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Efficient one-pot synthesis of 2,4-di(het)aryl and 2,4-diamino pyrido[3,2-*d*]pyrimidines involving regioselective S_NAr and palladium-catalyzed reactions†

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An efficient and original synthesis of various 2,4-disubstituted pyrido[3,2-*d*]pyrimidines is reported. One-pot di(het)arylation and diamination approaches were used to obtain highly functionalized products in very good yields. The two one-pot processes were compared to their step-by-step related synthesis. Both routes started from 2,4-dichloropyrido[3,2-*d*]pyrimidine **1** and included a chlorine discrimination during the first reaction.

Introduction

In anticancer chemotherapy, the pyridopyrimidine scaffold has generated a great number of biologically active drugs and very promising PDGF, DHFR, p38 MAP kinase, PI3 kinase, tyrosine kinase, adenosine kinase and cyclin-dependant kinases inhibitors.[1–7] However, the pyrido[3,2-*d*]pyrimidine regioisomer is the least described in the literature because of its difficult and expensive syntheses. Recently, our group has developed an original synthesis of 2,4-disubstituted pyrido[3,2-*d*]pyrimidines.[8,9]

We have previously demonstrated that a fully regioselective palladium insertion or S_NAr reaction occurred at the C-4 position of the 2,4-dichloropyrido[3,2-*d*]pyrimidine **1** and also designed, in two distinct steps, 2,4 disubstituted pyrido[3,2-*d*]pyrimidines (Fig. 1).[8,9] Nevertheless, one-pot syntheses including the same type of reaction twice are quite rare.[10]

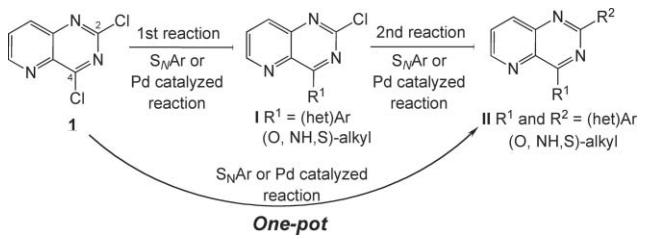
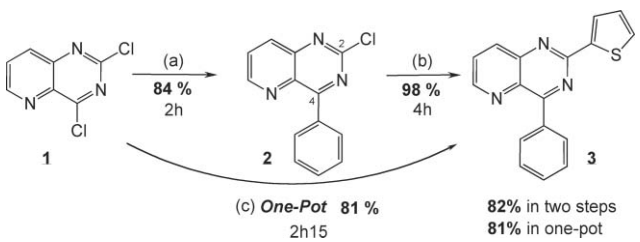


Fig. 1 Step-by-step and one-pot strategies leading to **II** from **1**.

The realization of several reactions in one flask has been attracting greater attention in recent years.[11] However, as a matter of fact, our previous results could be extrapolated to give chemists more attractive methods to synthesize 2,4-di(het)aryl and 2,4-diamino pyrido[3,2-*d*]pyrimidines **II** in a single step.[12] To highlight the usefulness and flexibility of this new process we have used our 2,4-dichloropyrido[3,2-*d*]pyrimidine **1** as a common starting material. A double Suzuki cross-coupling achieved di(het)arylation, and a double S_NAr or S_NAr/Buchwald combination completed the amination reaction panel. The assays described herein were either carried out in an oil bath by classical heating, or under microwave irradiation. This new "one-pot" work offers a useful perspective in heterocyclic functionalization and for the design of original active drugs.

