

Supporting Information

Unexpected Chemistry of Thiacalix[4]arene Monosulfoxide

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1. Spectral characterization of compounds

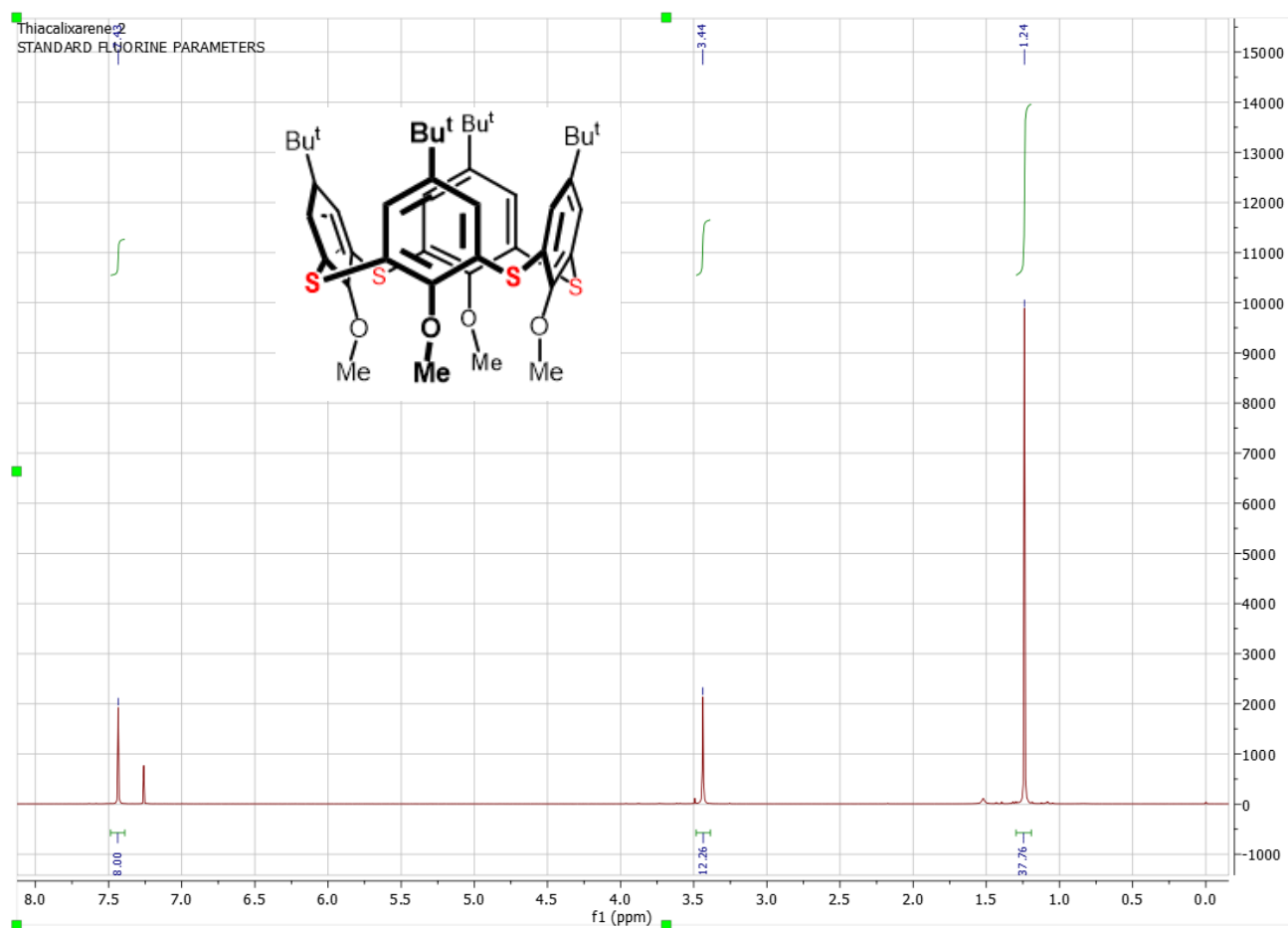


Figure S1: ¹H NMR of compound tetramethoxy derivative **2** (CDCl₃, 400 MHz).

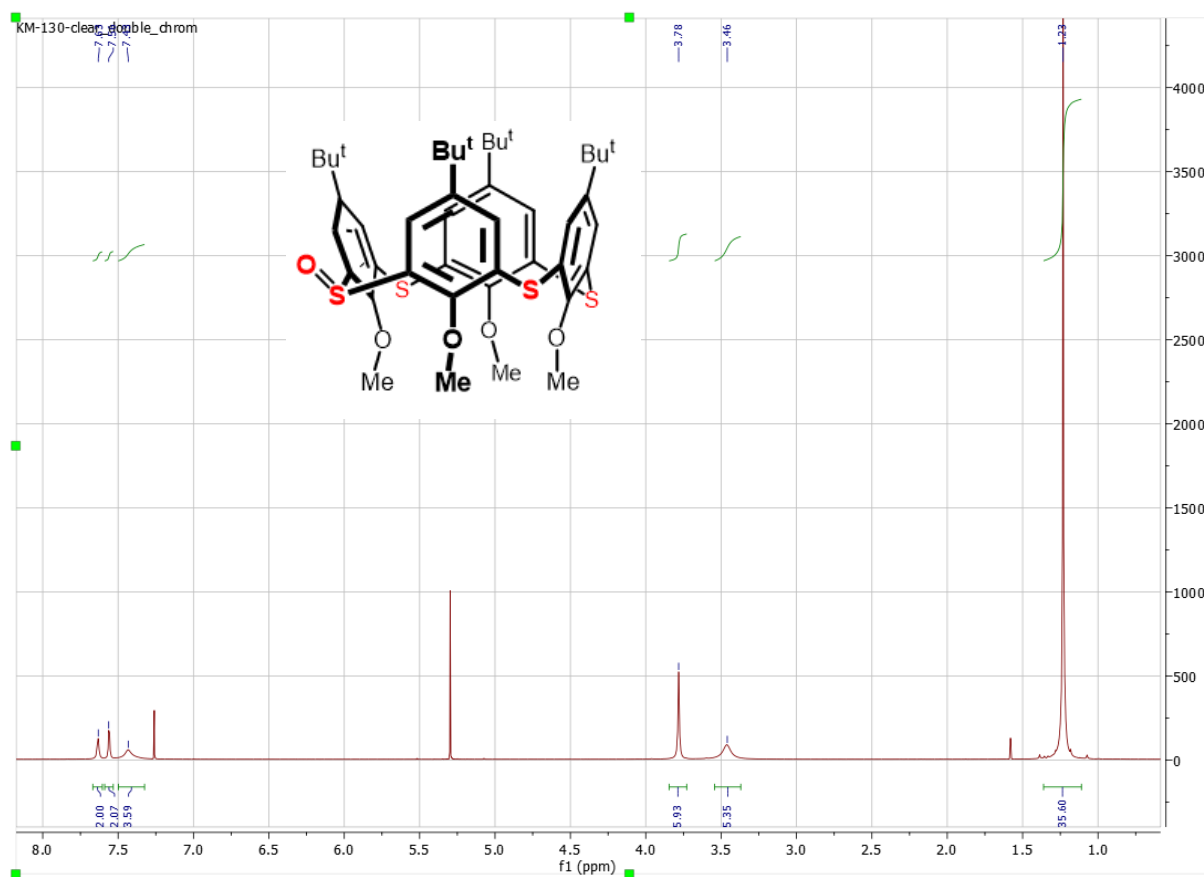


Figure S2: ¹H NMR of compound 3 (CDCl₃, 400 MHz).

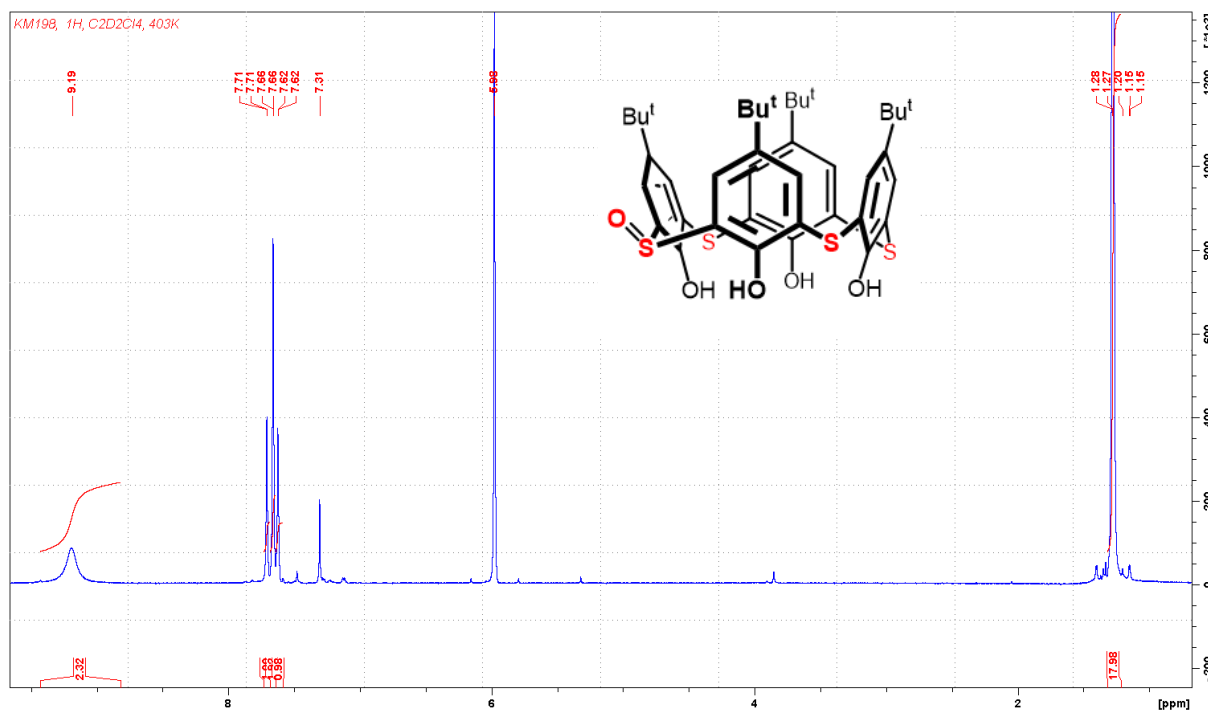


Figure S3: ¹H NMR of compound 4 (C₂D₂Cl₄, 500 MHz, 403 °K).

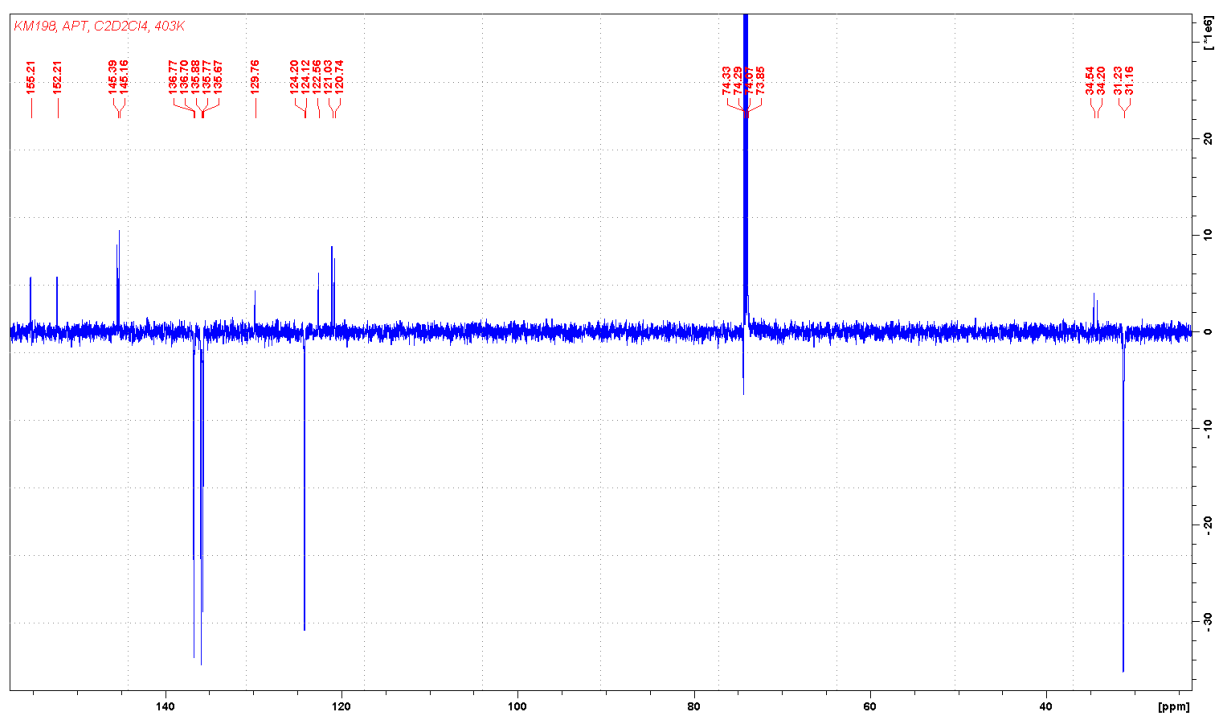


Figure S4: ^{13}C (APT) NMR of compound 4 ($\text{C}_2\text{D}_2\text{Cl}_4$, 100 MHz, 403 °K)

