

Supplementary Material

Rings of Rings: Calixpyrrole Cyclotrimers

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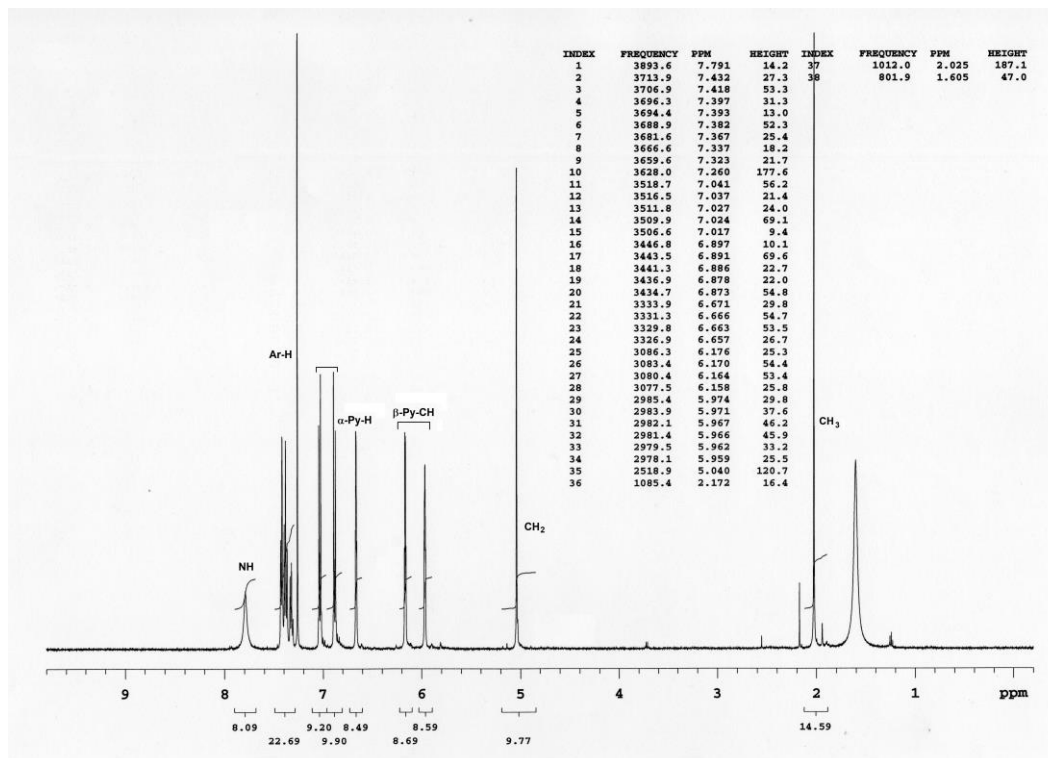


Figure S1a. ^1H NMR (500 MHz, CDCl_3) for compound **3** with resonances assignments.

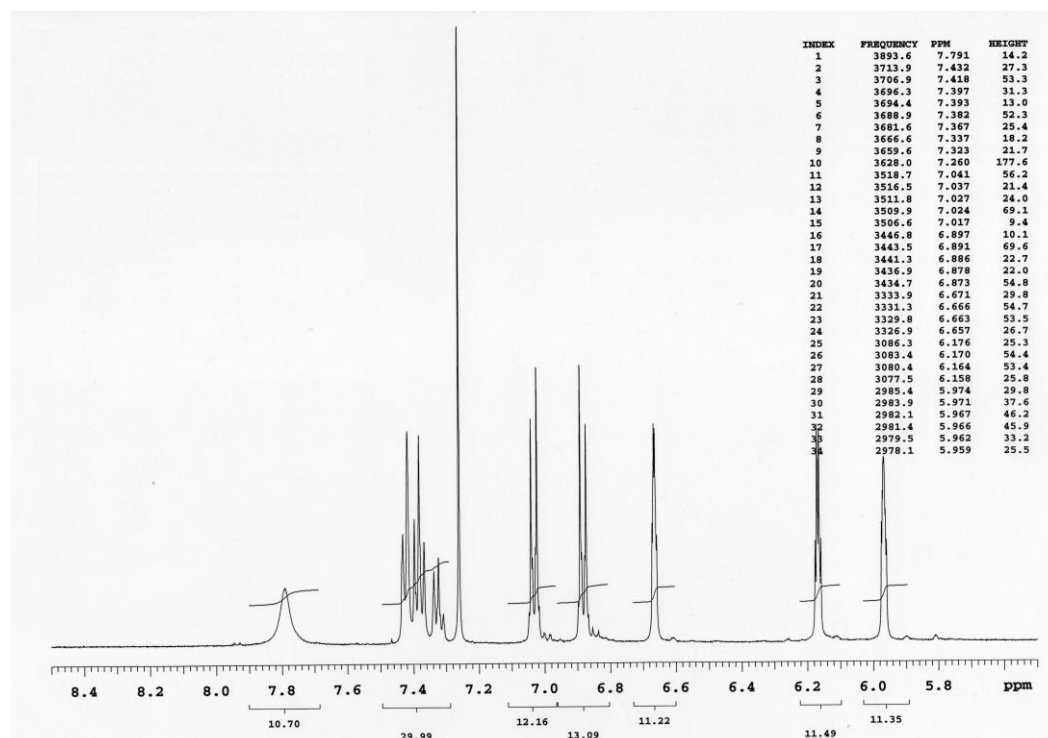


Figure S1b. ^1H NMR (500 MHz, CDCl_3) for compound **3** (Expansion).

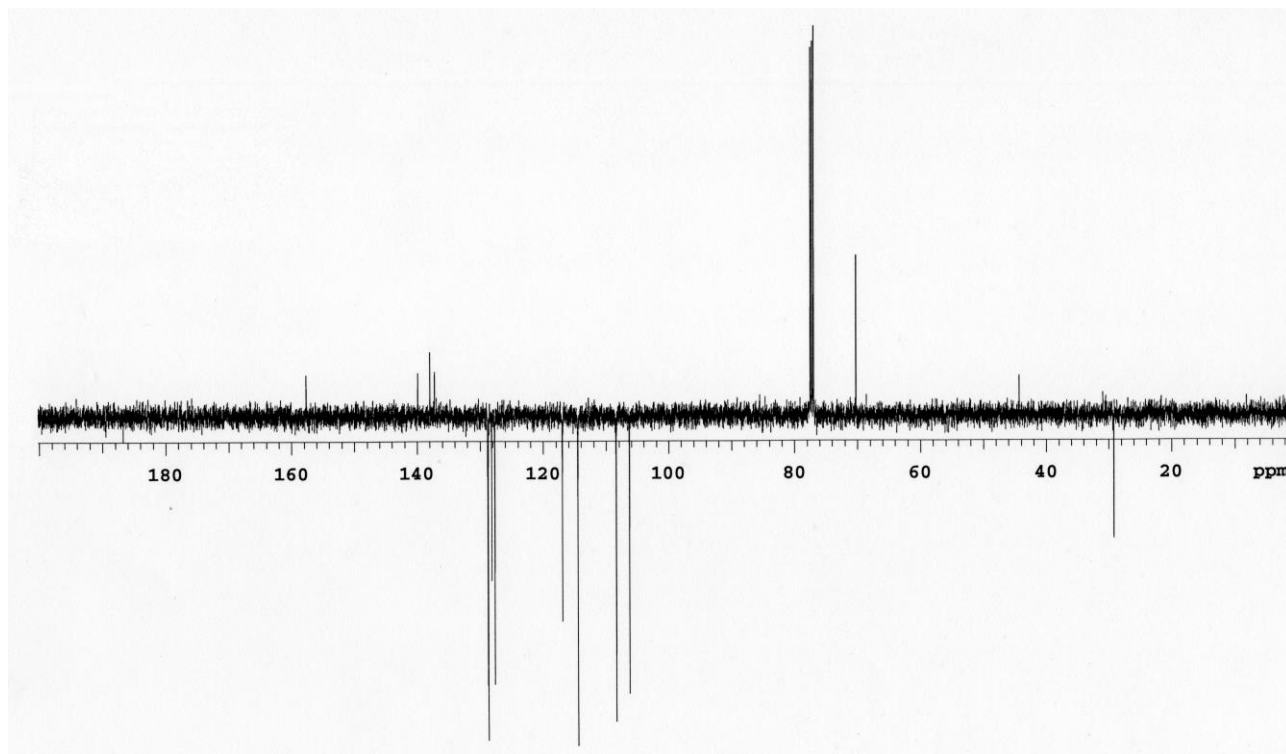


Figure S1c ¹³C NMR (125 MHz, CDCl₃) for compound **3**.

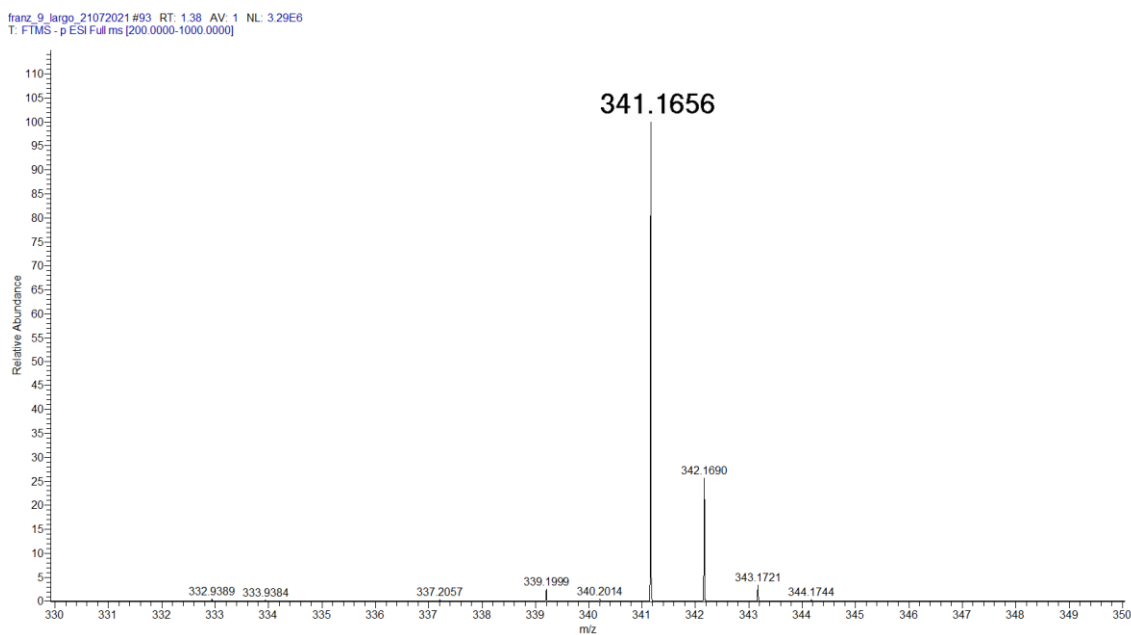


Figure S1d. ESI-MS for compound **3**. Calc. m/z for C₂₃H₂₀N₂O₂ 342.1732.

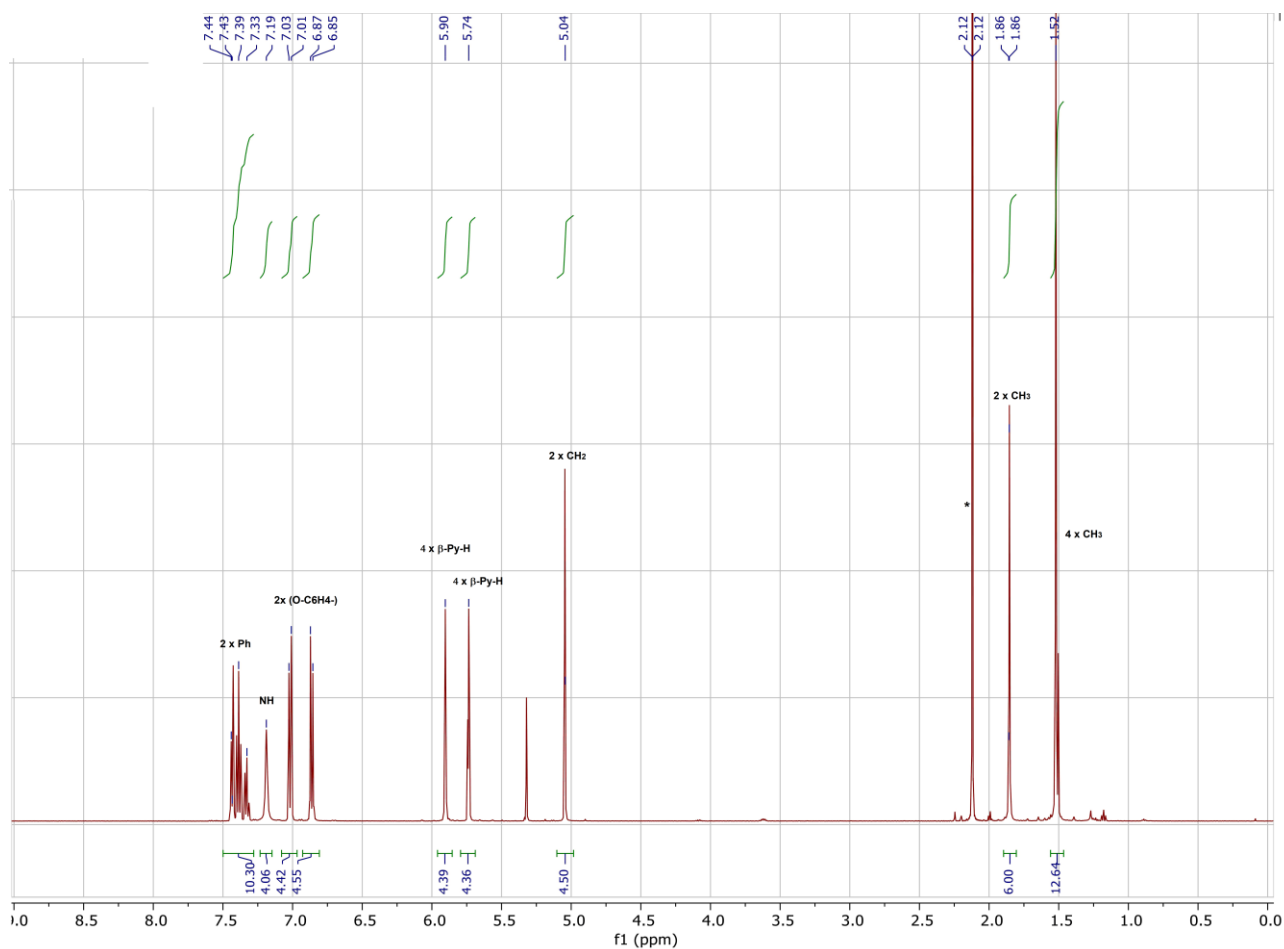


Figure S2a. ¹H NMR (500 MHz, CD₂Cl₂) for compound *anti*-4 with resonances assignments. * Adventitious water.

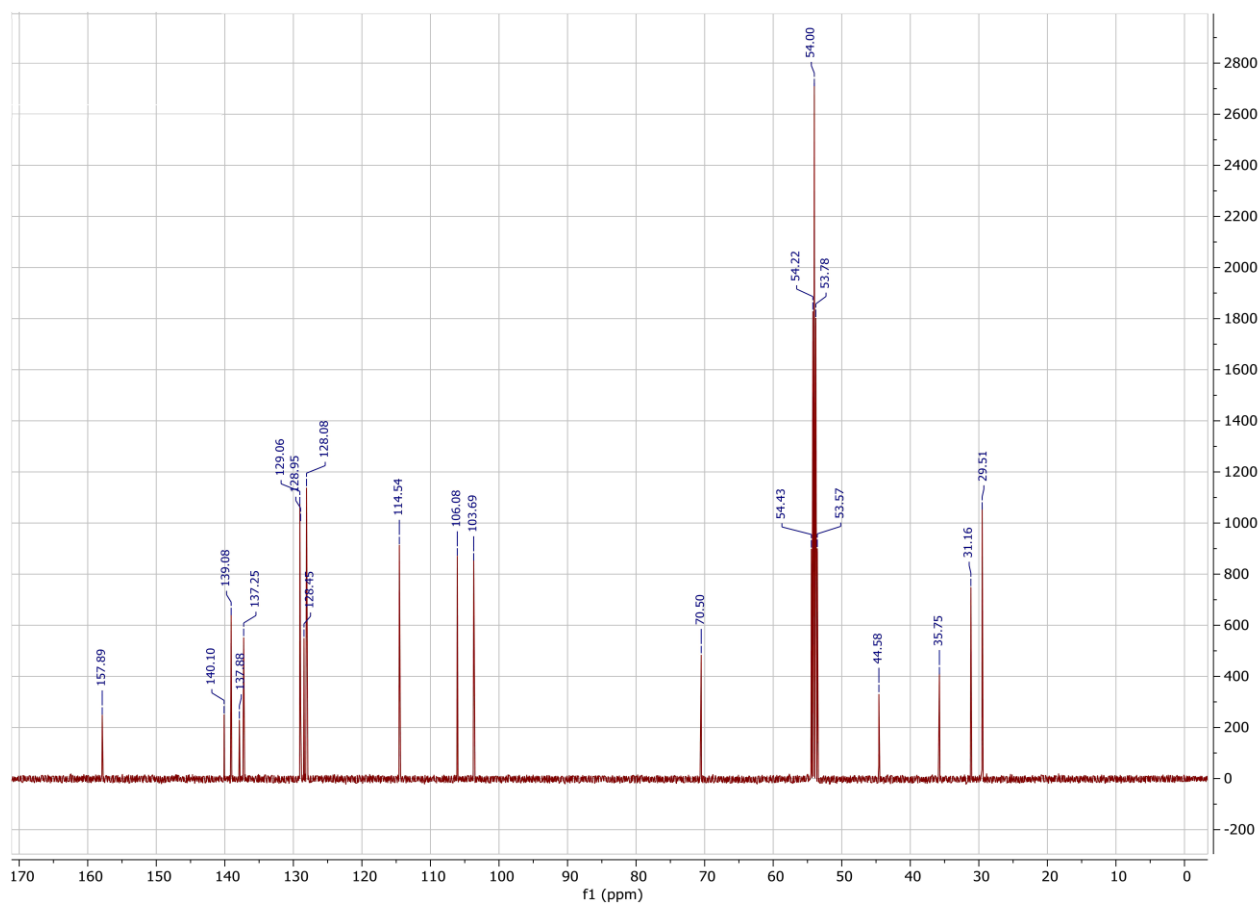


Figure S2b. ¹³C NMR (125 MHz, CD₂Cl₂) for compound *anti*-4.

