Three-spin correlations in double electron electron resonance

Gunnar Jeschke,\textsuperscript{a} Muhammad Sajid\textsuperscript{b}, Miriam Schulte\textsuperscript{b} and Adelheid Godt\textsuperscript{b}

\textsuperscript{a} ETH Zürich, Lab. Phys. Chem., CH-8093 Zürich, Switzerland.
E-mail: gunnar.jeschke@phys.chem.ethz.ch

\textsuperscript{b} Bielefeld University, Department of Chemistry, Universitätsstr. 25, D-33615 Bielefeld, Germany.
E-mail: godt@uni-bielefeld.de

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Supporting Information

1 Synthesis of bi- and triradicals

General information

All reactions were performed under argon. In case of alkynyl-aryl cross-coupling reactions, the solutions containing both coupling components, the solvent and the amine were degassed through several freeze-pump-thaw-cycles prior to addition of the catalysts. THF was distilled from sodium/benzophenone. Piperidine was distilled from CaH\textsubscript{2}. Diethylamine and triethyamine were used as received. 1-Oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid was purchased from Acros. Triiodobenzene 1\textsuperscript{[1]} and the alkynes 7\textsuperscript{[1, 2]} were prepared as described in the literature.

For flash chromatography, Merck silica gel (40-63 \textmu m) and Acros silica gel (35-70 \textmu m) was used. For the preparation of the chromatotron plates (centrifugal preparative thin layer chromatography) Merck silica gel 60 PF\textsubscript{254} was used. Thin layer chromatography (TLC) was carried out on silica gel coated aluminum foils (Merck, 60 F\textsubscript{254}). Ratios of solvents in mixtures are given as volume to volume.

The melting points were determined in open capillaries. Elemental analyses were made at the analytical laboratory of Bielefeld University or at an external analytical laboratory. MALDI
TOF mass spectra were recorded with a Voyager DE Instrument mounted with a 1.2 m flight tube. Ionisation was achieved using an LSI nitrogen laser (337 nm beam wavelength, 3 ns pulse width, 3 Hz repetition rate). The ions were accelerated with 15 to 20 kV. 1,8,9-trihydroxyanthracene was used as the matrix and THF or CHCl₃ as the solvent to prepare the samples.

Unless specified otherwise, NMR spectra were recorded at 27-30 °C on a Bruker 250 or a Bruker 500 instrument. The solvent was used as an internal standard. The coupling constants are given in Hz. For ¹³C NMR signal assignment the carbon multiplicity (quaternary carbon (C), tertiary carbon (CH), secondary carbon (CH₂), primary carbon (CH₃)) was determined by a DEPT-135 experiment. The detailed assignment is based on reported shift increments[3] and on our own data obtained from related compounds.[1, 2, 4, 5]

![Figure S 1: A fictive molecule to define the labeling of the benzene moieties with α–ε.](image)

**Diiodo compound 2**

Pd(PPh₃)₂Cl₂ (4 mg, 0.006 mmol) and CuI (3 mg, 0.02 mmol) were added to a degassed solution of alkyne 7₀ (81 mg, 0.40 mmol) and triiodobenzene 1 (609 mg, 1.34 mmol) in diethylamine (10 mL). After stirring the reaction mixture at room temperature for 16 h, Et₂NH was distilled.
off at room temperature and slightly reduced pressure. The residue was dissolved in Et₂O, THF and water, the aqueous phase was extracted with a mixture of Et₂O and THF, and the combined organic extracts were washed with saturated aqueous NH₄Cl, dried over Na₂SO₄, and concentrated at reduced pressure giving a colorless solid. This crude product was adsorbed onto a small quantity of silica gel through dissolving it in CH₂Cl₂, adding silica gel to this solution, and removing the solvent (40 °C, reduced pressure). The resulting freely flowing powder was applied to a silica gel column by pouring it into a small amount of solvent overlaying the silica gel column. Column chromatography (n-pentane/CH₂Cl₂ 12:1) yielded triiodobenzene 1 (347 mg, 57%; Rₜ = 0.72) as a colorless solid and diiodo compound 2 (121 mg, 57%; Rₜ = 0.52) as a colorless solid (mp 122 °C; Found C, 43.15; H, 3.06. Calc. for C₁₉H₁₆O₂I₂ (530.145): C, 43.04; H, 3.04%) containing a trace (about 1 % as judged from ¹H NMR spectrum) of disubstitution product 3. Analytical data of diiodo compound 2: δH(250 MHz; CDCl₃) 7.97 (1 H, t, J 1.5, Hα ortho to both I), 7.80 (2 H, d, J 1.5, Hα ortho to one I and to C≡C), 7.41 and 7.02 (2 H each, AA'XX' spinsystem, Hβ meta to OTHP and Hβ ortho to OTHP, respectively), 5.44 (1 H, t-shaped, J 3, O₂CH), 3.87 and 3.61 (1 H each, 2 m, OCH₂), 2.1-1.5 (6 H, m, CH₂); δC(62.8 MHz; CD₂Cl₂) 158.2 (C, Cβ O), 144.9 and 139.6 (CH, Cα H), 133.5 (CH, Cβ H meta to OTHP), 127.6 (C, Cα C≡C), 117.0 (CH, Cβ H ortho to OTHP), 115.4 (C, Cα C≡C), 96.8 (CH, O₂CH), 94.3 and 92.4 (C, C≡C), 85.2 (C, CαI), 62.5 (CH₂, OCH₂), 30.6, 25.5, and 19.1 (CH₂, CH₂ of THP).

