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Preparation of Multi-spin Systems: a Case Study of Tolane-bridged Verdazyl-based Hetero-diradicals

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Abstract: Iodine- and ethynyl-containing 'Kuhn'-verdazyls, oxoverdazyls, and nitronyl nitroxides were investigated as building blocks for the preparation of multi-spin systems *via* the Sonogashira reaction, and, as a result, eleven diradicals were prepared with fair yields. The reactivity of the building blocks indicates that oxoverdazyl iodides are effective starting components for the synthesis of diradicals *via* the Sonogashira coupling. The described one-step protocol allows combining different spin units, thereby facilitating the design of tolane-bridged diradicals and screening of their properties. The novel compounds were characterized by cyclic voltammetry, UV-Vis and electron spin resonance (ESR) spectroscopies. Although the electrochemical investigation and electronic spectra showed a negligible influence of radical moieties on each other, ESR data revealed a strong exchange interaction between two unpaired electrons. The prepared verdazyl-nitronylnitroxide diradicals have high stability at storage and hold promise for further investigation and application.

Introduction

The purely organic high-spin systems based on nitroxides, verdazyls, trityls, and phenoxides are widely applied as labels for structural studies of biological objects with the EPR technique,[1] as agents for dynamic nuclear polarisation,[2] and as potential components of a quantum computer.[3] Furthermore, such high-spin paramagnets have been used for the tuning of magneto-optic properties of a chiral polymer[4] and fabrication of electronic devices, e.g., as electrochemical switchers and memory devices,[5] hole-transporting materials[6], and spin filters.[7]

Despite the high demand for multi-spin systems in various fields of science and technology, the development of an efficient synthetic pathway towards exchange-coupled hetero-spin molecules still remains a challenge. The synthesis of high-spin systems based on the nitronyl nitroxide building blocks (Figure 1: **A**,[8a] **B**[6] and **C**[8b]) requires a multi-step complicated experimental procedures. The main limitations are related to the low stability of radical moieties under reaction conditions as well as the influence of unpaired electron on the chemical transformation processes.[9]

In this paper, we focus on the general approach to prepare a wide range of organic high-spin systems based on verdazyl radicals. The significance of this study is strongly related to a range of issues that arose in verdazyl chemistry. First of all, verdazyl high-spin systems have not been systematically studied previously: there are only two examples of verdazyl-containing hetero-diradicals; namely, compound **D**[10] developed by Y. Takahashi and tolane-bridged diradical **E** (Figure 1).[11a] In addition, combination of verdazyls and nitroxides, as predicted[12] and reported,[10d,11] could be considered promising for the synthesis of multi-spin molecules and possible materials for two-dimensional (2D) and 3D ordering of triplon excitations of spin dimers in a crystal lattice.

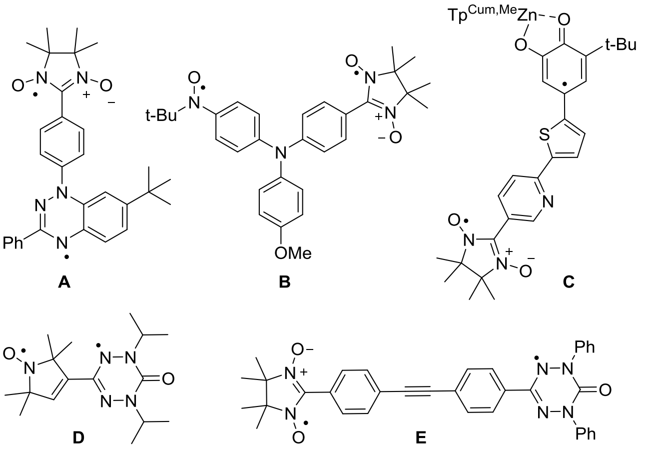


Figure 1. Examples of known hetero-diradicals.

For the preparation of the systematic series of high-spin molecules, we applied the same strategy that was used for the preparation of diradical **E**, where Sonogashira coupling of iodophenyl- and ethynylphenyl-substituted radical blocks was employed.[11a] Moreover, the same reaction was successfully applied to obtain nitronylnitroxide derivatives. [13] Considering the previous efforts, here we describe a convenient and reliable one-step approach for the coupling of different spin-carriers *via* the Sonogashira reaction. Eleven verdazyl-verdazyl and verdazyl-nitronylnitroxide diradicals were prepared with moderate yields and fully characterized by cyclic voltammetry (CVA), UV-Vis and ESR spectroscopies. The molecular and crystal structure of one verdazyl-nitronylnitroxide diradical was solved by X-Ray structural analysis.

Results and Discussion

Our study was focused on the Sonogashira coupling of iodine-substituted radicals **1a**-**1f** with ethynyl-containing building blocks **2a**-**2f** (Figure 2). The reaction was carried out in the previously optimized conditions[10c] for stable radical alkynylation: iodide **1** (1 eq.) and ethynyl building block **2** (1.5 eq.) with Pd(PPh$_3$)$_4$ (10% mol.) and CuI (10% mol.) as catalysts, Et$_3$N as a base in THF at room temperature under inert atmosphere. Reaction times, yields, and structures of the products are summarised in Table 1. General information about the preparation of starting compounds **1** and **2** is given in the Experimental part.

Previously we have shown[9] that the reactivity of verdazyl-halides in Sonogashira coupling depends on the radical structure: 6-oxoverdazyls are more reactive than 'Kuhn'-verdazyls. It was interesting to confirm this trend further, so two pairs of building blocks that give the same product **3ca** were involved in Sonogashira coupling: iodine-containing 6-oxoverdazyl **1c** with ethynyl-containing 'Kuhn'-verdazyl **2a** and *vice versa* **1d** plus **2c**. The last combination gave only an 8% yield of desired **3ca** (Table 1, Entry 2) after 24 hours of reaction. On the contrary, the reaction of **1c** and **2a** gave target diradical **3ca** in 50% isolated yield after 6 hours (Table 1, Entry 1). These observations were considered in the development of a synthetic route to 'Kuhn'-verdazyl-oxoverdazyl diradicals **3ba** (Table 1, Entry 4) and **3bb** (Table 1, Entry 5), which were prepared with acceptable yields (56% and 21% respectively).

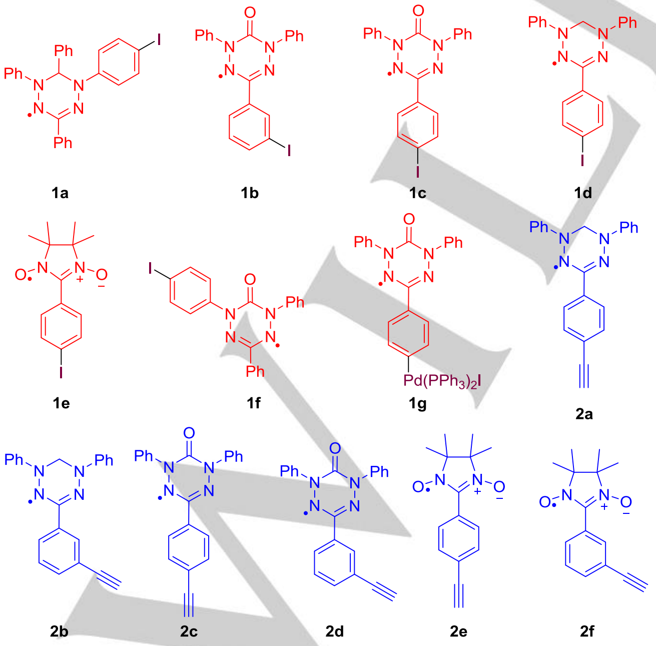


Figure 2. Structures of the building blocks under study.

As has been reported previously, the position of the iodo-phenyl substituent in 'Kuhn'-verdazyl structure dramatically affects on the reaction rate: 'Kuhn'-verdazyl **1a** with the 4-iodophenyl substituent at N1 demonstrates higher reactivity than **1d** in Sonogashira coupling[10c] and oxidative addition.[9] In our study, we observed a similar effect in the reactions of **1a** with **2c** or **2d**, yielding hetero-diradicals **4ac** and **4ad**, respectively (Table 1, Entries 6 and 7).

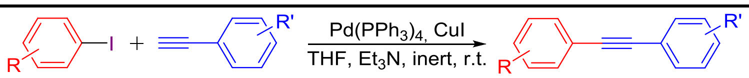
It is also possible to synthesise oxoverdazyl-nitronylnitroxides **5** using two approaches similar to diradicals **3**. The reaction of iodine-containing oxoverdazyl **1c** with the ethynyl-substituted nitronyl nitroxide **2e** gives the corresponding diradical **5ce** with higher yields than the *vice versa* cross-coupling of **1e** with **2c** (Table 1, Entries 8 and 9). Lower reactivity of **1e** in comparison with **1c** may be explained by the results of oxidative addition to Pd(PPh$_3$)$_4$, as shown previously for verdazyl halides.[9] After the reaction of **1e** with Pd(PPh$_3$)$_4$ in THF, we isolated Pd-nitronylnitroxide derivative only in 40% yield (see SI Section S1). At the same time, radical **1c** gave Pd-verdazyl derivative in a 92% yield.[9] Keeping this in mind, other hetero-spin diradicals **5be** (Table 1, Entry 11) and **5bf** (Table 1, Entry 12) were prepared in the same way by the cross-coupling of **1b** with **2e** or **2f**, respectively. Moreover, hetero-diradical **8fe** was successfully isolated after the reaction between oxoverdazyl **1f** and nitroxide **2e** in 51% yield (Table 1, Entry 17).

