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SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF PYRROLO[2,3-*d*]PYRIMIDINE-CORE BASED OLIGOARYLENES

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The research was carried out at Vilnius University, Faculty of Chemistry, Department of Organic Chemistry in the period of 2008-2012.

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VILNIAUS UNIVERSITETAS

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PIROLO[2,3-*d*]PIRIMIDINO OLIGOARILENŲ SINTEZĖ IR FOTOFIZIKINĖS SAVYBĖS

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CONTENTS

List of Abbreviations and Physical Units

AIE – aggregation-induced emission

AIEE – aggregation-induced emission enhancement

All - allyl

Ar – aryl

Bn – benzyl

Boc – *tert*-butoxycarbonyl

BOM – benzyloxymethyl

Bu – butyl

CCD – spectrometer with a charge coupled device

Cy – cyclohexane

dba – dibenzylideneacetone

Diglyme – diethyleneglycol dimethylether

DIPEA – diisopropylethylamine

dippf – bis(diisopropylphosphino)ferrocene

DMAP – *N*,*N*-dimethyl-4-aminopyridine

DME – dimethoxyethane

DMF – *N*,*N*-dimethylformamide

DMSO – dimethyl sulfoxide

DMT – di(*p*-methoxyphenyl)phenylmethyl

DNA – deoxyribonucleic acid

dppf – bis(diphenylphosphino)ferrocene

Et – ethyl

FE-SEM – field-emission scanning electron microscope

FlM – fluorescence microscope

Φ_F – fluorescence quantum yield

HOMO – the highest occupied molecular orbital

HRMS – high resolution mass spectrometry

LUMO – the lowest unoccupied molecular orbital

Me – methyl

MOM – methoxymethyl

MW – microwave irradiation

NMP – *N*-methylpyrrolidone

NMR – nuclear magnetic resonance

NOE – nuclear Overhauser effect

OLED – organic light-emitting diode

Ph – phenyl

Piv – pivaloyl

PL – photoluminescence

POM – pivaloyloxymethyl

ppm – parts per million

Pr – propyl

PS – polystyrene

Py – pyridine

rt – room temperature

SEM – 2-(trimethylsilyl)ethoxymethyl

TBS – *tert*-butyldimethylsilyl

TEA – triethylamine

TFA – trifluoroacetic acid

THF – tetrahydrofuran

TLC – thin layer chromatography

Tol – tolyl

Tp – triphosphate

TPPTS – 3,3',3"-phosphinetriyltris(benzenesulfonic acid) trisodium salt

Tr – trityl

Ts - tosyl

UV-Vis – ultraviolet-visible spectroscopy

δ – chemical shift

INTRODUCTION

Organic molecules with a π-conjugated backbone have attracted growing interest over recent years owing to their applications in a wide range of electronic and optoelectronic devices [1-13]. Non-linear molecules are of interest in materials science owing to their light-emitting [14-19], self-assembling [20-22] and complex forming properties with metal ions or organic molecules [20-25]. Therefore, novel structures and new synthetic methods are continuously being introduced into this field. Incorporation of azaheterocycles such as pyridine [18, 26], pyrazine [27], pyrimidine [28-33], s-triazine [34-37], or quinoxaline [38] at the centre of the backbone of such molecules leads to a strong enhancement of physical and photophysical properties.

Pyrrolo[2,3-*d*]pyrimidine occupies an exclusive place, mainly due to its structural resemblance to biogenic purines. This, for example, includes the naturally occurring nucleoside antitumor antibiotics such as Tubercidin, Toyocamycin, Sangivamycin, Cadeguomycin [39, 40], selective and potent inhibitors of phosphatidylinositol-4-kinase – Echiguanines A and B [41] and non-naturally occurring antifolate antimetabolites such as Pemetrexed [42]. These properties indicate to bio-compatibility of pyrrolo[2,3-*d*]pyrimidine skeleton. Although the parent pyrrolo[2,3-*d*]pyrimidine was found to possess fluorescence properties [43] and some derivatives were demonstrated to be suitable for probing the structure of DNA [44], exploitation of this heteroaromatic core in functional π-systems is insufficient. Thus, pyrrolo[2,3-*d*]pyrimidine represents an attractive scaffold for the development of analogs and for the synthesis of novel derivatives by modification of the substitution pattern. One particularly efficient way to introduce various substituents into molecules is the direct carbon–carbon bond formation reactions. These reactions are important processes in chemistry, because they provide key steps in the building of complex bioactive molecules developed as medicines and agrochemicals. They are also vital in developing the new generation of ingeniously designed organic materials with novel electronic, optical, or

mechanical properties, likely to play a significant role in the burgeoning area of nanotechnology [45-48].

During the past 40 years, most important carbon–carbon bond forming methodologies have involved using transition metals to mediate the reactions in a controlled and selective manner [49-55]. The palladium-catalyzed Suzuki cross-coupling reaction between different types of organoboron compounds and various organic electrophiles including halides or triflates in the presence of base provides a powerful and general methodology for the formation of carbon–carbon bonds in the construction of biaryls [56-65].

Such coupling reactions offer several advantages:

(1) ready availability of reactants;

(2) mild reaction conditions and high product yields;

(3) water stability;

(4) easy use of the reaction both under aqueous and heterogeneous conditions;

(5) toleration of a broad range of functional groups;

(6) high regio- and stereoselectivity;

(7) insignificant affect of steric hindrance;

(8) use of a small amount of catalyst;

(9) application in one-pot synthesis;

(10) nontoxic reaction;

(11) easy separation of inorganic boron compound;

(12) environmentally friendly process.

As one of the defects of the reaction, one would point out the use of bases. However, the difficulty can be overcome by using suitable solvent systems and adequate bases. Consequently, these coupling reactions have been actively utilized not only in academic laboratories, but also in industrial processes. In aromatic–aromatic cross-coupling reactions, cheap and readily accessible aryl and heteroaryl chlorides are particularly important from an industrial viewpoint as starting materials [66].

Literature survey has shown that palladium catalyzed processes constitute an efficient strategy for functionalization of pyrrolo[2,3-

d]pyrimidine scaffold by C–C bond formation and continue to offer new applications to synthesize an increasingly wide range of polyfunctionalized compounds with biochemical, medicinal or materials science applications. Taking all this into account, the Pd(0) and Cu(I) catalyzed arylation reactions were chosen in this investigation for introduction of various aryl functionalities into pyrrolo[2,3-*d*]pyrimidine scaffold.

The main goal of the present work was to synthesize pyrrolo[2,3-*d*]pyrimidine-core based oligoarylenes and to evaluate their photophysical properties.

The tasks proposed for the achievement of the above stated aim were as follows:

- to study the palladium-catalyzed cross-coupling reaction of chloropyrrolo[2,3-*d*]pyrimidines with arylboronic acids and to elaborate efficient methods for the synthesis of 4-aryl- and 2,4-diarylpyrrolo[2,3-*d*]pyrimidines;
- to study Cu(I)-catalyzed *N*-arylation reaction of 7*H*-pyrrolo[2,3-*d*]pyrimidines with haloarenes and to synthesize pyrrolo[2,3-*d*]pyrimidine-core based oligoarylenes with π-extended conjugated system - triarylpyrrolo[2,3-*d*]pyrimidines, bis(pyrrolo[2,3-*d*]pyrimidin-7-yl)carbazoles and the corresponding fluorenes;
- to investigate synthetic routes for the preparation of pyrrolo[2,3-*d*]pyrimidines bearing different aryl moieties in positions 2-, 4- and 7 of the heterocycle;
- to study photophysical properties of pyrrolo[2,3-*d*]pyrimidine-core based oligoarylenes and to evaluate influence of structure of aryl groups onto photophysical characteristics of the synthesized compounds.

Scientific novelty*:* The Suzuki reaction of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine with arylboronic acids was studied and novel 4-aryl- and 2,4-diarylpyrrolo[2,3-*d*]pyrimidines were synthesized. The reaction conditions

including an effective catalyst system for the Suzuki cross-coupling reaction were proposed to achieve site-selectivity of the reaction studied. An efficient synthesis of 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines, bis(pyrrolo[2,3-*d*]pyrimidin-7-yl)carbazoles and -fluorenes were developed by copper-catalyzed *N*-arylation reaction of 2,4-diarylpyrrolo[2,3-*d*]pyrimidines with aryl halogenides, dihalocarbazoles or dihalofluorenes, respectively. Synthetic strategies leading to pyrrolo[2,3-*d*]pyrimidines with different aryl moieties in positions 2, 4 and 7 of the heterocycle were studied and an efficient method for their synthesis was developed. The synthesized pyrrolo[2,3-*d*]pyrimidine-core based oligoarylenes were found to exhibit blue-UV fluorescence in solution and in solid state. Influence of structure of aryl groups, their position in the pyrrolo[2,3-*d*]pyrimidine nucleous and extent of π-conjugated aromatic system on the photoluminescent characteristics were evaluated. Some pyrrolo[2,3-*d*]pyrimidine derivatives were found to exhibit positive solvatofluorochromism and to form nanoaggregates in THF/water mixtures with aggregation induced enhanced emission. Pyrrolo[2,3-*d*]pyrimidine-core based oligomers with π-extended conjugation system were found to exibit better fluorescence quantum yields in a solid state than in solution.

***Main statements for the defence**:*

- 4-Aryl-2-chloro- and 2,4-diarylpyrrolo[2,3-*d*]pyrimidines can be synthesized by the Suzuki cross-coupling reaction of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine with aryl boronic acids in the presence of $Pd(OAc)_2$/(2-biphenyl)dicyclohexylphosphine/K_3PO_4 as a catalyst system. The site-selectivity of the reaction can be effectively controlled by an amount of arylboronic acid and reaction conditions.

- A simple and facile synthesis of novel 2,4-diaryl- and 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines bearing different 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 were developed. The necessity of protection-deprotection methodology of *N*(7)-position of pyrrolo[2,3-*d*]pyrimidine for their synthesis was shown.

- Photoluminescent properties of the synthesized arylpyrrolo[2,3-*d*]pyrimidines depend on the origin of the aryl branches, their position in the pyrrolo[2,3-*d*]pyrimidine moiety, solvent and aggregation state. Derivatives with 4-dimethylamino- and 4-diphenylaminophenyl groups at the position 7 of the pyrrolo[2,3-*d*]pyrimidine exhibit aggregation induced emission enhancement and form fluorescent nanoaggregates in a mixtures of THF and water.

- Pyrrolo[2,3-*d*]pyrimidine-core based oligomers with extended π-conjugated systems due to considerable suppression of nonradiative torsional deactivation processes are more efficient light-emitters in a solid PS matrix than in solution.

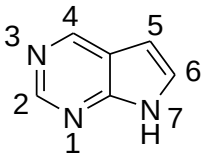
The main results of the present work were published in 5 articles in the international peer-reviewed scientific journals and were presented at 13 scientific conferences.

I. LITERATURE REVIEW

Functionalization of pyrrolo[2,3-*d*]pyrimidine by palladium-catalyzed cross-coupling reactions.

In this review we present a literature survey on the palladium-catalyzed reactions used for functionalization of pyrrolo[2,3-*d*]pyrimidine scaffold. For clarity, the presentation of data is organized on the basis of the position of pyrrolo[2,3-*d*]pyrimidine carbon atom, which participates in the formation of C–C bond.

Pyrrolo[2,3-*d*]pyrimidine is often named as 7-deazapurine, which results in different numbering of the parent heterocycle. In the present review pyrrolo[2,3-*d*]pyrimidine system is numbered and derivatives are named according to systematic nomenclature as shown below.

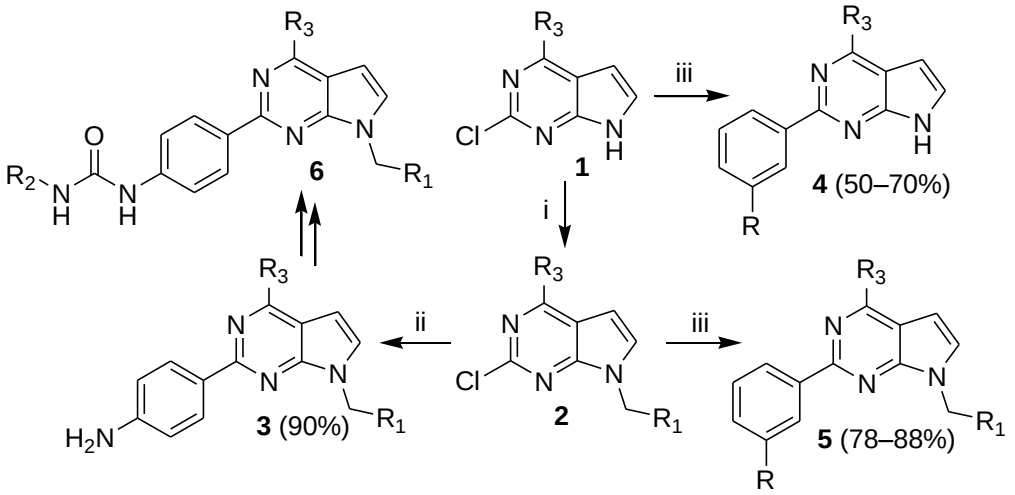


7*H*-Pyrrolo[2,3-*d*]pyrimidine

I.1. Synthesis of 2-substituted pyrrolo[2,3-*d*]pyrimidines.

There are only few reports in the literature on the synthesis of 2-substituted pyrrolo[2,3-*d*]pyrimidines by the palladium catalyzed cross-coupling reactions. Thus, in search of potent phosphatidylinozitol-3-kinase inhibitors a series of 4-(morpholin-4-yl)pyrrolo[2,3-*d*]pyrimidines **6**, bearing ureidophenyl structural units in the position 2 of the heterocycle, were synthesized and evaluated for biological activity [67]. 2-(4-Aminophenyl)pyrrolo[2,3-*d*]pyrimidines **3**, needed for the synthesis of the target compounds **6**, were obtained by the Suzuki coupling of 2-chloropyrrolo[2,3-*d*]pyrimidine **2** with pinacol ester of 4-aminophenylboronic acid in dimethoxyethane in the presence of $Pd(PPh_3)_4$/aq. 2M Na_2CO_3 at 130 °C under microwave irradiation (MW). These conditions were also applied for the synthesis of 2-(3-substituted)phenylpyrrolo[2,3-*d*]pyrimidines **4** and **5** by

reaction of 2-chloro-4-(morpholin-4-yl)pyrrolo[2,3-*d*]pyrimidines **1** and **2** with the corresponding arylboronic acids.

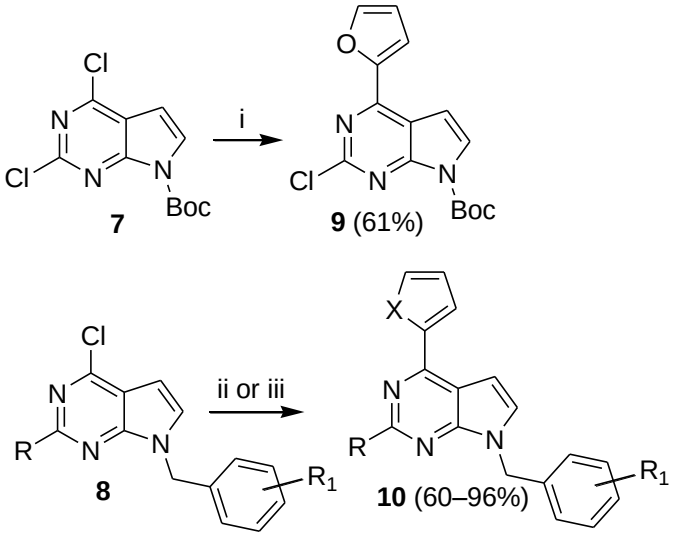


R = CH_2OH, OH; R_1 = $CH_2N(CH_3)_2$, CF_3, $CH(OCH_3)_2$;
R_2 = 2-Py, 3-Py, 4-Py, 4-F-C_6H_4, 4-$HO_2CC_6H_4$, Et, Me; R_3 = morpholin-4-yl

Reagents and conditions: (i) $(CH_3)_2NCH_2CH_2Cl$ or CF_3CH_2I or $(CH_3O)_2CHBr$, Cs_2CO_3, DMF; (ii) 4-aminophenylboronic acid pinacol ester, $Pd(PPh_3)_4$, DME, Na_2CO_3, MW; (iii) $RC_6H_4B(OH)_2$, $Pd(PPh_3)_4$, DME, Na_2CO_3, MW.

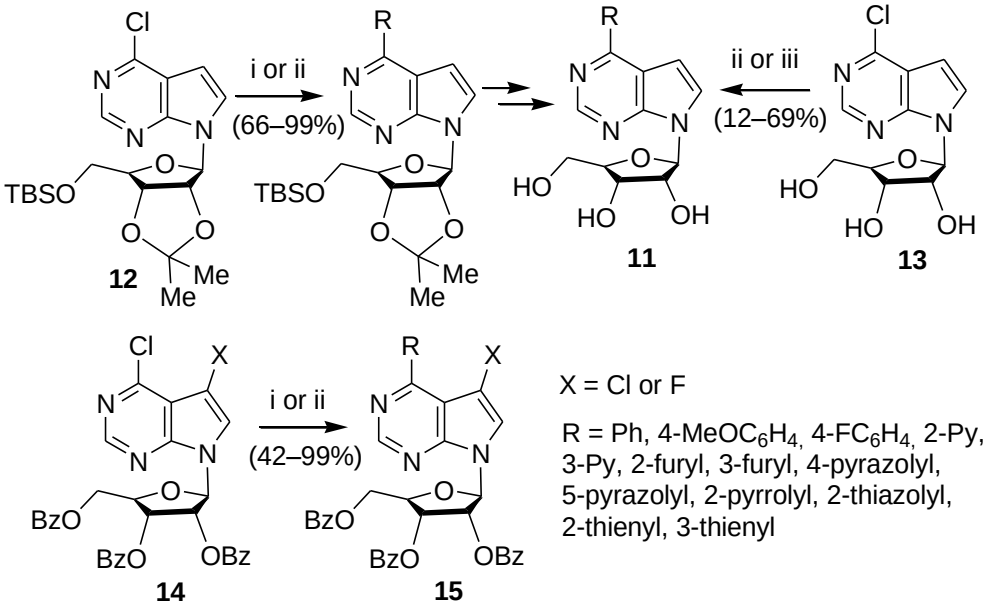
I.2. Synthesis of 4-substituted pyrrolo[2,3-*d*]pyrimidines.

In several papers, Pd(0)-catalyzed reactions of 2,4-dichloropyrrolo-[2,3-*d*]pyrimidine with heteroaryltributylstannanes or arylboronic acids were investigated in order to obtain potent adenosine A_{2A} antagonists [68], or compounds with antimycobacterial activities [69]. The reactions of 7-substituted derivatives **7** and **8** with corresponding heterocyclic organotin compounds were carried out at room temperature or at 50 °C in the presence of Pd catalyst in DMF [68, 69]. The formation of 4-regioisomers **9** and **10** (R = Cl) was presumably because of mild reaction conditions applied.



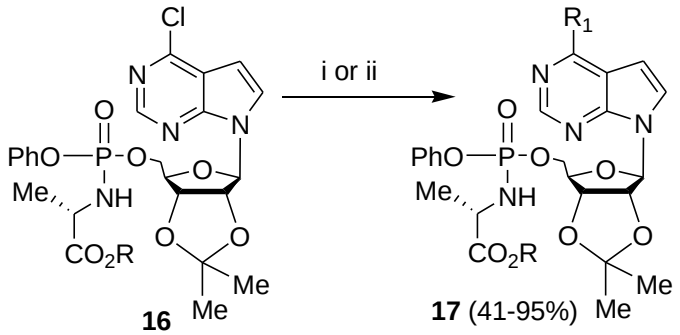
Reagents and conditions: (i) (2-furyl)$SnBu_3$, $(PPh_3)_2PdCl_2$, DMF, r.t.; (ii) R = H: (2-furyl)$SnBu_3$ or (2-thienyl)$SnBu_3$, $(PPh_3)_2PdCl_2$, DMF, 90 °C; (iii) R = Cl: (2-furyl)$SnBu_3$ or (2-thienyl)$SnBu_3$, $[(2\text{-furyl})_3P]_4Pd$ or $(PPh_3)_2PdCl_2$, DMF, 50 °C.

A series of pyrrolo[2,3-*d*]pyrimidine ribonucleosides **11, 15** as potent cytostatic agents bearing an aryl or (het)aryl group in position 4 and H, F, or Cl atom in position 5 has been prepared either by Pd-catalyzed cross-coupling reactions (Suzuki or Stille) of the corresponding protected 4-chloropyrrolo[2,3-*d*]pyrimidine ribonucleosides **12, 14** with (het)arylorganometallics followed by deprotection, or by single-step aqueous phase cross-coupling reactions of unprotected 4-chloropyrrolo[2,3-*d*]pyrimidine ribonucleoside **13** with (het)arylboronic acids [70]. The preferred position for cross-coupling in 4,5-dichloro- (X = Cl) or 4-chloro-5-fluoropyrrolo[2,3-*d*]pyrimidine **14** (X = F) is the position 4. Both in the Suzuki and Stille cross-coupling reactions compound **14** (X = Cl, F) gave 5-chloro- or 5-fluoropyrrolo[2,3-*d*]pyrimidine **15** as the only reaction product.



Reagents and conditions: (i) $RB(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, toluene or DME/H_2O, 100 °C; (ii) $RSnBu_3$, $PdCl_2(PPh_3)_2$, DMF, 100 °C; (iii) $RB(OH)_2$, $Pd(OAc)_2$, TPPTS, Na_2CO_3, H_2O/MeCN, 100 °C.

Similarly, 4-chloropyrrolo[2,3-*d*]pyrimidine pronucleotide **16** with (het)arylboronic acids in presence of $Pd(PPh_3)_4/K_2CO_3$ in toluene at 85 °C furnished 4-(het)arylpyrrolo[2,3-*d*]pyrimidine **17** [71]. It was noticed, that 2-thienyl- and 2-furylboronic acids were not sufficiently reactive in these reactions. Therefore, the Stille coupling with the corresponding stannanes was used instead and the corresponding products **17** (R_1 = 2-thienyl, 2-furyl) were obtained in good yields.

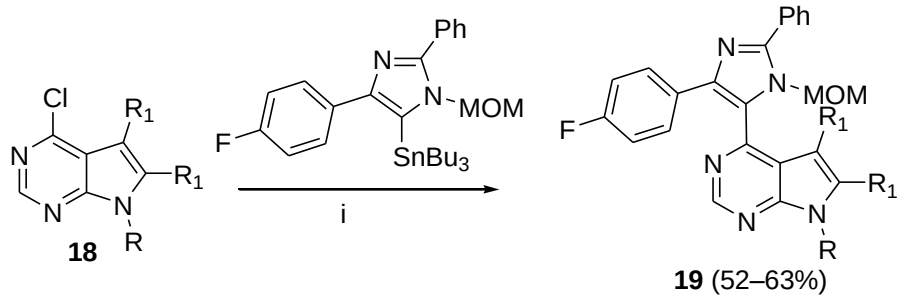


R = Me, Et, Bn; R_1 = Ph, 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 4-dibenzofuryl

Reagents and conditions: (i) $R_1B(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, toluene, 85 °C, 1-3 h; (ii) R_1SnBu_3, $PdCl_2(PPh_3)_2$, DMF, 105 °C, 1-3 h.

Synthesis of 2-pivaloylamino-4-vinylpyrrolo[2,3-*d*]pyrimidine, useful precursor for the synthesis of antifolates of pyrrolo[2,3-*d*]pyrimidine series, was synthesized by Stille cross-coupling reaction of 2-pivaloylamino-4-chloropyrrolo[2,3-*d*]pyrimidine with tributylvinylstannane [72].

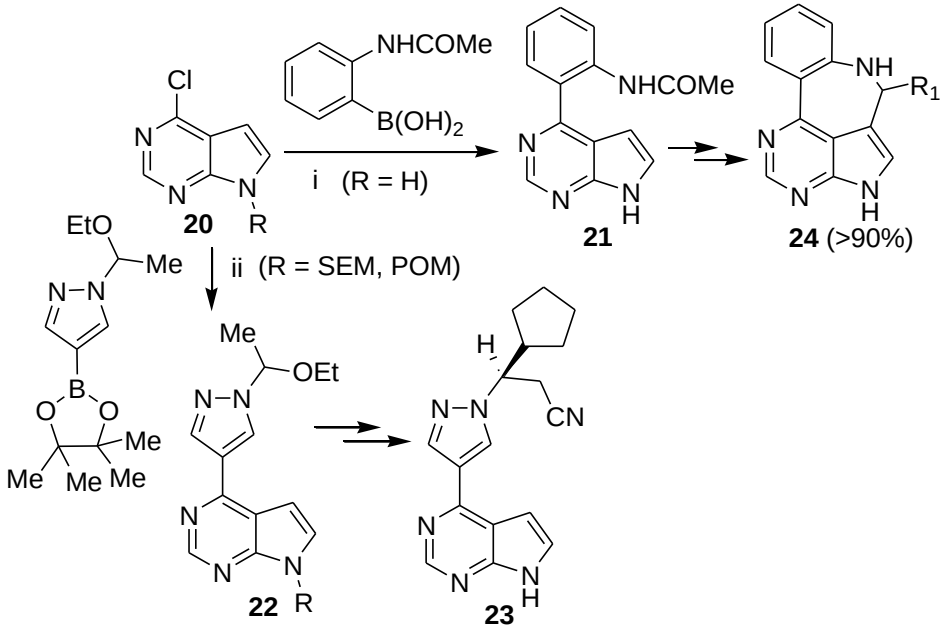
Recently, investigating the peculiarities of the Stille reaction between halogenated purine isosteric heterocycles, several 4-(5-imidazolyl)pyrrolo-[2,3-*d*]pyrimidines **19** have been synthesized by coupling of 4-chloropyrrolo-[2,3-*d*]pyrimidines **18** with the corresponding imidazolylstannane in the presence of $PdCl_2(PPh_3)_2$ at reflux for 4 h in tetrahydrofuran [73].



R = Bn, MOM, Ts; R_1 = H, Me

Reagents and conditions: (i) $PdCl_2(PPh_3)_2$, THF, Δ.

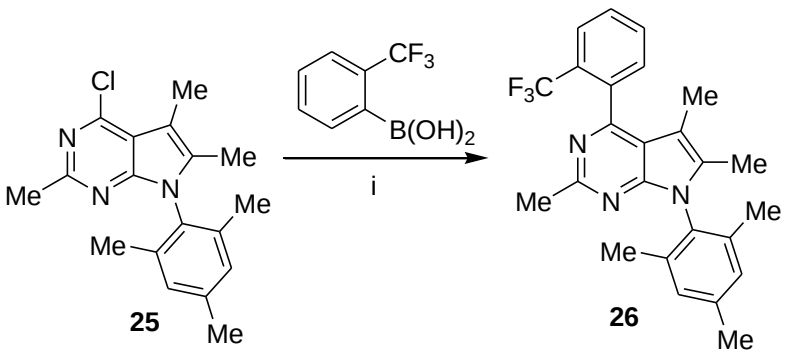
The Suzuki cross-coupling of 4-chloropyrrolo[2,3-*d*]pyrimidines **20** with 2-acetamidophenylboronic acid or (pyrazol-4-yl)boronic acid pinacol ester were used for the synthesis of intermediates **21** and **22**, from which 4-(4-pyrazolyl)pyrrolo[2,3-*d*]pyrimidine **23** [74] and derivatives of tetracyclic heterosystem **24** possessing Janus kinase (JAK2) inhibitory activity were synthesized [75].



R_1 = CF_3, $CH_2OCH_2C_6H_4$, Ph, 3-F-C_6H_4, 2-F-4-HO-C_6H_4, 3-F-4-HO-C_6H_4, 2-Cl-4-HO-C_6H_4

Reagents and conditions: (i) $Pd(PPh_3)_4$, K_2CO_3, DME, 128 °C, overnight; (ii) $Pd(PPh_3)_4$, K_2CO_3, 1-BuOH/H_2O or DME/H_2O, Δ.

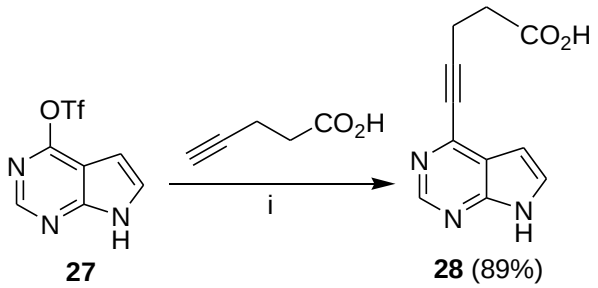
4-Chloropyrrolo[2,3-*d*]pyrimidine **25** reacted with electron-deficient (2-trifluoromethyl)phenylboronic acid in the presence of $Pd(PPh_3)_4/Na_2CO_3$ to give 4-(2-trifluoromethyl)phenylpyrrolo[2,3-*d*]pyrimidine **26** - antagonist of corticotropin releasing hormone (CRH_1) [76].



Reagents and conditions: (i) $Pd(PPh_3)_4$, Na_2CO_3, benzene, EtOH, Δ.

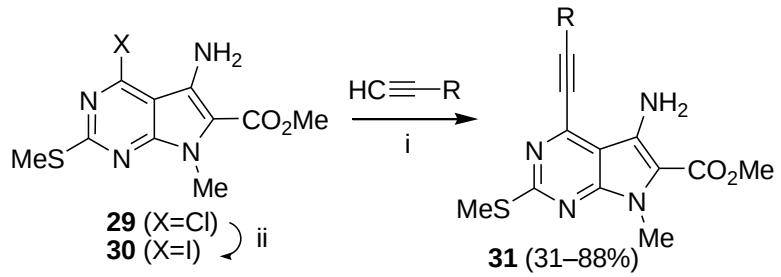
The formation of C–C bond at position 4 of the pyrrolo[2,3-*d*]pyrimidine by the Sonogashira cross-coupling reaction was first reported in 1991 by S. Cacchi [77]. The pyrrolo[2,3-*d*]pyrimidine-4-triflate **27** was employed in the reaction with 4-pentynecarboxylic acid using

$Pd(OAc)_2(PPh_3)_2$/CuI/*i*-Pr_2NH as the catalyst system. Compound **28** was obtained in 89% yield.



Reagents and conditions: (i) $Pd(OAc)_2(PPh_3)_2$, CuI, *i*-Pr_2NH, DMSO, rt.

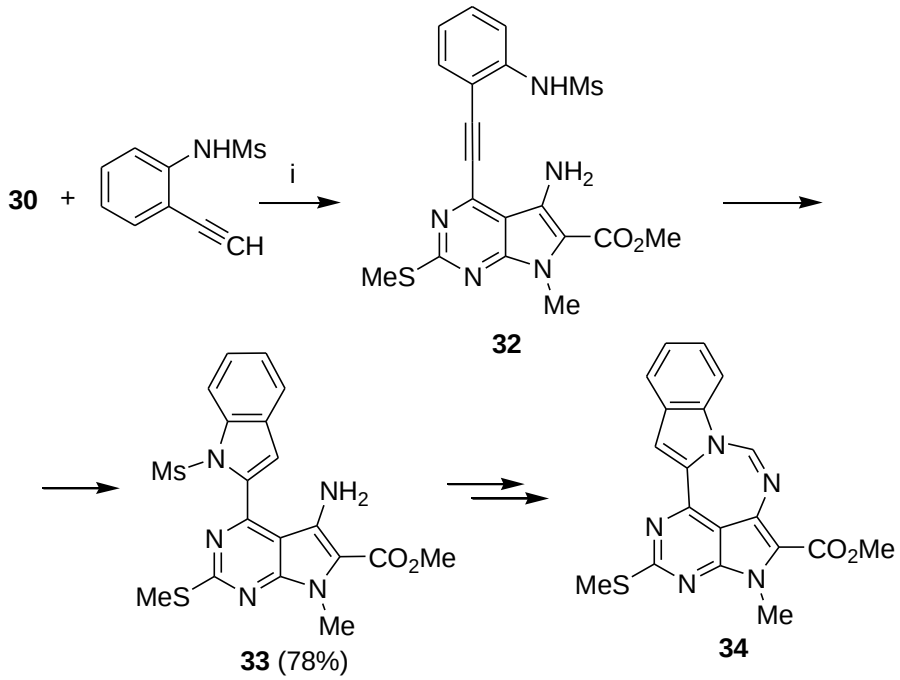
More extensive study on the Sonogashira coupling of 4-halopyrrolo[2,3-*d*]pyrimidines with different terminal alkynes was conducted with pyrrolo[2,3-*d*]pyrimidine **29** bearing various reactive functional groups in the molecule [78, 79]. It was found, that the reaction was very sluggish. In order to achieve full conversion, a large excess of alkyne (10 equiv.) has to be used. Diacetylenes, as byproducts of cross-coupling reaction, often accompany the formation of target compounds. Therefore, palladium catalyst and copper iodide must be used in reasonable quantity (up to 10 mol% $PdCl_2(PPh_3)_2$ and 20 mol% CuI). All these disadvantages disappeared when 4-iodopyrrolo-[2,3-*d*]pyrimidine **30** was employed in the reaction. The cross-coupling reaction was shown to proceed at room temperature using 2–3 mol% $PdCl_2(PPh_3)_2$, and the corresponding 4-alkynylpyrrolo[2,3-*d*]pyrimidines **31** were obtained in good yields. Moreover, there was no necessity to use an additional ligand in the reaction.



R = Ph, 4-MeC_6H_4, 4-FC_6H_4, 2-$NH_2C_6H_4$, 2-$EtO_2CNHC_6H_4$, C_4H_9, $SiMe_3$, CH_2OH

Reagents and conditions: (i) $PdCl_2(PPh_3)_2$, PPh_3, CuI, Et_3N, DMF; (ii) HI, Me_2CO, rt, 8 h.

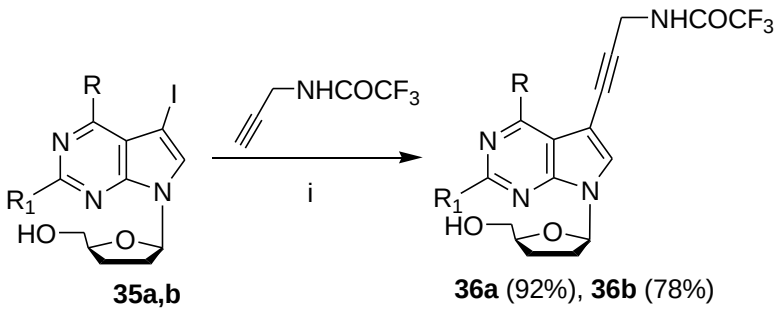
In the Sonogashira reaction of compound **30** with 2-ethynyl-*N*-mesylaniline the formation of cyclized product – 4-(2-indolyl)pyrrolo[2,3-*d*]pyrimidine **33** – was observed along with the cross-coupling product **32**. Thus, one-pot method of the synthesis of **33** was elaborated adding CuI at the end of the Sonogashira cross-coupling reaction. Compound **33** was further used for the construction of fused heterocycle **34** containing a 1,3-diazepine ring [78, 79].



Reagents and conditions: (i) $PdCl_2(PPh_3)_2$, CuI, NEt_3, DMF, rt, then CuI, 55-60 °C.

I.3. Synthesis of 5-substituted pyrrolo[2,3-*d*]pyrimidines.

The first report on a formation of C–C bond at position 5 of pyrrolo-[2,3-*d*]pyrimidine nucleosides using cross-coupling reaction was reported in 1989 by F. W. Hobbs [80]. 5-Iodopyrrolo[2,3-*d*]pyrimidine nucleoside analogs **35** reacted with *N*-(prop-2-yn-1-yl)trifluoroacetamide under the Sonogashira reaction conditions and 5-alkynylpyrrolo[2,3-*d*]pyrimidines **36** were obtained in good yields. The ratio of palladium(0) to copper(I) was found to be very important. For example, when a Pd(0) to Cu(I) ratio of 1:1 was used no reaction occurred. The best result was obtained when the Sonogashira reaction was carried out in DMF and the ratio of Pd(0) to Cu(I) was 1:2. The nucleoside analogs **36** were synthesized as tagged substrates for DNA polymerases.



35a,b **36a** (92%), **36b** (78%)

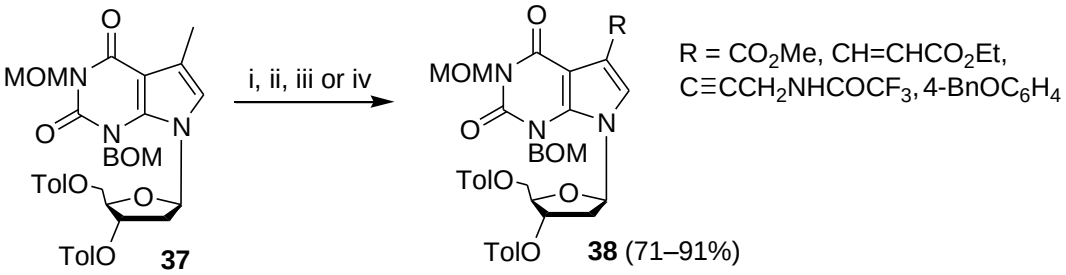
a R = NH_2, R_1 = H, **b** R = OH, R_1 = NH_2

Reagents and conditions: (i) $Pd(PPh_3)_4$, CuI, NEt_3, DMF, rt, 4 h.

The same reaction was investigated by M. J. Robins *et al.* [81]. They have found that cross-coupling reaction of compound **35** proceeded smoothly at ambient temperature using either $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$/CuI and triethylamine as a base. Slightly higher yields were obtained with $Pd(PPh_3)_4$. The most important factor on the reaction outcome was found to be the solvent. The highest yields of products and no appreciable amounts of byproducts were obtained when the reaction was carried out in DMF.

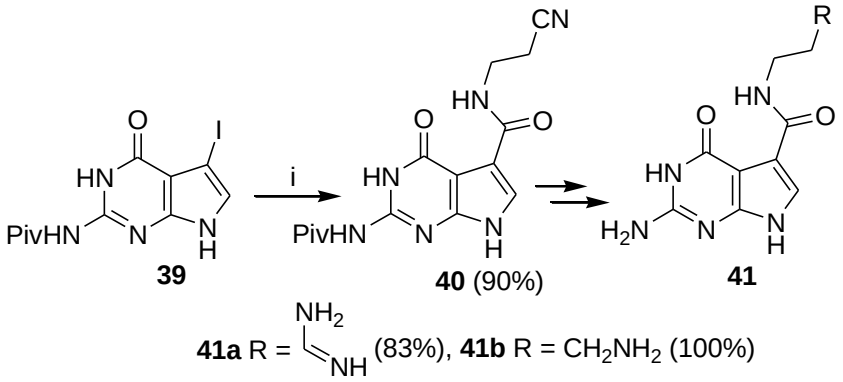
E. D. Edstrom and Y. Wei in 1994 showed that 7-(β-2'-deoxyribosyl)-pyrrolo[2,3-*d*]pyrimidine-5-triflate **37** is useful for the synthesis of a variety of

5-substituted pyrrolo[2,3-*d*]pyrimidine nucleosides **38** using methoxycarbonylation, Sonogashira, Heck, and Stille palladium-catalyzed reactions [82].



Reagents and conditions: (i) $Pd(OAc)_2$, PPh_3, CO, Et_3N, DMF, MeOH, 68 °C, 2h; (ii) $Pd(PPh_3)_4$, CuI, Et_3N, DMF, $HC{\equiv}CCH_2NHCOCF_3$, 30 °C, 1h; (iii) $Pd(PPh_3)_4$, Et_3N, DMF, $H_2C{=}CHCO_2Et$, 90 °C, 17h; (iv) Pd_2dba_3, $(furyl)_3P$, $(4\text{-}BnOC_6H_4)Sn(n\text{-}Bu)_3$, NMP, 55 °C, 16h.

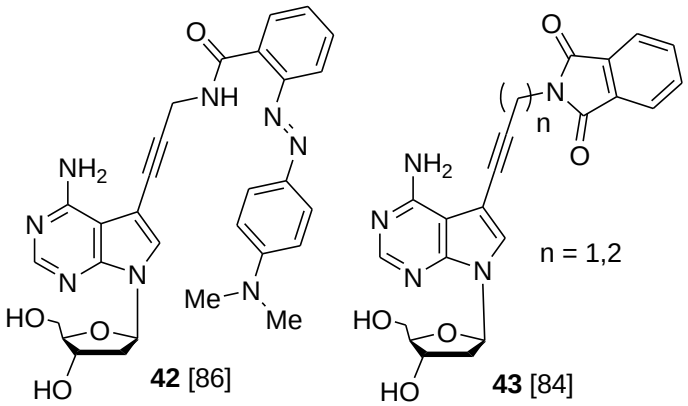
Palladium-catalyzed carbonylation reaction in a pyrrolo[2,3-*d*]pyrimidine series was successfully applied in the synthesis of potent inhibitors of phosphatidylinositol-4-kinase derived from the A-431 cell membrane – Echiguanines A (**41a**) and B (**41b**) [83]. A key step was the reaction of 5-iodo-2-pivaloylaminopyrrolo[2,3-*d*]pyrimidin-4(3*H*)-one (**39**) with carbon monoxide and 2-aminopropionitrile in the presence of $PdCl_2(PPh_3)_2$ at 80 °C in DMF.



Reagents and conditions: (i) $H_2NCH_2CH_2CN$, CO, $PdCl_2(PPh_3)_2$, DMF, 80 °C, 5 h.

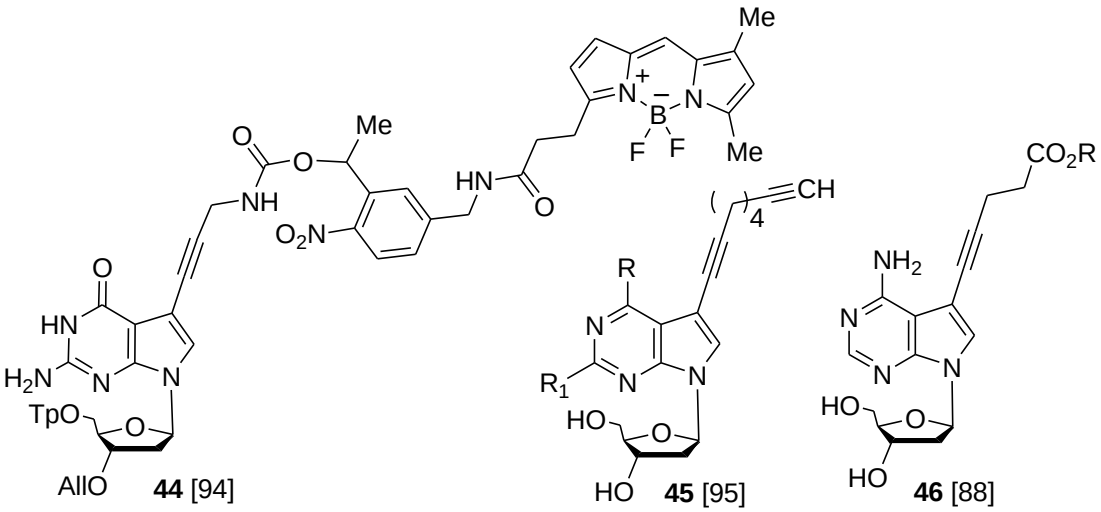
5-Alkynylpyrrolo[2,3-*d*]pyrimidine nucleoside analogs are of interest in the development of antisense nucleotides, substrates for DNA polymerases and in incorporating of non-radioactive fluorescent labels into nucleic acids.

Alkynyl group at the position 5 of pyrrolo[2,3-*d*]pyrimidine was usually introduced by Sonogashira reaction of the corresponding 5-iodopyrrolo[2,3-*d*]pyrimidine nucleoside with suitable terminal alkyne or by functional group transformations of intermediates, for example, 5-(3-trifluoroacetylamino)propynylpyrrolo[2,3-*d*]pyrimidine moiety containing nucleosides [84-100]. Further, several structures **42**-**49** of 5-alkynylpyrrolo[2,3-*d*]pyrimidine nucleosides with fluorescent tags and moieties suitable for further modifications or stabilizing DNA duplex are shown.



