

Electrochemically triggered co-conformational switching in a [2]catenane comprising a non-symmetric calix[6]arene wheel and a two-station oriented macrocycle

Valeria Zanichelli¹, Luca Dallacasagrande¹, Arturo Arduini¹, Andrea Secchi^{1,*}, Giulio Ragazzon^{2,3}, Serena Silvi^{2,4} and Alberto Credi^{4,5,6,*}

¹ Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy. andrea.secchi@unipr.it

² Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126, Italy.

³ Current address: Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova, Italy.

⁴ Center for Light Activated Nanostructures (CLAN), Università di Bologna and Consiglio Nazionale delle Ricerche, via Gobetti 101, 40129 Bologna, Italy. alberto.credi@unibo.it

⁵ Dipartimento di Scienze e Tecnologie Agro-alimentari, Università di Bologna, viale Fanin 50, 40127 Bologna, Italy.

⁶ Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche, via Gobetti 101, 40129 Bologna, Italy.

Supplementary Material

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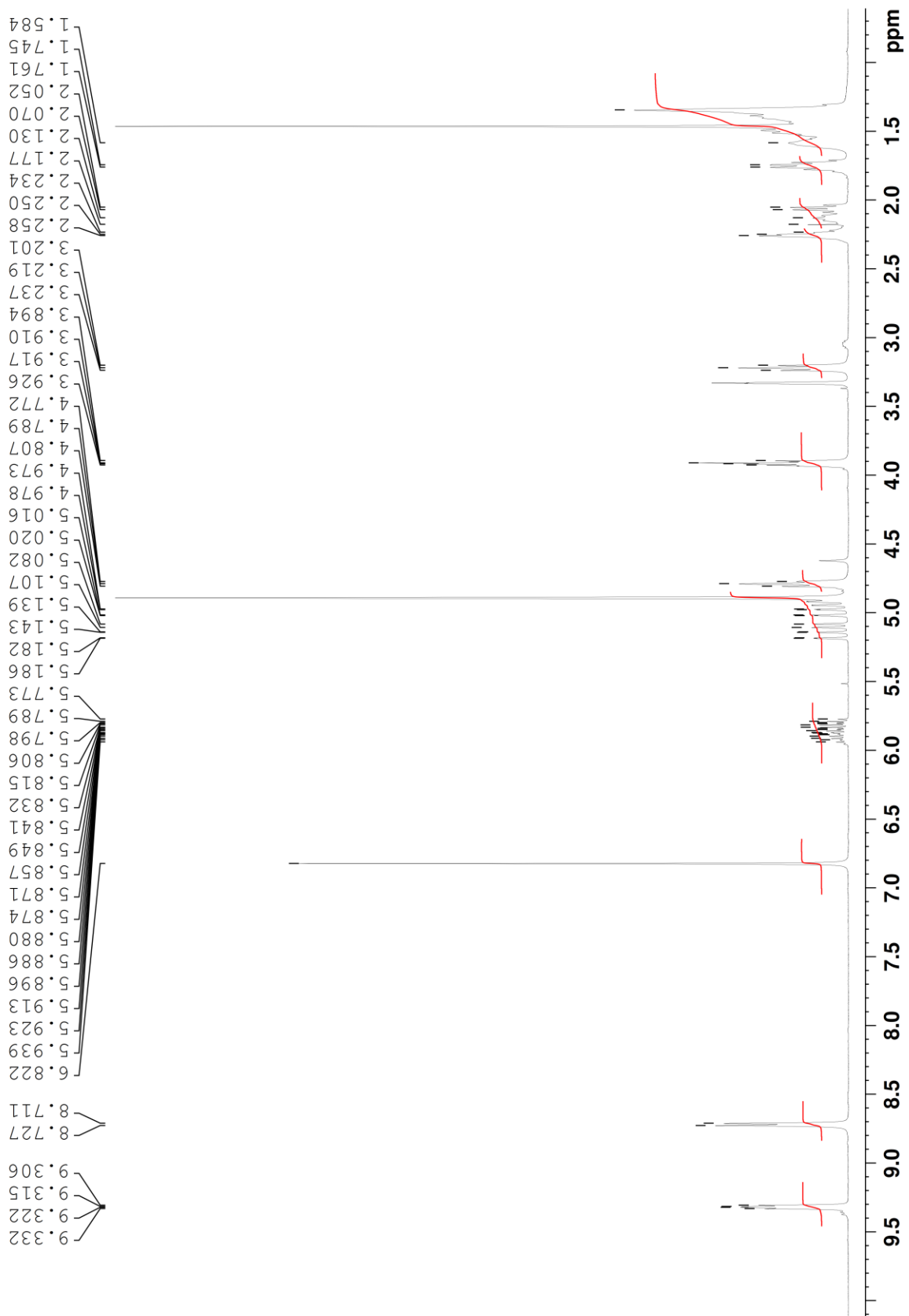


Figure S1. ^1H NMR spectrum (300 MHz, CD_3OD) of axle **9**.

