CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Efficient Synthesis of Calix[6]tmpa: a New Calix[6]aza-cryptand with Unique Conformational and Host-Guest Properties

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All the NMR spectra have been recorded in $CDCl_3$.

Figure S1. Variable temperature ^{1}H NMR study of **11** (300 MHz, 330K to 263 K).

Figure S2. ^{1}H NMR spectra recorded upon the progressive addition of PicH to **11** (300 MHz, 293K and 263 K).

Figure S3. Variable temperature ^{1}H NMR study of **11? $PrNH_3^+$** (300 MHz, 293 K to 220 K).

Figure S4. ^{1}H NMR spectra recorded upon the progressive addition of a solution of EtONa (21 %) in EtOH to calix[6]tmpa **11** (300 MHz, 293K).

Figure S5. ^{1}H NMR spectrum (300 MHz, 293 K) of methyl 6-(hydroxymethyl)picolinate **3**.

Figure S6. ^{13}C NMR spectrum (75 MHz, 293 K) of methyl 6-(hydroxymethyl)picolinate **3**.

Figure S7. ^{1}H NMR spectrum (300 MHz, 293 K) of methyl 6-(bromomethyl)picolinate **4**.

Figure S8. ^{13}C NMR spectrum (75 MHz, 293 K) of methyl 6-(bromomethyl)picolinate **4**.

Figure S9. ^{1}H NMR spectrum (250 MHz, 300 K) of tris[6-(methoxycarbonyl)-2-pyridylmethyl]amine **5**.

Figure S10. ^{13}C NMR spectrum (75 MHz, 300 K) of tris[6-(methoxycarbonyl)-2-pyridylmethyl]amine **5**.

Figure S11. ^{1}H NMR spectrum (200 MHz, 293 K) of tris[6-(hydroxymethyl)-2-pyridylmethyl]amine **6**.

Figure S12. ^{13}C NMR spectrum (75 MHz, 300 K) of tris[6-(hydroxymethyl)-2-pyridylmethyl]amine **6**.

Figure S13. ^{1}H NMR spectrum (300 MHz, 293 K) of tris[6-(chloromethyl)-2-pyridylmethyl]amine **7**.

Figure S14. ^{13}C NMR spectrum (75 MHz, 293 K) of tris[6-(chloromethyl)-2-pyridylmethyl]amine **7**.

Figure S15. ^{1}H NMR spectrum (300 MHz, 293 K) of calix[6]arene derivative **8**.

Figure S16. ^{13}C NMR spectrum (75 MHz, 293 K) of calix[6]arene derivative **8**.

Figure S17. ^{1}H NMR spectrum (300 MHz, 293 K) of calix[6]arene derivative **9**.

Figure S18. ^{13}C NMR spectrum (75 MHz, 293 K) of calix[6]arene derivative **9**.

Figure S19. ^{1}H NMR spectrum (300 MHz, 293 K) of calix[6]arene derivative **10**.

Figure S20. ^{13}C NMR spectrum (75 MHz, 293 K) of calix[6]arene derivative **10**.

Figure S21. ^{13}C NMR spectrum (75 MHz, 293 K) of calix[6]tmpa **11**.

Figure S22. ^{1}H NMR spectrum (300 MHz, 220 K) of compound **11.H^+,ClO_4^-**.

Figure S23. HMBC spectrum (293 K) of calix[6]tmpa **11**.

Figure S24. ^{13}C NMR spectrum (75 MHz, 293 K) of endo-complex **11.Na^{+}⋯EtOH**.

Figure S25. COSY spectrum (293 K) of endo-complex **11.Na^{+}⋯EtOH**.

Figure S26. HMBC spectrum (293 K) of endo-complex **11.Na^{+}⋯EtOH**.

Figure S27. NOESY spectrum (293 K) of endo-complex **11.Na^{+}⋯EtOH**.

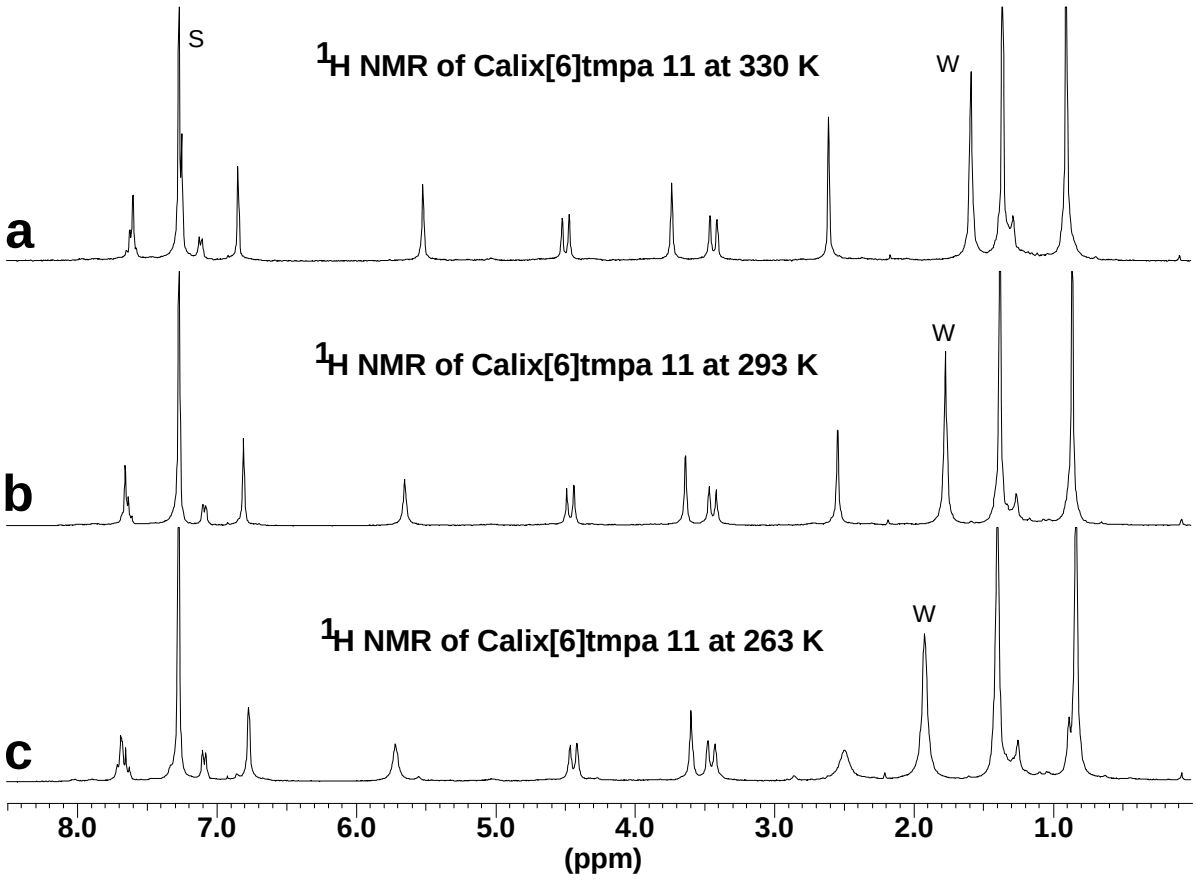


Figure S1. ^{1}H NMR spectra of **11** (300 MHz): (a) 330K; (b) 293 K; (c) 263 K. Residual solvents and water have been labeled "S" and "W", respectively.

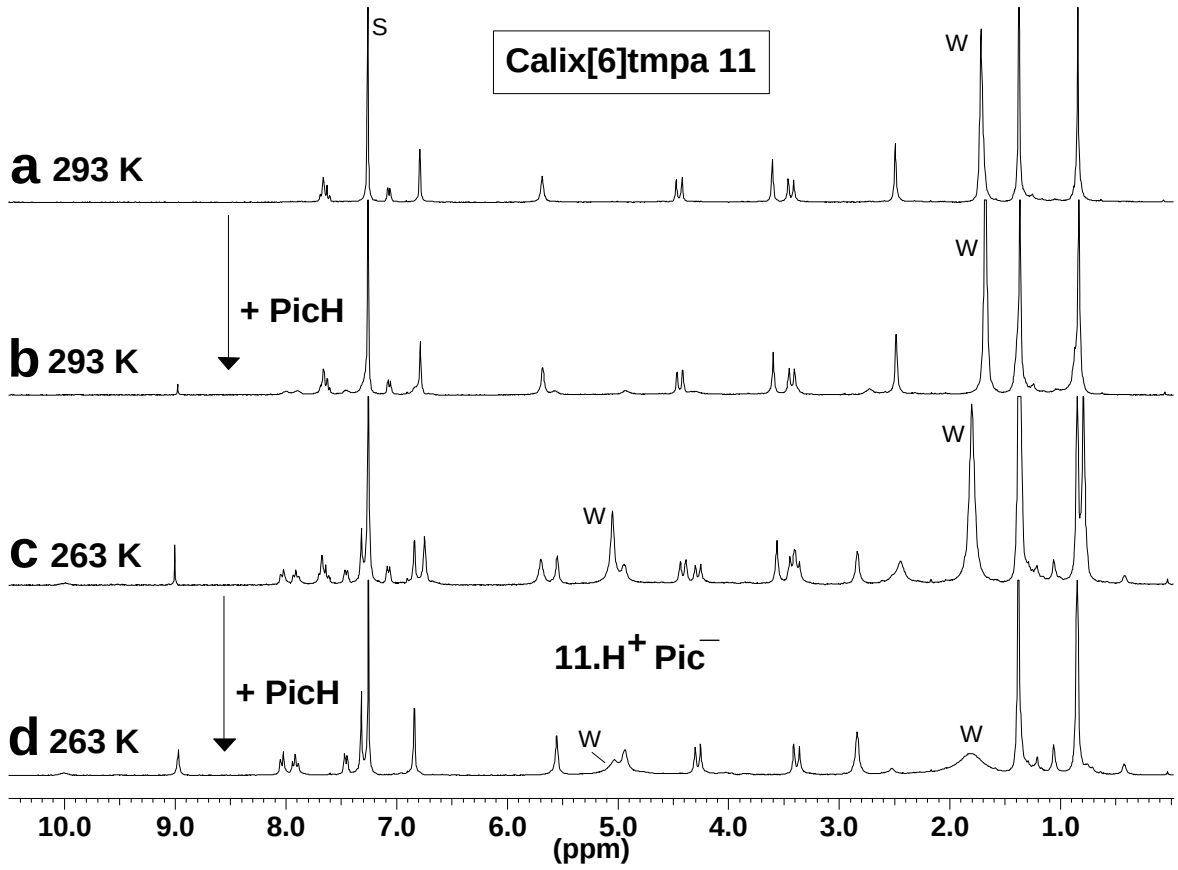


Figure S2. ^{1}H NMR spectra (300 MHz) of: (a) Calix[6]tmpa **11** (293 K); (b) after the addition of 0.5 equiv. of PicH (293K); (c) after the lowering of the temperature at 263 K; (d) after the addition of 1 equiv. of PicH (263K). Residual solvents and water have been labeled “S” and “W”, respectively.