Protected triol 5a
To a degassed solution of alkyne 7₁ (136 mg, 0.29 mmol) and diiodo compound 2 (60 mg, 0.11 mmol) in diethylamine (5 mL), Pd(PPh₃)₂Cl₂ (3 mg, 0.004 mmol) and CuI (2 mg, 0.01 mmol) were added. The reaction mixture was stirred at room temperature for 15 h. Then Et₂NH was distilled off at slightly reduced pressure/room temperature, the residue was dissolved in Et₂O and water, the aqueous phase was extracted with Et₂O, the combined organic extracts were washed with saturated aqueous NH₄Cl, dried over Na₂SO₄, and concentrated under reduced pressure giving a yellow oil. This was diluted with a very small amount of CH₂Cl₂ and applied as such to a chromatotron plate. Chromatography (n-pentane/CH₂Cl₂ 5:1 → 1:1) yielded 5a (126 mg, 92%; Rₜ(n-pentane/CH₂Cl₂ 1:1) = 0.08) as a yellowish fluorescent oil (Found C, 83.97; H, 8.26. Calc. for C₈₅H₉₈O₆ (1215.713): C 83.98, H 8.13%). Ahead of this product, diiodo compound 2 in mixture of an unidentified compound (27 mg, Rₜ(n-pentane/CH₂Cl₂ 1:1) = 0.35 and 0.29), oxidative dimer (Glaser coupling product) of the alkyne 7₁ (10 mg, 7%; Rₜ(n-pentane/CH₂Cl₂ 1:1) = 0.26), and the monocoupling product 3 (2 mg, 1%; Rₜ(n-pentane/CH₂Cl₂ 1:1) = 0.17) were eluted. Analytical data of protected triol 5a: δH(250 MHz; CDCl₃) 7.60-7.57 (3 H, m, Hα), 7.46 (2 H, half of AA’XX’ spinsystem, Hβ meta to OTHP; short arm), 7.44 (4 H, 2 halves of 2 AA’XX’ spinnets, Hβ meta to OTHP; long arms), 7.34 (4 H, slightly broadened s, Hγ), 7.03 (6 H, 3 halves of 3 AA’XX’ spinnets, Hβ ortho to OTHP; short and long arms), 5.45 (3 H, t-shaped, J 3, O₂CH), 3.89 and 3.62 (3 H each, 2 m,
OCH$_2$), 2.78 (8 H, m, ArCH$_2$), 2.1-1.2 (50 H, m, CH$_2$), 0.885 and 0.875 (6 H each, t, J 6.9, CH$_3$); $\delta_{C}$ (62.8 MHz; CD$_2$Cl$_2$) 158.1 and 157.8 (C, C$_{\beta}$O), 143.0 and 142.6 (C, C$_{\gamma}$Hex), 134.0 - 132.5[6] (CH, C$_{\alpha}$H, C$_{\beta}$H meta to OTHP, C$_{\gamma}$H), 124.9 and 124.7 (C, C$_{\alpha}$C≡C), 123.8 and 122.1 (C, C$_{\gamma}$C≡C), 117.0 (CH, C$_{\beta}$H ortho to OTHP), 116.7 and 115.9 (C, C$_{\beta}$C≡C), 96.9 (CH, O$_2$CH), 94.6, 92.5, 91.1, 90.0, 87.4, and 86.9 (C, C≡C), 62.5 (CH$_2$, OCH$_2$), 34.5, 32.20, 32.17, 31.12, 31.0, 30.7, 29.6, 25.6, 23.1, 23.0, and 19.2 (CH$_2$, CH$_2$ of THP and Hex), 14.32 and 14.26 (CH$_3$).

