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Synthesis and Electrochemical Properties of 2-(4-R^1-Phenyl)-6-(4-R^2-phenyl)-4-phenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yls

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Abstract—A new methodology for creating electroactive components for organic batteries, based on the construction of a molecular platform including stable 3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl radicals was described. A series of 2-(4-R^1-phenyl)-6-(4-R^2-phenyl)-4-phenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yls with substituents of various nature was obtained. It was shown that the substituents R^1 in the aromatic ring at position 2 of the tetrazinyl fragment influence the value of the oxidation potential in the radical, but do not influence the value of the reduction potentials, while the substituent R^2 of the aromatic ring at position 6 influence the values of the reduction potentials and practically do not influence oxidation potential values. Based on the obtained electrochemical data, a correlation structure–potential value was revealed for the cathodic and anodic process, with the help of which triarylsubstituted 3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl radicals with high values of the electrochemical gap were obtained.

Keywords: 3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl radicals, cyclic voltammetry, electron-donating substituent, electron-withdrawing substituent, electrode potential, electrochemical gap

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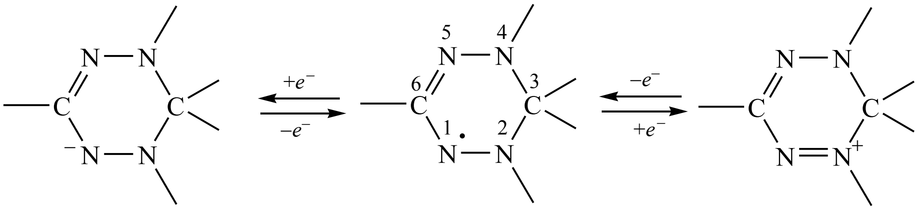
Tetrazinyl radicals (verdazyls), the preparation of which has been first reported in 1964 [1], are related to “electron amphoteric” [2], i.e., capable of both oxidizing and reducing, thus forming stable cations and anions (Scheme 1).

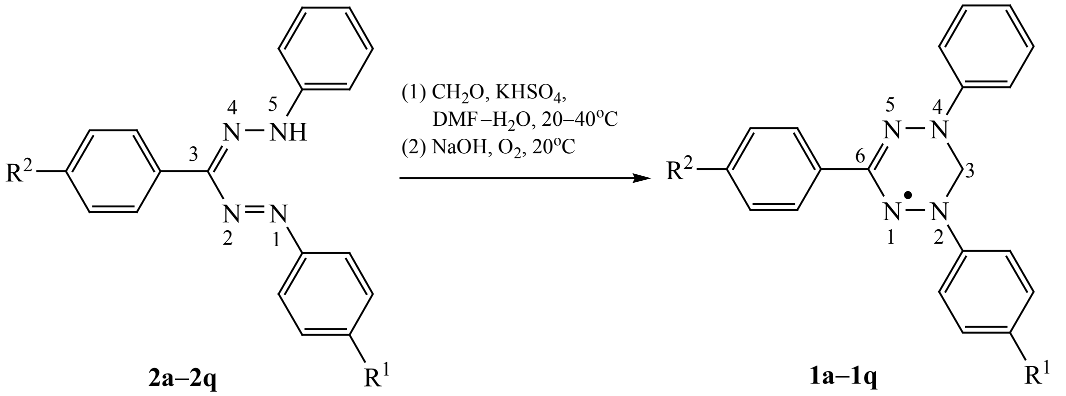
Verdazyls are the only family of neutral radicals whose stability competes with the stability of known nitroxyl radicals [3]. Versatile properties of verdazyl radicals that make them suitable for use in organic radical batteries [4] are the lack of a tendency to dimerization, as well as air and water resistance [5].

Currently, the main lines of research for verdazyl radicals are the study of their magnetic properties [6–10] and complexation ability [11–15]. At the same time, the redox properties of radicals of this type were studied much less. For example, the electrochemical behavior of the triphenylverdazyl radical in DMF in the presence of carboxylic acids has been studied in [16]. Authors [17] have studied the redox properties of some verdazyl radicals by cyclic voltammetry method. A correlation between the distribution of electron spins and redox properties was found. It was shown that the boundary orbitals along which oxidation and reduction processes

Scheme 1.



Scheme 2.



$R^1 = R^2 = H$ (**a**); $R^1 = H$, $R^2 = Me$ (**b**); $R^1 = H$, $R^2 = OMe$ (**c**); $R^1 = H$, $R^2 = NMe_2$ (**d**); $R^1 = H$, $R^2 = NO_2$ (**e**); $R^1 = H$, $R^2 = CN$ (**f**); $R^1 = Me$, $R^2 = H$ (**g**); $R^1 = OMe$, $R^2 = H$ (**h**); $R^1 = NMe_2$, $R^2 = H$ (**i**); $R^1 = NO_2$, $R^2 = H$ (**j**); $R^1 = CN$, $R^2 = H$ (**k**); $R^1 = CN$, $R^2 = Me$ (**l**); $R^1 = CN$, $R^2 = OMe$ (**m**); $R^1 = CN$, $R^2 = NMe_2$ (**n**); $R^1 = Me$, $R^2 = CN$ (**o**); $R^1 = OMe$, $R^2 = CN$ (**p**); $R^1 = NMe_2$, $R^2 = CN$ (**q**).

occur are localized in different parts of the molecule: the largest contribution to the oxidation process is made by the HOMO of the nitrogen atom in position 2, and the largest contribution to the reduction process is made by the LUMO of the carbon atom in position 6. The symmetric all-organic non-aqueous redox flow battery was studied using 3-phenyl-1,5-di-*p*-tolylverdazyl as a charge storage material, which can be reversibly oxidized and reduced through the one-electron processes [18]. The possibility of using verdazyl radicals as materials for storing electricity has also been mentioned in the review [19]. The synthesis of 6-oxo-verdazyl radical polymers with tunable electrochemical properties has been described in [20], which confirms the possibility of their use for functional redox thin films production.

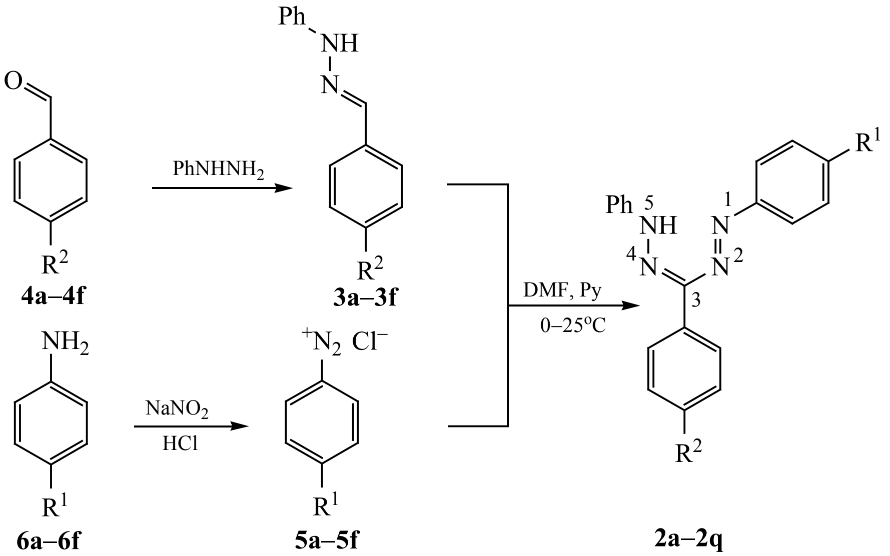
The unique structure of tetrazinyl radicals allows one to finely control the redox properties by varying the nature of the substituents at the nitrogen (position 2) and carbon atom (position 6) of the 3,4-dihydro-1,2,4,5-tetrazine fragment. Herein, we reported the synthesis of verdazyl radicals with substituents of various nature located at the para positions of benzene rings. It was shown that the substituents at position 6 of the 3,4-dihydro-1,2,4,5-tetrazine fragment strongly influence the values of the reduction potentials and practically do not influence the values of the oxidation potential, while the substituents at position 2 strongly influence the value of the oxidation potential, but do not influence the value of the reduction potentials. Based on the obtained electrochemical data, a structure–potential correlation was revealed for the cathodic and anodic process, with the help of which substituted triaryl-verdazyl radicals with high values of the electrochemical gap were obtained. The cyclic voltametry (CVA) method was used as an express method for estimating the values of the electrochemical gap of the obtained verdazyl radicals.

