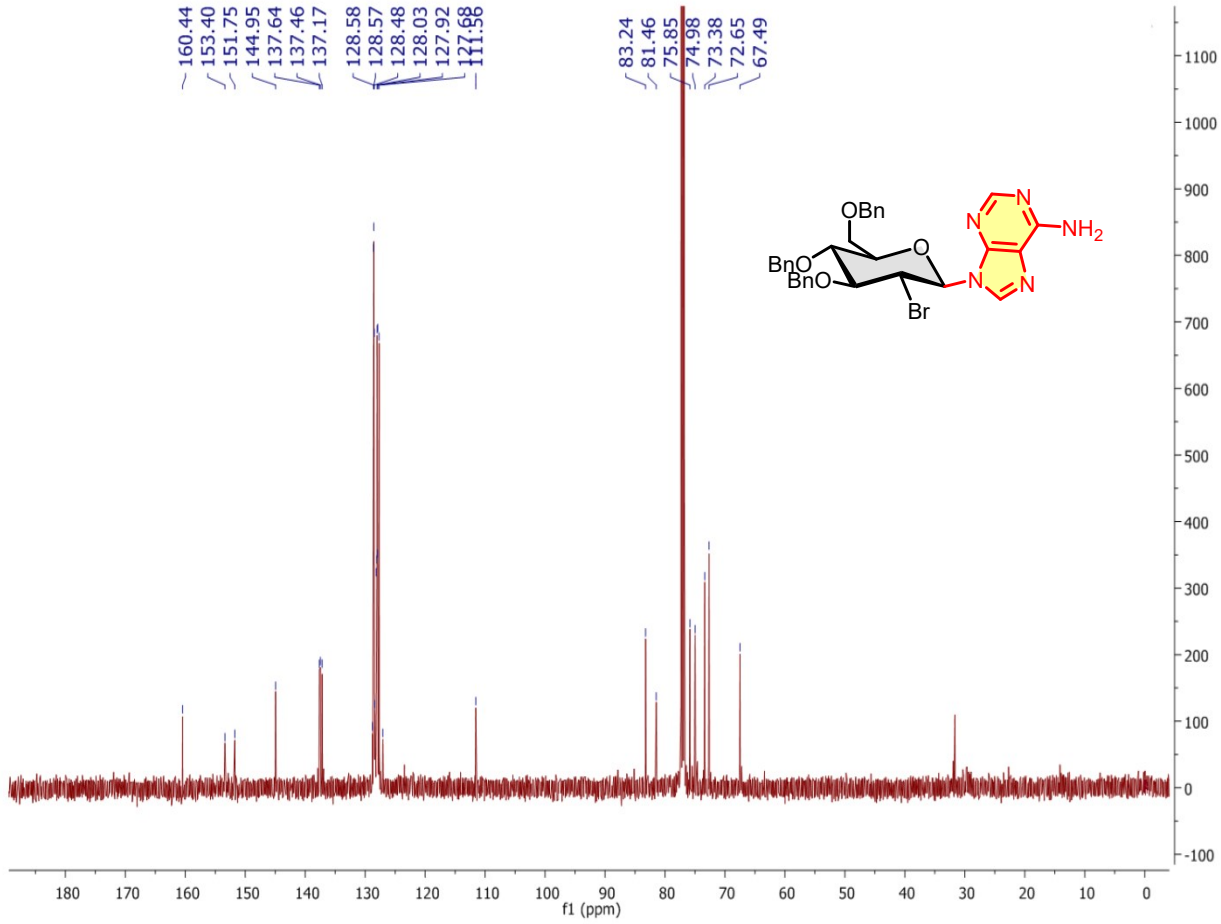
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 7a



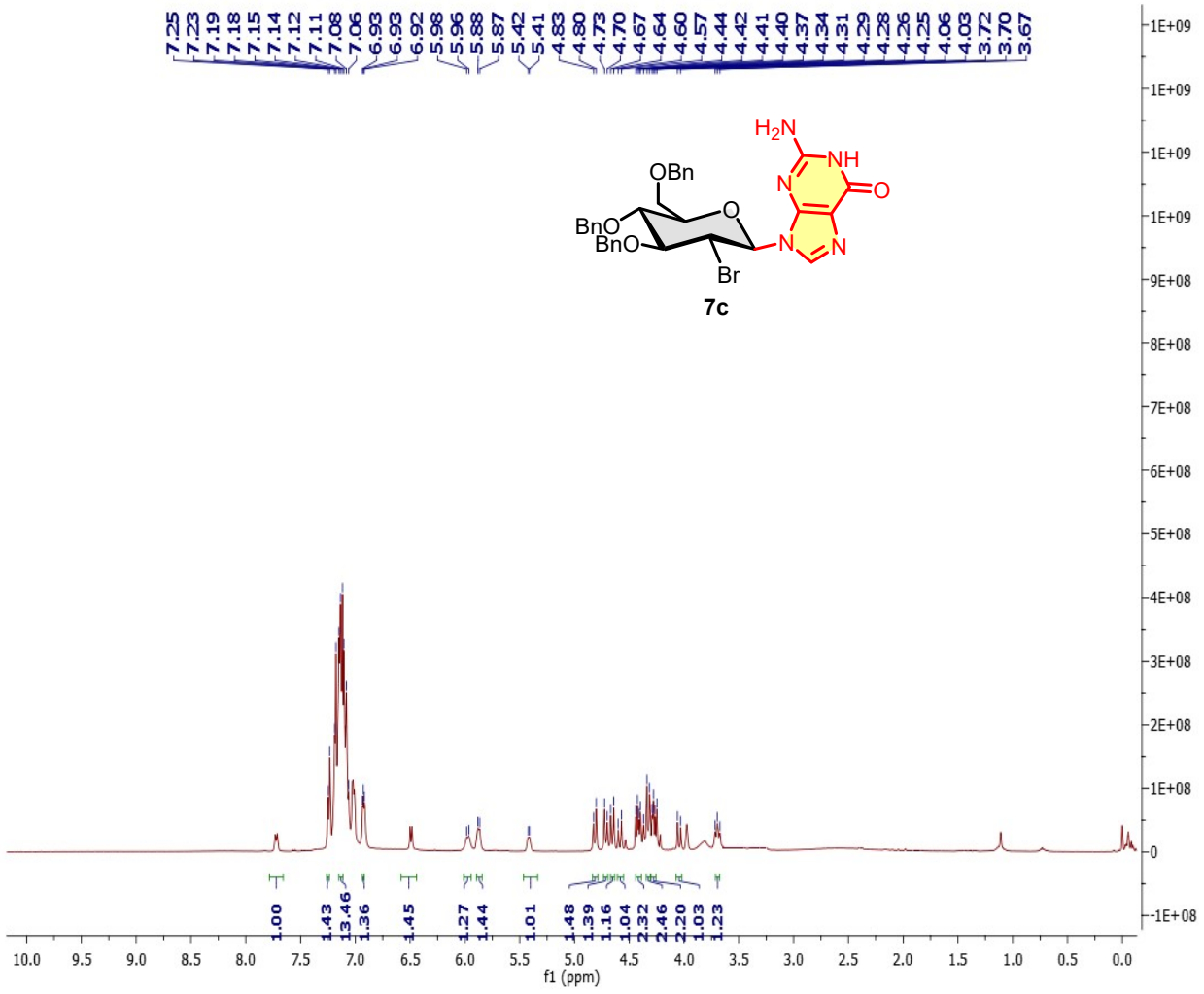
^{1}H NMR (400 MHz, $CDCl_3$) of compound 7b



