

Supplementary Information For:

## The first supramolecular ion triplet complex

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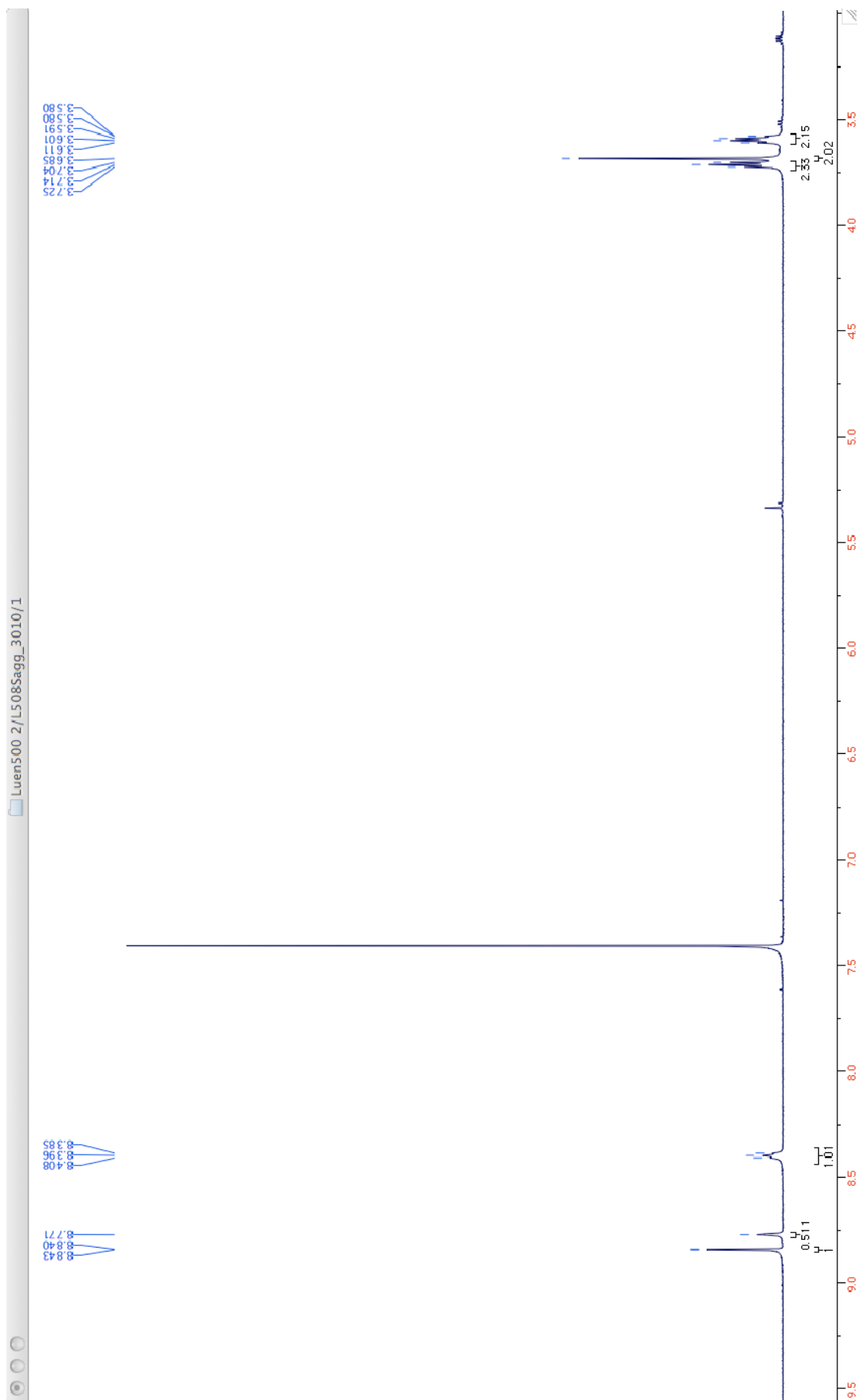
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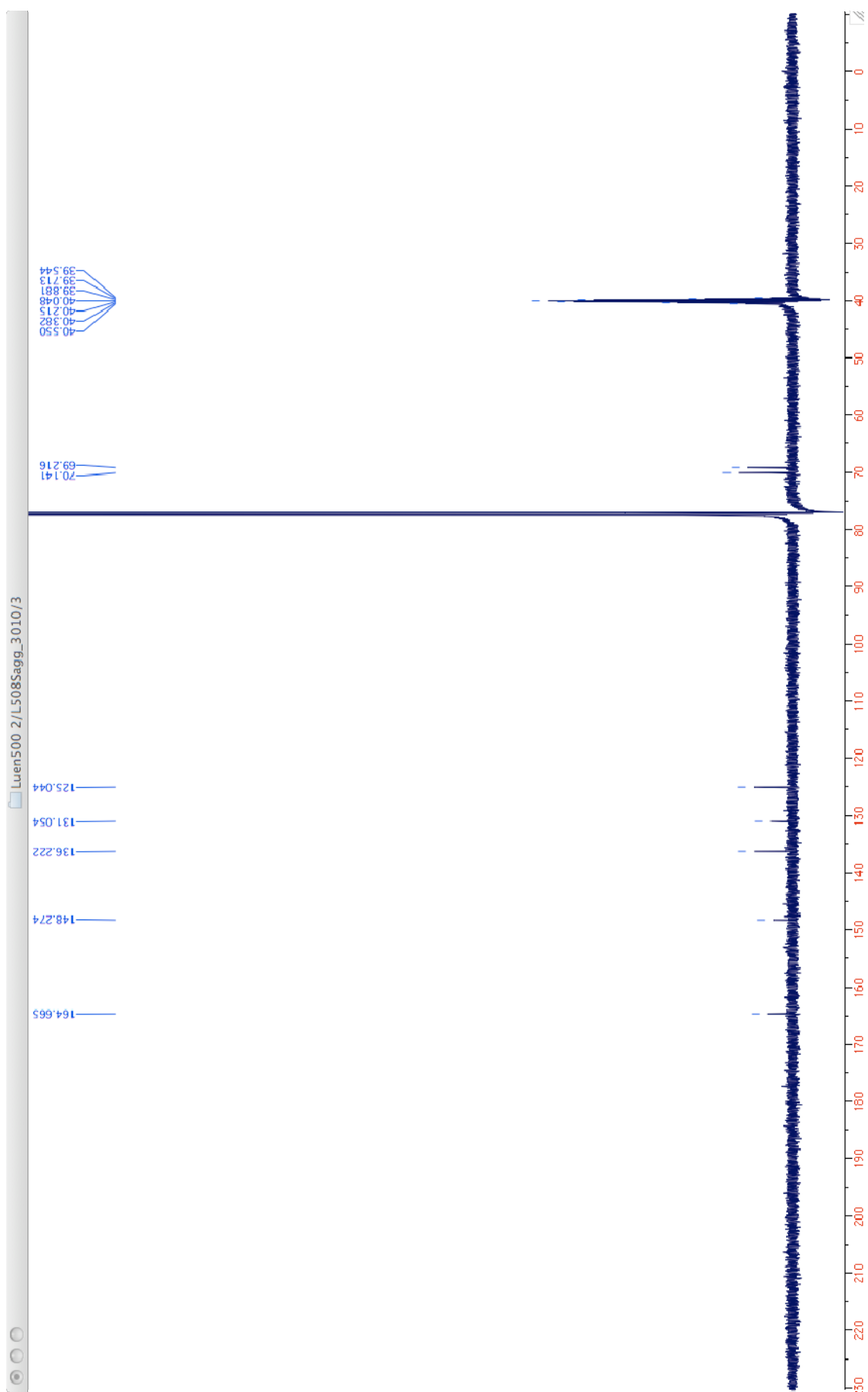
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## General Remarks

