Supporting Information

C-C Cross Coupling reactions of Trityl Radicals: Spin Density Delocalization, Exchange Coupling and a Spin Label

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1. Crystallographic Data

Figure S1: Crystal structure of trityl alcohol 5. The ellipsoid contour was set to 30% probability level.

The CIF-file containing all structural information can be obtained online as additional Supporting Information.
Crystallographic data for 5

Crystal Habitus  clear greenish yellow plate
Device Type   Bruker X8-KappaApexII
Empirical formula  C_{41}H_{47}I_{3}O_{2}S_{12}
Moiety formula  C_{37}H_{37}I_{3}O_{12}, C_{4}H_{10}O
Formula weight  1337.20
Temperature/K  100
Crystal system  orthorhombic
Space group  Pca2_{1}
a/Å  26.4750(8)
b/Å  10.6566(3)
c/Å  18.4500(6)
α/°  90
β/°  90
γ/°  90
Volume/Å^3  5205.4(3)
Z  4
ρ_{calc} / g/cm^3  1.706
μ/mm^{-1}  2.316
F(000)  2640.0
Crystal size/mm^3  0.2 × 0.09 × 0.04
Absorption correction  empirical
T_{min}; T_{max}  0.3729; 0.7460
Radiation  MoKα (λ = 0.71073)
2Θ range for data collection/°  4.674 to 55.996°
Completeness to theta  0.998
Index ranges  -34 ≤ h ≤ 26, -14 ≤ k ≤ 13, -24 ≤ l ≤ 24
Reflections collected  87159
Independent reflections  12545 [R_{int} = 0.1364, R_{sigma} = 0.0917]
Data/restraints/parameters  12545/1/538
Goodness-of-fit on F^2  1.027
Final R indexes [I>=2σ (I)]  R_{1} = 0.0653, wR_{2} = 0.1403
Final R indexes [all data]  R_{1} = 0.0789, wR_{2} = 0.1497
Largest diff. peak/hole / e Å^{-3}  1.89/-1.32
Flack parameter  0.068(19)
2. Computational results

2.1 Inclusion of spin density distribution in 16\textsuperscript{**} for distance calculation

The dipolar coupling constant considering the delocalization of spin density can be described by an extended point-dipole approach:\(^1\):

\[
D = \frac{\mu_0 g^2 \beta_e^2}{4\pi\hbar} \sum_{a=1}^{i} \sum_{b=i+1}^{N} \frac{1}{r_{ab}^3} \rho_a \rho_b \quad (eq. S1)
\]

Here, \( g \) equals the trityl g-factor of 2.0032, \( \beta_e \) is the Bohr magneton, and \( \hbar \) the reduced Planck constant. \( r_{ab} \) indicates the distance between two atoms bearing the spin densities \( \rho_a \) and \( \rho_b \). From this dipolar coupling constant, the effective interspin distance \( r_{\text{eff}} \) can be determined as:

\[
r_{\text{eff}} = \sqrt{\frac{3\mu_0 g^2 \beta_e^2}{4\pi\hbar} \frac{1}{D}} \quad (eq. S2)
\]

Figure S2 shows the distribution of spin density within 15\textsuperscript{**} schematically. Whereas the central carbon atom of the trityl core exhibit each about 30\% of the spin density, approximately 5\% is delocalized in each phenyl ring (purple) and 0.5\% into each phenyl ring (blue). Note that the spin density on the hydrogen atoms was neglected as only 0.07\% of the spin density was localized on all 108 hydrogen atoms together. The percentage values refer to the entire spin density of 2 electrons. Since the spin density in the phenyl rings decays rapidly with the distance from the central carbon (first phenyl ring: 5\%, second phenyl ring 0.5\%), it was assumed that spin A is not delocalized across the dashed line in Figure S2 and vice versa. By this, only distances across the dashed line contribute to the dipolar coupling constant between spin A and spin B. This yields an effective interspin distance of 1.75 nm for the optimized structure of 15\textsuperscript{**}, which is in a stretched conformation. Thus, any bending of the structure shortens the distance between the two trityl centers and therefore also the effective interspin distance. In order to account for this, a molecular dynamics (MD) simulation was performed, which was then convoluted with the spin density distribution in order to obtain a distribution of the effective interspin distances. The MD simulation was carried out using the \( GFN-xTB^2 \) program with a simulation time of 250 ps, a time step of 4 fs and a temperature of 298 K. The DFT-optimized structure was used as an input. Then, a home-written \textit{MATLAB} script was used to calculate the effective interspin distance for each frame of the MD simulation based on the procedure described above. The distance distribution was then obtained as a histogram of these effective interspin distances yielding the plot in Figure 7b in the main text.
2.2 Spin density distribution in 12

The Mulliken spin density populations in 12 were obtained from DFT calculations (PBE, def2-SVP). As shown by the $^1$H-NMR spectrum in the main text (Figure 4), one signal in the pyrrolic region is strongly shifted compared to the other ones. The spin densities for the hydrogen atoms, which occur in the $^1$H-NMR of 12 are provided below in figure S3. Since $H_{p1}$ features the largest spin density among the pyrrolic hydrogens, it was therefore assigned to the most-shifted signal in the NMR-spectrum (Figure 4, main text). The signals, which do not encounter a paramagnetic shift in the $^1$H-NMR also do not hold spin density according to the DFT calculations.

Figure S2: Schematic representation of the spin density distribution in 15. The central carbon atoms of the trityl core exhibit each a spin density of 0.58, the phenyl rings in purple of app. 0.10 and the phenyl rings in blue of app. 0.01.

