Electronic Supplementary Material (ESI) for Dalton Transactions


# [*2*]Catenanes and inclusion complexes derived from self-assembled rectangular $Pd^{II}$ and $Pt^{II}$ metallocycles

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- Supporting Information -

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## NMR spectra

### Inclusion complex (2a)⊂1a·6$NO_3$

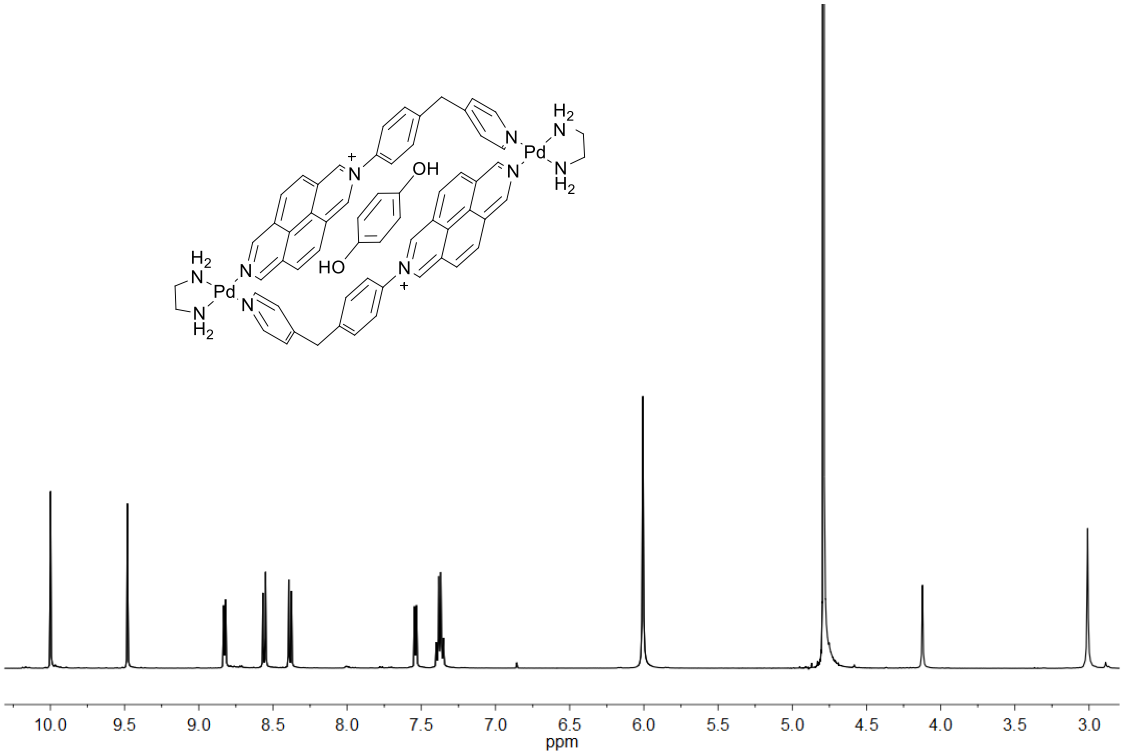



**Figure S1:** $^{1}$H NMR ($D_2O$, 500 MHz) spectrum of (**2a**)⊂**1a**·6$NO_3$.

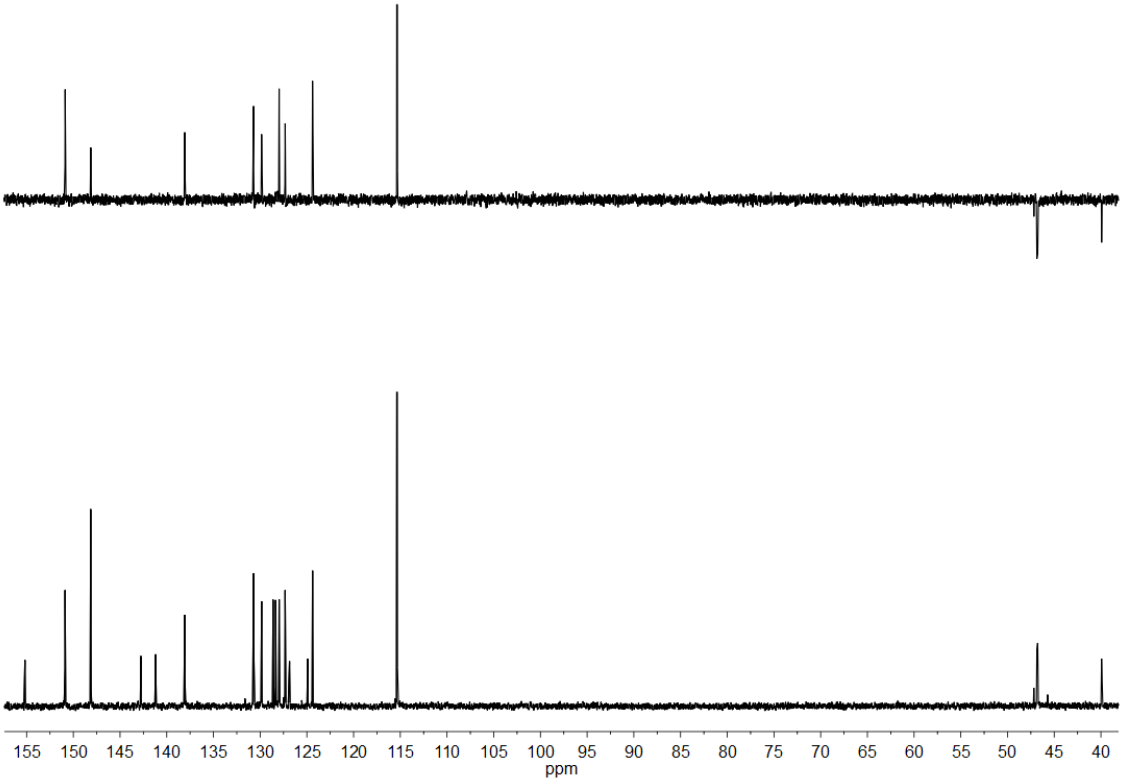



**Figure S2:** $^{13}$C NMR ($D_2O$, 125 MHz) spectrum of (**2a**)⊂**1a**·6$NO_3$.

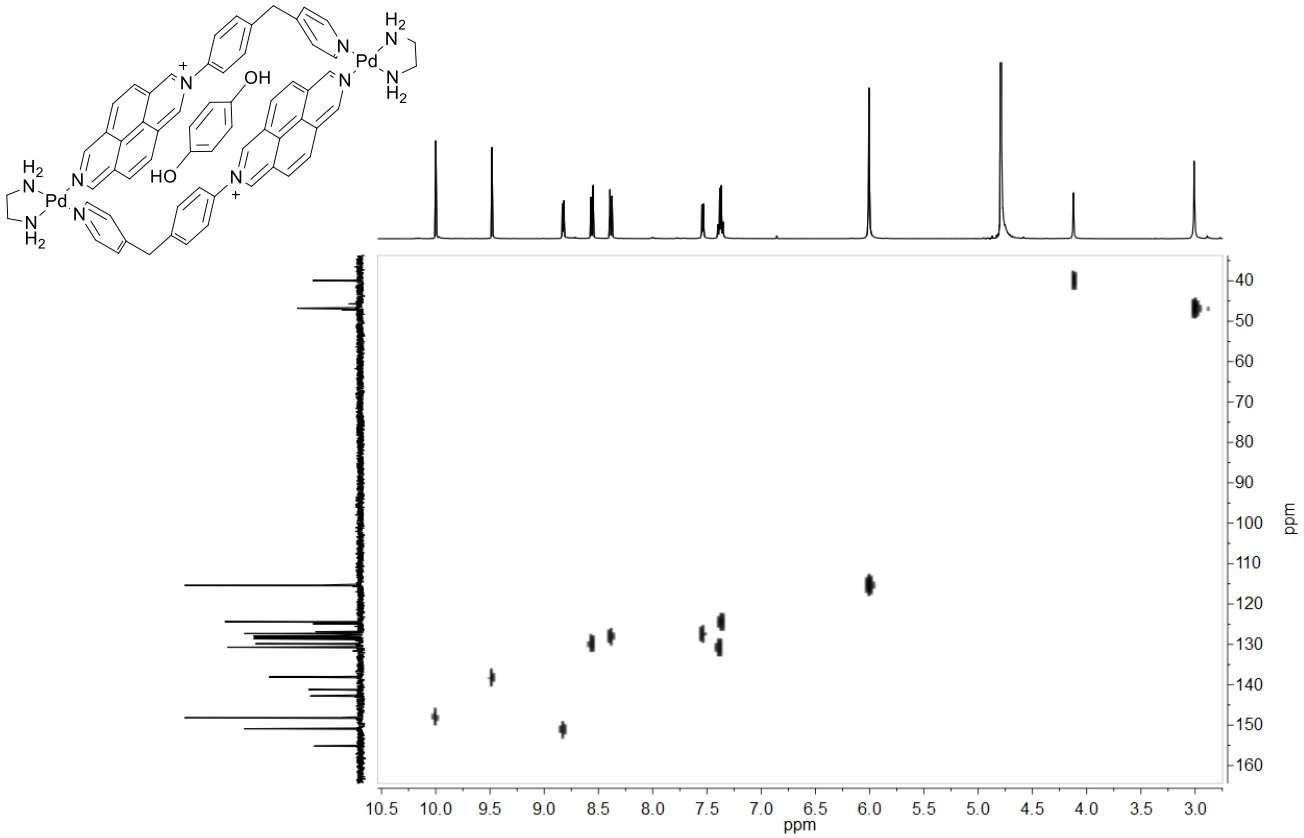



**Figure S3:** HSQC ($D_2O$, 500 and 125 MHz) spectrum of (**2a**)⊂**1a**·6$NO_3$.

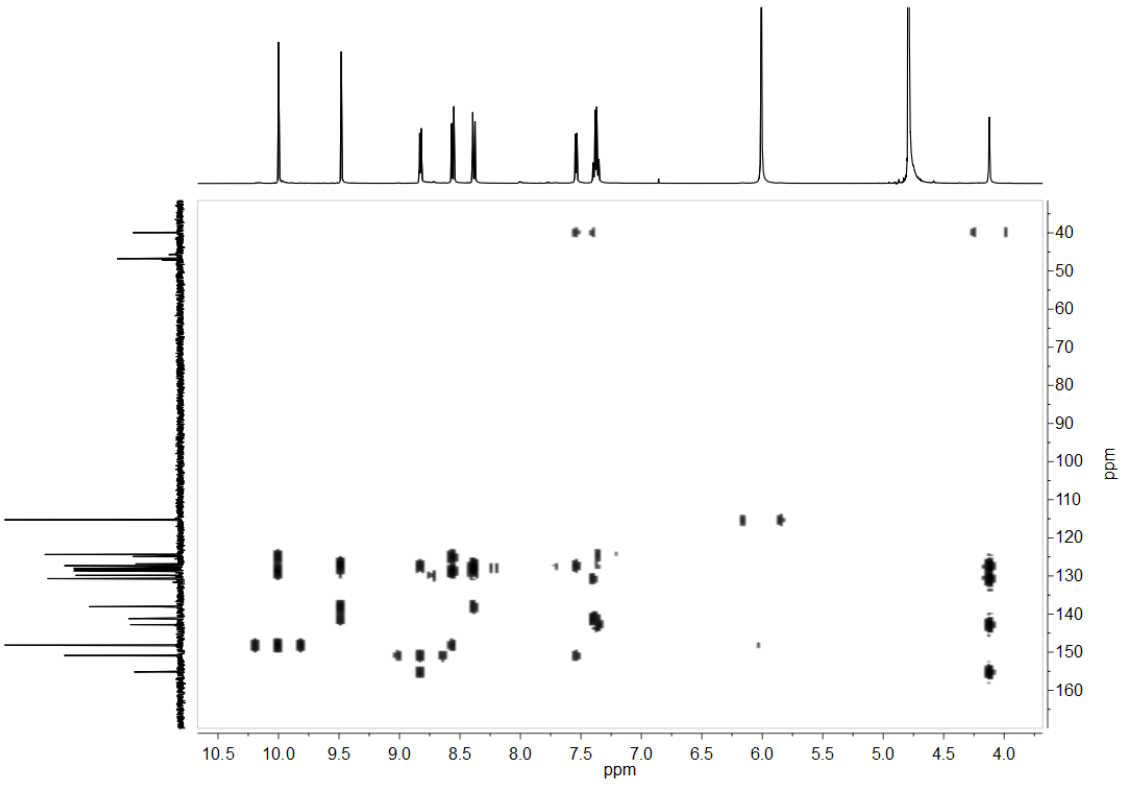



**Figure S4:** HMBC ($D_2O$, 500 and 125 MHz) spectrum of (**2a**)⊂**1a**·6$NO_3$.

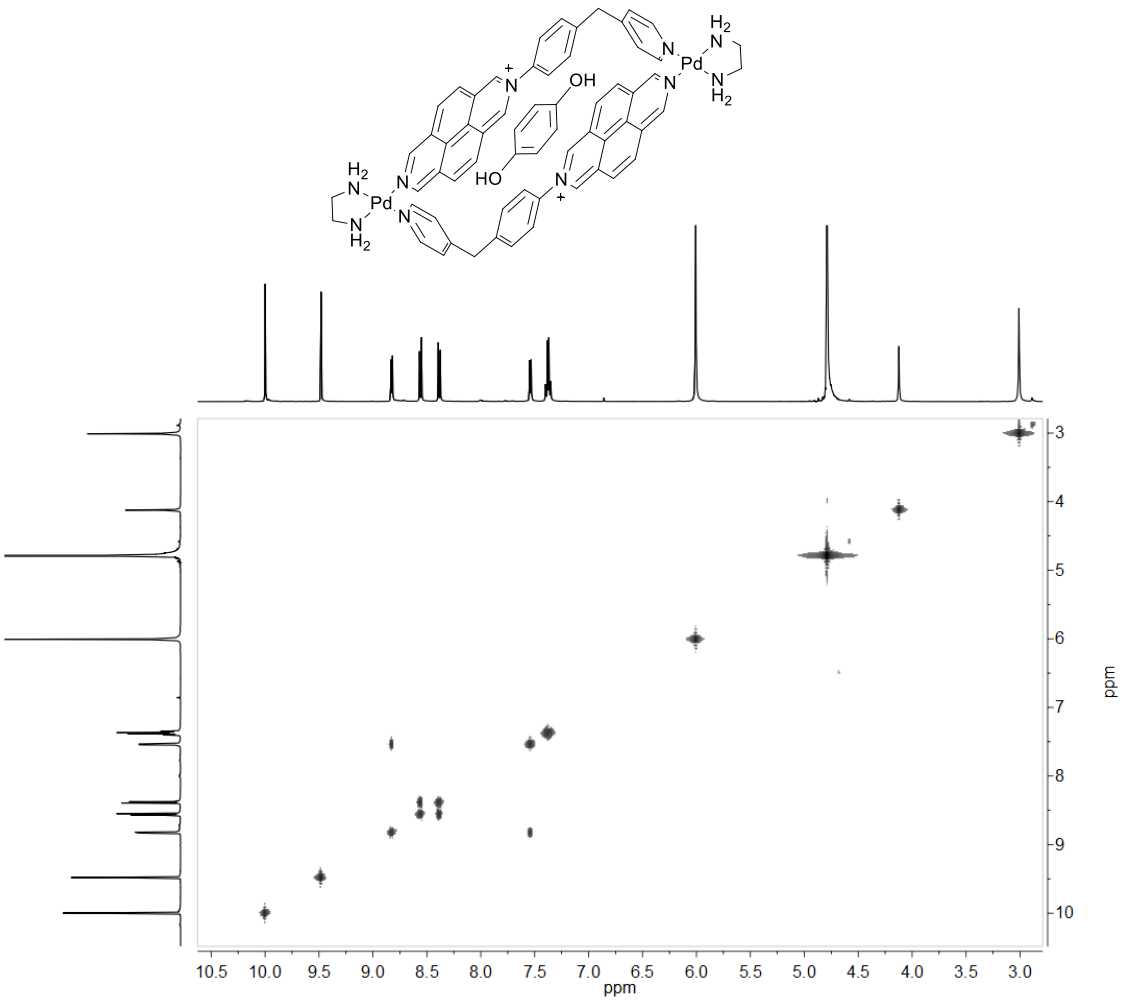



**Figure S5:** COSY ($D_2O$, 500 MHz) spectrum of (**2a**)⊂**1a**·$6NO_3$.

**Inclusion complex (2b)⊂1a·6NO$_3$**

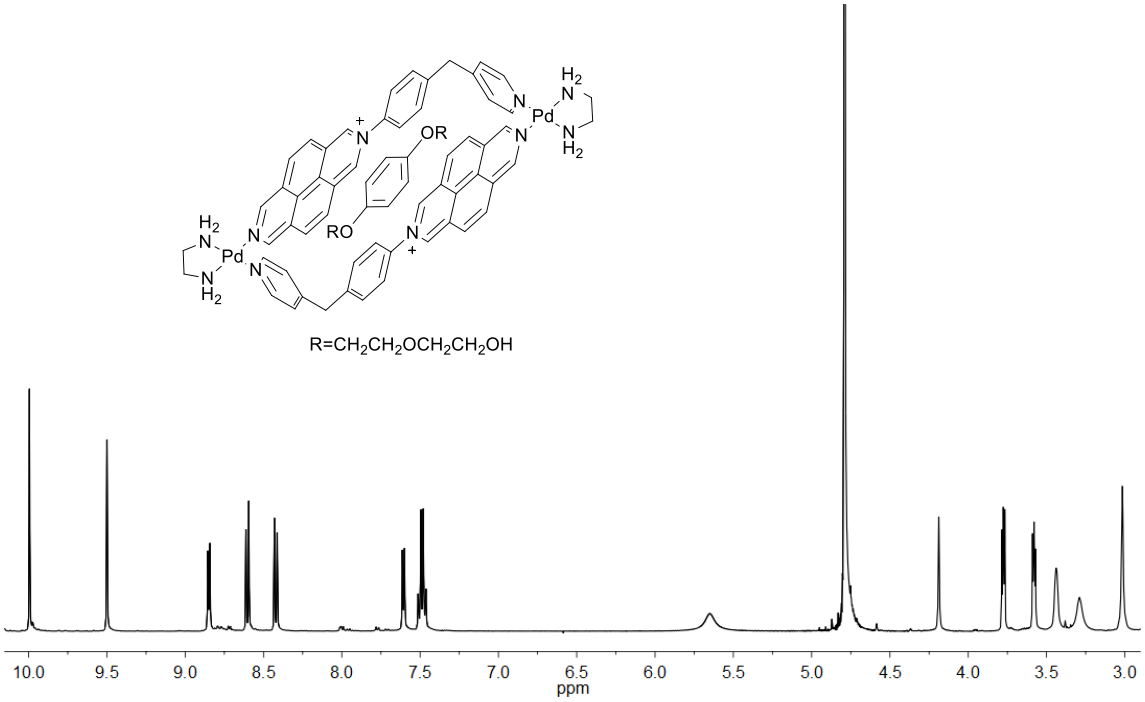



