

Materials and instruments

All the chemicals were purchased from commercial suppliers and used as received. Thin-layer chromatography (TLC) analysis was carried out on pre-coated silica plates. Column chromatography was performed using silica gel (200-300 mesh) using eluents in the indicated v/v ratio. ^1H NMR and ^{13}C NMR spectra were acquired on a Bruker ultrashield 300 MHz spectrometer at 25 °C. Chemical shifts (δ) are given in parts per million (ppm) relative to CHCl_3 (7.26 ppm for ^1H and 77.0 ppm for ^{13}C) or THF-d_8 (1.72, 3.58 ppm for ^1H and 25.3, 67.2 ppm for ^{13}C). Fluorescence spectra were recorded on an Agilent Cary Eclipse fluorescence spectrophotometer (with temperature controller). Light irradiation experiments were carried with a Camlin Atlas 300 W UV flash lamp and Bilber Lourmat 254 nm lamp.

Light irradiation experiments with coumarin^[1]

$3\text{-}^2\text{H}$ coumarin (1.0 mg) and benzophenone (0.16 mg) were dissolved in CDCl_3 (400 μL) and placed into a gas tight J-young NMR tube. The sample was prepared under an inert gas (nitrogen) atmosphere and T_1 experiments conducted on the monomer. It was then exposed to the 300W UV light. After 6 hours, the ^1H NMR spectrum shows that $3\text{-}^2\text{H}$ coumarin was converted into the dimer for which T_1 and T_s were determined. After the completion of T_1 and T_s measurement, the sample was irradiated under 254 nm for another 12 hours and the ^1H NMR shows that the dimer partly transferred back to $3\text{-}^2\text{H}$ coumarin. We did not observe significant degradation of the chloroform signal during the experiments. To further verify this, we performed the same experiment with 90% protonated chloroform and 10% deuterated chloroform (figure S1) which did not show significant signs of degradation or volume change after 12 hours of irradiation.

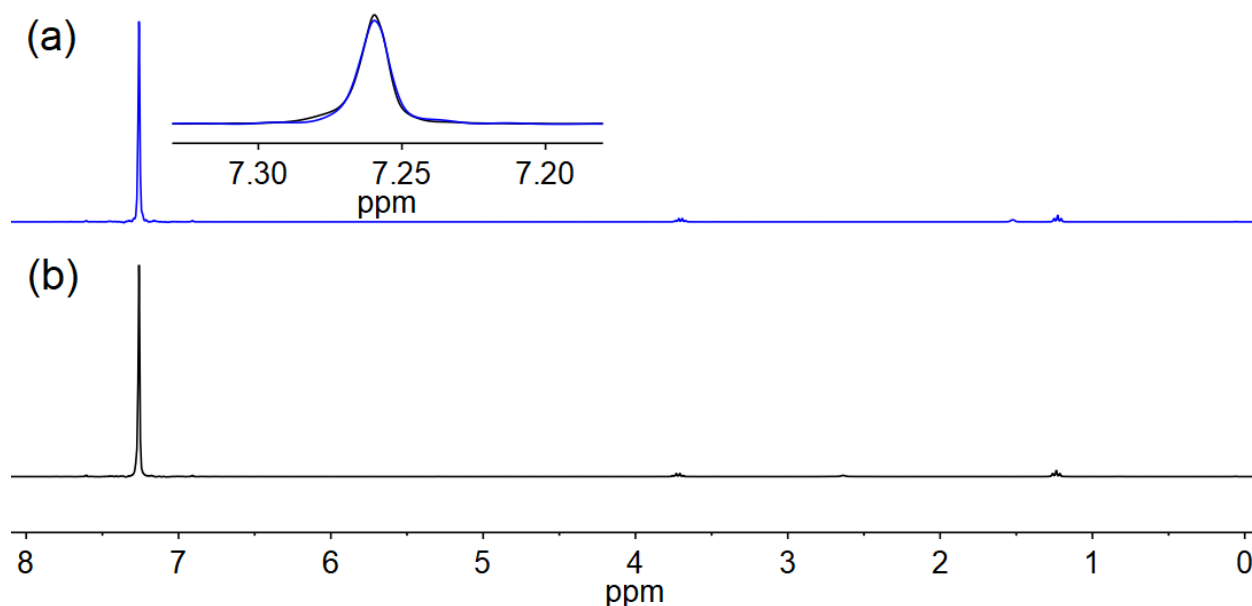


Figure S1. ^1H NMR spectrum of 3- ^2H -coumarin (1.0 mg) in the presence of benzophenone (0.16 mg) in 90% protonated CHCl_3 (containing 10% CDCl_3) (a) before and (b) after irradiation by light for 12 hours with the 300W flash lamp. The insert shows a magnification of the spectra (a) and (b) in the region between 7.30 ppm and 7.20 ppm, which shows no change in signal intensity.

