Supporting Information

Adaptation to Shape Switching by Component Selection in a Constitutional Dynamic System

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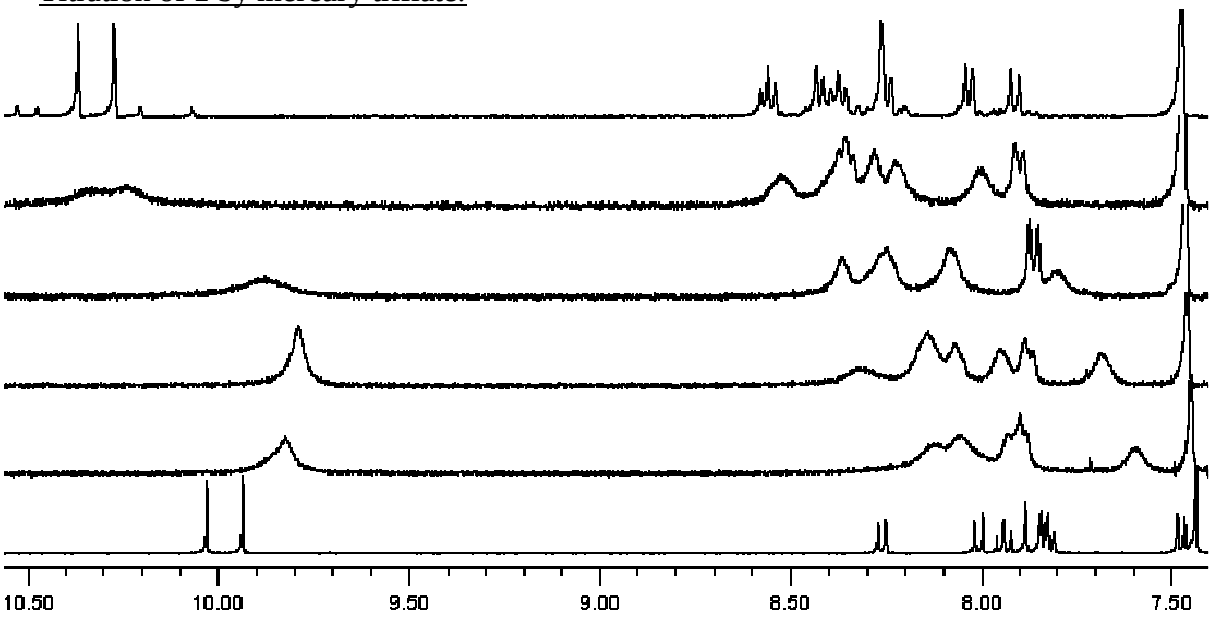
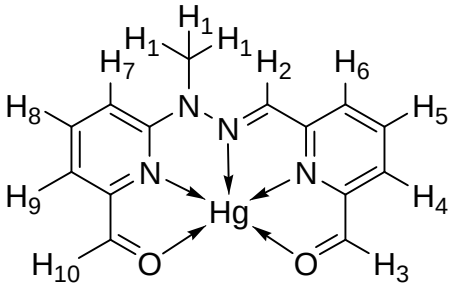
I. Structural features and shape switching of the morphological switches.

Titration of **1** by mercury triflate:



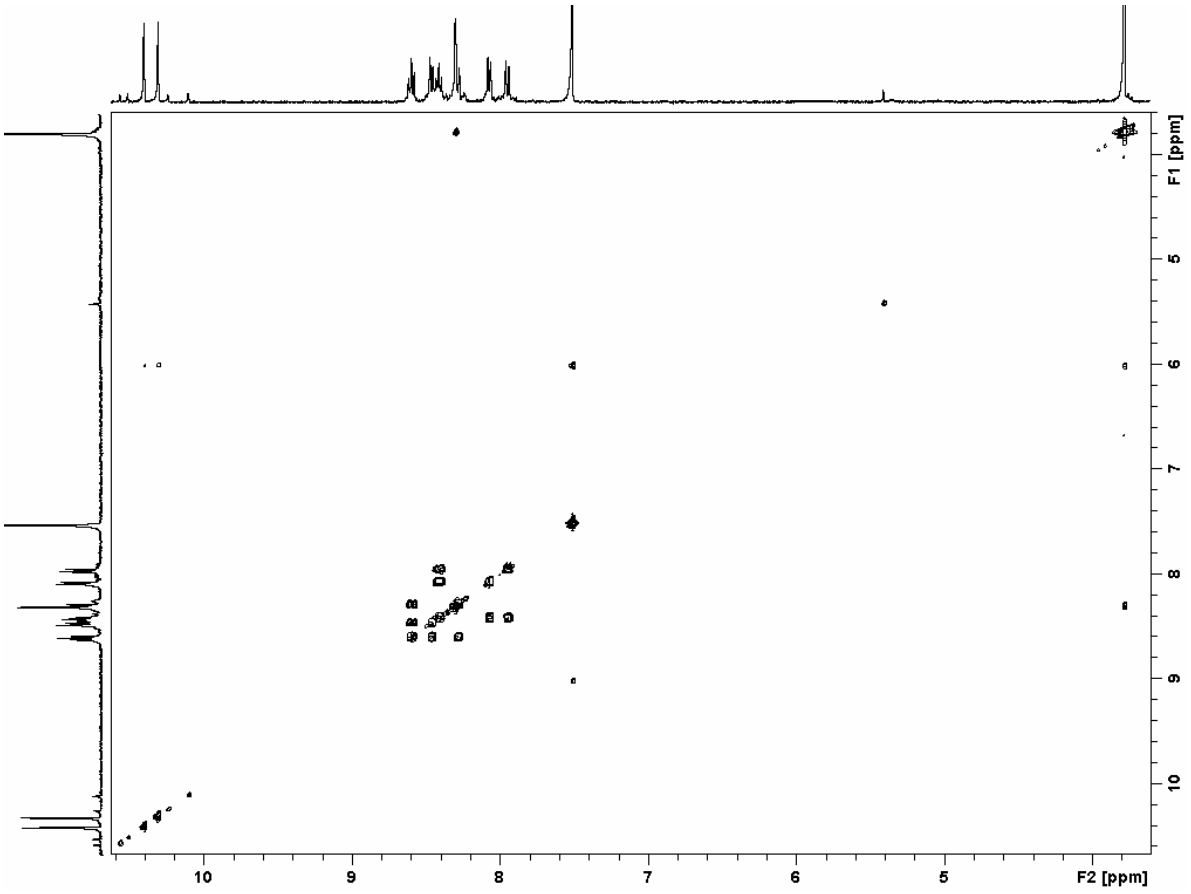
^{1}H NMR titration of ligand **1** by mercury triflate in $CDCl_3/CD_3CN$: 6/4. From bottom to top: addition of 0.0, 0.3, 0.5, 0.7, 0.9 and 1.0 equivalent of metal ion. Thermodynamic equilibrium was reached within the time needed to record the NMR spectra after addition of the metal salt containing solution, i.e. a few tens of seconds. The intermediate spectra show that the equilibria between all species are comparable to the NMR time-scale.

2D NMR analyses of **Hg.1**:

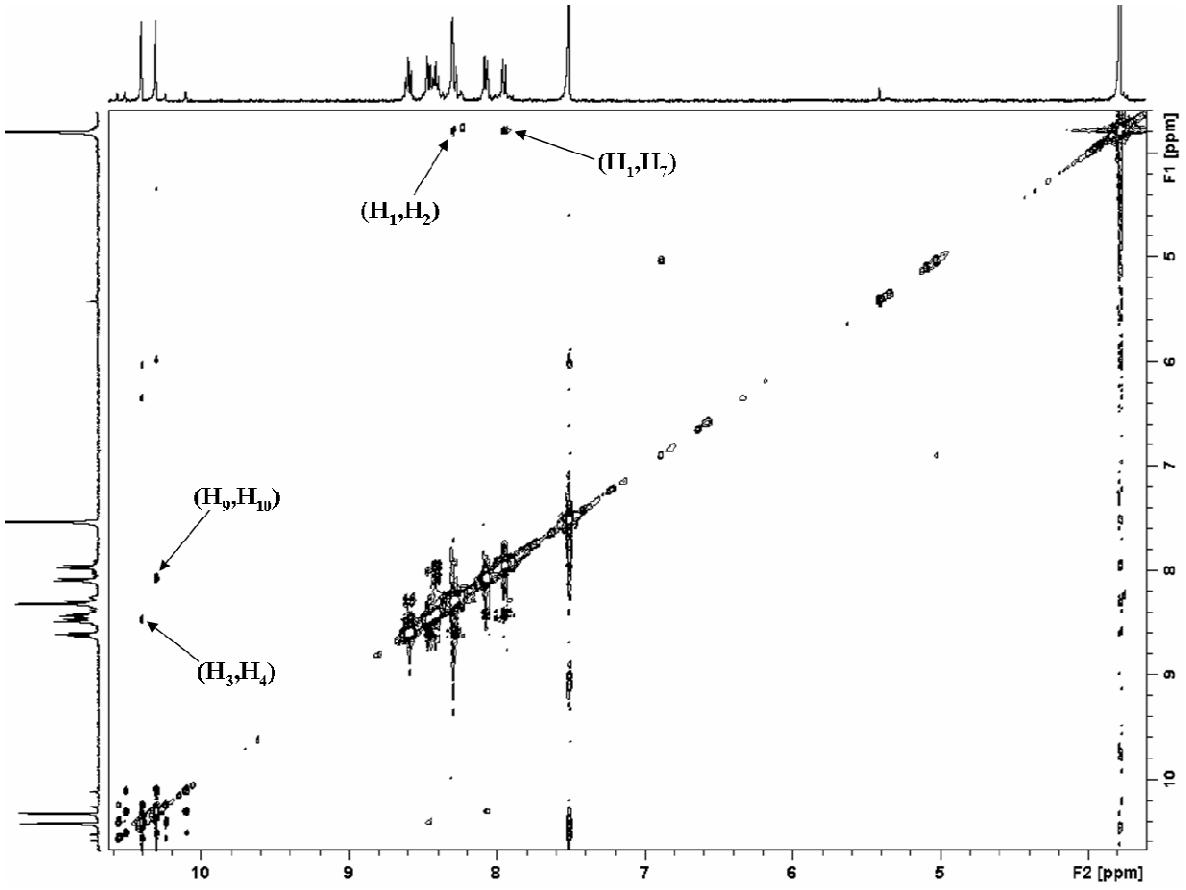


$(OTf)_2$

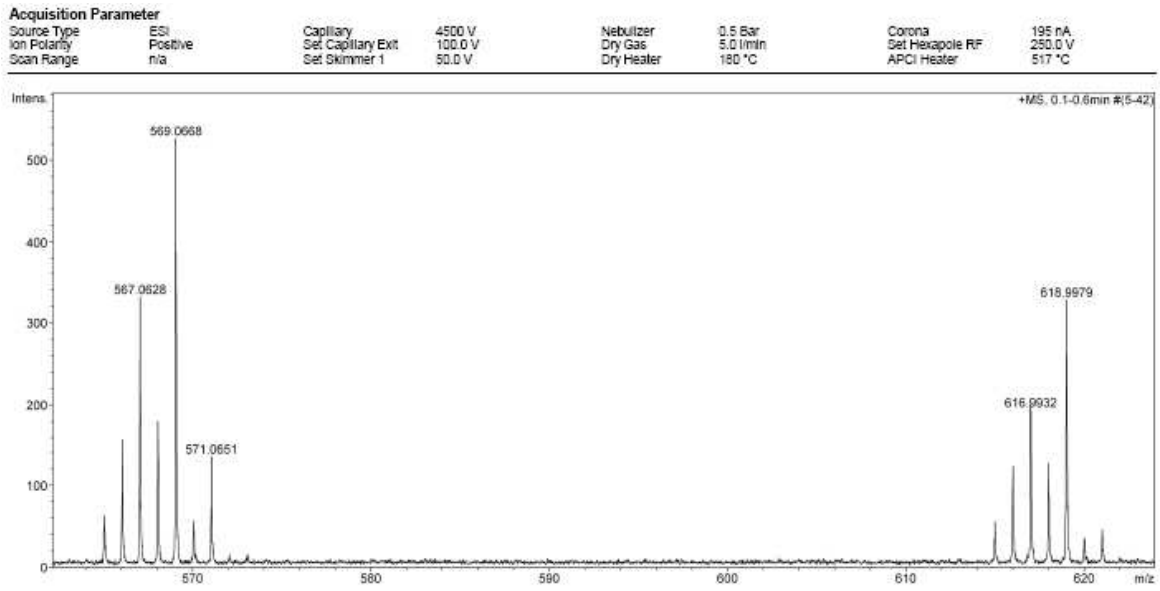
COSY ($CDCl_3^*/CD_3CN$: 51/49):



ROESY ($CDCl_3$*/CD_3CN: 51/49):

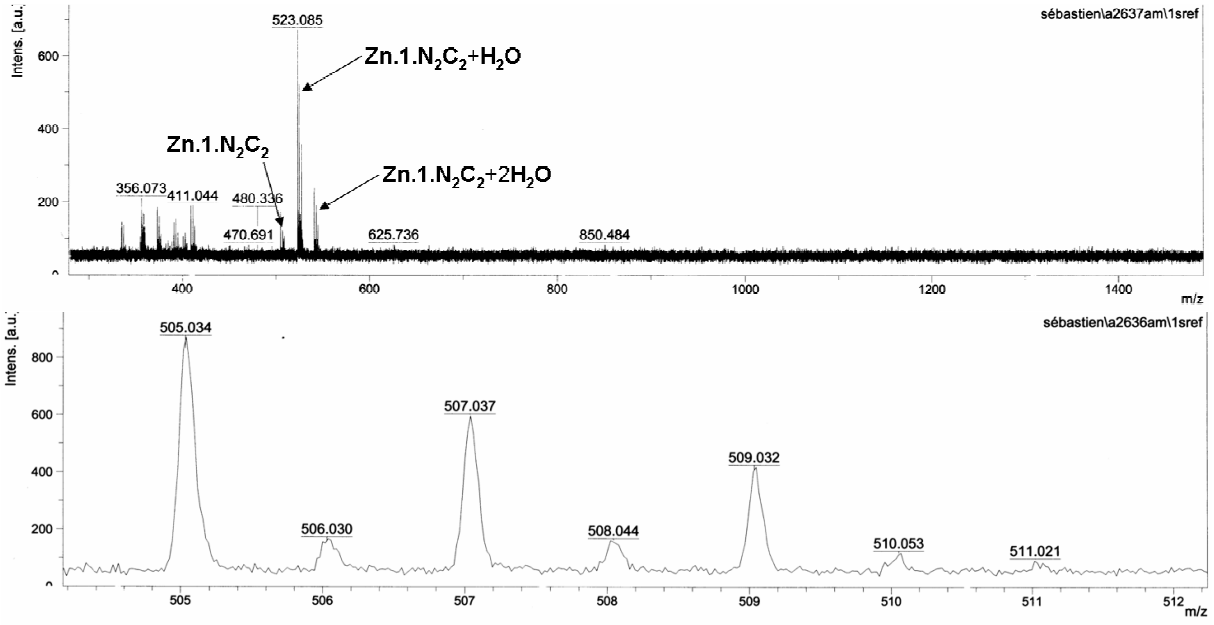


HR-ESI-MS:

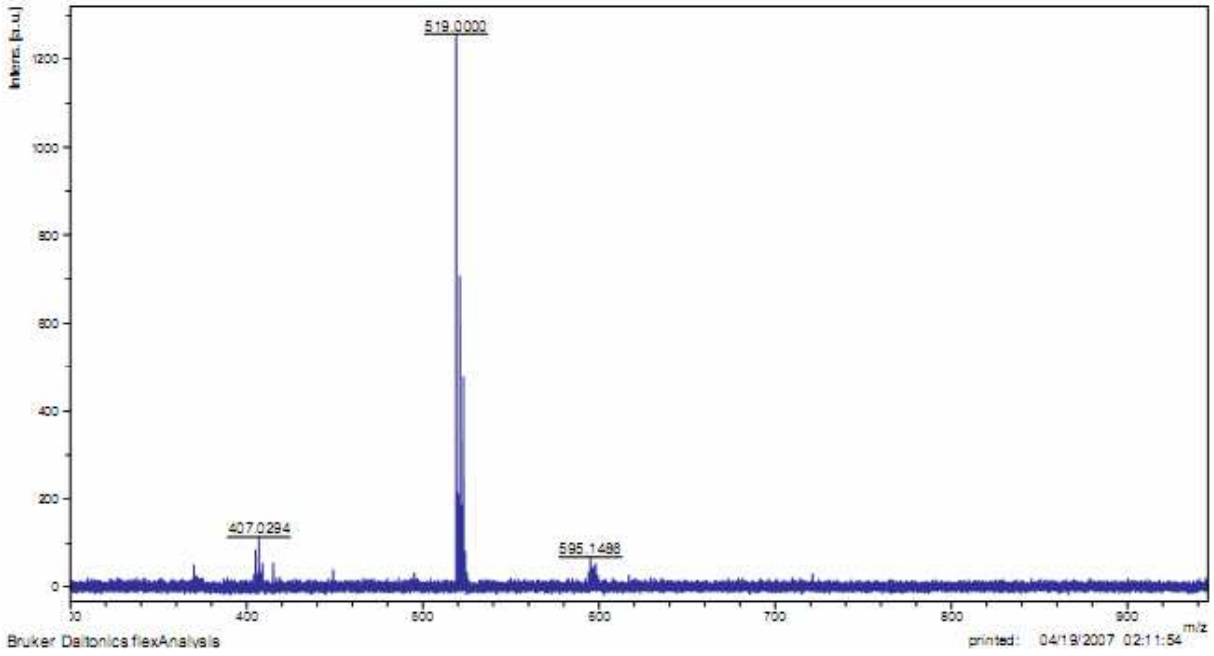


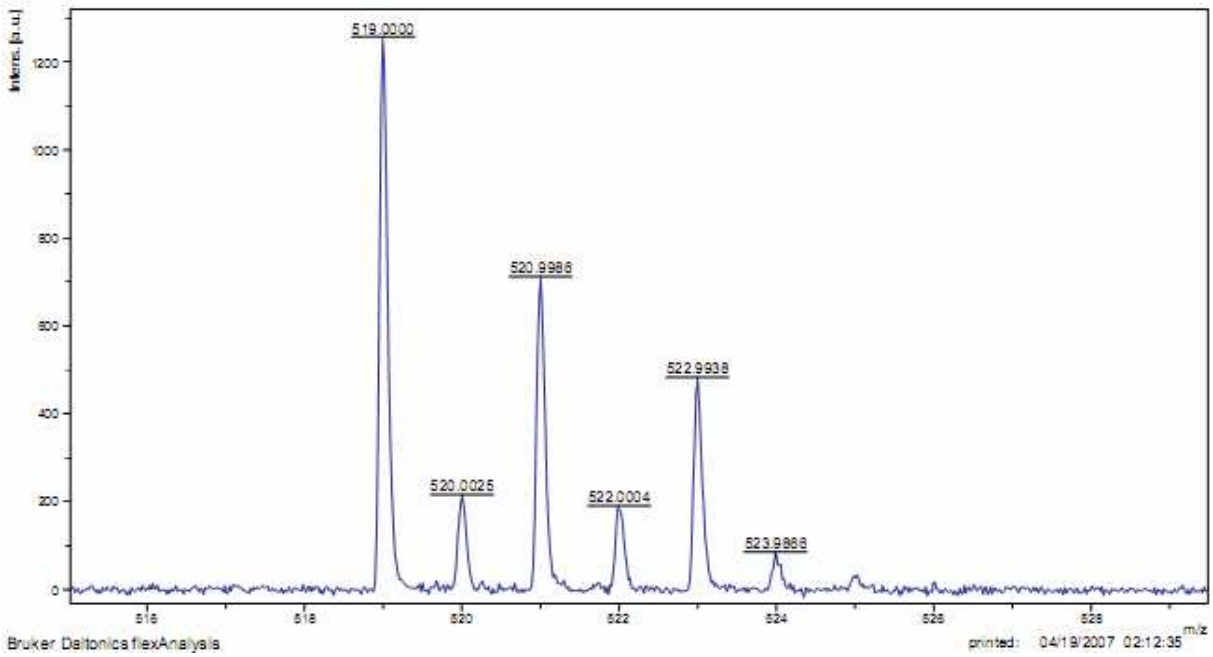
II. Characterizations of the imine macrocycles.

