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C–H Bond Functionalization of Arylpyrimidines Catalyzed by an in situ Generated Ruthenium(II) Carboxylate System and the Construction of Tris(heteroaryl)-Substituted Benzenes

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A ruthenium(II) carboxylate catalyst, generated in situ from $[RuCl_2(p\text{-cymene})]_2$ and 1-phenyl-1-cyclopentanecarboxylic acid (PCCA) in the presence of K_2CO_3, allowed activation of the C–H bond in phenyl-substituted pyrimidines and their direct functionalization with both electron-deficient and electron-rich aryl halides. The scope of this process can be extended to the use of heteroaryl bromides and less reactive aryl chlorides. This Ru^{II}-PCCA complex constitutes a better catalytic system in comparison to other carboxylates.

Introduction

Transition-metal-catalyzed activations of C–H bonds [1] followed by their functionalization with proelectrophiles have undoubtedly led to one of the most elegant strategies for the arylation of arenes, heterocycles, and alkenes. Recently, the majority of direct catalytic arylations have become feasible by using palladium,[2] rhodium,[3] or ruthenium[4,5] catalysts, although some other metal compounds[6–8] have also emerged as alternatives for catalyzing these reactions.

The Fagnou[2i–2k] and Maseras and Echavarren[9] groups have made significant contributions to understanding the concerted metalation–deprotonation mechanism for the direct functionalization of C–H bonds by activating them with palladium catalysts. A DFT (density functional theory) analysis performed with Ru^{II} complexes supports an initial cyclometalated intermediate formed by deprotonation of the C–H bond, from the reaction between the coordinated carbonate and the metal center.[4d] Very recently, an efficient in situ generated ruthenium(II) acetate catalyst allowed the direct arylation of 2-pyridylbenzene with aryl chlorides.[4b] The use of potassium pivalate, instead of acetate, enabled the same reaction to be performed under mild conditions in the nontoxic solvent diethyl carbonate.[4c] More importantly, this catalyst operates and is more active in water.[4a] These results clearly show the beneficial effect of a coordinated carboxylate ligand, acting as a proton shuttle from the C–H bond to the external base, and thus enhancing the activity of the catalytic system. Similar observations of increased activity in the presence of carboxylates have also been reported with Pd^{II}[2h–2k] and Ru^{II}[5d,5j,10] catalysts.

To the best of our knowledge, efficient methods for the direct catalytic arylation of arylpyrimidines at the *ortho* position of the phenyl substituent are relatively rare, and there are no reports of a direct arylation with an Ru^{II} catalytic system. Nakamura and co-workers succeeded in arylating 2- and 4-phenylpyrimidine by activating the C–H bond of the benzene ring with an iron catalyst in the presence of 1,10-phenanthroline acting as the ligand.[7b,7d] However, a drawback for this reaction is the need for a large excess amount of phenylmagnesium bromide along with $ZnCl_2$·TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and a stoichiometric amount of 1,2-dichloro-2-methylpropane. Furthermore, a low yield of the diphenylated product was obtained after starting from 4-phenylpyrimidine. Cheng et al. reported on an example of the successful phenylation of 2-phenylpyrimidine, catalyzed by $RuCl_3$, but the method required the more reactive iodobenzene and the presence of organic peroxides.[11] Similarly, Chen et al. reported on a direct arylation of 2-phenoxypyrimidines with arylboronic acids using $Pd(OAc)_2/Cu(OTf)_2/Ag_2O$ as a catalytic system.[12] This encouraged us to conduct an investigation of the Ru^{II}-catalyzed direct arylation of arylpyrimidines with organic halides.

Herein, we report that a new in situ generated ruthenium(II) carboxylate complex allowed the cleavage of the C–H bond in *ortho* position of the benzene ring of 2- and 4-phenylpyrimidine followed by functionalization with organic halides, affording mono- and disubstituted products in good to excellent yields.

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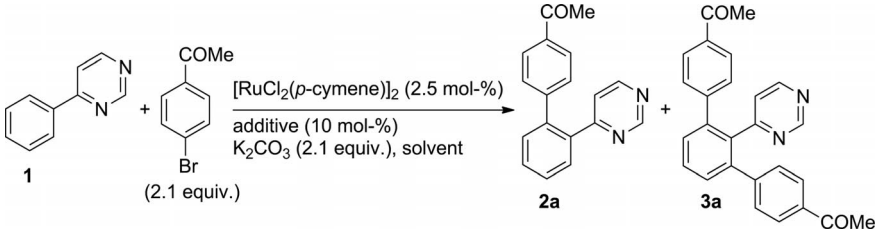
Results and Discussion

Initially, we chose 4-phenylpyrimidine (**1**) and 4-bromoacetophenone as the model substrates to evaluate the reaction parameters, although the remote nitrogen atom in **1** might cause a nonproductive coordination with the metal center and decrease the rate of metalation. The results are summarized in Table 1. According to the previously applied reaction conditions[4b] for the direct arylation of 2-pyridylbenzene, we heated **1** and 4-bromoacetophenone (2.1 equiv.) in the presence of the precatalyst $[RuCl_2(p\text{-cymene})]_2$ together with a catalytic amount of KOAc in *N*-methyl-2-pyrrolidone (NMP) as the solvent. Unfortunately, these conditions afforded only a 13% conversion of **1** and resulted in a 1:1 molar ratio of the monoarylated and diarylated products **2a** and **3a** in the crude mixture (Table 1, Entry 1). In other reactions we preferred to use dioxane as a solvent, as it allowed an easier workup due to its lower boiling point. When the same reaction was performed in dioxane, but at 150 °C, the conversion increased to 26% (Table 1, Entry 2). For the remainder of the paper, the influence of various carboxylate ligands, formed in situ by reaction with a stoichiometric amount of potassium carbonate, was investigated. Increasing the steric bulk by using pivalic acid (PivOH) or 1-adamantanecarboxylic acid (1-$AdCO_2H$) did not significantly improve the outcome of the reaction, although the sterically more hindered 1-$AdCO_2H$ led to a 53% conversion (Table 1, Entries 3 and 4). By employing benzoic acid as an example of an aromatic acid resulted in a very low conversion (Table 1, Entry 5), and the dicarboxylic acids phthalic and succinic acid effectively inhibited the arylation process.

