

Measurements of short distances between trityl spin labels with CW-EPR, DQC and PELDOR

Supporting Information

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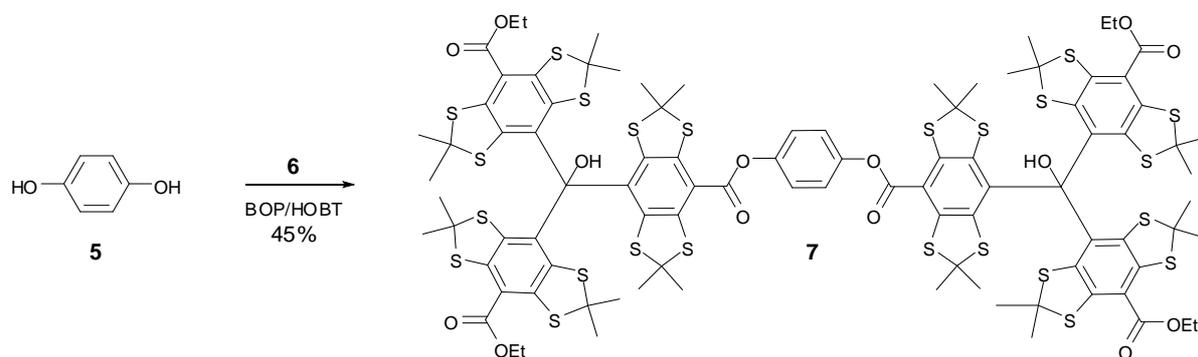
General procedures

All reagents were purchased from Sigma-Aldrich. All solvents were dried over molecular sieves (3Å) prior to use. All moisture- and oxygen-sensitive reactions were carried out under an inert atmosphere of argon unless otherwise stated. Silica gel was purchased from Silicycle. Analytical thin layer chromatography (TLC) was performed on glass plates (Silicycle 60 F₂₅₄).

NMR spectra for all compounds were recorded on an Avance 400 MHz Bruker NMR spectrometer and the chemical shifts were reported parts per million (ppm) relative to the deuterated NMR solvent used [¹H-NMR CDCl₃ (7.26 ppm), DMSO-*d*₆ (2.50 ppm); ¹³C-NMR: CDCl₃ (77.16 ppm), DMSO-*d*₆ (39.52 ppm)].

Mass spectra were recorded on Bruker, Micro Tof-Q. Compounds **1**, **2** and **3** were purified on RP-HPLC using a GL Sciences Inertsustain C18 14 × 250 mm preparative column with UV detection at 360 nm on Beckman Coulter Gold HPLC. Analytical RP-HPLC samples for compounds **1**, **2** and **3** were run on the same instrument, using a GL Sciences Inertsustain C18 4.6 × 150 mm analytical column with UV detection at 360 nm. Solvent gradients for analytical and preparative RP-HPLC are described for compounds **1**, **2** and **3**. Compounds having mass higher than 1000 mass units were analysed by MALDI-TOF using an Autoflex III matrix assisted laser desorption/ionization time of flight mass spectrometer (Bruker). The MALDI was operated with a Nb-YAG smartbeam laser of wavelength 354 nm and repetition rate up to 1000 Hz. The spectra were recorded in positive ion mode with ion reflectron and pulsed ion extraction (PIE) of 10 ns. The laser power was kept below 50% of total laser power in all measurements. The matrix solution was prepared by dissolving 10 mg of the matrix α -cyano-4-hydroxy cinnamic acid methyl ester in 1 mL (50:50 v/v) CH₃CN and 0.1% trifluoroacetic acid in water. Compounds were dissolved 50:50 CH₃CN and EtOAc. The sample spots were prepared by co-spotting 0.5 μ L of compound in 50:50 (v/v) acetonitrile (CH₃CN) and ethyl acetate (EtOAc) and 0.5 μ L of matrix solution on a clean polished steel sample plate, after which the solvent was allowed to evaporate at 22 °C. The instrument was internally calibrated using peptide calibration standard (nr. 206195, Bruker, Germany) and an in-house prepared calibration standard mixture prior to measurements.

Organic synthesis procedures



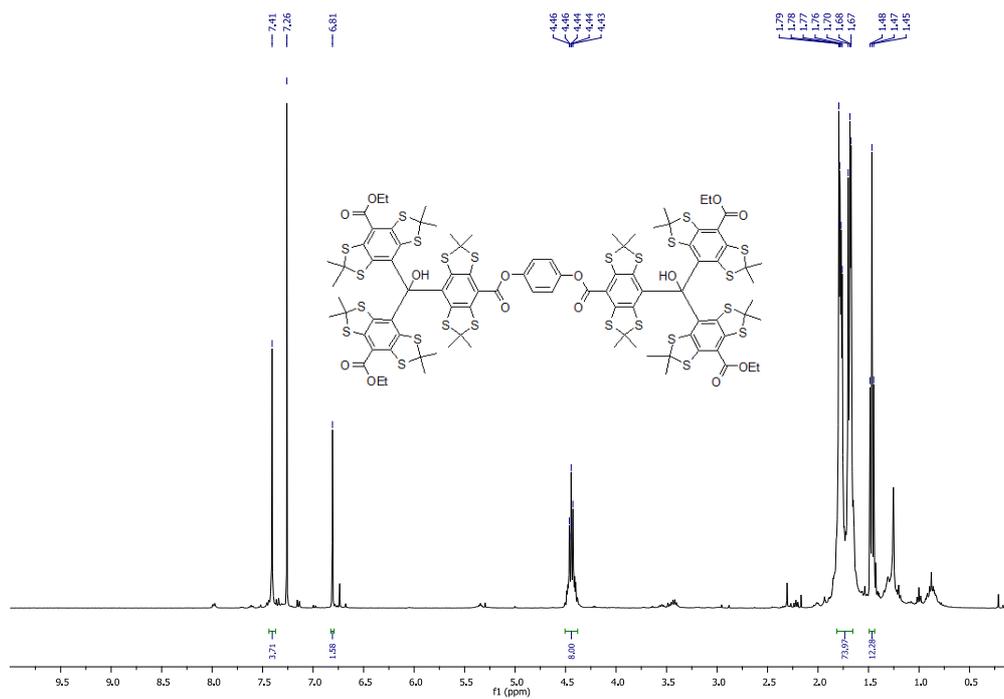
Compound 7. To a solution of hydroquinone **5** (0.005 g, 0.045 mmol) and monoacid trityl alcohol **6**¹ (0.410 g, 2.42 mmol) and Et₃N (1.5 mL) in anhydrous DMF (5 mL) were added BOP (0.080 g, 0.182 mmol) and HOBT (0.025 g, 0.182 mmol). The resulting suspension was stirred at 25 °C for 12 h, after which the reaction mixture was concentrated *in vacuo*. The crude product was purified by column chromatography using silica gel (5:95 to 40:60, EtOAc:hexane) to give **7** (0.454 g, 45%) as a yellow solid.

TLC (Silica gel, 30% EtOAc /hexane): Rf (**5**) = 0.3, Rf (**6**) = 0.1, Rf (**7**) = 0.50.

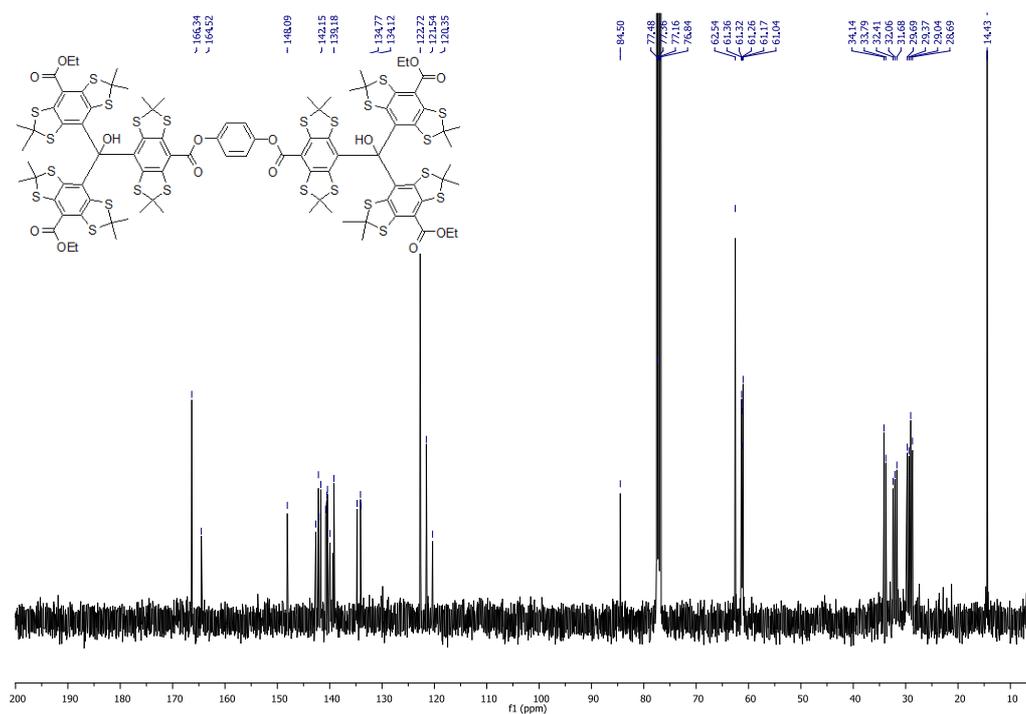
¹H NMR (CDCl₃) δ 7.41 (s, 4H), 6.81 (s, 2H), 4.51 – 4.38 (m, 8H), 1.81 – 1.66 (m, 74H), 1.47 (t, *J* = 7.1 Hz, 12H).

¹³C NMR (CDCl₃) δ 166.34, 164.52, 148.09, 142.65, 142.10, 141.68, 140.78, 140.49, 139.94, 139.18, 134.77, 134.08, 122.72, 121.54, 120.35, 84.50, 77.42, 77.16, 76.84, 62.54, 61.49 – 60.91, 34.14, 33.79, 32.41, 32.06, 31.68, 29.69, 29.37, 29.04, 28.69, 14.43.