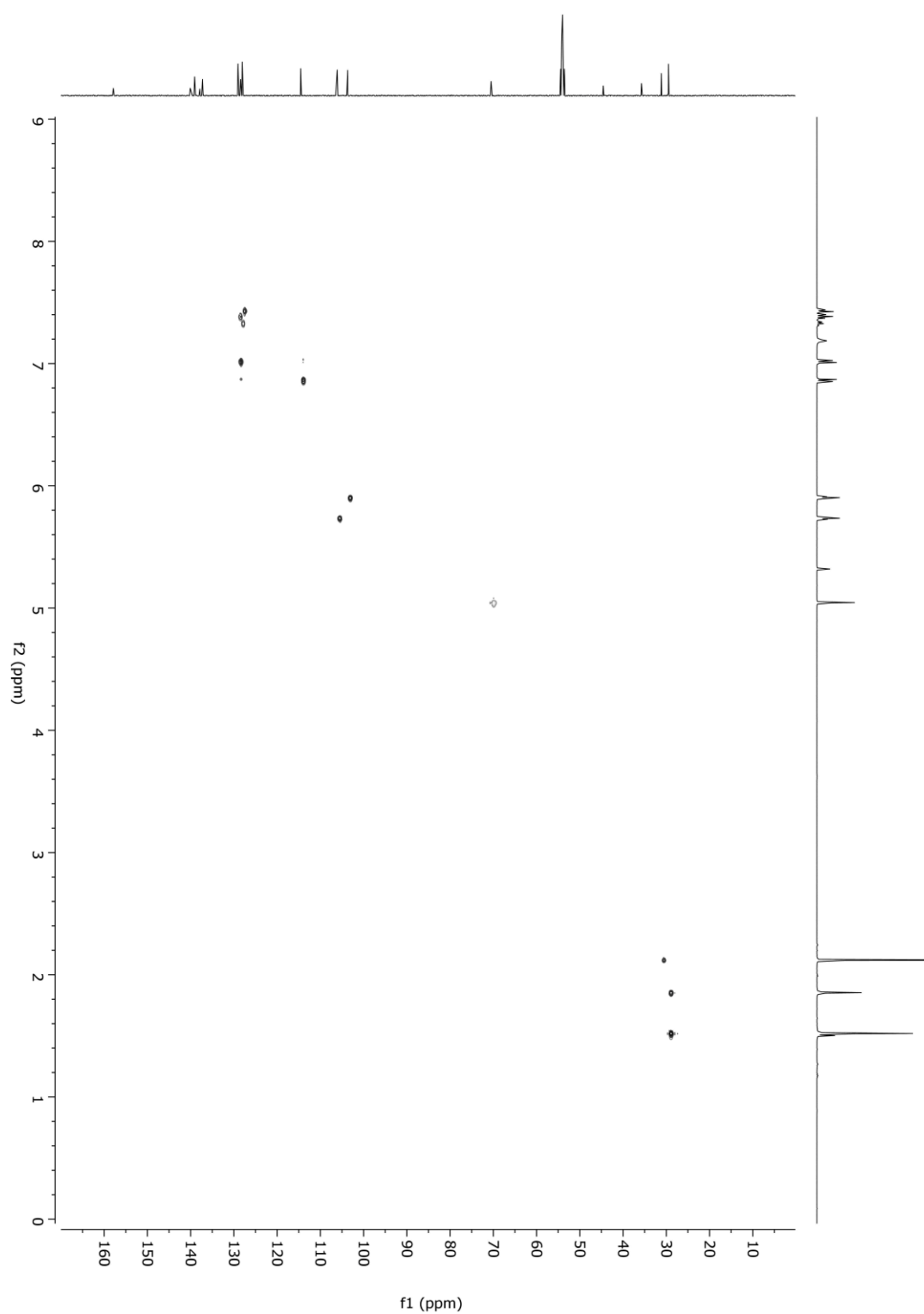


Figure S2c. HSQC (CD₂Cl₂) for compound *anti*-4.

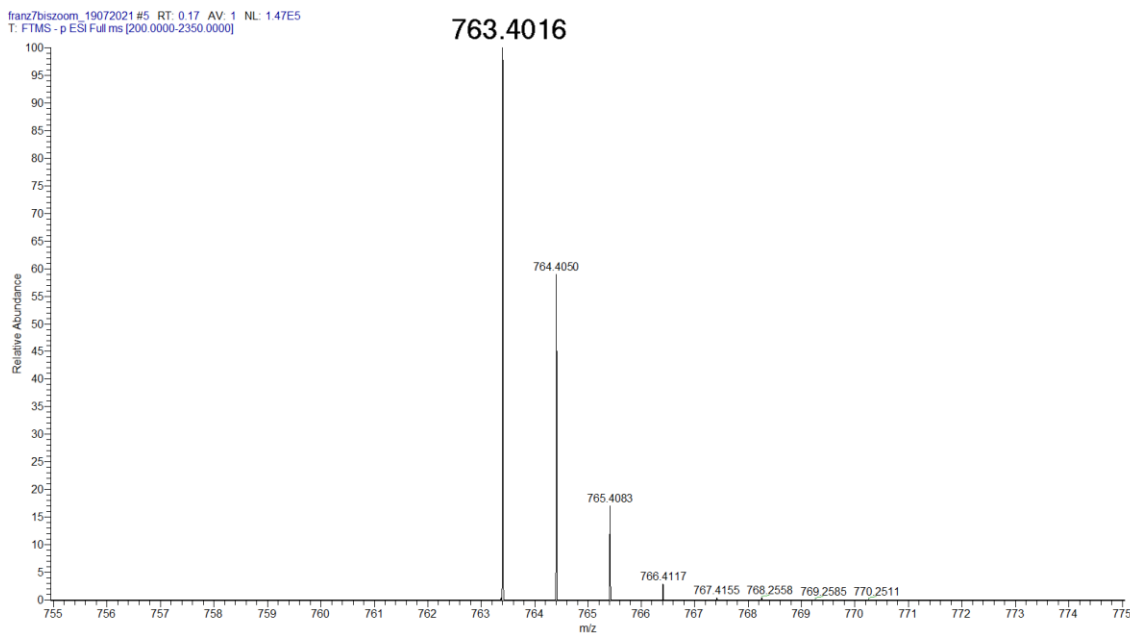


Figure S2d. ESI-MS for compound *anti*-4. Calc. m/z for $C_{52}H_{52}N_4O_2$ 764.4090.

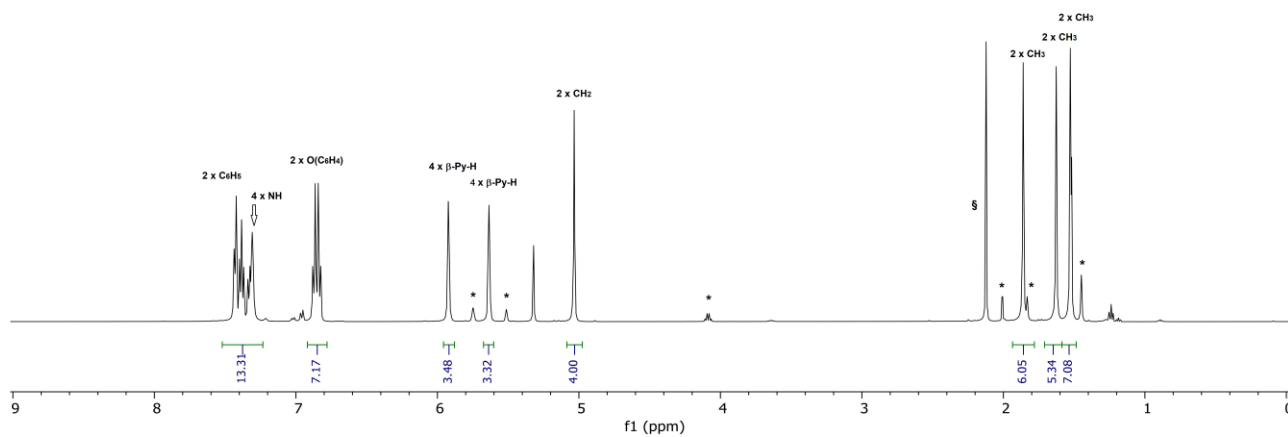


Figure S3a. 1H NMR (500 MHz, CD_2Cl_2) for compound *syn*-4 with resonances assignments. (*) Impurities from solvent; (§) water.

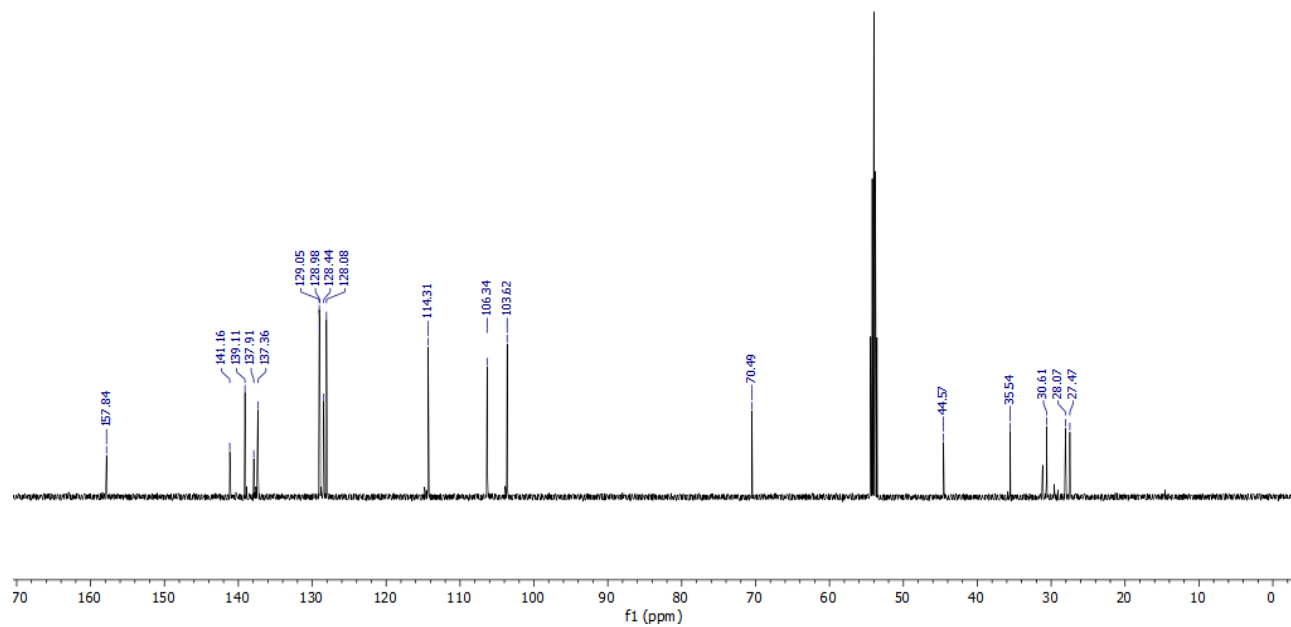


Figure S3b. ¹³C NMR (125 MHz, CD₂Cl₂) for compound *syn-4*.

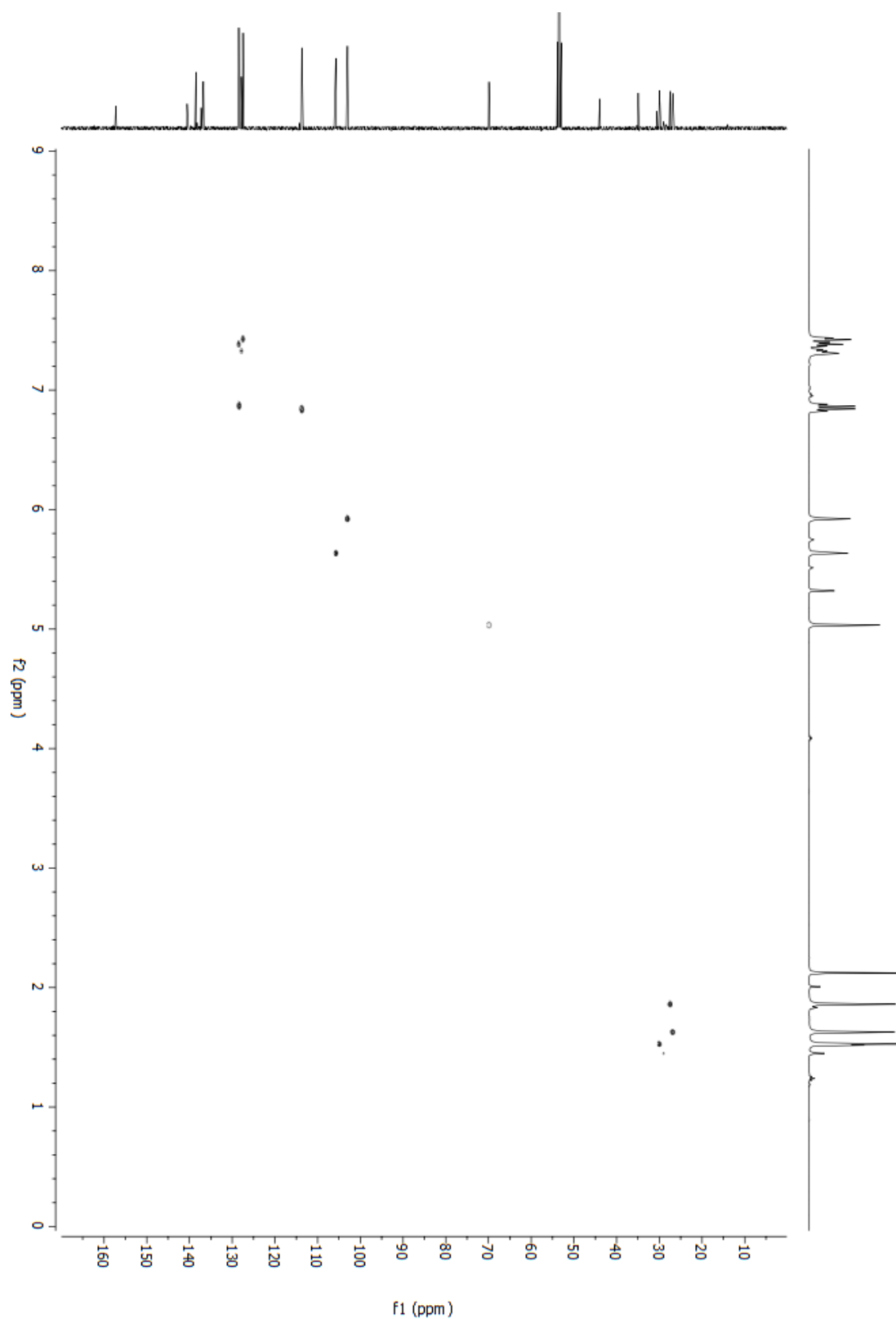


Figure S3c. HSQC (CD_2Cl_2) for compound *syn-4*.

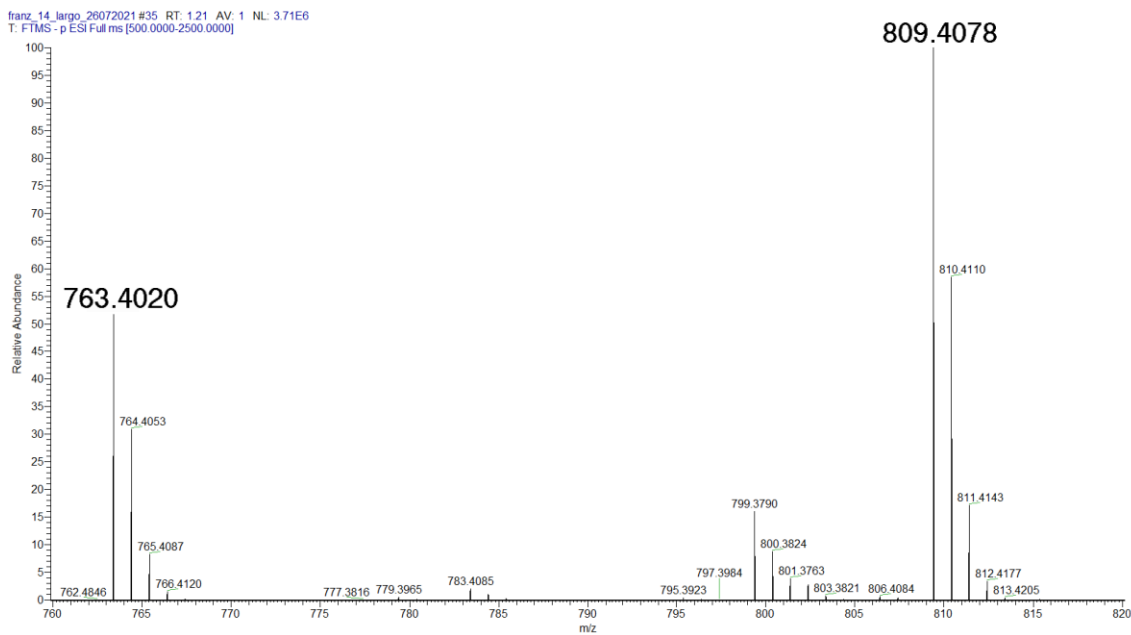


Figure S3d. ESI-MS for compound *syn-4*. Calc. m/z for $C_{52}H_{52}N_4O_2$ 764.4090; (calc. for $M+[HCOO]^-$: 809.4066).

