SUPPORTING INFORMATION

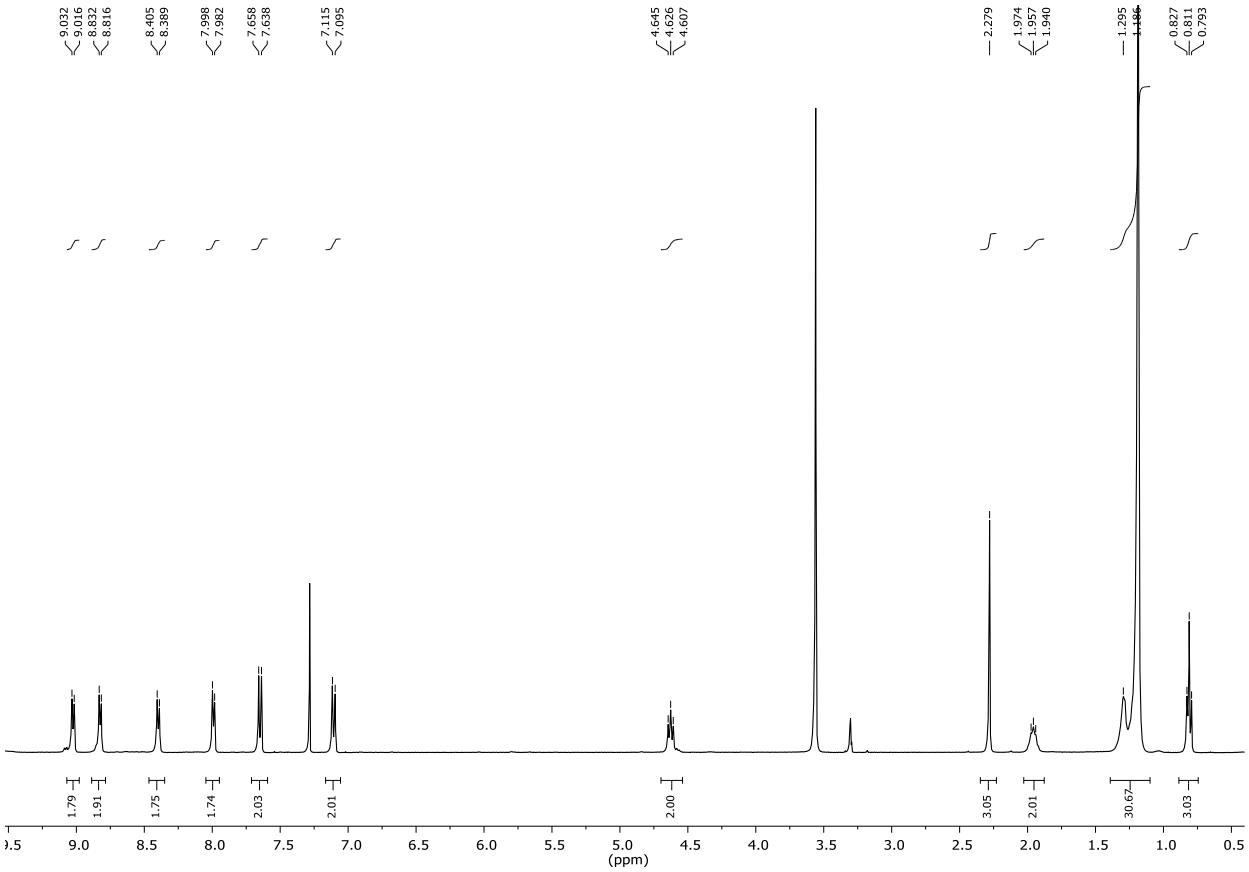

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$/MeOD) of **PpyC18**$^{+}$.

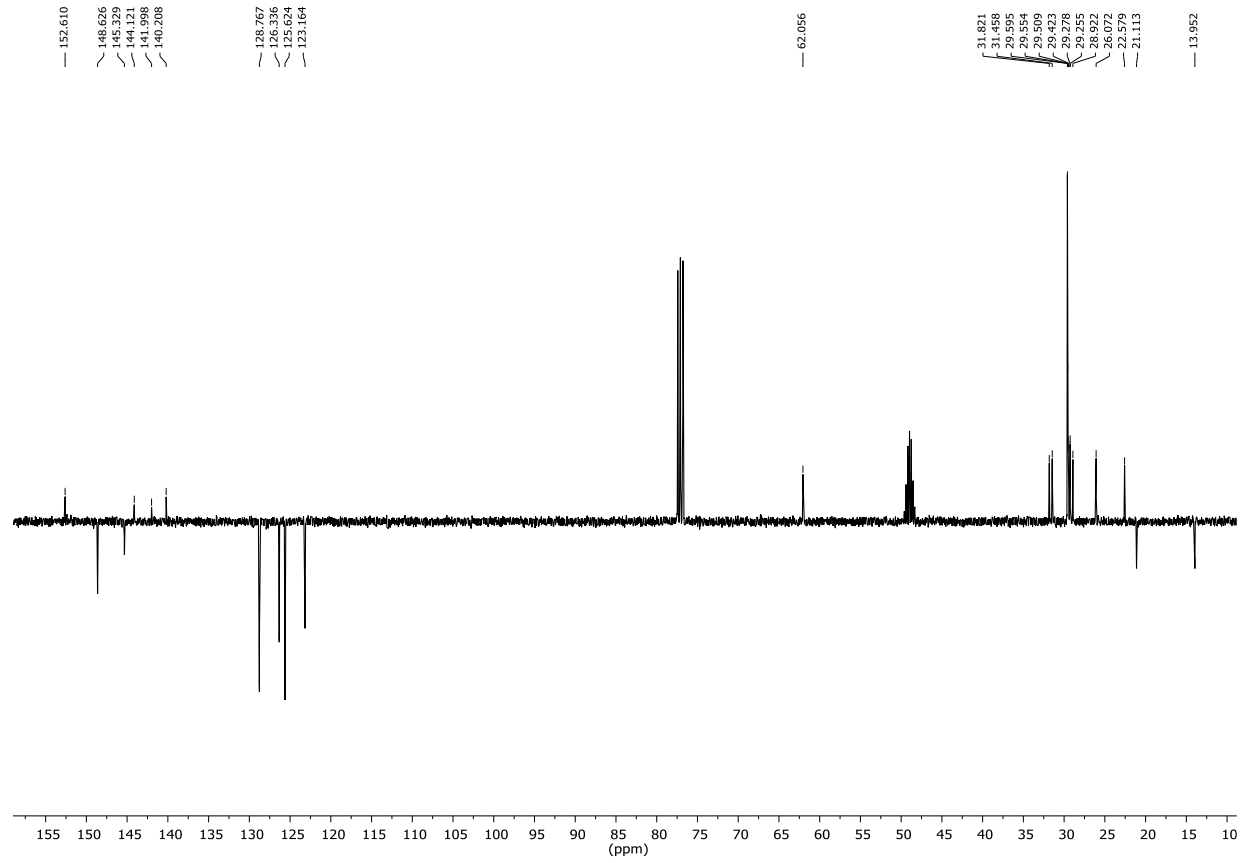

Figure S2. APT-^{13}C NMR spectrum (100 MHz, $CDCl_3$/MeOD) of **PpyC18**$^{+}$.

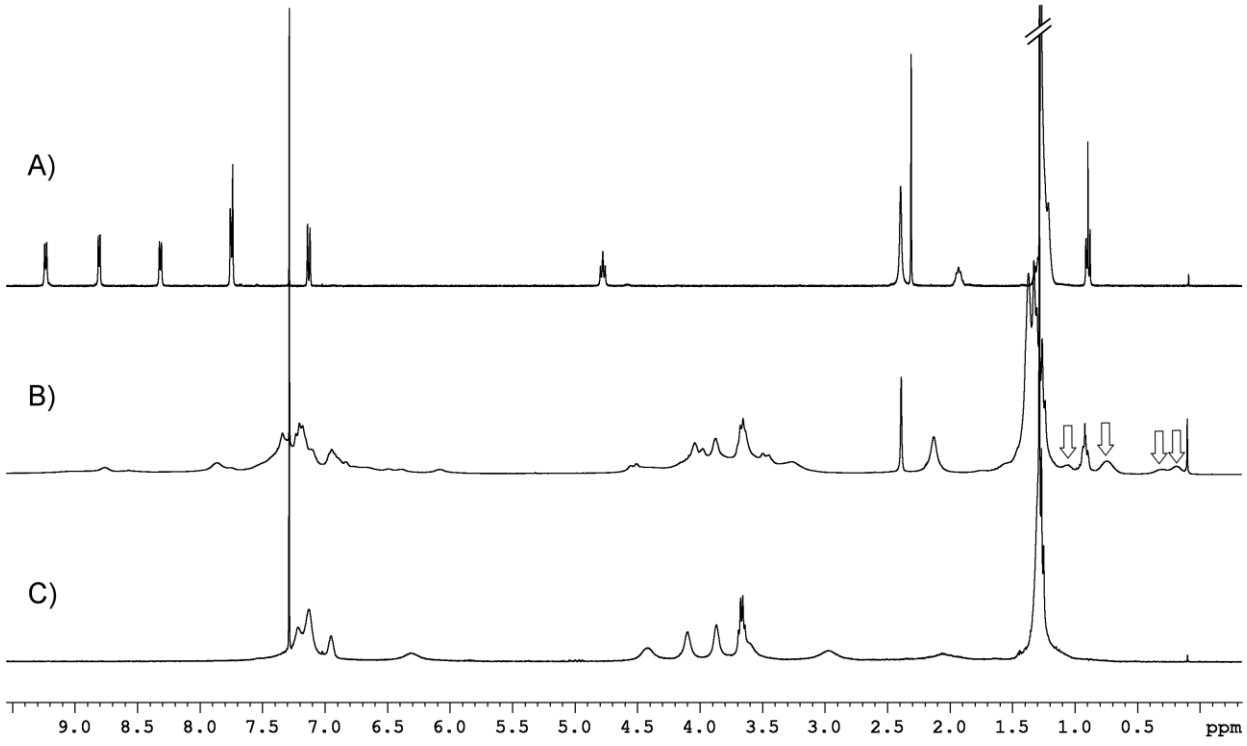

Figure S3. ^{1}H NMR stack plot ($CDCl_3$, 400 MHz, T = 296 K) of the spectra relative to: A) **PpyC18**$^{+}$; B) **PuCxEtE** and C) of their 1:1 mixture (white arrows indicate some signals of the pyridylpyridinium C18 alkyl chain which were upfield shifted upon complexation).

