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# Revisiting the Synthesis of Functionally Substituted 1,4-Dihydrobenzo[*e*][1,2,4]triazines

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**Abstract:** A series of novel 1,4-dihydrobenzo[1,2,4][*e*]triazines bearing an acetyl or ester moiety as a functional group at the C(3) atom of the 1,2,4-triazine ring were synthesized. The synthetic protocol is based on an oxidative cyclization of functionally substituted amidrazones in the presence of DBU and Pd/C. It was found that the developed approach is suitable for the preparation of 1,4-dihydrobenzo[*e*][1,2,4]triazines, but the corresponding Blatter radicals were isolated only in few cases. In addition, a previously unknown dihydrobenzo[*e*][1,2,4]triazolo[3,4-*c*][1,2,4]triazine tricyclic open-shell derivative was prepared. Studies of thermal behavior of the synthesized 1,4-dihydrobenzo[1,2,4][*e*]triazines revealed their high thermal stability (up to 240–250 °C), which enables their application potential as components of functional organic materials.

**Keywords:** 1,4-dihydrobenzo[*e*][1,2,4]triazine; Blatter radicals; oxidative cyclization; aerial oxidation; amidrazones; thermal stability

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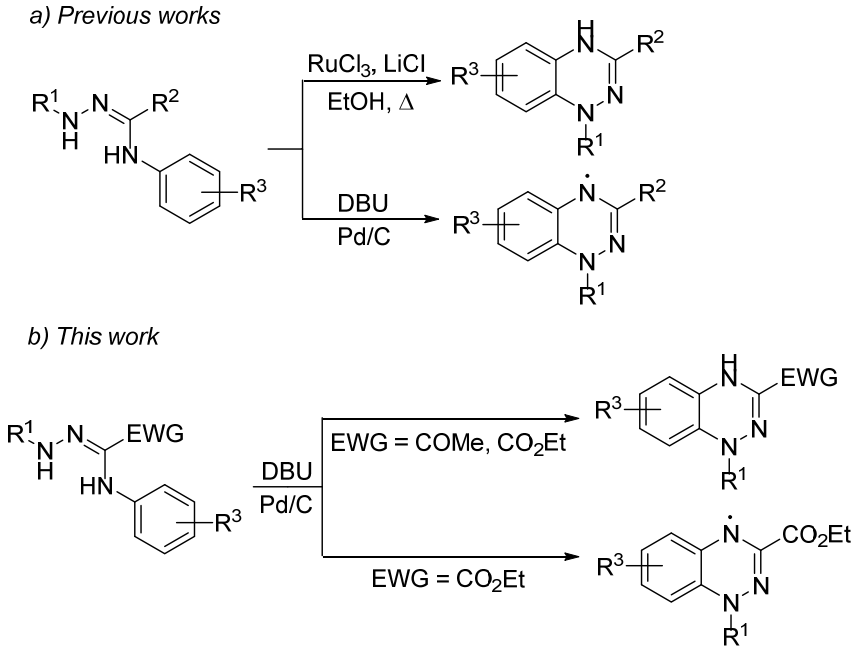
## 1. Introduction

A creation of novel functional organic materials remains one of the urgent goals in modern chemistry and materials science [1–4]. Such materials constitute a large variety of usually conjugated organic compounds with different chemical and physical properties. Recent achievements of numerous research groups worldwide confirmed that an incorporation of a nitrogen heteroaromatic motif usually enhances the quality of materials compared to their carbocyclic analogues [5–7].

Among nitrogen heterocyclic species, 1,4-dihydrobenzo[*e*][1,2,4]triazine motif is of special importance due to a wide range of applications inherent to compounds derived thereof. Such fused heterocyclic systems display various pharmacological activities, including antibacterial and antiproliferative activity [8–10]. Moreover, dihydrobenzo[*e*][1,2,4]triazines are direct precursors to the corresponding nitrogen-centered benzotriazinyl radicals, also known as Blatter radicals [11–13], which possess ferromagnetic and antiferromagnetic properties [14–17], and are valuable components of functional organic materials used in molecular grafting [18], preparation of liquid crystals [19,20], molecular electronics and spintronics [21,22], and for some other applications [23–25]. Therefore, synthetic strategies toward the construction of the 1,4-dihydrobenzo[*e*][1,2,4]triazine scaffold need to be constantly explored.

There are a number of commonly used synthetic methods for the assembly of the 1,4-dihydrobenzo[*e*][1,2,4]triazine framework from various acyclic precursors [8,12]. The most widely explored protocol is based on an oxidative cyclization of (arylamino)hydrazones, also known as amidrazones. An interesting feature of this approach is its regiodiversity: $RuCl_3$-mediated oxidation of amidrazones affords dihydrobenzo[*e*][1,2,4]triazines [26], while DBU-catalyzed aerial oxidation in the presence of Pd/C results in a direct formation of stable Blatter radicals (Scheme 1a) [12,27–29]. The latter protocol is generally used, and usually provides benzotriazinyl radicals in moderate to good yields, although only

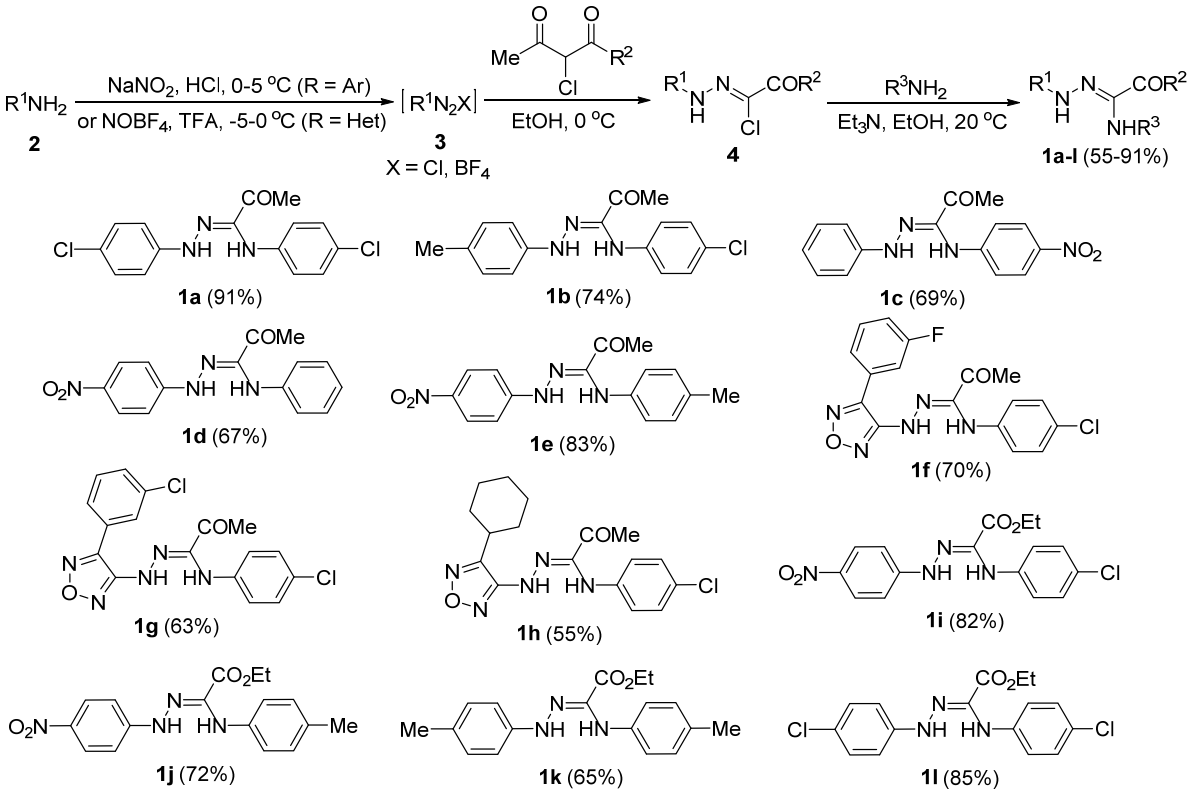
aromatic and heteroaromatic substituents are known to be installed onto the 1,2,4-triazine ring [11,12,27]. In this regard, a thorough investigation of scope and limitations of this approach for an assembly of the 1,4-dihydrobenzo[*e*][1,2,4]triazine core (either as Blatter radical or not) bearing additional functional groups remains relevant. It should be noted that electron-withdrawing groups at the fused benzo[1,2,4]triazine system may significantly affect both the reactivity and stability of Blatter radicals, and may be used for tuning functional properties of the resulted compounds. Herein, we disclose a divergent approach toward the construction of 1,4-dihydrobenzo[*e*][1,2,4]triazines bearing functional moieties at the triazine ring via DBU-catalyzed aerial oxidation of amidrazones in the presence of Pd/C (Scheme 1b).