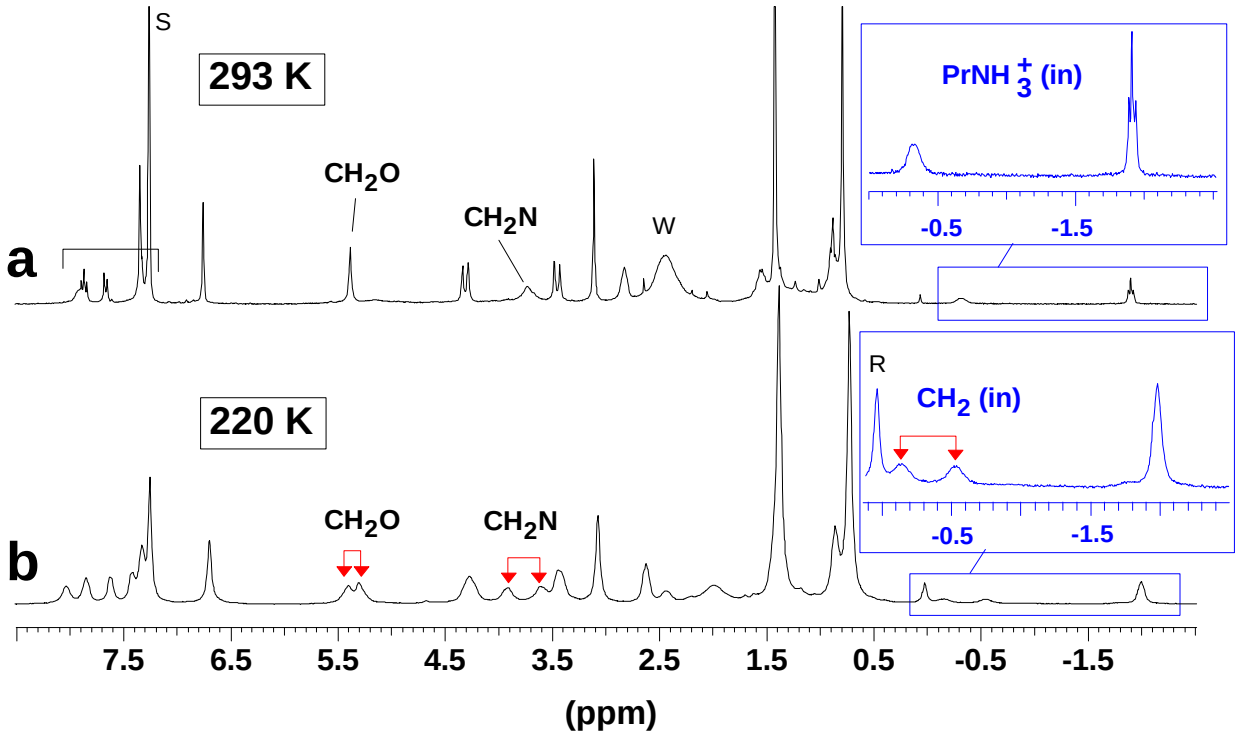


Figure S3. ^{1}H NMR spectra of **11? $PrNH_3^+$** (300 MHz): (a) 293 K; (b) 220 K. Residual solvents, reference and water have been labeled “S”, ”R” and “W”, respectively.

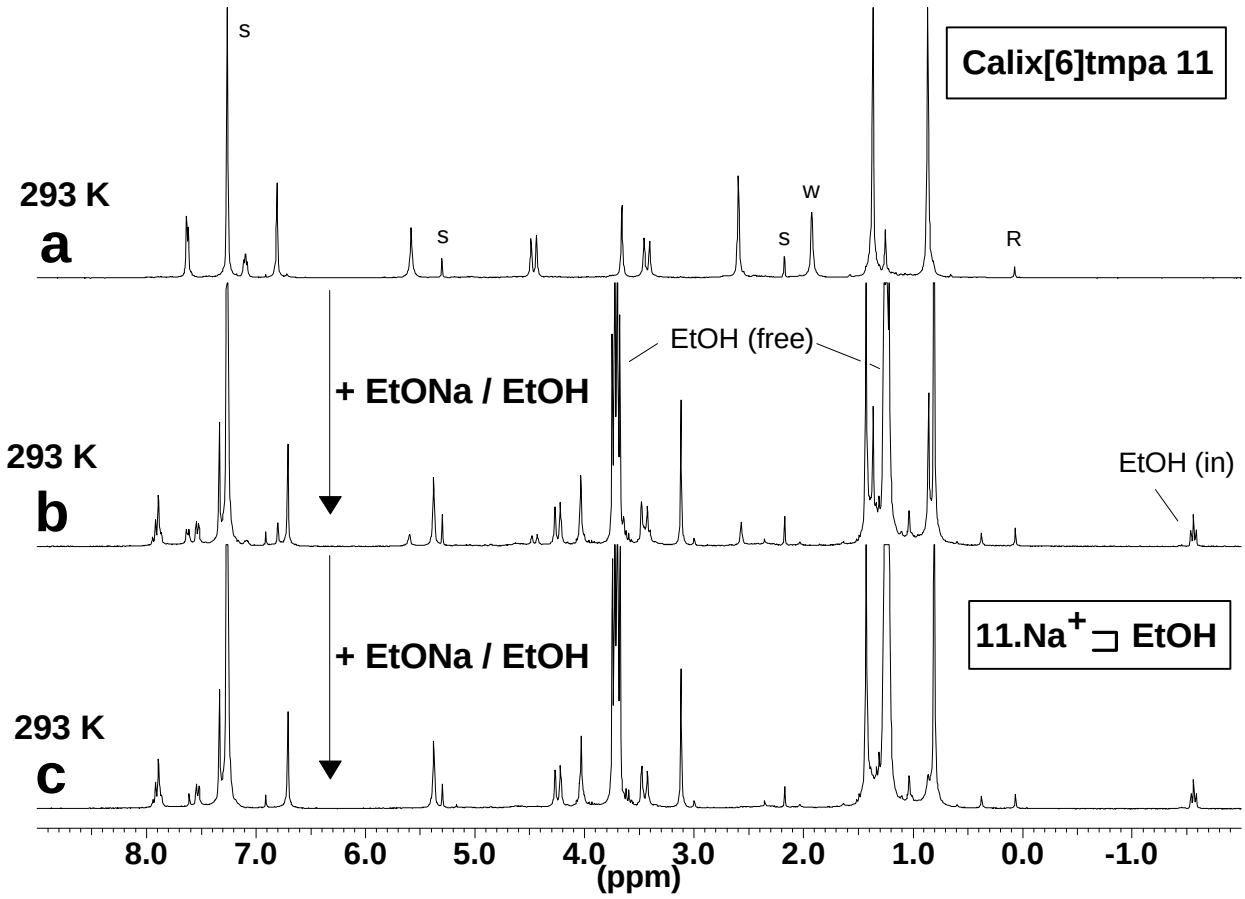


Figure S4. ^{1}H NMR spectra (300 MHz, 293 K) of: (a) Calix[6]tmpa **11**; (b) and (c) after the progressive addition of a solution of EtONa (21 %) in EtOH. Residual solvents, reference and water have been labeled “S”, ”R” and “W”, respectively.

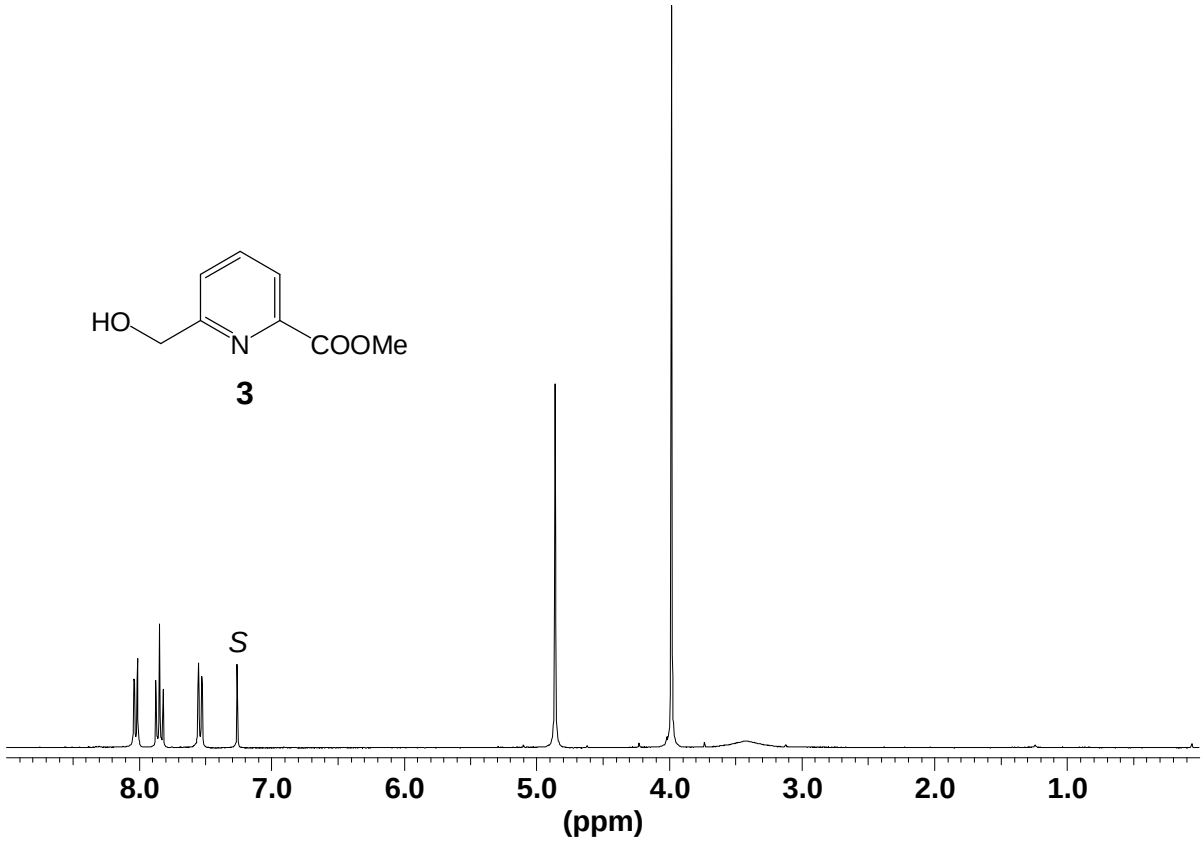


Figure S5. ^{1}H NMR spectrum (300 MHz, 293 K) of methyl 6-(hydroxymethyl)picolinate **3**. Residual solvent has been labeled “S”.

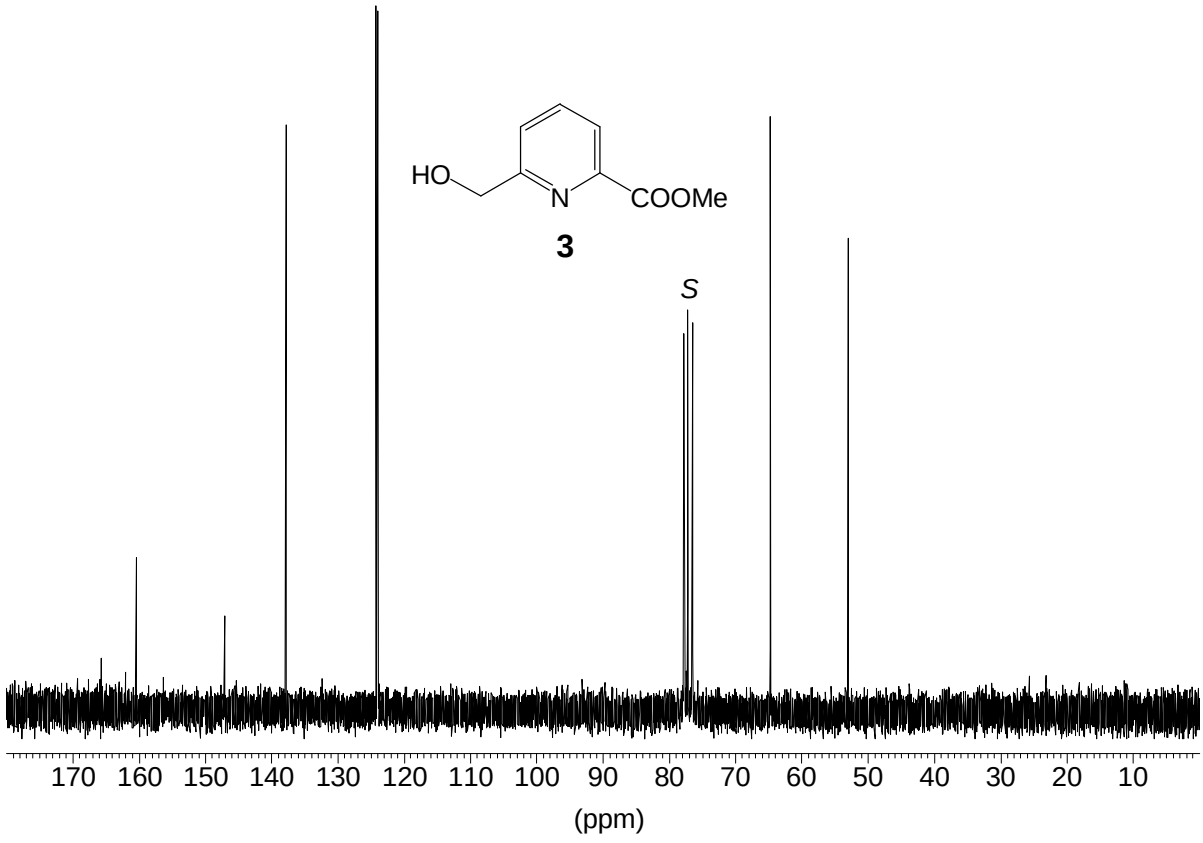


Figure S6. ^{13}C NMR spectrum (75 MHz, 293 K) of methyl 6-(hydroxymethyl)picolinate **3**. Residual solvent has been labeled “S”.