To our delight, we found that arylcycloalkyl-substituted 1-phenyl-1-cyclopentanecarboxylic acid formed an excellent catalyst with Ru^{II}, and **1** was coupled with 4-bromoacetophenone to afford predominantly the diarylated product **3a** (Table 1, Entry 6) in just 2 h with an 83% conversion. Prolonged heating for 18 h led to a quantitative conversion of **1**, giving almost exclusively the diarylated product **3a** in an 84% isolated yield (Table 1, Entry 7). With only K_2CO_3, the transformation was not as efficient as with the addition of PCCA (Table 1, Entry 6). Note that the solvent dioxane gave results comparable to those with NMP (Table 1, Entries 7 and 8). By increasing the amount of PCCA to 40 mol-%, there was still 100% conversion of **1**, but the selectivity was affected, thus providing a larger amount of the monoarylated product **2a** in the crude mixture in comparison with 10 mol-% of PCCA (Table 1, Entry 8). It is worth pointing out that our Ru^{II}-PCCA catalyst system was also operative in toluene, a significantly less polar solvent. The reaction proceeded with quantitative conversion in 18 h, though with a much lower selectivity compared to that in the dioxane (Table 1, Entry 9 vs. 7). As dioxane can be regarded as a double cyclic ether, we probed other cyclic and acyclic ethers as solvents in the direct arylations using our catalyst system (Table 1, Entries 10 and 11). These results proved that the direct arylations can be performed not only in the commonly used solvent NMP, but also in ethers, such as dioxane which was the solvent of choice for our catalyst system and led to the quantitative conversion of **1** with excellent selectivity. In addition, we probed other metal complexes as potential catalysts for the arylation reaction of **1** with 4-bromoacetophenone. Surprisingly, $Pd(OAc)_2$ was inefficient as a precatalyst, whereas the Ru–

Table 1. Direct arylation of 4-phenylpyrimidine (**1**).[a]



Entry	Additive	Solvent	T [°C]	t [h]	Conversion of **1** [%][b]	**2a/3a**
1	KOAc	NMP	120	2	13	50:50
2	KOAc	dioxane	150	2	26	77:23
3	PivOH	dioxane	150	2	38	38:62
4	1-$AdCO_2H$	dioxane	150	2	53	70:30
5	$PhCO_2H$	dioxane	150	2	24	77:23
6	PCCA	dioxane	150	2	83 (22)[c]	40:60 (72:28)[c]
7	PCCA	dioxane	150	18	100	6:94 (84)[d]
8	PCCA	NMP	150	18	100 (100)[e]	4:96 (20:80)[e]
9	PCCA	PhMe	150	18	100	33:67
10	PCCA	THF[f]	150	18	94	22:78
11	PCCA	*t*BuOMe	150	18	90	50:50 (34):(39)[d]

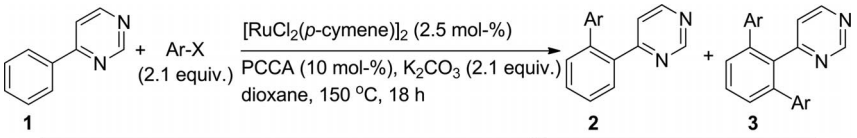
[a] Reagents and conditions: **1** (0.5 mmol), 4-bromoacetophenone (1.05 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.0125 mmol), additive (0.05 mmol), K_2CO_3 (1.05 mmol), solvent (2 mL), argon. [b] Conversion based on **1**, and the molar ratio determined by ^1H NMR spectroscopic data of the crude reaction mixture. [c] Values in parentheses: reaction performed without the addition of an additive. [d] Isolated yield. [e] 40 mol-% of PCCA was used. [f] THF = tetrahydrofuran.

alkylidene carbene complex $[Cl_2(PCy_3)(IMes)Ru{=}CHPh]$ gave a 70% conversion in the presence of PCCA and K_2CO_3 in dioxane at 150 °C after 2 h. Finally, we also tested our Ru^{II}-PCCA catalyst system in combination with other inorganic bases in dioxane at 150 °C for 2 h. Cs_2CO_3 gave a significantly lower conversion than K_2CO_3 (27% vs. 83%), whereas $KHCO_3$ gave practically the same outcome as K_2CO_3.

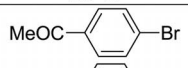
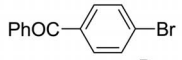
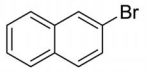
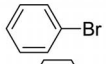
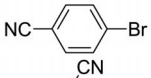
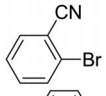
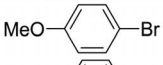
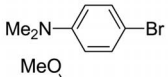
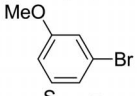
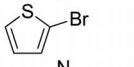
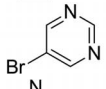
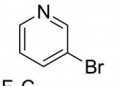
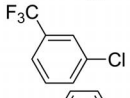
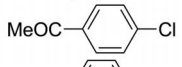
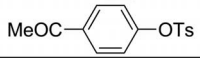
We assumed that the decreased reactivity of 4-phenylpyrimidine (**1**) in comparison to 2-phenylpyridine[4b] might have several causes, the unproductive competitive coordination of the metal center to the N-1 atom and the weaker coordinating ability of the pyrimidine, because of its lower basicity[13] compared to pyridine, which results in the lower stability of the cycloruthenated intermediate.

With an efficient, in situ generated catalyst in hand, we probed its scope and limitations in the direct arylation of **1** with selected electron-withdrawing and electron-donating aryl bromides. Using 4-bromobenzophenone and 2-bromonaphthalene, we succeeded in isolating the diarylated products **3b** and **3c** in 73% and 75% yields, respectively (Table 2, Entries 2 and 3). The unsubstituted bromobenzene gave an 88% conversion of **1** with the diarylated product **3d** dominating over the monoarylated product **2d**. The 4-bromobenzonitrile afforded an almost quantitative conversion with a larger amount of diarylated product **3e** in the mixture, whereas the *ortho*-substituted 2-bromobenzonitrile exhibited a lower reactivity (Table 2, Entries 5 and 6). Electron-rich 4-bromoanisole gave a satisfactory conversion of **1** with almost equimolar quantities of the mono- and diarylated

Table 2. Direct functionalization of 4-phenylpyrimidine (**1**).[a]



1 **2** **3**

Entry	Ar–X	Conversion of **1** [%][b]	**2**/**3**
1		100	**2a**/**3a** (6:94), (84)[c]
2		100	**2b**/**3b** (10:90),[d] (73)[c]
3		98	**2c**/**3c** (9:91),[d] (75)[c]
4		88	**2d**/**3d** (40:60), (20):(38)[c]
5		99	**2e**/**3e** (27:73), (10):(60)[c]
6		73	**2f**/**3f** (62:38), (32):(19)[c]
7		87	**2g**/**3g** (47:53), (29):(36)[c]
8		98	**2h**/**3h** (25/75), (10)/(63)[c]
9		100	**2i**/**3i** (0:100), (89)[c]
10		90	**2j**/**3j** (10:90),[d] (68)[c]
11		48	**2k**/**3k** (75:25), (24):(5)[c]
12		100[e]	**2l**/**3l** (23:77), (9):(56)[c]
13		71 100[e]	**2m**/**3m** (16:84)[d] **2m**/**3m** (0:100), (82)[c]
14		90	**2a**/**3a** (65:35)
15		0	–