**Figure S6:** $^{1}$H NMR ($D_2O$, 500 MHz) spectrum of (**2b**)⊂**1a**·6$NO_3$.

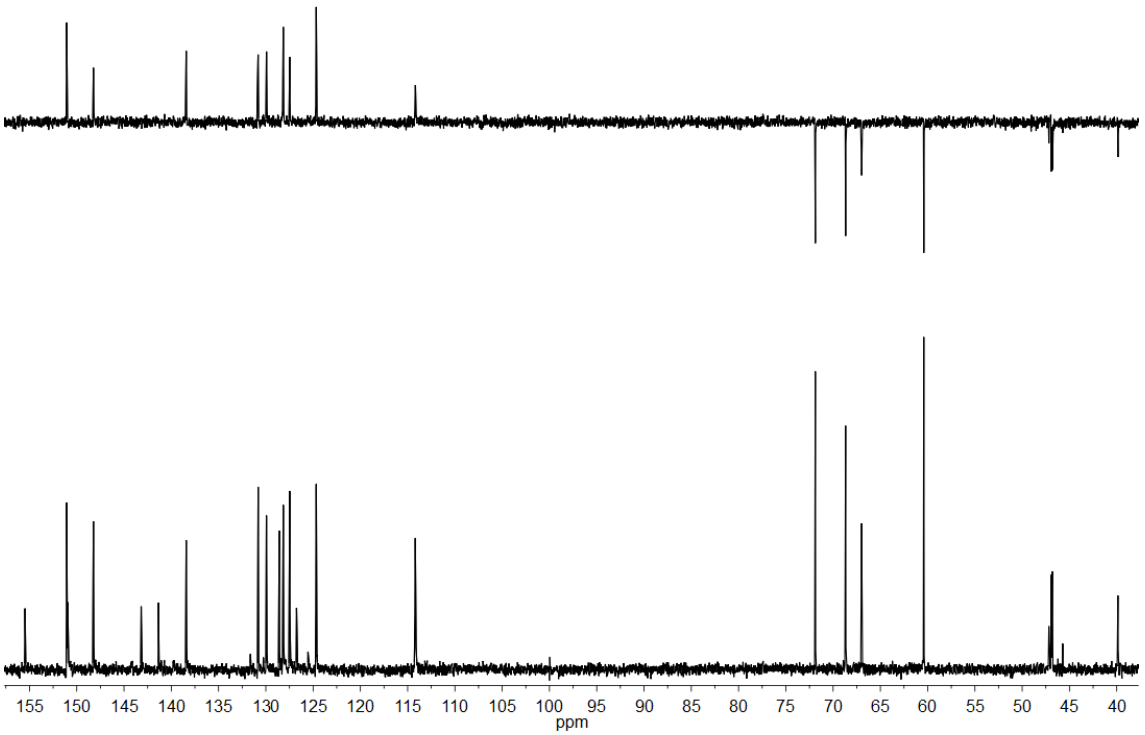



**Figure S7:** $^{13}$C NMR ($D_2O$, 125 MHz) spectrum of (**2b**)⊂**1a**·6$NO_3$.

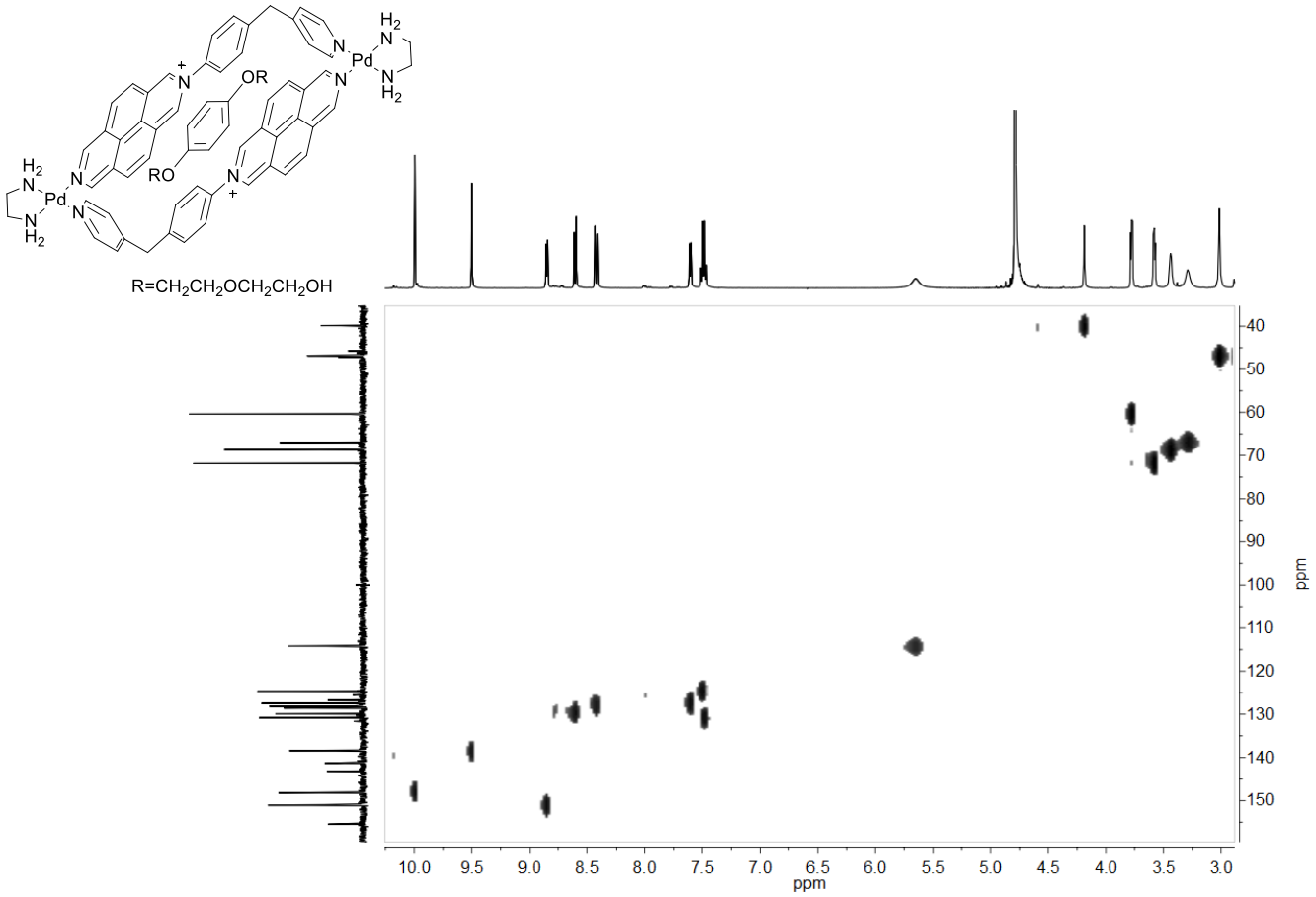



**Figure S8:** HSQC ($D_2O$, 500 and 125 MHz) spectrum of (**2b**)⊂**1a**·6$NO_3$.

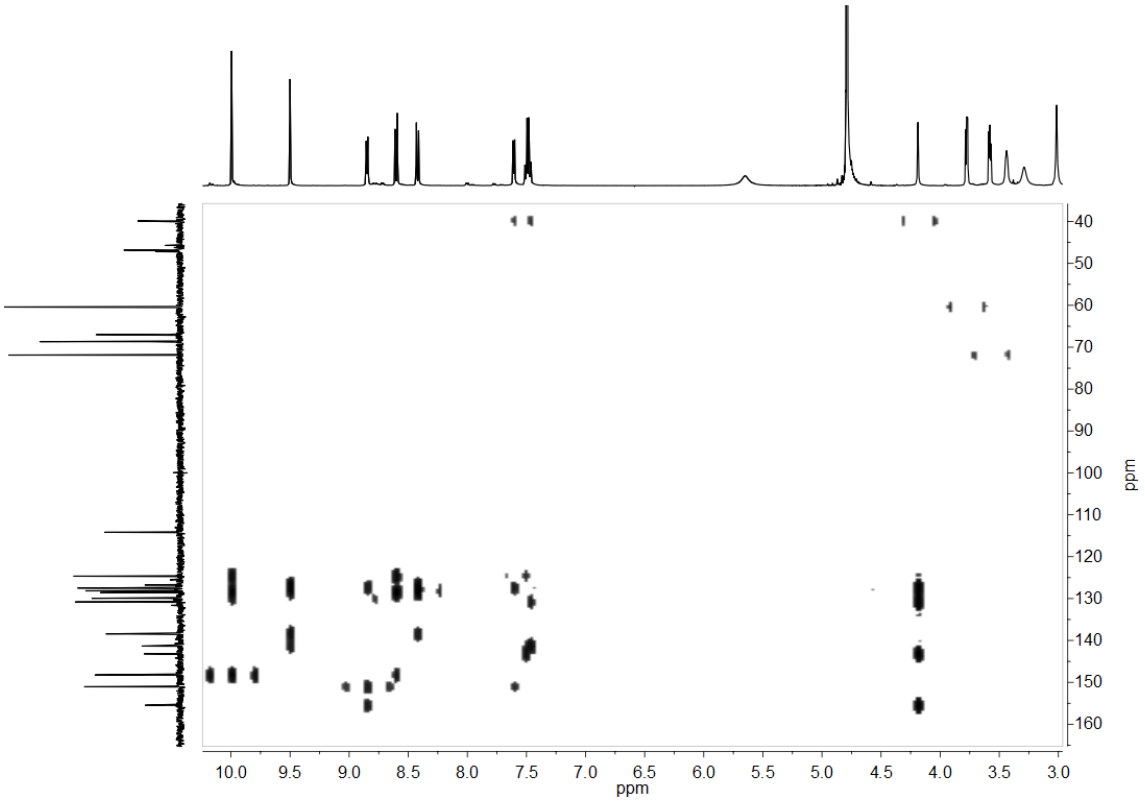



**Figure S9:** HMBC ($D_2O$, 500 and 125 MHz) spectrum of (**2b**)⊂**1a**·6$NO_3$.

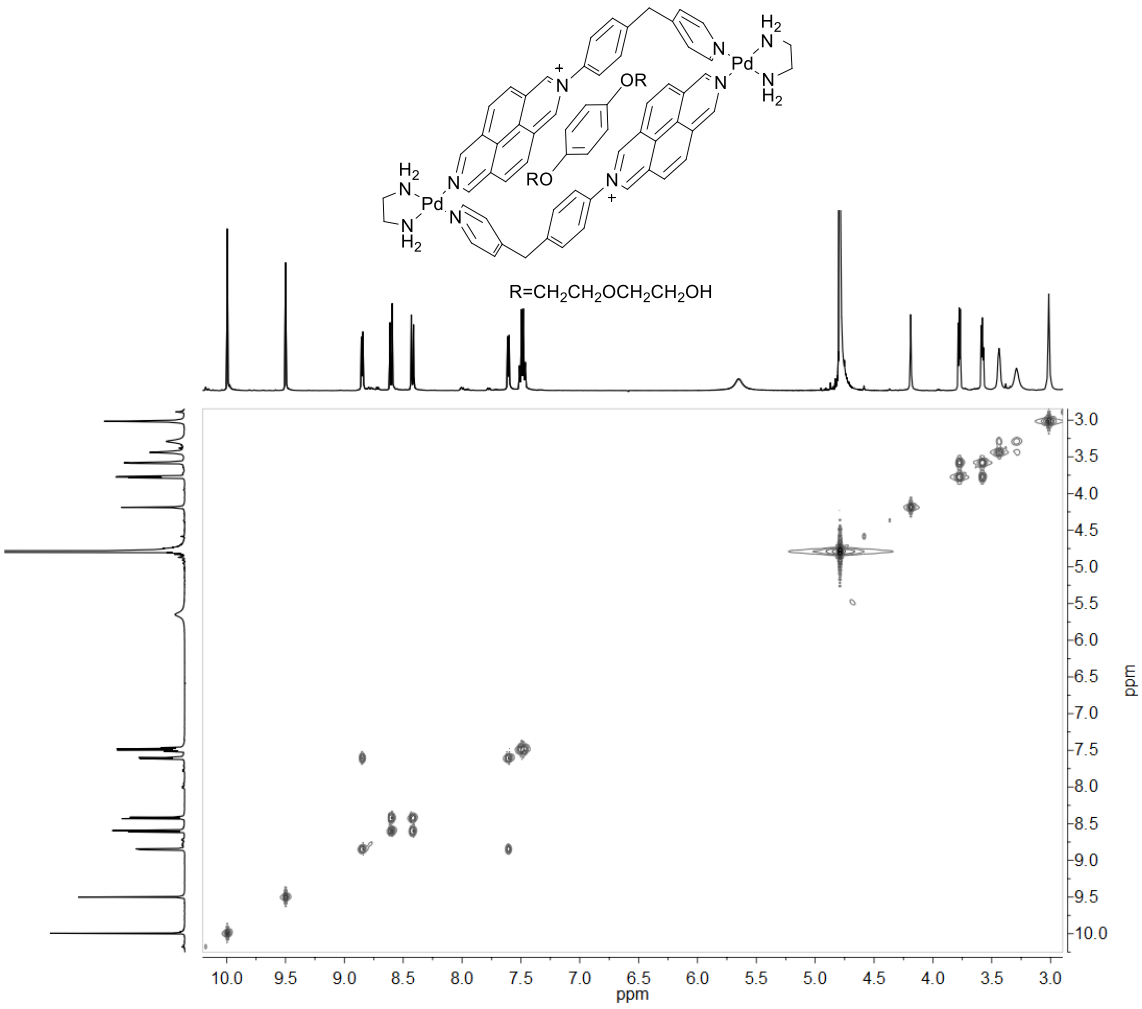



**Figure S10:** COSY ($D_2O$, 500 MHz) spectrum of (**2b**)⊂**1a**·$6NO_3$.

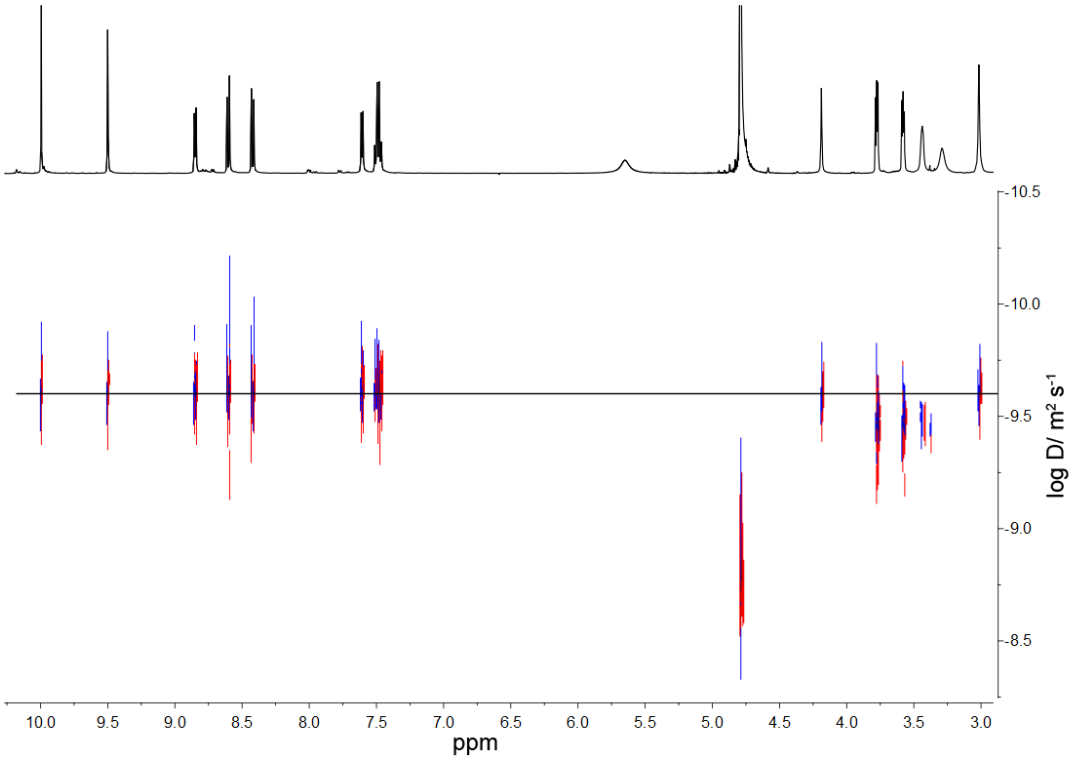



**Figure S11:** DOSY ($D_2O$, 500 MHz, 298 K) experiment of (**2b**)⊂**1a**·$6NO_3$.

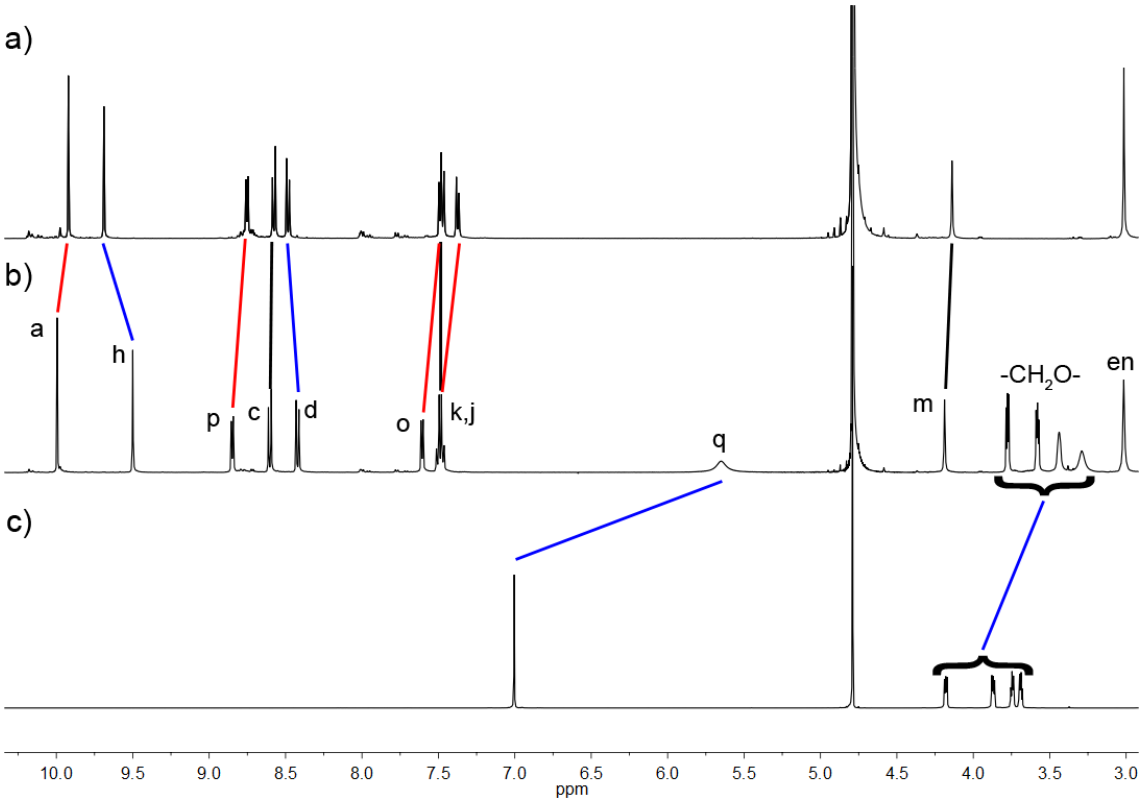



**Figure S12:** $^{1}$H NMR ($D_2O$, 500 MHz) spectrum of: a) **1a**·6$NO_3$. b) (**2b**)⊂**1a**·6$NO_3$. C) **2b**.

**Inclusion complex (3a)⊂1a·6NO$_3$**

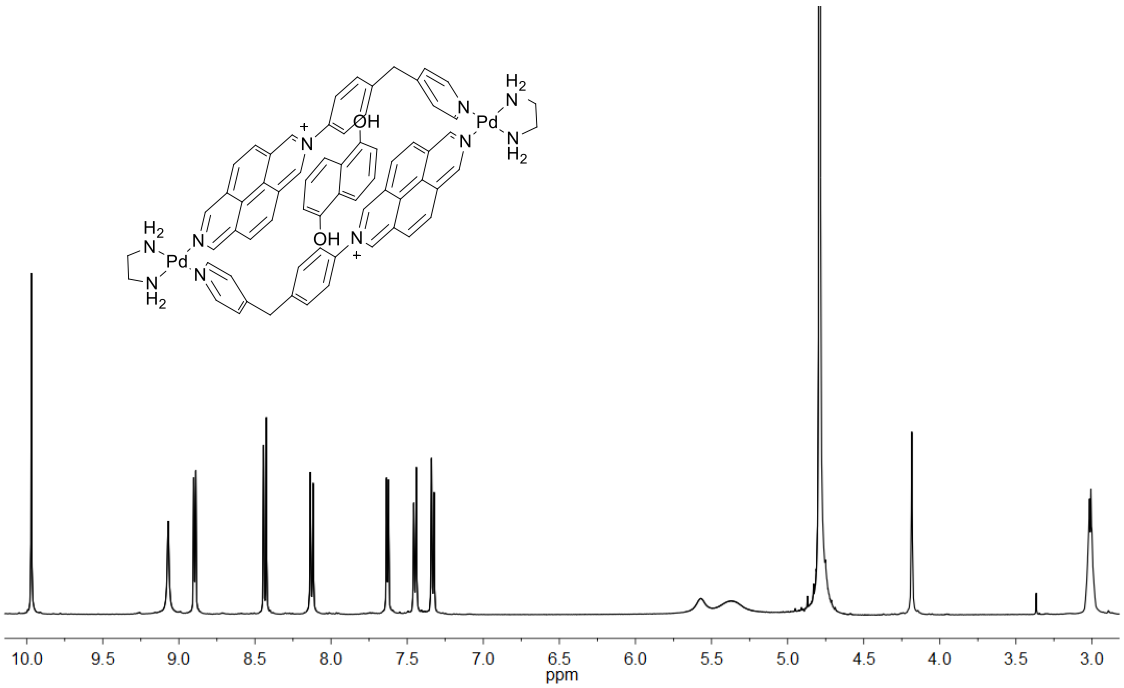