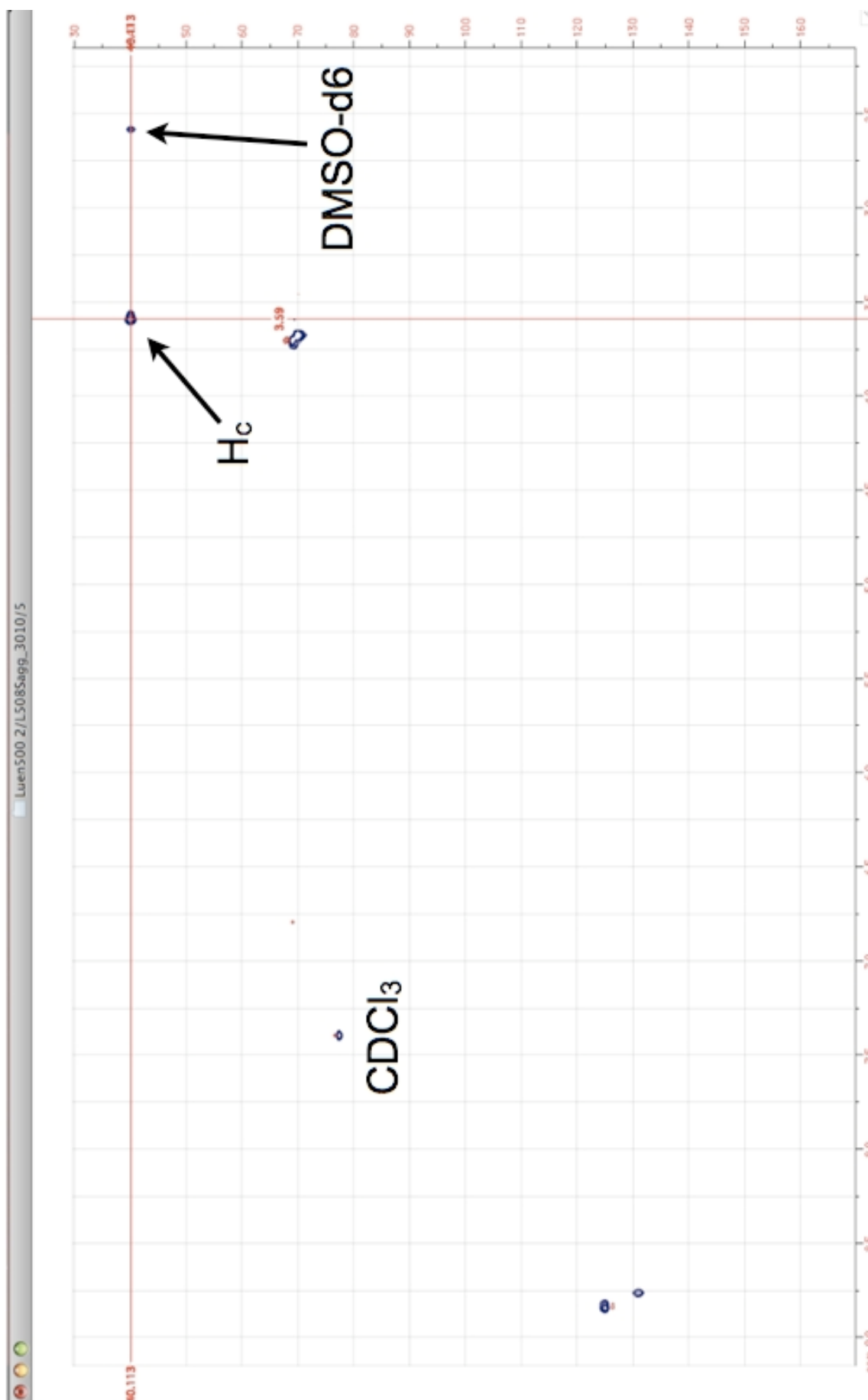
All reagents were obtained from commercial sources and used without additional purification unless otherwise indicated. 5-Nitroisophthaloyl dichloride was prepared from 5-nitroisophthalic acid and thionyl chloride according to Vögtle and De Cola.<sup>1</sup> 1,8-Diamino-3,6-dioxaoctane was obtained from Fluka. THF was freshly distilled from lithium aluminum hydride (triphenylmethane as indicator). All reactions were carried out in an atmosphere of nitrogen. NMR spectra were recorded with Bruker DRX 500 or AV 600 instruments. Assignments are supported by COSY, HSQC and HMBC. All chemical shifts are referenced to TMS. Mass spectra were recorded with a Finnigan MAT 8200 or MAT 8230. ESI mass spectra were recorded with an Applied Biosystems Mariner Spectrometry Workstation. IR spectra were recorded with a Perkin-Elmer Spectrum 100, equipped with an ATR unit. Elemental analyses were carried out with a EuroEA 3000 Elemental Analyzer from Euro Vector. MALDI-TOF spectra were recorded with a Bruker-Daltonics Biflex III. 4-Chloro- $\alpha$ -cyanocinnamic acid (Cl-CCA) was used as a matrix.



