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Star- and Banana-Shaped Oligomers with a Pyrimidine Core: Synthesis and Light-Emitting Properties

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By using Suzuki–Miyaura cross-coupling reactions we have synthesised a series of star- and banana-shaped oligomers with a pyrimidine unit as the central core and π-conjugated arms consisting of aromatics bearing electron-donor substituents. The position of the arms as well as the nature of their substituents were investigated with a view to accessing compounds that exhibit interesting light-emitting properties. The best fluorescence quantum yields were obtained with banana-shaped pyrimidines substituted with *p*-(dimethylamino)phenyl or 2-furyl groups. Comparison of the optical properties of oligomers with benzene, pyrimidine or *s*-triazine as the central unit revealed that the pyrimidinic compounds gave the best results. Some of the oligomers synthesised exhibit solvatochromic properties and pH sensibility, which could allow their use as polarity or pH sensors.

Introduction

Over the past decade there has been considerable interest in the synthesis and characterisation of conjugated organic compounds, which are attractive candidates for numerous applications in various fields, for example, as liquid crystals,[1] components of organic light-emitting devices (OLEDs) for display and lighting,[2] field-effect transistors (FETs),[3] single molecular electronics[4] and non-linear optical materials.[5] Fluorescent chromophores, generally known to have planar and rigid π-conjugated systems, are also of interest as functional materials in molecular probes.[6] The advantages of molecular fluorescence for sensing and switching are very important.[7] Indeed, they enable high sensitivity in detection, "on–off" switchability, subnanometre spatial resolution and submillisecond temporal resolution. Recently, star- and banana-shaped molecules have become highly interesting as chemical materials with greatly enhanced physical properties.[8] The incorporation of a π-deficient heterocycle such as pyridine,[9] *s*-triazine,[10] pyrazine,[11] quinoxaline[12] or pyrimidine[13] in the centre of the backbone of such molecules leads to a significant enhancement of some of their physical properties such as mesomorphism, fluorescence and solvatochromism. If the arms of these oligomers are substituted by donor groups, fluorescence with internal charge transfer (ICT) or twisted internal charge transfer (TICT) excited states is expected with interesting solvatochromic properties. The aim of this paper is to present the synthesis and physical properties of various star- and banana-shaped oligomers with a central pyrimidine core. The effect of the position of the arms as well as the nature of their substituents has been investigated. This study is a part of our work dedicated to the use of diazines as building blocks for the synthesis of organic molecular materials.[14]

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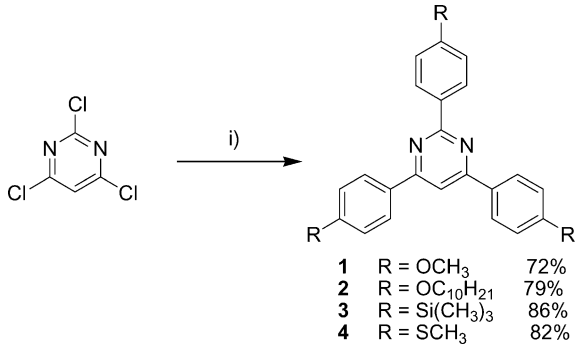
Results and Discussion

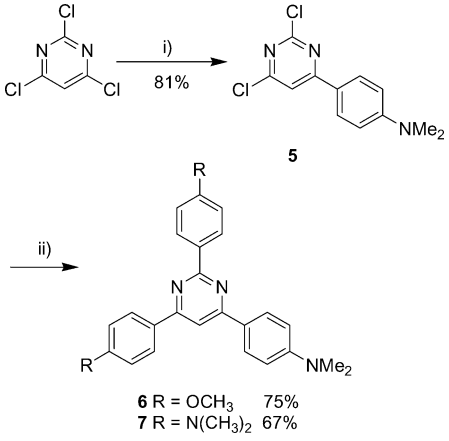
Synthesis

Two general methods for the synthesis of 2,4,6-triarylpyrimidines are described in the literature. The first method consists in the construction of the pyrimidine ring by condensation reactions,[15] the second involves the functionalisation of the pyrimidine ring.[13a–16] The advantages of this latter method are a greater versatility and the use of easily available starting materials. This led us to carry out the synthesis of various star- and bent-shaped molecules with a pyrimidine core by Suzuki cross-coupling of the commercially available 2,4,6-trichloropyrimidine. It should be noted that the π-electron-deficient character of the pyrimidine ring makes easier the oxidative addition of palladium to a chlorine–carbon bond without the use of specialised and expensive ligands.[17] A range of star-shaped triarylpyrimidines were synthesised in good yields under Suzuki conditions with an excess of arylboronic acids (5 equiv.; Scheme 1).



Scheme 1. Reagents and conditions: i) p-$RC_6H_4B(OH)_2$, [Pd-$(PPh_3)_4$], Cs_2CO_3, toluene, H_2O, Δ, 40 h.

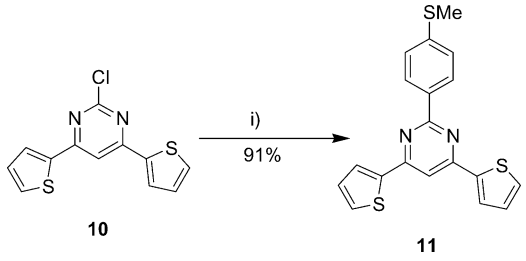
When [4-(dimethylamino)phenyl]boronic acid was used, despite a large excess of the reagent (5 equiv.), only the monocoupled compound **5** was obtained. However, when a further coupling reaction was performed with **5** and a further 5 equiv. of boronic acid, the expected 2,4,6-triarylpyrimidines **6** and **7** were obtained in good yields (Scheme 2). This result can be explained by the higher electron-donating effect of the dimethylamino group, which makes the oxidative addition of palladium to the carbon–chorine bond more difficult.



Scheme 2. Reagents and conditions: i) p-$(Me_2N)C_6H_4B(OH)_2$, [$Pd(PPh_3)_4$], Cs_2CO_3, toluene, H_2O, Δ, 40 h; ii) p-$RC_6H_4B(OH)_2$, [$Pd(PPh_3)_4$], Cs_2CO_3, toluene, H_2O, Δ, 40 h.

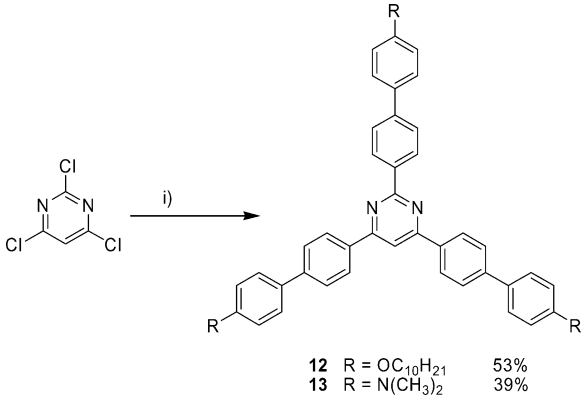
By using this methodology, it is possible to link π-electron-donor five-membered heterocycles such as furan or thiophene to the pyrimidine ring. With 2-furylboronic acid, the di- and trifurylpyrimidines **8** and **9** were obtained in equal amounts, whereas only the 2-chloro-4,6-dithienylpyrimidine (**10**) was obtained in moderate yield (34%) when the reaction was performed with 2-thienylboronic acid (Scheme 3).

The formation of the dithienyl compound **10** can be explained by the lower stability of the thienylboronic acid and palladium catalyst poisoning by the sulfur atom of the thiophene ring. However, as previously, reaction of **10** with [p-(methylthio)phenyl]boronic acid under Suzuki conditions allowed a further cross-coupling reaction with the residual chlorine atom at C-2 to give **11** in good yield (Scheme 4).

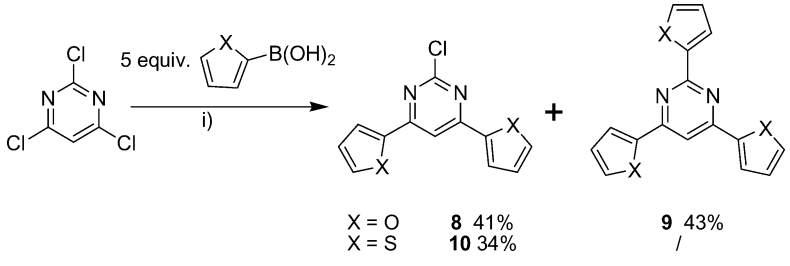


Scheme 4. Reagents and conditions: i) p-$MeSC_6H_4B(OH)_2$, [$Pd(PPh_3)_4$], Cs_2CO_3, toluene, H_2O, Δ, 40 h.

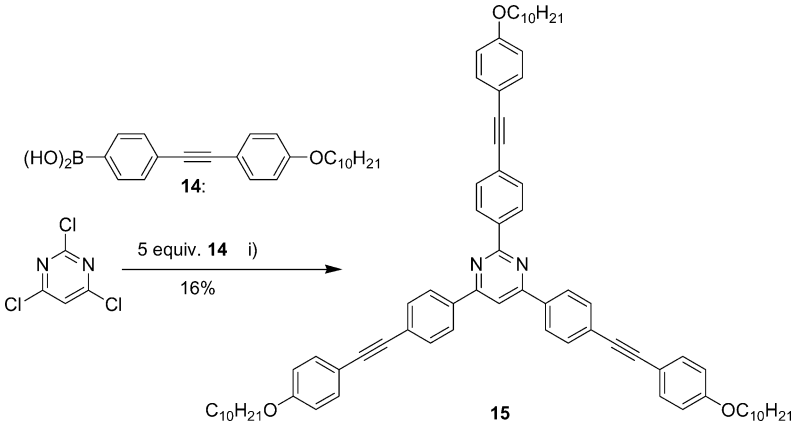
In order to increase the electronic delocalisation along each arm, star-shaped oligomers with seven rings were synthesised by reaction of 2,4,6-trichloropyrimidine with (biphenylyl)boronic acids. The lower yields observed are probably due to difficulties in purifying these oligomers by column chromatography (Scheme 5).



