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Chemoselective Synthesis of Arylpyridines via Suzuki–Miyaura Cross-Coupling Reactions

Rodisnel Perdomo Rivera,[a,c] Peter Ehlers,[a,b] Lars Ohlendorf,[a] Eugenio Torres Rodríguez,[c] Alexander Villinger,[a] Peter Langer[a,b,*]

[a] Universität Rostock, Institut für Chemie, A.-Einstein-Str. 3a, 18059 Rostock, Germany
E-mail: peter.langer@uni-rostock.de; https://www.langer.chemie.uni-rostock.de/
[b] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, A.-Einstein-Str. 29a, 18059 Rostock, Germany
[c] University of Granma, Study Center of Applied Chemistry, Carretera de Manzanillo Km 17½, 85100, Bayamo, Granma, Cuba.

Abstract:

4-Bromo-2,3,5-trichloro-6-iodopyridine has been synthesized for the first time and applied in chemo- and site-selective Suzuki-Miyaura cross-coupling reactions. This novel starting material allows the selective synthesis of pentaarylpyridines with up to four different aryl substituents.

Keywords: Cross-coupling; Suzuki–Miyaura reaction; chemoselectivity; palladium; pyridines

Introduction

Pyridine and its derivatives are associated with diverse pharmacological properties, such as antimicrobial,[1,2] anticancer,[3] anticonvulsant,[4] antiviral,[5] anti-HlV,[6] antifungal and antimycobacterial activities.[7] In addition to medicinal properties of pyridine derivatives, important other applications have been reported in the field of synthetic chemistry, such as catalysis, supramolecular chemistry as well as materials science.[8] All these results have increased the interest of the international scientific community in the development of new and efficient procedures for the synthesis of polyfunctionalized pyridines. Although several methodologies have been described for the synthesis of polysubstituted pyridines so far, many of those are limited, because they are not

economically viable or require many synthetic transformation steps. In 2014, Schmitt *et al*. reported the first synthesis of pentaarylpyridine with five different aryl groups in 13 steps.[9] Later, Yamaguchi and co-workers presented a regiocontrolled thermal [4+2] cycloaddition of tetraarylthiophene *S*-oxide and 2-cyanopyridine to give various pentaarylpyridines.[10] Recently, the same group completed the synthesis of pentaarylpyridines containing five different aryl groups by a ring transformation / coupling approach.[11] Although this method introduces different aryl substituents on the pyridine moiety with good regioselectivity, the diversity of functional groups is limited by the presence of three fixed aryl groups of the key intermediate, namely, 3-hydroxy-2,5,6-triarylpyridine. Additionally, Nishiwaki and co-workers published the synthesis of various polyarylated pyridines using condensation reactions of enamino esters with enones assisted by microwave.[12]

The Palladium catalyzed Suzuki-Miyaura reaction displays one of the most relevant methodologies for the construction of biaryls or polyarylated compounds, what is mainly based on the low toxicity and stability against air and moisture of the employed boronic acids as well as its good functional group tolerance.[13] In these reactions arylchlorides are favorable coupling partners, despite their low reactivity, due to their broader availability and lower costs compared to corresponding aryl bromides or –iodides.[14] To overcome the low reactivity of arylchlorides several electron-rich and sterical encumbered phosphine and NHC ligands have been developed allowing the cross-coupling of arylchlorides in high yield under mild conditions.[15]

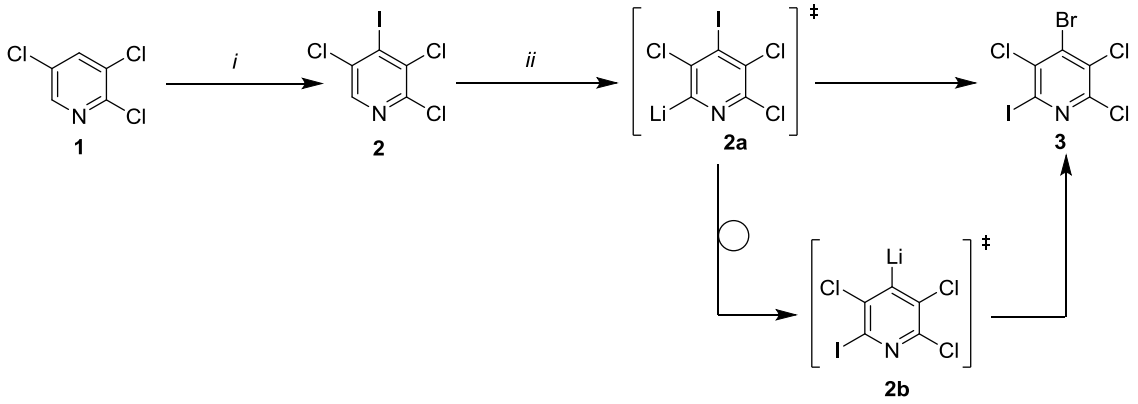
During the last years, the use of palladium catalysts in site-selective cross-coupling reactions of polyhalogenated heterocycles gained an increasing interest.[16] Recently, our group described the synthesis of pentaarylpyridines[17] as well as the site-selective synthesis of other arylated pyridines[18] using cheap and commercially available pentachloropyridine as substrate. These reactions give access to highly functionalized pyridines by cross-coupling reactions. However, in some cases, it was difficult to achieve site-selective reactions at specific positions of the pyridine core. In particular, the synthesis of tri- and tetraarylated pyridines was not possible by employment of pentachloropyridine as starting material, as the sequential coupling of aryl rings to the pyridine ring led to changes of the electronic situation of the central pyridine core structure. Thus, we envisioned that such compounds might be accessible by a chemo-

selective approach overwriting electronic effects responsible for the poor site-selectivity.

