VILNIUS UNIVERSITY

CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY INSTITUTE
OF CHEMISTRY

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SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF NON-LINEAR ARYLPYRIMIDINES

Summary of Doctoral Dissertation

Physical Sciences, Chemistry (03P)

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FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRO CHEMIJOS INSTITUTAS

Andžejus Voitechovičius

NELINIJINĖS STRUKTŪROS ARILPIRIMIDINŲ SINTEZĖ IR FOTOFIZIKINĖS SAVYBĖS

Daktaro disertacijos santrauka
Fiziniai mokslai, chemija (03P)

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1. Introduction

Organic compounds, possessing optical, photoelectric or magnetic properties, are used in many modern technologies. As emitters and photosemiconductors they are used in organic light-emitting diodes (OLED), optical switches and sensors, information collection and storage devices. From the point of view of application, low molar mass compounds have several important advantages in comparison with polymeric materials. First of all, Low molecular mass materials that are particularly interesting in such functional systems due to their well-defined molecular structures and molecular weights, and also because they can be easily purified. Most recently, materials with non-linear structure, so-called "star" and "banana" shaped, have become an inspiring aspect of material chemistry because it can lead to a strong enhancement of physical properties. Its combination with conjugated character within the arms brings novel electrical, optical, and morphological properties, In the last decade, research has shown that incorporation of aromatic nitrogen heterocycles (eg, pyrrole, pyridine, pyrazine, quinoline, chinazoline, etc.) into molecules with π-conjugated systems also often improve these properties. In this respect, the pyrimidine ring is suitable as a structural unit. Pyrimidine derivatives as functional materials are not widely investigated. Nevertheless, there are indications in the literature that some of the heterocycle-based π-conjugated systems can be used in electroluminescent devices. So, it was decided to synthesize pyrimidines with various arylgroup in different positions of the pyrimidine ring. For the synthesis of these compounds the Suzuki reaction, which is one of the most effective method for formation of the C-C bonds between aromatic rings, has been chosen. Moreover, the Suzuki reaction often shortens the synthesis of conjugated systems consisting of several aromatic rings and heterocycles.

The main goal of the present work was to synthesize non-linear pyrimidine derivatives and to investigate their photophysical properties.

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

1. to elaborate an economic synthesis of arylboronic acid using intermediate arylmagnesium organic compounds and to apply it for the synthesis of arylboronic acids in multigram scale (20-300g).
2. to study the palladium-catalysed cross-coupling reactions of various 2-chloro, -4-chloro-, 4,6-dichloro-, 2,4-dichloropyrimidines with arylboronic acids and to elaborate methods for the synthesis of the corresponding arylpyrimidines.
3. to develop the synthesis of 2,4-diarylpyrimidines with different aromatic side branches.
4. to study the optical properties of some synthesized compounds.

Scientific novelty: The influence of catalyst, ligand, base, and solvent on the Suzuki cross-coupling reaction of 4,6-dichloropyrimidines bearing methylthio-, methyl-, amino-, cyano-, formyl and nitro groups in the 2nd and/or 5th positions of the pyrimidine ring with arylboronic acids was studied and the method for the preparation of the corresponding 4,6-diarylpyirimidines was elaborated. Synthesis of novel 2,4-diarylpyrimidines with different and identical aryl groups and isomeric 2,4-diarylpyrimidines was accomplished. Using the condensation reaction of 4,6-dimethylpyrimidines with 2-bromo-5-formylpyridine 4,6-di{(E)-2-[5-bromopyridin-2-yl]vinyl}pyrimidines were synthesized their cross-coupling reaction with arylboronic acids was accomplished to give novel 4,6-bis{(*E*)-2-[6-arylpyridin-3-yl]vinyl} pyrimidines. Investigation of the photoluminescence properties of some synthesized pyrimidine derivatives in THF solutions showed that the fluorescence efficiency depends not only on the nature of the π-conjugated aromatic systems, but also on their position in the pyrimidine ring. The arrangement of the π-conjugated aromatic systems in the fourth and sixth

positions of the pyrimidine ring were found to be more favorable for the fluorescence properties.

Practical implications: The synthesis of arylboronic acids was optimized and applied for their production in large scale. General methods for the synthesis of 2,4-diaryl-, 4.6- diaryl-,, and 2,4,6-diaryl-triarylpyrimidines were developed. The performed optical studies of the synthesized compounds suggest that some of them can be of interest as potential light-emitters for OLED.

Main statements for the defence:

1. In the Suzuki reaction of 4,6-dichloropyrimidines bearing various substituents in the second and fifth positions of the pyrimidine ring, with equivalent amounts of arylboronic acids mono- and diarylpyrimidine derivatives are formed. Using an excess of arylboronic acids and $Pd(OAc)_2/PPh_3/K_3PO_4$ and $Pd(PPh_3)_2Cl_2/K_3PO_4$ as catalytic systems leads to the formation of the corresponding 4,6-diarylpyrimidines in good yields.

2. Using $Pd(OAc)_2/PPh_3/Na_2CO_3$ and $Pd(OAc)_2$/ (2-biphenyl) dicyclohexylphosphine/K_3PO_4 catalytic systems enables to perform a sequential Suzuki cross-coupling reactions in the fourth and the second positions of 2,4-dichloro-6-methylpyrimidine. and to synthesize 2,4-diaryl-6-methylpyrimidines with different or identical aryl groups.

3. The reaction of 4,6-dimethylpyrimidines with aromatic aldehydes, in the presence of anhydrous zinc chloride produces 4,6-distyrylpyrimidines.

4. Pyrimidine derivatives containing conjugated aromatic side chains exhibit UV-fluorescence. Fluorescence characteristics (emission maxima, fluorescence quantum yield) are strongly influenced not only by the nature of aryl groups but also by their position in the pyrimidine ring. The

fluorescence of the pyrimidine compounds can be controlled by aryl groups.

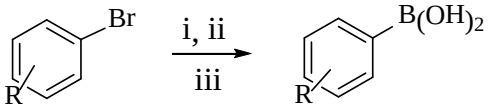
The main results of the present work were published in 2 articles in the international peer-reviewed scientific journals and were presented at 8 scientific conferences.

2. Results and discussion

2.1. Synthesis of initial compounds

2.1.1. Synthesis of arylboronic acids.

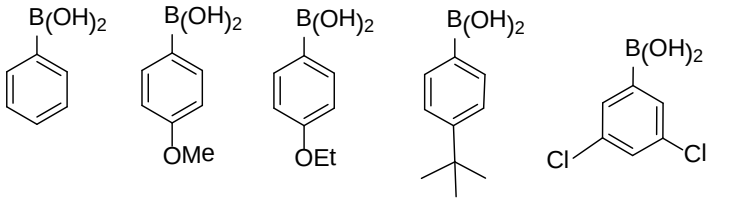
The target arylboronic acids **c, e-j** were synthesized by one-pot procedure from the corresponding aryl bromides through the reaction of intermediate Grignard reagents with trimethylborate and following hydrolysis of the formed esters (Scheme 1, Figure 1). It is worthy of note, that this method allows to synthesize arylboronic acids in multigram scale. Phenyl- (**a),** 4-methoxyphenyl- (**b)** and 4-*tret*-butylphenylboronic acids (**d)** were purchased and used in the reactions without further purification.



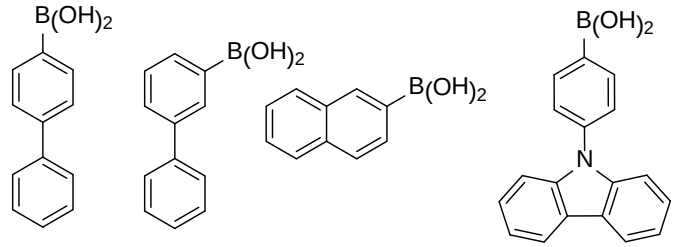
c, e-j

Scheme 1. *Reagents and conditions:* (i) Mg, THF, Δ; (ii) $B(OMe)_3$, THF, -70 °C; (iii) H_2SO_4.

Figure 1. A set of synthesized arylboronic acids.



a **b** **c(80%)** **d** **e(69-73%)**

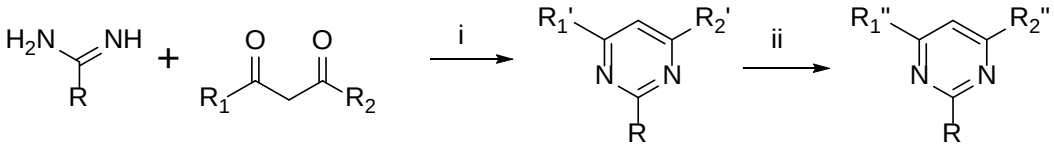


f(80-85%) **g(79%)** **h(55%)** **j(50-53%)**

2.1.2 Synthesis of 4,6-dichloro- and 4-chloropyrimidines.

4,6-Dichloropyrimidines (4,6-dichloro-2-methylpyrimidine (**1**), 4,6-dichloro-2-methylthiopyrimidine (**2**), 4,6-dichloro-5-cyano-2-methylthiopyrimidine (**3**), 4,6-dichloro-5-formyl-2-methylthiopyrimidine (**4**), 2-amino-4,6-dichloro-5-formylpyrimidine (**5**), 2-amino-4,6-dichloropyrimidine (**6**), 4,6-dichloro-5-nitropyrimidine (**7**)) were synthesized from the corresponding 4,6-dihydroxypyrimidines according to the procedures described in the literature. Other 2-substituted 4,6-dichloro- and 4-chloro-6-methylpyrimidines **12-15** were synthesized by condensation of the corresponding 1,3-dicarbonyl compounds with the corresponding amidines in the presence of sodium methoxide and following reaction of the obtained pyrimidinones **8-11** with phosphorus oxychloride to give the target compounds in good yields (Scheme 2, Table 1).

