

Extracting the Sign of Small Exchange Couplings Constants from PELDOR Data[†]

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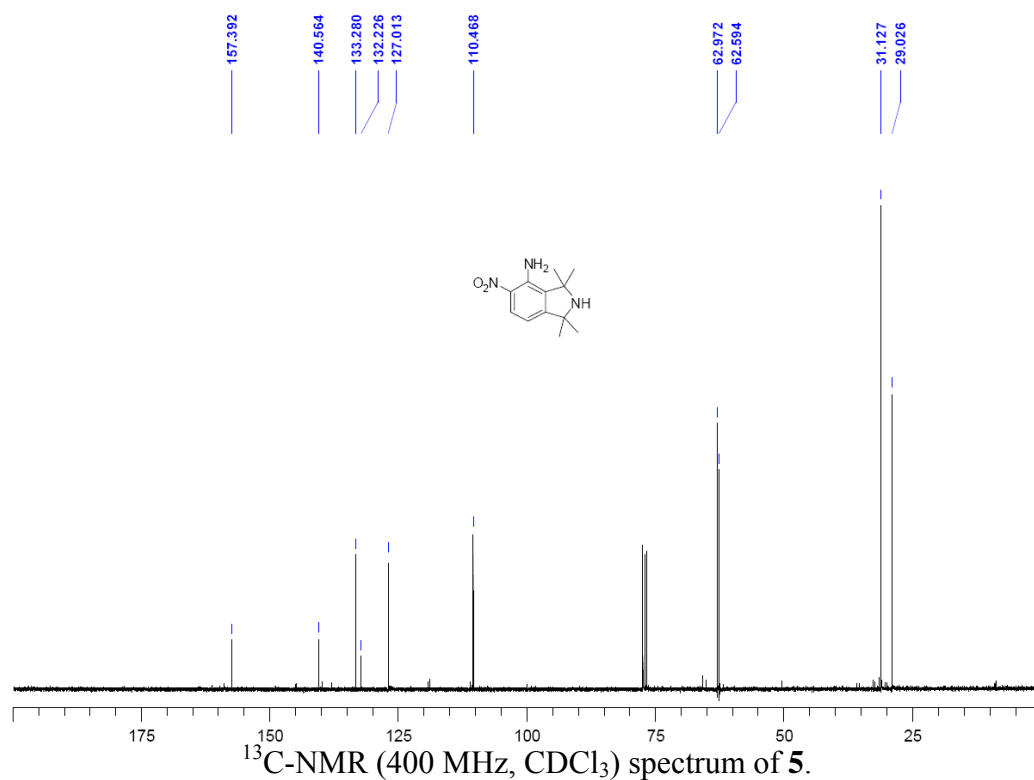
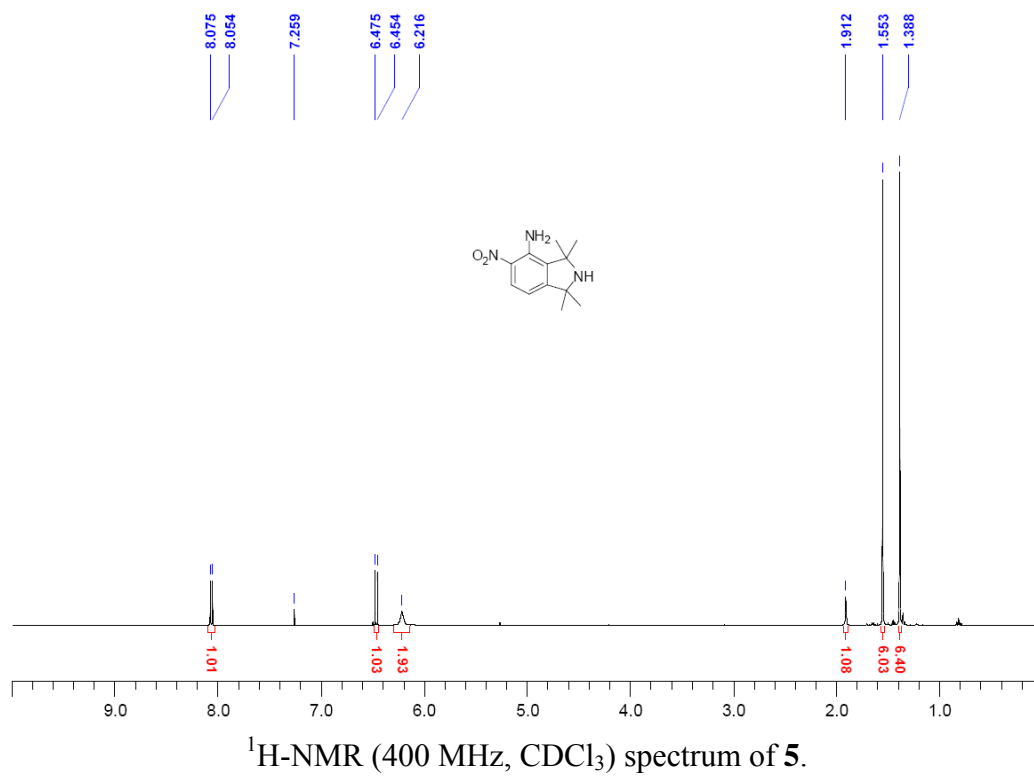
