Synthesis of Diheteroarylamine Ligands by Palladium-Catalyzed Mono- and Diamination of Dichloroheteroarenes with Heteroarenamines

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The syntheses of bidentate (see **6** and **12**), bis-bidentate (**7**, **10**, and **13**) up to oligo-bidentate (see **11** and **14**) diheteroarylamine-based N,N-ligands are reported (*Tables 2*, *4*, and *5*). In the course of investigations on heteroaromatic (C–N)-bond formations, a protocol for the Pd-catalyzed mono- and diamination of 2,6-dichloropyridine (**1**) and 4,6-dichloropyrimidines **5** with heteroaren-2-amines **2** and pyrimidine-4,6-diamines **8** is developed. The results are applied to the syntheses of the 'pentamers' **11a**–**11d** and the 'heptamer' **14** based on 4,6-disubstituted 2-alkylpyrimidines **5** and **8**, respectively.

Introduction. – Over the last decades, a central topic of our research activities have been correlations between molecular structure and fluorescence [1–3]. In addition to the synthesis and investigation of boron chelates **II** of bidentate heteroaromatic N,N-ligands **I**, one field of interest has been the investigation of bis- and oligo-BR_2 complexes of oligo-bidentate heteroaromatic N,N-ligands. Aside from the potential pharmacological activity of the title compounds, our interest in an easy and convenient availability of a great variety of amines **I** originates from the fact that the complexation of **I** with boron reagents results in dyes **II** that generally show high room-temperature fluorescence quantum yields [3]. Apart from their interesting spectroscopic features, we recommend dyes of type **II** as efficient laser dyes and attractively active emitters in OLEDs (organic light-emitting diodes) for a long time. In this context, we compared C-bridged 6-membered-ring ligand systems (*i.e.*, diheteroarylacetonitriles [4][5], X = C–CN in *Fig. 1*) with N-bridged 6-membered-ring ligand systems (*i.e.*, diheteroarylamines [6], X = N in *Fig. 1*). However, the access to the latter is very limited due to synthetic difficulties [7].

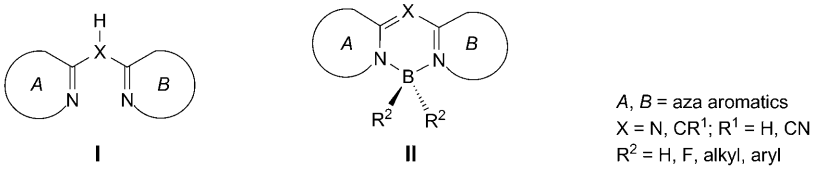


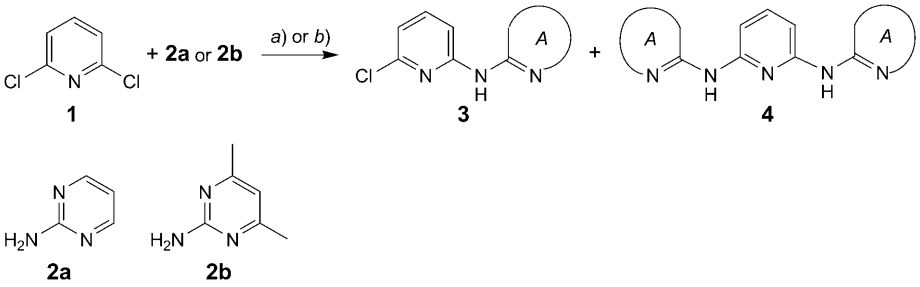
Fig. 1. *General formulas of diheteroarylamine ligands* **I** *and boron chelates* **II** *thereof*

The basic condensation of heteroaren-2-amines with leaving-group-substituted heteroaromatics resulting in diheteroarylamines **I** is well-known for *A*, *B* = pyridin-2-yl or quinolin-2-yl; however, the yields are unsatisfactory and the reaction does not work at all for many other combinations of heteroaromatic reactants. To overcome the

problems known from established syntheses of **I**, we studied the applicability of the *Buchwald–Hartwig* procedure with heteroaromatic substrates. In addition to the syntheses of a great variety of compounds **I**, the use of dichloro- and/or diamino-substituted heteroarenes as bi-functionalized reactants with the possibility of multiple combinations were taken into consideration from the very beginning of our studies. In contrast to a few reported Pd-catalyzed aminations of chloroheteroarenes with heteroarenamines [8–11], to the best of our knowledge, no reliable amination protocol for both the mono- and the diamination of dichloroheteroarenes has been established so far, with exception of the syntheses of oligo-pyridin-2-amines based on 2,6-dibromopyridines as precursors [12–17]. Furthermore, *Dommisse* and co-workers did not observe any formation of the diaminated products when reacting dichloropyridines even with a large excess of pyridin-2-amine for 40 h under *Buchwald–Hartwig* conditions. Hence, they reported the *selectivity* of the mild Pd-catalyzed monoamination on dichloropyridines with heteroarenamines [8]. Caused by the straightforward and low-cost access to chloroheteroarenes compared to bromo- and iodoheteroarenes or heteroaryl triflates, we investigated the Pd-catalyzed mono- and diamination of dichloroheteroarenes, namel, 2,6-dichloropyridine (**1**), 4,6-dichloropyrimidine (**5a**), and several 2-alkylated 4,6-dichloropyrimidines **5b**–**5d**, accepting the comparatively disadvantageous chloride leaving group (*cf. Tables 1*, *2*, *4*, and *5*) to obtain bidentate (see **6** and **12**), bis-bidentate (see **7**, **10**, and **13**) up to oligo-bidentate (see **11** and **14**) diheteroarylamine-based N,N-ligands. Also the reversed reactant functionalities regarding the amino function and leaving group were taken into consideration for the syntheses of bidentate (see **6′**) and bis-bidentate (see **7′**) ligands (*cf. Table 3*). The results were applied for the syntheses of the 'pentamers' **11a**–**11d** (*cf. Table 4*) and the 'heptamer' **14** (*cf. Table 5*) based on 4,6-disubstituted 2-alkylpyrimidines **5** and **8**, respectively.

Results and Discussion. – When reacting 2,6-dichloropyridine (**1**) with the pyrimidin-2-amines **2a** or **2b** (*Table 1*) by using 17 equiv. of K_2CO_3 as base and [Pd(OAc)$_2$]/BINAP (=1,1′-[1,1′-binaphthalene]-2,2′-diylbis[1,1-diphenylphosphine]) as catalyst in toluene (reaction condition *a*) in *Table 1*), we obtained mixtures of mono- and diaminated products and unreacted starting materials nearly independent of the chosen reactant stoichiometry. No constitutional selectivity in favor of either mono- or diamination was observed. However, when using the Pd^0 source [Pd(dba)$_2$] (dba = dibenzylideneacetone = 1,5-diphenylpenta-1,4-dien-3-one) and 2.2 equiv. of ^{t}BuONa as base, the yield of the diamination product increased significantly while the mono-amination product was only observed as an intermediate during the reaction (reaction condition *b*) in *Table 1*). We interprete this as a major result of the increased 'effective' catalytic amount of the Pd^0 catalyst complex, which is able to cleave the remaining second C–Cl bond by insertion within the oxidative addition step and, therefore, to promote the second amination, assisted by the higher basicity of the alkoxide compared to that of the carbonate. When using a Pd^{II} source, the *in situ* reduction to the efficient Pd^0 catalyst resting state has to take place before the catalyst complex can enter the catalytic cycle with the oxidative addition step [18]. Hence, it is not necessary to use a more electron-rich chelating phosphine coligand other than common BINAP when a Pd^0 source is used for the diamination of dichloroheteroarenes. We transferred these

Table 1. *Mono-* vs. *Diamination of 2,6-Dichloropyridine* (**1**) *with Pyrimidin-2-amines* **2a** *and* **2b**: *Reaction Conditions and Yields of Mono- and Diaminated Products* **3** *and* **4**, *respectively*



Reactants	Approx. ratio	Reaction condition[a])	Pd Source	Yield [%] of **3**	Yield [%] of **4**
1/**2a**	1:1	*a*)	Pd^{II}	10 (**3a**)	3 (**4a**)
1/**2a**	1:2	*b*)	Pd^{0}	not det. (**3a**)	58 (**4a**)
1/**2b**	1:1	*a*)	Pd^{II}	73 (**3b**)	5 (**4b**)
1/**2b**	1:2	*b*)	Pd^{0}	not det. (**3b**)	90 (**4b**)

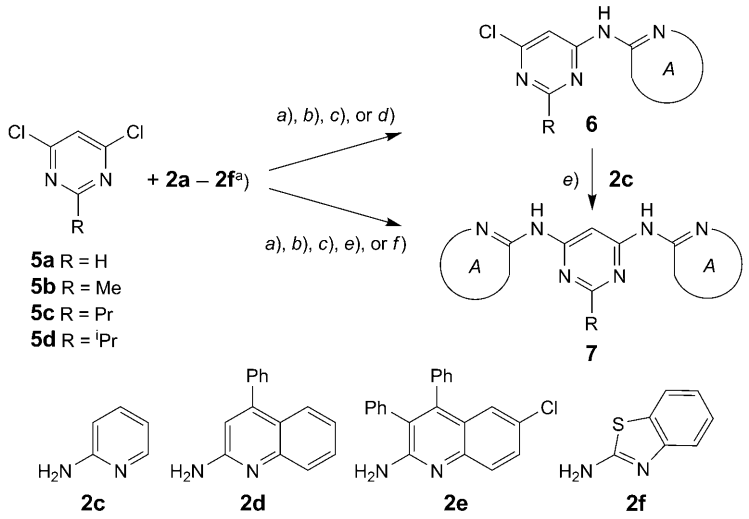
[a]) Reaction conditions: *a*) >9 equiv. of carbonate, Pd^{II} salt, chelating phosphine, toluene (reflux). *b*) 1–3 equiv. of alkoxide, Pd^{0} complex, chelating phosphine, toluene (reflux).

findings to the mono- and diamination of 4,6-dichloropyrimidines **5a**–**5d** with several heteroaren-2-amines **2a**–**2f** (*Table 2*) to obtain the 4,6-disubstituted pyrimidines **7a**–**7i**. The used catalyst loadings were typically between 2 and 6 mol-%. Higher loadings were only applied when necessary for completion of the individual reaction. The phosphine/Pd ratio was chosen to be 1.5 or higher to increase the amount of the BINAP-stabilized catalytically active Pd^{0} complex, to compensate partial phosphine oxidation, and to inhibit complexation of Pd by reactants and products, which is the most critical issue.