**Scheme 1.** Methods for the construction of the 1,4-dihydrobenzo[*e*][1,2,4]triazine scaffold: (**a**) known methods and (**b**) method described in this manuscript.

## 2. Results and Discussion

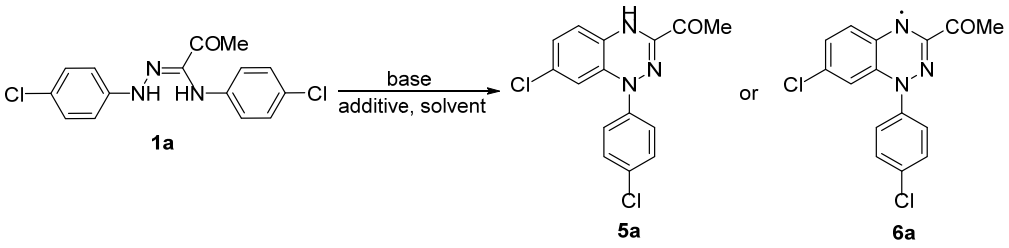
Our investigations towards the desired approach for the formation of 1,4-dihydrobenzo [*e*][1,2,4]triazines began from the preparation of a wide set of amidrazones **1**. The synthesis of compound **1** is based on a simple three-step reaction sequence starting from readily available amine **2**. It includes diazotization of amine **2**, followed by the introduction of formed (het)arene diazonium salts **3** into the Japp–Klingemann reaction with chloroacetylacetone or chloroacetoacetic ester. This one-pot procedure enables an easy preparation of functionalized chlorohydrazone **4** bearing an acetyl or an ester moiety. Subsequent treatment of compound **4** with anilines afforded a series of amidrazones **1** (Scheme 2).




**Scheme 2.** Synthesis of amidrazones **1a–l**.

To optimize the reaction conditions for the desired synthesis of 1,4-dihydrobenzo[*e*][1,2,4]triazines, amidrazone **1a** was selected as a model substrate. Various bases, additives, solvents, temperatures and reaction times were varied (Table 1). It was found that conditions used in the fundamental work by Koutentis et al. [27] for the synthesis of Blatter radicals (a combination of catalytic amounts of DBU and 5% Pd/C) were inappropriate in the case of amidrazone **1a** (Table 1, entry 1), and neither benzotriazine **5a** nor Blatter radical **6a** were formed. The same result was observed upon using a stoichiometric amount of DBU in the absence of Pd/C (entry 2). An increase of the amount of Pd/C up to 15 mol.% catalyzed the oxidative cyclization of amidrazone **1a**, but only benzotriazine **5a** was formed as a sole product (entry 3). An increase of the reaction temperature decreased the reaction time, but also slightly decreased the yield of **5a** (entry 4). More promising results were obtained upon utilization of two equiv. of DBU: target product **5a** was obtained in a yield of 69% (entry 5). Further replacements of base, additive or solvent were less effective and provided benzotriazine **5a** in poor yields (entries 6–11). Therefore, the optimal conditions for the synthesis of benzotriazine **5a** were using two equiv. of DBU, 15 mol.% of 5% Pd/C in $CH_2Cl_2$ at 25 °C for 8 h (entry 5). Interestingly, in all optimization experiments, the formation of Blatter radical **6a** was not observed, despite in all cases chromatography being used to isolate reaction products. Arguably, aerial oxidation of benzotriazine **5a** does not proceed under these conditions, or acetyl-substituted Blatter radical **6a** is substantially destabilized by the electron-withdrawing effect of the acetyl moiety. Our attempts to oxidize compound **5a** to the Blatter radical **6a** using $MnO_2$ or $NaIO_4$ or upon prolonged refluxing in *o*-xylene were unsuccessful and returned the starting material without decomposition, confirming the resistance of the thus obtained 1,4-dihydrobenzo[*e*][1,2,4]triazine **5a** towards oxidation.

**Table 1.** Optimization of oxidative cyclization of amidrazone **1a** [a].




| Entry | Base (Equiv.) | Additive (mol.%) | Solvent | T, °C | Time, h | Product (Yield, %) [b] |
|---|---|---|---|---|---|---|
| 1 | DBU (0.1) | 5% Pd/C (1.6) | $CH_2Cl_2$ | 25 | 72 | - [c] |
| 2 | DBU (1) | - | $CH_2Cl_2$ | 25 | 72 | - [c] |
| 3 | DBU (1) | 5% Pd/C (15) | $CH_2Cl_2$ | 25 | 10 | **5a** (43) |
| 4 | DBU (1) | 5% Pd/C (15) | $CH_2Cl_2$ | 40 | 7 | **5a** (36) |
| 5 | DBU (2) | 5% Pd/C (15) | $CH_2Cl_2$ | 25 | 8 | **5a** (69) |
| 6 | $Et_3N$ (2) | 5% Pd/C (15) | $CH_2Cl_2$ | 25 | 48 | **5a** (29) |
| 7 | DBU (2) | $C_{act}$ (200) | $CH_2Cl_2$ | 40 | 24 | **5a** (35) |
| 8 | DBU (2) | $TiO_2$ (50) | $CH_2Cl_2$ | 40 | 24 | **5a** (8) |
| 9 | $Cs_2CO_3$ (1) | - | $CH_2Cl_2$ | 25 | 48 | **5a** (10) |
| 10 | - | $MnO_2$ (100) | $CH_2Cl_2$ | 25 | 72 | - [c] |
| 11 | DBU (2) | 5% Pd/C (15) | MeCN | 50 | 8 | **5a** (23) |

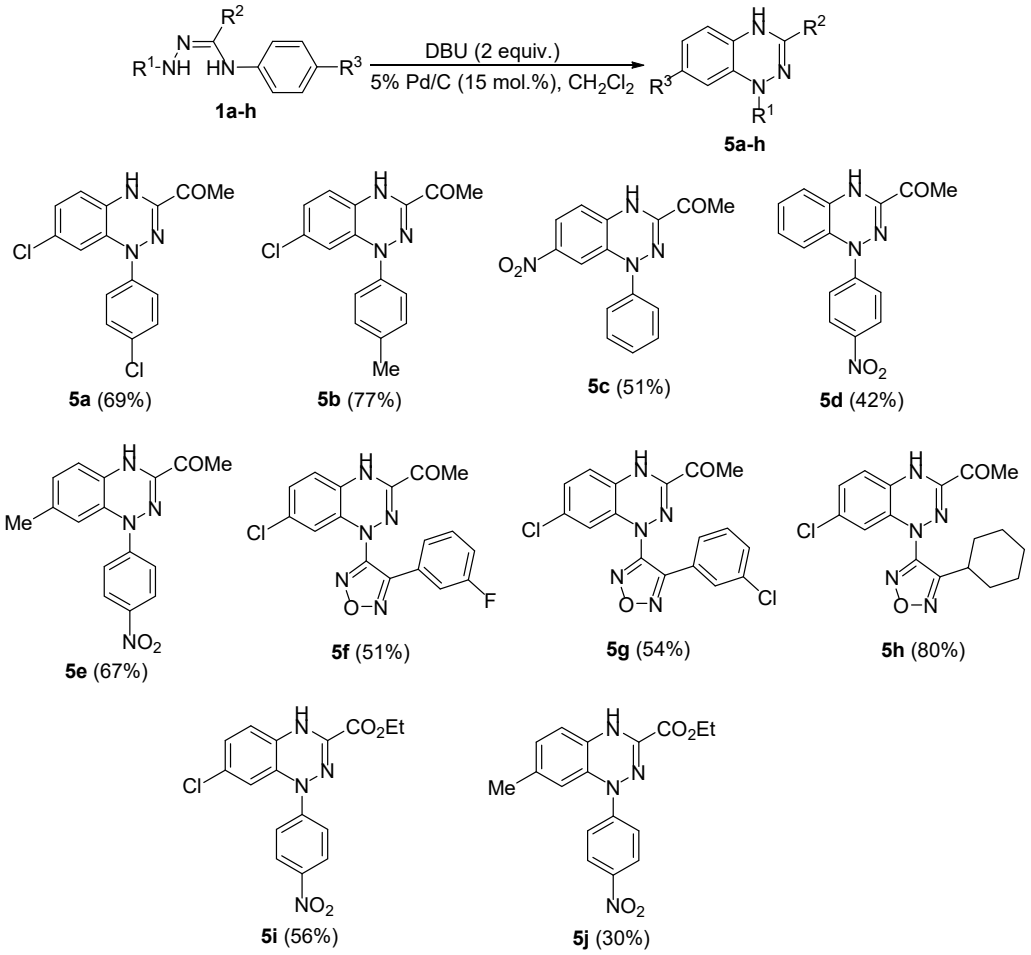
[a] Reaction conditions: amidrazone **1a** (2 mmol), base, additive, solvent (4 mL), stirring at indicated temperature for indicated time. [b] Isolated yield of analytically pure product **5a** is given. [c] No reaction.