Scheme 5. Reagents and conditions: i) p-$RC_6H_4C_6H_4B(OH)_2$, [$Pd(PPh_3)_4$], Cs_2CO_3, toluene, H_2O, Δ, 40 h.



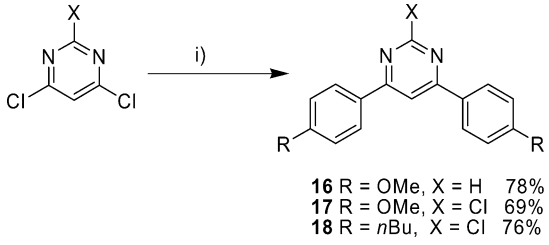
Scheme 3. Reagents and conditions: i) [$Pd(PPh_3)_4$], Cs_2CO_3, toluene, H_2O, Δ, 40 h.



Scheme 6. Reagents and conditions: i) $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene, H_2O, Δ, 40 h.

Following the same procedure, the conjugation could be extended by introducing an acetylenic linkage between the two phenyl rings of each arm by reaction of 2,4,6-trichloropyrimidine with the {4-[(4-decyloxyphenyl)ethynyl]phenyl}-boronic acid (**14**). Compound **15** was obtained in low yield, as previously, due to the difficulties of purification (Scheme 6).

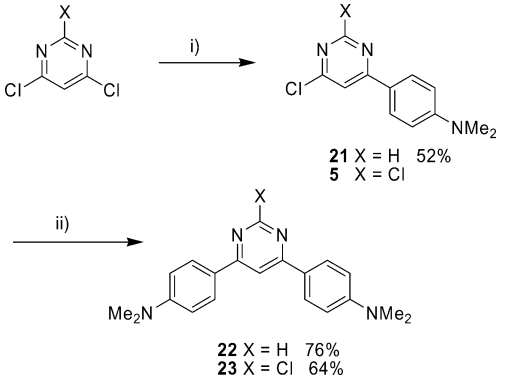
Banana-shaped molecules were obtained by Suzuki cross-coupling reactions either with 4,6-dichloropyrimidine or with 2,4,6-trichloropyrididine. By using 2 or 3 equiv. of arylboronic acid, the diaryl compounds **16**–**18** were synthesised in good yields (Scheme 7).



Scheme 7. Reagents and conditions: *p*-$RC_6H_4B(OH)_2$, $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene, H_2O, Δ, 40 h.

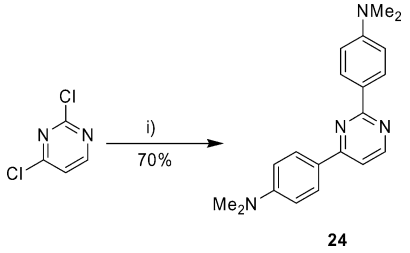
A banana-shaped conjugated structure with long alkoxy groups on the termini with potential liquid crystal properties was synthesised by a Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine with (6-octyloxy-3-pyridinyl)boronic acid (**19**). The reaction was performed with 5 equiv. of the boronic acid in dioxane for 8 h; compound **20** was isolated in 54% yield (Scheme 8).

With [4-(dimethylamino)phenyl]boronic acid, reaction with 4,6-dichloropyrimidine or 2,4,6-trichloropyrididine led to the dicoupled compound **22** or **23**, respectively, in two steps by successive coupling reactions with 3 equiv. of boronic acid in each step (Scheme 9).

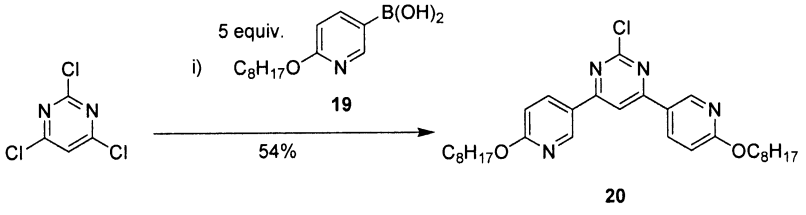


Scheme 9. Reagents and conditions: i) *p*-$Me_2NC_6H_4B(OH)_2$, $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene, H_2O, Δ, 24 h; ii) *p*-$Me_2NC_6H_4B(OH)_2$, $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene, H_2O, Δ, 48 h.

Note that 2,4-bis[4-(dimethylamino)phenyl]pyrimidine (**24**) was obtained directly in one step by the coupling of 4 equiv. of boronic acid with 2,4-dichloropyrimidine (Scheme 10).

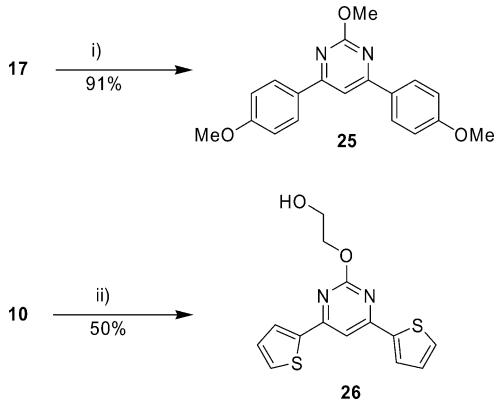


Scheme 10. Reagents and conditions: i) *p*-$Me_2NC_6H_4B(OH)_2$, $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene, H_2O, Δ, 40 h.

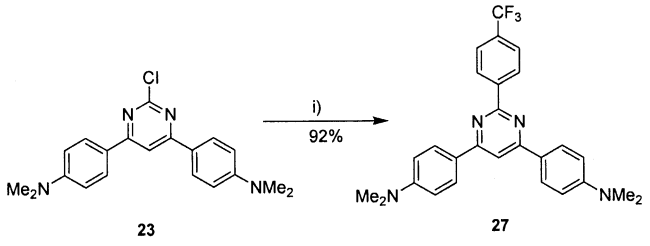


Scheme 8. Reagents and conditions: i) $[Pd(PPh_3)_2Cl_2]$, dioxane, Na_2CO_3, Δ, 8 h.

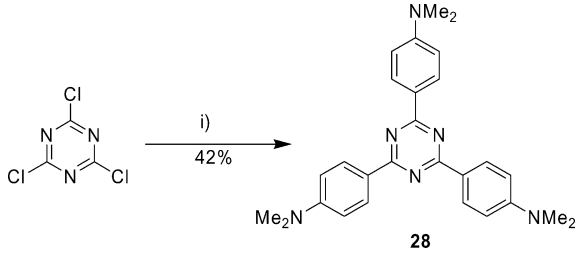
The presence of a chlorine atom at the 2-position allows the easy replacement of chlorine by other groups by nucleophilic substitution. Reaction of **17** with sodium methoxide led to 2-methoxy-4,6-bis(4-methoxyphenyl)pyrimidine (**25**), and reaction of **10** with sodium 2-hydroxyethoxide gave the derivative **26**. This last compound, which possesses an alcoholic function, could be used to form links with polymers or various biocompounds (Scheme 11).



Scheme 11. Reagents and conditions: i) MeONa/MeOH, 60 °C, 24 h; ii) $HOCH_2CH_2ONa/HOCH_2CH_2OH$, 15 h, room temp.



Scheme 12. Reagents and conditions: i) p-$F_3CC_6H_4B(OH)_2$, $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene, H_2O, Δ, 40 h.



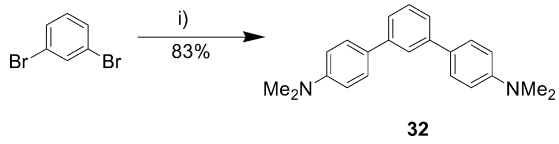
Scheme 13. Reagents and conditions: i) p-$Me_2NC_6H_4B(OH)_2$, $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene, H_2O, Δ, 24 h.

In order to improve the electron-attracting character of the pyrimidine core, incorporation of a phenyl group bearing an electron-withdrawing substituent could be envisaged. A Suzuki cross-coupling reaction with *p*-(trifluoromethylphenyl)boronic acid was carried out on the residual chlorine atom at the 2-position of compound **23** to give compound **27** in good yield (Scheme 12).

With the aim of evaluating the effect of the central core on the physical properties of such oligomers, analogous banana- or star-shaped molecules with a benzene or triazine ring as the central core were synthesised. Compound **28**, analogous to **7** but with an *s*-triazine central core, was obtained by a Suzuki coupling reaction of cyanuric chloride with [4-(dimethylamino)phenyl]boronic acid (Scheme 13).

Structures analogous to compounds **1** and **13** with a benzene ring as the central core were obtained by cyclotrimerization of *para*-substituted acetophenones with silicon tetrachloride,[18] leading to compounds **29** and **30** (analogous to **1**). A further Suzuki coupling reaction of the tribromide derivative **29** with [*p*-(dimethylamino)phenyl]boronic acid afforded compound **31** (analogous to **13**) (Scheme 14).

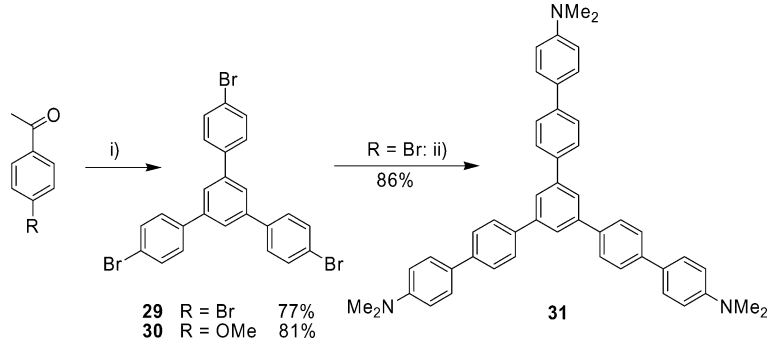
The banana-shaped compound **32**, analogous to **22** with a benzene core, was obtained by Suzuki coupling reaction of 1,3-dibromobenzene with [4-(dimethylamino)phenyl]-boronic acid (Scheme 15).



