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A PASE Approach towards (Adamantyl-1)-, Alkyl- and (Het) Aryl-Substituted [1,2,4]triazolo[1,5-d][1,2,4]triazines: A Sequence of Two Solvent-Free Reactions Bearing Lower E-Factors

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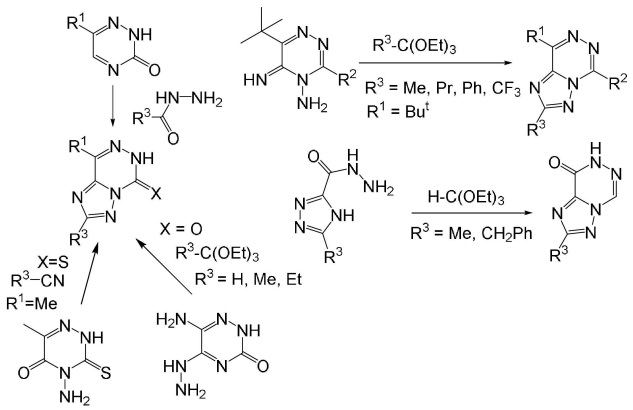
A Pot, Atom, Step Economic (PASE) approach is reported towards [1,2,4]triazolo[1,5-d][1,2,4]triazines, substituted with the azole ring with pharmacophore residues, such as 1-adamantyl or 2-furanyl moieties, naproxen residues, as well aliphatic and (het)aromatic substituents, starting from easily available 1,2,4-triazine-5-carbonitriles and carboxylic acids hydrazides. This approach involves a sequence of two solvent-free reactions accompanied by the Dimroth rearrangement on the last step. The structures of the final Dimroth rearrangement products were confirmed based on the DFT studies as well as the single crystal X-ray analysis for the admantane-substituted product. In addition, this method possesses lower E-factors.

Introduction

Among synthetic purine analogs,[1] including *aza*-purines[2] and some fluorescent analogs,[3] 1,2,4-triazole annelated di- and triazines are of considerable interest due to their various biological activities, such as antidiabetic activity[4] as well as antiviral activity.[5] In addition, these scaffolds were incorporated in some commercially available drugs such as Triazavirin (TZV) (non-nucleoside antiviral drug), Aciclovir (antiviral drug) etc. (Figure 1).[6] Additionally, these compounds are reported as synthons and building blocks for the further preparation of polynuclear heterocycles.[7,8] On the other hand, adamantane derivatives have also found practical applications as common drug components,[9] including antiviral drugs.[9a–c] Very recently Roberge and co-authors reported C-adamantylated azoles, including imidazoles, as new inhibitors of the influenza A virus M2 proton channel.[9d] Adamantylated nucleosides of fluorouracil have indicated some activities against certain types of cancer, cytotoxic activity, as well as antiviral activity.[9e]

Among the azolo[1,2,4]triazines, [1,2,4]triazolo[1,5-d][1,2,4]triazines are reported in very few articles. According to literature a small number of synthetic approaches is proposed for the construction of this heterocyclic system (Scheme 1). In particular, one strategy was developed involving building up of the triazine ring to the triazole one starting from 1,2,4-triazole-3-carboxylic acid hydrazide.[10] In addition, a number of synthetic approaches need to mention, which involved the construction of the 1,2,4-triazole moiety, in particular starting



Scheme 1. Some common approaches towards [1,2,4]triazolo[1,5-d][1,2,4]triazines.