Highly reactive 'Kuhn'-verdazyl **1a** was successfully coupled with ethynyl-substituted nitronyl nitroxides **2e**, **2f** to prepare hetero-diradicals **6ae** and **6af** in average yields (Table 1, Entries 13 and 14). Similar to **4ac** and **4ad**, the full conversion of starting compounds into **6ae** and **6af** required ~8 h. Therefore, there are significant differences in reactivity between *C*-linked iodophenyl-substituted 'Kuhn'-verdazyls (like **1d**) and their *N*-linked analogue **1a** that seems to be more reactive (Table 1, Entry 2 vs. Entries 6, 7, 13 and 14).

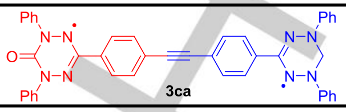
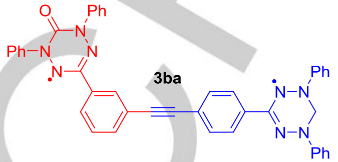
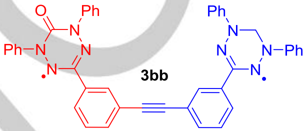
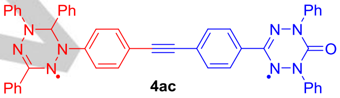
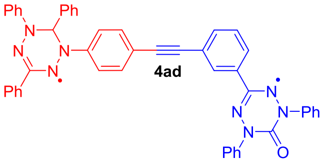
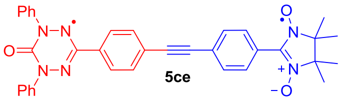
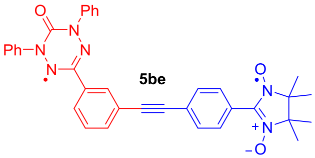
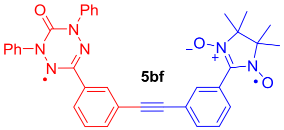
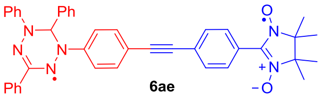
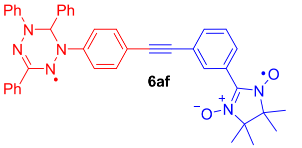
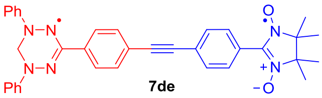
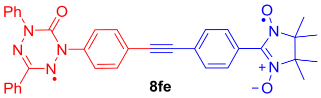
It is interesting that diradicals **3bb** and **5bf** were isolated only in low yields. A possible reason could be associated with the steps of hindered *trans/cis*-isomerization and reductive elimination of bulky organic moieties, which blocked the rotation and decreased the torsional freedom.[14]

Unfortunately, hetero-diradical **7de** was unstable (Table 1, Entries 15, 16) and was not isolated for both combinations of the starting compounds (**1d** plus **2e** and **1e** plus **2a**). We observed the formation of the diradical by thin-layer chromatography (TLC) and its full decomposition after several minutes of elution. Supposedly, one or both radical moieties in **7de** were oxidized by atmospheric oxygen, and only by-products were observed after the column chromatography. Changing the substituent position did not improve stability of this hetero-diradical type.

Table 1 The synthesis of verdazyl hetero-diradicals via Sonogashira coupling [a]



1a-1f **2a-2f** *R and R' = verdazyl or nitroxide radicals*

Entry	Iodine/ethynyl blocks	Time [b]	Yield, % [c]	Product
1	**1c** (1 eq.)/**2a** (1.5 eq.)	6 h	50	 **3ca**
2	**1d** (1 eq.)/**2c** (1.5 eq.)	24 h	8	
3	**1g** (1 eq.)/**2a** (1.5 eq.)	15 min	55	
4	**1b** (1 eq.)/**2a** (1.5 eq.)	6 h	56	 **3ba**
5	**1b** (1 eq.)/**2b** (1.5 eq.)	6 h	21	 **3bb**
6	**1a** (1 eq.)/**2c** (1.5 eq.)	8 h	46	 **4ac**
7	**1a** (1 eq.)/**2d** (1.5 eq.)	8 h	42	 **4ad**
8	**1c** (1 eq.)/**2e** (1.5 eq.)	6 h	46	 **5ce**
9	**1e** (1.5 eq.)/**2c** (1 eq.)	6 h	31	
10	**1g** (1 eq.)/**2e** (1.5 eq.)	15 min	51	
11	**1b** (1 eq.)/**2e** (1.5 eq.)	6 h	34	 **5be**
12	**1b** (1 eq.)/**2f** (1.5 eq.)	6 h	15	 **5bf**
13	**1a** (1 eq.)/**2e** (1.5 eq.)	8 h	54	 **6ae**
14	**1a** (1 eq.)/**2f** (1.5 eq.)	8 h	46	 **6af**
15	**1d** (1 eq.)/**2e** (1.5 eq.)	12 h	0	 **7de**
16	**1e** (1 eq.)/**2a** (1.5 eq.)	6 h	0	
17	**1f** (1 eq.)/**2e** (1.5 eq.)	6 h	51	 **8fe**

[a] Reaction conditions: iodine-containing compound **1** (0.1 mmol) and ethynyl-containing compound **2** (0.15 mmol) were stirred in a deoxygenated mixture of THF (3 mL) and Et_3N (1 mL) with $Pd(PPh_3)_4$ (10% mol) and CuI (10% mol) as catalysts; [b] reaction progress was monitored by thin-layer chromatography; [c] preparative yields.

In total, the four series of hetero-diradicals were prepared *via* Sonogashira coupling. The presented approach may be considered universal, versatile, and widely applicable. The reactivity of the radical iodides in Sonogashira coupling decreases in the following order: oxoverdazyls > *N*-linked 'Kuhn'-verdazyl > nitronyl nitroxides > *C*-linked 'Kuhn'-verdazyls. This experimentally confirmed pattern can be of great help in the choice of the building blocks to obtain the exchange-coupled verdazyl-verdazyl and verdazyl-nitronylnitroxide diradicals.

In all experiments, 1.5 eq. of ethynyl-containing building blocks were used to achieve the full conversion of the iodo-derivatives. We have performed control experiments with the ethynyl derivatives **2a** and **2c** that confirmed their significant decomposition (60–80% after 24 h) in the presence of catalysts in THF in an inert atmosphere but in the absence of iodine compound (see Supporting Information, Section S1). At the same time, the verdazyl iodides were relatively stable under the same conditions, as the previously reported.[9] It is not possible to unambiguously describe the decomposition pathway of the ethynyl compounds. However, it is worth noting that neither the formation of any paramagnetic by-products nor the dimerisation into buta-1,3-diyne derivatives was not observed. Several attempts to optimize the reaction conditions in order to avoid decomposition of ethynyls **2** in the reaction were made. However, neither increasing the temperature up to 60 °C nor changing the solvent to DMF or benzene or the base from Et_3N to *N*,*N*-diisopropylethylamine was not successful. Moreover, coupling reaction with ethynyl derivatives **2a** or **2e** in the presence of CuI with the specially synthesised Pd-verdazyl derivative **1f**[9] gave only a minor (5%) increase in the reaction yields, despite a decrease in the reaction time (Table 1, Entries 3 and 10). This experiment indicates that the yields in Sonogashira coupling are mainly affected by the decomposition of the ethynyl building blocks during transmetalation and elimination processes but not during the oxidative addition of iodides to the Pd catalyst.

A stability test was performed on crystal powders of all the prepared diradicals (**3–6** and **8**) at the refrigerator and room temperatures in air. 'Kuhn'-verdazyl-oxoverdazyls **3** and **4** demonstrated the shortest lifetime; a significant amount of a by-product was observed after one month of storage in the refrigerator and after one week of storage at room temperature. Nitroxide-containing diradicals **5**, **6,** and **8** did not demonstrate significant decomposition, and only traces of by-products were observed on TLC after three months of storage at 3°C and after one month at room temperature.

Numerous attempts to grow diradical crystals suitable for X-ray diffraction led to the formation of fine powders. Suitable single crystals were obtained only for diradical **8fe** (crystal structure of diradical **5ce** was solved previously [10d]), and its molecular and crystal structure was successfully solved (see SI, Section S2).

The obtained diradicals have conjugated linker, so the expected mutual influence of the unpaired electrons was studied using spectral and electrochemical methods. The diradical **3bb** was used as an example to demonstrate the general trends. Figure 3 shows the electronic absorption spectrum of diradical **3bb** together with spectra of building blocks **2d** as ethynyl-containing analogue of **1b** and **2b** in CH_2Cl_2 at room temperature. The spectra of the starting monoradicals agree well with the existing data[15]: **2b** has a broad charge transfer characteristic band in the visible region at ~700 nm, and **2d** has a double peak at ~540 and ~565 nm. The resulting spectrum of diradical **3bb** is a superposition of electronic spectra of initial compounds **2d** as ethynyl-containing analogue of **1b** and **2b**, meaning that two radical moieties influence each other only in a slight manner. The same trend is present in the electronic absorption spectra of other synthesised diradicals (see Supporting Information).

