Regioselective synthesis of *cis*- and *trans*-2,4,5-triarylimidazolines and 2,4,5-triarylimidazoles from available reagents*

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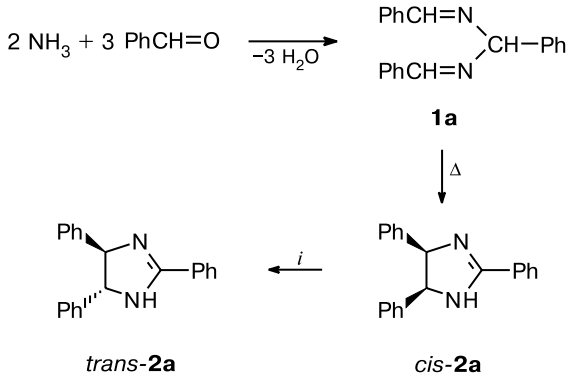
Novel data were obtained concerning the reaction of aromatic aldehydes with ammonia. A preparative method for the synthesis of new substituted 1,3,5-triaryl-2,4-diazapenta-1,4-dienes was developed. These products are the starting reactants for syntheses of *cis*- and *trans*-2,4,5-triaryl-2-imidazolines and 2,4,5-triarylimidazoles.

Key words: aromatic aldehydes, 1,3,5-triaryl-2,4-diazapenta-1,4-dienes, hydrobenzamide, imidazolines, imidazoles.

It is known[1,2] that benzaldehyde reacts with ammonia to form the trimeric product, *viz.*, 1,3,5-triphenyl-2,4-diazapenta-1,4-diene (**1a**). The thermal ring closure of compound **1a** affords *cis*-2,4,5-triphenyl-2-imidazoline (*cis*-**2a**).[2—4] The third isomer, *trans*-2,4,5-triphenyl-2-imidazoline (*trans*-**2a**), was prepared by the treatment of the *cis*-isomer with a strong base (Scheme 1).[3—7]

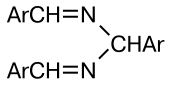
Scheme 1



Reagent and conditions: *i*. NaOH/ethylene glycol, 150 °C.

Substituted *cis*-imidazolines *cis*-**2** and *trans*-imidazolines *trans*-**2** are, as known, of great synthetic interest as the starting reactants in the synthesis of *meso*- and *d,l*-isomers of vicinal diamines[4—6] and imidazole derivatives.[8] Therefore, the ring closure of 1,3,5-triaryl-2,4-diazapenta-1,4-dienes **1** is a convenient synthetic method. Previously, such strong bases as sodium amide and phenyllithium were used for the ring closure of triphenyldiazapentadiene (**1a**) to *cis*-imidazoline *cis*-**2a** along with the thermal ring closure, which occurs in a low yield. To synthesize *trans*-triphenylimidazoline (*trans*-**2a**), the two-step method was proposed, including the synthesis of *cis*-imidazoline (*cis*-**2a**)[9,10] and its isolation followed by recyclization under the action of a strong base (PhLi, Bu^tOK in Bu^tOH, and NaOH in diethylene glycol). The ring closure of triphenyldiazapentadiene (**1a**) by a 0.41 *N* solution of Bu^tOK in Bu^tOH at 100 °C was also described.[11] However, the yield of compound **3a** was low. The attempt[12] to use ultraviolet irradiation for the direct ring closure of the anion of triphenyldiazapentadiene (**1a**) to form *trans*-imidazoline *trans*-**2a** was unsuccessful: the reaction occurred in a low yield (7—16%).

We synthesized several 1,3,5-triaryl-2,4-diazapentadienes **1a—f** (77—94% yields) by the interaction of the corresponding aromatic aldehydes with an ammonia solution to use them in subsequent ring closure.



1a—f

Ar = Ph (**a**), 4-BrC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 2-thienyl (**d**), 3-$NO_2C_6H_4$ (**e**), 4-FC_6H_4 (**f**)

The interaction of 2,6-dichlorobenzaldehyde with an ammonia solution in ethanol immediately afforded the corresponding *cis*-2,4,5-triarylimidazoline *cis*-**2g** in 97% yield. This fact can be explained by a greater easiness of proton elimination in the formed compound **1g**, which facilitates ring closure even under the action of such a weak base as ammonia. To check this assumption, we studied the reactions of 2-nitrobenzaldehyde and 3-nitrobenzaldehyde with am-