One-pot C-4 and C-2 diarylation by double Suzuki–Miyaura cross-coupling

We initially envisaged the synthesis of 2,4-di(het)aryl-pyrido[3,2-*d*]pyrimidines starting from **1** *via* Suzuki–Miyaura cross-coupling reactions. We have thus recently shown that the 2,4-dichloropyrido[3,2-*d*]pyrimidine **1** reacts with 1 equiv. of phenylboronic acid and then with 2-thiopheneboronic acid to afford the 2,4-unsymmetrically substituted pyrido[3,2-*d*]pyrimidine **3** (Scheme 1, steps (a) and (b)).[9]



Scheme 1 Optimized conditions for a double (het)arylation of **1**. *Reagents and conditions*: (a) $PhB(OH)_2$ 1.05 equiv., $Pd(PPh_3)_4$ 0.05 equiv., K_2CO_3 1.5 equiv., toluene, 100 °C, 2 h; (b) 2-thiopheneboronic acid 1.2 equiv., $Pd(PPh_3)_4$ 0.05 equiv., Na_2CO_3 2.0 equiv., toluene/EtOH (2 : 1), 100 °C, 4 h; (c) $PhB(OH)_2$ 1.05 equiv., K_2CO_3 2.0 equiv., $Pd(OAc)_2$ 0.05 equiv., PPh_3 0.1 equiv., toluene, 100 °C, 2 h then 2-thiopheneboronic acid 1.2 equiv., EtOH (2 : 1), 100 °C, 15 min.

The difference in reactivity of the two chlorine atoms prompted us to attempt an unprecedented one-pot Pd-catalyzed preparation of **3** from **1**. Each step has been independently optimized and unfortunately the conditions demonstrate incompatible differences

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† Electronic supplementary information (ESI) available: Synthesis and ^1H and ^{13}C NMR spectra of compounds **11–20**. See DOI: 10.1039/b913657f

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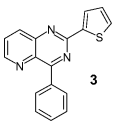
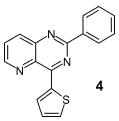
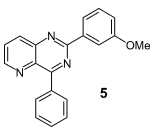
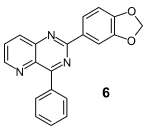
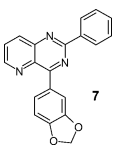
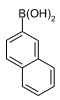
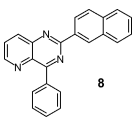
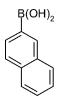
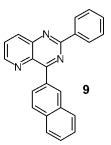
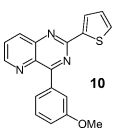
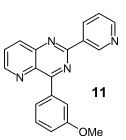
Table 1 One-pot di(het)arylation of compound **1**[13]

Entry	(het)Ar^{1}BOH)$_2$	(het)Ar^{2}B(OH)$_2$	Compound	Step-by-step sequence		One-pot synthesis	
				Time[a]	Yield	Time[a]	Yield
1			 **3**	6 h	82%	2 h 15	81%
2			 **4**	28 h	47%	18 h 20	40%
3			 **5**	8 h	75%	2 h 15	70%
4			 **6**	9 h	82%	2 h 15	75%
5			 **7**	29 h	67%	12 h 15	69%
6			 **8**	6 h	82%	2 h 15	78%
7			 **9**	12 h	69%	3 h 15	75%
8			 **10**	[b]	—	4 h 10	86%
9			 **11**	[b]	—	4 h 30	78%

[a] Global reaction times are reported. [b] Not performed.

(base and solvent) preventing the realization of the two steps in a single flask. Thus, we propose modifications to pursue our new one-pot strategy (Scheme 2, Table 1).

First, compound **2** was prepared using K_2CO_3 and 5 mol% of $Pd(PPh_3)_4$ in toluene at 100 °C.[9] After completion of the reaction (monitored by TLC), the second boronic acid was added but the derivative **3** was isolated after one day in only 42% yield.

Fortunately, introduction of the second boronic acid in EtOH decreased the global reaction time to 3 h and enhanced the yield of **3** to 64%. In each assay, compound **2** is the only other isolated product and its yield fully completed the amount of organic material. With a near stoichiometric amount of reagents, no trace of biphenyl compound was observed, emphasizing the lack of reactivity of the 2-Cl *vs.* the 4-Cl atom. As a last idea, we now

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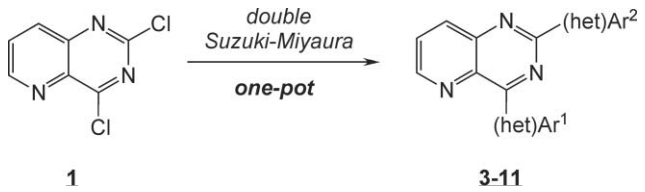


Scheme 2 *Reagents and conditions*: (het)$Ar^1B(OH)_2$ 1.05 equiv., K_2CO_3 2.0 equiv., $Pd(OAc)_2$ 0.05 equiv., PPh_3 0.1 equiv., toluene, 100 °C, then (het)$Ar^2B(OH)_2$ 1.2 equiv., EtOH (2 : 1), 100 °C.