42 [86]

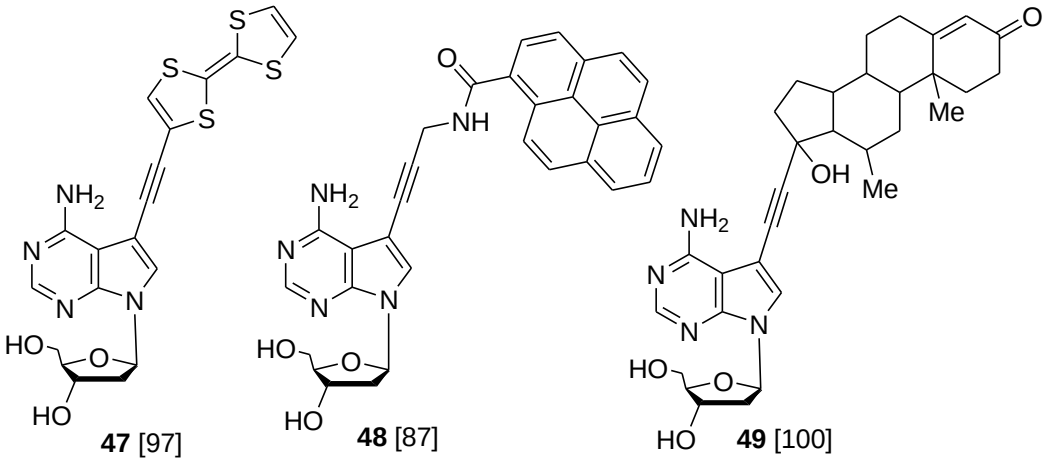
43 [84]



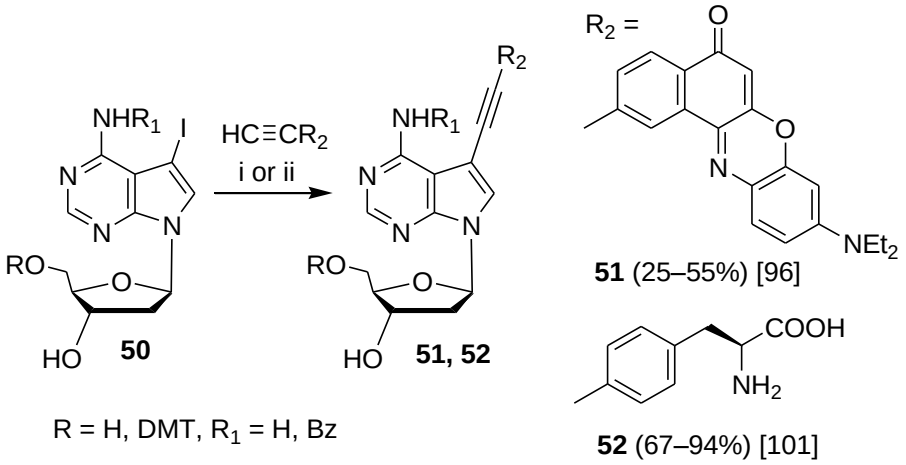
44 [94]

45 [95]

46 [88]

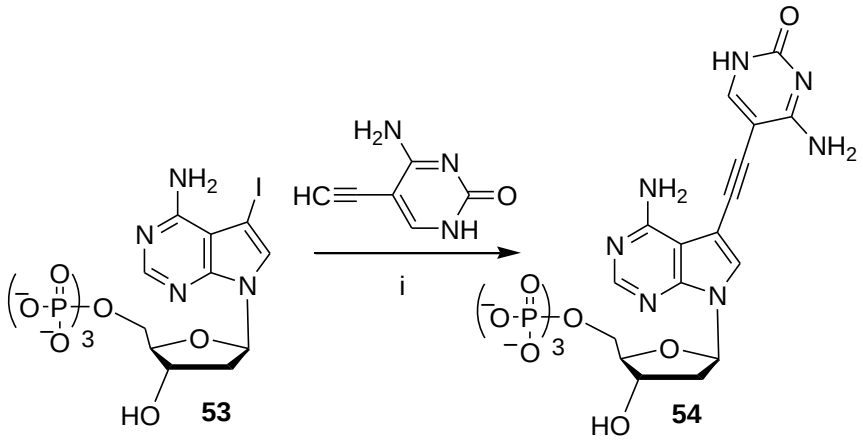


Using Sonogashira coupling reaction between 5-iodo-pyrrolo[2,3-*d*]pyrimidine nucleosides **50** and ethynyl Nile Red [96] and 4-ethynylphenylalanine [101], respectively, pyrrolopyrimidine nucleosides **51**, **52**, labeled through a rigid acetylene linker, have been synthesized. Study on the synthesis of **51** [96] revealed, that protection of 5'-OH or amino group of pyrrolo[2,3-*d*]pyrimidine significantly increases the yields of the cross-couplings, while the ratio of Pd(0) to CuI, catalyst load or reaction temperature have no effect on the reaction outcome. Synthesis of compound **52** was performed in the presence of $Pd(OAc)_2$, $P(3\text{-}NaSO_3C_6H_4)_3$, CuI and *i*-$Pr_2NEt$ in water-acetonitrile, 2:1, mixture at 80 °C [101]. Pyrrolo[2,3-*d*]pyrimidine nucleosides, modified in the position 5, were shown to be suitable substrates for DNA polymerases.



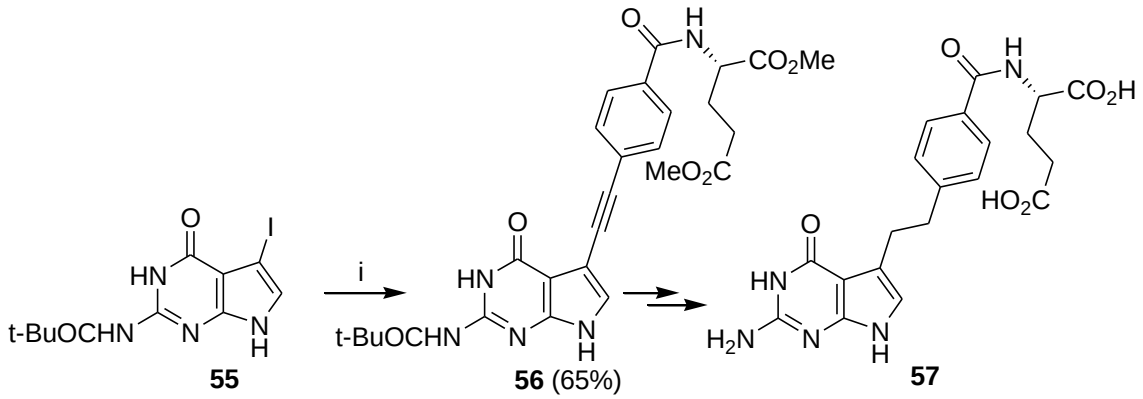
Reagents and conditions: (i) $Pd(PPh_3)_4$, CuI, DMF, Et_3N, 90 °C, 4h; (ii) $Pd(OAc)_2$, $P(3\text{-}NaSO_3C_6H_4)_3$, *i*-$Pr_2NEt$, CuI, H_2O/MeCN, 80 °C.

It is worthy of note, that Sonogashira coupling was successfully performed under aqueous conditions using the corresponding 5'-triphosphates, such as **53** [102]. Aqueous cross-coupling reactions of triphosphates suffer from lower yields of modified nucleotides **54** due to partial hydrolysis of triphosphates to diphosphates. As noted in [102], the reactions must be performed in short time (max 1 h).



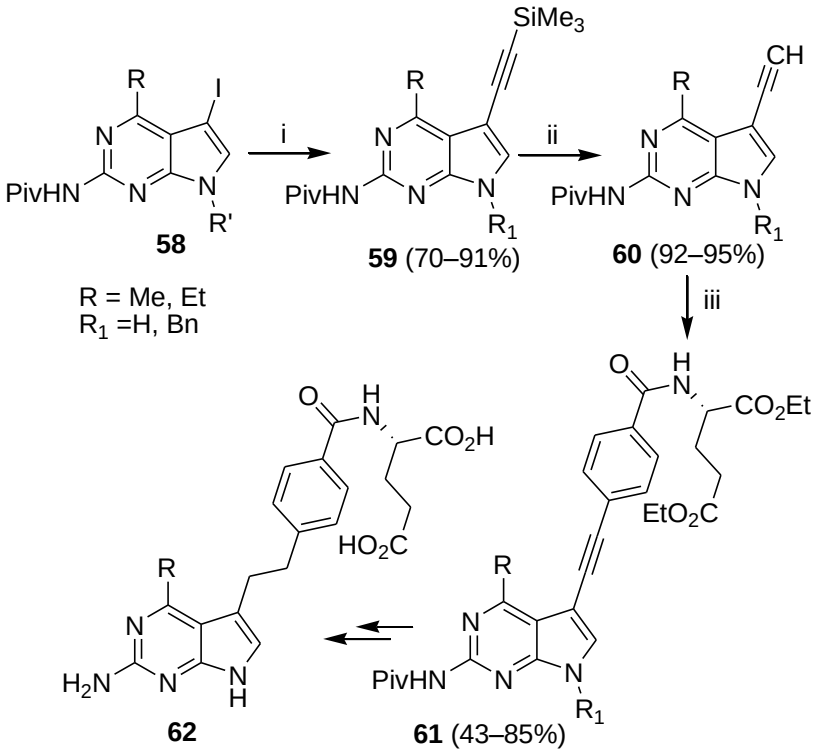
Reagents and conditions: (i) $Pd(OAc)_2$, TPPTS, CuI, *i*-Pr_2NEt, H_2O/MeCN, 105 °C, 1h.

Sonogashira reaction has been also exploited in the development of thymidylate synthase (TS) and dihydrofolate reductase (DHFR) inhibitors useful as anticancer and antibacterial agents. E. C. Taylor *et al.* developed an approach for potent TS and DHFR inhibitor Pemetrexed **57**, in which the Sonogashira reaction was used in the synthesis of the key intermediate **56** from 5-iodopyrrolo[2,3-*d*]pyrimidine **55** and dimethyl *N*-(4-ethynylbenzoyl)-L-glutamate [42].



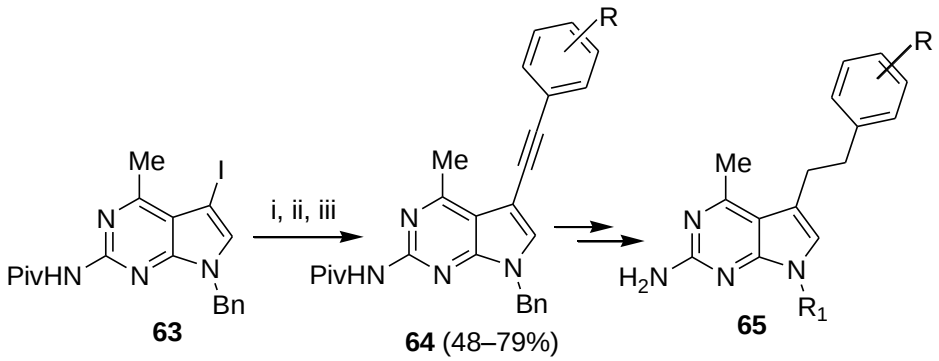
Reagents and conditions: (i) Dimethyl *N*-(4-ethynylbenzoyl)-L-glutamate, $Pd(PPh_3)_4$, CuI, Et_3N, DMF, rt, 2h.

However, attempts to synthesize 4-methyl and 4-ethyl analogs of Pemetrexed by analogous methodology using the Sonogashira coupling of the corresponding 5-iodopyrrolopyrimidines with *N*-(4-ethynylbenzoyl)-L-glutamate have failed [103, 72]. The use of different solvents (DMF, toluene, 1,2-dichloroethane, dichloromethane) or temperatures did not give the desired result. A. Gangjee *et al.* elaborated an alternative method for the synthesis of compounds **62** [103]. 5-Iodopyrrolo[2,3-*d*]pyrimidines **58** were coupled with trimethylsilylacetylene. The silyl protecting group was removed by fluoride ion to give 5-ethynylpyrrolo[2,3-*d*]pyrimidines **60**. Compound **60** was then successfully coupled with 4-iodobenzoyl-L-glutamate under the Sonogashira conditions to give diester **61** in 43–85% yield. Subsequent catalytic hydrogenation and hydrolysis afforded the corresponding classical antifolates **62**.



Reagents and conditions: (i) $Me_3SiC{\equiv}CH$, $Pd(PPh_3)_4$, CuI, NEt_3, THF, rt; (ii) *n*-Bu_4NF, THF, rt; (iii) diethyl *N*-(4-iodobenzoyl)-L-glutamate, $Pd(PPh_3)_4$, CuI, NEt_3, THF, rt.

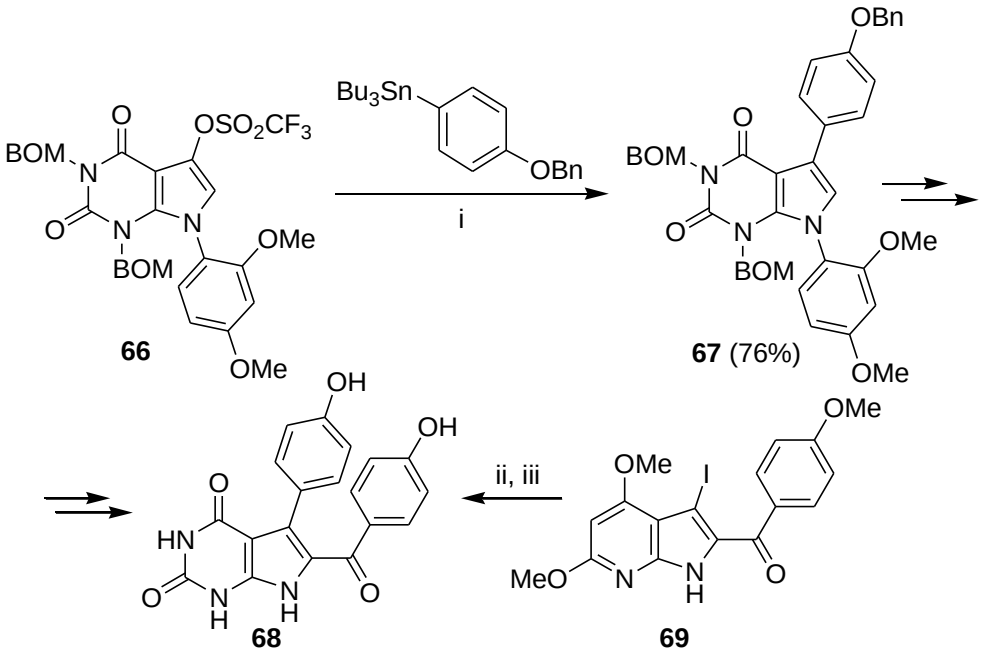
The depicted reaction sequences were also applied by the same team for the synthesis of 5-(2-arylethyl)-7-benzyl-4-methylpyrrolo[2,3-*d*]pyrimidin-2-amines (**65**) possessing antimitotic and antitumor activities against antimitotic-sensitive as well as resistant tumor cells [104].



R = 3,4,5-$(MeO)_3$, 4-MeO, 3-MeO, 2-MeO, H; R_1 = H, Bn

Reagents and conditions: (i) $Me_3SiC{\equiv}CH$, $Pd(PPh_3)_4$, CuI, NEt_3, THF, rt; (ii) *n*-Bu_4NF, THF, rt; (iii) RC_6H_4I, $Pd(PPh_3)_4$, CuI, NEt_3, CH_2Cl_2, dark, rt.

Aromatic substituents at position 5 of pyrrolo[2,3-*d*]pyrimidine were introduced by the Suzuki or Stille reactions. Thus, E. D. Edstrom and Y. Wei [105] reported the total synthesis of marine alkaloid rigidin (**68**), which inhibits caldomulin-activated brain phosphodiesterase. In one of the steps, Stille cross-coupling of pyrrolo[2,3-*d*]pyrimidine-5-triflate **66** with 4-benzyloxyphenyl-tributylstannane, using $Pd_2(dba)_3$ and tri(2-furyl)phosphine, was applied to furnish the intermediate **67**.

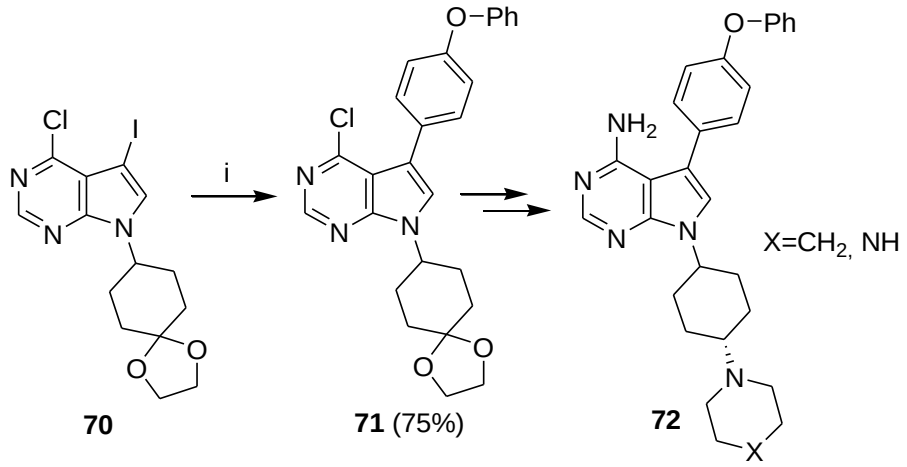


Reagents and conditions: (i) $Pd_2dba_3{\times}CHCl_3$, $ZnCl_2$, $P(2\text{-furyl})_3$, NMP, 55 °C, 24 h; (ii) 2-(4-methoxyphenyl)-1,3,2-dioxaborinane, $Pd(PPh_3)_4$, DMF, 100 °C, 60%; (iii) BBr_3, $ClCH_2CH_2Cl$, 41%.

A year later, another route for the synthesis of rigidin (**68**), including the Suzuki coupling of 5-iodopyrrolo[2,3-*d*]pyrimidine **69** with a 2-(4-methoxyphenyl)-1,3,2-dioxaborinane in DMF at 100 °C in the presence of $Pd(PPh_3)_4$, was reported by T. Sakamoto *et al.* [106].

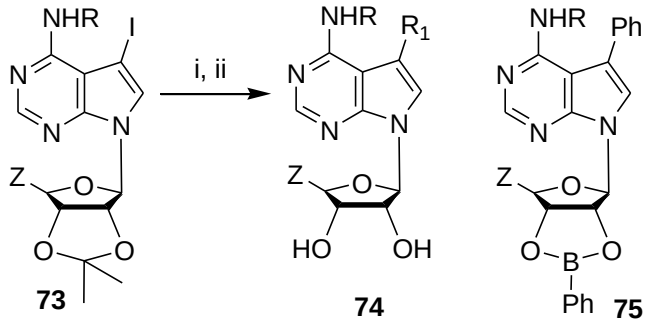
D. J. Calderwood *et al.* reported the synthesis of pyrrolo[2,3-*d*]pyrimidines **72** as potent inhibitors of *Lck*, a *Src* family tyrosine kinase, expressed primarily in T lymphocytes [107]. The key step of the sequence of

reactions leading to compound **72** is the Suzuki coupling between 4-chloro-5-iodopyrrolo[2,3-*d*]pyrimidine **70** and 4-phenoxyphenylboronic acid.



Reagents and conditions: (i) 4-(PhO)$C_6H_4B(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O.

Diaryltubercidine analogs **74**, as adenosine kinase inhibitors, were synthesized by the arylation of 5-iodopyrrolo[2,3-*d*]pyrimidine nucleoside analogs **73** *via* the Suzuki reaction. It was found, that protected nucleosides furnish 5-aryl derivatives in higher yields in comparison with the reaction of unprotected ones. Lower yields of the desired products in the latter case are presumably due to partial formation of 2',3'-*O*-cyclic boronates **75** [108, 109].

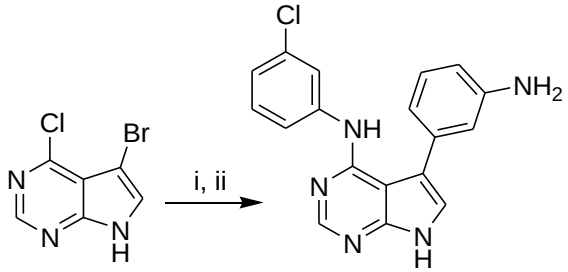


[108]: Z = Me, CH_2OH, CH_2OTBS; R = Ph, Bn, 4-FC_6H_4, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-HOC_6H_4, 4-CNC_6H_4, Cy, 3-Py; R_1 = Ph, 4-ClC_6H_4, 4-FC_6H_4, 4-$MeOC_6H_4$, 2-furyl (50–88%)

[109]: Z = Me; R = 4-FC_6H_4, 4-CNC_6H_4, 3,4-$O(CH_2)_2OC_6H_3$, 2-$MeOC_6H_4$; R_1 = 3-$NH_2C_6H_4$, 4-$EtOC_6H_4$, 4-ClC_6H_4, 2-MeC_6H_4 (76–94%)

Reagents and conditions: (i) $R_1B(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3, diglyme, EtOH, Δ; (ii) 70% TFA or HCl, MeOH.

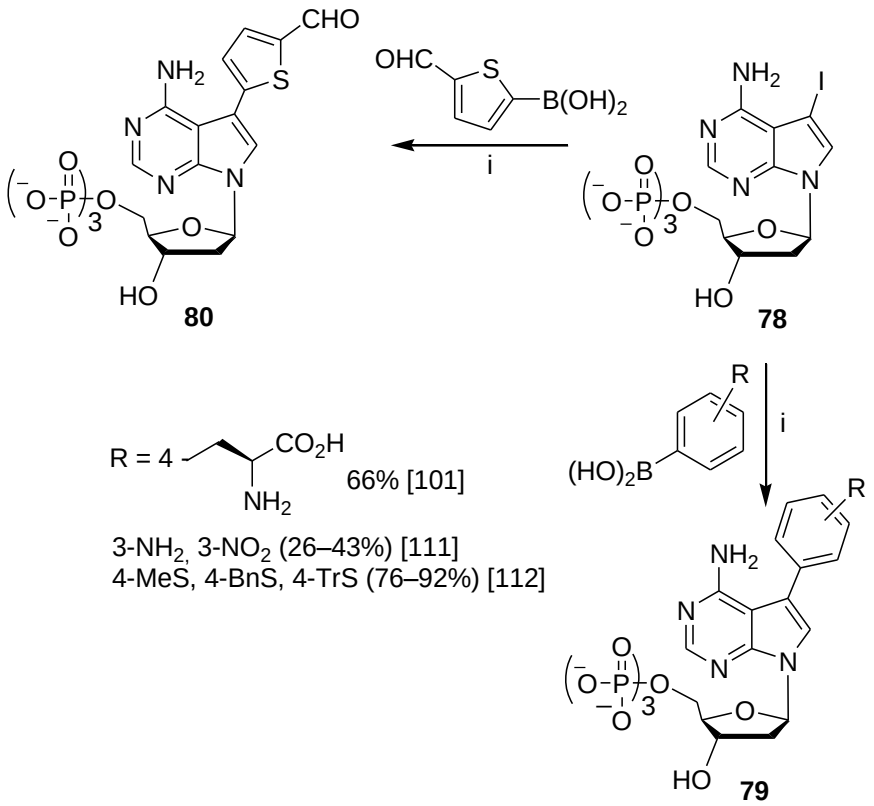
A microwave-assisted reaction was developed to facilitate the construction of 4,5-disubstituted pyrrolopyrimidine **77** [110]. The one-pot two-step process involves a sequential S_NAr displacement of the 4-chloro substituent in 5-bromo-4-chloropyrrolo[2,3-*d*]pyrimidine (**76**) with 3-chloroaniline, followed by Suzuki coupling reaction with boronic acid. The use of microwave irradiation leads to high product conversion, low side product formation, and shorter reaction time.



76 **77** (65%)

Reagents and conditions: (i) 3-Chloroaniline, AcOH, 1,4-dioxane, MW, 150 °C, 10 min; (ii) 2-$H_2NC_6H_4B(OH)_2$, $Pd(dppf)Cl_2 \times CH_2Cl_2$, K_3PO_4, 1,4-dioxane, MW, 180 °C, 10 min.

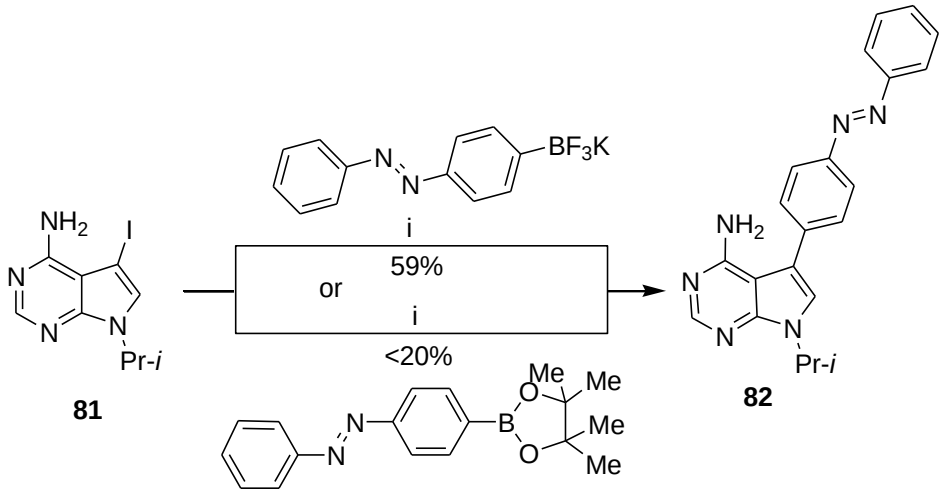
For the synthesis of corresponding 5-aryl- or 5-arylethynylpyrrolo-[2,3-*d*]pyrimidine nucleosides M. Hocek *et al.* applied aqueous-phase cross-coupling reactions of 5-iodopyrrolo[2,3-*d*]pyrimidine derivatives **78** with 3-nitro-, 3-amino [111], 4-methylsulfanyl-, 4-benzylsulfanyl-, 4-tritylsulfanyl-phenylboronic acids [112]. For this purpose, $Pd(OAc)_2$ and a water soluble ligand, $P(3\text{-}NaSO_3C_6H_4)_3$, were used in the presence of Cs_2CO_3 in acetonitrile-water mixture. The synthesized 5-arylpyrrolo[2,3-*d*]pyrimidine nucleosides were tested as substrates for DNA polymerases in the enzymatic construction of functionalized DNA. 3-Amino and 3-nitrophenyl modifications **79** were found to be the excellent electrochemical labels detectable by either oxidation (NH_2) or reduction (NO_2), which allows perfect discrimination between the two tags incorporated in the same DNA molecule. Successful synthesis of compound **80**, bearing formyl group, under the analogous conditions showed that aldehyde group (attached through a thiophene moiety) withstands both Suzuki cross-coupling and polymerase incorporation [113].



Reagents and conditions: (i) $Pd(OAc)_2$, $P(3\text{-}NaSO_3C_6H_4)_3$, Cs_2CO_3 or Na_2CO_3, MeCN, H_2O.

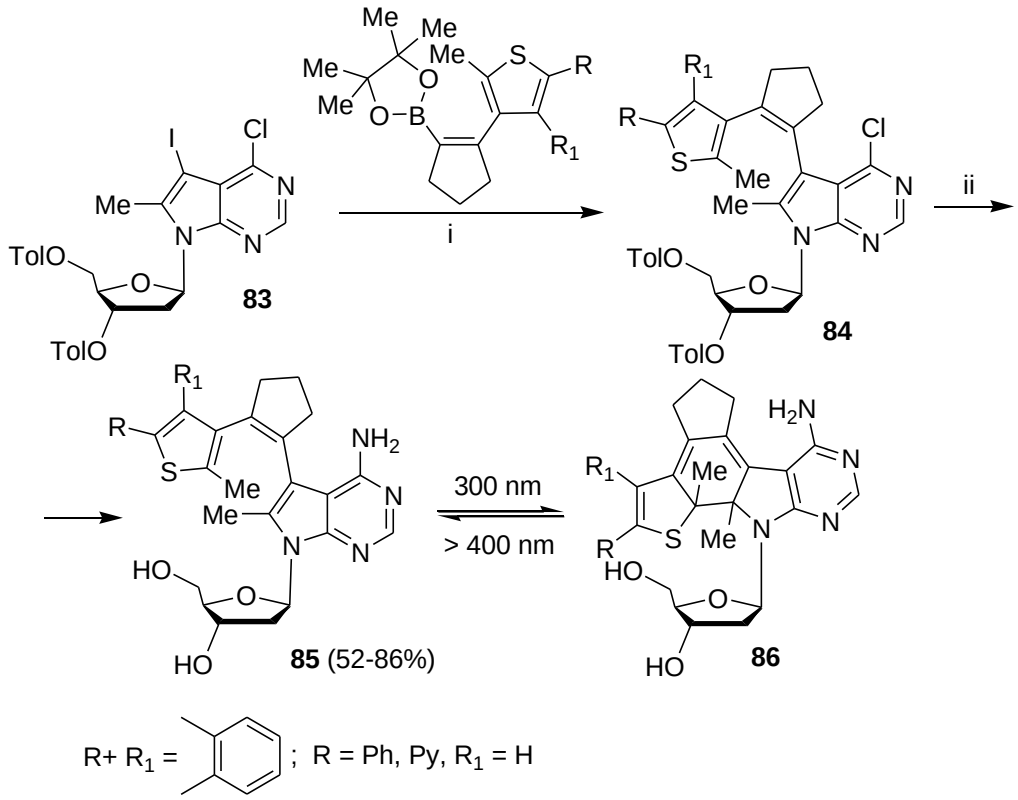
In order to introduce azobenzene moiety into the position 5 of pyrrolo[2,3-*d*]pyrimidine and to obtain photoswitchable kinase inhibitors, arylation of 4-amino-5-iodo-7-isopropylpyrrolo[2,3-*d*]pyrimidine (**81**) in the Suzuki reaction was investigated [114].

It was found, that coupling of compound **81** with potassium azobenzenetrifluoroborate gives better results, and the product **82** is obtained in higher yield (59%) when compared with the coupling reaction using the corresponding boronate (<20%). The reaction was carried out in refluxing ethanol in the presence of $PdCl_2$(dppf). When triphenylphosphine was used as a ligand or reaction was performed under microwave irradiation, yields were typically decreased.



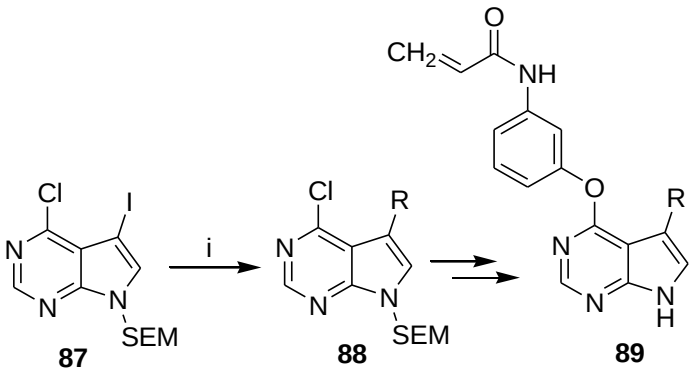
Reagents and conditions: (i) $PdCl_2(dppf)\times CH_2Cl_2$, DIPEA, EtOH, Δ.

In a recent paper [115], reversibly photoswitchable pyrrolo[2,3-*d*]pyrimidine nucleosides **85** combining the structural features and molecular recognition properties of nucleic acids with the light-sensitivity of diarylethenes have been designed. Their synthesis was accomplished by the Suzuki coupling of protected nucleoside **83** with boronic esters, using $PdCl_2(dppf)$ as a catalyst in the presence of potassium phosphate in THF–water mixture.



Reagents and conditions: (i) $Pd(dppf)Cl_2$, TEA, K_3PO_4, H_2O, THF; (ii) aq. NH_3, 1,4-dioxane.

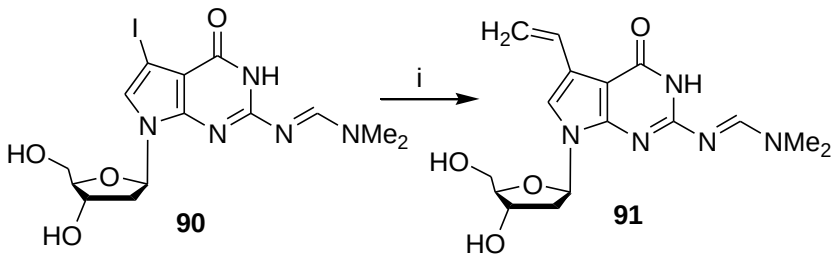
The initially very low yields of this reaction were improved by addition of triethylamine. Under these conditions coupling products were obtained in 50–85% yields. It should be mentioned, that no reaction occurred with chlorine group at position 4 of pyrrolo[2,3-*d*]pyrimidine. Such chemoselectivity of the coupling reaction was also observed in the reaction of protected pyrrolo[2,3-*d*]pyrimidines **87** with (het)arylboronic acid [116].



R = 3-Py, 3-quinolyl, 4-$MeOC_6H_4$

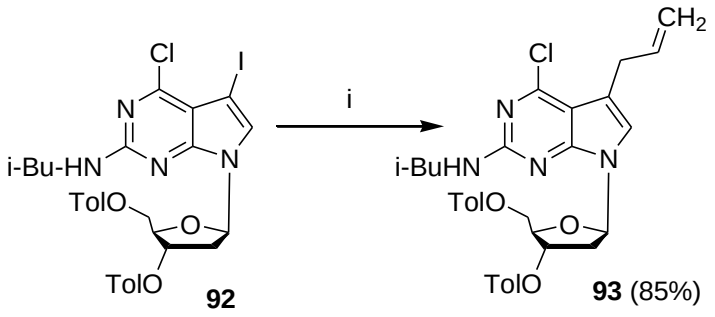
Reagents and conditions: (i) $RB(OH)_2$, $Pd(dppf)Cl_2$, dppf, Na_2CO_3, 1,4-dioxane, H_2O.

Stille cross-coupling reaction for the functionalization of position 5 of pyrrolo[2,3-*d*]pyrimidine was used to introduce vinyl, allyl or aryl moieties. Thus, reaction of 5-iodopyrrolo[2,3-*d*]pyrimidine nucleoside **90** with tributylvinylstannane in DMF at 100 °C in the presence of $Pd(PPh_3)_4$ led to nucleoside **91** [117], which was found to be capable to stabilize DNA duplex due to π-stacking of vinyl group with 5'-flanking base.



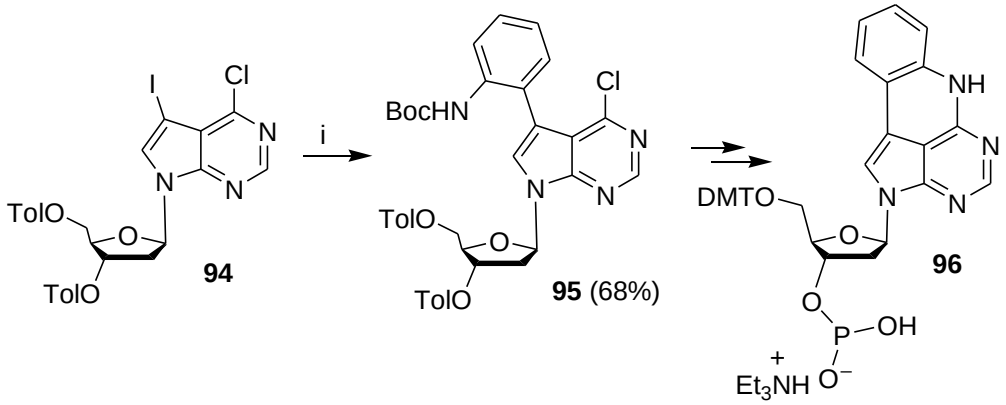
Reagents and conditions: (i) $Bu_3SnCH=CH_2$, $Pd(PPh_3)_4$, DMF, 100 °C, 5 h, 60%.

Similarly, allyl group at the position 5 of pyrrolo[2,3-*d*]pyrimidine was introduced by the reaction of **92** with allyltributylstannane [118].



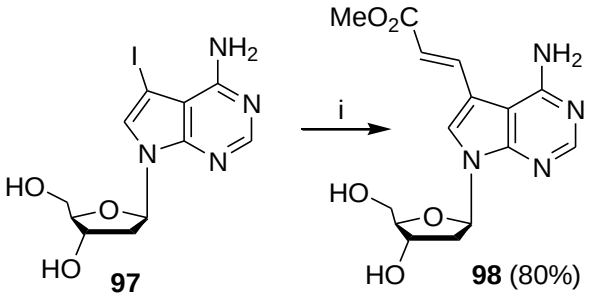
Reagents and conditions: (i) $Bu_3SnCH_2CH=CH_2$, $Pd(PPh_3)_4$, toluene, 95 °C.

Stille coupling of 4-chloro-5-iodopyrrolo[2,3-*d*]pyrimidine nucleoside **94** with 2-(*t*-butoxycarbonylamino)phenyltrimethylstannane allowed to prepare the coupling product **95**, which appeared to be useful intermediate for the synthesis of a tetracyclic nucleoside **96** [119].



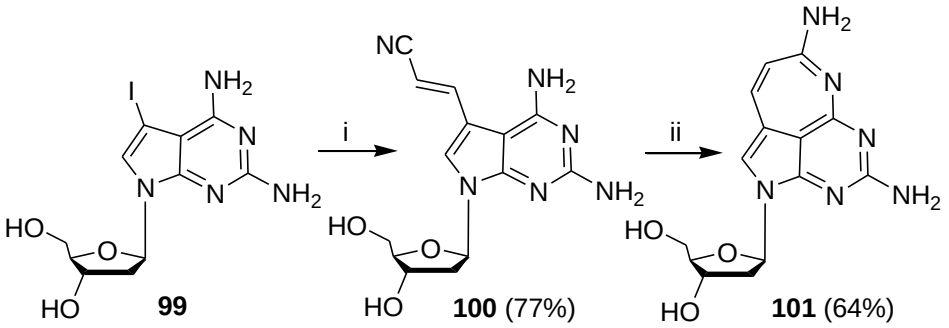
Reagents and conditions: (i) 2-(*t*-BuCONH)$C_6H_4SnMe_3$, $Pd(PPh_3)_2Cl_2$, DMF, 60 °C, 24h.

Heck reaction for the C–C bond formation at position 5 of pyrrolo-[2,3-*d*]pyrimidine was used only by several authors. For example, nucleoside **98** was synthesized in 80% yield by reaction of 5-iodo derivative **97** with methyl acrylate by heating of the reaction mixture at 80 °C in DMF [100, 120].



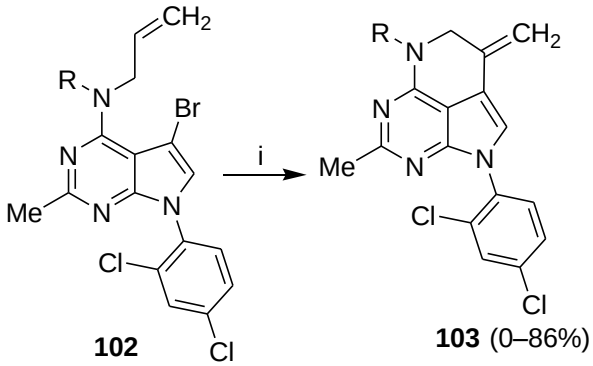
Reagents and conditions: (i) $H_2C=CHCO_2Me$, $Pd(PPh_3)_4$, CuI, Et_3N, DMF, 80 °C, 8h.

The use of Heck reaction of the 5-iodo-2,4-diaminopyrrolo[2,3-*d*]pyrimidine **99** with acrylonitrile and following cyclization under basic conditions allowed the synthesis of nucleoside derivative **101** possessing a 2,3,5,6-tetraazabenzo[*cd*]azulene skeleton [121].



Reagents and conditions: (i) MeCN, $Pd(PhCN)_2Cl_2$, CuI, Et_3N, DMF, 70 °C, 24h; (ii) NaSPh, NaOMe, MeOH, 70 °C, 24h.

Intramolecular Heck cyclization also served as the critical step in the construction of six membered ring in the development of a synthetic route to pharmaceutically important tricyclic pyrrolopyrimidines **103** [122].



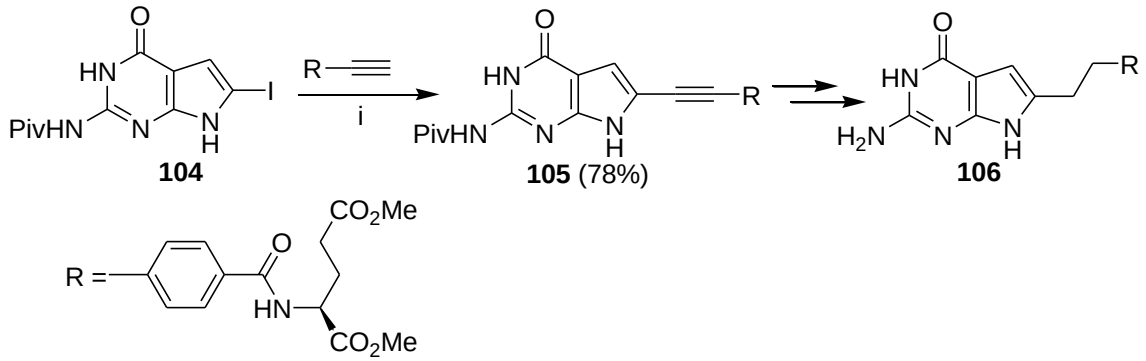
R = H, Me, Cy, 4-heptyl

Reagents and conditions: (i) $Pd(PPh_3)_4$, KOAc, DMF, 85 °C.

I.4. Synthesis of 6-substituted pyrrolo[2,3-*d*]pyrimidines.

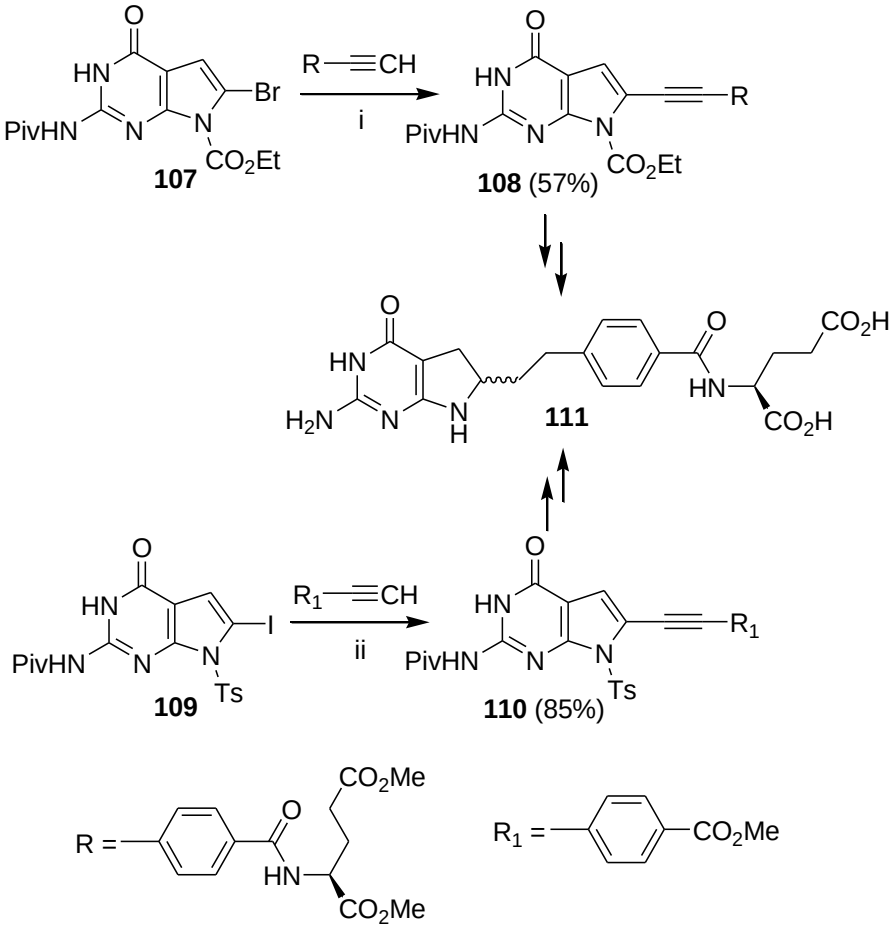
E. C. Taylor *et al.* prepared a regioisomer **106** of the potent TS inhibitor and antitumor agent Pemetrexed using the synthetic route that involved Sonogashira coupling of 6-iodo-2-pivaloylaminopyrrolo[2,3-*d*]pyrimidine **104**

with dimethyl *N*-(4-ethynylbenzoyl)-L-glutamate in the presence of $Pd(PPh_3)_4$/CuI/Et_3N in DMF [123].