Results and Discussion

Starting Material Synthesis

In order to improve the selectivity of Suzuki cross-coupling reactions at positions 4 and 6 of the pyridine ring, we focused on the synthesis of the novel starting material 4-bromo-2,3,5-trichloro-6-iodopyridine (**3**). Commercially available 2,3,5-trichloropyridine was transformed, following the procedure described by Bobbio *et al.*,[19] to 2,3,5-trichloro-4-iodopyridine (**2**) in 75 % yield. Subsequently, the desired pyridine derivative **3** could be synthesized in 77 % yield adapting a similar procedure by lithiation, followed by bromination using 1,2-dibromotetrachloroethane (Scheme 1). It is important to note that the initially generated 6-lithiated species **2a** instantaneously isomerized by migration of the heavy halogen to the less basic 4-lithiated isomer **2b**. The constitution of **3** was independently confirmed by X-ray crystallographic analysis (Figure 1).



Scheme 1. Synthesis of starting material **3**. *i:* 1) **1**(1.0 equiv.), LDA (1.0 equiv.), THF, -78 °C, 2 h; 2) I_2 (1.2 equiv.), THF, -78 °C, 2 h. *ii:* 1) **2** (1.0 equiv.), LiTMP (1.0 equiv.), THF, -100 °C, 2 h; 2) $C_2Br_2Cl_4$ (3.3 equiv.), THF, -78 °C, 2 h.

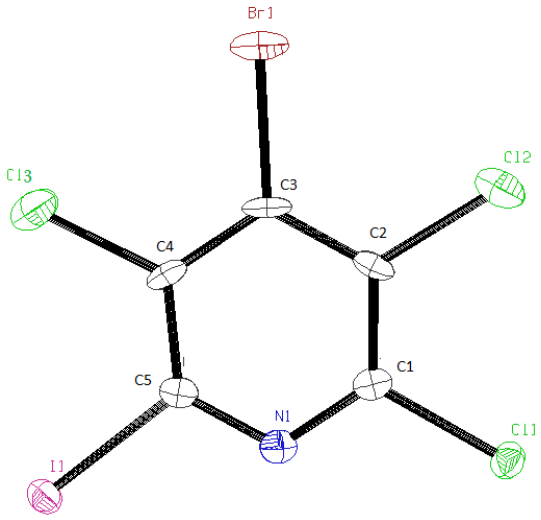


Figure 1. Ortep of compound **3**[20]

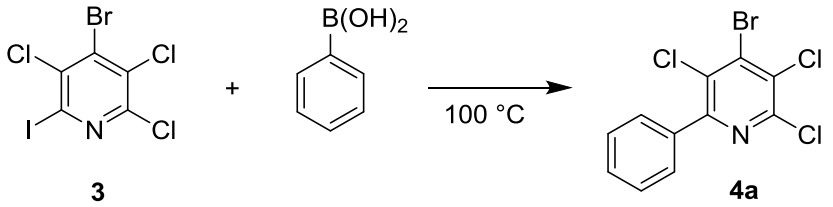
Site selective Suzuki-Miyaura reactions

Synthesis of 4-Bromo-2,3,5-trichloro-6-arylpyridines 4

With substrate **3** in hand, we optimized the reaction conditions for the synthesis of monoarylpyridines **4** (Table 1). As the C-I bond in postion 2 of starting material should be highly active, we started our optimization with the cheap and easy available $Pd(PPh_3)_4$ as catalyst and chose K_3PO_4 as base and toluene as solvent based on our

previous experiences on the arylation of pyridines.[17] After some experimentation, we found that the best yield of **4a** (78%) was obtained when the reaction was carried out using $Pd(PPh_3)_4$ (5 mol%) as the catalyst in a solvent mixture of toluene, water and ethanol (entry 3). However, employment of $Pd(OAc)_2$ and PCy_3 as a more active catalyst system did not give the desired product. Instead, the diarylated pyridine was formed as the main product (entry 4).

Table 1. Optimization for the synthesis of **4a**.



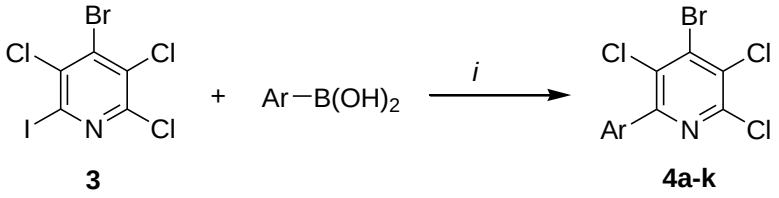
3 **4a**

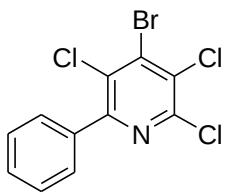
Entry	Catalyst (mol%)	Base (equiv.)	Solvent	$PhB(OH)_2$ (equiv.)	4a (%)[a]
1	$Pd(PPh_3)_4$ (5)	K_3PO_4 (1.1)	Toluene	1.1	40
2	$Pd(PPh_3)_4$ (5)	K_3PO_4 (1.5)	Toluene	1.5	60
3	$Pd(PPh_3)_4$ (5)	K_3PO_4 (1.5)	Toluene/H_2O/ EtOH (6:1:1)	1.5	78
4	$Pd(OAc)_2$ (5), $P(Cy)_3$(10)	K_3PO_4 (1.1)	Toluene	1.1	-

[a] Yield of isolated products.