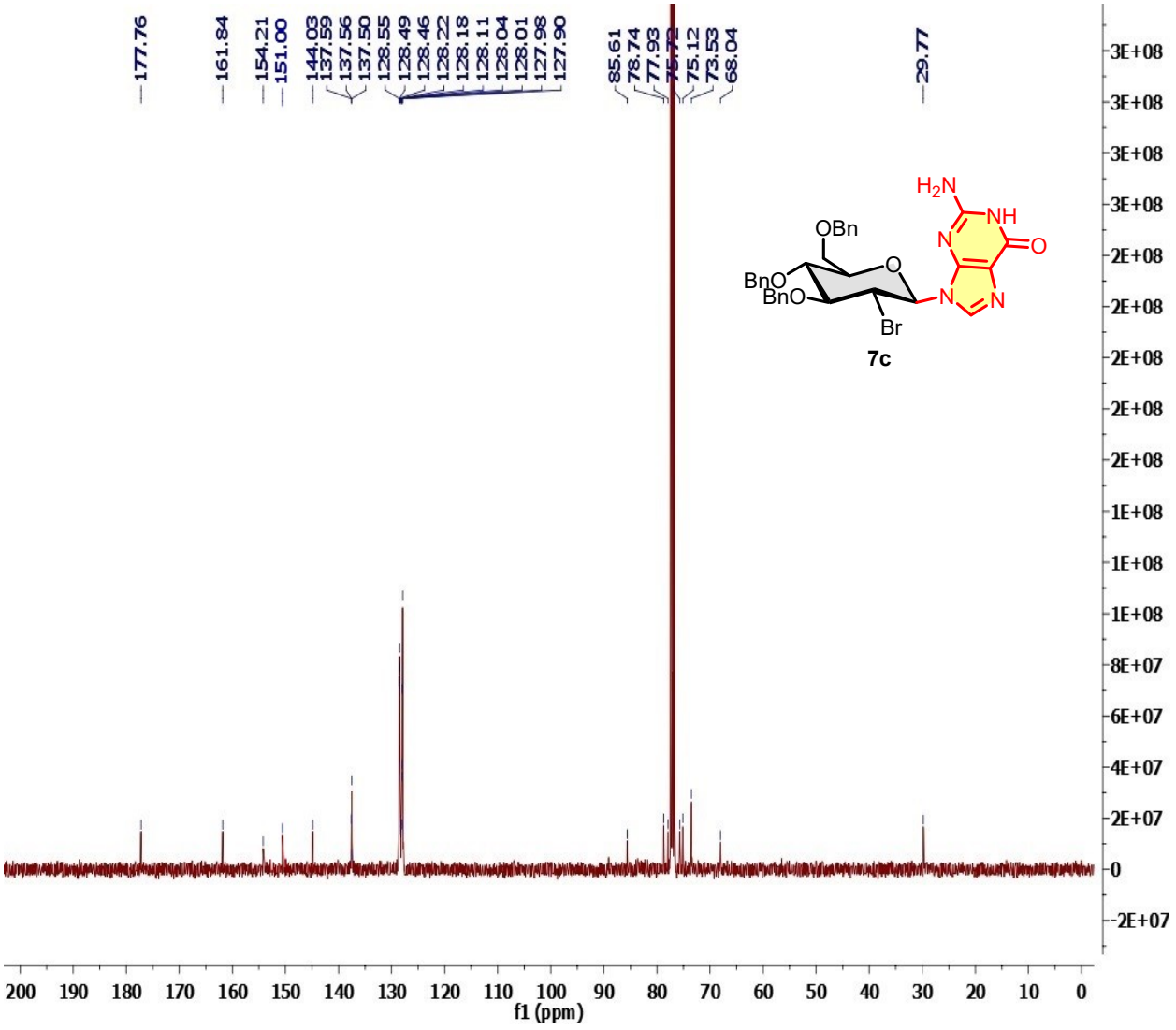
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 7b



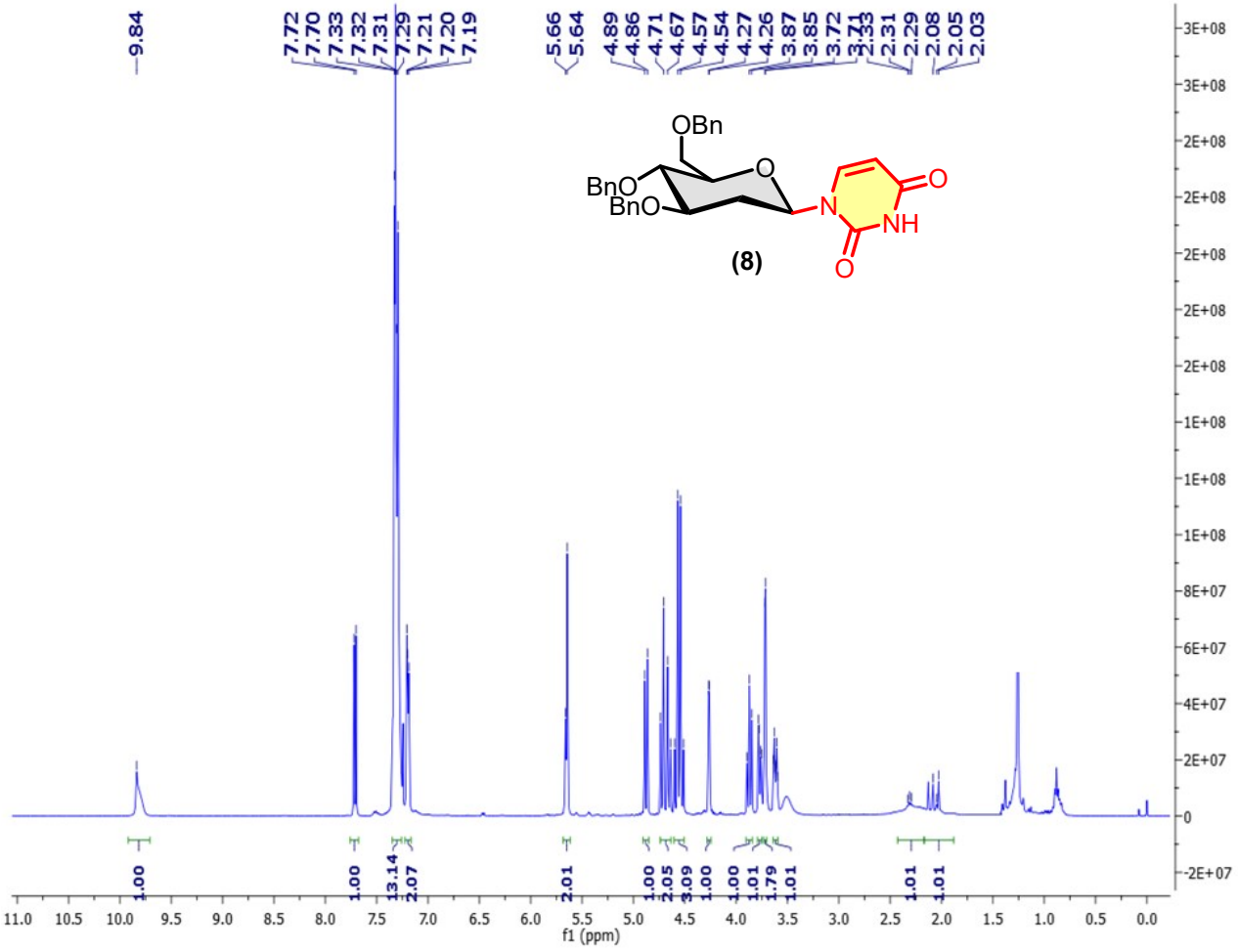
^{1}H NMR (400 MHz, $CDCl_3$) of compound 7c



