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Synthesis of 4-aryl-, 2,4-diaryl- and 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines by a combination of the Suzuki cross-coupling and *N*-arylation reactions

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ABSTRACT

A simple and facile synthesis of novel 4-aryl-2-chloro-, 2,4-diaryl- and 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines with various aryl and heteroaryl assemblies in the heterocyclic framework by a combination of Suzuki cross-coupling and *N*-arylation reactions of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine with arylboronic acids and haloarenes are described. A majority of the synthesized compounds were found to emit in a near UV-blue spectral range with fluorescence quantum yields up to 67%. The impact of aryl groups attached to the pyrrole ring of pyrrolopyrimidine derivatives on optical properties is discussed.

1. Introduction

The introduction of a heteroaryl moiety into extended π-systems often brings about a number of interesting properties that are useful in the development of advanced electronic and photonic materials.[1] Owing to the light-emitting,[2] self-assembling[3] and complex forming[4] properties with metal ions or organic molecules such materials are of interest in biological, chemical and materials science. Otherwise, arylpyrrolo[2,3-*d*]pyrimidines were found to display a wide range of biological activities, such as antimicrobial,[5] inhibition of protein kinases[6] and dihydrofolate reductase,[7] antagonist effects to receptors,[8] cytostatic and antiproliferative effects,[9] etc. Although the parent pyrrolo[2,3-*d*]pyrimidine is known to possess fluorescence properties[10] and some derivatives were demonstrated to be suitable for probing the structure of DNA,[11] exploitation of this heteoaromatic core in functional π-systems is insufficient. Only recently, we have found that pyrrolo[2,3-*d*]pyrimidine-core based oligoarylenes possess interesting fluorescent properties.[12] To develop more efficient light-emitting materials we report herein on the sequential assembly of π-systems, such as aryl groups, onto the pyrrolo[2,3-*d*]pyrimidine core as a useful method for the construction of mono-, di- and triarylpyrrolo[2,3-*d*]pyrimidines bearing various aryl branches in positions 2, 4 and 7 of the heterocycle. Our synthetic strategy towards the target compounds was based on a combination of the palladium-catalyzed Suzuki cross-coupling reaction of 2,4-dichloropyrolo[2,3-*d*]pyrimidine (**1**) with arylboronic acids and copper-catalyzed *N*-arylations of pyrrolo[2,3-*d*]pyrimidines with aryl halides. The Suzuki cross-coupling reaction has received much attention in the past years due to its versatility in the C–C bond formation and construction of biaryl skeleton.[13] However, a literature survey on the arylpyrrolo[2,3-*d*]pyrimidines revealed that the Suzuki reaction in a pyrrolo[2,3-*d*]pyrimidine series is explored insufficiently. To the best of our knowledge, only few examples were reported on the application of the palladium-catalyzed cross-coupling reactions for the arylation of a pyrrole[6b,14] and pyrimidine rings[9a,12,15] of pyrrolo[2,3-*d*]pyrimidine and there were no data on a site-selectivity of the Suzuki coupling of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine.

2. Results and discussion

As mentioned above, our synthetic strategy towards the target compounds was based on a combination of the palladium-catalyzed Suzuki cross-coupling reactions of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine[16] (**1**) with arylboronic acids and copper-catalyzed *N*-arylations of 7*H*-pyrrolo[2,3-*d*]pyrimidines with aryl halides. Therefore, a set of seven phenylboronic acids (**2a**–**g**) and four phenyl iodides and bromides (**3a**–**d**) has been chosen (Fig. 1) as the reagents for the particular arylations in different position.

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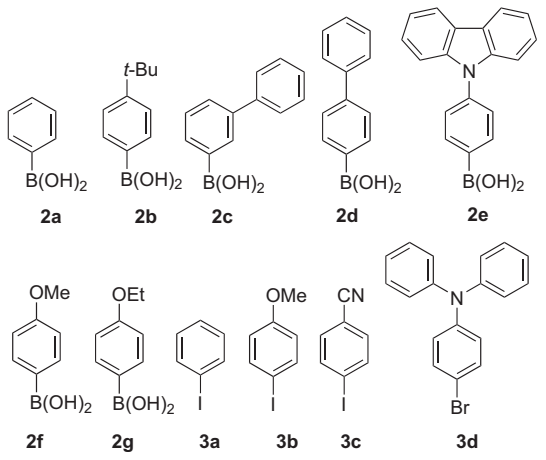
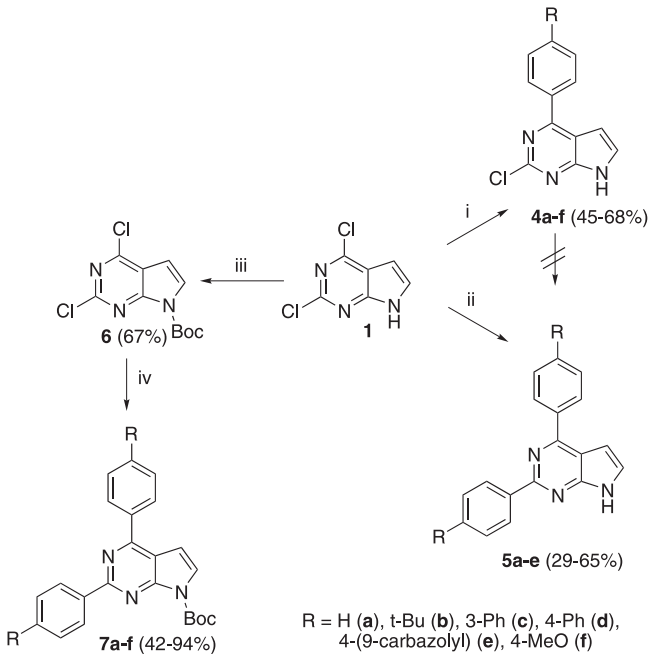


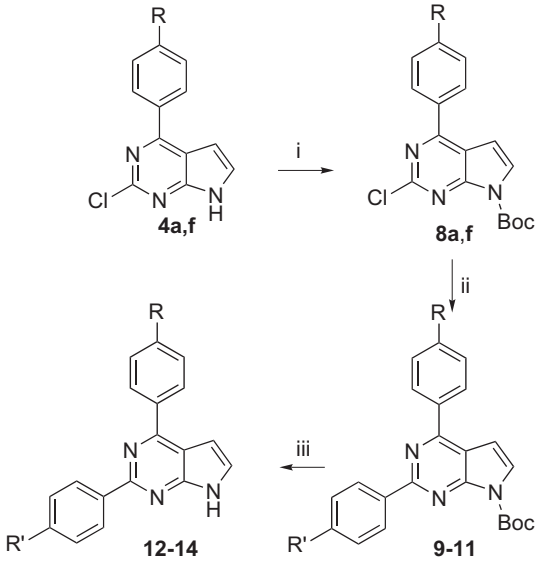
Fig. 1. Set of arylboronic acids and aryl halides.

We have found that the Suzuki coupling of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine (**1**) with arylboronic acids **2** depending on the amount of arylboronic acid and reaction conditions gives 4-aryl-2-chloro- (**4a**–**f**) or 2,4-diarylpyrrolo[2,3-*d*]pyrimidines (**5a**–**e**), respectively[12] (Scheme 1).



Scheme 1. Reagents and conditions: (i) 2 mol % $Pd(OAc)_2$, 4 mol % PCy_2(2-biphenyl), 1.2 equiv $ArB(OH)_2$, 2.4 equiv K_3PO_4, 1,4-dioxane, 60–70 °C, Ar; (ii) 2 mol % $Pd(OAc)_2$, 4 mol % PCy_2(2-biphenyl), 2.4 equiv $ArB(OH)_2$, 4.8 equiv K_3PO_4, 1,4-dioxane, Δ, Ar; (iii) Boc_2O, DMAP, DIPEA, CH_2Cl_2; (iv) 2 mol % $Pd(OAc)_2$, 4 mol % PCy_2(2-biphenyl), 2.4 equiv $ArB(OH)_2$, 4.8 equiv K_3PO_4, 1,4-dioxane, Δ, Ar.

Mono cross-coupling reaction of **1** with arylboronic acids **2** to give compounds **4a**–**f** was accomplished at 60–70 °C in 1,4-dioxane using 1.2 equiv of the corresponding boronic acid and $Pd(OAc)_2/PCy_2$(2-biphenyl)/K_3PO_4 as a catalyst system. Reflux of **1** with 2.4 equiv of **2** using the same catalytic system led to the corresponding 2,4-diarylpyrrolo[2,3-*d*]pyrimidines **5a**–**e** in moderate yields. Low yield (29%) of **5d** was obtained mainly because of the formation in considerable amount of a side-product—*p*-quaterphenyl. The presence of a *N*(7)-Boc group in **6** increased the reactivity of the 2-chlorine group and compounds **7a**–**f** were obtained in higher yields. However, all attempts to obtain 4-aryl-2-chloro-7-*tert*-butoxycarbonylpyrrolo[2,3-*d*]pyrimidines by the reaction of **6** with arylboronic acids **2** failed. In order to obtain 2,4-diarylpyrrolopyrimidines with different aryl groups the second Suzuki coupling of 4-aryl-2-chloropyrrolo[2,3-*d*]pyrimidines (**4**) with arylboronic acids was investigated. But compounds **4** were found to be inert to the selected arylboronic acids although various catalyst systems were examined. The catalysts and ligands employed were $PdCl_2(PPh_3)_2$, $PdCl_2$(dppf), $Pd(OAc)_2$ and PCy_2(2-biphenyl), PCy_2[2′,6′-$(MeO)_2$-2-biphenyl], P(*t*-Bu)$_2$(2-biphenyl), P(*i*-Pr)$_2$(2-biphenyl) and dppf, correspondingly. Otherwise, the Suzuki coupling of the *N*(7)-Boc derivatives **8a**,**f**, obtained by the reaction of **4a**,**f** with Boc_2O in the presence of DMAP and DIPEA, with the selected arylboronic acids furnished pyrrolopyrimidines **9**–**11** bearing different aryl groups in positions 2 and 4 of heterocyclic moiety in good yields (Scheme 2, Table 1). The second Suzuki coupling was accomplished by reflux of the reaction mixture in 1,4-dioxane for 4–7 h in the presence of $Pd(OAc)_2/PCy_2$(2-biphenyl)/K_3PO_4 as a catalyst system. Deprotection of *N*(7)-Boc group with hydrochloric acid in acetone or TFA in dichloromethane afforded the corresponding 2,4-diarylpyrrolopyrimidines **12**–**14**.

