Supporting Information

A catalytic and solvent-free approach for the synthesis of diverse functionalized dipyrromethanes (DPMs) and calix[4]pyrroles (C4Ps)

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Materials and methods: All commercially available reagents were used without further purification and purchased from Sigma Aldrich, Alfa Aesar, TCI, GLR, and Spectrochem. Pyrrole was used after distillation and acetone used was of HPLC grade. Analytical thin layer chromatography (TLC) was performed on aluminium plates coated with silica gel by using a suitable mixture of EtOAc and petroleum ether for development. Column chromatography was performed by using silica gel (100-200 mesh) with an appropriate mixture of EtOAc and petroleum ether. ^{1}H-NMR spectra (400 MHz and 500 MHz) and ^{13}C-NMR spectra were recorded on a Bruker spectrometer in $CDCl_3$ and DMSO. The "*'' wherever present denotes solvent residual peak. The high-resolution mass spectrometric measurements were carried out by using electrospray ionization (ESI, Q-ToF) spectrometer. TGA analysis was carried out on a Bruker spectrometer. pH studies of diverse deep eutectic solvents (DESs) have been carried out on digital pH meter (Decibel DB-1101).

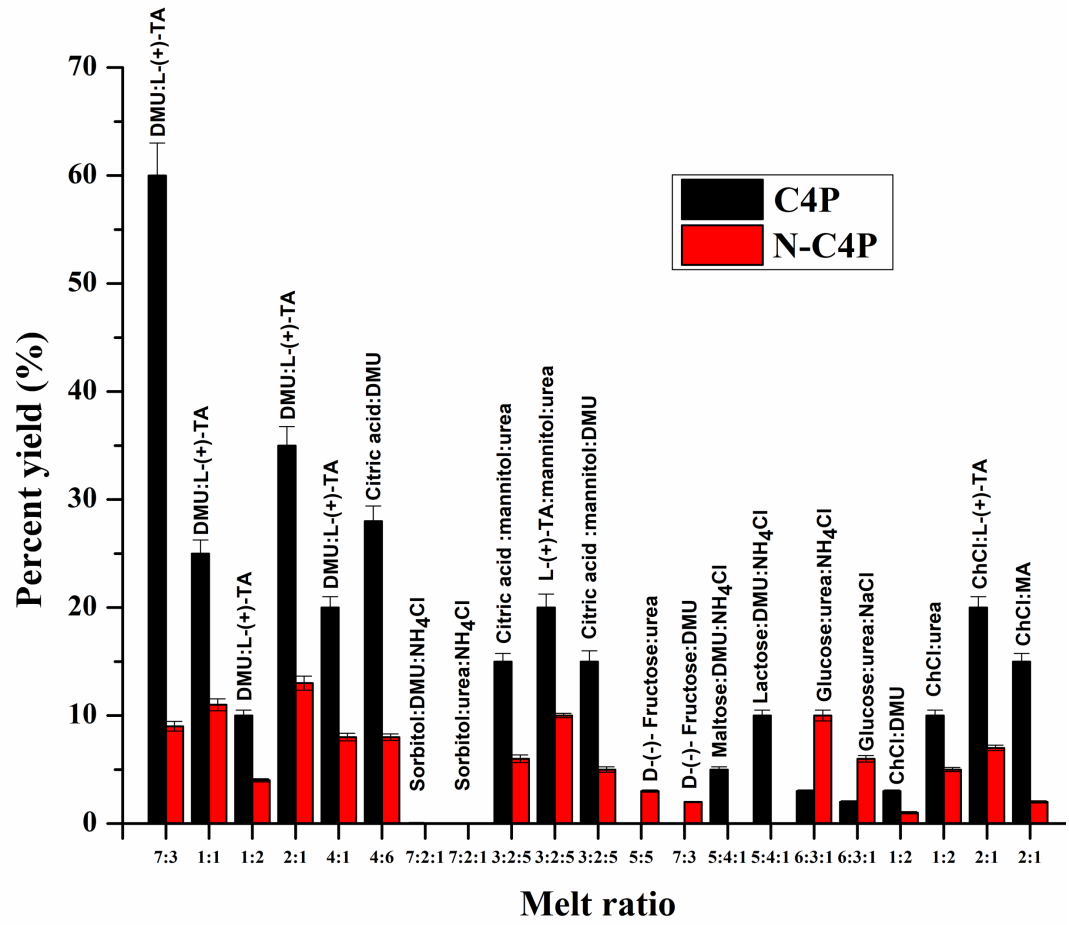

Fig. S1. Bar graph depicting % yields of compounds **3** and **4** using diverse melts.

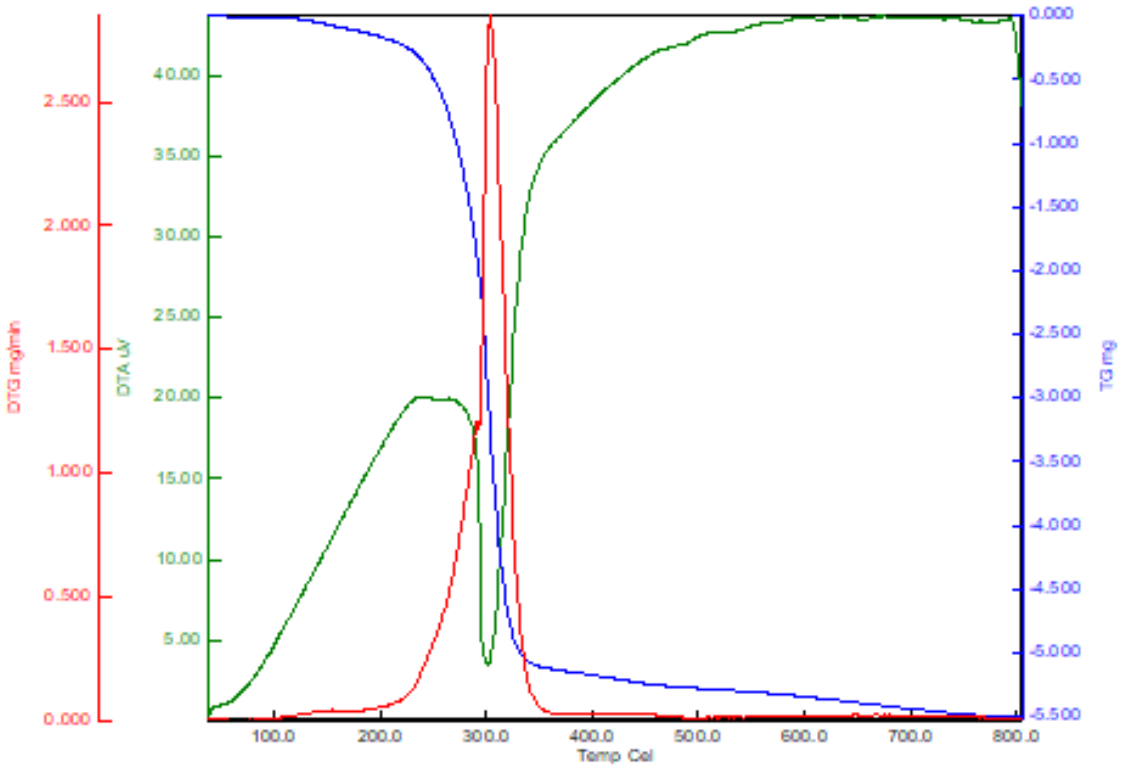

Fig. S2. TGA, DTG, and DTA spectra of compounds **3** and **4**.

Table S1. Recyclability test of DMU:L-(+)-TA (7:3) melt in the condensation reaction of pyrrole with acetone.

Entry	Cycle	Time (h)	3 (% Yield)	4 (% Yield)
1	1st run	4_5	60	9
2	2nd run	4_5	55	7
3	3rd run	4_5	44	5

Table S2. pH studies of diverse low melting mixtures.

Melt	pH	Melt	pH
DMU:L-(+)-TA (7:3)	3.34	DMU:L-(+)- TA (4:1)	3.5
DMU:L-(+)- TA (1:1)	3.26	Citric acid:DMU (4:6)	3.42
DMU:L-(+)- TA (1:2)	3.20	Sorbitol:DMU:NH_4Cl (7:2:1)	5.72
DMU:L-(+)- TA (2:1)	3.39	Sorbitol:Urea:NH_4Cl (7:2:1)	5.75

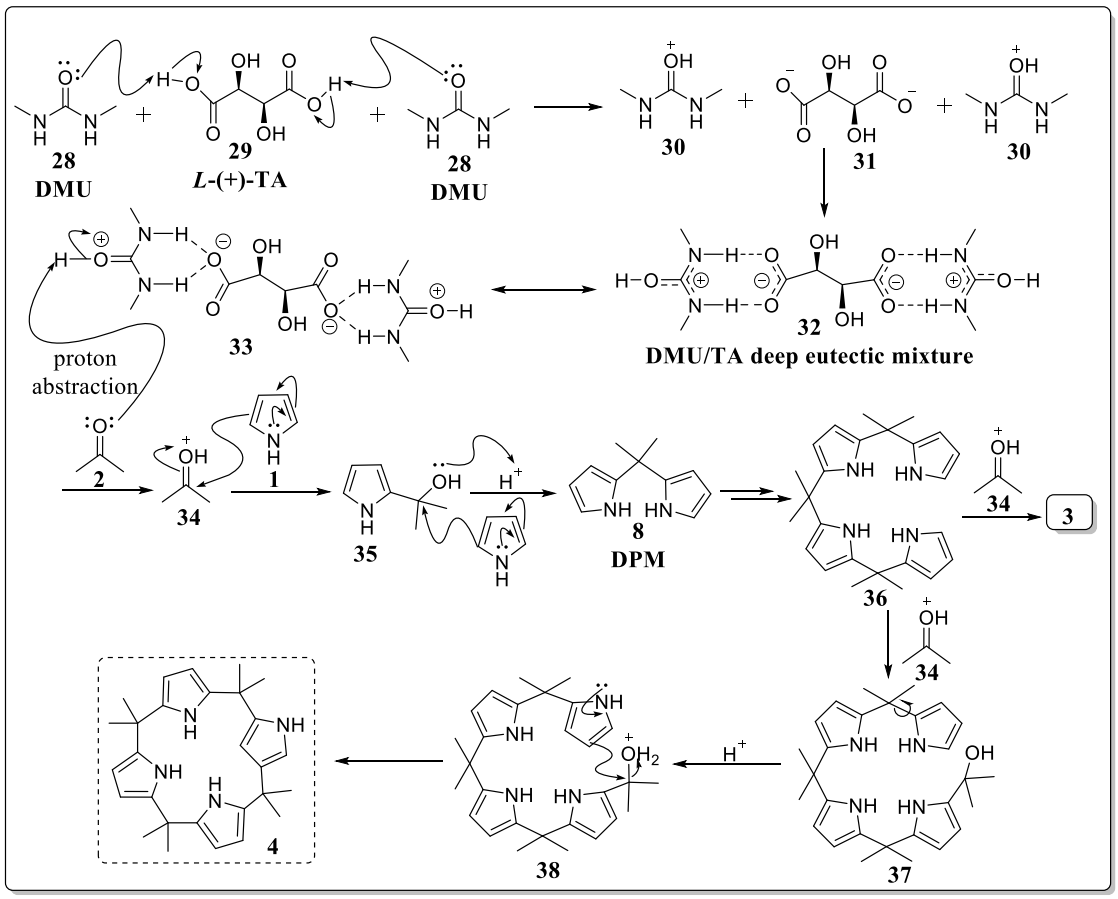

Fig. S3. DMU:L-(+)-TA mediated mechanism for the synthesis of DPMs and C4Ps.