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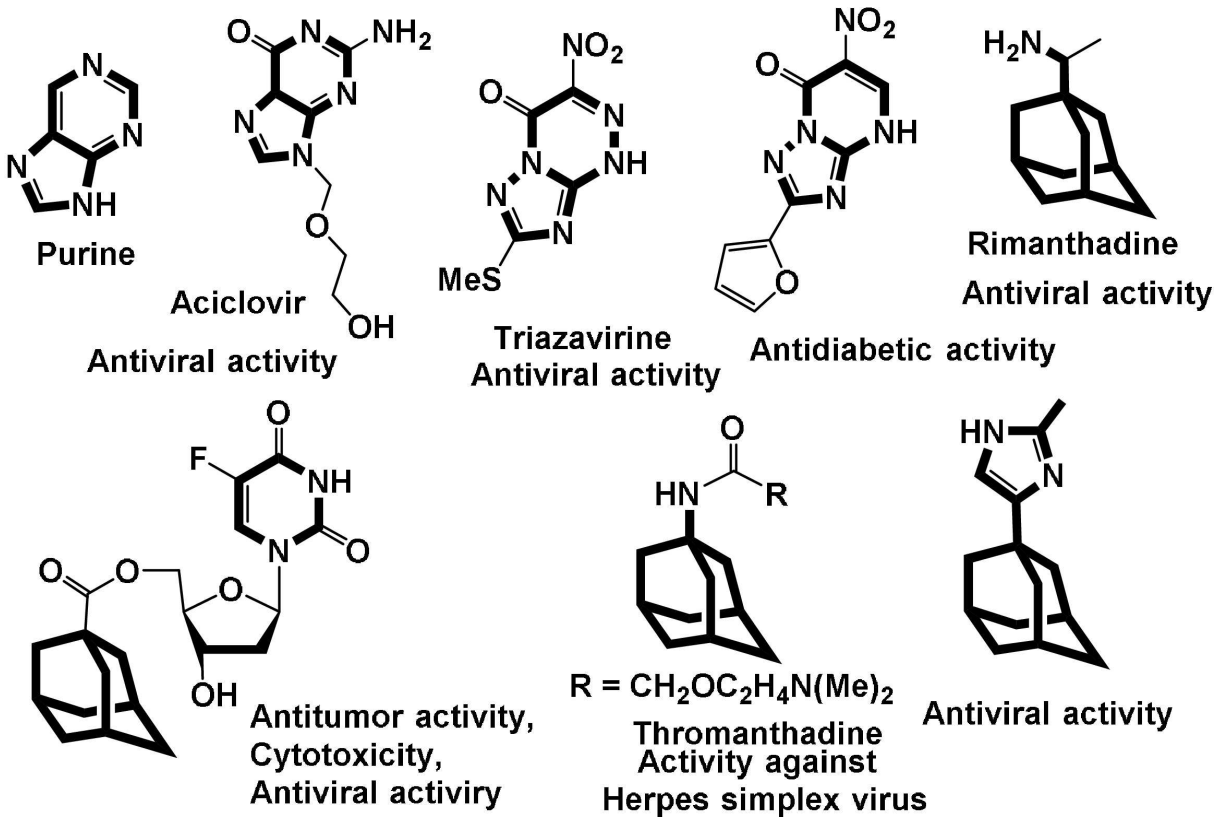


Figure 1. Some biologically active (*aza*)-purines and adamantanes.

