"Choose-a-Size" Control in the Synthesis of Sucrose Based Urea and Thiourea Macrocycles

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Supporting Information

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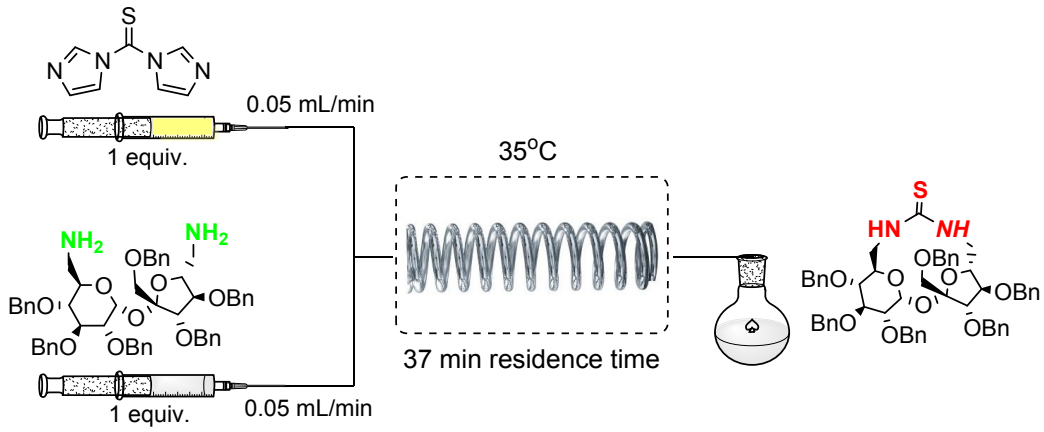
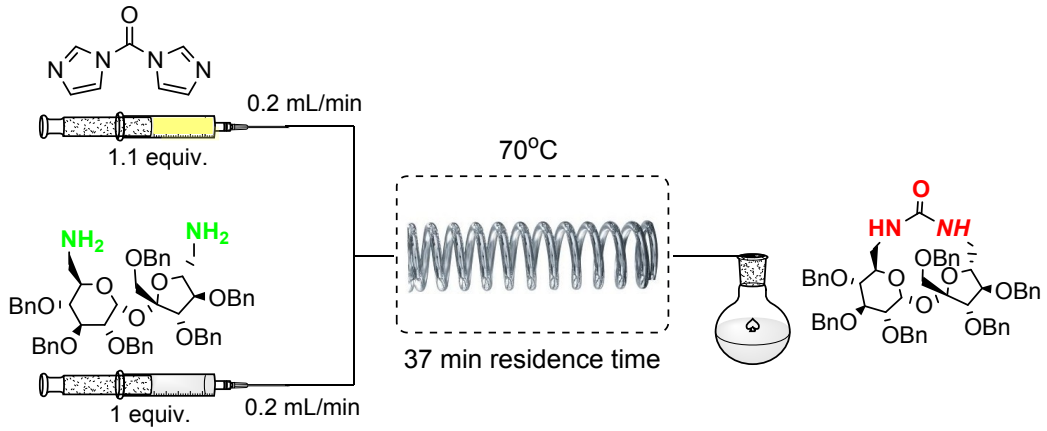
1. **The synthesis of monomeric macrocyclic derivative 3 in a flow mode**



2. The synthesis of monomeric macrocyclic derivative 5 in a flow mode



2. Copies of NMR spectra

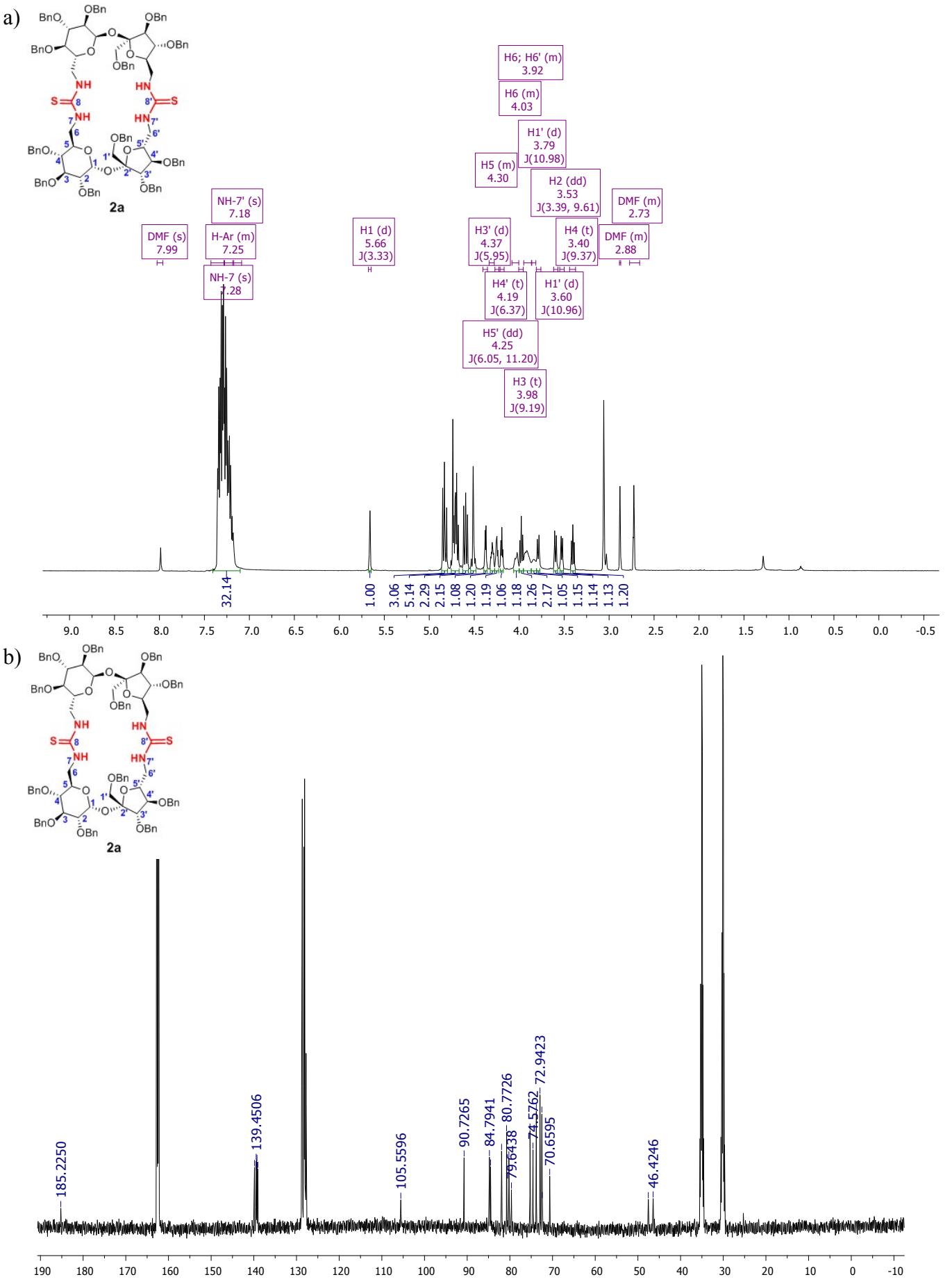
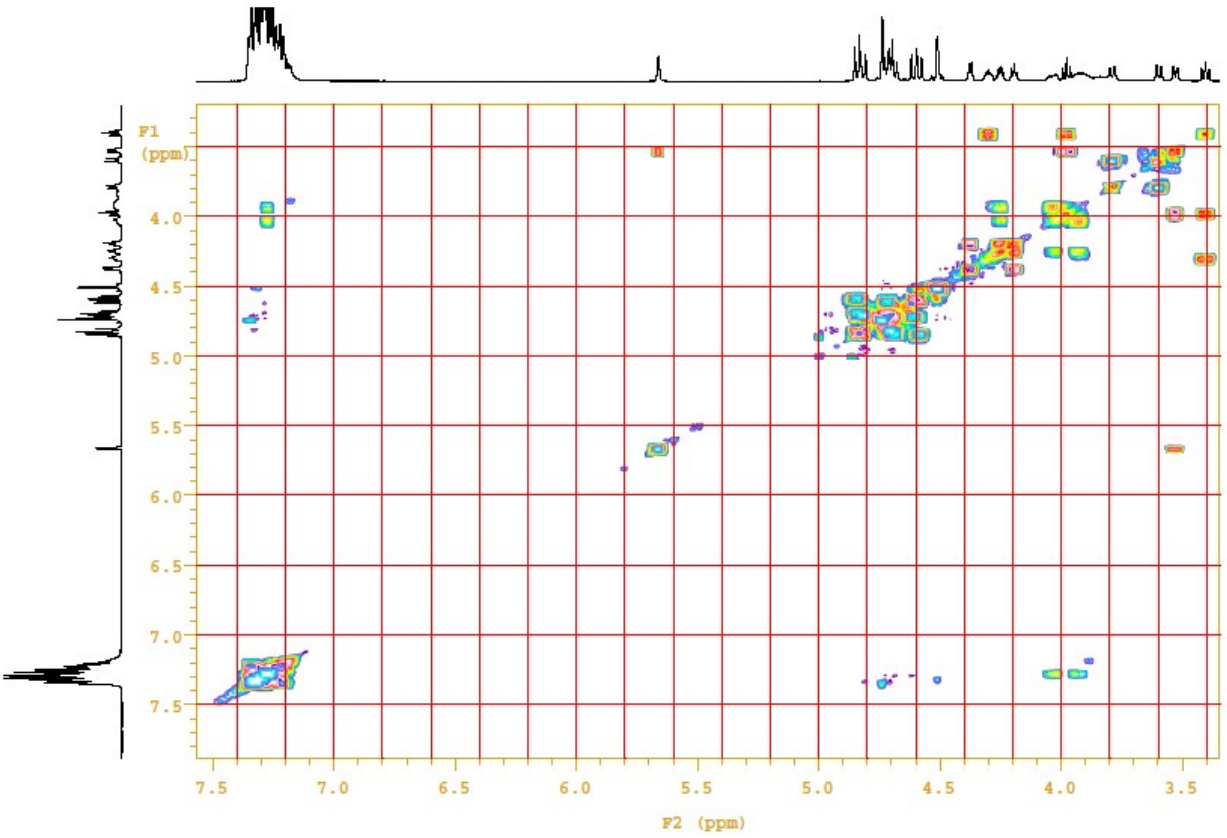


Fig. S1. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **2a** in DMF-d_6.

a)



