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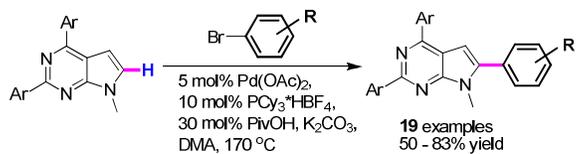
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## PAPER

An access to 6-arylpyrrolo[2,3-*d*]pyrimidines via palladium-catalyzed direct C-H arylation reaction

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# An access to 6-arylpyrrolo[2,3-*d*]pyrimidines via palladium-catalyzed direct C-H arylation reaction

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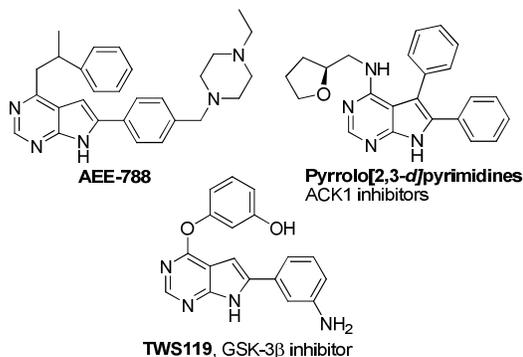
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**Abstract.** An efficient method of the palladium-catalyzed direct arylation has been developed for the selective functionalization of the C6 position of 2,4-diarylpyrrolo[2,3-*d*]pyrimidines. Under optimal conditions various aryl bromides were successfully applied to provide a wide range of 6-arylpyrrolo[2,3-*d*]pyrimidines.

**Keywords:** aryl halides; arylation; C-H activation; nitrogen heterocycles, palladium.

## Introduction

Pyrrolo[2,3-*d*]pyrimidine, its aryl and heteroaryl derivatives were found to display a wide range of biological activities, such as inhibition of protein kinases<sup>[1]</sup>, thymidylate synthase<sup>[2]</sup> and dihydrofolate reductase,<sup>[3]</sup> antitumor,<sup>[4]</sup> antimicrobial,<sup>[5]</sup> antagonist effects to receptors,<sup>[6]</sup> cytostatic and antiproliferative effects.<sup>[6a,7]</sup> Several examples of synthetic biologically active compounds possessing pyrrolo[2,3-*d*]pyrimidine core could be EGFR-tyrosine kinases inhibitor AEE-788,<sup>[8]</sup> ACK1 inhibitors<sup>[4]</sup> and neurogenesis inductors by GSK-3 $\beta$  inhibition (TWS119)<sup>[9]</sup> (Figure 1).



**Figure 1.** Biologically active pyrrolo[2,3-*d*]pyrimidines.

In addition to these applications, oligoarylenes with pyrrolo[2,3-*d*]pyrimidine core were shown to exhibit strong UV-blue fluorescence and are promising candidates as fluorescent functional materials.<sup>[10]</sup> Moreover, some pyrrolo[2,3-*d*]pyrimidine derivatives form fluorescent nanoaggregates and show aggregation induced emission enhancement.<sup>[11]</sup> Compounds possessing functionalized pyrrolo[2,3-*d*]pyrimidine scaffold can be prepared by cyclocondensation reactions starting either from the appropriately substituted pyrrole<sup>[5b,12]</sup> or pyrimidine<sup>[6c,13]</sup> derivatives as common intermediates. However, these strategies often require multistep syntheses and, thus the synthesis of polysubstituted pyrrolopyrimidines using such methods tends to be rather long and time-consuming. On the other hand, pyrrolo[2,3-*d*]pyrimidine can be functionalized using the late-stage functionalization methods, for example various transition metal catalyzed cross-coupling reactions. Generally, such methods allow the introduction of different aryl moieties into various positions of the heterocycle and diversely functionalized pyrrolo[2,3-*d*]pyrimidines can be obtained in good yields.<sup>[3,10,13c,14]</sup> Despite significant advances of cross-coupling reactions, multiple steps for installation of active groups are usually required and none of the preactivation groups appear in the final product. Therefore, in recent years direct arylation reactions as more atom-economic and step-simplified have emerged as attractive alternatives to these more commonly employed cross-coupling reactions.<sup>[15]</sup> Although direct arylation has been demonstrated on a wealth of aromatic heterocycles so far, there still remains a multitude of heteroaromatic ring systems that have not been investigated. Pyrrolo[2,3-*d*]pyrimidine is one of them. To the best of our knowledge, the only attempt to synthesize 6-arylpyrrolopyrimidines by direct arylation of 7-benzyl-4-phenylpyrrolo[2,3-*d*]pyrimidine with iodoarenes and heteroarenes was made by *M. Hocek*.<sup>[14a]</sup> However, the reaction gave products (3 examples) in low 35-41% yields or did not take place. Taking into consideration that pyrrolo[2,3-*d*]pyrimidine ring system represents an important pharmacophore in drug discovery and its

aryl derivatives possess valuable photophysical properties, efficient and economic methods for the synthesis of arylpyrrolo[2,3-*d*]pyrimidines are highly required. Therefore, we have been interested in studying direct arylation of the pyrrolopyrimidine to provide easy access to 6-arylpyrrolo[2,3-*d*]pyrimidines.

## Results and discussion

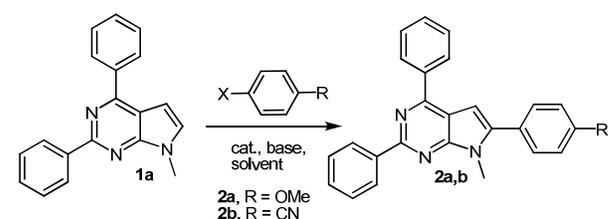
Initially, our efforts were focused on identifying the catalytic system and reaction conditions for direct arylation of compound **1a** with 4-iodoanisole (Table 1). We began our study with the arylation of pyrrolo[2,3-*d*]pyrimidine **1a** applying catalyst system used by *Hocek*.<sup>[14a]</sup> After heating the reaction mixture at 170 °C for 72 hours in the presence of Pd(OAc)<sub>2</sub>/CuI/Cs<sub>2</sub>CO<sub>3</sub> product **2a** was obtained in low 21% yield (Table 1, entry 1). A little higher yield of **2a** (34%) was obtained when a catalyst system composed of Pd(OAc)<sub>2</sub>, P(2-biPh)Cy<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> was employed (Table 1, entry 2). These results together with the reported ones<sup>[14a, 16]</sup> indicate that catalyst system suitable for the direct arylation of purines does not work well in a pyrrolo[2,3-*d*]pyrimidine series. Otherwise, using conditions similar to those of *Fagnou's* heteroaryl direct arylation procedure,<sup>[17]</sup> we were pleased to observe that C6 direct arylation of pyrrolo[2,3-*d*]pyrimidine **1a** proceeded at 170 °C to provide **2a** in 80% yield (Table 1, entry 3). Decreasing the loading of the catalyst from 5 mol% to 2 mol% led to the lower yield of compound **2a** (40%) (Table 1, entry 4). It is also worthy to note the role of pivalic acid - the reaction performed without pivalic acid under the same conditions furnished **2a** only in 46% (Table 1, entry 5). Addition of pivalic acid (30 mol%) to a catalyst system Pd(OAc)<sub>2</sub>/P(2-biPh)Cy<sub>2</sub>/K<sub>2</sub>CO<sub>3</sub> also increased the reactivity of **1a** and product **2a** was obtained in 51% (Table 1, compare entry 6 with entry 2).

