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Synthesis and photophysical properties of oligoarylenes with a pyrrolo[2,3-*d*]pyrimidine core

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ABSTRACT

The palladium-catalyzed Suzuki–Miyaura reaction of 2,4-dichloropyrrolo[2,3-*d*]pyrimidine with aryl boronic acids has been studied. $Pd(OAc)_2$/dicyclohexyl(2-biphenyl)phosphine/K_3PO_4 was found to be an efficient catalyst system to prepare 4-aryl-2-chloro- and 2,4-diarylpyrrolo[2,3-*d*]pyrimidines. Novel non-linear molecules consisting of a pyrrolo[2,3-*d*]pyrimidine core and aryl branches have been elucidated as blue light-emitters with fluorescence quantum yields ranging from 4% to 67% in THF solution. The impact of an electron-withdrawing *t*-BuOCO group attached to the pyrrole ring of pyrrolopyrimidine derivatives on optical properties is discussed.

Organic molecules with a π-conjugated backbone have attracted growing interest over recent years owing to their applications in a wide range of electronic and optoelectronic devices.[1] Non-linear (so-called star-shaped and banana-shaped) molecules are of interest in materials science owing to their light-emitting,[2] self-assembling[3] and complex forming properties with metal ions or organic molecules.[3,4] New synthetic methods and novel structures are continuously being introduced into this field. Incorporation of azaheterocycles such as pyridine,[2e,5] pyrazine,[2b] pyrimidine,[2f,6] *s*-triazine[7] or quinoxaline[8] at the centre of the backbone of such molecules leads to a strong enhancement of physical and photophysical properties. It is worth mentioning that pyrrolo[2,3-*d*]pyrimidine derivatives constitute a very important class of compounds exhibiting antiviral[9] and antitumor[10] activities. Owing to the site-specific incorporation of fluorescent pyrrolo[2,3-*d*]pyrimidine derivatives into oligonucleotides, they have been demonstrated to be ideally suitable for probing the structure of DNA.[11] In view of the growing importance of highly efficient light-emitting materials in biological, chemical and materials science, we report herein our results on the synthesis and light-emitting properties of non-linear oligoarylenes containing a pyrrolo[2,3-*d*]pyrimidine moiety.

For the synthesis of novel pyrrolo[2,3-*d*]pyrimidine derivatives, 2,4-dichloro[2,3-*d*]pyrimidine (**1**)[12] was used as the starting material. The Suzuki–Miyaura reaction is a powerful tool for C–C bond formation in the construction of biaryl skeletons.[13] However, a literature survey on arylpyrrolo[2,3-*d*]pyrimidines revealed that the Suzuki–Miyaura reaction on pyrrolo[2,3-*d*]pyrimidines has not been explored in detail. To the best of our knowledge, only a few examples have been reported on the application of palladium-catalyzed cross-coupling for the arylation of the pyrrole ring of a pyrrolo[2,3-*d*]pyrimidine,[14] and no work on functionalization of the pyrimidine moiety in pyrrolo[2,3-*d*]pyrimidines has been published.

Initially, we conducted a brief screen of common palladium catalysts and ligands using 4-*tert*-butylphenylboronic acid and 2,4-dichloropyrrolo[2,3-*d*]pyrimidine (**1**) as coupling partners in the Suzuki–Miyaura cross-coupling. The catalysts and ligands employed were $PdCl_2(PPh_3)_2$, $PdCl_2$(dppf), $Pd(OAc)_2$ and PCy_2(2-biphenyl), PCy_2(2′,6′-$(MeO)_2$-2-biphenyl), P(*t*-Bu)$_2$(2-biphenyl), P(*i*-Pr)$_2$(2-biphenyl) and dppf, respectively. The reaction of **1** with 2.16 equiv of 4-*tert*-butylphenylboronic acid in the presence of $PdCl_2(PPh_3)_2$/K_3PO_4, which was previously found to be an efficient catalyst system for the synthesis of densely substituted 4,6-diarylpyrimidines,[15] resulted in the formation of only mono-coupled product **2b** in 41% yield. Analogous results were obtained employing $Pd(OAc)_2$/dppf/K_3PO_4 or $Pd(OAc)_2$/PCy_2(2′,6′-$(MeO)_2$-2-biphenyl)/K_3PO_4 as catalyst systems. The yields of **2b** were 29% and 35%, respectively. The use of $Pd(OAc)_2$ with P(*t*-Bu)$_2$(2-biphenyl) or P(*i*-Pr)$_2$(2-biphenyl) as a ligand led to the formation of a complex mixture of products. Only $PdCl_2$(dppf) or $Pd(OAc)_2$/PCy_2(2-biphenyl) gave the double cross-coupling product **3b** in 28% and 48% yields, respectively. Performing the reaction of **1** with 1.2 equiv of 4-*tert*-butylphenylboronic acid in