MALDI-TOF (THAP) of **Zn.1.N_2C_2**:

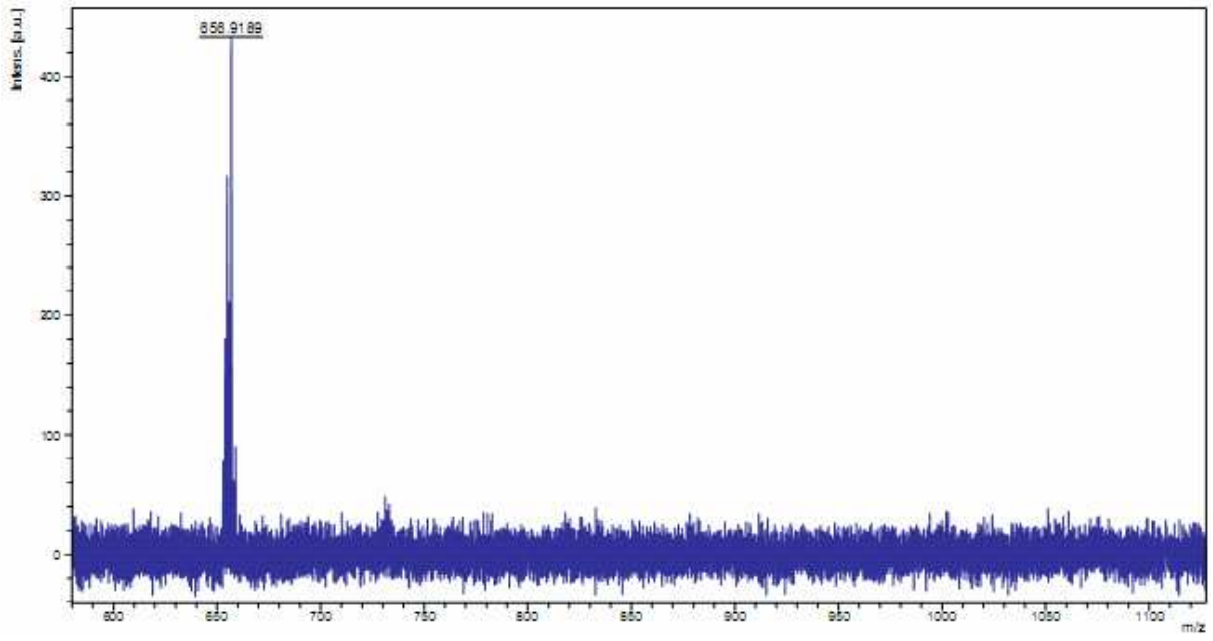


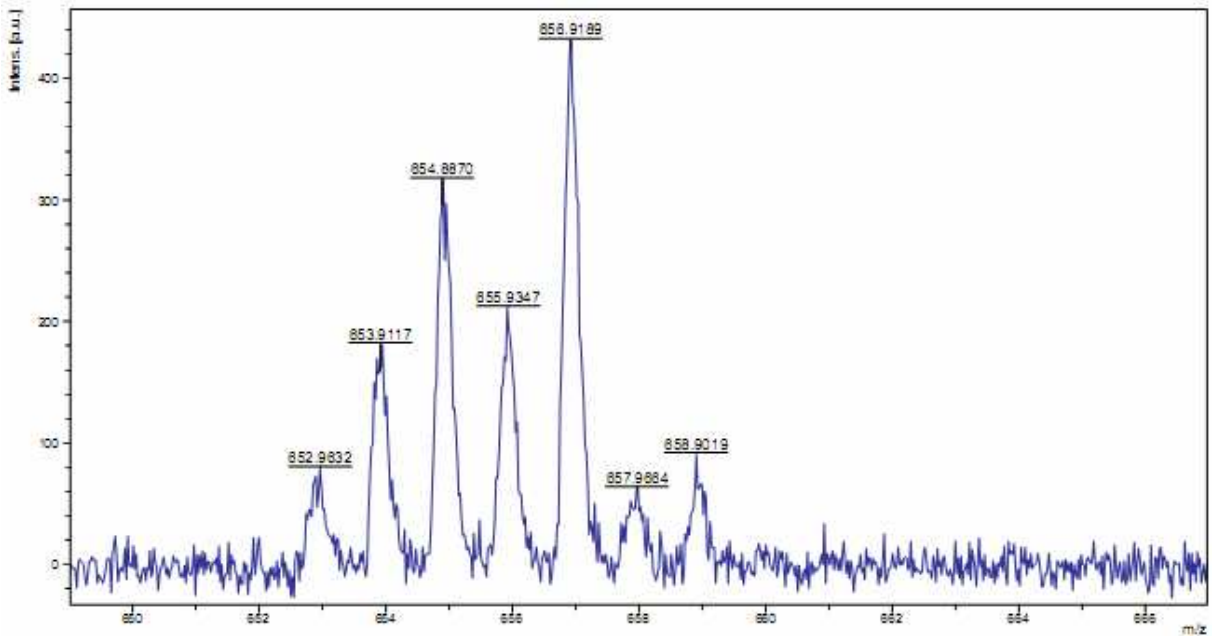
MALDI-TOF (dithranol) of **Zn.1.N_2C_3**:



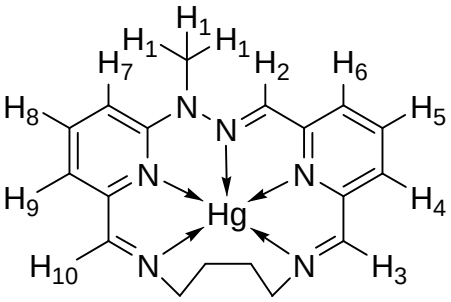


MALDI-TOF (dithranol) of **Hg.1.$N_2$$C_3$**:



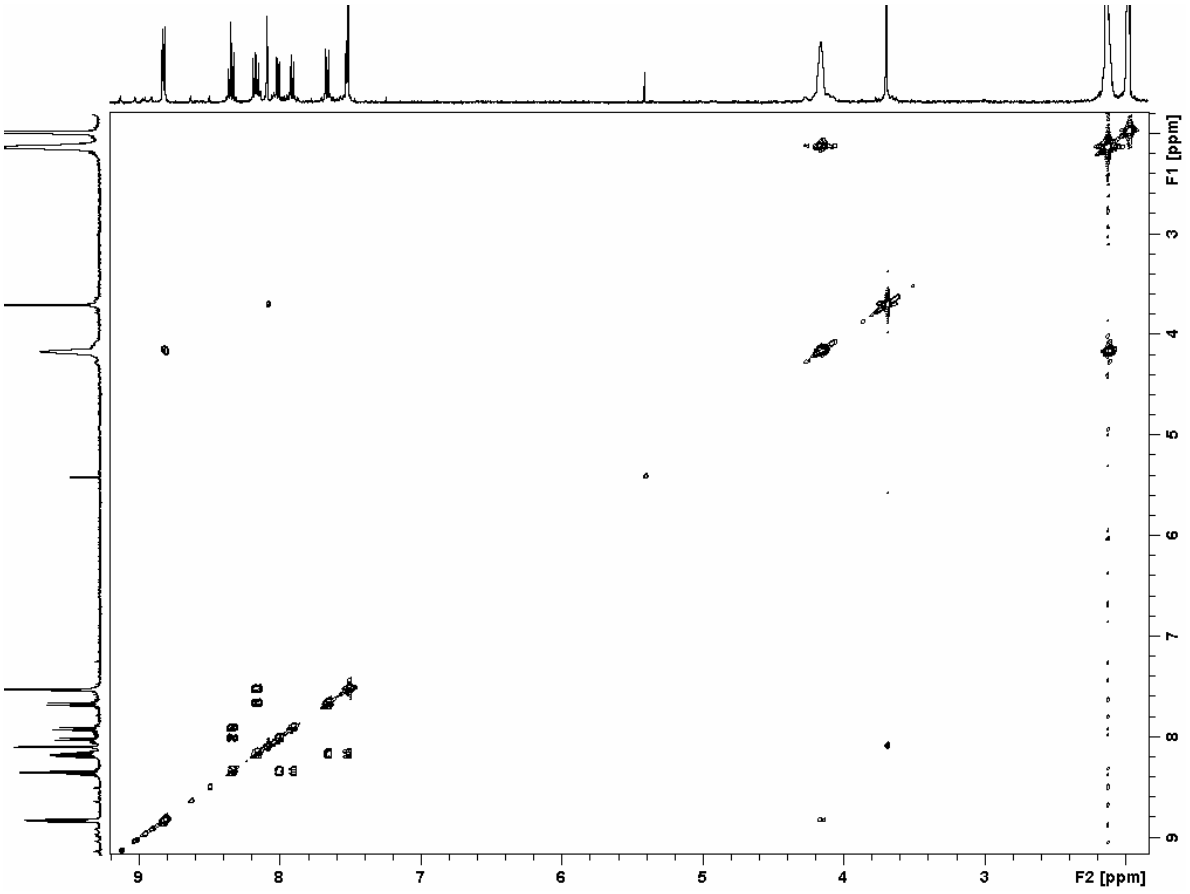


2D NMR analyses of **Hg.1.$N_2$$C_4$**:

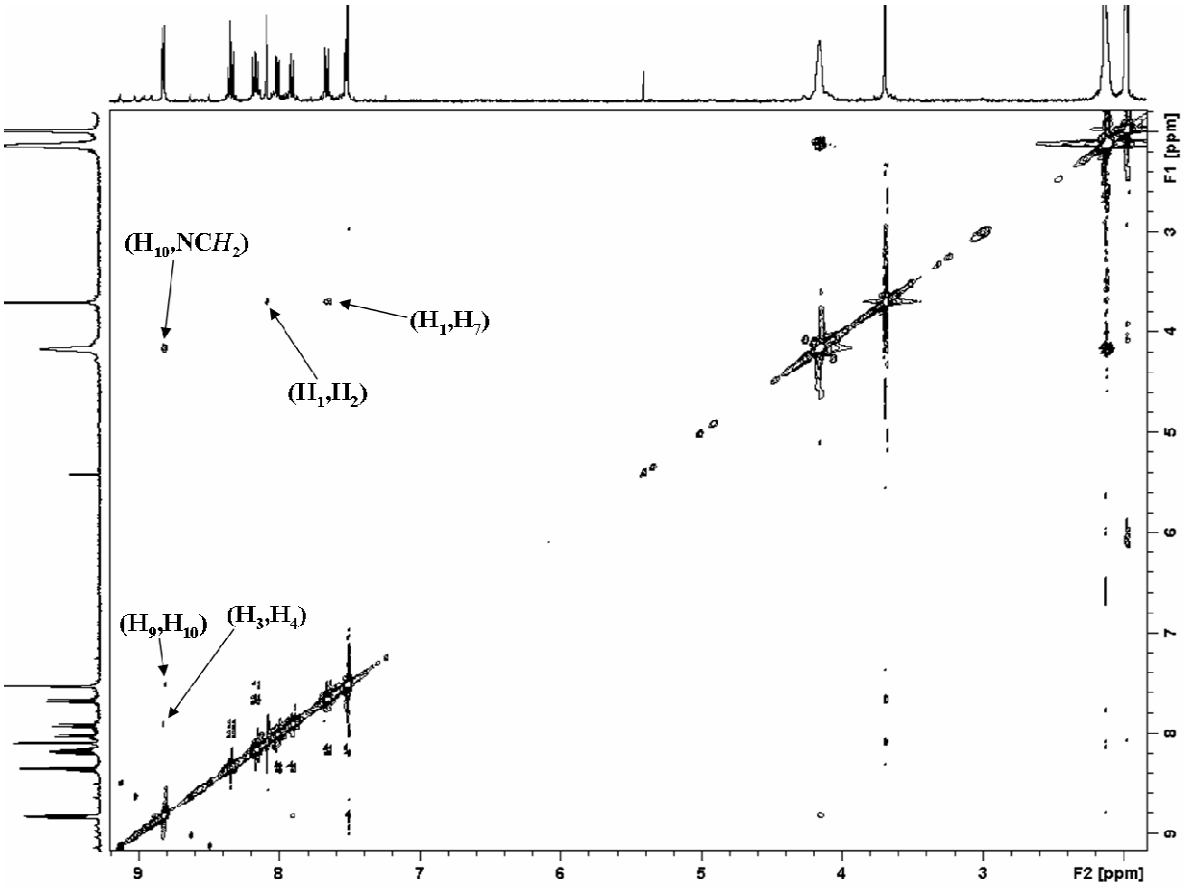


$(OTf)_2$

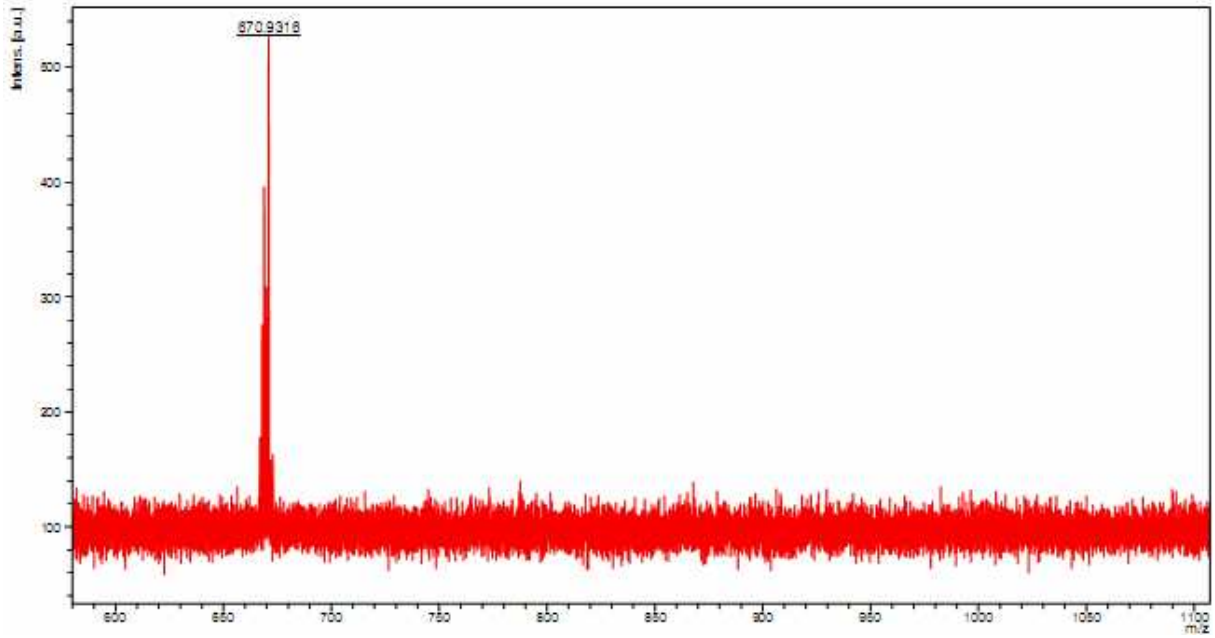
COSY ($CDCl_3$*/CD_3CN: 52/48):

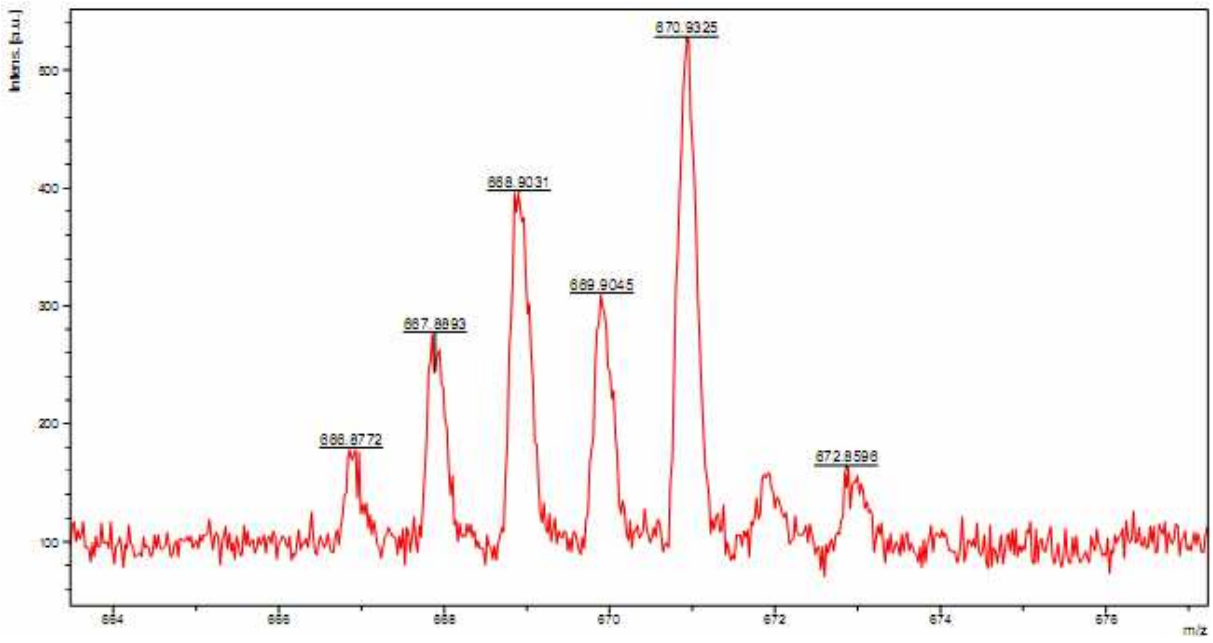


ROESY ($CDCl_3$*/CD_3CN: 52/48):

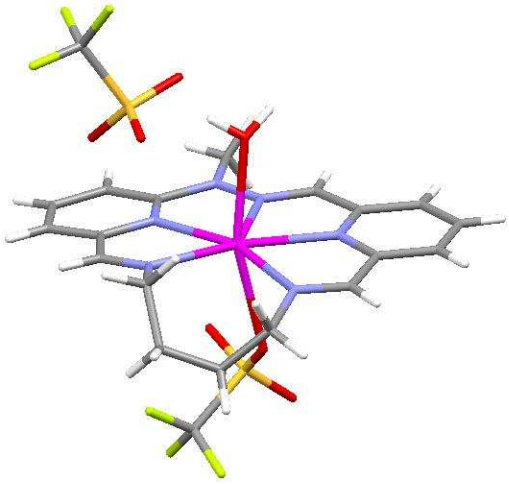


MALDI-TOF (dithranol) of **Hg.1.N_2C_4**:

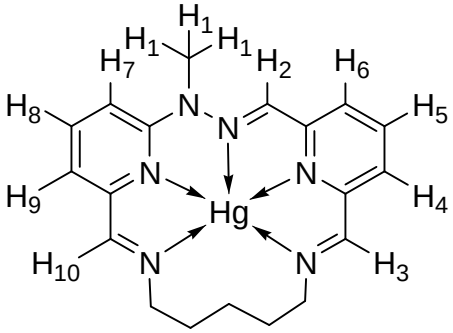




Solid state structure of **Hg.1.N_2C_4**:

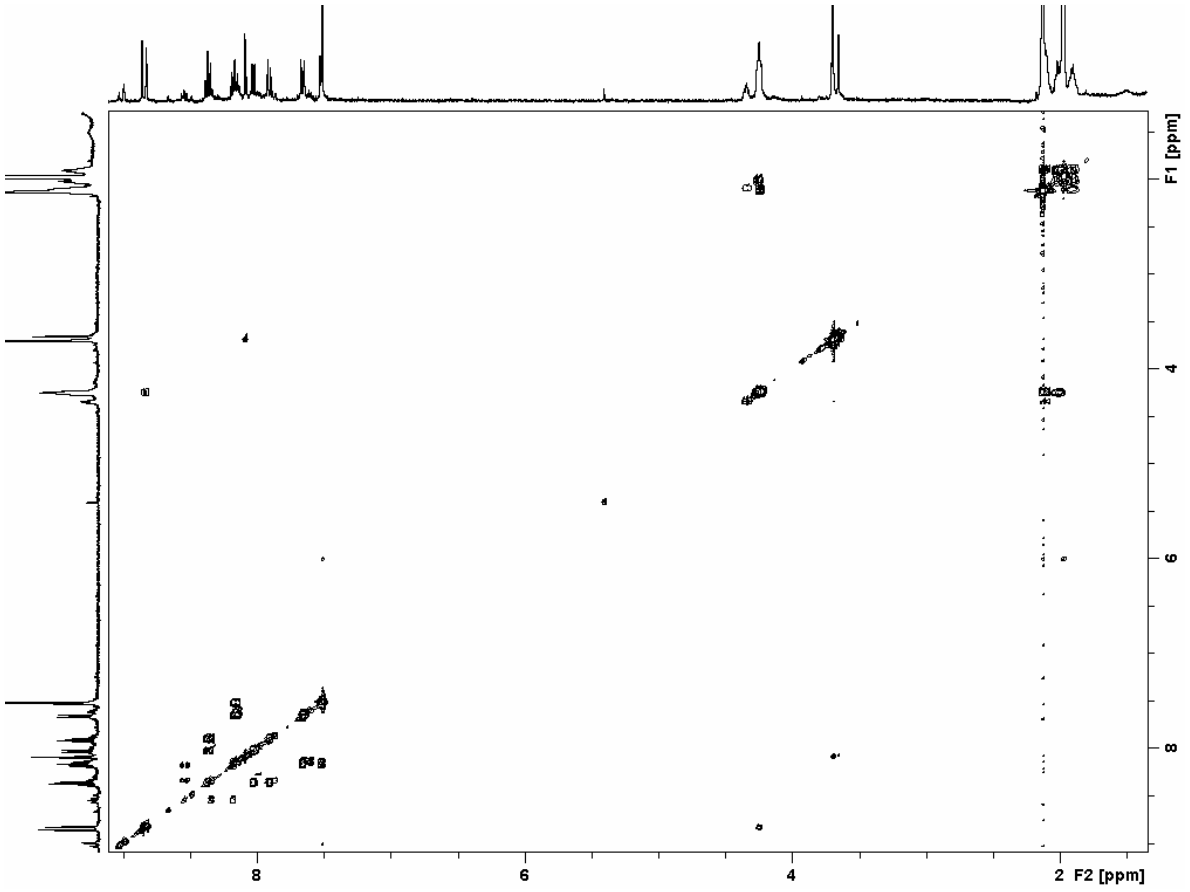


2D NMR analyses of **Hg.1.N_2C_5**:

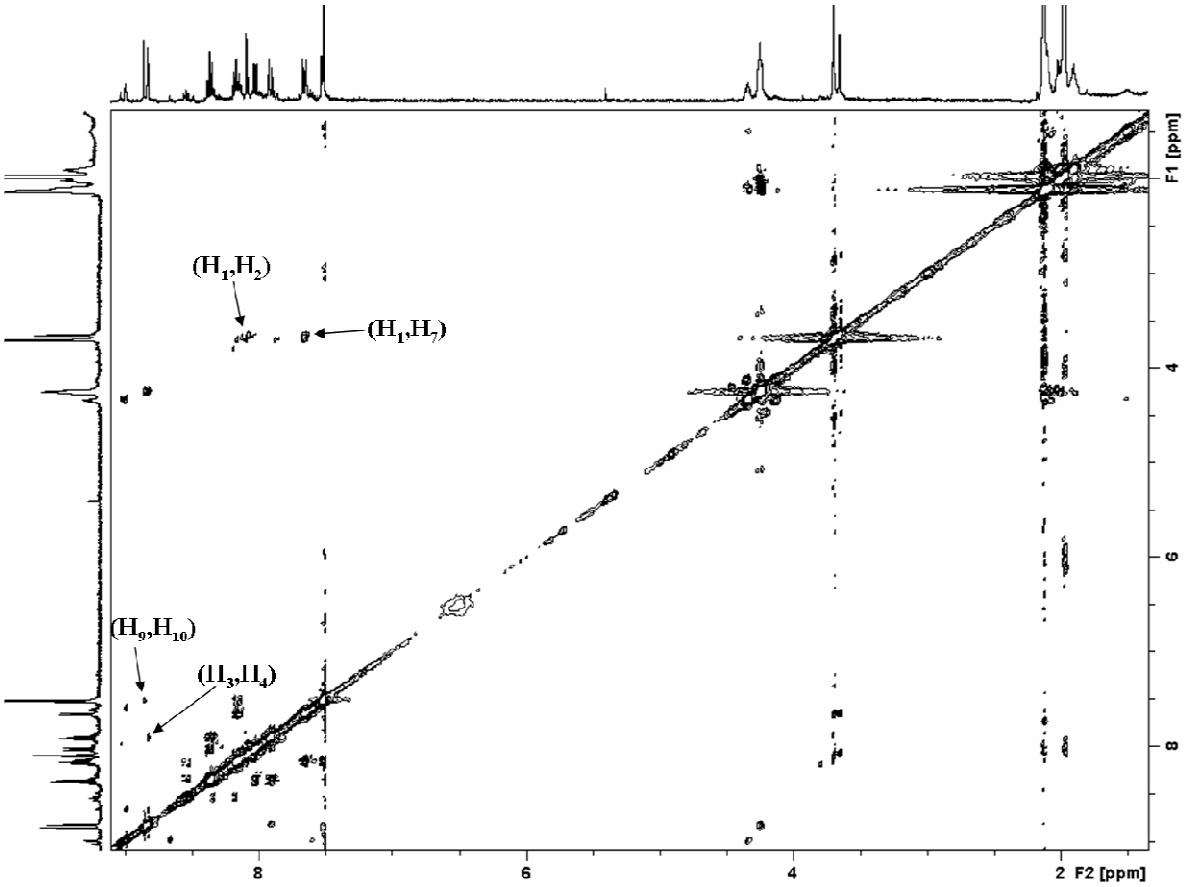


$(OTf)_2$

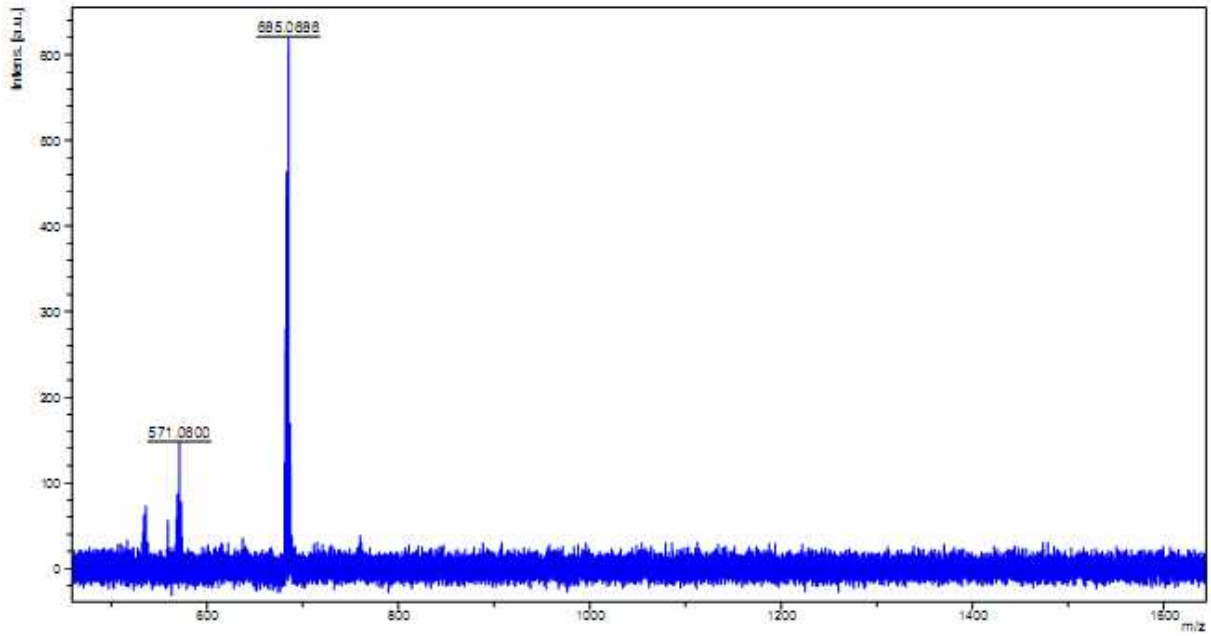
COSY ($CDCl_3$*/CD_3CN: 52/48):

