Hydroalkoxylation of alkynes by a nitroxyl containing alcohol, 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl: synthesis of spin-labeled enol ethers

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Abstract

A series of spin-labeled enol ethers has been synthesized in 53–67% yields by superbase-catalyzed (KOH/DMSO suspension as a catalyst) hydroalkoxylation of alkynes (acetylene, phenylacetylene, 4-*tert*-butylphenylacetylene and 3-ethynylpyridine) by 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-hydroxy-TEMPO) under mild conditions (70–80 °C, 1.5–2 h). With unsubstituted acetylene, the hydroalkoxylation readily occurs at atmospheric pressure, yield of the corresponding vinyl ether being 53%.

Keywords: Alkynes, enol ethers, hydroalkoxylation, superbases, stable radicals

Introduction

Stable free radicals of nitroxyl type are under ever-increasing studies due to their importance in a variety of developing areas of modern science and technology, particularly in design of high-tech materials.[1-3] Among such species, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) and its congeners are of special interest. They have found wide applications as reagents and catalysts in organic synthesis,[3] antioxidants,[4] materials for radical batteries,[5,6] magneto-active materials,[7] agents for DNP-NMR,[8,9] as well as radiation protective agents[10] and polymerization catalysts.[11] Furthermore, 4-hydroxy-TEMPO exhibits an antihypertensive effect.[12]

Special attention has been devoted to the use of TEMPO derivatives as spin probes in various fields of biochemistry and biophysics.[13,14] The incorporation of TEMPO labels into such vital molecules as sugars, lipids, proteins, DNA provides valuable information (by EPR spectroscopy) about key metabolic processes and drug docking and targeting. The TEMPO-tailored labels allow evaluation (by EPR technique) of the structure and dynamics of the local environment of biologically important molecules at the labeling site.[15-17] Clearly, for this purpose

the TEMPO derivatives should contain reactive linkers, ensuring site-specific binding of the spin label with the target molecule under mild conditions.

For these considerations, the design of new TEMPO-based spin labels bearing appropriate chemically active linkers is a synthetic challenge. An attractive route to functionalization of the TEMPO skeleton might be the introduction into its molecule of the enol ether (vinyloxy) moiety that, thanks to its rich chemistry,[18-21] can be easily linked with the desired molecules such as sugars, amino acids, proteins, DNA, etc. Furthermore, the presence of easily polymerizable vinyloxy groups[22,23] in the molecules of paramagnetic compounds considerably extends their possible application in advanced technologies.

However, the practical possibilities of spin-labeled vinyl ethers generally, and TEMPO-labeled ones particularly, has been virtually overlooked, despite their above mentioned importance: only one such compound, *viz.* 4-vinyloxy-TEMPO (2,2,6,6-tetramethyl-4-(vinyloxy)piperidin-1-oxyl), first synthesized in 1986,[24] is so far known. In recent years a number of works (mainly patents) describing applications of 4-vinyloxy-TEMPO have appeared. For instance, polymers and copolymers based on this vinyl ether have been proposed as efficient cathode materials for greener organic radical batteries,[25-35] and a nano-scale memory device was constructed by nanolithographic patterning of oxidized poly(4-vinyloxy-TEMPO).[36] The first synthesis of 4-vinyloxy-TEMPO, which goes back to 1986, comprised the hydroalkoxylation of acetylene with 4-hydroxy-2,2,6,6-tetramethylpiperidine in KOH/DMSO followed by oxidation (Na_2WO_4 as catalyst).[24] In the same work, an attempt at direct vinylation of 4-hydroxy-TEMPO (KOH/DMSO, 90 ^{o}C, 4 h, acetylene pressure 12 atm at ambient temperature) led to a mixture of 4-vinyloxy-TEMPO and its reduced form, *i.e.* 4-vinyloxy-2,2,6,6-tetramethylpiperidine, as the major product. The target 4-vinyloxy-TEMPO was isolated chromatographically in a yield of just 13%.[24] The first polymer of 4-vinyloxy-TEMPO was obtained *via* polymerization of its reduced form (4-vinyloxy-2,2,6,6-tetramethylpiperidine) followed by its oxidation.[24] Twenty years later, during the last decade, publications in this area have mushroomed (total number of works being 37, selected works[25-36]), although the synthesis of the monomer was based mainly on transvinylation of 4-hydroxy-TEMPO with vinyl acetate in presence of expensive metal complex catalyst, [IrCl(cod)$_2$] (~ 8 mass% relative to the alcohol).[25-36] Since the first synthesis of 4-vinyloxy-TEMPO,[24] no attempt to develop an expedient hydroalkoxylation of alkynes with 4-hydroxy-TEMPO has been undertaken. Meanwhile, having in mind that direct superbase-catalyzed hydroalkoxylation of alkynes with hydroxyl compounds has proved to be highly efficient,[37-42] we decided to revisit the vinylation of 4-hydroxy-TEMPO with various alkynes exploiting our expertise gained during the last decade.

Therefore, this work focuses on the development of a general and efficient route to spin-labeled vinyl ethers by direct vinylation of the available 4-hydroxy-TEMPO with alkynes in the superbasic KOH/DMSO system under readily accessible conditions, *viz.* at atmospheric pressure and mild temperatures.

It is relevant to note that some KOH/DMSO-catalyzed vinylations, e.g. NH- and CH-functionalization of pyrroles and indoles with acetylenes,[43-46] involve single electron transfer

steps (the expected radicals were trapped as spin-adducts). Therefore, the KOH/DMSO-catalyzed vinylation of a free radical such as 4-hydroxy-TEMPO with acetylenes could be affected by involvement of this radical in the vinylation process. In view of these data, and the earlier result of predominant reduction of 4-hydroxy-TEMPO during its vinylation by acetylene in the KOH/DMSO system, it remains unclear whether efficient base-catalyzed hydroalkoxylation of nitroxyl-containing alcohols with alkynes is possible. This issue is of fundamental importance to the question of the mechanism of nucleophilic addition of alkoxide to the C≡C triple bond.

Results and Discussion

To develop an efficient synthesis of 4-vinyloxy-TEMPO, the reaction of 4-hydroxy-TEMPO (**1**) with acetylene in the KOH/DMSO system was studied under atmospheric pressure (acetylene flow). The **1**/KOH molar ratio, reaction temperature and time were optimization parameters. The GLC monitoring of the reaction revealed that, along with the hoped-for vinylation to afford vinyl ether **2**, reduction leading to compounds **3** and **4** also took place (Table 1).