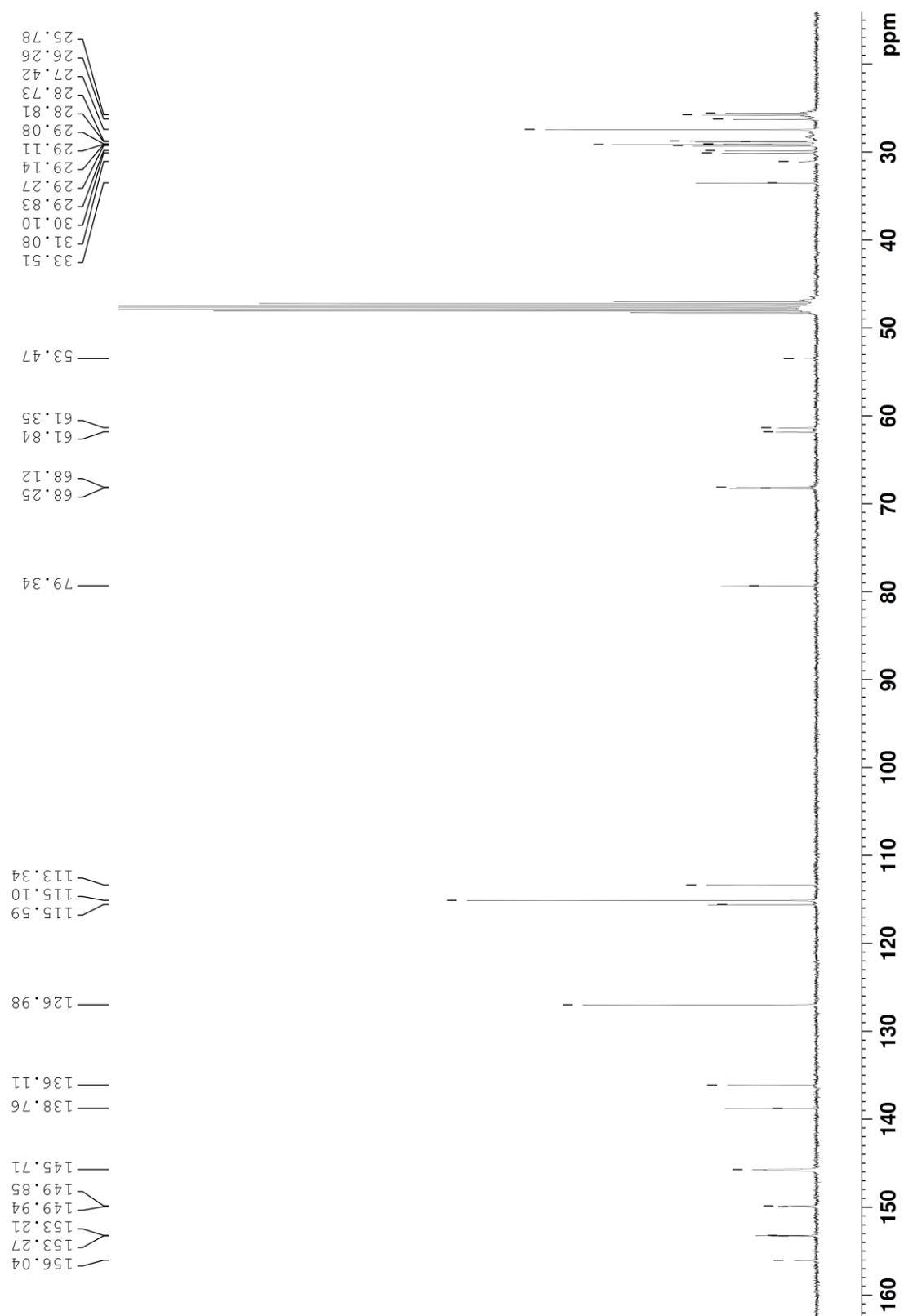


Figure S2. ^{13}C NMR spectrum (100 MHz, CD_3OD) of axle 9.

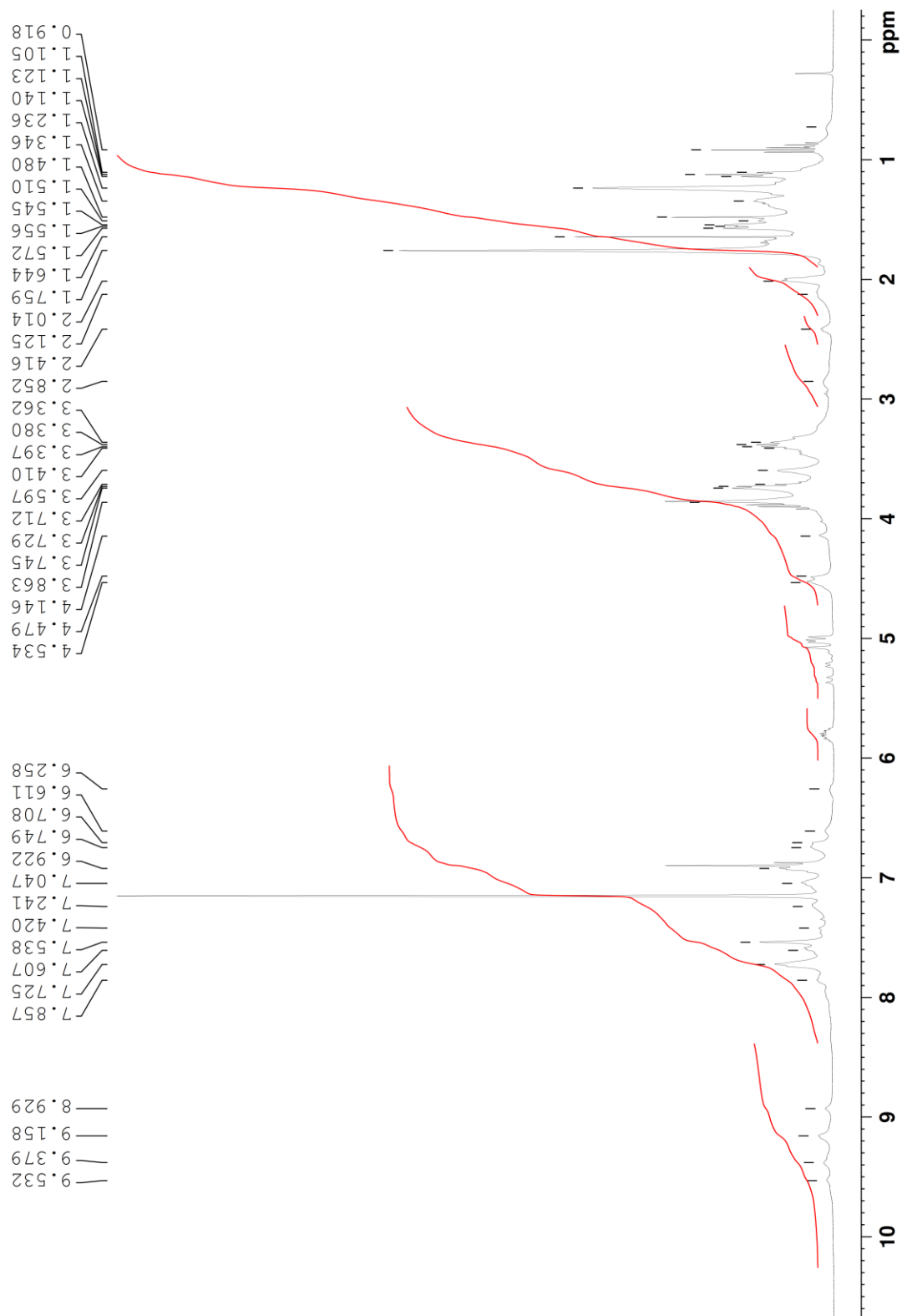


Figure S3. ^1H NMR spectrum (400 MHz, C_6D_6) of pseudorotaxane $[1-9]_{up}$.