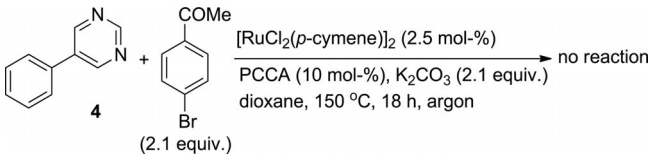
[a] Reagents and conditions: **1** (0.5 mmol), Ar–X (1.05 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.0125 mmol), PCCA (0.05 mmol), K_2CO_3 (1.05 mmol), dioxane (2 mL), 150 °C, 18 h, argon. [b] Conversion based on **1**, and the molar ratio determined by the ^1H NMR spectroscopic data of the crude reaction mixture. [c] Isolated yield. [d] The monoarylated product **2** was not isolated. [e] Ar–X (1.5 mmol), 48 h.

products **2g** and **3g**, but 4-bromo-*N*,*N*-dimethylaniline exhibited both a better reactivity and selectivity and favored the diarylated product **3h** (Table 2, Entries 7 and 8). Surprisingly, 3-bromoanisole afforded exclusively the diarylated product **3i** with an excellent isolated yield of 89%.

Given the results obtained for the direct arylation of **1** with aryl bromides, the scope of the process for the preparation of multiheteroaryl-substituted benzenes as potential ligands was explored. The use of multidentate pyrimidine-core ligands was demonstrated by Johansson et al. in the preparation of high-nuclearity ruthenium complexes with interesting electronic properties.[14] As shown in Table 2, our arylation protocol, though less effective than with aryl bromides, proved to be applicable for the C–H functionalization of **1** with heteroaryl bromides. Accordingly, the reaction with 2-bromothiophene led to the disubstituted product **3j** in a 68% isolated yield, but the conversion of **1** was not complete after 18 h (Table 2, Entry 10). The arylation reaction of **1** with 5-bromopyrimidine resulted in only a 48% conversion, giving low yields of the monosubstituted product **2k** and the disubstituted product **3k** (Table 2, Entry 11). Prolonged heating for 48 h and the use of 3 equiv. of 3-bromopyridine afforded a 100% conversion of **1** and a mixture of mono- and diarylated products **2l** and **3l** (Table 2, Entry 12). There are no previous reports of the direct functionalization of phenylpyrimidines with heteroaryl bromides in the literature.

Notably, our in situ generated catalytic system was not limited to organic bromides, but in two examples, **1** was arylated with less reactive aryl chlorides. The reaction of 1-chloro-3-(trifluoromethyl)benzene led to a 71% conversion after 18 h. Quantitative conversion was reached with 3 equiv. of 1-chloro-3-(trifluoromethyl)benzene and 48 h of heating, giving only the diarylated product **3m** in an 82% isolated yield (Table 2, Entry 13). 4-Chloroacetophenone afforded a good conversion and a mixture of **2a** and **3a** (Table 2, Entry 14). It has been reported that the less-reactive aryl tosylates, in contrast to aryl chlorides, gave preferentially monoarylated products.[15] Unfortunately, according to our protocol, the lower reactivity of 4-acetylphenyl tosylate resulted in the recovery of the unreacted starting materials (Table 2, Entry 15).

The importance of a functional group forcing the metal center close to the *ortho*-C–H bond of the benzene ring, thereby allowing selective metalation–functionalization, was demonstrated in the reaction of 5-phenylpyrimidine (**4**) with 4-bromoacetophenone catalyzed by the Ru^{II}-PCCA system under optimized conditions (Scheme 1). Heating for 18 h did not afford the products, presumably because the formation of the reactive cycloruthenated intermediate was impossible, and consequently the starting materials were recovered.

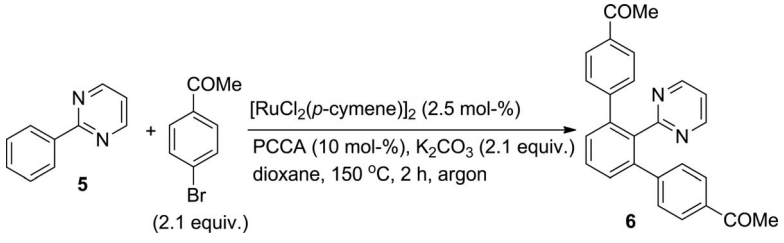


Scheme 1. Coupling of 5-phenylpyrimidine (**4**) with 4-bromoacetophenone.

To show the diversity of the arylpyrimidine, we used 2-phenylpyrimidine (**5**) with the Ru^{II}-PCCA catalytic system. We expected that 2-phenylpyrimidine (**5**) would react very smoothly, because the two nitrogen atoms are capable of bringing the ruthenium center close to the *ortho*-C–H bond of the benzene ring. Consequently, cleavage is allowed followed by arylation at this position through the metallacyclic intermediate. Indeed, the reaction of **5** with 2.1 equiv. of 4-bromoacetophenone in the presence of catalytic amounts of $[RuCl_2(p\text{-cymene})]_2$ and PCCA led to the quantitative conversion of **5** in 2 h, giving exclusively the diarylated product **6** in an 88% isolated yield (Scheme 2). This reaction clearly showed the superior reactivity of 2-phenylpyrimidine (**5**) compared to 4-phenylpyrimidine (**1**), which afforded an 83% conversion and a mixture of the monoarylated and diarylated products (Table 1, Entry 6) under otherwise identical conditions.