Triaryl-verdazyl radicals **1a**–**1q** bearing various *para*-substituted benzene fragments at positions 2 and 6 of the 3,4-dihydro-1,2,4,5-tetrazine ring were the objects of our study. The radicals **1a**–**1q** were obtained according to the classical scheme starting from the corresponding formazans **2a**–**2q** (Scheme 2).

Compounds **2a**–**2q** were synthesized by the reaction of phenylhydrazones **3a**–**3f** of substituted benzaldehydes **4a**–**4f** with aryldiazonium salts **5a**–**5f** derived from *para*-substituted anilines **6a**–**6f**. The target verdazyls **1a**–**1q** were produced by condensation of formazans **2a**–**2q** with formaldehyde in the presence of $KHSO_4$ (Scheme 3). However, in the case of substituted formazans **2b**–**2q**, cyclization is more difficult; therefore, the reactions were carried out at 40°C. The intermediate leucobases were oxidized with air to radicals **1a**–**1q**. It should be noted that in the presence of substituents, the last oxidation step required a longer time.

This method of producing verdazyl radicals is widely used, although with some restrictions. For example, in the presence of strong electron-withdrawing substituents in the aromatic ring of benzaldehyde, the yields of formazans are usually low [17]. Using the synthesis of 1,5-diphenyl-3-arylverdazyls as an example, it has been

Scheme 3.



R^1, R^2 = H (**a**), Me (**b**), MeO (**c**), NMe$_2$ (**d**), NO$_2$ (**e**), CN (**f**).

shown that the yields of formazans increase when the DMF–pyridine system is used as a solvent [21].

Hydrazones **3a**–**3f** were obtained in 60–90% yield by condensation of aldehydes **4a**–**4f** with phenylhydrazine according to the known methods; their physico-chemical constants correspond to the literature data.

Structure of formazans **2a**–**2q** was confirmed by IR, ^{1}H, ^{13}C NMR spectroscopy, and mass spectrometry data. Thus, in the IR spectra there are absorption characteristic bands of the C=N (1600–1590 cm^{-1}), N–H (3400–3300 cm^{-1}) and N=N (1500–1480 cm^{-1}) bonds. Verdazyl radicals **1a**–**1q** were characterized using IR, UV, ESR spectroscopy and mass spectrometry methods. In general, all 2,6-diaryl-4-phenyl-3,4-dihydro-1,2,4,5-tetrazin-1 (2*H*)-yls **1a**–**1q** are finely crystalline substances of green or brown color. In the IR spectra of these compounds there is a vibration band in the region of ~1150–1160 cm^{-1}, which characterizes the verdazyl radicals. For benzene solutions of radicals **1a**–**1q**, typical time-stable ESR spectra are recorded, containing 9 wide lines with an intensity ratio of 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1, due to the interaction of an unpaired electron with four

Table 1. Electrochemical characteristics of 2-(4-R^1-phenyl)-6-(4-R^2-phenyl)-4-phenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yls **1a**–**1q**

Comp. no.	R^1	R^2	E_{ox}, V	E_{red}, V	E_{gap}, V	Comp. no.	R^1	R^2	E_{ox}, V	E_{red}, V	E_{gap}, V
1a	H	H	0.31	–0.81	1.12	**1j**	NO$_2$	H	0.32	–0.64	0.96
1b	H	Me	0.24	–0.81	1.01	**1k**	CN	H	0.34	–0.65	0.99
1c	H	OMe	0.20	–0.85	1.05	**1l**	CN	Me	0.23	–0.70	0.93
1d	H	NMe$_2$	0.16	–0.86	1.02	**1m**	CN	OMe	0.20	–0.67	0.87
1e	H	NO$_2$	0.41	–0.65	1.06	**1n**	CN	NMe$_2$	0.17	–0.67	0.84
1f	H	CN	0.38	–0.67	1.05	**1o**	Me	CN	0.33	–0.86	1.19
1g	Me	H	0.29	–0.82	1.11	**1p**	OMe	CN	0.36	–0.87	1.23
1h	OMe	H	0.26	–0.87	1.13	**1q**	NMe$_2$	CN	0.38	–0.88	1.24
1i	NMe$_2$	H	0.24	–0.88	1.12						

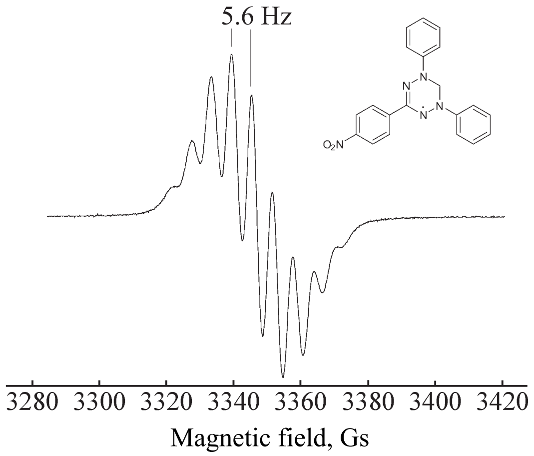


Fig. 1. ESR spectrum of verdazyl **1e**.

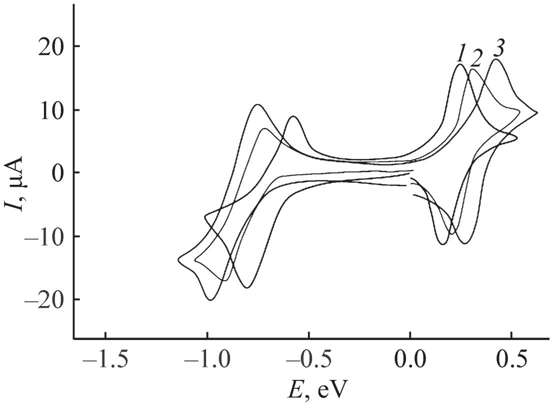


Fig. 2. Cyclic voltammograms of compounds **1a**, **1l** and **1q**.

spectrally equivalent nitrogen atoms of tetrazine ring. Figure 1 shows the ESR spectrum of verdazyl **1d**.

The electrochemical properties of radicals **1a**–**1q** were studied by cyclic voltammetry method in an acetonitrile solution using Bu_4NBF_4 as supporting electrolyte. A glassy carbon electrode was used as the working electrode, platinum was the counter electrode, and the standard silver chloride electrode was used as the reference electrode. Almost all radicals, with the exception of the nitro derivative **1d**, exhibit completely reversible oxidation and reduction processes. The oxidation potentials of verdazyls **1a**–**1q** are in the range from 0.17 to 0.41 V (Ag/AgCl/KCl). The reduction of these radicals occurs at negative potentials from –0.64 to –0.88 V (Ag/AgCl/KCl). Table 1 shows the electrochemical characteristics of compounds **1a**–**1q**.

