Triarylverdazyl radicals as promising redox-active components of rechargeable organic batteries*

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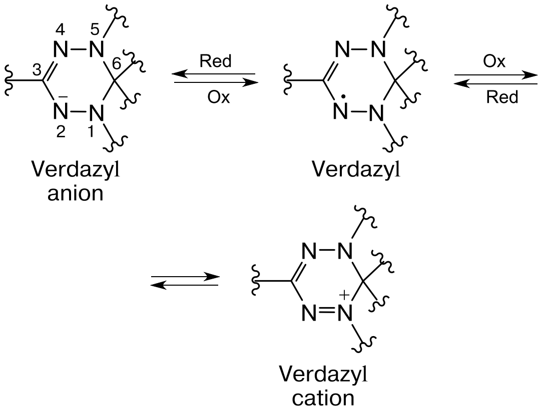
A novel design of electroactive components of rechargeable organic batteries based on stable verdazyl radicals bearing various substituents is proposed. 3-Positioned aromatic substituents at the verdazyl moiety affect the reduction potentials and almost do not affect the oxidation potential, while 1-positioned aromatic substituents affect contrariwise the oxidation potential of this radical without any influence on the reduction potential. The acquired electrochemical data allowed us to reveal the structure—potential relationship for the cathodic and anodic processes, which provided the design of triarylverdazyl radicals possessing record-breaking parameters of the "electrochemical gap".

Key words: verdazyl radicals, cyclic voltammetry, electron-donating substituent, electron-withdrawing substituent, electrode potential, electrochemical gap.

Verdazyl (tetrazinyl) radicals first reported in 1964 by Kuhn and Trischman[1] are "electron amphoteric", *i.e.* capable of both oxidizing and reducing[2] to give stable cations and anions (Scheme 1).

Scheme 1



Red is reduction, and Ox is oxidation.

Verdazyls are the only family of neutral radicals, whose stability approaches to that of the known nitroxyl radicals. The favorable properties of verdazyls include tolerance to dimerization, as well as resistance to air and moisture.[3]

Until quite recently, mostly magnetic[4—7] and complexing properties[8—10] of verdazyls were considered. The redox properties of these radicals remain much less explored. In particular, electrochemical investigations of a verdazyl series aimed to find a correlation between their redox properties and structure[11] have revealed such a correlation between the distribution of electron spins and redox properties. The boundary orbitals that are involved in the redox processes are localized in different parts of the molecule: the HOMO of nitrogen atom at the position 1 makes the largest contribution to the oxidation process, while a carbon atom at the position 3 makes the most significant contribution to the reduction process proceeding *via* LUMO.

As a material for the storage of charge, 3-phenyl-1,5-di(*p*-tolyl)verdazyl has been applied since it can be reversibly oxidized and reduced in single-electron processes[12] and employed it in a symmetric all-organic non-aqueous redox battery of the flow-type. The opportunity to utilize verdazyl radicals as materials for the electricity storage has been also mentioned in the review.[13]

Results and Discussion

The unique structure of verdazyl radicals allows one to finely tune the redox properties by varying the nature of substituents at the N(1) and C(3) atoms of the verdazyl moiety. In the present work, we report on the synthesis and electrochemical properties of verdazyl radicals **1a—m** bearing substituents of the various nature.

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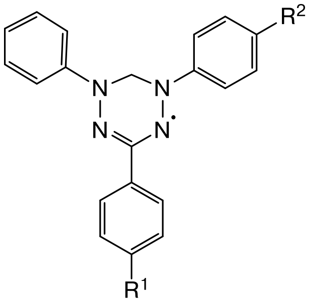


1a—m

Compounds **1**	R^1	R^2	Compounds **1**	R^1	R^2
a	H	H	**h**	H	NO_2
b	Br	H	**i**	H	CN
c	MeO	H	**j**	MeO	NO_2
d	NO_2	H	**k**	MeO	CN
e	CN	H	**l**	NO_2	MeO
f	H	Br	**m**	CN	MeO
g	H	MeO			

It has been assumed[11] that substituents in the 3-positioned aromatic ring of the verdazyl moiety would strongly affect the reduction potential and cause no significant effect on the oxidation potential, while substituents in the 1-positioned aromatic ring of the verdazyl moiety would affect the oxidation potential, but not the reduction one. To verify this hypothesis, we computed the electron density distribution for the boundary orbitals of the considered compounds within the density functional theory (DFT) method using the B3LYP hybrid functional[14] and the standard 6-31G basic set[15] implemented in the Firefly software package.[16] Figure 1 shows the localization of boundary orbitals for verdazyl radical **1j**, where one can see the HOMO localized at the nitrogen atoms of the verdazyl moiety and the LUMO located at the C(3) atom. Therefore, the computational data confirms the individual effect of substituents at the different positions on the redox processes.

Taking into account the calculated data, we selected a set of verdazyls **1a—m** bearing substituents of the different natures at *para*-positions of the benzene moieties attached to the positions 1 and 3 of verdazyl ring, whose "structure—potential value" relationship was estimated for the cathodic and anodic processes. Cyclic voltammetry (CV) was used as the express method for evaluating values of the "electrochemical gap" for the obtained verdazyl radicals.

Radicals **1a—m** were prepared from the corresponding formazans **2a—m** according to the classical approach. Compounds **2a—m** were obtained by the reaction of phenylhydrazones **3a—e** of substituted benzaldehydes **4a—e** with aryldiazonium salts **5a—e** synthesized from *para*-substituted anilines **6a—e** (Scheme 2). Formazans **2a—m** were cyclized with formaldehyde in the presence of potassium hydrogen sulfate and subsequently oxidized with atmospheric oxygen under alkaline conditions to give verdazyls **1a—m**. The duration of air bubbling through the reaction mixture was monitored by changing its color from red-violet to green.

This approach to verdazyls is used quite successfully. Some limitations may arise, *e.g.*, in the case of the presence of strong electron-withdrawing substituents at the benzaldehyde aromatic ring, while yields of the intermediate formazans are usually low.[11] Using the synthesis of 1,5-diphenyl-3-arylverdazyls as the example, it has been revealed that the yields of formazans are increased upon using a DMF—pyridine mixture as the solvent.[17]

The structure of formazans **2a—m** was confirmed by ^1H and ^{13}C NMR spectroscopy and mass spectrometry.

