Cross-coupling of aryl iodides with paramagnetic terminal acetylenes derived from 4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide

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2-(Arylylethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxides **12** and **13** were synthesized by cross-coupling of aryl iodides with 1-alkynes containing the 4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide fragment. A procedure was developed for the preparation of 3- and 4-ethynylbenzaldehydes with the use of 2-methylbut-3-yn-2-ol.

Key words: alkynes, cross-coupling, nitroxyl radicals, aryl iodide, imidazoline oxide.

Previously,[1] we have demonstrated that compounds with the structure A—Sp—R$^\bullet$, where A is the aromatic group, R$^\bullet$ is the stable radical center, and Sp is the bridging fragment (spacer), are convenient models for studying spin catalysis. It was found that the presence of the radical center R$^\bullet$ in the ion-radical pair (alkane)$^{\bullet+}$/$^{-\bullet}$A—Sp—R$^\bullet$ leads to the disappearance or rapid (nanoseconds) attenuation of the magnetic effect in luminescence arising from recombination of these pairs. This effect was observed for *p*-terphenyl derivatives. To answer the question about the influence of the nature of the luminophore A on the magnetic effect, it is necessary to study substrates of the A—Sp—R$^\bullet$ type in which the luminophore is varied, while the Sp and R$^\bullet$ fragments remain unchanged. In this connection, we undertook the present investigation in order to synthesize paramagnetic linear aromatic compounds in which the aromatic group A is regularly changed (phenyl, biphenylyl, and *p*-terphenylyl).

Generally, derivatives of 2-imidazoline nitroxyls are synthesized by condensation of aldehydes or their synthetic equivalents with 2,3-bis(hydroxyamino)-2,3-dimethylbutane (BHA) or its monosulfate followed by oxidation of cyclic adducts with sodium periodate or lead dioxide.[2] This procedure was used for the preparation of derivatives of 2-(ethynylphenyl)-2-imidazoline nitroxyls.[3—8] Previously,[1] we have failed to apply this procedure to the synthesis of 2-(terphenylylethynylphenyl)-2-imidazoline nitroxyl from *p*-(terphenylylethynyl)benzaldehyde. The target paramagnetic arylacetylene has been synthesized in low yield by the reaction of iodoterphenyl with 4,4,5,5-tetramethyl-2-(4-ethynylphenyl)-2-imidazoline-1-oxyl 3-oxide.

In the present study, the reactions of (arylethynyl)benzaldehydes with BHA and cross-coupling of aryl iodides with paramagnetic terminal acetylenes, *viz.*, derivatives of 4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide, were examined in detail with the aim of preparing new 2-(arylethynylphenyl)imidazoline nitroxyls.

Results and Discussion

As mentioned above, the key stage of the synthesis of 2-(arylethynylphenyl)-2-imidazoline-1-oxyl 3-oxides according to Ullman's procedure[2] involves the reactions of aldehydes with BHA. With this in mind, we prepared a series of arylethynylbenzaldehydes **3a—c** by cross-coupling of aryl iodides **1a—c** with *p*-ethynylbenzaldehyde (**2a**) and then treated them with BHA. However, the reactions of 4-(phenylethynyl)benzaldehyde (**3a**) or 4-(biphenylyl-4-ethynyl)benzaldehyde (**3b**) with BHA in the presence of atmospheric oxygen led to oxidation of aldehydes (instead of condensation) to form the corresponding carboxylic acids **4a,b** in 55—65% yields irrespective of whether the reactions were carried out in ethanol, benzene, or tetrahydrofuran and regardless of the temperature (ambient or higher). The reaction of BHA with 4-([1,1′;4′,1″]terphenyl-4″-ylethynyl)benzaldehyde (**3c**) in tetrahydrofuran afforded a poorly soluble compound whose structure was not unambiguously established (Scheme 1).

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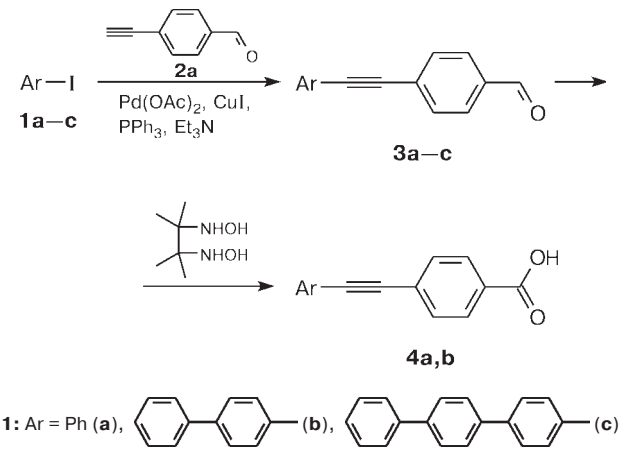
Scheme 1



Apparently, these results are associated with low reactivities of tolan-like aldehydes **3a,b**, which reacted not with BHA but with hydrogen peroxide generated due to oxidation of BHA with atmospheric oxygen.[9] Actually, aldehydes **3a—c** were not oxidized under an inert atmosphere to yield carboxylic acids; however, their reactions with BHA did not proceed as well. Under the reaction conditions in the absence of BHA, aldehydes were not transformed into acids **4**.