As can be seen from the obtained data, the nature of the substituent in the *para*-position of 2-aryl fragment has a stronger effect on the oxidation process and much less on the reduction process. Thus, donor substituents facilitate the oxidation process by shifting E_{ox} value to the cathode region [by 0.07 V for verdazyl **1b** (Me), 0.11 V for **1c** (OMe), 0.15 V **1d** (NMe_2) in comparison to radical **1a**]. The methyl radical does not influence the reduction process; methoxy and dimethylamino groups slightly shift E_{red} value to the anode region by 0.04 and 0.05 V, respectively, in comparison with verdazyl **1a**. Electron-withdrawing substituents facilitate the reduction process by shifting E_{red} value to the cathode region [by 0.16 V for verdazyl **1e** (NO_2) and 0.14 V for verdazyl **1f** (CN) in comparison to radical **1a**].

The substituent at position 6 of the aromatic ring has a stronger effect on the reduction process and much less on the oxidation process. Thus, the oxidation potential (E_{ox}) is slightly shifted to the cathode region in the case of compounds with electron-withdrawing groups **1i** (NO_2) and **1k** (CN), and in the case of compounds with donor substituents (Me, OMe, NMe_2) to the anode region. At the same time, a rather strong effect on the reduction potential (E_{red}) is observed. Thus, electron-withdrawing nitro and cyano groups shift the E_{red} value to the cathode region by 0.17 V for compounds **1k** (NO_2) and **1k** (CN) as compared to verdazyl **1a**. Donor substituents slightly influence the reduction potential, shifting the E_{red} value to the anode region: by 0.02 (**1g**, Me), 0.05 (**1h**, OMe) and 0.07 V (**1i**, NMe_2) in comparison to verdazyl **1a**.

In general, for verdazyl radicals **1b**–**1k**, the magnitude of the electrochemical gap ($E_{gap} = |E_{ox} - E_{red}|$) does not change much in comparison to radical **1a**.

With the simultaneous presence of donor (at position 2) and acceptor (at position 6) substituents (verdazyl radicals **1o**–**1q**), a more significant increase in the value of the electrochemical gap is observed. This is due to the fact that the electron-donating groups in position 2 shift the E_{ox} value to the cathode region, and the electron-withdrawing CN group in position 6 shifts the E_{ox} value to the anode region, thereby increasing the difference between the peak values of oxidation and reduction potentials.

With the reverse distribution of substituents (verdazyl **1l**–**1n**), a narrowing of the electrochemical gap is observed, since the acceptor nitrile group at position 6 shifts the E_{ox} value to the anode region, and the donor groups shift the E_{ox} value to the cathode region, thereby reducing the difference between the peak values of oxidation and reduction potentials.

Figure 2 shows the CV curves of some verdazyl radicals that best demonstrate the changes in the electrochemical behavior of compounds **1a**, **1n**, and **1q** due to the substituents effect.

The magnitude of the electrochemical gap influences the capacity of a battery based on neutral radicals [22]; therefore, the use of radicals in organic batteries having a significant difference between the electrochemical potentials of oxidation and reduction can significantly increase the capacity of an energy storage device.

EXPERIMENTAL

The solvents were dried and distilled before use. All reagents (Sigma Aldrich, Merck) were used without further purification.

^1H and ^{13}C NMR spectra were recorded on a JNM-ECX400 Jeol spectrometer (400.1 and 100.6 MHz, respectively) from $CDCl_3$ solutions. IR spectra were registered from KBr pellets on an InfraLUM FT-02 Fourier spectrometer. Elemental analysis was performed on a Vario MICRO CHNS analyzer. Analytical TLC conditions: Silufol UV-245, eluents—benzene, methylene chloride–ethyl acetate (2 : 1), display by iodine. For column chromatography, silica gel L40/100µ was used; the eluent was benzene. The melting points were determined in sealed glass capillaries using an MP-50 melting point analyzer (Mettler Toledo, Switzerland). Mass spectra (EI, 70 eV) were registered on a KONIK RBK-HRGC 5000B-MSQ12 spectrometer (Spain) in the positive ionization mode. Visible electron spectra were recorded on a Shimadzu UV-2600 spectrophotometer. ESR spectra were recorded using an ESP 70–03XD/2 ESR spectrometer. Electrochemical data were taken by cyclic voltametry in an acetonitrile solution (0.1 M n-Bu_4NBF_4) using a Gamry potentiostat (Canada) in a 5 mL electrochemical cell. A glassy carbon electrode, $S^2 = 0.125$ cm^2, was used as the working electrode. The electrode was carefully polished and washed before measurements. The counter electrode was platinum, the reference electrode was the standard silver chloride electrode ($E^0 = 0.33$ V in CH_3CN vs Fc/Fc^+). All solutions were completely deaerated by purging with argon through them.

General procedure for the synthesis of phenylhydrazones 3a–3f. To a solution of 4.34 g (0.03 mol) of phenylhydrazine hydrochloride and 2.46 g of anhydrous sodium acetate in 70 mL of water a solution of 0.02 mol of aldehyde **4a**–**4f** in 25 mL of dioxane was added with stirring in small portions. Upon completion of the addition, the reaction mixture was stirred at room temperature for ~20–60 min. The precipitate was filtered off and washed on the filter with water, then dried in air. The desired products were purified by recrystallization. Melting points and spectral characteristics coincided with published data.

1-Benzylidene-2-phenylhydrazone (3a). Yield 4.19 g (72.6%), mp 155–156°C (ethanol).

1-(4-Methylbenzylidene)-2-phenylhydrazone (3b). Yield 4.35 g (68.9%), mp 113–114°C (ethanol).

1-(4-Methoxybenzylidene)-2-phenylhydrazone (3c). Yield 4.42 g (65.2%), mp 119–120°C (ethanol).

1-(4-Dimethylaminobenzylidene)-2-phenylhydrazone (3d). Yield 3.90 g (54.3%), mp 147–148°C (ethanol).

1-(4-Nitrobenzylidene)-2-phenylhydrazone (3e). Yield 5.43 g (75.1%), mp 158–159°C (ethanol).

1-(4-Cyanobenzylidene)-2-phenylhydrazone (3f). Yield 4.72 g (71.2%), mp 177–178°C (ethanol).

General procedure for the synthesis of formazans 2a–2q. A solution of 0.01 mol of phenylhydrazone **3a**–**3f** in a mixture of 5 mL of pyridine and 10 mL of DMF was cooled to –10–5°C. Aryldiazonium salt **5a**–**5f** was prepared separately: to 0.011 mol of aniline **6a**–**6f** a solution of 0.011 mol of $NaNO_2$ in 3 mL of H_2O was added, then 3.5 mL of concentrated hydrochloric acid was added, maintaining the temperature in the range of 0–5°C. The resulting suspension of the corresponding arenediazonium salt **5a**–**5f** was added in small portions to the solution of phenylhydrazone **3a**–**3f**, preventing the temperature from rising above 5°C. In this case, the reaction mixture acquired dark cherry color. The reaction mixture was kept for 3 h at a temperature of ~ 5°C and then for 12 h at room temperature, then diluted with 20 mL of water. Formazan was extracted with CH_2Cl_2 (3×20 mL). The combined organic extracts were washed with water (3×10 mL), then passed through a layer of neutral Al_2O_3 and the solvent was removed in vacuum. The resulting product was triturated with methanol.