To further evaluate the scope of the observed transformation, other acetyl-substituted amidrazones **1b–h** were subjected to the optimized reaction conditions. Aside from dichloro derivative **5a**, benzotriazine **5b** bearing electron-donor *p*-tolyl substituent was formed in a good yield. Importantly, amidrazones **1c–e** incorporating electron-withdrawing *p*-nitrophenyl moiety either at the hydrazone or amine motifs also smoothly underwent cyclization to form corresponding heterocyclic products **5c–e** (Scheme 3). Similar results were obtained in the case of 1,2,5-oxadiazolyl substituted substrates **1f–h**, which confirmed the lack of influence of electronic effects of aromatic or heteroaromatic subunits on the cyclization outcome. In addition, 1,4-dihydrobenzo[*e*][1,2,4]triazines **5i,j**, bearing an ester functionality at the C(3) carbon atom of the heterocyclic moiety and electron-withdrawing *p*-nitrophenyl fragments at the N(1) nitrogen atom, were obtained in fair yields under the same conditions. All compounds were fully characterized by IR, $^1$H and $^{13}$C NMR spectroscopy (see Supplementary Materials), as well as high-resolution mass spectrometry and elemental analysis.

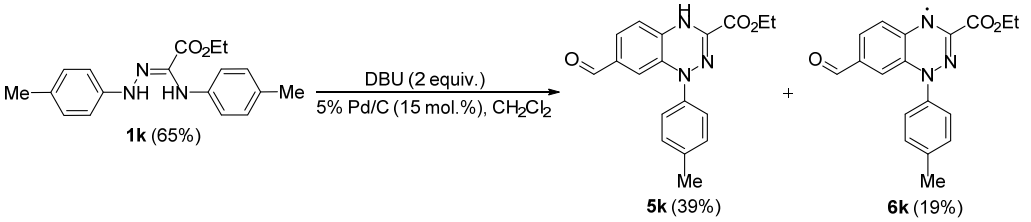
More intriguing results were obtained upon oxidative cyclization of amidrazones **1k** and **1l**. Introduction of substrate **1k** into the studied transformation provided two compounds **5k** and **6k** in a ratio 2:1, both of which possessed a formyl functionality as a result of oxidation of one of the methyl groups in the *p*-tolyl motif (Scheme 4). According to the $^1$H and $^{13}$C NMR spectroscopy data, the structure of the major product was assigned to as benzo[1,2,4]triazine **5k**. At the same time, the structure of compound **6k** was determined as a Blatter radical, which was confirmed by the presence of the multiplet signal in the EPR spectrum and HRMS data.

Oxidative cyclization of amidrazone **1l** also resulted in the formation of two compounds **6l** and **7** in moderate yields, although both of these derivatives were found to possess an unpaired electron (Scheme 5). Based on the EPR and HRMS data, the structure of **6l** was assigned as the corresponding Blatter radical. The formation of Blatter radicals from amidrazones **1k,l** is arguably attributed to the presence of electron-donating *p*-tolyl and *p*-chlorophenyl moieties at the N(1) atom of the benzo[1,2,4]triazine scaffold, while in the case of substrates **1i,j**, the electron-withdrawing effect of the *p*-nitrophenyl substituent suppresses the oxidation to Blatter radicals. The structure of compound **7** was unambiguously confirmed by X-ray diffraction study and was characterized as dihydrobenzo[*e*][1,2,4]triazolo [3,4-*c*][1,2,4]triazine derivative (Figure 1). According to the

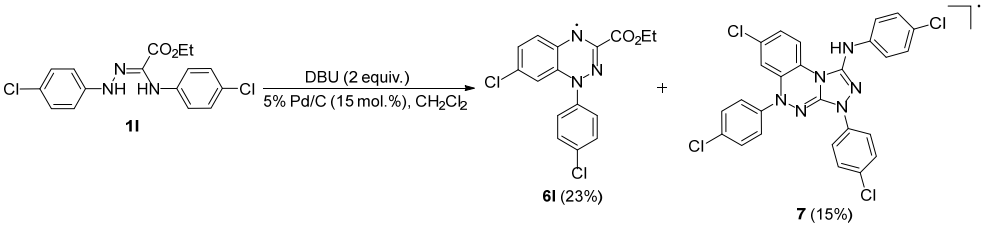
EPR spectrum, compound **7** also represents an organic radical, although the corresponding signal is broadened due to the delocalization of the unpaired electron in the tricyclic system.




**Scheme 3.** Synthesis of benzotriazines **5a–j** using the conditions indicated in the entry 5 of Table 1.




**Scheme 4.** Oxidative cyclization of amidrazone **1k** using the conditions indicated in entry 5 of Table 1.




**Scheme 5.** Oxidative cyclization of amidrazone **1l** using the conditions indicated in entry 5 of Table 1.

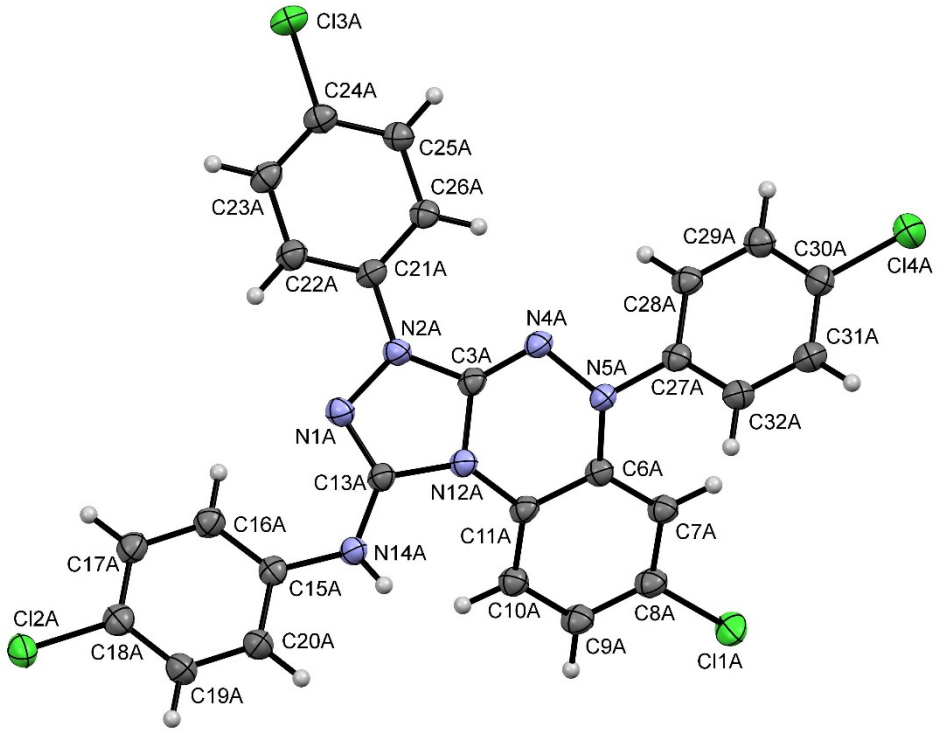
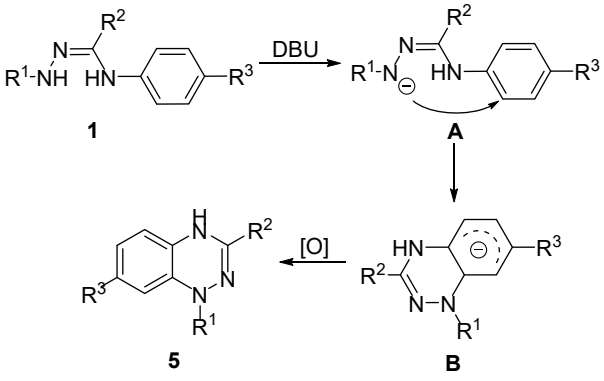