Figure S3: Spin density distribution within 12 according to DFT.
3. Pulsed EPR

Pulsed EPR measurements were conducted on a Bruker (Bruker BioSpin GmbH, Rheinstetten, Germany) ELEXSYS E580 EPR spectrometer equipped with a CF935 helium gas-flow cryostat (Oxford Instruments, Abington, United Kingdom) and an Oxford Instruments ITC 502 temperature controller. An ER 5106QT-II resonator was used at Q-Band frequencies in combination with a 150 W TWT-amplifier (model: 187 Ka) from Applied Systems Engineering, Texas, USA. All data was acquired using quadrature detection.

Before setting up the DQC experiment, an echo-detected field sweep based on the Hahn echo sequence was conducted. Herein, the $\pi/2$ and $\pi$ pulse lengths were set to 12 ns and 24 ns, respectively. The phase of the microwave was adjusted for subsequent experiments already at the stage of Hahn echo optimization. Care was taken that the full signal intensity was detected in the real channel, whereas signal contributions of the imaginary channel were minimized. By means of the echo-detected field sweep, the resonance field of the trityl signal was determined.

For the DQC-measurement, a 6-pulse sequence was used in conjunction with a 64-step phase cycling in order to filter out single-quantum coherences. All pulse lengths, interpulse delay times and further relevant parameters are given in table S1.

![Figure S4: Applied DQC pulse sequence.](image)

<table>
<thead>
<tr>
<th>Table S1: DQC parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Quantity</strong></td>
</tr>
<tr>
<td>$\pi/2$-Pulse</td>
</tr>
<tr>
<td>$\pi$-Pulse</td>
</tr>
<tr>
<td>$\tau_1, \tau_2$</td>
</tr>
<tr>
<td>T</td>
</tr>
<tr>
<td>SRT</td>
</tr>
</tbody>
</table>
Data analysis was performed using the *MATLAB* toolkit *DeerAnalysis*\(^4\),\(^5\). The time trace was preprocessed by applying a background correction. Applying Fast Fourier Transformation as implemented in the *DeerAnalysis* software to the background-corrected time trace yields the Pake pattern shown in Figure S5.

Due to the fast oscillation with a period of 60 ns, a time increment of 4 ns was used for the DQC-experiment. However, *DeerAnalysis 2018* imposes a lower limit of 8 ns as time increment, so that half of the points are discarded prior to analysis, leading to insufficient fits of the time trace. Upon request, the program was modified by its author, *Gunnar Jeschke*, so that time steps of 4 ns could also be handled. Applying a regularization parameter \(\alpha = 0.794\) yields the corresponding distance distribution. The regularization parameter was chosen from the L-curve shown in Figure S2 according to the GCV-criterion as implemented in *DeerAnalysis*.

![Figure S5: a) Pake pattern obtained from the Fourier Transformation of the DQC time trace. b) L-Curve of the Tikhonov-regularization. The regularization parameter chosen for data analysis is marked in red.](image)

\(\text{Figure S5: a) Pake pattern obtained from the Fourier Transformation of the DQC time trace. b) L-Curve of the Tikhonov-regularization. The regularization parameter chosen for data analysis is marked in red.}\)
4. cw EPR spectroscopy

4.1 cw-EPR spectroscopy on 15** in the liquid state

The cw X-band EPR spectrum of 15** was simulated with EasySpin\textsuperscript{6} in combination with a home-written MATLAB script. The position of the $^{13}$C-hyperfine satellites is sensitive to an increasing $J$ up to 550 MHz. While spectra simulated with lower $J$-values can be distinguished, higher $J$ values do not change the shape of the spectrum further, as the strong coupling regime is accessed as shown in fig. S6.

![Figure S6: Room temperature cw-EPR spectra (X-Band) simulated for 15** assuming different values of $J$. The experimental spectrum of 15** is overlaid as a dotted line.](image-url)
4.2 cw-EPR spectroscopy on 15** in the frozen state

Figure S7: Bleany-Bowers fit of the intensity of the half-field signal $I_{p2p}$ versus the temperature $T$. The best fit for the experimental data provided $J = -2.81 \text{ cm}^{-1}$. ● exp. Data; — $J = -2.81 \text{ cm}^{-1}$; △ $J = +1.00 \text{ cm}^{-1}$; + $J = -1.00 \text{ cm}^{-1}$; × $J = -10.0 \text{ cm}^{-1}$.

The frozen-solution cw-EPR spectrum of 15** was measured as described in the main text. In the main-field region, two transitions occur. One being the $\Delta m_s = 1$ transition and yielding the Pake pattern, the other one is a $\Delta m_s = 2$ double-quantum transition giving the central line. The latter transition requires two coherent photons and therefore its intensity scales differently from the $\Delta m_s = 1$ transition with the microwave power as shown below in figure S78.

Figure S8: cw-EPR spectrum of 15** at 100 K at different microwave power.
4.3 cw-EPR spectra of new compounds
In the section below, *continuous wave (cw) X-band* EPR spectra of the radical compounds presented in the main text are shown together with the respective fits. A summary of hyperfine coupling constants, isotropic g-values and linewidths obtained from the fits is provided in Table S2.

Figure S9: Trityl radical 3• *cw*-EPR, X-Band, 298K.

Figure S10: Trityl radical 6• *cw*-EPR, X-Band, 298K.
Figure S11: Trityl radical $^7\text{cw-EPR}$, X-Band, 298K.

Figure S12: Trityl radical $^8\text{cw-EPR}$, X-Band, 298K.
Figure S13: Trityl porphyrin 12$^*$ cw-EPR, X-Band, 298K.