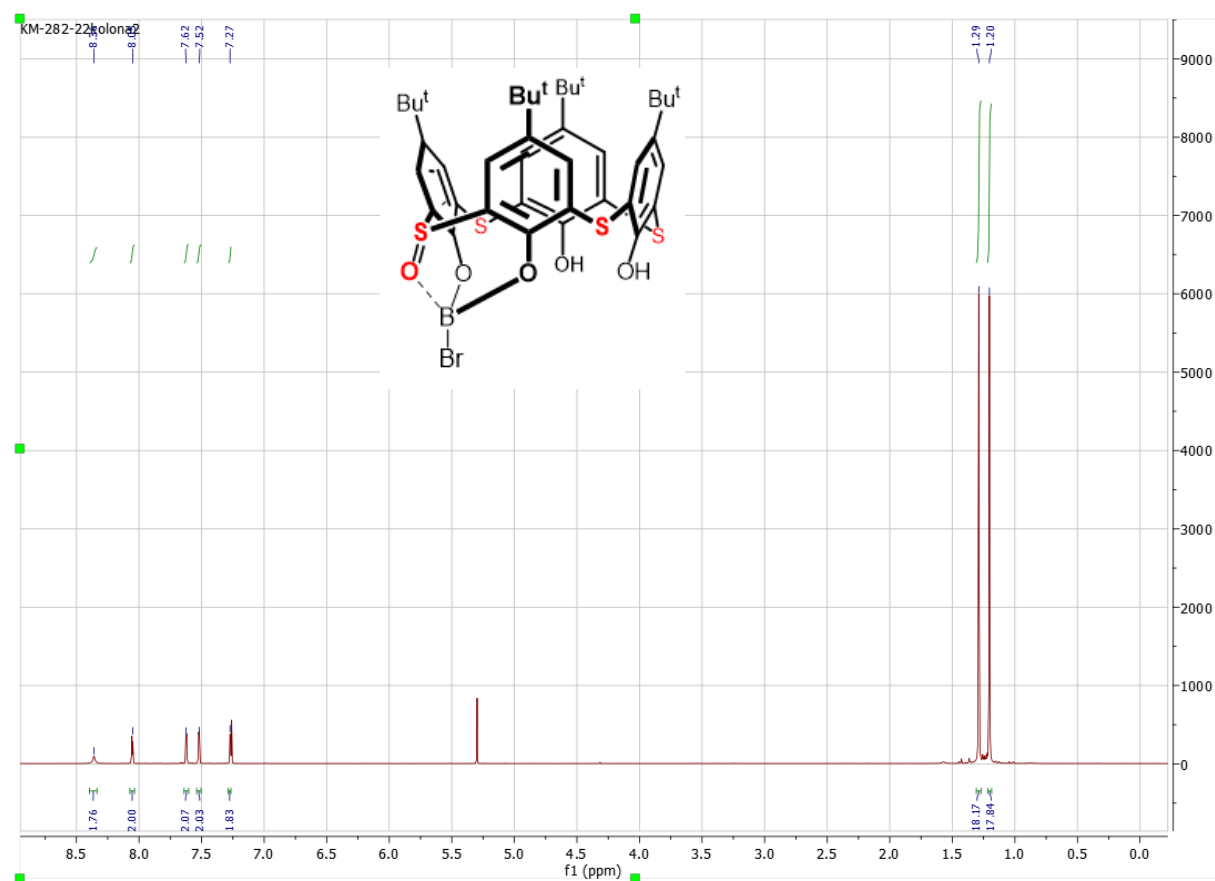


Figure S5: ^1H NMR of compound 5 (CDCl_3 , 400 MHz).

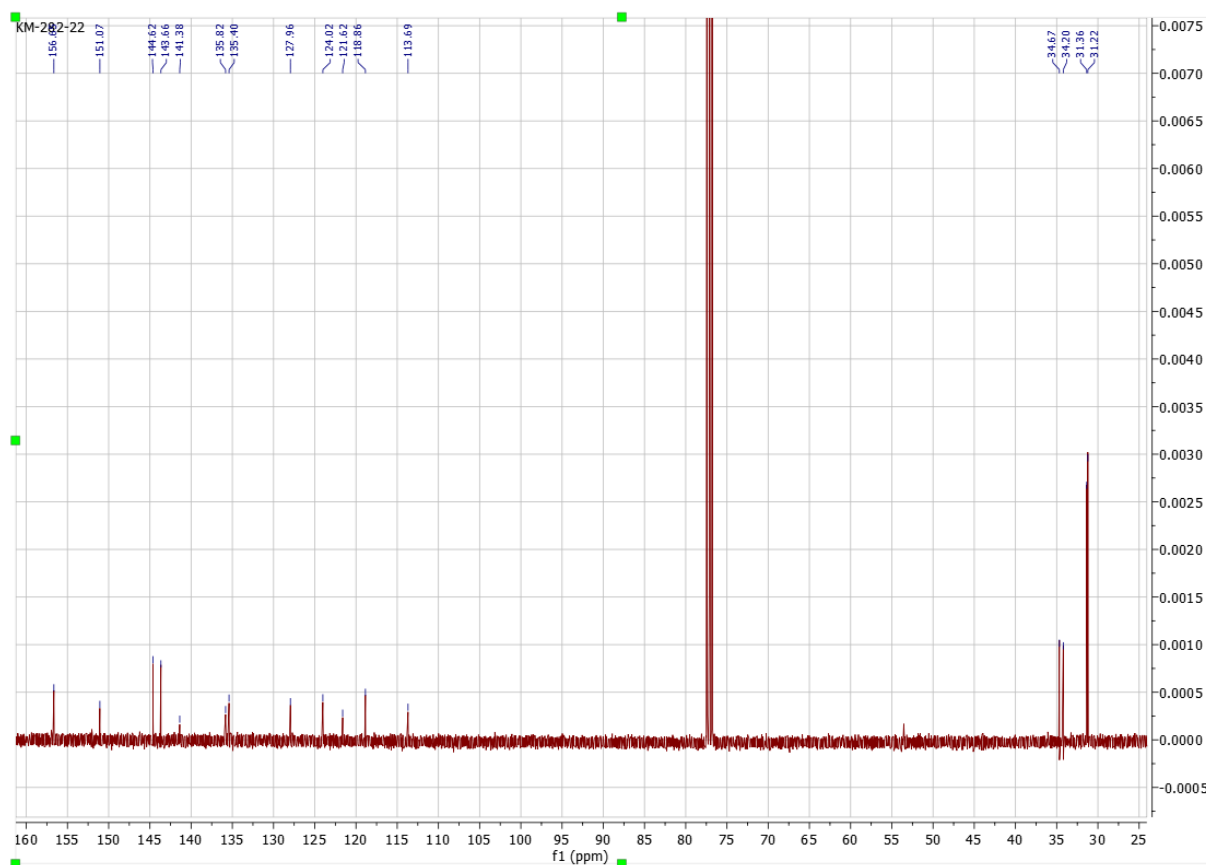


Figure S6: ^{13}C NMR of compound **5** (CDCl_3 , 100 MHz)

335_Mamleev_ESIpos_KM-259-C_1
MetOH

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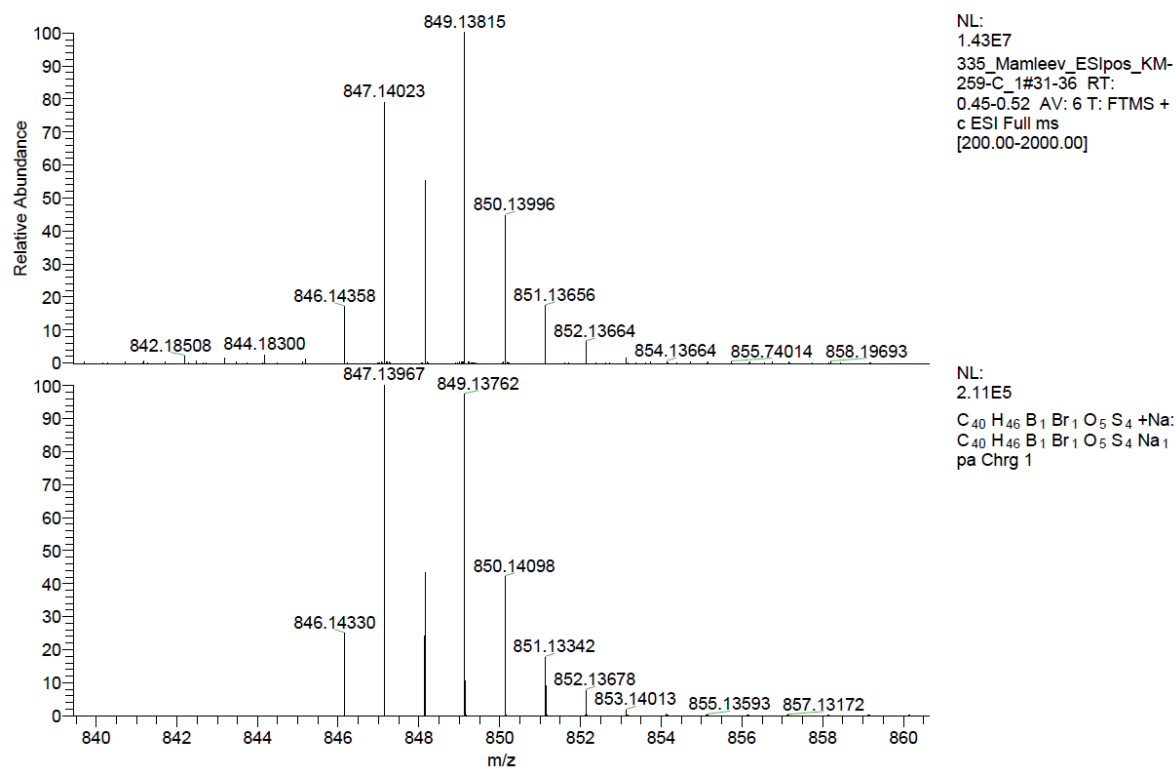


Figure S7: HRMS of compound **5** (ESI^+).

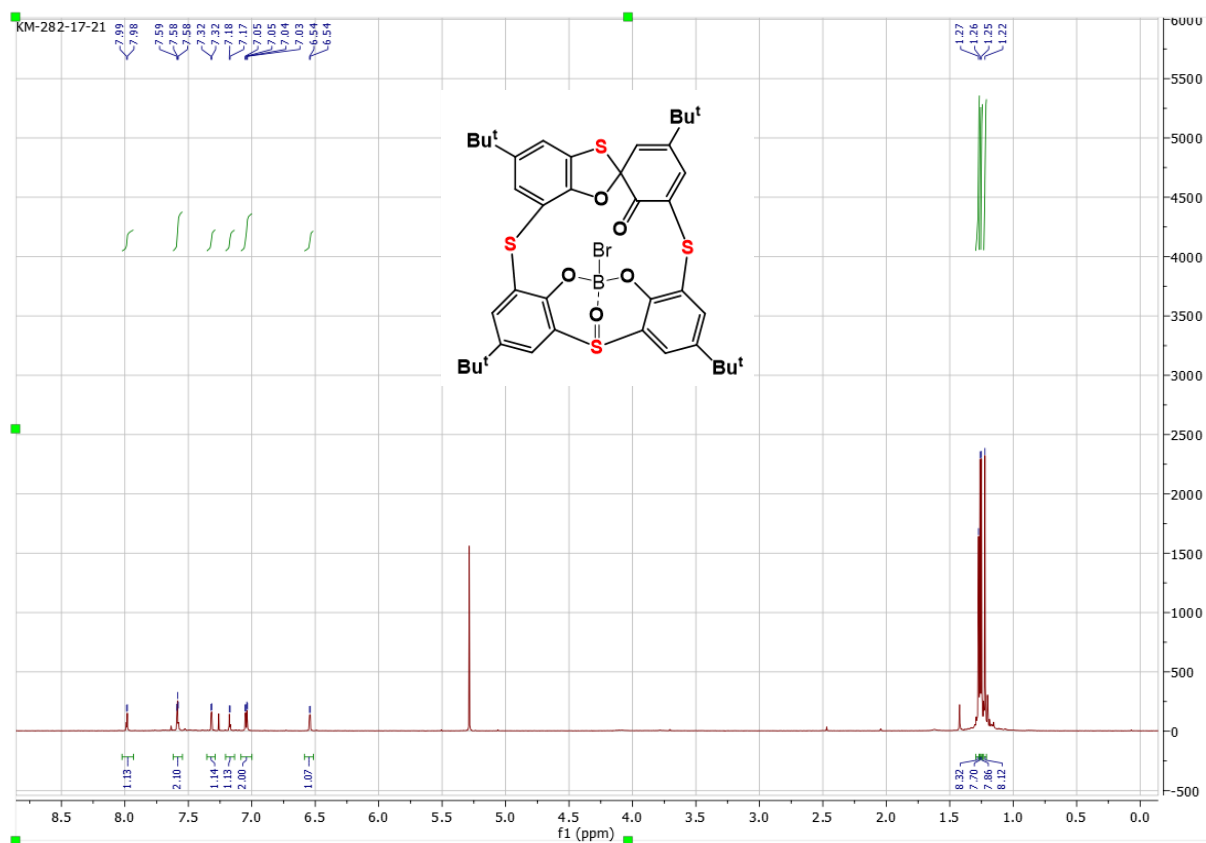


Figure S8: ¹H NMR of compound 6 (CDCl₃, 400 MHz).

