Supporting Information

Improved hemicryptophane hosts for stereoselective recognition of glucopyranosides.

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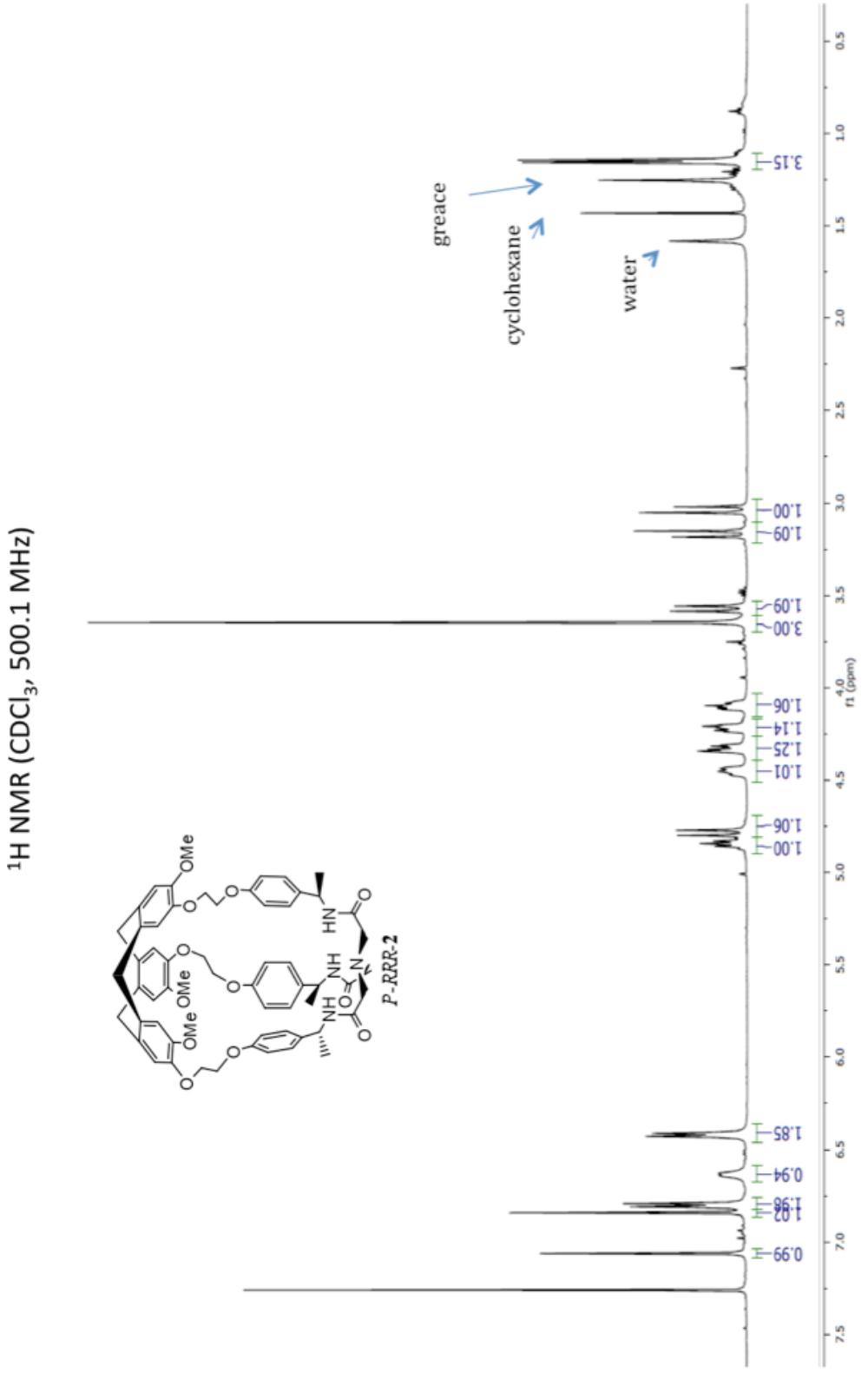
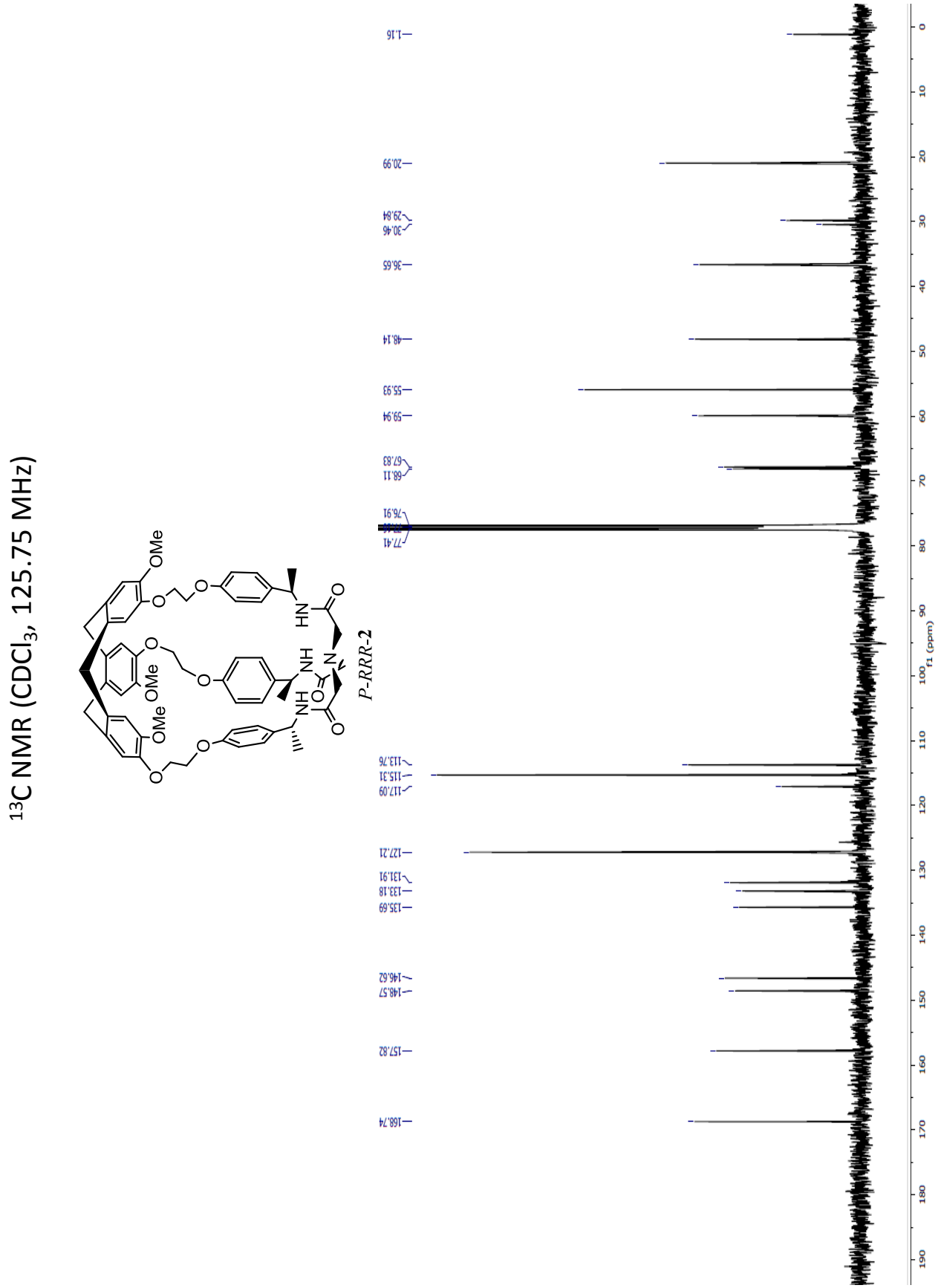
3/ Spectral characterization