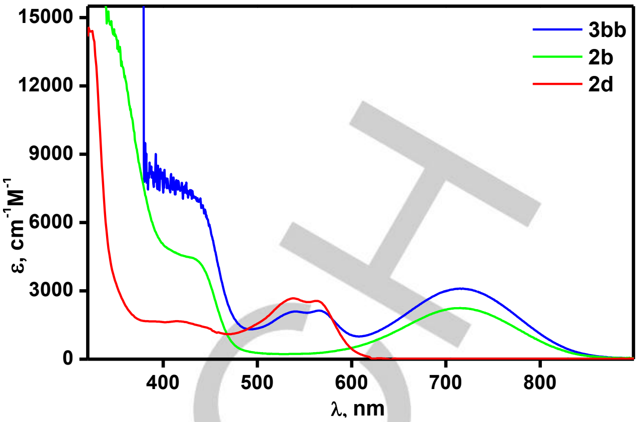


Figure 3. UV-Vis spectra in CH_2Cl_2 solution of biradical **3bb** as superposition of spectra of starting building blocks: **2d** as ethynyl-containing equivalent of **1b** and **2b**.

Electrochemical analysis of diradicals **3**–**6** and **8** was carried out in the deoxygenated CH_2Cl_2 solution. For compounds **3**, **5,** and **8**, the observed CVA curves seem to be the superposition of redox waves of the two independent radical moieties with negligible differences (less than 0.1 V) in comparison with the starting building blocks (Figure 4, Supporting Information Section S3). It is noteworthy that the sufficiently different redox potentials of the two spin moieties may allow the selective reduction or oxidation of one of two paramagnetic groups, opening the possibilities for the electronic devices design.

In the CVA data for diradicals **4** and **6,** there is only one reduction process, but at the same time, two reversible oxidation waves are present, corresponding to the oxidation of two different radical groups (SI, Section S3). It is not possible to correctly assign the reduction process to a certain radical moiety since the reduction potential is different from those of the

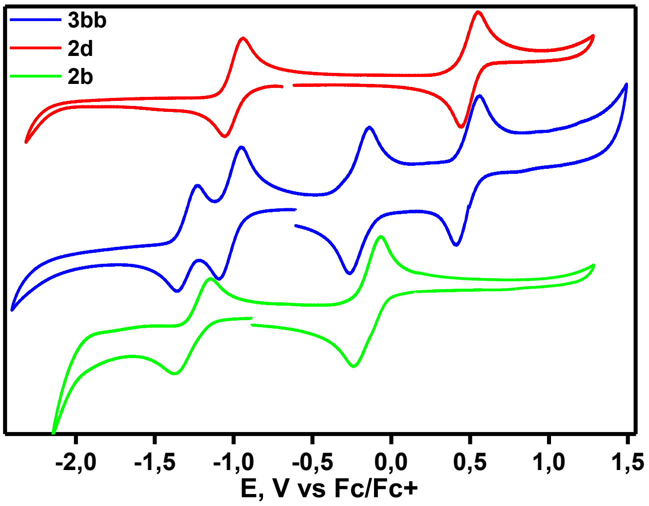


Figure 4. Cyclic voltammogram of biradical **3bb** as superposition of redox waves of starting building blocks: **2d** as ethynyl-containing equivalent of **1b** and **2b**. CVAs of all compounds were recorded in CH_2Cl_2 solution (100 mV/s with 0.1 M Bu_4NPF_6 electrolyte).

corresponding starting monoradicals. Some conjugation of molecular orbitals undetectable in the UV-Vis spectra may be responsible for the absence of the second reduction peak in the diradical systems **4** and **6**.

Continuous-wave ESR spectra of the prepared monoradicals **1** and **2** and diradicals **3–8** were recorded at room temperature in deoxygenated toluene solution (Figure 5 and SI, Section S1). ESR spectra of monoradicals were successfully simulated, and the hyperfine coupling constants were measured that are in good agreement with known data.[9,15] The ESR spectra of diradicals have rather complex line shapes because of the significant contributions of electron-electron spin-spin interactions and the hyperfine interactions. For example, the ESR spectra of diradicals **3ba**, **3bb,** and **3ca** have unique spectral line shapes in each case, significantly different from that of initial radicals. The strong exchange interaction is confirmed by the distinctly reduced splitting between small peaks in comparison with the characteristic value of hyperfine splitting, as observed for some other diradicals.[16] It should be noted, that the beautiful single narrow line of the ESR spectrum of **3ca** has peak-to-peak linewidth of 1.6 G. In the case of motional averaging of the ESR spectrum, such a narrow line should be caused by decreasing in the hyperfine interaction between electron spins and nitrogen atoms because of a specific electron spin density distribution over **3ca** backbones. Strict determination of exchange interaction strength and explanation of the narrow ESR line of **3ca** are a question of further investigation.

Conclusion

A series of verdazyl-verdazyl and verdazyl-nitronylnitroxide hetero-diradicals was synthesized *via* Sonogashira coupling with fair to moderate yields. The described synthetic pathway allowed us to combine different spin-carriers in one conjugated molecule by a one-step procedure. As a result, eleven hetero-diradicals were obtained, and their stability, ESR and UV-Vis spectra, and electrochemical properties were studied. The mutual influence of the unpaired electrons in the diradicals with a conjugated linker was not observed in the UV-Vis spectroscopy studies but was clearly present in the ESR spectra. In addition, the observed changes in the CVA data for some diradicals indirectly confirm the presence of the radical moieties' interaction. The reactivity and applicability of the radical-containing building blocks in Sonogashira coupling were described, and it is shown that iodine-containing oxoverdazyls perform as the most reactive building blocks for the Sonogashira reaction, and the reactivity of radical iodides decreases as follows: oxoverdazyls > *N*-linked 'Kuhn'-verdazyl > nitronyl nitroxides > *C*-linked 'Kuhn'-verdazyls. As for diradicals stability, 'Kuhn'-verdazyl-oxoverdazyls have the shortest lifetime, and the nitronyl nitroxide-containing diradicals are much more stable. The diradicals have sufficient differences in the redox potentials of the spin moieties; therefore, they may be independently reduced or oxidized, providing novel opportunities for the switchable materials design.[17] In general, the Sonogashira cross-coupling reaction represents a versatile synthetic tool for the fast and straightforward screening of novel organic magnetic materials based on multi-spin systems. Authors would like to encourage further research into the magnetic characteristics of the hetero-diradicals, revealing their magneto-structural correlations.

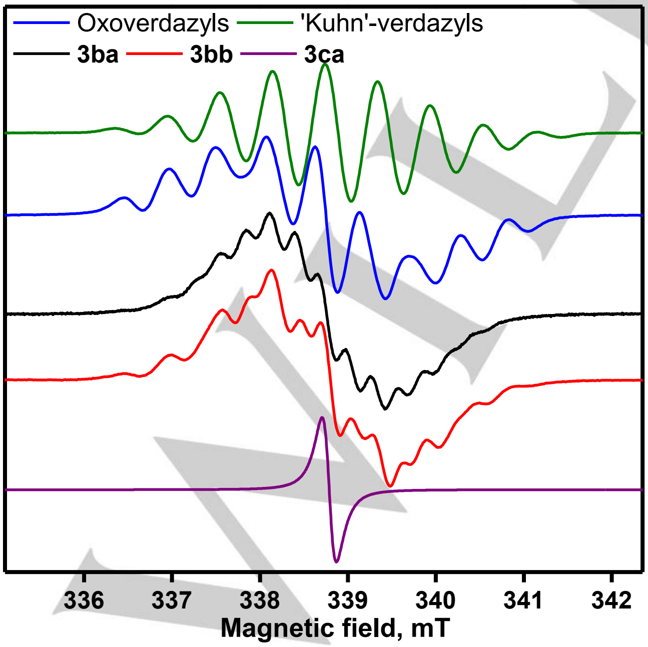


Figure 5. Experimental ESR spectra in deoxygenated toluene solution of compound **3ba**, **3bb** and **3ca** in comparison with starting building blocks.

Experimental Section

General information. All organic reagents and solvents were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, and others) and were used as received. THF was purified according to a previously reported procedure.[18] Radicals **1a**,[10c] **1b**,[9] **1c**[9] and acetylene-substituted nitronyl nitroxide radicals **2e**[15] and **2f**[15] were obtained according to previously reported procedures. The synthesis of 1,3,5-substituted verdazyls **1d**,[10c] **2a,** and **2b**[10c] and nitroxide **1e**[19] was carried out using procedures adapted from other papers. Synthetic pathways for the building blocks are given in SI, Section S1. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD (400 MHz) instrument. Elemental analysis was performed using a Euro EA 3000 (EuroVector). Absorption spectra were registered on a Specord 250 PLUS UV-Vis spectrophotometer. Melting points were measured using the Mettler Toledo Melting point system MP50. High-resolution mass spectra were recorded on an Agilent 6550 Q-TOF LC-MS instrument with electrospray ionization (ESI) and a Thermo Fisher Scientific LC-MS LTQ-Orbitrap Velos instrument with ESI.