Scheme 15. Reagents and conditions: i) p-$Me_2NC_6H_4B(OH)_2$, $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene, H_2O, Δ, 24 h.

Geometric and Electronic Properties

The X-ray crystal structure of **1** is shown in Figures 1 and 2.[19] Single crystals of **1** suitable for X-ray analysis were obtained by slow evaporation at room temperature from a



Scheme 14. Reagents and conditions: i) $SiCl_4$, EtOH, room temp., 15 h; ii) p-$Me_2NC_6H_4B(OH)_2$, $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene, H_2O, Δ, 24 h.

mixed solvent of chloroform/heptane (1:4). As shown in Figure 1, it can be observed that compound **1** is slightly twisted; the dihedral angle between the pyrimidine central core and the benzene ring at the 2-position is 3.58°, whereas the dihedral angles between the pyrimidinic central core and the benzene rings at the 4- and 6-positions are 13.05 and 13.93°, respectively. These angles are sufficiently small for the conjugation along the three arms of the molecule to be preserved. Compound **1** crystallises in the form of a monoclinic array with the following parameters: a = 9.17, b = 14.43, c = 15.60 Å, α = 90.00, β = 103.15, γ = 90.00° (Figure 2).

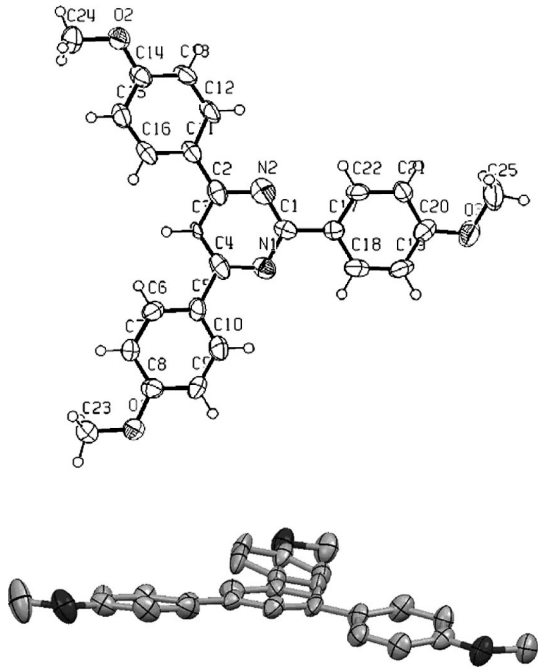


Figure 1. Molecular structure of compound **1** with the atomic labelling scheme. Selected bond lengths [Å]: C(1)–C(17) 1.483, C(2)–C(11) 1.501, C(1)–C(5) 1.479, C(1)–N(2) 1.355, N (2)-C(2) 1.361, C(2)–C(3) 1.314, C(3)–C(4) 1.332, C(4)–N(1) 1.400, N(1)–C(1) 1.364.

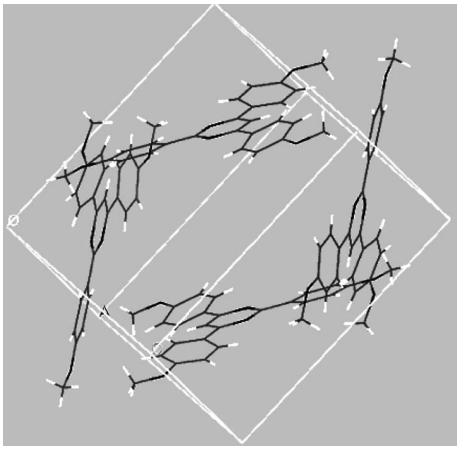


Figure 2. Crystal structure of **1**.

Quantum mechanical calculations by DFT methods at the B3LYP level of theory with the 6-31G* basis set were performed to determine the geometries and electronic structures of compounds **1** and **29**. For compound **1**, there is generally a good agreement between the calculated and X-ray experimental bond lengths; the mean discrepancies are less than 3%. However, the dihedral angles determined by calculation correlate poorly with the experimental values: the calculated dihedral angle between the pyrimidine core and the benzene ring at the 2-position (4.26°) is similar to the experimental value (3.58°), whereas those calculated between the pyrimidine central ring and the benzene rings at the 4- and 6-positions (respectively, 17.07 and 18.32°) are much higher than the experimentally determined values. The results of the calculations performed for compound **30**, analogous to compound **1** with a benzene ring as the central core, gave a value of about 38° for the dihedral angles between the central benzene ring and those in the arms. The high values of these dihedral angles are due to steric hindrance between the *ortho* hydrogen atoms.

The electron-attracting nature of the pyrimidine ring and the geometry of compound **1** allow high charge transfer between the donor methoxy groups and the central core, whereas the geometry of compound **30** reduces the amount of charge transfer.

The energy levels of the HOMOs and LUMOs for compounds **1** and **30** (Table 1) show a narrower HOMO–LUMO gap for **1** than for **30**.

Table 1. HOMO and LUMO energies and dipole moments for compounds **1** and **30** from quantum mechanical calculations.

Compd.	HOMO [eV]	LUMO [eV]	$\Delta E_{HOMO-LUMO}$ [eV]	$\|\mu\|$ [debye]
1	–6.61	–1.31	5.30	2.00
30	–6.72	–0.55	6.17	2.22

Solution Electrochemical Properties

The redox properties of some of these compounds, studied by cyclic voltammetry (CV) in dry deoxygenated dichloromethane solution, are given in Table 2.

Table 2. Redox properties determined by cyclic voltammetry.

Compound	$E^{1/2}_{red}$ [V][a]	$E^{1/2}_{ox}$ [V][a]
2	–2.75 (R)	–
4	–2.55 (R)	–
5	–3.00 (R)	–
6	–2.80 (R)	+0.25 (NR)
7	–2.85 (R)	+0.40 (NR)
8	–2.85 (R)	–
9	–2.45 (R)	–
11	–1.35 (R), –2.70 (R)	+0.70 (NR)
13	–2.70 (R)	+0.45 (NR)
16	–2.85 (R)	–
23	–2.95 (R)	+0.30 (NR)

[a] Potential values measured vs. Ag/Ag^+ and standardised in comparison to Fc/Fc^+. 1 mM sample in dichloromethane/0.1 M Bu_4NPF_6 (20 °C), scan rate: 0.1 V/s, 20 °C. R indicates a reversible peak and NR a non-reversible peak.

All the compounds showed a quasi-reversible reduction peak between –1.35 and –3.00 V. Non-reversible oxidation peaks were only observed for the compounds substituted by strong electron-donating groups such as dimethylamino groups (compounds **6**, **7**, **13** and **23**) between +0.25 and +0.45 V as well as for compound **11** at +0.70 V. For the other compounds, determination of the E_{ox} potentials, which could be at much more positive potential values and out of the range of the electrochemical transparency of dichloromethane, was impossible.

Absorption and Fluorescence Properties

The UV/Vis and fluorescence spectroscopic data of various oligomers measured in chloroform at 25 °C are summarised in Tables 3 and 4.

All the compounds collected in Table 3 have a pyrimidine core; their absorption wavelengths (λ_{abs}) are in the UV region (269–394 nm) and their emission wavelengths (λ_{em}) in the UV or blue region (306–495 nm). Star-shaped compounds with one benzene ring per arm (compounds **1**, **2** and **4**) substituted by alkoxy or sulfanyl groups exhibit absorption and emission wavelengths in the UV region (λ_{abs} = 296–321 nm, λ_{em} = 372–398 nm) with low quantum yields. In the case of the unsymmetrical compound **6**, with a 4-(dimethylamino)phenyl group at the 4-position, we observed lower λ_{abs} and λ_{em} values, a lower Stokes shift and a marked increase in the quantum yield (Φ_F = 0.53). When each arm bears a *p*-(dimethylamino)phenyl group (compound **7**), higher λ_{abs} and λ_{em} values were observed, this bathochromic shift due to the high electron-donating character of the dimethylamino group, with a decrease in Φ_F. Generally, when higher λ_{abs} and λ_{em} values are observed the fluorescence quantum yield Φ_F decreases, so, in order to have the best fluorescence properties (high quantum yields Φ_F, large Stokes shifts), it seems important to find a compromise between the number and the strength of the peripheral electron-donor groups.

The star-shaped pyrimidinic compounds **12** and **13** (with a biphenyl unit per arm) have higher values of λ_{abs}, λ_{em} and Φ_F than the analogous compounds **2** and **7** (with only one benzene ring per arm). The bathochromic effect observed is due to the extension of the conjugation. Comparison between compounds **12** and **15** reveals that incorporation of a triple bond between the benzene rings does not significantly influence the optical properties.

Banana-shaped compounds **8** and **10** with electron-donor groups such as thienyl or furyl groups have λ_{abs} and λ_{em} wavelengths in the UV region with high Φ_F values of 0.62 and 0.42, respectively, whereas their Stokes shifts are relatively low.

Note that replacement in compounds **8** and **10** of the chlorine atom at the 2-position with an electron-donor aromatic fragment leads to compounds **9** and **11** which have low Φ_F (0.17 and 0.04).

When the banana-shaped compound **22** is compared with the star-shaped compound **7**, the lack of a electron-donating substituent at the 2-position of the central pyrimidine core causes an notable increase in Φ_F (0.72). Comparison of the data for compounds **22** and **23** reveals that the presence of the chlorine atom in compound **23** lowers the value of Φ_F (0.57). The position of the two arms at the 2,4- or the 4,6-positions is of high importance as compound **24**, disubstituted at the 2,4-positions, has a very low Φ_F (0.06). Thus, it seems that the presence of a strongly electron-donating arm at the 2-position of pyrimidine is unfavourable for a high quantum yield. The spectroscopic data for **27** compared with **22** show that incorporation of an electron-attracting substituent at the 2-position does not increase the fluorescence properties.