Reagents and conditions: (i) Dimethyl *N*-(4-ethynylbenzoyl)-L-glutamate, $Pd(PPh_3)_4$, NEt_3, CuI, DMF, 60 °C, 4h.

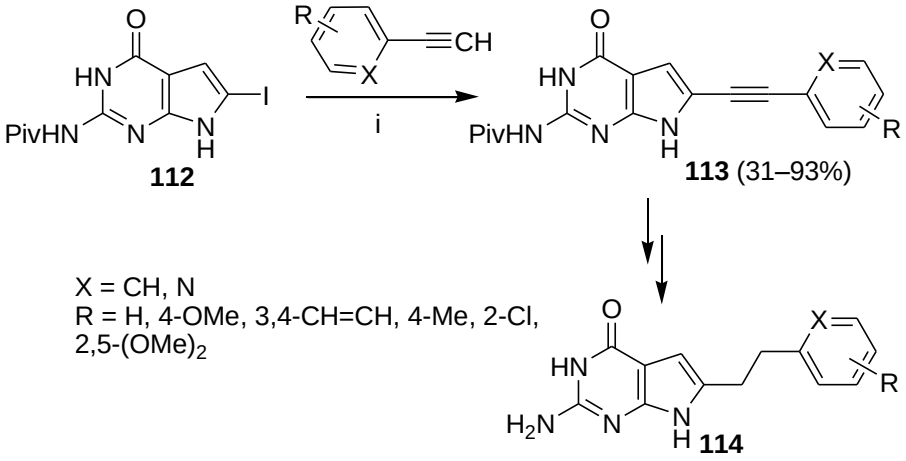
The same research team reported two routes for the synthesis of **111**, which can be viewed as a ring-contracted analogue of Lometrexol [124].



Reagents and conditions: (i) $Pd(PPh_3)_4$, NEt_3, CuI, MeCN, Δ, 6h; (ii) $Pd(PPh_3)_4$, TEA, CuI, CH_2Cl_2, Δ, 3h.

The synthesis of compound **111** was accomplished using the Sonogashira coupling reaction between the 6-bromo(or iodo)-7*H*-pyrrolo[2,3-*d*]pyrimidine derivatives **107** or **109** and corresponding acetylenic compounds. Compound **111** exhibits significant activity as an inhibitor of the growth of human lymphoblastic leukemic cells *in vitro* and apparently acts by blocking *de novo* purine biosynthesis through inhibition of glycinamide ribonucleotide formyltransferase.

In search of potent TS inhibitors A. Gangjee *et al.* [125] designed and synthesized several 6-substituted pyrrolo[2,3-*d*]pyrimidines **114**. One of the steps was Sonogashira coupling reaction of **112** with an appropriately substituted arylacetylene.



Reagents and conditions: (i) $Pd(PPh_3)_4$, CuI, TEA, DMF, rt.

In summary, this review demonstrates that palladium(0) catalyzed processes constitute an efficient strategy for functionalization of pyrrolo[2,3-*d*]pyrimidine scaffold by C–C bond formation and continue to offer new applications to synthesize an increasingly wide range of polyfunctionalized compounds with biochemical, medicinal or materials science applications. The possibility to use easily accessible halopyrrolo[2,3-*d*]pyrimidines, as well as to attain the target in a few steps is of considerable importance. Such a goal may not be easily obtainable by other methods. Moreover, these reactions proceed under relatively mild reaction conditions and tolerate a wide variety of functional groups. There are some uncertainties, however, with regard to the

selection of ligand, catalyst, solvent, base, additives, *etc*. The results reviewed also demonstrate that the selectivity pattern in halopyrrolo[2,3-*d*]pyrimidines usually follows the pattern for a nucleophilic aromatic substitution. However, regioselectivity also depends on the halogen attached to the pyrrolo[2,3-*d*]pyrimidine moiety. Iodine reacts first, even though it is attached to the less electron-deficient position of pyrrolo[2,3-*d*]pyrimidine. An important aspect which requires further attention, especially in the synthesis of biologically active compounds, is contamination of products with residual palladium and other heavy metals originated from organometallics used in the cross-coupling reactions. In the literature reviewed, removal of palladium has usually not been considered. Despite that, removal of residual amounts of metals from products and post-reaction solutions is of great importance and can be a major purity concern [126-129].

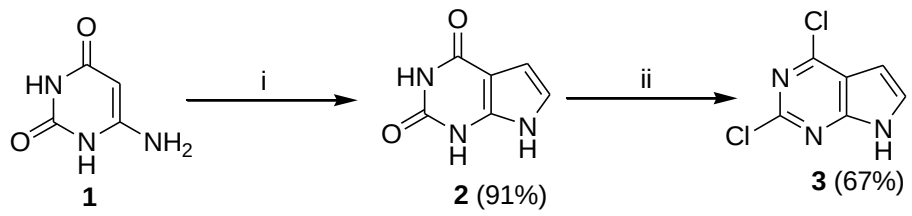
II. RESULTS AND DISCUSSION

II.1. Study on the palladium-catalyzed cross-coupling reaction of chloropyrrolo[2,3-*d*]pyrimidines with arylboronic acids.

II.1.1. Synthesis of 4-aryl- and 2,4-diarylpyrrolo[2,3-*d*]pyrimidines.

For the synthesis of 4-aryl-2-chloro- and 2,4-diaryl-7*H*-pyrrolo[2,3-*d*]pyrimidines 2,4-dichloropyrrolo[2,3-*d*]pyrimidine (**3**) was chosen as starting material. The choice was made because of several reasons. Firstly, the successful Suzuki reaction of **3** would provide the target compounds in one step. Secondly, substrates containing chlorine groups are the cheapest substrates for cross-coupling reactions in comparison with the corresponding bromine or iodine derivatives. Furthermore, 2,4-dichloropyrrolo[2,3-*d*]pyrimidine (**3**) can be easily synthesized from commercially available 6-aminouracil (**1**) by two step procedure [130, 131]. And finally, the site-selectivity of pyrrolo[2,3-*d*]pyrimidines containing halogen groups in different positions was not studied till the present investigation. Therefore, study of site-selectivity of cross-coupling reaction of **3** as well as discovery of reaction conditions and effective catalyst systems for the Suzuki coupling is of great importance from point of development of synthetic methods for novel arylpyrrolopyrimidines.

As mentioned above, 2,4-dichloropyrrolo[2,3-*d*]pyrimidine (**3**) was synthesized by cyclization of commercially available 6-aminouracil (**1**) with chloroacetaldehyde to give pyrrolo[2,3-*d*]pyrimidine-2,4-dione (**2**) and following reaction of compound **2** with dichloro(phenyl)phosphorous oxide according to the literature described method [131] (Scheme 1).



Scheme 1. *Reagents and conditions:* (i) $ClCH_2CHO$, NaOAc, H_2O, 80 °C to rt; (ii) $PhPOCl_2$, 165 °C, 1 h.

However, attempts to reach the reported yield of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine using the procedure described in [131] failed. The best yield of **3** was achieved only 24% instead of 41% reported in the literature. Taking into account, that compound **3** was chosen as an initial material for all investigations it was necessary to improve its synthetic procedure. It was noticed that isolation of compound **3** from the reaction mixture according to the reported procedure is not complete. Thus, we modified it by changing the solvent for the extraction of **3** from diethyl ether/dichloromethane mixture to water/ethyl acetate mixture and applying a continuous extraction for approx. 12 hours. After the evaporation of solvent the product **3** was extracted from the obtained residue with a large amount of hot toluene. After these modifications compound **3** was obtained in 64%-67% yield. Moreover, it was pure enough for use in cross-coupling reactions without additional purification.

With successfully prepared 2,4-dichloropyrrolo[2,3-*d*]pyrimidine in hand, we examined its ability to participate in the Suzuki cross-coupling reaction. For this purpose, a set of nine phenyl boronic acids (**4a-i**) has been chosen (Figure 1).

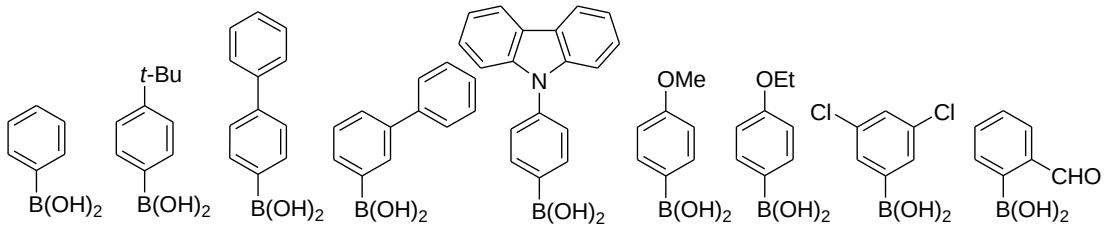
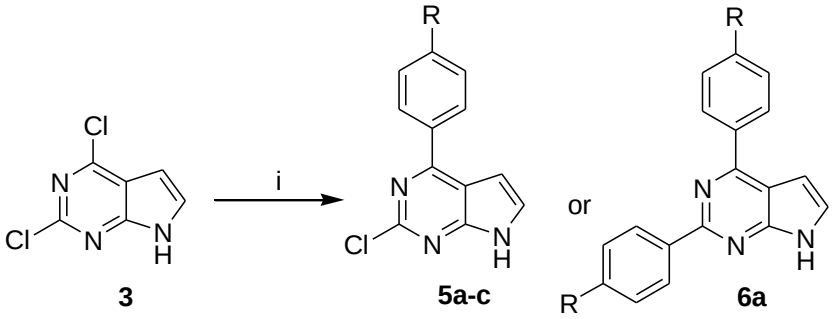


Figure 1. Phenyl boronic acids used for the Suzuki reaction.

Recently, it has been shown the utility of the Suzuki reaction for the synthesis of densely substituted 4,6-diarylpyrimidines [132]. Two catalytic systems were found to be efficient for these purposes - $Pd(OAc)_2/PPh_3/K_3PO_4$ and $PdCl_2(PPh_3)_2/K_3PO_4$. Taking into account, that 2,4-dichloropyrrolo[2,3-*d*]pyrimidine (**3**) is structurally similar to dichloropyrimidines studied in [132] (it can be considered as tetrasubstituted pyrimidine), we decided to apply these

conditions for arylation of compound **3**. Initially, $Pd(OAc)_2/PPh_3/K_3PO_4$ was used as a catalyst system for cross-coupling reaction of compound **3** with phenylboronic acid (**4a**). However, the performed experiments showed that no product was formed neither using 1 eq. of **4a** at 70 °C nor 2 eq. of **4a** at reflux temperature of dioxane.



Scheme 2. *Reagents and conditions*: (i) $RC_6H_4B(OH)_2$, 2.5 mol% $Pd(PPh_3)_2Cl_2$, K_3PO_4, 1,4-dioxane, Ar.

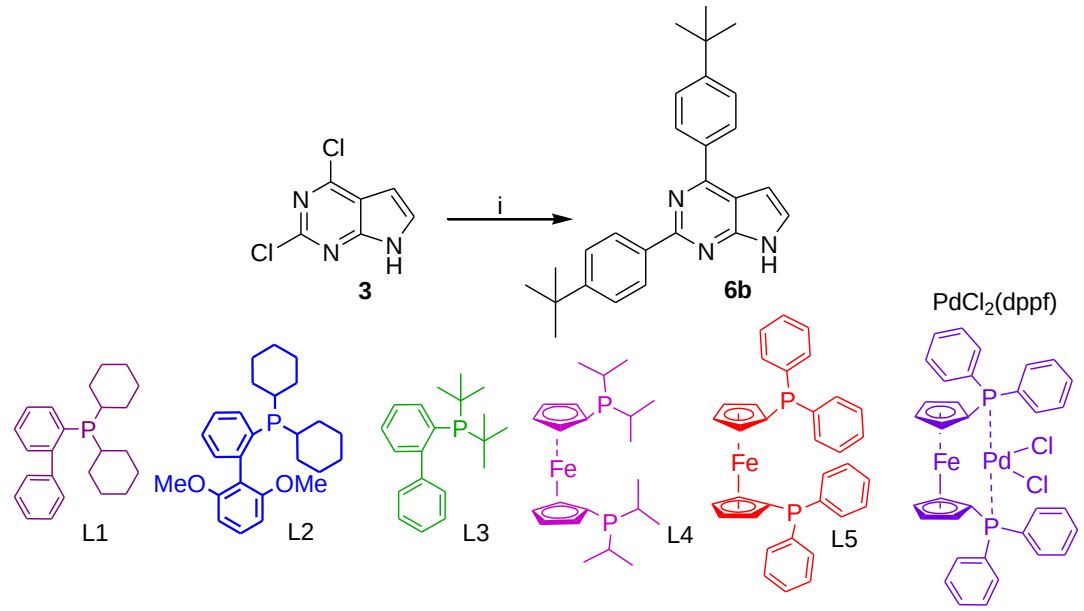
Employing $PdCl_2(PPh_3)_2/K_3PO_4$ in anhydrous dioxane as a catalyst system in the Suzuki reaction of pyrrolopyrimidine **3** with 2.16 eq. of phenylboronic acid (**4a**) resulted in the formation of mono-coupled product **5a** with 41% yield (Scheme 2, Table 1, entry 1). Similarly, the reaction with 2.16 eq. of 4-*tert*-butylphenylboronic acid (**4b)** and 4-biphenylboronic acid (**4c)** furnished compounds **5b** and **5c** in 57% and 12% yield, respectively (Table 1, entries 3, 5). Efforts to perform the Suzuki coupling under milder conditions (room temperature) and using less amount of boronic acid failed and only starting material **3** was recovered (Table 1, entries 4, 6). It was found that a large excess of phenylboronic acid (**4a**) has to be used to perform the double cross-coupling reaction of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine (**3**). Thus, 2,4-diphenylpyrrolo[2,3-*d*]pyrimidine (**6a**) was obtained when 8.32 eq. of phenylboronic acid (**4a**) were used in the reaction. The yield was only 24% (Table 1, entry 2).

Table 1. The Suzuki reaction results of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine (**3**) using $Pd(PPh_3)_2Cl_2$ as a catalyst.

Entry	$ArB(OH)_2$	Amount $ArB(OH)_2$, equiv.	Reaction temp.,°C/ Duration	Product (Yield,* %)
1	**4a**	2,16	Δ/2 h	**5a** (41)
2		8,32	Δ/6 h	**6a** (24)
3	**4b**	2,16	Δ/2 h	**5b** (57)
4		1,08	r.t./3 days	recovered **3**
5	**4c**	2,16	Δ/3 h	**5c** (12)
6		1,08	r.t./3 days	recovered **3**

* The yields are after isolation and purification by the column chromatography.

Taking into account, that $Pd(PPh_3)_2Cl_2$ enabled to synthesize the desired mono- and double cross-coupling products only with a great excess of corresponding boronic acid, we conducted further screen of common palladium catalysts and ligands using 4-*tert*-butylphenylboronic acid (**4b**) as the coupling partner of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine (**3**) in the Suzuki cross-coupling reaction.



Scheme 3. *Reagents and conditions*: (i) 2.4 eq. 4-*tert*-butylphenylboronic acid (**4b**), Pd(0), ligand, K_3PO_4, 1,4-dioxane, Δ.

The catalysts employed were $PdCl_2$(dppf) and $Pd(OAc)_2$. The ligands examined were PCy_2(2-biphenyl) (**L1**), PCy_2(2',6'-$(MeO)_2$-2-biphenyl) (**L2**), P(*t*-Bu)$_2$(2-biphenyl) (**L3**), dippf (**L4**) and dppf (**L5**) (Scheme 3).

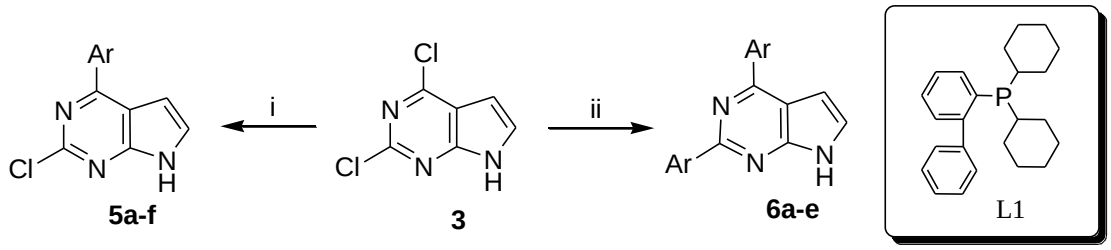
Table 2. Ligand influence on the Suzuki reaction of **3** with 4-*tert*-butylphenylboronic acid (**4b**).

Entry	Catalyst	Ligand	Reaction time	Yield, %
1	2 mol% $Pd(OAc)_2$	4 mol% **L1**	15 min	48
2	2 mol% $Pd(OAc)_2$	4 mol% **L2**	3 h	35
3	10 mol% $Pd(OAc)_2$	20 mol% **L2**	1 h	28
4	2 mol% $Pd(OAc)_2$	4 mol% **L3**	3 h	ND
5	2 mol% $Pd(OAc)_2$	2 mol% **L4**	8 h	ND
6	2 mol% $Pd(OAc)_2$	2 mol% **L5**	2 h	29
7	2 mol% $PdCl_2$(dppf)	-	4 h	28

Ratio boronic acid (2,4 eq.):K_3PO_4 = 1:2.

Performing the reaction of **3** with 2.4 equiv. of 4-*tert*-butylphenylboronic acid (**4b**) in the presence of $Pd(OAc)_2$/**L5**, $Pd(OAc)_2$/**L2** or $PdCl_2$(dppf) gave the double cross-coupling product **6b** only in 28-35% yield (Table 2, entries 2, 6, 7). It is worthy of note, that using 10 mol% of $Pd(OAc)_2$ and 20 mol% **L2** resulted in lower yield of compound **6b** (Table 2, compare entries 2 and 3). Exploitation of $Pd(OAc)_2$ with **L3** or **L4** as ligands in the reaction led to formation of a complex mixture of products (Table 2, entries 4, 5). Using $Pd(OAc)_2$/**L1**/K_3PO_4 as a catalyst system gave the double cross-coupling product **6b** in 48% yield (Table 2, entry 1). Performing the reaction of **3** with 1.2 equiv. of 4-*tert*-butylphenylboronic acid (**4b**) in the presence of $Pd(OAc)_2$/**L1**/K_3PO_4 as catalyst system at 60-70 °C allowed to obtain compound **5b** in 66% yield (Table 3, entry 3). Among the catalyst systems studied only $Pd(OAc)_2$/**L1**/K_3PO_4 resulted in the cleanest conversion and enabled to perform mono- and double cross-coupling reactions and, therefore, it was selected as the most suitable catalyst for further development.

As a result, mono cross-coupling reaction of **3** with arylboronic acids **4a-f** to give compounds **5a-f** was accomplished at 60-70 °C in 1,4-dioxane using 1.2 equivalent of the corresponding boronic acid and $Pd(OAc)_2$/L1/K_3PO_4 as a catalyst system. Performing reaction under reflux temperature of dioxane and using 2.4 eq. of boronic acid led to the formation of double cross-coupling products **6a-e**. The results are summarized in Scheme 4 and Table 3.



Scheme 4. *Reagents and conditions*: (i) 2 mol% $Pd(OAc)_2$, 4 mol% L1, 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% L1, 2.4 equiv. $ArB(OH)_2$, 4.8 equiv. K_3PO_4, 1,4-dioxane, Δ, Ar.

In almost all cases besides the target coupling products the side products including homo-coupling products of arylboronic acids were also formed. Lower yield of compound **6c** (Table 3, entry 6) was obtained, presumably because of more complex purification by column chromatography. However, formation of the corresponding 2-aryl-4-chloropyrrolo[2,3-*d*]pyrimidines was not observed.

Table 3. Preparation of compounds **5a-f** and **6a-e**.

Entry	$ArB(OH)_2$	Amount $ArB(OH)_2$, equiv.	Reaction temp.,°C/ Duration	Product (Yield,* %)
1	**4a**	1.2	60-70/4 h	**5a** (45)
2		2.4	Δ/4 h	**6a** (65)
3	**4b**	1.2	60-70/2 h	**5b** (66)
4		2.4	Δ/15 min	**6b** (48)

Table 3 *(continued)*

Entry	$ArB(OH)_2$	Amount $ArB(OH)_2$, equiv.	Reaction temp., °C/ Duration	Product (Yield,* %)
5	**4c**	1.2	60-70/2 h	**5c** (46)
6		2.4	Δ/2 h	**6c** (29)
7	**4d**	1.2	60-70/1.5 h	**5d** (68)
8		2.4	Δ/2.5 h	**6d** (49)
9	**4e**	1.2	Δ/2.5 h	**5e** (47)
10		2.4	Δ/3 h	**6e** (63)
11	**4f**	1.2	60-70/3.5 h	**5f** (51)

* The yields are after isolation and purification by the column chromatography.

Assignment of the structures **5a-f** was based on NOE ^{1}H NMR experiments. Increase of the signal intensities of 5-*H* and 2'-*H* protons located in the vicinity was observed to be 7-12% (Figure 2). This indicated that 4-chlorine group in the pyrrolopyrimidine **3** reacted first in the Suzuki reaction to yield the corresponding 4-aryl derivatives **5a-f**.

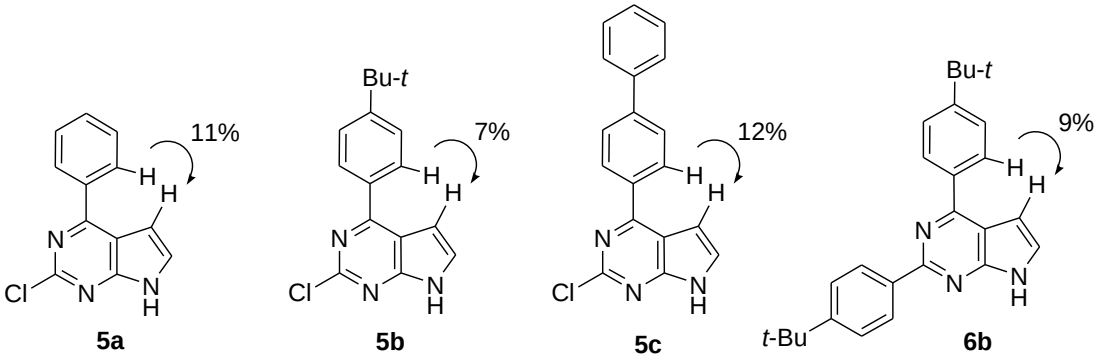
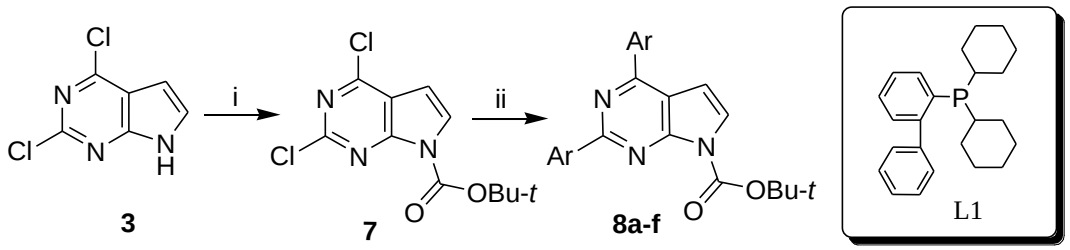


Figure 2. NOE ^{1}H NMR experiments.

Although the performed investigation of the Suzuki reaction of **3** with arylboronic acids enabled to synthesize arylpyrrolopyrimidines with sufficient site-selectivity, the yields of the target compounds **5** and **6** were low or moderate. We supposed that the reason can be an interaction of the pyrrole NH group in the anion form under the basic conditions with boronic acids or palladium catalyst similar to that observed for 4-amino-2-chloropyrimidine

[133]. For this reason, we examined, whether the protection of the N7-amino group could influence the outcome of the Suzuki reaction. Therefore, N7-protected pyrrolo[2,3-*d*]pyrimidine **7** was synthesized by the reaction of **3** with Boc_2O in the presence of DMAP and DIPEA in abs. dichloromethane (Scheme 5). Further the Suzuki cross-coupling reactions of compound **7** were investigated under the conditions previously described. It was found that using 2.4 equiv. of the corresponding boronic acid the double cross-coupling reaction gave compounds **8a-f** in good to excellent yields (Scheme 5, Table 4). However, 7-*tert*-butoxycarbonyl group increased the reactivity of 2-chlorine atom in **7** and all attempts to obtain 4-aryl-2-chloropyrrolo[2,3-*d*]pyrimidines failed. Formation of the diarylpyrrolopyrimidines **8a-f** was observed even when an equivalent amount of boronic acid was used in the reaction.



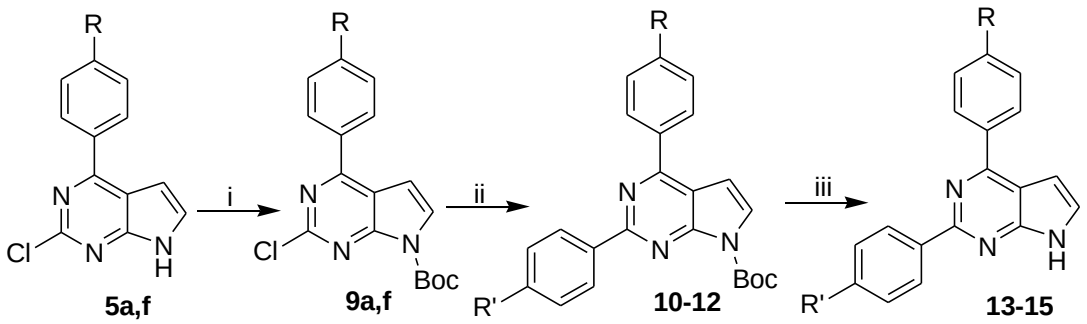
Scheme 5. *Reagents and conditions*: (i) Boc_2O, DMAP, DIPEA, CH_2Cl_2, Δ; (ii) 2 mol% $Pd(OAc)_2$, 4 mol% L1, 2.4 equiv. $ArB(OH)_2$, 4.8 equiv. K_3PO_4, 1,4-dioxane, Δ, Ar.

Table 4. Preparation of compounds **8a-f**.

Entry	$ArB(OH)_2$	Duration	Product (Yield,* %)
1	**4a**	3.5 h	**8a** (78)
2	**4b**	2 h	**8b** (76)
3	**4c**	2 h	**8c** (66)
4	**4d**	3 h	**8d** (42)
5	**4e**	4 h	**8e**** (86)
6	**4f**	1 h	**8f** (94)

*The yields are after isolation and purification by the column chromatography.
4.8 equiv. of 4-(9-carbazolyl)phenylboronic (4e**) acid and 9.6 equiv. K_3PO_4 were used in the reaction.

In order to obtain 2,4-diarylpyrrolopyrimidines with different aryl groups the second Suzuki coupling of 4-aryl-2-chloropyrrolo[2,3-*d*]pyrimidines (**5**) with arylboronic acids was investigated. Unfortunately, compounds **5** were found to be inert to the selected arylboronic acids.



Scheme 6. *Reagents and conditions*: (i) Boc_2O, DMAP, DIPEA, CH_2Cl_2, rt or Δ; (ii) 2 mol% $Pd(OAc)_2$, 4 mol% L1, 1.2 equiv. $R'C_6H_4B(OH)_2$, 2.4 equiv. K_3PO_4, 1,4-dioxane, Δ, Ar; (iii) HCl, Me_2CO, Δ or TFA, CH_2Cl_2, rt.

Otherwise, the Suzuki coupling of the *N*(7)-Boc derivatives **9a,f**, obtained by the reaction of **5a,f** with Boc_2O in the presence of DMAP and DIPEA, with the selected arylboronic acids furnished pyrrolopyrimidines **10-12** bearing different aryl groups in positions 2 and 4 of heterocyclic moiety in good yields (Scheme 6, Table 5). The second Suzuki coupling was accomplished by reflux of the reaction mixture in 1,4-dioxane for 4-7 hours in the presence of $Pd(OAc)_2$/L1/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 **13-15**. It should be mentioned, that remove of Boc group is much more efficient with TFA. For example, deprotection of *N*(7)-Boc group of compound **10** with hydrochloric acid in acetone furnished the desired product **13** only under reflux for 70 hours, whereas deprotection of compound **12** with TFA in dichloromethane was over already after 5 minutes of stirring at room temperature.

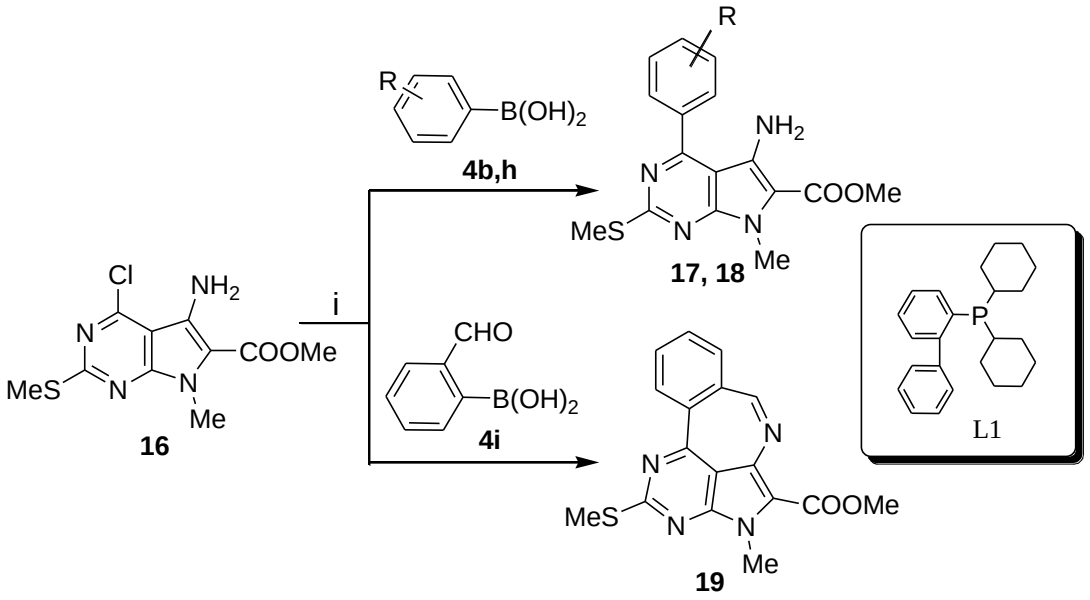
Table 5. Data of synthesis of compounds **10-15.**

Compound	R	R’	Yield,* %
10	H	4-Ph	76
11	H	4-EtO	79
12	4-MeO	4-EtO	69
13	H	4-Ph	73
14	H	4-EtO	80
15	4-MeO	4-EtO	77

* The yields are after isolation and purification by the column chromatography.

II.1.2. The Suzuki reaction of methyl 5-amino-2-methylthio-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine-6-carboxylate with arylboronic acids.

Taking into account the obtained results, it was of interest to examine whether the found catalyst system, $Pd(OAc)_2$/L1/K_3PO_4, works well in the reaction of densely substituted chloropyrrolo[2,3-*d*]pyrimidines. For this purpose, an easily obtainable methyl 5-amino-2-methylthio-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine-6-carboxylate (**16**) [134] bearing various reactive groups was chosen (Scheme 7). Employing the reaction conditions for the synthesis of 2,4-diarylpyrrolo[2,3-*d*]pyrimidines compound **16** was allowed to react with the selected arylboronic acids **4b,h,i**. Indeed, catalyst system - $Pd(OAc)_2$/L1/K_3PO_4 appeared to be suitable in the cross-coupling reaction of **16** with arylboronic acids and compounds **17, 18** were obtained in 80% and 64% yields, respectively.



Scheme 7. *Reagents and conditions*: (i) 2 mol% $Pd(OAc)_2$, 4 mol% L1, 1.3 equiv. $RC_6H_4B(OH)_2$, 2.6 equiv. K_3PO_4, 1,4-dioxane, Δ, Ar.

The reaction of **16** with 2-formylphenylboronic acid (**4i**) under the analogous conditions proceeded with the formation of a tetracyclic heterocycle - 1,3,4,6-tetraazadibenzo[*cd*,*f*]azulene, i.e. along with the Suzuki reaction of **16** with 2-formylphenylboronic acid (**4i**) the cyclocondensation reaction between formyl group of the boronic acid and 5-amino group of the pyrrolopyrimidine took place. Structure assignment of **19** was based on IR, ^1H, ^{13}C NMR spectral and elemental analysis data. For example, in the IR spectrum of compound **19** there were no absorption bands for the amino group, which is observed in the IR spectra of **16** and **17, 18** in a region 3269-3453 cm^{-1}. The IR spectrum of **19** contains only one CO absorption band at 1702 cm^{-1}. It is shifted to a region of higher wavenumbers for *ca*. 30 cm^{-1} in comparison with that of compounds **16-18** containing the primary amino group capable to form intramolecular hydrogen bonds with the adjacent ester group. In the ^1H NMR spectrum of **19** along with other proton signals a singlet due to resonance of the CH=N group proton at 8.14 ppm is observed. The ^{13}C NMR spectrum of **19** is also consistent with the proposed structure.

* * *

In summary, the performed investigation provides an easy access to novel pyrrolo[2,3-*d*]pyrimidine derivatives bearing various peripheral aromatic π-conjugated units. Catalyst system and reaction conditions for the synthesis of 4-aryl-2-chloro- and 2,4-diarylpyrrolo[2,3-*d*]pyrimidines bearing the same or different aryl assemblies in the molecule have been developed. The investigation of synthetic routes for the preparation of 2,4-diarylpyrrolo[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.

II.1.3. Photophysical properties of 2,4-diaryl-7*H*-pyrrolo[2,3-*d*]pyrimidines.

The synthesized pyrrolo[2,3-*d*]pyrimidine derivatives **6a-e** and **8a,b,d-f** were subjected to optical absorption and fluorescence studies[1]. The emission and absorption characteristics of compounds **6a-e** and **8a,b,d-f** together with the radiative rate constants (k_r), radiationless rate constants (k_{nr}), and emission lifetimes (τ) are collected in Table 6. Since the k_r and k_{nr} values are related to the corresponding emission quantum yields and lifetimes by $k_r=\Phi_F/\tau$ and $k_r + k_{nr}=\tau^{-1}$, it is possible to calculate the values of k_r and k_{nr} whenever quantum yield and lifetime data are available [18].

[1] All photophysical measurements were performed by prof. habil. dr. S. Juršėnas, dr. K. Kazlauskas, L. Skardžiūtė at Institute of Applied Research, Vilnius University.

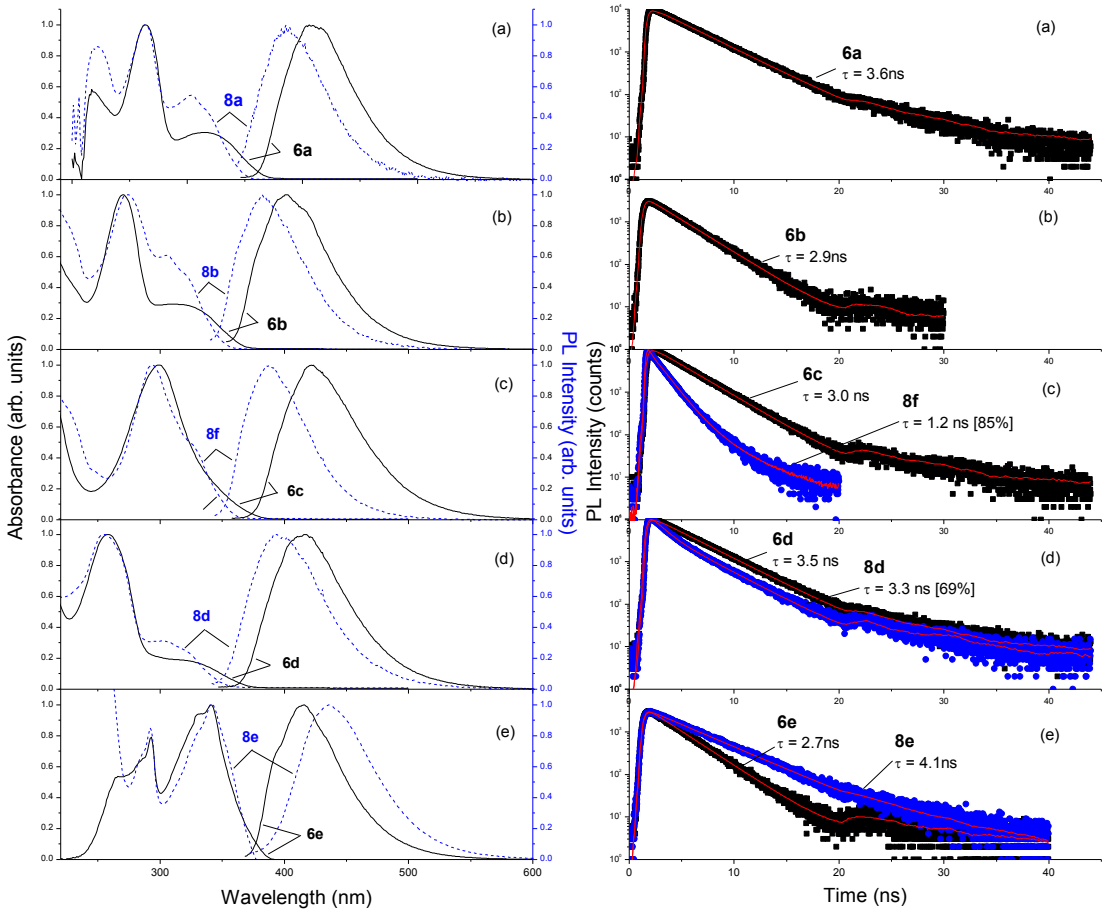


Figure 3. Normalized absorption, PL spectra and lifetimes of the compounds (a) **6a** and **8a**, (b) **6b** and **8b**, (c) **6c** and **8f**, (d) **6d** and **8d**, (e) **6e** and **8e** in 10^{-5} M THF solutions. Solid lines correspond to compounds **6a-e**, dashed lines - to compounds **8a,b,d-f**. *Lifetimes of compounds **8a** and **8b** were shorter than 0.1 ns.

All the compounds in diluted THF solution exhibit strong absorption with their absorption maxima positioned in the range of 255 - 342 nm and emission maxima located in the range of 382 - 436 nm (Figure 3). For the **6a-e** series of compounds the following spectral features can be highlighted. The shape and maxima of the absorption and fluorescence spectra of the compounds **6a,b,d** resemble those of pyrrolo[2,3-*d*]pyrimidine [43, 135]. Slight modifications of the spectra might be induced by the aryl substituents attached to the pyrimidine. Similar fluorescence efficiency (see Table 6, Φ_F: 42% for **6a,** Φ_F: 41% for **6b** and Φ_F: 43% for **6d**) estimated for the solutions of these compounds obviously indicates similar influence of radiation and radiationless processes and similar extension of π-conjugation governing the optical

transitions. The resemblance in the spectrum and quantum yield of the compound **6a** and **6d** possessing additional phenyl groups in the *meta*- position of the benzene ring attached to pyrrolopyrimidine core can be justified by the out-of-plane twisting of the phenyl end-groups of the compound **6d** resulting in broken π-conjugation. Such twisted molecular conformations are well-known and were also observed in 4,6-di(heteroaryl)pyrimidines [20]. As opposed to this, introduction of additional phenyl (**6c**) end-groups to the *para*- position of phenyl groups of pyrrolopyrimidine derivatives results in extended conjugation, and thus, in a red shift of the spectral bands (Figure 3).

Table 6. UV-VIS absorption and PL data for the series of compounds **6a-e** and **8a,b,d-f** in 10^{-5} M THF solution.

Compd.	λ_{abs}, nm	ε, l·mol^{-1}· cm^{-1}	λ_{em},* nm	Φ_f, %	Stokes shift, cm^{-1}	τ, ns	$k_r \cdot 10^9$, s^{-1}	$k_{nr} \cdot 10^9$, s^{-1}
6a	264 318	39969 12185	403 419	42	6633	3.6	0.12	0.16
6b	270 321	42810 11721	401 419	41	6215	2.9	0.14	0.20
6c	299	74472	421	53	9692	3.0	0.18	0.16
6d	258 325	68076 12302	415	43	6673	3.5	0.13	0.16
6e	265 282 293 331 341	19693 22984 29529 35003 37219	415	50	5229	2.7	0.18	0.18
8a	263 303	36692 20357	386	3.6	7097	<0.1	-	-
8b	274 307 325	38480 23346 17005	382	5.7	6395	<0.1	-	-
8d	256 305	63463 19802	391	13	7211	3.3	0.04	0.26
8e	255 293 342	44475 24940 29822	436	67	6304	4.1	0.16	0.08
8f	294 327	50131 23801	387	15	8174	1.2	0.13	0.71

*fluorescence was excited at 330 nm

The extension of the conjugation length in the compound **6c** also manifests in dramatically increased absorbance of the lowest-energy optical transitions as well as in enhanced fluorescence quantum yield (up to 53%, see Table 6). Attachment of carbazolyl end-groups (**6e**) to the *para*-position of phenyl groups of pyrrolopyrimidine derivatives also results in an enhancement of quantum yield up to 50%. This enhancement of fluorescence efficiency is mainly dealt with the increase of radiation processes of **6c**, **6e** (k_r = 0.18 for both compounds, Table 6), while radiationless constant for these compounds remains the same as for compound **6a** (k_{nr} = 0.16 for **6a** and **6c** or increases slightly: k_{nr} = 0.18 for **6e**). The fluorescence lifetimes estimated for the pyrrolopyrimidine series **6a-e** span the range from 2.7 to 3.6 ns, which is typical for fluorescent organic molecules featuring significant radiative relaxation probability. Interestingly, the maxima of the absorption spectrum of the compound **6e** possessing carbazolyl end-groups are in close correspondence to those of the ethylcarbazole [136].

Attachment of additional electron-withdrawing Boc group to the pyrrole ring of pyrrolo[2,3-*d*]pyrimidine core (series **8a,b,d-f**) invokes the following spectral changes. Almost 2-fold increase in absorbance (from 12000 $l \cdot mol^{-1} \cdot cm^{-1}$ to 20000 $l \cdot mol^{-1} \cdot cm^{-1}$) and a blue shift by ~20 nm of the lowest absorption bands for compounds **8a,b,d** as compared to **6a,b,d** compounds is observed. The changes in absorption are accompanied by the similar blue shift of fluorescence spectra and remarkable drop in fluorescence quantum yield. In the limiting case of compound **8a**, reduction of quantum yield amounts to one order of magnitude, i.e. from 42% to 3.6%. The reduction is not so significant (only 3.5 times) for compounds possessing more bulky end-groups, like methoxy (**8f**) and phenyl (**8d**). It is likely that bulky end-groups inhibit twisting of intermediate phenyl groups, thus enhancing probability of radiative decay from an excited state. Fluorescence decay time measurements support the later consideration indicating short decay times (<0.1 ns) for compounds **8a,b** and prolonged decay times (1.2 – 3.3 ns) for compounds **8d,f**. General influence of Boc group that is the blue shift of absorption and fluorescence spectra, the

reduction of fluorescence quantum yields and decay times observed for compounds **8a,b,d,f** strongly contrasts with the influence observed for compound **8e**. The attachment of electron-withdrawing Boc group to **6e** results in a red shift of the fluorescence spectrum from 415 to 436 nm, an enhancement of the quantum yield from 50% to 67% and an increase of the decay time from 2.7 to 4.1 ns [see Table 6 and Figure 3(e)]. Interestingly, this increase of fluorescence quantum yield is caused not by increase of radiation processes, but by more than two-fold decrease of radiationless processes of compound **8e** (k_r = 0.18 for **6e** and 0.16 for **8e**; k_{nr} = 0.18 for **6e** and 0.08 for **8e**, Table 6). This exceptional behavior induced by the presence of polar Boc group might be also explained by a forced planarization of the intermediate phenyl groups, which increases extent of π-conjugation in the excited state. A close similarity of the absorption spectra of compounds **6e** and **8e**, and also similarity of the lowest absorption bands of the spectra with those of ethylcarbazole [136] evidences orthogonal-like orientation of the intermediate phenyl rings of the derivatives in the ground state, and thus, poor conjugation between carbazolyl end-groups with the rest fragments. However, in the excited state charge redistribution induced by the presence of the polar Boc group in compound **8e** results in more planar conformation of the molecule than in the case of compound **6e**, which does not contain this group.

