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DIRECT C–C COUPLING OF CYCLIC ALDONITRONES WITH 1,2,4-TRIAZINES USING S_N^H REACTIONS

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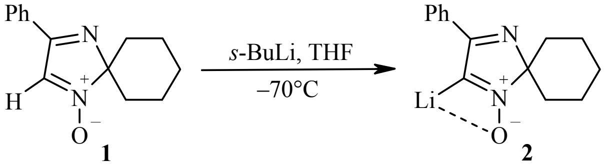
New nitrogen heterocyclic derivatives were obtained by a direct uncatalyzed by metals C–C cross-coupling of a cyclic aldonitrone lithium derivative with 1,2,4-triazines.

Keywords: aldonitrones, 1,2,4-triazines, S_N^H reactions.

The development of efficient methods for the construction of new C–C bonds in aromatic and heteroaromatic compounds is a very important strategic problem in synthetic organic chemistry. Such methods are the Suzuki, Negishi, Stille, Kumada, Hiyama and other cross-coupling reactions catalyzed by transition metals, such as Pd, Ni, Cu etc. [1, 2]. As a rule, these are reactions of organoelement compounds (boron, zinc, tin, silicon, and magnesium derivatives) with halides or triflates. Although this approach is commonly employed in the creation of $C(sp^3,sp^2,sp)$–$C(sp^3,sp^2)$ bonds, it has several limitations arising from the need for prior introduction of auxiliary groups into the reagent structure and the use of metal complex catalysts.

An alternative method for the formation of $C(sp^2)$–$C(sp^3,sp^2)$ bonds is the direct C–H functionalization of arenes and hetarenes [3]. A variation of this method is the nucleophilic aromatic substitution of hydrogen (S_N^H reactions) [4, 5], which may be seen as an atom-economical and "green" synthetic approach. The economical advantage of this strategy lies in minimization of the number of auxiliary steps and additional reagents, especially, expensive noble metal catalysts. The "green" advantage arises since S_N^H reactions, as a rule, proceed under mild conditions, and the side products are usually environmentally harmless compounds, most often water.

In the present work, we present a simple and convenient method for the preparation of functionally-substituted azaheterocycles, based on S_N^H reactions of a aldonitrone lithium derivative with 1,2,4-triazines. The synthesis of such compounds is of interest since promising materials containing nitrones [6-8] and triazines [9-11] have been reported.



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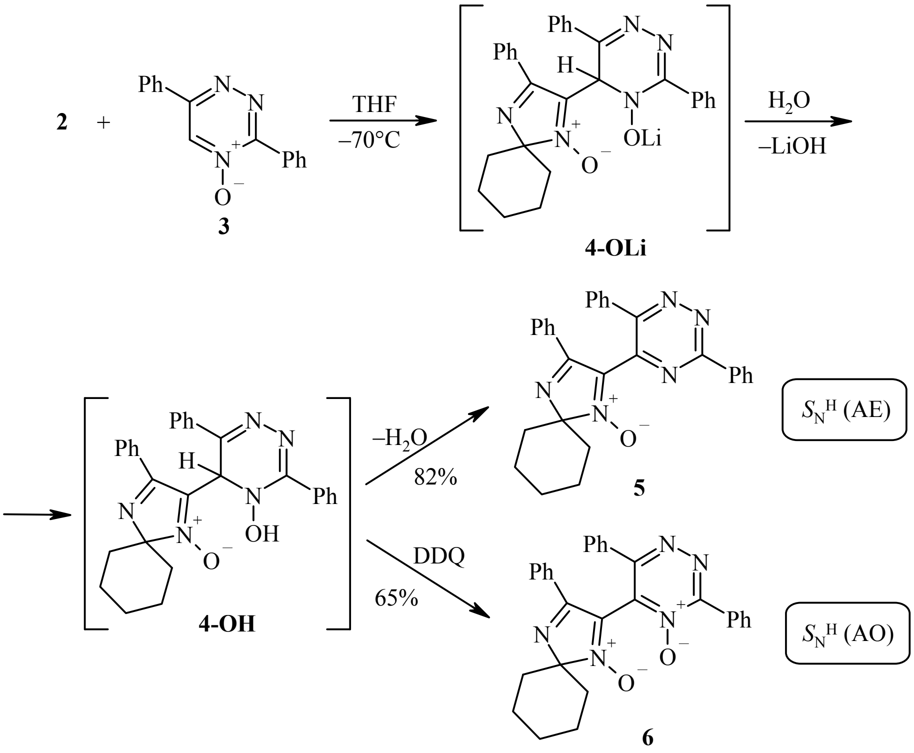
It is known that nitrones **1**, which contain a hydrogen atom at the α-carbon atom relative to the *N*-oxide group, display acidic properties and form the corresponding lithium derivatives **2** upon reaction with organometallic bases such as *s*-BuLi and lithium diisopropylamide (LDA) [12]. The relative stability of the intermediates, which are dipole-stabilized carbanions [13], is attributed to a thermodynamically-advantageous intramolecular coordination bond.