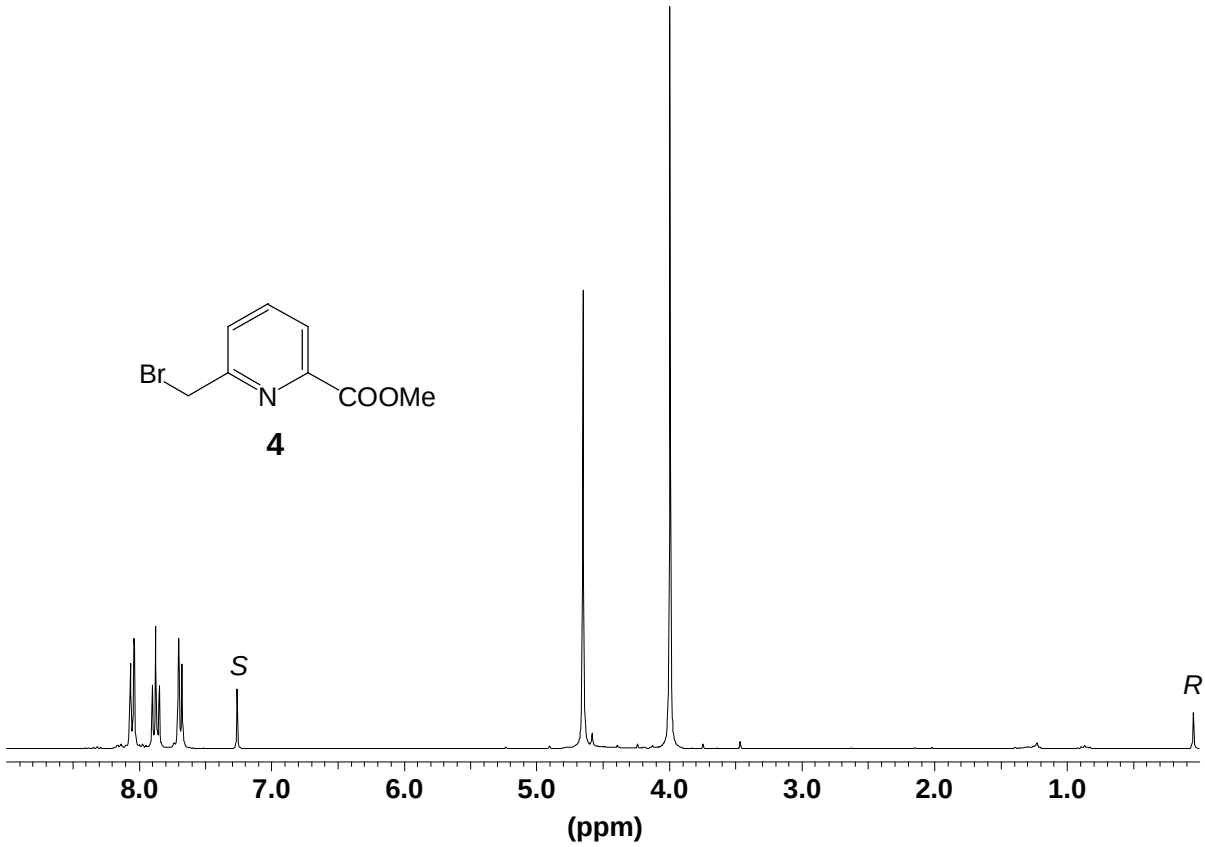


Figure S7. ^{1}H NMR spectrum (300 MHz, 293 K) of methyl 6-(bromomethyl)picolinate **4**. Residual solvents and reference have been labeled “S” and ”R” respectively.

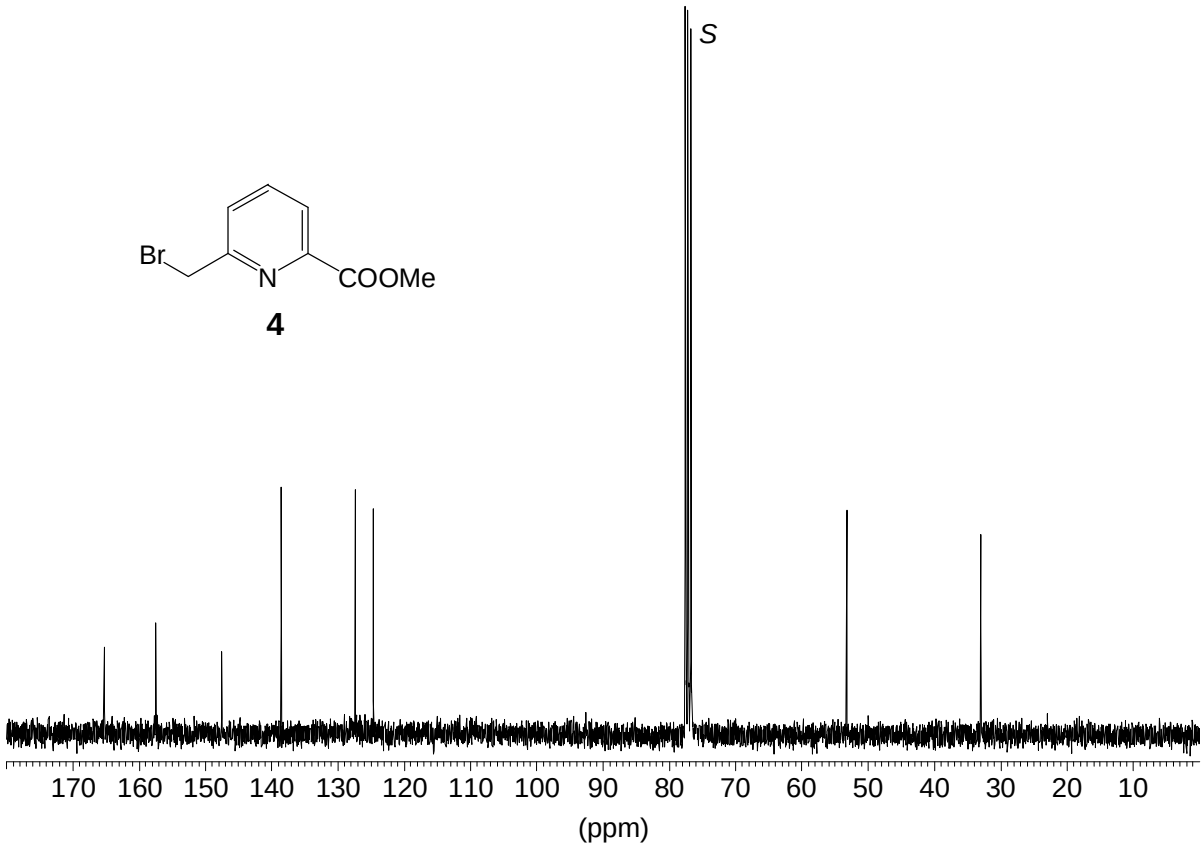


Figure S8. ^{13}C NMR spectrum (75 MHz, 293 K) of methyl 6-(bromomethyl)picolinate **4**. Residual solvent has been labeled “S”.

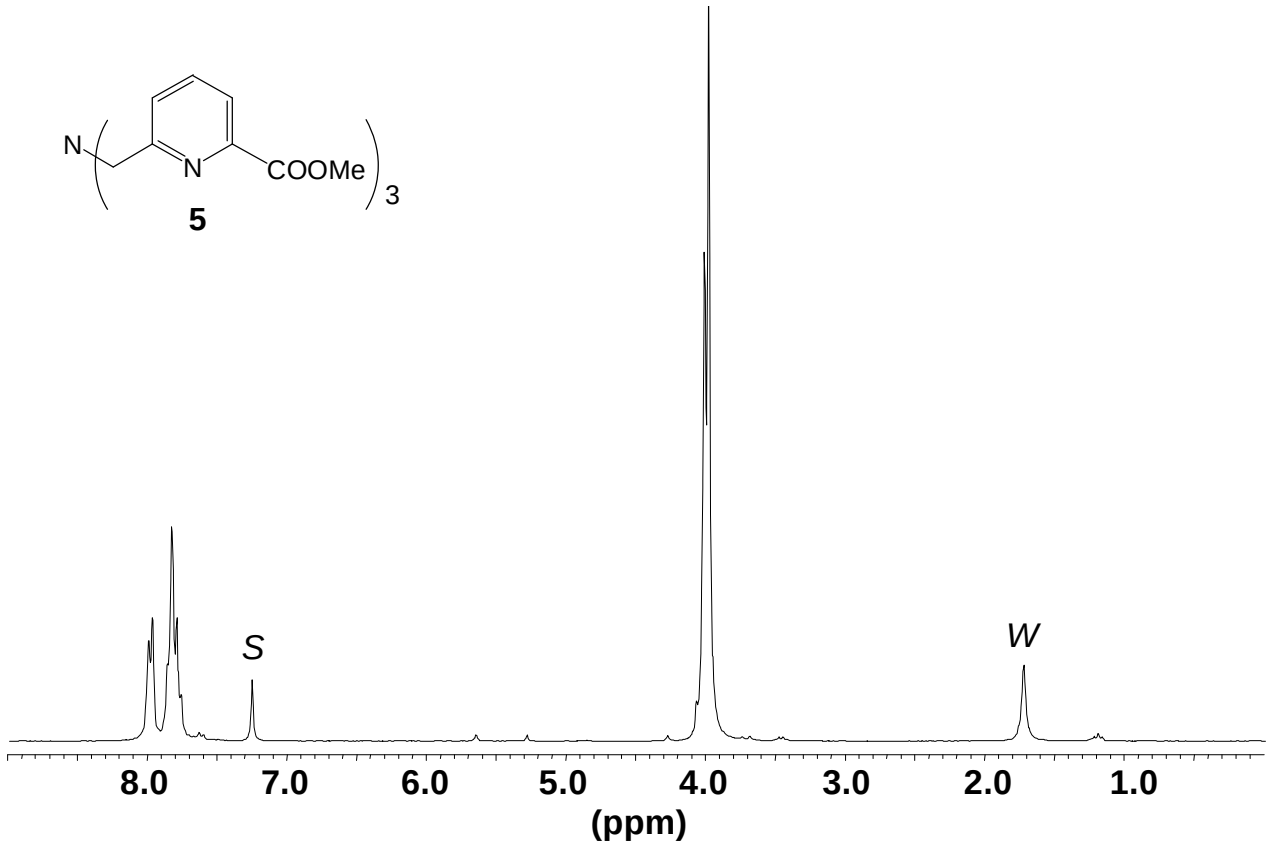


Figure S9. ^{1}H NMR spectrum (250 MHz, 300 K) of tris[6-(methoxycarbonyl)-2-pyridylmethyl]amine **5**. Residual solvent and water have been labeled “S” and “W” respectively.