In addition, influence of solvent (chloroform, tetrahydrofuran and dimethyl sulfoxide) on the fluorescence characteristics of compounds **6a,e** and **8a,e** was investigated. The results are presented in Table 7 and Figure 4.

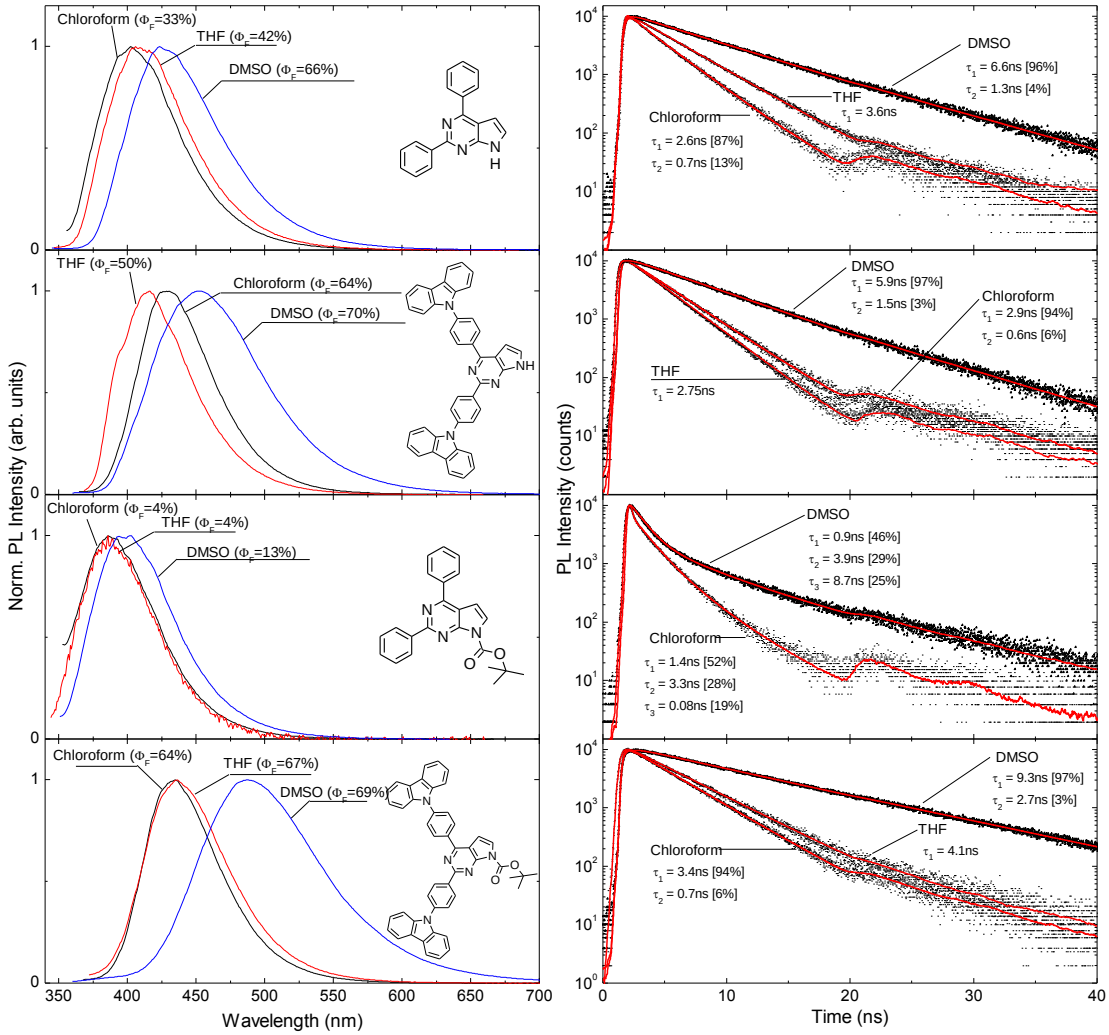


Figure 4. The PL spectra and characteristics of compounds **6a,e** and **8a,e** in — $CHCl_3$, — THF, — DMSO.

From these data we can conclude that emission maxima of all compounds are almost the same in THF and $CHCl_3$ (exception is compound **6e**, the difference between emission bands in THF and $CHCl_3$ is 12 nm). These solvents do not differ very much in polarity. The situation changes dramatically with significant increase of the solvent polarity (DMSO): emission maxima of all compounds are significantly red shifted up to 50 nm (compound **8e**, Table 7, compare entries 10 and 12). Moreover, emission quantum yields and decay times in DMSO are in general higher than those in other solvents. In that respect the most significant effect of DMSO was observed for compounds **6a,e** and **8a** (Table 7, entries 1→3, 4→6 and 7→9). For example, emission quantum yield of compound **6a** changes from 33% in

$CHCl_3$ to 66% in DMSO and decay time from 2.6 ns in $CHCl_3$ to 6.6 ns in DMSO. Interestingly, increase of fluorescence quantum yield of compounds **6a,e** is caused not by increase of radiation processes, but by more than four-fold decrease of radiationless processes of compounds **6a,e** (compare k_r and k_{nr} of compounds **6a,e** in DMSO and in THF or $CHCl_3$, Table 7, entries 1, 3 and 5, 6). As for compound **8e**, increase of solvent polarity resulted in decreasing radiation processes, but radiationless processes were decreasing even faster resulting in higher fluorescence quantum yield in DMSO, than in $CHCl_3$ (k_r decreased from 0.19 in $CHCl_3$ to 0.07 in DMSO, Φ_F increased from 64% to 69%, Table 7, entries 10→12).

Table 7. PL data for compounds **6a,e** and **8a,e** in $CHCl_3$, THF and DMSO.

Entry	Compound	Solvent*	λ_{em}, nm	Φ_F, %	τ, ns	$k_r \cdot 10^9$, s^{-1}	$k_{nr} \cdot 10^9$, s^{-1}
1		$CHCl_3$	402	33	2.6	0.13	0.26
2	**6a**	THF	406	42	3.6	0.12	0.16
3		DMSO	423	66	6.6	0.1	0.05
4		$CHCl_3$	428	64	2.9	0.22	0.12
5	**6e**	THF	416	50	2.7	0.19	0.19
6		DMSO	451	70	5.9	0.12	0.05
7		$CHCl_3$	386	4	1.4	0.03	0.69
8	**8a**	THF	386	3.6	<0.1	-	-
9		DMSO	401	13	0.9	0.14	0.97
10		$CHCl_3$	435	64	3.4	0.19	0.11
11	**8e**	THF	436	67	4.1	0.16	0.08
12		DMSO	486	69	9.3	0.07	0.03

*Dipole moments of solvents: $CHCl_3$ – 1.04 D, THF – 1.75 D, DMSO – 3.96 D.

One of the reasons can be different interaction of ground and excited states of **6a,e** with DMSO *via* hydrogen bonds between hydrogen at *N*(7) of pyrrolo[2,3-*d*]pyrimidine and oxygen of DMSO. Such a presumption is supported by an insignificant influence of solvent onto the fluorescence

characteristics of **8e.** Compound **8e** has no protons capable to form hydrogen bonds and, presumably, is less polar in a series due to electron-donating character of carbazolyl groups. Thus, the performed investigation indicates that depending on the nature of aryl branches attached to the pyrrolo[2,3-*d*]pyrimidine and substituent at *N*(7)-position of the heterocycle compounds can show more or less expressed solvatofluorochromism.

Fluorescence studies of the compounds **6a-e** and **8a,b,d-f** in THF solution led to an assumption that a reason of fluorescence efficiency of the compounds studied could be dealt with twisting of the phenyl rotors and that this phenomena can be influenced by the Boc group at the position 7 of pyrrolo[2,3-*d*]pyrimidine. Taking this into account, we decided to investigate solid state fluorescence of several selected compounds to find out how their optical properties would change in the rigid matrix. For this purpose, compounds **6a, 8a**, which showed significant fluorescence quenching with Boc group incorporation, and compounds **6e, 8e**, which, on the contrary, showed enhanced fluorescence, have been chosen. Solid state fluorescence of compounds **6a,e** and **8a,e** was measured at four different concentrations in polystyrene (PS) matrix. The details of their photophysical properties are summarized in Table 8.

Table 8. Fluorescence data for compounds **6a,e** and **8a,e** in a polystyrene matrix.

Entry	Compound	Concentration (%)	λ_{em}, nm	Φ_F (%)	τ, ns
1	**6a**	0.25	392	7	5.3
2		1	392	11	3.8
3		4	395	10	3.8
4		16	421	6	3.1
5	**6e**	0.25	406	34	2.3
6		1	408	42	2.2
7		4	416	28	1.9
8		16	419	18	1.0

Table 8 *(continued)*

Entry	Compound	Concentration (%)	λ_{em}, nm	Φ_F (%)	τ, ns
9	**8a**	0.25	372	<1	5.8
10		1	376	<1	5.6
11		4	410	<1	-
12		16	392	<1	5.2
13	**8e**	0.25	403	25	1.7
14		1	404	35	2.2
15		4	410	31	2.4
16		16	419	24	3.1

As seen from the table, emission maximum of each compound shifts to the longer wavelengths with increase of concentration. The most significant shifts showed compounds **6a** (29 nm) and **8a** (20 nm). In general, emission maximum of all compounds at the highest concentrations is shifted bathochromically compared to those in the solution. It is worthy of note, that the highest quantum yields were observed at 1% concentration almost for all compounds. Only compound **8a** showed less than 1% quantum yield at all concentrations (Table 8, entries 9-12). However, emission quantum yields in solid state are much lower than those in solution (especially for compounds **6a** and **8e**). The reduction of fluorescence efficiency in the solid state is common for majority of fluorophores and is, probably, dealt with an excitation migration-related quenching in the solid state. Fluorescence decay times of compounds **6a,e** and **8a** in solid state decreased with increasing of their concentration in PS. As opposed to this, decay time of compound **8e** increases from 1.7 ns at the lowest concentration to the 3.1 ns at the highest (Table 8, entries 13→16).

* * *

In summary, the synthesized pyrrolo[2,3-*d*]pyrimidines with various peripheral chromophoric aromatic units in positions 2 and 4 of the heterocycle were found to exhibit blue-UV fluorescence ranging from 380 to 440 nm with

emission quantum yields in the range of 41 – 53% in THF solutions. Introduction of highly polar Boc group was found to have a dramatic impact on the fluorescence properties of the pyrrolopyrimidine derivatives. For **8a,b,d,f** derivatives, where pyrrolo[2,3-*d*]pyrimidine core acts as a fluorophore, intramolecular charge transfer results in a significant quenching of fluorescence (down to 3.6%), whereas for **8e** derivative, where carbazolyl moiety is invoked in formation of the lowest excited states, intramolecular charge transfer facilitates a significant increase in emission quantum yield up to 67%. Investigation of emission behavior of selected 2,4-diarylpyrrolo[2,3-*d*]pyrimidines in different solvents revealed that the studied compounds exhibit strong positive solvatofluorochromic effect. In solid state (polystyrene matrix) fluorescence efficiency of studied compounds was reduced.

II.2. Synthesis and Properties of 2,4,7-Triaryl-7*H*-pyrrolo[2,3-*d*]pyrimidines.

II.2.1. Synthesis of 2,4,7-triaryl-7*H*-pyrrolo[2,3-*d*]pyrimidines.

π-conjugated small molecules have attracted much attention in the area of organic chemistry and materials science. They have some very interesting electronic and optical properties and have been investigated as advanced molecular electronic materials [10-13]. The advantages of oligomers are that their physical properties can be easily tuned to the desired properties by changing the structure e.g. solubilizing chains, end-capping groups, insertion of certain groups, and different oligomer lengths.

Above mentioned fluorescence studies of 2,4-diarylpyrrolo[2,3-*d*]pyrimidines showed the necessity of further seeking of more efficient compounds. Molecules with expanded π-system could have better optoelectronic properties than already synthesized pyrrolo[2,3-*d*]pyrimidines. Therefore, we decided to expand conjugated π-system by introducing aromatic moieties into the pyrrole scaffold through *N*-arylation reaction. Introduction of different aryl functionalities at various positions of pyrrolo[2,3-*d*]pyrimidine is

also important for tuning of structure and photophysical properties of the pyrrolo[2,3-*d*]pyrimidine derivatives.

Copper-promoted *N*-arylation of aromatic amines, originally diarylamines, has been known for a century as the classical Ullmann reaction [137]. The reaction requires harsh prolonged heating at 200 °C or higher, in the presence of simple Cu(I) or Cu(II) salts or oxides, or Cu bronze, *etc.*, in the presence of base in polar high-boiling solvents. In spite of modest yields and severe limitations imposed on both amine and aryl halide reagents, this reaction has until recently been regarded as the only available approach to triarylamines, compounds with rich and versatile practical potential. The discovery of Pd-catalyzed amination (the Buchwald–Hartwig reaction) has been a major breakthrough in the chemistry of amines, opening access to huge numbers of previously inaccessible compounds. A new interest in much cheaper and more practical copper-catalyzed chemistry has been brought about by the observations that appropriate ligands can modulate the reactivity of catalyst, and thus enable us to achieve more effective and more versatile catalytic systems [138, 139]. Unlike the classical Ullmann method, the reactions with copper complexes are best performed in non-polar solvents, such as toluene or dioxane, at reflux or lower temperatures, using (mono-) or bidentate ligands, including aliphatic diamines, 1,10-phenanthroline and its derivatives, 2,2'-bipyridine, 8-hydroxyquinoline, bidentate phosphines and *etc*. A number of effective protocols have been put forward for the arylation of aromatic amines or heterocycles by ligand-assisted methods [140-147].

Taking into account the mentioned arguments, the obtained compounds **6a**,**e** and **13-15** were subjected to *N*-arylation reaction using a set of six phenyl iodides and bromides **20a-f** (Figure 5, Scheme 8).

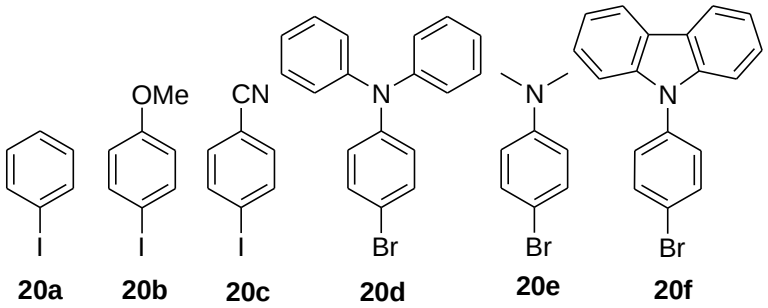
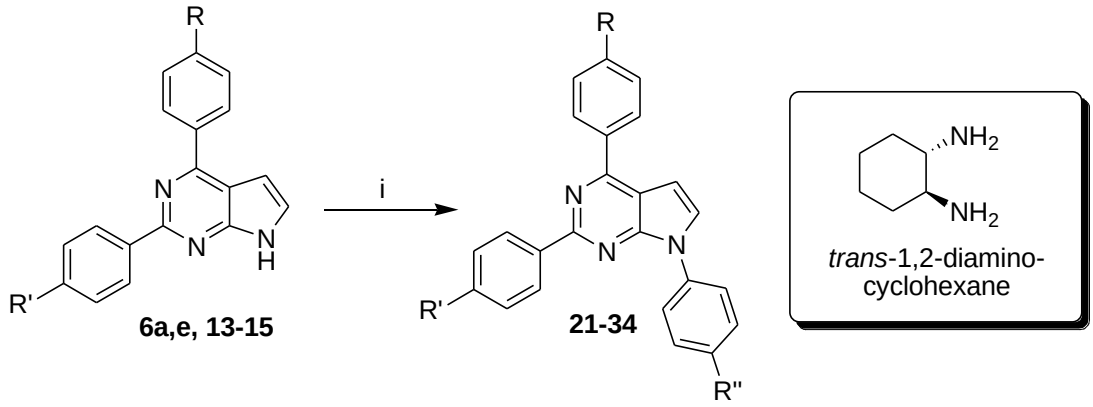


Figure 5. Aryl iodides and bromides used for *N*-arylation reaction.

Compounds **6a,e** as starting materials for the *N*-arylation reaction were chosen because of their interesting fluorescence properties. Moreover, compound **6a** could serve as a standard for the evaluation of influence of *N*-aryl moieties on fluorescence properties of the synthesized 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines. Compounds **13-15** were interesting because of the possibility to obtain pyrrolopyrimidines with three different aryl branches.



Scheme 8. *Reagents and conditions:* (i) 4-R"C_6H_4-I(Br), CuI, *trans*-1,2-diaminocyclohexane, K_3PO_4, 1,4-dioxane, Δ, Ar.

CuI/*trans*-1,2-diaminocyclohexane/K_3PO_4 was used as a catalyst system of choice [140]. Employing other ligands and bases in the reaction gave worse results. For example, the reaction of **6e** with iodobenzene **20a** using CuI/*trans*-1,2-diaminocyclohexane/K_3PO_4 as a catalyst system furnished **25** in 85% yield (Table 9, entry 5), while using in the reaction CuI/1,10-phenanthroline/Cs_2CO_3 as a catalyst system gave the target compound **25** in 49% yield (experimental,

method B). Even worse situation was observed, when CuI/1,10-phenanthroline/Cs_2CO_3 was used for the synthesis of compound **27**, after 11 hours of stirring under reflux only traces of the target compound were obtained. So, in further reactions only CuI/*trans*-1,2-diaminocyclohexane/K_3PO_4 was used as a catalyst system. To achieve full conversion of compounds **6a**,**e** and **13-15** in the *N*-arylation reaction an amount of CuI ranging from 3 mol% to 15 mol% was used (Table 9). 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 (**21-34**) varied from good to excellent (Table 9). Lower yields of compounds **26-28** (Table 9, entries 6-8) were obtained, presumably because of more complex their purification by column chromatography.

Table 9. Preparation of 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines (**21-34**).

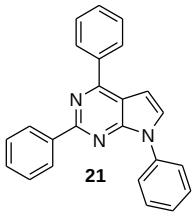
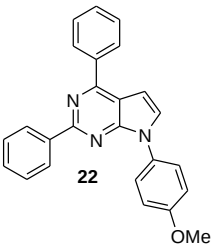
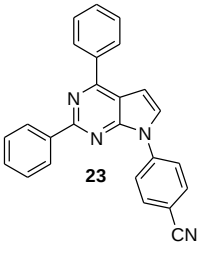
Entry	Comp. **6a,e** or **13-15**	ArX **20a-f**	CuI, mol%	Reac. time, hr.	Product **21-34**	Yield,* %
1	**6a**	**20a**	4	13	 **21**	94
2	**6a**	**20b**	5	12	 **22**	92
3	**6a**	**20c**	5	12	 **23**	82

Table 9 *(continued)*

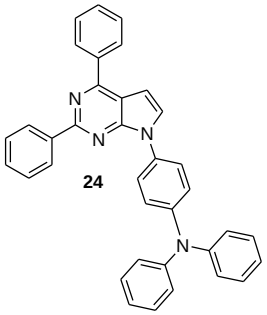
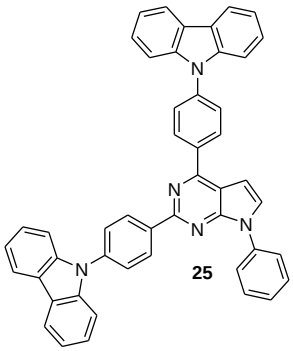
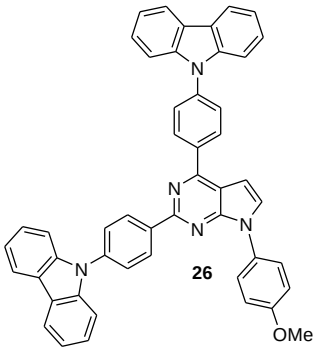
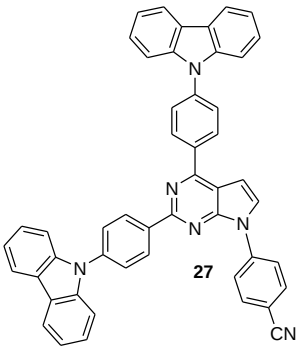
Entry	Comp. **6a,e** or **13-15**	ArX **20a-f**	CuI, mol%	Reac. time, hr.	Product **21-34**	Yield,* %
4	**6a**	**20d**	6	22	 **24**	72
5	**6e**	**20a**	5	10	 **25**	85
6	**6e**	**20b**	7	19	 **26**	51
7	**6e**	**20c**	7	22	 **27**	57

Table 9 *(continued)*

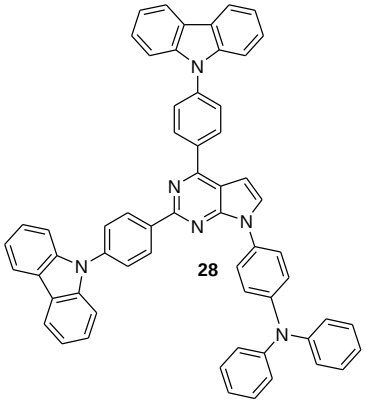
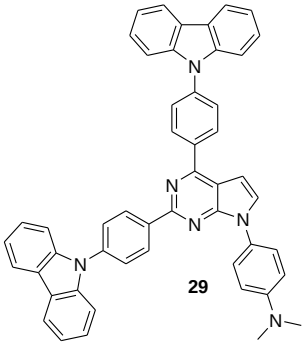
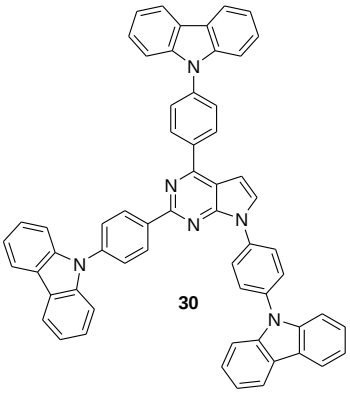
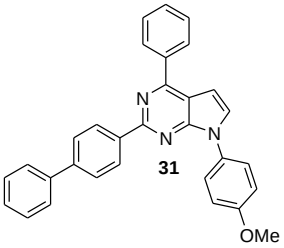
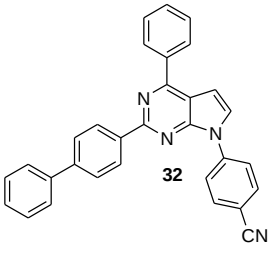
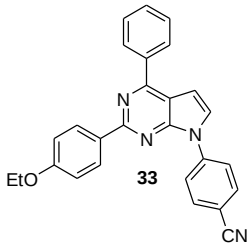
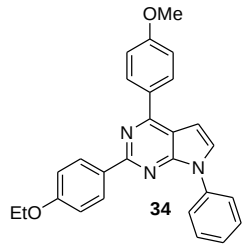
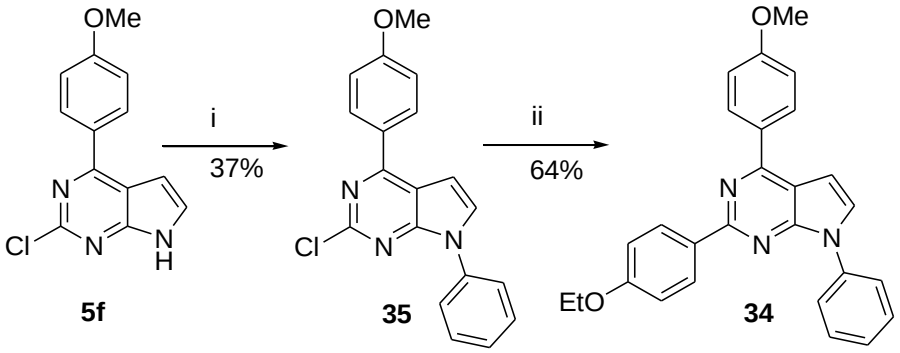
Entry	Comp. **6a,e** or **13-15**	ArX **20a-f**	CuI, mol%	Reac. time, hr.	Product **21-34**	Yield,* %
8	**6e**	**20d**	8	29	 **28**	59
9	**6e**	**20e**	14	32	 **29**	65
10	**6e**	**20f**	15	35	 **30**	59
11	**13**	**20b**	5	11	 **31**	93
12	**13**	**20c**	10	25	 **32**	95

Table 9 *(continued)*

Entry	Comp. **6a,e** or **13-15**	ArX **20a-f**	CuI, mol%	Reac. time, hr.	Product **21-34**	Yield,* %
13	**14**	**20c**	3	6	 **33**	90
14	**15**	**20a**	5	9.5	 **34**	99

* The yields are after isolation and purification by the 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-triarylpyrrolopyrimidines by an alternate and shorter route. This is exemplified by the synthesis of compound **34** by *N*-arylation of **5f** with iodobenzene **20a** and following Suzuki coupling of the obtained **35** with boronic acid **4g** (experimental, method B) (Scheme 9). Total conversion of **5f** in its *N*-arylation reaction with iodobenzene to give **35** was achieved after 33 hours and using 12 mol% CuI and 30 mol% *trans*-diaminocyclohexane. However, a complex mixture of products was formed in the reaction and compound **35** was isolated only in 37% yield.



Scheme 9. *Reagents and conditions*: (i) **20a**, CuI, *trans*-1,2-diaminocyclohexane, K_3PO_4, 1,4-dioxane, Δ, Ar; (ii) 2 mol% $Pd(OAc)_2$, 4 mol% L1, 1.5 equiv. **4g**, 3.0 equiv. K_3PO_4, 1,4-dioxane, Δ, Ar.

The Suzuki coupling of **35** with 4-ethoxyphenylboronic acid (**4g**) gave the desired **34** in 64% yield. It is worthy of note, that the latter reaction appeared to be much slower (20 hrs.) than that of *N*(7)-Boc derivative **9f** with the same boronic acid (6 hrs.). This supports our observation in the synthesis of **8a-f** that Boc group increases the reactivity of the chlorine atom in the position 2 of pyrrolopyrimidine. Yield of compound **34** (24%) calculated for two reactions (Scheme 9) was considerably lower than the yield of its synthesis using four reaction sequence (42%) including the *N*(7)-protection and deprotection reactions (Schemes 6, 8).

* * *

In summary, 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 was developed. The investigation of alternate synthetic routes for the preparation of 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines bearing different aryl branches revealed that more efficient way for their synthesis is, primarily the synthesis of 2,4-diarylpyrrolo[2,3-*d*]pyrimidines with different aryl groups and following arylation of *N*(7)-position of the heterocycle. *N*-arylation reaction was found to proceed well with aryl iodides and aryl bromides to give 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines in good to excellent yields in the presence of CuI/*trans*-1,2-diaminocyclohexane/K_3PO_4 as a catalyst system.

II.2.2. Photophysical properties of 2,4,7-triaryl-7*H*-pyrrolo[2,3-*d*]pyrimidines.

The synthesized 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines (**21-34**) were subjected to optical absorption and fluorescence studies. The results of these investigations are summarized in Table 10 and depicted in Figure 6.

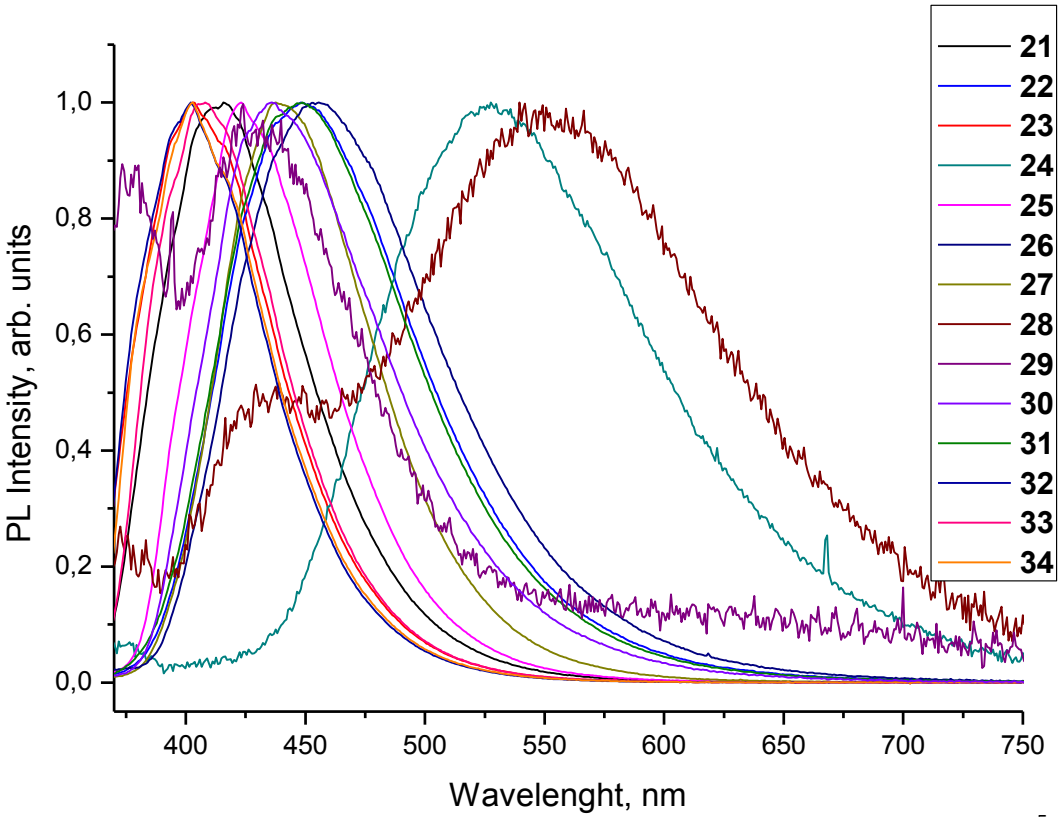


Figure 6. PL spectra of 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines (**21-34**) in 10^{-5} M THF.

Table 10. UV-VIS absorption and PL data for the series of compounds **21-34** in 10^{-5} M THF solution.

Entry	Comp.	λ_{abs}, nm	ε, $l \cdot mol^{-1} \cdot cm^{-1}$	λ_{em},* nm	Stokes shift, cm^{-1}	Φ_F, %	τ, ns	$k_r \cdot 10^9$, s^{-1}	$k_{nr} \cdot 10^9$, s^{-1}
1	**21**	256 327	42432 10759	416	6543	30	4.6	0.06	0.15
2	**22**	210 259 341	116315 100284 20855	448	7004	21	12.2	0.02	0.07

Table 10 *(continued)*

Entry	Comp.	λ_{abs}, nm	ε, $l \cdot mol^{-1} \cdot cm^{-1}$	λ_{em},* nm	Stokes shift, cm^{-1}	Φ_F, %	τ, ns	$k_r \cdot 10^9$, s^{-1}	$k_{nr} \cdot 10^9$, s^{-1}
3	**23**	210 265 292 326	51091 54001 26948 15588	403	5861	23	2.6	0.09	0.30
4	**24**	210 267 308	80942 41473 39999	528	13527	4	6.5	0.01	0.15
5	**25**	210 236 254 281 292 342	83354 95604 73364 40217 40074 40627	423	5600	36	3.7	0.10	0.17
6	**26**	210 237 255 292 342	80911 97694 71874 44901 41076	456	7310	20	10.4	0.02	0.08
7	**27**	210 236 256 284 291 342	121627 99333 76639 54569 53153 41433	438	6409	40	3.9	0.10	0.16
8	**28**	237 255 293 341	115282 75367 62155 63694	539	10772	2	3.8	0.01	0.26
9	**29**	239 257 293 342	48484 38535 26738 23614	373 424	5656	<1	-	-	-

Table 10 *(continued)*

Entry	Comp.	λ_{abs}, nm	ε, $l \cdot mol^{-1} \cdot cm^{-1}$	λ_{em},* nm	Stokes shift, cm^{-1}	Φ_F, %	τ, ns	$k_r \cdot 10^9$, s^{-1}	$k_{nr} \cdot 10^9$, s^{-1}
10	**30**	245 282 292 341	53446 26794 33339 21447	436	6389	35	8.85	0.04	0.07
11	**31**	242 260 297 344	13928 17523 20932 7897	449	6798	30	10.59	0.03	0.07
12	**32**	280 332	28639 13226	402	5244	34	2.33	0.15	0.29
13	**33**	235 275 324	10753 27097 9602	408	6354	23	2.14	0.11	0.36
14	**34**	291 330	20441 7079	403	5489	31	2.39	0.13	0.29

*fluorescence was excited at 340 nm

2,4,7-Triarylpyrrolo[2,3-*d*]pyrimidines (**21-30**) were found to exhibit strong absorption in dilute THF solution with their absorption maxima positioned in the range 210 - 344 nm. The absorption maxima of compounds **21-23** at the longest wavelengths show bathochromic shifts at about 10-20 nm with respect to their precursor **6a** (318 nm). In contrast, absorption maximum of compound **24** is blue shifted at about 10 nm as compared to that of **6a**. As for compounds **25-28**, they show additional absorption bands at 210 and 236-237 nm and no absorption band at 331 nm as compared to that of **6e**. Moreover, compounds **22**, **27**, **28** show strong absorbance up to 122000 $l \cdot mol^{-1} \cdot cm^{-1}$ (compound **27**, Table 10, entry 7).

Depending on the origin of aryl branches emission maxima of compounds **21-30** are located in the range 402 - 539 nm with fluorescence quantum yields ranging from 1% to 40%. Emission maxima of compounds **21** and **23** are blue shifted comparing with their precursor **6a** emission maxima (419 nm). Rest of the compounds (**22**, **24**, **25-30**) have emission maxima

positioned in the longer wavelengths with respect to emission maxima of their precursors **6a**,**e**. It could be noticed, that introduction of electron-donating groups to the pyrrole scaffold led to the bathochromic shift of emission maxima and major Stokes shift (Table 10, compare entries 1 and 2 or 5 and 6). The largest Stokes shift was observed for compounds **24** and **28** bearing 4-diphenylaminophenyl group at the position 7 of the pyrrolo[2,3-*d*]pyrimidine. The values for **24** and **28** are 13527 cm^{-1} and 10772 cm^{-1}, respectively (Table 10, entries 4, 8). All 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines showed lower quantum yields (20-40%) with respect to their precursors **6a,e** (42% and 50%, respectively). This, mainly, is caused by decrease of radiation processes when compared with the corresponding precursors. For example, the value $k_r = 0.06$ (Table 10, entry 1) for compound **21** is two times lower than $k_r = 0.12$ for **6a** (Table 6, entry 1), whereas the k_{nr} value for both compounds remains almost the same (**21**: $k_{nr} = 0.15$; **6a**: $k_{nr} = 0.16$). Generally, for all compounds of 7-aryl-2,4-diphenyl- (**21**-**24**) and 2,4-di[4-(9*H*-carbazol-9-yl)phenyl]pyrrolo[2,3-*d*]pyrimidine (**25**-**30**) series radiation processes are reduced comparing with corresponding data for 7-unsubstituted precursors (compare data in Tables 10 and 6).

A strong fluorescence quenching was observed for compounds **24**, **28**, **29** bearing diphenylamino or dimethylamino groups in the 4^{th} position of *N*(7)-phenyl group. The fluorescence quantum yields in THF solutions of **24**, **28**, **29** were found to be 4%, 2% and <1%, respectively (Table 10, entries 4, 8, 9). For compounds **24** and **28** the drop of fluorescence efficiency is reflected by a significant decrease of radiation processes and increase of radiationless processes (**24**: $k_r = 0.01$, $k_{nr} = 0.15$; **28**: $k_r = 0.01$, $k_{nr} = 0.26$) (Table 10, entries 4, 8). This could be caused at least by two reasons. First of all, introduction of bulky NPh_2 group (compounds **24**, **28**) puts on more rotors twisting of which quenches the fluorescence. Another reason can be attributed to the electron-donating character of NPh_2 and NMe_2 groups. The significance of number of rotors on fluorescence efficiency can be concluded comparing Φ_F of compounds **28** and **30**. Fluorescence quantum yield of compound **30** is more

than 17 times higher than that of compound **28** (Table 10, entries 8, 10). Structures of **28** and **30** are quite similar. In compound **30** phenyl groups in diphenylamino fragment (see structure **28**) are connected by C-C bond to the rigid carbazole ring. This rigidity in structure causes essential improvement of fluorescence efficiency. On the other hand, compound **29** with NMe_2 group showed even worse result, than compound **28** with more bulky NPh_2 group. Such a result is consistent with more expressed electron-donating character of NMe_2 group.

So, it seemed interesting to ascertain the influence of the electronic effect of dimethylamino group on the fluorescence characteristics of compound **29**. For this purpose, it was decided to protonate amino group of compound **29** using CF_3COOH and investigate its fluorescence properties. Data presented in Figure 7 indicate that protonation of **29** enhances the fluorescence more than 10 times (Φ_F of protonated **29** is 12%). However, performing the analogous experiment with compound **28** gave quite different result. Fluorescence quantum yield of the protonated form of compound **28** was even lower (1.5%) than that of compound **28** in THF solution (2%). The emission maximum of protonated **28** is strongly shifted to blue region of spectrum and was observed at 410 nm (neutral form emitted light at 539 nm, Table 10, entry 8). Such a difference in emission of protonated forms of compounds **28** and **29** can be a result of different structure of protonated forms. Most probably, the protonation of **28** occurs not on the nitrogen of NPh_2 group, as it happens in case of NMe_2 group, but on one of the nitrogens of pyrimidine ring of the pyrrolo[2,3-*d*]pyrimidine heterocycle. Protonation of compound **29** on NMe_2 group was proved by ^1H NMR and ^{13}C NMR spectra. After protonation NMe_2 group proton signal was shifted to weaker fields by approx. 0.5 ppm and carbon signal by approx. 7 ppm.

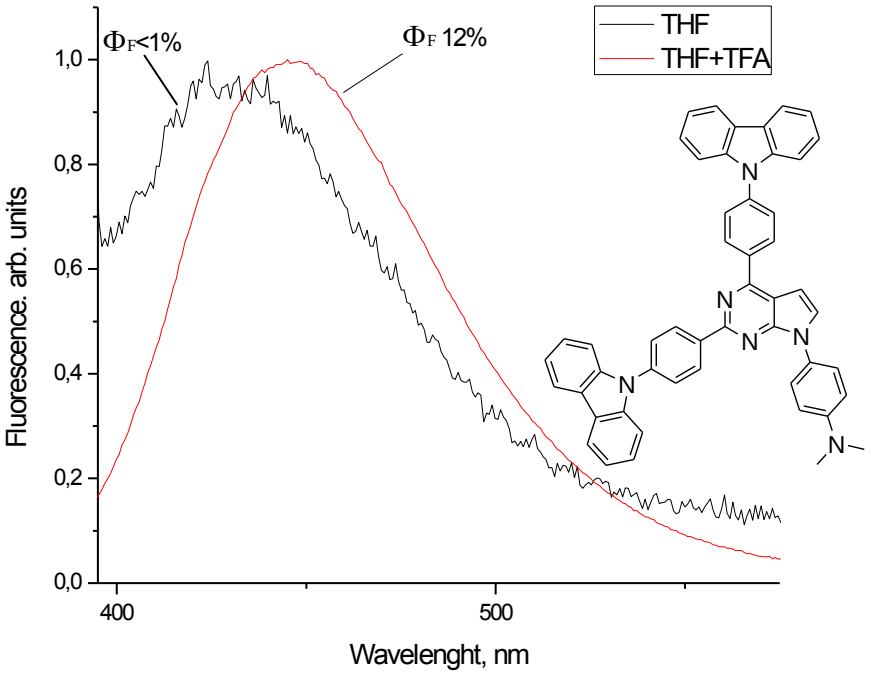


Figure 7. PL spectra of neutral and protonated forms of compound **29**.

The fluorescence lifetimes estimated in THF solutions span the range from 2.14 to 12.2 ns. Most of compounds show decay times, which are in good agreement with decay times of precursors **6a,e** (3.6 and 2.7 ns accordingly). Although, compounds **22**, **26** and **30** with electron-donating groups show prolonged lifetimes up to 12.2 ns (Table 10, entries 2, 6, 10).

Optical properties of compounds **31-34** possessing different aryl groups in positions 2 and 4 of pyrrolopyrimidine were also investigated. They were found to exhibit strong absorption in dilute THF solution with their absorption maxima positioned in the range 235 - 344 nm (Table 10). Emission maxima of compounds **31-34** were positioned in the range 402-449 nm. Compound **31** bearing electron-donating methoxy group in the *N*(7)-phenyl group has the largest Stokes shift (Table 10, entry 11). Fluorescence quantum yields of these compounds vary from 23 to 34%. Change of phenyl group by 4-biphenyl group at position 2 of pyrrolopyrimidine led to the higher quantum yields of compounds **31** and **32** compared with those of compounds **22** and **23** (Table 10, entries 2, 3, 11, 12). However, ethoxy substituent in 2-phenyl group of pyrrolopyrimidine has no effect neither on quantum yields nor decay times of

the studied compounds (compare data for **23** and **33**, Table 10, entries 3 and 13).

Solid state fluorescence of compounds **21-30** was measured at three different concentrations in polystyrene matrix (Table 11).

Table 11. Fluorescence data for compounds **21-30** in polystyrene matrix.

Entry	Compound	Concentration (%)	λ_{em}, nm	Φ_F, %	τ, ns
1		0.6	402	23	4.13
2	**21**	1.2	402	29	3.89
3		9	404 (416)*	32 (30)*	5.38
4		0.6	418	35	7.77
5	**22**	1.2	418	35	10.69
6		9	423 (448)	46 (21)	10.65
7		0.6	392	21	2.12
8	**23**	1.2	392	21	2.23
9		5	395 (403)	23 (23)	2.84
11		0.6	449	20	7.74
12	**24**	1.2	450	21 (4)	12.13
13		12	461 (528)	18	14.54
14		0.6	415	34 (36)	2.27
15	**25**	1.2	416	32	2.51
16		1.6	416 (423)	33	2.68
17		0.6	421	32	3.26
18	**26**	1.2	422	35 (20)	3.10
19		9	426 (456)	32	3.78
20	**27**	0.6	403 (438)	33 (40)	2.40
21		0.6	462	24	14.69
22	**28**	1.2	465	24 (2)	14.65
23		9	475 (539)	21	16.82
24		0.6	490	28	20.81
25	**29**	1.2	490	28	21.88
26		9	496 (424)	32 (<1)	19.60
27		0.6	417	39 (35)	20.81
28	**30**	1.2	418	35	2.22
29		9	423 (436)	31	2.74

*in parentheses data in THF solution are presented for comparison

One of the general features of PL spectra of triarylpyrrolopyrimidines in PS matrix is that emission maxima of almost all compounds are shifted hypsochromically compared to those in the solution, except compound **29**, which showed strong bathochromic shift ~ 72 nm in a solid state (Table 11). Moreover, emission maxima shift to the longer wavelength with increase of concentration (Table 11, entries 17-19). The most significant shift was observed for compounds **24** (13 nm) and **28** (20 nm) (Table 11, entries 11-13, 21-23). Emission quantum yields at higher concentrations in case of compounds **21**, **22**, **24**, **26**, **28**, **29** were higher, for compounds **23**, **25**, **30** - almost the same, and for compound **27** – lower, than those in the solution. It is worthy to note, that compounds **24**, **28**, **29** showed pronounced solid state fluorescence on the contrary to their results in solution: 5-fold, 12-fold and 32-fold increase, respectively (Table 11, entries 12, 22, 26). Dramatic increase of fluorescence efficiency in compounds **24**, **28**, **29** can be attributed to considerable suppression of nonradiative torsional deactivation processes due to the rigid environment in the solid PS matrix. Compounds **22** and **26** showed less significant progress, their quantum yields were approximately two times higher (46% and 35%) than those in the solution (Table 11, entries 6, 18). It should be mentioned, that almost in all cases quantum yields at the highest concentrations were lower compared to moderate concentrations. From the data obtained we can not conclude about any relationship between fluorescence decay times and concentration. As it was mentioned earlier, compounds **22** and **26** exhibited very long fluorescence lifetimes in solution, but in a solid state only compound **22** had 10.69 ns lifetime and lifetime of compound **26** decreased almost 3 times (Table 11, entries 5, 18). On the other hand, compounds **24** and **28-30** showed prolonged lifetimes: 14.54 ns, 16.82 ns, 21.88 ns, 20.81 ns respectively (Table 11, entries 13, 23, 25, 27).

II.2.3. Nanoaggregates and aggregation-induced emission enhancement of compounds 24, 28.

