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HAL Id: hal-01880133
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Submitted on 28 Sep 2018

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2,4-Distyryl- and 2,4,6-tristyrylpyrimidines: Synthesis and photophysical properties.

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Synopsis TOC

Abstract
The synthesis of a series of twenty new 2,4,6-tristyrilpyrimidines and three new 2,4-distyrylpyrimidines by means of combination of Knoevenagel condensation and Suzuki-Miyaura cross coupling reaction is reported. This methodology enables to obtain chromophores with identical or different substituent on each arm. The photophysical properties of the compounds are described. Optical properties and TD-DFT calculations indicate that photophysical properties of target compounds are mainly affected by the nature of the electron-donating group in C4/C6 positions, except when the C2 substituent is a significantly stronger electron-donating group. However, the C2 substituent has a strong influence on emission quantum yield: addition of a strong electron-donating group tends to decrease the fluorescence quantum yield whereas a moderate electron-withdrawing group results in a significant increase of fluorescence quantum yield.

**Introduction**

During the past two decades, there has been a great interest in the synthesis of pyrimidine fluorophores.\(^1\) The pyrimidine is a six-membered heterocycle with two nitrogen atoms (1,3-diazine) that exhibits a strong electron-withdrawing character. When the pyrimidine ring is combined with electron-donating fragments via \(\pi\)-conjugated linkers, intramolecular charge transfer (ICT) occurs leading, generally, to a strong emission.\(^1\) Recently, pyrimidine-based thermally activated fluorescent emitters (TADF) have been developed and have been used for high external quantum efficiency organic light-emitting diodes (OLEDs).\(^2\) 4,6-Distyrilpyrimidines have also been developed as two-photon excitation emitters for biological microscopy\(^3\) and photoinitiator for multiphoton lithography.\(^4\)

Due to the electron lone pair of its two nitrogen atoms, the pyrimidine ring can catch protons, coordinate metal cations, and link to various (bio)organic molecules leading to modification of its emission properties. Various pyrimidine chromophores have been used as pH,\(^5\) metal
cations, nitroaromatic, and protein fluorescent sensors. Mixtures of neutral and protonated forms of pyrimidine fluorophores have also been used as white light emitters. Recently, Kato and coworkers have highlighted the influence of substituent in C2 position on the emission properties of pyrimidine derivatives.

Y-shaped centripetal molecules have been subject to intensive research. In this context, the triazine core has been extensively used. In these structures, periphery-to-core multidimensional charge transfer lead to large second-order optical response and large two photon absorption cross section. Numerous 2,4,6-aryl- and 2,4,6-arylthynylpyrimidine chromophores have been designed for their luminescence properties.

Styrylpyrimidines are generally obtained by Knoevenagel condensation of an aldehyde with methylpyrimidine under basic or acidic conditions. This reaction can be easily carried out on the methyl group in positions C2, C4 and/or C6. Using this strategy, 2-styryl, 4-styryl and 4,6-distrylpyrimidine as well as 4,4′,6,6′-tetraarylpyrimidine chromophores have been prepared so far; selected known 4,6-distrylpyrimidines are presented in Chart 1. To the best of our knowledge, only the unsubstituted 2,4,6-tristyrlpyrimidine has been described to date.

![Chart 1. Structures of selected known chromophores 4,6-distyrylpyrimidines.](image-url)

In this contribution, we describe the design and synthesis of 2,4,6-tristyrlpyrimidines and 2,4-distyrylpyrimidines by combining Suzuki-Miyaura cross coupling reaction and Knoevenagel condensation. This strategy enables the synthesis of compounds with different substituents on each arm and, thus, allows modification of their electron donating or withdrawing abilities. The molecular structure obtained by X-ray analysis of a selected...
The photophysical properties of target chromophores were studied and thoroughly compared with the corresponding 4,6-distyrylpyrimidines. The DFT and TD-DFT calculations were also performed on selected chromophores to rationalize their photophysical properties.

**Results and discussion**

**Synthesis**

Various strategies have been considered for the synthesis of 2,4,6-tristyrylpyrimidines. Threefold Knoevenagel condensation from 2,4,6-trimethylpyrimidine has been envisioned. However, the pyrimidine starting material cannot be isolated easily in a good yield.\(^{21}\) The synthesis of 2-methyl-4,6-distyrylpyrimidine was also considered by treating 4,6-distyrylpyrimidine with methylolithium followed by \textit{in-situ} rearomatization with DDQ according to known procedure\(^{22}\) but we failed in obtaining the desired product. We therefore proposed a third strategy, starting from commercially available 2-chloro-4,6-dimethylpyrimidine and 2,4-dichloro-6-methylpyrimidine. A combination of Suzuki cross-coupling and Knoevenagel condensation has been developed leading to twenty-one tristyrylpyrimidine chromophores (Schemes 1–2).

Chromophores 2 with identical substituents in C4 and C6 positions were obtained in two steps from 2-chloro-4,6-dimethylpyrimidine. The first step consists of the \textit{in-situ} conversion of arylalkynes into styrylboronic acid by action of catecholborane followed by palladium-catalyzed Suzuki-Miyaura cross coupling reaction.\(^{23}\) 2-Styrylpyrimidine intermediates 1 were obtained in moderate to good yields. 2,4,6-Tristyrylpyrimidines 2 were obtained by condensation between the C4 and C6 methyl group and the corresponding aromatic aldehyde in boiling aqueous 5 M NaOH using Aliquat 336 as catalyst.\(^{5a,17a}\) Moderate to good yields
were generally observed. The lower yields, observed in particular for unsubstituted styryl derivatives, were due to more complicated purification process.

Scheme 1: Synthesis of compounds 2.

To obtain 2,4,6-tristyrylpyrimidines 5 with three different arms, a three-step synthetic route employed 2,4-dichloro-6-methylpyrimidine as a starting material (Scheme 2). The first step consisted in a C4 regioselective Suzuki-Miyaura cross coupling reaction with \textit{in situ} formed styrylboronic acid leading to intermediates 3. The observed regioselectivity of cross coupling reaction in C4 over C2 position of the pyrimidine ring is in accordance with the literature.\textsuperscript{15b,16a,24} The second step consisted in a second Suzuki-Miyaura cross coupling reaction in C2 position leading to 2,4-dististyrylpyrimidines intermediates 4 and finally a Knoevenagel condensation of 4-(\textit{N},\textit{N}-diphenylamino)benzaldehyde on the methyl group in C6 position lead to chromophores 5.
Starting from 2-chloro-4-methylpyrimidine, 2,4-distyrylpyrimidines were obtained in a similar two-step synthetic pathway (Scheme 3).

Scheme 2: Synthesis of compounds 5.

(i): catecholborane, THF, reflux, 3.5h
(ii): 2,4-dichloro-6-methylpyrimidine, Pd(PPh₃)₄, Na₂CO₃, reflux, 15h
(iii): 3a or 3b, Pd(PPh₃)₄, Na₂CO₃, reflux, 15h
(iv): 4-R²C₆H₄-CH₃, aliquat 336, NaOHaq 5M, reflux, 3h
Scheme 3: Synthesis of compounds 7.

All new compounds are well soluble especially in chlorinated solvents (DCM, CHCl₃) and were characterized by ¹H, ¹³C NMR and HRMS spectroscopic techniques. The selectivity of the Suzuki-Miyaura cross coupling as well as condensation reactions was sufficiently high to generate all trans-isomer within the limits of NMR detection as observed previously. The stereochemistry of the double bounds was unequivocally established on the basis of coupling constant for the vinylic proton in the ¹H NMR (J ≈ 16 Hz). No trans/cis isomerisation were observed during photophysical experiments.

X-ray Analysis

Chromophore 2h provided crystals for X-ray analysis by slow evaporation of its dichloromethane/ethyl acetate (1/1, v/v) solution. The measured crystal, a large fragment of a large yellow and transparent prism, confirms the proposed molecular structure; in particular the E configuration of the three vinylic linkers is confirmed (Figure 1). An orthorhombic crystal system is observed with a Pna2₁ space group. The presence of a (modelled) disorder
on one of the two C4/C6 arm, already observed for similar structures,\textsuperscript{19b} can be shown. Solid state supramolecular assembly of the chromophore revealed an orthorhombic crystal system with a Pna\textsubscript{2}$_{1}$ space group. The crystal structure shows that the angles between the planes of three benzene rings and the pyrimidine central core lower than 20°, indicating that they are not completely planar, in accordance with other 4-styryl- and 4,6-distyrylpyrimidines.\textsuperscript{9a,25} It should be noted that the dihedral angle between the phenyl ring in C2 position and the pyrimidine core is the lowest (∼7°). Bond length alternation (BLA) were calculated for the vinylic linker on each arm and were revealed to be slightly lower for the C2 arm (0.1185 Å), than for C4/C6 arms (0.1205, 0.1600 and 0.1775 Å) indicating that the C2 arm imparts stronger ICT.
**Figure 1**: ORTEP drawing of the chromophore 2h with thermal ellipsoid at 50%.

**Thermal properties**

Thermal behaviour of the final compounds 2, 5 and 7 as well as compounds A2 and A3 was studied by differential scanning calorimetry (DSC). Figure 2 shows thermograms of representative compounds 2i, 2m, A2 and A3 while Table 1 lists all measured melting points \( T_m \) and temperatures of thermal decompositions \( T_d \). All DCS curves are given in the SI. The measured melting points range from 128 to 243 °C. The temperature of decomposition was estimated within the range of 195-320 °C. Further discussion on the thermal properties is provided in the SI.
Figure 2: Representative DSC thermographs of compounds 2i, 2m, A₂ and A₃ obtained with a scanning rate of 3°C/min in the range 50-400°C.