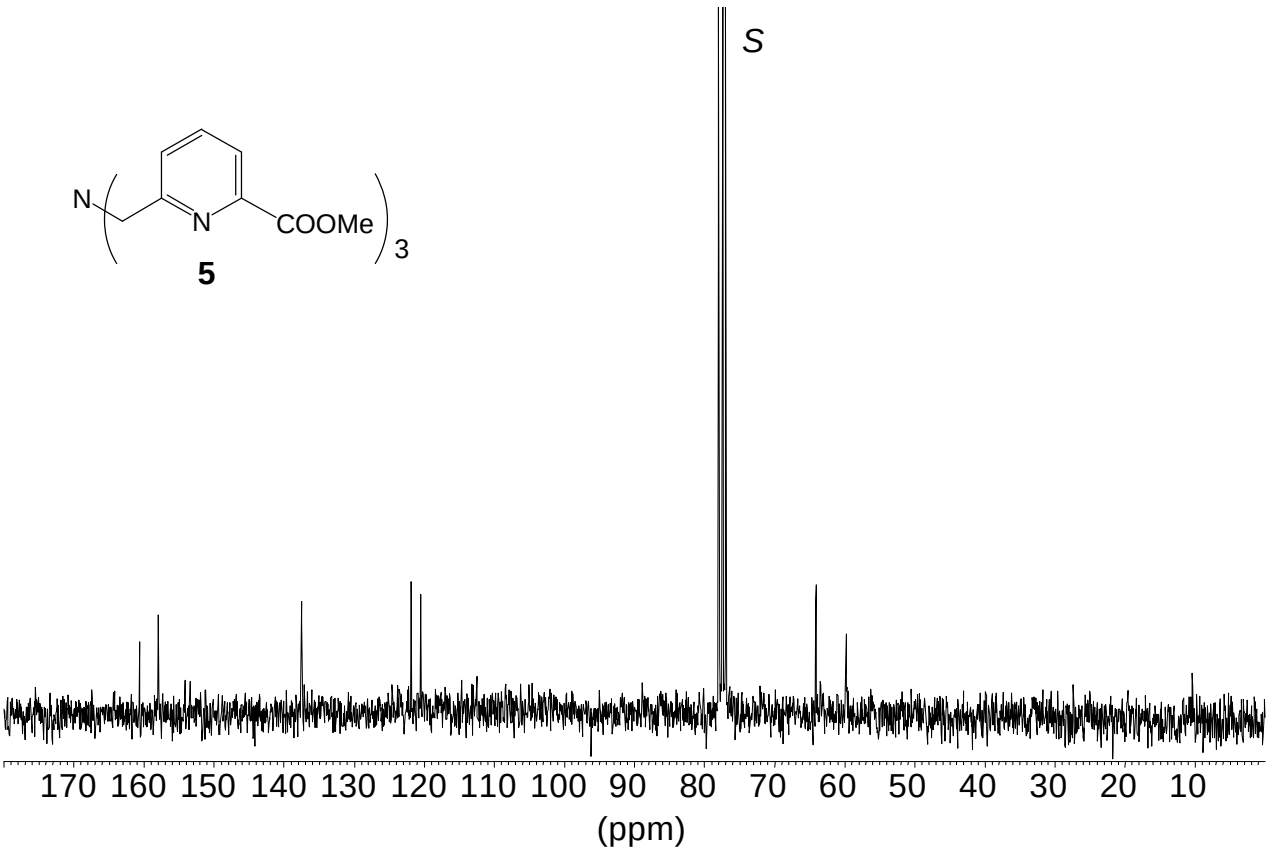


Figure S10. ^{13}C NMR spectrum (75 MHz, 300 K) of tris[6-(methoxycarbonyl)-2-pyridylmethyl]amine **5**. Residual solvent has been labeled “S”.

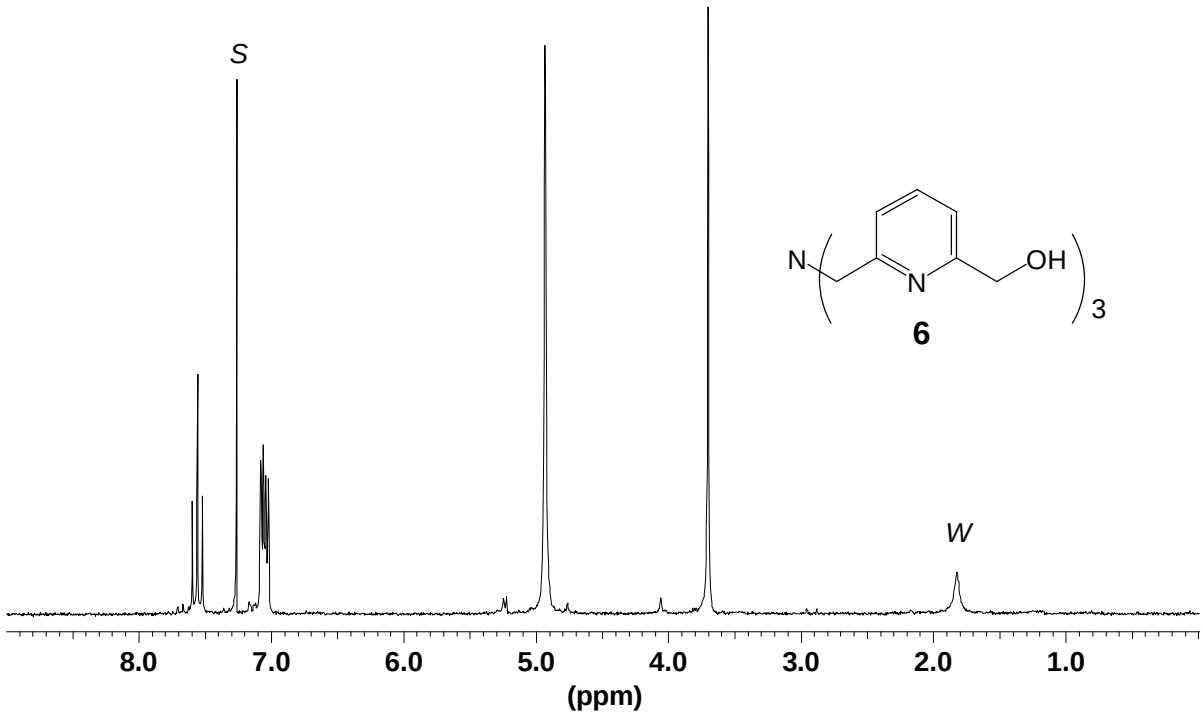


Figure S11. ^{1}H NMR spectrum (200 MHz, 293 K) of tris[6-(hydroxymethyl)-2-pyridylmethyl]amine **6**. Residual solvent and water have been labeled “S” and “W” respectively.

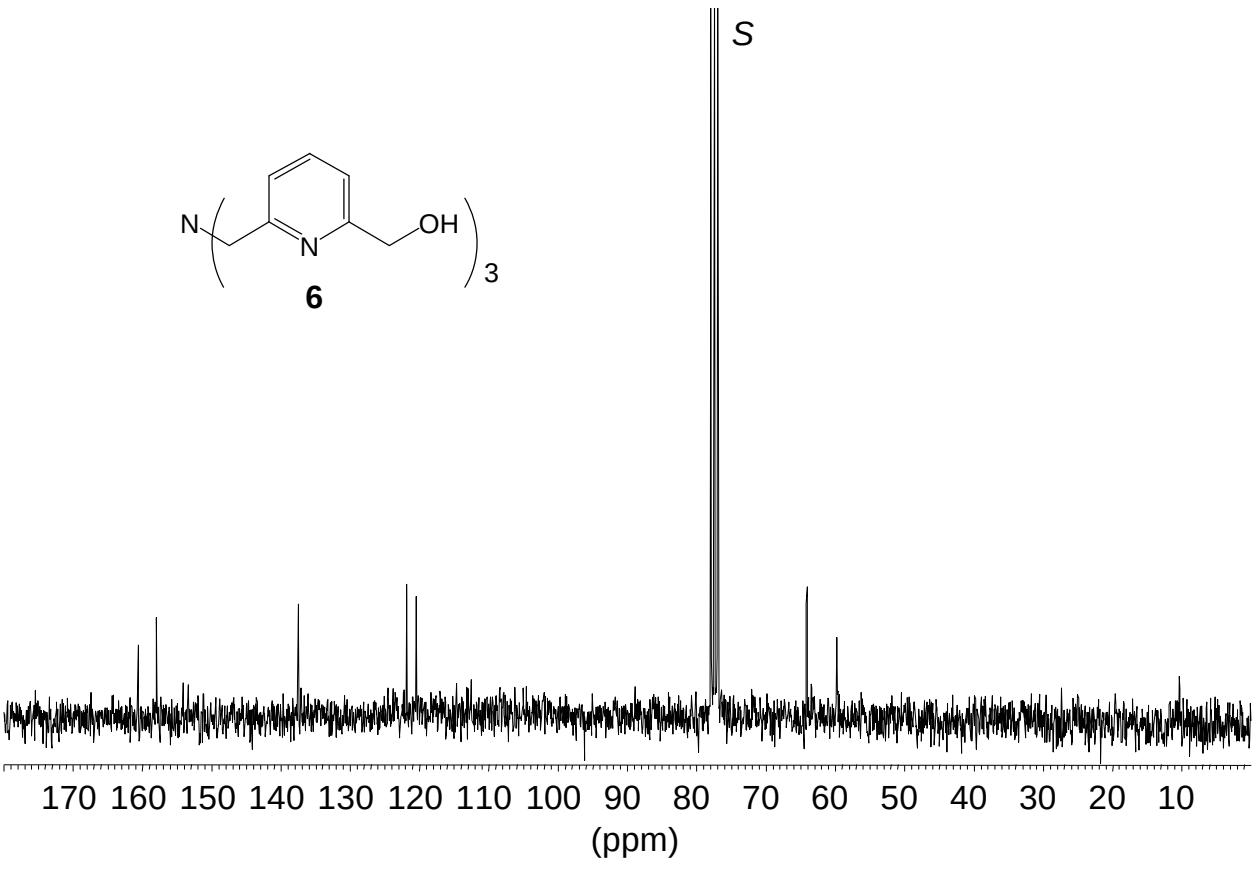


Figure S12. ^{13}C NMR spectrum (75 MHz, 300 K) of tris[6-(hydroxymethyl)-2-pyridylmethyl]amine **6**. Residual solvent has been labeled “S”.

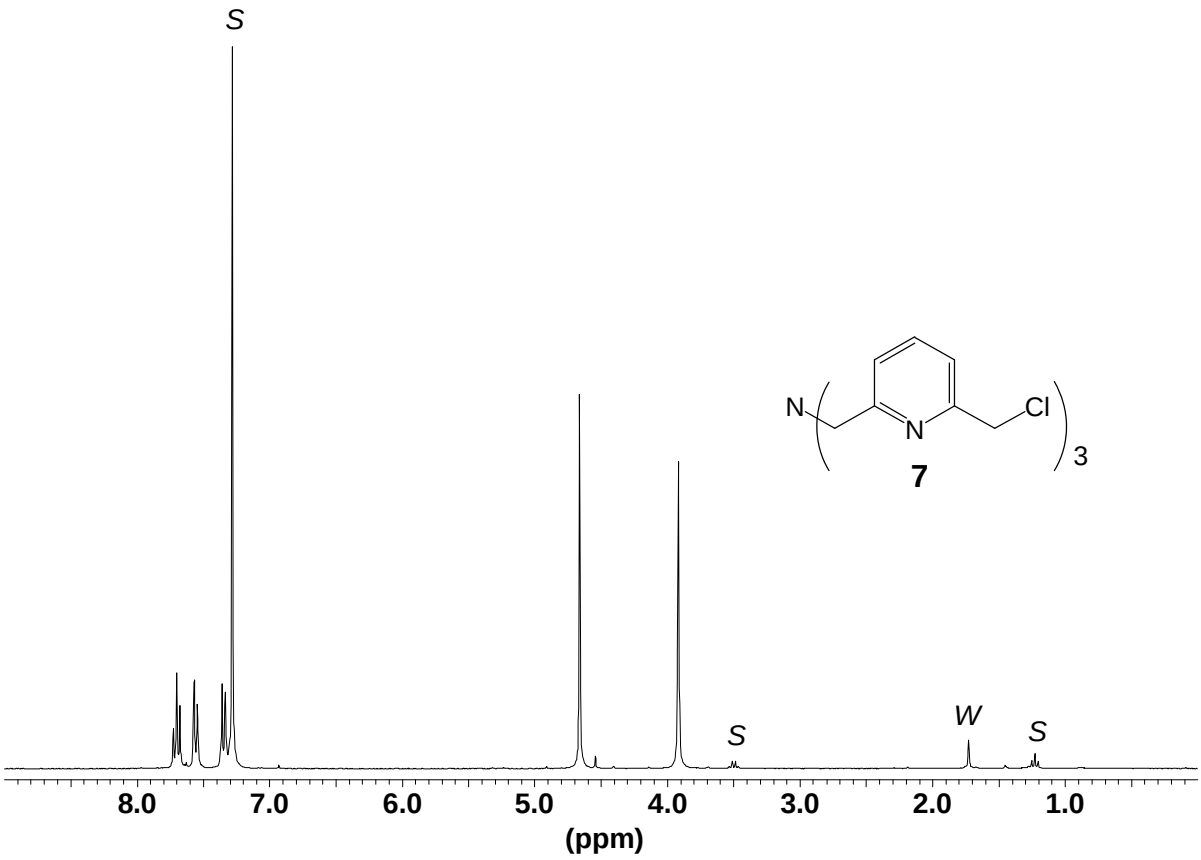


Figure S13. ^{1}H NMR spectrum (300 MHz, 293 K) of tris[6-(chloromethyl)-2-pyridylmethyl]amine **7**. Residual solvents and water have been labeled “S” and “W” respectively.