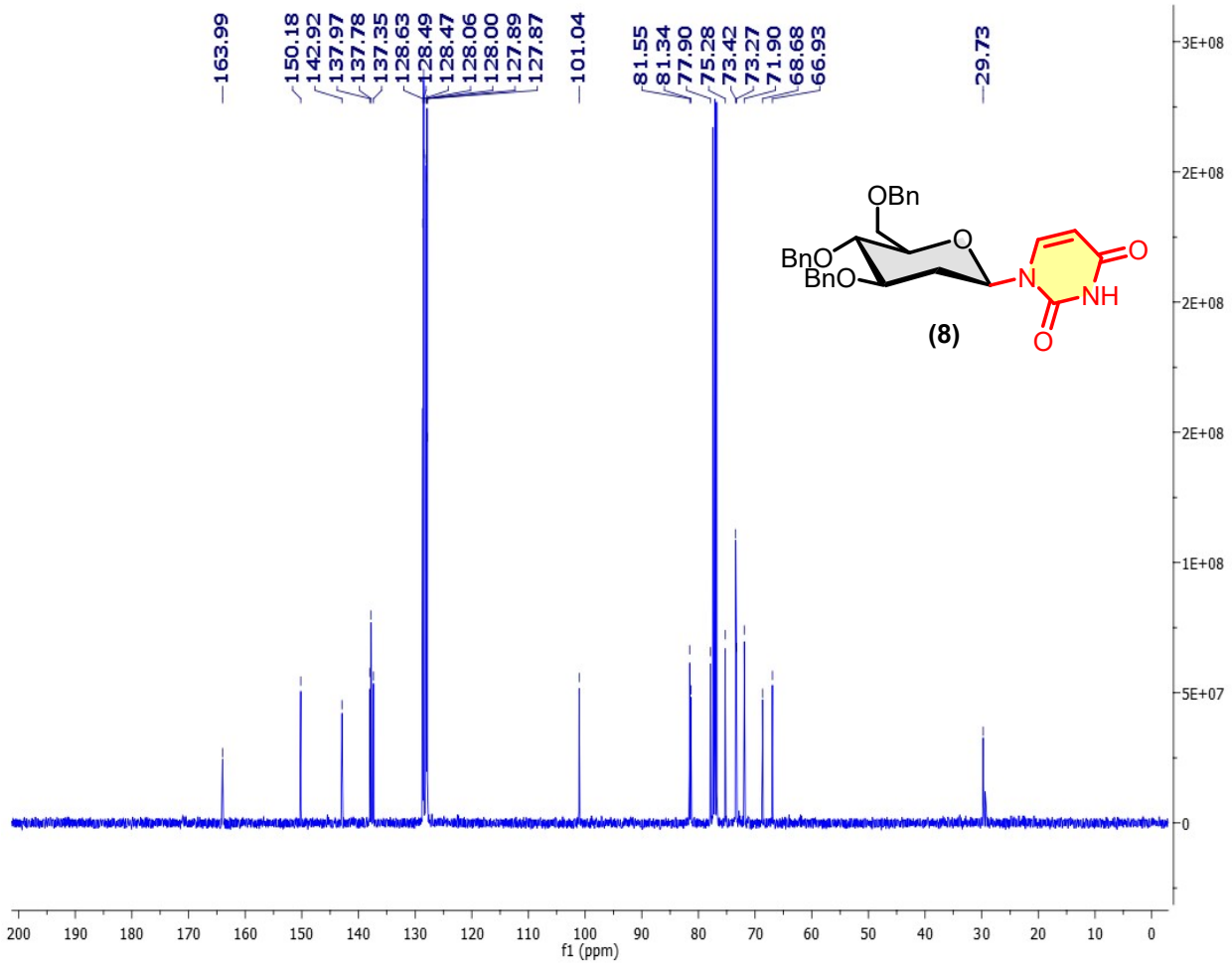
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 7c