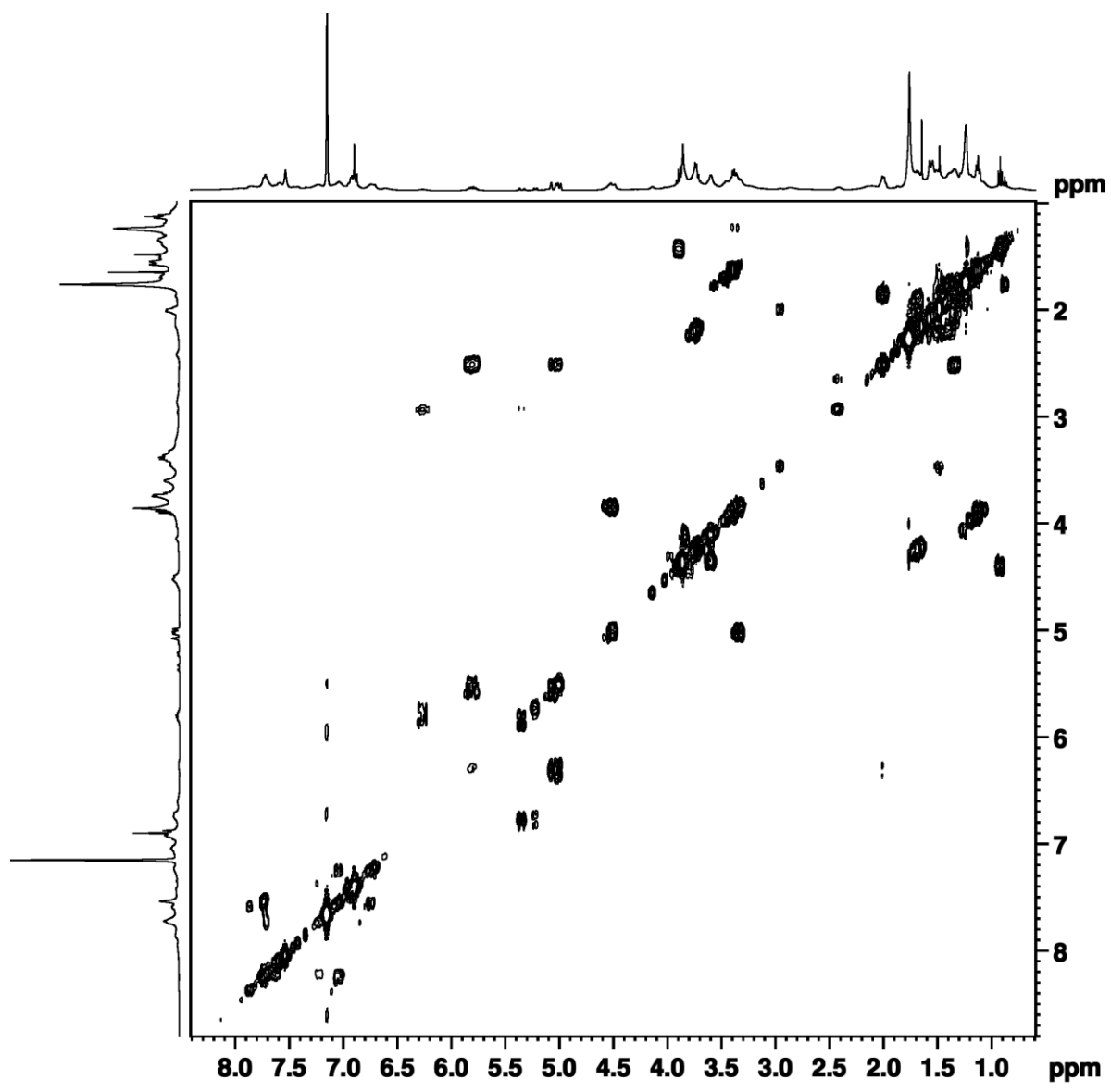


Figure S4. 2D COSY (top) spectrum (400 MHz, C₆D₆) of pseudorotaxane [1-9]_{up}

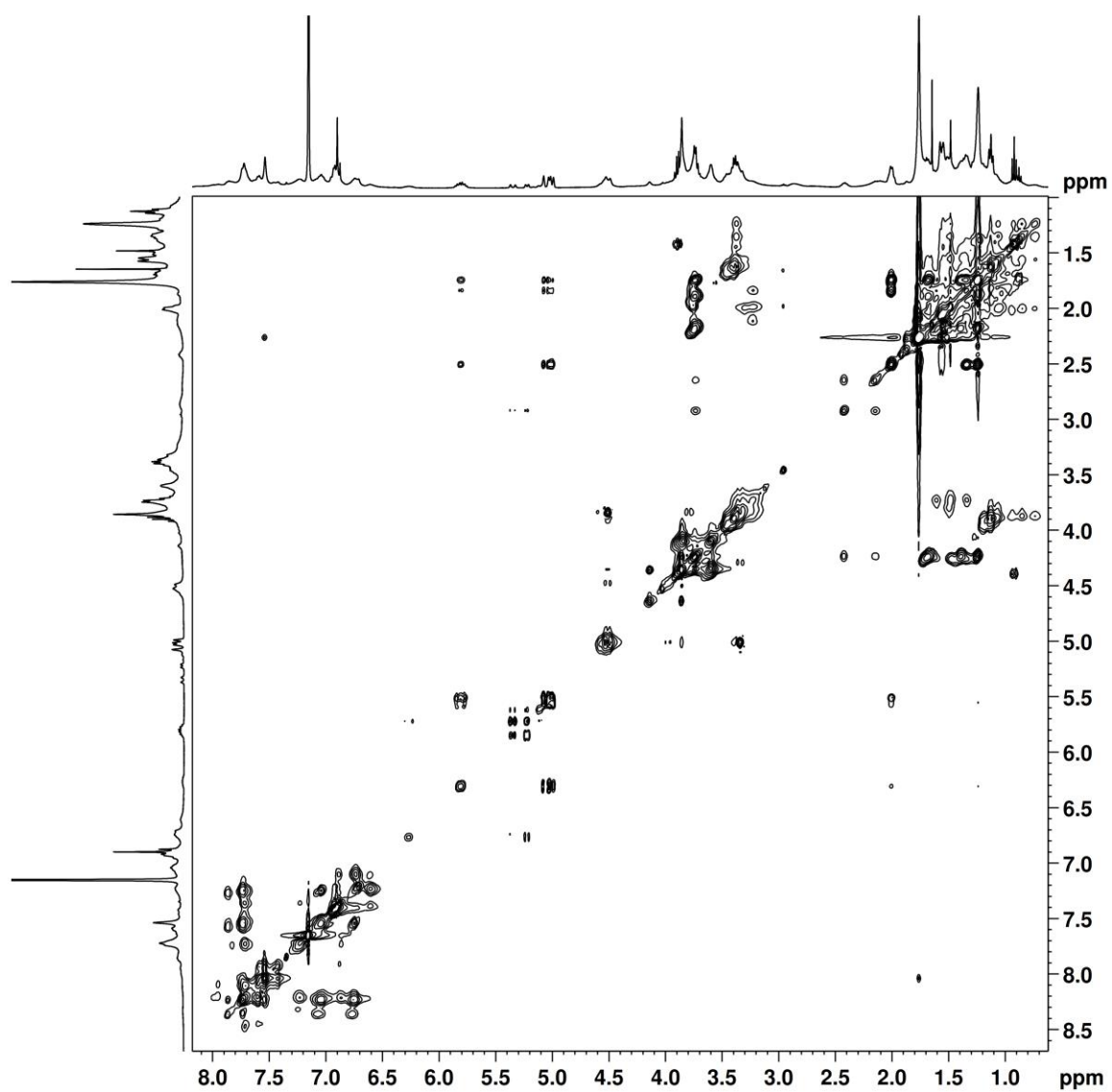


Figure S5. 2D TOCSY (MT = 0.08 s) spectrum (400 MHz, C₆D₆) of pseudorotaxane [1-9]_{up}.