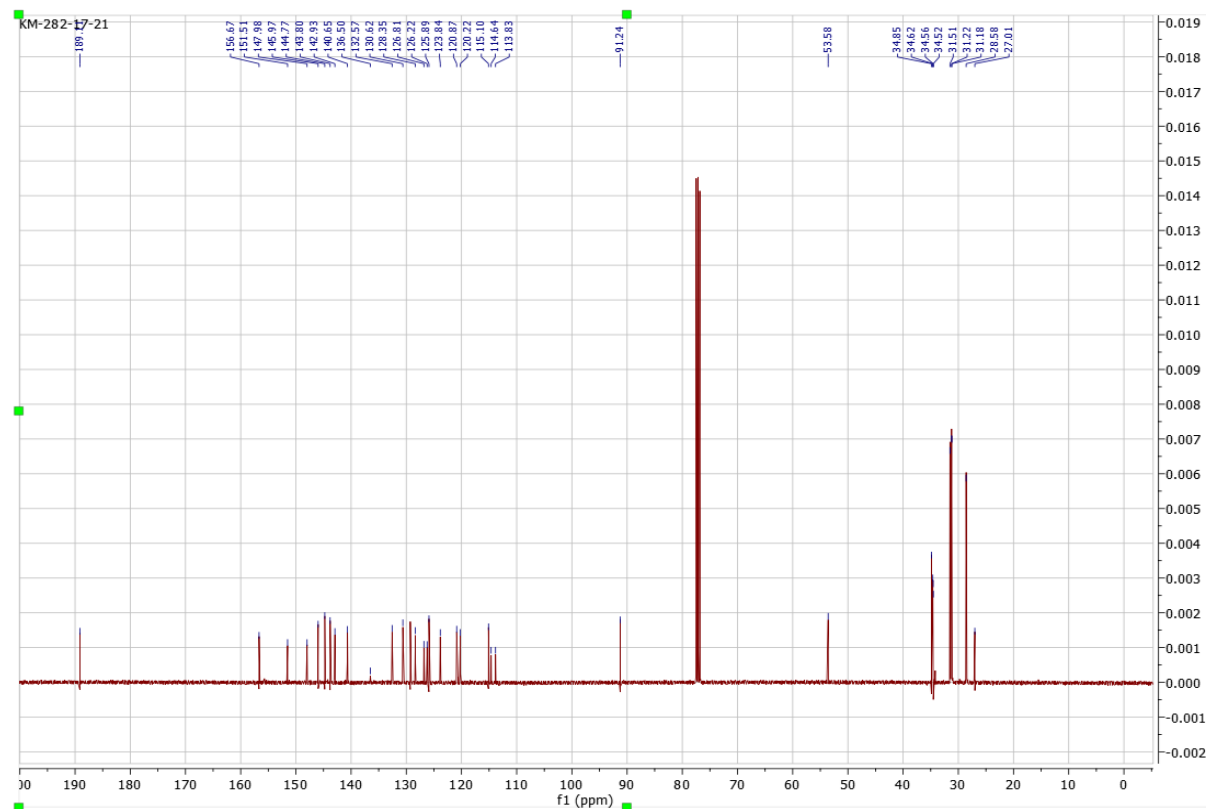


Figure S9: ¹³C NMR of compound 6 (CDCl₃, 100 MHz)

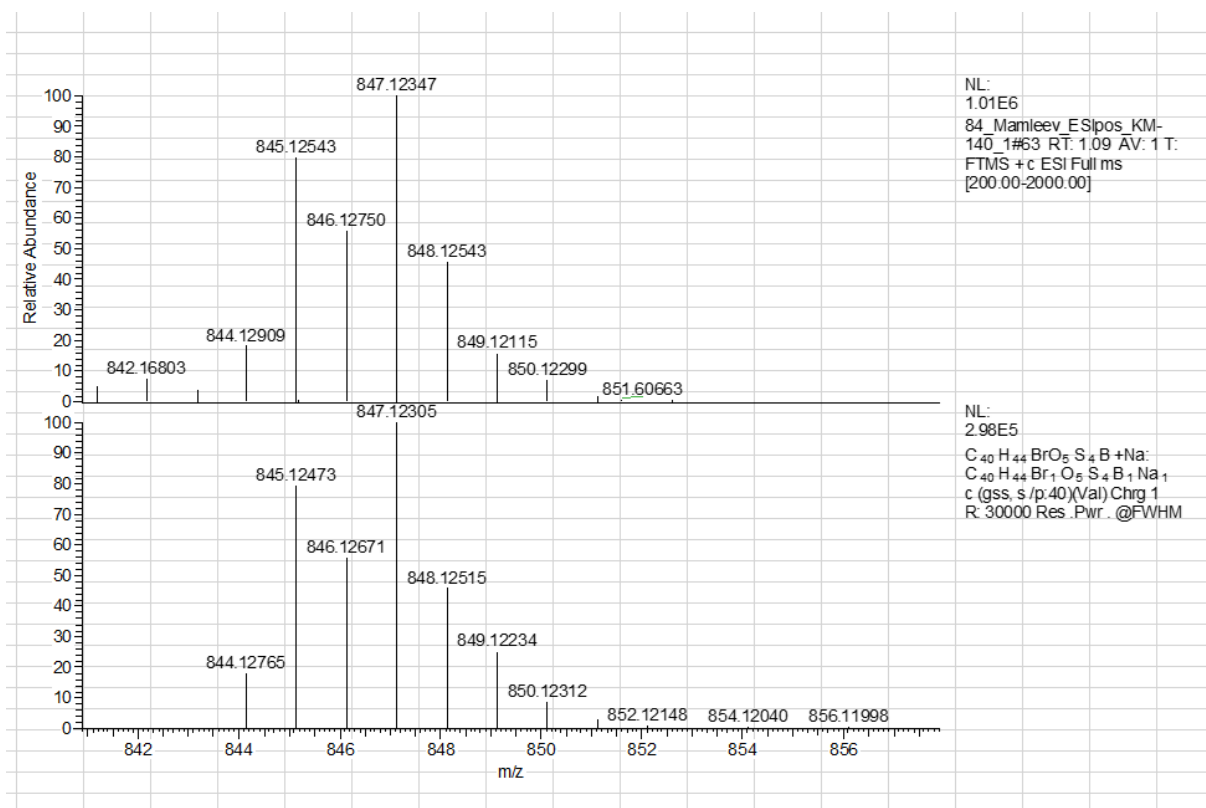


Figure S10: HRMS of compound 6 (ESI⁺).

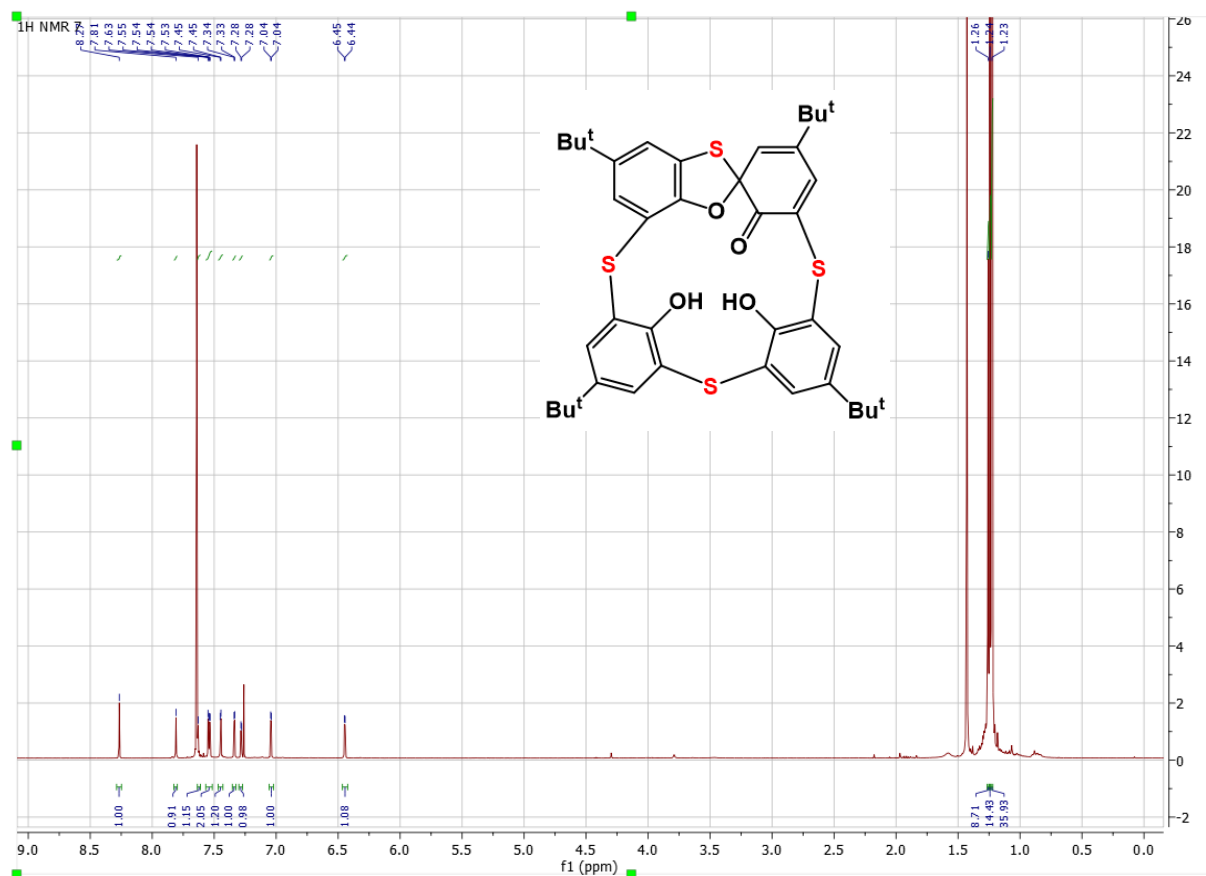


Figure S11: ¹H NMR of compound 7 (CDCl₃, 400 MHz).

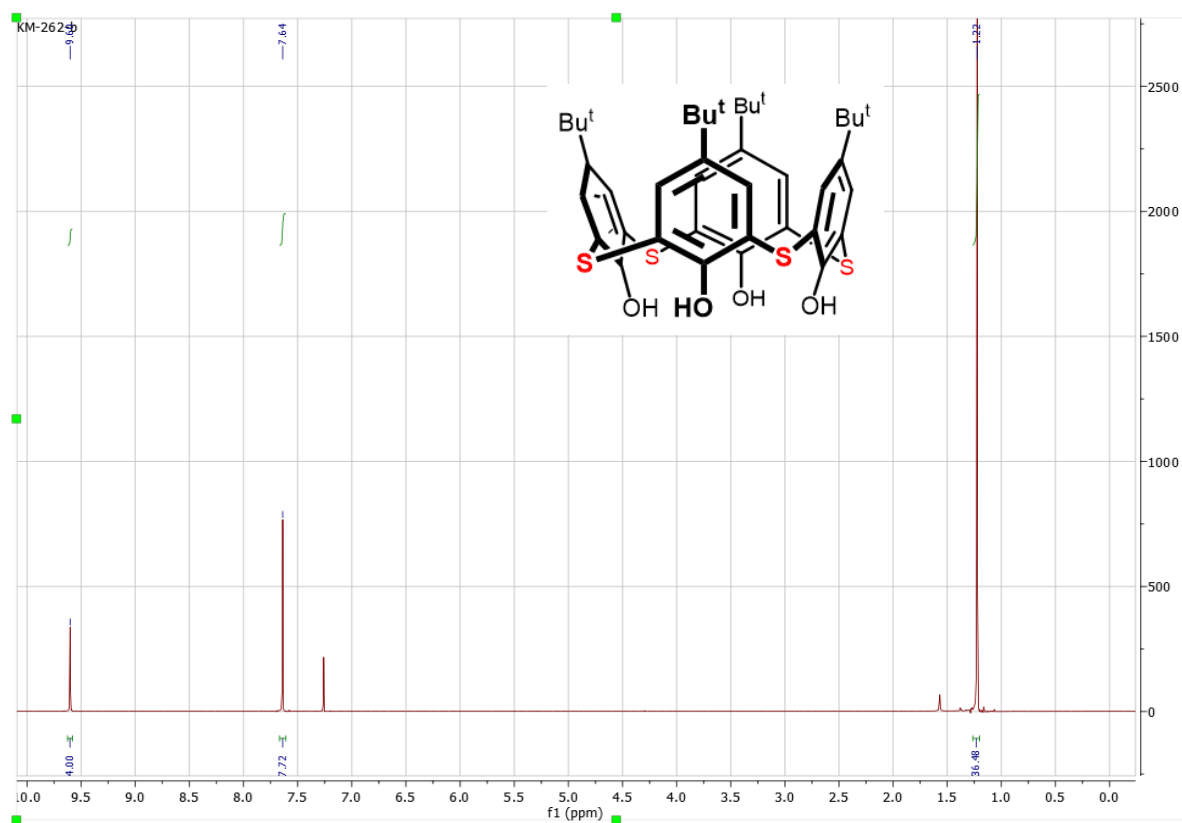


Figure S12: ^1H NMR of compound **1** (CDCl_3 , 400 MHz).

