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Bis- and tris(arylethynyl)pyrimidine oligomers: synthesis and light-emitting properties

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Abstract

In this contribution, we describe the synthesis of bis- and tris(arylethylnyl)pyrimidine oligomers using Sonogashira, Negishi and Suzuki cross-coupling reactions and starting from chloro or iodopyrimidines. When the arms of such banana-shaped and star-shaped molecules are substituted by electron-donating groups, interesting fluorescence properties were observed. The influence of the nature of the electron-donating groups was studied and a comparison with banana-shaped and star-shaped pyrimidine core molecules without ethynyl moities was carried out, showing that the triple bonds generally enable a red shift of the absorption and emission spectra and upgrade fluorescence properties in terms of quantum yield.

Keywords: Pyrimidine; Cross-coupling reactions; Fluorescence; Conjugation

1. Introduction

Organic materials with a π-conjugated backbone have received intensive research interest both in academic and industry due to their applications in a wide range of electronic and optoelectronic devices.[1] Among them, star-shaped and banana-shaped molecules have attracted a growing interest over recent years owing to their applications in various fields such as liquid crystalline,[2] light-emitting,[3] self assembling[4] and octupolar nonlinear optical[5] properties. Incorporation of a π-deficient heterocycle such as pyridine,[6] *s*-triazine,[7] pyrazine,[8] quinoxaline,[9] naphthyridine[10] or pyrimidine[11] in the centre of the backbone of such molecules leads to a strong enhancement of physical properties such as mesomorphism, fluorescence and solvatochromism. In π-conjugated materials, azaheterocycles such as pyrimidine can be used as the electron-deficient unit, its combination with conjugated character within the arms bearing donating groups would provide fluorescence with internal charge transfer (ICT) or twisted internal charge transfer (TICT) excited states upon electronic excitation with interesting solvatochromic properties. Such molecules can then be used as luminescent sensors in molecular biology and medical diagnostics, as active materials in self-assembled molecular devices.[12] The advantages of molecular fluorescence for sensing and switching are very important:[13] indeed they enable a high sensitivity of detection, an 'on−off' switchability, a subnanometer spatial resolution and a submillisecond temporal resolution.

Ethynyl moities added in the backbone lead to ethynyl aromatic/heteroaromatic systems which are versatile rigid molecules that have been successively exploited for the construction of a range of nanosized hydrocarbon molecular architectures such as rings, cages and dendritic macromolecules.[14] The main advantage of them compared to their arylenevinylene counterparts is the lack of possible *Z*/*E* isomerism and their higher stability.[15]

In a recent paper,[16] we have shown that some di- and triarylpyrimidines present good fluorescence properties with quantum yields reaching 0.72 and Stokes shifts generally superior to 6000 cm^{-1}. These fluorophores present also interesting fluorosolvatochromic properties and pH-sensibility.

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In order to extend the conjugation within the arms of the star-shaped and banana-shaped oligomers with the aim to improve their fluorescence properties, we have incorporated alkyne linkages between the pyrimidine central core and phenyl moieties. We report herein the synthesis of bis- and tris(arylethylnyl)-pyrimidine oligomers and their light-emitting properties. This study is a part of our work dedicated to the use of diazines as building blocks for the synthesis of new molecular materials.[17]

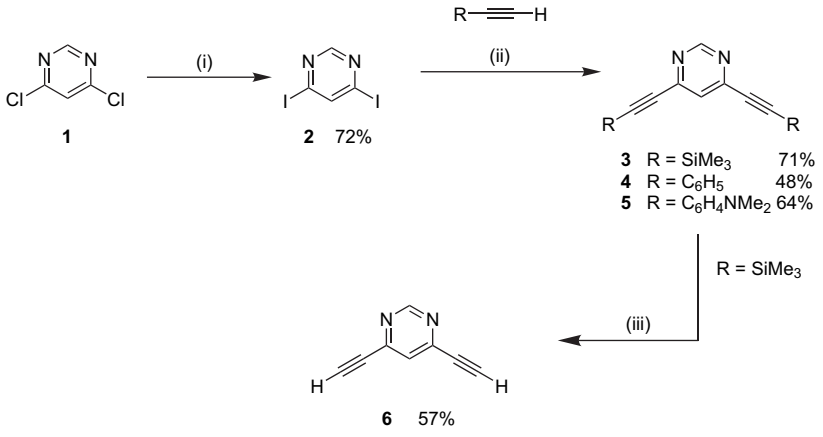
2. Results and discussion

2.1. Synthesis

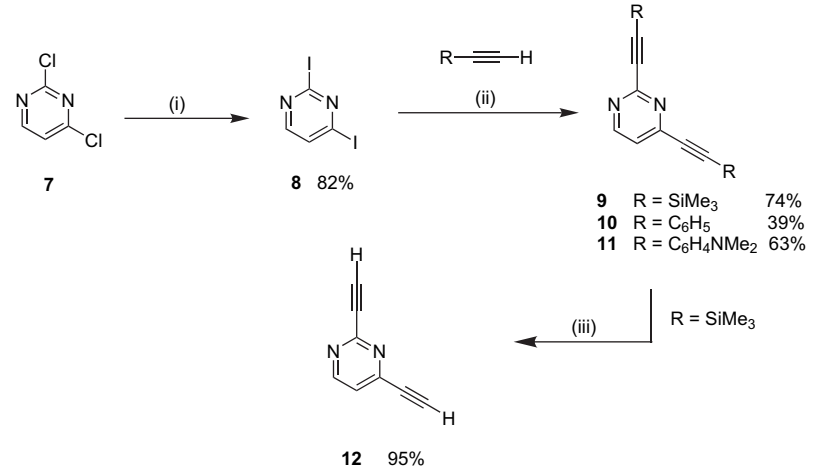
The Sonogashira cross-coupling reaction[18] is one of the most common method to introduce an ethynyl moiety on aryl compounds. The π-deficient character of the pyrimidine ring makes easier the oxidative addition of palladium on the chlorine–carbon bond,[19] allowing to carry out Sonogashira cross-coupling reactions with chloropyrimidines. However, the yields kept low,[20] and this latter coupling is generally performed with iodopyrimidines. First examples of the synthesis of diethynylpyrimidines were reported by Yamanaka and co-workers with medium yields.[21] Starting from 2,4-diiodopyrimidine and 4,6-diiodopyrimidine, easily obtained from chloro derivatives by nucleophilic substitutions,[22] we synthesized the expected dialkynylpyrimidines using this methodology. Dialkynylpyrimidines were then obtained with medium to good yields, when the alkyne used is trimethylsilylacetylene. Further cleavage of the trimethylsilyl groups with potassiun hydroxide in methanol led to compounds **6** and **12**, which could be used as building blocks for the synthesis of nanoarchitectures (Schemes 1 and 2).