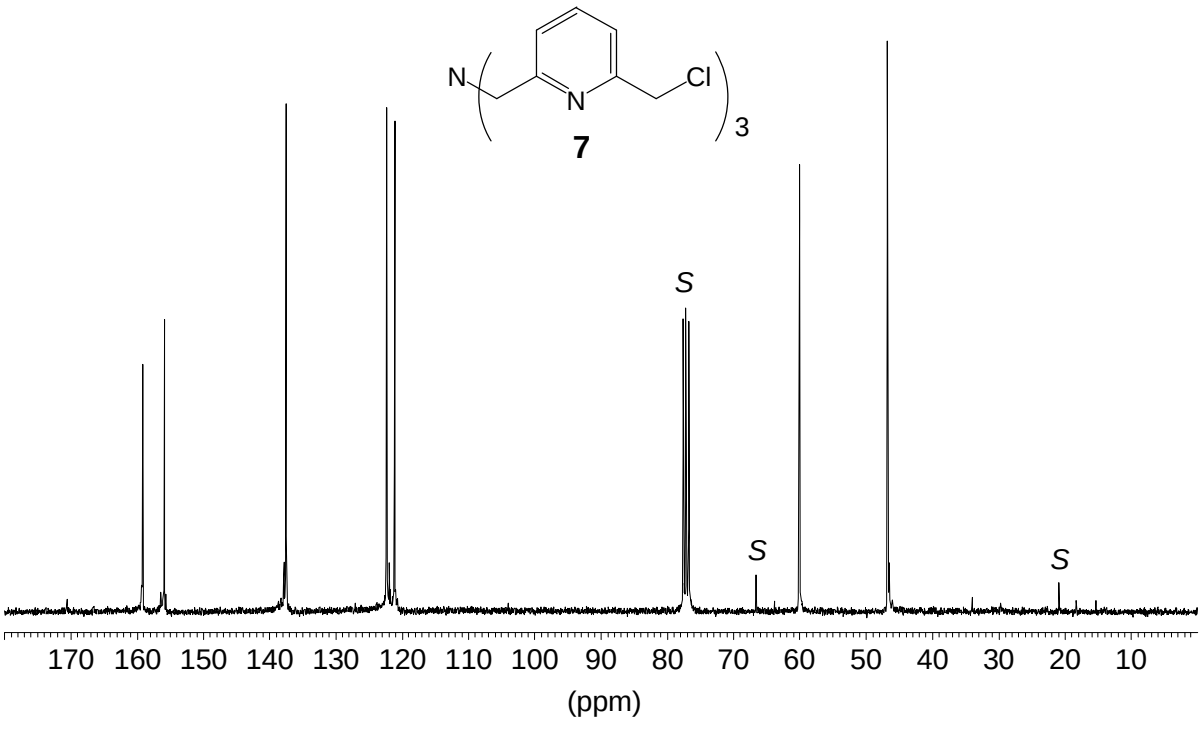


Figure S14. ^{13}C NMR spectrum (75 MHz, 293 K) of tris[6-(chloromethyl)-2-pyridylmethyl]amine **7**. Residual solvents have been labeled “S”.

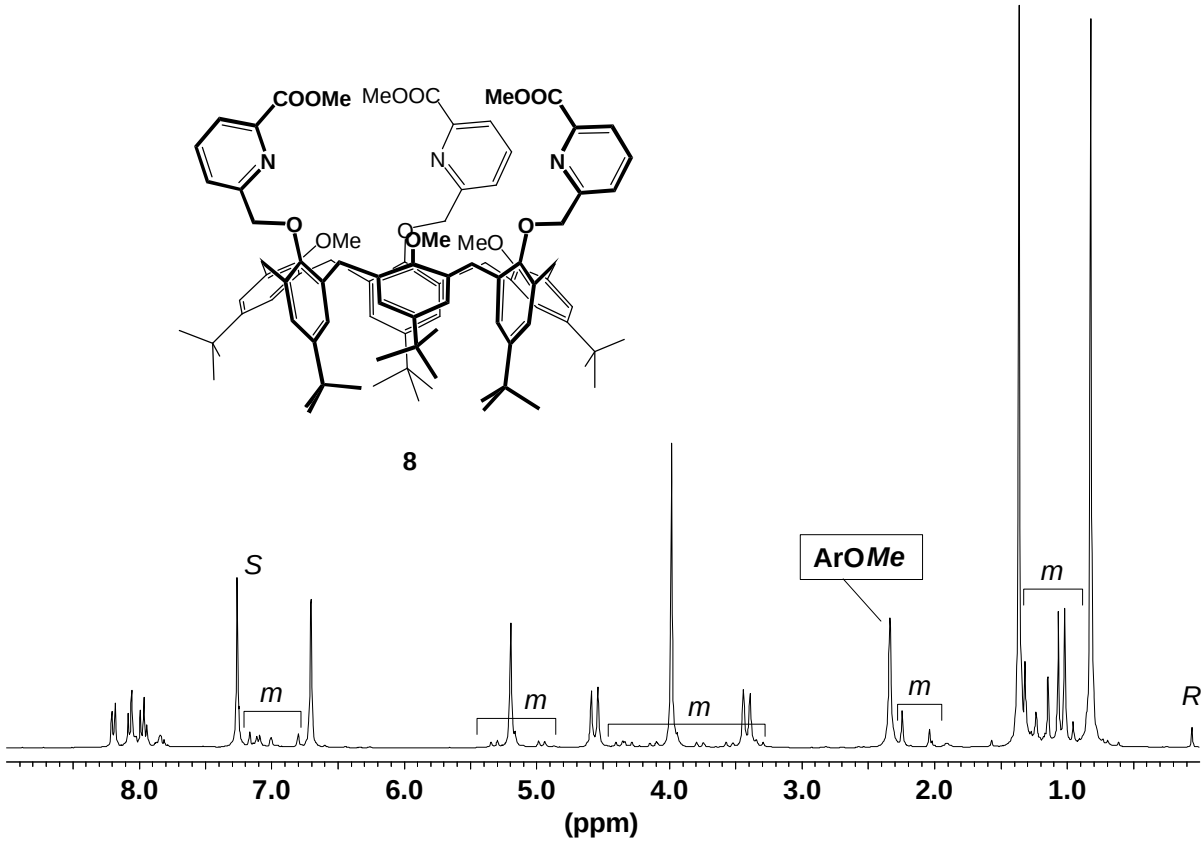


Figure S15. ^{1}H NMR spectrum (300 MHz, 293 K) of calix[6]arene derivative **8**. Residual solvent, reference and the minor conformation of **8** (see the theoretical part) have been labeled “S”, “R” and “m” respectively.

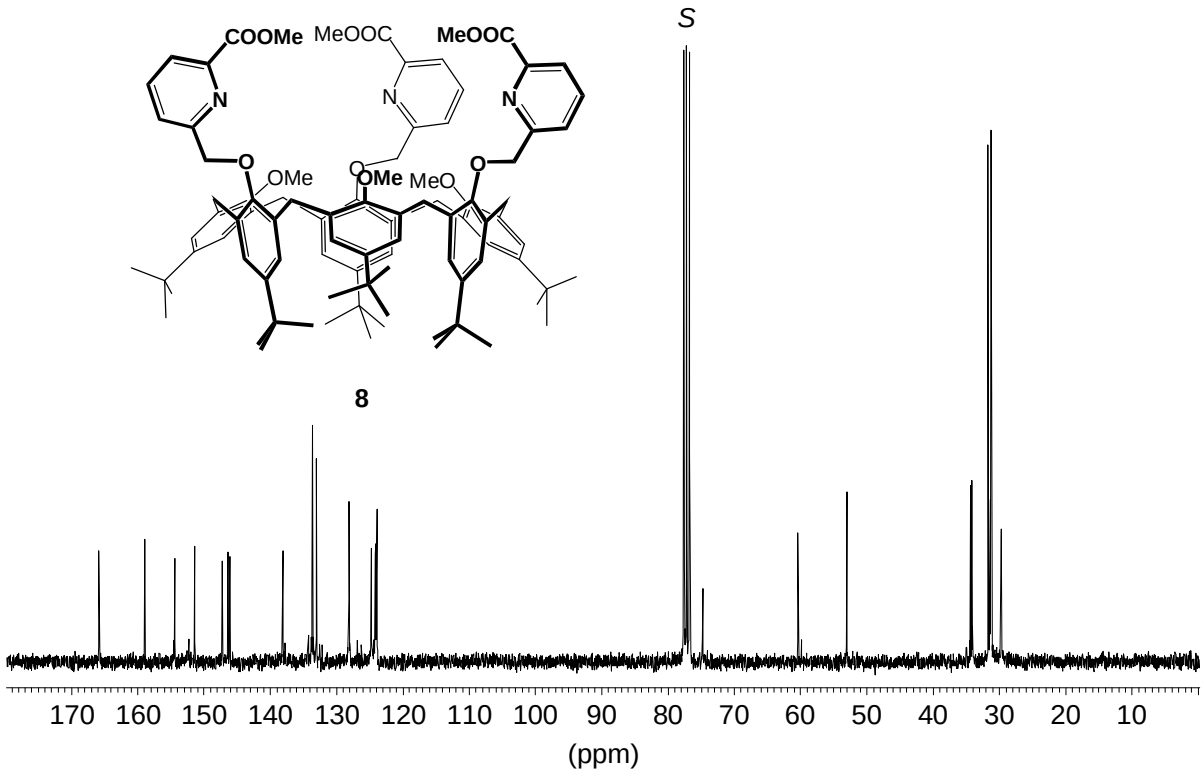


Figure S16. ^{13}C NMR spectrum (75 MHz, 293 K) of calix[6]arene derivative **8**. Residual solvent has been labeled “S”.

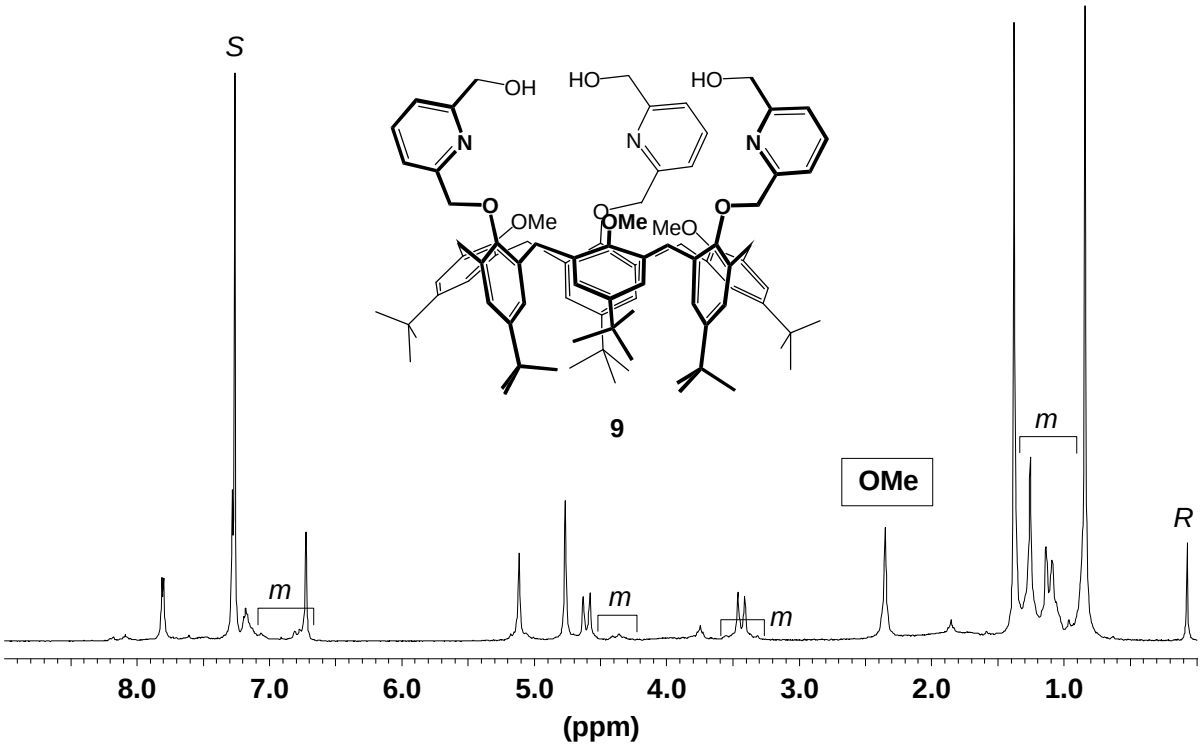


Figure S17. ^{1}H NMR spectrum (300 MHz, 293 K) of calix[6]arene derivative **9**. Residual solvent, reference and the minor conformation of **9** (see the theoretical part) have been labeled “S”, “R” and “m” respectively.