Since attempts to prepare nitroxyl-containing tolans according to Ullman's procedure failed, we examined an alternative approach to the synthesis in more detail. The latter approach is based on cross-coupling of the corresponding iodoarenes with paramagnetic arylacetylenes synthesized beforehand. This procedure for the preparation of 2-(arylethynylphenyl)-2-imidazoline nitroxyls has been described in the literature.[1,10] For example, cross-coupling of *m*-diiodobenzene with 2-(3,5-diethynylphenyl)-2-imidazoline nitroxyl[10] was applied in the synthesis of nitroxyl polyradicals; the reaction was carried out in pyridine in the presence of triethylamine using $PdCl_2(PPh_3)_2$ and CuI as the catalysts.

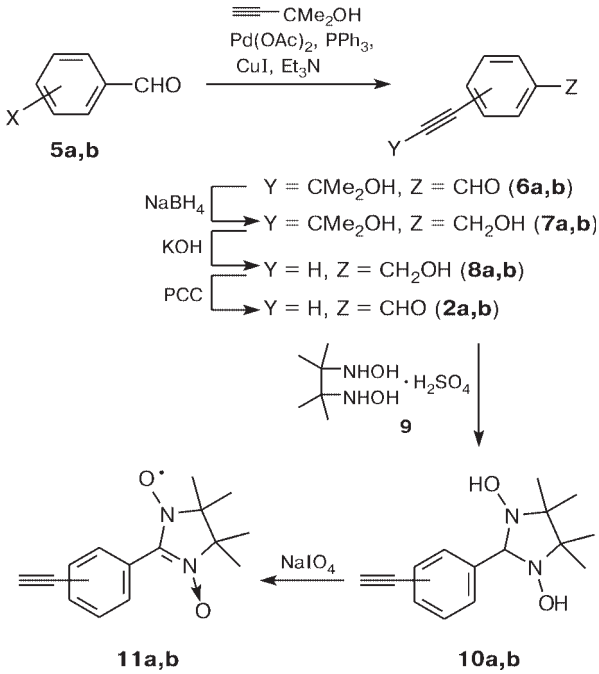
The starting paramagnetic alkynes **11a,b** were prepared according to Scheme 2.

A procedure has been proposed[11] for the preparation of isomeric ethynylbenzaldehydes **2a,b** based on the reactions of bromobenzaldehydes with trimethylsilylacetylene followed by the removal of the trimethylsilyl group. We synthesized aldehydes **2a,b** based on the alkaline cleavage of tertiary arylacetylenic alcohols (the retro-Favorskii reaction[12]), which were prepared by cross-coupling of aryl halides with 2-methylbut-3-yn-2-ol. The reactions of halobenzaldehydes **5a,b** with 2-methylbut-3-yn-2-ol in the presence of $Pd(OAc)_2$, PPh_3, CuI, and Et_3N afforded acetylenic alcohols **6a,b** in 90% yields. Tertiary acetylenic alcohols are generally decomposed in anhydrous benzene at 75—80 °C in the presence of catalytic amounts of a calcined KOH powder or in an apparatus for sublimation in the presence of KOH and vacuum oil.[13] Under these reaction conditions, compounds **6a,b** underwent resinification. Because of this, the aldehyde group in compounds **6a,b** was reduced with $NaBH_4$, the resulting alcohols **7a,b** were decomposed with KOH, and then compounds **8a,b** were oxidized with PCC to obtain the target ethynylbenzaldehydes **2a,b**. We failed to apply this procedure to the synthesis of the *ortho*-isomer. *o*-Ethynylbenzaldehyde was prepared from 2-iodobenzaldehyde according to a procedure described previously.[11]

Condensation of aldehydes **2a,b** with BHA monosulfate **9** gave rise to adducts **10a,b** in 85% yields. Adducts **10a,b** were oxidized with $NaIO_4$ to obtain nitroxyls **11a,b**. Sulfate **9** was preferred over the free base (the reaction with the use of the latter was described in the literature[3]) because it is, first, more readily accessible and, second, allowed us to obtain adducts **10a,b** in higher yields. The reaction of *o*-ethynylbenzaldehyde with BHA or its monosulfate **9** afforded a complex mixture of products, which we failed to separate.

The reaction of spin-labeled acetylene **11a** with *p*-iodotoluene (**1d**) in benzene in the presence of $PdCl_2(PPh_3)_2$, CuI, and Et_3N at 55—80 °C gave rise to 2-(4-ethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl (**19**) (the yield was 12%) and compounds **16—18** (the yield was ~65%). The structure of **16** was established by comparing with the authentic sample.[3] The structure of compound **18** was proved by its independent synthesis

Scheme 2



a is *para*-isomer, **b** is *meta*-isomer, X = 4-Br (**5a**), 3-I (**5b**)

involving reduction of biradical **16**. The qualitative composition of the reaction mixtures remained the same irrespective of whether the reaction was carried out in Et_3N or in a mixture of Et_3N and pyridine[10] and regardless of the reaction temperature (either ambient or higher). Conceivably, symmetrical biradicals **16** and **18** and unsymmetrical biradical **17** were formed due to successive or competitive oxidation of the paramagnetic terminal alkyne by another molecule of the starting nitronyl nitroxide giving rise to disubstituted butadiyne with the loss of the nitroxide oxygen atom. To confirm this suggestion, we carried out cross-coupling of paramagnetic iodoarene (2-(4-iodophenyl)-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide) with phenylacetylene in Et_3N. Actually, the latter reaction gave rise to diphenylbuta-1,3-diyne, 2-(4-iodophenyl)-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl, and a small amount of the starting compound.

In continuation of the studies aimed at examining the possibilities of the use of cross-coupling for the preparation of the target compounds, we attempted to perform the reactions with adducts **10a,b** and obtain copper acetylides from compounds **10a,b** and **11a,b** in an effort to employ the acetylide version of acetylenic condensation. However, all our attempts failed.