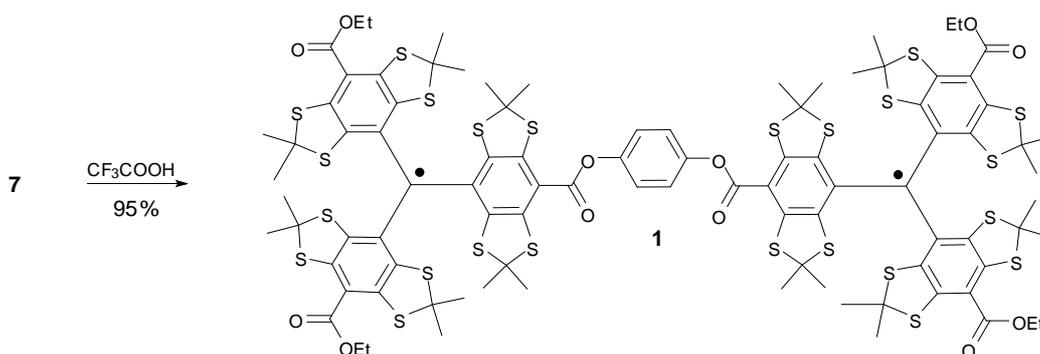
MALDI-TOF: calcd. for C₉₄H₉₈O₁₄S₂₄ [M+Na] 2241.015, found 2241.666



¹H-NMR (400 MHz, CDCl₃) spectrum of **7**.



¹³C-NMR (400 MHz, CDCl₃) spectrum of **7**.



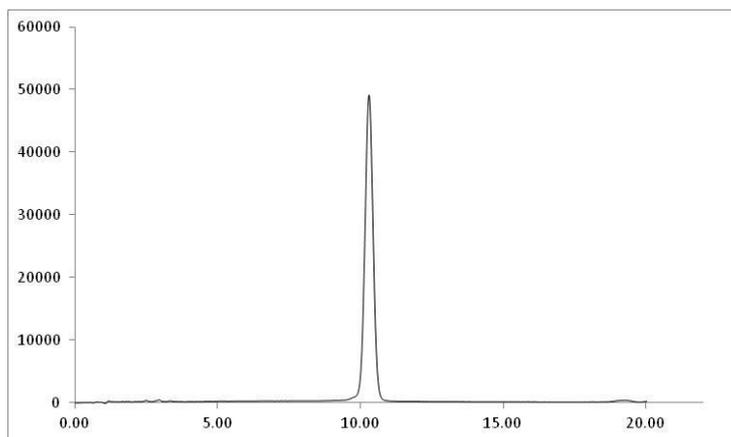
Compound 1. Trifluoroacetic acid (2 mL) was added to a solution of compound **7** (0.020 g, 0.020 mmol) in CH_2Cl_2 (5mL). The reaction mixture was stirred at 25 °C for 3 h and concentrated *in vacuo*. The product was purified by column chromatography using silica gel (5:95 to 40:60, EtOAc:hexane) to give **1** (0.019 g, 95%) as a green solid.

TLC (Silica gel, 30% EtOAc/hexane): Rf (**7**) = 0.50, Rf (**1**) = 0.70.

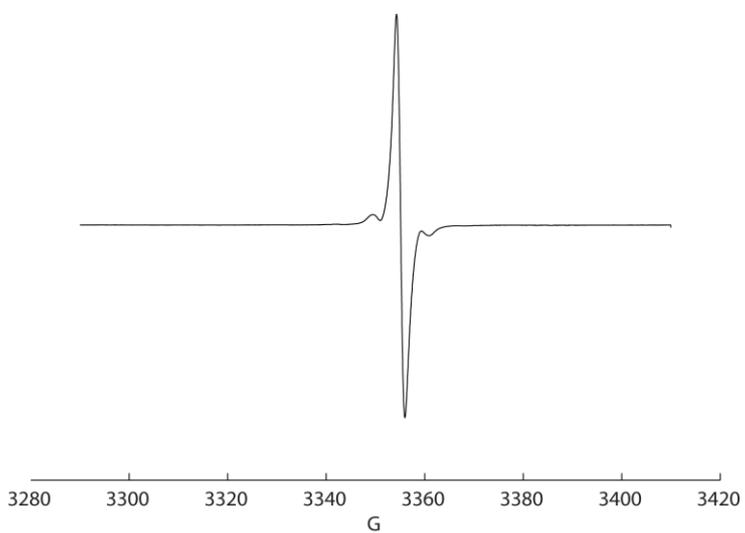
MALDI-TOF: calcd. for $\text{C}_{94}\text{H}_{96}\text{O}_{12}\text{S}_{24}^-$ [M+] 2184.019, found 2184.070

Preparative HPLC run (flow rate = 7 mL/min). Solvent A, 100% CH_3CN ; Solvent B, 100% EtOAc; 5 min linear gradient from 0% to 10% B, 15% B isocratic for 25 min. 1 min linear gradient from 10% to 0% B to initial conditions (100% A).

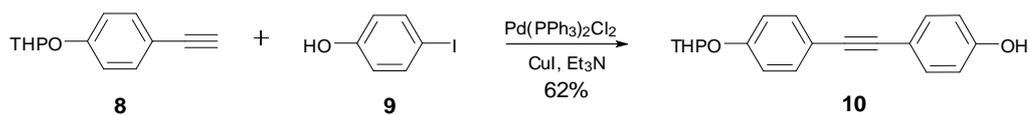
Analytical HPLC run (Flow rate = 1 mL/min). Solvent A, 100% CH_3CN ; Solvent B, 100% EtOAc; 15 min linear gradient from 0% to 10% B, 10% B isocratic for 4 min. 1 min linear gradient from 10% to 0% B to initial conditions (100% A).



HPLC chromatogram of **1**.



EPR spectrum of **1** (10% MeOH/CH₂Cl₂ at 22 °C).



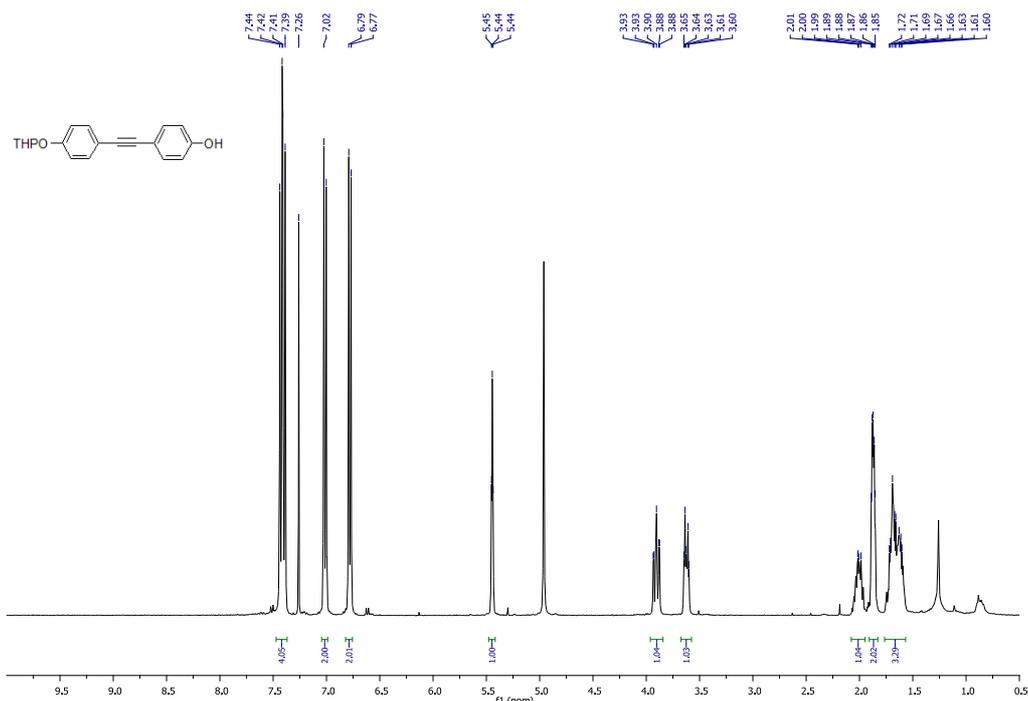
4-((4-(tetrahydro-2H-pyran-2-yloxy)phenyl)ethynyl)phenol (10). To a solution of compound **8** (0.368 g, 1.818 mmol), 4-iodophenol (0.200 g, 0.909 mmol) and freshly distilled Et₃N (5 mL) in anhydrous THF (10 mL) were added Pd[PPh₃]₂Cl₂ (0.032 g, 5 mol %) and CuI (0.014 g, 8 mol %) and the reaction mixture was stirred at 25 °C for 12 h. The reaction mixture was diluted with water (20 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed successively with water (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na₂SO₄ and concentrated *in vacuo* to give the crude product, which was purified by column chromatography using silica gel (5:95 to 40:60, EtOAc:hexane) to yield **10** (0.166 g, 62%) as a brown solid.

TLC (Silica gel, 30% EtOAc/hexane): R_f (**8**) = 0.50, R_f (**9**) = 0.40, R_f (**10**) = 0.20.