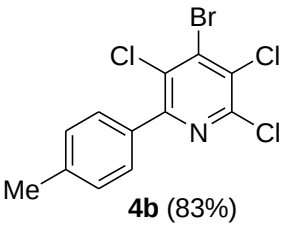
The reaction of **3** with various arylboronic acids, using our optimized conditions (Table 1, entry 3), afforded 4-bromo-2,3,5-trichloro-6-arylpyridines **4a-k** in 60 – 86 % yield (Table 2). The best yields were obtained for the reactions of **3** with 2-methoxyphenylboronic acid **4i** and 4-tolylboronic acid **4b**. Slightly lower yields were obtained when electron-poor arylboronic acids were employed (cf. compounds **4h, j, k**). A reaction at another position was not observed, showing the high degree of chemoselectivity at position 6. The structure of **4b** was independently confirmed by X-ray crystallographic analysis (Figure 2).

Table 2. Chemoselective synthesis of monoarylated pyridines **4a-k**.

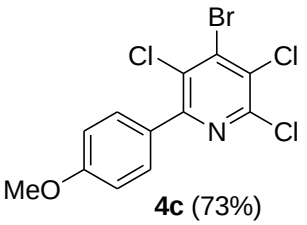




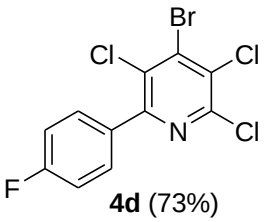
4a (78%)



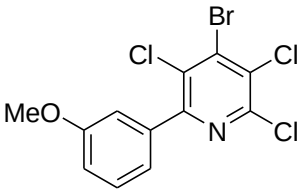
4b (83%)



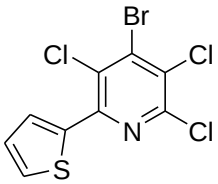
4c (73%)



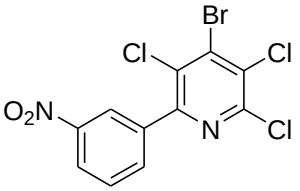
4d (73%)



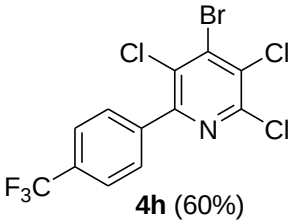
4e (77%)



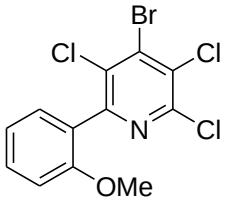
4f (81%)



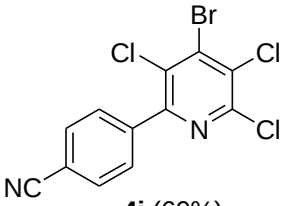
4g (78%)



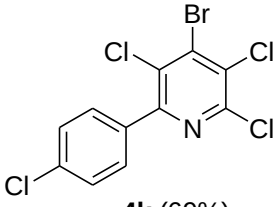
4h (60%)



4i (86%)



4j (60%)



4k (69%)

Reaction conditions *i*: **3** (0.3 mmol), $ArB(OH)_2$ (1.5 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (5 mol%), Toluene/EtOH/H_2O (6:1:1), 22 h, 100 °C; yield of isolated products.

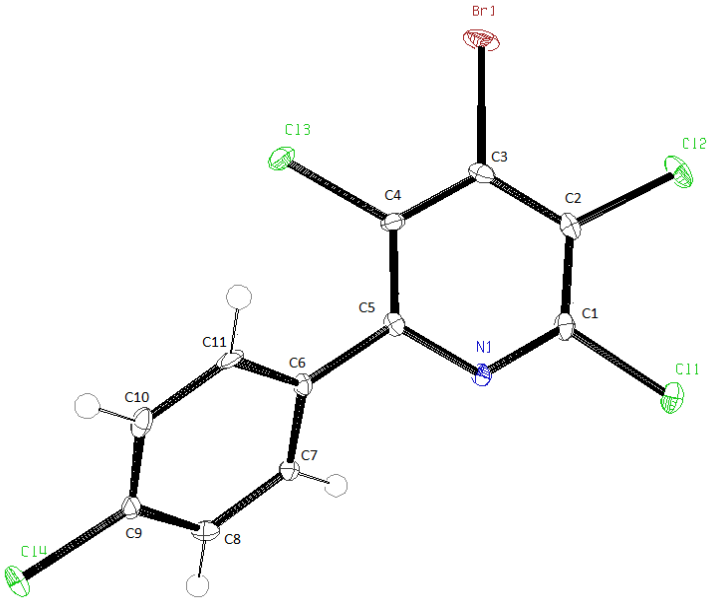
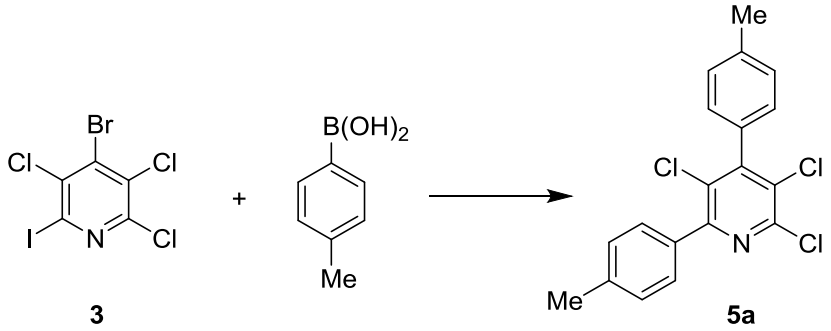