It is known, that organic conjugated molecules generally exhibit strong luminescence in diluted solutions. However, the fluorescence turn-on in the solid phase or in solutions with high concentrations is very uncommon, since usually, intermolecular interactions enhance non-radiative deactivation resulting in emission quenching. Thus, many efforts were attempted to suppress the aggregation of organic luminophores. On the other hand, another way to solve this problem would be to develop new luminophoric materials whose aggregates could emit more efficiently than their solutions. Thus, two novel photoluminescence processes have been identified: "aggregation-induced emission enhancement" (AIEE) and "aggregation-induced emission" (AIE) [148-166]. These phenomena usually occur due to the restriction of intramolecular rotational/vibrational motions of the aromatic rings around the carbon-carbon single bonds in the aggregation state and subsequent enhanced light emission.

Majority of the obtained 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines are soluble in common solvents, such as chloroform, tetrahydrofurane, dichloromethane and so on. However, their solubility in water is very poor. To determine whether some triarylpyrrolopyrimidines were AIEE active or not, the fluorescent behaviour of their diluted solutions were studied in the mixture of water and THF solvents with different water fractions. For this purpose compounds **24** and **28** were chosen, since they showed very low fluorescence quantum yields in diluted THF solution (only 4% and 2% accordingly) and enhanced quantum yields in polystyrene matrix (21% and 24% accordingly). Figures 8, 9 and 10 show the obtained results for compound **24**.

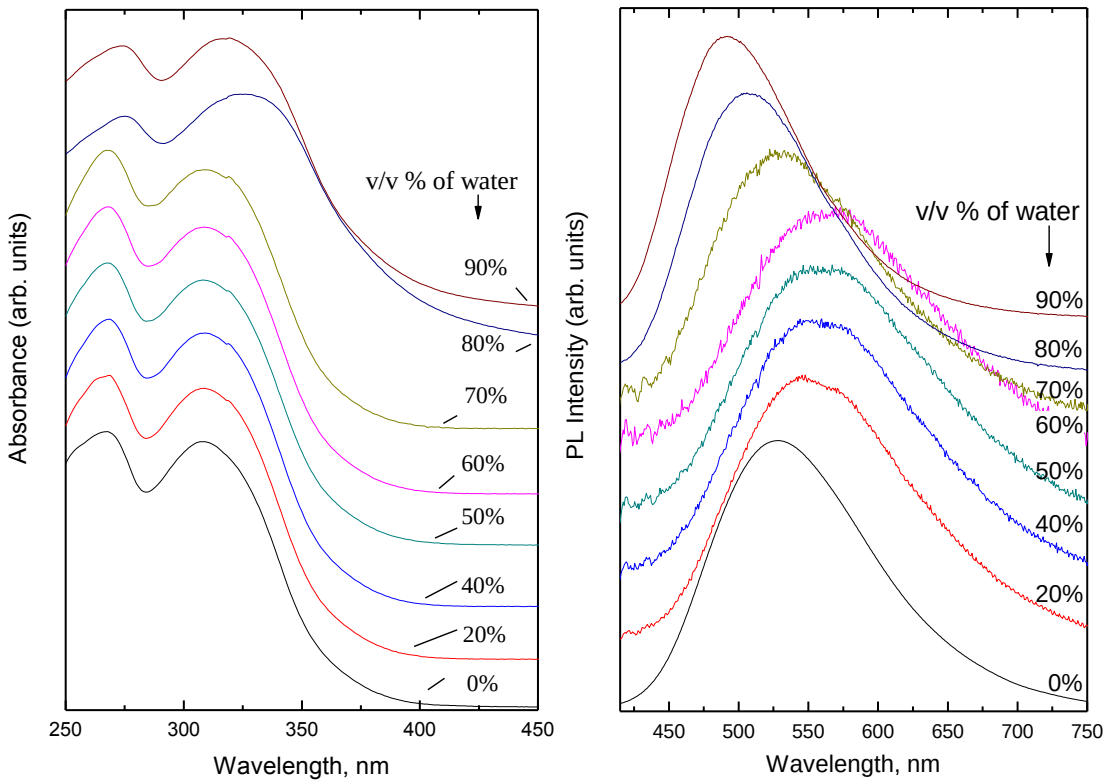
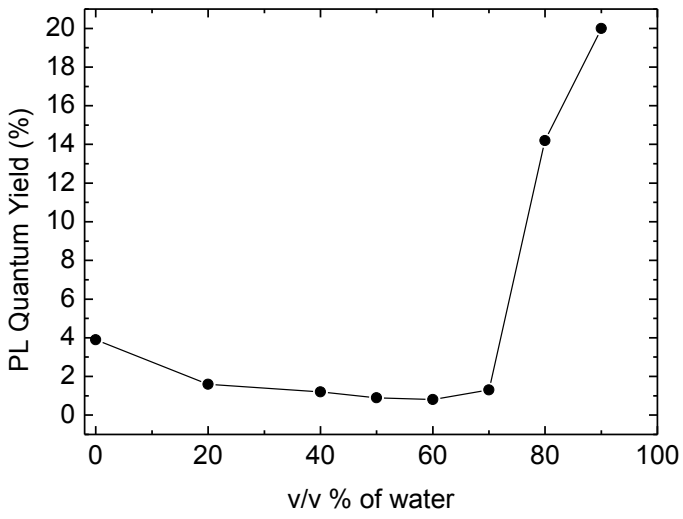
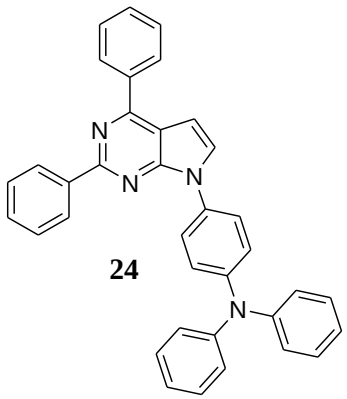


Figure 8.UV-Vis and PL spectra of dilute solution of **24** (10^{-5} M) in water/THF mixtures with different water contents.





24

Figure 9. Changes in quantum yield of dilute solution **24** (10^{-5} M) with different water fractions in the water/THF mixtures.

While the water fraction was increased from 0% to 70%, fluorescence quantum yields were almost the same or even lower (at 60% of water in the mixture) (Figure 8, 9). Since compound **24** was insoluble in water, the increase

of the water fraction in the mixture solvent would reduce the solubility of this compound. Then, the existing formation of compound **24** would change from molecules in the pure THF to particles of molecular aggregation in the mixture of solvents step by step. Thus, further increase of the water fraction from 70% to 90% led to the enhanced fluorescence quantum yield up to 20% (Figure 8, 9). Essentially, the enhancement of fluorescence quantum yield is directly related to the diminishing number of free molecules and growing number/volume of aggregates. Since both free molecules and aggregates are capable of absorbing excitation energy, but only aggregates produce efficient emission, the increase number of the later is thus responsible for the fluorescence quantum yield enhancement. In other words, compound **24** emitted stronger fluorescence upon aggregation, than in dilute solution and, thus, it was AIEE active. It is worthy of note, that increase of the water fraction in the mixture led to the prolonged fluorescence lifetimes up to 22.36 ns (Figure 10).

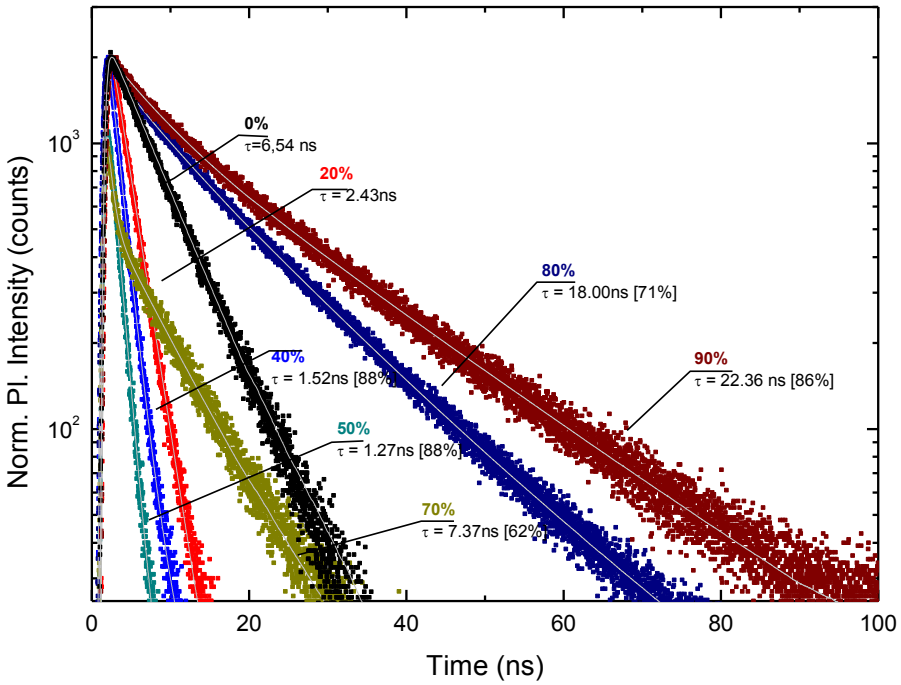


Figure 10. PL lifetimes of dilute solution of **24** (10^{-5} M) in water/THF mixtures with different water contents.

Just as obtained in the fluorescence behavior of compound **24**, nearly the same trend was observed in case of compound **28** (Figures 11, 12, 13). However, if we compare the results of these two compounds in detail, we could find some differences.

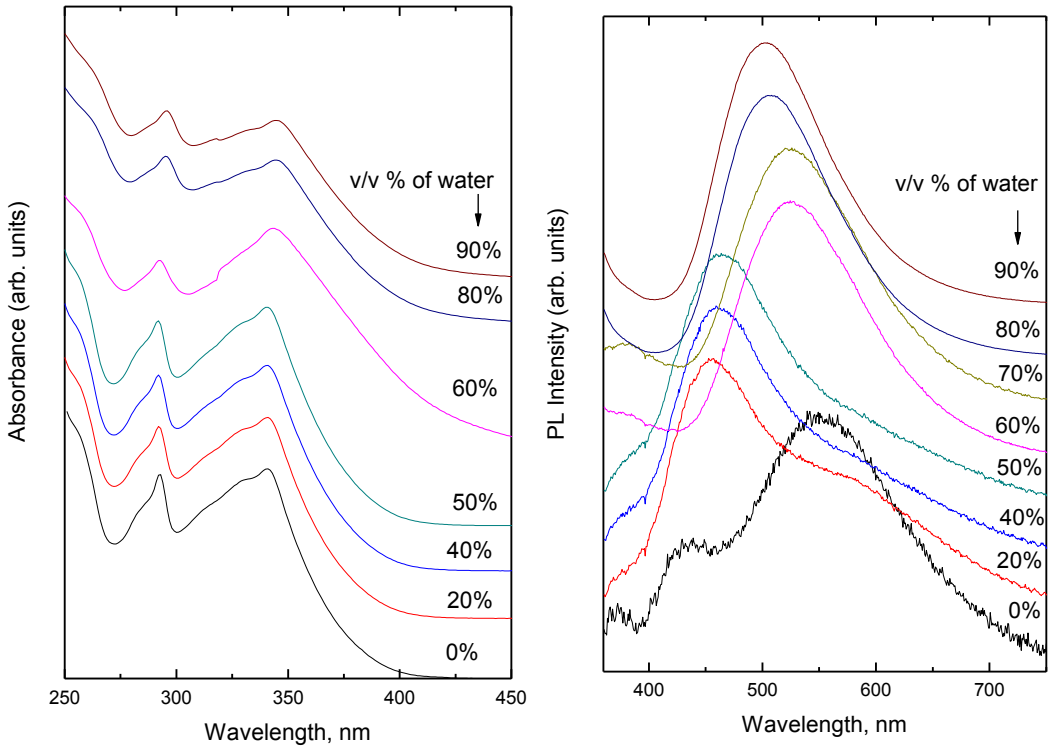


Figure 11.UV-Vis and PL spectra of dilute solution of **28** (10^{-5} M) in water/THF mixtures with different water contents.

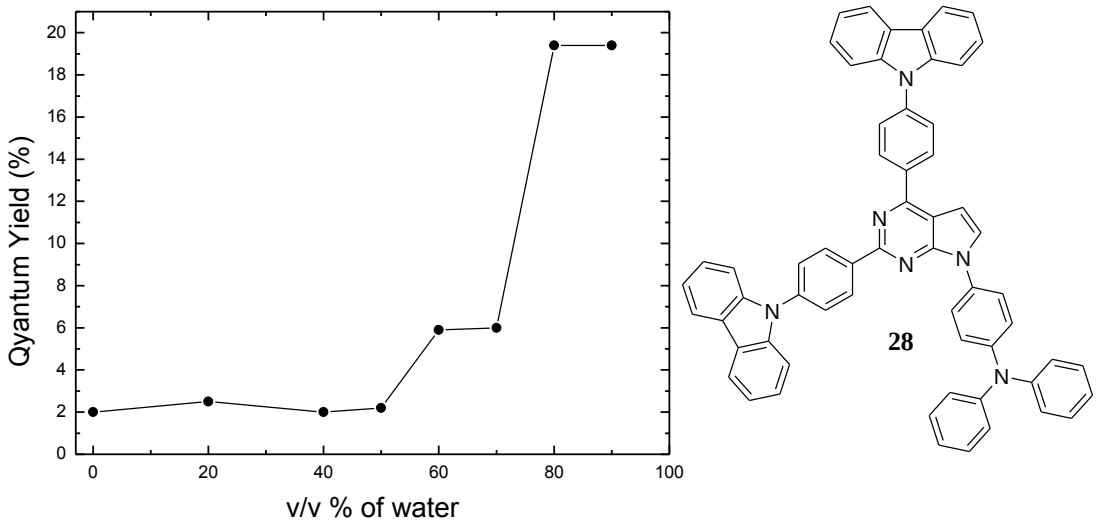


Figure 12. Changes in quantum yield of dilute solution **28** (10^{-5} M) with different water fractions in the water/THF mixtures.

While the water fraction was increased from 0% to 50%, the fluorescence quantum yields were almost the same (Figures 11, 12). Further increase of water fraction in the mixture led to the significant enhance of fluorescence quantum yield up to 19%. It is worthy of note, that fluorescence quantum yield was the same at 80% and 90% of water fraction in the mixture (Figures 11, 12). Thus, compound **28** also was AIEE active. Again, increase of the water fraction in the mixture led to the prolonged fluorescence lifetimes up to 22.54 ns (Figure 13).

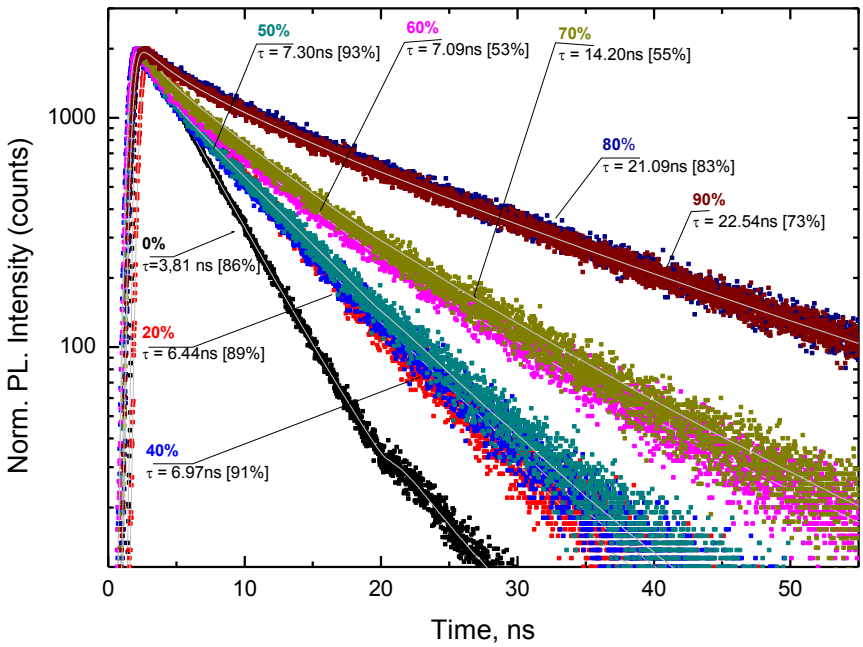


Figure 13. PL lifetimes of dilute solution of **28** (10^{-5} M) in water/THF mixtures with different water contents.

Taking into account complete water miscibility of THF, increase of the water content unavoidably reduces size of the THF droplets and, consequently, average intermolecular separation of molecules inside the droplets thus forcing them to aggregate. So, nanoparticle sizes should be reduced with increase of the water content in the THF/water mixture. And indeed, the visualization of nanoparticles of compounds **24**, **28** formed at different THF/water ratios, casted on the silicon pads and accomplished using field emission scanning electron microscope (FE-SEM), clearly indicated reduction of nanoparticle sizes. The mean diameters of nanoparticles of compound **24** obtained by

averaging over the large ensemble attained the values of 100 and 200 nm for 90 and 80 v/v% of water, respectively (Figure 14), whereas for nanoparticles of compound **28** the mean diameter ranged from 50 to 500 nm for 90 and 70 v/v% of water (Figure 15).

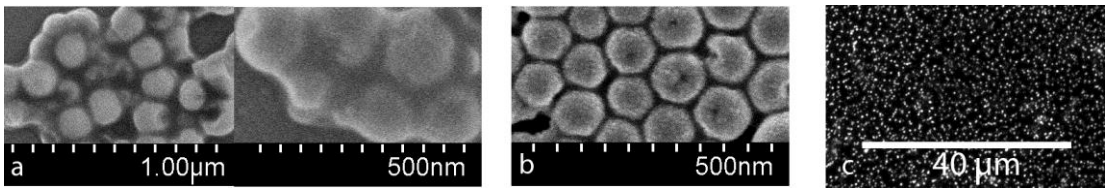


Figure 14. FE-SEM (a, b) and FlM (c) images of compound **24** nanoparticles formed in THF/water mixtures with 80 (a) and 90 (b, c) volume percent of water. The solute concentration in the mixture was kept constant (1×10^{-5} M).

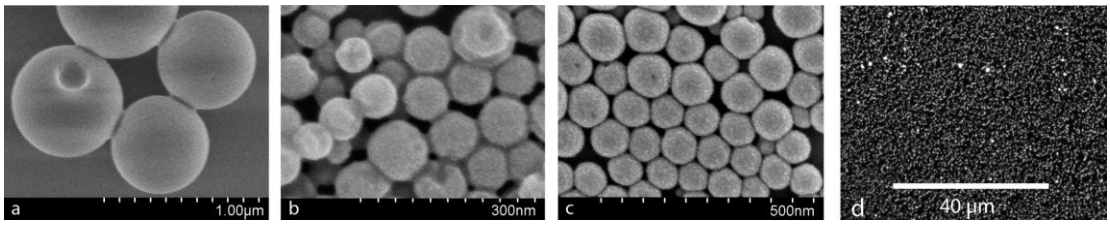


Figure 15. FE-SEM (a, b, c) and FlM (d) images of compound **28** nanoparticles formed in THF/water mixtures with 70 (a), 80 (b) and 90 (c, d) volume percent of water. The solute concentration in the mixture was kept constant (1×10^{-5} M).

Taking into account the constant concentration of compounds **24** and **28** maintained in the THF/water mixtures irrespective of the solvent/nonsolvent ratio, descending nanoparticle size with increasing water content indicates increasing local concentration of the molecules in the THF droplets as well as in the casted nanoparticles. More dense packing of the molecules in the nanoparticles and diminishing number of free molecules with increasing water content is responsible for the steady enhancement of the fluorescence quantum yields as it was demonstrated above.

* * *

In summary, the synthesized 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines exhibit blue-UV fluorescence with emission maxima in THF solution ranging from 402 nm to 539 nm with emission quantum yields in the range of 1-40%.

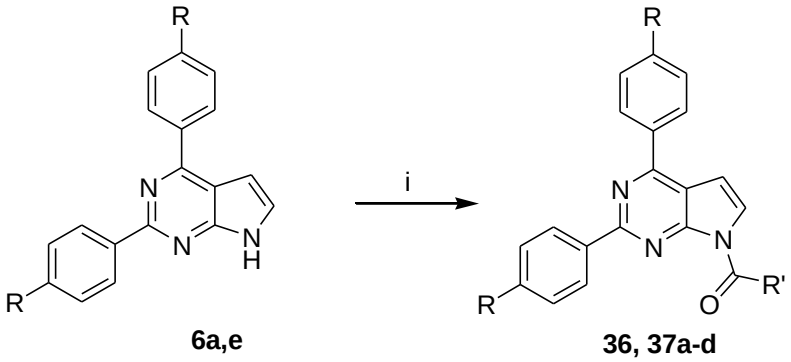
In general, attachment of an additional aromatic system at the position 7 of pyrrolo[2,3-*d*]pyrimidine reduces the fluorescence quantum yields of the studied compounds. Especially significant drop of fluorescence is observed for compounds, containing 4-(diphenylamino)- and 4-(dimethylamino)phenyl groups at *N*(7) position of the heterocycle. However, in the polystyrene matrix 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines exhibit pronounced fluorescence. Depending on the aryl branches at position 7 of the heterocycle emission maxima of 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines measured at three different concentrations varied from 402 nm to 496 nm and emission quantum yields from 18% to 46%. Increase of the fluorescence efficiency in a solid state of compounds possessing more number of aryl rotors was attributed to a considerable suppression of nonradiative torsional deactivation processes. 7-[4-(Diphenylamino)phenyl]pyrrolo[2,3-*d*]pyrimidines were found to exhibit an aggregation induced emission enhancement by formation of nanoaggregates in THF/water mixtures. The fluorescence of pyrrolopyrimidine derivatives containing amino groups is sensitive to acids and its efficiency depends on a protonation site.

II.3. Synthesis and Properties of 7-acyl-2,4-diaryl-7*H*-pyrrolo[2,3-*d*]pyrimidines.

II.3.1. Synthesis of 7-acyl-2,4-diaryl-7*H*-pyrrolo[2,3-*d*]pyrimidines.

As we have seen, fluorescence quantum yields of the synthesized 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines, despite the fact that they have more π-extended aromatic system were moderate and/or lower with respect to *N*-unsubstituted pyrrolopyrimidines **6a,e**. This could be explained by a steric interaction of 6-*H* proton of pyrrolo[2,3-*d*]pyrimidine with 2,6-*H* protons of *N*(7)-aryl scaffold resulting in out-of-plane conformation of this fragment and broken π-conjugation. Otherwise, electron-withdrawing 7-*tert*-butoxycarbonyl group in 2,4-di[4-(9*H*-carbazol-9-yl)phenyl]pyrrolo[2,3-*d*]pyrimidine (**8e**) enhanced the fluorescence quantum yield up to 67% in THF. Thus, in order to obtain additional information about the influence of structural features at the

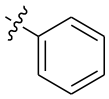
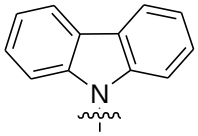
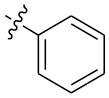
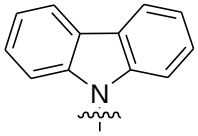
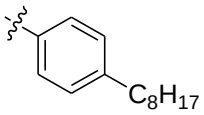
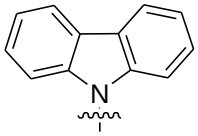
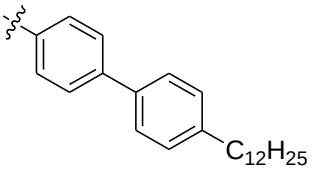
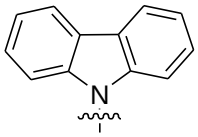
position 7 of pyrrolopyrimidine on their photophysical properties we designed compounds which contain aroyl group in position 7. Aroyl group as Boc is electron-withdrawing group and aromatic ring is separated from the heterocyclic moiety by a linker - C=O group. Thus, the steric interaction of aromatic and heterocyclic parts of molecule will be reduced, while the conjugation between these two parts should have maintained through C=O group.



Scheme 10. *Reagents and conditions*: (i) R'COCl, DMAP, DIPEA or TEA, CH_2Cl_2, 12-16 h, rt or Δ.

Synthesis of 7-acylpyrrolo[2,3-*d*]pyrimidines **36**, **37a-d** was carried out by acylation of pyrrolopyrimidines **6a** and **6e** with chloranhydrides of the corresponding carboxylic acids in the presence of DMAP and DIPEA applying the method described in [167] (Scheme 10, Table 12). Compound **36** and 7-pivaloyl derivative **37d** were prepared for comparative study of photophysical properties. Yields of all synthesized compounds were moderate or low mostly because of the side product formation and further complex purification by column chromatography. It should be noted, that for the synthesis of compound **37d** triethylamine was used as a base instead of DIPEA (Table 12).

Table 12. Data of synthesis of 7-acyl-2,4-diaryl-*7H*-pyrrolo[2,3-*d*]pyrimidines (**36**, **37a-d**).

Compound	R	R’	Yield,* %
36	H		65
37a			51
37b			17
37c			51
37d			57

* The yields are after isolation and purification by the column chromatography.

II.3.2. Photophysical properties of 7-acyl-2,4-diaryl-7*H*-pyrrolo[2,3-*d*]pyrimidines (36, 37a-d).

The synthesized 7-acyl-2,4-diarylpyrrolo[2,3-*d*]pyrimidines **36** and **37a-d** were subjected to optical absorption and fluorescence studies. The results of these investigations are presented in Table 13. The corresponding data of compound **8e** are shown in the table for convenience.

Table 13. UV-VIS absorption and PL data for the series of compounds **36, 37a-d** in 10^{-5} M THF solution.

Entry	Comp.	λ_{abs}, nm	ε, $l \cdot mol^{-1} \cdot cm^{-1}$	λ_{em},* nm	Stokes shift, nm	Φ_F, %	τ, ns	$k_r \cdot 10^9$, s^{-1}	$k_{nr} \cdot 10^9$, s^{-1}
1	**36**	258 310	20368 8492	405	7567	2	3.41	0.01	0.29
2	**37a**	239 254 292 342	48341 40325 20688 21765	444	6718	48	3.89	0.12	0.13
3	**37b**	256 292 342	62096 50562 49966	444	6718	54	4.03	0.13	0.11
4	**37c**	255 292 342	71458 60256 52070	443	6667	16	2.08	0.08	0.40
5	**37d**	243 256 292 342	39921 32228 18736 21141	438	6409	52	4.10	0.13	0.12
6	**8e**	255 293 342	44475 24940 29822	436	6304	67	4.1	0.16	0.08

*fluorescence was excited at 340 nm

They were found to exhibit strong absorption in dilute THF solution with their absorption maxima positioned in the range 239 - 342 nm. Depending on the origin of acyl branches emission maxima of compounds **36, 37a-d** are located in the range 405 - 444 nm with fluorescence quantum yields ranging from 2% to 54%. In general, emission maxima of compounds **37a-d** are shifted to the longer wavelengths with respect to the reference compound **8e** emission maxima. It should be mentioned, that emission maxima of compounds **37a-c** lies in the same range of 444 nm. Quantum yield of compound **36** is 21 times lower comparing to its precursor **6a** (42%) and almost two times lower than emission quantum yield of protected compound **8a** (3.6%) (Table 13, entry 1 and Table 6). This is in a good agreement with changes of radiative and

nonradiative rate constants: radiative rate constant k_r of compound **36** is twelve times lower than k_r of compound **6a** (k_r = 0.12). On the other hand, nonradiative rate constant k_{nr} of compound **36** is almost two times higher, than k_{nr} of compound **6a**. Thus, in a series of 2,4-diphenylpyrrolo[2,3-*d*]pyrimidines introduction of electron-withdrawing substituent at *N*(7)-position reduces the efficiency of fluorescence. However, acyl substituents at *N*(7) in a series of 2,4-di[4-(9*H*-carbazol-9-yl)phenyl]pyrrolo[2,3-*d*]pyrimidine can increase their fluorescence efficiency. Compounds **37a,b,d** showed the same or even higher quantum yields than their precursor **6e** (50%). Nevertheless, *N*(7)-Boc derivative **8e** was still better and had higher quantum yield (Table 13, compare entries 2, 3, 5 and 6). Although, compounds **37a,b,d** had slightly lower radiative rate constants k_r than compound **8e**, nonradiative rate constant k_{nr} of compound **8e** is significantly lower, and, thus, it showed better fluorescence results (Table 13, compare entries 2, 3, 5 with 6). Lower fluorescence quantum yield of **37c** indicates that introduction of an additional rotor, in spite of its π-aromatic character, is very important for photoluminescence properties of these compounds. Compounds **37a,b,d** showed almost the same lifetimes as compound **8e** (Table 13, entries 2, 3, 5). Compound with the lowest quantum yield (**37c**) showed shorter lifetimes with respect to the reference compound **8e** (Table 13, entries 4, 6).

Solid state fluorescence of compounds **37a-d** was measured at 0.6% concentration in polystyrene matrix. The results are presented in Table 14 together with reference compound **8e**.

Table 14. Characteristics of PL spectra of 7-acyl-2,4-diaryl-7*H*-pyrrolo[2,3-*d*]pyrimidines (**37a-d**) in PS matrix at 0.6% concentration.

Entry	Compound	λ_{em}, nm	Φ_F, %	τ, ns	$k_r \cdot 10^9$, s^{-1}	$k_{nr} \cdot 10^9$, s^{-1}
1	**37a**	401	30	2.59	0.12	0.27
2	**37b**	401	34	2.48	0.14	0.26
3	**37c**	401	23	2.32	0.10	0.33
4	**37d**	402	36	2.68	0.13	0.24
5	**8e**	404	35	2.2	0.16	0.30

As seen from the table, all compounds have their emission maxima in the same range at 401-404 nm and are blue shifted at about 40 nm with respect to their emission maxima in solution. Fluorescence quantum yields of compounds **37b,d** could be compared with fluorescence efficiency of compound **8e** (Table 14, compare entries 2, 4 and 5). Although, compound **37a,b,d** had slightly lower radiative rate constant k_r, than compound **8e**, their nonradiative rate constants k_{nr} are lower, too. For this reason, their fluorescence quantum yields do not differ too much (Table 14, compare entries 1, 2, 4 with 5). However, all compounds showed lower quantum yields in a solid state as compared with those in the solution (just like compound **8e**). Only compound **37c** showed enhance of quantum yield up to 23% (Table 14, entry 3). This result is in agreement with our earlier observation about significance of number of rotors on the fluorescence efficiency. Emission lifetimes in a solid state for compounds **37a-d** were almost the same with respect to the compound **8e**.

* * *

In summary, the performed investigation provides an easy access to the 2,4-diaryl-7*H*-pyrrolo[2,3-*d*]pyrimidine derivatives with various acyl branches in position 7 of heterocyclic moiety. Although the photoluminescence properties of the synthesized compounds were better than those of 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines, improvement of π-conjugation between the pyrrolopyrimidine and aryl branches at *N*(7)-position did not give an expected enhancement of fluorescence efficiency. The obtained results support our earlier observation about the significance of considerable nonradiative torsional processes with increase of number of rotors.

II.4. Synthesis and Properties of Bis(2,4-diarylpyrrolo[2,3-*d*]pyrimidin-7-yl)carbazoles and -fluorenes.

II.4.1. Synthesis of bis(2,4-diarylpyrrolo[2,3-*d*]pyrimidin-7-yl)carbazoles and -fluorenes.

Carbazole and fluorene are well-known fluorophores and their derivatives have been extensively investigated [168]. Carbazole, due to its unique optical, electrical and chemical properties has been used widely as a functional building block or substituent in the construction of organic molecules for use as light-emitting and hole-transporting layers in OLED devices [169-175], as host materials for electrophosphorescent applications [176, 177], and as active component in solar cells [178, 179]. Moreover, the thermal stability and glassy durability of the organic molecules were found to be significantly improved upon incorporation of a carbazole moiety into the structure [180, 181]. Fluorene derivatives have also attracted much attention in the synthesis of organic optoelectronic materials [182-184], and in particular blue-emitting fluorophores for OLEDs due to its large HOMO-LUMO energy gap, availability and facile chemical functionalization. For this reason, incorporation of carbazole or fluorene moieties into conjugated π-system could improve optical and electronic properties of the pyrrolo[2,3-*d*]pyrimidine compounds.

It was decided to incorporate carbazole and fluorene moieties between two 2,4-diarylpyrrolo[2,3-*d*]pyrimidine fragments. Such molecules can be constructed by *N*-arylation reaction of the corresponding pyrrolopyrimidine derivatives with dihalocarbazoles or dihalofluorenes. For this purpose, earlier mentioned compounds **6a,e** and a set of four different “diiodo- and dibromo-“ carbazoles (**38**, **39**) and fluorenes (**40**, **41**) (Figure 16) were used as coupling partners. Compound **39** is commercially available, while compounds **38** and **40** were synthesized according to the procedures described in the literature [185, 186].

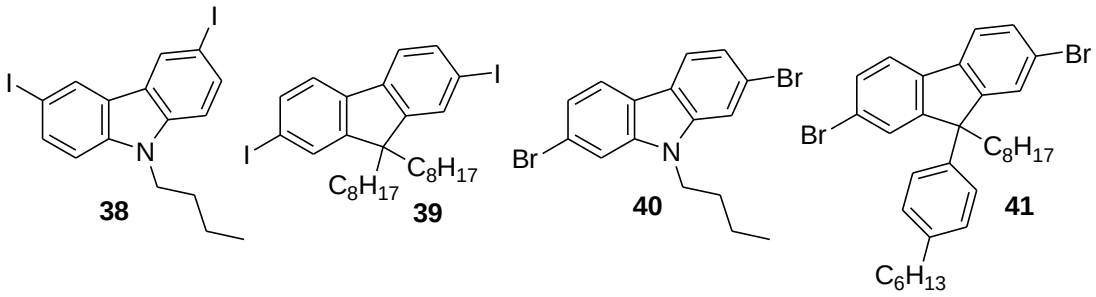
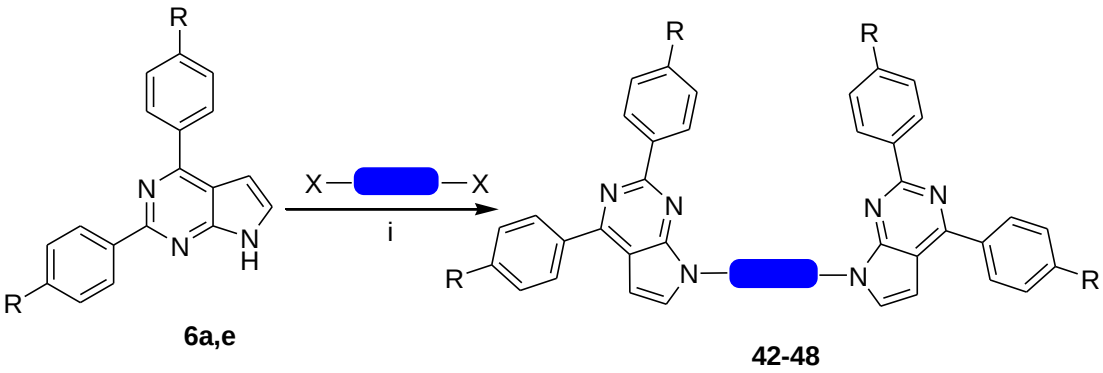


Figure 16. Set of carbazoles and fluorenes used in *N*-arylation reaction.

N-arylation reactions were performed using catalytic system and conditions previously elaborated by us (Section II.2.1.). The principal scheme of synthesis is depicted in Scheme 11 and the data of synthesis is presented in Table 15.



6a, R = H; **6e**, R = Carbazolyl

Scheme 11. *Reagents and conditions*: (i) CuI, *trans*-1,2-diaminocyclohexane or *trans*-*N*,*N*'-dimethyl-1,2-diaminocyclohexane, K_3PO_4, 1,4-dioxane, Δ, Ar.

Table 15. Data of synthesis of compounds **42-48**.

Entry	Compound	X—▬—X	CuI, mol%	Duration	Product, (Yield,* %)
1	**6a**	**38**	13	37 h	**42** (72)
2	**6a**	**39**	9	18 h	**43** (87**)
3	**6a**	**40**	8	16 h	**44** (78**)
4	**6a**	**41**	23	59 h	**45** (67)
5	**6e**	**38**	17	36 h	**46** (71)
6	**6e**	**39**	13	39 h	**47** (61)
7	**6e**	**40**	15	42 h	**48** (60**)

* The yields are after isolation and purification by the column chromatography.
**Reactions were performed using *trans*-*N*,*N*'-dimethyl-1,2-diaminocyclohexane as a ligand.

Compound **6a** showed better results in earlier mentioned synthesis of 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines, probably because of less bulky aryl groups. For this reason, firstly we examined compound **6a** in *N*-arylation reaction with 9-butyl-3,6-diiodo-9*H*-carbazole (**38**) and after 37 hours of stirring under reflux compound **42** was isolated in 72% yield (Table 15, entry 1). Again, 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 same reaction was performed using **6e** as a starting material and after 36 hours compound **46** was isolated in 71% yield (Table 15, entry 5). The reaction of compound **6e** with 2,7-diiodo-9,9-dioctylfluorene (**39)** led to the formation of the target product **47** in a moderate yield (Table 15, entry 6). However, the efforts to perform reaction of **6e** with 2,7-dibromo-9-butylcarbazole (**40**) using the same procedure led to a complex mixture of products and after purification only small amount of the target compound **48** was isolated. S. L. Buchwald *et al.* examined several ligands in *N*-arylation reaction and have found, that using *trans*-*N*,*N*'-dimethyl-1,2-diaminocyclohexane in many cases gives better results [141, 142]. For this reason, we repeated reaction of compound **6e** with 2,7-dibromo-9-butylcarbazole (**40**) and after 42 hours of stirring under reflux in dioxane the target compound **48** was isolated already in 60% yield (Table 15, entry 7). Further reactions of 2,4-diphenylpyrrolo[2,3-*d*]pyrimidine (**6a**) with halides **39** and **40** using *trans*-*N*,*N*'-dimethyl-1,2-diaminocyclohexane as a ligand furnished the target compounds **43**, **44** in 87% and 78% yields, correspondingly (Table 15, entries 2, 3). It should be noted, that the *N*-arylation reaction using *trans*-*N*,*N*'-dimethyl-1,2-diaminocyclohexane as a ligand required less amount of CuI (8-9 mol%) and proceeded faster. Performing the reaction of **6a** with fluorene **41** under usual conditions (CuI/*trans*-1,2-diaminocyclohexane) required a great amount of CuI (Table 15, entry 4) and prolonged heating. Compound **45** was obtained in a moderate yield.

II.4.2. Photophysical properties of bis(2,4-diarylpyrrolo[2,3-*d*]pyrimidin-7-yl)carbazoles and -fluorenes 42-48.

The synthesized compounds **42-48** were subjected to optical absorption and fluorescence studies. The results of these investigations are presented in Table 16.

Table 16. UV-VIS absorption and PL data for the series of compounds **42-48** in 10^{-5} M THF solution.

Entry	Compd.	λ_{abs}, nm	ε, l·mol^{-1}·cm^{-1}	λ_{em},* nm	Stokes shift, cm^{-1}	Φ_F, %	τ, ns
1	**42**	252 295 353	47848 34620 9280	483	7624	16	12.05
2	**43**	266 289 328	73980 56480 55571	437	7604	25	7.21
3	**44**	321 341	52675 44367	454	7299	20	7.84
4	**45**	263 294 331	39475 27397 27427	436	7275	30	6.92
5	**46**	292 342	59337 49001	493	8956	14	11.31
6	**47**	250 292 341	48377 37314 38727	449	7054	31	6.87
7	**48**	292 342	48938 57970	461	7548	25	8.47

*fluorescence was excited at 340 nm

Bis(2,4-diarylpyrrolo[2,3-*d*]pyrimidin-7-yl)carbazoles and -fluorenes (**42-48**) were found to exhibit strong absorption in dilute THF solution with their absorption maxima positioned in the range 250 - 353 nm. Emission maxima of compounds **42-48** are positioned in the range 436-493 nm with emission quantum yields 14-31%. It should be noted, that compounds with carbazole moiety in the middle are shifted to the longer wavelengths, than

compounds with fluorene moiety in the middle of the molecule (Table 16, compare entries 1, 3, 5 with 2, 4, 6). Moreover, compounds **42, 46** have a larger Stokes shifts than their 2,7-isomers **44, 48** (Table 16, compare entries 1, 5 and 3, 7). However, compounds **42, 46** bearing 3,6-disubstituted carbazole in the middle of molecules have lower emission quantum yields and longer lifetimes (Table 16, entries 1, 5) than their isomers **44**, **48**. Emission maxima of compounds with 2,4-di(4-(9*H*-carbazol-9-yl)phenyl)pyrrolo[2,3-*d*]pyrimidine fragment are shifted bathochromically (at about 7-12 nm) compared to those with 2,4-diphenylpyrrolo[2,3-*d*]pyrimidine fragment.

Solid state fluorescence of compounds **42-48** was measured at 0.6% concentration in polystyrene matrix. The results are presented in Table 17.

Table 17. Characteristics of PL spectra of bis(2,4-diarylpyrrolo[2,3-*d*]pyrimidin-7-yl)carbazoles and -fluorenes (**42-48**) in PS matrix at 0.6% concentration.

Entry	Compound	λ_{em}, nm	Φ_F, %	τ, ns
1	**42**	423	34	9.65
2	**43**	417	42	5.34
3	**44**	419	39	5.68
4	**45**	402	23	2.31
5	**46**	424	35	3.65
6	**47**	403, 422	37	1.97
7	**48**	422	40	2.31

Emission maxima of compounds **42-48** in a solid state are positioned in the range 402-424 nm and are blue shifted comparing with those in the solution. The most significant shifts showed compounds **42** (~ 60 nm) and **46** (~ 70 nm) (Table 17, entries 1, 5). It is worthy of note, that almost all compounds (except compound **45**) showed up to two-fold increase in solid state emission quantum yields. Increase of fluorescence efficiency of all compounds can be attributed to considerable suppression of nonradiative torsional deactivation processes due to the rigid environment in the solid PS matrix. It should be noted, that emission lifetimes of compounds **42-48** were much shorter compared to those in the solution. PL data in PS matrix of

compounds bearing 3,6-disubstituted (**42, 46**) and 2,7-disubstituted carbazole derivatives (**44, 48**) indicates that their fluorescence quantum yields vary in the same trend as in solution.

* * *

In summary, a high yielding synthesis of bis(2,4-diarylpyrrolo[2,3-*d*]pyrimidin-7-yl)carbazoles and -fluorenes by the reaction of 2,4-diarylpyrrolo[2,3-*d*]pyrimidines with 3,6- or 2,7-dihalocarbazoles and fluorenes in the presence of CuI/*trans*-1,2-diaminocyclohexane/K_3PO_4 or CuI/*trans*-*N*,*N*'-dimethyl-1,2-diaminocyclohexane/K_3PO_4 as catalyst systems has been accomplished. It was found, that extension of π-conjugated system by connection of pyrrolo[2,3-*d*]pyrimidine skeletons *via* well known chromophores - carbazole or fluorene did not lead to an adequate change of photoluminescence properties of the synthesized oligoarylenes. However, the structural changes made were found to have positive effects on the photoluminescence properties in a solid state. The synthesized pyrrolopyrimidine-core based oligoarylenes exhibit up to two-fold higher fluorescence quantum yields in PS matrix than in THF solution. Moreover, connection of pyrrolopyrimidine moieties *via* 2,7-positions of carbazole seems to be more favorable for distribution of π-electronic density in the whole molecule than 3,6-connection mode.

III. EXPERIMENTAL PART

III.1. Instrumentation

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 330 or 340 nm wavelength light-emitting diode and measured using backthinned 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. 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), which was coupled to the CCD spectrometer by an optical fiber. Fluorescence transients of the sample solutions were measured using time-correlated single photon counting system (Pico-Quant PicoHarp 300). Fluorescence lifetime estimated at λ_{em}.

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).

Mass spectrometry analyses were carried out on a quadrupole, time-of-flight mass spectrometer (microTOF-Q II, Bruker Daltonik GmbH, Bremen, Germany) or on Dual-ESI Q-TOF 6520 (Agilent Technologies) mass spectrometer. The instrument was modified for detection of medium masses (50 – 1500 amu). The samples were introduced directly as 50 μM solutions in $CHCl_3$ and CH_3CN solution (v:v, 3:1) with mechanical syringe (KdScientific, Holliston, MA, USA), at 180 μL/h rates. All mass spectra were calibrated

internally using low concentration tuning mix (ESI – L, Agilent Technologies, USA) and were processed with DataAnalysis 4.0 software (Bruker Daltonik GmbH, Bremen, Germany).