Figure S14: Trityl porphyrin 13$^*$ cw-EPR, X-Band, 298K.
Figure S15: Trityl radical $16^\bullet$ cw-EPR, X-Band, 298K.

Figure S16: Trityl radical $17^\bullet$ cw-EPR, X-Band, 298K.
Table S2: EPR parameters obtained from the fit of the *cw*-EPR spectra.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Isotropic g-value</th>
<th>A / MHz</th>
<th>lwpp Gaussian / mT</th>
<th>lwpp Lorenzian / mT</th>
</tr>
</thead>
<tbody>
<tr>
<td>3*</td>
<td>2.0051</td>
<td>$^{13}\text{C}<em>{\text{central}}$: 68.94 $^{13}\text{C}</em>{\text{ipso}}$: 32.80 $^{13}\text{C}_{\text{ortho}}$: 26.08</td>
<td>0.0020</td>
<td>0.1224</td>
</tr>
<tr>
<td>6*</td>
<td>2.0032</td>
<td>$^{13}\text{C}<em>{\text{central}}$: 65.16 $^{13}\text{C}</em>{\text{ipso}}$: 31.56 $^{13}\text{C}_{\text{ortho}}$: 25.56</td>
<td>0.0502</td>
<td>0.0626</td>
</tr>
<tr>
<td>7*</td>
<td>2.0038</td>
<td>$^{13}\text{C}<em>{\text{central}}$: 67.67 $^{13}\text{C}</em>{\text{ipso}}$: 31.56 $^{13}\text{C}_{\text{ortho}}$: 25.56</td>
<td>0</td>
<td>0.0966</td>
</tr>
<tr>
<td>8*</td>
<td>2.0044</td>
<td>$^{13}\text{C}<em>{\text{central}}$: 67.09 $^{13}\text{C}</em>{\text{ipso}}$: 31.80 $^{13}\text{C}_{\text{ortho}}$: 25.20</td>
<td>0</td>
<td>0.1415</td>
</tr>
<tr>
<td>12*</td>
<td>2.0032</td>
<td>$^{13}\text{C}<em>{\text{central}}$: 66.19 $^{13}\text{C}</em>{\text{ipso}}$: 31.42 $^{13}\text{C}<em>{\text{ortho}}$: 25.38 $^{13}\text{C}</em>{\text{para}}$: 6.57 $^{13}\text{C}_{\text{meta}}$: 4.02</td>
<td>0.0482</td>
<td>0.0244</td>
</tr>
<tr>
<td>13*</td>
<td>2.0031</td>
<td>$^{13}\text{C}<em>{\text{central}}$: 66.75 $^{13}\text{C}</em>{\text{ipso}}$: 31.09 $^{13}\text{C}<em>{\text{ortho}}$: 25.32 $^{13}\text{C}</em>{\text{para}}$: 6.77 $^{13}\text{C}_{\text{meta}}$: 4.50</td>
<td>0.0473</td>
<td>0.0282</td>
</tr>
<tr>
<td>15**</td>
<td>2.0036</td>
<td>$^{13}\text{C}<em>{\text{ipso}}$: 31.25 $^{13}\text{C}</em>{\text{ortho}}$: 25.30</td>
<td>0.0160</td>
<td>0.0551</td>
</tr>
<tr>
<td>15** (100K)</td>
<td>g&lt;sub&gt;xx&lt;/sub&gt; = 2.0036 g&lt;sub&gt;yy&lt;/sub&gt; = 2.0036 g&lt;sub&gt;zz&lt;/sub&gt; = 2.0034</td>
<td>$^{13}\text{C}<em>{\text{ipso}}$: 31.25 $^{13}\text{C}</em>{\text{ortho}}$: 25.30 $^{1H}_{\text{alkyne}}$: 3.72</td>
<td>0.0787</td>
<td>0.0402 (2x$\Delta m_s = 1$) 0.0635 (2x$\Delta m_s = 1$)</td>
</tr>
<tr>
<td>16*</td>
<td>2.0032</td>
<td>$^{13}\text{C}<em>{\text{central}}$: 66.44 $^{13}\text{C}</em>{\text{ipso}}$: 31.01 $^{13}\text{C}<em>{\text{ortho}}$: 24.94 $^{13}\text{C}</em>{\text{para}}$: 7.87 $^{13}\text{C}_{\text{meta}}$: 5.74</td>
<td>0.0396</td>
<td>0.0172</td>
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<tr>
<td>17*</td>
<td>2.0032</td>
<td>$^{13}\text{C}<em>{\text{central}}$: 67.82 $^{13}\text{C}</em>{\text{ipso}}$: 31.93 $^{13}\text{C}<em>{\text{ortho}}$: 25.54 $^{1H}</em>{\text{alkyne}}$: 3.72</td>
<td>0.0135</td>
<td>0.1095</td>
</tr>
</tbody>
</table>
5. Reaction of 3* with n-butyl lithium

Trityl radical 3* (100 mg, 79 µmol) was dissolved in 8 mL dry THF and n-butyl lithium (98 µL 2.5 M in hexanes, 3.00 eq.) was added at -78 °C. The deep green solution turns deep purple upon the addition of butyl lithium. After 1 h, 0.5 mL methanol was added and the solution was warmed up to room temperature and stirred for 30 min. Then, solvents were removed under reduced pressure and the crude product was subjected to MALDI(+)-MS analysis, which revealed the product composition displayed above. Interestingly, the main products were coupling products with butyl lithium and not the exchange products.