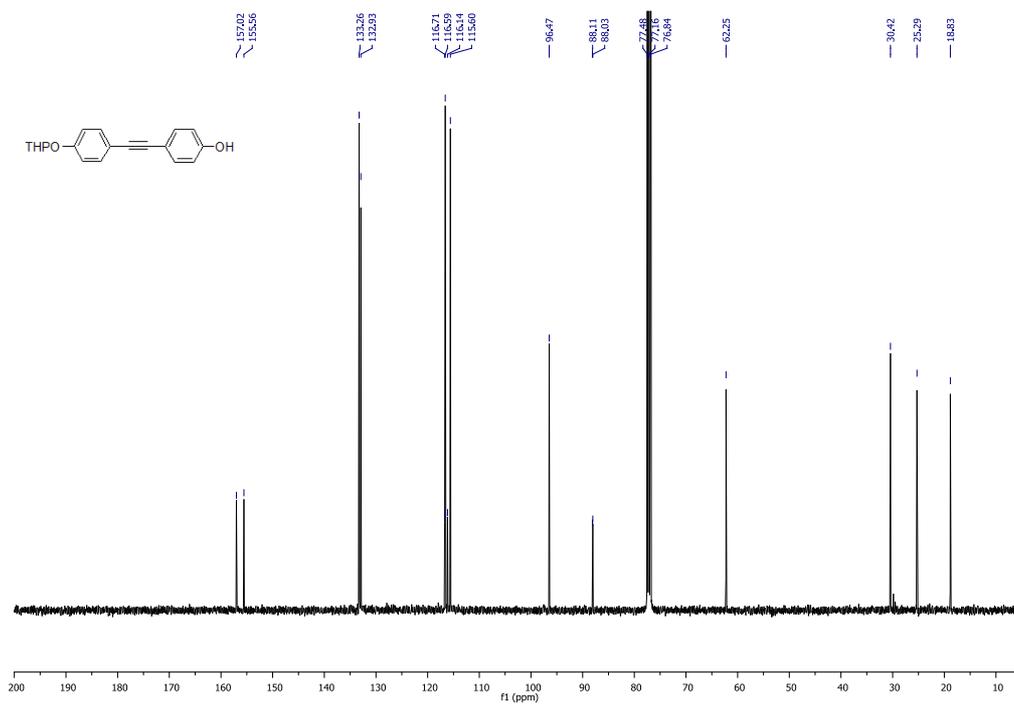
¹H NMR (CDCl₃) δ 7.41 (dd, *J* = 11.4, 8.8 Hz, 4H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 5.44 (t, *J* = 3.1 Hz, 1H), 3.96 – 3.84 (m, 1H), 3.67 – 3.58 (m, 1H), 2.08 – 1.95 (m, 1H), 1.91 – 1.83 (m, 2H), 1.66 (ddd, *J* = 23.1, 11.2, 4.1 Hz, 3H).

¹³C NMR (CDCl₃) δ 157.02, 155.56, 133.26, 132.93, 116.65, 116.14, 115.60, 96.47, 88.07, 77.48, 77.16, 76.84, 62.25, 30.42, 25.29, 18.83.

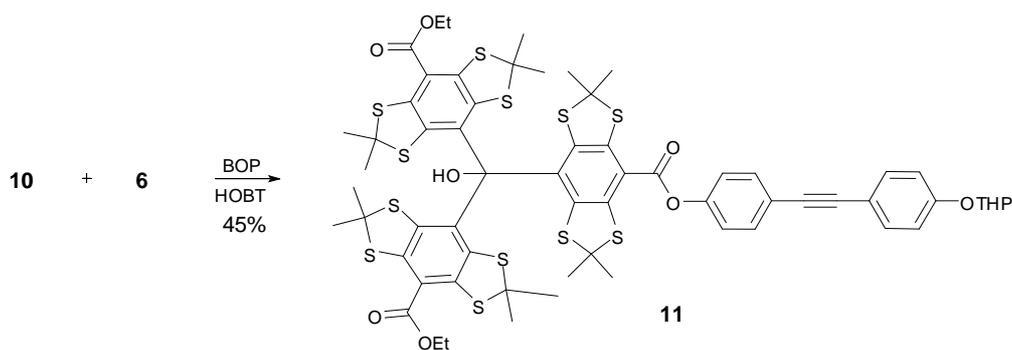
MS (ESI) calcd. for C₁₉H₁₈O₃ [M+Na] 317.1154, found 317.1148.



$^1\text{H-NMR}$ (400 MHz, CDCl_3) spectrum of **10**.



$^{13}\text{C-NMR}$ (400 MHz, CDCl_3) spectrum of **10**.



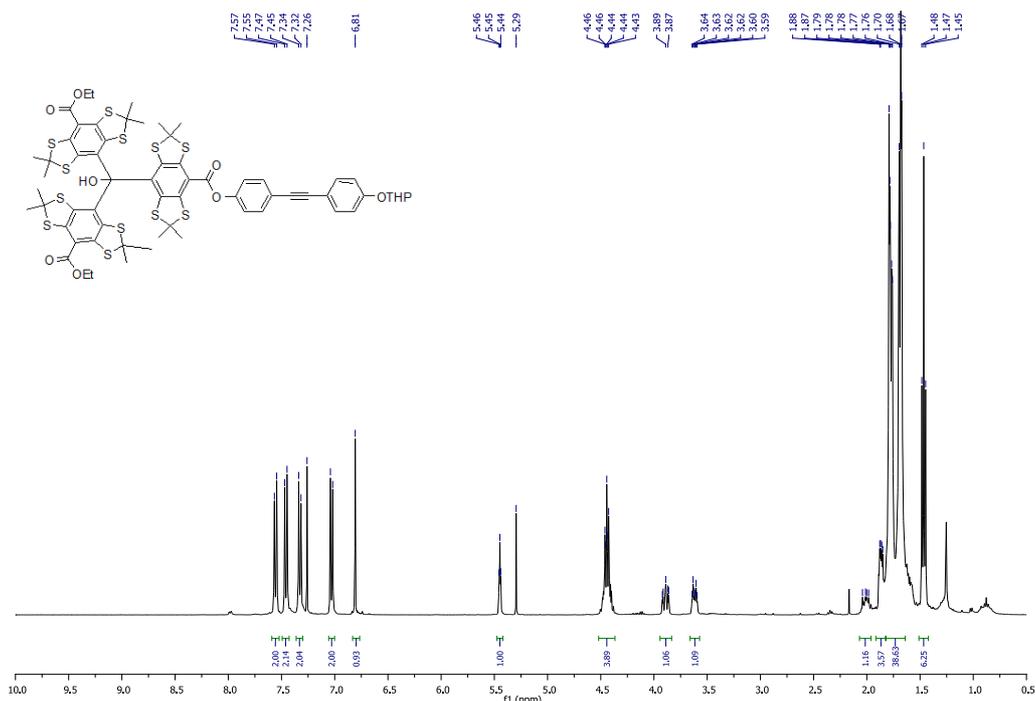
Compound 11. To a solution of compound **10** (0.040 g, 0.136 mmol), monoacid trityl alcohol (0.100 g, 0.136 mmol) and Et₃N (1.5 mL) in anhydrous DMF (5 mL) were added BOP (0.082 g, 0.272 mmol) and HOBT (0.037 g, 0.272 mmol). The resulting suspension was stirred at 25 °C for 12 h, after which the reaction mixture was concentrated *in vacuo*. The crude product was purified by column chromatography using silica gel (5:95 to 40:60, EtOAc:hexane) to give **11** (0.083 g, 45%) as a yellow solid.

TLC (Silica gel, 30% EtOAc/hexane): R_f (**10**) = 0.20, R_f (**6**) = 0.1, R_f (**11**) = 0.50.

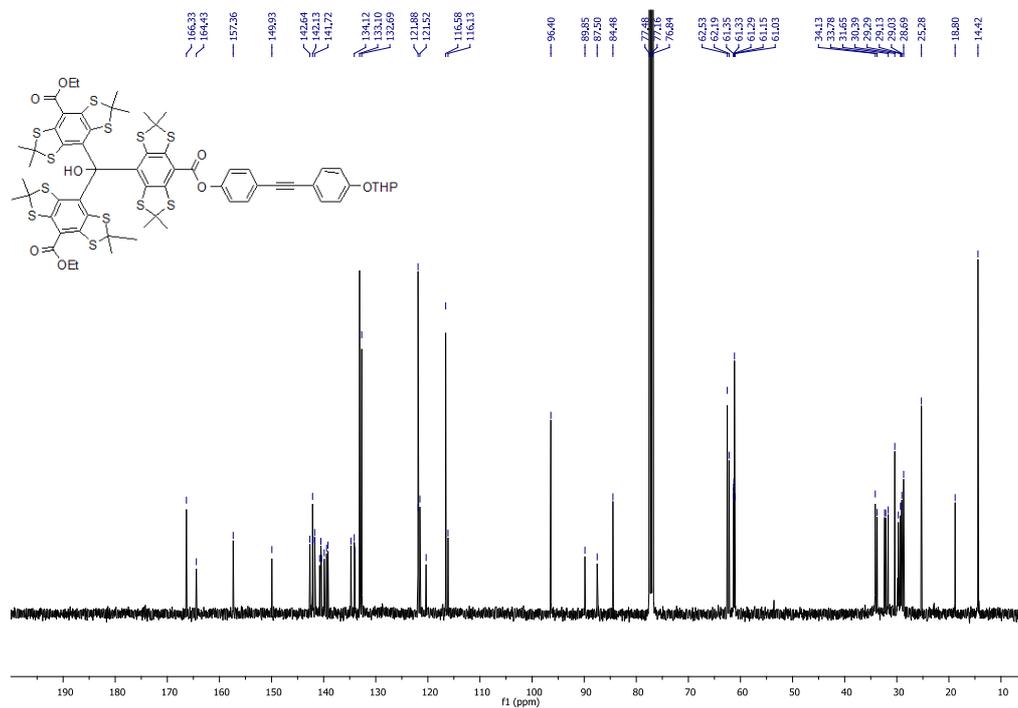
¹H NMR (CDCl₃) δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.81 (s, 1H), 5.45 (t, *J* = 3.1 Hz, 1H), 4.52 – 4.37 (m, 4H), 3.94 – 3.83 (m, 1H), 3.62 (dt, *J* = 8.2, 3.7 Hz, 1H), 2.01 (dd, *J* = 13.9, 9.2 Hz, 1H), 1.86 (dd, *J* = 7.9, 3.4 Hz, 4H), 1.74 (ddd, *J* = 34.5, 7.1, 3.3 Hz, 39H), 1.47 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (CDCl₃) δ 166.33, 164.43, 157.36, 149.93, 142.64, 142.08, 141.70, 140.77 (s, 2C), 140.47, 139.89, 139.43, 139.16, 134.77, 134.05, 133.10, 132.69, 121.86, 121.52, 120.33, 116.58, 116.13, 96.40, 89.85, 87.50, 84.48, 77.48, 77.16, 76.84, 62.53, 62.19, 61.49 – 60.93, 34.13, 33.78, 32.34, 32.11, 31.65, 30.39, 29.69, 29.44 – 28.89, 28.69, 25.28, 18.80, 14.42.