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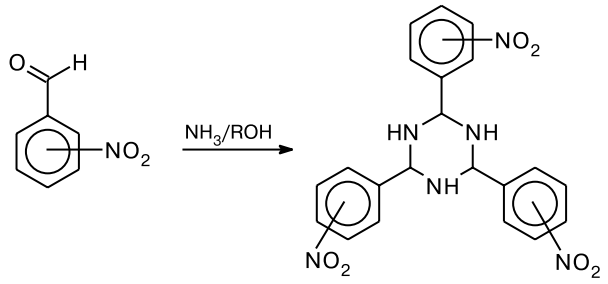
monia. We found that the nature of products of the reactions of these aldehydes with ammonia depends on the chosen solvent. For example, the interaction of 2- and 3-nitrobenzaldehydes with a saturated alcoholic solution of ammonia (ethyl, isopropyl, and *tert*-butyl alcohols were used) afforded hexahydrotriazines **3a,b** (Scheme 2), and when a saturated solution of ammonia in THF was used, the corresponding *cis*-imidazolines *cis*-**2e,h** immediately formed. Anhydrous solvents decrease the yield of by-products. It is known that the formation of triazine structure is more characteristic of aliphatic than aromatic aldehydes[9,13] because, in the case of aromatic aldehydes, similar triazines can transform with ejection of an ammonia molecule into diazapentadienes **1**. This transformation readily occurs on slight heating.[14] 1,3,5-Triaryldiazapentadiene **1e** was synthesized from 3-nitrobenzaldehyde by the reaction with a saturated ammonia solution in methylene chloride or benzene. Under these conditions, 2-nitrobenzaldehyde transformed into the 1 : 1 mixture of the corresponding diazapentadiene and hexahydrotriazine.

Scheme 2



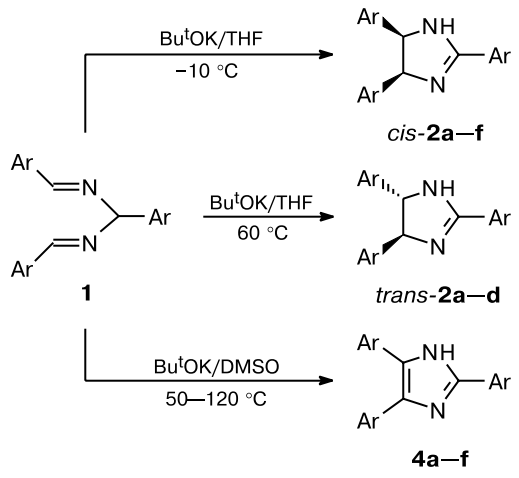
3a,b

The results obtained for 2- and 3-nitrobenzaldehydes correlate well with the previous data for the reaction of pyridine-2-carbaldehyde with ammonia.[13]

Studying the ring closure of compounds **1** by the action of Bu^{t}OK, we showed that a change in the reaction conditions allowed one to easily obtain any of three desired products (*cis*-**2**, *trans*-**2**, or **4**) in a high yield. This procedure provides the easy isolation of all these compounds. A simple and convenient method for syntheses of *cis*- and *trans*-2,4,5-triaryl-2-imidazolines *cis*-**2** and *trans*-**2** and 2,4,5-triarylimidazolines **4** using the ring closure of the corresponding 1,3,5-triaryl-2,4-diazapenta-1,4-dienes was proposed (Scheme 3).

The reaction of triphenyldiazapentadiene (**1a**) with the stoichiometric amount of Bu^{t}OK in anhydrous THF at −10 °C for 20 min affords the corresponding *cis*-imidazoline *cis*-**2a** in 80% yield. The reaction in anhydrous THF on boiling for 15 min results in the formation of *trans*-imidazoline *trans*-**2a** in 90% yield, and 2,4,5-triphenylimidazole **4a** forms in ~100% yield when

Scheme 3

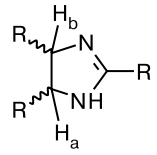


Ar = Ph (**2a**, **4a**), 4-BrC_6H_4 (**2b**, **4b**), 4-$MeOC_6H_4$ (**2c**, **4c**), 2-thienyl (**2d**, **4d**), 3-$NO_2C_6H_4$ (*cis*-**2e**, **4e**), 4-FC_6H_4 (*cis*-**2f**), 4-pyridyl (**4f**)

the reaction is performed with the stoichiometric amount of Bu^{t}OK in DMSO at 50 °C for 2 h. Products of ring closure of compound **1a** can easily be identified, because the structures of *cis*-**2a** and *trans*-**2a** are known and their *cis*- and *trans*-configurations have been proved earlier[7] by X-ray diffraction analysis.