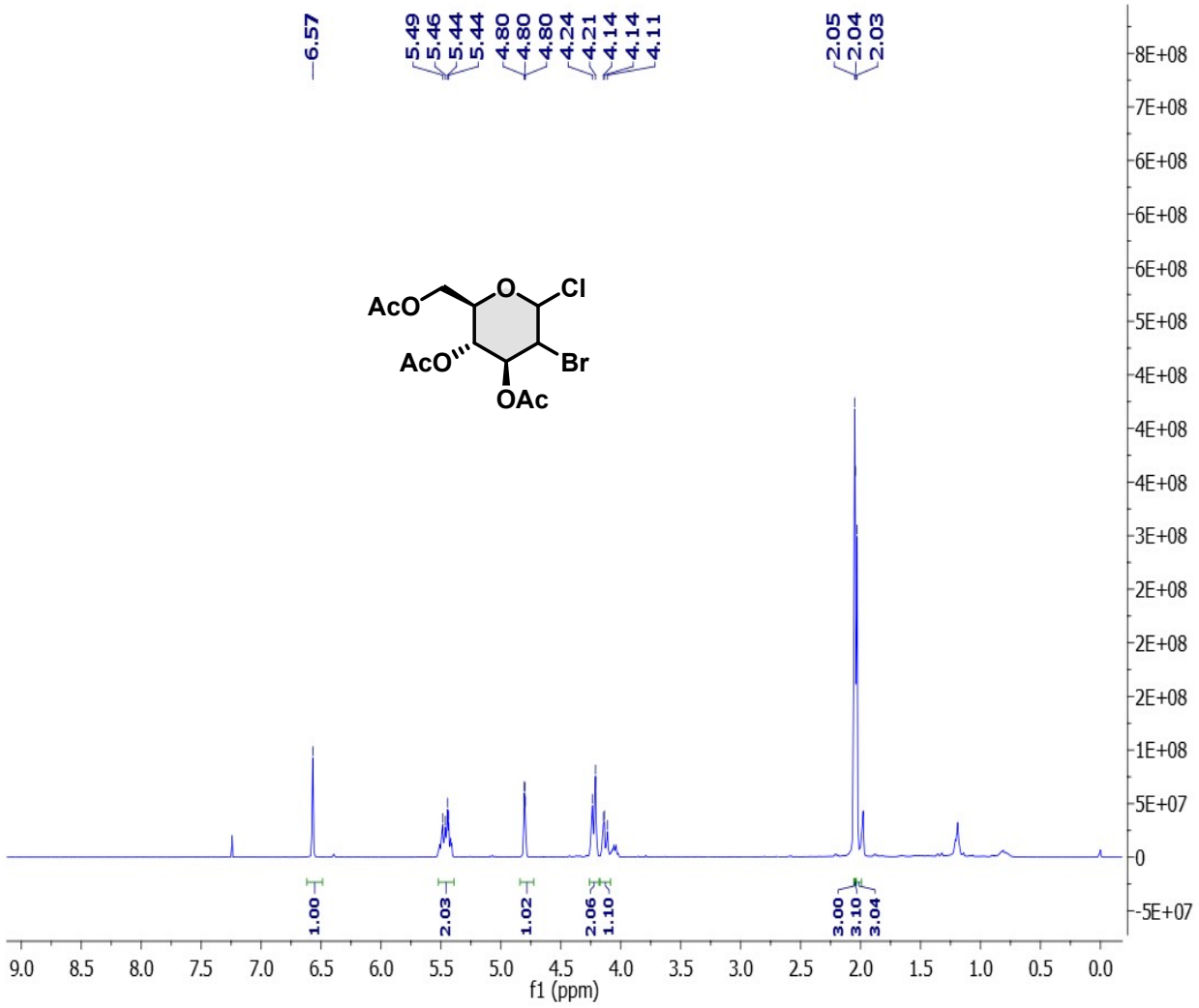
^{1}H NMR (400 MHz, $CDCl_3$) of compound 8



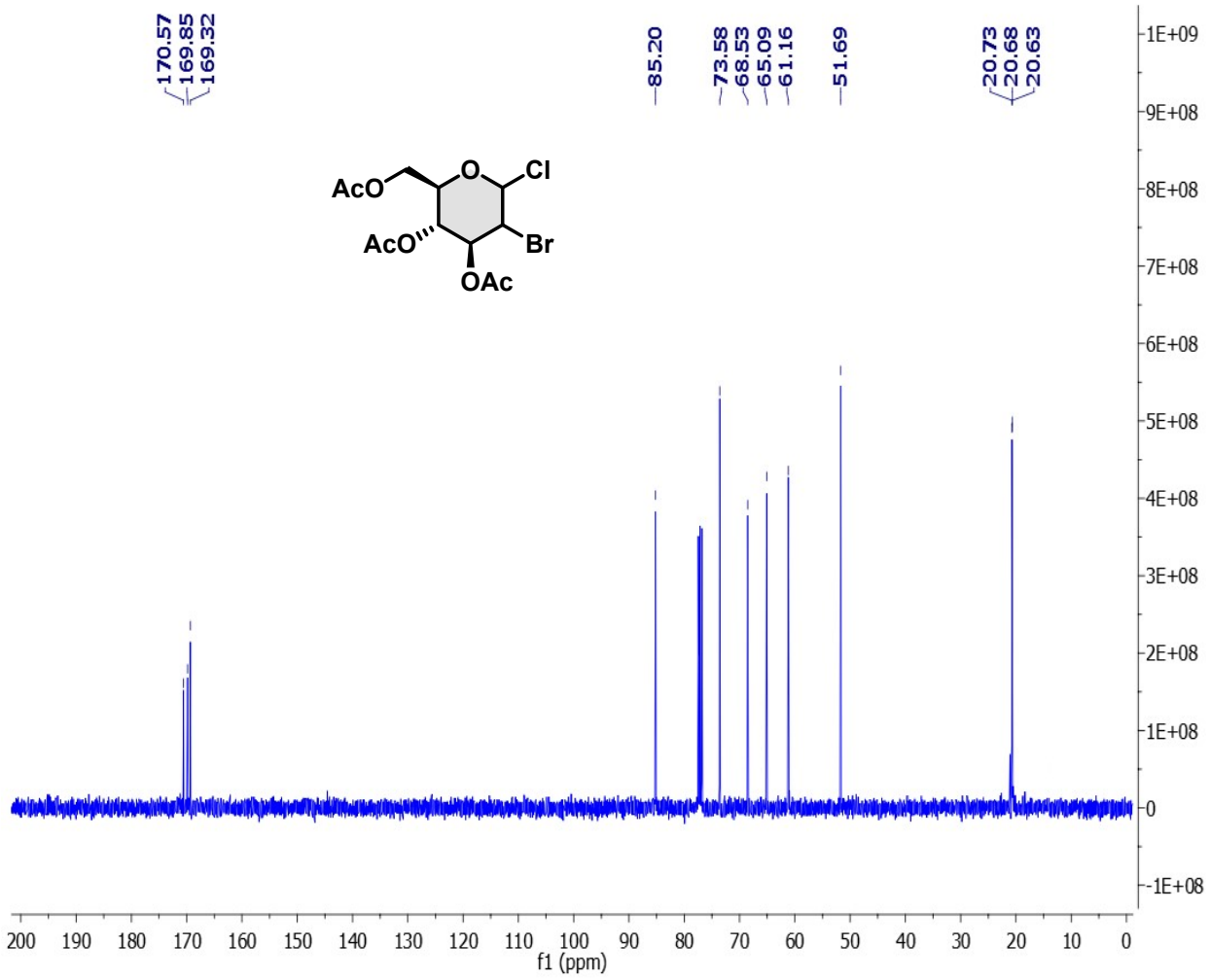
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 8