Synthesis of $^{13}\text{C}_2$ -TPE

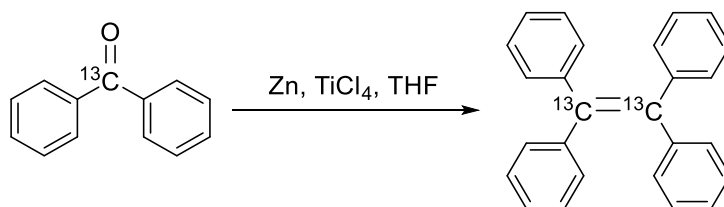


Figure S2. Synthesis of $^{13}\text{C}_2$ -TPE.

A three-neck flask equipped with magnetic bar was charged with zinc powder (162 mg). Anhydrous THF (10 mL) was subsequently added under nitrogen atmosphere. After the suspension cooled in the ice-water bath, TiCl_4 (1.30 mL) was added slowly by a syringe. The suspension mixture was warmed up to room temperature and stirred for 0.5 h, then heated at reflux for another 2.5 h. The suspension mixture was cooled down to room temperature again and benzophenone (89 mg) in THF (mL) was added slowly. After the completion of the addition, the suspension was heated to reflux overnight. The reaction mixture was quenched by 10% K_2CO_3 solution, extracted by ethyl acetate (20 mL \times 3). The organic layer was collected and washed with brine (15 mL), followed by drying with anhydrous Na_2SO_4 . After filtration, the filtrate was concentrated under reduced pressure. Crude material was then purified by column chromatography on silica gel (Eluent: petroleum ether : ethyl acetate = 50 : 1 to 10 : 1) to give a white solid. ^1H NMR (300 MHz, CDCl_3): δ 7.12-7.08 (m, 12 H), 7.07-7.02 (m, 8 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 143.73 (dd, ^{13}C - ^{13}C , $^1J_{\text{CC}} = 30.00$ Hz, $^2J_{\text{CC}} = 27.00$ Hz), 140.90 (dd (apparent singlet), ^{13}C - ^{13}C , $^1J_{\text{CC}} = 77.2$ Hz, estimated from SLIC experiments^[2]), 131.30 (dd, ^{13}C - ^{13}C , $^2J_{\text{CC}} = 2.4$ Hz, $^3J_{\text{CC}} = 2.0$ Hz), 127.61 (dd, ^{13}C - ^{13}C , $^3J_{\text{CC}} = 2.2$ Hz, $^4J_{\text{CC}} = 1.7$ Hz), 126.37 (s).