At elevated temperatures, the pyrimidine moiety is sensitive to strong bases such as the alkoxides, which are commonly used in the standard *Buchwald–Hartwig*-amination protocols. Therefore, it was necessary to decrease the amount of base or substitute alkoxides by the milder carbonates for both the mono- and the desirable diamination. In general, the monoamination products **6** were obtained in moderate to good yields when using Pd^{II} sources for the catalyst and equimolar reactant ratios, whereas the diamination products **7** for many combinations of substrates required Pd^{0} sources (*Table 2*). In some cases, the diaminated products could also be isolated in moderate to good yields by using Pd^{II} sources; however, higher catalyst loadings were necessary in these reactions. With Pd^{0} sources, the diaminated products were also obtained in a mixture with the monoaminated products when the amine reactants were used in substoichiometric amounts[1]). Thus, the diaminated products could be obtained

[1]) The yields of the (2:1)-condensation products given in *Tables 1–3* are calculated on the basis of the amount of the limiting reactant when the reactants' ratio was 1:1. Thus, the effective yields of the diaminated products are always significantly higher (up to a factor of 2, when no monoaminated product is formed at all).

Table 2. *Mono-* vs. *Diamination of 4,6-Dichloropyrimidines* **5a**–**5d** *with Heteroaren-2-amines* **2a**–**2f**: *Reaction Conditions and Yields of Mono- and Diaminated Products* **6** *and* **7**, *respectively*



Reactants[a])	Approx. ratio	Reaction conditions[b])	Pd Source	Yield [%] of **6**	Yield [%] of **7**
5a/**2a**	1:1	*a*)	Pd^0	69 (**6a**)	not det. (**7a**)
5a/**2a**	1:2	*a*)	Pd^0	not det. (**6a**)	31 (**7a**)
5a/**2b**	1:1	*a*)	Pd^0	75 (**6b**)	not det. (**7b**)
5a/**2b**	1:2	*a*)	Pd^0	not det. (**6b**)	66 (**7b**)
5b/**2b**	1:0.8	*b*)	Pd^0	29 (**6c**)	36 (**7c**)
5b/**2b**	1:2	*c*)	Pd^{II}	not det. (**6c**)	75 (**7c**)
5a/**2c**	1:1	*d*)	Pd^{II}	41 (**6d**)	not det. (**7d**)
5a/**2c**	1:2	*e*)	Pd^0	not det. (**6d**)	82 (**7d**)
6d/**2c**	1:1	*e*)	Pd^0	n/a (**6d**)	52 (**7d**)
5a/**2d**	1:2	*d*)	Pd^{II}	38 (**6e**)	not det. (**7e**)
5a/**2d**	1:2	*f*)	Pd^0	not det. (**6e**)	81 (**7e**)
5d/**2e**	1:2	*a*)	Pd^0	not det. (**6f**)	86 (**7f**)
5a/**2f**	1:2	*c*)	Pd^{II}	not det. (**6g**)	77 (**7g**)
5b/**2f**	1:1	*c*)	Pd^{II}	30 (**6h**)	10 (**7h**)
5c/**2f**	1:2	*d*)	Pd^{II}	67 (**6i**)	27 (**7i**)

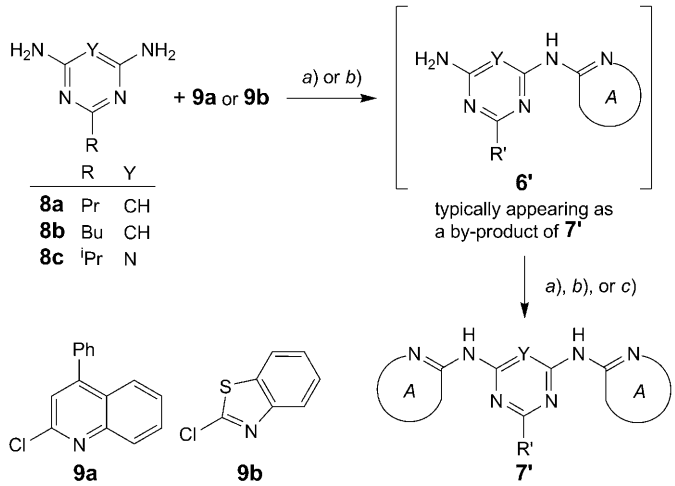
[a]) For the formulas of **2a** and **2b**, see *Table 1*. [b]) Reaction conditions: *a*) >9 equiv. of carbonate, Pd^0 complex, chelating phosphine, toluene (reflux). *b*) 2–6 equiv. of carbonate, Pd^0 complex, chelating phosphine, dioxane (reflux). *c*) 2–6 equiv. of carbonate, Pd^{II} salt, chelating phosphine, dioxane (reflux). *d*) 1–5 equiv. of carbonate, Pd^{II} salt, chelating phosphine, toluene (reflux). *e*) >9 equiv. of carbonate, Pd^{II} salt, chelating phosphine, toluene (reflux). *c*) 1–3 equiv. of alkoxide, Pd^{II} salt, chelating phosphine, toluene (reflux).

in reasonably high yields by using Pd^0 sources and excess of amine reactants and base.

When reversing the reactant functionality by conducting the 1:1 and 2:1 condensation of the pyrimidine-4,6-diamines **8a**–**8c** with the 2-chloroheteroarenes **9a**

and **9b**, different results regarding the yields of mono- *vs.* diaminated products were obtained (*Table 3*). In these cases, the monoaminated products were only observed as intermediates during reaction when using Pd^0 sources or in a mixture with the diaminated products when using Pd^{II} sources. This fact was nearly independent of the excess of the chlorinated reactants **9**. We interprete this as a consequence of the reactivity of the heteroarenediamines **8**, which is not decreased after monoamination. Hence, it is not necessary to activate a second C–Cl bond in the pyrimidine moiety for further reaction as it is in case of the nonreversed reactant functionality as described above.

Table 3. *Reversed Reactant Functionality: Reaction Conditions and Yields of Mono- and Diaminated Products* **6′** *and* **7′**, *respectively*



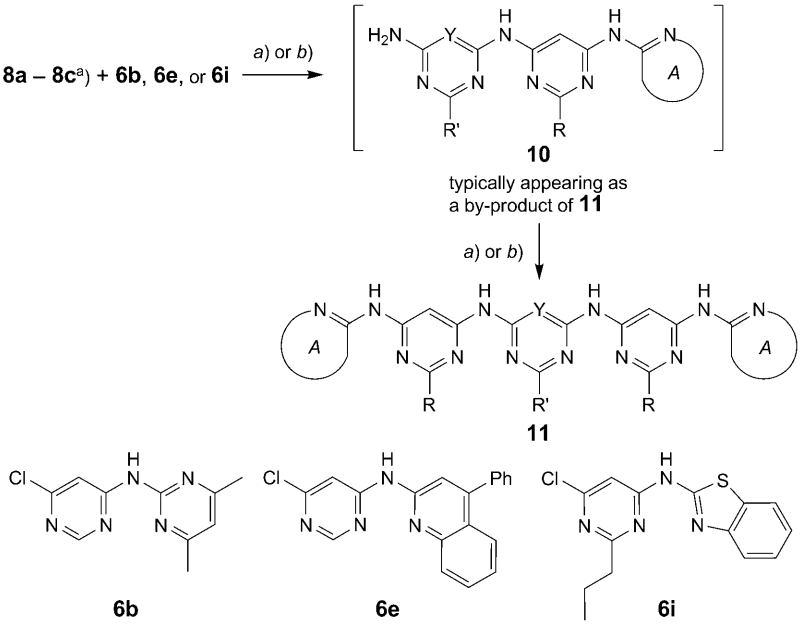
Reactants	Approx. ratio	Reaction conditions[a])	Pd Source	Yield [%] of **6′**	Yield [%] of **7′**
8a/9a	1 : 1	*a*)	Pd^{II}	18 (**6′k**)	41 (**7′k**)
8a/9a	1.2 : 1	*b*)	Pd^0	not det. (**6′k**)	53 (**7′k**)
8b/9a	1 : 1	*c*)	Pd^{II}	not det. (**6′l**)	44 (**7′l**)
8c/9a	1 : 2	*b*)	Pd^0	not det. (**6′m**)	83 (**7′m**)
8a/9b	1 : 1	*c*)	Pd^{II}	17[b]) (**6′n**)	12 (**7′n** $\hat{=}$ **7i**)
8c/9b	1 : 2	*c*)	Pd^{II}	22 (**6′o**)	9 (**7′o**)

[a]) Reaction conditions: *a*) 1–5 equiv. of carbonate, Pd^{II} salt, chelating phosphine, toluene (reflux). *b*) > 9 equiv. of carbonate, Pd^0 complex, chelating phosphine, toluene (reflux). *c*) > 9 equiv. of carbonate, Pd^{II} salt, chelating phosphine, toluene (reflux). [b]) Compound **6′n** was also obtained, in 56% yield, by reacting the bifunctional 6-chloropyrimidin-4-amine with **2f** (1 : 1 ratio) under condition *c*).

The results of the reversed reactant functionality were applied for the syntheses of the 'pentamers' **11a**–**11d** (*Table 4*) by using a Pd^0 source and excess of the dichloroheteroarene reactants **6b**, **6e**, and **6i**.