**Figure S13:** $^1$H NMR (D$_2$O, 500 MHz) spectrum of (**3a**)⊂**1a**·6NO$_3$

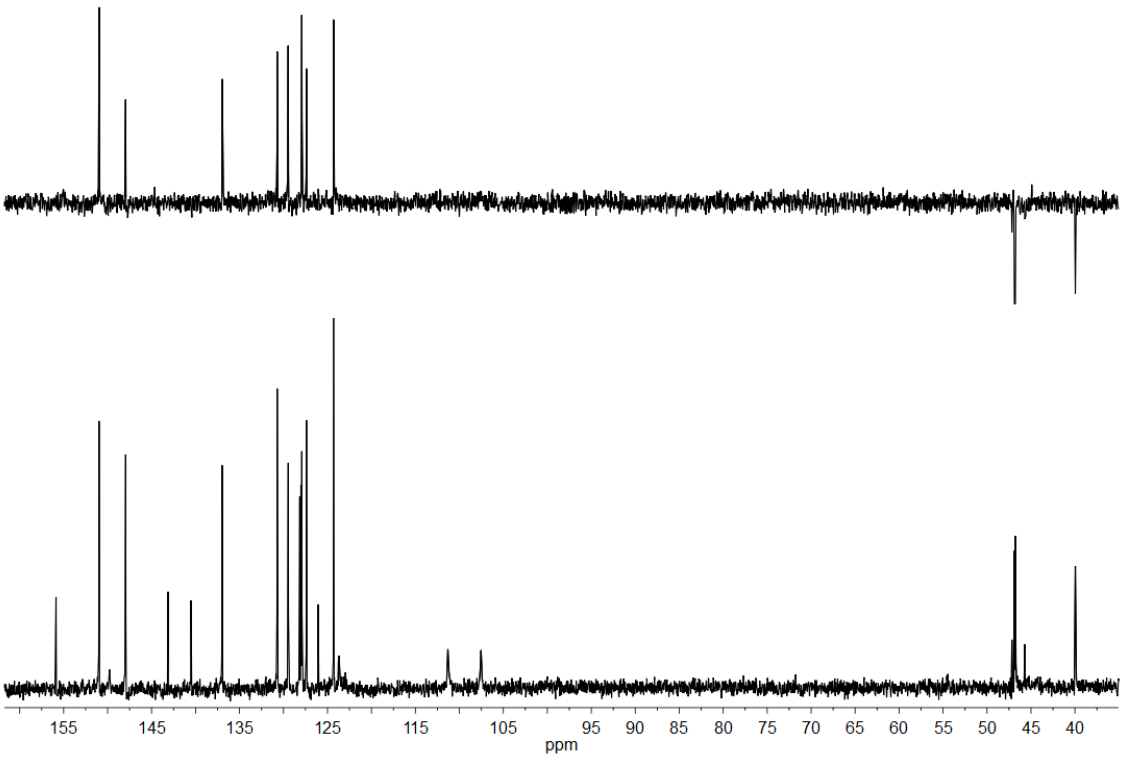



**Figure S14:** $^{13}$C NMR (D$_2$O, 125 MHz) spectrum of (**3a**)⊂**1a**·6NO$_3$.

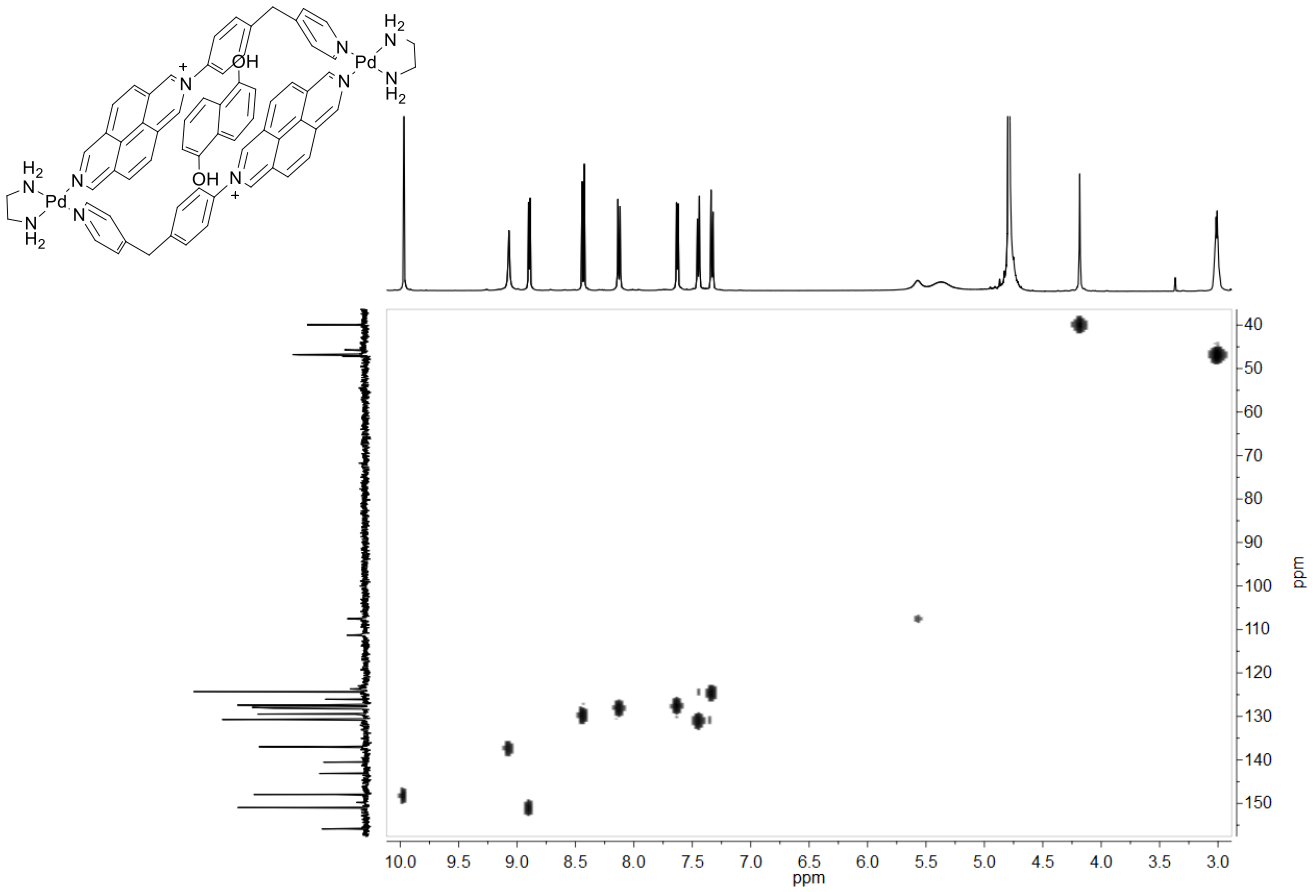



**Figure S15:** HSQC ($D_2O$, 500 and 125 MHz) spectrum of (**3a**)⊂**1a**·$6NO_3$.

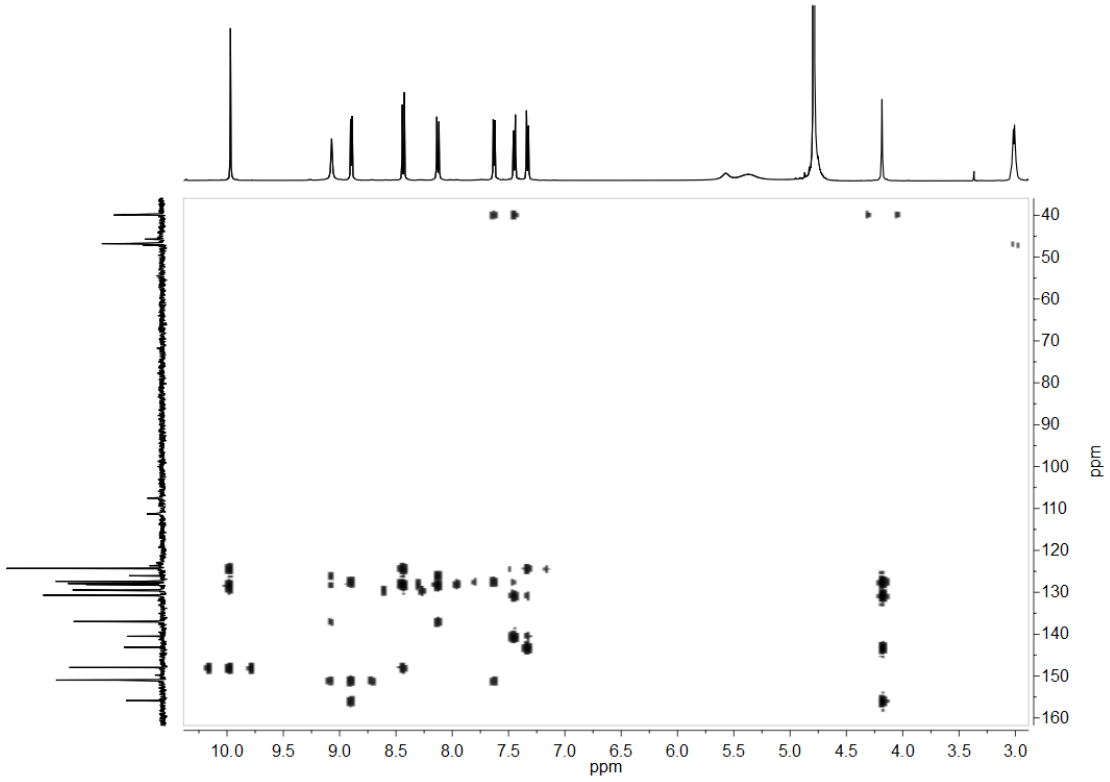



**Figure S16:** HMBC ($D_2O$, 500 and 125 MHz) spectrum of (**3a**)⊂**1a**·$6NO_3$.

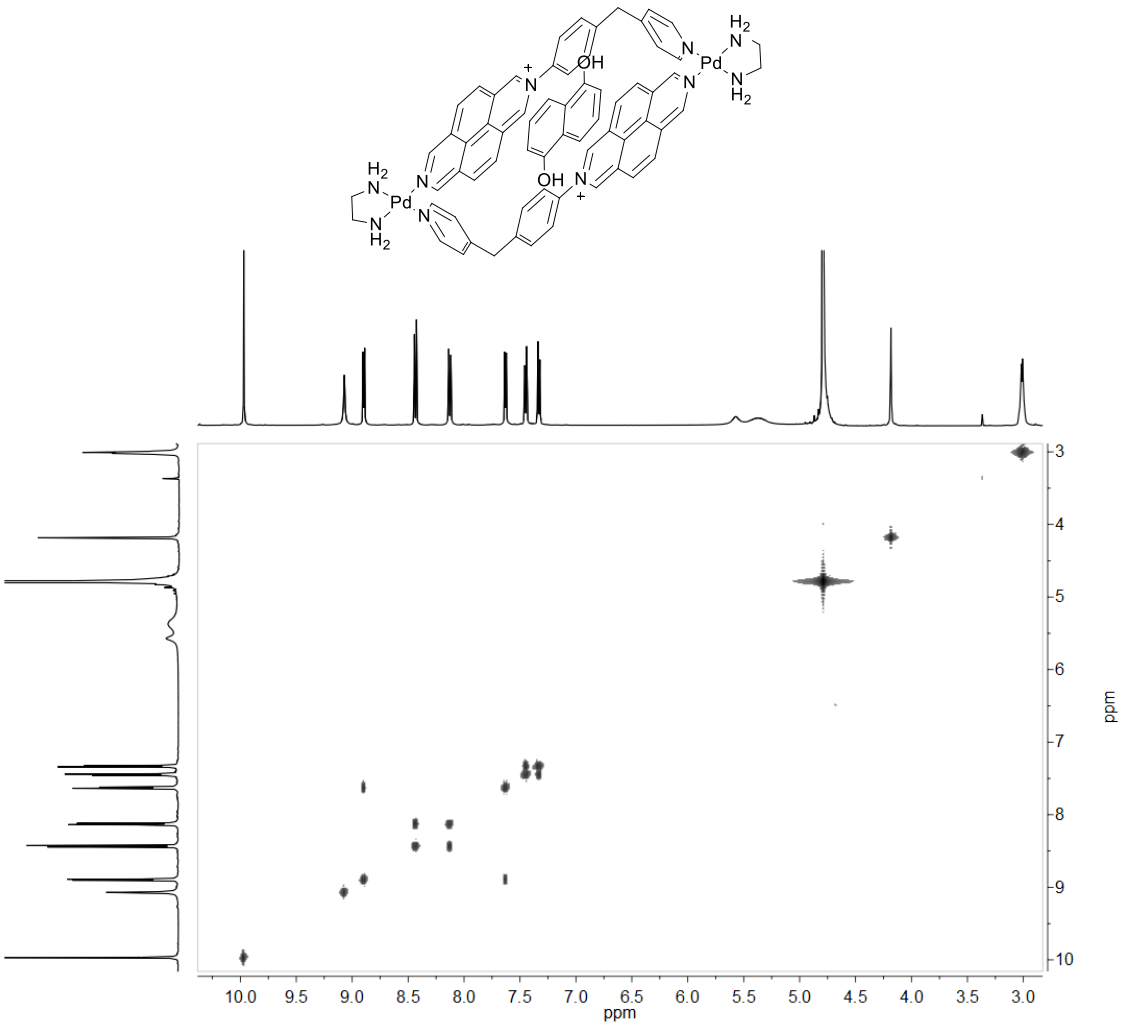



**Figure S17:** COSY ($D_2O$, 500 MHz) spectrum of (**3a**)⊂**1a**·6$NO_3$.

**Inclusion complex (3b)⊂1a·6NO$_3$**

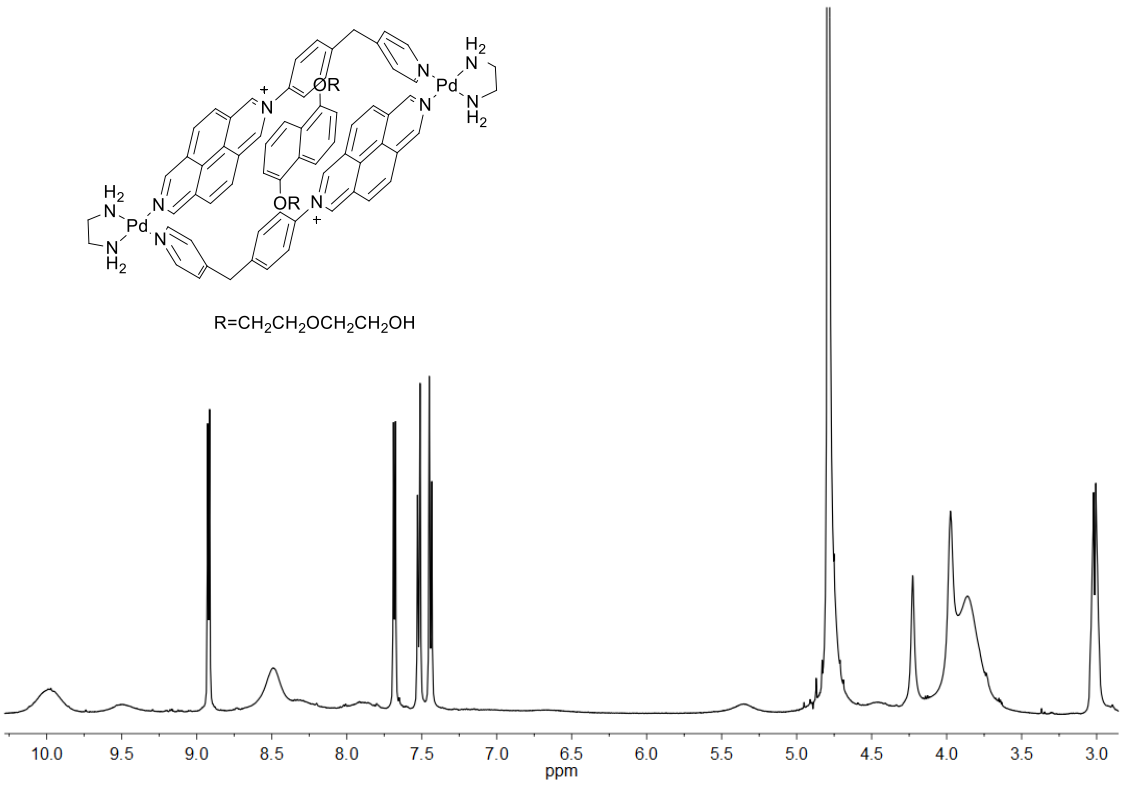



**Figure S18:** $^1$H NMR (D$_2$O, 500 MHz, 298 K) spectrum of (**3b**)⊂**1a**·6NO$_3$

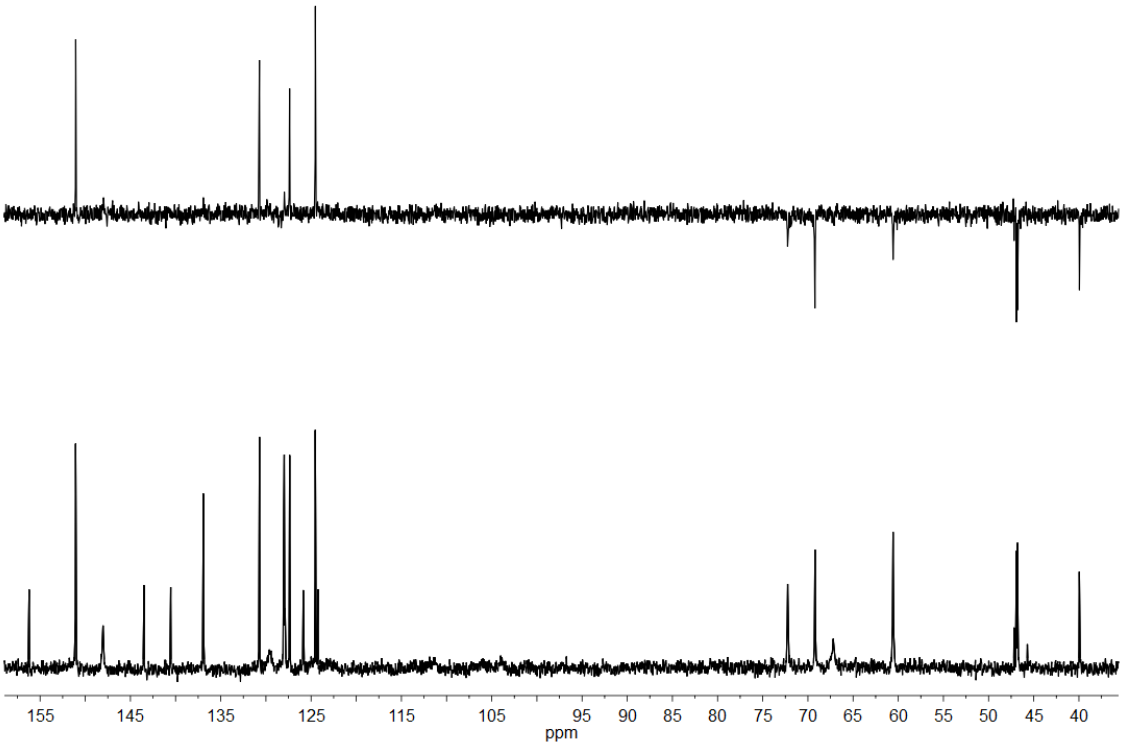



**Figure S19:** $^{13}$C NMR (D$_2$O, 125 MHz, 298 K) spectrum of (**3b**)⊂**1a**·6NO$_3$

**Inclusion complex (4a)⊂1a·6NO$_3$**

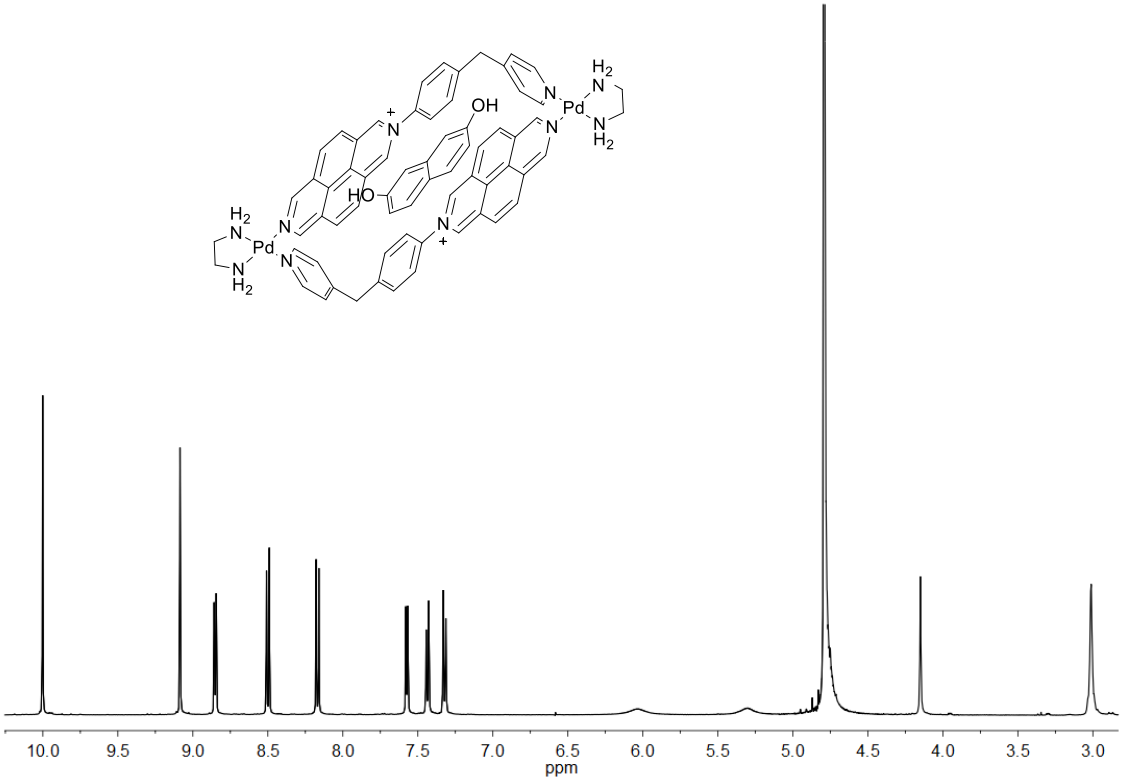



**Figure S20:** $^{1}$H NMR ($D_2O$, 500 MHz) spectrum of (**4a**)⊂**1a**·6$NO_3$.

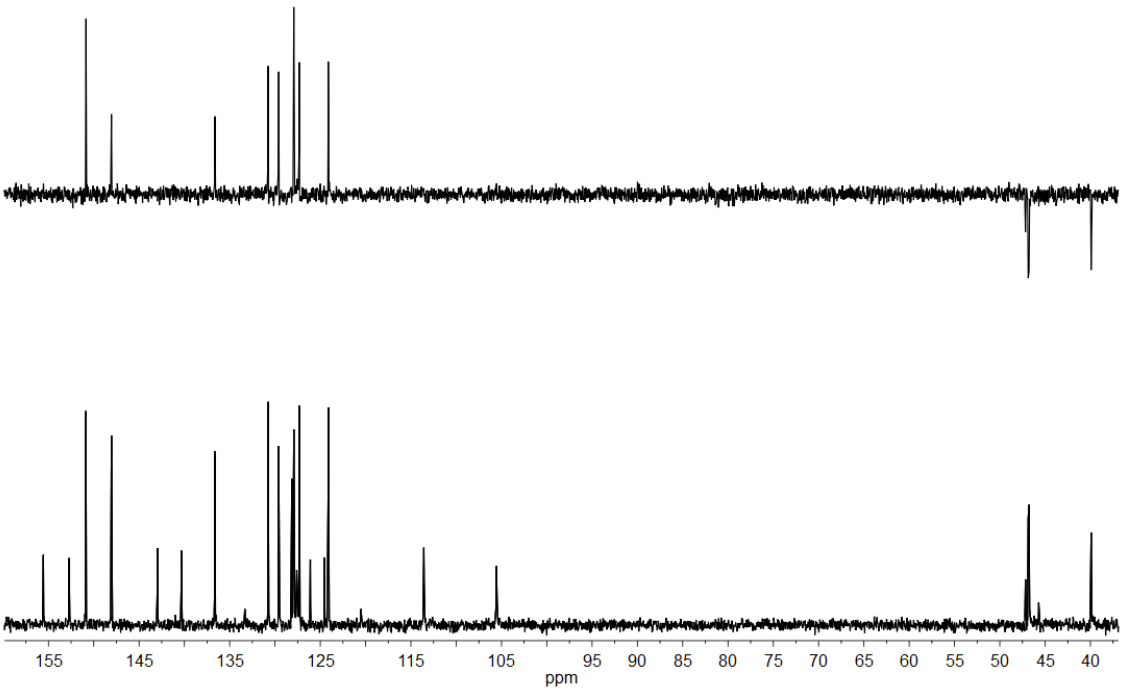