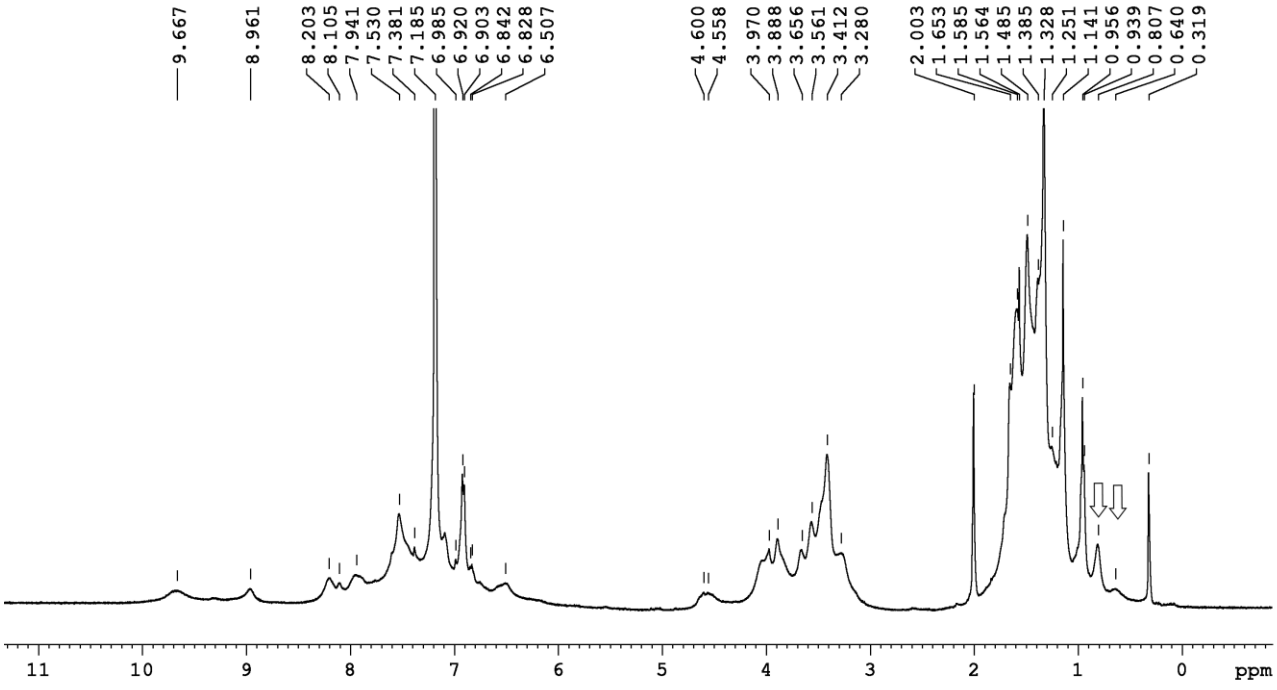

Figure S4. ^{1}H NMR spectrum in C_6D_6 (400 MHz) of the 1:1 **PuCxEtE**/**PpyC18**$^{+}$ mixture (white arrows indicate some upfield-shifted guest signals).

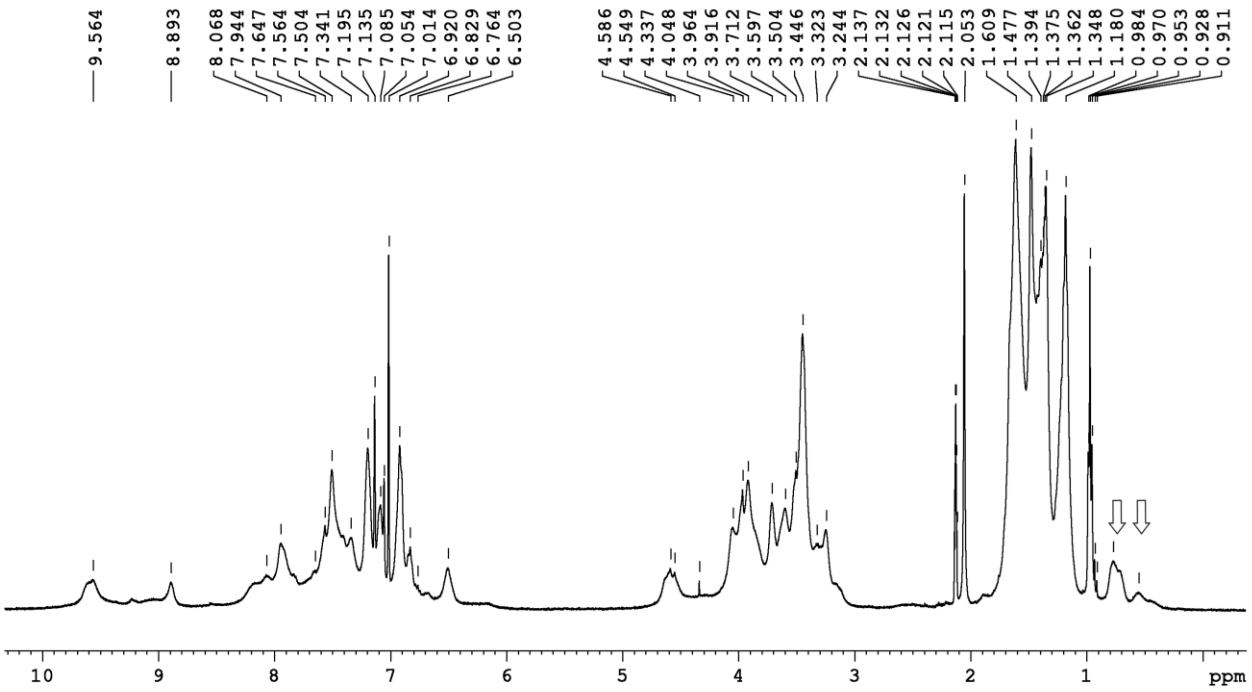

Figure S5. ^{1}H NMR spectrum in toluene[D8] (400 MHz) of the 1:1 **PuCxEtE**/**PpyC18**$^{+}$ mixture (white arrows indicate some upfield-shifted guest signals).

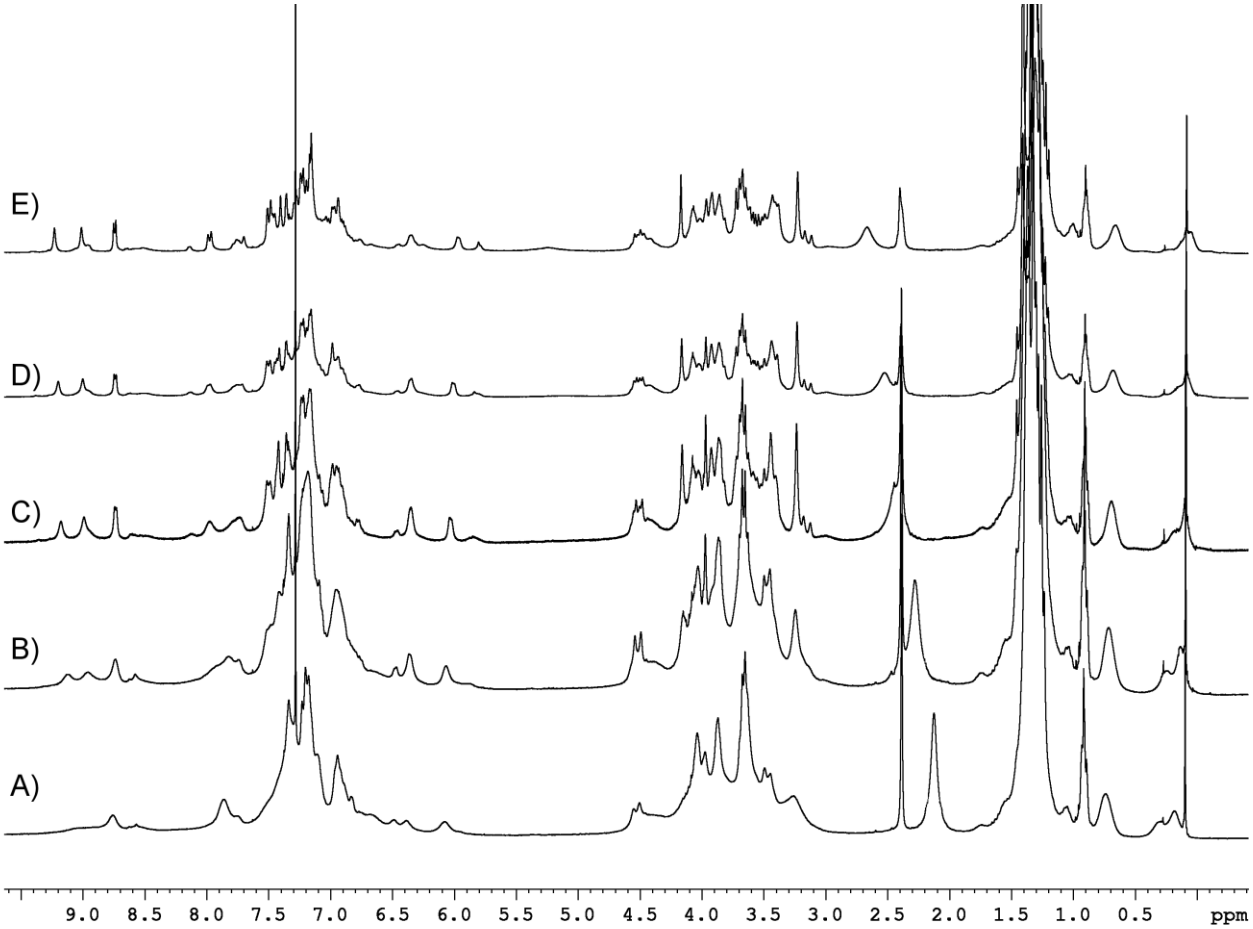

Figure S6. Variable temperature ^{1}H NMR stack plot ($CDCl_3$, 400 MHz) of the 1:1 **PuCxEtE**/**PpyC18**$^{+}$ mixture: A) T = 296 K; B) T = 283 K; C) T = 273 K; D) T = 268 K; and E) T = 253 K.