Figure S17: MALDI(+)-spectrum of crude product of the reaction of 3* with nBuLi.
6. Catalysts for Suzuki-Coupling

For the reaction of 5 to 6-OH, the suitability of catalyst Pd(OAc)$_2$ + 2 $t$Bu$_3$P was also tested. The aim of this was to test whether the oxidative addition of Pd$^0$ is inhibited by the steric situation, since the electron-rich $t$Bu$_3$P would accelerate this step. However, one sees a decrease in the reaction rate, presumably due to the large cone-angle of $t$Bu$_3$P and the steric demand associated with it. The reaction was carried out under the same conditions as described in the synthesis section. $^1$H-NMR allowed to analyze the product mixture, since the signal of the central OH-group is quite sensitive to para-functionalization.

![Figure S18: $^1$H-NMR-spectrum (500 MHz) of the crude product. Signal A refers to the starting material 5, signal D to 6-OH. Signals C and B are originated from the bis- and mono-coupling product, respectively.](image-url)
7. Oxygen sensitivity of 15**

During purification of the trityl biradical 15**, a bleaching of the deep green color during column chromatography was observed. This was attributed to an enhanced sensitivity towards oxygen and partial oxidation, which was also observed for a similar trityl biradical before7. This behavior might be explained by the triplet state for 15**, which is populated by 49.5 % at a \( J \) of -2.8 cm\(^{-1}\) and at 298 K according to the Boltzmann distribution. Since atmospheric oxygen is also a triplet, the kinetic inhibition of the oxidation could be reduced compared to a doublet trityl radical or a singlet trityl alcohol. Figure S19 shows the ESI(+) mass spectrum of 15** synthesized directly from trityl radical 7*, the intensity of the \([M+17]^+/[M+16]^+\) peak is remarkable here. Note that both peaks overlap and correspond to the trityl alcohol (15-OH*) and the sulfoxide oxidation products. The mass spectrum in figure S20 was recorded from 15** synthesized via the trityl alcohol approach as described in the main text. Here, the peaks assigned to oxidation products exhibit less intensity. The remaining intensity accounts for the monoradical content as seen in the \(cw\) EPR spectrum.

![Figure S19: ESI(+)-MS of 15** synthesized from trityl radical 7* after column chromatography.](image)
Figure S20: ESI(+)‐MS of 15** synthesized from trityl alcohol 9.
8. Sonogashira reactions

8.1 General procedure for Sonogashira-Hagihara reactions

150 mg of 5 (120 µmol), Pd-catalyst (6 µmol, 5 mol%), CuI (12 µmol, 10 mol%) were dissolved in 20 mL of the solvent mixture. Then, the corresponding acetylene (480 µmol, 4 eq.) was added and the reaction mixture was stirred at the corresponding temperature. Solvents were removed under reduced pressure subsequently and the residue was taken up in dichloromethane (30 mL). After washing with 0.1M Na₂EDTA and brine, the organic phase was separated, dried over MgSO₄ and the solvents were removed under reduced pressure. The crude product was then dried in oil-pump vacuum (10⁻³ mbar) and subjected to analysis without further purification.

8.2 General remarks

The C-C cross coupling under Sonogashira-coupling conditions was tested on trityl alcohol 5 with 2-methyl-3-butyn-2-ol, trimethylsilyl acetylene (TMS-acetylene), and triisopropylsilyl acetylene (TIPS-acetylene) as alkynes and using common solvents and catalysts (THF/DIPEA or Et₃N, Pd(Ph₃P)₂Cl₂, CuI, 70°C, 16h). These reaction conditions showed several side products in the MALDI-MS spectra alongside to the coupling products, as shown in figures S21, S36, and S37. The sum formulas of the side products were obtained via APCI-HRMS (S23-30, S38) and revealed an uptake of alkyne equivalents additional to the desired coupling reaction. Therefore, these side-products are called “insertion products”, as they presumably emerge from an insertion of alkyne into the trityl backbone. It is noteworthy, that this unusual reactivity was observed systematically for all alkynes mentioned above. Using only the copper catalyst led to no reaction at all, whereas the sole use of Pd(Ph₃P)₂Cl₂ provided both coupling and insertion products. Other palladium catalysts such as Pd(OAc)₂ + P(Bu₃P)₃ or Pd(dppf)Cl₂ proved to be inferior both for the coupling and the insertion reaction. Moreover, the choice of either DIPEA or Et₃N as cosolvent did not influence the product composition. Except for the C-I bond, the C-S bonds of the annulated 1,3-dithianes are the only reactive bonds within the molecule. Interestingly, also Iovine et al.⁸ observed a competitive carbothiolation process via alkyne insertion into the C-S bond of phenylthioacetate under palladium catalysis condition. We thus assume an analogous migratory insertion of alkyne into a C-S bond of the trityl moiety.
Figure S21: Reaction of 5 with 4 eq. TIPS-acetylene, Pd(Ph₃P)₂Cl₂, and Cul in THF/DIPEA (3:1). The MALDI(+)-spectrum of the product mixture obtained is shown. Notation: CₓIᵧ = x times coupling (x = 1 – 3) and y times insertion of alkyne. Assignment of peaks [m/z]: 1315.7 (C₁I₀), 1370.1 (C₂I₀), 1424.4 (C₁I₀), 1552.3 (C₂I₁), 1606.6 (C₃I₁), 1734.5 (C₂I₂), 1788.8 (C₃I₂). The peak at 1244.2 corresponds to a C₂-product with a remaining hydrogen instead of iodine.