**Figure S21:** $^{13}$C NMR ($D_2O$, 125 MHz) spectrum of (**4a**)⊂**1a**·6$NO_3$.

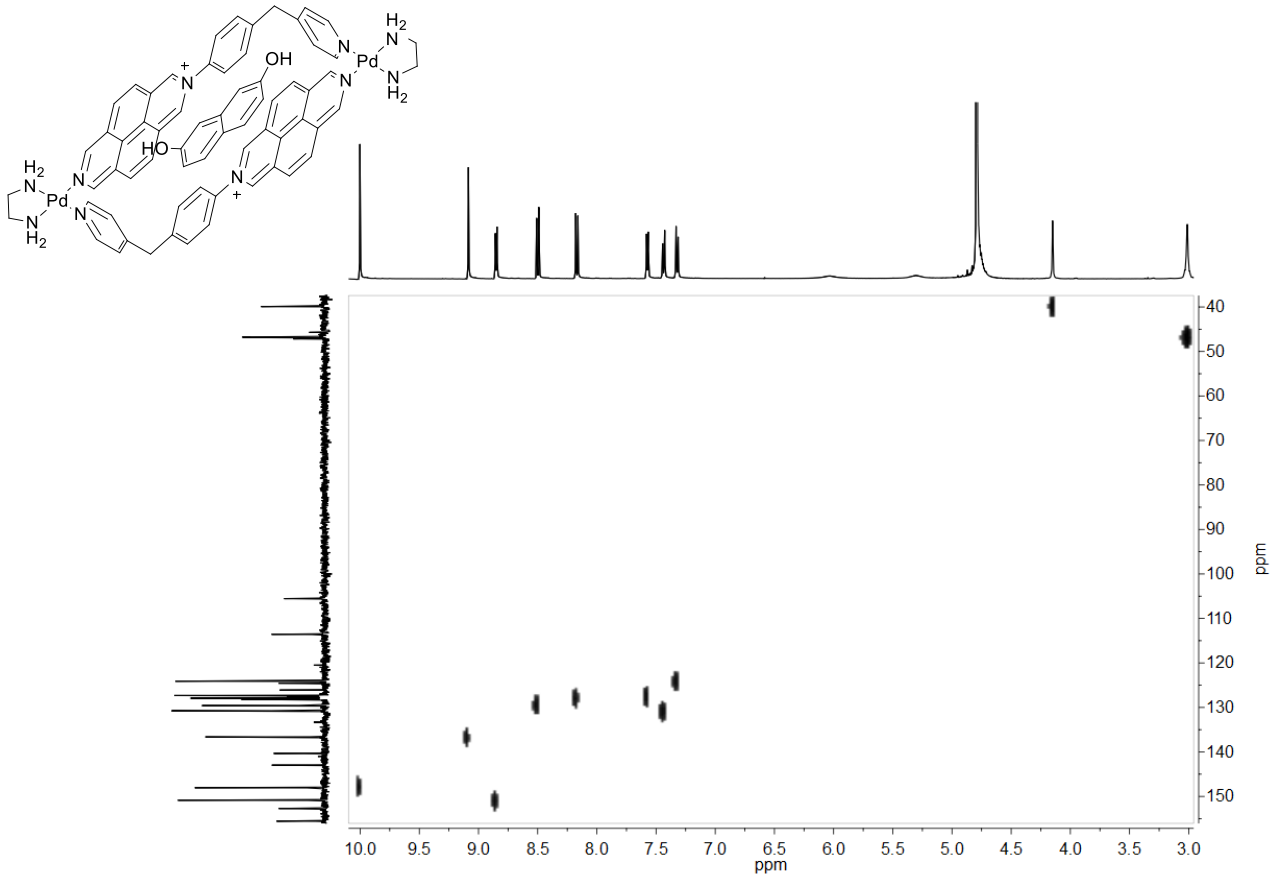



**Figure S22:** HSQC ($D_2O$, 500 and 125 MHz) spectrum of (**4a**)⊂**1a**·6$NO_3$.

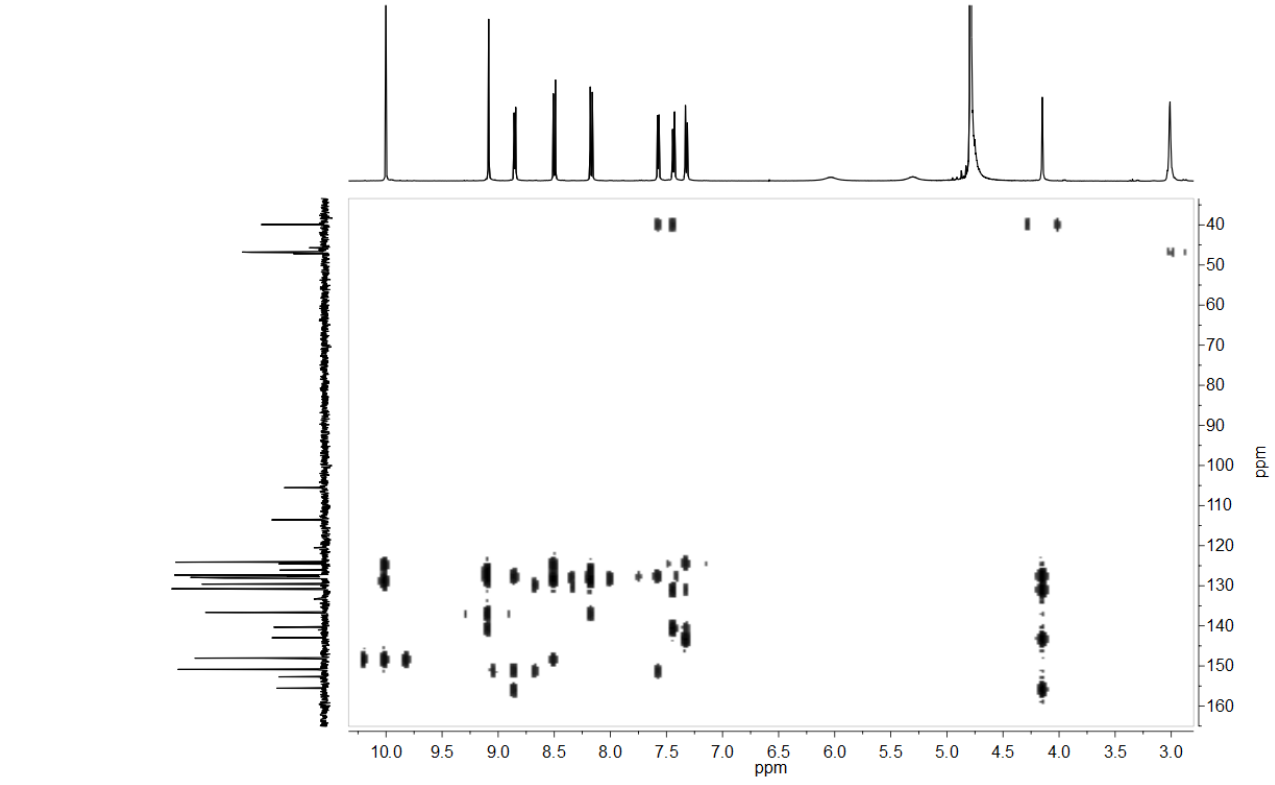



**Figure S23:** HMBC ($D_2O$, 500 and 125 MHz) spectrum of (**4a**)⊂**1a**·6$NO_3$.

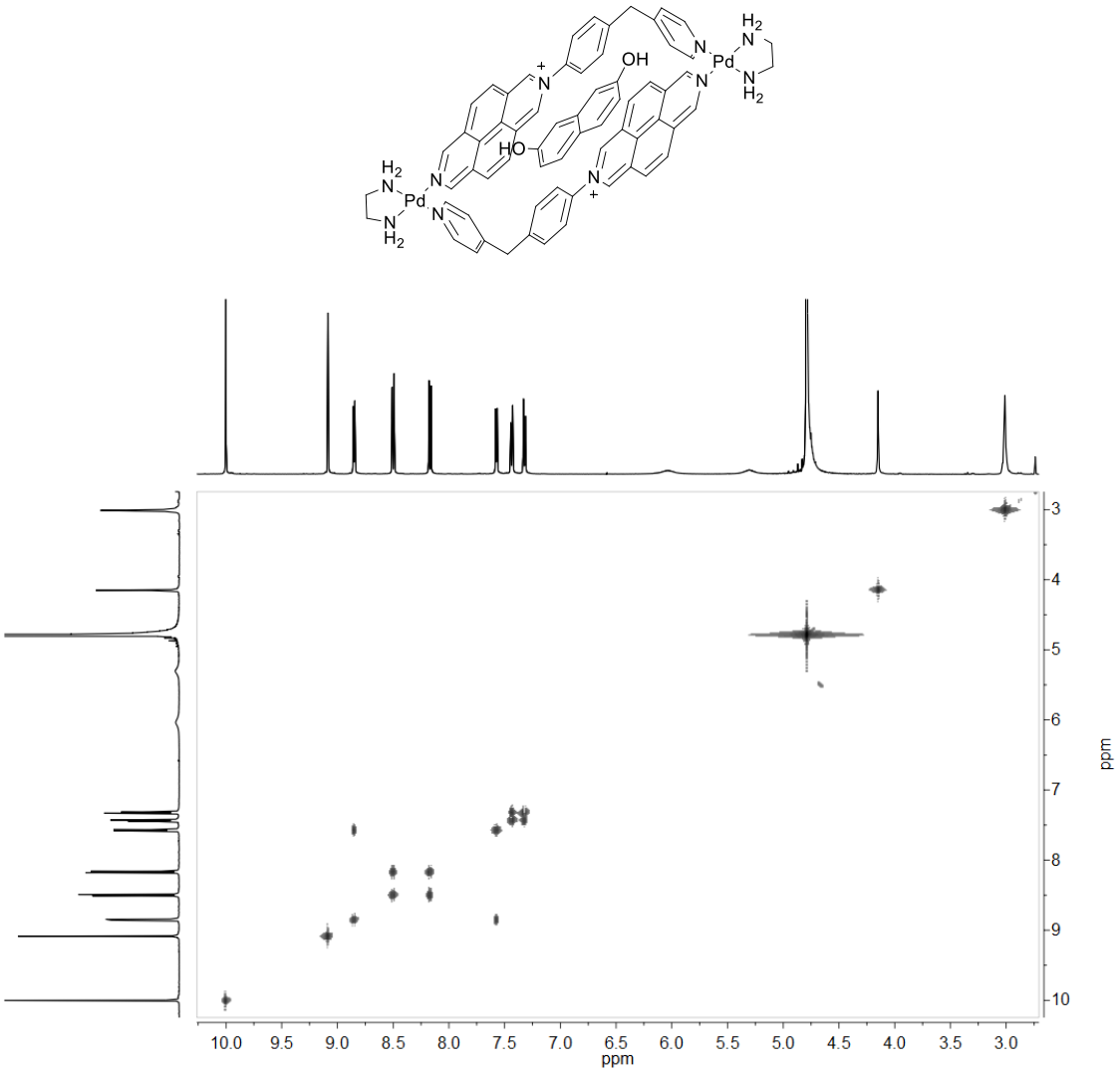



**Figure S24:** COSY ($D_2O$, 500 MHz) spectrum of (**4a**)⊂**1a**·$6NO_3$.

**Inclusion complex (4b)⊂1a·6NO$_3$**

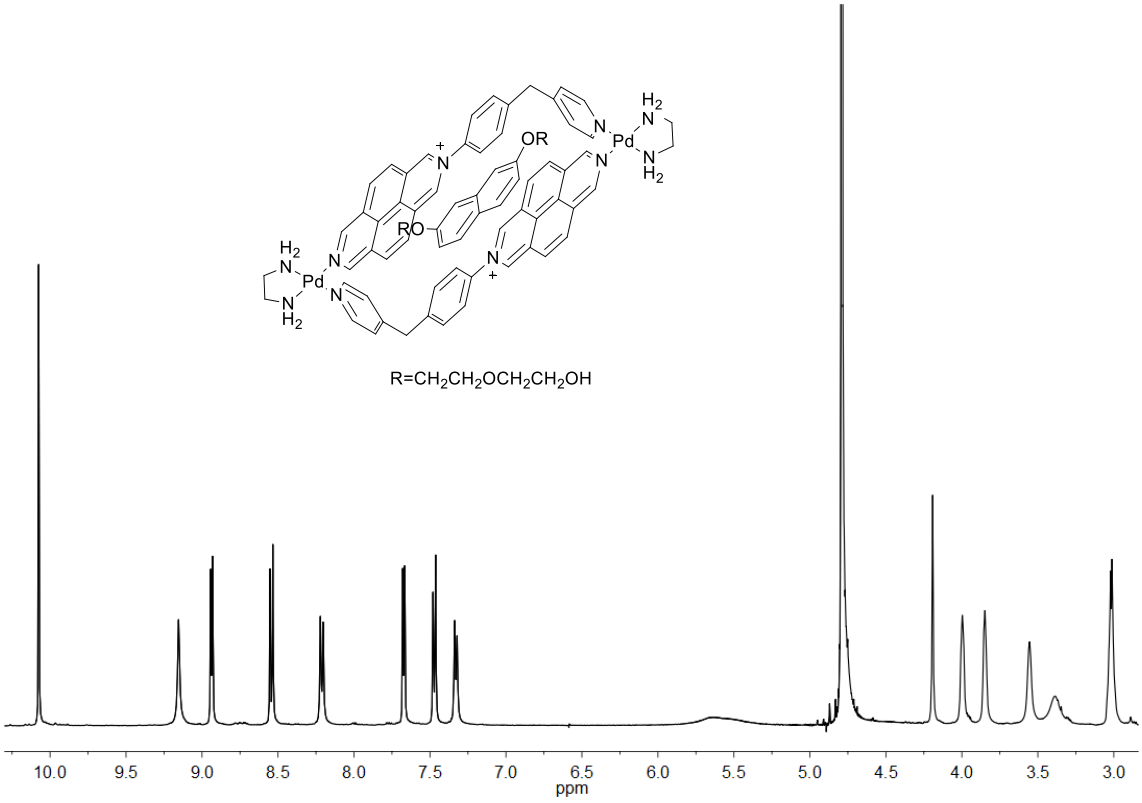



**Figure S25:** $^1$H NMR ($D_2O$, 500 MHz) spectrum of (**4b**)⊂**1a**·6$NO_3$.

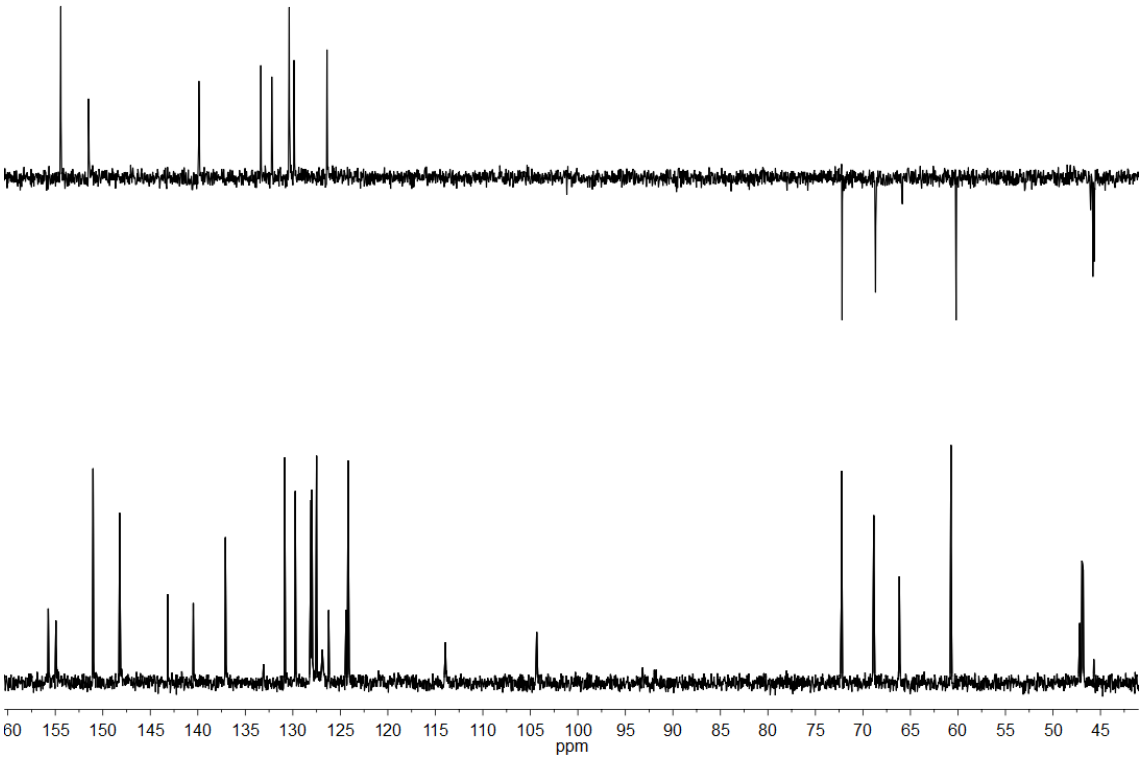



**Figure S26:** $^{13}$C NMR ($D_2O$, 125 MHz) spectrum of (**4b**)⊂**1a**·6$NO_3$.

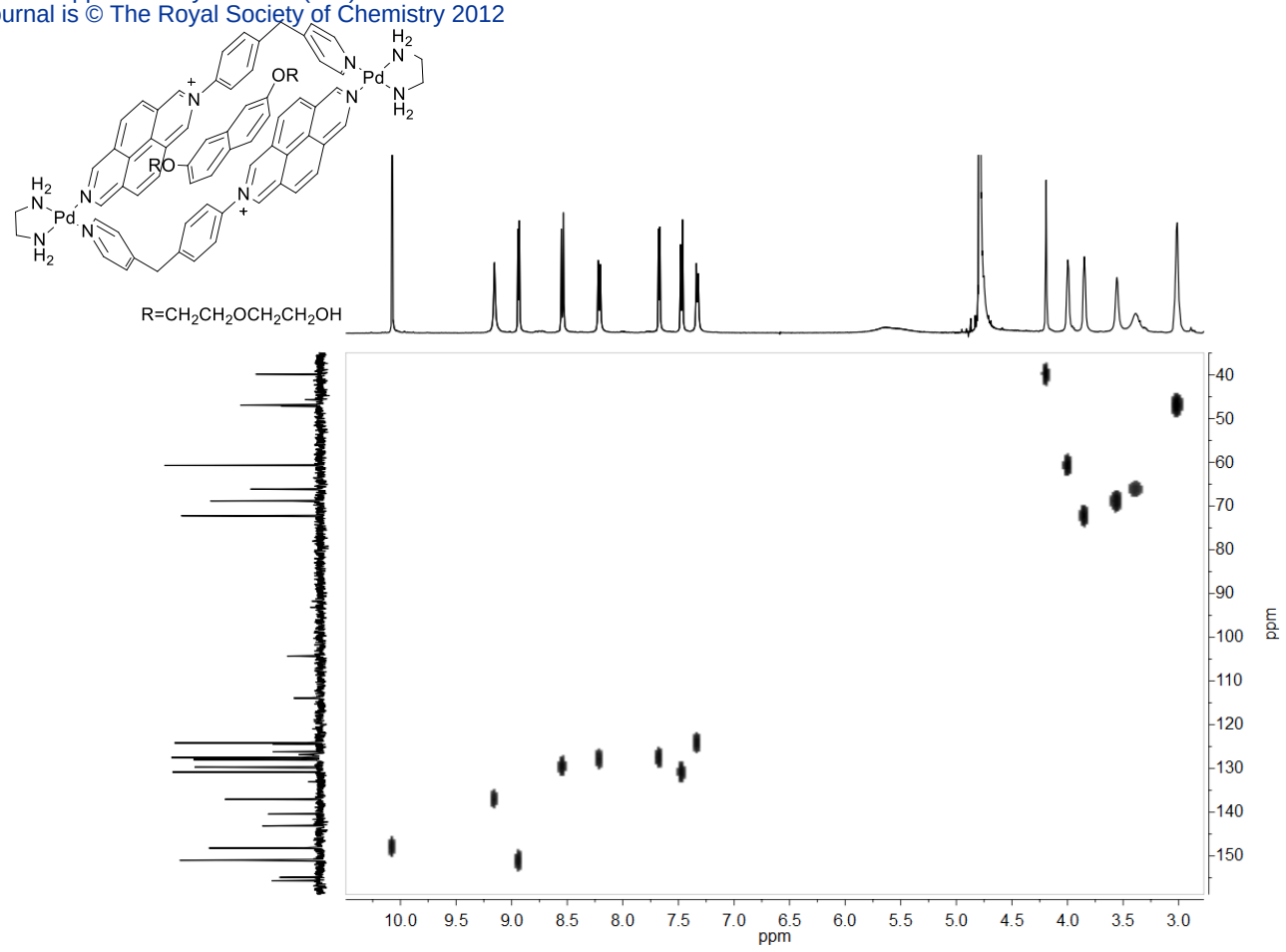



**Figure S27:** HSQC ($D_2O$, 500 and 125 MHz) spectrum of (**4b**)⊂**1a**·6$NO_3$.

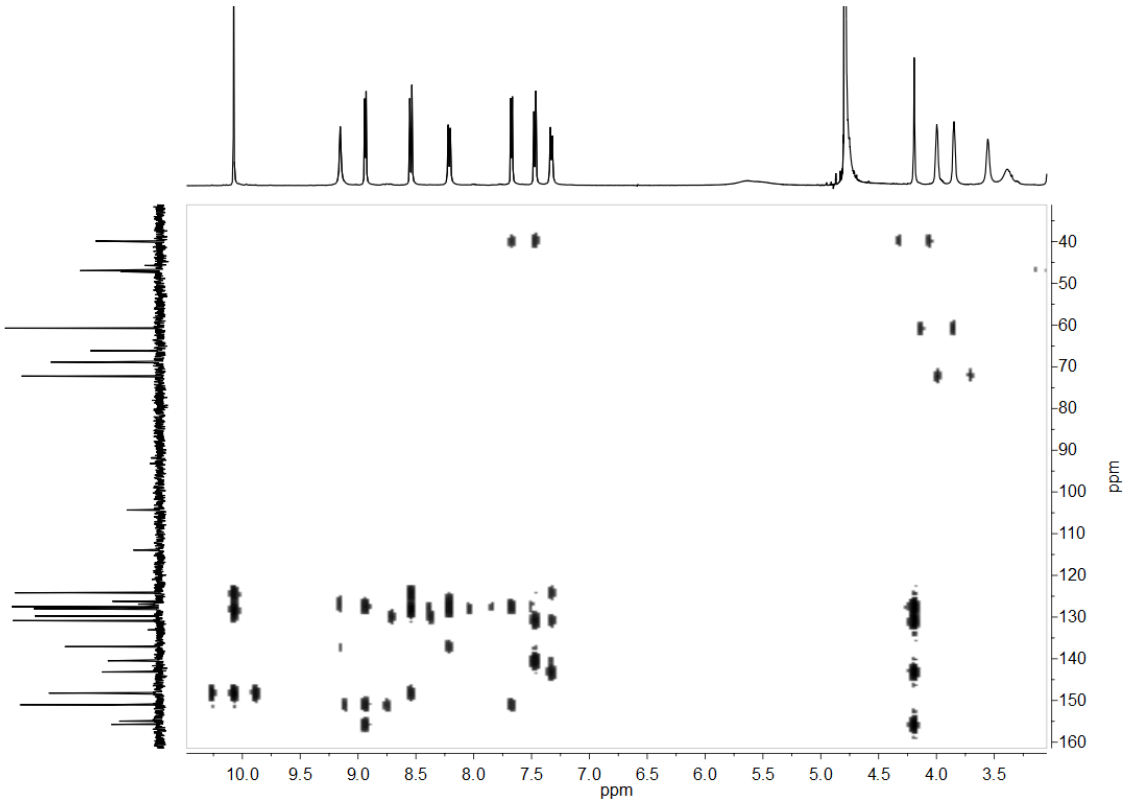



**Figure S28:** HMBC ($D_2O$, 500 and 125 MHz) spectrum of (**4b**)⊂**1a**·6$NO_3$.

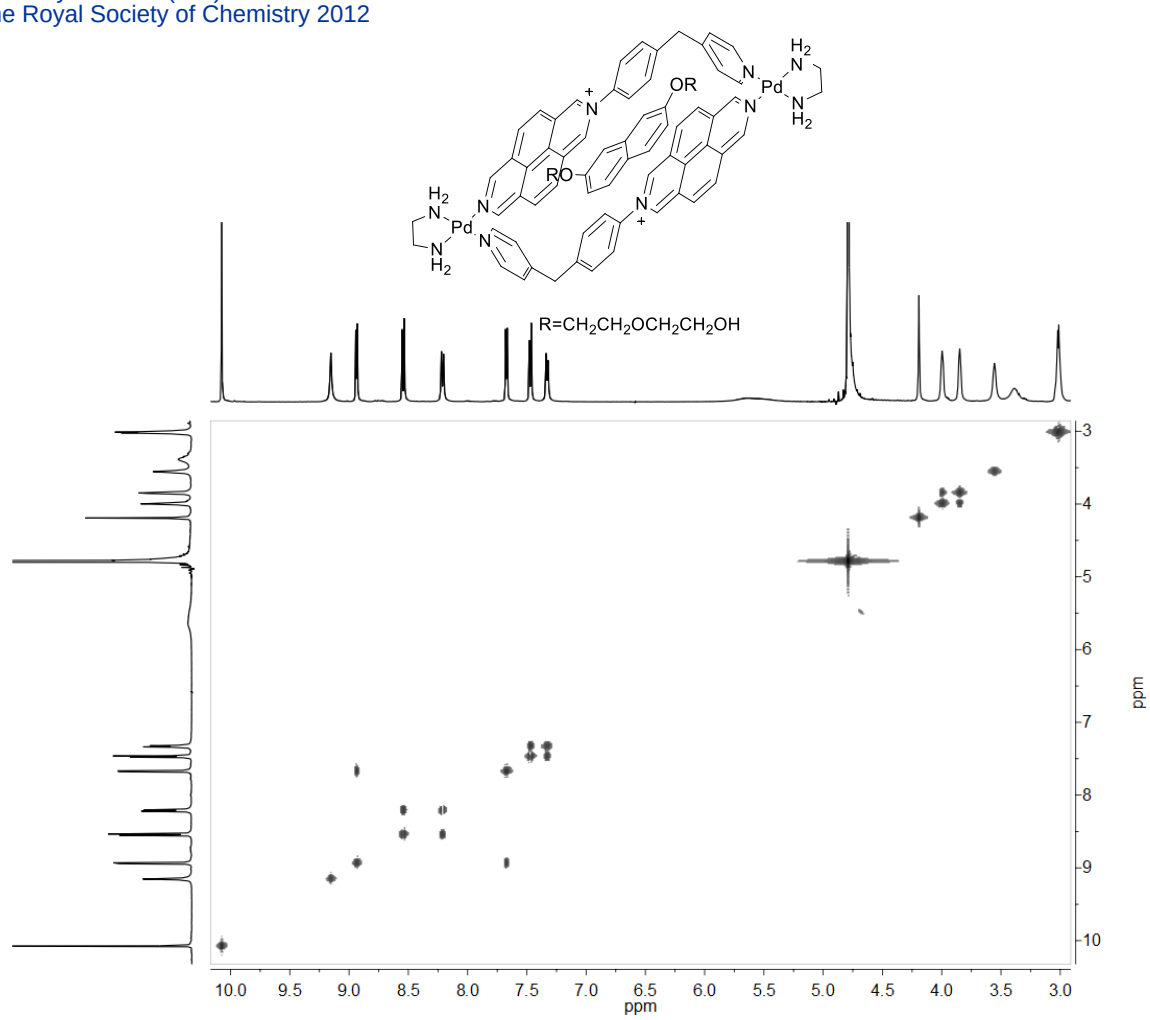