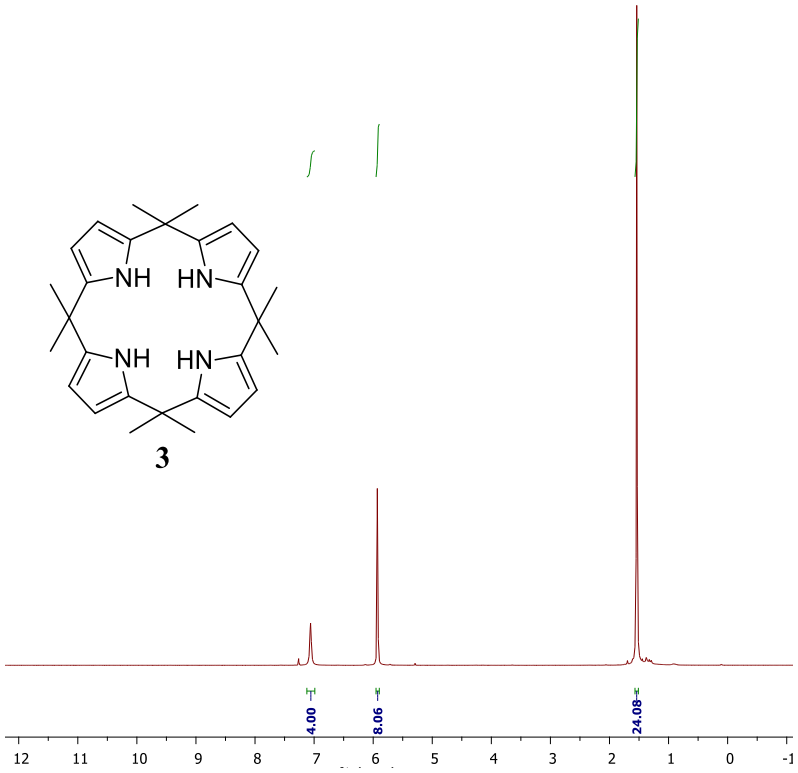

Fig. S4. ^{1}H-NMR spectrum of compound **3** recorded in $CDCl_3$.

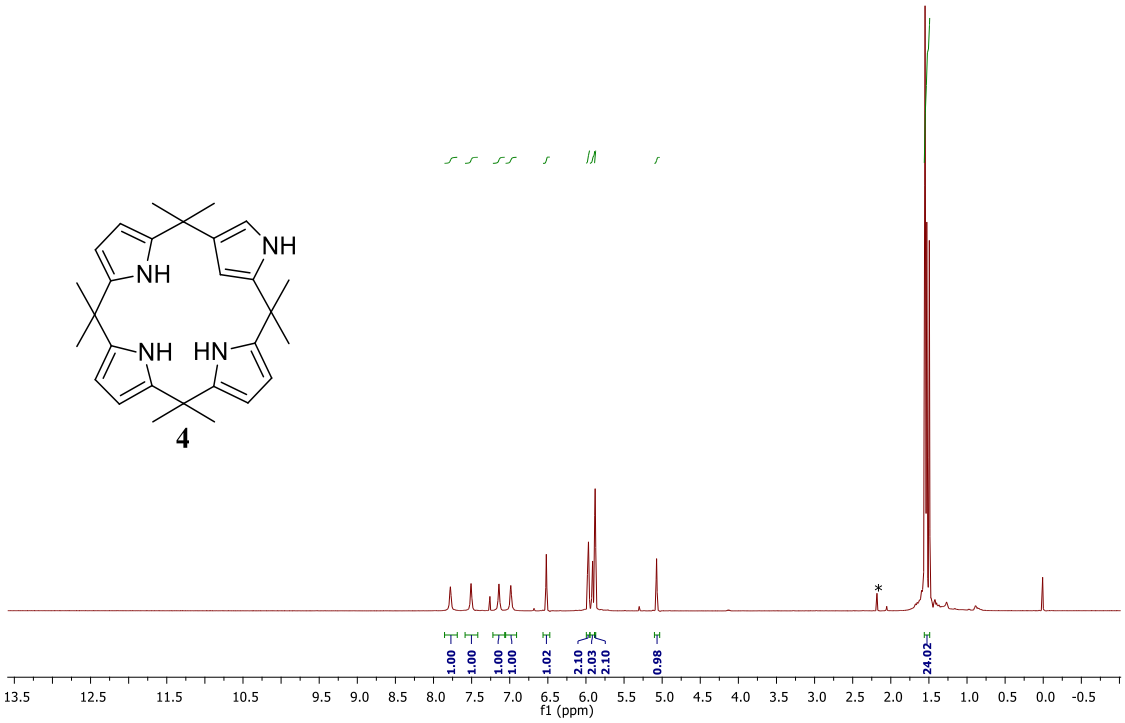

Fig. S5. ^{1}H-NMR spectrum of compound **4** recorded in $CDCl_3$. (*Represents a peak due to residual solvent acetone)

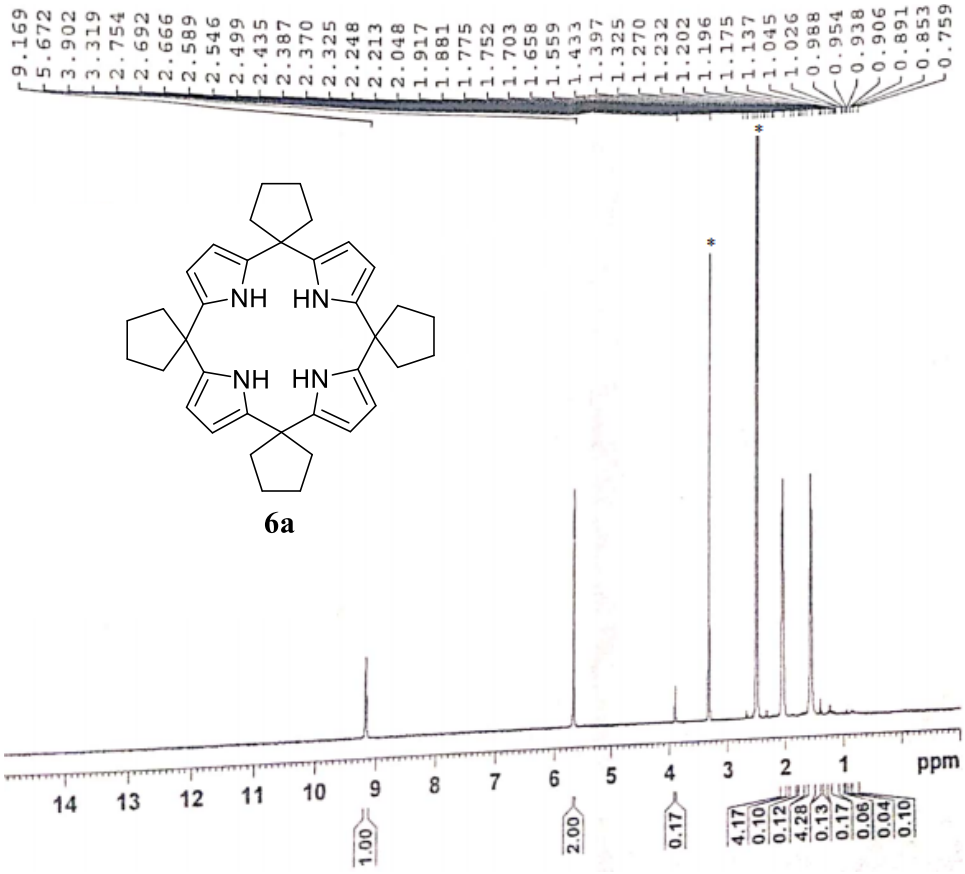

Fig. S6. ^{1}H-NMR spectrum of compound **6a** recorded in d_6-DMSO. (*Represents peaks due to residual solvents dimethylsulfoxide and water)

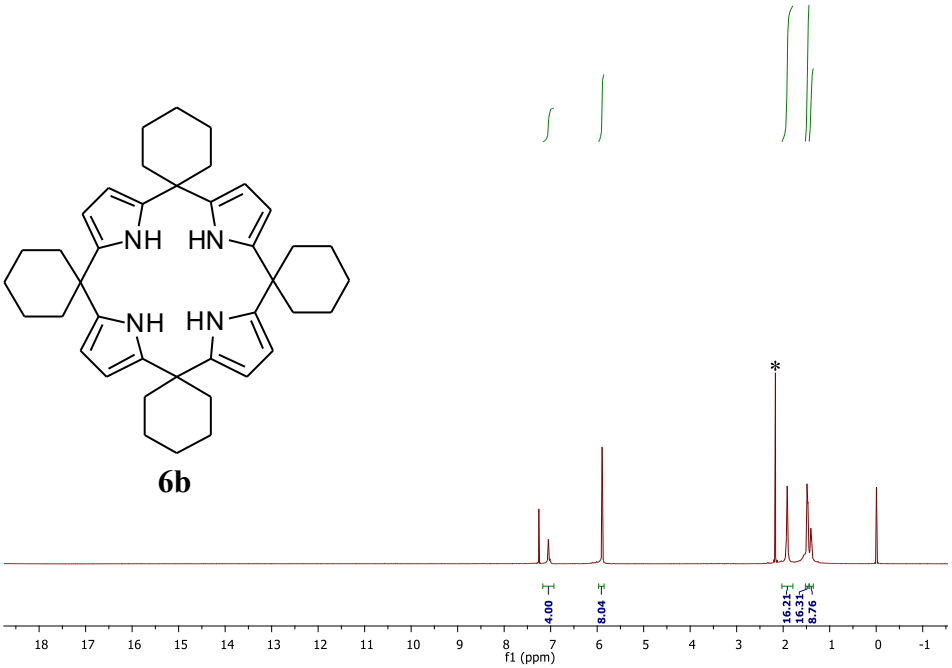

Fig. S7. ^{1}H-NMR spectrum of compound **6b** recorded in $CDCl_3$. (*Represents a peak due to residual solvent acetone)

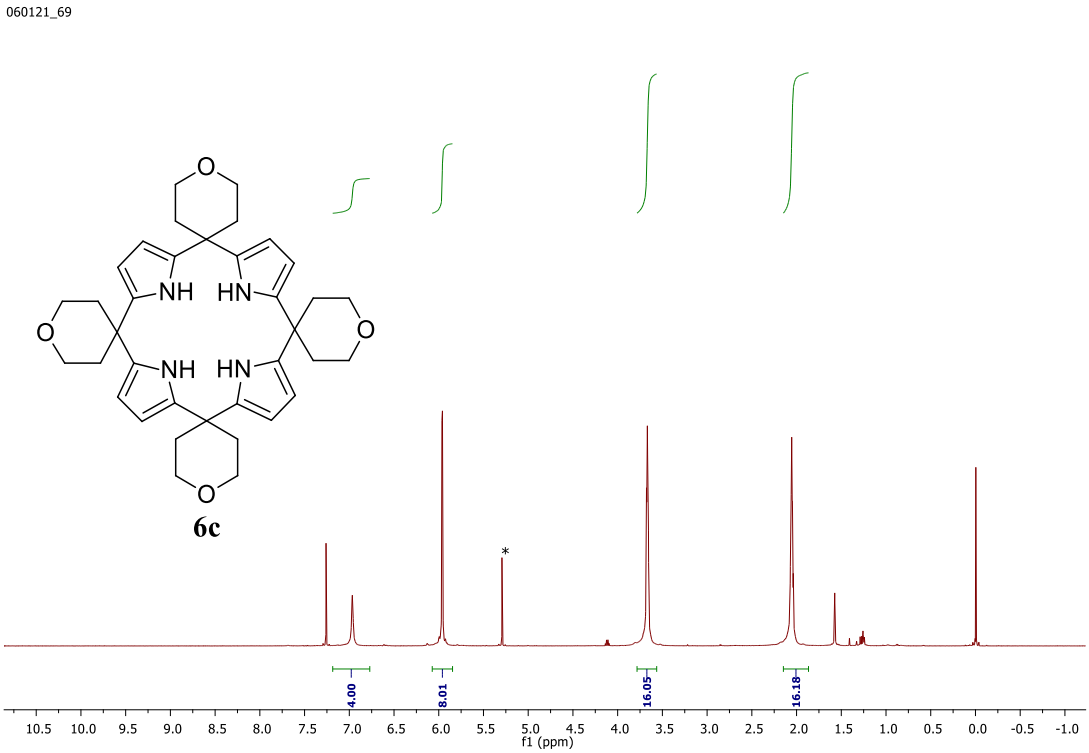

Fig. S8. ^{1}H-NMR spectrum of compound **6c** recorded in $CDCl_3$. (*Represents a peak due to residual solvent dichloromethane)