Table 1: DSC results for chromophores 2, 5, 7, A₂ and A₃.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Tₘ (°C)</th>
<th>Tₖ (°C)</th>
<th>Comp.</th>
<th>Tₘ (°C)</th>
<th>Tₖ (°C)</th>
<th>Comp.</th>
<th>Tₘ (°C)</th>
<th>Tₖ (°C)</th>
<th>Comp.</th>
<th>Tₘ (°C)</th>
<th>Tₖ (°C)</th>
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<tbody>
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<td>193</td>
<td>300</td>
<td>2h</td>
<td>200</td>
<td>295</td>
<td>2o</td>
<td>/</td>
<td>250</td>
<td>7a</td>
<td>137</td>
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<td>2b</td>
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<td>290</td>
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<td>/</td>
<td>250</td>
<td>2p</td>
<td>/</td>
<td>220</td>
<td>7b</td>
<td>185</td>
<td>305</td>
</tr>
<tr>
<td>2c</td>
<td>/</td>
<td>245</td>
<td>2j</td>
<td>/</td>
<td>240</td>
<td>2q</td>
<td>/</td>
<td>280</td>
<td>7c</td>
<td>243</td>
<td>265</td>
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<td>2r</td>
<td>210</td>
<td>265</td>
<td>7d</td>
<td>/</td>
<td>250</td>
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<tr>
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<td>305</td>
<td>2l</td>
<td>/</td>
<td>195</td>
<td>2s</td>
<td>/</td>
<td>300</td>
<td>A₂</td>
<td>191</td>
<td>260</td>
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<td>/</td>
<td>250</td>
<td>2m</td>
<td>/</td>
<td>310</td>
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<td>/</td>
<td>210</td>
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</table>

Tₘ = melting point (the point of intersection of a baseline and a tangent of thermal effect = onset). Tₖ = thermal decomposition (pyrolysis in N₂ atmosphere).

Common feature of tripodal (D-π)₃-A or (D-π)₂-A-(π-A) chromophores 2a–s and 5a–b is their resistance to crystallize and they often occur as solid glasses and amorphous solid. This suggests a more sophisticated thermal behaviour of centripetal star-shaped systems. Hence, their DSC curves are frequently similar and decorated by solid-solid or glass transitions. Based on the DSC analysis there are no evident general trends between type or position of particular donor used and thermal behavior of tripodal chromophores.
modifications (donor variation) often influences the thermal properties of tripodal chromophores only negligibly because the intrinsic nature of these molecules remains the same.

In general, 2,4- and 4,6-disubstituted pyrimidines (7a–d, A2 and A3) have demonstrated a similar thermal behaviour. A presence of donor groups (NMe2, OMe) in quadrupolar molecules 7b and 7c increases the melting point up to 100 °C compared to “donor free” analogue 7a.

The $T_d$ of tripodal molecules 2i/2m and their quadrupolar analogous A2/A3 are comparable (Figure 2) and dictated by the type of attached donors on the periphery. Therefore, DMA 2i/A2 and TPA analogous 2m/A3 have demonstrated almost identical $T_d$ values (250/260 and 310/320 °C, see Table 1).

**Photophysical properties**

The UV/Vis and photoluminescence (PL) spectroscopic data of compounds 2, 5 and 7 measured in CH$_2$Cl$_2$ at room temperature are presented in Table 2. The analyses were carried out by using low concentrations of chromophores (0.5–1.5 × 10$^{-5}$ M). To facilitate comparison of photophysical properties, 4,6-distyrylpyrimidines A$^{5a}$ were also included in Table 1. As an example, the spectra of compounds 2b, 2c and 2d are provided in Figure 3.
Figure 3: Normalized absorption (solid lines) and emission spectra (dashed lines) of compounds 2b (black), 2c (green) and 2d (green) in CH$_2$Cl$_2$ solution.

For all the compounds, the less energetic absorption band ($\lambda_{\text{max}} = 312-429$ nm) is attributed to charge transfer. Except compounds 2a, 2h, 7a and 7b, that are however slightly emissive in non polar heptane, all the compounds exhibit significant emission. In case of 2h, the absence of emission is attributed to twisted intramolecular charge transfer excited state. For these compounds, as generally observed for pyrimidine push-pull chromophores,$^1$ large Stokes shifts were obtained, indicating large difference (vibrational, electronic, geometric) between the Franck-Condon state and the excited state. For tristyrylpyrimidines 2 and 5, the position of absorption and emission wavelength maxima depends mainly on C4/C6 substituents. However, it should be noted that a significant red-shift in emission is observed when the C2
substituent is a significantly stronger electron-donating groups than C4/C6 substituents (2j and 2k). Whereas the ICT generally occurs over the C4/C6 arm, in this case, the ICT is probably prevailing on the C2 arm. The fluorescence quantum yield varies significantly when the C2 substituent is modified. When tristrylpyrimidines 2b-2d with unsubstituted styryl group in C2 position are compared with 2,6-distyrylpyrimidines A1-A3, it appears that the addition of the styryl group in C2 position leads to a slight red shift of the emission maxima and a significant increase of the fluorescence quantum yield. The presence of an electron-donating group (methoxy, dimethylamino or diphenylamino) on the C2 arm (compounds 2e-2g, 2i, 2l, 2m) results in a slight blue shift of emission regarding the corresponding unsubstituted styryl derivatives 2b-2d. The opposite trend is observed for 2j and 2k probably due to change in the ICT direction over the C2 arm. Whereas chromophores with dimethylamino group on C4/C6 arms (compounds A2, 2c, 2f, 2l, 2o, 2r and 5a) are generally highly luminescent, the incorporation of this fragment on C2 (chromophores 2h-2j, 5b and 7c) leads to a dramatic decrease of fluorescence quantum yield. On the other hand, the addition of a trifluoromethyl fragment, a moderately electron-withdrawing group, on C2 arm (chromophores 2q-2s) results in a significant increase of the fluorescence quantum yield up to 1.00 for 2s. 2,4-Distyrylpyrimidines 7 exhibits significantly blue shifted absorption and emission with regards to their 4,6-distyryl and 2,4,6-tristyrylpyrimidines analogues. All these trends are in accordance with the observation made on arylpyrimidine series.\(^{1a,15a-b}\)

**Table 2:** UV/Vis and PL data in CH\(_2\)Cl\(_2\).

<table>
<thead>
<tr>
<th>Compd(^{a})</th>
<th>UV/vis (\lambda_{max}), nm</th>
<th>PL</th>
<th>Stokes shift</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((\varepsilon, \text{mM}^{-1}\cdot\text{cm}^{-1}))</td>
<td>(\lambda_{max}), nm</td>
<td>(\Phi_F^{b})</td>
</tr>
<tr>
<td>A1(^{1a})</td>
<td>359 (36.0)</td>
<td>439</td>
<td>-</td>
</tr>
<tr>
<td>A2(^{5a})</td>
<td>429 (42.1)</td>
<td>530</td>
<td>0.40</td>
</tr>
<tr>
<td>A3(^{5a})</td>
<td>427 (47.6)</td>
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<td>0.55</td>
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<td></td>
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<td>312 (74.3)</td>
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<tr>
<td></td>
<td>2b</td>
<td>369 (35.9)</td>
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<tr>
<td></td>
<td>2c</td>
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<td></td>
<td>2d</td>
<td>430 (55.0)</td>
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<td></td>
<td>2g</td>
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<tr>
<td></td>
<td>2h</td>
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<tr>
<td></td>
<td>2i</td>
<td>402 (97.3)</td>
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<td></td>
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</table>

All spectra were recorded at room temperature at \( c = 0.5 \times 10^{-5} \) M to \( 1.5 \times 10^{-5} \). Flourescence quantum yield (±10%) determined relative to 9,10-bisphenylethynylantracene in cyclohexane (\( \Phi_F = 1.00 \)).

In order to gain further insights into the photophysical properties of these compounds, their absorption and emission behavior was studied in a variety of aprotic solvents. While the absorption maxima were not significantly shifted, an increase in solvent polarity, estimated by Dimroth-Reichardt polarity parameter, led to bathochromic shifts of the emission maxima. The results of emission solvatochromism are summarized in Table 3. As an example, the spectra registered for compound 2g are shown in Figure 4 and the change in emission color under UV irradiation for compound 2k, easily seen by the naked eye, can be seen in Figure 5.

This solvatochromic behavior, characteristic for fluorophore featuring intramolecular charge transfer, can be explained by the stabilization of the highly polar emitting state by polar solvents. For all the compounds, the emission maxima were plotted versus Dimroth-Reichardt polarity parameter (see Figures S106-S112) and, in all cases, a good linearity was observed. The emission solvatochromic behavior can be quantified by the slope of the corresponding regression line. Once again, with the exception of compound 2k, the substituents in C4/C6 arm are the most affected by the emission solvatochromism with decreasing order: NMe₂ > NPh₂ > OMe. This is in accordance to the electron-donating strength of the substituents. The slopes for 2,4-distyrylpyrimidines 7c and 7d are significantly lower than that of their 2,4,6-tristyrylpyrimidine analogues 2i and 2m, indicating that both arms in C4 and C6 position play a role on the emission solvatochromism and, therefore on ICT into the chromophores.
Table 3: Emission solvatochromism of pyrimidine derivatives in various aprotic solvents.

<table>
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<tr>
<th>Compd</th>
<th>Heptane</th>
<th>Toluene</th>
<th>THF</th>
<th>CH₂Cl₂</th>
<th>Acetone</th>
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$^a$ Dimroth–Reichardt polarity parameter, kcal·mol$^{-1}$
Figure 4: Normalized emission spectra of $2g$ in different aprotic solvents.

Figure 5: Fluorescence color changes experienced by $2k$ in various solvents. Picture was taken in the dark upon irradiation with a hand-held UV lamp ($\lambda_{em} = 366$ nm).

The ability of protonation of pyrimidine chromophores has been already demonstrated.$^{5,9}$ Generally, the protonation of amino-substituted stryrylpyrimidines results in quenching of emission; however, in the case of less electron-donating substituents, such as methoxy groups,
the protonation lead to a red-shifted emission. The changes in the emission spectra of 2q upon addition of (1S)-(+) camphorsulfonic acid are illustrated in Figure 6. The progressive disappearance of the emission band of the neutral form at 441 nm is observed, whereas a new red-shifted absorption band at 540 nm progressively appear corresponding to the monoprotonated species. As shown on Figure 7, the neutral form of 2q emits dark blue light under UV-irradiation whereas the protonated form emits green light. A mixture of the two forms enables to obtain cyan light.

![Figure 6](image)

**Figure 6** Changes in the emission spectra of a CH$_2$Cl$_2$ solution of 2q (c = 0.9642 ×10$^{-5}$ M) upon addition of (1S)-(+) camphorsulfonic acid (0.1 – 50 eq.). $\lambda_{exc} = 380$ nm.
Figure 7 Change in the color of a CH$_2$Cl$_2$ solution of 2q (c = 0.9642 $\times$ 10$^{-5}$ M) after the addition of 0.8 equiv (middle) and 50 equiv of (1S)-(+)10-camphorsulfonic acid (right). Picture was taken in the dark upon irradiation with a hand-held UV lamp ($\lambda_{em}$ = 366 nm).