Conclusions

The combination of $[RuCl_2(p\text{-cymene})]_2$ and a catalytic amount of 1-phenyl-1-cyclopentanecarboxylic acid generates a relatively active catalyst for the direct *ortho*-arylation of pyrimidylbenzenes with the corresponding organic halides. The potential for this new Ru^{II}-catalytic system is illustrated in the first examples of high-yielding, catalytic, phenyl-substituted pyrimidine metalation–arylation reactions. The arylation of 4-phenylpyrimidine was possible with electron-deficient as well as with electron-rich aryl bromides and gave good to excellent yields of mono- and disubstituted products. This method tolerated several functional groups, such as acyl, methoxy, dimethylamino, cyano, and trifluoromethyl. Importantly, the approach was appli-



Scheme 2. Coupling of 2-phenylpyrimidine (**5**) with 4-bromoacetophenone.

cable, not only to aryl bromides, but also to less reactive 1-chloro-3-(trifluoromethyl)benzene and 4-chloroacetophenone, though the scope of this process with aryl chlorides still has to be explored. Moreover, the arylation reactions were extended to heteroarylation reactions by using heteroaryl bromides to construct the tris(heteroaryl)-substituted benzenes, which could serve as potential multidentate ligands. The coupling of 2-phenylpyrimidine with 4-bromoacetophenone proceeded very smoothly, giving exclusively the diarylated product in only 2 h, thus exhibiting a superior reactivity compared to 4-phenylpyrimidine. Finally, our results showed that the proper choice of carboxylic acid is crucial for the successful Ru^{II}-catalyzed direct arylation assisted by a carboxylate ligand.

Experimental Section

General Information: All reagents and solvents were used as obtained from commercial suppliers. ^1H and ^{13}C NMR spectra were recorded at 29 °C with a Bruker Avance DPX 300 in $CDCl_3$. ^1H NMR spectra were recorded at 300 MHz by using TMS as an internal standard. ^{13}C NMR spectra were recorded at 75.5 MHz and are referenced against the central line of the $CDCl_3$ triplet at δ = 77.0 ppm. Mass spectra were recorded with a VG-Analytical AutoSpec Q instrument. Merck silica gel 60 PF_{254} containing gypsum was used to prepare the chromatotron plates.

Representative Procedure for the Direct Arylation of 4-Phenylpyrimidine: See Table 1, Entry 7. A suspension of $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 0.0125 mmol, 2.5 mol-%), 1-phenyl-1-cyclopentanecarboxylic acid (9.5 mg, 0.05 mmol, 10 mol-%), powdered K_2CO_3 (145 mg, 1.05 mmol), 4-phenylpyrimidine (78 mg, 0.5 mmol), and 4-bromoacetophenone (209 mg, 1.05 mmol) in dioxane (2 mL) was stirred at 150 °C under argon in a sealed tube for 18 h. To the cold reaction mixture, CH_2Cl_2 (10 mL) was added, and the inorganic salts were filtered off and washed with a small amount of CH_2Cl_2. The filtrate was concentrated, and the remaining residue was purified by radial chromatography on silica gel (petroleum ether/EtOAc, 5:3) to yield **3a** (165 mg, 84%).

1-[2′-(Pyrimidin-4-yl)biphenyl-4-yl]ethanone (2a) and 1-(4-Acetyl-2′-pyrimidin-4-yl-[1,1′:3′,1′′-terphenyl]-4′′-yl)ethanone (3a): The representative procedure was applied by using *t*BuOMe as a solvent, see Table 1, Entry 11. Radial chromatography (petroleum ether/EtOAc, 5:1) afforded **2a** (47 mg, 34%) and **3a** (77 mg, 39%). Data for **2a**: ^1H NMR (300 MHz, $CDCl_3$): δ = 2.60 (s, 3 H, Me), 6.89 (dd, $J_{2,5}$ = 1.5 Hz, $J_{5,6}$ = 5.3 Hz, 1 H, 5-Pym), 7.27 (AA′BB′, J = 8.4 Hz, 2 H, Ar), 7.46 (m, 1 H, Ar), 7.56 (m, 2 H, Ar), 7.77 (m, 1 H, Ar), 7.88 (AA′BB′, J = 8.4 Hz, 2 H, Ar), 8.44 (d, $J_{5,6}$ = 5.3 Hz, 1 H, 6-Pym), 9.21 (d, $J_{2,5}$ = 1.5 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.5, 122.1, 128.4, 128.5, 129.7, 130.0, 130.5, 130.6, 135.8, 136.8, 139.8, 145.4, 155.9, 159.0, 166.0, 197.5 ppm. HRMS (ESI+): calcd. for $C_{18}H_{15}N_2O$ $[M + H]^+$ 275.1184; found 275.1180. Data for **3a**: ^1H NMR (300 MHz, $CDCl_3$): δ = 2.56 (s, 6 H, 2 Me), 6.88 (dd, $J_{2,5}$ = 1.5 Hz, $J_{5,6}$ = 5.2 Hz, 1 H, 5-Pym), 7.20 (AA′BB, J = 8.4 Hz, 4 H, Ar), 7.499 (d, J = 8.4 Hz, 1 H, Ar), 7.50 (d, J = 6.9 Hz, 1 H, Ar), 7.63 (dd, J = 6.9 Hz, 8.4 Hz, 1 H, Ar), 7.80 (AA′BB′, J = 8.4 Hz, 4 H, Ar), 8.36 (d, $J_{5,6}$ = 5.2 Hz, 1 H, 6-Pym), 8.92 (d, $J_{2,5}$ = 1.5 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.5, 124.0, 128.0, 129.3, 129.7, 130.0, 135.6, 135.8, 140.8, 145.4, 155.9, 158.2, 166.1, 197.5 ppm. HRMS (ESI+): calcd. for $C_{26}H_{21}N_2O_2$ $[M + H]^+$ 393.1603; found 393.1584.

(4-Benzoyl-2′-pyrimidin-4-yl-1,1′:3′,1′′-terphenyl-4′′-yl)(phenyl)-methanone (3b): The representative procedure was applied by using 4-bromobenzophenone (274 mg, 1.05 mmol), see Table 2, Entry 2. Radial chromatography (petroleum ether/EtOAc, 5:1→5:3) afforded **3b** (189 mg, 73%). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.93 (dd, $J_{2,5}$ = 1.3 Hz, $J_{5,6}$ = 5.2 Hz, 1 H, 5-Pym), 7.24 (AA′BB′, J = 8.3 Hz, 4 H, Ar), 7.41 (m, 4 H, Ar), 7.56 (m, 4 H, Ar), 7.63 (m, 1 H, Ar), 7.67 (AA′BB′, J = 8.3 Hz, 4 H, Ar), 7.75 (AA′BB′, J = 7.2 Hz, 4 H, Ar), 8.40 (d, $J_{5,6}$ = 5.2 Hz, 1 H, 6-Pym), 8.95 (d, $J_{2,5}$ = 1.3 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 124.1, 128.3, 129.4, 129.86, 129.87, 130.1, 132.4, 135.9, 136.0, 137.4, 140.8, 144.8, 156.0, 158.2, 166.2, 196.1 (one signal is hidden) ppm. HRMS (ESI+): calcd. for $C_{36}H_{25}N_2O_2$ $[M + H]^+$ 517.1916; found 517.1909.