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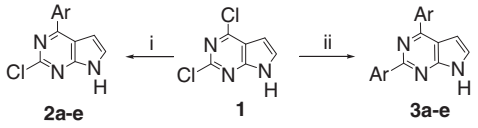
the presence of $Pd(OAc)_2/PCy_2$(2-biphenyl)/K_3PO_4 as the catalyst system at 50–60 °C led to compound **2b** in 66% yield (Table 1, entry 3). Among the catalyst systems studied, only $Pd(OAc)_2/PCy_2$(2-biphenyl)/K_3PO_4 resulted in clean conversions and enabled mono- and double cross-coupling reactions and, therefore, it was selected as the most suitable catalyst system for further development. Using the reaction conditions presented in Scheme 1 and Table 1, a series of 4-aryl-2-chloro- (**2a–e**)[16] and 2,4-diarylpyrrolo[2,3-*d*]pyrimidines (**3a–e**)[17] were synthesized. Formation of the corresponding 2-aryl-4-chloropyrrolo[2,3-*d*]pyrimidines was not observed. Assignment of the structures **2a–e** was based on NOE ^{1}H NMR experiments. An increase in the signal intensities of the 5-H and 2′-H protons was observed to be 7–12% (Fig. 1). This indicated that the 4-Cl group in the pyrrolopyrimidine **1** reacted first in the Suzuki–Miyaura reaction to yield the corresponding 4-aryl derivatives **2a–e**.

Although the Suzuki–Miyaura reaction of **1** with arylboronic acids enabled the synthesis of arylpyrrolopyrimidines with sufficient site-selectivity, the yields of compounds **2** and **3** were low or moderate.

We suppose that the reason for this is an interaction between the pyrrole aza-group in the anion form under basic conditions with the boronic acid or palladium catalyst, similar to that observed for 4-amino-2-chloropyrimidine.[18] Therefore, we studied the Suzuki–Miyaura reaction of N7-protected pyrrolo[2,3-*d*]pyrimidine **4**[19] under analogous conditions. It was found that using 2.4 equiv of the corresponding boronic acid enabled the double cross-coupling reaction to give compounds **5a–e**[20] in good to excellent yields (Scheme 2, Table 2).

However, the presence of a 7-*tert*-butoxycarbonyl group increased the reactivity of the 2-chlorine group in **4** and all attempts to obtain 4-aryl-2-chloro-7-*tert*-butoxycarbonylpyrrolo[2,3-*d*]pyrimidines failed. Formation of the diarylpyrrolopyrimidines **5a–e** was observed even when only 1 equiv amount of boronic acid was used in the reaction.