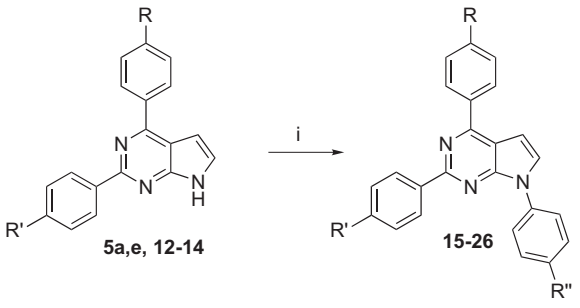


Scheme 2. Reagents and conditions: (i) Boc_2O, DMAP, DIPEA, CH_2Cl_2; (ii) 2 mol % $Pd(OAc)_2$, 4 mol % PCy_2(2-biphenyl), 1.2 equiv $ArB(OH)_2$, 2.4 equiv K_3PO_4, 1,4-dioxane, Δ, Ar; (iii) HCl, Me_2CO, Δ or TFA, DCM, rt.

Table 1
Preparation of compounds **8a**,**f** and **9**–**14**

Compd	R	R′	Yield, %
8a	H	—	61
8f	4-MeO	—	80
9	H	4-Ph	76
10	H	4-EtO	79
11	4-MeO	4-EtO	69
12	H	4-Ph	73
13	H	4-EtO	80
14	4-MeO	4-EtO	77

The obtained **5a**, **5e** and **12**–**14** were subjected to *N*-arylation reaction (Scheme 3). CuI/(±)-*trans*-1,2-diaminocyclohexane/K_3PO_4 was used as a catalyst system of choice.[17] Employing other ligands and bases in the reaction gave worse results. For example, the reaction of **5e** with iodobenzene using CuI/(±)-*trans*-1,2-diaminocyclohexane/K_3PO_4 as a catalyst system furnished **22** in 85% yield (Table 2, entry 8), while using in the reaction CuI/1,10-phenanthroline/Cs_2CO_3 as a catalyst system gave the target



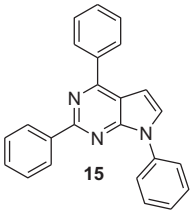
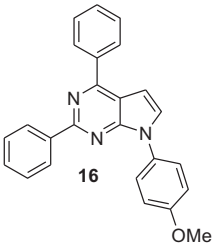
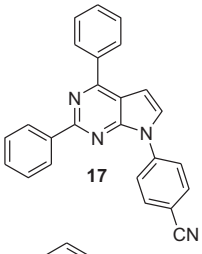
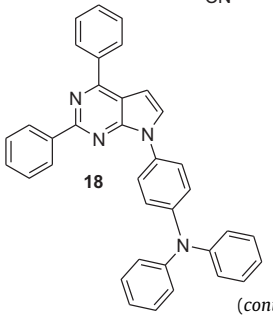
Scheme 3. Reagents and conditions: (i) 4-R″C_6H_4-I(Br), CuI, (±)-*trans*-1,2-diaminocyclohexane, K_3PO_4, 1,4-dioxane, Δ, Ar.

compound **22** in 49% yield (experimental, method B). To achieve full conversion of compounds **5a**, **5e** and **12**–**14** in the *N*-arylation reaction an amount of CuI ranging from 3 mol % to 10 mol % was used (Table 2). The reaction proceeded at reflux temperature of dioxane and worked well with aryl iodides and bromides bearing electron-donating or electron-withdrawing groups. It should be noted that better results of *N*-arylation reaction were obtained when the indicated amount of CuI was added to the reaction mixture in portions during the reaction. The yields of 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines (**15**–**26**) varied from good to excellent (Table 2). Lower yields of compounds **23**–**25** (Table 2, entries 9–11) were obtained, presumably because of more complex their purification by column chromatography.

Taking into account that introduction of aryl groups by the Suzuki coupling into position 2 of 4-arylpyrrolopyrimidines was successful only when *N*(7)-protected derivatives were employed, it was of interest to evaluate the possibility of the synthesis of 2,4,7-triarylpyrrolo pyrimidines by an alternate and shorter route. This is exemplified by the synthesis of compound **26** by *N*-arylation of **4f** with iodobenzene and following Suzuki coupling of the obtained **27** with boronic acid **2g** (method B) (Scheme 4). Total conversion of **4f** in its *N*-arylation reaction with iodobenzene to give **27** was achieved after 33 h and using 12 mol % CuI and 30 mol % (±)-*trans*-diaminocyclohexane. However, a complex mixture of products was formed in the reaction and compound **27** was isolated only in 37% yield.

The Suzuki coupling of **27** with 4-ethoxyphenylboronic acid gave the desired **26** in 64% yield. It is worthy of note that the latter reaction appeared to be much slower (20 h) than that of *N*(7)-Boc derivative **8f** with the same boronic acid (6 h). This supports our observation in the synthesis of **7a**–**f** that Boc group increases the reactivity of the chlorine group in the position 2 of pyrrolopyrimidine. Yield of compound **26** (24%) calculated for two reactions (Scheme 4) was considerably lower than the yield of its synthesis

Table 2
Preparation of 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines (**15**–**26**)

Entry	Compd **5a**,**e** or **12**–**14**	Aryl halide **3a**–**d**	CuI, mol %	Reaction time, hr	Product **15**–**26**	Yield, %
1	**5a**	**3a**	4	13	 **15**	94
2	**5a**	**3b**	5	12	 **16** OMe	92
3	**5a**	**3c**	5	12	 **17** CN	82
4	**5a**	**3d**	6	22	 **18**	72

(*continued on next page*)

Table 2 (*continued*)

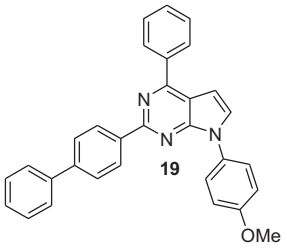
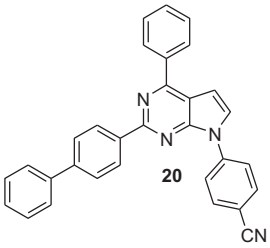
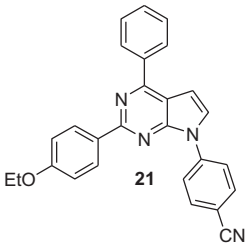
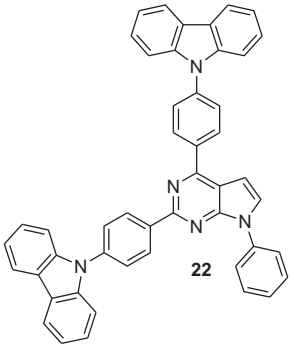
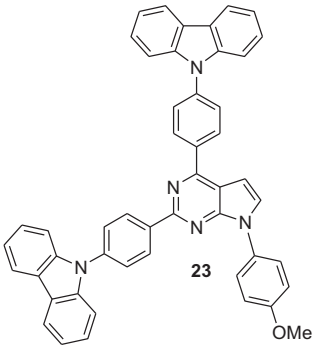
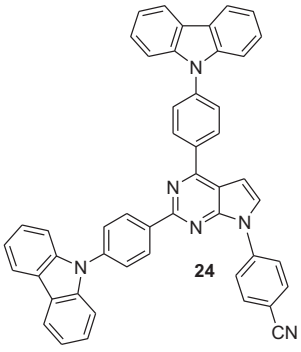
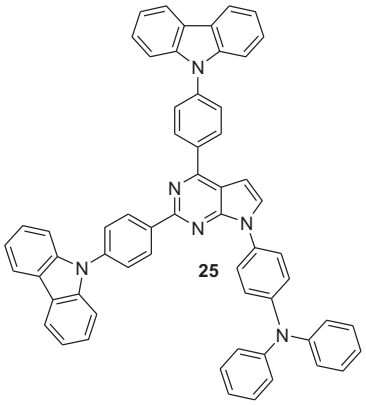
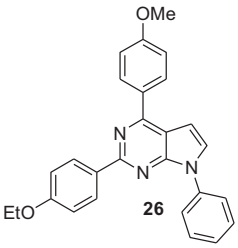
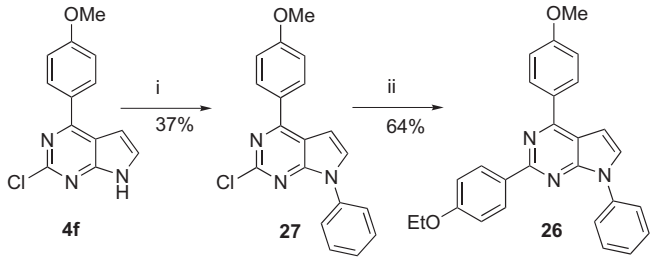
Entry	Compd **5a**,**e** or **12**–**14**	Aryl halide **3a**–**d**	CuI, mol %	Reaction time, hr	Product **15**–**26**	Yield, %
5	**12**	**3b**	5	11	 **19**	93
6	**12**	**3c**	10	25	 **20**	95
7	**13**	**3c**	3	6	 **21**	90
8	**5e**	**3a**	5	10	 **22**	85
9	**5e**	**3b**	**7**	19	 **23**	51
10	**5e**	**3c**	7	22	 **24**	57

Table 2 (*continued*)

Entry	Compd **5a**,**e** or **12**–**14**	Aryl halide **3a**–**d**	CuI, mol %	Reaction time, hr	Product **15**–**26**	Yield, %
11	**5e**	**3d**	8	29	 **25**	59
12	**14**	**3a**	5	9.5	 **26**	99



Scheme 4. Reagents and conditions: (i) PhI, CuI, (±)-*trans*-1,2-diaminocyclohexane, K_3PO_4, 1,4-dioxane, Δ, Ar; (ii) 2 mol % $Pd(OAc)_2$, 4 mol % PCy_2(2-biphenyl), 1.5 equiv 4-$EtOC_6H_4B(OH)_2$, 3.0 equiv K_3PO_4, 1,4-dioxane, Δ, Ar.

using four reaction sequence (42%) including the *N*(7)-protection and deprotection reactions (Schemes 2 and 3).