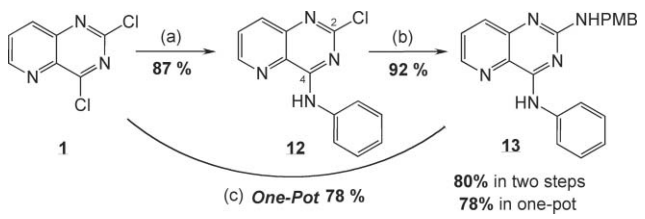
switched the catalyst to the more simple $Pd(OAc)_2/PPh_3$ system at the beginning of the one-pot sequence. The first reaction was regioselectively achieved in only 2 h whereas the second reaction required only a few minutes and compound **3** was isolated in the best yield of 81%.

Other indicators in favour of our new green one-pot methodology include the diminishing of the global reaction time (6 h to 2 h 15), the amount of the catalytic system required (2 × 5% for two independent steps *versus* 5% for a single step) and the production of **3** in fairly good yield by a single purification. Thus, we performed additional assays in order to complete our study (Scheme 2, Table 1). In entries 1–7, we indicated the reaction times and the yields of the two step-by-step and one-pot reactions. Regardless of the chosen method, the attempted 2,4-disubstituted pyrido[3,2-*d*]pyrimidines **3–9** were isolated in quite similar and good yields (69–81%) except compound **4** does not exceed 40% due to its degradation. Interestingly, the one-pot reactions are 3–4 times faster than the step-by-step syntheses.

During the one-pot synthesis, the second boronic acid was added when starting material **1** fully disappeared (monitored by TLC). Most of the first cross-coupling reactions were achieved after 2–4 hours (entries 1, 3, 4, 6–9). The use of 2-thienyl and 3,4-methylenedioxyphenyl boronic acids (entries 2, 5) increased the reaction time to 18 and 12 h respectively. In both aromatic and heteroaromatic series, the second Suzuki reaction required only a few minutes (10–30 mins). Our new one-pot method constitutes easier access to 2,4-di(het)aryl-pyrido[3,2-*d*]pyrimidines, independent of the nature of the (het)arylboronic acid.

One-pot C-4 and C-2 diamination by double S_NAr reaction

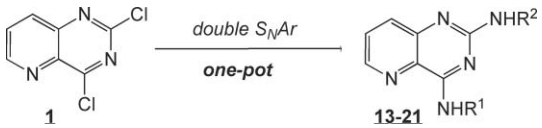
Alkyl amination of **1** regioselectively occurred at C-4.[8] From this point of view, we now considered the synthesis of C-2 and C-4 bis-aminated pyrido[3,2-*d*]pyrimidines (Scheme 3). Under a sequential route, compound **1** reacted first with aniline in the presence of a stoichiometric amount of Et_3N in THF to produce



Scheme 3 *Reagents and conditions*: (a) $PhNH_2$ 1.0 equiv., Et_3N 1.0 equiv., THF, r.t., 12 h; (b) $PMBNH_2$ 1.2 equiv., 1,4-dioxane, reflux, 24 h; (c) $PhNH_2$ 1.0 equiv., Et_3N 2.0 equiv., 1,4-dioxane, r.t., 2 h then $PMBNH_2$ 1.2 equiv., reflux, 22 h, see also ref. 15.

compound **12** after 12 h at room temperature in 87% yield whereas the second S_NAr reaction was achieved with 1.2 equiv. of $PMBNH_2$ in refluxing dioxane to afford compound **13** after 24 h in a high (92%) yield. Furthermore, the step-by-step synthesis of **13** from **1** required the purification of the intermediate **12**.