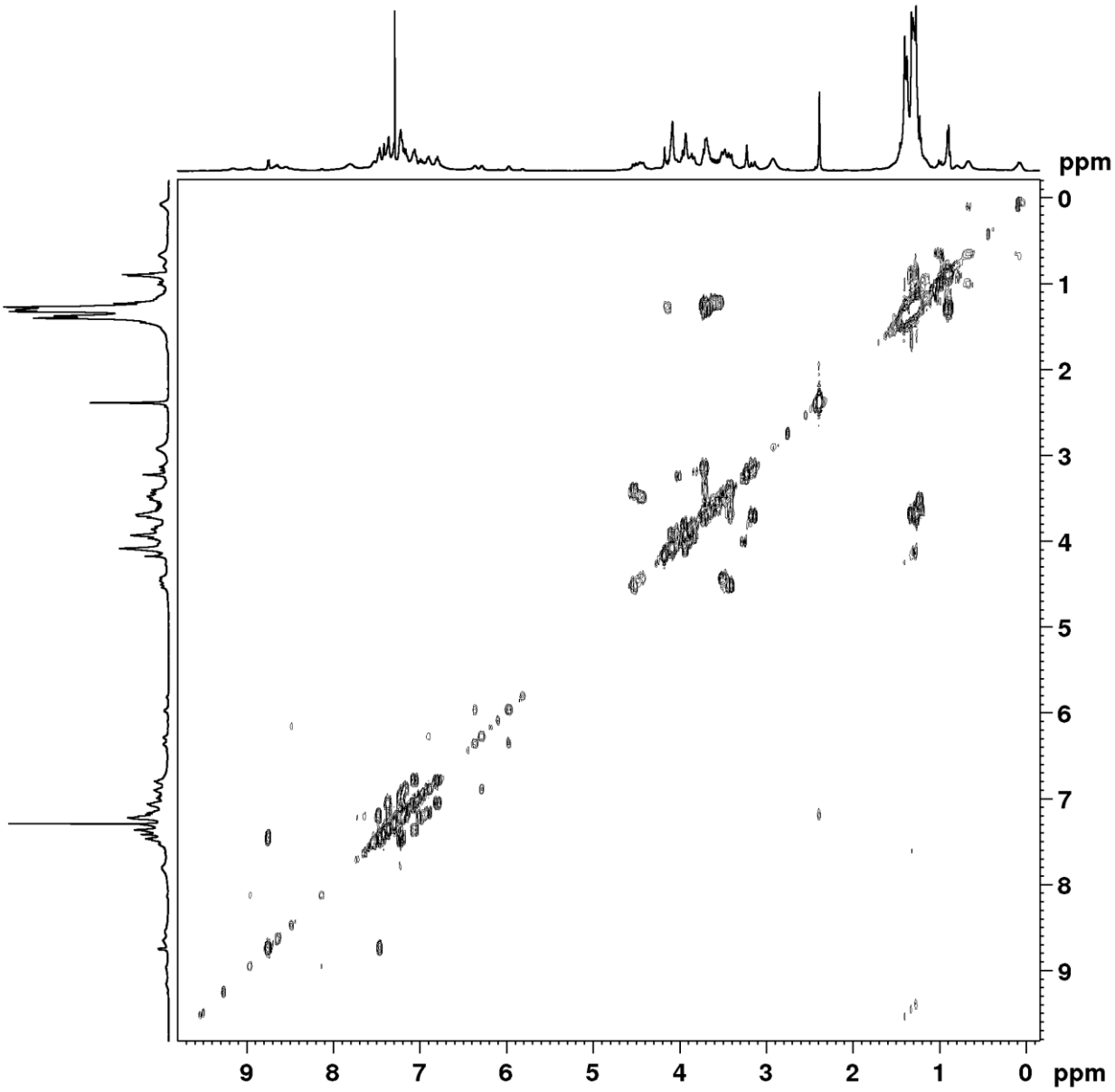

Figure S7. COSY-90 NMR spectrum (400 MHz, $CDCl_3$, T = 253 K) of the 1:1 **PuCxEtE**/**PpyC18**$^+$ mixture.

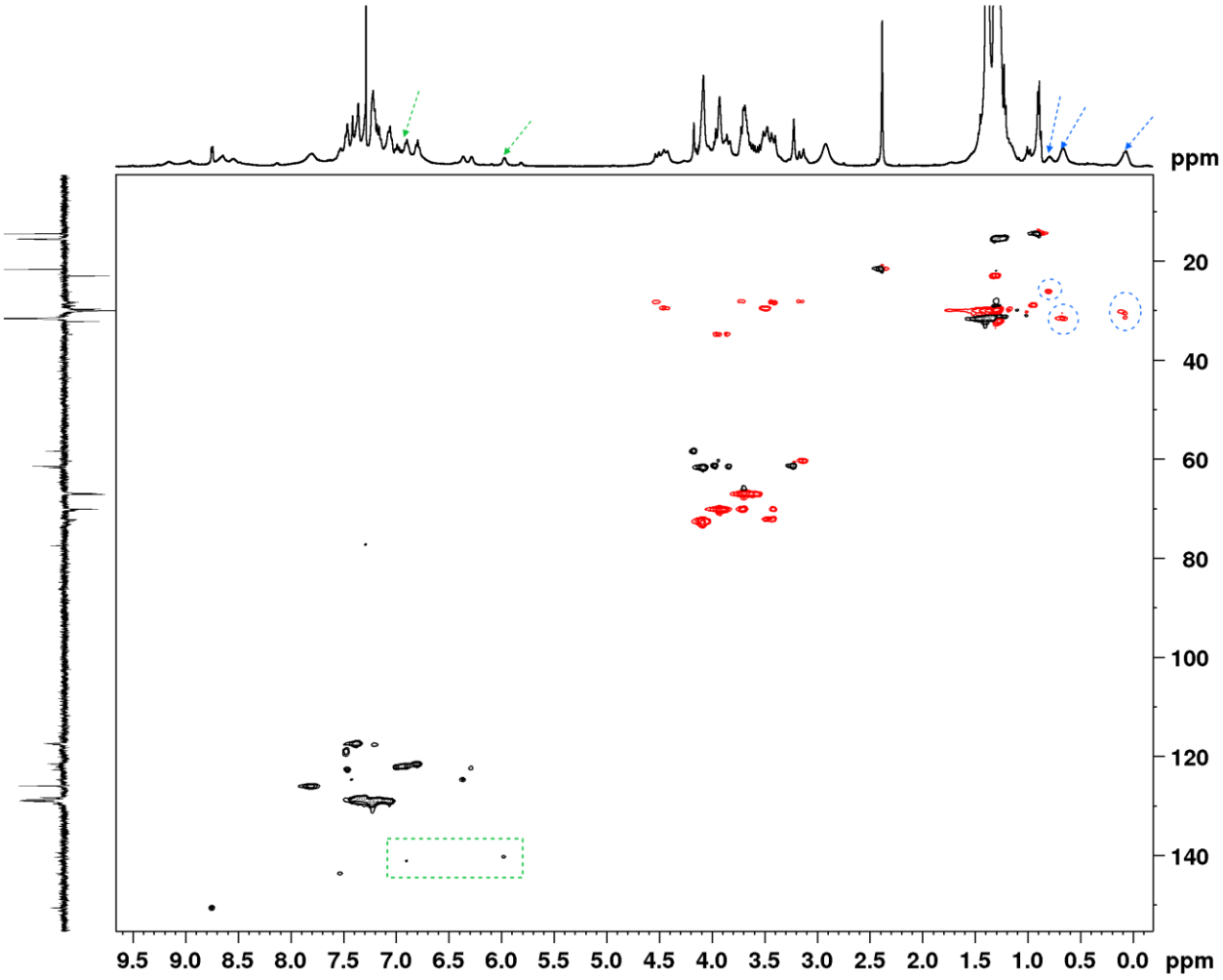

Figure S8. Edited HSQC NMR spectrum (400 MHz, $CDCl_3$, T = 253 K) of the 1:1 **PuCxEtE**/**PpyC18**$^+$ mixture (cross-peaks relative to CH_2 carbons are indicated in red). The blue dashed arrows and circles indicated the methylene groups of the octadecyl chain of **PpyC18**$^+$ which are upfield-shifted upon complexation with **PuCxEt**. Similarly, the green arrows and the rectangle indicate the aromatic signal of the pyridinium ring of **PpyC18**$^+$ deeply embedded and shielded by the aromatic calix[6]arene cavity.