*K. Fagnou* established that reactivity of aryl iodides is sometimes reduced due to the accumulation of iodide anions in the reaction mixture and that this catalyst poisoning can be overcome by adding AgOTf or Ag<sub>2</sub>CO<sub>3</sub> to the reaction mixture.<sup>[18]</sup> However, in our case addition of Ag<sub>2</sub>CO<sub>3</sub> was useless and the product **2a** was obtained almost in the same yield (Table 1, entry 7).

In order to compare reactivity of aryl bromides and aryl iodides, we decided to examine the reaction of pyrrolo[2,3-*d*]pyrimidine **1a** with 4-bromoanisole using the same catalytic system - Pd(OAc)<sub>2</sub>/PCy<sub>3</sub>\*HBF<sub>4</sub>/PivOH/K<sub>2</sub>CO<sub>3</sub>/DMA. Gratifyingly, after 72 hours heating at 170 °C the desired product was obtained in 79% yield (Table 1, entry 8). However, when free tricyclohexylphosphine was used as a ligand, only traces of target compound **2a** were isolated (Table 1, entry 9). Change of the reaction solvent from DMA to dioxane resulted in the formation of compound **2a** only in 10% yield (Table 1, entry 10). To clarify reactivity of aryl iodides and bromides with electron-withdrawing group, C-H

arylation using 4-iodo(or bromo)benzonitrile has been carried out. In contrast to 4-iodoanisole, 4-iodobenzonitrile reacted with pyrrolo[2,3-*d*]pyrimidine **1a** very poorly and compound **2b** was obtained only in 17% yield (Table 1, entry 11). Moreover, along with the target C6-arylated product **2b** 5,5'-bipyrrolo[2,3-*d*]pyrimidine **3** was isolated, as well.

**Table 1.** Optimization for direct C6 arylation of pyrrolopyrimidine **1a**.<sup>a)</sup>



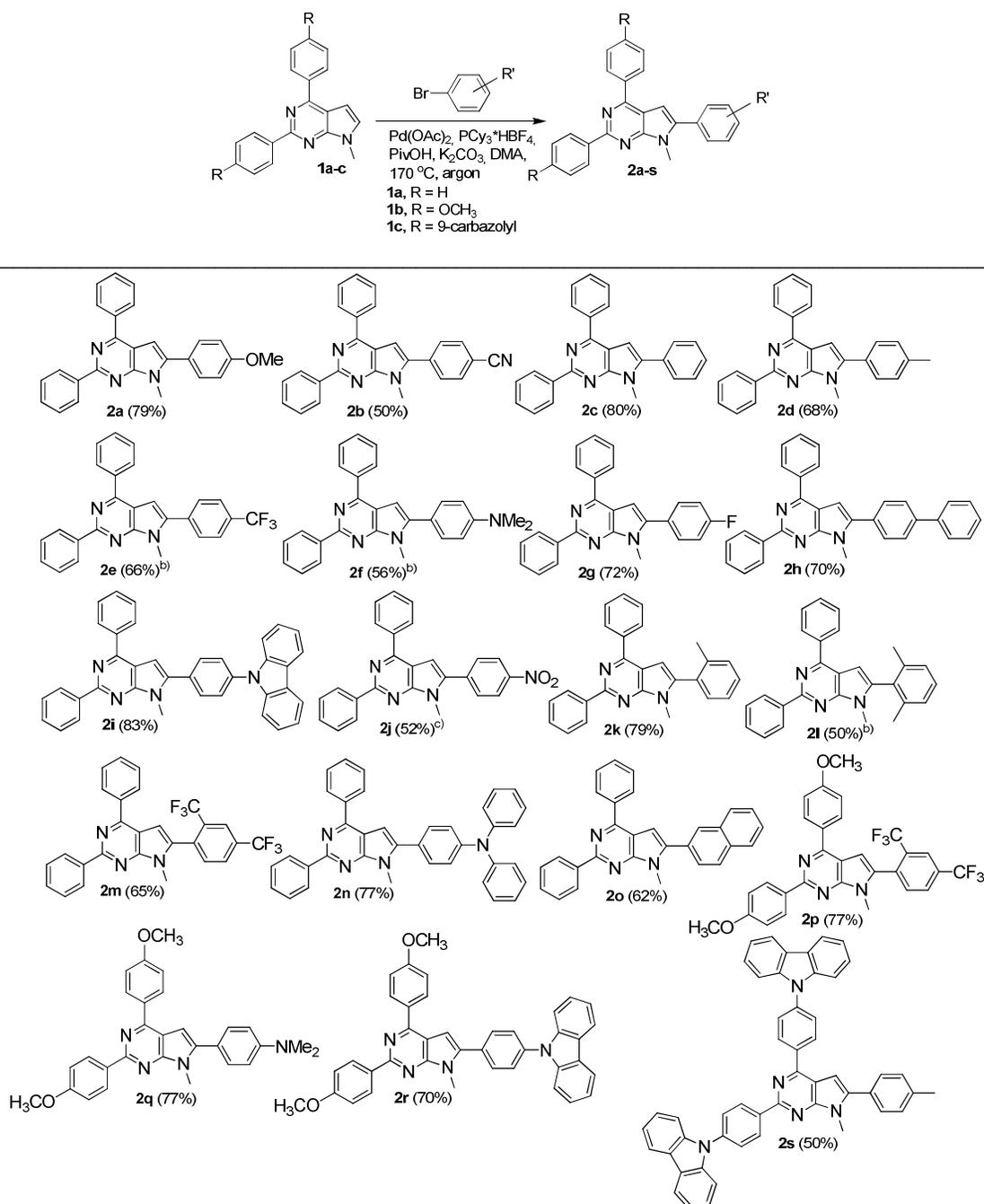
Entry	RC <sub>6</sub> H <sub>4</sub> X	Reaction conditions	Yield, % <sup>b)</sup>
1	4-MeOC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> , CuI, Cs <sub>2</sub> CO <sub>3</sub>	<b>2a</b> , 21 <sup>c)</sup>
2	4-MeOC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> , P(2-biPh)Cy <sub>2</sub> , K <sub>2</sub> CO <sub>3</sub>	<b>2a</b> , 34
3	4-MeOC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> , PCy <sub>3</sub> *HBF <sub>4</sub> , PivOH, K <sub>2</sub> CO <sub>3</sub>	<b>2a</b> , 80
4	4-MeOC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> , PCy <sub>3</sub> *HBF <sub>4</sub> , PivOH, K <sub>2</sub> CO <sub>3</sub>	<b>2a</b> , 40 <sup>d)</sup>
5	4-MeOC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> , PCy <sub>3</sub> *HBF <sub>4</sub> , K <sub>2</sub> CO <sub>3</sub>	<b>2a</b> , 46
6	4-MeOC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> , P(2-biPh)Cy <sub>2</sub> , PivOH, K <sub>2</sub> CO <sub>3</sub>	<b>2a</b> , 51
7	4-MeOC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> , PCy <sub>3</sub> *HBF <sub>4</sub> , PivOH, K <sub>2</sub> CO <sub>3</sub> , Ag <sub>2</sub> CO <sub>3</sub>	<b>2a</b> , 78
8	4-MeOC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> , PCy <sub>3</sub> *HBF <sub>4</sub> , PivOH, K <sub>2</sub> CO <sub>3</sub>	<b>2a</b> , 79
9	4-MeOC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> , PCy <sub>3</sub> , PivOH, K <sub>2</sub> CO <sub>3</sub>	<b>2a</b> , 2 <sup>e)</sup>
10	4-MeOC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> , PCy <sub>3</sub> *HBF <sub>4</sub> , PivOH, K <sub>2</sub> CO <sub>3</sub> , Dioxane	<b>2a</b> , 10 <sup>e)</sup>
11	4-CNC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> , PCy <sub>3</sub> *HBF <sub>4</sub> , PivOH, K <sub>2</sub> CO <sub>3</sub>	<b>2b</b> , 17
12	4-CNC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> , PCy <sub>3</sub> *HBF <sub>4</sub> , PivOH, K <sub>2</sub> CO <sub>3</sub>	<b>2b</b> , 50