^{1}H NMR (400 MHz, $CDCl_3$) of compound 9

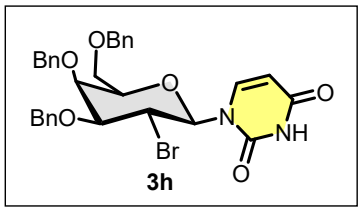


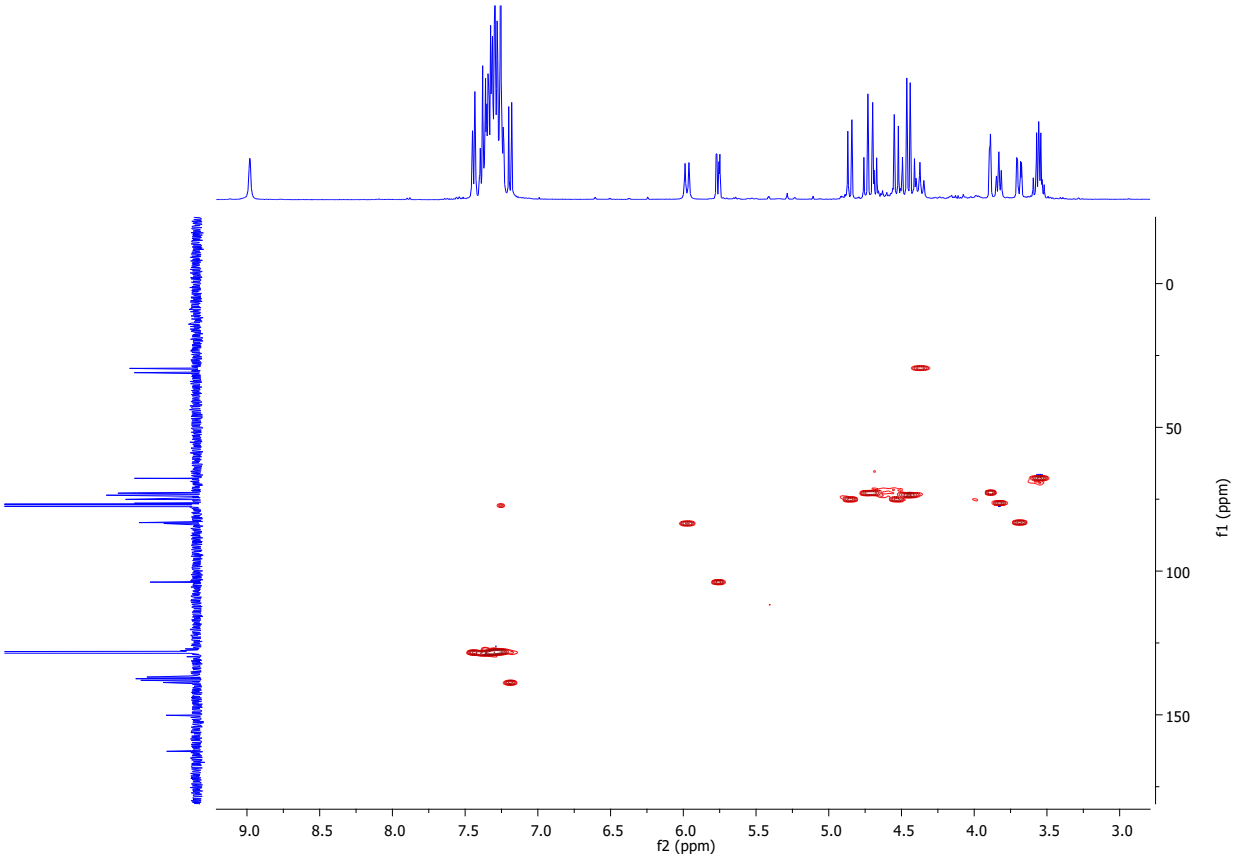
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 9