The presence of acceptor substituents in the aromatic cycle is shown to facilitate both the ring closure and subsequent oxidation to imidazole. For example, 2,4,5-tris(pyridin-4-yl)imidazole (**4f**) forms already in the interaction of pyridine-4-carbaldehyde with an aqueous solution of ammonia, while the syntheses of 2,4,5-tris(2-thienyl)imidazole (**4d**) and 2,4,5-tris(4-methoxyphenyl)imidazole (**4c**) require drastic conditions: refluxing of the starting diazapentadienes or imidazolines *cis*-**2** and *trans*-**2** with Bu^{t}OK in DMSO in an oxygen flow for 1—7 days, the yield being ~50%. In these cases, it is difficult to oxidize imidazolines to imidazoles likely because the reaction proceeds through deprotonation at the nitrogen atom to form an anionic structure, and the deprotonation is hindered by donor substituents.

In studying the ring closure of various diazapentadienes, we faced the problem of identification of *cis*- and *trans*-products of the reaction, because it has previously been reported for the only well-studied similar compounds, *viz*., benzaldehyde derivatives, that signals from the H_a and H_b protons in the ^{1}H NMR spectrum coincide for *cis*- and *trans*-imidazolines.



To prove the structure, imidazolines were either transformed into those acylated at the nitrogen atom of the system, which allowed one to distinguish signals from the *cis*- and *trans*-protons,[9] or X-ray diffraction analysis was

Table 1. Chemical shifts of the H_a and H_b protons in the ^1H NMR spectra and melting points of imidazolines ***cis*-2** and ***trans*-2***

Compound	R	δ	M.p./°C
***cis*-2**			
a	Ph	5.25—5.35 (br.s, 2 H)	129
b	4-BrC_6H_4	5.40 (s, 2 H)	120
c	4-$MeOC_6H_4$	5.25 (s, 2 H)	86
d	2-Thienyl	5.53 (s, 2 H)	97
e	3-$NO_2C_6H_4$	5.55 (d, 1 H) 5.85 (d, 1 H)	150—154
f	4-FC_6H_4	5.38 (br.s, 2 H)	123—125
g	2,6-$Cl_2C_6H_4$	6.05 (d, 1 H), 6.45 (d, 1 H)	138—143
h	2-$NO_2C_6H_4$	5.98 (d, 1 H) 6.18 (d, 1 H)	244—246
***trans*-2**			
a	Ph	4.85—5.00 (br.s, 2 H)	202
b	4-BrC_6H_4	4.75 (s, 2 H)	196
c	4-$MeOC_6H_4$	4.66 (c, 2 H)	135
d	2-Thienyl	5.05 (d, 1 H), 5.15 (d, 1 H)	158—160

* Signals from the H_a and H_b protons in compounds *cis*-**2e**, *cis*-**2g**, and *trans*-**2d** have the shape of doublets, which is caused by hindrances of internal rotation about the R—C(4) and R—C(5) bonds. The spin-spin coupling constants are presented in Experimental.

used.[7] We propose to use a DMSO-d_6/CCl_4 (1 : 2) system for recording ^1H NMR spectra. Since the configuration for compounds *cis*-**2a** and *trans*-**2a** has previously[7] been proved by X-ray diffraction analysis, at first the signals of the indicated protons in *trans*- and *cis*-imidazolines were exactly assigned. It was found that in the DMSO-d_6/CCl_4 (1 : 2) system the signals from H_a and H_b differed for the *cis*- and *trans*-isomers and, as expected, for *cis*-imidazolines the signals of protons demonstrated downfield shifts compared to the *trans*-isomers. The established *cis*- and *trans*-configurations were indirectly confirmed by the regularities in the melting temperatures: the melting point is higher for the *trans*-isomer (Table 1).

The validity of determination of the configuration of imidazolines from the ^1H NMR spectrum was verified for compound *cis*-**2g**, for which we assumed the *cis*-configuration due to the strong upfield shift of characteristic protons. The proposed configuration was confirmed by the X-ray diffraction data to be published elsewhere.

Experimental

^1H NMR spectra were recorded on Bruker AC-300, Bruker AC-200, and Varian 400 instruments. Melting points were determined in a glass capillary.

1,3,5-Triphenyl-2,4-diazapenta-1,4-diene (1a).[4] A solution (100 mL) of ammonia in 95% ethanol and ammonium chloride (1 g) were added to benzaldehyde (20 g, 0.188 mol). The mixture was stirred for 6 h at ~20 °C. Colorless crystals were filtered off. The yield was 80% (15 g), m.p. 105 °C (95% ethanol).

1,3,5-Tris(4-bromophenyl)-2,4-diazapenta-1,4-diene (1b). A solution of ammonia (50 mL) in ethanol and ammonium chloride (0.5 g) were added to 4-bromobenzaldehyde (10 g, 0.054 mol). The mixture was stirred for 24 h at ~20 °C. Colorless crystals were filtered off. The yield was 79% (7.6 g), m.p. 120 °C (95% ethanol). ^1H NMR (300.13 MHz, $CDCl_3$), δ: 5.90 (s, 1 H); 7.35 (d, 2 H, J = 13 Hz); 7.50 (d, 2 H, J = 13 Hz); 7.55 (d, 4 H, J = 12 Hz); 7.70 (d, 4 H, J = 12 Hz); 8.49 (s, 2 H). Found (%): C, 47.06; H, 3.04; N, 6.02. $C_{21}H_{15}Br_3N_2$. Calculated (%): C, 47.14; H, 2.83; N, 5.24.