Whereas the same reactivity was observed for 3* (Figure S31) and 6, no insertion reactivity was observed for the unsubstituted parent compound, suggesting that the vicinal iodine seems to be crucial for the insertion reaction. According to the mechanism proposed below in Figure S22, the insertion reaction starts with an oxidative addition of palladium(0) into the C₄-I bond analogous to the coupling reaction. Followed by a 1,2-palladium shift, the insertion reaction runs further through a π-coordination of the alkyne to the palladium and a subsequent migratory insertion into the C-S bond. Such a reaction step would be sensitive to steric demands, which is in agreement with our observation, that the insertion reaction becomes disfavored for the bulky TIPS-acetylene compared to 2-methyl-3-butyn-2-ol and TMS-acetylene.

Moreover, the product with presumably one coupled and one inserted 2-methyl-3-butyn-2-ol (C₁I₁) was isolated by column chromatography and in an amount sufficient for ¹H-NMR. As only singlets appeared in the olefin region (Figure S39), a cyclic structure was proposed as given in fig. S22. Surprisingly, the insertion reaction can be suppressed by the use of refluxing CH₂Cl₂/Et₃N as solvent, which is, however, less common for Sonogashira couplings. For TIPS-acetylene with Pd(Ph₃P)₂Cl₂, this leads solely to coupling products and no insertion (Figure S32), whereas for the sterically less demanding 2-methyl-3-butyl-2-ol, insertion products are observed, again. However, in that case both the insertion and the coupling reaction seem to be equitable,
since they always occurred side by side throughout the entire reaction progress (fig. S42 – S46). Moreover, the use of Pd(dppf)Cl₂ in CH₂Cl₂/Et₃N caused less insertion compared to Pd(Ph₃P)₂Cl₂ for 2-methyl-3-butyn-2-ol as coupling substrate (fig. S47).

**Figure S22:** Proposed mechanism of alkyne uptake into the trityl scaffold by a Pd-catalyzed carbothiolation process. Note that X can be either –OH or a radical center and R is a thioaryl-substituent.

All in all, the palladium catalyst is responsible for a presumed migratory insertion of alkyne into the C-S bonds of the thioacetal and which is competing with the *Sonogashira* coupling. By choosing an appropriate solvent, CH₂Cl₂, and a sterically demanding alkyne, TIPS-acetylene, this side reaction can be suppressed. Nonetheless, also the coupling reaction suffers from the steric demand both of the trityl moiety and the TIPS-acetylene, and thus becomes slow. Accordingly, the *Sonogashira-Hagihara* coupling reaction is not versatile with trityl alcohols/ radicals and can only be taken into account for bulky acetylenes, such as TIPS-acetylene.
8.3 Reaction with TIPS-acetylene

Following the general procedure, 5 was reacted with triisopropylsilylacetylene in THF/Et3N 3:1 (v/v) yielding a mixture of insertion and coupling products. An assignment of the peaks to sum formulas and products is presented in table S3. The APCI-spectra are shown below in order of ascending mass is indicated in table S3 (Figures S23-S30).

In the following, products will be denominated with a $C_x$I_y notation, where $x$ indicates the number of coupled alkynes and $y$ the number of inserted alkynes according to the sum formula. Note, that APCI-data is presented here. During the ionization process, an $\alpha$-cleavage at the central carbon is observed leading to an abstraction of the –OH group. Therefore, the $[M-17]^+$ peaks are shown here, whereas the MALDI(+) spectrum shows $[M]^+$ peaks. The signal intensities in MALDI(+) spectra do not correspond to the sample composition in a quantitative manner, though a qualitative estimate can be obtained from these.

**Table S3:** Mass spectrometric data for the product mixture obtained with TIPS-acetylene

<table>
<thead>
<tr>
<th>MALDI(+) peak [M]$^+$</th>
<th>APCI-peak [M-17]$^+$</th>
<th>sum formula of the corr. trityl alcohol</th>
<th>product type</th>
<th>HRMS figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1244.2</td>
<td>1227.2450</td>
<td>$C_{59}H_{80}OS_{12}Si_2$</td>
<td>[M-I] $C_2$I_0</td>
<td>S22</td>
</tr>
<tr>
<td>1315.4</td>
<td>1298.9026</td>
<td>$C_{48}H_{58}I_2OS_{12}Si$</td>
<td>$C_1$I_0</td>
<td>S23</td>
</tr>
<tr>
<td>1370.1</td>
<td>1353.1399</td>
<td>$C_{59}H_{79}OS_{12}Si_2$</td>
<td>$C_2$I_0</td>
<td>S24</td>
</tr>
<tr>
<td>1424.4</td>
<td>1407.3796</td>
<td>$C_{58}H_{100}OS_{12}Si_3$</td>
<td>$C_3$I_0</td>
<td>S25</td>
</tr>
<tr>
<td>1552.3</td>
<td>1535.2886</td>
<td>$C_{76}H_{101}OS_{12}Si_3$</td>
<td>$C_2$I_1</td>
<td>S26</td>
</tr>
<tr>
<td>1606.6</td>
<td>1589.5247</td>
<td>$C_{81}H_{122}OS_{12}Si_4$</td>
<td>$C_3$I_1</td>
<td>S27</td>
</tr>
<tr>
<td>1734.5</td>
<td>1717.4338</td>
<td>$C_{81}H_{122}OS_{12}Si_4$</td>
<td>$C_2$I_2</td>
<td>S28</td>
</tr>
<tr>
<td>1788.8</td>
<td>1771.6735</td>
<td>$C_{92}H_{144}OS_{12}Si_5$</td>
<td>$C_3$I_2</td>
<td>S29</td>
</tr>
</tbody>
</table>
Figure S23: APCI-HRMS of the [M-I] $\text{C}_2\text{I}_0$ product.