SEM images were taken by a FE-SEM Hitachi SU-70. Before measurements samples were coated by thin chromium film to avoid charging.

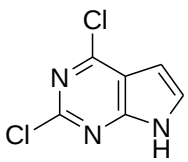
Organic nanoagregates were casted from solution on silicon substrates and visualized using fluorescence microscope Olympus BX51. The nanoaggregates were imaged through the high magnification (100x, numerical aperture 0.90) objective using thermoelectrically cooled CCD camera QImaging Exi Blue for fluorescence detection. Nanoparticle solutions were obtained by a re-precipitation method from molecularly dispersed 2,4-diphenyl-7-[4-(diphenylamino)phenyl]-7*H*-pyrrolo[2,3-*d*]pyrimidine and 2,4-di[4-(9*H*-carbazol-9-yl)phenyl]-7-(4-diphenylamino)phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine solutions in THF by injecting purified water at different volume percent under vigorous stirring. The final solute concentration in THF/water mixtures was kept constant (1×10^{-5} M).

All reactions and purity of the synthesized compounds were monitored by TLC using Silica gel 60 F254 aluminium plates (Merck). Visualization was accomplished by UV light. Column chromatography was performed using Silica gel 60 (0.040-0.063 mm) (Merck).

In description of ^{1}H NMR spectra such abbreviations were used: s – singlet, d - doublet, dd – doublet of doublet, t - triplet, q – quartet, m - multiplet, pp – protons of pyrrolo[2,3-*d*]pyrimidine.

III.2. Materials

*2,4-Dichloro-7H-pyrrolo[2,3-d]pyrimidine (**3**)*

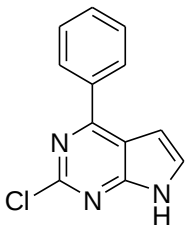


Mixture of 7*H*-pyrrolo[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (**2**) [130] (1.0 g, 6.6 mmol) and dichloro(phenyl)phosphorous oxide (5 ml) was stirred at

165 °C for 1 hour under argon flow. The resulted viscous residue was poured into a mixture of water (23 ml) and ethyl acetate (12 ml) and stirred at room temperature overnight. The mixture was then filtered through a layer of silica gel. The layers were separated and water solution was extracted with ethyl acetate (6×25 ml). Organic layers were combined, dried over Na_2SO_4 and evaporated under reduced pressure. Product was extracted from the solid residue with hot toluene 10x100 mL to give 831 mg (67%) of compound **3**, mp 249 °C. UV (ethanol), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 228 ($2{,}78 \cdot 10^4$); 291 ($4{,}2 \cdot 10^3$); ν_{max} (KBr) 3444 cm^{-1} (NH); δ_H (DMSO-d_6): 6,67 (1H, d, *J* = 3,6 Hz, 5-H), 7,74 (1H, d, *J* = 3,3 Hz, 6-H), 12,79 (1H, br. s, NH); δ_C (DMSO-d_6): 100.1, 116.5, 130.2, 150.8, 151.6, 153.5.

Lit. [131]: yield 41%, mp 249 °C; Lit. [187]: yield 52%, mp 249 °C.

*2-Chloro-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (**5a**)*

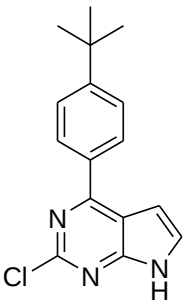


Method A. A solution of compound (**3**) (0.2 g, 1.06 mmol) in anhydrous dioxane (5 ml) was flushed with argon and K_3PO_4 (1.39 g, 6.59 mmol), phenylboronic acid (**4a**) (0.28 g, 2.29 mmol), 2.5 mol% $Pd(PPh_3)_2Cl_2$ were added under stirring and argon flow. The reaction mixture was stirred under reflux for 2 hours. Then reaction mixture was cooled on standing and water (5 mL) was added to dissolve inorganic salts. The solid obtained was purified by column chromatography using chloroform as an eluent to give compound **5a** (0.1 g, 41%) as a yellowish solid, mp 210 °C.

Method B. A solution of compound **3** (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 (**4a**) (0.39 g, 3.20 mmol) and K_3PO_4 (1.35 g,

6.37 mmol) were added. The reaction mixture was stirred at 60-70 °C (bath temperature) for 4 hours. 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 **5a** (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%]; UV (ethanol), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 224 ($2\times10^4$); 231 ($2{,}2 \times 10^4$); 252 ($1x10^4$); 318 ($6\times10^3$); ν_{max} (KBr) 3449 cm^{-1} (NH); δ_H ($CDCl_3$): 6.92 [1H, dd, J^3 = 3.6 Hz, J^4 = 2.1 Hz, 5-H (pp)], 7.47 [1H, dd, J^3 = 3.6 Hz, J^3 = 2.1 Hz, 6-H (pp)], 7.59-7.63 [3H, m, 3-5-H (Ph)], 8.18-8.21 [2H, m, 2,6-H (Ph)], 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-(4-tert-Butylphenyl)-2-chloro-7H-pyrrolo[2,3-d]pyrimidine (**5b**)*

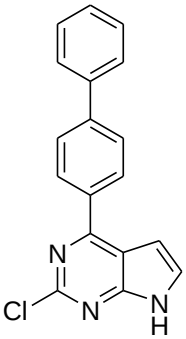


Method A. Compound **5b** was synthesized and isolated according to the procedure described for the preparation of compound **5a** (Method A). The reaction time 2 h. Yield 57%, yellowish solid, mp 164-165 °C.

Method B. Compound **5b** was synthesized and isolated according to the procedure described for the preparation of compound **5a** (Method B). The reaction time 2 h. Yield 66%, yellowish solid, mp 164-165 °C. [Found: C, 67.27; H, 6.05; N, 14.83. $C_{16}H_{16}ClN_3$ requires C, 67.25; H, 5.64; N, 14.70%]; UV (ethanol), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 226 ($3\times10^4$); 266 ($1 \times 10^3$); ν_{max} (KBr) 3434 cm^{-1} (NH); δ_H ($CDCl_3$): 1.44 (9H, s, $C(CH_3)_3$), 6.93 [1H, dd, J^3 = 3.6 Hz,

J^4 = 1.8 Hz, 5-H (pp)], 7.45 [1H, dd, J^3 = 3.6 Hz, J^3= 2.4 Hz, 6-H (pp)], 7.60–7.63 [2H, m, 3,5-H (4-Ph)], 8.12–8.15 [2H, m, 2,6-H (4-Ph)], 10.35 (1H, br s, NH); δ_C (DMSO-d_6): 31.7, 35.4, 101.3, 114.2, 120.7, 126.5, 129.3, 134.5, 152.9, 154.3, 154.7, 158.3.

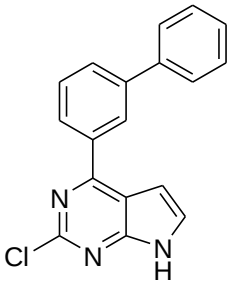
*4-(Biphenyl-4-yl)-2-chloro-7H-pyrrolo[2,3-d]pyrimidine (**5c**)*



Method A. Compound **5c** was synthesized and isolated according to the procedure described for the preparation of compound **5a** (Method A). The reaction time 3 h. Yield 12%, yellow solid, mp 254-255 ^{o}C.

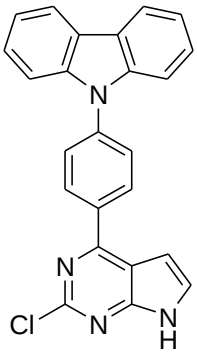
Method B. Compound **5c** was synthesized and isolated according to the procedure described for the preparation of compound **5a** (Method B). The reaction time 2 h. Yield 46%, yellow solid, mp 254-255 °C. [Found: C, 70.93; H, 4.11; N, 13.59. $C_{18}H_{12}ClN_3$ requires C, 70.71; H, 3.96; N, 13.74%]; UV (ethanol), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 225 ($2\times10^4$); 287 ($1.6\times10^4$); 328 ($1.5 \times 10^4$); ν_{max} (KBr) 3452 cm^{-1} (NH); δ_H ($CDCl_3$): 7.03 [H, dd, J^3 = 3.6 Hz, J^4 = 1.2 Hz, 5-H (pp)], 7.45–7.57 [3H, m, 3'-5'-H (4-biPh)], 7.75 [1H, dd, J^3 = 3.45 Hz, J^3 = 2.1 Hz, 6-H (pp)], 7.79–7.81 [2H, m, 2',6'-H (4-biPh)], 7.91–7.94 [2H, m, 3,5-H (4-biPh)], 8.28–8.30 [2H, m, 2,6-H (4-biPh)], 12.53 (1H, br s, NH); δ_C (DMSO-d_6 + two drops CF_3COOD): 101.0, 114.3, 120.7, 127.4, 127.7, 128.5, 128.9, 129.6, 129.9, 136.3, 139.9, 143.0, 152.9, 154.6, 157.8.

*4-(Biphenyl-3-yl)-2-chloro-7H-pyrrolo[2,3-d]pyrimidine (**5d**)*



Compound **5d** was synthesized and isolated according to the procedure described for the preparation of compound **5a** (Method B). The reaction time 1.5 h. Yield 68% (eluent for column chromatography chloroform:ethyl acetate (8:1)), yellowish solid, mp 184.6-185.0 °C. δ_H (DMSO-d_6): 6.99 [1H, k, J^3 = 3.6 Hz, J^4 = 1.8 Hz, 5-H (pp)], 7.42-7.56 [3H, m, 4, 2',6'-H (biPh)], 7.69-7.91 [4H, m, 6-H (pp), 3'-5'-H (biPh)], 7.88-7.91 [1H, m, 5-H (biPh)], 8.09-8.20 [1H, m, 6-H (biPh)], 8.31-8.33 [1H, m, 2-H (biPh)]; δ_C (DMSO-d_6): 101.3, 114.6, 127.5, 127.6, 128.6, 129.1, 129.7, 129.8, 129.9, 130.5, 137.9, 140.4, 141.7, 152.9, 154.8, 158.3; HRMS (ESI): MH^+, found 306.0793. $C_{18}H_{13}ClN_3$ requires 306.0793.

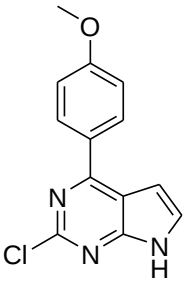
*4-[4-(9H-Carbazol-9-yl)phenyl]-2-chloro-7H-pyrrolo[2,3-d]pyrimidine (**5e**)*



Compound **5e** was synthesized and isolated according to the procedure described for the preparation of compound **5a** (Method B). 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%]; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 238 ($23.5 \times 10^4$), 256 ($10.8 \times 10^4$), 280 ($5.8 \times 10^4$), 291 ($6.3 \times 10^4$), 342 ($6.2 \times 10^4$); δ_H ($CDCl_3$): 7.01 [1H, dd, J^3 = 3.6 Hz, J^4 = 2.1 Hz, 5-H (pp)], 7.34-7.39 [2H,

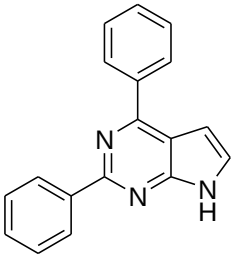
m, 3,5-H (Ph)], 7.46-7.58 [5H, m, 2,3,6,7-H (carb.), 6-H (pp)], 7.84 [2H, dm, *J* = 8.7 Hz, 1,8-H (carb.)], 8.21 [2H, dm, *J* = 7.5 Hz, 4,5-H (carb.)], 8.44 (2H, dm, *J* = 9 Hz, 2,6-H (Ph)], 9.49 (1H, s, NH); δ_C (DMSO-d_6): 101.3, 110.5, 114.4, 121.2, 121.4, 123.8, 127.1, 127.5, 129.8, 131.3, 135.9, 139.7, 140.4, 152.9, 154.9, 157.3.

*2-Chloro-4-(4-methoxyphenyl)-7H-pyrrolo[2,3-d]pyrimidine (**5f**)*



Compound **5f** was synthesized and isolated according to the procedure described for the preparation of compound **5a** (Method B). 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 (pp)], 7.11 [2H, dm, *J* = 9 Hz, 3,5-H (Ph)], 7.42 [1H, dd, J^3 = 3.8 Hz, J^3 = 2.4 Hz, 6-H (pp)], 8.19 [2H, dm, *J* = 8.7 Hz, 2,6-H (Ph)], 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.

*2,4-Diphenyl-7H-pyrrolo[2,3-d]pyrimidine (**6a**)*

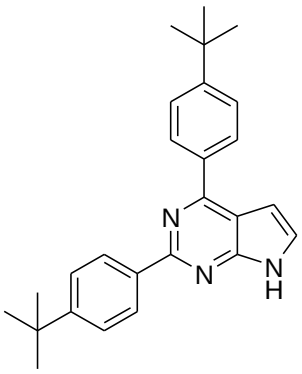


Method A. A solution of compounds **3** (0.2 g, 1.06 mmol) in anhydrous dioxane (5 ml) was flushed with argon and K_3PO_4 (2.79 g, 0.013 mol), phenylboronic acid (**4a**) (1.08 g, 8.85 mmol), 2.5 mol% $Pd(PPh_3)_2Cl_2$ were added under stirring and argon flow. The reaction mixture was stirred under

reflux for 6 hours. Then reaction mixture was cooled on standing and water (5 mL) was added to dissolve inorganic salts. The solid obtained was purified by column chromatography using chloroform as an eluent to give compound **6a** (0.07 g, 24%) as a yellowish solid, mp 210 °C.

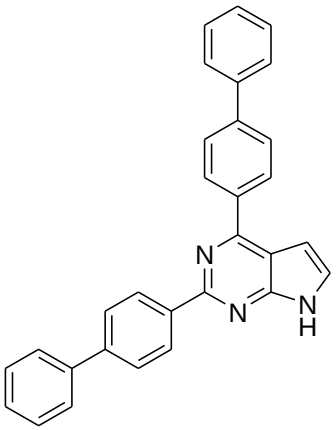
Method B. A solution of compound **3** (0.3 g, 1.60 mmol) in anhydrous dioxane (10 ml) was flushed with argon and 2.0 mol% $Pd(OAc)_2$ and 4.0 mol% (2-biphenyl)dicyclohexylphosphine were added under stirring and argon flow. After 10 min. phenylboronic acid (**4a**) (0.47 g, 3.83 mmol) and K_3PO_4 (1.62 g, 7.66 mmol) were added. The reaction mixture was stirred under reflux for 4 hours. 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 **6a** (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, $l \cdot mol^{-1} \cdot cm^{-1}$): 216 ($3\times10^4$), 264 ($4x10^4$), 316 ($1\times10^4$); δ_H ($CDCl_3$): 6.94 [1H, dd, J^3 = 3.75 Hz, J^4 = 1.8 Hz, 5-H (pp)], 7.39 [1H, dd, J^3 = 3.6 Hz, J^3 = 2.4 Hz, 6-H (pp)], 7.55-7.64 [6H, m, 2×3-5-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.

*2,4-Di(4-tert-butylphenyl)-7H-pyrrolo[2,3-d]pyrimidine (**6b**)*



Compound **6b** was synthesized and isolated according to the procedure described for the preparation of compound **6a** (Method B). The reaction time 15 min. Eluent for column chromatography – chloroform. Yield 48%, yellow solid, mp 265 °C. [Found: C, 81.54; H, 7.78; N, 10.82. $C_{26}H_{29}N_3$ requires C, 81.42; H, 7.62; N, 10.96%]; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 215 ($2.9x10^4$); 270 ($4.3\times10^4$); 327 ($1.2\times10^4$); ν_{max} (KBr) 3412 cm^{-1} (NH); δ_H (DMSO-d_6): 1.44 (9H, s, 2-C$(CH_3)_3$), 1.45 (9H, s, 4-C$(CH_3)_3$), 6.93 [1H, dd, J^3 = 3.6 Hz, J^4 = 1.8 Hz, 5-H (pp)], 7.36 (1H, dd, J^3 = 3.3 Hz, J^3= 2.4 Hz, 6-H (pp)], 7.61 [2H, dm, J = 8.7 Hz, 3,5-H (4-Ph)], 7.65 [2H, dm, J = 8.4 Hz, 3,5-H (2-Ph)], 8.29 [2H, dm, J = 8.7 Hz, 2,6-H (4-Ph)], 8.55 [2H, dm, J = 8.4 Hz, 2,6-H (2-Ph)], 11.19 (1H, br s, NH); δ_C (DMSO-d_6): 31.74, 31.81, 35.19, 35.29, 100.9, 113.6, 125.9, 126.4, 127.9, 128.5, 129.1, 136.3, 136.8, 152.9, 153.5, 154.4, 156.2, 157.1.

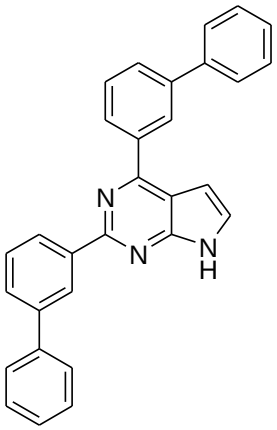
*2,4-Di(biphenyl-4-yl)-7H-pyrrolo[2,3-d]pyrimidine (**6c**)*



Compound **6c** was synthesized and isolated according to the procedure described for the preparation of compound **6a** (Method B). The reaction time 2

h. Eluent for column chromatography – chloroform. Yield 29%, yellow solid, mp 281 °C. [Found: C, 85.29; H, 5.13; N, 9.87. $C_{30}H_{21}N_3$ requires C, 85.08; H, 5.00; N, 9.92%]; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 217 ($5.5 \times 10^4$); 299 ($7.4 \times 10^4$); ν_{max} (KBr) 3435 cm^{-1} (NH); δ_H ($CDCl_3$): 7.02 [1H, dd, J^3 = 3.9 Hz, J^4 = 1.8 Hz, 5-H (pp)], 7.46–7.55 [7H, m, 6-H (pp), 2×3'-5'-H (2-biPh, 4-biPh)], 7.74–7.77 [m, 4H, 2×2',6'-H (2-biPh, 4-biPh)], 7.84 [2H, dm, J = 8.4 Hz, 3,5-H (4-biPh)], 7.89 [2H, dm, J = 8.4 Hz, 3,5-H (2-biPh)], 8.45 [2H, dm, J = 8.7 Hz, 2,6-H (4-biPh)], 8.75 [2H, dm, J = 8.7 Hz, 2,6-H (2-biPh)], 10.14 (1H, br s, NH); δ_C (DMSO-d_6+ two drops CF_3COOD): 101.4, 114.0, 127.4, 127.5, 127.8, 128.5, 128.7, 129.1, 129.6, 129.7, 129.8, 130.2, 136.6, 137.4, 140.1, 140.3, 142.3, 142.8, 154.1, 154.3, 155.2, 156.2.

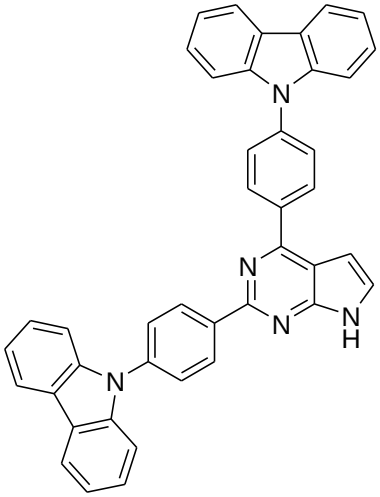
*2,4-Di(biphenyl-3-yl)-7H-pyrrolo[2,3-d]pyrimidine (**6d**)*



Compound **6d** was synthesized and isolated according to the procedure described for the preparation of compound **6a** (Method B). The reaction time 2.5 hrs. Eluent for column chromatography – chloroform. Yield 49%, yellowish solid, mp 226-227 °C. ν_{max} 3028 cm^{-1} (NH); UV (THF), λ_{max} (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 215 ($4.4 \times 10^4$), 258 ($6.8 \times 10^4$), 325 ($1.2 \times 10^4$); δ_H ($CDCl_3$): 6.96 [1H, dd, J^3 = 3.6 Hz, J^4 = 1.8 Hz, 5-H (pp)], 7.36-7.81 [15H, m, 6-H (pp), 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,

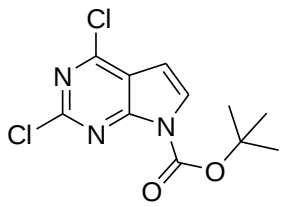
129.9, 130.0, 130.4; HRMS (ESI): MH^+, found 424.1800 $C_{30}H_{21}N_3$ requires 424.1808.

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



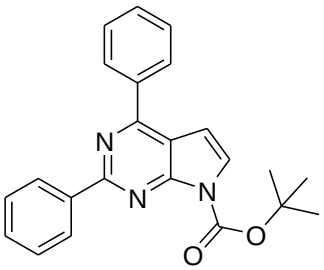
Compound **6e** was synthesized and isolated according to the procedure described for the preparation of compound **6a** (Method B). The reaction time 3 hours. Eluent for column chromatography – chloroform. Yield 63%, yellow solid, mp 310 °C (dec.). [Found: C, 83.96; H, 4.59; N, 11.72. $C_{42}H_{27}N_5$ requires C, 83.84; H, 4.52; N, 11.64%]; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 265 ($1.9 \times 10^4$), 282 ($2.3 \times 10^4$), 293 ($2.9 \times 10^4$), 331 ($3.5 \times 10^4$), 341 ($3.7 \times 10^4$); ν_{max} (KBr) 3400 cm^{-1} (NH); δ_H (DMSO-d_6): 7.14 [1H, dd, J^3 = 3.6 Hz, J^4 = 1.8 Hz, 5-H (pp)], 7.33–7.39 [4H, m, 2×3,5-H (2-Ph, 4-Ph)], 7.48–7.63 [8H, m, 2×2,3,6,7-H (2-carb., 4-carb.)], 7.82 [1H, t, *J* = 2.7 Hz, 6-H (pp)], 7.87 [2H, d, *J* = 8.4 Hz, 1,8-H (4-carb.)], 7.95 [2H, d, *J* = 8.4 Hz, 1,8-H (2-carb.)], 8.29–8.34 [4H, m, 2×4,5-H (2-carb., 4-carb.)], 8.71 [2H, d, *J* = 8.7 Hz, 2,6-H (4-Ph)], 8.91 [2H, d, *J* = 8.4 Hz, 2,6-H (2-Ph)], 12.49 (1H, br s, NH); δ_C (DMSO-d_6): 101.1, 110.6, 114.1, 121.0, 121.1, 121.3, 121.4, 123.6, 123.7, 127.1, 127.2, 127.3, 127.5, 127.6, 129.5, 129.9, 131.2, 137.7, 138.3, 138.8, 139.3, 140.6, 140.7, 154.6, 155.3, 156.4.

*tert-Butyl 2,4-dichloro-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**7**)*



To a solution of compound **3** (0.4 g, 2.13 mmol) in anhydrous CH_2Cl_2 (10 mL), DIPEA (0.56 mL, 2.55 mmol), DMAP (0.052 g, 0.43 mmol) and Boc_2O (0.7 g, 3.19 mmol) were added. The reaction mixture was stirred under reflux for 10 min. The solvent was evaporated under reduced pressure and the obtained solid was purified by column chromatography (eluent-chloroform) to give 0.41 g (67%) of compound 4, mp 136–136.5 °C (from 2-propanol); [Found: C, 46.21; H, 3.94; N, 14.55. $C_{11}H_{11}Cl_2N_3O_2$ requires : C, 45.85; H, 3.85; N, 14.58%]; ν_{max} (KBr) 1750 cm^{-1} (CO); δ_H ($CDCl_3$): 1.72 (9H, s, $C(CH_3)_3$), 6.68 [1H, d, *J* = 3.9 Hz, 5-H (pp)], 7.73 [1H, d, *J* = 3.9 Hz, 6-H (pp)]; δ_C (DMSO-d_6): 28.2, 86.7, 102.9, 118.9, 128.4, 146.9, 153.1, 153.6, 154.6.

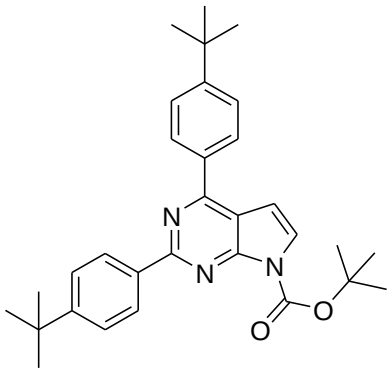
*tert-Butyl 2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**8a**)*



A solution of compound **7** (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 (**4a**) (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 hours. 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 **8a** (0.10 g, 78%) as a colourless solid, mp 121-122.4 °C (from 2-propanol). UV (THF), λ_{max} (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 213 ($4\times10^4$), 263 ($4\times10^4$), 303 ($2\times10^4$); δ_H ($CDCl_3$): 1.81 (9H, s, *tert*-Boc), 6.93 [1H, d, *J* = 4.2 Hz, 5-H (pp)], 7.52-7.63 [6H, m, 2×3-5-H (2-Ph, 4-Ph)], 7.81 [1H, d, *J* = 4.2 Hz, 6-H (pp)], 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.

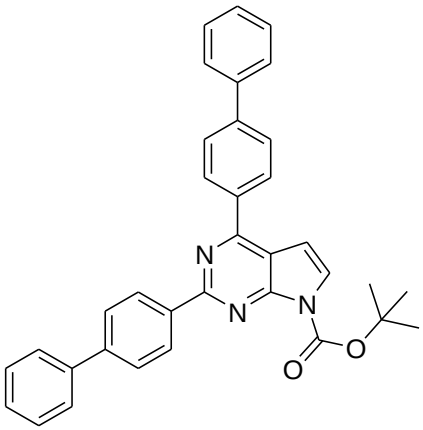
*tert-Butyl 2,4-bis(4-tert-butylphenyl)-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**8b**)*



Compound **8b** was synthesized and isolated according to the procedure described for the preparation of compound **8a**. Eluent for column chromatography – hexane:benzene (1:2). The reaction time 2 hours. Yield 76%, colourless solid, mp 190-192 °C (from 2-propanol). [Found: C, 76.52; H, 7.94; N, 8.88. $C_{31}H_{37}N_3O_2$ requires : C, 76.98; H, 7.71; N, 8.69%]; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 213 ($3.8\times10^4$), 274 ($3.8\times10^4$), 307 ($2.3\times10^4$), 325 ($1.7\times10^4$); ν_{max} (KBr) 1736 cm^{-1} (CO); δ_H ($CDCl_3$): 1.42 (9H, s, 4-C(CH_3)$_3$), 1.44 (9H, s, 2-C(CH_3)$_3$), 1.82 (9H, s, N_7-C(CH_3)$_3$), 6.93 [1H, d, *J* = 4.2 Hz, 5-H (pp)], 7.55 [2H, dm, *J* = 8.7 Hz, 3,5-H (4-Ph)], 7.64 [2H, dm, *J* = 8.7 Hz, 3,5-H (2-Ph)], 7.78 [1H, d, *J* = 4.2 Hz, 6-H (pp)], 8.17 [2H, dm, *J* = 8.7 Hz, 2,6-H (4-Ph)], 8.64 [2H, dm, *J* = 8.7 Hz, 2,6-H (2-Ph)]; δ_C ($CDCl_3$): 28.5, 31.5, 31.6,

35.1, 35.2, 85.0, 104.5, 116.1, 125.6, 126.1, 127.2, 128.3, 129.0, 135.6, 136.2, 148.8, 153.5, 153.8, 154.1, 158.1, 160.0.

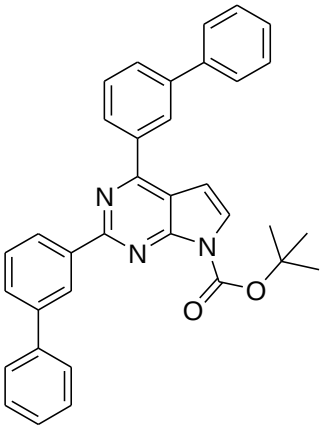
tert-Butyl 2,4-di(biphenyl-4-yl)-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate ***(8c)***



Compound **8c** was synthesized and isolated according to the procedure described for the preparation of compound **8a**. The reaction time 2 hours. 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 (pp)], 7.41-7.89 [15H, m, 6-H, 2×3,5,2‘-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.

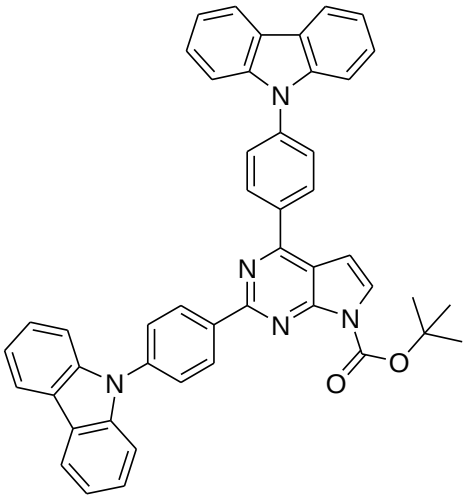
tert-Butyl 2,4-di(biphenyl-3-yl)-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate

(8d)



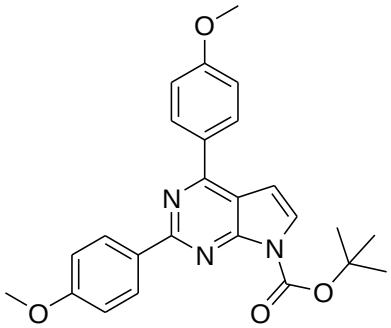
Compound **8d** was synthesized and isolated according to the procedure described for the preparation of compound **8a**. The reaction time 3 hrs. Yield 42%, colourless solid, mp 139-139.6 °C (from 2-propanol). UV (THF), λ_{max} (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 256 ($6.3 \times 10^4$), 305 ($2 \times 10^4$); δ_H ($CDCl_3$): 1.82 (9H, s, *tert*-Boc), 6.97 [1H, d, *J* = 4.2 Hz, 5-H (pp)], 7.39-7.81 [14H, m, 2×4,5,2‘-6‘-H (2-biPh, 4-biPh)], 7.85 [1H, d, *J* = 4.2 Hz, 6-H (pp)], 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

*tert-Butyl 2,4-di(4-(9H-carbazol-9-yl)phenyl)-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**8e**)*



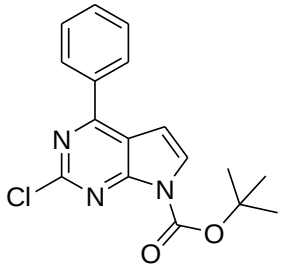
Compound **8e** was synthesized and isolated according to the procedure described for the preparation of compound **8a**, 4.8 equivalents of boronic acid and 9.6 equivalents of K_3PO_4 were used. The reaction time 4 hours. Eluent for column chromatography – benzene. Yield 86%, yellow solid, mp 230 °C (dec.) (from 2-propanol). [Found: C, 80.58; H, 5.17; N, 9.93. $C_{47}H_{35}N_5O_2$ requires : C, 80.43; H, 5.03; N, 9.98%]; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 236 ($7.3\times10^4$), 255 ($4.4\times10^4$), 293 ($2.5\times10^4$), 342 ($3\times10^4$); ν_{max} (KBr) 1738 cm^{-1} (CO); δ_H ($CDCl_3$): 1.87 (9H, s, $C(CH_3)_3$), 7.07 [1H, d, *J* = 4.2 Hz, 5-H (pp)], 7.34–7.63 [m, 12H, 2×3,5-H (2-Ph, 4-Ph), 2×2,3,6,7-H (2-carb., 4-carb.)], 7.81 [2H, d, *J* = 8.4 Hz, 1,8-H (4-carb.)], 7.87–7.92 [3H, m, 6-H (pp), 1,8-H (2-carb.)], 8.21–8.23 [4H, m, 2×4,5-H (2-carb., 4-carb.)], 8.53 [2H, d, *J* = 8.4 Hz, 2,6-H (4-Ph)], 9.02 [2H, d, *J* = 8.7 Hz, 2,6-H (2-Ph)]; δ_C ($CDCl_3$): 28.5, 85.4, 104.2, 110.1, 110.2, 116.6, 120.4, 120.6, 120.64, 120.7, 123.8, 124.0, 126.3, 126.4, 127.1, 127.5, 128.2, 130.2, 130.8, 137.0, 137.7, 139.7, 140.0, 140.9, 141.0, 148.4, 154.4, 157.4, 159.3.

*tert-Butyl 2,4-di(4-methoxyphenyl)-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**8f**)*



Compound **8f** was synthesized and isolated according to the procedure described for the preparation of compound **8a**. The reaction time 1 hour. Yield 94%, colourless solid, mp 129.5-130 °C (from 2-propanol). [Found: C, 69.91; H, 5.99; N, 9.71. $C_{25}H_{25}N_3O_4$ requires : C, 69.59; H, 5.84; N, 9.74%]; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 215 ($4.4 \times 10^4$), 294 ($5.0 \times 10^4$), 327 ($2.4 \times 10^4$); ν_{max} (KBr) 1735 cm^{-1} (CO); δ_H ($CDCl_3$): 1.80 (9H, s, $C(CH_3)_3$), 3.93 (3H, s, 4-OCH_3), 3.95 (3H, s, 2-OCH_3), 6.89 [1H, d, *J* = 4 Hz, 5-H (pp)], 7.05 [2H, dm, *J* = 9 Hz, 3,5-H (4-Ph)], 7.13 [2H, dm, *J* = 9 Hz, 3,5-H (2-Ph)], 7.74 [1H, d, *J* = 4 Hz, 6-H (pp)], 8.20 [2H, dm, *J* = 9 Hz, 2,6-H (4-Ph)], 8.67 [2H, dm, *J* = 9 Hz, 2,6-H (2-Ph)]; δ_C ($CDCl_3$): 28.5, 55.6, 55.7, 84.9, 104.5, 113.9, 114.4, 115.4, 126.8, 130.1, 130.8, 131.0, 131.6, 148.7, 154.3, 157.7, 159.7, 161.6, 161.8.

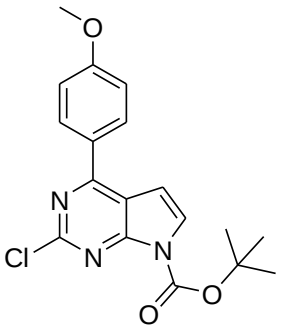
*tert-Butyl 2-chloro-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**9a**)*



To a solution of compound **5a** (0.42 g, 1.83 mmol) in anhydrous CH_2Cl_2 (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 CH_2Cl_2 was evaporated, the obtained residue was purified

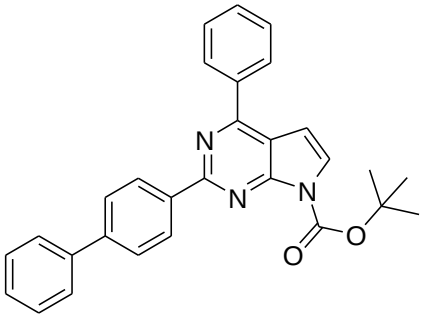
by column chromatography using chloroform as an eluent to give compound **9a** (0.37 g, 61%) as a colourless solid, mp 76-77 °C (from 2-propanol). δ_H ($CDCl_3$): 1.74 (9H, s, *tert*-Boc), 6.89 [1H, d, *J* = 4.2 Hz, 5-H (pp)], 7.58-7.61 [3H, m, 3-5-H (Ph)], 7.74 [1H, d, *J* = 4.2 Hz, 6-H (pp)], 8.06-8.09 [2H, m, 2,6-H (Ph)]; 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.

*tert-Butyl 2-chloro-4-(4-methoxyphenyl)-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**9f**)*



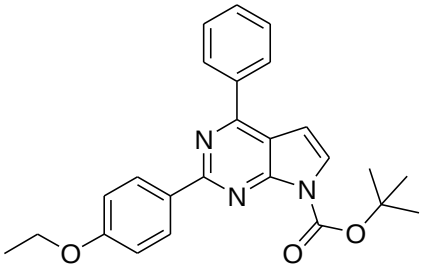
To a solution of compound **5f** (0.18 g, 0.69 mmol) in anhydrous CH_2Cl_2 (5 mL) DIPEA (0.14 ml, 0.83 mmol), DMAP (0,017 g, 0.14 mmol) and Boc_2O (0.23 g, 1.04 mmol) were added. The reaction mixture was stirred at room temperature for 0.5 h. Then CH_2Cl_2 was evaporated, the obtained residue was purified by column chromatography using chloroform as an eluent to give compound **9f** (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 (pp)], 7.09 [2H, dm, *J* = 9 Hz, 3,5-H (Ph)], 7.71 [1H, d, *J* = 4.2 Hz, 6-H (pp)], 8.09 [2H, dm, *J* = 9 Hz, 2,6-H (Ph)]; 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.

*tert-Butyl 2-(biphenyl-4-yl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**10**)*



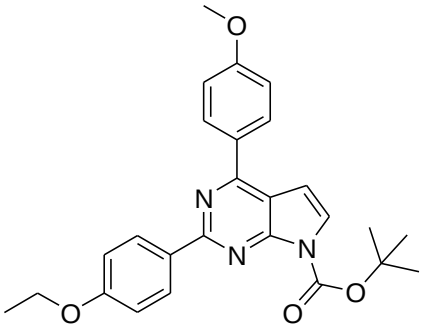
A solution of compound **9a** (0.14 g, 0.42 mmol) in an anhydrous dioxane (10 ml) was flushed with argon and 2.0 mol% $Pd(OAc)_2$ and 4.0 mol% (2-biphenyl)dicyclohexylphosphine were added under stirring and argon flow. After 10 min. 4-biphenylboronic acid (**4c**) (0.10 g, 0.51 mmol) and K_3PO_4 (0.22 g, 1.02 mmol) were added. The reaction mixture was stirred under reflux for 7 hours. 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 **10** (0.145 g, 76%) as a colourless solid, mp 150-150.2 °C (from 2-propanol); UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 225 ($1.5 \times 10^4$), 288 ($1.6 \times 10^4$), 317 ($1.7 \times 10^4$); δ_H ($CDCl_3$): 1.83 (9H, s, *tert*-Boc), 6.94 [1H, d, *J* = 4.2 Hz, 5-H (pp)], 7.49-7.79 [10H, m, 3,5,2‘-6‘-H (4-biPh), 3-5-H (Ph)], 7.81 [1H, d, *J* = 3.9 Hz, 6-H (pp)], 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.

*tert-Butyl 2-(4-ethoxyphenyl)-4-phenyl-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 **10**. Eluent for column chromatography – chloroform. The reaction time 4 hours. Yield 79%, yellowish solid, mp 141-141.9 °C (from 2-propanol); UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 227 ($1.4 \times 10^4$), 252 ($1.0 \times 10^4$), 288 ($1.4 \times 10^4$), 308 ($1.3 \times 10^4$); 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 (pp)], 7.05 [2H, dm, *J* = 9 Hz, 3,5-H (2-Ph)], 7.58-7.61 [3H, m, 3-5-H (4-Ph)], 7.75 [1H, d, *J* = 4.2 Hz, 6-H (pp)], 8.19-8.22 [2H, m, 2,6-H (4-Ph)], 8.68 [2H, dm, *J* = 9 Hz, 2,6-H (2-Ph)]; 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.

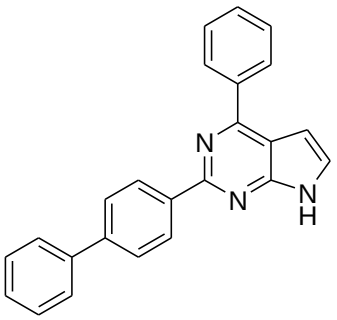
*tert-Butyl 2-(4-ethoxyphenyl)-4-(4-methoxyphenyl)-7H-pyrrolo[2,3-d]pyrimidine-7-carboxylate (**12**)*



Compound **12** was synthesized and isolated according to the procedure described for the preparation of compound **10**. Eluent for column chromatography – chloroform. The reaction time - 6 hours. Yield 69%,

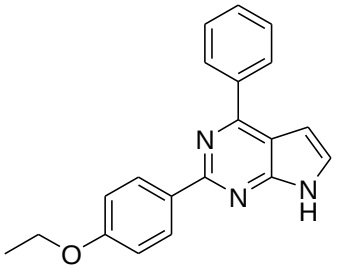
colourless solid, mp 145-145.5 °C (from 2-propanol); UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 227 ($1.5 \times 10^4$), 248 ($0.7 \times 10^4$), 294 ($2.4 \times 10^4$), 329 ($1.1 \times 10^4$); δ_H ($CDCl_3$): 1.49 (3H, t, *J* = 7.2 Hz, Me), 1.79 (9H, s, *tert*-Boc), 3.95 (3H, s, OCH_3), 4.16 (2H, q, *J* = 6.9 Hz, CH_2O), 6.88 [1H, d, *J* = 3.9 Hz, 5-H (pp)], 7.03 [2H, dm, *J* = 9 Hz, 3,5-H (2-Ph)], 7.13 [2H, dm, *J* = 8.7 Hz, 3,5-H (4-Ph)], 7.73 [1H, d, *J* = 4.2 Hz, 6-H (pp)], 8.20 [2H, dm, *J* = 9 Hz, 2,6-H (4-Ph)], 8.66 [2H, dm, *J* = 9 Hz, 2,6-H (2-Ph)]; 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.

2-*(Biphenyl-4-yl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (**13**)*



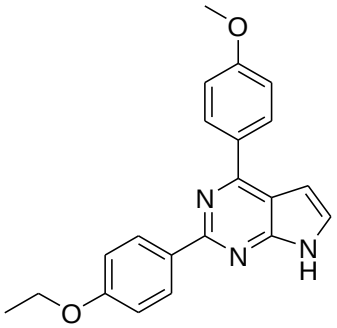
To a solution of compound **10** (0.145 g, 0.32 mmol) in a mixture of acetone (15 mL) and water (5 mL) concd. hydrochloric acid (0.08 mL, 0.97 mmol) was added. The reaction mixture was stirred under reflux for 70 hours, then cooled to room temperature, the precipitate was filtered off to give compound **13** (0.08 g, 73%) as a colourless solid, mp 278.2-278.9 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 226 ($1.2 \times 10^4$), 286 ($2.1 \times 10^4$), 321 ($1.3 \times 10^4$); δ_H (DMSO-d_6): 6.95 [1H, dd, J^3 = 3.3 Hz, J^4 = 1.5 Hz, 5-H (pp)], 7.54-7.89 [11H, m, 6-H (pp), 3,5, 2‘-6‘-H (2-biPh), 3-5-H (4-Ph)], 8.34-8.36 [2H, m, 2,6-H (4-Ph)], 8.66 [2H, dm, *J* = 8.4 Hz, 2,6-H (2-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.

*2-(4-Ethoxyphenyl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (**14**)*



Compound **14** was synthesized and isolated according to the procedure described for the preparation of compound **13**. The reaction time - 7 days. Yield 80%, colourless solid, mp 275-276 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 219 ($0.6 \times 10^4$), 231 ($0.8 \times 10^4$), 280 ($1.6 \times 10^4$), 336 ($0.5 \times 10^4$); 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 (pp)], 7.08 [2H, dm, *J* = 9.0 Hz, 3,5-H (2-Ph)], 7.59-7.65 [4H, m, 6-H (pp), 3-5-H (4-Ph)], 8.31 [2H, dm, *J* = 7.9 Hz, 2,6-H (4-Ph)], 8.49 [2H, dm, *J* = 9.0 Hz, 2,6-H (2-Ph)], 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.

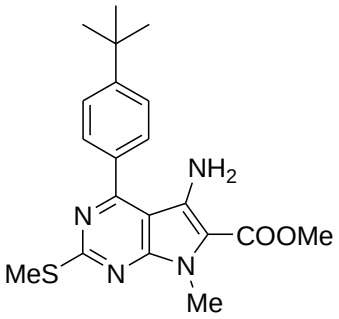
*2-(4-Ethoxyphenyl)-4-(4-methoxyphenyl)-7H-pyrrolo[2,3-d]pyrimidine (**15**)*



To a solution of compound **12** (0.17 g, 0.38 mmol) in an anhydrous CH_2Cl_2 (10 mL) TFA (6.3 mL) was added. The reaction mixture was stirred at room temperature for 5 min. Then CH_2Cl_2 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 **15** (0.10 g, 77%) as a yellowish solid, mp 225.3-226.3 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-}$

$^{1}\cdot cm^{-1}$): 224 (1.2 $\times 10^4$), 287 (2.3×10^4), 338 (0.7×10^4); 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 (pp)], 7.08 [2H, dm, *J* = 9 Hz, 3,5-H (2-Ph)], 7.18 [2H, dm, *J* = 8.7 Hz, 3,5-H (4-Ph)], 7.60 [1H, dd, J^3 = 3.5 Hz, J^3 = 2.1 Hz, 6-H (pp)], 8.32 [2H, dm, *J* = 8.7 Hz, 2,6-H (4-Ph)], 8.48 [2H, dm, *J* = 9 Hz, 2,6-H (2-Ph)], 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.