Table 1. Vinylation of 4-hydroxy-TEMPO (**1**) with acetylene: effect of the conditions on the product yields and ratio[a]
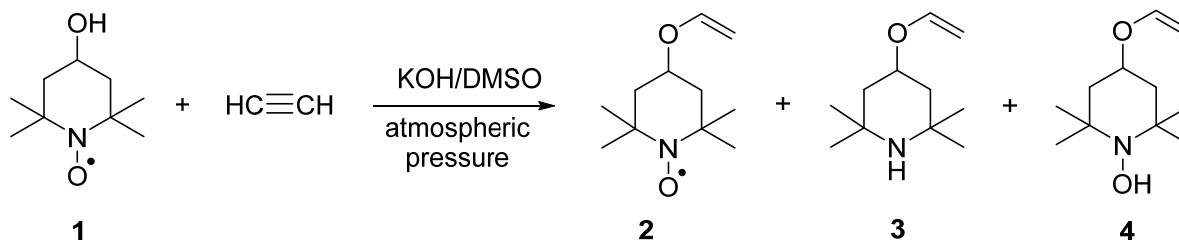
Entry	KOH (mol%)[b]	Temp. (°C)	Time (h)	Crude product composition, % (GLC)			
				1	**2**	**3**	**4**
1	50	60	1	96.9	3.1	0	0
2	50	80	1.5	28.4	65.4	4.0	2.1
3	75	80	0.75	39.7	56.6	1.2	2.3
4	75	80	1.5	7.4	62.2	15.9	14.5
5	75	80	3	0	51.6	24.8	23.6
6	75	90	2	0	46.2	39.7	14.1
7	100	90	4	0	2.8	93.2	4.0

[a] Reaction conditions: alcohol **1** (20 mmol), DMSO (50 mL), atmospheric pressure, acetylene flow rate ~1 L/h. [b] Relative to **1**.

As may be seen from Table 1, the selectivity of formation of the vinyl ether radical **2** significantly depends on the reaction temperature and time. Under the mildest conditions (60

°C), the rate of alcohol **1** vinylation is insignificant: after 1 h only traces of vinyl ether **2** are present in the reaction mixture (entry 1). At 80 °C, and with 75 mol% of KOH, increase of the reaction time (from 0.75 to 3 h) results in complete conversion of the starting alcohol **1**, while the content of vinyl ether **2** in the crude product decreases from 62.2% to 51.6% due to its reduction to products **3** and **4** (entries 3-5, Table 1). The elevated temperature also facilitates the reduction processes**.** A longer reaction time (4 h, other conditions being the same) diminishes the content of **2** in the crude product from 46.2 to 2.8% (entries 6, 7, Table 1). In this case, the major product becomes the vinyl ether **3** (entry 7, Table 1), isolated in 59% yield. Eventually, the best result (65.4% content of **2** in the crude product) is achieved at **1** : KOH molar ratio of 2:1, 80 °C and the reaction time of 1.5 h (entry 2, Table 1). The vinyl ether **2** is isolated in 53% yield by column chromatography (basic Al_2O_3) along with unreacted alcohol **1** (71% conversion).

The reduction of the nitroxyl moiety of **1** and/or **2** during the vinylation under the above conditions is nontrivial since the nitroxyl radicals are known to be quite stable in basic media. In this case the reducing agent may be either DMSO (being further oxidized to dimethylsulfone) or acetaldehyde (the product of side hydration of acetylene).

To suppress the reduction of alcohol **1** and vinyl ether **2**, leading to the formation of side products **3**, **4**, the vinylation of **1** was conducted in an autoclave under elevated pressure of acetylene (initial loading pressure at room temperature 10-12 atm, maximum pressure at the reaction temperature 9 atm). At 70 °C with 100 mol% KOH the vinylation proceeds rapidly (about 20 min for 10 mmol loading of **1**) so that the undesirable reduction of the nitroxyl moiety of **1** and **2** does not take place, and hence the target vinyl ether **2** is a major product; its isolated yield reaches 67%.

Further, aiming to develop an efficient synthesis of other spin-labeled enol ethers (hitherto unknown), we extended the reaction studied to aryl- and hetarylacetylenes. The experiments showed that, under the modified conditions, in a suspension of KOH (50 mol%) in DMSO, alcohol **1** regioselectively reacts with phenylacetylene, 4-*tert*-butylphenylacetylene and 3-ethynylpyridine (70 °C, 2 h) to give vinyl ethers **5a-c** as mixtures of *E*- and *Z*-isomers in 58-64% total yields (Table 2). Because ^{1}H NMR analysis of the products **5** is impossible because of their paramagnetic nature, to determine the *Z/E*-isomeric ratio of alkenes **5a-c** their crude mixtures were reduced to the corresponding nonparamagnetic hydroxylamines with hydrazine hydrate under mild conditions (ethanol, 40-45 °C, 2 h), in which the *Z/E*-isomerization is assumed to be improbable. Thus, the ratio of the formed diamagnetic hydroxylamines, according to ^{1}H NMR analysis, closely corresponds to the ratio of parent vinyl ethers **5a-c**. As can be seen from Table 2, *Z*-isomers always predominate over the *E*-adducts as is typical for nucleophilic addition to alkynes.[41]

Table 2. Regioselective vinylation of alcohol **1** with arylacetylenes[a]

R = Ph (**a**), 4-^{t}BuC$_6$H$_4$ (**b**), 3-Py (**c**)
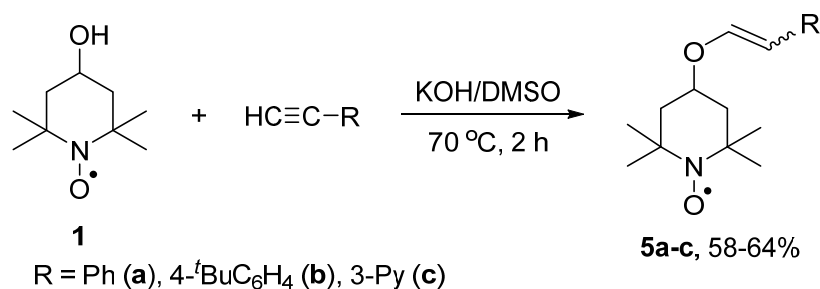
Entry	Alkyne	Product	*Z/E* ratio of **5a-c** in the reaction mixture[b]	Isolated yield of **5a-c** (%) (*Z/E* ratio)[c]
1		(5a)	74:26	58 (5:2)
2		(5b)	80:20	64 (3:1)
3		(5c)	60:40	60 (3:1)

[a] Reaction conditions: alcohol **1** (10 mmol), alkyne (10 mmol), KOH·0.5H$_2$O (5 mmol), DMSO (50 mL), atmospheric pressure, 70 °C, 2 h.   [b] Determined by ^{1}H NMR analysis of the reaction mixtures, pre-treated with hydrazine hydrate (40-45 °C, EtOH, 2 h).   [c] Isolated yields after chromatographic purification.