The reactivity of 2,4,6-triiodopyrimidine **13** is efficient enough to allow its triarylation under the Suzuki cross-coupling conditions,[23] whereas reaction of **13** with 5 equiv of alkyne under Sonogashira conditions did not afford the expected trialkynylpyrimidines. In this latter case only tarry products were obtained probably due to the low stability of the triiodo derivative (Scheme 3).

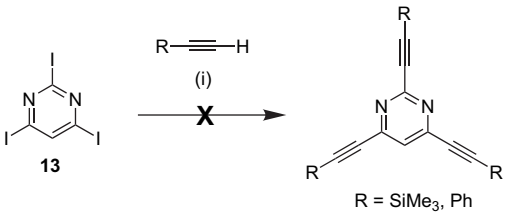
An other well-known method to introduce ethynyl moieties on aryl compounds is the palladium-catalyzed Negishi cross-coupling reaction using alkynylzinc chlorides easily accessible from alkynyllithiums.[24] Recently, using this method, Tobe and co-workers[25] described the synthesis of triethynyltriazines starting from cyanuric chloride with good yields. However,



Scheme 1. (i) HI 57%, rt, 72 h; (ii) $PdCl_2(PPh_3)_2$/CuI, THF/NEt_3, rt, 15 h; (iii) KOH/MeOH, 15 min, rt.

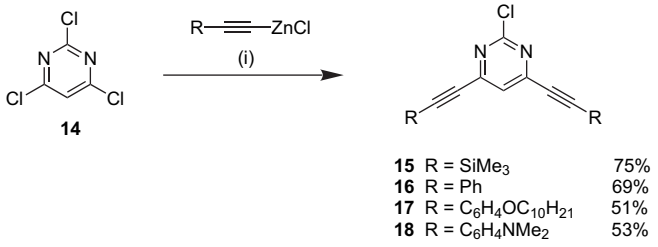


Scheme 2. (i) HI 57%, rt, 2 h; (ii) $PdCl_2(PPh_3)_2$/CuI, THF/NEt_3, rt, 15 h; (iii) KOH/MeOH, 15 min, rt.



Scheme 3. (i) $PdCl_2(PPh_3)_2$/CuI, THF/NEt_3, rt, 15 h.

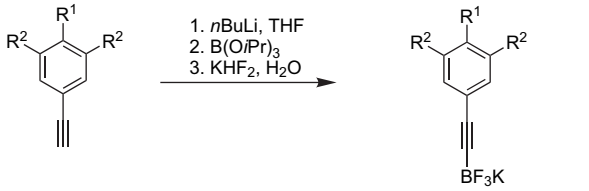
when the reaction was carried out under the same conditions with the 2,4,6-trichloropyrimidine **14**, only 4,6-dialkynylpyrimidines were obtained. This result could be explained by a lower π-deficient character of the pyrimidine than for triazine, making the pyrimidine ring less reactive versus alkynylzinc reagents. Modification of experimental conditions like temperature, reaction time, amount of equivalents of alkynylzinc chloride and the use of the iodo derivative **13** instead of **14** did not allow to perform the Negishi reaction at the 2-position of the pyrimidine which is known to be less reactive for oxidative addition of palladium than positions 4 and 6.[26] However, this method proved to be very efficient to obtain 2-chloro-4,6-dialkynylpyrimidines **15**–**18** starting from **14** (Scheme 4).



Scheme 4. (i) $Pd(PPh_3)_4$, THF, 30 °C, 3 h.

The presence of a chlorine atom at the 2-position allows the easy replacement of chlorine by other group using nucleophilic substitutions. Reaction of **16** with sodium alkoxide of ethylene glycol gave the derivative **19**. This compound possessing a terminal alcoholic function could be grafted on polymers or on various biocompounds (Scheme 5).

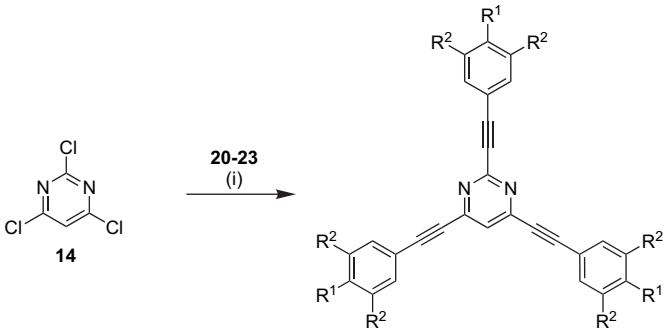
An other way was tested with the aim to access 2,4,6-trialkynylpyrimidines. The palladium-catalyzed cross-coupling reaction of air and moisture-stable potassium alkynyltrifluoroborates with aryl halides can be a good alternative to Sonogashira and Negishi coupling reactions.[27] Various potassium phenylalkynyltrifluoroborates were obtained by metallation of phenylalkynes with *n*-BuLi followed by the action of triisopropylborate and subsequent treatment with KHF_2 (Scheme 6).



20 $R^1 = R^2 = H$ 85%
21 R^1 = OMe $R^2 = H$ 91%
22 $R^1 = NMe_2$ $R^2 = H$ 87%
23 $R^1 = R^2$ = OMe 76%

Scheme 6.

Potassium alkynyltrifluoroborates obtained were then used in cross-coupling reaction with **14**. This method allowed us to obtain in one step the expected 2,4,6-trialkynylpyrimidines **24**–**27** with medium to good yields (Scheme 7).