Comparison of the spectroscopic data for compounds **30**, **31** and **32** with a benzene core (Table 4) with the analogous compounds **1**, **13** and **22** with a pyrimidine central unit

Table 3. Optical absorption and emission spectroscopic data for compounds with a pyrimidine core in chloroform solution (10^{-4}–10^{-7} M) at 25 °C.

Compound	$\lambda_{abs,max}$ [nm]	ε [$M^{-1}cm^{-1}$]	$\lambda_{em,max}$ [nm]	Φ_F[a]	Stokes shift [cm^{-1}]
1	296	29734	372	0.04[b]	6902
2	297	31277	387	0.04[b]	7830
4	321	51663	398	0.14[b]	6027
5	382	67965	438	0.34[b]	3347
6	269	61226	306	0.53[b]	4495
7	349	39286	427	0.14[c]	5234
8	352	26476	382	0.62[b]	2231
9	302	47284	386	0.17[b]	7206
10	339	18277	386	0.42[b]	3592
11	314	26177	415	0.04[c]	7751
12	323	64959	409	0.54[b]	6510
13	366	75772	495	0.57[c]	7120
15	348	66578	422	0.48[c]	5039
16	269/298/319	19692/23678/27744	365	0.04[b]	3951
18	317	26306	364	0.03[b]	4073
20	323	25491	368	0.18[b]	3786
22	299/378	16025/38060	429	0.72[b]	3145
23	394	58182	441	0.57[c]	2705
24	354	50085	465	0.06[c]	6743
27	376	30739	429	0.39[c]	3286

[a] ±10%. [b] Quantum yield of fluorescence determined using 2-aminopyridine in 0.1 M H_2SO_4 as standard (Φ_F = 0.60),[20] excitation at 299 nm. [c] Quantum yield of fluorescence determined using harmane in 0.1 M H_2SO_4 as standard (Φ_F = 0.83),[20] excitation at 366 nm.

Table 4. Optical absorption and emission spectroscopic data for benzenic and triazinic compounds in chloroform solution (10^{-4}–10^{-7} M) at 25 °C.

Compd.	$\lambda_{abs,max}$ [nm]	ε [$M^{-1}cm^{-1}$]	$\lambda_{em,max}$ [nm]	Φ_F[a]	Stokes shift [cm^{-1}]
28	368	62411	419	0.15[b]	3308
30	270	52298	367	0.04[c]	9789
31	333	33795	416	0.21[c]	5992
32	309	29190	–[d]	–	–

[a] ±10%. [b] Quantum yield of fluorescence determined using harmane in 0.1 M H_2SO_4 as standard (Φ_F = 0.83),[20] excitation at 366 nm. [c] Quantum yield of fluorescence determined using 2-aminopyridine in 0.1 M H_2SO_4 as standard (Φ_F = 0.60),[20] excitation at 299 nm. [d] Compound **31** in not fluorescent.

(Table 3) enable us to appreciate the effect of the central core. Replacement of the benzene by a pyrimidine ring causes a bathochromic effect and increases significantly the value of Φ_F in the case of compounds **13** and **22**, whereas compounds **30** and **1** with *p*-methoxyphenyl substituents have similar optical properties (λ_{abs}, λ_{em} and Φ_F). The triazinic compound **28** and the pyrimidinic compound **7** can be compared and have similar values for λ_{abs}, λ_{em} and Φ_F. However, the Stokes shift is superior in the case of the pyrimidinic compound **7**.

The pyrimidinic compound **13** exhibits fluorosolvatochromism; its absorption and emission spectra in various solvents are shown in Figure 3 and the data are summarised in Table 5.

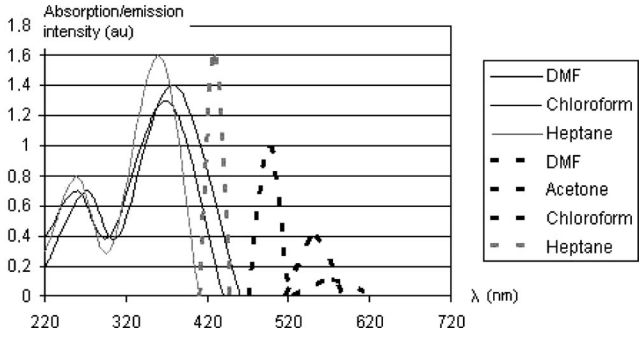


Figure 3. Normalised absorbance and emission (dotted line) spectra of compound **13** in various solvents.

Table 5. Optical absorption and emission spectroscopic data for compound **13** in various solvents (10^{-4}–10^{-7} M) at 25 °C.

Solvent	$\lambda_{abs,max}$ [nm]	$\lambda_{em,max}$ [nm]	Φ_F[a]	Stokes shift [cm^{-1}]
Heptane	359	427	0.77[b]	4436
Chloroform	366	495	0.57[b]	7120
Acetone	363	552	0.14[b]	9432
DMF	378	573	0.04[b]	9003
Methanol	377	–[c]	< 0.01	–

[a] ±10%. [b] Quantum yield of fluorescence determined using 2-aminopyridine in 0.1 M H_2SO_4 as standard (Φ_F = 0.60),[20] excitation at 299 nm. [c] Compound **13** is not fluorescent in methanol.

A slight bathochromic shift of the absorption maximum is observed when going from non-polar *n*-heptane (ε = 1.9) to polar aprotic DMF (ε = 36.7): $\Delta\lambda_{abs}$ = 19 nm (positive solvatochromism); the variation of the emission maximum is more important ($\Delta\lambda_{em}$ = 146 nm) and is associated with a large increase in the Stokes shift. It should be noted that the fluorescence quantum yield Φ_F dramatically decreases as the polarity of the solvent increases to become almost null in methanol. This means that the dipole moment of the molecule is higher in the excited state than in the ground state, which indicates its aptitude for charge transfer in the excited state. The fact that solvatochromism is more important for emission than for absorption suggests that the molecule is more solvated in the excited state than in the ground state,[21] which implies charge transfer from the dimethylamino groups to the π-deficient pyrimidine central ring.

For compound **22**, the solvatochromic properties (Table 6) indicate that λ_{abs} and λ_{em} increase with the polarity of the solvent, but unlike the case of compound **13**, the Φ_F quantum yield increases with the polarity of the solvent from a non-polar solvent (heptane, ε = 1.9) to a moderately polar solvent (chloroform, ε = 4.7), but with a high polar solvent (DMF, ε = 37.5) an unexpected decrease in Φ_F is observed. This indicates that two solvatochromic effects (negative and positive) coexist.[21]

Table 6. Optical absorption and emission spectroscopic data for compound **22** in various solvents (10^{-4}–10^{-7} M) at 25 °C.

Solvent	$\lambda_{abs,max}$ [nm]	$\lambda_{em,max}$ [nm]	Φ_F[a]	Stokes shift [cm^{-1}]
Heptane	275/363	393	0.42[b]	2103
Chloroform	299/374	429	0.72[b]	3428
DMF	378	470	0.63[b]	5178

[a] ±10%. [b] Quantum yield of fluorescence determined using 2-aminopyridine in 0.1 M H_2SO_4 as standard (Φ_F = 0.60),[19] excitation at 299 nm.

The effect of protonation on the optical properties of compounds **7** and **13** was also studied (Table 7). The absorption maxima λ_{abs} slightly decrease or remain constant, whereas the emission maxima λ_{em} dramatically increase when TFA is added to a chloroform solution. Significant Stokes shifts (superior to 10000 cm^{-1}) are observed, whereas at the same time a decrease in the fluorescence quantum yield Φ_F is noted. A similar tendency is observed for the quantum yield of compound **22**. The spectroscopic data for compound **5** are quite different: protonation does not modify the absorption and emission profiles but causes an increase in the fluorescence quantum yield. These variations in the fluorescence properties indicate an important modification of the electronic state of the chromophores and/or of the mechanism by which fluorescence is generated. The spectroscopic data for compound **8** are unaltered after addition of TFA to the chloroform solution. In this case, only the pyrimidine ring can be protonated, which does not lead to a modification of the spectroscopic data. The modifications of the spectroscopic data observed during the protonation of compounds **5**, **7** and **13** bearing one or more di-

Table 7. Optical absorption and emission data in chlroform solution (10^{-4}–10^{-7} M) with addition of TFA at 25 °C; data obtained without the addition of TFA are given in parentheses.

Compd.	$\lambda_{abs,max}$ [nm]	$\lambda_{em,max}$ [nm]	Φ_F[a]	Stokes shift [cm^{-1}]
5	382 (382)	431 (438)	0.77[b] (0.34[b])	2976 (3347)
7	350 (349)	539 (427)	0.11[c] (0.14[d])	10019 (5234)
8	351 (352)	383 (382)	0.62[b] (0.62[b])	2380 (2231)
13	300 (366)	512 (495)	0.15[b] (0.57[b])	13802 (7120)
22	484 (374)	530 (429)	0.17[d] (0.72[b])	1793 (3145)

[a] ±10%. [b] Quantum yield of fluorescence determined using 2-aminopyridine in 0.1 M H_2SO_4 as standard (Φ_F = 0.60),[19] excitation at 299 nm. [c] Quantum yield of fluorescence determined using fluorescein in 0.1 M NaOH as standard (Φ_F = 0.79),[19] excitation at 442 nm. [d] Quantum yield of fluorescence determined using harmane in 0.1 M H_2SO_4 as standard (Φ_F = 0.83),[19] excitation at 366 nm.

methylamino groups could be due to protonation of the nitrogen atom of the amino group and thus compounds **7** and **13** are pH sensors.