The cyclic aldonitrone lithium derivative **2** reacts with 3,6-diphenyl-1,2,4-triazine *N*-oxide (**3**). The selection of bicyclic nitrone **2** as the nucleophilic synthon and 3,6-disubstituted 1,2,4-triazines as the electrophilic components was made in light of the synthetic availability of these reagents. This reaction most likely proceeds through the formation of an unstable σ^H-adduct **4-OLi**, which is the product of the addition of lithium derivative **2** to the triazine *N*-oxide **3** [14]. Intermediate **4-OLi** converts into **4-OH** by the action of an equimolar amount of water. The aromatization of intermediate **4-OH** may be carried out by either elimination (S_N^H(AE)) or oxidation (S_N^H(AO)). The dihydro derivative **4-OH** gives triazine **5** in 82% yield as the result of loss of a water molecule. The use of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) as the oxidizing agent leads to triazine *N*-oxide **6** in 65% yield. DDQ was selected since this reagent has already proved effective in other S_N^H(AO) reactions [15, 16].



The structures of the resultant heterocycles **5** and **6** were supported by elemental analysis, mass spectrometry, and IR, ^{1}H NMR, and ^{13}C NMR spectroscopy data. The ^{1}H NMR spectra show signals for the protons of the spirofused cyclohexyl fragment as broad multiplets (1.17-2.01 ppm) and of the phenyl substituents at 7.29-8.32 ppm. The ^{13}C NMR spectra show characteristic resonance signals for the carbon nuclei [17]. The mass spectra display characteristic peaks of *m/z* 460 and 476, corresponding to the $[\mathrm{M+H}]^+$ molecular ions of products **5** and **6**.

X-ray structural analysis was carried out to confirm the position of the *N*-oxide fragment in triazine **5** (Fig. 1). The analysis showed that the triazine **5** forms orthorhombic crystals with space group $Pna2_1$. No significant deviations of the bond lengths and angles from standard values [18] were found. The triazine and imidazole rings are planar, and the deviations of the atoms from the mean planes in both cases are not more than

0.008 Å. The dihedral angle between the planes of the five- and six-membered azaheterocycles is 64.58°.

In our study of this S_N^H reaction, we discovered that the dipole-stabilized carbanion **2** reacts smoothly not only with the highly electrophilic triazine *N*-oxide **3**, but also with less reactive species, namely, unactivated 1,2,4-triazines **7a-d**. This transformation should also be seen as a two-step S_N^H reaction leading to previously unreported triazinyl-containing 2*H*-imidazole derivatives. The first step most likely also involves nucleophilic addition of lithium derivative **2** to the HC=N bond of azine **7a-d** to give σ^H-adducts **(8a-d)-NLi**. These intermediates have limited stability and are converted irreversibly in the presence of water into dihydro derivatives **(8a-d)-NH**, which are capable of existing in two tautomeric forms: **A-(8a-d)-NH** and **B-(8a-d)-NH**. The second step features loss of a water molecule to form heterocyclic derivatives **9a-d** without an *N*-oxide function in the structure. The yield of reaction products **9a-d** is 75-85%. We should note that the loss of a water molecule from the imidazole fragment permits classification of this S_N^H reaction as a vicarious nucleophilic substitution of hydrogen [19, 20].