DFT calculations

DFT calculations implemented in Gaussian 16 software package$^{29}$ were employed to investigate the fundamental properties of representative pyrimidines A$_3$, 2g, 2j, 2k, and 2m with a systematically varied structural arrangement. Their optimized geometries, the HOMO/LUMO energies, and ground state dipole moments $\mu$ (Table 4) were obtained by DFT B3LYP/6-311+g(2d,p) method. The calculated HOMO/LUMO levels were further visualized in the energy level diagram as shown in Figure 8. Whereas the HOMO-LUMO gaps of all molecules are almost identical (2.97-3.02 eV), the principal variations are seen at both HOMO/LUMO levels. Hence, decoration of the central pyrimidine acceptor with two or three donor arms affects the position of the HOMO and LUMO rather than the HOMO-LUMO difference. This is in accordance to our latest observation and generalization on multipodal chromophores.$^{30}$ The frontier molecular orbitals are further visualized in Figure 9. In the parent molecule A$_3$, the HOMO is localized on both $N,N$-diphenylamino donors but is also
mixed with the LUMO spread over the central pyrimidine and adjacent π-linkers. This implies lower charge separation. The situation is similar in 2g bearing weak additional 4-methoxystyryl donor appended at C2 (the second N,N-diphenylamino donor is occupied by the HOMO-1). However, by attaching strong electron releasing moieties, such as N,N-dimethylamino or N,N-diphenylamino groups, the HOMO has completely moved on the arms appended at C2 regardless what type of donors are connected at C4/C6. Hence, for 2j, 2k, and 2m, the ICT dominates from the arm connected at pyrimidine C2.

**Table 4**: DFT calculated data of representative chromophores.

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<th>Compd</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>$\Delta E$ (eV)</th>
<th>$\mu$ (D)</th>
<th>$\lambda_{\text{max}}$ (nm/eV)</th>
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<td>2.94</td>
<td>1.60</td>
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**Figure 8** Energy level diagram of the DFT-derived HOMO/LUMO energies.

**Figure 9** Optimized geometries and HOMO (red) and LUMO (blue) localizations in representative chromophores.

The electronic absorption spectra of representative chromophores were further calculated using TD-SCF (nstates = 10) B3LYP/6-311+g(2d,p) method. The spectra are listed in Figure S113 jointly with the experimental data; the calculated longest-wavelength absorption maxima are given in Table 3. Their correlation with the experimental $\lambda_{\text{max}}$ values is very tight.
as shown in Figure S114. This implies that, despite the calculated values are generally red-shifted, the employed method is capable to described trends within the given series of molecules. The spectra of representative chromophores feature a low energy lying CT-band with the $\lambda_{\text{max}}$ appearing between 403-475 nm (376-428 nm experimentally). Compared to tripodal molecules 2, the quadrupolar chromophore $A_3$ showed the most bathochromically shifted CT-band ($\lambda_{\text{max}} = 428$ nm). This may be explained by the Frenkel exciton model, which predicts splitting of the singlet excited state into two and three bands for quadrupolar and tripodal molecules, as compared to their linear analogue. Whereas for quadrupolar molecules is the low energy band dominant, the low energy lying two states of a tripodal molecule are degenerate while the third high energy state has zero oscillator strength. Hence, the absorption spectra of both types of molecules are characterized by a single CT-band, eventually accompanied by a shoulder for quadrupolar molecules and a blue-shift for tripodal ones. According to the performed calculations, the CT-bands of quadrupolar $A_3$ and tripodal $2g$, bearing weak methoxy electron donor, are almost exclusively generated by the HOMO→LUMO transition. On the other hand, the CT bands of $2j$ and $2m$, bearing all amino donors, are dominated by the HOMO→LUMO, HOMO-1→LUMO, and HOMO→LUMO+1 transitions. Replacement of two amino donors at C4/C6 as in $2k$ led to a significantly red-shifted HOMO→LUMO transition (~468 nm, see Figure S113) but with diminished oscillator strength. Hence, the observed CT-band is generated by the HOMO→LUMO+1 and HOMO-1→LUMO transitions.

**Conclusions**

In conclusion, we have successfully synthesized 2,4,6-tristyrylpyrimidine and 2,4-distyrylpyrimidine chromophores with identical or different substituent on each arm. In terms of absorption and emission maxima, and calculated HOMO-LUMO gaps, 2,4,6-tristyrylpyrimidines exhibits generally the similar properties as the corresponding 4,6-
distyrylpyrimidines. Nevertheless, when the C2 substituent is a significantly stronger electron-donating substituents than C4/C6 ones, the ICT occurs mainly on this branch and dictates the photophysical properties. In all cases, the C2 substituent play a key role on the emission quantum yield. As one would expected, all these materials exhibit strong emission solvatochromism and pH sensibility. Comparison of the two-photon absorption properties of 2,4,6-tristyrylpyrimidine with the corresponding 4,6-distyrylpyrimidines are currently under investigation.

**Experimental Section**

**General Conditions.** In air- and moisture-sensitive reactions, all glassware was flame-dried and cooled under nitrogen. Thermal behavior of the target compounds was measured in open aluminous crucibles under N$_2$ inert atmosphere. DSC curves were determined with a scanning rate of 3 °C/min within the range 25–400 °C. NMR spectra were acquired at room temperature. Chemical shifts are given in parts per million relative to TMS (1H, 0.0 ppm) and CDCl$_3$ (13C, 77.0 ppm). Acidic impurities in CDCl$_3$ were removed by treatment with anhydrous K$_2$CO$_3$. High resolution MALDI MS spectra were measured on a MALDI mass spectrometer equipped with nitrogen UV laser (337 nm, 60 Hz) and quadrupole analyser (positive-ion mode over a normal mass range (m/z 50-2000) with resolution 100 000 at m/z = 400). Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as a matrix. Mass spectra were averaged over the whole MS record for all measured samples. UV-vis and fluorescence spectra were recorded using standard 1 cm quartz cells. Compounds were excited at their absorption maxima (band of lowest energy) to record the emission spectra. The $\Phi_F$ values were calculated using a well-known procedure with 9,10-diphenylethynylantracene in cyclohexane as standard.$^{26}$ Stokes shifts were calculated by considering the lowest energetic absorption band. All calculations were carried out in Gaussian 09W package at the DFT level of theory. The initial geometry optimizations were carried out by the PM3 method implemented in program ArgusLab and subsequently by the DFT B3LYP method using the 6-311G++(2d,f,p) basic
set. The energies of the HOMO and LUMO ($E_{\text{HOMO}}$ and $E_{\text{LUMO}}$), their differences ($\Delta E$) and ground state dipole moments ($\mu$) were calculated by the DFT B3LYP/6-311++G(2d,f,p) method.

**General procedure for Suzuki-Miyaura cross-coupling reaction.** The corresponding acetylene (1.57 equiv) was dissolved in THF (20 mL) and nitrogen was bubbled through the solution for 10 min. Catecholborane (1.9 equiv of 1 M solution in THF) was added and the reaction mixture was heated to reflux for 1.5 h. The second portion of catecholborane (0.7 equiv) was added and heating was continued for 2 h. The reaction mixture was cooled to room temperature and Pd(PPh$_3$)$_4$ (0.025 equiv) and corresponding pyrimidine (1 equiv) were added. Solution was stirred for 20 min before 20% aqueous Na$_2$CO$_3$ (5 mL) was added and the mixture was stirred under nitrogen at reflux for 15 h. The reaction mixture was cooled and then diluted with CH$_2$Cl$_2$ (20 mL). The organic layer was washed with water (3x20 mL), then with brine (20 mL), separated, dried over MgSO$_4$ and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (SiO$_2$, indicated solvents).

**General procedure for Knoevenagel condensation.** Aldehyde (1 equiv) and corresponding 4-methylpyrimidine (1 equiv) or 4,6-dimethylpyrimidine (0.5 equiv) were added in 5 M aqueous NaOH (15 mL) containing Aliquat 336 (0.1 equiv). Solution was heated to reflux for 3 h and then cooled to room temperature. The precipitate was filtered off, washed with water, and purified by recrystallization from CH$_2$Cl$_2$/n-heptane and/or by column chromatography (SiO$_2$, indicated solvents).

**(E)-2-Styryl-4,6-dimethylpyrimidine (1a).** Synthesized from phenylacetylene (161 mg, 1.57 mmol) and 2-chloro-4,6-dimethylpyrimidine (143 mg, 1 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 7:3). Yield: 78 mg (37 %); white solid. $R_f$: 0.7 (SiO$_2$; petroleum ether:EtOAc, 7:3). Mp: 47.5–49.4 °C (lit.$^{31}$ 47-50°C). $^1$H NMR (300
MHz, CDCl₃): δ = 2.50 (s, 6H), 6.86 (s, 1H), 7.21 (d, J = 15.9 Hz, 1H), 7.29–7.41 (m, 3H), 7.61–7.64 (m, 2H), 7.97 (d, J = 15.9 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 24.1, 117.7, 127.7, 127.9, 128.8, 128.9, 136.4, 137.6, 164.3, 166.6 ppm. IR (ATR): ν = 3057, 1533, 1367, 978, 747, 692 cm⁻¹. HR-MALDI-MS (DCTB): m/z calculated for C₁₄H₁₅N₂ [(M+H)⁺] 211.1230, found 211.1227.

(E)-2-(4-Methoxystyryl)-4,6-dimethylpyrimidine (1b). Synthesized from 4-ethynylanisole (415 mg, 3.14 mmol) and 2-chloro-4,6-dimethylpyrimidine (286 mg, 2 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude product was purified by column chromatography (SiO₂, petroleum ether:EtOAc, 7:3). Yield: 257 mg (54 %); brownish solid. Rᶠ: 0.4 (SiO₂; petroleum ether:EtOAc, 7:3). Mp: 87.9–90.2 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.48 (s, 6H), 3.82 (s, 3H), 6.82 (s, 1H), 6.89–6.92 (m, 2H), 7.07 (d, J = 15.9 Hz, 1H), 7.54–7.57 (m, 2H), 7.92 (d, J = 15.9 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 24.1, 55.4, 114.3, 117.4, 125.6, 129.1, 129.2, 137.3, 160.4, 164.6, 166.6 ppm. IR (ATR): ν = 3004, 1574, 1511, 1242, 1178, 1028, 981, 839, 818, 770 cm⁻¹. HR-MALDI-MS (DCTB): m/z calculated for C₁₅H₁₆N₂O [M⁺] 240.1257, found 240.1256.