Despite of the high yields, the development of an attractive one-pot strategy would constitute a major advance in the poly substitution of pyrido[3,2-*d*]pyrimidines (Scheme 4). After several assays, we opted for dioxane as solvent. The first reaction was also performed with $PhNH_2$ at room temperature to preserve the C-4 regioselectivity. After the complete disappearance of **1** on TLC (2 h), 1.2 equiv. of $PMBNH_2$ was added and the reaction mixture was refluxed. After nearly one additional day, the expected product **13** was isolated in 78% yield. Our new one-pot strategy greatly decreased the reaction time and this process was generalized as demonstrated by the results summarized in Table 2.



Scheme 4 *Reagents and conditions*: R^1NH_2 1.01 equiv., Et_3N 2.0 equiv., 1,4-dioxane, r.t. then R^2NH_2 1.2 equiv., reflux or MW irradiation 140 °C.

The first S_NAr reaction was mostly completed after 1 or 2 h whatever the nature of the primary amine (aliphatic, benzylamine or anilines, entries 1–7). With 6-aminoquinoline (entry 8), a strongly deactivated nucleophile, completion occurred only after 12 h. Introduction of the second primary amines (alkyl, benzyl and phenyl) and refluxing the mixture achieved the C-2 S_NAr reaction. Assays 1–8 were nearly quantitative on TLC but some of the synthesized compounds were not easy to purify, explaining why the diaminated derivatives **13–20** were isolated in the 63–89% yield range.

In spite of the good yields obtained for compounds **13–20**, the second reaction times strongly increased (12–47 h). The lack of reactivity of the residual C-2 chlorine atom may be due to the presence of electron-donating groups on the C-4 position. This hypothesis was confirmed when the less nucleophilic 6-aminoquinoline was used. The desired product **21** was not identified and only 81% of **12** was isolated. So we switched the thermal conditions for microwave irradiation.[14] After only one or two hours, complete conversion was seen on TLC and compounds **13–20** were isolated in good yields (63–84%). Despite the change in the activation mode, the use of 6-aminoquinoline (entry 9) failed again and only 86% of **12** was recovered.

In summary, we have proposed a straightforward one-pot bisamination of pyrido[3,2-*d*]pyrimidines and successfully introduced onto positions C-2 and C-4 alkyl, benzyl and aryl primary amines.[15] The two chlorine atoms of **1** were successfully and regioselectively displaced after two successive S_NAr reactions. The first one was achieved on C-4 at room temperature, whereas the second one on C-2 required harsh thermal conditions. Microwave irradiation retrieved the situation and reduced the global reaction time to a few hours. Nevertheless, the use of deactivated amines remains unsolved.

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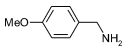
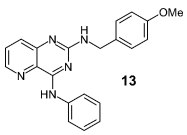
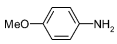
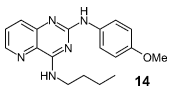
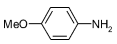
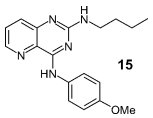
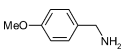
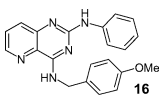
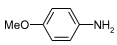
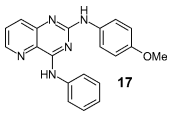
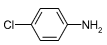
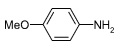
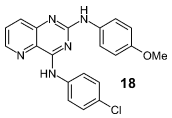
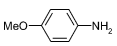
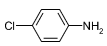
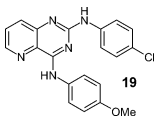
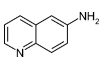
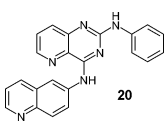
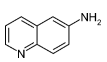
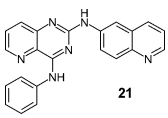
Table 2 One-pot diamination of compound **1**

Entry	R^1NH_2	R^2NH_2	Compound	1st S_NAr	2nd S_NAr under thermal conditions		2nd S_NAr under MW irradiation	
				Time	Time	Yield	Time	Yield
1			 **13**	2 h	22 h	78%	1 h	75%
2			 **14**	2 h	12 h	63%	1 h	67%
3			 **15**	1 h	47 h	83%	2 h	78%
4			 **16**	1 h	23 h	89%	1 h	84%
5			 **17**	2 h	22 h	60%	1 h	67%
6			 **18**	2 h	22 h	72%	1 h	74%
7			 **19**	1 h	47 h	64%	2 h	63%
8			 **20**	12 h	12 h	68%	1 h	70%
9			 **21**	2 h	46 h	[a]	2 h	[b]

[a] 81% of **12** was isolated. [b] 86% of **12** was isolated.

