

Synthesis, photophysical and redox properties of the 2,5,7-tri(het)aryl-[1,2,4]triazolo[1,5-*a*]pyrimidines

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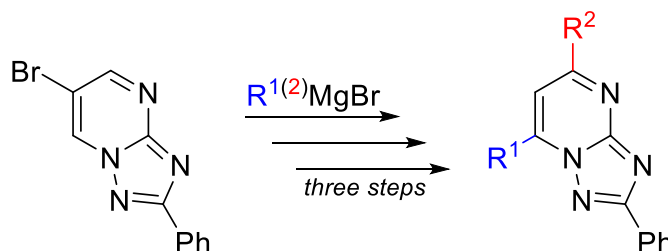
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Abstract

A number of Y-type push-pull compounds based on the [1,2,4]triazolo[1,5-*a*]pyrimidine core, namely 5,7-di(het)aryl-substituted 2-phenyl-[1,2,4]triazolo[1,5-*a*]pyrimidines, were obtained by transition metal free nucleophilic C–H functionalization. Substituents at both the C-5 and C-7 positions were introduced by successive treatment of the starting 6-bromo-2-phenyl-[1,2,4]triazolo[1,5-*a*]pyrimidine with Grignard reagents. In addition, the optical and electrochemical properties of the synthesized push-pull systems were studied.



Keywords: [1,2,4]triazolo[1,5-*a*]pyrimidine, Grignard reagents, direct (het)arylation, nucleophilic aromatic substitution of hydrogen (S_{NH})

Introduction

Over the past few decades pyrimidine-cored compounds have gained considerable attention due to their promising application in designing different types of organic electronic devices.¹ For instance, pyrimidine-based π -conjugated compounds are widely and successfully used as active layers of thin-film (opto)electronic devices, including polymer solar cells,^{2,3} different types of OLEDs (e.g., compounds **1**⁴ and **2**⁵),⁴⁻⁹ or even portable detectors of explosives (e.g., compound **3**)¹⁰ (Figure 1).

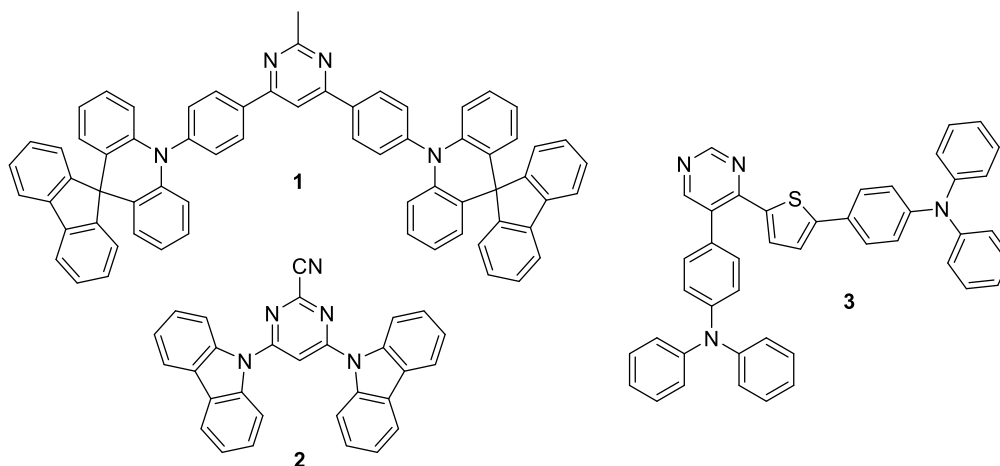


Figure 1. Pyrimidine-based (opto)electronic materials.

Such popularity of pyrimidines is explained by their highly π -deficient nature and ability to be an electron acceptor in various push-pull scaffolds providing an internal charge transfer upon excitation, and, therefore, inducing luminescence properties.¹ In this context, the electron-deficient system of the pyrimidine derivative [1,2,4]triazolo[1,5-*a*]pyrimidine (TAP) can also be of interest for the elaboration of donor-acceptor molecules. Indeed, substituted TAPs show good fluorescence features, especially in the blue region of spectra.¹¹ Since there is still a great demand for blue emitting materials with high efficiency,^{12,13} TAPs seem to be an attractive object for the further research.

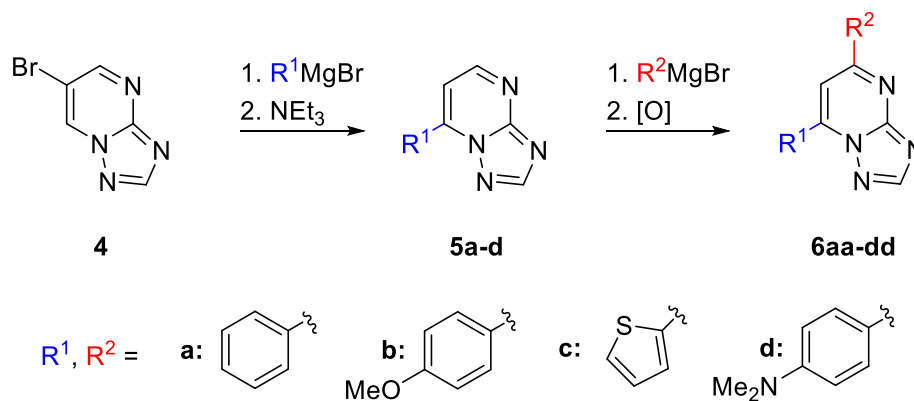
One of the main routes to substituted pyrimidines is the direct C-H functionalization,^{1,14} otherwise known as nucleophilic aromatic substitution of hydrogen (S_N^H).^{15,16} This approach can also be applied to the TAP-system, as already demonstrated by Jie Wu and colleagues who synthesized 2,7-diaryl-substituted TAPs using direct copper-catalyzed CH functionalization.¹⁷ However, in general, S_N^H method requires the pre-functionalization of substrates with auxiliary groups, e.g. halogens, and the catalysis by expensive transition metals, which does not satisfy the atom-economy principle in terms of green chemistry and increases the process cost. As such, we have attempted to improve the C-H functionalization approach to substituted TAPs using organomagnesium compounds as nucleophilic species, thus avoiding the above-mentioned disadvantages and obtaining 5,7-di(het)aryl-substituted TAPs with promising luminescence features.¹¹

Continuing our previous work¹¹ on the functionalization of TAPs by Grignard reagents, we present below the synthesis and study of more π -extended 2,5,7-tri(het)aryl-substituted TAPs, obtained with the aim of improving the optical properties.