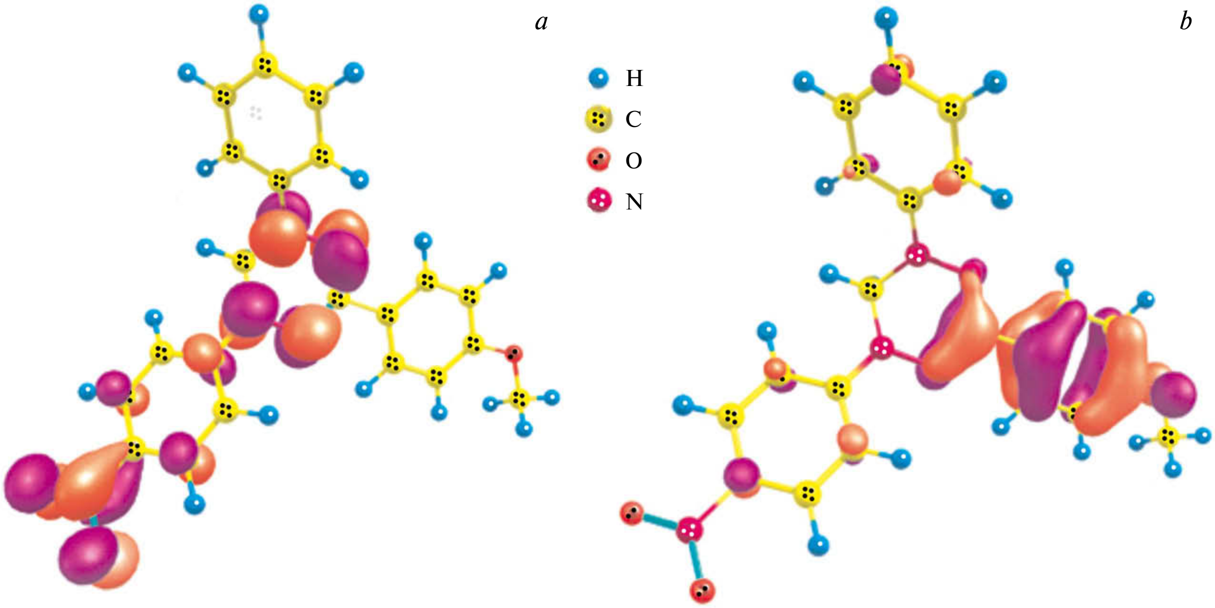
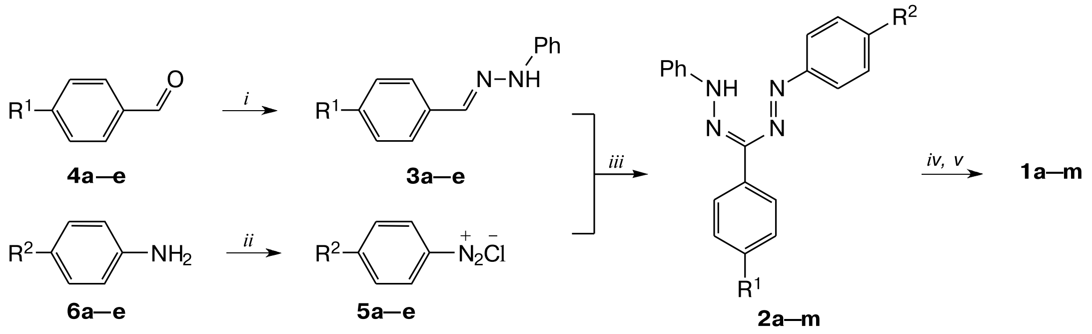


Fig. 1. LUMO (*a*) and HOMO (*b*) for compound **1j**.

Scheme 2



3–6: R^1, R^2 = H (**a**), Br (**b**), MeO (**c**), NO_2 (**d**), CN (**e**)

Compounds **1**, **2**	R^1	R^2	Compounds **1**, **2**	R^1	R^2
a	H	H	**h**	H	NO_2
b	Br	H	**i**	H	CN
c	MeO	H	**j**	MeO	NO_2
d	NO_2	H	**k**	MeO	CN
e	CN	H	**l**	NO_2	MeO
f	H	Br	**m**	CN	MeO
g	H	MeO			

Reagents and conditions: *i*. $PhNHNH_2$, EtOH, AcONa, 20 °C; *ii*. $NaNO_2$, HCl, 0 °C; *iii*. DMF, Py, 0—25 °C; *iv*. CH_2O, $KHSO_4$, DMF, H_2O, 20 °C; *v*. 1) NaOH, 2) O_2, 20 °C.

Verdazyl radicals **1a—m** were characterized using IR, UV—Vis, and EPR spectroscopy and mass spectrometry. In general, all verdazyls **1a—m** are fine-crystalline substances colored in various shades of green. Their IR spectra contain vibration bands in the range of ~1150—1160 cm^{-1}, which is characteristic of verdazyl radicals. The benzene solutions of radicals **1a—m** exhibit typical time-stable EPR spectra containing nine broad lines with the intensity ratio of 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1 caused by a coupling of the unpaired electron with four spectroscopically equivalent nitrogen atoms of the tetrazine ring. Figure 2 exemplifies the EPR spectrum of verdazyl **1d**. Although there are two chemically nonequivalent pairs of the nitrogen atoms (N(1), N(5) and N(2), N(4)), the hyperfine coupling constants for radicals **1a—m** have close values of ~5.6 G.

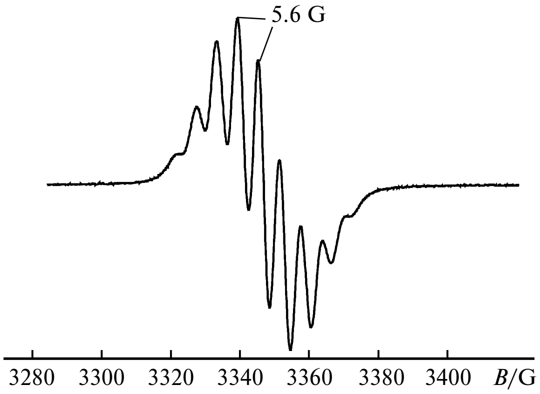


Fig. 2. EPR spectrum of verdazyl **1d**.