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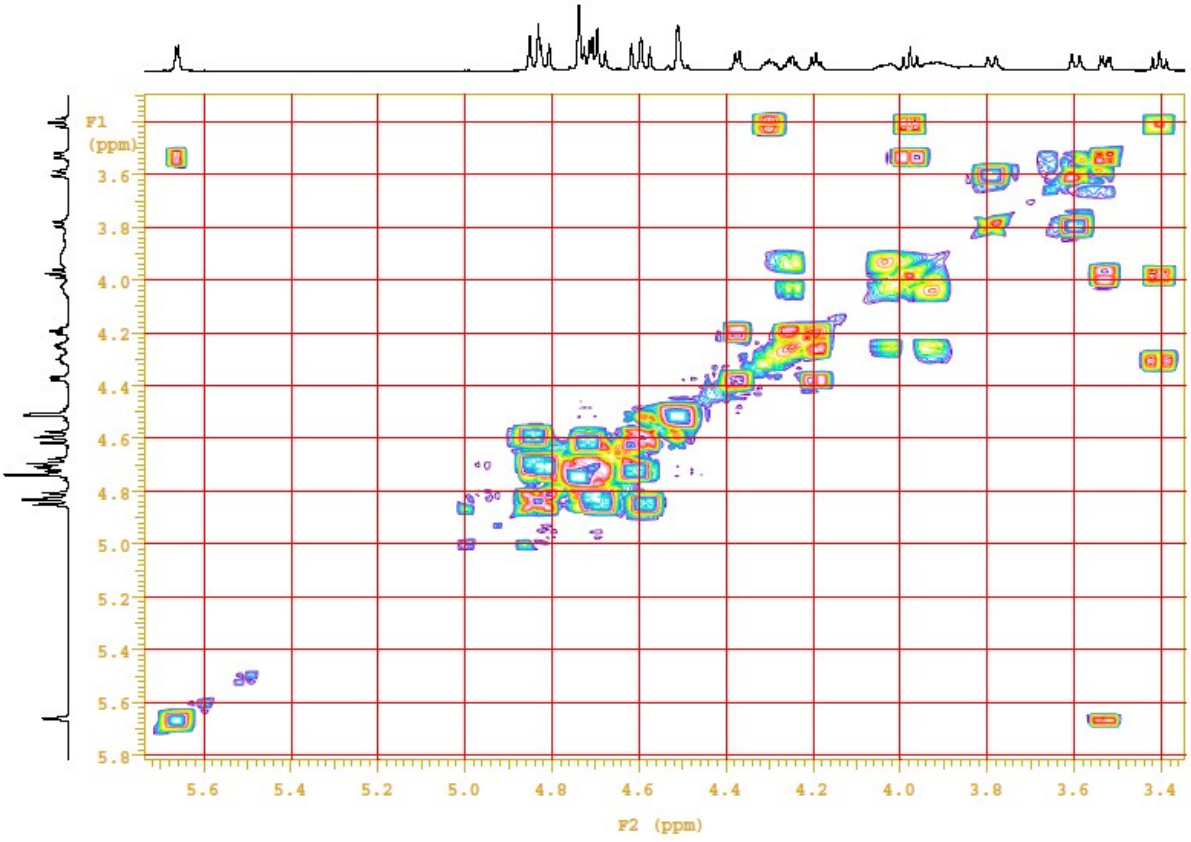
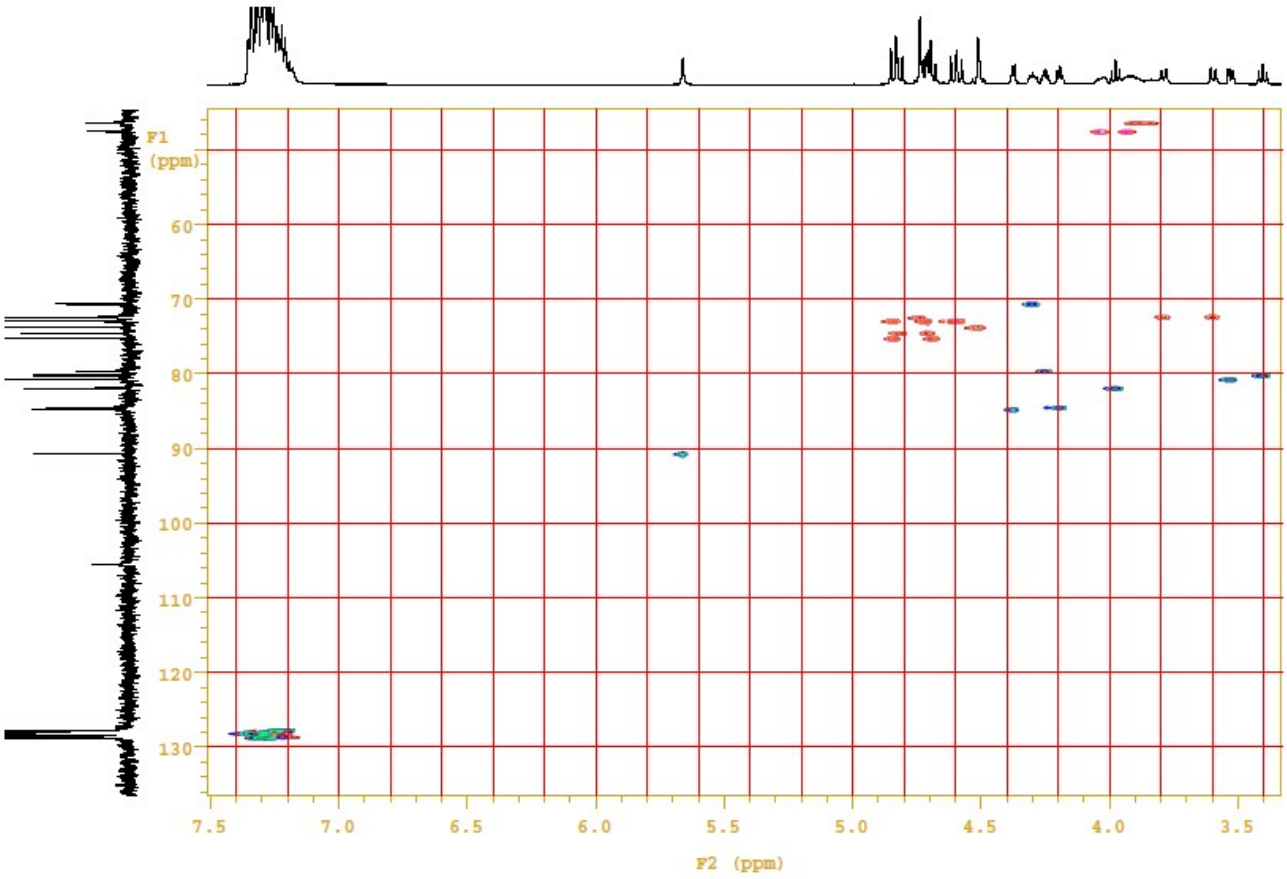


Fig. S2. COSY (^{1}H-^{1}H) spectra of compound **2a** in DMF-d_6.

a)



b)

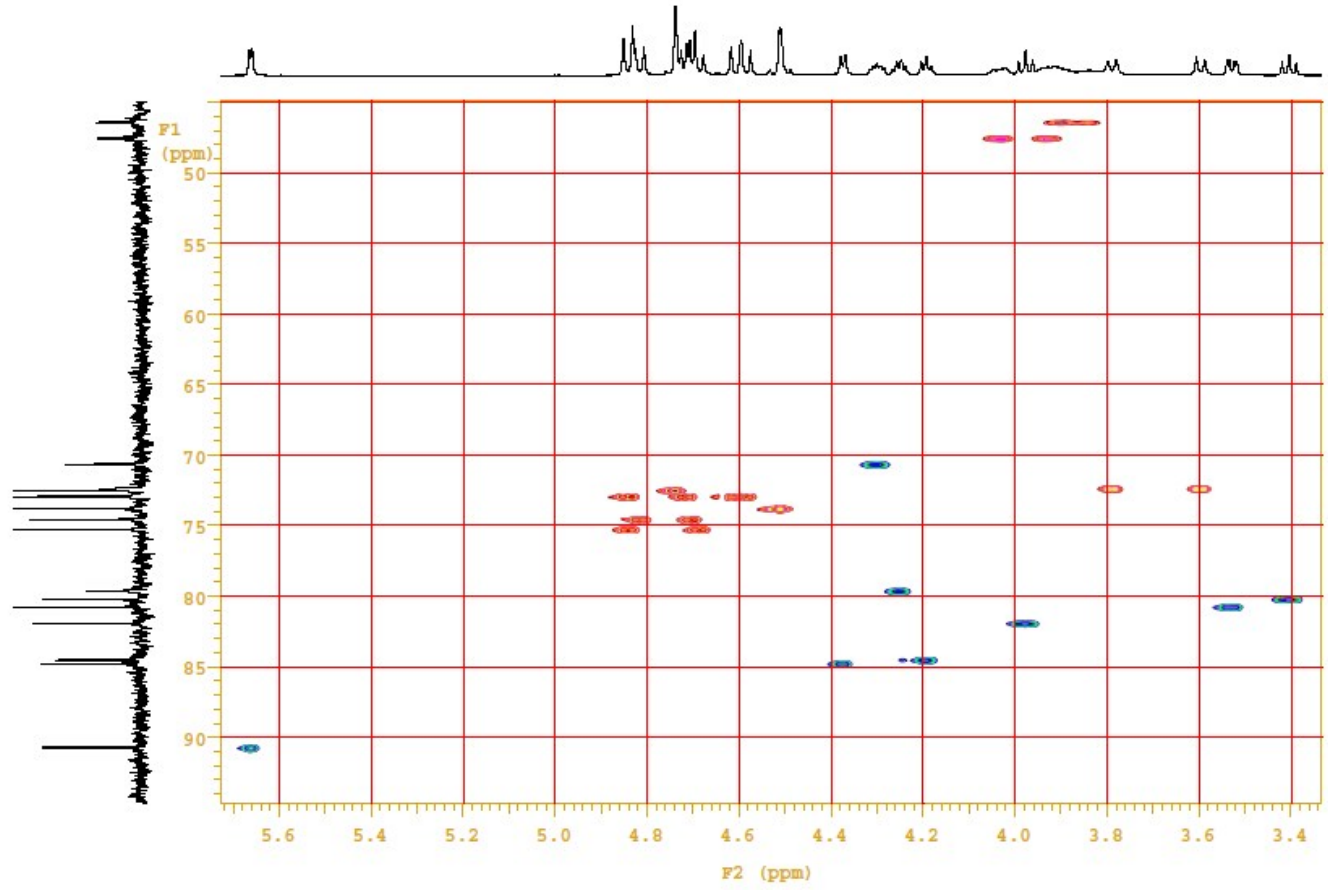


Fig. S3. HSQC (^{1}H-^{13}C) spectra of compound **2a** in DMF-d_6.