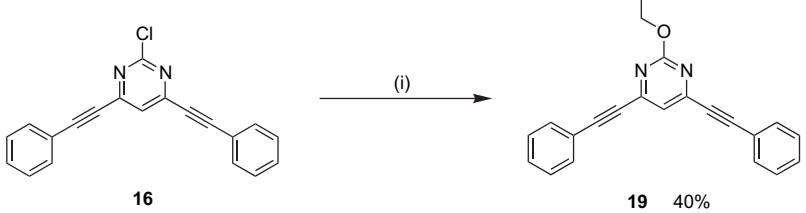


24 $R^1 = R^2 = H$ 74%
25 R^1 = OMe $R^2 = H$ 35%
26 $R^1 = NMe_2$ $R^2 = H$ 51%
27 $R^1 = R^2$ = OMe 45%

Scheme 7. (i) $PdCl_2(dppf)\cdot CH_2Cl_2/Cs_2CO_3$, THF/$H_2O$, Δ, 12 h.

2.2. Photophysical properties

To determine the optical properties of the oligomers in solution, UV/vis, excitation and fluorescence spectra were measured (Table 1, Figs. 1 and 2). All the compounds have their absorption wavelenghts λ_{abs} in UV or in blue (335–433 nm) whereas their emission λ_{em} wavelenghts are in visible



Scheme 5. (i) $NaOCH_2CH_2OH/HOCH_2CH_2OH$, 15 h, rt.

Table 1
Spectroscopic data of **5**, **11**, **18** and **24**–**27**

Compound	λ_{abs}, max (nm)	ε (M^{-1} cm^{-1})	λ_{em}, max (nm)	ϕ_F[a]	Stokes shift (cm^{-1})
5	410	49,346	491	0.55[d]	4024
11	384	27,849	478	0.05[c]	5121
18	434	35,445	516	0.37[d]	3662
24	341	38,539	370	0.06[b]	2298
25	335	45,073	406	0.48[b]	5220
26	433	26,155	522	0.24[d]	3938
27	368	10,384	513	0.18[c]	7681

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

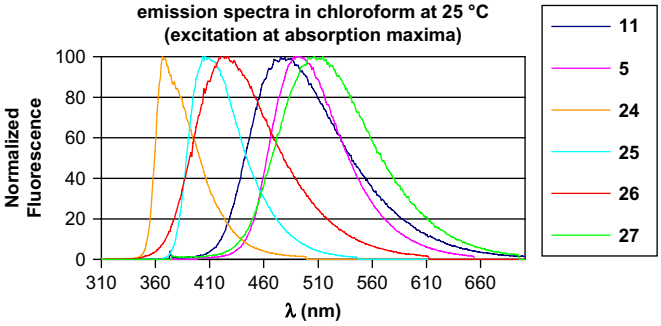


Figure 1.

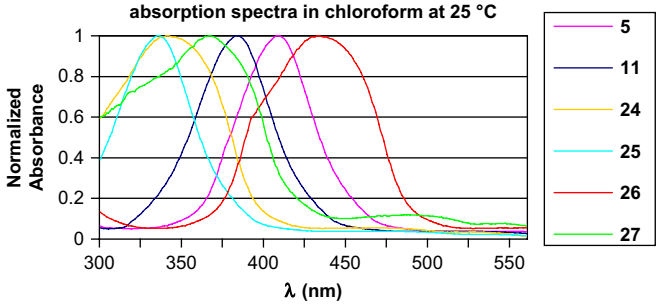


Figure 2.

(406–522 nm). Comparison of the banana-shaped compounds **5**, **11** and **18**, substituted with *p*-dimethylaminophenyl groups, revealed a bathochromic shift and a better quantum yield when the substituents are at the 4,6-positions rather at the 2,4-positions for which the lowest optical properties were observed. Comparison of **24** with the substituted star-shaped compounds **25**–**27** allows to appreciate influence of the electron-donating groups on the phenyl rings. Replacement of a hydrogen by a methoxy or a dimethylamino group increases the absorption and emission wavelengths (λ_{abs}, λ_{em}), the highest bathochromic effect is observed for the dimethylamino group which is prone to have the stronger donating effect. An enhancement of the quantum yield ϕ_F is also noted. Consideration of compound **27** bearing three methoxy groups on each phenyl ring highlighted the lower ϕ_F but the greatest Stokes shift. Generally, it can be noted that introduction of a third arm on the pyrimidine moiety did not increase significantly the optical properties.

The optical properties of the compounds **5**, **11**, **24**–**26** were compared with already described analogous banana-shaped and star-shaped compounds **28**–**32**[11a,16] (Fig. 3, Table 2). Incorporation of a triple bond within the arms of the molecules brings about a significant red shift of the absorption and emission wavelengths.

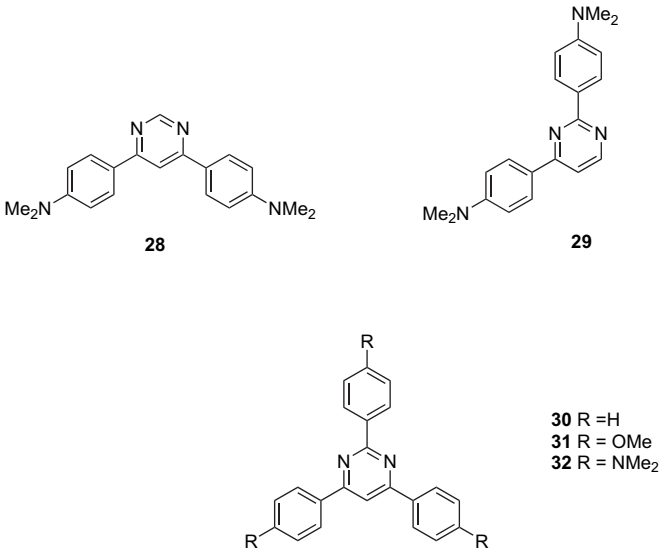


Figure 3.