Results and Discussion

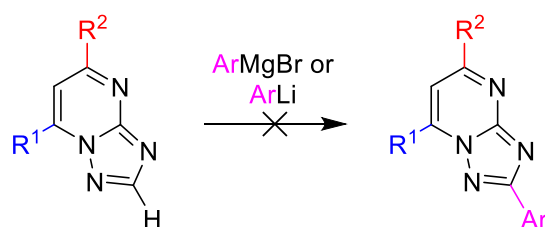
Synthesis of TAP compounds

As previously highlighted, TAPs have electron deficient character, so they tend to enter into addition reactions with nucleophiles. Previously, we reported that the reaction of 6-bromo-TAP **4** with (het)aryl magnesium bromides proceeds regioselectively at the C-7 position. The resulting σ^H -adducts can undergo an eliminative aromatization, thus giving 7-substituted TAPs **5a-d**, which can be further treated with additional Grignard reagents to afford the 5,7-disubstituted TAPs **6aa-dd** (Scheme 1).¹¹



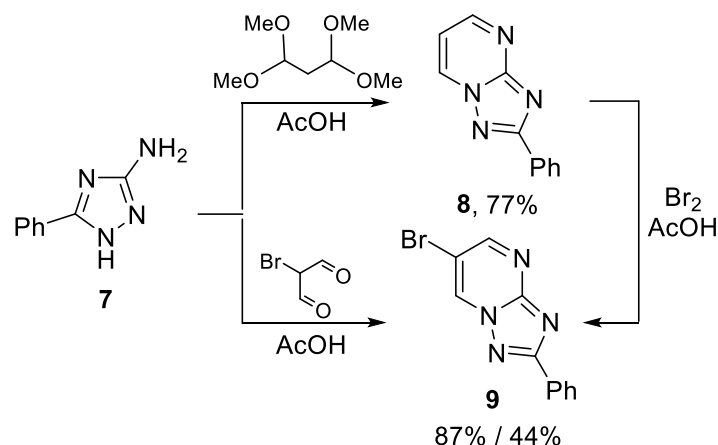
Scheme 1. General pathway to 5,7-disubstituted TAPs.

In accordance with our approach, we tried to construct 2,5,7-tris(het)aryl-TAPs by attacking the C-2 position of 5,7-di(het)aryl-TAP with Grignard reagents as well as stronger nucleophiles - aryllithium compounds, but in both cases the attempts failed (Scheme 2). Thus, we decided to synthesize the desired 2,5,7-tri(het)aryl-TAPs by the successive functionalization of 2-aryl-substituted TAP at its C-5 and C-7 positions using Grignard reagents, similar to the manner described above.



Scheme 2. Interaction 5,7-di(het)aryl-TAPs with aryl lithium reagents.

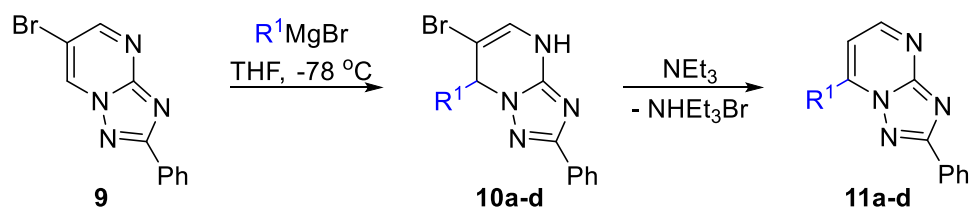
To this end, 2-phenyl-TAP **8**, formed from 3-phenyl-1,2,4-triazol-5-amine (**7**), obtained by earlier reported procedure,¹⁸ and 1,1,3,3-tetramethoxypropane, was selected as a model compound to realize our strategy and treated with Grignard reagents prepared *in situ* from the corresponding aryl bromides and magnesium in THF. However, in the course of this reaction the regioselectivity was not observed, thus giving the mixture of products of the C-5 and C-7 addition. Thus, we turned our attention to another TAP derivative, namely 6-bromo-2-phenyl-TAP **9**. Substrate **9** was prepared by the condensation of 3-phenyl-1,2,4-triazol-5-amine (**7**) with 2-bromomalonaldehyde in glacial acetic acid solution (Scheme 3) in 87% yield. Compound **9** can also be obtained by the direct bromination of 2-phenyl-TAP **8** but only in 44% yield.



Scheme 3. Preparation route of 6-bromo-2-phenyl-TAP **9**.

The first addition of (het)aryl magnesium bromides to compound **9** proceeded regioselectively at low temperatures and afforded σ^H -adducts **10a-d** in 68-91% yields. The latter adducts were aromatized by dehydrobromination with triethylamine, resulting in 2,7-disubstituted TAPs **11a-d** (Table 1).

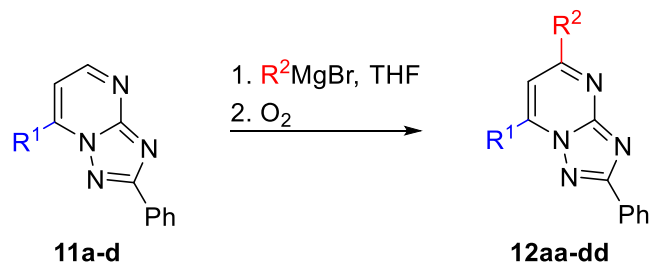
Table 1. Scope and yields of 2,7-disubstituted TAPs



R^1	Entry	Yield (%)	Entry	Yield (%)
Ph	10a	91	11a	88
4-MeOC ₆ H ₄	10b	68	11b	85
Thien-2-yl	10c	71	11c	91
4-Me ₂ NC ₆ H ₄	10d	85	11d	92

The second attachment of Grignard reagents to derivatives **11a-d** led to the formation of 2,5,7-trisubstituted TAPs **12aa-dd** after the one-pot oxidation of addition intermediates (Table 2), which, however, proceeded slowly and required prolonged bubbling of oxygen through the reaction mixture.

It is worth noting that the synthesized compounds, due to the presence of an additional phenyl group in theazole moiety, have poorer solubility compared to the substances described in our previous article. However, this did not prevent us to obtain analytically pure forms of these compounds in the all cases. Nevertheless, it is clear, that to construct similar TAP molecules with bulk (hetero)aromatic moieties, fragments bearing long-chain or branched alkyl or alkoxy groups should be inserted to improve solubility of the desired final TAPs.

Table 2. Scope and yields of 2,5,7-trisubstituted TAPs **12**

Entry	R ²	Com-d	Yield (%)
11a	Ph	12aa	63
	4-MeOC ₆ H ₄	12ab	53
	Thien-2-yl	12ac	83
	4-Me ₂ NC ₆ H ₄	12ad	64
11b	Ph	12ba	58
	4-MeOC ₆ H ₄	12bb	55
	Thien-2-yl	12bc	64
	4-Me ₂ NC ₆ H ₄	12bd	60
11c	Ph	12ca	76
	4-MeOC ₆ H ₄	12cb	61
	Thien-2-yl	12cc	57
	4-Me ₂ NC ₆ H ₄	12cd	58
11d	Ph	12da	54
	4-MeOC ₆ H ₄	12db	52
	Thien-2-yl	12dc	53
	4-Me ₂ NC ₆ H ₄	12dd	56

Optical and electrochemical measurements

The UV-vis absorption and photoluminescence spectra of compounds **11** and **12** were recorded in CH₂Cl₂ solution (2×10^{-5} mol · L⁻¹) at ambient temperature (Table 3). E_{HOMO/LUMO} values were estimated from the corresponding onset potentials in electrochemical studies, E_{gap} = E_{LUMO} - E_{HOMO} (for additional data see SI). Measurements of E_g^{opt} were carried out by the optical method¹⁹ in a solid form. The quantum yields were determined by the relative method;¹⁹ the comparison sample was quinine bisulfate.