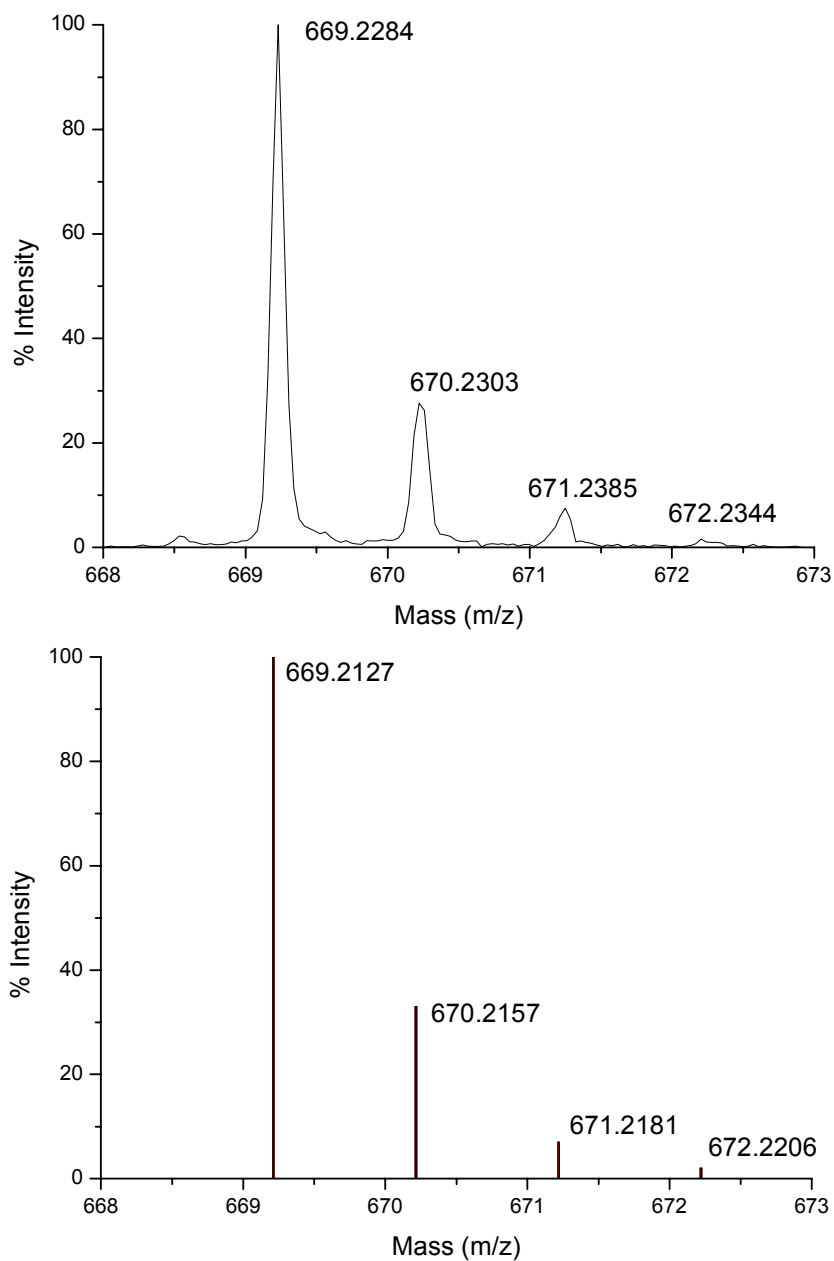
**Figure 1:**  $^1\text{H-NMR}$  (500 MHz; 298 K;  $\text{CDCl}_3/\text{DMSO-d}_6$  95:5 v/v; TMS) of **1**.



**Figure 2:**  $^{13}\text{C}$ -NMR (125 MHz, 298 K,  $\text{CDCl}_3/\text{DMSO-d}_6$  95:5 v/v, TMS) of **1**.



**Figure 3:** HSQC of **1**. The CH<sub>2</sub>NH carbon is overlapping with DMSO-d6 carbons.



**Figure 4:** Measured (top) and predicted (bottom): ESI-MS spectra (positive mode) of **1** ( $C_{28}H_{34}N_6O_{12}+Na^+$ ).