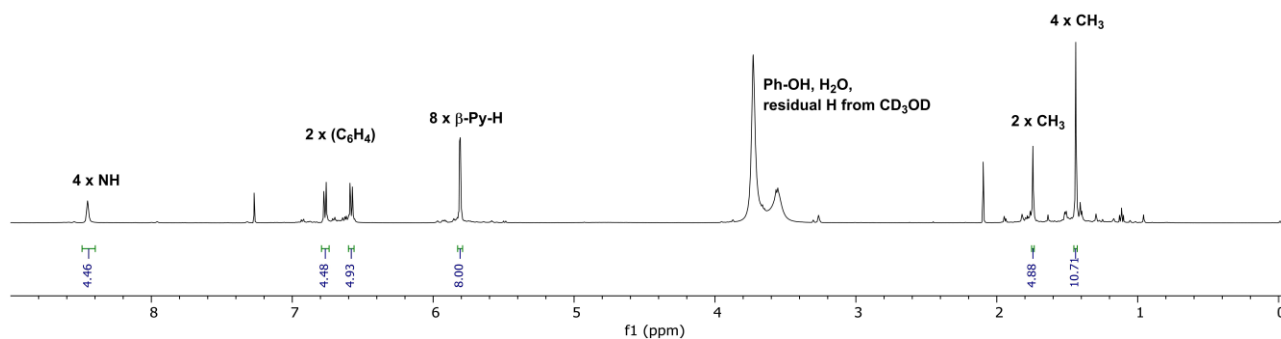


Figure S4a. 1H NMR (500 MHz, $CDCl_3/CD_3OD$ 6:1) for compound *anti-5* with assignments.

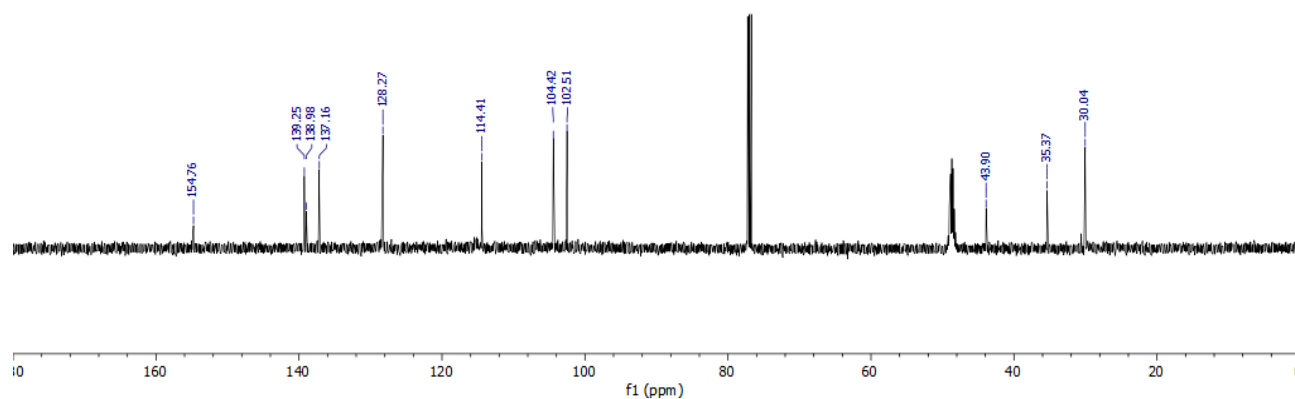


Figure S4b. ¹³C NMR (500 MHz, CDCl₃/CD₃OD 6:1) for compound *anti*-5.

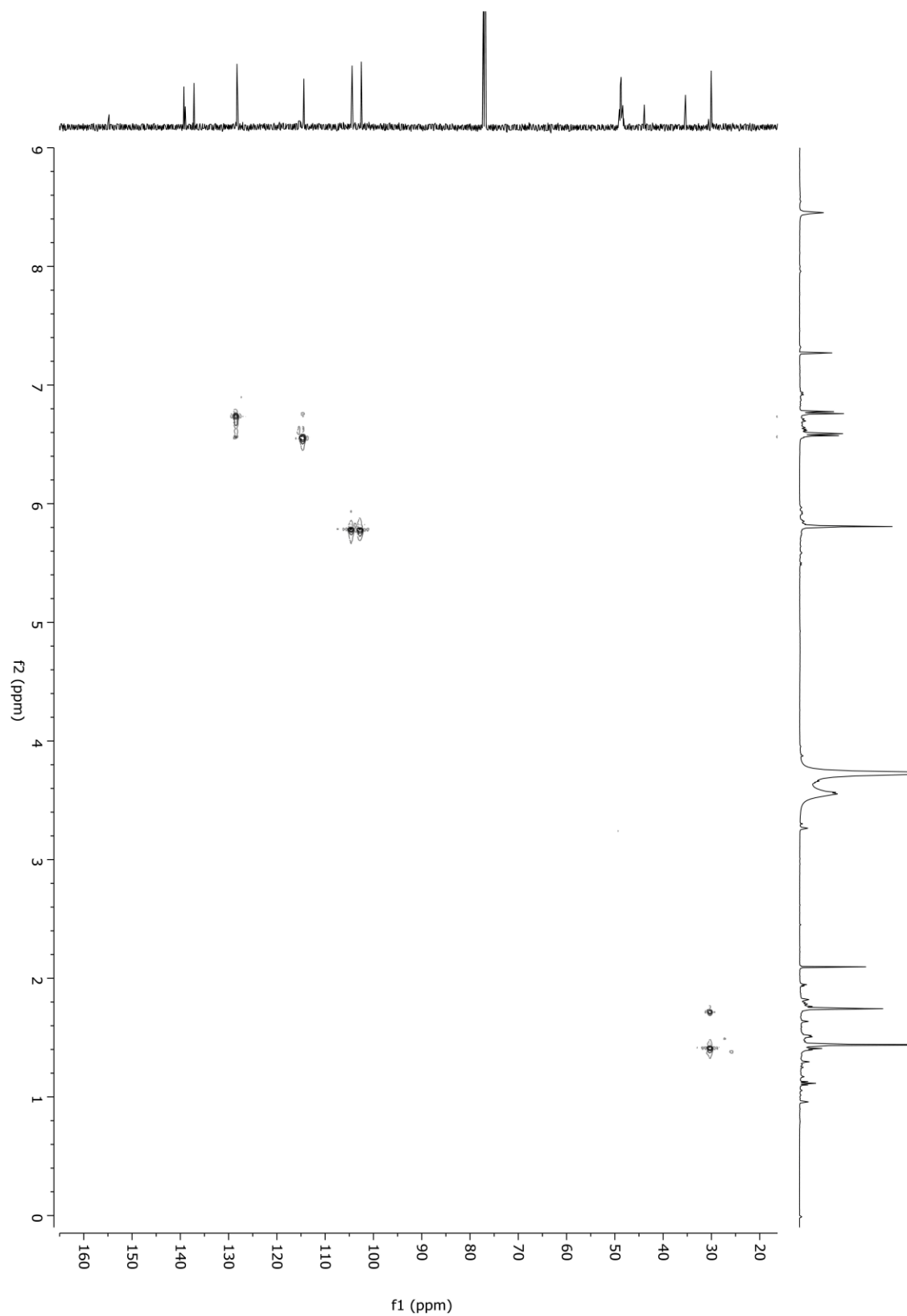


Figure S4c. HSQC ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 6:1) for compound *anti*-5.

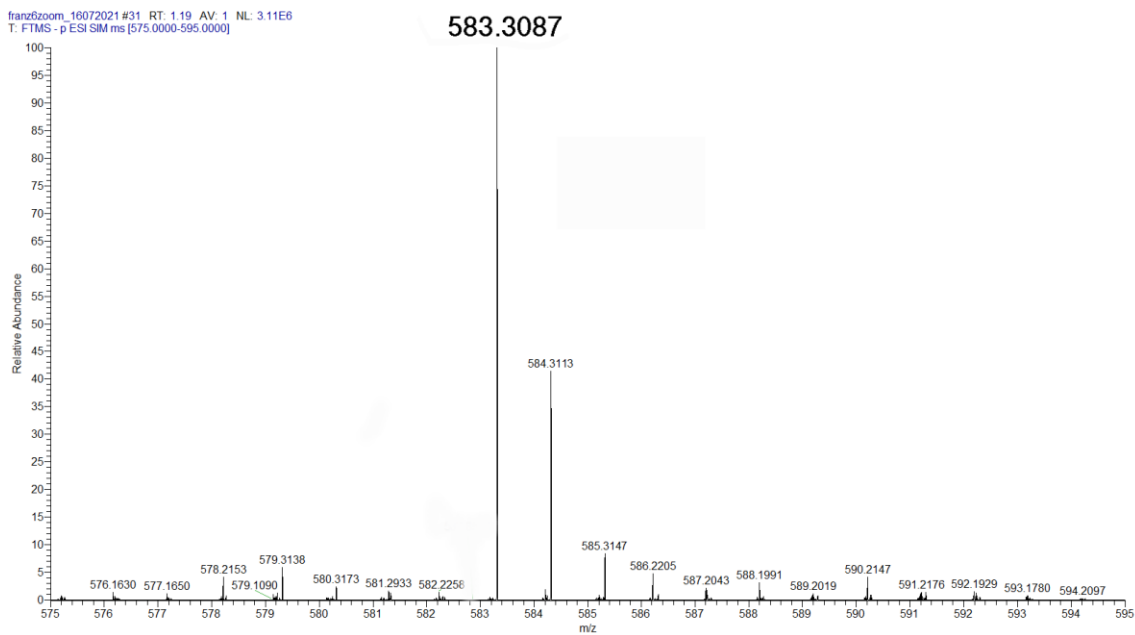


Figure S4d. ESI-MS for compound *anti*-5. Calc. m/z for $C_{38}H_{40}N_4O_2$ 584.3151.

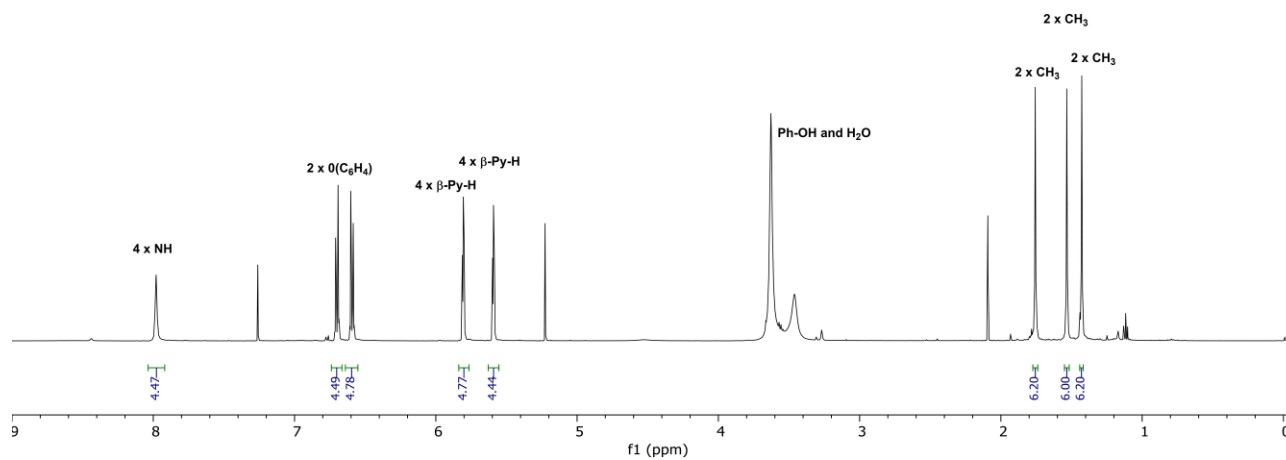


Figure S5a. 1H NMR (500 MHz, $CDCl_3/CD_3OD$ 6:1) for compound *syn*-5 with resonances assignments.

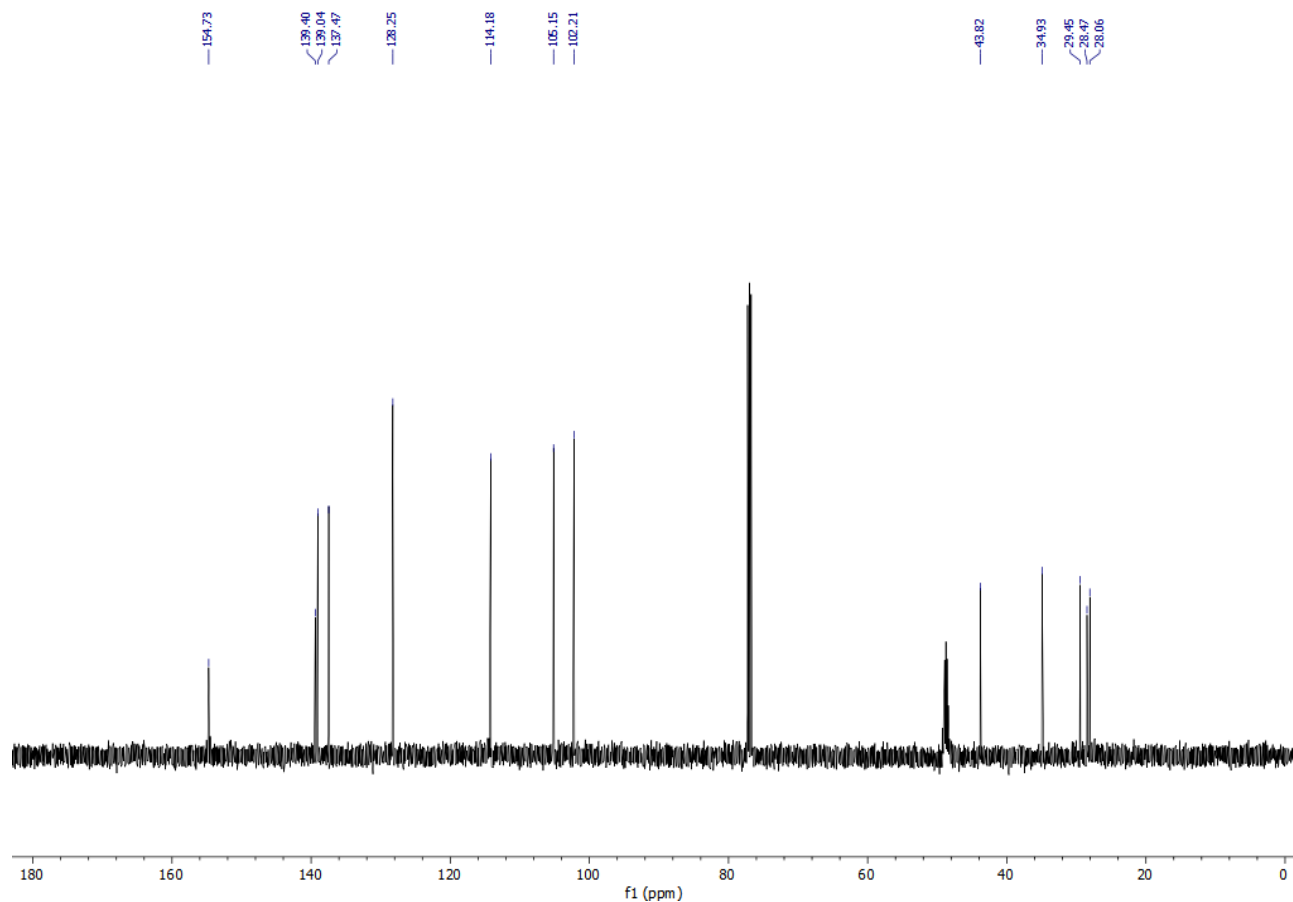


Figure S5b. ¹³C NMR (125 MHz, CDCl₃/CD₃OD 6:1) for compound *syn-5*.