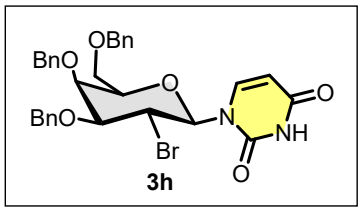
5. 2D spectrum ($CDCl_3$) of 3h

HSQC Spectrum of **3h**

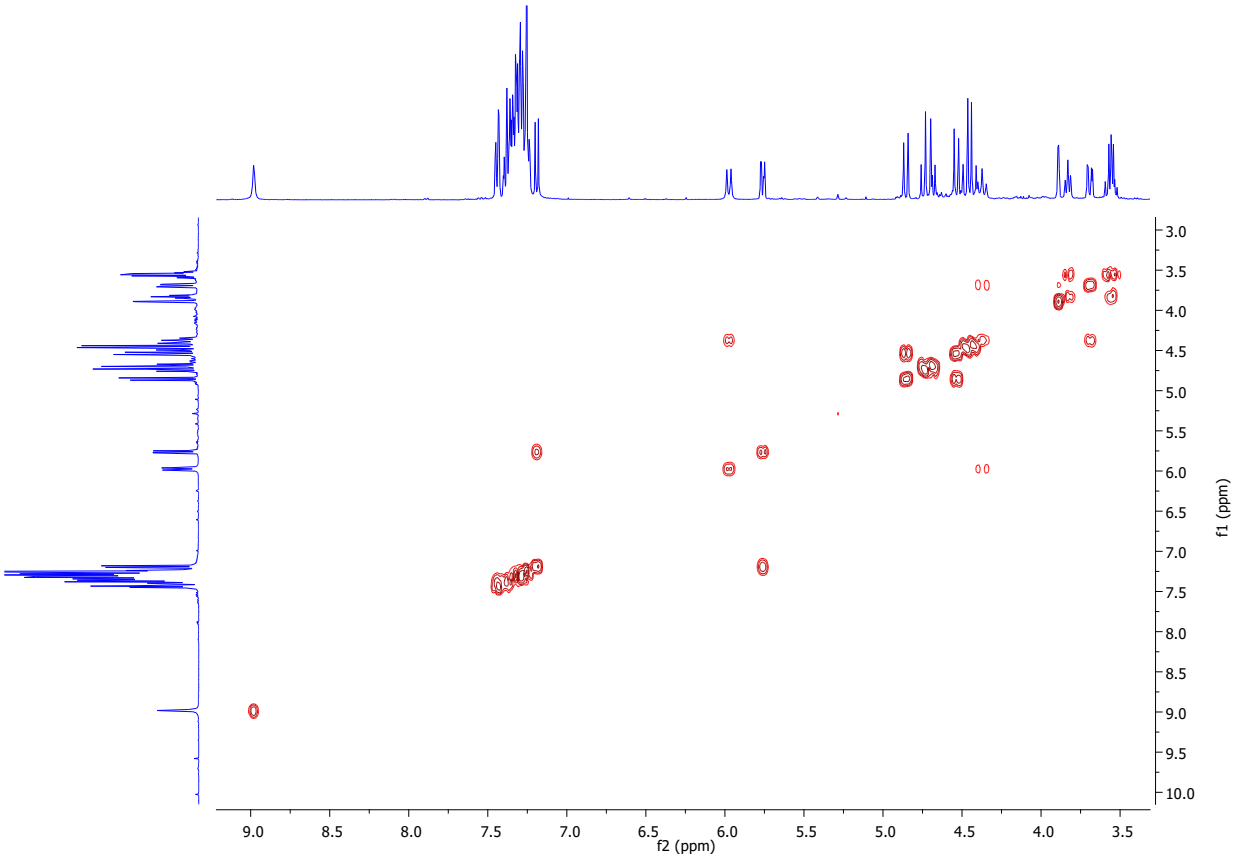




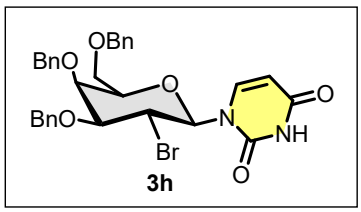
COSY Spectrum of **3h**

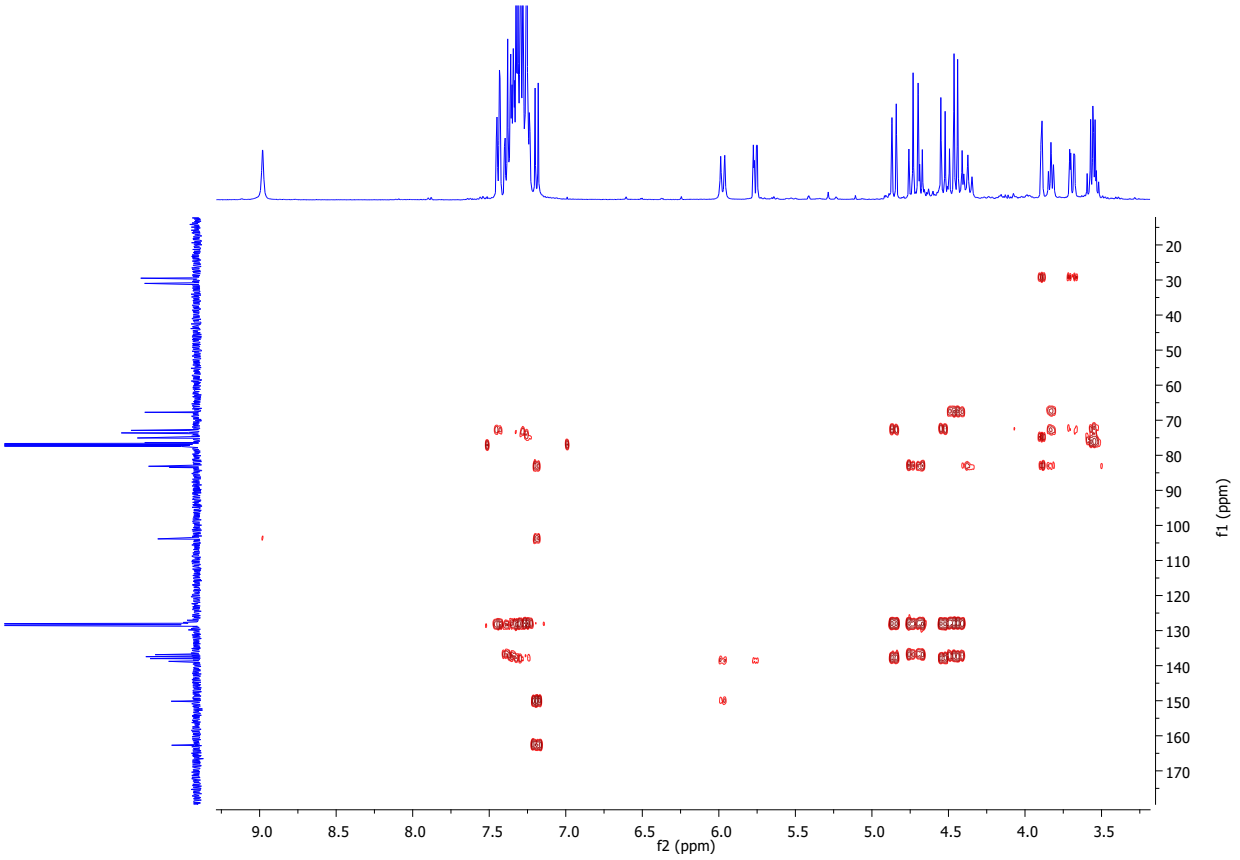


3h

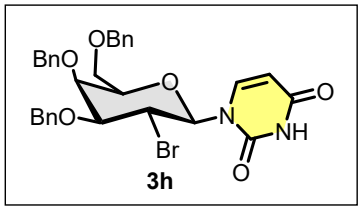