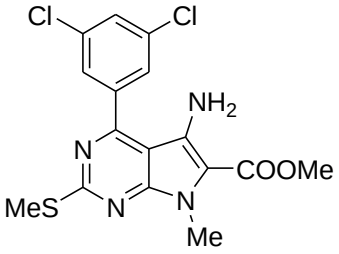
*Methyl 5-amino-4-(4-tert-butylphenyl)-7-methyl-2-methylthio-7H-pyrrolo[2,3-d]pyrimidine-6-carboxylate (**17**)*



A solution of compound **16** [134] (0.15 g, 0.52 mmol) in anhydrous dioxane (5 ml) was flushed with argon, and 4-*tert*-butylphenylboronic acid (**4b**) (0.12 g, 0.68 mmol), 2 mol% $Pd(OAc)_2$, 4 mol% (2-biphenyl)dicyclohexylphosphine, and K_3PO_4 (0.29 g, 1.37 mmol) were added under stirring and argon flow. The reaction mixture was refluxed under argon for 5 h. Then the dioxane was evaporated to dryness and water was added to the residue. The obtained solution was extracted with benzene, and the organic layer dried with Na_2SO_4, filtered, and the solvents evaporated to dryness. The obtained solid was purified by column chromatography (eluent – benzene) to give compound **17** (0.16 g, 80%) as yellow solid, mp 153-155°C. [Found: C, 62.66; H, 6.39; N, 14.51. $C_{20}H_{24}N_4O_2S$ requires: C, 62.48; H, 6.29; N, 14.57%]; ν_{max} (KBr): 3453, 3350 (NH_2), 1667 (CO) cm^{-1}; δ_H ($CDCl_3$): 1.40 (9H, s, *t*-Bu), 2.69 (3H, s, SCH_3), 3.96 (3H, s, NCH_3), 3.99 (3H, s, OCH_3), 5.29

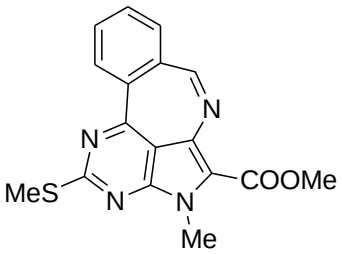
(2H, br. s, NH_2), 7.60 [(2H, d, *J* = 8.1, 3,5-H (Ph)], 7.76 [(2H, d, *J* = 8.1, 2,6-H (Ph)]; δ_C ($CDCl_3$): 14.6, 31.1, 31.5, 35.2, 51.4, 103.5, 107.3, 125.4, 126.2, 129.0, 136.8, 151.3, 154.2, 161.8, 163.6, 168.6.

*Methyl 5-amino-4-(3,5-dichlorophenyl)-7-methyl-2-methylthio-7H-pyrrolo[2,3-d]pyrimidine-6-carboxylate (**18**)*



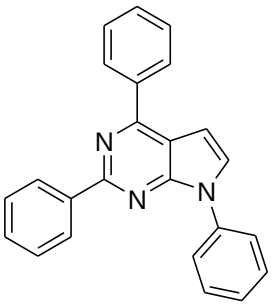
A solution of compound **16** [134] (0.1 g, 0.35 mmol) in anhydrous dioxane (5 ml) was flushed with argon, and 3,5-dichlorophenylboronic acid (**4h**) (0.09 g, 0.46 mmol), 2 mol% $Pd(OAc)_2$, 4 mol% (2-biphenyl)dicyclohexylphosphine, and K_3PO_4 (0.19 g, 0.9 mmol) were added. The reaction mixture was refluxed under argon for 3 h. Then the dioxane was evaporated to dryness and water was added to a residue. The obtained solution was extracted with benzene, the organic layer dried with Na_2SO_4 and filtered, and the filtrate concentrated to 1/3 of the initial volume. The solution was filtered through a layer of silica gel, and the silica gel was washed once with benzene. After the evaporation of solvents the residue was recrystallized to give compound **18** (0.089 g, 64%) as a yellow solid, mp 202–204°C (from 2-propanol). [Found: C, 48.63; H, 3.50; N, 14.32. $C_{16}H_{14}Cl_2N_4O_2S$ requires: C, 48.37; H, 3.55; N, 14.10%]; ν_{max} (KBr): 3377, 3269 (NH_2), 1679 (CO) cm^{-1}; δ_H ($CDCl_3$): 2.69 (3H, s, SCH_3), 3.97 (3H, s, NCH_3), 4.00 (3H, s, OCH_3), 4.77 (2H, br. s, NH_2), 7.56-7.57 [1H, dd, *J* = 1.8, *J* = 2.1, (Ph)], 7.70-7.71 [2H, dd, *J* = 1.8, *J* = 2.1, (Ph)]; δ_C ($CDCl_3$): 14.6, 31.1, 51.6, 103.5, 108.1, 127.7, 130.5, 135.6, 135.8, 140.3, 151.4, 158.8, 163.5, 169.0.

*Methyl 4-methyl-2-methylthio-4H-1,3,4,6-tetraazadibenzo[cd,f]azulene-5-carboxylate (**19**)*



Compound **19** was synthesized from compound **16** [134] and 2-formylphenylboronic acid (**4i**) according to the procedure described for compound **18**. The reaction time was 2 h. Yield 88%, mp 199–201°C. [Found: C, 60.22; H, 3.98; N, 16.39. $C_{17}H_{14}N_4O_2S$ requires: C, 60.34; H, 4.17; N, 16.56%]; ν_{max} (KBr): 1702 (CO) cm^{-1}; δ_H ($CDCl_3$): 2.70 (3H, s, SCH_3), 4.06 (3H, s, NCH_3), 4.07 (3H, s, OCH_3); 7.60–7.65 [3H, m, (Ph)], 8.14 (1H, s, CH), 8.88–8.91 [1H, m, (Ph)]; δ_C ($CDCl_3$): 14.7, 31.4, 52.7, 109.6, 120.7, 128.6, 129.0, 132.8, 133.1, 135.1, 136.0, 138.1, 151.7, 157.6, 160.0, 162.2, 169.8.

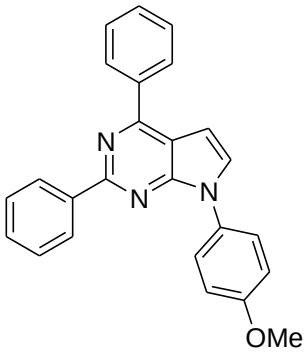
*2,4,7-Triphenyl-7H-pyrrolo[2,3-d]pyrimidine (**21**)*



A solution of compound **6a** (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 (**20a**) (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 hours and 1.0 mol% of CuI was added. Then every 2 hours 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 hours. Then after cooling to room temperature ethylacetate (5 mL) was added to the reaction mixture and resulting solution was filtered through a layer of silica gel eluting

with ethylacetate. 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 **21** (0.15 g, 94%) as a colourless solid, mp 155.2-155.8 °C. UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 256 ($4.2 \times 10^4$), 327 ($1.1 \times 10^4$); δ_H ($CDCl_3$): 7.04 [1H, d, *J* = 3.9 Hz, 5-H (pp)], 7.41-7.68 [10H, m, 6-H (pp), 3×3-5-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.

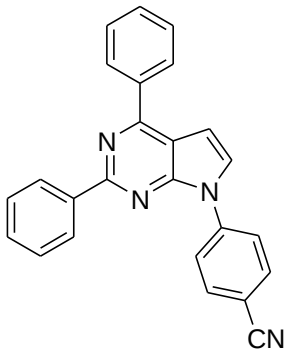
*7-(4-Methoxyphenyl)-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (**22**)*



Compound **22** was synthesized according to the procedure described for compound **21**. The reaction time – 12 hours. Addition of an additional CuI in an amount 1.0 mol% was started after 4 hours of reflux and repeated every 2 hours till the total amount CuI reached 5.0 mol%. The isolation and purification was carried out analogously **21** by column chromatography using hexane:ethyl acetate (20:1) as an eluent to give compound **22** (92%) as a colourless solid, mp 184.9-185.4 °C. UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 210 ($5.2 \times 10^4$), 259 ($4.5 \times 10^4$), 341 ($0.9 \times 10^4$); δ_H ($CDCl_3$): 3.95 (3H, s, CH_3O), 7.01 [d, 1H, *J* = 3.9 Hz, 5-H (pp)], 7.13-7.16 [m, 2H, 3,5-H (N_7-Ph)], 7.49-7.64 [m, 7H, 6-H (pp), 2×3-5-H (2-Ph, 4-Ph)], 7.79-7.83 [m, 2H, 2,6-H (N_7-Ph)], 8.31-8.35 [m, 2H, 2,6-H (4-Ph)], 8.66-8.69 [m, 2H, 2,6-H (2-Ph)]; δ_C ($CDCl_3$): 55.9,

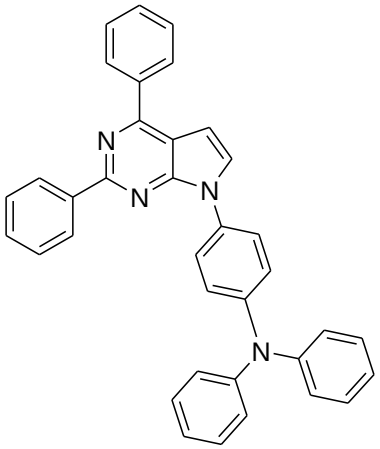
101.9, 114.8, 114.9, 125.5, 128.4, 128.6, 128.9, 129.2, 129.3, 129.9, 130.2, 131.2, 139.0, 139.2, 152.9, 157.9, 158.5, 158.6; HRMS (ESI): MH^+, found 378.1598. $C_{25}H_{19}N_3O$ requires 378.1601.

*7-(4-Cyanophenyl)-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (**23**)*



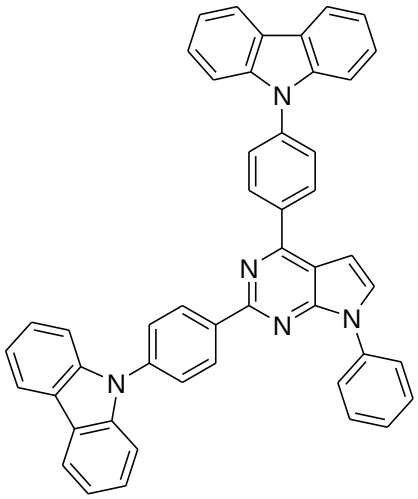
Compound **23** was synthesized according to the procedure described for compound **21**. The reaction time – 12 hours. Addition of an additional CuI in an amount 1.0 mol% was started after 2 hours of reflux and repeated every 2 hours till the total amount CuI reached 5.0 mol%. The isolation and purification was carried out analogously **21** by column chromatography using benzene as an eluent to give compound **23** (82%) as a yellowish solid, mp 209-210 °C. IR (KBr): 2227 (CN); UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 210 ($5.1 \times 10^4$), 265 ($5.4 \times 10^4$), 292 ($2.7 \times 10^4$), 326 ($1.6 \times 10^4$); δ_H ($CDCl_3$): 7.11 [1H, d, *J* = 3.6 Hz, 5-H (pp)], 7.51-7.66 [7H, m, 6-H (pp), 2×3-5-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.

*2,4-Diphenyl-7-[4-(diphenylamino)phenyl]-7H-pyrrolo[2,3-d]pyrimidine (**24**)*



Compound **24** was synthesized according to the procedure described for compound **21**. The reaction time – 22 hours. Addition of an additional CuI in an amount 1.0 mol% was started after 2 hours of reflux and repeated every 2 hours till the total amount CuI reached 6.0 mol%. The isolation and purification was carried out analogously **21** by column chromatography using hexane:ethyl acetate (27:1) as an eluent to give compound **24** (72%) as a yellowish solid, mp 166-166.2 °C. UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 210 ($8.1 \times 10^4$), 267 ($4.1 \times 10^4$), 308 ($4.0 \times 10^4$); δ_H ($CDCl_3$): 7.02 [1H, d, *J* = 3.6 Hz, 5-H (pp)], 7.08-7.18 [2H, m, 3,5-H (N_7Ph)], 7.23-7.39 [10H, m, 2×2‘-6‘-H ($N(Ph)_2$)], 7.48-7.68 [7H, m, 6-H, 2×3-5-H (2-Ph, 4-Ph)], 7.80-7.83 [2H, m, 2,6-H (N_7Ph)], 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.

*2,4-Di[4-(9H-carbazol-9-yl)phenyl]-7-phenyl-7H-pyrrolo[2,3-d]-pyrimidine (**25**)*

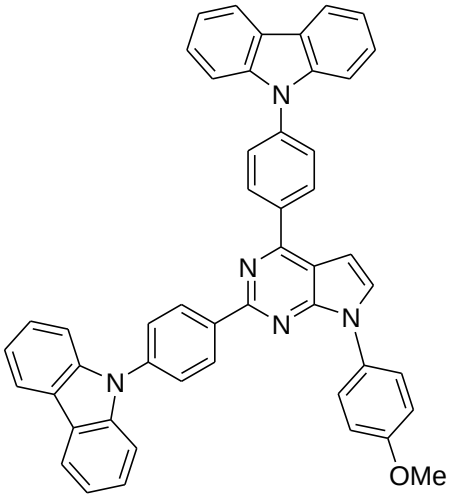


Method A. Compound **25** was synthesized according to the procedure described for compound **21**. The reaction time – 10 hours. Addition of an additional CuI in an amount 2.0 mol% was started after 2 hours of reflux and repeated after every 2 hours till the total amount CuI reached 5.0 mol%. The isolation and purification was carried out analogously **21** by column chromatography using hexane:ethyl acetate (10:1) as an eluent to give compound **25** as a yellow solid. Yield 85%, mp 267-268 °C.

Method B. A solution of compound **6e** (0.20 g, 0.33 mmol) in anhydrous toluene (5 ml) was flushed with argon and iodobenzene **20a** (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 hours. 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 **25** (0.11 g, 49%) as a yellow solid, mp 267-268 °C. UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 210 ($8.3 \times 10^4$), 236 ($9.6 \times 10^4$), 254 ($7.3 \times 10^4$), 281 ($4.0 \times 10^4$), 292 ($4.0 \times 10^4$), 342 ($4 \times 10^4$); δ_H ($CDCl_3$): 7.19 [1H, d,

J = 3.6 Hz, 5-H (pp)], 7.35-7.79 [18H, m, 6-H (pp), 2,6-H (N_7-Ph), 2×3,5-H (2-Ph, 4-Ph), 2×2,3,6,7-H (2-carb., 4-carb.)], 7.88-7.99 [2H, m, 1,8-H (4-carb.)], 7.99-8.02 [2H, m, 1,8-H (2-carb.)], 8.19-8.24 [4H, m, 2×4,5-H (2-carb., 4-carb.)], 8.63 [2H, dm, *J* = 8.7 Hz, 2,6-H (4-Ph)], 8.95 [2H, dm, J = 8.7 Hz, 2,6-H (2-Ph)]; 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.

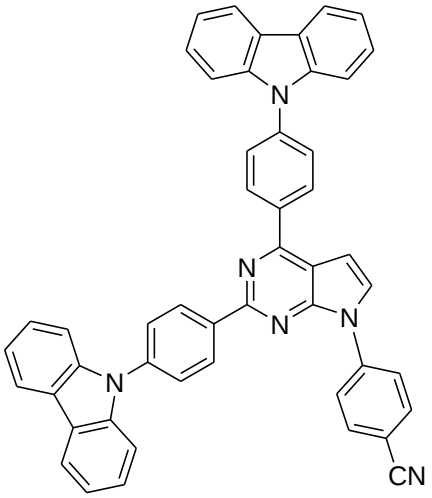
*2,4-Di[4-(9H-carbazol-9-yl)phenyl]-7-(4-methoxyphenyl)-7H-pyrrolo[2,3-d]pyrimidine (**26**)*



A solution of compound **6e** (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 (**20b**) (0.06 g, 0.25 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 hours 1.0 mol% of CuI was added to the reaction mixture till total amount of CuI reached 5.0 mol%. Then after 2 hours 2.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. Total reaction time was 19 hours. 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 **26** (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, $l \cdot mol^{-1} \cdot cm^{-1}$): 210 ($8.1 \times 10^4$), 237 ($9.8 \times 10^4$), 255 ($7.2 \times 10^4$), 292 ($4.5 \times 10^4$), 342 ($4.1 \times 10^4$); δ_H ($CDCl_3$): 3.97 (3H, s, CH_3O), 7.14 [1H, d, *J* = 3.6 Hz, 5-H (pp)], 7.18-7.21 [2H, m, 3,5-H (4-Ph)], 7.36-7.66 [13H, m, 6-H (pp), 3,5-H (N_7-Ph), 3,5-H (2-Ph), 2,3,6,7-H (2-carb.), 2,3,6,7-H (4-carb.)], 7.77 [2H, dm, *J* = 8.7 Hz, 2,6-H (N_7-Ph)], 7.84-7.91 [4H, m, 2×1,8-H (2-carb., 4-carb.)], 8.20-8.25 [4H, m, 2×4,5-H (2-carb., 4-carb.)], 8.62 [2H, dm, *J* = 8.4 Hz, 2,6-H (4-Ph)], 8.95 [2H, dm, *J* = 8.4 Hz, 2,6-H (2-Ph)]; 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.

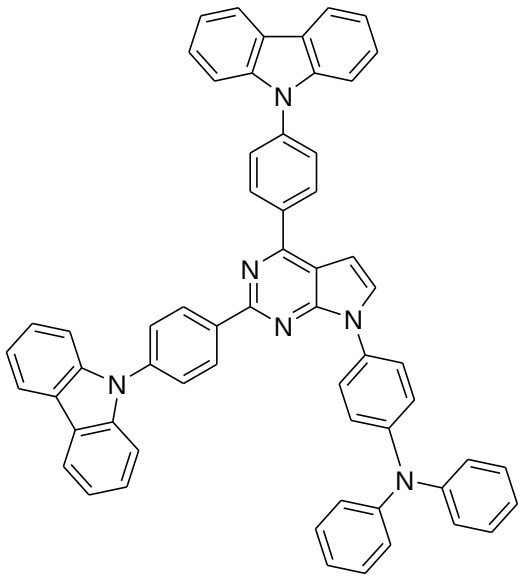
*2,4-Di[4-(9H-carbazol-9-yl)phenyl]- 7-(4-cyanophenyl)-7H-pyrrolo[2,3-d]pyrimidine (**27**)*



Compound **27** was synthesized according to the procedure described for compound **26**. Addition of an additional CuI in an amount 1.0 mol% was started after 2 hours of reflux and repeated after every 2 hours till the total amount of CuI reached 5.0 mol%. Then after 2 hours 2.0 mol% CuI and 10 mol% *trans*-1,2-diaminocyclohexane were added. Total reaction time – 22

hours. The isolation and purification was carried out analogously **26** by column chromatography using benzene as an eluent to give compound **27** (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, $l \cdot mol^{-1} \cdot cm^{-1}$): 210 ($12.2 \times 10^4$), 236 ($9.9 \times 10^4$), 256 ($7.7 \times 10^4$), 284 ($5.5 \times 10^4$), 291 ($5.3 \times 10^4$), 342 ($4.1 \times 10^4$); δ_H ($CDCl_3$): 7.23 [1H, d, *J* = 3.9 Hz, 5-H (pp)], 7.32-7.41 [4H, m, 2×3,5-H (2-Ph, 4-Ph)], 7.48-7.61 [8H, m, 2×2,3,6,7-H (2-carb., 4-carb.)], 7.72 [1H, d, *J* = 3.9 Hz, 6-H (pp)], 7.79-7.91 [4H, m, 2×1,8-H (2-carb., 4-carb.)], 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), 2×4,5-H (2-carb., 4-carb.)], 8.59 [2H, dm, *J* = 8.4 Hz, 2,6-H (4-Ph)], 8.94 [2H, dm, *J* = 8.7 Hz, 2,6-H (2-Ph)]; 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.

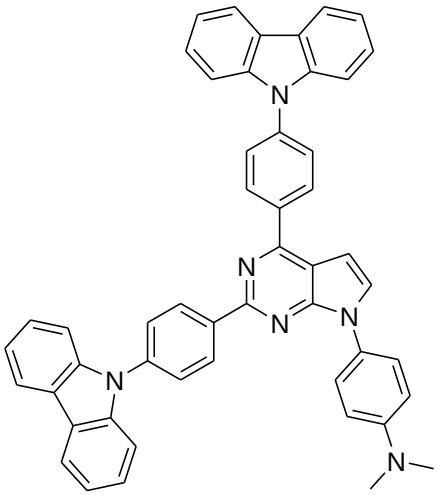
*2,4-Di[4-(9H-carbazol-9-yl)phenyl]-7-[4-(diphenylamino)phenyl]-7H-pyrrolo[2,3-d]pyrimidine (**28**)*



Compound **28** was synthesized according to the procedure described for compound **26**. Addition of an additional CuI in an amount 1.0 mol% was started after 2 hours of reflux and repeated after every 2 hours till the total amount of CuI reached 5.0 mol%. Then after 2 hours 1.0 mol% CuI and 10

mol% *trans*-1,2-diaminocyclohexane were added. Addition of an additional CuI in an amount 1.0 mol% was continued every 2 hours of reflux till the total amount of CuI reached 8.0 mol%. Total reaction time – 29 hours. The isolation and purification was carried out analogously **26** by column chromatography using benzene as an eluent to give compound **28** (59%) as a yellowish solid, mp 290-291 °C. UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 237 ($11.5 \times 10^4$), 255 ($7.5 \times 10^4$), 293 ($6.2 \times 10^4$), 341 ($6.4 \times 10^4$); δ_H ($CDCl_3$): 7.13-7.65 [25H, m, 5-H (pp), 2×3,5-H (2-Ph, 4-Ph), 2×2,3,6,7-H (2-carb., 4-carb.), 3,5-H (N_7-Ph), 2×2'-6'-H ($N(Ph)_2$)], 7.70 [1H, d, *J* = 3.6 Hz, 6-H (pp)], 7.78 [2H, dm, *J* = 8.4 Hz, 2,6-H (N_7-Ph)], 7.84-7.91 [4H, m, 2×1,8-H (2-carb., 4-carb.)], 8.20-8.25 [4H, m, 2×4,5-H (2-carb., 4-carb.)], 8.63 [2H, dm, *J* = 8.7 Hz, 2,6-H (4-Ph)], 8.95 [2H, dm, *J* = 8.7 Hz, 2,6-H (2-Ph)]; 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.

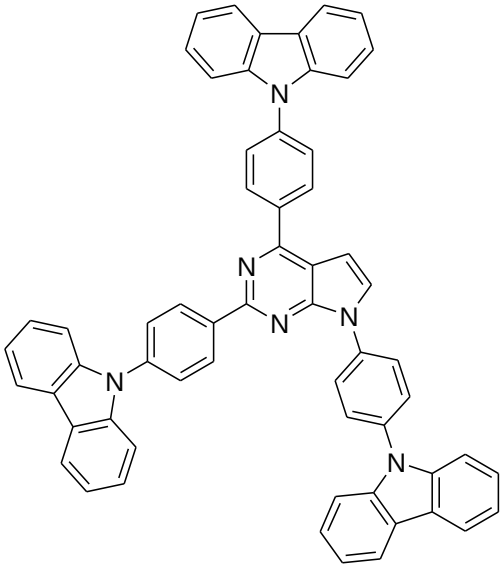
*2,4-Di[4-(9H-carbazol-9-yl)phenyl]-7-[4-(dimethylamino)phenyl]-7H-pyrrolo[2,3-d]pyrimidine (**29**)*



A solution of compound **6e** (0.1 g, 0.17 mmol) in anhydrous dioxane (3 ml) was flushed with argon and 1.0 mol% CuI, anhydrous K_3PO_4 (0.062 g, 0.29 mmol), 4-bromo-*N*,*N*-dimethylbenzeneamine (**20e**) (0.028 g, 0.14 mmol),

10.0 mol% *trans*-1,2-diaminocyclohexane were added under stirring and argon flow. Addition of portions 1.0 mol% CuI to the reaction mixture was continued every two hours till amount of CuI reached 5.0 mol%. Then after 2 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 10.0 mol%. Then after 2 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 14.0 mol%. Total reaction time was 32 hours. 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 chloroform and purified by column chromatography using hexane:ethyl acetate (16:1) as an eluent to give compound **29** (0.065 g, 65%) as a yellow solid, mp 281.4-282.6 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 239 ($4.8 \times 10^4$), 257 ($3.9 \times 10^4$), 293 ($2.7 \times 10^4$), 342 ($2.4 \times 10^4$); δ_H ($CDCl_3$): 3.11 (6H, s, N(CH_3)$_2$), 6.98 [2H, dm, *J* = 9.3 Hz, 3,5-H (N_7-Ph)], 7.12 [1H, d, *J* = 3.6 Hz, 5-H (pp)], 7.35-7.66 [13H, m, 6-H (pp), 2×7-9,12-14-H (2-carb., 4-carb.)], 7.75-7.79 [4H, m, 2×3,5-H (2-Ph, 4-Ph)], 7.89 [2H, dm, *J* = 8.7 Hz, 2,6-H (N_7-Ph)], 8.21 [2H, dm, *J* = 6.3 Hz, 10,11-H (4-carb.)], 8.23 [2H, dm, *J* = 6.6 Hz, 10,11-H (2-carb.)], 8.63 [2H, dm, *J* = 8.7 Hz, 2,6-H (4-Ph)], 8.95 [2H, dm, *J* = 9 Hz, 2,6-H (2-Ph)]; δ_C ($CDCl_3$): 40.9, 101.4, 110.2, 110.3, 113.0, 114.9, 120.3, 120.5, 120.6, 120.7, 123.8, 123.9, 125.5, 126.3, 126.4, 127.0, 127.3, 127.4, 129.9, 130.2, 130.8, 137.9, 138.3, 139.1, 139.6, 140.9, 141.0, 149.9, 153.0, 156.8, 157.7. HRMS (ESI): MH^+, found 721.3053. $C_{50}H_{36}N_6$ requires 721.3074.

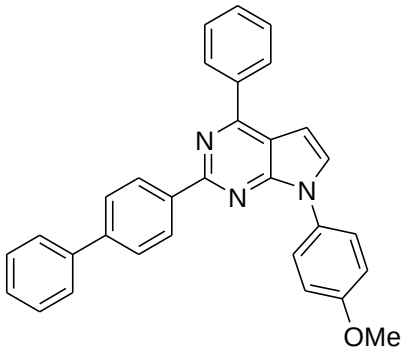
*2,4,7-Tri[4-(9H-carbazol-9-yl)phenyl]-7H-pyrrolo[2,3-d]pyrimidine (**30**)*



A solution of compound **6e** (0.1 g, 0.17 mmol) in anhydrous dioxane (3 ml) was flushed with argon and 5.0 mol% CuI, anhydrous K_3PO_4 (0.0.62 g, 0.29 mmol), 9-(4-bromophenyl)-9*H*-carbazole (**20f**) (0.045 g, 0.14 mmol), 10.0 mol% *trans*-1,2-diaminocyclohexane were added under stirring and argon flow. Then after 10 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 10.0 mol%. Then after 2 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 15.0 mol%. Total reaction time was 35 hours. 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 chloroform and purified by column chromatography using hexane→hexane:ethyl acetate as an eluent to give compound **30** (0.042 g, 59%) as a colourless solid, mp 326.8-327.7 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 245 ($5.3 \times 10^4$), 282 ($2.7 \times 10^4$), 292 ($3.3 \times 10^4$), 329 ($2.1 \times 10^4$); δ_H ($CDCl_3$): 7.26 [1H, d, *J* = 3.9 Hz, 5-H (pp)], 7.35-7.64 [18H, m, 3×7-9,12-14-H (2-carb., 4-carb., N_7-carb.), 7.80-7.94 [7H, m, 6-H (pp), 3×10,11 (2-carb., 4-carb., N_7-carb.)], 8.19-8.28 [8H, m, 2,6-H (N_7-Ph), 3×3,5-

H (2-Ph, 4-Ph, N_7-Ph)], 8.65 [2H, dm, *J* = 8.4 Hz, 2,6-H (4-Ph)], 9.00 [2H, dm, *J* = 8.4 Hz, 2,6-H (2-Ph)]; δ_C ($CDCl_3$): 103.1, 109.9, 110.1, 110.2, 115.4, 120.4, 120.5, 120.61, 120.62, 120.73, 120.74, 123.82, 123.83, 123.9, 125.3, 126.3, 126.4, 126.43, 127.1, 127.5, 128.4, 129.4, 130.1, 130.9, 136.6, 136.8, 137.1, 137.5, 139.6, 140.0, 140.8, 140.9, 141.1, 153.1, 157.3, 158.2. HRMS (ESI): MH^+, found 843.3189. $C_{60}H_{38}N_6$ requires 843.3230.

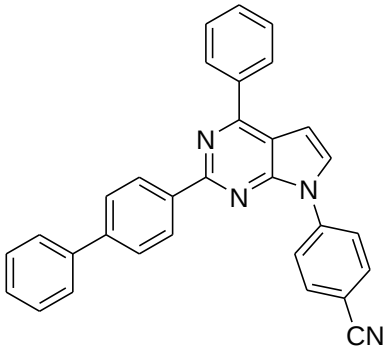
2-(Biphenyl-4-yl)-7-(4-methoxyphenyl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine ***(31)***



Compound **31** was synthesized according to the procedure described for compound **21**. The reaction time – 11 hours. Addition of an additional CuI in an amount 1.0 mol% was started after 4 hours of reflux and repeated after every 2 hours till the total amount CuI reached 5.0 mol%. The isolation and purification was carried out analogously **21** by column chromatography using hexane:ethyl acetate (8:1) as an eluent to give compound **31** (93%) as a colourless solid, mp 178.8-179.9 °C. UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 242 ($1.4 \times 10^4$), 260 ($1.8 \times 10^4$), 297 ($2.1 \times 10^4$), 344 ($0.8 \times 10^4$); δ_H (DMSO-d_6): 3.89 (3H, s, CH_3O), 7.17 [1H, d, *J* = 3.9 Hz, 5-H (pp)], 7.22 [2H, dm, *J* = 9 Hz, 3,5-H (N_7-Ph)], 7.39-7.91 [12H, m, 6-H (pp), 3,5,2‘-6‘-H (2-biPh), 3-5-H (4-Ph), 2,6-H (N_7-Ph)], 8.06 [1H, d, *J* = 3.6 Hz, 6-H (pp)], 8.34-8.37 [2H, m, 2,6-H (4-Ph)], 8.62 [2H, dm, *J* = 8.4 Hz, 2,6-H (2-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.

2-(Biphenyl-4-yl)- 7-(4-cyanophenyl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine

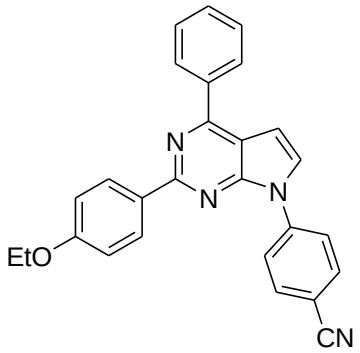
(32)



A solution of compound **13** (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 (**20c**) (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 hours 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 hours. 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 **32** (0.051 g, 95%) as a yellowish solid, mp 222-222.7 °C. UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 280 ($2.9 \times 10^4$), 332 ($1.3 \times 10^4$); δ_H (DMSO-d_6): 7.26 [1H, d, *J* = 3.9 Hz, 5-H (pp)], 7.43-7.87 [10H, m, 6-H (pp), 3,5,2‘-6‘-H (2-biPh), 3-5-H (4-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 (pp)], 8.31-8.39 [4H, m, 2,6-H (4-Ph), 3,5-H (N_7-Ph)], 8.63 [2H, dm, *J* = 8.7 Hz, 2,6-H (2-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,

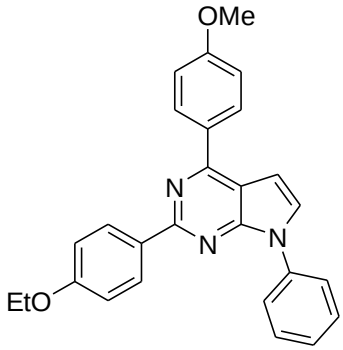
153.2, 157.6, 157.7, 167.7; HRMS (ESI): MH^+, found 449.1758. $C_{31}H_{20}N_4$ requires 449.1761.

*7-(4-Cyanophenyl)-2-(4-ethoxyphenyl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (**33**)*



Compound **33** was synthesized according to the procedure described for compound **21**. The reaction time – 6 hours. Addition of an additional CuI in an amount 1.0 mol% was started after 1 hour of reflux and repeated after 2 hours till the total amount CuI reached 3.0 mol%. The isolation and purification was carried out analogously **21** by column chromatography using hexane:ethyl acetate (27:1) as an eluent to give compound **33** (90%) as a colourless solid, mp 206.3-206.8 °C (from 2-PrOH-EtOAc). UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 235 ($1.1 \times 10^4$), 275 ($2.7 \times 10^4$), 324 ($0.9 \times 10^4$); 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 (pp), 3,5-H (2-Ph)], 7.61-7.62 [4H, m, 6-H (pp), 3-5-H (4-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 (4-Ph)], 8.1 [2H, dm, *J* = 9.0 Hz, 2,6-H (2-Ph)]; 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.

*2-(4-Ethoxyphenyl)-4-(4-methoxyphenyl)-7-phenyl-7H-pyrrolo[2,3-d]pyrimidine (**34**)*

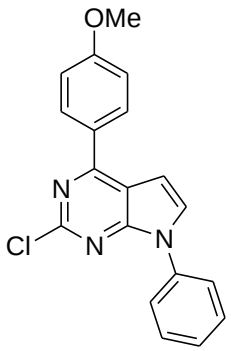


Method A. Compound **34** was synthesized according to the procedure described for compound **21**. The reaction time – 9.5 hours. Addition of an additional CuI in an amount 1.0 mol% was started after 1 hour of reflux and repeated after every 2 hours till the total amount CuI reached 5.0 mol%. The isolation and purification was carried out analogously **21** by column chromatography using CH_2Cl_2 as an eluent to give compound **34** (0.05 g, 99%) as a colourless solid, mp 188.3-189.8 °C.

Method B. A solution of compound **35** (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 hours and 0.3 equiv. of 4-ethoxyphenylboronic acid and 0.6 eq of K_3PO_4 were added additionally. Total reaction time was 20 hours. 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 CH_2Cl_2 to give compound **34** (0.04 g, 64%) as a colourless solid, mp 188.3-189.8 °C. UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 291 ($2.0 \times 10^4$), 330 ($0.7 \times 10^4$); 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 (pp)],

7.04 [2H, dm, *J* = 9 Hz, 3,5-H (2-Ph)], 7.15 [2H, dm, *J* = 9 Hz, 3,5-H (4-Ph)], 7.40-7.43 [1H, m, 4-H (N_7-Ph)], 7.55 [1H, d, *J* = 3.9 Hz, 6-H (pp)], 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-Ph)], 8.63 [2H, dm, *J* = 9 Hz, 2,6-H (2-Ph)]; 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.

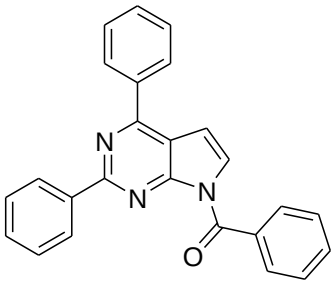
*2-Chloro-4-(4-methoxyphenyl)-7-phenyl-7H-pyrrolo[2,3-d]pyrimidine (**35**)*



A solution of compound **5f** (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 (**20a**) (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 hours 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 hours 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 hours 2.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. Total reaction time was 33 hours, 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 **35** (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 (pp)], 7.11 [2H, dm, *J* = 8.7 Hz, 3,5-H (4-Ph)], 7.44-7.62 [4H, m, 6-H (pp), 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 (4-Ph)]; 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.

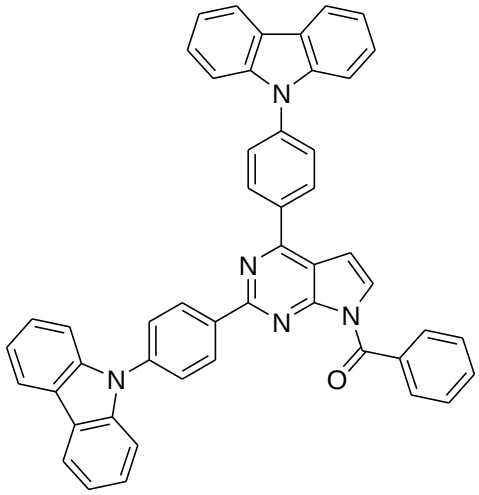
*7-Benzoyl-2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidine (**36**)*



To a solution of 2,4-diphenylpyrrolo[2,3-d]pyrimidine (**6a**) (0.2 g, 0.74 mmol) in anhydrous CH_2Cl_2 (10 mL), DIPEA (0.13 mL, 0.74 mmol), DMAP (0.018 g, 0.15 mmol) and benzoyl chloride (0.085 mL, 0.74 mmol) were added. The reaction mixture was stirred at room temperature for 16 hours. The solvent was evaporated under reduced pressure and the obtained solid was quenched with water, extracted with ethyl acetate, dried over Na_2SO_4, concentrated in vacuo. The residue was dissolved in a minimal amount of tetrachloromethane and purified by column chromatography (eluent-ethyl acetate:hexane, 1:9, then hexane:CH_2Cl_2, 2:1) to give compound **36** (0.18 g, 65%) as a colourless solid, mp 143.6-144.6 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 216 ($1.1 \times 10^4$), 258 ($2.0 \times 10^4$), 309 ($0.8 \times 10^4$); ν_{max} (KBr) 1698 cm^{-1} (CO); δ_H ($CDCl_3$): 7.09 [1H, d, *J* = 4.5 Hz, 5-H (pp)], 7.30-7.42 [3H, m, 3-5-H (2-Ph)], 7.61-7.80 [6H, m, 3-5-H (N_7CO-Ph), 3-5-H (4-Ph)], 7.92 [2H, dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 2,6-H (N_7CO-Ph)], 8.03 [1H, d, *J* = 4.2 Hz, 6-H (pp)], 8.16-8.25 [4H, m, 2×2,6-H (2-Ph, 4-Ph)]; δ_C ($CDCl_3$): 105.9, 116.5, 127.9, 128.3,

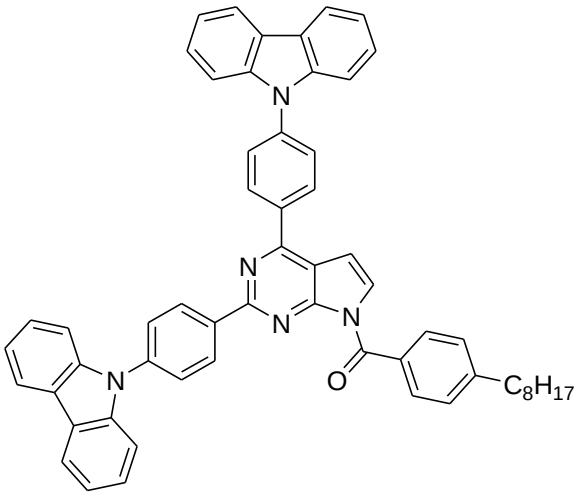
128.5, 129.1, 129.3, 130.4, 130.5, 130.7, 132.9, 134.3, 138.0, 138.1, 154.2, 158.5, 1568.9, 168.0. HRMS (ESI): MH^+, found 376.1452. $C_{25}H_{17}N_3O$ requires 376.1444.

7-Benzoyl-2,4-di[4-(9H-carbazol-9-yl)phenyl]-7H-pyrrolo[2,3-d]pyrimidine ***(37a)***



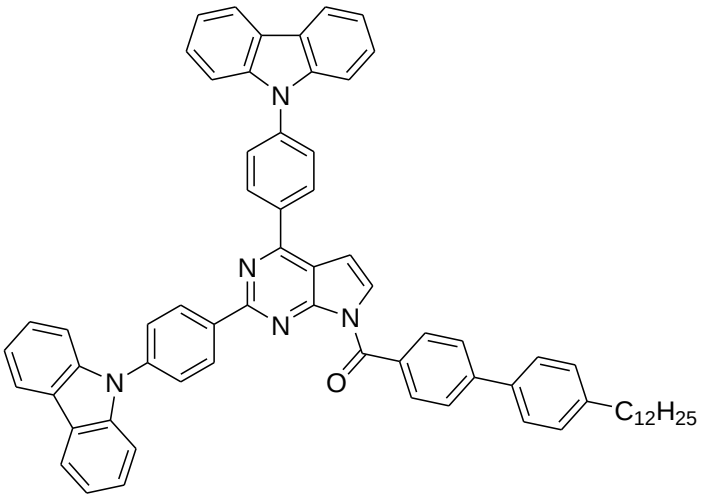
Compound was synthesized according to the procedure described for compound **36**. The isolation and purification was carried out analogously **36** by column chromatography using benzene as an eluent to give compound **37a** (0.06 g, 51%) as a yellow solid, mp 232.6-234 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 239 ($4.8\times10^4$), 254 ($4.0\times10^4$), 292 ($2.1\times10^4$); ν_{max} (KBr) 1690 cm^{-1} (CO); δ_H ($CDCl_3$): 7.23 [1H, d, *J* = 3.9 Hz, 5-H (pp)], 7.33-7.69 [16H, m, 2×3,5-H (2-Ph, 4-Ph),7-9,12-14-H (2-carb., 4-carb.)], 7.75-7.82 [1H, m, 4-H (N_7CO-Ph)], 7.91 [2H, dd, *J* = 8.4 Hz, 3,5-H (N_7CO-Ph)], 7.99 [2H, dd, *J* = 6.9 Hz, 2,6-H (N_7CO-Ph)], 8.13 [1H, d, *J* = 4.2 Hz, 6-H (pp)], 8.20 [2H, dm, *J* = 7.8 Hz, 10,11-H (4-carb.)], 8.23 [2H, dm, *J* = 8.4 Hz, 10,11-H (2-carb.)], 8.45 [2H, dm, *J* = 8.4 Hz, 2,6-H (4-Ph)], 8.54 [2H, dm, *J* = 8.4 Hz, 2,6-H (2-Ph)]; δ_C ($CDCl_3$): 105.8, 110.1, 110.2, 116.6, 120.4, 120.6, 120.7, 120.75, 123.8, 123.9, 126.3, 126.4, 126.9, 127.5, 128.4, 128.5, 129.9, 130.6, 130.8, 133.2, 134.2, 136.8, 136.9, 139.8, 140.2, 140.8, 140.9, 154.3, 157.6, 158.4, 167.9. HRMS (ESI): MH^+, found 706.2606. $C_{49}H_{31}N_5O$ requires 706.2601.