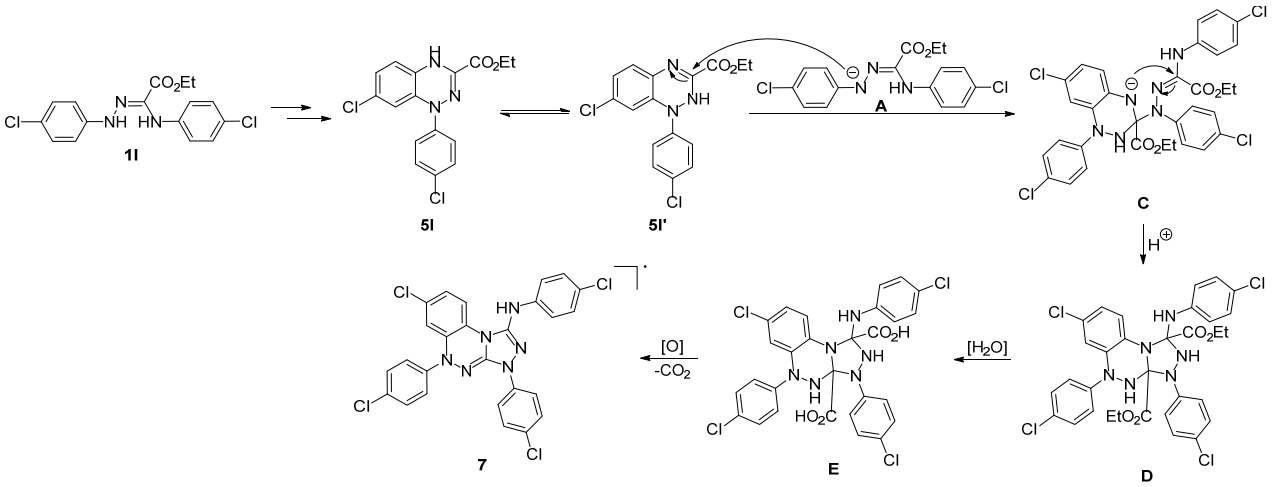

**Figure 1.** The crystal structure of compound **7**. All atoms are shown as probability ellipsoids of atomic displacements ($p$ = 50%).

A plausible mechanism for the formation of benzo[1,2,4]triazines **5** is depicted in Scheme 6. At the first step, DBU acts as a strong base to deprotonate the N-NH-fragment and the generated anion **A** undergoes intramolecular nucleophilic attack onto the benzene ring with the formation of anionic σ-complex **B**. Further oxidation of intermediate **A** furnishes the formation of benzo[1,2,4]triazine **5**.



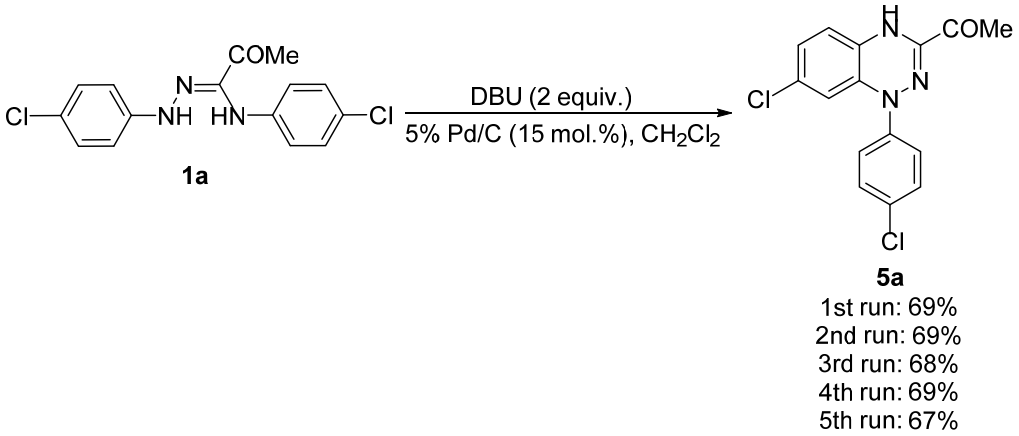

**Scheme 6.** A plausible mechanism for the formation of benzo [1,2,4]triazines **5**.

For the formation of the previously unknown compound **7**, the following mechanism was proposed (Scheme 7). Introduction of amidrazone **1l** into oxidative cyclization under standard reaction conditions affords benzo[1,2,4]triazine **5l**, which tautomerizes to the N(2)H form **5l′** with subsequent nucleophilic addition of the amidrazone anion **A**. Intermediate **C** undergoes cyclization to the perhydro[1,2,4]triazolo[3,4-*c*][1,2,4]triazine derivative **D**. Hydrolysis of both ester moieties in D under traces of moisture affords intermediate **E**, which undergoes oxidative decarboxylation to the final dihydrobenzo[*e*][1,2,4]triazolo[3,4-*c*][1,2,4]triazine derivative **7**.




**Scheme 7.** A plausible mechanism for the formation of compound **7**.

To further elucidate the synthetic utility of the developed protocol, we conducted a set of experiments on recycling of the Pd/C catalyst on the example of oxidative cyclization of amidrazone **1a**. After the reaction was completed, the catalyst was filtered off, washed with organic solvents, and dried at 100 °C for 24 h until the constant mass in each case. It was found that the catalyst could be reused at least 5 times without loss of activity, which was confirmed by nearly equal yields of benzo[1,2,4]triazine **5a** (Scheme 8).




**Scheme 8.** Recyclability of the Pd/C catalyst.

Since benzo[1,2,4]triazine derivatives are of special importance in the preparation of functional organic materials, we also studied the thermal behavior of the synthesized compounds using differential scanning calorimetry (DSC). Thermal stability is a crucial parameter which strictly defines the applicability of materials in a construction of functional devices or molecular grafting. To our delight, all synthesized benzo[1,2,4]triazines, except formyl-derived Blatter radical **6k** and tricycle **7**, were thermally stable up to 240–250 °C (for DSC curves, see SI). It should also be pointed out that no phase transitions or mass loss were observed during DSC studies, which strongly support the application potential of the synthesized compounds in material science.

## 3. Conclusions

In summary, a divergent approach toward the construction of 1,4-dihydrobenzo[*e*][1,2,4]triazines bearing functional moieties at the triazine ring via DBU-catalyzed aerial oxidation of amidrazones in the presence of Pd/C was realized. It was found that the synthesized 1,4-dihydrobenzo[*e*][1,2,4]triazines are substantially resistible towards various oxidants,

which is attributed to the strong electron-withdrawing effect of the functional groups incorporated in the heterocyclic system. In addition, the dihydrobenzo[*e*][1,2,4]triazolo[3,4-*c*][1,2,4]triazine open-shell compound was also prepared for the first time as a minor product. Recyclability of the Pd/C catalyst was also demonstrated by conducting the oxidative cyclization for at least five times on the same substrate. The majority of the synthesized fused heterocyclic systems exhibited high thermal stability, which further enables their application potential in material science and related fields.