<sup>a)</sup> Unless otherwise specified, all reactions were carried out using 5 mol% Pd(OAc)<sub>2</sub>, 10 mol% PCy<sub>3</sub>\*HBF<sub>4</sub> or P(2-biPh)Cy<sub>2</sub>, 30 mol% PivOH, 1.5 equiv. RC<sub>6</sub>H<sub>4</sub>X, 3 equiv. K<sub>2</sub>CO<sub>3</sub> in DMA at 170 °C, 72 h, argon. <sup>b)</sup> Isolated yields. <sup>c)</sup> 5 mol% Pd(OAc)<sub>2</sub>, 3 equiv. CuI, 2 equiv. RC<sub>6</sub>H<sub>4</sub>X, 2.5 equiv. Cs<sub>2</sub>CO<sub>3</sub>, argon. <sup>d)</sup> 2 mol% Pd(OAc)<sub>2</sub>, 4 mol% PCy<sub>3</sub>\*HBF<sub>4</sub>. <sup>e)</sup> the rest of **1a** recovered.

Meanwhile, 4-bromobenzonitrile under the same reaction conditions furnished the C6 arylation product **2b** in 50% yield (Table 1, entry 12). Finally, brief screening of bases employing  $\text{Cs}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , KOAc and AgOAc revealed that  $\text{K}_2\text{CO}_3$  is the most suitable base for C6 arylation reaction of the pyrrolo[2,3-*d*]pyrimidine.

Having established the optimal reaction conditions, that is  $\text{Pd}(\text{OAc})_2/\text{PCy}_3\cdot\text{HBF}_4/\text{PivOH}$  as the catalyst system,  $\text{K}_2\text{CO}_3$  as a base and DMA as a solvent, we next turned our attention to the scope of the direct arylation of 7-methyl-2,4-diarylpyrrolo[2,3-*d*]pyrimidines (**1a-c**) with aryl bromides as a result of their stability and ease of preparation on the laboratory scale.

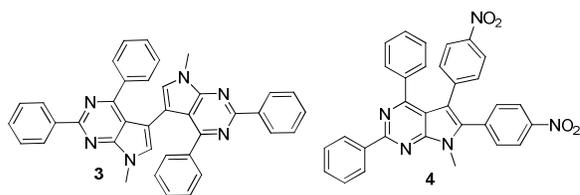
**Scheme 1.** Scope of C6 arylation of 7-methyl-2,4-diarylpyrrolo[2,3-*d*]pyrimidines.<sup>a)</sup>



<sup>a)</sup> Reaction conditions (isolated yields): Compound **1a-c** (70 mg),  $\text{Pd}(\text{OAc})_2$  (5 mol%),  $\text{PCy}_3\cdot\text{HBF}_4$  (10 mol%), PivOH (30 mol%), aryl halide (1.5 equiv.),  $\text{K}_2\text{CO}_3$  (3 equiv.), DMA. <sup>b)</sup> 7-10 mg of compound **3** were isolated. <sup>c)</sup> 4 mg of compound **4** were isolated.

As shown in Scheme 1, a variety of aryl bromides with either electron-donating or electron-withdrawing groups attached at the *ortho*- and/or *para*-positions to benzene ring were able to undergo arylation and furnished the corresponding products **2a-s** in moderate to good yields. The reaction showed good compatibility with many valuable functional groups such as methoxy, cyano, nitro, dimethylamino, fluoro, and trifluoromethyl substituents. Pyrrolo[2,3-*d*]pyrimidines also reacted with sterically encumbered aryl bromides, such as 2-bromotoluene, 1-bromo-2,6-dimethylbenzene or 1-bromo-2,4-di(trifluoromethyl)benzene to afford the corresponding products **2k-m,p** in 50-79% yields.