For the stepwise syntheses of the 'heptamer' **14** (*Table 5*), a comparatively inefficient Pd^{II} source (instead of a Pd^0 source as discussed above) was used to avoid

Table 4. *Amination of the Chlorinated Diheteroarylamines* **6b**, **6e**, *and* **6i** *with Pyrimidine-4,6-diamines* **8a** *and* **8b** *or Triazine-2,4-diamine* **8c**: *Reaction Conditions and Yields of Mono- and Diaminated Products* **10** *and* **11**, *respectively*



Reactants	Approx. ratio	Reaction conditions[b])	Pd Source	Yield [%] of **10**	Yield [%] of **11**
8a/**6b**	1 : 2	*a*)	Pd^0	47 (**10a**)	33 (**11a**)
8b/**6e**	1 : 1.7	*a*)	Pd^0	30 (**10b**)	48 (**11b**)
8b/**6i**	1 : 2	*a*)	Pd^0	not det. (**10c**)	46 (**11c**)
8c/**6b**	1 : 2	*a*) or *b*)	Pd^0	5 (**10d**)	23 (**11d**)

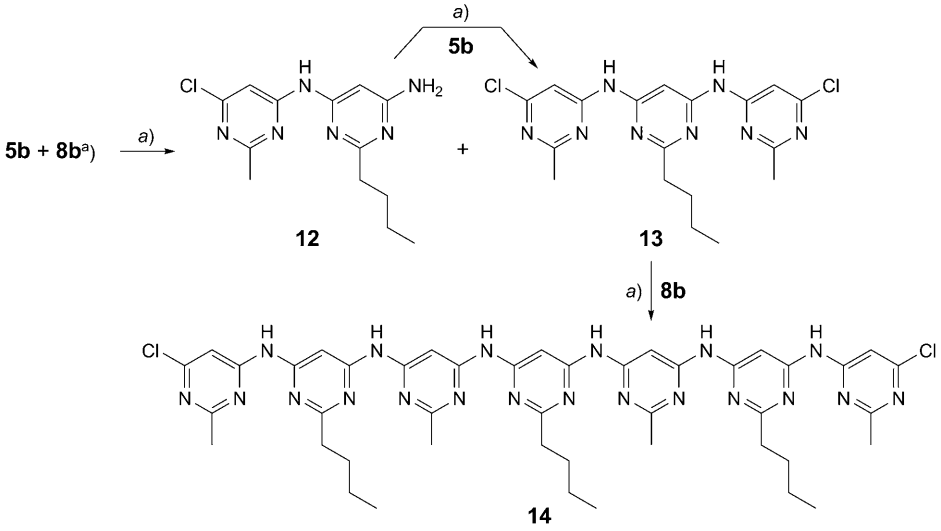
[a]) For the formulas of **8a**–**8c**, see *Table 3*. [b]) Reaction conditions: *a*) >9 equiv. of carbonate, Pd^0 complex, chelating phosphine, toluene (reflux). *b*) 1–3 equiv. of alkoxide, Pd^0 complex, chelating phosphine, toluene (reflux).

side reactions or uncontrolled oligomerization. For the synthesis of **14**, Ph_3P was added to the catalyst mixture to avoid partial BINAP oxidation.

The solubilities of the 'oligomers' **11** and **14** were increased by using the 2-alkylated pyrimidine reactants **5b**–**5d**, **6i**, and **8a**–**8c**. The crude product mixtures were washed carefully with H_2O before drying and subsequent purification because of the adsorption of the products on the heterogeneous base. To our surprise, the wastage of the Pd catalyst by the formation of Pd chelates with the ligands described in this work was not a problem. In contrast to this finding, we isolated and characterized Pd complexes containing a 2 : 1 ratio of the bidentate diheteroarylamine ligands and the metal from Pd-catalyzed syntheses with quinolin-2-amines [6].

For all reported products **3**, **4**, **6**, **7**, and **10**–**14**, the temperature- and solvent-dependent tautomer equilibria in neutral solution preferably exist on the side of the

Table 5. *Amination of* **5b** *with* **8b** *and Synthesis of the 'Heptamer'* **14**: *Reaction Conditions and Yields of Mono- and Diaminated Products* **12** *and* **13** *or* **14**, *respectively*

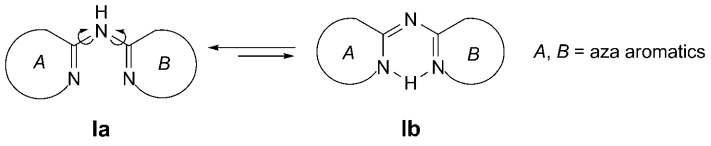


Reactants	Approx. ratio	Reaction conditions[a])	Pd Source	Yield [%] of **12**	Yield [%] of **13** or **14**
5b/**8b**	2 : 1	*a*)	Pd^{II}	23 (**12**)	48 (**13**)
13/**8b**	2 : 1	*a*)	Pd^{II}	not det.	88 (**14**)

[a]) Reaction conditions: *a*) > 9 equiv. of carbonate, Pd^{II} salt, chelating phosphine, toluene (reflux).

tautomers containing central NH bridges. Due to the electron-withdrawing forces of the connected azaaromatics and dependent on the solvent, always minor parts of the systems exist on the side of **Ib** (X = N, *Fig. 1*), as evidenced by a longer-wavelength absorption (*Scheme*).

Scheme. *Tautomers* **Ia** *and* **Ib** *in Neutral Solution*



Monoprotonation of diheteroarylamines results in the formation of the H-chelate structures **IIIa** and *not* of the azacyanine-type structures **IIIb** as it results from alkylation (*Fig. 2*). This structural assignment clearly follows from the UV/VIS spectra of the derivatives **III** with $A = B$, showing the characteristic differences for the $S_0 \rightarrow S_1$ transition which are typical for C_{2v} and C_s symmetry of the chromophoric systems, respectively [3]. Spectra/structure correlations and a detailed discussion of the tautomeric species occurring by protonation of oligo-bidentate compounds will be presented elsewhere [19].

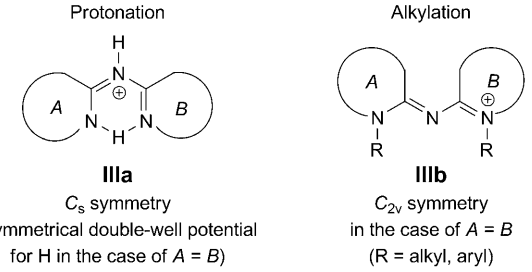


Fig. 2. *Comparison of the protonated species* **IIIa** *with the corresponding* N,N′*-dialkylated azacyanine-type species* **IIIb**

Summary. – When conducting Pd-catalyzed aminations of dichloropyridines or dichloropyrimidines with heteroarenamines, the (1:1)-condensation products were preferably formed when using Pd^{II} sources, nearly independent of the reactant ratio. However, the (2:1)-condensation products could be obtained in reasonably high yields by using Pd^0 sources. When reversing the reactant functionality, the monoamination products were only observed as intermediates during reaction when using Pd^0 sources or in a mixture with the diamination products when using Pd^{II} sources.

Experimental Part

General. All catalysts were purchased from commercial sources and used without further purification. Toluene was distilled on sodium/benzophenone before use. Flash chromatography (FC): *Merck* silica gel *60* (63–200 μm), if not otherwise noted. UV/VIS Spectra: *Varian-Cary-50* spectrometer; λ_{max} in nm. ^{1}H-NMR Spectra: *Jeol-GX-400* spectrometer; residual solvent peaks as internal reference; chemical shifts δ rel. to Me_4Si in ppm ($CHCl_3$ in $CDCl_3$ at δ 7.26, (D_5)DMSO in (D_6)DMSO at δ 2.49), coupling constants *J* in Hz. MS: *Finnigan-MAT-312* instrument for EI; *Bruker-Biflex-III* instrument for MALDI TOF, with α-cyano-4-hydroxycinnamic acid (CHCA) as the matrix; in *m*/*z* (rel. %). Elemental analyses: Elemental CHN analyzer *Vario EL*.

Reactants. Compounds **1**, **2a**–**2c**, **2f**, and **8c** were purchased from commercial sources. The other compounds were synthesized as follows: **2d** and **2e** by a modified protocol [20][21] as described in detail in [6], **5a** as described in [4][6][22], **5b**–**5d** by optimized procedures as described in [4][23], and **8a**–**8d** and **9b** as described in [24–26].

4-Phenylquinolin-2-amine (**2d**). NaH (6.2 g, 0.26 mol) was added to pyridine (400 ml) at r.t. under N_2, then MeCN (21.1 g, 0.52 mol) was added dropwise followed by 2-aminobenzophenone (=(2-aminophenyl)phenylmethanone; 34.1 g, 0.17 mol). The mixture was stirred and heated to 100° for 20 h. After quenching with ice water, the precipitate was washed with dist. H_2O, digested with MeOH, and dried *in vacuo:* 33.5 g (88%) of **2d**. UV/VIS (MeOH): 340. ^{1}H-NMR ($CDCl_3$, 25°): 7.73 (*dd*, *J* = 8.3, 1.2, H–C(8)); 7.66 (*dd*, *J* = 8.3, 1.2, H–C(5)); 7.56 (*dt*, *J* = 8.3, 1.5, H–C(7)); 7.21 (*dt*, *J* = 8.3, 1.5, H–C(6)); 6.67 (*s*, H–C(3)); 4.80 (br. *s*, NH_2–C(2)). EI-MS (100°): 220.0 (100). Anal. calc. for $C_{15}H_{12}N_2$: C 81.79, H 5.49, N 12.72; found: C 81.84, H 5.67, N 12.79.

6-Chloro-3,4-diphenylquinolin-2-amine (**2e**). As described for **2d**, with NaH (5.9 g, 0.25 mol), pyridine (300 ml), phenylacetonitrile (83.8 g, 0.49 mol), and 2-amino-6-chlorobenzophenone (=(2-amino-6-chlorophenyl)phenylmethanone; 37.7 g, 0.16 mol): 36.2 g of crude **2d**. Purification by vacuum sublimation gave 18.1 g (35%) of **2e**. UV/VIS (MeOH): 345. ^{1}H-NMR ($CDCl_3$, 25°): 7.65 (*d*, *J* = 9.0, H–C(8)); 7.48 (*dd*, *J* = 8.9, 2.2, H–C(7)); 7.29 (*d*, *J* = 2.4, H–C(5)); 7.28–7.18 (*m*, 6 arom. H (H_m and H_p

of 2 Ph); 7.15–7.06 (*m*, 4 arom. H (H_o of 2 Ph)); 4.86 (br. *s*, NH_2–C(2)). EI-MS (120°): 330.2 (100). Anal. calc. for $C_{21}H_{15}ClN_2$: C 76.24, H 4.57, N 8.47; found: C 76.28, H 4.55, N 8.50.