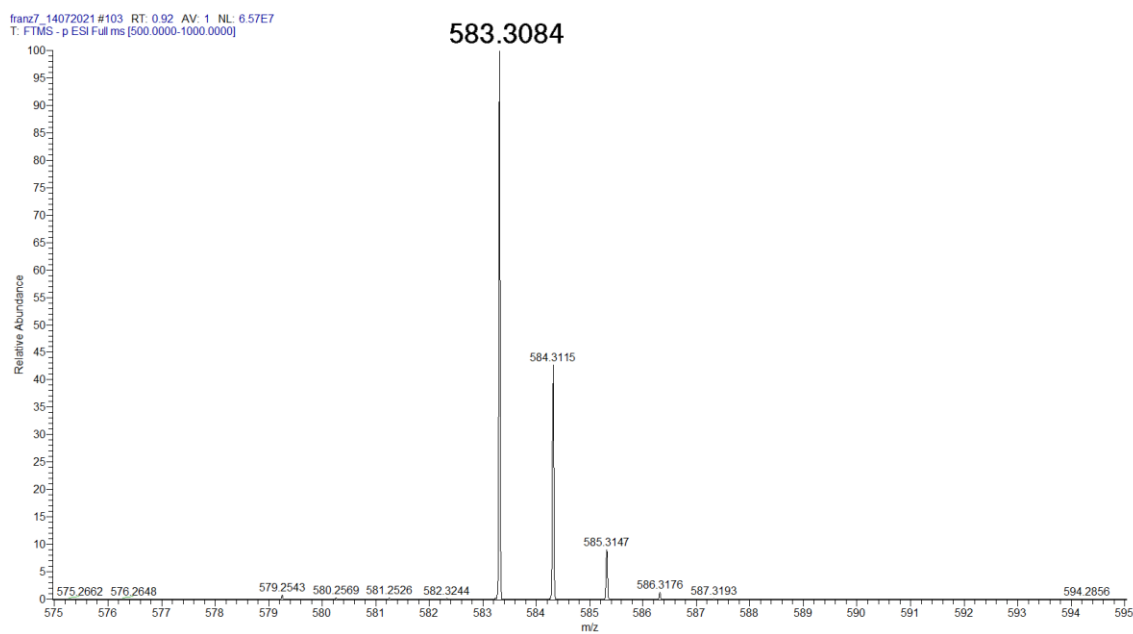


Figure S5c. ESI-MS for compound *syn-5*. Calc. *m/z* for C₃₈H₄₀N₄O₂ 584.3151.

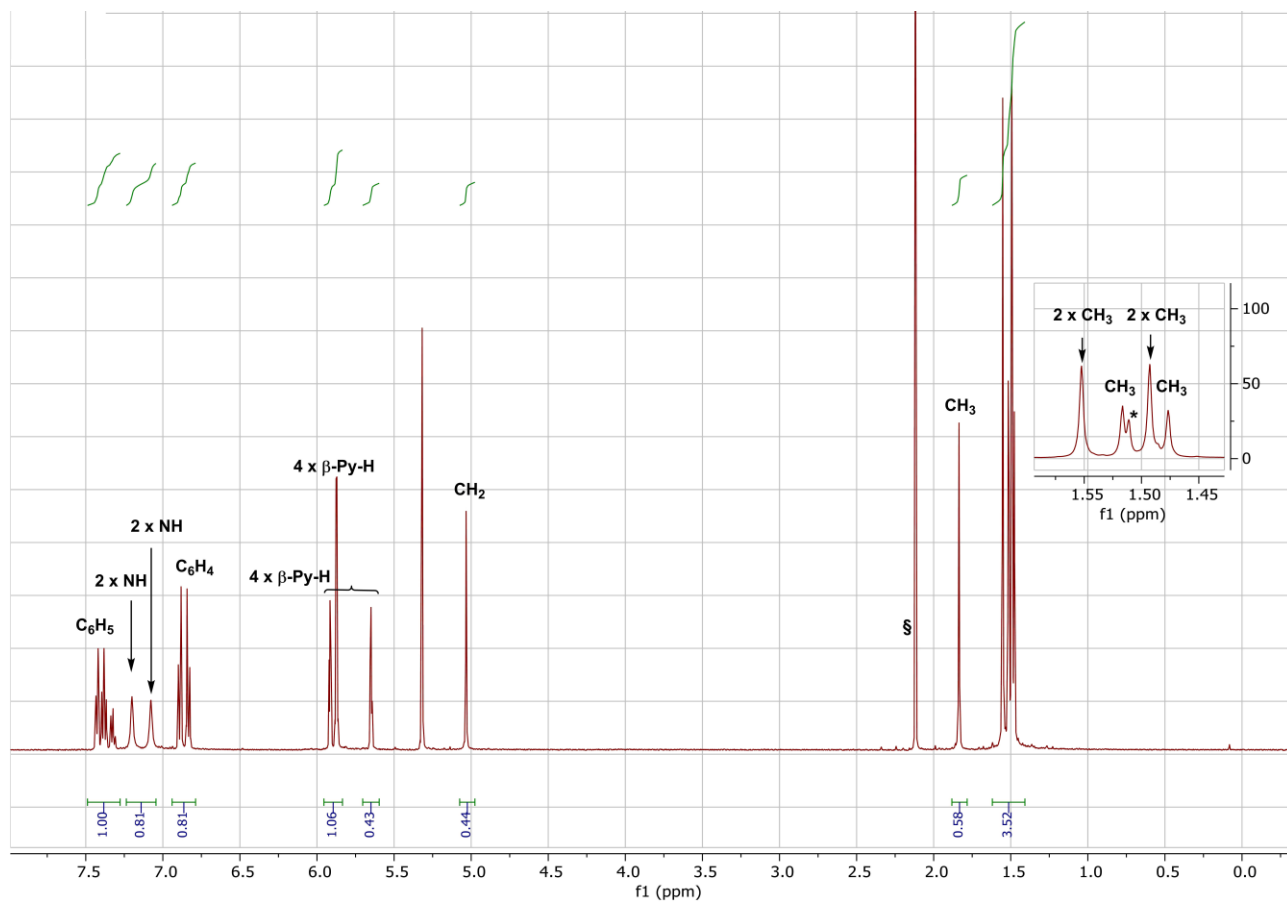


Figure S6a ^1H NMR (500 MHz, CD_2Cl_2) for compound **7**. § Adventitious water; * solvent impurity.

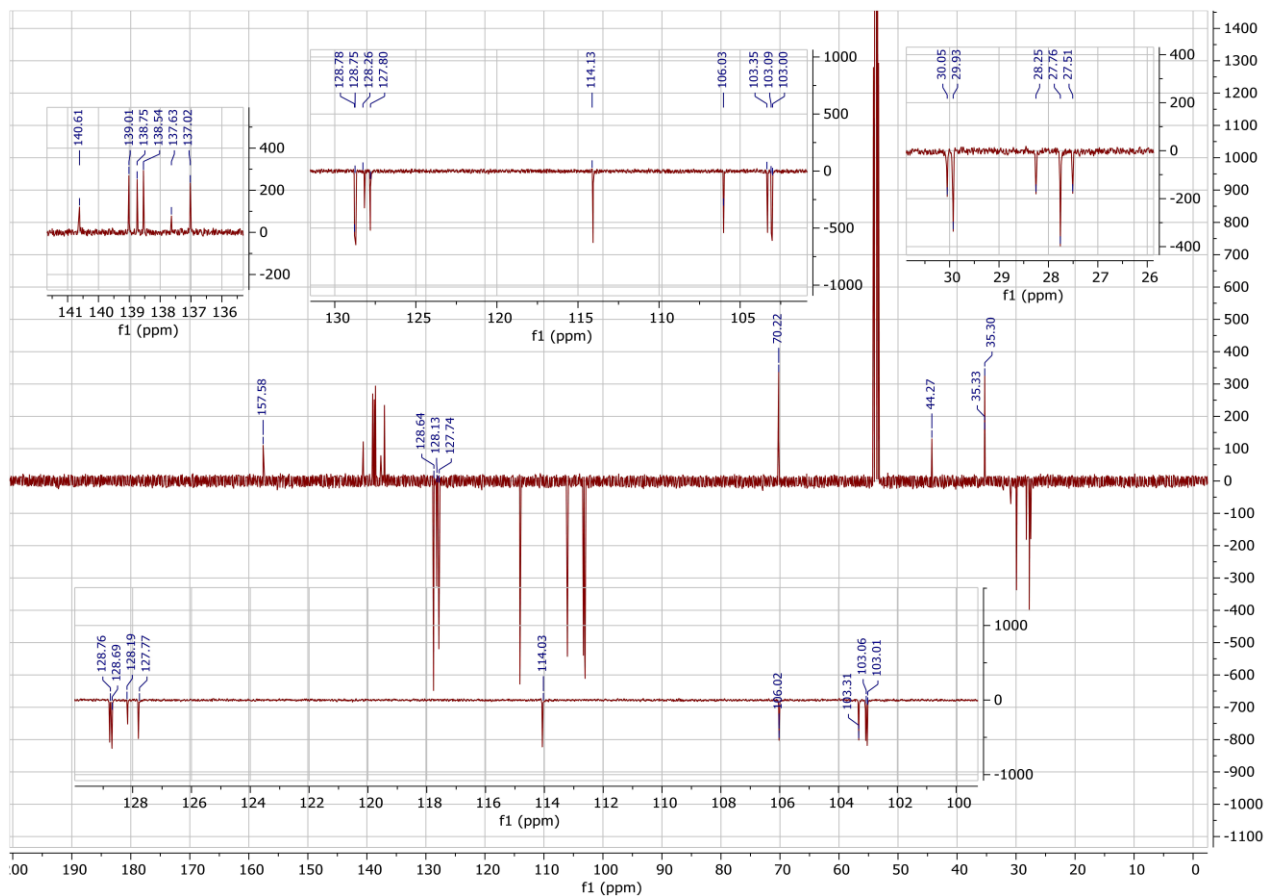


Figure S6b. APT ^{13}C NMR (125 MHz, CD_2Cl_2) for compound 7.

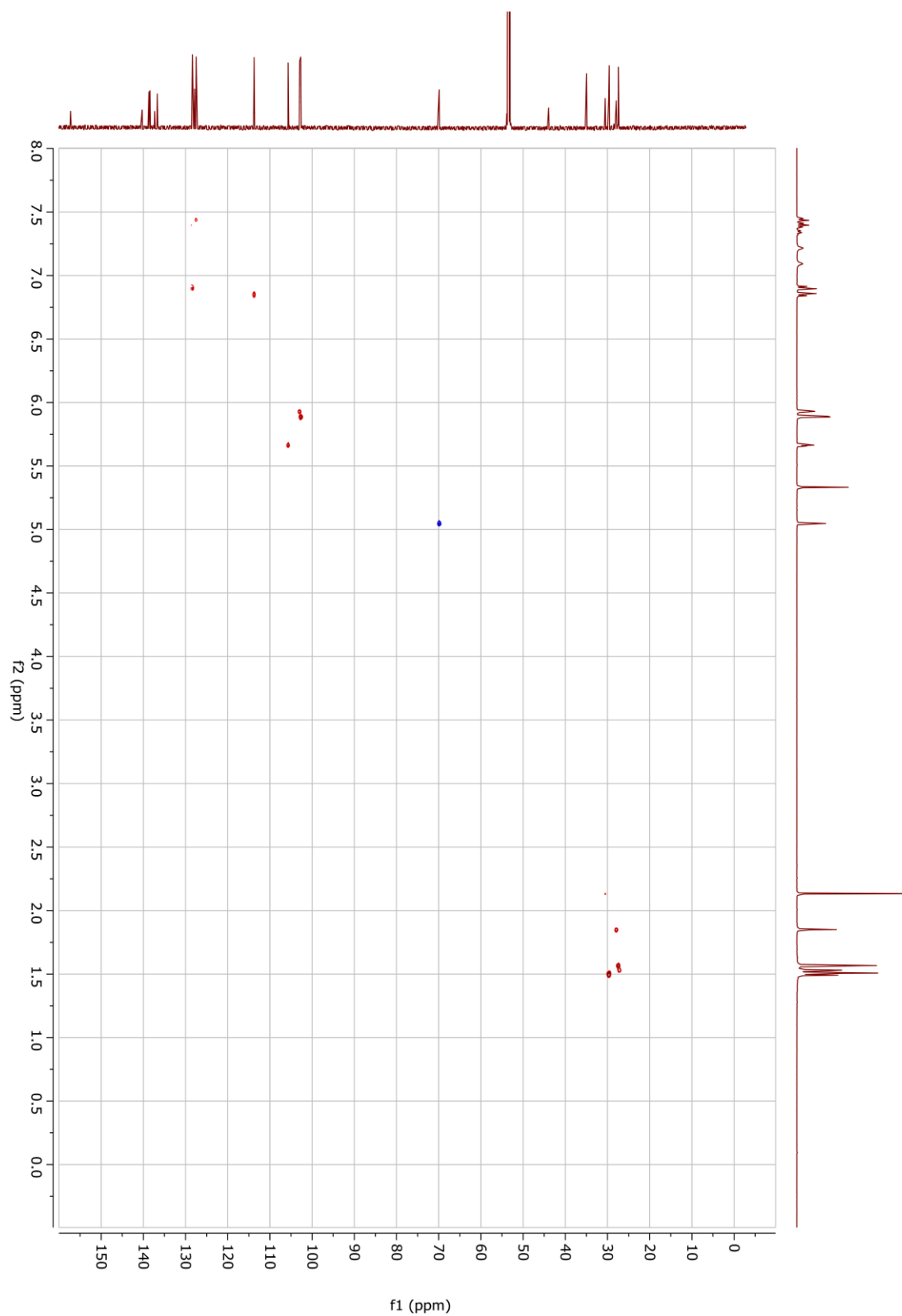


Figure S6c. HSQC (CD₂Cl₂) for compound 7.

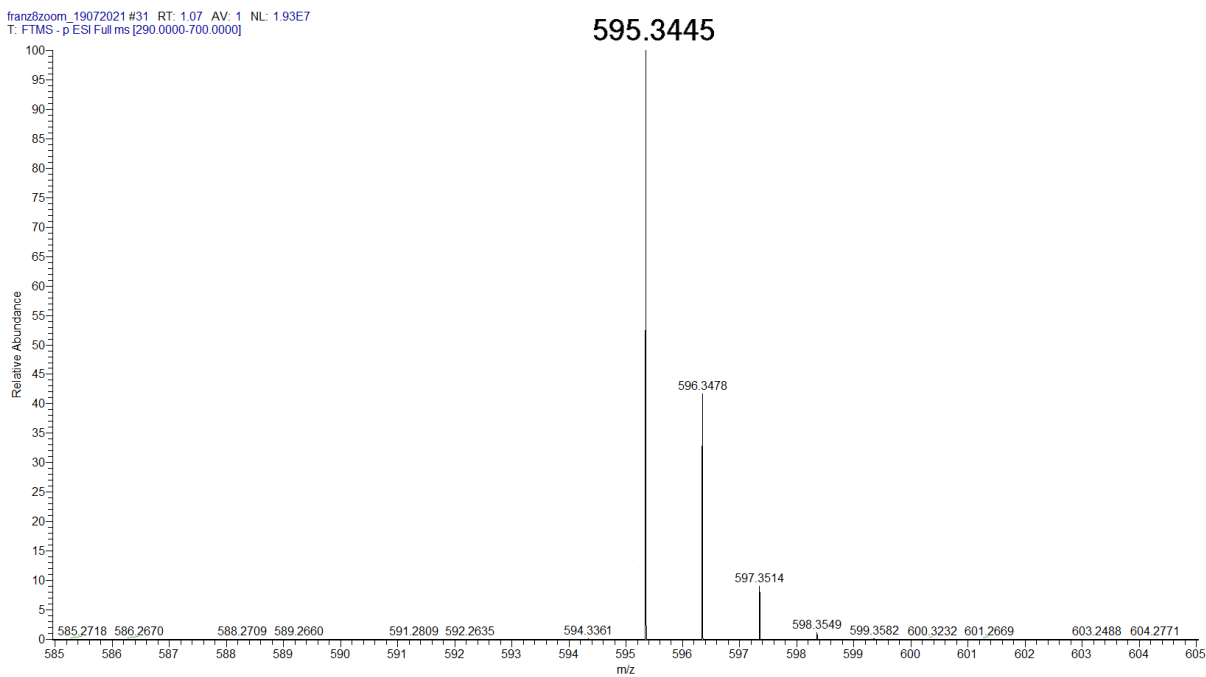


Figure S6d. ESI-MS for compound **7**. Calc. m/z for $C_{40}H_{44}N_4O$: 596.3515.