3.1) NMR spectra of *P-RRR*-**2**

a) ^{1}H NMR spectrum of *P-RRR*-**2**

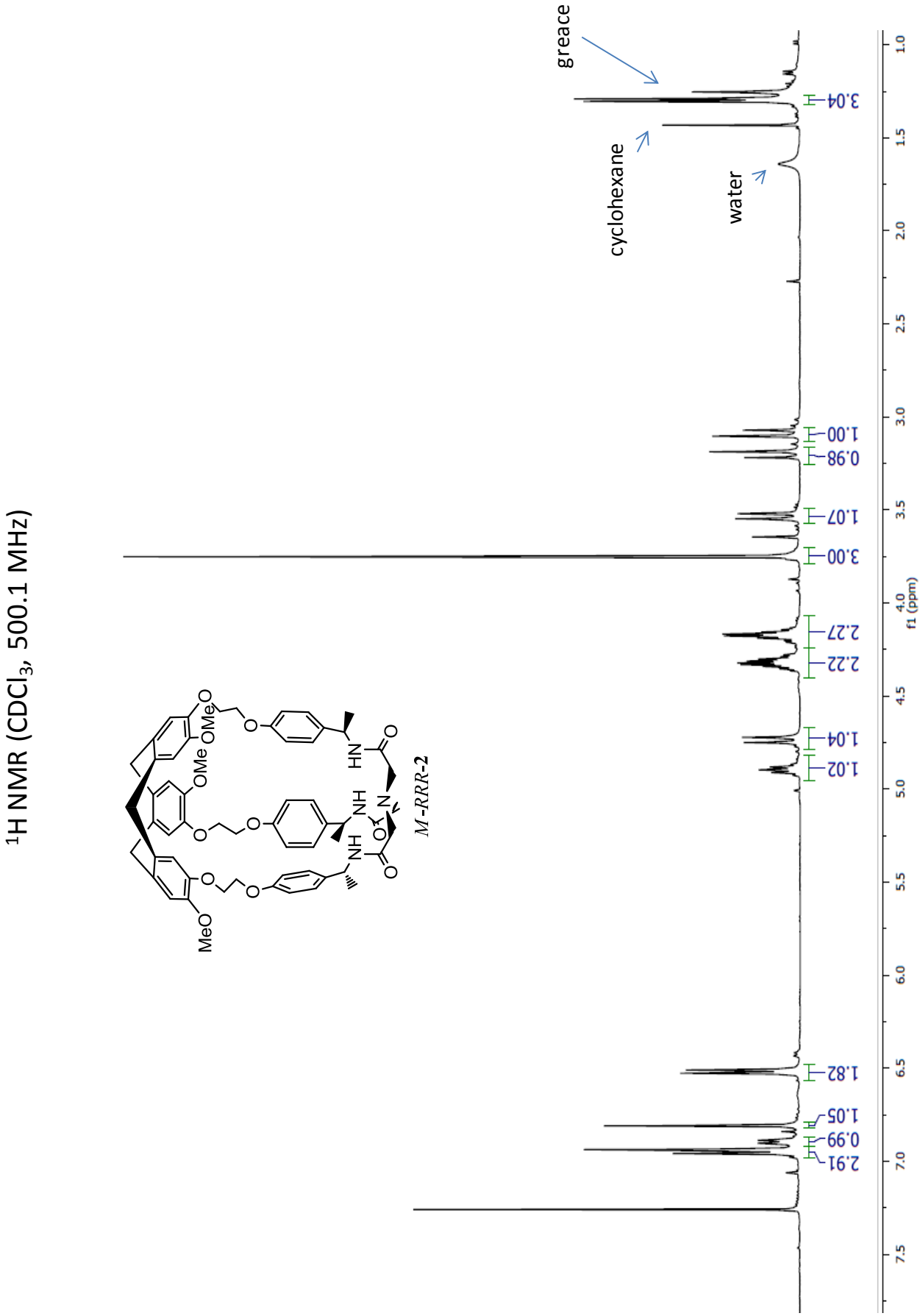


b) ^{13}C NMR spectrum of *P-RRR*-**2**

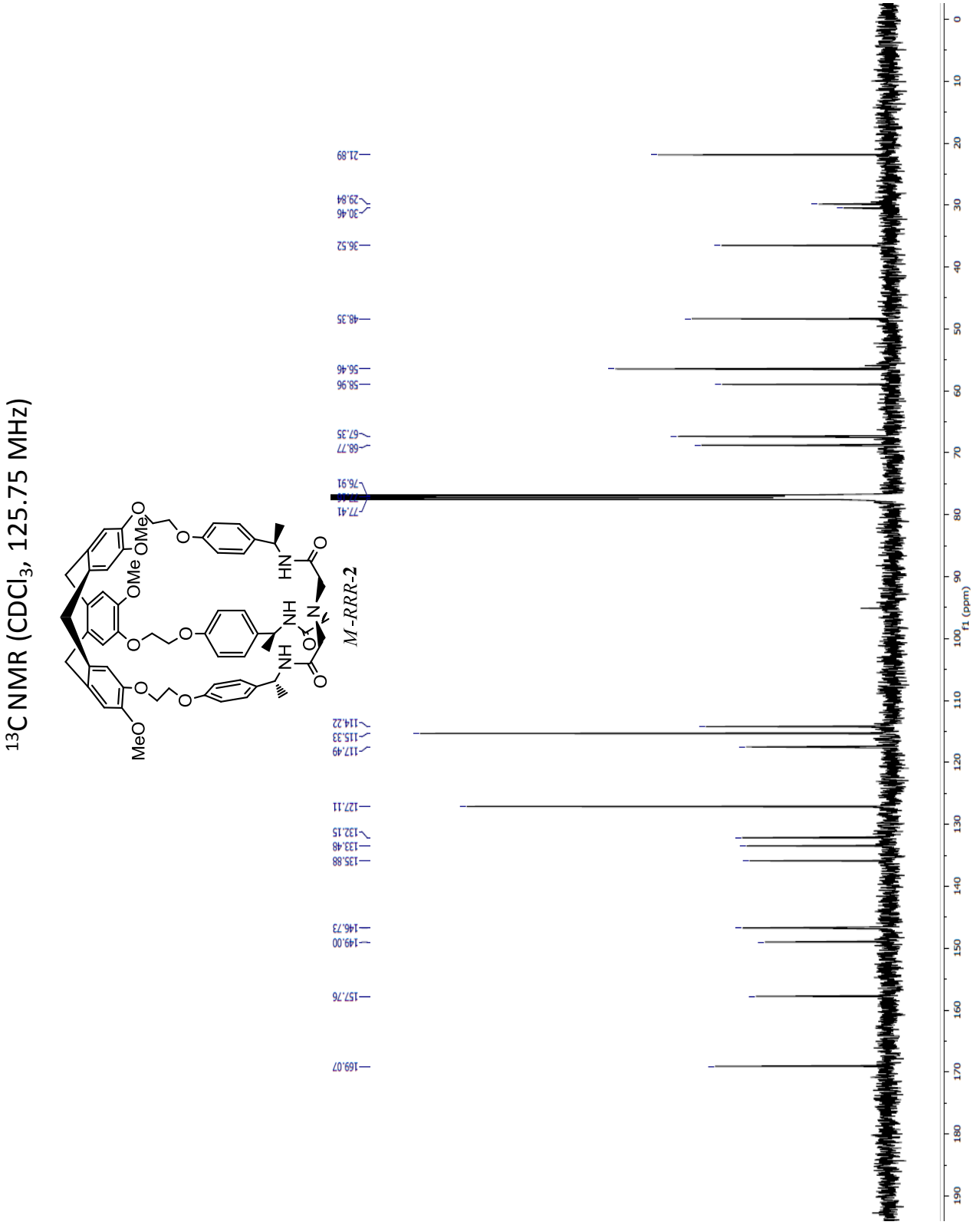


3.2) NMR spectra of *M-RRR*-**2**

a) ^{1}H NMR spectrum of *M-RRR*-**2**

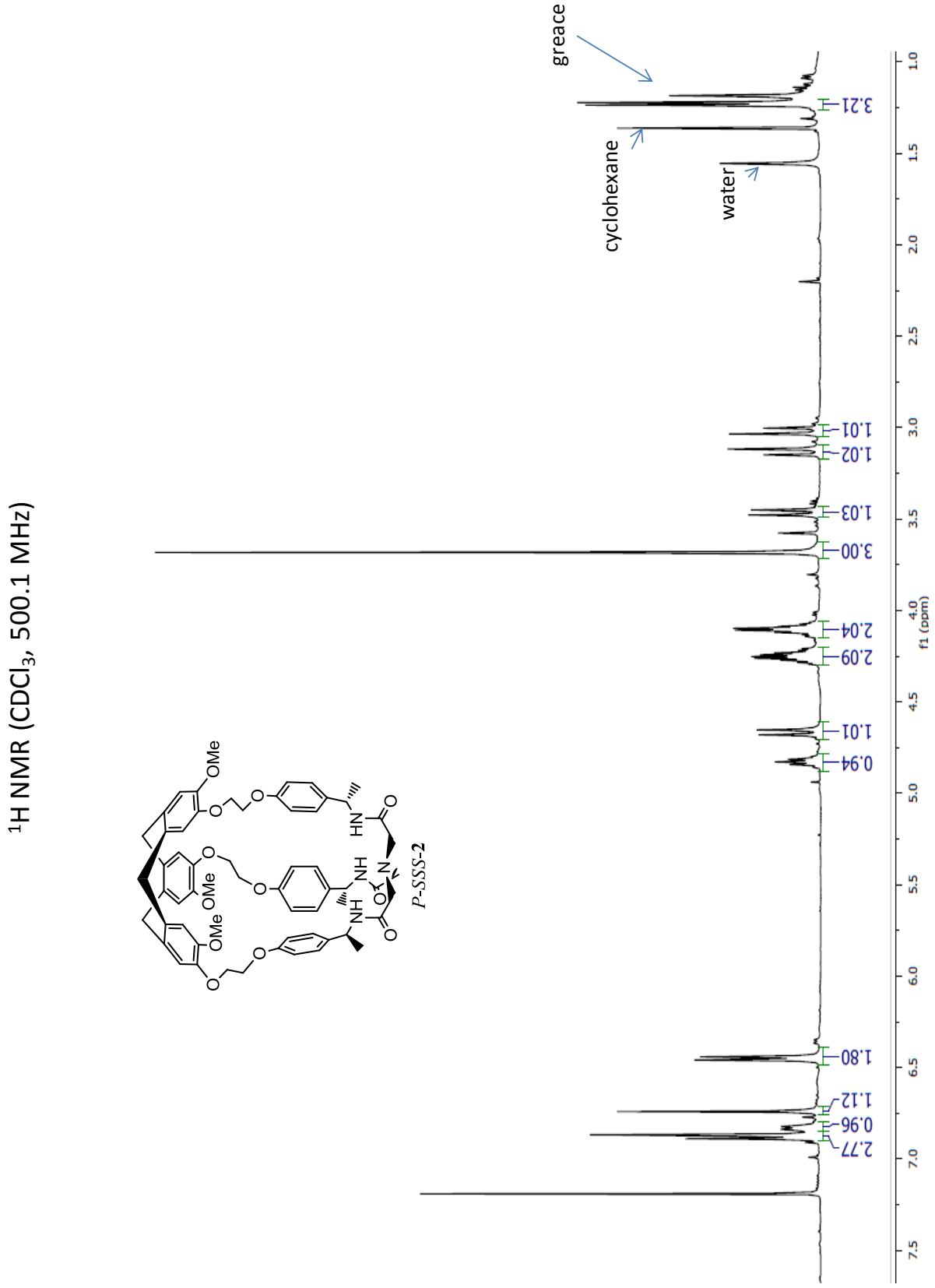