2-Chloro-4-phenylquinoline (**9a**). This compound was obtained by chlorination of 4-phenylquinoline-2(1*H*)-one (28.1 g, 0.12 mol) with PCl_5 (29.8 g, 0.15 mol) in PhCl (100 ml) for 60 min at 120°: 21.1 g (70%) of **9a**. UV/VIS (MeOH): 295. ^{1}H-NMR ($CDCl_3$, 25°): 8.09 (*dd*, *J* = 8.6, 0.5, H–C(8)); 7.88 (*dd*, *J* = 8.6, 1.0, H–C(5)); 7.74 (*dt*, *J* = 7.8, 1.5, H–C(7)); 7.47–7.57 (*m*, H–C(6), Ph); 7.35 (*s*, H–C(3)). EI-MS (60°): 241.0 (41). Anal. calc. for $C_{15}H_{10}ClN$: C 75.16, H 4.21, N 5.84; found: C 75.15, H 4.20, N 5.91.

Ligands. Typical procedure for the Pd-catalyzed amination of dichloroheteroarenes with heteroarenamines and for the amination of chloroheteroarenes with heteroarenediamines; for conditions, see *Tables 1–5:* The reactants, base, palladium source, and chelating phosphine were refluxed (if not otherwise noted) in toluene or in dioxane, resp. (*Tables 1–5*). After cooling, the precipitate was filtered off, dried under reduced pressure, and washed properly with H_2O to remove inorganic components. The combined dried org. phase was concentrated and the residue purified by FC, recrystallization, digestion, or vaccum sublimation as noted.

N^2-*(6-Chloropyridin-2-yl)pyrimidin-2-amine* (**3a**). Condition *a*), *Table 1*: **1** (5.96 g, 40 mmol), **2a** (4.22 g, 45 mmol), K_2CO_3 (92 g, 0.67 mol), [$Pd(OAc)_2$] (0.15 g, 0.67 mmol, 1.7 mol-%), and BINAP (0.62 g, 0.99 mmol, 2.5 mol-%). Purification by vacuum sublimation yielded 0.84 g (10%) of **3a**[2]). UV/VIS (MeCN): 302. ^{1}H-NMR ($CDCl_3$, 25°): 9.01 (br. *s*, NH–C(2)); 8.60 (*d*, *J* = 4.9, H–C(4), H–C(6)); 8.35 (*d*, *J* = 8.3, H–C(3′)); 7.66 (*dd*, *J* = 8.3, 7.8, H–C(4′)); 6.99 (*d*, *J* = 7.8, H–C(5′)); 6.92 (*t*, *J* = 4.9, H–C(5)).

N^2,N^6-*Dipyrimidin-2-ylpyridine-2,6-diamine* (**4a**). Condition *b*), *Table 1*: **1** (2.5 g, 17 mmol), **2a** (3.54 g, 38 mmol), ^{t}BuONa (3.57 g, 38 mmol), [$Pd(dba)_2$] (0.26 g, 0.9 mmol, 5.2 mol-%), and BINAP (0.73 g, 1.4 mmol, 8.2 mol-%). Purification by recrystallization from 1,2-dichlorobenzene yielded 2.60 g (58%) of **4a**. UV/VIS (MeOH): 307. ^{1}H-NMR ($CDCl_3$, 25°): 9.82 (br. *s*, NH–C(2), NH–C(6)); 8.53 (*d*, *J* = 4.9, 4 H, H–C(4′), H–C(6′)); 7.95 (*d*, *J* = 8.3, H–C(3), H–C(5)); 7.66 (*t*, *J* = 8.3, H–C(4)); 6.79 (*t*, *J* = 4.9, 2 H, H–C(5′)). EI-MS (150°): 265.0 (100). Anal. calc. for $C_{13}H_{11}N_7 \cdot 0.2$ 1,2-dichlorobenzene: C 57.88, H 4.04, N 33.27; found: C 56.99, H 4.33, N 33.50.

N^2-*(6-Chloropyridin-2-yl)-4,6-dimethylpyrimidin-2-amine* (**3b**). Condition *a*), *Table 1*: **1** (5.96 g, 40 mmol), **2b** (5.41 g, 44 mmol), K_2CO_3 (92 g, 0.66 mol), [$Pd(OAc)_2$] (0.15 g, 0.67 mmol, 1.7 mol-%), and BINAP (0.62 g, 0.99 mmol, 2.5 mol-%). Purification by vacuum sublimation yielded 6.73 g (73%) of **3b**[3]). EI-MS (80°): 233.8 (100). UV/VIS (MeOH): 292. ^{1}H-NMR ($CDCl_3$, 25°): 8.44 (*d*, *J* = 8.3, H–C(3′)); 7.77 (br. *s*, NH–C(2)); 7.61 (*dd*, *J* = 8.3, 7.8, H–C(4′)); 6.91 (*d*, *J* = 7.8, H–C(5′)); 6.59 (*s*, H–C(5)); 2.39 (*s*, Me–C(4), Me–C(6)). Anal. calc. for $C_{11}H_{11}ClN_4$: C 56.30, H 4.72, N 23.87; found: C 56.49, H 4.98, N 24.00.

N^2,N^6-*Bis(4,6-dimethylpyrimidin-2-yl)pyridine-2,6-diamine* (**4b**). Condition *b*), *Table 1*: **1** (5 g, 34 mmol), **2b** (9.54 g, 74 mmol), ^{t}BuONa (7.14 g, 74 mmol), [$Pd(dba)_2$] (0.56 g, 1 mmol, 3 mol-%), and BINAP (1.47 g, 2.4 mmol, 7.2 mol-%). Purification by recrystallization from toluene yielded 9.80 g (90%) of **4b**. UV/VIS (MeCN): 316. ^{1}H-NMR ($CDCl_3$, 25°): 8.17 (br. *s*, NH–C(2), NH–C(6)); 8.07 (*d*, *J* = 8.1, H–C(3), H–C(5)); 7.67 (*t*, *J* = 8.1, H–C(4)); 6.53 (*s*, 2 H, H–C(5′)); 2.39 (*s*, 12 H, Me–C(4′), Me–C(6′)). EI-MS (160°): 321.1 (100). Anal. calc. for $C_{17}H_{19}N_7$: C 63.53, H 5.96, N 30.51; found: C 63.53, H 6.26, N 30.46.

N^2-*(6-Chloropyrimidin-4-yl)pyrimidin-2-amine* (**6a**). Condition *a*), *Table 2*: **5a** (0.5 g, 3.35 mmol), **2a** (0.32 g, 3.35 mmol), K_2CO_3 (4.6 g, 33.5 mmol), [$Pd(dba)_2$] (0.038 g, 0.066 mmol, 2 mol-%), and BINAP (0.063 g, 0.1 mmol, 3 mol-%). Purification by FC ($CHCl_3$) and subsequent recrystallization from toluene yielded 0.48 g (69%) of **6a**. UV/VIS (MeCN): 270. ^{1}H-NMR ($CDCl_3$, 25°): 9.29 (br. *s*, NH–C(2)); 8.71 (*s*, H–C(2′)); 8.66 (*d*, *J* = 4.9, H–C(4), H–C(6)); 8.56 (*s*, H–C(5′)); 7.00 (*t*, *J* = 4.9, H–C(5)). EI-MS (100°): 206.6 (100).

N^4,N^6-*Dipyrimidin-2-ylpyrimidine-4,6-diamine* (**7a**). Condition *a*), *Table 2*: **5a** (0.5 g, 3.38 mmol), **2a** (0.64 g, 6.7 mmol), K_2CO_3 (9.3 g, 68 mmol), [$Pd(dba)_2$] (0.038 g, 0.06 mmol, 1.8 mol-%), and BINAP (0.063 g, 0.1 mmol, 2.9 mol-%). Purification by vacuum sublimation yielded 0.28 g (31%) of **7a**. UV/VIS (MeCN): 263. ^{1}H-NMR ($CDCl_3$, 25°): 9.39 (*d*, *J* = 1.0, H–C(5)); 8.58 (*d*, *J* = 4.9, 4 H, H–C(4′), H–C(6′));

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[2]) Additionally, 0.30 g (3%) of the diaminated product **4a** was obtained.

[3]) Additionally, 0.58 g (5%) of the diaminated product **4b** was obtained.

8.53 (*d*, *J* = 1.0, H–C(2)); 8.13 (br. *s*, NH–C(4), NH–C(6)); 6.90 (*t*, *J* = 4.9, 2 H, H–C(5′)). EI-MS (200°): 265.8 (100). Anal. calc. for $C_{12}H_{10}N_8$: C 54.13, H 3.79, N 42.08; found: C 53.03, H 3.77, N 40.11.

N^2-*(6-Chloropyrimidin-4-yl)-4,6-dimethylpyrimidin-2-amine* (**6b**). Condition *a*), *Table 2*: **5a** (2.5 g, 15 mmol), **2b** (1.9 g, 15 mmol), K_2CO_3 (23 g, 0.17 mmol), [Pd(dba)$_2$] (0.24 g, 0.45 mmol, 3 mol-%), and BINAP (0.73 g, 1.18 mmol, 7.8 mol-%). Purification by FC ($CHCl_3$) yielded 2.63 g (75%) of **6b**. UV/VIS (MeCN): 270. ^{1}H-NMR ($CDCl_3$, 25°): 8.84 (br. *s*, NH–C(2)); 8.73 (*d*, *J* = 1.0, H–C(2′)); 8.59 (*d*, *J* = 1.0, H–C(5′)); 6.70 (*s*, H–C(5)); 2.46 (*s*, Me–C(4), Me–C(6)). EI-MS (80°): 234.7 (100). Anal. calc. for $C_{10}H_{10}ClN_5$: C 50.96, H 4.28, N 29.72; found: C 50.89, H 4.25, N 29.65.

N^4,N^6-*Bis(4,6-dimethylpyrimidin-2-yl)pyrimidine-4,6-diamine* (**7b**). Condition *a*), *Table 2*: **5a** (5 g, 33.8 mmol), **2b** (9.3 g, 74.4 mmol), K_2CO_3 (93 g, 0.68 mol), [Pd(dba)$_2$] (0.48 g, 0.9 mmol, 2.6 mol-%), and BINAP (1.47 g, 2.36 mmol, 6.9 mol-%). Purification by recrystallization from 1,2-dichlorobenzene yielded 7.2 g (66%) of **7b**. UV/VIS (MeCN): 267. ^{1}H-NMR ((D$_6$)DMSO, 30°): 9.68 (*s*, NH–C(4), NH–C(6)); 9.01 (*d*, *J* = 1.0, H–C(5)); 8.35 (*d*, *J* = 1.0, H–C(2)); 6.81 (*s*, 2 H, H–C(5′)); 2.35 (*s*, 12 H, Me–C(4′), Me–C(6′)). EI-MS (180°): 322.1 (40). Anal. calc. for $C_{16}H_{18}N_8$: C 59.61, H 5.63, N 34.76; found: C 59.56, H 5.67, N 34.66.

