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Synthetic and mechanistic aspects of cross-coupling of nitroxyl radicals of 3-imidazoline series with terminal alkynes

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ABSTRACT

Practical synthetic approaches to the new class of acetylenic derivatives of 3-imidazolyl-3-oxide-1-oxyls, including biradicals, were developed through cross-coupling reactions of 3-imidazolyl halides with either terminal alkynes or their copper salts. The presence of nitroxyl functional group as an internal oxidant leads to a competition between the formation of cross-coupling products and the products of oxidative homocoupling. The balance in this competition can be shifted toward the cross-coupling products through the combination of factors that includes nature of the catalyst, reactivity of the halides, and reaction conditions.

1. Introduction

Stable nitroxyl radicals continue to draw significant attention of researchers working at the interface between chemistry, physics, and biology. Traditionally, radicals of this family have been widely used as spin probes in biochemistry[1] and in the design of paramagnetic complexes in coordination chemistry.[2] New areas of application for these molecules continue to emerge, most recently in studies of intricate details of intramolecular interactions and spin catalysis.[3,4]

Stringent requirements to structural, electronic, and steric parameters often complicate development of new materials with designed magnetic and optical properties. In this context, radicals with ethynyl moieties are promising because the HC≡C-group is a rigid, convenient scaffold for construction of spin-labeled molecules with programmable electronic, geometric, and magnetic parameters. On one hand, increased acidity of the methine protons allows facile functionalization of such molecules through the creation of new C–C bonds. On the other hand, the –C≡C-linkage ensures the rigid spatial arrangement of functional moieties and can participate in electron delocalization. Both of these factors are often important for studies of magnetic and optical properties. If needed, partial hydrogenation of the C≡C-bond allows one to prepare the respective *cis*- and *trans*-alkene derivatives in transformations, which change molecular geometry but preserve conjugation. Another valuable property of alkyne functionality is its ability to undergo facile cycloaddition reactions[5–7] useful for the attachment of spin labels to biomolecules. Finally, full hydrogenation of the triple bond can be used to drastically decrease the exchange interaction. For example, this problem had to be addressed in the studies of the fundamental aspects of spin catalysis in recombination of spin-correlated ion-radical pairs. In these studies, hydrogenation of acetylenic derivatives of nitroxyl radicals of 2-imidazolyl family permitted for the first time detection of the magnetic effect (15%) in recombination of ion-radical pairs.[3] However, more detailed quantitative studies required the further decrease in the exchange interaction between the spin center and the ion-radical pair. Such decrease could be achieved in nitroxyls of 3-imidazolyl family where the paramagnetic center is separated from the aromatic molecule with two single bonds.

It is important to emphasize that although chemistry of 3-imidazolylnitroxyls is well-developed, information regarding synthesis of acetylenic derivatives with this core has not been available before the initiation of our research program in this field. From our point of view, this situation is not due to the lack of interest to

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acetylenyl-3-imidazolinyl nitroxyls but rather a result of synthetic difficulties illustrated in this paper.

From this perspective, the development of synthetic approaches to acetylenic derivatives of 3-imidazolyl is necessary for the general progress of chemistry of nitroxyl radicals because the reactivity of the triple bond opens access to numerous transformations of the paramagnetic molecules. The presence of two highly reactive functional groups establishes the significance of acetylenyl-3-imidazoline-3-oxide-1-oxyls as promising building blocks of multipurpose utility.

Recently, we published two short communications describing the first representatives of this class of compounds.[8,9] In the present paper, we provide full experimental details and spectral properties of these molecules and expand the list of prepared nitroxyls through the introduction of a more diverse set of substituents of different chemical nature. In addition, we will compare three alternative cross-coupling techniques, and analyze their scope, limitations, and mechanistic features.

2. Results and discussion

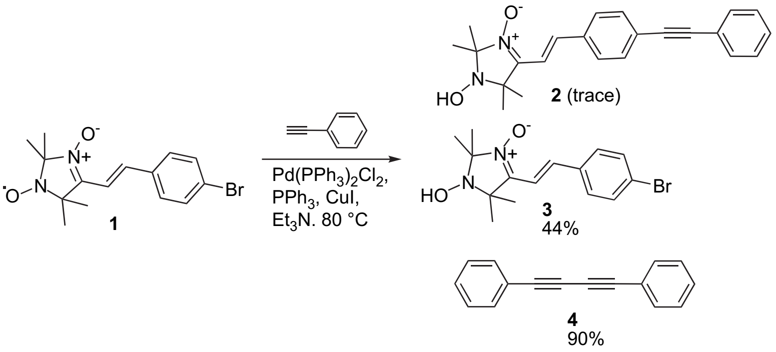
Our initial attempts of using the classic approach to the preparation of alkynes through dehydrohalogenation of the respective *vic*-dihalides with such strong bases as KOH in DMSO or refluxing ethanol, or with KOH in the presence of tetrabutylammonium bromide (TBAB) turned out to be unsuccessful and only led to considerable decomposition.[8] This result prompted us to consider the most widely applied alternative modern method for the preparation of aryl(hetaryl)alkynes—the Sonogashira cross-coupling of terminal alkynes with aryl(hetaryl)halides.[10] However, interaction of paramagnetic bromide **1** with phenylacetylene under the Sonogashira conditions [$Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N, 80 °C] in benzene was unsuccessful as well (Scheme 1).

In the course of this reaction, we observed only trace amounts of the desired product **2**. The main reaction path included formation of ca. 90% of the dehydrodimer (homocouple) of phenylacetylene **4** along with the hydroxylamine derived from the starting *p*-bromoimidazoline **3**.

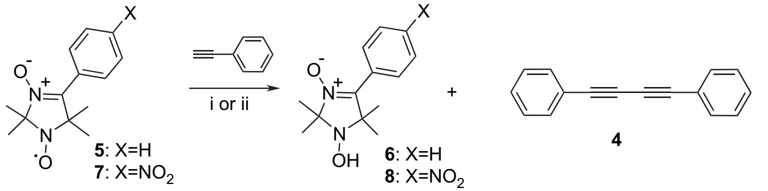
Earlier,[11] we observed for the first time the anomalous formation of such oxidative coupling products from terminal alkynes in the absence of an external oxidant in the reaction of 3-acylamino-1-methyl-4-iodopyrazole with phenylacetylene or hexyne-1. However, in the earlier report, dehydrodimers were formed through a sequence, which included oxidative addition/reductive elimination of the alkyne derivatives and exchange of hydride to iodide anion. At the end, the iodine atom of aryl halide played the role of the oxidant. In the present case, the mechanism may be different due to the possible involvement of either the nitrone or the nitroxyl groups as the oxidant (Scheme 2).