The arylation reaction of pyrrolo[2,3-*d*]pyrimidines **1a-c** can occur at the position 5 or 6 of the pyrrolopyrimidine. However, structure elucidation of the obtained products by NMR spectroscopy showed that arylation reaction is site-selective and only 6-aryl derivatives were obtained. In the <sup>1</sup>H NMR spectra of compounds **2** the pyrrole 5-*H* proton signal remains almost in the same range at 6.8-7.0 ppm as in the starting compounds **1**. Moreover, NOESY spectra of products showed two significant types of cross-signals – one between *N*-methyl group and *ortho*-protons of the aromatic ring at position 6, and the second between 5-*H* proton of the pyrrole ring and *ortho*-protons of the aromatic rings at positions 4 and 6 of the pyrrolopyrimidine. Additionally, in the NOESY spectra no interaction between *N*-methyl group protons and proton of the pyrrole ring was observed. This incontrovertibly proved that only C6 arylated products were obtained.



**Figure 2.** Structures of 7,7'-dimethyl-2,2',4,4'-tetraphenyl-7*H*,7'*H*-5,5'-bipyrrolo[2,3-*d*]pyrimidine (**3**) and 7-methyl-5,6-di(4-nitrophenyl)-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (**4**).

Nevertheless, in some cases the formation of two types of byproducts was observed (Figure 2). The first one was identified as a dimerization product **3**. This byproduct in small amounts (up to 7%) was formed in the reaction of pyrrolo[2,3-*d*]pyrimidine **1a** with 1-bromo-4-trifluoromethyl-, 1-bromo-4-dimethylamino- and 1-bromo-2,6-dimethylbenzenes. Compound **3**, probably, is formed during side-reaction of the palladium-catalyzed oxidative C5-H activation with Pd(OAc)<sub>2</sub>. Another byproduct – 5,6-diarylated derivative **4** (3%) was observed only in the reaction of compound **1a** with 4-nitrophenyl bromide (Figure 2). Formation of these byproducts caused some problems in purification of the target

compounds. Therefore, lower final yields of the corresponding C6 arylation products **2f,j,l** were obtained.

As it was mentioned, the yields of the selective C6 arylation were dramatically lower without a palladium-pivalate co-catalyst combination. These results suggest that the C6 arylation proceeds *via* a concerted metallation-deprotonation mechanism (CMD).<sup>[19]</sup>

## Conclusion

In summary, an efficient regioselective Pd-catalyzed direct arylation of 7-methyl-2,4-diarylpyrrolo[2,3-*d*]pyrimidines with aryl bromides has been developed. The procedure tolerates many functional groups and allows to generate a wide library of novel pyrrolo[2,3-*d*]pyrimidine derivatives including those with  $\pi$ -extended conjugated systems. The results presented here may find use in materials and pharmaceutical research programs.

## Experimental Section

**General procedure for the synthesis of 2,4-diaryl-7-methylpyrrolo[2,3-*d*]pyrimidines 1a-c:** A solution of 2,4-dichloro-7-methylpyrrolo[2,3-*d*]pyrimidine (150 mg, 0.74 mmol) in anhydrous dioxane (5 ml) was flushed with argon and Pd(OAc)<sub>2</sub> (3.32 mg, 0.015 mmol, 2 mol%) and (2-biphenyl)dicyclohexylphosphine (10.4 mg, 0.03 mmol, 4 mol%) were added under stirring and argon flow. After 10 min. arylboronic acid (1.78 mmol, 2.4 equiv.) and K<sub>3</sub>PO<sub>4</sub> (0.76 g, 3.56 mmol, 4.8 equiv.) were added. The reaction mixture was stirred under reflux. 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 over Na<sub>2</sub>SO<sub>4</sub>, and chloroform removed by distillation under reduced pressure and residue was purified by column chromatography using benzene as an eluent.

**7-Methyl-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (1a).** After 15 min. compound **1a** was obtained as a yellowish solid (190 mg, 90%), mp 159.8-161.4 °C. Lit.<sup>[20]</sup> mp 159-160 °C. All spectra matched literature values. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.00 (3H, s, NCH<sub>3</sub>), 6.85 [1H, d, *J* = 4 Hz, 5-*H* (pp)], 7.25 [1H, d, *J* = 4 Hz, 6-*H* (pp)], 7.46-7.63 [6H, m, 2×3-5-*H* (2-Ph, 4-Ph)], 8.31 [2H, dm, *J* = 8 Hz, 2,6-*H* (4-Ph)], 8.72 [2H, dm, *J* = 8 Hz, 2,6-*H* (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 31.1, 100.3, 113.9, 128.1, 128.4, 128.7, 129.0, 129.6, 129.9, 130.0, 138.8, 139.1, 153.1, 157.0, 157.6 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>19</sub>H<sub>16</sub>N<sub>3</sub>): 286.1339, found: 286.1342.

**2,4-Di(4-methoxyphenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (1b).** After 4 h compound **1b** was obtained as a yellowish solid (182 mg, 71%), mp 138.4-139.7 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.92 (3H, s, OCH<sub>3</sub>), 3.93 (3H, s, OCH<sub>3</sub>), 3.96 (3H, s, NCH<sub>3</sub>), 6.81 [1H, d, *J* = 4 Hz, 5-*H* (pp)], 7.05 [2H, d, *J* = 8 Hz, 3,5-*H* (2-Ph)], 7.11 [2H, d, *J* = 8 Hz, 3,5-*H* (4-Ph)], 7.19 [1H, d, *J* = 4 Hz, 6-*H* (pp)], 8.29 [2H, dm, *J* = 8 Hz, 2,6-*H* (4-Ph)], 8.66 [2H, dm, *J* = 8 Hz, 2,6-*H* (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 31.0, 55.4, 55.42, 100.3, 112.9, 113.7, 114.1, 129.2, 129.5, 130.5, 131.6, 132.1, 153.1, 156.5, 157.5, 161.0, 161.1 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>21</sub>H<sub>20</sub>N<sub>3</sub>O<sub>2</sub>): 346.1550, found: 346.1548.

**2,4-Di[4-(9H-carbazol-9-yl)phenyl]-7-methyl-7H-pyrrolo[2,3-d]pyrimidine (1c).** After 9.5 h compound **1c** was obtained as a reddish solid (410 mg, 90%), mp 284-285.8 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.08 (3H, s, NCH<sub>3</sub>), 7.00 [1H, d, *J* = 4 Hz, 5-H (pp)], 7.33–7.39 [m, 5H, 6-H (pp), 2×3,6-H (2-carb., 4-carb.)], 7.46–7.52 [4H, m, 2×2,7-H (2-carb., 4-carb.)], 7.58–7.62 [4H, m, 2×1,8-H (2-carb., 4-carb.)], 7.79 [2H, d, *J* = 8 Hz, 3,5-H (4-Ph)], 7.86 [2H, d, *J* = 8 Hz, 3,5-H (2-Ph)], 8.20–8.23 [4H, m, 2×4,5-H (2-carb., 4-carb.)], 8.61 [2H, d, *J* = 8.4 Hz, 2,6-H (4-Ph)], 9.00 [2H, d, *J* = 8.7 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 31.3, 100.3, 109.9, 110.0, 114.1, 120.0, 120.3, 120.4, 120.42, 123.5, 123.7, 126.0, 126.1, 126.9, 127.1, 129.7, 130.56, 130.6, 137.6, 138.1, 138.9, 139.4, 140.7, 140.8, 153.3, 156.1, 157.1 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>43</sub>H<sub>30</sub>N<sub>5</sub>): 616.2496, found: 616.2490.