N^2-*(6-Chloro-2-methylpyrimidin-4-yl)-4,6-dimethylpyrimidin-2-amine* (**6c**). Condition *b*), *Table 2*: **5b** (2.5 g, 15 mmol), **2b** (1.57 g, 12.5 mmol), Na_2CO_3 (2.67 g, 25 mmol), [Pd(dba)$_2$] (0.28 g, 0.4 mmol, 3.2 mol-%), and BINAP (0.9 g, 1.4 mmol, 11 mol-%). Purification by repeated FC ($CHCl_3$) yielded 0.91 g (29%) of **6c**[4]). UV/VIS (MeCN): 272. ^{1}H-NMR ($CDCl_3$, 25°): 8.37 (*s*, H–C(5′)); 7.96 (br. *s*, NH–C(2)); 6.68 (*s*, H–C(5)); 2.57 (*s*, Me–C(2′)); 2.44 (*s*, Me–C(4), Me–C(6)). EI-MS (80°): 248.7 (100). Anal. calc. for $C_{11}H_{12}ClN_5$: C 52.91, H 4.84, N 28.05; found: C 52.88, H 4.82, N 27.72.

N^4,N^6-*Bis(4,6-dimethylpyrimidin-2-yl)-2-methylpyrimidine-4,6-diamine* (**7c**). Condition *c*), *Table 2*: **5b** (2.5 g, 15 mmol), **2b** (4.5 g, 36.5 mmol), Na_2CO_3 (8.16 g, 85 mmol), [Pd(OAc)$_2$] (0.27 g, 1.2 mmol, 8 mol-%), and BINAP (1.14 g, 2.2 mmol, 14 mol-%). Purification by recrystallization from toluene and subsequent vacuum sublimation yielded 3.78 g (75%) of **7c**. UV/VIS (MeCN): 265. ^{1}H-NMR ((D$_6$)DMSO, 30°): 9.48 (*s*, NH–C(4), NH–C(6)); 8.89 (*s*, H–C(5)); 6.79 (*s*, 2 H–C(5′)); 2.35 (*s*, Me–C(2)); 2.34 (*s*, 12 H, Me–C(4′), Me–C(6′)). EI-MS (140°): 336.7 (61). Anal. calc. for $C_{17}H_{20}N_8$: C 60.70, H 5.99, N 33.31; found: C 61.72, H 5.81, N 29.26.

6-Chloro-N^4*-pyridin-2-ylpyrimidin-4-amine* (**6d**). Condition *d*), *Table 2*: **5a** (2.0 g, 13.5 mmol), **2c** (1.27 g, 13.5 mmol), Na_2CO_3 (2.0 g, 53 mmol), [Pd(OAc)$_2$] (0.12 g, 0.53 mmol, 3.9 mol-%), and BINAP (0.50 g, 0.8 mmol, 5.9 mol-%). Purification by FC ($CHCl_3$) yielded 1.13 g (41%) of **6d**. UV/VIS (MeCN): 300. ^{1}H-NMR ($CDCl_3$, 25°): 8.57 (*d*, *J* = 1.0, H–C(2)); 8.36 (*ddd*, *J* = 4.9, 2.0, 1.0, H–C(6′)); 7.94 (br. *s*, NH–C(4)); 7.91 (*d*, *J* = 1.0, H–C(5)); 7.68 (*dq*, *J* = 8.3, 7.3, 2.0, H–C(4′)); 7.31 (br. *d*, *J* = 8.3, H–C(3′)); 7.01 (*ddd*, *J* = 7.3, 4.9, 1.0, H–C(5′)). EI-MS (150°): 207.8 (20). Anal. calc. for $C_9H_7ClN_4$: C 52.31, H 3.41, N 27.11; found: C 52.46, H 3.36, N 26.82.

N^4,N^6-*Dipyridin-2-ylpyrimidine-4,6-diamine* (**7d**). This compound could be obtained 1) by direct Pd^0-catalyzed diamination of **5a** with **2c** or 2) by stepwise Pd^0-catalyzed amination of the isolated monoamination product **6d** with **2c**.

1) Condition *e*), *Table 2*: **5a** (1 g, 6.75 mmol), **2c** (1.4 g, 14.9 mmol), K_2CO_3 (18.6 g, 134 mmol), [Pd(dba)$_2$] (0.116 g, 0.2 mmol, 3 mol-%), and BINAP (0.25 g, 0.4 mmol, 6 mol-%). Purification by digestion with MeOH yielded 1.48 g (82%) of **7d**.

2) Condition *e*), *Table 2*: **6d** (1 g, 4.84 mmol), **2c** (0.54 g, 5.8 mmol), K_2CO_3 (13.3 g, 96 mmol), [Pd(dba)$_2$] (0.08 g, 0.14 mmol, 2.9 mol-%), and BINAP (0.18 g, 0.29 mmol, 6 mol-%). Purification by digestion with MeOH yielded 0.67 g (52%) of **7d**. UV/VIS (MeCN): 312. ^{1}H-NMR ((D$_6$)DMSO, 30°): 9.84 (*s*, NH–C(4), NH–C(6)); 8.35 (*s*, H–C(5)); 8.26 (*d*, *J* = 5.0, 2 H, H–C(6′)); 8.18 (*s*, H–C(2)); 7.67 (*dd*, *J* = 8.3, 6.8, 2 H, H–C(4′)); 7.62 (*d*, *J* = 8.3, 2 H, H–C(3′)); 6.92 (*dd*, *J* = 6.8, 5.0, 2 H, H–C(5′)). EI-MS (160°): 263.9 (100). Anal. calc. for $C_{14}H_{12}N_6$: C 63.62, H 4.58, N 31.80; found: C 63.07, H 4.48, N 31.48.

N^2-*(6-Chloropyrimidin-4-yl)-4-phenylquinolin-2-amine* (**6e**). Condition *d*), *Table 2*: **2d** (7.13 g, 32 mmol), **5a** (2.4 g, 16 mmol), Na_2CO_3 (5.4 g, 51 mmol), [Pd(OAc)$_2$] (0.28 g, 1.2 mmol, 7.5 mol-%), and DPEPhos (= bis[2-(diphenylphosphino)phenyl] ether; 0.88 g, 1.6 mmol, 10 mol-%). Purification by digestion with EtOH and subsequent FC ($CHCl_3$) yielded 2.0 g (38%) of **6e**. UV/VIS (MeCN): 345.

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[4]) Additionally, 1.52 g (36%) of the diaminated product **7c** was obtained.

^{1}H-NMR ($CDCl_3$, 25°): 8.68 (*s*, NH–C(2)); 8.60 (*d*, *J* = 0.7, H–C(2′)); 8.03 (br. *d*, *J* = 8.3, H–C(8)); 7.89 (*d*, *J* = 0.7, H–C(5′)); 7.80 (br. *d*, *J* = 8.3, H–C(5)); 7.71 (*ddd*, *J* = 8.3, 7.1, 1.5, H–C(7)); 7.57–7.48 (*m*, Ph–C(4)); 7.40 (*ddd*, *J* = 8.3, 7.1, 1.2, H–C(6)); 7.09 (*s*, H–C(3)). EI-MS (180°): 332.1 (100). Anal. calc. for $C_{19}H_{13}ClN_4$: C 68.57, H 3.94, N 16.84; found: C 68.47, H 4.19, N 16.54.

N^4,N^6-*Bis(4-phenylquinolin-2-yl)pyrimidine-4,6-diamine* (**7e**). Condition *f*), *Table 2*: **2d** (3.8 g, 17 mmol), **5a** (1.3 g, 8.7 mmol), ^{t}BuONa (2.3 g, 24 mmol), [Pd(dba)$_2$] (0.28 g, 0.49 mmol, 5.7 mol-%), and BINAP (0.32 g, 0.5 mmol, 5.9 mol-%). Purification by FC ($CHCl_3$) and subsequent vacuum sublimation yielded 3.58 g (81%) of **7e**. UV/VIS (MeCN): 352. ^{1}H-NMR ((D$_6$)DMSO, 30°): 10.40 (*s*, NH–C(4), NH–C(6)); 9.42 (*d*, *J* = 0.7, H–C(5)); 8.45 (*d*, *J* = 0.7, H–C(2)); 7.94 (br. *d*, *J* = 8.5, 2 H, H–C(8′)); 7.69 (br. *d*, *J* = 8.5, 2 H, H–C(5′)); 7.65 (*s*, 2 H, H–C(3′)); 7.65 (*ddd*, *J* = 8.5, 7.1, 1.0, 2 H, H–C(7′)); 7.6–7.5 (*m*, 10 H, Ph–C(4′)); 7.40 (*ddd*, *J* = 8.5, 7.1, 1.0, 2 H, H–C(6′)). EI-MS (280°): 516.1 (70). Anal. calc. for $C_{34}H_{24}N_6$: C 79.05, H 4.68, N 16.27; found: C 79.09, H 4.76, N 15.44.

N^4,N^6-*Bis(6-chloro-3,4-diphenylquinolin-2-yl)-2-isopropylpyrimidine-4,6-diamine* (**7f**). Condition *a*), *Table 2*: **2e** (4.82 g, 14.6 mmol), **5d** (1.35 g, 7.1 mmol), K_2CO_3 (9.3 g, 67 mmol), [Pd(dba)$_2$] (0.27 g, 0.47 mmol, 6.6 mol-%), and BINAP (0.33 g, 0.53 mmol, 7.4 mol-%). Purification by digestion with toluene and subsequent recrystallization from 1,2-dichlorobenzene yielded 4.83 g (86%) of **7f**. UV/VIS (MeCN): 359. ^{1}H-NMR ((D$_6$)DMSO, 50°): 9.82 (*s*, H–C(5)); 7.90 (*d*, *J* = 9.0, 2 H, H–C(8′)); 7.75 (*dd*, *J* = 8.8, 2.4, 2 H, H–C(7′)); 7.40–7.22 (*m*, 24 H, NH–C(4), NH–C(6), H–C(5′), Ph–C(3′), Ph–C(4′)); 2.67 (*sept.*, *J* = 6.8, Me$_2$C*H*); 1.01 (*d*, *J* = 6.8, *Me*$_2$CH). MALDI-MS: 778.9 (100).