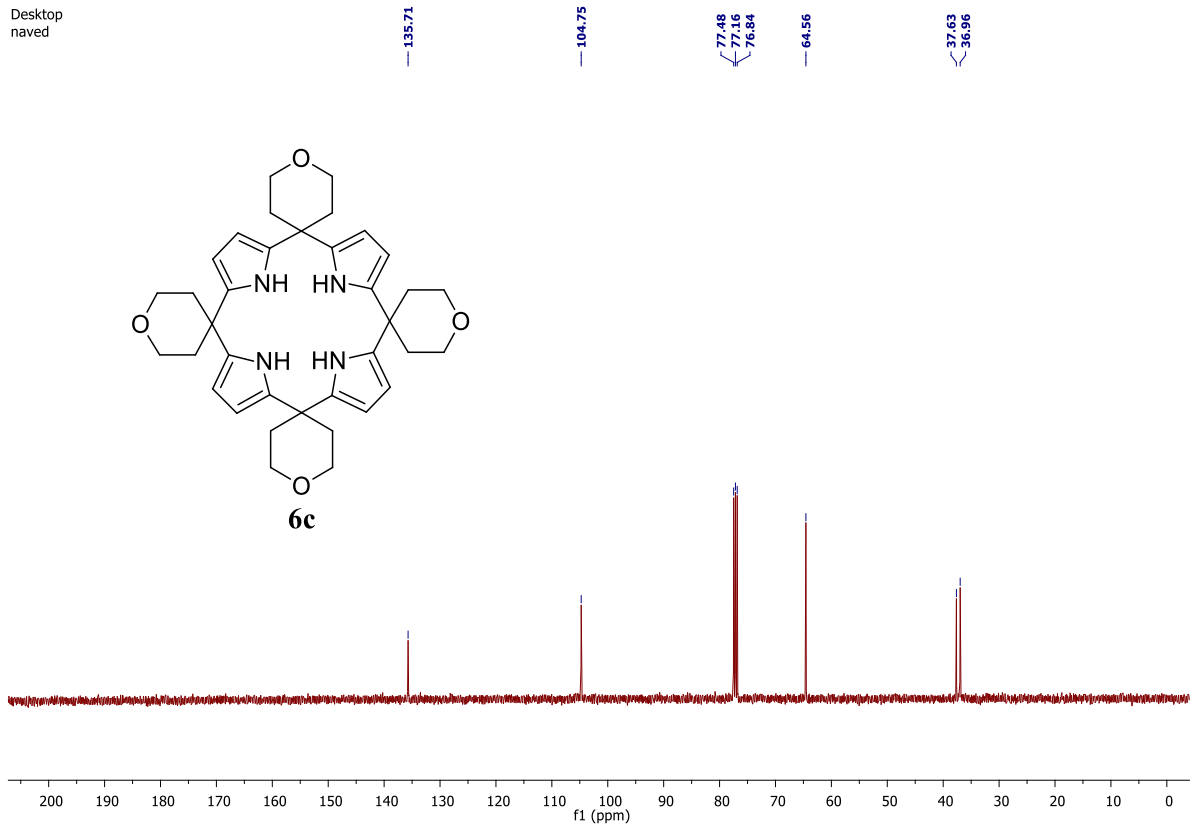

Fig. S9. ^{13}C-NMR spectrum of compound **6c** recorded in $CDCl_3$.

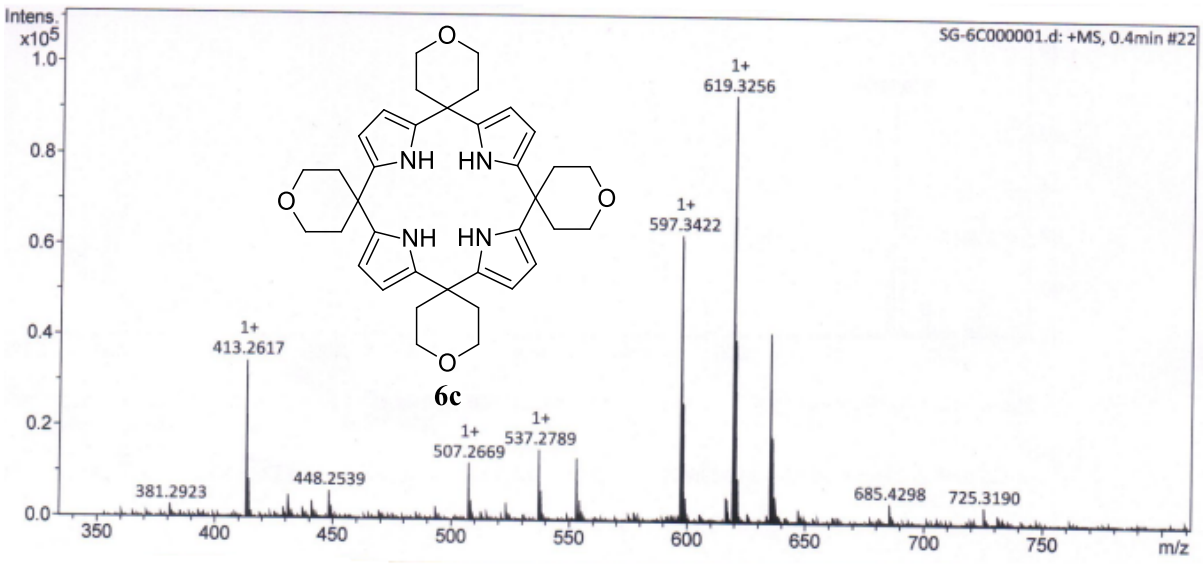

Fig. S10. HRMS spectrum of compound **6c** (*m/z* calculated for $C_{28}H_{36}N_4$ $[M+Na]^+$ = 619.3255)

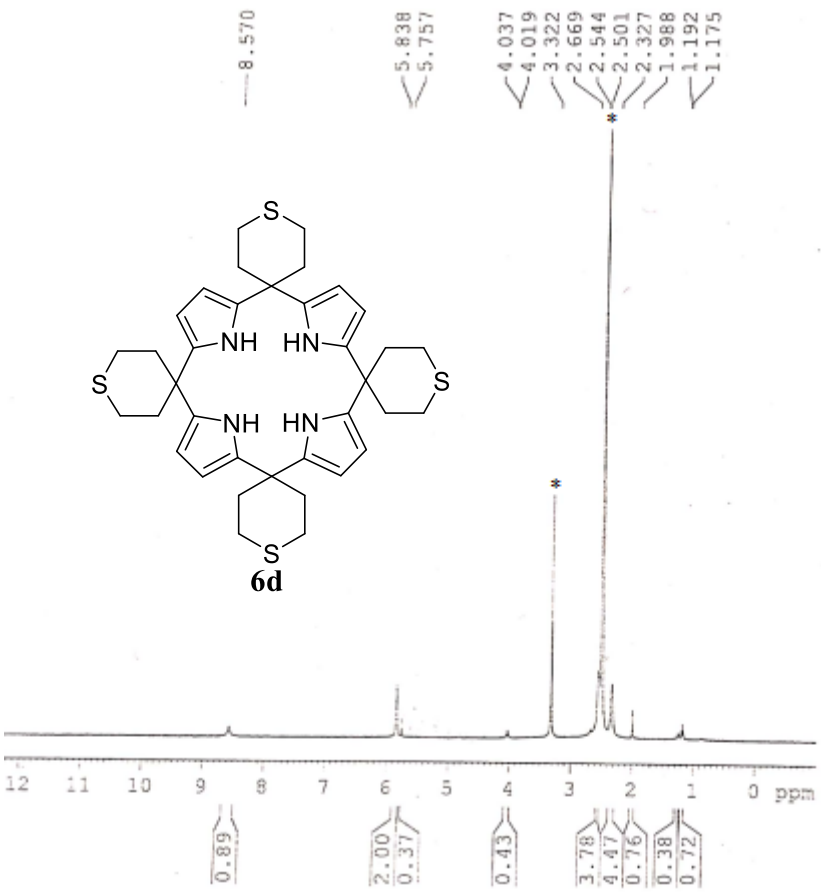

Fig. S11. ^{1}H-NMR spectrum of compound **6d** recorded in d_6-DMSO. (*Represents peaks due to residual solvents dimethylsulfoxide and water)

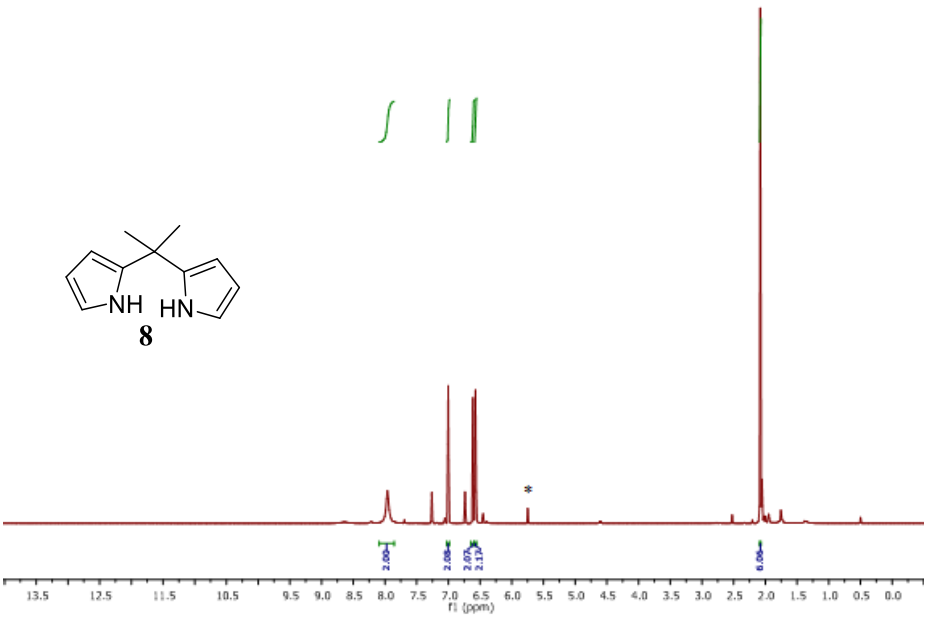

Fig. S12. ^{1}H-NMR spectrum of compound **8** recorded in $CDCl_3$. (*Represents a peak due to residual solvent dichloromethane)

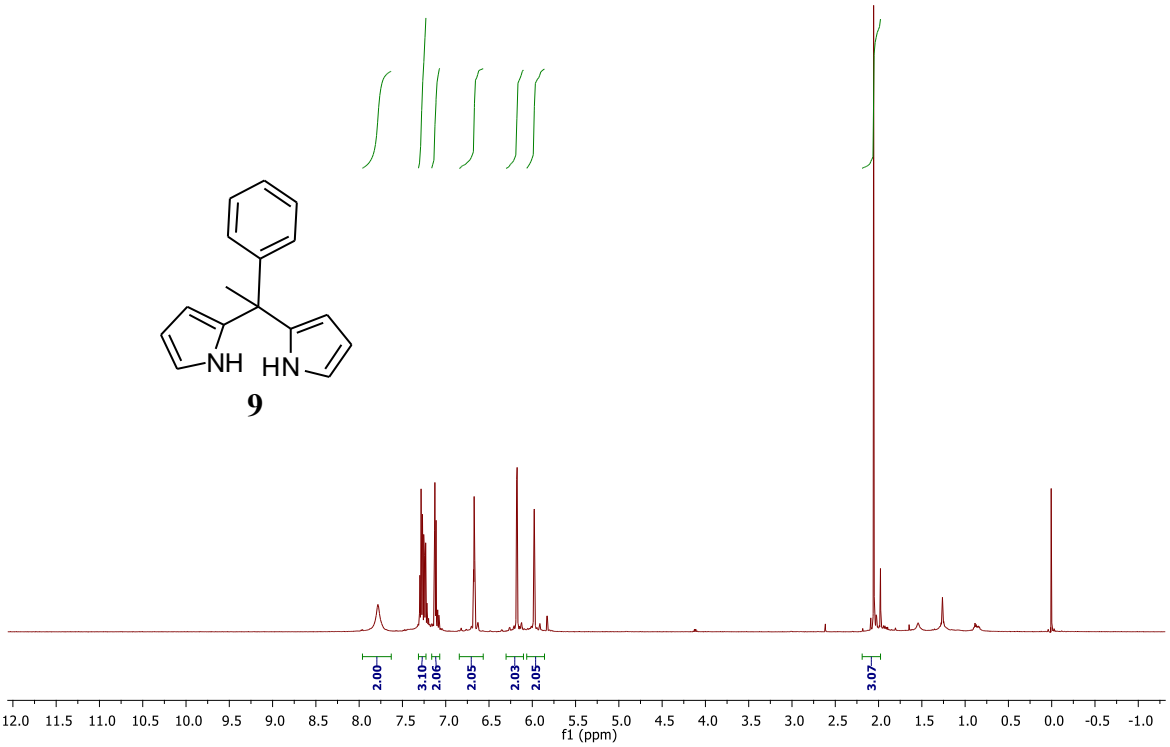

Fig. S13. ^{1}H-NMR spectrum of compound **9** recorded in $CDCl_3$.