Scheme 2.



8-11 **12-15**

Scheme 2. *Reagents and conditions*: (i) NaOMe, MeOH, 6-12 h, Δ; (ii) $POCl_3$, 4-8 h, Δ.

Table 1. Preparation of 2-substituted 4,6-dichloro-, 4-chloro-6-methyl- and 4-chloro-6-methoxypyrimidines **8-15**

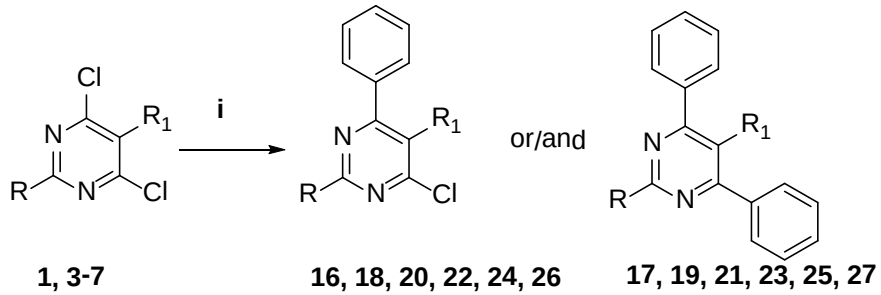
№	R	R_1	R_2	R_1‘	R_2‘	Yield (%)	№	R_1“	R_2“	Yield (%)
8	4- EtC_6H_4	OMe	OMe	OH	OH	86	**12**	Cl	Cl	78
9	4-$NMe_2C_6H_4$	OMe	OMe	OH	OH	26	**13**	Cl	Cl	70
10	4-EtC_6H_4	OMe	Me	OH	Me	70	**14**	Cl	Me	60
11	4-$NMe_2C_6H_4$	OMe	Me	OH	Me	25	**15**	Cl	Me	76

It should be noted, that compounds **1**, **8** were synthesized using the corresponding amidine hydrochlorides, and for the synthesis of 2-(4-*N*, *N*-

dimethylaminophenyl)-4,6-dihydroxypyrimidine (**9**) and 2-(4-*N*,*N*-dimethylaminophenyl)-4-methyl-6-pyrimidone (**11**) 4-(*N*,*N*-dimetylamino)-benzamidine acetate was used as a starting material.

2.2. Study on the Suzuki reaction of 2- and/or 5-disubstituted-4,6-dichloropyrimidines (1, 3-7) with arylboronic acids.

Our investigation on *Suzuki* reaction conditions started with the cross-coupling of 4,6-dichloropyrimidines **1**, **3-7** with phenylboronic acid **a** (Scheme 3).



1, 3-7 **16, 18, 20, 22, 24, 26** **17, 19, 21, 23, 25, 27**

Scheme 3. *Reagents and conditions*: .(i).$C_6H_5B(OH)_2$, base, catalyst, solvent, reaction temperature. **1**) R=Me, R_1=H; **3**) R=SMe, R_1=CN; **4**) R=SMe, R_1=CHO; **5**) R=NH_2, R_1=CHO; **6**) R=NH_2, R_1=H; **7**) R=H, R_1=NO_2.

Initially, compound **3** [3] was coupled with a slight excess of phenylboronic acid using $Pd(OAc)_2/PPh_3/Na_2CO_3$ (aqueous 1M solution) as a catalyst system in tetrahydrofurane. However, conversion of **3** was very slow and led to a complex mixture of products (Table 2, entry 1). Almost the same result was obtained when Cs_2CO_3 was used as a base instead of Na_2CO_3 (Table 2, entry 2). Using $Pd_2(dba)_3$ as a catalyst instead of $Pd(OAc)_2$ did not give the desirable result and a mixture of **18** and **19** with the latter compound as major product was isolated in negligible amount. It should be mentioned that in spite of the fact that equivalent amount of phenylboronic acid was used both chlorine groups of compound **3** took part in the coupling reaction (Table 2, entries 2 and 3). Performing the reaction of **3** with 2.16 equiv. of phenylboronic acid

resulted in the formation of the corresponding 4,6-diphenylpyrimidine **19** only in 29% yield (Table 2, entry 4).

Table 2: Results of the Suzuki reaction of compounds **1, 3-7** with phenylboronic acid.

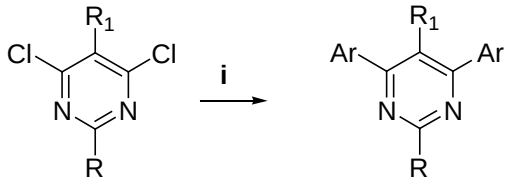
Entry	Compd.	$PhB(OH)_2$ equiv.	Catalyst/Ligand	Base/Solvent	Reaction. temp.°C/ Duration (h)	Product yield (%)*
1	**3**	1.08	$Pd(OAc)_2/PPh_3$	Na_2CO_3/ H_2O/THF	Δ/35 h	ND
2	**3**	1.08	$Pd(OAc)_2/PPh_3$	Cs_2CO_3/ H_2O /THF	Δ/33h.	**18+19** (traces) **
3	**3**	1.08	$Pd_2(dba)_3/PPh_3$	Cs_2CO_3/ H_2O /THF	Δ/28 h.	**18:19=** 1:3**
4	**3**	2.16	$Pd(OAc)_2/PPh_3$	Cs_2CO_3/ H_2O /THF	Δ/11 h.	**19** (29)
5	**3**	1.08	$Pd(OAc)_2/PPh_3$	K_3PO_4/ dioxane	70°C /25 h.	**18** (26)
6	**3**	2.16	$Pd(OAc)_2/PPh_3$	K_3PO_4/ dioxane	Δ/2.7 h.	**19** (51)
7	**4**	1.08	$Pd(OAc)_2/PPh_3$	K_3PO_4/ dioxane	70°C /35 h.	**20** (34)
8	**4**	1.08	$Pd_2(dba)_3/PPh_3$	K_3PO_4/ dioxane	rt/72 h.	**20**(42)
9	**4**	2.16	$Pd(OAc)_2/PPh_3$	K_3PO_4/ dioxane	Δ/2,75 h.	**21** (62)
10	**5**	2.16	$Pd(OAc)_2/PPh_3$	K_3PO_4/ dioxane	Δ/13 h.	**23** (68)
11	**5**	2.16	$Pd(OAc)_2$/dppb	K_3PO_4/ dioxane	Δ/3 h.	ND
12	**5**	2.16	$Pd(OAc)_2/P(o\text{-tolil})_3$	K_3PO_4/ dioxane	Δ/13 h.	ND
13	**5**	2.16	$Pd(OAc)_2$/(2-biph)PCy_2	K_3PO_4/ dioxane	Δ/5 h.	recovered **5**
14	**5**	2.16	$Pd(PPh_3)_2Cl_2$	K_3PO_4/ dioxane	Δ/7 h.	**23**(85)
15	**6**	2.16	$Pd(OAc)_2/PPh_3$	K_3PO_4/ dioxane	Δ/25 h.	**25** (59)***
16	**6**	2.16	$Pd(PPh_3)_2Cl_2$	K_3PO_4/ dioxane	Δ/3.5 h.	**25**(51)
17	**1**	2.16	$Pd(PPh_3)_2Cl_2$	K_3PO_4/ dioxane	Δ/3 h.	**17**(75)***
18	**7**	2.16	$Pd(OAc)_2/PPh_3$	K_3PO_4/ dioxane	Δ/2 h.	**27 (**21)

*The yields are after isolation and purification by the column chromatography.
**Determined by ^1H NMR spectra.
***Physical properties of compounds **17, 25** corresponded to the reported data [4] where they were synthesized from acyclic precursors by cyclocondensation reactions