**General procedure for C-H arylation:** 7-Methyl-2,4-diphenylpyrrolo[2,3-d]pyrimidine (**1a**) (70 mg, 0.245 mmol), Pd(OAc)<sub>2</sub> (2.75 mg, 0.0125 mmol, 5 mol %), PCy<sub>3</sub>\*HBF<sub>4</sub> (9.0 mg, 0.0244 mmol, 10 mol%), PivOH (7.5 mg, 0.0734 mmol, 30 mol%), aryl halide (0.37 mmol, 1.5 equiv.) and K<sub>2</sub>CO<sub>3</sub> (100 mg, 0.724 mmol, 3 equiv.) and DMA (1-2 mL) were placed in a screw-cap vial equipped with a magnetic stir bar. The vial was purged with argon and the reaction mixture was stirred vigorously at 170 °C for 72 h. After completion of the reaction, water (10 ml) was added and the aqueous solution was extracted with ethyl acetate (3×25 ml). The combined extract was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, ethyl acetate removed by distillation under reduced pressure and residue was purified by column chromatography using gradient elution hexane/benzene → benzene.

**6-(4-Methoxyphenyl)-7-methyl-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2a).** Product **2a** was obtained as a yellow solid (76 mg, 79%), mp 152.2-153.8 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.92 (3H, s, OCH<sub>3</sub>), 3.98 (3H, s, NCH<sub>3</sub>), 6.85 [1H, s, 5-H (pp)], 7.07 [2H, dm, *J* = 8 Hz, 3,5-H (6-Ph)], 7.48–7.62 [8H, m, 2×3-5-H (2-Ph, 4-Ph), 2,6-H (6-Ph)], 8.35 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.74 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 29.9, 55.4, 99.3, 114.27, 114.3, 124.1, 128.0, 128.4, 128.7, 129.0, 129.4, 129.8, 130.4, 139.0, 139.3, 143.0, 154.6, 155.9, 157.2, 160.1 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>26</sub>H<sub>22</sub>N<sub>3</sub>O): 392.1757, found: 392.1767.

**6-(4-Cyanophenyl)-7-methyl-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2b).** Product **2b** was obtained as a yellowish green solid (47 mg, 50%), mp 225-226.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.02 (3H, s, NCH<sub>3</sub>), 7.00 [1H, s, 5-H (pp)], 7.50–7.64 [6H, m, 2×3-5-H (2-Ph, 4-Ph)], 7.75 [2H, dm, *J* = 8 Hz, 2,6-H (6-Ph)], 7.84 [2H, dm, *J* = 8 Hz, 3,5-H (6-Ph)], 8.32 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.74 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 30.2, 101.8, 112.2, 114.0, 118.5, 127.9, 128.2, 128.4, 128.8, 129.0, 129.4, 129.8, 130.2, 132.6, 132.9, 138.5, 138.8, 155.0, 157.3, 158.2 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>26</sub>H<sub>19</sub>N<sub>4</sub>): 387.1603, found: 387.1604.

**7-Methyl-2,4,6-triphenyl-7H-pyrrolo[2,3-d]pyrimidine (2c).** Product **2c** was obtained as a yellowish solid (71 mg, 80%), mp 134-134.9 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.00 (3H, s, NCH<sub>3</sub>), 6.92 [1H, s, 5-H (pp)], 7.49–7.64 [11H, m, 2×3-5-H (2-Ph, 4-Ph), 2,6-H (6-Ph)], 8.36 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.75 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 30.0, 100.0, 114.2, 128.1, 128.4, 128.7, 128.76, 128.8, 129.0, 129.1, 129.5, 129.9, 131.7, 138.9, 139.2, 143.0, 154.7, 156.3, 157.5 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>25</sub>H<sub>20</sub>N<sub>3</sub>): 362.1652, found: 362.1652.

**7-Methyl-6-(4-methylphenyl)-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2d).** Product **2d** was obtained as a bright yellow solid (63 mg, 68%), mp 196-197.8 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.48 (3H, s, CH<sub>3</sub>), 3.99 (3H, s, NCH<sub>3</sub>), 6.88 [1H, s, 5-H (pp)], 7.36 [2H, dm, *J* = 8 Hz, 3,5-H (6-Ph)], 7.46–7.62 [8H, m, 2×3-5-H (2-Ph, 4-Ph), 2,6-H (6-Ph)], 8.34 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.74 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 21.4, 29.9, 99.6, 114.3, 128.0, 128.4, 128.7, 128.8, 128.98, 128.99, 129.4, 129.5, 129.8, 138.8, 139.0, 139.3, 143.2, 154.7, 156.1, 157.3 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>26</sub>H<sub>22</sub>N<sub>3</sub>): 376.1808, found: 376.1814.

**6-(4-Trifluoromethylphenyl)-7-methyl-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2e).** Product **2e** was obtained as a bright yellow solid (66 mg, 66%), mp 200-201.7 °C. 7 mg (5%) of compound **3** were isolated, as well. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.00 (3H, s, NCH<sub>3</sub>), 6.97 [1H, s, 5-H (pp)], 7.49–7.61 [6H, m, 2×3-5-H (2-Ph, 4-Ph)], 7.75 [2H, dm, *J* = 8 Hz, 2,6-H (6-Ph)], 7.81 [2H, dm, *J* = 8 Hz, 3,5-H (6-Ph)], 8.33 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.75 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 30.1, 101.2, 114.0, 124.0 (*J* = 273 Hz), 125.8 (*J* = 4 Hz), 128.1, 128.4, 128.7, 129.0, 129.3, 129.7, 130.1, 130.7 (*J* = 33 Hz), 135.3, 138.7, 139.0, 141.1, 154.8, 156.9, 157.9 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): -62.65 (CF<sub>3</sub>) ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>26</sub>H<sub>19</sub>F<sub>3</sub>N<sub>3</sub>): 430.1526, found: 430.1531.