1,3,5-Triphenylformazan (2a). Yield 1.97 g (65.6%), mp 148–150°C (methanol). IR spectrum, ν, cm^{-1}: 752.3 m, 1018.3 s, 1234.5 s, 1493.1 s (N=N), 1511.9 s (N=N), 1597.2 s (C=N), 3353.2 w (N–H). ^1H NMR spectrum, δ, ppm: 7.60–7.25 m (9H), 7.73 d. d (4H, *J* = 8.0, 1.2 Hz), 8.15 d. t (2H, *J* = 8.0, 1.4 Hz), 15.38 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 119.3, 122.7, 126.4, 128.1, 128.4, 129.0, 129.5, 129.6, 130.0, 130.4, 138.0, 141.7, 148.5. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 270 (17250), 300 (22000), 488 (14250). Mass spectrum, *m/z* (I_{rel}, %): 300 (30) $[M]^+$, 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-(*p*-Tolyl)-1,5-diphenylformazan (2b). Yield 1.51 g (48.3%), mp 156–157°C (methanol). IR spectrum, ν, cm^{-1}: 812.3 m, 1015.3 s, 1226.5 s, 1493.1 s (N=N), 1509.4 s (N=N), 1598.2 s (C=N), 3353.2 w (N–H). ^{1}H NMR spectrum, δ, ppm: 2.22 s (3H, CH_3), 7.20–7.30 m (4H), 7.34 t. t (1H, *J* = 7.6, 1.2 Hz), 7.42 d. d. d (2H, *J* = 8.1, 7.6, 1.5 Hz), 7.51–7.68 m (5H), 7.62 d. d (2H, *J* = 8.0, 1.7 Hz), 15.36 s (1H NH). ^{13}C NMR spectrum, δ_C, ppm: 21.3, 114.5, 122.2, 124.7, 125.5, 129.2, 129.4, 131.7, 139.7, 145.4, 153.1, 154. 5. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 279 (18600), 306 (25500), 498 (17000). Mass spectrum, *m/z* (I_{rel}, %): 314 (14) $[M]^+$, 299 (25), 286 (23), 222 (49), 209 (100), 63 (50). Found, %: C 76.36; H 5.74; N 17.96. $C_{20}H_{18}N_4$. Calculated, %: C 76.41; H 5.77; N 17.82.

3-(4-Methoxyphenyl)-1,5-diphenylformazan (2c). Yield 1.48 g (45.0%), mp 172–173°C (methanol). IR spectrum, ν, cm^{-1}: 1172.3 s, 1226.0 s, 1250.2, 1358.7, 1487.1 s (N=N), 1512.4 s (N=N), 1597.3 s (C=N), 3354.2 w (N–H). ^{1}H NMR spectrum, δ, ppm: 3.85 s (3H, CH_3O), 7.58–7.27 m (6H), 7.76 d (4H, *J* = 8.0 Hz), 8.02 d (2H, *J* = 9.0 Hz), 8.31 d (2H, *J* = 9.0 Hz), 15.45 s (1H NH). ^{13}C NMR spectrum, δ_C, ppm: 55.8, 113.6, 120.4, 123.1, 124.8, 127.0, 128.3, 129.2, 129.9, 131.8, 145.4, 148.2, 154.1, 160.3. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 279 (20700), 308 (27400), 522 (15900). Mass spectrum, *m/z* (I_{rel}, %): 330 (10) $[M]^+$, 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-(Dimethylamino)phenyl]-1,5-diphenylformazan (2d). Yield 1.48 g (43.0%), mp 207–209°C (methanol). IR spectrum, ν, cm^{-1}: 739.4 s, 1172.3 s, 1226.0 s, 1250.2, 1358.7, 1487.1 s (N=N), 1512.4 s (N=N), 1597.3 s (C=N), 2987.5 m, 3354.2 w (N–H). ^{1}H NMR spectrum, δ, ppm: 2.81 s [6H, $(CH_3)_2N$], 6.60 d. d (2H, *J* = 8.2, 1.1 Hz), 7.26 d. t (2H, *J* = 8.1, 1.2 Hz), 7.31–7.46 m (3H), 7.54 d. d. d (2H, *J* = 8.1, 1.4, 1.3 Hz), 7.58–7.68 m (4H), 7.65 t. t (1H, *J* = 7.7, 1.4 Hz), 15.45 s (1H NH). ^{13}C NMR spectrum, δ_C, ppm: 40.31 [$(CH_3)_2N$], 113.8, 114.5, 122.2, 124.7, 126.2, 129.2, 129.2, 131.7, 145.4, 151.4, 153.1, 155.1. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 276 (20200), 405 (17000), 530 (21500). Mass spectrum, *m/z* (I_{rel}, %): 343 (10) $[M]^+$, 327 (20), 251 (35), 239 (55), 93 (100). Found, %: C 73.52; H 6.20; N 20.51. $C_{21}H_{21}N_5$. Calculated, %: C 73.44; H 6.16; N 20.39.

3-(4-Nitrophenyl)-1,5-diphenylformazan (2e). Yield 1.52 g (44.0%), mp 207–209°C (methanol). IR spectrum, ν, cm^{-1}: 740.3 m, 1242.5 s, 1350.7 (NO_2), 1493.1 s (N=N), 1527.1 (NO_2), 1561.9 s (N=N), 1597.2 s (C=N), 3353.2 w (N–H). ^{1}H NMR spectrum, δ, ppm: 7.58–7.27 m (10H), 7.77 d (2H, *J* = 8.0 Hz), 8.41 d (2H, *J* = 9.0 Hz), 15.80 s (1H). ^{13}C NMR spectrum, δ_C, ppm: 113.6, 120.6, 122.8, 124.6, 127.5, 128.4, 129.8, 140.7, 144.4, 148.5, 152.3, 154.9. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 266 (20200), 419 (17000), 490 (20900). Mass spectrum, *m/z* (I_{rel}, %): 345 (56) $[M]^+$, 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 (2f). Yield 1.30 g (41.0%), mp 177–178°C (methanol). IR spectrum, ν, cm^{-1}: 741.3 m, 1243.5 s, 1473.1 s (N=N), 1512.4 s (N=N), 1598.2 s (C=N), 2255.1 (CN), 3359.2 w (N–H). ^{1}H NMR spectrum, δ, ppm: 7.58–7.27 m (10H), 7.65 d (2H, *J* = 8.0 Hz), 8.37 d (2H, *J* = 9.0 Hz), 15.78 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 113.1, 118.6 (CN), 119.6, 120.8, 121.6, 123.4, 126.5, 127.8, 139.7, 141.4, 145.5, 148.3, 150.9. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 272 (30200), 338 (27000), 488 (21000). Mass spectrum, *m/z* (I_{rel}, %): 325 (28) $[M]^+$, 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-(*p*-Tolyl)-3,5-diphenylformazan (2g). Yield 1.69 g (54.1%), mp 153–154°C (methanol). IR spectrum, ν, cm^{-1}: 815.3 m, 1017.3 s, 1228.5 s, 1494.1 s (N=N), 1510.4 s (N=N), 1599.2 s (C=N), 3352.2 w (N–H). ^{1}H NMR spectrum, δ, ppm: 2.15 s (3H, CH_3), 7.11 d. d (2H, *J* = 8.0, 1.6 Hz), 7.22–7.30 m (3H), 7.34 t. t (1H, *J* = 7.6, 1.2 Hz), 7.43–7.57 m (4H), 7.63 d. d (2H, *J* = 8.1, 1.5 Hz), 8.26 d. t (2H, *J* = 8.5, 1.4 Hz), 15.33 s (1H). ^{13}C NMR spectrum, δ_C, ppm: 21.2 (CH_3), 114.5, 122.3, 124.7, 125.4, 128.9, 129.2, 131.7, 132.4, 145.4, 149.5, 154.1. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 275 (16600), 310 (26700), 496 (16800). Mass spectrum, *m/z* (I_{rel}, %):

314 (7), 286 (24), 207 (30), 195 (55), 105 (100). Found, %: C 76.25; H 5.84; N 17.91. $C_{20}H_{18}N_4$. Calculated, %: C 76.41; H 5.77; N 17.82.