Triol 5b
To a solution of protected triol 5a (110 mg, 0.09 mmol) in THF (10 mL) and methanol (7 mL) toluenesulphonic acid monohydrate (47 mg, 0.25 mmol) was added. The reaction mixture was stirred at room temperature for 5 h (TLC monitoring; n-pentane/Et$_2$O 1:3). Then Et$_2$O and water were added, the phases were separated, the aqueous phase was extracted with Et$_2$O, and the combined organic extracts were washed with saturated aqueous K$_2$CO$_3$, then 2 N HCl, and finally brine. After drying over MgSO$_4$, the solvents were removed under reduced pressure and the residue was freeze-dried from benzene giving triol 5b (86 mg, 99%) as a slightly yellow solid (mp 138°C). The elemental analysis of this material deviated largely from the expected values. The $^1$H NMR spectrum showed an intense peak for silicon grease which may account for the elemental analysis result. However other experiments in which THP was removed from similar compounds indicate that in general the material obtained in the way that is described above is impure. A satisfying elemental analysis (Found C, 87.08; H, 87.86. Calc. for C$_{70}$H$_{74}$O$_3$ (963.359): C 87.27, H 7.74%) was obtained from material which had been chromatographed (n-pentane/Et$_2$O 1:1). The crude triol 5b was used as obtained for the next synthetic step, i.e. the preparation of triradical T011. $\delta_{H}$ (250 MHz; CDCl$_3$) 7.60-7.57 (3 H, m, H$_{\alpha}$), 7.43 (2 H, half of AA’XX’ spinsystem, H$_{\beta}$ meta to OH, short arm), 7.42 (4 H, 2 halves of 2 AA’XX’ spinsystems, H$_{\beta}$ meta to OH, long arms), 7.35 and 7.34 (2 H each, 2 s, H$_{\gamma}$), 6.82 (6 H, 3 halves of 3 AA’XX’ spinsystems, H$_{\beta}$ ortho to OH; short and long arms), 4.92 (1 H, s, OH of short arm), 4.89 (2 H, s, OH of long arms), 2.79 (8 H, m, ArCH$_2$), 1.69 (8 H, m, CH$_2$), 1.34 (24 H, m, CH$_2$), 0.885 and 0.875 (6 H each, 2 t, J 6.9, CH$_3$); $\delta_{C}$ (62.8 MHz; CD$_2$Cl$_2$) 156.7 and 156.4 (C, C$_{\beta}$O), 143.0 and 142.6 (C, C$_{\gamma}$Hex), 133.8, 133.7, and 133.5 (CH, C$_{\alpha}$H, C$_{\beta}$H meta to OH), 132.8 and 132.5 (CH, C$_{\gamma}$H) 124.9 and 124.7 (C, C$_{\alpha}$C≡C), 123.8 and 122.1 (C, C$_{\gamma}$C≡C), 116.1 (C, C$_{\beta}$C≡C), 116.02 and 115.99 (CH, C$_{\beta}$H ortho to OH), 115.4 (C, C$_{\beta}$C≡C), 94.5, 92.5, 90.9, 90.0, 87.3, and 86.8 (C, C≡C), 34.5, 32.20, 32.17, 31.12, 31.0, 29.6, 23.1, and 23.0 (CH$_2$), 14.33 and 14.26 (CH$_3$); m/z (MALDI-TOF) 964.1 (100%, M$^+$. C$_{70}$H$_{74}$O$_3$ requires 963.4).

Triradical T011
N,N’-Dicyclohexylcarbodiimide (45.0 mg, 0.22 mmol) was added to a solution of triol 5b (35 mg, 0.036 mmol), 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid (40.5 mg, 0.220 mmol), and DMAP (26.8 mg, 0.22 mmol) in THF (5 mL). After stirring of the reaction mixture at room temperature for 3 days, the precipitate was filtered off and washed with THF until the
solid was colorless. The solvent of the filtrate, which contained the triradical, was removed. In order to get rid of trapped THF, the crude product was dissolved in CH₂Cl₂ and the solvent was removed. The crude product was suspended in a small amount of CH₂Cl₂ (the colorless insoluble material is most probably the urea compound) and applied to a chromatotron plate. Elution with CH₂Cl₂ \((R_f = 0.12)\) gave triradical **T011** (25 mg, 47%) as a yellow oil which solidified upon freeze-drying from benzene \(\text{mp} 54-56 ^\circ \text{C}\); Found C, 78.95; H, 7.58; N, 3.09. Calc. for C₉₇H₁₁₀O₉N₃ (1461.959): C, 79.69; H, 7.58; N, 2.87%.