The pyrrolo[2,3-*d*]pyrimidine derivatives (**3a–e** and **5a–e**) were subjected to optical absorption and fluorescence studies. The details of their photophysical properties are summarized in Table 3. All the compounds in dilute THF solution exhibited strong absorption with their absorption maxima positioned in the range 263–342 nm and emission maxima located in the range 382–436 nm (Fig. 2). For compounds **3a–e** the following spectral features can be highlighted. The shape and maxima of the absorption and fluorescence spectra of compounds **3a,b,d** resemble those of pyrrolo[2,3-*d*]pyrimidine.[21] Slight modifications of the spectra might be induced by the aryl substituents attached to the pyrimidine. Similar fluorescence quantum yields (Φ_f = 41–43%) estimated for the solutions of these compounds obviously indicate similar extension of π-conjugation governing the optical transitions. The similarities in the absorption and fluorescence spectra and quantum yields of **3a** and **3d** possessing additional phenyl groups at the *meta*-position of the benzene ring attached to the pyrrolopyrimidine core can be justified by the out-of-plane twisting of the phenyl end-groups of compound **3d** resulting in broken π-conjugation. Such twisted molecular conformations are well-known and were observed in 4,6-di(heteroaryl)pyrimidines.[3a] As opposed to this, introduction of additional phenyl end-groups to the *para*-position of the phenyl groups of the pyrrolopyrimidine (compound **3c**) results in extended conjugation, and thus, in a red shift of the spectral bands (Fig. 2c). The extension of the conjugation length in **3c** also manifests in a dramatically increased absorbance of the lowest-energy optical transitions, as well as in an enhanced fluorescence quantum yield (up to 53%, see Table 3).



Scheme 1. Reagents and conditions: (i) 2 mol % $Pd(OAc)_2$, 4 mol % PCy_2(2-biphenyl), 1.2 equiv $ArB(OH)_2$, 2.4 equiv K_3PO_4, 1,4-dioxane, 50–60 °C, Ar; (ii) 2 mol % $Pd(OAc)_2$, 4 mol % PCy_2(2-biphenyl), 2.4 equiv $ArB(OH)_2$, 4.8 equiv K_3PO_4, 1,4-dioxane, Δ, Ar.

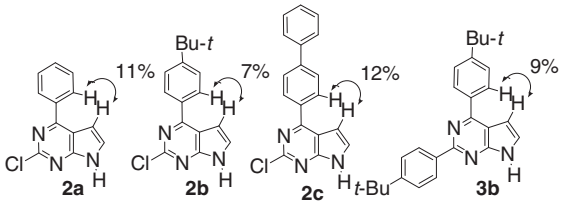
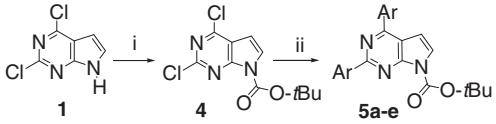
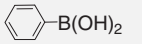
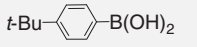
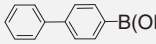
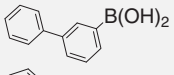
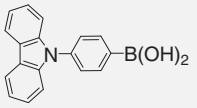


Figure 1. NOE experiments on **2a–c** and **3b**.



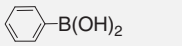
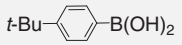
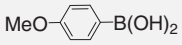
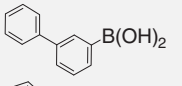
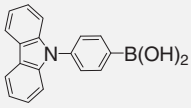
Scheme 2. Reagents and conditions: (i) Boc_2O, DMAP, DIPEA, CH_2Cl_2, Ar; (ii) 2 mol % $Pd(OAc)_2$, 4 mol % PCy_2(2-biphenyl), 2.4 equiv $ArB(OH)_2$, 4.8 equiv K_3PO_4, 1,4-dioxane, Δ, Ar.

Table 1
Preparation of compounds **2a–e** and **3a–e**

Entry	Arylboronic acid	Equiv	Temp (°C)/time	Product (Yield,[a] %)
1		1.2	50–60/3 h	**2a** (13)
2		2.4	Δ/9 h	**3a** (24)
3		1.2	50–60/2 h	**2b** (66)
4		2.4	Δ/15 min	**3b** (48)
5		1.2	50–60/2 h	**2c** (46)
6		2.4	Δ/2 h	**3c** (29)
7		1.2	70/1.5 h	**2d** (68)
8		2.4	Δ/2 h	**3d** (49)
9		1.2	Δ/2.5 h	**2e** (47)
10		2.4	Δ/3 h	**3e** (63)

[a] Yield after isolation and purification by column chromatography.

Table 2
Preparation of compounds **5a–e**

Entry	Arylboronic acid	Reaction time (h)	Product (Yield,[a] %)
1		3.5	**5a** (78)
2		2	**5b** (76)
3		1	**5c** (94)
4		5	**5d** (42)
5		3	**5e** (86)[b]

[a] Yield after isolation and purification by column chromatography.
[b] 4.8 equiv of 4-(9-carbazolyl)phenylboronic acid and 9.6 equiv of K_3PO_4 were used.

