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Microwave-assisted palladium-catalyzed C–C coupling versus nucleophilic aromatic substitution of hydrogen (S_N^H) in 5-bromopyrimidine by action of bithiophene and its analogues

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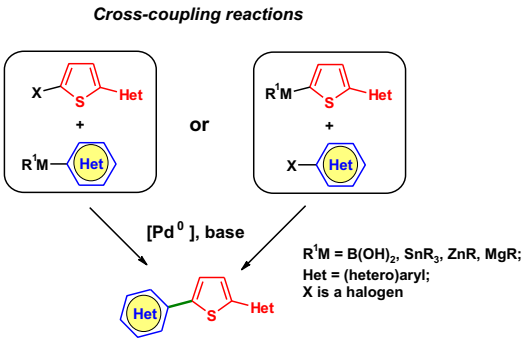
ABSTRACT

5-Bromopyrimidine reacts with 2,2′-bithiophene, [2,2′:5′,2″]terthiophene and 2-phenylthiophene in the presence of a palladium catalyst to give 5-(het)aryl substituted pyrimidines due to the palladium-catalyzed aryl–aryl C–C coupling. However 5-bromo-4-(het)aryl-pyrimidines have been prepared from the same starting materials through the S_N^H-reaction catalyzed by a Lewis acid. Conditions for both types of reactions were optimized. All components of the reaction mixtures, including by-products, have been elucidated by gas–liquid chromatography/mass-spectrometry. Evidence for the structure of 4- and 5-bithiophenyl-substituted pyrimidines has first been obtained by means of X-ray crystallography analysis. Molecular orbital calculations (TDDFT), as well as the redox and optical measurements for all new compounds have also been performed.

1. Introduction

During the last decade, organic molecules bearing both electron-donating and electron-withdrawing fragments, for instance pyrimidine–thiophene conjugated monomers and polymers, have received considerable attention due to their promising optical and electronic properties.[1] Therefore, a search for an access to novel (hetero)arylated bithiophenes is an important task in organic and organometallic chemistry.[2]

The palladium-catalyzed Suzuki, Stille, and Negishi cross-coupling reactions provide a valuable synthetic basis to prepare such compounds.[3] However, these reactions require a preliminary preparation of organometallic intermediates (Scheme 1).



Scheme 1.

It is known that aryl halides can be coupled with a number of electron π-excessive five-membered heteroaromatics,[4] including thiophenes[5] in the presence of a palladium catalyst (Scheme 2).

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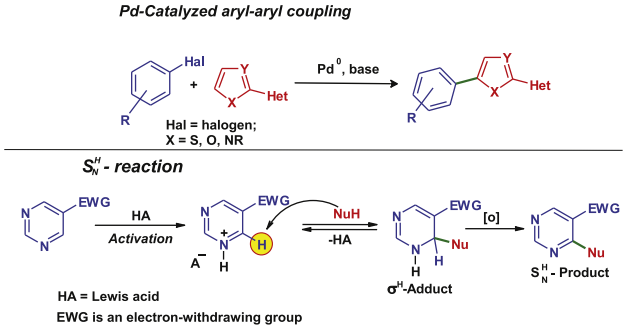


Scheme 2.

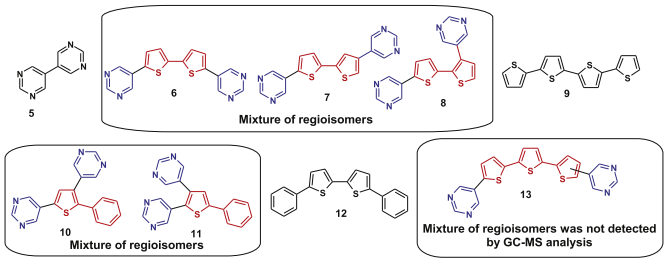


Fig. 1. Structures of by-products derived from the reactions of bithiophene and its analogues with 5-bromopyrimidine, according to the GC–MS analysis.

Indeed, the palladium-catalyzed arylation of heteroaromatics with aryl halides has proved to be a very powerful method for the synthesis of a wide range of aryl substituted heteroaromatics. Aryl-aryl cross-coupling reactions with simple thiophenes have been well elucidated,[5] whereas the palladium-catalyzed arylations of bi-, ter-, and polythiophenes have been scarcely studied.[2] It should be noted that only a few examples of the preparation of monoarylated bithiophenyls by direct arylation reactions have been reported.[2,6]

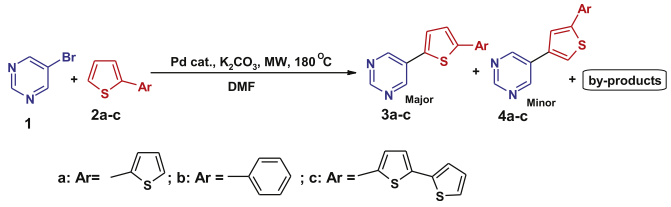
Another synthetic methodology to form the C–C and C–X (X is a heteroatom) bonds is based on nucleophilic aromatic substitution of hydrogen (S_N^H) (Scheme 2).[7] The advantage of this approach is that it does require the presence of a halogen atom in aromatic substrate nor an expensive metal catalyst.

In this paper we wish to report new protocols for the direct monoarylation of 2,2′-bithiophene and its analogues by action of 5-bromopyrimidine. These reactions have been shown to proceed in a regioselective manner to give the corresponding C–C coupling products at C-5 of 2,2′-bithiophene, although the outcome of these reactions appears to depend on the nature of the activating agents and reaction conditions.

2. Results and discussion

It has previously been shown that 2,2′-bithiophene reacts with a number of bromo-substituted (hetero)aromatic compounds, including 5-bromopyrimidine, in the presence of air-stable [PdCl(C_3H_5)dppb] complex as catalyst at 150 °C for 16 h to form 5-(het)aryl-2,2′-bithiophenes.[2]

In order to determine the reactivity of 5-bromopyrimidine (**1**) toward bithiophene (**2a**), 2-phenylthiophene (**2b**), and [2,2′:5′,2″] terthiophene (**2c**), a series of microwave-assisted palladium-catalyzed C–C cross-coupling reactions have been performed under various reaction conditions (see Scheme 3, Fig. 1, Table 1).



Scheme 3.

Initially we explored the activity of $Pd(OAc)_2$ (taking into account that it is one of the best catalysts[8] for direct arylations), in combination with two phosphorus ligands, such as triphenylphosphine or tricyclohexylphosphine. Also we have examined some classical catalysts of organometallic chemistry, such as $Pd(PPh_3)_4$ and $Pd(dba)_2$.