Table 3. The maxima of absorption, excitation and emission spectra, energy gaps and quantum yields of compounds **11** and **12**

Entry	^{abs} λ_{\max} (nm)	^{em} λ_{\max} (nm)	E_{LUMO} , eV	E_{HOMO} , eV	E_{gap}	$E_{\text{g}}^{\text{opt}}$, eV	Φ (%)
11a	309	391	-3.01	-6.66	3.65	3.36	13
11b	317	395	-2.95	-6.41	3.46	3.19	62
11c	330	395	-3.28	-6.28	3.00	3.06	45
11d	390	475	-3.29	-5.49	2.20	2.69	61
12aa	330	400	-3.26	-6.38	3.12	3.22	29
12ab	344	436	-3.01	-6.32	3.31	3.01	48
12ac	351	425	-3.12	-6.30	3.18	3.01	30
12ad	310	400	-3.01	-5.45	2.44	2.53	7
12ba	334	408	-2.99	-6.34	3.35	3.17	53
12bb	344	430	-2.94	-6.25	3.31	3.06	62
12bc	350	418	-2.97	-6.31	3.34	2.97	35
12bd	336	416	-2.90	-5.44	2.54	2.57	17
12ca	348	407	-3.12	-6.34	3.22	3.01	24
12cb	351	446	-3.10	-5.49	2.39	2.89	45
12cc	355	430	-3.35	-6.20 ^a	2.85 ^b	2.85	31
12cd	342	402	-3.09	-5.46	2.37	2.38	12
12da	402	518	-2.93	-5.62	2.69	2.53	29
12db	400	497	-2.76	-5.61	2.85	2.33	41
12dc	359	530	-3.00	-5.56	2.56	2.52	24
12dd	406	538	-2.76	-5.40	2.64	2.53	15

^a Calculated by equation: $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g}}^{\text{opt}}$. It was not possible to determine the oxidation peak. Probably, it coincides with the oxidation potential of the supporting electrolyte salt;

^b $E_{\text{gap}} = E_{\text{g}}^{\text{opt}}$

All obtained substituted TAPs exhibit a very strong light absorption in violet and near UV regions of the spectrum (Figure 4). The luminescence of compounds **11** and **12** varies from near UV (**11a-c**) and violet (**12aa-12cd**) to blue (**11d**) and green (**12da, 12dc, 12dd**). Compound **11a** with the simplest structure has a minimum quantum yield among the studied 2,7-disubstituted TAPs. Replacement of the C-7 phenyl group by 4-methoxyphenyl or 4-(*N,N*-dimethylamino)phenyl groups leads to significant increase in quantum yields to above 60%. All TAPs containing 2-thienyl-group show average quantum yields with maximum value of 45% for **11c** and **12cb**. TAPs **11b** and **12bb** containing 4-methoxyphenyl group show significant quantum yields of 62%. At the same time, there is a small bathochromic and significant bathofluoric shift.

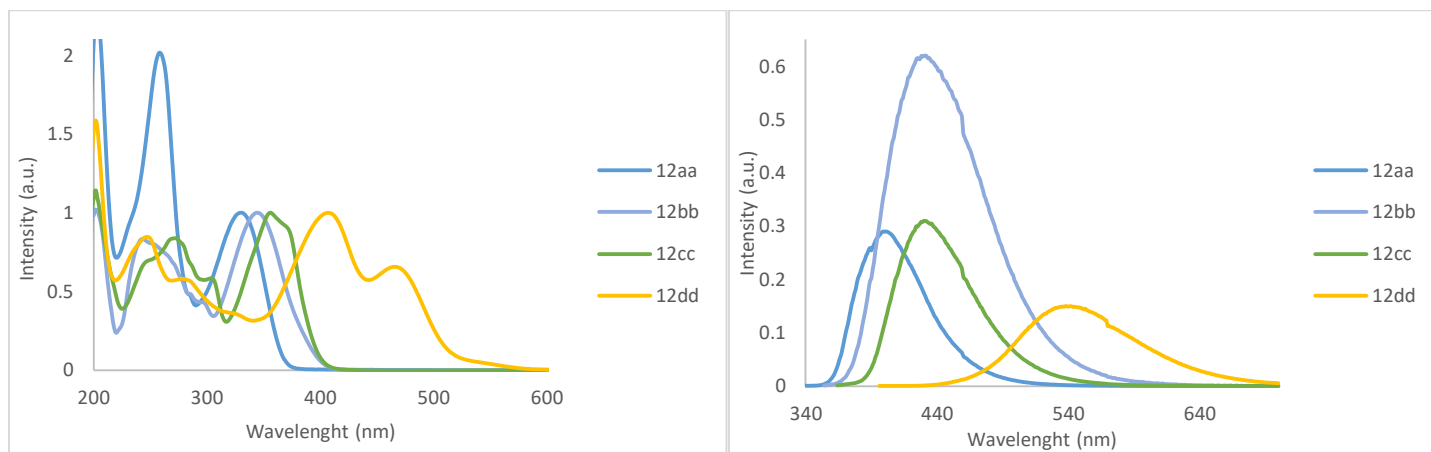


Figure 1. UV-vis absorption (left) and emission (right) spectra of some 2,5,7-tri(het)aryl TAPs in CH_2Cl_2 after normalization. Intensity of emission spectra is based on relative quantum yields.

The greatest bathofluoric effect is achieved by introducing 4-(*N,N*-dimethylamino)phenyl at C-5 and C-7 positions (compound **12dd**). The emission maximum shifts to 538 nm (Figure 4). A similar effect can be achieved by replacing the substituent at C-5 position on thienyl as in **12dc** (emission maximum at 530 nm). At the same time, quantum yields of these compounds are relatively low, 15 and 24%, respectively. Compound **12db**, containing 4-methoxyphenyl and 4-(*N,N*-dimethylamino)phenyl substituents, shows good quantum yield, which is higher than the group average (41%), as well as strong bathofluoric shift with emission maximum at 497 nm. The swap of substituents in compound **12db** gives compound **12bd** with an almost minimum quantum yield in the group (17%) and an insignificant bathofluoric shift (emission maximum at 416 nm).

Comparing the series of compounds **11** and **12** with the previous one of compounds **6**,¹¹ it should be noted that entering additional phenyl at C-2 position of TAP led to some increase in quantum yields, however, the luminescence maxima are on average shifted to the region of shorter wavelengths. If comparing 5-phenyl-7-(het)aryl- and 2-phenyl-7-(het)aryl TAPs, a significant increase of quantum yields is observed, in the case of 5-phenyl-7-[4-(*N,N*-dimethylamino)phenyl]-TAP **6da** and corresponding compound **11d** – twofold.

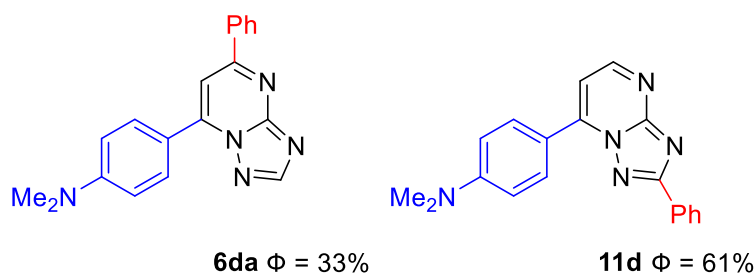


Figure 5. Quantum yields of **6da** and **11d**.