1-(4-Methoxyphenyl)-3,5-diphenylformazan (2h). Yield 1.33 g (40.1%), mp 119–120°C (methanol). IR spectrum, ν, cm^{-1}: 1176.3 s, 1229.0 s, 1255.2, 1348.7, 1485.9 s (N=N), 1511.4 s (N=N), 1598.4 s (C=N), 3355.1 w (N–H). ^{1}H NMR spectrum, δ, ppm: 3.82 s (3H, CH_3O), 7.60–7.15 m (10H), 7.92 d (2H, *J* = 9.0 Hz), 8.15 d (2H, *J* = 8.0 Hz), 15.40 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 55.7 (CH_3O), 113.6, 115.1, 122.1, 125.0, 128.0, 128.8, 129.6, 131.8, 135.4, 140.4, 144.2, 153.1, 160.6. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M m^{-1}): 280 (20200), 310 (25100), 520 (14700). Mass spectrum, *m/z* (I_{rel}, %): 330 (10) $[M]^+$, 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-Dimethylaminophenyl)-3,5-diphenylformazan (2i). Yield 1.51 g (44.0%), mp 147–149°C (methanol). IR spectrum, ν, cm^{-1}: 740.4 s, 1171.5 s, 1225.8 s, 1251.6, 1359.2, 1481.7 s (N=N), 1509.4 s (N=N), 1596.9 s (C=N), 2986.5 cp, 3355.2 w (N–H). ^{1}H NMR spectrum, δ, ppm: 2.90 s [6H, $(CH_3)_2N$], 7.05 d. d (2H, *J* = 8.2, 2.0 Hz), 7.19–7.29 m (3H), 7.34 t. t (1H, *J* = 7.6, 1.2 Hz), 7.42 d. d (2H, *J* = 8.2, 1.5 Hz), 7.52 d. d . d (2H, *J* = 8.5, 7.6, 1.3 Hz), 7.63 d. d . d (2H, *J* = 8.1, 7.6, 1.5 Hz), 8.25 d. t (2H, *J* = 8.5, 1.4 Hz), 15.40 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 40.4 [$(CH_3)_2N$], 111.6, 114.5, 124.7, 125.4, 125.5, 128.9, 127.7, 129.2, 131.7, 145.4, 150.5, 153.0, 155.1. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 278 (17900), 420 (20400), 520 (19800). Mass spectrum, *m/z* (I_{rel}, %): 343 (9), 328 (59), 315 (37), 195 (94), 135 (100). Found, %: C 73.48; H 6.20; N 20.31. $C_{21}H_{21}N_5$. Calculated, %: C 73.44; H 6.16; N 20.39.

1-(4-Nitrophenyl)-3,5-diphenylformazan (2j). Yield 1.86 g (54.0%), mp 197–198°C (methanol). IR spectrum, ν, cm^{-1}: 739.9 m, 1241.5 s, 1352.7 (NO_2), 1492.1 s (N=N), 1526.7 (NO_2), 1562.1 s (N=N), 1598.7 s (C=N), 3358.2 w (N–H). ^{1}H NMR spectrum, δ, ppm: 7.58–7.27 m (10H), 7.79 d (2H, *J* = 8.0 Hz), 8.33 d (2H, *J* = 9.0 Hz), 15.40 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 113.9. 122.4, 123.6, 124.7, 126.8, 127.9, 128.8, 130.1, 135.7, 144.2, 148.2, 153.3, 155.8. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 266 (20800), 424 (17100), 490 (20200). Mass spectrum, *m/z* (I_{rel}, %): 345 (10) $[M]^+$, 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 (2k). Yield 1.79 g (55.0%), mp 173–175°C (methanol). IR spectrum, ν, cm^{-1}: 741.3 m, 1243.9 s, 1473.1 s (N=N), 1511.9 s (N=N), 1597.2 s (C=N), 2253.1 (CN), 3359.2 w. ^{1}H NMR spectrum, δ, ppm: 7.65–7.30 m (10H), 8.09 d. d (2H, *J* = 8.0, 1.5 Hz), 8.27 d. d (2H, *J* = 9.0, 1.5 Hz), 15.40 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 106.3, 113.9, 118.4 (CN), 123.0, 124.1, 125.4, 127.3, 128.5, 129.1, 131.9, 136.2, 146.2, 150.3, 155.1. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 273 (33400), 340 (26000), 489 (21500). Mass spectrum, *m/z* (I_{rel}, %): 325 (22) $[M]^+$, 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.

1-(4-Cyanophenyl)-3-(*p*-tolyl)-5-phenylformazan (2l). Yield 1.46 g (43.0%), mp 152–153°C (methanol). IR spectrum, ν, cm^{-1}: 743.5 m, 1244.5 s, 1463.8 s (N=N), 1510.4 s (N=N), 1599.0 s (C=N), 2235.1 (CN), 2967.5, 3359.2 w (NH). ^{1}H NMR spectrum, δ, ppm: 2.22 s (3H, CH_3), 7.24 d. d (2H, *J* = 7.9, 1.2 Hz), 7.30–7.45 m (3H), 7.59–7.69 m (6H), 8.20 d. d (2H, *J* = 8.3, 1.6 Hz), 15.66 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 21.3 (CH_3), 106.3, 114.5, 118.5 (CN), 123.1, 124.7, 125.5, 129.2, 129.3, 131.7, 133.4, 139.7, 145.4, 150.5, 155.05. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 276 (14300), 428 (12500), 498 (16800). Mass spectrum, *m/z* (I_{rel}, %): 325 (24), 297 (43), 220 (63), 194 (100), 130 (50), 91 (67). Found, %: C 74.43; H 5.07; N 20.57. $C_{21}H_{17}N_5$. Calculated, %: C 74.32; H 5.05; N 20.63.

1-(4-Cyanophenyl)-3-(4-methoxyphenyl)-5-phenylformazan (2m). Yield 1.53 g (43.1%), mp 142–144°C (methanol). IR spectrum, ν, cm^{-1}: 742.3 m, 1223.5 s, 1244.5 cp, 1470.1 s (N=N), 1510.4 s (N=N), 1598.2 s (C=N), 2255.1 (CN), 2996.1 m, 3359.2 w (N–H). ^{1}H NMR spectrum, δ, ppm: 3.80 s (3H, CH_3O). 7.05 d. d (2H, *J* = 8.5, 1.2 Hz), 7.30–7.45 m (3H), 7.56 d. d (2H, *J* = 8.3, 1.8 Hz), 7.59–7.69 m (4H), 8.20 d. d (2H, *J* = 8.5, 1.6 Hz), 14.66 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 55.5 (CH_3O), 106.4, 114.0, 114.8, 118.6 (CN), 123.1, 124.7, 127.0, 129.3, 131.2, 133.5, 145.3, 150.4, 155.1, 160.2. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, Mcm^{-1}): 272 (12900), 420 (10500), 492 (15800). Mass spectrum, *m/z* (I_{rel}, %): 355 (12) $[M]^+$, 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-Cyanophenyl)-3-(4-dimethylaminophenyl)-5-phenylformazan (2n). Yield 1.80 g (49.0%), mp

151–152°C (methanol). IR spectrum, ν, cm^{-1}: 741.2 m, 1220.1 s, 1240.8 cp, 1469.2 s (N=N), 1508.4 s (N=N), 1596.9 s (C=N), 2254.1 (CN), 2995.8 s, 3355.2 w (N–H). ^{1}H NMR spectrum, δ, ppm: 2.82 s [6H, $(CH_3)_2N$], 6.61 d. d (2H, *J* = 8.2, 1.1 Hz), 7.35 t. t (1H, *J* = 7.6, 1.3 Hz), 7.42 d. t (2H, *J* = 8.0, 1.3 Hz), 7.59–7.70 m (6H), 8.19 d. d (2H, *J* = 8.3, 1.6 Hz), 14.66 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 40.3 [$(CH_3)_2N$], 106.4, 113.8, 114.5, 118.6 (CN), 123.0, 124.7, 126.2, 129.2, 131.7, 133.4, 145.4, 150.5, 151.4, 155.1. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 277 (14700), 436 (14500), 505 (20800). Mass spectrum, *m/z* (I_{rel}, %): 368 (11) [*M*]$^+$, 353 (65), 340 (39), 261 (65), 238 (60), 118 (90), 93 (100). Found, %: C 71.78; H 5.49; N 22.75. $C_{22}H_{20}N_6$. Calculated, %: C 71.72; H 5.47; N 22.81.