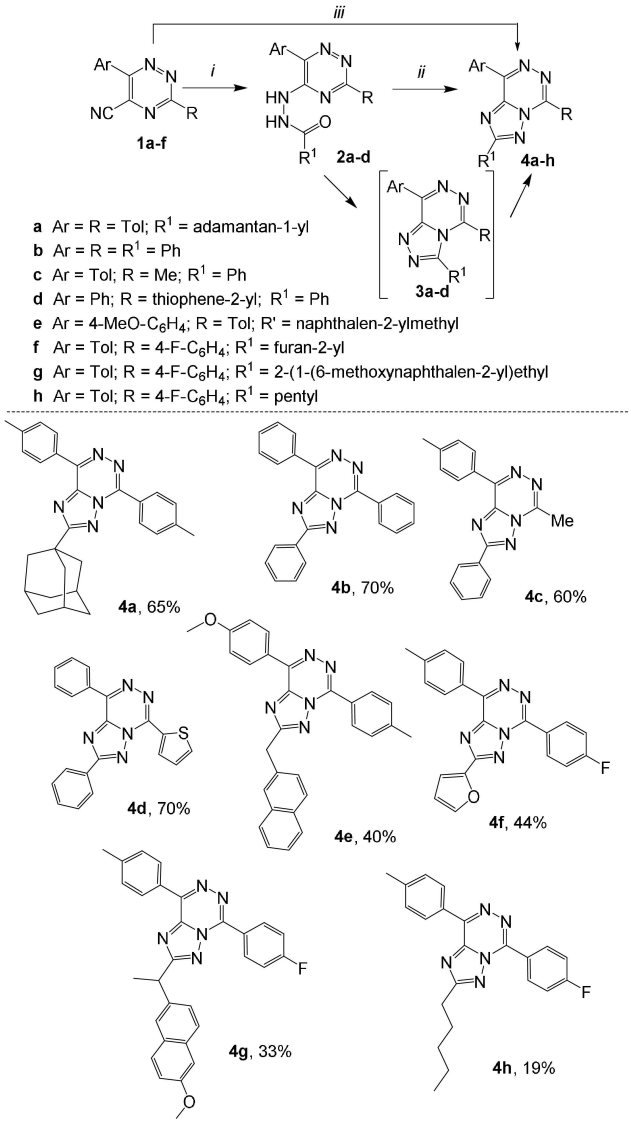
from 5-hydrazino-6-amino-[11] or 4,5-diamino-substituted 1,2,4-triazines[12] by the reactions with orthoesters. In addition, a similar heterocyclization is possible in reaction between 4-amino-1,2,4-triazin-5-one and aromatic nitriles.[13] Finally, the S_N^H reaction of 5-*H*-6-aryl-1,2,4-triazin-3-ones was also reported under the reaction with carboxylic acid hydrazides followed by cyclocondensation reaction accompanied by the Dimroth rearrangement.[14]

In continuation of our studies on PASE-approach[15] towards (oligo)azine-containing ligands/fluorophores and on the new synthetic approaches towards biologically active compounds[16] we attempted to synthesize new (het)aryl-, alkyl- and adamantane-substituted *as*-triazines and their azoloannelated derivatives starting from 5-cyano-1,2,4-triazines **1** by means of the *ipso*-substitution of the C5-cyanogrop by the reaction with carboxylic acid hydrazides (Scheme 2).

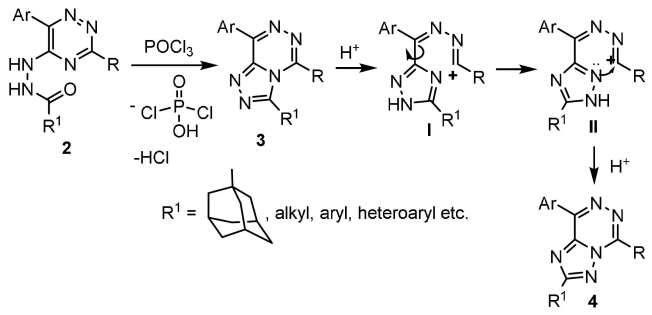
Results and Discussion

5-Cyano-1,2,4-triazines (**1**) are easily accessible and could be obtained using previously reported approaches *via* S_N^H reactions of 1,2,4-triazine-4-oxides,[17] and the starting 1,2,4-triazines **1** and their derivatives could be prepared as described earlier.[18–21] The *ipso*-substitution of the 5-cyano group in 1,2,4-triazines is widely reported for various nucleophiles, for instance amines,[22–24] alcohols,[18][13] lithium carboranes,[25] etc. Recently, we also reported a solvent-free method for the substitution of 5-cyano-group in 1,2,4-triazines by the reaction between aromatic amines[20] and carboxylic acids hydrazides.[26]