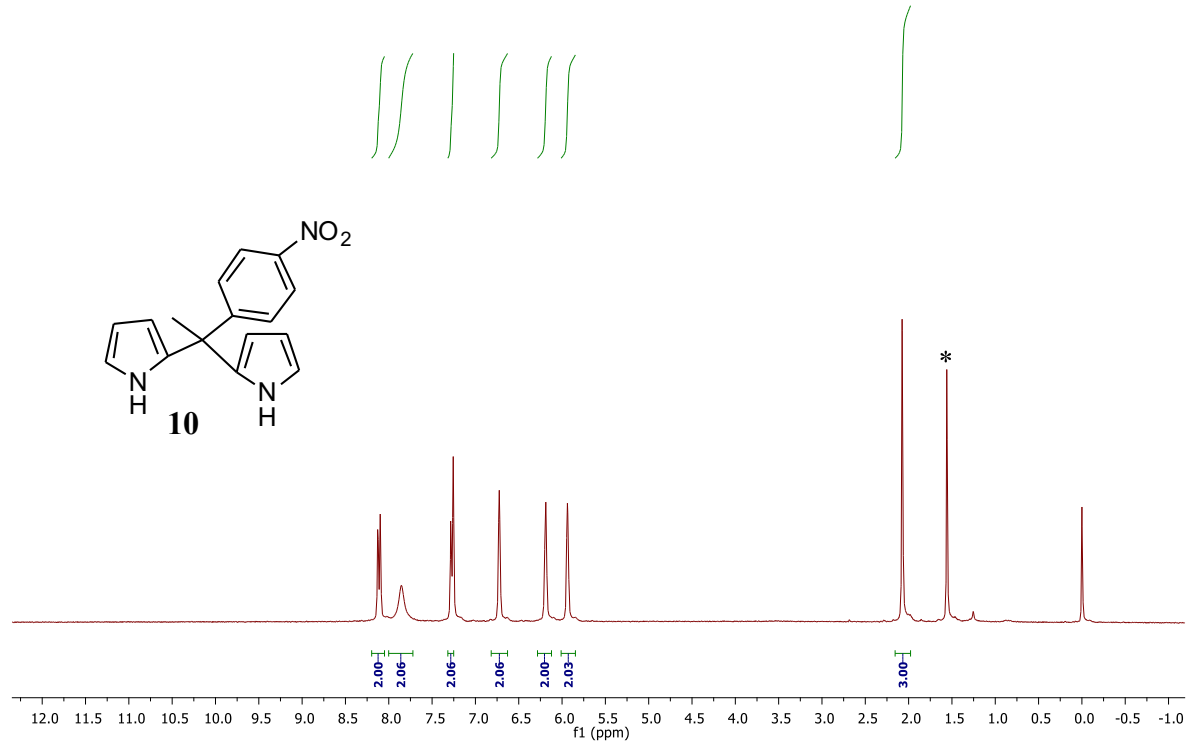

Fig. S14. ^{1}H-NMR spectrum of compound **10** recorded in $CDCl_3$. (*Represents a peak due to residual solvent water)

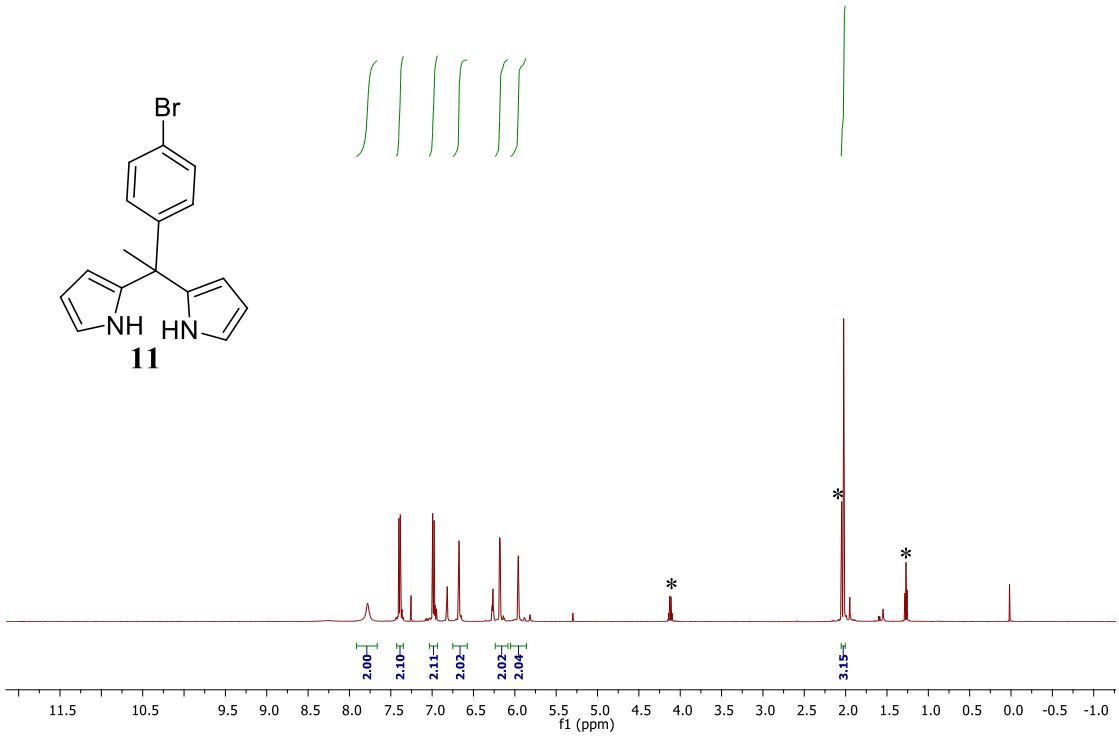

Fig. S15. ^{1}H-NMR spectrum of compound **11** recorded in $CDCl_3$. (*Represents peaks due to residual solvent ethyl acetate)

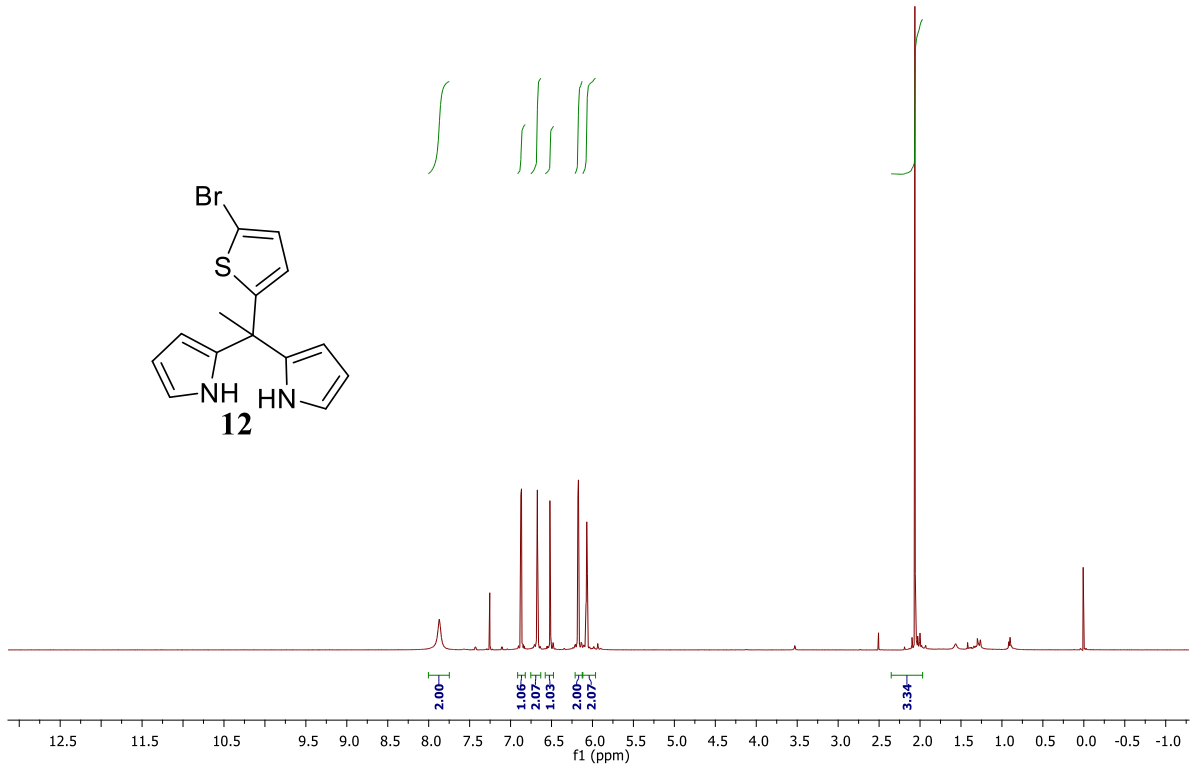

Fig. S16. ^{1}H-NMR spectrum of compound **12** recorded in $CDCl_3$.