Table 1
Microwave-assisted arylation of 2,2′-bithiopene (**2a**), 2-phenylthiophene (**2b**), and [2,2′:5′,2″]terthiophene (**2c**) with 5-bromopyrimidine (**1**)[a]

Entry	Thiophene	Conditions[b]	Time (min)	Reaction mixtures GC–MS (%)	Product, isolated yield (%)
1	2a	A	60	**2a**—55.3 **3a**—32.2 **4a**—0.5 **5**—1.7 Cy_3PO—10.3	**3a**—52
2	**2a**	B	10	**2a**—29.1 **3a**—45.1 **4a**—0.7 **5**—3.3 **6**—1.2 **7**—0.6 **8**—0.3 **9**—0.3 Cy_3PO— Impurities—0.4	**3a**—49
3	**2a**	C	10	**2a**—25.5 **3a**—34.6 **4a**—0.5 **5**—9.2 **6**—1.1 **7**—0.7 **8**—0.3 **9**—0.3 Ph_3PO—27.2 Impurities—0.6	**3a**—30
4	**2b**	B	10	**2b**—34.3 **3b**—39.9 **4b**—0.2 **5**—6.0 **10**—0.4 **11**—0.1 **12**—0.8 Cy_3PO—16.7 Impurities—1.6	**3b**—52
5	**2b**	D	10	**2b**—32.0 **3b**—37.7 **4b**—0.2 **5**—6.0 **10**—0.3 **11**—0.1 **12**—0.8 Ph_3PO—21.5 Impurities—1.4	**3b**—44
6	**2c**	A	60	**2c**—42.5 **3c**—34.3 **4c**—1.0 **5**—4.8 Cy_3PO—17.4	**3c**—56

Table 1 (*continued*)

Entry	Thiophene	Conditions[b]	Time (min)	Reaction mixtures GC–MS (%)	Product, isolated yield (%)
7	**2c**	B	10	**2c**—60.8 **3c**—31.5 **4c**—1.3 Cy_3PO—6.4	**3c**—50
8	**2c**	D	60	**2c**—61.3 **3c**—29.8 **4c**—0.9 Ph_3PO—17.4	**3c**—40
9	**2c**	E	60	**2c**—75.3 **3c**—4.9 **5**—4.5 Ph_3PO—15.3	**3c**[c]
10	**2c**	F	60	**2c**—83.2 **3c**—13.0 **5**—2.9 dba—0.9	**3c**[c]

[a] In DMF under argon unless noted otherwise.
[b] Method A: [**1**]/[**2**]/[$Pd(OAc)_2$]/[PCy_3]/K_2CO_3=1:3:0.1:0.2:5 (in mmol); method B: [**1**]/[**2**]/[$Pd(OAc)_2$]/[PCy_3]/K_2CO_3=1:2:0.1:0.2:3 (in mmol); method C: [**1**]/[**2**]/[$Pd(OAc)_2$]/[PPh_3]/K_2CO_3=1:1:0.1:0.2:3 (in mmol); Method D: [**1**]/[**2**]/[$Pd(OAc)_2$]/[PPh_3]/K_2CO_3=1:2:0.1:0.2:3 (in mmol); method E: [**1**]/[**2**]/[$Pd(PPh_3)_4$]/K_2CO_3=1:2:0.1:3 (in mmol); method F: [**1**]/[**2**]/[$Pd(dba)_2$]/K_2CO_3=1:2:0.1:3 (in mmol); Cy—cyclohexyl; dba—dibenzylideneacetone.
[c] The product was not isolated.

It has also been shown that the formation of the diaryl derivatives of 2,2′-bithiophene (**6**–**8**) and its analogues (**10**, **11**, **13**) in these reactions is possible. In order to minimize the formation of these by-products, we used an excess of 2-(het)aryl substituted thiophenes **2a**–**c**. Since 2,2′-bithiophene, 2-phenylthiophene, and [2,2′:5′,2″]terthiophene are relatively stable under the reaction conditions, an excess of these reagents can easily be recovered after the reaction.

We have established that the reaction of 5-bromopyrimidine with 2 equiv of 2-(het)aryl-thiophenes **2a**–**c** in DMF under microwave irradiation at 180 °C in the presence of mixture 10 mol % of $Pd(OAc)_2$ and 20 mol % PCy_3 (catalyst) with 3 equiv K_2CO_3 (base) provides the best yields of 5-[2,2′]bithiopen-5-yl-pyrimidine (**3a**), 5-(5-phenylthiophen-2-yl)-pyrimidine (**3b**), and 5-[2,2′;5′,2″]thethiophen-5-yl-pyrimidine (**3c**) (Table 1, entries 2, 4, and 7, method B). All of these reaction mixtures have been analyzed by GC–MS and several by-products were identified. Moreover, the crystal structure of 5-[2,2′]bithiopen-5-yl-pyrimidine (**3a**) was established unequivocally by X-ray diffraction study (see Fig. 2).

Another approach for the direct (hetero)arylation of five-membered π-electron-excessive heterocycles by action of 5-bromopyrimidine is the S_N^H-reaction catalyzed by a Lewis acid. Previously, we have used this S_N^H-protocol for coupling of rather simple heterocycles, such as thiophene, pyrrole, and indole, with 5-substituted pyrimidines.[9,10] In this paper we wish to report application of the S_N^H-methodology to more complex 2-(het)arylthiophenes **2a**–**c**.

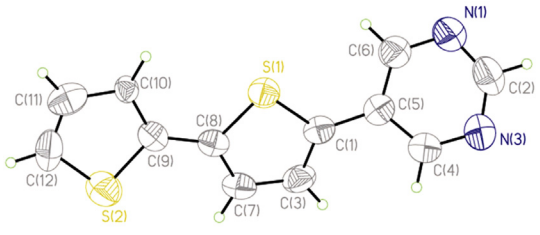
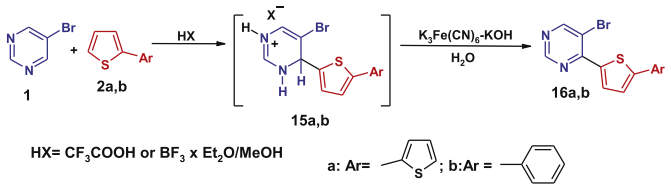


Fig. 2. X-ray structure of **3a**.

It has been found that 5-bromopyrimidine (**1**) reacts with bithiophene (**2a**) and 2-phenylthiophene (**2b**) in CF_3COOH (method G) or methanol in the presence of boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$) (methods H and I) to afford the corresponding σ^H-adducts—5-bromo-4-[5-(het)aryl-thiophen-2-yl]-3,4-dihydropyrimidin-1-ium salts **15a**,**b**. After removal of the solvent these salts **15a**,**b** were oxidized with $K_3Fe(CN)_6$ in an aqueous solution of KOH (Scheme 4, Table 2). The reaction mixtures were analyzed by GC–MS. 5-Bromo-4-(het)aryl substituted pyrimidines **16a**,**b** were obtained in moderate yields due to side reactions (see Fig. 3). The structure of 4-[2,2′]-bithiophenyl-5-yl-5-bromopyrimidine (**16a**) and 5-bromo-4-(5-phenylthiophen-2-yl)-pyrimidine (**16b**) has been established unequivocally by X-ray crystallography (Figs. 4 and 5). Unfortunately, the reaction of pyrimidine **1** with thiophene **2c** under the same conditions gave a mixture of tar products, which could not been identified by GC–MS.



Scheme 4.