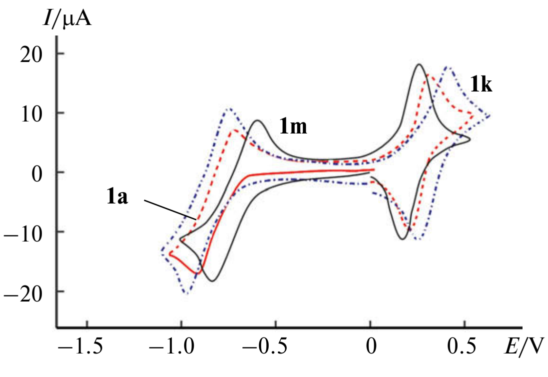
Electrochemical properties of radicals **1a—m** were evaluated using the CV method in solutions in MeCN. Completely reversible oxidation and reduction processes were observed for almost all the verdazyls, except for the nitro derivatives. The oxidation potentials of verdazyls **1a—m** are in the range from 0.18 to 0.41 V (Ag/AgCl/KCl). The reduction of these radicals proceeds at negative potentials varying from –0.63 to –0.87 V (Ag/AgCl/KCl). The electrochemical parameters of verdazyl radicals **1a—m** are given in Table 1.

Table 1. Electrochemical parameters for verdazyl radicals **1a—m**

Verdazyl	E_{Ox}	$-E_{Red}$	E_{ec}
		V	
1a	0.31	0.81	1.12
1b	0.30	0.80	1.10
1c	0.26	0.87	1.13
1d	0.35	0.61	0.96
1e	0.34	0.65	0.99
1f	0.25	0.81	1.06
1g	0.20	0.85	1.15
1h	0.41	0.65	1.06
1i	0.38	0.67	1.05
1j	0.36	0.87	1.23
1k	0.34	0.86	1.20
1l	0.18	0.63	0.81
1m	0.19	0.64	0.83

As one can see from Table 1, the nature of substituent at the *para*-position of aromatic ring attached at the position 3 of the verdazyl affects slightly the oxidation potential ($E_{\rm Ox}$). Thus, the $E_{\rm Ox}$ value is slightly shifted to the cathodic region in the case of compounds bearing the electron-withdrawing substituents, *viz.*, **1d** ($R^1 = NO_2$, $R^2 = H$) and **1e** ($R^1 = CN$, $R^2 = H$), while that for compound with the electron-donating substituent, **1c** ($R^1 = MeO$, $R^2 = H$), is shifted to the anodic region. At the same time, a fairly strong influence of the substituent R^1 on the reduction potential ($E_{\rm Red}$) was observed. Thus in the cases of compounds **1d** and **1e**, the electron-withdrawing nitro and cyano groups shift $E_{\rm Red}$ to the cathodic region by 0.2 and 0.16 V relative to **1a**, respectively. A bromine atom causes no significant effect, while a methoxy group slightly shifts the $E_{\rm Red}$ value to the anodic region (by 0.06 V as compared to compound **1a**).

The substituent at the aromatic ring linked to the position 1 of the verdazyl moiety causes a more pronounced effect on the oxidation and much weaker one on the reduction. At this end, electron-donating substituents facilitate the oxidation process, shifting $E_{\rm Ox}$ to the cathodic region by 0.06 and 0.11 V as compared to compound **1a** in the cases of **1f** ($R^1 = H$, $R^2 = Br$) and **1g** ($R^1 = H$, $R^2 = MeO$), respectively. Electron-withdrawing substituents hinder the oxidation, shifting $E_{\rm Ox}$ to the anodic region by 0.10 and 0.07 V relative to **1a** in the cases of **1h** ($R^1 = H$, $R^2 = NO_2$) and **1i** ($R^1 = H$, $R^2 = CN$). The bromine atom does not affect the reduction process, while the methoxy group slightly shifts the $E_{\rm Red}$ value to the anodic region (by 0.05 V as compared to compound **1a**). The electron-withdrawing groups facilitate the reduction, shifting $E_{\rm Red}$ to the cathodic region by 0.16 and 0.14 V as compared to **1a** for **1h** ($R^1 = H$, $R^2 = NO_2$) and **1i** ($R^1 = H$, $R^2 = CN$). Considering all the acquired results, a magnitude of the "electrochemical gap" ($E_{\rm ec} = |E_{\rm Ox} - E_{\rm Red}|$) has been only insignificantly changed for verdazyl radicals **1b—i** as compared to radical **1a**. Figure 3 shows the CV curves recorded for verdazyls **1a,k,m**.



PFig. 3. CV curves recorded for compounds **1a**,**k**,**m**. The solvent was MeCN, the supporting electrolyte was 0.1 *M* Bu_4NBF_4, the potential scan rate was 200 mW s^{-1}.

In the case of simultaneous presence of electron-donating (at the position 3) and electron-withdrawing (at the position 1) substituents at the verdazyl moiety, a more pronounced increase in the "electrochemical gap" value was observed due to shifting the $E_{\rm Ox}$ value to the cathodic region by the MeO-substituted aromatic ring at the position 3 of verdazyl with simultaneous shifting the $E_{\rm Ox}$ value to the anodic region by the NO_2- and CN-substituted aromatic rings, thereby increasing the difference between the highest oxidation and reduction potential values. A reverse "distribution" of the substituents results in narrowing the "electrochemical gap", since the electron-withdrawing groups (NO_2 and CN) at the aromatic ring linked to the position 3 of verdazyl shift the $E_{\rm Ox}$ value to the anodic region, while the electron-donating methoxy group at the aromatic ring shifts it to the cathodic region, thereby decreasing the difference between the highest oxidation and reduction potential values.

In summary, in the present work the disubstituted triarylverdazyl radicals exhibiting record values of the "electrochemical gap" were synthesized. The magnitude of "electrochemical gap" affects a capacity of the battery based on neutral radicals,**[18]** thus the radicals possessing a significant difference between the electrochemical potentials of oxidation and reduction can be employed in organic batteries, allowing one to significantly increase the capacity of energy storage devices.