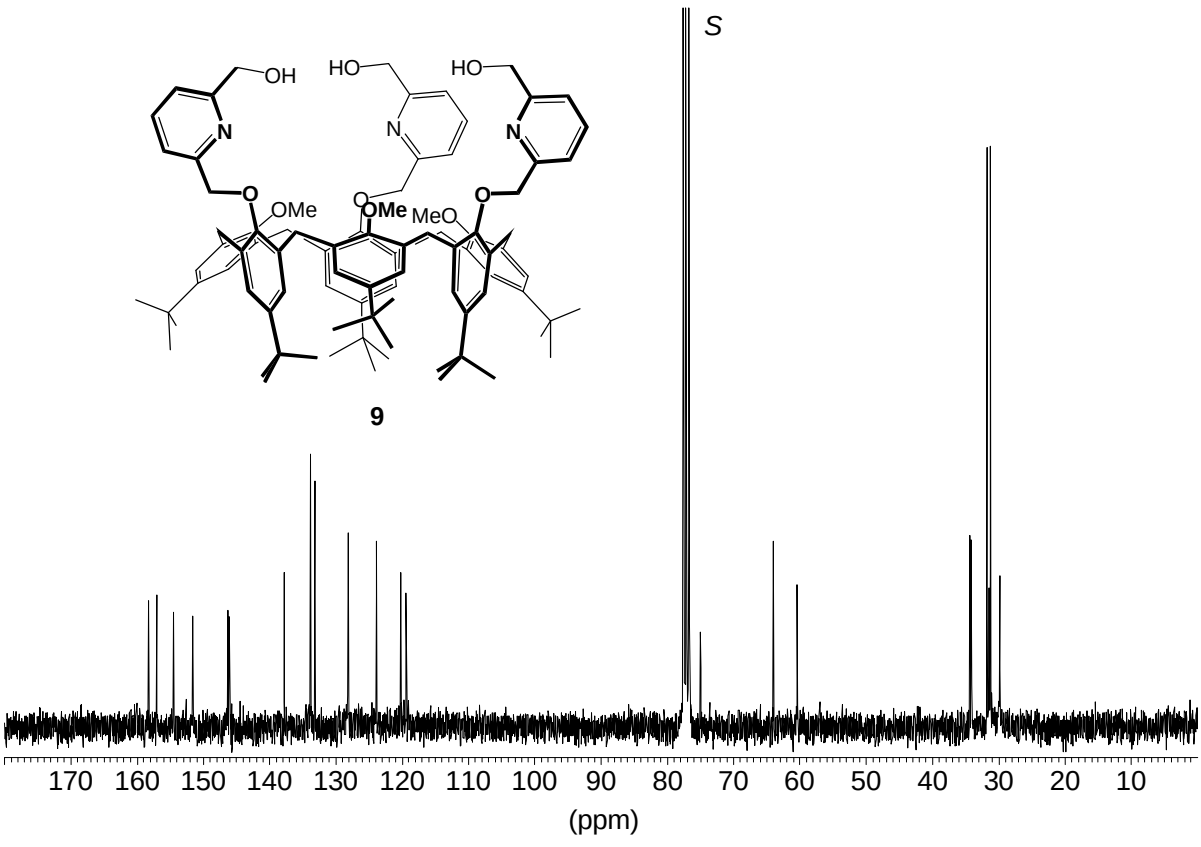


Figure S18. ^{13}C NMR spectrum (75 MHz, 293 K) of calix[6]arene derivative **9**. Residual solvent has been labeled “S”.

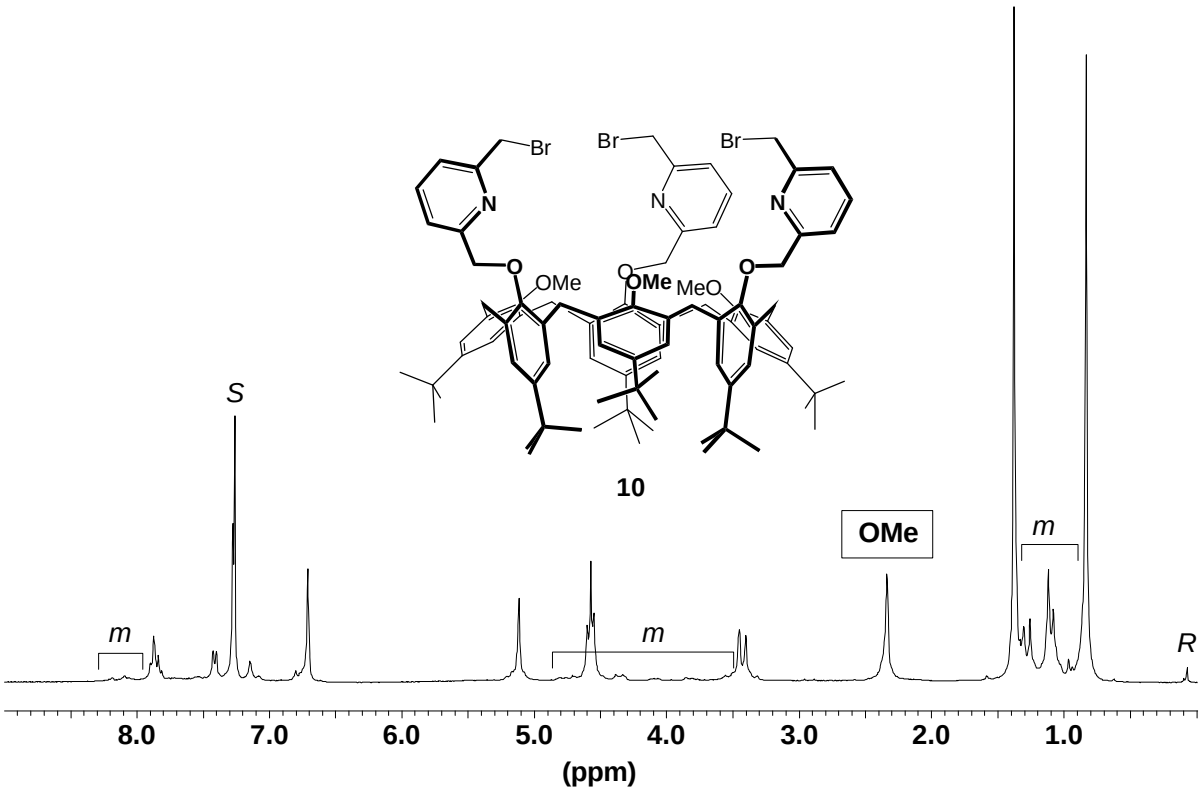


Figure S19. ^{1}H NMR spectrum (300 MHz, 293 K) of calix[6]arene derivative **10**. Residual solvent, reference and the minor conformation of **10** (see the theoretical part) have been labeled “S”, “R” and “m” respectively.

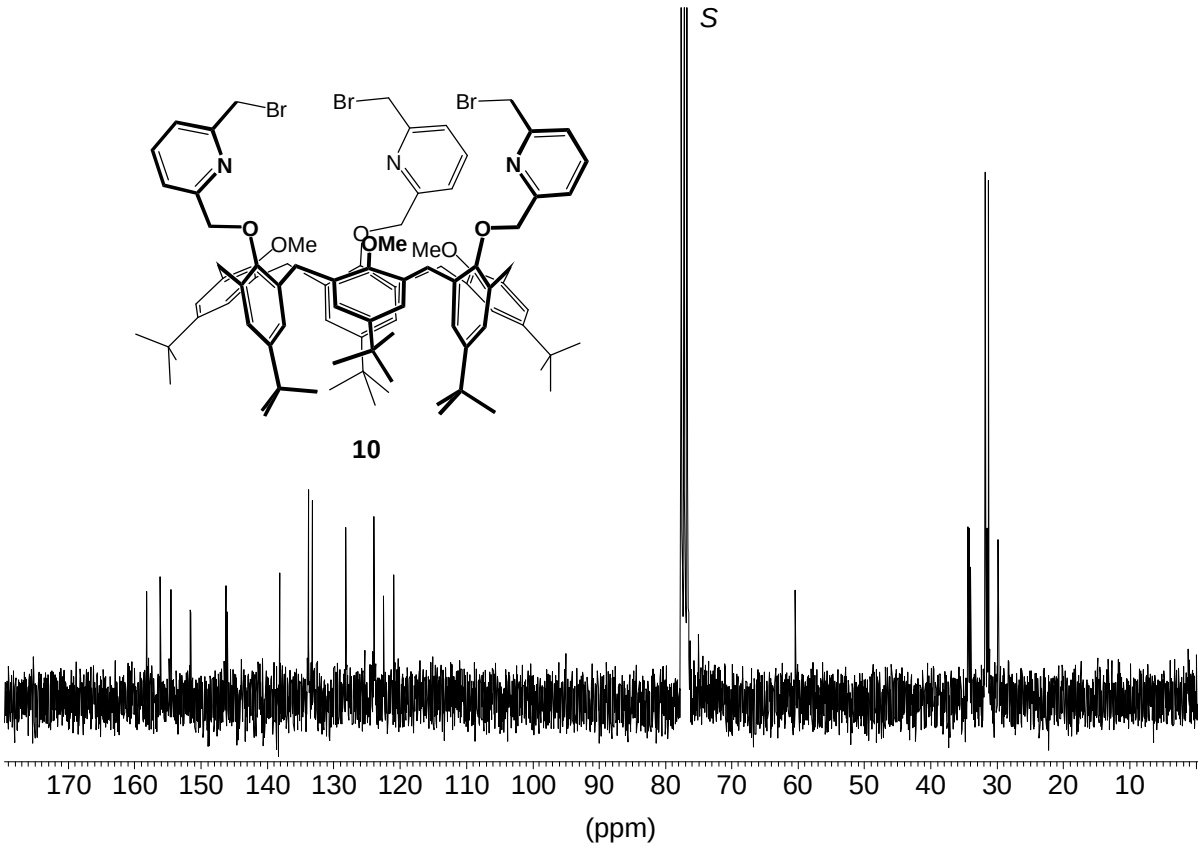


Figure S20. ^{13}C NMR spectrum (75 MHz, 293 K) of calix[6]arene derivative **10**. Residual solvent has been labeled “S”.