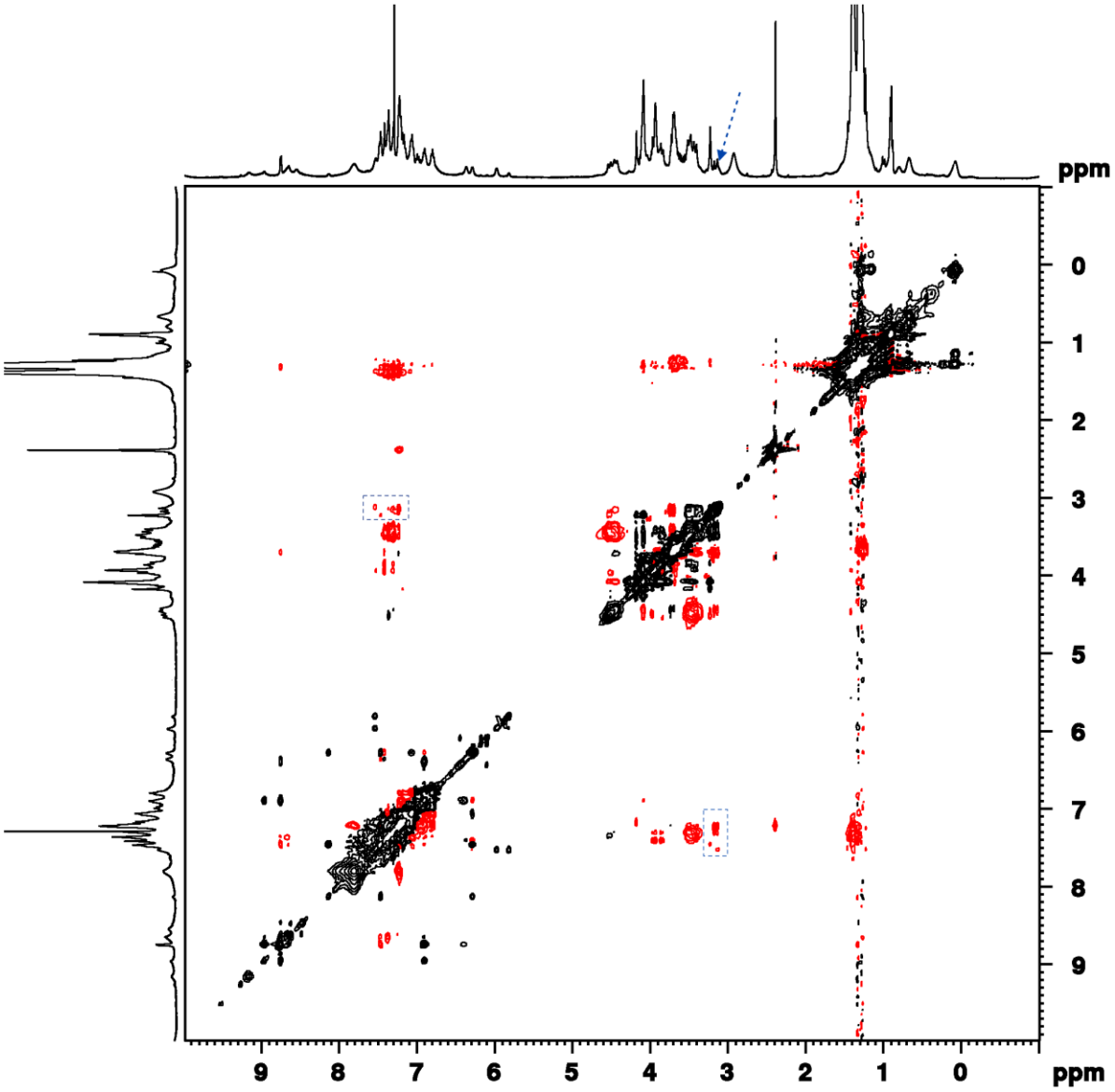

Figure S9. ROESY NMR spectrum (400 MHz, $CDCl_3$, *T* = 253 K, ROESY spin-lock = 200 ms) of the 1:1 **PuCxEtE**/**PpyC18**$^+$ mixture (cross-peaks relative to CH_2 carbons are indicated in red). The two dashed boxes indicate the spatial correlation between the -C*H*$_2$-N$^+$ methylene protons (blue arrow) of **PpyC18**$^+$ and several aromatic protons of the calix[6]arene cavity. The black spots are TOCSY artifacts.

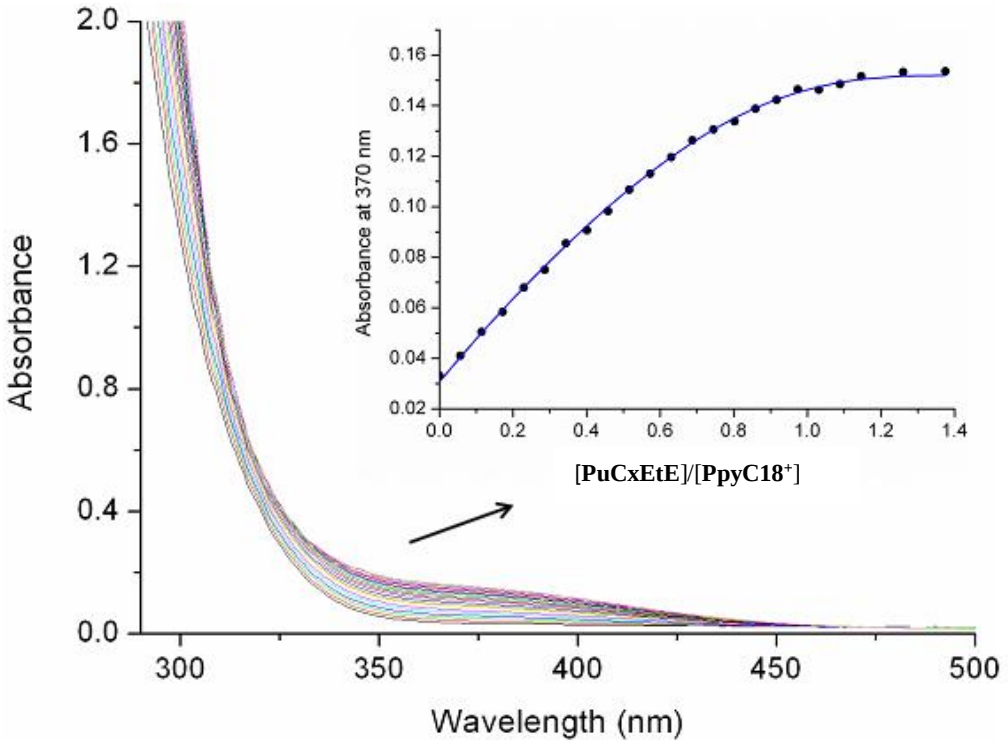

Figure S10. Collection of absorption spectra obtained during the titration of a 2.4×10^{-4} M toluene solution of **PpyC18**$^{+}$ with **PuCxEt**. The titration experiment was carried out at T = 333 K for solubility reasons. Inset: fitting of the absorbance at 370 nm.

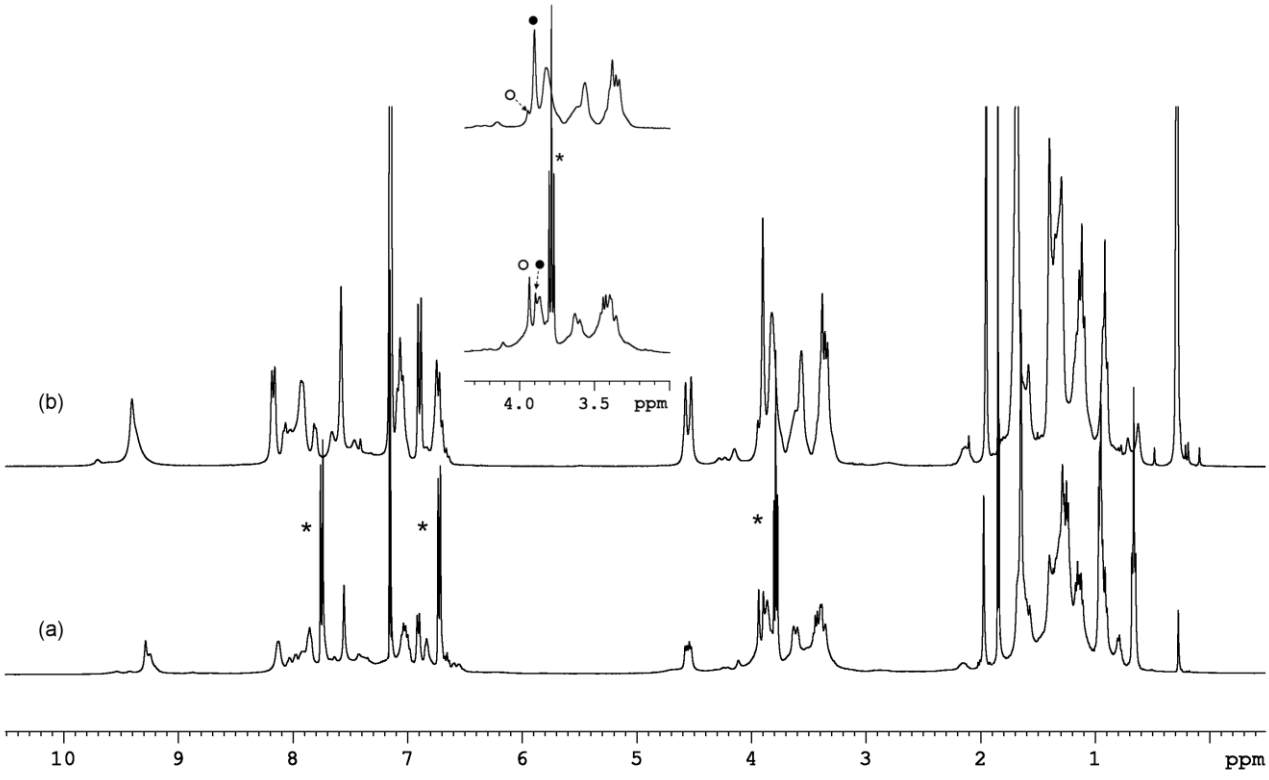

Figure S11. ^{1}H NMR spectrum (400 MHz, C_6D_6) of (a) the outcome of experiment ***A*** (t = 24 h), and (b) of the orientational pseudorotaxane isomer [**PuCxEt⊃C$_{18}$BpyC$_5$**]$^{2+}$ reported for comparison. Inset: expansion of 3.0-4.4 ppm region where the resonances of the calix[6]arene methoxy groups in the two orientational isomers [**PuCxEt⊃C$_5$BpyC$_{18}$**]$^{2+}$ and [**PuCxEt⊃C$_{18}$BpyC$_5$**]$^{2+}$ have been highlighted with white and black circles, respectively. Several resonances of free **1a** are indicated with asterisks.

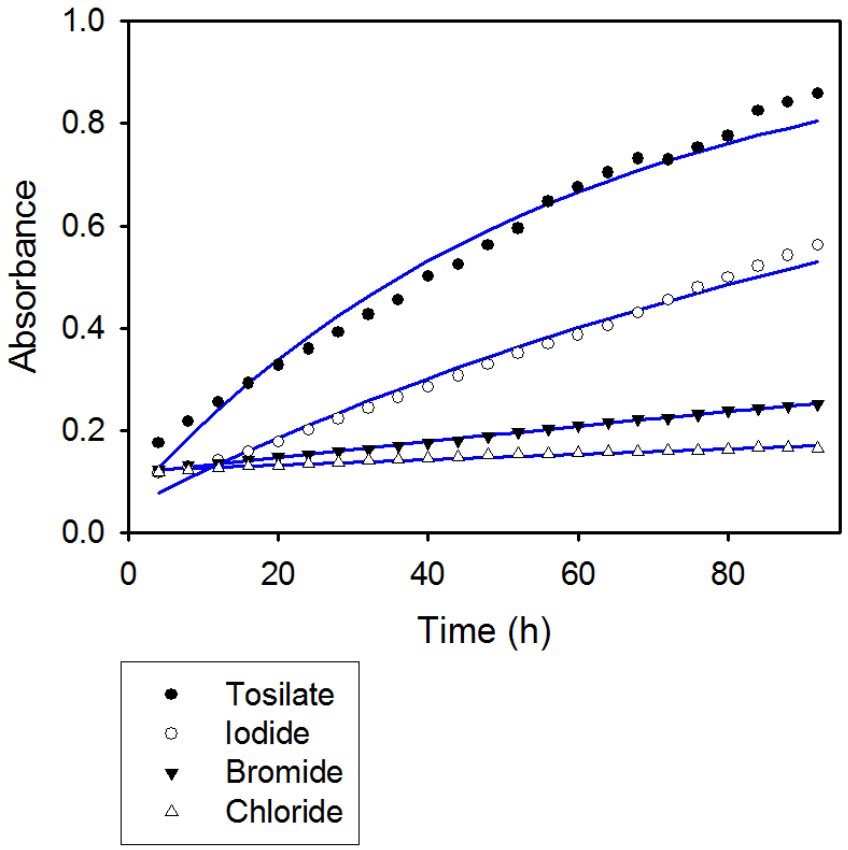

Figure S12. Fitting of the absorbance data at λ = 370 nm for experiment ***A*** performed with **1a-d**.