## **<sup>1</sup>H-NMR Experiment**

8.0 mg (1.2 μmol) of **1** was dissolved in 5.0 mL of a mixture of CDCl<sub>3</sub>/DMSO-d<sub>6</sub> (95:5, v/v). 600 μL of this stock solution was then transferred into different NMR tubes containing various excess of salts. The tubes were fluxed with nitrogen, capped and sealed with PARAFILM<sup>®</sup>. The NMR spectra were recorded after 12 h.

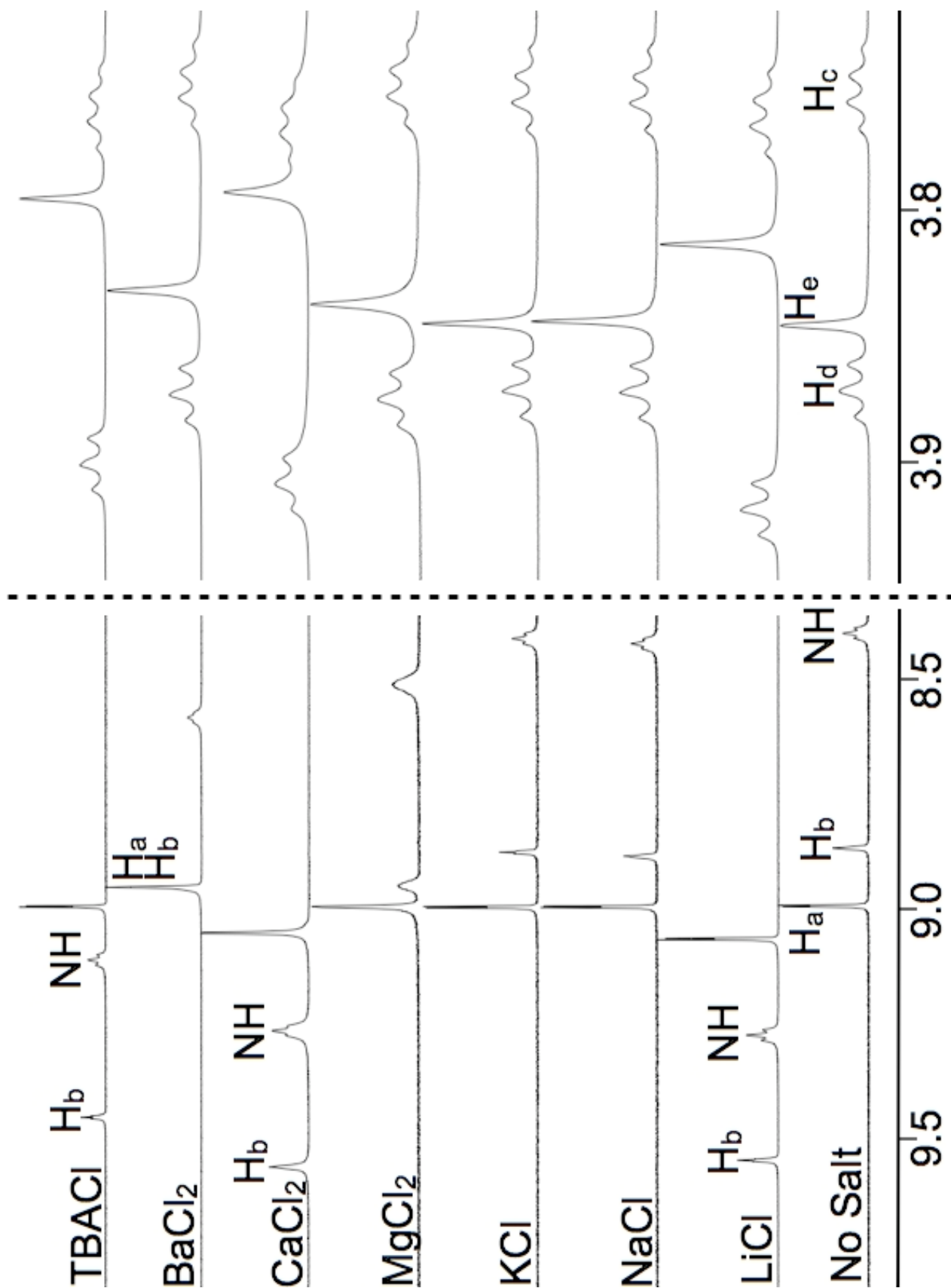
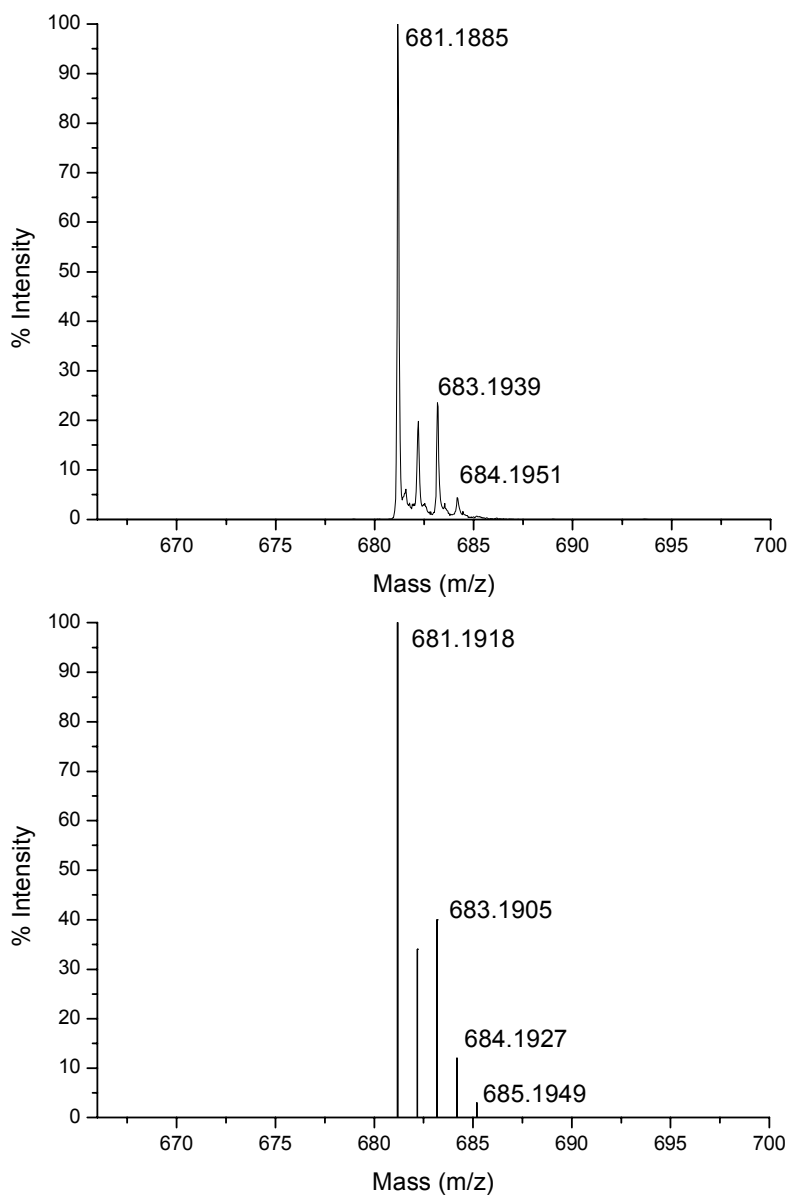