Apart from the major products **5a-c**, the reaction mixtures contained, according to GC/MS analysis, minor amounts of the starting alcohol **1** and the corresponding piperidines **6a-c**, which were formed by reduction of nitroxyls **5a-c**. One of the piperidines, 2,2,6,6-tetramethyl-4-[(*Z*)-(2-phenylethenyl)oxy]piperidine (**6b**), was isolated in 2% yield by column chromatography.

The fractional crystallization of crude products **5a**,**b** from hexane allows their *Z*-isomers to be isolated in pure form. Interestingly, the heating of (*Z*)-**5b** in the KOH (50 mol%) / DMSO suspension (70 °C, 2 h) does not lead to its isomerization into the thermodynamically preferable *E*-isomer. This result clearly suggests that the *E*-isomers are formed during the nucleophilic

addition of alcohol **1** to the alkynes, and their formation is not due to isomerization of the kinetically preferable *Z*-isomers.

The synthesized paramagnetic vinyl ethers **2** and **5a-c** were characterized by X-ray crystallography (for **2**, (*Z*)-**5a** and (*Z*)-**5b**), EPR, EI-MS and FT-IR techniques. In the EI-MS spectra of adducts **2** and **5a-c**, the intense peaks of the molecular ions, [M]$^{+\bullet}$, are presented. In the FT-IR spectra of these compounds, the stretching vibration of the N–O bonds appears as a medium intensity band at 1364-1365 cm^{-1}.

Compounds **2**, (*Z*)-**5a** and (*Z*)-**5b** crystallized from hexane in the monoclinic P21/c space group with four molecules per unit cell. Their molecular structures are shown in Figures 1-3. The piperidine rings in these compounds adopt the expected chair conformation.[47-49] The N–O bonds are in an equatorial position of the piperidine ring. The N(1)–O(2) distances are nearly equal in length (1.286-1.291 Å) and comparable with these in similar compounds.[47-49] Within (*Z*)-**5a** and (*Z*)-**5b** molecules, short intramolecular C-H⋯O contacts (2.383 and 2.367 Å, respectively) between an *ortho*-hydrogen atom of the benzene ring and the oxygen atom of the vinyloxy moiety are observed. The C(3)–O(1)–C(2)–C(1) and C(4)–O(1)–C(5)–C(6) torsion angles in **2** and (*Z*)-**5b,** respectively, are -151.78º and -150.39º, while the values of the C(7)–O(1)–C(6)–C(5) torsion angle in (*Z*)-**5a** are -179.67º.
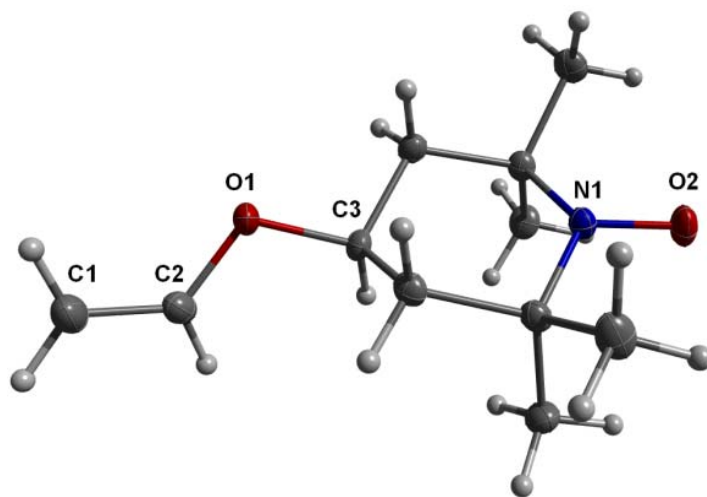

Figure 1. The X-Ray structure of **2**. Selected bond distances (Å) and angles (°): O(2)–N(1) 1.2879(11), O(1)–C(2) 1.3653(13), O(1)–C(3) 1.4430(11), C(1)–C(2) 1.3183(15), C(2)–O(1)–C(3) 113.36(8), C(1)–C(2)–O(1) 122.37(11).
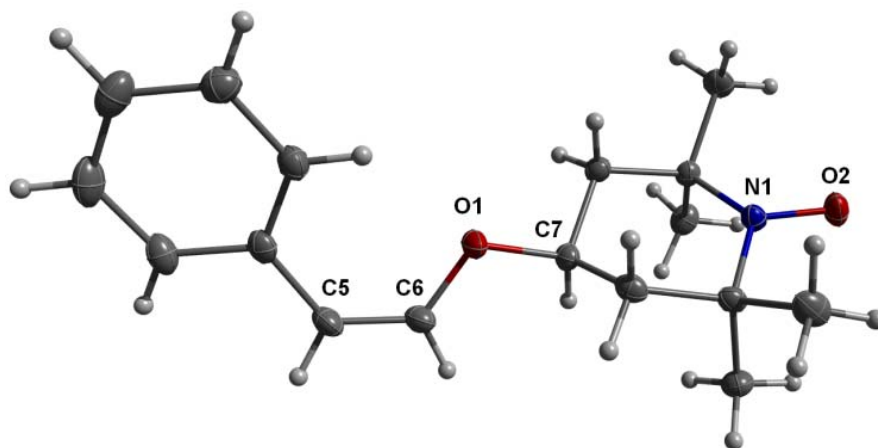
Figure 2. The X-Ray structure of **5a**. Selected bond distances (Å) and angles (°): O(2)–N(1) 1.2909(11), O(1)–C(6) 1.3583(12), O(1)–C(7) 1.4474(11), C(5)–C(6) 1.3364(15), C(6)–O(1)–C(7) 114.95(8), C(5)–C(6)–O(1) 123.64(10).
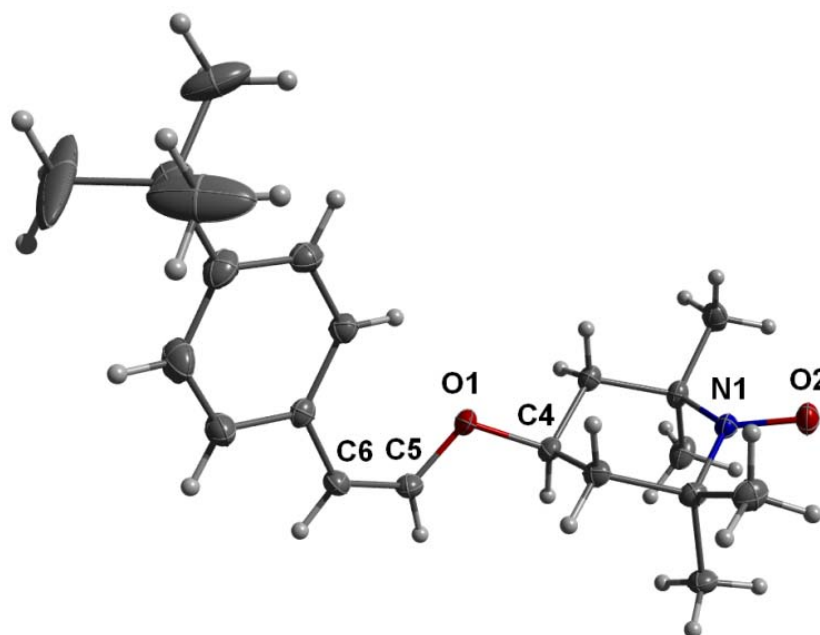