Figure 2. Ortep of compound **4k**[20]

Synthesis of 4,6-Diaryl-2,3,5-trichloropyridines 5

We envisioned that **3** might also be an ideal substrate for chemoselective diarylation of pyridine by Suzuki–Miyaura reactions, directed at positions 4 and 6 (Table 3), while previously employed pentachloropyridine resulted in selective formation of 2,6-diarylpyridines.

Table 3. Optimization of the synthesis of **5a**



3 **5a**

Entry	Catalyst (mol%)	Base (equiv.)	4-TolB(OH)$_2$ (equiv.)	Temp. (°C)	t (h)	**5a** (%)[a]
1	$Pd(PPh_3)_4$ (5)	K_3PO_4 (2.5)	2.5	100	19	50

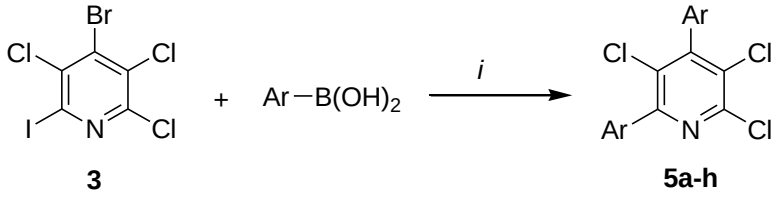
2[b]	$Pd(PPh_3)_4$ (5)	K_3PO_4 (2.5)	2.5	130	31	59
3[b]	$Pd(PPh_3)_4$ (5)	K_3PO_4 (3.0)	3.0	130	31	62
4	$Pd(OAc)_2$ (5), $P(Cy)_3$ (10)	K_3PO_4 (2.0)	2.0	100	19	75
5	$Pd(OAc)_2$ (5), $P(Cy)_3$ (10)	K_3PO_4 (2.1)	2.1	100	19	81
6	$Pd(OAc)_2$ (5), $P(Cy)_3$ (10)	K_3PO_4 (2.5)	2.5	100	19	67
7	$Pd(OAc)_2$ (5), $P(Cy)_3$ (10)	K_3PO_4 (3.0)	3.0	100	19	58
8	$Pd(OAc)_2$ (5), $P(Cy)_3$ (10)	K_3PO_4 (3.5)	3.5	100	19	38

[a] Yield of isolated products; [b] using xylene (mixture of isomers) was used as solvent

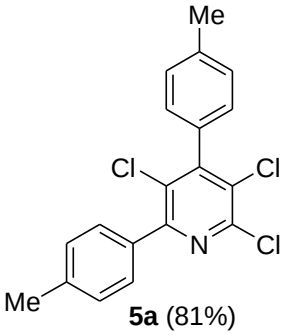
During the optimization process (Table 3), it became apparent that a catalytic system based on $Pd(OAc)_2$ and PCy_3 is superior to the employment of $Pd(PPh_3)_4$. Moreover, we realized that the isolated yield is highly sensitive to the employed amount of K_3PO_4 and the arylboronic acid. Hence, the best yield (81%) of product **5a** was obtained when the reaction was carried out using $Pd(OAc)_2/PCy_3$ and 2.1 equivalents of the arylboronic acid (entry 5). Generally, in all cases trace amounts of monoarylated and triarylated product have been detected by TLC analysis, leading to slightly diminished yields of the isolated product.

Using our optimized conditions, we were able to synthesize various 2,3,5-trichloro-4,6-diarylpyridines **5** in moderate to very good yield (Table 4). All reactions took place selectively at positions 4 and 6 of the pyridine moiety. The moderate yields of some products (**5g, 5h**) can be explained by the formation of substantial amounts of triarylated side-products using electron-poor arylboronic acids by electronically activating intermediates and products.