(E)-2-(4-Dimethylaminostyryl)-4,6-dimethylpyrimidine (1c). Synthesized from 4-ethynyl-N,N-dimethylaniline (362 mg, 2.50 mmol) and 2-chloro-4,6-dimethylpyrimidine (230 mg, 1.61 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude product was purified by column chromatography (SiO₂, petroleum ether:EtOAc, 7:3). Yield: 244 mg (59 %); yellow solid. Rᶠ: 0.6 (SiO₂; petroleum ether:EtOAc, 7:3). Mp: 112.8–115.2 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.47 (s, 6H), 3.00 (s, 6H), 6.69–6.72 (m, 2H), 6.78 (s, 1H), 7.01 (d, J = 15.9 Hz, 1H), 7.51–7.54 (m, 2H), 7.91 (d, J = 15.9 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 24.2, 40.4, 112.2, 116.9, 123.2, 124.6, 129.1, 138.0, 151.0, 165.1, 166.4 ppm. IR (ATR): ν = 2919, 1580, 1443, 1356, 1165, 986, 820, 748 cm⁻¹. HR-MALDI-MS (DCTB): m/z calculated for C₁₆H₁₉N₃ [M⁺] 253.1574, found 253.1562.
(E)-2-(4-Diphenylaminostyryl)-4,6-dimethylpyrimidine (1d). Synthesized from 4-ethynyl-
N,N-diphenylaniline (790 mg, 2.94 mmol) and 2-chloro-4,6-dimethylpyrimidine (267 mg,
1.87 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude product
was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 8:2). Yield: 200 mg
(28 %); yellow solid. $R_f$ 0.4 (SiO$_2$; petroleum ether:EtOAc, 8:2). Mp: 132.7–135.7 °C. $^1$H
NMR (300 MHz, CDCl$_3$): $\delta$ = 2.49 (s, 6H), 6.83 (s, 1H), 7.02–7.14 (m, 9H), 7.25–7.30 (m,
4H), 7.46–7.49 (m, 2H), 7.91 (d, $^3J$ = 15.9 Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$
= 24.1, 117.3, 122.6, 123.5, 125.1, 125.6, 128.6, 129.4, 129.9, 137.3, 147.4, 148.6, 164.6, 166.5
ppm. IR (ATR): $\nu$ = 3030, 1585, 1488, 1273, 749, 692 cm$^{-1}$. HR-MALDI-MS (DCTB): m/z
calculated for C$_{26}$H$_{23}$N$_3$ [M$^+$] 377.1887, found 377.1888.

(E)-2-[(6-Methoxynaphtalen-2-yl)ethenyl]-4,6-dimethylpyrimidine (1e). Synthesized from
2-ethynyl-6-methoxynaphtalene (286 mg, 1.57 mmol) and 2-chloro-4,6-dimethylpyrimidine
(143 mg, 1 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude
product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 7:3). Yield:
230 mg (79 %); yellowish solid. $R_f$ 0.3 (SiO$_2$; petroleum ether:EtOAc, 7:3). Mp: 133.5–134.9
°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 2.45 (s, 6H), 3.86 (s, 3H), 6.75 (s, 1H), 7.06–7.13 (m,
2H), 7.26 (d, $^3J$ = 15.9 Hz, 1H), 7.66–7.77 (m, 3H), 7.88 (s, 1H), 8.09 (d, $^3J$ = 15.9 Hz, 1H)
ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 24.0, 55.3, 105.9, 117.4, 119.1, 124.4, 127.0, 127.3,
128.4, 128.9, 129.9, 131.7, 134.9, 137.7, 158.2, 164.3, 166.4 ppm. IR (ATR): $\nu$ = 2931, 1582,
1364, 1163, 1027, 860, 803, 665 cm$^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for
C$_{19}$H$_{18}$N$_2$O [M$^+$] 290.1414, found 290.1414.

(E)-2-(4-Trifluoromethylstyryl)-4,6-dimethylpyrimidine (1f). Synthesized from 4-
trifluoromethylphenylacetylene (426 mg, 2.50 mmol) and 2-chloro-4,6-dimethylpyrimidine
(228 mg, 1.59 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude
product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 7:3). Yield:
222 mg (50%); yellowish solid. \( R_f \): 0.4 (SiO\(_2\); petroleum ether:EtOAc, 7:3). Mp: 94.9–96.5°C. \(^{1}\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 2.50 \) (s, 6H), 6.89 (s, 1H), 7.26 (d, \(^3\)J = 15.9 Hz, 1H), 7.60–7.71 (m, 4H), 7.97 (d, \(^3\)J = 15.9 Hz, 1H) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 24.1, 118.2, 124.2 \) (q, \(^1\)J\(_{CF} = 270 \) Hz), 125.8 (q, \(^3\)J\(_{CF} = 4 \) Hz), 127.7, 130.4, 130.5 (q, \(^2\)J\(_{CF} = 32 \) Hz), 135.8, 139.9 (d, \(^4\)J\(_{CF} = 1 \) Hz), 163.7, 166.8 ppm. IR (ATR): \( \nu = 2929, 1583, 1319, 1103, 1064, 831, 714 \) cm\(^{-1}\). HRMALDIMMS (DCTB): m/z calculated for C\(_{15}\)H\(_{14}\)F\(_3\)N\(_2\) [(M+H)\(^+\)] 279.1104, found 279.1102.

\((E,E,E)-2,4,6\)-Tristyrylpyrimidine (2a). Synthesized from 1a (300 mg, 1.43 mmol) and benzaldehyde (303 mg, 2.85 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by column chromatography (SiO\(_2\), petroleum ether:EtOAc, 9:1) and then by recrystallization from CH\(_2\)Cl\(_2\)/n-heptane. Yield: 155 mg (28%); white solid. \( R_f \): 0.4 (SiO\(_2\); petroleum ether:EtOAc, 9:1). Mp: 193°C (lit.\(^{20}\) 197–199°C). \(^{1}\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.08–7.16 \) (m, 3H), 7.28–7.43 (m, 10H), 7.62–7.69 (m, 6H), 7.93 (d, \(^3\)J = 15.9 Hz, 2H), 8.11 (d, \(^3\)J = 15.9 Hz, 1H) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 113.7, 126.5, 127.7, 128.5, 128.8, 128.9, 129.3, 136.0, 135.8, 137.9, 162.9, 164.6 \) ppm All the atoms of carbon were not observed. IR (ATR): \( \nu = 3025, 1635, 1564, 1514, 1368, 963, 739, 689 \) cm\(^{-1}\). HRMALDIMMS (DCTB): m/z calculated for C\(_{28}\)H\(_{23}\)N\(_2\) [(M+H)\(^+\)] 387.1856, found 387.1855.

\((E,E,E)-2\)-Styryl-4,6-bis(4-methoxystyryl)pyrimidine (2b). Synthesized from 1a (78 mg, 0.37 mmol) and 4-methoxybenzaldehyde (102 mg, 0.74 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by column chromatography (SiO\(_2\), petroleum ether:EtOAc, 8:2) and then by recrystallization from CH\(_2\)Cl\(_2\)/n-heptane. Yield: 40 mg (24%); yellowish solid. \( R_f \): 0.4 (SiO\(_2\); petroleum ether:EtOAc, 8:2). Mp: 128°C. \(^{1}\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 3.86 \) (s, 6H), 6.93–7.01 (m, 6H), 7.11 (s, 1H), 7.29–7.44 (m, 4H), 7.58–7.61 (m, 4H), 7.68–7.70 (m, 2H), 7.89 (d, \(^3\)J =
15.9 Hz, 2H), 8.11 (d, J = 15.9 Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 55.5, 113.2, 114.5, 124.4, 127.8, 128.5, 128.9, 128.90, 128.91, 136.2, 136.6, 137.6, 160.7, 163.1, 164.5 ppm. IR (ATR): ν = 2837, 1604, 1560, 1501, 1251, 1171, 1152, 967, 749 cm$^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for C$_{30}$H$_{27}$N$_2$O$_2$ [(M+H)$^+$] 447.2067, found 447.2064.

(E,E,E)-2-Styryl-4,6-bis(4-dimethylaminostyryl)pyrimidine (2c). Synthesized from 1a (150 mg, 0.71 mmol) and 4,N,N-dimethylaminobenzaldehyde (213 mg, 1.43 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 8:2) and then by recrystallization from CH$_2$Cl$_2$/n-heptane. Yield: 63 mg (17 %); black solid. $R_f$: 0.2 (SiO$_2$; petroleum ether:EtOAc, 8:2). $T_d$: 245 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ = 3.03 (s, 12 H), 6.71–6.74 (m, 4H), 6.91 (d, J = 15.9 Hz, 2H), 7.08 (s, 1H), 7.28–7.35 (m, 4H), 7.53–7.56 (m, 4H), 7.68–7.70 (m, 2H), 7.86 (d, J = 15.9 Hz, 2H), 8.10 (d, J = 15.9 Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 40.4, 112.2, 112.4, 114.2, 114.7, 121.9, 124.3, 127.8, 128.7, 128.8, 129.2, 136.8, 137.2, 151.2, 163.4, 164.3 ppm. IR (ATR): ν = 2892, 1602, 1555, 1503, 1363, 1162, 965, 800, 746 cm$^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for C$_{32}$H$_{32}$N$_4$ [M$^+$] 472.2622, found 472.2620.

(E,E,E)-2-Styryl-4,6-bis(4-diphenylaminostyryl)pyrimidine (2d). Synthesized from 1a (300 mg, 1.43 mmol) and 4-N,N-diphenylaminobenzaldehyde (780 mg, 2.85 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 9:1) and then by recrystallization from CH$_2$Cl$_2$/n-heptane. Yield: 220 mg (21 %); yellow solid. $R_f$: 0.4 (SiO$_2$; petroleum ether:EtOAc, 9:1). $T_d$: 305 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ = 6.98 (d, J = 15.9 Hz, 2H), 7.05–7.17 (m, 17H), 7.27–7.43 (m, 12H), 7.48–7.51 (m, 4H), 7.67–7.70 (m, 2H), 7.87 (d, J = 15.9 Hz, 2H), 8.10 (d, J = 15.9 Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 113.1, 122.5, 123.8, 124.4, 125.2, 127.8, 128.6, 128.77, 128.85, 128.88, 129.56, 129.59, 136.1, 136.6, 137.2, 151.2, 163.4, 164.3 ppm.
137.6, 147.3, 149.0, 163.1, 164.6 ppm. IR (ATR): \( \nu = 3033, 1559, 1490, 1274, 969, 748, 693 \) cm\(^{-1}\). HR-MALDI-MS (DCTB): m/z calculated for C\(_{52}\)H\(_{40}\)N\(_4\) [M\(^+\)] 720.3248, found 720.3252.