## 4. Materials and Methods

**General**. All reactions were carried out in well-cleaned oven-dried glassware with magnetic stirring. $^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker AM-300 (300.13 and 75.47 MHz, respectively) spectrometer and referenced to a residual solvent peak. The chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. The IR spectra were recorded on a Bruker "Alpha" spectrometer in the range 400–4000 cm$^{-1}$ (resolution 2 cm$^{-1}$). Elemental analyses were performed by the CHN Analyzer Perkin-Elmer 2400. High resolution mass spectra were recorded on a Bruker microTOF spectrometer with electrospray ionization (ESI). All measurements were performed in a positive (+MS) ion mode (interface capillary voltage: 4500 V) with scan range *m*/*z*: 50–3000. External calibration of the mass spectrometer was performed with Electrospray Calibrant Solution (Fluka). A direct syringe injection was used for all analyzed solutions in MeCN (flow rate: 3 μL min$^{-1}$). Nitrogen was used as nebulizer gas (0.4 bar) and dry gas (4.0 L min$^{-1}$); interface temperature was set at 180 °C. All spectra were processed by using Bruker DataAnalysis 4.0 software package. Thermal behaviour of the synthesized compounds was studied using differential scanning calorimeter Netzsch DSC 204 HP. Analytical thin-layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 $F_{254}$ aluminum sheets. The visualization of the TLC plates was accomplished with a UV light. All solvents were purified and dried using standard methods prior to use. All standard reagents were purchased from Aldrich or Acros Organics and used without further purification. Initial chlorohydrazones **4** were prepared according to previously published procedures [30]. Preparation of amidrazones **1** was accomplished similarly to the procedure reported in [31].

**Synthesis of amidrazones 1a-l (general procedure)**. $Et_3N$ (1 mL, 7 mmol) was added to a magnetically stirred mixture of the corresponding chlorohydrazone **4** (5 mmol) and substituted aniline (5 mmol) in absolute EtOH (10 mL) at 20 °C. The reaction mixture was refluxed until the consumption of substrate **4** (TLC monitoring, eluent—$CHCl_3$), and then cooled to 20 °C. If the crude product precipitated from the solution (in the case of compounds **1a,b,d,h,k**), it was filtered off, washed with water (2 × 5 mL) and 50% EtOH (1 × 4 mL), dried in air and recrystallized from 95% EtOH. If the precipitate did not form, the solvent was evaporated to dryness and the residue was triturated with water until the precipitation did not occur. The solid formed was filtered off, washed with water (2 × 5 mL) and 50% EtOH (1 × 4 mL), dried in air, and recrystallized from 95% EtOH.

*1-(4-Chlorophenylamino)-1-(4-chlorophenylhydrazono)-2-propanone* (**1a**). Yellow solid, yield 1.47 g (91%), mp 102–103 °C, $R_f$ 0.52 ($CHCl_3$). IR (KBr): 3354, 3281, 1660, 1581, 1489, 1361, 1091 cm$^{-1}$. $^{1}$H NMR (300 MHz, [$D_6$]DMSO): 2.50 (s, 3H), 6.58 (d, *J* 8.5 Hz, 2H), 7.20 (d, *J* 8.5 Hz, 2H), 7.33 (s, 4H), 8.02 (s, 1H), 9.91 (s, 1H). $^{13}$C NMR (75.5 MHz, [$D_6$]DMSO): 24.9, 115.5, 117.3, 122.7, 124.5, 128.3, 128.9, 135.9, 141.3, 142.8, 192.9. Anal. calcd. for $C_{15}H_{13}Cl_2N_3O$ (%): C, 55.92; H, 4.07; N, 13.04. Found (%): C, 56.06; H, 4.24; N, 12.81.

*1-(4-Chlorophenylamino)-1-(4-tolylhydrazono)-2-propanone* (**1b**). Yellowish solid, yield 1.06 g (74%), mp 133–134 °C, $R_f$ 0.48 ($CHCl_3$). IR (KBr): 3349, 3320, 1672, 1582, 1523, 1495, 1350, 1184 cm$^{-1}$. $^{1}$H NMR (300 MHz, $CDCl_3$): 2.34 (s, 3H), 2.62 (s, 3H), 6.57 (d, *J* 8.5 Hz, 2H), 7.04 (d, *J* 8.2 Hz, 2H), 7.14 (d, *J* 8.2 Hz, 2H), 7.22 (d, *J* 8.5 Hz, 2H), NH protons are significantly broadened. $^{13}$C NMR (75.5 MHz, $CDCl_3$): 20.7, 23.9, 113.9, 118.7, 126.9, 129.2,

129.9, 131.9, 134.9, 138.0, 140.5, 193.8. Anal. calcd. for $C_{16}H_{16}ClN_3O$ (%): C, 63.68; H, 5.34; N, 13.92. Found (%): C, 63.52; H, 5.52; N, 13.69.

*1-(4-Nitrophenylamino)-1-phenylhydrazono-2-propanone* (**1c**). Yellow solid, yield 1.02 g (69%), mp 167–168 °C, $R_f$ 0.54 ($CHCl_3$). IR (KBr): 3357, 3277, 1674, 1601, 1555, 1508, 1463, 1339, 1111, $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): 2.64 (s, 3H), 6.64 (d, *J* 8.8 Hz, 2H), 7.07 (t, *J* 7.3 Hz, 1H), 7.17–7.21 (m, 2H), 7.36 (t, *J* 7.3 Hz, 2H), 8.14 (d, *J* 8.8 Hz, 2H), NH protons are significantly broadened. $^{13}C$ NMR (75.5 MHz, $CDCl_3$): 24.1, 114.3, 115.9, 123.2, 125.7, 129.6, 133.6, 141.7, 142.3, 146.0, 193.6. Anal. calcd. for $C_{15}H_{14}N_4O_3$ (%): C, 60.40; H, 4.73; N, 18.78. Found (%): C, 60.23; H, 4.90; N, 18.52.

*1-(4-Nitrophenylhydrazono)-1-phenylamino-2-propanone* (**1d**). Yellowish solid, yield 1.00 g (67%), mp 162–163 °C, $R_f$ 0.47 ($CHCl_3$). IR (KBr): 3352, 3274, 1677, 1594, 1496, 1328, 1164, 1108 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): 2.66 (s, 3H), 6.74 (d, *J* 8.8 Hz, 2H), 7.06–7.11 (m, 4H), 7.29–7.35 (m, 2H), 7.51 (s, 1H), 8.18 (d, *J* 8.8 Hz, 2H), another NH proton is significantly broadened. $^{13}C$ NMR (75.5 MHz, $CDCl_3$): 24.0, 112.9, 118.9, 123.3, 126.0, 129.5, 137.2, 138.0, 141.7, 148.0, 194.2. Anal. calcd. for $C_{15}H_{14}N_4O_3$ (%): C, 60.40; H, 4.73; N, 18.78. Found (%): C, 60.62; H, 4.66; N, 18.55.

*1-(4-Nitrophenylhydrazono)-1-(4-tolylamino)-2-propanone* (**1e**). Yellowish solid, yield 1.29 g (83%), mp 154–155 °C, $R_f$ 0.56 ($CHCl_3$). IR (KBr): 3384, 3258, 1672, 1592, 1513, 1479, 1327, 1158, 1108 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): 2.34 (s, 3H), 2.65 (s, 3H), 6.68 (d, *J* 8.7 Hz, 2H), 7.04 (d, *J* 7.7 Hz, 2H), 7.13 (d, *J* 7.7 Hz, 2H), 7.49 (br.s, 1H), 8.17 (d, *J* 8.7 Hz, 2H). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): 20.8, 24.0, 112.7, 119.5, 126.0, 130.0, 133.3, 135.3, 137.4, 141.5, 148.1, 194.2. Anal. calcd. for $C_{16}H_{16}N_4O_3$ (%): C, 61.53; H, 5.16; N, 17.94. Found (%): C, 61.75; H, 5.01; N, 17.71.