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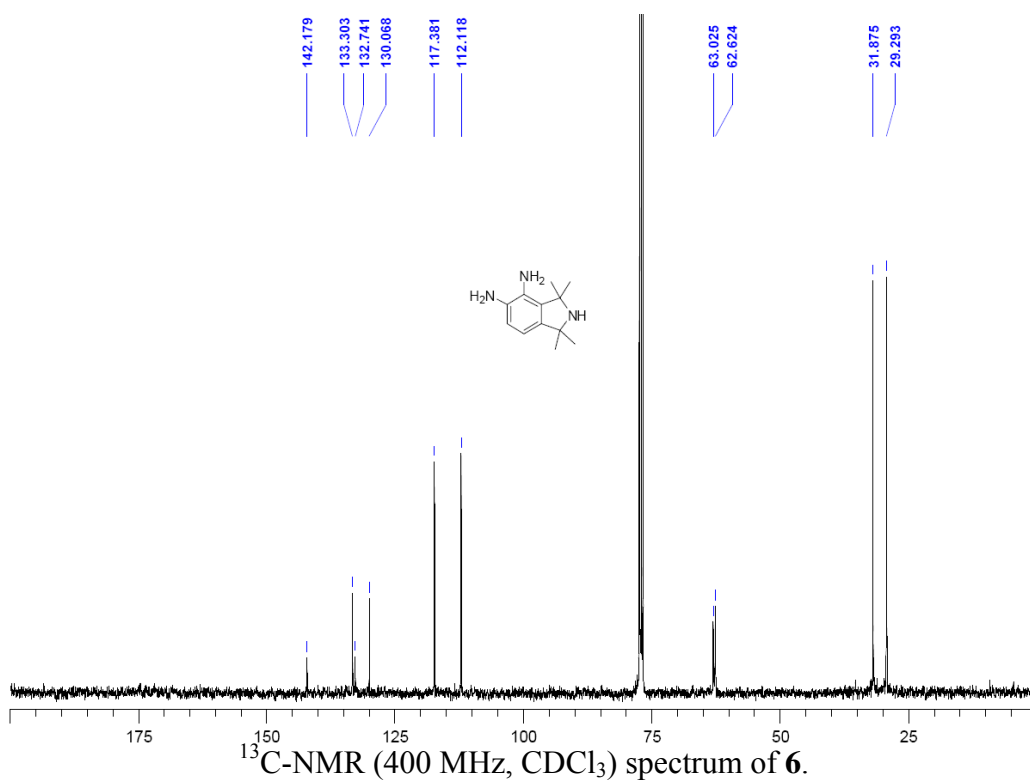
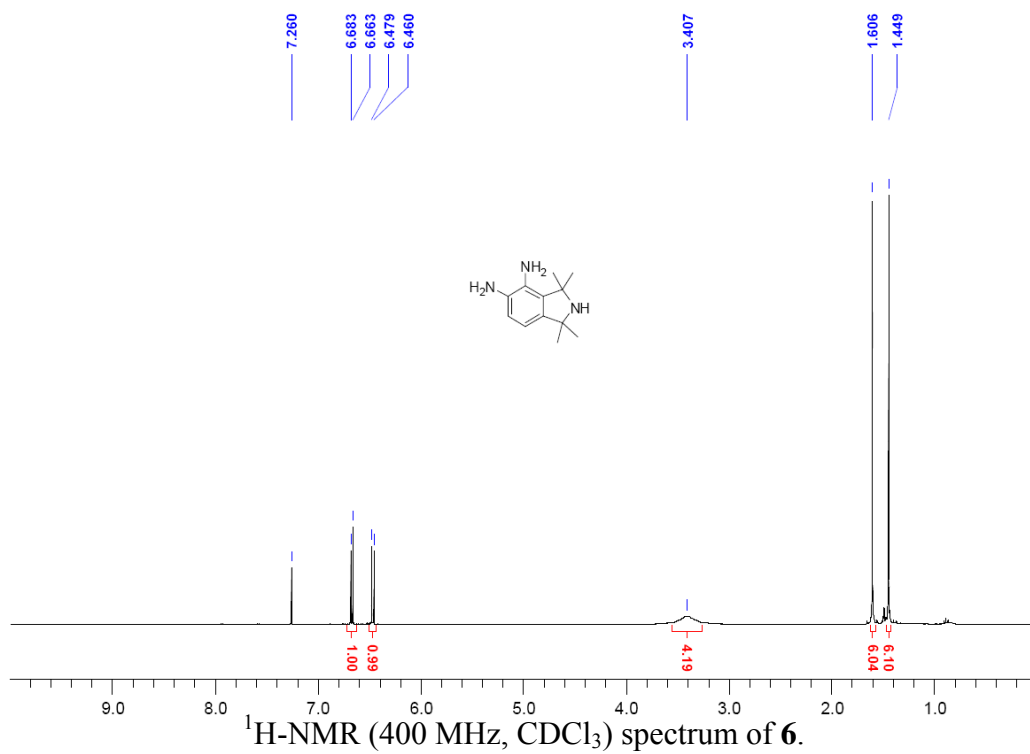
[‡] Both, D. Margraf and P. Cekan contributed equally to this work.