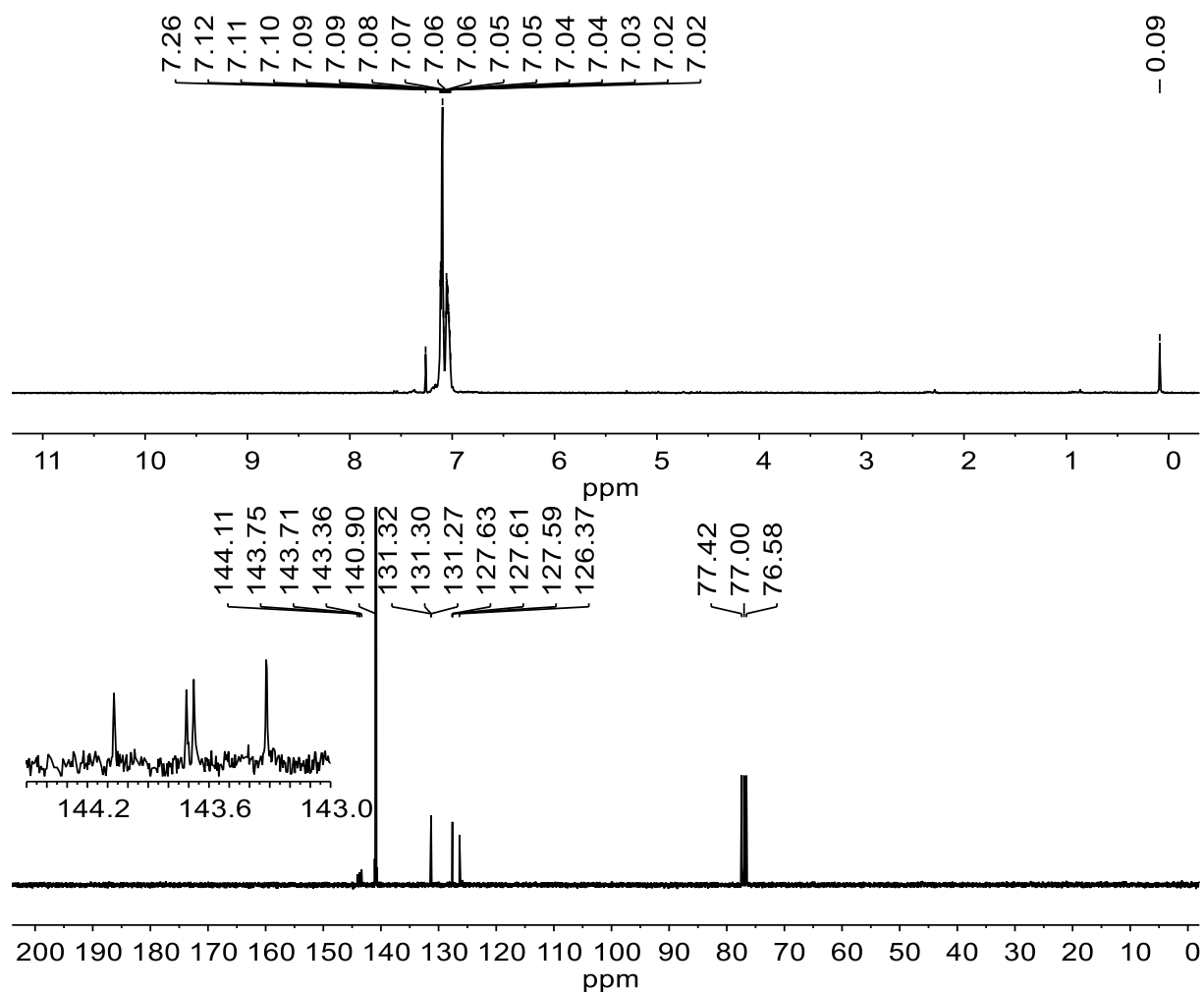


Figure S3. ^1H (top) and ^{13}C NMR (bottom) spectrum of $^{13}\text{C}_2$ -TPE recorded on a Bruker 300 MHz spectrometer in CDCl_3 .

Synthesis of 3- ^2H -coumarin

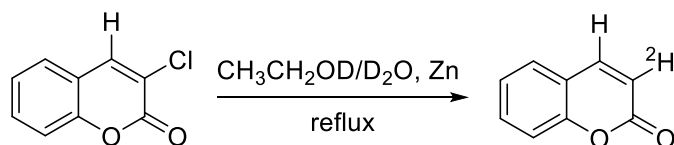


Figure S4. Synthesis of 3- ^2H -coumarin.

3- ^2H -coumarin was synthesized according to the literature^[3]. To a round-bottom pressure flask, equipped with a magnetic stirring bar, 3-chlorocoumarin (1.0 g) was added to a zinc powder (0.65 g) suspension in $\text{CH}_3\text{CH}_2\text{OD}$ and D_2O (30 mL, 1:1/v:v). The suspension was sealed and then heated to reflux for 48 hours. After filtration, the filtrate was concentrated. The residue was redissolved and crystallized from petroleum ether and benzene to give a solid.

^1H NMR (300 MHz, CDCl_3): δ 7.70 (s, 1 H), 7.55-7.46 (m, 2 H), 7.34-7.24 (m, 2 H).