In order to test this hypothesis and get further insight into the mechanism, we carried out the model experiments, which utilized nitroxyls **5** and **7** lacking halogen atoms in the aromatic ring (Scheme 2). The TLC analysis confirmed that neither the hydroxylamines **6** and **8** nor the dehydrodimer **4** are formed when radicals **5** and **7** are stirred with triethylamine and phenylacetylene in benzene at 80 °C for 5 h in the atmosphere of argon. However, once $Pd(PPh_3)_2Cl_2$ catalyst (20 mol %) was added, nitroxyl radicals **5** and **7** were reduced in the respective hydroxylamines **6** (66%) and **8** (91%) with the concomitant formation of dehydrodimer **4** (66–74%). In the presence of $PdCl_2$ and a stronger base ($AcONa\cdot 3H_2O$), formation of dehydrodimer **4** (66–90%) and hydroxylamines **6** or **8** was observed even at the room temperature in the course of 8 h. The yields of diamagnetic products **6** and **8** were 28% and 94%, respectively.

These observations illustrate that the nitroxyl group needs the assistance of the Pd salts to serve as an oxidant. Although the exact mechanism of this assistance is unknown, it is possible that the role of Pd catalyst is in the formation of π-complex possessing a weakened C–H bond, which increases the reductive properties of the terminal alkyne. On the other hand, direct homolytic cleavage of



Scheme 1.

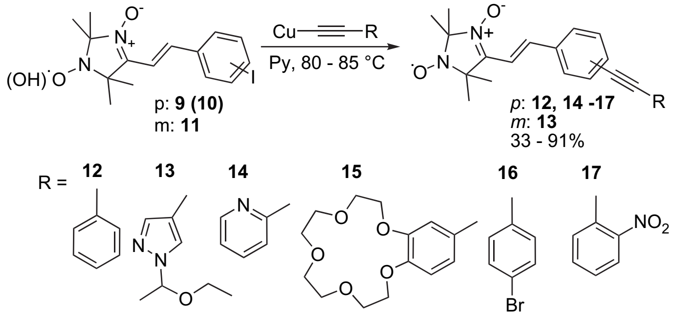


i: $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, C_6H_6, Ar, 80 °C	**6** (66%), **4** (66%); **8** (91%), **4** (74%)
ii: $PdCl_2$, $AcONa\cdot 3H_2O$, CuI, CH_3CN, Ar,80 °C	**6** (28%), **4** (90%); **8** (94%), **4** (66%)

Scheme 2.

the very strong sp-hybridized C–H bond is thermodynamically unfavorable. It is worth noting that this is the first example of oxidative coupling of a terminal alkyne under the cross-coupling conditions in the absence of an external oxidant.

Considering the formation of the side products in the reactions of nitroxyls catalyzed by Pd-complexes, we applied the acetylide method[12] for the synthesis of spin-labeled acetylenic compounds using both the paramagnetic and the diamagnetic *p*-iodoimidazolines (**9** and **10**) and *m*-iodoimidazoline **11** as the substrates (Scheme 3).



Scheme 3.

Interaction of iodoimidazolines **9**–**11** with copper acetylides in refluxing pyridine under the argon atmosphere[13] led to the formation of the spin-labeled acetylenes **12**–**17** in 33–91%. Either the paramagnetic iodide **9** or its diamagnetic precursor **10** can be used in the reaction without the need to oxidize the hydroxylamine **10**. The yields and selected properties of the spin-labeled alkynes **12**–**17** are summarized in Section 4.

However, despite the overall attractiveness of acetylide method for the modification of 3-imidazolinenitroxyles, this approach has an important shortcoming since it requires an additional step for the preparation of copper acetylides. Not only some compounds of this class are explosive but also many terminal alkynes, in particular such simple acetylenic alcohols and amines as 3-methylbut-1-yn-3-ol, *N*-morpholinoprop-1-yne, etc., cannot form the copper salts.

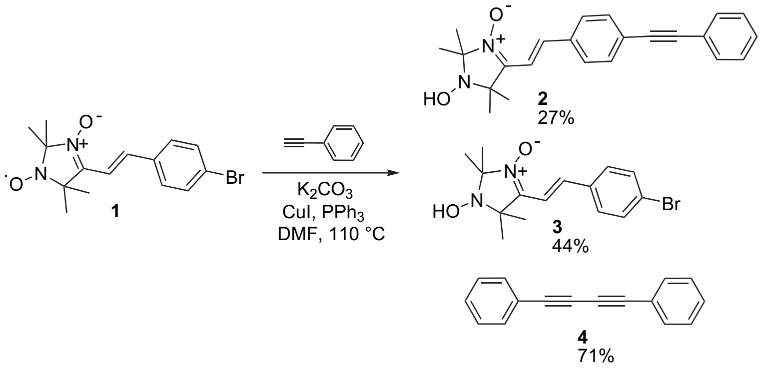
Considering all of the above, we decided to utilize a different modification of cross-coupling, which used Cu catalysis in the absence of Pd in the [K_2CO_3, CuI, Et_3N, PPh_3, DMF, 110 °C] system[14] (Scheme 4). Under these conditions (110 °C, DMF, 13 h), we were able to isolate the diamagnetic target cross-coupling product **2**. However, the yield was low (27%) and, again, the reaction was accompanied by the formation of hydroxylamine **3** (44%) and dehydrodimer **4** (71%).

We supposed that the copper salt plays the same role here as in the Pd-catalyzed processes described above. In order to test this hypothesis, we carried out a model experiment described in Scheme 5.