4-[2,6-Bis(naphthalen-2-yl)phenyl]pyrimidine (3c): The representative procedure was applied by using 2-bromonaphthalene (215 mg, 1.05 mmol), see Table 2, Entry 3. Radial chromatography (petroleum ether/EtOAc, 5:1) afforded **3c** (153 mg, 75%). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.90 (dd, $J_{2,5}$ = 1.4 Hz, $J_{5,6}$ = 5.2 Hz, 1 H, 5-Pym), 7.14 (dd, J = 1.8, 8.4 Hz, 2 H, Ar), 7.41 (m, 4 H, Ar), 7.55–7.63 (m, 5 H, Ar), 7.66–7.77 (m, 6 H, Ar), 8.18 (d, $J_{5,6}$ = 5.2 Hz, 1 H, 6-Pym), 8.83 (d, $J_{2,5}$ = 1.4 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 124.1, 126.0, 126.2, 127.4, 127.45, 127.48, 127.9, 128.5, 129.1, 130.0, 132.0, 133.0, 136.3, 138.2, 141.6, 155.6, 158.0, 166.9 ppm. HRMS (ESI+): calcd. for $C_{30}H_{21}N_2$ $[M + H]^+$ 409.1705; found 409.1718.

4-(Biphenyl-2-yl)pyrimidine (2d) and 4-(1,1′:3′,1′′-Terphenyl-2′-yl)-pyrimidine (3d): The representative procedure was applied by using bromobenzene (165 mg, 1.05 mmol), see Table 2, Entry 4. Radial chromatography (CH_2Cl_2/MeOH, 150:1) afforded **2d** (23 mg, 20%) and **3d** (59 mg, 38%). NMR spectroscopic data for **2d** are consistent with reported data.[7d] Data for **2d**: ^1H NMR (300 MHz, $CDCl_3$): δ = 6.83 (dd, $J_{2,5}$ = 1.3 Hz, $J_{5,6}$ = 5.3 Hz, 1 H, 5-Pym), 7.13–7.20 (m, 2 H, Ar), 7.25–7.32 (m, 3 H, Ar), 7.46 (m, 1 H, Ar), 7.49–7.56 (m, 2 H, Ar), 7.78 (m, 1 H, Ar), 8.38 (d, $J_{5,6}$ = 5.3 Hz, 1 H, 6-Pym), 9.23 (d, $J_{2,5}$ = 1.3 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 122.4, 127.3, 127.9, 128.4, 129.6, 129.9, 130.3, 130.8, 136.7, 140.5, 141.1, 155.5, 159.0, 166.4 ppm. HRMS (ESI+): calcd. for $C_{16}H_{13}N_2$ $[M + H]^+$ 233.1079; found 233.1070. Data for **3d**: ^1H NMR (300 MHz, $CDCl_3$): δ = 6.87 (dd, $J_{2,5}$ = 1.3 Hz, $J_{5,6}$ = 5.1 Hz, 1 H, 5-Pym), 7.07–7.12 (m, 4 H, Ar), 7.16–7.21 (m, 6 H, Ar), 7.463 (d, J = 8.4 Hz, 1 H, Ar), 7.465 (d, J = 6.8 Hz, 1 H, Ar), 7.57 (dd, J = 6.8, 8.4 Hz, 1 H, Ar), 8.31 (d, $J_{5,6}$ = 5.1 Hz, 1 H, 6-Pym), 8.89 (d, $J_{2,5}$ = 1.3 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 124.2, 126.8, 127.9, 129.0, 129.5, 129.6, 136.0, 140.7, 141.6, 155.4, 158.0, 167.1 ppm. HRMS (ESI+): calcd. for $C_{22}H_{17}N_2$ $[M + H]^+$ 309.1392; found 309.1389.

2′-(Pyrimidin-4-yl)biphenyl-4-carbonitrile (2e) and 2′-Pyrimidin-4-yl-1,1′:3′,1′′-terphenyl-4,4′′-dicarbonitrile (3e): The representative procedure was applied by using 4-bromobenzonitrile (191 mg, 1.05 mmol), see Table 2, Entry 5. Radial chromatography (petroleum ether/EtOAc, 7:1) afforded **2e** (13 mg, 10%) and **3e** (108 mg, 60%). Data for **2e**: ^1H NMR (300 MHz, $CDCl_3$): δ = 6.94 (dd, $J_{2,5}$ = 1.2 Hz, $J_{5,6}$ = 5.2 Hz, 1 H, 5-Pym), 7.28 (AA′BB′, J = 8.4 Hz, 2 H, Ar), 7.44 (m, 1 H, Ar), 7.58 (m, 4 H, Ar), 7.75 (m, 1 H, Ar), 8.51 (d, $J_{5,6}$ = 5.2 Hz, 1 H, 6-Pym), 9.19 (d, $J_{2,5}$ = 1.2 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 111.2, 118.5, 122.0, 128.9, 130.1, 130.2, 130.60, 130.63, 132.1, 136.9, 139.1, 145.5, 156.3, 159.0, 165.8 ppm. HRMS (ESI+): calcd. for $C_{17}H_{12}N_3$ $[M + H]^+$ 258.1031; found 258.1036. Data for **3e**: ^1H NMR (300 MHz, $CDCl_3$): δ = 6.83 (dd, $J_{2,5}$ = 1.2 Hz, $J_{5,6}$ = 5.1 Hz, 1 H, 5-Pym), 7.21 (AA′BB′, J = 8.4 Hz, 4 H, Ar), 7.47–7.54 (m, 6 H, Ar), 7.65

(dd, J = 7.2, 8.1 Hz, 1 H, Ar), 8.41 (d, $J_{5,6}$ = 5.1 Hz, 1 H, 6-Pym), 8.94 (d, $J_{2,5}$ = 1.2 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 111.0, 118.3, 123.7, 129.6, 130.1, 130.2, 131.8, 135.7, 140.1, 145.0, 156.2, 158.2, 165.4 ppm. HRMS (ESI+): calcd. for $C_{24}H_{15}N_4$, $[M + H]^+$ 359.1297; found 359.1289.