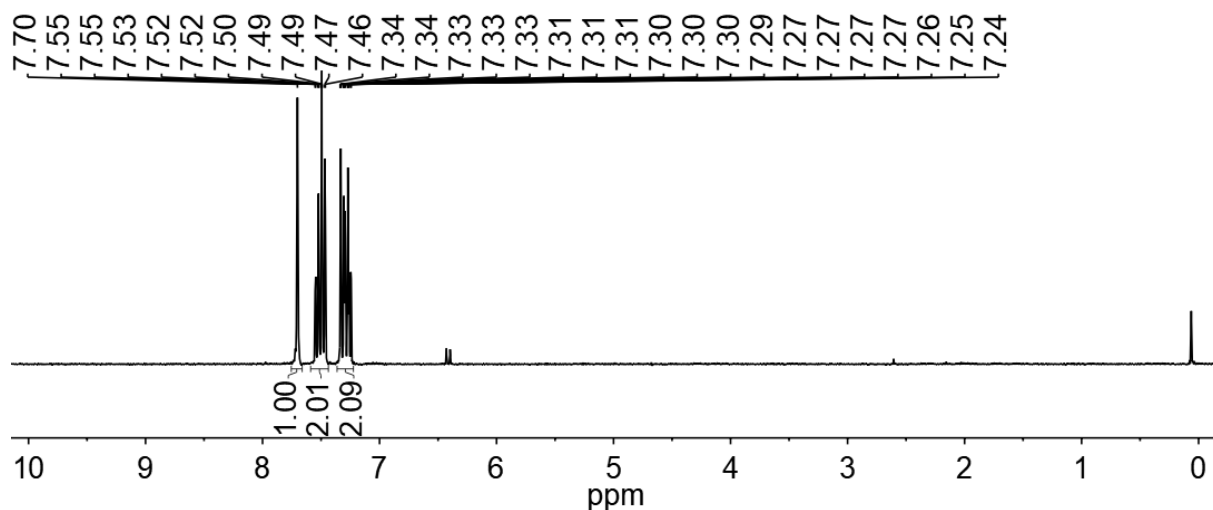


Figure S5. ^1H NMR spectrum of 3- ^2H -coumarin recorded on a Bruker 300 MHz spectrometer in CDCl_3 .