Conclusions

By using Suzuki–Miyaura cross-coupling reactions we have synthesised a series of star- and banana-shaped oligomers with a pyrimidine as the central core and arms consisting of aromatic groups bearing electron-donating substituents. The position of the arms as well as the nature of their substituents were investigated with a view to accessing compounds with interesting light-emitting properties. The best fluorescence quantum yields were obtained with the banana-shaped pyrimidines substituted with 4-(dimethylamino)phenyl or 2-furyl groups. Comparison of the optical properties of oligomers with benzene, pyrimidine or *s*-triazine as the central unit showed that the best results were obtained for the pyrimidinic compounds. Some of the oligomers synthesised exhibit solvatochromic properties and pH sensibility, which could allow their use as polarity or pH sensors.

Experimental Section

General: Melting points were determined on an Electrothermal 1100 instrument. The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with a Bruker AC 300 (300 MHz ^{1}H, 75 MHz ^{13}C, 282.5 MHz ^{19}F) instrument. Microanalyses were performed with a Carlo Erba CHNOS 1160 apparatus. The IR spectra were obtained as potassium bromide pellets with a Perkin-Elmer 16 PC FT-IR spectrometer. Mass spectra were recorded with an ATI-Unicam Automass® apparatus. UV/Vis spectra were obtained with a Varian Can 50 scan spectrophotometer in chloroform solution. Fluorescence spectroscopic studies were performed in chloroform solution in a semi-micro fluorescence cell (Hellma®, 104F-QS, 10 × 4 mm, 1400 μL) with a Varian Cary Eclipse spectrophotometer. Fluorescence quantum yields were determined by comparison with standards, as described in literature.[19] Cyclic voltammetry was performed with a Metrohm PGSTAT 100 potentiostat with a Pt auxiliary electrode, a 100 micron diameter Pt working electrode and a double junction Ag/AgCl reference electrode.

General Procedure A for Cross-Coupling Reactions Under Suzuki Conditions: A mixture of chloropyrimidine (or bromobenzene) derivatives, arylboronic acid, tetrakis(triphenylphosphane)palladium(0) (0.05 equiv. per coupling reaction), caesium carbonate (1 equiv. per coupling reaction), aqueous 2 M potassium carbonate (1 equiv. per coupling reaction.) and ethanol (1.5 mL) in degassed toluene (20 mL) was heated at reflux under nitrogen for a time *t*. The reaction mixture was cooled, diluted with a mixture of water and ethyl acetate (20 mL, 1:1) and the organic layer separated. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried with magnesium sulfate and the solvents evaporated.

2,4,6-Tris(4-methoxyphenyl)pyrimidine (1): Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine (803 mg, 4.40 mmol) with (4-methoxyphenyl)boronic acid (3.87 g, 22.1 mmol) according to the general procedure (t = 40 h) gave after purification by column chromatography [silica gel, eluent heptane/ethyl acetate (9:1)] 1.28 g (72%) of **1** as a pale-yellow solid; m.p. 182 °C (ref.[15a] 174 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 6 H, OCH_3), 3.85 (s, 3 H, OCH_3), 7.01–6.97 (m, 6 H, Ph-H), 7.72 (s, 1 H, 5-H), 8.17 (d, J = 8.8 Hz, 4 H, Ph-H), 8.62 (d, J = 8.8 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.8, 108.2, 114.0, 114.5, 129.1, 130.4, 130.6, 131.6, 162.0, 162.1, 164.1 ppm. IR: $\tilde{\nu}$ = 1606, 1510, 1364, 1242, 1175, 1021, 844, 787 cm^{-1}. $C_{25}H_{22}N_2O_3$ (398.16): calcd. C 75.36, H 5.57, N 7.03; found C 75.02, H 5.36, N 6.83.

2,4,6-Tris(4-decyloxyphenyl)pyrimidine (2): Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine (250 mg, 1.4 mmol) with (4-decyloxyphenyl)boronic acid (1.38 g, 7.0 mmol) according to the general procedure (t = 40 h) gave after purification by column chromatography [silica gel, eluent heptane/ethyl acetate (9:1)] 858 mg (79%) of **2** as a colourless solid; m.p. 70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.0 Hz, 9 H, 3 × CH_3), 1.42–1.22 (m, 42 H, 21 × CH_2), 1.79–1.74 (m, 6 H, 3 × OCH_2CH_2), 3.97 (t, J = 6.6 Hz, 4 H, OCH_2), 4.02 (t, J = 6.6 Hz, 2 H, OCH_2), 7.01–6.97 (m, 6 H, Ph-H), 7.72 (s, 1 H, 5-H), 8.17 (d, J = 8.8 Hz, 4 H, Ph-H), 8.62 (d, J = 8.8 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.1, 27.7, 25.0, 28.2, 28.3, 28.4, 28.5, 28.6, 30.9, 66.8, 67.0, 106.5, 113.1, 113.6, 125.6, 127.0, 128.9, 129.1, 160.2, 162.6, 164.8 ppm. IR: $\tilde{\nu}$ = 2920, 2851, 1608, 1586, 1510, 1284, 1173, 825 cm^{-1}. $C_{52}H_{76}N_2O_3$ (776.59): calcd. C 80.36, H 9.86, N 3.60; found C 80.99, H 10.02, N 3.55.

2,4,6-Tris(4-trimethylsilanylphenyl)pyrimidine (3): Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine (500 mg, 2.7 mmol) with [4-(trimethylsilanyl)phenyl]boronic acid[22] (2.90 g, 15 mmol) according to the general procedure (t = 40 h) gave after purification by column chromatography [silica gel, eluent heptane/ethyl acetate (9:1)] 1.22 g (86%) of **3** as a colourless solid; m.p. 142 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.27 [s, 27 H, $Si(CH_3)_3$], 7.66–7.61 (m, 6 H, Ph-H), 7.85 (s, 1 H, 5-H), 8.15 (d, J = 8.1 Hz, 4 H, Ph-H), 8.64 (d, J = 7.9 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.3, 111.5, 127.5, 128.8, 134.6, 135.0, 139.0, 139.7, 144.4, 144.8, 165.7 ppm. IR: $\tilde{\nu}$ = 2953, 1576, 1516, 1362, 1247, 1100, 857, 821 cm^{-1}. $C_{31}H_{40}N_2Si_3$ (524.25): calcd. C 70.93, H 7.68, N 5.34; found C 70.87, H 7.61, N 5.35.

2,4,6-Tris(4-methylsulfanylphenyl)pyrimidine (4): Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine (300 mg, 1.6 mmol) with [4-(methylsulfanyl)phenyl]boronic acid (1.4 g, 8.1 mmol) according to the general procedure (t = 40 h) gave after purification by column chromatography [silica gel, eluent heptane/ethyl acetate (9:1)] 596 mg (82%) of **4** as a colourless solid; m.p. 134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 6 H, 2 × SCH_3), 2.46 (s, 3 H, SCH_3), 7.27–7.24 (m, 6 H, Ph-H), 7.72 (s, 1 H, 5-H), 8.05 (d, J = 8.6 Hz, 4 H, Ph-H), 8.48 (d, J = 8.7 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.6, 109.1, 126.0, 126.3, 127.8, 129.1, 134.2, 135.2, 142.1, 142.7, 164.2 ppm. IR: $\tilde{\nu}$ = 1578, 1556, 1514, 1491, 1362, 1088, 817, 776 cm^{-1}. $C_{25}H_{22}N_2S_3$ (446.09): calcd. C 67.23, H 4.96, N 6.27, S 21.54; found C 67.41, H 5.21, N 6.32, S 21.39.

2,6-Dichloro-4-[4-(dimethylamino)phenyl]pyrimidine (5): Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine (1 g, 5.4 mmol) with [4-(dimethylamino)phenyl]boronic acid (1.31 g, 8 mmol) according to the general procedure (t = 40 h) gave after purification by recrystallisation in methylcyclohexane 1.18 g (81%) of **5** as a yellow solid; m.p. 183 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.07 [s, 6 H, $N(CH_3)_2$], 6.68 (d, J = 9.0 Hz, 2 H, Ph-H), 7.42 (s, 1 H, 5-H), 7.94 (d, J = 9.0 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.5, 111.9, 113.0, 121.0, 129.5, 153.5, 161.3, 162.1, 168.2 ppm. IR: $\tilde{\nu}$ = 1606, 1557, 1532, 1500, 1402, 1372, 1339, 1261, 1199, 1123, 813 cm^{-1}. MS (IC+): m/z (%) = 268 (100)

[MH]$^+$, 270 (13) [MH]$^+$, 272 (64) [MH]$^+$. $C_{12}H_{11}Cl_2N_3$ (268.14): calcd. C 53.75, H 4.13, N 15.67; found C 53.72, H 4.13, N 15.63.

4-[4-(Dimethylamino)phenyl]-2,6-bis(4-methoxyphenyl)pyrimidine (6): Suzuki cross-coupling reaction of **5** (100 mg, 0.37 mmol) with (4-methoxyphenyl)boronic acid (281 mg, 1.85 mmol) according to the general procedure (t = 40 h) gave after purification by column chromatography [silica gel, eluent petroleum ether/ethyl acetate (8:2)] 120 mg (75%) of **6** as an orange solid; m.p. 157 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.00 [s, 6 H, $N(CH_3)_2$], 3.84 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 6.76 (d, J = 9 Hz, 2 H, Ph-H), 7.04–7.00 (m, 4 H, Ph-H), 7.74 (s, 1 H, 5-H), 8.22–8.16 (m, 4 H, Ph-H), 8.67 (d, J = 9.0 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.4, 40.6, 55.8, 108.3, 114.0, 114.6, 125.3, 128.1, 129.0, 129.1, 130.4, 131.0, 132.0, 152.5, 163.7, 164.1, 164.5 ppm. IR: $\tilde{\nu}$ = 1609, 1568, 1510, 1363, 1245, 1170 cm^{-1}. $C_{26}H_{25}N_3O_2$ (411.19): calcd. C 75.89, H 6.12, N 10.21; found C 75.85, H 6.09, N 10.15.