Figure S24: APCI-HRMS of the $\text{C}_1\text{I}_0$ product
Figure S25: APCI-HRMS of the C$_3$I$_0$ product

Figure S26: APCI-HRMS of the C$_3$I$_0$ product
Figure S27: APCI-HRMS of the C$_2$I$_1$ product

Figure S28: APCI-HRMS of the C$_3$I$_1$ product
Figure S29: APCI-HRMS of the C$_2$I$_2$ product

Figure S30: APCI-HRMS of the C$_3$I$_2$ product
For radical $3^\bullet$, an analogous reactivity was observed. However, $3^\bullet$ is decently less soluble in THF/Et$_3$N than 5, leading to unreacted starting material within the product mixture. Nonetheless, insertion products occur here as well.

Figure S31: MALDI(+)—spectrum of the product mixture.

Table S4: Mass spectrometric data for the product mixture obtained from the reaction of $3^\bullet$ with TIPS-acetylene.

<table>
<thead>
<tr>
<th>MALDI(+)—peak [M]$^+$</th>
<th>sum formula of the corr. trityl alcohol</th>
<th>product type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1244.7</td>
<td>C$<em>{37}$H$</em>{36}$I$<em>3$S$</em>{12}$</td>
<td>C$_0$I$_0$</td>
</tr>
<tr>
<td>1299.0</td>
<td>C$<em>{48}$H$</em>{57}$I$<em>2$S$</em>{12}$Si</td>
<td>C$_1$I$_0$</td>
</tr>
<tr>
<td>1353.2</td>
<td>C$<em>{59}$H$</em>{78}$I$S_{12}$Si$_2$</td>
<td>C$_2$I$_0$</td>
</tr>
<tr>
<td>1407.4</td>
<td>C$<em>{70}$H$</em>{99}$I$<em>2$S$</em>{12}$Si$_2$</td>
<td>C$_3$I$_0$</td>
</tr>
<tr>
<td>1481.1</td>
<td>C$<em>{59}$H$</em>{78}$I$<em>2$S$</em>{12}$Si$_2$</td>
<td>C$_1$I$_1$</td>
</tr>
<tr>
<td>1535.3</td>
<td>C$<em>{70}$H$</em>{100}$I$<em>2$S$</em>{12}$Si$_3$</td>
<td>C$_2$I$_1$</td>
</tr>
<tr>
<td>1589.6</td>
<td>C$<em>{81}$H$</em>{121}$S$_{12}$Si$_4$</td>
<td>C$_3$I$_1$</td>
</tr>
</tbody>
</table>
In the solvent system CH$_2$Cl$_2$/Et$_3$N 1:1 (v/v), no insertion products were observed as the MALDI(+) spectrum below shows (Figure S32), even though no quantitative conversion was achieved. The corresponding HRMS-APCI data is provided below in order of ascending mass and indicated in table S5 (Figures S33-35).

![MALDI(+) spectrum of the product mixture](image)

**Figure S32:** MALDI(+) spectrum of the product mixture.

**Table S5:** Mass spectrometric data for the product mixture obtained from the reaction of 5 with TIPS-acetylene in dichloromethane/triethylamine

<table>
<thead>
<tr>
<th>MALDI(+) peak [M]$^+$</th>
<th>APCI-peak [M-17]$^+$</th>
<th>sum formula of the corr. trityl alcohol</th>
<th>product type</th>
<th>HRMS figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1315.9</td>
<td>1298.8998</td>
<td>C$<em>{48}$H$</em>{55}$I$<em>5$OS$</em>{12}$Si</td>
<td>C$_1$I$_0$</td>
<td>S32</td>
</tr>
<tr>
<td>1370.2</td>
<td>1353.1340</td>
<td>C$<em>{59}$H$</em>{70}$IOS$_{12}$Si$_2$</td>
<td>C$_2$I$_0$</td>
<td>S33</td>
</tr>
<tr>
<td>1424.4</td>
<td>1407.3715</td>
<td>C$<em>{70}$H$</em>{100}$OS$_{12}$Si$_3$</td>
<td>C$_3$I$_0$</td>
<td>S34</td>
</tr>
</tbody>
</table>
Figure S33: APCI-HRMS of the C$_1$I$_0$ product

Figure S34: APCI-HRMS of the C$_2$I$_0$ product
Figure S35: APCI-HRMS of the C$_3$I$_0$ product
8.4 Reaction with trimethylsilylacetylene

Following the general procedure, 5 was reacted with trimethylsilylacetylene in THF/Et₃N 3:1 (v/v) yielding a mixture of insertion and coupling products as shown by the MALDI spectrum below.

Figure S36: MALDI(+)-spectrum of the product mixture

Table S6: MALDI data for the product mixture from the reaction of 5 with TMS-acetylene.

<table>
<thead>
<tr>
<th>MALDI(+)‐peak [M]⁺</th>
<th>sum formula of the corr. trityl alcohol</th>
<th>product type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1368.1</td>
<td>C₆₂H₈₄OS₁₂Si₅</td>
<td>C₃I₂</td>
</tr>
<tr>
<td>1466.1</td>
<td>C₆₇H₉₄OS₁₂Si₆</td>
<td>C₃I₃</td>
</tr>
<tr>
<td>1564.2</td>
<td>C₇₂H₁₀₄OS₁₂Si₇</td>
<td>C₃I₄</td>
</tr>
</tbody>
</table>
8.5 Reaction with 2-Methyl-3-butyn-2-ol
Following the general procedure, 5 was reacted with 2-Methyl-3-butyn-2-ol in THF/Et$_3$N 3:1 (v/v) yielding a mixture of insertion and coupling products as shown by the MALDI spectrum below.