Table 2
Composition of the reaction mixtures of 5-bromopyrimidine (**1**) with 2,2′-bithiopene (**2a**) and 2-phenylthiophene (**2b**) and yields of 5-bromo-4-(het)aryl substituted pyrimidines **16a**,**b**[a]

Entry	Thiophene	Conditions[b]	Reaction mixtures GC–MS (%)	Product, isolated yield (%)
1	**2a**	G	**2a**—25.1 **16a**—55.7 **17a**—19.2	**16a**—23
2	**2a**	H	**2a**—9.4 **16a**—90.1 **17a**—0.5	**16a**—64
3	**2a**	I	**16a**—95.4 Impurities—4.6	**16a**—87
4	**2b**	G	**2b**—6.6 **16b**—82.0 **17b**—7.5 Impurities—3.9	**16b**—76
5	**2b**	H	**2b**—8.4 **16b**—89.1 **17b**—1.2 Impurities—1.3	**16b**—84
6	**2b**	I	**2b**—5.4 **16b**—72.2 **17b**—14.9 Impurities—7.5	**16b**—56

[a] The reaction was carried out in the corresponding solvent on air at room temperature, followed by oxidation with aqueous solution $K_3Fe(CN)_6$/KOH=2:4 (in mmol); oxidation time=6 h.
[b] Method G: [**1**]/[**2**]=1:1.2 (in mmol) in CF_3COOH, reaction time=24 h; method H: [**1**]/[**2**]/[$BF_3 \cdot Et_2O$]=1:1.2:2.4 (in mmol) in MeOH, reaction time=1 week; method I: [**1**]/[**2**]/[$BF_3 \cdot Et_2O$]=1:1.2:2.4 (in mmol) in MeOH, reaction time=1 month.

It is worth noting that in the reactions of 5-bromopyrimidine (**1**) with 2-(het)aryl-thiophenes **2a**,**b** compounds **17a** and **17b** are formed as by-products. 4-([2,2′]-Bithiophenyl-5-yl)-pyrimidine

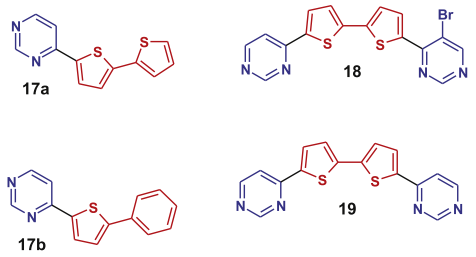


Fig. 3. By-products derived from the S_N^H-reactions of bithiophene and its analogues with 5-bromopyrimidine, determined by GC–MS analysis.

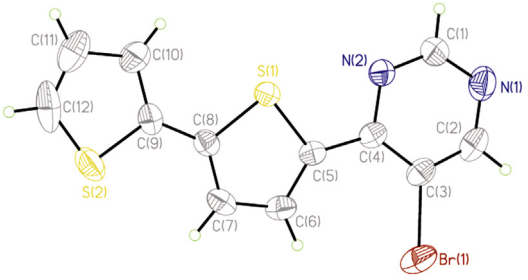


Fig. 4. X-ray structure of **16a**.

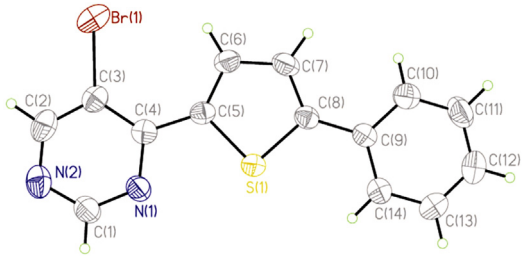
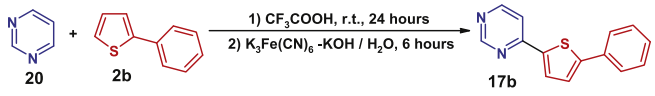


Fig. 5. X-ray structure of **16b**.

(**17a**) was prepared previously by other way[12] and this compound was identified by GC–MS data.

In order to prove the structure of by-product **17b**, the synthesis of **17b** was carried out by reacting unsubstituted pyrimidine (**20**) with 2-phenylthiophene (**2b**) in CF_3COOH under the same reaction conditions (method G) (Scheme 5). 4-(5-Phenylthiophen-2-yl)-pyrimidine (**17b**) was obtained as an off-white crystalline product in rather good yield (69%). The retention time (in GC–MS) for the obtained compound **17b** proved to coincide with that for the by-product derived from the reaction of **1** with **2b**. The crystal structure of 4-(5-phenylthiophen-2-yl)pyrimidine (**17b**) was also confirmed by the X-ray diffraction analysis (see Fig. 6).



Scheme 5.

Unfortunately, all attempts to use a combination of the cross-coupling and S_N^H-reactions for pyrimidines bearing the bithiophene fragment have been unsuccessful. Indeed, 5-[2,2′]bithiophenyl-5-yl-pyrimidine (**3b**) proved to react with thiophene (**2d**) in CF_3COOH followed by oxidation with $K_3Fe(CN)_6$, affording a mixture with the major component **3c**, instead of 5-[2,2′]bithio-phenyl-5-yl-4-thiophen-2-yl-pyrimidine (**21a**) (Scheme 6, Table 3, entry 1). It seems the production of side-products **3c** and **22** arises from the electrophilic aromatic substitution reactions of thiophene **2d** with **3b**.

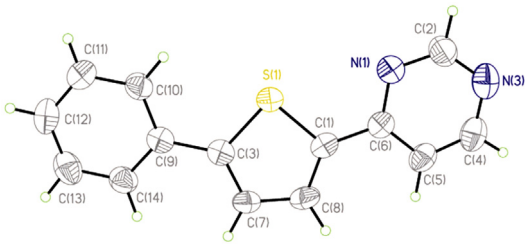
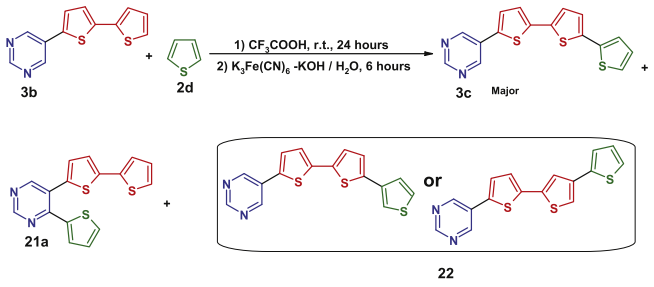


Fig. 6. X-ray structure of **17b**.



Scheme 6.