It was decided that a reason of such poor reaction course may be the presence of water in the reaction mixture. It is known, that chlorine groups in positions 4 and 6 of the pyrimidine ring are very reactive toward various nucleophiles [5]. Thus, in addition to other possible side reactions, such as, dehalogenation, homocoupling and *etc.*, hydrolysis of chlorine atoms under the alkaline reaction conditions could also occur to give several side products. Therefore, for further study, K_3PO_4/anhydrous dioxane was chosen as a base/solvent

system. Using $Pd(OAc)_2/PPh_3/K_3PO_4$ as a catalyst system, the reaction of **3** with 1.08 equiv. of phenylboronic acid gave a complex mixture of products and after purification compound **18** was isolated only in 26% yield (Table 2, entry 5). When the cross-coupling reaction was carried out with 2.16 equiv. of phenylboronic acid in an anhydrous dioxane with K_3PO_4 as a base double cross-coupling occurred to give compound **19**in 51% yield (Table 2, entry 6). The Suzuki reaction of 4,6-dichloro-2-methylthiopyrimidine-5-carbaldehyde (**4**) with 1.08 equiv. phenylboronic acid using $Pd(OAc)_2/PPh_3/K_3PO_4$ in dioxane at 70°C furnished 4-chloro-2-methylthio-6-phenylpyrimidine-5-carbaldehyde (**20**) in 34% yield (Table 2, entry 7). A slightly better yield of **20** (42%) was obtained when $Pd_2(dba)_3$ was used as a catalyst and reaction was carried out at room temperature (Table 2, entry 8). In the reaction of **4** with 2.16 equiv. of phenylboronic acid at reflux temperature of dioxane, the corresponding 4,6-diphenylpyrimidine **21** was obtained in 62% yield (Table 2, entry 9). Compounds **5**, **6** [6, 7] bearing strong electron-donating and capable to form complexes with palladium species amino group in the position 2 of the pyrimidine ring reacted with phenylboronic acid only at elevated temperatures. Moreover, possibly due to decreased reactivity of chlorine groups, the cross-coupling reaction with 1.08 equiv. phenylboronic acid did not give monophenyl derivatives **22, 24**. With both substrates **5**, **6**, the side reactions competed with the cross-coupling reaction and, at best, formation of both monophenyl and diphenyl derivatives was observed. However, performing the reaction of **5**, **6** with double amount of phenylboronic acid using $Pd(OAc)_2/PPh_3/ K_3PO_4$ as a catalyst system gave **23, 25** in 68% and 59% yields, respectively (Table 2, entries 10 and 15). To increase the yield of the cross-coupling product **23** bidentate ligand 1,4-di(triphenylphosphino)butane (dppb) and more electron rich and sterically hindered ligands—tri(*o*-tolyl)phosphane and (2-biphenyl)dicyclohexylphosphine were used in the reaction. However, the side reactions competed again and complex mixtures of products were formed (Table 2, entries 11 and 12) or no reaction was observed (Table 2, entry 13). It was found that using $Pd(PPh_3)_2Cl_2$ instead $Pd(OAc)_2$

sometimes gives better results (Table 2, entries 14 and 16) and there is no necessity to add an additional amount of ligand when $Pd(PPh_3)_2Cl_2$ is used as a catalyst. Under these conditions, 4,6-diphenyl-2-methylpyrimidine (**17**) was obtained in 73% yield (Table 2, entry 17). The cross-coupling of 4,6-dichloro-5-nitropyrimidine (**7**) with phenylboronic acid proceeded ambiguously. Nitro group due to its electron-withdrawing nature activates chlorine groups in the positions 4 and 6 of the pyrimidine ring, but this, perhaps, increases chances of side reactions to take place. Thus, after 2 h substrate **26** disappeared from the reaction mixture (TLC data), but the desirable 4,6-diphenyl-5-nitropyrimidine (**27**) was isolated only in 21% yield (Table 2, entry 18).



1, 5

28 (50%)
29 (20%)
30 (65%)

Scheme 4. *Reagents and conditions*: (i).2.16 equiv. Ar-$B(OH)_2$, 2.5 mol% $Pd(PPh_3)_2Cl_2$, 6.2 equiv. K_3PO_4, dioxane, argon, Δ. **28**) R=NH_2, R_1=CHO, Ar=4-biphenyl; **29**) R=NH_2, R_1=CHO, Ar=4-*tert*-butylphenyl; **30**) R=Me, R_1=H, Ar=4-*tert*-butylphenyl.

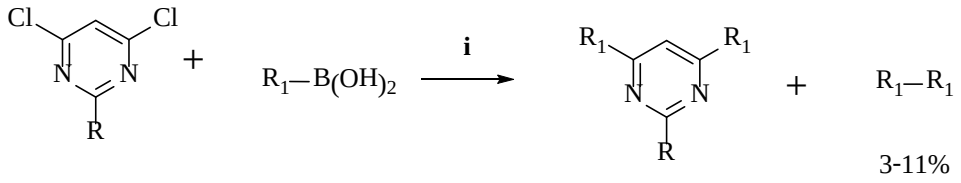
Taking into account the results of the cross-coupling reactions of **1**, **5** with phenylboronic acid some 4,6-diarylpyrimidines **28-30** using $Pd(PPh_3)_2Cl_2/K_3PO_4$ as a catalyst system were synthesized (Scheme 4).

In conclusion, the performed investigation showed that the synthesis of 6-aryl-4-chloropyrimidines bearing various substituents in the second and fifth positions of the pyrimidine ring by the Suzuki cross-coupling reaction is problematic. The reaction proceeds with the formation of mixtures of mono- and diarylpyrimidines. Otherwise, the *Suzuki* cross-coupling reaction of the corresponding 4,6-dichloropyrimidines with double amount of arylboronic acids using $Pd(OAc)_2/PPh_3/K_3PO_4$ or $Pd(PPh_3)_2Cl_2/K_3PO_4$ as catalyst systems

in dioxane furnishes the corresponding 2- and/or 5-substituted 4,6-diarylpyrimidines in reasonable yields.

2.3. Synthesis of 2-substituted 4,6-diarylpyrimidines.

Taking into account our results on the synthesis of 4,6-diarylpyrimidines bearing various substituents in positions 2 and 5 of the pyrimidine ring by the Suzuki reaction $Pd(PPh_3)_2Cl_2/K_3PO_4$ was chosen in the present investigation as a catalyst system. Thus, 4,6-dichloropyrimidines **1, 2, 12, 13** reacted with a slight excess of the corresponding arylboronic acids in the presence of 2.5 mol% of $Pd(PPh_3)_2Cl_2$ to give the corresponding 4,6-diarylpyrimidines **32(c, f, j) 31, 33, 34(c, e-j)** in moderate yields (Scheme 5, Table 3). Lower yields of compounds **31g, 31h, 33h, 34c, 34g** were obtained, presumably because of formation of homo-coupling products of boronic acids in reasonable amounts. All the reactions were carried out by reflux in anhydrous dioxane under argon atmosphere. The reaction time depending on the nature of arylboronic acids varied from 4 to 10 hours. The structure of the obtained compounds **32(c, f, j) 31, 33, 34(c, e-j)** was consistent with their ^1H and ^{13}C NMR spectra and elemental analysis data.



1,2,12, 13

32(c, f, j), 31, 33, 34(c, e-j)

Scheme 5. *Reagents and conditions*: (i) $Pd(PPh_3)_2Cl_2$, K_3PO_4, dioxane, Δ, argon.

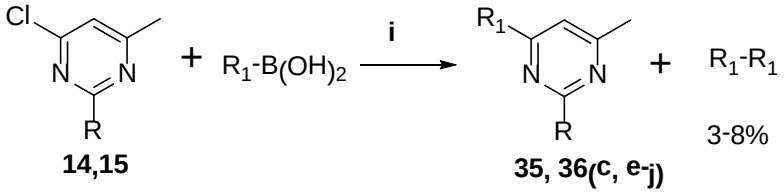
Table 3: Results of synthesis of compounds **32(c, f, j) 31, 33, 34(c, e-j)**.

Entry	Compd.	R\R$_1$	**c***	**e***	**f***	**g***	**h***	**j***
1	**31**	Me	60%	50%	82%	13%	30%	55%
2	**32**	SMe	60%	-	60%	-	-	51%
3	**33**	4-EtC_6H_4	65%	53%	91%	43%	25%	76%
4	**34**	4-N$Me_2C_6H_4$	25%	64%	42%	30%	49%	64%

*** c)** 4-ethoxyphenyl, **e)** 3,5-dichlorophenyl, **f)** 4-biphenyl, **g)** 3-biphenyl, **h)** 2-naphthyl, **j)** 4-(9-carbazolyl)phenyl.

2.4. Synthesis of 2-substituted 4-methyl-6-arylpyrimidines.

2-Substituted 6-chloro-4-methylpyrimidines **14, 15** reacted with a slight excess (1.2 equiv.) of the corresponding arylboronic acid (**c, e-j**) in the presence of 2 mol% of $Pd(PPh_3)_2Cl_2$ to give the target 2-substituted 6-aryl-4-methylpyrimidines **35, 36(c, e-j)** (Scheme 6, Table 4). All the reactions were carried out by reflux in anhydrous dioxane under argon atmosphere. The reaction time depending on the nature of arylboronic acids varied from 4 to 16 hours. The structure of the obtained compounds **35, 36(c, e-j)** was consistent with their ^1H and ^{13}C NMR spectra and elemental analysis data.



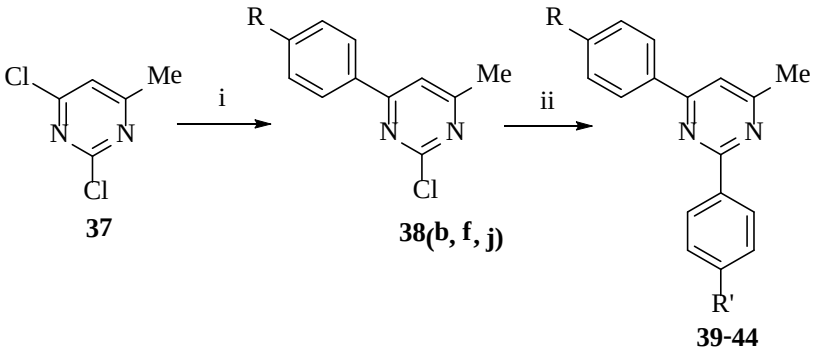
Scheme 6. *Reagents and conditions*: (i) $Pd(PPh_3)_2Cl_2$, K_3PO_4, dioxane, Δ, argon.

Table 4: Results of synthesis of compounds **35, 36(c, e-j)**.