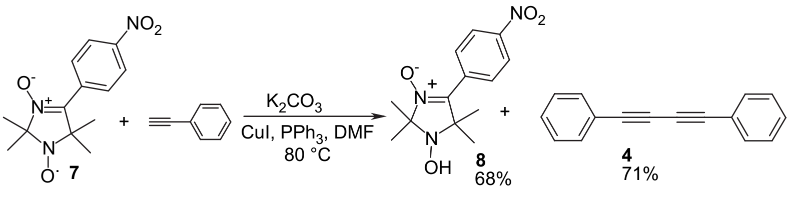
Neither hydroxylamine **8** nor dehydrodimer **4** was formed when a mixture of radical **7**, phenylacetylene, and potassium carbonate was refluxed in DMF for 4 h under the atmosphere of argon. On the other hand, addition of a catalytic amount of CuI to the reaction mixture led to the reduction of the nitroxyl radical **7** to the respective hydroxylamine **8** (68%) and to the formation of the dehydrodimer **4** (71%) in 2 h. These results show that the nitroxyl moiety can behave as an oxidant not only in the presence of Pd catalyst but also in the presence of the Cu(I) salts as well.

Although examples of oxidative coupling of terminal alkynes in the presence of Pd catalysts can be found in the literature, only external oxidants (such as iodine,[15] triethylamine oxide,[16] chloroacetone,[17] etc.) were used. Thus, we were the first to describe the cases when the substrate itself serves as an oxidant in such catalytic processes.

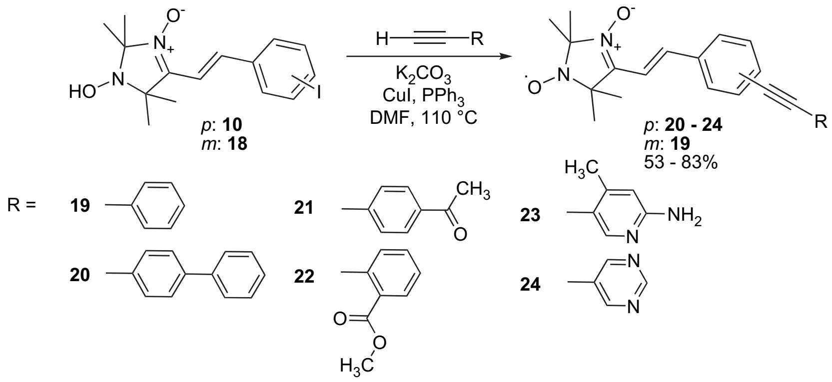
Nevertheless, formation of the target products even in the low yields suggested that use of more reactive iodides instead of bromides may increase the relative importance of cross-coupling. Indeed, when the iodohydroxylamine **10** or **18** was used, the reaction promoted by the [K_2CO_3, CuI, Et_3N, PPh_3, DMF] system at 110 °C led to the formation of the target acetylenyl derivatives **19**–**24** (53–83%, Scheme 6). This method was also successfully applied for the synthesis of the biradical product **25** (45%, Scheme 7).



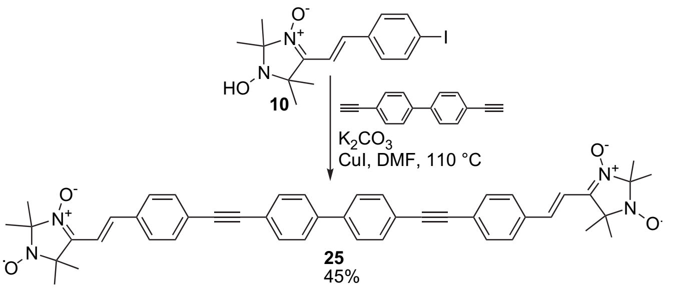
Scheme 4.



Scheme 5.



Scheme 6.

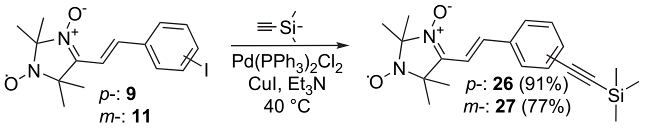


Scheme 7.

Section 4 summarizes the reaction yields and times as well as the selected physical and spectral properties for compounds obtained via this method. The formation of dehydrodimers from the aryl bromides and successful cross-coupling of their iodo analogues suggests that homocoupling and cross-coupling compete with each other and that the latter process dominates when the more reactive iodides are used.

Although this method seems the most general, it also has a shortcoming because the high reaction temperature (110 °C) is necessary. This requirement does not allow one to carry out the reactions with low-boiling reagents such as trimethylsilyl acetylene (bp 53 °C), which is the key reagent for the preparation of terminal alkynes.

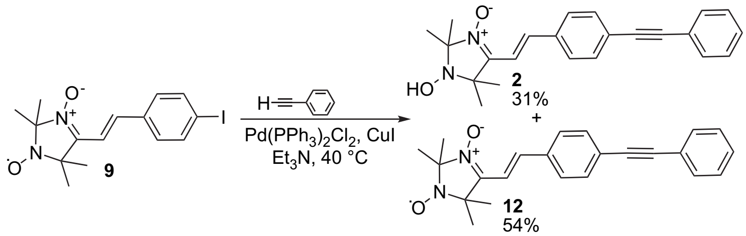
The successful results obtained for the iodo derivatives prompted us to reinvestigate the efficiency of Pd-catalyzed cross-coupling processes at the lower temperatures. Considering that the cross- and homocoupling are competing processes, one can expect that the competition between them may be perturbed by a change in temperature. Indeed, such approach allowed us to carry out successful synthesis of the spin-labeled alkynes. For example, in the reaction of *p*- and *m*-iodides **9** and **11** with trimethylsilyl acetylene under the standard Sonogashira conditions ([Pd(PPh$_3$)$_2$]Cl$_2$–CuI, Et$_3$N) at 40 °C in benzene, the yields of TMS-alkynes **26** and **27** reached 91% and 77%, respectively (Scheme 8).



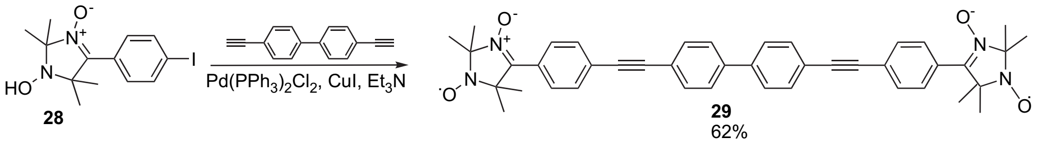
Scheme 8.