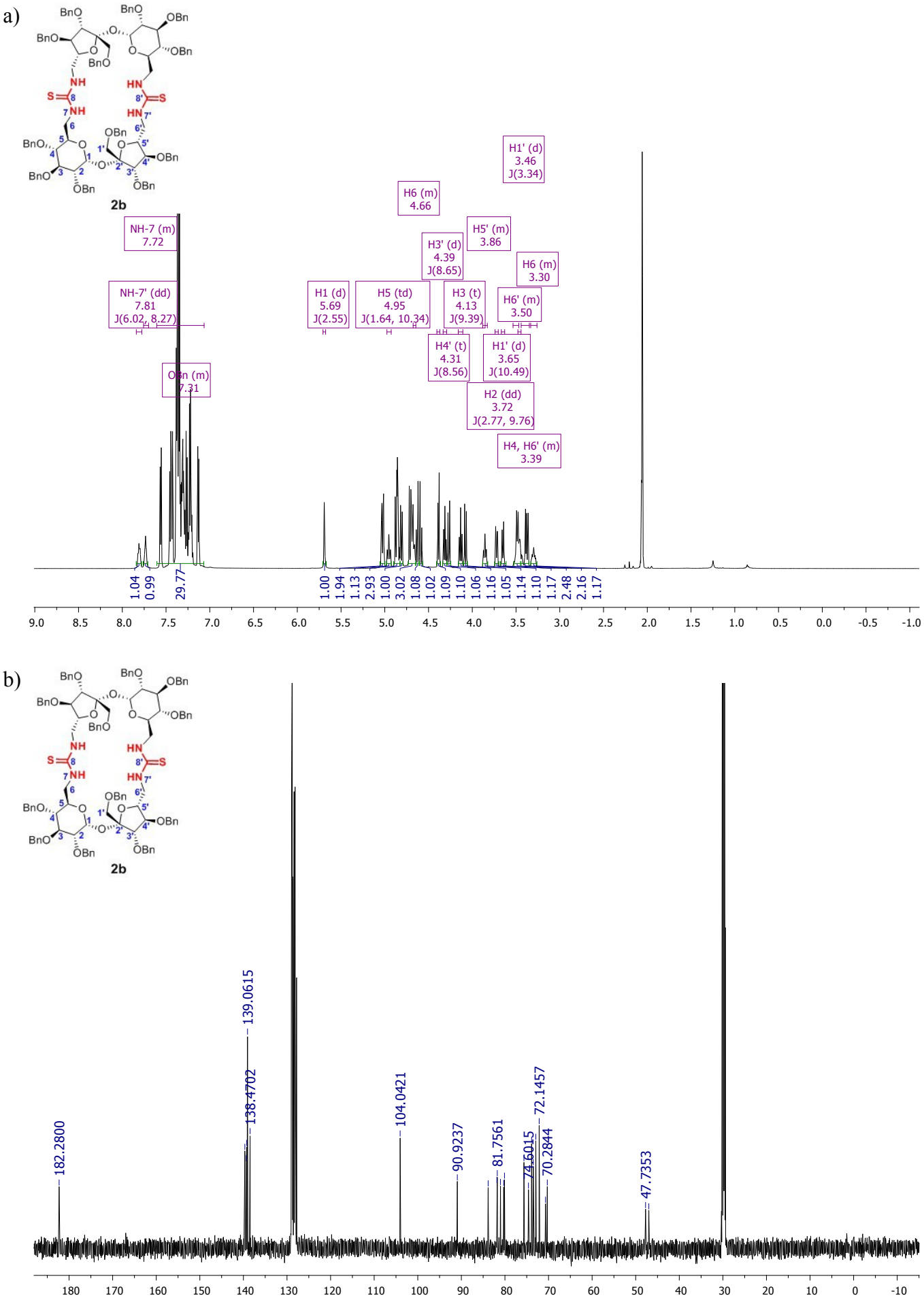
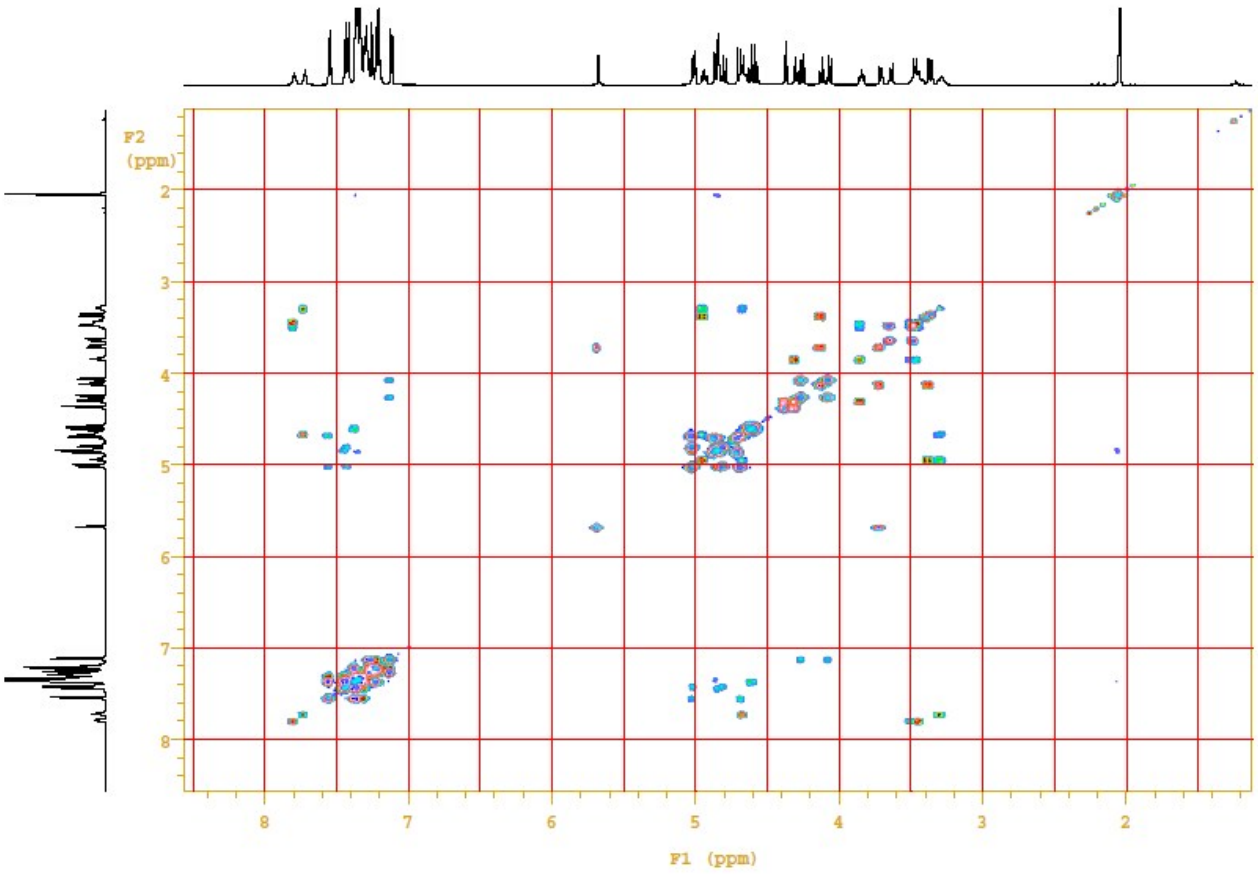


Fig. S4. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **2b** in acetone-d_6.

a)



b)

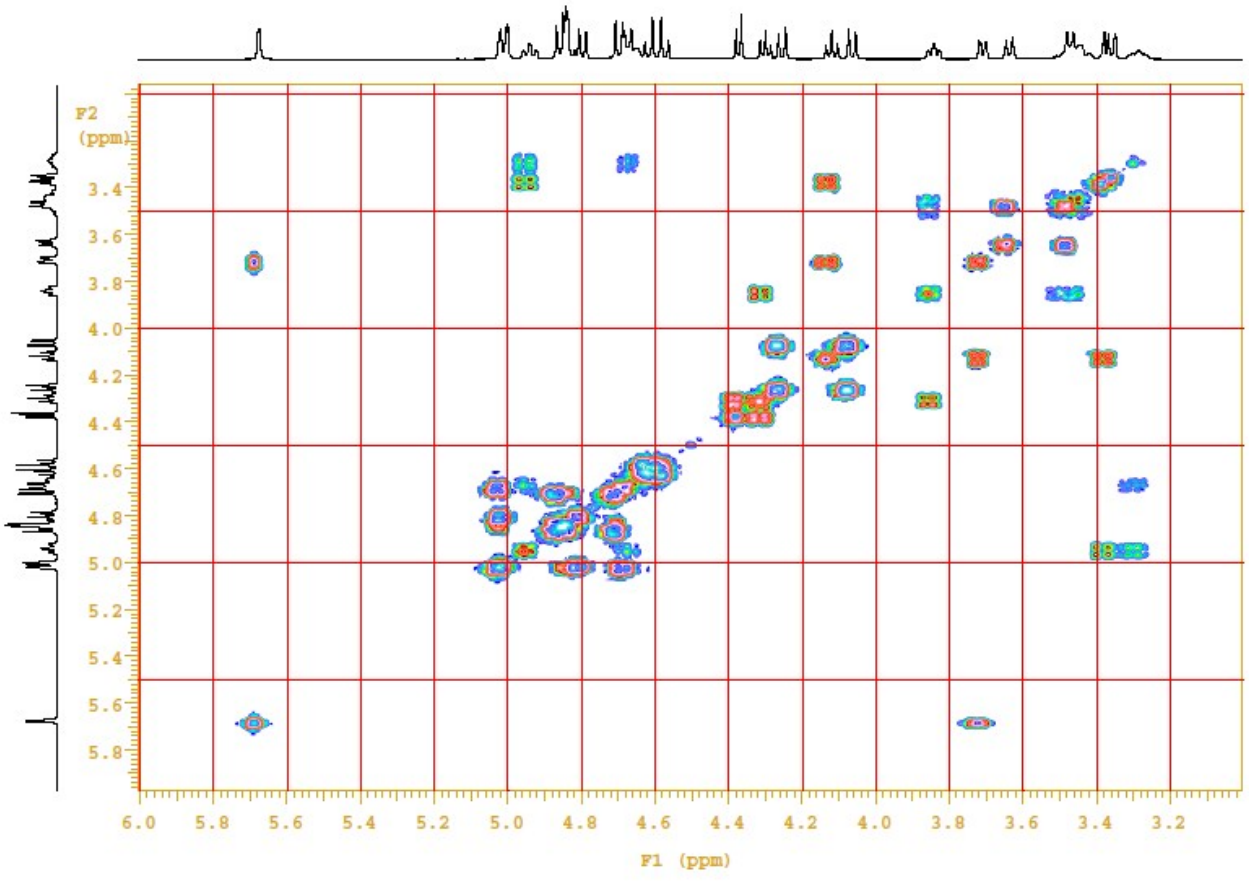
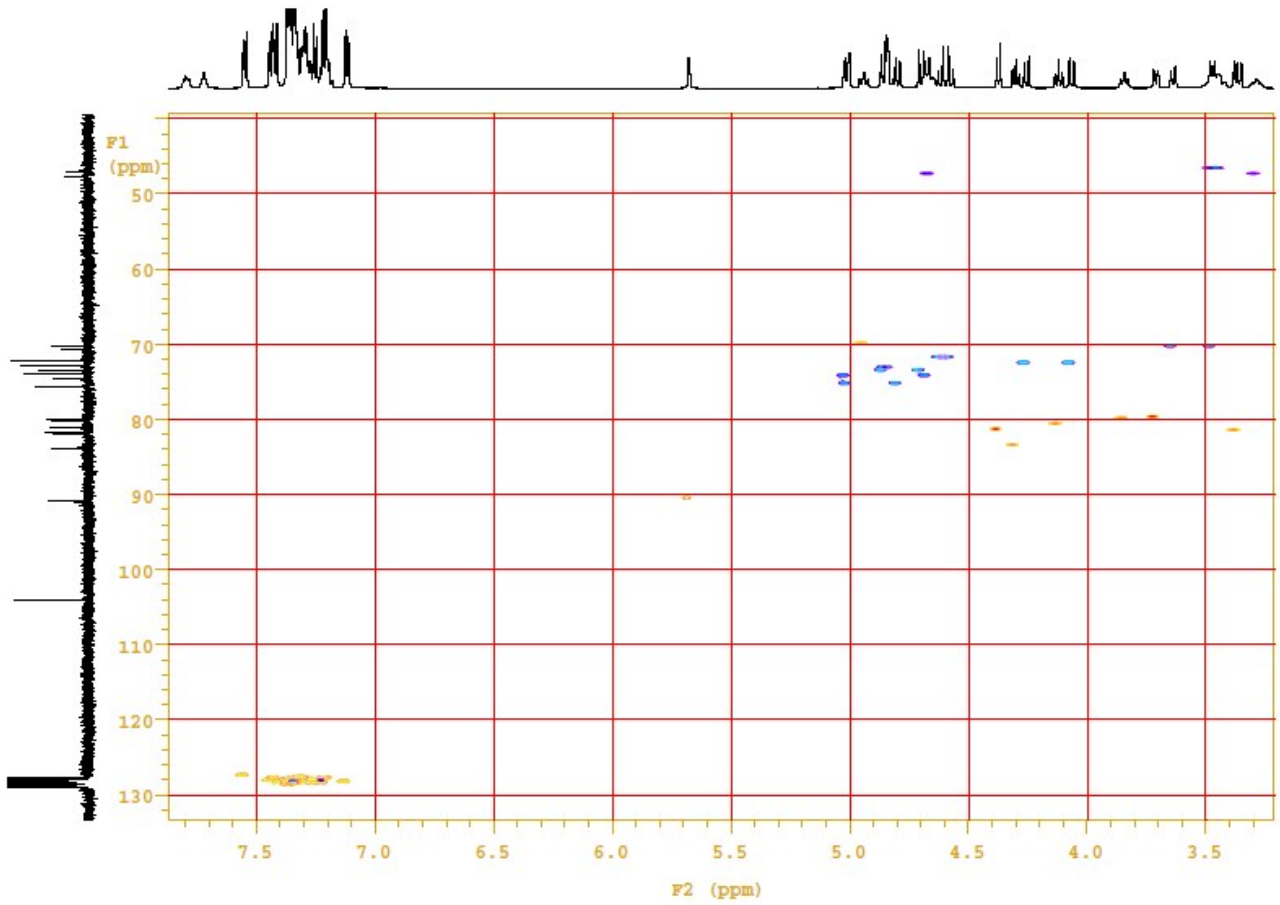