**Monoiodo compound 3**

Starting from alkyne 7₁ (114 mg, 0.24 mmol), diiodo compound 2 (256 mg, 0.48 mmol), Pd(PPh₃)₂Cl₂ (3 mg, 0.004 mmol) and CuI (2 mg, 0.01 mmol) in diethylamine (10 mL) and working as described for the synthesis of protected triol 5a, with the difference that the crude product was dissolved in \(n\)-pentane/Et₂O 12:1 for being applied onto the chromatotron plate and the compounds were eluted with \(n\)-pentane/Et₂O 12:1, monoiodo compound 3 (92 mg, 44%; \(R_f = 0.14\)) was obtained as a yellow solid \(\text{mp} 49-50 ^\circ \text{C}\); Found C, 71.30; H, 6.61. Calc. for C₅₂H₅₇O₄I (872.929): C, 71.55; H, 6.58%.

Analytical data of monoiodo compound 3: \(\delta_H (250 \text{ MHz}; \text{CDCl}_3)\) 7.80 and 7.78 (1 H each, 2 dd, \(J = 1.5 \text{ and } 1.5\), Hα ortho to I), 7.59 (1 H, t, \(J = 1.5\), Hα para to I), 7.44 (4 H, 2 halves of 2 AA’XX’ spinsystems, Hβ meta to OTHP), 7.33 and 7.32 (1 H each, 2 s, Hγ), 7.03 (4 H, 2 halves of 2 AA’XX’ spinsystems, Hβ ortho to OTHP), 5.44 (2 H, t-shaped, \(J = 3\), O₂CH), 3.89 and 3.61 (2 H each, 2 m, OCH₂), 2.77 (4 H, m, ArCH₂), 2.1-1.5 (16 H, m, CH₂ of THP and Hex), 1.34 (12 H, m, CH₂ of Hex), 0.89 and 0.87 (3 H each, 2 t, \(J = 6.9\), CH₃); \(\delta_C (62.8 \text{ MHz}; \text{CDCl}_3)\) 158.2 and 157.8 (C, C’βO), 143.0 and 142.6 (C, C’αHex), 139.9 and 139.6 (CH, C’αH), 133.6 - 132.5 (6) (CH, C’βH meta to OTHP, CαH, C’γH), 126.1 and 125.9 (C, C’αC≡C), 123.9 and 121.8 (C, C’γC≡C), 117.0 (CH, C’βH ortho to OTHP), 116.6 and 115.7 (C, C’βC≡C), 96.9 (CH, O₂CH), 94.7, 93.6, 91.8, 91.7, 90.7, and 87.4 (C, C≡C), 86.1 (C, C’-I), 62.5 (CH₂, OCH₂), 34.5, 32.19, 32.18, 31.12, 31.0, 30.7, 29.6, 25.6, 23.1, 23.0, and 19.2 (CH₂, CH₂ of THP and Hex), 14.35 and 14.27 (CH₃).
Protected triol 4a

Pd(PPh₃)₂Cl₂ (9 mg, 0.01 mmol) and CuI (5 mg, 0.03 mmol)[12] were added to a degassed solution of monoiodo compound 3 (115 mg, 0.13 mmol) and alkyne 7₂ (107 mg, 0.14 mmol) in piperidine (3 mL) and THF (10 mL). The reaction mixture was stirred at room temperature for 23 h. Et₂O and water were added, the aqueous phase was extracted with Et₂O, the combined organic extracts were washed with saturated aqueous NH₄Cl, dried over Na₂SO₄, and the solvents were removed under reduced pressure. The dirty-yellow colored solid residue was dissolved in a minimum amount of CH₂Cl₂ and applied to a chromatotron plate. Chromatography (n-pentane/CH₂Cl₂ 2:1 → 1:1) furnished protected triol 4a (95 mg, 48%; R_f (n-pentane/CH₂Cl₂ 1:1) = 0.32) as a yellow oil. Ahead of 4a, the oxidative dimer (Glaser coupling product) of alkyne 7₂ (37 mg, 34%; R_f = 0.58) was eluted. Analytical data of protected triol 4a:

δ_H (250 MHz; CDCl₃) 7.61-7.58 (3 H, m, H_α), 7.46 (2 H, half of AA’XX’ spin system, H_β meta to OTHP; short arm), 7.45 (4 H, 2 halves of 2 AA’XX’ spin systems, H_β meta to OTHP; medium and long arm), 7.37 and 7.36 (1 H each, 2 s, H_γ), 7.35 and 7.34 (al llover 4 H, 2 s, H_γ), 7.03 (6 H, 3 halves of 3 AA’XX’ spin systems, H_β ortho to OTHP), 5.45 (3 H, t-shaped, J_3, O_2 CH), 3.89 and 3.62 (3 H each, 2 m, OCH₂), 2.80 (12 H, m, ArCH₂), 2.1-1.5 (30 H, m, CH₂), 1.34 (36 H, m, CH₂), 0.88 (18 H, m, CH₃).