Table 3
UV–Vis absorption and fluorescence data for compounds **3a–e** and **5a–e** in 10^{-5} M THF solution

Compound	λ_{abs} (nm)	ε (l mol^{-1} cm^{-1})	λ_{em}[a] (nm)	Φ_f[b] (%)	Stokes shift (cm^{-1})	τ[c] (ns)
3a	216, 264, 318	27,208, 39,969, 12,185	403	42	6633	3.6
3b	215, 270, 321	28,665, 42,810, 11,721	401	41	6215	2.9
3c	217, 299	55,035, 74,472	421	53	9692	3.0
3d	215, 258, 325	44,226, 68,076, 12,302	415	43	6673	3.5
3e	265, 282, 293, 331, 341	19,693, 22,984, 29,529, 35,003, 37,219	415	50	5229	2.75
5a	213, 263, 303	37,454, 36,692, 20,357	386	3.6	7097	<0.1
5b	213, 274, 307	37,623, 38,480, 23,346, 17,005	382	5.7	6395	<0.1
5c	215, 294	44,437, 50,131, 23,801	387	15	8174	1.5
5d	256, 305	63,463, 19,802	391	13	7211	2.6
5e	236, 255, 293, 342	72,903, 44,475, 24,940, 29,822	436	67	6304	4.1

[a] Excited at 320 nm.
[b] Fluorescence quantum yield determined using two methods, that is, the integrating sphere method and by comparison with a standard (quinine sulfate in 0.1 M H_2SO_4).
[c] Fluorescence lifetime estimated at λ_{em}.

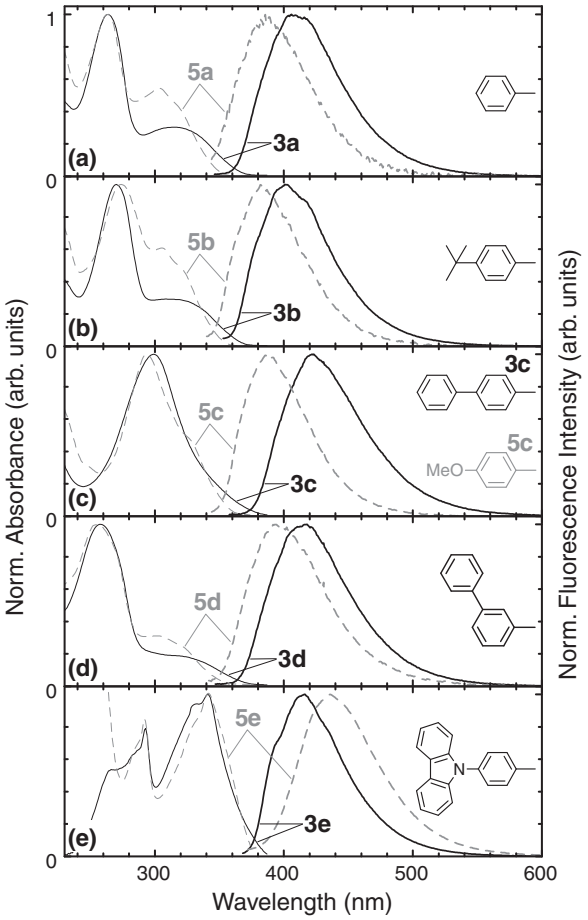


Figure 2. Normalized absorption and fluorescence spectra of compounds (a) **3a** and **5a**, (b) **3b** and **5b**, (c) **3c** and **5c**, (d) **3d** and **5d**, (e) **3e** and **5e** in 10^{-5} M THF solution. Solid lines correspond to compounds **3a–e**, dashed lines to compounds **5a–e**.