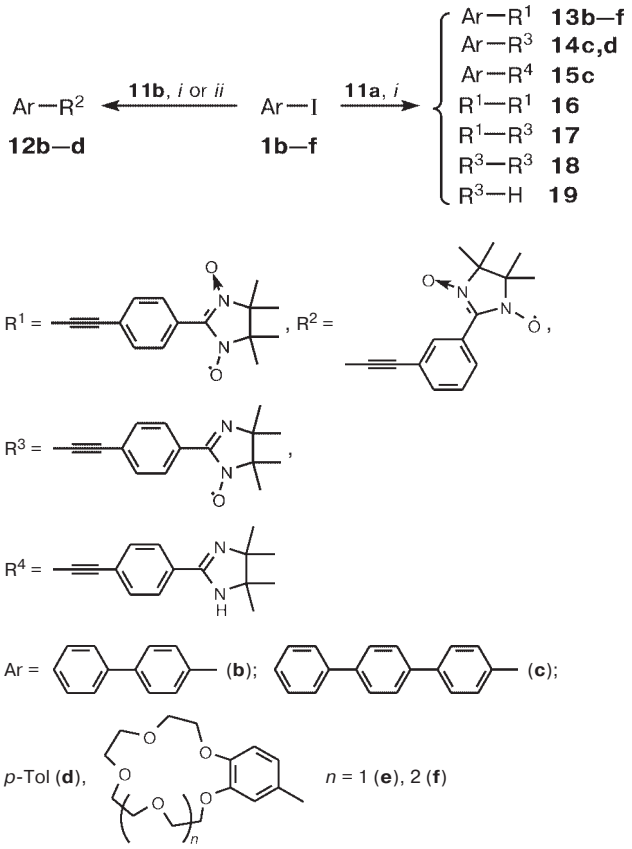
It is known that cross-coupling with the use of piperidine as a base proceeded much faster.[14] Actually, cross-coupling of alkyne **11a** with *p*-iodotoluene (**1d**) in piperidine in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$ and CuI afforded imidazoline-1-oxyl 3-oxide (**13d**) in 58% yield. Simultaneously, we obtained 4,4,5,5-tetramethyl-2-[4-(4-tolylethynyl)phenyl]-2-imidazoline-1-oxyl (**14d**) (the yield was 16%) and biradicals **16**, **17**, and **18** (the total yield was ~10%) (Scheme 3). The reactions with iodides **1b,c,e,f** gave rise to analogous series of the products; the target nitronylnitroxyls **13b,c,e,f** were obtained in 20—60% yields. In addition, we isolated compound **15c** from the products of the reaction of iodide **1c** with alkyne **11a**. This fact indicates that the nitroxyl group can be reduced to the amino group under the conditions of cross-coupling (Scheme 3).

In cross-coupling, *meta*-isomer **11b** behaved differently. In this case, the reaction take place not only in piperidine but also in a pyridine—triethylamine mixture,[10] the target nitronylnitroxyls **12b—d** being obtained in higher yields (65—85%) (see Scheme 3).

Hence, the course of cross-coupling depends substantially on the reaction conditions and the structure of the spin-labeled alkyne.

It should be noted that compounds **13b—f** are rather labile under the conditions of cross-coupling. Thus, nitronylnitroxyl **13c**, which was prepared by the reaction of **1c** with **11a**, underwent complete deoxygenation to compound **14c** in ~16 h. Hence, after completion of the reaction, the solvents must be immediately removed at

Scheme 3



Reagents and conditions: *i*. $Pd(PPh_3)_2Cl_2$, CuI, piperidine, 20—25 °C; *ii*. $Pd(PPh_3)_2Cl_2$, CuI, Et_3N (or Et_3N—Py), 35—40 °C.

~20 °C and the residue must be dissolved in benzene and filtered through a layer of Al_2O_3. After this treatment, the product was obtained in 65% yield and it was stable upon storage.

To summarize, paramagnetic acetylenes of the aromatic series were synthesized by cross-coupling of aryl iodides with 4,4,5,5-tetramethyl-2-phenylethynyl-2-imidazoline-1-oxyl 3-oxide.

Experimental

The ^1H NMR spectra were recorded on a Bruker Avance-300 spectrometer. The IR spectra were measured on a Bruker IFS-66 spectrometer in KBr pellets. The ESR spectra were recorded on a Bruker EMX radiospectrometer at ~20 °C; the concentrations of the solutions were $5 \cdot 10^{-5}$—$5 \cdot 10^{-4}$ mol L^{-1}. The mass spectra were obtained on a Finnigan SSQ–710 instrument using a direct inlet system (EI, the ionizing voltage was 70 eV, the temperature of the ionization chamber was 220—270 °C). The electronic absorption spectra were recorded on a Specord UV-VIS spectrophotometer in MeOH at ~20 °C. Column chromatography was carried out on KSK silica gel (60/200 μm).