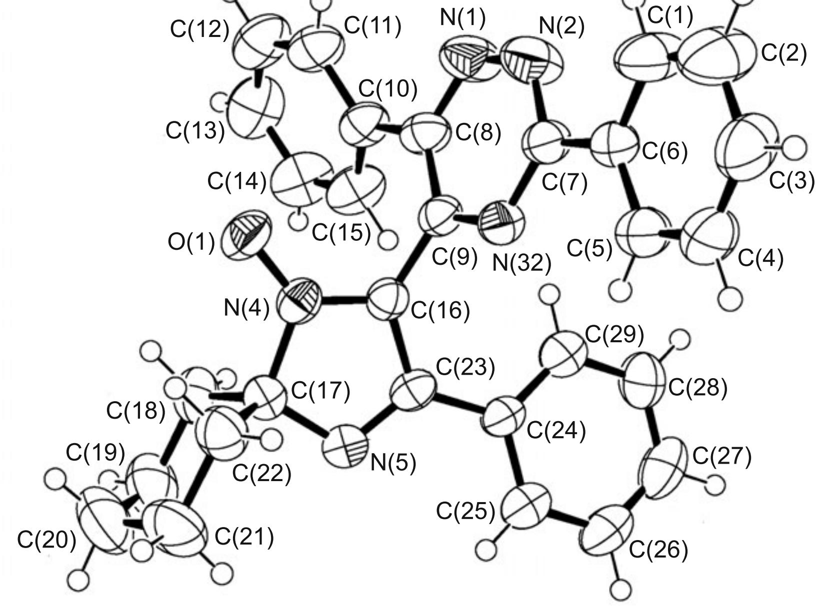
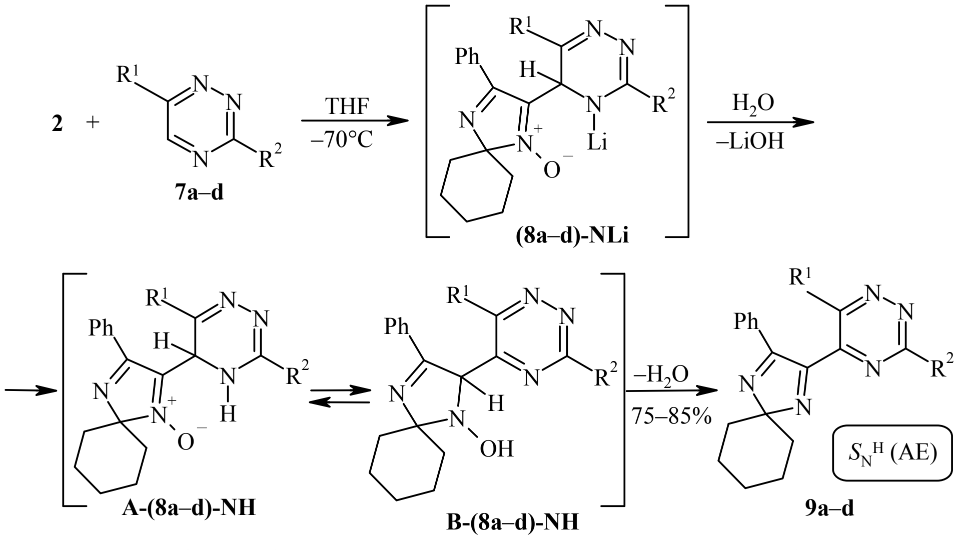


Fig. 1. Molecular structure of triazine **5**. The hydrogen atoms are represented by thermal vibration ellipsoids of 50% probability.



a $R^1 = R^2 = Ph$; **b** $R^1 = Ph$, $R^2 = 2\text{-Py}$; **c** $R^1 = 4\text{-MeOC}_6H_4$, $R^2 = 2\text{-Py}$; **d** $R^1 = Ph$, $R^2 = 4\text{-MeOC}_6H_4$

The ^{1}H NMR spectra of triazines **9a-d** show resonance signals for the aliphatic (1.59-1.90 ppm) as well as aromatic and heteroaromatic fragments (6.86-8.85 ppm), while the ^{13}C NMR spectra of these compounds show characteristic carbon atom signals [17]. The mass spectra display molecular ion peaks.