Conclusions

An effective route to obtain 2,7-di(het)aryl- and 2,5,7-tri(het)aryl-substituted [1,2,4]triazolo[1,5-*a*]pyrimidines based on the nucleophilic aromatic substitution of hydrogen ($\text{S}_\text{N}^\text{H}$) in the 2-aryl-substituted TAP substrate has

been developed. Successive nucleophilic addition of Grignard reagents on 6-bromo-2-phenyl-TAP enables substitution first at C-7 and then at C-5 via direct C-H functionalization. Basic optical and electrochemical properties of 2,7-di(het)aryl- and 2,5,7-tri(het)aryl-substituted derivatives have been also investigated. Most of the studied compounds exhibit strong fluorescence with high quantum yields up to 61%.

Experimental Section

General. All reagents, except for 3-phenyl-1,2,4-triazol-5-amine, and solvents were purchased from commercial sources and dried by using standard procedures before use. 3-Phenyl-1,2,4-triazol-5-amine was prepared according to the literature.¹¹ Analytical studies were carried out using equipment of the Center for Joint Use "Spectroscopy and Analysis of Organic Compounds" at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Division). Melting points were determined on Boetius combined heating stages and are uncorrected. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. ¹H and ¹³C NMR spectra were recorded on AVANCE-400 and AVANCE-500 instruments in DMSO-*d*₆ or CDCl₃ with TMS as an internal standard. The GC-MS analysis of all samples was carried out using an Agilent GC 7890A MS 5975C Inert XL EI/CI GC-MS spectrometer with a quadrupole mass-spectrometric detector with electron ionization (70 eV), and scan over the total ionic current in the range *m/z* 20-1000 and a quartz capillary column HP-5MS (30 m × 0.25 mm, film thickness 0.25 mm). Column chromatography was carried out using Alfa Aesar silica gel 0.040–0.063 mm (230–400 mesh), eluting with ethyl acetate/hexane (50:50) or ethyl acetate containing 0.5% of triethylamine. The progress of the reactions and the purity of compounds were checked by TLC on Sorbfil plates (Russia), in which the spots were visualized with UV light (λ 254 or 365 nm). Optical spectra were obtained using a Shimadzu UV-2600 double-beam UV-vis spectrophotometer, a Varian Cary Eclipse fluorescence spectrophotometer and a Hèllma QS-101 high precision quartz cell in CH₂Cl₂ solution. Solutions of compounds with 4-(*N,N*-dimethylaminophenyl) substituents were made with the addition of Me₄NOH base. Bi-quinine sulfate was used as the standard for relative quantum yield measuring. Cyclic voltammetry was carried out on a Metrohm Autolab PGSTAT128N potentiostat with a standard three-electrode configuration. Typically, a three electrodes cell equipped with a glass carbon working electrode, a Ag/AgNO₃ (0.01 M) reference electrode, and a glass carbon rod counter electrode was employed. The measurements were done in dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte under an argon atmosphere at a scan rate of 100 mV/s. The potential of Ag/AgNO₃ reference electrode was calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc⁺).

2-Phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (8). To solution of 3-amino-5-phenyl[1,2,4]triazole (**7**) (16 g, 0.1 mol) in glacial acid (200 mL) was added 1,1,3,3-tetramethoxypropane (16.45 mL, 0.1 mol) and water (5 mL). After stirring for 30 min, the mixture was heated to boiling and refluxed for 4 h. All volatiles were then removed under reduce pressure. To the residue was added 2-PrOH (200 mL) and the mixture was boiled, then cooled. The formed precipitate was filtered off and dried in air to give the *title compound* **8** (15.2 g, 77%), as colorless crystals mp 184–185 °C (2-PrOH); ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 9.45 (dd, *J* 6.8, 1.9 Hz, 1H), 8.89 (dd, *J* 4.3, 1.9 Hz, 1H), 8.28–8.20 (m, 2H), 7.62–7.52 (m, 3H), 7.38 (dd, *J* 6.8, 4.3 Hz, 1H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ_C 164.5, 155.52, 155.47, 137.2, 130.7, 130.2, 129.0, 126.9, 110.9. Anal. Calcd. for C₁₁H₈N₄: C: 67.34; H: 4.11; N: 28.55. Found C: 67.41; H: 4.08; N: 28.51.

5-Bromo-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (9) (Route A). To stirred solution of 2-phenyl-[1,2,4]triazolo[1,5-*a*]pyrimidine (**8**) (1.5 g, 0.01 mol) in glacial acid (30 mL) dropwise was added a solution of

bromine (1.9 g, 0.012 mol) in glacial acid (20 mL). After adding bromine solution, reaction mixture was set aside for 2 h. To this mixture was added water (200 mL), and the crude residue was filtered off, boiled with 2-PrOH (50 mL) and cooled. The formed precipitate was filtered off and dried in air to give the *title compound 9* (1.2 g, 44%) as colorless crystals mp 151-153 °C (2-PrOH). ¹H NMR (400 MHz, DMSO-*d*₆) δ_H 9.92 (d, *J* 2.4 Hz, 1H), 8.98 (d, *J* 2.4 Hz, 1H), 8.27–8.17 (m, 2H), 7.63–7.48 (m, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ_C 165.0, 155.9, 154.2, 137.4, 130.9, 129.9, 129.0, 126.9, 105.7. Anal. Calcd. for C₁₁H₇BrN₄: C: 48.02; H: 2.56; Br: 29.04; N: 20.37. Found C: 48.09; H: 2.60; Br: 29.11; N: 20.31.

5-Bromo-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (9) (Route B). To stirred solution of 3-amino-5-phenyl-[1,2,4]triazole (**7**) (16 g, 0.1 mol) in glacial acid (200 mL) was added 2-bromomalonaldehyde (15.1 g, 0.1 mol). After stirring for 30 min, the mixture was heated to boiling and refluxed for 4 h. All volatiles were removed under reduce pressure. The crude residue was poured onto 2-PrOH (200 mL) and boiled, then cooled. The precipitate filtered off and dried in air to give the title compound **9** (23.9 g, 87%), identical to that described above.

6-Bromo-2-phenyl-7-substituted-4,7-dihydro-[1,2,4]triazolo[1,5-*a*]pyrimidines (10a-d) (General procedure). Magnesium powder (36 mg, 1.5 mmol) was immersed in abs. THF (10 mL) under argon or nitrogen, and the appropriate bromo(het)arene (1.5 mmol) was added. The reaction mixture was stirred at room temperature until the formation of a clear solution, cooled to -78 °C and charged with 6-bromo-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (**4**) (200 mg, 1 mmol). After 1 h the bath temperature was elevated to 50 °C. Two hours later the flask was cooled, and to the reaction mixture was added cold water (3 mL) and ammonium chloride (107 mg, 2 mmol). After that, the solvent was distilled off *in vacuo*, the precipitate was filtered off, washed with water and ethyl acetate, dried and recrystallized to give compounds **10a-d**.