*1-(4-Chlorophenylamino)-1-[4-(3-fluorophenyl)-1,2,5-oxadiazolyl-3-yl]hydrazono-2-propanone* (**1f**). Creme solid, yield 1.31 g (70%), mp 174–175 °C, $R_f$ 0.17 ($CHCl_3$). IR (KBr): 3322, 1691, 1594, 1550, 1483, 1089 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 2.28 (s, 3H), 6.75 (d, *J* 5.8 Hz, 2H), 7.28–7.41 (m, 6H), 8.57 (s, 1H), 9.56 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 24.6, 115.2 (d, *J* 23.8 Hz), 117.2 (d, *J* 20.9 Hz), 119.8, 124.4 (d, *J* 2.6 Hz), 124.7, 127.4 (d, *J* 9.0 Hz), 128.1, 130.7 (d, *J* 8.4 Hz), 138.6, 140.4, 146.5 (d, *J* 3.1 Hz), 153.9, 161.9 (d, *J* 245.2 Hz), 193.7. Anal. calcd. for $C_{17}H_{13}ClFN_5O_2$ (%): C, 54.63; H, 3.51; N, 18.74. Found (%): C, 54.39; H, 3.39; N, 18.63.

*1-[4-(3-Chlorophenyl)-1,2,5-oxadiazolyl-3-yl]hydrazono-1-(4-chlorophenylamino)-2-propanone* (**1g**). Creme solid, yield 1.23 g (63%), mp 162–163 °C, $R_f$ 0.15 ($CHCl_3$). IR (KBr): 3316, 1687, 1594, 1549, 1506, 1270, 1077 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 2.25 (s, 3H), 6.74 (d, *J* 8.0 Hz, 2H), 7.29 (d, *J* 8.0 Hz, 2H), 7.44–7.50 (m, 2H), 7.60–7.65 (m, 2H), 8.54 (s, 1H), 9.68 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 24.6, 119.6, 124.6, 126.9, 127.5, 128.0, 128.2, 130.1, 130.4, 133.4, 138.7, 140.4, 146.5, 154.0, 193.7. Anal. calcd. for $C_{17}H_{13}Cl_2N_5O_2$ (%): C, 52.33; H, 3.36; N, 17.95. Found (%): C, 52.49; H, 3.23; N, 17.73.

*1-(4-Chlorophenylamino)-1-[(4-cyclohexyl-1,2,5-oxadiazol-3-yl)hydrazono]-2-propanone* (**1h**). Slightly orange solid, yield 0.99 g (55%), mp 97–98 °C, $R_f$ 0.38 ($CHCl_3$). IR (KBr): 3325, 2933, 2856, 1691, 1586, 1495, 1402, 1357, 1088 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 1.27–1.43 (m, 5H), 1.62–1.90 (m, 5H), 2.49 (s, 3H), 3.03 (t, *J* 7.5 Hz, 1H), 6.70 (d, *J* 6.8 Hz, 2H), 7.24 (d, *J* 6.8 Hz, 2H), 8.45 (s, 1H), 9.74 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 25.1, 25.3, 25.4, 30.7, 33.0, 119.4, 124.2, 128.0, 139.2, 139.8, 152.1, 153.8, 193.4. Anal. calcd. for $C_{17}H_{20}ClN_5O_2$ (%): C, 56.43; H, 5.57; N, 19.36. Found (%): C, 56.67; H, 5.45; N, 19.02.

*Ethyl 2-(4-chlorophenylamino)-2-(4-nitrohydrazono)acetate* (**1i**). Orange solid, yield 1.50 g (82%), mp 198–199 °C, $R_f$ 0.25 ($CHCl_3$). IR (KBr): 3403, 3278, 1708, 1591, 1532, 1489, 1322, 1110, 1009 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): 1.50 (t, *J* 7.1 Hz, 3H), 4.51 (q, *J* 7.1 Hz, 2H), 7.03 (d, *J* 8.8 Hz, 2H), 7.33 (d, *J* 8.7 Hz, 2H), 7.49 (d, *J* 8.7 Hz, 2H), 8.18 (d, *J* 8.8 Hz, 2H), 11.19 (s, 1H), another NH proton is significantly broadened. $^{13}C$ NMR (75.5 MHz, $CDCl_3$): 14.2, 63.4, 111.5, 113.2, 119.6, 126.0, 126.4, 129.1, 129.6, 137.9, 149.4, 159.4. Anal. calcd. for $C_{16}H_{15}ClN_4O_4$ (%): C, 52.97; H, 4.17; N, 15.44. Found (%): C, 53.20; H, 4.01; N, 15.22.

*Ethyl 2-(4-nitrophehylhydrazono)-2-(4-tolylamino)acetate* (**1j**). Orange solid, yield 1.23 g (72%), mp 162–163 °C, $R_f$ 0.27 ($CHCl_3$). IR (KBr): 3410, 3282, 1709, 1605, 1532, 1491, 1321,

1113 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): 1.45 (t, *J* 6.7 Hz, 3H), 2.37 (s, 3H), 4.45 (q, *J* 6.7 Hz, 2H), 6.71 (d, *J* 7.7 Hz, 1H), 7.13 (d, *J* 7.7 Hz, 1H), 7.20 (d, *J* 8.0 Hz, 1H), 7.42 (d, *J* 8.0 Hz, 1H), 7.65 (br s, 1H), 11.04 (br s, 1H). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): 14.2, 20.9, 63.3, 111.4, 112.9, 118.9, 119.0, 125.9, 126.3, 129.7, 130.1, 131.8, 132.5, 133.4, 135.4, 136.5, 140.0, 141.5, 148.4, 149.7, 159.42, 162.7. Anal. calcd. for $C_{17}H_{18}N_4O_4$ (%): C, 59.64; H, 5.30; N, 16.37. Found (%): C, 59.38; H, 5.54; N, 16.13.

*Ethyl 2-(4-tolylamino)-2-(4-tolylhydrazono)acetate* (**1k**). Brown solid, yield 1.01 g (65%), mp 69–70 °C, $R_f$ 0.49 ($CHCl_3$). IR (KBr): 3359, 3291, 1702, 1567, 1512, 1472, 1370, 1105, 1021 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 1.19 (t, *J* 7.0 Hz, 3H), 2.21 (s, 3H), 2.23 (s, 3H), 4.15 (q, *J* 7.0 Hz, 2H), 6.54 (d, *J* 8.1 Hz, 2H), 7.01 (d, *J* 8.1 Hz, 2H), 7.04–7.12 (m, 4H), 7.72 (s, 1H), 9.39 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 14.1, 14.4, 20.6, 62.1, 111.4, 119.0, 126.3, 129.7, 132.5, 135.4, 140.0, 148.4, 159.4, 162.7. Anal. calcd. for $C_{18}H_{21}N_3O_2$ (%): C, 69.43; H, 6.80; N, 13.49. Found (%): C, 69.26; H, 7.02; N, 13.22.

*Ethyl 2-(4-chlorophenylamino)-2-(4-chlorophenylhydrazono)acetate* (**1l**). Pale yellow solid, yield 1.49 g (85%), mp 94–95 °C, $R_f$ 0.52 ($CHCl_3$). IR (KBr): 3351, 3299, 1704, 1595, 1567, 1490, 1278, 1091 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): 1.42 (t, 3H, *J* 7.0 Hz, $CH_3$), 4.39 (q, 2H, *J* 7.0 Hz, $CH_2$), 6.63 (d, *J* 8.4 Hz, 2H), 6.99–7.06 (m, 2H), 7.23–7.42 (m, 5H), 10.23 (br s, 1H, exchangeable proton). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): 14.3, 62.2, 112.9, 114.0, 118.1, 119.0, 126.8, 129.0, 129.3, 129.8, 138.5, 163.3. Anal. calcd. for $C_{16}H_{15}Cl_2N_3O_2$ (%): C, 54.56; H, 4.29; N, 11.93. Found (%): C, 54.35; H, 4.47; N, 11.65.

**Synthesis of benzo[1,2,4[triazine derivatives 5–7 (general procedure)**. DBU (0.3 mL, 2 mmol) and 5% Pd/C (15 mol.%, 640 mg, 0.3 mmol) were added to a magnetically stirred mixture of amidrazone **1** (2 mmol) in $CH_2Cl_2$ (4 mL) at 25 °C. The reaction mixture was stirred at 25 °C until the consumption of starting amidrazone **1** (TLC monitoring, eluent—$CHCl_3$), then Pd/C was filtered off and thoroughly washed with $CH_2Cl_2$ until the filtrate became completely colorless. The solvent was evaporated, and the residue was purified by preparative TLC (eluent—$CHCl_3$).