Figure 5:  $^1\text{H-NMR}$  spectra in presence of different salts.

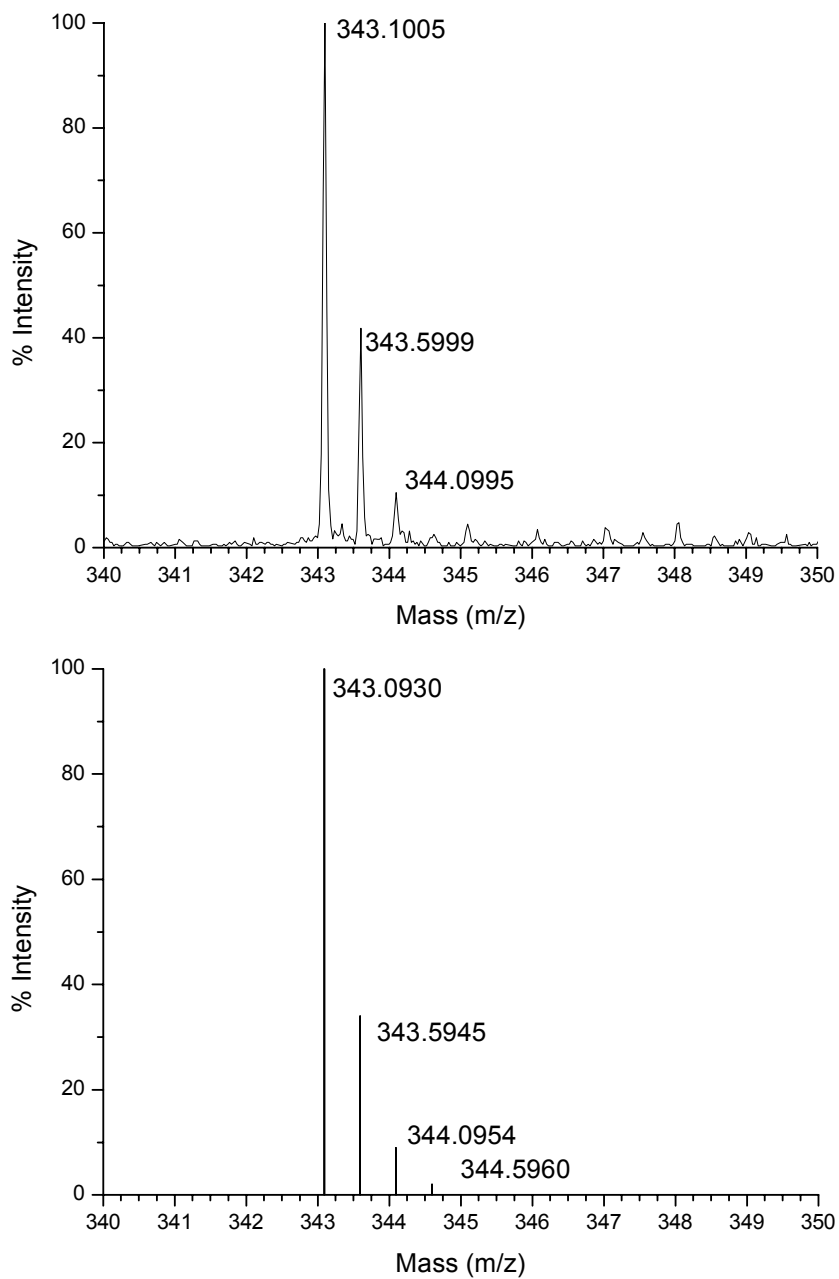


## MS experiments :

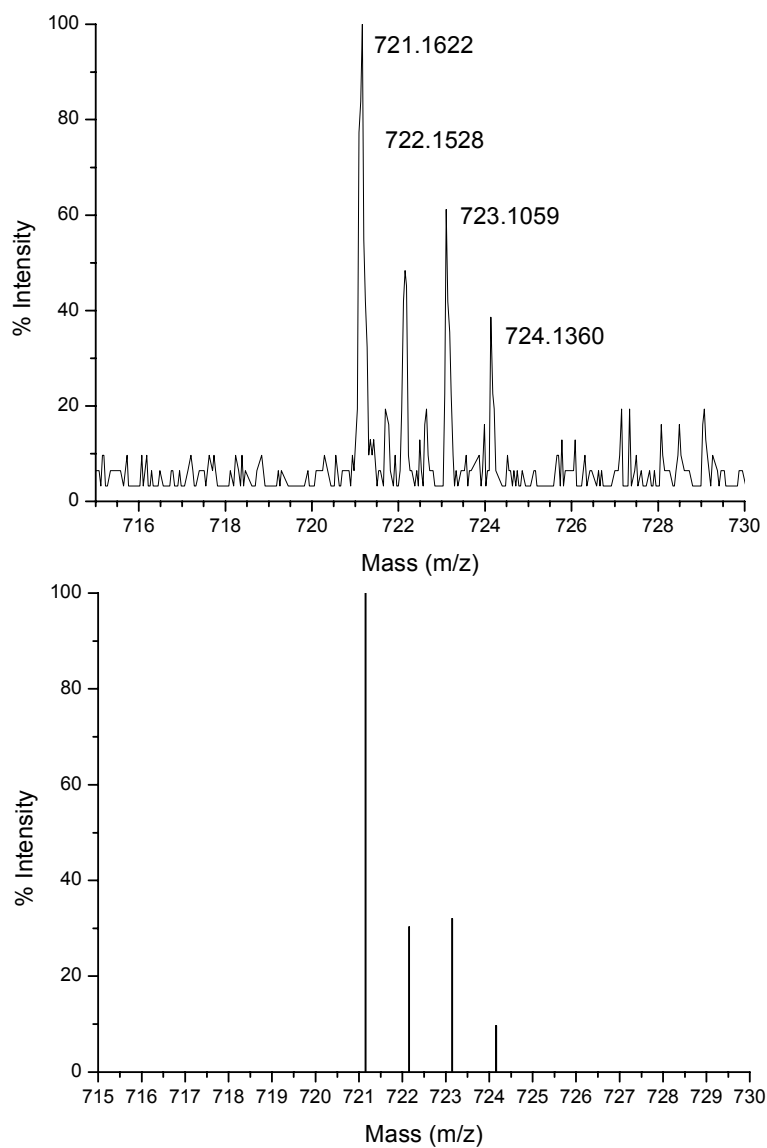
Directly from the NMR tubes, a drop of solution was used to carry out the mass spectrometry experiments.



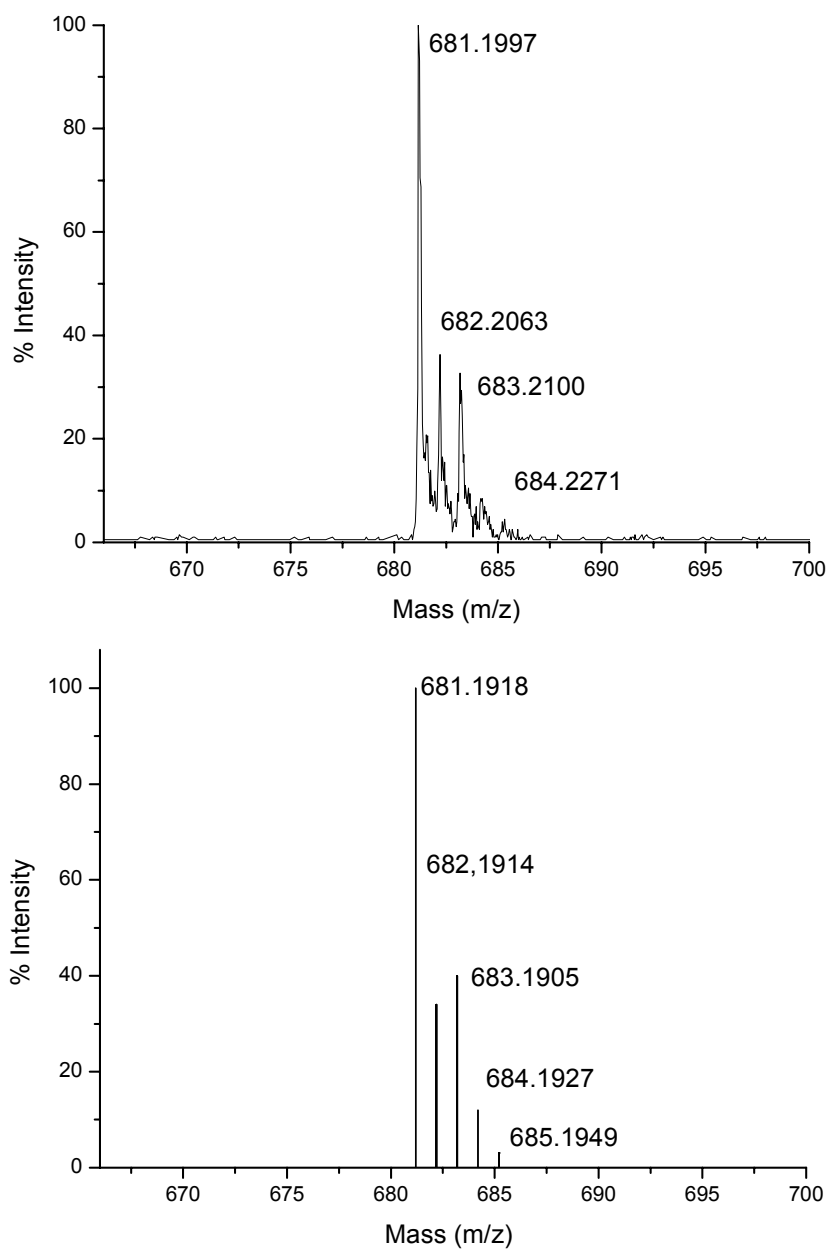
**Figure 6:** Measured (top) and predicted (bottom): ESI-MS spectra (negative mode) of  $1 \cdot \text{CaCl}_2$  ( $\text{C}_{28}\text{H}_{34}\text{N}_6\text{O}_{12} + \text{Cl}^-$ ).