\((E.E,E)-2,4,6\text{-Tris(4-methoxystyryl)pyrimidine (2e).}\) Synthesized from 1b (100 mg, 0.42 mmol) and 4-methoxybenzaldehyde (114 mg, 0.83 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by recrystallization from CH\(_2\)Cl\(_2\)/n-heptane. Yield: 156 mg (79 %); yellowish solid. \( R_f \): 0.4 (SiO\(_2\); petroleum ether:EtoAc, 8:2). Mp: 183 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 3.85 \) (s, 9H), 6.93–7.00 (m, 8H), 7.08 (s, 1H), 7.18 (d, \(^3\)J = 15.9 Hz, 1H), 7.57–7.65 (m, 6H), 7.88 (d, \(^3\)J = 15.9 Hz, 2H), 8.06 (d, \(^3\)J = 15.9 Hz, 1H) ppm. \(^13\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 55.46, 55.49, 112.8, 114.3, 114.4, 124.5, 126.3, 129.0, 129.2, 129.4, 136.1, 137.3, 160.4, 160.7, 163.1, 164.8 \) ppm All the atoms of carbon were not observed. IR (ATR): \( \nu = 2933, 1602, 1559, 1506, 1245, 1169, 1028, 959, 868, 810, 767 \) cm\(^{-1}\). HRMALDI-MS (DCTB): m/z calculated for C\(_{31}\)H\(_{28}\)N\(_2\)O\(_3\) [M\(^+\)] 476.2094, found 476.2094.

\((E,E,E)-2-(4\text{-Methoxystyryl})-4,6\text{-bis(4-dimethylaminostyryl)pyrimidine (2f).}\) Synthesized from 1b (100 mg, 0.42 mmol) and 4-N,N-dimethylaminobenzaldehyde (125 mg, 0.83 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by recrystallization from CH\(_2\)Cl\(_2\)/n-heptane. Yield: 154 mg (74 %); red solid. \( R_f \): 0.3 (SiO\(_2\); petroleum ether:EtoAc, 8:2). \( T_d \): 250 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 3.03 \) (s, 12H), 3.85 (s, 3H), 6.71–6.74 (m, 4H), 6.88–6.95 (m, 4H), 7.07 (s, 1H), 7.17 (d, \(^3\)J = 15.9 Hz, 1H), 7.52–7.55 (m, 4H), 7.62–7.65 (m, 2H), 7.84 (d, \(^3\)J = 15.9 Hz, 2H), 8.05 (d, \(^3\)J = 15.9 Hz, 1H) ppm. \(^13\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 40.4, 55.4, 112.1, 112.2, 114.3, 122.0, 124.3, 126.6, 129.1, 129.6, 136.6, 136.8, 151.1, 160.2, 163.3, 164.7 \) ppm All the atoms of carbon were not observed. IR (ATR): \( \nu = 2933, 1602, 1559, 1506, 1472, 1417, 1355, 1244, 1142, 971, 806 \) cm\(^{-1}\). HR-MALDI-MS (DCTB): m/z calculated for C\(_{33}\)H\(_{34}\)N\(_4\)O [M\(^+\)] 502.2727, found 502.2731.
(E,E,E)-2-(4-Methoxystyryl)-4,6-bis(4-diphenylaminostyryl)pyrimidine (2g). Synthesized from 1b (100 mg, 0.42 mmol) and 4-N,N-diphenylaminobenzaldehyde (228 mg, 0.83 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by recrystallization from CH₂Cl₂/n-heptane. Yield: 225 mg (72 %); yellow solid. Rᵣ: 0.7 (SiO₂; petroleum ether:EtOAc, 8:2). Tᵣ: 270 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.85 (s, 3H), 6.92–7.21 (m, 24H), 7.27–7.32 (m, 6H), 7.48–7.50 (m, 4H), 7.61–7.64 (m, 2H), 7.86 (d, 3J = 15.9 Hz, 2H), 8.06 (d, 3J = 15.9 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 55.5, 112.8, 114.3, 122.6, 123.7, 124.5, 125.2, 126.3, 128.7, 129.2, 129.4, 129.5, 129.7, 136.0, 137.2, 147.4, 149.0, 160.4, 163.0, 164.9 ppm. IR (ATR): ν = 3033, 1562, 1489, 1271, 1242, 1168, 972, 818, 749, 691 cm⁻¹. HR-MALDI-MS (DCTB): m/z calculated for C₅₃H₄₂N₄O [M⁺] 750.3353, found 750.3361.

(E,E,E)-2-(4-Dimethylaminostyryl)-4,6-bis(4-methoxystyryl)pyrimidine (2h). Synthesized from 1c (110 mg, 0.43 mmol) and 4-methoxybenzaldehyde (119 mg, 0.87 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by recrystallization from CH₂Cl₂/n-heptane. Yield: 121 mg (57 %); brown solid. Rᵣ: 0.3 (SiO₂; petroleum ether:EtOAc, 8:2). Mp: 200 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.02 (s, 6H), 3.85 (s, 6H), 6.72–6.75 (m, 2H), 6.93–7.00 (m, 6H), 7.05 (s, 1H), 7.12 (d, 3J = 15.9 Hz, 1H), 7.57–7.61 (m, 6H), 7.87 (d, 3J = 15.9 Hz, 2H), 8.05 (d, 3J = 15.9 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 40.4, 55.5, 112.2, 112.4, 114.4, 123.7, 124.7, 124.8, 129.0, 129.2, 135.9, 138.1, 151.0, 160.6, 163.0, 165.4 ppm All the atoms of carbon were not observed. IR (ATR): ν = 2924, 1603, 1558, 1502, 1357, 1249, 1168, 1028, 961, 810 cm⁻¹. HR-MALDI-MS (DCTB): m/z calculated for C₃₂H₃₁N₃O₂ [M⁺] 489.2411, found 489.2414.

(E,E,E)-2,4,6-Tris(4-dimethylaminostyryl)pyrimidine (2i). Synthesized from 1c (244 mg, 0.96 mmol) and 4-N,N-dimethylaminobenzaldehyde (287 mg, 1.92 mmol) following the
general procedure for Knoevenagel condensation. The crude product was purified by recrystallization from CH$_2$Cl$_2$/n-heptane. Yield: 212 mg (43 %); brown solid. $R_f$: 0.1 (SiO$_2$; petroleum ether:EtOAc, 8:2). $T_d$: 250 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.02–3.03 (m, 18H), 6.71–6.75 (m, 6H), 6.91 (d, $^3J = 15.9$ Hz, 2H), 7.05 (s, 1H), 7.11 (d, $^3J = 15.6$ Hz, 1H), 7.53–7.61 (m, 6H), 7.83 (d, $^3J = 15.9$ Hz, 2H), 8.03 (d, $^3J = 15.9$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 40.4, 40.5, 111.6, 112.3, 122.3, 124.2, 124.4, 125.0, 129.1, 136.4, 137.6, 150.9, 151.1, 163.2, 165.2 ppm All the atoms of carbon were not observed. IR (ATR): $\nu$ = 2888, 1599, 1502, 1356, 1167, 965, 797 cm$^{-1}$. HRMALDI-MS (DCTB): m/z calculated for C$_{34}$H$_{37}$N$_5$ [M$^+$] 515.3044, found 515.3044.

(E,E,E)-2-(4-Dimethylaminostyryl)-4,6-bis(4-diphenylaminostyryl)pyrimidine (2j). Synthesized from 1c (110 mg, 0.43 mmol) and 4,N,N-diphenylaminobenzaldehyde (238 mg, 0.87 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by recrystallization from CH$_2$Cl$_2$/n-heptane. Yield: 225 mg (68 %); yellow solid. $R_f$: 0.6 (SiO$_2$; petroleum ether:EtOAc, 8:2). $T_d$: 240 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.02 (s, 6H), 6.72–6.75 (m, 2H), 6.99 (d, $^3J = 15.9$ Hz, 2H), 7.05–7.16 (m, 18H), 7.27–7.32 (m, 8H), 7.48–7.50 (m, 4H), 7.57–7.60 (m, 2H), 7.85 (d, $^3J = 15.9$ Hz, 2H), 8.04 (d, $^3J = 15.9$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 40.4, 112.2, 112.3, 122.6, 123.7, 124.76, 124.78, 125.2, 128.7, 129.2, 129.5, 129.8, 135.8, 138.0, 147.4, 148.9, 151.0, 163.0, 165.4 ppm All the atoms of carbon were not observed. IR (ATR): $\nu$ = 3034, 1564, 1490, 1361, 1273, 1167, 971, 810, 749, 692 cm$^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for C$_{54}$H$_{45}$N$_5$ [M$^+$] 763.3670, found 763.3673.

(E,E,E)-2-(4-Diphenylaminostyryl)-4,6-bis(4-methoxystyryl)pyrimidine (2k). Synthesized from 1d (70 mg, 0.19 mmol) and 4-methoxybenzaldehyde (51 mg, 0.37 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 8:2). Yield: 83 mg (73 %); yellow solid. $R_f$: 
0.5 (SiO$_2$; petroleum ether:EtOAc, 8:2). $T_d$: 310 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.86$ (s, 6H), 6.93–7.20 (m, 16H), 7.27–7.32 (m, 4H), 7.53–7.60 (m, 6H), 7.87 (d, $^3J = 15.9$ Hz, 2H), 8.05 (d, $^3J = 15.9$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 55.5, 112.8, 114.4, 122.8, 123.6, 124.5, 126.4, 128.8, 128.9, 129.2, 129.5, 130.3, 136.1, 137.2, 147.5, 148.6, 160.7, 163.1, 164.9 ppm. IR (ATR): $\nu = 3033, 1562, 1506, 1279, 1248, 1031, 972, 808, 752, 695$ cm$^{-1}$. HRMALDI-MS (DCTB): m/z calculated for C$_{42}$H$_{35}$N$_3$O$_2$ [M$^+$] 613.2724, found 613.2728.