6-Bromo-2,7-diphenyl-4,7-dihydro-[1,2,4]triazolo[1,5-*a*]pyrimidine (10a). Pale crystals: (321 mg, 91%), mp 182-184 °C (2-PrOH); ¹H NMR (400 MHz, DMSO-*d*₆) δ_H 10.29 (d, *J* 5.1 Hz, 1H), 7.89–7.78 (m, 2H), 7.46–7.35 (m, 5H), 7.36–7.28 (m, 3H), 7.01 (dd, *J* 5.1, 0.8 Hz, 1H), 6.21 (d, *J* 0.8 Hz, 1H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ_C 158.9, 148.3, 139.3, 130.8, 129.1, 129.0, 128.6, 128.5, 127.6, 125.5, 125.5, 92.6, 65.0. Anal. Calcd. for C₁₇H₁₃BrN₄: C: 57.81; H: 3.71; Br: 22.62; N: 15.86. Found C: 57.84; H: 3.67; Br: 22.59; N: 15.81.

6-Bromo-7-(4-methoxyphenyl)-2-phenyl-4,7-dihydro-[1,2,4]triazolo[1,5-*a*]pyrimidine (10b). Colorless crystals: (260 mg, 68%), mp 184-186 °C (MeCN); ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 10.24 (d, *J* 4.9 Hz, 1H), 7.86–7.80 (m, 2H), 7.43–7.32 (m, 3H), 7.28–7.22 (m, 2H), 6.99 (d, *J* 4.2 Hz, 1H), 6.97–6.91 (m, 2H), 6.15 (s, 1H), 3.74 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ_C 159.4, 158.8, 148.1, 131.4, 130.8, 129.0, 128.9, 128.5, 125.5, 125.4, 113.9, 93.0, 64.5, 55.1. Anal. Calcd. for C₁₈H₁₅BrN₄O: C: 56.41; H: 3.95; Br: 20.85; N: 14.62. Found C: 57.44; H: 3.88; Br: 20.89; N: 14.61.

6-Bromo-7-(thiophen-2-yl)-2-phenyl-4,7-dihydro-[1,2,4]triazolo[1,5-*a*]pyrimidine (10c). Pale crystals: (255 mg, 71%), mp 204-206 °C (2-PrOH); ¹H NMR (400 MHz, DMSO-*d*₆) δ_H 10.37 (d, *J* 5.1 Hz, 1H), 7.90–7.82 (m, 2H), 7.55 (ddd, *J* 5.1, 1.3, 0.7 Hz, 1H), 7.48–7.33 (m, 3H), 7.26 (ddd, *J* 3.5, 1.3, 0.5 Hz, 1H), 7.06–6.99 (m, 2H), 6.59 (q, *J* 0.7 Hz, 1H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ_C 159.0, 147.8, 142.9, 130.7, 129.1, 128.6, 127.9, 127.3, 126.8, 125.8, 125.5, 92.1, 60.2. Anal. Calcd. for C₁₅H₁₁BrN₄S: C: 50.15; H: 3.09; Br: 22.24; N: 15.60; S: 8.92. Found C: 50.14; H: 3.06; Br: 22.20; N: 15.64; S: 8.95.

6-Bromo-7-(4-(*N,N*-dimethylaminophenyl))-2-phenyl-4,7-dihydro-[1,2,4]triazolo[1,5-*a*]pyrimidine (10d). Light yellow crystals: (337 mg, 85%), mp 202-204 °C (MeCN); ¹H NMR (400 MHz, DMSO-*d*₆) δ_H 10.17 (d, *J* 5.0 Hz, 1H), 7.87–7.79 (m, 2H), 7.43–7.31 (m, 3H), 7.16–7.08 (m, 2H), 6.96 (dd, *J* 5.0, 0.8 Hz, 1H), 6.73–6.65 (m, 2H), 6.04 (d, *J* 0.7 Hz, 1H), 2.88 (s, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ_C 158.7, 150.4, 148.1, 130.9, 128.9,

128.5, 128.3, 126.5, 125.5, 125.1, 112.0, 93.5, 64.8, 40.0. Anal. Calcd. for C₁₉H₁₈BrN₅: C: 57.59; H: 4.58; Br: 20.16; N: 17.67. Found C: 57.64; H: 4.60; Br: 20.19; N: 17.61.

2,7-Disubstituted [1,2,4]triazolo[1,5-*a*]pyrimidines (11a-d) (General procedure). The relevant 6-bromo-7-substituted-2-phenyl-4,7-dihydro-[1,2,4]triazolo[1,5-*a*]pyrimidine **5a-d** (1 mmol) and triethylamine (TEA) (0.216 mL, 1.5 mmol) were added to acetonitrile (10 mL) and heated at reflux until the initial substance completely disappeared (by TLC). The reaction mixture was then diluted with water (5 mL), cooled, then the precipitate was filtered, washed with water, dried and recrystallized to afford the desired products **11a-d**.

2,7-Diphenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (11a). Colorless needles: (240 mg, 88%), mp 170-171 °C (2-PrOH); ¹H NMR (400 MHz, DMSO-*d*₆) δ_H 8.93 (d, *J* 4.7 Hz, 1H), 8.33–8.27 (m, 2H), 8.27–8.22 (m, 2H), 7.73–7.67 (m, 3H), 7.62 (d, *J* 4.7 Hz, 1H), 7.60–7.54 (m, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ_C 164.2, 156.7, 154.9, 147.0, 131.7, 130.6, 130.3, 129.7, 129.6, 128.9, 128.7, 126.9, 109.7. Anal. Calcd. for C₁₇H₁₂N₄: C: 74.98; H: 4.44; N: 20.58. Found C: 75.07; H: 4.39; N: 20.52.

7-(4-Methoxyphenyl)-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (11b). Pale powder: (257 mg, 85%), mp 167-169 °C (2-PrOH); ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 8.87 (d, *J* 4.8 Hz, 1H), 8.42–8.36 (m, 2H), 8.29–8.23 (m, 2H), 7.61 (d, *J* 4.8 Hz, 1H), 7.60–7.54 (m, 3H), 7.28–7.21 (m, 2H), 3.91 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ_C 164.0, 162.0, 156.8, 154.6, 146.6, 131.5, 130.6, 130.4, 128.9, 126.9, 121.6, 114.2, 108.5, 55.5. Anal. Calcd. for C₁₈H₁₄N₄O: C: 71.51; H: 4.67; N: 18.53. Found C: 71.54; H: 4.70; N: 18.57.

2-Phenyl-7-(thien-2-yl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (11c). Light brown powder: (253 mg, 91%), mp 198-200 °C (2-PrOH); ¹H NMR (400 MHz, DMSO-*d*₆) δ_H 8.87 (d, *J* 5.0 Hz, 1H), 8.65 (dd, *J* 4.0, 1.2 Hz, 1H), 8.39–8.31 (m, 2H), 8.24 (dd, *J* 5.0, 1.2 Hz, 1H), 7.99 (d, *J* 5.0 Hz, 1H), 7.61 (qt, *J* 5.0, 2.0 Hz, 3H), 7.47 (dd, *J* 5.0, 3.9 Hz, 1H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ_C 164.0, 156.3, 154.1, 140.7, 135.6, 133.2, 130.8, 130.1, 129.9, 129.0, 128.4, 127.0, 106.0. Anal. Calcd. for C₁₅H₁₀N₄S: C: 64.73; H: 3.62; N: 20.13; S: 11.52. Found C: 64.79; H: 3.67; N: 20.19; S: 11.49.