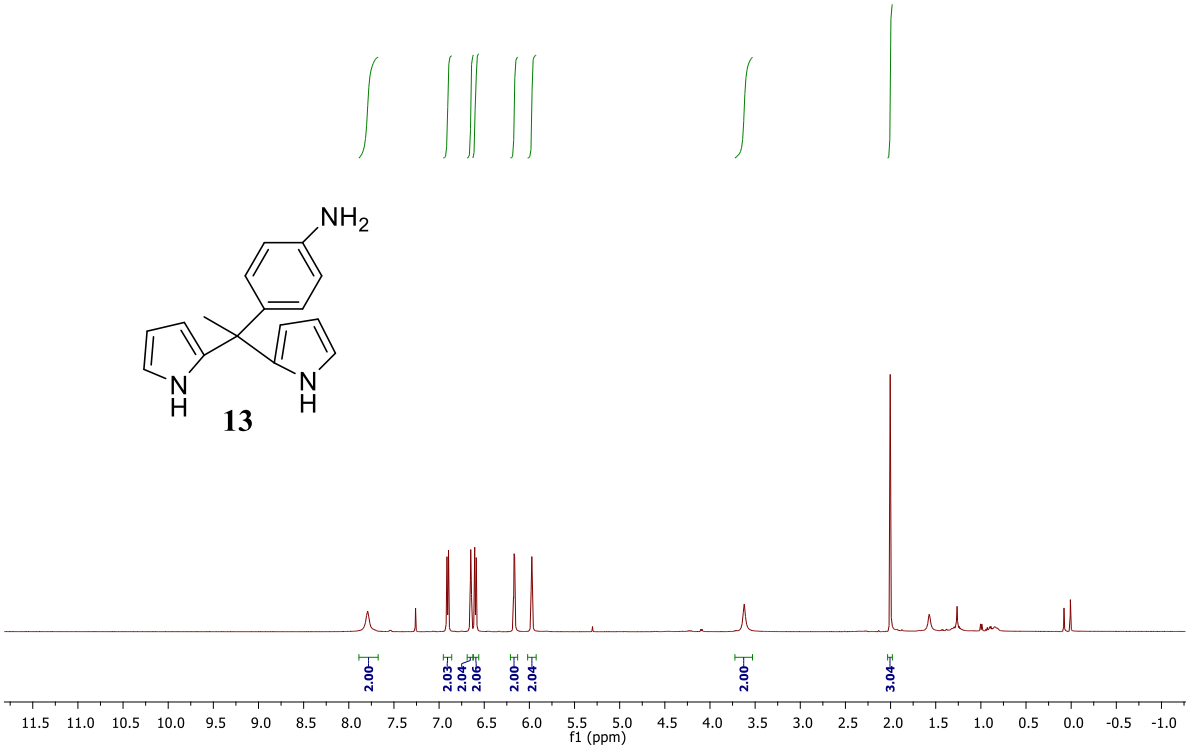

Fig. S17. ^{1}H-NMR spectrum of compound **13** recorded in $CDCl_3$.

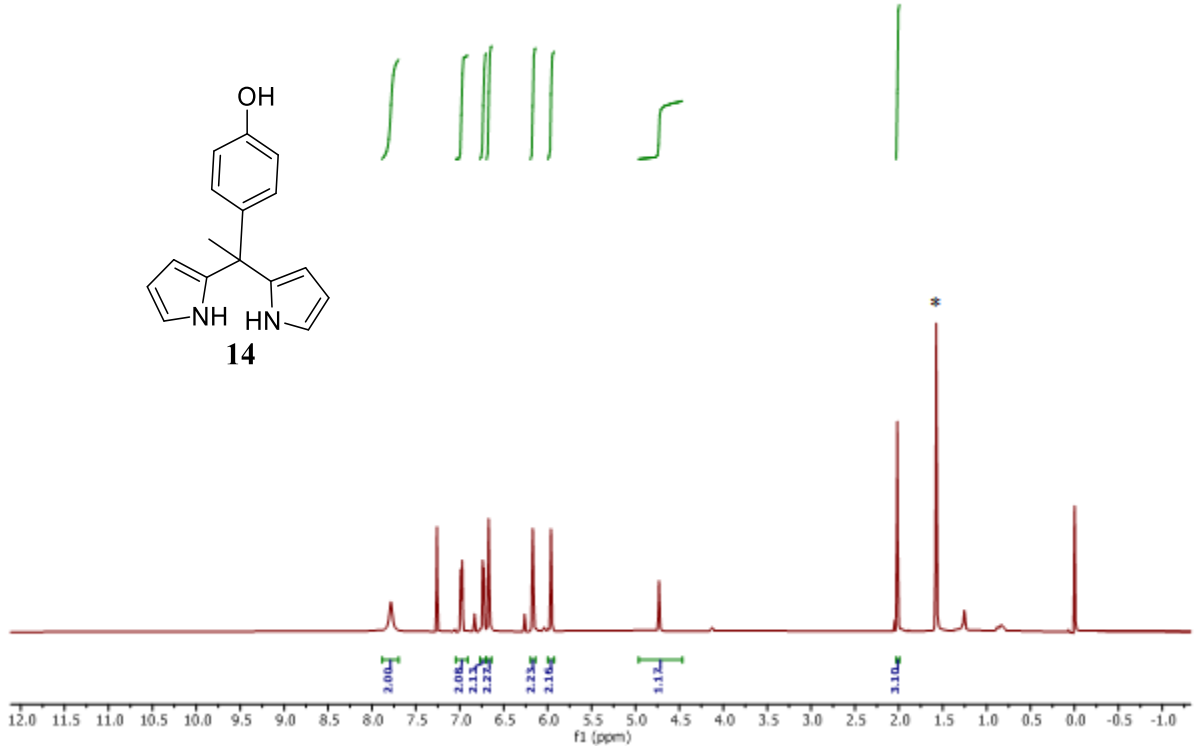

Fig. S18. ^{1}H-NMR spectrum of compound **14** recorded in $CDCl_3$. (*Represents a peak due to residual solvent water)

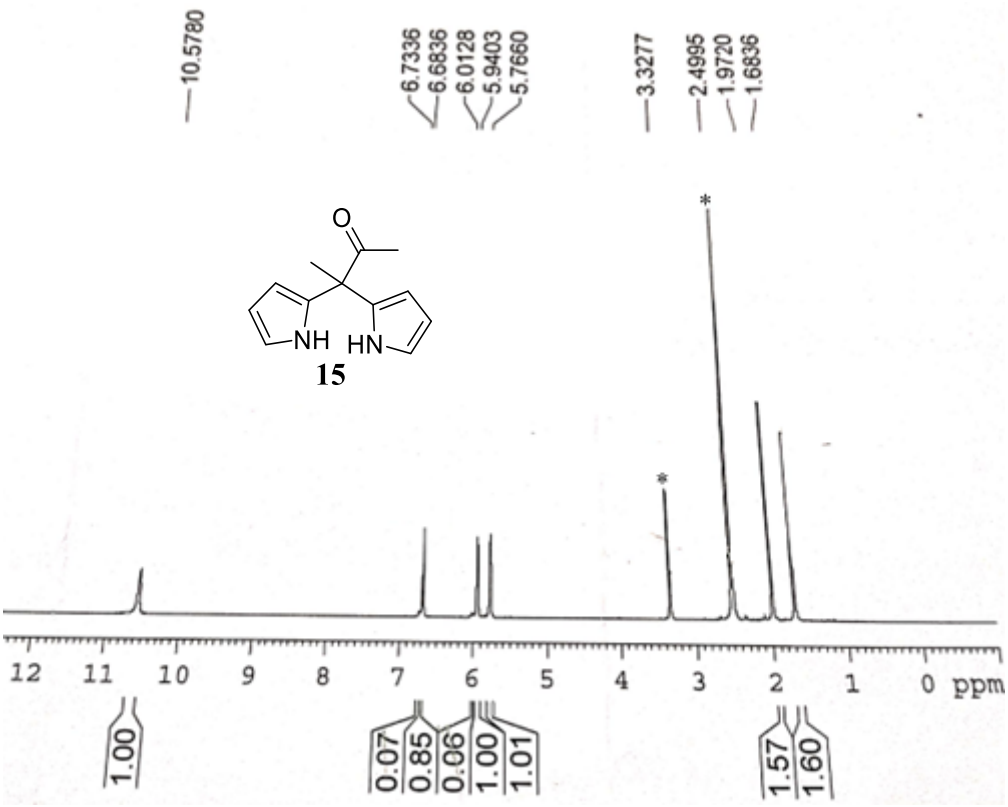

Fig. S19. [1]H-NMR spectrum of compound **15** recorded in d_6-DMSO. (*Represents peaks due to residual solvent dimethylsulfoxide and water)

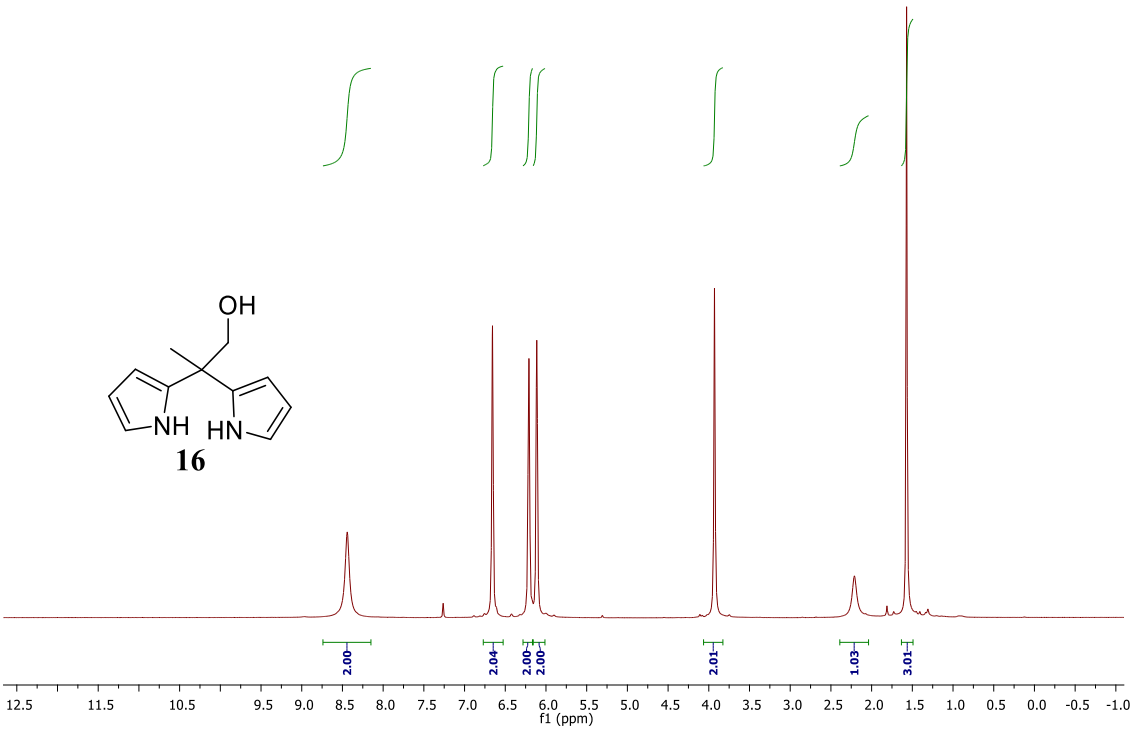

Fig. S20. [1]H-NMR spectrum of compound **16** recorded in $CDCl_3$.

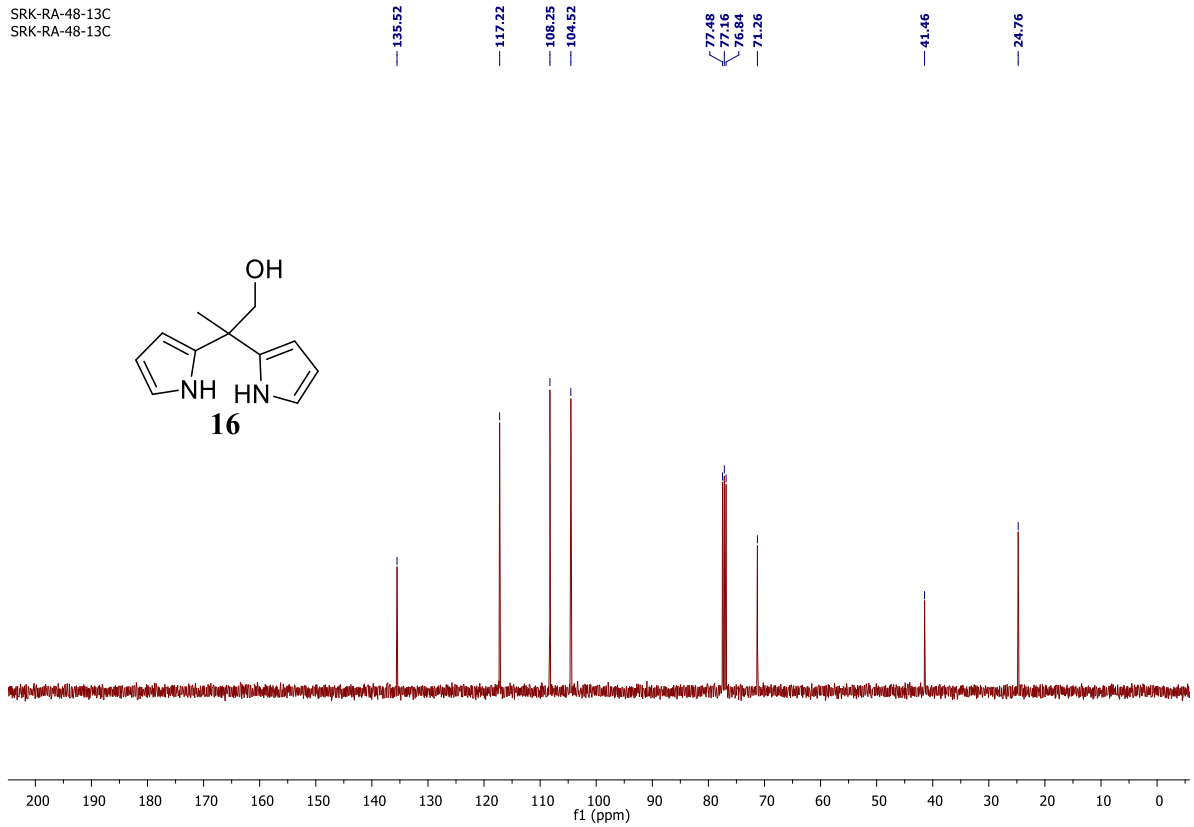

Fig. S21. ^{13}C-NMR spectrum of compound **16** recorded in $CDCl_3$.