Figure 3. The X-Ray structure of **5b**. Selected bond distances (Å) and angles (°): O(2)–N(1) 1.2868(14), O(1)–C(5) 1.3586(17), O(1)–C(4) 1.4504(15), C(5)–C(6) 1.335(2), C(5)–O(1)–C(4) 114.41(10), C(6)–C(5)–O(1) 123.94(13).

The EPR spectra of all nitroxyl radicals in various solvents (CHCl$_3$, benzene, DMSO) reveal a stable signal of three intense equidistant lines (see typical signal in Figure 4). The isotropic hyperfine coupling constants for the ^{14}N of all nitroxyl radicals are 15.4-15.8 G and are almost independent of the functionalization of the vinyl fragment and solvent (Table 3). Clearly, the

modification of the vinyl ethers **2** and **5a-b** at hydroxyl oxygen atom does not change the geometry of the six-membered ring and the radical center on the oxygen atom at which the electron spin is localized. Stability of the electron-spin values, depending on structure of the substituents in the nitroxyl radicals, is one of the essential conditions for the successful application of the radicals as spin probes.[2,13,14]
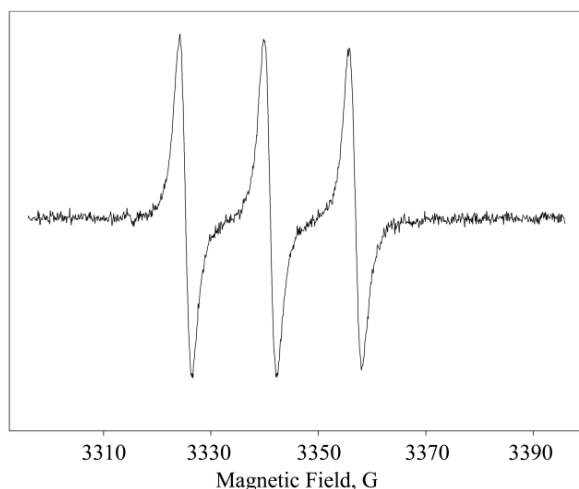

Figure 4. Typical EPR spectrum for vinyl ethers **2** and **5a-c.**

Table 3. EPR characteristics of **2** and **5a-c** in different solvents (288 K)

Compound	Solvent	g-factor	Constant A_N, G	Width ΔH, G
2	CHCl₃	2.0064	15.8	2.5
	benzene	2.0066	15.4	2.5
	DMSO	2.0065	15.7	1.6
5a	CHCl₃	2.0062	15.8	2.2
	benzene	2.0065	15.4	2.5
	DMSO	2.0064	15.7	1.5
5b	CHCl₃	2.0064	15.8	2.4
	benzene	2.0066	15.4	2.5
	DMSO	2.0065	15.7	1.6
5c	CHCl₃	2.0063	15.7	2.3
	benzene	2.0066	15.4	2.5
	DMSO	2.0065	15.7	1.6

Expectedly, when dissolved in polar solvent like DMSO, the linewidth becomes significantly narrower (Table 3, Figure 5). In a DMSO solution (at 288 K), anisotropy of the EPR

spectra is observed due to orientation of the radical relative to external magnetic field. Only in the polar solvent is resolution of each line of the triplet detected from coupling to ^{1}H nuclei.
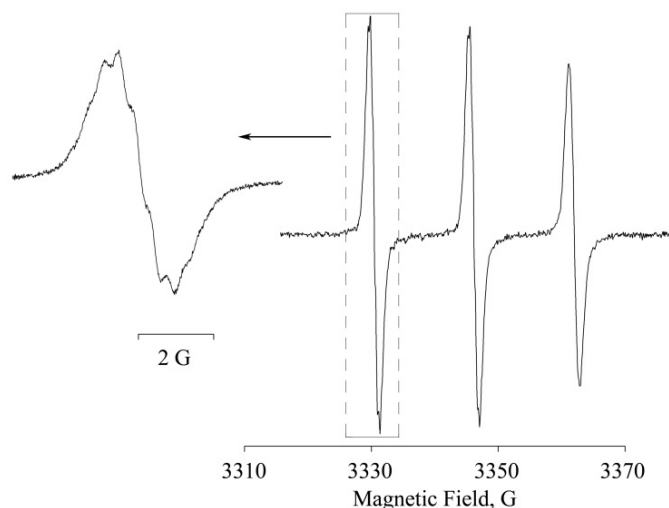

Figure 5. EPR Spectrum **2** in DMSO (288 K).

Conclusions

In summary, a general and efficient methodology for the synthesis of enol ethers bearing paramagnetic TEMPO moieties has been developed using the KOH/DMSO-catalyzed regioselective hydroalkoxylation of diverse alkynes by available 4-hydroxy-TEMPO. This reaction readily proceeds under environmentally benign transition metal free conditions at atmospheric pressure and mild heating (up to 80 ^{o}C). The methodology represents a facile and concise route to prospective spin labels containing reactive enol ether groups.