Optical properties of the synthesized 2,4-diaryl- and 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines were assessed by performing absorption and fluorescence spectroscopy, fluorescence lifetime and fluorescence quantum yield measurements. Photophysical properties of the compounds **5a**–**e** and **7a**–**f** in THF solutions are discussed in our preliminary communication.[12] Absorption and fluorescence data of 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines (**15**–**26**) are summarized in Table 3. Triarylpyrrolopyrimidines **15**–**26** were found to exhibit strong UV absorption in dilute THF solution with their absorption maxima positioned below 342 nm. Aryl groups in position 7 enhances the absorption of triarylpyrrolopyrimidines as compared with the corresponding 2,4-diaryl derivatives.[12] The most prominent hyperchromic effect is observed for compounds **16**, **18**, **23**, **25** containing electron-donating methoxy and diphenylamino groups in the *N*(7)-aryl group (Table 3, entries 2, 4, 9, 11) when compared with the corresponding data of compounds **5a**,**e**.[12] Depending on the origin of aryl branches of the compounds **15**–**26** their emission maxima are located in the range of 402–539 nm with fluorescence quantum yields ranging from 2% to 40%. Substituents in the *para*-position of *N*(7)-aryl groups of the compounds have a dramatic effect on a position of their fluorescence bands. Introduction of electron-donating methoxy and diphenylamino groups (compounds **16**, **18**, **23**, and **25**) results in a significant red shift of the spectral bands. This effect for methoxy group is about 32–33 nm, whereas for diphenylamino group it amounts to 112–116 nm (Table 3, compare entry 1 with entries 2, 4 and entry 8 with entries 9, 11).

Conversely, cyano group in the *para*-position of *N*(7)-aryl groups causes a blue shift of the fluorescence bands (Table 3, compare entry 1 with entry 3). However, 7-(4-cyanophenyl)pyrrolopyrimidines **17**, **20**, **24** exhibit a slightly better fluorescence quantum yield than corresponding 7-(4-methoxyphenyl) derivatives **16**, **19**, **23** (Table 3). Comparing the fluorescence quantum yields of pyrrolopyrimidines **15**–**26** with those obtained for corresponding compounds **5a**–**e**[12] it can be concluded that aryl groups in the position 7 of pyrrolo[2,3-*d*]pyrimidine reduce fluorescence quantum yield. Especially significant drop of fluorescence is observed for compounds **18**, **25** containing 4-(diphenylamino)phenyl group at the nitrogen atom of the pyrrole ring (Table 3, entries 4, 11). Considering the fluorescence lifetimes estimated in THF solutions of the studied compounds it is seen that most of them span the range from 2.1 to 4.6 ns, which is typical for fluorescent organic molecules featuring significant radiative probability. Exception is observed for 7-(4-methoxyphenyl)pyrrolopyrimidines **16**, **19** and **23**, which demonstrate prolonged fluorescence decay times ranging from 10.4 to 12.2 ns (Table 3, entries 2, 5, 9).

3. Conclusions

In summary, we have developed a simple synthetic strategy that permits the assembly of aromatic π-systems onto a pyrrolo[2,3-*d*]pyrimidine core in a programmable and diversity-oriented format. The investigation of synthetic routes for the preparation of 2,4-diaryl- and 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines bearing different aryl branches revealed the necessity of protection–deprotection methodology of *N*(7)-position of pyrrolo[2,3-*d*]pyrimidine. The vast majority of the synthesized 2,4-diaryl- and

Table 3
UV absorption and PL data of 2,4,7-triarylpyrrolo-[2,3-*d*]pyrimidines (**15**–**26**) in 10^{-5} THF solution

Entry	Compd	λ_{abs}, nm	ε, l mol^{-1} cm^{-1}	λ_{em},[a] nm	Φ_F, %	τ,[b] ns
1	**15**	256	42,432	416	30	4.6
		327	10,759			
2	**16**	210	116,315	448	21	12.2
		259	100,284			
		341	20,855			
3	**17**	210	51,091	403	23	2.6
		265	54,001			
		292	26,948			
		326	15,588			
4	**18**	210	80,942	528	4	6.5
		267	41,473			
		308	39,999			
5	**19**	242	13,928	449	30	10.6
		260	17,523			
		297	20,932			
		344	7897			
6	**20**	280	28,639	402	34	2.33
		332	13,226			
7	**21**	235	10,753	408	23	2.14
		275	27,097			
		324	9602			
8	**22**	210	83,354	423	36	3.7
		236	95,604			
		254	73,364			
		281	40,217			
		292	40,074			
		342	40,627			
9	**23**	210	80,911	456	20	10.4
		237	97,694			
		255	71,874			
		292	44,901			
		342	41,076			
10	**24**	210	121,627	438	40	3.9
		236	99,333			
		256	76,639			
		284	54,569			
		291	53,153			
		342	41,433			
11	**25**	237	115,282	539	2	3.8
		255	75,367			
		293	62,155			
		341	63,694			
12	**26**	291	20,441	403	31	2.39
		330	7079			

[a] Excited at 340 nm.
[b] Fluorescence lifetime estimated at λ_{em}.

2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines exhibit near UV-blue fluorescence with emission maxima in THF solution ranging from 380 nm to 460 nm. A more detailed study of the photophysical properties of the synthesized compounds in various solvents and in the solid state and further variations of oligoarylene branches at the pyrrolo[2,3-*d*]pyrimidine are currently in progress and the results will be reported in due course.

4. Experimental section

4.1. General

Melting points were determined in open capillaries with a digital melting point IA9100 series apparatus (ThermoFischer Scientific) and are uncorrected. The absorption spectra were recorded on a Perkin–Elmer UV–vis spectrophotometer Lambda 20 in THF solutions. Fluorescence of the sample solutions was excited by 340 nm wavelength light-emitting diode and measured using back-thinned CCD spectrometer (Hamamatsu PMA-11). The fluorescence quantum yield of the solutions was estimated by comparing wavelength-integrated fluorescence intensity of the solution with that of the reference. Quinine sulfate dissolved in 0.1 M H_2SO_4 has been used as a reference.[18] Optical densities of the reference and the sample solutions were ensured to be below 0.05 to avoid reabsorption effects. Estimated quantum yield was verified by using an alternative method of an integrating sphere (Sphere Optics),[19] which was coupled to the CCD spectrometer by an optical fibre. Fluorescence transients of the sample solutions were measured using time-correlated single photon counting system (PicoQuant PicoHarp 300). IR spectra were run on a Perkin–Elmer FT-IR spectrophotometer Spectrum BX II in KBr. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA spectrometer (300 MHz and 75 MHz, respectively). HRMS spectra were obtained on a mass spectrometer Dual-ESI Q-TOF 6520 (Agilent Technologies). Column chromatography was performed using Silica gel 60 (0.040–0.063 mm) (Merck). All reactions and purity of the synthesized compounds were monitored by TLC using Silica gel 60 F_{254} aluminium plates (Merck). Visualization was accomplished by UV light. Physical and spectral characteristics of compounds **4b**, **4d**, **5b**, **5d**, **5e**, **6** and **7b**, **7e**, **7f** are presented in our preliminary communication.[12]

*4.1.1. 2-Chloro-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (**4a**).* A solution of compound **1** (0.5 g, 2.66 mmol) in anhydrous dioxane (10 mL) was flushed with argon and 2.0 mol % $Pd(OAc)_2$ and 4.0 mol % (2-biphenyl)dicyclohexylphosphine were added under stirring and argon flow. After 10 min phenylboronic acid (**2a**) (0.39 g, 3.20 mmol) and K_3PO_4 (1.35 g, 6.37 mmol) was added. The reaction mixture was stirred at 60–70 °C (bath temperature) for 4 h. Then dioxane was evaporated under reduced pressure to dryness and water (5 mL) was added to dissolve inorganic salts. The obtained solution was extracted with chloroform (3×25 mL), organic layer dried with Na_2SO_4, chloroform removed by distillation under reduced pressure and the solid obtained was purified by column chromatography using chloroform as an eluent to give compound **4a** (0.27 g, 45%) as a yellowish solid, mp 210 °C. [Found: C, 63.02; H, 3.71. $C_{12}H_8ClN_3$ requires C, 62.76; H, 3.51%]; ν_{max} 3449 cm^{-1} (NH); δ_H ($CDCl_3$): 6.92 (1H, dd, J^3=3.6 Hz, J^4=2.1 Hz, 5-H), 7.47 (1H, dd, J^3=3.6 Hz, J^3=2.1 Hz, 6-H), 7.59–7.63 (3H, m, 3′-5′-H), 8.18–8.21 (2H, m, 2′,6′-H), 10.69 (1H, s, NH); δ_C (DMSO-d_6): 101.2, 114.5, 129.4, 129.7, 129.8, 131.4, 137.3, 152.8, 154.9, 158.2.

*4.1.2. 4-[4-(9-Carbazolyl)phenyl]-2-chloro-7H-pyrrolo[2,3-d]pyrimidine (**4e**).* Compound **4e** was synthesized and isolated according to the procedure described for the preparation of compound **4a**. The reaction time 2.5 h. Yield 47%, yellow solid, mp 309.6–309.8 °C. [Found: C, 73.39; H, 4.02. $C_{24}H_{15}ClN_4$ requires C, 73.00; H, 3.83%]; δ_H ($CDCl_3$): 7.01 (1H, dd, J^3=3.6 Hz, J^4=2.1 Hz, 5-H), 7.34–7.39 (2H, m, 3′,5′-H), 7.46–7.58 [5H, m, 2″,3″,6″,7″-H (carbazolyl), 6-H], 7.84 [2H, dm, J=8.7 Hz, 1″,8″-H (carbazolyl)], 8.21 [2H, dm, J=7.5 Hz, 4″,5″-H (carbazolyl)], 8.44 (2H, dm, J=9 Hz, 2′,6′-H), 9.49 (1H, s, NH); δ_C (DMSO-d_6): 101.3, 110.5, 114.4, 121.2, 121.4, 123.8, 127.1, 127.5, 129.8, 131.3, 135.9, 139.7, 140.4, 152.9, 154.9, 157.3.