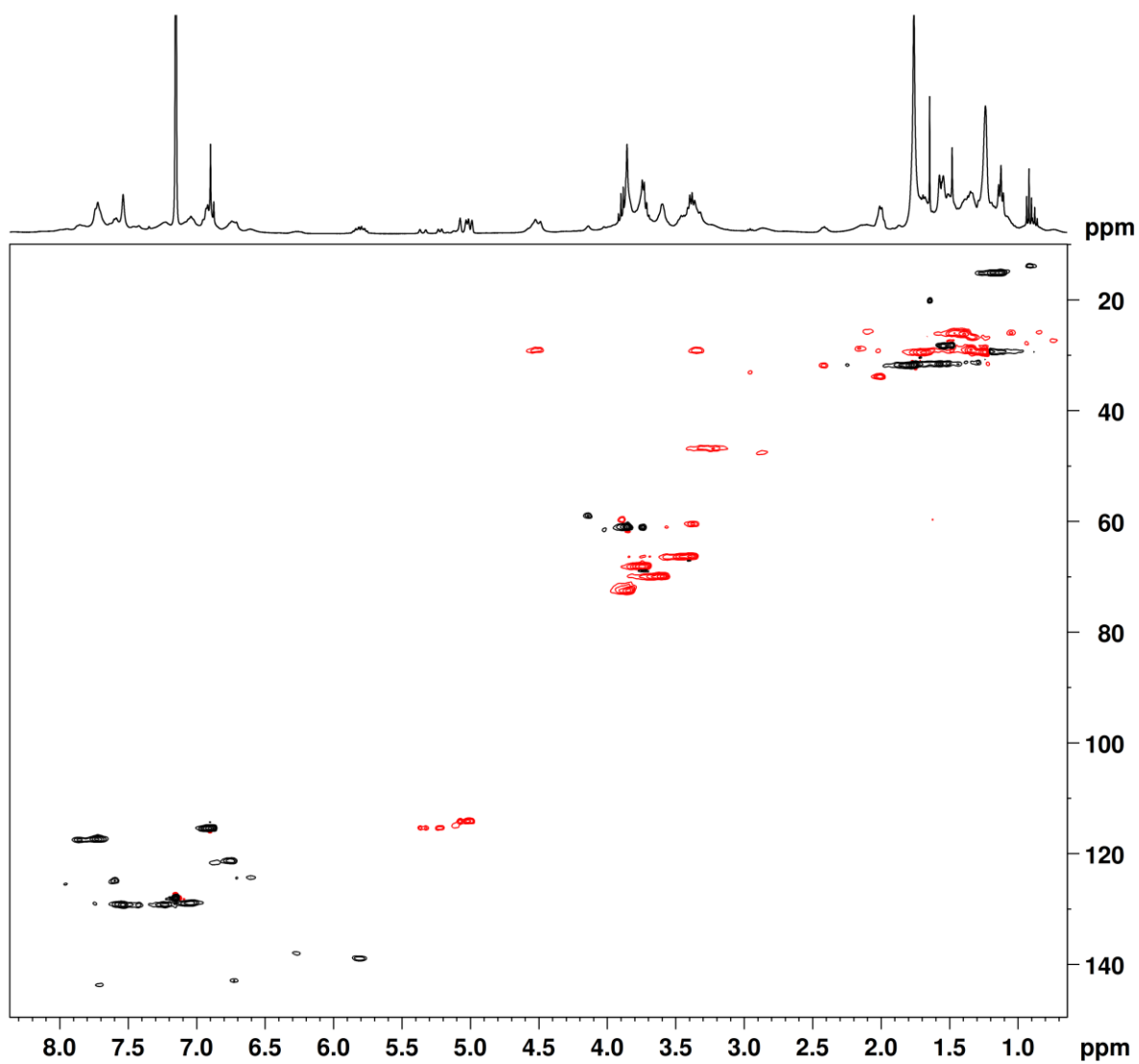


Figure S6. Edited 2D HSQC spectrum (400 MHz, C_6D_6) of pseudorotaxane $[\mathbf{1}\rightarrow\mathbf{9}]_{up}$