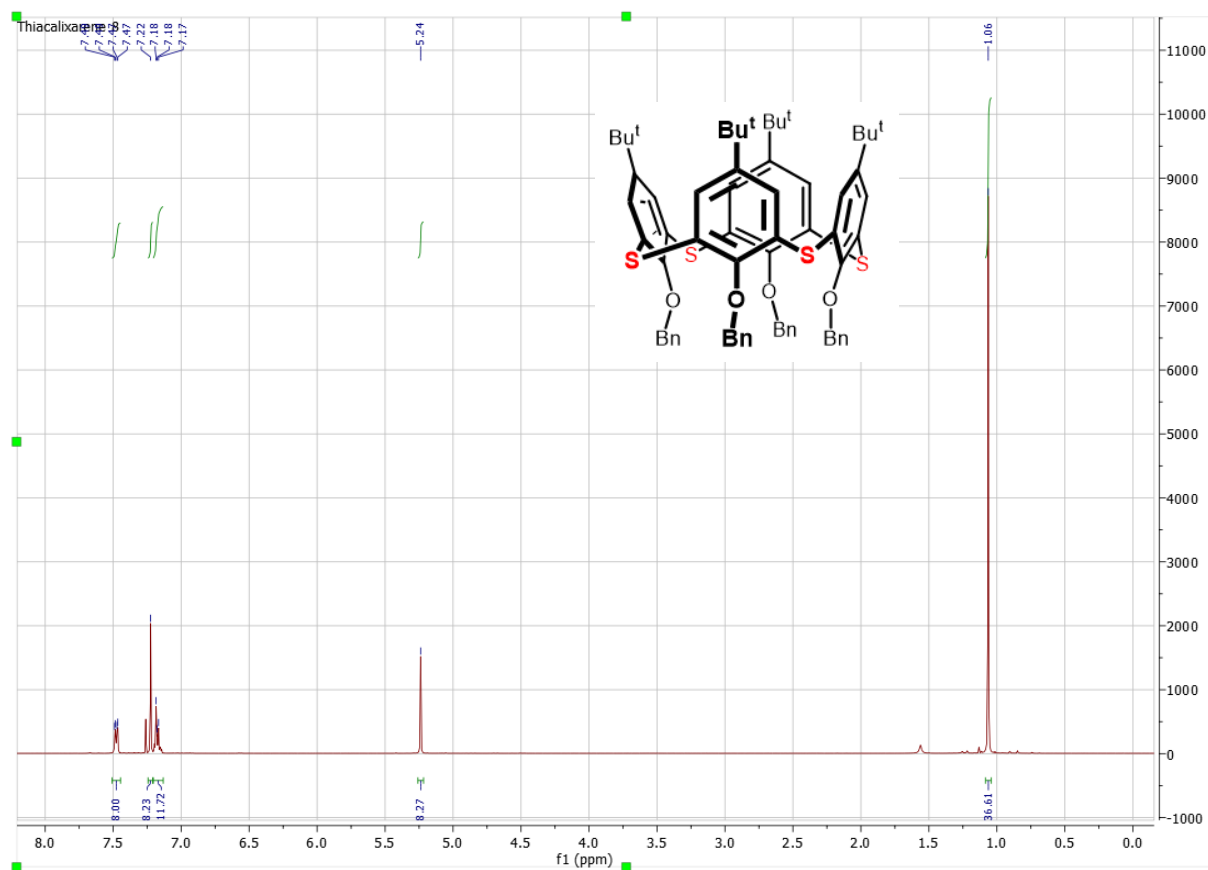


Figure S13: ^1H NMR of compound **8** (CDCl_3 , 400 MHz).

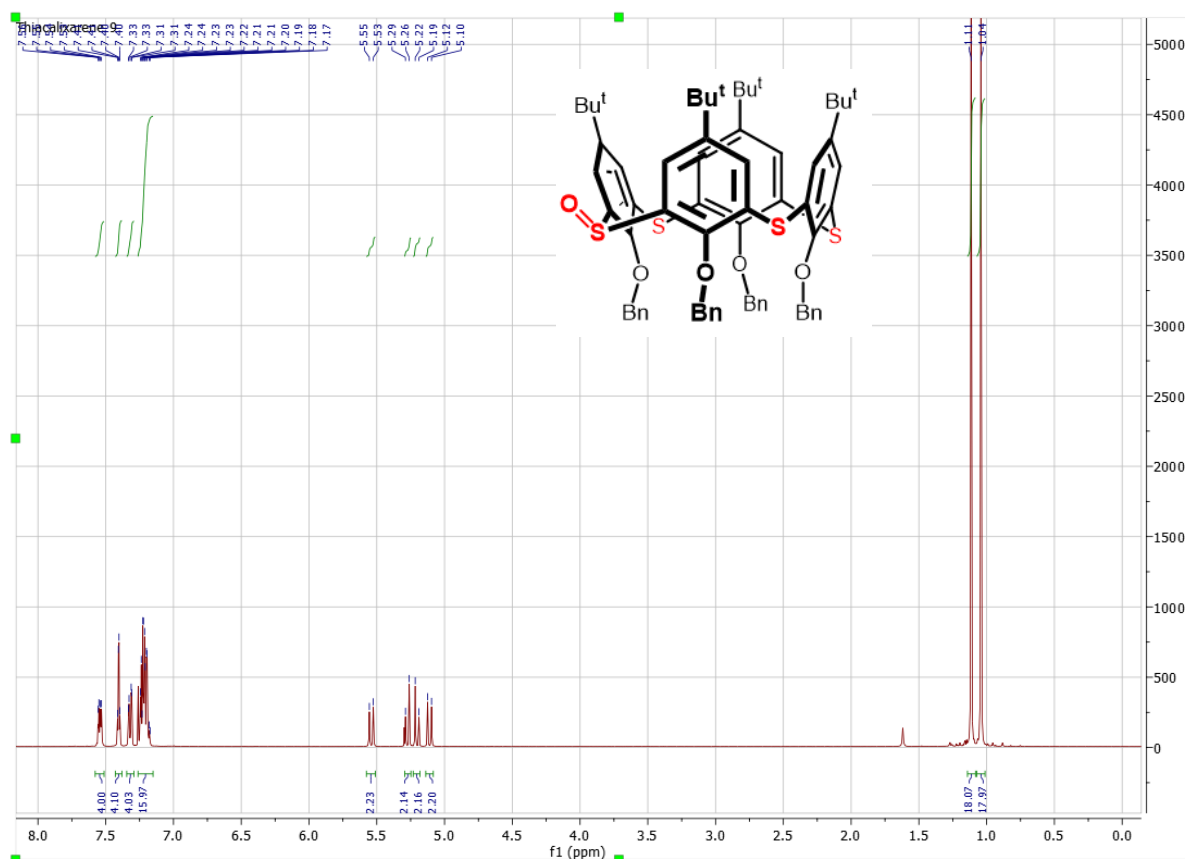


Figure S14: ¹H NMR of compound **9** (CDCl₃, 400 MHz).

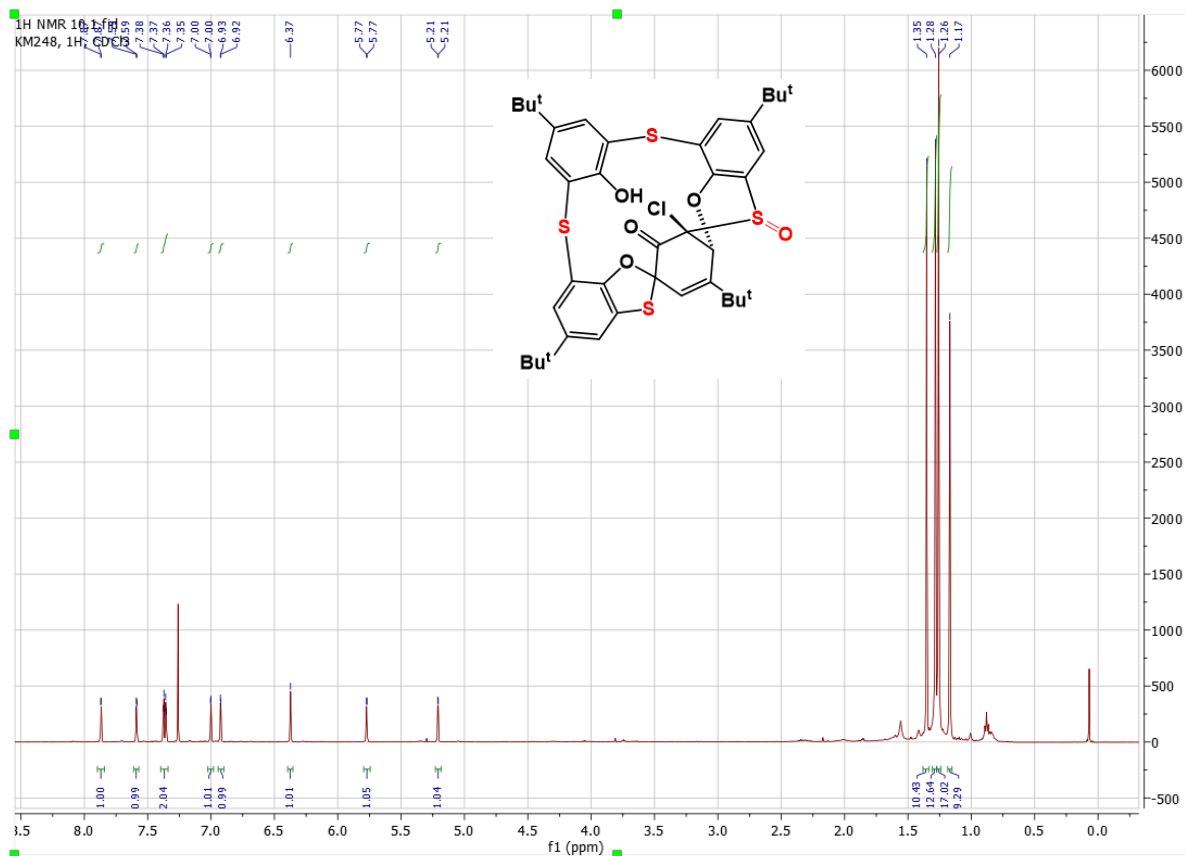


Figure S15: ¹H NMR of compound **10** (CDCl₃, 400 MHz).

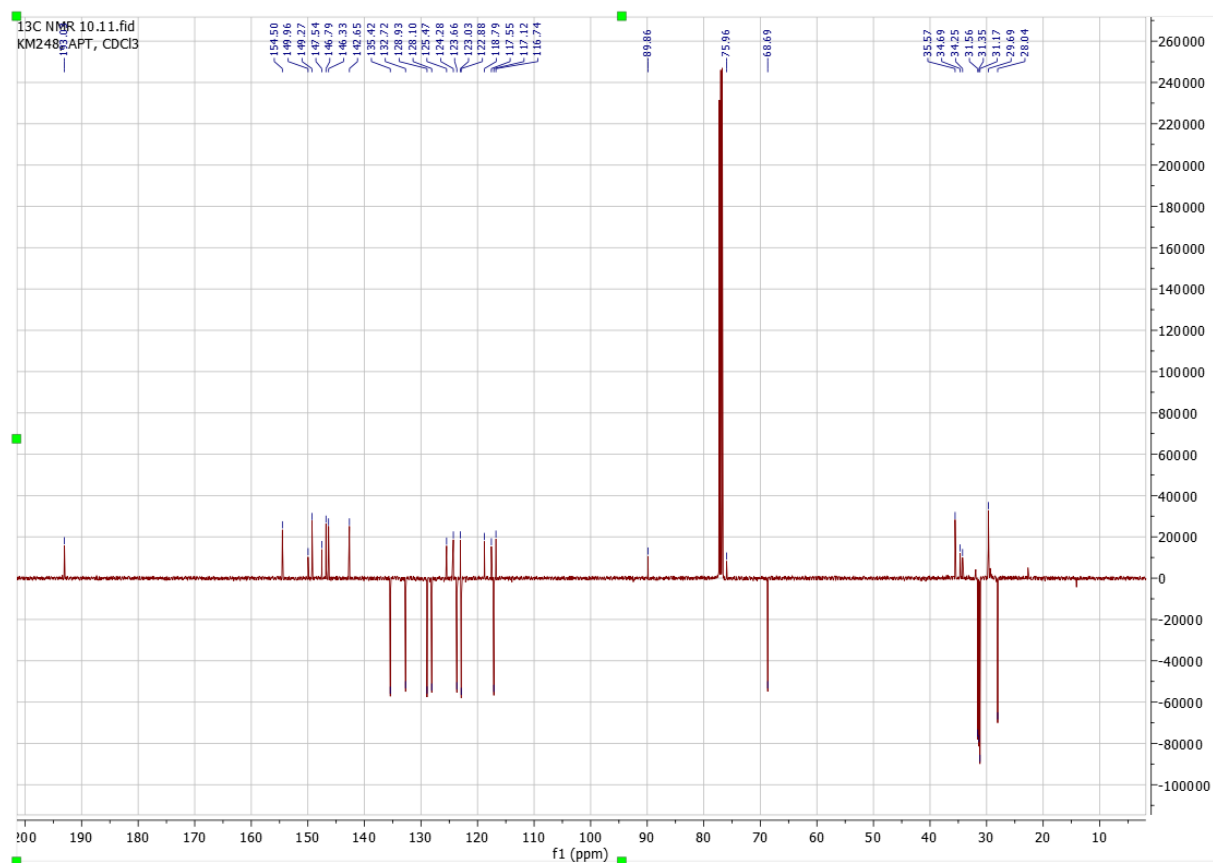


Figure S16: ¹³C(APT) NMR of compound **10** (CDCl₃, 100 MHz)

194_Mamleev_ESIpos_KM-248_1
MeOH

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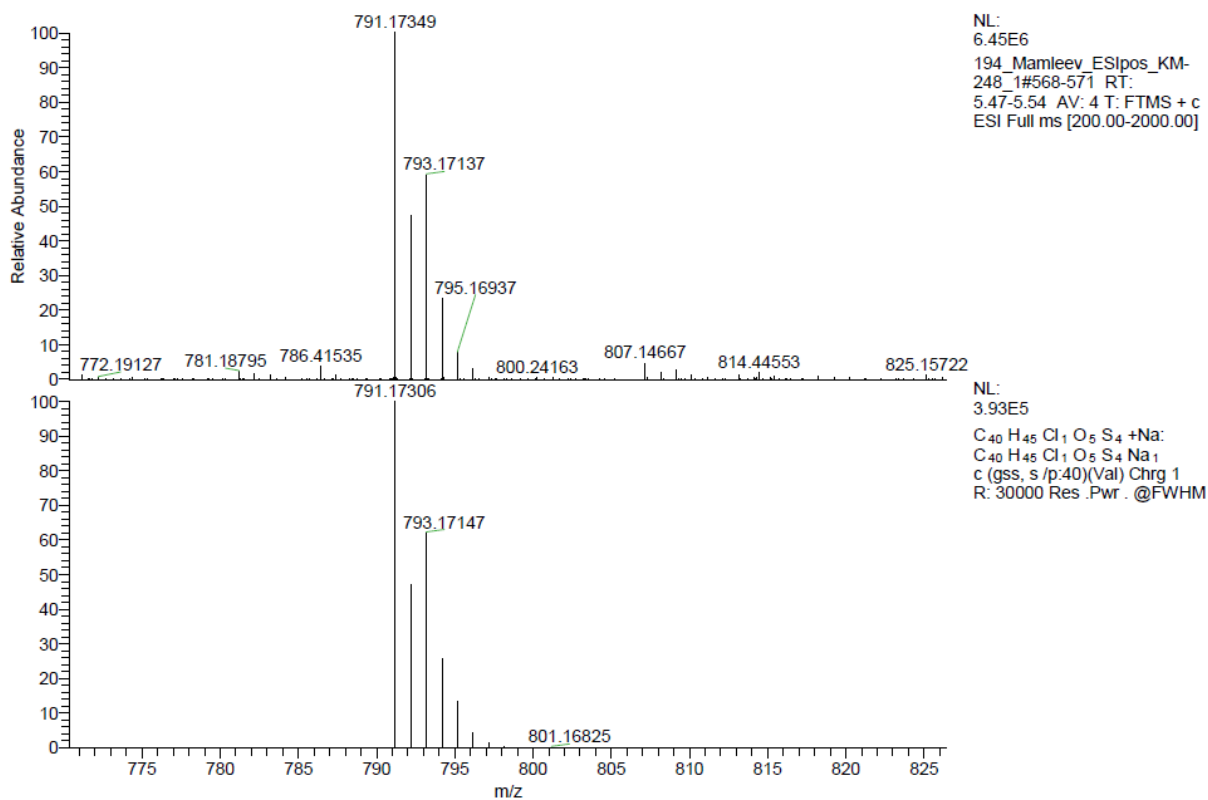


Figure S17: HRMS of compound **10** (ESI⁺).