The course of the reactions and the purities of the compounds were monitored by TLC on Silufol UV-254 plates. 4″-Iodo-[1,1′;4′,1″]terphenyl,[1] 4-bromobenzaldehyde,[15] 3-iodobenzaldehyde,[16] 4-phenylethynylbenzaldehyde,[17] 2,3-bis(hydroxyamino)-2,3-dimethylbutane, and its monosulfate,[18] 2-iodo-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecene, 2-iodo-6,7,9,10,12,13,15,16,18,19-decahydro-5,8,11,14,17,20-hexaoxabenzocyclooctadecene,[19] and PCC[20] were prepared according to known procedures. 2-Iodobenzaldehyde[21] was prepared from 2-iodobenzyl alcohol[22] according to a procedure described previously.[20] 2-Methylbut-3-yn-2-ol (Aldrich), trimethylsilylacetylene (Fluka), CuI, $NaBH_4$, PPh_3, $Pd(OAc)_2$, and $Pd[PPh_3]_2Cl_2$ (all from Lancaster) were used without additional purification. Other reagents and organic solvents were prepared according to standard procedures.

4-(3-Hydroxy-3-methylbut-1-yn-1-yl)benzaldehyde (6a). A mixture of 4-bromobenzaldehyde (**5a**) (10.0 g, 54.1 mmol), 2-methylbut-3-yn-2-ol (7.9 mL, 81 mmol), $Pd(OAc)_2$ (90 mg, 0.40 mmol), CuI (45 mg, 0.24 mmol), and PPh_3 (180 mg, 0.69 mmol) in Et_3N (11 mL) and benzene (20 mL) was stirred under argon at 75—80 °C for 40 min. After completion of the reaction, the cooled mixture was filtered through a layer of SiO_2 (2.5×2 cm) and the solvent was removed *in vacuo*. The yield of **6a** was 9.61 g (93%), oil. ^{1}H NMR ($CDCl_3$), δ: 1.68 (s, 6 H, C(3)Me_2); 1.85 (br.s, 1 H, OH); 7.56 (d, 2 H, H(3), H(5), J = 7.5 Hz); 7.85 (d, 2 H, H(2), H(6), J = 7.5 Hz); 10.03 (s, 1 H, CHO). IR, ν/cm^{-1}: 1702 (C=O); 2226 (C≡C); 3404 (OH). Found (%): C, 76.32; H, 6.52. $C_{12}H_{12}O_2$. Calculated (%): C, 76.57; H, 6.43.

4-[4-(Hydroxymethyl)phenyl]-2-methylbut-3-yn-2-ol (7a). Solid $NaBH_4$ (0.70 g, 19.0 mmol) was added to a stirred solution of aldehyde **6a** (9.60 g, 51.1 mmol) in MeOH (20 mL) at ~20 °C. After completion of the reaction, the reaction mixture was filtered, the solvent was removed *in vacuo*, and the residue was crystallized from trichloroethylene. The yield of **7a** was 8.92 g (92%), m.p. 83—84 °C. ^{1}H NMR (DMSO-d_6), δ: 1.48 (s, 6 H, C(2)Me_2); 4.51 (d, 2 H, CH_2, J = 5 Hz); 5.22 (t, 1 H, $CH_2O\underline{H}$, J = 5 Hz); 5.42 (s, 1 H, OH); 7.29—7.35 (m, 4 H, Ar). IR, ν/cm^{-1}: 2230 (C≡C); 3485 (OH). Found (%): C, 75.69; H, 7.46. $C_{12}H_{14}O_2$. Calculated (%): C, 75.76; H, 7.42.

(4-Ethynylphenyl)methanol (8a). A mixture of alcohol **7a** (6.80 g, 35.8 mmol) and calcined powdered KOH (2.10 g, 37.5 mmol) in benzene (30 mL) was refluxed for 2 h. After cooling, the reaction mixture was filtered through a layer of SiO_2 (2.5×2 cm) and the solvent was removed *in vacuo*. The product was extracted from the resulting oil with hot hexane (5×40 mL) and the solvent was removed from the extract *in vacuo*. The yield of **8a** was 3.11 g (66%), m.p. 37—38.5 °C. ^{1}H NMR ($CDCl_3$), δ: 3.12 (s, 1 H, C≡CH); 4.74 (s, 2 H, CH_2); 7.38 (d, 2 H, H(2), H(6), J = 7.5 Hz); 7.53 (d, 2 H, H(3), H(5), J = 7.5 Hz). IR, ν/cm^{-1}: 2260 (C≡C); 3260 (≡C—H); 3480 (OH). Found (%): C, 81.61; H, 6.15. C_9H_8O. Calculated (%): C, 81.79; H, 6.10.

4-Ethynylbenzaldehyde (2a). A mixture of alcohol **8a** (3.11 g, 23.5 mmol), PCC (5.65 g, 25.8 mmol), and CH_2Cl_2 (30 mL) was stirred at ~20 °C for 1 h. Then the reaction mixture was filtered through a layer of silica gel, the solvent was distilled off *in vacuo*, and the reaction product was sublimed at 100—110 °C (15 Torr). The yield of **2a** was 2.31 g (74%), m.p. 88—90 °C.[11]

3-(3-Hydroxy-3-methylbut-1-yn-1-yl)benzaldehyde (6b) was prepared from 3-iodobenzaldehyde (**5b**) analogously to **6a**, the yield was 94%, oil. ^{1}H NMR (CD_2Cl_2), δ: 1.63 (s, 6 H, C(3)Me_2); 2.08 (br.s, 1 H, OH); 7.54 (t, 1 H, H(5), J = 8.5 Hz); 7.71 (d, 1 H, H(4), J = 8.5 Hz); 7.86 (d, 1 H, H(6), J = 8.5 Hz); 7.97 (s, 1 H, H(2)); 9.97 (s, 1 H, CHO). IR, ν/cm^{-1}: 1710 (C=O); 2220 (C≡C); 3560 (OH). Found (%): C, 76.82; H, 6.48. $C_{12}H_{12}O_2$. Calculated (%): C, 76.57; H, 6.43.