ESR spectra were acquired using a Bruker Elexsys ESP-580E X-band instrument with the ER 4118 X-MD5 dielectric cavity and neutron-irradiated LiF as a standard ($g = 2.00229 \pm 0.00001$[20]). The spectra were obtained in a deoxygenated toluene solution (three freeze-pump-thaw cycles) at a concentration of ~5 mM in glass tubes of a 4.8 mm outer diameter. Microwave power was 20 mW, modulation frequency 100 kHz, and modulation amplitude 0.1 G. Simulation of ESR spectra was conducted in the Winsim2002 freeware, and hyperfine coupling constants were measured directly from the simulation.[21] CVA measurements were performed in a deoxygenated CH_2Cl_2 solution by a computer-controlled P-8nano potentiostat/galvanostat (Elins, Russia) in combination with a three-electrode cell (Gamry), with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. Pt, a Pt wire and Ag/AgCl served as a working, counter, and reference electrode, respectively. The reference electrode was calibrated by measurement of the redox potentials of ferrocene. Routine monitoring of the reactions was performed using silica gel–coated aluminum plates (Merck, Silica gel 60, F254), which were analyzed under UV light at 254 nm.

X-ray diffraction analysis. Single crystals for compound **8fe** were grown from a CH_2Cl_2–hexane solution in an open flask at –5 °C. X-ray crystallography of a single crystal of **8ef** was carried out in a Bruker Kappa Apex II CCD diffractometer *via* φ,ω-scans of narrow (0.5°) frames with MoKα radiation (λ = 0.71073 Å) and a graphite monochromator. The structure was solved by direct methods in the SHELX-97 software[22] and was refined by the full-matrix least-squares method against all F2 in anisotropic approximation using the SHELXL-2014/7 software.[23] The hydrogen atoms' positions were calculated via the riding model. Absorption correction was applied by the empirical multi-scan method in the SADABS software.[24]

Free solvent-accessible volume in the crystal of **8ef** derived from PLATON routine analysis[25] was found to be 26.4% (988.0 Å^3). This volume is occupied by highly disordered solvent molecules that could not be modeled as a set of discrete atomic sites. We employed the PLATON/SQUEEZE procedure to calculate the contribution to the diffraction from the solvent region and thereby obtained a set of solvent-free diffraction intensities.

Crystallographic data on the structure of **8fe** were deposited in the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1961924, containing supplementary crystallographic data for this paper. A copy of the data can be obtained, free of charge, by contacting Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 122 3336033 or e-mail: deposit@ccdc.cam.ac.uk; Internet: https://www.ccdc.cam.ac.uk).

The general procedure for the preparation of verdazyls 1d, 2a, and 2b: $Ba(OH)_2·8H_2O$ (473 mg, 1.5 mmol) and 1,3,5-substituted formazan (0.5 mmol) were dissolved in DMF (8 mL), and the resulting mixture was heated to 65 °C. After 15 min, the mixture was cooled to room temperature, MeI (125 µL, 2 mmol) was added, and the reaction mixture was stirred at room temperature for 10 min, at 60 °C for 30 min and 90 °C for 10 min. $Ba(OH)_2$ was separated by centrifugation, and the verdazyl radical was precipitated from the solution with cracked ice (70 g). The solid product was filtered out and washed with water (20 mL).

1,5-Diphenyl-3-(4-iodophenyl)verdazyl radical 1d. According to the general procedure, the reaction of 3-(4-iodophenyl)-1,5-diphenylformazan[10c] (213 mg, 0.5 mmol) with MeI afforded compound **1d** (198 mg, 90% yield) as light-green solids, mp = 130.0–131.4 °C. UV-vis (CH_2Cl_2): $λ_{max}$ (log ε) = 413 (3.72), 438 (3.72), 721 (3.42) nm. Fourier transform infrared spectroscopy (FT-IR; KBr disk): 3058, 2925, 2856, 1744, 1591, 1489, 1393, 1215, 1139, 1121, 1004, 828, 752, 688 cm^{-1}. ESR (toluene, 9.5 GHz): nonet, $a_{N1,5}$ = 5.48 G, $a_{N2,4}$ = 5.49 G, g-value 2.0033. Anal. calcd. for $C_{20}H_{16}IN_4$: C, 54.68; H, 3.67; N, 12.75. Found: C, 54.71; H, 3.66; N, 12.76. High-resolution mass spectrometry (HRMS; ESI/Q-TOF) m/z: [M]$^+$ calcd. for $C_{20}H_{16}IN_4$: 439.0420. Found: 439.0417.

1,5-Diphenyl-3-(4-ethynylphenyl)verdazyl radical 2a. According to the general procedure, the reaction of 3-(4-ethynylphenyl)-1,5-diphenylformazan **12a** (162 mg, 0.5 mmol) with MeI produced compound **2a** (144 mg, 85% yield) as light-green solids, mp = 95.2–95.9 °C. UV-vis (CH_2Cl_2): $λ_{max}$ (log ε) = 362 (3.86), 448 (3.65), 725 (3.34) nm. FT-IR (KBr disk): 3281, 3062, 2924, 2852, 2104, 1598, 1565, 1495, 1448, 845, 754, 690 cm^{-1}. ESR (toluene, 9.5 GHz): nonet, $a_{N1,5}$ = 5.88 G, $a_{N2,4}$ = 5.88 G, g-value 2.0033. Anal. calcd. for $C_{22}H_{17}N_4$: C, 78.32; H, 5.08; N, 16.61. Found: C, 78.29; H, 5.06; N, 16.60. HRMS (ESI/Q-TOF) m/z: [M]$^+$ calcd. for $C_{22}H_{17}N_4$: 337.1453. Found: 337.1451.

1,5-Diphenyl-3-(3-ethynylphenyl)verdazyl radical 2b. According to the general procedure, the reaction of 3-(3-ethynylphenyl)-1,5-diphenylformazan **12b** (162 mg, 0.5 mmol) with MeI generated compound **2b** (149 mg, 88% yield) as light-green solids, mp = 87.3–88.4 °C. UV-vis (CH_2Cl_2): $λ_{max}$ (log ε) = 432 (3.65), 715 (3.35) nm. FT-IR (KBr disk): 3411, 3285, 3060, 3032, 2924, 2852, 2106, 1597, 1563, 1495, 1377, 1297, 1197, 1076, 800, 748, 688 cm^{-1}. ESR (toluene, 9.5 GHz): nonet, $a_{N1,5}$ = 5.89 G, $a_{N2,4}$ = 5.88 G, g-value 2.0033. Anal. calcd. for $C_{22}H_{17}N_4$: C, 78.32; H, 5.08; N, 16.61. Found: C, 78.25; H, 5.07; N, 16.59. HRMS (ESI/Q-TOF) m/z: [M]$^+$ calcd. for $C_{22}H_{17}N_4$: 337.1453. Found: 337.1449.

Synthesis of 2-(4-iodophenyl)-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl 1e. To a solution of 2-(4-iodophenyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol **13** (362 mg, 1 mmol) in CH_2Cl_2 (25 mL), a solution of $NaIO_4$ (214 mg, 1 mmol) in water (15 mL) was added, and the mixture was stirred vigorously for 30 min until the organic phase turned deep blue. The organic layer was separated, washed with water (2 × 20 mL), and dried with Na_2SO_4, and the solvent was evaporated *in vacuo*. The radical was purified via column chromatography (hexane:CH_2Cl_2 at 1:1 to 1:4) to obtain blue crystals after evaporation of the eluent (298 mg, 83% yield). Mp = 141.7 °C (decomposition). UV-vis (CH_2Cl_2): $λ_{max}$ (log ε) = 370 (4.12), 585 (2.60), 629 (2.60) nm. FT-IR (KBr disk): 2992, 2928, 1584, 1467, 1415, 1361, 1301, 1165, 1008, 816 cm^{-1}. ESR (toluene, 9.5 GHz): quintet, a_N = 7.42 G (2N), g-value 2.0062. Anal. calcd. for $C_{13}H_{16}IN_2O_2$: C, 43.47; H, 4.49; N, 7.80. Found: C, 43.49; H, 4.50; N, 7.81. HRMS (ESI/Q-TOF) m/z: [M+H]$^+$ calcd. for $C_{13}H_{17}IN_2O_2$: 360.0335. Found: 360.0329.

The general procedure for the preparation of 1,3,5-substituted 6-oxoverdazyl radicals 1f, 2c and 2d. A solution of Na_2CO_3 (2.12 g, 20 mmol) and $K_3[Fe(CN)_6]$ (2.963 g, 9 mmol) in 20 mL of water was added to a solution (50 mL) of tetrazinan-3-ones **11** (2 mmol) and Et_4NBr (84 mg, 0.4 mmol) in CH_2Cl_2 (50 mL). Radicals **1f**, **2c** and **2d** were extracted with CH_2Cl_2 (2 × 30 mL), washed with water, dried over Na_2SO_4 and subjected to flash chromatography (hexane:CH_2Cl_2 at 2:1). Pure radicals **1f**, **2c** and **2d** were obtained after evaporation of the eluate *in vacuo*.