1,3,5-Tris(4-methoxyphenyl)-2,4-diazapenta-1,4-diene (1c). A saturated solution of ammonia (100 mL) in ethanol and ammonium chloride (0.5 g) were added to 4-methoxybenzaldehyde (10 g, 0.073 mol). The mixture was stirred for 24 h at ~20 °C. Colorless crystals of compound **1c** were filtered off (8 g, 84%), m.p. 127 °C (95% ethanol). ^1H NMR spectrum (300.13 MHz, DMSO-d_6/CCl_4), δ: 5.81 (s, 1 H); 6.85 (d, 2 H, J = 10 Hz); 6.95 (d, 4 H, J = 11 Hz); 7.35 (d, 2 H, J = 10); 7.75 (d, 4 H, J = 11 Hz); 8.48 (s, 2 H). Found (%): C, 74.29; H, 6.38; N, 7.32. $C_{24}H_{24}N_2O_3$. Calculated (%): C, 74.21; H, 6.23; N, 7.21.

1,3,5-Tris(2-thienyl)-2,4-diazapenta-1,4-diene (1d). A saturated solution of ammonia (100 mL) in ethanol and ammonium chloride (1 g) were added to thiophene-2-carbaldehyde (20 g, 0.178 mol). The mixture was stirred for 6 h at ~20 °C. Colorless crystals of compound **1d** were filtered off. The yield was 14.9 g (84%), m.p. 120 °C (95% ethanol). ^1H NMR (300.13 NHz, DMSO-d_6/CCl_4), δ: 6.18 (s, 1 H); 6.90 (t, 1 H, J = 6 Hz); 7.03 (d, 1 H, J = 6 Hz); 7.12 (t, 2 H, J = 6 Hz); 7.45 (d, 1 H, J = 6 Hz); 7.50 (d, 2 H, J = 6 Hz); 7.65 (d, 2 H, J = 6 Hz); 8.65 (s, 2 H). Found (%): C, 56.33; H, 3.77; N, 9.05. $C_{14}H_{13}N_2S_3$. Calculated (%): C, 56.93; H, 3.82; N, 8.85.

1,3,5-Tris(3-nitrophenyl)-2,4-diazapenta-1,4-diene (1e). Compound **1e** was obtained from 3-nitrobenzaldehyde (5 g, 0.033 mol) and a saturated solution (40 mL) of ammonia in methylene chloride or benzene. The yield was 4.5 g (94%), white crystals, m.p. 178 °C (95% ethanol). ^1H NMR (399.95 MHz, DMSO-d_6/CCl_4), δ: 6.35 (s, 1 H); 7.70 (t, 1 H, J = 9 Hz); 7.85 (t, 2 H, J = 8 Hz); 8.00 (d, 1 H, J = 9 Hz); 8.15 (d, 1 H, J = 8 Hz); 8.30 (m, 4 H); 8.40 (s, 1 H); 8.70 (s, 2 H); 8.85 (s, 2 H). Found (%): C, 57.96; H, 3.47; N, 16.99. $C_{21}H_{17}N_5O_7$. Calculated (%): C, 58.20; H, 3.49; N, 16.16.

1,3,5-Tris(4-fluorophenyl)-2,4-diazapenta-1,4-diene (1f). Compound **1e** was synthesized from *p*-fluorobenzaldehyde (10 g, 0.054 mol), an aqueous 25% solution of ammonia (50 mL), and ammonium chloride (0.5 g). The yield was 6 g (77%), colorless crystals, m.p. 93—95 °C (95% ethanol). ^1H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 5.95 (s, 1 H); 7.10 (t, 2 H, J = 9 Hz); 7.20 (t, 4 H, J = 9 Hz); 7.50 (t, 2 H, J = 7 Hz); 7.20 (t, 4 H, J = 7 Hz); 8.69 (s, 2 H). Found (%): C, 71.68; H, 4.25; N, 8.12. $C_{21}H_{15}F_3N_2$. Calculated (%): C, 71.58; H, 4.29; N, 7.95.