δ_C (62.8 MHz; CD₂Cl₂) 158.1, 157.80 and 157.78 (C, C_β O), 143.00, 142.96, 142.61, 142.57, 142.50, and 142.46 (C, C_γ Hex), 134.0-132.5 [6] (CH, C_β H meta to OTHP, C_α H, C_γ H), 125.0, 124.8, 124.7 (C, C_α C≡C), 123.8, 123.7, 123.4, 122.8, 122.4, and 122.1 (C, C_β C≡C), 117.0 (CH, C_β H ortho to OTHP), 116.70, 116.65, and 115.9 (C, C_β C≡C), 96.9 (CH, O_2 CH), 94.6, 94.5, 93.7, 93.1, 92.7, 92.5, 91.1, 90.05, 89.98, 87.5, 87.4, and 86.9 (C, C≡C), 62.5 (CH₂, OCH₂), 34.5, 32.25, 32.21, 32.18, 31.13, 31.02, 30.7, 29.7, 29.6, 25.6, 23.1, and 19.2 (CH₂), 14.33 and 14.27 (CH₃); m/z (MALDI-TOF) 1488.1 (35%, M⁺), 1404.1 (45, [M - dihydropyrrane]⁺), 1319.1 (30, [M - 2 dihydropyranes]⁺), 1234.4 (100, [M - 3 dihydropyranes]⁺).

Triol 4b

Crude triol 4b was obtained starting from protected triol 4a (90 mg, 0.06 mmol) and toluenesulphonic acid monohydrate (36 mg, 0.19 mmol) in THF (10 mL) and methanol (7 mL), following the same procedure as described for the synthesis of triol 5b, but omitting the freeze drying. Through twofold chromatography on a chromatotron plate (n-pentane/Et₂O 1:1) triol 4b (55 mg, 74%; R_f = 0.10) was obtained as a yellow colored solid (mp 69-70 °C; Found C, 87.59; H, 8.47. Calc. for C₉₀H₁₀₃O₃ (1231.803): C, 87.76; H, 8.35%); δ_H (250 MHz; CDCl₃) 7.60-7.58 (3 H, m, H_α), 7.43 (2 H, half of AA’XX’ spin system, H_β meta to OH; short arm), 7.42 (4 H, 2 halves of 2 AA’XX’ spin systems, H_β meta to OH; medium and long arm), 7.37 and 7.36 (1 H each, 2 s, H_γ), 6.83 and 6.82 (al llover 6 H, 3 halves of 3 AA’XX’ spin systems, H_β ortho to OH), 4.98, 4.95, 4.94 (1 H each, 3 s, OH), 2.81 (12 H, m, ArCH₂), 1.70 (12 H, m, CH₂), 1.34 (36 H, m, CH₂), 0.88 (18 H, m, CH₃); δ_C (125.6 MHz; CD₂Cl₂) 156.7, 156.41 and 156.38 (C, C_β O), 142.96, 142.92, 142.54, 142.50, 142.46, and 142.42
(C, C\textsubscript{\textgamma}Hex), 133.9, 133.8, 133.7, 133.48, and 133.47 (CH, C\textbeta H meta to OH, C\textalpha H), 132.84, 132.78, 132.5, and 132.4 (CH, C\textgamma H), 124.9, 124.7, and 124.6 (C, C\textalpha C=C), 123.7, 123.6, 123.3, 122.7, 122.3, and 122.0 (C, C\textgamma C=C), 116.00 (CH, C\textbeta H meta to OH), 115.96, and 115.92 (CH, C\textbeta H ortho to OH), 115.2 (C, C\textbeta C=C), 94.4, 94.3, 93.6, 93.1, 92.7, 92.5, 90.9, 89.97, 89.92, 87.3, 87.2, and 86.7 (C, C=C), 34.5, 32.21, 32.17, 32.14, 31.10, 31.06, 31.04, 30.99, 29.6, 23.07, 23.05, and 23.03 (CH\textsubscript{2}), 14.32 and 14.26 (CH\textsubscript{3}).