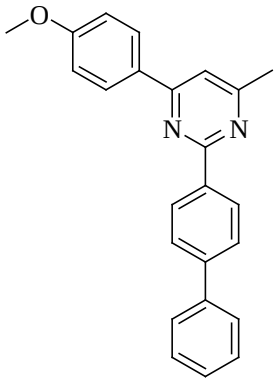
Entry	Compd.	R\R$_1$	**c***	**e***	**f***	**g***	**h***	**j***
1	**35**	4-C_6H_4Et	78%	72%	59%	24%	70%	17%
2	**36**	4-$C_6H_4NMe_2$	75%	34%	93%	36%	70%	23%

***c)** 4-ethoxyphenyl, **e)** 3,5-dichlorophenyl, **f)** 4-biphenyl, **g)** 3-biphenyl, **h)** 2-naphthyl, **j)** 4-(9-carbazolyl)phenyl.

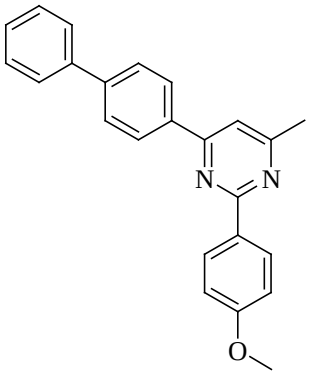
We have found that monoarylation of compound **37** with arylboronic acids can be achieved using a slight excess (1.2 equiv.) of the corresponding arylboronic acids in the presence of $Pd(OAc)_2/PPh_3/Na_2CO_3$ (aq.) as a catalyst system (Scheme 7). However, the yields of 4-aryl-2-chloro-6-methylpyrimidines **38(b, f, j)** because of a more complex isolation from the reaction mixture were moderate or low. All attempts to accomplish substitution of 2-chlorine group with aryl moieties by the Suzuki coupling of **38(b, f, j)** with arylboronic acids using the same catalytic system failed. In this case catalyst system – $Pd(OAc)_2/PCy_2$(2-biphenyl)/K_3PO_4 appeared to be more suitable.



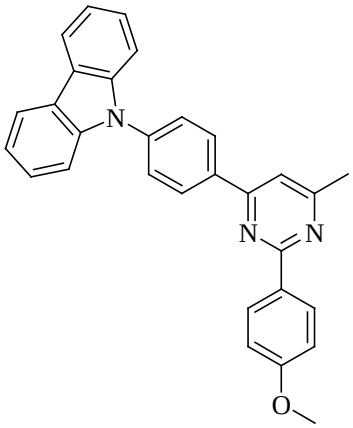
Scheme 7. *Reagents and conditions*: (i) 2 equiv. $ArB(OH)_2$, 5 mol% $Pd(OAc)_2$, 10 mol% PPh_3, Na_2CO_3(aq.), dioxane, argon, Δ. (ii) 1.2 equiv. $ArB(OH)_2$, 2 mol% $Pd(OAc)_2$, 4 mol% P(2-biPh)Cy_2, K_3PO_4, dioxane, argon, Δ. **38b**) R=OMe (40%); **38f**) R=Ph (33%); **38j**) R=9-carbazolyl (59%).



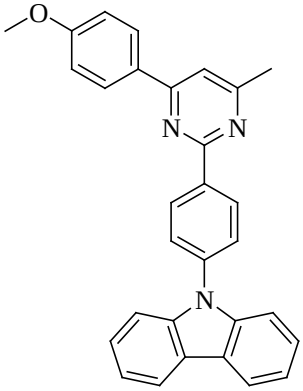
39(72%)



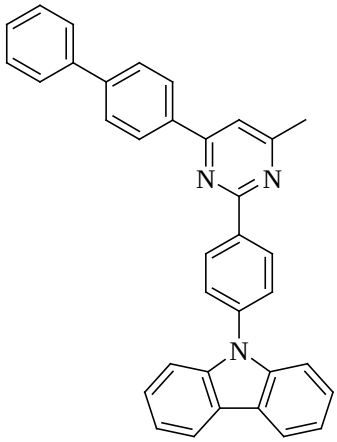
40(66%)



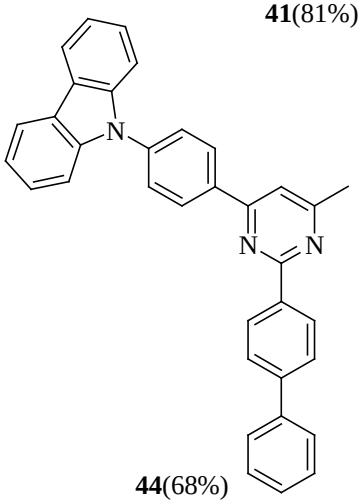
41(81%)



42(68%)

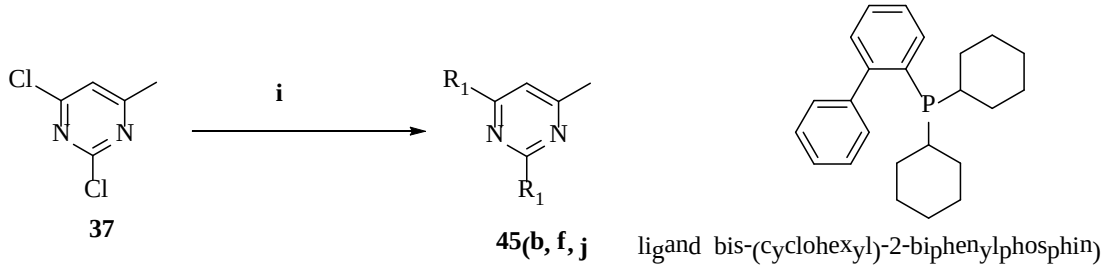


43(77%)

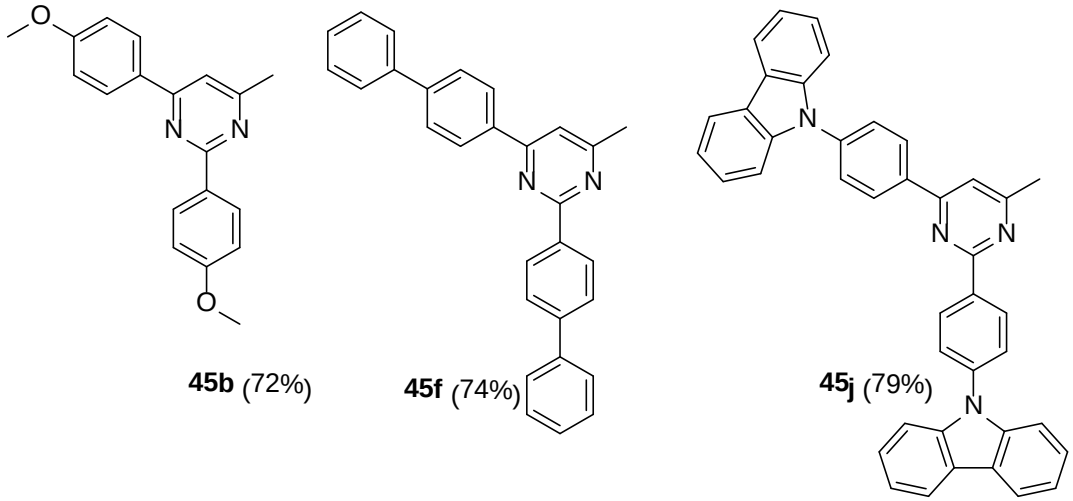


44(68%)

Thus, reaction of compounds **38(b, f, j)** with a slight excess of arylboronic acids using $Pd(OAc)_2/PCy_2$(2-biphenyl)/K_3PO_4 as a catalyst system led to the corresponding 2,4-diaryl-6-methylpyrimidines **39-44** in 66-81% yields (Scheme 7). Employing this catalyst system, the Suzuki reaction of 2,4-dichloro-6-methylpyrimidine (**37**) with boronic acids **b, f, j** gave the coresponding pyrimidines **(45b, f, j)** with yields 72%/74%/79%, respectively (Scheme 8). It is worthy to note that catalyst system - $Pd(OAc)_2/PCy_2$(2-biphenyl)/K_3PO_4 appeared to be unsuitable for the synthesis of 4-aryl-2-chloropyrimidines **38(b, f, j)** starting from dichloropyrimidine **37**.



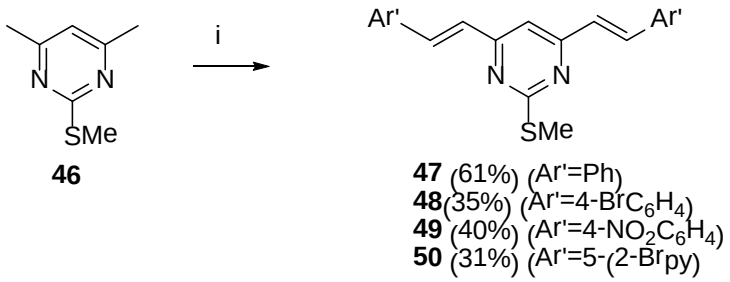
Scheme 8. *Reagents and conditions*: (i) 2.4 equiv. R_1-$B(OH)_2$, 2 mol% $Pd(OAc)_2$, 4 mol% P(2-biPh)Cy_2, K_3PO_4, dioxane, argon, Δ.