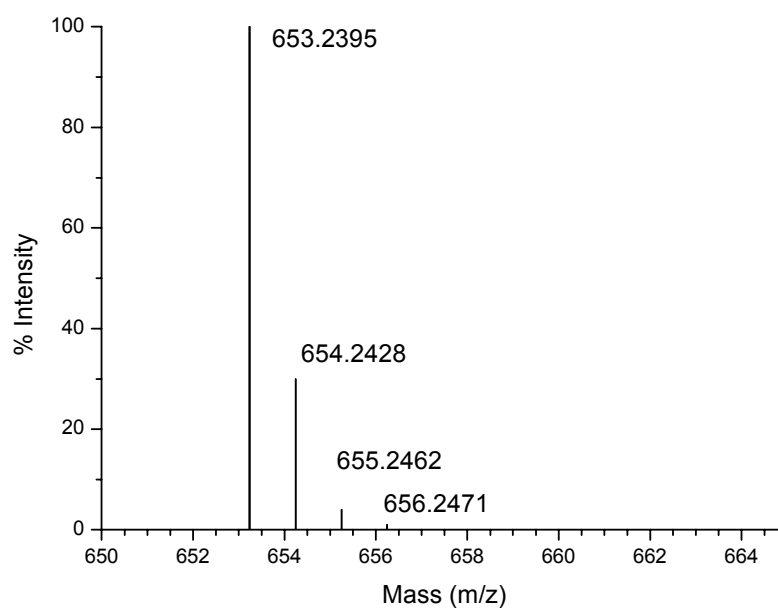
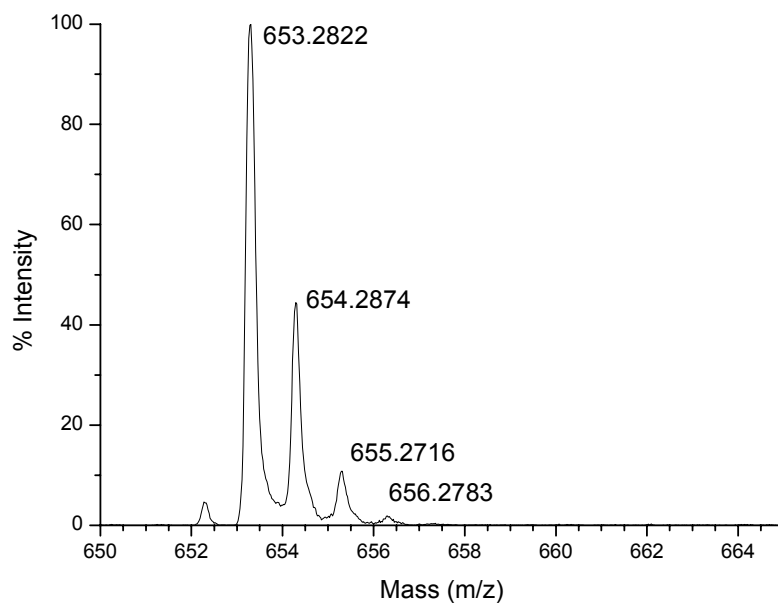
**Figure 7:** Measured (top) and predicted (bottom): ESI-MS spectra (positive mode) of  $1 \cdot \text{CaCl}_2$  ( $\text{C}_{28}\text{H}_{34}\text{N}_6\text{O}_{12} + \text{Ca}^{2+}/2$ ).



**Figure 8:** Measured (top) and predicted (bottom): ESI-MS spectra (positive mode) of  $1 \cdot \text{CaCl}_2$  ( $\text{C}_{28}\text{H}_{34}\text{N}_6\text{O}_{12} + \text{CaCl}^+$ ).



**Figure 9:** Measured (top) and predicted (bottom): ESI-MS spectra (negative mode) of  $1 \cdot \text{LiCl}$  ( $\text{C}_{28}\text{H}_{34}\text{N}_6\text{O}_{12} + \text{Cl}^-$ ).



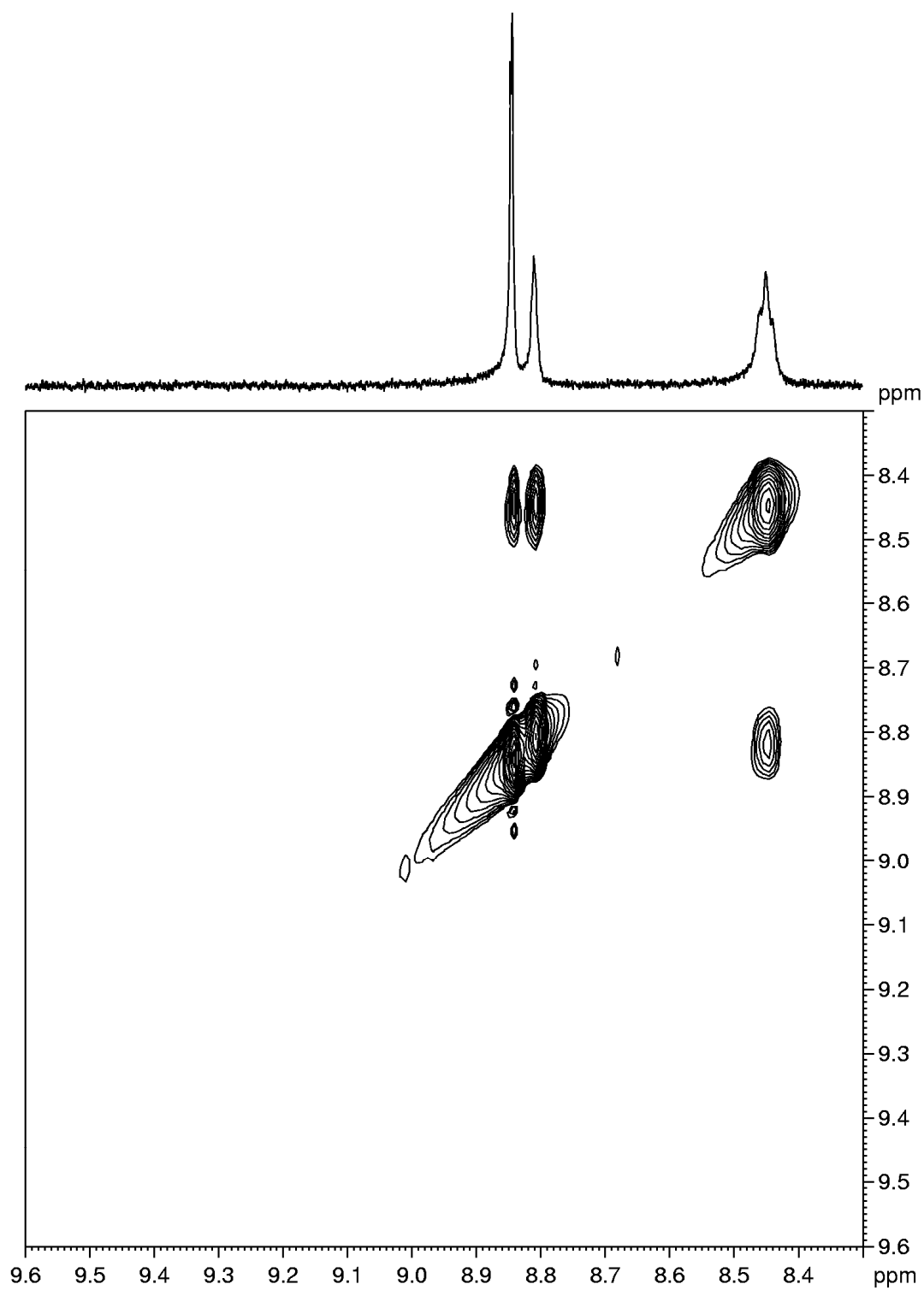
**Figure 10:** Measured (top) and predicted (bottom): MALDI-TOF spectra (CI-CCA) of 1-LiCl ( $C_{28}H_{34}N_6O_{12}+Li^+$ ).