Experimental

The solvents were dried and distilled before use. All the rewere agents were purchased from Sigma-Aldrich Rus and Merck and used as received. IR spectra were recorded in KBr pellets using an InfraLUM FT-02 Fourier spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a JNM-ECX400 spectrometer (JEOL) operating at the frequencies of 400.1 and 100.6 MHz, respectively.

Elemental analysis was performed using a Vario MICRO CHNS-analyzer. Analytical TLC was performed on Silufol UV-245 plates using benzene or dichloromethane—ethyl acetate (2 : 1) as the eluents; the spots of the compounds were visualized by iodine vapors. Column chromatography was carried out on L40/100 μ silica gel using benzene as the eluent. Melting points were measured in sealed glass capillaries on a MP-50 apparatus (Mettler Toledo, Switzerland). Electron impact mass spectra were recorded on a Konik RBK-HRGC 5000B—MSQ12 spectrometer (Spain); ionization potential was 70 eV. UV—Vis spectra were recorded on a Shimadzu UV-2600 spectrophotometer (in benzene), and EPR spectra were recorded on an ESP 70-03 XD/2 EPR spectrometer.

The molecular geometry was completely optimized without any symmetry restrictions, taking into account the influence of solvent (MeCN) within the framework of polarized continuum model (PCM),**[14]** wherein a cavity containing the dissolved particle is an ensemble of the intersected atomic spheres of certain radius. The dielectric constant inside the cavity is equal to the dielectric constant *in vacuo* and outside the cavity, to that of the solvent. Data for the solvent consideration (dielectric constant, molecule radius) were taken from the online source (https://www.scm.com/doc/ADF/Input/COSMO.html). To confirm the achievement of true minimum during the geometry optimization, the frequencies of normal vibrations were calculated. The absence of imaginary frequencies in the vibrational spectrum of the optimized structure indicates that the resulting structure corresponds to a minimum on the full surface of potential energy.

Electrochemical data were acquired by the cyclic voltammetry in acetonitrile solution (0.1 *M* Bu_4NBF_4 as the supporting electrolyte) in an electrochemical cell (5 mL) using a Gamry potentiostat (Canada); the concentration of test compounds was 0.001 mol L^{-1}. A glassy carbon (GC) electrode with $S = 0.125$ cm^2 was used as the working electrode. The electrode was carefully polished and washed before measurements. A platinum electrode was the auxiliary one, and a standard silver chloride electrode ($E° = 0.33$ V in MeCN *vs.* the Fc/Fc^+ couple) was the reference. All the solutions were deaerated before use by passing an Ar flow.

Phenylhydrazones 3a—e (general procedure). A solution of the corresponding aldehyde **4a—e** (0.02 mol) in 1,4-dioxane (25 mL) was added by small portions under stirring to a solution of phenylhydrazine hydrochloride (4.34 g, 0.03 mol) and anhydrous sodium acetate (2.46 g) in water (70 mL). The mixture was stirred at room temperature for ~20—60 min. The precipitate formed was filtered off, washed on the filter with water, and dried in air. The target products were purified by recrystallization. The melting points and spectral characteristics of the obtained compounds **3a—e** coincide with those reported previously.

1-Benzylidene-2-phenylhydrazine (3a). Yield 4.19 g (73%), m.p. 155—156 °C (EtOH).[19]

1-(4-Bromobenzylidene)-2-phenylhydrazine (3b). Yield 5.86 g (71%), m.p. 116—117 °C (EtOH).[19]

1-(4-Methoxybenzylidene)-2-phenylhydrazine (3c). Yield 4.42 g (65%), m.p. 119—120 °C (EtOH).[19]

1-(4-Nitrobenzylidene)-2-phenylhydrazine (3d). Yield 5.43 g (75%), m.p. 158—159 °C (EtOH).[20]

1-(4-Cyanobenzylidene)-2-phenylhydrazine (3e). Yield 4.72 g (71%), m.p. 177—178 °C (EtOH).[19]

Formazans 2a—m (general procedure). Aryldiazonium salts **5a—d** were synthesized preliminarily as follows. An aqueous solution of $NaNO_2$ (3 mL, 0.011 mol) and concentrated hydrochloric acid (3.5 mL) were subsequently added to the corresponding aniline **6a—e** (0.011 mol) at 0—5 °C. The resulting suspension of aryldiazonium salt **5a—e** was added in small portions to a stirred and cooled (−5÷−10 °C) solution of phenylhydrazone **3a—e** (0.01 mol) in a mixture of pyridine (5 mL) and DMF (10 mL), at the addition rate to maintain the temperature of the reaction mixture below 5 °C. The mixture became intensively dark cherry colored. The mixture was kept at ~5 °C for 3 h and at room temperature for 12 h, diluted with water (20 mL), and extracted with CH_2Cl_2 (3×20 mL). The combined organic extracts were washed with water (3×10 mL), passed through a layer of neutral Al_2O_3, and the solvent was evaporated *in vacuo*. The resulting product was triturated with methanol.

1,3,5-Triphenylformazan (2a). Yield 1.97 g (66%), m.p. 148—150 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 15.38 (s, 1 H, NH); 8.15 (d, 2 H, *J* = 8.0 Hz); 7.73 (d, 4 H, *J* = 8.0 Hz); 7.60—7.25 (m, 9 H). ^{13}C NMR ($CDCl_3$), δ: 148.5, 141.7, 138.0, 130.4, 130.0, 129.7, 129.6, 129.5, 129.0, 128.4, 128.2, 128.1, 126.4, 122.7, 119.3. IR (KBr), ν/cm^{-1}: 1597 (s), 1512 (s), 1493 (s), 1235 (s), 1018 (s), 752 (s). UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 270 (17250), 300 (22000), 488 (14250). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 300 $[M]^+$ (30), 285 (25), 272 (33), 246 (34), 194 (100), 167 (40), 103 (40), 63 (50). Found (%): C, 76.16; H, 5.54; N, 18.36. $C_{19}H_{16}N_4$. Calculated (%): C, 75.98; H, 5.37; N, 18.65.