7-[4-(*N,N*-Dimethylaminophenyl)]-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine 11d. Yellow needles: (290 mg, 92%), mp 213-214 °C (2-PrOH); ¹H NMR (400 MHz, DMSO-*d*₆) δ_H 8.76 (d, *J* 5.0 Hz, 1H), 8.46–8.38 (m, 2H), 8.32–8.24 (m, 2H), 7.63–7.51 (m, 4H), 6.98–6.90 (m, 2H), 3.09 (s, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ_C 163.8, 157.1, 154.0, 152.4, 147.0, 131.1, 130.53, 130.51, 128.9, 126.9, 115.2, 111.3, 106.7, 39.6. Anal. Calcd. for C₁₉H₁₇N₅: C: 72.36; H: 5.43; N: 22.21. Found C: 72.29; H: 5.47; N: 22.19.

2,5,7-Trisubstituted [1,2,4]triazolo[1,5-*a*]pyrimidines (12aa-dd) (General procedure). Grignard reagent solution was prepared from magnesium powder (36 mg, 1.5 mmol) and the appropriate bromo(het)arene (1.5 mmol) in THF (10 mL). It was cooled to -78 °C and the corresponding 7-substituted-TAP **6** (1 mmol) was added. After 1 h the bath temperature was elevated to 50 °C, and the reaction mixture was stirred for another 2 h. Then the oxygen atmosphere was created and kept for 2 h. When the reaction was completed, the flask was cooled, and the reaction mixture was charged with cold water (2-3 mL) and ammonium chloride (107 mg, 2 mmol). The volatiles were then distilled off *in vacuo*, the residue was filtered, washed with cold water and hexane, dried and recrystallized to afford the desired products **12aa-dd**.

2,5,7-Triphenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (12aa). Colorless powder: (220 mg, 63%), mp 176-178 °C (2-PrOH); ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 8.47–8.42 (m, 2H), 8.42–8.37 (m, 2H), 8.29–8.23 (m, 2H), 8.17 (s, 1H), 7.75–7.67 (m, 3H), 7.65–7.61 (m, 3H), 7.61–7.52 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ_C 166.1, 161.0, 157.4, 147.5, 136.5, 131.7, 131.2, 130.6, 130.5, 130.3, 129.4, 129.0, 128.9, 128.6, 127.7, 127.6, 106.1. Anal. Calcd. for C₂₃H₁₆N₄: C: 79.17; H: 4.63; N: 16.08. Found C: 79.21; H: 4.67; N: 16.09.

5-(4-Methoxyphenyl)-2,7-diphenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (12ab). Colorless powder: (313 mg, 53%), mp 232-233 °C (MeCN); ¹H NMR (400 MHz, DMSO-*d*₆) δ_H 8.44–8.40 (m, 2H), 8.38–8.34 (m, 2H), 8.28–8.20 (m, 2H), 8.10 (s, 1H), 7.74–7.66 (m, 3H), 7.62–7.51 (m, 3H), 7.20–7.12 (m, 2H), 3.89 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ_C 165.7, 162.3, 160.6, 157.3, 147.2, 131.6, 130.68, 130.65, 130.4, 129.4, 129.3, 128.9, 128.8, 128.6, 127.5, 114.4, 105.6, 55.5. Anal. Calcd. for C₂₄H₁₈N₄O: C: 76.17; H: 4.79; N: 14.81. Found C: 76.22; H: 4.74; N: 14.84.

2,7-Diphenyl-5-(thien-2-yl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (12ac). Pale powder: (294 mg, 83%), mp 191-193 °C (2-PrOH); ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 8.38–8.30 (m, 3H), 8.25–8.19 (m, 2H), 8.14 (s, 1H), 7.94 (dd, *J* 5.0, 1.1 Hz, 1H), 7.75–7.66 (m, 3H), 7.61–7.51 (m, 3H), 7.32 (dd, *J* 5.0, 3.7 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ_C 165.9, 157.0, 156.0, 147.4, 142.4, 131.7, 131.4, 130.6, 130.5, 130.1, 129.4, 128.9, 128.6, 128.52, 128.45, 127.5, 105.1. Anal. Calcd. for C₂₁H₁₄N₄S: C: 71.17; H: 3.98; N: 15.81; S: 9.05. Found C: 71.19; H: 3.96; N: 15.88; S: 9.03.

5-[4-(*N,N*-Dimethylaminophenyl)]-2,7-diphenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (12ad). Yellow powder: (250 mg, 64%), mp 241-243 °C (MeCN); ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 8.37–8.27 (m, 4H), 8.28–8.18 (m, 2H), 7.98 (s, 1H), 7.72–7.65 (m, 3H), 7.60–7.50 (m, 3H), 6.90–6.83 (m, 2H), 3.06 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ_C 165.3, 160.9, 152.4, 146.6, 131.3, 131.0, 130.8, 130.2, 129.4, 129.0, 128.9, 128.7, 128.5, 127.4, 123.5, 111.7, 105.1, 40.1. Anal. Calcd. for C₂₅H₂₁N₅: C: 76.70; H: 5.41; N: 17.89. Found C: 76.72; H: 5.38; N: 17.85.

7-(4-Methoxyphenyl)-2,5-diphenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (12ba). Pale powder: (220 mg, 58%), mp 207-209 °C (MeCN); ¹H NMR (400 MHz, DMSO-*d*₆) δ_H 8.46 (dd, *J* 26.0, 6.4 Hz, 4H), 8.31–8.24 (m, 2H), 8.13 (s, 1H), 7.65–7.55 (m, 6H), 7.26 (d, *J* 8.5 Hz, 2H), 3.93 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ_C 165.9, 162.4, 160.8, 157.5, 147.2, 136.7, 131.3, 131.1, 130.7, 130.4, 129.0, 128.6, 127.7, 127.5, 122.4, 114.3, 105.1, 55.6. Anal. Calcd. for C₂₄H₁₈N₄O: C: 76.17; H: 4.79; N: 14.81. Found C: 76.21; H: 4.77; N: 14.79.

5,7-Bis(4-methoxyphenyl)-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (12bb). Pale powder: (224 mg, 55%), mp 200-203 °C (MeCN); ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 8.49–8.44 (m, 2H), 8.43–8.38 (m, 2H), 8.29–8.22 (m, 2H), 8.05 (s, 1H), 7.62–7.51 (m, 3H), 7.29–7.21 (m, 2H), 7.19–7.11 (m, 2H), 3.92 (s, 3H), 3.88 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ_C 165.6, 162.2, 162.2, 160.4, 157.5, 146.9, 131.2, 130.8, 130.3, 129.3, 129.1, 128.5, 127.5, 122.6, 114.3, 114.2, 104.5, 55.5, 55.4. Anal. Calcd. for C₂₀H₂₀N₄O₂: C: 73.51; H: 4.94; N: 13.72. Found C: 73.57; H: 4.89; N: 13.79.

7-(4-Methoxyphenyl)-2-phenyl-5-(thien-2-yl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (12bc). Light brown powder: (245 mg, 64%), mp 221-223 °C (MeCN); ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 8.47–8.38 (m, 2H), 8.35 (dd, *J* 3.8, 1.2 Hz, 1H), 8.29–8.21 (m, 2H), 8.11 (s, 1H), 7.93 (dd, *J* 5.0, 1.1 Hz, 1H), 7.63–7.51 (m, 3H), 7.31 (dd, *J* 5.0, 3.7 Hz, 1H), 7.30–7.22 (m, 2H), 3.93 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ_C 165.8, 162.4, 157.1, 155.9, 147.1, 142.5, 131.3, 131.2, 130.7, 130.4, 128.6, 128.4, 128.3, 127.5, 122.2, 114.3, 104.1, 55.6. Anal. Calcd. for C₂₂H₁₆N₄OS: C: 68.73; H: 4.20; N: 14.57; S: 8.34. Found C: 68.78; H: 4.18; N: 14.60; S: 8.29.