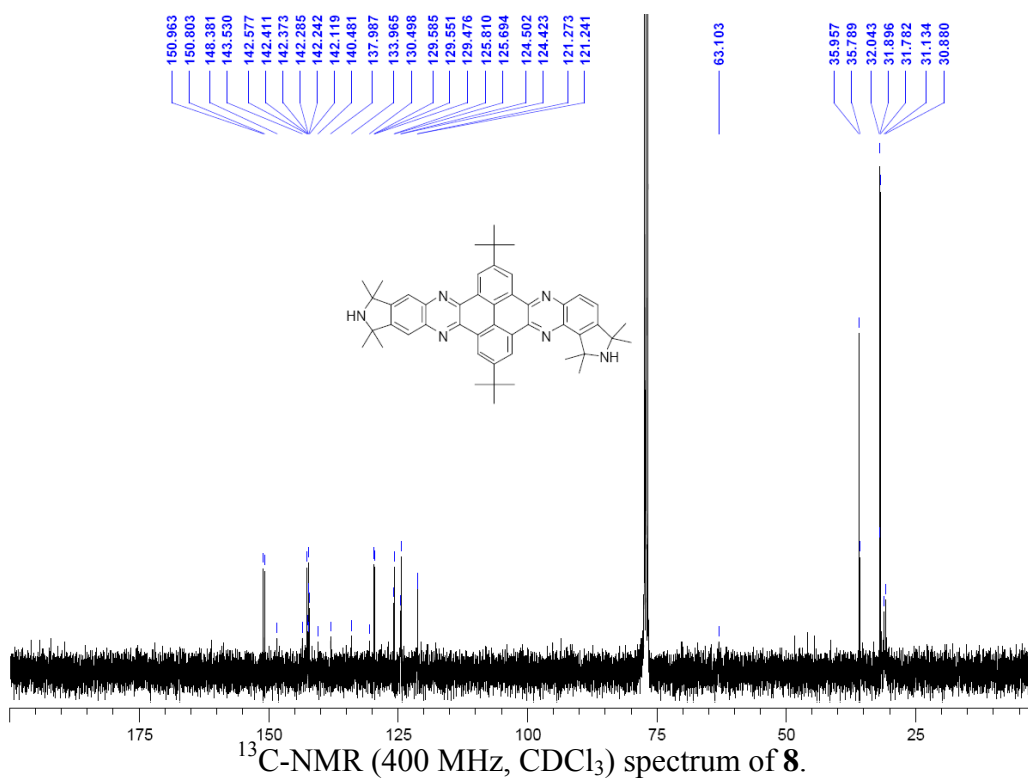
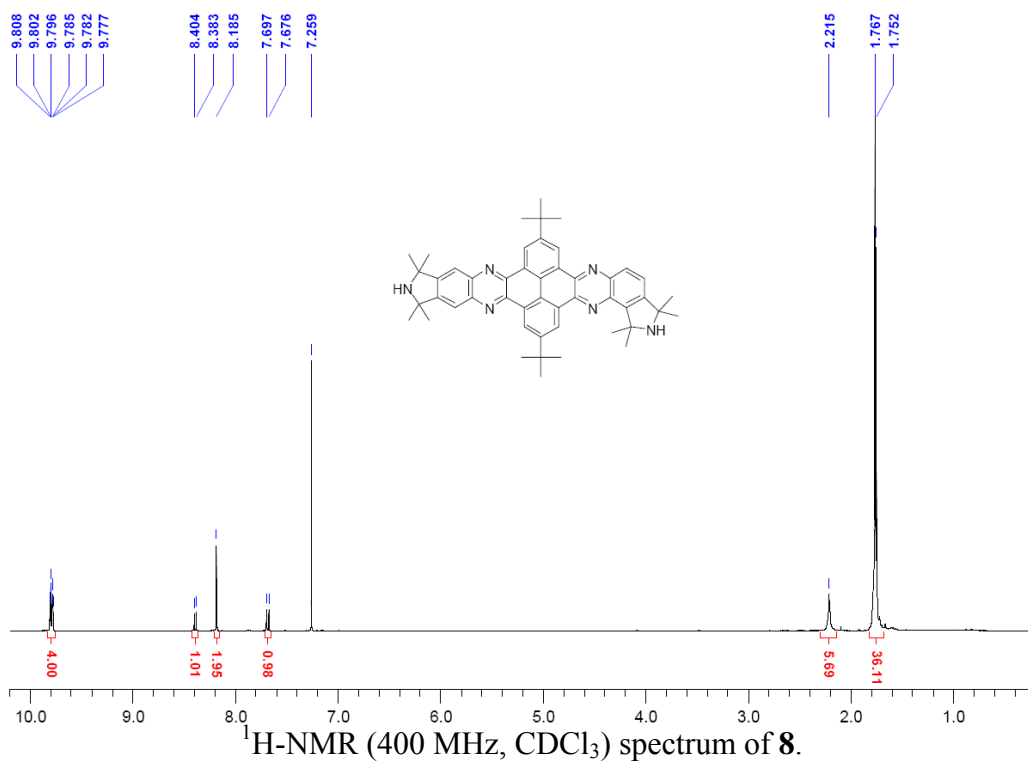
Supporting Information