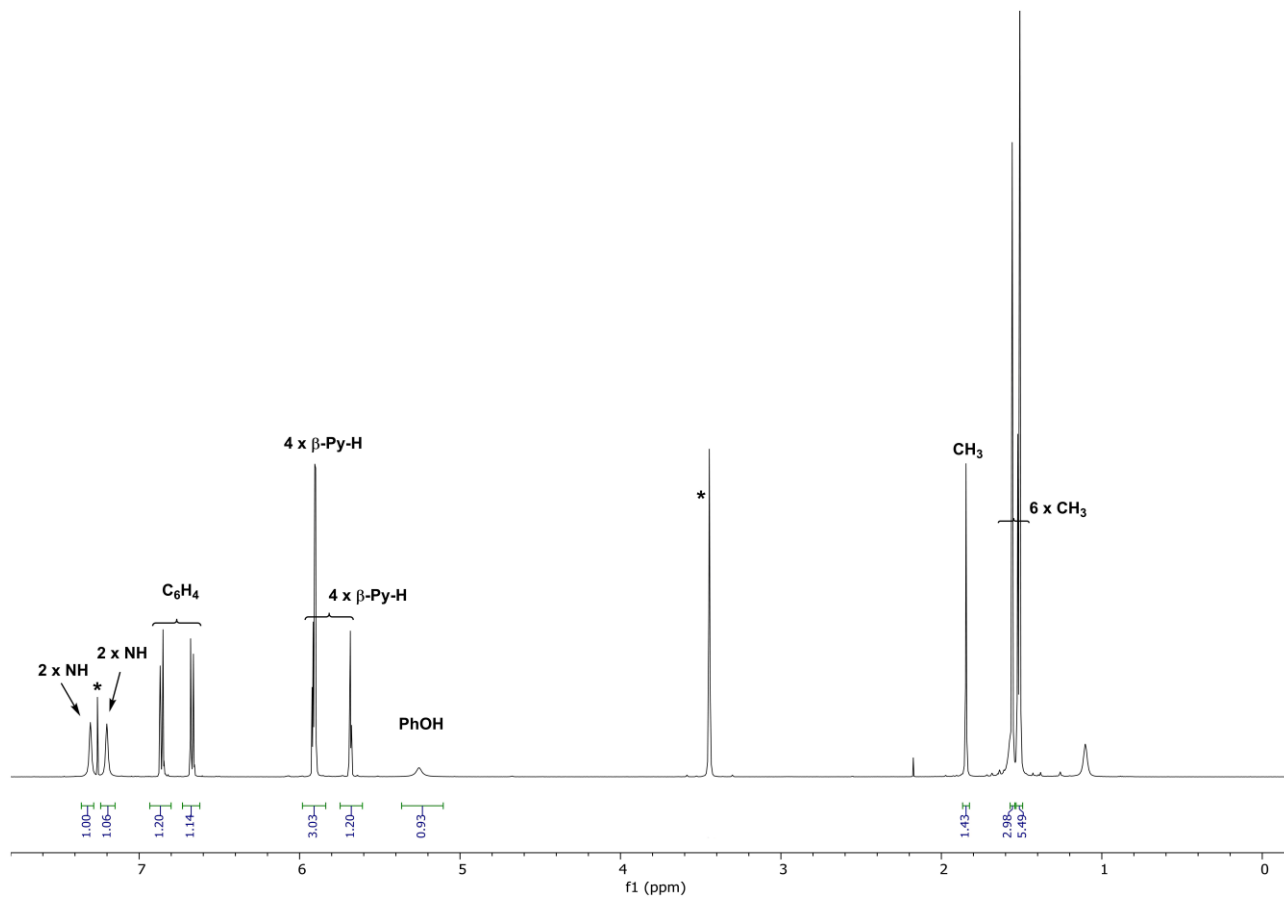


Figure S7a. ^1H NMR (500 MHz, CDCl_3) for compound **8**. *MeOH solvent.

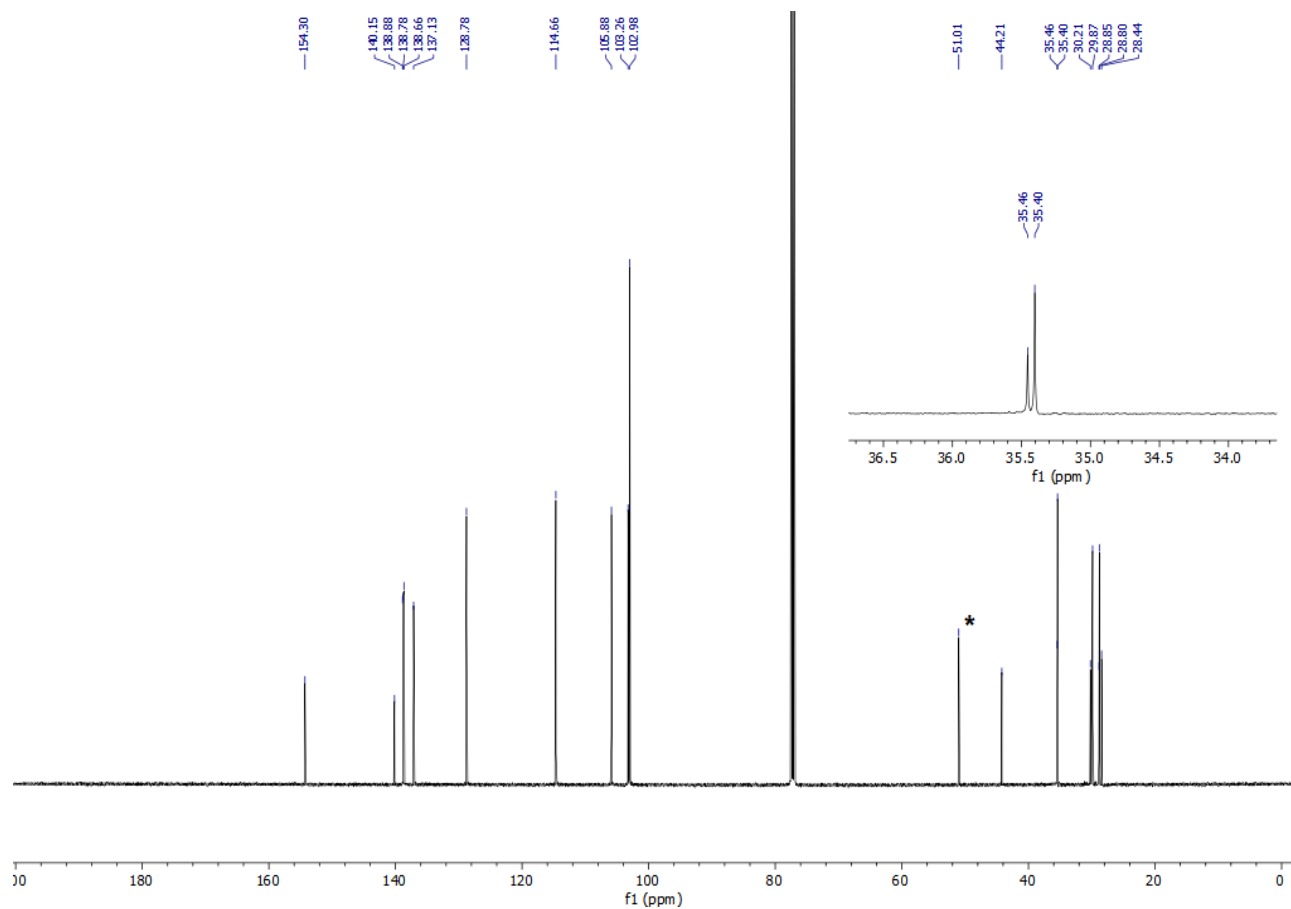


Figure S7b. ¹³C HNMR (125 MHz, CDCl₃) for compound **8**. * Methanol.

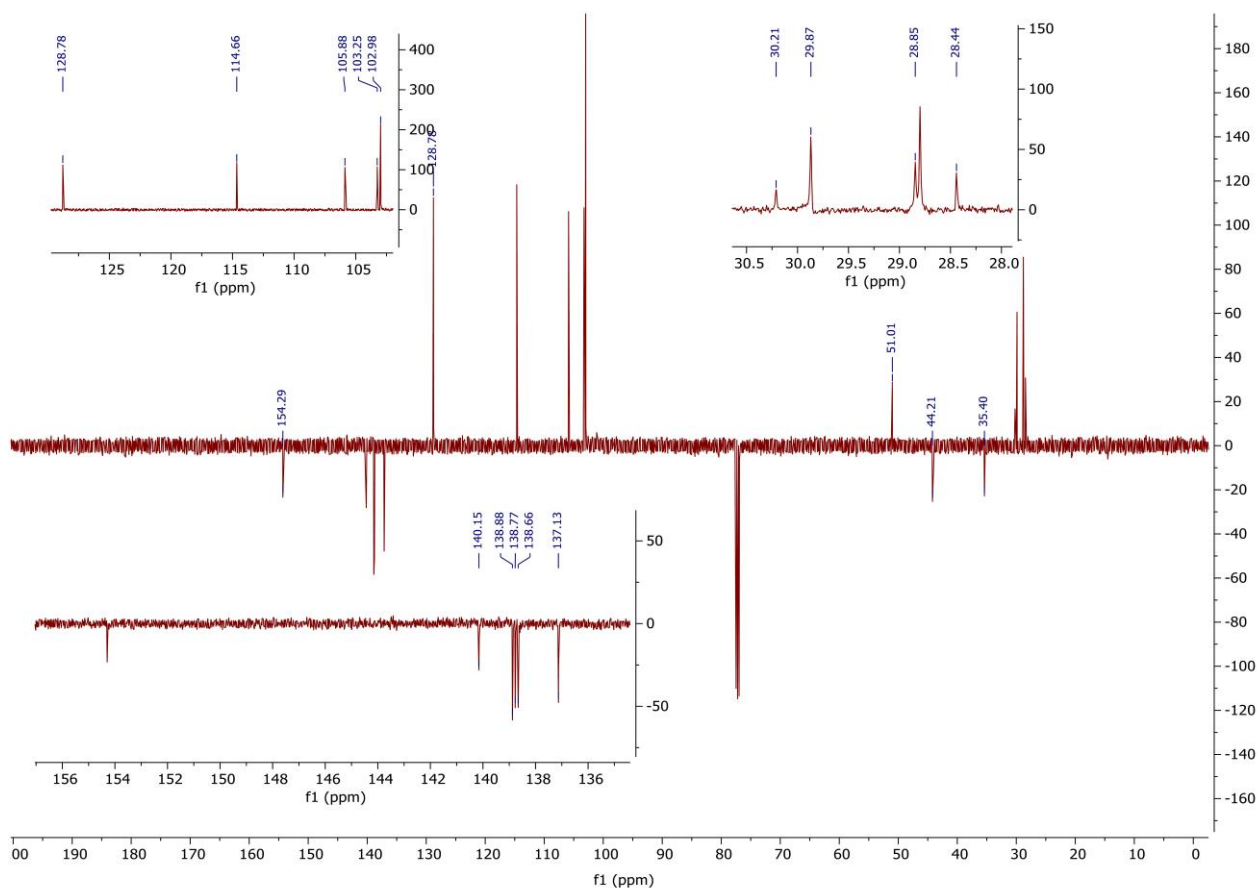


Figure S7c. APT ^{13}C NMR (125 MHz, CDCl_3) for compound **8**. * Methanol; the two quaternary carbon atoms at 35.4 ppm are not resolved and resonate as a single signal.

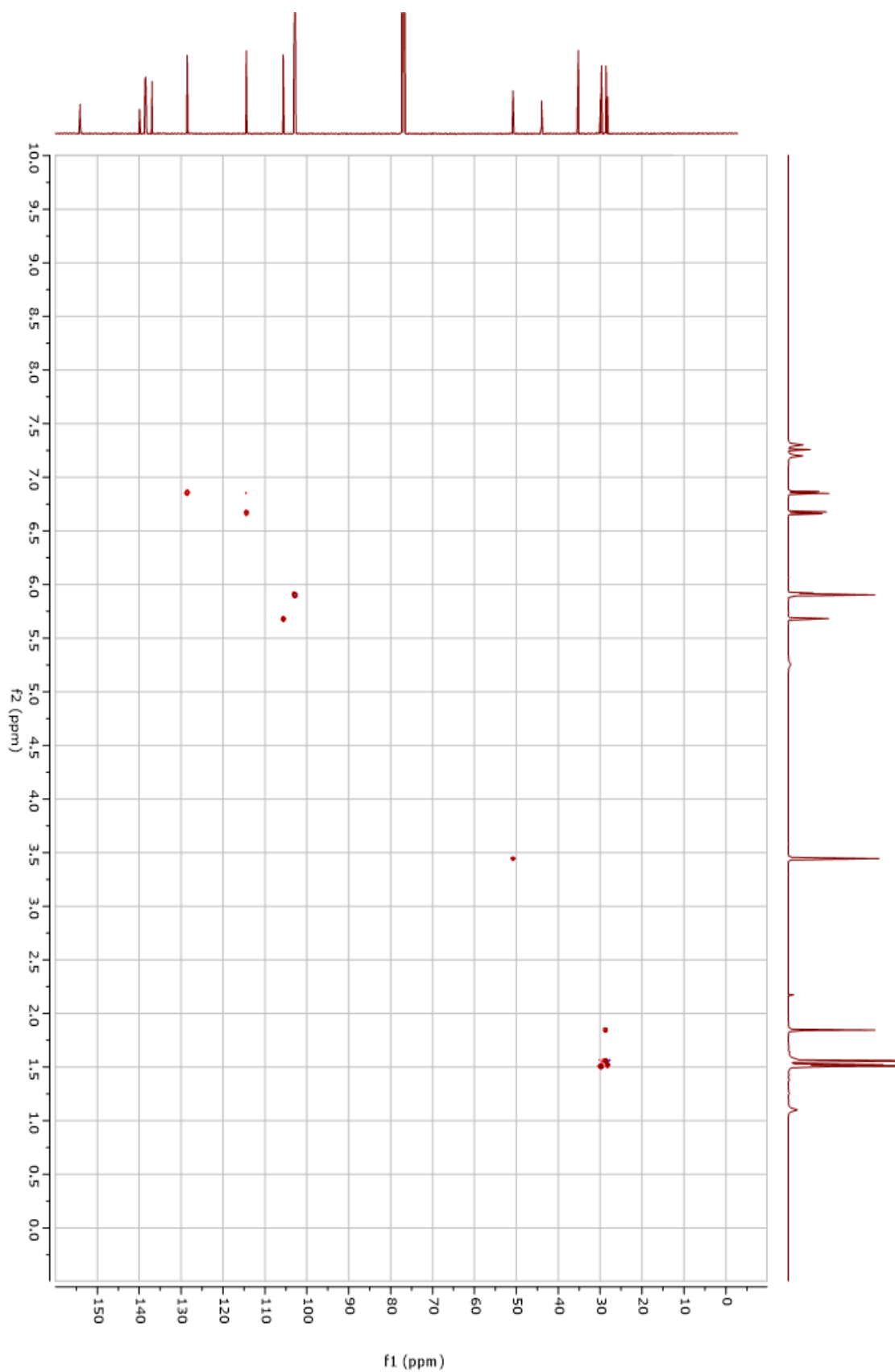


Figure S7d. HSQC (CDCl₃) for compound **8**.

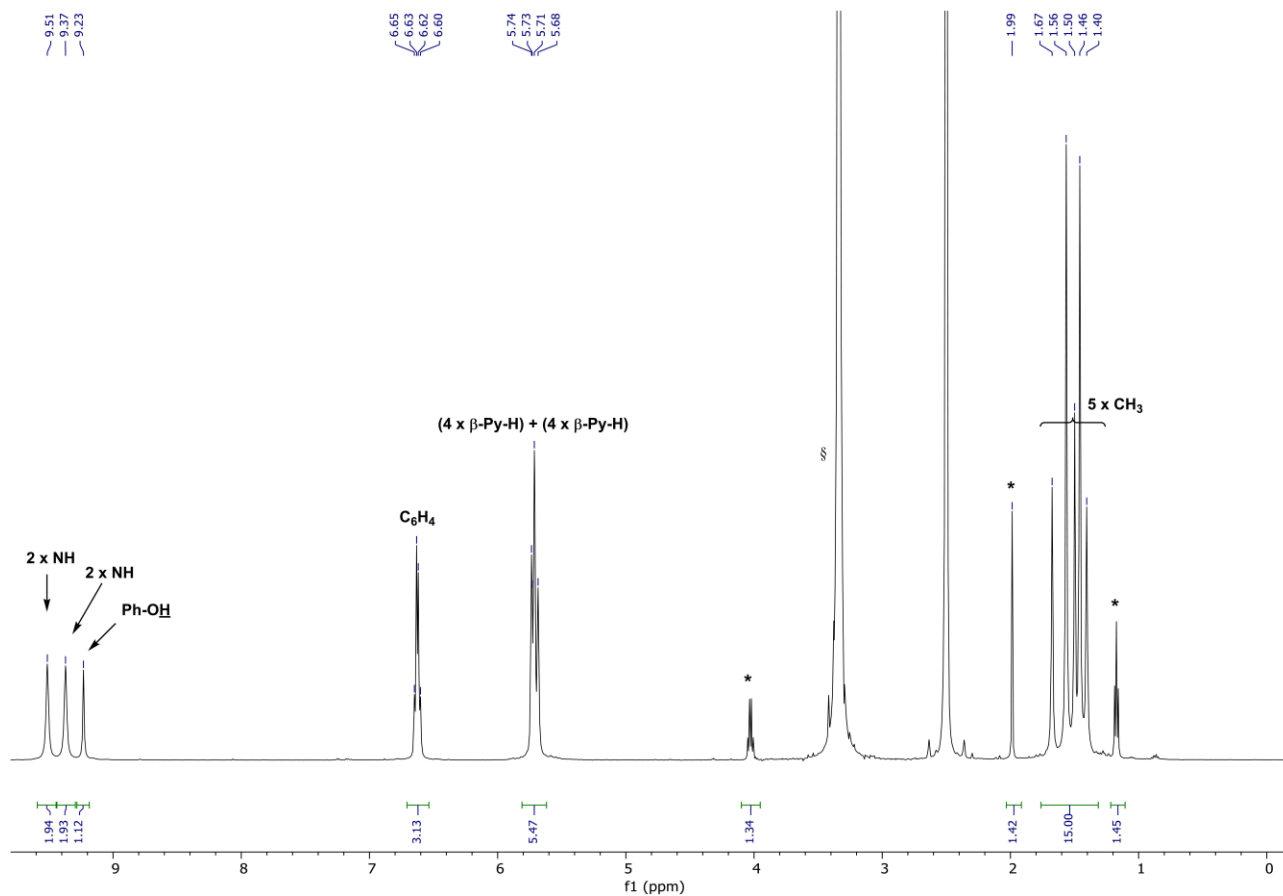


Figure S7e. ¹H NMR (500MHz, DMSO-d₆) for compound **8**. * Ethyl acetate, § water.