2,4,6-Tris[4-(dimethylamino)phenyl]pyrimidine (7): Suzuki cross-coupling reaction of **5** (100 mg, 0.37 mmol) with [4-(dimethylamino)phenyl]boronic acid (305 mg, 1.85 mmol) according to the general procedure (t = 40 h) gave after purification by column chromatography [silica gel, eluent petroleum ether/ethyl acetate (8:2)] 108 mg (67%) of **7** as a red solid; m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.06 [s, 18 H, $N(CH_3)_2$], 6.85–6.81 (m, 6 H, Ph-H), 7.73 (s, 1 H, 5-H), 8.22 (d, J = 9.1 Hz, 4 H, Ph-H), 8.63 (d, J = 9.0 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.7, 40.8, 106.2, 112.0, 112.3, 126.2, 127.5, 128.8, 130.0, 152.3, 163.9, 165.0 ppm. IR: $\tilde{\nu}$ = 1610, 1570, 1523, 1361, 1193, 1169, 810 cm^{-1}. $C_{28}H_{31}N_5$ (437.26): calcd. C 76.85, H 7.14, N 16.00; found C 76.55, H 6.98, N 16.09.

2-Chloro-4,6-di(furan-2-y)pyrimidine (8) and 2,4,6-Tri(furan-2-yl)-pyrimidine (9): Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine (634 mg, 3.46 mmol) with (furan-2-yl)boronic acid (1.93 g, 17.3 mmol) according to the general procedure (t = 40 h) gave after purification by column chromatography [silica gel, eluent heptane/ethyl acetate (9:1)] 348 mg (41%) of **8** and 410 mg (43%) of **9** both as colourless solids. **8**: M.p. 188 °C (ref.[23] 187–188 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.64 (dd, J_1 = 1.7, J_2 = 3.6 Hz, 2 H, 4'-H), 7.41 (d, J_2 = 3.6 Hz, 2 H, 5′-H), 7.67 (d, J_1 = 1.7 Hz, 2 H, 3'-H), 7.85 (s, 1 H, 5-H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 106.8, 113.3, 114.5, 146.3, 151.1, 158.5, 161.9 ppm. IR: $\tilde{\nu}$ = 1608, 1548, 1482, 1265, 756 cm^{-1}. $C_{12}H_7ClN_2O_2$ (246.02): calcd. C 58.43, H 2.86, N 11.36; found C 58.35, H 2.69, N 11.20. **9**: M.p. 168 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.64 (m, 3 H, 4′- and 4′′-H), 7.41 (d, J_2 = 3.4 Hz, 2 H, 5'-H), 7.43 (d, J_2 = 3.4 Hz, 1 H, 5''-H), 7.66 (d, J_1 = 1.7 Hz, 2 H, 3'-H), 7.68 (d, J_1 = 1.7 Hz, 1 H, 3''-H), 7.78 (s, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 106.2, 112.4, 112.9, 113.0, 114.1, 145.4, 145.5, 152.3, 152.6, 156.6, 158.2 ppm. IR: $\tilde{\nu}$ = 1608, 1535, 1486, 1006, 760, 739 cm^{-1}. $C_{16}H_{10}N_2O_3$ (278.0): calcd. C 69.06, H 3.62, N 10.07; found C 68.96, H 3.75, N 9.95.

2-Chloro-4,6-di(2-thienyl)pyrimidine (10): Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine (300 mg, 1.63 mmol) with 2-thienylboronic acid (1.1 g, 8.1 mmol) according to the general procedure (t = 40 h) gave after purification by column chromatography [silica gel, eluent heptane/ethyl acetate (9:1)] 155 mg (34%) of **10** as a yellow solid; m.p. 191 °C (ref.[23] 195–196°°C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20 (dd, J_1 = 4.9, J_2 = 3.8 Hz, 2 H, 4'-H), 7.59 (dd, J_1 = 4.9, J_2 = 1.0 Hz, 2 H, 5'-H), 7.67 (s, 1 H, 5-H), 7.87 (dd, J_1 = 3.8, J_2 = 1.0 Hz, 2 H, 3'-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 106.3, 127.5, 127.6, 130.1, 139.6, 160.4, 160.8 ppm. IR: $\tilde{\nu}$ = 1573, 1490, 1434, 1259, 714 cm^{-1}. $C_{12}H_7ClN_2S_2$ (277.97): calcd. C 51.70, H 2.53, N 10.05, S 23.00; found C 51.61, H 2.60, N 10.03, S 22.78.

2-(4-Methylsulfanylphenyl)-4,6-di(2-thienyl)pyrimidine (11): Suzuki cross-coupling reaction of **10** (100 mg, 0.36 mmol) with (4-methylsulfanylphenyl)boronic acid (1.1 g, 8.1 mmol) according to the general procedure (t = 40 h) gave after purification by recrystallisation in heptane 120 mg (91%) of **11** as a yellow solid; m.p. 192 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.59 (s, 3 H, SCH_3), 7.22 (dd, J_1 = 4.9, J_2 = 3.8 Hz, 2 H, 4'-H), 7.39 (d, J = 8.8 Hz, 2 H, Ph-H), 7.58 (dd, J_1 = 4.9, J_2 = 1.0 Hz, 2 H, 5'-H), 7.69 (s, 1 H, 5-H), 7.91 (dd, J_1 = 3.8, J_2 = 1.0 Hz, 2 H, 3'-H) 8.56 (d, J = 8.8 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.7, 106.7, 126.0, 126.3, 127.5, 128.7, 129.1, 130.2, 134.4, 142.5, 143.6, 159.8 ppm. IR: $\tilde{\nu}$ = 1575, 1557, 1524, 1365, 822, 716, 702 cm^{-1}. $C_{19}H_{14}N_2S_3$ (366.52): calcd. C 62.26, H 3.85, N 7.64, S 26.25; found C 62.60, H 3.61, N 7.41, S 25.93.

2,4,6-Tris[4′-(decyloxy)biphenyl-4-yl]pyrimidine (12): Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine (103 mg, 0.55 mmol) with [4′-(decyloxy)biphenyl-4-yl]boronic acid (990 mg, 2.79 mmol) according to the general procedure (t = 40 h) gave after purification by column chromatography [silica gel, eluent heptane/ethyl acetate (9:1)] and by recrystallisation in methylcyclohexane 293 mg (53%) of **12** as a pale-yellow solid; m.p. 191 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.0 Hz, 9 H, 3 × CH_3), 1.42–1.22 (m, 42 H, 21 × CH_2), 1.79–1.74 (m, 6 H, 3 × OCH_2CH_2), 3.92 (t, J = 6.6 Hz, 6 H, 3 × OCH_2), 7.07 (d, J = 8.8 Hz, 6 H, Ph-H), 7.68 (d, J = 8.8 Hz, 6 H, Ph-H), 7.78 (d, J = 8.8 Hz, 6 H, Ph-H), 8.06 (s, 1 H, 5-H), 8.35 (d, J = 8.8 Hz, 4 H, Ph-H), 8.82 (d, J = 8.8 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 23.1, 26.5, 29.7, 29.8 (2 C), 29.9, 30.0, 32.2, 68.5, 110.0, 115.2, 127.0, 127.4, 128.1, 128.6, 129.3, 132.9, 133.4, 136.1, 136.9, 143.2, 143.5, 159.6, 164.7 ppm. IR: $\tilde{\nu}$ = 2923, 2852, 1604, 1574, 1497, 1248, 1192, 821 cm^{-1}. $C_{70}H_{88}N_2O_3$ (1004.68): calcd. C 83.62, H 8.82, N 2.79; found C 83.61, H 8.79, N 2.81.

2,4,6-Tris[4′-(dimethylamino)biphenyl-4-yl]pyrimidine (13): Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine (143 mg, 0.78 mmol) with (4′-decyloxybiphenyl-4-yl)boronic acid (937 mg, 3.0 mmol) according to the general procedure A (t = 40 h) gave after purification by recrystallisation in methylcyclohexane 195 mg (39%) of **13** as a yellow solid; m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.05 (s, 18 H, NCH_3), 6.87 (d, J = 8.8 Hz, 6 H, Ph-H), 7.65 (d, J = 8.8 Hz, 6 H, Ph-H), 7.78 (d, J = 8.8 Hz, 6 H, Ph-H), 8.06 (s, 1 H, 5-H), 8.38 (d, J = 8.8 Hz, 4 H, Ph-H), 8.80 (d, J = 8.8 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.9, 41.0, 109.7, 113.1, 126.5, 126.8, 128.0, 128.2, 128.5, 129.0, 129.3, 135.6, 136.5, 143.5, 143.8, 150.6, 150.7, 164.7, 164.8 ppm. IR: $\tilde{\nu}$ = 1603, 1501, 1361, 1200, 1166, 811, 787 cm^{-1}. $C_{46}H_{43}N_5$ (665.35): calcd. C 82.97, H 6.51, N 10.52; found C 83.02, H 6.40, N 10.64.