Fig. S5. COSY (^{1}H-^{1}H) spectra of compound **2b** in acetone-d_6.

a)



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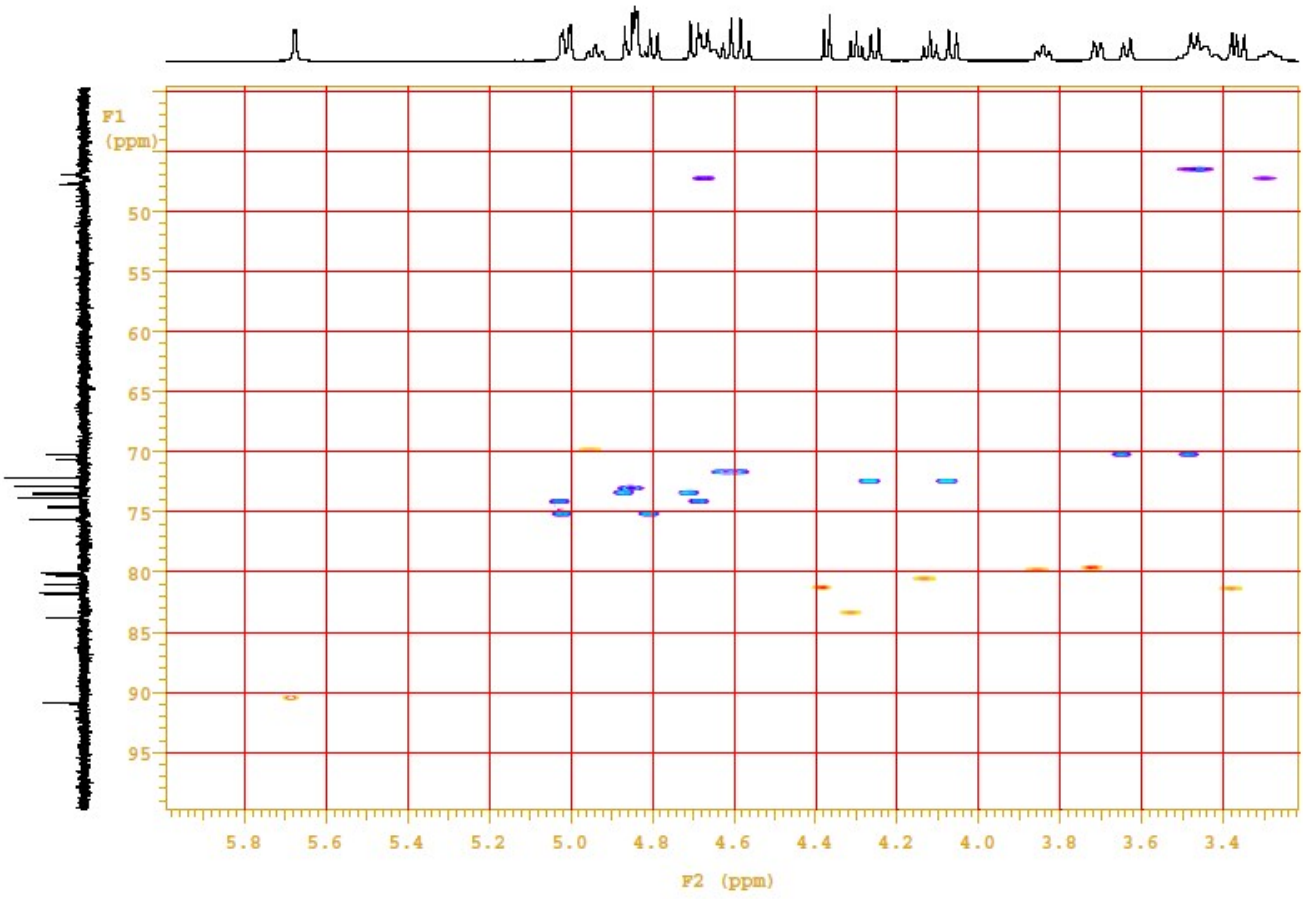


Fig. S6. HSQC (^{1}H-^{13}C) spectra of compound **2b** in acetone-d_6.

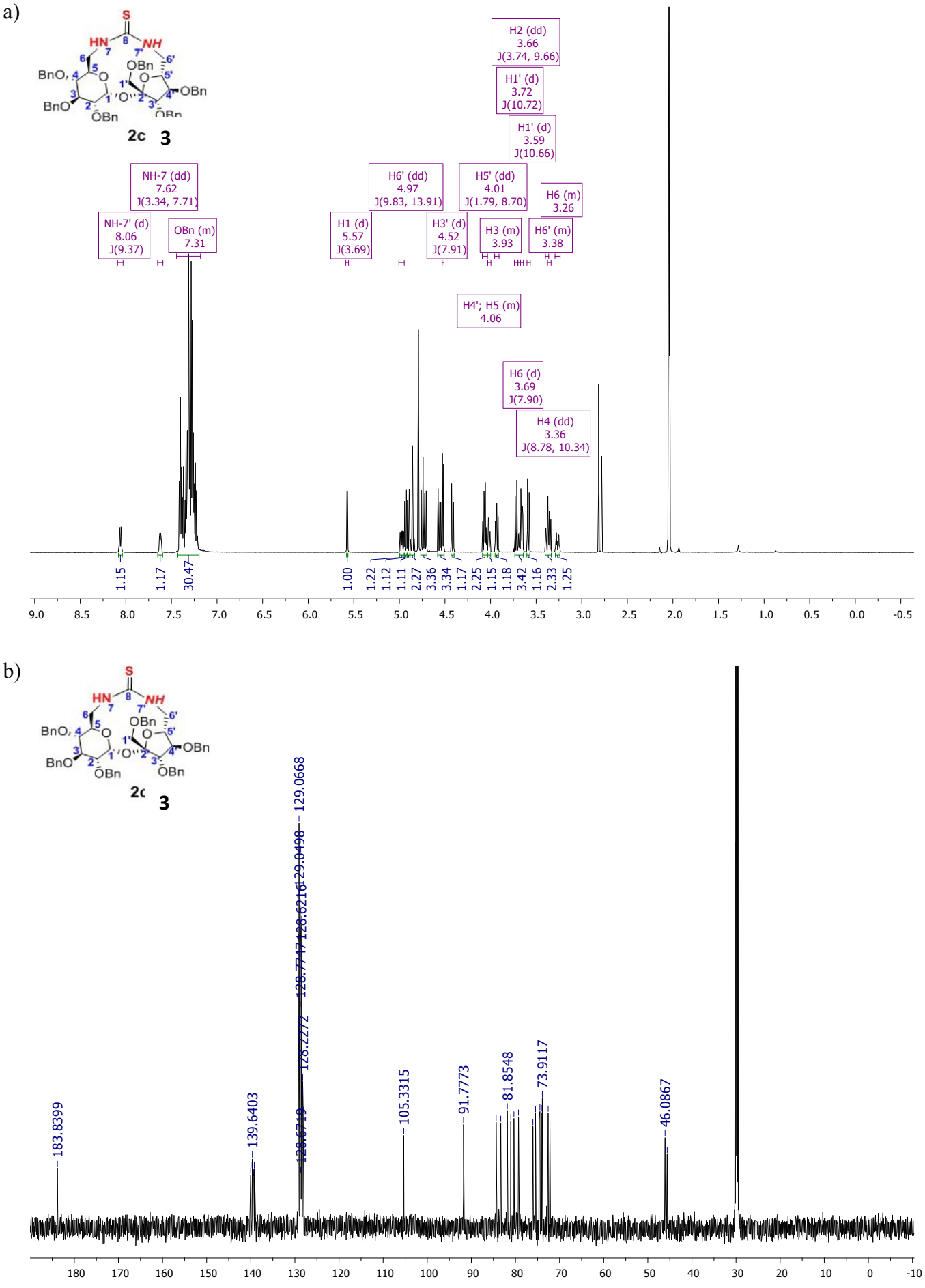
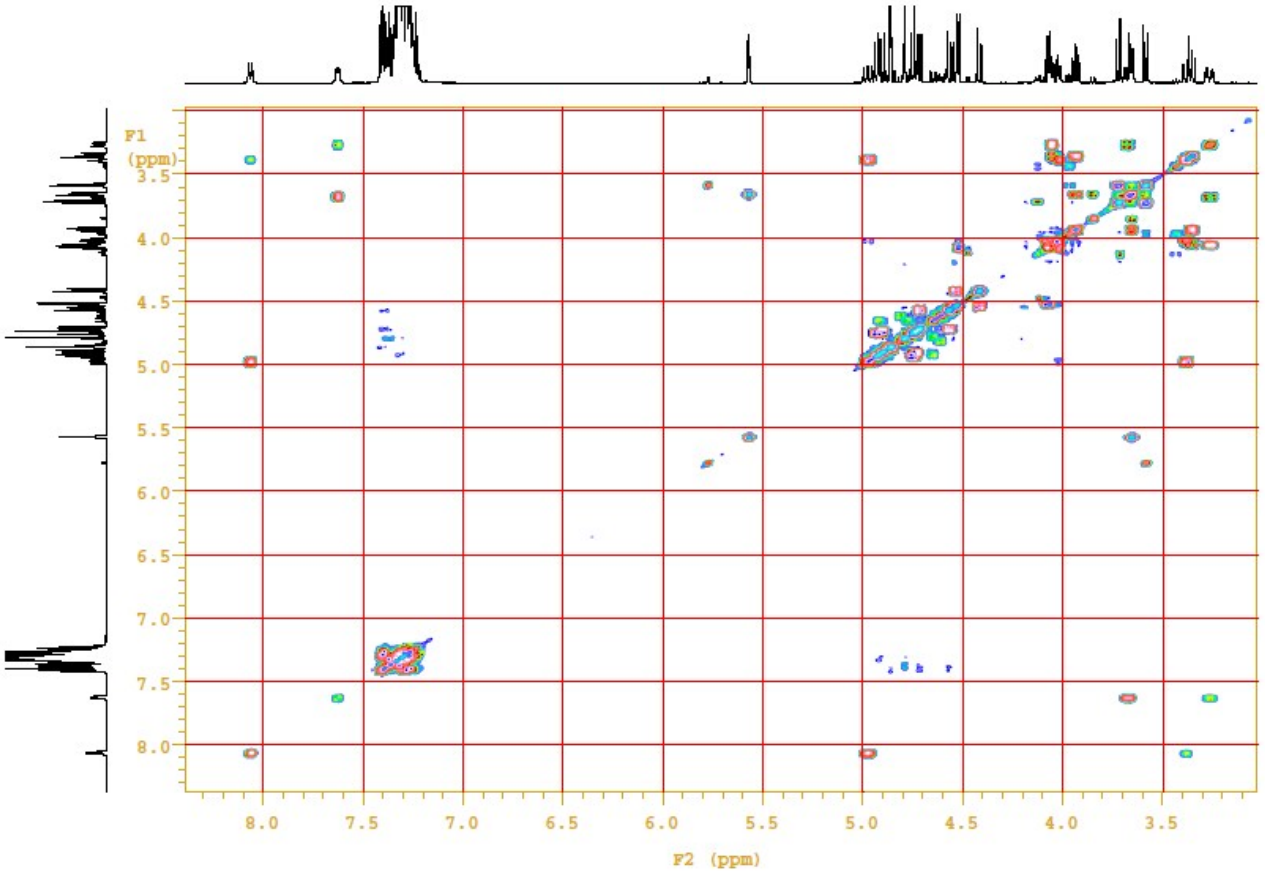