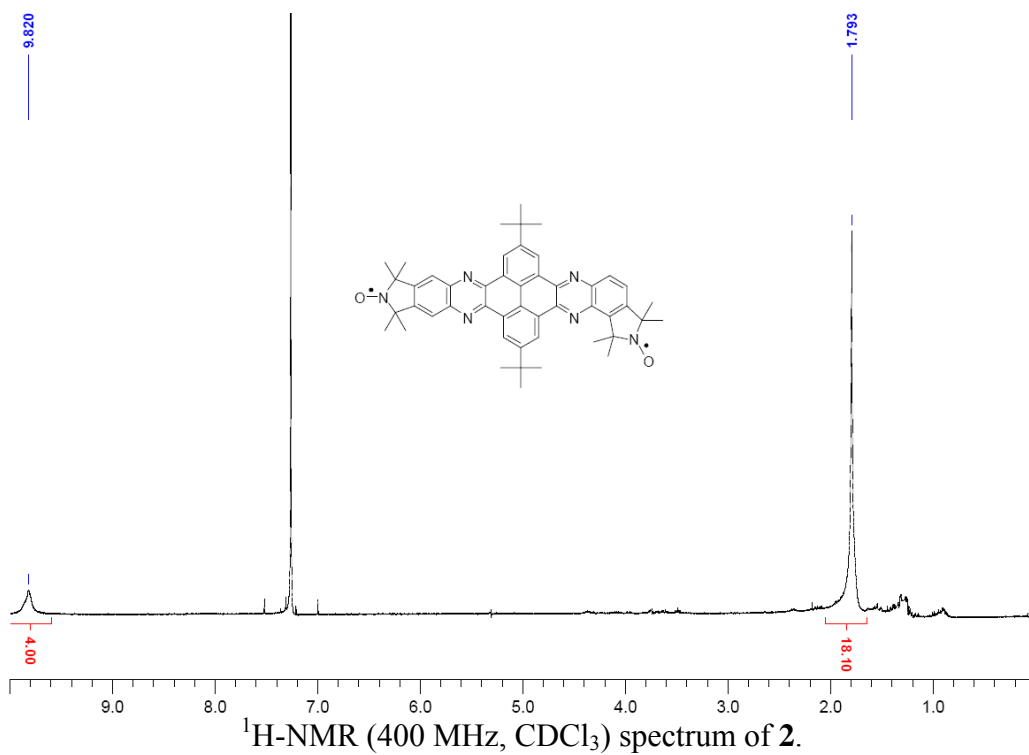
Table of Contents

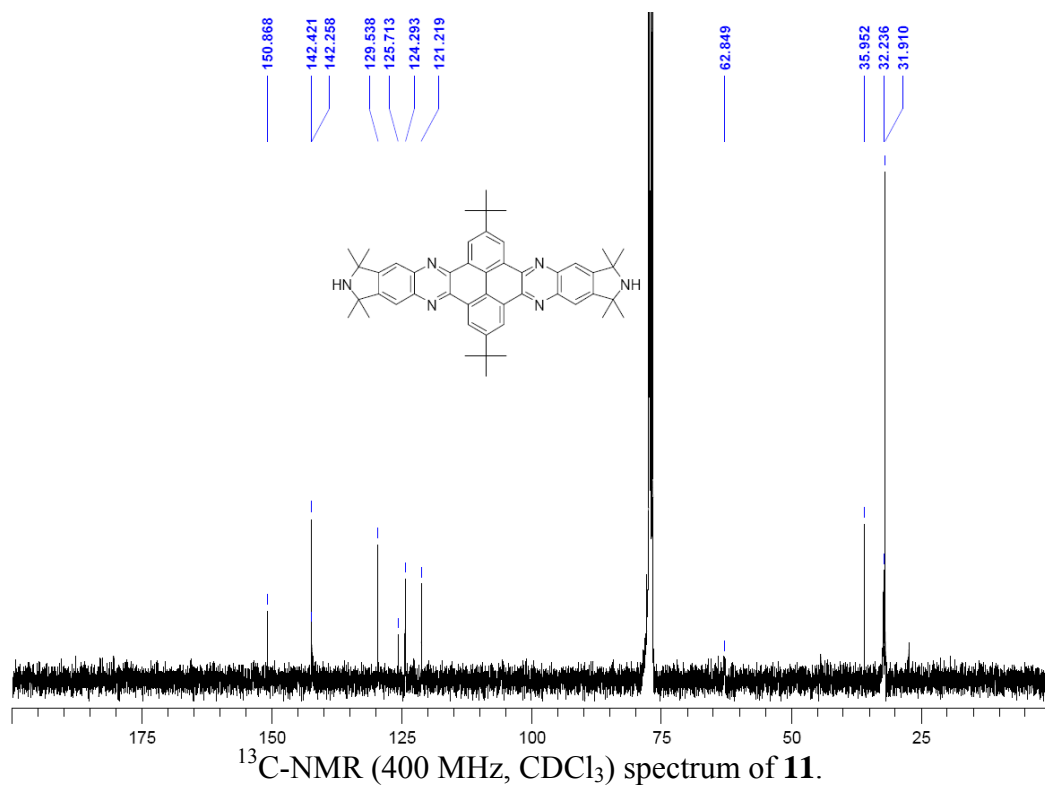
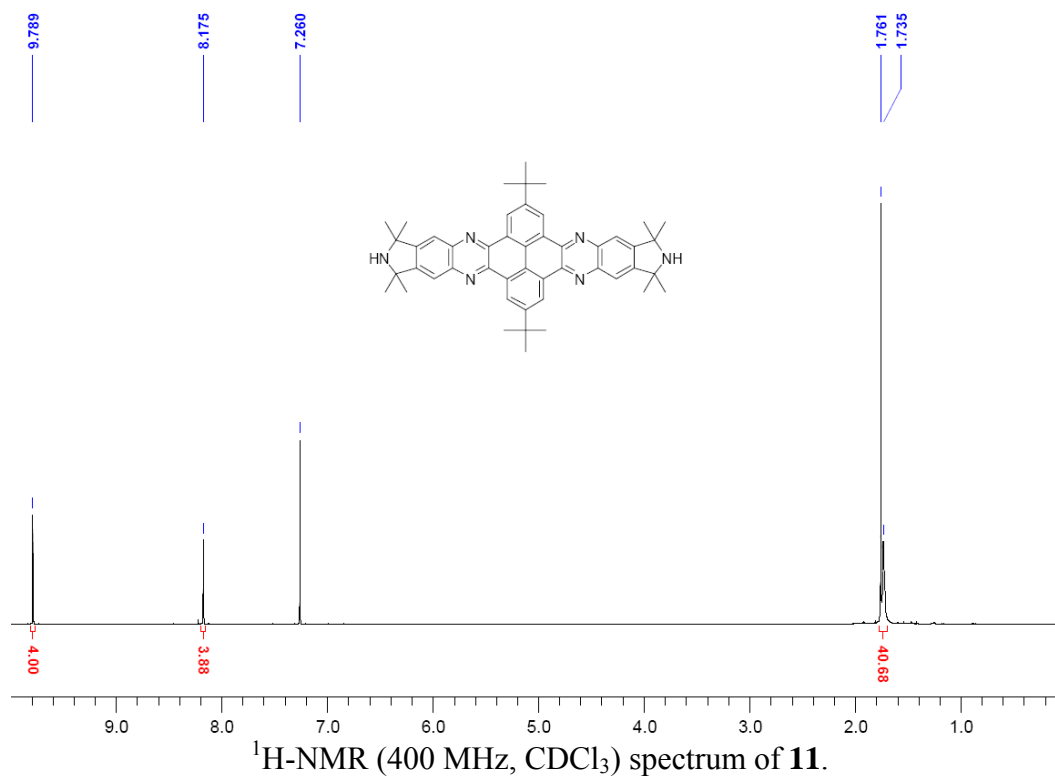
¹ H-NMR and ¹³ C-NMR spectrum of 5	page S2
¹ H-NMR and ¹³ C-NMR spectrum of 6	page S3
¹ H-NMR and ¹³ C-NMR spectrum of 8	page S4
¹ H-NMR spectrum of 2	page S5
¹ H-NMR and ¹³ C-NMR spectrum of 11	page S6
¹ H-NMR and ¹³ C-NMR spectrum of 3	page S7
Variation of detection pulse lengths.....	page S8
Simulations.....	page S8
Determination of errors.....	page S8
Literature.....	page S9