*3-Acetyl-7-chloro-1-(4-chlorophenyl)-1,4-dihydrobenzo[e][1,2,4]triazine* (**5a**). Red solid, yield 0.442 g (69%), mp 198 °C, $T_d$ 254 °C, $R_f$ 0.67 ($CHCl_3$). IR (KBr): 3336, 1678, 1631, 1485, 1363, 1061 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): 2.41 (s, 3H), 6.27–6.31 (m, 2H), 6.40 (br s, 1H), 6.71 (dd, *J* 6.3, 1.9 Hz, 1H), 7.37–7.44 (m, 4H). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): 23.7, 112.7, 114.3, 124.0, 124.3, 129.1, 129.6, 130.9, 131.3, 133.7, 141.0, 143.8, 191.1. HRMS (ESI) $[M + H]^+$ *m*/*z* calcd. for $C_{15}H_{11}{}^{35}Cl_2N_3O^{\cdot}$: 319.0266, found: 319.0274; calcd. for $C_{15}H_{11}{}^{35}Cl^{37}ClN_3O^{\cdot}$: 321.0243, found: 321.0245.

*3-Acetyl-7-chloro-1-(4-p-tolyl)-1,4-dihydrobenzo[e][1,2,4]triazine* (**5b**). Purple solid, yield 0.461 g (77%), mp 170 °C, $T_d$ 255 °C, $R_f$ 0.50 ($CHCl_3$). IR (KBr): 3342, 1675, 1493, 1362, 1291, 1067 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 2.29 (s, 3H), 2.34 (s, 3H), 5.94 (s, 1H), 6.63–6.71 (m, 2H), 7.29 (br s, 4H), 8.53 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 20.5, 23.8, 110.8, 114.6, 123.1, 123.3, 126.7, 129.9, 132.4, 134.8, 135.1, 139.9, 144.6, 190.6. Anal. calcd. for $C_{16}H_{14}ClN_3O$ (%): C, 64.11; H, 4.71; N, 14.02. Found (%): C, 63.89; H, 4.88; N 13.78.

*3-Acetyl-7-nitro-1-phenyl-1,4-dihydrobenzo[e][1,2,4]triazine* (**5c**). Pale brown solid, yield 0.300 g (51%), $T_d$ 272 °C (decomposed without melting), $R_f$ 0.27 ($CHCl_3$). IR (KBr): 3334, 1679, 1573, 1506, 1371, 1315, 1087 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 2.29 (s, 3H), 6.68–6.71 (m, 3H), 7.34 (t, *J* 6.7 Hz, 1H), 7.45–7.60 (m, 4H), 9.24 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 23.7, 104.6, 112.3, 112.5, 122.0, 123.3, 126.3, 129.7, 133.7, 141.6, 141.7, 142.9, 143.3, 190.1. HRMS (ESI) Calcd. for: $C_{15}H_{12}N_4O_3^{\cdot}$ $[M^{\cdot}+ H]^+$: 296.0904, found: 296.0897.

*3-Acetyl-1-(4-nitrophenyl)-1,4-dihydrobenzo[e][1,2,4]triazine* (**5d**). Brown solid, yield 0.249 g (42%), mp 219 °C, $T_d$ 256 °C, $R_f$ 0.47 ($CHCl_3$). IR (KBr): 3349, 1682, 1585 1490, 1448, 1371, 1339, 1283, 1059 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 2.46 (s, 3H), 6.86–6.98 (m, 4H), 7.63 (d, *J* 9.1 Hz, 2H), 8.22 (d, *J* 9.1 Hz, 2H), 9.16 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 24.3, 114.7, 115.5, 116.4, 123.6, 125.4, 126.1, 127.4, 134.8, 140.3, 147.4, 147.7, 191.3. Anal. calcd. for $C_{15}H_{12}N_4O_3$ (%): C, 60.81; H, 4.08; N, 18.91. Found (%): C, 61.03; H, 3.94; N, 18.68.

*3-Acetyl-1-(4-nitrophenyl)-7-methyl-1,4-dihydrobenzo[e][1,2,4]triazine* (**5e**). Dark-brown solid, yield 0.415 g (67%), mp 252 °C, $T_d$ 252 °C, $R_f$ 0.44 ($CHCl_3$). IR (KBr): 3342, 1682, 1586, 1505, 1331, 1284, 1066 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 2.14 (s, 3H), 2.46 (s, 3H), 6.76–6.87 (m, 3H), 7.63 (d, *J* 9.2 Hz, 2H), 8.22 (d, *J* 9.2 Hz, 2H), 9.10 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 20.4, 24.3, 115.2, 115.3, 116.4, 125.4, 126.3, 127.3, 132.0, 132.9, 140.2, 147.4, 147.7, 191.4. Anal. calcd. for $C_{16}H_{14}N_4O_3$ (%): C, 61.93; H, 4.55; N, 18.06. Found (%): C, 61.65; H, 4.74; N, 17.82.

*3-Acetyl-1-[4-(3-fluorophenyl)-1,2,5-oxadiazol-3-yl]-7-chloro-1,4-dihydrobenzo[e][1,2,4]triazine* (**5f**). Orange solid, yield 0.379 g (51%), mp 159 °C, $T_d$ 254 °C, $R_f$ 0.42 ($CHCl_3$). IR (KBr): 3306, 1708, 1597, 1530, 1505, 1476, 1410, 1266 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 1.55 (s, 3H), 6.71 (d, *J* 8.3 Hz, 1H), 6.88 (dd, *J* 6.2, 2.1 Hz, 1H), 7.28 (br s, 1H), 7.36–7.42 (m, 1H), 7.57–7.65 (m, 3H), 9.05 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 22.7, 114.8, 115.2, 115.8 (d, *J* 23.6 Hz), 116.7 (d, *J* 20.9 Hz), 125.0, 125.1 (d, *J* 3.0 Hz), 126.8, 128.4, 128.6, 128.7, 130.4 (d, *J* 8.5 Hz), 131.3, 145.2, 148.7 (d, *J* 2.7 Hz), 152.9, 161.7 (d, *J* 244.5 Hz), 190.4. Anal. calcd. for $C_{17}H_{11}ClFN_5O_2$ (%): C, 54.92; H, 2.98; N, 18.84. Found (%): C, 54.70; H, 3.12; N, 18.57.

*3-Acetyl-1-[4-(3-chlorophenyl)-1,2,5-oxadiazol-3-yl]-7-chloro-1,4-dihydrobenzo[e][1,2,4]triazine* (**5g**). Red solid, yield 0.419 g (54%), mp 179 °C, $T_d$ 256 °C, $R_f$ 0.50 ($CHCl_3$). IR (KBr): 3363, 1697, 1651, 1495, 1411, 1362, 1080 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 1.54 (s, 3H), 6.71 (d, *J* 8.3 Hz, 1H), 6.87 (dd, *J* 6.3, 2.0 Hz, 1H), 7.32 (s, 1H), 7.54–7.63 (m, 2H), 7.70–7.73 (m, 1H), 7.86 (s, 1H), 9.06 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 22.7, 114.9, 115.3, 125.0, 126.8, 127.6, 128.6, 128.7 (2 C), 129.7, 130.2, 131.4, 133.0, 145.3, 148.6, 152.8, 190.4. Anal. calcd. for $C_{17}H_{11}Cl_2N_5O_2$ (%): C, 52.60; H, 2.86; N, 18.04. Found (%): C, 52.34; H, 3.02; N, 17.78.

*3-Acetyl-1-[4-cyclohexyl-1,2,5-oxadiazol-3-yl]-7-chloro-1,4-dihydrobenzo[e][1,2,4]triazine* (**5h**). Carmine solid, yield 0.575 g (80%), mp 218 °C, $R_f$ 0.47 ($CHCl_3$). IR (KBr): 3315, 2928, 2863, 1699, 1594, 1499, 1306, 1073 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 1.32–1.81 (m, 8H), 2.10 (d, *J* 12.1 Hz, 2H), 2.32 (s, 3H), 3.13–3.23 (m, 1H), 6.70–6.74 (m, 1H), 6.85 (dd, *J* 6.2, 2.1 Hz, 1H), 7.21 (d, *J* 1.9 Hz, 1H), 9.06 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 24.2, 25.3, 25.5, 31.2, 34.1, 114.6, 115.2, 124.9, 126.8, 129.2, 131.6, 145.9, 152.8, 154.4, 190.4. Anal. calcd. for $C_{17}H_{18}ClN_5O_2$ (%): C, 56.75; H, 5.04; N, 19.46. Found (%): C, 56.97; H, 4.83; N, 19.19.