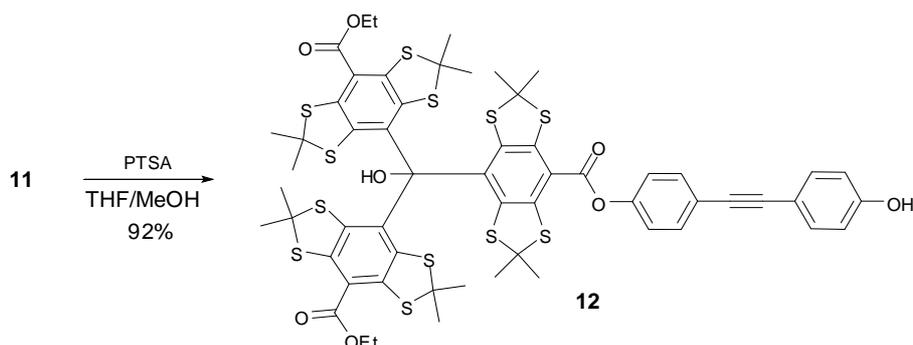
MALDI-TOF: calcd. for C₆₃H₆₄O₉S₁₂ [M+Na] 1371.119, found 1371.279.



¹H-NMR (400 MHz, CDCl₃) spectrum of **11**.



¹³C-NMR (400 MHz, CDCl₃) spectrum of **11**.



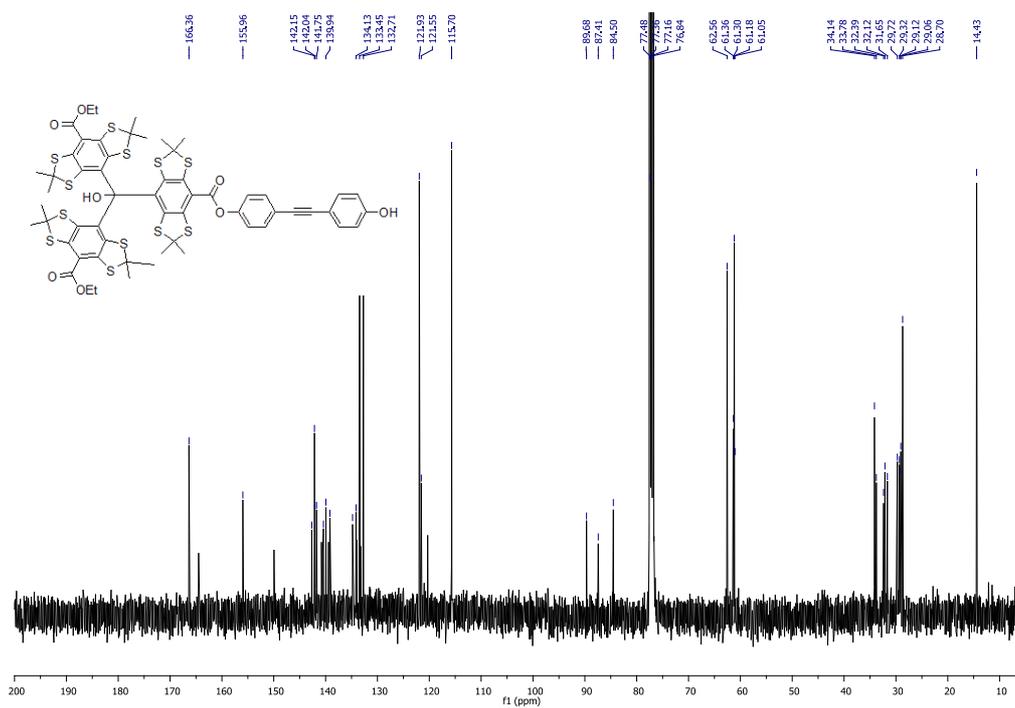
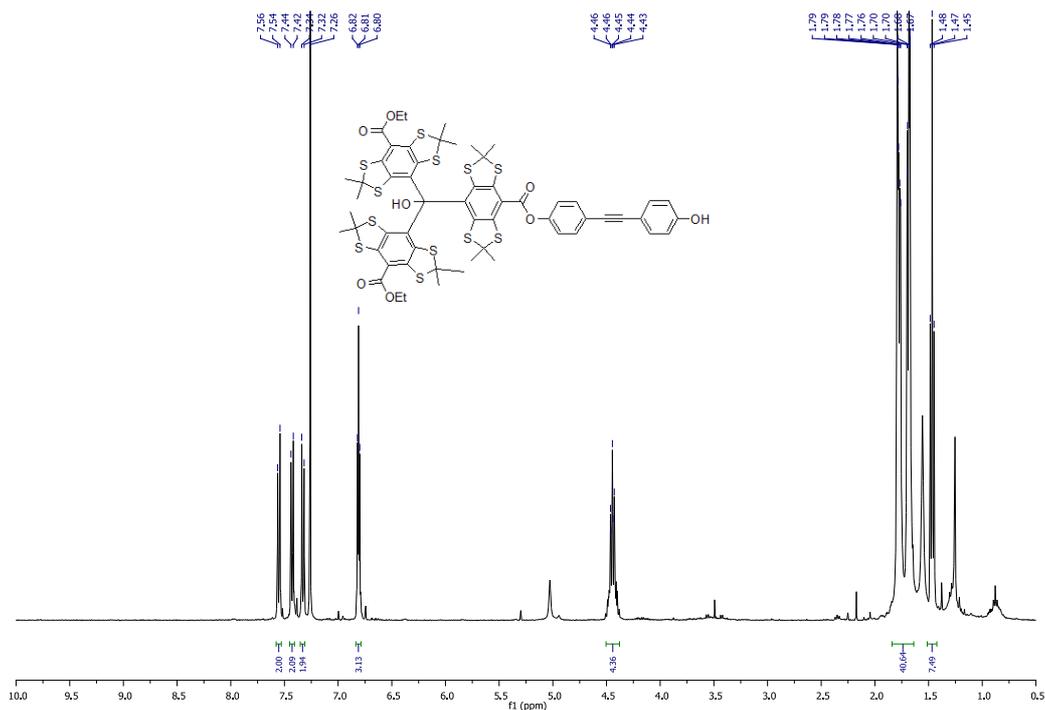
Compound 12. 4-toluenesulfonic acid (0.003 g, 0.019 mmol) was added to a solution of compound **11** (0.050 g, 0.037 mmol) in anhydrous THF and methanol (1:1, 10 mL). After stirring the reaction mixture at 25 °C for 12 h, it was diluted with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed successively with water (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na₂SO₄ and concentrated *in vacuo* to give the crude product, which was purified by column chromatography using silica gel (2:98, EtOAc:hexane) to yield **12** (0.043 g, 92%) as a yellow solid.

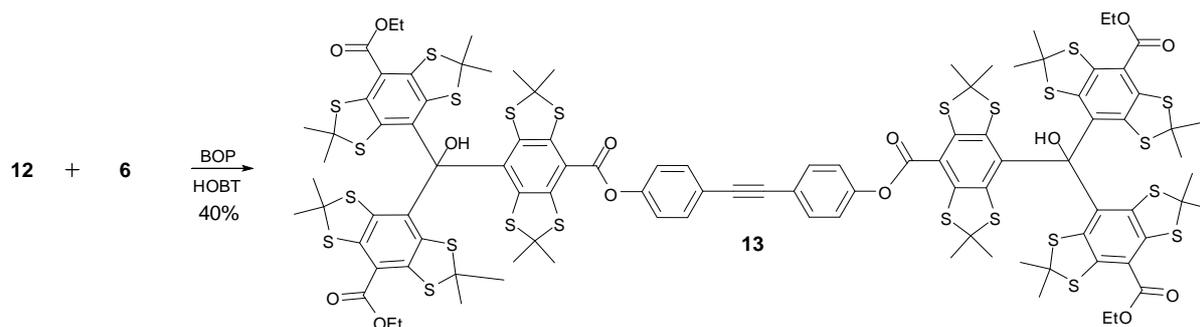
TLC (Silica gel, 30% EtOAc/hexane): R_f (**11**) = 0.5, R_f (**12**) = 0.30.

¹H NMR (CDCl₃) δ 7.55 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 6.81 (t, *J* = 4.3 Hz, 3H), 4.50 – 4.38 (m, 4H), 1.84 – 1.64 (m, 41H), 1.47 (t, *J* = 7.1 Hz, 7H).

¹³C NMR (CDCl₃) δ 142.10, 141.75, 140.42, 134.13, 133.45, 132.71, 121.93, 121.55, 115.70, 77.48, 77.26, 76.84, 62.56, 61.22, 34.14, 33.78, 32.39, 32.12, 31.65, 29.72, 29.58 – 28.92, 28.70, 14.43, 1.17.