Under the same conditions, the paramagnetic *p*-iodoimidazoline **9** interacts with phenylacetylene to yield a mixture of dia- and paramagnetic products **2** and **12** (31% and 54%, respectively, Scheme 9). As expected from the formation of product **2**, the homocoupling product **4** was also observed (25% isolated yield). This observation suggests that the balance between cross- and homocoupling in Pd-catalyzed reactions of nitroxyl radicals remains rather subtle and can be potentially controlled by a number of experimental variables.

Under these conditions, the diamagnetic iodide **28** reacts with 4,4′-diethynylbiphehyl with the formation of biradical **29** in 62% yield (Scheme 10).

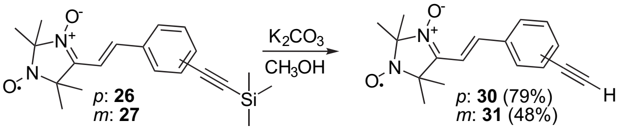


Scheme 9.



Scheme 10.

The paramagnetic TMS-substituted nitronylnitroxides **26** and **27** can be converted into terminal acetylenylimidazolines **30** (79%) and **31** (48%) via removal of the silyl protecting group under mild conditions (MeOH, K_2CO_3, 40 °C, Scheme 11).



Scheme 11.

3. Conclusions

In summary, we investigated three modifications of the cross-coupling of halogen-substituted nitroxyles of 3-imidazolyl family with terminal alkynes and their copper salts. We found that only iodides are suitable substrates for cross-coupling of halo-3-imidazolylnitroxyls with terminal alkynes. The Castro method is applicable to copper salts of a variety of alkynes with the exception of several simplest amines and alcohols. The catalytic version of cross-coupling with the [K_2CO_3, CuI, Et_3N, PPh_3, DMF] system is general for all terminal alkynes with sufficiently high boiling points but requires a high temperature (110 °C). On the other hand, the catalytic Sonogashira [$Pd(PPh_3)_2Cl_2$, CuI, Et_3N] system has the advantage of allowing cross-coupling under the lower temperatures but, sometimes, at the expense of partial conversion of the alkyne to the respective oxidative homocoupling product. Under the Sonogashira conditions, the bromo-3-imidazoline nitroxyls act mainly as oxidants and transform terminal acetylenes into their dehydrodimers.

Overall, this work developed convenient practical approaches to acetylenic 3-imidazolyl nitroxyles, compounds, which can serve as the multipurpose building blocks for the preparation of spin probes of a new generation.

4. Experimental

4.1. General

Melting points were determined with a hot-stage microscope. Column chromatography was performed on silica gel (Merck 60, 70–230 mesh). The R_f values were measured on aluminum backed TLC plates (silica gel 60 F_{254}, Merck, 0.2 mm) with the indicated eluent. Mass spectra (HRMS) were measured on a Finnigan SSQ—710 at 70 eV using electron impact modes. Combustion elemental analysis was performed for the non-volatile compounds **25** and **29** instead of high-resolution mass spectrometry. The IR-spectra were recorded on a Bruker IFS 66 spectrometer (potassium bromide). ESR spectra were taken in degassed solutions on a Bruker EMX CW ESR spectrometer, all hyperfine coupling constants and field offsets from standard DPPH line are given in Gauss with accuracy ±0.02 G, except for the couplings with methyl carbon-13 for which the accuracy is ±0.1 G, concentration of radicals 10^{-5} to 10^{-4} M in the indicated solvent. ^{1}H NMR spectra were recorded on a Bruker DRX 400 (9.4 Tesla, 400.13 MHz) spectrometer. Chemical shifts (δ, ppm) are given from internal $CHCl_3$ (7.24). Coupling constants (J, Hz) were accurate to ±0.2 Hz for ^{1}H. Compound **1** was prepared by previously reported methods.[10] Copper(I) acetylides were prepared according to the published procedure[11] from the corresponding acetylenes.[18–20] Commercial phenylacetylene, (trimethylsilyl)acetylene, and $PdCl_2(PPh_3)_2$ ('Aldrich') were used without additional purification.

4.2. Method A. General procedure of acetylides cross-coupling reaction

A mixture of copper(I) salt of acetylene (0.36 mmol) and paramagnetic iodides **9** or **11** or diamagnetic iodide **10** (130 mg, 0.33 mmol) in 10 mL of pyridine was stirred at 80–85 °C in argon atmosphere till absence of iodide (TLC-control). Then $CHCl_3$ (30 ml) and water (40 mL) were added. The organic layer was separated, the water layer was extracted with $CHCl_3$ (2×25 mL), and the combined organic layers were washed with 25% NH_{3aq} (2×15 mL), dried over Na_2SO_4, filtered off through Al_2O_3, and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on Al_2O_3 (elution with chloroform). Subsequent recrystallization gave pure compounds **12**–**17**.

*4.2.1. 2,2,5,5-Tetramethyl-4-{2-[p-(phenyl)ethynylphenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**12**)*

The time of reaction is 6 h, the yield of **12** is 83.3%, mp 197.5–198.5 °C (from benzene). IR, cm^{-1}, ν: 1253 (N→O), 1364 (N–O), 2216 (C≡C). HRMS, m/z (%): 359.1 [M$^+$] (15.40), 344.2 (31.44), 329.2 (37.78), 314.2 (44.47), 312.2 (70.76), 271.2 (38.51), 257.1 (64.78), 242.1 (56.20), 215.1 (52.66). Found: m/z 359.17540 [M$^+$]. $C_{23}H_{23}N_2O_2$ calcd: M=359.17594. UV (EtOH), λ_{max}/nm (lg ε): 201 (2.15), 235 (0.87), 273 (0.54), 283 (0.61), 360 (2.18). ESR: g_{iso}=2.0058 (ΔH_{DPPH}=3.79 G), A_N=14.05 G, $A_{H(CH3)}$(12H)=0.23 G, A(^{13}C)=5.66 G. Solvent: toluene.