4-[3-(Hydroxymethyl)phenyl]-2-methylbut-3-yn-2-ol (7b) was prepared from acetylenic alcohol **6b** analogously to **7a**, the yield was 91%, m.p. 63—64 °C. ^{1}H NMR (CD_2Cl_2), δ: 1.51 (s, 6 H, C(2)Me_2); 1.84 (t, 1 H, $CH_2O\underline{H}$, J = 5 Hz); 2.22 (s, 1 H, OH); 4.67 (d, 2 H, CH_2, J = 5 Hz); 7.28—7.37 (m, 3 H, H(4), H(5), H(6)); 7.44 (s, 1 H, H(2)). IR, ν/cm^{-1}: 2226 (C≡C); 3550 (OH). Found (%): C, 75.91; H, 7.51. $C_{12}H_{14}O_2$. Calculated (%): C, 75.76; H, 7.42.

(3-Ethynylphenyl)methanol (8b) was prepared from tertiary acetylenic alcohol **7b** analogously to **8a**, the yield was 62%, oil. ^{1}H NMR ($CDCl_3$), δ: 3.06 (s, 1 H, C≡CH); 4.79 (s, 2 H, CH_2); 7.14—7.18 (m, 3 H, H(4), H(5), H(6)); 7.32 (s, 1 H, H(2)). IR, ν/cm^{-1}: 2260 (C≡C); 3260 (≡C—H); 3480 (OH). Found (%): C, 81.81; H, 6.14. C_9H_8O. Calculated (%): C, 81.79; H, 6.10.

3-Ethynylbenzaldehyde (2b) was prepared from alcohol **8b** analogously to **2a**, the yield was 74%, m.p. 76—76.5 °C.[11]

4-(Biphenyl-4-ylethynyl)benzaldehyde (3b). A mixture of 4-iodobiphenyl **1b** (1.57 g, 5.6 mmol), 4-ethynylbenzaldehyde (**2b**) (0.78 g, 6.0 mmol), $Pd(OAc)_2$ (60 mg, 0.27 mmol), CuI (45 mg, 0.24 mmol), and PPh_3 (180 mg, 0.69 mmol) in Et_3N (5 mL) and benzene (20 mL) was stirred under argon at 75—80 °C for 6.5 h. After completion of the reaction, the cooled mixture was filtered through a layer of SiO_2 (2.5×2 cm), the solvent was removed *in vacuo*, and the residue was crystallized from a benzene—hexane mixture. The yield of **3b** was 9.61 g (93%), m.p. 162—164 °C. ^{1}H NMR (DMSO-d_6), δ: 7.41 (t, 1 H, J = 8 Hz); 7.51 (t, 2 H, J = 8 Hz); 7.66—7.85 (m, 8 H); 7.97 (d, 2 H, J = 9 Hz); 10.05 (s, 1 H, CHO). IR, ν/cm^{-1}: 1697 (C=O); 2214 (C≡C). Found (%): C, 89.12; H, 5.08. $C_{21}H_{14}O$. Calculated (%): C, 89.34; H, 5.00.

4-([1,1′;4′,1″]Terphenyl-4″-ylethynyl)benzaldehyde (3c) was prepared from 4-phenylethynylbenzaldehyde and **2b** analogously to **3b**, the yield was 64%, m.p. with decomp. 240—245 °C (from Py). ^{1}H NMR (DMSO-d_6), δ: 7.41 (t, 1 H, J = 8 Hz); 7.51 (t, 2 H, J = 8 Hz); 7.66—7.85 (m, 8 H); 7.97 (d, 2 H, J = 9 Hz); 10.05 (s, 1 H, CHO). IR, ν/cm^{-1}: 1697 (C=O); 2214 (C≡C). Found (%): C, 90.21; H, 5.21. $C_{27}H_{18}O$. Calculated (%): C, 90.47; H, 5.06.

4-Phenylethynylbenzoic acid (4a). A mixture of **3a** (0.1 g, 0.49 mmol), BHA (75 mg, 0.51 mmol), C_6H_6 (3 mL), and MeOH (3 mL) was stirred at ~20 °C for 5 days and the solvents were distilled off. The residue was dissolved in THF, filtered through a layer of SiO_2, and crystallized from C_6H_6. The yield of **4a** was 60 mg (55%). ^{1}H NMR (Py-d_5), δ: 7.11—7.34 (m, 2 H); 7.45—7.68 (m, 5 H); 8.22 (d, 2 H, J = 9 Hz). IR, ν/cm^{-1}: 2220 (C≡C); 3480 (OH). High-resolution mass spectrum. Found: m/z 222.06880 $[M]^+$. $C_{15}H_{10}O_2$. Calculated: M = 222.06807.

4-(Biphenyl-4-ylethynyl)benzoic acid (4b) was isolated in the reaction of aldehyde **3b** with BHA, the yield was 61%, m.p. 297—298 °C (from C_6H_6). ^{1}H NMR (Py-d_5), δ: 7.11—7.34 (m, 3 H); 7.45—7.68 (m, 8 H); 8.19 (d, 2 H, J = 9 Hz). IR, ν/cm^{-1}: 2220 (C≡C); 3420 (OH). High-resolution mass spec-

trum. Found: *m/z* 298.10020 $[M]^+$. $C_{21}H_{14}O_2$. Calculated: M = 298.09937.