MALDI-TOF: calcd. for C₅₈H₅₆O₈S₁₂ [M+Na] 1287.062, found 1287.945





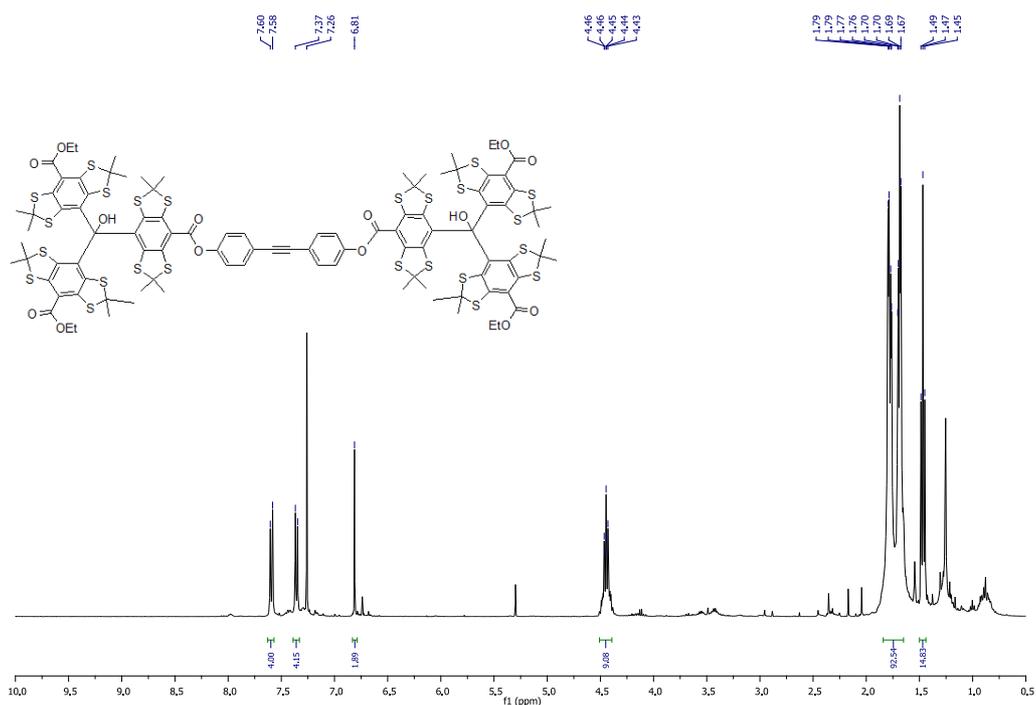
Compound 13. To a solution of compound **12** (0.050 g, 0.039 mmol), monoacid trityl alcohol (0.042 g, 0.039 mmol) and Et₃N (1.5 mL) in anhydrous DMF (5 mL) were added BOP (0.079 g, 0.079 mmol) and HOBT (0.010 g, 0.079 mmol). The resulting suspension was stirred at 25 °C for 12 h, after which the reaction mixture was concentrated *in vacuo*. The crude product was purified by column chromatography using silica gel (5:95 to 40:60, EtOAc:hexane) to give **13** (0.037 g, 40%) as a yellow solid.

TLC (Silica gel, 30% EtOAc/hexane): R_f (**12**) = 0.30, R_f (**6**) = 0.1, R_f (**13**) = 0.50.

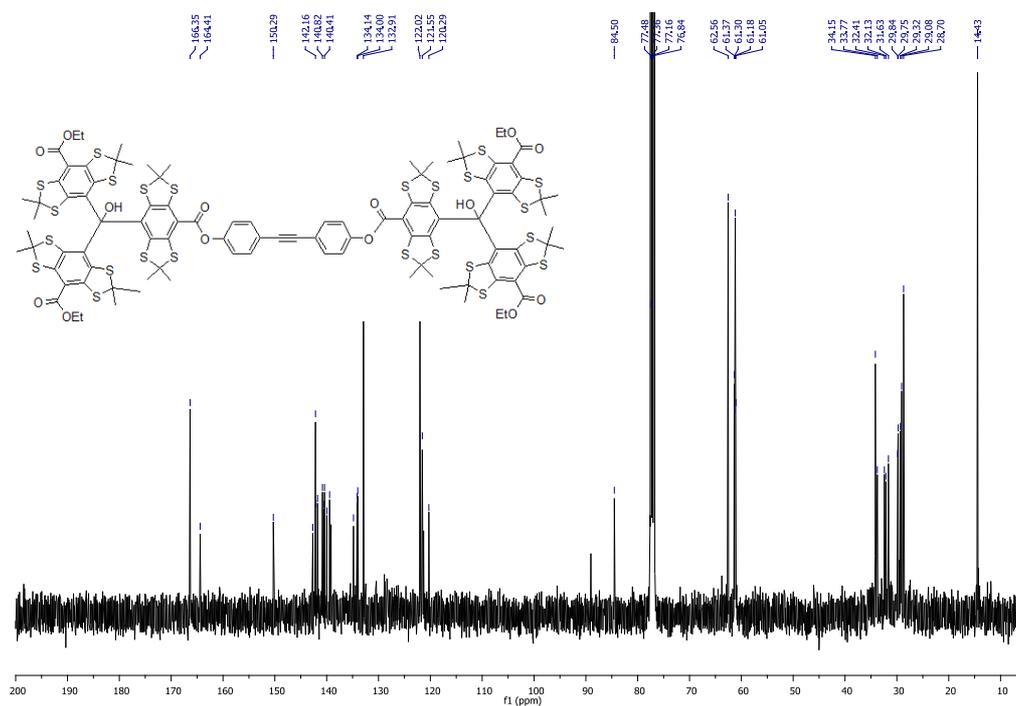
¹H NMR (CDCl₃) δ 7.59 (d, *J* = 8.7 Hz, 4H), 7.36 (d, *J* = 8.7 Hz, 4H), 6.81 (s, 2H), 4.51 – 4.39 (m, 9H), 1.73 (ddd, *J* = 11.8, 9.6, 3.9 Hz, 93H), 1.47 (t, *J* = 7.1 Hz, 15H).

¹³C NMR (CDCl₃) δ 166.35, 142.10, 141.76, 140.69, 140.41, 139.97, 139.44, 134.07, 132.91, 122.02, 121.55, 120.29, 84.50, 77.42, 77.16, 76.84, 62.56, 61.22, 34.15, 33.77, 32.41, 31.88, 31.57 – 31.25, 29.80, 29.32, 29.08, 28.70, 14.43, 1.17.

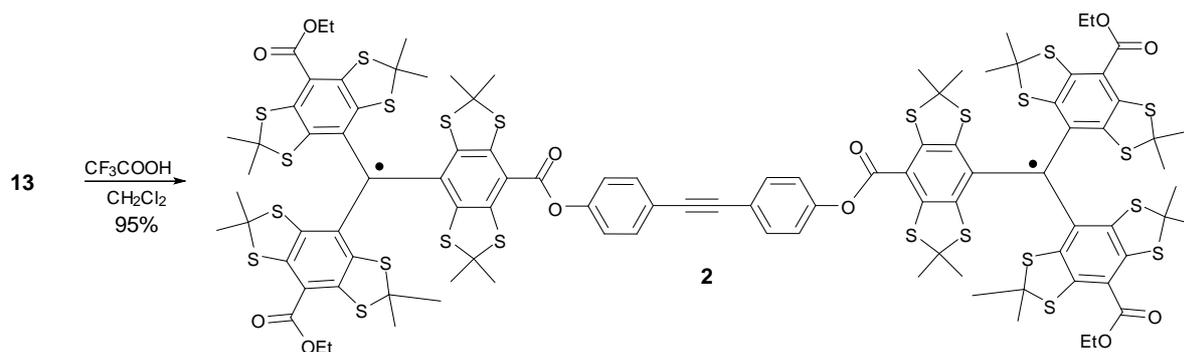
MALDI-TOF: calcd. for C₁₀₂H₁₀₂O₁₄S₂₄ [M+Na] 2341.056, found 2344.555



¹H-NMR (400 MHz, CDCl₃) spectrum of **13**.



¹³C-NMR (400 MHz, CDCl₃) spectrum of **13**.



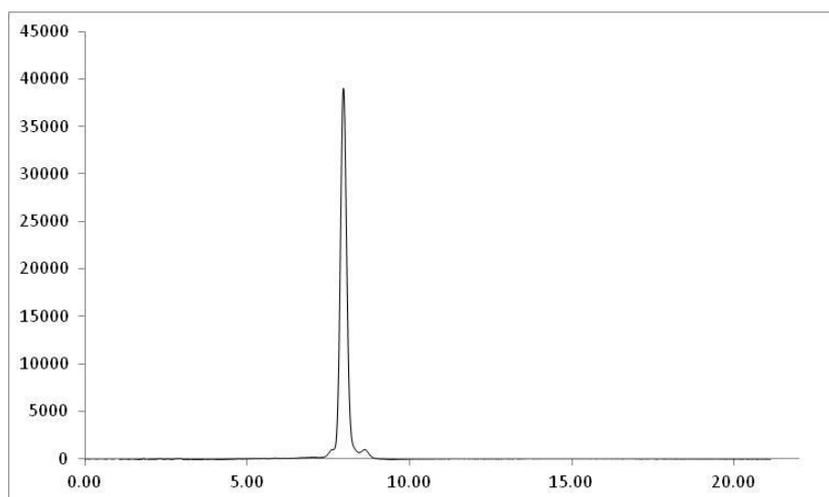
Compound 2. Trifluoroacetic acid (2 mL) was added to a solution of compound **13** (0.025 g, 0.010 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at 25 °C for 3 h and concentrated *in vacuo*. The product was purified by column chromatography using silica gel (5:95 to 40:60, EtOAc:hexane) to give **2** (0.023 g, 95%) as a green solid.

TLC (Silica gel, 30% EtOAc/hexane): Rf (**13**) = 0.50, Rf (**2**) = 0.60.