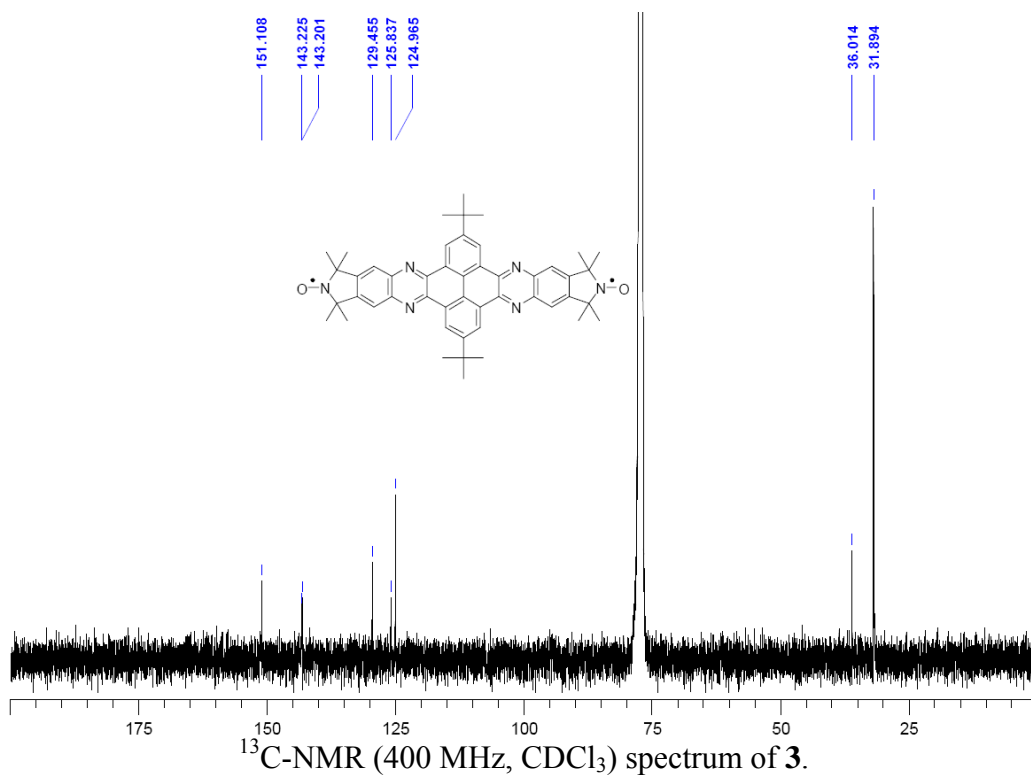
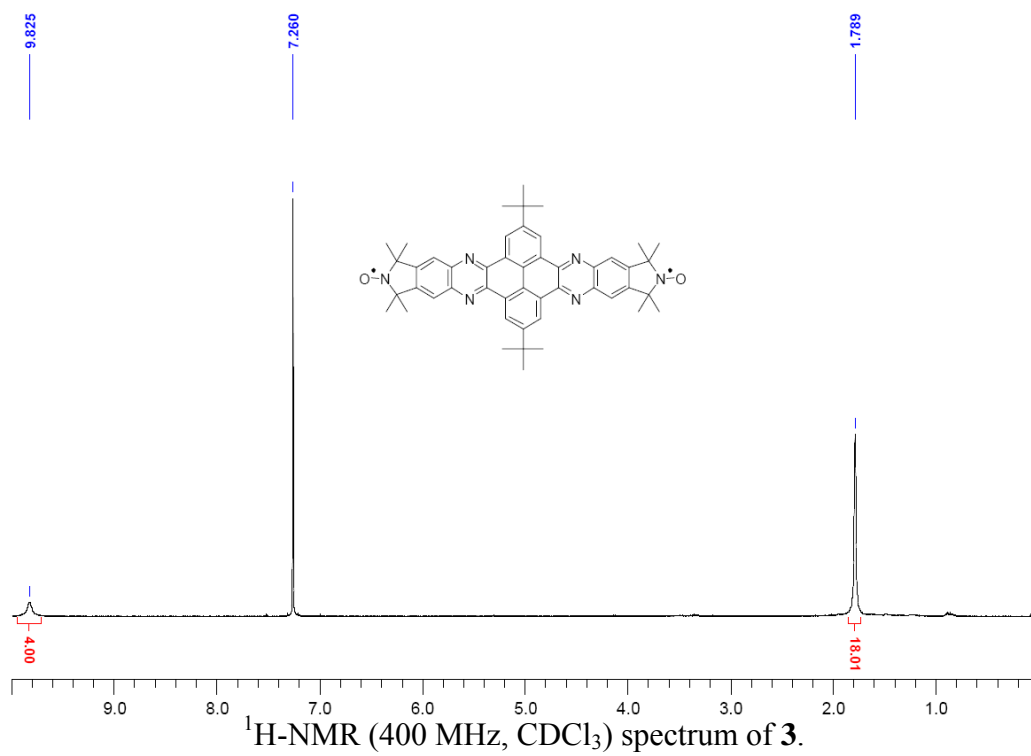