*4.1.3. 2-Chloro-4-(4-methoxyphenyl)-7H-pyrrolo[2,3-d]pyrimidine (**4f**).* Compound **4f** was synthesized and isolated according to the procedure described for the preparation of compound **4a**. The reaction time 3.5 h. Yield 51%, yellow solid, mp 249–249.6 °C. δ_H ($CDCl_3$): 3.94 (3H, s, CH_3O), 6.91 (1H, dd, J^3=3.8 Hz, J^4=2.1 Hz, 5-H), 7.11 (2H, dm, J=9 Hz, 3′,5′-H), 7.42 (1H, dd, J^3=3.9 Hz, J^3=2.4 Hz, 6-H), 8.19 (2H, dm, J=8.7 Hz, 2′,6′-H), 9.99 (1H, s, NH); δ_C (DMSO-d_6): 56.1, 101.4, 115.1, 128.9, 129.6, 131.1, 132.4, 152.9, 154.6, 157.9, 162.1; HRMS (ESI): MH^+, found 260.0587. $C_{13}H_{10}ClN_3O$ requires 260.0585.

*4.1.4. 2,4-Diphenyl-7H-pyrrolo[2,3-d]pyrimidine (**5a**).* A solution of compound **1** (0.3 g, 1.60 mmol) in anhydrous dioxane (10 mL) was flushed with argon and 2.0 mol % $Pd(OAc)_2$ and 4.0 mol % (2-biphenyl)dicyclohexylphosphine were added under stirring and argon flow. After 10 min phenylboronic acid (**2a**) (0.47 g,

3.83 mmol) and K_3PO_4 (1.62 g, 7.66 mmol) were added. The reaction mixture was stirred under reflux for 4 h. Then dioxane was evaporated under reduced pressure to dryness and water (5 mL) was added to dissolve inorganic salts. The obtained solution was extracted with chloroform (3×25 mL), organic layer was dried with Na_2SO_4, chloroform removed by distillation under reduced pressure and the solid was purified by column chromatography using benzene as an eluent to give compound **5a** (0.28 g, 65%) as a yellowish solid, mp 210 °C. [Found: C, 79.47; H, 4.95. $C_{18}H_{13}N_3$ requires C, 79.68; H, 4.83%]; ν_{max} 3435 cm^{-1} (NH); UV (THF), λ_{max} (ε, l mol^{-1} cm^{-1}): 216 (3×10^4), 264 (4×10^4), 316 (1×10^4); δ_H ($CDCl_3$): 6.94 (1H, dd, J^3=3.75 Hz, J^4=1.8 Hz, 5-H), 7.39 (1H, dd, J^3=3.6 Hz, J^3=2.4 Hz, 6-H), 7.55–7.64 [6H, m, 3′,4′,5′-H (2-Ph, 4-Ph)], 8.34 [2H, dm, J=9.6 Hz, 2′,6′-H (4-Ph)], 8.64 [2H, dm, J=9.9 Hz, 2′,6′-H (2-Ph)], 10.05 (1H, s, NH); δ_C (DMSO-d_6): 100.9; 113.9; 128.2; 128.9; 129.3; 129.4; 129.6; 130.3; 130.8; 138.9; 139.3; 154.4; 156.2; 156.9.

*4.1.5. 2,4-Di(biphenyl-3-yl)-7H-pyrrolo[2,3-d]pyrimidine (**5c**).* Compound **5c** was synthesized and isolated according to the procedure described for the preparation of compound **5a**. The reaction time 2.5 h. Eluent for column chromatography—chloroform. Yield 49%, yellowish solid, mp 226–227 °C. ν_{max} 3028 cm^{-1} (NH); UV (THF), λ_{max} (ε, l mol^{-1} cm^{-1}): 215 (4×10^4), 258 (7×10^4), 325 nm (1×10^4); δ_H ($CDCl_3$): 6.96 (1H, dd, J^3=3.6 Hz, J^4=1.8 Hz, 5–H), 7.36–7.81 [15H, m, 6-H, 4′,5′,2″-6″-H (2-biPh), 3′,4′,2″-6″-H (4-biPh)], 8.29–8.32 [1H, m, 2′-H (4-biPh)], 8.55–8.56 [1H, m, 2′-H (2-biPh)], 8.62–8.65 [1H, m, 6′-H (4-biPh)], 8.90–8.91 [1H, m, 6′-H (2-biPh)], 9.80 (1H, s, NH); δ_C (DMSO-d_6): 101.0, 114.2, 126.4, 127.2, 127.3, 127.4, 127.5, 127.6, 128.4, 128.5, 128.7, 129.0, 129.3, 129.8, 129.9, 130.0, 130.4; HRMS (ESI): MH^+, found 424.1800. $C_{30}H_{21}N_3$ requires 424.1808.

*4.1.6. tert-Butyl 2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**7a**).* A solution of compound **6** (0.1 g, 0.35 mmol) in anhydrous dioxane (10 mL) was flushed with argon and 2.0 mol % $Pd(OAc)_2$ and 4.0 mol % (2-biphenyl)dicyclohexylphosphine were added under stirring and argon flow. After 10 min phenylboronic acid (0.10 g, 0.83 mmol) and K_3PO_4 (0.35 g, 1.67 mmol) were added. The reaction mixture was stirred under reflux for 3.5 h. Then dioxane was evaporated under reduced pressure to dryness and water (5 mL) was added to dissolve inorganic salts. The obtained solution was extracted with chloroform (3×25 mL), organic layer was dried with Na_2SO_4, chloroform removed by distillation under reduced pressure and residue was purified by column chromatography using chloroform as an eluent to give compound **7a** (0.10 g, 78%) as a colourless solid, mp 121–122.4 °C (from 2-propanol). UV (THF), λ_{max} (ε, l mol^{-1} cm^{-1}): 213 (4×10^4), 263 (4×10^4), 303 (2×10^4); δ_H ($CDCl_3$): 1.81 (9H, s, *tert*-Boc), 6.93 (1H, d, J=4.2 Hz, 5-H), 7.52–7.63 [6H, m, 3′,4′,5′-H (2-Ph, 4-Ph)], 7.81 (1H, d, J=4.2 Hz, 6-H), 8.22 [2H, dm, J=5.4 Hz, 2′,6′-H (4-Ph)], 8.73 [2H, dm, J=6.6 Hz, 2′,6′-H (2-Ph)]; δ_C (DMSO-d_6): 28.5, 85.1, 104.4, 116.5, 127.6, 128.6, 128.7, 129.1, 129.3, 130.4, 130.5, 138.3, 138.8, 148.6, 154.2, 158.3, 159.9.

*4.1.7. tert-Butyl 2,4-di(biphenyl-3-yl)-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**7c**).* Compound **7c** was synthesized and isolated according to the procedure described for the preparation of compound **7a**. The reaction time 3 h. Yield 42%, colourless solid, mp 139–139.6 °C (from 2-propanol). UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 256 (6×10^4), 305 (2×10^4); δ_H ($CDCl_3$): 1.82 (9H, s, *tert*-Boc), 6.97 (1H, d, J=4.2 Hz, 5-H), 7.39–7.81 [14H, m, 4′,5′,2″-6″-H (2-biPh, 4-biPh)], 7.85 (1H, d, J=4.2 Hz, 6-H), 8.20 [1H, dm, J=7.5 Hz, 6′-H (4-biPh)], 8.44 [1H, t, J=1.8 Hz, 2′-H (4-biPh)], 8.75 [1H, dm, J=7.8 Hz, 6′-H (2-biPh)], 8.99 [1H, t, J=1.8 Hz, 2′-H (2-biPh)]; δ_C ($CDCl_3$): 28.5, 85.3, 104.4, 116.8, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.2, 128.9, 129.2, 129.25, 129.3, 129.6, 138.8, 139.2, 141.1, 141.6, 141.7, 142.2, 148.8, 156.0, 157.8, 158.3; HRMS (ESI): MH^+, found 524.2327. $C_{35}H_{29}N_3O_2$ requires 524.2333.

*4.1.8. tert-Butyl 2,4-di(biphenyl-4-yl)-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**7d**).* Compound **7d** was synthesized and isolated according to the procedure described for the preparation of compound **7a**. The reaction time 2 h. Yield 66%, yellowish solid, mp 165–165.4 °C (from 2-propanol). [Found: C, 80.14; H, 5.56. $C_{35}H_{29}N_3O_2$ requires C, 80.28; H, 5.58%]; δ_H ($CDCl_3$): 1.85 (9H, s, *tert*-Boc), 6.98 (1H, d, J=4.2 Hz, 5-H), 7.41–7.89 [15H, m, 6-H, 3′,5′,2″-6″-H (2-biPh, 4-biPh)], 8.34 [2H, dm, J=8.1 Hz, 2′,6′-H (4-biPh)], 8.84 [2H, dm, J=8.4 Hz, 2′,6′-H (2-biPh)]; δ_C ($CDCl_3$): 28.5, 85.2, 104.5, 116.5, 127.3, 127.4, 127.4, 127.5, 127.7, 127.8, 128.1, 129.0, 129.1, 129.2, 129.8, 137.2, 137.8, 140.7, 141.1, 142.9, 143.3, 148.6, 154.2, 157.9, 159.7.

*4.1.9. tert-Butyl 2-chloro-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**8a**).* To a solution of compound **4a** (0.42 g, 1.83 mmol) in anhydrous dichloromethane (5 mL) DIPEA (0.48 mL, 2.75 mmol), DMAP (0.07 g, 0.57 mmol) and Boc_2O (0.6 g, 2.75 mmol) were added. The reaction mixture was stirred under reflux for 1 h 20 min. Then dichloromethane was evaporated, the obtained residue was purified by column chromatography using chloroform as an eluent to give compound **8a** (0.37 g, 61%) as a colourless solid, mp 76–77 °C (from 2-propanol). δ_H ($CDCl_3$): 1.74 (9H, s, *tert*-Boc), 6.89 (1H, d, J=4.2 Hz, 5-H), 7.58–7.61 (3H, m, 3′,4′,5′-H), 7.74 (1H, d, J=4.2 Hz, 6-H), 8.06–8.09 (2H, m, 2′,6′-H); δ_C ($CDCl_3$): 28.3, 86.0, 104.1, 116.9, 128.0, 129.2, 129.3, 131.2, 136.6, 147.3, 154.4, 156.2, 160.6; HRMS (ESI): MH^+, found 330.1000. $C_{17}H_{16}ClN_3O_2$ requires 330.1004.