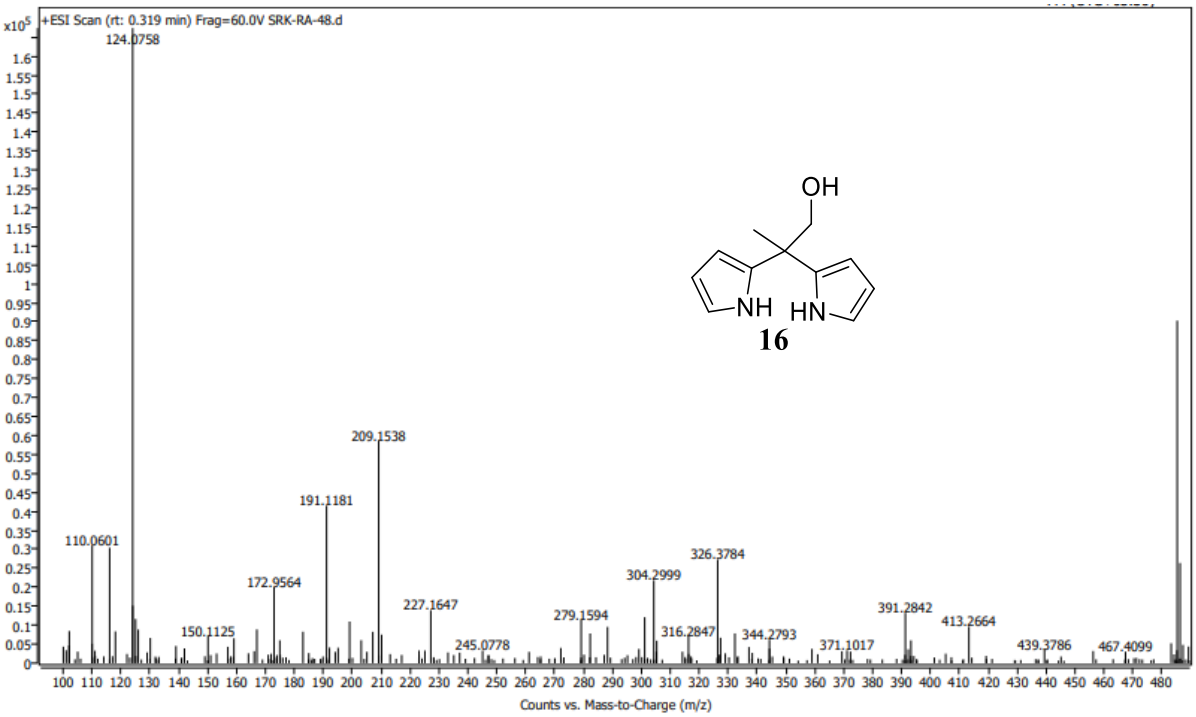

Fig. S22. HRMS spectrum of compound **16** (*m/z* calculated for $C_{11}H_{14}N_2O$ $[M+H]^+$ = 191.1179)

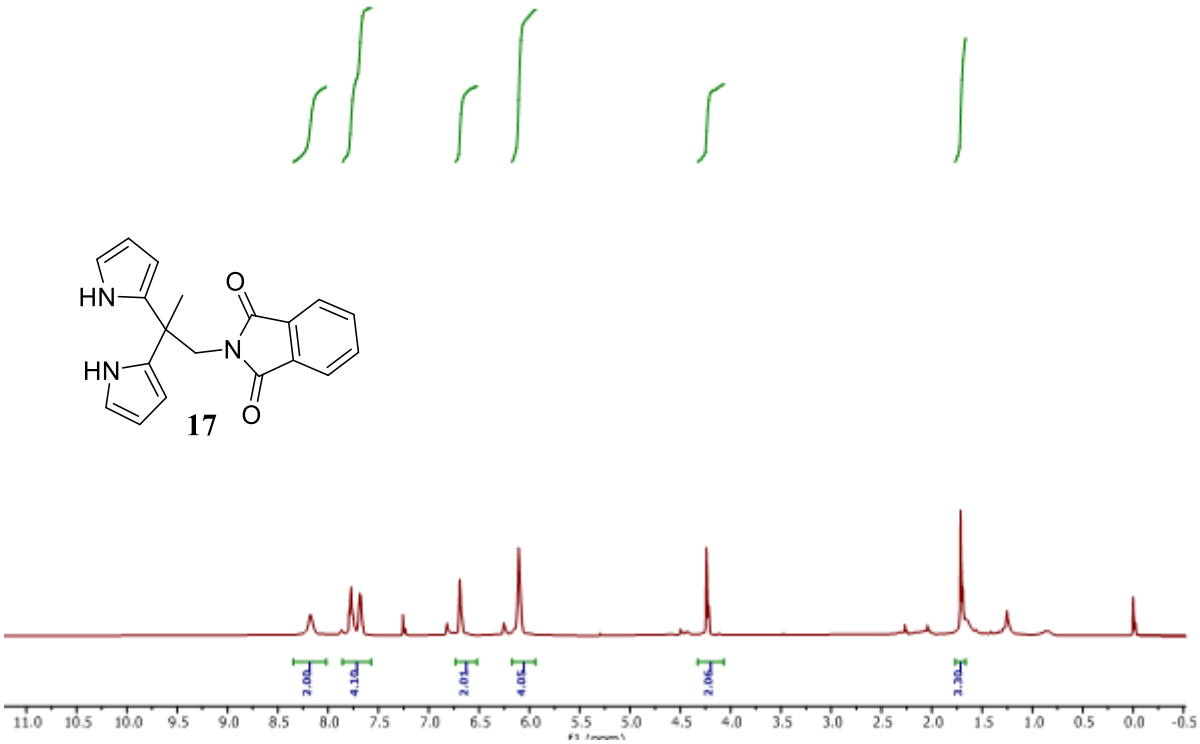

Fig. S23. ^{1}H-NMR spectrum of compound **17** recorded in $CDCl_3$.

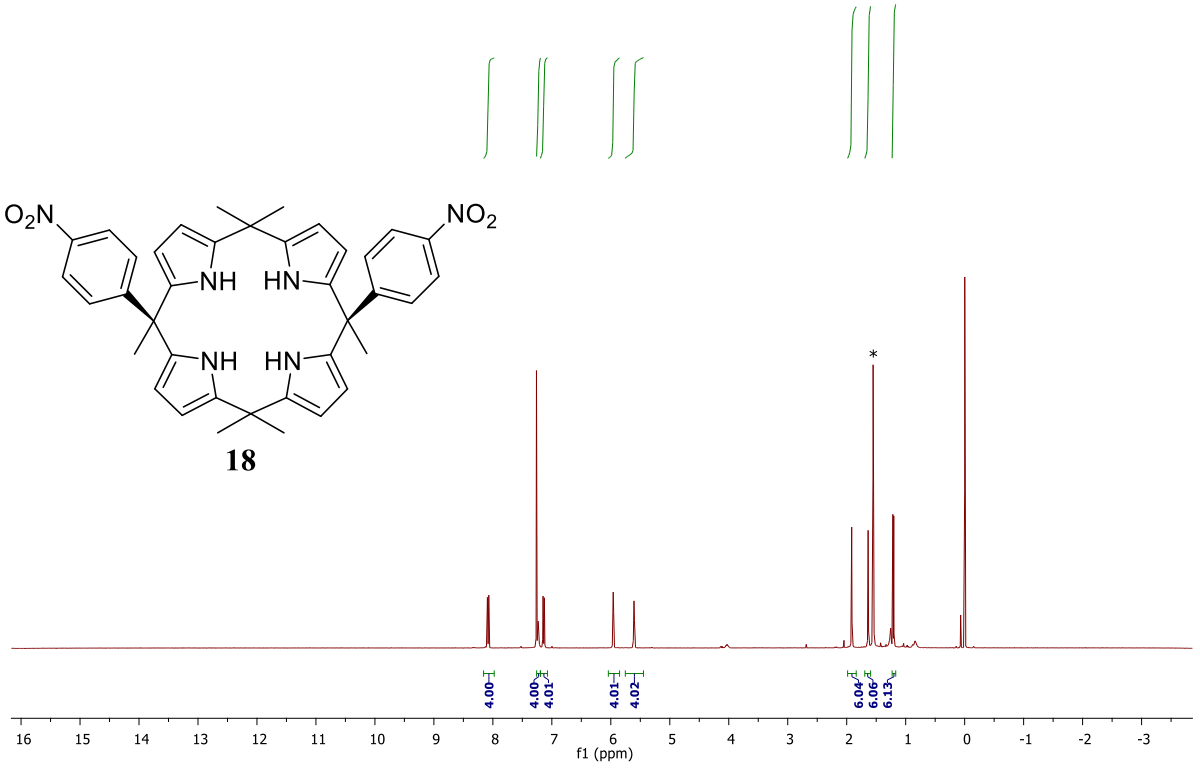

Fig. S24. ^{1}H-NMR spectrum of compound **18** recorded in $CDCl_3$. (*Represents a peak due to residual solvent water)

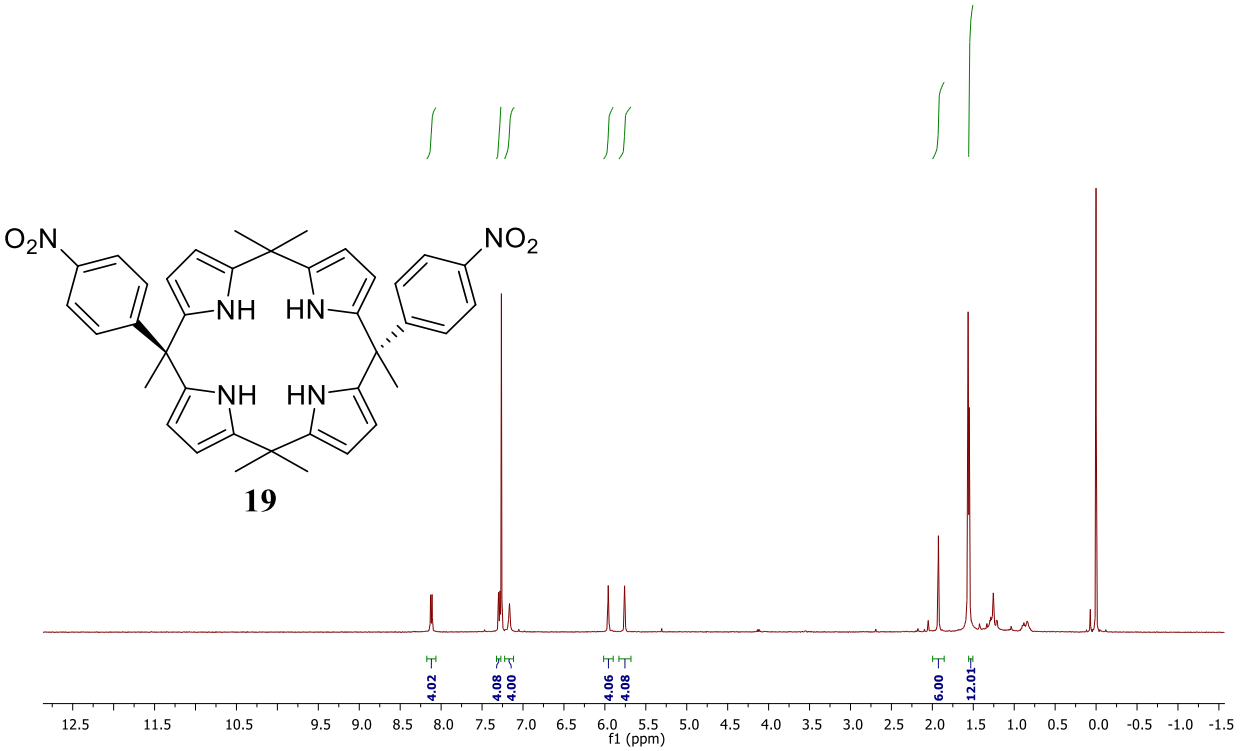

Fig. S25. ^{1}H-NMR spectrum of compound **19** recorded in $CDCl_3$.