3-(4-Bromophenyl)-1,5-diphenylformazan (2b). Yield 2.12 g (56%), m.p. 201—202 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 15.41 (s, 1 H, NH); 8.21 (d, 2 H, *J* = 8.9 Hz); 8.02 (d, 2 H, *J* = 8.9 Hz); 7.75 (d, 4 H, *J* = 8.0 Hz); 7.60—7.25 (m, 6 H). ^{13}C NMR ($CDCl_3$), δ: 153.0, 147.1, 145.0, 137.4, 132.1, 131.7, 129.2, 129.2, 127.1, 124.7, 124.0, 122.2, 114.5. IR (KBr), ν/cm^{-1}: 1589 (s), 1488 (s), 1396 (s), 1232 (s), 1019 (s), 756 (s). UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 274 (18100), 310 (25000), 492 (16400). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 380 $[M + 1]^+$ (22), 378 $[M - 1]^+$ (22), 350 (25), 352 (25), 299 (80), 272 (100), 270 (98), 223 (38), 103 (80), 65 (60). Found (%): C, 76.16; H, 5.54; N, 18.36. $C_{19}H_{15}BrN_4$. Calculated (%): C, 75.98; H, 5.37; N, 18.65.

3-(4-Methoxyphenyl)-1,5-diphenylformazan (2c). Yield 1.48 g (45%), m.p. 172—173 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 15.45 (s, 1 H, NH); 8.31 (d, 2 H, *J* = 8.9 Hz); 8.02 (d, 2 H, *J* = 8.9 Hz); 7.76 (d, 4 H, *J* = 8.0 Hz); 7.58—7.27 (m, 6 H); 3.85 (s, 3 H, CH_3O). ^{13}C NMR ($CDCl_3$), δ: 160.3, 154.1, 148.2, 145.4, 131.8, 129.9, 129.2, 128.3, 127.0, 124.8, 123.1, 120.4, 113.6, 55.8. IR (KBr), ν/cm^{-1}: 1597.2, 1512.1, 1454.2, 1358.7, 1250.2, 1226.0, 1172.4. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 279 (20700), 308 (27400), 522 (15900). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 330 $[M]^+$ (10), 315 (37), 238 (40), 226 (58), 224 (55), 93 (100), 65 (30). Found (%): C, 72.36; H, 5.51; N, 17.01. $C_{20}H_{18}N_4O$. Calculated (%): C, 72.71; H, 5.49; N, 16.96.

3-(4-Nitrophenyl)-1,5-diphenylformazan (2d). Yield 1.52 g (44%), m.p. 207—209 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 15.80 (s, 1 H, NH); 8.41 (d, 2 H, *J* = 8.9 Hz); 7.77 (d, 2 H, *J* = 8.0 Hz); 7.58—7.27 (m, 10 H). ^{13}C NMR ($CDCl_3$), δ: 155, 152, 149, 144, 141, 130, 129, 128, 125, 129, 121, 114. IR (KBr), ν/cm^{-1}: 1597.2, 1527.1 (NO_2), 1454.5, 1350.7 (NO_2), 1242.2, 740.2. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 266 (20200), 419 (17000), 490 (20900). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 345 $[M]^+$ (56), 328 (46), 299 (66), 241 (100), 105 (62). Found (%): C, 65.96; H, 4.41; N, 20.21. $C_{19}H_{15}N_5O_2$. Calculated (%): C, 66.08; H, 4.38; N, 20.28.

3-(4-Cyanophenyl)-1,5-diphenylformazan (2e). Yield 1.30 g (41%), m.p. 177—178 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 15.78 (s, 1 H, NH); 8.37 (d, 2 H, *J* = 8.9 Hz); 7.65 (d, 2 H, *J* = 8.0 Hz); 7.58—7.27 (m, 10 H). ^{13}C NMR ($CDCl_3$), δ: 150.9, 148.3, 145.5, 141.4, 139.7, 127.8, 126.5, 125.3, 123.5, 121.6, 120.8, 119.6, 118.6 (CN), 113.1. IR (KBr), ν/cm^{-1}: 2255 (CN), 1598, 1451, 1243, 741. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 272 (30200), 338 (27000), 488 (21000). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 325 $[M]^+$ (28), 297 (31), 271 (22), 219 (100), 192 (40), 105 (40). Found (%): C, 73.96; H, 4.61; N, 21.41. $C_{20}H_{15}N_5$. Calculated (%): C, 73.83; H, 4.65; N, 21.52.

1-(4-Bromophenyl)-3,5-diphenylformazan (2f). Yield 2.20 g (58%), m.p. 189—190 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 15.38 (s, 1 H, NH); 8.21 (d, 2 H, *J* = 8.0 Hz); 8.05 (d, 2 H, *J* = 8.9 Hz); 7.65 (d, 2 H, *J* = 8.9 Hz); 7.55—7.25 (m, 8 H). ^{13}C NMR ($CDCl_3$), δ: 153.3, 147.2, 144.8, 136.4, 134.7, 131.6, 130.4, 129.3, 128.1, 125.7, 124.0, 122.2, 113.9. IR (KBr), ν/cm^{-1}: 1588, 1488, 1393, 1230, 1010, 746. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 240 (15100), 276 (18300), 320 (29600), 490 (16000). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 380 $[M + 1]^+$ (12), 378 $[M - 1]^+$ (12), 352 (22), 350 (22), 299 (40), 194 (100), 167 (43), 91 (65). Found (%): C, 76.16; H, 5.54; N, 18.36. $C_{19}H_{15}BrN_4$. Calculated (%): C, 75.98; H, 5.37; N, 18.65.