**6-[4-(Dimethylamino)phenyl]-7-methyl-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2f).** Product **2f** was obtained as a dark yellow solid (55 mg, 56%), mp 214.4-215.5 °C. 7 mg (5%) of compound **3** were isolated, as well. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.07 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 4.00 (3H, s, NCH<sub>3</sub>), 6.83-6.86 [3H, m, 5-H (pp), 3,5-H (6-Ph)], 7.49-7.61 [8H, m, 2×3-5-H (2-Ph, 4-Ph), 2,6-H (6-Ph)], 8.37 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.75 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 30.0, 40.4, 98.3, 112.1, 114.6, 119.1, 128.0, 128.4, 128.6, 129.0, 129.3, 129.6, 130.0, 139.2, 139.4, 144.0, 150.6, 154.7, 155.3, 156.8 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>27</sub>H<sub>25</sub>N<sub>4</sub>): 405.2074, found: 405.2077.

**6-(4-Fluorophenyl)-7-methyl-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2g).** Product **2g** was obtained as a yellowish solid (67 mg, 72%), mp 150-151.4 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.98 (3H, s, NCH<sub>3</sub>), 6.88 [1H, s, 5-H (pp)], 7.23-7.27 [2H, m, 3,5-H (6-Ph)], 7.48-7.62 [8H, m, 2×3-5-H (2-Ph, 4-Ph), 2,6-H (6-Ph)], 8.34 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.74 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 29.9, 100.1, 114.1, 115.9 [d, *J* = 22 Hz, 3,5-C (6-Ph)], 127.84 [d, *J* = 4 Hz, 1-C(6-Ph)], 128.1, 128.4, 128.7, 129.0, 129.6, 129.9, 130.9 [d, *J* = 8 Hz, 2,6-C (6-Ph)], 138.8, 139.1, 141.9, 154.6, 156.4, 157.6, 163.1 [d, *J* = 247 Hz, 4-C (6-Ph)] ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): -112.17 (F) ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>25</sub>H<sub>19</sub>FN<sub>3</sub>): 380.1558, found: 380.1559.

**6-(Biphenyl-4-yl)-7-methyl-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2h).** Product **2h** was obtained as a yellowish solid (76 mg, 70%), mp 242.3-244 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.06 (3H, s, NCH<sub>3</sub>), 6.97 [1H, s, 5-H (pp)], 7.40-7.79 [15H, m, 2×3-5-H (2-Ph, 4-Ph), 2,3,5,6,2'-6'-H (6-biPh)], 8.36 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.75 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 30.1, 100.1, 114.3, 127.1, 127.5, 127.8, 128.1, 128.4, 128.7, 128.9, 129.0, 129.4, 129.5, 129.9, 130.6, 138.9, 139.2, 140.3, 141.6, 142.7, 154.8, 156.3, 157.5 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>31</sub>H<sub>24</sub>N<sub>3</sub>): 438.1965, found: 438.1970.

**6-[4-(9H-carbazol-9-yl)phenyl]-7-methyl-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2i).** Product **2i** was obtained as a yellowish solid (107 mg, 83%), mp 258.5-259.8 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.12 (3H, s, NCH<sub>3</sub>), 7.04 [1H, s, 5-H (pp)], 7.37-7.64 [12H, m, 2×3-5-H (2-Ph, 4-Ph), 1-3,6-8-H (6-carb.)], 7.77 [2H, dm, *J* = 8 Hz, 3,5-H (6-Ph)], 7.87 [2H, dm, *J* = 8 Hz, 2,6-H (6-Ph)], 8.21 [2H, dm, *J* = 8 Hz, 4,5-H (6-carb.)], 8.39 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.78 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 30.2, 100.6, 109.8, 114.2, 120.3, 120.5, 123.7, 126.1, 127.2, 128.1, 128.4, 128.8, 129.0, 129.6, 130.0, 130.5, 130.6, 138.2, 138.8, 139.1, 140.6, 142.0, 154.9, 156.6, 157.7 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>37</sub>H<sub>27</sub>N<sub>4</sub>): 527.2230, found: 527.2242.

**7-Methyl-6-(4-nitrophenyl)-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2j).** Product **2j** was obtained as an orange solid (52 mg, 52%), mp 263.1-264.5 °C. 4 mg (3%) of compound **4** were isolated, as well. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.05 (3H, s, NCH<sub>3</sub>), 7.05 [1H, s, 5-H (pp)], 7.52-7.62 [6H, m, 2×3-5-H (2-Ph, 4-Ph)], 7.82 [2H, dm, *J* = 8 Hz, 2,6-H (6-Ph)], 8.33 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.41 [2H, dm, *J* = 8 Hz, 3,5-H (6-Ph)], 8.74 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 30.3, 102.3, 114.0, 124.1, 128.2, 128.4, 128.8, 129.0, 129.5, 129.9, 130.2, 138.1, 138.5, 138.8, 140.1, 147.6, 155.1, 157.5, 158.4 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>25</sub>H<sub>19</sub>N<sub>4</sub>O<sub>2</sub>): 407.1503, found: 407.1506.

**7-Methyl-6-(2-methylphenyl)-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2k).** Product **2k** was obtained as a yellowish oil (73 mg, 79%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.30 (3H, s, CH<sub>3</sub>), 3.76 (3H, s, NCH<sub>3</sub>), 6.84 [1H, s, 5-H (pp)], 7.36-7.64 [10H, m, 2×3-5-H (2-Ph, 4-Ph), 3-6-H (6-Ph)], 8.39 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.79 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 20.0, 29.2, 100.1, 114.2, 125.9, 128.1, 128.4, 128.7, 129.1, 129.4, 129.5, 129.9, 130.4, 130.8, 131.4, 137.9, 139.0, 139.3, 142.3, 153.9, 156.2, 157.4 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>26</sub>H<sub>22</sub>N<sub>3</sub>): 376.1808, found: 376.1811.

**7-Methyl-6-(2,6-dimethylphenyl)-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2l).** Product **2l** was obtained as a colorless oil (48 mg, 50%). 10 mg (7%) of compound **3** were isolated, as well. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.16 (6H, s, 2×CH<sub>3</sub>), 3.67 (3H, s, NCH<sub>3</sub>), 6.77 [1H, s, 5-H (pp)], 7.22-7.34 [3H, m, 3-5-H (6-Ph)], 7.51-7.61 [6H, m, 2×3-5-H (2-Ph, 4-Ph)], 8.38 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.76 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 20.4, 28.6, 99.5, 114.3, 127.5, 128.0, 128.4, 128.7, 129.1, 129.2, 129.5, 129.8, 131.1, 138.4, 139.0, 139.2, 141.0, 153.7, 156.0, 157.1 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>27</sub>H<sub>24</sub>N<sub>3</sub>): 390.1965, found: 390.1972.