NMR spectra of $^{13}\text{C}_2$ -TPE in a solution containing 50% water

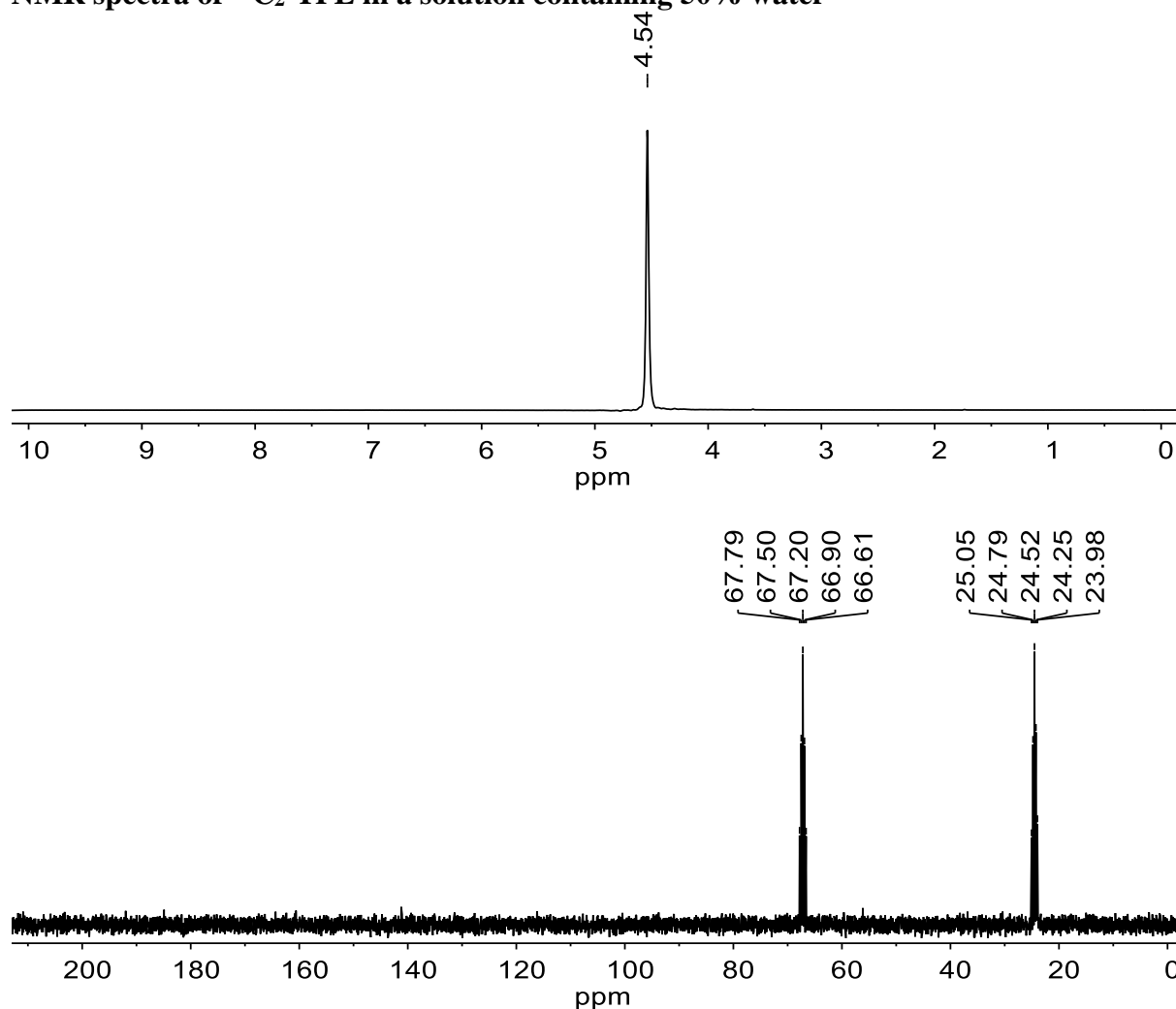


Figure S6. ^1H (top), and ^{13}C NMR (bottom) spectra of $^{13}\text{C}_2$ -TPE in the solution of THF-d_8 and water (1 : 1, v : v), which were measured with 1 scan each.