2.5. Synthesis of styrylpyrimidines.

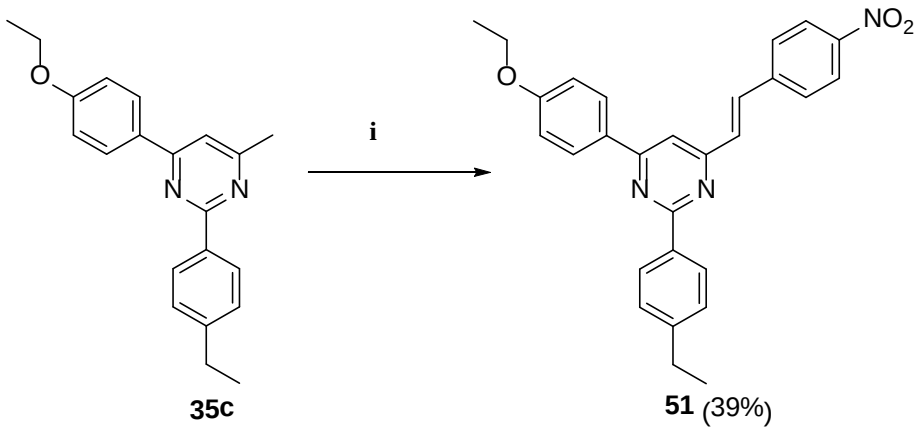
In order to obtain compounds with extended π-conjugated system, we decided to synthesize the corresponding 2-styrylpyrimidine derivatives. The investigation was performed on the example of 4,6-di(4-biphenyl)-2-methylpyrimidine (**31f**) using several methods: one of the method for the synthesis of *trans*-olefins is *Wittig* reaction. In order to apply this reaction for the synthesis of the desired compounds, an attempt to synthesize 2-bromomethylpyrimidine derivative was made. It was found that the method was not so good because bromination reaction of 2-methyl-4,6-di(4-biphenyl)pyrimidine (**31f**) was very slow and yield of the target compound was lower than 22%. Another way to get these derivatives is condensation between methyl group and aldehyde in the presence of zinc chloride [10] or potassium hydroxide with transphase catalyst (for example, tetrabutylammonium hydrosulphate [11] or other amonium salts). All these methods were tried and

the best results were obtained by the condensation reaction of corresponding pyrimidines with aldehydes using anhydrous zinc chloride (Scheme 9).



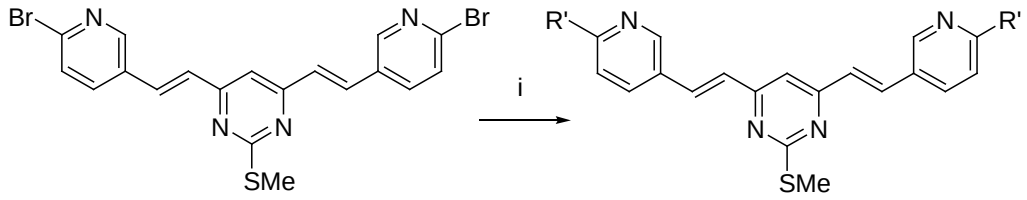
Scheme 9. *Reagents and conditions*: $ZnCl_2$, Ar'CHO, 150°C.

Moreover, attempts to synthesize derivatives with one stilbene group (Scheme10) were made. However, all products appeared to be unstable and the only pyrimidine **51** was purified successfully.



Scheme 10. *Reagents and conditions*: $ZnCl_2$, p-$NO_2C_6H_4CHO$, 150°C.

After purification of the obtained pyrimidines **47-50** it was decided to accomplish Suzuki reaction of pyrimidine **50** with different arylboronic acids in the presence of $Pd(PPh_3)_2Cl_2/K_3PO_4$ as a catalyst system. Thus, derivative **50** reacted with a slight excess of the corresponding arylboronic acid in the presence of 2 mol% of $Pd(PPh_3)_2Cl_2$ to give the desired pyrimidines **52(c, f, h, j)** (Scheme 11). All the reactions were carried out by reflux in anhydrous dioxane under argon atmosphere.



50

52c (55%) (R'= 4-OEtC_6H_4)
52f (15%) (R'= 4-PhC_6H_4)
52h (23%) (R'= 2-naftil)
52j (8%) (R'= N-(4-phenyl)carbazolyl)

Scheme 11. *Reagents and conditions*: (i) 2 mol% $Pd(PPh_3)_2Cl_2$, 2.5 equiv., R_1-$B(OH)_2$, K_3PO_4, dioxane, Δ.

2.6. Photophysical properties of 2-substituted-4,6-diarylpyrimidines.

The synthesized pyrimidine derivatives **31j, 32j, 33f, 33j, 34j** were subjected to optical absorption and fluorescence studies in tetrahydrofuran solutions. The emission and absorption characteristics of compounds **31j, 32j, 33f, 33j, 34j** together with the radiative rate constants (k_r), radiationless rate constants (k_{nr}), and emission lifetimes (τ) are collected in Table 5. Since the k_r and k_{nr} values are related to the corresponding emission quantum yields and life times by $k_r=\Phi_\Phi/\tau$ 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. An investigation of photophysical properties of the synthesized compounds has shown that they exhibit strong absorption in dilute THF solution with their absorption maxima positioned in the range 237-363 nm. It should be noted, that almost all compounds show UV-blue fluorescence in THF solution except compound **34j** (enrty 5), which show yellow fluorescence. However, it's fluorescence quantum yield is quite low. Depending on the origin of aryl branches emission maxima of compounds **31j, 32j, 33f, 33j, 34j** are located in the range 345-576 nm (Table 5).

Table 5. UV-VIS absorption and PL data for the series of compounds **31j, 32j, 33f, 33j, 34j** THF solution (c = 10^{-5} M).

Entry	Compd.	λ_{abs}, nm	ε, $l \cdot mol^{-1} \cdot cm^{-1}$	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}
1	**31j**	291 343	$3.50 \cdot 10^4$ $3.64 \cdot 10^4$	437	85	5514	4.1	0.21	0.04
2	**32j**	292 343 363	$3.42 \cdot 10^4$ $2.71 \cdot 10^4$ $3.63 \cdot 10^4$	447	65.4	5177	3.22	0.20	0.11
3	**33f**	295 333	$6.32 \cdot 10^4$ $3.21 \cdot 10^4$	369	0.5	2930	<0.1	-	-
4	**33j**	265 287 343	$4.11 \cdot 10^4$ $2.49 \cdot 10^4$ $2.13 \cdot 10^4$	436	60	7552	3.72	0.16	0.11
5	**34j**	282 291 344	$1.72 \cdot 10^4$ $1.71 \cdot 10^4$ $2.98 \cdot 10^4$	576	3.5	11624	9.18	0.004	0.11

Excited at 350-360 nm

Compound **31j,** bearing carbazolylphenyl units in positions 4 and 6 of the pyrimidine moiety and methyl group in position 2, exhibits strong fluorescence in THF at 437 nm with fluorescence quantum yield 85%. Fluorescence lifetime of compound **31j** (entry 1) is 4.1 ns (Table 5, entry 1, figure 2).

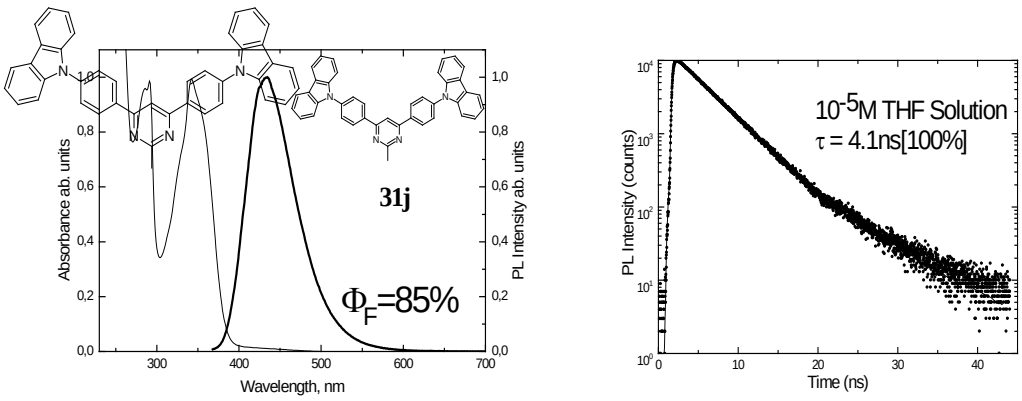


Figure 2. Absorption and PL spectra, fluorescence lifetimes of compound **31j** in THF solution.

Compounds **32j, 33j** with (carbazolyl)phenyl fragments in positions 4 and 6 of the pyrimidine moiety and methylthio and 4-ethylphenyl groups in position 2, respectively, exhibit lower fluorescence quantum yield (**32j** - 65.4%; **33j** -

60%) when compared with that of compound **31j**. However, methylthio group causes a bathochromic shift of fluorescence band of about 10 nm (Table 5, entries 1, 2). Compound **33f** containing 4-biphenyl groups has its emission maxima in dilute THF solution at 369 nm with extremely low fluorescence quantum yield 0.5%. Interestingly, compound **34j** in spite of the presence of (carbazolyl)phenyl groups in the molecule showed low fluorescence quantum yield (3.5%). This is caused by very low contribution of radiation processes. Kr for compound 34j is more than 50 times lower than kr for **31j** (Table 5, entries 1, 5). Moreover, for this compound very large Stokes shift and bathochromic shift of the fluorescence band was observed. Fluorescence maximum of **34j** was observed at 576 nm. This can be attributed to electronic influence of 4-dimethylaminophenyl group compound **34j**.