1-(*p*-Tolyl)-3-(4-cyanophenyl)-5-phenylformazan (2o). Yield 1.46 g (43.0%), mp 152–153°C (methanol). IR spectrum, ν, cm^{-1}: 747.5 m, 1249.5 s, 1468.1 s (N=N), 1515.1 s (N=N), 1598.8 s (C=N), 2237.0 (CN), 2969.5, 3358.2 w (NH). ^{1}H NMR spectrum, δ, ppm: 2.15 s (3H, CH_3), 7.12 d. d (2H, *J* = 8.0, 1.6, 0.5 Hz), 7.35 t. t (1H, *J* = 7.6, 1.3 Hz), 7.39–7.51 m (4H), 7.64 d. d. d (2H, *J* = 8.1, 7.6, 1.5 Hz), 7.87 d. d (2H, *J* = 8.6, 1.5 Hz), 8.01 d. d (2H, *J* = 8.3, 1.6 Hz), 15.60 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 21.2 (CH_3), 112.2, 114.5, 118.4 (CN), 122.2, 124.7, 127.1, 128.9, 129.2, 131.7, 132.0, 132.4, 145.4, 150.5, 155.0. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 275 (15300), 426 (13500), 496 (15900). Mass spectrum, *m/z* (I_{rel}, %): 325 (24), 297 (43), 220 (63), 194 (100), 130 (50), 91 (67). Found, %: C 74.39; H 5.01; N 20.59. $C_{21}H_{17}N_5$. Calculated, %: C 74.32; H 5.05; N 20.63.

1-(4-Methoxyphenyl)-3-(4-cyanophenyl)-5-phenylformazan (2p). Yield 1.10 g (31.0%), mp 135–137°C (methanol). IR spectrum, ν, cm^{-1}: 742.0 m, 1222.9 s, 1243.8 cp, 1468.1 s (N=N), 1509.5 s (N=N), 1597.8 s (C=N), 2250.9 (CN), 2996.1 m, 3359.2 w (N–H). ^{1}H NMR spectrum, δ, ppm: 3.82 s (3H, CH_3O), 6.99 d. d (2H, *J* = 8.3, 2.4 Hz), 7.35 т. т (1H, *J* = 7.6, 1.3 Hz), 7.42 d. t (2H, *J* = 8.1, 1.3 Hz), 7.59–7.69 m (4H), 7.85 d. d (2H, *J* = 8.6, 1.7 Hz), 8.00 d. d (2H, *J* = 8.6, 1.7 Hz), 14.65 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 55.2, 112.2, 114.5, 114.6, 118.5, 124.7, 125.5, 127.1, 129.2, 131.7, 132.2, 145.4, 150.5, 154.9, 159.8. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 273 (12900), 424 (10500), 490 (15800). Mass spectrum, *m/z* (I_{rel}, %): 355 (10) [*M*]$^+$, 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.

1-(4-Dimethylaminophenyl)-3-(4-cyanophenyl)-5-phenylformazan (2q). Yield 1.18 (32.1%), mp 144–145°C (methanol). IR spectrum, ν, cm^{-1}: 745.2 m, 1224.1 s, 1242.1 cp, 1470.1 s (N=N), 1510.2 s (N=N), 1598.1 s (C=N), 2255.3 (CN), 2996.1 s, 3353.8 w (N–H). ^{1}H NMR spectrum, δ, ppm: 2.90 s [6H, $(CH_3)_2N$], 7.05 d. d (2H, *J* = 8.2, 1.5 Hz), 7.30–7.47 m (5H), 7.64 d. d. d (2H, *J* = 8.1, 7.6, 1.4 Hz), 7.84 d. d (2H, *J* = 8.6, 1.7 Hz), 8.00 d. d (2H, *J* = 8.6, 1.7 Hz), 14.87 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 40.7 [$(CH_3)_2N$), 111.6, 112.2, 114.5, 118.5 (CN), 124.7, 125.5, 127.1, 129.2, 131.7, 132.3, 145.4, 150.5, 153.3, 159.5. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 280 (15900), 440 (14500), 510 (19800). Mass spectrum, *m/z* (I_{rel}, %): 368 (8) [*M*]$^+$, 353 (23), 340 (33), 234 (52), 220 (75), 134 (100), 93 (76). Found, %: C 71.69; H 5.44; N 22.79. $C_{22}H_{20}N_6$. Calculated, %: C 71.72; H 5.47; N 22.81.

General procedure for synthesis of verdazyls 1a–1q. A mixture of 0.001 mol of formazan **2a**–**2q**, 50 mL of DMF, 1.36 g (0.01 mol) of $KHSO_4$, and 1.5 g of paraform was stirred for 24 h at room temperature, then the reaction mixture was filtered. Under stirring, 12 mL of a 37% formalin solution and 10 mL of 2 N NaOH solution were successively added dropwise to the filtrate with stirring. Stirring was continued, depending on the starting formazan, from 0.5 h to 24 h with constant air purging, after which the reaction mixture was diluted with 100 mL of water. The product was extracted with C_6H_6 (3×50 mL). The combined organic extracts were washed with water (3 × 50 mL), then dried with anhydrous $MgSO_4$ and filtered through a pad of silica gel. The solvent was removed in vacuum. The resulting product was crystallized from methanol.

2,4,6-Triphenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1a). The duration of oxidation by air is 0.5 h. Yield 0.173 g (55.2%), mp 139–140°C (methanol). IR spectrum, ν, cm^{-1}: 752.5 s, 1145.6 m, 1207.3 m, 1265.1 m, 1323.0 m, 1488.9 s, 1585.3 s. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 273 (62300), 405 (7500), 716 (3600). Mass spectrum, *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.

2,4-Diphenyl-6-(*p*-tolyl)-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1b). The duration of oxidation by air is 2 h. Yield 0.17 g (52.0%), mp 111–112°C (methanol).

IR spectrum, ν, cm^{-1}: 780.1 s, 820.1 m, 1146.2 m, 1208.7 m, 1260.3 m, 1385.1 m, 1490.1 s, 1586.0 s, 2967.1 s. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 245 (12300), 284 (19500), 325 (9500), 395 (6500), 720 (3900). Mass spectrum, *m/z* (I_{rel}, %): 327 (30) $[M]^+$, 301 (80), 254 (44), 223 (52), 133 (49), 120 (100). Found, %: C 77.09; H 5.81; N 17.09. $C_{21}H_{19}N_4$. Calculated, %: C 77.04; H 5.85; N 17.11.