Variation of detection pulse lengths

In order to assure full excitation of the broad electron-electron coupling tensor in **2** the detection pulse length was varied from 32 ns to 12 ns at a detection frequency offset of 40 MHz using a video amplifier bandwidth of 50 MHz. The shape of the Pake pattern remained constant with a detection pulse length of 16 ns or 12 ns.

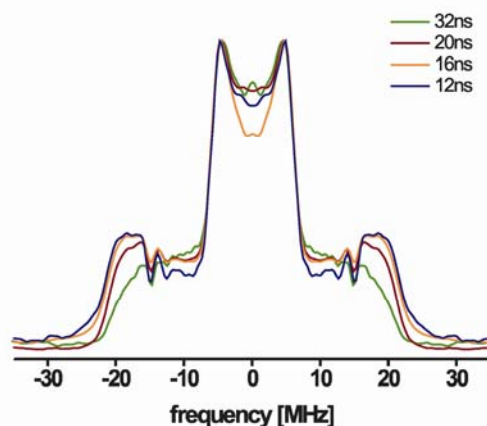


Fig. S1: Fourier Transformations of **2** at $\Delta\nu = 40$ MHz for detection pulse lengths of 32 ns, 20 ns, 16 ns and 12 ns in olive, wine, orange and navy, respectively.