1,3-Diphenyl-5-(4-iodophenyl)-6-oxoverdazyl radical 1f. Oxidation of 2-(4-ethynylphenyl)-4,6-diphenyl-1,2,4,5-tetrazinan-3-one[26] (913 mg, 2 mmol) according to the general procedure afforded **1f** (725 mg, 80% yield) as deep-violet solids, mp = 178.3–182.9 °C. UV-vis (CH_2Cl_2): $λ_{max}$ (log ε) = 413 (3.16), 541 (3.43), 565 (3.45) nm. FT-IR (KBr disk): 3441, 3062, 3030, 1694, 1481, 1409, 1363, 1309, 1249, 1121, 1001, 824, 748, 684, 654, 606, 501 cm^{-1}. ESR (toluene, 9.5 GHz): multiplet, a_N = 6.43 G (N2, N4), a_N = 4.45 G (N1, N5), g-value 2.0040. Anal. calcd. for $C_{20}H_{14}IN_4O$: C, 53.00; H, 3.11; N, 12.36. Found: C, 53.04; H, 3.10; N, 12.32. HRMS (ESI/Q-TOF) m/z: [M]$^+$ calcd. for $C_{20}H_{14}IN_4O$: 453.0212. Found: 453.0213.

1,5-Diphenyl-3-(4-ethynylphenyl)-6-oxoverdazyl radical 2c. Oxidation of 6-(4-ethynylphenyl)-2,4-diphenyl-1,2,4,5-tetrazinan-3-one **11c** (709 mg, 2 mmol) according to the general procedure produced **2c** (816 mg, 84% yield) as violet solids, mp = 318.3–319.1 °C. UV-vis (CH_2Cl_2): $λ_{max}$ = 429 (3.29), 548 (3.41), 580 (3.32) nm. FT-IR (KBr disk): 3435, 3377, 3070, 3038, 1694, 1589, 1487, 1357, 1249, 1123, 1005, 754, 692 cm^{-1}. ESR (toluene, 9.5 GHz): nonet, a_N = 6.27 G (N2, N4), a_N = 4.62 G (N1, N5), g-value 2.0039. Anal. calcd. for $C_{22}H_{15}N_4O$: C, 75.20; H, 4.30; N, 15.94. Found: C, 75.28; H, 4.29; N, 16.01. HRMS (ESI/Q-TOF) m/z: [M]$^+$ calcd. for $C_{22}H_{15}N_4O$: 351.1246. Found: 351.1279.

1,5-Diphenyl-3-(3-ethynylphenyl)-6-oxoverdazyl radical 2d. Oxidation of 6-(3-ethynylphenyl)-2,4-diphenyl-1,2,4,5-tetrazinan-3-one **11d** (709 mg, 2 mmol) according to the general procedure gave **2d** (597 mg, 85% yield) as violet solids, mp = 148.8–150.4 °C. UV-vis (CH_2Cl_2): $λ_{max}$ (log ε) = 415 (3.23), 538 (3.43), 563 (3.41) nm. FT-IR (KBr disk): 3439, 3270, 3064, 2114, 1692, 1595, 1485, 1359, 1257, 1187, 760, 734, 682, 622, 602 cm^{-1}. ESR (toluene, 9.5 GHz): nonet, a_N = 6.34 G (N2, N4), a_N = 4.54 G (N1, N5), g-value 2.0039. Anal. calcd. for $C_{22}H_{15}N_4O$: C, 75.20; H, 4.30; N, 15.94. Found: C, 75.03; H, 4.31; N, 15.96. HRMS (ESI/Q-TOF) m/z: [M]$^+$ calcd. for $C_{22}H_{15}N_4O$: 351.1246. Found: 351.1239.

The general procedure for the Sonogashira cross-coupling reaction: $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) was added to a deoxygenated (freeze-pump-thaw method, 3 cycles) solution of iodine-containing building block **1a–1e** (0.1 mmol), ethynyl-containing building block **2a–2g** (0.15 mmol) and CuI (1.9 mg, 0.01 mmol) in a mixture of THF (3 mL) and Et_3N (1 mL). The solution was stirred until full conversion of one of the building blocks, **1** or **2**, according to thin-layer chromatography (reaction times are reported in Table 1). The product was isolated by column chromatography with an appropriate eluent (see below), the solvent was evaporated, and the resultant solid product was reprecipitated from a CH_2Cl_2–hexane system to obtain pure diradicals **3–6** and **8**.

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Compound 3ca. According to the general procedure, the reaction of **1c** (45.3 mg, 0.1 mmol) with **2a** (50.6 mg, 0.15 mmol) was followed by column chromatography (hexane:CH_2Cl_2 at 1:1 to 0:1), which afforded compound **3ca** (33.1 mg, 50% yield) as olive solids, mp = 210.3–210.8 °C. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 539 (3.29), 565 (3.30), 723 (3.48) nm. FT-IR (KBr disk): 3422, 3068, 3040, 2212, 1695, 1595, 1495, 1407, 1357, 1304, 1246, 1147, 1122, 845, 751, 690, 654 cm^{-1}. Anal. calcd. for $C_{42}H_{30}N_8O$: C, 76.12; H, 4.56; N, 16.91. Found: C, 76.19; H, 4.57; N, 16.88. HRMS (ESI/LTQ Orbitrap) m/z: $[M]^+$ calcd. for $C_{42}H_{30}N_8O$: 662.2542. Found: 662.2540.

Compound 3ba. According to the general procedure, the reaction of **1b** (45.3 mg, 0.1 mmol) with **2a** (50.6 mg, 0.15 mmol) was followed by column chromatography (hexane:CH_2Cl_2 at 1:1 to 0:1), which afforded compound **3ba** (37.1 mg, 56% yield) as olive solids, mp = 170.5–171.5 °C. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 450 (3.79), 538 (3.21), 566 (3.21), 728 (3.44) nm. FT-IR (KBr disk): 3439, 3065, 3037, 2210, 1700, 1590, 1493, 1399, 1144, 745, 687, 607 cm^{-1}. Anal. calcd. for $C_{42}H_{30}N_8O$: C, 76.12; H, 4.56; N, 16.91. Found: C, 76.11; H, 4.58; N, 16.89. HRMS (ESI/LTQ Orbitrap) m/z: $[M]^+$ calcd. for $C_{42}H_{30}N_8O$: 662.2542. Found: 662.2534.

Compound 3bb. According to the general procedure, the reaction of **1b** (45.3 mg, 0.1 mmol) with **2b** (50.6 mg, 0.15 mmol) followed by column chromatography (hexane:CH_2Cl_2 at 1:1 to 0:1) gave compound **3bb** (13.9 mg, 21% yield) as olive solids, mp = 151.2–151.5 °C. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 537 (3.32), 566 (3.33), 716 (3.49) nm. FT-IR (KBr disk): 3400, 3059, 2924, 2855, 2150, 1700, 1595, 1493, 748, 690, 610, 515 cm^{-1}. Anal. calcd. for $C_{42}H_{30}N_8O$: C, 76.12; H, 4.56; N, 16.91. Found: C, 76.22; H, 4.59; N, 16.83. HRMS (ESI/LTQ Orbitrap) m/z: $[M]^+$ calcd. for $C_{42}H_{30}N_8O$: 662.2542. Found: 662.2545.

Compound 4ac. According to the general procedure, the reaction of **1a** (51.5 mg, 0.1 mmol) with **2c** (50.6 mg, 0.15 mmol) followed by column chromatography (hexane:CH_2Cl_2 at 1:1 to 0:1) afforded compound **4ac** (34.0 mg, 46% yield) as olive solids, mp = 174.1–175.5 °C. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 443 (4.16), 543 (3.40), 590 (3.23), 736 (3.46) nm. FT-IR (KBr disk): 3314, 3057, 2923, 2204, 1700, 1595, 1493, 1252, 1136, 748, 693, 518 cm^{-1}. Anal. calcd. for $C_{48}H_{34}N_8O$: C, 78.03; H, 4.64; N, 15.17. Found: C, 78.19; H, 4.63; N, 15.10. HRMS (ESI/LTQ Orbitrap) m/z: $[M]^+$ calcd. for $C_{48}H_{34}N_8O$: 738.2856. Found: 738.2849.

Compound 4ad. According to the general procedure, the reaction of **1a** (51.5 mg, 0.1 mmol) with **2d** (50.6 mg, 0.15 mmol) followed by column chromatography (hexane:CH_2Cl_2 at 1:1 to 0:1) generated compound **4ad** (31.0 mg, 46% yield) as olive solids, mp = 150.9–151.8 °C. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 434 (4.14), 524 (3.48), 567 (3.36), 731 (3.52) nm. FT-IR (KBr disk): 3437, 3063, 2927, 2207, 1703, 1593, 1510, 1493, 1249, 1133, 754, 690 cm^{-1}. Anal. calcd. for $C_{48}H_{34}N_8O$: C, 78.03; H, 4.64; N, 15.17. Found: C, 77.99; H, 4.66; N, 15.18. HRMS (ESI/LTQ Orbitrap) m/z: $[M]^+$ calcd. for $C_{48}H_{34}N_8O$: 738.2856. Found: 738.2848.