b) ^{13}C NMR spectrum of *M-RRR*-**2**



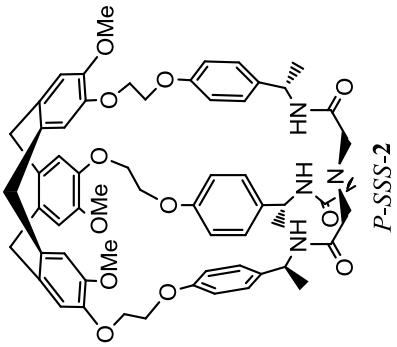
3.3) NMR spectra of *P-SSS*-**2**

a) ^{1}H NMR spectrum of *P-SSS*-**2**

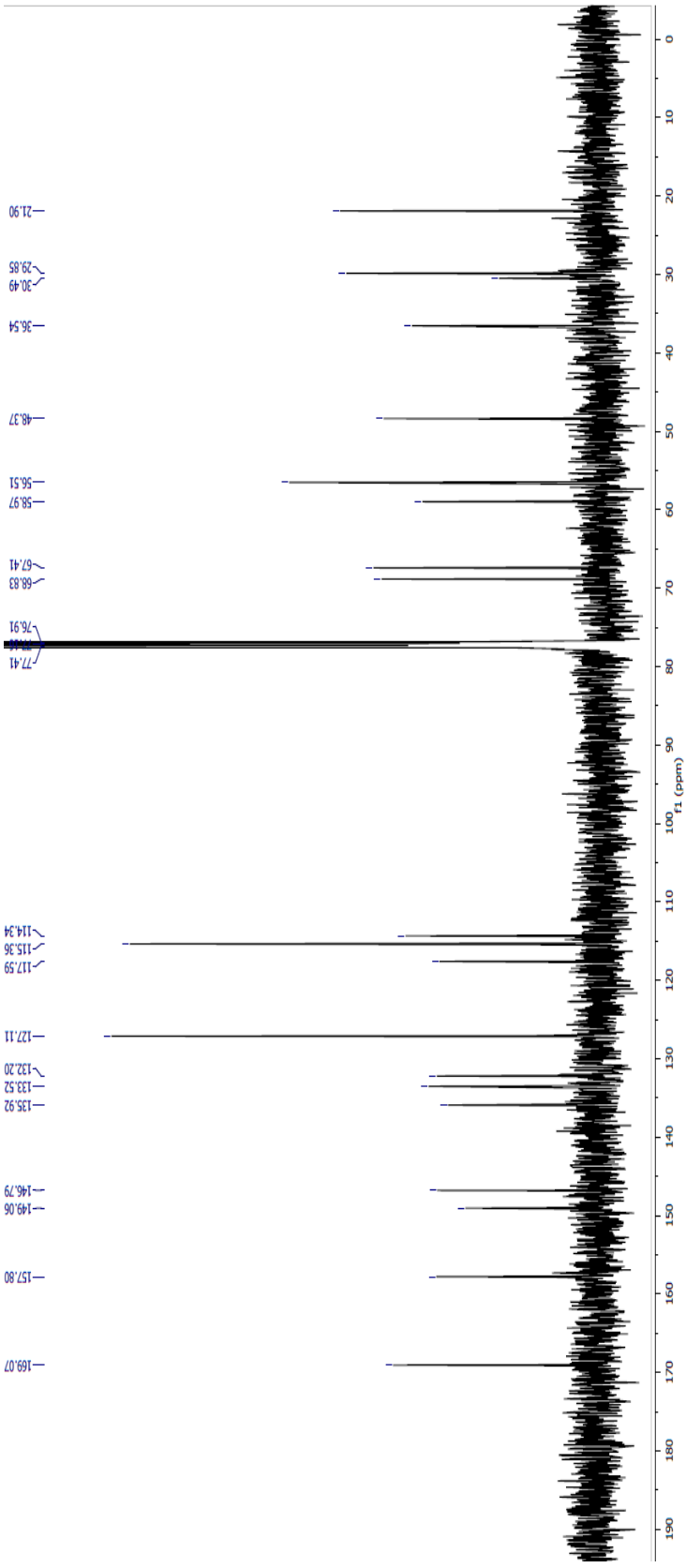


b) ^{13}C NMR spectrum of *P-SSS*-**2**

^{13}C NMR ($CDCl_3$, 125.75 MHz)