2,4-Diphenyl-6-(4-methoxyphenyl)-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1c). The duration of oxidation by air is 3 h. Yield 0.197 g (50.2%), mp 71–72°C (methanol). IR spectrum, ν, cm^{-1}: 825.5 c, 1105.6 cp, 1207.7 m, 1233.6 m, 1399.5 s, 1488.8 s, 1589.1 s. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 280 (28400), 319 (10500), 388 (7300), 730 (3200). Mass spectrum, *m/z* (I_{rel}, %): 343 (15) $[M]^+$, 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.

2,4-Diphenyl-6-(4-dimethylaminophenyl)-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1d). The duration of oxidation by air is 5 h. Yield 0.135 g (38.0%), mp 124–125°C (methanol). IR spectrum, ν, cm^{-1}: 765.9 s, 800.1 m, 1126.2 m, 1212.7 m, 1270.9 m, 1390.1 m, 1491.9 s, 1592.1 s, 2969.1 s. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 290 (29400), 325 (11500), 405 (7300), 740 (4200). Mass spectrum, *m/z* (I_{rel}, %): 356 (23) $[M]^+$, 342 (47), 330 (80), 315 (44), 254 (78), 239 (60), 149 (100), 106 (83). Found, %: C 74.11; H 6.31; N 19.59. $C_{22}H_{22}N_5$. Calculated, %: C 74.13; H 6.22; N 19.65.

2,4-Diphenyl-6-(4-nitrophenyl)-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1e). The duration of oxidation by air is 10 h. Yield 0.147 g (41.1%), mp 120–122°C (methanol). IR spectrum, ν, cm^{-1}: 740.5 s, 1152.3 m, 1208.9 m, 1349.7 s (NO_2), 1495.1 s, 1532.1 s (NO_2), 1589.9 s. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 293 (45300), 350 (14500), 738 (8400). Mass spectrum, *m/z* (I_{rel}, %): 358 (21) $[M]^+$, 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.

2,4-Diphenyl-6-(4-cyanophenyl)-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1f). The duration of oxidation by air is 10 h. Yield 0.121 g (36.0%), mp 117–119°C (methanol). IR spectrum, ν, cm^{-1}: 740.5 m, 1152.3 m, 1208.9 m, 1495.1 s, 1589.9 s, 2241.0 m (CN). UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 287 (34300), 334 (12500), 740 (9400). Mass spectrum, *m/z* (I_{rel}, %): 338 (17) $[M]^+$, 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.

2-(*p*-Tolyl)-4,6-diphenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1g). The duration of oxidation by air is 5 h. Yield 0,104 g (32.0%), mp 138–139°C (methanol). IR spectrum, ν, cm^{-1}: 746.1 s, 1143.2 s, 1205.7 m, 1387.1 m, 1494.1 s, 1590.0 s. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 246 (9900), 280 (22500), 320 (12400), 398 (7400), 721 (3400). Mass spectrum, *m/z* (I_{rel}, %): 327 (17) $[M]^+$, 301 (85), 251 (60), 224 (65), 120 (74), 106 (100). Found, %: C 77.08; H 5.91; N 17.16. $C_{21}H_{19}N_4$. Calculated, %: C 77.04; H 5.85; N 17.11.

2-(4-Methoxyphenyl)-4,6-diphenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1h). The duration of oxidation by air is 3 h. Yield 0.197 g (50.2%), mp 71–72°C (methanol). IR spectrum, ν, cm^{-1}: 880.5 m, 1120.7 m, 1249.6 s, 1506.8 s, 1609.1 m, 1708.1 m. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 280 (28400), 319 (10500), 388 (7300), 730 (3200). Mass spectrum, *m/z* (I_{rel}, %): 343 (15) $[M]^+$, 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.

2-(4-Dimethylaminophenyl)-4,6-diphenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1i). The duration of oxidation by air is 3 h. Yield 0.181 g (51.1%), mp 95–96°C (methanol). IR spectrum, ν, cm^{-1}: 770.9 s, 812.1 m, 1131.2 m, 1227.0 m, 1280.2 m, 1395.2 m, 1495.9 s, 1595.1 s, 2970.1 s. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 288 (28400), 320 (10600), 400 (6300), 736 (3200). Mass spectrum, *m/z* (I_{rel}, %): 356 (11) $[M]^+$, 342 (36), 330 (80), 255 (65), 164 (50), 149 (65), 106 (100). Found, %: C 74.21; H 6.21; N 19.59. $C_{21}H_{19}N_4O$. Calculated, %: C 74.13; H 6.22; N 19.65.

2-(4-Nitrophenyl)-4,6-диphenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1j). The duration of oxidation by air is 10 h. Yield 0.147 g (41.1%), mp 120–122°C (methanol). IR spectrum, ν, cm^{-1}: 755.5 s, 1161.3 m, 1210.8 m, 1350.7 s (NO_2), 1490.1 s, 1536.1 s (NO_2), 1591.0 s UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 290 (35300), 340 (12500), 735 (7400). Mass spectrum, *m/z* (I_{rel}, %): 358 (21) $[M]^+$, 334 (100), 275 (56), 261 (83), 257 (85), 151 (62), 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.

2-(4-Cyanophenyl)-4,6-diphenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1k). The duration of oxidation by air is 10 h. Yield 0.122 g (36.0%), mp 103–104°C (methanol). IR spectrum, ν, cm^{-1}: 745.6 m, 1160.3 m, 1211.9 m, 1489.1 s, 1592.1 s, 2245.0 m (CN). UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 290 (29300), 344 (10500), 756 (7300). Mass spectrum, *m/z* (I_{rel}, %): 338 (17) $[M]^+$, 312 (90), 286 (35), 286 (35), 237 (80), 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.

2-(4-Cyanophenyl)-6-(*p*-tolyl)-4-phenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1l). The duration of oxidation by air is 24 h. Yield 0.117 (33.2%), mp 125–126°C (methanol). IR spectrum, ν, cm^{-1}: 740.6 m, 856.1 s, 1165.3 m, 1219.2 m, 1490.4 s, 1596.0 s, 2245.6 m (CN). UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 292 (29800), 346 (11800), 760 (6300). Mass spectrum, *m/z* (I_{rel}, %): 352 (17) $[M]^+$, 326 (100), 300 (32), 276 (45), 237 (73), 223 (47), 133 (60), 122 (90). Found, %: C 74.88; H 5.13; N 19.79. $C_{22}H_{18}N_5$. Calculated, %: C 74.98; H 5.15; N 19.87.

2-(4-Cyanophenyl)-6-(4-methoxyphenyl)-4-phenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1m). The duration of oxidation by air is 24 h. Yield 0.1915 g (52.1%), mp 83–84°C (methanol). IR spectrum, ν, cm^{-1}: 820.2 s, 1157.6 s, 1205.2 m, 1494.0 s, 1587.8 s, 2241.1 m (CN). UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 282 (48400), 330 (11500), 393 (8300), 742 (4000). Mass spectrum, *m/z* (I_{rel}, %): 368 (14) $[M]^+$, 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.

2-(4-Cyanophenyl)-6-(4-dimethylaminophenyl)-4-phenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1n). The duration of oxidation by air is 24 h. Yield 0.126 g (33.1%), mp 122–123°C (methanol). IR spectrum, ν, cm^{-1}: 820.2 s, 1076 s, 1157.6 m, 1205.2 m, 1494.0 s, 1587.8 s, 2241.1 m (CN), 2982.6 m. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 293 (38400), 356 (14500), 420 (9200), 761 (4400). Mass spectrum, *m/z* (I_{rel}, %): 381 (14) $[M]^+$, 355 (90), 262 (50), 254 (81), 237 (68), 149 (84), 133 (76), 106 (106). Found, %: C 72.35; H 5.58; N 22.09. $C_{23}H_{21}N_6$. Calculated, %: C 72.42; H 5.55; N 22.03.