One-pot C-4 and C-2 diamination by a S_NAr/Buchwald combination

The poor reactivity of 2-chloro-4-aminopyrido[3,2-*d*]pyrimidine and the use of deactivated amines led to disappointing failure in the double S_NAr one-pot strategy. So, we envisioned to perform the second S_NAr reaction *via* a Buchwald amination. To exemplify our new proposal, we started with the compound **21** as the target (Scheme 5).

Starting from **1**, we first realized the selective S_NAr reaction with aniline at room temperature and then we added to the reaction mixture the 6-aminoquinoline and the $Pd(OAc)_2$/Xantphos catalytic system, which proved its efficiency in Buchwald aminations.[16]

After a nearly two-day period at reflux, compound **21** was isolated in 82% yield.[17] So we were able to restore the reactivity at position C-2 with poor nucleophilic amines.

The great interest of a one-pot methodology intimately relies on a fast turnover and good yields. In a final assay, we performed the palladium-catalyzed reaction under microwave irradiation. Interestingly, the reaction time decreased to only 2 h with a minor impact on the global yield. Including this original

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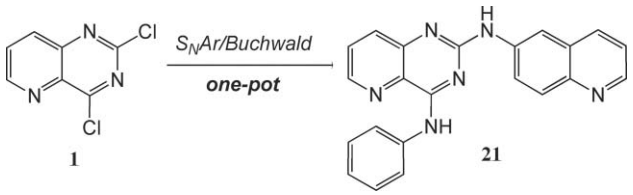

Scheme 5 One pot S_NAr/Buchwald synthesis. *Reagents and conditions*: $PhNH_2$ 1.0 equiv., Et_3N 2.0 equiv., 1,4-dioxane, r.t., 2 h; then 6-aminoquinoline 1.2 equiv., $Pd(OAc)_2$ 0.05 equiv., Xantphos 0.1 equiv., (reflux, 46 h, 82% or MW irradiation 140 °C, 2 h, 78%).

microwave irradiation step, we efficiently performed a double one-pot amination of pyrido[3,2-*d*]pyrimidine **1** using successive S_NAr and Buchwald-type reactions to get around the lack of reactivity of strongly deactivated amines.

Conclusion

Herein, we have described three original one-pot procedures to generate 2,4-disubstituted pyrido[3,2-*d*]pyrimidines from 2,4-dichloropyrido[3,2-*d*]pyrimidine **1** using S_NAr and palladium-catalyzed reactions. This unprecedented work included a double Suzuki–Miyaura cross-coupling, a double S_NAr reaction and an S_NAr/Buchwald combination, which proved to be very efficient. The C-4 *versus* C-2 chlorine discrimination under Suzuki or S_NAr conditions is the key to achieving the first steps in only a few hours. The second C-2 arylations were realized in a few minutes under thermal activation, whereas the second C-2 aminations required microwave irradiation to be achieved in a few hours. The C-2 aminations were mostly performed by S_NAr reactions and, last but not least, the deactivated amines were introduced under Buchwald-type conditions. This strategy has also proved to be very useful in the double substitution of pyrido[3,2-*d*]pyrimidine. Efforts are already in progress to broaden the methodology to other heterocycles.