*4.2.2. 2,2,5,5-Tetramethyl-4-{2-[p-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecen-15-yl-ethynyl)-phenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**15**)*

The time of reaction is 2 h, the yield of **15** is 57.0%, mp 178.5–180.0 °C (from mixture benzene–hexane). IR, cm^{-1}, ν: 2205 (C≡C), 2868, 2934, 2930, 2983 (CH_3). HRMS, m/z (%): 549.2 [M$^+$] (15.31), 534.1 (31.71), 504.1 (24.31), 502.2 (45.38), 448.3 (12.07), 447.3 (35.54), 343.1 (11.61), 295.2 (18.03), 189.2 (6.38), 180.1 (23.58), 163.1 (33.76), 98.2 (28.67). Found: m/z 549.25942 [M$^+$]. $C_{31}H_{37}N_2O_7$ calcd: M=549.26006. UV (EtOH), λ_{max}/nm (lg ε): 205 (1.43), 245 (0.63), 271 (0.52), 326 (0.73), 349 (1.11), 3.72 (1.21). ESR: g_{iso}=2.0059 (ΔH_{DPPH}=4.10 G), A_N=13.74 G, $A_{H(CH3)}$(12H)=0.22 G, A (^{13}C)=5.57 G. Solvent: toluene.

*4.2.3. 2,2,5,5-Tetramethyl-4-{2-[p-(bromophenyl)ethynyl-phenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**16**)*

The time of reaction is 5 h, the yield of **16** is 91.0%, mp 192.4–193.6 °C (from benzene). IR, cm^{-1}, ν: 2212 (C≡C). HRMS, m/z (%): 437.0 [M$^+$] (6.34), 410.1 (7.24), 407.0 (35.07), 394.0 (39.32), 391.9 (100.00), 350.9 (37.18), 349.9 (45.67), 294.9 (37.56), 257.1 (9.18), 239.1 (50.58), 176.0 (23.43), 150.0 (11.40), 135.1 (30.55), 98.1 (24.57). Found: m/z 437.08795 [M$^+$]. $C_{23}H_{22}N_2O_2Br$ calcd: M=437.08651. UV (EtOH), λ_{max}/nm (lg ε): 200 (1.56), 236 (0.65), 288 (0.48), 364 (1.61). ESR: g_{iso}=2.0057 (ΔH_{DPPH}=3.6 G), A_N=14.09 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.72 G. Solvent: toluene.

*4.2.4. 2,2,5,5-Tetramethyl-4-{2-[m-(N-ethoxyethyl-1H-pyrazol-4-ylethynyl)phenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**13**)*

The time of reaction is 4.5 h, the yield of **13** is 76.5%, mp 141.0–142.0 °C (from mixture benzene–hexane). IR, cm^{-1}, ν: 2224 (C≡C). HRMS, m/z (%): 421.2 [M$^+$] (3.90), 391.1 (63.55), 374.1 (43.14), 261.1 (38.46), 260.1 (22.86), 247.2 (22.34), 205.1 (34.52), 73.1 (43.57), 45.1 (100.00). Found: m/z 421.22844 [M$^+$]. $C_{24}H_{29}N_4O_3$ calcd: M=421.22395. UV (EtOH), λ_{max}/nm (lg ε): 202 (1.22), 237 (1.11), 282 (1.44), 294 (1.56), 335 (1.23). ESR: g_{iso}=2.0059 (ΔH_{DPPH}=3.85 G), A_N=14.06 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.73 G. Solvent: toluene.

*4.2.5. 2,2,5,5-Tetramethyl-4-{2-[p-(2-pyridinylethynyl)-phenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**14**)*

The time of reaction is 2.5 h, the yield of **14** is 33.0%, mp 179.9–180.0 °C (from mixture benzene–hexane). IR, cm^{-1}, ν: 2221 (C≡C), 2862, 2936, 2981 (CH_3). HRMS, m/z (%): 363.0 [M^+] (11.73), 361.9 (44.62), 359.9 (19.52), 330.0 (61.01), 314.9 (73.31), 312.9 (100.00), 271.8 (54.00), 257.9 (88.27), 241.9 (37.30), 231.8 (30.33), 215.9 (51.74). Found: m/z 360.17256 [M^+]. $C_{22}H_{22}N_3O_2$ calcd: M=360.17119. UV (EtOH), λ_{max}/nm (lg ε): 200 (1.57), 228 (0.76), 270 (0.48), 359 (2.18). ESR: g_{iso}=2.0059 (ΔH_{DPPH}=4.05 G), A_N=13.81 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.60 G. Solvent: toluene.

*4.2.6. 2,2,5,5-Tetramethyl-4-{2-[p-(o-nitrophenyl)ethynyl-phenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**17**)*

The time of reaction is 2 h, the yield of **16** is 53.0%, mp 179.0–180.0 °C (from benzene). IR, cm^{-1}, ν: 1252 (N→O), 1341 (N–O), 2216 (C≡C). HRMS, m/z (%): 404.2 [M^+] (12.86), 374.2 (61.66), 359.1 (62.03), 358.1 (25.08), 357.1 (100.00), 299.1 (25.59), 258.1 (19.88), 239.0 (15.16), 183.1 (43.56). Found: m/z 404.16220 [M^+]. $C_{23}H_{22}N_3O_4$ calcd: M=404.16102. UV (EtOH), λ_{max}/nm (lg ε): 203 (1.81), 228 (1.21), 264 (0.85), 373 (2.78), 382 (2.27). ESR: g_{iso}=2.0059 (ΔH_{DPPH}=3.85 G), A_N=14.06 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.736 G. Solvent: toluene.

4.3. Method B. General procedure of Pd-free cross-coupling reaction

A mixture of iodide **10** or **18** (150 mg, 0.39 mmol), PPh_3 (0.04 mmol), CuI (0.02 mmol), potassium carbonate (0.6 mmol), and alkyne (0.4 mmol) in 10 mL of DMF was stirred under stream of argon at 90–100 °C until the full consumption of iodide (TLC-control, 'Silufol'). Then $CHCl_3$ (30 ml) and water (40 mL) were added, organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (2×25 mL). The combined organic layers were washed with 25% aqueous NH_3 (2×15 mL), dried over K_2CO_3, filtered through Al_2O_3, and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on Al_2O_3 (elution with chloroform). Subsequent recrystallization gave pure compounds **19**–**25**. Physical and spectral data for the products are given in following sections. Note for compound **25**: a mixture of iodide **10** (130 mg, 0.33 mmol), PPh_3 (0.04 mmol), CuI (0.02 mmol), potassium carbonate (0.6 mmol), and 4,4′-diethynylbiphehyl (33 mg, 0.16 mmol) in 10 mL of DMF was used.