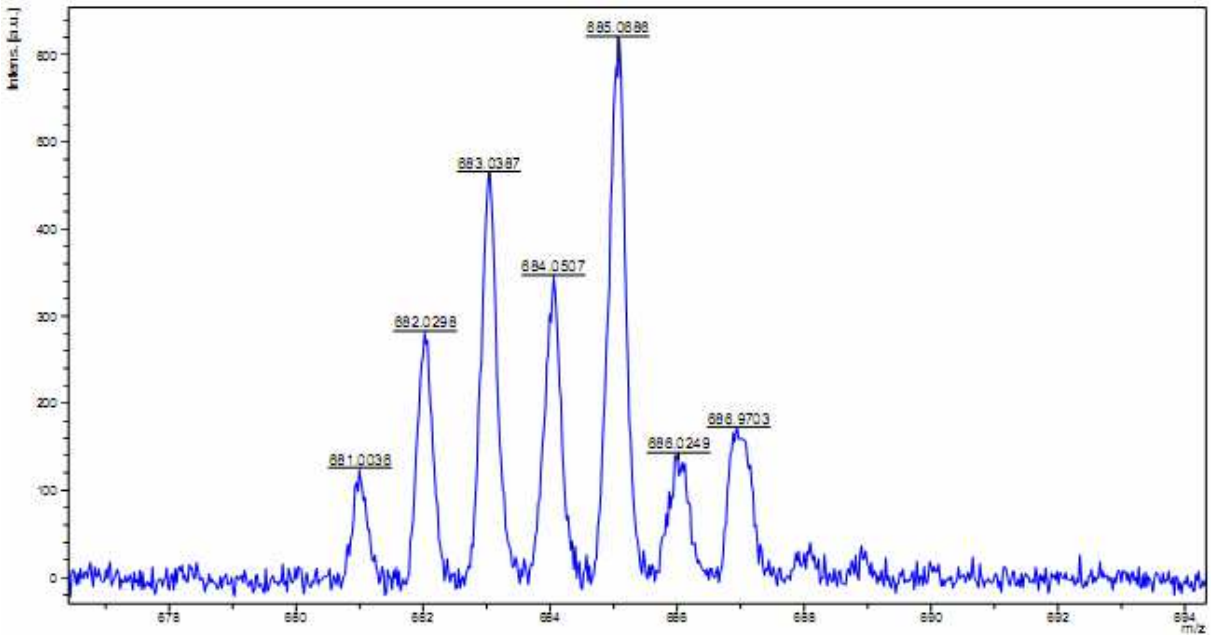


ROESY ($CDCl_3$*/CD_3CN: 52/48):

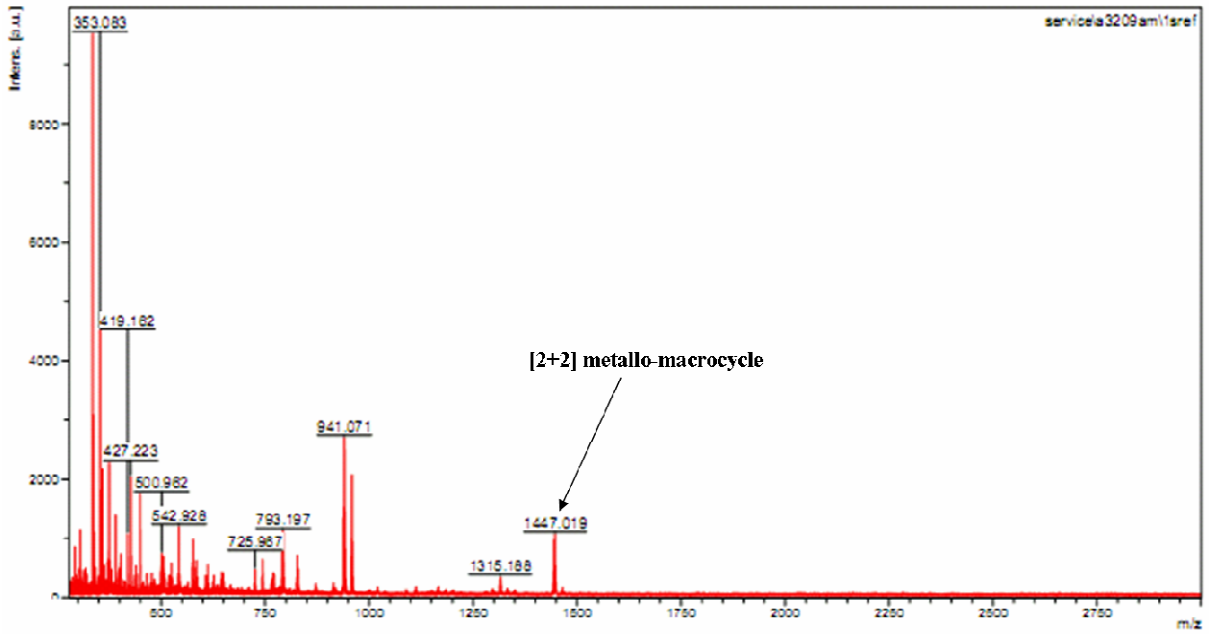


MALDI-TOF (dithranol) of **Hg.1.$N_2$$C_5$**:



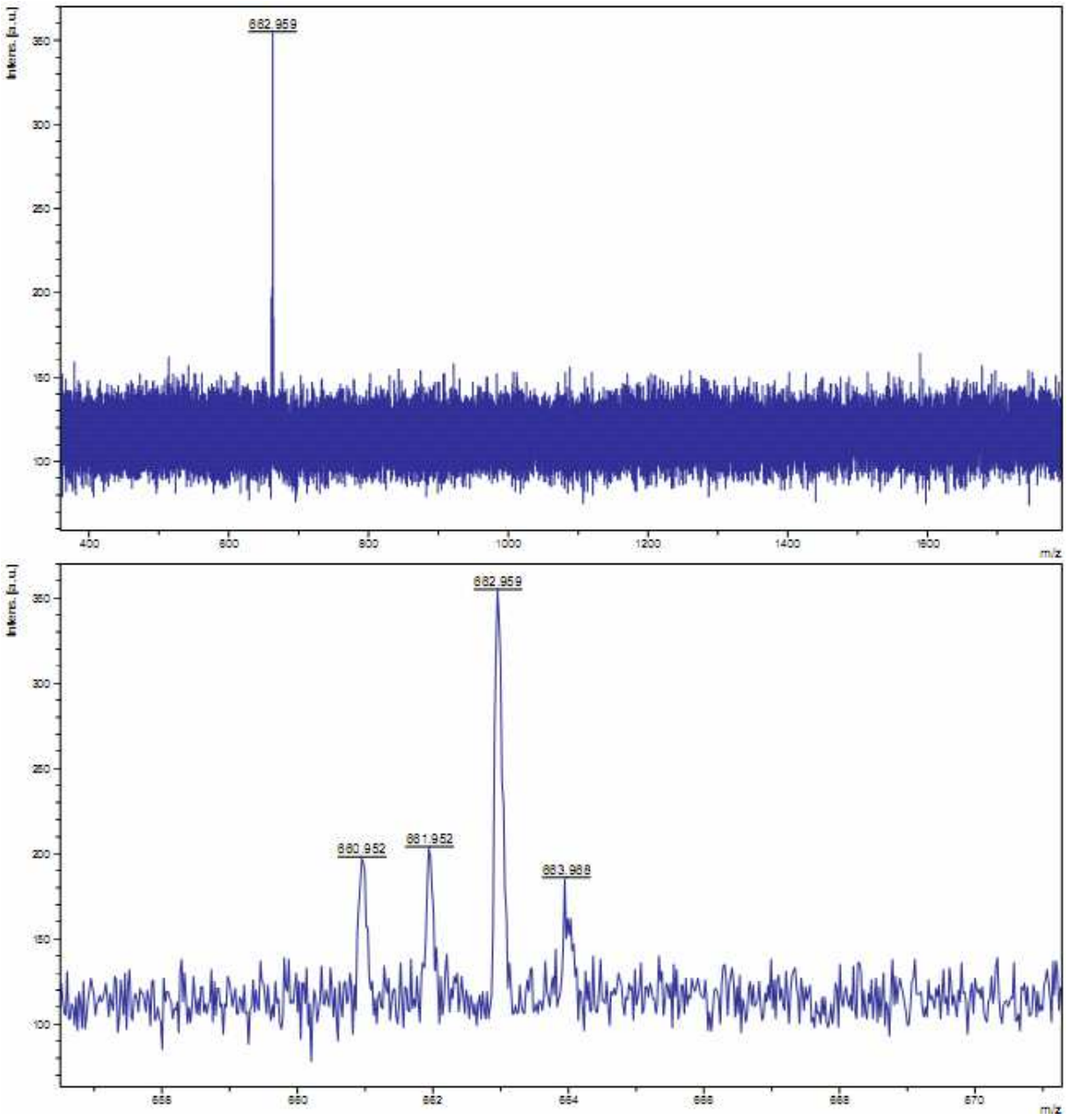


MALDI-TOF (THAP) analysis of the precipitate resulting from the mixing of **Pb.1** and **N_2C_2**:

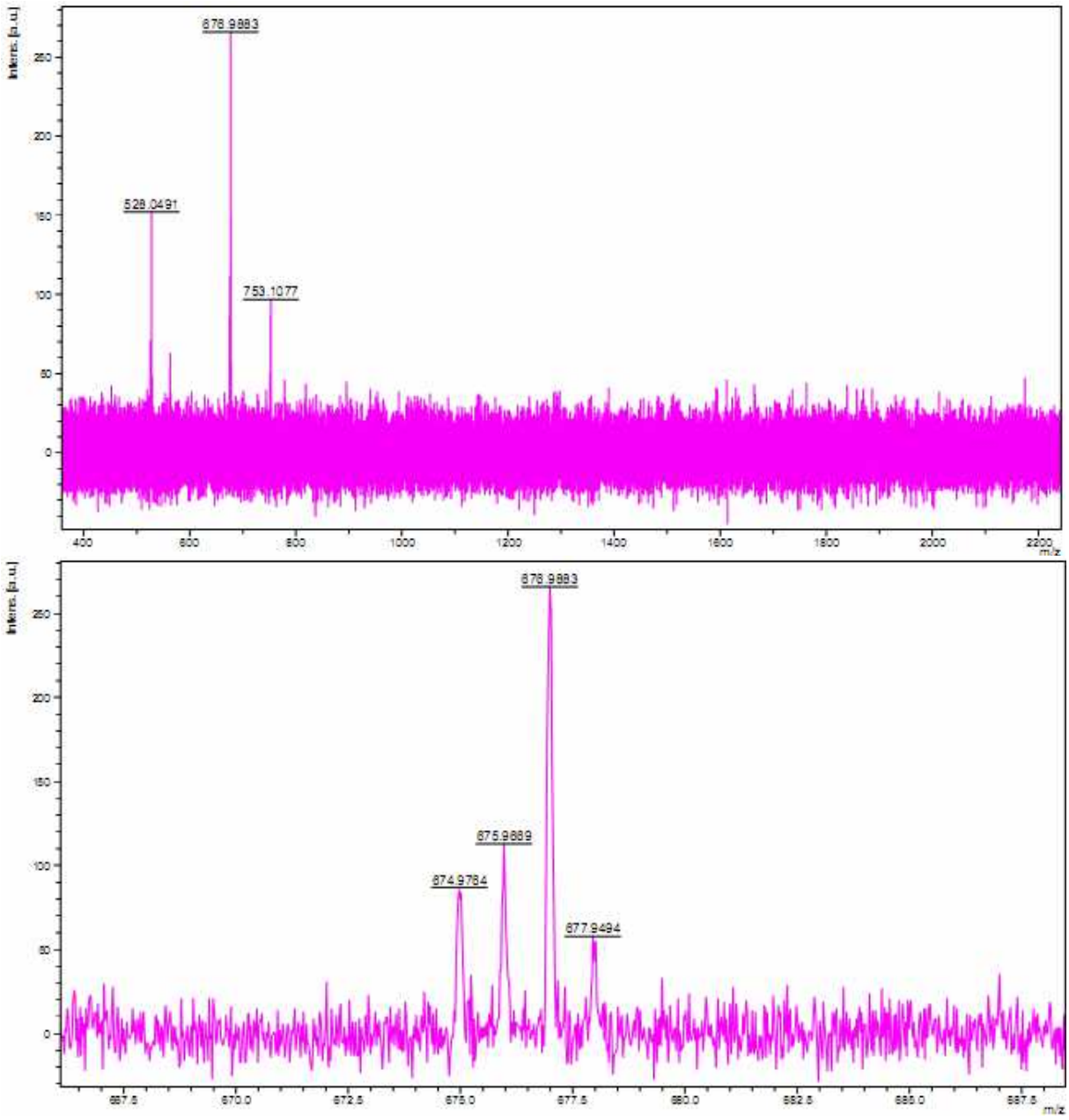


Calculated for $[C_{35}H_{32}F_9N_{12}O_9Pb_2S_3]^+$ 1447.097, found 1447.019.

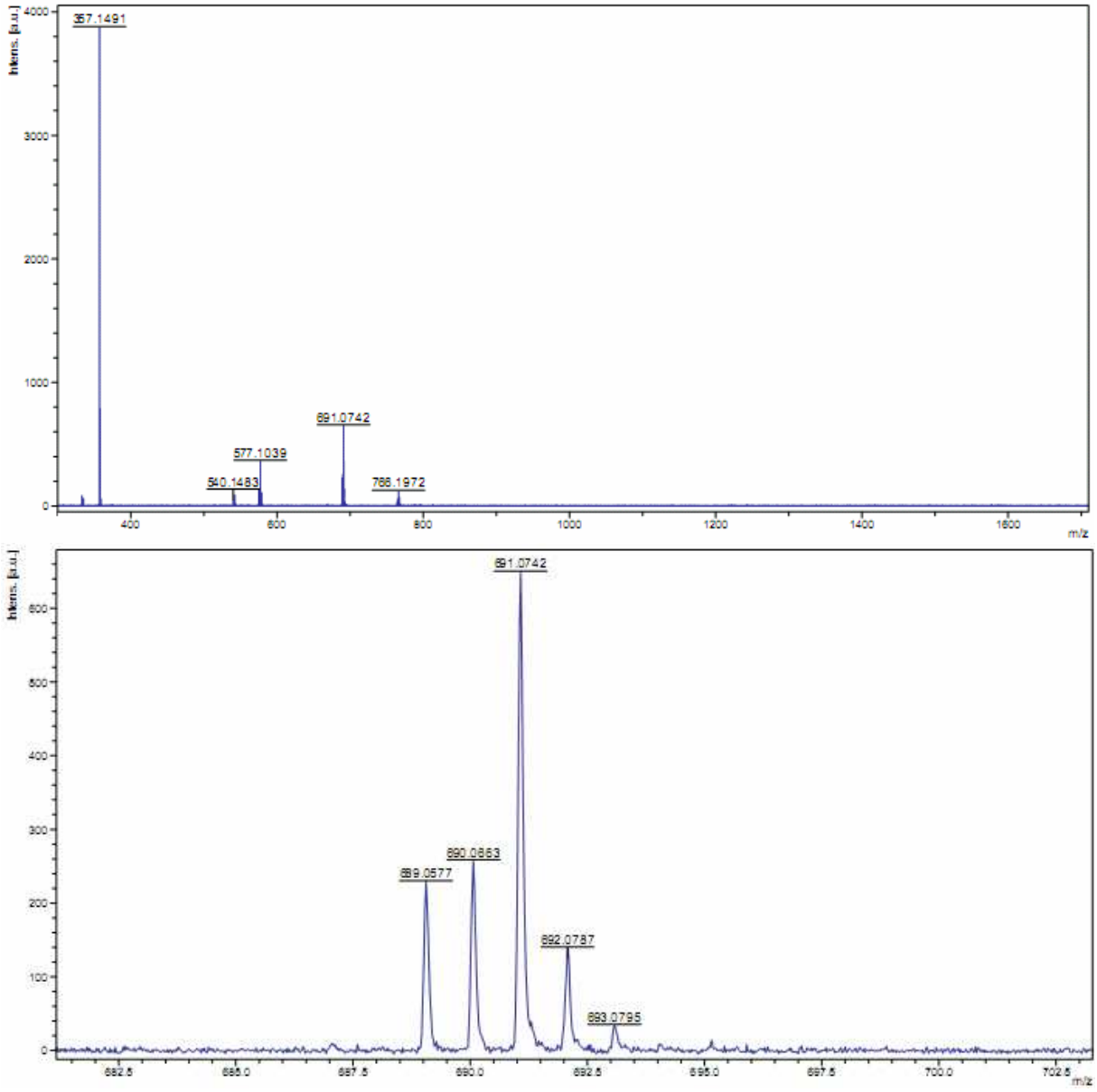
MALDI-TOF (dithranol) of **Pb.1.N_2C_3**:



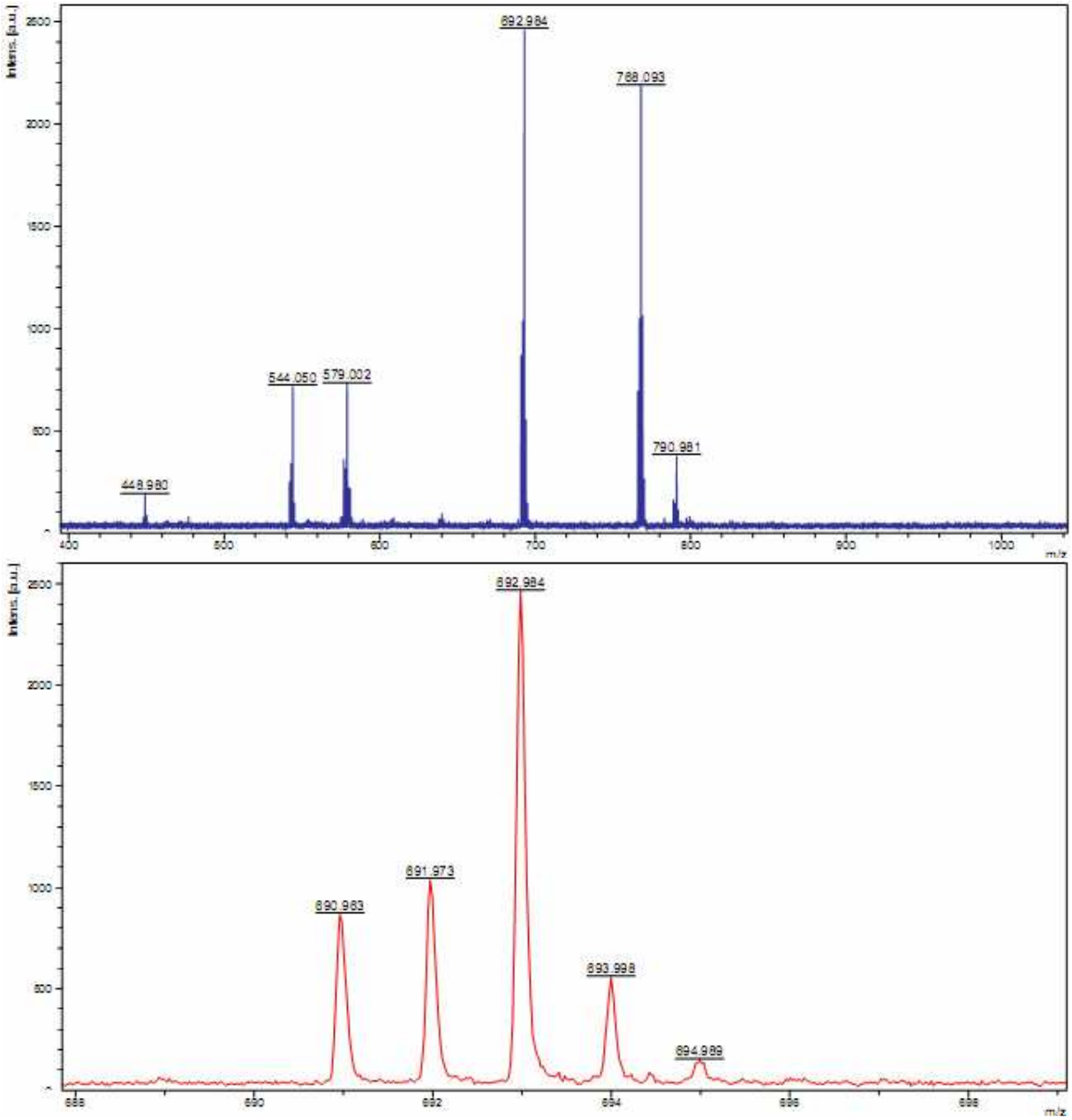
MALDI-TOF (dithranol) of **Pb.1.N_2C_4**:



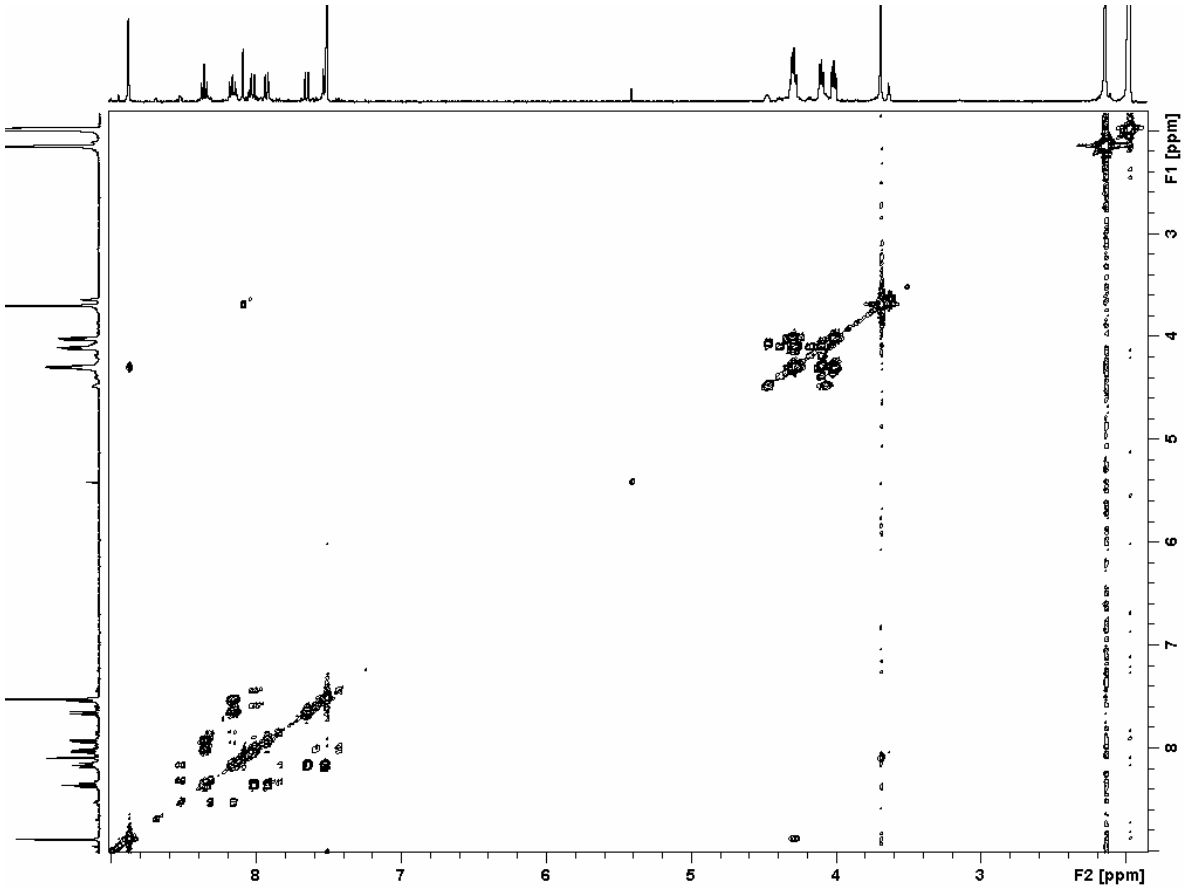
MALDI-TOF (dithranol) of **Pb.1.N_2C_5**:



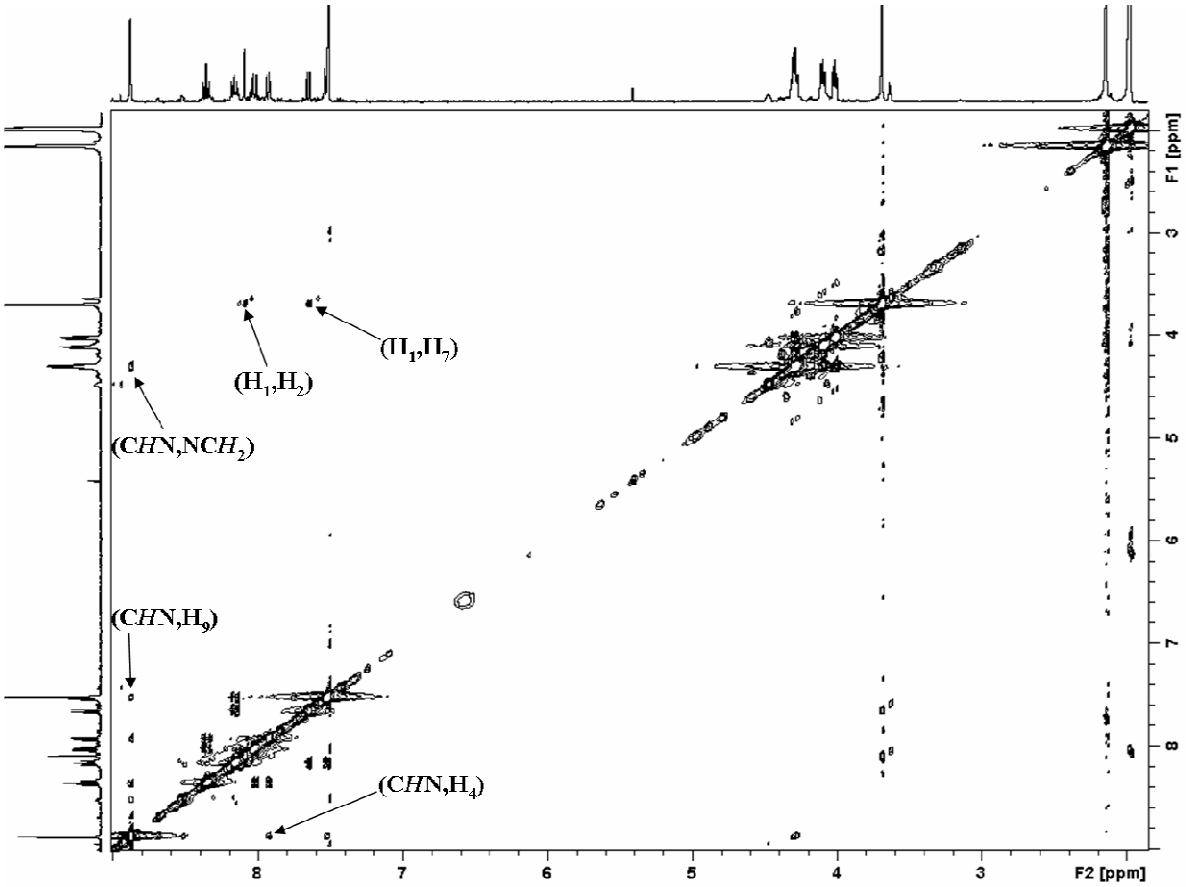
MALDI-TOF (dithranol) of **Pb.1.N_2O**:



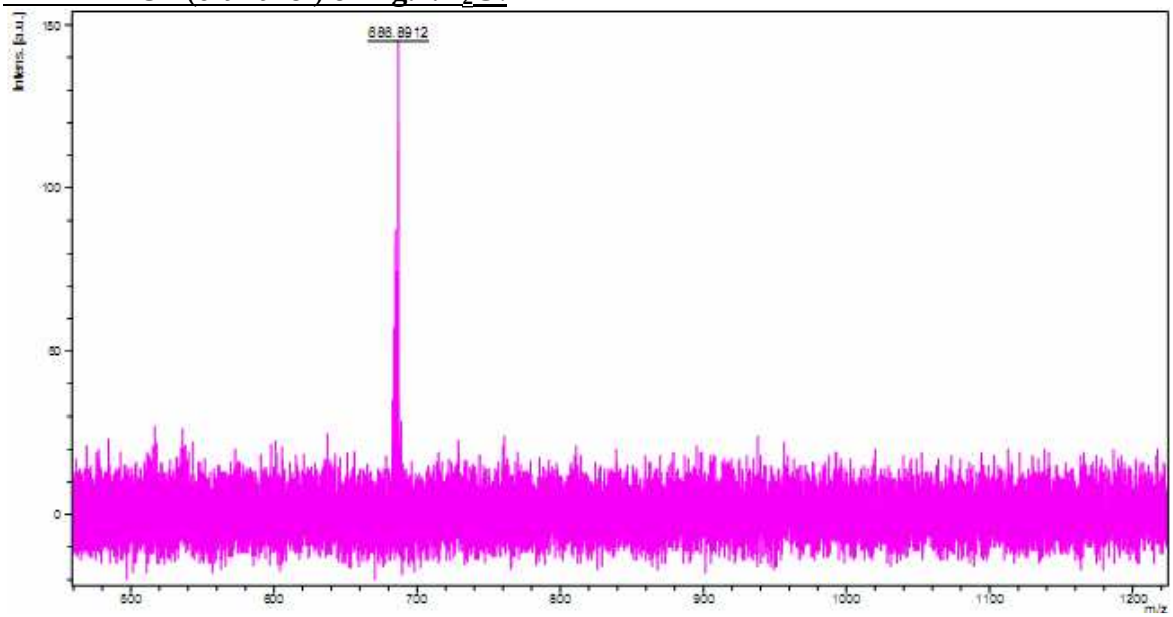
2D NMR analyses of **Hg.1.N_2O**:
COSY ($CDCl_3$*/CD_3CN: 52/48):

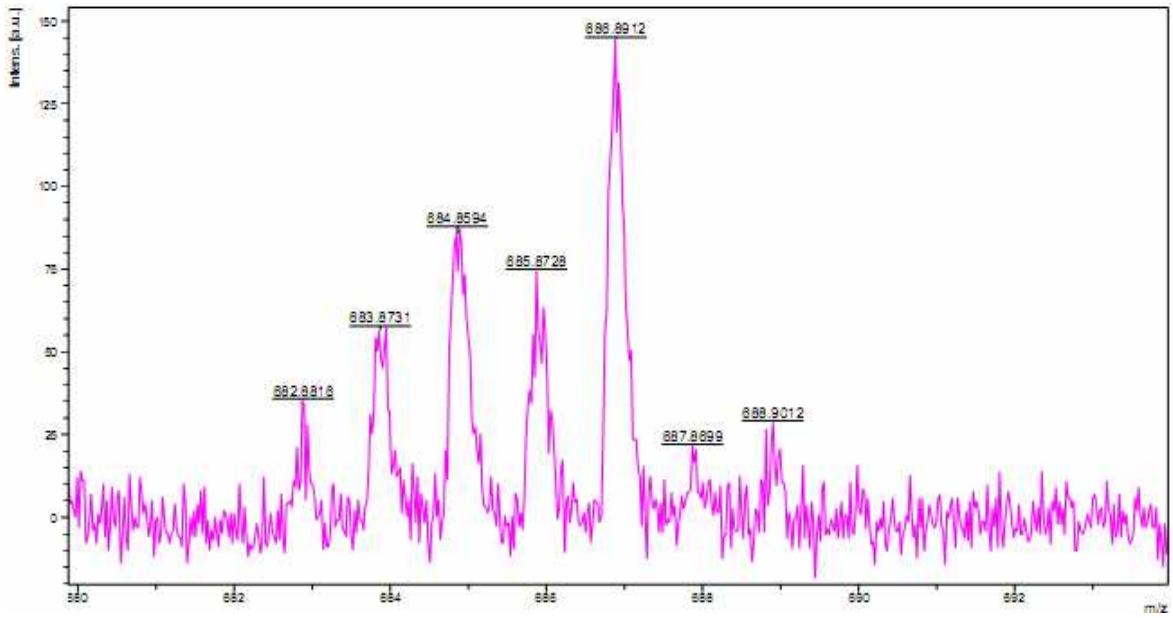


ROESY ($CDCl_3$*/CD_3CN: 52/48):

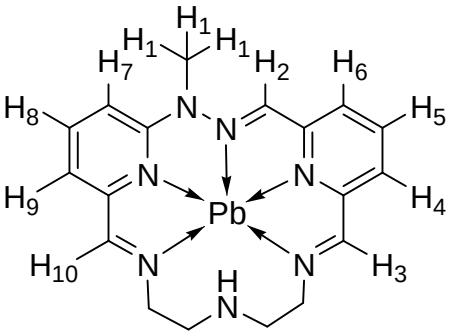


MALDI-TOF (dithranol) of **Hg.1.N_2O**:



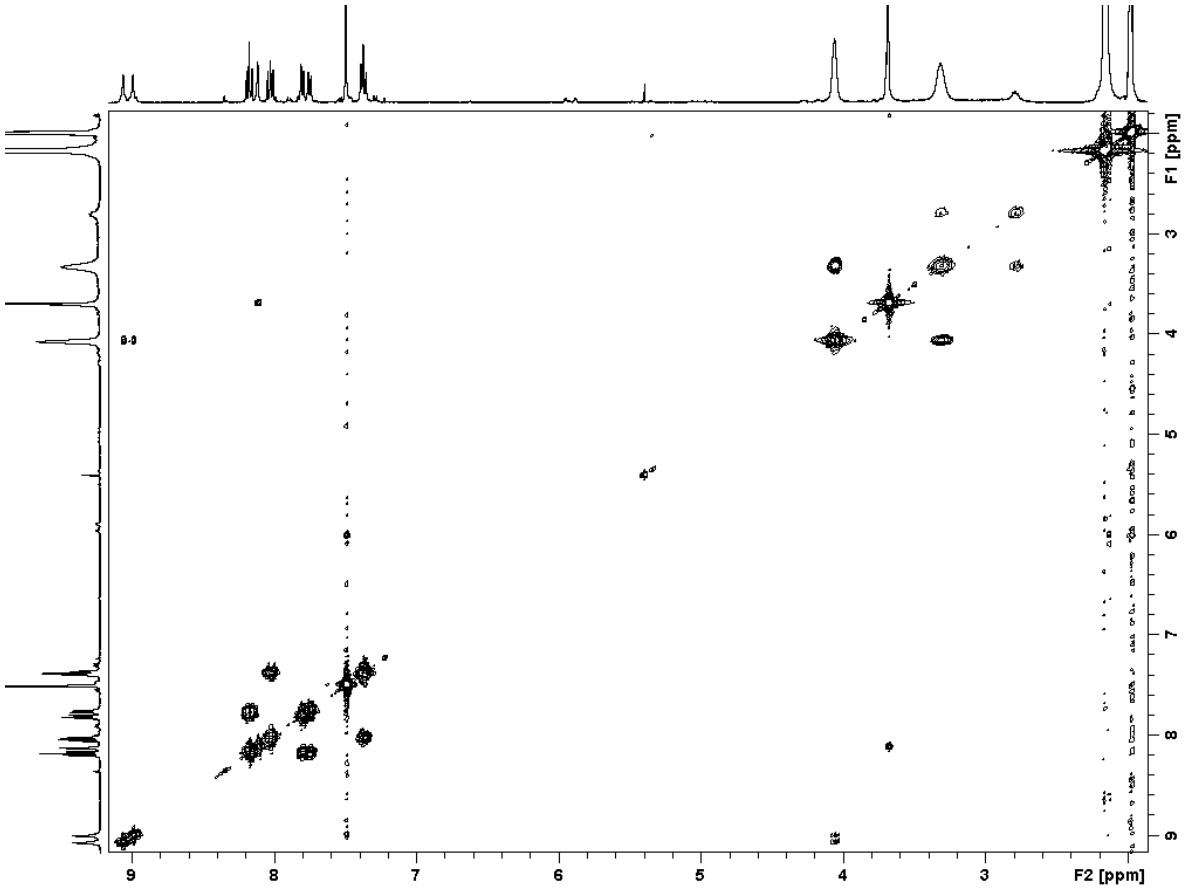


2D NMR analyses of **Pb.1.N_2NH**:

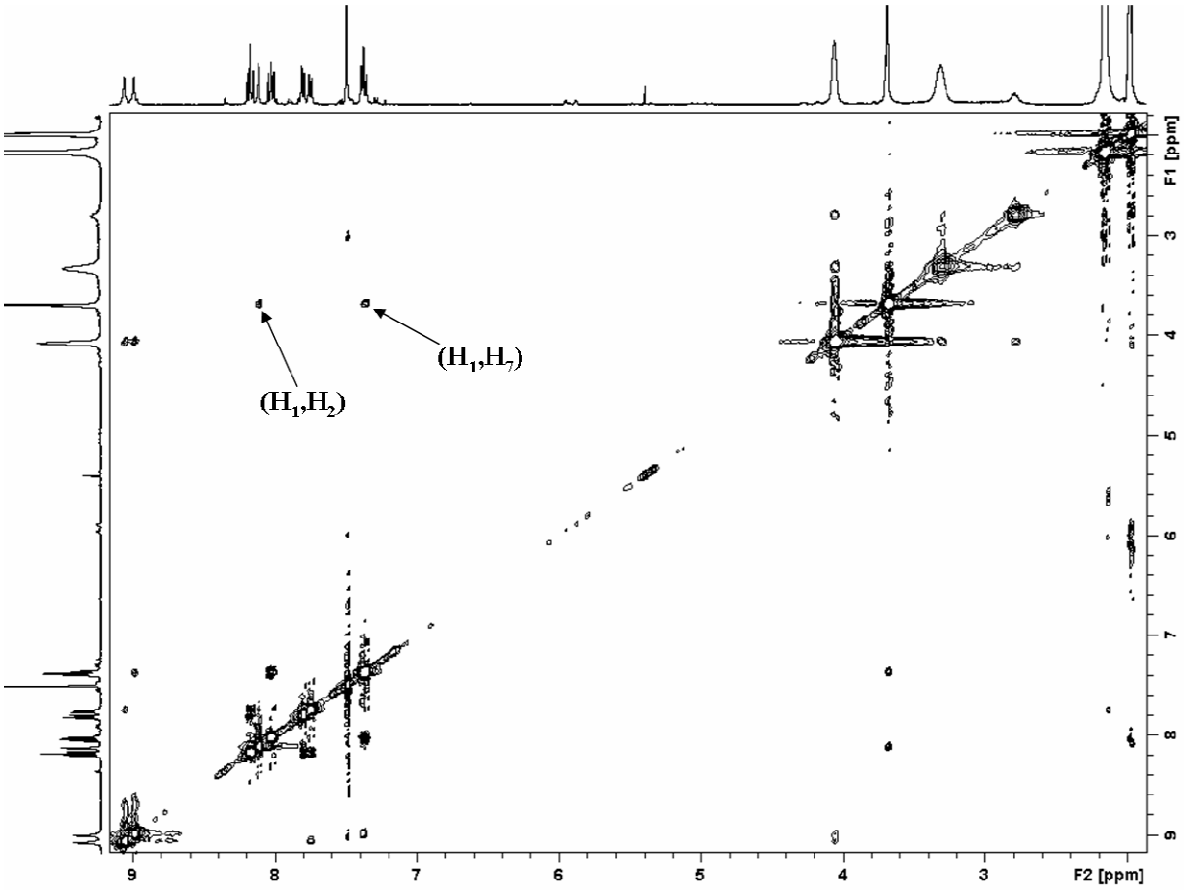


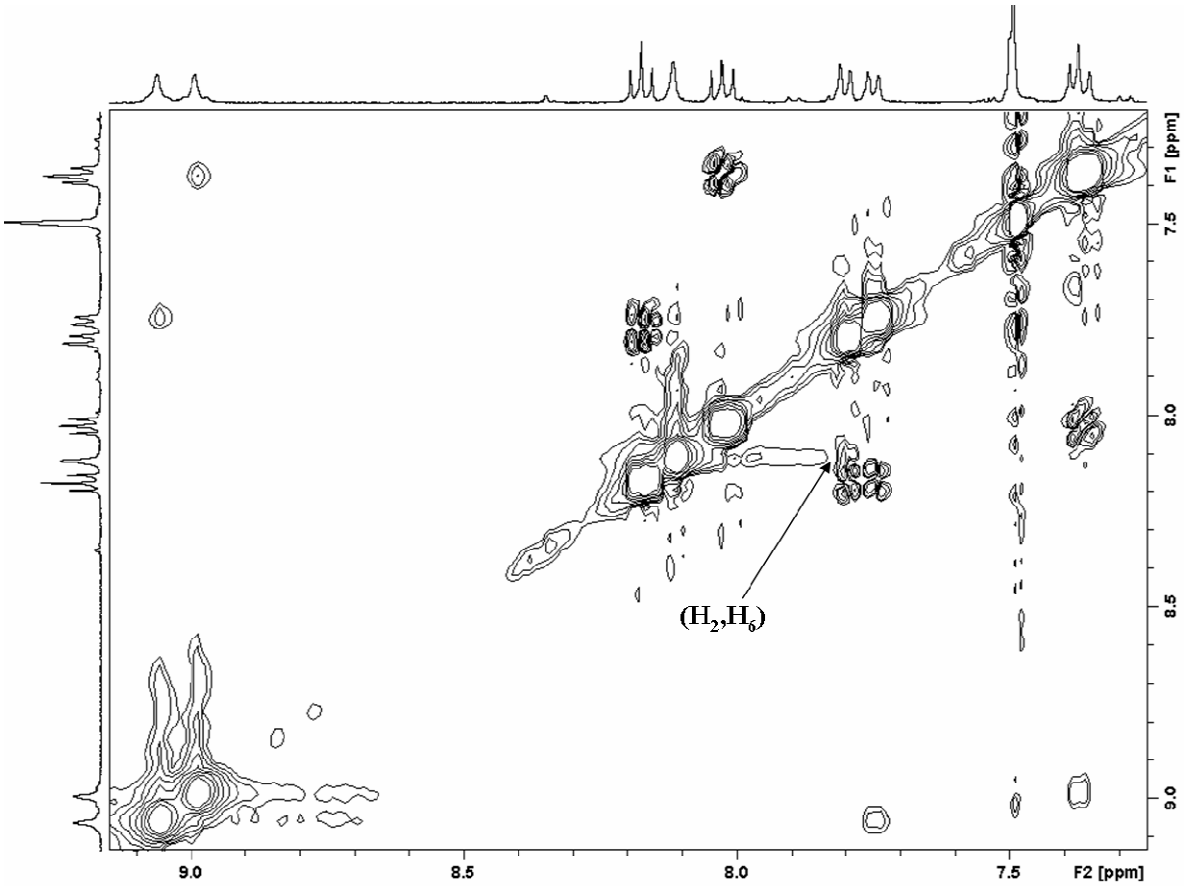
$(OTf)_2$

COSY ($CDCl_3$*/CD_3CN: 56/44):