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12 J. Koubachi, S. El Kazzouli, S. Berteina-Raboin, A. Mouaddib and G. Guillaumet, *J. Org. Chem.*, 2007, **72**, 7650–7665.
13 **General procedure for the one-pot double Suzuki–Miyaura cross-coupling reactions (compounds 3–11):** To an argon degassed solution of 2,4-dichloropyrido[3,2-*d*]pyrimidine **1** (100 mg, 0.5 mmol) in toluene (6 mL), the desired (het)Ar boronic acid (1.05 equiv.), K_2CO_3 (138 mg, 2 equiv.), $Pd(OAc)_2$ (6.0 mg, 0.05 equiv.) and PPh_3 (13 mg, 0.1 equiv.) were successively added. The reaction mixture was heated at 100 °C under vigorous stirring. After complete disappearance of **1** on TLC, the second (het)aryl boronic acid (1.2 equiv.) in EtOH (3 mL) was added. After complete conversion of the C-4 monoarylated non-isolated intermediate, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. Water (10 mL) and CH_2Cl_2 (10 mL) were successively added. After extraction of the aqueous phase with CH_2Cl_2 (3 × 10 mL), the combined organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude material was purified by flash chromatography to afford the attempted compounds **3–11**. **4-(3-Methoxyphenyl)-2-(thien-2-yl)-pyrido[3,2-*d*]pyrimidine (10)**. Compound **10** was isolated after a flash chromatography (petroleum ether/EtOAc, 9/1) as a pale yellow solid in 86% yield. Mpt 119–120 °C; IR (ATR-Ge, cm^{-1}) ν 3063, 2832, 1594, 1532, 1451, 1323, 1256, 1036, 867, 790; ^1H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3H, CH_3), 7.10 (dd, 1H, $J = 2.1$ Hz, $J = 7.8$ Hz), 7.18 (dd, 1H, $J = 3.8$ Hz, $J = 5.0$ Hz), 7.43 (t, 1H, $J = 8.0$ Hz), 7.56 (dd, 1H, $J = 1.0$ Hz, $J = 5.0$ Hz), 7.70 (dd, 1H, $J = 4.1$ Hz, $J = 8.6$ Hz, H_7), 8.03-8.04 (m, 1H), 8.07 (d, 1H, $J = 7.8$ Hz), 8.37 (d, 1H, $J = 3.8$ Hz), 8.46 (dd, 1H, $J = 1.6$ Hz, $J = 8.6$ Hz, H_8), 8.92 (dd, 1H, $J = 1.6$ Hz, $J = 4.1$ Hz, H_6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4 (CH_3), 117.2 (CH), 117.3 (CH), 124.8 (CH), 128.4 (CH), 129.0 (CH), 129.2 (CH), 131.4 (CH), 132.2 (CH), 134.9 (CH), 136.7 (Cq), 137.2 (Cq), 141.6 (Cq), 146.3 (Cq), 150.7 (CH), 156.3 (Cq), 159.3 (Cq), 167.0 (Cq); HRMS (EI-MS) : m/z calcd for $C_{18}H_{14}N_3OS$: 320.0858, found: 320.0867.
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15 **General procedure for the one-pot double S_NAr (compounds 13–20):** To a solution of 2,4-dichloropyrido[3,2-*d*]pyrimidine **1** (100 mg, 0.5 mmol) in dry 1,4-dioxane (5 mL), the first primary amine R^1NH_2 (1.01 equiv.) and Et_3N (130 µL, 2.1 equiv.) were successively added. The reaction mixture was stirred at room temperature and after the complete disappearance of **1**, the second amine R^2NH_2 (1.2 equiv.) was added and the reaction was subject to microwave irradiation at 140 °C. After complete conversion of the non-isolated C-4 monoaminated intermediate, the reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The crude residue was purified by silica gel column chromatography or by triturating with Et_2O to