Compound 5ce. According to the general procedure, the reaction of **1c** (45.3 mg, 0.1 mmol) with **2e** (38.6 mg, 0.15 mmol) followed by column chromatography (hexane:$CHCl_3$ at 1:1 to 0:1) produced compound **5ce** (26.8 mg, 46% yield) as violet solids, mp = 209.2–210.8 °C. UV-vis (CH_2Cl_2): λ_{max} = 387 (4.22), 452 (3.35), 554 (2.41), 590 (3.33) nm. FT-IR (KBr disk): 3447, 3068, 2987, 2924, 2212, 1701, 1487, 1363, 845, 756, 693 cm^{-1}. Anal. calcd. for $C_{35}H_{30}N_6O_3$: C, 72.15; H, 5.19; N, 14.42. Found: C, 72.21; H, 5.17; N, 14.56. HRMS (ESI/LTQ Orbitrap) m/z: $[M]^-$ calcd. for $C_{35}H_{30}N_6O_3$: 582.2379. Found: 582.2465.

Compound 5be. According to the general procedure, the reaction of **1b** (45.3 mg, 0.1 mmol) with **2e** (38.6 mg, 0.15 mmol) was followed by column chromatography (hexane:$CHCl_3$ at 1:1 to 0:1), which afforded compound **5be** (19.8 mg, 34% yield) as violet solids, mp = 165.1–165.9 °C. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 384 (3.84), 539 (3.08), 567 (3.07) nm. FT-IR (KBr disk): 3444, 3068, 2987, 2932, 2212, 1702, 1484, 1363, 1301, 1235, 1130, 837, 759, 693, 612 cm^{-1}. Anal. calcd. for $C_{35}H_{30}N_6O_3$: C, 72.15; H, 5.19; N, 14.42. Found: C, 72.20; H, 5.21; N, 14.46. HRMS (ESI/LTQ Orbitrap) m/z: $[M]^-$ calcd. for $C_{35}H_{30}N_6O_3$: 582.2379. Found: 582.2466.

Compound 5bf. According to the general procedure, the reaction of **1b** (45.3 mg, 0.1 mmol) with **2f** (38.6 mg, 0.15 mmol) followed by column chromatography (hexane:$CHCl_3$ at 1:1 to 0:1) gave compound **5bf** (8.8 mg, 15% yield) as violet solids, mp = 132.2–133.0 °C. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 369 (4.28), 539 (3.47), 566 (3.47) nm. FT-IR (KBr disk): 3445, 3066, 2992, 2930, 2211, 1702, 1485, 1361, 800, 761, 690, 602, 541 cm^{-1}. Anal. calcd. for $C_{35}H_{30}N_6O_3$: C, 72.15; H, 5.19; N, 14.42. Found: C, 72.11; H, 5.20; N, 14.40. HRMS (ESI/LTQ Orbitrap) m/z: $[M]^-$ calcd. for $C_{35}H_{30}N_6O_3$: 582.2379. Found: 582.2465.

Compound 6ae. According to the general procedure, the reaction of **1a** (51.5 mg, 0.1 mmol) with **2e** (38.6 mg, 0.15 mmol) was followed by column chromatography (hexane:CH_2Cl_2 at 4:1 to 1:2), which afforded compound **6ae** (34.8 mg, 54% yield) as olive solids, mp = 129.1–129.9 °C. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 445 (4.15), 517 (3.20), 734 (3.54) nm. FT-IR (KBr disk): 3453, 3056, 2986, 2926, 2207, 1591, 1495, 1391, 1363, 1261, 1131, 836, 746, 692, 517 cm^{-1}. Anal. calcd. for $C_{41}H_{36}N_6O_2$: C, 76.38; H, 5.63; N, 13.03. Found: C, 76.43; H, 5.65; N, 12.99. HRMS (ESI/LTQ Orbitrap) m/z: $[M]^-$ calcd. for for $C_{41}H_{36}N_6O_2$: 644.2900. Found: 644.2993.

Compound 6af. According to the general procedure, the reaction of **1a** (51.5 mg, 0.1 mmol) with **2f** (38.6 mg, 0.15 mmol) followed by column chromatography (hexane:CH_2Cl_2 at 4:1 to 1:2) produced compound **6af** (29.6 mg, 46% yield) as olive solids, mp = 130.0–130.7 °C. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 366 (4.28), 436 (4.13), 518 (3.19), 731 (3.58) nm. FT-IR (KBr disk): 3439, 3058, 2952, 2926, 2856, 2205, 1591, 1505, 1389, 1363, 1263, 1137, 746, 690, 515 cm^{-1}. Anal. calcd. for $C_{41}H_{36}N_6O_2$: C, 76.38; H, 5.63; N, 13.03. Found: C, 76.36; H, 5.64; N, 13.00. HRMS (ESI/LTQ Orbitrap) m/z: $[M]^-$ calcd. for $C_{41}H_{36}N_6O_2$: 644.2900. Found: 644.2988.

Compound 8fe. According to the general procedure, the reaction of **1f** (45.3 mg, 0.1 mmol) with **2e** (38.6 mg, 0.15 mmol) was followed by column chromatography (hexane:CH_2Cl_2 at 1:1 to 1:3), which afforded compound **8fe** (29.7 mg, 51% yield) as violet solids, mp = 114.4–116.3 °C. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 381 (4.35), 571 (3.48) nm. FT-IR (KBr disk): 3459, 3060, 2990, 2928, 2858, 2212, 2118, 1702, 1600, 1487, 1421, 1389, 1365, 1307, 1247, 1167, 1125, 838, 756, 692, 521 cm^{-1}. Anal. calcd. for $C_{35}H_{30}N_6O_3$: C, 72.15; H, 5.19; N, 14.42. Found: C, 72.20; H, 5.18; N, 14.45. HRMS (ESI/Q-TOF) m/z: $[M]^-$ calcd. for $C_{35}H_{30}N_6O_3$: 582.2379. Found: 582.2398.

The general procedure for the preparation of hydrazones 9a and 9b. A solution of phenyl hydrazine (6 mmol) and aromatic aldehyde (6 mmol) in EtOH (20 mL) was refluxed for 1 h in an inert atmosphere. Water (8 mL) was added, and hydrazone was isolated by filtration followed by washing with 70% EtOH (10 mL).

1-(4-Ethynylbenzylidene)-2-phenylhydrazine 9a. According to the general procedure, the reaction of phenyl hydrazine (594 μL, 6 mmol) with 4-ethynylbenzaldehyde (781 mg, 6 mmol) afforded compound **9a** (1.084 g, 82% yield) as light-yellow solids, mp = 112.5–113.2 °C. ^1H NMR (DMSO-d_6, 400 MHz): δ 4.25 (s, 1H), 6.77 (t, *J* = 7.26 Hz, 1H), 7.09 (d, *J* = 7.62 Hz, 2H), 7.21–7.25 (m, 2H), 7.48 (d, *J* = 8.28 Hz, 2H), 7.65 (d, *J* = 8.30 Hz, 2H), 7.85 (s, 1H), 10.51 (s, 1H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 81.6, 83.7, 112.2, 119.1, 120.7, 125.6, 129.2, 129.2, 132.0, 135.3, 136.4, 145.0 ppm. FT-IR (KBr disk): 3303, 3284, 3054, 3029, 2924, 2102, 1603, 1581, 1523, 1498, 1257, 1141, 751, 698, 659, 546, 510 cm^{-1}. Anal. calcd. for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.71; H, 5.50; N, 12.69.

1-(3-Ethynylbenzylidene)-2-phenylhydrazine 9b. According to the general procedure, the reaction of phenyl hydrazine (594 μL, 6 mmol) with 3-ethynylbenzaldehyde (781 mg, 6 mmol) produced compound **9b** (1.123 g, 85% yield) as light-yellow solids, mp = 108.8–109.7 °C. ^1H NMR (DMSO-d_6, 400 MHz): δ 4.23 (s, 1H), 6.76 (t, J = 7.14 Hz, 1H), 7.08 (d, J = 7.96 Hz, 2H), 7.21–7.24 (m, 2H), 7.38–7.42 (m, 2H), 7.69 (d, J = 6.24 Hz, 1H), 7.73 (s, 1H), 7.84 (s, 1H), 10.47 (s,1H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ 80.9, 83.3, 112.1, 119.0, 122.1, 126.0, 128.6, 129.1, 129.2, 130.9, 135.1, 136.4, 145.1 ppm. FT-IR (KBr disk): 3315, 3291, 3271, 3056, 3034, 2962, 2926, 2108, 1593, 1563, 1519, 1475, 1447, 1257, 1143, 908, 800, 752, 692, 630, 509 cm^{-1}. Anal. calcd. for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.76; H, 5.48; N, 12.70.