Simulations

Structural flexibility was induced by a bending described by the angle δ (see Figure S2).

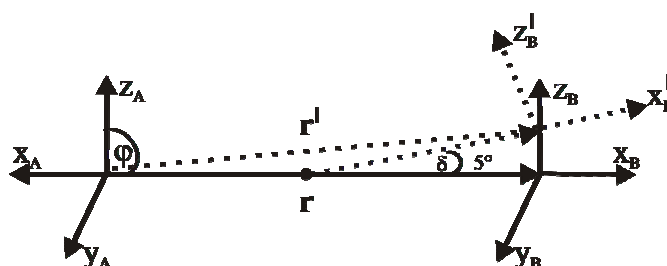


Figure S2: Geometric model with an average bending of the ring system in the xz -plane and around the centre of the molecule of $\pm 5^\circ$ for **1**, **2** and **3**.

The flexibility yielded from the average bending of $\pm 5^\circ$ of the ring system mimics accessible non-planar structures of polycyclic aromatic hydrocarbons.^[S1] The influence of the consequential structural diversity might already be overestimated from a chemical point of view, and its influence on the simulated PELDOR time traces are indeed negligible compared to simulations neglecting any flexibility. However, different molecular structures with different orbital overlap are a requirement for a distribution in J for **2** and **3** and a distribution in J is needed to fit the modulation damping and to circumvent even larger bending angles.

The resulting ensemble typically contains 1000 different structures each characterized via an interconnecting spin-spin distance vector r , with polar angles (ψ, η) in the axis system of spin A. Euler angles Ω were used to characterize the mutual orientation of spin centre B with respect to A. Hyperfine and g-tensor axes were considered to be collinear to the molecular axis system. For all orientations (typically 20000) of the

magnetic field vector B_0 in the molecular axis frame of spin A, the resonance positions of spins A and B were calculated. Transforming the hyperfine and g-tensor of spin B in the coordinate system of spin A yields spin B resonance frequencies. Final resonance frequencies of spin A and B were obtained taking a Gaussian distributed inhomogeneous line width into account. Pulse excitation profiles for detection and pump pulses were calculated based on the Bloch equations for uncoupled spins.^[S2] This gives rise to the excitation functions of spin A and B and the resulting dipolar distribution function for each conformer. The final PELDOR signal for a given frequency offset $\Delta\nu$ is the sum over all conformers and all magnetic field values. Full details of the home-written MATLAB® routine are described elsewhere.^[S3]

Determination of errors

The error in φ for molecule **1** is described in one of our previous publications and assumed to be the same for **2**.^[S4] For **3** φ cannot be determined (see main text). The error in r for **1** was deduced by a visual comparison of simulated PELDOR time traces with $r = 26.8$ and 27.0 Å, both leading to observable differences of the oscillation frequency as compared to the experiment. For **2** and **3**, the error in r was estimated from simulations varying r and J with a constant ΔJ in order to investigate a compensation of e.g. a large r -value with a decreased J -value. Small compensation effects were observed, but r and J can be independently yielded within the errors stated in Table 1. An analogous procedure was carried out for the analysis of the error of ΔJ , varying J and ΔJ at a constant r -value. The errors could be independently deduced. In contrast to previous publications yielding insight towards the conformational flexibility of rigid rod-like molecules^[S3] the bending described by the angle δ for **1**, **2** and **3** is in such a small regime that it cannot be reliably gathered via our simulation routine.

Literature

S1 S. Pogodin and I. Agranat, *J. Org. Chem.* 2002, **67**, 265-270.

S2 A. Schweiger and G. Jeschke, *Principles of pulse electron paramagnetic resonance*, Oxford University Press, New York, 2001.

S3 D. Margraf, B. E. Bode, A. Marko, O. Schiemann and T. F. Prisner, *Mol. Phys.*, 2007, **105**, 2153-2160.

S4 O. Schiemann, P. Cekan, D. Margraf, T. F. Prisner and S. T. Sigurdsson, *S., Angew. Chem. Int. Ed. Engl.*, 2009, in press.