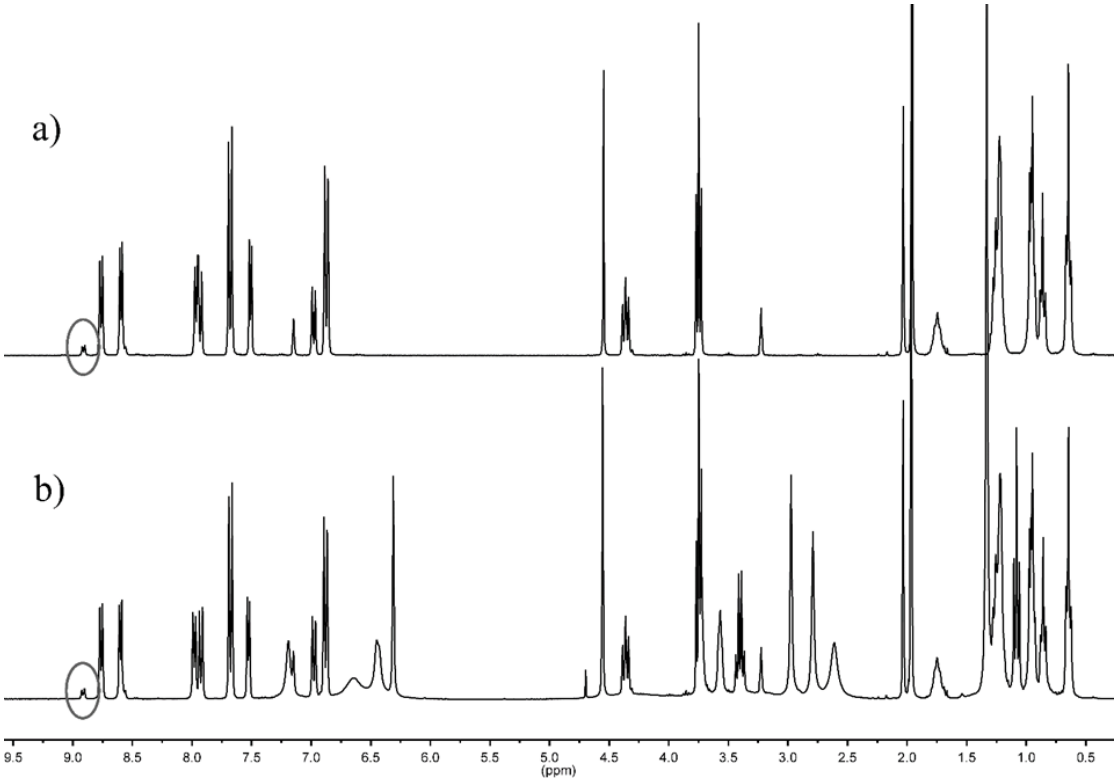

Figure S13. ^{1}H NMR spectra (C_6D_6/CD_3OD = 95:5, 400 MHz) of the reaction mixtures obtained from experiments *B* (a) and *C* (b). The negligible amount of **C5BpyC18**$^{2+}$ in solution is evidenced by the small encircled doublet at very low fields (ca. 8.9 ppm) relative to the ortho aromatic protons (deuterated methanol was added to the benzene solution to assure the complete solubility of the formed salt).

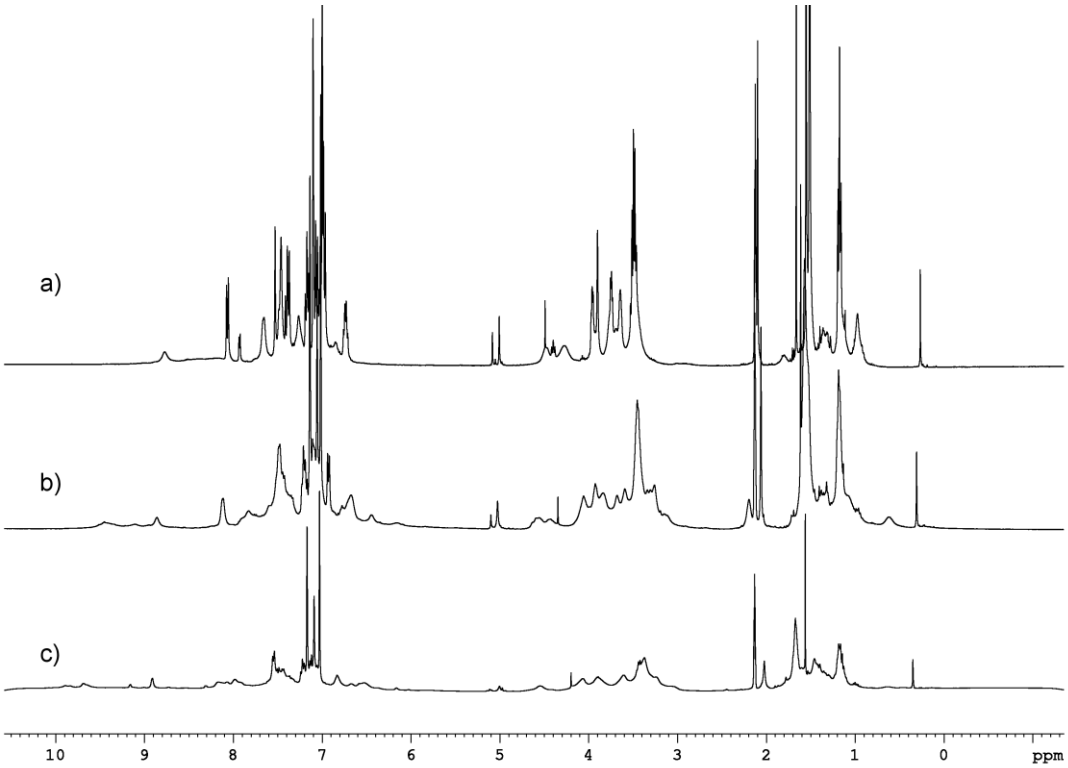

Figure S14. ^{1}H NMR spectra (400 MHz, toluene-d8) of the mixture of the orientational pseudorotaxane isomers [**PuCxEt⊃PpyC$_6$S**]$^+$ and [**PuCxEt⊃SC$_6$Ppy**]$^+$ at a) 353 K, b) 295 K and c) 253 K.

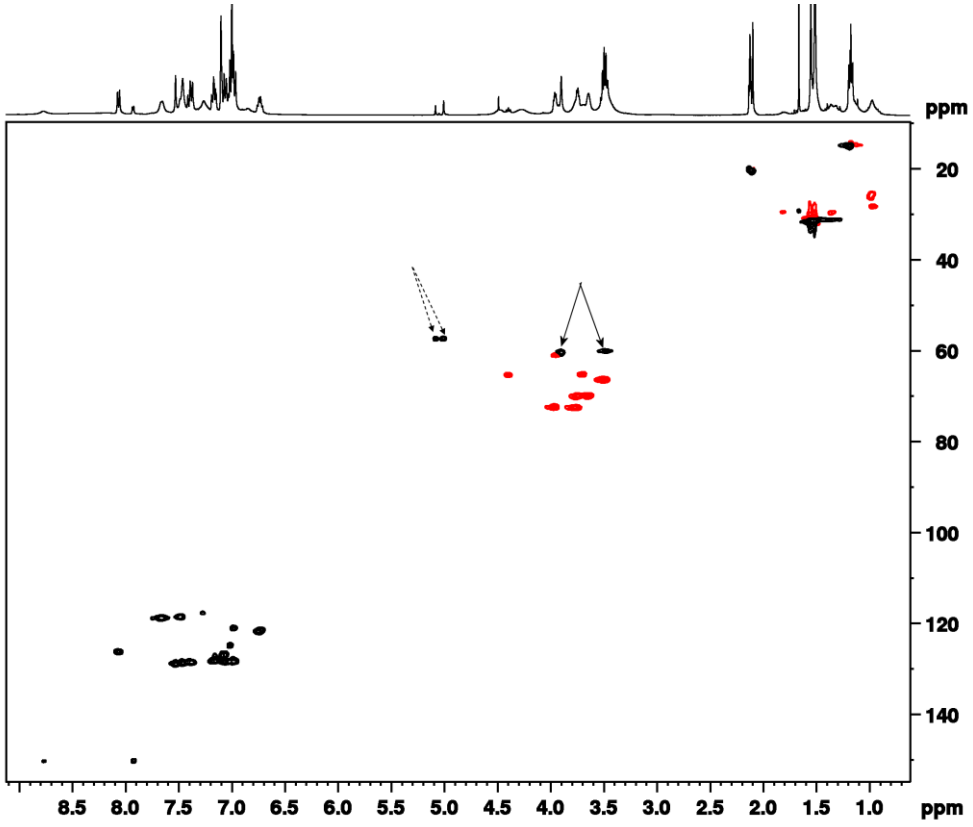

Figure S15. Edited HSQC NMR spectrum (400 MHz, toluene-d8) of the mixture of the orientational pseudorotaxane isomers [**PuCxEt⊃PpyC$_6$S**]$^+$ and [**PuCxEt⊃SC$_6$Ppy**]$^+$ at T = 353 K. The methyl and methyne carbons are indicated with black cross-peaks: the dashed arrows identify the diphenylacetyl methyne carbons of the stopper, while the plain arrows the methoxy carbons of the calix[6]arene wheel.