Interestingly, the maxima of the absorption spectrum of compound **3e** possessing carbazolyl end-groups were similar to those of ethylcarbazole.[22] Attachment of carbazolyl end-groups (**3e**) to the *para*-position of the phenyl groups of the pyrrolopyrimidine derivatives also results in an enhancement of quantum yield up to 50%. The fluorescence lifetimes estimated for the pyrrolopyrimidines **3a–e** span the range from 2.75 to 3.6 ns, which is typical for fluorescent organic molecules featuring significant radiative relaxation probability. Attachment of an additional electron-withdrawing *t*-BuOCO group to the pyrrole ring of the pyrrolo[2,3-*d*]pyrimidine core (**5a–e**) invokes the following spectral changes: an almost twofold increase in absorbance (from 12,000 l mol^{-1} cm^{-1} to 20,000 l mol^{-1} cm^{-1}) and a blue shift by ~20 nm of the lowest absorption bands for compounds **5a**,**b**,**d** as compared to **3a**,**b**,**d**.

The changes in absorption are accompanied by a similar blue shift of the fluorescence spectra and a remarkable drop in the fluorescence quantum yield. In the limiting case of compound **5a**, reduction of the quantum yield amounts to one order of magnitude, that is, from 42% to 3.6%. The reduction is not so significant (only 3.5 times) for compounds possessing more bulky end-groups such as methoxy (**5c**) and phenyl (**5d**). It is likely that bulky end-groups inhibit twisting of intermediate phenyl groups, thus enhancing the probability of radiative decay from an excited state. Fluorescence decay time measurements support the latter consideration indicating short decay times (<0.1 ns) for compounds **5a**,**b** and prolonged decay times (1.5–2.6 ns) for compounds **5c**,**d**. The general influence of the *t*-BuOCO group is that the blue shift of the absorption and fluorescence spectra, the reduction of fluorescence quantum yields and the decay times observed for compounds **5a–d** strongly contrast with the influence observed for compound **5e**. The attachment of the electron-withdrawing *t*-BuOCO group to **3e** results in a red shift of the fluorescence spectrum from 415 to 436 nm, an enhancement of the quantum yield from 50% to 67%, and an increase of the decay time from 2.75 to 4.1 ns (see Table 3 and Fig. 2e). This exceptional behaviour induced by the presence of the polar *t*-BuOCO group might be explained by the forced planarization of the phenyl groups, which increases the extent of π-conjugation in the excited state. A close similarity in the absorption spectra of compounds **3e** and **5e**, and also similarities in the lowest absorption bands of the spectra with those of ethylcarbazole[22] are evidences of orthogonal-like orientation of the phenyl and carbazolyl groups in the ground state, and thus, poor conjugation between the carbazolyl end-groups and the remaining fragments. However, in the excited state, charge redistribution induced by the presence of the polar *t*-BuOCO group in compound **5e** results in a more planar conformation of the molecule than in the case of compound **3e**, which does not possess this group.

In conclusion, this investigation provides access to novel fluorescent molecules consisting of a pyrrolo[2,3-*d*]pyrimidine core and various peripheral chromophoric units. The pyrrolo[2,3-*d*]pyrimidine derivatives were found to exhibit blue-UV fluorescence ranging from 380 nm to 440 nm with emission quantum yields in the range of 4–67%. Introduction of a polar *t*-BuOCO group was found to have a dramatic impact on the fluorescence properties of the pyrrolopyrimidine derivatives. With derivatives **5a–d**, where the pyrrolo[2,3-*d*]pyrimidine core acts as a fluorophore, intramolecular charge transfer results in a significant quenching of fluorescence (down to 3.6%), whereas for **5e**, where a carbazolyl

moiety is invoked in formation of the lowest excited states, intramolecular charge transfer facilitates a significant increase in the emission quantum yield up to 67%. A more detailed study of the photophysical properties of the synthesized compounds and a further modification of the pyrrolo[2,3-*d*]pyrimidine skeleton to create more efficient light-emitting materials are currently being carried out and the results will be reported in due course.