**6-[2,4-Di(trifluoromethyl)phenyl]-7-methyl-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2m).** Product **2m** was obtained as a colorless solid (79 mg, 65%), mp 189-190.8 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.74 (3H, s, NCH<sub>3</sub>), 6.93 [1H, s, 5-H (pp)], 7.50-7.62 [6H, m, 2×3-5-H (2-Ph, 4-Ph)], 7.69 [1H, d, *J* = 8 Hz, 5-H (6-Ph)], 7.99 [1H, d, *J* = 8 Hz, 6-H (6-Ph)], 8.16 [1H, s, 3-H (6-Ph)], 8.32 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.75 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 29.3, 102.5, 113.6, 122.8 (*J* = 273 Hz), 123.1 (*J* = 271 Hz), 123.79 (*J* = 4 Hz), 123.84 (*J* = 4 Hz), 128.1, 128.41, 128.42, 128.8, 129.0, 129.8, 130.1, 131.8 (*J* = 31 Hz), 132.0 (*J* = 34 Hz), 133.76, 133.77, 134.3, 136.3, 138.6, 138.9, 153.8, 157.3, 158.2 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): -59.11 (CF<sub>3</sub>), -63.00 (CF<sub>3</sub>) ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>27</sub>H<sub>18</sub>F<sub>6</sub>N<sub>3</sub>): 498.1399, found: 498.1396.

**7-Methyl-6-[(4-diphenylamino)phenyl]-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2n).** Product **2n** was obtained as a bright yellow film (100 mg, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.03 (3H, s, NCH<sub>3</sub>), 6.88 [1H, s, 5-H (pp)], 7.12-7.22 [8H, m, 3,5-H (6-Ph), 2×2',4',6'-H (NPh<sub>2</sub>)], 7.32-7.36 [4H, m, 2×3',5'-H (NPh<sub>2</sub>)], 7.46-7.62 [8H, m, 2,6-H (6-Ph), 2×3-5-H (2-Ph, 4-Ph)], 8.35 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.74 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 30.1, 99.3, 114.4, 122.5, 123.7, 124.7, 125.0, 125.1, 128.0, 128.4, 128.7, 129.0, 129.4, 129.5, 129.8, 139.0, 139.3, 143.1, 147.3, 148.4, 154.7, 155.9, 157.2 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>37</sub>H<sub>29</sub>N<sub>4</sub>): 529.2387, found: 529.2385.

**7-Methyl-6-(naphthalen-2-yl)-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (2o).** Product **2o** was obtained as a yellow solid (63 mg, 62%), mp 185.5-187 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.06 (3H, s, NCH<sub>3</sub>), 7.02 [1H, s, 5-H (pp)], 7.50-7.62 [8H, m, 2×3-5-H (2-Ph, 4-Ph), 4,5-H (6-naph)], 7.73 [1H, dd, *J* = 8 Hz, 8-H (6-naph)], 7.95-7.98 [2H, m, 3,6-H (6-naph)], 8.01 [1H, d, *J* = 8 Hz, 7-H (6-naph)], 8.10 [1H, s, 2-H (6-naph)], 8.38 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.77 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 30.2, 100.4, 114.3, 126.5, 126.86, 126.9, 127.9, 128.1, 128.3, 128.4, 128.41, 128.5, 128.7, 129.0, 129.1, 129.6, 129.9, 133.1, 133.2, 138.9, 139.2, 143.1, 154.8, 156.4, 157.5 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>29</sub>H<sub>22</sub>N<sub>3</sub>): 412.1808, found: 412.1812.

**6-(2,4-Di(trifluoromethyl)phenyl)-2,4-di(4-methoxyphenyl)-7-methyl-7H-pyrrolo[2,3-d]pyrimidine (2p).** Compound **2p** was synthesized by the general procedure for C-H arylation, starting from 2,4-di(4-methoxyphenyl)-7-methylpyrrolo[2,3-d]pyrimidine (**1b**) (70 mg, 0.20 mmol). After 72 h (170 °C) product **2p** was obtained as a colorless solid (87 mg, 77%), mp 185.5-186.2 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.71 (3H, s, NCH<sub>3</sub>), 3.93 (6H, s, 2×OCH<sub>3</sub>), 6.88 [1H, s, 5-H (pp)], 7.07 [2H, d, *J* = 8 Hz, 3,5-H (2-Ph)], 7.11 [2H, d, *J* = 8 Hz, 3,5-H (4-Ph)], 7.68 [1H, d, *J* = 8 Hz, 5-H (6-Ph)], 7.98 [1H, d, *J* = 8 Hz, 6-H (6-Ph)], 8.15 [1H, s, 3-H (6-Ph)], 8.29 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.68 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 29.2, 55.4, 55.43, 102.6, 112.6, 112.9, 113.7, 114.3, 122.9 (*J* = 272 Hz), 123.2 (*J* = 272 Hz), 123.77 (*J* = 4 Hz), 123.8 (*J* = 4 Hz), 124.2, 124.5, 128.3, 129.6, 130.5, 131.3, 131.7 (*J* = 34 Hz), 131.8, 131.9 (*J* = 34 Hz), 133.8, 133.81, 134.6, 135.4, 153.9, 156.8, 158.1, 161.1, 161.3 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): -59.07 (CF<sub>3</sub>), -62.97 (CF<sub>3</sub>) ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>29</sub>H<sub>22</sub>F<sub>6</sub>N<sub>3</sub>O<sub>2</sub>): 558.1611, found: 558.1613.