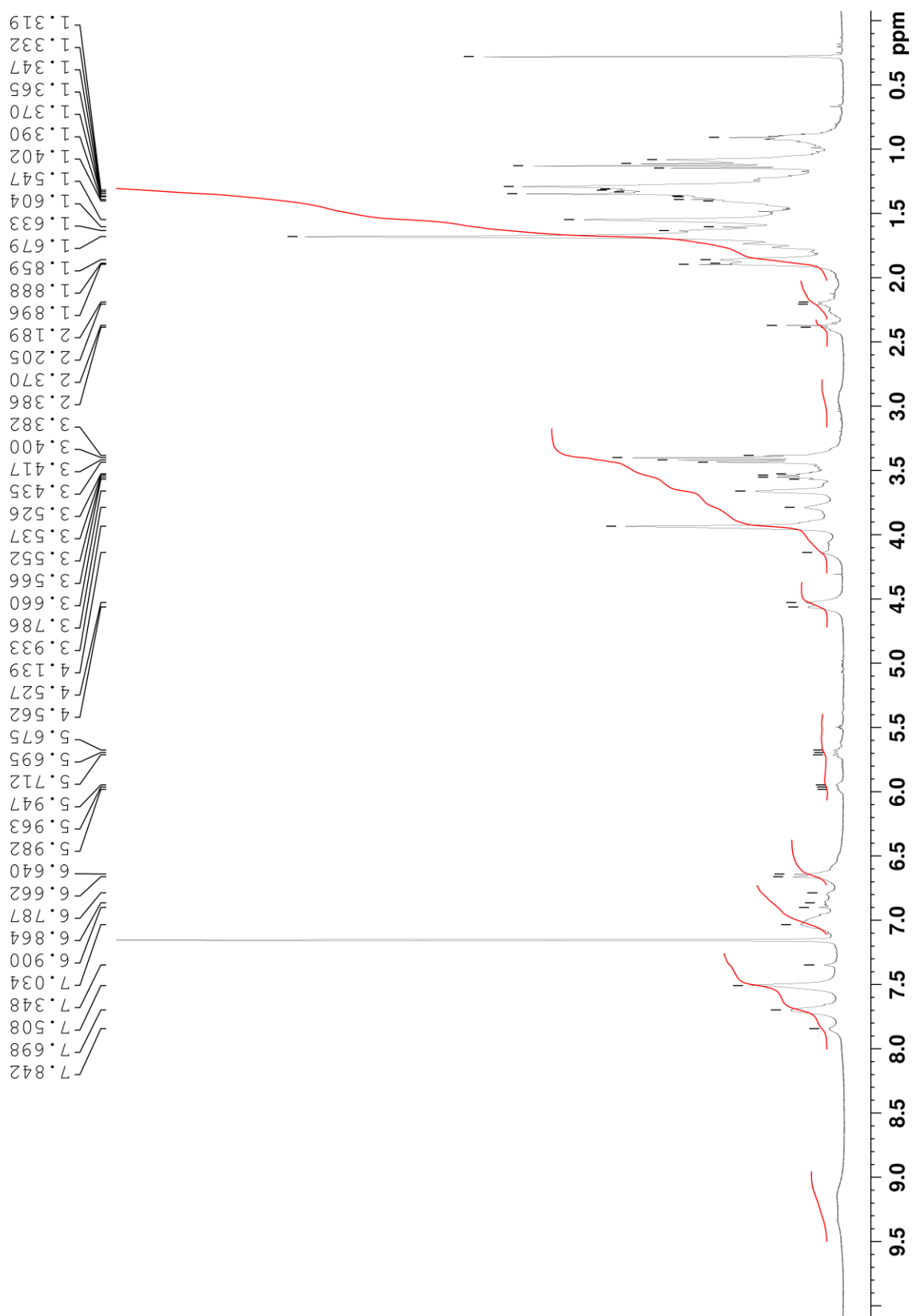


Figure S7. ^1H NMR spectrum (400 MHz, C_6D_6) of [2]catenane **10**

Id14b_160208114925 #1-10 RT: 0.01-0.22 AV: 10 NL: 1.51E6
T: FTMS + p ESIFull ms [900.00-3000.00]

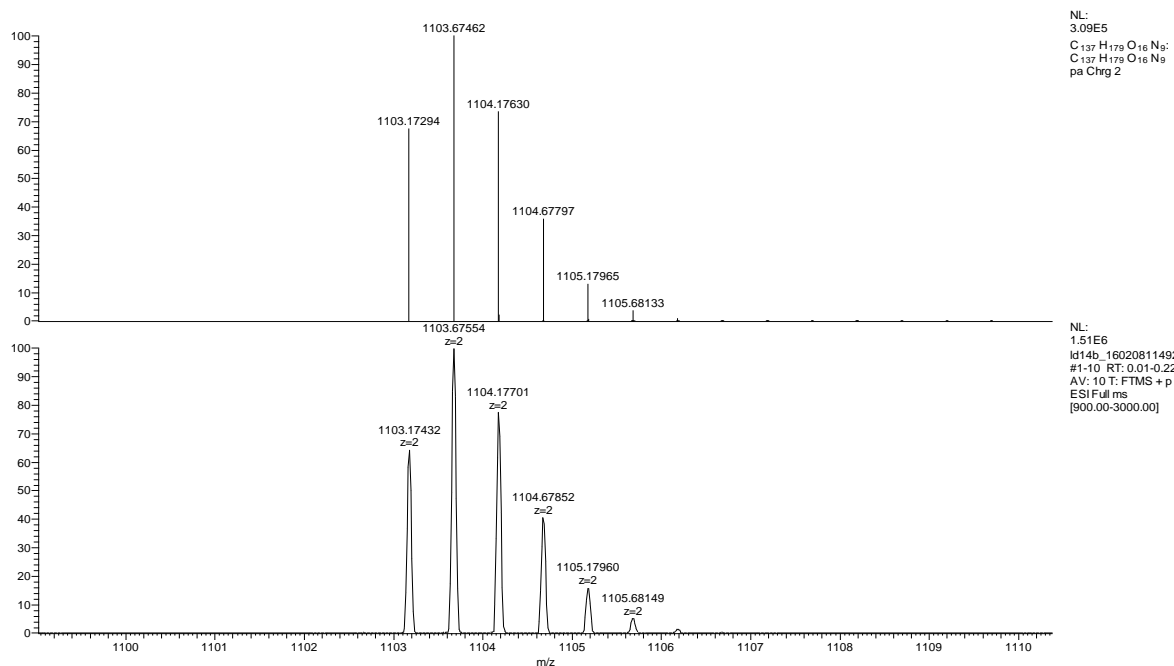
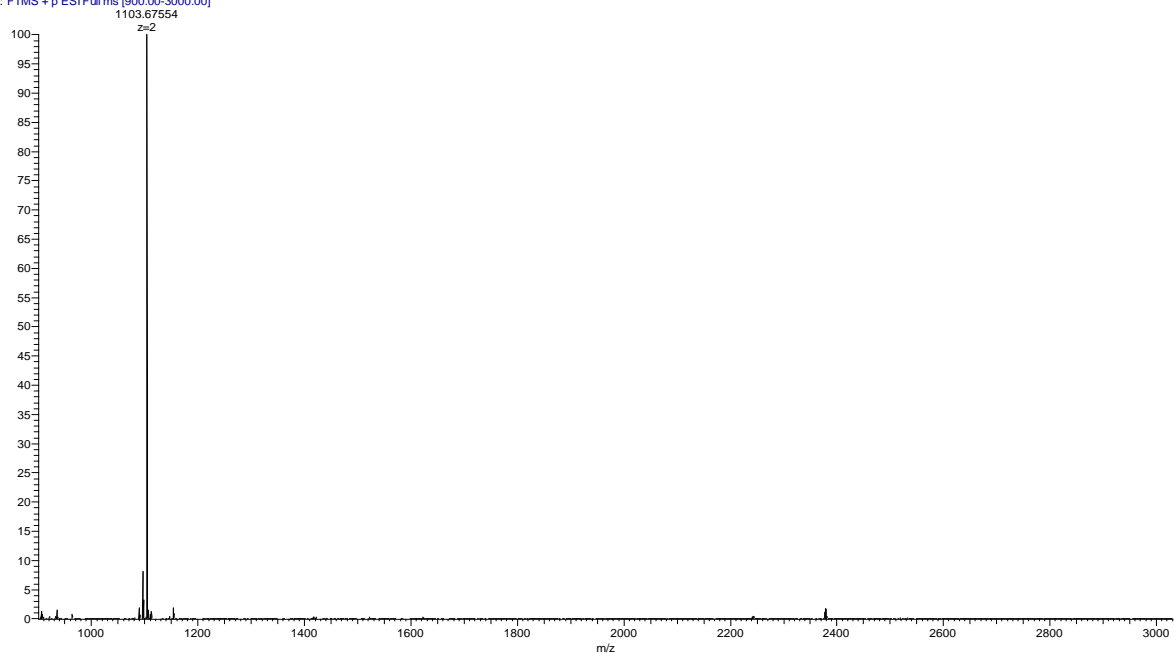


Figure S8. HR-MS (Orbitrap-LQ) of [2]catenane **10** (top) and comparison between the calculated and experimental isotopic distribution for the doubly charged specie (bottom).