X-ray structural analysis was carried out to confirm the structure of triazines **9a-d**. These results indicated that triazine **9c** forms monoclinic crystals with space group $P2_1/c$ (Fig. 2). No significant deviations were found for the bond lengths and angles from standard values [18]. The triazine and imidazole rings are planar. The deviations of the ring atoms from the mean planes do not exceed 0.014 Å. The dihedral angle between the planes of the five- and six-membered azaheterocycles is 78.63°.

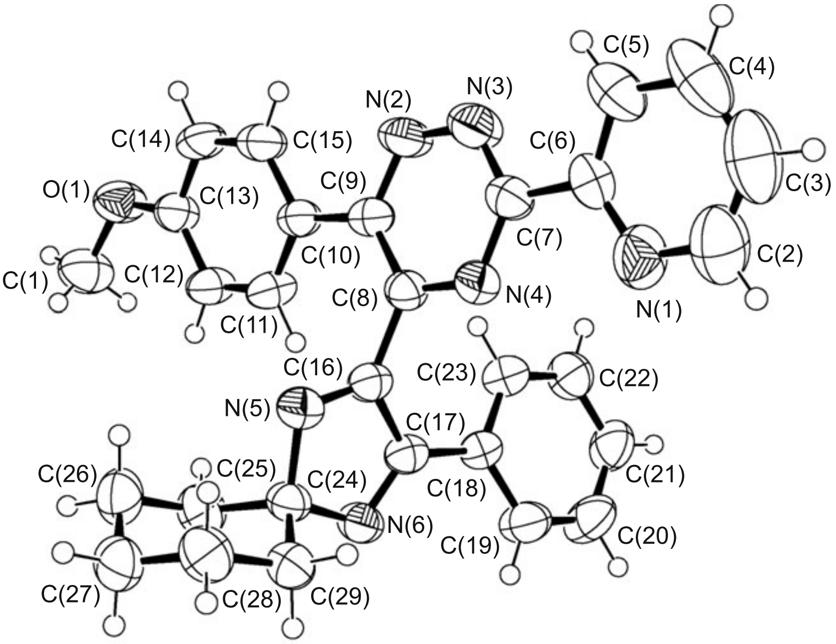


Fig. 2. The molecular structure of **9c** with representation of the hydrogen atoms as thermal vibration ellipsoids of 50% probability.

Thus, a new method is proposed for the preparation of previously unreported heterocycles by the uncatalyzed C–C coupling of aldonitrones and 1,2,4-triazines.

EXPERIMENTAL

The IR spectra were recorded for neat samples on a Perkin Elmer Spectrum One B FTIR spectrometer (DRA). The ^{1}H NMR (400 MHz) and ^{13}C NMR spectra (100 MHz, APT mode) were recorded on a Bruker Avance II spectrometer in 1:1 DMSO-d_6–CCl_4 (for the ^{1}H NMR spectra) and DMSO-d_6 (for the ^{13}C NMR spectra) with TMS as internal standard. The ESI mass spectra were recorded on a Bruker Daltonics micrOTOF-Q II spectrometer. The elemental analysis was carried out on a Perkin Elmer 2400-II CHNS/O analyzer. The melting points were measured on a Boetius hot stage apparatus. The R_f values were obtained on Macheray-Nagel Alugram Sil G/UV-254 plates. Merck silica gel (0.063-0.200 mm) was used for column chromatography.

The solvents were purified and dried by standard methods. *s*-BuLi (1.3 M in 92:8 cyclohexane–hexane mixture) and DDQ from Alfa Aesar were used in the work.

2-Phenyl-1,4-diazaspiro[4,5]decane-1,3-diene 4-oxide (1) [21], **3,6-diphenyl-1,2,4-triazine 4-oxide (3)** [22], **3,6-diphenyl-1,2,4-triazine (7a)** [23], **6-phenyl-3-(2-pyridyl)-1,2,4-triazine (7b), 6-(4-methoxyphenyl)-3-(2-pyridyl)-1,2,4-triazine (7d)** [24], **3-(4-methoxyphenyl)-6-phenyl-1,2,4-triazine (7c)** [25] were prepared according to literature procedures.