*4.1.10. tert-Butyl 2-chloro-4-(4-methoxyphenyl)-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**8f**).* To a solution of compound **4f** (0.18 g, 0.69 mmol) in anhydrous dichloromethane (5 mL) DIPEA (0.14 mL, 0.83 mmol), DMAP (0.017 g, 0.14 mmol) and Boc_2O (0.23 g, 1.04 mmol) were added. The reaction mixture was stirred at room temperature for 0.5 h. Then dichloromethane was evaporated, the obtained residue was purified by column chromatography using chloroform as an eluent to give compound **8f** (0.20 g, 80%) as a colourless solid, mp 170.3–170.8 °C (from 2-propanol). δ_H ($CDCl_3$): 1.73 (9H, s, *tert*-Boc), 3.94 (3H, s, OMe), 6.88 (1H, d, J=4.2 Hz, 5-H), 7.09 (2H, dm, J=9 Hz, 3′,5′-H), 7.71 (1H, d, J=4.2 Hz, 6-H), 8.09 (2H, dm, J=9 Hz, 2′,6′-H); δ_C ($CDCl_3$): 28.3, 55.7, 85.9, 104.2, 114.6, 116.2, 127.6, 129.1, 130.9, 147.3, 154.4, 156.1, 160.1, 162.2; HRMS (ESI): MH^+, found 360.1112. $C_{18}H_{18}ClN_3O_3$ requires 360.1109.

*4.1.11. tert-Butyl 2-(biphenyl-4-yl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**9**).* A solution of compound **8a** (0.14 g, 0.42 mmol) in an anhydrous dioxane (10 mL) was flushed with argon and 2.0 mol % $Pd(OAc)_2$ and 4.0 mol % (2-biphenyl)dicyclohexylphosphine were added under stirring and argon flow. After 10 min. 4-biphenylboronic acid (0.10 g, 0.51 mmol) and K_3PO_4 (0.22 g, 1.02 mmol) were added. The reaction mixture was stirred under reflux for 7 h. Then dioxane was evaporated under reduced pressure to dryness and water (5 mL) was added to dissolve inorganic salts. The obtained solution was extracted with chloroform (3×25 mL), organic layer was dried with Na_2SO_4, chloroform removed by distillation under reduced pressure, the residue was dissolved in a minimal amount of tetrachloromethane and purified by column chromatography using hexane/ethyl acetate (27:1) as an eluent to give compound **9** (0.145 g, 76%) as a colourless solid, mp 150–150.2 °C (from 2-propanol). δ_H ($CDCl_3$): 1.83 (9H, s, *tert*-Boc), 6.94 (1H, d, J=4.2 Hz, 5-H), 7.49–7.79 [10H, m, 3′,5′,2″-6″-H (4-biPh), 3′,4′,5′-H (Ph)], 7.81 (1H, d, J=3.9 Hz, 6-H), 8.22–8.25 [2H, m, 2′,6′-H (Ph)], 8.80 [2H, dm, J=8.7 Hz, 2′,6′-H (4-biPh)]; δ_C ($CDCl_3$): 28.5, 85.2, 104.5, 116.5, 127.4, 127.5, 127.6, 127.8, 129.0, 129.1, 129.2, 129.3, 130.5, 137.8, 138.3, 141.1, 142.9, 148.6, 154.2,

158.3, 159.7; HRMS (ESI): MH^+, found 448.2013. $C_{29}H_{25}N_3O_2$ requires 448.2020.

*4.1.12. tert-Butyl 2-(4-ethoxyphenyl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**10**).* Compound **10** was synthesized and isolated according to the procedure described for the preparation of compound **9**. Eluent for column chromatography—chloroform. The reaction time 4 h. Yield 79%, yellowish solid, mp 141–141.9 °C (from 2-propanol). δ_H ($CDCl_3$): 1.49 (3H, t, J=6.9 Hz, Me), 1.81 (9H, s, *tert*-Boc), 4.16 (2H, q, J=6.9 Hz, CH_2O), 6.88 (1H, d, J=4.2 Hz, 5-H), 7.05 [2H, dm, J=9 Hz, 3′,5′-H ($EtOC_6H_4$)], 7.58–7.61 [3H, m, 3′,4′,5′-H (Ph)], 7.75 (1H, d, J=4.2 Hz, 6-H), 8.19–8.22 [2H, m, 2′,6′-H (Ph)], 8.68 [2H, dm, J=9 Hz, 2′,6′-H ($EtOC_6H_4$)]; δ_C ($CDCl_3$): 15.1, 28.5, 63.7, 84.9, 104.4, 114.5, 115.9, 127.1, 129.0, 129.3, 130.1, 130.4, 131.4, 138.4, 148.6, 154.3, 158.2, 159.9, 161.1; HRMS (ESI): MH^+, found 416.1962. $C_{25}H_{25}N_3O_3$ requires 416.1969.

*4.1.13. tert-Butyl 2-(4-ethoxyphenyl)-4-(4-methoxyphenyl)-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**11**).* Compound **11** was synthesized and isolated according to the procedure described for the preparation of compound **9**. Eluent for column chromatography—chloroform. The reaction time—6 h. Yield 69%, colourless solid, mp 145–145.5 °C (from 2-propanol). δ_H ($CDCl_3$): 1.49 (3H, t, J=7.2 Hz, Me), 1.79 (9H, s, *tert*-Boc), 3.95 (3H, s, OCH_3), 4.16 (2H, q, J=6.9 Hz, CH_2O), 6.88 (1H, d, J=3.9 Hz, 5-H), 7.03 [2H, dm, J=9 Hz, 3′,5′-H ($EtOC_6H_4$)], 7.13 [2H, dm, J=8.7 Hz, 3′,5′-H ($MeOC_6H_4$)], 7.73 (1H, d, J=4.2 Hz, 6-H), 8.20 [2H, dm, J=9 Hz, 2′,6′-H ($MeOC_6H_4$)], 8.66 [2H, dm, J=9 Hz, 2′,6′-H ($EtOC_6H_4$)]; δ_C ($CDCl_3$): 15.1, 28.5, 55.7, 63.7, 84.9, 104.5, 114.4, 114.5, 115.3, 126.8, 130.1, 130.8, 131.0, 131.5, 148.6, 154.3, 157.7, 159.8, 161.0, 161.6; HRMS (ESI): MH^+, found 446.2066. $C_{26}H_{27}N_3O_4$ requires 446.2074.

*4.1.14. 2-(Biphenyl-4-yl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (**12**).* To a solution of compound **9** (0.145 g, 0.32 mmol) in a mixture of acetone (15 mL) and water (5 mL) concd hydrochloric acid (0.08 mL, 0.97 mmol) was added. The reaction mixture was stirred under reflux for 70 h, then cooled to room temperature, the precipitate was filtered off to give compound **12** (0.08 g, 73%) as a colourless solid, mp 278.2–278.9 °C. δ_H (DMSO-d_6): 6.95 (1H, dd, J^3=3.3 Hz, J^4=1.5 Hz, 5-H), 7.54–7.89 [11H, m, 6-H, 3′,5′,2″-6″-H (biPh), 3′-5′-H (Ph)], 8.34–8.36 [2H, m, 2′,6′-H (Ph)], 8.66 [2H, dm, J=8.4 Hz, 2′,6′-H (biPh)], 12.36 (1H, s, NH); δ_C (DMSO-d_6): 101.0, 113.9, 127.4, 127.5, 128.5, 128.8, 129.0, 129.4, 129.6, 129.8, 130.9, 138.4, 138.9, 140.4, 141.9, 154.4, 156.2, 156.7; HRMS (ESI): MH^+, found 348.1493. $C_{24}H_{17}N_3$ requires 348.1495.

*4.1.15. 2-(4-Ethoxyphenyl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (**13**).* Compound **13** was synthesized and isolated according to the procedure described for the preparation of compound **12**. The reaction time—7 days. Yield 80%, colourless solid, mp 275–276 °C. δ_H (DMSO-d_6): 1.39 (3H, t, J=6.9 Hz, Me), 4.13 (2H, q, J=6.9 Hz, OCH_2), 6.90 (1H, dd, J^3=3.5 Hz, J^4=1.8 Hz, 5-H), 7.08 [2H, dm, J=9.0 Hz, 3′,5′-H (EtOPh)], 7.59–7.65 [4H, m, 6-H, 3′-5′-H (Ph)], 8.31 [2H, dm, J=7.9 Hz, 2′,6′-H (Ph)], 8.49 [2H, dm, J=9.0 Hz, 2′,6′-H (EtOPh)], 12.21 (1H, s, NH); δ_C (DMSO-d_6): 15.4, 63.9, 100.9, 113.4, 114.9, 128.4, 129.3, 129.6, 129.7, 130.8, 131.7, 138.9, 154.5, 156.1, 157.0, 160.6; HRMS (ESI): MH^+, found 316.1446. $C_{20}H_{17}N_3O$ requires 316.1444.

*4.1.16. 2-(4-Ethoxyphenyl)-4-(4-methoxyphenyl)-7H-pyrrolo[2,3-d]pyrimidine (**14**).* To a solution of compound **11** (0.17 g, 0.38 mmol) in an anhydrous dichloromethane (10 mL) TFA (6.3 mL) was added. The reaction mixture was stirred at room temperature for 5 min. Then dichloromethane and TFA were evaporated under reduced pressure to dryness and the obtained residue was purified by column chromatography using chloroform as an eluent to give compound **14** (0.10 g, 77%) as a yellowish solid, mp 225.3–226.3 °C. δ_H (DMSO-d_6): 1.39 (3H, t, J=6.9 Hz, Me), 3.89 (3H, s, OMe), 4.12 (2H, q, J=6.9 Hz, OCH_2), 6.89 (1H, dd, J^3=3.6 Hz, J^4=1.5 Hz, 5-H), 7.08 [2H, dm, J=9 Hz, 3′,5′-H (EtOPh)], 7.18 [2H, dm, J=8.7 Hz, 3′,5′-H (MeOPh)], 7.60 (1H, dd, J^3=3.5 Hz, J^3=2.1 Hz, 6-H), 8.32 [2H, dm, J=8.7 Hz, 2′,6′-H (MeOPh)], 8.48 [2H, dm, J=9 Hz, 2′,6′-H (EtOPh)], 12.16 (s, 1H, NH); δ_C (DMSO-d_6): 15.4, 56.1, 63.8, 101.0, 112.7, 114.9, 127.9, 129.6, 130.9, 131.4, 131.8, 154.4, 155.7, 156.9, 160.6, 161.6; HRMS (ESI): MH^+, found 346.1546. $C_{21}H_{19}N_3O_2$ requires 346.1550.