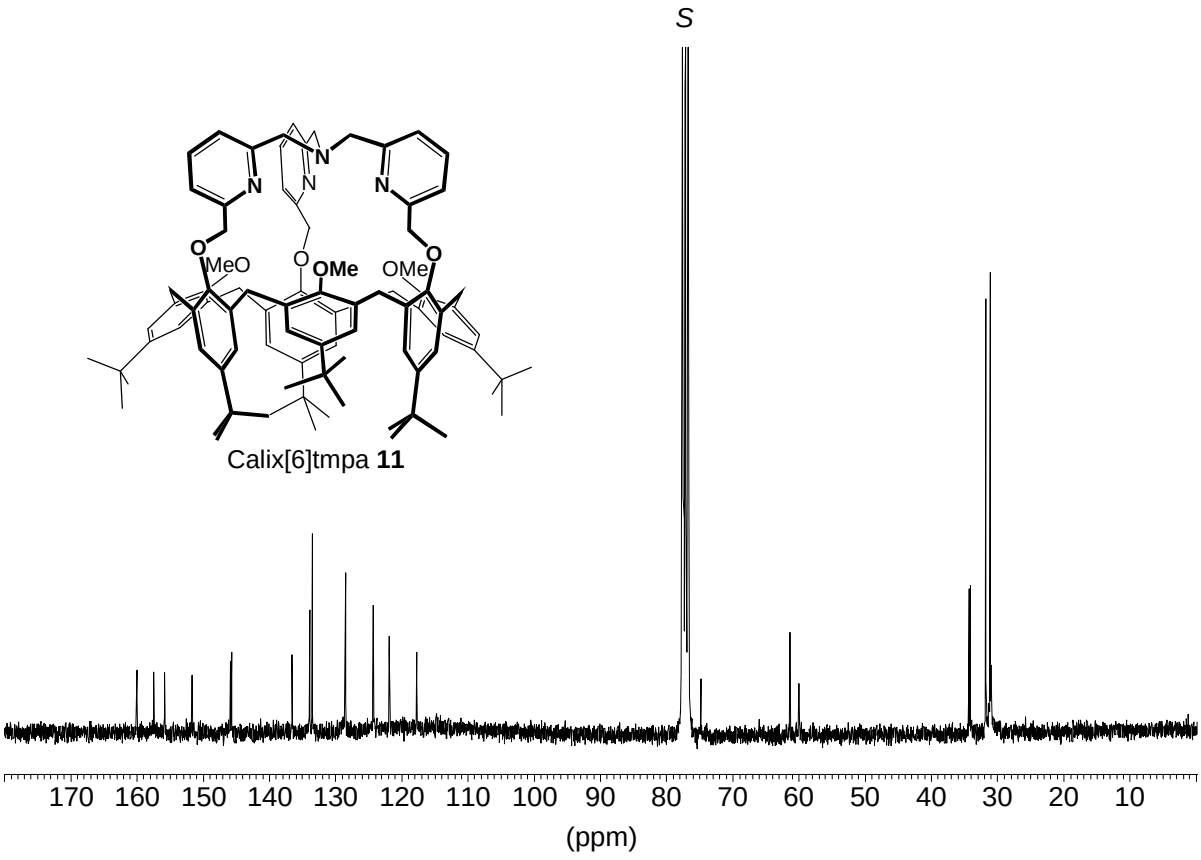


Figure S21. ^{13}C NMR spectrum (75 MHz, 293 K) of calix[6]tmpa **11**. Residual solvent has been labeled “S”.

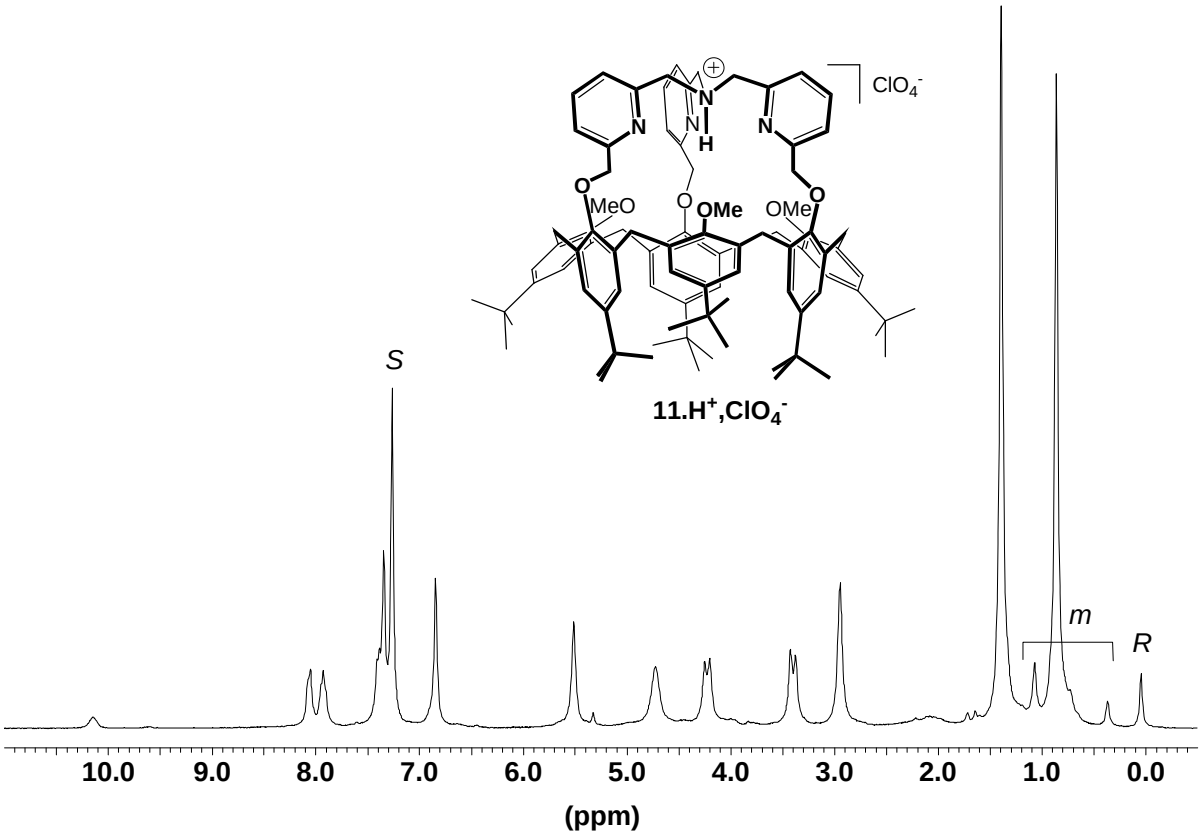


Figure S22. ^{1}H NMR spectrum (300 MHz, 220 K) of compound **11.H^{+},ClO$_4^{-}$**. Residual solvent, reference and the minor conformation of **11.H^{+},ClO$_4^{-}$** (see the theoretical part) have been labeled “S”, “R” and “m” respectively.

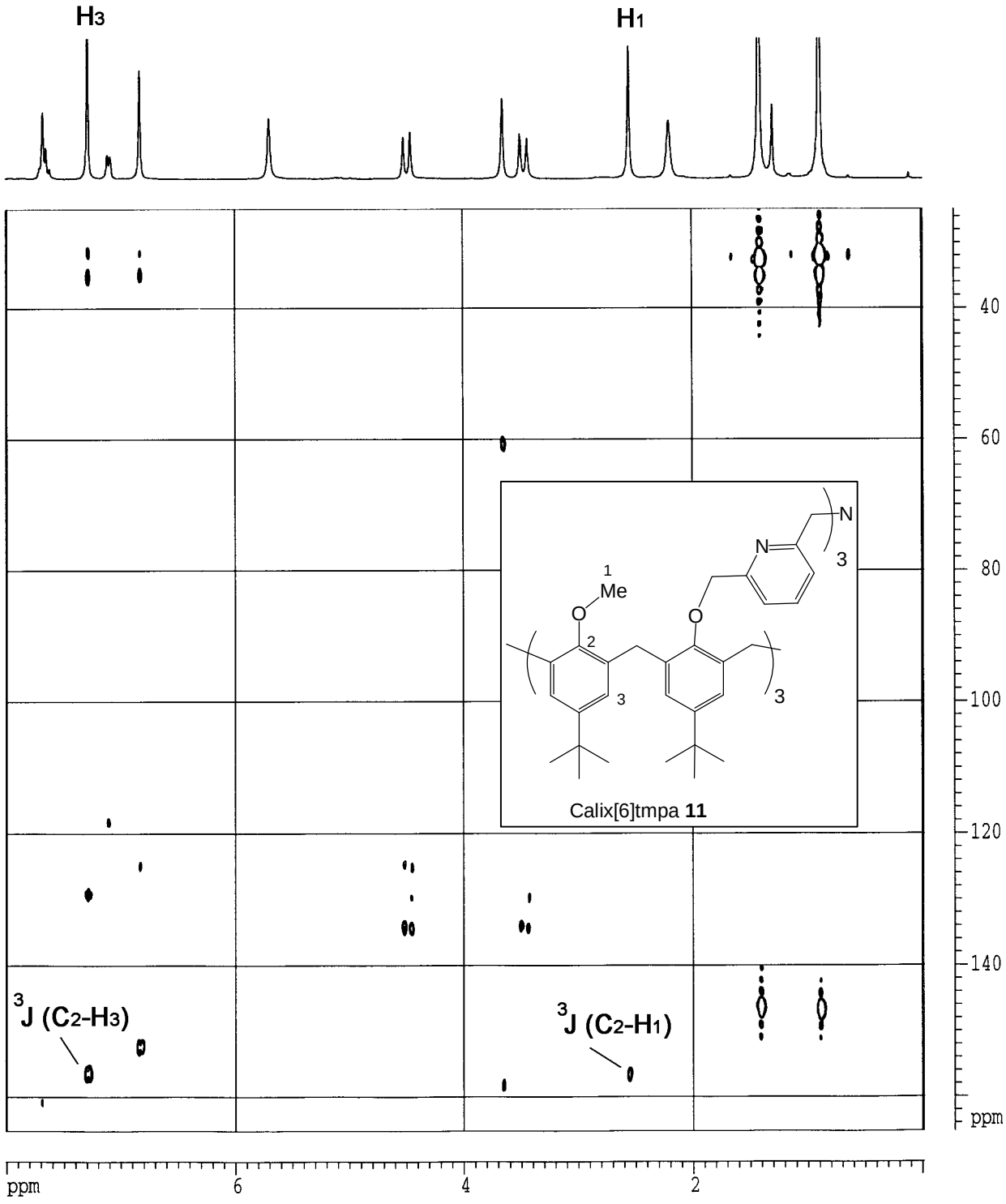


Figure S23. HMBC spectrum (293 K) of calix[6]tmpa **11**.

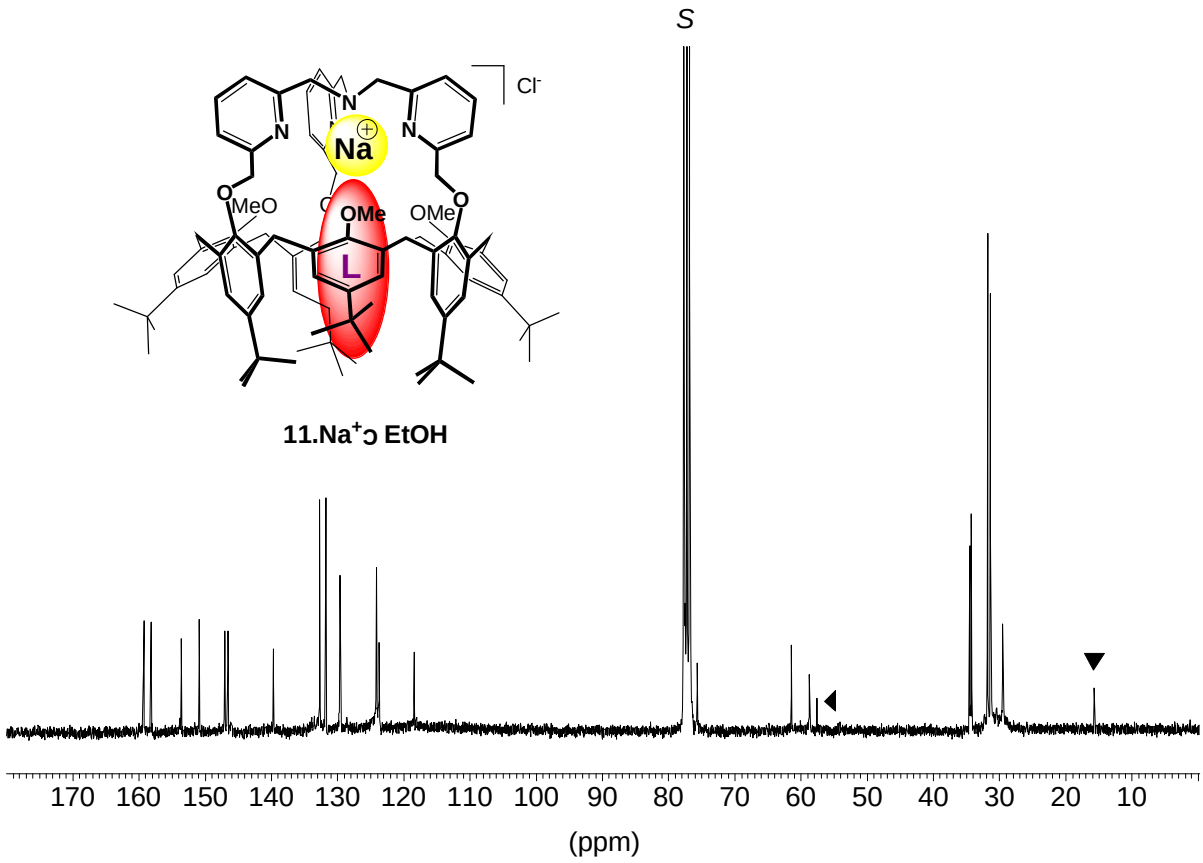


Figure S24. ^{13}C NMR spectrum (75 MHz, 293 K) of endo-complex **11.Na$^+$? EtOH**. Residual solvent has been labeled "S". ? : included EtOH.