NMR spectra of $^{13}\text{C}_2$ -TPE in a solution containing 80% water

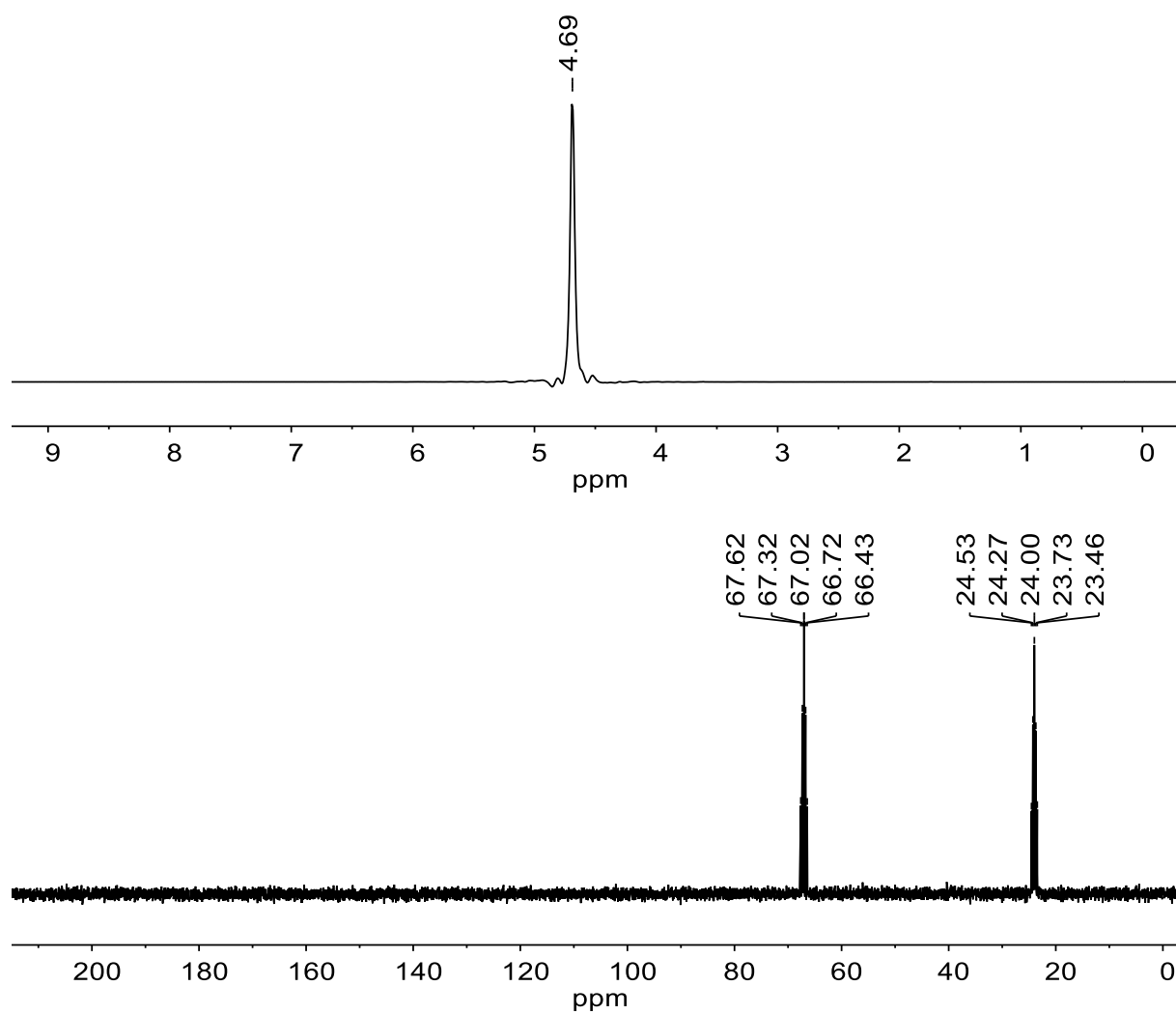


Figure S7. ^1H (top), and ^{13}C NMR spectra (bottom) of $^{13}\text{C}_2$ -TPE in the solution of THF- d_8 and water (1 : 4, v : v), which were measured with 1 and 64 scans, respectively.