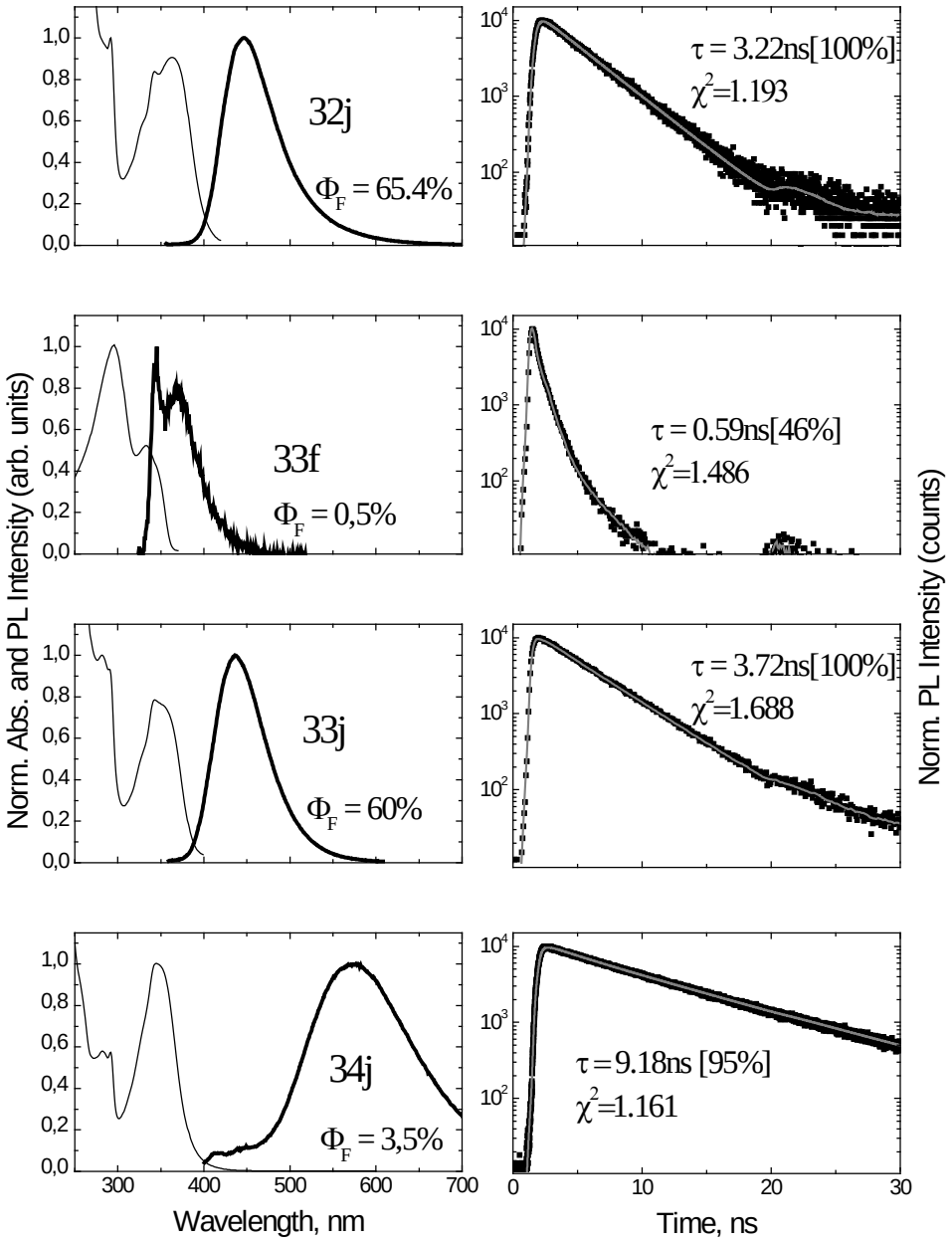


Figure 3. Absorption and PL spectra, fluorescence lifetimes of compounds **32j, 33f, 33j, 34j** in THF solution ($c = 10^{-5}$ M).

1.7 Photophysical properties of pyrimidines 41-44, 45j.

The emission and absorption characteristics of compounds and **41-44, 45j** together with the radiative rate constants (k_r), radiationless rate constants (k_{nr}), and emission lifetimes (τ) are collected in table 6. Absorption spectra of the

synthesized compounds in dilute THF solution are characterized by several absorption bands positioned in the UV region (λ_{abs} = 255–341 nm) (Table 6, Figure 4). Although absorption spectra of compounds containing one (carbazolyl)phenyl group (**41-44)** particularly resemble each other, some features in the absorption spectra of isomeric compounds **41, 42** and **43, 44** can be highlighted. The absorption band of $\pi \rightarrow \pi^*$ transient at 292 nm of compounds **41-44** has almost two times higher extinction coefficient when compared with the value ε for the absorption band in a region at 340 nm (Table 6).

Table 6. UV-VIS absorption and PL data for the series of compounds **41-44, 45j** in THF solution (c = 10^{-5} M).

Entry	Compd.	λ_{abs}, nm	ε, $l \cdot mol^{-1} \cdot cm^{-1}$	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}
1	**41**	255 291 340	$3.43 \cdot 10^4$ $3.42 \cdot 10^4$ $1.89 \cdot 10^4$	418	47.2	5488	3.76	0.13	0.14
2	**42**	257 292 312 339	$3.28 \cdot 10^4$ $2.92 \cdot 10^4$ $2.14 \cdot 10^4$ $1.53 \cdot 10^4$	402	46.5	4623	2.56	0.18	0.21
3	**43**	258 292 314 341	$3.21 \cdot 10^4$ $3.53 \cdot 10^4$ $2.94 \cdot 10^4$ $1.78 \cdot 10^4$	418	22.3	5402	3.63	0.06	0.21
4	**44**	257 293 341	$3.46 \cdot 10^4$ $4.19 \cdot 10^4$ $1.97 \cdot 10^4$	422	62.2	5715	4.02	0.15	0.09
5	**45j**	292 341	$3.40 \cdot 10^4$ $4.23 \cdot 10^4$	423	59	5684	4.26	0.14	0.10

Excited at 356 nm.

The absorption bands with maxima at around 292 nm and 341 nm are more intense for derivatives **41, 44** in which (carbazolyl)phenyl group is attached at position 4 of the pyrimidine ring in comparison with the absorption of compounds **42, 43** (Table 6)**.** Introduction of the second (carbazolyl)phenyl group into the molecule of dye **45j** does not have significant effect on the

position of these bands. However, the extension of the conjugation in **45j** manifests in a dramatically increased absorbance of the lowest-energy optical transitions (Table 6). The λ_{em}, Φ_F values for the synthesized compounds **41-44, 45j** markedly depend on the nature of aryl branches and their position in the pyrimidine ring. Emission maxima of compounds containing (carbazolyl)phenyl groups in the position 4 and 6 of the pyrimidine ring (**41, 44**) are observed in a longer wavelengths region when compared with 2-[(carbazolyl)phenyl] derivatives **42, 43**. The fluorescence efficiency of isomeric compounds **41** and **42** is very similar (Φ_F: 46.5%, λ_{em},: 402 nm for **42)** and (Φ_F: 47.2%, λ_{em},: 418 nm for **41**). For both compounds radiationless processes are predominant. More expressed differences were observed in the fluorescence characteristics of isomeric compounds **43** and **44**. The higher fluorescence efficiency of **44** (Φ_F: 62.2%, λ_{em},: 422 nm) in comparison with **43** (Φ_F: 22.3%, λ_{em},: 41 nm) is caused by an increase of radiation processes in compound **44** almost in the same extent as radiationless process decreases.