*4.3.1. 2,2,5,5-Tetramethyl-4-{2-[m-(phenyl)ethynylphenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**19**)*

The time of reaction is 5 h, the yield of **19** is 83.3%, mp 156.5–158.0 °C (from benzene). IR, cm^{-1}, ν: 1255 (N→O), 1364 (N–O), 2116 (C≡C). HRMS, m/z (%): 359.1 [M^+] (6.62), 354.9 (83.62), 329.1 (96.31), 312.0 (60.45), 270.0 (39.74), 214.9 (71.07), 170.0 (52.00). Found: m/z 359.17647 [M^+]. $C_{23}H_{23}N_2O_2$ calcd: M=359.17594. UV (EtOH), λ_{max}/nm (lg ε): 217 (0.71), 284 (098), 300 (0.98), 335 (0.67). ESR: g_{iso}=2.0061 (ΔH_{DPPH}=4.42 G), A_N=14.07 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.90 G. Solvent: toluene.

*4.3.2. 2,2,5,5-Tetramethyl-4-{2-[p-(diphenyl)ethynylphenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**20**)*

The time of reaction is 4 h, the yield of **20** is 71.4%, mp 147.0–148.0 °C (from benzene). IR, cm^{-1}, ν: 1255 (N→O), 1368 (N–O), 2213 (C≡C). HRMS, m/z (%): 435.2 [M^+] (13.79), 405.2 (29.00), 390.2 (56.62), 388.2 (100.00), 347.2 (62.17), 318.3 (34.32), 291.2 (54.24), 252.2 (19.13). Found: m/z 435.20869 [M^+]. $C_{29}H_{27}N_2O_2$ calcd: M=435.20724. UV (EtOH), λ_{max}/nm (lg ε): 203 (1.56), 240 (0.96), 257 (1.04), 342 (1.97). ESR: g_{iso}=2.0060 (ΔH_{DPPH}=4.05 G), A_N=14.05 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.72 G. Solvent: toluene.

*4.3.3. 2,2,5,5-Tetramethyl-4-{2-[p-(acetylphenyl)ethynyl-phenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**21**)*

The time of reaction is 4.5 h, the yield of **21** is (53.3%), mp 179.0–180.5 °C (from mixture benzene–hexane). IR, cm^{-1}, ν: 1264 (N→O), 1361 (N–O), 1674 (C═O), 2212 (C≡C). HRMS, m/z (%): 401.2 [M^+] (5.31), 386.2 (14.34), 371.1 (21.04), 356.1 (32.30), 354.1 (44.52), 312.9 (20.09), 299.0 (32.62). Found: m/z 401.18722 [M^+]. $C_{25}H_{25}N_2O_3$ calcd: M=401.18650. UV (EtOH), λ_{max}/nm (lg ε): 324 (4.39). ESR g_{iso}=2.0062 (ΔH_{DPPH}=4.29 G), A_N=14.04 G, $A_{H(CH3)}$(12H)=0.23 G. Solvent: toluene.

*4.3.4. 2,2,5,5-Tetramethyl-4-{2-[p-(2-carbomethoxyphenyl)-ethynylphenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**22**)*

The time of reaction is 2.5 h, the yield of **22** is 56.2%, mp 239.0–239.5 °C (from benzene). IR, cm^{-1}, ν: 1254 (N→O), 1367 (N–O), 1739 (C═O), 2214 (C≡C). HRMS, m/z (%): 417.2 [M^+] (17.48), 387.2 (38.26), 372.1 (56.79), 370.1 (100.00), 329.1 (29.87), 314.1 (40.57), 283.1 (51.02). Found: m/z 417.17921 [M^+]. $C_{25}H_{25}N_2O_4$ calcd: M=417.18142. UV (EtOH), λ_{max}/nm (lg ε): 238 (4.28), 285(3.95), 365 (4.61). ESR g_{iso}=2.0061 (ΔH_{DPPH}=4.5 G), A_N=14.06 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.575 G. Solvent: toluene.

*4.3.5. 2,2,5,5-Tetramethyl-4-{2-[p-(2-amino-4-methylpyridinyl-5)-ethynylphenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**23**)*

The time of reaction is 3.5 h, the yield of **23** is 75.0%, mp 202.5–203.0 °C (from benzene). IR, cm^{-1}, ν: 1253 (N→O), 1364 (N–O), 2206 (C≡C). HRMS, m/z (%): 389.0 [M^+] (7.90), 359.1(5.30), 344.1 (11.32), 342.1 (22.28), 286.9 (9.81), 244.9 (10.78). Found: m/z 389.19693 [M^+]. $C_{23}H_{25}N_4O_2$ calcd: M=389.19774. UV (EtOH), λ_{max}/nm (lg ε): 255 (4.18), 277 (4.21), 377 (4.59). ESR: g_{iso}=2.0060 (ΔH_{DPPH}=4.05 G), A_N=14.05 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.72 G. Solvent: toluene.

*4.3.6. 2,2,5,5-Tetramethyl-4-{2-[p-(pyrimidinyl-5)ethynylphenyl]-vinyl}-3-imidazoline-3-oxide-1-oxyl (**24**)*

The time of reaction is 7 h, the yield of **24** is 53.0%, mp 147.0–148.0 °C (from benzene). IR, cm^{-1}, ν: 1255 (N→O), 1366 (N–O), 2216 (C≡C). HRMS, m/z (%): 361.2 [M^+] (11.17), 346.2 (32.86), 331.2 (64.91), 314.2 (95.94), 273.1 (64.75), 272.1 (66.67), 244.0 (78.94), 217.2 (82.34), 177.1 (40.24), 78.0 (60.81). Found: m/z 361.16545 [M^+]. $C_{21}H_{21}N_4O_2$ calcd: M=361.16644. UV (EtOH), λ_{max}/nm (lg ε): 226 (4.16), 357 (4.49). ESR g_{iso}=2.0061 (ΔH_{DPPH}=4.39 G), A_N=14.05 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.88 G. Solvent: toluene.