*Ethyl 7-chloro-1-(4-nitrophenyl)-1,4-dihydrobenzo[e][1,2,4]triazine-3-carboxylate* (**5i**). Brown solid, yield 0.404 g (56%) mp 242 °C, $T_d$ 242 °C, $R_f$ 0.18 ($CHCl_3$). IR (KBr): 3363, 3353, 1702, 1589, 1502, 1376, 1343, 1289, 1056 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 1.32 (t, *J* 7.1 Hz, 3H), 4.35 (q, *J* 7.1 Hz, 2H), 6.85 (s, 1H), 6.91 (d, *J* 8.3 Hz, 1H), 6.99 (d, *J* 8.3 Hz, 1H), 7.58 (d, *J* 9.1 Hz, 2H), 8.25 (d, *J* 9.1 Hz, 2H), 9.46 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 14.4, 62.9, 114.4, 116.7, 117.7, 125.8, 125.9, 128.0, 130.0, 134.2, 141.5, 143.5, 147.6, 159.6. Anal. calcd. for $C_{16}H_{13}ClN_4O_4$ (%): C, 53.27; H, 3.63; N, 15.53. Found (%): C, 52.98; H, 3.79; N, 15.29.

*Ethyl 7-methyl-1-(4-nitrophenyl)-1,4-dihydrobenzo[e][1,2,4]triazine-3-carboxylate* (**5j**). Dark red solid, yield 0.204 g (30%), mp 200 °C, $T_d$ 252 °C, $R_f$ 0.35 ($CHCl_3$). IR (KBr): 3368, 3353, 1715, 1589, 1517, 1375, 1328, 1111 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 1.31 (t, *J* 7.1 Hz, 3H), 2.14 (s, 3H), 4.33 (q, *J* 7.1 Hz, 2H), 6.76–6.86 (m, 3H), 7.52 (d, *J* 9.3 Hz, 2H), 8.19 (d, *J* 9.3 Hz, 2H), 9.33 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 14.4, 21.0, 62.8, 115.8, 115.9, 116.5, 125.9, 126.8, 127.8, 132.6, 133.9, 140.5, 143.9, 148.0, 159.9. Anal. calcd. for $C_{17}H_{16}N_4O_4$ (%): C, 60.00; H, 4.74; N, 16.46. Found (%): C, 59.82; H, 4.87; N, 16.23.

*Ethyl 7-formyl-1-(4-p-tolyl)-1,4-dihydrobenzo[e][1,2,4]triazine-3-carboxylate* (**5k**). Dark-red solid, yield 0.252 g (39%), mp 224 °C, $T_d$ 259 °C, $R_f$ 0.21 ($CHCl_3$). IR (KBr): 3217, 1718, 1659, 1569, 1504, 1433, 1376, 1323, 1109 $cm^{-1}$. $^1H$ NMR (300 MHz, [$D_6$]DMSO): 1.26 (t, *J* 7.1 Hz, 3H), 2.36 (s, 3H), 4.26 (q, *J* 7.1 Hz, 2H), 6.25 (s, 1H), 6.72 (d, *J* 7.7 Hz, 1H), 7.22–7.32 (m, 5H), 9.09 (s, 1H), 9.48 (s, 1H). $^{13}C$ NMR (75.5 MHz, [$D_6$]DMSO): 13.9, 20.6, 61.9, 107.7, 112.8, 124.0, 130.1, 130.7, 132.5, 134.7, 135.6, 137.6, 140.1, 140.2, 159.2, 190.2. HRMS (ESI) Calcd. for $C_{18}H_{17}N_3NaO_3$ $[M + Na]^+$: 346.1162, found: 346.1153.

*3-Ethoxycarbonyl-7-formyl-1-(4-p-tolyl)-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl* (**6k**). Red-brown solid, yield 0.122 g (19%), mp 176 °C, $T_d$ 191 °C, $R_f$ 0.20 ($CHCl_3$). IR (KBr): 3220, 1734, 1719, 1676, 1660, 1571, 1507, 1434, 1278, 1102 $cm^{-1}$. EPR (toluene) $g$ = 2.0034. HRMS

(ESI) Calcd. for $C_{18}H_{16}N_3NaO_3$ $[M + Na]^+$: 345.1099, found: 345.1097. Anal. calcd. for $C_{18}H_{16}N_3O_3$ (%): C, 67.07; H, 5.00; N, 13.04. Found (%): C, 66.83; H, 5.26; N, 12.78.

*3-Ethoxycarbonyl-7-chloro-1-(4-chlorophenyl)-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl* (**6l**). Red-brown solid, yield 0.419 g (23%), mp 167 °C, $T_d$ 254 °C, $R_f$ 0.54 ($CHCl_3$). IR (KBr): 3368, 1703, 1486, 1373, 1059 $cm^{-1}$. EPR (toluene) $g$ = 2.0035. HRMS (ESI) Calcd. for $C_{16}H_{12}{}^{35}Cl_2N_3NaO_2$ $[M + Na]^+$: 371.0199, found: 371.0197; calcd. for $C_{16}H_{12}{}^{35}Cl^{37}ClN_3NaO_2$ $[M + Na]^+$: 373.0170, found: 373.0175. Anal. calcd. for $C_{16}H_{12}Cl_2N_3O_2$ (%): C, 55.03; H, 3.46; N, 12.03. Found (%): C, 54.79; H, 3.59; N, 11.79.

*7-Chloro-3,5-di(4-chlorophenyl)-1-(4-chlorophenylamino)-3,5-dihydro-benzo[e][1,2,4]triazolo [3,4-c][1,2,4]-triazinyl* (**7**). Gray solid, yield 0.083 g (15%), mp 194 °C, $T_d$ 194 °C, $R_f$ 0.60 ($CHCl_3$). IR (KBr): 3397, 1681, 1621, 1594, 1490, 1403, 1093 $cm^{-1}$. EPR (toluene) $g$ = 2.0024. HRMS (ESI) Calcd. for $C_{26}H_{16}{}^{35}Cl_4N_6^{\cdot}$ $[M^{\cdot}+ H]^+$: 552.0186, found: 552.0185; calcd. for $C_{26}H_{16}{}^{35}Cl_3{}^{37}ClN_6^{\cdot}$: 554.0159, found: 554.0159; calcd. for $C_{26}H_{16}{}^{35}Cl_2{}^{37}Cl_2N_6^{\cdot}$: 556.0133, found: 556.0127. Anal. calcd. for $C_{26}H_{16}Cl_4N_6$ (%): C, 56.34; H, 2.91; N, 15.16. Found (%): C, 56.57; H, 2.79; N, 14.89.

**X-ray crystallographic data and refinement details**. Crystals of **7** suitable for X-ray diffraction were grown from DMSO-$CH_2Cl_2$ mixture (2:1). X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (kappa geometry, shutterless ω-scan technique), using graphite monochromatized Cu Kα-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program [32]. The structure was solved by direct methods using SHELXT [33] and refined on $F^2$ using SHELXL-2018 [34] in the OLEX2 program [35]. All non-hydrogen atoms were refined with individual anisotropic displacement parameters. The location of hydrogen atoms H14A and H14B were found from the electron density-difference map; these hydrogen atoms were refined with an individual isotropic displacement parameter. All other hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The Mercury program suite [36] was used for molecular graphics. Three molecules of the solvent (DMSO) are disordered onto two positions. Deposition number 2160590 contain the supplementary crystallographic data. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27082575/s1, S1. Thermal behavior; S2. Crystallographic data (Tables S1–S7); S3. EPR spectra; S4. NMR and HRMS spectra.

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**Conflicts of Interest:** The authors declare no conflict of interest.

**Sample Availability:** Samples of the compounds are not available from the authors.

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