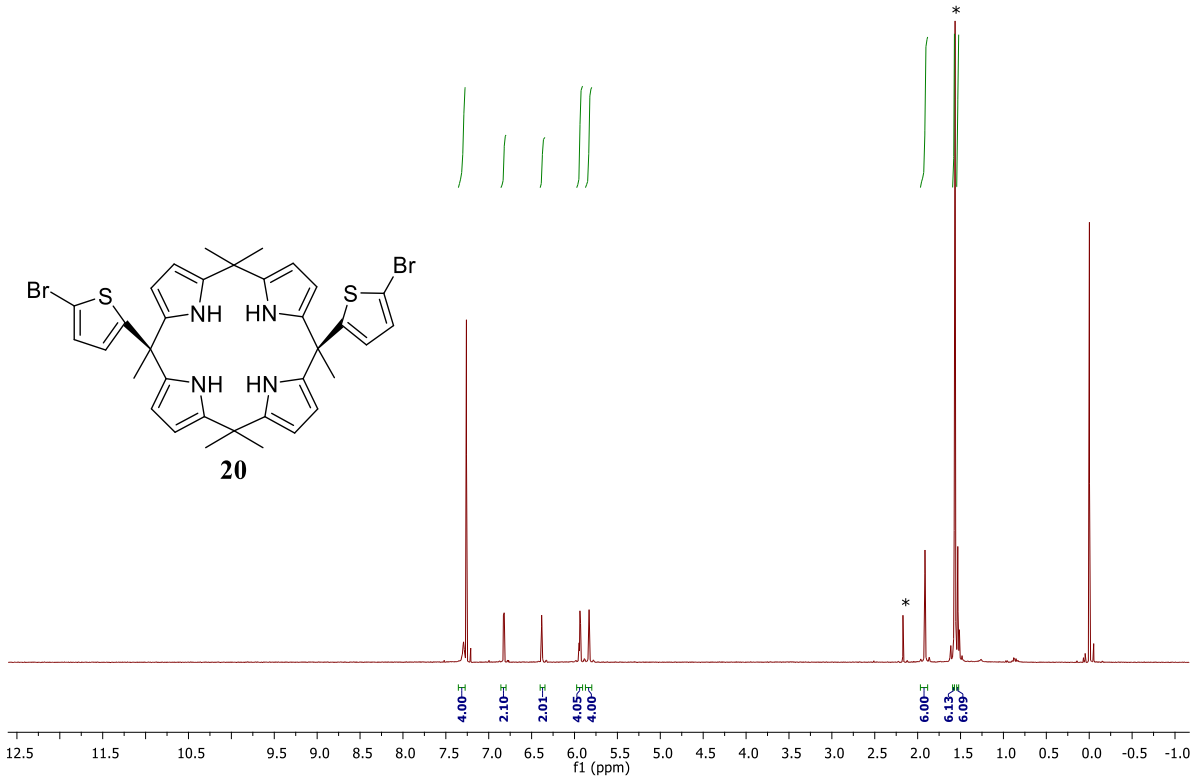

Fig. S26. ^{1}H-NMR spectrum of compound **20** recorded in $CDCl_3$. (*Represents peaks due to residual solvents water and acetone)

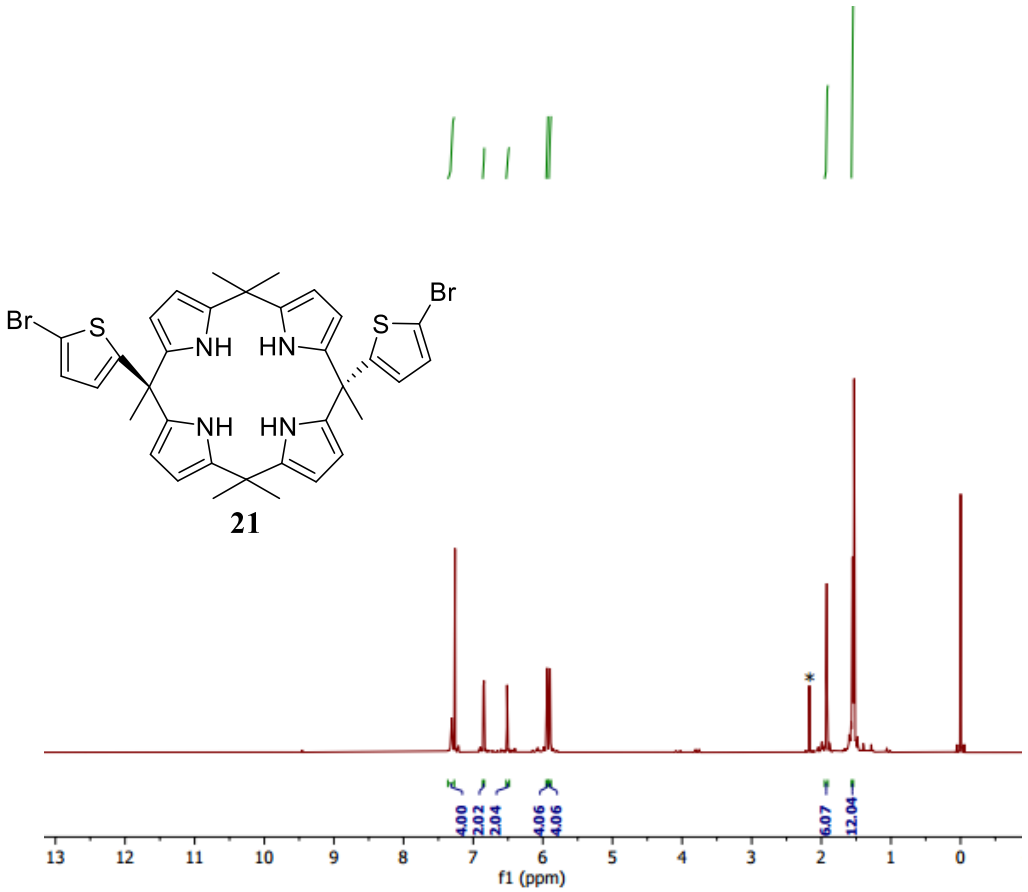

Fig. S27. ^{1}H-NMR spectrum of compound **21** recorded in $CDCl_3$. (*Represents a peak due to residual solvent acetone)

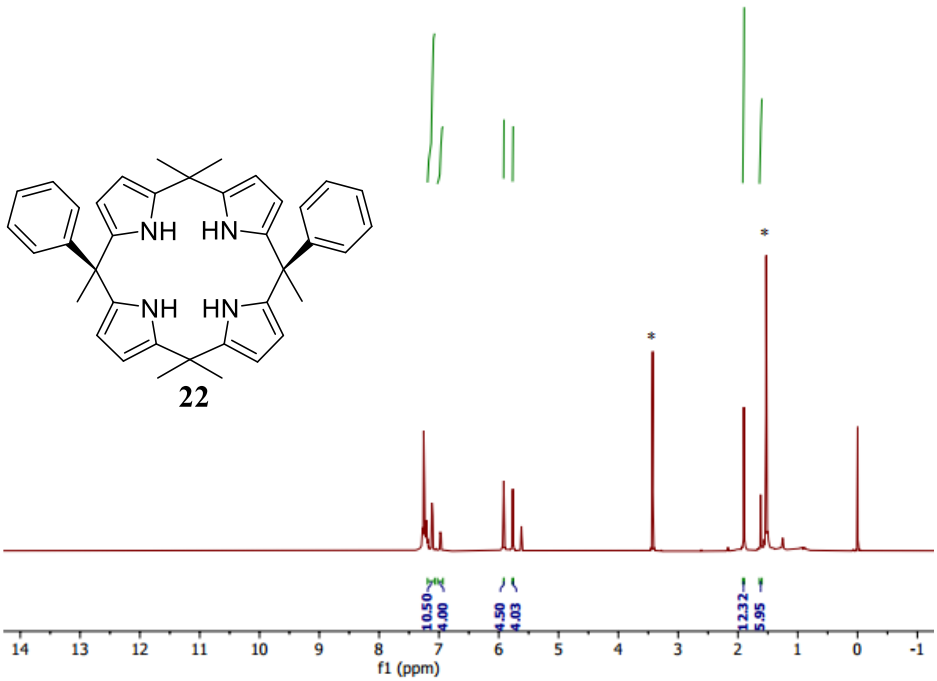

Fig. S28. ^{1}H-NMR spectrum of compound **22** recorded in $CDCl_3$. (*Represents peaks due to residual solvents water and methanol)

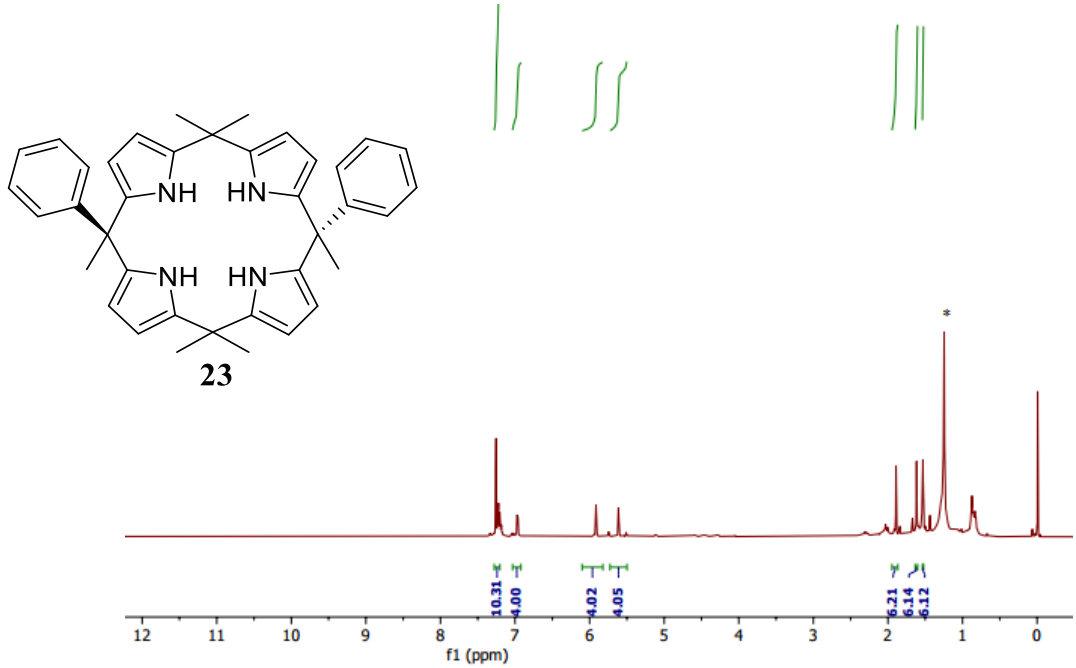

Fig. S29. ^{1}H-NMR spectrum of compound **23** recorded in $CDCl_3$. (*Represents a peak due to residual solvent ethanol)