*4.3.7. Bis-4,4′-{2,2,5,5-tetramethyl-4-[2-(p-ethynylphenyl)vinyl]-3-imidazoline-3-oxide-1-oxyl}-biphenyl (**25**)*

The time of reaction is 3 h, the yield of **25** is 45.5%, mp 254.0–255.5 °C (from benzene). IR, cm^{-1}, ν: 1255 (N→O), 1364 (N–O), 2211 (C≡C). Anal. Calcd for $C_{46}H_{44}N_4O_4$: C, 77.07; H, 6.19; N, 7.82. Found: C, 76.95; H, 6.42; N, 7.80. UV spectra were not taken due to low solubility in ethanol. ESR g_{iso}=2.0060 (ΔH_{DPPH}=4.22 G), A_N=14.13 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.83 G. Solvent: toluene.

4.4. Method C. General procedure of Pd catalyst cross-coupling reaction

A mixture of iodide **9** or **11** (150 mg, 0.39 mmol), $[Pd(PPh_3)_2]Cl_2$ (20 mg), PPh_3 (40 mg), CuI (20 mg), Et_3N (5 mL), and alkyne (0.4 mmol) in 20 mL of benzene was stirred under stream of argon at 80 °C until the full consumption of iodide (TLC-control, 'Silufol'). Then the mixture filtered through Al_2O_3 and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on Al_2O_3 (elution with benzene). Subsequent recrystallization gave pure compounds **2**, **12**, **26**, **27**, and **29**. Physical and spectral data for the products are given in the following sections. Note for biradical **25**: a mixture of iodide **28** (150 mg, 0.40 mmol), $[Pd(PPh_3)_2]Cl_2$ (20 mg), PPh_3 (40 mg), CuI (20 mg),

Et_3N (5 mL), and 4,4′-diethynylbiphehyl (42 mg, 0.20 mmol) in 20 mL of benzene was used.

*4.4.1. 1-Hydroxy-2,2,5,5-tetramethyl-4-{2-[p-(phenyl)ethynylphenyl]vinyl}-3-imidazoline-3-oxide (**2**)*

The time of reaction is 4.5 h, the yield of **2** is 31%, mp 218–219.5 °C (from benzene). IR, cm^{-1}, ν: 1257 ($N\rightarrow O$), 2217 ($C\equiv C$), 3230 (OH). ^1H NMR: 1.52 (s, 6H, CH_3), 1.62 (s, 6H, CH_3), 4.85 (br s, 1H, OH), 6.86 (d, 1H, =CH–Im, J=16.2), 7.26–7.57 (m, 9H, Ar), 8.42 (d, 1H, =CH–Ar, J=16.2). HRMS, m/z (%): 360.0 [M^+] (25.11), 312.0 (20.85), 286.9 (21.52), 257.9 (42.73), 256.9 (100.00), 241.8 (79.39), 240.9 (34.38), 218.8 (19.20), 214.8 (24.10). Found: m/z 360.18393 [M^+]. $C_{23}H_{24}N_2O_2$. calcd: M=360.18377. UV (EtOH), λ_{max}/nm (lg ε): 227 (0.12), 284 (0.10), 359 (0.24). 1,4-Diphenylbuta-1,3-diyne **4** [10 mg (25%)] was isolated as well.

*4.4.2. 2,2,5,5-Tetramethyl-4-{2-[p-(phenyl)ethynylphenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**12**)*

The time of reaction is 4.5 h, the yield of **12** is 54.0%, mp 197.5–198.5 °C (from benzene). Spectral and analytical data see above (in Section 4.2).

*4.4.3. 2,2,5,5-Tetramethyl-4-{2-[p-(trimethylsilyl)-ethynylphenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl] (**26**)*

The time of reaction is 3 h, the yield of **26** is 91.0%, mp 184.0–185.0 °C (from mixture benzene–hexane), $mp_{(lit.)}$ 184.0–185.0 °C.[21] IR, cm^{-1}, ν: 1252 ($N\rightarrow O$), 1362 (N–O), 2157 ($C\equiv C$), HRMS, m/z (%): 355.1 [M^+] (22.84), 325.1 (43.98), 310.1 (56.54), 309.1 (22.75), 308.1 (73.41), 267.1 (38.07), 266.1 (33.91), 252.1 (24.26), 211.0 (16.03). Found: m/z 355.18055 [M^+]. $C_{20}H_{27}N_2O_2Si$ calcd: M=355.18417. UV (EtOH), λ_{max}/nm (lg ε): 243 (4.08), 251 (4.08), 352 (4.52). ESR g_{iso}=2.0060 (ΔH_{DPPH}=4.184 G), A_N=14.29 G, $A_{H(CH3)}$(12H)=0.24 G, A (^{13}C)=5.82 G. Solvent: toluene.

*4.4.4. 2,2,5,5-Tetramethyl-4-{2-[m-(trimethylsilyl)-ethynylphenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**27**)*

The time of reaction is 7 h, the yield of **27** is 77.0%, mp 144.0–144.5 °C (from mixture benzene–hexane), $mp_{(lit.)}$ 144.0–144.5 °C.[21] IR, cm^{-1}, ν: 1258 ($N\rightarrow O$), 1368 (N–O), 2156 ($C\equiv C$). HRMS, m/z (%): 360.0 [M^+] (25.11), 312.0 (20.85), 286.9 (21.52), 257.9 (42.73), 256.9 (100.00), 241.8 (79.39), 240.9 (34.38), 218.8 (19.20), 214.8 (24.10). Found: m/z 355.18373 $[M]^+$. $C_{20}H_{27}N_2O_2Si$ calcd: M=355.18417. UV (EtOH), λ_{max}/nm (lg ε): 202 (4.21), 231 (4.34), 247 (4.35), 263 (4.01), 272 (4.27), 336 (4.32). ESR g_{iso}=2.0061 (ΔH_{DPPH}=4.262 G), A_N=14.09 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.913 G. Solvent: toluene.

*4.4.5. Bis-4,4′-[4-(p-ethynylphenyl)-2,2,5,5-tetramethyl-3-imidazoline-3-oxide-1-oxyl]-biphenyl (**29**)*

The time of reaction is 5 h, the yield of **29** is 61.5%, mp 242.0–242.5 °C (from mixture benzene–hexane). IR, cm^{-1}, ν: 1256 ($N\rightarrow O$), 1360 (N–O), 2213 ($C\equiv C$). Anal. Calcd for $C_{42}H_{40}N_4O_4$: C, 75.88; H, 6.06; N, 8.43. Found: C, 76.60; H, 6.07; N, 8.54. UV spectra were not taken due to low solubility of compounds **25** and **29** in ethanol. ESR g_{iso}=2.0059 (ΔH_{DPPH}=3.95 G), A_N=14.16 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=6.3 G. Solvent: toluene.