1-(4-Methoxyphenyl)-3,5-diphenylformazan (2g). Yield 1.33 g (40%), m.p. 119—120 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 15.40 (d, 1 H, NH); 8.15 (d, 2 H, *J* = 8.0 Hz); 7.92 (d, 2 H, *J* = 8.9 Hz); 7.60—7.15 (m, 10 H); 3.82 (s, 3 H, CH_3O). ^{13}C NMR ($CDCl_3$), δ: 160.6, 153.1, 144.2, 140.4, 135.4, 131.8, 129.6, 128.8, 128.0, 125.0, 122.1, 115.1, 113.6, 55.7 (CH_3O). IR (KBr), ν/cm^{-1}: 1598 (s), 1513 (s), 1454, 1347, 1249, 1225, 1176. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 280 (20200), 310 (25100), 520 (14700). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 330 $[M]^+$ (10), 303 (25), 276 (20), 195 (55), 122 (100), 104 (51), 93 (70). Found (%): C, 72.36; H, 5.51; N, 17.01. $C_{20}H_{18}N_4O$. Calculated (%): C, 72.71; H, 5.49; N, 16.96.

1-(4-Nitrophenyl)-3,5-diphenylformazan (2h). Yield 1.86 g (54%), m.p. 197—198 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 15.40 (s, 1 H, NH); 8.33 (d, 2 H, *J* = 8.9 Hz); 7.79 (d, 2 H, *J* = 8.0 Hz); 7.58—7.27 (m, 10 H). ^{13}C NMR ($CDCl_3$), δ: 154.8, 153.3, 148.2, 144.2, 135.7, 130.1, 128.8, 127.9, 126.8, 124.7, 123.6, 122.4, 113.9. IR (KBr), ν/cm^{-1}: 1598, 1538 (NO_2), 1453, 1351 (NO_2), 1244, 741. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 266 (20800), 424 (17100), 490 (20200). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 345 $[M]^+$ (10), 317 (12), 299 (14), 224 (19), 195 (100), 123 (12). Found (%): C, 65.96; H, 4.41; N, 20.21. $C_{19}H_{15}N_5O_2$. Calculated (%): C, 66.08; H, 4.38; N, 20.28.

1-(4-Cyanophenyl)-3,5-diphenylformazan (2i). Yield 1.79 g (55%), m.p. 173—175 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 15.40 (s, 1 H, NH); 8.27 (dd, 2 H, *J* = 8.9 Hz, *J* = 1.5 Hz); 8.09 (dd, 2 H, *J* = 8.0 Hz, *J* = 1.5 Hz); 7.65—7.30 (m, 10 H). ^{13}C NMR ($CDCl_3$), δ: 155.1, 150.3, 146.2, 136.2, 131.9, 129.1, 128.5, 127.3, 125.4, 124.1, 123.0, 118.4 (CN), 113.9, 106.3. IR (KBr), ν/cm^{-1}: 2254 (CN), 1598, 1528, 1453, 1244, 741. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 273 (33400), 340 (6000), 489 (21500). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 325 $[M]^+$ (22), 310 (30), 297 (43), 271 (30), 220 (61), 194 (100), 167 (40), 130 (50). Found (%): C, 73.91; H, 4.68; N, 21.47. $C_{20}H_{15}N_5$. Calculated (%): C, 73.83; H, 4.65; N, 21.52.

3-(4-Methoxyphenyl)-1-(4-nitrophenyl)-5-phenylformazan (2j). Yield 2.14 g (57%), m.p. 171—172 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 14.75 (s, 1 H, NH); 8.23 (d, 2 H, *J* = 8.9 Hz); 7.70 (d, 2 H, *J* = 8.9 Hz); 7.65 (d, 2 H, *J* = 8.5 Hz); 7.55 (d, 2 H, *J* = 8.0 Hz); 7.35 (t, 1 H, *J* = 7.1 Hz); 7.12 (d, 2 H, *J* = 8.0 Hz); 6.99 (d, 2 H, *J* = 8.5 Hz); 3.82 (s, 3 H, CH_3O). ^{13}C NMR ($CDCl_3$), δ: 160.3, 155.8, 150.3, 146.2, 142.1, 132.5, 129.4, 127.5, 124.7, 123.6, 114.9, 113.9, 55.6 (CH_3O). IR (KBr), ν/cm^{-1}: 15989, 1528, 1454, 1351, 1244, 1226, 741. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 270 (20300), 422 (16500), 490 (19600). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 375 $[M]^+$ (12), 360 (40), 347 (22), 238 (35), 224 (52), 138 (100). Found (%): C, 63.96; H, 4.61; N, 18.72. $C_{20}H_{17}N_5O_3$. Calculated (%): C, 63.99; H, 4.56; N, 18.66.

1-(4-Cyanophenyl)-3-(4-methoxyphenyl)-5-phenylformazan (2k). Yield 1.66 g (45%), m.p. 142—144 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 14.66 (s, 1 H, NH); 8.20 (d, 2 H, *J* = 8.5 Hz); 7.58—7.69 (m, 6 H); 7.30—7.45 (m, 3 H); 7.05 (d, 2 H, *J* = 8.5 Hz); 3.80 (s, 3 H, CH_3O). ^{13}C NMR ($CDCl_3$), δ: 160.2, 155.1, 150.4, 145.3, 133.5, 131.2, 129.3, 127.0, 124.7, 123.1, 118.6 (CN), 114.8, 114.0, 106.4, 55.5 (CH_3O). IR (KBr), ν/cm^{-1}: 2223 (CN), 1598, 1509, 1455, 1245, 1223, 743. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 273 (12900), 424 (10500), 490 (15800). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 355 $[M]^+$ (12), 340 (38), 327 (35), 250 (45), 238 (37), 226 (68), 118 (90), 93 (100). Found (%): C, 70.88; H, 4.89; N, 19.65. $C_{21}H_{17}N_5O$. Calculated (%): C, 70.97; H, 4.82; N, 19.71.