1,3-Dihydroxy-2-(4-ethynylphenyl)-4,4,5,5-tetramethylimidazolidine (10a). A hot (50—56 °C) solution of 2,3-bis(hydroxyamino)-2,3-dimethylbutane monosulfate monohydrate (**9**) (3.55 g, 13 mmol) in H_2O (20 mL) was added to a hot (50—55 °C) solution of aldehyde **2a** (1.71 g, 13 mmol) in MeOH (13 mL). Then the reaction mixture was kept at ~20 °C for one day and neutralized with $NaHCO_3$ (1.55 g). The residue was filtered off and recrystallized from a benzene—$CHCl_3$ mixture. The yield of **10a** was 2.84 g (83%), m.p. 184—185 °C.[3]

2-(4-Ethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide (11a). Solid $NaIO_4$ (4.11 g, 19.1 mmol) was added portionwise to a stirred mixture of adduct **10a** (3.32 g, 12.8 mmol), water (60 mL), and CH_2Cl_2 (60 mL) at 10—15 °C for 1 h. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3×20 mL). The combined organic extracts were filtered through a layer of Al_2O_3 (2×5 cm), the solvent was distilled off, and the residue was crystallized from a 3 : 1 hexane—benzene mixture. The yield of **11a** was 2.55 g (78%), m.p. 131—132 °C.[3]

1,3-Dihydroxy-2-(3-ethynylphenyl)-4,4,5,5-tetramethylimidazolidine (10b) was prepared from aldehyde **2b** analogously to **10a**, the yield was 87%, m.p. 161—162 °C (from $CHCl_3$—AcOEt, 1 : 1) (*cf.* lit. data[5]: m.p. 151—153 °C). ^{1}H NMR (DMSO-d_6), δ: 0.99 (s, 6 H, C(4)Me, C(5)Me); 1.12 (s, 6 H, C(4)Me, C(5)Me); 4.13 (s, 1 H, C≡CH); 4.49 (s, 1 H, CH); 7.29—7.41 (m, 2 H, H(5), H(6)); 7.48 (d, 1 H, H(4), *J* = 8.5 Hz); 7.59 (s, 1 H, H(2)); 7.83 (s, 2 H, NOH).

2-(3-Ethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide (11b) was prepared from adduct **10b** analogously to **11a**, the yield was 89%, m.p. 138—139 °C (from a 2 : 1 hexane—benzene mixture).[6]

4,4,5,5-Tetramethyl-2-[4-([1,1′;4′,1″]terphenyl-4-ylethynyl)phenyl]-2-imidazoline-1-oxyl 3-oxide (13c). Alkyne **11a** (0.45 g, 1.8 mmol) was added portionwise to a mixture of iodoterphenyl **1c** (0.42 g, 1 mmol), $Pd[PPh_3]_2Cl_2$ (40 mg, 0.057 mmol), CuI (20 mg, 0.11 mmol), and piperidine (10 mL) under a stream of argon for 1 h. The solvent was removed *in vacuo* with the use of an oil pump (~0.1 Torr) at ~20 °C, the residue was dissolved in benzene, the solution was filtered through a layer of Al_2O_3, and the solvent was distilled off. The residue was dissolved in benzene and twice chromatographed on silica gel. Elution with benzene afforded 0.1 g of 4,4,5,5-tetramethyl-2-[4-([1,1′;4′,1″]terphenyl-4-ylethynyl)phenyl]-4,5-dihydro-1*H*-imidazole (**15c**) (the yield was 19%), 60 mg of 4,4,5,5-tetramethyl-2-[4-([1,1′;4′,1″]terphenyl-4-ylethynyl)phenyl]imidazoline-1-oxyl (**14c**) (the yield was 10%), and 0.11 g of imidazoline-1-oxyl 3-oxide (**13c**) (20%). Elution with chloroform yielded a mixture (0.16 g) containing dimer **16** and its iminonitroxyl analogs **17** and **18**.

Imidazoline-1-oxyl 3-oxide (13c). Blue-green crystals (from benzene); at 238 °C, the compounds was transformed into orange imidazoline-1-oxyl **14c**. IR, ν/cm^{-1}: 2213 (C≡C); 2988 (Me); 3030 (C—H arom.). MS, *m/z* (I_{rel} (%)): 485.0 $[M]^+$ (14.39), 454.0 (9.04), 439.0 (3.74), 398.0 (17.40), 396.9 (52.65), 356.9 (15.70), 355.9 (44.46), 354.9 (100), 329.0 (2.12), 327.90 (3.38), 253.0 (1.25), 251.9 (3.99), 151.9 (1.43), 114.0 (28.70), 84.1 (88.31), 69.1 (27.46), 56.0 (11.29), 41.0 (14.64), 28.0 (4.78). High-resolution mass spectrum. Found: *m/z* 485.2166 $[M]^+$. $C_{33}H_{29}N_2O_2$. Calculated: M = 485.2189. ESR: a_N (2 N) = 0.73 mT, $a_{H\text{-}o}$ (2 H) = 0.075 mT, $a_{H(Me)}$ (12 H) = 0.021 mT.