![MALDI spectrum](image)

Figure S37: MALDI(+) -spectrum of the product mixture

Table S7: MALDI-data for the product mixture obtained from the reaction of 5 with 2-Methyl-3-butyn-2-ol.

<table>
<thead>
<tr>
<th>MALDI(+) -peak [M]$^+$</th>
<th>sum formula of the corr. trityl alcohol</th>
<th>product type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1257.9</td>
<td>C$<em>{52}$H$</em>{59}$IO$<em>4$S$</em>{12}$</td>
<td>C$_2$I$_1$</td>
</tr>
<tr>
<td>1301.8</td>
<td>C$<em>{47}$H$</em>{52}$I$_3$O$<em>3$S$</em>{12}$</td>
<td>C$_1$I$_1$</td>
</tr>
<tr>
<td>1342.0</td>
<td>C$<em>{57}$H$</em>{67}$IO$<em>2$S$</em>{12}$</td>
<td>C$_2$I$_2$</td>
</tr>
<tr>
<td>1382.2</td>
<td>C$<em>{67}$H$</em>{82}$O$<em>7$S$</em>{12}$</td>
<td>C$_3$I$_3$</td>
</tr>
<tr>
<td>1426.2</td>
<td>C$<em>{62}$H$</em>{75}$IO$<em>6$S$</em>{12}$</td>
<td>C$_2$I$_3$</td>
</tr>
</tbody>
</table>
The C$_{11}$I$_{1}$-product of this batch could be isolated by column chromatography on silica eluting with cyclohexane/ethyl acetate 2:1 (v/v). The HRMS-spectrum shown below confirms the assumed sum formula.

Figure S38: APCI-HRMS of the C$_{11}$I$_{1}$ product
The structure of this $C_1I_1$ product was then further studied by $^1$H-NMR at 700 MHz, these spectra are shown below.

Figure S39: $^1$H-NMR (700 MHz, CD$_2$Cl$_2$, 298K) of the $C_1I_1$ product with 2-methyl-3-butyne-2-ol, olefinic region.

Figure S40: $^1$H-NMR (700 MHz, CD$_2$Cl$_2$, 298K) of the $C_1I_1$ product with 2-methyl-3-butyne-2-ol, aliphatic region.
In the aliphatic region between 1.60 and 1.95 ppm, the methyl protons of the thioacetal give resonances. Clearly, more than 12 peaks – as it would be expected for an asymmetric trityl alcohol – are visible, which means that more than one isomer of the C1I1 product exists. According to the mechanism proposed in the main text, six isomers plus their enantiomers can exist:

![Structure A1](image1)

![Structure B1](image2)

![Structure C1](image3)

![Structure A2](image4)

![Structure B2](image5)

![Structure C2](image6)

Figure S41: Suggested structures of the insertion products.

For the products A1, B1, and C1, a steric clash of the OH-group with the 7-membered ring can be expected, which disfavors the formation of these products. Regarding the NMR-spectra, the olefinic proton of the 7-membered ring and the central OH-proton are expected to give signals between 6 and 7 ppm, both with an equal integral. As shown in the 1H-NMR spectrum, three signal pairs (A, B, C) with equal integrals occur between 6 and 7 ppm, presumably originating from A2, B2, and C2.

For this kind of product structure, no scalar coupling is present, so that only singlets are expected corresponding to the experiment. However, the regioselectivity of the alkyne insertion cannot be determined this way and remains unclear.
In a further experiment, 5 was reacted with 2-methyl-3-butyn-2-ol in CH₂Cl₂/Et₃N and samples for MALDI(+)-analysis were extracted after 2 h (fig. S42), 4 h (fig. S43), 6 h (fig. S44), 8 h (fig. S45), and 10 h (fig. S46).

This examination revealed that the coupling- and insertion reaction both occur side by side. At no time, only coupling products without insertion products were observed, meaning that neither of both reaction pathways is kinetically strongly preferred.

The corresponding MALDI(+)-spectra are shown below, the following table presents a peak assignment.

Table S8: MALDI-data for the product mixtures obtained from the reaction of 5 with 2-methyl-3-butyn-2-ol in dichloromethane/triethylamine.

<table>
<thead>
<tr>
<th>MALDI(+)-peak [M]+</th>
<th>sum formula of the corr. trityl alcohol</th>
<th>product type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1130.0</td>
<td>C₅₂H₅₈O₄S₁₂</td>
<td>C₃I₀</td>
</tr>
<tr>
<td>1173.8</td>
<td>C₄₇H₅₁O₅S₁₂</td>
<td>C₂I₀</td>
</tr>
<tr>
<td>1217.6</td>
<td>C₄₂H₄₄I₂O₂S₁₂</td>
<td>C₁I₀</td>
</tr>
<tr>
<td>1257.9</td>
<td>C₅₂H₅₉O₄S₁₂</td>
<td>C₂I₁</td>
</tr>
<tr>
<td>1261.5</td>
<td>starting material</td>
<td></td>
</tr>
<tr>
<td>1301.8</td>
<td>C₄₇H₅₂I₂O₃S₁₂</td>
<td>C₁I₁</td>
</tr>
<tr>
<td>1342.0</td>
<td>C₅₇H₆₇I₀O₅S₁₂</td>
<td>C₂I₂</td>
</tr>
<tr>
<td>1382.2</td>
<td>C₆₇H₈₂O₂S₁₂</td>
<td>C₃I₃</td>
</tr>
<tr>
<td>1426.2</td>
<td>C₆₂H₇₄I₀O₆S₁₂</td>
<td>C₂I₃</td>
</tr>
</tbody>
</table>
Figure S42: MALDI(+) –spectrum after 2 hours reaction time.