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afford the expected compounds **13–20**. **2-(4-Methoxybenzylamino)-4-phenylaminopyrido[3,2-*d*]pyrimidine (13)**. Compound **13** was isolated after flash chromatography (DCM/MeOH, 98/2) as a yellow solid in 78% yield. Mpt 157–158 °C; IR (ATR-Ge, cm^{-1}) ν 3360, 3247, 2833, 1622, 1546, 1453, 1339, 1227, 1041, 811; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.77 (s, 3H, OCH_3), 4.66 (d, 2H, $J = 5.6$ Hz, CH_2), 5.62 (sl, 1H, NH), 6.85 (d, 2H, $J = 8.8$ Hz), 7.08 (t, 1H, $J = 7.5$ Hz), 7.30-7.37 (m, 4H), 7.45 (dd, 1H, $J = 4.1$ Hz, 8.5 Hz, H_7), 7.73 (d, 1H, $J = 8.5$ Hz, H_8), 7.84 (d, 2H, $J = 7.5$ Hz), 8.36 (dd, 1H, $J = 1.6$ Hz, $J = 4.1$ Hz, H_6), 9.05 (sl, 1H, NH); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 45.4 (CH_2), 55.4 (CH_3), 114.0 (3CH), 120.2 (3CH), 123.5 (CH), 126.0 (Cq), 127.8 (CH), 129.0 (3CH), 131.5 (Cq), 133.0 (Cq), 138.7 (Cq), 143.3 (CH), 147.1 (Cq), 157.6 (Cq), 158.9 (Cq); HRMS (EI-MS): m/z calcd for $C_{21}H_{20}N_5O$: 358.1668, found: 358.1673.

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17 **Synthesis of 21 by a one-pot S_NAr/Buchwald sequence**. To a solution of 2,4-dichloropyrido[3,2-*d*]pyrimidine **1** (100 mg, 0.5 mmol) in 1,4-dioxane (5 mL), aniline (47 mg, 1.01 equiv.) and Et_3N (130 µL, 2.1 equiv.) were added. The reaction mixture was stirred for 2 h at room temperature. 6-Aminoquinoline (86 mg, 1.2 equiv.), $Pd(OAc)_2$ (6 mg, 0.05 equiv.), Xantphos (29 mg, 0.1 equiv.) were successively added to the reaction mixture and the reaction was refluxed for 46 h or subjected to microwave irradiation (140 °C) for 2 h. Whereas in the chosen method, the purification steps were similar. The reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. Water (10 mL) and CH_2Cl_2 (10 mL) were added. After extraction of the aqueous phase with CH_2Cl_2 (3 × 10 mL), the combined organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude residue was purified by silica gel column chromatography (DCM/MeOH 98/2) to afford compound **21** in 82% yield with thermal activation and 78% including the microwave irradiation step. **4-Phenylamino-2-(6-quinolinamino)-pyrido[3,2-*d*]pyrimidine (21)**. Compound **21** was isolated after flash chromatography (petroleum ether/EtOAc, 98/2) as a beige solid in 82% yield. Mpt 198–199 °C; IR (ATR-Ge, cm^{-1}) ν 3043, 2285, 1599, 1563, 1486, 1420, 1348, 1297, 1102, 831; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, 1H, $J = 7.3$ Hz), 7.38-7.42 (m, 2H), 7.45 (dd, 1H, $J = 4.2$ Hz, $J = 8.3$ Hz), 7.76 (dd, 1H, $J = 4.2$ Hz, $J = 8.5$ Hz, H_7), 7.94 (d, 1H, $J = 9.1$ Hz), 8.00 (dd, 1H, $J = 1.2$ Hz, $J = 8.4$ Hz), 8.09-8.18 (m, 4H), 8.61 (dd, 1H, $J = 1.5$ Hz, $J = 4.2$ Hz), 8.73 (dd, 1H, $J = 1.6$ Hz, $J = 4.1$ Hz, H_6), 8.76 (sl, 1H), 9.82 (s, 1H, NH), 10.06 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.6 (CH), 121.5 (CH), 121.6 (CH), 123.5 (CH), 124.2 (CH), 128.4 (2CH), 128.6 (2CH). 128.9 (CH), 129.1 (Cq), 133.5 (CH), 134.9 (CH), 138.8 (Cq), 138.9 (Cq), 144.1 (Cq), 144.7 (CH), 146.2 (Cq), 147.9 (CH), 156.4 (2Cq), 157.6 (Cq); HRMS (EI-MS) : m/z calcd for $C_{22}H_{17}N_6$: 365.1515, found: 365.1510.

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