2,4,6-Tris(2-nitrophenyl)hexahydro-1,3,5-triazine (3a). A saturated solution of ammonia (50 mL) in anhydrous ethanol and ammonium chloride (0.1 g) were added to 2-nitrobenzaldehyde (4.7 g, 0.031 mol). The mixture was stirred for 48 h at ~20 °C, and a light pink precipitate was filtered off from the formed dark cherry-colored solution. The yield was 2 g

(44.7%), m.p. 117 °C (95% ethanol). ^{1}H NMR (200.13 MHz, DMSO-d_6/CCl_4), δ: 2.41 (t, 3 H, *J* = 10 Hz); 5.55 (t, 3 H, *J* = 10 Hz); 7.48 (t, 3 H, *J* = 7 Hz); 7.61 (t, 3 H, *J* = 7 Hz); 7.68—7.79 (m, 6 H). Found (%): C, 55.88; H, 4.00; N, 18.56. $C_{21}H_{18}N_6O_3$. Calculated (%): C, 56.00; H, 4.03; N, 18.66.

2,4,6-Tris(3-nitrophenyl)hexahydro-1,3,5-triazine (3b). A saturated solution of ammonia (50 mL) in anhydrous ethanol was added to 3-nitrobenzaldehyde (5 g, 0.033 mol). The mixture was stirred for 5 days at ~20 °C. A light yellow crystalline precipitate was filtered off from the formed dark cherry-colored solution. The yield was 3.82 g (80%), m.p. 118 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 2.45 (t, 3 H, *J* = 10 Hz); 5.25 (t, 3 H, *J* = 10 Hz); 7.65 (t, 3 H, *J* = 7 Hz); 8.15 (d, 3 H, *J* = 7 Hz); 8.20 (d, 2 H, *J* = 7 Hz); 8.55 (s, 3 H). Found (%): C, 55.93; H, 4.08; N, 18.66. $C_{21}H_{18}N_6O_3$. Calculated (%): C, 56.00; H, 4.03; N, 18.66.

***cis*-2,4,5-Tris(2,6-dichlorophenyl)-2-imidazoline (*cis*-2g).** 2,6-Dichlorobenzaldehyde (4.7 g, 0.027 mol) was stirred in 95% ethanol in the presence of ammonium chloride (0.2 g) at ~20 °C for 8 days. The precipitate was filtered off. The yield was 4.15 g (99%), colorless crystals, m.p. 138—143 °C (95% ethanol). ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 6.05 (d, 1 H, *J* = 17 Hz); 6.45 (d, 1 H, *J* = 17 Hz); 7.05—7.20 (m, 4.5 H); 7.43—7.60 (m, 1 H); 8.5 (d, 1 H, *J* = 4 Hz). Found (%): C, 50.06; H, 2.34; N, 5.25. $C_{21}H_{10}Cl_6N_2$. Calculated (%): C, 49.94; H, 2.39; N, 5.55.

***cis*-2,4,5-Tris(2-nitrophenyl)-2-imidazoline (*cis*-2h)** was synthesized from 2-nitrobenzaldehyde (1.5 g, 0.01 mol) and a saturated solution of ammonia (50 mL) in anhydrous THF. The yield was 0.71 g (50%), m.p. 244—246 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6), δ: 5.98 (d, 1 H, *J* = 9 Hz); 6.18 (d, 1 H, *J* = 9 Hz); 7.25—7.56 (m, 6 H); 7.65 (d, 1 H, *J* = 7 Hz); 7.73 (d, 1 H, *J* = 7 Hz); 7.80 (d, 1 H, *J* = 7 Hz); 7.88 (t, 1 H, *J* = 7 Hz); 8.00 (d, 1 H); 8.50 (d, 1 H); 8.30 (s, 1 H). Found (%): C, 58.26; H, 3.39; N, 16.42. $C_{21}H_{15}N_5O_6$. Calculated (%): C, 58.20; H, 3.49; N, 16.16.

Synthesis of *cis*-2,4,5-triaryl-2-imidazolines *cis*-2 (general procedure). Diazapentadienes **1** were dissolved in a minor amount of anhydrous THF, the solution was cooled to −20 °C, argon was passed through the solution for 5 min, and Bu^{t}OK was added with vigorous stirring. The solution changed its color to intense blue or violet and then became colorless. As soon as the color of the solution changed to light yellow, the reaction was stopped adding a threefold excess of cold water. The precipitate that formed was recrystallized from an ethyl acetate—hexane (1 : 6) mixture.

***cis*-2,4,5-Triphenyl-2-imidazoline (*cis*-2a)** [7] was synthesized from **1a** (1 g, 3.3 mmol) and Bu^{t}OK (0.3 g, 2.6 mmol) in anhydrous THF (10 mL). The yield was 0.9 g (90%), m.p. 129 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/$CDCl_3$), δ: 5.25 (d, 1 H, *J* = 8 Hz); 5.35 (d, 1 H, *J* = 8 Hz); 5.65—5.75 (br.s, 1 H); 6.9—7.05 (m, 10 H); 7.48—7.55 (m, 3 H); 7.95 (d, 2 H).