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16. *Typical procedure for the preparation of 4-aryl-2-chloro-7H-pyrrolo[2,3-d]pyrimidines* (**2a**–**e**). A solution of compound **1** (1.06 mmol) in anhydrous 1,4-dioxane (5 mL) was degassed with argon, and K_3PO_4 (0.54 g, 2.55 mmol), arylboronic acid (1.28 mmol), 2.0 mol % $Pd(OAc)_2$ and 4.0 mol % dicyclohexyl(2-biphenyl)phoshine were added with stirring under argon. The mixture was stirred at 40–50 °C for 1.5–3 h until compound **1** had been consumed (TLC). The solvent was evaporated under reduced pressure and H_2O (5 mL) was added to dissolve inorganic salts. The obtained solution was extracted with $CHCl_3$ (3 × 25 mL), and the combined organic layer was dried over Na_2SO_4, and evaporated under reduced pressure. The resulting solid was purified by column chromatography using $CHCl_3$ as an eluent. Data for selected compounds. Compound **2b**: yield 66%; mp 165 °C. IR (KBr): 3434 cm^{-1} (NH). ^1H NMR (300 MHz, $CDCl_3$): δ 1.44 (s, 9H, CMe_3), 6.93 (dd, 1H, J^3 = 3.6 Hz, J^4 = 1.8 Hz, 5-H), 7.45 (dd, 1H, J^3 = 3.6 Hz, J^4 = 2.4 Hz, 6-H), 7.60–7.63 (m, 2H, 3′,5′-H), 8.12–8.15 (m, 2H, 2′,6′-H), 10.35 (br s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 31.7, 35.4, 101.3, 114.2, 120.7, 126.5, 129.3, 134.5, 152.9, 154.3, 154.7, 158.3. Anal. Calcd for $C_{16}H_{16}ClN_3$: C, 67.25; H, 5.64; N, 14.70. Found: C, 67.27; H, 6.05; N, 14.83. Compound **2c**: yield 46%, mp 255 °C. IR (KBr): 3452 cm^{-1} (NH). ^1H NMR (300 MHz, $CDCl_3$): δ 7.03 (dd, 1H, J^3 = 3.6 Hz, J^4 = 1.2 Hz, 5-H), 7.45–7.57 (m, 3H, 3″, 4″, 5″-H), 7.75 (dd, 1H, J^3 = 3.45 Hz, J^4 = 2.1 Hz, 6-H), 7.79–7.81 (m, 2H, 2″,6″-H), 7.91–7.94 (m, 2H, 3′,5′-H), 8.28–8.30 (m, 2H, 2′,6′-H), 12.53 (br s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6 + two drops CF_3COOD): δ 101.0, 114.3, 120.7, 127.4, 127.7, 128.5, 128.9, 129.6, 129.9, 136.3, 139.9, 143.0, 152.9, 154.6, 157.8. Anal. Calcd for $C_{18}H_{12}ClN_3$: C, 70.71; H, 3.96; N, 13.74. Found: C, 70.93; H, 4.11; N, 13.59.
17. *Preparation of 2,4-diaryl-7H-pyrrolo[2,3-d]pyrimidines* (**3a**–**e**). Compounds **3a-e** were synthesized and isolated according to the procedure described for **2a**–**e** except that the reaction was carried out at reflux and double the amount of K_3PO_4 and arylboronic acid were used. Data for selected compounds. Compound **3b**: yield 48%, mp 265 °C. IR (KBr): 3412 cm^{-1} (NH). ^1H NMR (300 MHz, DMSO-d_6): δ 1.44 (s, 9H, CMe_3), 1.45 (s, 9H, CMe_3), 6.93 (dd, 1H, J^3 = 3.6 Hz, J^4 = 1.8 Hz, 5-H), 7.36 (dd, 1H, J^3 = 3.3 Hz, J^4 = 2.4 Hz, 6-H), 7.61 (dm, 2H, J = 8.7 Hz, 3′,5′-H), 7.65 (dm, 2H, J = 8.4 Hz, 3′,5′-H), 8.29 (dm, 2H, J = 8.7 Hz, 2′,6′-H), 8.55 (dm, 2H, J = 8.4 Hz, 2′,6′-H), 11.19 (br s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 31.74, 31.81, 35.19, 35.29, 100.9, 113.6, 125.9, 126.4, 127.9, 128.5, 129.1, 136.3, 136.8, 152.9, 153.5, 154.4, 156.2, 157.1. Anal. Calcd for $C_{26}H_{29}N_3$: C, 81.42; H, 7.62; N, 10.96. Found: C, 81.54; H, 7.78; N, 10.82. Compound **3c:** yield 29%, mp 281 °C. IR (KBr): 3435 cm^{-1} (NH). ^1H NMR (300 MHz, $CDCl_3$): δ 7.02 (dd, 1H, J^3 = 3.9 Hz, J^4 = 1.8 Hz, 5-H), 7.46–7.55 (m, 7H, 6-H, 2 × 3″,4″,5″-H), 7.74–7.77 (m, 4H, 2 × 2″,6″-H), 7.84 (dm, 2H, J = 8.4 Hz, 3′,5′-H), 7.89 (dm, 2H, J = 8.4 Hz, 3′,5′-H), 8.45 (dm, 2H, J = 8.7 Hz, 2′,6′-H), 8.75 (dm, 2H, J = 8.7 Hz, 2′,6′-H), 10.14 (br s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6 + two drops CF_3COOD): δ 101.4, 114.0, 127.4, 127.5, 127.8, 128.5, 128.7, 129.1, 129.6, 129.7, 129.8, 130.2, 136.6, 137.4, 140.1, 140.3, 142.3, 142.8, 154.1, 154.3, 155.2, 156.2. Anal. Calcd for $C_{30}H_{21}N_3$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.29; H, 5.13; N, 9.87. Compound **3e**: yield 63%, mp 310 °C (dec.). IR (KBr): 3400 cm^{-1} (NH). ^1H NMR (300 MHz, DMSO-d_6): δ 7.14 (dd, 1H, J^3 = 3.6 Hz, J^4 = 1.8 Hz, 5-H), 7.33–7.39 (m, 4H, 3′,5′-H), 7.48–7.63 (m, 8H, 2″,3″,6″,7″-H), 7.82 (t, 1H, J = 2.7 Hz, 6-H), 7.87 (d, 2H, J = 8.4 Hz, 1″,8″-H), 7.95 (d, 2H, J = 8.4 Hz, 1″,8″-H), 8.29–8.34 (m, 4H, 4″,5″-H), 8.71 (d, 2H, J = 8.7 Hz, 2′,6′-H), 8.91 (d, 2H, J = 8.4 Hz, 2′,6′-H), 12.49 (br s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 101.1, 110.6, 114.1, 121.0, 121.1, 121.3, 121.4, 123.6, 123.7, 127.1, 127.2, 127.3, 127.5, 127.6, 129.5, 129.9, 131.2, 137.7, 138.3, 138.8, 139.3, 140.6, 140.7, 154.6, 155.3, 156.4. Anal. Calcd for $C_{42}H_{27}N_5$: C, 83.84; H, 4.52; N, 11.64. Found: C, 83.96; H, 4.59; N, 11.72.
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19. *2,4-Dichloro-7-tert-butoxycarbonyl-7H-pyrrolo[2,3-d]pyrimidine* (**4**). To a solution of compound **1** (0.4 g, 2.13 mmol) in anhydrous CH_2Cl_2 (10 mL), DIPEA (0.56 mL, 2.55 mmol), DMAP (0.052 g, 0.43 mmol) and Boc_2O (0.7 g, 3.19 mmol) were added. The reaction mixture was stirred under reflux for 10 min. The solvent was evaporated under reduced pressure and the obtained solid was purified by column chromatography (eluent—$CHCl_3$) to give 0.41 g (67%) of compound **4**, mp 136–136.5 °C (from 2-propanol). IR (KBr): 1750 cm^{-1} (CO). ^1H NMR (300 MHz, $CDCl_3$): δ 1.72 (s, 9H, CMe_3), 6.68 (d, 1H, J = 3.9 Hz, 5-H), 7.73 (d, 1H, J = 3.9 Hz, 6-H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 28.2, 86.7, 102.9, 118.9, 128.4, 146.9, 153.1, 153.6, 154.6. Anal. Calcd for $C_{11}H_{11}Cl_2N_3O_2$: C, 45.85; H, 3.85; N, 14.58. Found: C, 46.21; H, 3.94; N, 14.55.
20. *Preparation of 2,4-diaryl-7-tert-butoxycarbonyl-7H-pyrrolo[2,3-d]pyrimidines* (**5a**–**e**). Compounds **5a**–**e** were synthesized and isolated according to the procedure described for **3a**–**e** but starting from compound **4** (0.1 g, 0.35 mmol), and using the corresponding arylboronic acid (0.83 mmol), K_3PO_4 (0.35 g, 1.67 mmol), 2.0 mol % $Pd(OAc)_2$, and 4.0 mol % dicyclohexyl(2-biphenyl)-phosphine. Data for selected compounds. Compound **5b**: yield 76%, mp 190–192 °C. IR (KBr): 1736 cm^{-1} (CO). ^1H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 9H, CMe_3), 1.44 (s, 9H, CMe_3), 1.82 (s, 9H, CMe_3), 6.93 (d, 1H, J = 4.2 Hz, 5-H), 7.55 (dm, 2H, J = 8.7 Hz, 3′,5′-H), 7.64 (dm, 2H, J = 8.7 Hz, 3′,5′-H), 7.78 (d, 1H, J = 4.2 Hz, 6-H), 8.17 (dm, 2H, J = 8.7 Hz, 2′,6′-H), 8.64 (dm, 2H, J = 8.7 Hz, 2′,6′-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.5, 31.5, 31.6, 35.1, 35.2, 85.0, 104.5, 116.1, 125.6, 126.1, 127.2, 128.3, 129.0, 135.6, 136.2, 148.8, 153.5, 153.8, 154.1, 158.1, 160.0. Anal. Calcd for $C_{31}H_{37}N_3O_2$: C, 76.98; H, 7.71; N, 8.69. Found: C, 76.52; H, 7.94; N, 8.88. Compound **5c**: yield 94%, mp 129.5–130 °C. IR (KBr): 1735 cm^{-1} (CO). ^1H NMR (300 MHz, $CDCl_3$): δ 1.80 (s, 9H, CMe_3), 3.93 (s, 3H, OMe), 3.95 (s, 3H, OMe), 6.89 (d, 1H, J = 4 Hz, 5-H), 7.05 (dm, 2H, J = 9 Hz, 3′,5′-H), 7.13 (dm, 2H, J = 9 Hz, 3′,5′-H), 7.74 (d, 1H, J = 4 Hz, 6-H), 8.20 (dm, 2H, J = 9 Hz, 2′,6′-H),