Table 2
Spectroscopic data of **28**–**32**

Compound	λ_{abs}, max (nm)	ε (M^{-1} cm^{-1})	λ_{em}, max (nm)	ϕ_F[a]	Stokes shift (cm^{-1})
28	299/378	16,025/38,060	429	0.72[16]	3145
29	354	50,085	465	0.06[16]	6743
30	265	—	381	<0.01[23]	11,489
31	296	29,734	372	0.04[16]	6902
32	349	39,286	427	0.14[16]	5234

[a] ±10%.

We also performed molecular orbital calculations at the DFT 6-31G* level of theory on molecules **5**, **11**, **26** possessing an ethynyl link and molecules **28**, **29**, **32** where the phenyl rings are directly connected to the pyrimidine core. The geometry of these six molecules was fully optimized and the energies of their frontier orbitals were calculated (Table 3). The presence

Table 3
HOMO/LUMO energy levels for compounds **5**, **11**, **26**, **28**, **29** and **32** from B3LYP/6-31G* calculations

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{LUMO}-E_{HOMO}$ (eV)
5	−5.05	−1.55	3.50
11	−4.94	−1.50	3.44
26	−4.94	−1.50	3.44
28	−5.01	−1.08	3.93
29	−4.87	−0.95	3.92
32	−4.74	−0.90	3.84

of phenylethynyl moities linked to the pyrimidine central unit allows the molecules to be absolutely planar and so enforced the conjugation whereas direct linkage of the phenyl rings brings out a twisted geometry with dihedral angle between the pyrimidine and the phenyl rings in the range 8–16°. Moreover, for compounds **5**, **11**, **26** the differences between the energies of HOMOs and LUMOs (around 3.5 eV) are significantly lower compared to those of molecules **28**, **29**, **32** (around 3.9 eV) possessing no ethynyl link. These facts could explain the bathochromic effect observed for the absorption and emission wavelengths of the compounds possessing an ethynyl moiety.

3. Conclusion

In summary, we have described the synthesis of bis- and tris(arylethylnyl)pyrimidine oligomers using Sonogashira, Negishi and Suzuki cross-coupling reactions starting from chloro and iodopyrimidines. When the arms of such banana-shaped and star-shaped molecules are substituted by electron-donating groups, interesting fluorescence properties were observed. The influence of the nature of the electron-donating groups was studied and a comparison between banana-shaped and star-shaped substituted pyrimidines with or without ethynyl moities was carried out highlighting that presence of triple bonds generally increases the optical properties (bathochromic effect, quantum yield and Stokes shift).

4. Experimental section

4.1. General methods

Melting points were determined on an Electrothermal 1100 instrument. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 (300 MHz ^{1}H, 75 MHz ^{13}C, 282.5 MHz ^{19}F) instrument. Microanalyses were performed on a Carlo Erba CHNOS 1160 apparatus. The IR spectra were obtained from potassium bromide pellets with a Perkin–Elmer 16 PC FT-IR spectrometer. Mass spectra were recorded on an ATI-Unicam Automass® apparatus. UV/vis spectra were recorded on 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 yield was determined by comparison with standards as described in literature.[28] Molecular orbital calculations were performed with the Gaussian 03 suite of programs[29] employing the three parameter hybrid functional of Becke based on the correlation functional of Lee, Yang and Parr (B3LYP).[30] The 6-31G* basis sets were used for all atoms.

4.2. General procedure A for cross-coupling of iodopyrimidines with alkyne under Sonogashira conditions

To iodoaryl in THF (5 mL) were added alkyne, NEt_3 (0.5 mL), CuI (6 mol %) and $Pd(PPh_3)_2Cl_2$ (6 mol %). The suspension was stirred at room temperature for 8 h. The reaction mixture was cooled, diluted with a mixture of water and dichloromethane (1:1, 20 mL) and the organic layer separated. The aqueous layer was extracted with dichloromethane (2×20 mL). The combined organic extracts were dried over magnesium sulfate, filtered and evaporated.

4.3. General procedure B for trimethylsilyl groups' deprotection

A mixture of trimethylsilanylethynylpyrimidine and a solution of potassium hydroxide in methanol (1 M, 10 mL) was stirred at room temperature for 15 min. The solution was then neutralized with 1 M aqueous HCl and extracted with dichloromethane (3×20 mL). The combined organic extracts were dried over magnesium sulfate, filtered and evaporated.

4.4. General procedure C for cross-coupling of 2,4,6-trichloropyrimidine with alkynylzinc chlorides under Negishi conditions

To a solution of alkyne in THF (5 mL) under nitrogen at 0 °C was added a solution of *n*-BuLi (1.6 M, 1 equiv), then the solution was stirred at room temperature for 1 h, cooled at −50 °C and a solution of anhydrous $ZnCl_2$ (1.2 equiv) in THF (10 mL) was added dropwise. The solution was then stirred at room temperature for 1 h, added to a mixture of 2,4,6-trichloropyrimidine (0.2 equiv), $Pd(PPh_3)_4$ (3 mol %) and THF (2 mL). The reaction mixture was heated at 30 °C for 3 h. Then, 0.1 M HCl (10 mL) was added, the reaction mixture was extracted with ether (3×20 mL). The combined organic layers were washed with brine (20 mL) and dried over $MgSO_4$, filtered and evaporated.

4.5. General procedure D for potassium alkynyltrifluoroborate synthesis

A solution of alkyne (10 mmol) in dry THF (20 mL) was cooled to −78 °C under nitrogen. *n*-BuLi (1.6 M, 1 equiv) was added dropwise, and the solution was stirred for 1 h at this temperature. Triisopropylborate (1.5 equiv) was then added dropwise at −78 °C. The solution was stirred at this temperature for 1 h and then allowed to warm to −20 °C for 1 h. A saturated aqueous solution of potassium hydrogen difluoride (6.0 equiv) was added to the vigorously stirred solution. The resulting mixture was allowed to stir for 1 h at −20 °C and then allowed to warm to room temperature for 1 h. The solvent was removed under reduced pressure, and the resulting white solid was dried under high vacuum to remove all water. The solid was then washed with acetone and with hot acetone. The resulting organic solution was evaporated.