Table 3
Composition of the reaction mixtures of 5-[2,2′]-bithiophenyl-5-yl-pyrimidine (**3**) with thiophene (**2d**) and 5-bromo-4-thiophen-2-yl-pyrimidine (**23**) with 2,2′-bithiopene (**2a**) and 2-phenylthiophene (**2b**)

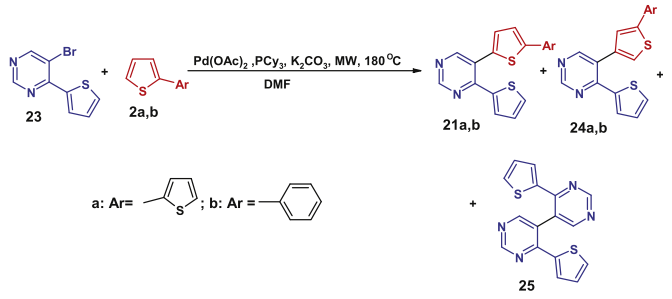
Entry	Reaction	Conditions	Reaction mixtures GC–MS (%)	Retention time t_R for the products[a] (min)
1	**3b**+**2d**	G	**3b**—3.1	
			3c—87.2	**3c**—32.60
			21a—5.5	**21a**—29.54
			22—4.2	**22**—29.62
2	**23**+**2a**	B	**23**—34.5	
			21a—27.4	**21a**—29.55
			24a—17.1	**24a**—29.94
			25—1.2	**25**—28.34
			Cy_3PO—18.9	
			Impurities—0.9	
3	**23**+**2b**	B	**23**—49.0	
			21b—10.2	**21a**—29.49
			24b—18.3	**24a**—29.85
			25—1.3	**25**—28.34
			Cy_3PO—19.7	
			Impurities—1.5	

[a] Analyzed by GC–MS for reaction mixtures.

Attempts to cause (hetero)arylation of thiophenes **2a**,**b** with previously[12] obtained 5-bromo-4-thiophen-2-yl-pyrimidine (**23**) have also been unsuccessful. The reactions proved to be non-selective and led to complex mixtures including arylated products **21a**,**b** and **24a**,**b** and by-product **25** (Scheme 7, Table 3, entries 2 and 3). Unfortunately, due to close retention times (in GC–MS) for compounds **21** and **24** we were unable to isolate these products.

3. Electrochemical and optical properties of (het)aryl substituted pyrimidines

Cyclic voltammetry of each isolated thiophenyl-substituted pyrimidine was done to determine their redox potentials (see Table 4). Both the reduction and oxidation processes of compounds **3a**–**c**,



Scheme 7.

comparison with **3a**–**c** probably due to the different positions of the (het)aryl substituent in these pyrimidines: the C(4) position of pyrimidine cycle seems to be more favorable. Meanwhile, the presence of a bromine atom leads to a decrease of quantum yields.

4. Molecular orbital calculations

Oligothiophenes are well known as photoactive compounds due to their ability to conduct electrons along the highly π-conjugated system of thiophene rings.[12] Our personal interest is focused on using them as sensitizers of semiconducting surfaces in dyes sensitized solar cells (DSSC), namely in classical 'titanium dioxide–I_3^-/I^- redox couple' photovoltaic Grätzel cell.[13]

Table 4
Molecular orbital calculations, electrochemical and optical properties of 4- and 5-(het)aryl substituted pyrimidines

Compound	E_{pa} (V)	E_{pc} (V)	HOMO[a] (eV)	LUMO[a] (eV)	ΔE_{abs}[b] (eV)	λ_{abs}^{calcd}[b]/λ_{abs}^{exp} (nm)	f[b]	ε (l mol^{-1} cm^{-1})	ΔE_{em}[b] (eV)	λ_{em}^{calcd}[b]/λ_{em}^{exp} (nm)	f[b]	Φ
3a	1.39; 1.65	−1.97	−7.29	−0.94	3.87	320.6/346	0.857	23,183	2.83	438.6/420	0.920	0.06
3b	1.65	−2.05	−7.46	−0.84	4.09	303.1/330	0.864	22,630	3.01	412.3/394	0.975	0.09
3c	1.19	−1.90	−6.94	−1.14	3.45	359.8/386	1.204	29,698	2.45	505.2/472	1.311	0.11
16a	1.49; 1.80	−1.53; −1.78	−7.35	−1.38	3.57	347.1/378	0.883	26,400	2.78	445.4/450	0.954	0.88
16b	1.69	−1.57, −1.79	−7.54	−1.31	3.78	328.1/358	0.898	28,859	2.98	416.5/421	0.997	0.82
17b	1.68	−1.82	−7.53	−1.19	3.86	321.4/348	0.925	35,259	3.25	411.6/409	0.995	1.00

ΔE—vertical excitation energy.
Φ—quantum yield of the photoluminescence.
[a] Calculated at CAM-B3LYP/6-311++G**.
[b] Calculated by TDDFT at CAM-B3LYP/6-311++G** level.

16a,**b**, and **17b** are not reversible, as seen in Figs. S1–S6 (see Supplementary data). This is expected, since the radical ions, which can be obtained in these processes, are highly reactive and able to cross-couple to form their corresponding dimers[11] as thin electroactive films on the platinum electrode. Unfortunately, we had no large-surface-area mesh electrode and could not obtain sufficient quantities of dimers for characterization.

UV–vis absorption and photoluminescent spectra of **3a**–**c**, **16a**,**b**, and **17b** were carried out and the results were summarized in Table 4 and Fig. 7. The absorption maxima of 4- and 5-(het)arylated pyrimidine were bathochromically shifted in **3b**, **3a**, **17b**, **16b**, **16a**, **3c** sequence. The bathochromic shift suggests an introduction of a bromine atom (**17b** compared with **16a** and **16b**). On the other hand, the bathochromic shift implies an increased degree of conjugation resulting from the terthiophene unit relative to bithiophene (**3c** compared with **3a**) and conjugation with the nitrogen atom (**17b** compared with **3b**).

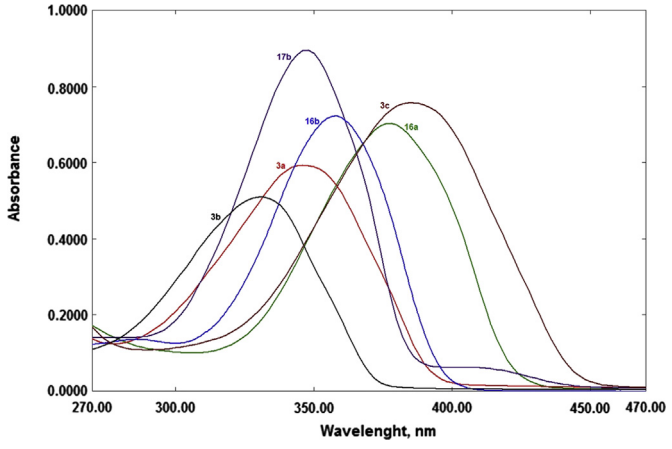


Fig. 7. UV–vis absorption spectra of **3a**–**c**, **16a**,**b**, **17b**.