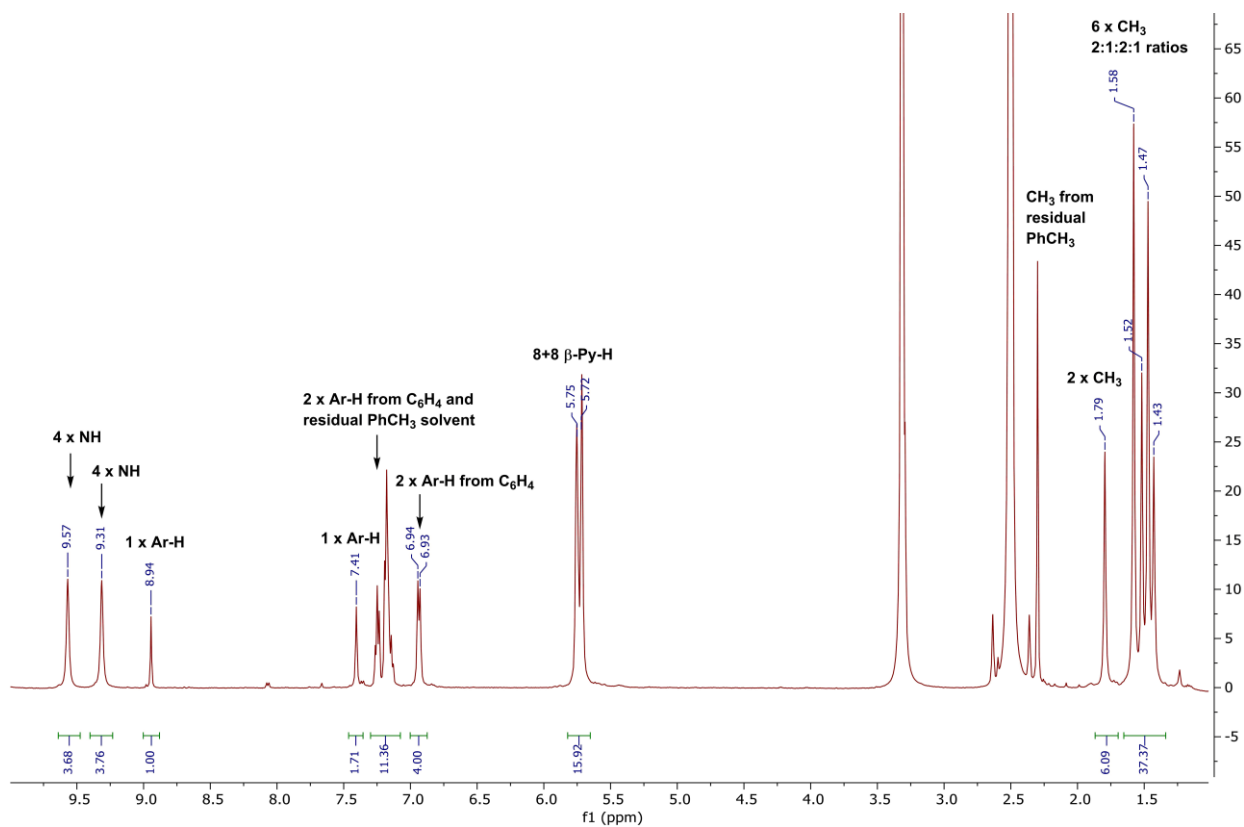


Figure S8a. ¹H NMR (500 MHz, DMSO-d₆) for compound **10** with assignments.

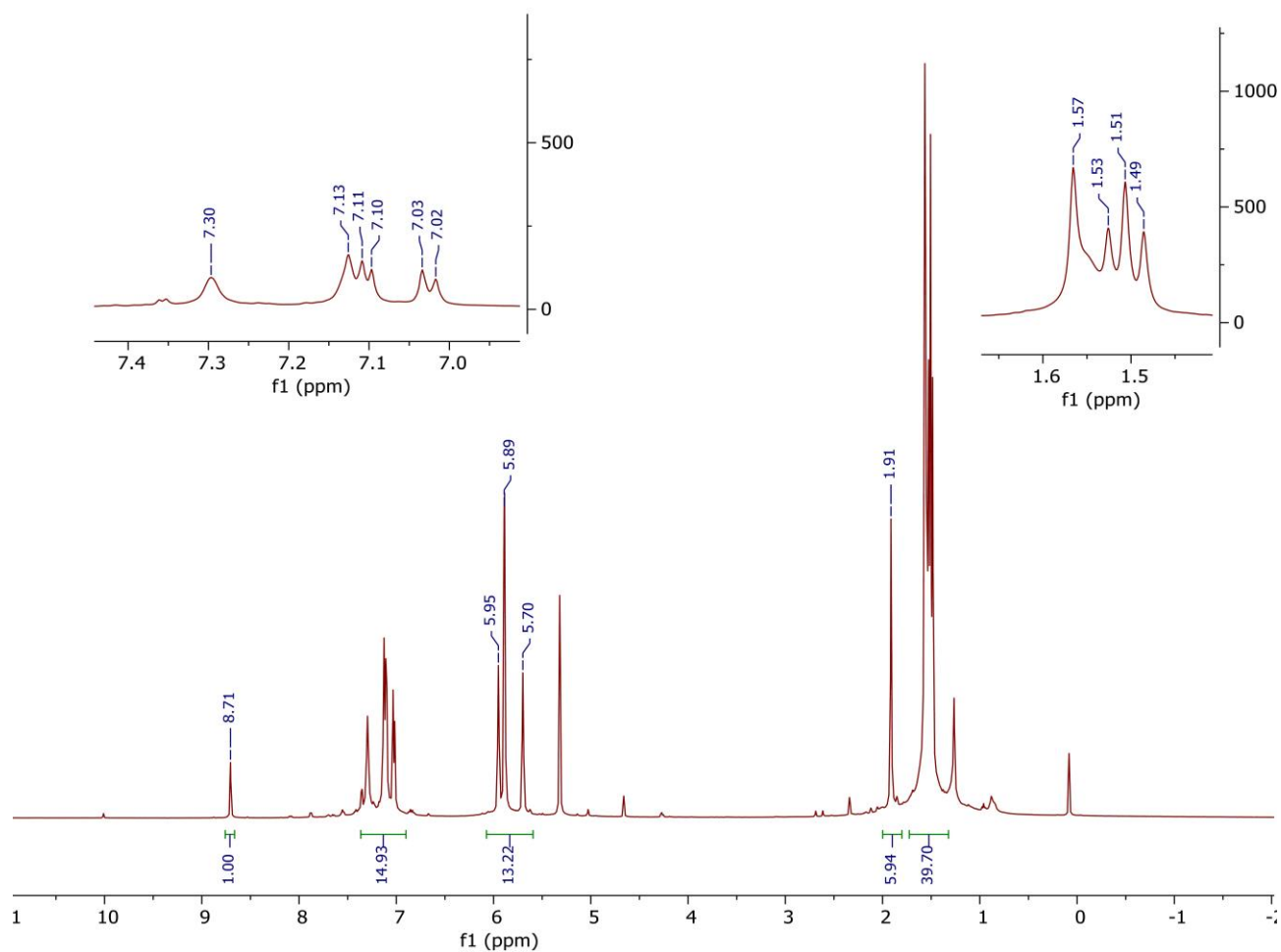


Figure S8b. ¹H NMR (500 MHz, CD₂Cl₂) for compound **10**.

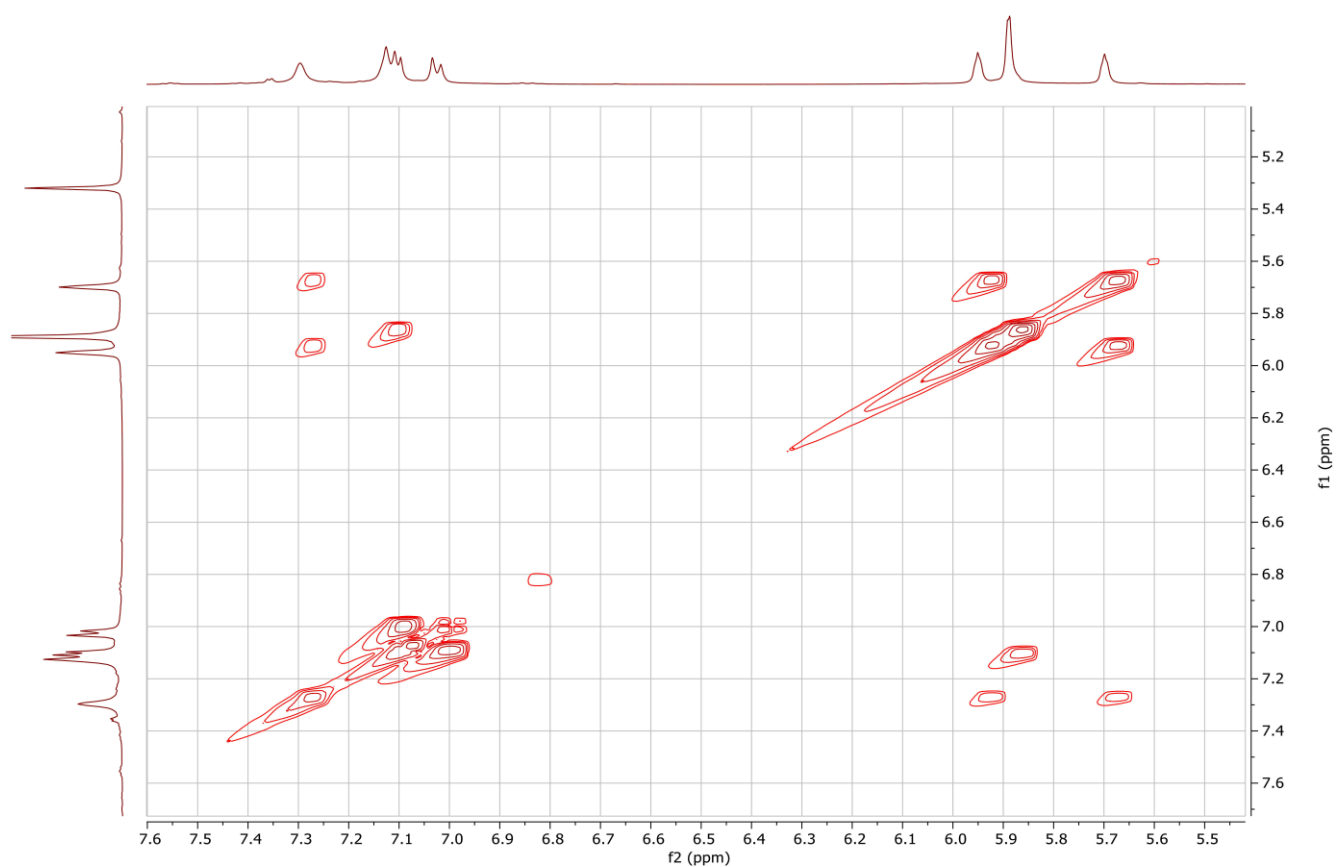


Figure S8c. COSY (500 MHz, CD₂Cl₂) Partial spectrum for compound **10** showing the correlation between the pyrrole b-CH resonances and the NH resonances contained in the signals system at 7.00-7.35 ppm.

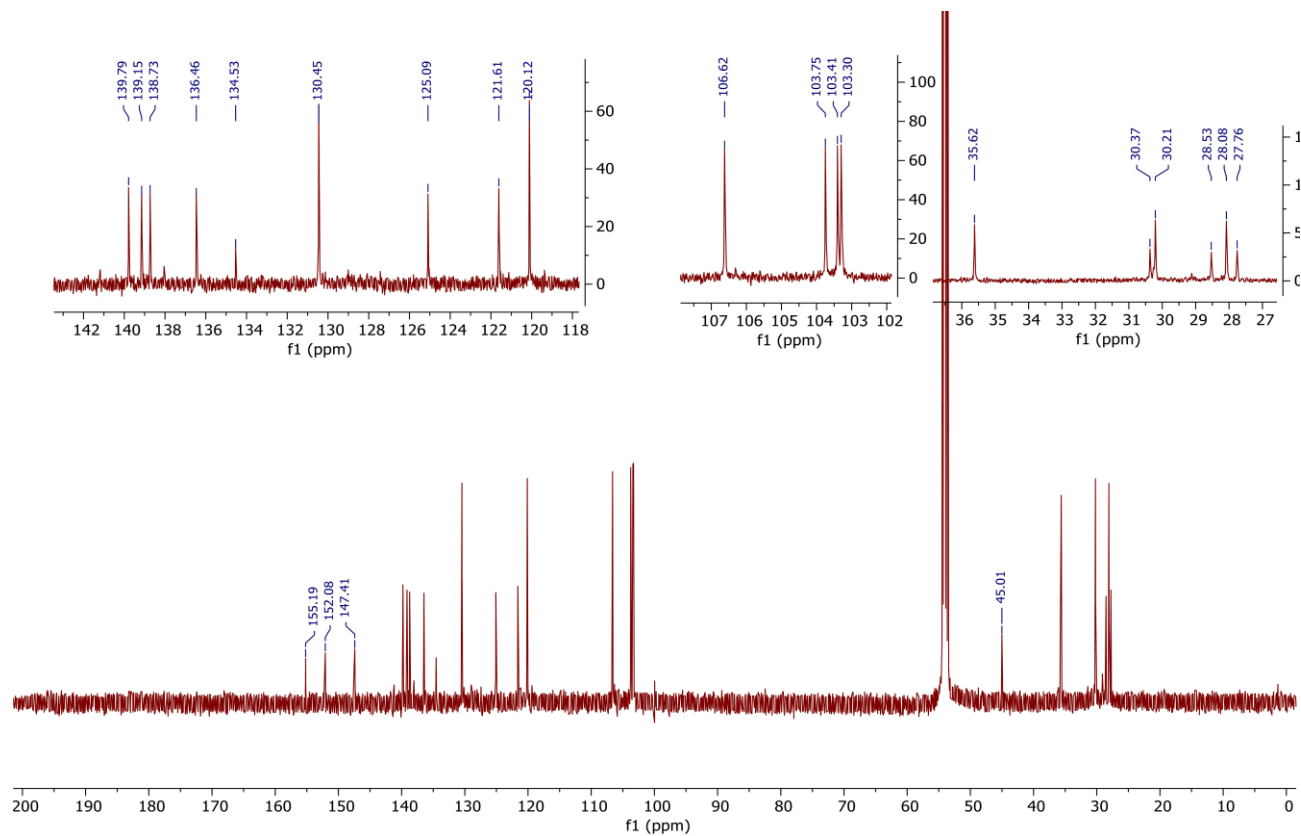


Figure S8d. ¹³C NMR (500 MHz, CD₂Cl₂) for compound **10**.

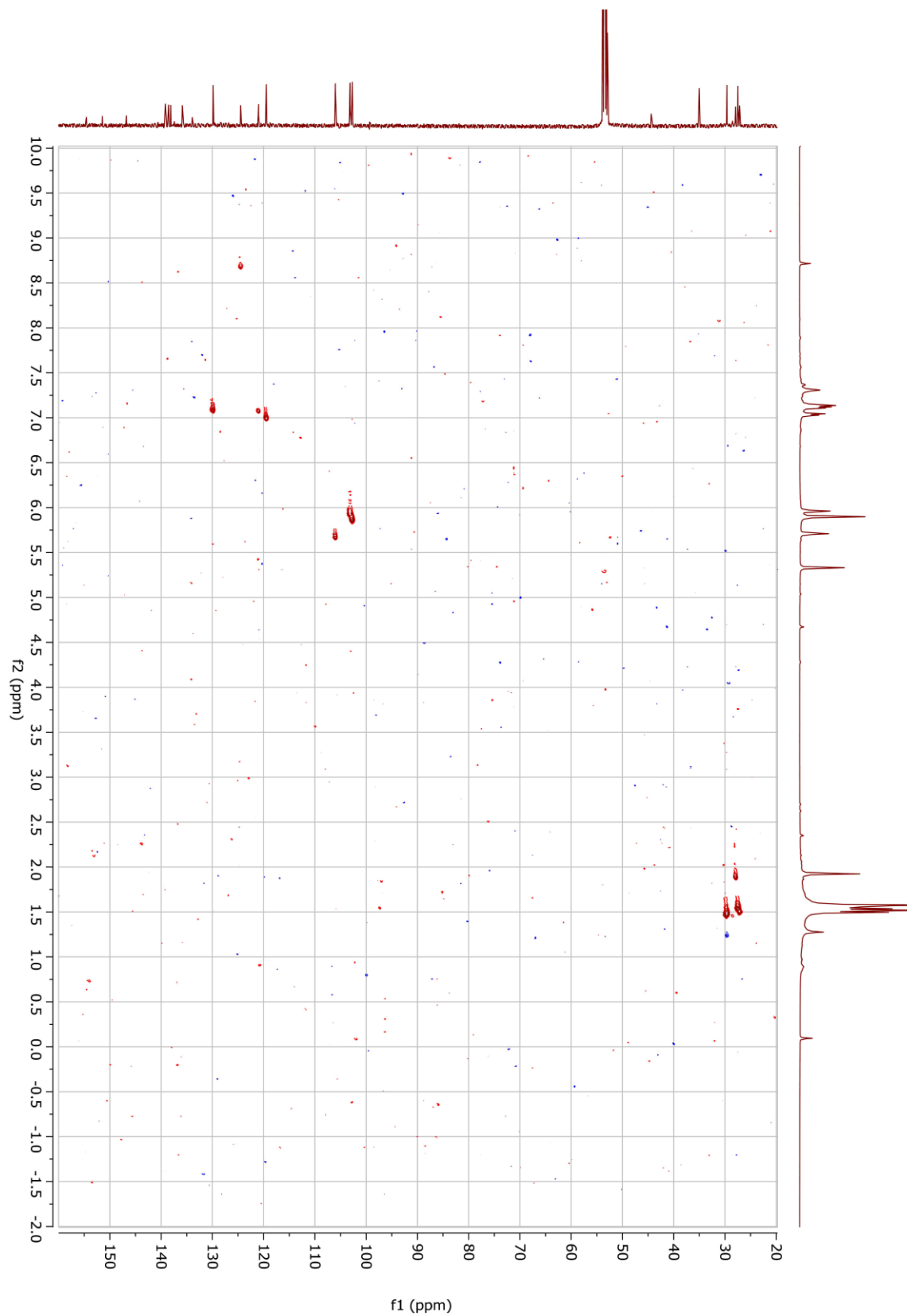


Figure S8e. HSQC (CD₂Cl₂) for compound **10**.