*(E,E,E)*-2-(4-Diphenylaminostyryl)-4,6-bis(4-dimethylaminostyryl)pyrimidine (2l). Synthesized from 1d (70 mg, 0.19 mmol) and 4$N,N$-dimethylaminobenzaldehyde (56 mg, 0.37 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 8:2) and then by recrystallization from CH$_2$Cl$_2$/n-heptane. Yield: 62 mg (52 %); yellow solid. $R_f$: 0.5 (SiO$_2$; petroleum ether:EtOAc, 8:2). $T_d$: 195 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.03$ (s, 12H), 6.71–6.74 (m, 4H), 6.90 (d, $^3J = 15.9$ Hz, 2H), 7.03–7.08 (m, 5H), 7.13–7.19 (m, 5H), 7.28–7.31 (m, 4H), 7.52–7.55 (m, 6H), 7.83 (d, $^3J = 15.9$ Hz, 2H), 8.03 (d, $^3J = 15.9$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 40.4, 112.0, 112.2, 122.1, 122.9, 123.5, 124.3, 125.1, 126.8, 128.7, 129.2, 129.5, 130.5, 136.6, 136.8, 147.5, 148.4, 151.2, 163.3, 164.7 ppm. IR (ATR): $\nu = 2853, 1602, 1553, 1492, 1358, 1276, 974, 808, 751, 696$ cm$^{-1}$. HRMALDI-MS (DCTB): m/z calculated for C$_{44}$H$_{41}$N$_5$ [M$^+$] 639.3357, found 639.3359.

*(E,E,E)*-2,4,6-Tris(4-diphenylaminostyryl)pyrimidine (2m). Synthesized from 1d (33 mg, 0.09 mmol) and 4$N,N$-diphenylaminobenzaldehyde (48 mg, 0.17 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by recrystallization from CH$_2$Cl$_2$/n-heptane. Yield: 44 mg (57 %); yellow solid. $R_f$: 0.8 (SiO$_2$; petroleum ether:EtOAc, 8:2). $T_d$: 310 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 6.97$ (d, $^3J = 15.9$ Hz, 2H), 7.04–7.20 (m, 26H), 7.27–7.32 (m, 12H), 7.47–7.55 (m, 6H), 7.85 (d, $^3J = 15.9$ Hz, 2H), 8.04 (d, $^3J = 15.9$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 112.7, 122.6, 122.8,
123.5, 123.7, 124.3, 124.6, 125.1, 125.2, 126.4, 128.7, 129.49, 129.54, 129.6, 130.3, 136.0, 137.2, 147.3, 147.5, 148.6, 148.9, 163.0, 164.9 ppm. IR (ATR): $\nu = 3034, 1588, 1558, 1489, 1273, 1174, 970, 750, 693 \text{ cm}^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for $C_{64}H_{49}N_5 [M^+]$ 887.3983, found 887.3982.

$(E,E,E)$-2-[(6-Methoxynaphtalen-2-yl)ethenyl]-4,6-bis(4-methoxystyryl)pyrimidine (2n). Synthesized from 1e (56 mg, 0.19 mmol) and 4-methoxybenzaldehyde (52 mg, 0.38 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by recrystallization from CH$_2$Cl$_2$/n-heptane. Yield: 77 mg (77 %); yellowish solid. $R_f$: 0.3 (SiO$_2$; petroleum ether:EtOAc, 8:2). $T_d$: 290 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.86 (s, 6H), 3.94 (s, 3H), 6.94–7.19 (m, 9H), 7.38 (d, $^3J = 15.9$ Hz, 1H), 7.59–7.61 (m, 4H), 7.74–7.98 (m, 6H), 8.24 (d, $^3J = 15.9$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 55.5, 106.1, 113.1, 114.5, 119.2, 124.5, 124.8, 127.4, 127.8, 128.6, 128.9, 129.1, 129.2, 130.0, 132.1, 135.1, 136.2, 137.9, 158.4, 160.7, 163.1, 164.7 ppm. IR (ATR): $\nu = 2935, 1601, 1559, 1505, 1366, 1246, 1169, 938, 809 \text{ cm}^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for $C_{35}H_{30}N_2O_3 [M^+]$ 526.2252, found 526.2252.

$(E,E,E)$-2-[(6-Methoxynaphtalen-2-yl)ethenyl]-4,6-bis(4-dimethylaminostyryl)pyrimidine (2o). Synthesized from 1e (53 mg, 0.18 mmol) and 4-N,N-dimethylaminobenzaldehyde (54 mg, 0.36 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by recrystallization from CH$_2$Cl$_2$/n-heptane. Yield: 70 mg (70 %); orange solid. $R_f$: 0.2 (SiO$_2$; petroleum ether:EtOAc, 8:2). $T_d$: 250 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.03 (s, 12H), 3.94 (s, 3H), 6.72–6.75 (m, 4H), 6.92 (d, $^3J = 15.9$ Hz, 2H), 7.07–7.18 (m, 3H), 7.38 (d, $^3J = 15.9$ Hz, 1H), 7.54–7.57 (m, 4H), 7.74–7.90 (m, 5H), 7.99 (s, 1H), 8.23 (d, $^3J = 15.9$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 40.4, 55.5, 106.1, 112.2, 112.3, 119.1, 122.0, 124.3, 124.8, 127.3, 128.2, 128.4, 129.2, 130.0, 132.2, 135.0, 136.7, 137.4, 151.2, 158.3, 163.4, 164.5 ppm. All the atoms of
carbon were not observed. IR (ATR): $\nu = 2853, 1600, 1552, 1357, 1144, 969, 851, 804 \text{ cm}^{-1}$.
HR-MALDI-MS (DCTB): m/z calculated for C$_{37}$H$_{36}$N$_4$O [M$^+$] 552.2884, found 552.2889.

**$E,E,E$-2-[(6-Methoxynaphtalen-2-yl)ethenyl]-4,6-bis(4-diphenylaminostyryl)pyrimidine (2p).** Synthesized from 1e (37 mg, 0.12 mmol) and 4-N,N-diphenylaminobenzaldehyde (69 mg, 0.25 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by recrystallization from CH$_2$Cl$_2$/n-heptane. Yield: 30 mg (30 %); orange solid. $R_f$: 0.6 (SiO$_2$; petroleum ether:EtOAc, 8:2). $T_d$: 220 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.94$ (s, 3H), 6.97–7.17 (m, 22H), 7.28–7.40 (m, 8H), 7.49–7.52 (m, 4H), 7.74–7.79 (m, 2H), 7.84–7.92 (m, 3H), 7.98 (s, 1H), 8.23 (d, $^3J = 15.9$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 55.5, 106.1, 113.0, 119.2, 122.6, 123.8, 124.5, 124.8, 125.2, 127.4, 127.8, 128.6, 128.8, 129.1, 129.5, 129.6, 130.0, 132.1, 135.1, 136.1, 137.8, 147.4, 149.0, 154.8, 163.1, 164.8 ppm. IR (ATR): $\nu = 3034, 1588, 1558, 1490, 1268, 1174, 969, 849, 751, 694 \text{ cm}^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for C$_{57}$H$_{44}$N$_4$O [M$^+$] 800.3510, found 800.3518.

**$E,E,E$-2-(4-Trifluoromethylstyryl)-4,6-bis(4-methoxystyryl)pyrimidine (2q).** Synthesized from 1f (90 mg, 0.32 mmol) and 4-methoxybenzaldehyde (88 mg, 0.65 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 7:3). Yield: 71 mg (43 %); yellowish solid. $R_f$: 0.7 (SiO$_2$; petroleum ether:EtOAc, 7:3). $T_d$: 280 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 3.86 (s, 6H), 6.94–7.02 (m, 6H), 7.13 (s, 1H), 7.38 (d, $^3J = 15.9$ Hz, 1H), 7.58–7.61 (m, 4H), 7.65–7.68 (m, 2H), 7.76–7.79 (m, 2H), 7.91 (d, $^3J = 15.9$ Hz, 2H), 8.11 (d, $^3J = 15.9$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 55.5, 113.6, 114.5, 124.2, 124.3 (q, $^1J_{CF} = 270$ Hz), 125.8 (q, $^3J_{CF} = 4$ Hz), 127.8, 128.8, 129.3, 130.4 (q, $^2J_{CF} = 32$ Hz), 131.1, 135.8, 136.5, 140.1, 160.8, 163.2, 163.9 ppm. IR (ATR): $\nu = 2838, 1568, 1588, 1558, 1490, 1268, 1174, 969, 849, 751, 694 \text{ cm}^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for C$_{37}$H$_{36}$N$_4$O [M$^+$] 552.2884, found 552.2889.
976, 818 cm\(^{-1}\). HR-MALDI-MS (DCTB): m/z calculated for C\(_{31}H_{23}F_3N_2O_2\) [M\(^+\)] 514.1863, found 514.1861.

**(E,E,E)-2-(4-Trifluoromethylstyryl)-4,6-bis(4-dimethylaminostyryl)pyrimidine (2r).**

Synthesised from 1f (90 mg, 0.32 mmol) and 4-N,N-dimethylaminobenzaldehyde (97 mg, 0.65 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by column chromatography (SiO\(_2\), petroleum ether:EtOAc, 8:2). Yield: 69 mg (40 %); orange solid. \(R_f\) 0.3 (SiO\(_2\); petroleum ether:EtOAc, 8:2). Mp: 210 °C. 

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 3.04\) (s, 12H), 6.72–6.75 (m, 4H), 6.91 (d, \(^3\)J = 15.9 Hz, 2H), 7.10 (s, 1H), 7.37 (d, \(^3\)J = 15.9 Hz, 1H), 7.53–7.56 (m, 4H), 7.64–7.67 (m, 2H), 7.76–7.79 (m, 2H), 7.86 (d, \(^3\)J = 15.9 Hz, 2H), 8.09 (d, \(^3\)J = 15.9 Hz, 1H) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 40.4, 112.2, 112.9, 121.7, 124.1, 124.3\) (q, \(^1\)J\(_{CF}\) = 270 Hz), 125.8 (q, \(^3\)J\(_{CF}\) = 4 Hz), 127.8, 129.2, 130.2 (q, \(^2\)J\(_{CF}\) = 32 Hz), 131.4, 135.4, 137.0, 140.2, 151.2, 163.5, 163.8 ppm. IR (ATR): \(\nu = 2892, 1494, 1318, 1116, 1065, 974, 809\) cm\(^{-1}\). HR-MALDI-MS (DCTB): m/z calculated for C\(_{33}H_{31}F_3N_4\) [M\(^+\)] 540.2495, found 540.2501.