Concerning the photoluminescent spectra of **3a**–**c**, **16a**,**b**, **17b**, all compounds emitted in the violet/blue electromagnetic wavelength range (see Table 4). Quantum yields were high for **16a**,**b**, **17b** in

To evaluate their ability to transfer electrons to the conducting band of TiO_2 we have performed time-dependent density functional theory (TDDFT) calculations at CAM-B3LYP/6-311++G** level. The choice of level of theory was based on the published benchmark done for coumarin dyes.[14] Authors have shown that the best estimates for excitation energies in photoactive systems can be achieved if long-corrected density functionals are used (LC-PBE, CAM-B3LYP, etc.). Previously published 2,2′-bithiophene case study on the quality of standard sulfur basis sets has shown the importance of inclusion of polarized and diffusion functions in basis set and recommended 6-311++G** basis for oligo- and polythiophenes.[15] To improve the accuracy of calculated values, polarizable continuum model (PCM) was implied, using dichloromethane as a solvent. Calculated energy gaps between HOMO/LUMO levels and parameters of the most intensive electron transitions for absorption and excitation are listed in Table 4. Additionally cyclic voltammetry was performed to evaluate HOMO/LUMO energy levels and to estimate the accuracy of calculations. Oxidation and reduction potentials are listed in Table 4. Details of measurement are explained in 'Supplementary data' section. In general computations reproduced experimentally observed trends. Errors in calculated wavelengths for absorption and emission peaks were in range 1÷30 nm. Oscillator strengths (f) for the strongest transitions were in good agreement with experimentally observed intensities for most compounds.

As one can see from this table, the energy gaps associated with light absorption are relatively higher than is desired for sensitizing agents for DSSC: ~3–4 eV versus ~2 eV. Indeed, the system is photoactively responsible to the change of structure and thus it will be possible to tune them up to the conducting level of TiO_2 (−4.0 eV) and I_3^-/I^- redox potential (−4.8 eV).[16] For example, elongating the structure with extra thiophene ring (from **3a** to **3c**) shifted the absorption band closer to NIR area: from 320.6 to 359.8 nm, as calculated. The effect of structural change was even more drastic for the luminescent properties of compound **3a**. The maximum of excitation was moved to 505.2 nm and by ~67 nm. The elongation of conjugation was also reflected in higher intensities of light absorption/emission. Calculated oscillatory strength of associated transitions rose from 0.857/0.920 to 1.204/1.311.

Introduction of an electron-withdrawing substituent to the pyrimidine ring (from **3a** to **16a**) created a subtle charge separation in the entire molecule. This resulted in a decreased energy gap, by 0.13 eV, and led to the small shift of wavelengths for absorption and emission, by around 17 and 7 nm, respectively.

The obtained energies of highest occupied molecular orbitals are in direct correlation with the oxidation potentials obtained by cyclic voltammetry. HOMO values were increasing and, consequentially, E_{pa} values were decreasing in the following order: **16b**<**17b**<**3b**<**16a**<**3a**<**3c**.

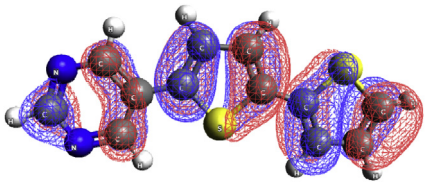
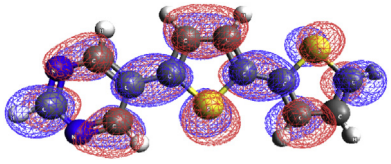
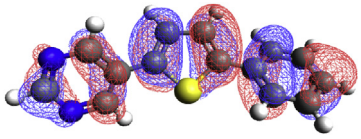
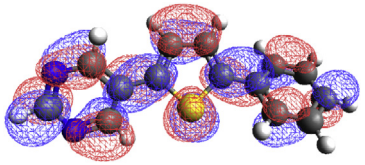
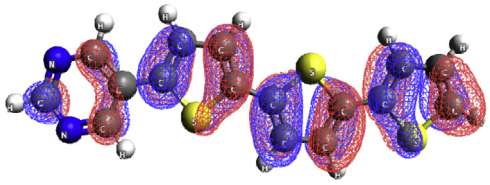
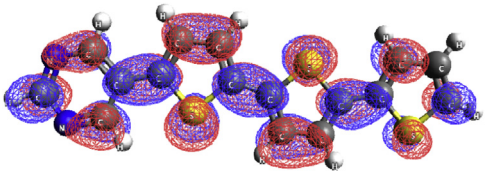
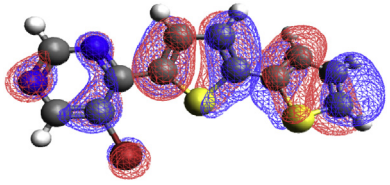
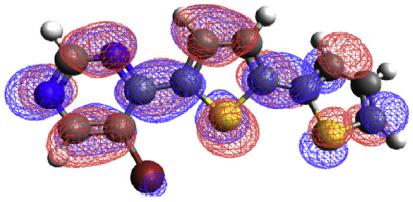
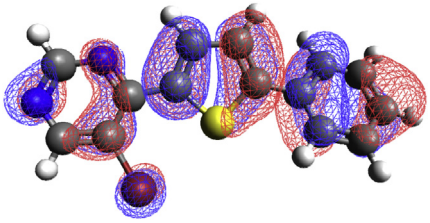
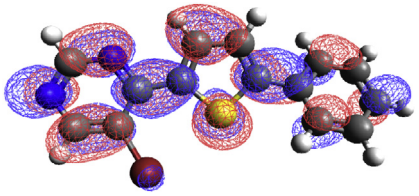
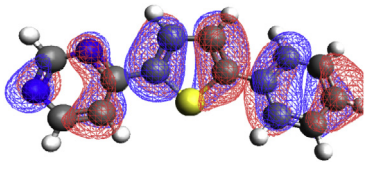
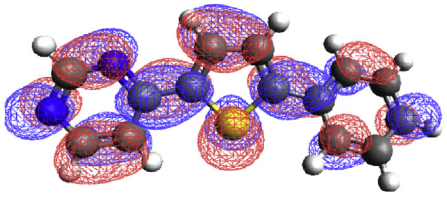
Visual representation of boundary molecular orbitals reflecting orbitals responsible for the absorption suggests that in order to increase it, stronger donor and acceptor groups should be introduced (Table 5). Otherwise the electron density will stay located on the same atoms along the whole molecule and no absorption—enhanced charge separation will be introduced.

5. Conclusion

Microwave-assisted palladium-catalyzed C–H bond functionalization and S_N^H-reactions have proved to be versatile tools for the synthesis of regioisomeric 4- or 5-monothiophenyl-substituted pyrimidines, some of which showed relatively high fluorescent efficiency. The X-ray crystallography data for a number of new monothiophenyl-substituted pyrimidines have been presented.

In summary, it is legitimate to say that the studied compounds can be potentially used for DSSC application, but additional modifications are required in order to do so. Future direction for the syntheses we are planning to follow is to create push–pull systems with stronger donor and acceptor groups attached to the opposite sides of the oligothiophene motif.