**Figure S29:** COSY ($D_2O$, 500 MHz) spectrum of (**4b**)⊂**1a**·6$NO_3$.

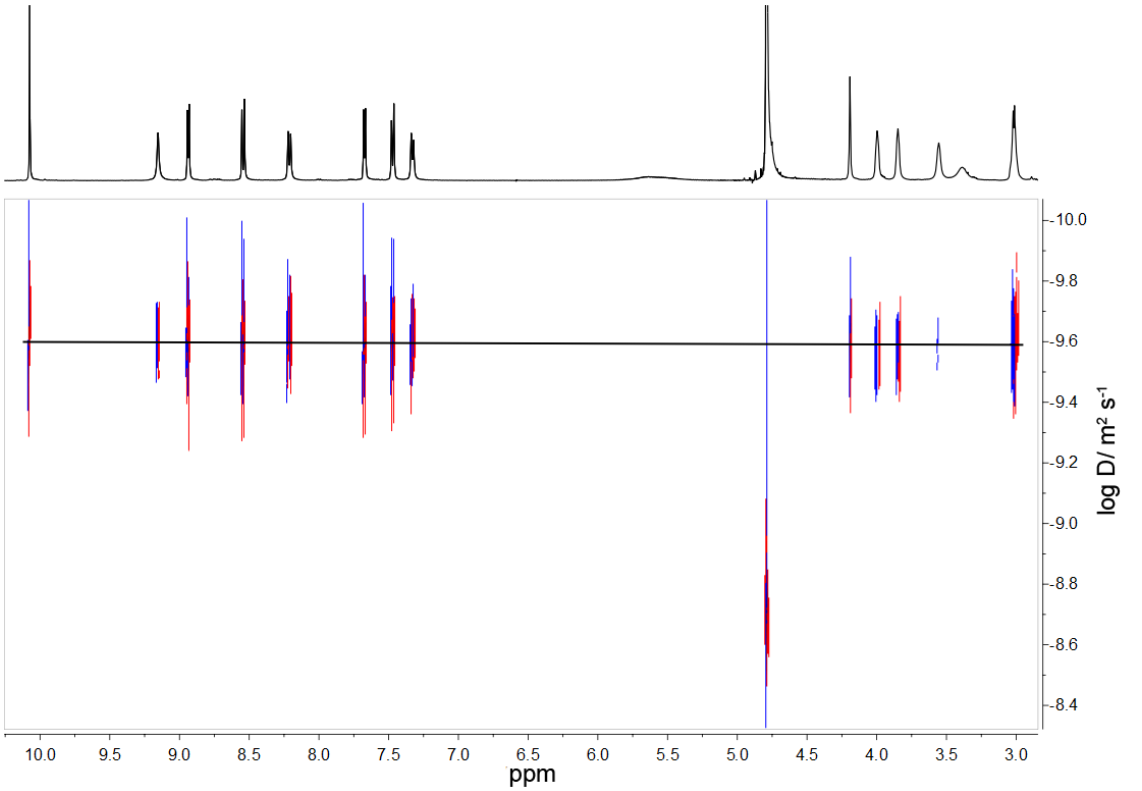



**Figure S30:** DOSY ($D_2O$, 500 MHz, 298 K) experiment of (**4b**)⊂**1a**·6$NO_3$.

**Inclusion complex (5a)⊂1a·6NO$_3$**

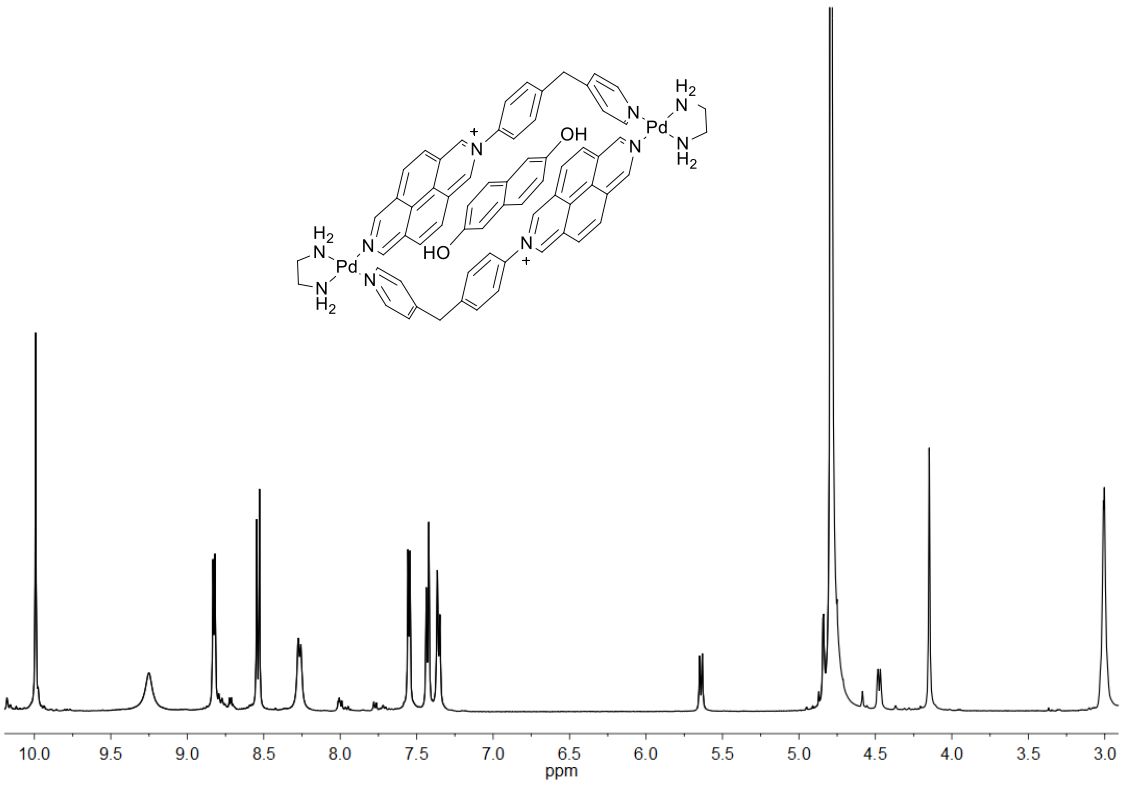



**Figure S31:** $^{1}$H NMR ($D_2O$, 500 MHz) spectrum of (**5a**)⊂**1a**·6$NO_3$.

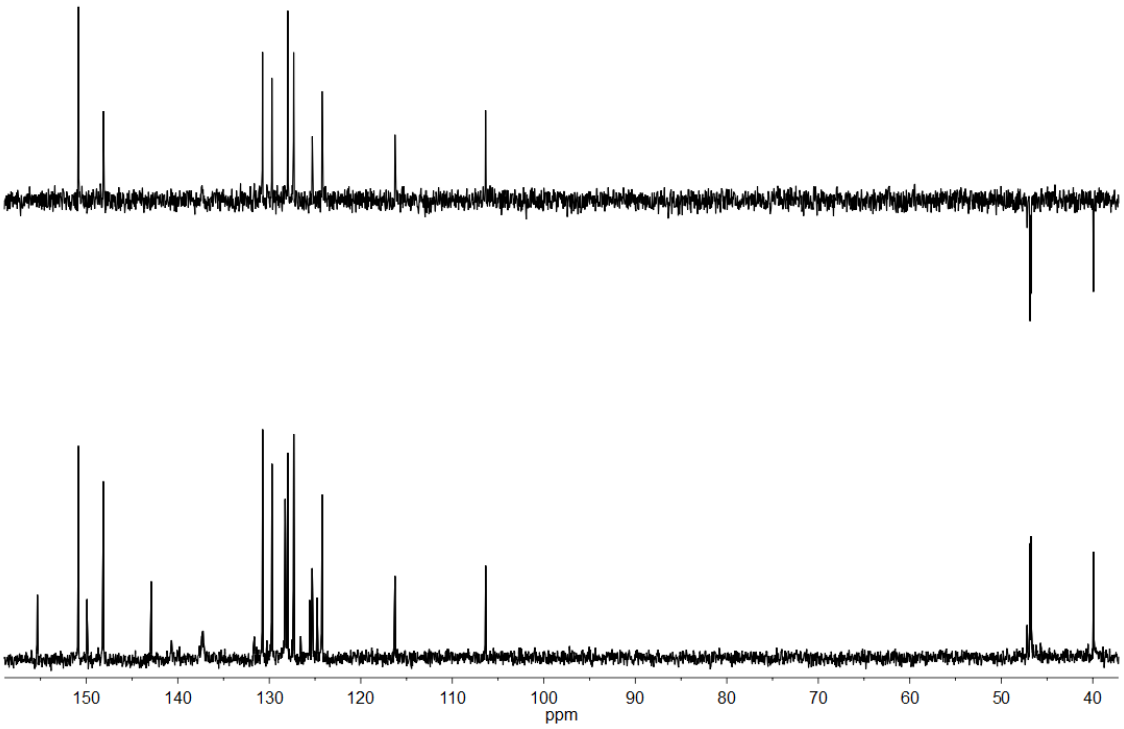



**Figure S32:** $^{13}$C NMR ($D_2O$, 125 MHz) spectrum of (**5a**)⊂**1a**·6$NO_3$.

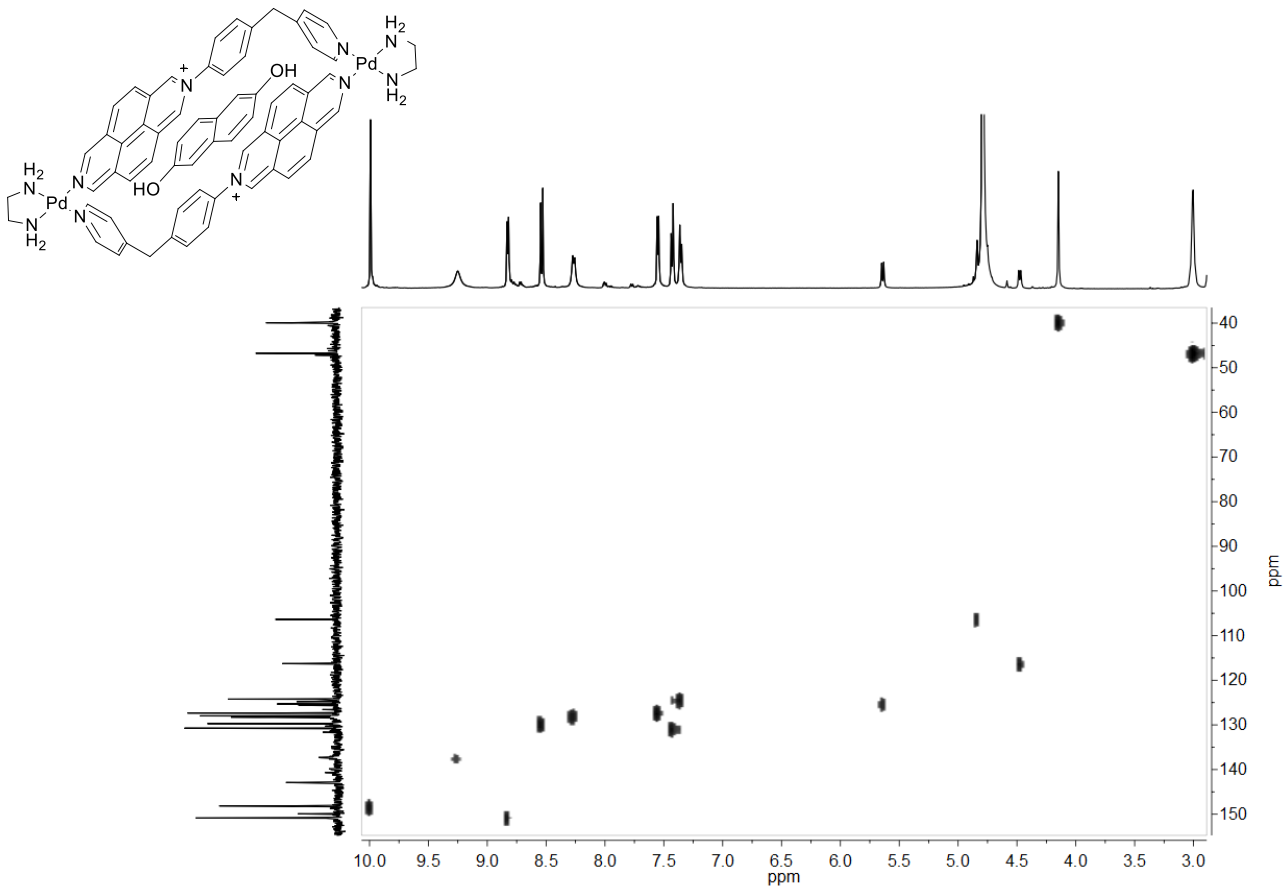



**Figure S33:** HSQC ($D_2O$, 500 and 125 MHz) spectrum of (**5a**)⊂**1a**·6$NO_3$.

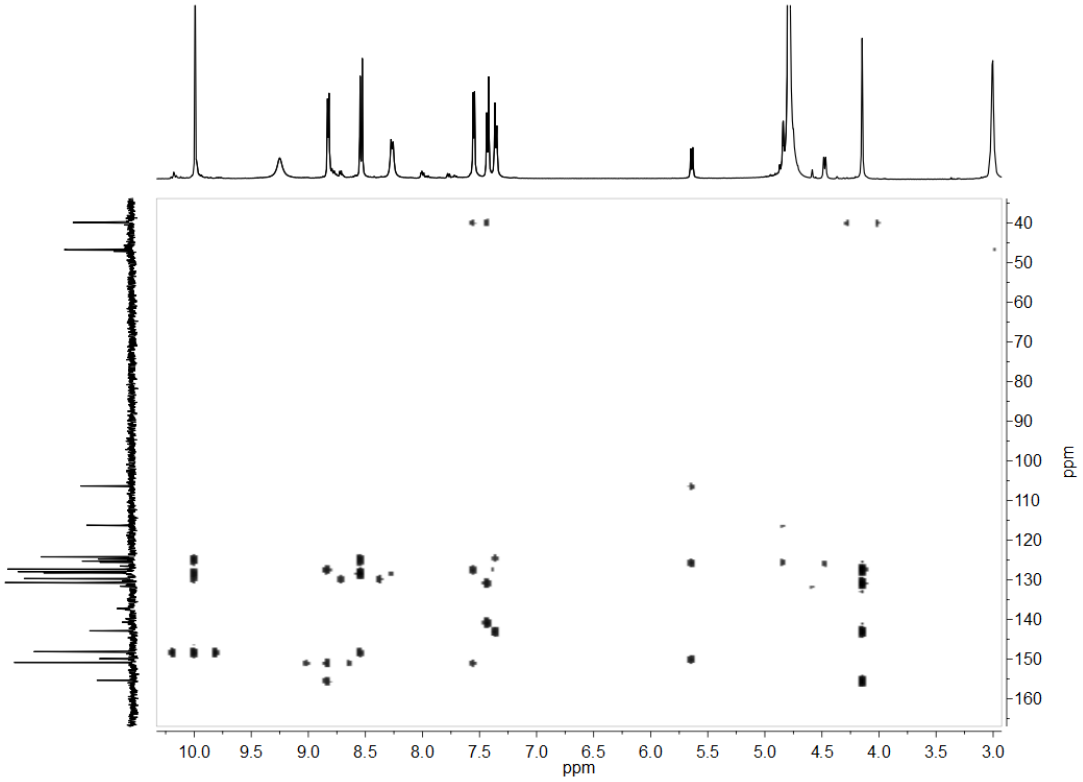



**Figure S34:** HMBC ($D_2O$, 500 and 125 MHz) spectrum of (**5a**)⊂**1a**·6$NO_3$.

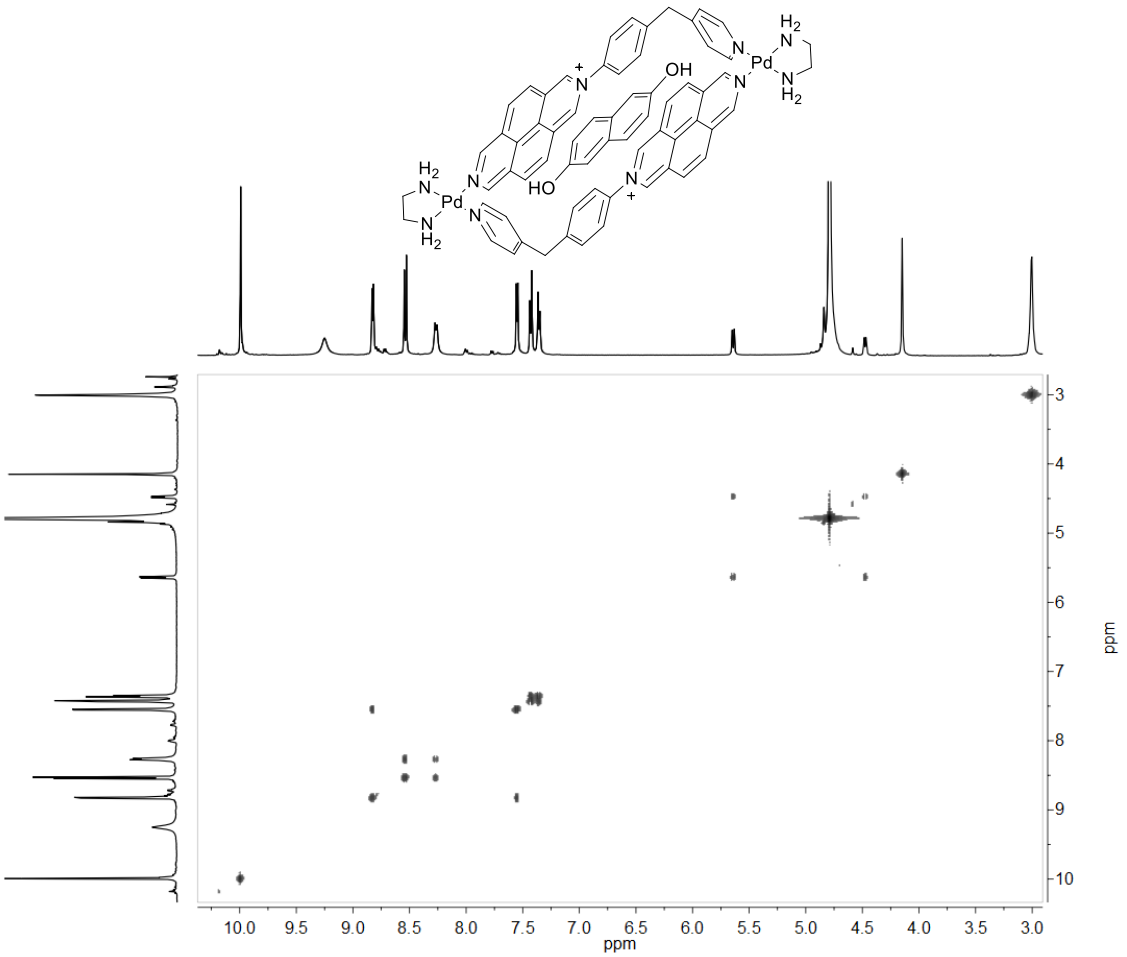



**Figure S35:** COSY ($D_2O$, 500 MHz) spectrum of (**5a**)⊂**1a**·6$NO_3$.

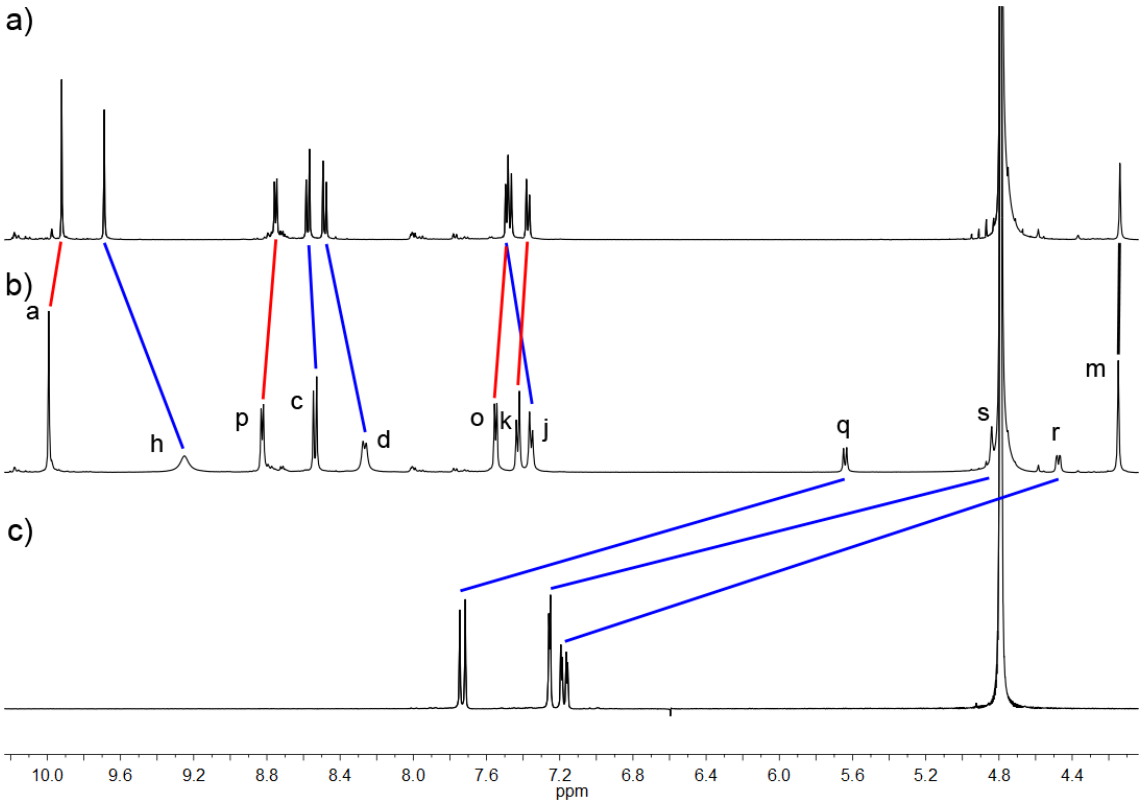



**Figure S36:** Partial $^1$H NMR ($D_2O$, 500 MHz) spectrum of: a) **1a**·6$NO_3$. b) (**5a**)⊂**1a**·6$NO_3$. C) **5a**.