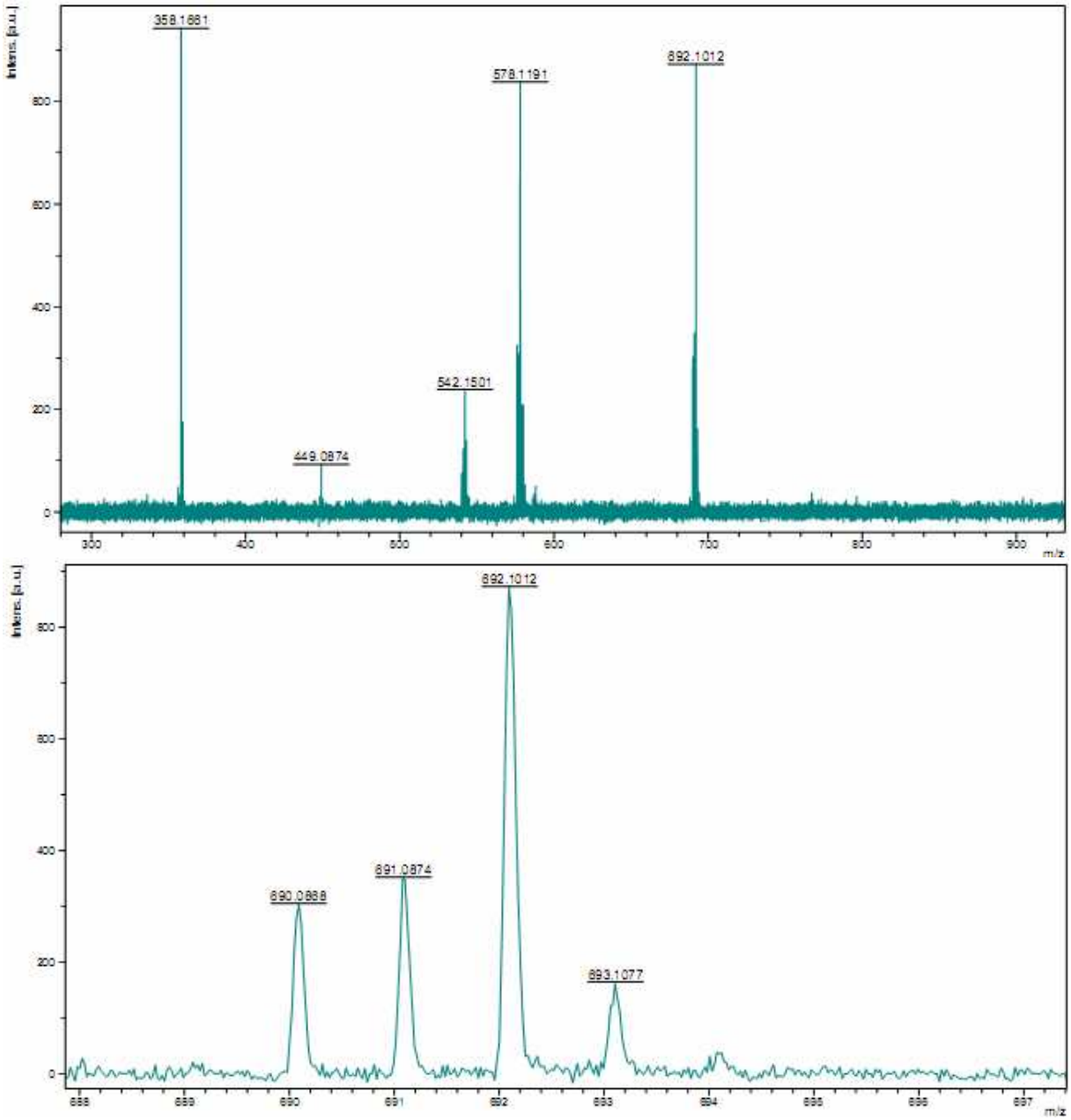


ROESY ($CDCl_3$*/CD_3CN: 56/44):

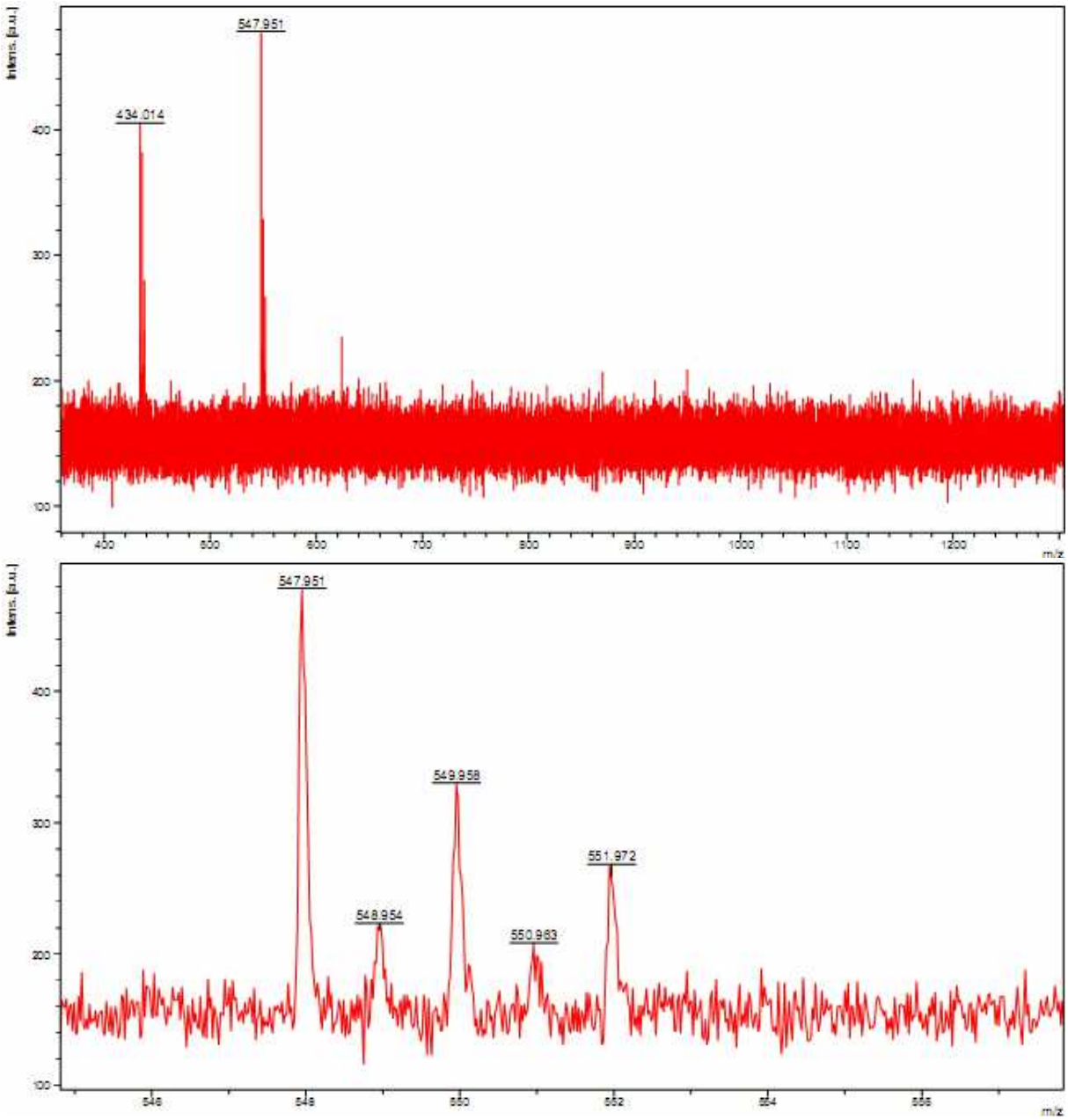

(H1,H2)
(H1,H7)
F1 [ppm]
F2 [ppm]


(H2,H6)
F1 [ppm]
F2 [ppm]

MALDI-TOF (dithranol) of **Pb.1.N_2NH**:

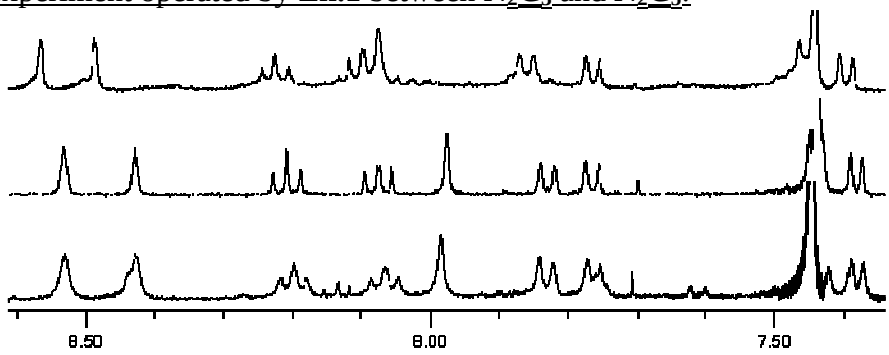


MALDI-TOF (dithranol) of **Zn.1.N_2NH**:



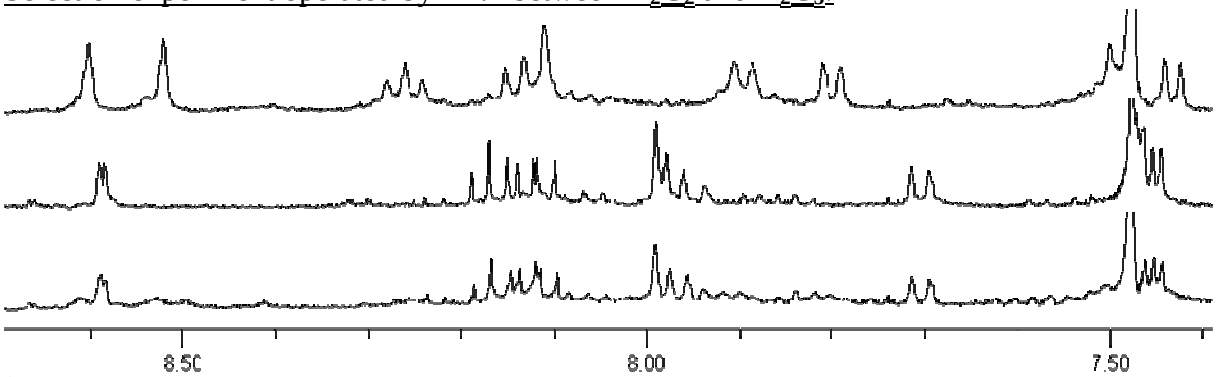
III. Component selection in covalent dynamic self-assembly processes of M.1.

Selection experiment operated by **Zn.1** between $\mathbf{N_2C_3}$ and $\mathbf{N_2C_5}$:



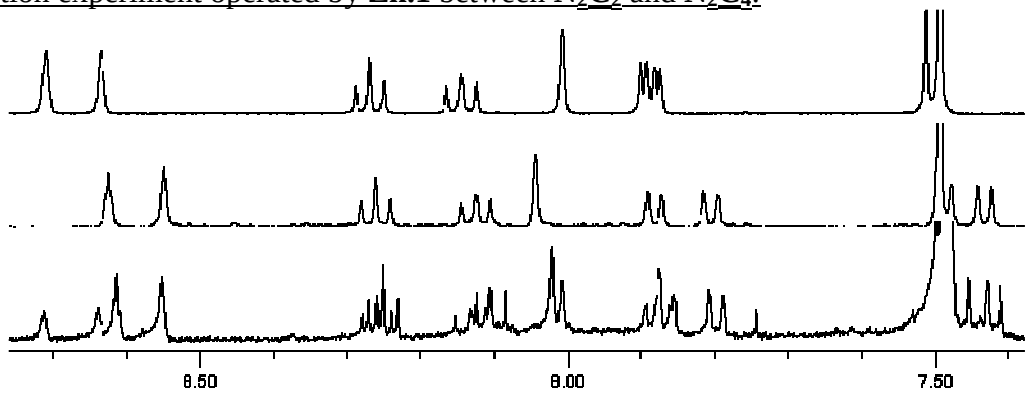
^{1}H NMR spectra showing the selection operated by **Zn.1** between $\mathbf{N_2C_3}$ and $\mathbf{N_2C_5}$, in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. Bottom: competition experiment between $\mathbf{N_2C_3}$ and $\mathbf{N_2C_5}$, spectrum recorded after 3 days at 65°C ; middle: macrocycle $\mathbf{Zn.1.N_2C_3}$; top: macrocycle $\mathbf{Zn.1.N_2C_5}$.

Selection experiment operated by **Zn.1** between $\mathbf{N_2C_2}$ and $\mathbf{N_2C_5}$:



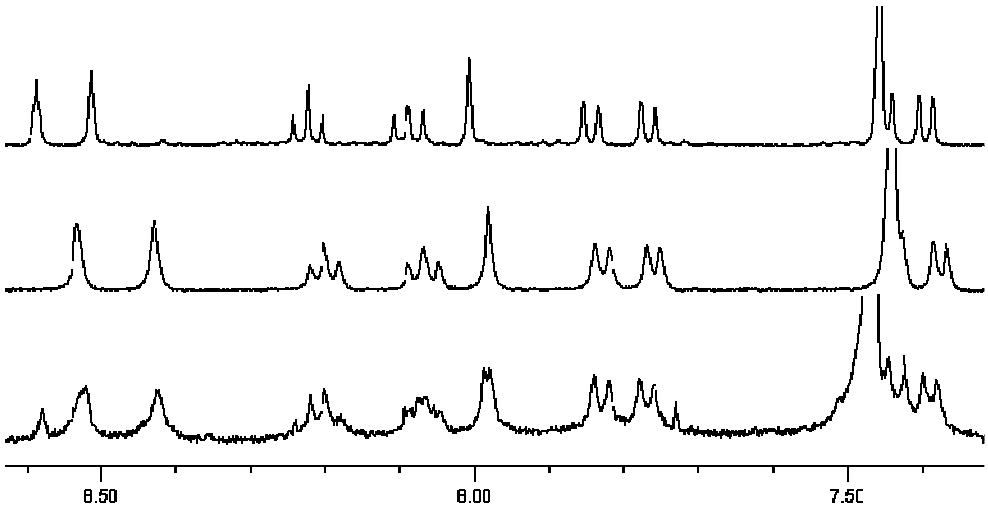
^{1}H NMR spectra showing the selection operated by **Zn.1** between $\mathbf{N_2C_2}$ and $\mathbf{N_2C_5}$, in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. Bottom: competition experiment between $\mathbf{N_2C_2}$ and $\mathbf{N_2C_5}$, spectrum recorded after 1 day at 50°C ; middle: macrocycle $\mathbf{Zn.1.N_2C_2}$; top: macrocycle $\mathbf{Zn.1.N_2C_5}$.

Selection experiment operated by **Zn.1** between $\mathbf{N_2C_2}$ and $\mathbf{N_2C_4}$:



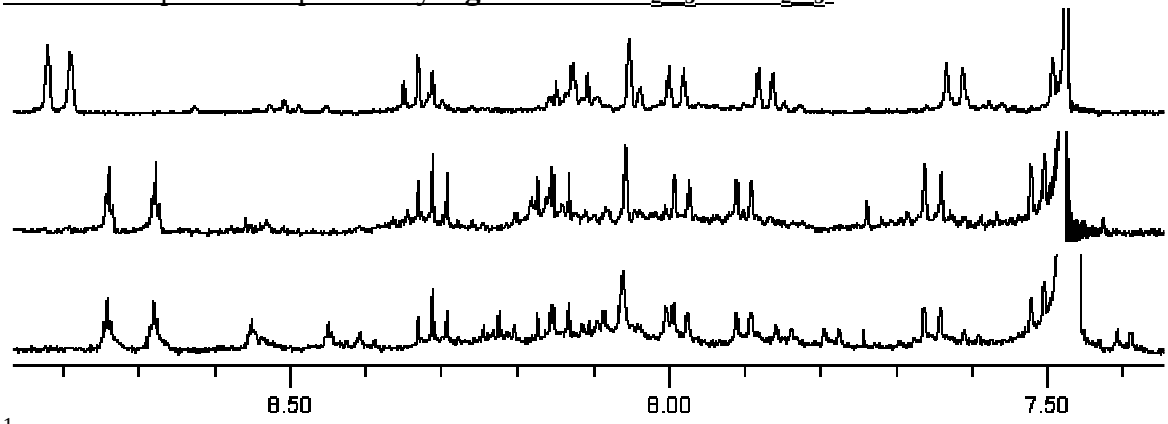
^{1}H NMR spectra showing the selection operated by **Zn.1** between $\mathbf{N_2C_2}$ and $\mathbf{N_2C_4}$, in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. Bottom: competition experiment between $\mathbf{N_2C_2}$ and $\mathbf{N_2C_4}$, spectrum recorded after 6 days at 60°C ; middle: macrocycle $\mathbf{Zn.1.N_2C_4}$; top: macrocycle $\mathbf{Zn.1.N_2C_2}$.

Selection experiment operated by **Zn.1** between $\mathbf{N_2C_3}$ and $\mathbf{N_2C_4}$:



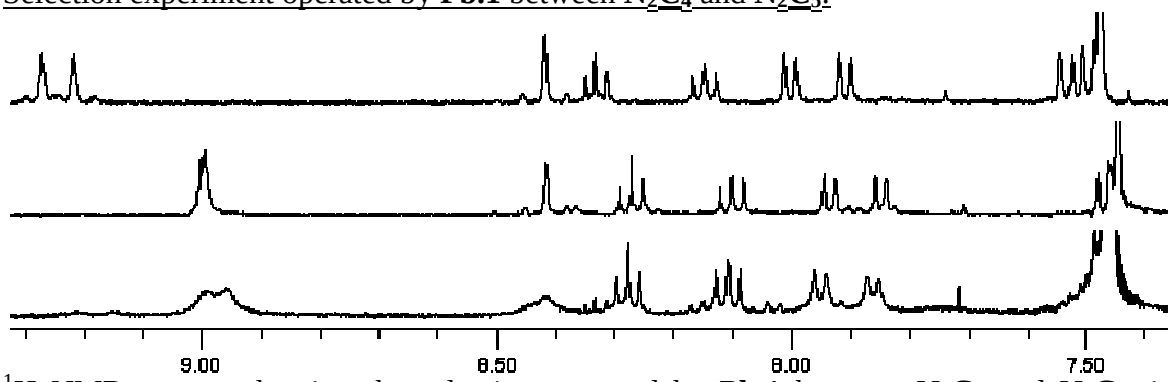
^{1}H NMR spectra showing the selection operated by **Zn.1** between $\mathbf{N_2C_3}$ and $\mathbf{N_2C_4}$, in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. Bottom: competition experiment between $\mathbf{N_2C_3}$ and $\mathbf{N_2C_4}$, spectrum recorded after 6 days at 60°C ; middle: macrocycle **Zn.1.**$\mathbf{N_2C_3}$; top: macrocycle **Zn.1.**$\mathbf{N_2C_4}$.

Selection experiment operated by **Hg.1** between $\mathbf{N_2C_3}$ and $\mathbf{N_2C_5}$:



^{1}H NMR spectra showing the selection operated by **Hg.1** between $\mathbf{N_2C_3}$ and $\mathbf{N_2C_5}$, in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. Bottom: competition experiment between $\mathbf{N_2C_3}$ and $\mathbf{N_2C_5}$, spectrum recorded after 1 day at 60°C ; middle: macrocycle **Hg.1.**$\mathbf{N_2C_3}$; top: macrocycle **Hg.1.**$\mathbf{N_2C_5}$. The spectrum of the competition experiment contains also peaks due to unidentified species.

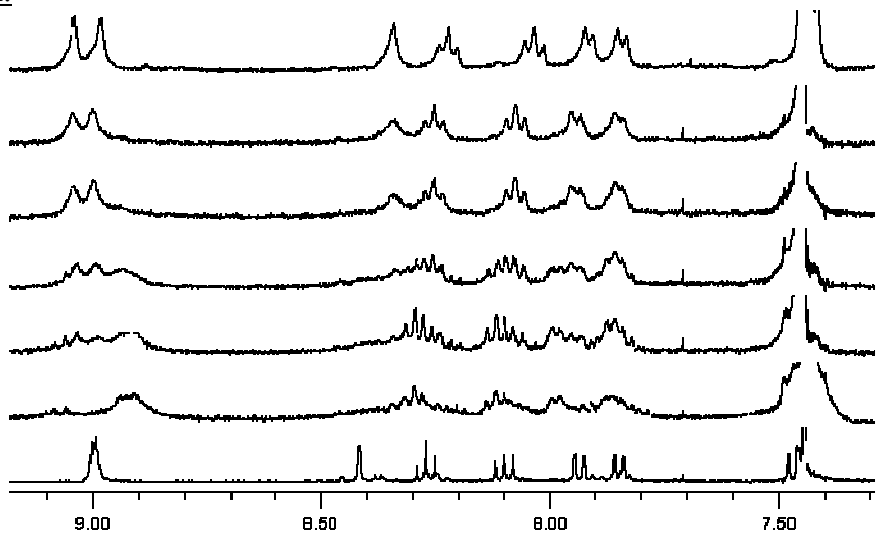
Selection experiment operated by **Pb.1** between $\mathbf{N_2C_4}$ and $\mathbf{N_2C_5}$:



^{1}H NMR spectra showing the selection operated by **Pb.1** between $\mathbf{N_2C_4}$ and $\mathbf{N_2C_5}$, in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. Bottom: competition experiment between $\mathbf{N_2C_4}$

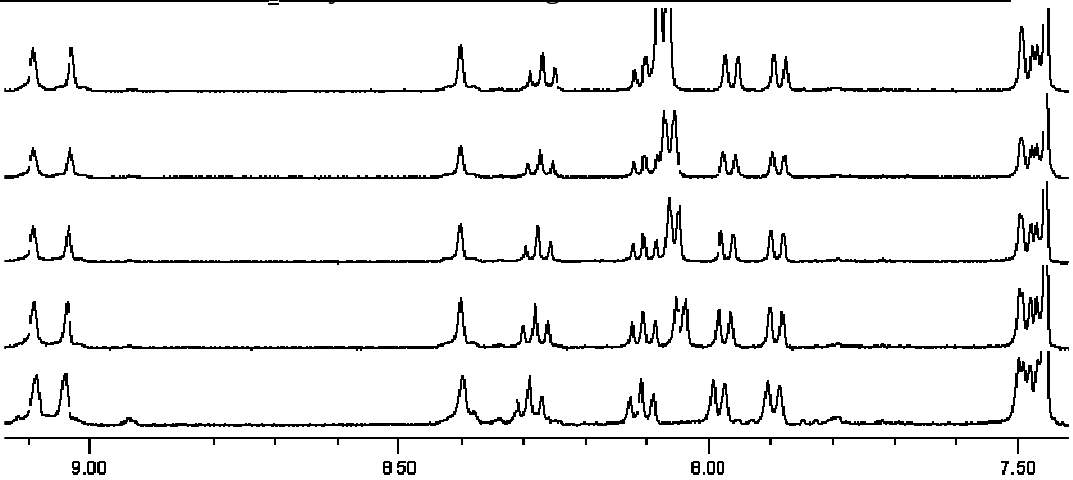
and **N_2C_5**, spectrum recorded after 4 days at 65°C ; middle: macrocycle **Pb.1.N_2C_5** ; top: macrocycle **Pb.1.N_2C_4**.