Table 5
Schematic representation of the frontier molecular orbitals of the HOMO and LUMO energy levels calculated at the CAM-B3LYP/6-311++G** level of **3a**–**c**, **16a**,**b**, and **17b**

Compound	HOMO	LUMO
3a		
3b		
3c		
16a		
16b		
17b		

6. Experimental section

6.1. General information

All reagents and solvents were obtained from commercial sources and dried by standard procedures before use. Starting materials, such as 5-bromopyrimidine (**1**), bithiophene (**2a**), 2-phenylthiophene (**2b**), [2,2′:5′,2″]terthiophene (**2c**), and pyrimidine (**20**) were purchased from Sigma–Aldrich and used without additional purification. 5-Bromo-4-thiophen-2-yl-pyrimidine (**23**) was prepared according to the earlier reported method.[9] *N*,*N*-Dimethylformamide (DMF) for the microwave-assisted cross-coupling reaction were deoxygenated by bubbling with argon for 1 h.

^{1}H and ^{13}C NMR spectra were recorded on an AVANCE-500 instrument using Me_4Si as an internal standard. All signals in the ^{1}H and ^{13}C NMR spectra were assigned on the basis of 2D ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC, and HMBC experiments. Elemental analysis was carried on an Eurovector EA 3000 automated analyzer. Melting points were determined on Boetius combined heating stages and were not corrected.

The GC–MS analysis of all samples was carried out using an Agilent GC 7890A MS 5975C Inert XL EI/CI GC–MS spectrometer with a quadrupole mass-spectrometric detector with electron ionization (70 eV) and scan over the total ionic current in the range m/z 20÷1000 and a quartz capillary column HP-5MS (30 m×0.25 mm, film thickness 0.25 mm). Helium served as a carrier gas, the split ratio of the flow was 1:50, and the consumption through the column was 1.0 mL min^{-1}; the initial temperature of the column was 40 °C (storage 3 min), programming rate was 10 °C min^{-1} to 290 °C (storage 20 min), the temperature of the evaporator was 250 °C, the temperature of the source was 230 °C, the temperature of the quadrupole was 150 °C, and the temperature of the transition chamber was 280 °C. Solutions of the samples with a concentration of 3–4 mg mL^{-1} were prepared in THF. Samples of 1 mL of the obtained solutions were analyzed. Column chromatography was carried out using Lancaster silica gel 0.040–0.063 mm (230–400 mesh), eluting with ethyl acetate/hexane, 1:2. The progress of reactions and the purity of compounds were checked by TLC on Sorbfil plates (Russia), in which the spots were visualized with UV light (λ 254 or 365 nm).

Microwave experiments were carried out in a Discover unimodal microwave system (CEM, USA) with a working frequency of 2.45 GHz and the power of microwave radiation ranged from 0 to 300 W. The reactions were carried out in a 10 mL reaction tube with the hermetic Teflon cork. The temperature of the reaction was monitored using an inserted IR sensor by the external surface of the reaction vessel.

X-ray intensity data were collected with an Xcalibur S diffractometer on standard procedure (Mo Kα (λ=0.71069 Å) radiation, T=295(2) K ω-scanning with step 1°). Crystal data and data collection parameters are summarized in Table 6 (see Supplementary data). Unit cell parameters were refined using all collected spots after the integration process. The details of the refinement and the final R indices are presented in Table 6. Deposition numbers CCDC 921369 for **3a**, CCDC 921368 for **16a**, CCDC 921367 for **16b**, and CCDC 921370 for **17 b** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6.2. Redox and optical properties

Cyclic voltammetry (CV) was performed with a potentiostat/galvanostat Autolab *PGSTAT128N* at ambient temperature. The measurements were performed in anhydrous and deaerated dichloromethane solution containing the compound (2 mM) and Bu_4NClO_4 (0.1 M) as a supporting electrolyte by the use of a platinum disk working electrode (2 mm diameter), a glassy carbon as a counter electrode, and a Ag/AgCl electrode as a reference electrode at a scan rate of 100 mV/s.

UV–vis spectra were recorded for a 1×10^{-5} M dichloromethane solution with Shimadzu UV-2401PC spectrophotometer. Photoluminescent spectra were recorded for a 1×10^{-6} M dichloromethane solution on a Varian Cary Eclipse fluorescence spectrophotometer. Quantum yields (Φ) were estimated with 1N H_2SO_4 solution of quinine bisulfate (Φ=0.55) as a reference.[17]

IR spectra of samples (solid powders) were recorded on a Spectrum One Fourier transform IR spectrometer (Perkin Elmer) equipped with a diffuse reflectance attachment (DRA) in the frequency range 4000÷400 cm^{-1}. Spectrum processing and band intensity determination were carried out using the special software supplied with the spectrometer.

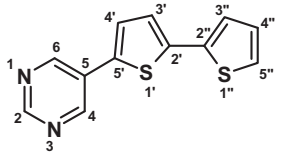
6.3. Molecular orbital calculation

Quantum chemical calculations were performed by employing the Gaussian 09 program.[18] Compounds were fully optimized at CAM-B3LYP/6-311++G** level. The minima were confirmed by frequency calculations. Then compounds were fully reoptimized at the same level of theory, but within PCM framework. TDDFT was done at CAM-B3LYP/6-311++G** level. Solvent effects were simulated by polarizable continuum model including SCRF=(Solvent=Dichloromethane) keyword in the input file.

6.4. General procedure for the microwave-assisted palladium-catalyzed C–C coupling reactions

5-Bromopyrimidine (**1**) (79 mg, 0.5 mmol), the corresponding 2-(het)aryl substituted thiophene (**2a**, **2b** or **2c**) (1.0 mmol), $Pd(OAc)_2$ (11 mg, 10 mol %), PCy_3 (28 mg, 0.1 mmol), and K_2CO_3 (207 mg, 1.5 mmol) were dissolved in DMF (5 mL). The resulting reaction mixture was deaerated by bubbling argon and irradiated in a microwave apparatus at 180 °C (250 W) for 10 min. After that the solvent was distilled off under reduced pressure, and the residue was purified by flash column chromatography (hexane/ethyl acetate, 1:2) to afford the desired product (**3a**, **3b** or **3c**). Yields of reaction products are based on the molar amount of 5-bromopyrimidine used. The regioisomeric products **4a**, **4b**, and **4c** were not isolated.

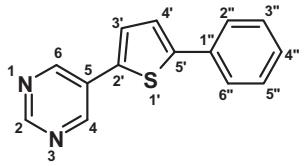
6.4.1. 5-[2,2′]Bithiophenyl-5-yl-pyrimidine (**3a**).[2]



3a

Yield (see Table 1, entry 2), yellow powder; mp 97–99 °C (lit.[2] mp not available). δ_H (500 MHz, $CDCl_3$) 7.05 (dd, 1H, H-4″, J=5.0, 3.7 Hz), 7.21 (d, 1H, H-3′, J=3.8 Hz), 7.25 (d, 1H, H-3″, J=3.7 Hz), 7.28 (d, 1H, H-5″, J=5.0 Hz), 7.33 (d, 1H, H-4′, J=3.8 Hz), 8.94 (s, 2H, H-4,6), 9.11 (s, 1H, H-2); δ_C (126 MHz, $CDCl_3$) 124.52 (C-3″), 124.82 (C-3′), 125.32 (C-5″), 125.93 (C-4′), 128.02 (C-4″), 128.41 (C-5), 134.54 (C-5′), 136.38 (C-2″), 139.43 (C-2′), 153.03 (C-4,6), 157.14 (C-2); GC t_R 24.47 min; MS m/z (rel intensity) 244 (M^+, 100). Anal. Calcd for $C_{12}H_8N_2S_2$ (244.34): C, 58.99; H, 3.30; N, 11.46. Found: C, 59.02; H, 3.08; N, 11.39. ν (DRA) 405, 458, 495, 550, 577, 591, 631, 700, 716, 735, 744, 805, 838, 886, 906, 956, 977, 1045, 1062, 1083, 1121, 1185, 1205, 1226, 1270, 1320, 1351, 1409, 1421, 1462, 1509, 1545, 1578, 1614, 1770, 1796, 1878, 1951, 2351, 3017, 3051, 3071, 3086, 3808, 3911.