**Inclusion complex (5b)⊂1a·6NO$_3$**

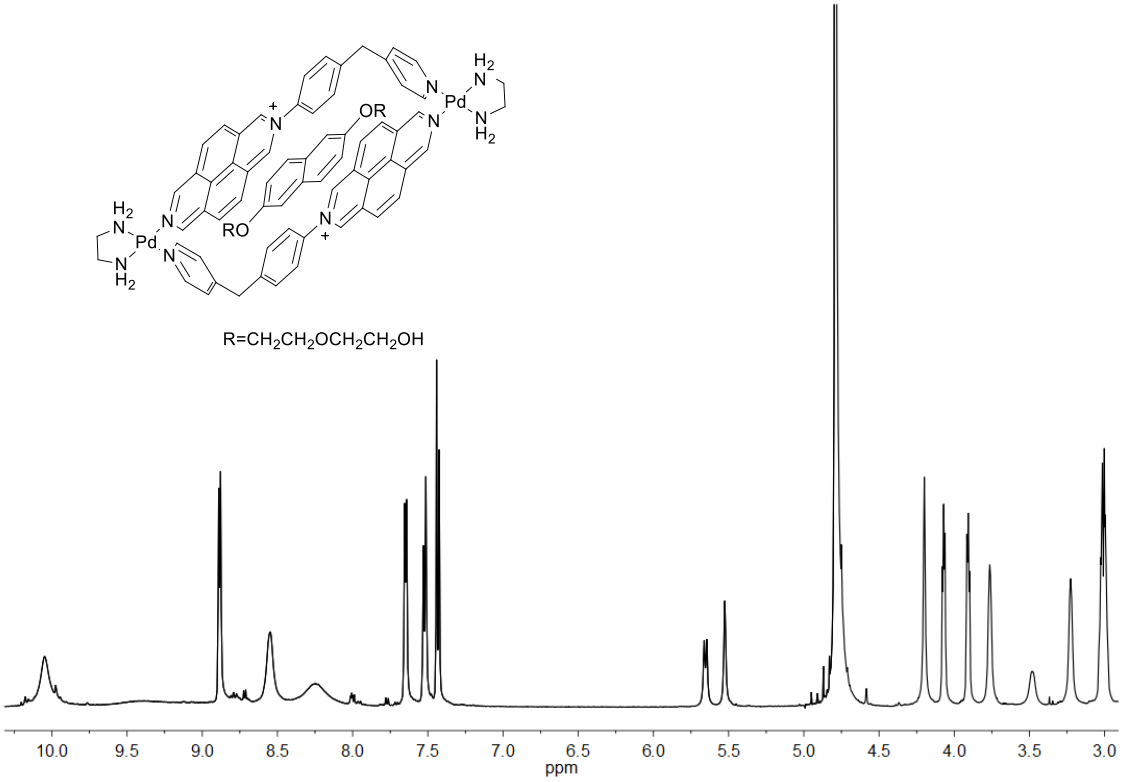



**Figure S37:** $^{1}$H NMR ($D_2O$, 500 MHz) spectrum of (**5b**)⊂**1a**·6$NO_3$.

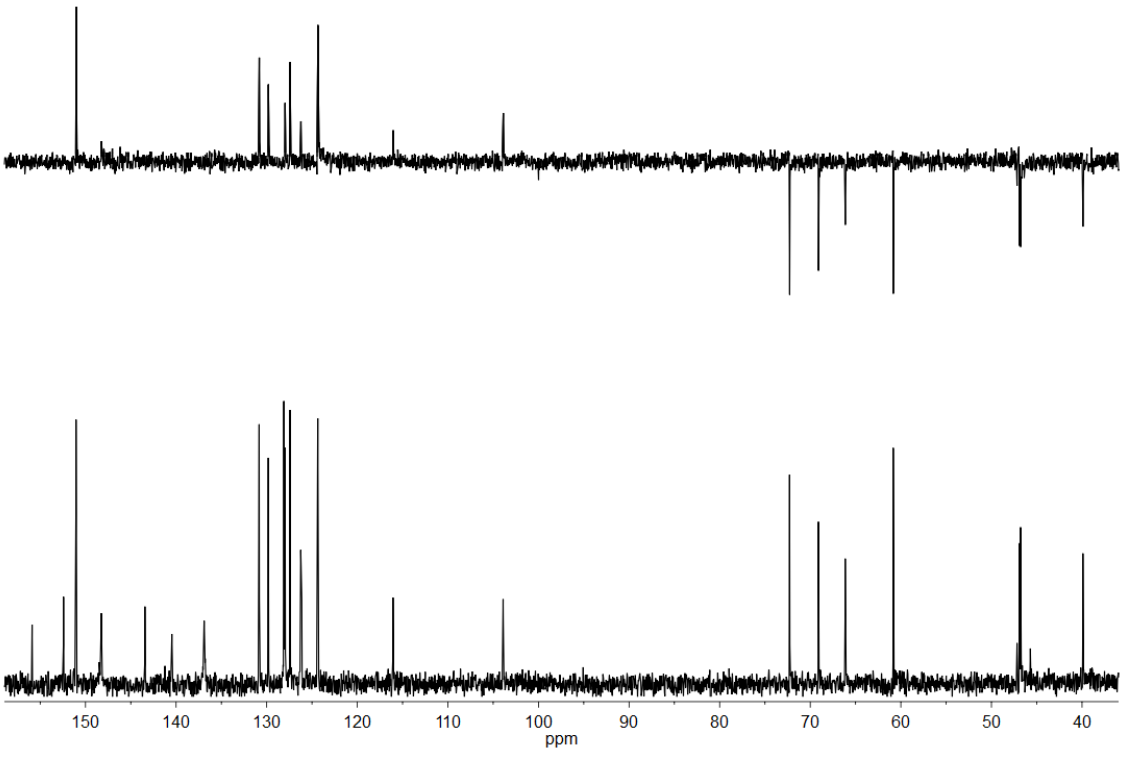



**Figure S38:** $^{13}$C NMR ($D_2O$, 125 MHz) spectrum of (**5b**)⊂**1a**·6$NO_3$.

**Catenane 1a(6)·6PF$_6$**

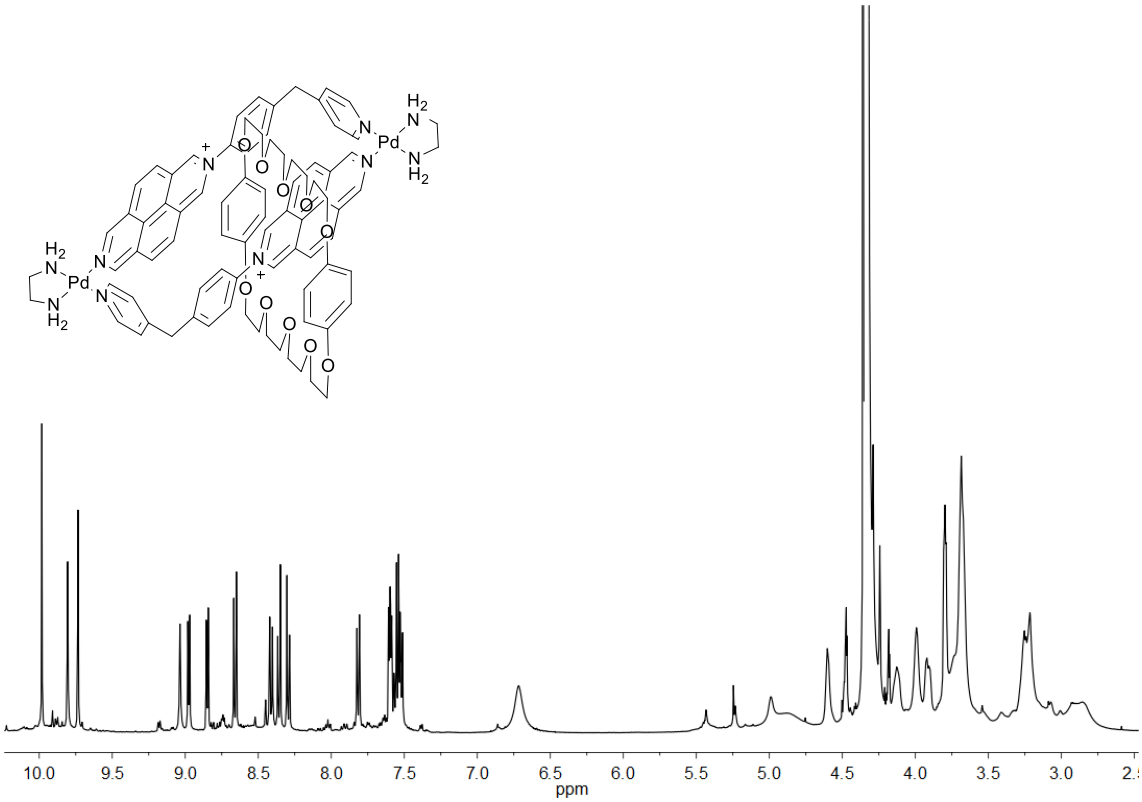



**Figure S39:** $^1$H NMR ($CD_3NO_2$, 500 MHz) spectrum of **1a**(**6**)·6PF$_6$.

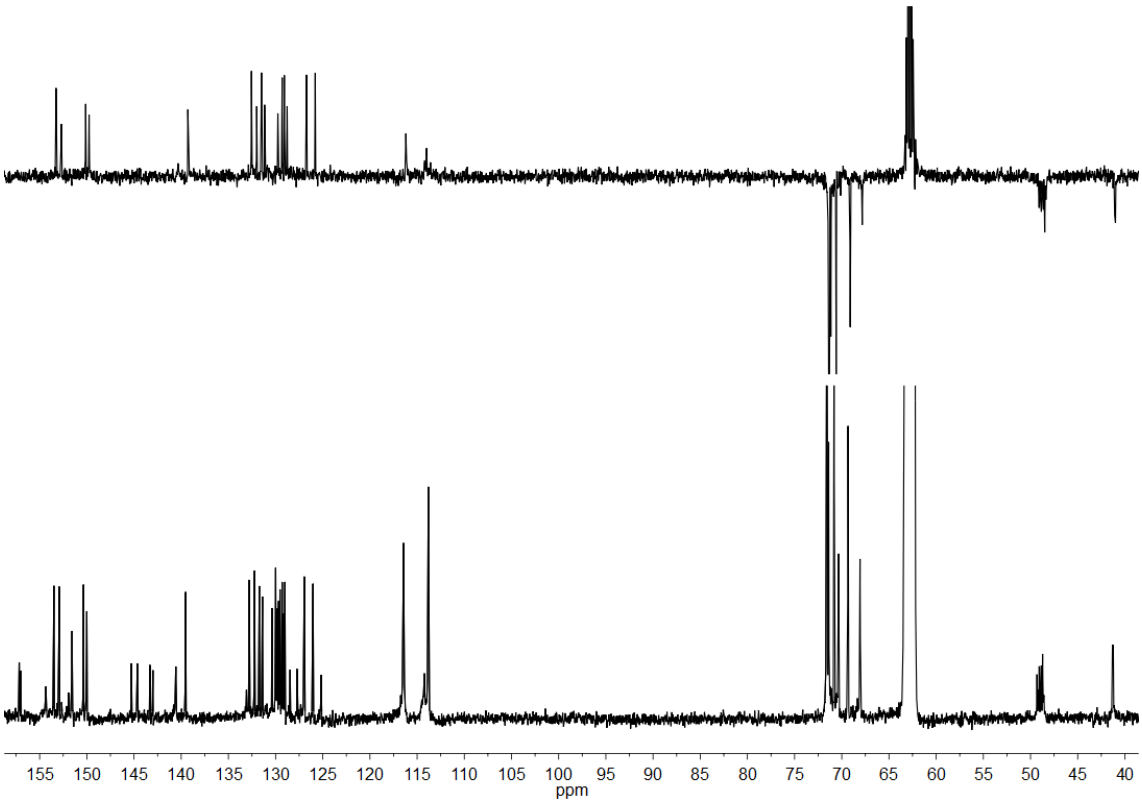



**Figure S40:** $^{13}$C NMR ($CD_3NO_2$, 125 MHz) spectrum of **1a**(**6**)·6PF$_6$.

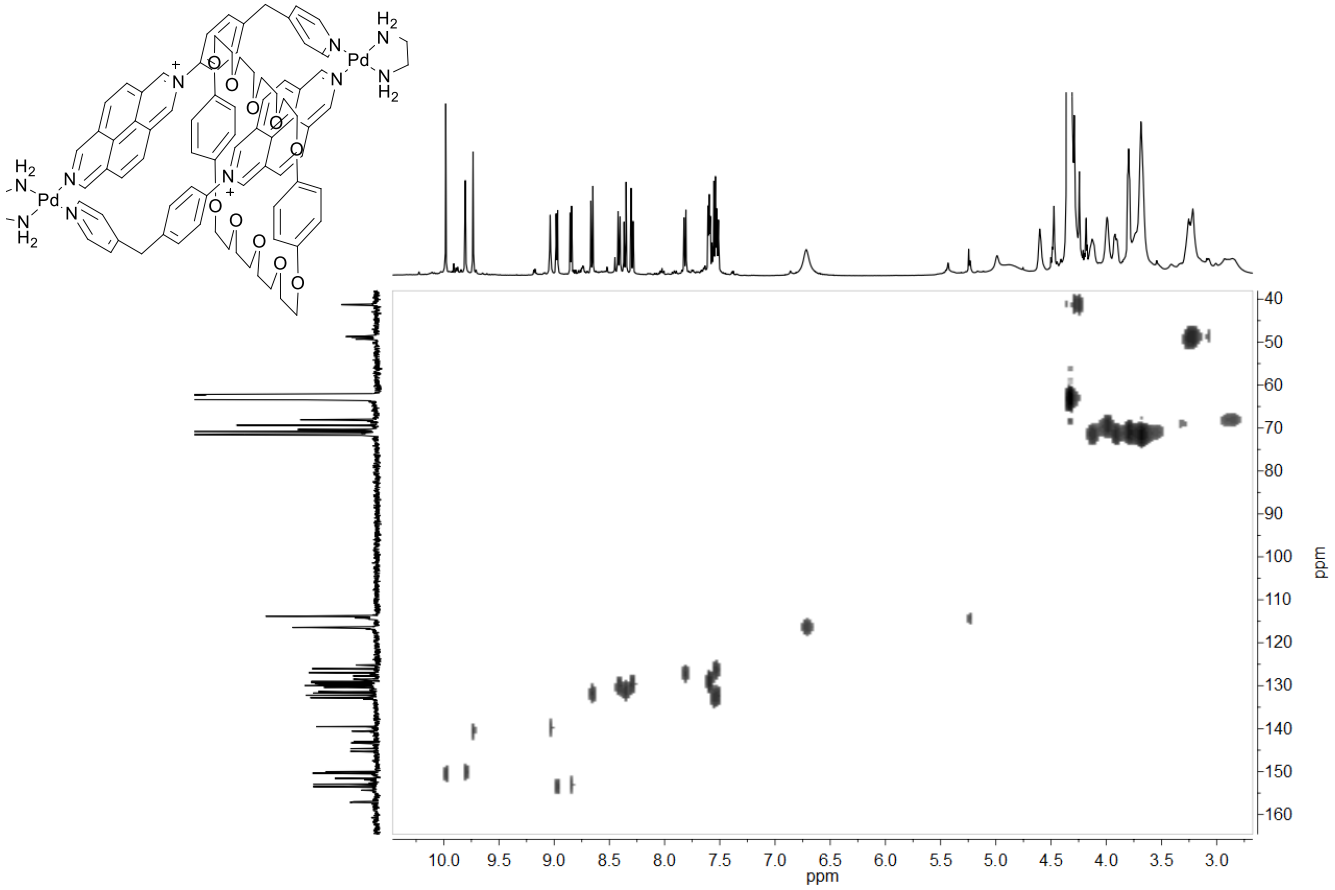



**Figure S41:** HSQC ($CD_3NO_2$, 500 and 125 MHz) spectrum of **1a**(**6**)·$6PF_6$.

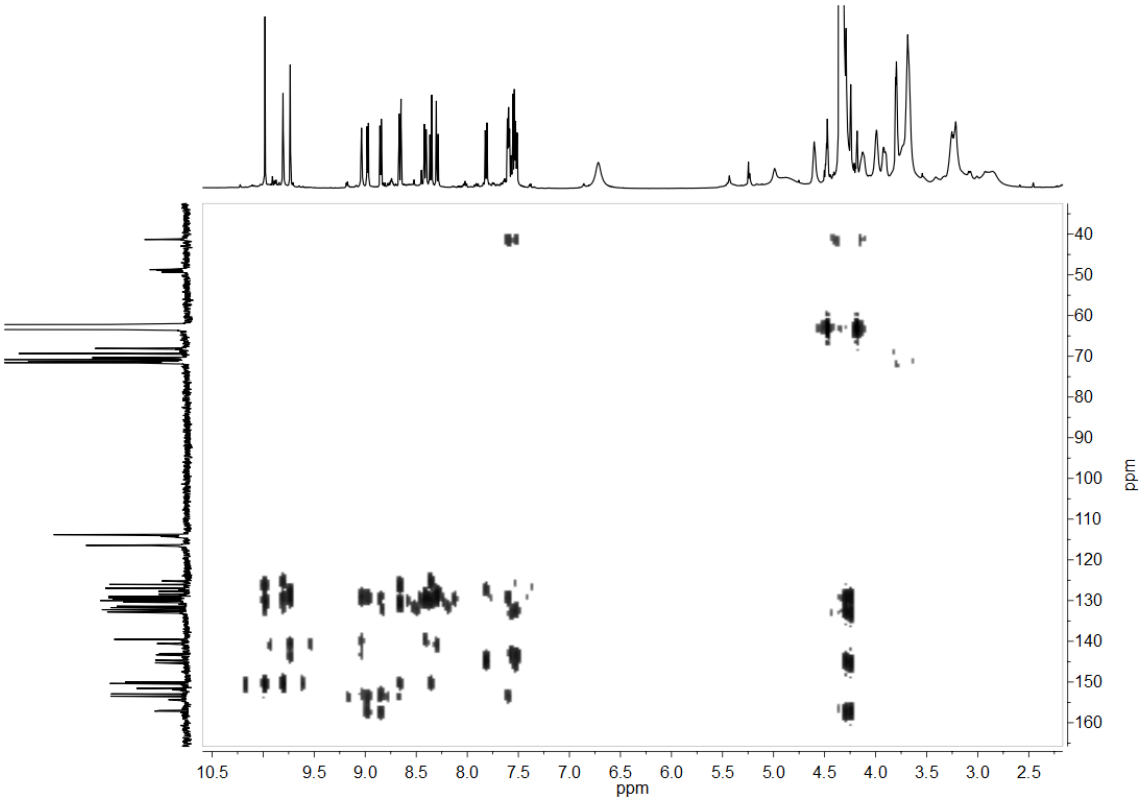



**Figure S42:** HMBC ($CD_3NO_2$, 500 and 125 MHz) spectrum of **1a**(**6**)·$6PF_6$.

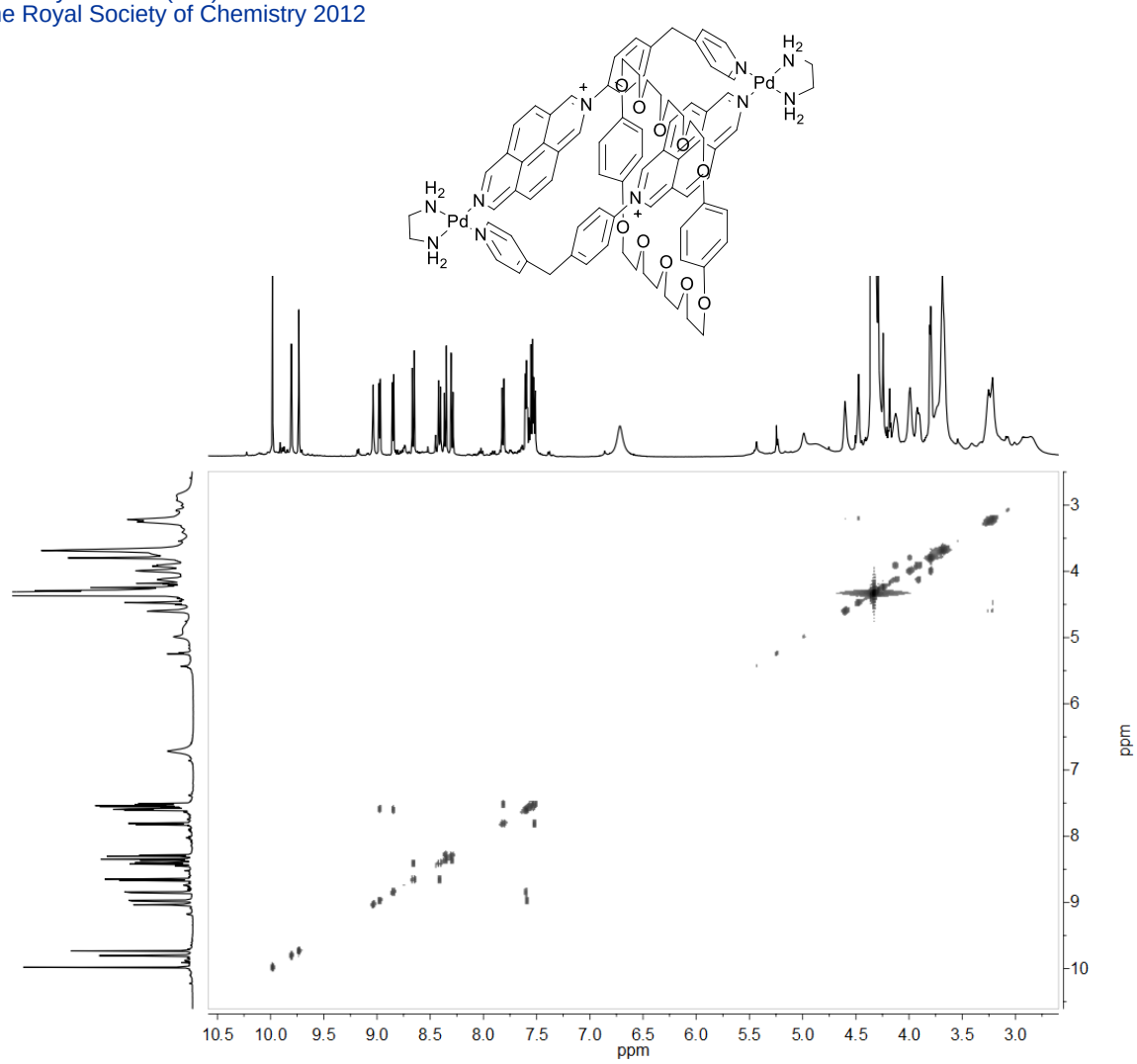



**Figure S43:** COSY ($CD_3NO_2$, 500 MHz) spectrum of **1a**(**6**)·$6PF_6$.

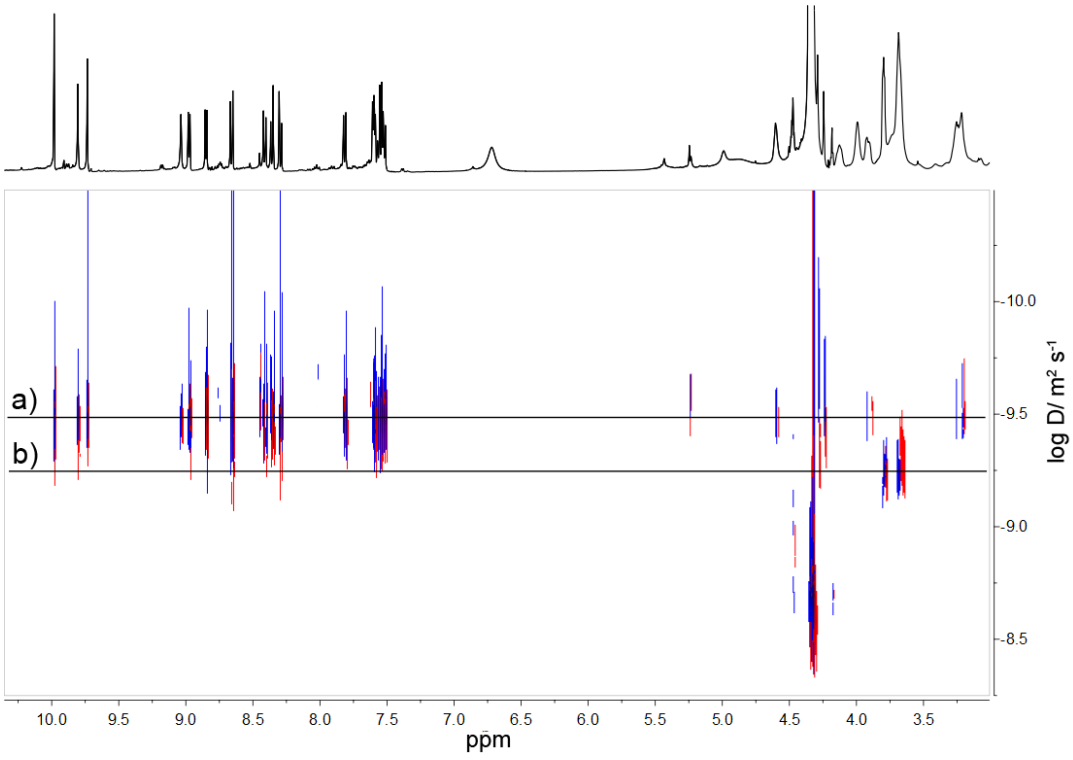



**Figure S44:** DOSY ($CD_3NO_2$, 500 MHz, 298 K) experiment of: a) catenane **1a**(**6**)·$6PF_6$. b) excess of **6**.

**Catenane 1a(7)·6PF$_6$**

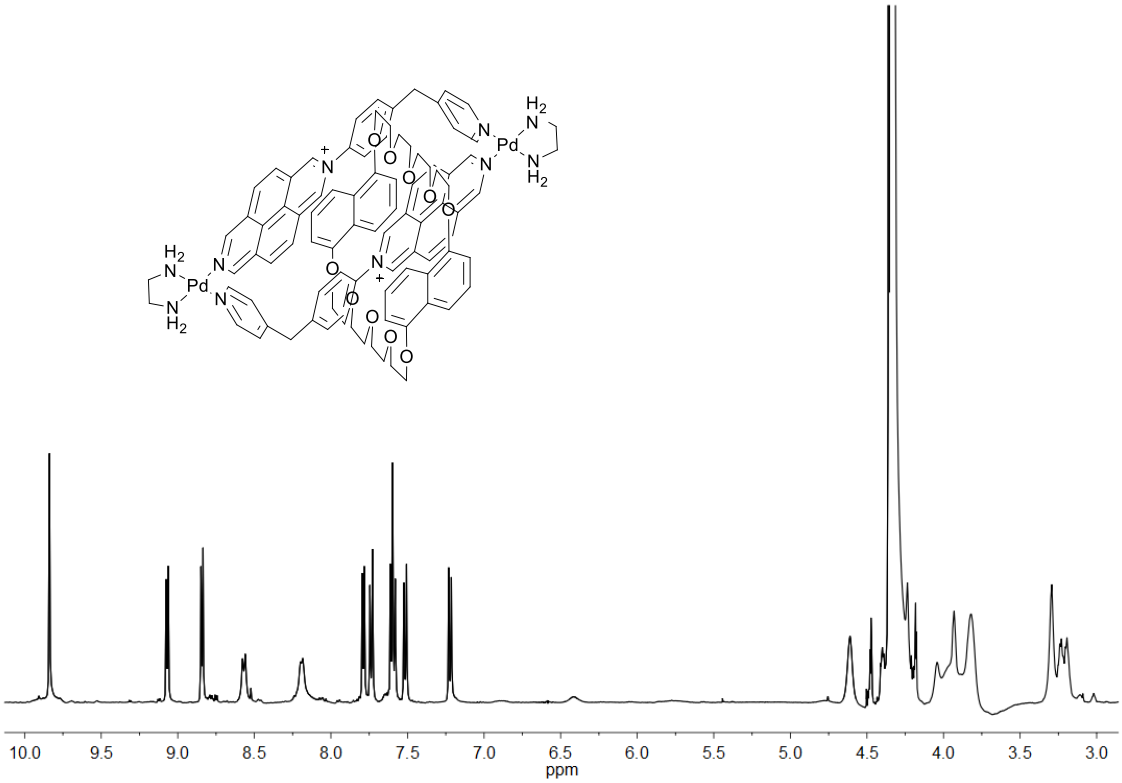