2′-(Pyrimidin-4-yl)biphenyl-2-carbonitrile (2f) and 2′-Pyrimidin-4-yl-1,1′:3′,1′′-terphenyl-2,2′′-dicarbonitrile (3f): The representative procedure was applied by using 2-bromobenzonitrile (191 mg, 1.05 mmol), see Table 2, Entry 6. Radial chromatography (petroleum ether/EtOAc, 5:1) afforded **2f** (41 mg, 32%) and **3f** (34 mg, 19%). Data for **2f**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.08 (dd, $J_{2,5}$ = 1.4 Hz, $J_{5,6}$ = 5.2 Hz, 1 H, 5-Pym), 7.25 (dd, J = 1.4, 7.7 Hz, 1 H, Ar), 7.39 (dt, J = 1.4, 7.7 Hz, 1 H, Ar), 7.45–7.53 (m, 2 H, Ar), 7.57–7.63 (m, 2 H, Ar), 7.65 (dd, J = 1.4, 7.7 Hz, 1 H, Ar), 7.79 (m, 1 H, Ar), 8.53 (d, $J_{5,6}$ = 5.2 Hz, 1 H, 6-Pym), 9.08 (d, $J_{2,5}$ = 1.4 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 112.6, 117.9, 121.6, 127.7, 129.3, 129.9, 130.3, 131.06, 131.15, 132.4, 133.0, 137.2, 137.4, 144.8, 156.4, 158.6, 165.6 ppm. HRMS (ESI+): calcd. for $C_{17}H_{12}N_3$ $[M + H]^+$ 258.1031; found 258.1029. Data for **3f**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.95 (br., 1 H, 5-Pym), 7.16 (br., 2 H, Ar), 7.28–7.43 (m, 4 H, Ar), 7.55–7.73 (m, 5 H, Ar), 8.32 (d, $J_{5,6}$ = 5.2 Hz, 1 H, 6-Pym), 8.82 (d, $J_{2,5}$ = 1.5 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 112.9, 117.9, 123.8, 127.8, 129.2, 130.9, 131.2, 132.0, 132.7, 137.0, 138.1, 144.0, 155.8, 157.9, 164.9 ppm. HRMS (ESI+): calcd. for $C_{24}H_{15}N_4$ $[M + H]^+$ 359.1297; found 359.1296.

4-(4′-Methoxybiphenyl-2-yl)pyrimidine (2g) and 4-(4,4′′-Dimethoxy-1,1′:3′,1′′-terphenyl-2′-yl)pyrimidine (3g): The representative procedure was applied by using 4-bromoanisol (196 mg, 1.05 mmol), see Table 2, Entry 7. Radial chromatography (petroleum ether/EtOAc, 5:1) afforded **2g** (38 mg, 29%) and **3g** (66 mg, 36%). Data for **2g**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, Me), 6.82 (AA′BB′, J = 9.0 Hz, 2 H, Ar), 6.85 (dd, $J_{2,5}$ = 1.3 Hz, $J_{5,6}$ = 5.4 Hz, 1 H, 5-Pym), 7.08 (AA′BB′, J = 9.0 Hz, 2 H, Ar), 7.41–7.55 (m, 3 H, Ar), 7.76 (m, 1 H, Ar), 8.40 (d, $J_{5,6}$ = 5.4 Hz, 1 H, 6-Pym), 9.24 (d, $J_{2,5}$ = 1.3 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.2, 113.9, 122.4, 127.5, 129.9, 130.3, 130.68, 130.75, 132.8, 136.6, 140.7, 155.5, 159.0, 159.1, 166.6 ppm. HRMS (ESI+): calcd. for $C_{17}H_{15}N_2O$ $[M + H]^+$ 263.1184; found 263.1181. Data for **3g**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74 (s, 6 H, 2 Me), 6.72 (AA′BB′, J = 8.7 Hz, 4 H, Ar), 6.87 (dd, $J_{2,5}$ = 1.2 Hz, $J_{5,6}$ = 5.1 Hz, 1 H, 5-Pym), 6.99 (AA′BB′, J = 8.7 Hz, 4 H, Ar), 7.402 (d, J = 8.2 Hz, 1 H, Ar), 7.404 (d, J = 6.9 Hz, 1 H, Ar), 7.51 (dd, J = 6.9, 8.2 Hz, 1 H, Ar), 8.34 (d, $J_{5,6}$ = 5.1 Hz, 1 H, 6-Pym), 8.94 (d, $J_{2,5}$ = 1.2 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.1, 113.3, 124.2, 128.9, 129.3, 130.5, 133.1, 136.0, 141.2, 155.5, 158.0, 158.4, 167.5 ppm. HRMS (ESI+): calcd. for $C_{24}H_{21}N_2O_2$ $[M + H]^+$ 369.1603; found 369.1604.

4-[4′-(Dimethylamino)biphenyl-2-yl]pyrimidine (2h) and 4-[4,4′′-Bis(dimethylamino)-1,1′:3′,1′′-terphenyl-2′-yl]pyrimidine (3h): The representative procedure was applied by using 4-bromo-*N*,*N*-dimethylaniline (210 mg, 1.05 mmol), see Table 2, Entry 8. Radial chromatography (petroleum ether/EtOAc, 5:1) afforded **2h** (14 mg, 10%) and **3h** (124 mg, 63%). Data for **2h**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.95 (s, 6 H, 2 Me), 6.63 (AA′BB′, J = 8.7 Hz, 2 H, Ar), 6.88 (dd, $J_{2,5}$ = 1.3 Hz, $J_{5,6}$ = 5.4 Hz, 1 H, 5-Pym), 7.02 (AA′BB′, J = 8.7 Hz, 2 H, Ar), 7.40–7.52 (m, 3 H, Ar), 7.75 (m, 1 H, Ar), 8.38 (d, $J_{5,6}$ = 5.4 Hz, 1 H, 6-Pym), 9.25 (d, $J_{2,5}$ = 1.3 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 40.4, 112.2, 122.5, 127.0, 128.1, 129.8, 130.3, 130.4, 130.7, 136.4, 141.3, 149.7, 155.4, 159.1, 167.0 ppm. HRMS (ESI+): calcd. for $C_{18}H_{18}N_3$ $[M + H]^+$ 267.1501; found 267.1503. Data for **3h**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.90 (s, 12 H, 4 Me), 6.53 (AA′BB′, J = 8.7 Hz, 4 H, Ar), 6.92 (dd, $J_{2,5}$ = 1.5 Hz, $J_{5,6}$ = 5.2 Hz, 1 H, 5-Pym), 6.94 (AA′BB′, J = 8.7 Hz, 4 H, Ar), 7.376 (d, J = 8.4 Hz, 1 H, Ar), 7.378 (d, J = 6.6 Hz, 1 H, Ar), 7.48 (dd, J = 6.6, 8.4 Hz, 1 H, Ar), 8.35 (d, $J_{5,6}$ = 5.2 Hz, 1 H, 6-Pym), 8.97 (d, $J_{2,5}$ = 1.5 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 40.4, 111.9, 124.4, 128.8, 128.9, 130.2, 135.7, 141.6, 149.1, 155.3, 158.0, 168.3 (one signal is hidden) ppm. HRMS (ESI+): calcd. for $C_{26}H_{27}N_4$ $[M + H]^+$ 395.2236; found 395.2234.