***cis*-2,4,5-Tris(4-bromophenyl)-2-imidazoline (*cis*-2b)** was synthesized from **1b** (0.5 g, 0.9 mmol) and Bu^{t}OK (0.3 g, 2.6 mmol) in anhydrous THF (10 mL). The yield was 0.3 g (60%), m.p. 120 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 3.0 (s, 1 H); 5.4 (s, 2 H); 6.9 (d, 4 H, *J* = 11 Hz); 7.2 (d, 4 H, *J* = 8 Hz); 7.65 (d, 2 H, *J* = 8 Hz); 8.00 (d, 2 H, *J* = 8 Hz). Found (%): C, 47.00; H, 2.69; N, 5.15. $C_{21}H_{15}Br_3N_2$. Calculated (%): C, 47.14; H, 2.83; N, 5.24.

***cis*-2,4,5-Tris(4-methoxyphenyl)-2-imidazoline (*cis*-2c)** was synthesized from **1c** (0.5 g, 1.3 mmol) and Bu^{t}OK (0.3 g, 2.6 mmol) in anhydrous THF (10 mL). The yield was 0.47 g (94%), m.p. 86 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 3.65 (s, 6 H); 3.85 (s, 3 H); 5.25 (s, 2 H); 6.55 (d, 4 H, *J* = 9 Hz); 6.85 (d, 4 H, *J* = 9 Hz); 6.95 (d, 2 H, *J* = 9 Hz); 7.98 (d, 2 H, *J* = 9 Hz). Found (%): C, 81.69; H, 6.71; N, 8.00. $C_{24}H_{24}N_2O_3$. Calculated (%): C, 81.78; H, 6.86; N, 7.95.

***cis*-2,4,5-Tris(2-thienyl)-4-imidazoline (*cis*-2d)** was synthesized from **1d** (0.5 g, 1.6 mmol) and Bu^{t}OK (0.3 g, 2.6 mmol) in anhydrous THF (10 mL). The yield was 0.5 g (100%), m.p. 97 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 5.53 (s, 2 H); 6.65 (d, 2 H, *J* = 4 Hz); 6.75 (t, 2 H, *J* = 4 Hz); 7.10 (d, 2 H, *J* = 3 Hz); 7.20 (t, 1 H, *J* = 3 Hz); 7.61 (d, 1 H, *J* = 3 Hz); 7.75 (d, 1 H, *J* = 3 Hz). Found (%): C, 56.82; H, 3.81; N, 8.73. $C_{15}H_{12}N_2S_3$. Calculated (%): C, 56.93; H, 3.82; N, 8.85.

***cis*-2,4,5-Tris(3-nitrophenyl)-4-imidazoline (*cis*-2e). *A*.** Compound ***cis*-2e** was synthesized from diazapentadiene **1e** (1.3 g, 2.8 mmol) and Bu^{t}OK (0.4 g, 3.5 mmol) in a mixture of anhydrous THF (10 mL) and anhydrous DMF (5 mL). The yield was 1.3 g (100%).

***B*.** Compound ***cis*-2e** was synthesized by the reaction of 3-nitrobenzaldehyde (1 g) with a saturated solution of NH_3 (20 mL) in anhydrous THF for 3 days. The yield was 0.8 g (73%), m.p. 150—154 °C.

^{1}H NMR (399.95 MHz, DMSO-d_6/$CDCl_3$), δ: 5.55 (d, 1 H, *J* = 14 Hz); 5.85 (d, 1 H, *J* = 14 Hz); 7.2 (t, 2 H, *J* = 7 Hz); 7.3 (t, 2 H, *J* = 7 Hz); 7.7 (t, 1 H, *J* = 7 Hz); 7.5 (s, 1 H); 7.80—7.85 (m, 3 H); 8.3 (d, 2 H, *J* = 7 Hz); 8.50 (d, 2 H, *J* = 7 Hz); 9.0 (s, 1 H). Found (%): C, 57.40; H, 2.99; N, 15.54. $C_{21}H_{17}N_5O_7$. Calculated (%): C, 58.20; H, 3.49; N, 16.16.

***cis*-2,4,5-Tris(4-fluorophenyl)imidazoline (*cis*-2f)** was synthesized from diazapentadiene **1f** (1 g, 2.8 mmol) and Bu^{t}OK (0.3 g, 2.6 mmol) in anhydrous THF (10 mL). The yield was 1 g (100%), m.p. 123—125 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 5.38 (br.s, 2 H); 6.74 (t, 4 H, *J* = 3 Hz); 6.85—6.89 (m, 4 H); 7.14 (t, 2 H, *J* = 3 Hz); 7.91—7.96 (m, 2 H). Found (%): C, 67.97; H, 4.27; N, 7.98. $C_{21}H_{15}N_2F_3 \cdot H_2O$. Calculated (%): C, 68.10; H, 4.68; N, 7.56.