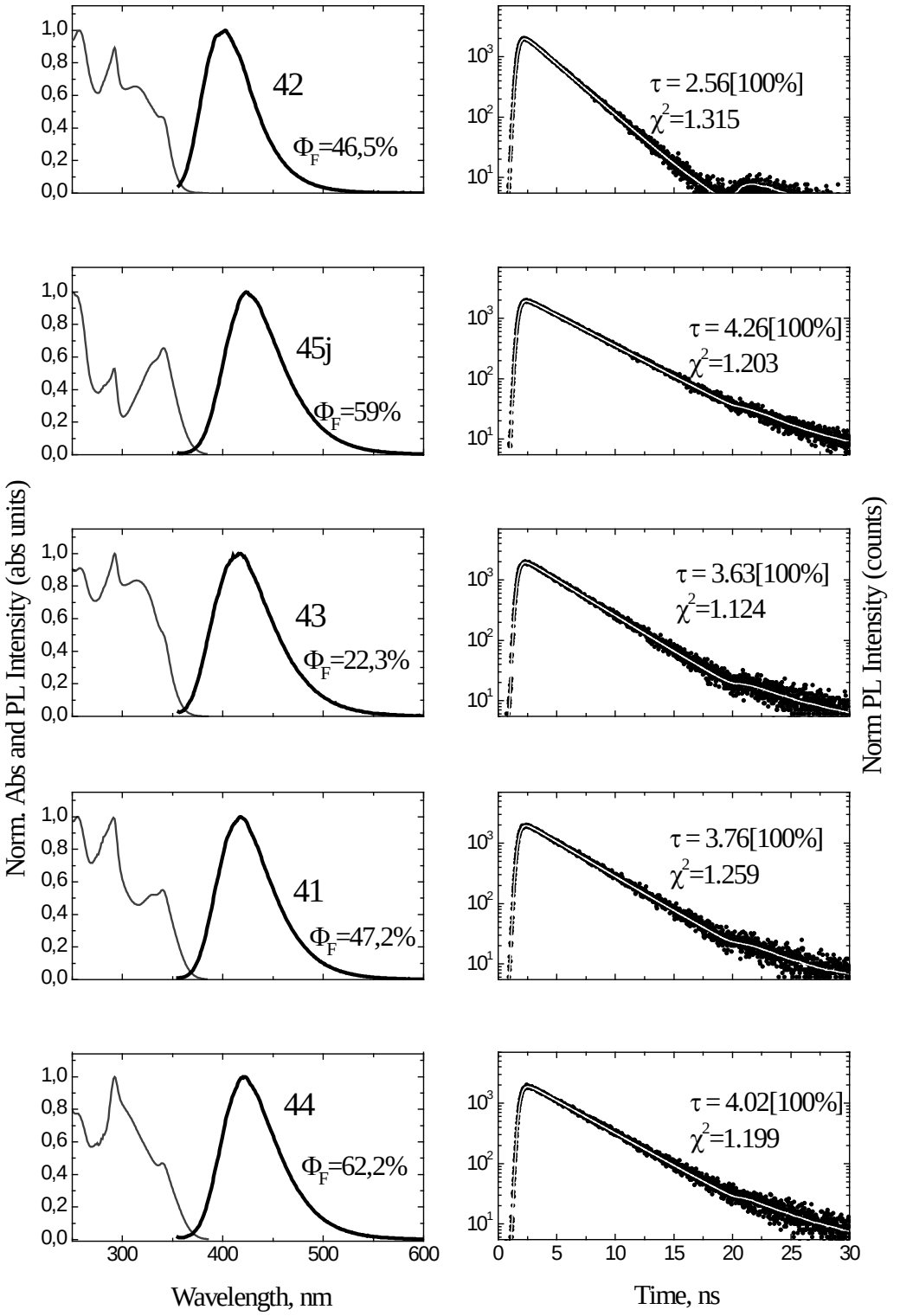


Figure 4. Absorption and PL spectra, fluorescence lifetimes of compounds **41-44, 45j** in THF solution (c = 10^{-5} M).

1.8 Photophysical properties of 4,6-bis{(*E*)-2-[6-arylpyridin-3-yl]vinyl}-2-methylthiopyrimidines 52(c, f, h, j).

It should be noted, that the fluorescent spectra of compounds **52f** and **52h** has two peaks, which indicates that it could be a combination of several modes of excitation and fluorescence extinction kinetics have 2-3 lifetimes (Figure 4), while compound **52j** has a fluorescence peak at 512 nm and a lifetime –2.79 ns. Compound **52f** bearing bulky 4-biphenyl units in positions 4 and 6 of the pyrimidine moiety exhibits strong fluorescence in THF at 425 nm and 445 nm (Table7, Figure 4) with fluorescence quantum yield 9.8%. Derivative **52c** with 4-etoxyphenyl groups in positions 4 and 6 of the pyrimidine moiety exhibits strong blue fluorescence in THF at 456 nm with pronounced fluorescence quantum yield 55% (Table7, Figure 5). Pyrimidine **52h** with 2-naphtyl groups in positions 4 and 6 of the pyrimidine moiety exhibits fluorescence in THF at 423 nm with fluorescence quantum yield 12% (Table7, Figure 5).

Table 7. UV-VIS absorption and PL data for the series of compounds **52(c, f, h, j)** in THF solution (c = 10^{-5} M).

Entry	Compd.	λ_{abs}, nm	ε, $l \cdot mol^{-1} \cdot cm^{-1}$	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}
1	**52c**	276 382 391 412	$1.25 \cdot 10^4$ $2.46 \cdot 10^4$ $2.44 \cdot 10^4$ $1.99 \cdot 10^4$	456	55	2343	1.06	0.52	0.39
2	**52f**	257 313 381	$2.03 \cdot 10^4$ $1.63 \cdot 10^4$ $1.38 \cdot 10^4$	425 445	9.8	2717 3776	-**	-	-
3	**52h**	260 336 382	$21.94 \cdot 10^4$ $2.04 \cdot 10^4$ $2.11 \cdot 10^4$	423 448	12	2538 3857	-	-	-
4	**52j**	255 292 325 339 382	$2.65 \cdot 10^4$ $2.79 \cdot 10^4$ $2.40 \cdot 10^4$ $2.22 \cdot 10^4$ $2.75 \cdot 10^4$	512	61.4	6647	2.79	0.22	0.14

*Excited to 400 nm

** The change is not only exponential and we can not calculate the constants

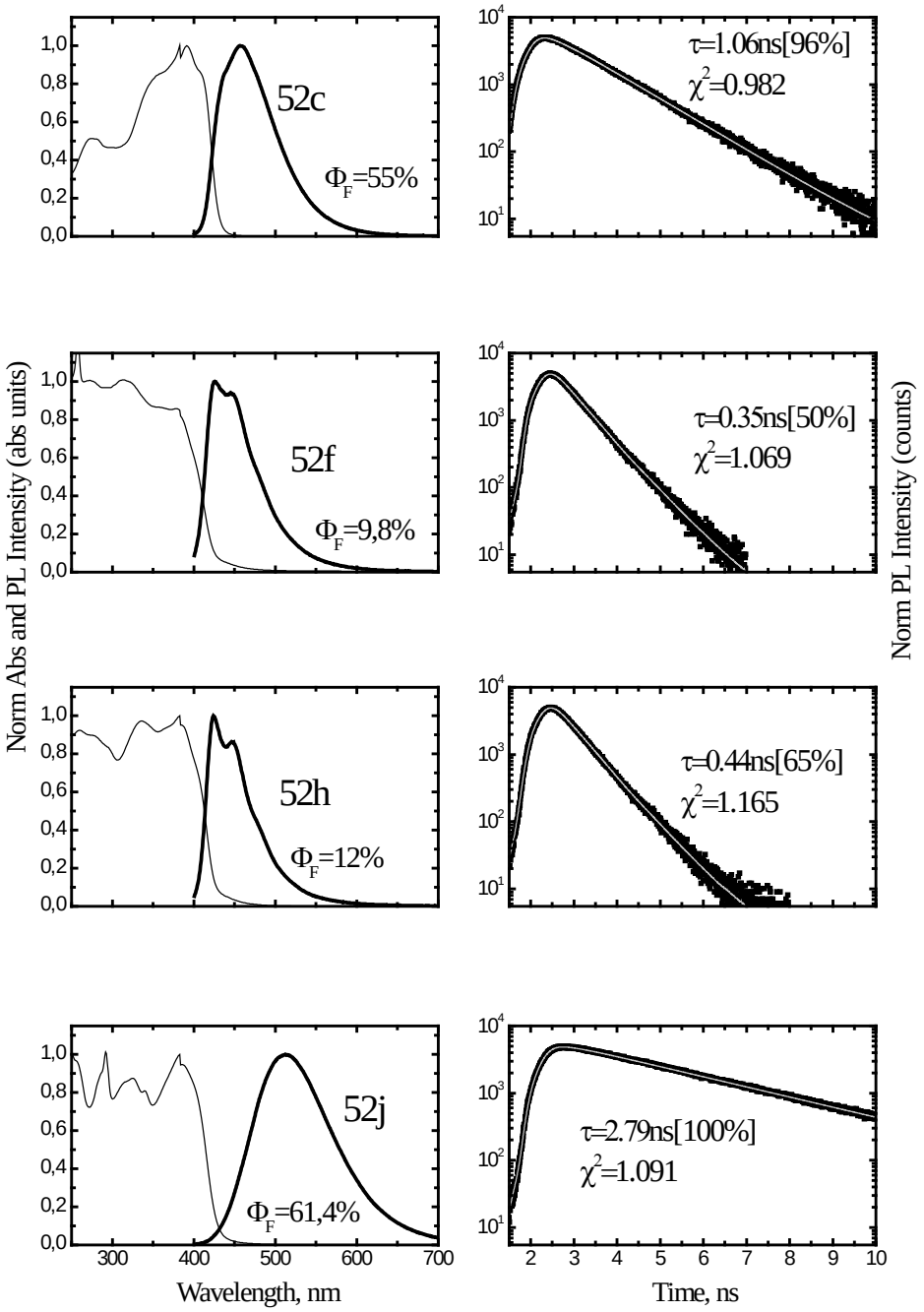


Figure 5. Absorption and PL spectra, fluorescence lifetimes of compounds **52(c, f, h, j)** in THF solution (c = 10^{-5} M).

In summary, the obtained results show that almost all compounds exhibit fluorescence in blue range of 402-456 nm (1-3 tables). However, depending on the nature of the groups in the side chains fluorescence can be monitored in a

range of other colors. For example, compound **32j** λ_{em} = 576 nm, compound **61j** λ_{em} = 512 nm. Fluorescent properties of the pyrimidine derivatives depend not only on the nature of the aromatic side chain, but also on their position in the pyrimidine ring. In addition, photoluminescent properties of the pyrimidine derivatives can be controlled by the electronic nature of aryl groups in the pyrimidine ring. The synthesized 4,6-di[4-(9-carbazolyl)phenyl]-2-methylpyrimidine (**31j**), exhibited the fluorescence quantum yield 85%, which, to the best of our knowledge, is the highest among the fluorescent pyrimidine derivatives.