Chlorocarbamoyl hydrazones 10c and 10d. Hydrazone **9a** or **9b** (1.101 g, 5 mmol) was dissolved in dry CH_2Cl_2 (50 mL) in a Schlenk flask in an inert atmosphere. Anhydrous pyridine (495 μL, 6.1 mmol) and a solution of triphosgene (1.484 g, 5 mmol) in 15 mL of dry CH_2Cl_2 were added, and the resulting solution was stirred for 3 h at room temperature. Next, 1 M HCl (20 mL) was added to the mixture, and the product was extracted with CH_2Cl_2, washed with water (3 × 35 mL) and dried with $MgSO_4$. Chlorocarbamoyls **10c** and **10d** were purified by flash chromatography (CH_2Cl_2 as an eluent) with subsequent evaporation of the solvent.

2-(4-Ethynylphenyl)-α-chloroformyl-4-phenylhydrazone 10c. According to the general procedure, the reaction of 1-(4-ethynylbenzylidene)-2-phenylhydrazine **9a** (1.102 g, 5 mmol) with triphosgene afforded compound **10c** (1.117 g, 79% yield) as light-yellow solids, mp = 96.0–96.9 °C. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 4.26 (s, 1H), 6.75 (t, J = 7.25 Hz, 1H), 7.09 (d, J = 8.51, 1H), 7.21 (dd, *J* = 8.47 Hz, J = 7.30 Hz, 1H), 7.46 (d, J = 8.31 Hz, 1H), 7.63 (d, J = 8.32 Hz, 1H), 7.88 (s, 1H) ppm. ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 81.7, 83.7, 112.2, 119.1, 120.7, 120.8, 124.3, 125.6, 129.2, 132.1, 135.2, 136.5, 145.1 ppm. FT-IR (KBr disk): 3267, 1706, 1389, 1321, 1291, 1233, 1185, 886, 840, 829, 710, 660, 547, 312 cm^{-1}. Anal. calcd. for $C_{16}H_{11}ClN_2O$: C, 67.97; H, 3.92; N, 9.91. Found: C, 67.92; H, 3.93; N, 9.89.

2-(3-Ethynylphenyl)-α-chloroformyl-4-phenylhydrazone 10d. According to the general procedure, the reaction of 1-(3-ethynylbenzylidene)-2-phenylhydrazine **9b** (1.102 g, 5 mmol) with triphosgene gave compound **10d** (1.117 g, 79% yield) as light-yellow solids, mp = 91.2–91.6 °C. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 4.23 (s, 1H), 6.75 (t, J = 7.21 Hz, 1H), 7.08 (d, *J* = 7.79 Hz, 2H), 7.19–7.23 (m, 2H), 7.35–7.41 (m, 2H), 7.67 (d, *J* = 6.65 Hz, 1H), 7.71 (s, 1H), 7.86 (s, 1H) ppm. ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 81.0, 83.4, 112.1, 119.0, 122.1, 124.3, 126.0, 128.6, 129.2, 130.9, 135.1, 136.5, 145.1 ppm. FT-IR (KBr disk): 3281, 1732, 1377, 1293, 1195, 832, 708, 620 cm^{-1}. Anal. calcd. for $C_{16}H_{11}ClN_2O$: C, 67.97; H, 3.92; N, 9.91. Found: C, 67.92; H, 3.93; N, 9.89.

2,4,6-Substituted 1,2,4,5-tetrazenane-3-ones 11c and 11d. Chlorocarbamoyl hydrazone **10c** or **10d** (565.5 mg, 2 mmol) was dissolved in deoxygenated EtOH (20 mL), and Et_3N (304 μL, 2.2 mmol) and phenylhydrazine (236 μL, 2.2 mmol) were added. The mixture was heated at 65 °C for 8 h in an inert atmosphere and cooled to 0 °C. Water (2 mL) was added, and the precipitate was filtered off and washed with 80% EtOH (5 mL).

6-(4-Ethynylphenyl)-2,4-diphenyl-1,2,4,5-tetrazinan-3-one 11c. According to the general procedure, the reaction of 2-(4-ethynylphenyl)-α-chloroformyl-4-phenylhydrazone **10c** with phenylhydrazine produced compound **11c** as greyish-white solids (638 mg, 90% yield) mp = 230.1–234.7 °C (decomp.). ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 4.21 (s, 1H), 5.42–5.44 (m, 1H), 6.46 (d, J = 8.68 Hz, 1H), 7.08 (t, J = 7.32 Hz, 2H), 7.32–7.35 (m, 4H), 7.47 (d, J = 8.16 Hz, 1H), 7.55 (d, J = 8.06 Hz, 1H), 7.60 (d, J = 7.71 Hz, 2H) ppm. ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 72.5, 81.2, 83.2, 121.1, 121.5, 123.4, 127.4, 128.1, 131.7, 138.6, 142.7, 157.1 ppm. FT-IR (KBr disk): 3286, 3245, 3065, 3037, 2927, 2103, 1706, 1620, 1598, 1493, 1376, 1307, 917, 831, 759, 695 cm^{-1}. Anal. calcd. for $C_{22}H_{18}N_4O$: C, 74.56; H, 5.12; N, 15.81. Found: C, 74.52; H, 5.14; N, 15.85.

6-(3-Ethynylphenyl)-2,4-diphenyl-1,2,4,5-tetrazinan-3-one 11d. According to the general procedure, the reaction of 2-(3-ethynylphenyl)-α-chloroformyl-4-phenylhydrazone **10d** with phenylhydrazine afforded compound **11d** as greyish-white solids (581 mg, 82% yield) mp = 215.3–217.1 °C (decomp.). ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 4.19 (s, 1H), 5.41 (t, J = 8.92 Hz, 1H), 6.46 (d, J = 8.99 Hz, 2H), 7.07 (t, J = 7.30 Hz, 2H), 7.31–7.44 (m, 6H), 7.56-7.63 (m, 6H) ppm. ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 72.5, 81.0, 121.1, 121.7, 123.4, 127.7, 128.1, 128.8, 130.3, 131.5, 138.4, 142.7, 157.2 ppm. FT-IR (KBr disk): 3286, 3248, 3062, 2927, 2102, 1708, 1620, 1595, 1493, 1376, 1307, 756, 697 cm^{-1}. Anal. calcd. for $C_{22}H_{18}N_4O$: C, 74.56; H, 5.12; N, 15.81. Found: C, 74.51; H, 5.14; N, 15.79.

The general procedure for the preparation of formazans 12a and 12b: Phenyldiazonium tosylate (2.4 mmol, 553 mg) was added in six portions to a solution of hydrazone **9a** or **9b** (441 mg, 2 mmol) and Et_3N (557 μL, 4 mmol) in $CHCl_3$ (20 mL) at room temperature. The resulting solution was stirred for 10 min until full consumption of diazonium salts. Then, the solvent was removed in a rotary evaporator *in vacuo*, cold 90% EtOH (10 mL) was added to the residue, and the precipitated formazan was filtered off and washed with cold 90% EtOH (2 × 20 mL).

3-(4-Ethynylphenyl)-1,5-diphenylformazan 12a. According to the general procedure, the reaction of phenyldiazonium tosylates with **9a** produced compound **12a** as dark violet solids (396 mg, 61% yield), mp = 204.8–205.4 °C. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 489 (4.34) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.12 (s, 1H), 7.30 (t, 2H, J = 7.31 Hz), 7.45–7.49 (m, 4H), 7.56 (d, 2H, J = 8.33 Hz), 7.68 (d, 4H, J = 7.91 Hz), 8.11 (d, 2H, J = 8.17 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 77.9, 84.2, 119.0, 121.0, 125.6, 127.9, 129.6, 132.4, 138.1, 140.4, 147.8 ppm. FT-IR (KBr disk): 3281, 3062, 2926, 2854, 2098, 1746, 1597, 1501, 1453, 1355, 1241, 1185, 1034, 838, 764, 746, 688, 660, 636, 485 cm^{-1}. Anal. calcd. for $C_{21}H_{16}N_4$: C, 77.76; H, 4.97; N, 17.27. Found: C, 77.65; H, 4.98; N, 17.28.

3-(3-Ethynylphenyl)-1,5-diphenylformazan 12b. According to the general procedure, the reaction of phenyldiazonium tosylates with **9b** afforded compound **12b** as dark violet solids (402 mg, 62% yield), mp = 126.9–127.1 °C. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 485 (4.24) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.13 (s, 1H), 7.30 (t, 2H, J = 7.29 Hz), 7.38–7.42 (m, 1H), 7.45–7.49 (m, 5H), 7.69 (d, 4H, J = 7.92 Hz), 8.14 (d, 1H, J = 7.80 Hz), 8.27 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 77.1, 84.2, 119.0, 122.3, 126.3, 127.8, 128.6, 129.5, 129.6, 131.3, 137.8, 140.2, 147.8 ppm. FT-IR (KBr disk): 3303, 3062, 2926, 2854, 2106, 1744, 1597, 1509, 1481, 1453, 1351, 1241, 1167, 1044, 904, 764, 686, 652, 483 cm^{-1}. Anal. calcd. for $C_{21}H_{16}N_4$: C, 77.76; H, 4.97; N, 17.27. Found: C, 77.68; H, 4.99; N, 17.26.