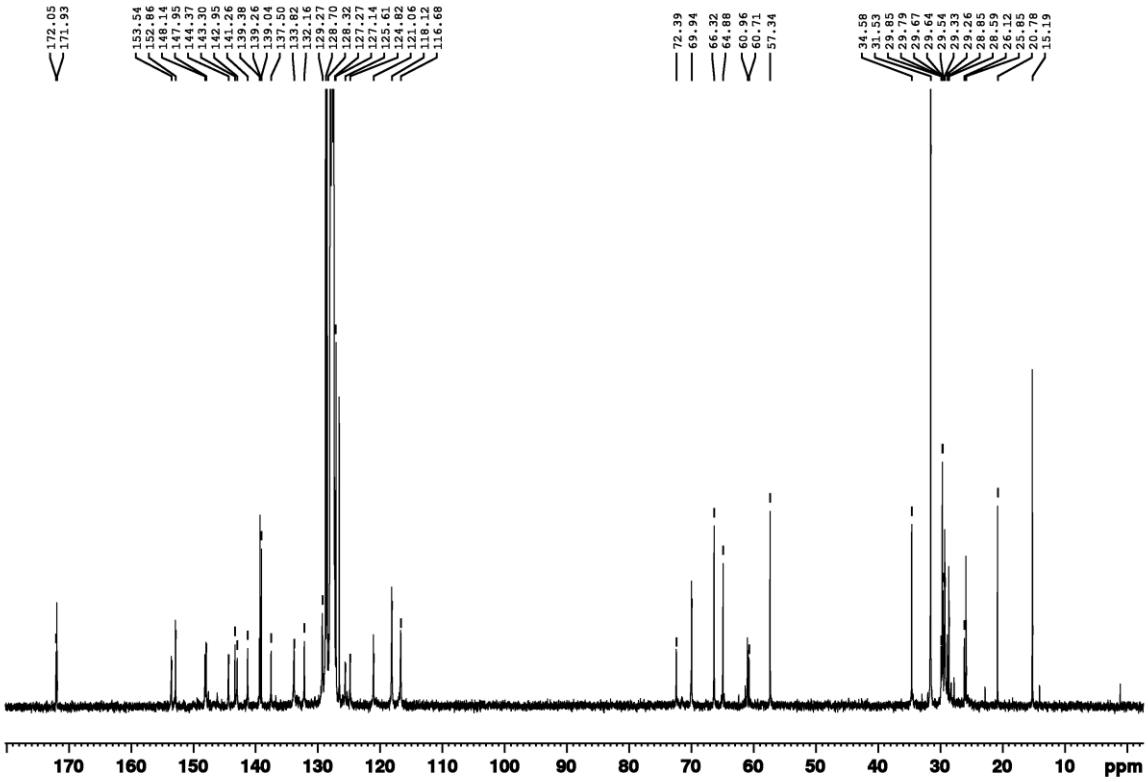

Figure S16. ^{13}C NMR spectrum (100 MHz, C_6D_6) of rotaxane [**PuCxEt•SC$_{12}$BpyC$_6$S**]$^{2+}$.

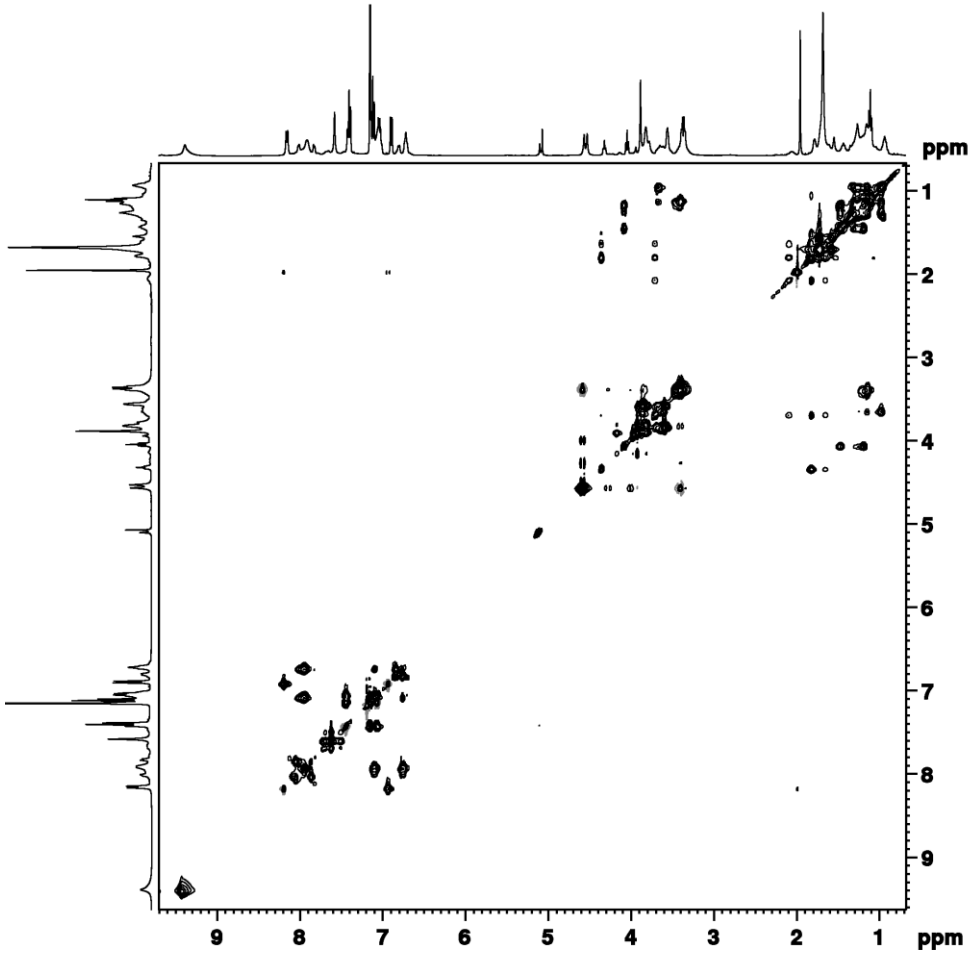

Figure S17. TOCSY NMR spectrum (400 MHz, C_6D_6) of rotaxane [**PuCxEt•SC$_{12}$BpyC$_6$S**]$^{2+}$.

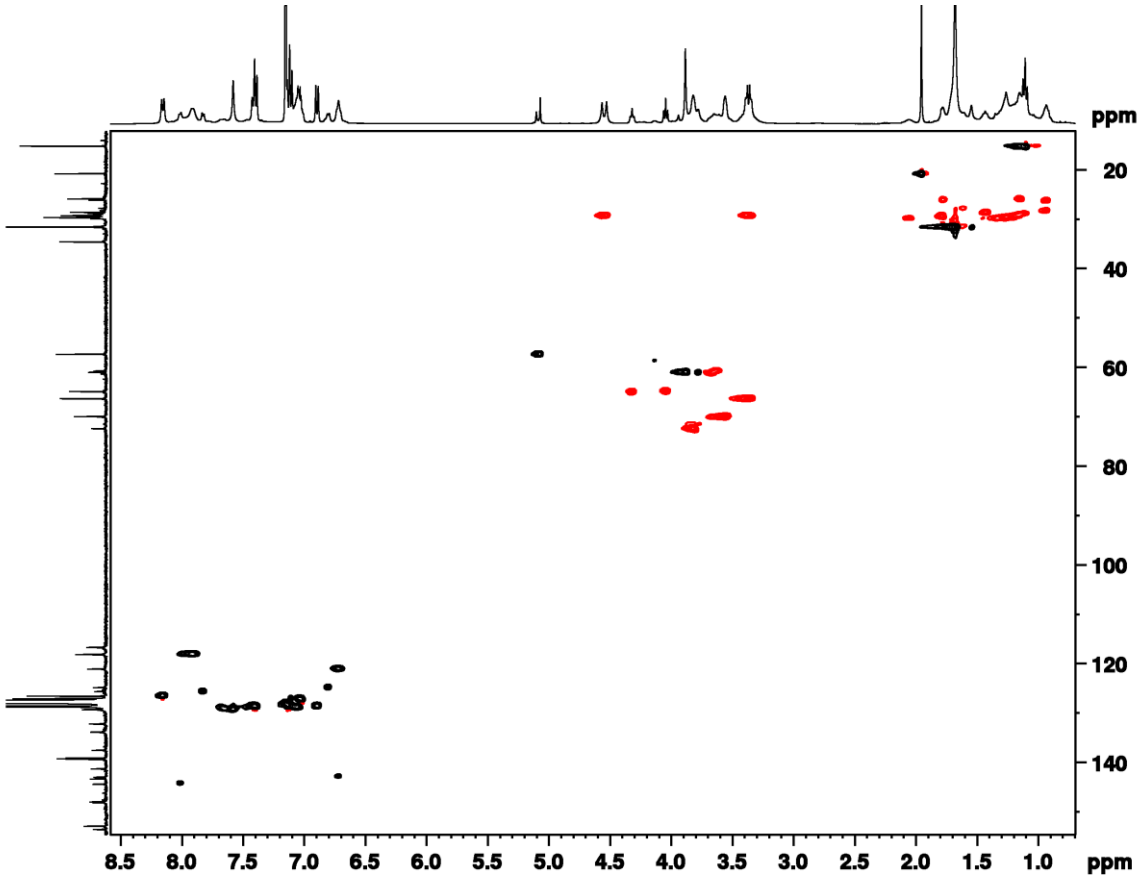

Figure S18. Edited HSQC NMR spectrum (400 MHz, C_6D_6) of rotaxane [**PuCxEt•SC$_{12}$BpyC$_6$S**]$^{2+}$

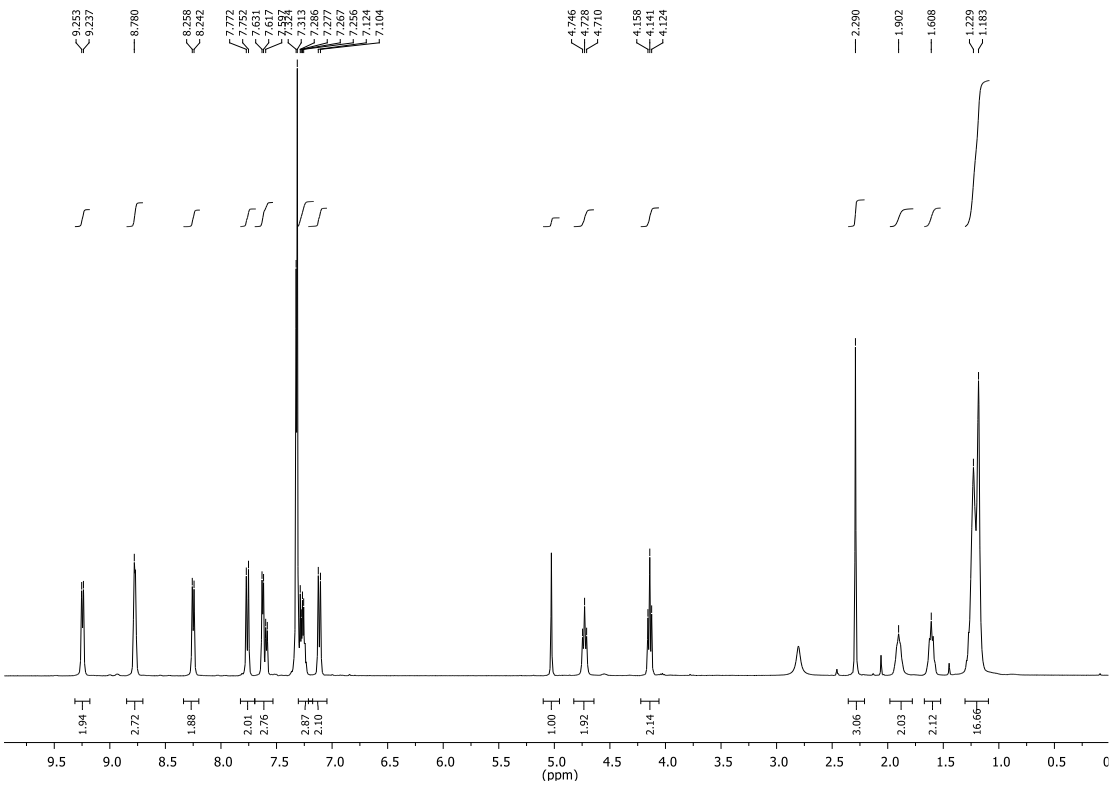

Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **PpyC$_{12}$S$^+$**.