Conclusions

1. The synthetic procedure of arylboronic acids was optimized. Using reaction of arylmagnesium intermediates with trimethylborate, arylboronic acids were synthesized and the developed procedure employed for the synthesis of arylboronic acids in multigram scale.
2. Effects of catalyst, ligand, base, and solvent on the Suzuki cross-coupling reaction of 4,6-dichloropyrimidines bearing methylthio, methyl, amino, cyano, formyl and nitro groups in the 2nd and/or 5th pyrimidine ring positions, with arylboronic acids were studied and method for the synthesis of the corresponding 4,6-diarylpyirimidines was elaborated.
3. A general method for the synthesis of 2,4-diaryl-6-methylpyrimidines, 4,6-diarylpyrimidines, 2-aryl-4,6-dimethylpyrimidines, 2-substituted 4,6-bis{(E) -2-[6-arylpyridin-3-yl]vinyl}pyrimidines was developed. The gist of the synthesis is the Suzuki cross-coupling reaction of the corresponding 2-aryl-4-chloro-6-methylpyrimidines, 2-chloro-4,6-dimethylpyrimidine and 4,6-di{(E)-2-[6-bromopiridin-3-yl]vinyl}pyrimidines with arylboronic acids in dioxane in the presence of $Pd(PPh_3)_2Cl_2/K_3PO_4$ as a catalyst system.
4. It was shown that mono-and dicross-coupling reactions of 2,4-dichloro-6-methylpyrimidine with arylboronic acids could be controlled by the catalyst system, reaction conditions and amount of arylboronic acids. The methods for the synthesis of 4-aryl-2-chloro-6-methylpyrimidines and 2,4-diaryl-6-methylpyrimidines with the same or different aryl groups were elaborated.
5. Condensation reaction of 2-substituted 4,6-dimetylpyrimidines with aldehydes was studied. It was shown that using a catalytic amount of anhydrous zinc chloride 2-substituted-4,6-distirylpyrimidines are obtained in good yields.
6. Some of the synthesized pyrimidine derivatives with various aromatic fragments in the 2nd, 4th and/or 6th positions of the heterocycle exhibit

UV-blue fluorescence. Depending on the nature of arylgroups and their position in the pyrimidine ring the emission maxima in THF solutions of the majority of the investigated compounds were observed in the range 402-456 nm, the fluorescence lifetimes ranged from 2.56 to 4.26 ns.

7. It was found that among the investigated compounds pyrimidine derivatives containing 4-(9-carbazolyl)phenyl group exhibited the best fluorescence characteristics.

a) The fluorescence efficiency of 4,6-di[4-(9-carbazolyl)phenyl]-2-substituted pyrimidines depends on the nature of groups at the second position of the pyrimidine ring. 4,6-Di[4-(9-carbazolyl)phenyl]-2-methylpyrimidine was found to possess the highest fluorescence quantum yield (Φ_F = 85%). The extension of π-conjugated system by introducing the aromatic ring at the second position of the pyrimidine ring does not improve photoluminescence characteristics of compounds. Particularly strong fluorescence quench (up to Φ_F = 3.5%) causes [(4-dimetilamino)phenyl] group in the second position of the pyrimidine ring.

b) The fluorescence studies of isomeric 2,4-diaryl-6-methylpyrimidines in THF solutions showed that the pyrimidine derivatives containing [4-(9-carbazolyl) phenyl] group in the fourth position of the pyrimidine ring have a higher fluorescence quantum yield. Established fluorescence characteristics of isomeric 2,4-di [4 - (9-carbazolyl) phenyl]-6-methyl- and 4,6-di[4-(9-carbazolyl)phenyl]-2-methylpyrimidine indicate that arrangement of π-conjugated electronic systems in 4,6-positions of the pyrimidine ring is more efficient than in 2,4-positions.

c) 2-(3-pyridyl)ethenyl fragment inserted between the pyrimidine ring and arilgroups have no significant effect on the fluorescence quantum efficiency. However, a significant shortening of the fluorescence lifetimes (up to 1.06 ns) and batochromic shift of emission bands was observed.

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3. A. Voitechovičius, K. Karpavičius, A. Voitechovičiūtė, P. Adomėnas, S.Tumkevičius. Synthesis of Novel 4,6-Diaryl- and 4,6-Bis(2-arylvinyl)pyrimidines. Riga Technical University, Faculty of Materials Science and Applied Chemistry „*Paul Walden 7th Symposium on Organic Chemistry*" Riga (Latvia), September 12-13 d., **2011**; *Latv. J. Chem*., **2012**, No. *1*, 77

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Curriculum Vitae

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2007 - 2011	Vilnius University, Department of Chemistry Department of Organic Chemistry, postgraduate study.
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Santrauka

Organinės medžiagos, kurių molekulės yra sudarytos iš π-konjuguotų elektroninių sistemų, šiuo metu sulaukia didelio dėmesio dėl jų taikymo įvairiuose elektroniniuose ir optoelektroniniuose įrenginiuose. Ieškant efektyvesnių organinių fotopuslaidininkių ir spinduolių, yra kuriamos ir atrandamos naujos medžiagos. Pastaruoju metu didelis dėmesys yra skiriamas nelinijinės struktūros junginiams, kurie dėl gerų šviesą spinduliuojančių, puslaidininkinių savybių, savitvarkos ir gebėjimo sudaryti kompleksus su metalų jonais ar organinėmis molekulėmis yra taikomi OLED, įvairių jutiklių ir jungiklių technologijose.

Šio darbo pagrindiniai tikslas - susintetinti nelinijinės struktūros 2,4,6-tripakeistus pirimidino oligoarilenus ir ištirti jų fotofizikines savybes.

Nustatyta, kad 6-aril-4-chlorpirimidinų, turinčių įvairius pakaitus antroje ir penktoje pirimidino žiedo padėtyse, sintezė iš atitinkamų 4,6-dichlorpirimidinų Suzuki kryžminio jungimo reakcija yra problematiška. Reakcijos metu susidaro mono- ir diarilpirimidino dariniai. Kita vertus, 4,6-dichlorpirimidinų Suzuki reakcijoje su arilborono rūgščių pertekliumi, esant $Pd(OAc)_2/PPh_3/K_3PO_4$ ar $Pd(PPh_3)_2Cl_2/K_3PO_4$ katalitinėms sistemoms, geromis išeigomis susidaro atitinkami 4,6-diarilpirimidinai, turintys antroje ir/ar penktoje pirimidino padėtyse įvairias grupes. Parodyta, kad katalitinė sistema - $Pd(PPh_3)_2Cl_2/K_3PO_4$ - dioksane yra tinkama ir 2,4-diaril-6-metilpirimidinų, 2-aril-4,6-dimetilpirimidinų, 4,6-bis{(*E*)-2-[6-arilpiridin-3-il]vinil}-2-pakeistų pirimidinų sintezėje atitinkamų 2-aril-4-chloro-6-metilpirimidinų, 2-chloro-4,6-dimetilpirimidino bei 4,6-di{(*E*)-2-[6-brompiridin-3-il]vinil}pirimidinų Suzuki kryžminio jungimo reakcijomis su arilborono rūgštimis. Ištirta katalizatoriaus, ligando ir bazės įtaka 2,4-dichlor-6-metilpirimidino paladžio katalizuojamai kryžminio jungimo reakcijai su įvairiomis borono rūgštimis. Nustatyta, kad 2,4-dichlor-6-metilpirimidino mono-kryžminio jungimo reakcijos su įvairiomis arilborono rūgštimis, susidarant atitinkamiems 4-aril-2-chlor-6-metilpirimidinams, geriausiai vyksta naudojant

$Pd(OAc)_2/PPh_3/Na_2CO_3$ katalitinę sistemą. Pasiūlytas 2,4-diaril-6-metilpirimidinų, turinčių skirtingas arba vienodas arilgrupes antroje ir ketvirtoje pirimidino žiedo padėtyse, sintezės būdas. Nustatyta, kad katalitinė sistema - $Pd(OAc)_2$/(2-bifenil)dicikloheksilfosfinas/K_3PO_4 – yra tinkama 2,4-diaril-6-metilpirimidinų sintezėje, atliekant 4-aril-2-chlor-6-metilpirimidinų ir 2,4-dichlor-6-metilpirimidino kryžminio jungimo reakcijas su arilborono rūgštimis. Susintetinti izomeriniai 2,4-diaril-6-metilpirimidino dariniai. Ištirta 2-pakeistų 4,6-dimetilpirimidinų metilgrupės kondensacija su aldehidais. Parodyta, kad naudojant katalitinį bavandenio cinko chlorido kiekį kondensacijos reakcijos produktai - 2-pakeisti-4,6-distirilpirimidinai yra gaunami geromis išeigomis.

Nustatyta, kad susintetinti pirimidino dariniai su įvairiais aromatiniais fragmentais 2-oje, 4-oje ir/arba 6-oje heterociklo padėtyse pasižymi UV-fluorescencinėmis savybėmis. Pastebėta, kad ne tik arilgrupės bet ir jų padėtis pirimidino žiede turi didelę įtaką 2,4-diaril- arba 4,6-diarilpirimidinų fluorescencinėms savybėms. Priklausomai nuo arilgrupių padėties ir prigimties tirtų junginių emisijos maksimumai tetrahidrofurano tirpaluose yra 369 - 576 nm intervale, fluorescencijos kvantiniai našumai kinta nuo 3.5% iki 85%.

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