2,4,6-Tris{4-[4-(decyloxyphenyl)ethynyl]phenyl}pyrimidine (15): Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine (166 mg, 0.91 mmol) with **14**[24] (1.72 g, 4.55 mmol) according to the general procedure A (t = 40 h) gave after purification by column chromatography [silica gel, eluent heptane/ethyl acetate (9:1)], recrystallisation in a mixture of methylcyclohexane and ethyl acetate and washings with toluene 157 mg (16%) of **15** as an orange solid; m.p. 64 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.0 Hz, 9 H, 3 × CH_3), 1.42–1.22 (m, 42 H, 21 × CH_2),1.79–1.74 (m, 6 H, 3 × OCH_2CH_2), 3.97 (t, J = 6.6 Hz, 6 H, OCH_2), 6.90 (d, J = 8.9 Hz, 6 H, Ph-H), 7.53–7.51 (d, J = 8.9 Hz, 6 H, Ph-H), 7.69 (d, J = 8.9 Hz, 6 H, Ph-H), 8.01 (s, 1 H, 5-H), 8.27 (d, J = 8.9 Hz, 4 H, Ph-H), 8.69 (d, J = 8.9 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 23.1, 26.4, 29.6, 29.7, 29.8, 29.9, 30.0, 32.3, 68.5, 88.2, 88.7, 91.9, 92.4, 114.9, 115.0, 115.1, 115.3, 126.4, 126.7, 127.5 (2 C), 128.7, 132.3 (2 C), 133.6 (2 C), 138.8, 137.7,

159.8, 159.9, 164.3 (2 C) ppm. IR: ṽ = 2923, 2853, 2213, 1578, 1514, 1248, 830 cm^{-1}. MS (IC+): *m*/*z* (%) = 1078 (100) [MH]$^+$. $C_{76}H_{88}N_2O_3$ (1076.68): calcd. C 84.71, H 8.23, N 2.60; found C 85.06, H 8.46, N 2.41.

4,6-Bis(4-methoxyphenyl)pyrimidine (16): Suzuki cross-coupling reaction of 4,6-dichloropyrimidine (300 mg, 2.0 mmol) with (4-methoxyphenyl)boronic acid (607 mg, 4.0 mmol) according to the general procedure (*t* = 40 h) gave after purification by column chromatography [silica gel, eluent petroleum ether/ethyl acetate (5:5)] 456 mg (78%) of **16** as a colourless solid; m.p. 148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.90 (s, 6 H, OCH_3), 7.04 (d, *J* = 9.0 Hz, 4 H, Ph-H), 7.98 (d, *J* = 1.1 Hz, 1 H, 5-H), 8.12 (d, *J* = 9.0 Hz, 4 H, Ph-H), 9.22 (d, *J* = 1.1 Hz, 1 H, 2-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.8, 111.4, 114.7, 129.0, 129.9, 159.4, 162.3, 164.3 ppm. IR: ṽ = 1600, 1590, 1575, 1510, 1405 cm^{-1}. $C_{18}H_{16}N_2O_2$ (292.33): calcd. C 73.95, H 5.52, N 9.58; found C 73.81, H 5.29, N 9.68.

2-Chloro-4,6-bis(4-methoxyphenyl)pyrimidine (17): Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine (367 mg, 2.0 mmol) with (4-methoxyphenyl)boronic acid (607 mg, 4.0 mmol) according to the general procedure (*t* = 40 h) gave after purification by recrystallisation in methylcyclohexane and ethyl acetate 450 mg (69%) of **17** as an ivory solid; m.p. 182 °C (ref.[25] 187–189°°C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.90 (s, 6 H, OCH_3), 7.04 (d, *J* = 9.0 Hz, 4 H, Ph-H), 7.88 (s, 1 H, 5-H), 8.12 (d, *J* = 9.0 Hz, 4 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.9, 109.4, 114.7, 128.5, 129.4, 160.7, 162.9, 167.1 ppm. IR: ṽ = 1584, 1575, 1512, 1259, 1234, 1175, 825 cm^{-1}. $C_{18}H_{15}ClN_2O_2$ (326.08): calcd. C 66.16, H 4.63, N 8.57; found C 66.22, H 4.70, N 8.70.

2-Chloro-4,6-bis(4-butylphenyl)pyrimidine (18): Suzuki cross-coupling reaction of 2,4,6-trichloropyrimidine (149 mg, 0.81 mmol) with (4-butylphenyl)boronic acid (430 mg, 2.43 mmol) according to the general procedure (*t* = 40 h) gave after purification by column chromatography [silica gel, eluent petroleum ether/dichloromethane (7:3)] 233 mg (76%) of **18** as a colourless solid; m.p. 54 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 8 Hz, 6 H, CH_3), 1.40–1.28 (m, 4 H, CH_2), 1.64–1.54 (m, 4 H, CH_2), 2.63 (t, *J* = 7.7 Hz, 4 H, CH_2), 7.25 (d, *J* = 8.2 Hz, 2 H, Ph-H), 7.80 (s, 1 H, 5-H), 7.98 (d, *J* = 8.2 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 22.8, 33.8, 36.0, 110.5, 127.7, 129.5, 133.5, 147.5, 162.3, 167.7 ppm. IR: ṽ = 2952, 2930, 1588, 1501, 1233, 1065, 828 cm^{-1}. MS (IC+): *m*/*z* (%) = 378 (100) [M]$^+$, 379 (27) [M]$^+$, 380 (33) [M]$^+$. $C_{24}H_{27}ClN_2$ (378.19): calcd. C 76.07, H 7.18, N 7.39; found C 76.15, H 7.09, N 7.45.

2-Chloro-4,6-bis[6-(octyloxy)pyridin-3-yl]pyrimidine (20): A mixture of [6-(octyloxy)pyridin-3-yl]boronic acid (**19**) (1.1 g, 4.43 mmol), 2,4,6-trichloropyrimidine (161 mg, 0.88 mmol), $[Pd(PPh_3)_2Cl_2]$ (60 mg, 0.09 mmol) in degassed 1,4-dioxane (10 mL) was stirred at 20 °C for 30 min. A degassed 1 M aqueous Na_2CO_3 solution (4.4 mL) was added and the reaction mixture was heated under nitrogen at reflux for 8 h. Solvent was removed in vacuo, ethyl acetate was added and the organic layer was washed with brine, separated and dried with $MgSO_4$. The mixture was purified by column chromatography (silica gel, eluent dichloromethane) to give 245 mg (54%) of **20** as a pale-yellow solid; m.p. <50 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (t, *J* = 6.6 Hz, 6 H, CH_3), 1.35–1.15 (m, 20 H, 10 × CH_2), 1.71–1.67 (m, 4 H, 2 × CH_2), 4.25 (t, *J* = 6.7 Hz, 4 H, OCH_2), 6.71 (d, *J* = 8.6 Hz, 2 H, 5'-H), 7.69 (s, 1 H, 5-H), 8.20 (d, *J* = 8.6 Hz, 2 H, 4'-H), 8.74 (s, 2 H, 2′-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 23.0, 26.4, 29.3, 29.6, 29.7, 32.2, 67.2, 108.6, 111.8, 124.8, 137.7, 147.3, 162.4, 164.5, 166.6 ppm. IR: ṽ = 2927, 2856, 1604, 1579, 1493, 1397, 1290, 1234, 832 cm^{-1}. $C_{30}H_{41}ClN_4O_2$ (524.29): calcd. C 68.62, H 7.87, N 10.67; found C 68.41, H 7.60, N 10.90.

6-Chloro-4-[4-(dimethylamino)phenyl]pyrimidine (21): Suzuki cross-coupling reaction of 4,6-dichloropyrimidine (300 mg, 1.29 mmol) with [4-(dimethylamino)phenyl]boronic acid (639 mg, 3.87 mmol) according to the general procedure (*t* = 24 h) gave after purification by column chromatography [silica gel, eluent petroleum ether/ethyl acetate (9:1)] 156 mg (52%) of **21** as a yellow solid; m.p. 182 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.06 [s, 6 H, $N(CH_3)_2$], 6.74 (d, *J* = 9.0 Hz, 2 H, Ph-H), 7.58 (s, 1 H, 5-H), 7.98 (d, *J* = 9.0 Hz, 2 H, Ph-H), 8.88 (s, 1 H, 2-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.6, 109.7, 112.2, 124.9, 128.6, 152.5, 159.2, 164.1 ppm. IR: ṽ = 1610, 1556, 1456, 1199, 1105, 822, 752 cm^{-1}. $C_{12}H_{12}ClN_3$ (233.70): calcd. C 61.67, H 5.18, N 17.98; found C 61.58, H 5.23, N 17.82.

4,6-Bis[4-(dimethylamino)phenyl]pyrimidine (22): Suzuki cross-coupling reaction of **21** (300 mg, 1.29 mmol) with [4-(dimethylamino)phenyl]boronic acid (659 mg, 4.0 mmol) according to the general procedure (*t* = 40 h) gave after purification by column chromatography [silica gel, eluent petroleum ether/ethyl acetate (8:2)] 311 mg (76%) of **22** as an orange solid; m.p. 172 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.08 [s, 12 H, $N(CH_3)_2$], 6.81 (d, *J* = 9.0 Hz, 4 H, Ph-H), 7.92 (d, *J* = 1.1 Hz, 1 H, 5-H), 8.08 (d, *J* = 9.0 Hz, 4 H, Ph-H), 9.13 (d, *J* = 1.1 Hz, 1 H, 2-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.5, 112.1, 115.2, 122.5, 129.0, 153.1, 159.1 ppm. IR: ṽ = 1608, 1574, 1524, 1439, 1362, 1182, 819 cm^{-1}. $C_{20}H_{22}N_4$ (318.42): calcd. C 75.44, H 6.96, N 17.60; found C 75.31, H 7.12, N 17.37.

2-Chloro-4,6-bis[4-(dimethylamino)phenyl]pyrimidine (23): Suzuki cross-coupling reaction of **5** (300 mg, 1.12 mmol) with [4-(dimethylamino)phenyl]boronic acid (221 mg, 1.34 mmol) according to the general procedure (*t* = 40 h) gave after purification by column chromatography [silica gel, eluent petroleum ether/ethyl acetate (95:5)] 252 mg (64%) of **23** as a yellow solid; m.p. 172 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.08 [s, 12 H, $N(CH_3)_2$], 6.77 (d, *J* = 9.0 Hz, 4 H, Ph-H), 7.77 (s, 1 H, 5-H), 8.06 (d, *J* = 9.0 Hz, 4 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.5, 107.4, 112.0, 123.5, 129.0, 152.8, 160.6, 166.9 ppm. IR: ṽ = 2937, 1557, 1518, 1413, 1223, 1185, 818 cm^{-1}. $C_{20}H_{21}ClN_4$ (352.15): calcd. C 68.08, H 6.00, N 15.88; found C 69.37, H 6.16, N 15.63.