4,5-Dihydro-1*H*-imidazole (15c). Pale-yellow crystals, m.p. 249—251 °C (C_6H_6—hexane). IR, ν/cm^{-1}: 825, 846, 880, 956, 1002, 1018, 1110, 1140, 1157, 1182, 1221, 1264, 1292, 1308, 1366, 1403, 1448, 1482, 1508, 1534, 1609, 2214, 2930, 2976 3034, 3441. ^{1}H NMR (CD_2Cl_2), δ: 1.55 (s, 12 H, Me); 7.10 (br.s, 1 H, NH); 7.22 (t, 1 H, 4″-H); 7.32 (t, 2 H, 3″, 5″-H); 7.41—7.54 (m, 4 H, H arom.); 7.63—7.77 (m, 8 H, H arom.); 7.88 (d, 2 H, 2,6-H). MS, *m/z* (I_{rel} (%)): 454.2 $[M]^+$ (2.76), 397.0 (14.27), 357.0 (6.69), 355.9 (33.34), 354.9 (86.68), 326.0 (1.78), 252.0 (3.63), 226.0 (0.74), 151.9 (1.0), 84.0 (100), 69.0 (46.45), 57.0 (1.49), 42.0 (7.64), 41.0 (22.19), 39.0 (1.02), 27.9 (53.33). High-resolution mass spectrum. Found: *m/z* 454.2388 $[M]^+$. $C_{33}H_{30}N_2$. Calculated: M = 454.2409.

2-Imidazoline-1-oxyl (14c). The yield was 15%, the IR spectrum and R_f are identical with those of authentic radical **14c** (see below).

2,2′-[(Buta-1,3-diyne-1,4-diyl)di-*p*-phenylene]-bis(4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide) (biradical 16): the IR spectrum and R_f are identical with those of authentic radical **16**.[3]

1-[4-(4,4,5,5-Tetramethyl-2-imidazoline-1-oxyl-2-yl 3-oxide)phenyl]-4-[4-(4,4,5,5-tetramethyl-2-imidazoline-1-oxyl-2-yl)phenyl]buta-1,3-diyne (biradical 17): R_f and the color of the spot of biradical **17** are identical with those of an intermediate in the reaction of **16** with $NaNO_2$.

Biradical 18: the IR spectrum and R_f are identical with those of authentic radical **18** (see below).

4,4,5,5-Tetramethyl-2-[4-(*p*-tolylethynyl)phenyl]-2-imidazoline-1-oxyl 3-oxide (13d) was prepared analogously to **13c**, the yield was 58%, m.p. 148.5—150 °C (from a 3 : 1 hexane—benzene mixture). IR, ν/cm^{-1}: 819, 841, 1127, 1166, 1216, 1300, 1362, 1388, 1421, 1449, 1478, 1509, 1599, 2213, 2979, 3030. ESR: a_N (2 N) = 0.73 mT, $a_{H(Me)}$ (12 H) = 0.024 mT. Found (%): C, 76.15; H, 6.53; N, 8.03. $C_{22}H_{23}N_2O_2$. Calculated (%): C, 76.05; H, 6.67; N, 8.06. In addition, **4,4,5,5-tetramethyl-2-[4-(*p*-tolylethynyl)phenyl]-2-imidazoline-1-oxyl (14d)** was isolated from the reaction mixture. The yield was 16%, m.p. 126—127 °C (from a 3 : 1 hexane—benzene mixture). ESR: a_{N1} (1 N) = 0.91 mT, a_{N3} (1 N) = 0.45 mT. Found (%): C, 79.75; H, 6.91; N, 8.29. $C_{22}H_{23}N_2O$. Calculated (%): C, 79.73; H, 6.99; N, 8.45. In addition, biradicals **16—18** were isolated (the total yield was 10%).

Compounds **13b,e,f** were prepared analogously to **13c** (by-products, which were identified by TLC and were not isolated).

2-[4-(Biphenyl-4-ylethynyl)phenyl]-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide (13b). The yield was 29%, m.p. 188—190 °C (from a hexane—benzene mixture). IR, ν/cm^{-1}: 815, 837, 1000, 1019, 1065, 1103, 1129, 1166, 1214, 1302, 1363, 1388, 1423, 1449, 1485, 1526, 1600, 2213, 2928, 2987, 3032. ESR: a_N (2 N) = 0.73 mT, $a_{H(Me)}$ (12 H) = 0.024 mT. Found (%): C, 79.31; H, 6.23; N, 6.63. $C_{27}H_{25}N_2O_2$. Calculated (%): C, 79.19; H, 6.15; N, 6.84.

4,4,5,5-Tetramethyl-2-[4-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecen-15-ylethynyl)phenyl]-2-imidazoline-1-oxyl 3-oxide (13e). The yield was 41%, m.p. 175—176 °C (from a hexane—benzene mixture). IR, ν/cm^{-1}: 813, 833, 907, 938, 964, 1050, 1129, 1166, 1208, 1254, 1303,

1331, 1360, 1389, 1420, 1453, 1513, 1564, 1603, 2207, 2868, 2929, 2981, 3027. ESR: a_N (2 N) = 0.74 mT, $a_{H(Me)}$ (12 H) = 0.023 mT. Found (%): C, 66.81; H, 6.58; N, 5.13. $C_{29}H_{35}N_2O_7$. Calculated (%): C, 66.52; H, 6.74; N, 5.35.