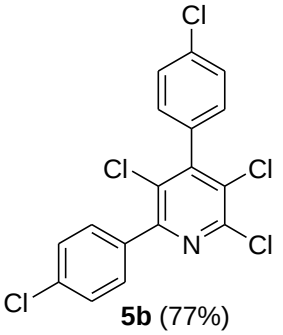
Table 4. Synthesis of 2,4-diarylated pyridines **5a-h**



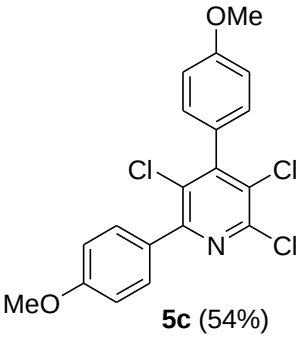
3 **5a-h**



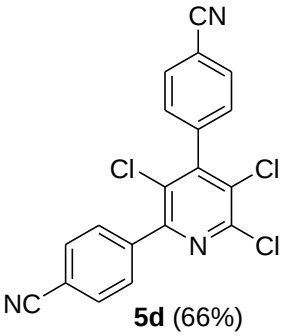
5a (81%)



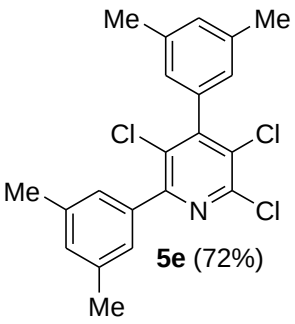
5b (77%)



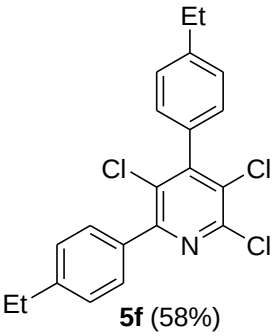
5c (54%)



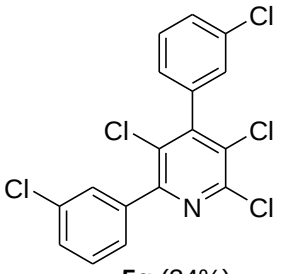
5d (66%)



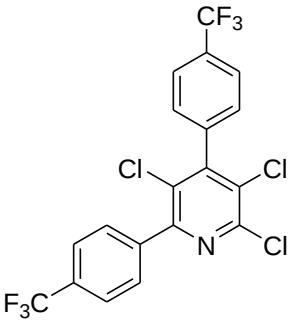
5e (72%)



5f (58%)



5g (34%)



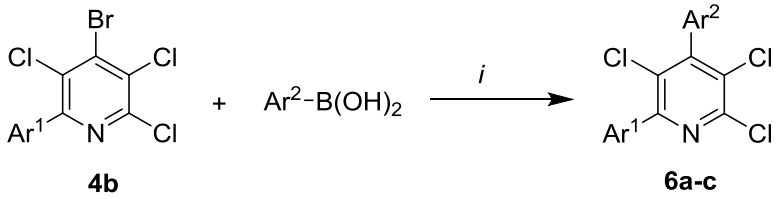
5h (35%)

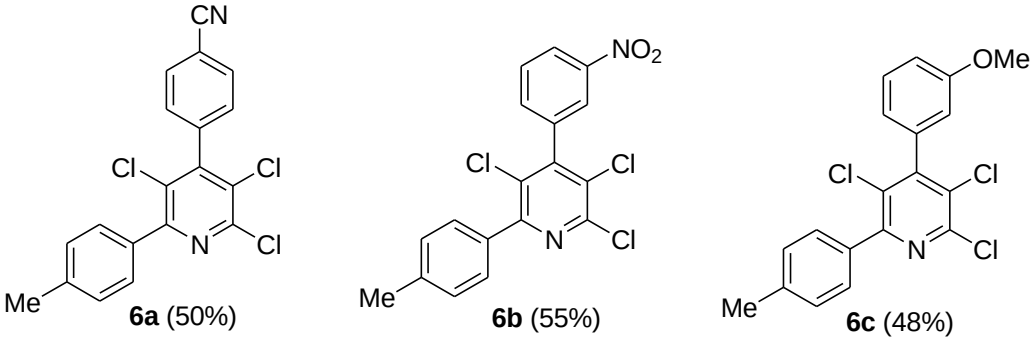
Reaction conditions *i*: **3** (0.26 mmol), $ArB(OH)_2$ (2.1 equiv.), K_3PO_4 (2.1 equiv.), $Pd(OAc)_2$ (5 mol%), PCy_3 (10 mol%), Toluene/*n*BuOH/H_2O (6:1:1), 19 h, 100 °C.

Next, we studied the chemoselective synthesis of diarylated pyridines **6a-c**, containing two different aryl substituents. These compounds were prepared in a two-step procedure, starting from compound **4b** (Table 5). The yields are not affected by the

nature of the substituents employed. However, practical separation problems of the corresponding triarylated side products are the main reason for the moderate isolated yields.

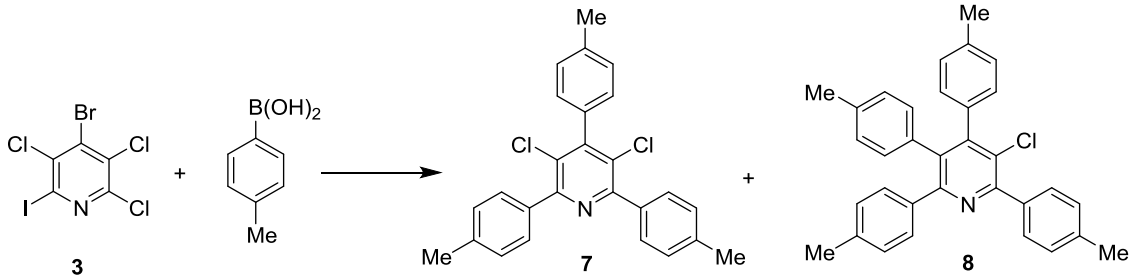
Table 5. Synthesis of 2,4-diarylated pyridines **6a-c**





Reaction conditions *i*: **4b** (0.29 mmol), $ArB(OH)_2$ (1.5 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (5 mol%), Toluene/*n*BuOH/H_2O (6:1:1), 19 h, 100 °C.