2.4-Bis[4-(dimethylamino)phenyl]pyrimidine (24): Suzuki cross-coupling reaction of 2,4-dichloropyrimidine (209 mg, 1.40 mmol) with [4-(dimethylamino)phenyl]boronic acid (924 mg, 5.60 mmol) according to the general procedure (*t* = 40 h) gave after purification by column chromatography [silica gel, eluent petroleum ether/ethyl acetate (9:1)] 311 mg (70%) of **24** as a beige solid; m.p. 252 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.06 [s, 6 H, $N(CH_3)_2$], 3.07 [s, 6 H, $N(CH_3)_2$], 6.81 (d, *J* = 9.0 Hz, 4 H, Ph-H), 6.82 (d, *J* = 9.0 Hz, 4 H, Ph-H), 7.37 (d, *J* = 5.3 Hz, 1 H, 5-H), 8.17 (d, *J* = 9.0 Hz, 4 H, Ph-H), 8.48 (d, *J* = 9.0 Hz, 4 H, Ph-H), 8.64 (d, *J* = 5.3 Hz, 1 H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.2, 110.4, 110.6, 110.8, 123.6, 125.1, 127.3, 128.4, 151.0 151.2, 159.8, 162.3, 163.4 ppm. IR: ṽ = 1608, 1574, 1524, 1439, 1362, 1182, 819 cm^{-1}. $C_{20}H_{22}N_4$ (318.42): calcd. C 75.44, H 6.96, N 17.60; found C 75.09, H 6.69, N 17.83.

2-Methoxy-4,6-bis(4-methoxyphenyl)pyrimidine (25): A solution of sodium methoxide prepared with Na (51 mg, 2.24 mmol) in methanol (15 mL) was added dropwise to **17** (180 mg, 1.12 mmol) in methanol (5 mL) at 0 °C. The mixture was allowed to stir at 60 °C during 24 h and then hydrolysed with water (20 mL). The methanol was evaporated in vacuo, the aqueous layer extracted with dichloromethane (3 × 20 mL) and the combined organic extracts dried with magnesium sulfate and the solvents evaporated. The residue was

purified by column chromatography [silica gel, eluent petroleum ether/ethyl acetate (9:1)] to give 328 mg (91%) of **25** as a beige solid; m.p. 134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 6 H, OCH_3), 4.12 (s, 3 H, OCH_3), 7.00 (d, J = 9 Hz, 4 H, Ph-H), 7.61 (s, 1 H, 5-H), 8.10 (d, J = 8.9 Hz, 4 H, Ph-H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 55.0, 55.8, 105.1, 114.5, 129.2, 129.8, 162.3, 166.5 (2 C) ppm. IR: $\tilde{\nu}$ = 1511, 1257, 1169, 1019, 825 cm^{-1}. $C_{19}H_{18}N_2O_3$ (322.13): calcd. C 70.79, H 5.63, N 8.69; found C 71.11, H 5.48, N 8.72.

2-[4,6-Di(2-thienyl)pyrimidin-2-yloxy]ethanol (26): NaH (60%) in a mineral oil dispersion (50 mg, 1.25 mmol) was added to ethylene glycol (5 mL) in an ice bath. After 5 min, **10** (27 mg, 0.1 mmol) was added and the mixture was allowed to stir at room temperature overnight, acidified with 10% aqueous HCl, diluted with H_2O and extracted twice with EtOAc (10 mL). The combined organic extracts were washed with H_2O and brine, dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography [silica gel, eluent petroleum ether/ethyl acetate (9:1)] to give 15 mg (50%) of **26** as a beige solid; m.p. 108 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.10–4.07 (m, 2 H, CH_2), 4.69–4.66 (m, 2 H, CH_2), 7.20 (dd, J_1 = 4.9, J_2 = 3.8 Hz, 2 H, 4'-H), 7.54 (s, 1 H, 5-H), 7.58 (dd, J_1 = 4.9, J_2 = 1.0 Hz, 2 H, 5'-H), 7.87 (dd, J_1 = 3.8, J_2 = 1.0 Hz, 2 H, 3'-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 62.2, 70.0, 104.0, 128.3, 128.8, 130.7, 142.2, 162.0, 165.6 ppm. IR: $\tilde{\nu}$ = 3413, 2928, 1580, 1528, 1404, 1347, 1327, 1060, 826, 715 cm^{-1}. $C_{14}H_{12}N_2O_2S_2$ (304.39): calcd. C 55.24, H 3.97, N 9.20, S 21.07; found C 55.56, H 4.29, N 8.84, S 20.72.

4,6-Bis[4-(dimethylamino)phenyl]-2-[4-(trifluoromethyl)phenyl]-pyrimidine (27): Suzuki cross-coupling reaction of **23** (115 mg, 0.32 mmol) with [4-(trifluoromethyl)phenyl]boronic acid (62 mg, 0.64 mmol) according to the general procedure (t = 40 h) gave after purification by recrystallisation from methylcyclohexane 134 mg (92%) of **27** as a colourless solid; m.p. 236 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.07 [s, 12 H, $N(CH_3)_2$], 6.83 (d, J = 9.0 Hz, 4 H, Ph-H), 7.77 (d, J = 9.0 Hz, 2 H, Ph-H), 7.84 (s, 1 H, 5-H), 8.20 (d, J = 9.0 Hz, 4 H, Ph-H), 8.82 (d, J = 9.0 Hz, 2 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.2, 106.4, 110.8, 123.8, 124.1, 125.2, 127.3, 127.6, 130.3 (q), 141.3, 151.0, 161.4, 162.9 ppm. ^{19}F NMR (282.5 MHz, $CDCl_3$): δ = –62.9 ppm. IR: $\tilde{\nu}$ = 1588, 1567, 1520, 1324, 1194, 1167, 1118, 1066, 1017, 809 cm^{-1}. $C_{27}H_{25}F_3N_4$ (462.51): calcd. C 70.12, H 5.45, N 12.11; found C 70.34, H 5.21, N 12.37.

2,4,6-Tris[4-(dimethylamino)phenyl]-1,3,5-triazine (28): Suzuki cross-coupling reaction of cyanuric chloride (184 mg, 1.0 mmol) with [4-(dimethylamino)phenyl]boronic acid (825 mg, 5.0 mmol) according to the general procedure (t = 24 h) gave after purification by column chromatography [silica gel, eluent petroleum ether/ethyl acetate (7:3)] 184 mg (42%) of **28** as a red solid; m.p. 116 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.11 [s, 18 H, $N(CH_3)_2$], 6.82 (d, J = 9.0 Hz, 6 H, Ph-H), 8.65 (d, J = 9.0 Hz, 4 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.6, 111.7, 124.9, 130.6, 153.3, 170.8 ppm. IR: $\tilde{\nu}$ = 3226, 2924, 1494, 1429, 1364, 1193, 1145, 803 cm^{-1}. $C_{27}H_{30}N_6$ (438.25): calcd. C 73.94, H 6.89, N 19.16; found C 74.26, H 6.98, N 18.89.

1,3,5-Tris[4′-(dimethylamino)biphenyl-4-yl]benzene (31): Suzuki cross-coupling reaction of **29**[18] (543 mg, 1.0 mmol) with [4-(dimethylamino)phenyl]boronic acid (825 mg, 5.0 mmol) according to the general procedure (t = 24 h) gave after purification by recrystallisation in chloroform 570 mg (86%) of **31** as a yellow solid; m.p. 236 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.03 (s, 18 H, NCH_3), 6.86 (d, J = 8.1 Hz, 6 H, Ph-H), 7.61 (d, J = 8.7 Hz, 6 H, Ph-H), 7.70 (d, J = 8.1 Hz, 6 H, Ph-H), 7.78 (d, J = 8.4 Hz, 6 H, Ph-H), 7.89 (s, 3 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$ + TFA): δ = 47.7, 121.0, 125.8, 128.2, 128.5, 129.7, 138.4, 141.5, 141.6, 142.2, 143.8 ppm. IR: $\tilde{\nu}$ = 1610, 1503, 1441, 1355, 1212, 1196, 809, 754 cm^{-1}. $C_{48}H_{45}N_3$ (663.89): calcd. C 86.84, H 6.83, N 6.33; found C 86.91, H 6.81, N 6.39.

1,3-Bis[4′-(dimethylamino)phenyl]benzene (32): Suzuki cross-coupling reaction of 1,3-dibromobenzene (300 mg, 1.30 mmol) with [4-(dimethylamino)phenyl]boronic acid (825 mg, 5.0 mmol) according to the general procedure (t = 24 h) gave after purification by column chromatography [silica gel, eluent petroleum ether/ethyl acetate (9:1)] 343 mg (83%) of **32** as a beige solid; m.p. 196 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.03 (s, 12 H, NCH_3), 6.85 (d, J = 8.7 Hz, 4 H, Ph-H), 7.49–7.46 (m, 3 H, Ph-H), 7.59 (d, J = 8.7 Hz, 4 H, Ph-H), 7.78 (s, 1 H, Ph-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 41.0, 113.2, 124.6, 124.9, 128.2, 129.4, 129.9, 142.0, 150.4 ppm. IR: $\tilde{\nu}$ = 1610, 1534, 1480, 1349, 1229, 1206, 708 cm^{-1}. $C_{22}H_{24}N_2$ (316.44): calcd. C 83.50, H 7.64, N 8.85; found C 83.71, H 7.79, N 8.54.

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