## **2D-NOESY experiments:**

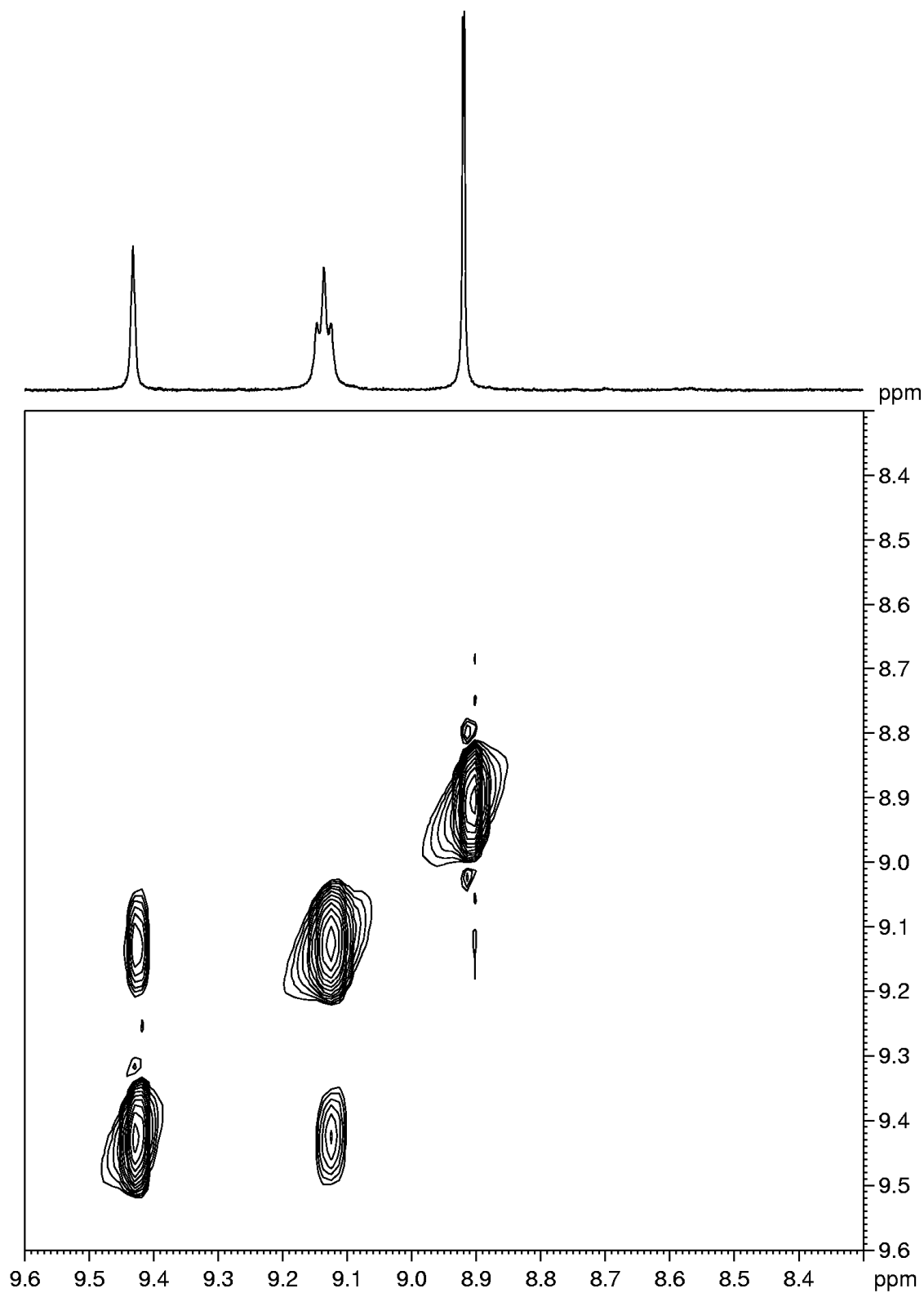
Using the NMR samples prepared as described above, phase sensitive 2D-NOESY experiments were acquired at 298 K with mixing times of 300 and 600 ms on a Bruker DRX500 instrument.

Spectra were acquired with 8 scans and a repetition delay of 2 sec, spectral widths of 4300 Hz, and 2048/128 total data points in F2 and F1 dimensions, respectively.

The data was zero-filled in F1 to 1028 real data points, weighted in both dimension with 90°-shifted squared sinebell function. Cross peaks were integrated after baseline correction. The obtained peak volumes were converted into distances using a two-spin approximation. For intensity calibration, the constant distance of H<sub>a</sub>-H<sub>b</sub> was used as a reference. When this NOE cross peak was not available due to overlap, the NOE between NH and H<sub>c</sub> was used, assuming an average distance of 3.1 Å. All processing was performed with Topspin 2.1 (Bruker Biospin, Germany).