2. The Variable Temperature (VT) NMR experiments

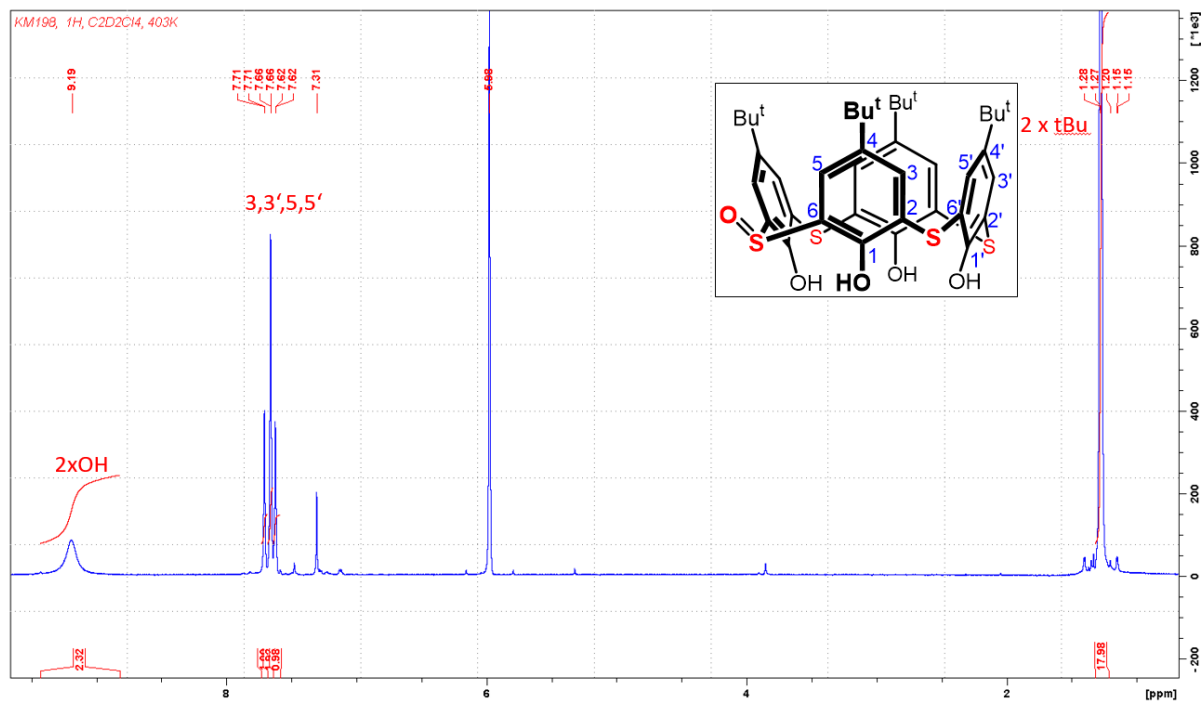


Figure S18: ^1H NMR of compound 4 ($\text{C}_2\text{D}_2\text{Cl}_4$, 500 MHz, 403 °K)

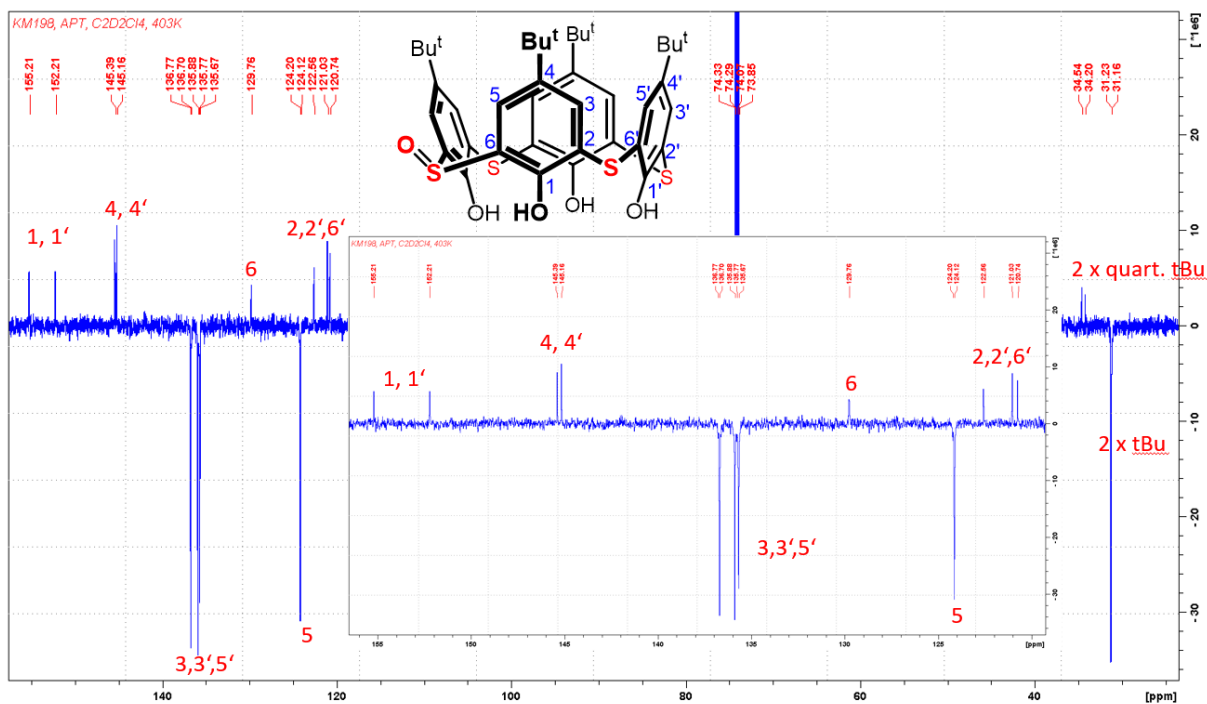


Figure S19: ^{13}C NMR of compound 4 ($\text{C}_2\text{D}_2\text{Cl}_4$, 100 MHz, 403 °K)

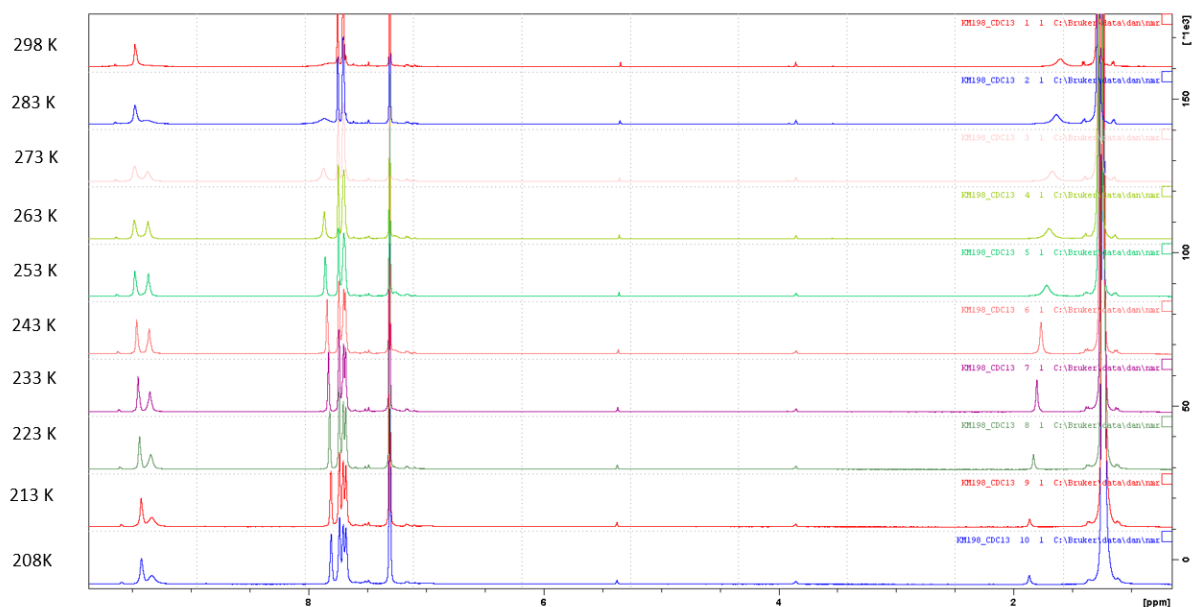


Figure S20: ^1H NMR of compound **4** (CDCl_3 , 500 MHz).

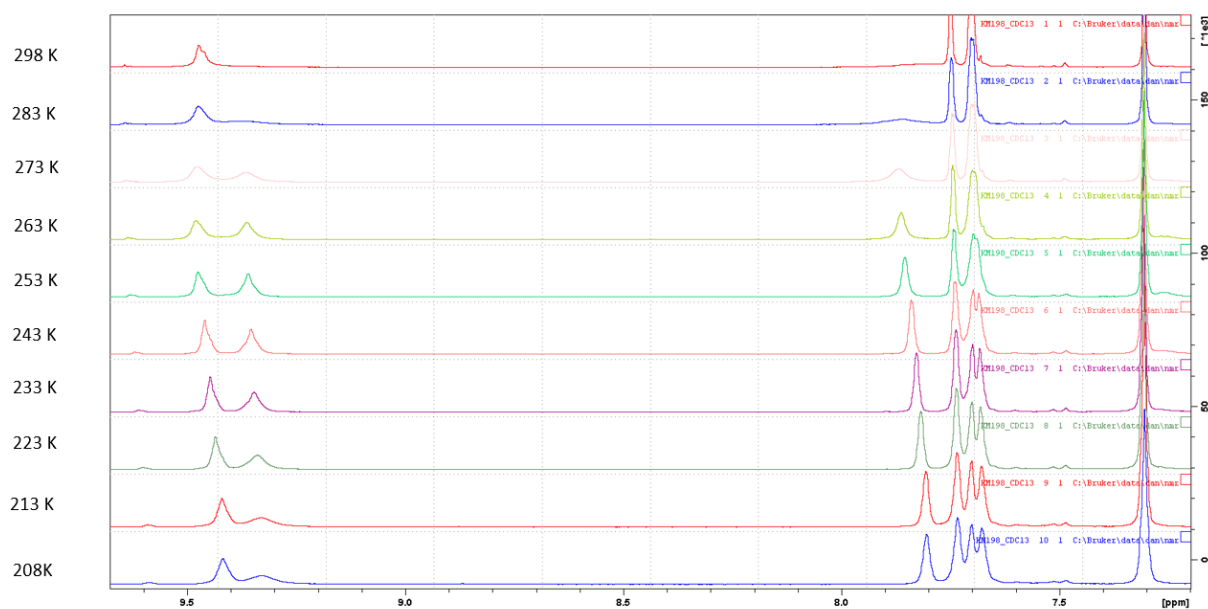


Figure S21: ^1H NMR of compound **4** (Aromatic part) (CDCl_3 , 500 MHz).

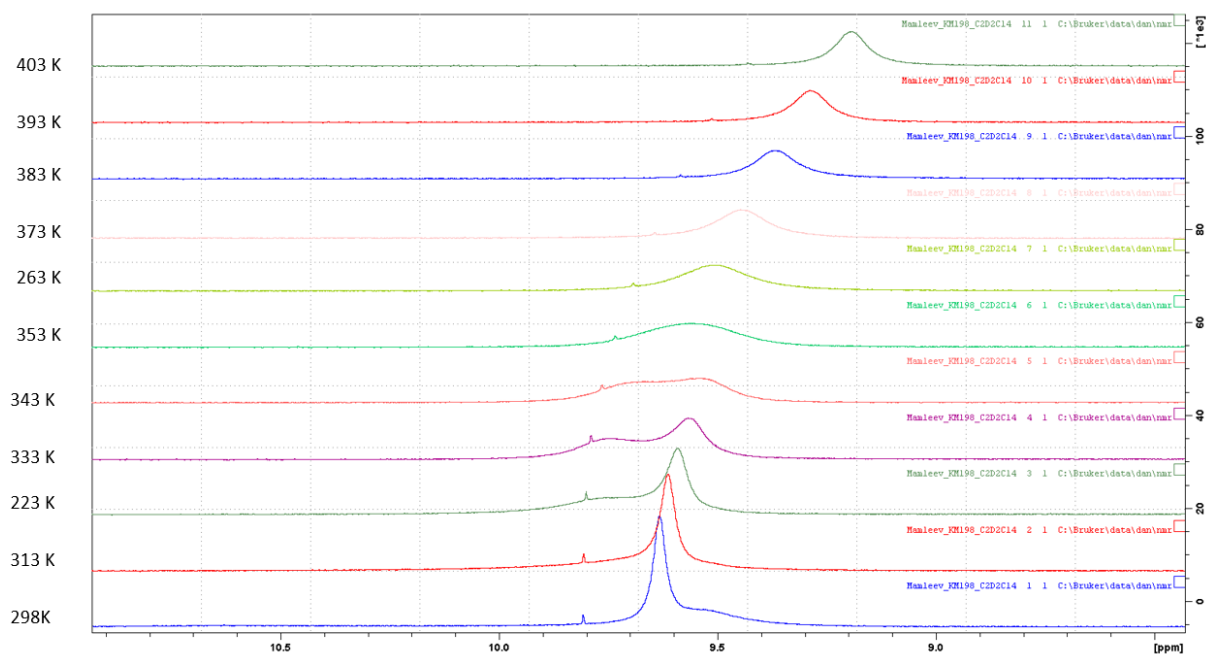


Figure S22: ^1H NMR of compound **4** (OH- groups part) (CDCl_3 , 500 MHz).