*4.1.17. 2,4,7-Triphenyl-7H-pyrrolo[2,3-d]pyrimidine (**15**).* A solution of compound **5a** (0.15 g, 0.55 mmol) in anhydrous dioxane (3 mL) was flushed with argon and 1.0 mol % CuI, anhydrous K_3PO_4 (0.21 g, 0.99 mmol), iodobenzene (0.052 mL, 0.46 mmol), 10.0 mol % (±)-*trans*-1,2-diaminocyclohexane were added under stirring and argon flow. The reaction mixture was stirred under reflux for 6 h and 1.0 mol % of CuI was added. Then every 2 h 1.0 mol % of CuI was added to the mixture till the total amount of CuI reached 4.0 mol %. Total reaction time was 13 h. Then after cooling to room temperature ethyl acetate (5 mL) was added to the reaction mixture and resulting solution was filtered through a layer of silica gel eluting with ethyl acetate. The filtrate was concentrated under reduced pressure, the residue was dissolved in a minimal amount of tetrachloromethane and purified by column chromatography using hexane/ethyl acetate (40:1) as an eluent to give compound **15** (0.15 g, 94%) as a colourless solid, mp 155.2–155.8 °C. UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 256 (4×10^4), 327 (1×10^4); δ_H ($CDCl_3$): 7.04 (1H, d, J=3.9 Hz, 5-H), 7.41–7.68 [10H, m, 6-H, 3′-5′-H (2-Ph, 4-Ph, N_7–Ph)], 7.97–7.94 [2H, m, 2′,6′-H (N_7–Ph)], 8.29–8.34 [2H, m, 2′,6′-H (4-Ph)], 8.67–8.71 [2H, m, 2′,6′-H (2-Ph)]; δ_C ($CDCl_3$): 102.5, 115.2, 124.1, 126.9, 128.4, 128.6, 128.8, 128.9, 129.3, 129.6, 129.9, 130.3, 138.1, 138.9, 139.1, 152.9, 158.0, 158.6; HRMS (ESI): MH^+, found 348.1489. $C_{24}H_{17}N_3$ requires 348.1495.

*4.1.18. 7-(4-Methoxyphenyl)-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (**16**).* Compound **16** was synthesized according to the procedure described for compound **15**. The reaction time—12 h. Addition of CuI in an amount 1.0 mol % was started after 4 h of reflux and repeated every 2 h till the total amount CuI reached 5.0 mol %. The isolation and purification was carried out analogously **15** by column chromatography using hexane/ethyl acetate (20:1) as an eluent to give compound **16** (92%) as a colourless solid, mp 184.9–185.4 °C. UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 210 (12×10^4), 259 (10×10^4), 341 (2×10^4); δ_H ($CDCl_3$): 3.95 (3H, s, CH_3O), 7.01 (d, 1H, J=3.9 Hz, 5-H), 7.13–7.16 (m, 2H, N_7-(4-MeO–Ph): 3′,5′-H), 7.49–7.64 (m, 7H, 6-H, 2-Ph, 4-Ph: 3′-5′-H), 7.79–7.83 (m, 2H, N_7-(4-MeO–Ph): 2′,6′-H), 8.31–8.35 (m, 2H, 4-Ph: 2′,6′-H), 8.66–8.69 (m, 2H, 2-Ph: 2′,6′-H); δ_C ($CDCl_3$): 55.9, 101.9, 114.8, 114.9, 125.5, 128.4, 128.6, 128.9, 129.2, 129.3, 129.9, 130.2, 131.2, 139.0, 139.2, 152.9, 157.9, 158.5, 158.6; HRMS (ESI): MH^+, found 378.1598. $C_{25}H_{19}N_3O$ requires 378.1601.

*4.1.19. 4-(2,4-Diphenyl-7H-pyrrolo[2,3-d]pyrimidin-7-yl)benzonitrile (**17**).* Compound **17** was synthesized according to the procedure described for compound **15**. The reaction time—12 h. Addition of CuI in an amount 1.0 mol % was started after 2 h of reflux and repeated every 2 h till the total amount CuI reached 5.0 mol %. The isolation and purification was carried out analogously **15** by column chromatography using benzene as an eluent to give compound **17** (82%) as a yellowish solid, mp 209–210 °C. IR (KBr): 2227 (CN); UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 210 (5×10^4), 265 (5×10^4), 292 (3×10^4), 326 (2×10^4); δ_H ($CDCl_3$): 7.11 (1H, d, J=3.6 Hz, 5-H), 7.51–7.66 [7H, m, 6-H, 3′-5′-H (2-Ph, 4-Ph)], 7.92–7.95 [2H, m, 2′,6′-H (N_7–Ph)], 8.19–8.22 [2H, m, 3′,5′-H (N_7–Ph)], 8.29–8.32 [2H, m, 2′,6′-H (4-Ph)], 8.66–8.69 [2H, m, 2′,6′-H (2-Ph)]; δ_C ($CDCl_3$): 104.2, 109.9, 115.5, 118.7, 123.6, 127.4, 128.4, 128.7, 129.1, 129.3, 130.4, 130.6, 133.7, 138.5, 138.6, 141.7,

153.3, 158.6, 159.1; HRMS (ESI): MH^+, found 373.1446. $C_{25}H_{16}N_4$ requires 373.1448.

*4.1.20. 4-(2,4-Diphenyl-7H-pyrrolo[2,3-d]pyrimidin-7-yl)-N,N-diphenylaniline (**18**).* Compound **18** was synthesized according to the procedure described for compound **15**. The reaction time—22 h. Addition of CuI in an amount 1.0 mol % was started after 2 h of reflux and repeated every 2 h till the total amount CuI reached 6.0 mol %. The isolation and purification was carried out analogously **15** by column chromatography using hexane/ethyl acetate (27:1) as an eluent to give compound **18** (72%) as a yellowish solid, mp 166–166.2 °C. UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 210 (8×10^4), 267 (4×10^4), 308 (4×10^4); δ_H ($CDCl_3$): 7.02 (1H, d, J=3.6 Hz, 5-H), 7.08–7.18 [2H, m, 3′,5′-H (N_7–Ph)], 7.23–7.39 [10H, m, 2×2″-6″-H ($N(Ph)_2$)], 7.48–7.68 [7H, m, 6-H, 3′-5′-H (2-Ph, 4-Ph)], 7.80–7.83 [2H, m, 2′,6′-H (N_7–Ph)], 8.32–8.35 [2H, m, 2′,6′-H (4-Ph)], 8.68–8.71 [2H, m, 2′,6′-H (2-Ph)]; δ_C ($CDCl_3$): 102.2, 115.2, 123.5, 124.4, 124.7, 124.8, 128.4, 128.7, 128.9, 129.0, 129.3, 129.7, 129.9, 130.3, 132.5, 138.9, 139.1, 146.7, 147.9, 152.8, 157.9, 158.6; HRMS (ESI): MH^+, found 515.2225. $C_{36}H_{26}N_4$ requires 515.2230.

*4.1.21. 2-(Biphenyl-4-yl)-7-(4-methoxyphenyl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (**19**).* Compound **19** was synthesized according to the procedure described for compound **15**. The reaction time—11 h. Addition of CuI in an amount 1.0 mol % was started after 4 h of reflux and repeated after every 2 h till the total amount CuI reached 5.0 mol %. The isolation and purification was carried out analogously **15** by column chromatography using hexane/ethyl acetate (8:1) as an eluent to give compound **19** (93%) as a colourless solid, mp 178.8–179.9 °C. UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 242 (1×10^4), 260 (2×10^4), 297 (2×10^4), 344 (1×10^4); δ_H (DMSO-d_6): 3.89 (3H, s, CH_3O), 7.17 (1H, d, J=3.9 Hz, 5-H), 7.22 [2H, dm, J=9 Hz, 3′,5′-H (N_7–Ph)], 7.39–7.91 [12H, m, 6-H, 3′,5′,2″-6″-H (4-biPh), 3′-5′-H (4-Ph), 2′,6′-H (N_7–Ph)], 8.06 (1H, d, J=3.6 Hz, 6-H), 8.34–8.37 [2H, m, 2′,6′-H (4-Ph)], 8.62 [2H, dm, J=8.4 Hz, 2′,6′-H (4-biPh)]; δ_C (DMSO-d_6): 56.2, 102.2, 114.9, 115.3, 125.9, 127.4, 127.6, 128.5, 128.9, 129.5, 129.7, 129.7, 130.9, 131.1, 131.5, 137.9, 138.5, 140.3, 142.2, 152.7, 157.2, 157.3, 158.7; HRMS (ESI): MH^+, found 454.1910. $C_{31}H_{23}N_3O$ requires 454.1914.