As a first step, the adamantane-substituted 5-hydrazino-1,2,4-triazine **2a** was prepared by the reaction of 5-cyano-1,2,4-triazine **1a** with adamantane-1-carboxylic hydrazide at 150 °C under neat conditions following our previously reported procedures[20,26] (Scheme 2). As a next step, aiming to synthesize the [1,2,4]triazolo[4,3-d][1,2,4]triazines **3** the cyclocondensation reaction of hydrazide **2a** was carried out also under neat conditions in the presence of phosphorus oxychloride as dehydrating agent. However, based on the X-ray data of compound **4a** it was found that the reaction afforded the [1,2,4]triazolo[1,5-d][1,2,4]triazines **4** as the only product. The same products **4b-d** were obtained in the reaction of hydrazides **2b-d**, which were obtained in the same way as it was described for **2a,** with phosphorous oxychloride under neat conditions. Based on the literature[14] we assumed that the product **4** is formed *via* the Dimroth rearrangement of *in situ* generated [1,2,4]triazolo[4,3-d][1,2,4]triazine **3** through the formation of acid promoted triazine ring opening product **I**; rotation of 1,2,4-triazole ring along the C–C bond affording intermediate **II** and the 1,2,4-triazine ring closure into product **4** (Scheme 3). After the purification by column chromatography products **4** were isolated in up to 70% yields. Additionally, it was found that the compounds **4a-h** can be obtained from **1a-f** in a one-pot manner, without isolation of the intermediate products **2**, by means of a stepwise addition of carboxylic acid



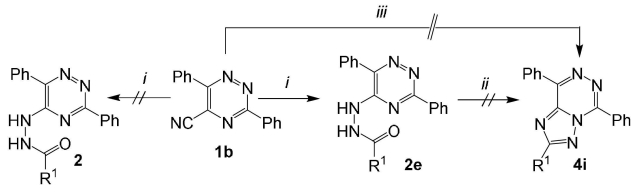
Scheme 2. Synthesis of [1,2,4]triazolo[1,5-d][1,2,4]triazines **4**. *Reagents and conditions: i)* $R^1C(O)NHNH_2$, 150 °C, neat, 8 h; *ii)* $POCl_3$, 100 °C, 2 h, neat; *iii)* $R^1C(O)NHNH_2$, 150 °C, neat, 6 h, then $POCl_3$, 150 °C, 2 h, neat.



Scheme 3. Proposed mechanism of the Dimroth rearrangement affording [1,2,4]triazolo[1,5-d][1,2,4]triazines **4**.

hydrazide and $POCl_3$ with a little bit increase in yields. It is worthy to mention that by using this approach the (*S*)-naproxen moiety can be introduced in **4** to afford an enantiopure mutual prodrug candidate,[27] namely **4g**. In addition, we have developed a greener reaction condition bearing lower E-factors[28] in cases of this PASE approach towards [1,2,4]triazolo[1,5-d][1,2,4]triazines which is consistent with the principles of the atom economy (Supporting Information).

It is worthy to mention that in case of other hydrazides (R^1 = Me, CCl_3, 3-pyridyl, 4-pyridyl), their "solvent-free" reaction (way *i*) with 1,2,4-triazine **1b** did not afford any products, most probably, due to the sublimation of the above mentioned hydrazides at high temperature, and only starting 1,2,4-triazine **1b** was isolated, The reaction between **1a** and 2-pyridyl carboxylic acid hydrazide afforded the *ipso*-substitution product **2e**,[26] however, neither the following cyclocondensation reaction of **2e** (way *ii)* nor the one-pot reaction between the above mentioned hydrazide and **1b** (way *iii*) afforded the expected [1,2,4]triazolo[1,5-d][1,2,4]triazine **4i**, while mixture of several products was obtained (unidentified) (Scheme 4).



Scheme 4. Attempted synthesis of other 1,2,4-triazines **2** and [1,2,4]triazolo [1,5-d][1,2,4]triazines **4**. Reagents and conditions: i) $R^1C(O)NHNH_2$, 150 °C, neat, 8 h; ii) $POCl_3$, 100 °C, 2 h, neat; *iii*) $R^1C(O)NHNH_2$, 150 °C, neat, 6 h, then $POCl_3$, 150 °C, 2 h, neat.