NMR titration of **Pb.1.N_2C_5** by **N_2O** showing that constitutional rearrangement occurs leading to the formation of the most stable metallo-macrocycle **Pb.1.N_2O** through transimination:



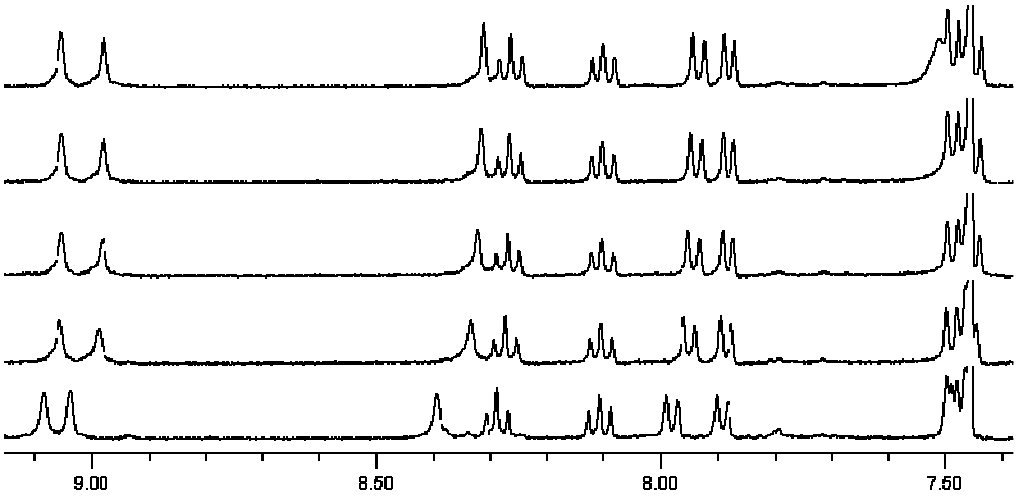
^{1}H NMR spectra showing the conversion, by transimination, from **Pb.1.N_2C_5** to **Pb.1.N_2O** upon addition of **N_2O** in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration and room temperature. From bottom to top: **Pb.1.N_2C_5**, after addition of 1.0 equivalent of **N_2O**, then after 2.5, 8.5, 21.75, 32.25 hours, spectrum recorded at -50°C.

NMR titration of **Pb.1.N_2O** by DMAP showing an interaction in the solution state:



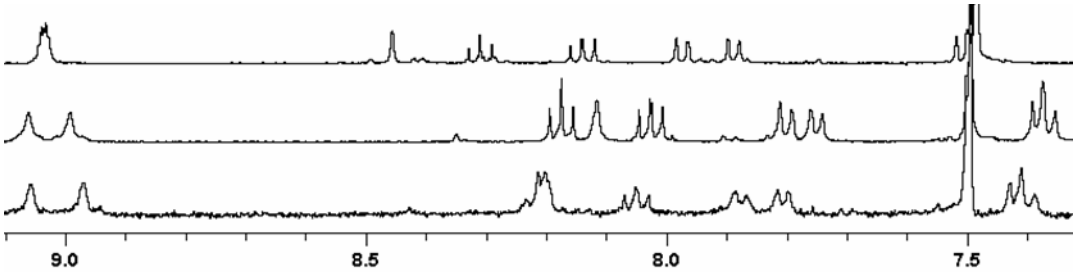
^{1}H NMR titration of **Pb.1.N_2O** by DMAP in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration and room temperature. From bottom to top: 0.0, 0.6, 1.0, 1.4, 2.0 equivalent of DMAP.

NMR titration of **Pb.1.N_2O** by imidazole showing an interaction in the solution state:



^{1}H NMR titration of **Pb.1.N_2O** by imidazole in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration and room temperature. From bottom to top: 0.0, 0.6, 1.0, 1.4, 2.0 equivalent of imidazole.

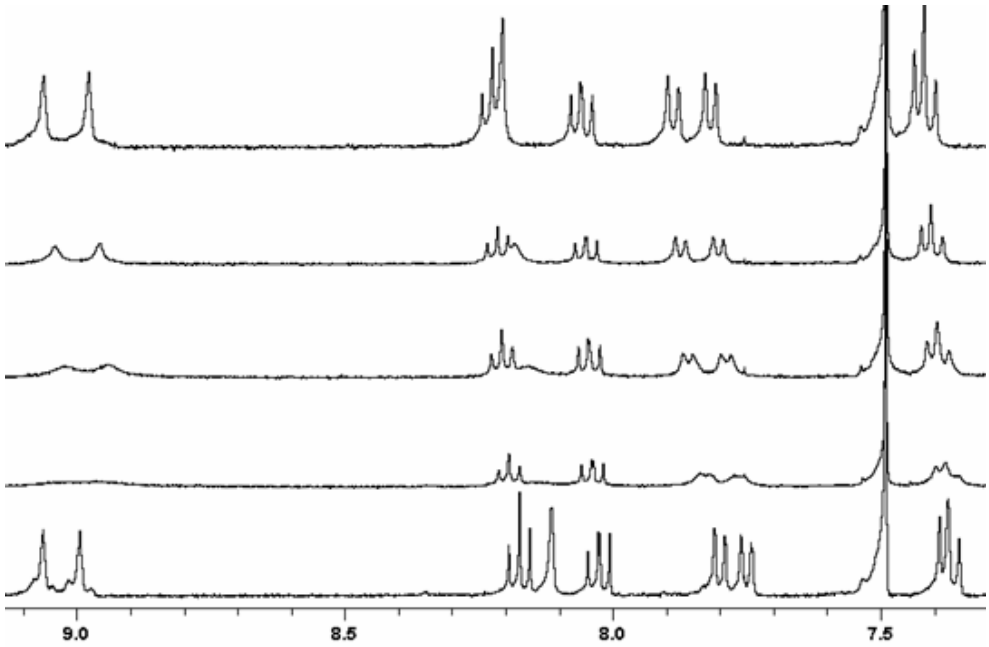
Selection experiment operated by **Pb.1** between **N_2C_5** and **N_2NH**:



^{1}H NMR spectra showing the selection operated by **Pb.1** between **N_2NH** and **N_2C_5**, in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. Bottom: competition experiment between **N_2NH** and **N_2C_5**, spectrum recorded after 1 day at room temperature ; middle: macrocycle **Pb.1.N_2NH** ; top: macrocycle **Pb.1.N_2C_5**.

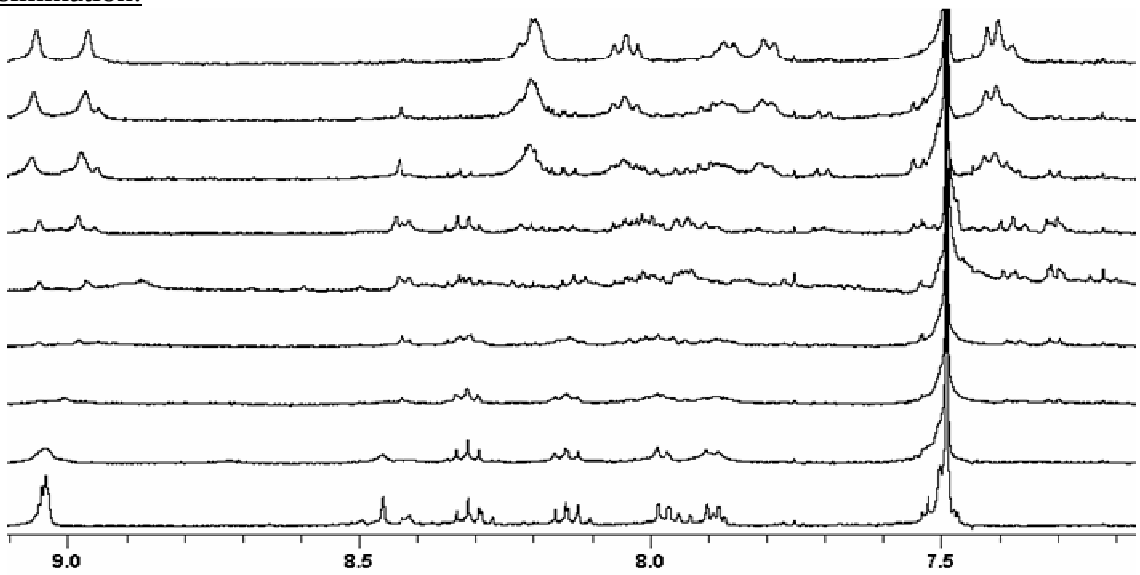
Even if the imine region (ca. 9.0 ppm) strongly suggests that selection of **N_2NH** has occurred, the other peaks do not perfectly fit with those of **Pb.1.N_2NH**. This is again explained by an intermolecular interaction between the metallo-macrocycle and the remaining diamine. Indeed, addition of **N_2C_5** to **Pb.1.N_2NH** induces immediate changes of the chemical shifts, which eventually reach those displayed in the competition experiment (see below). On the other hand, addition of **N_2NH** onto **Pb.1.N_2C_5** induces, by a transimination reaction which requires hours to reach completion, the formation of the more stable macrocycle **Pb.1.N_2NH** (see below).

Titration of **Pb.1.N_2NH** by **N_2C_5**:



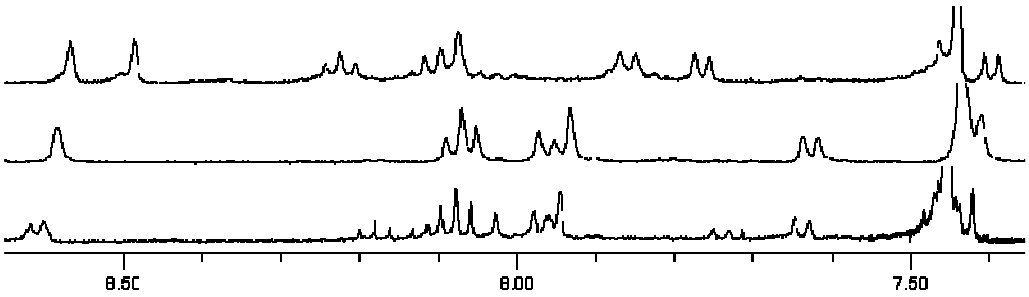
^{1}H NMR titration of **Pb.1.N_2NH** by **N_2C_5** in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. From bottom to top: 0.0, 0.3, 0.5, 0.7 and 1.0 equivalent of **N_2C_5**. Thermodynamic equilibrium was reached within the time needed to record the NMR spectrum after addition of the diamine, i.e. a few tens of seconds.

NMR titration of **Pb.1.N_2C_5** by **N_2NH** showing that constitutional rearrangement occurs leading to the formation of the most stable metallo-macrocycle **Pb.1.N_2NH** through transimination:



^{1}H NMR spectra showing the conversion, by transimination, from **Pb.1.N_2C_5** to **Pb.1.N_2NH** upon addition of **N_2NH** in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration and room temperature. From bottom to top: 0.0, 0.3, 0.5, 0.7, 1.0 equivalent of **N_2NH**, then after 3, 19, 27, 51 hours.

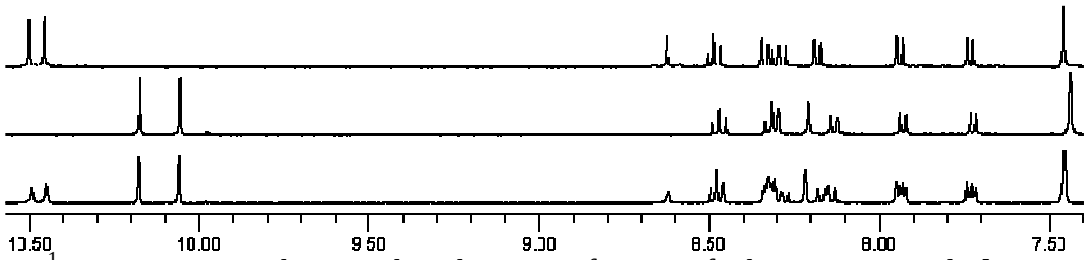
Competition experiment operated by **Zn.1** between **N_2C_5** and **N_2NH**:



^{1}H NMR spectra showing the selection operated by **Zn.1** between $\mathbf{N_2C_5}$ and $\mathbf{N_2NH}$, in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. Bottom: competition experiment between $\mathbf{N_2C_5}$ and $\mathbf{N_2NH}$, spectrum recorded after 2 days at 60°C ; middle: macrocycle $\mathbf{Zn.1.N_2NH}$; top: macrocycle $\mathbf{Zn.1.N_2C_5}$.

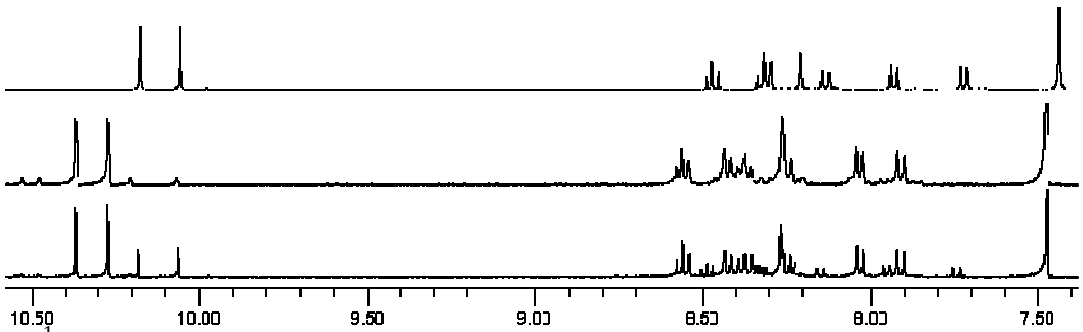
IV. Diamine-dependent selection of metal ions.

Competition experiment between $\mathbf{Zn(OTf)_2}$ and $\mathbf{Pb(OTf)_2}$ of the complex formation from **1**:



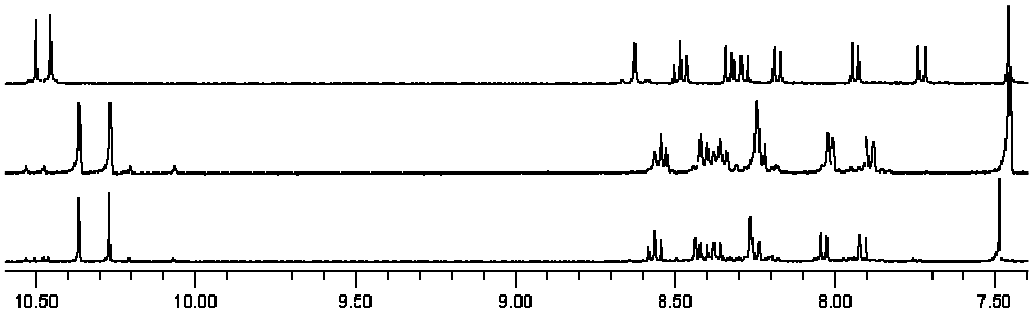
^{1}H NMR spectra showing the inherent preference of **1** between **Zn** and **Pb**, in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. Bottom: competition experiment between $Zn(OTf)_2$ and $Pb(OTf)_2$, spectrum recorded after a few hours at room temperature ; middle: **Zn.1** ; top: **Pb.1**.

Competition experiment between $\mathbf{Zn(OTf)_2}$ and $\mathbf{Hg(OTf)_2}$ of the complex formation from **1**:



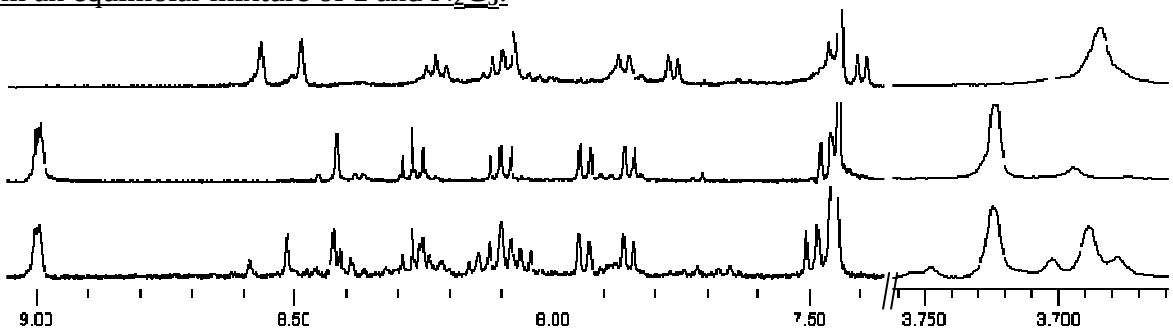
^{1}H NMR spectra showing the inherent preference of **1** between **Zn** and **Hg**, in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. Bottom: competition experiment between $Zn(OTf)_2$ and $Hg(OTf)_2$, spectrum recorded after 1 day at 60°C ; middle: **Hg.1** ; top: **Zn.1**.

Competition experiment between $\mathbf{Pb(OTf)_2}$ and $\mathbf{Hg(OTf)_2}$ on the complex formation from **1**:



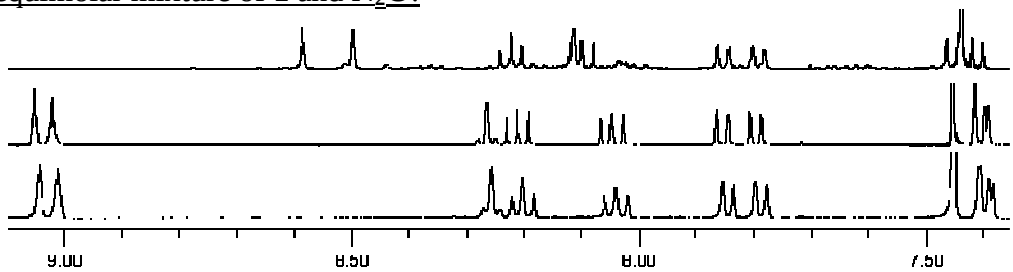
^{1}H NMR spectra showing the inherent preference of **1** between Pb(II) and Hg(II), in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. Bottom: competition experiment between $Pb(OTf)_2$ and $Hg(OTf)_2$, spectrum recorded after 1 day at 60°C ; middle: **Hg.1** ; top: **Pb.1**.

Competition experiment between **Zn(OTf)$_2$** and **Pb(OTf)$_2$** on the macrocycle formation from an equimolar mixture of **1** and **N_2C_5**:



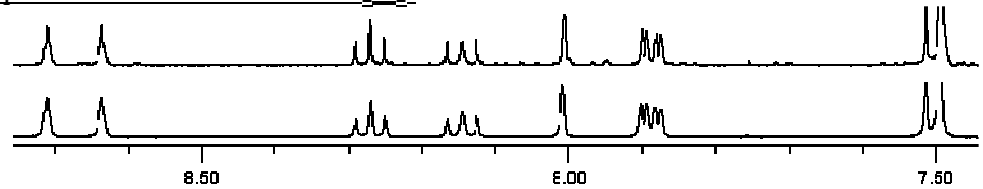
$CDCl_3/CD_3CN$: 6/4, 5 mM concentration. Bottom: competition experiment between $Zn(OTf)_2$ and $Pb(OTf)_2$ with an equimolar mixture of **1** and **N_2C_5**, spectrum recorded after a few hours at room temperature ; middle: **Pb.1.N_2C_5** ; top: **Zn.1.N_2C_5**.

Competition experiment between **Zn(OTf)$_2$** and **Pb(OTf)$_2$** on the macrocycle formation from an equimolar mixture of **1** and **N_2O**:



$CDCl_3/CD_3CN$: 6/4, 5 mM concentration. Bottom: competition experiment between $Zn(OTf)_2$ and $Pb(OTf)_2$ with an equimolar mixture of **1** and **N_2O**, spectrum recorded after 1 day at room temperature ; middle: **Pb.1.N_2O** ; top: **Zn.1.N_2O**.

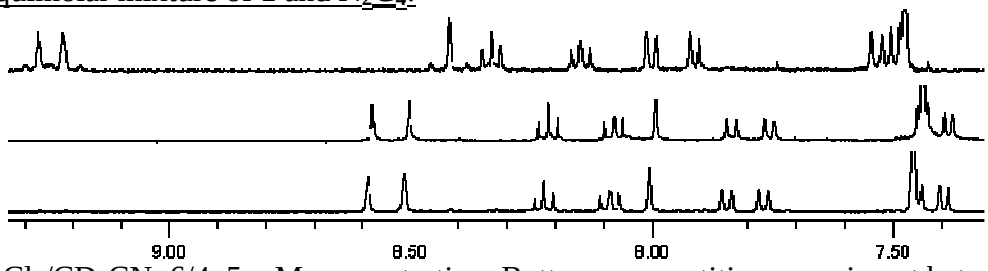
Competition experiment between **Zn(OTf)$_2$** and **Pb(OTf)$_2$** on the macrocycle formation from an equimolar mixture of **1** and **N_2C_2**:



$CDCl_3/CD_3CN$: 6/4, 5 mM concentration. Bottom: competition experiment between $Zn(OTf)_2$ and $Pb(OTf)_2$ with an equimolar mixture of **1** and **N_2C_2**, spectrum recorded after 2

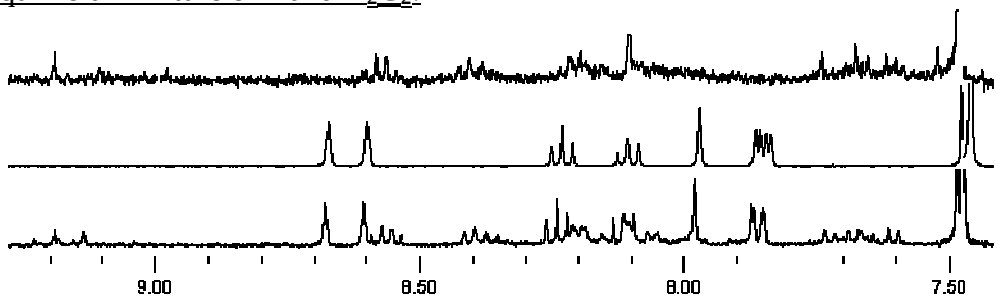
days at 65°C ; top: **Zn.1.N_2C_2**. Note that the [1+1] macrocycle **Pb.1.N_2C_2** does not form under those conditions (see text).

Competition experiment between **Zn(OTf)$_2$** and **Pb(OTf)$_2$** on the macrocycle formation from an equimolar mixture of **1** and **N_2C_4**:



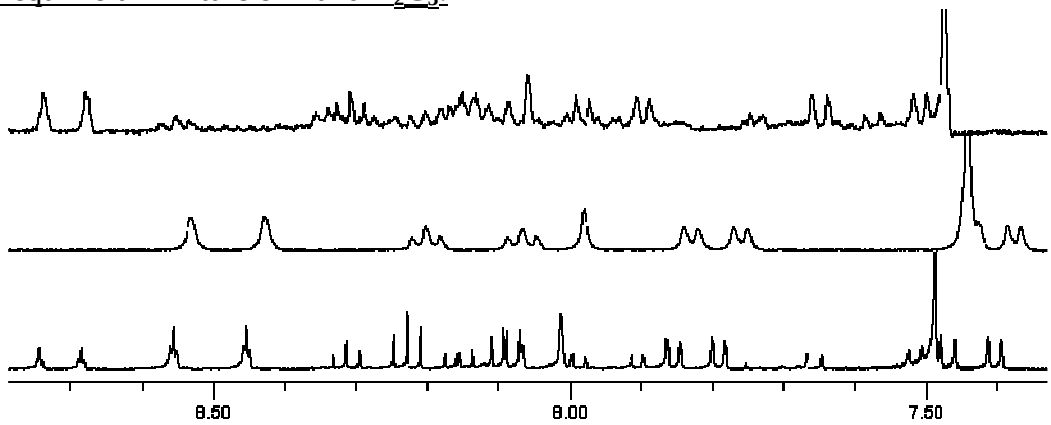
$CDCl_3/CD_3CN$: 6/4, 5 mM concentration. Bottom: competition experiment between $Zn(OTf)_2$ and $Pb(OTf)_2$ with an equimolar mixture of **1** and **N_2C_4**, spectrum recorded after 2 days at 65°C ; middle: **Zn.1.N_2C_4** ; top: **Pb.1. N_2C_4**.