1-(4-Methoxyphenyl)-3-(4-nitrophenyl)-5-phenylformazan (2l). Yield 1.01 g (27%), m.p. 168—169 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 14.75 (s, 1 H, NH); 8.23 (d, 2 H, *J* = 8.9 Hz); 7.70 (d, 2 H, *J* = 8.9 Hz); 7.65 (d, 2 H, *J* = 8.5 Hz); 7.55 (d, 2 H, *J* = 8.0 Hz); 7.35 (t, 1 H, *J* = 7.1 Hz); 7.12 (d, 2 H, *J* = 8.0 Hz); 6.99 (d, 2 H, *J* = 8.5 Hz); 3.82 (s, 3 H, CH_3O). ^{13}C NMR ($CDCl_3$), δ: 160.3, 155.8, 150.3, 146.2, 142.1, 132.5, 129.4, 127.5, 124.7, 123.6, 114.9, 113.9, 55.6 (CH_3O). IR (KBr), ν/cm^{-1}: 1599, 1528, 1454, 1351, 1248, 1226, 741. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 269 (22400), 424 (16000), 490 (19200). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 375 $[M]^+$ (11), 360 (38), 347 (24), 254 (34), 241 (52), 121 (100). Found (%): C, 63.92; H, 4.55; N, 18.64. $C_{20}H_{17}N_5O_3$. Calculated (%): C, 63.99; H, 4.56; N, 18.66.

3-(4-Cyanophenyl)-1-(4-methoxyphenyl)-5-phenylformazan (2m). Yield 1.10 g (31%), m.p. 135—137 °C (MeOH). ^{1}H NMR ($CDCl_3$), δ: 14.65 (s, 1 H, NH); 8.20 (d, 2 H, *J* = 8.5 Hz); 7.58—7.69 (m, 6 H); 7.30—7.45 (m, 3 H); 7.05 (d, 2 H, *J* = 8.5 Hz); 3.80 (s, 3 H, CH_3O). ^{13}C NMR ($CDCl_3$), δ: 160.2, 155.1, 150.4, 145.3, 133.5, 131.2, 129.3, 127.0, 124.7, 123.1, 118.6 (CN), 114.8, 114.0, 106.4, 55.5 (CH_3O). IR (KBr), ν/cm^{-1}: 2224 (CN), 1598, 1509, 1454, 1244, 1223, 742. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 273 (12900), 424 (10500), 490 (15800). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 355 $[M]^+$ (10), 340 (22), 327 (25), 234 (49), 220 (56), 129 (55), 121 (100), 93 (71). Found (%): C, 70.88; H, 4.89; N, 19.65. $C_{21}H_{17}N_5O$. Calculated (%): C, 70.97; H, 4.82; N, 19.71.

Verdazyls 1a—m (general procedure). A mixture of the corresponding formazan **2a—m** (1 mol), DMF (50 mL), potassium hydrosulfate (1.36 g, 0.01 mol), and paraformaldehyde (1.5 g) was stirred at room temperature for 24 h. The reaction mixture was filtered, and formaldehyde solution (37%, 12 mL) and 2 *M* NaOH solution (10mL) were subsequently added dropwise to the filtrate under stirring. The resulting mixture was stirred at 50 °C for 1 h and cooled down to room temperature, and 2 *M* NaOH solution (~10 mL) was added to pH 10. The mixture was stirred under continuous air bubbling for 0.5—24 h (depending on the nature of starting formazan) and then diluted with water (100 mL). The product was extracted with benzene (3×50 mL); the combined extracts were washed with water (3×50 mL), dried over anhydrous $MgSO_4$, and filtered through a layer of silica gel. The solvent was evaporated *in vacuo*. The resulting product was crystallized from methanol.

1,3,5-Triphenylverdazyl (1a). The duration of air oxidation was 0.5 h. Yield 0.173 g (55%), m.p. 139—140 °C (MeOH). IR (KBr), ν/cm^{-1}: 1585, 1489, 1323, 1265, 1207, 1146, 752. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 273 (62300), 405 (7500), 716 (3600). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 313 $[M]^+$ (32), 299 (15), 286 (16), 209 (60), 104 (100). Found (%): C, 76.92; H, 5.51; N, 17.74. $C_{20}H_{17}N_4$. Calculated (%): C, 76.65; H, 5.47; N, 17.88.

3-(4-Bromophenyl)-1,5-diphenylverdazyl (1b). The duration of air oxidation was 2 h. Yield 0.197 g (50%), m.p. 162—163 °C (MeOH). IR (KBr), ν/cm^{-1}: 1597, 1505, 1486, 1374, 1234, 1207, 1151, 826. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 280 (65300), 410 (8500), 720 (3900). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 391 $[M - 1]^+$ (27), 367 (60), 291 (55), 219 (67), 183 (82), 121 (80), 106 (100). Found (%): C, 61.32; H, 4.21; N, 14.41. $C_{20}H_{16}BrN_4$. Calculated (%): C, 61.24; H, 4.11; N, 14.28.

3-(4-Methoxyphenyl)-1,5-diphenylverdazyl (1c). The duration of air oxidation was 3 h. Yield 0.197 g (50%), m.p. 122—123 °C (MeOH). IR (KBr), ν/cm^{-1}: 1590, 1489, 1401, 1234, 1207, 1155, 826. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 283 (27300), 323 (11500), 390 (7300), 735 (3400). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 343 [M]$^+$ (25), 315 (43), 301 (45), 277 (38), 241 (61), 212 (44), 136 (100). Found (%): C, 73.51; H, 5.51; N, 16.29. $C_{21}H_{19}N_4O$. Calculated (%): C, 73.45; H, 5.58; N, 16.32.

3-(4-Nitrophenyl)-1,5-diphenylverdazyl (1d). The duration of air oxidation was 5 h. Yield 0.161 g (45%), m.p. 153—155 °C (MeOH). IR (KBr), ν/cm^{-1}: 1590, 1534 (NO_2), 1497, 1349 (NO_2), 1207, 1154, 737. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 290 (47300), 345 (13500), 740 (9400). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 358 [M]$^+$ (19), 334 (50), 332 (46), 275 (49), 261 (42), 219 (35), 151 (100). Found (%): C, 67.11; H, 4.53; N, 19.49. $C_{20}H_{16}N_5O_2$. Calculated (%): C, 67.03; H, 4.50; N, 19.54.

3-(4-Cyanophenyl)-1,5-diphenylverdazyl (1e). The duration of air oxidation was 5 h. Yield 0.149 g (44%), m.p. 137—138 °C (MeOH). IR (KBr), ν/cm^{-1}: 2243 (CN), 1587, 1495, 1210, 1152, 739. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 288 (35300), 344 (11500), 735 (8400). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 338 [M]$^+$ (30), 312 (70), 234 (60), 212 (42), 131 (100), 121 (45). Found (%): C, 74.61; H, 4.79; N, 20.62. $C_{21}H_{16}N_5$. Calculated (%): C, 74.54; H, 4.77; N, 20.70.