*2,4-Di[4-(9H-carbazol-9-yl)phenyl]-7-(4-octylbenzoyl)-7H-pyrrolo[2,3-d]pyrimidine (**37b**)*



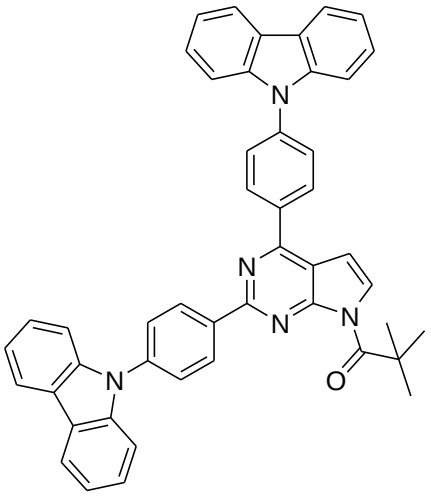
Compound **37b** was synthesized according to the procedure described for compound **36**. The isolation and purification was carried out analogously **36** by column chromatography using benzene as an eluent to give compound **37b** (0.023 g, 17%) as a yellowish solid, mp 231.5-232.3 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 252 ($6.2 \times 10^4$), 256 ($6.2 \times 10^4$), 292 ($5.1 \times 10^4$), 342 ($5.0 \times 10^4$); ν_{max} (KBr) 1699 cm^{-1} (CO); δ_H ($CDCl_3$): 0.86 (3H, t, *J* = 5.1 Hz, *CH*$_3$), 1.08-1.50 (10H, m, C_6H_4-CH_2-CH_2-*(CH*$_2$*)*$_5$-), 2.70-2.81 (2H, m, C_6H_4-CH_2-*CH*$_2$-), 2.80 (2H, t, *J* = 3.9 Hz, C_6H_4-*CH*$_2$-), 7.22 [1H, d, *J* = 4.2 Hz, 5-H (pp)], 7.35-7.55 [12H, m, 2×7-9,12-14-H (2-carb., 4-carb.)], 7.64 [4H, dm, *J* = 8.4 Hz, 2×3,5-H (2-Ph, 4-Ph)], 7.90 [2H, dm, *J* = 9 Hz, 3,5-H (N_7CO-Ph)], 7.93 [2H, dm, *J* = 9, 2,6-H (N_7CO-Ph)], 8.12 [1H, d, *J* = 4.2 Hz, 6-H (pp)], 8.20 [2H, dm, *J* = 7.8 Hz, 10,11-H (4-carb.)], 8.23 [2H, dm, *J* = 8.1 Hz, 10,11-H (2-carb.)], 8.49 [2H, dm, *J* = 8.7 Hz, 2,6-H (4-Ph)], 8.54 [2H, dm, *J* = 8.7 Hz, 2,6-H (2-Ph)]; δ_C ($CDCl_3$): 14.3, 22.9, 29.5, 29.6, 29.7, 31.9, 32.0, 36.5, 105.5, 110.1, 110.2, 116.5, 120.4, 120.6, 120.66, 120.7, 123.8, 123.9, 126.3, 126.4, 126.9, 127.5, 128.4, 128.7, 129.9, 130.8, 131.1, 131.4, 136.9, 137.1, 139.7, 140.1, 140.8, 140.9, 149.4, 154.3, 157.6, 158.3, 167.9. HRMS (ESI): MH^+, found 818.3873. $C_{57}H_{47}N_5O$ requires 818.3853.

*2,4-Di[4-(9H-carbazol-9-yl)phenyl]-7-(4'-dodecylbiphenyl-1-oyl)-7H-pyrrolo[2,3-d]pyrimidine (**37c**)*



Compound **37c** was synthesized according to the procedure described for compound **36**. The isolation and purification was carried out analogously **36** by column chromatography using benzene as an eluent to give compound **37c** (0.08 g, 51%) as a yellowish solid, mp 207.9-209.1 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 244 ($7.5 \times 10^4$), 255 ($7.1 \times 10^4$), 292 ($6.0 \times 10^4$), 342 ($5.2 \times 10^4$); ν_{max} (KBr) 1698 cm^{-1} (CO); δ_H ($CDCl_3$): 0.92 (3H, t, *J* = 6.6 Hz, *CH_3*), 1.21-1.41 (18H, m, C_6H_4-CH_2-CH_2-*$(CH_2)_9$*-CH_3), 1.50-1.71 (2H, m, C_6H_4-CH_2-*CH_2*-), 2.63 (2H, t, *J* = 3.9 Hz, C_6H_4-*CH_2*-CH_2-), 7.25 [1H, d, *J* = 4.2 Hz, 5-H (pp)], 7.29-7.68 [18H, m, 2×7-9, 12-14-H (2-carb., 4-carb.), 3,5, 2‘,3‘,5‘,6‘-H (N_7CO-biPh)], 7.85-7.92 [4H, m, 2×3,5-H (2-Ph, 4-Ph)], 8.05 [2H, dm, *J* = 8.7 Hz, 2,6-H (N_7CO-biPh)], 8.16-8.24 [5H, m, 6-H (pp), 10,11-H (2-carb., 4-carb.)], 8.46 [2H, dm, *J* = 8.7 Hz, 2,6-H (4-Ph)], 8.55 [2H, dm, *J* = 8.7 Hz, 2,6-H (2-Ph)]; δ_C ($CDCl_3$): 14.4, 22.9, 29.6, 29.7, 29.8, 29.9, 31.6, 32.2, 35.9, 105.7, 110.1, 110.2, 116.5, 120.4, 120.5, 120.6, 120.7, 123.8, 123.9, 126.3, 126.4, 126.8, 126.9, 127.3, 127.5, 128.5, 129.5, 129.9, 130.8, 131.2, 132.5, 136.8, 136.9, 137.5, 139.7, 140.2, 140.8, 143.8, 146.2, 154.3, 157.6, 158.3, 167.7. HRMS (ESI): MH^+, found 950.4776. $C_{67}H_{59}N_5O$ requires 950.4792.

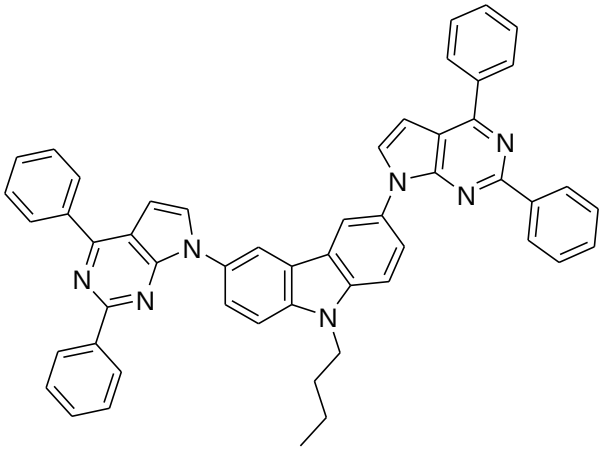
*2,4-Di[4-(9H-carbazol-9-yl)phenyl]-7-(2,2-dimethylethanoyl)-7H-pyrrolo[2,3-d]pyrimidine (**37d**)*



Pivaloyl chloride (0.03 mL, 0.25 mmol) was added at 0 °C (ice-bath) to a stirred solution containing compound **6e** (0.1 g, 0.166 mmol), triethylamine (0.034 mL, 0.25 mmol), DMAP (0.002 g, 0.017 mmol) in anhydrous CH_2Cl_2. Ice-bath was removed and the mixture was stirred at room temperature for 16 hours. The solvent was evaporated under reduced pressure and the obtained solid was quenched with water, washed with brine, extracted with chloroform, dried over Na_2SO_4, concentrated in vacuum. The residue was purified by column chromatography (eluent-benzene) to give compound **37d** (0.065 g, 57%) as a yellow solid, mp 249.5-251.2 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 243 ($4.0 \times 10^4$), 256 ($3.2 \times 10^4$), 292 ($1.9 \times 10^4$), 342 ($2.1 \times 10^4$); δ_H ($CDCl_3$): 1.88 (9H, s, $C(CH_3)_3$), 7.14 [1H, d, *J* = 4.2 Hz, 5-H (pp)], 7.37-7.63 [12H, m, 2×7-9,12-14-H (2-carb., 4-carb.)], 7.83 [2H, dm, *J* = 8.7 Hz, 3,5-H (4-Ph)], 7.89 [2H, dm, *J* = 8.4 Hz, 3,5-H (2-Ph)], 8.18 [1H, d, *J* = 4.2 Hz, 6-H (pp)], 8.23 [4H, dm, *J* = 7.8 Hz, 2×10,11-H (2-carb., 4-carb.)], 8.51 [2H, dm, *J* = 8.7 Hz, 2,6-H (4-Ph)], 8.96 [2H, dm, *J* = 8.7 Hz, 2,6-H (2-Ph)]; δ_C ($CDCl_3$): 27.1, 27.4, 42.7, 104.8, 110.1, 110.2, 117.2, 120.5, 120.6, 120.7, 123.8, 123.9, 126.3, 126.4, 127.2, 127.5, 129.9, 130.0, 130.9, 136.8, 137.4, 139.9, 140.1, 140.8, 140.9, 153.0, 157.5, 158.1, 178.2. HRMS (ESI): MH^+, found 686.2887. $C_{47}H_{35}N_5O$ requires 686.2914.

9-Butyl-3,6-bis(2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidin-7-yl)-9H-carbazole

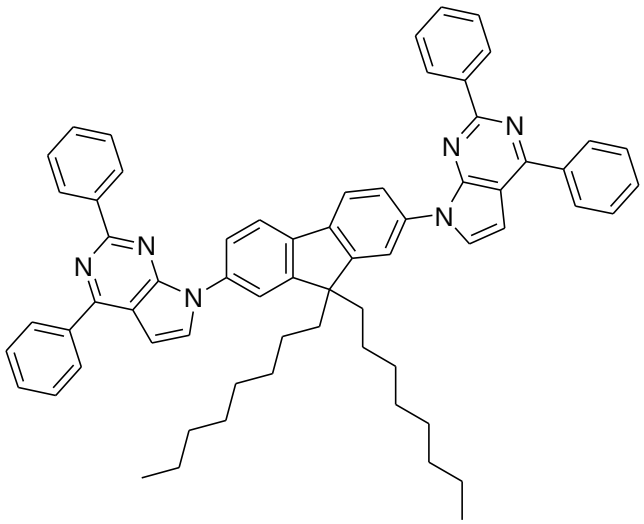
(42)



A solution of compound **6a** (0.1 g, 0.37 mmol) in anhydrous dioxane (3 ml) was flushed with argon and 1.0 mol% CuI, anhydrous K_3PO_4 (0.068 g, 0.32 mmol), 9-butyl-3,6-diiodo-9*H*-carbazole (**38**) (0.073 g, 0.15 mmol), 10.0 mol% *trans*-1,2-diaminocyclohexane were added under stirring and argon flow. The reaction mixture was stirred under reflux. Addition of portions 1.0 mol% CuI to the reaction mixture was continued every two hours till amount of CuI reached 5.0 mol%. Then after 2 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 10.0 mol%. After 20 hours anhydrous K_3PO_4 (0.068 g, 0.32 mmol), 9-butyl-3,6-diiodo-9*H*-carbazole (0.014 g, 0.03 mmol) and 2,4-diphenylpyrrolo[2,3-*d*]pyrimidine (0.018 g, 0.066 mmol) were added. Then after 2 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 13.0 mol%. Total reaction time was 37 hours. 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 **42** (0.1 g, 72%) as a colourless solid, mp 241-242.4 °C; UV (THF),

λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 252 ($4.8 \times 10^4$), 295 ($3.5 \times 10^4$), 353 ($0.9 \times 10^4$); δ_H ($CDCl_3$): 1.09 (3H, t, *J* = 7.2 Hz, CH_3), 1.51-1.59 (2H, m, CH_2CH_3), 2.01-2.04 (2H, m, $CH_2CH_2CH_3$), 4.51 (2H, t, *J* = 7.2 Hz, $CH_2CH_2CH_2CH_3$), 7.06 [2H, d, *J* = 3.6 Hz, 2×5-H (pp)], 7.43-7.51 [6H, m, 2×3-5-H (2-Ph)], 7.61-7.71 [10H, m, 2,7-H (carb.), 2×6-H (pp), 2×3-5-H (4-Ph)], 8.09 [2H, dd, *J* = 2.1 Hz, *J* = 1.8 Hz, 1,8-H (carb.)], 8.36 [4H, dd, *J* = 1.8 Hz, *J* = 6.6 Hz, 2×2,6-H (4-Ph)], 8.51 [2H, d, *J* = 1.8 Hz, 4,5-H (carb.)], 8.70 [4H, dd, *J* = 1.8 Hz, *J* = 6.6 Hz, 2×2,6-H (2-Ph)]; δ_C ($CDCl_3$): 14.2, 20.9, 31.5, 43.6, 101.9, 109.7, 115.0, 116.7, 123.3, 123.6, 128.4, 128.6, 129.0, 129.4, 129.8, 129.9, 130.2, 130.3, 139.0, 139.2, 140.0, 153.1, 157.9, 158.5; HRMS (ESI): MH^+, found 762.3323. $C_{52}H_{39}N_7$ requires 762.3340.

*2,7-Bis(2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidin-7-yl)-9,9-dioctyl-9H-fluorene (**43**)*

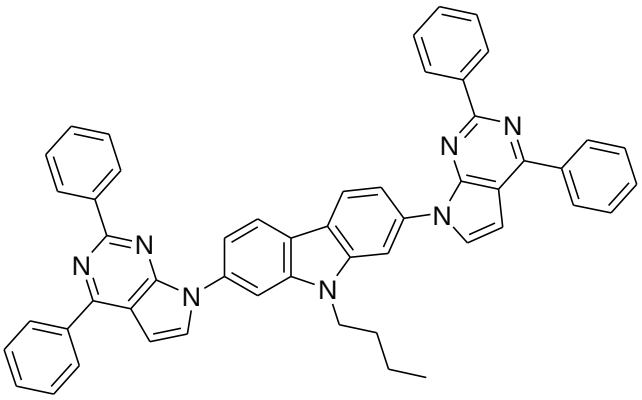


A solution of compound **6a** (0.1 g, 0.37 mmol) in anhydrous dioxane (3 ml) was flushed with argon and 1.0 mol% CuI, anhydrous K_3PO_4 (0.14 g, 0.64 mmol), 2,7-diiodo-9,9-dioctyl-9*H*-fluorene (**39**) (0.099 g, 0.15 mmol), 10.0 mol% *trans-N,N'*-dimethyl-1,2-diaminocyclohexane were added under stirring and argon flow. The reaction mixture was stirred under reflux, and after 2 hours 1.0 mol% CuI were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 5.0 mol%. Then after 2 hours 1.0 mol% CuI and 10.0 mol% *trans-N,N'*-dimethyl-1,2-

diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 9.0 mol%. Total reaction time was 18 hours. After cooling the reaction mixture to room temperature chloroform (5 mL) was added, resulting solution was filtered through a layer of silica gel eluting with chloroform. The filtrate was concentrated under reduced pressure, the residue was dissolved in a minimal amount of chloroform and purified by column chromatography using hexane: chloroform (2.3:1) → hexane: chloroform (1:1.2) as an eluent to give compound **43** (0.125 g, 87%) as a colorless solid, mp 194.7-195.2 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 237 ($1.2 \times 10^5$), 292 ($5.9 \times 10^4$), 342 ($4.9 \times 10^4$); δ_H ($CDCl_3$): 0.78 (6H, t, *J* = 6.9 Hz, 2×*CH*$_3$), 0.92-1.27 (24H, m, 12×*CH*$_2$), 2.24-2.29 [4H, m, (*CH*$_2$)C(*CH*$_2$)], 7.09 [2H, d, *J* = 3.6 Hz, 2×5-H (pp)], 7.53-7.67 [12H, m, 2×3-5-H (2-Ph), 2×3-5-H (4-Ph)], 7.75 [2H, d, *J* = 3.9 Hz, 2×6-H (pp)], 7.83 [2H, dd, *J* = 8.1 Hz, J = 2.1 Hz, 3,6-H (fluor.)], 7.98 [2H, d, *J* = 8.1 Hz, 4,5-H (fluor.)], 8.18 [2H, d, *J* = 2.1 Hz, 1,8-H (fluor.)], 8.36 [4H, dd, *J* = 8.1 Hz, 2×2,6-H (4-Ph)], 8.76 [4H, dd, *J* = 8.1 Hz, 2×2,6-H (2-Ph)]; δ_C ($CDCl_3$): 14.3, 22.8, 24.4, 29.6, 29.7, 30.6, 31.9, 41.1, 56.2, 102.5, 115.4, 119.2, 120.7, 122.5, 128.4, 128.7, 129.0, 129.1, 129.4, 130.1, 130.4, 137.3, 138.9, 139.1, 139.1, 152.5. 152.9, 158.1, 158.5. HRMS (ESI): MH^+, found 929.5249. $C_{65}H_{64}N_6$ requires 929.5265.

9-Butyl-2,7-bis(2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidin-7-yl)-9H-carbazole

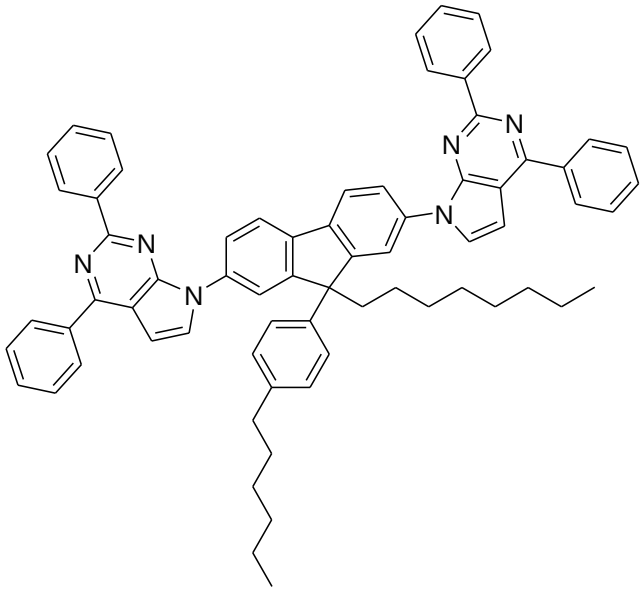
(44)



A solution of compound **6a** (0.12 g, 0.44 mmol) in anhydrous dioxane (3 ml) was flushed with argon and 1.0 mol% CuI, anhydrous K_3PO_4 (0.16 g, 0.77 mmol), 2,7-dibromo-9-butyl-9*H*-carbazole (**40**) (0.07 g, 0.18 mmol), 10.0 mol% *trans-N,N'*-dimethyl-1,2-diaminocyclohexane were added under stirring and argon flow. The reaction mixture was stirred under reflux, and after 2 hours 1.0 mol% CuI were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 5.0 mol%. Then after 2 hours 1.0 mol% CuI and 10.0 mol% *trans-N,N'*-dimethyl-1,2-diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 8.0 mol%. Total reaction time was 16 hours. After cooling the reaction mixture to room temperature the solid precipitate, which formed during the reaction, was filtered, diluted in chloroform and filtered one more time to separate inorganic salts. The resulted solution was concentrated under reduced pressure, the residue was dissolved in a minimal amount of chloroform and purified by column chromatography using hexane: chloroform (1:1.3) as an eluent to give compound **44** (0.11 g, 78%) as a colorless solid, mp 292.5-293.0 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 266 ($7.4 \times 10^4$), 289 ($5.6 \times 10^4$), 328 ($5.6 \times 10^4$); δ_H ($CDCl_3$): 1.02 (3H, t, *J* = 7.2 Hz, CH_3), 1.55-1.58 (2H, m, CH_2CH_3), 2.10-2.14 (2H, m, $CH_2CH_2CH_3$), 4.51 (2H, t, *J* = 7.2 Hz, NCH_2), 7.08 [2H, d, *J* = 3.9 Hz, 2×5-H (pp)], 7.49-7.69 [14H, m, 3,6-H (carb.), 2×3-5-H (2-Ph), 2×3-5-H (4-Ph)], 7.77 [2H, d, *J* = 3.6 Hz, 2×6-H (pp)], 8.23 [2H, d, *J* = 1.5 Hz, 1,8-H

(carb.)], 8.30 [2H, d, *J* = 8.4 Hz, 4,5-H (carb.)], 8.36 [4H, dd, *J* = 8.1 Hz, 2×2,6-H (4-Ph)], 8.75 [4H, dd, *J* = 8.1 Hz, 2×2,6-H (2-Ph)]; δ_C ($CDCl_3$): 14.3, 21.1, 31.6, 43.7, 102.4, 105.3, 115.4, 115.43, 121.2, 121.4, 128.4, 128.6, 129.1, 129.4, 129.6, 130.0, 130.4, 136.1, 138.9, 139.1, 141.8, 153.1, 158.1, 158.5. HRMS (ESI): MH^+, found 762.3314. $C_{52}H_{39}N_7$ requires 762.3339.

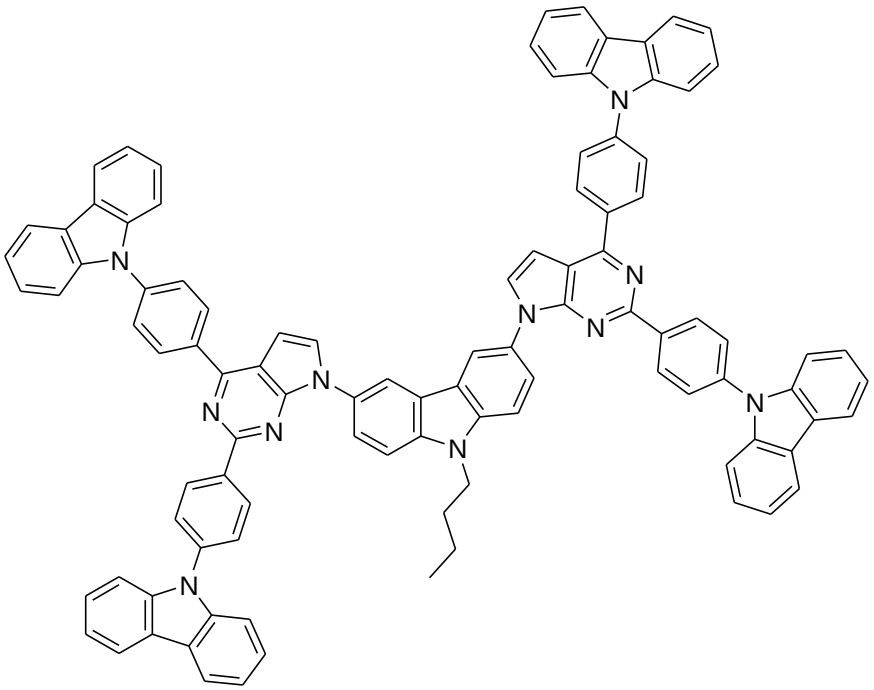
*9-(4-Hexylphenyl)-2,7-bis(2,4-diphenyl-7H-pyrrolo[2,3-d]pyrimidin-7-yl)-9-octyl-9H-fluorene (**45**)*



A solution of compound **6a** (0.1 g, 0.37 mmol) in anhydrous dioxane (3 ml) was flushed with argon and 1.0 mol% CuI, anhydrous K_3PO_4 (0.14 g, 0.64 mmol), 2,7-dibromo-9-(4-hexylphenyl)-9-octyl-9*H*-fluorene (**41**) (0.092 g, 0.15 mmol), 10.0 mol% *trans*-1,2-diaminocyclohexane were added under stirring and argon flow. The reaction mixture was stirred under reflux. Addition of portions 1.0 mol% CuI to the reaction mixture was continued every two hours till amount of CuI reached 5.0 mol%. Then after 2 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 10.0 mol%. In this way every 2 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane (after every 5.0 mol% CuI) were added till total amount of CuI was 23.0 mol%, and *trans*-1,2-

diaminocyclohexane – 50 mol%. Total reaction time was 59 hours. 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 (10:1) as an eluent to give compound **45** (0.1 g, 67%) as a colourless solid, mp 175.4-176.9 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 226 ($2.6 \times 10^4$), 232 ($2.9 \times 10^4$), 263 ($3.9 \times 10^4$), 294 ($2.7 \times 10^4$), 332 ($2.7 \times 10^4$); δ_H ($CDCl_3$): 0.79-0.86 (6H, m, 2x*CH_3*), 1.19-1.31 (20H, m, 4×*CH_2*, 6×*CH_2*), 2.59 (2H, t, *J* = 7.2 Hz, C_6H_4-*CH_2*), 2.74-2.79 (2H, m, fluor-*CH_2*), 7.04 [2H, d, *J* = 3.6 Hz, 2×5-H (pp)], 7.15 [2H, dm, *J* = 8.1 Hz, 3,5-H (fluor-*C_6H_4*)], 7.33 [2H, dm, *J* = 8.4 Hz, 2,6-H (fluor-*C_6H_4*)], 7.52-7.68 [14H, m, 1,3,6,8-H (fluor.), 2×6-H (pp), 2×3-5-H (2-Ph), 2×4-H (4-Ph)], 7.89 [2H, dd, *J* = 1.8 Hz, *J* = 1.8 Hz, 4,5-H (fluor.)], 8.02-8.04 [4H, m, 2×3,5-H (4-Ph)], 8.33 [4H, m, *J* = 6.6 Hz, *J* = 1.8 Hz, 2×2,6-H (4-Ph)], 8.68 [4H, m, *J* = 7.8 Hz, *J* = 1.8 Hz, 2×2,6-H (2-Ph)]; δ_C ($CDCl_3$): 14.2, 14.3, 22.8, 24.5, 29.5, 29.6, 29.7, 30.7, 31.5, 31.9, 32.0, 35.8, 38.6, 59.5, 102.5, 115.3, 120.4, 120.9, 122.9, 126.9, 128.4, 128.7, 128.9, 129.0, 129.1, 129.4, 130.0, 130.4, 137.6, 138.7, 138.8, 138.9, 141.5, 141.6, 152.9, 153.9, 157.9, 158.4. HRMS (ESI): MH^+, found 977.5250. $C_{69}H_{64}N_6$ requires 977.5265.

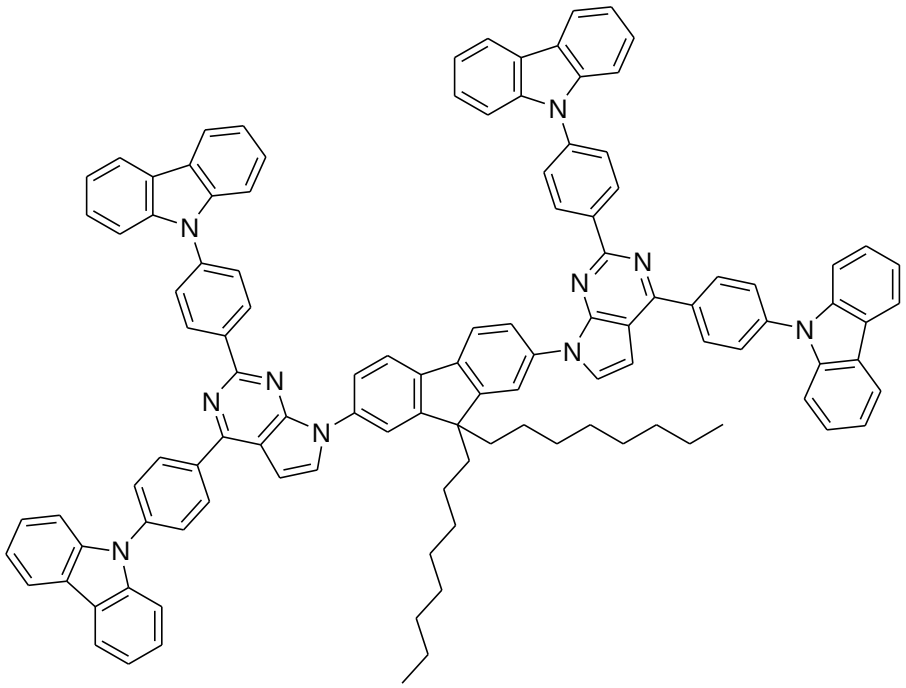
*9-Butyl-3,6-bis{2,4-di[4-(9-carbazolyl)phenyl]-7H-pyrrolo[2,3-d]pyrimidin-7-yl}-9H-carbazole (**46**)*



A solution of compound **6e** (0.1 g, 0.17 mmol) in anhydrous dioxane (3 ml) was flushed with argon and 1.0 mol% CuI, anhydrous K_3PO_4 (0.062 g, 0.29 mmol), 9-butyl-3,6-diiodo-9*H*-carbazole (**38**) (0.033 g, 0.07 mmol), 10.0 mol% *trans*-1,2-diaminocyclohexane were added under stirring and argon flow. The reaction mixture was stirred under reflux. Addition of portions 1.0 mol% CuI to the reaction mixture was continued every two hours till amount of CuI reached 5.0 mol%. Then after 2 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. In this way every 2 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane (after every 5.0 mol% CuI) were added till total amount of CuI was 17.0 mol%, and *trans*-1,2-diaminocyclohexane – 40 mol%. Total reaction time was 36 hours. 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) → hexane:ethyl acetate (2.7:1) as an eluent to give compound **46** (0.07 g, 71%) as a yellow

solid, mp 262.2-264.0 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 237 ($12.2 \times 10^4$), 292 ($5.9 \times 10^4$), 342 ($4.9 \times 10^4$); δ_H ($CDCl_3$): 1.09 (3H, t, *J* = 7.5 Hz, *CH*$_3$), 1.54-1.59 (2H, m, *CH*$_2$CH$_3$), 2.07-2.09 (2H, m, *CH*$_2$CH$_2$CH$_3$), 4.54 (2H, t, *J* = 6.9 Hz, *CH*$_2$CH$_2$ CH$_2$CH$_3$), 7.18 [2H, d, *J* = 3.9 Hz, 2×5-H (pp)], 7.27-7.55 [20H, m, 2×3,5-H (4-Ph), 4×7,8,13,14-H (2×2-carb., 2×4-carb.)], 7.64 [8H, dm, *J* = 8.7 Hz, 4×9,12-H (2×2-carb., 2×4-carb.)], 7.75 [2H, dm, *J* = 8.7 Hz, 2,7-H (carb.)], 7.82 [2H, d, *J* = 3.6 Hz, 2×6-H (pp)], 7.89 [4H, dm, *J* = 8.7 Hz, 2×3,5-H (2-Ph)], 8.13 [2H, dd, *J* = 8.7 Hz, *J* = 2.1 Hz, 1,8-H (carb.)], 8.17 [4H, dm, *J* = 7.8 Hz, 2×10,11-H (4-carb.)], 8.24 [4H, dm, *J* = 7.8 Hz, 2×10,11-H (2-carb.)], 8.63 [4H, dm, *J* = 8.4 Hz, 2×2,6-H (4-Ph)], 8.69 [2H, d, *J* = 2.1 Hz, 4,5-H (carb.)], 8.92 [4H, dm, *J* = 8.7 Hz, 2×2,6-H (2-Ph)]; δ_C ($CDCl_3$): 14.2, 20.9, 31.5, 43.7, 101.9, 109.9, 110.2, 115.1, 116.8, 116.9, 120.2, 120.5, 120.6, 120.7, 123.4, 123.6, 123.7, 123.9, 126.2, 126.4, 126.9, 127.4, 129.9, 130.2, 130.5, 130.9, 137.7, 138.0, 139.2, 139.7, 140.2, 140.8, 140.9, 153.3, 156.9, 157.9. HRMS (ESI): MH^+, found 1422.5512. $C_{100}H_{67}N_{11}$ requires 1422.5654.

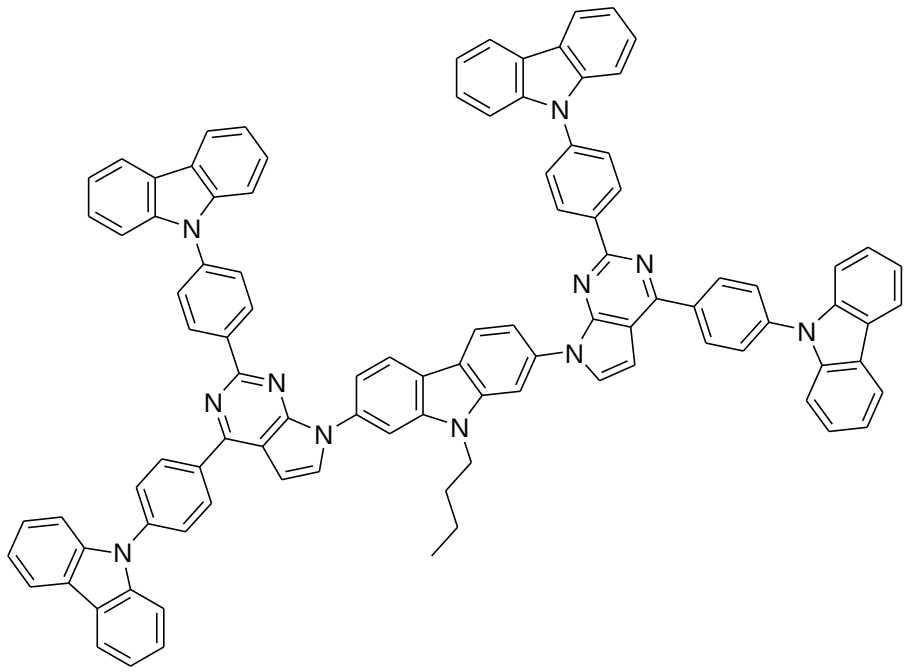
*2,7-Bis{2,4-di[4-(9-carbazolyl)phenyl]-7H-pyrrolo[2,3-d]pyrimidin-7-yl}-9,9-dioctyl-9H-fluorene (**47**)*



A solution of compound **6e** (0.12 g, 0.20 mmol) in anhydrous dioxane (3 ml) was flushed with argon and 5.0 mol% CuI, anhydrous K_3PO_4 (0.074 g, 0.35 mmol), 2,7-diiodo-9,9-dioctyl-9*H*-fluorene (**39**) (0.053 g, 0.083 mmol), 10.0 mol% *trans*-1,2-diaminocyclohexane were added under stirring and argon flow. The reaction mixture was stirred under reflux, and after 10 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 10.0 mol%. Then after 2 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 13.0 mol%. Total reaction time was 39 hours. 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 1). hexane:ethyl acetate (10:1) as an eluent and 2). benzene as an eluent to give compound **47** (0.08 g, 61%) as a yellow solid, mp

224.5-225.0 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 292 ($4.9 \times 10^4$), 342 ($5.8 \times 10^4$); δ_H ($CDCl_3$): 0.6-0.7 (6H, m, 2×*CH*$_3$), 0.9-1.3 (24H, m, 12×*CH*$_2$), 2.2-2.3 [4H, m, (*CH*$_2$)C(*CH*$_2$)], 7.24 [2H, d, *J* = 3.9 Hz, 2×5-H (pp)], 7.30-7.80 [26H, m, 3,6-H (fluor.), 2×3,5-H (2-Ph), 2×3,5-H (4-Ph), 4×8,9,12,13-H (2-carb., 4-carb.)], 7.86 [2H, d, *J* = 3.6 Hz, 2×6-H (pp)], 7.91-7.97 [8H, m, 4×7,14-H (2-carb., 4-carb.)], 8.06 [2H, d, *J* = 8.4 Hz, 4,5-H (fluor.)], 8.17 [2H, d, *J* = 1.5 Hz, 1,8-H (fluor.)], 8.19-8.25 [8H, m, 4×10,11-H (2-carb., 4-carb.)], 8.65 [4H, dm, *J* = 8.4 Hz, 2×2,6-H (4-Ph)], 9.01 [4H, dm, *J* = 8.7 Hz, 2×2,6-H (2-Ph)]; δ_C ($CDCl_3$): 14.2, 22.7, 24.4, 29.5, 29.7, 30.6, 32.0, 41.2, 56.3, 102.5, 110.1, 110.2, 115.5, 119.1, 120.4, 120.6, 120.61, 120.7, 120.9, 122.9, 123.8, 123.9, 126.3, 126.4, 127.1, 127.5, 129.8, 129.9, 130.9, 137.2, 137.5, 137.9, 139.4, 139.5, 139.9, 140.91, 140.94, 152.6, 153.1, 157.1, 157.8. HRMS (ESI): MH^+, found 1589.7538. $C_{113}H_{92}N_{10}$ requires 1589.7579.

*9-Butyl-2,7-bis{2,4-di[4-(9-carbazolyl)phenyl]-7H-pyrrolo[2,3-d]pyrimidin-7-yl}-9H-carbazole (**48**)*



A solution of compound **6e** (0.12 g, 0.20 mmol) in anhydrous dioxane (3 ml) was flushed with argon and 1.0 mol% CuI, anhydrous K_3PO_4 (0.074 g, 0.35 mmol), 2,7-dibromo-9-butyl-9*H*-carbazole (**40**) (0.032 g, 0.083 mmol),

10.0 mol% *trans-N,N'*-dimethyl-1,2-diaminocyclohexane were added under stirring and argon flow. The reaction mixture was stirred under reflux, and after 2 hours 1.0 mol% CuI was added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 5.0 mol%. Then after 2 hours 1.0 mol% CuI and 10.0 mol% *trans-N,N'*-dimethyl-1,2-diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 10.0 mol%. Then after 2 hours 1.0 mol% CuI and 10.0 mol% *trans*-1,2-diaminocyclohexane were added. Addition of CuI was continued every two hours in portions 1.0 mol% till amount of CuI reached 15.0 mol%. Total reaction time was 42 hours. After cooling the reaction mixture to room temperature chloroform (5 mL) was added, resulting solution was filtered through a layer of silica gel eluting with chloroform. The filtrate was concentrated under reduced pressure, the residue was dissolved in a minimal amount of chloroform and purified by column chromatography using hexane:chloroform (9:1) → chloroform as an eluent to give compound **48** (0.07 g, 60%) as a yellowish solid, mp 257.0-258.5 °C; UV (THF), λ, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$): 232 ($2.9 \times 10^4$), 263 ($3.9 \times 10^4$), 294 ($2.7 \times 10^4$), 331 ($2.7 \times 10^4$); δ_H ($CDCl_3$): 1.05 (3H, t, *J* = 7.2 Hz, *CH*$_3$), 1.59-1.67 (2H, m, *CH*$_2$CH$_3$), 2.10-2.19 (2H, m, *CH*$_2$CH$_2$CH$_3$), 4.59 (2H, t, *J* = 7.2 Hz, N*CH*$_2$), 7.24 [2H, d, *J* = 3.9 Hz, 2×5-H (pp)], 7.28-7.66 [24H, m, 4×7-9,12-14-H (2-carb., 4-carb.)], 7.75-7.80 [6H, m, 2×3,5-H (4-Ph), 3,6-H (carb.)], 7.88 [2H, d, *J* = 3.6 Hz, 2×6-H (pp)], 7.92 [4H, dm, *J* = 8.4 Hz, 2×3,5-H (2-Ph)], 8.17-8.25 [10H, m, 1,8-H (carb.), 4×10,11-H (2-carb., 4-carb.)], 8.39 [2H, d, *J* = 8.1 Hz, 4,5-H (carb.)], 8.65 [4H, dm, *J* = 8.7 Hz, 2×2,6-H (4-Ph)], 8.99 [4H, dm, *J* = 8.7 Hz, 2×2,6-H (2-Ph)]; δ_C ($CDCl_3$): 14.4, 21.1, 31.7, 43.7, 102.4, 105.4, 110.1, 110.15, 115.5, 115.9, 120.3, 120.5, 120.6, 120.7, 121.5, 121.6, 123.8, 123.9, 126.3, 126.4, 127.0, 127.5, 129.9, 130.3, 130.9, 136.0, 137.6, 138.0, 139.4, 139.8, 140.9, 140.93, 141.9, 153.3, 157.2, 157.9. HRMS (ESI): MH^+, found 1422.5660. $C_{100}H_{67}N_{11}$ requires 1422.5654.

IV. CONCLUSIONS

1. Influence of catalyst, base and ligand on the palladium-catalyzed cross-coupling reaction of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine with arylboronic acids was studied. $Pd(OAc)_2$/dicyclohexyl(2-biphenyl)phosphine/K_3PO_4 was found to be an efficient catalyst system in the arylation reaction of pyrrolo[2,3-*d*]pyrimidine. Mono- or double cross-coupling reactions of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine with arylboronic acids to give the corresponding 4-aryl-2-chloro- and 2,4-diarylpyrrolo[2,3-*d*]pyrimidines can be controlled by an amount of boronic acids and reaction conditions.

2. The Suzuki reaction was demonstrated to be suitable for the synthesis of densely substituted and bearing reactive groups pyrrolo[2,3-*d*]pyrimidine derivatives - methyl 5-amino-4-aryl-2-methylthiopyrrolo[2,3-*d*]pyrimidine-6-carboxylates. The applied approach led to a novel *ortho,peri*-fused heterocyclic system - 1,3,4,6-tetraazadibenzo[*cd*,*f*]azulene, containing structural units of pyrimidine, pyrrole and benzazepine.

3. *N*-arylation reaction of 7*H*-pyrrolo[2,3-*d*]pyrimidine with aryl halogenides was studied. CuI/*trans*-1,2-diaminocyclohexane/K_3PO_4 catalyst system was found to be effective for the introduction of aryl moieties into the position 7 of the heterocycle. An efficient high yielding synthesis of 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines and bis(2,4-diarylpyrrolo[2,3-*d*]pyrimidin-7-yl)carbazoles and the corresponding fluorenes has been developed.

4. Method for the synthesis of 7-acyl-2,4-diarylpyrrolo[2,3-*d*]pyrimidines has been developed by the acylation reaction of 2,4-diarylpyrrolo[2,3-*d*]pyrimidines with acyl chlorides in the presence of DMAP and DIPEA.

5. 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 has been developed. 2,4-Diaryl- and 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines with different aryl branches were synthesized by a combination of Pd(0) and Cu(I) catalyzed cross-coupling

reactions. The investigation of the synthetic routes for the preparation of these compounds revealed the necessity of protection-deprotection methodology of *N*(7)-group of pyrrolo[2,3-*d*]pyrimidine.

6. The synthesized pyrrolo[2,3-*d*]pyrimidines with various aromatic units in positions 2 and 4 of the heterocycle were found to exhibit blue-UV fluorescence ranging from 380 to 440 nm with emission quantum yields in the range of 41 – 53% in THF solutions. Introduction of highly polar Boc group was found to have a dramatic impact on the fluorescence properties of the pyrrolopyrimidine derivatives. For derivatives, where pyrrolo[2,3-*d*]pyrimidine core acts as a fluorophore, intramolecular charge transfer results in a significant quenching of fluorescence (down to 3.6%), whereas for derivative, where carbazolyl moiety is invoked in formation of the lowest excited states, intramolecular charge transfer facilitates a significant increase in emission quantum yield up to 67%. Investigation of emission behavior of the selected 2,4-diarylpyrrolo[2,3-*d*]pyrimidines in different solvents revealed that the studied compounds exhibit positive solvatofluorochromic effect. In the polystyrene matrix fluorescence efficiency of 2,4-diarylpyrrolo[2,3-*d*]pyrimidines is less expressed.

7. Aryl groups in position 7 enhance the absorption of triarylpyrrolo[2,3-*d*]pyrimidines as compared with the corresponding 2,4-diaryl derivatives. However, the fluorescence quantum yields of 2,4,7-triarylpyrrolo[2,3-*d*]pyrimidines in THF solution are lower than those obtained for corresponding 2,4-diarylpyrrolo[2,3-*d*]pyrimidines. Especially significant drop of fluorescence is observed for compounds, containing 4-(diphenylamino)- and 4-(dimethylamino)phenyl groups at the nitrogen atom of the pyrrole ring. Otherwise, these compounds showed the pronounced solid state fluorescence with up to 32-fold increase as compared to their results in solution. The tendency of the increase of the fluorescence quantum yield in a solid state in comparison with that in solution is also maintained in a series of 7-acyl-2,4-diarylpyrrolo[2,3-

d]pyrimidines as well as in series of 3,6- and 2,7-bis(2,4-diarylpyrrolo[2,3-*d*]pyrimidin-7-yl)carbazoles and -fluorenes.

8. 2,4-Diphenyl- and 2,4-di[4-(9*H*-carbazol-9-yl)phenyl]-7-[(4-diphenylamino)phenyl]pyrrolo[2,3-*d*]pyrimidines were found to form nanoaggregates and exhibited aggregation induced emission enhancement effect in THF/water solution. The size of nanoparticles depends on the water content - increase of water fraction in a THF/water mixture reduces the size of nanoaggregates. Emission of 2,4-di[4-(9*H*-carbazol-9-yl)phenyl]-7-[(4-dimethylamino)phenyl]pyrrolo[2,3-*d*]pyrimidine exhibits pH sensibility.

9. The disclosed light-emitting properties of some synthesized pyrrolo[2,3-*d*]pyrimidine-core based oligoarylenes could allow their use as fluorescent solvent detection and pH sensors. Moreover, presence of carbazole and fluorene structural units, often responsible for the charge transporting properties of organic materials, makes the synthesized compounds promising candidates for multifunctional materials with optoelectronic applications.

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LIST OF PUBLICATIONS

Publications in the journals inscribed into the list approved by Information Scientific Institute (ISI):

1. S. Tumkevicius, J. Dodonova. Functionalization of pyrrolo[2,3-*d*]pyrimidine by palladium-catalyzed cross-coupling reactions (review). *Chem. Heterocycl. Comp.* **2012**, *48(2)*, 258-279.
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