**Triradical T012**

The procedure reported for the synthesis of triradical T011 was followed. Starting from triol 4b (25 mg, 0.02 mmol), 1-oxyl-2,2,5,5-tetramethylpyrroline -3-carboxylic acid (22 mg, 0.12 mmol), DMAP (15 mg, 0.12 mmol), and N,N\textprime dicyclohexylcarbodiimide (25 mg, 0.12 mmol) in THF (5 mL), triradical T012 (22 mg, 63%; \textit{Rf} (CH\textsubscript{2}Cl\textsubscript{2}) = 0.14) was obtained as a yellow oil which solidified upon freeze-drying from benzene. (mp 63-64 \textdegree C; Found C, 80.61; H, 8.12; N, 2.47. Calc. for C\textsubscript{117}H\textsubscript{138}N\textsubscript{3}O\textsubscript{9} (1730.403): C, 81.21; H, 8.04; N, 2.43%). Ahead of the triradical T012 a yellow oil (7 mg) containing unidentified compounds was eluted [7]. Analytical data of triradical T012:

\[ \delta_H (500 MHz; CD_2Cl_2) \] All signals are broadened. 7.68 and 7.67 (allover 3 H, 2 s, H\textalpha), 7.62 (6 H, very broad, H\textgamma meta to OR), 7.43, 7.42, 7.41, and 7.40 (allover 6 H, 4 s, H\textgamma), 7.21 (extremely broad, 6 H, H\textbeta ortho to OR), 2.86 (12 H, m, ArCH\textsubscript{2}), 1.72 (12 H, m, ArCH\textsubscript{2}), 1.44 and 1.35 (alover about 36 H, 2 m, CH\textsubscript{2}), 0.90 (18 H, m, CH\textsubscript{3}); \[ m/z \text{ (MALDI-TOF)} 1732.1 (95%, M\textsuperscript{+}. C\textsubscript{117}H\textsubscript{138}N\textsubscript{3}O\textsubscript{9} requires 1730.4), 1716.6 (30), 1698.4 (20), 1669.3 (13), 1563.6 (55), 1549.2 (42), 1532.1 (35, 1519.5 (23), 1397.7 (50), 1382.2 (50), 1366.6 (17), 1230.6 (100).

**Triradical precursor 9**

Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (3.7 mg, 0.005 mmol) and CuI (2.0 mg, 0.010 mmol) were added to a degassed solution of 1,3,5-triiodobenzene (1) (20.0 mg, 0.044 mmol) and alkyne 8 (121.0 mg, 0.197 mmol) in THF (10 mL) and Et\textsubscript{3}N (5.0 mL). After two further freeze-pump thaw cycles the reaction mixture was stirred at room temperature for 5 days. The solvent was evaporated at 45 \textdegree C and reduced pressure. The brown residue was dissolved in chloroform (5.0 mL) and applied as such onto a silica gel column. Chromatography (CHCl\textsubscript{3}/MeOH 97:3) furnished triradical precursor 9 as a light-yellow colored solid (37 mg, 44%; \textit{Rf} = 0.35; mp 143 \textdegree C). Ahead of this product the oxidative dimer (Glaser coupling product) of the alkyne 9 was eluted (\textit{Rf} = 0.28). Analytical data of triradical precursor 9:

\[ \delta_H (500 MHz; CDCl_3) \] 7.70 (6 H, s, H\textepsilon), 7.65 (6 H, half of AA'XX' spinsystem, H\textdelta meta to N), 7.47 (6 H, half of AA'XX' spinsystem,ortho to N), 7.40 and 7.38 (3 H each, 2 s, H\textgamma), 2.83 and 2.82 (6 H each, 2 t, J=6.4, ArC\textsubscript{H}2), 1.78 (9 H, broad, NH and H\textsubscript{2}O), 1.72 and 1.71 (6 H each, 2 quint, J=8, ArCH\textsubscript{2}CH\textsubscript{2}), 1.53 (36 H, s, CH\textsubscript{3} of isoindoline), 1.42 (12 H, CH\textsubscript{2}), 1.35 (24 H, m, CH\textsubscript{2}), 0.892 and 0.888 (9 H each, 2 t, J=7, CH\textsubscript{3} of Hex); \[ \delta_C (62.8 MHz; CDCl_3) \] 166.9 (C, CO), 156.4 (C, C\textalpha), 142.45 and 142.43 (C, C\textgamma Hex), 133.7 (C\textalpha H), 132.5 and 132.4 (CH, C\textalpha H), 132.1 (CH, C\textgamma H meta to N), 131.6 (C, C\textalpha N), 131.5 (C, C\textepsilon), 126.2 (CH, C\textgamma H ortho to N), 124.3 (C, C\textalpha C=C), 123.1 (C, C\textgamma C=C), 122.7 and 122.2 (C, C\textgamma C=C), 117.6 (CH, C\textalpha H), 93.4, 92.3, 89.7, and 89.3 (C, C=C), 63.1 (C, Me\textsubscript{2}CN),
34.2 and 34.1 (CH₂), 31.8 (CH₃ of isoindoline), 30.7, 30.6, 29.3, 29.2, 22.7, and 22.6 (CH₂), 14.2 and 14.1 (CH₃); m/z (MALDI-TOF) 1909.8 (100%, M⁺. C₁₃₂H₁₄₄N₆O₆ requires 1910.6), 1893.8 (60%).