7-(4-Methoxyphenyl)-5-[4-(*N,N*-dimethylaminophenyl)]-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (12bd). Orange powder: (253 mg, 60%), mp 211-214 °C [Chromatographed with EtOAc/hexane (50:50)]; ¹H NMR (400 MHz, DMSO-*d*₆) δ_H 8.45–8.38 (m, 2H), 8.33–8.20 (m, 4H), 7.94 (s, 1H), 7.62–7.49 (m, 3H), 7.27–7.20 (m, 2H), 6.86 (d, *J* 9.1 Hz, 2H), 3.92 (s, 3H), 3.06 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ_C 162.2, 160.8, 151.7, 146.5, 131.3, 131.3, 131.2, 130.4, 129.1, 128.6, 128.6, 127.5, 122.5, 114.3, 114.2, 112.5, 104.5, 55.5, 40.7. Anal. Calcd. for C₂₆H₂₃N₅O: C: 74.09; H: 5.50; N: 16.62. Found C: 74.12; H: 5.53; N: 16.56.

2,5-Diphenyl-7-(thien-2-yl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (12ca). Pale powder: (269 mg, 76%), mp 186-187 °C (2-PrOH); ¹H NMR (500 MHz, CDCl₃) δ_H 8.57 (dd, *J* 3.9, 1.2 Hz, 1H), 8.51–8.45 (m, 2H), 8.32–8.24 (m, 2H), 7.87–7.79 (m, 2H), 7.60–7.48 (m, 6H), 7.35 (dd, *J* 5.0, 3.9 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ_C 166.8–164.4 (m), 160.7, 158.2–153.1 (m), 141.0, 136.6, 133.1, 132.6, 131.3, 131.2, 130.7, 130.5, 129.0, 128.7, 128.4, 127.7,

102.7, 77.2. Anal. Calcd. for C₂₁H₁₄N₄S: C: 71.17; H: 3.98; N: 15.81; S: 9.05. Found C: 71.14; H: 4.01; N: 15.86; S: 9.09.

5-(4-Methoxyphenyl)-2-phenyl-7-(thien-2-yl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (12cb). Pale powder: (234 mg, 61%), mp 211–213 °C (MeCN); ¹H NMR (400 MHz, DMSO-*d*₆) δ_H 8.83 (d, *J* 3.9 Hz, 1H), 8.46–8.39 (m, 3H), 8.37–8.30 (m, 2H), 8.23 (d, *J* 5.0 Hz, 1H), 7.65–7.56 (m, 3H), 7.52–7.45 (m, 1H), 7.20–7.13 (m, 2H), 3.89 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ_C 165.7, 162.2, 160.1, 157.1, 140.7, 132.7, 132.4, 131.5, 130.7, 130.5, 129.3, 129.0, 128.7, 128.3, 127.6, 114.3, 102.0, 55.5. Anal. Calcd. for C₂₂H₁₆N₄OS: C: 68.73; H: 4.20; N: 14.57; S: 8.34. Found C: 68.65; H: 4.18; N: 14.59; S: 8.32.

2-Phenyl-5,7-di(thien-2-yl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (12cc). Light brown powder: (205 mg, 57%), mp 227–229 °C (2-PrOH); ¹H NMR (400 MHz, DMSO-*d*₆) δ_H 8.79 (dd, *J* 4.0, 1.2 Hz, 1H), 8.48 (s, 1H), 8.39 (d, *J* 3.8 Hz, 1H), 8.36–8.29 (m, 2H), 8.25 (dd, *J* 5.1, 1.1 Hz, 1H), 7.96–7.89 (m, 1H), 7.67–7.54 (m, 3H), 7.49 (t, *J* 4.5 Hz, 1H), 7.34 (dd, *J* 5.0, 3.7 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ_C 156.0, 142.1, 141.0, 133.5, 133.4, 133.0, 131.6, 131.5, 130.9, 130.76, 130.75, 129.8, 128.8, 128.6, 128.4, 127.7, 102.0. Anal. Calcd. for C₁₉H₁₂N₅S₂: C: 63.31; H: 3.36; N: 15.54; S: 17.79. Found C: 63.25; H: 3.38; N: 15.49; S: 17.82.

7-(Thien-2-yl)-5-[4-(*N,N*-dimethylaminophenyl)]-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (12cd). Orange powder: (230 mg, 58%), mp 203–205 °C [Chromatographed with EtOAc/hexane (50:50)]; ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 8.80 (dd, *J* 4.0, 1.2 Hz, 1H), 8.34–8.29 (m, 5H), 8.20 (dd, *J* 5.0, 1.1 Hz, 1H), 7.63–7.56 (m, 3H), 7.47 (dd, *J* 5.1, 3.9 Hz, 1H), 6.91–6.83 (m, 2H), 3.06 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ_C 165.1, 160.5, 157.2, 152.1, 140.1, 132.1, 132.0, 131.7, 130.8, 130.6, 130.3, 128.9, 128.7, 128.6, 128.6, 111.8, 101.6, 40.2. Anal. Calcd. for C₂₃H₁₉N₅S: C: 69.50; H: 4.82; N: 17.62; S: 8.07. Found C: 69.52; H: 4.85; N: 17.68; S: 8.01.

7-[4-(*N,N*-Dimethylaminophenyl)]-2,5-diphenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (12da). Yellow needles: (211 mg, 54%), mp 230–233 °C (MeCN); ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 8.55–8.49 (m, 2H), 8.44–8.38 (m, 2H), 8.32–8.26 (m, 2H), 8.06 (s, 1H), 7.65–7.52 (m, 20H), 6.98–6.93 (m, 2H), 3.10 (s, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ_C 164.3, 159.7, 157.1, 152.3, 147.2, 136.6, 131.3, 130.9, 130.6, 130.4, 128.9, 127.6, 126.9, 126.8, 115.7, 111.2, 103.7, 39.6. Anal. Calcd. for C₂₅H₂₁N₅: C: 76.70; H: 5.41; N: 17.89. Found C: 76.76; H: 5.47; N: 17.83.

7-[4-(*N,N*-Dimethylaminophenyl)]-5-(4-methoxyphenyl)-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (12db). Orange powder: (219 mg, 52%), mp 216–217 °C (MeCN); ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 8.51–8.45 (m, 2H), 8.41–8.35 (m, 2H), 8.30–8.24 (m, 2H), 7.97 (s, 1H), 7.62–7.51 (m, 3H), 7.17–7.11 (m, 2H), 6.97–6.91 (m, 2H), 3.88 (s, 3H), 3.09 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ_C 162.1, 160.3, 152.1, 147.3, 131.1, 131.0, 130.5, 129.3, 129.1, 128.8, 128.6, 128.5, 127.6, 127.5, 114.2, 111.7, 103.5, 55.4, 40.3. Anal. Calcd. for C₂₆H₂₃N₅O: C: 74.09; H: 5.50; N: 16.62. Found C: 74.01; H: 5.56; N: 16.59.