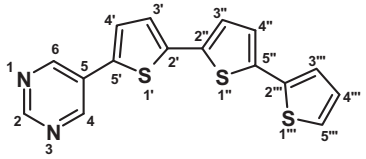
*6.4.2. 5-(5-Phenylthiophen-2-yl)-pyrimidine (**3b**).*



3b

Yield (see Table 1, entry 4), pale yellow powder; mp 130–131 °C. δ_H (500 MHz, $CDCl_3$) 7.34 (tt, 1H, H*p*, *J*=7.3, 1.1 Hz), 7.36 (d, 1H, H-4′, *J*=3.8 Hz), 7.41 (d, 1H, H-3′, *J*=3.8 Hz), 7.42 (dd, 2H, H*m*, *J*=8.1, 7.3 Hz), 7.65 (dd, 2H, H*o*, *J*=8.3, 1.1 Hz), 8.97 (s, 2H, H-4,6), 9.12 (s, 1H, H-2); δ_C (126 MHz, $CDCl_3$) 124.38 (C-4′), 125.88 (C*o*), 126.19 (C-3′), 128.27 (C*p*), 128.65 (C-5), 129.08 (C*m*), 133.49 (C*i*), 135.13 (C-2′), 146.49 (C-5′), 153.11 (C-4,6), 157.13 (C-2); GC t_R 24.52 min; MS *m*/*z* (rel intensity) 238 (M^+, 100); Anal. Calcd for $C_{14}H_{10}N_2S$ (238.31): C, 70.56; H, 4.23; N, 11.75. Found: C, 70.34; H, 4.04; N, 11.64. ν (DRA) 425, 417, 462, 494, 567, 590, 633, 690, 717, 735, 761, 808, 885, 902, 940, 968, 982, 999, 1028, 1045, 1076, 1100, 1163, 1184, 1211, 1237, 1287, 1308, 1338, 1354, 1413, 1427, 1447, 1461, 1498, 1537, 1551, 1574, 1596, 1678, 1769, 1878, 1905, 1956, 2368, 3030, 3078, 3822.

*6.4.3. 5-[2,2′:5′,2″]Terthiophenyl-5-yl-pyrimidine (**3c**).*



3c

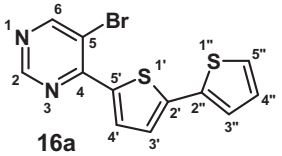
Yield (see Table 1, entry 7), dark yellow powder; mp 170–172 °C. δ_H (500 MHz, $CDCl_3$) 7.04 (dd, 1H, H-4‴, *J*=5.1, 3.6 Hz), 7.12 (d, 1H, H-4″, *J*=3.8 Hz), 7.16 (d, 1H, H-3″, *J*=3.8 Hz), 7.20 (dd, 1H, H-3‴, *J*=3.6, 1.1 Hz), 7.21 (d, 1H, H-3′, *J*=3.8 Hz), 7.25 (dd, 1H, H-5‴, *J*=5.1, 1.1 Hz), 7.35 (d, 1H, H-4′, *J*=3.8 Hz), 8.94 (s, 2H, H-4,6), 9.12 (s, 1H, H-2); δ_C (126 MHz, $CDCl_3$) 124.05 (C-3‴), 124.45 (C-4″), 124.72 (C-3′), 124.90 (C-5‴), 125.13 (C-3″), 126.05 (C-4′), 127.97 (C-4‴), 128.40 (C-5), 134.57 (C-5′), 135.02 (C-5″), 136.75 (C-2‴), 137.29 (C-2″), 139.15 (C-2′), 153.05 (C-4,6), 157.17 (C-2); GC t_R 32.55 min; MS *m*/*z* (rel intensity) 326 (M^+, 100). Anal. Calcd for $C_{16}H_{10}N_2S_3$ (326.46): C, 59.87; H, 3.09; N, 8.58. Found: C, 59.64; H, 2.90; N, 8.31. ν (DRA) 404, 444, 470, 482, 524, 554, 574, 588, 607, 631, 707, 719, 741, 796, 834, 866, 876, 906, 956, 982, 1047, 1067, 1118, 1180, 1201, 1213, 1223, 1232, 1242, 1272, 1306, 1338, 1355, 1409, 1425, 1451, 1468, 1551, 1603, 1655, 1755, 1790, 1884, 1946, 2342, 2853, 2924, 3030, 3063, 3077, 3115, 3802.

6.5. General procedure for the synthesis of S_N^H-products—5-bromo-4-(het)aryl-pyrimidines

Pathway A: 2-(Het)aryl-thiophene (**2a**, **2b** or **2c**) (1.2 mmol) was added to a solution of 5-bromopyrimidine (**1**) (159 mg, 1.0 mmol) in CF_3COOH (5 mL). The reaction mixture was stirred at room temperature for 24 h and evaporated. The solution of KOH (224 mg, 4.0 mmol, 4 equiv) and $K_3Fe(CN)_6$ (658 mg, 2.0 mmol, 2 equiv) in 5 mL water was added to residue. The resulting mixture was stirred for appropriate time (see Table 2) at room temperature, the precipitate or semisolid formed was filtered off, washed with H_2O, and air-dried. The residue was purified by flash column chromatography (hexane/ethyl acetate, 1:2) to afford the desired S_N^H-product.

Pathway B: To a stirred mixture of 5-bromopyrimidine (**1**) (79 mg, 0.5 mmol) and corresponding 2-(het)aryl-thiophene (**2a**, **2b** or **2c**) (0.6 mmol) in MeOH (3 mL) was added $BF_3 \cdot Et_2O$ (1.1 mmol). The reaction mixture was stirred at room temperature for appropriate time (see Table 2) and evaporated. A solution of KOH (112 mg, 2.0 mmol, 4 equiv) and $K_3Fe(CN)_6$ (329 mg, 1.0 mmol, 2 equiv) in water (5 mL) was added to residue. The resulting mixture was stirred for the appropriate time (see Table 2) at room temperature, the precipitate or semisolid formed was filtered off, washed with H_2O, and air-dried. The residue was purified by flash column chromatography (hexane/ethyl acetate, 1:2) to afford the desired S_N^H-products.