1-(4-Bromophenyl)-3,5-diphenylverdazyl (1f). The duration of air oxidation was 3 h. Yield 0.157 g (40%), m.p. 145—146 °C (MeOH). IR (KBr), ν/cm^{-1}: 1598, 1508, 1484, 1373, 1236, 1209, 1156, 824. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 278 (35300), 405 (9500), 715 (4100). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 391 [M – 1]$^+$ (10), 367 (45), 290 (37), 261 (27), 183 (44), 121 (40), 106 (100). Found (%): C, 61.32; H, 4.21; N, 14.41. $C_{20}H_{16}BrN_4$. Calculated (%): C, 61.24; H, 4.11; N, 14.28.

1-(4-Methoxyphenyl)-3,5-diphenylverdazyl (1g). The duration of air oxidation was 3 h. Yield 0.197 g (50%), m.p. 71—72 °C (MeOH). IR (KBr), ν/cm^{-1}: 1589, 1489, 1400, 1234, 1208, 1106, 826. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 280 (28400), 319 (10500), 388 (7300), 730 (3200). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 343 [M]$^+$ (15), 317 (100), 315 (50), 301 (60), 267 (50), 242 (70), 151 (44), 136 (90). Found (%): C, 73.51; H, 5.51; N, 16.29. $C_{21}H_{19}N_4O$. Calculated (%): C, 73.45; H, 5.58; N, 16.32.

1-(4-Nitrophenyl)-3,5-diphenylverdazyl (1h). The duration of air oxidation was 10 h. Yield 0.147 g (41%), m.p. 120—122 °C (MeOH). IR (KBr), ν/cm^{-1}: 1590, 1532 (NO_2), 1495, 1350 (NO_2), 1209, 1152, 741. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 293 (45300), 350 (14500), 738 (8400). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 358 [M]$^+$ (21), 334 (100), 308 (48), 275 (59), 261 (80), 257 (82), 151 (60), 106 (100). Found (%): C, 67.11; H, 4.53; N, 19.49. $C_{20}H_{16}N_5O_2$. Calculated (%): C, 67.03; H, 4.50; N, 19.54.

1-(4-Cyanophenyl)-3,5-diphenylverdazyl (1i). The duration of air oxidation was 10 h. Yield 0.121 g (36%), m.p. 117—119 °C (MeOH). IR (KBr), ν/cm^{-1}: 2241 (CN), 1590, 1495, 1209, 1152, 741. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 287 (34300), 334 (12500), 741 (9400). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 338 [M]$^+$ (17), 324 (80), 312 (86), 286 (35), 237 (74), 146 (48), 131 (85), 106 (100). Found (%): C, 74.48; H, 4.73; N, 20.59. $C_{21}H_{15}N_5$. Calculated (%): C, 74.54; H, 4.77; N, 20.70.

3-(4-Methoxyphenyl)-1-(4-nitrophenyl)-5-phenylverdazyl (1j). The duration of air oxidation was 24 h. Yield 0.2097 g (54%), m.p. 90—92 °C (MeOH). IR (KBr), ν/cm^{-1}: 1590, 1522, 1495, 1346, 1208, 1155, 824. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 280 (58400), 325 (13500), 390 (7300), 740 (4200). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 388 [M]$^+$ (10), 372 (30), 360 (100), 343 (69), 317 (42), 291 (46), 244 (50), 224 (60), 134 (70), 106 (50). Found (%): C, 64.88; H, 4.71; N, 18.09. $C_{21}H_{18}N_5O_3$. Calculated (%): C, 64.94; H, 4.67; N, 18.03.

1-(4-Cyanophenyl)-3-(4-methoxyphenyl)-5-phenylverdazyl (1k). The duration of air oxidation was 24 h. Yield 0.1915 g (52%), m.p. 83—84 °C (MeOH). IR (KBr), ν/cm^{-1}: 2241 (CN), 1588, 1494, 1205, 1158, 820. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 282 (48400), 330 (11500), 393 (8300), 742 (4000). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 368 [M]$^+$ (14), 344 (60), 342 (85), 340 (76), 326 (54), 237 (74), 146 (63), 133 (86), 131 (100), 106 (75). Found (%): C, 71.81; H, 4.88; N, 19.09. $C_{22}H_{18}N_5O$. Calculated (%): C, 71.72; H, 4.92; N, 19.01.

1-(4-Methoxyphenyl)-3-(4-nitrophenyl)-5-phenylverdazyl (1l). The duration of air oxidation was 24 h. Yield 0.113 g (29%), m.p. 111—113 °C (MeOH). IR (KBr), ν/cm^{-1}: 1590, 1534 (NO_2), 1496, 1350 (NO_2), 1210, 1155, 822. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 285 (46500), 325 (13800), 392 (7200), 735 (3500). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 388 [M]$^+$ (11), 372 (28), 362 (81), 360 (100), 343 (60), 291 (46), 284 (49), 257 (48), 136 (60). Found (%): C, 64.88; H, 4.71; N, 18.09. $C_{21}H_{18}N_5O_3$. Calculated (%): C, 64.94; H, 4.67; N, 18.03.

3-(4-Cyanophenyl)-1-(4-methoxyphenyl)-5-phenylverdazyl (1m). The duration of air oxidation was 24 h. Yield 0.141 g (41%), m.p. 91—93 °C (MeOH). IR (KBr), ν/cm^{-1}: 2223 (CN), 1592, 1489, 1401, 1234, 1207, 1155, 826. UV—Vis (CH_2Cl_2), λ_{max}/nm (ε): 286 (37500), 330 (12500), 390 (7500), 730 (4200). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 368 [M]$^+$ (14), 342 (78), 326 (51), 300 (38), 236 (69), 151 (49), 131 (100), 121 (84), 106 (89). Found (%): C, 71.77; H, 4.98; N, 19.08. $C_{22}H_{18}N_5O$. Calculated (%): C, 71.72; H, 4.92; N, 19.01.

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