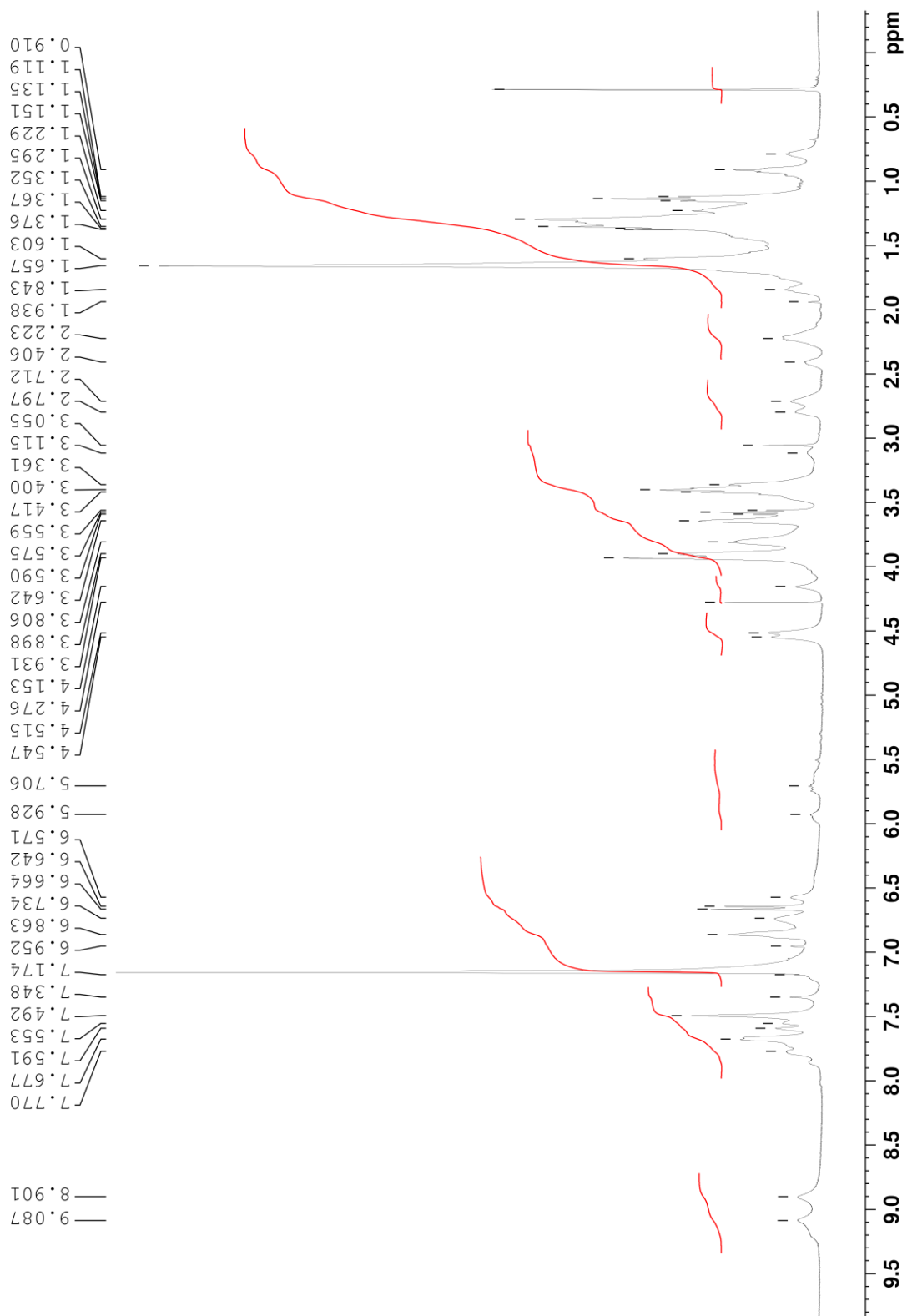


Figure S9. ^1H NMR spectrum (400 MHz, C_6D_6) of [2]catenane **3**

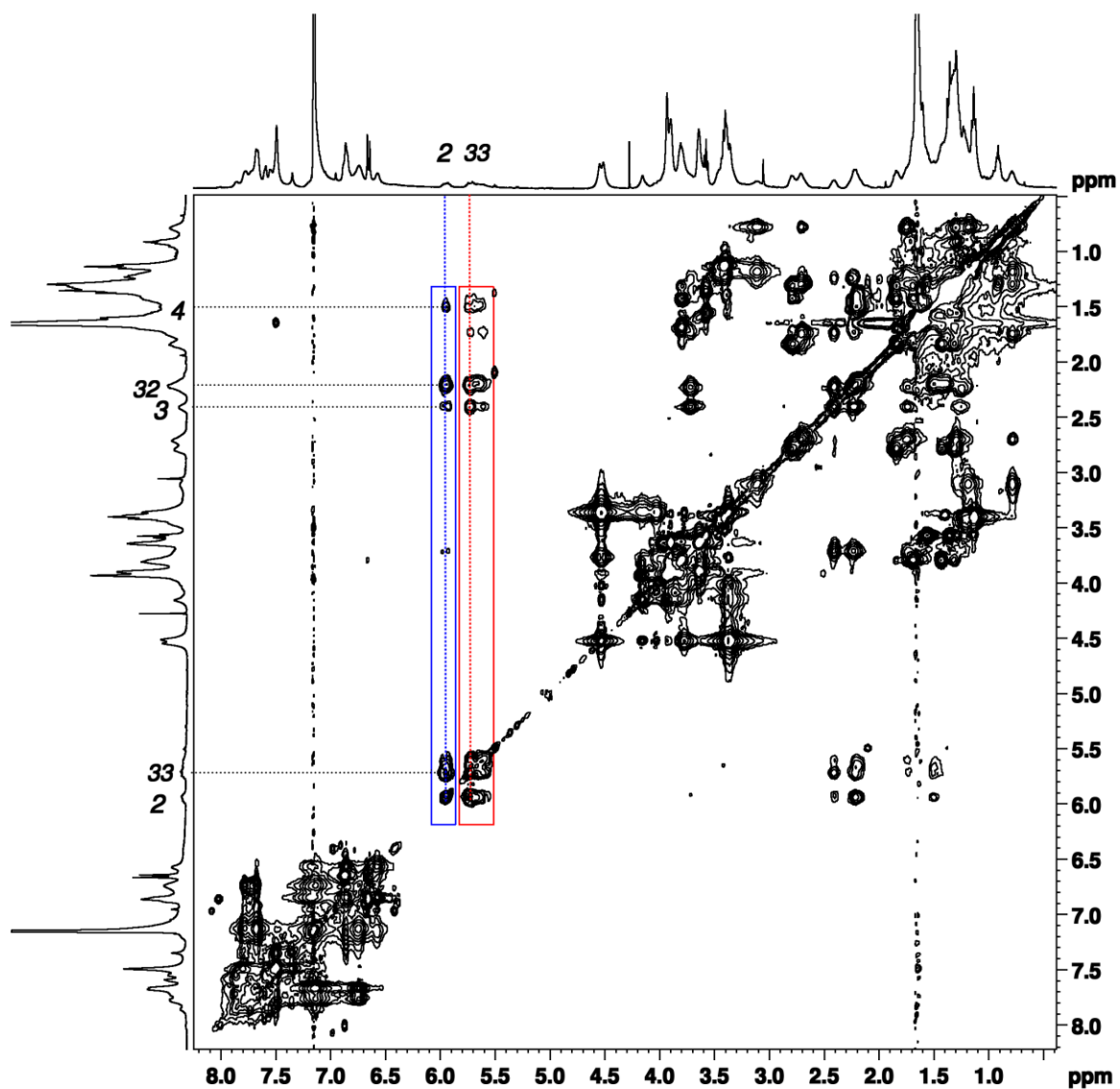


Figure S10. 2D TOCSY (MT = 0.04 s) spectrum (400 MHz, C₆D₆) of [2]catenane **3**. The scalar correlations linking proton 2 to proton 32 have been enclosed in a blue box. These series are also related with proton 33 (red box).