Competition experiment between **Zn(OTf)$_2$** and **Hg(OTf)$_2$** on the macrocycle formation from an equimolar mixture of **1** and **N_2C_2**:



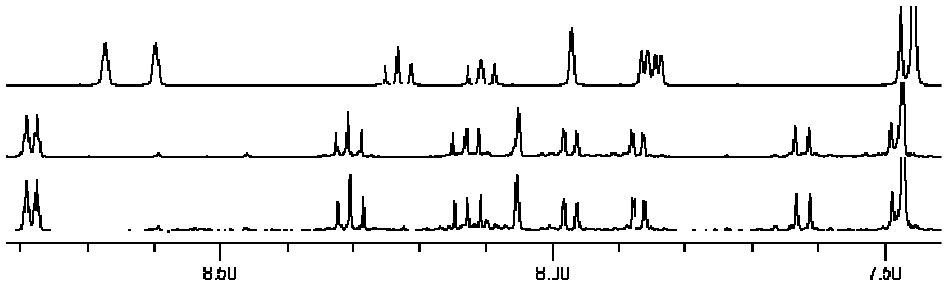
$CDCl_3/CD_3CN$: 6/4, 5 mM concentration. Bottom: competition experiment between $Zn(OTf)_2$ and $Hg(OTf)_2$ with an equimolar mixture of **1** and **N_2C_2**, spectrum recorded after 1 day at 60°C ; middle: **Zn.1.N_2C_2** ; top: equimolar mixture of $Hg(OTf)_2$, **1** and **N_2C_2**.

Competition experiment between **Zn(OTf)$_2$** and **Hg(OTf)$_2$** on the macrocycle formation from an equimolar mixture of **1** and **N_2C_3**:



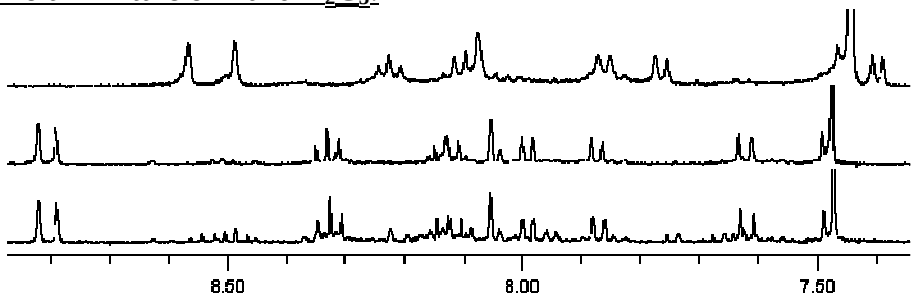
$CDCl_3/CD_3CN$: 6/4, 5 mM concentration. Bottom: competition experiment between $Zn(OTf)_2$ and $Hg(OTf)_2$ with an equimolar mixture of **1** and **N_2C_3**, spectrum recorded after 2 days at 60°C ; middle: **Zn.1.N_2C_3** ; top: **Hg.1.N_2C_3**.

Competition experiment between **Zn(OTf)$_2$** and **Hg(OTf)$_2$** on the macrocycle formation from an equimolar mixture of **1** and **N_2C_4**:



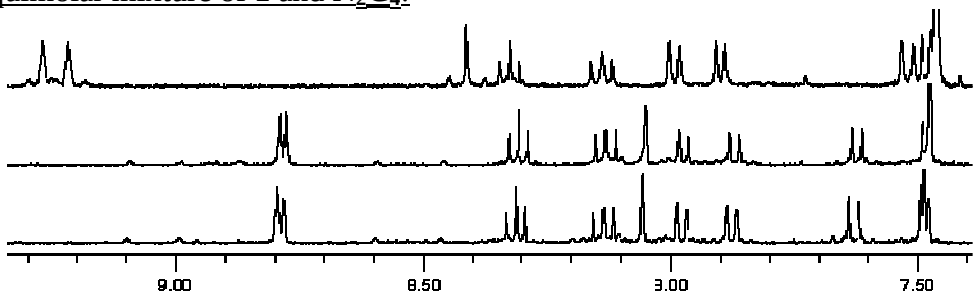
$CDCl_3/CD_3CN$: 6/4, 5 mM concentration. Bottom: competition experiment between $Zn(OTf)_2$ and $Hg(OTf)_2$ with an equimolar mixture of **1** and $\mathbf{N_2C_4}$, spectrum recorded after 2 days at 60°C ; middle: $\mathbf{Hg.1.N_2C_4}$; top: $\mathbf{Zn.1.N_2C_4}$.

Competition experiment between $\mathbf{Zn(OTf)_2}$ and $\mathbf{Hg(OTf)_2}$ on the macrocycle formation from an equimolar mixture of **1** and $\mathbf{N_2C_5}$:



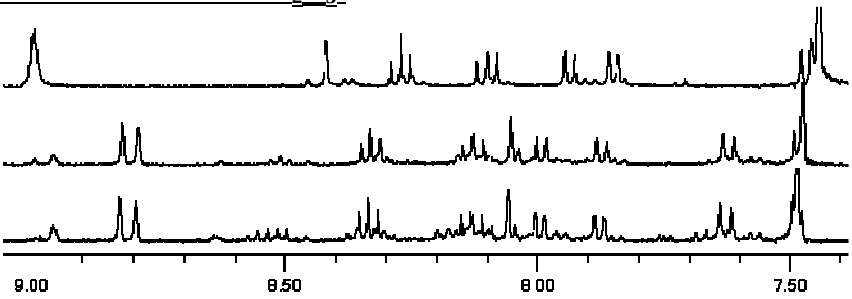
$CDCl_3/CD_3CN$: 6/4, 5 mM concentration. Bottom: competition experiment between $Zn(OTf)_2$ and $Hg(OTf)_2$ with an equimolar mixture of **1** and $\mathbf{N_2C_5}$, spectrum recorded after 2 days at 60°C ; middle: $\mathbf{Hg.1.N_2C_5}$; top: $\mathbf{Zn.1.N_2C_5}$.

Competition experiment between $\mathbf{Pb(OTf)_2}$ and $\mathbf{Hg(OTf)_2}$ on the macrocycle formation from an equimolar mixture of **1** and $\mathbf{N_2C_4}$:



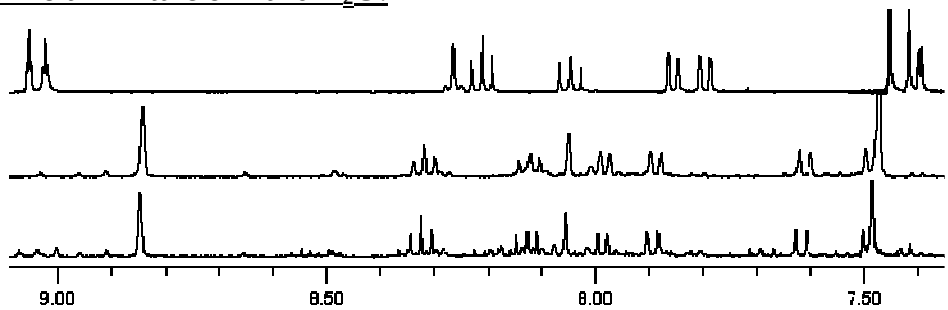
$CDCl_3/CD_3CN$: 6/4, 5 mM concentration. Bottom: competition experiment between $Pb(OTf)_2$ and $Hg(OTf)_2$ with an equimolar mixture of **1** and $\mathbf{N_2C_4}$, spectrum recorded after 2 days at 60°C ; middle: $\mathbf{Hg.1.N_2C_4}$; top: $\mathbf{Pb.1.N_2C_4}$.

Competition experiment between $\mathbf{Pb(OTf)_2}$ and $\mathbf{Hg(OTf)_2}$ on the macrocycle formation from an equimolar mixture of **1** and $\mathbf{N_2C_5}$:



$CDCl_3/CD_3CN$: 6/4, 5 mM concentration. Bottom: competition experiment between $Pb(OTf)_2$ and $Hg(OTf)_2$ with an equimolar mixture of **1** and $\mathbf{N_2C_5}$, spectrum recorded after 2 days at 60°C ; middle: $\mathbf{Hg.1.N_2C_5}$; top: $\mathbf{Pb.1.N_2C_5}$.

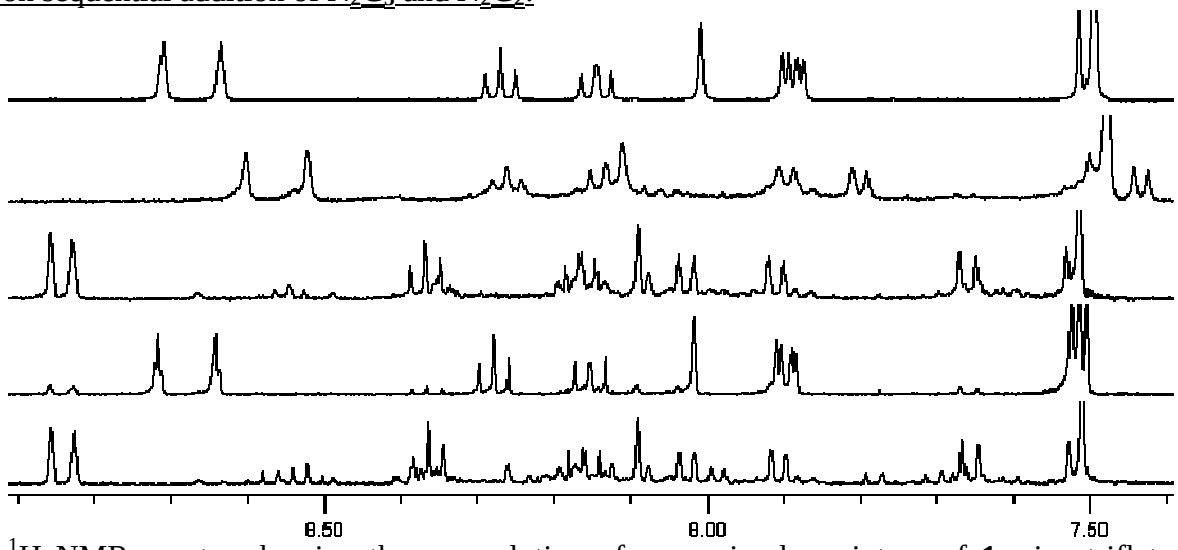
Competition experiment between $\mathbf{Pb(OTf)_2}$ and $\mathbf{Hg(OTf)_2}$ on the macrocycle formation from an equimolar mixture of **1** and $\mathbf{N_2O}$:



$CDCl_3/CD_3CN$: 6/4, 5 mM concentration. Bottom: competition experiment between $Pb(OTf)_2$ and $Hg(OTf)_2$ with an equimolar mixture of **1** and $\mathbf{N_2O}$, spectrum recorded after 2 days at 60°C ; middle: $\mathbf{Hg.1.N_2O}$; top: $\mathbf{Pb.1.N_2O}$.

V. Constitutional co-evolution in response to reciprocal metal ion/diamine effects.

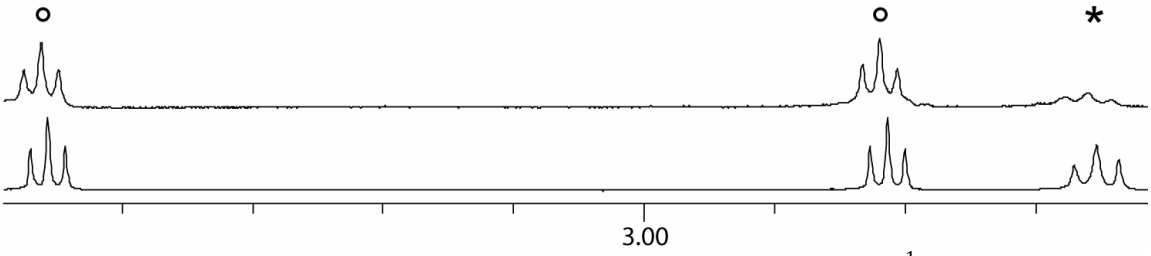
Constitutional evolution of an equimolar mixture of **1**, zinc triflate and mercury triflate upon sequential addition of $\mathbf{N_2C_5}$ and $\mathbf{N_2C_2}$:



^{1}H NMR spectra showing the co-evolution of an equimolar mixture of **1**, zinc triflate, mercury triflate upon sequential addition of $\mathbf{N_2C_5}$ and $\mathbf{N_2C_2}$, in $CDCl_3/CD_3CN$: 6/4 at 5 mM. From bottom to top: equimolar mixture of **1**, zinc triflate and mercury triflate after addition of one equivalent of $\mathbf{N_2C_5}$, after further addition of one equivalent of $\mathbf{N_2C_2}$ (spectrum recorded after 3 days at 60°C) ; $\mathbf{Hg.1.N_2C_5}$; $\mathbf{Zn.1.N_2C_5}$; $\mathbf{Zn.1.N_2C_2}$.

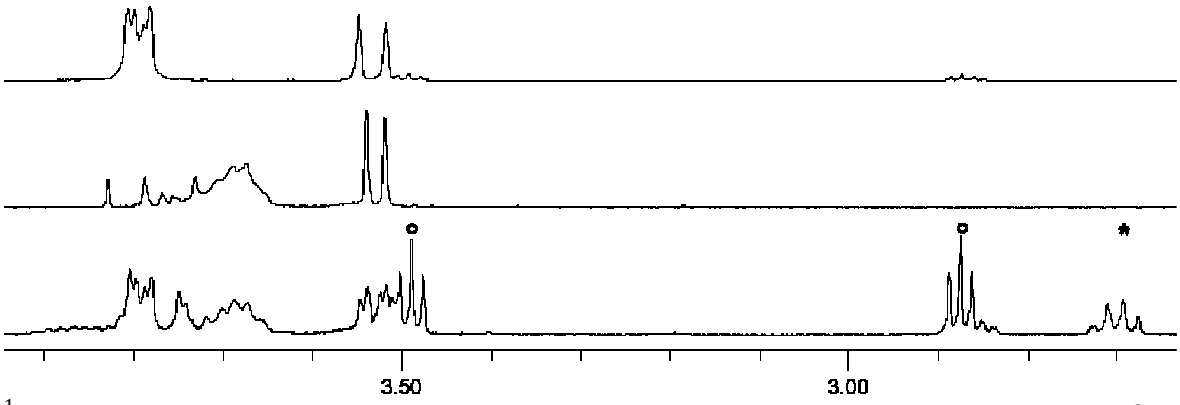
VI. Constitutional adaptation in response to shape changes.

Selection between $\mathbf{N_2O}$ and $\mathbf{N_2C_5}$ upon addition of **1**:



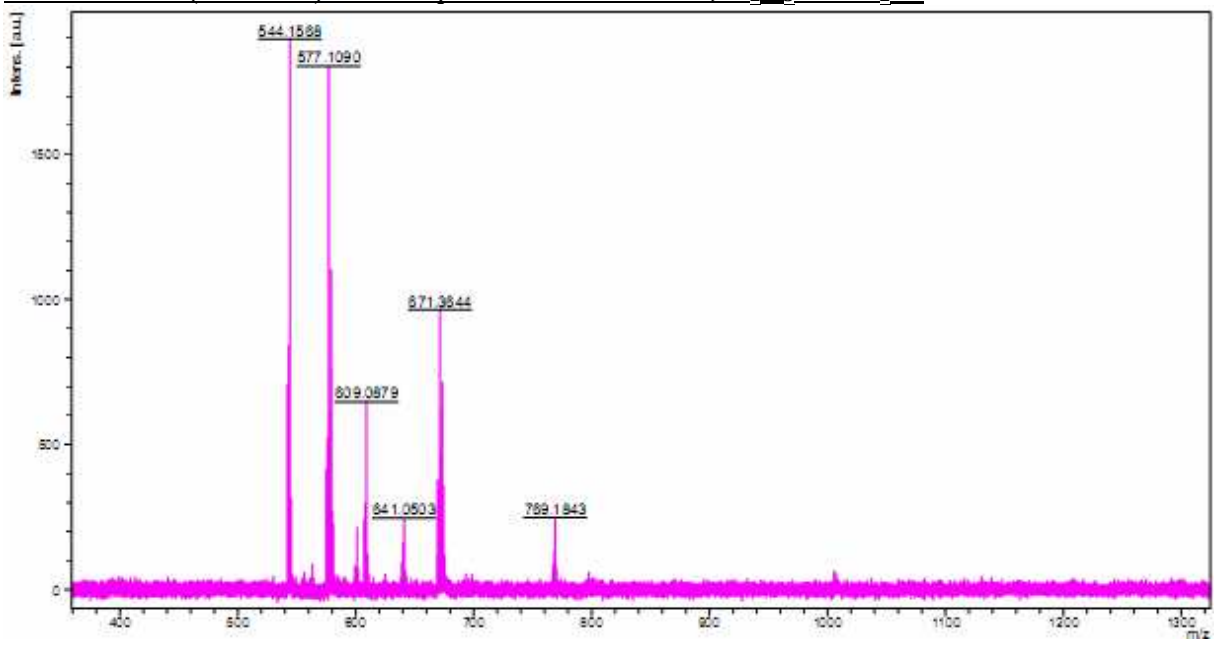
Selection between **N_2O** and **N_2C_5** upon addition of **1** (400 MHz ^{1}H NMR spectra in $CDCl_3/CD_3CN$ 6/4). Bottom: equimolar mixture of **N_2O** and **N_2C_5** ; top: after addition of 1 equivalent of **1**. The peaks belonging to **N_2O** are marked with a circle and the peak belonging to **N_2C_5** is marked with a star.

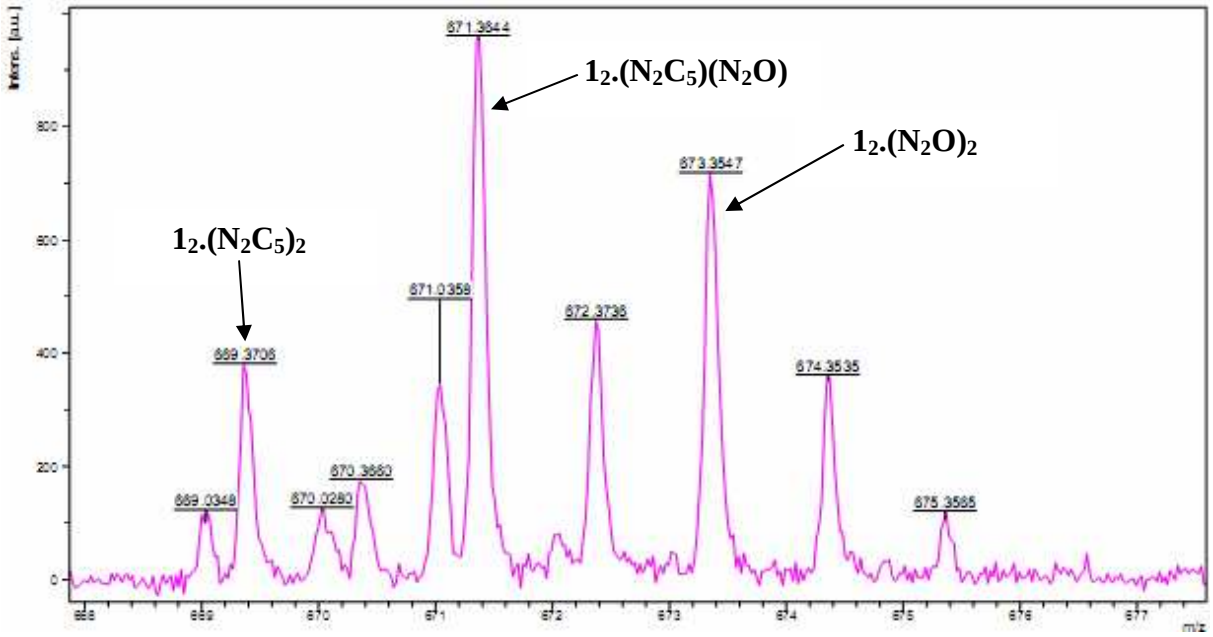
NMR spectra showing the non-selective solution state consisting in the mixture of **1**, **N_2O** and **N_2C_5** in $CDCl_3$:



^{1}H NMR spectra showing the non-selective solution state consisting in the mixture of **1**, **N_2O** and **N_2C_5** in $CDCl_3$. Bottom: equimolar mixture of **1**, **N_2O** and **N_2C_5** ; middle: self-assembly between **1** and **N_2C_5** ; top: macrocycle **$1_2.(N_2O)_2$**. The peaks belonging to the free **N_2O** are marked with a circle and the peak belonging to the free **N_2C_5** is marked with a star.