Experimental Section

General. The FT-IR spectra were recorded on a Bruker Vertex 70 spectrometer. NMR spectra were recorded on Bruker DPX-400 spectrometer (400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C) at ambient temperature for CDCl$_3$ solutions. Chemical shifts were reported in δ (ppm) relative to CDCl$_3$ (^{1}H, ^{13}C) as internal standard. Prior to recording of NMR spectra, the paramagnetic compounds were reduced with ~5 equivalets of hydrazine hydrate (EtOH, 40-45 ^{o}C, 2 h). The EI-MS spectra were on an Agilent 5975C MSD instrument. Samples were introduced into the source by means of the gas chromatograph GC-6890N (Agilent Technologies) through capillary column HP-5MS (30 m × 0.25 mm × 0.25 mm), the helium being the gas-carrier. The source temperature was approximately 150 °C. The elemental analyses were carried out on a Flash EA

1112 analyzer. Melting points were determined on a Kofler micro-hot stage. The high-pressure experiments were carried out in a stainless steel, high-pressure batch reactor (Parr 4572, Parr Instrument Co.) equipped with an electrical heating jacket, a gas inlet, a mechanical stirrer and 4848A temperature controller. Basic Al_2O_3 was used for column chromatography and SiO_2 plates for TLC (50% Et_2O/hexane). Visualization was performed with iodine vapor. Alcohol **1**, $KOH \cdot 0.5H_2O$, DMSO (up to 0.5% of water) and all other reagents are commercially available and were used without further purification.

Crystallography

The single crystals of **2**, **5a** and **5b** were obtained by slow evaporation of solutions in hexane. The data were collected on a Bruker D8 Venture diffractometer by using graphite monochromatic MoKα radiation (λ = 0.71073 Å). Structures were solved by direct method and were refined against the least-squares methods on F^2 with the SHELXL-97 package,[50] incorporated in SHELXTL-PC V6.14.8. All non-hydrogen atoms were refined anisotropically. CCDC 990980 (**2**), 990592 (**5a**) and 1054445 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for 2. $C_{11}H_{20}NO_2$ (M = 198.28), monoclinic, space group P21/c, a =11.5408(4) Å, b = 10.0341(4) Å, c = 11.2571(5) Å, β = 115.9670(10)°, V = 1171.99(8) Å^3, Z = 4, T = 100.0 K, μ(MoK$_\alpha$) = 0.075 mm^{-1}, D_{calc} = 1.157 g/mm^3. 24498 reflections measured (2.32° < 2θ < 30.04°), 3440 of which were independent (R$_{int}$ = 4.69%) and 2760 (80.23%) were greater than 2σ(F^2). The final anisotropic full-matrix least-squares refinement on F^2 with 131 variables converged at R1 = 4.28%, for the observed data and wR2 = 11.49% for all data. The goodness-of-fit was 1.088.

Crystal data for 5a. $C_{17}H_{24}NO_2$ (M = 274.37), monoclinic, space group P21/c, a = 14.5414(11) Å, b = 10.1248(7), c = 11.1582(8) Å, V = 1575.6(2) Å^3, Z = 4, T = 100.0 K, μ(MoK$_\alpha$) = 0.075 mm^{-1}, D_{calc} = 1.157 g/mm^3. 47329 reflections measured (2.49 ≤ 2θ ≤ 30.07), 4617 of which were independent (R$_{int}$ = 5.23%) and 3841 (83.19%) were greater than 2σ(F^2). The final anisotropic full-matrix least-squares refinement on F^2 with 185 variables converged at R1 = 4.37%, for the observed data and wR2 = 12.03% for all data. The goodness-of-fit was 1.028.

Crystal data for 5b. $C_{21}H_{32}NO_2$ (M = 330.47), monoclinic, space group P21/c, a = 6.0530(3) Å, b = 11.9835(6), c = 27.0370(12) Å, β = 94.756(2)º, V = 1954.41(16) Å^3, Z = 4, T = 100.0 K, μ(MoK$_\alpha$) = 0.071 mm^{-1}, D_{calc} = 1.123 g/mm^3. 66186 reflections measured (2.49 ≤ 2θ ≤ 30.07), 5739 of which were independent (R$_{int}$ = 8.99%) and 4280 (74.58%) were greater than 2σ(F^2). The final anisotropic full-matrix least-squares refinement on F^2 with 254 variables converged at R1 = 5.89%, for the observed data and wR2 = 14.61% for all data. The goodness-of-fit was 1.053.

EPR Spectroscopy. CW Spectra were recorded with FT X-band Bruker ELEXSYS E-580 spectrometer (X-wave range 9.7 GHz). Precision of the measurement of g-factor was ±0.0002. Spectra were recorded at the following conditions: amplitude modulation 0.3 G, receiver gain 60

dB, time constant 0.02 s, conversion time 0.06 s, microwave power 0.6325 mW at room temperature in quartz tubes (3 mm caliber tube were used for CHCl$_3$ and benzene solutions, whereas 1 mm caliber was used for DMSO solutions). Concentration of the samples was $1 \cdot 10^{-6}$ M.

Synthetic procedures

Vinylation of 4-hydroxy-TEMPO (1) with acetylene in the KOH/DMSO system at atmospheric pressure

Method A. The dry acetylene was fed into the heated (80 $^{\mathrm{o}}$C) mixture of alcohol **1** (3.44 g, 20 mmol), KOH·0.5H$_2$O (0.65 g, 10 mmol) and DMSO (50 mL) for 1.5 h. The reaction mixture was cooled to room temperature, diluted with an aqueous 1% solution of NH$_4$Cl (50 mL) and extracted with diethyl ether (6 × 20 mL). The combined extracts were washed with water (3 × 15 mL) and dried over K$_2$CO$_3$. Removal of the solvent gave a crude product containing vinyl ethers **2** (65.4%), **3** (4.0%), **4** (2.1%) and unreacted alcohol **1** (28.4%) (GLC). The crude product was separated by column chromatography (basic Al$_2$O$_3$): first vinyl ether **2** was washed off with hexane, and then initial alcohol **1** was washed with chloroform / benzene / ethanol mixture (20:4:1).