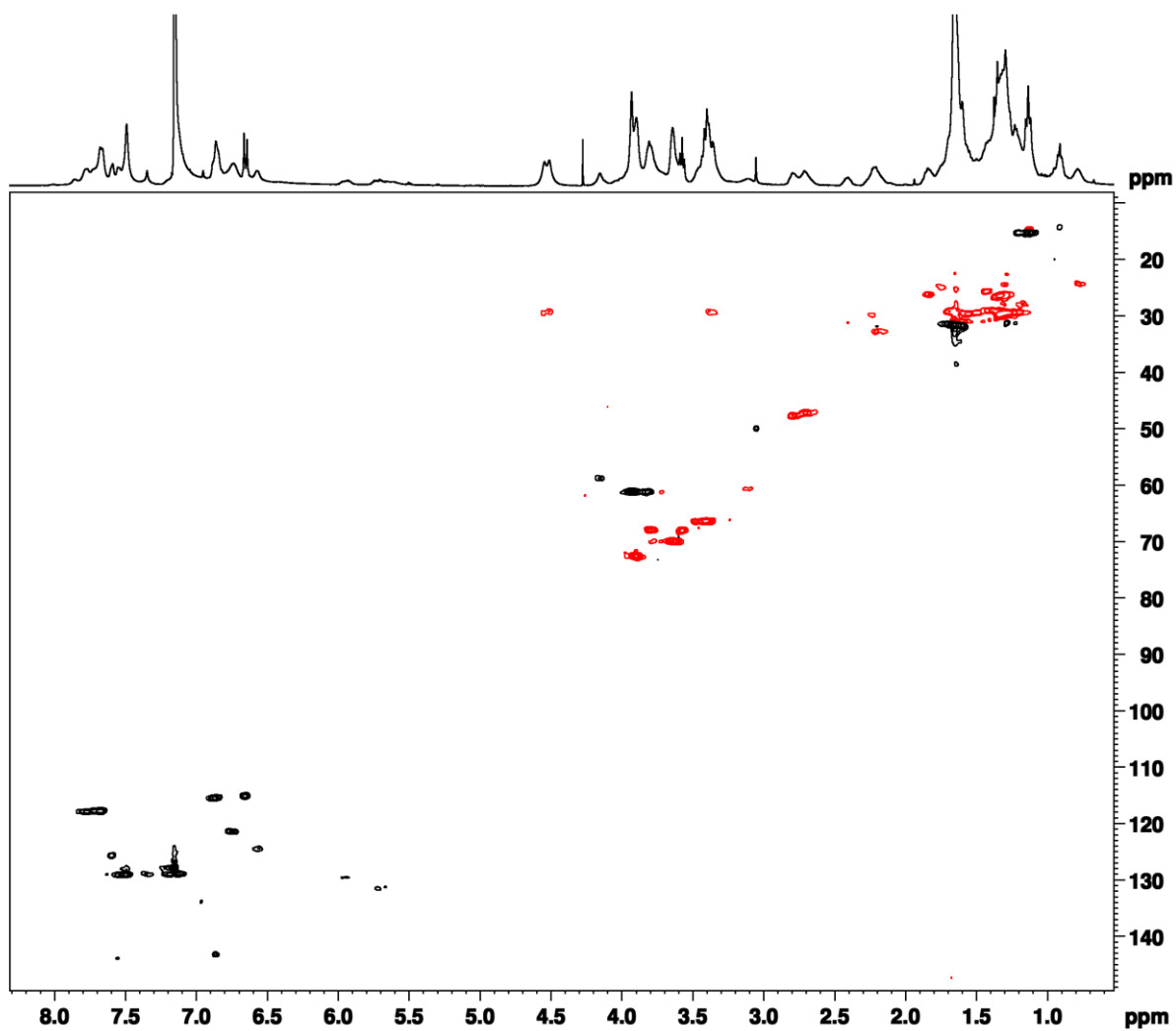


Figure S11. Edited 2D HSQC spectrum (400 MHz, C₆D₆) of [2]catenane **3**

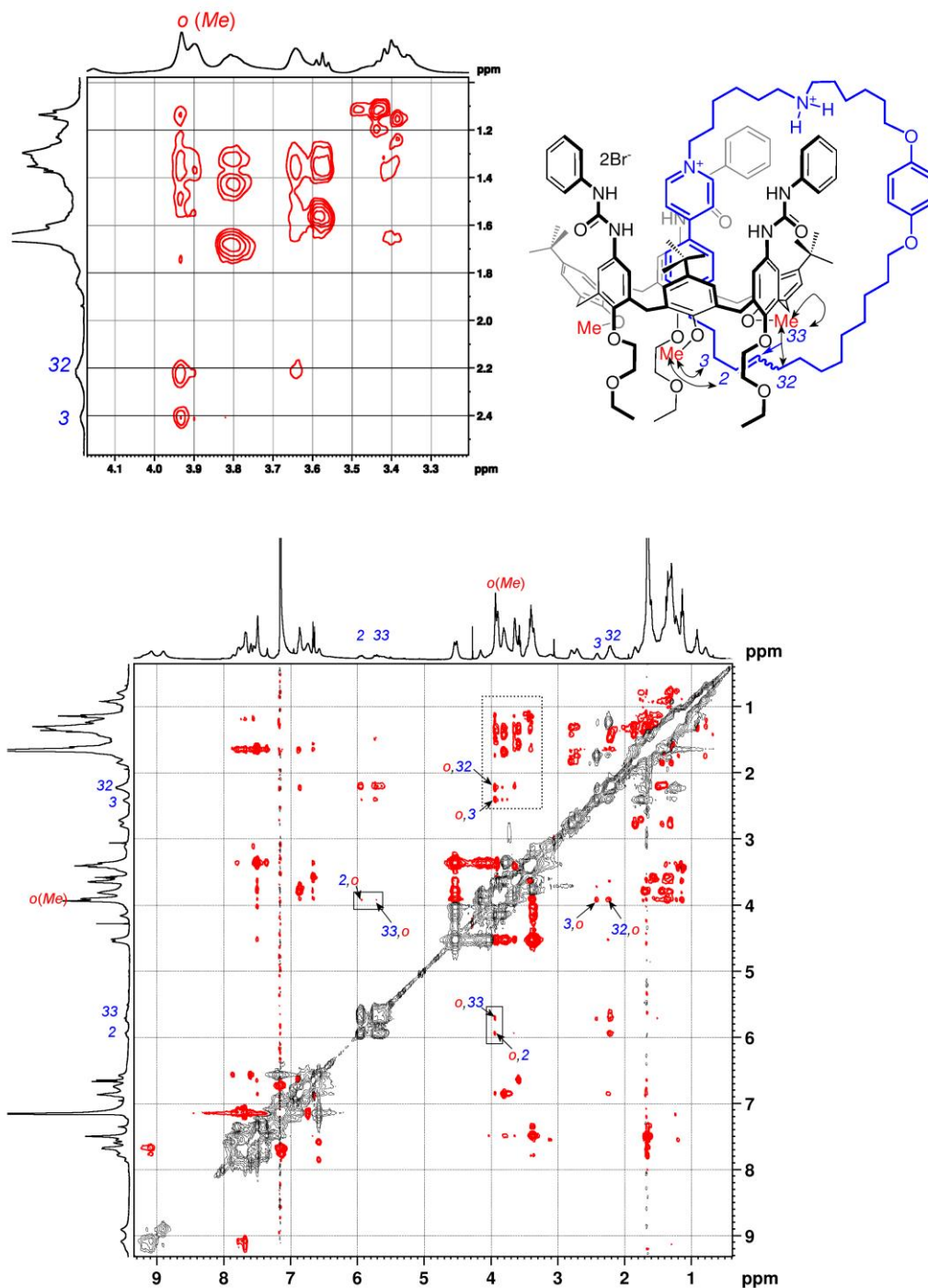


Figure S12. (Bottom) 2D ROESY spectrum (400 MHz, C_6D_6 , SpinLock = 200 ms) of [2]catenane **3**. The cross-peaks showing the spatial proximity of protons 2,3, 32 and 33 with the methoxy groups at the calix[6]arene lower rim have been indicated with arrows. (Top, left) Inset of the ROESY spectrum enlightening the cross-peaks generated by the dipolar interaction between the protons of the methoxy groups and the allylic protons 3 and 32 of the annulated thread of **3**. (Top, right) Molecular sketch showing the possible dipolar interaction (double arrows) at the calix[6]arene lower rim.