Synthesis of *trans*-2,4,5-triaryl-2-imidazolines *trans*-2 (general procedure). Diazapentadiene **1** was dissolved in a minor amount of anhydrous THF (in the case of donating substituents, in anhydrous DMSO), argon was passed through the solution for 5 min, and Bu^{t}OK was added with vigorous stirring. The solution changed its color to intense blue or violet, which then gradually disappeared. The mixture was heated for 0.3—24 h, monitoring the formation of a recyclization product by TLC using an ethyl acetate—hexane (1 : 1) mixture as eluent. The reaction was stopped by the addition of a triple excess of cold water. The precipitate that formed was washed with a hot ethyl acetate—hexane (1 : 6) mixture.

***trans*-2,4,5-Triphenyl-2-imidazoline (*trans*-2a)** [7] was synthesized from **1a** (1 g, 3.3 mmol) and Bu^{t}OK (0.3 g, 2.6 mmol) on refluxing for 2 h in anhydrous THF (10 mL). The yield was 0.9 g (90%), m.p. 202 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 4.85—5.00 (br.s, 2 H); 5.35—5.50 (br.s, 1 H); 7.25—7.40 (m, 10 H); 7.42—7.55 (m, 3 H); 7.95 (d, 2 H, *J* = 3 Hz).

***trans*-2,4,5-Tris(4-bromophenyl)-2-imidazoline (*trans*-2b)** was synthesized from **1b** (0.5 g, 0.9 mmol) and Bu^{t}OK (0.3 g, 2.6 mmol) in anhydrous THF (10 mL). The yield was 0.3 g (60%), m.p. 196 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4),

δ: 3.0 (s, 1 H); 4.75 (s, 2 H); 7.22 (d, 4 H, J = 10 Hz); 7.50 (d, 4 H, J = 10 Hz); 7.65 (d, 2 H, J = 10 Hz); 7.95 (d, 2 H, J = 10 Hz). Found (%): C, 47.12; H, 2.72; N, 5.23. $C_{21}H_{15}Br_3N_2$. Calculated (%): C, 47.14; H, 2.83; N, 5.24.

***trans*-2,4,5-Tris(4-methoxy)-2-imidazoline (*trans*-2c)** was synthesized from **1c** (0.5 g, 1.3 mmol) and Bu^{t}OK (0.3 g, 2.6 mmol) in THF (10 mL). The yield was 0.47 g (94%), m.p. 86 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 3.65 (s, 6 H); 3.85 (s, 3 H); 4.66 (s, 2 H); 6.50 (d, 4 H, J = 9 Hz); 6.75 (d, 4 H, J = 9 Hz); 6.95 (d, 2 H, J = 9 Hz); 7.98 (d, 2 H, J = 9 Hz). Found (%): C, 74.19; H, 6.21; N, 7.10. $C_{24}H_{24}N_2O_3$. Calculated (%): C, 74.21; H, 6.23; N, 7.21.

***trans*-2,4,5-Tris(2-thienyl)-2-imidazoline (*trans*-2d)** was synthesized from **1d** (1 g, 3.2 mmol) and Bu^{t}OK (0.3 g, 2.6 mmol) in DMSO (10 mL). The yield was 0.6 g (60%), m.p. 158—160 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 5.05 (d, 1 H, J = 6 Hz); 5.15 (d, 1 H, J = 6 Hz); 6.90—7.10 (m, 3 H); 7.15—7.20 (t, 1 H, J = 4 Hz); 7.40 (d, 1 H, J = 4 Hz); 7.50 (d, 1 H, J = 4 Hz); 7.65 (d, 1 H, J = 4 Hz); 7.75 (d, 1 H, J = 4 Hz); 8.15 (br.s, 1 H). Found (%): C, 56.88; H, 3.85; N, 8.94. $C_{15}H_{12}N_2S_3$. Calculated (%): C, 56.93; H, 3.82; N, 8.85.

Synthesis of 2,4,5-triarylimidazoles 4 (general procedure). Compound **1** was dissolved in a minor amount of anhydrous DMSO, and Bu^{t}OK was added with vigorous stirring. The color of the solution changed to intense blue or violet and then gradually transformed into intense crimson. The mixture was heated for some time, passing an air or oxygen flow to accelerate the process and monitoring the formation of an oxidation product by TLC using an ethyl acetate—hexane (1 : 1) mixture as eluent. The mixture was poured into cold water. The precipitate that formed was recrystallized from an ethyl acetate—hexane (1 : 1) mixture.