Synthesis of 2-(4-iodophenyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol 13. 4-Iodobenzaldehyde (464 mg, 2 mmol) and N,N′-(2,3-dimethylbutane-2,3-diyl)bis(hydroxylamine) (326 mg, 2.2 mmol) were dissolved in MeOH (8 mL), and the mixture was deoxygenated. The reaction mass was stirred for 12 h at gentle reflux then cooled to –15 °C, and the precipitate was filtered off and washed with 70% MeOH (10 mL). Yield: 616 mg, 85%, mp = 219.5 °C (decomp.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.02 (s, 6H), 1.06 (s, 6H), 4.46 (s, 1H), 7.28 (d, J = 8.18 Hz, 2H), 7.69 (d, J = 8.17 Hz, 2H), 7.79 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.3, 24.4, 66.2, 89.7, 93.2, 130.9, 136.4, 141.9 ppm. FT-IR (KBr disk): 3238, 2976, 2926, 2910, 1589, 1485, 1461, 1373, 1147, 1086, 1006, 917, 872, 796 cm^{-1}. Anal. calcd. for $C_{13}H_{19}IN_2O_2$: C, 43.11; H, 5.29; N, 7.73. Found: C, 43.22; H, 5.28; N, 7.77.

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Keywords: stable radicals • verdazyl radicals • nitroxides • multi-spin systems • Sonogashira coupling

[1] a) Y. D. Tsvetkov, M. K. Bowman, Y. A. Grishin, *Pulsed Electron–Electron Double Resonance*, Springer International Publishing, Cham, **2019**. b) Y. Liu, F. A. Villamena, A. Rockenbauer, J. L. Zweier, *Chem. Commun.* **2010**, *46*, 628–630;

[2] a) D. Wisser, G. Karthikeyan, A. Lund, G. Casano, H. Karoui, M. Yulikov, G. Menzildjian, A. C. Pinon, A. Purea, F. Engelke, et al., *J. Am. Chem. Soc.* **2018**, *140*, 13340–13349; b) S. Bothe, J. Nowag, V. Klimavičius, M. Hoffmann, T. I. Troitskaya, E. V. Amosov, V. M. Tormyshev, I. Kirilyuk, A. Taratayko, A. Kuzhelev, D. Parkhomenko, E. Bagryanskaya, T. Gutmann, G. Buntkowsky, *J. Phys. Chem. C* **2018**, *122*, 11422–11432; c) B. Plainchont, P. Berruyer, J. N. Dumez, S. Jannin, P. Giraudeau, *Anal. Chem.* **2018**, *90*, 3639–3650;

[3] R. Gaudenzi, J. De Bruijckere, D. Reta, I. D. P. R. Moreira, C. Rovira, J. Veciana, H. S. J. Van Der Zant, E. Burzurí, *ACS Nano* **2017**, *11*, 5879–5883.

[4] C. K. Lim, M. J. Cho, A. Singh, Q. Li, W. J. Kim, H. S. Jee, K. L. Fillman, S. H. Carpenter, M. L. Neidig, A. Baev, M.T. Swihart, P.N. Prasad, *Nano Lett.* **2016**, *16*, 5451–5455;

[5] a) C. Simão, M. Mas-Torrent, N. Crivillers, V. Lloveras, J. M. Artés, P. Gorostiza, J. Veciana, C. Rovira, *Nat. Chem.* **2011**, *3*, 359–364; b) C. Simão, M. Mas-Torrent, J. Veciana, C. Rovira, *Nano Lett.* **2011**, *11*, 4382–4385;

[6] T. Kurata, K. Koshika, F. Kato, J. Kido, H. Nishide, *Chem. Commun.* **2007**, *2*, 2986–2988;

[7] S. Shil, D. Bhattacharya, A. Misra, D. J. Klein, *Phys. Chem. Chem. Phys.* **2015**, *17*, 23378–23383;

[8] a) N. M. Gallagher, J. J. Bauer, M. Pink, S. Rajca, A. Rajca, *J. Am. Chem. Soc.* **2016**, *138*, 9377–9380; b) M. L. Kirk, D. A. Shultz, J. Zhang, R. Dangi, L. Ingersol, J. Yang, N. S. Finney, R. D. Sommer, L. Wojtas, *Chem. Sci.* **2017**, *8*, 5408–5415;

[9] P. V. Petunin, D. E. Votkina, M. E. Trusova, T. V. Rybalova, E. V. Amosov, M. N. Uvarov, P. S. Postnikov, M. S. Kazantsev, E. A. Mostovich, *New J. Chem.* **2019**, *43*, 15293–15301;

[10] Y. Takahashi, Y. Miura, N. Yoshioka, *ChemPhysChem* **2018**, *19*, 175–179;

[11] a) P. V. Petunin, T. V. Rybalova, M. E. Trusova, M. N. Uvarov, M. S. Kazantsev, E. A. Mostovich, L. Postulka, P. Eibisch, B. Wolf, M. Lang, P. S. Postnikov, M. Baumgarten, *ChemPlusChem* **2019**, DOI: cplu.201900709; b) H. Jobelius, N. Wagner, G. Schnakenburg, A. Meyer, *Molecules* **2018**, *23*, 1758; c) T. N. Le, T. Trevisan, E. Lieu, D. J. R. Brook, *European J. Org. Chem.* **2017**, *2017*, 1125–1131; d) P. V. Petunin, E. A. Martynko, M. E. Trusova, M. S. Kazantsev, T. V. Rybalova, R. R. Valiev, M. N. Uvarov, E. A. Mostovich, P. S. Postnikov, *European J. Org. Chem.* **2018**, *2018*, 4802–4811;

[12] K. C. Ko, D. Cho, J. Y. Lee, *J. Phys. Chem. A* **2012**, *116*, 6837–6844;

[13] a) E. V. Tretyakov, V. I. Ovcharenko, *Russ. Chem. Rev*. **2009**, *78*, 971–1012; b) C. Stroh, M. Mayor, C. von Hanisch, *Tetrahedron Lett*. **2004**, *45*, 9623–9626; c) S. V. Klyatskaya, E. V. Tretyakov , S. F. Vasilevsky. *Russ. Chem. Bull*. **2002**, *51*, 128–134.; d) F. B. Sviridenko, D. V. Stass, T. V. Kobzeva, E. V. Tretyakov, S. V. Klyatskaya, E. V. Mshvidobadze, S. F. Vasilevsky, Yu. N. Molin, *J. Am. Chem. Soc*. **2004**, *126*, 2807–2819;

[14] M. Schilz, H. Plenio, *J. Org. Chem.* **2012**, *77*, 2798–2807;

[15] [R. G. Hicks, *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds*, **2010**.

[16] M. Shinomiya, K. Higashiguchi, K. Matsuda, *J. Org. Chem.* **2013**, *78*, 9282–9290.

[17] Yu. A. Ten, N. M. Troshkova, E. V. Tretyakov, *Russ. Chem. Rev*., **2020**, 89, DOI:10.1070/RCR4923;

[18] A. B. C. Simas, V. L. P. Pereira, C. B. Barreto, D. L. De Sales, L. L. De Carvalho, *Quim. Nova* **2009**, *32*, 2473–2475;

[19] K. Oyaizu, T. Sukegawa, H. Nishide, *Chem. Lett.* **2011**, *40*, 184–185;

[20] F. G. Cherkasov, I. V. Ovchinnikov, A. N. Turanov, S. G. L'vov, V. A. Goncharov, A. Y. Vitols, *Low Temp. Phys.* **1997**, *23*, 174–176.

[21] https://www.niehs.nih.gov/research/resources/software/tox-pharm/tools/index.cfm

[22] G. M. Sheldrick, SHELX-97, Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany, **1997;**

[23] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2015**, *71*, 3–8;

[24] SADABS, v. 2008-1, Bruker AXS, Madison, WI, USA, **2008;**

[25] a) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13; b) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool (Version 10M), Utrecht University, Utrecht, The Netherlands, **2003;**

[26] E. Di Piazza, A. Merhi, L. Norel, S. Choua, P. Turek, S. Rigaut, *Inorg. Chem.* **2015**, *54*, 6347–6355.

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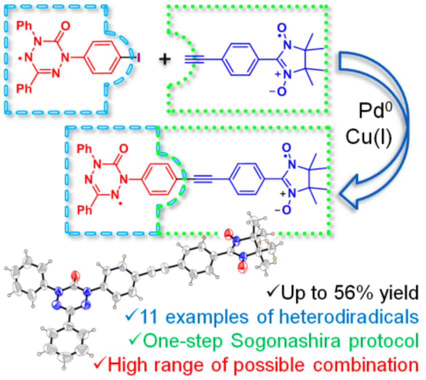

✓Up to 56% yield
✓11 examples of heterodiradicals
✓One-step Sogonashira protocol
✓High range of possible combination

Sonogashira coupling was investigated as a promising strategy for the synthesis of a multi-spin system based on ‘Kuhn’-verdazyls, oxoverdazyls, and nitronyl-nitroxides. Eleven hetero-diradicals were isolated in up to 56% yields using a one-step protocol. Oxoverdazyl radicals manifested the highest reactivity among the studied radicals. This research opens up access to simple design and investigation of conjugated diradicals.

Keywords: stable radicals; verdazyl radicals; nitroxides; multi-spin systems; Sonogashira coupling

Key Topic: high-spin systems