The structures of products **2** and **4** were confirmed based on the ^1H and ^{13}C NMR, as well as mass-spectroscopy and elemental analysis. Thus, the formation of hydrazides **2** is confirmed based on the presence of the proton signals of the substituents in C3- and C6- positions of the 1,2,4-triazine moiety, as well as the signals of protons of the disubstituted hydrazide residues. For the compounds **4** the absence of the proton signals belonging to the disubstituted hydrazide was the evidence for the formation of [1,2,4]triazolo[1,2,4]triazines. In addition to ^1H and ^{13}C NMR the final determination of the structure of products **4** was performed on the basis of the X-ray diffraction analysis for the compound **4a** in order to attribute the structure of these products as [1,2,4]triazolo[1,5-d][1,2,4] triazines.

The single crystal structure of compound **4a** is presented in Figure 2,[29] and the crystal packing is represented in Figure 3. According to XRD data, the compound **4a** is crystallized in the centrosymmetric space group as solvate with $C_2H_4Cl_2$ (1,2-dichloroethane) (2:1). The molecule of the $C_2H_4Cl_2$ is placed in the special position and demonstrated the strong thermal disordering. The solvent was included in the refinement with the restrained C–Cl bond distance and anisotropic displacement parameters. This restriction of the model lead to significant $\Delta\rho_{\bar{e}}$ = 0.402/-0.361 $\bar{e}Å^{-3}$ and R_1 = 0.0603 ($I > 2\sigma(I)$),

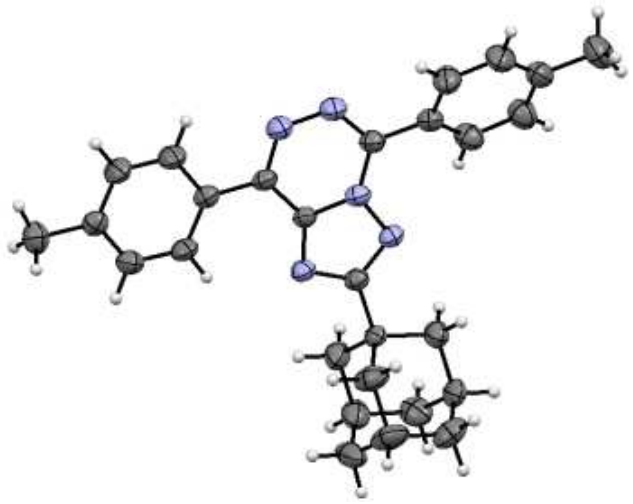


Figure 2. X-ray structure of compound **4a**.

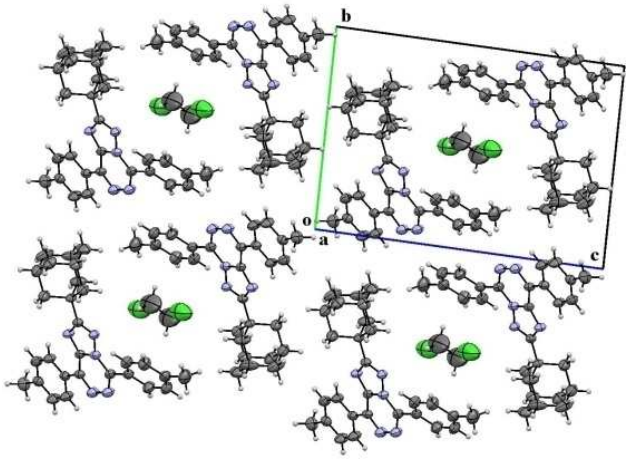


Figure 3. The crystal packing of the compound **4a** along 0a axe.

however, in general, the structural model did not cause any doubts.

The heterocycle does not show any deviation in the expected bond distances and angles. The conjugation effect in the heterocycle is well observed, however, the single sp^2-sp^2 and double sp^2-sp^2 bond distances are quite distinguished. The distances for double bonds in the molecule are less than 1.33 Å and distances for single bond are more than 1.35 Å. The *p*-tolyl substituent at C(6) is placed approximately in the heterocyclic plane (the dihedral angle between the planes of the rings is 3.75°), the *p*-tolyl substituent at C(9) is turned toward heterocycle on the angle of 30.6°. Any significant shortened intermolecular contacts did not observe in the crystal.