2-(*p*-Tolyl)-6-(4-cyanophenyl)-4-phenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1o). The duration of oxidation by air is 24 h. Yield 0.158 g (45.0%), mp 130–131°C (methanol). IR spectrum, ν, cm^{-1}: 755.1 m, 862.7 s, 1196.3 m, 1224.2 m, 1495.4 s, 1599.0 s, 2246.1 m (CN). UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 285 (42400), 335 (12500), 398 (7300), 750 (4000). Mass spectrum, *m/z* (I_{rel}, %): 352 (18) $[M]^+$, 328 (70), 326 (100), 324 (65), 249 (50), 228 (65), 121 (70), 106 (74), 79 (63). Found, %: C 74.88; H 5.13; N 19.79. $C_{22}H_{18}N_5$. Calculated, %: C 74.98; H 5.15; N 19.87.

2-(4-Methoxyphenyl)-6-(4-cyanophenyl)-4-phenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1p). The duration of oxidation by air is 24 h. Yield 0.141 g (41.0%), mp 91–93°C (methanol). IR spectrum, ν, cm^{-1}: 825.5 s, 1155.1 s, 1207.5 m, 1234.1 m, 1400.5 m, 1488.6 s, 1591.6 s, 2223.1 (CN). UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 286 (37500), 330 (12500), 390 (7500), 730 (4200). Mass spectrum, *m/z* (I_{rel}, %): 368 (14) $[M]^+$, 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.

2-(4-Dimethylaminophenyl)-6-(4-cyanophenyl)-4-phenyl-3,4-dihydro-1,2,4,5-tetrazin-1(2*H*)-yl (1q). The duration of oxidation by air is 24 h. Yield 0.171 g (45.0%), mp 101–102°C (methanol). IR spectrum, ν, cm^{-1}: 817.2 s, 1066 s, 1145.6 m, 1200.9 m, 1496.9 s, 1590.8 s, 2245.1 m (CN), 2989.6 m. UV spectrum (CH_2Cl_2), λ_{max}, nm (ε, M cm^{-1}): 290 (35500), 335 (14500), 400 (8500), 735 (3600). Mass spectrum, *m/z* (I_{rel}, %): 381 (15) $[M]^+$, 367 (40), 355 (100), 326 (54), 277 (49), 255 (74), 236 (67), 149 (65), 106 (69). Found, %: C 72.35; H, 5.58; N 22.09. $C_{23}H_{21}N_6$. Calculated, %: C 72.42; H 5.55; N 22.03.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

1. Kuhn, R. and Trischman, H., *Monatsh. Chem.*, 1964, vol. 95, no. 2, p. 457. https://doi.org/10.1007/BF00901311
2. Fabian, J. and Hartmann, H., *J. Pr. Chem.*, 1984, vol. 326, no. 5, p. 443. https://doi.org/10.1002/prac.19843260313
3. Chemistnick, V., Chambers, D., and Brook, D.J.R., *J. Org. Chem.*, 2009, vol. 74, no. 5, p. 1850. https://doi.org/10.1021/jo8019829
4. Nishide, H., Iwasa, S., Pu, Y.-J., Suga, T., Nakahara, K., and Satoh, M., *Electrochim. Acta*, 2004,

vol. 50, nos. 2–3, p. 827.
https://doi.org/10.1016/j.electacta.2004.02.052

5. Lipunova, G.N., Fedorchenko, T.G., and Chupakhin, O.N., *Russ. Chem. Rev*., 2013, vol. 82, no. 8, p. 701. https://doi.org/10.1070/RC2013v082n08ABEH004341
6. Koivisto, B.D. and Hicks, R.G., *Coord. Chem. Rev*., 2005, vol. 249, no. 23, p. 2612. https://doi.org/10.1016/j.ccr.2005.03.012
7. Miyamoto, S., Iwasaki, Y., Uemoto, N., Hosokoshi, Y., Fujiwara, H., Shimono, S., and Yamaguchi, H., *Phys. Rev. Mater.*, 2019, vol. 3, no. 6, p. 064410. https://doi.org/10.1103/PhysRevMaterials.3.064410
8. Brook, D.J.R., Fleming, C., Chung, D., Richardson, C., Ponce, S., Das, R., Srikanth, H., Heindl, R., and Noll, B.C., *Dalton Trans*., 2018, vol. 47, no. 18, p. 6351. https://doi.org/10.1039/c8dt00805a
9. Solea, A.B., Wohlhauser, T., Abbasi, P., Mongbanziama, Y., Crochet, A., Fromm, K.M., Novitchi, G., Train, C., Pilkington, M., and Mamul, O., *Dalton Trans*., 2018, vol. 47, no. 14, p. 4785. https://doi.org/10.1039/c8dt00840j
10. Iwase, K., Yamaguchi, H., Ono, T., Shimokawa, T., Nakano, H., Matsuo, A., Kindo, K., Nojiri, H., and Hosokoshi, Y., *J. Phys. Soc. Japan*, 2013, vol. 82, no. 7, p. 074719. https://doi.org/10.7566/JPSJ.82.074719
11. Brook, D.J.R., *Comm. Inorg. Chem*., 2015, vol. 35, no. 1, p. 1. https://doi.org/10.1080/02603594.2014.974805
12. Kumar, V., Shova, S., Novitchi, G., and Train, C., *Compt. Rend. Chim*., 2019, vol. 22, no. 6–7, p. 541. https://doi.org/10.1016/j.crci.2019.03.008
13. Sanz, C.A., McKay, Z.R., Maclean, S.W.C., Patrick, B.O., and Hicks, R.G., *Dalton Trans*., 2017, vol. 46, no. 33, p. 12674. https://doi.org/10.1039/c9dt02549a
14. Wang, C., Lin, S.-Y., Shi, W., Cheng, P., and Tang, J., *Dalton Trans*., 2015, vol. 44, no. 12, p. 5364. https://doi.org/10.1039/c4dt03354j
15. McKinnon, S.D.J., Patrick, B.O., Lever, A.B.P., and Hicks, R.G., *Inorg. Chem*., 2013, vol. 52, no. 14, p. 8053. https://doi.org/10.1021/ic400704j
16. Jaworski, J.S. and Krawczyk, I., *Monat. Chem*., 1992, vol. 123, nos. 1–2, p. 43. https://doi.org/10.1007/BF01045295
17. Gilroy, J.B., McKinnon, S.D.J., Koivisto, B.D., and Hicks, R.G., *Org. Lett*., 2007, vol. 9, no. 9, p. 4837. https://doi.org/10.1021/ol702163a
18. Charlton, G.D., Barbon, S.M., Gilroy, J.B., and Dyker, C.A., *J. Energy Chem*., 2019, vol. 34, p. 52. https://doi.org/10.1016/j.jechem.2018.09.020
19. Nevers, D.R., Brushett, F.R., and Wheeler, D.R., *J. Power Sources*, 2017, vol. 352, p. 226. https://doi.org/10.1016/j.jpowsour.2017.03.077
20. Price, J.T., Paquette, J.A., Harrison, C.S., Bauld, R., Fanchini, G., and Gilroy, J.B., *Polym. Chem*., 2014, vol. 5, p. 5223. https://doi.org/10.1039/c4py00829d
21. Tsebulaeva, Yu.V., Pryanichnikova, M.K., and Tanaseichuk, B.S., *Izv. Vuzov. Ser. Khim. i Khim. Tekhnol*., 2018, vol. 61, no. 1, p. 23.
22. Wilcox, D.A., Agarkar, V., Mukherjee, S., and Boudouris, B.W., *Ann. Rev. Chem. Biomol. Eng*., 2018, vol. 9, p. 83. https://doi.org/10.1146/annurev-chembioeng-060817-083945