8.67 (dm, 2H, J = 9 Hz, 2′,6′-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.5, 55.6, 55.7, 84.9, 104.5, 113.9, 114.4, 115.4, 126.8, 130.1, 130.8, 131.0, 131.6, 148.7, 154.3, 157.7, 159.7, 161.6, 161.8. Anal. Calcd for $C_{25}H_{25}N_3O_4$: C, 69.59; H, 5.84; N, 9.74. Found: C, 69.91; H, 5.99; N, 9.71. Compound **5e:** yield 86%, mp 230 °C (dec.). IR (KBr): 1738 cm^{-1} (CO). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.87 (s, 9H, CMe_3), 7.07 (d, 1H, J = 4.2 Hz, 5-H), 7.34–7.63 (m, 12H, 2 × 3′,5′, 2″,3″,6″,7″-H), 7.81 (d, 2H, J = 8.4 Hz, 1″,8″-H), 7.87–7.92 (m, 3H, 6-H, 1″,8″-H), 8.21–8.23 (m, 4H, 2 × 4″,5″-H), 8.53 (d, 2H, J = 8.4 Hz, 2′,6′-H), 9.02 (d, 2H, J = 8.7 Hz, 2′,6′-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.5, 85.4, 104.2, 110.1, 110.2, 116.6, 120.4, 120.6, 120.64, 120.7, 123.8, 124.0, 126.3, 126.4, 127.1, 127.5, 128.2, 130.2, 130.8, 137.0, 137.7, 139.7, 140.0, 140.9, 141.0, 148.4, 154.4, 157.4, 159.3. Anal. Calcd for $C_{47}H_{35}N_5O_2$: C, 80.43; H, 5.03; N, 9.98. Found: C, 80.58; H, 5.17; N, 9.93.

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