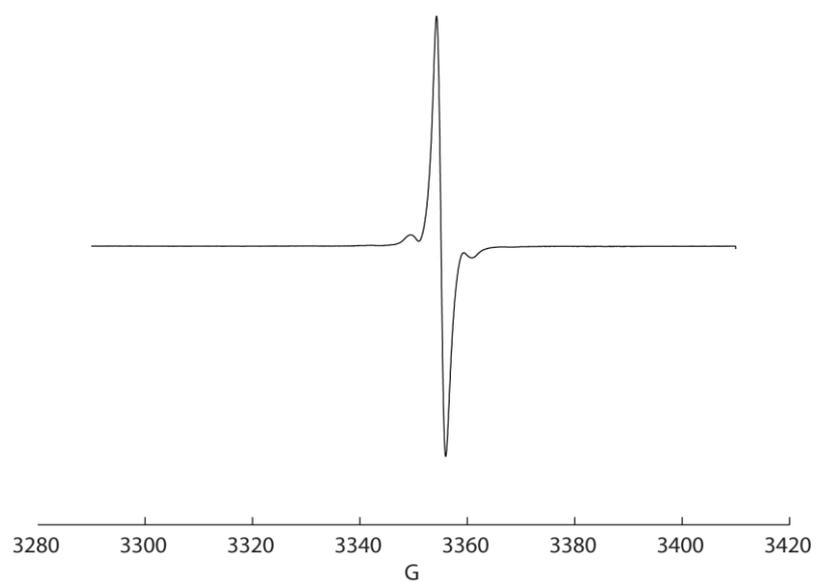
MALDI-TOF: calcd. for $\text{C}_{102}\text{H}_{100}\text{O}_{12}\text{S}_{24}$ [M+Na] 2307.040, found 2307.697

Preparative HPLC run (Flow rate = 7 mL/min). Solvent A, 100% CH_3CN ; Solvent B, 100% EtOAc; 5 min linear gradient from 0% to 5% B, 5% B isocratic for 15 min. 1 min linear gradient from 5% to 0% B to initial conditions (100% A).

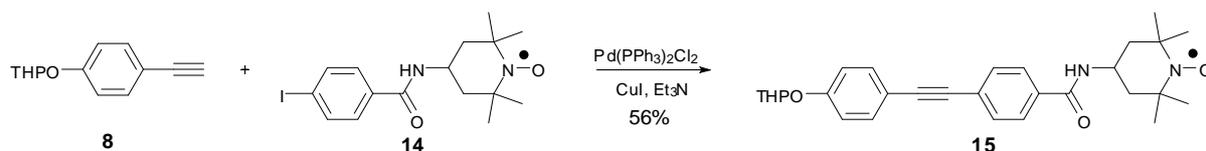
Analytical HPLC run (Flow rate = 1 mL/min). Solvent A, 100% CH_3CN ; Solvent B, 100% EtOAc; 5 min linear gradient from 0% to 15% B, 15% B isocratic for 15 min. 1 min linear gradient from 15% to 0% B to initial conditions (100% A).



HPLC Chromatogram of **2**



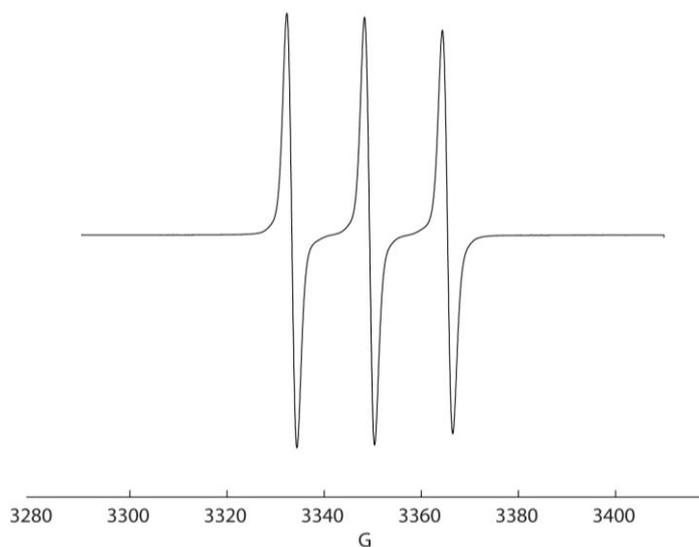
EPR spectrum of **2** (10% MeOH/CH₂Cl₂ at 22 °C).



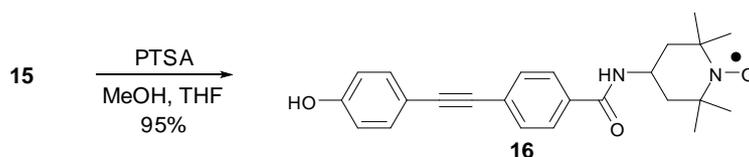
Compound 15. To a solution of compound **8** (0.202 g, 0.997 mmol), compound **14** (0.200 g, 0.498 mmol) and freshly distilled Et₃N (5 mL) in anhydrous THF (10 mL) were added Pd[PPh₃]₂Cl₂ (0.017 g, 5 mol %) and CuI (0.007 g, 8 mol %) and the reaction mixture was stirred at 25 °C for 12 h. The reaction mixture was diluted with water (20 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed successively with water (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na₂SO₄ and concentrated *in vacuo* to give the crude product, which was purified by column chromatography using silica gel (5:95 to 40:60, EtOAc:hexane) to yield **15** (0.133 g, 56%) as a red solid.

TLC (Silica gel, 30% EtOAc/hexane): R_f (**8**) = 0.50, R_f (**14**) = 0.40, R_f (**15**) = 0.30.

MS (ESI) calcd. for C₃₀H₃₇N₂O₃ [M+Na] 496.2702, found.



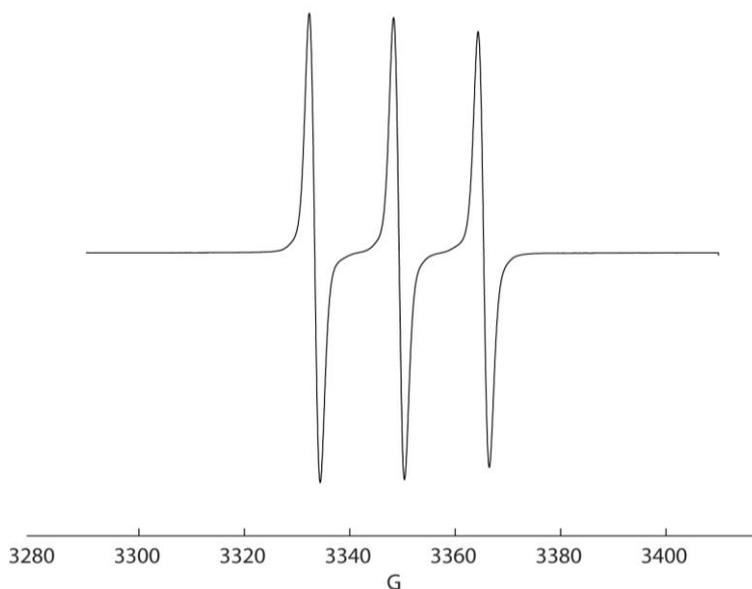
EPR spectrum of **15** (10% MeOH/CH₂Cl₂ at 22 °C).



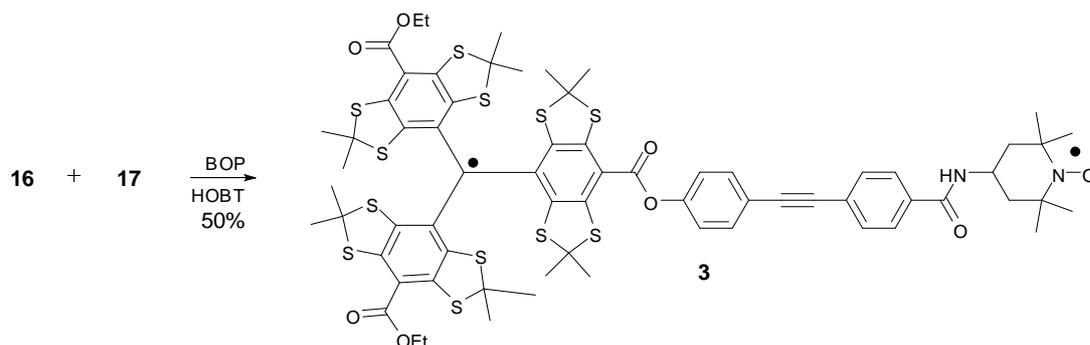
Compound 16. 4-toluenesulfonic acid (0.020 g, 0.105 mmol) was added to a solution of compound **15** (0.100 g, 0.210 mmol) in anhydrous THF and methanol (1:1, 10 mL). After stirring the reaction mixture at 25 °C for 12 h, it was diluted with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed successively with water (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na₂SO₄ and concentrated *in vacuo* to give the crude product, which was purified by column chromatography using neutral silica gel (2:98, EtOAc:hexane) to yield **16** (0.078 g, 95%) as a red solid.

TLC (Silica gel, 30% EtOAc/hexane): R_f (**15**) = 0.3, R_f (**16**) = 0.20.

MS (ESI) calcd. for C₂₄H₂₇N₂O₃ [M+Na] 414.1919, found 414.1914.



EPR spectrum of **16** (10 % MeOH/CH₂Cl₂ at 22 °C).



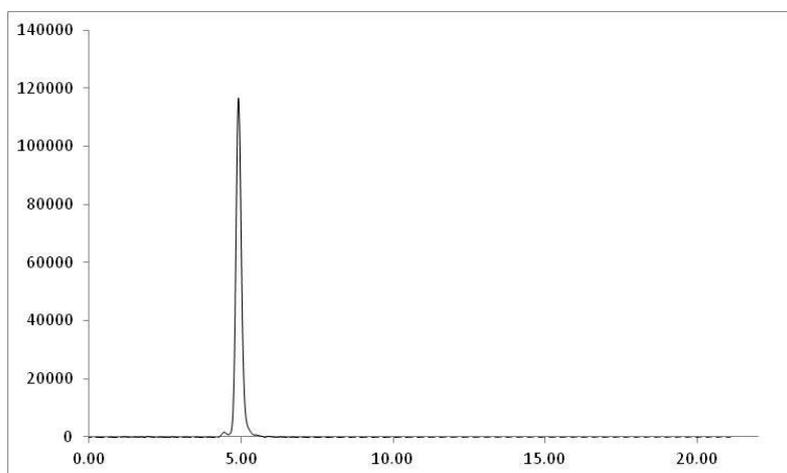
Compound 3. To a solution of trityl radical **17** (0.081 g, 0.077 mmol) and compound **16** (0.030 g, 0.077 mmol) in dry DMF (5 mL) was added BOP (0.068 g, 0.153 mmol) and HOBT (0.021 g, 0.153 mmol) followed by addition of Et₃N (0.5 mL). The reaction mixture was stirred at 25 °C for 12 h and concentrated to remove DMF. The crude product was purified by column chromatography using silica gel (5:95 to 40:60, EtOAc:hexane) to give **3** as a green solid (0.055 g, 50 %).