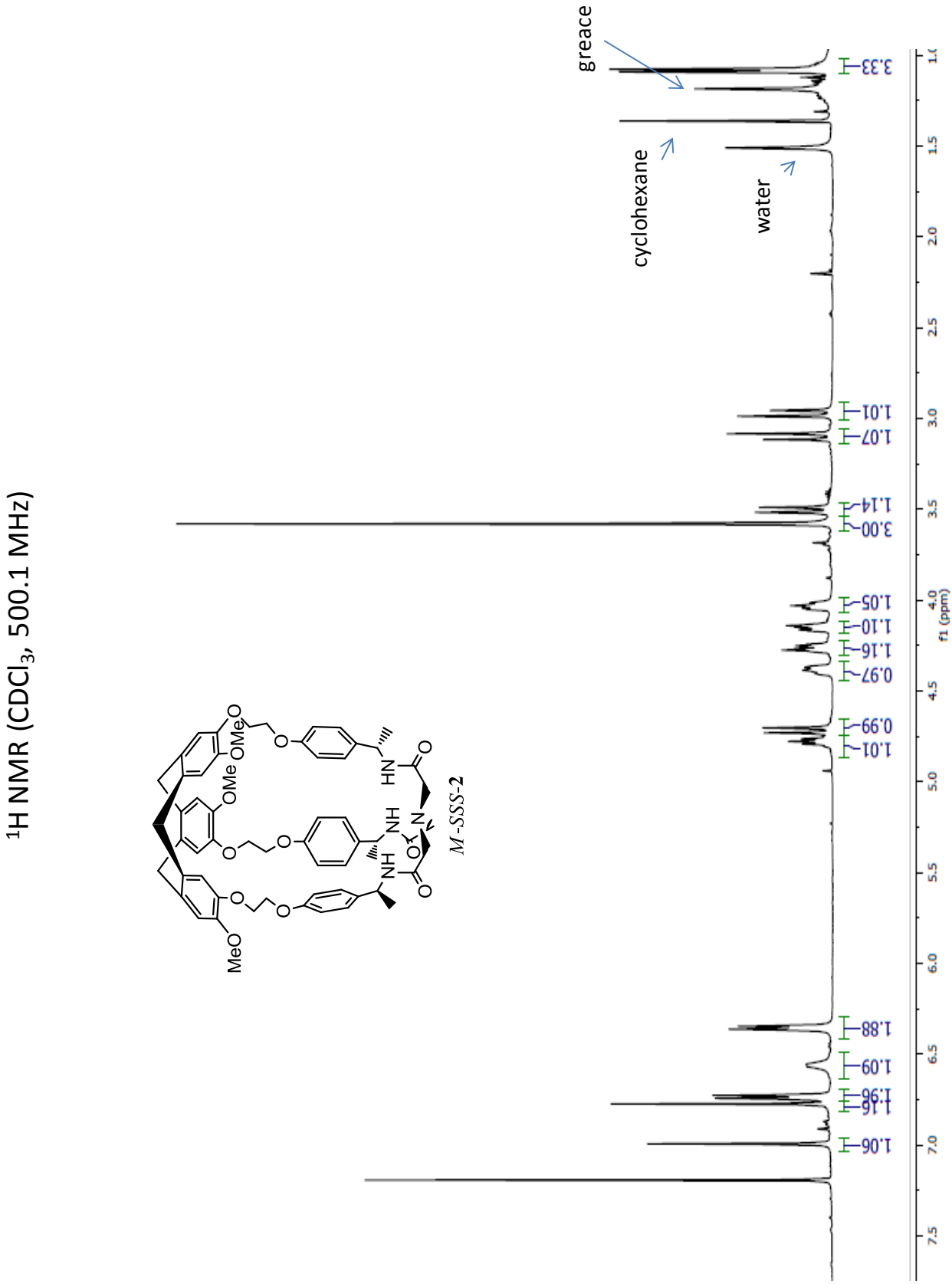


P-SSS-**2**

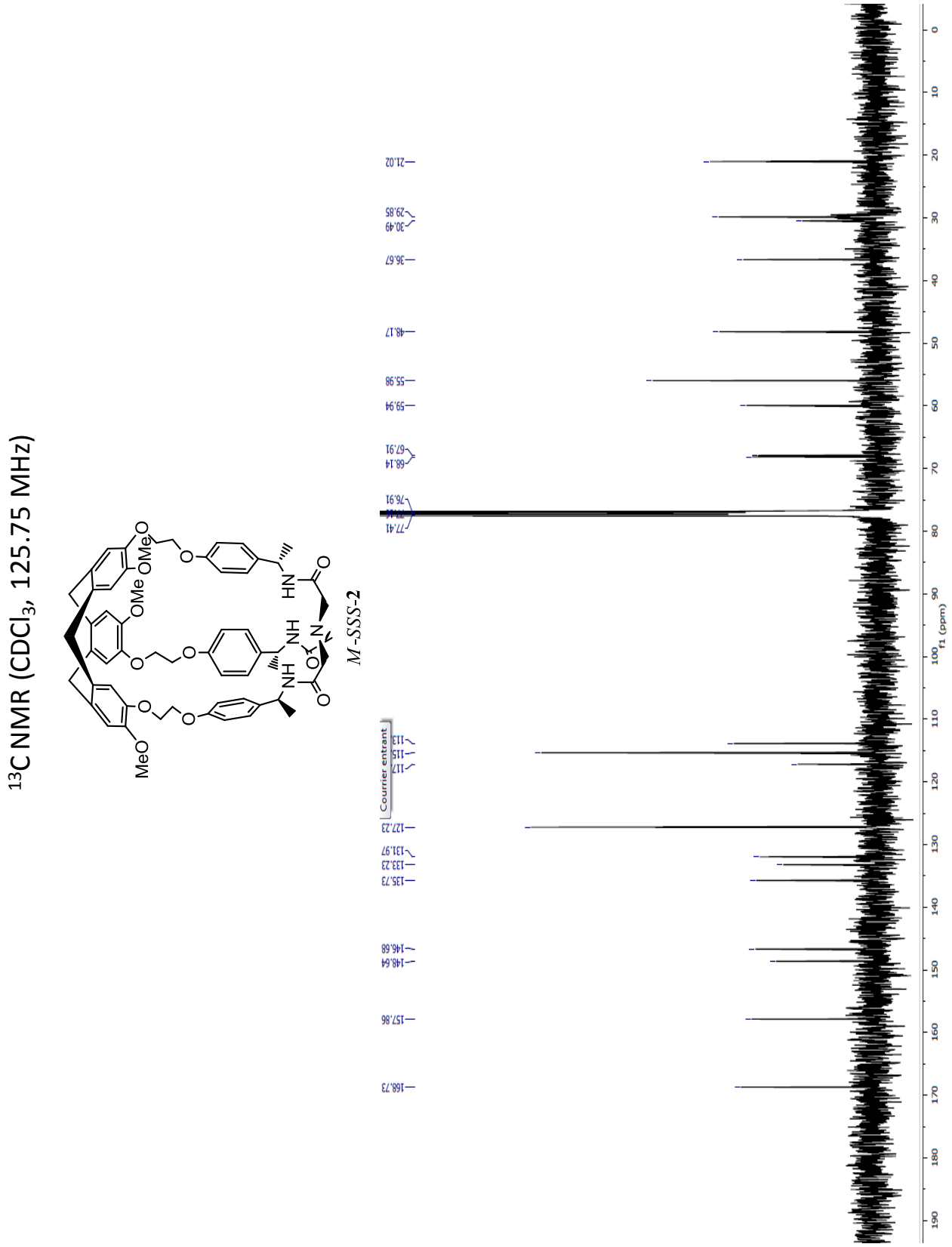


3.4) NMR spectra of *M-SSS*-**2**

a) ^{1}H NMR spectrum of *M-SSS*-**2**

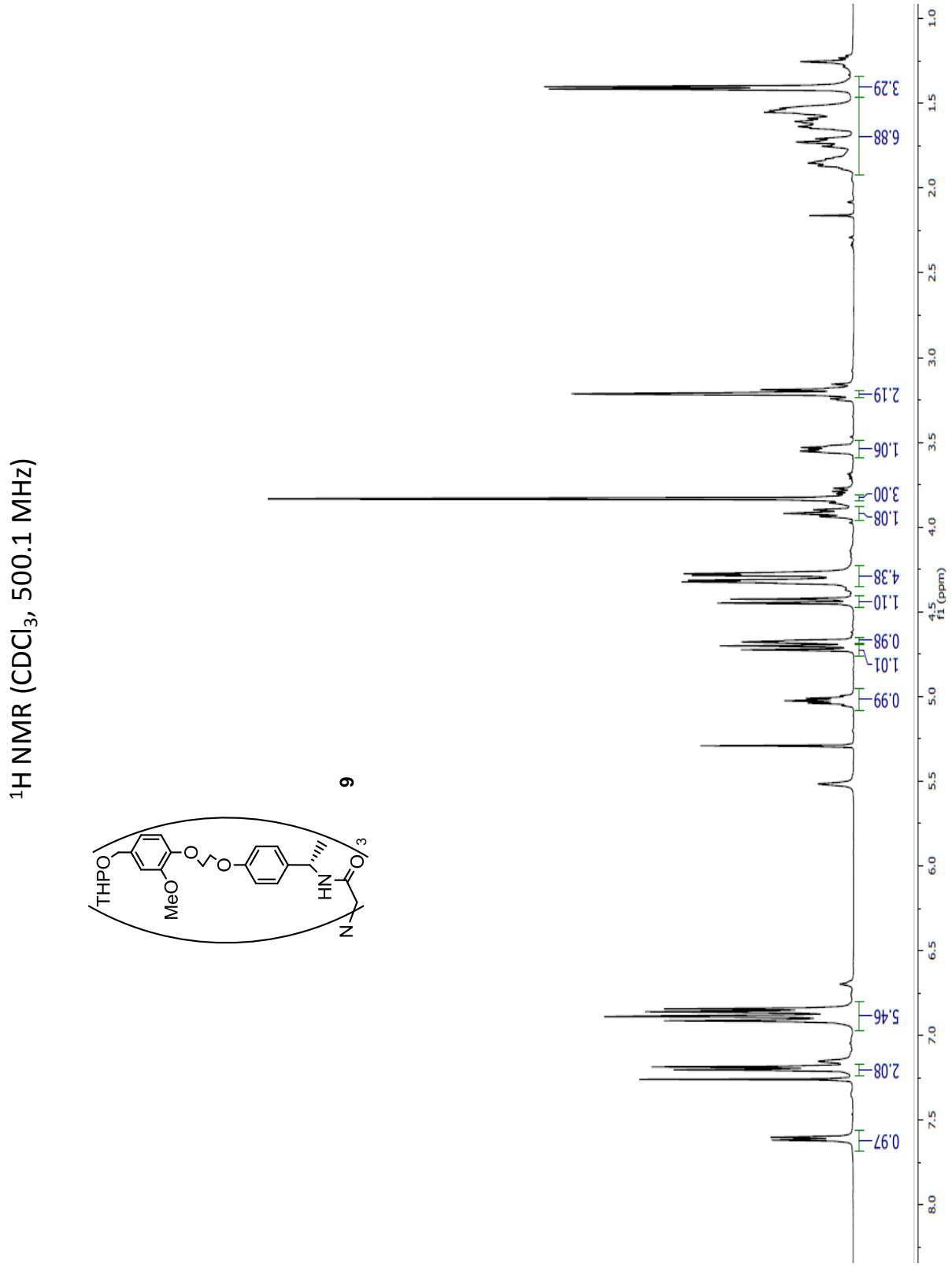


b) ^{13}C NMR spectrum of *M-SSS*-**2**

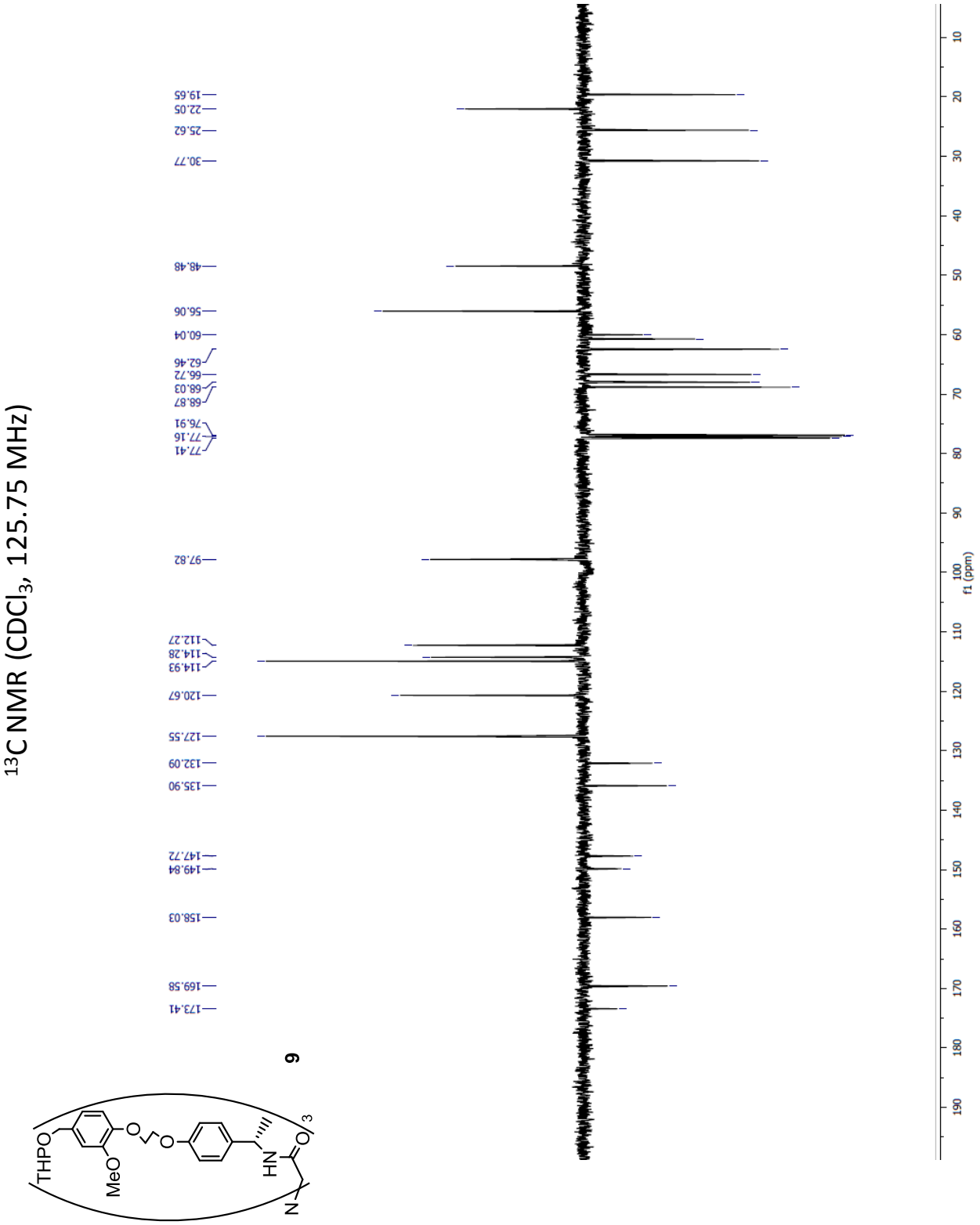


3.5) NMR spectra of **9**

a) ^{1}H NMR spectrum of **9**

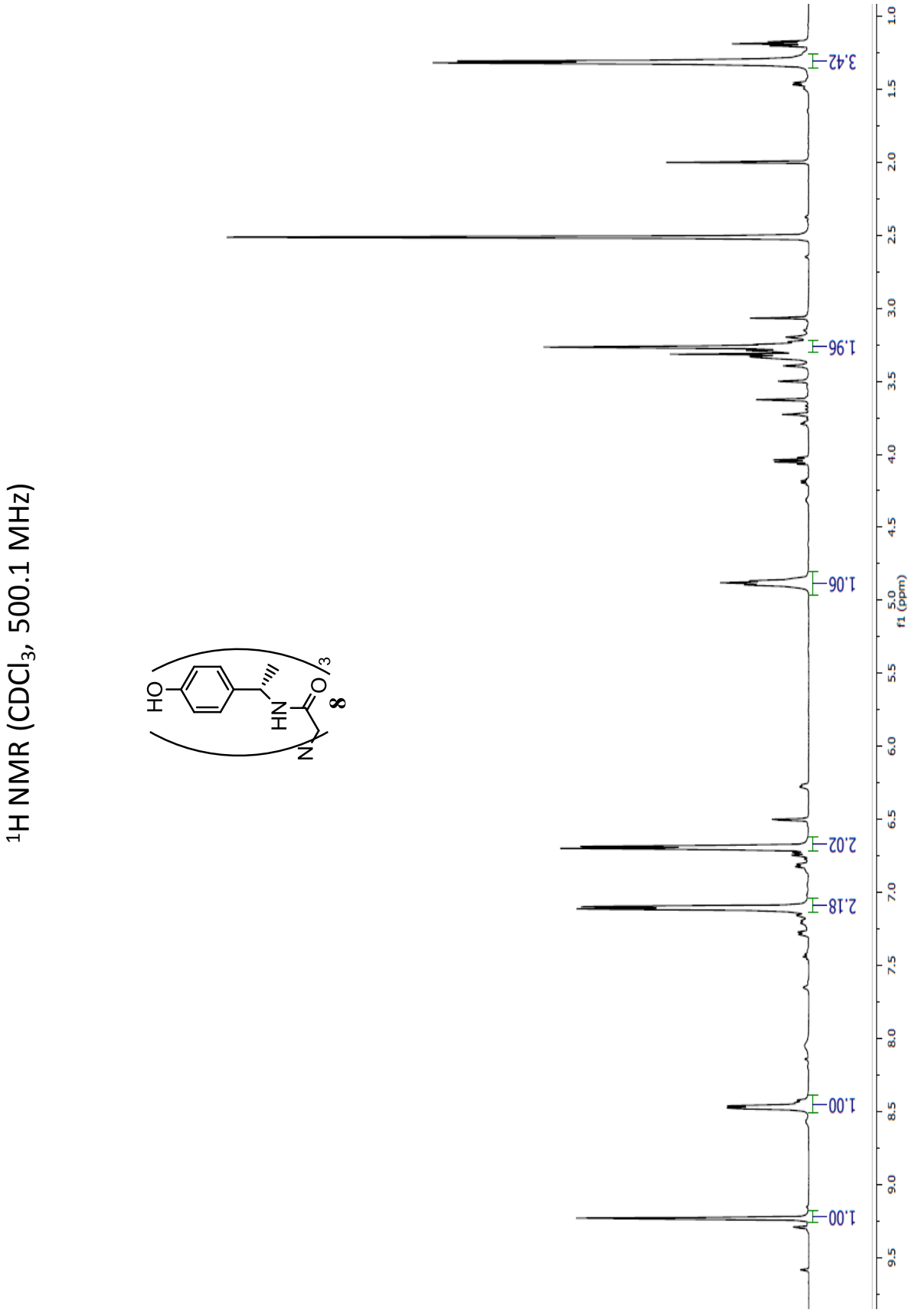