N^4,N^6-*Bis(benzothiazol-2-yl)pyrimidine-4,6-diamine* (**7g**). Condition *c*), *Table 2*: **5a** (2.0 g, 13.5 mmol), **2f** (4.04 g, 27 mmol), Na_2CO_3 (5.4 g, 50 mmol), [Pd(OAc)$_2$] (0.24 g, 1 mmol, 7.9 mol-%), and BINAP (1.06 g, 1.7 mmol, 12.6 mol-%). Purification by recrystallization from 1,2-dichlorobenzene yielded 3.91 g (77%) of **7g**. UV/VIS (MeOH): 328. ^{1}H-NMR ((D$_6$)DMSO, 30°): 11.87 (*s*, NH–C(4), NH–C(6)); 8.69 (*d*, *J* = 0.7, H–C(2)); 7.92 (*d*, *J* = 7.6, 2 H, H–C(4′)); 7.67 (*d*, *J* = 8.1, 2 H, H–C(7′)); 7.40 (*ddd*, *J* = 8.1, 7.1, 1.2, 2 H, H–C(6′)); 7.24 (*ddd*, *J* = 7.6, 7.1, 1.0, 2 H, H–C(5′)); 7.08 (br. *s*, H–C(5)). EI-MS (320°): 376.1 (100). Anal. calc. for $C_{18}H_{12}N_6S_2$: C 57.43, H 3.21, N 22.32; found: C 57.04, H 3.30, N 22.02.

N^2-*(6-Chloro-2-methylpyrimidin-4-yl)benzothiazol-2-amine* (**6h**) *and* N^4,N^6-*Bis(benzothiazol-2-yl)-2-methylpyrimidine-4,6-diamine* (**7h**). Condition *c*), *Table 2*: **5b** (2.5 g, 15 mmol), **2f** (2.2 g, 15 mmol), Na_2CO_3 (5.45 g, 51 mmol), [Pd(OAc)$_2$] (0.14 g, 0.6 mmol, 4 mol-%), and BINAP (0.57 g, 0.9 mmol, 6 mol-%). Separation by FC ($CHCl_3$) yielded 1.36 g (30%) of **6h** and 0.60 g (10%) of **7h**.

Data of **6h**: UV/VIS (MeCN): 311. ^{1}H-NMR ((D$_6$)DMSO, 30°): 12.10 (br. *s*, NH–C(2)); 7.96 (*d*, *J* = 7.6, H–C(4)); 7.70 (*d*, *J* = 8.1, H–C(7)); 7.41 (*ddd*, *J* = 8.1, 7.3, 1.2, H–C(6)); 7.26 (*ddd*, *J* = 8.1, 7.3, 1.2, H–C(5)); 7.05 (*s*, H–C(5′)); 2.59 (*s*, Me–C(2′)). EI-MS (150°): 275.8 (100). Anal. calc. for $C_{12}H_9ClN_4S$: C 52.08, H 3.28, N 20.24; found: C 51.58, H 3.47, N 19.76.

Data of **7h**: UV/VIS (MeCN): 326. ^{1}H-NMR ((D$_6$)DMSO, 30°): 11.78 (br. *s*, NH–C(4), NH–C(6)); 7.92 (*d*, *J* = 7.8, 2 H, H–C(4′)); 7.66 (*d*, *J* = 8.1, 2 H, H–C(7′)); 7.38 (*ddd*, *J* = 8.3, 8.1, 1.0, 2 H, H–C(6′)); 7.22 (*dd*, *J* = 8.3, 7.8, 2 H, H–C(5′)); 6.82 (*s*, H–C(5)); 2.62 (*s*, Me–C(2)). EI-MS (300°): 390.3 (100). Anal. calc. for $C_{19}H_{14}N_6S_2 \cdot 0.2\ CHCl_3$: C 55.65, H 3.45, N 20.28; found: C 56.32, H 3.75, N 20.91.

N^2-*(6-Chloro-2-propylpyrimidin-4-yl)benzothiazol-2-amine* (**6i**) *and* N^4,N^6-*Bis(benzothiazol-2-yl)-2-propylpyrimidine-4,6-diamine* (**7i** ≙ **7′n**). Condition *d*), *Table 2*: **5c** (1.93 g, 10 mmol), **2f** (3.04 g, 20 mmol), Na_2CO_3 (4.15 g, 39 mmol), [Pd(OAc)$_2$] (0.18 g, 0.8 mmol, 8 mol-%), and BINAP (0.75 g, 1.2 mmol, 12 mol-%) After FC ($CHCl_3$), purification by recrystallization from 1,2-dichlorobenzene yielded 2.05 g (67%) of **6i** and 1.14 g (27%) of **7i**.

Data of **6i**: UV/VIS (MeCN): 310. ^{1}H-NMR ((D$_6$)DMSO, 30°): 12.11 (br. *s*, NH–C(2)); 7.97 (*d*, *J* = 7.8, H–C(4)); 7.71 (*d*, *J* = 8.1, H–C(7)); 7.41 (*ddd*, *J* = 8.1, 7.1, 1.0, H–C(6)); 7.27 (*ddd*, *J* = 7.8, 7.1, 1.2, H–C(5)); 7.03 (*s*, H–C(5′)); 2.83 (*t*, *J* = 7.3, MeCH$_2$C*H*$_2$); 1.88 (*sext.*, *J* = 7.3, MeC*H*$_2$CH$_2$); 0.97 (*t*, *J* = 7.3, *Me*CH$_2$CH$_2$). EI-MS (150°): 303.9 (100). Anal. calc. for $C_{14}H_{13}ClN_4S$: C 55.17, H 4.30, N 18.38; found: C 55.51, H 4.36, N 18.21.

Data of **7i**: MALDI-MS: 419.0 (100). UV/VIS (MeCN): 327. ^{1}H-NMR ((D$_6$)DMSO, 80°): 11.57 (br. *s*, NH–C(4), NH–C(6)); 7.90 (*d*, *J* = 7.6, 2 H, H–C(4′)); 7.66 (*d*, *J* = 8.1, 2 H, H–C(7′)); 7.38 (*ddd*, *J* = 8.1, 7.3, 1.2, 2 H, H–C(6′)); 7.22 (*ddd*, *J* = 8.1, 7.3, 1.2, 2 H, H–C(5′)); 6.88 (*s*, H–C(5)); 2.90 (*t*, *J* = 7.3, MeCH$_2$C*H*$_2$); 2.03 (*sext.*, *J* = 7.3, MeC*H*$_2$CH$_2$); 1.05 (*t*, *J* = 7.3, *Me*CH$_2$CH$_2$). EI-MS (300°): 418.2 (100). Anal. calc. for $C_{21}H_{18}N_6S_2$: C 60.26, H 4.33, N 20.08; found: C 61.03, H 5.05, N 19.40.

N^4-*(4-Phenylquinolin-2-yl)-2-propylpyrimidine-4,6-diamine* (**6′k**). Condition *a*), *Table 3*: **9a** (0.66 g, 2.75 mmol), **8a** (0.50 g, 3.28 mmol), K_2CO_3 (1.05 g, 7.6 mmol), [Pd(OAc)$_2$] (0.017 g, 0.07 mmol, 2.5 mol-%), and BINAP (0.10 g, 0.01 mmol, 5.8 mol-%). Purification by recrystallization from toluene yielded 0.175 g (18%) of **6′k**[5]). UV/VIS (MeCN): 348. ^{1}H-NMR ((D$_6$)DMSO, 80°): 9.58 (br. *s*, NH–C(4)); 7.88 (*dd*, *J* = 8.7, 1.2, H–C(8′)); 7.64 (*ddd*, *J* = 8.7, 7.5, 1.5, H–C(7′)); 7.64 (*dd*, *J* = 8.2, 1.7, H–C(5′)); 7.59–7.48 (*m*, H–C(5), Ph–C(4′)); 7.32 (*ddd*, *J* = 7.8, 7.5, 1.5, 1.2, H–C(6′)); 6.25 (*s*, NH_2–C(6)); 2.49 (*t*, *J* = 7.1, $MeCH_2CH_2$); 1.71 (*sext.*, *J* = 7.3, $MeCH_2CH_2$); 0.89 (*t*, *J* = 7.3, $MeCH_2CH_2$). EI-MS (160°): 355.3 (100).

N^4,N^6-*Bis(4-phenylquinolin-2-yl)-2-propylpyrimidine-4,6-diamine* (**7′k**). Condition *b*), *Table 3*: **9a** (5.0 g, 20.8 mmol), **8a** (2.65 g, 17 mmol), K_2CO_3 (47 g, 340 mmol), [Pd(dba)$_2$] (0.39 g, 0.68 mmol, 4 mol-%), and BINAP (0.63 g, 1 mmol, 5.9 mol-%). Purification by digestion with MeOH yielded 5.12 g (53%) of **7′k**. EI-MS (250°): 558.6 (23). UV/VIS (MeCN): 352. ^{1}H-NMR ((D$_6$)DMSO, 80°): 10.06 (br. *s*, NH–C(4), NH–C(6)); 9.09 (*s*, H–C(5)); 7.94 (*d*, *J* = 8.3, 2 H, H–C(8′)); 7.76 (*s*, 2 H, H–C(3′)); 7.69 (*dd*, *J* = 8.3, 1.2, 2 H, H–C(5′)); 7.63 (*ddd*, *J* = 8.3, 7.6, 1.5, 2 H, H–C(7′)); 7.6–7.5 (*m*, 10 H, Ph–C(4′)); 7.37 (*ddd*, *J* = 8.3, 7.6, 1.5, 2 H, H–C(6′)); 2.67 (*t*, *J* = 7.3, $MeCH_2CH_2$); 1.82 (*sext.*, *J* = 7.3, $MeCH_2CH_2$); 0.94 (*t*, *J* = 7.3, $MeCH_2CH_2$). Anal. calc. for $C_{37}H_{30}N_6$: C 79.54, H 5.41, N 15.04; found: C 79.61, H 5.46, N 14.99.