Method B. A 0.3-L Parr reactor equipped with a magnetic stirrer (250 rpm) was charged with alcohol **1** (1.72 g, 10 mmol), KOH·0.5H$_2$O (0.65 g, 10 mmol) and DMSO (50 mL). The reactor was fed with nitrogen and then decompressed to atmospheric pressure to remove air. The reactor was fed with acetylene (initial pressure was 10 atm) and heated at 70 °C for 20 min (the pressure maximum was about 9 atm). After cooling to room temperature the reaction mixture was discharged, the DMSO solution was poured into ice water (100 mL), neutralized with NH$_4$Cl, and extracted with diethyl ether (5 × 50 mL). The organic layers were combined, washed with H$_2$O (3 × 50 mL) and dried over K$_2$CO$_3$. After distilling off the solvents, the residue was chromatographed on the column (1.0 × 10 cm) to afford vinyl ether **2**.

Synthesis of vinyl ether 3. The dry acetylene was fed into the heated (90 $^{\mathrm{o}}$C) mixture of alcohol **1** (3.44 g, 20 mmol), KOH·0.5H$_2$O (1.05 g, 15 mmol) and DMSO (50 mL) for 4 h. The reaction mixture was cooled to room temperature, diluted with an aqueous 1% solution of NH$_4$Cl (50 mL) and extracted with diethyl ether (6 × 20 mL). The combined extracts were washed with water (3 × 15 mL) and dried over K$_2$CO$_3$. After removal of the solvent, 3.31 g of a crude residue was obtained, which was distilled in vacuum to give 2,2,6,6-tetramethyl-4-(vinyloxy)piperidine (**3**).

Vinylation of 4-hydroxy-TEMPO (1) with arylacetylenes in the KOH/DMSO system (general procedure). A mixture of alcohol **1** (1.72 g, 10 mmol), arylacetylene (10 mmol), KOH·0.5H$_2$O (0.33 g, 5 mmol) and DMSO (50 mL) was stirred at 70 $^{\mathrm{o}}$C for 2 h. After cooling (20-25 $^{\mathrm{o}}$C), the reaction mixture was diluted with water (20 mL), neutralized with NH$_4$Cl and extracted with Et$_2$O (6 × 10 mL). The organic extract was washed with water (3 × 10 mL) and dried over Na$_2$SO$_4$. Column chromatography (basic Al$_2$O$_3$, eluent hexane/diethyl ether with gradient 1:0 to 0:1) of a crude residue after removal of the solvent gave the pure adducts **5** and **6b**.

Characterization data for synthesized compounds

2,2,6,6-Tetramethyl-4-(vinyloxy)piperidine-1-oxyl (2). Bright red crystals, mp 32 ^{o}C (*n*-hexane). Yield: 2.09 g, 53% (method A), 1.33 g, 67% (method B). IR (KBr): 3116 (=C−H), 1637, 1618 (C=C), 1439 (=CH$_2$), 1364 (N−O·), 1327 (=CH), 1198 (C−O−C), 965, 822 (OCH=CH$_2$) cm^{-1}. ^{1}H NMR (400.13 MHz, CDCl$_3$ + NH$_2$-NH$_2$): δ 1.17 and 1.21 (two s, each 6 H, Me), 1.53 (t, 2 H, $^3J_{HH} \approx {}^2J_{HH}$ 11.7 Hz, H$_a^{3,5}$), 2.07 (dd, 2 H, $^2J_{HH}$ 11.7 Hz, $^3J_{HH}$ 2.3 Hz, H$_e^{3,5}$), 4.01 (d, 1 H, $^3J_{cis}$ 6.7 Hz, CH$_2$=), 4.05-4.10 (m, 1 H, H^4), 4.28 (d, 1 H, $^3J_{trans}$ 14.2 Hz, CH$_2$=), 6.33 (dd, 1 H, $^3J_{cis}$ 6.6 Hz, $^3J_{trans}$ 14.1 Hz, CH=). ^{13}C NMR (100.62 MHz, CDCl$_3$ + NH$_2$-NH$_2$): d 20.0 (Me), 31.4 (Me), 43.7 (C^{3,5}), 58.4 (C^{2,6}), 70.1 (C^4), 87.6 (CH$_2$=), 149.7 (CH=). Anal. Calcd. for C$_{11}$H$_{20}$NO$_2$: C, 66.57; H, 10.09; N, 7.06. Found: C, 66.64; H, 10.18; N, 7.33. Mass spectrum (EI), *m/z*: 198 [M]$^{+}$. The analytical data are in agreement with the literature.[24]

2,2,6,6-Tetramethyl-4-(vinyloxy)piperidine (3). Colorless liquid, b.p. 50-52 ^{o}C/2 mmHg, n$_D^{20}$ 1.4640. Yield: 2.16 g, 59%. IR (film): 3324 (NH), 3116 (=C−H), 1634, 1607 (C=C), 1440 (=CH$_2$), 1326 (=CH), 1196 (C−O−C), 965, 813 (OCH=CH$_2$) cm^{-1}. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 1.10 (t, 2 H, $^3J_{HH} \approx {}^2J_{HH}$ 11.8 Hz, H$_a^{4,6}$), 1.14 and 1.19 (two s, each 6 H, Me), 1.96 (dd, 2 H, $^2J_{HH}$ 12.7 Hz, $^3J_{HH}$ 4.0 Hz, H$_e^{4,6}$), 3.99 (dd, 1 H, $^3J_{HH}$ 6.5 Hz, $^2J_{HH}$ 1.3 Hz, CH$_{cis}$=), 4.16 (m, 1 H, H^4), 4.27 (dd, 1 H, $^3J_{HH}$ 14.2 Hz, $^2J_{HH}$ 1.3 Hz, CH$_{trans}$=), 6.33 (dd, 1 H, $^3J_{HH}$ 14.2 Hz, $^3J_{HH}$ 6.5 Hz, CH=). ^{13}C NMR (100.62 MHz, CDCl$_3$): δ 29.0 (Me), 34.7 (Me), 44.3 (C^{3,5}), 51.4 (C^{2,6}), 72.8 (C^4), 88.2 (CH$_2$=), 150.2 (CH=). Anal. Calcd for C$_{11}$H$_{21}$NO: C, 72.08; H, 11.55; N, 7.64. Found: C, 72.52; H, 11.78; N, 7.44. Mass spectrum (EI), *m/z*: 168 [M-15]$^{+}$. The analytical data are in agreement with the literature.[24]