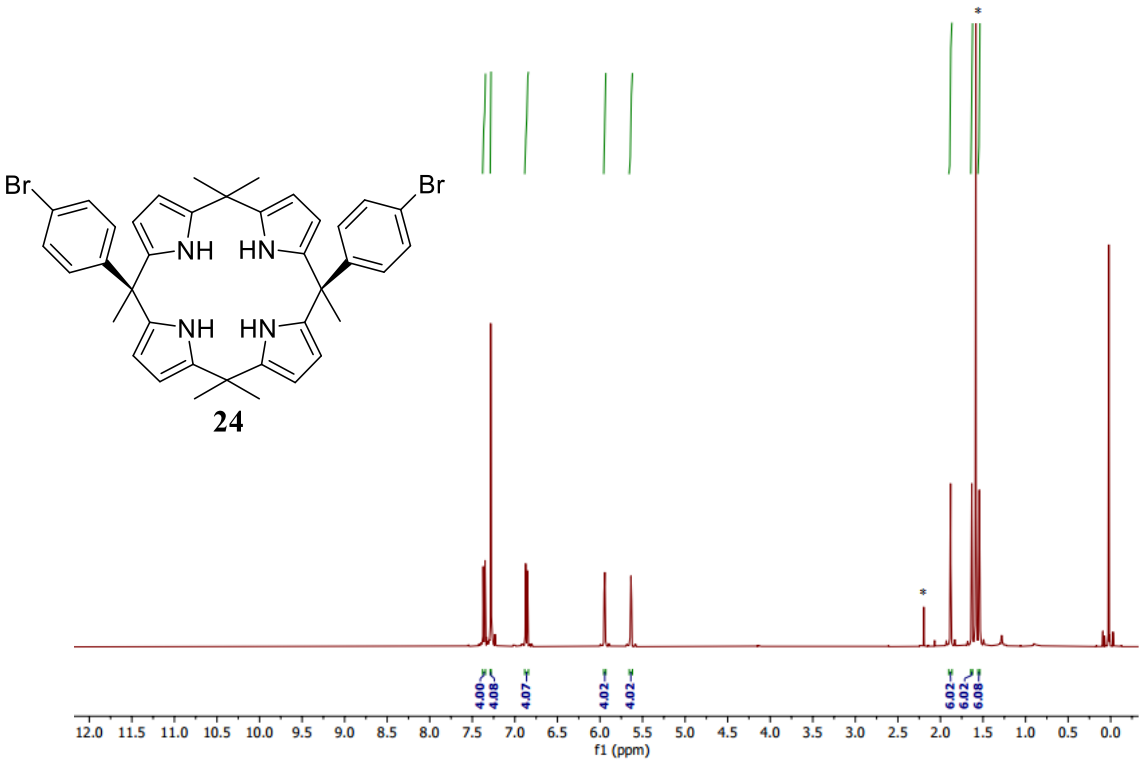

Fig. S30. ^{1}H-NMR spectrum of compound **24** recorded in $CDCl_3$. (*Represents peaks due to residual solvents water and acetone)

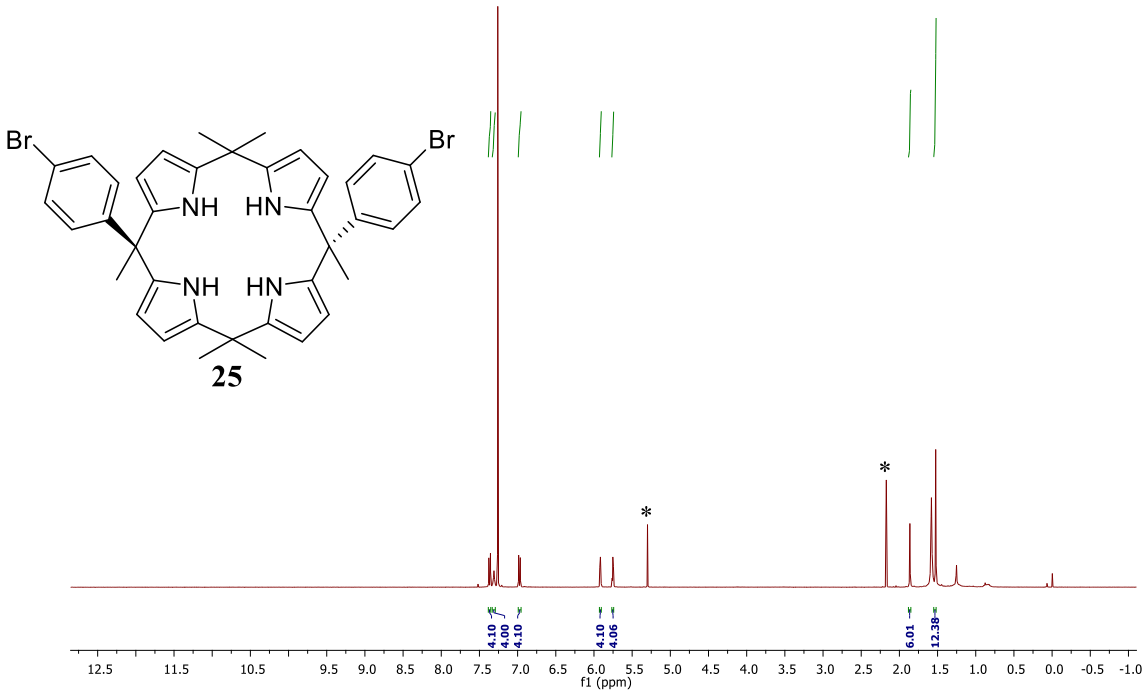

Fig. S31. ^{1}H-NMR spectrum of compound **25** recorded in $CDCl_3$. (*Represents peaks due to residual solvents acetone and dichloromethane)

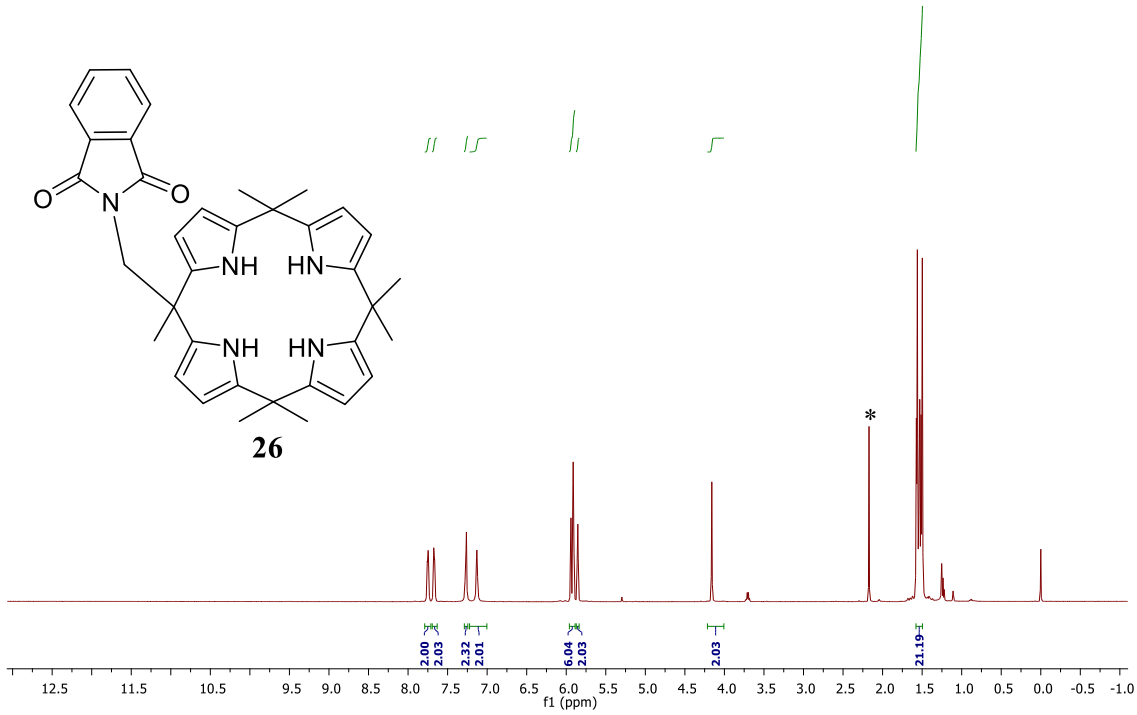

Fig. S32. ^{1}H-NMR spectrum of compound **26** recorded in $CDCl_3$. (*Represents a peak due to residual solvent acetone)

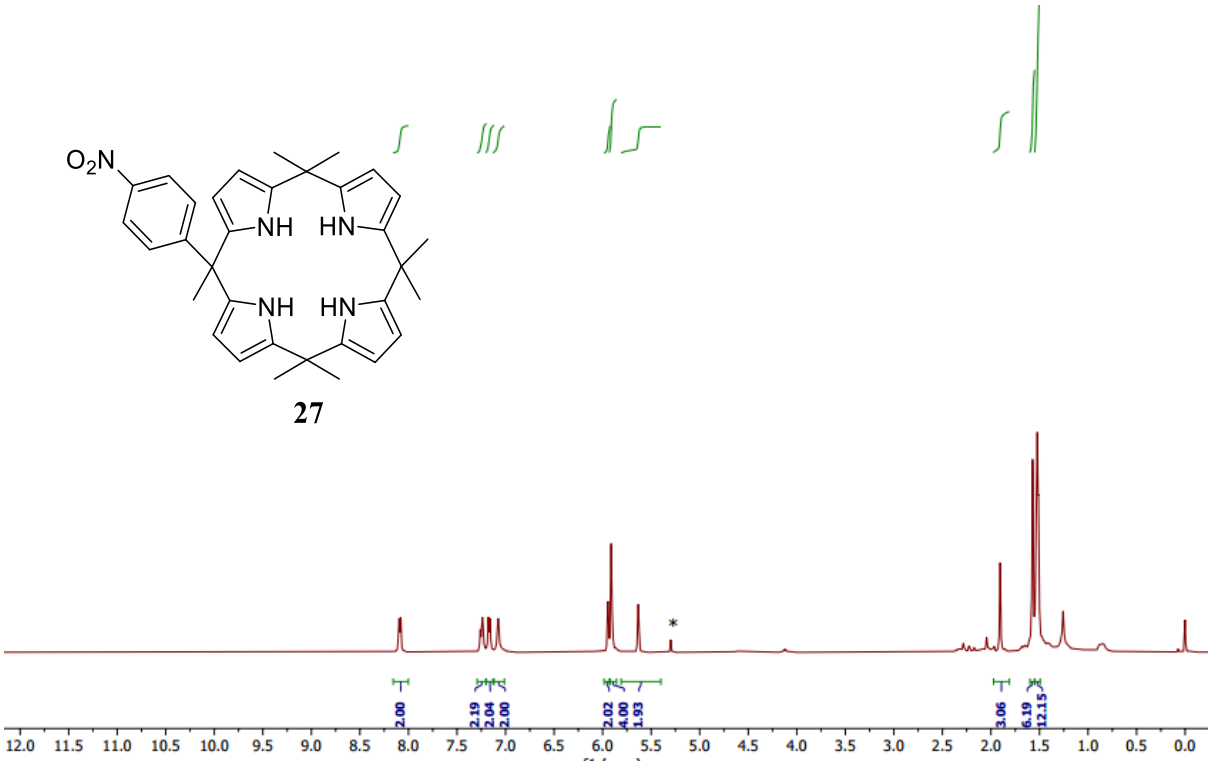

Fig. S33. ^{1}H-NMR spectrum of compound **27** recorded in $CDCl_3$. (*Represents a peak due to residual solvent dichloromethane)