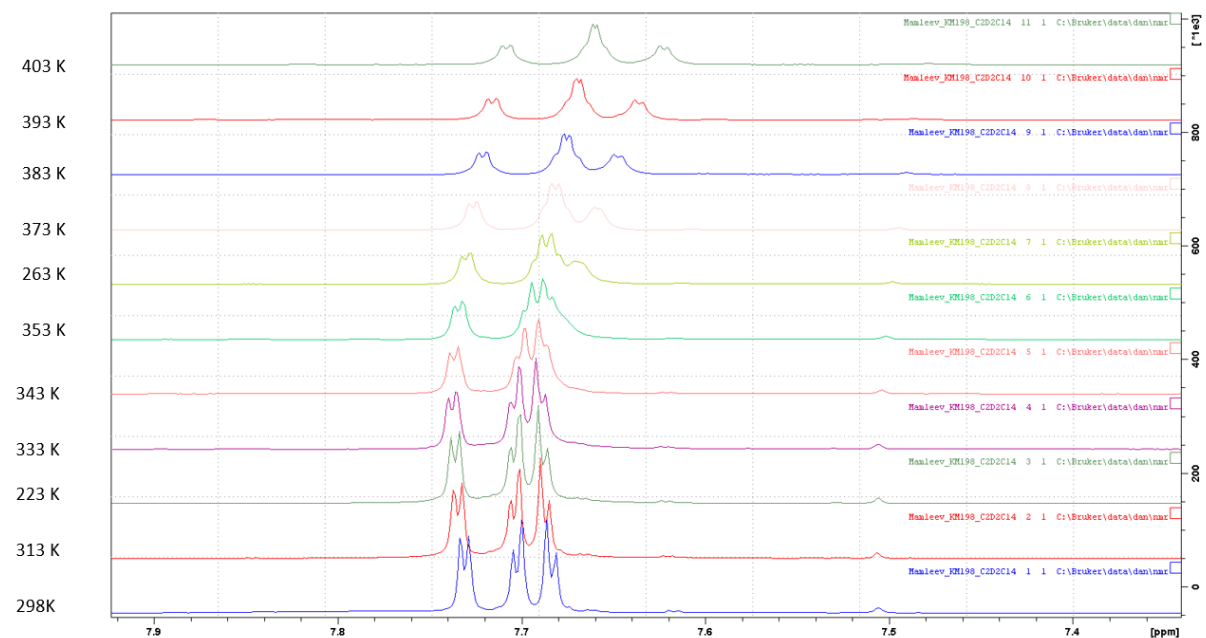


Figure S23: ^1H NMR of compound **4** (Aromatic part) (CDCl_3 , 500 MHz).

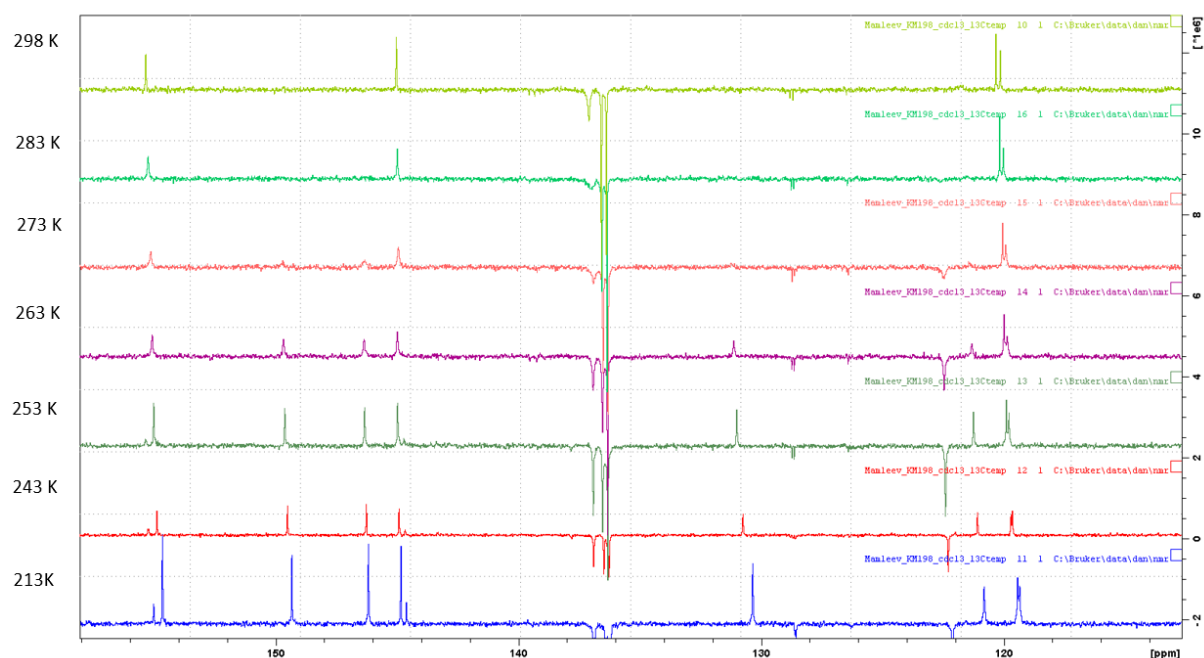


Figure S24: ^{13}C (APT) NMR of compound **4** (Aromatic part) (CDCl_3 , 100 MHz)

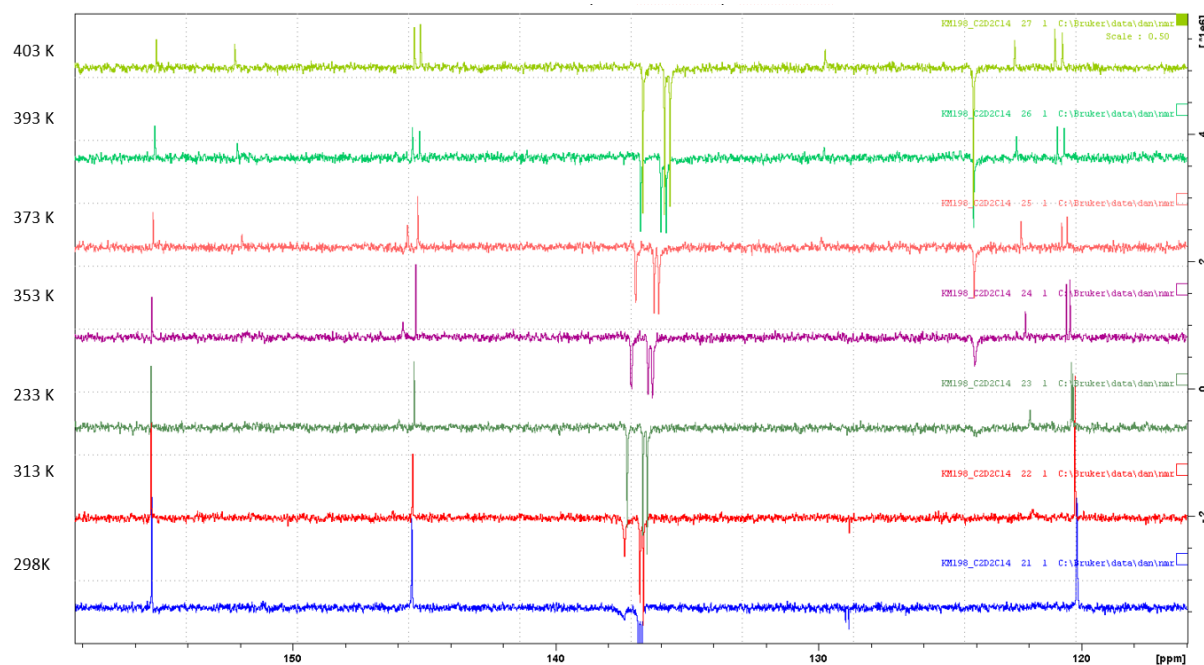


Figure S25: ^{13}C (APT) NMR of compound **4** (Aromatic part) (CDCl_3 , 100 MHz)

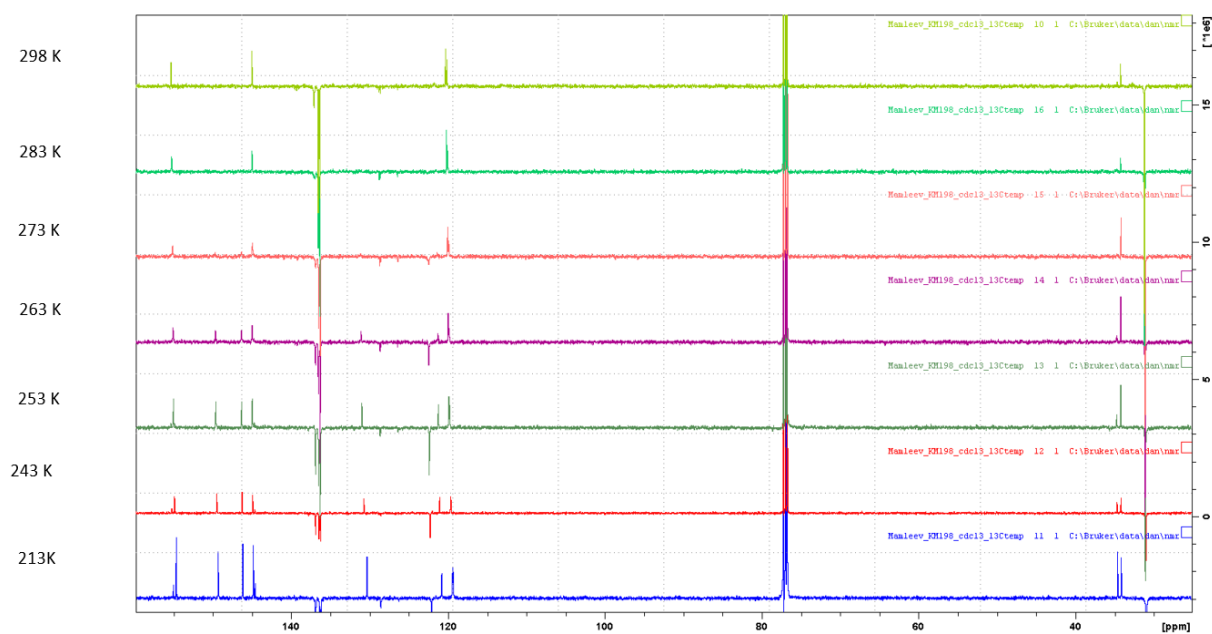


Figure S26: ^{13}C (APT) NMR of compound **4** (CDCl_3 , 100 MHz)

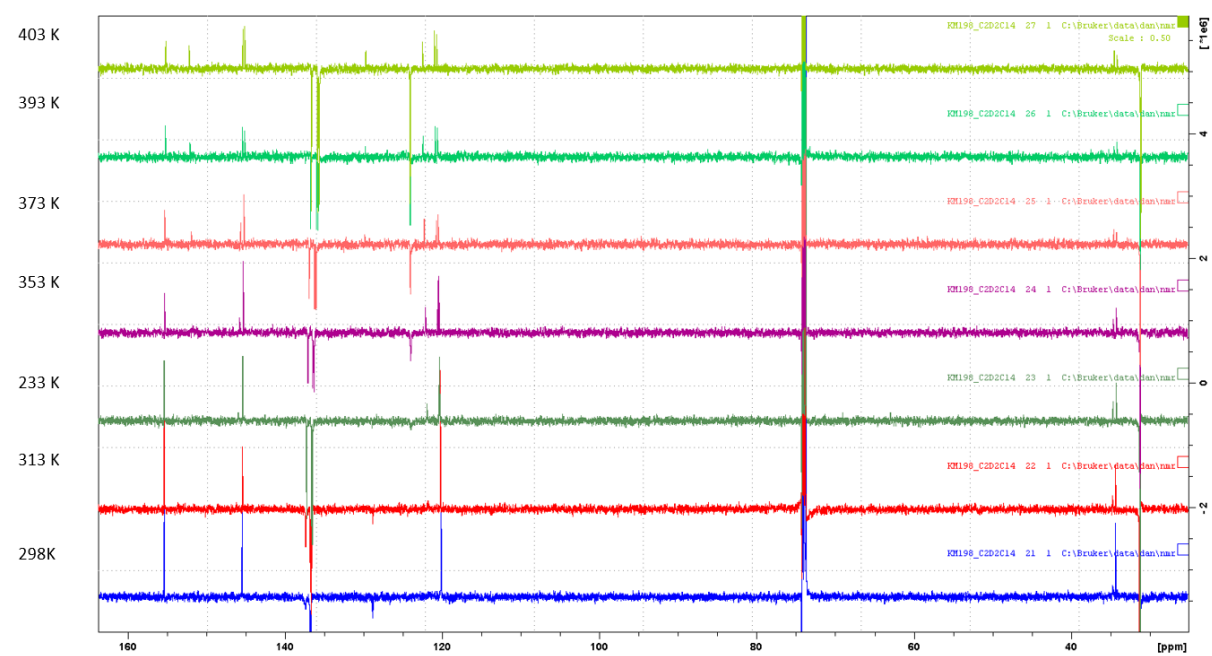


Figure S27: ^{13}C (APT) NMR of compound **4** (CDCl_3 , 100 MHz)