Fig. S7. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **3** in acetone-d_6.

a)



b)

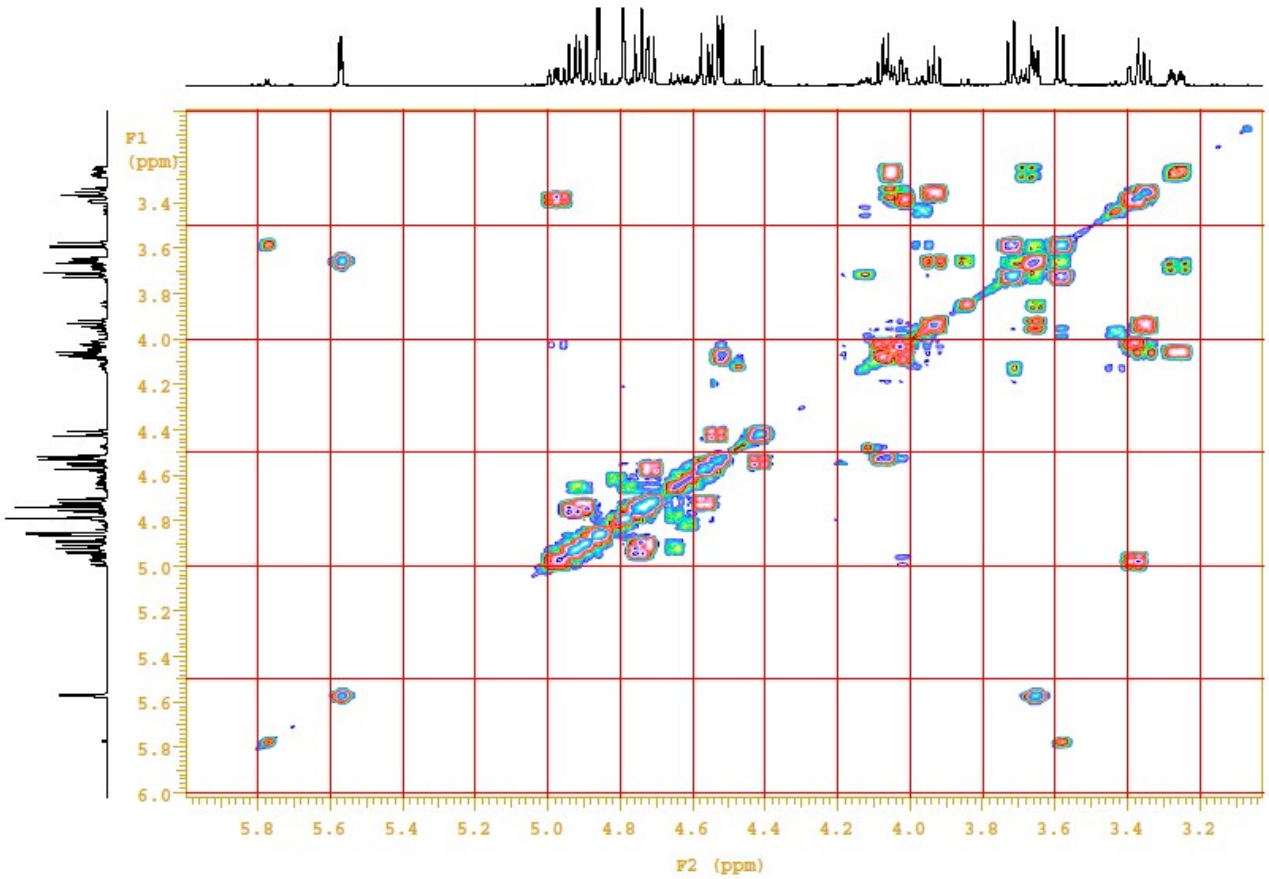
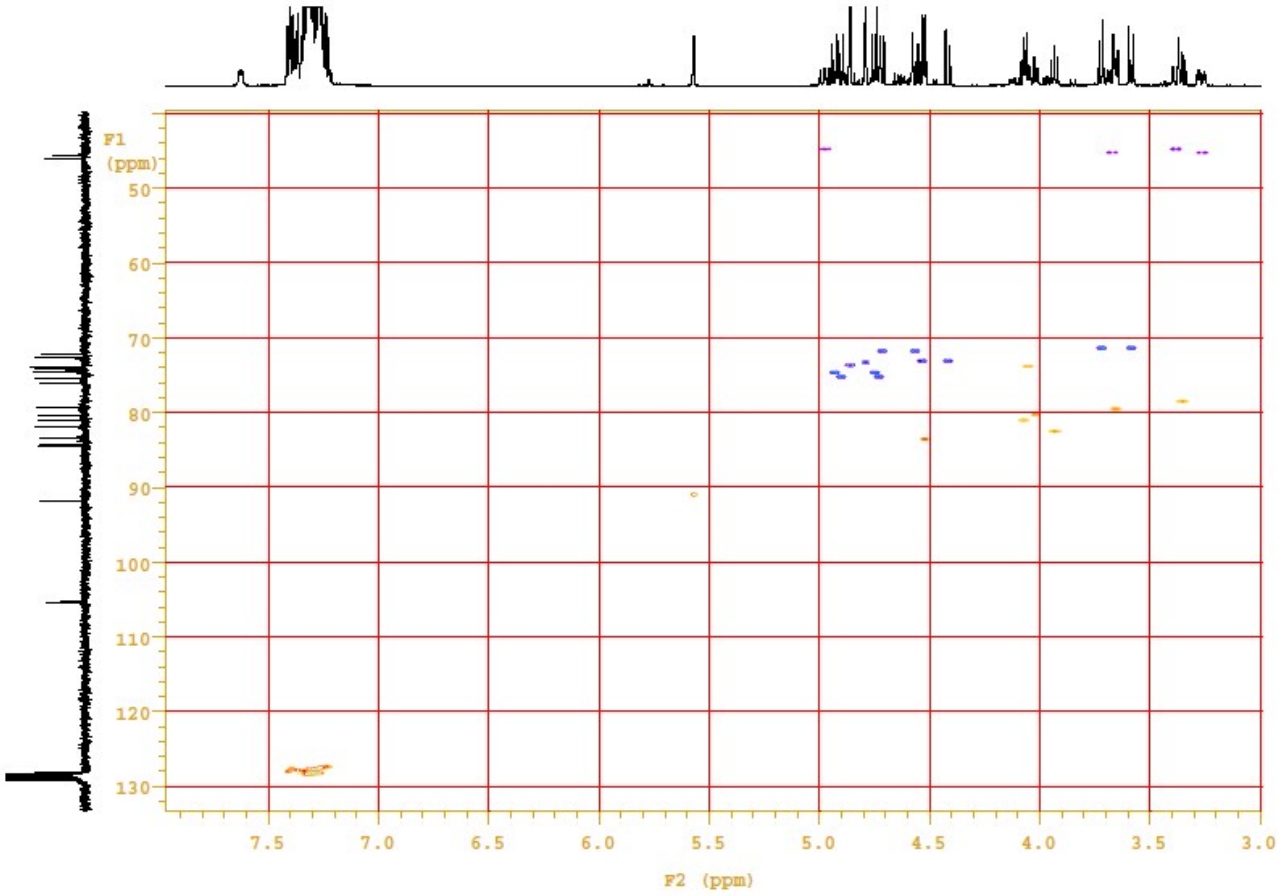


Fig. S8. COSY (^{1}H-^{1}H) spectra of compound **3** in acetone-d_6.

a)