7-[4-(*N,N*-Dimethylaminophenyl)]-5-(thien-2-yl)-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (12dc). Dark yellow powder: (210 mg, 53%), mp 261–263 °C (Chromatographed with EtOAc/hexane (50:50)); ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 8.52–8.45 (m, 2H), 8.33 (dd, *J* 3.8, 1.1 Hz, 1H), 8.31–8.22 (m, 2H), 8.04 (s, 1H), 7.89 (dd, *J* 5.0, 1.1 Hz, 1H), 7.62–7.51 (m, 7H), 7.30 (dd, *J* 5.0, 3.7 Hz, 1H), 6.99–6.91 (m, 2H), 3.10 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ_C 165.4, 157.4, 155.5, 152.5, 147.6, 143.0, 131.0, 131.0, 130.6, 130.2, 128.5, 128.3, 127.9, 127.5, 116.5, 111.4, 102.7, 40.0. Anal. Calcd. for C₂₃H₁₉N₅S: C: 69.50; H: 4.82; N: 17.62; S: 8.07. Found C: 69.45; H: 4.80; N: 17.59; S: 8.12.

5,7-Bis[4-(*N,N*-dimethylaminophenyl)]-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (12dd). Orange powder: (243 mg, 56%), mp 205–207 °C (Chromatographed with EtOAc/hexane (50:50)); ¹H NMR (500 MHz, DMSO-*d*₆) δ_H 8.46–8.40 (m, 2H), 8.30–8.22 (m, 4H), 7.87 (s, 1H), 7.61–7.50 (m, 3H), 6.97–6.91 (m, 2H), 6.88–6.83 (m, 2H), 3.09 (s, 12H), 3.05 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ_C 164.8, 160.4, 157.8, 152.2, 152.1, 146.9, 131.3, 130.8, 129.9, 128.9, 128.4, 127.4, 124.1, 117.2, 111.6, 111.3, 102.8, 40.12, 40.06. Anal. Calcd. for C₂₇H₂₆N₆: C: 74.63; H: 6.03; N: 19.34. Found C: 74.54; H: 6.07; N: 19.39.

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Supplementary Material

Supplementary material contains: copies of ^1H and ^{13}C NMR spectra of all synthesized compounds, 2D NMR HSQC/HMBC spectra for **11d**, **12bb**, **12da**, copies of absorption, excitation, emission and IR spectra, CV curves, of **11a-d** and **12aa-dd** compounds.

References

1. Achelle, S.; Baudequin, C. *Targets Heterocycl. Syst.* **2013**, *17*, 1–34.
ISBN: 9788886208512
2. Kim, J.; Chae, S.; Yi, A.; Kim, M.; Kim, H. J.; Suh, H. *Macromol. Res.* **2018**, *26*, 438–445.
<https://doi.org/10.1007/s13233-018-6063-7>
3. Sun, H.; Liu, D.; Wang, T.; Li, P.; Bridgmohan, C. N.; Li, W.; Lu, T.; Hu, W.; Wang, L.; Zhou, X. *Org. Electron.* **2018**, *61*, 35–45.
<https://doi.org/10.1016/j.orgel.2018.06.045>
4. Li, B.; Li, Z.; Hu, T.; Zhang, Y.; Wang, Y.; Yi, Y.; Guo, F.; Zhao, L. *J. Mater. Chem. C* **2018**, *6*, 2351–2359.
<https://doi.org/10.1039/c7tc05746f>
5. Li, S. W.; Yu, C. H.; Ko, C. L.; Chatterjee, T.; Hung, W. Y.; Wong, K. T. *ACS Appl. Mater. Interfaces* **2018**, *10*, 12930–12936.
<https://doi.org/10.1021/acsami.8b02766>
6. Jang, S.; Han, S. H.; Lee, J. Y.; Lee, Y. *Synth. Met.* **2018**, *239*, 43–50.
<https://doi.org/10.1016/j.synthmet.2018.03.002>
7. Nakao, K.; Sasabe, H.; Komatsu, R.; Hayasaka, Y.; Ohsawa, T.; Kido, J. *Adv. Opt. Mater.* **2017**, *5*, 1600843 (Article No.).
<https://doi.org/10.1002/adom.201600843>
8. Nosova, E. V.; Achelle, S.; Lipunova, G. N.; Charushin, V. N.; Rennes, F. *Russ. Chem. Rev.* **2019**, *88*, 1128–1178.
<https://doi.org/10.1070/RCR4887>
9. Zak, P. P.; Lapina, V. A.; Pavich, T. A.; Trofimov, A. V.; Trofimova, N. N.; Tsaplev, Y. B. *Russ. Chem. Rev.* **2017**, *86*, 831–844.
<https://doi.org/10.1070/rcr4735>
10. Verbitskiy, E. V.; Baranova, A. A.; Lugovik, K. I.; Khokhlov, K. O.; Cheprakova, E. M.; Shafikov, M. Z.; Rusinov, G. L.; Chupakhin, O. N.; Charushin, V. N. *Dyes Pigm.* **2017**, *137*, 360–371.
<https://doi.org/10.1016/j.dyepig.2016.10.039>
11. Rasputin, N. A.; Demina, N. S.; Irgashev, R. A.; Rusinov, G. L.; Chupakhin, O. N.; Charushin, V. N. *Tetrahedron* **2017**, *73*, 5500–5508.
<https://doi.org/10.1016/j.tet.2017.07.042>
12. Miwa, T.; Kubo, S.; Shizu, K.; Komino, T.; Adachi, C.; Kaji, H. *Sci. Rep.* **2017**, *7*, 284 (Article No.).

- <https://doi.org/10.1038/s41598-017-00368-5>
13. Lee, S. Y.; Adachi, C.; Yasuda, T. *Adv. Mater.* **2016**, *28*, 4625–4625.
<https://doi.org/10.1002/adma.201670160>
14. Verbitskiy, E. V.; Rusinov, G. L.; Chupakhin, O. N.; Charushin, V. N. *Synthesis* **2018**, *50*, 193–210.
<https://doi.org/10.1055/s-0036-1589520>
15. Chupakhin, O. N.; Charushin, V. N. *Tetrahedron Lett.* **2016**, *57*, 2665–2672.
<https://doi.org/10.1016/j.tetlet.2016.04.084>
16. Chupakhin, O. N.; Charushin, V. N. *Pure Appl. Chem.* **2011**, *89*, 1195–1208.
<https://doi.org/10.1515/pac-2017-0108>
17. Wu, J.; Cheng, Y.; Lan, J.; Wu, D.; Qian, S.; Yan, L.; He, Z.; Li, X.; Wang, K.; Zou, B.; You, J. *J. Am. Chem. Soc.* **2016**, *138*, 12803–12812.
<https://doi.org/10.1021/jacs.6b03890>
18. Dolzhenko, A. V.; Dolzhenko, A. V.; Chui, W.-K. *Tetrahedron* **2007**, *63*, 12888–12895.
<https://doi.org/10.1016/J.TET.2007.10.046>
19. Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. *Adv. Mater.* **2011**, *23*, 2367–2371.
<https://doi.org/10.1002/adma.201004554>

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