4.6. General procedure E for cross-coupling of 2,4,6-trichloropyrimidine with potassium alkynyltrifluoroborate under Suzuki conditions

Potassium alkynyltrifluoroborate, $PdCl_2(dppf)\cdot CH_2Cl_2$, 2,4,6-trichloropyrimidine and Cs_2CO_3 (3 equiv related to alkynyltrifluoroborate) were mixed with THF (5 mL) and degassed

water under nitrogen (20:1 THF/water ratio). The solution was heated at reflux for 12 h. The mixture was then cooled, and water (10 mL) was added to the flask. The resulting solution was then extracted with diethyl ether. The combined organic extracts were washed with 1 M HCl and brine and then dried over $MgSO_4$. After filtering off the solid, the solvent was removed under reduced pressure.

4.6.1. 4,6-Bis-trimethylsilylethynylpyrimidine (3)

Sonogashira cross-coupling reaction of **2** (300 mg, 0.9 mmol) with ethynyltrimethylsilane (354 μL, 2.5 mmol) according to the general procedure A gave after purification by column chromatography (silica gel, eluent petroleum ether/ethyl acetate (90:10)) 173 mg (71%) of **3** as an orange oil. ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 18H, $Si(CH_3)_3$), 7.45 (d, J=1.3 Hz, 1H, H_5), 9.05 (d, J=1.3 Hz, 1H, H_2). ^{13}C ($CDCl_3$): δ 0.0, 101.5, 102.5, 126.5, 151.0, 159.5. IR: 2961, 1567, 1498, 1251, 948, 847 cm^{-1}. Anal. Calcd for $C_{14}H_{20}N_2Si_2$ (272.12): C, 61.71; H, 7.40; N, 10.28. Found: C, 62.04; H, 7.51; N, 10.19.

4.6.2. 4,6-Bis-phenylethynylpyrimidine (4)

Sonogashira cross-coupling reaction of **2** (500 mg, 1.51 mmol) with ethynylbenzene (485 μL, 4.59 mmol) according to the general procedure A gave after purification by column chromatography (silica gel, eluent dichloromethane) 203 mg (48%) of **4** as a brown solid. Mp 105–107 °C. ^{1}H NMR ($CDCl_3$): δ 7.65–7.57 (m, 6H, H_{Ph}), 7.86–7.82 (m, 5H, H_{Ph}+H_5), 9.39 (d, J=1.3 Hz, 1H, H_2). ^{13}C ($CDCl_3$): δ 86.9, 85.3, 121.3, 126.0, 129.0, 130.5, 132.8, 151.3, 159.5. IR: 2218, 1568, 1494, 762, 752, 685 cm^{-1}. Anal. Calcd for $C_{20}H_{12}N_2$ (280.10): C, 85.69; H, 4.31; N, 9.99. Found: C, 85.79; H, 4.48; N, 9.81.

4.6.3. 4,6-Bis-4-(N,N-dimethylamino)phenylethynylpyrimidine (5)

Sonogashira cross-coupling reaction of **2** (500 mg, 1.51 mmol) with 4-ethynyl-*N*,*N*-dimethylaniline (666 mg, 4.59 mmol) according to the general procedure A gave after purification by column chromatography (silica gel, eluent dichloromethane) 354 mg (64%) of **5** as a brown solid. Mp 161–163 °C. ^{1}H NMR ($CDCl_3$): δ 3.00 (s, 12H, $N(CH_3)_2$), 6.62 (d, J=8.9 Hz, 4H, H_{Ph}), 7.44 (s, 1H, H_5), 7.48 (d, J=8.9 Hz, 4H, H_{Ph}), 9.04 (s, 1H, H_2). ^{13}C ($CDCl_3$): δ 40.4, 86.5, 97.8, 107.5, 112.0, 124.7, 134.4, 151.4, 151.5, 159.3. IR: 2192, 1605, 1556, 1526, 1366, 1160, 1103, 811 cm^{-1}. Anal. Calcd for $C_{24}H_{22}N_4$ (366.18): C, 78.66; H, 6.05; N, 15.29. Found: C, 78.75; H, 6.01; N, 15.02.

4.6.4. 4,6-Diethynylpyrimidine (6)

Trimethylsilyl deprotection reaction of **3** (100 mg, 0.37 mmol) according to the general procedure B gave 27 mg (57%) of **6** as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 3.06 (s, 2H, $H_{2'}$), 7.37 (d, J=1.3 Hz, 1H, H_5), 9.07 (d, J=1.3 Hz, 1H, H_2). ^{13}C ($CDCl_3$): δ 81.8, 103.7, 124.6, 159.0, 166.8. IR: 3444, 3242, 2932, 3114, 1724, 1582, 1523, 1119, 1071 cm^{-1}. Anal. Calcd for $C_8H_4N_2$ (128.04): C, 74.99; H, 3.15; N, 21.86. Found: C, 74.72; H, 3.02; N, 21.69.

4.6.5. 2,4-Bis-trimethylsilylethynylpyrimidine (9)

Sonogashira cross-coupling reaction of **8** (501 mg, 1.51 mmol) with ethynyltrimethylsilane (570 μL, 4.00 mmol) according to the general procedure A gave after purification by column chromatography (silica gel, eluent petroleum ether/diethyl ether (5:1)) 303 mg (74%) of **9** as a brown solid. Mp 79–80 °C. ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 18H, $Si(CH_3)_3$), 7.26 (d, J=5 Hz, 1H, H_5), 8.63 (d, J=5 Hz, 1H, H_6). ^{13}C ($CDCl_3$): δ −0.47, −0.40, 95.1, 100.9, 102.0, 102.1, 122.4, 150.8, 152.6, 157.5. IR: 2962, 2900, 2360, 2107, 1555, 1527, 1414, 1363, 1251, 1233, 959, 845, 761 cm^{-1}. Anal. Calcd for $C_{14}H_{20}N_2Si_2$ (272.12): C, 61.71; H, 7.40; N, 10.28. Found: C, 61.84; H, 7.03; N, 10.19.