MALDI-TOF (dithranol) of the equimolar mixture of **1**, **N_2C_5** and **N_2O**:



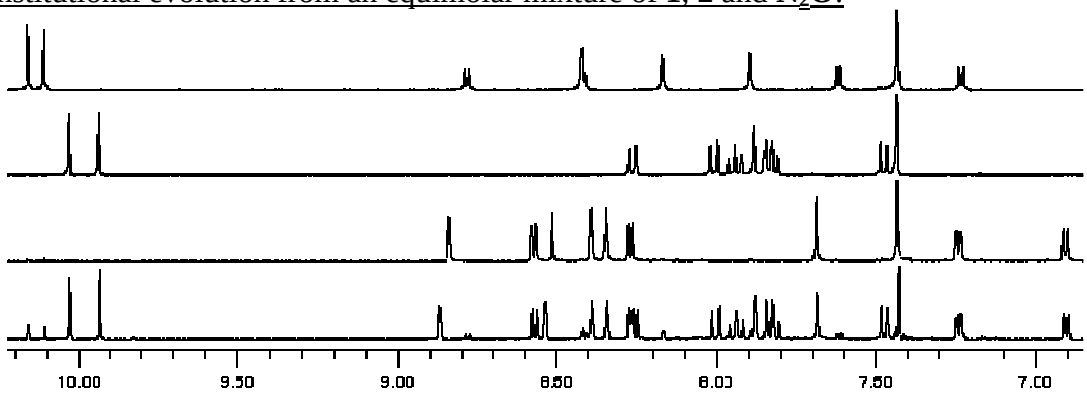


$1_2.(N_2C_5)(N_2O)$

$1_2.(N_2O)_2$

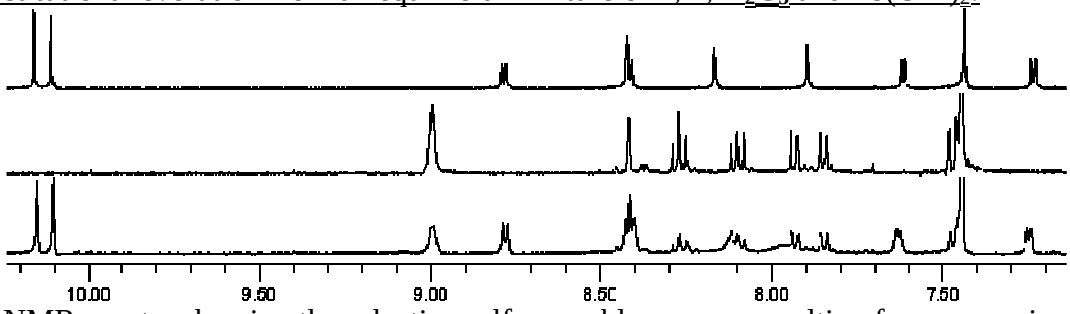
$1_2.(N_2C_5)_2$

Constitutional evolution from an equimolar mixture of **1**, **2** and N_2O:



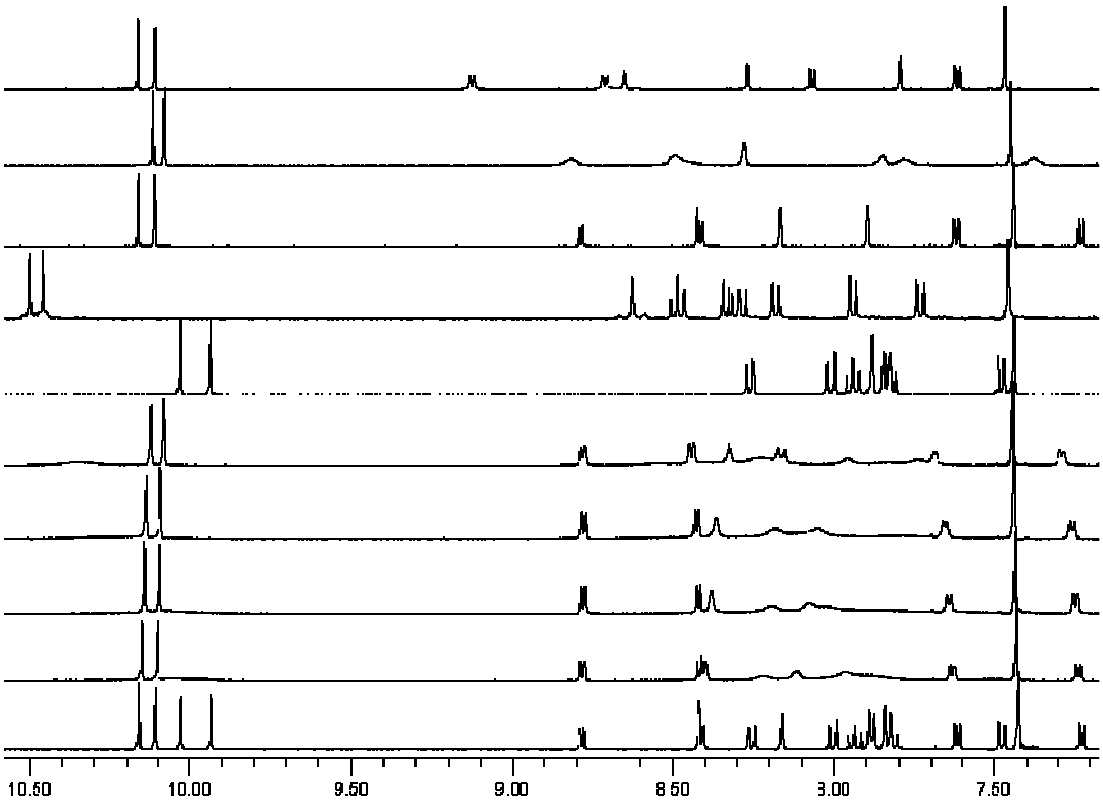
^{1}H NMR spectra showing the selective self-assembly process resulting from an equimolar mixture of **1**, **2** and N_2O in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. From bottom to top: mixture after 2 days at room temperature ; Macrocycle $\mathbf{2_2.(N_2O)_2}$; **1** ; **2**.

Constitutional evolution from an equimolar mixture of **1**, **2**, N_2C_5 and $Pb(OTf)_2$:



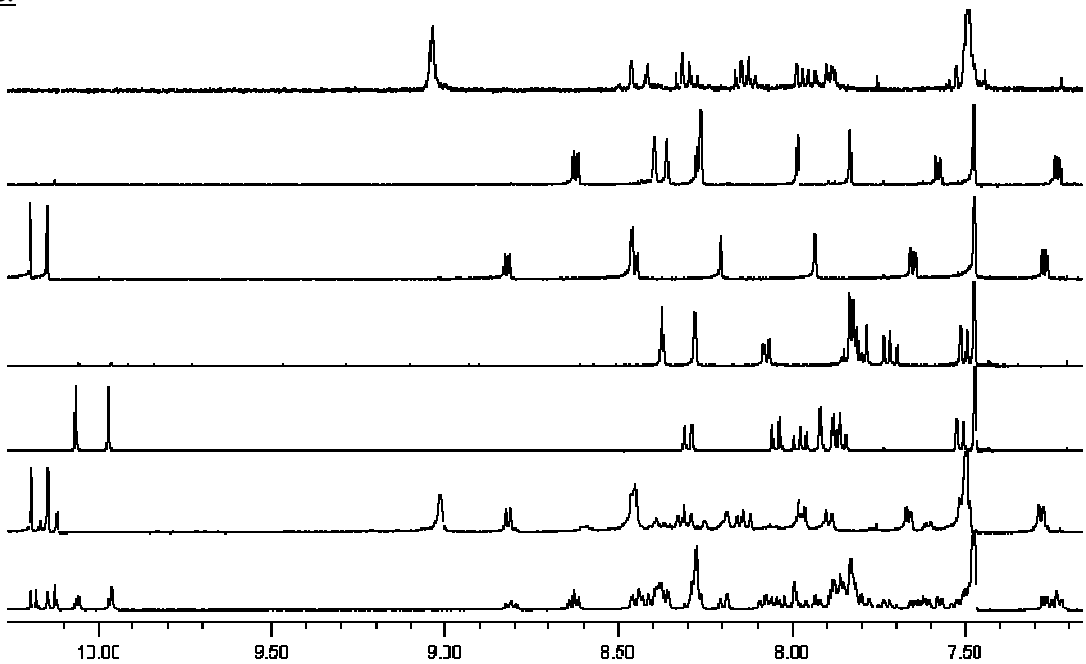
^{1}H NMR spectra showing the selective self-assembly process resulting from an equimolar mixture of **1**, **2**, N_2C_5 and lead triflate in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. From bottom to top: mixture after 1 day at room temperature ; $\mathbf{Pb.1.N_2C_5}$; **2**.

^{1}H NMR titration of an equimolar mixture of **1** and **2**, by $Pb(OTf)_2$:



^{1}H NMR spectra showing the titration of an equimolar mixture of **1** and **2** by lead triflate in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. From bottom to top: 0.0, 0.3, 0.5, 0.7, 1.0 equivalent of lead triflate ; **1** ; **Pb.1** ; **2** ; **Pb.2**$_2$; **Pb.2**.

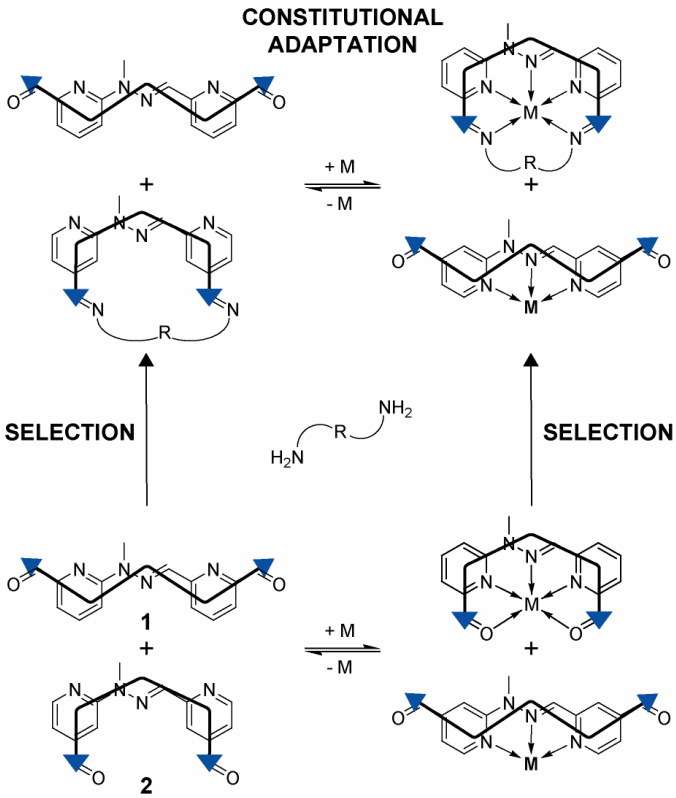
Analysis of an equimolar mixture of **1** and **2** after sequential addition of **NC**$_8$ and lead triflate:



^{1}H NMR spectra of an equimolar mixture of **1** and **2** after sequential addition of **NC$_8$** and lead triflate in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. From bottom to top: equimolar mixture of **1** and **2** after addition of 2.0 eq. of **NC$_8$**, after further addition of 1.0 eq. of lead triflate ; **1** ; **1.(NC$_8$)$_2$** ; **2** ; **2.(NC$_8$)$_2$** ; **Pb.1.(NC$_8$)$_2$**.

Discussion on the studies of the constitutional adaptation by using zinc triflate:

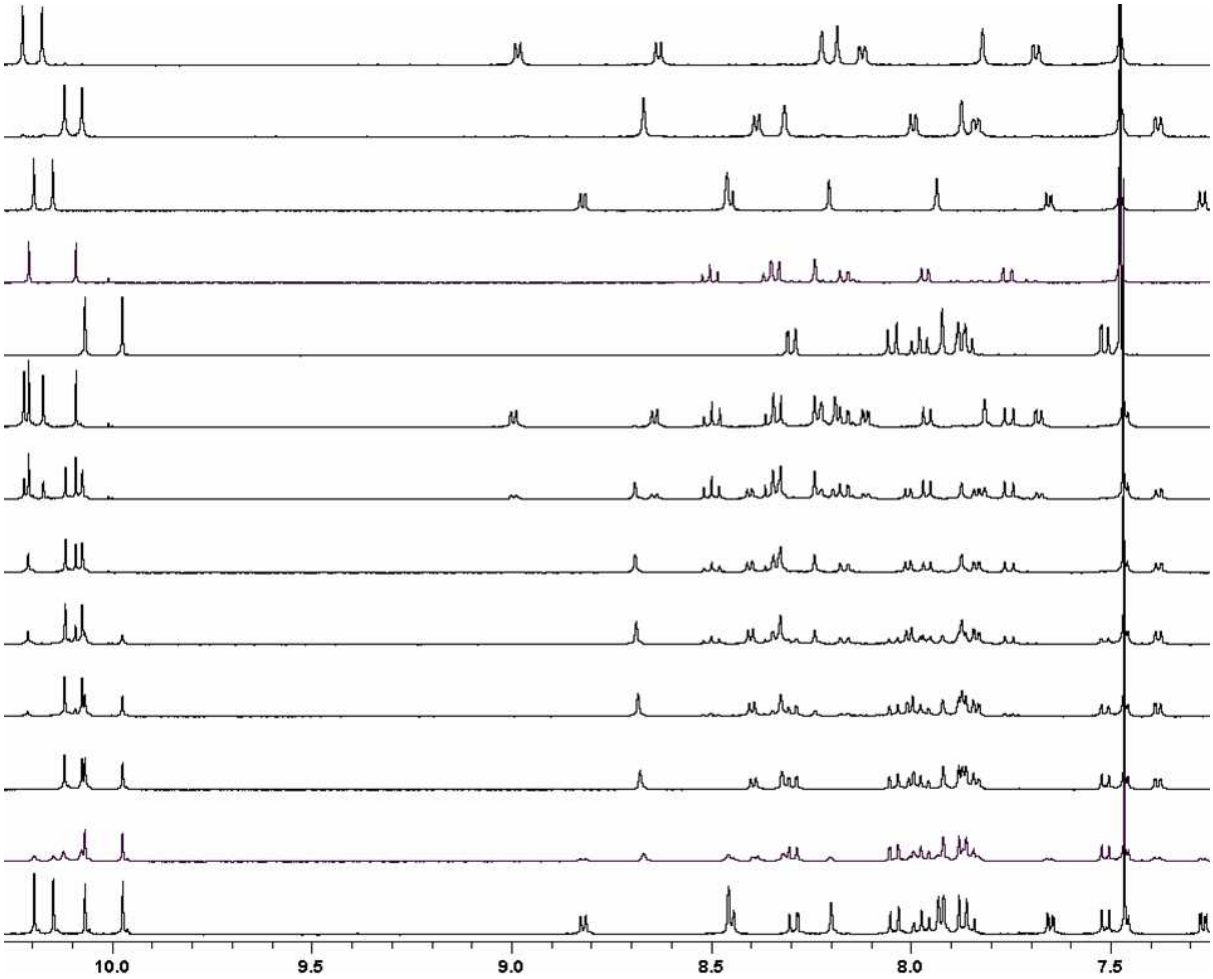
A selective self-assembled state was also achieved after addition of zinc triflate to the mixture of **1**, **2** and $\mathbf{N_2C_5}$ but it required in all cases the addition of 2.0 equivalent of zinc triflate (see below).



Representative illustration of an adaptation process induced by molecular shape change and correlated self-assembly through imine bond in the case where "M"=Zn(II).

Noteworthy, in the case of the diamine $\mathbf{N_2O}$, a more complex mixture was obtained indicating once again that the zinc(II) ion can not well accommodate the additional oxygen atom.

Complexation of a mixture of ligands **1** and **2** by zinc triflate reveals the sequential formation of each complex. $\mathbf{Zn.2_2}$ is formed at 0.5 equivalent of zinc while ligand **1** stay free. Further addition of 0.5 equivalent induces the partial formation of **Zn.1**. **Zn.1** is then formed quantitatively after addition of an other 0.5 equivalent of zinc triflate, i.e. at 1.5 equivalent of metal ion. Further addition of 0.5 equivalent then yields the complexes **Zn.1** and **Zn.2**.

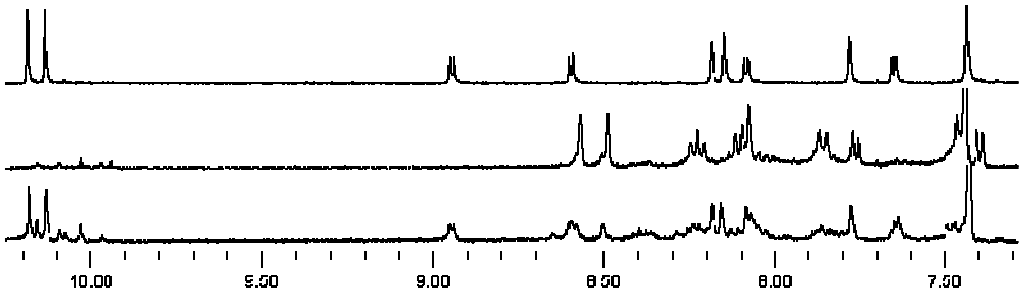


^{1}H NMR titration of an equimolar mixture of **1** and **2** by zinc triflate in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. From bottom to top: 0.0, 0.3, 0.5, 0.7, 1.0, 1.3, 1.5, 2.0 equivalent of zinc triflate, then **1**, **Zn.1**, **2**, **Zn.2$_2$**, **Zn.2**.

The titration therefore shows a strong preference for the formation of **Zn.2$_2$** which is in agreement with the binding constants of complexation previously reported.[1] Such behaviour then explains why 2.0 equivalent are needed in the case of zinc triflate whereas only one equivalent of lead triflate is able induce the adaptation process in response to shape change. At one equivalent of zinc triflate there is only partial formation of **Zn.1**. As observed, addition of a diamine then induces only the partial formation of the corresponding metallo-macrocycle. Whereas in the case of lead triflate the formation of the macrocyclic species shifts all equilibria towards the formation of this product in a amplificating process, such behaviour is not possible in the case of zinc triflate due to the high stability of **Zn.2$_2$**. The free energy of macrocycle formation through imine self-assembly is not sufficient to break that strong complex. That is why additional zinc triflate is needed, the selective self-assembly being then a linear process since the complex **Zn.1** must be already quantitatively present before the addition of the diamine.

Furthermore, addition of hexacyclen to sequestrate the zinc cation induces the whole system to go back to its original constitution characteristic of the metal-free states.

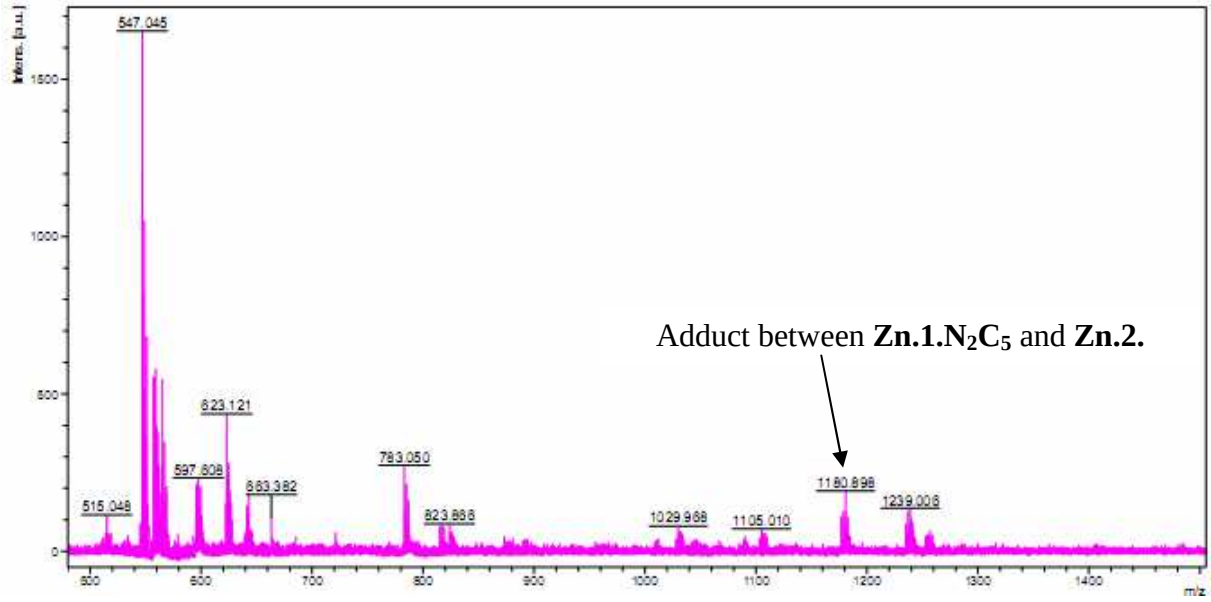
Constitutional evolution from an equimolar mixture of **1**, **2**, **N_2C_5** with 2.0 equivalents of $Zn(OTf)_2$:

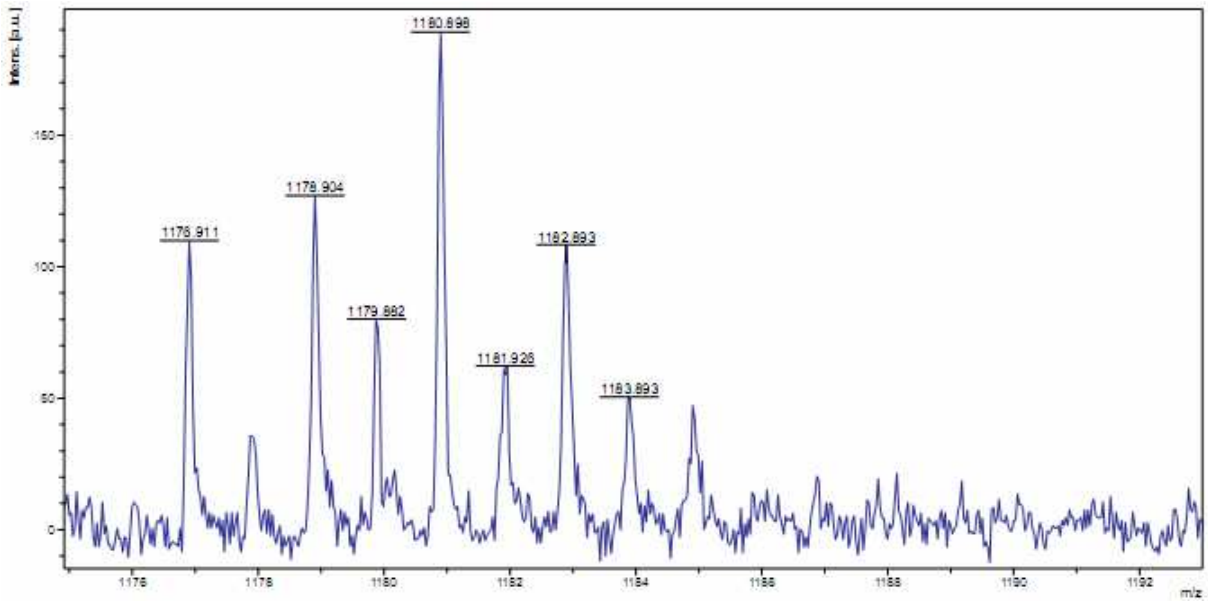


^{1}H NMR spectra showing the selective self-assembly process resulting from an equimolar mixture of **1**, **2**, **N_2C_5** after addition of 2.0 equivalents of zinc triflate in $CDCl_3/CD_3CN$: 6/4 at 5 mM concentration. From bottom to top: mixture after 1 day at 60°C ; **Zn.1.N_2C_5** ; **Zn.2**.

Noteworthy, there are some peaks in the mixture which belong to neither **Zn.1.N_2C_5** nor **Zn.2**. These peaks belong to an intermolecular non-covalent association between **Zn.1.N_2C_5** and **Zn.2**. That was proved by MALDI-TOF mass spectrometry (see below) and by ^{1}H NMR spectrometry on the mixing of **Zn.1.N_2C_5** and **Zn.2** which immediately after the mixing showed these peaks.

MALDI-TOF of the equimolar mixture of **1**, **2**, **N_2C_5** after addition of 2.0 equivalents of zinc triflate:





Since this behaviour is not observed in the case of the system containing the diamine $\mathbf{N_2C_4}$, it again reflects the fact that $\mathbf{Zn.1.N_2C_5}$ has a higher energy than $\mathbf{Zn.1.N_2C_4}$ due to the presence of the longer diamine.

(1) Ulrich, S.; Buhler, E.; Lehn, J.-M. *New J. Chem.* **2009**, Accepted for publication.