2-Butyl-N^4,N^6-*bis(4-phenylquinolin-2-yl)pyrimidine-4,6-diamine* (**7′l**). Condition *c*), *Table 3*: **9a** (2.5 g, 10.4 mmol), **8b** (1.75 g, 10.5 mmol), K_2CO_3 (28.2 g, 200 mmol), [Pd(OAc)$_2$] (0.09 g, 0.4 mmol, 3.8 mol-%), and BINAP (0.38 g, 0.6 mmol, 5.7 mol-%). Purification by digestion with MeOH and subsequent recrystallization from toluene yielded 2.67 g (44%) of **7′l**. UV/VIS (CH_2Cl_2): 352. ^{1}H-NMR ((D$_6$)DMSO, 80°): 10.08 (br. *s*, NH–C(4), NH–C(6)); 9.04 (*s*, H–C(5)); 7.94 (*d*, *J* = 8.3, 2 H, H–C(8′)); 7.77 (*s*, 2 H, H–C(3′)); 7.75 (*d*, *J* = 7.8, 2 H, H–C(5′)); 7.63 (*dd*, *J* = 8.3, 7.3, 2 H, H–C(7′)); 7.6–7.5 (*m*, 10 H, Ph–C(4′)); 7.36 (*dd*, *J* = 7.8, 7.3, 2 H, H–C(6′)); 2.67 (*t*, *J* = 7.4, $MeCH_2CH_2CH_2$); 1.74 (*quint.*, *J* = 7.4, $MeCH_2CH_2CH_2$); 1.35 (*sext.*, *J* = 7.4, $MeCH_2CH_2CH_2$); 0.86 (*t*, *J* = 7.4, $MeCH_2CH_2CH_2$). MALDI-MS: 573.1 (100).

N^4,N^6-*Bis(4-phenylquinolin-2-yl)-6-isopropyl-1,3,5-triazine-2,4-diamine* (**7′m**). Condition *b*), *Table 3*: **9a** (3.94 g, 16 mmol), **8c** (1.20 g, 7.8 mmol), K_2CO_3 (21 g, 150 mmol), [Pd(dba)$_2$] (0.09 g, 0.16 mmol, 2.1 mol-%), and BINAP (0.29 g, 0.47 mmol, 6 mol-%). Purification by digestion with toluene and subsequent recrystallization from 1,2-dichlorobenzene yielded 3.66 g (83%) of **7′m**. UV/VIS (MeCN): 340. ^{1}H-NMR ((D$_6$)DMSO, 30°): 10.4 (*s*, NH–C(2), NH–C(4)); 8.30 (*s*, 2 H, H–C(3′)); 7.88 (*d*, *J* = 8.1, 2 H, H–C(8′)); 7.7 (*m*, 4 H, H–C(5′), H–C(6′)); 7.45–7.35 (*m*, 12 H, H–C(7′), Ph–C(4′)); 2.82 (*sept.*, *J* = 6.8, Me_2CH); 1.24 (*d*, *J* = 6.8, Me_2CH). EI-MS (250°): 559.6 (27). Anal. calc. for $C_{36}H_{29}N_7$: C 77.26, H 5.22, N 17.52; found: C 77.13, H 5.28, N 17.54.

N^4-*(Benzothiazol-2-yl)-2-propylpyrimidine-4,6-diamine* (**6′n**). 1) Condition *c*), *Table 3*: **9b** (2.53 g, 15 mmol), **8a** (2.5 g, 16 mmol), K_2CO_3 (41 g, 290 mmol), [Pd(OAc)$_2$] (0.13 g, 0.44 mmol, 2.9 mol-%), and BINAP (0.55 g, 0.88 mmol, 5.9 mol-%). Purification by FC ($CHCl_3$) and subsequent vacuum sublimation yielded 0.71 g (17%) of **6′n**[6]).

2) Same condition as in 1), with 6-chloropyrimidin-4-amine (1.98 g, 11.5 mmol), **2f** (1.90 g, 12.6 mmol), K_2CO_3 (31 g, 220 mmol), $PdCl_2$ (0.06 g, 0.35 mmol, 3 mol-%), and DPEPhos (0.25 g, 0.46 mmol, 4 mol-%). Purification by FC (AcOEt/MeOH 95 : 5, basic Al_2O_3) yielded 1.84 g (56%) of **6′n**. UV/VIS (MeCN): 307. ^{1}H-NMR ((D$_6$)DMSO, 30°): 11.25 (*s*, NH–C(4)); 7.86 (*d*, *J* = 7.8, H–C(4′)); 7.56 (*d*, *J* = 7.8, H–C(7′)); 7.30 (*ddd*, *J* = 7.8, 7.3, 1.0, H–C(6′)); 7.15 (*ddd*, *J* = 7.8, 7.3, 1.0, H–C(5′)); 6.57 (*s*, NH_2–C(6)); 5.91 (*s*, H–C(5)); 2.55 (*t*, *J* = 7.3, $MeCH_2CH_2$); 1.80 (*sext.*, *J* = 7.3, $MeCH_2CH_2$); 0.93 (*t*, *J* = 7.3, $MeCH_2CH_2$). EI-MS (170°): 284.9 (100). Anal. calc. for $C_{14}H_{15}N_5S$: C 58.92, H 5.30, N 24.54; found: C 59.03, H 5.30, N 24.46.

N^2-*(Benzothiazol-2-yl)-6-isopropyl-1,3,5-triazine-2,4-diamine* (**6′o**) *and* N^2,N^4-*Bis(benzothiazol-2-yl)-6-isopropyl-1,3,5-triazine-2,4-diamine* (**7′o**). Condition *c*), *Table 3*: **9b** (2.79 g, 16.5 mmol), **8c** (1.2 g, 7.8 mmol), K_2CO_3 (21.5 g, 156 mmol), [Pd(OAc)$_2$] (0.09 g, 0.4 mmol, 5.1 mol-%), and BINAP (0.29 g, 0.47 mmol, 6 mol-%). After fractionated recrystallization from $CHCl_3$, purification by vacuum sublimation yielded 0.48 g (22%) of **6′o**. UV/VIS (CH_2Cl_2): 301. ^{1}H-NMR ((D$_6$)DMSO, 80°): 11.29 (*s*,

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[5]) Additionally, 0.71 g of a mixture of the monoaminated product **6′k** and the diaminated product **7′k** was obtained from the filtrate.

[6]) Additionally, 0.75 g (12%) of the diaminated product **7′n** (≙ **7i**) was obtained.

NH–C(2)); 7.86 (*d*, *J* = 7.8, H–C(4′)); 7.65 (*d*, *J* = 8.1, H–C(7′)); 7.36 (*dd*, *J* = 8.1, 7.3, H–C(6′)); 7.22 (*dd*, *J* = 7.8, 7.3, H–C(5′)); 7.07 (*s*, NH_2–C(4)); 2.80 (*sept.*, *J* = 6.8, Me_2CH); 1.41 (*d*, *J* = 6.8, Me_2CH). EI-MS (180°): 286.0 (100). Anal. calc. for $C_{13}H_{14}N_6S$: C 54.53, H 4.93, N 29.35; found: C 54.43, H 4.94, N 29.26.

After fractionated crystallization from $CHCl_3$, purification by vacuum sublimation and subsequent digestion with MeOH yielded 0.30 g (9%) of **7′o**. UV/VIS (CH_2Cl_2): 307. ^{1}H-NMR ((D_6)DMSO, 80°): 11.48 (br. *s*, NH–C(2), NH–C(4)); 7.80 (*d*, *J* = 8.3, 2 H, H–C(4′)); 7.59 (*d*, *J* = 8.1, 2 H, H–C(7′)); 7.30 (*dd*, *J* = 8.1, 7.3, 2 H, H–C(6′)); 7.12 (*dd*, *J* = 8.3, 7.3, 2 H, H–C(5′)); 2.92 (*sept.*, *J* = 7.1, Me_2CH); 1.41 (*d*, *J* = 7.1, Me_2CH). EI-MS (300°): 419.2 (100).

N^4*-(6-Amino-2-propylpyrimidin-4-yl)*-N^6*-(4,6-dimethylpyrimidin-2-yl)pyrimidine-4,6-diamine* (**10a**) *and* N^4,N^6*-Bis{6-[(4,6-dimethylpyrimidin-2-yl)amino]pyrimidin-4-yl}-2-propylpyrimidine-4,6-diamine* (**11a**). Condition *a*), *Table 4*: **6b** (2.0 g, 8.5 mmol), **8a** (0.65 g, 4.2 mmol), K_2CO_3 (11.7 g, 85 mmol), [$Pd(dba)_2$] (0.07 g, 0.13 mmol, 3 mol-%), and BINAP (0.16 g, 0.25 mmol, 6 mol-%). Purification by fractionated crystallization from DMF yielded 0.69 g (47%) of **10a** and 0.76 g (33%) of **11a**.

Data of **10a***:* UV/VIS (CH_2Cl_2): 312. EI-MS (150°): 351.5 (100).

Data of **11a***:* UV/VIS (CH_2Cl_2): 312. ^{1}H-NMR ((D_6)DMSO, 80°): 9.85 (br. *s*, 2 H, NH–C(6′)); 9.04 (*s*, NH–C(4), NH–C(6)); 8.40 (*s*, 4 H, H–C(2′), H–C(5′)); 6.79 (*s*, 2 H, H–C(5″)); 2.68 (br. *t*, *J* = 6–7, $MeCH_2CH_2$); 2.40 (*s*, 12 H, Me–C(4″), Me–C(6″)); 1.76 (*sext.*, *J* = 6.8, $MeCH_2CH_2$); 0.90 (*t*, *J* = 6.8, $MeCH_2CH_2$). MALDI-MS: 551.0 (100).

N^4*-(6-Amino-2-butylpyrimidin-4-yl)*-N^6*-(4-phenylquinolin-2-yl)pyrimidine-4,6-diamine* (**10b**) *and 2-Butyl*-N^4,N^6*-bis{6-[(4-phenylquinolin-2-yl)amino]pyrimidin-4-yl}pyrimidine-4,6-diamine* (**11b**). Condition *a*), *Table 4*: **6e** (0.77 g, 2.3 mmol), **8b** (0.23 g, 1.38 mmol), K_2CO_3 (4.3 g, 31 mmol), [$Pd(dba)_2$] (0.024 g, 0.04 mmol, 2.9 mol-%), and BINAP (0.07 g, 0.11 mmol, 7.9 mol-%). Purification by fractionated crystallization from DMF yielded 0.19 g (30%) of **10b** and 0.51 g (48%) of **11b**.