4.6.6. 2,4-Bis-phenylethynylpyrimidine (10)

Sonogashira cross-coupling reaction of **8** (500 mg, 1.51 mmol) with ethynylbenzene (485 μL, 4.59 mmol) according to the general procedure A gave after purification by column chromatography (silica gel, eluent dichloromethane) 164 mg (39%) of **10** as a brown solid. Mp 125–126 °C. ^{1}H NMR ($CDCl_3$): δ 7.39 (m, 7H, H_{Ph}+H_5), 7.63 (d, J=6.2 Hz, 2H, H_{Ph}), 7.68 (d, J=6.2 Hz, 2H, H_{Ph}), 8.73 (d, J=5.3 Hz, 1H, H_6). ^{13}C ($CDCl_3$): δ 93.8, 94.2, 95.2, 97.3, 128.8, 128.9, 129.0, 130.2, 130.3, 130.5 (2C), 132.9, 133.1, 133.3, 151.7, 157.8. Anal. Calcd for $C_{20}H_{12}N_2$ (280.10): C, 85.69; H, 4.31; N, 9.99. Found: C, 85.51; H, 4.18; N, 9.71.

4.6.7. 2,4-Bis-4-(N,N-dimethylamino)phenylethynylpyrimidine (11)

Sonogashira cross-coupling reaction of **8** (500 mg, 1.51 mmol) with 4-ethynyl-*N*,*N*-dimethylaniline (666 mg, 4.59 mmol) according to the general procedure A gave after purification by column chromatography (silica gel, eluent petroleum ether/ethyl acetate (50:50)) 348 mg (63%) of **11** as a black solid. Mp 193–195 °C. ^{1}H NMR ($CDCl_3$): δ 3.02 (s, 6H, $N(CH_3)_2$), 3.04 (s, 6H, $N(CH_3)_2$), 6.66 (d, J=8.9 Hz, 4H, H_{Ph}), 7.22 (d, J=5.3 Hz, 1H, H_5), 7.50 (d, J=8.9 Hz, 2H, H_{Ph}), 7.56 (d, J=8.9 Hz, 2H, H_{Ph}), 9.04 (d, J=5.3 Hz, 1H, H_6). ^{13}C ($CDCl_3$): δ 40.5, 86.5, 87.6, 91.0, 97.8, 107.6, 108.0, 111.9, 112.0, 120.6, 134.4, 134.6, 151.3, 151.5, 152.3, 154.2, 157.2. IR: 2196, 1604, 1551, 1526, 1416, 1367, 1163, 981, 808 cm^{-1}. Anal. Calcd for $C_{24}H_{22}N_4$ (366.18): C, 78.66; H, 6.05; N, 15.29. Found: C, 78.57; H, 5.59; N, 15.18.

4.6.8. 2,4-Diethynylpyrimidine (12)

Trimethylsilyl deprotection reaction of **9** (153 mg, 0.56 mmol) according to the general procedure B gave after purification by column chromatography (silica gel, eluent dichloromethane) 68 mg (95%) of **12** as a brown oil. ^{1}H NMR ($CDCl_3$): δ 3.05 (s, 1H, $H_{2'}$), 3.07 (s, 1H, $H_{2''}$), 7.22 (d, J=5.0 Hz, 1H, H_5), 8.59 (d, J=5.0 Hz, 1H, H_6). ^{13}C ($CDCl_3$): δ 82.3 (2C), 103.7 (2C), 121.5, 152.0, 157.3, 167.0. IR: 3246, 2939, 2114, 1473, 1548, 1432, 1369, 1119,

1070, 984, 682 cm^{-1}. Anal. Calcd for $C_8H_4N_2$ (128.04): C, 74.99; H, 3.15; N, 21.86. Found: C, 74.72; H, 3.02; N, 21.69.

4.6.9. 2-Chloro-4,6-bis-trimethylsilylethynylpyrimidine (**15**)

Negishi cross-coupling reaction of **14** (226 mg, 1.24 mmol) with ethynyltrimethylsilane according to the general procedure C gave after purification by column chromatography (silica gel, eluent petroleum ether/ethyl acetate (90:10)) 285 mg (75%) of **15** as a beige solid. Mp 129–130 °C. ^{1}H NMR ($CDCl_3$): δ 0.27 (s, 18H, $Si(CH_3)_3$), 7.40 (s, 1H, H_5). ^{13}C ($CDCl_3$): δ 0.0, 100.5, 104.9, 125.0, 153.4, 162.1. IR: 2964, 2167, 1563, 1538, 1493, 1245, 970, 911, 844, 763 cm^{-1}. MS (IC^+) *m/z*: 307 (MH^+, 100), 308 (MH^+, 26), 309 (MH^+, 39). Anal. Calcd for $C_{14}H_{19}ClN_2Si_2$ (306.08): C, 54.78; H, 6.24; N, 9.13. Found: C, 54.71; H, 6.32; N, 9.20.

4.6.10. 2-Chloro-4,6-bis-phenylethynylpyrimidine (**16**)

Negishi cross-coupling reaction of **14** (226 mg, 1.24 mmol) with ethynylbenzene according to the general procedure C gave after purification by column chromatography (silica gel, eluent petroleum ether/ethyl acetate (90:10)) 262 mg (69%) of **16** as a pale yellow solid. Mp 148–149 °C. ^{1}H NMR ($CDCl_3$): δ 7.32–7.21 (m, 7H, H_{Ph}+H_5), 7.48–7.45 (m, 4H, H_{Ph}). ^{13}C ($CDCl_3$): δ 86.2, 97.1, 120.9, 124.2, 129.0, 130.9, 132.9, 153.4, 161.7. IR: 2218, 1562, 1482, 1249, 880, 760, 688 cm^{-1}. MS (EI) *m/z*: 314 (M^+, 100), 315 (M^+, 26), 316 (M^+, 39). Anal. Calcd for $C_{20}H_{11}ClN_2$ (314.16): C, 76.31; H, 3.52; N, 8.90. Found: C, 56.29; H, 3.54; N, 8.88.