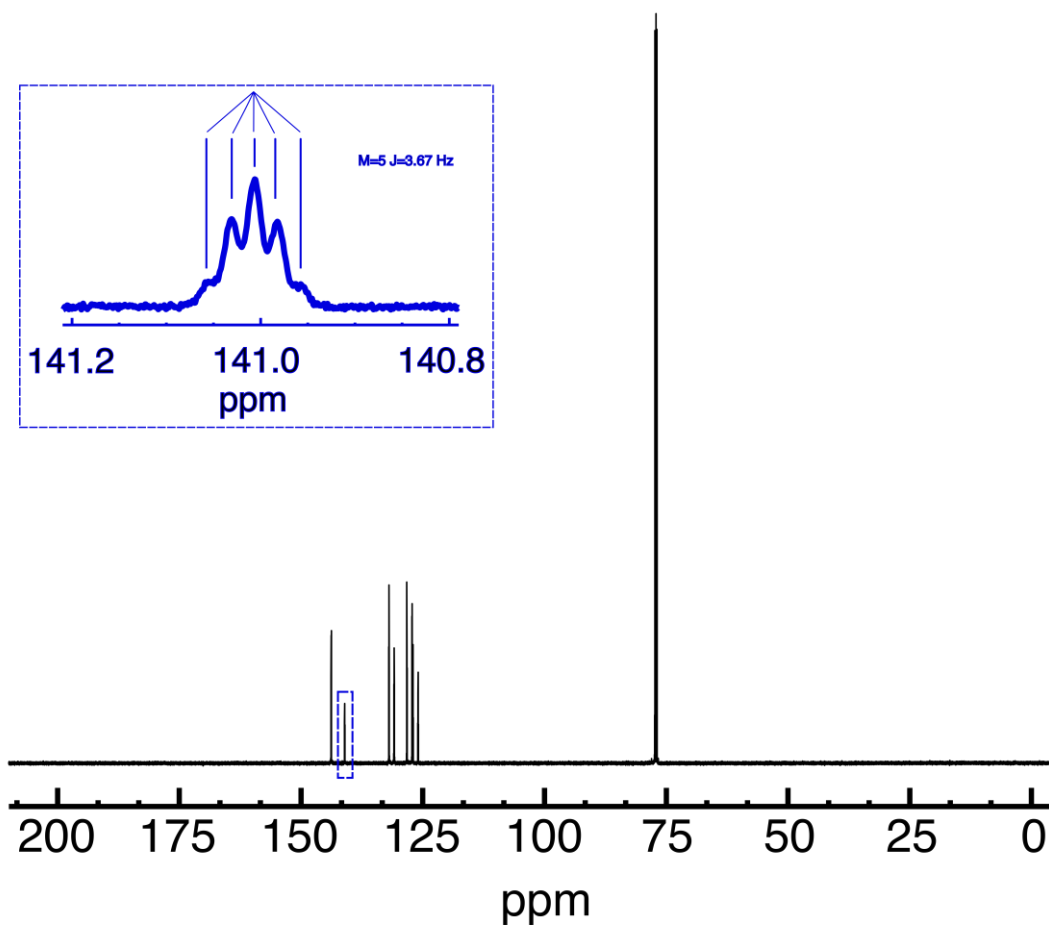


Figure S8. ^{13}C NMR spectrum of TPE at natural abundance as recorded on a 14T spectrometer at 298K. The inset in blue color shows a zoom on the olefinic carbon ^{13}C NMR signal. The quintet structure originates from the 3-bond J-coupling of the ^{13}C nucleus with the protons in the ring, where $^3J(\text{CH})=3.7\text{Hz}$. Based on the spectral resolution, the 4-bond coupling is estimated to be smaller than 0.4 Hz.

Singlet State Experiments

The NMR experiments were performed on a 7.05 T NMR spectrometer (Bruker Biospin, DE) at 298 K. Data were acquired and analysed via the proprietary spectrometer software TopSpin 3.5pl6 (Bruker Biospin, DE).

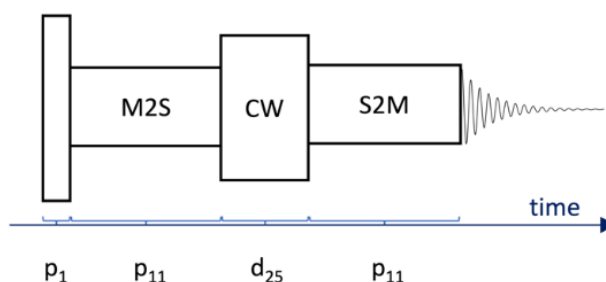


Figure S9. Schematic of the SLIC pulse sequence for converting longitudinal magnetization into singlet (first hard $\pi/2$ pulse followed by the M2S block) and back to observable transverse magnetization (after the S2M block).

The spin-lattice relaxation times T_1 were measured by using an inversion recovery experiment. The pulse programs t1irig and t1ir in the standard Bruker pulse sequence library were used to measure the ^{13}C T_1 in the $^{13}\text{C}_2$ -TPE sample and the ^1H T_1 in the coumarin and its dimer sample, respectively.

The spin density operator was converted from magnetization into singlet and back to magnetization for observation using the SLIC sequence⁴² (Figure 3), by exploiting the asymmetry in the J -couplings with the closest ^1H nuclei. During the sequence, radio-frequency pulses were applied on-resonance at the frequency of the spin pair bearing the singlet. CW decoupling was applied during the sustaining period d_{25} . The principal condition for spin order transfer is that the power level of the conversion blocks M2S and S2M matches the intra-nuclear J -coupling. With reference to Figure 3, the power level during the conversion blocks corresponded to a nutation frequency of 77.2 Hz for the $^{13}\text{C}_2$ -TPE sample and of 6.95 Hz for the coumarin dimer sample, respectively. The M2S and S2M blocks had a duration of $p11 = 90$ ms and $p11 = 200$ ms in the $^{13}\text{C}_2$ -TPE sample and in the coumarin dimer sample, respectively. The singlet relaxation time T_s was measured by monitoring the NMR signal decay during the variable delay d_{25} .

References

- [1] M. Jiang, N. Paul, N. Bieniek, T. Buckup, N. Hampp, M. Motzkus, *Phys. Chem. Chem. Phys.*, **2017**, *19*, 4597.
- [2] S. J. DeVience, R. L. Walsworth, M. S. Rosen, *Phys. Rev. Lett.*, **2013**, *111*, 173002.
- [3] D. A. Zykov, V. A. Zagorevskii, *Khimiya Geterotsiklicheskikh Soedinenii* **1969**, *5*, 1135.