HMBC Spectrum of **3h**

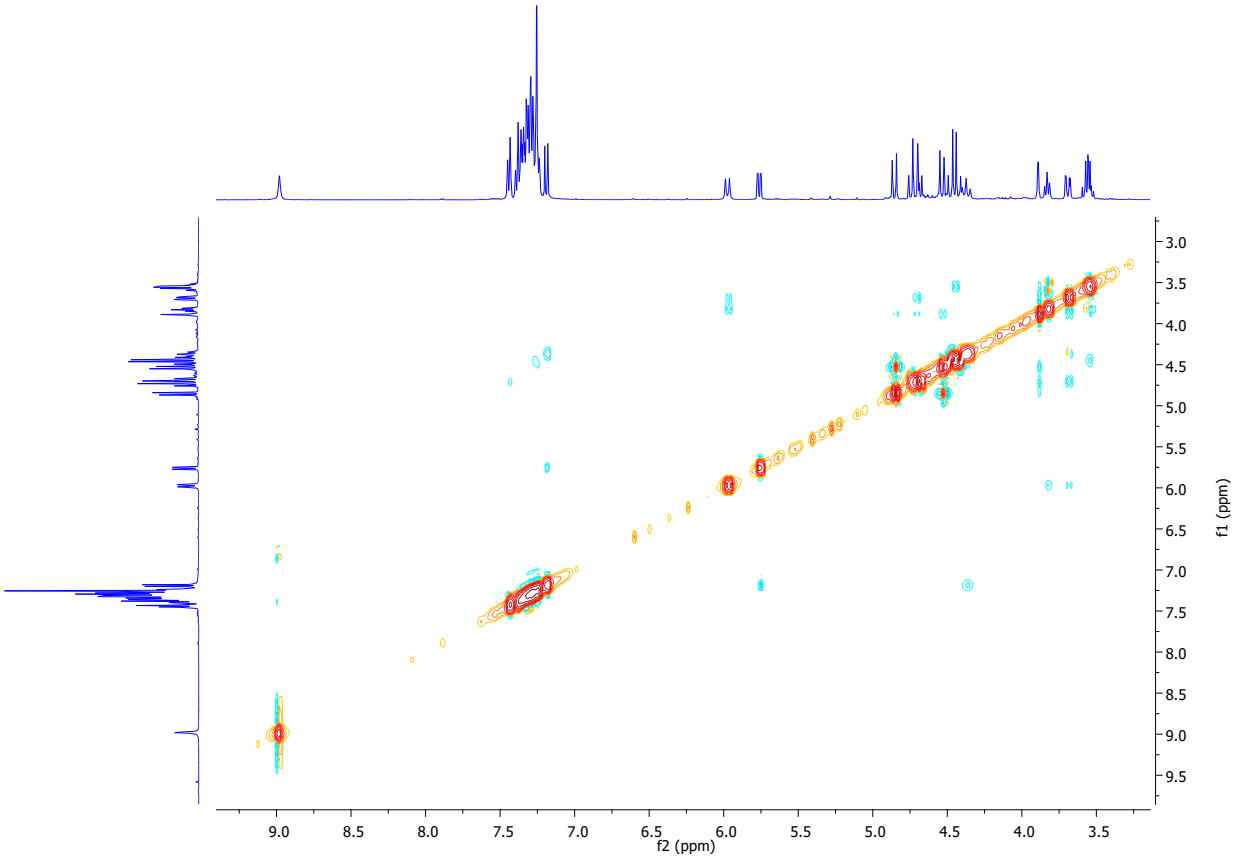




NOESY Spectrum of **3h**

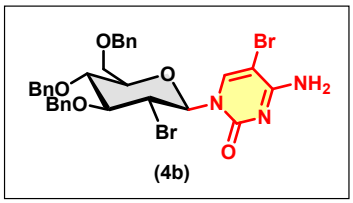


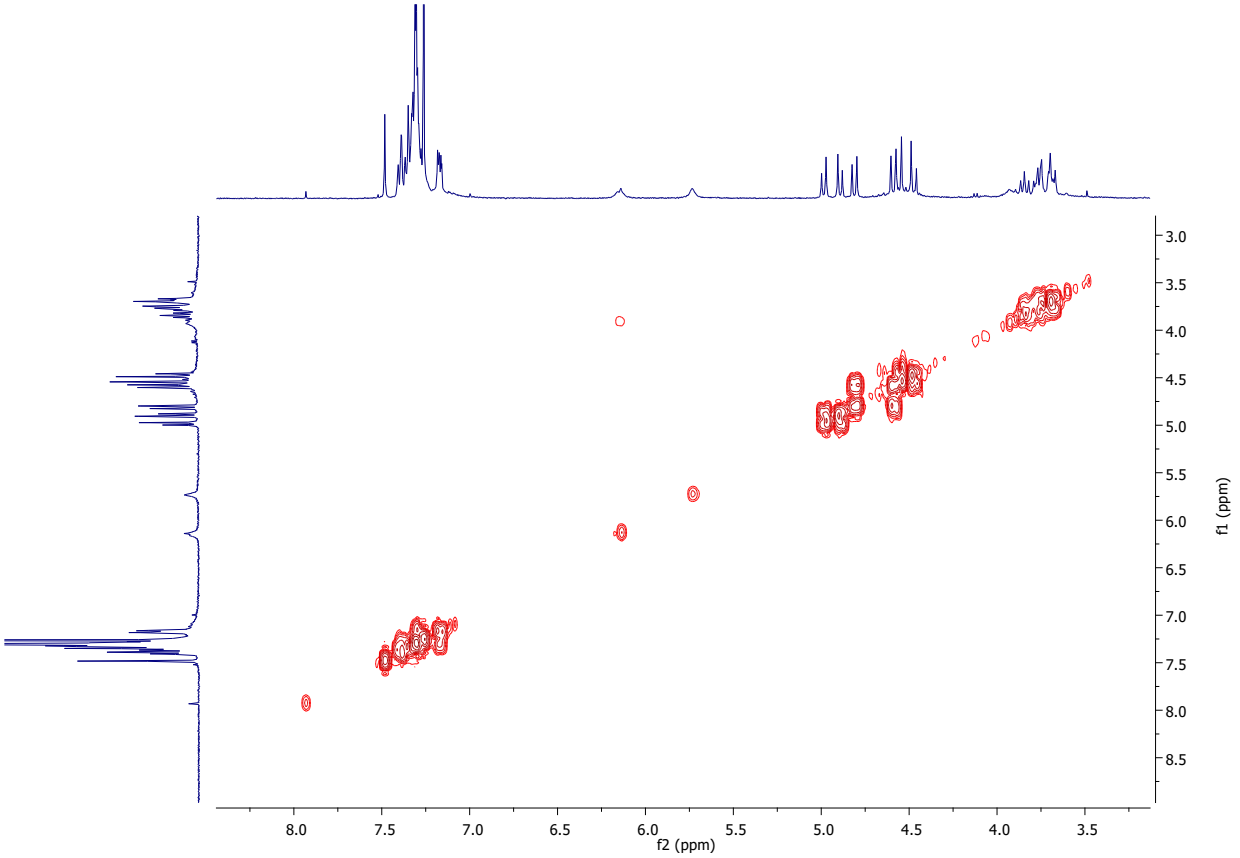
3h



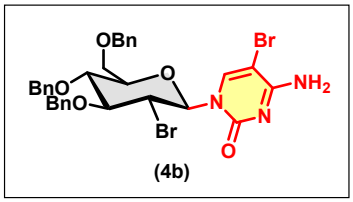
6. 2D Spectrum ($CDCl_3$) of compound 4b