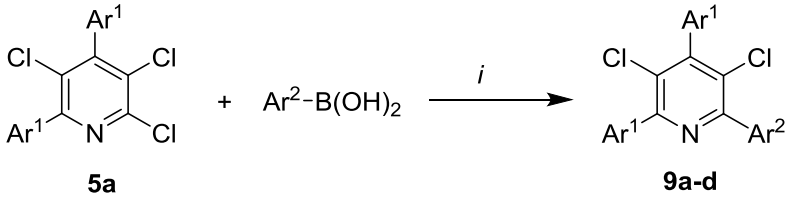
In the following studies, we attempted to realize the selective synthesis of triarylated pyridines using 2.5-4.5 equiv. of the appropriate arylboronic acid. However, in all cases, we isolated only inseparable mixtures of the expected 3,5-dichloro-2,4,6-triarylpyridine **7a** and of tetraarylated 3-chloro-2,4,5,6-tetraarylpyridine **8a** (cf. Supporting Information; Scheme 2). This is surprising, as position 6, located adjacent to the nitrogen atom, was expected to be significantly more reactive than positions 3 and 5, due to electronic reasons.

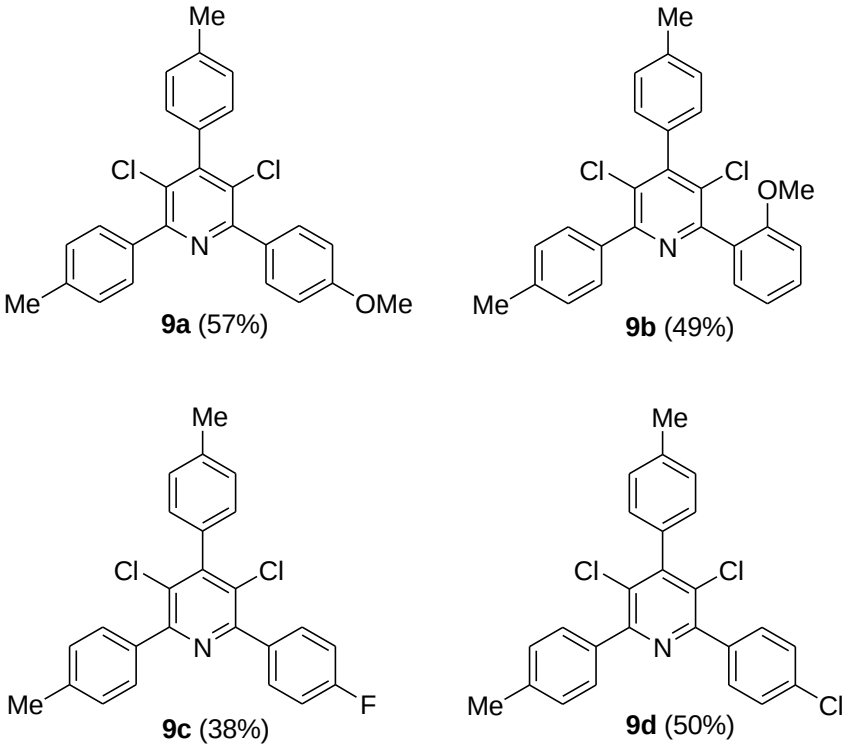


Scheme 2. Synthesis of a mixture of pyridines **7** and **8**

To overcome this drawback, we studied the applicability of pyridines **5** and **6** as starting materials for the synthesis of 2,4,6-triarylated pyridines **9** and **10**. To our delight, the Suzuki-Miyaura reaction of **5a** with 1.2 equivalents of the corresponding arylboronic acids, in the presence of $Pd(PPh_3)_4$, delivered the triarylated products **9a-d** (Table 6). The moderate yield can be explained by difficulties during column chromatography and are independent from the substitution pattern of the employed arylboronic acid.

Table 6. Synthesis of triarylated pyridines **9a-d**.