b) ^{13}C NMR spectrum of **9**

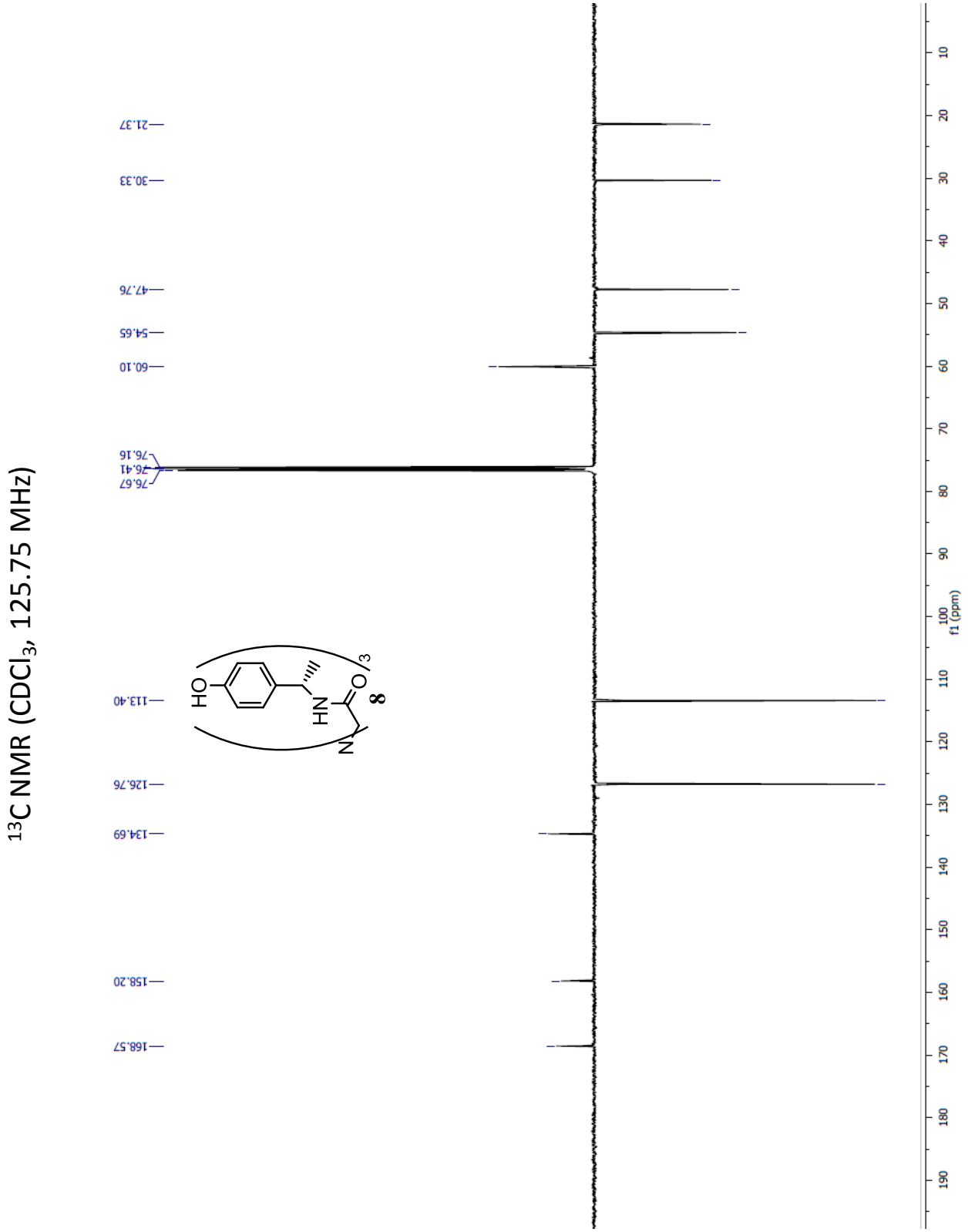


3.6) NMR spectra of **8**

a) ^{1}H NMR spectrum of **<u>8</u>**

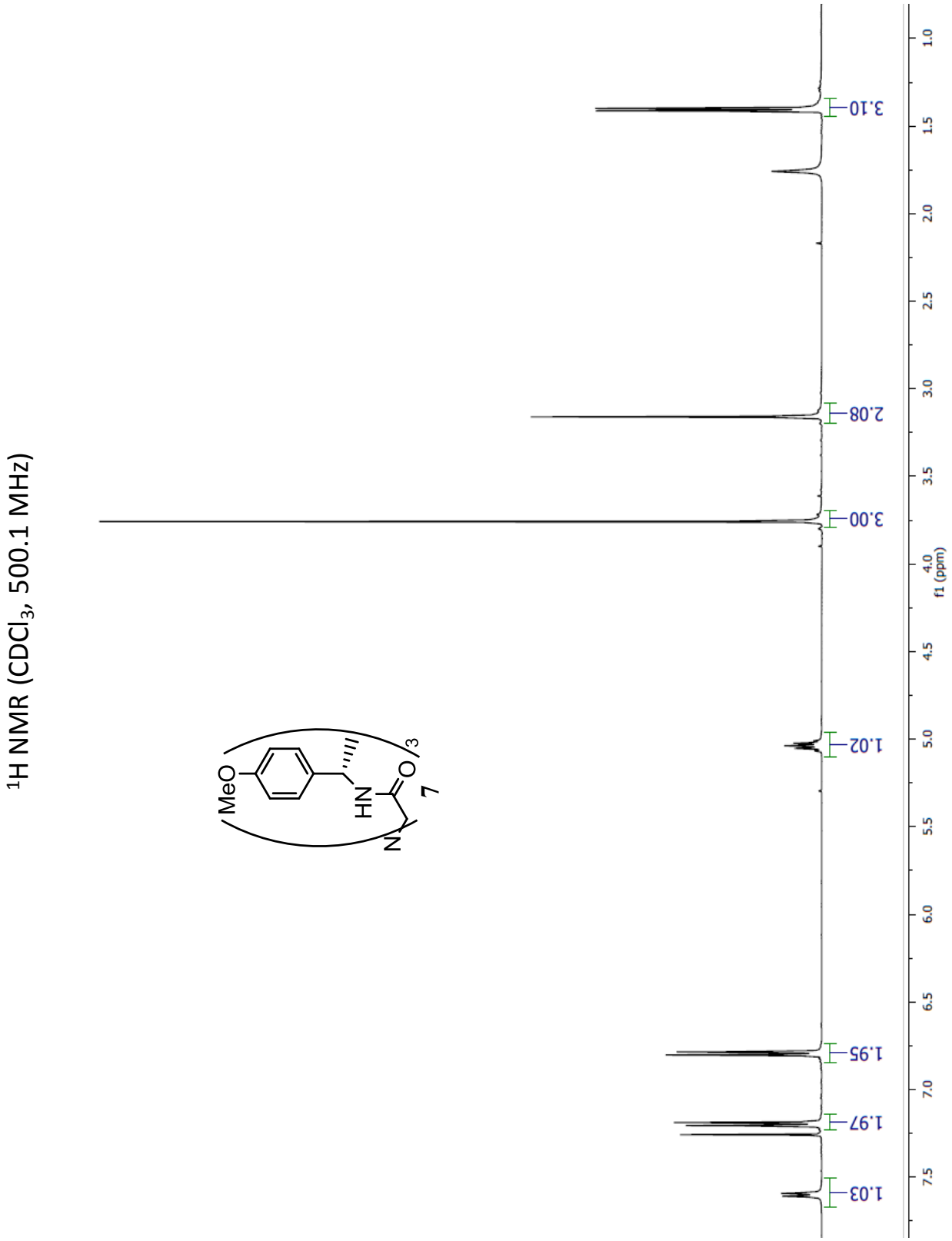


b) ^{13}C NMR spectrum of **8**

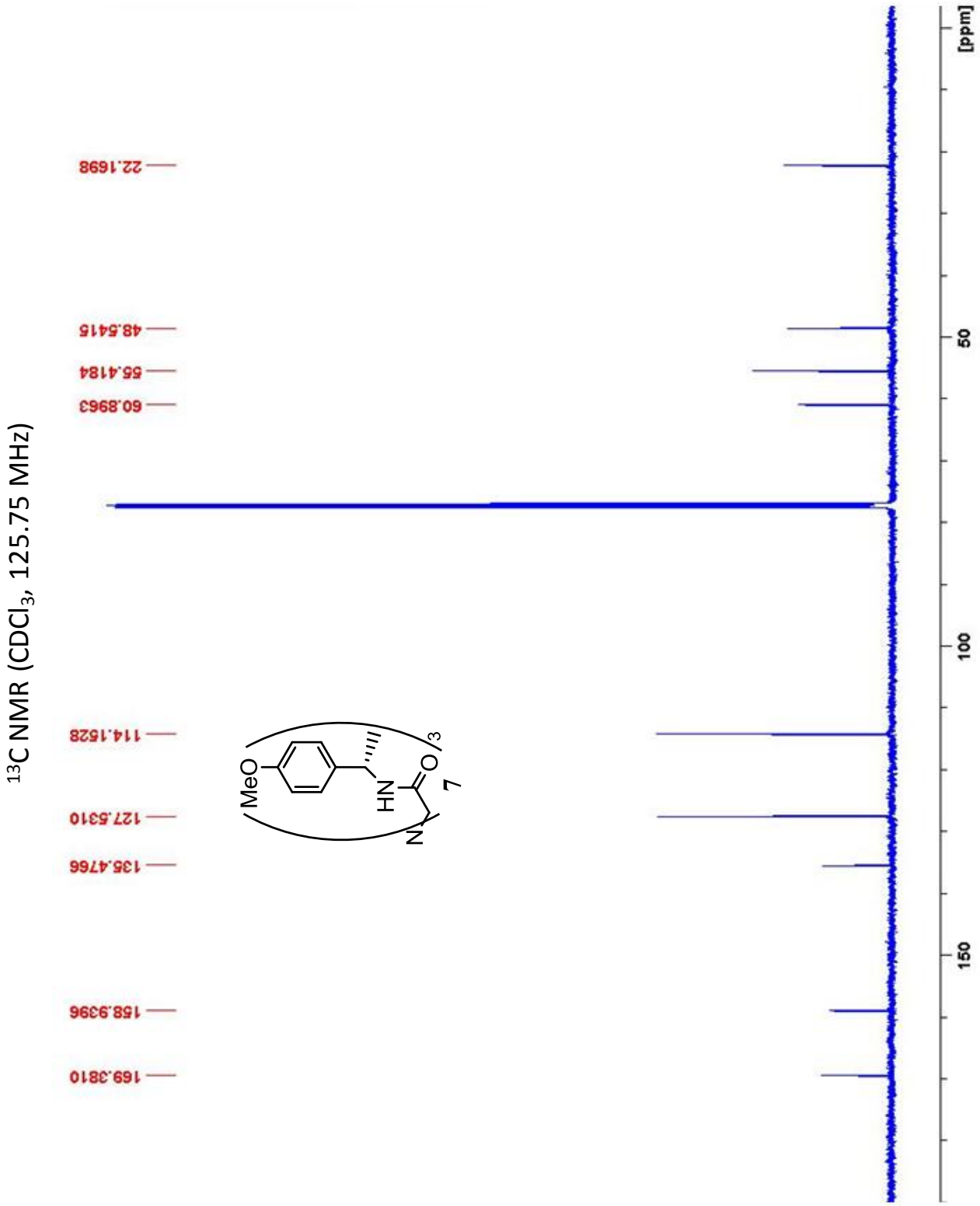


3.7) NMR spectra of **7**

a) ^{1}H NMR spectrum of **7**



b) ^{13}C NMR spectrum of **7**



4/ ^{1}H NMR titrations:

Solutions of hosts (2.0 mM in $CDCl_3$, 500 μL) were titrated in NMR tubes with small aliquots of concentrated solutions (10 or 20 mM in $CDCl_3$) of guests. Complexation induced shifts $\Delta\delta$ of the aromatic protons or the NH protons of the host were measured after each addition and plotted as a function of the guest/host ratio. Mathematical analysis of data and graphic representation of results were performed using the HypNMR 2008 program,[2] handling general host-guest association equilibria under fast exchange regime on the NMR time scale. This allows obtaining the binding constant Ka. Complexation induced shifts were measured on the aromatic protons or the NH protons since in all these cases, they displayed sharp signals and no overlapping region.