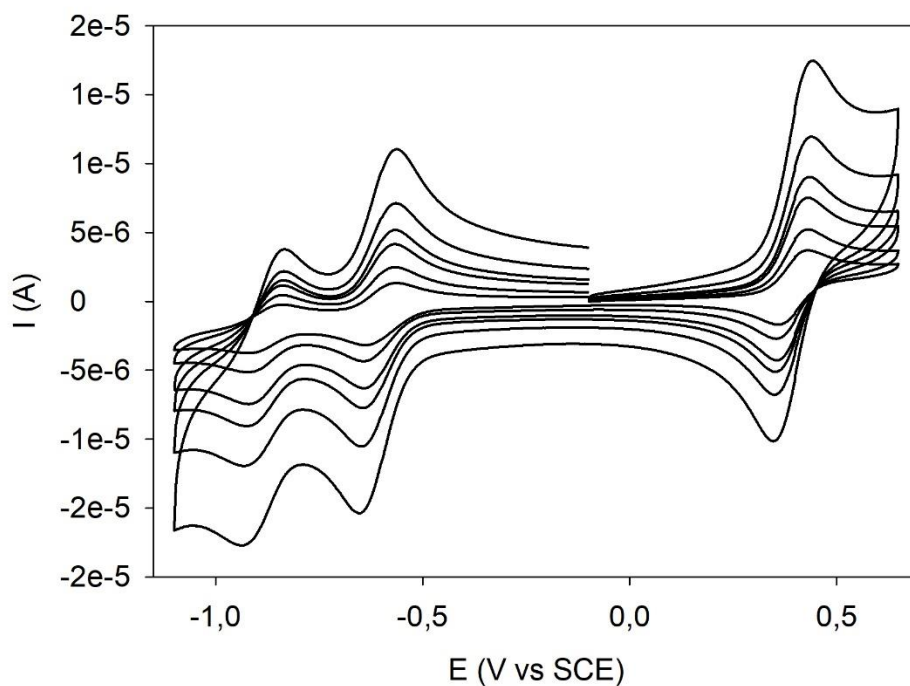


Figure S13. Cyclic voltammetric patterns of [2]catenane **3** at different scan rates (from 50 to 1000 mV s^{-1}). Conditions: argon-purged acetonitrile, 0.03 mM, 0.4 M TEAPF₆, glassy carbon electrode, r.t. The process at +0.395 V vs SCE is that of the ferrocene used as an internal standard.

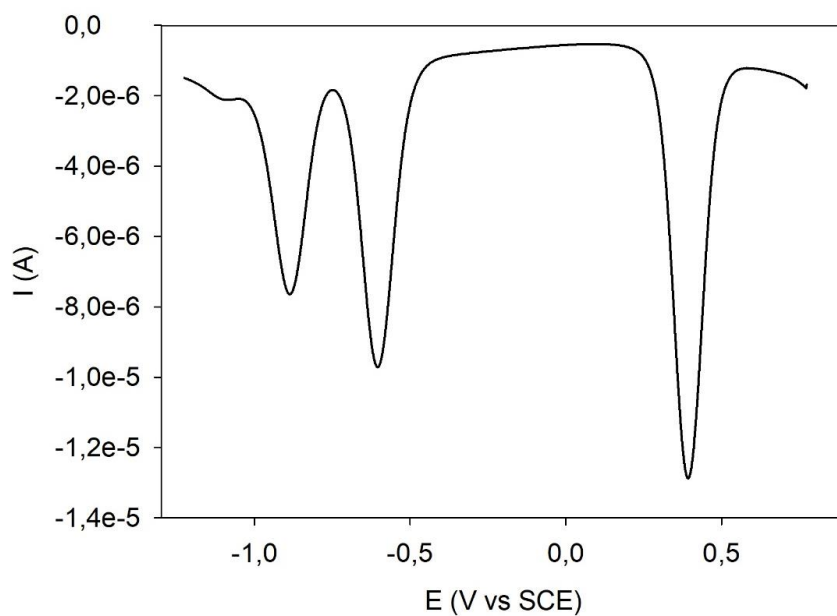


Figure S14. Differential pulse voltammogram of [2]catenane **3**. Conditions: argon-purged acetonitrile, 0.03 mM, 0.4 M TEAPF₆, glassy carbon electrode, r.t.; scan rate 20 mV s^{-1} , pulse height 75 mV, pulse duration 40 ms. The process at +0.395 V vs SCE is that of the ferrocene used as an internal standard.