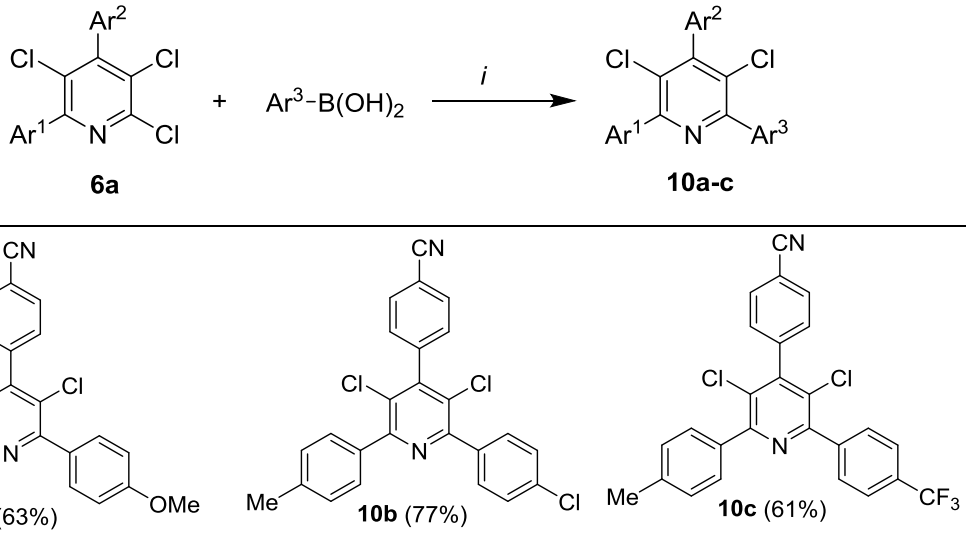




Reaction conditions *i*: **5a** (0.28 mmol), $ArB(OH)_2$ (1.2 equiv.), K_3PO_4 (1.2 equiv.), $Pd(PPh_3)_4$ (5 mol%), Toluene, 20 h, 100 °C.

The Suzuki-Miyaura reaction of **6a**, containing two different aryl groups, afforded the triarylated pyridines **10a-c**, which contain three different aryl rings, in good yields ranging from 61-77 % (Table 7).

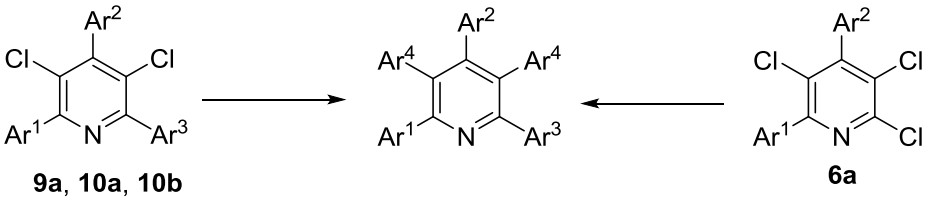
Table 7. Synthesis of triarylated pyridines **10a-c**.



Reaction conditions *i*: **6a** (0.27 mmol), $ArB(OH)_2$ (1.2 equiv.), K_3PO_4 (1.2 equiv.), $Pd(PPh_3)_4$ (5 mol%), Toluene, 20 h, 100 °C.

Finally, we studied the employment of synthesized compounds **6**, **9** and **10** for the synthesis of pentaarylpyridines, using our previously reported conditions.[14] Pentaarylated pyridines **11a,b**, containing three different aryl groups, were formed in excellent yields by reacting triarylated pyridine **9a** with 4-tolylboronic acid and 4-*tert*-butylphenylboronic acid, respectively (Table 8). Single crystal X-ray analysis independently proved the structure of pentaarylpyridine **11a** (Figure 3). Furthermore, the Suzuki-Miyaura reaction of **6a** gave pentaarylpyridines **12a** and **12b**, containing three different aryls groups, in 93 and 75 % yields, respectively. In the same manner, the Suzuki-Miyaura reaction of pyridines **10a** and **10b** resulted in arylation of positions 3 and 5 of the pyridine nucleus. The yields vary considerably, 90 % for **13a** and 50 % for **13b**, which might be due to side reactions of the aryl chloride moiety in position 2 of the starting material **10b**. However, the catalyst favors reaction at positions 3 and 5 of the pyridine, although two aryl rings are located in both *ortho*-positions, leaving the aryl chloride moiety in position 2 intact for further functionalization.

Table 8. Synthesis of Pentaarylpyridines **11**, **12** and **13**.