Lithium derivatives 4-OLi and (8a-d)-NLi (General Method). 1.3 M *s*-BuLi solution (0.920 ml, 1.2 mmol) was added with vigorous stirring to a solution of 2-phenyl-1,4-diazaspiro[4,5]decane-1,3-diene 4-oxide (**1**) (0.228 g, 1.0 mmol) in THF (6 ml) under an argon atmosphere at -70°C. The reaction mixture was stirred for 10 min at -70°C. A solution of the corresponding triazine **3** or **7a-d** (1.2 mmol) in a minimal amount of THF was added to the solution of the formed lithium derivative **2**. The reaction mixture, which was a solution of the respective intermediate **4-OLi** or **(8a-d)-NLi**, was warmed to room temperature and stirred for an additional 2 h.

Triazines 5 and 9a-d (General Method). Water (0.02 ml, 1.0 mmol) was added to the previously prepared solution of lithium derivative **4-OLi** or **(8a-d)-NLi** cooled to 0°C, and the reaction mixture was stirred for 15 min at room temperature. The mixture was concentrated in vacuum. Triazines **5** and **9a-d** were isolated by column chromatography.

2-(3,6-Diphenyl-1,2,4-triazin-5-yl)-3-phenyl-1,4-diazaspiro[4,5]decane-1,3-diene 1-Oxide (5). Yield 0.376 g (82%). Yellow powder, mp 166-168°C. R_f 0.2 (hexane–EtOAc, 4:1). IR spectrum, ν, cm^{-1}: 652, 690, 737, 1002, 1025, 1342, 1385, 1415, 1446, 1506, 1557, 1606 (C=N), 2853, 2929, 2940, 3060. ^{1}H NMR spectrum, δ, ppm: 1.38-1.45 (3H, m) and 1.72-1.88 (7H, m, $(CH_2)_5$); 7.29-7.40 (4H, m, H Ph); 7.44-7.51 (4H, m, H Ph); 7.52-7.58 (3H, m, H Ph); 7.61-7.66 (2H, m, H Ph); 8.28-8.32 (2H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 22.4 (CH_2); 24.0 (CH_2); 34.0 (CH_2); 103.7; 127.0 (CH); 127.5 (CH); 127.7 (CH); 128.3 (CH); 128.5 (CH); 128.8 (CH); 129.9 (CH); 130.7 (CH); 131.2; 131.7 (CH); 132.8; 133.6; 133.9; 144.9; 156.0; 160.6; 163.6. Found, *m*/*z*: 460.2086 [M+H]$^+$. $C_{29}H_{26}N_5O$. Calculated, *m*/*z*: 460.2132. Found, %: C 75.64; H 5.67; N 15.09. $C_{29}H_{25}N_5O$. Calculated, %: C 75.80; H 5.48; N 15.24.

2-(3,6-Diphenyl-1,2,4-triazin-5-yl)-3-phenyl-1,4-diazaspiro[4,5]decane-1,3-diene (9a). Yield 0.377 g (85%). Yellow powder, mp 173-175°C. R_f 0.2 (hexane–EtOAc, 9:1). IR spectrum, ν, cm^{-1}: 558, 649, 677, 950, 985, 1320, 1371, 1445, 1486, 1499, 1607 (C=N), 2846, 2923, 3058. ^{1}H NMR spectrum, δ, ppm: 1.59-1.85 (10H, m, $(CH_2)_5$); 7.21-7.32 (6H, m, H Ph); 7.38-7.43 (4H, m, H Ph); 7.52-7.57 (3H, m, H Ph); 8.39-8.43 (2H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 23.2 (CH_2); 24.6 (CH_2); 32.9 (CH_2); 106.0; 127.6 (2CH); 127.9 (CH); 128.1 (CH); 128.7 (CH); 128.8 (CH); 129.4; 129.9; 130.8; 131.6 (CH); 133.3; 133.6; 150.5; 155.7; 160.1; 160.4; 161.9. Found, *m*/*z*: 444.2147 [M+H]$^+$. $C_{29}H_{26}N_5$. Calculated, *m*/*z*: 444.2183. Found, %: C 78.67; H 5.68; N 15.96. $C_{29}H_{25}N_5$. Calculated, %: C 78.53; H 5.68; N 15.79.