**(E,E,E)-2-(4-Trifluoromethylstyryl)-4,6-bis(4-diphenylaminostyryl)pyrimidine (2s).**

Synthesised from 1f (90 mg, 0.32 mmol) and 4-N,N-diphenylaminobenzaldehyde (177 mg, 0.65 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by column chromatography (SiO\(_2\), petroleum ether:EtOAc, 9:1). Yield: 70 mg (28 %); yellow solid. \(R_f\) 0.7 (SiO\(_2\); petroleum ether:EtOAc, 9:1). \(T_d\): 300 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.00\) (d, \(^3\)J = 15.9 Hz, 2H), 7.08–7.19 (m, 18H), 7.30–7.43 (m, 8H), 7.50–7.53 (m, 4H), 7.66–7.69 (m, 2H), 7.78–7.80 (m, 2H), 7.90 (d, \(^3\)J = 15.9 Hz, 2H), 8.12 (d, \(^3\)J = 15.9 Hz, 1H) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 113.6, 123.8, 124.0, 124.1, 124.5\) (q, \(^1\)J\(_{CF}\) = 276 Hz), 125.3, 125.8 (q, \(^3\)J\(_{CF}\) = 4 Hz), 127.8, 128.8, 129.4, 129.6, 130.4 (q, \(^2\)J\(_{CF}\) = 32 Hz), 131.1, 135.7, 136.3, 140.0 (q, \(^4\)J\(_{CF}\) = 1 Hz), 147.3, 149.1, 163.2, 163.9 ppm. IR (ATR): \(\nu\)
= 3033, 1559, 1490, 1320, 1066, 968, 751 cm\(^{-1}\). HR-MALDI-MS (DCTB): m/z calculated for C\(_{53}\)H\(_{39}\)F\(_3\)N\(_4\) [M\(^+\)] 788.3121, found 788.3111.

**\((E)-2\)-Chloro-4-(4-dimethylaminostyryl)-6-methylpyrimidine (3a).** Synthesized from 4-ethynyl-N,N-dimethylaniline (250 mg, 1.72 mmol) and 2,4-dichloro-6-methylpyrimidine (179 mg, 1.1 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude product was purified by column chromatography (SiO\(_2\), petroleum ether:EtOAc, 8:2). Yield: 156 mg (52 %); brown solid. \(R_f\): 0.4 (SiO\(_2\); petroleum ether:EtOAc, 8:2). Mp: 163.4–165.7 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.49\) (s, 3H), 3.03 (s, 6H), 6.68–6.78 (m, 3H), 6.99 (s, 1H), 7.47–7.50 (m, 2H), 7.83 (d, \(^3J = 15.9\) Hz, 1H) ppm. \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 24.0, 40.3, 112.1, 115.6, 119.2, 123.3, 129.6, 139.5, 151.6, 161.1, 166.2, 169.9\) ppm. IR (ATR): \(\nu = 2913, 2193, 1566, 1258, 979, 809, 751, 765\) cm\(^{-1}\). HR-MALDI-MS (DCTB): m/z calculated for C\(_{15}\)H\(_{16}\)ClN\(_3\) [M\(^+\)] 273.1027, found 273.1023.

**\((E)-2\)-Chloro-4-(4-methoxystyryl)-6-methylpyrimidine (3b).** Synthesized from 4-ethynylanisole (311 mg, 2.35 mmol) and 2,4-dichloro-6-methylpyrimidine (245 mg, 1.5 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude product was purified by column chromatography (SiO\(_2\), petroleum ether:EtOAc, 7:3). Yield: 215 mg (55 %); yellowish solid. \(R_f\): 0.4 (SiO\(_2\); petroleum ether:EtOAc, 7:3). Mp: 78.9–81.8 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.51\) (s, 3H), 3.85 (s, 3H), 6.83 (d, \(^3J = 15.9\) Hz, 1H), 6.90–6.95 (m, 2H), 7.04 (s, 1H), 7.51–7.56 (m, 2H), 7.86 (d, \(^3J = 15.9\) Hz, 1H) ppm. \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 24.1, 55.5, 114.6, 116.2, 122.0, 128.2, 129.6, 138.7, 161.18, 161.21, 165.6, 170.5\) ppm. IR (ATR): \(\nu = 2924, 1570, 1512, 1256, 1020, 967, 819\) cm\(^{-1}\). HR-MALDI-MS (DCTB): m/z calculated for C\(_{14}\)H\(_{13}\)ClN\(_2\)O [M\(^+\)] 260.0711, found 260.0710.

**\((E,E)-2\)-(4-Methoxystyril)-4-(4-dimethylaminostyryl)-6-methylpyrimidine (4a).** Synthesized from 4-ethynylanisole (91 mg, 0.69 mmol) and 3a (120 mg, 0.44 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude product was purified
by column chromatography (SiO₂, petroleum ether:EtOAc, 7:3). Yield: 65 mg (40 %); orange solid. Rf: 0.3 (SiO₂; petroleum ether:EtOAc, 7:3). Mp: 79.9–81.5 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.51 (s, 3H), 3.02 (s, 6H), 3.84 (s, 3H), 6.70–6.73 (m, 2H), 6.83–6.94 (m, 4H), 7.13 (d, ³J = 15.9 Hz, 1H), 7.50–7.53 (m, 2H), 7.58–7.61 (m, 2H), 7.81 (d, ³J = 15.9 Hz, 1H), 7.99 (d, ³J = 15.9 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 24.3, 40.4, 55.4, 112.2, 114.3, 114.4, 121.6, 124.1, 126.1, 129.1, 129.2, 129.4, 137.1, 151.2, 160.3, 163.2, 164.6, 166.7 ppm All the atoms of carbon were not observed. IR (ATR): ν = 2922, 1602, 1509, 1352, 1242, 1169, 973, 809 cm⁻¹. HRMALDI-MS (DCTB): m/z calculated for C₂₄H₂₅N₃O [M⁺] 371.1992, found 371.1988.

(E,E)-2-(4-Dimethylaminostyryl)-4-(4-methoxystyryl)-6-methylpyrimidine (4b). Synthesized from 4-ethynyl-N,N-dimethylaniline (155 mg, 1.06 mmol) and 3b (177 mg, 0.68 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude product was purified by column chromatography (SiO₂, petroleum ether:EtOAc, 7:3). Yield: 190 mg (75 %); brown solid. Rf: 0.2 (SiO₂; petroleum ether:EtOAc, 7:3). Mp: 123.5–125.7 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.52 (s, 3H), 3.01 (s, 6H), 3.84 (s, 3H), 6.70–6.73 (m, 2H), 6.90–6.95 (m, 4H), 7.07 (d, ³J = 15.9 Hz, 1H), 7.54–7.58 (m, 4H), 7.83 (d, ³J = 15.9 Hz, 1H), 7.99 (d, ³J = 15.9 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 24.4, 40.4, 55.5, 112.2, 114.3, 123.3, 124.4, 124.6, 128.9, 129.1, 136.0, 138.1, 151.0, 160.6, 162.5, 165.2, 166.9 ppm All the atoms of carbon were not observed. IR (ATR): ν = 2918, 1599, 1509, 1352, 1242, 1169, 973, 809 cm⁻¹. HRMALDI-MS (DCTB): m/z calculated for C₂₄H₂₅N₃O [M⁺] 371.1992, found 371.1993.

(E,E,E)-2-(4-Methoxystyryl)-4-(4-dimethylaminostyryl)-6-(4-diphenylaminostyryl)pyrimidine (5a). Synthesized from 4a (45 mg, 0.12 mmol) and 4-N,N-diphenylaminobenzaldehyde (33 mg, 0.12 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by column chromatography
(SiO$_2$, petroleum ether:EtOAc, 8:2). Yield: 46 mg (61 %); orange solid. $R_f$: 0.5 (SiO$_2$; petroleum ether:EtOAc, 8:2). $T_d$: 240 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.03 (s, 6H), 3.85 (s, 3H), 6.71–6.74 (m, 2H), 6.88–7.20 (m, 14H), 7.27–7.32 (m, 4H), 7.48–7.55 (m, 4H), 7.62–7.65 (m, 2H), 7.85 (d, $^3J = 15.9$ Hz, 2H), 8.05 (d, $^3J = 15.9$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 40.4, 55.5, 112.2, 112.5, 114.3, 121.9, 122.6, 123.7, 124.2, 124.7, 125.2, 126.5, 128.7, 129.2, 129.50, 129.54, 129.8, 135.7, 136.9, 137.0, 147.4, 148.9, 151.2, 160.3, 162.7, 163.6, 164.8 ppm. IR (ATR): $\nu$ = 2925, 1561, 1490, 1247, 1170, 1144, 971, 694 cm$^{-1}$.

HR-MALDI-MS (DCTB): m/z calculated for C$_{43}$H$_{38}$N$_4$O [M$^+$] 626.3040, found 626.3038.

($E,E,E$)-2-(4-Dimethylaminostyril)-4-(4-methoxystyril)-6-(4-diphenylaminostyril)pyrimidine (5b). Synthesized from 4b (150 mg, 0.40 mmol) and 4-$N,N$-diphenylaminobenzaldehyde (110 mg, 0.40 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 7:3). Yield: 84 mg (33 %); orange solid. $R_f$: 0.5 (SiO$_2$; petroleum ether:EtOAc, 7:3). $T_d$: 210 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.02 (s, 6H), 3.85 (s, 3H), 6.72–6.75 (m, 2H), 6.93–7.16 (m, 14H), 7.27–7.32 (m, 4H), 7.48–7.51 (m, 2H), 7.57–7.60 (m, 4H), 7.82–7.90 (m, 2H), 8.05 (d, $^3J = 15.9$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 40.4, 55.5, 112.3, 112.3, 114.4, 122.6, 123.7, 124.2, 124.4, 124.7, 124.8, 125.2, 128.4, 128.7, 129.0, 129.2, 129.4, 129.5, 129.8, 135.9, 138.1, 147.4, 148.9, 151.0, 160.6, 162.9, 163.0, 165.4 ppm. IR (ATR): $\nu$ = 2921, 1500, 1359, 1248, 1166, 971, 809, 693 cm$^{-1}$.

HR-MALDI-MS (DCTB): m/z calculated for C$_{43}$H$_{38}$N$_4$O [M$^+$] 626.3040, found 626.3058.

($E$)-2-Styryl-4-methylpyrimidine (6a). Synthesized from phenylacetylene (176 mg, 1.72 mmol) and 2-chloro-4-methylpyrimidine (142 mg, 1.1 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 8:2). Yield: 70 mg (32 %); white solid. $R_f$: 0.4 (SiO$_2$; petroleum ether:EtOAc, 8:2). Mp: 67.2–69.9 °C (lit. $^{32}$ 65–67°C). $^1$H NMR (300 MHz, CDCl$_3$):
$\delta = 2.54$ (s, 3H), 6.97 (d, $^3J = 4.8$ Hz, 1H), 7.22 (d, $^3J = 15.9$ Hz, 1H), 7.30–7.41 (m, 3H), 7.61–7.63 (m, 2H), 7.98 (d, $^3J = 15.9$ Hz, 1H), 8.56 (d, $^3J = 4.8$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 24.4, 118.3, 127.7, 128.9, 129.1, 136.3, 137.9, 156.8, 164.7, 167.1$ ppm. All the atoms of carbon were not observed. IR (ATR): $\nu = 2918, 1547, 1440, 1385, 978, 790, 747$ cm$^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for C$_{13}$H$_{13}$N$_2$ [(M+H)$^+$] 197.1073, found 197.1073.