2,4,5-Triphenylimidazole (4a) was synthesized from **1a** (1 g, 3 mmol) and Bu^{t}OK (0.3 g, 2.6 mmol) on refluxing for 2 h in anhydrous DMSO (20 mL). The yield was 1 g (100%), m.p. 270 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 7.25—7.60 (m, 10 H); 8.10 (d, 2 H, J = 4 Hz); 12.45 (s, 1 H). Found (%): C, 85.80; H, 5.42; N, 9.45. $C_{21}H_{10}Cl_6N_2$. Calculated (%): C, 85.11; H, 5.44; N, 9.45.

2,4,5-Tris(4-bromophenyl)imidazole (4b) was synthesized from **1b** (0.5 g, 0.9 mmol) and Bu^{t}OK (0.1 g, 0.8 mmol) on refluxing in anhydrous DMSO (14 mL) for 12 h. The yield was 0.47 g (94%), m.p. 235 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ: 4.85—5.00 (br.s, 2 H); 5.35—5.50 (br.s, 1 H); 7.25—7.40 (m, 10 H); 7.42—7.55 (m, 3 H); 7.95 (d, 2 H, J = 9 Hz). Found (%): C, 47.28; H, 2.43; N, 5.20. $C_{21}H_{13}Br_3N_2$. Calculated (%): C, 47.32; H, 2.46; N, 5.26.

2,4,5-Tris(4-methoxyphenyl)imidazole (4c) was synthesized from **1c** (0.5 g, 1.3 mmol) and Bu^{t}OK (0.2 g, 1.8 mmol) on refluxing in anhydrous DMSO (10 mL) for 4 days. The yield was 0.2 g (40%), m.p. 215 °C. ^{1}H NMR (399.95 MHz, $CDCl_3$), δ: 3.80 (s, 3 H); 6.80—6.90 (m, 6 H); 7.39—7.43 (d, 4 H, J = 10 Hz); 7.78—7.82 (d, 2 H, J = 10 Hz). Found (%): C, 74.51; H, 5.70; N, 7.16. $C_{24}H_{22}N_2O_3$. Calculated (%): C, 74.59; H, 5.74; N, 7.25.

2,4,5-Tris(2-thienyl)imidazole (4d) was synthesized from **1d** (1 g, 3.2 mmol) and Bu^{t}OK (0.3 g, 2.6 mmol) on refluxing in anhydrous DMSO (10 mL) for 2 days. The yield was 0.6 g (60%), m.p. 270—272 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 7.10 (m, 3 H); 7.30 (d, 2 H, J = 4 Hz); 7.55 (m, 3 H); 7.75 (d, 1 H, J = 4 Hz); 13.20 (br.s, 1 H). Found (%): C, 57.28; H, 3.30; N, 9.13. $C_{15}H_{10}N_2S_3$. Calculated (%): C, 57.29; H, 3.21; N, 8.91.

2,4,5-Tris(3-nitrophenyl)imidazole (4e) was synthesized from **1e** (0.5 g, 1.2 mmol) and Bu^{t}OK (0.2 g, 1.8 mmol) on refluxing in anhydrous DMSO (6 mL) for 3 h. The yield was 0.2 g (40%), m.p. 235 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6/CCl_4), δ: 7.65 (t, 2 H, J = 9 Hz); 7.75 (t, 1 H, J = 9 Hz); 7.95 (m, 3 H); 8.2 (m, 3 H); 8.45 (s, 3 H); 8.60 (d, 1 H, J = 9 Hz); 9.00 (s, 1 H); 13.20—13.40 (br.s, 1 H). Found (%): C, 56.59; H, 3.61; N, 15.97. $C_{21}H_{15}N_5O_7 \cdot H_2O$. Calculated (%): C, 56.13; H, 3.36; N, 15.58.

2,4,5-Tris(4-pyridin-4-yl)imidazole (4f). Pyridine-4-carbaldehyde (2 g, 0.018 mol) and a saturated solution of ammonia (50 mL) in 95% ethanol in the presence of ammonium chloride (0.2 g) were stored at ~20 °C for 8 days. The yield was 1.36 g (72%), m.p. 333 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6), δ: 7.50 (s, 4 H); 8.00 (s, 2 H); 8.60 (d, 5.5 H, J = 8 Hz); 13.2 (br.s, 1 H). ^{13}C NMR (100.13 MHz, DMSO-d_6), δ: 120, 122.9, 136.8, 145.1, 149.9, 150, 163.8. Found (%): C, 68.28; H, 4.83; N, 23.12. $C_{18}H_{13}N_5 \cdot H_2O$. Calculated (%): C, 68.13; H, 4.76; N, 22.07.

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