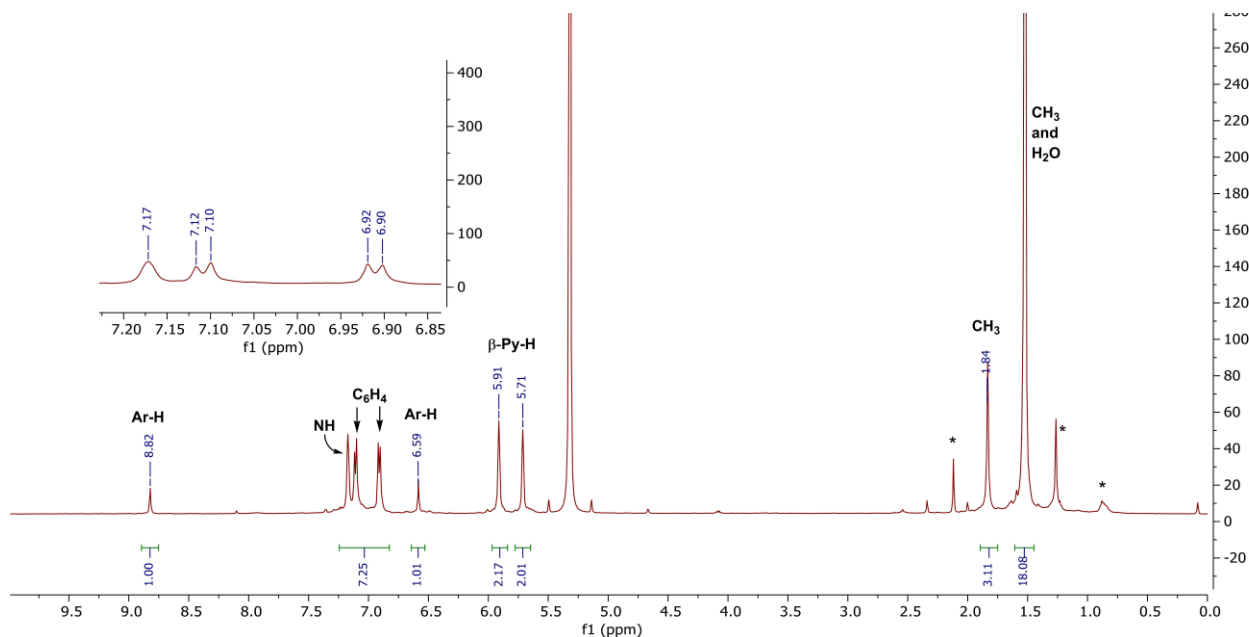


Figure S9a. ^1H NMR (500 MHz, CD_2Cl_2) for compound *anti-anti-anti-11*. * Solvent impurity.

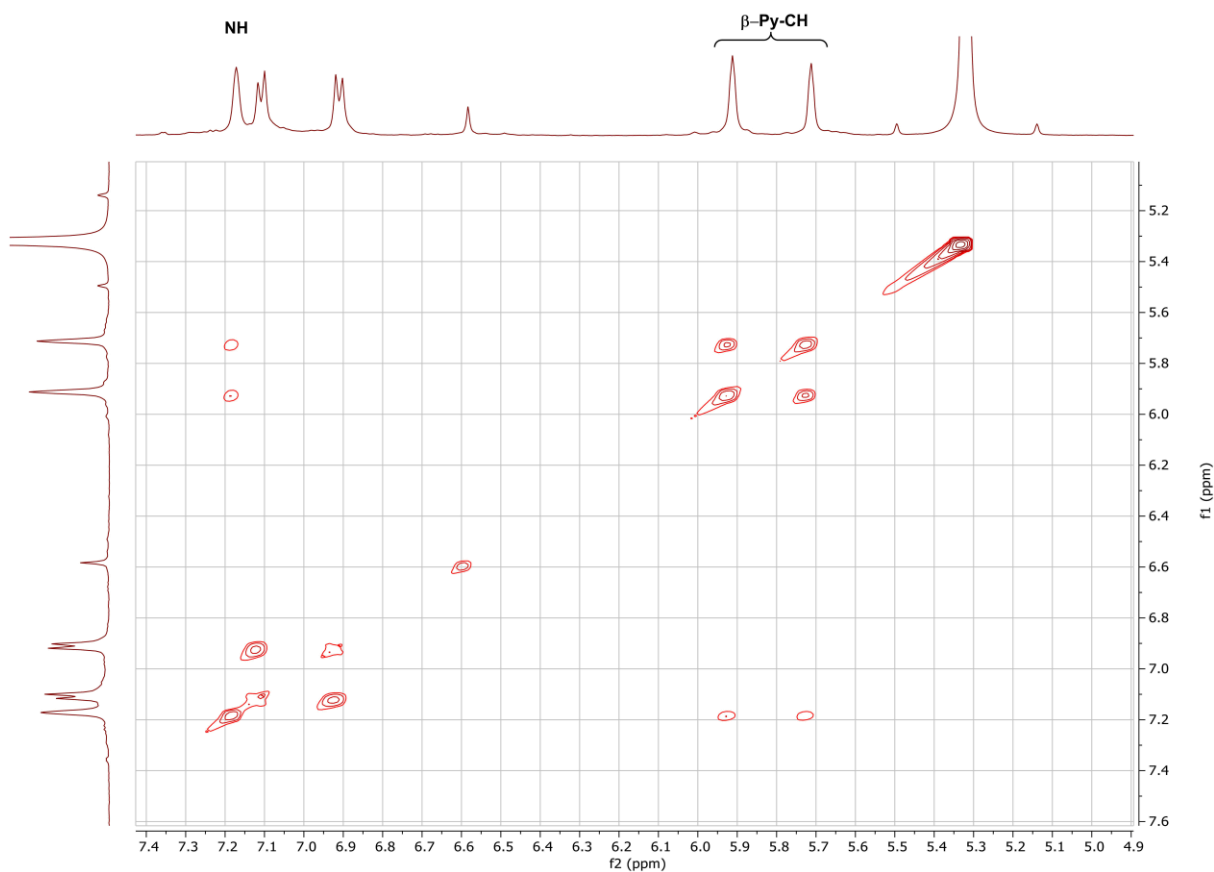


Figure S9b. ^1H NMR COSY (500 MHz, CD_2Cl_2) Partial spectrum for compound *anti-anti-anti-11* showing the correlation between the pyrrole b-CH resonances and the resonance at 7.17 ppm for the NH units.

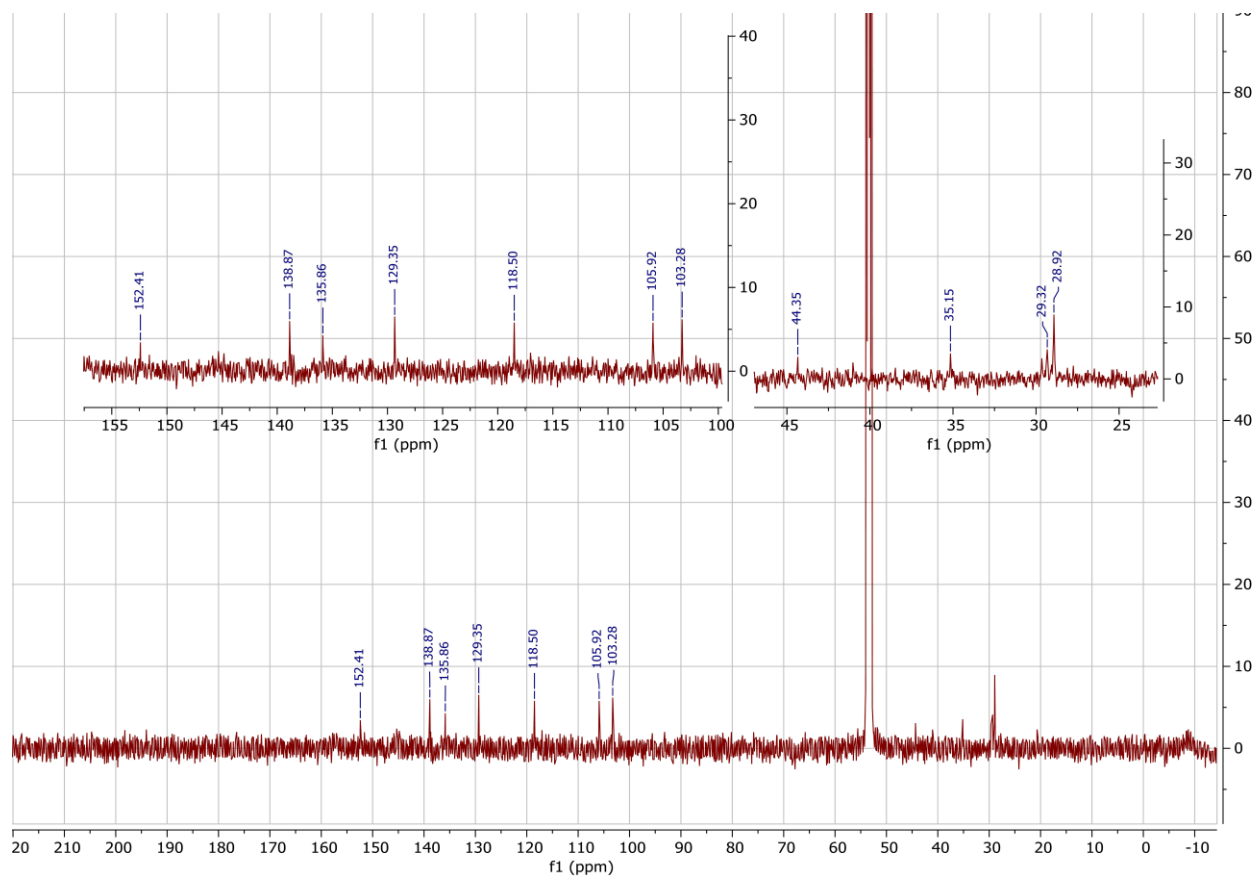


Figure S9c. ^{13}C NMR (125 MHz, CD_2Cl_2) for compound *anti-anti-anti-11*.

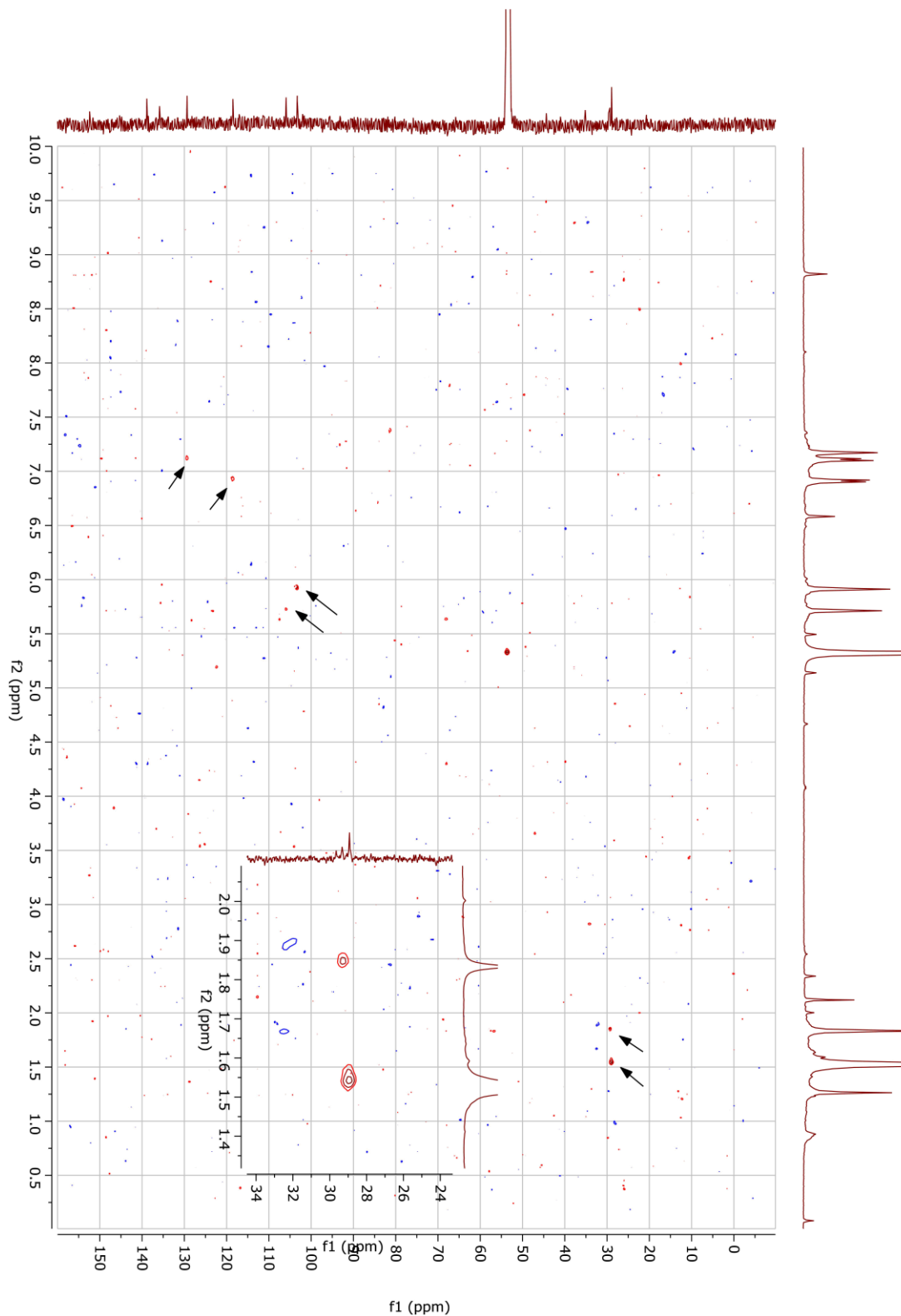


Figure S9d. HSQC (CD_2Cl_2) for compound *anti-anti-anti-11*. The arrows are to evidence the correlated signals (red dots) in the noisy background. The inset expansion shows that the strong resonance at 1.52 ppm contains the four symmetry-related CH_3 units under the water signal.

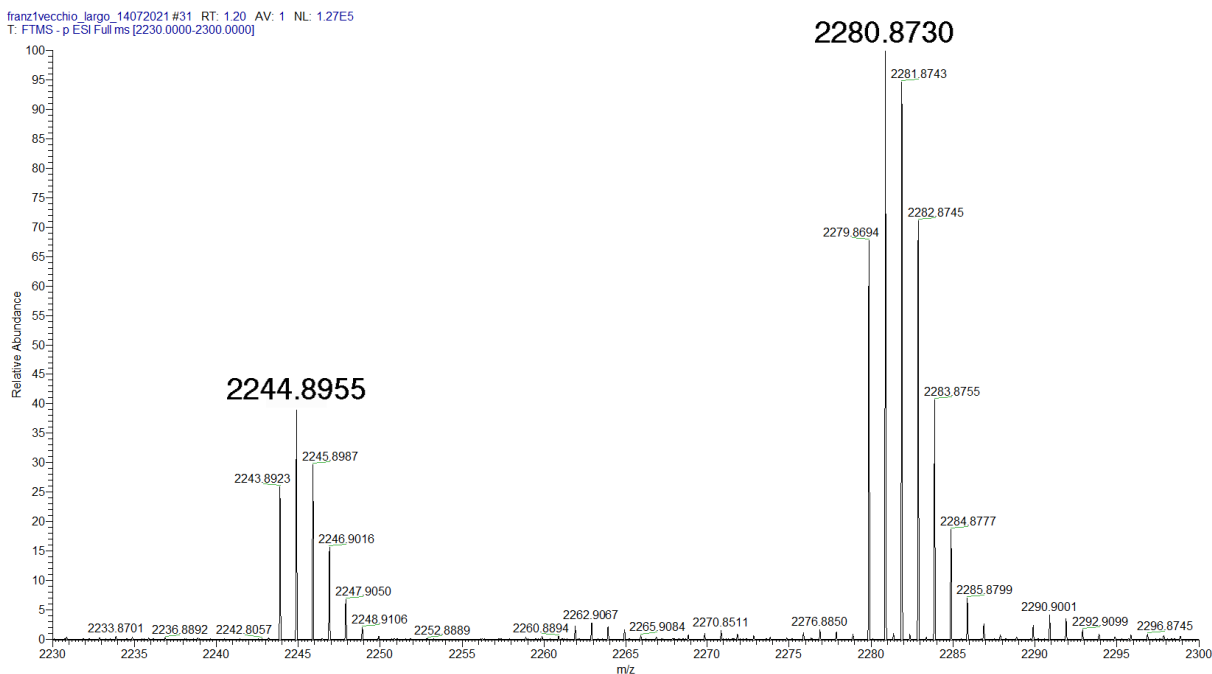


Figure S9e. ESI-MS for compound *anti-anti-anti-11*. Calculated m/z for $C_{132}H_{120}N_{18}O_{18}$: 2244.9028 and for $C_{132}H_{120}N_{18}O_{18}Cl$: 2279.9028.