*(E)-2-(4-Methoxystyryl)-4-methylpyrimidine (6b).*

Synthesized from 4-ethynylanisole (311 mg, 2.35 mmol) and 2-chloro-4-methylpyrimidine (193 mg, 1.50 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 7:3). Yield: 206 mg (61 %); brownish solid. $R_f$: 0.2 (SiO$_2$; petroleum ether:EtOAc, 7:3). Mp: 102.3–104.9°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 2.53$ (s, 3H), 3.83 (s, 3H), 6.90–6.95 (m, 3H), 7.09 (d, $^3J = 15.9$ Hz, 1H), 7.55–7.58 (m, 2H), 7.93 (d, $^3J = 15.9$ Hz, 1H), 8.54 (d, $^3J = 5.1$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 24.4, 55.5, 114.4, 117.9, 125.5, 129.1, 129.2, 137.6, 156.7, 160.6, 165.0, 167.1$ ppm. IR (ATR): $\nu = 2937, 1566, 1509, 1249, 1178, 1028, 981, 821, 775$ cm$^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for C$_{14}$H$_{14}$N$_2$O [M$^+$] 226.1101, found 226.1100.

*(E)-2-(4-Dimethylaminostyryl)-4-methylpyrimidine (6c).*

Synthesized from 4-ethynyl-$N,N$-dimethylaniline (250 mg, 1.72 mmol) and 2-chloro-4-methylpyrimidine (142 mg, 1.1 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 8:2). Yield: 85 mg (32 %); brown solid. $R_f$: 0.3 (SiO$_2$; petroleum ether:EtOAc, 8:2). Mp: 117.3–119.8°C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 2.51$ (s, 3H), 2.99 (s, 6H), 6.68–6.71 (m, 2H), 6.89 (d, $^3J = 5.1$ Hz, 1H), 7.02 (d, $^3J = 15.9$ Hz, 1H), 7.49–7.52 (m, 2H), 7.92 (d, $^3J = 15.9$ Hz, 1H), 8.50 (d, $^3J = 5.1$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 24.3,$
40.3, 112.2, 117.3, 122.6, 124.3, 129.2, 138.5, 151.1, 156.5, 165.3, 166.9 ppm. IR (ATR): $\nu = 2912, 1602, 1435, 1363, 1167, 987, 805, 768, 750 \text{ cm}^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for C$_{15}$H$_{17}$N$_3$ [M$^+$] 239.1417, found 239.1415.

(E)-2-(4-Diphenaminostyryl)-4-methylpyrimidine (6d). Synthesized from 4-ethynyl-$N,N$-diphenylaniline (275 mg, 1.02 mmol) and 2-chloro-4-methylpyrimidine (84 mg, 0.65 mmol) following the general procedure for Suzuki-Miyaura reaction. The crude product was purified by column chromatography (SiO$_2$, petroleum ether:EtOAc, 8:2). Yield: 102 mg (43 %); yellow solid. $R_f$: 0.2 (SiO$_2$; petroleum ether:EtOAc, 8:2). Mp: 120.9–123.5 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 2.53$ (s, 3H), 6.94 (d, $^3J = 5.1$ Hz, 1H), 7.02–7.15 (m, 10H), 7.25–7.31 (m, 3H), 7.46–7.49 (m, 2H), 7.92 (d, $^3J = 15.9$ Hz, 1H), 8.54 (d, $^3J = 5.1$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 24.4, 117.9, 122.6, 123.6, 125.2, 125.4, 128.7, 129.5, 129.8, 137.6, 147.4, 148.8, 156.7, 165.0, 167.1$ ppm. All the atoms of carbon were not observed. IR (ATR): $\nu = 3036, 1572, 1487, 1266, 984, 831, 750, 695 \text{ cm}^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for C$_{25}$H$_{21}$N$_3$ [(M+H)$^+$] 363.1730, found 363.1723.

(E,E)-2,4-Distyrylpyrimidine (7a). Synthesized from 6a (50 mg, 0.25 mmol) and benzaldehyde (28 mg, 0.25 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by column chromatography (SiO$_2$; petroleum ether:EtOAc, 8:2). Yield: 41 mg (57 %); white solid. $R_f$: 0.4 (SiO$_2$; petroleum ether:EtOAc, 8:2). Mp: 137 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.08–7.15$ (m, 2H), 7.32–7.41 (m, 7H), 7.63–7.68 (m, 4H), 7.92 (d, $^3J = 15.9$ Hz, 1H), 8.05 (d, $^3J = 15.9$ Hz, 1H), 8.67 (d, $^3J = 5.1$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 115.9, 126.3, 127.8, 128.0, 128.9, 129.0, 129.1, 129.5, 135.9, 136.3, 137.2, 138.1, 157.6, 162.5, 164.9$ ppm All the atoms of carbon were not observed. IR (ATR): $\nu = 3054, 3026, 1637, 1558, 1537, 1388, 975, 876, 738, 688 \text{ cm}^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for C$_{20}$H$_{17}$N$_2$ [(M+H)$^+$] 285.1386, found 285.1385.
(E,E)-2,4-Bis(4-methoxystyryl)pyrimidine (7b). Synthesized from 6b (170 mg, 0.75 mmol) and 4-methoxybenzaldehyde (103 mg, 0.75 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by recrystallization from CH$_2$Cl$_2$/n-heptane. Yield: 218 mg (84 %); silver solid. $R_f$: 0.1 (SiO$_2$; petroleum ether:EtOAc, 7:3). Mp: 185 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.85 (s, 6H), 6.92–6.98 (m, 5H), 7.07 (d, $^3J = 5.1$ Hz, 1H), 7.14 (d, $^3J = 15.9$ Hz, 1H), 7.56–7.62 (m, 4H), 7.85 (d, $^3J = 15.9$ Hz, 1H), 7.99 (d, $^3J = 15.9$ Hz, 1H), 8.60 (d, $^3J = 5.1$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 55.47, 55.49, 114.4, 114.5, 115.3, 124.1, 125.8, 128.7, 129.1, 129.2, 129.3, 136.7, 137.5, 157.3, 160.5, 160.8, 162.8, 165.1 ppm. IR (ATR): $\nu$ = 2964, 1560, 1250, 1177, 1028, 972, 826 cm$^{-1}$. HRMALDI-MS (DCTB): m/z calculated for C$_{22}$H$_{21}$N$_2$O$_2$ [(M+H)$^+$] 345.1598, found 345.1592.

(E,E)-2,4-Bis(4-dimethylaminostyryl)pyrimidine (7c). Synthesized from 6c (41 mg, 0.17 mmol) and 4-N,N-dimethylaminobenzaldehyde (26 mg, 0.17 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by recrystallization from CH$_2$Cl$_2$/n-heptane. Yield: 55 mg (85 %); brown solid. $R_f$: 0.2 (SiO$_2$; petroleum ether:EtOAc, 8:2). Mp: 243 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.02–3.03 (m, 12H), 6.70–6.74 (m, 4H), 6.88 (d, $^3J = 15.9$ Hz, 1H), 7.01–7.09 (m, 2H), 7.51–7.57 (m, 4H), 7.80 (d, $^3J = 15.9$ Hz, 1H), 7.96 (d, $^3J = 15.9$ Hz, 1H), 8.54 (d, $^3J = 5.1$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 40.4, 40.5, 112.2, 112.3, 114.3, 121.7, 123.4, 124.1, 124.6, 129.2, 129.3, 137.3, 138.0, 151.1, 151.3, 156.9, 163.3, 165.5 ppm. IR (ATR): $\nu$ = 2920, 1602, 1550, 1520, 1359, 1163, 970, 810, 781 cm$^{-1}$. HRMALDI-MS (DCTB): m/z calculated for C$_{24}$H$_{26}$N$_4$ [M$^+$] 370.2152, found 370.2150.

(E,E)-2,4-Bis(4-diphenylaminostyryl)pyrimidine (7d). Synthesized from 6d (76 mg, 0.21 mmol) and 4-N,N-diphenylaminobenzaldehyde (58 mg, 0.21 mmol) following the general procedure for Knoevenagel condensation. The crude product was purified by recrystallization
from CH$_2$Cl$_2$/n-heptane. Yield: 51 mg (39 %); yellow solid. $R_f$: 0.3 (SiO$_2$; petroleum ether:EtOAc, 8:2). $T_d$: 250 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ = 6.92–6.97 (m, 2H), 7.04–7.15 (m, 19H), 7.29–7.32 (m, 6H), 7.46–7.52 (m, 4H), 7.82 (d, $^3J = 15.9$ Hz, 1H), 7.97 (d, $^3J = 15.9$ Hz, 1H), 8.59 (d, $^3J = 5.4$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 115.1, 122.5, 122.7, 123.6, 123.8, 124.1, 125.2, 125.3, 125.9, 128.78, 128.82, 129.3, 129.5, 129.6, 130.0, 136.7, 137.5, 147.3, 147.4, 148.8, 149.1, 157.2, 162.9, 165.1 ppm. IR (ATR): $\nu = 3034, 2924, 1588, 1556, 1490, 1274, 1174, 972, 831, 751, 693$ cm$^{-1}$. HR-MALDI-MS (DCTB): m/z calculated for C$_{44}$H$_{34}$N$_4$ [M$^+$] 618.2778, found 618.2779.

**Associated contents**

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Experimental and calculated absorption spectra in dichloromethane as well as correlation between experimental and emission maxima for A$_3$, 2g, 2j, 2m, 2k, cartesian coordinates, total energies for A$_3$, 2g, 2j, 2m, 2k emission maxima ($\lambda_{em}$) vs $E_T$ (30) for compounds 2b-g, 2i-s, 5a-b, 7c-d, DSC curves of chromophores 2, 5, 7, A2 and A3, $^1$H and $^{13}$C NMR spectra for compounds 1-7, ORTEP drawing of the chromophore 2h with thermal ellipsoid at 50% (pdf).

X-ray crystallographic data of compound 2h (CIF)

**Conflicts of interest**

There are no conflict to declare.

**Acknowledgements**

M. F. thanks the Région Bretagne, France for funding.
References