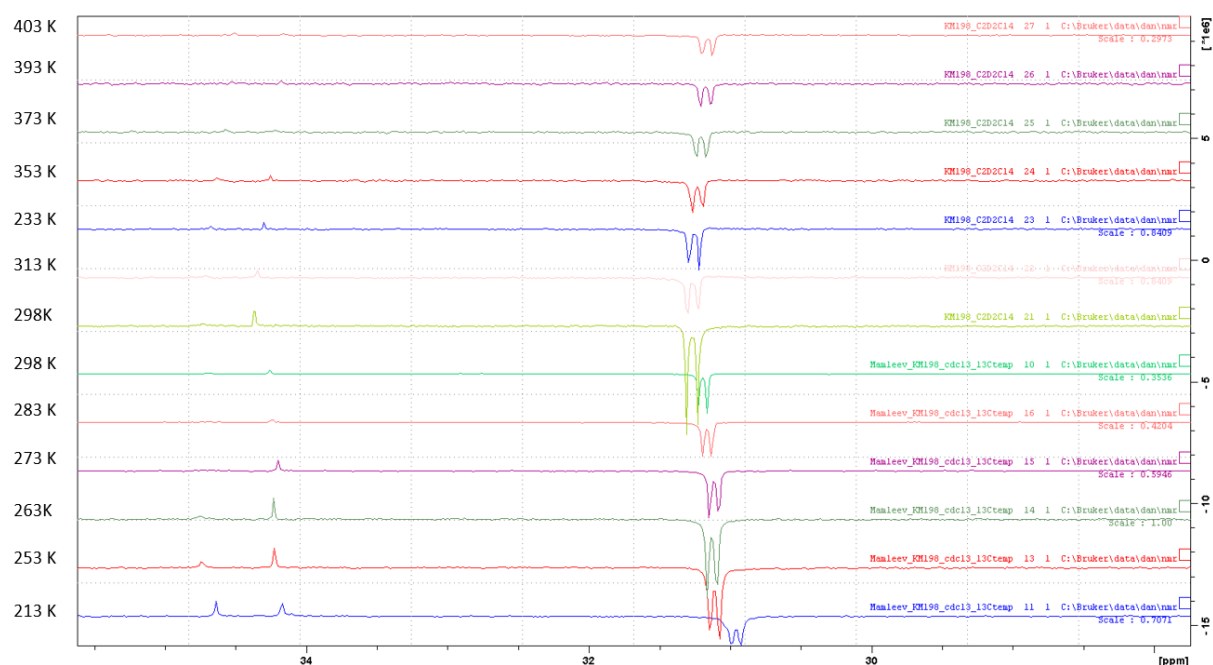


Figure S28: ^{13}C (APT) NMR of compound **4** (*tert*-butyl part) (CDCl_3 , 100 MHz)

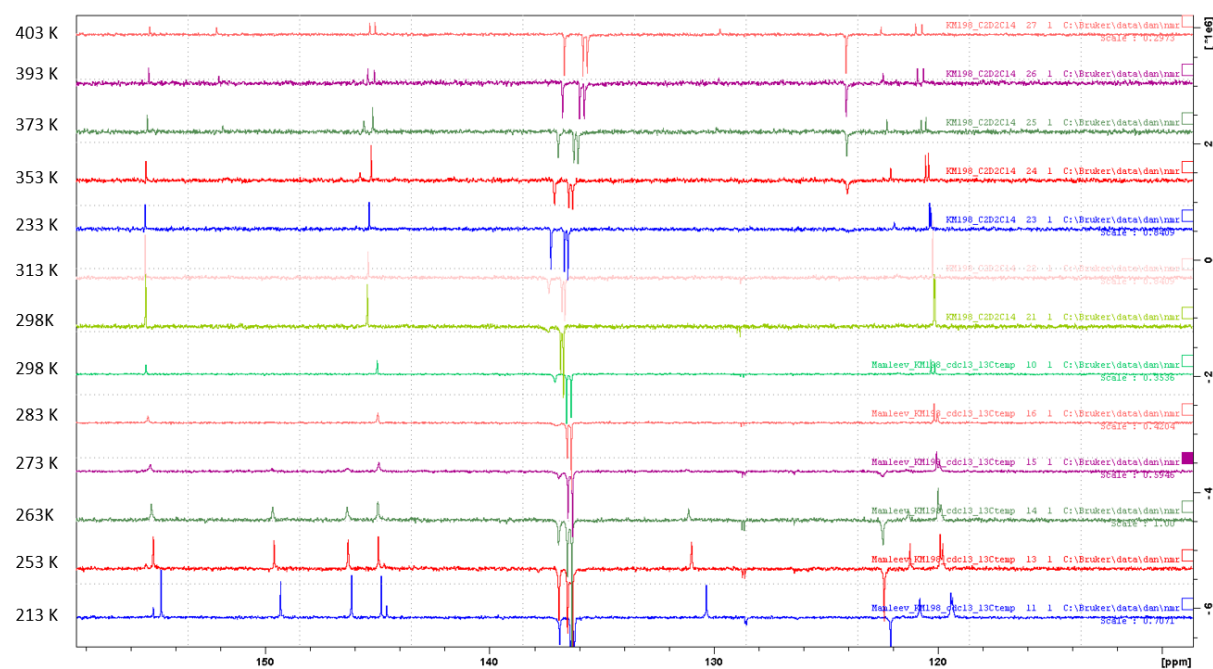


Figure S29: ^{13}C (APT) NMR of compound **4** (Aromatic part) (CDCl_3 , 100 MHz)

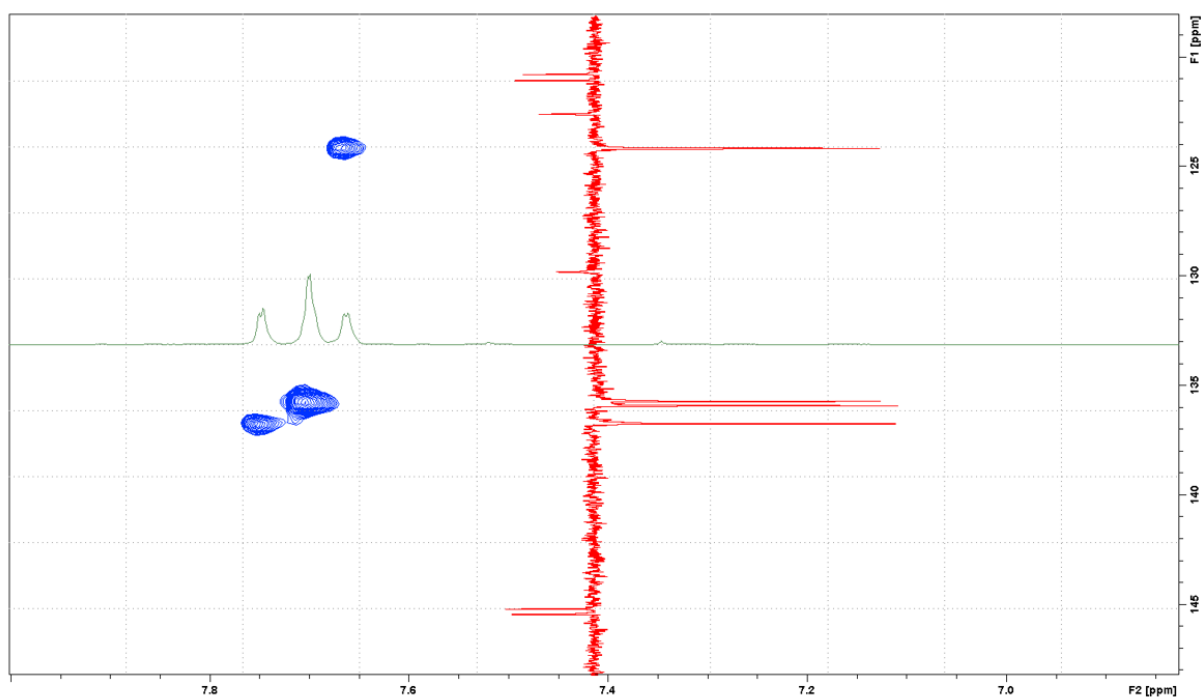


Figure S30: HMQC NMR of compound 4 (Aromatic part, 403 °K) (CDCl₃, 100 MHz)

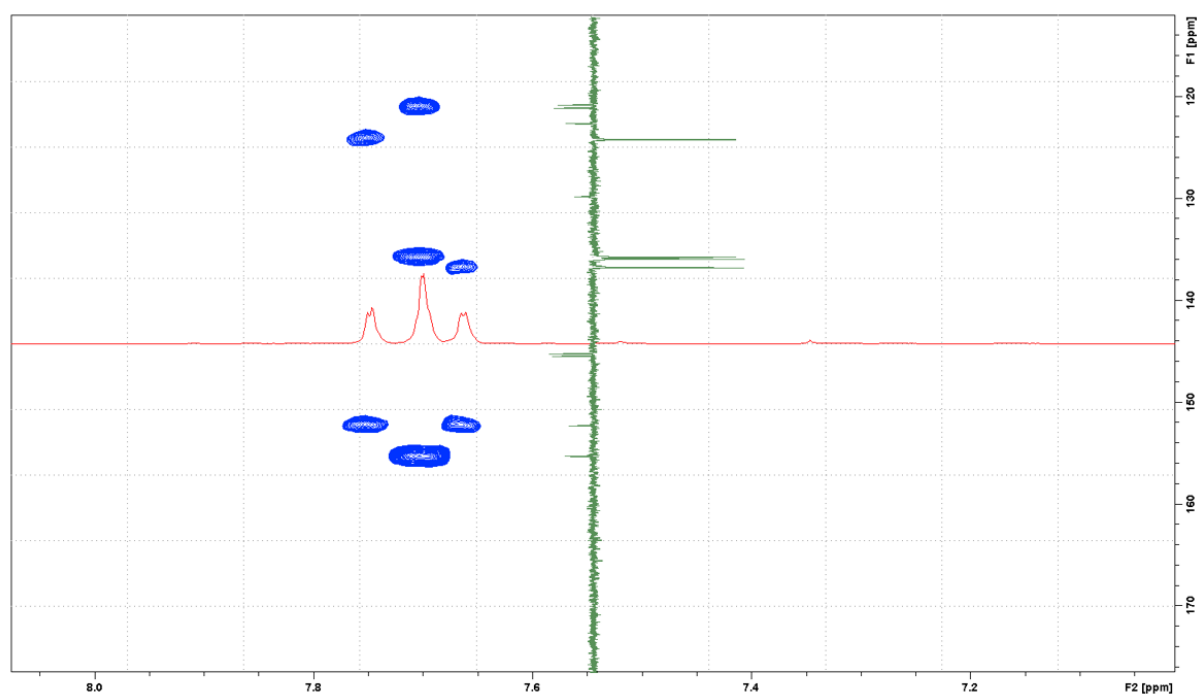


Figure S31: HMBC NMR of compound 4 (Aromatic part 403 °K) (CDCl₃, 100 MHz)

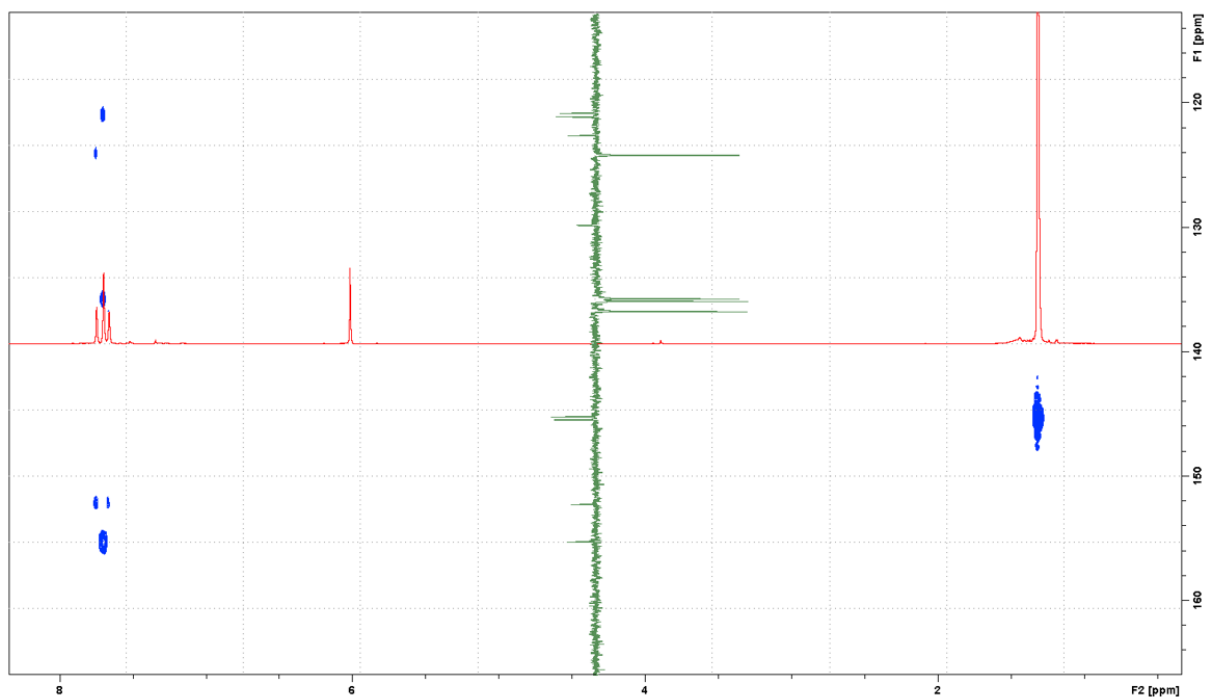


Figure S32: HMBC NMR of compound **4** (Aromatic and *tert*-butyl parts, 403 °K) (CDCl₃, 100 MHz)