4-(3,3′′-Dimethoxy-1,1′:3′,1′′-terphenyl-2′-yl)pyrimidine (3i): The representative procedure was applied by using 3-bromoanisol (196 mg, 1.05 mmol), see Table 2, Entry 9. Radial chromatography (petroleum ether/EtOAc, 5:1) afforded **3i** (164 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.63 (s, 6 H, 2 Me), 6.63 (dd, J = 1.6, 2.5 Hz, 2 H, Ar), 6.69 (ddd, J = 0.9, 1.6, 7.6 Hz, 2 H, Ar), 6.74 (ddd, J = 0.9, 2.5, 8.4 Hz, 2 H, Ar), 6.92 (dd, $J_{2,5}$ = 1.5 Hz, $J_{5,6}$ = 5.2 Hz, 1 H, 5-Pym), 7.10 (t, J = 7.6 Hz, 2 H, Ar), 7.465 (d, J = 8.7 Hz, 1 H, Ar), 7.468 (d, J = 6.3 Hz, 1 H, Ar), 7.55 (dd, J = 6.3, 8.7 Hz, 1 H, Ar), 8.35 (d, $J_{5,6}$ = 5.2 Hz, 1 H, 6-Pym), 8.94 (d, $J_{2,5}$ = 1.5 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.0, 112.9, 114.8, 122.0, 124.0, 128.9, 129.0, 129.5, 135.9, 141.5, 142.0, 155.5, 157.9, 159.0, 167.2 ppm. HRMS (ESI+): calcd. for $C_{24}H_{21}N_2O_2$ $[M + H]^+$ 369.1603; found 369.1610.

4-[2,6-Bis(thiophen-2-yl)phenyl]pyrimidine (3j): The representative procedure was applied by using 2-bromothiophene (171 mg, 1.05 mmol), see Table 2, Entry 10. Radial chromatography (petroleum ether/EtOAc, 7:1) afforded **3j** (109 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.66 (dd, J = 1.2, 3.5 Hz, 2 H, thiophene), 6.84 (dd, J = 3.5, 5.1 Hz, 2 H, thiophene), 7.09 (dd, $J_{2,5}$ = 1.5 Hz, $J_{5,6}$ = 5.1 Hz, 1 H, 5-Pym), 7.19 (dd, J = 1.2, 5.1 Hz, 2 H, thiophene), 7.50 (dd, J = 6.1, 9.0 Hz, 1 H, Ar), 7.567 (d, J = 6.1 Hz, 1 H, Ar), 7.572 (d, J = 9.0 Hz, 1 H, Ar), 8.50 (d, $J_{5,6}$ = 5.1 Hz, 1 H, 6-Pym), 9.13 (d, $J_{2,5}$ = 1.5 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 123.7, 126.2, 127.0, 127.6, 129.1, 130.5, 134.3, 136.4, 141.6, 156.2, 158.3, 166.8 ppm. HRMS (ESI+): calcd. for $C_{18}H_{13}N_2S_2$ $[M + H]^+$ 321.0520; found 321.0525.

4-[2-(Pyrimidin-5-yl)phenyl]pyrimidine (2k) and 5,5′-[-2-(Pyrimidin-4-yl)-1,3-phenylene]dipyrimidine (3k): The representative procedure was applied by using 5-bromopyrimidine (167 mg, 1.05 mmol), see Table 2, Entry 11. Radial chromatography (petroleum ether/EtOAc, 5:1→3:1) afforded **2k** (28 mg, 24%) and **3k** (8 mg, 5%). Data for **2k**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14 (dd, $J_{2,5}$ = 1.5 Hz, $J_{5,6}$ = 5.1 Hz, 1 H, 5-Pym), 7.46 (m, 1 H, Ar), 7.63 (m, 2 H, Ar), 7.74 (m, 1 H, Ar), 8.56 (s, 2 H, 4,6-Pym′), 8.63 (d, $J_{5,6}$ = 5.1 Hz, 1 H, 6-Pym), 9.14 (s, 2 H, 2-Pym and 2-Pym′) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 121.6, 129.5, 130.4, 130.8, 130.9, 133.7, 134.5, 137.3, 156.6, 157.0, 157.2, 158.9, 165.4 ppm. HRMS (ESI+): calcd. for $C_{14}H_{11}N_4$, $[M + H]^+$ 235.0984; found 235.0988. Data for **3k**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.87 (dd, $J_{2,5}$ = 1.3 Hz, $J_{5,6}$ = 5.1 Hz, 1 H, 5-Pym), 7.568 (d, J = 8.2 Hz, 1 H, Ar), 7.569 (d, J = 7.3 Hz, 1 H, Ar), 7.76 (dd, J = 7.3, 8.2 Hz, Ar), 8.48 (d, $J_{5,6}$ = 5.1 Hz, 1 H, 6-Pym), 8.54 (s, 4 H, 4,6-Pym′), 9.05 (d, $J_{2,5}$ = 1.3 Hz, 1 H, 2-Pym), 9.09 (s, 2 H, 2-Pym′) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 123.7, 130.2, 131.1, 133.8, 135.1, 137.0, 156.6, 157.0, 157.5, 158.8, 164.3 ppm. HRMS (ESI+): calcd. for $C_{18}H_{13}N_6$ $[M + H]^+$ 313.1202; found 313.1192.