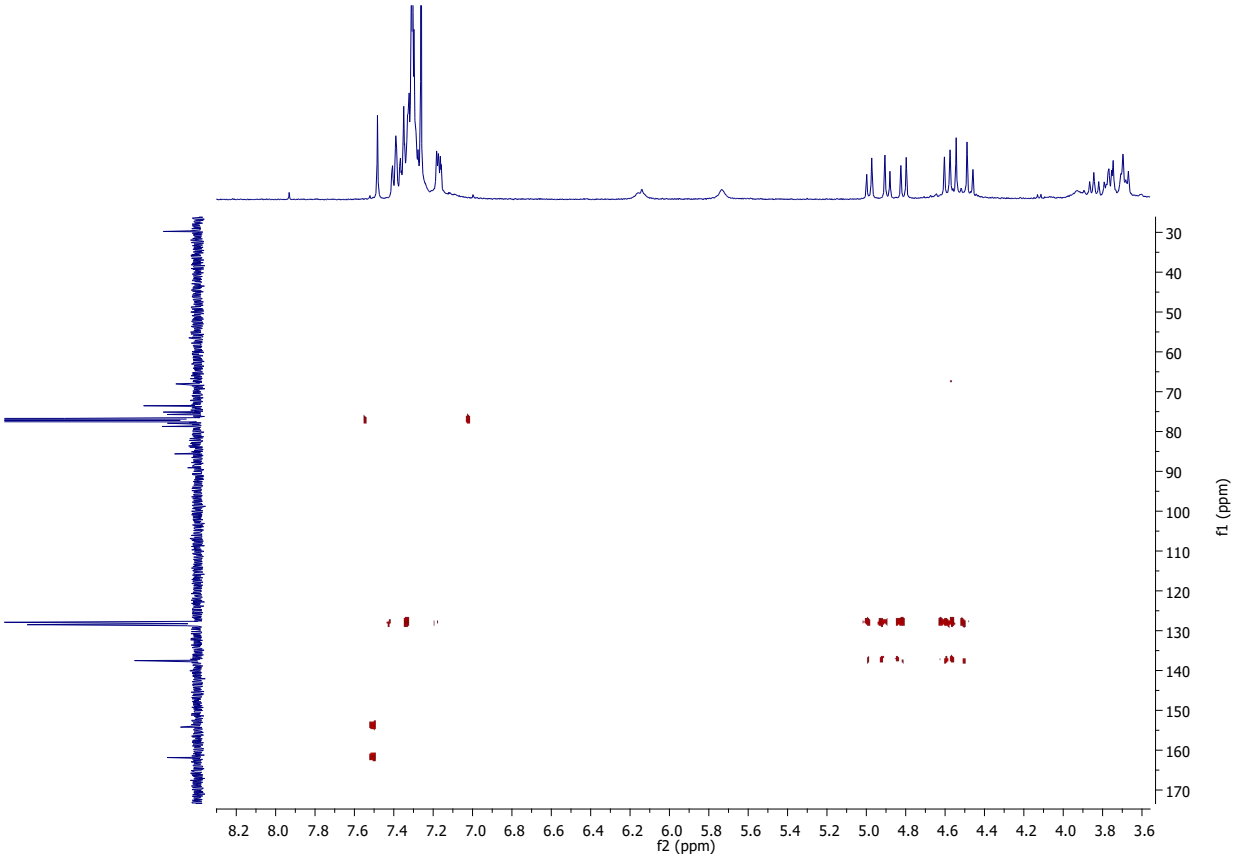
COSY Spectrum of 4b



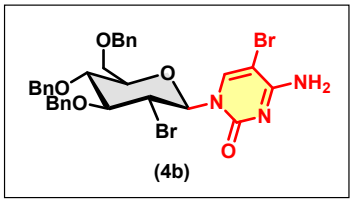


HMBC Spectrum of 4b

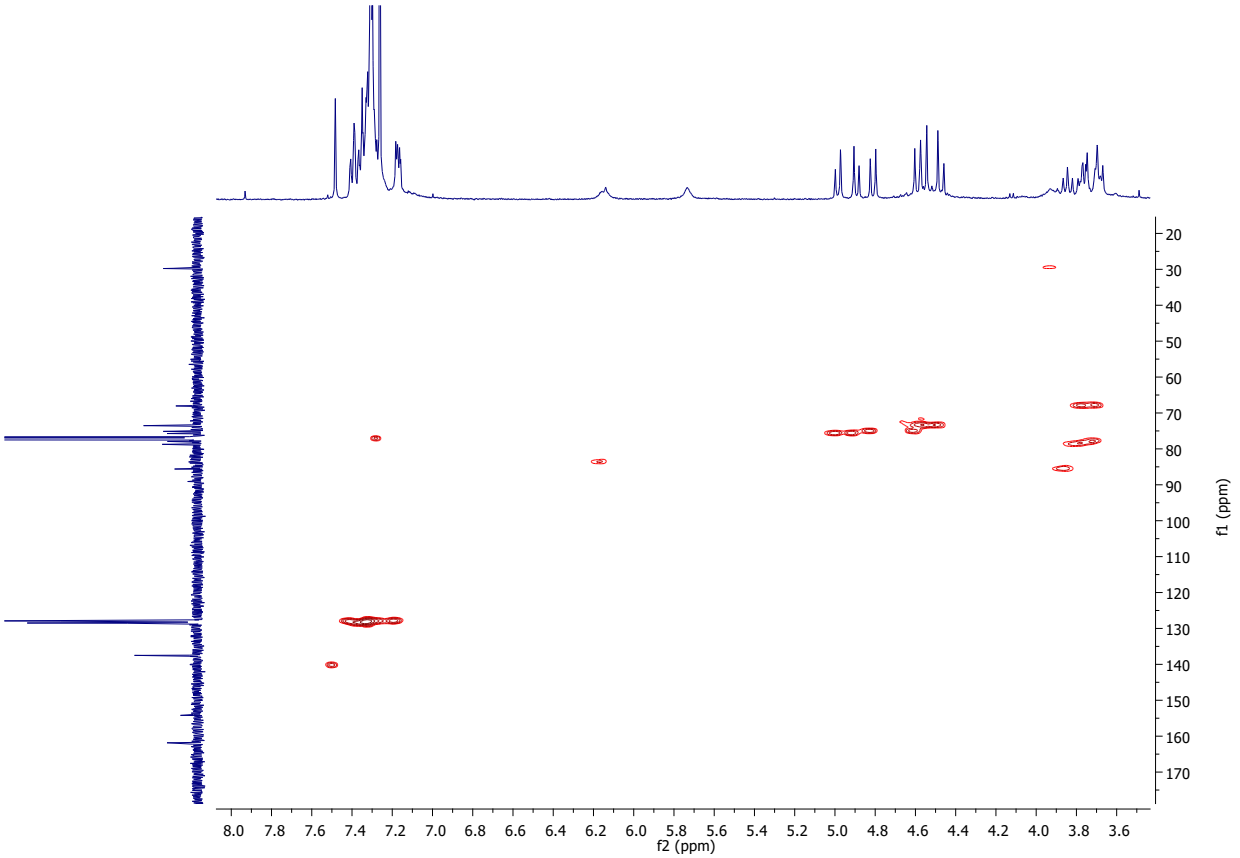




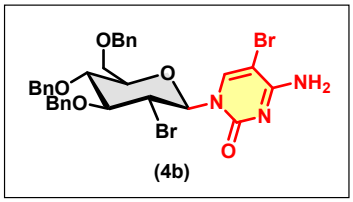
HSQC Spectrum of 4b



(4b)



NOESY Spectrum of 4b



(4b)