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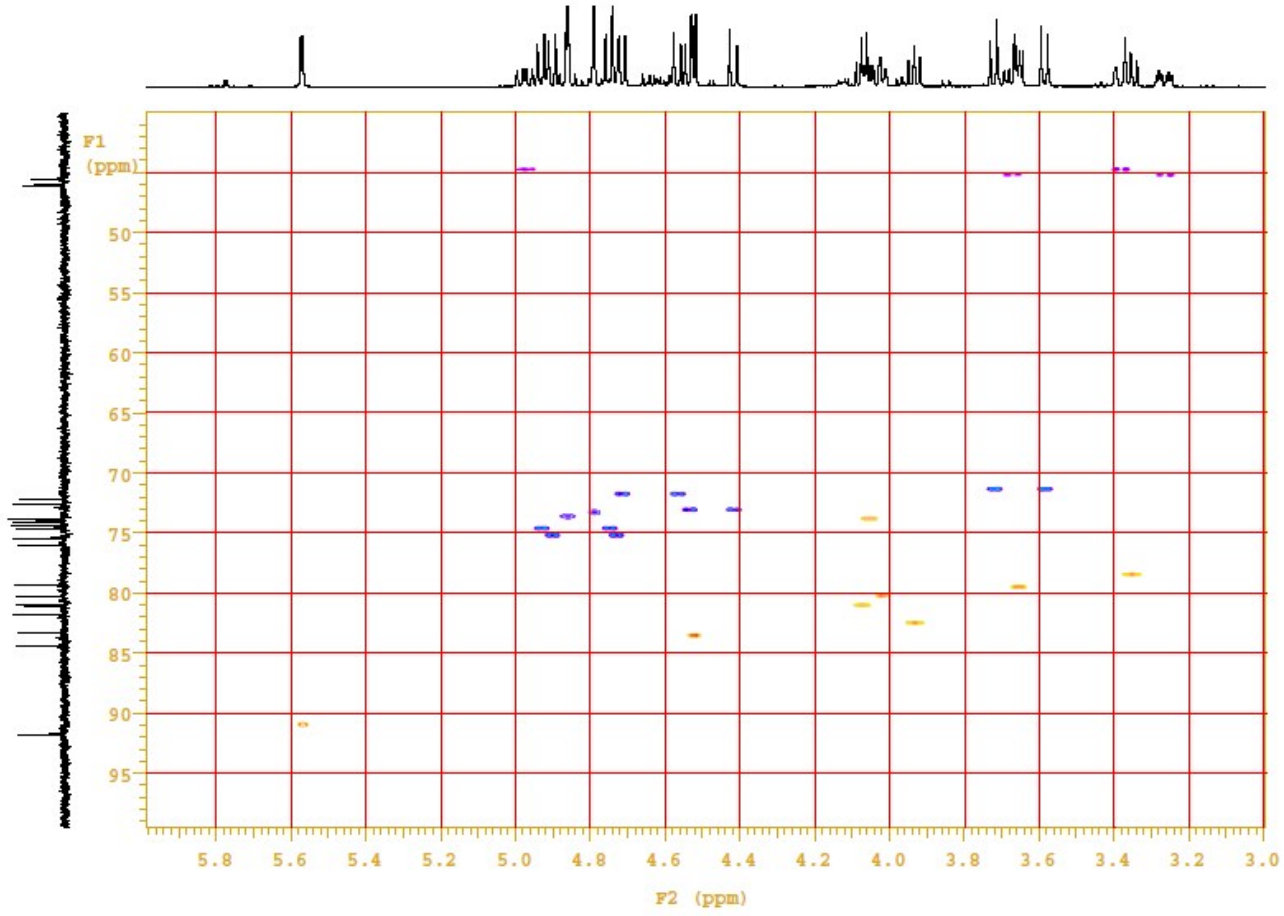

Fig. S9. HSQC (^{1}H-^{13}C) spectra of compound **3** in acetone-d_6.

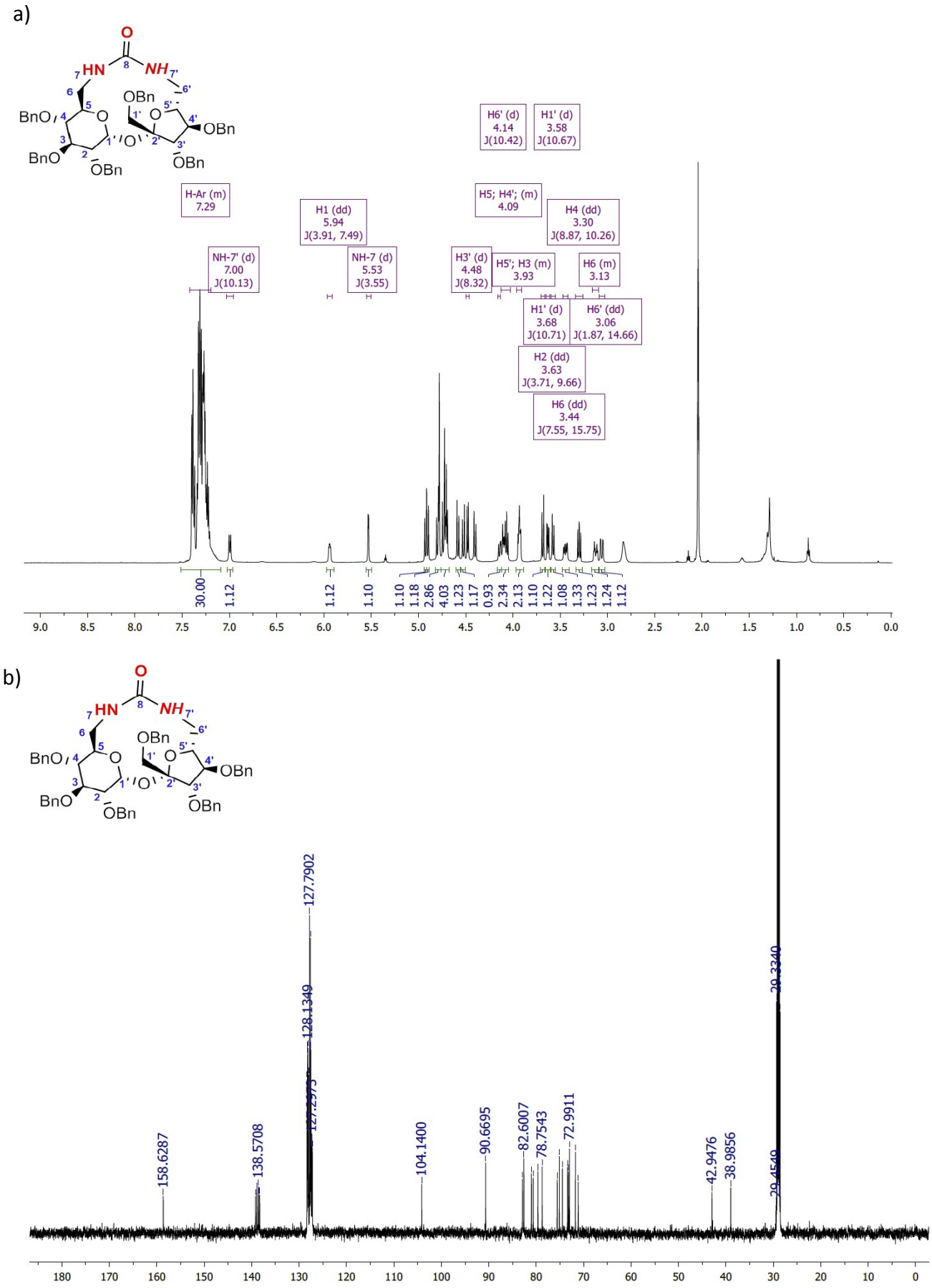

Fig. S10. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **3** in acetone-d_6.

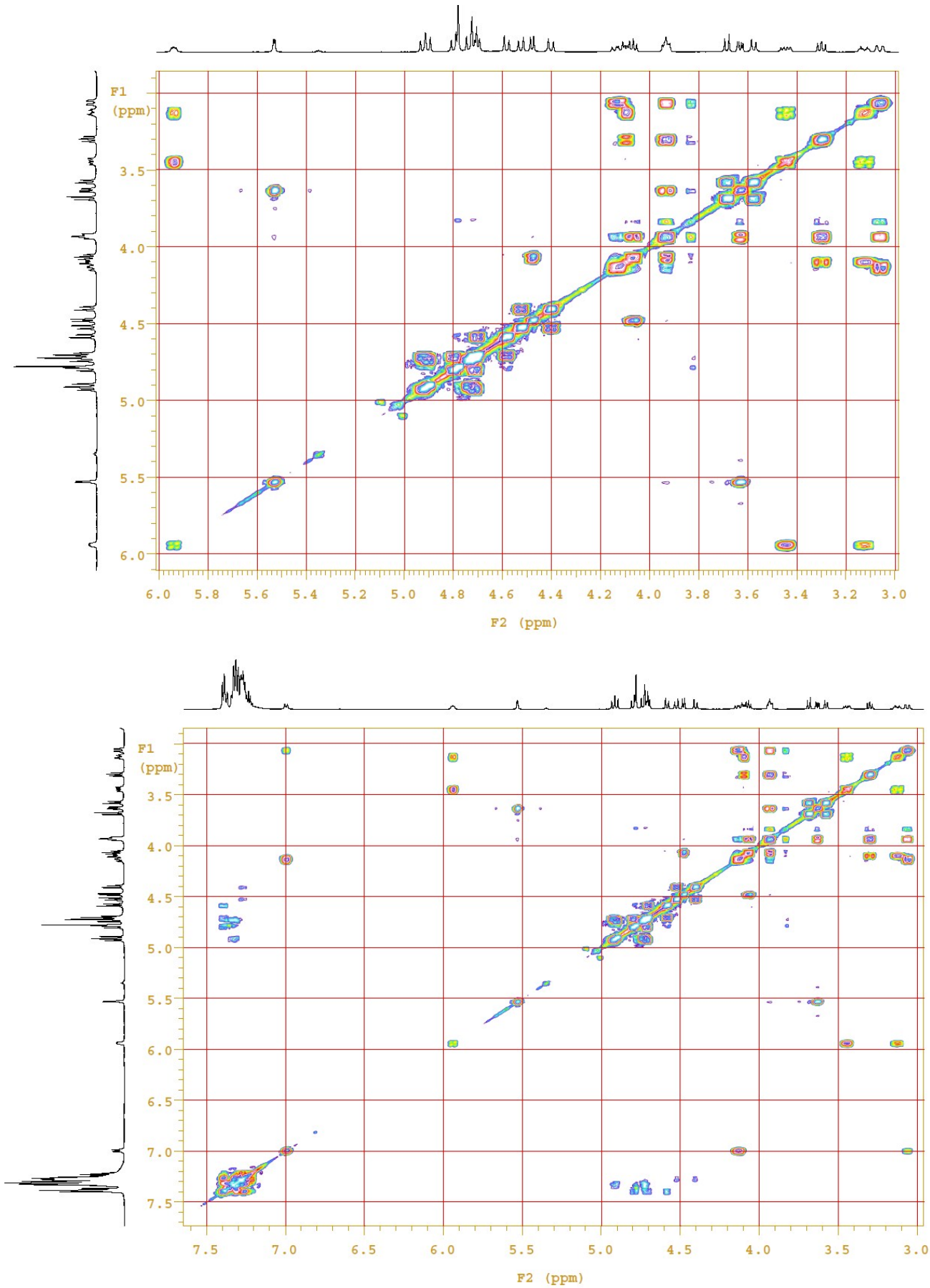

Fig. S11. COSY (^{1}H-^{1}H) spectra of compound **5** in acetone-d_6.