Data of **10b***:* UV/VIS (CH_2Cl_2): 349. MALDI-MS: 463.9 (100).

Data of **11b***:* UV/VIS (CH_2Cl_2): 349. ^{1}H-NMR ((D_6)DMSO, 30°): 10.33 (*s*, NH–C(6′)); 10.30 (*s*, NH–C(4), NH–C(6)); 8.81 (*s*, 2 H, H–C(2′)); 8.50 (*s*, 3 H, H–C(5), H–C(5′)); 8.04 (*d*, *J* = 8.1, 2 H, H–C(8″)); 7.68 (*ddd*, *J* = 8.1, 7.1, 1.0, 2 H, H–C(7″)); 7.66 (*d*, *J* = 8.3, 2 H, H–C(5″)); 7.44 (*s*, 2 H, H–C(3″)); 7.37 (*ddd*, *J* = 8.3, 7.1, 1.0, 2 H, H–C(6″)); 2.72 (*t*, *J* = 7.3, $MeCH_2CH_2CH_2$); 1.69 (*tt*, *J* = 7.8, 7.6, $MeCH_2CH_2CH_2$); 1.17 (*sext.*, *J* = 7.3, $MeCH_2CH_2CH_2$); 0.70 (*t*, *J* = 7.3, $MeCH_2CH_2CH_2$). MALDI-MS: 759.3 (100).

N^4,N^6*-Bis[6-(benzothiazol-2-ylamino)-2-propylpyrimidin-4-yl)-2-butylpyrimidine-4,6-diamine* (**11c**). Condition *a*), *Table 4:* **6i** (0.91 g, 3 mmol), **8b** (0.21 g, 1.3 mmol), K_2CO_3 (3.9 g, 28 mmol), [$Pd(dba)_2$] (0.026 g, 0.024 mmol, 1.5 mol-%), and BINAP (0.15 g, 0.24 mmol, 15 mol-%). Purification by digestion with toluene yielded 0.41 g (46%) of **11c**. UV/VIS (CH_2Cl_2): 325. ^{1}H-NMR ((D_6)DMSO, 80°): 11.59 (br. *s*, 2 H, NH–C(6′)); 9.97 (br. *s*, NH–C(4), NH–C(6)); 7.89 (*d*, *J* = 7.8, 2 H, H–C(4″)); 7.63 (*d*, *J* = 7.8, 2 H, H–C(7″)); 7.61 (*s*, H–C(5)); 7.56 (*s*, 2 H, H–C(5′)); 7.34 (*dd*, *J* = 7.8, 7.6, 2 H, H–C(6″)); 7.19 (*dd*, *J* = 7.8, 7.6, 2 H, H–C(5″)); 2.89 (*t*, *J* = 7.3, $MeCH_2CH_2CH_2$); 2.81 (*t*, *J* = 7.3, $MeCH_2CH_2$); 1.95 (*sext.*, *J* = 7.3, $MeCH_2CH_2$); 1.48 (*sext.*, *J* = 7.3, $MeCH_2CH_2CH_2$); 1.41 (*sext.*, *J* = 7.3, $MeCH_2CH_2CH_2$); 1.02 (*t*, *J* = 7.3, $MeCH_2CH_2$); 0.95 (*t*, *J* = 7.3, $MeCH_2CH_2CH_2$). EI-MS (300°): 701.4 (100).

N^2*-{6-[(4,6-Dimethylpyrimidin-2-yl)amino]pyrimidin-4-yl}-6-isopropyl-1,3,5-triazine-2,4-diamine* (**10d**) *and* N^4,N^6*-Bis{6-[(4,6-dimethylpyrimidin-2-yl)amino]pyrimidin-4-yl}-6-isopropyl-1,3,5-triazine-2,4-diamine* (**11d**). 1) Condition *a*), *Table 4*: **6b** (2.0 g, 8.5 mmol), **8c** (0.62 g, 4.05 mmol), K_2CO_3 (11.7 g, 85 mmol), [$Pd(dba)_2$] (0.15 g, 0.25 mmol, 5.9 mol-%), and BINAP (0.37 g, 0.51 mmol, 12.6 mol-%). 2) Condition *b*), *Table 4*: **6b** (2.36 g, 10 mmol), **8c** (0.77 g, 5 mmol), ^{t}BuONa (1.06 g, 11 mmol), [$Pd(dba)_2$] (0.12 g, 0.2 mmol, 4 mol-%), and BINAP (0.19 g, 0.51 mmol, 6 mol-%). The crude material of both syntheses was combined for workup (1.88 g). Purification by fractionated crystallization from DMF yielded 0.15 g (5%) of **10d** and 1.16 g (23%) of **11d**.

Data of **10d***:* UV/VIS (CH_2Cl_2): 265. EI-MS (150°): 352.3 (13).

Data of **11d***:* UV/VIS (CH_2Cl_2): 264. ^{1}H-NMR ((D_6)DMSO, 80°): 9.65 (br. *s*, NH–C(6′)); 8.93 (*s*, 4 H, NH–C(2), NH–C(4), H–C(2′)); 8.35 (*s*, 2 H, H–C(5′)); 6.65 (*s*, 2 H, H–C(5″)); 2.89 (*sept.*, *J* = 6.8, Me_2CH); 2.22 (*s*, 12 H, Me–C(4″), Me–C(6″)); 1.26 (*d*, *J* = 6.8, Me_2CH). MALDI-MS: 552.3 (100). EI-MS (200°): 551.6 (100). Anal. calc. for $C_{26}H_{29}N_{15}$: C 56.61, H 5.30, N 38.09; found: C 56.47, H 5.33, N 38.05.

2-Butyl-N^4-(6-chloro-2-methylpyrimidin-4-yl)pyrimidine-4,6-diamine (**12**). Condition *b*) at 105°, *Table 5*: **5b** (4.92 g, 30 mmol), **8b** (2.5 g, 15 mmol), K_2CO_3 (14.5 g, 104 mmol), and $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (0.25 g, 0.3 mmol, 2 mol-%; dppf = 1,1′-bis(diphenylphosphino)ferrocene). Purification by FC (petroleum ether/AcOEt 2:1) yielded 1.01 g (23%) of **12**[7]). UV/VIS (MeCN): 294. ^{1}H-NMR ((D$_6$)DMSO, 30°): 10.1 (br. *s*, NH–C(4)); 7.78 (*s*, H–C(5′)); 6.59 (*s*, NH_2–C(6)); 6.47 (*s*, H–C(5)); 2.48 (*t*, *J* = 7.6, $MeCH_2CH_2CH_2$); 2.46 (*s*, Me–C(2′)); 1.64 (*quint.*, *J* = 7.6, $MeCH_2CH_2CH_2$); 1.28 (*sext.*, *J* = 7.6, $MeCH_2CH_2CH_2$); 0.87 (*t*, *J* = 7.4, $MeCH_2CH_2CH_2$). EI-MS (150°): 292.1 (10). Anal. calc. for $C_{13}H_{17}ClN_6$: C 53.33, H 5.85, N 28.71; found: C 53.08, H 5.87, N 28.71.

2-Butyl-N^4,N^6-bis(6-chloro-2-methylpyrimidin-4-yl)pyrimidine-4,6-diamine (**13**). Condition *a*) at 105°, *Table 5*: **5b** (5.28 g, 32 mmol), **8b** (2.5 g, 15 mmol), K_2CO_3 (14.5 g, 104 mmol), and $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (0.33 g, 0.4 mmol, 2.6 mol-%). Purification by digestion with petroleum ether and subsequent FC (petroleum ether/AcOEt 2:1) yielded 3.02 g (48%) of **13**. UV/VIS (MeCN): 309. ^{1}H-NMR ((D$_6$)DMSO, 30°): 10.7 (*s*, NH–C(4), NH–C(6)); 7.90 (*s*, H–C(5)); 7.75 (*s*, 2 H, H–C(5′)); 2.75 (*t*, *J* = 7.6, $MeCH_2CH_2CH_2$); 2.48 (*s*, 6 H, Me–C(2′)); 1.76 (*quint.*, *J* = 7.6, $MeCH_2CH_2CH_2$); 1.37 (*sext.*, *J* = 7.6, $MeCH_2CH_2CH_2$); 0.92 (*t*, *J* = 7.6, $MeCH_2CH_2CH_2$). EI-MS (150°): 420.6 (11). Anal. calc. for $C_{18}H_{20}Cl_2N_8$: C 51.56, H 4.81, N 26.72; found: C 51.40, H 4.85, N 26.66.

2-Butyl-N^4,N^6-bis{6-{[2-butyl-6-[(6-chloro-2-methylpyrimidin-4-yl)amino]pyrimidin-4-yl}amino}-2-methylpyrimidin-4-yl}pyrimidine-4,6-diamine (**14**). Condition *a*) at 105°, *Table 5*: **13** (3.02 g, 7.2 mmol), **8b** (0.53 g, 3.28 mmol), K_2CO_3 (9.05 g, 65 mmol), $Pd(OAc)_2$ (0.04 g, 0.17 mmol, 5.1 mol-%), BINAP (0.08 g, 0.12 mmol, 4 mol-%), and PPh_3 (0.018 g, 0.06 mmol, 2 mol-%). Purification by recrystallization from 1,2-dichlorobenzene yielded 2.67 (88%) of **14**. UV/VIS (MeCN): 319. ^{1}H-NMR ((D$_5$)pyridine, 80°): 11.2–10.4 (3 br. *s*, 6 NH); 8.50 (*s*, H–C(5)); 8.24–8.20 (3*s*, 6 H, H–C(5′), H–C(5″), H–C(5‴)); 2.9–2.8 (br. *m*, 3 $MeCH_2CH_2CH_2$); 2.55, 2.53 (2*s*, 4 Me); 2.0–1.7 (br. *m*, $MeCH_2CH_2CH_2$); 1.5–1.3 (br. *m*, $MeCH_2CH_2CH_2$); 1.0–0.8 (br. *m*, $MeCH_2CH_2CH_2$). MALDI-MS: 931.8 (100). Anal. calc. for $C_{44}H_{52}Cl_2N_{20}$: C 56.71, H 5.62, N 30.06; found: C 56.83, H 5.68, N 30.12.

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7) Additionally, 1.61 g (25%) of the diaminated product **13** was obtained.

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Received April 9, 2010