Titration Plots: experimental (symbols) and calculated (lines) chemical shifts are shown in Figure 5 of the article.

Results

Receptor: *M-SSS*-**2** guest: OctαGlc
HypNMR2008
Refinement concluded
Converged in 4 iterations with sigma = 0,588186

	value	standard deviation	Comments
1 log beta(HCsucre)	2.7745	0.0924	2.77(9)

Receptor: *M-SSS*-**2** guest: OctβGlc
HypNMR2008
Refinement concluded
Converged in 5 iterations with sigma = 0,877167

	value	standard deviation	Comments
1 log beta(HCsucre)	3.2202	0.0973	3.22(1)

Receptor: *P-SSS*-**2** guest: OctαGlc
Refinement concluded
Converged in 5 iterations with sigma = 0,091442

	value	standard deviation	Comments
1 beta(HCsucre)	-2.8E+01	0.2407	Log beta cannot be updated

Receptor: *P-SSS*-**2** guest: OctβGlc

HypNMR2008

Refinement concluded

Converged in 5 iterations with sigma = 0,179391

	value	standard deviation	Comments
1 log beta(HCsucre)	2.2619	0.0825	2.26(8)

Receptor: *M-RRR*-**2** guest: OctαGlc

HypNMR2008

Refinement

Converged in 4 iterations with sigma = 0,067908

	value	standard deviation	Comments
1 log beta(HCsucre)	1.7467	0.1071	1.7(1)

Receptor: *M-RRR*-**2** guest: OctβGlc

HypNMR2008

Refinement concluded

Converged in 4 iterations with sigma = 0,115243

	value	standard deviation	Comments
1 log beta(HCsucre)	2.2822	0.0427	2.28(4)

Receptor: *P-RRR*-**2** guest: OctαGlc

HypNMR2008

Refinement concluded

Converged in 3 iterations with sigma = 0,068269

	value	standard deviation	Comments
1 log beta(HCsucre)	1.528	0.066	1.53(7)

Receptor: *P-RRR*-**2** guest: OctβGlc

HypNMR2008

Refinement concluded

Converged in 4 iterations with sigma = 0,075097

	value	standard deviation	Comments
1 log beta(HCsucre)	2.5841	0.0428	2.58(4)

4/ Job's Plot

^{1}H NMR continuous variation methods (Job's plot)

Stock solutions (1.0 mM in $CDCl_3$) of **1** and of the guest were prepared and mixed in NMR tubes in different ratios. In this way, relative concentrations α were varied continuously but their sum was kept constant (1.0 mM). ^{1}H NMR spectra were recorded for each sample and values of host's chemical shift δ_{obs} were measured. Job's plots were obtained by plotting $(\delta_{obs} - \delta_{free})\alpha$ versus α, where δ_{free} is the chemical shift of the proton in the uncomplexed host. The stoichiometry of the complexes was obtained from the value of the molar fraction α which corresponds to a maximum of the curve: a 1:1 complexation is obtained for $\alpha_{max} = 0.5$.

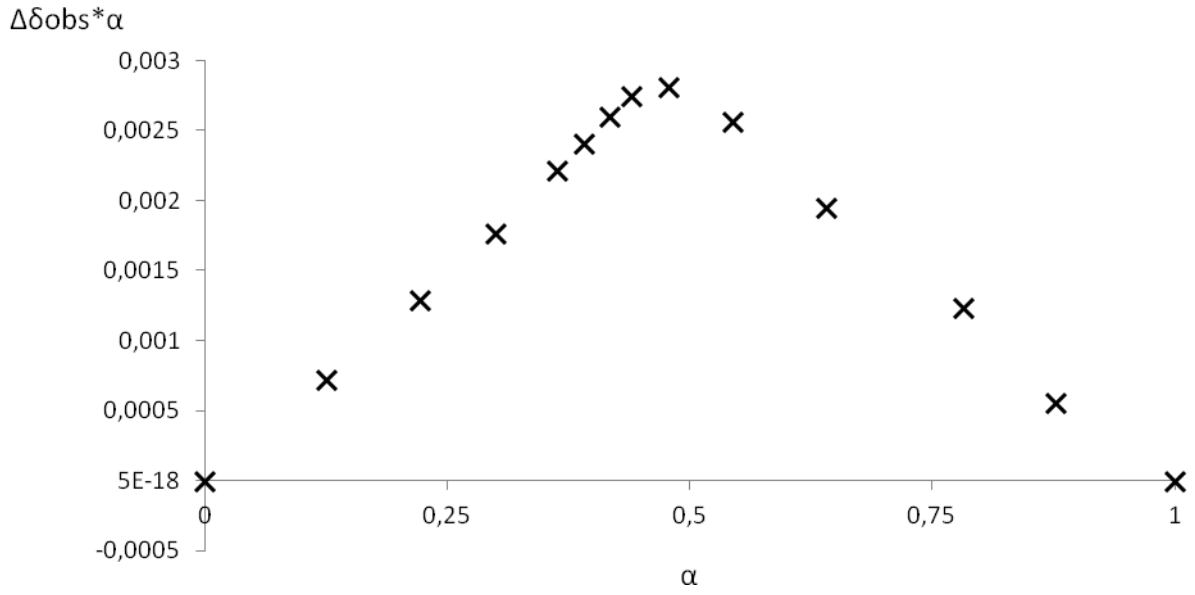
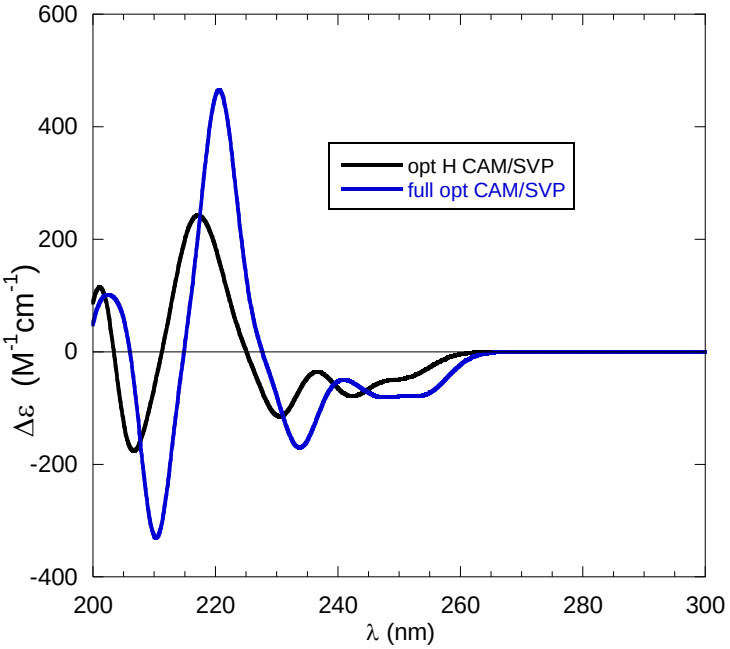


Figure S1. Job's plot of ***M-SSS*-2** with OctβGlc. The chemical induced shifts Δδ of the H_4 protons of ***M-SSS*-2** were measured, α is the molar ratio of ***M-SSS*-2**.

5/ ECD



Comparison between the calculated ECD spectra of *M-SSS*-**2** calculated on fully optimized and hydrogen-only optimized structures (at CAM/SVP level). Small differences can be observed between the two data sets. Such small differences between the spectra calculated on the fully optimized and on the hydrogen optimized structures allowed us to use the former in order to save time in the computational procedure.

References

1. Dimitrov-Raytchev, P.; Perraud, O.; Aronica, C.; Martinez, A.; Dutasta, J.-P. *J. Org. Chem.* 2010, **75**, 2099-2102.
2. C. Frassineti, S. Ghelli, P. Gans, A. Sabatini, M.S. Moruzzi, A. Vacca, *Anal. Biochem.* 1995, **231**, 374-382.