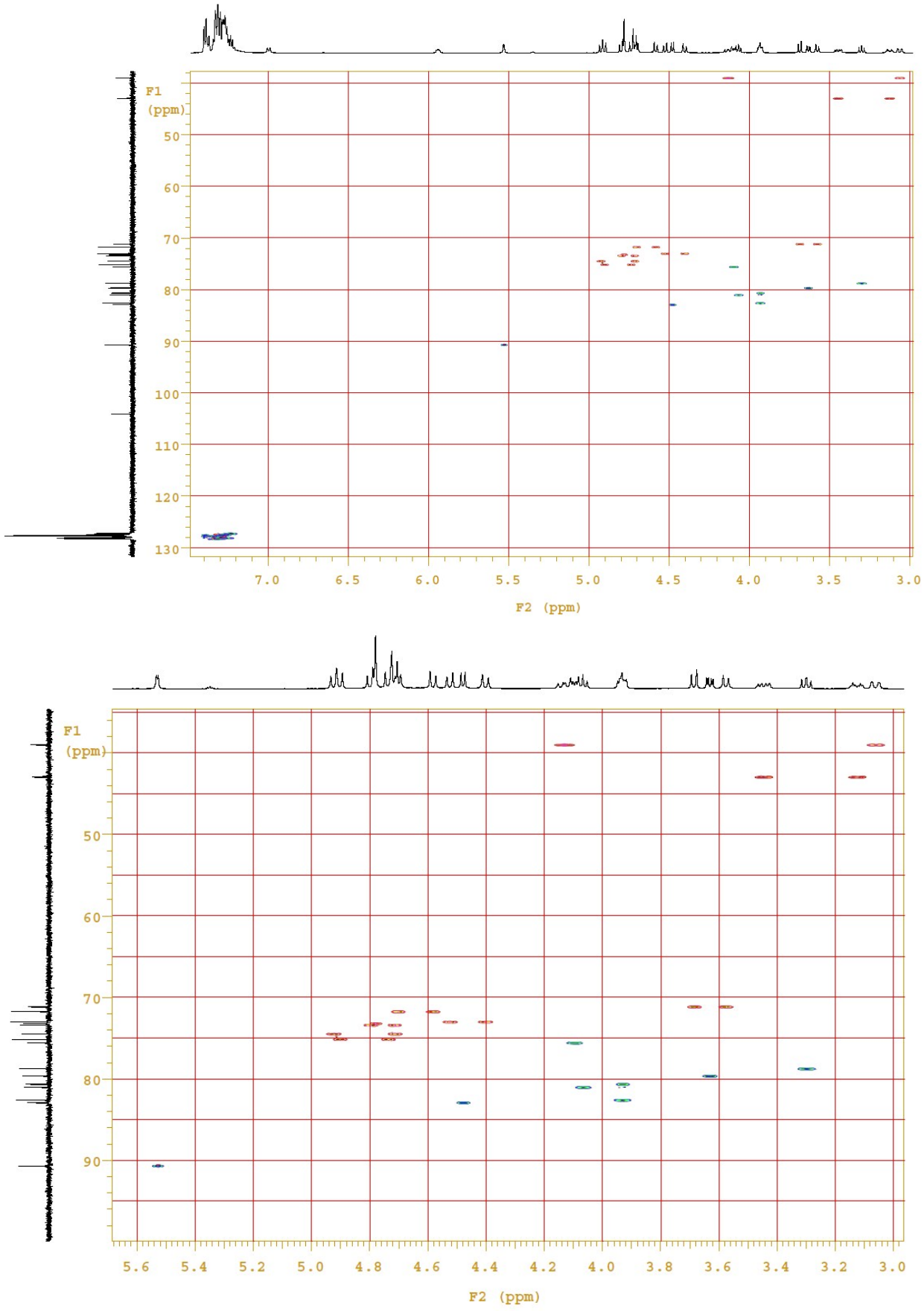

Fig. S12. HSQC (^{1}H-^{13}C) spectra of compound **5** in acetone-d_6.

3. Titration experiments

All solutions were prepared in the HPLC gradient-grade acetronitrile. TBA salts (TBACl, $TBAH_2PO_4$, $CH_3COOTBA$, and PhCOOTBA) were dried overnight at room temperature under high vacuum (1 mbar) directly before use. A 1 cm cuvette was filled with ~2.2 mL of the host solution and aliquots of the guest solution were added by a syringe pump. UV-Vis spectrum was recorded after each step once the mixture was homogenised by magnetic stirrer (30 s). The collected data were then analysed by HyperSpec. In case of hosts **3** and **5**, addition of guest had no effect on the spectra. In case of **2a** and **2b** the data were fitted with 1:1 and 1:1+1:2 models. Low values of the residuals are obtained with simple 1:1 model and no significant improvement in fitting quality is observed with 1:1+1:2 model. The residuals are most likely to arise from small errors in concentrations of the reagents. .

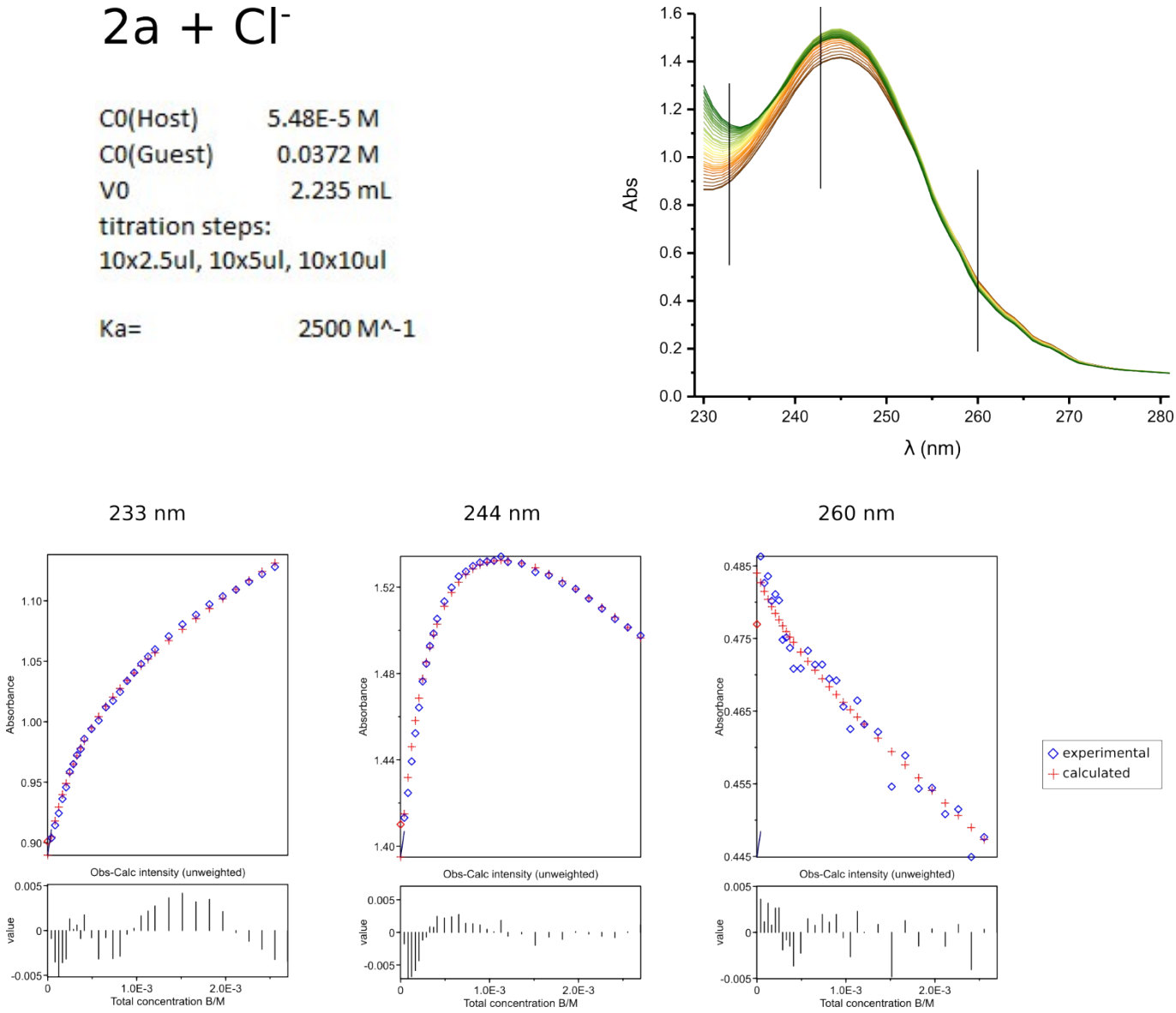

Fig. 13 Plots of UV-Vis titration of host **2a** with TBACl.