(*Z/E*)-2,2,6,6-Tetramethyl-4-[(2-phenylethenyl)oxy] piperidine-1-oxyl (5a). Mixture of *Z*- and *E*-isomers (5:2), combined yield: 1.60 g (58%). Individual *Z*-isomer **5a** is light salmon solid, mp 117-118 °C (*n*-hexane). *E*-isomer was not isolated in a pure state. Its structure was determined after transformation of mixture *Z*- and *E*-**5a** (obtained after column chromatography) into the *N*-hydroxylamine compounds. IR (KBr) for *Z*-isomer: 3088 (=C−H), 1650 (C=C), 1448 (=CH$_2$), 1365 (N−O·), 1351 (=CH), 1198 (C−O−C), 990, 806 (OCH=CH) cm^{-1}. ^{1}H NMR (400.13 MHz, CDCl$_3$ + NH$_2$-NH$_2$) for *Z*-isomer: δ 1.20 and 1.24 (two s, each 6 H, Me), 1.70 (t, 2 H, $^2J_{HH} \approx {}^3J_{HH}$ 11.8 Hz, H$_a^{3,5}$), 2.02 (dd, 2 H, $^2J_{HH}$ 11.8 Hz, $^3J_{HH}$ 2.2 Hz, H$_e^{3,5}$), 4.02-4.08 (m, 1 H, H^4), 5.25 (d, 1 H, $^3J_{HH}$ 6.8 Hz, C*H*Ph), 6.26 (d, 1 H, $^3J_{HH}$ 6.8 Hz, OCH=), 7.12-7.57 (m, 5 H in Ph); for *E*-isomer: δ 1.20 and 1.24 (two s, each 6 H, Me), 1.61 (t, 2 H, $^2J_{HH} \approx {}^3J_{HH}$ 11.7 Hz, H$_a^{3,5}$), 2.02 (dd, 2 H, $^2J_{HH}$ 11.8 Hz, $^3J_{HH}$ 2.2 Hz, H$_e^{3,5}$), 4.14 (m, 1 H, H^4), 5.94 (d, 1 H, $^3J_{HH}$ 12.7 Hz, C*H*Ph), 6.88 (d, 1 H, $^3J_{HH}$ 12.7 Hz, OCH=), 7.12-7.57 (m, 5 H in Ph). ^{13}C NMR (100.62 MHz, CDCl$_3$+ NH$_2$-NH$_2$) for *Z*-isomer: δ = 20.1 (Me), 28.5 (Me), 44.6 (C^{3,5}), 58.6 (C^{2,6}), 74.4 (C^4), 105.6 (Ph*C*H=), 125.2 (*p*-C in Ph), 127.6, 127.7 (*o,m*-C in Ph), 135.6 (*ipso*-C in Ph), 144.5 (OCH=); for *E*-isomer: δ = 20.2 (Me), 28.3 (Me), 44.4 (C^{3,5}), 58.6 (C^{2,6}), 72.6 (C^4), 107.5 (Ph*C*H=), 125.6 (*p*-C in Ph), 127.4, 127.6 (*o,m*-C in Ph), 135.8 (*ipso*-C in Ph), 145.7 (OCH=). Anal. Calcd. for C$_{17}$H$_{24}$NO$_2$: C, 74.35; H, 8.75; N, 5.10. Found: C, 74.48; H, 8.88; N, 5.25. Mass spectrum (EI), *m/z*: 274 [M]$^{+}$.

(*Z/E*)-2,2,6,6-Tetramethyl-4-{[2-(4-tert-butyl)phenyl]ethenyloxy}piperidine-1-oxyl   **(5b)**.
Mixture of *Z*- and *E*-isomers (3:1), combined yield: 2.11 g (64%). Individual *Z*-isomer **5b** is pink
solid, mp 131-133 °C (*n*-hexane). *E*-isomer was not isolated in a pure state. Its structure was
determined after transformation mixture (*Z*)- and (*E*)-**5b** (obtained after column
chromatography) into the *N*-hydroxylamine compounds. IR (KBr) for *Z*-isomer: 3089 (=C−H),
1649 (C=C), 1465 (=CH$_2$), 1365 (N−O·), 1352 (=CH), 1191 (C−O−C), 990, 839 (OCH=CH)
cm^{-1}. ^{1}H NMR (400.13 MHz, CDCl$_3$ + NH$_2$-NH$_2$) for *Z*-isomer: δ 1.20 and 1.24 (two s, each 6 H,
Me), 1.31 (s, 9 H, *t*-Bu), 1.70 (t, 2 H, $^2J_{HH} \approx {}^3J_{HH}$ 11.8 Hz, H$_a^{3,5}$), 2.04 (dd, 2 H, $^2J_{HH}$ 11.8 Hz,
$^3J_{HH}$ 3.9 Hz, H$_e^{3,5}$), 4.01-4.10 (m, 1 H, H^4), 5.24 (d, 1 H, $^3J_{HH}$ 7.0 Hz, =C*H*Ar), 6.24 (d, 1 H, $^3J_{HH}$
7.0 Hz, OCH=), 7.33 (d, 2 H, $^3J_{HH}$ 8.2 Hz, H^{3,5} in Ar), 7.54 (d, 2 H, $^3J_{HH}$ 8.2 Hz, H^{2,6} in Ar); for
E-isomer: δ 1.20 and 1.24 (two s, each 6 H, Me), 1.31 (s, 9 H, *t*-Bu), 1.60 (t, 2 H, $^2J_{HH} \approx {}^3J_{HH}$
11.6 Hz, H$_a^{3,5}$), 1.99 (dd, 2 H, $^2J_{HH}$ 11.8 Hz, $^3J_{HH}$ 3.9 Hz, H$_e^{3,5}$), 4.10-4.16 (m, 1 H, H^4), 5.94 (d,
1 H, $^3J_{HH}$ 12.7 Hz, =C*H*Ar), 6.83 (d, 1 H, $^3J_{HH}$ 12.7 Hz, OCH=), 7.17 (d, 2 H, $^3J_{HH}$ 8.0 Hz, H^{3,5} in
Ar), 7.29 (d, 2 H, $^3J_{HH}$ 8.0 Hz, H^{2,6} in Ar). ^{13}C NMR (100.62 MHz, CDCl$_3$+ NH$_2$-NH$_2$) for *Z*-
isomer: δ 19.7 (Me), 30.5 (Me in *t*-Bu), 31.4 (Me), 33.6 (C in *t*-Bu), 44.2 (C^{3,5}), 58.2 (C^{2,6}), 73.7
(C^4), 105.0 (Ar*C*H=), 124.2 (C^{3,5} in Ar), 127.0 (C^{2,6} in Ar), 132.4 (C^4 in Ar), 143.6 (OCH=),
147.6 (C^1 in Ar); for *E*-isomer: δ = 19.9 (Me), 30.5 (Me in *t*-Bu), 31.1 (Me), 33.6 (C in *t*-Bu),
43.8 (C^{3,5}), 58.2 (C^{2,6}), 71.7 (C^4), 107.0 (Ar*C*H=), 124.0 (C^{3,5} in Ar), 124.6 (C^{2,6} in Ar), 132.6 (C^4
in Ar), 145.0 (OCH=), 147.9 (C^1 in Ar). Anal. Calcd. for C$_{21}$H$_{32}$NO$_2$: C, 76.25; H, 9.68; N, 4.24.
Found: C, 75.93; H, 9.81; N, 3.98. Mass spectrum (EI), *m/z*: 330 [M]$^+$.