**Figure S45:** $^1$H NMR ($CD_3NO_2$, 500 MHz) spectrum of **1a**(**7**)·6PF$_6$.

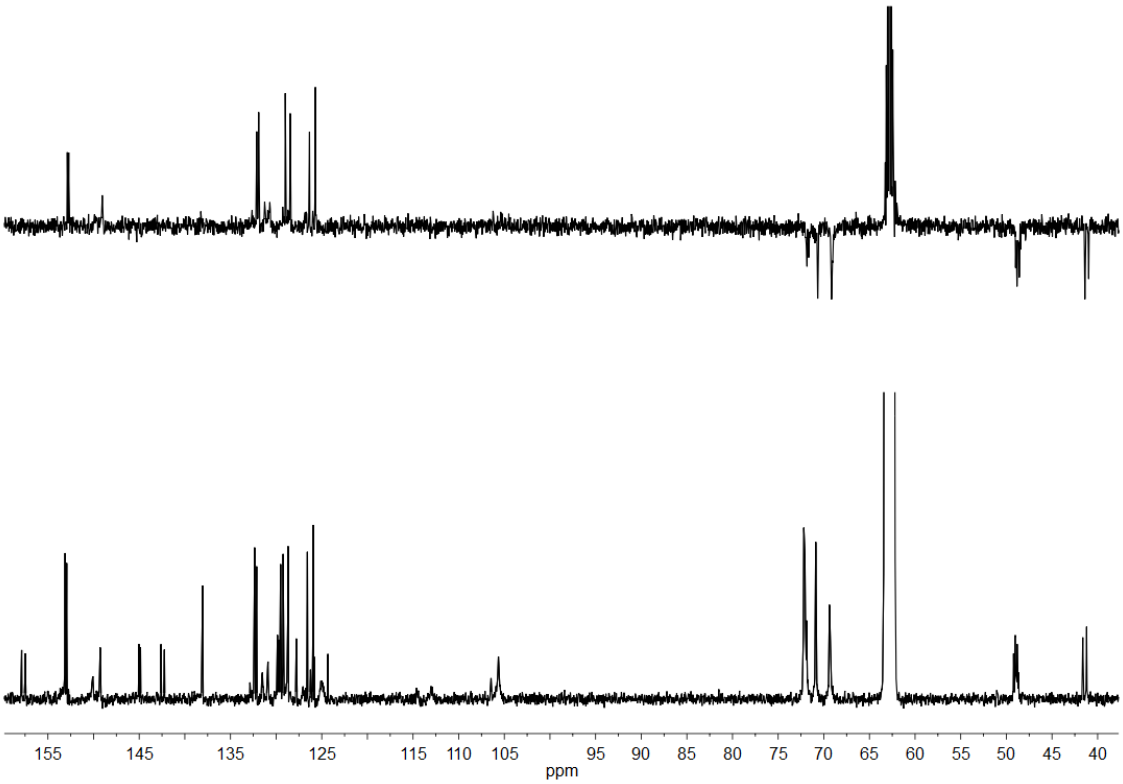



**Figure S46:** $^{13}$C NMR ($CD_3NO_2$, 125 MHz) spectrum of **1a**(**7**)·6PF$_6$.

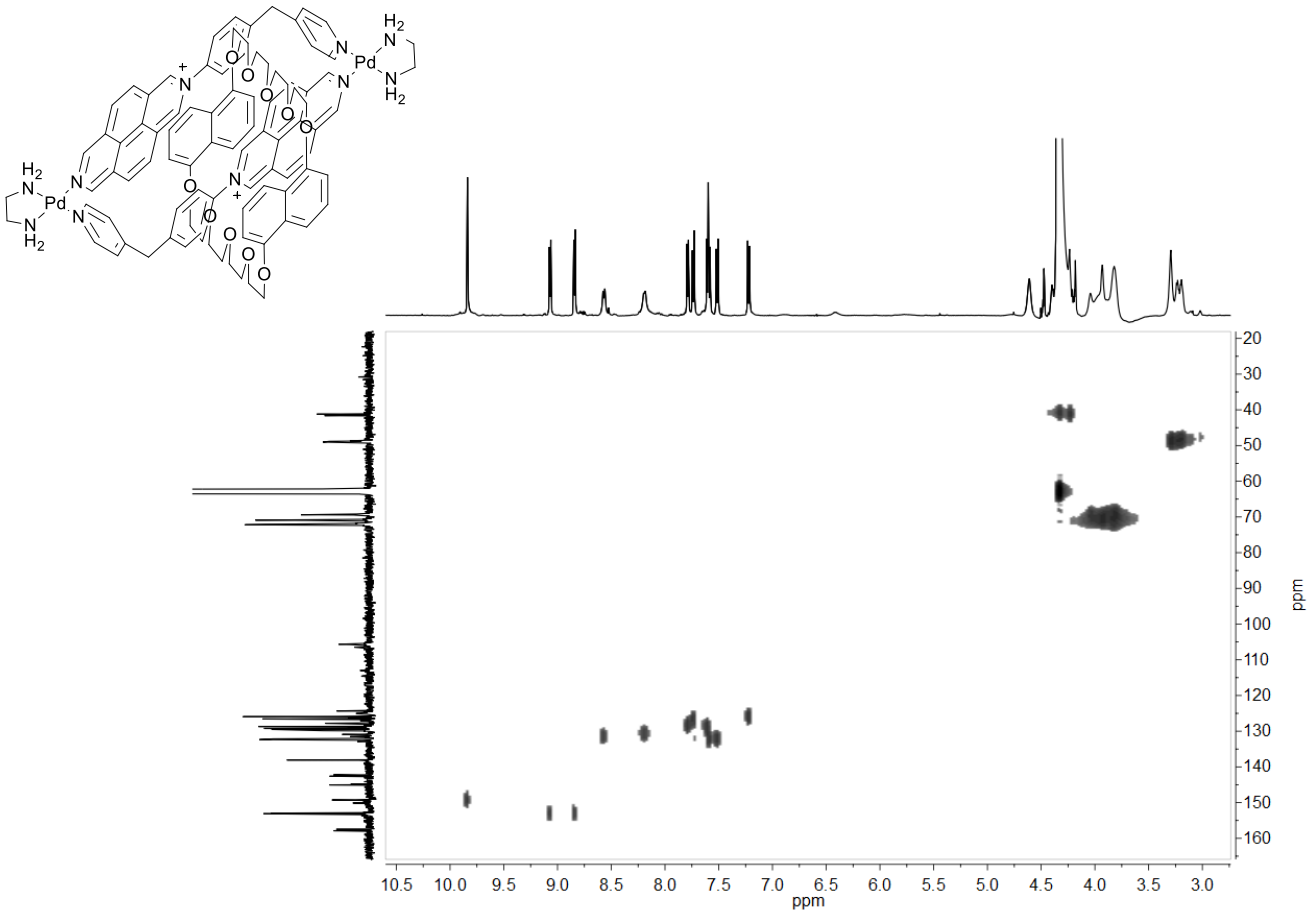



**Figure S47:** HSQC ($CD_3NO_2$, 500 and 125 MHz) spectrum of **1a**(**7**)·$6PF_6$.

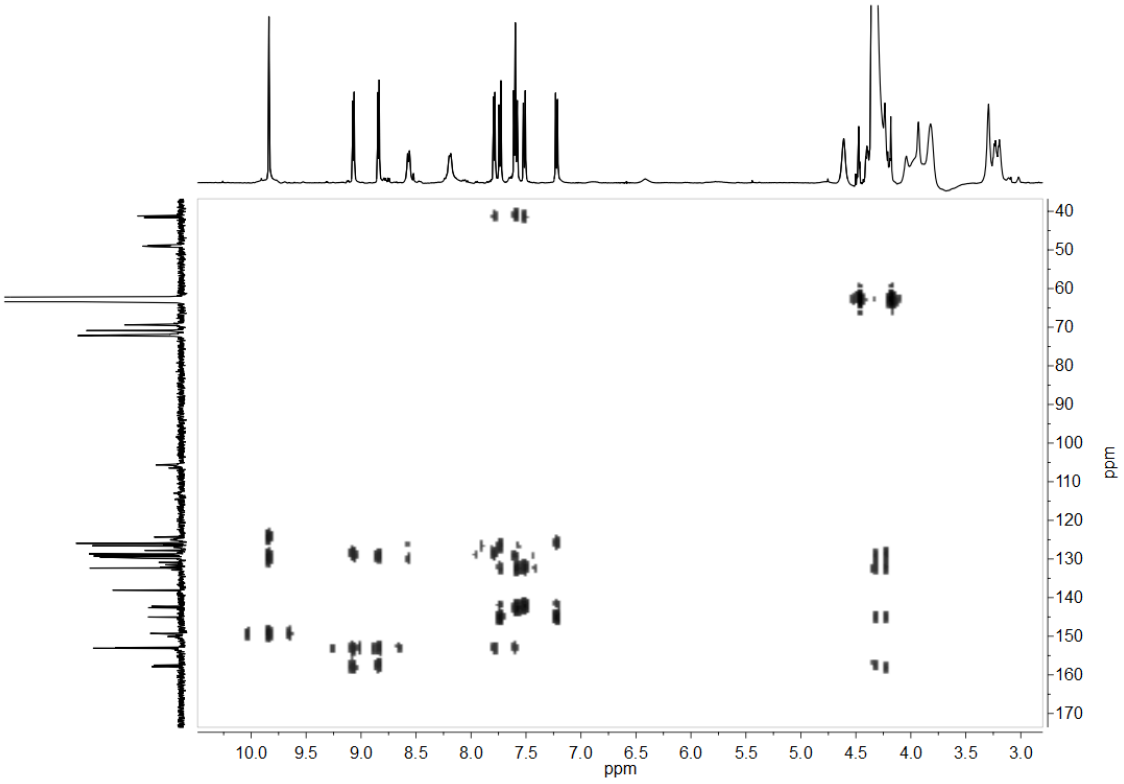



**Figure S48:** HMBC ($CD_3NO_2$, 500 and 125 MHz) spectrum of **1a**(**7**)·$6PF_6$.

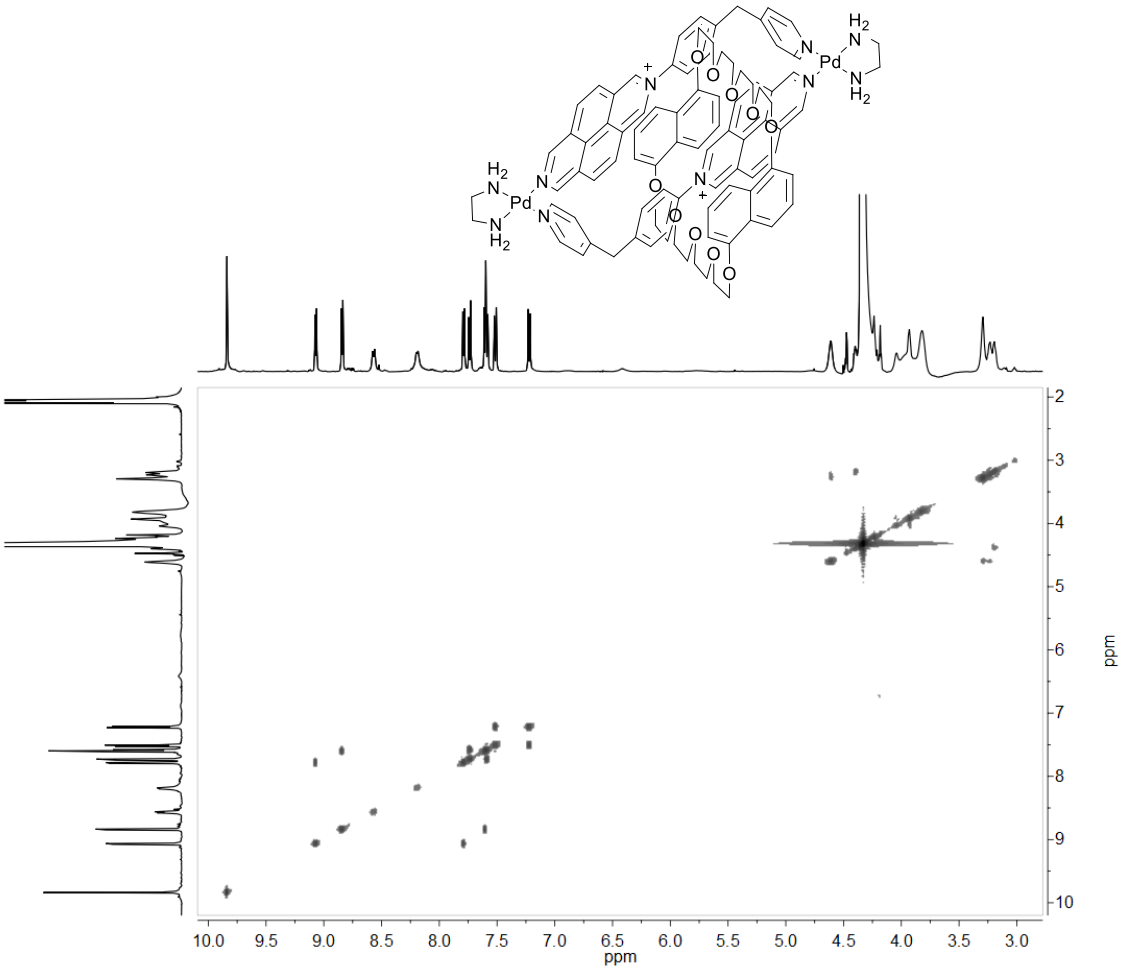



**Figure S49:** COSY ($CD_3NO_2$, 500 MHz) spectrum of **1a**(**7**)·$6PF_6$.

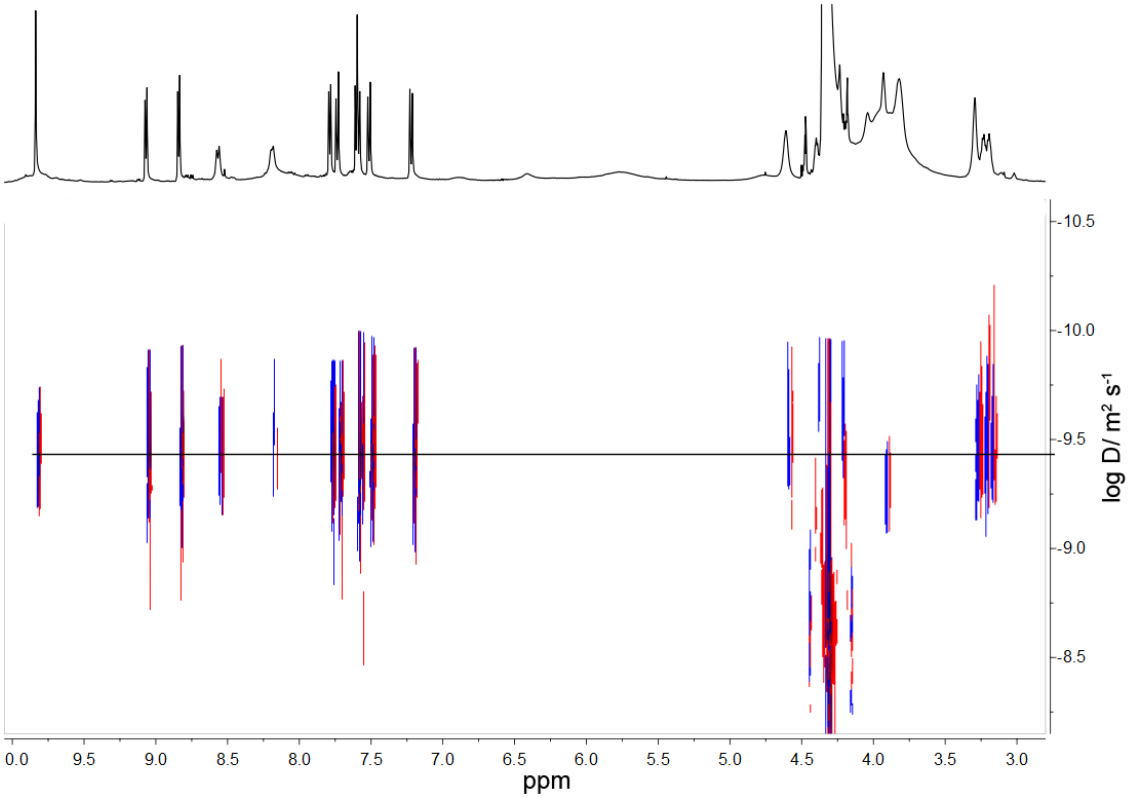



**Figure S50:** DOSY ($CD_3NO_2$, 500 MHz, 298 K) experiment of catenane **1a**(**7**)·$6PF_6$.

## ORTEP Representations

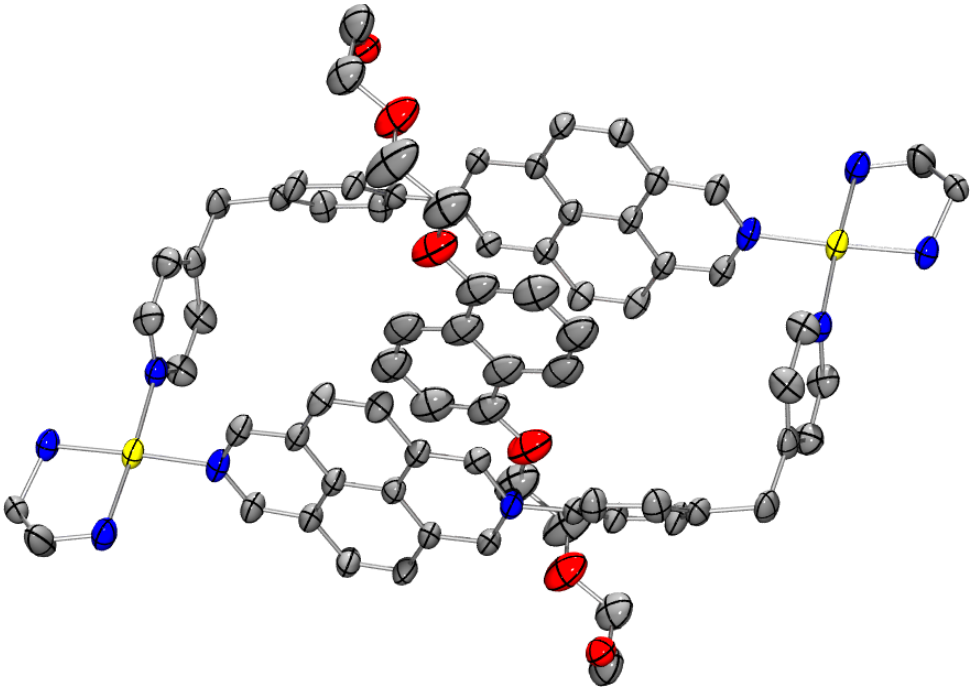


**Figure S51.** ORTEP plot of the X-ray structure of (**3b**)⊂**1a**·6$PF_6$. The displacement ellipsoids are shown at the 50% probability. Hydrogen atoms, counterions and solvent molecules are omitted for clarity.