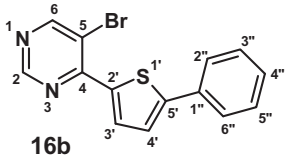
*6.5.1. 4-[2,2′]Bithiophenyl-5-yl-5-bromopyrimidine (**16a**).*



16a

Yield (see Table 2, entries 1–3), yellow crystal powder; mp 138–140 °C. δ_H (500 MHz, $CDCl_3$) 7.05 (dd, 1H, H-4″, *J*=5.1, 3.6 Hz), 7.22 (d, 1H, H-3′, *J*=4.1 Hz), 7.30 (d, 1H, H-5″, *J*=5.1, 1.1 Hz), 7.33 (dd, 1H, H-3″, *J*=3.6, 1.1 Hz), 8.33 (d, 1H, H-4′, *J*=4.1 Hz), 8.80 (s, 1H, H-6), 8.98 (s, 1H, H-2); δ_C (126 MHz, $CDCl_3$) 115.00 (C-5), 124.51 (C-3′), 125.17 (C-3″), 126.00 (C-5″), 128.15 (C-4″), 132.96 (C-4′), 136.49 (C-2″), 138.90 (C-5′), 143.55 (C-2′), 155.72 (C-4), 156.13 (C-2), 160.69 (C-6); GC t_R 26.93 min; MS *m*/*z* (rel intensity) 322 (M^+, 100) for ^{79}Br, 324 (M^+, 100) for ^{81}Br; Anal. Calcd for $C_{12}H_7BrN_2S_2$ (323.23): C, 44.59; H, 2.18; N, 8.67. Found: C, 44.75; H, 2.26; N, 8.65. ν (DRA) 418, 457, 475, 512, 586, 598, 611, 623, 639, 655, 675, 711, 733, 742, 759, 808, 835, 889, 923, 980, 1028, 1048, 1073, 1140, 1161, 1183, 1201, 1219, 1231, 1246, 1270, 1279, 1322, 1345, 1384, 1425, 1447, 1514, 1550, 1634, 1740, 1776, 1827, 1903, 1963, 2143, 2321, 2426, 2494, 2716, 2889, 2960, 3078, 3102, 3810, 3913.

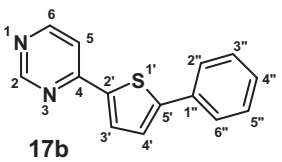
*6.5.2. 5-Bromo-4-(5-phenyl-thiophen-2-yl)-pyrimidine (**16b**).*



16b

Yield (see Table 2, entries 4–6), yellow crystal powder; mp 141–142 °C. δ_H (500 MHz, $CDCl_3$) 7.34 (t, 1H, H*p*, *J*=7.3, Hz), 7.37 (d, 1H, H-4′, *J*=4.1 Hz), 7.41 (t, 2H, H*m*, *J*=7.6 Hz), 7.68 (dd, 2H, H*o*, *J*=8.3, 1.1 Hz), 8.39 (d, 1H, H-3′, *J*=4.1 Hz), 8.81 (s, 1H, H-6), 9.00 (s, 1H, H-2); δ_C (126 MHz, $CDCl_3$) 115.10 (C-5), 124.20 (C-4′), 126.10 (C*o*), 128.66 (C*p*), 129.03 (C*m*), 133.14 (C-3′), 133.43 (C*i*), 139.53 (C-2′), 150.43 (C-5′), 155.94 (C-4), 156.17 (C-2), 160.72 (C-6); GC t_R 26.94 min; MS *m*/*z* (rel intensity) 316 (M^+, 100) for ^{79}Br, 318 (M^+, 100) for ^{81}Br. Anal. Calcd for $C_{14}H_9BrN_2S$ (317.21): C, 53.01; H, 2.86; N, 8.83. Found: C, 53.03; H, 2.70; N, 8.70. ν (DRA) 412, 453, 478, 514, 582, 598, 620, 663, 688, 699, 758, 809, 844, 913, 922, 951, 985, 998, 1025, 1072, 1086, 1098, 1139, 1156, 1183, 1248, 1288, 1308, 1333, 1350, 1384, 1427, 1440, 1453, 1509, 1549, 1594, 1619, 1748, 1784, 1879, 1905, 1969, 2321, 2995, 3055, 3092, 3115.

6.6. 4-(5-Phenylthiophen-2-yl)-pyrimidine (17b)



17b

2-Phenylthiophene (**2c**) (288 mg, 1.8 mmol) was added to a solution of pyrimidine (**20**) (120 mg, 1.5 mmol) in CF_3COOH (3 mL). The reaction mixture was stirred at room temperature for

24 h and evaporated. The solution of KOH (337 mg, 6.0 mmol, 4 equiv) and $K_3Fe(CN)_6$ (988 mg, 3.0 mmol, 2 equiv) in water (10 mL) was added to residue. The resulting mixture was stirred for 6 h at room temperature; the precipitate formed was filtered off, washed with H_2O, and air-dried. The residue was purified by flash column chromatography (hexane/ethyl acetate, 1:1) to afford the desired 4-(5-phenylthiophen-2-yl)-pyrimidine (**17b**). Yield (246 mg, 69%), off-white crystalline powder; mp 145–147 °C. δ_H (500 MHz, $CDCl_3$) 7.34 (tt, 1H, H*p*, *J*=7.3, 1.1 Hz), 7.35 (d, 1H, H-4′, *J*=3.9 Hz), 7.41 (dd, 2H, H*m*, *J*=8.1, 7.3 Hz), 7.53 (dd, 1H, H-5, *J*=5.3, 1.4 Hz), 7.66 (dd, 2H, H*o*, *J*=8.1, 1.1 Hz), 7.72 (d, 1H, H-3′ *J*=3.9 Hz), 8.65 (d, 1H, H-6, *J*=5.3 Hz), 9.13 (d, 1H, H-2, *J*=1.4 Hz); δ_C (126 MHz, $CDCl_3$) 114.81 (C-5), 124.31 (C-4′), 125.92 (C*o*), 128.47 (C*p*), 128.62 (C-3′), 129.02 (C*m*), 133.56 (C*i*), 140.58 (C-2′), 149.23 (C-5′), 156.98 (C-6), 158.62 (C-4), 159.02 (C-2); GC t_R 24.88 min; MS *m*/*z* (rel intensity) 238 (M^+, 100). Anal. Calcd for $C_{14}H_{10}N_2S$ (238.31): C, 70.56; H, 4.23; N, 11.75. Found: C, 70.54; H, 4.15; N, 11.68. ν (DRA) 450, 510, 575, 622, 661, 689, 727, 756, 773, 808, 847, 909, 949, 983, 995, 1031, 1069, 1088, 1101, 1168, 1213, 1244, 1287, 1307, 1332, 1390, 1447, 1466, 1501, 1532, 1574, 1594, 1671, 1696, 1746, 1802, 1875, 1892, 1948, 1967, 2032, 2236, 2555, 2751, 2911, 3021, 3076, 3823.

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Supplementary data

Crystallographic and cyclic voltammetry data summary, copies of the photoluminescent, IR, ^1H and ^{13}C NMR spectra of the new compounds. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.04.062. These data include MOL files and InChiKeys of the most important compounds described in this article.

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