(*Z/E*)-2,2,6,6-Tetramethyl-4-{[2-(3-pyridinyl)ethenyl]oxy}piperidine-1-oxyl **(5c).** Could not
separate *E*- and *Z*-isomers. Coral powder, mp 90-92 ^{o}C (*n*-hexane) (mixture of *Z*- and *E*-isomers,
3:1). Combined yield: 1.66 g (60%). IR (KBr): 3082 (=C−H), 1652 (C=C), 1437 (=CH$_2$), 1364
(N−O·), 1353 (=CH), 1192 (C−O−C), 990, 811 (OCH=CH) cm^{-1}. ^{1}H NMR (400.1 MHz, CDCl$_3$
+ NH$_2$-NH$_2$) for *Z*-isomer: δ 1.19 and 1.23 (two s, each 6 H, Me), 1.69 (t, 2 H, $^2J_{HH} \approx {}^3J_{HH}$ 11.5
Hz, H$_a^{3,5}$), 2.00 (dd, 2 H, $^2J_{HH}$ 11.5 Hz, $^3J_{HH}$ 3.5 Hz, H$_e^{3,5}$), 4.05-4.11 (m, 1 H, H^4), 4.44 (br s, 1
H, OH), 5.21 (d, 1 H, $^3J_{HH}$ 6.8 Hz, =C*H*Py), 6.38 (d, 1 H, $^3J_{HH}$ 6.8 Hz, OCH=), 7.15-7.19 (m, 1
H, H^5 in Py), 7.95 (d, 1 H, $^3J_{HH}$ 8.0 Hz, H^4 in Py), 8.35-8.38 (m, 1 H, H^6 in Py), 8.70 (s, 1 H, H^2
in Py); for *E*-isomer: δ 1.20 and 1.23 (two s, each 6 H, Me), 1.62 (t, 2 H, $^2J_{HH} \approx {}^3J_{HH}$ 11.6 Hz,
H$_a^{3,5}$), 1.97 (dd, 2 H, $^2J_{HH}$ 11.6 Hz, $^3J_{HH}$ 4.2 Hz, H$_e^{3,5}$), 4.12-4.19 (m, 1 H, H^4), 4.44 (br s, 1 H,
OH), 5.86 (d, 1 H, $^3J_{HH}$ 12.8 Hz, =C*H*Py), 6.91 (d, 1 H, $^3J_{HH}$ 12.8 Hz, OCH=), 7.15-7.19 (m, 1 H,
H^5 in Py), 7.51 (d, 1 H, $^3J_{HH}$ = 8.2 Hz, H^4 in Py), 8.35-8.38 (m, 1 H, H^6 in Py), 8.47 (s, 1 H, H^2 in
Py). ^{13}C NMR (100.62 MHz, CDCl$_3$+ NH$_2$-NH$_2$) for *Z*-isomer: δ 20.3 (Me), 32.2 (Me), 44.9
(C^{3,5}), 58.8 (C^{2,6}), 75.3 (C^4), 102.1 (=*C*HPy), 122.9 (C^5 in Py), 131.9 (C^1 in Py), 134.7 (C^6 in Py),
146.2 (CHO), 146.6 (C^2 in Py), 149.2 (C^4 in Py); for *E*-isomer: δ 20.7 (Me), 31.8 (Me), 44.5
(C^{3,5}), 58.8 (C^{2,6}), 73.1 (C^4), 104.0 (=*C*HPy), 123.2 (C^5 in Py), 131.5 (C^6 in Py), 132.2 (C^1 in Py),
146.8 (CHO, C^2 in Py), 147.7 (C^4 in Py). Anal. Calcd. for C$_{16}$H$_{23}$N$_2$O$_2$: C, 69.72; H, 8.35; N,
10.17. Found: C, 69.95; H, 8.02; N, 9.70. Mass spectrum (EI), *m/z*: 275 [M]$^+$.

4-{(*Z*)-2-[4-(tert-butyl)phenyl]ethenyloxy}-2,2,6,6-tetramethylpiperidine **(6b)**. Yellowish
solid. Yield: 0.065 g (2%). ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 1.20 and 1.24 (two s, each 6 H,

Me), 1.27 (t, 2 H, $^2J_{HH} \approx {}^3J_{HH}$ 12.2 Hz, H$_a^{3,5}$), 1.33 (s, 9 H, t-Bu), 2.09 (dd, 2 H, $^2J_{HH}$ 12.2 Hz, $^3J_{HH}$ 3.8 Hz, H$_e^{3,5}$), 4.13-4.20 (m, 1 H, H^4), 5.25 (d, 1 H, $^3J_{HH}$ 6.8 Hz, =CHAr), 6.30 (d, 1 H, $^3J_{HH}$ 6.8 Hz, OCH=), 7.32 (d, 2 H, $^3J_{HH}$ 8.2 Hz, H^{3,5} in Ar), 7.55 (d, 2 H, $^3J_{HH}$ 8.2 Hz, H^{2,6} in Ar). ^{13}C NMR (100.62 MHz, CDCl$_3$): δ 28.5 (Me), 30.8 (Me in t-Bu), 33.9 (C in t-Bu), 34.4 (Me), 44.6 (C^{3,5}), 51.0 (C^{2,6}), 76.3 (C^4), 105.6 (ArCH=), 124.5 (C^{3,5} in Ar), 127.3 (C^{2,6} in Ar), 132.8 (C^4 in Ar), 144.0 (OCH=), 147.9 (C^1 in Ar). Anal. Calcd for C$_{21}$H$_{33}$NO: C, 79.95; H, 10.54; N, 4.44. Found: C, 79.91; H, 10.46; N, 4.88. Mass spectrum (EI), m/z: 300 [M-15]$^+$.

Acknowledgements

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