**Triradical T111_inv**

A solution of m-chloroperbenzoic acid (28 mg, 0.16 mmol) in CH₂Cl₂ (1.5 mL) was added to an ice bath cooled solution of triradical precursor 9 (29.0 mg, 0.015 mmol) in CH₂Cl₂ (3.0 mL). The reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated at 40°C and reduced pressure. Methanol (5.0 mL) was added to the yellow residue, the precipitate was isolated through filtration and washed with methanol (10 mL). Surprisingly, the material was only partially soluble in solvents such as THF, CHCl₃, CH₂Cl₂, Et₂O, and toluene, despite the fact that the reaction mixture had been a clear solution (CH₂Cl₂) before work-up. The isolated solid was suspended in CHCl₃. The suspension was stirred at room temperature for overnight, then stirred at 80°C for 1 h, cooled to room temperature and filtered. The filtrate was concentrated (to about 5 mL) at room temperature and reduced pressure. The residual solution was diluted with THF (2.0 mL). This solution was applied to a silica gel column. Chromatography (CH₂Cl₂/Et₂O 10:1) yielded triradical T111_inv (9.3 mg, 31%; mp 132°C; Rf = 0.54) as a yellow solid. δH (500 MHz; CDCl₃) All signals are broad and structureless. 8.0 (ca 4 H, extremely broad, Hε), 7.67 (6 H, very broad, Hδ ortho to N), 7.63 (3 H, s, Hα), 7.48 (6 H, very broad, Hδ meta to N), 7.41 and 7.39 (3 H each, 2 s, Hγ), 2.82 (12 H, ArC₂H₃), 1.72 (ca. 12 H, ArCH₂CH₂), 1.53 (ca. 27 H, s, CH₃ of isoindoline), 1.43 and 1.34 (ca. 36 H, CH₂), 1.25 (ca. 4 H, sharp s, probably water), 0.89 (18 H, m, CH₃ of Hex); m/z (MALDI-TOF) 1984.5 (50), 1968.8 (70), 1955.3 (100%, M⁺. C₁₃₂H₁₄₁N₆O₉ requires 1955.6), 1941.3 (90), 1924.1 (75); All signals are of very low absolute intensity.

**Compound 10a**

To a degassed solution of diiodo compound 2 (30.0 mg, 0.057 mmol) and alkyne 8 (99.3 mg, 0.162 mmol) in THF (6.0 mL) and Et₃N (3.0 mL) were added Pd(PPh₃)₂Cl₂ (3.2 mg, 0.005 mmol) and CuI (1.8 mg, 0.009 mmol). Two further freeze-pump-thaw cycles were pursued. The reaction mixture was stirred at room temperature for 5 days. The solvent was evaporated at 45°C and reduced pressure. The lightly yellow colored solid residue was dissolved in CHCl₃ (5.0 mL) and applied as such to a silica gel column. Elution (CHCl₃/EtOH 97:3) gave two fractions of a faintly yellow solid (64 mg, 19 mg; Rf = 0.32) containing the coupling product 10a and the oxidative dimer (Glaser coupling product) of the alkyne 8 in a ratio of 3:1 and 20:1 (1H NMR spectroscopically determined), respectively. Ahead of this fraction a mixture (6 mg; Rf = 0.38 and 0.32) of these two products and an unidentified compound was eluted. Analytical data of compound 10a: δH (500 MHz; CDCl₃) 7.70 (4 H, s, Hε), 7.64 (4 H, half of AA‘XX’ spin system, Hδ meta to N), 7.62 and 7.60 (2 H and 1 H, respectively, AB₂ spinsystem, J 1, Hα), 7.471 (4 H, half of AA‘XX’ spin system, Hδ ortho to N), 7.466 (2 H, half of AA‘XX’ spinsystem, Hβ meta to OTHP), 7.39 and 7.38 (2 H each, 2 s, Hγ), 7.04 (2H, half of AA‘XX’
spinsystem, Hβ ortho to OTHP), 5.46 (1 H, t-shaped, J 3, O2CH), 3.89 and 3.62 (1 H each, 2 m, CH2O) and 2.81 (8 H, m, ArCH2), 2.1 - 1.5 (17 H, m, CH2 of Hex and THP, NH), 1.52 (24 H, s, CH3 of isoindoline), 1.42 and 1.34 (24 H, CH2 of Hex), 0.899 and 0.886 (6 H each, 2 t, J 7, CH3 of Hex); m/z (MALDI-TOF of the 20:1 mixture) 1499.3 (80%, M+. C103H110N4O6 requires 1500.0), 1482.9 (40), 1414.5 (50, [M+ - THP]), 1399.2 (100), 1383.9 (55), 1370.1 (85).