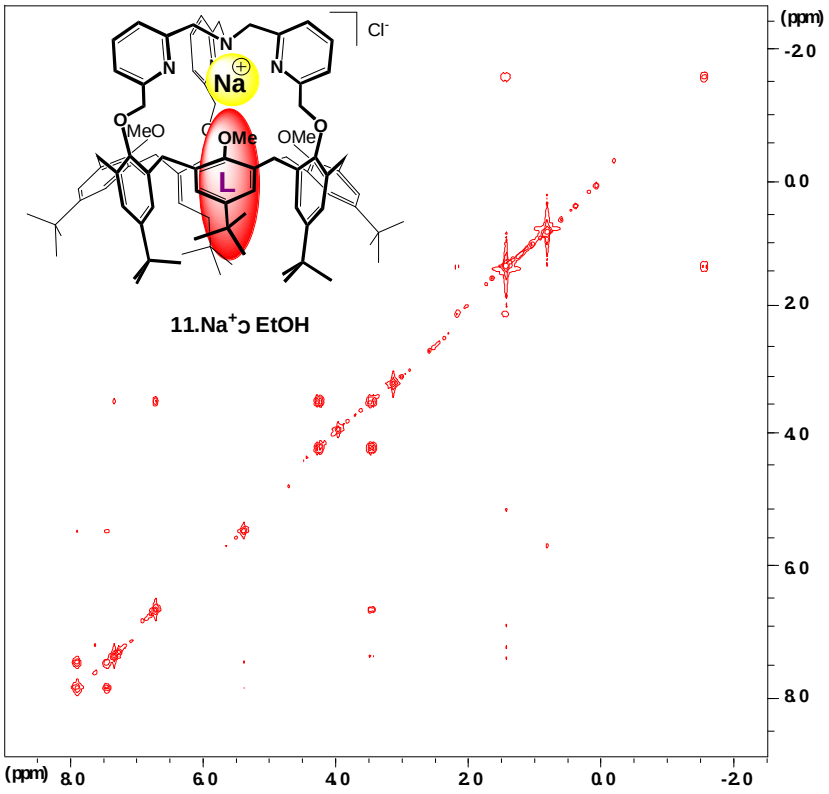
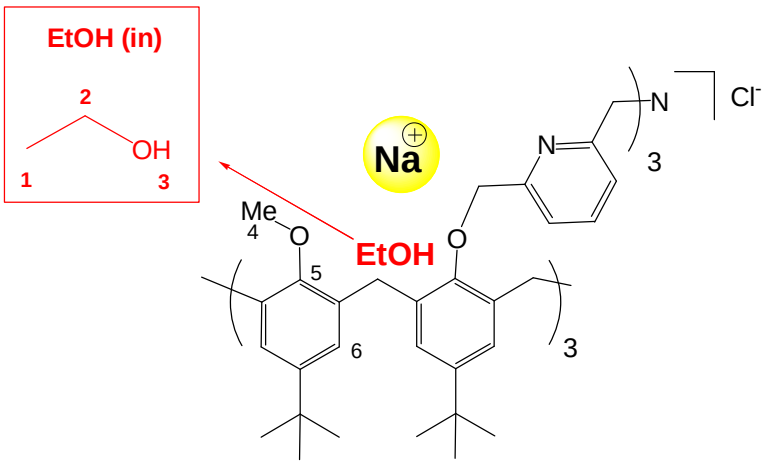


Figure S25. COSY spectrum (293 K) of endo-complex **11.Na$^+$? EtOH**.



Endo-complex **11.Na$^+$⊃EtOH**

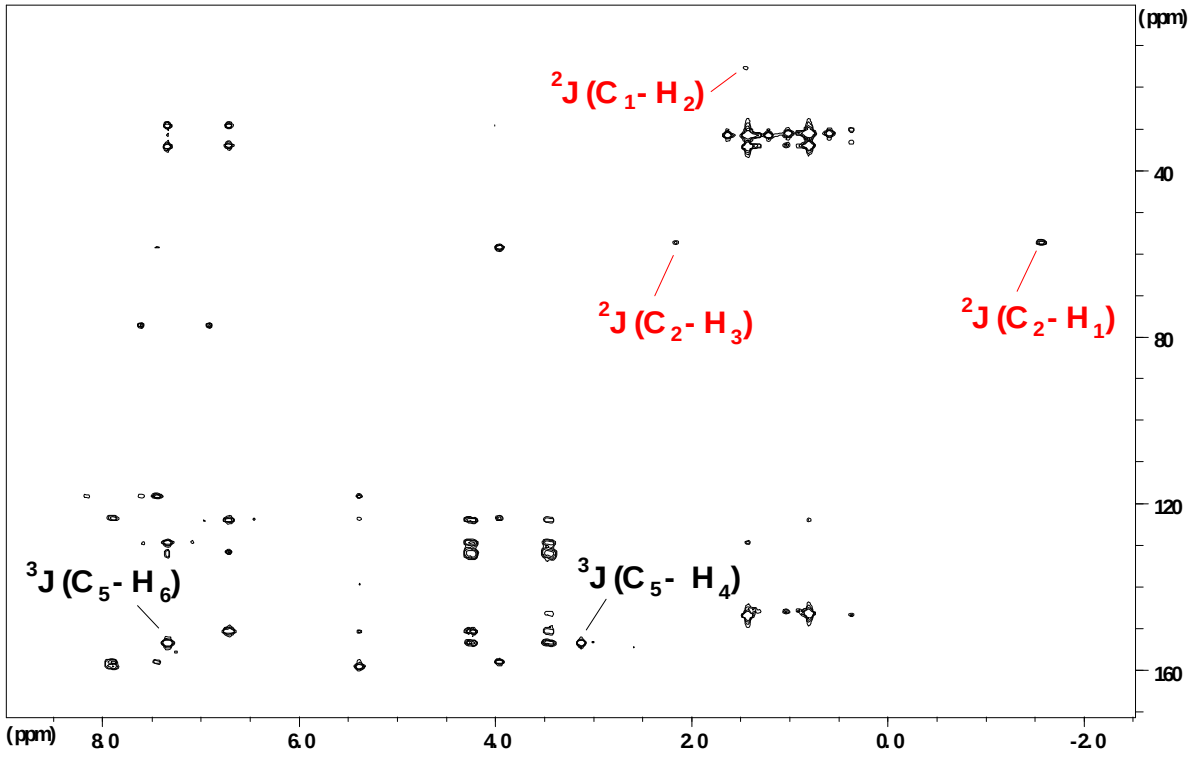
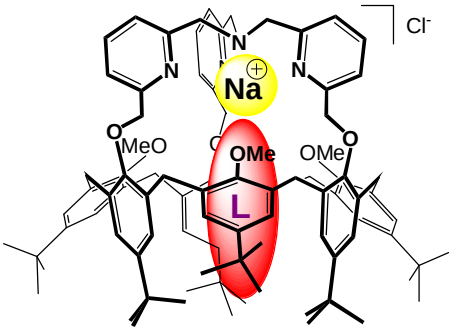


Figure S26. HMBC spectrum (293 K) of endo-complex **11.Na$^+$⊃EtOH**.



11.Na$^+$ EtOH

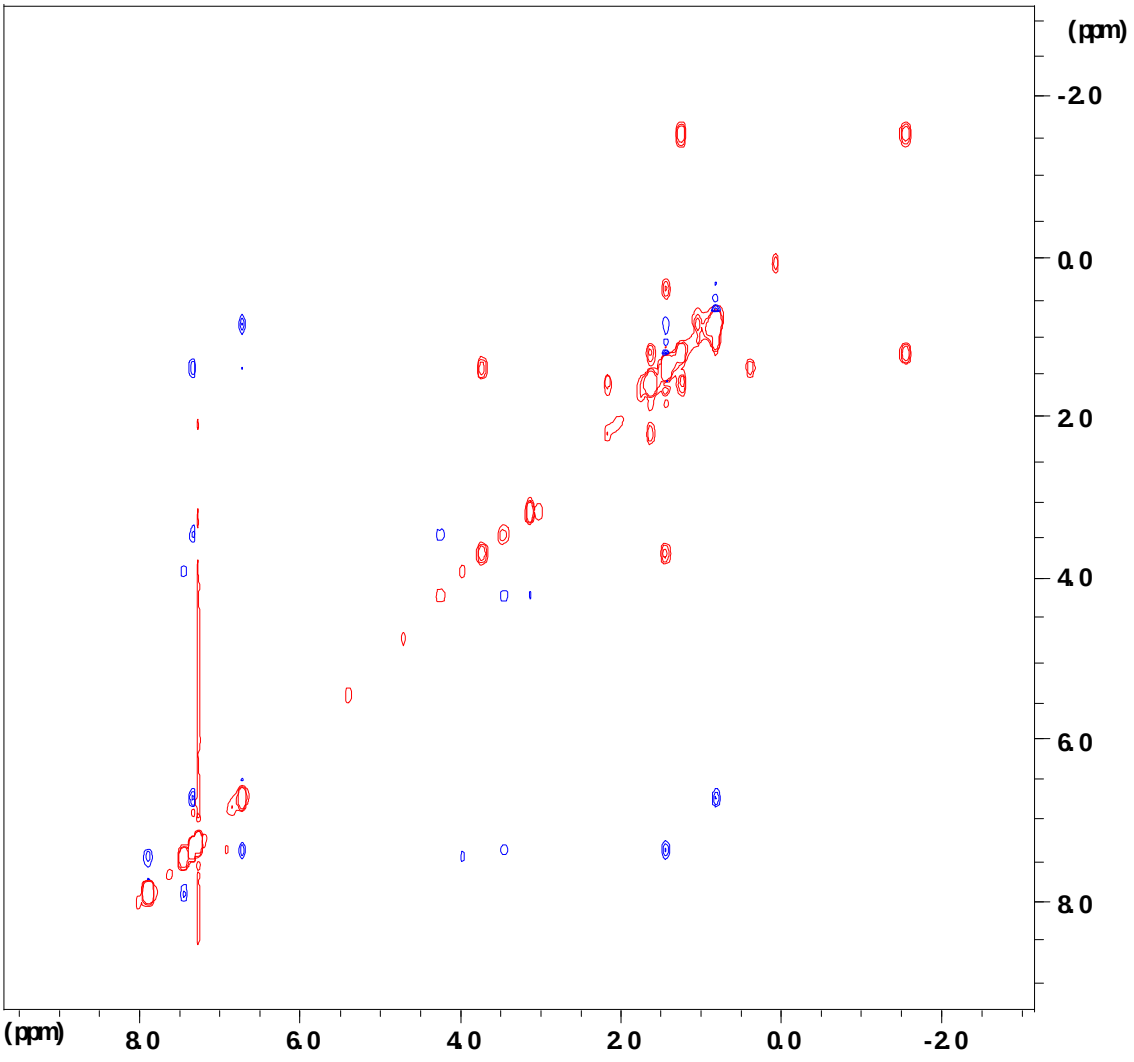


Figure S27. NOESY spectrum (293 K) of endo-complex **11.Na$^+$ EtOH**.