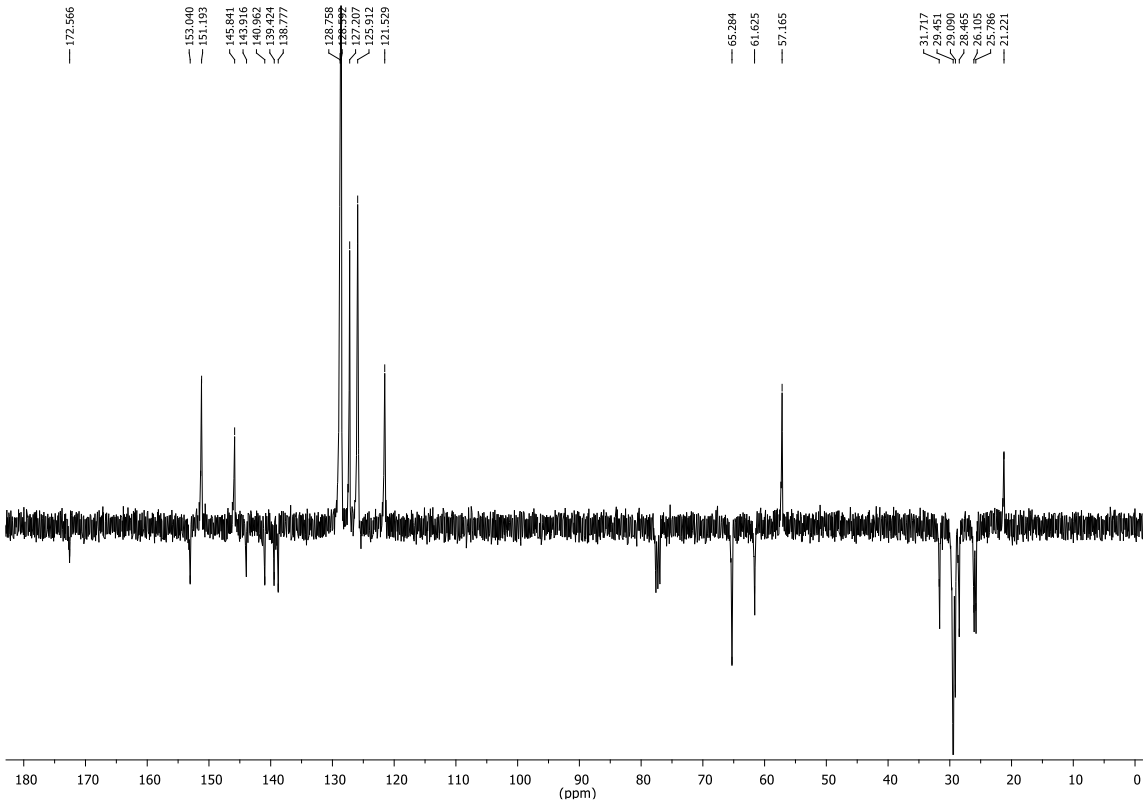

Figure S20. ^{13}C APT NMR spectrum (100 MHz, $CDCl_3$) of **PpyC$_{12}$S$^+$**.

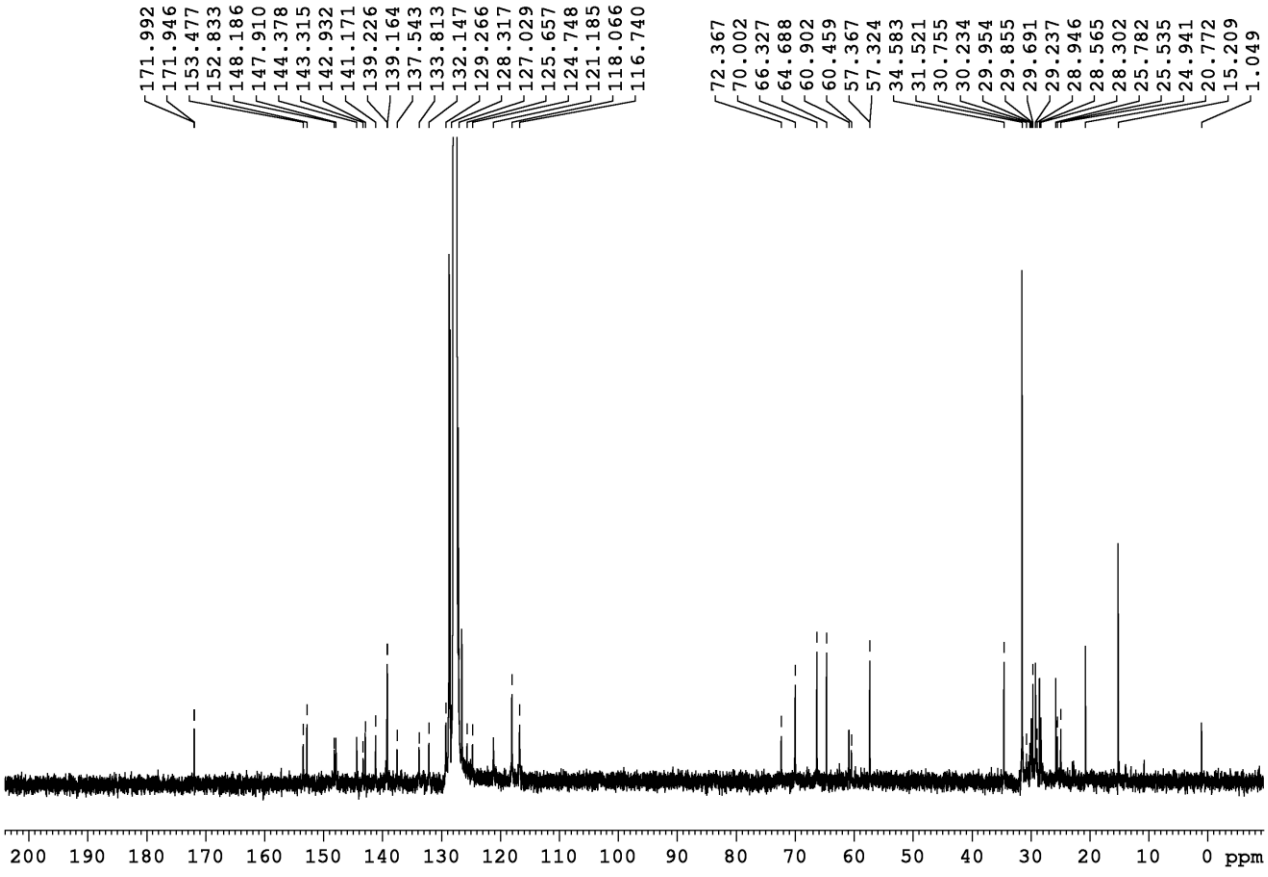

Figure S21. ^{13}C NMR spectrum (100 MHz, C_6D_6) of rotaxane [**PuCxEt•SC$_6$BpyC$_{12}$S**]$^{2+}$.

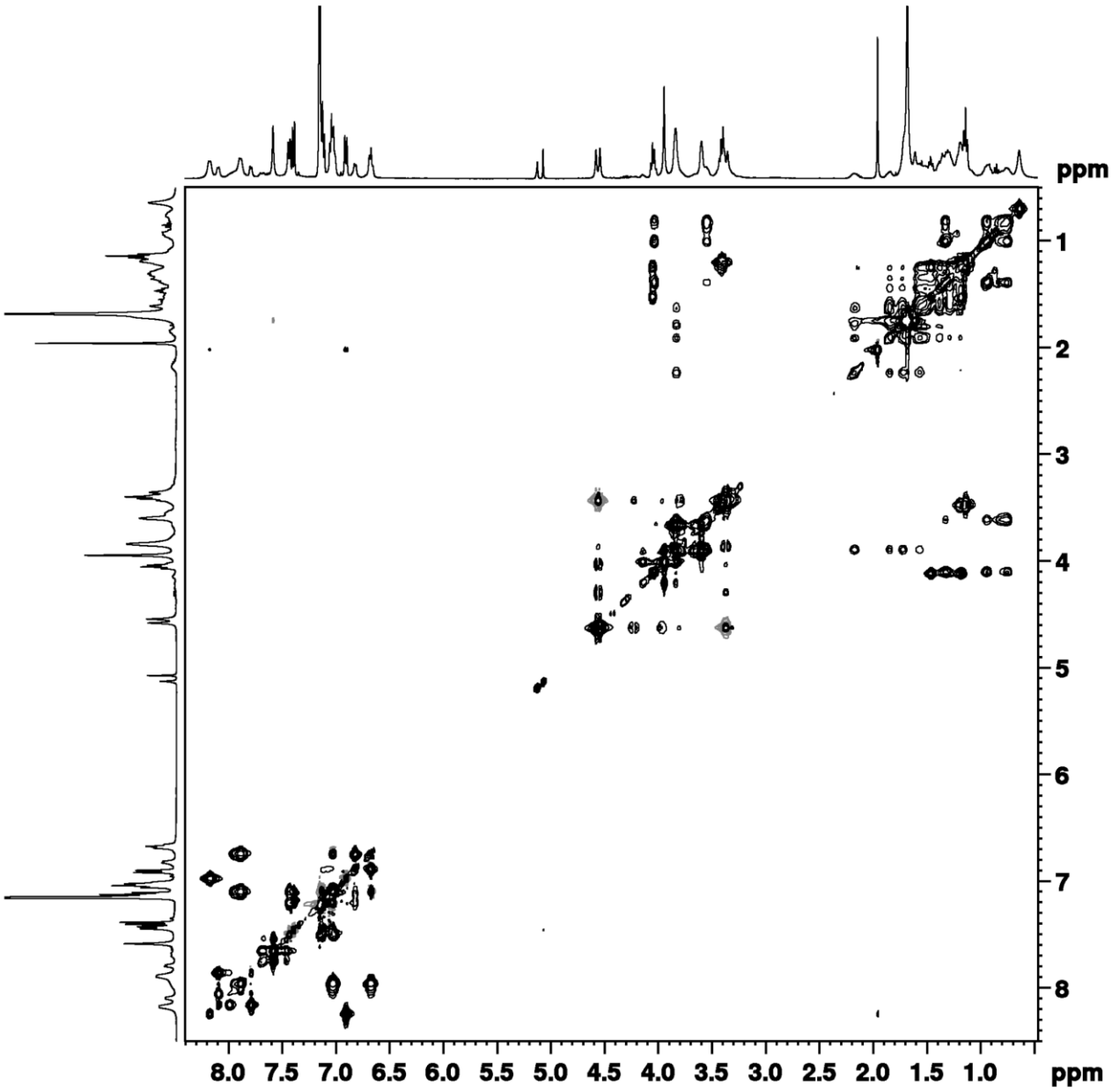

Figure S22. TOCSY NMR spectrum (400 MHz, C_6D_6) of rotaxane [**PuCxEt•SC$_6$BpyC$_{12}$S**]$^{2+}$.