2-[4-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-hexaoxabenzocyclooctadecen-18-ylethynyl)phenyl]-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide (13f). The yield was 39%, m.p. 134—136 °C (from a hexane—benzene mixture). IR, ν/cm^{-1}: 810, 839, 949, 982, 1054, 1123, 1218, 1254, 1302, 1329, 1360, 1390, 1420, 1451, 1513, 1595, 2206, 2870, 2924, 3032. ESR: a_N (2 N) = 0.74 mT, $a_{H(Me)}$ (12 H) = 0.024 mT. MS, *m/z* (I_{rel} (%)): 567.2 $[M]^+$ (1.63), 537.3 (5.56), 536.3 (13.32), 521.3 (6.84), 509.2 (3.38), 481.2 (5.76), 480.1 (33.0), 479.1 (100.0), 438.1 (6.05), 437.1 (24.46), 339.1 (6.28), 303.1 (3.10), 262.0 (14.52), 261.0 (43.24), 247.0 (4.0), 246.0 (10.86), 235.0 (4.48), 234.0 (4.18), 206.0 (5.78), 204.9 (10.09), 177.0 (7.79), 163.0 (8.21), 152.0 (3.24), 114.1 (8.10), 98.1 (9.10), 89.0 (5.31), 84.1 (65.54). High-resolution mass spectrum. Found: *m/z* 567.27100 $[M]^+$. $C_{31}H_{39}N_2O_8$. Calculated: M = 567.27062.

2-[3-(Biphenyl-4-ylethynyl)phenyl]-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide (12b) was prepared analogously to **13c**, except that the synthesis was carried out at 35—40 °C and a 1 : 10 Et_3N—Py mixture was used instead of piperidine. The yield was 79%, m.p. 161—163 °C (from a hexane—benzene mixture). IR, ν/cm^{-1}: 815, 837, 1000, 1019, 1065, 1103, 1129, 1166, 1214, 1302, 1363, 1388, 1423, 1449, 1485, 1526, 1600, 2213, 2928, 2987, 3032. ESR: a_N (2 N) = 0.73 mT, $a_{H(Me)}$ (12 H) = 0.024 mT. Found (%): C, 79.43; H, 6.03; N, 6.58. $C_{27}H_{25}N_2O_2$. Calculated (%): C, 79.19; H, 6.15; N, 6.84.

Compounds **12c,d** were prepared analogously to **12b**.

4,4,5,5-Tetramethyl-2-[3-([1,1′;4′,1″]terphenyl-4-ylethynyl)phenyl]-2-imidazoline-1-oxyl 3-oxide (12c). A mixture of 4-iodoterphenyl **1c** (0.42 g, 1.2 mmol), $Pd[PPh_3]_2Cl_2$ (40 mg, 0.057 mmol), CuI (20 mg, 0.11 mmol), Et_3N (1 mL), and Py (or Et_3N) (10 mL) was stirred under a stream of argon at 35—40 °C for 30 min. Then 2-imidazoline-1-oxyl 3-oxide **11b** (0.33 g, 1.3 mmol) was added and the reaction mixture was stirred for 2 h. The reaction product was isolated analogously to **13c**. The yield of nitroxyl **12c** was 66%, m.p. 226—228 °C (from benzene). IR, ν/cm^{-1}: 827, 865, 908, 1002, 1078, 1138, 1166, 1217, 1272, 1304, 1364, 1389, 1420, 1450, 1485, 1506, 1593, 2207, 2989, 3033. ESR: a_N (2 N) = 0.73 mT, $a_{H(Me)}$ (12 H) = 0.021 mT. Found (%): C, 81.35; H, 6.18; N, 5.64. $C_{33}H_{29}N_2O_2$. Calculated (%): C, 81.62; H, 6.02; N, 5.77.

4,4,5,5-Tetramethyl-2-[3-(*p*-tolylethynyl)phenyl]-2-imidazoline-1-oxyl 3-oxide (12d). The yield was 84%, m.p. 148.5—150 °C (from a 3 : 1 hexane—benzene mixture). IR, ν/cm^{-1}: 819, 841, 1127, 1166, 1216, 1300, 1362, 1388, 1421, 1449, 1478, 1509, 1599, 2213, 2979, 3030. ESR: a_N (2 N) = 0.73 mT, $a_{H(Me)}$ (12 H) = 0.024 mT. Found (%): C, 76.15; H, 6.53; N, 8.03. $C_{22}H_{23}N_2O_2$. Calculated (%): C, 76.05; H, 6.67; N, 8.06.

2,2′-[(Buta-1,3-diyne-1,4-diyl)di-*p*-phenylene]-bis(4,4,5,5-tetramethyl-2-imidazoline-1-oxyl) (18). A mixture of biradical **16** (0.24 g, 0.47 mmol), $NaNO_2$ (0.75 g, 11 mmol), and AcOH (150 μL) in $CHCl_3$ (15 mL) was refluxed with stirring for 1 h (until the color of the reaction mixture changed from blue to red). The reaction mixture was filtered through a layer of silica gel (2.5×1.5 cm), the solvent was distilled off *in vacuo*, and the residue was crystallized from a benzene—hexane mixture. The yield of **18** was 0.2 g (89%), with decomp. at 115—120 °C. IR, ν/cm^{-1}: 847, 879, 957, 1018, 1101, 1141, 1155, 1179, 1221, 1265, 1292, 1308, 1367, 1388, 1403, 1447, 1489, 1536, 1569, 1606, 2149, 2215, 2930, 2977, 3052. Found (%): C, 74.64; H, 6.89; N, 11.45. $C_{30}H_{32}N_4O_2$. Calculated (%): C, 74.97; H, 6.71; N, 11.66.

2-Imidazoline-1-oxyl (14c) was prepared from **13c** analogously to **18,** the yield was 66%, m.p. 239—241 °C (C_6H_6). ESR: a_{N1} (1 N) = 0.91 mT, a_{N3} (1 N) = 0.45 mT. Found (%): C, 84.35; H, 6.18; N, 5.94. $C_{33}H_{29}N_2O$. Calculated (%): C, 84.40; H, 6.22; N, 5.97.

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