Biradical B11inv
A solution of metachloroperbenzoic acid (25.3 mg, 0.147 mmol) in dichloromethane (1.5 mL) was added to an ice-bath cooled solution of the 3:1 mixture (27.2 mg) of compound 10a and the Glaser coupling product of the alkyne 8 dissolved in dichloromethane (2.0 mL). The reaction mixture was stirred at room temperature for 1.5 h. The solvent was evaporated at 40 °C and reduced pressure. Washing with methanol (8.0 mL) provided a yellowish solid (24 mg). This solid (23 mg) was dissolved in THF (2.0 mL) and CH3OH (1.0 mL) and p-toluenesulphonic acid monohydrate (5.6 mg, 0.03 mmol) was added. After stirring the reaction mixture at room temperature for 3 h, the solution was concentrated (to about 2 mL) at 38 °C and reduced pressure. The residual solution was diluted with CHCl3 (5 mL). This solution was applied to a silica gel column. Chromatography (CH2Cl2/Et2O 12:1) gave the oxidised Glaser coupling product of the alkyne 8 (RF(CH2Cl2/Et2O 10:1) = 0.73) and biradical B11inv as a yellowish solid (13 mg, 63% over two steps; RF(CH2Cl2/Et2O 10:1) = 0.34; mp 125 °C). Analytical data of biradical B11inv: δH(500 MHz; CDCl3) All signals are broad and structureless. 8.0-10 (extremely broad, Hε), 8.5-6.5 (extremely broad, Hβ ortho to OH), 7.69 (4 H, very broad, Hδ meta to N), 7.63 and 7.62 (3 H, 2 s, Hα), 7.49 (6 H, very broad, Hγ ortho to N and Hδ meta to OH), 7.42 and 7.40 (2 H each, 2 s, Hγ), 2.84 (8 H, ArCH2), 1.73 (8 H, ArCH2CH2), 1.44 and 1.36 (allover ca. 28 H, CH2, CH3 of isoindoline), 1.26 (2 H, sharp s, probably water), 0.92 and 0.91 (12 H, CH3 of Hex); m/z (MALDI-TOF) 1445.9 (55%, M+). C98H100N4O7 requires 1445.9, 1430.7 (75), 1415.8 (100), 1400.2 (75).
2 Supporting figures

Figure S 2: Total modulation depth $\Delta$ as a function of nominal inversion efficiency $\lambda_{\text{nominal}}$ for compounds T011 (A), T012 (B), T111 (C), and 2a from [1]. The data were fitted for models with up to two spins (blue lines) and up to three spins (red lines) by varying the polynomial coefficients and $\lambda_{\text{max}}$. 
Figure S 3: Distance distributions for triradicals T011 (A) and T111 (B). Red lines correspond to distributions obtained from original DEER data and solid lines to distributions obtained from the extracted pair contribution. Vertical arrows correspond to side lengths found in model fits. (A) $a = 2.90 \text{ nm}$, $b = 3.07 \text{ nm}$, $c = 3.69 \text{ nm}$. (B) $a = 3.52 \text{ nm}$, $b = 3.54 \text{ nm}$, $c = 3.60 \text{ nm}$.
Figure S 4: Fit of dipolar spectra by scalene triangle models with uniform normal distribution of all side lengths. Experimental spectra are shown as black lines and fits as red lines. Dotted red lines correspond to a range that was excluded from the fits. (A) Pair contribution of \textbf{T011}. (B) Three-spin contribution of \textbf{T011}. (C) Pair contribution of \textbf{T111}. (D) Three-spin contribution of \textbf{T111}. (E) Pair contribution of \textbf{T012}. (F) Three-spin contribution of \textbf{T012}. 

References


[6] When recording the spectra on the 250 MHz instrument the decoupling power was insufficient which resulted in signal broadening or splitting in the case of aromatic CH groups.

[7] An intensely yellow prefracion has been observed in all reaction in which we attached 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid to phenols in the way described here. See Refs. [1] and [5].

[8] This is a typical fragmentation pattern found for the esters of 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid. See Refs. [1, 5, 9, 10, 11]


[12] The large amounts of catalysts used in this reaction are due to a miscalculation.