*4.1.22. 4-[2-(Biphenyl-4-yl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidin-7-yl]benzonitrile (**20**).* A solution of compound **12** (0.05 g, 0.14 mmol) in anhydrous dioxane (6 mL) was flushed with argon and 1.0 mol % CuI, anhydrous K_3PO_4 (0.053 g, 0.25 mmol), 4-iodobenzonitrile (0.027 g, 0.12 mmol), 10.0 mol % (±)-*trans*-1,2-diaminocyclohexane were added under stirring and argon flow. The reaction mixture was stirred under reflux for 4 h and 1.0 mol % of CuI was added. Then every hour 1.0 mol % of CuI was added to the mixture till the total amount of CuI reached 5.0 mol %. Then after an hour 1.0 mol % CuI and 10.0 mol % (±)-*trans*-1,2-diaminocyclohexane were added. Addition of 1.0 mol % of CuI was continued every hour till amount of CuI reached 10.0 mol %. Total reaction time was 25 h. After cooling the reaction mixture to room temperature ethyl acetate (5 mL) was added, resulting solution was filtered through a layer of silica gel eluting with ethyl acetate. The filtrate was concentrated under reduced pressure, the residue was dissolved in a minimal amount of tetrachloromethane and purified by column chromatography using hexane/ethyl acetate (8:1) as an eluent to give compound **20** (0.051 g, 95%) as a yellowish solid, mp 222–222.7 °C. UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 280 (3×10^4), 332 (1×10^4); δ_H (DMSO-d_6): 7.26 (1H, d, J=3.9 Hz, 5-H), 7.43–7.87 [10H, m, 6-H, 3′,5′,2″-6″-H (4-biPh), 3′-5′-H (Ph)], 8.14 [2H, dm, J=8.7 Hz, 2′,6′-H (N_7–Ph)], 8.28 (1H, d, J=3.9 Hz, 6-H), 8.31–8.39 [4H, m, 2′,6′-H (Ph), 3′,5′-H (N_7–Ph)], 8.63 [2H, dm, J=8.7 Hz, 2′,6′-H (4-biPh)]; δ_C (DMSO-d_6): 104.1, 109.4, 115.6, 119.3, 124.2, 127.5, 127.6, 128.6, 129.0, 129.4, 129.5, 129.8, 131.3, 132.3, 134.4, 137.6, 138.1, 140.3, 142.4, 153.2, 157.6, 157.7, 167.7; HRMS (ESI): MH^+, found 449.1758. $C_{31}H_{20}N_4$ requires 449.1761.

*4.1.23. 4-[2-(4-Ethoxyphenyl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidin-7-yl]benzonitrile (**21**).* Compound **21** was synthesized according to the procedure described for compound **15**. The reaction time—6 h. Addition of CuI in an amount 1.0 mol % was started after 1 h of reflux and repeated after 2 h till the total amount CuI reached 3.0 mol %. The isolation and purification was carried out analogously **15** by column chromatography using hexane/ethyl acetate (27:1) as an eluent to give compound **21** (90%) as a colourless solid, mp 206.3–206.8 °C (from 2-PrOH/EtOAc). UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 235 (1×10^4), 275 (3×10^4), 324 (1×10^4); δ_H ($CDCl_3$): 1.51 (3H, t, J=6.9 Hz, Me), 4.17 (2H, q, J=6.9 Hz, OCH_2), 7.04–7.09 [3H, m, 5-H, 3′,5′-H (4-$EtOC_6H_4$)], 7.61–7.62 [4H, m, 6-H, 3′,4′,5′-H (Ph)], 7.93 [2H, dm, J=9.0 Hz, 3′,5′-H (N_7–Ph)], 8.21 [2H, dm, J=9.0 Hz, 2′,6′-H (N_7–Ph)], 8.30 [2H, m, J=7.9 Hz, 2′,6′-H (Ph)], 8.1 [2H, dm, J=9.0 Hz, 2′,6′-H (4-$EtOC_6H_4$)]; δ_C ($CDCl_3$): 15.1, 63.8, 104.2, 109.7, 114.6, 114.9, 118.8, 123.6, 126.9, 129.1, 129.3, 129.9, 130.5, 131.1, 133.7, 138.5, 141.8, 153.3, 158.5, 159.1, 161.1; HRMS (ESI): MH^+, found 417.1710. $C_{27}H_{20}N_4O$ requires 417.1710.

*4.1.24. 2,4-Bis[4-(9H-carbazol-9-yl)phenyl]-7-phenyl-7H-pyrrolo[2,3-d]pyrimidine (**22**). Method A.* Compound **22** was synthesized according to the procedure described for compound **15**. The reaction time—10 h. Addition of CuI in an amount 2.0 mol % was started after 2 h of reflux and repeated after every 2 h till the total amount CuI reached 5.0 mol %. The isolation and purification was carried out analogously **15** by column chromatography using hexane/ethyl acetate (10:1) as an eluent to give compound **22** as a yellow solid. Yield 85%, mp 267–268 °C. UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 210 (8×10^4), 236 (10×10^4), 254 (7×10^4), 281 (4×10^4), 292 (4×10^4), 342 (4×10^4); δ_H ($CDCl_3$): 7.19 (1H, d, J=3.6 Hz, 5-H), 7.35–7.79 [18H, m, 6-H, 2′,6′-H (N_7–Ph), 3′,5′,2″,3″,6″,7″-H (2-carbazolyl, 4-carbazolyl)], 7.88–7.99 [2H, m, 1″,8″-H (4-carbazolyl)], 7.99–8.02 [2H, m, 1″,8″-H (2-carbazolyl)], 8.19–8.24 [4H, m, 4″,5″-H (2-carbazolyl, 4-carbazolyl)], 8.63 [2H, dm, J=8.7 Hz, 2′,6′-H (4-carbazolyl)], 8.95 [2H, dm, J=8.7 Hz, 2′,6′-H (2-carbazolyl)]; δ_C ($CDCl_3$): 102.4, 110.2, 110.3, 115.3, 120.3, 120.6, 120.6, 120.7, 123.8, 123.9, 124.2, 126.3, 126.4, 127.0, 127.2, 127.4, 129.5, 129.8, 129.9, 130.9, 137.7, 137.8, 137.9, 139.3, 139.8, 140.9, 140.98, 153.1, 157.1, 158.0; HRMS (ESI): MH^+, found 678.2641. $C_{48}H_{31}N_5$ requires 678.2652.

Method B. A solution of compound **5e** (0.20 g, 0.33 mmol) in anhydrous toluene (5 mL) was flushed with argon and iodobenzene (0.08 mL, 0.73 mmol), 10.0 mol % 1,10-phenanthroline, Cs_2CO_3 (0.22 g, 0.66 mmol) were added under stirring and argon flow. The reaction mixture was heated to 100 °C and 10.0 mol % CuI was added. The reaction mixture was stirred under reflux for 16 h. Then toluene was evaporated under reduced pressure to dryness and water (5 mL) was added to dissolve inorganic salts. The obtained solution was extracted with ethyl acetate (3×25 mL), organic layer was dried with Na_2SO_4, ethyl acetate removed by distillation under reduced pressure and the solid purified by column chromatography using hexane→benzene as an eluent to give compound **22** (0.11 g, 49%) as a yellow solid, mp 267–268 °C.

*4.1.25. 2,4-Bis[4-(9H-carbazol-9-yl)phenyl]-7-(4-methoxyphenyl)-7H-pyrrolo[2,3-d]pyrimidine (**23**).* A solution of compound **5e** (0.15 g, 0.25 mmol) in anhydrous dioxane (3 mL) was flushed with argon and 1.0 mol % CuI, anhydrous K_3PO_4 (0.11 g, 0.52 mmol), 4-iodoanisole (0.06 g, 0.26 mmol), 10.0 mol % (±)-*trans*-1,2-diaminocyclohexane were added under stirring and argon flow. The reaction mixture was stirred under reflux and every 2 h 1.0 mol % of CuI was added to the reaction mixture till total amount

of CuI reached 5.0 mol %. Then after 2 h 2.0 mol % CuI and 10.0 mol % (±)-*trans*-1,2-diaminocyclohexane were added. Total reaction time was 19 h. After cooling the reaction mixture to room temperature ethyl acetate (5 mL) was added, resulting solution was filtered through a layer of silica gel eluting with ethyl acetate. The filtrate was concentrated under reduced pressure, the residue was dissolved in a minimal amount of tetrachloromethane and purified by column chromatography using hexane/ethyl acetate (8:1) as an eluent to give compound **23** (0.09 g, 51%) as a yellowish solid, mp 186.5–187.1 °C. ν_{max} (KBr) 1517 cm^{-1} (OCH_3); UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 210 (8×10^4), 237 (10×10^4), 255 (7×10^4), 292 (5×10^4), 342 (4×10^4); δ_H ($CDCl_3$): 3.97 (3H, s, CH_3O), 7.14 (1H, d, *J*=3.6 Hz, 5-H), 7.18–7.21 [2H, m, 3′,5′-H (4-carbazolyl)], 7.36–7.66 [13H, m, 6-H, 3′,5′-H (N_7–Ph), 3′,5′,2″,3″,6″,7″-H (2-carbazolyl), 2″,3″,6″,7″-H (4-carbazolyl)], 7.77 [2H, dm, *J*=8.7 Hz, 2′,6′-H (N_7–Ph)], 7.84–7.91 [4H, m, 1″,8″-H (2-carbazolyl, 4-carbazolyl)], 8.20–8.25 [4H, m, 4″,5″-H (2-carbazolyl, 4-carbazolyl)], 8.62 [2H, dm, *J*=8.4 Hz, 2′,6′-H (4-carbazolyl)], 8.95 [2H, dm, *J*=8.4 Hz, 2′,6′-H (2-carbazolyl)]; δ_C ($CDCl_3$): 55.9, 101.9, 110.2, 110.3, 114.9, 115.0, 120.3, 120.6, 120.6, 120.7, 123.8, 123.9, 125.7, 126.3, 126.4, 127.0, 127.4, 129.9, 129.98, 130.9, 131.0, 137.7, 138.0, 139.3, 139.7, 140.8, 140.9, 153.0, 156.9, 157.9, 158.8; HRMS (ESI): MH^+, found 708.2751. $C_{49}H_{33}N_5O$ requires 708.2758.