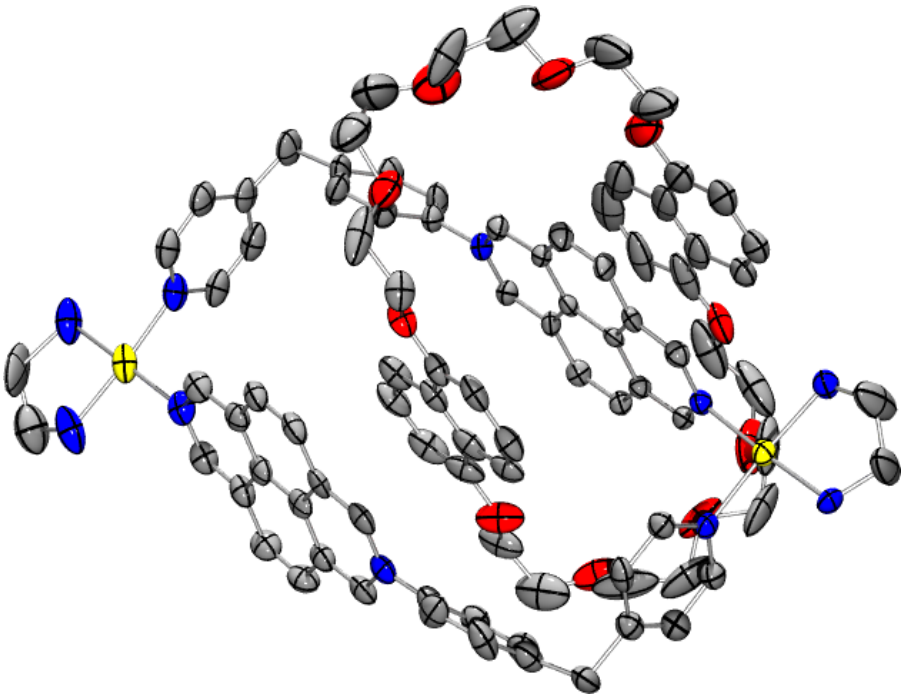


**Figure S52.** ORTEP plot of the X-ray structure of **1a**(**7**)·6$PF_6$. The displacement ellipsoids are shown at the 50% probability. Hydrogen atoms, counterions and solvent molecules are omitted for clarity.

## Job's plots for 2a⊂1b·6PF$_6$ and 3b⊂1b·6PF$_6$ in $CH_3NO_2$

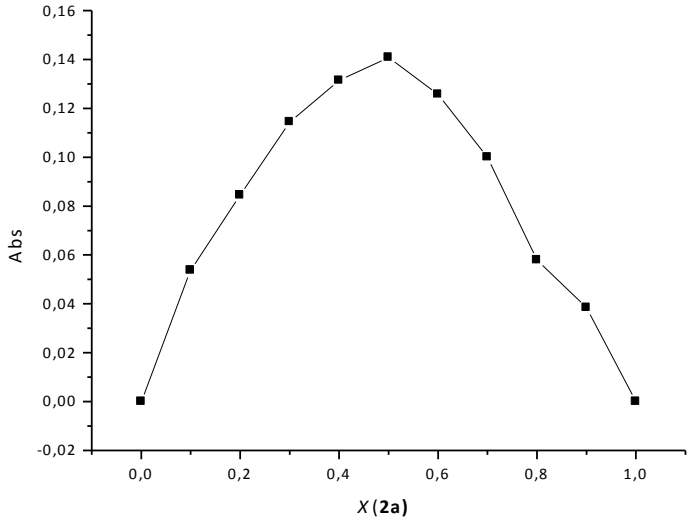



**Figure S53.** Job's plot showing the 1:1 (H:G) stoichiometry of a complex formed between **2a** and **1b**·6PF$_6$ (total concentration 1 mM) in $CH_3NO_2$ (443 nm).

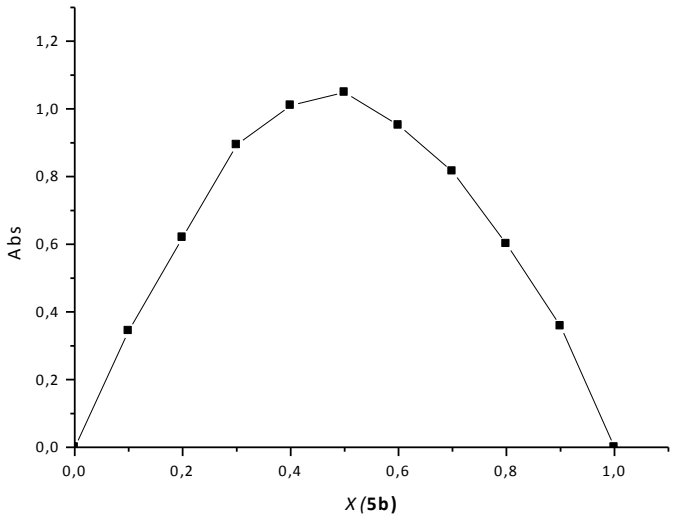
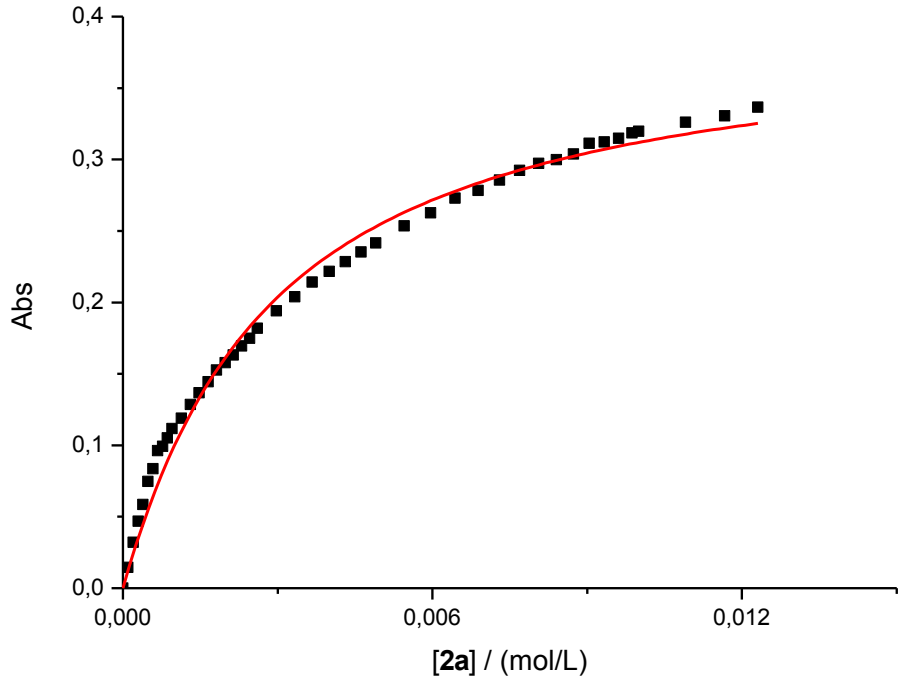



**Figure S54.** Job´s plot showing the 1:1 (H:G) stoichiometry of a complex formed between **3b** and **1b**·6PF$_6$ (total concentration 1 mM) in $CH_3NO_2$ (437nm).

## Determination of binding constants ($K_a$) for the inclusion complexes 2a⊂1b·6PF$_6$ and 3b⊂1b·6PF$_6$ in $CH_3NO_2$ using the UV/Vis dilution method

A 0.5 mM solution of host (**1b**·6PF$_6$) in $CH_3NO_2$, and a solution of host (0.5 mM) and the corresponding guest **2a**/**3b** (10 mM) in $CH_3NO_2$, were separately prepared. Aliquots of the host/guest solution (10 µL initially, then 20 µL, then 50 µL, and finally 100 µL) were added to the host solution (2 mL). The UV-vis spectrum was recorded after each addition, and overall 45 (**2a**⊂**1b**·6PF$_6$) and 40 (**3b**⊂**1b**·6PF$_6$) data points were obtained. The association constants were determined by using the nonlinear least squares fitting of the titration curves plotting A of the host-guest complex charge-transfer band against the molar equivalent of the guest. The titration curves were well fitted to the expression of a 1:1 binding isotherm.

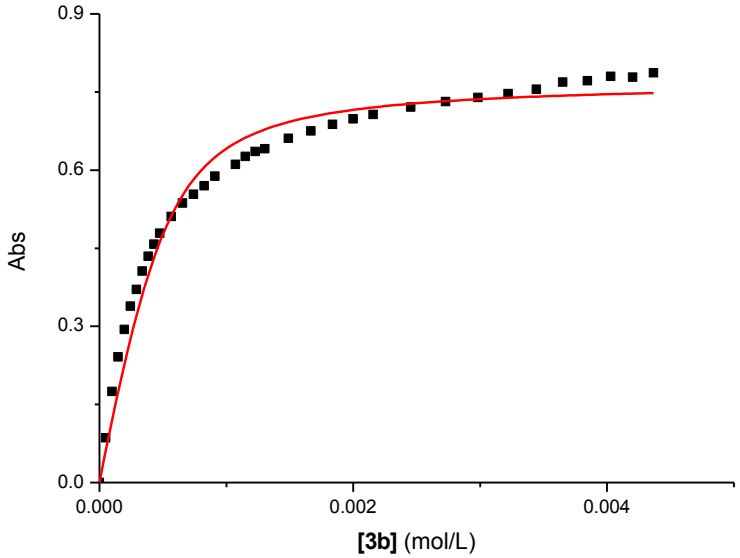
a) **2a⊂1b**·6$PF_6$**:**
T: 298 K
$\lambda_{max}$=443nm
$K_a$ = 386 ± 21 $M^{-1}$ (adj. $R^2$ = 0,98938)




| Total volumen added (mL) | Abs | $[\mathbf{2a}]_{total}$ (mol/L) |
|---|---|---|
| 0 | 0 | 0 |
| 0.01 | 0.01448 | 9.9502E-05 |
| 0.02 | 0.03209 | 0.00019802 |
| 0.03 | 0.04682 | 0.00029557 |
| 0.04 | 0.05857 | 0.00039216 |
| 0.05 | 0.07459 | 0.0004878 |
| 0.06 | 0.08348 | 0.00058252 |
| 0.07 | 0.09617 | 0.00067633 |
| 0.08 | 0.09924 | 0.00076923 |
| 0.09 | 0.105 | 0.00086124 |
| 0.1 | 0.11154 | 0.00095238 |
| 0.12 | 0.11887 | 0.00113208 |
| 0.14 | 0.12855 | 0.00130841 |
| 0.16 | 0.1366 | 0.00148148 |
| 0.18 | 0.14447 | 0.00165138 |
| 0.2 | 0.15249 | 0.00181818 |
| 0.22 | 0.15786 | 0.00198198 |
| 0.24 | 0.16323 | 0.00214286 |
| 0.26 | 0.16953 | 0.00230088 |
| 0.28 | 0.17492 | 0.00245614 |
| 0.3 | 0.1818 | 0.0026087 |
| 0.35 | 0.19397 | 0.00297872 |
| 0.4 | 0.20379 | 0.00333333 |
| 0.45 | 0.21411 | 0.00367347 |
| 0.5 | 0.22172 | 0.004 |

| | | |
|---|---|---|
| 0.55 | 0.22848 | 0.00431373 |
| 0.6 | 0.23524 | 0.00461538 |
| 0.65 | 0.24156 | 0.00490566 |
| 0.75 | 0.25344 | 0.00545455 |
| 0.85 | 0.26268 | 0.00596491 |
| 0.95 | 0.27301 | 0.00644068 |
| 1.05 | 0.27835 | 0.00688525 |
| 1.15 | 0.28545 | 0.00730159 |
| 1.25 | 0.29229 | 0.00769231 |
| 1.35 | 0.29724 | 0.0080597 |
| 1.45 | 0.29978 | 0.0084058 |
| 1.55 | 0.30387 | 0.00873239 |
| 1.65 | 0.31131 | 0.0090411 |
| 1.75 | 0.31222 | 0.00933333 |
| 1.85 | 0.31484 | 0.00961039 |
| 1.95 | 0.31855 | 0.00987342 |
| 2 | 0.31972 | 0.01 |
| 2.4 | 0.32595 | 0.01090909 |
| 2.8 | 0.33054 | 0.01166667 |
| 3.2 | 0.33658 | 0.01230769 |

b) **3b**⊂**1b**·6$PF_6$:
T: 298 K
$\lambda_{max}$ = 437
$K_a$ = 8477 ± 1253 (adj. $R^2$ = 0.97193)




| V/mL | Abs | [**3b**]total (mol/L) |
|---|---|---|
| 0 | 0 | 0 |
| 0.01 | 0.08598 | 4.9751E-05 |
| 0.02 | 0.17472 | 9.901E-05 |
| 0.03 | 0.2414 | 0.00014778 |
| 0.04 | 0.2936 | 0.00019608 |
| 0.05 | 0.3384 | 0.0002439 |
| 0.06 | 0.37077 | 0.00029126 |
| 0.07 | 0.40591 | 0.00033816 |

| | | |
|---|---|---|
| 0.08 | 0.4347 | 0.00038462 |
| 0.09 | 0.45781 | 0.00043062 |
| 0.1 | 0.47887 | 0.00047619 |
| 0.12 | 0.51064 | 0.00056604 |
| 0.14 | 0.53639 | 0.00065421 |
| 0.16 | 0.55333 | 0.00074074 |
| 0.18 | 0.56987 | 0.00082569 |
| 0.2 | 0.58849 | 0.00090909 |
| 0.22 | 0.59951 | 0.00099099 |
| 0.24 | 0.61074 | 0.00107143 |
| 0.26 | 0.62609 | 0.00115044 |
| 0.28 | 0.63543 | 0.00122807 |
| 0.3 | 0.64094 | 0.00130435 |
| 0.35 | 0.66097 | 0.00148936 |
| 0.4 | 0.67506 | 0.00166667 |
| 0.45 | 0.68752 | 0.00183673 |
| 0.5 | 0.6983 | 0.00200000 |
| 0.55 | 0.70665 | 0.00215686 |
| 0.65 | 0.72121 | 0.00245283 |
| 0.75 | 0.73144 | 0.00272727 |
| 0.85 | 0.73916 | 0.00298246 |
| 0.95 | 0.74698 | 0.00322034 |
| 1.05 | 0.7553 | 0.00344262 |
| 1.15 | 0.76882 | 0.00365079 |
| 1.25 | 0.77144 | 0.00384615 |
| 1.35 | 0.77987 | 0.00402985 |
| 1.45 | 0.7786 | 0.0042029 |
| 1.55 | 0.78652 | 0.0043662 |
| 1.65 | 0.79455 | 0.00452055 |
| 1.75 | 0.79753 | 0.00466667 |
| 1.82 | 0.80286 | 0.0047644 |
| 1.95 | 0.80964 | 0.00493671 |
| 2.40 | 0.82765 | 0.00545455 |
| 2.80 | 0.83102 | 0.00583333 |
| 3.20 | 0.83501 | 0.00615385 |
| 3.60 | 0.84021 | 0.00642857 |
| 4.00 | 0.8458 | 0.00666667 |

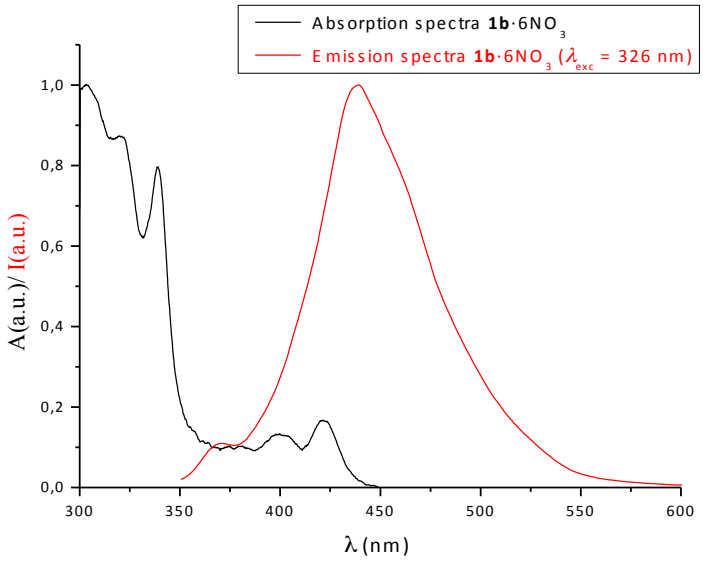



**Figure S55:** Normalised absorption (black line) and fluorescence emission spectra (red line) of metallocycle **1b**·6$NO_3$ in $H_2O$ (293K).

## Determination of binding constant ($K_a$) for the inclusion complex 3b⊂1b·6$NO_3$ in $H_2O$ using the fluorescence dilution method

A $1.010^{-6}$ M solution of host **1**·6$NO_3$ in water, and a solution of host ($1.0\times10^{-6}$ M) and guest **3b** ($1.0\times10^{-5}$ M) in water were separately prepared. Aliquots of 50 µL the guest/host solution were added to the host solution (2 mL). The spectrum was recorded after each addition, and overall 20 data points were obtained. The association constant was determined by using the nonlinear least squares fitting of the titration curve plotting the fluorescence quenching against the concentration of guest. The titration curve fits perfectly to the 1:1 binding isotherm.

Temperature: 300 K
$\lambda_{exc}$ = 326.3 nm; $\lambda_{em}$ = 439.1 nm;
$K_a = 4.4\times10^5 \pm 1.8\times10^4$ $M^{-1}$ ($R^2$ = 0.9991)

| $I_F$ | [**3b**]$_{total}$ (mol/L) |
|---|---|
| 498.816 | 0 |
| 474.628 | 2.439E-07 |
| 456.374 | 4.7619E-07 |
| 437.788 | 6.9767E-07 |
| 423.38 | 9.0909E-07 |
| 409.368 | 1.1111E-06 |
| 398337 | 1.3043E-06 |
| 388.971 | 1.4894E-06 |
| 379.347 | 1.6667E-06 |
| 376.737 | 1.8367E-06 |
| 364.468 | 0.000002 |
| 360.255 | 2.1569E-06 |
| 356.325 | 2.3077E-06 |
| 350.597 | 2.5926E-06 |
| 336.46 | 2.8571E-06 |
| 325.342 | 3.1034E-06 |
| 321.182 | 3.3333E-06 |
| 318.076 | 3.5484E-06 |
| 309.354 | 0.00000375 |
| 305.13 | 3.9394E-06 |
| 300.429 | 4.1176E-06 |
| 295.017 | 4.2857E-06 |
| 288.889 | 4.4444E-06 |

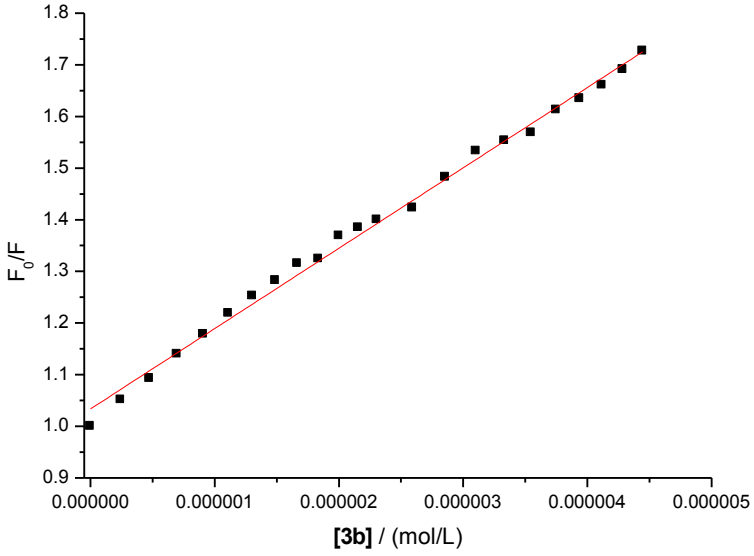



**Figure S56:** Stern-Volmer fitting of the tritation data for metallocycle **1b**·6$NO_3$ and **3b** in water: slope $K_{sv} = 5.5\times10^5 \pm 2\times10^3$ $M^{-1}$, intercept = 1.033 ± 0.006 $M^{-1}$.