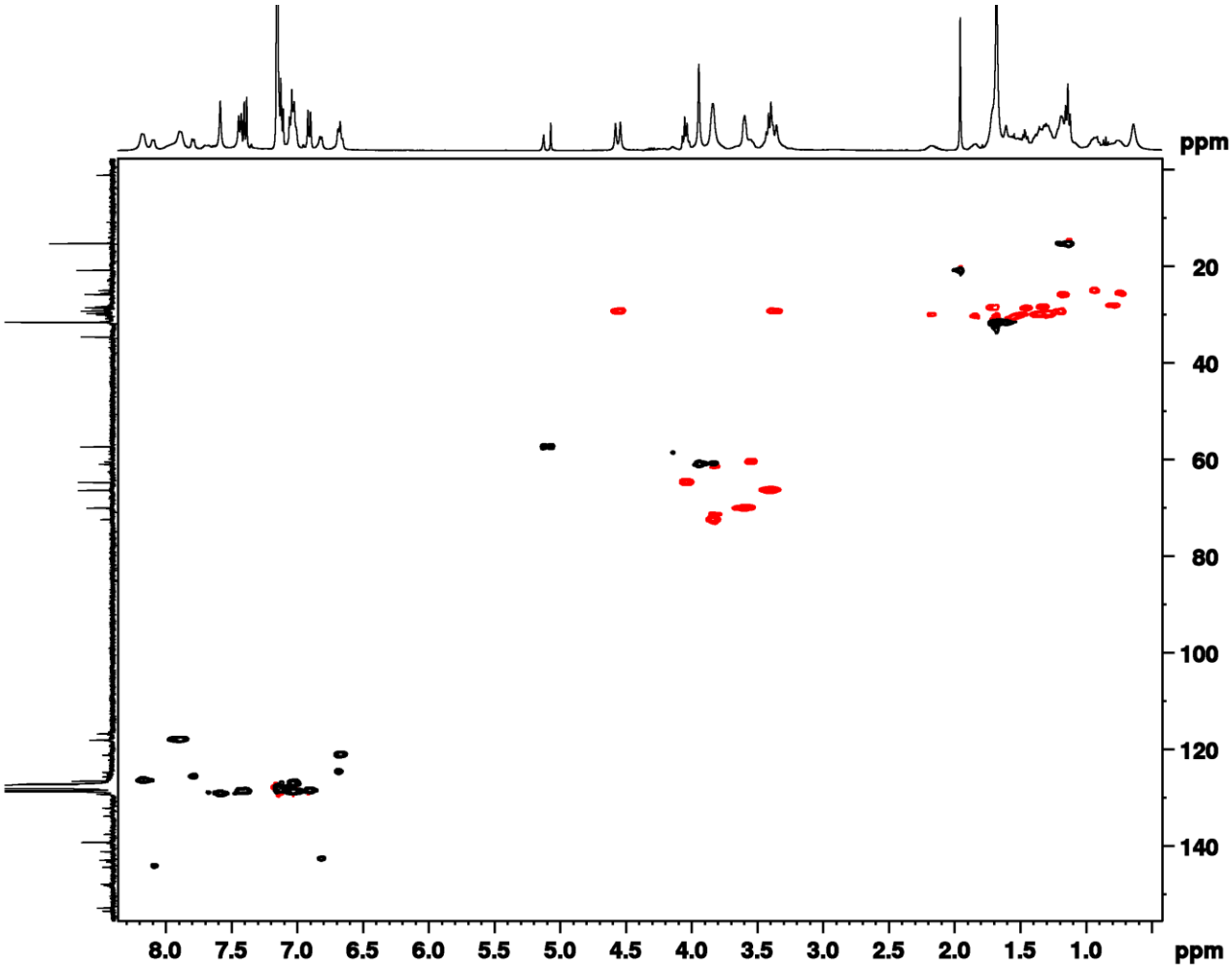

Figure S23. Edited HSQC NMR spectrum (400 MHz, C_6D_6) of rotaxane [**PuCxEt•SC$_6$BpyC$_{12}$S**]$^{2+}$.

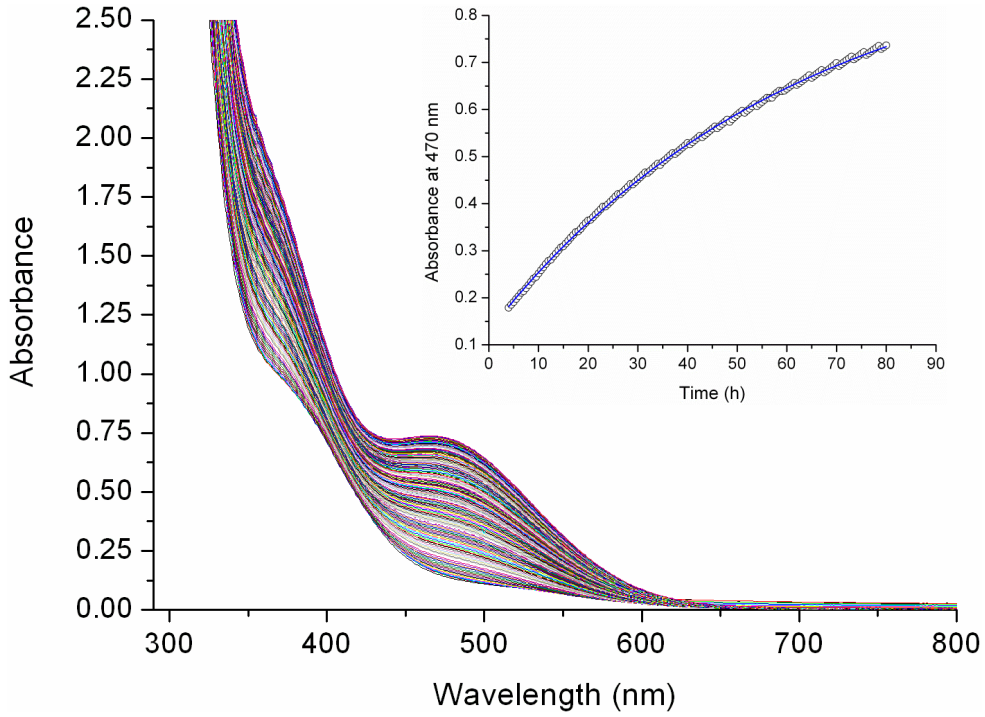

Figure S24. Collection of absorption spectra obtained following the reaction of **PpyC$_{18}^{+}$** with **1a** in the presence of **PuCxEt**. Conditions: toluene, 333 K. Inset: absorption changes at 470 nm (open circles) and fitting of the data points (solid line) according to a S_N2 mechanism.

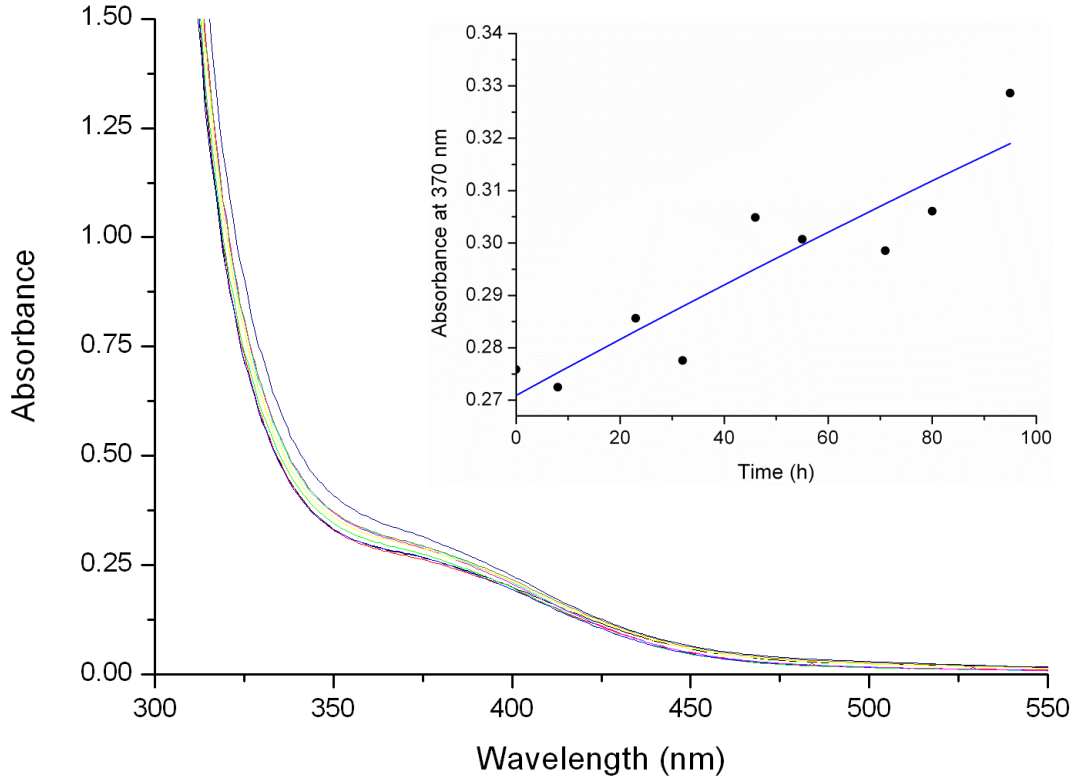

Figure S25. Collection of absorption spectra obtained following the reaction of **PpyC$_{18}^{+}$** with **1a** in the absence of **PuCxEt**. The spectra were obtained by adding a stoichiometric amount of **PuCxEt** to the reaction mixture at different and progressive times. Conditions: toluene, 333 K. Inset: absorption changes at 370 nm (circles) and fitting of the data points (solid line) according to a S_N2 mechanism.