Figure S43: MALDI(+) –spectrum after 4 hours reaction time
Figure S44: MALDI(+) – spectrum after 6 hours reaction time.

Figure S45: MALDI(+) – spectrum after 8 hours reaction time.
Replacing Pd(Ph$_3$P)$_2$Cl$_2$ by Pd(dppf)Cl$_2$ in the solvent system CH$_2$Cl$_2$/Et$_3$N (1:1) led to less insertion. Here, a quantitative coupling alongside insertion occurs, so that the coupling reactions seem to be favored here.
Table S9: MALDI data for the reaction of 5 with 2-methyl-3-butyn-2-ol catalyzed with Pd(dppf)Cl₂.

<table>
<thead>
<tr>
<th>MALDI(+) - peak [M]⁺</th>
<th>sum formula of the corr. trityl alcohol</th>
<th>product type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1130.0</td>
<td>C₅₂H₅₈O₄S₁₂</td>
<td>C₃I₀</td>
</tr>
<tr>
<td>1214.1</td>
<td>C₅₇H₆₆O₅S₁₂</td>
<td>C₃I₁</td>
</tr>
<tr>
<td>1298.2</td>
<td>C₆₂H₇₄O₆S₁₂</td>
<td>C₃I₂</td>
</tr>
</tbody>
</table>
9. NMR spectra of new compounds

9.1 Trityl alcohol 5

Figure S48: $^1$H-NMR, 400 MHz.

Figure S49: $^{13}$C{$^1$H}-NMR, 100 MHz.
9.2 Trityl alcohol 6-OH

Figure S50: $^1$H-NMR, 500 MHz.

Figure S51: $^{13}$C{$^1$H}-NMR, 125 MHz.
9.3 Trityl alcohol 9

Figure S52: $^1$H-NMR, 700 MHz.
Figure S53: $^{13}$C-${}^1$H-NMR, 175 MHz.

9.4 Trityl alcohol 10

Figure S54: ${}^1$H-NMR, 700 MHz.
**Figure S55**: $^{13}$C-$^1$H-NMR, 175 MHz.

**9.5 Trityl alcohol 14**

**Figure S56**: $^1$H-NMR, 700 MHz.
Figure S57a: $^{13}$C-$^1$H-NMR, 175 MHz.

Figure S57b: $^{13}$C-$^1$H-NMR, 175 MHz.
9.6 Trityl porphyrin 12-OH

Figure S57c: $^{13}$C($^1$H)-NMR, 175 MHz.

Figure S58: $^1$H-NMR, 700 MHz.
Figure S59: $^{13}$C-{$^1$H}-NMR, 175 MHz.
10. High-Resolution Mass Spectra

Figure S60: ESI(+)‐HRMS of trityl radical 3•.

Figure S61: ESI(+)‐HRMS of trityl alcohol 5.
Figure S62: APCI-HRMS of trityl alcohol 6-OH.

Figure S63: APCI-HRMS of trityl radical 6°.
Figure S64: APCI-HRMS of trityl radical 7*. 

Figure S65: APCI-HRMS of trityl radical 8*. 

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Figure S66: ESI(+)−HRMS of trityl alcohol 9.

Figure S67: ESI(+)−HRMS of trityl alcohol 10 (Figure S20).
Figure S68: ESI(+)-HRMS of trityl porphyrin 12*.

Figure S69: ESI(+)-HRMS of trityl porphyrin 13*.
Figure S70: ESI(+)-HRMS of trityl alcohol 14.

Figure S71: ESI(+)-HRMS of trityl biradical 15**.
Figure S72: ESI(+)-HRMS of trityl radical 16*.

Figure S73: ESI(+)-HRMS of trityl radical 17*.
Figure S74: ESI(+)–HRMS of trityl porphyrin 12-OH.
11. MALDI(+) and ESI(+) mass spectra of trityl radicals

In the following, MALDI(+) and ESI(+) mass spectra of all new trityl radicals will be presented serving as an additional purity assessment. Note, that the [M+17]-peak belongs to traces of the corresponding trityl alcohol. Peaks occurring for [M+16] belong to trityl radicals bearing sulfoxide groups due to incorporation of oxygen.

Figure S75: MALDI(+) mass spectrum of radical 3⁺.
Figure S76: MALDI(+) mass spectrum of radical 6*.

Figure S77: MALDI(+) mass spectrum of radical 7*.
Figure S78: MALDI(+) mass spectrum of radical 8*.

Figure S79: ESI(+) mass spectrum of radical 16*.
Figure S80: ESI(+) mass spectrum of radical 17*.
12. Medium pressure liquid chromatography

Additionally to mass spectrometry and cw-EPR, liquid chromatography (MPLC) was used to examine the purity of all new radical compounds which could not be subjected to NMR analysis. The instrumentation for the MPLC was set up as described in the main text. Besides from this, cyclohexane/ethyl acetate was used as solvent. In the following chromatograms, the green line indicates the ethyl acetate gradient. The initial signal in all chromatograms at a retention time of 00:00 min is artificial and belongs to the automatic zero-adjusting of the detector.

Figure S81: MPLC-chromatogram of radical 3\(^*\) (t = 11:48 min).

Figure S82: MPLC-chromatogram of radical 6\(^*\) (t = 12:04 min).
Figure S83: MPLC-chromatogram of radical 7* (t = 12:14 min).

Figure S84: MPLC-chromatogram of radical 8* (t = 11:00)
Figure S85: MPLC-chromatogram of biradical 15•• (t = 15:26).

Figure S86: MPLC-chromatogram of radical 16• (t = 11:31 min)

Figure S87: MPLC-chromatogram of radical 17• (t = 11:52 min).
13. References