3-Phenyl-2-[6-phenyl-3-(2-pyridyl)-1,2,4-triazin-5-yl]-1,4-diazaspiro[4,5]decane-1,3-diene (9b). Yield 0.377 g (80%). Yellow powder, mp 153-156°C. R_f 0.2 (hexane–EtOAc, 3:2). IR spectrum, ν, cm^{-1}: 565, 676, 696, 762, 949, 985, 1074, 1386, 1487, 1624 (C=N), 2851, 2926, 3057. ^{1}H NMR spectrum, δ, ppm: 1.63-1.85 (10H, m, $(CH_2)_5$); 7.23-7.43 (10H, m, H Ph); 7.58-7.61 (1H, m, H Py); 7.99-8.02 (1H, m, H Py); 8.45-8.48 (1H, m, H Py); 8.82-8.83 (1H, m, H Py). ^{13}C NMR spectrum, δ, ppm: 23.4 (CH_2); 24.8 (CH_2); 33.0 (CH_2); 106.3; 124.0 (CH); 125.9 (CH); 127.7 (CH); 128.2 (CH); 128.5 (CH); 129.1 (CH); 129.9 (CH); 130.3 (CH); 130.6; 133.2; 137.3 (CH); 150.1 (CH); 151.2; 151.8; 156.4; 160.5 (2C); 161.9. Found, *m*/*z*: 445.2180 [M+H]$^+$. $C_{28}H_{25}N_6$. Calculated, *m*/*z*: 445.2135. Found, %: C 75.25; H 5.53; N 18.68. $C_{28}H_{24}N_6$. Calculated, %: C 75.65; H 5.44; N 18.90.

2-[6-(4-Methoxyphenyl)-3-(2-pyridyl)-1,2,4-triazin-5-yl]-3-phenyl-1,4-diazaspiro[4,5]decane-1,3-diene (9c). Yield 0.370 g (78%). Yellow powder, mp 159–162°C. R_f 0.15 (hexane–EtOAc, 2:3). IR spectrum, ν, cm^{-1}: 693, 784, 948, 985, 1076, 1252, 1365, 1415, 1462, 1605 (C=N), 2853, 2927, 3055. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.72-1.78 (6H, m) and 1.84-1.90 (4H, m, $(CH_2)_5$); 3.83 (3H, s, OCH_3); 6.86 (2H, d, ^3J = 8.8, H Ar); 7.23-7.29 (4H, m, H Ph); 7.34 (2H, d, ^3J = 8.8, H Ar); 7.40-7.43 (1H, m, H Ph); 7.60-7.64 (1H, m, H Py); 8.01-8.04 (1H, m, H Py); 8.46-8.50 (1H, m, H Py); 8.84-8.87 (1H, m, H Py). ^{13}C NMR spectrum, δ, ppm: 23.3 (CH_2); 24.7 (CH_2); 32.9 (CH_2); 55.1 (CH_3); 106.1; 113.8 (CH); 123.6 (CH); 125.2; 125.4 (CH); 127.4 (CH); 128.1 (CH); 130.0 (CH); 130.5 (CH); 130.6; 136.9 (CH); 149.8 (CH); 150.6; 151.8; 155.6; 159.9; 160.5; 160.7; 161.7. Found, *m*/*z*: 475.2261 [M+H]$^+$. $C_{29}H_{27}N_6O$. Calculated, *m*/*z*: 475.2241. Found, %: C 73.51; H 5.65; N 17.55. $C_{29}H_{26}N_6O$. Calculated, %: C 73.40; H 5.52; N 17.71.

2-[3-(4-Methoxyphenyl)-6-phenyl-1,2,4-triazin-5-yl]-3-phenyl-1,4-diazaspiro[4,5]decane-1,3-diene (9d). Yield 0.355 g (75%). Yellow powder, mp 181–185°C. R_f 0.15 (hexane–EtOAc, 4:1). IR spectrum, ν, cm^{-1}: 695, 731, 845, 984, 1028, 1172, 1253, 1277, 1395, 1461, 1489, 1605 (C=N), 2851, 2914, 2925, 2937, 3001, 3056. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.63-1.88 (10H, m, $(CH_2)_5$); 3.91 (3H, s, OCH_3); 7.06 (2H, d, $^3J = 8.8$, H Ar); 7.28-7.43 (10H, m, H Ph); 8.38 (2H, d, $^3J = 8.8$, H Ar). ^{13}C NMR spectrum, δ, ppm: 23.1 (CH_2); 24.6 (CH_2); 32.9 (CH_2); 55.1 (CH_3); 105.9; 114.3 (CH); 125.9; 127.5 (CH); 127.8 (CH); 128.1 (CH); 128.5 (CH); 128.7 (CH); 129.2 (CH); 129.4 (CH); 129.9; 133.4; 150.3; 154.9; 160.1 (2C); 161.9; 162.3. Found, *m*/*z*: 474.2292 $[M+H]^+$. $C_{30}H_{28}N_5O$. Calculated, *m*/*z*: 474.2288. Found, %: C 76.44; H 5.66; N 14.66. $C_{30}H_{27}N_5O$. Calculated, %: C 76.09; H 5.75; N 14.79.