TLC (Silica gel, 40% EtOAc/hexane): Rf (**16**) = 0.30, Rf (**17**) = 0.1, Rf (**3**) = 0.50.

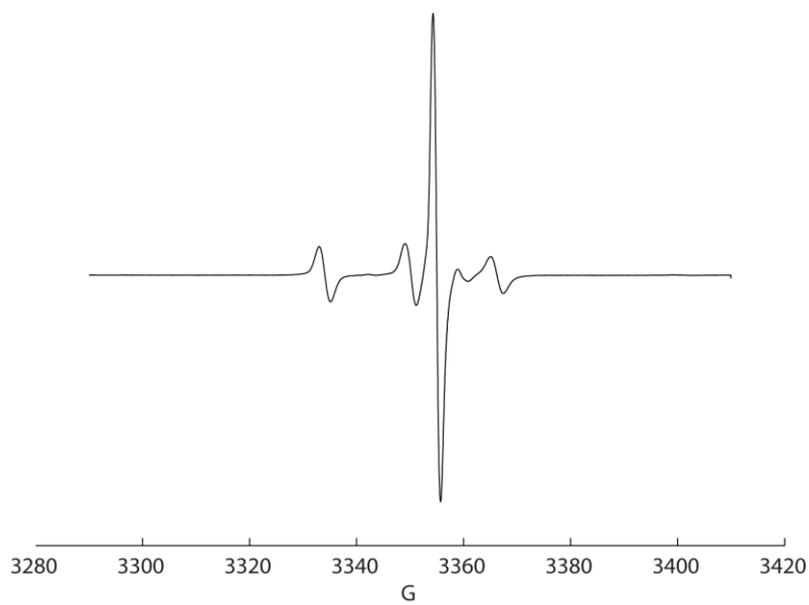
MALDI-TOF: calcd. for C₆₈H₇₂O₈S₁₂⁻ [M+]⁻ 1428.1937, found 1428.093

Preparative HPLC run (Flow rate = 7 mL/min). Solvent A, 100% CH₃CN; Solvent B, 100% CH₃CN. Run time = 21min.

Analytical HPLC run (Flow rate = 1 mL/min). Solvent A, 100% CH₃CN; Solvent B, 100% CH₃CN. Run time = 21min.



HPLC chromatogram of **3**.



EPR spectrum of **3** (10 % MeOH/CH₂Cl₂ at 22 °C).

Simulation of CW-EPR spectra

Simulation of CW-EPR spectrum for **1** was done using the EasySpin² toolbox with the following spin system definition:

```
Sys.S = [1/2 1/2];
```

```
gtensor = [2.0029 2.0030 2.0032];
```

```
Sys.g = [gtensor;gtensor];
```

```
Sys.ee = 0 + [1 1 -2]*9.5;
```

The CW-EPR simulation for **2** was done using the same spin system definition as above, except the dipole-dipole coupling constant was set to 3 MHz.

The CW-EPR spectrum of **3** was simulated both as a two-component spectrum (a combination of a trityl and a nitroxide spectra) and a two-spin system. For the two-component spectrum simulation the spin system was defined by the following:

```
SysTrityl.weight = 0.5;
```

```
SysTrityl.S = 1/2;
```

```
SysTrityl.g = [2.0029 2.0030 2.0031];
```

```
SysNitroxide.weight=0.5;
```

```
SysNitroxide.S = 1/2;
```

```
SysNitroxide.g = [2.0092 2.0059 2.0018];
```

For the two-spin system simulation the spin system was defined by the following:

```
Sys.S = [1/2 1/2];
```

```
Sys.Nucs = 'C,C,C,14N';
```

```
Sys.g = [2.0029 2.0030 2.0032;2.0093 2.0059 2.0018];
```

```
Sys.ee = 0+[1 1 -2]*4;
```

Table S1. Simulation parameters for **1-3** at 120 K.

| Parameters | 1-2 | 3 | |
|---|---------------------------|---------------------------|---------------------------|
| | | Nitroxide | Trityl |
| g_{xx}, g_{yy}, g_{zz} | 2.0029, 2.0030, 2.0032 | 2.0093, 2.0059, 2.0018 | 2.0029, 2.0030, 2.0032 |
| A_{xx}, A_{yy}, A_{zz} ^[a] | | | |
| ¹⁴ N Nitroxide nitrogen | - | 18, 18, 93 | - |
| ¹³ C Central carbon | 20.6, 20.6, 160.1 | - | 20.6, 20.6, 160.1 |
| ¹³ C 1-Phenyl carbon | 30, 30, 34 | - | 30, 30, 34 |
| ¹³ C 2,6-Phenyl carbon | 19, 19, 36.7 | - | 19, 19, 36.7 |
| Linewidth ^[b] | 1 | 0.08, 0.03 | 0.35, 0.02 |
| | 2 | 0.1, 0.03 | |
| Dipole-dipole coupling ^[c] | 1 | 9.5 | - |
| | 2 | 3 | |
| Weight | - | 0.5 | 0.5 |

[a] The hyperfine coupling values are in MHz. Only carbon atoms with the largest hyperfine couplings were included in the simulation for the trityl. [b] The linewidths (Gaussian, Lorentzian) is the peak to peak linewidth in mT. [c] The dipole-dipole coupling value is given in MHz and corresponds to the perpendicular component ($\theta = 90^\circ$).

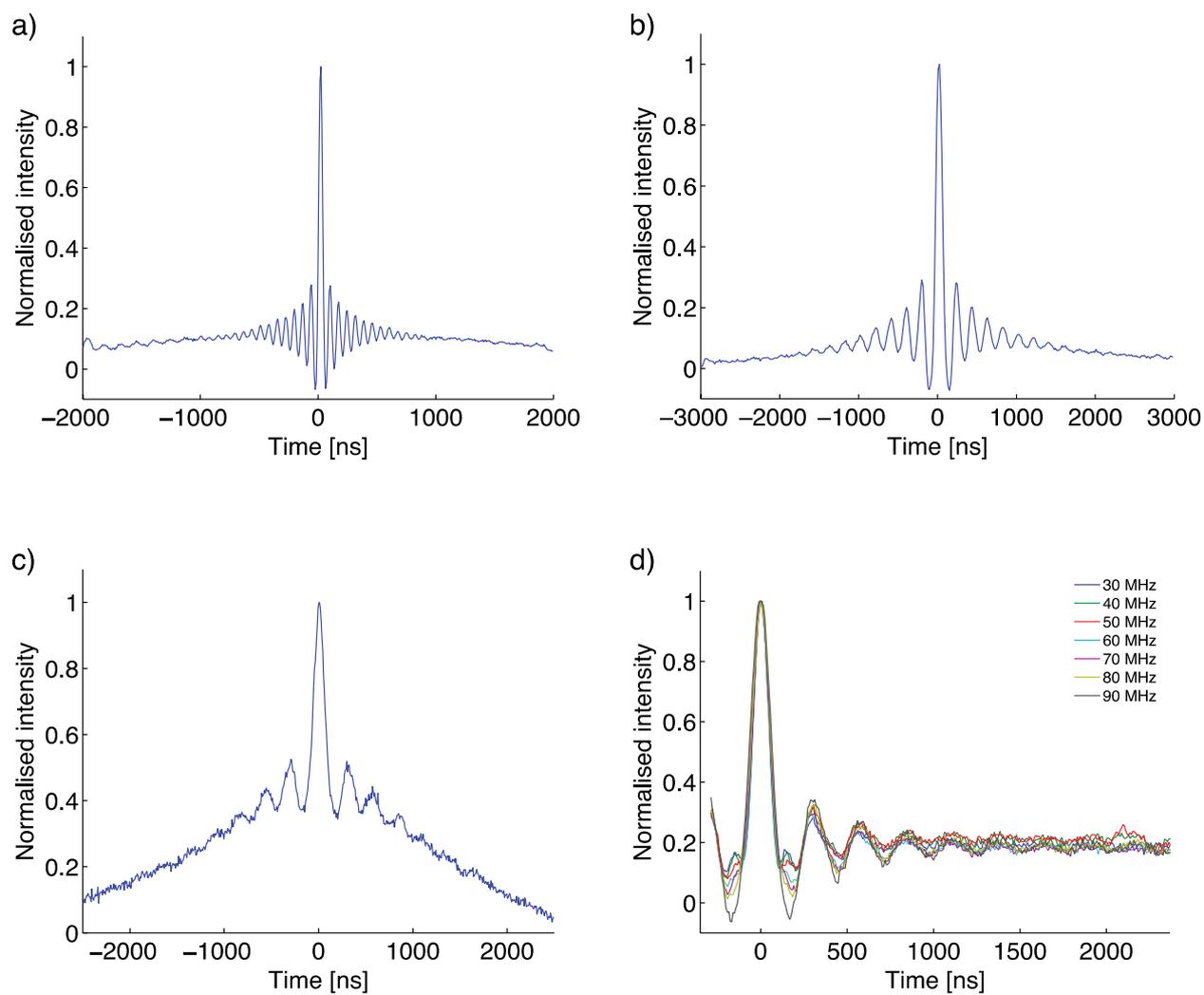


Figure S1. Original DQC and PELDOR time traces. a) Original DQC time trace for **1**. b) Original DQC time trace for **2**. c) Original DQC time trace for **3**. d) Original PELDOR time traces for **3**.