4.6.11. 2-Chloro-4,6-bis-(4-dodecyloxyphenylethynyl)-pyrimidine (**17**)

Negishi cross-coupling reaction of **14** (103 mg, 0.56 mmol) with 1-dodecyloxy-4-ethynylbenzene according to the general procedure C gave after purification by column chromatography (silica gel, eluent petroleum ether/ethyl acetate (90:10)) 194 mg (51%) of **17** as a pale yellow solid. Mp <50 °C. ^{1}H NMR ($CDCl_3$): δ 0.78 (t, J=6.0 Hz, 6H, 2×CH_3), 1.37–1.19 (m, 36H, 18×CH_2), 1.74–1.68 (m, 4H, 2×OCH_2CH_2), 3.92 (t, J=6.6 Hz, 2H, 2×OCH_2), 6.83 (d, J=8.9 Hz, 2H, H_{Ph}), 7.19 (s, 1H, H_5), 7.47 (d, J=8.9 Hz, 2H, H_{Ph}). ^{13}C ($CDCl_3$): δ 14.5, 23.1, 26.4, 29.5, 29.7, 29.9, 30.0 (3C), 30.1, 32.3, 68.7, 85.2, 99.2, 112.1, 115.3, 121.7, 135.0, 154.5, 161.6, 162.8. IR: 2918, 2852, 2214, 1554, 1497, 1260, 1244, 1111, 831 cm^{-1}. Anal. Calcd for $C_{44}H_{59}ClN_2O_2$ (682.54): C, 80.10; H, 8.92; N, 3.22. Found: C, 80.35; H, 9.06; N, 3.11.

4.6.12. 2-Chloro-4,6-bis-(4-(N,N-dimethylamino)-phenylethynyl)pyrimidine (**18**)

Negishi cross-coupling reaction of **14** (565 mg, 3.08 mmol) with 1-ethynyl-4-*N*,*N*-dimethylaminobenzene according to the general procedure C gave after purification by column chromatography (silica gel, eluent petroleum ether/dichloromethane (70:30)) 655 mg (53%) of **18** as a brown solid. Mp >250 °C. ^{1}H NMR ($CDCl_3$): δ 2.95 (s, 12H, $N(CH_3)_2$), 6.57 (d, J=8.9 Hz, 4H, H_{Ph}), 7.17 (s, 1H, H_5), 7.37 (d, J=8.9 Hz, 4H, H_{Ph}). ^{13}C ($CDCl_3$): δ 40.1, 85.3, 85.9, 99.7, 106.7, 111.6, 122.4, 134.3, 151.1, 153.2. MS (IC^+) *m/z*: 401 (MH^+, 100), 402 (MH^+, 26), 403 (MH^+, 38). Anal. Calcd for $C_{24}H_{21}ClN_4$ (400.90): C, 71.90; H, 5.28; N, 13.98. Found: C, 71.75; H, 5.39; N, 13.90.

4.6.13. 2-(4,6-Bis-phenylethynylpyrimidin-2-yloxy)-ethanol (**19**)

NaH (60%, mineral oil dispersion, 370 mg, 1.37 mmol) was added to freshly distilled ethylene glycol (10 mL) on an ice bath. After 5 min, **16** (386 mg, 1.22 mmol) was added and the mixture was allowed to stir at room temperature overnight. The resulting mixture was acidified with 10% aqueous HCl, diluted with H_2O and extracted twice with EtOAc (20 mL). The combined organic extracts were washed with H_2O and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (silica gel, eluent petroleum ether/ethyl acetate (1:1)) to give 167 mg (40%) of **19** as a brown solid. Mp 100–101 °C. ^{1}H NMR ($CDCl_3$): δ 2.88 (s, 1H, OH), 3.91–3.95 (m, 2H, CH_2), 4.50–4.47 (m, 2H, CH_2), 7.19 (s, 1H, H_5), 7.29–7.34 (m, 6H, H_{Ph}), 7.51–7.49 (m, 4H, H_{Ph}). ^{13}C ($CDCl_3$): δ 61.9, 70.2, 86.9, 94.9, 120.9, 121.4, 129.0, 130.5, 132.9, 153.3, 166.5. MS (IC^+) *m/z*: 341 (MH^+, 100), 342 (MH^+, 30). Anal. Calcd for $C_{22}H_{16}N_2O_2$ (340.37): C, 77.63; H, 4.74; N, 8.23. Found: C, 77.31; H, 4.52; N, 8.11.

4.6.14. Potassium (4-methoxyphenylethynyl)trifluoro-borate (**21**)

Alkynyltrifluoroborate synthesis from 1-methoxy-4-ethynylbenzene (776 mg, 5.87 mmol) according to the general procedure D gave 1.27 g (91%) of **21** as a colourless solid. Mp >250 °C. ^{1}H NMR (DMSO-d_6): δ 3.78 (s, 3H, OCH_3), 6.89 (d, J=8.9 Hz, 2H, H_{Ph}), 7.26 (d, J=8.9 Hz, 2H, H_{Ph}). ^{13}C (DMSO-d_6): δ 55.4, 93.4, 114.2, 118.0, 132.4, 158.3. ^{19}F (DMSO-d_6): δ −131.9. IR: 2192, 1606, 1510, 1250, 1052, 1029, 980, 836 cm^{-1}.

4.6.15. Potassium (4-N,N-dimethylaminophenylethynyl)-trifluoroborate (**22**)

Alkynyltrifluoroborate synthesis from 4-ethynyl-*N*,*N*-dimethylaniline (776 mg, 5.87 mmol) according to the general procedure D gave 612 mg (87%) of **22** as a colourless solid. Mp 184–185 °C. ^{1}H NMR (DMSO-d_6): δ 2.73 (s, 6H, $N(CH_3)_2$), 6.48 (d, J=8.9 Hz, 2H, H_{Ph}), 7.08 (d, J=8.9 Hz, 2H, H_{Ph}). ^{13}C (DMSO-d_6): δ 40.1, 90.0, 108.3, 112.1, 133.0, 150.5. ^{19}F (DMSO-d_6): δ −137.0. IR: 2922, 2099, 1609, 1520, 1359, 1166, 816 cm^{-1}.