DFT Calculations

In order to estimate the stability of [1,2,4]triazolo[4,3-d][1,2,4] triazines **3** compare to the isolated [1,2,4]triazolo[1,5-d][1,2,4] triazines **4** the DFT calculations were carried out using Gaussian 09[30] suit of programs by using 6–311 + G(2d,p) 41WB97XD and 6–311 + G(2d,p) WB97XD basis. Based on the obtained results (Table 1-Table 2) the formation of Dimroth rearrangement

Table 1. The DFT calculations for the enthalpy and Gibbs energy values for the products **3–4**.

	$\Delta_f H_0$ (M, 0 K) (kcal/mol)		$\Delta_f H_0$ (M, 298 K) (kcal/mol)		$\Delta_f G_0$ (M, 298 K) (kcal/mol)	
	WB97XD, 6–311 + G(2d,p)	M062X, 6–311 + G (2d,p)	WB97XD, 6–311 + G(2d,p)	M062X, 6–311 + G (2d,p)	WB97XD, 6–311 + G(2d,p)	M062X, 6–311 + G (2d,p)
3a	-177,44	-178,66	-152,44	-154,25	-706,93	-707,02
4a	-166,24	-164,81	-141,79	-139,78	-693,28	-694,26
3b	-227,52	-221,41	-214,60	-208,52	-595,05	-588,99
4b	-214,79	-208,19	-201,91	-195,28	-581,59	-575,49
3c	-182,42	-179,07	-169,74	-166,44	505,99	-503,27
4c	-167,49	-163,91	-154,88	151,26	-491,21	-488,31

Table 2. The DFT calculations for the enthalpy and free energy of the reactions for the formation of products **3–4**.

	$\Delta_r H_0$ (298.15 K) (kcal/mol)		$\Delta_r G_0$ (298.15 K) (kcal/mol)	
	41WB97XD, 6–311 + G(2d,p)	M062X, 6–311 + G(2d,p)	41WB97XD, 6–311 + G(2d,p)	M062X, 6–311 + G(2d,p)
3a	-3,9187968	-0,8534129	-2,4246967	-8,2944206
4a	-6,7363145	-14,0926084	-16,0717733	-21,7996800
3b	-0,1631525	-2,9442746	-7,1799637	-10,7084496
4b	-12,8526496	-18,1318870	-20,6331399	-25,6689036
3c	-1,5555961	-6,0090310	-9,4214276	-0,7235185
4c	-16,4162760	-8,4563180	-24,1967663	-13,4820416

products **4** is thermodynamically more favorable in all the cases since their enthalpy and the Gibbs energy as well as the free energy of the reaction and the enthalpy of the reaction are higher than that of [1,2,4]triazolo[4,3-d][1,2,4]triazines **3**.

Conclusions

In summary, we have reported a PASE-approach towards [1,2,4]triazolo[1,5-d][1,2,4]triazines bearing various substituents, including some important pharmacophore moieties, such as adamantane, furan, naproxen etc., as well as (hetero) aromatic substituents, starting from readily available 5-cyano-1,2,4-triazines and carboxylic acid hydrazides. The method involves the use of two successive solvent-free reactions: *ipso*-substitution of the cyano group in the position of C5 of the 1,2,4-triazine moiety by the carboxylic acid hydrazide residues and followed by cyclocondensation reaction in $POCl_3$ under neat, conditions accompanied by a Dimroth rearrangement. The reaction can also be carried out in one-pot manner. Moreover, this is the PASE approach towards [1,2,4]triazolo[1,5-d][1,2,4]triazines associated with the lowest generation of waste that we are aware of, as evidenced by the calculated E-factors. The structure of the adamantane-substituted product was confirmed based on single crystal X-ray diffraction analysis.

DFT calculations were carried out to get a better understanding on the mechanistic pathway of the reaction.

Experimental Section

The Supporting Information for this article contains the Experimental Section explaining all the experimental details along with general procedure, analytical and spectral data of all the synthesized compounds and scanned copies of their respective ^{1}H-NMR and ^{13}C-NMR spectra.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: adamantane · Dimroth rearrangement · DFT studies · E-factors · [1,2,4]triazolo[1,5-d][1,2,4]triazines

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