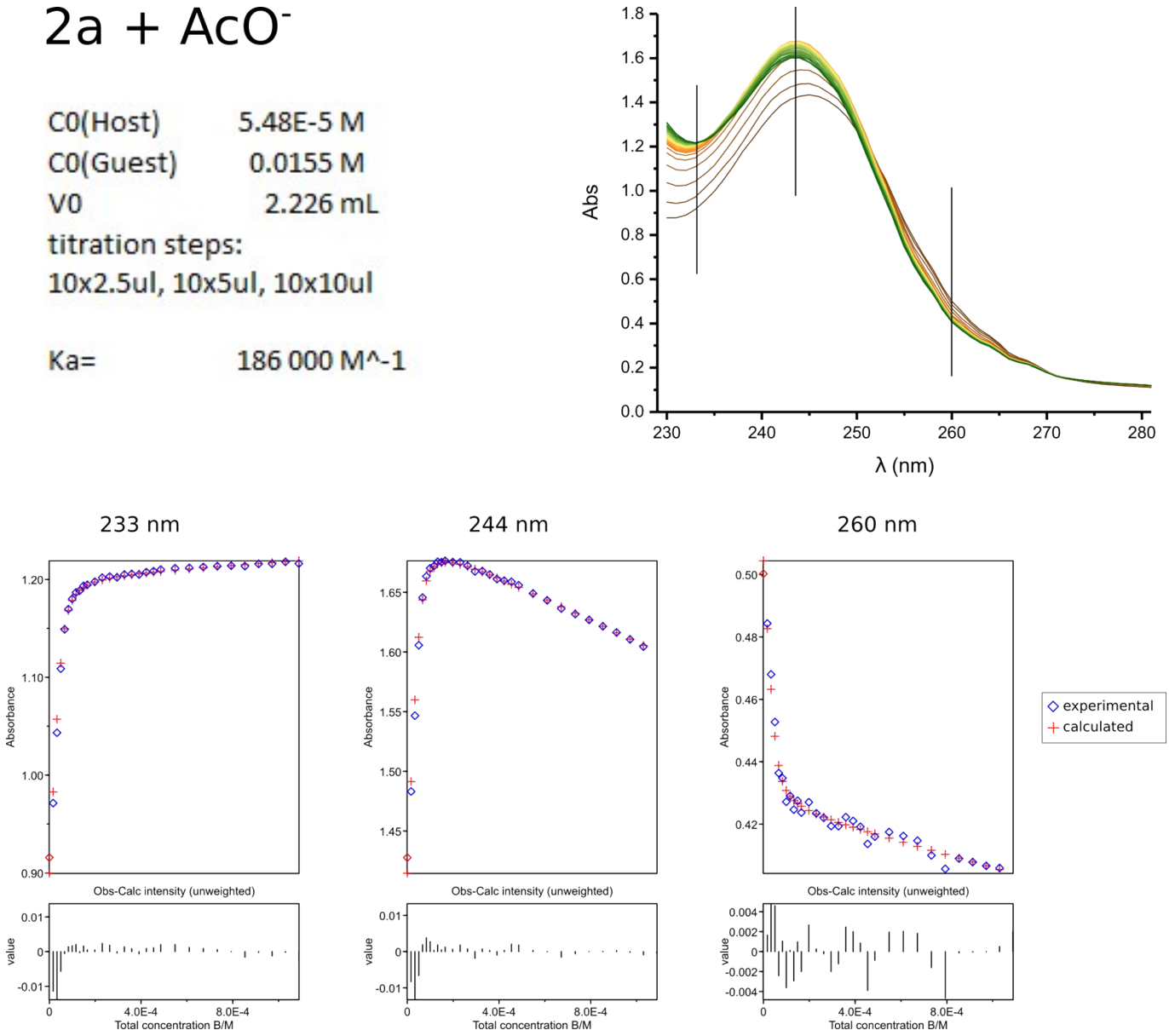

Fig. 14 Plots of UV-Vis titration of host **2a** with AcOTBA.

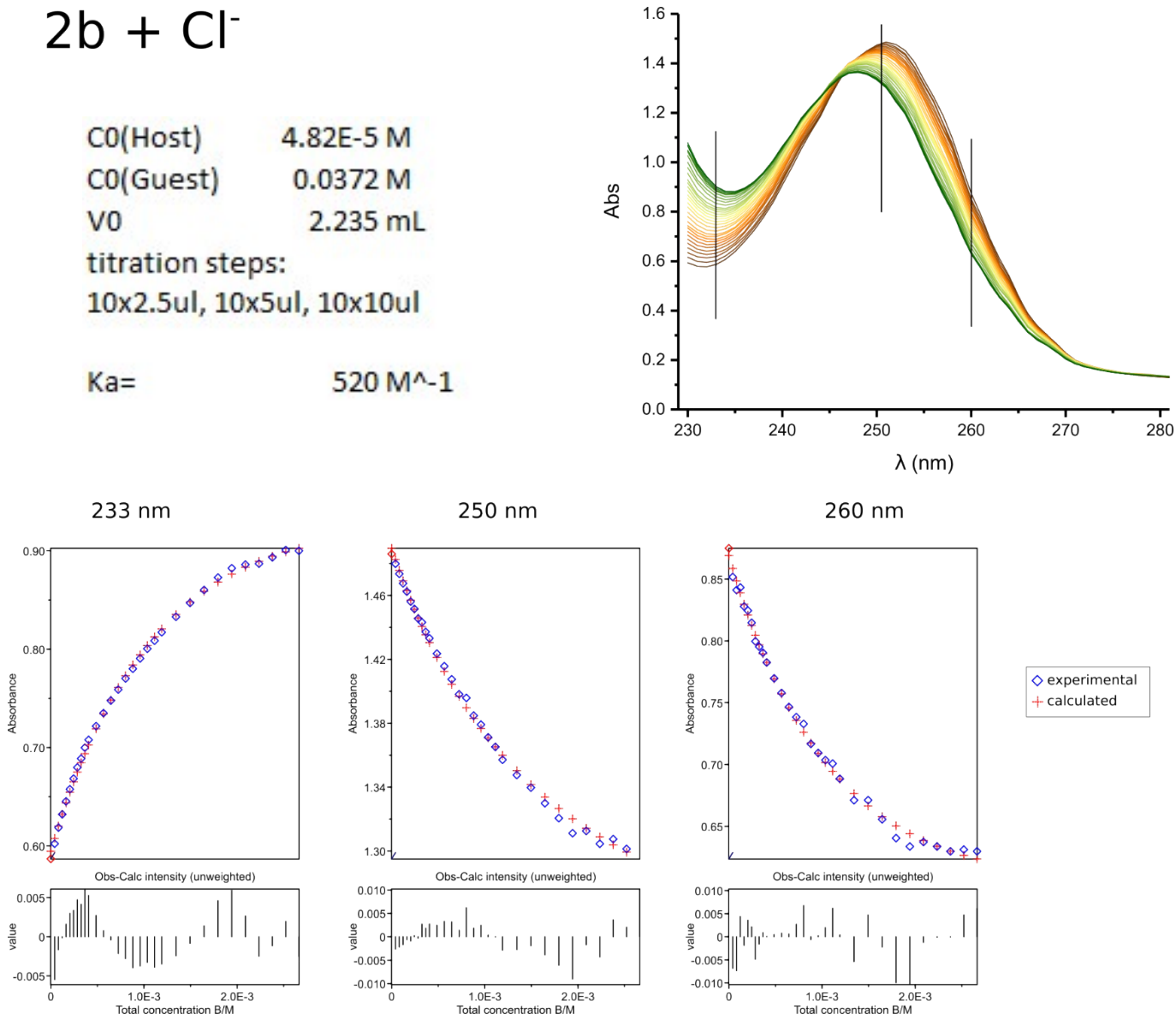

Fig. 15 Plots of UV-Vis titration of host **2b** with TBACl.

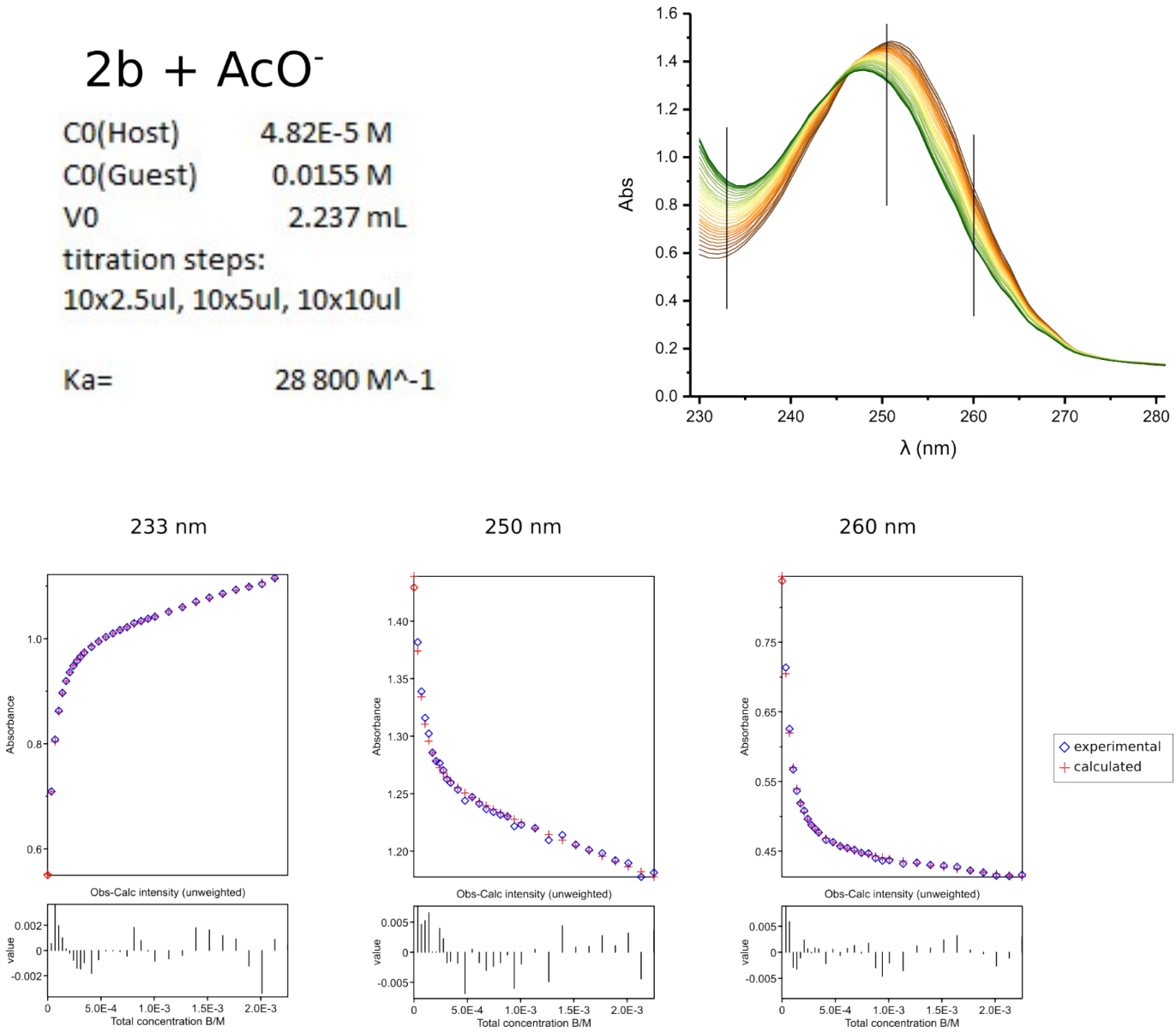

Fig. 16 Plots of UV-Vis titration of host **2b** with AcOTBA.

4. Single crystal X-ray measurement

Single crystal X-ray diffraction measurements were carried out on a Agilent Supernova diffractometer, at 100K with monochromated Mo Kα radiation (0.7107Å). The data reduction was made by using CrysAlisPRO [1] software. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares by using SHELXS97 and SHELXL97 [2]. All non-hydrogen atoms were refined as anisotropic while hydrogen atoms were placed in calculated positions, and refined in riding mode.

Crystal of 3. orthorhombic, P212121, a= 11.1611(7), b=18.4375(11), c= 23.2735(12)Å, V= 4789.3(5)Å^3, Z=4, D_{calc}=1.385g cm^{-1}, μ=1.782 mm^{-1}, R1=0.0635 for 6643 [Fo > 4σ(Fo)] and 0. 1075 for all data, wR2=0. 1795, S=0. 911

CCDC 1584391 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

5. References

[1] Agilent (**2011**). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.

[2] Sheldrick, G. M. (**2008**) *Acta Cryst*. A64 112-122.