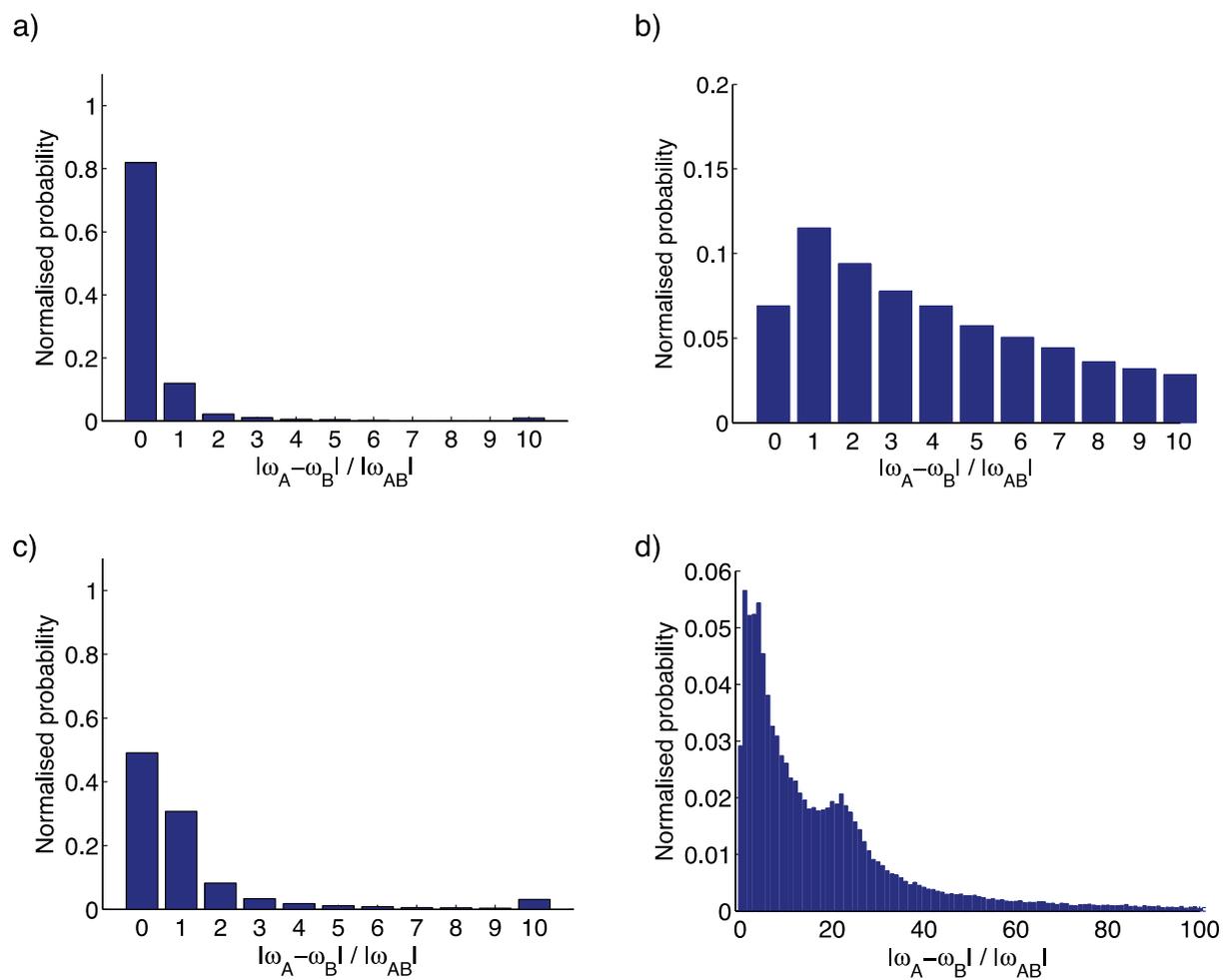


Figure S2. Histograms of the ratio $|\omega_A - \omega_B|$ to $|\omega_{AB}|$. a) Ratio histogram for **1**. b) Ratio histogram for compound **4**. c) Ratio histogram for **2**. d) Ratio histogram for **3**.

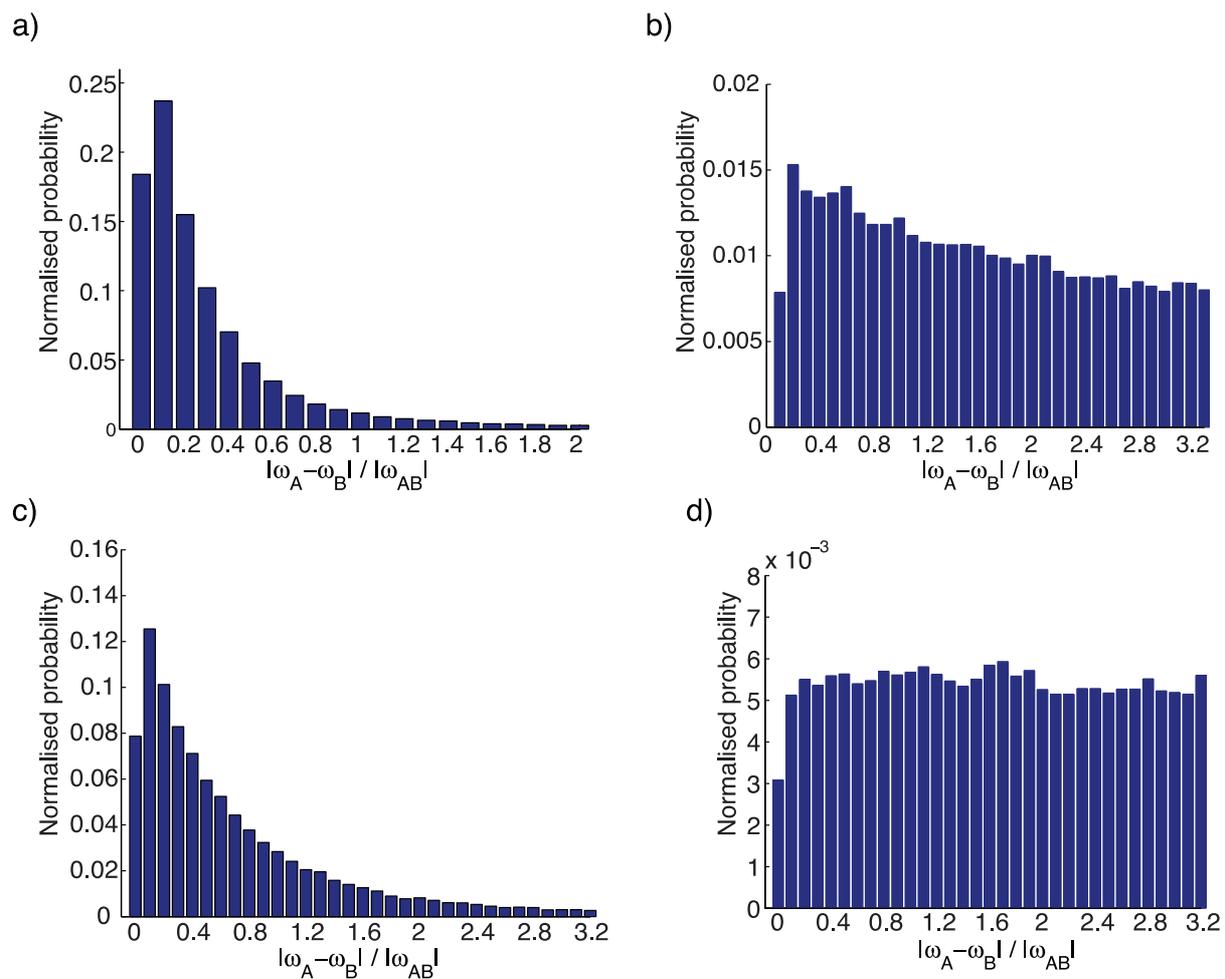
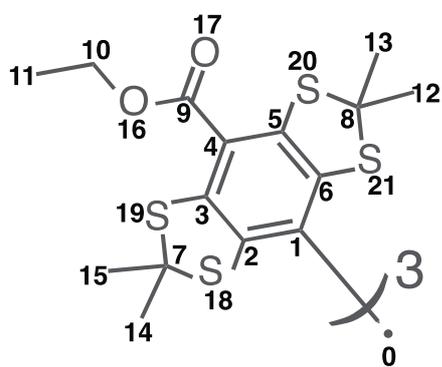


Figure S3. Histograms of the ratio $|\omega_A - \omega_B|$ to $|\omega_{AB}|$. a) Ratio histogram for **1**. b) Ratio histogram for compound **4**. c) Ratio histogram for **2**. d) Ratio histogram for **3**. The width of the bars in these histograms are smaller than in Figure S2, to better show the distribution of spin pairs in the high- and intermediate-coupling regimes.

Table S2. Average spin densities of carbon, oxygen and sulphur atoms in the trityl moiety of compounds **1-3**.

| Structure ^[a] | Position | Average spin density |
|--------------------------|----------|----------------------|
| | 0 | 0.695 |
| | 1 | -0.116 |
| | 2 | 0.102 |
| | 3 | -0.043 |
| | 4 | 0.088 |
| | 5 | -0.043 |
| | 6 | 0.098 |
| | 7 | -0.001 |
| | 8 | -0.001 |
| | 9 | -0.005 |
| | 10 | 0 |
| | 11 | 0 |
| | 12 | 0 |
| | 13 | 0 |
| | 14 | 0 |
| | 15 | 0 |
| | 16 | 0.002 |
| | 17 | 0.013 |
| | 18 | 0.008 |
| | 19 | -0.003 |
| | 20 | -0.003 |
| | 21 | 0.011 |



[a] Structure of the trityl moiety used for DFT calculations. The numbering of the atoms refers to the position of the spin-bearing atoms.

References

1. G. W. Reginsson, N. C. Kunjir, S. T. Sigurdsson, and O. Schiemann, *Chemistry - A European Journal*, 2012, **18**, 13580–13584.
2. S. Stoll and A. Schweiger, *J. Magn. Reson.*, 2006, **178**, 42–55.