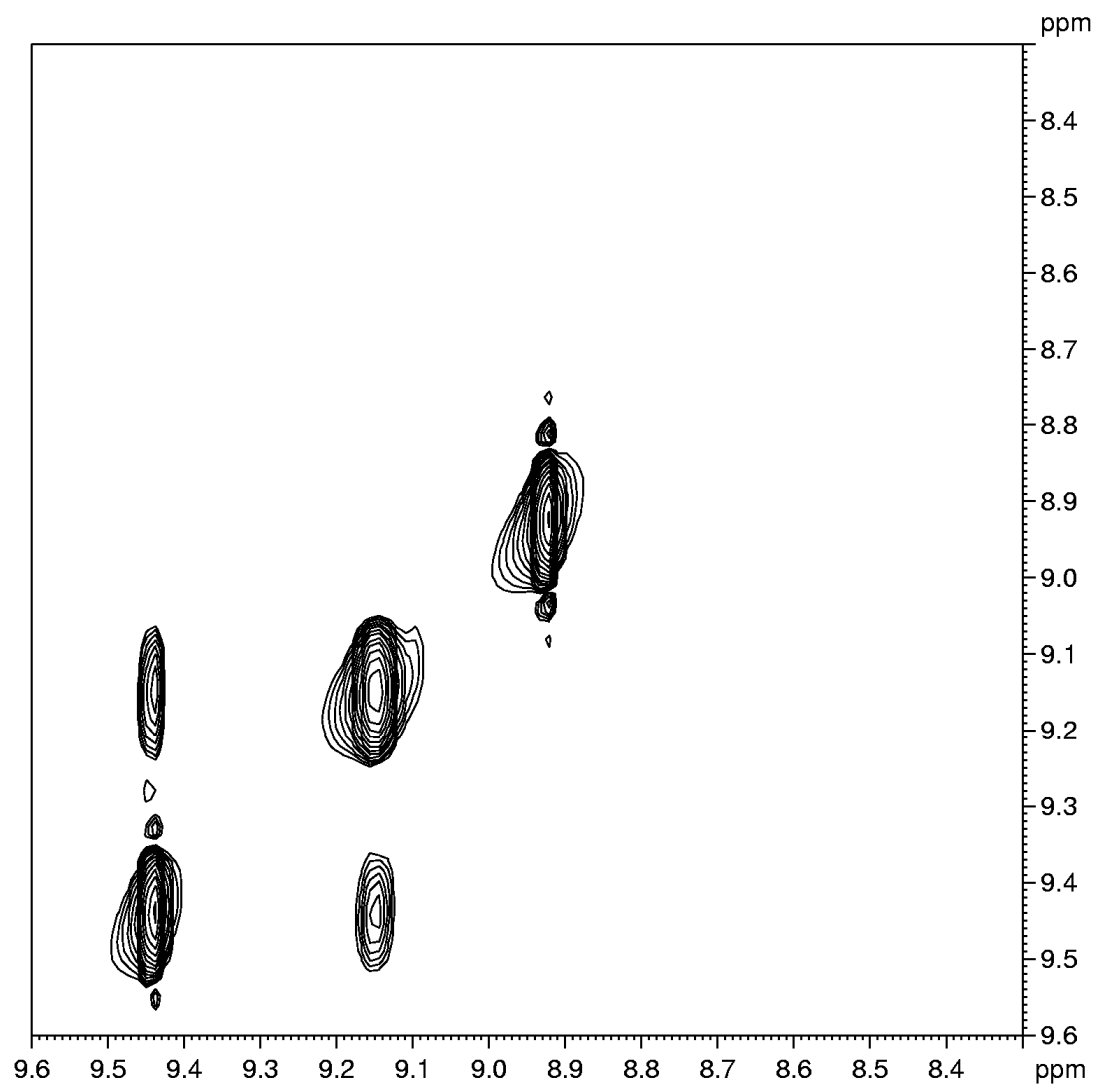


**Figure 11:** NOESY NMR (500 MHz; 298 K; CDCl<sub>3</sub>/DMSO-d<sub>6</sub> 93:7 v/v; TMS) spectrum of **1**.



**Figure 12:** NOESY NMR (500 MHz; 298 K; CDCl<sub>3</sub>/DMSO-d<sub>6</sub> 93:7 v/v; TMS) spectrum of 1·LiCl.

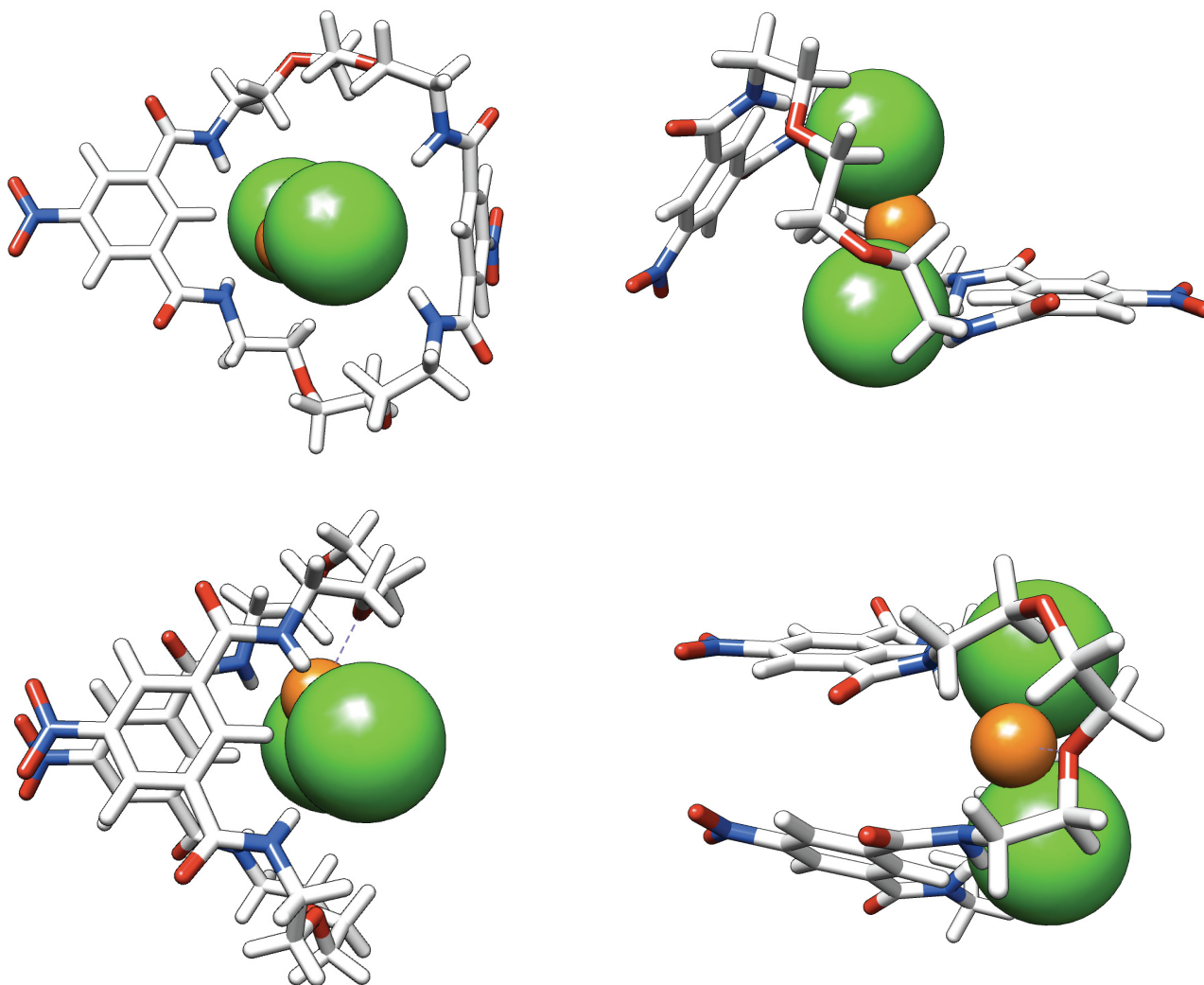




**Figure 13:** NOESY NMR (500 MHz; 298 K; CDCl<sub>3</sub>/DMSO-d<sub>6</sub> 93:7 v/v; TMS) spectrum of 1·CaCl<sub>2</sub>.

## Quantum mechanical calculations

Quantum mechanical calculations were carried out for  $1 \cdot \text{CaCl}_2$ . Top and side views for two minimized conformers (U- and S-shaped) are shown in Fig. 14. All calculations were done with Gaussian03.<sup>2</sup> Geometry optimizations were done using HF/6-31G(d). The calculations cannot reflect all aspects of the spectroscopic investigations because (i) those have been carried out in solvent, and (ii) the spectroscopic data are time averaged. Thus the conformers have to be viewed as snap-shots.



**Figure 14:** Two calculated conformers of  $1 \cdot \text{CaCl}_2$ .

<sup>1</sup> A. Dirksen, U. Hahn, F. Schwanke, M. Nieger, J. N. H. Reek, F. Vögtle, L. De Cola *Chem. Eur. J.*, 2004, **10**, 2036 - 2047.

<sup>2</sup> *Gaussian 03, Revision D.02*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N.

Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.