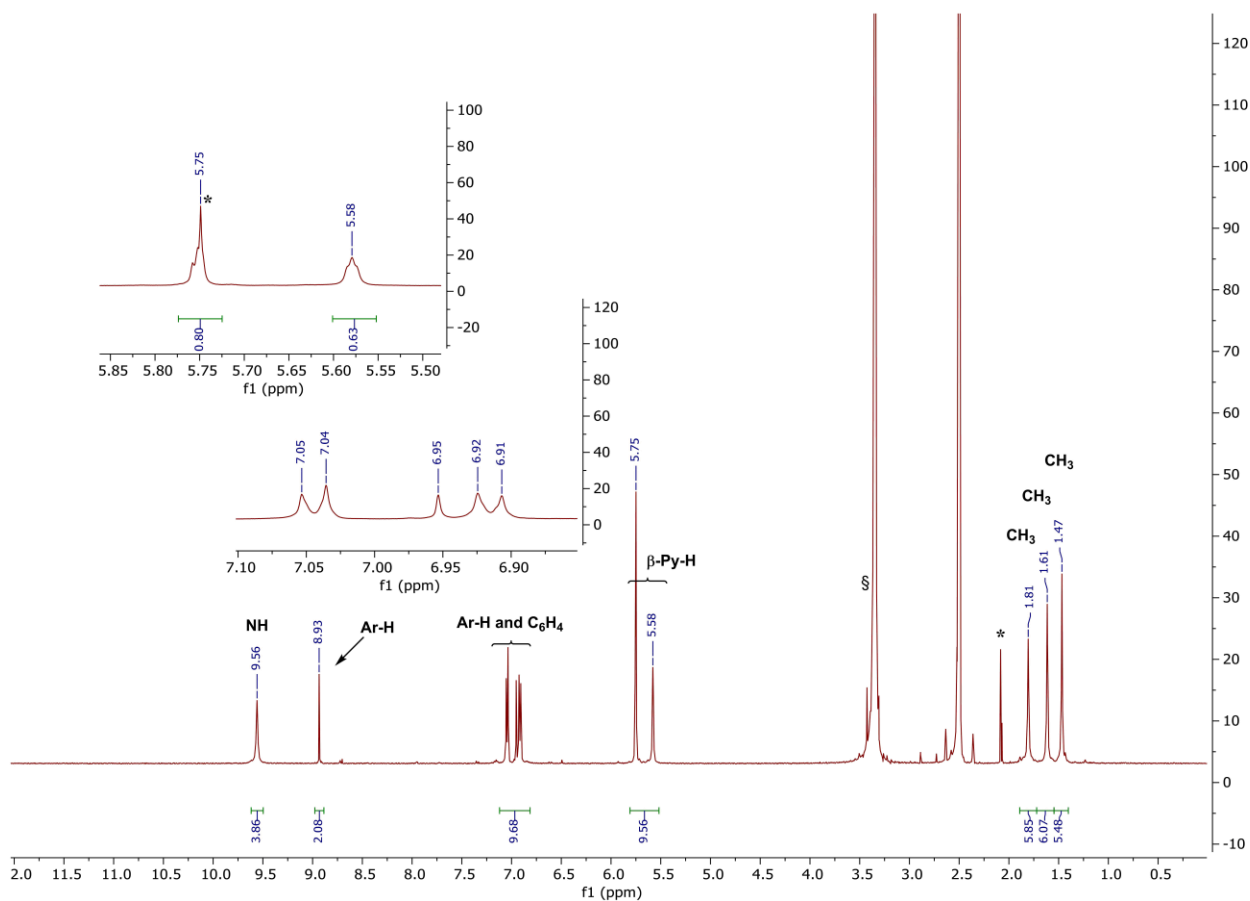


Figure S10a. ^1H NMR (500 MHz, DMSO-d_6) for *syn-syn-syn-11*. The peak at 5.75 ppm overlapping one set of the β -pyrrole resonances is DCM contaminant in the DMSO solvent; δ water; * other solvent impurity (see ref. R1).

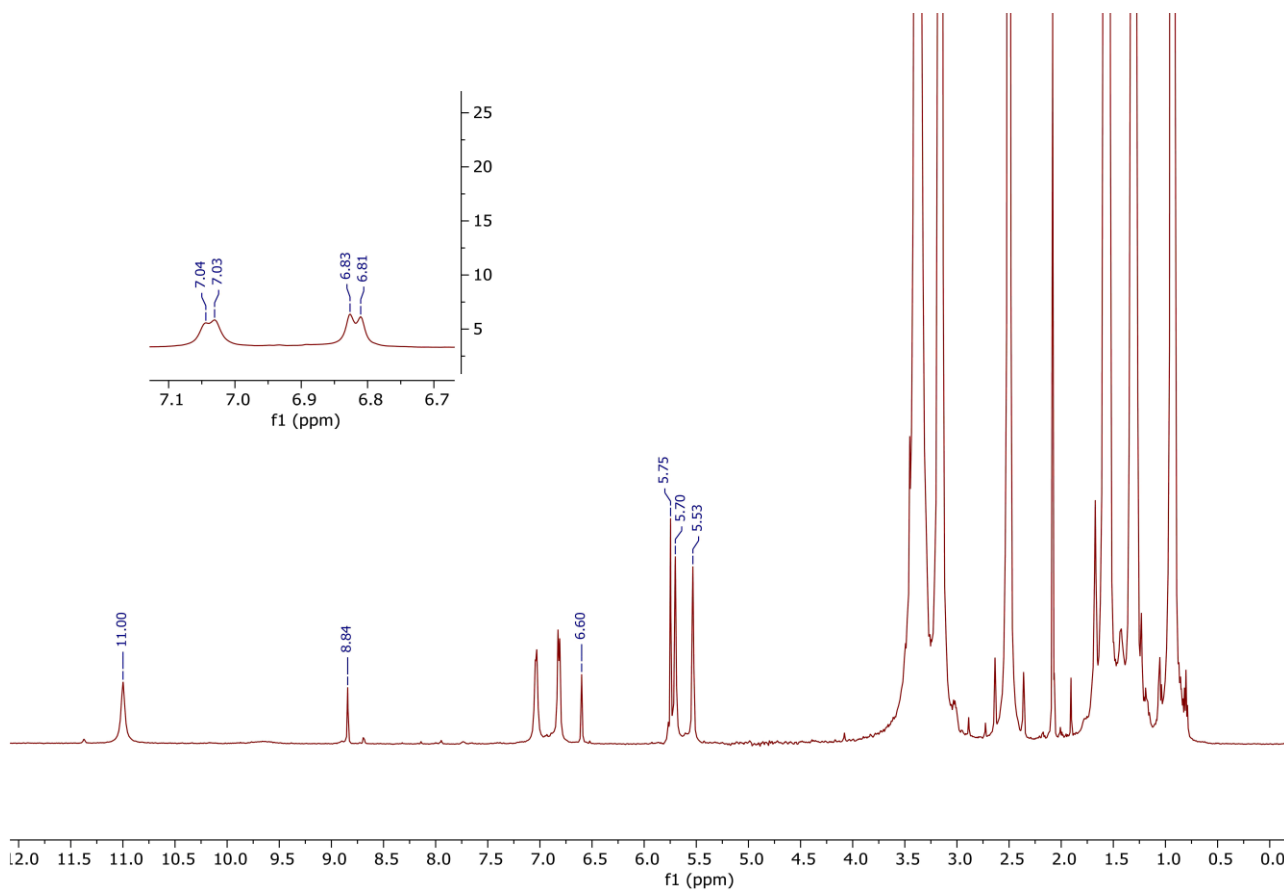


Figure S10b. ^1H NMR (500 MHz, DMSO-d_6) for *syn-syn-syn-11* in the presence of molar excess of TBACl. The peak at 5.75 ppm overlapping one set of the b-pyrrole resonances is DCM contaminant in the DMSO solvent (see ref. R1).

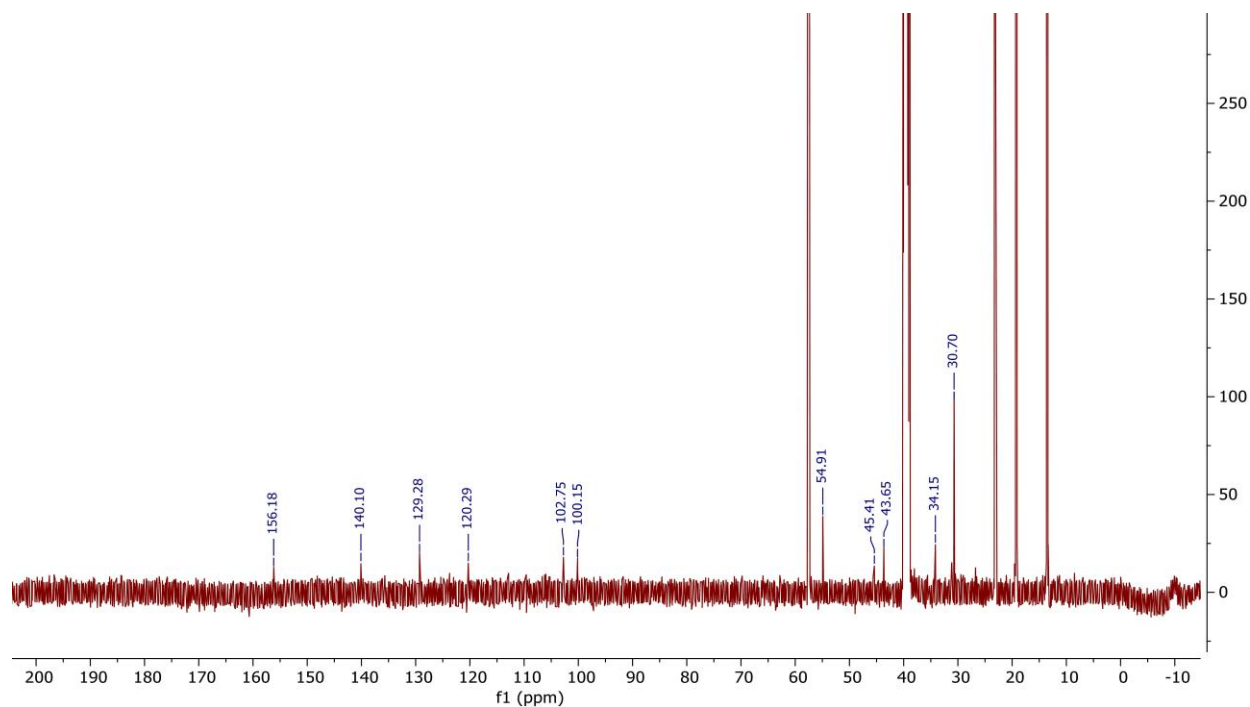


Figure S10c. ^{13}C NMR (125 MHz, DMSO-d_6) for *syn-syn-syn-11*. The peak at 54.91 ppm is DCM.

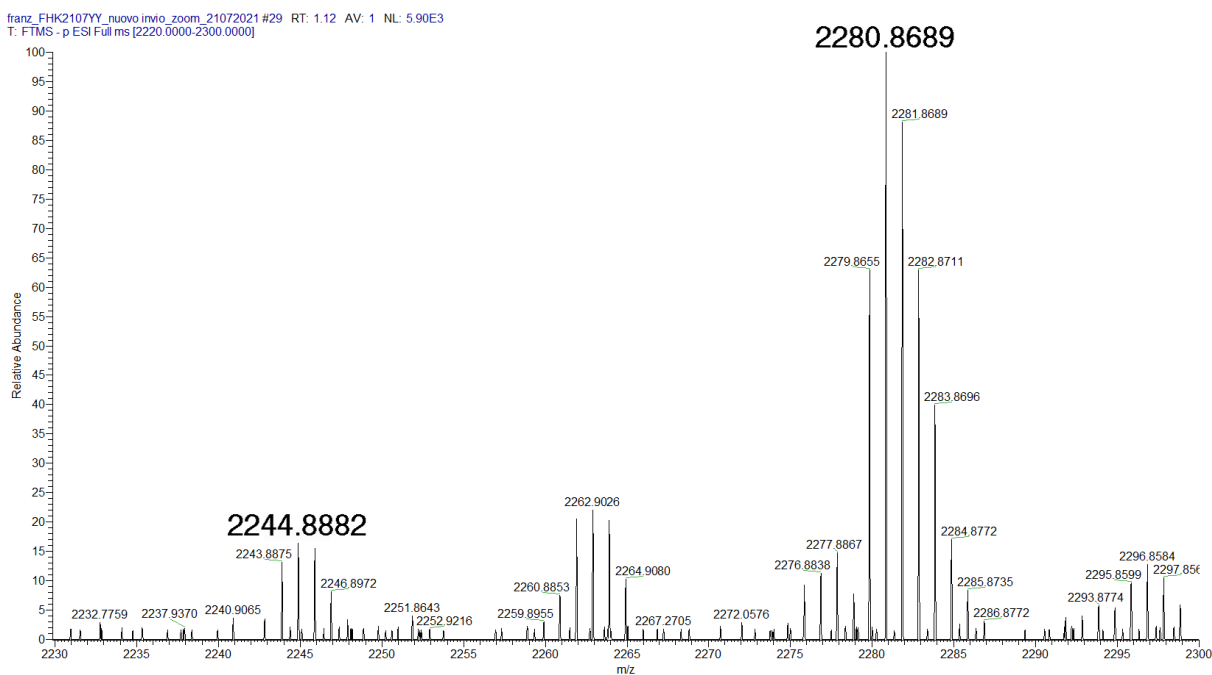


Figure S10d. ESI-MS for *syn-syn-syn-11*. Calc. m/z for $\text{C}_{132}\text{H}_{120}\text{N}_{18}\text{O}_{18}$: 2244.9028 and for $\text{C}_{132}\text{H}_{120}\text{N}_{18}\text{O}_{18}\text{Cl}$: 2279.9028.

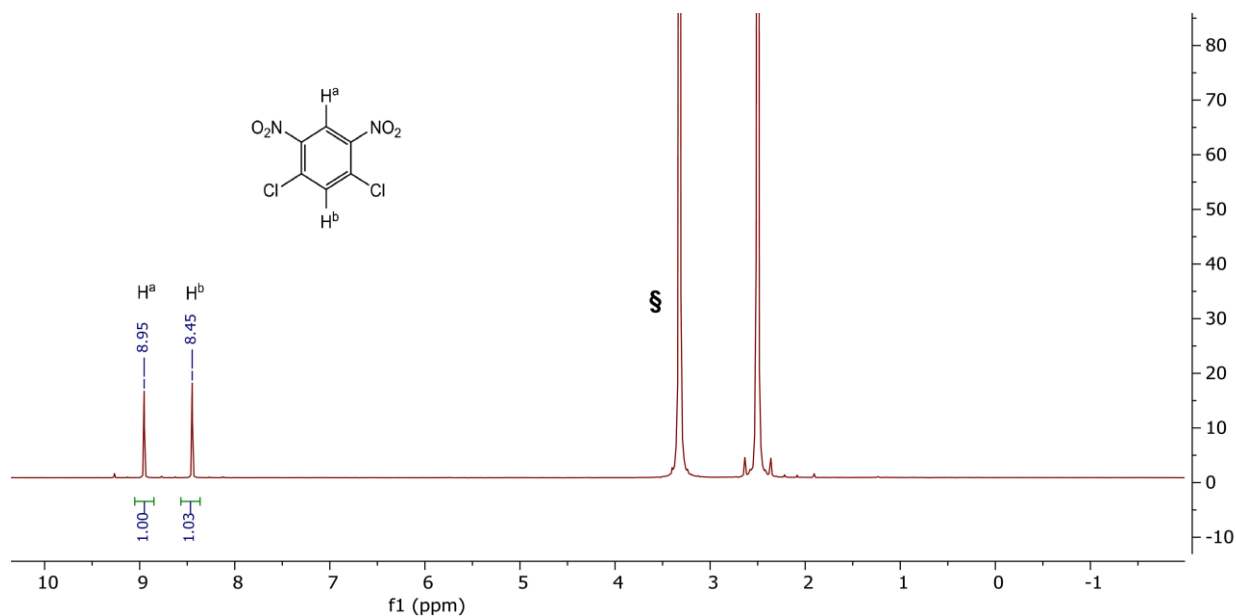


Figure S11a. ^1H NMR (DMSO-d_6) for 1,3-dichloro-4,6-dinitrobenzene **9**.

References

- R1 Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176-2179.
<https://doi.org/10.1021/om100106e>