2-(4-Oxido-3,6-diphenyl-1,2,4-triazin-5-yl)-3-phenyl-1,4-diazaspiro[4,5]decane-1,3-diene 1-Oxide (6). A solution of DDQ (0.273 g, 1.2 mmol) in THF (5 ml) was added to a previously prepared solution of **4-OLi** cooled to 0°C, and the mixture was stirred for 15 min. The reaction mixture was then filtered through an alumina layer and evaporated. The residue was purified by column chromatography. Yield 0.308 g (65%). Light-yellow powder, mp 172-175°C. R_f 0.15 (hexane–EtOAc, 4:1). IR spectrum, ν, cm^{-1}: 618, 672, 688, 994, 1021, 1261, 1338, 1416, 1483, 1563 (C=N), 2855, 2925, 3052. ^1H NMR spectrum, δ, ppm: 1.17-1.20 (1H, m), 1.37-1.41 (1H, m), 1.50-1.54 (1H, m), 1.78-1.88 (6H, m), and 1.97-2.01 (1H, m, $(CH_2)_5$); 7.33-7.39 (6H, m, H Ph); 7.43-7.48 (2H, m, H Ph); 7.55-7.63 (5H, m, H Ph); 8.24-8.28 (2H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 22.6 (CH_2); 22.7 (CH_2); 24.2 (CH_2); 33.9 (CH_2); 34.8 (CH_2); 103.9; 126.5 (CH); 127.6 (CH); 127.8; 128.2 (CH); 128.4; 128.6 (CH); 129.0 (CH); 129.8 (CH); 130.8 (CH); 131.3; 131.6 (CH); 131.8 (CH); 132.7; 134.1; 156.5; 157.8; 163.1. Found, *m*/*z*: 476.2143 $[M+H]^+$. $C_{29}H_{26}N_5O_2$. Calculated, *m*/*z*: 476.2081. Found, %: C 73.32; H 5.34; N 14.66. $C_{29}H_{25}N_5O_2$. Calculated, %: C 73.25; H 5.30; N 14.73.

X-ray Structural Analysis of Triazines 5 and 9c. Monocrystals of triazines **5** and **9c** were grown by slow evaporation of the corresponding solutions in ether. The unit cell parameters for the orthorhombic crystals of triazine **5** are as follows: *a* 17.2482(11), *b* 9.5284(7), *c* 15.0868(9) Å, β 90.00°, *V* 2479.5(3) $Å^3$, *F*(000) 968, μ 0.077, d_{calc} 1.231, *Z* 4, space group $Pna2_1$. The unit cell parameters for the monoclinic crystals of triazine **9c** are as follows: *a* 10.8579(7), *b* 10.5150(10), *c* 21.732(2) Å, β 102.199(7)°, *V* 2425.1(4) $Å^3$, *F*(000) 1000, μ 0.082, d_{calc} 1.300, *Z* 4, space group $P2_1/c$. The experimental sets of reflections were measured at 295(2) K on an Xcalibur 3 diffractometer using λMo radiation, graphite monochromator, ω-scanning, and scanning step 1°. The structures were solved by the direct method using the SHELXS97 program [26] and refined using the full-matrix anisotropic method of least squares (isotropic method for hydrogen atoms) and the SHELXL97 program [27]. The hydrogen atoms were located using the electron density peaks and included in the refinement using the" rider" model with dependent thermal parameters. The complete data of the X-ray structural studies were deposited at the Cambridge Crystallographic Data Center: deposit CCDC 865991 for triazine **5** and deposit CCDC 865992 for triazine **9c**.

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