**6-[4-(Dimethylamino)phenyl]-2,4-di(4-methoxyphenyl)-7-methyl-7H-pyrrolo[2,3-d]pyrimidine (2q).** Compound **2q** was synthesized by the general procedure for C-H arylation, starting from 2,4-di(4-methoxyphenyl)-7-methylpyrrolo[2,3-d]pyrimidine (**1b**) (70 mg, 0.20 mmol). After 72 h (170 °C) product **2q** was obtained as a yellow film (72 mg, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.07 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 3.92 (3H, s, OCH<sub>3</sub>), 3.94 (3H, s, OCH<sub>3</sub>), 3.97 (3H, s, NCH<sub>3</sub>), 6.78 [1H, s, 5-H (pp)], 6.86 [2H, d, *J* = 8 Hz, 3,5-H (6-Ph)], 7.06 [2H, d, *J* = 8 Hz, 3,5-H (2-Ph)], 7.11 [2H, d, *J* = 8 Hz, 3,5-H (4-Ph)], 7.50 [2H, d, *J* = 8 Hz, 3,5-H (6-Ph)], 8.33 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.67 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 29.9, 40.4, 55.4, 55.42, 98.4, 112.1, 113.5, 113.6, 114.0, 119.3, 129.38, 129.9, 130.4, 131.9, 132.3, 143.3, 150.5, 154.6, 154.9, 156.7, 160.8, 160.9 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>29</sub>H<sub>29</sub>N<sub>4</sub>O<sub>2</sub>): 465.2285, found: 465.2289.

**6-[4-(9H-carbazol-9-yl)phenyl]-2,4-di(4-methoxyphenyl)-7-methyl-7H-pyrrolo[2,3-d]pyrimidine (2r).** Compound **2r**

was synthesized by the general procedure for C-H arylation, starting from 2,4-di(4-methoxyphenyl)-7-methylpyrrolo[2,3-*d*]pyrimidine (**1b**) (70 mg, 0.20 mmol). After 72 h (170 °C) product **2r** was obtained as a yellow solid (83 mg, 70%), mp 265.2-266.6 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.94 (3H, s, OCH<sub>3</sub>), 3.95 (3H, s, OCH<sub>3</sub>), 4.10 (3H, s, NCH<sub>3</sub>), 7.01 [1H, s, 5-H (pp)], 7.08 [2H, d, *J* = 8 Hz, 3,5-H (4-Ph)], 7.14 [2H, d, *J* = 8 Hz, 3,5-H (2-Ph)], 7.34-7.38 [2H, m, 3,6-H (6-carb.)], 7.47-7.50 [2H, m, 2,7-H (6-carb.)], 7.77 [2H, dm, *J* = 8 Hz, 3,5-H (6-Ph)], 7.86 [2H, dm, *J* = 8 Hz, 2,6-H (6-Ph)], 8.21 [2H, dm, *J* = 8 Hz, 4,5-H (6-carb.)], 8.37 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.71 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 30.1, 55.4, 55.45, 100.7, 109.8, 113.2, 113.7, 114.1, 120.3, 120.5, 123.6, 126.1, 127.2, 129.6, 130.4, 130.5, 130.8, 131.6, 132.0, 138.1, 140.6, 141.3, 156.1, 161.0, 161.2 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>39</sub>H<sub>31</sub>N<sub>4</sub>O<sub>2</sub>): 587.2442, found: 587.2444.

#### 2,4-Di(4-(9*H*-carbazol-9-yl)phenyl)-7-methyl-6-(4-methylphenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (**2s**)

Compound **2s** was synthesized by the general procedure for C-H arylation, starting from 2,4-di(4-(9*H*-carbazol-9-yl)phenyl)-7-methylpyrrolo[2,3-*d*]pyrimidine (**1c**) (70 mg, 0.13 mmol). After 70 h (170 °C) product **2s** was obtained as a yellowish solid (47 mg, 50%), mp 305-306 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.52 (3H, s, CH<sub>3</sub>), 4.07 (3H, s, NCH<sub>3</sub>), 7.03 [1H, s, 5-H (pp)], 7.34-7.52 [10H, m, 3,5-H (6-Ph), 2×2,7-H (2-carb., 4-carb.), 2×3,6-H (2-carb., 4-carb.)], 7.58-7.62 [6H, m, 2,6-H (6-Ph), 2×1,8-H (2-carb., 4-carb.)], 7.80 [2H, dm, *J* = 8 Hz, 3,5-H (2-Ph)], 7.86 [2H, dm, *J* = 8 Hz, 3,5-H (6-Ph)], 8.22 [4H, m, 2×4,5-H (2-carb., 4-carb.)], 8.65 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 9.02 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 21.4, 30.1, 99.6, 109.9, 110.0, 114.4, 120.0, 120.2, 120.35, 120.42, 123.5, 123.6, 126.0, 126.1, 126.9, 127.1, 128.6, 129.0, 129.6, 129.62, 130.5, 137.8, 138.2, 138.8, 139.1, 139.3, 140.7, 140.8, 143.9, 154.8, 155.1, 156.7 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>50</sub>H<sub>36</sub>N<sub>5</sub>): 706.2965, found: 706.2961.

**7,7'-Dimethyl-2,2',4,4'-tetraphenyl-7*H*,7'*H*-5,5'-bipyrrolo[2,3-*d*]pyrimidine (**3**)**. Yellow solid, mp 269-270 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.00 (3H, s, NCH<sub>3</sub>), 7.13 [1H, s, 6-H (pp)], 7.55-7.64 [6H, m, 2×3-5-H (2-Ph, 4-Ph)], 8.36 [2H, dm, *J* = 8 Hz, 2,6-H (4-Ph)], 8.76 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 29.9, 103.6, 113.8, 129.2, 128.5, 128.9, 129.1, 129.9, 130.2, 131.9, 138.5, 138.8, 154.4, 157.5, 158.5 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>38</sub>H<sub>29</sub>N<sub>6</sub>): 569.2448, found: 569.2462.

**7-Methyl-5,6-di(4-nitrophenyl)-2,4-diphenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (**4**)**. Yellow solid, mp 274.5-275 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.96 (3H, s, NCH<sub>3</sub>), 6.90 [2H, dm, *J* = 8 Hz, 2,6-H (5-Ph)], 7.11-7.15 [2H, m, 2×4-H (2-Ph, 4-Ph)], 7.37-7.55 [8H, m, 2,6-H (6-Ph), 3,5-H (2-Ph), 2,3,5,6-H (4-Ph)], 7.82 [2H, dm, *J* = 8 Hz, 3,5-H (5-Ph)], 8.29 [2H, dm, *J* = 8 Hz, 3,5-H (6-Ph)], 8.73 [2H, dm, *J* = 8 Hz, 2,6-H (2-Ph)] ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 30.1, 112.7, 114.0, 122.9, 124.0, 127.6, 128.3, 128.5, 129.4, 129.6, 130.2, 131.2, 131.8, 136.6, 137.2, 137.5, 138.3, 140.6, 146.1, 148.0, 153.9, 158.6, 160.0 ppm. HRMS-ESI: *m/z* calcd. for MH<sup>+</sup> (C<sub>31</sub>H<sub>22</sub>N<sub>5</sub>O<sub>4</sub>): 528.1666, found: 528.1675.

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