3. Crystallographic data

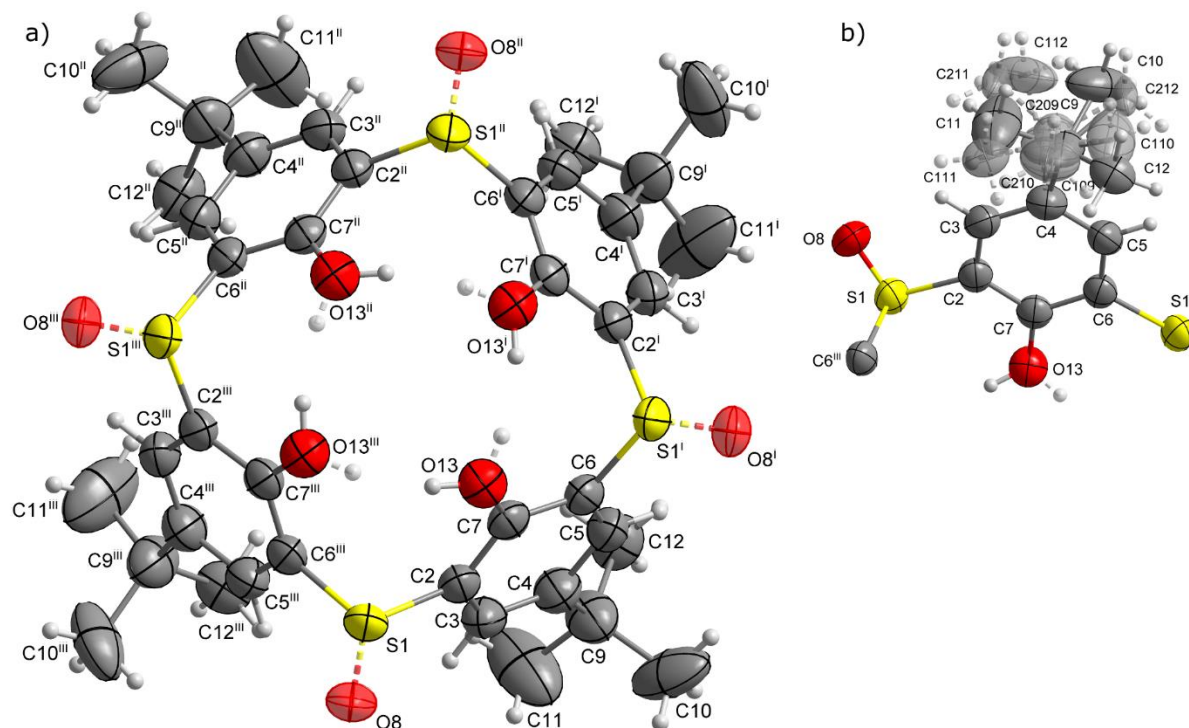


Figure S33: Numbering scheme of crystal structure **4**, with a) full calixarene visible, disordered tert-butyl groups omitted for clarity and b) the asymmetric unit with tert-butyl group disorder visible. Weakly occupied atoms depicted as transparent with dashed bonds. Symmetry codes: (i) 0.5-y, x, z; (ii) 0.5-x, 0.5-y, z; (iii) y, 0.5-x, z.

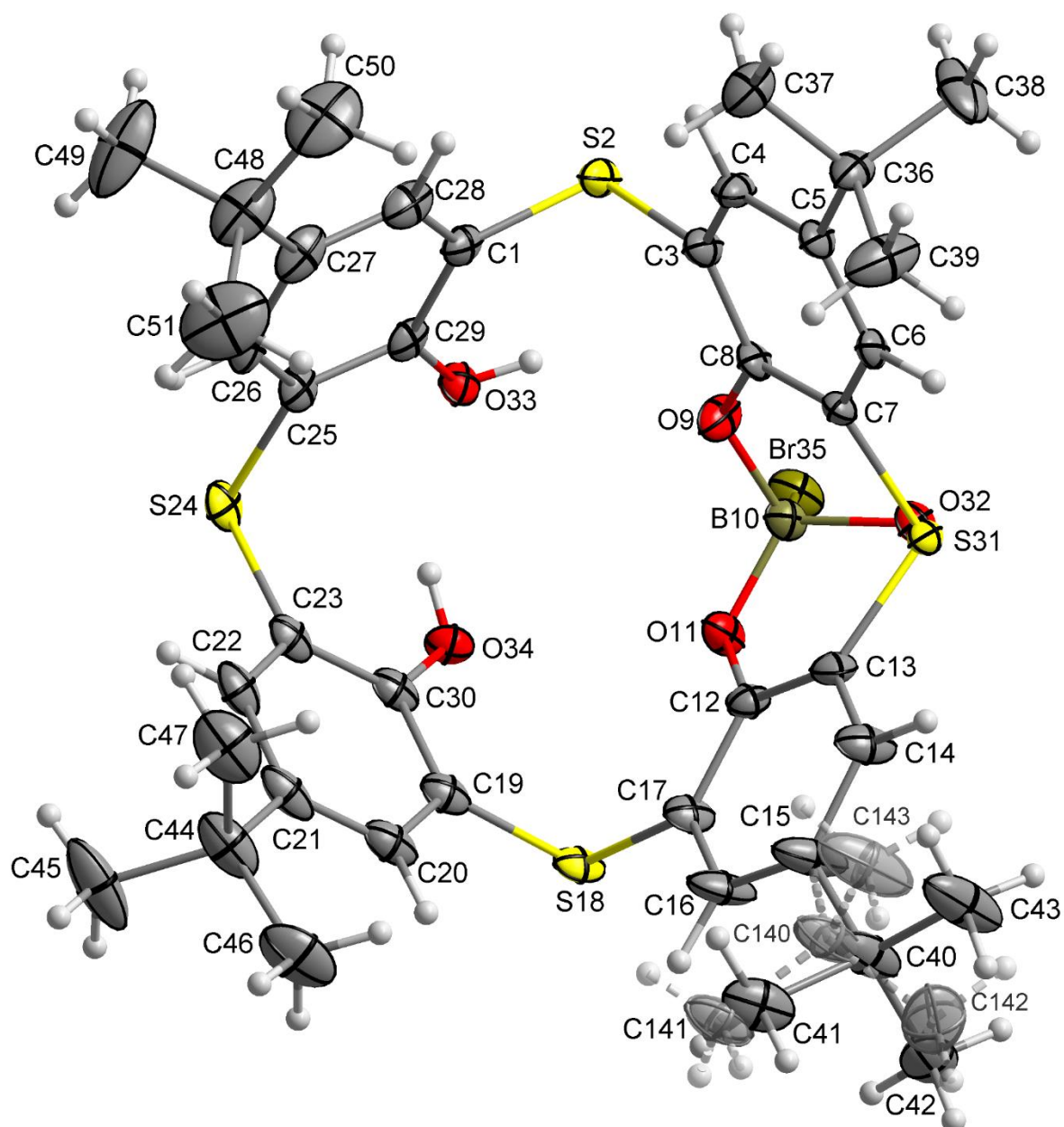


Figure S34: Numbering scheme of crystal structure 5. Weakly occupied atoms depicted as transparent with dashed bonds.

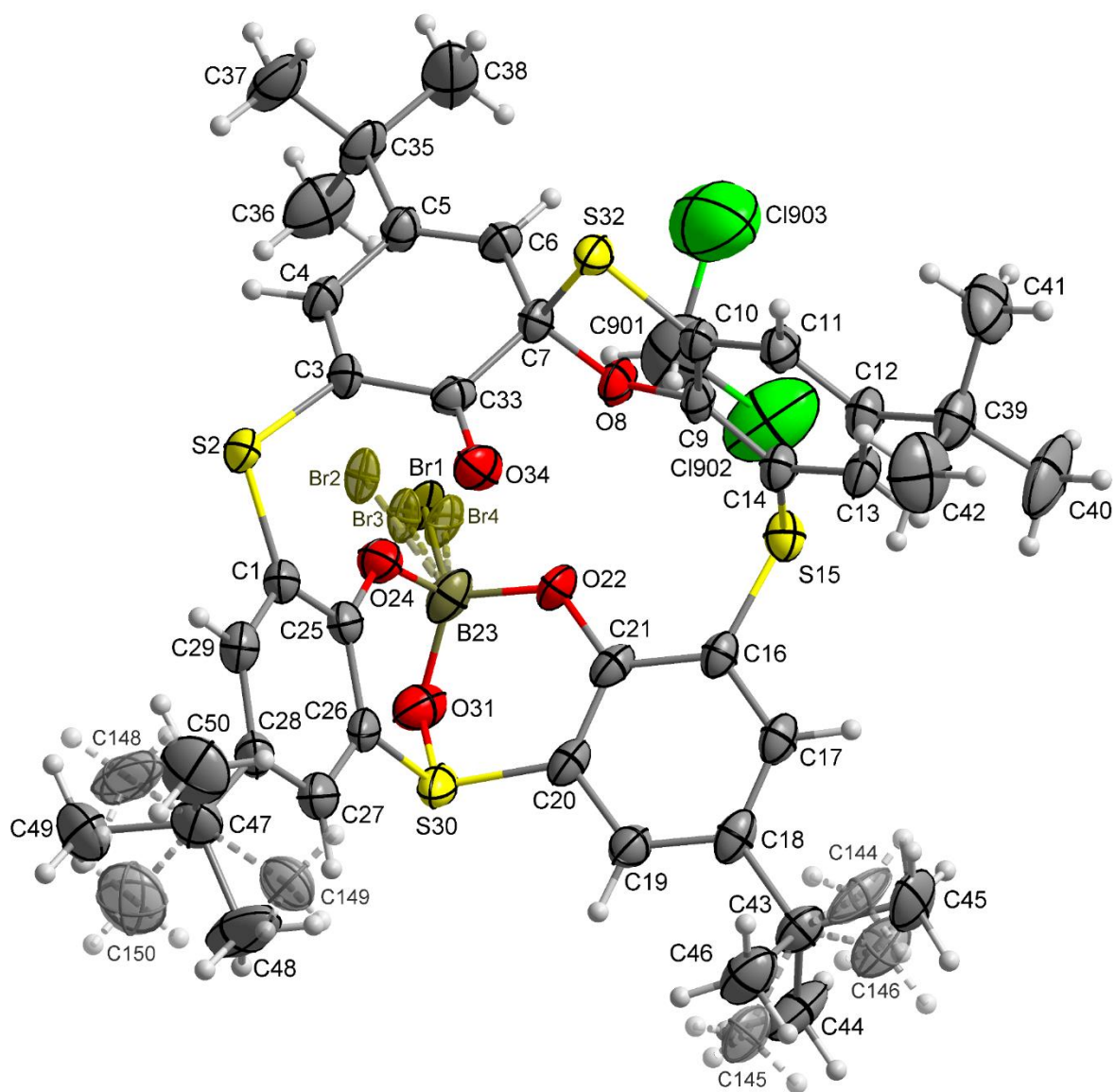


Figure S35: Numbering scheme of crystal structure **6**. Weakly occupied atoms depicted as transparent with dashed bonds.

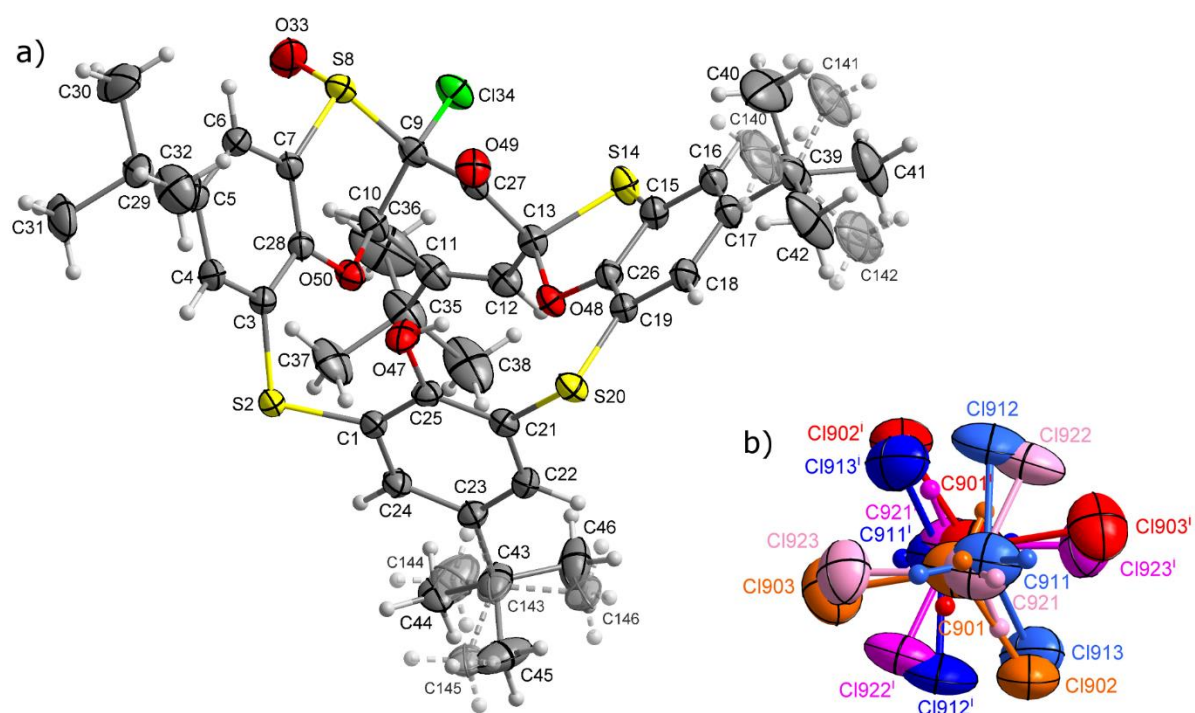


Figure S36: Numbering scheme of crystal structure **10** with a) disordered solvent omitted b) solvent disorder with color-coding. Weakly occupied atoms depicted as transparent with dashed bonds. Symmetry code: (i) $-x, 2-y, -z$.