4.5. General procedure of Pd catalyst cross-coupling reaction for model compounds 5 and 7

Method i: a solution of radical **5** or **7** (2.0 mmol), Et_3N (5 mL) and phenylacetylene (240 mg, 2.4 mmol, 0.30 mL) in 20 mL of benzene was stirred under stream of argon at 80 °C for 5 h. Then $[Pd(PPh_3)_2]Cl_2$ (20 mg) was added and the mixture was stirred at 80 °C for another 5 h. The mixture was filtered through Al_2O_3, and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on Al_2O_3 (elution with benzene). Subsequent recrystallization gave pure products.

For radical **5** the yield of 1-hydroxy-2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-3-oxide **6** is 66%, mp 188.5–189.5 °C (from mixture of benzene–hexane), $mp_{(lit.)}$ 193.0–194.0 °C.[22] The yield of 1,4-diphenylbuta-1,3-diyne **4** is 66.5%, mp 83.0–85.0 °C (from hexane), $mp_{(lit.)}$ 86.0–87.0 °C.

For radical **7** the yield of 1-hydroxy-2,2,5,5-tetramethyl-4-(p-nitrophenyl)-3-imidazoline-3-oxide **8** is 91%, mp 83.4–84.5 °C (from mixture of benzene–hexane), $mp_{(lit.)}$ 85.0–87.0 °C.[24] The yield of 1,4-diphenylbuta-1,3-diyne **4** is 74%, mp 85.5–86.5 °C (from hexane), $mp_{(lit.)}$ 86.0–87.0 °C.[23]

Method ii: a solution of radical **5** or **7** (2.0 mmol), $AcONa\cdot 3H_2O$ (0.08 g, 0.58 mmol) and phenylacetylene (2.4 mmol, 240 mg, 0.3 mL), $PdCl_2$ (5 mg) in 8 mL of CH_3CN was stirred under stream of argon at 20 °C for 8 h. Then the mixture was evaporated to dryness under reduced pressure and filtered through Al_2O_3 (elution with ethyl acetate). Subsequent recrystallization gave pure compounds **6** or **8** and **4**.

For radical **5** the yield of 1-hydroxy-2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-3-oxide **6** is 28%, mp 188.5–189.5 °C (from mixture of benzene–hexane), $mp_{(lit.)}$ 193.0–194.0 °C.[22] The yield of 1,4-diphenylbuta-1,3-diyne **4** is 90%, mp 85.5–86.5 °C (from hexane), $mp_{(lit.)}$ 86.0–87.0 °C.[23]

For radical **7** the yield of 1-hydroxy-2,2,5,5-tetramethyl-4-(p-nitrophenyl)-3-imidazoline-3-oxide **8** is 94%, mp 84.0–85.0 °C (from mixture of benzene–hexane), $mp_{(lit.)}$ 85.0–87.0 °C.[24] The yield of 1,4-diphenylbuta-1,3-diyne **4** is 66%, mp 83.5–85.0 °C (from hexane), $mp_{(lit.)}$ 86.0–87.0 °C.[23]

4.6. General procedure of desilylation of 26 and 27

A mixture of radical **26** or **27** (0.33 g, 0.9 mmol) and K_2CO_3 (0.12 g, 0.9 mmol) in 15 mL of methanol was stirred under of argon at room temperature until TLC-control ('Silufol') indicates absence of the starting materials (4 h). At this point, $CHCl_3$ (20 ml) and water (40 mL) were added, organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (2×25 mL). The organic layers were combined, dried over K_2CO_3, filtered through Al_2O_3, and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on Al_2O_3 (elution with chloroform). Subsequent recrystallization gave pure compounds **30** and **31**.

*4.6.1. 2,2,5,5-Tetramethyl-4-{2-[p-(ethynyl)phenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**30**)*

Yield is 78.9%, mp 176.0–176.6 °C (from mixture benzene–hexane), $mp_{(lit.)}$ 176.0–176.6 °C.[21] IR, cm^{-1}, ν: 1254 ($N\rightarrow O$), 1361 (N–O), 2110 ($C\equiv C$). HRMS, m/z (%): 283.1 [M^+] 33.31, 253.0 (100.00), 238.0 (72.42), 236.1 (84.63), 194.9 (47.73), 193.9 (75.10), 179.9 (48.82), 165.9 (54.81), 164.9 (70.52), 152.9 (40.80), 138.9 (97.80). Found: m/z 283.14430 [M^+]. $C_{17}H_{19}N_2O_2$ calcd: M=283.14463. UV (EtOH), λ_{max}/nm (lg ε): 242 (0.83), 249 (0.82), 346 (1.89). ESR g_{iso}=2.00587 (ΔH_{DPPH}=3.9 G), A_N=14.01 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.97 G. Solvent: toluene.

*4.6.2. 2,2,5,5-Tetramethyl-4-{2-[m-(ethynyl)phenyl]vinyl}-3-imidazoline-3-oxide-1-oxyl (**31**)*

Yield is 48.0%, mp 141.5–142.0 °C (from mixture benzene–hexane), $mp_{(lit.)}$ 141.5–142.0 °C.[21] IR, cm^{-1}, ν: 1254 ($N\rightarrow O$), 1361 (N–O), 2110 ($C\equiv C$). HRMS, m/z (%): 2853.1 [M^+] (11.92), 253.2 (100.00), 238.2 (42.99), 236.2 (44.49), 194.1 (54.97), 165.1 (64.51), 149.0 (37.29), 139.1 (71.73). Found: m/z 283.14521 $[M]^+$. $C_{17}H_{19}N_2O_2$ calcd: M=283.14464. UV (EtOH), λ_{max}/nm (lg ε): 201 (1.04), 224 (1.81), 256 (1.13), 265 (0.92), 333 (1.62). ESR g_{iso}=2.0060

(ΔH_{DPPH}=4.22 G), A_N=14.13 G, $A_{H(CH3)}$(12H)=0.23 G, A (^{13}C)=5.83 G. Solvent: toluene.

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