*4.1.26. 4-{2,4-Bis[4-(9H-carbazol-9-yl)phenyl]-7H-pyrrolo[2,3-d] pyrimidin-7-yl}benzonitrile (**24**).* A solution of compound **5e** in an anhydrous dioxane (3 mL) was flushed with argon and 1.0 mol % CuI, anhydrous K_3PO_4 (0.09 g, 0.43 mmol), 4-iodobenzonitrile (0.06 g, 0.26 mmol), 10 mol % (±)-*trans*-1,2-diaminocyclohexane were added under stirring and argon flow. The reaction mixture was stirred under reflux and every 2 h 1.0 mol % of CuI was added to the reaction mixture till an amount of CuI reached 5.0 mol %. Then after 2 h 2.0 mol % CuI and 10 mol % (±)-*trans*-1,2-diaminocyclohexane were added. Total reaction time was 22 h. After cooling the reaction mixture to room temperature ethyl acetate (5 mL) was added, resulting solution was filtered through a layer of silica gel eluting with ethyl acetate. The filtrate was concentrated under reduced pressure, the residue was dissolved in a minimal amount of tetrachloromethane and purified by column chromatography using benzene as an eluent to give compound **24** (0.10 g, 57%) as a yellowish solid, mp 199–199.1 °C. ν_{max} (KBr) 2226 cm^{-1} (CN); UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 210 (12×10^4), 236 (10×10^4), 256 (8×10^4), 284 (6×10^4), 291 (5×10^4), 342 (4×10^4); δ_H ($CDCl_3$): 7.23 (1H, d, *J*=3.9 Hz, 5-H), 7.32–7.41 [4H, m, 3′,5′-H (2-carbazolyl, 4-carbazolyl)], 7.48–7.61 [8H, m, 2″,3″,6″,7″-H (2-carbazolyl, 4-carbazolyl)], 7.72 (1H, d, *J*=3.9 Hz, 6-H), 7.79–7.91 [4H, m, 1″,8″-H (2-carbazolyl, 4-carbazolyl)], 7.97 [2H, dm, *J*=8.7 Hz, 2′,6′-H (N_7–Ph)], 8.20–8.24 [6H, m, 3′,5′-H (N_7–Ph), 4″,5″-H (2-carbazolyl, 4-carbazolyl)], 8.59 [2H, dm, *J*=8.4 Hz, 2′,6′-H (4-carbazolyl)], 8.94 [2H, dm, *J*=8.7 Hz, 2′,6′-H (2-carbazolyl)]; δ_C ($CDCl_3$): 104.1, 110.1, 110.2, 110.3, 115.6, 118.6, 120.4, 120.7, 120.7, 123.8, 123.9, 126.3, 126.4, 127.1, 127.5, 128.1, 128.6, 130.0, 130.9, 133.8, 137.1, 137.4, 139.7, 140.1, 140.8, 140.9, 141.6, 153.4, 157.7, 158.5; HRMS (ESI): MH^+, found 703.2597. $C_{49}H_{30}N_6$ requires 703.2605.

*4.1.27. 4-{2,4-Bis[4-(9H-carbazol-9-yl)phenyl]-7H-pyrrolo[2,3-d] pyrimidin-7-yl}-N,N-diphenylaniline (**25**).* Compound **25** was synthesized according to the procedure described for compound **24**. The reaction time—29 h. The isolation and purification was carried out analogously **24** by column chromatography using benzene as an eluent to give compound **25** (59%) as a yellowish solid, mp 290–291 °C. UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 237 (12×10^4), 255 (8×10^4), 293 (6×10^4), 341 (6×10^4); δ_H ($CDCl_3$): 7.13–7.65 [25H, m, 5-H, 3′,5′,2″,3″,6″,7″-H (2-carbazolyl, 4-carbazolyl), 3′,5′,2×(2″–6″)-H (N_7–Ph), N($Ph)_2$], 7.70 (1H, d, *J*=3.6 Hz, 6-H), 7.78 [2H, dm, *J*=8.4 Hz, 2′,6′-H (N_7–Ph)], 7.84–7.91 [4H, m, 1″,8″-H (2-carbazolyl, 4-carbazolyl)], 8.20–8.25 [4H, m, 4″,5″-H (2-carbazolyl, 4-carbazolyl)], 8.63 [2H, dm, *J*=8.7 Hz, 2′,6′-H (4-carbazolyl)], 8.95 [2H, dm, *J*=8.7 Hz, 2′,6′-H (2-carbazolyl)]; δ_C ($CDCl_3$): 102.1, 110.2, 110.3, 115.2, 120.3, 120.5, 120.6, 120.7, 123.6, 123.8, 123.9, 124.2, 124.8, 124.9, 126.3, 126.4, 127.1, 127.4, 129.6, 129.7, 129.9, 130.9, 132.2, 137.7, 138.0, 139.3, 139.8, 140.8, 140.9, 147.0, 147.8, 152.9, 157.1, 157.9; HRMS (ESI): MH^+, found 845.3370. $C_{60}H_{40}N_6$ requires 845.3387.

*4.1.28. 2-(4-Ethoxyphenyl)-4-(4-methoxyphenyl)-7-phenyl-7H-pyrrolo[2,3-d]pyrimidine (**26**). Method A.* Compound **26** was synthesized according to the procedure described for compound **15**. The reaction time—9.5 h. Addition of CuI in an amount 1.0 mol % was started after 1 h of reflux and repeated after every 2 h till the total amount CuI reached 5.0 mol %. The isolation and purification was carried out analogously **15** by column chromatography using dichloromethane as an eluent to give compound **26** (0.05 g, 99%) as a colourless solid, mp 188.3–189.8 °C. UV (THF), λ, nm (ε, l mol^{-1} cm^{-1}): 291 (2×10^4), 330 (1×10^4); δ_H ($CDCl_3$): 1.49 (3H, t, *J*=6.9 Hz, Me), 3.96 (3H, s, OCH_3), 4.15 (2H, q, *J*=6.9 Hz, CH_2O), 6.48 (1H, d, *J*=3.9 Hz, 5-H), 7.04 [2H, dm, *J*=9 Hz, 3′,5′-H (4-EtOC_6H_4)], 7.15 [2H, dm, *J*=9 Hz, 3′,5′-H (4-MeOC_6H_4)], 7.40–7.43 [1H, m, 4′-H (N_7–Ph)], 7.55 (1H, d, *J*=3.9 Hz, 6-H), 7.59–7.64 [2H, m, 3′,5′-H (N_7–Ph)], 7.93 [2H, dm, *J*=8.4 Hz, 2′,6′-H (N_7–Ph)], 8.31 [2H, dm, *J*=9 Hz, 2′,6′-H (4-MeOC_6H_4)], 8.63 [2H, dm, *J*=9 Hz, 2′,6′-H (4-EtOC_6H_4)]; δ_C ($CDCl_3$): 15.1, 55.7, 63.7, 102.5, 114.2, 114.3, 114.4, 124.0, 126.7, 128.0, 129.6, 129.9, 130.8, 131.6, 131.8, 138.2, 152.9, 157.5, 158.4, 160.7, 161.5; HRMS (ESI): MH^+, found 422.1856. $C_{27}H_{23}N_3O_2$ requires 422.1863.

Method B. A solution of compound **27** (0.05 g, 0.15 mmol) in anhydrous dioxane (5 mL) was flushed with argon and 2.0 mol % $Pd(OAc)_2$ and 4.0 mol % (2-biphenyl)dicyclohexylphosphine were added under stirring and argon flow. After 10 min. 4-ethoxyphenylboronic acid (0.03 g, 0.18 mmol) and K_3PO_4 (0.08 g, 0.38 mmol) were added. The reaction mixture was stirred under reflux for 5 h and 0.3 equiv of 4-ethoxyphenylboronic acid and 0.6 equiv of K_3PO_4 were added additionally. Total reaction time was 20 h. Then dioxane was evaporated under reduced pressure to dryness and water (5 mL) was added to dissolve inorganic salts. The obtained solution was extracted with ethyl acetate (3×25 mL), organic layer was dried with Na_2SO_4, ethyl acetate removed by distillation under reduced pressure, and the solid was purified by column chromatography using dichloromethane to give compound **26** (0.04 g, 64%) as a colourless solid, mp 188.3–189.8 °C.

*4.1.29. 2-Chloro-4-(4-methoxyphenyl)-7-phenyl-7H-pyrrolo[2,3-d] pyrimidine (**27**).* A solution of compound **4f** (0.20 g, 0.77 mmol) in anhydrous dioxane (10 mL) was flushed with argon and 1.0 mol % CuI, anhydrous K_3PO_4 (0.29 g, 1.37 mmol), iodobenzene (0.072 mL, 0.64 mmol), 10.0 mol % (±)-*trans*-1,2-diaminocyclohexane were added under stirring and argon flow. The reaction mixture was stirred under reflux for 2 h and 1.0 mol % of CuI was added. Addition of portions 1.0 mol % CuI to the reaction mixture was continued every hour till amount of CuI reached 5.0 mol %. Then after 2 h 1.0 mol % CuI and 10.0 mol % (±)-*trans*-1,2-diaminocyclohexane were added. Addition of CuI was continued every hour in portions 1.0 mol % till amount of CuI reached 10.0 mol %. Then after 2 h 2.0 mol % CuI and 10.0 mol % (±)-*trans*-1,2-diaminocyclohexane were added. Total reaction time was 33 h, total amount of CuI—12.0 mol %, (±)-*trans*-1,2-diaminocyclohexane—30.0 mol %. After cooling the reaction mixture to room temperature ethyl acetate (5 mL) was added, resulting solution was filtered through a layer of silica gel eluting with ethyl acetate. The filtrate was concentrated under reduced pressure and the residue purified by column chromatography using benzene as an eluent to give compound **27** (0.08 g, 37%) as a colourless solid, mp 164.4–165.1 °C. δ_H ($CDCl_3$): 3.95 (3H, s, OCH_3), 7.01

(1H, d, J=3.9 Hz, 5-H), 7.11 [2H, dm, J=8.7 Hz, 3′,5′-H ($MeOC_6H_4$)], 7.44–7.62 [4H, m, 6-H, 3′-5′-H (N_7–Ph)], 7.75 [2H, dm, J=8.1 Hz, 2′,6′-H (N_7–Ph)], 8.18 [2H, dm, J=8.7 Hz, 2′,6′-H ($MeOC_6H_4$)]; δ_C ($CDCl_3$): 55.7, 102.6, 114.6, 114.9, 124.3, 127.7, 129.3, 129.7, 129.9, 130.9, 137.3, 152.9, 154.6, 159.9, 162.1; HRMS (ESI): MH^+, found 336.0900. $C_{19}H_{14}ClN_3O$ requires 336.0898.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.10.040. These data include MOL files and InChiKeys of the most important compounds described in this article.

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