4-[2-(Pyridine-3-yl)phenyl]pyrimidine (2l) and 4-[2,6-Bis(pyridine-3-yl)phenyl]pyrimidine (3l): The representative procedure was applied by using 3-bromopyridine (166 mg, 1.05 mmol), see Table 2, Entry 12. After 48 h at 150 °C, radial chromatography (petroleum ether/EtOAc, 5:1) afforded **2l** (11 mg, 9%) and **3l** (87 mg, 56%). Data for **2l**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.94 (dd, $J_{2,5}$ =

1.3 Hz, $J_{5,6}$ = 5.3 Hz, 1 H, 5-Pym), 7.22 (dd, J = 5.0, 7.8 Hz, 1 H, pyridine), 7.46 (m, 2 H, Ar, pyridine), 7.58 (m, 2 H, Ar), 7.76 (m, 1 H, Ar), 8.47 (d, J = 1.6 Hz, 1 H, pyridine), 8.49 (d, $J_{5,6}$ = 5.3 Hz, 1 H, 6-Pym), 8.54 (dd, J = 1.6, 5.0 Hz, 1 H, pyridine), 9.20 (d, $J_{2,5}$ = 1.3 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 122.1, 123.0, 128.7, 130.1, 130.6, 130.9, 136.3, 136.7, 137.1, 137.3, 148.5, 150.0, 156.2, 159.1, 165.9 ppm. HRMS (ESI+): calcd. for $C_{15}H_{12}N_3$ [M + H]$^+$ 234.1031; found 234.1041. Data for **3l**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.88 (d, $J_{5,6}$ = 5.2 Hz, 1 H, 5-Pym), 7.14 (dd, J = 4.8, 8.0 Hz, 2 H, pyridine), 7.42 (d, J = 8.0 Hz, 2 H, pyridine), 7.52 (d, J = 7.5 Hz, 2 H, Ar), 7.66 (t, J = 7.5 Hz, 1 H, Ar), 8.39 (d, $J_{5,6}$ = 5.2 Hz, 1 H, 6-Pym), 8.42 (d, J = 1.8 Hz, 2 H, pyridine), 8.46 (d, J = 4.8 Hz, 2 H, pyridine), 8.96 (s, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 122.6, 123.8, 129.4, 130.2, 135.9, 136.47, 136.53, 138.1, 148.2, 149.8, 156.1, 158.2, 165.5 ppm. HRMS (ESI+): calcd. for $C_{20}H_{15}N_4$ [M + H]$^+$ 311.1297; found 311.1308.

4-[3,3′′-Bis(trifluoromethyl)-1,1′:3′,1′′-terphenyl-2′-yl]pyrimidine (3m): The representative procedure was applied by using 1-chloro-3-(trifluoromethyl)benzene (271 mg, 1.5 mmol), see Table 2, Entry 13. After 48 h at 150 °C, radial chromatography (petroleum ether/EtOAc, 7:1) afforded **3m** (182 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.86 (d, $J_{2,5}$ = 1.3 Hz, $J_{5,6}$ = 5.1 Hz, 1 H, 5-Pym), 7.28–7.36 (m, 4 H, Ar), 7.40 (m, 2 H, Ar), 7.46 (m, 2 H, Ar), 7.515 (d, J = 8.5 Hz, 1 H, Ar), 7.517 (d, J = 6.8 Hz, 1 H, Ar), 7.63 (dd, J = 6.8, 8.5 Hz, 1 H, Ar), 8.37 (d, $J_{5,6}$ = 5.1 Hz, 1 H, 6-Pym), 8.94 (d, $J_{2,5}$ = 1.3 Hz, 1 H, 2-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 123.78 (q, J = 3.6 Hz), 123.79 (q, J = 272.4 Hz), 123.9, 126.4 (q, J = 3.8 Hz), 128.5, 129.5, 130.0, 130.4 (q, J = 32.4 Hz), 132.7 (q, J = 1.3 Hz), 136.2, 140.3, 141.1, 156.0, 158.1, 166.1 ppm. HRMS (ESI+): calcd. for $C_{24}H_{15}N_2F_6$ [M + H]$^+$ 445.1139; found 445.1138.

5-Phenylpyrimidine (4): To a mixture of 5-bromopyrimidine (79.5 mg, 0.5 mmol) and Na_2CO_3 (318 mg, 3 mmol) in water (1.5 mL), mixtures of $Pd(PPh_3)_4$ (33 mg, 0.028 mmol) in *N*,*N*-dimethylacetamide (DMAc, 2 mL) and phenylboronic acid (79 mg, 0.65 mmol) in EtOH (2 mL) were successively added. The reaction mixture was heated under argon at 90 °C for 8 h. The cold reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by radial chromatography on silica gel (petroleum ether/EtOAc, 10:1) to yield **4** (72 mg, 92%). NMR spectroscopic data are consistent with reported data.[16] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.61 (m, 5 H, Ar), 8.95 (s, 2 H, 4,6-Pym), 9.20 (s, 1 H, 2-Pym) ppm. HRMS (ESI+): calcd. for $C_{10}H_9N_2$ [M + H]$^+$ 157.0766; found 157.0764.

2-Phenylpyrimidine (5): To a mixture of 2-bromopyrimidine (159 mg, 1 mmol) and Na_2CO_3 (636 mg, 6 mmol) in water (3 mL), mixtures of $Pd(PPh_3)_4$ (66 mg, 0.056 mmol) in DMAc (4 mL) and phenylboronic acid (159 mg, 1.3 mmol) in EtOH (4 mL) were successively added. The reaction mixture was heated under argon at 90 °C for 8 h. The cold reaction mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried with Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by radial chromatography on silica gel (petroleum ether/EtOAc, 10:1) to yield **5** (100 mg, 64%). NMR spectroscopic data are consistent with reported data.[17] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14 (t, J = 5.0 Hz, 1 H, 5-Pym), 7.48 (m, 3 H, Ar), 8.45 (m, 2 H, Ar), 8.78 (d, J = 5.0 Hz, 2 H, 4,6-Pym) ppm. HRMS (ESI+): calcd. for $C_{10}H_9N_2$ [M + H]$^+$ 157.0766; found 157.0762.

1-(4-Acetyl-2′-pyrimidin-2-yl-1,1′:3′,1′′-terphenyl-4′′-yl)ethanone (6): The representative procedure was applied by using 2-phenylpyrimidine (78 mg, 0.5 mmol) and 4-bromoacetophenone (209 mg, 1.05 mmol). After 2 h at 150 °C, purification by radial chromatography (CH_2Cl_2/MeOH, 50:1) afforded **6** (173 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.56 (s, 6 H, 2 Me), 6.96 (t, J = 4.9 Hz, 1 H, 5-Pym), 7.22 (AA′BB′, J = 8.3 Hz, 4 H, Ar), 7.505 (d, J = 8.4 Hz, 1 H, Ar), 7.507 (d, J = 6.8 Hz, 1 H, Ar), 7.61 (dd, J = 6.8, 8.4 Hz, 1 H, Ar), 7.78 (AA′BB′, J = 8.3 Hz, 4 H, Ar), 8.45 (d, J = 4.9 Hz, 2 H, 4,6-Pym) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.3, 118.3, 127.7, 128.7, 129.1, 129.4, 135.0, 137.3, 140.4, 145.8, 156.0, 167.0, 197.4 ppm. HRMS (ESI+): calcd. for $C_{26}H_{21}N_2O_2$ [M + H]$^+$ 393.1603; found 393.1603.

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