4.6.16. Potassium (3,4,5-trimethoxyphenylethynyl)-trifluoroborate (**23**)

Alkynyltrifluoroborate synthesis from 5-ethynyl-1,2,3-trimethoxybenzene (1.69 g, 8.8 mmol) according to the general procedure D gave 1.99 g (76%) of **23** as a colourless solid. Mp >250 °C. ^{1}H NMR (DMSO-d_6): δ 3.82 (s, 9H, OCH_3), 6.65 (s, 2H, $H_{2,6}$). ^{19}F (DMSO-d_6): δ −132.1. IR: 3661, 3505, 2953, 2172, 1578, 1509, 1412, 1242, 1131, 1049, 1026, 995 cm^{-1}.

*4.6.17. 2,4,6-Tris-phenylethynylpyrimidine (**24**)*

Cross-coupling reaction of 2,4,6-trichloropyrimidine (91 mg, 0.50 mmol) with potassium phenylethynyltrifluoroborate (520 mg, 2.50 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (108 mg, 0.13 mmol) according to the general procedure E gave after purification by column chromatography (silica gel, eluent petroleum ether/ethyl acetate (9:1)) 140 mg (74%) of **24** as a brown solid. Mp 181–183 °C. ^{1}H NMR ($CDCl_3$): δ 7.42 (m, 9H, H_{Ph}), 7.56 (s, 1H, H_5), 7.65 (dd, J_1=7.5 Hz, J_2=1.9 Hz, 4H, H_{Ph}), 7.71 (dd, J_1=7.5 Hz, J_2=1.9 Hz, 2H, H_{Ph}). ^{13}C ($CDCl_3$): δ 86.7, 88.2, 89.0, 95.7, 121.3, 121.6, 124.2, 128.8, 129.0, 130.2, 130.6, 132.9, 133.2, 151.9, 154.0. IR: 2216, 1557, 1495, 1362, 755, 690 cm^{-1}. Anal. Calcd for $C_{28}H_{16}N_2$ (380.13): C, 88.40; H, 4.24; N, 7.36. Found: C, 88.35; H, 4.31; N, 7.26.

*4.6.18. 2,4,6-Tris-(4-methoxyphenylethynyl)pyrimidine (**25**)*

Cross-coupling reaction of 2,4,6-trichloropyrimidine (183 mg, 1.00 mmol) with potassium 4-methoxy-phenylethynyltrifluoroborate (1.14 g, 5.00 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (215 mg, 0.27 mmol) according to the general procedure E gave after purification by column chromatography (silica gel, eluent petroleum ether/ethyl acetate (9:1)) 164 mg (35%) of **25** as a beige solid. Mp 202–203 °C. ^{1}H NMR ($CDCl_3$): δ 3.86 (s, 9H, 3×OCH_3), 6.94–6.89 (m, 6H, H_{Ph}), 7.44 (s, 1H, H_5), 7.58 (d, J=9.0 Hz, 4H, H_{Ph}), 7.60 (d, J=9.0 Hz, 2H, H_{Ph}). ^{13}C ($CDCl_3$): δ 55.8, 86.3, 87.6, 89.3, 90.5, 113.4, 113.7, 114.7, 123.4 (2C), 134.7 (2C), 151.9, 154.1, 161.2 (2C). IR: 2209, 1605, 1555, 1511, 1295, 1253, 1179, 827 cm^{-1}. Anal. Calcd for $C_{31}H_{22}N_2O_3$ (470.52): C, 79.13; H, 4.71; N, 5.95. Found: C, 79.44; H, 4.93; N, 5.73.

*4.6.19. 2,4,6-Tris-(4-N,N-dimethylamino-phenylethynyl)-pyrimidine (**26**)*

Cross-coupling reaction of 2,4,6-trichloropyrimidine (183 mg, 1 mmol) with potassium 4-*N*,*N*-dimethylaminophenylethynyltrifluoroborate (1.25 g, 5 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (215 mg, 0.27 mmol) according to the general procedure C gave after purification by column chromatography (silica gel, eluent petroleum ether/ethyl acetate (7:3)) 259 mg (51%) **26** as a brown solid. Mp 245–247 °C. ^{1}H NMR ($CDCl_3$): δ 3.02 (s, 18H, 3×$N(CH_3)_2$), 6.64 (d, J=9.0 Hz, 6H, H_{Ph}), 7.32 (s, 1H, H_5), 7.47 (d, J=9.0 Hz, 4H, H_{Ph}), 7.49 (d, J=9.0 Hz, 2H, H_{Ph}). ^{13}C ($CDCl_3$): δ 40.4, 86.2, 87.6, 91.0, 100.1, 107.0, 108.6, 111.9, 112.0, 122.8, 134.4, 134.6, 151.7, 152.3, 153.6, 161.5. IR: 2181, 1606, 1550, 1367, 1115 cm^{-1}. Anal. Calcd for $C_{34}H_{31}N_5$ (509.26): C, 80.13; H, 6.13; N, 13.74. Found: C, 79.84; H, 5.93; N, 13.94.

*4.6.20. 2,4,6-Tris-(3,4,5-trimethoxyphenylethynyl)-pyrimidine (**27**)*

Cross-coupling reaction of 2,4,6-trichloropyrimidine (183 mg, 1.0 mmol) with potassium phenylethynyltrifluoroborate (1.62 g, 5.4 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (216 mg, 0.26 mmol) according to the general procedure E gave after purification by column chromatography (silica gel, eluent heptane/ethyl acetate (5:5)) and recrystallization in a mixture of methylcyclohexane/ethyl acetate 293 mg (45%) of **27** as a beige solid. Mp 246–247 °C. ^{1}H NMR ($CDCl_3$): δ 3.88 (s, 18H, 6×OCH_3), 3.89 (s, 9H, 3×OCH_3), 6.88 (s, 6H, H_{Ph}), 7.52 (s, 1H, H_5). ^{13}C ($CDCl_3$): δ 56.6, 61.4, 85.6, 87.8, 92.3, 97.5, 110.3, 111.3, 115.6, 117.9, 123.7, 141.1, 142.4, 153.4 (2C), 153.6 (2C). IR: 2217, 1578, 1563, 1504, 1472, 1238, 1123 cm^{-1}. Anal. Calcd for $C_{37}H_{34}N_2O_9$ (650.67): C, 68.30; H, 5.27; N, 4.31. Found: C, 68.66; H, 5.44; N, 3.99.

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