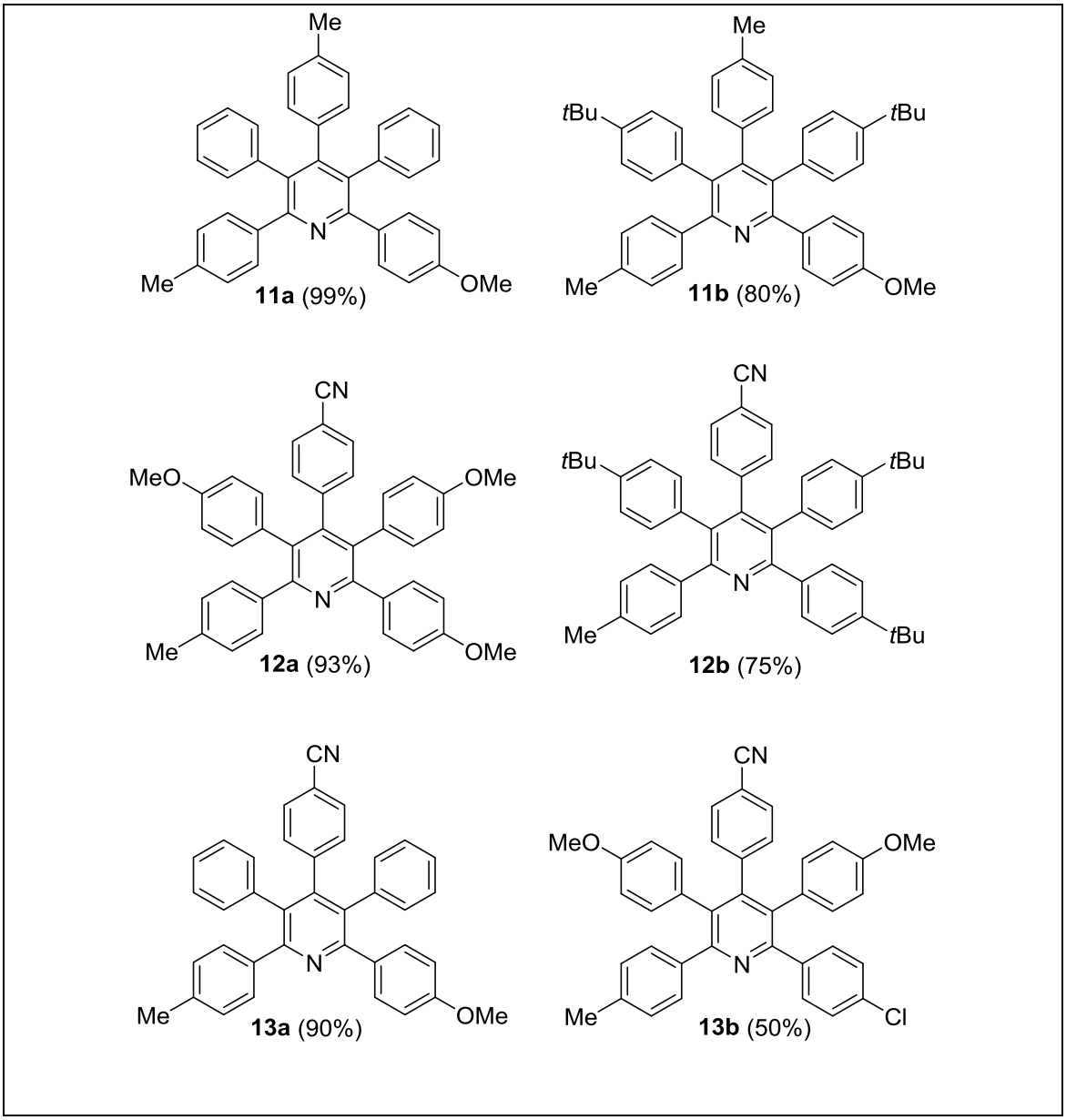


9a, **10a**, **10b**

11a,b $Ar^1=Ar^2\neq Ar^3\neq Ar^4$

12a,b $Ar^1\neq Ar^2\neq Ar^3=Ar^4$

13a,b $Ar^1\neq Ar^2\neq Ar^3\neq Ar^4$



Reaction conditions *i*: **6a**, **9a**, **10a** or **10b**, $ArB(OH)_2$ (2.0 equiv. per C-Cl bond.), K_3PO_4 (2.0 equiv. per C-Cl bond), $PdCl_2(CH_3CN)_2$ (5 mol%), SPhos (10 mol%), Toluene, 20 h, 100 °C.

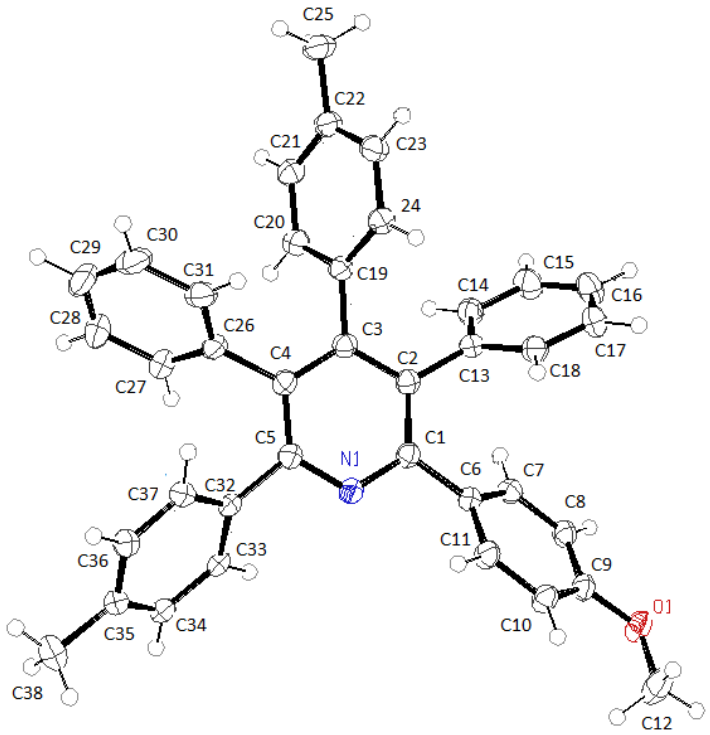


Figure 3. Ortep of compound **11a**[20]

Conclusions

In conclusion, we have developed an efficient method for the chemo- and site-selective synthesis of various substituted arylated pyridines by palladium-catalyzed cross-coupling reactions of newly synthesized 4-bromo-2,3,5-trichloro-6-iodopyridine (**3**). Our developed methodology shows a very good functional group tolerance for the selective synthesis of mono-, di- and triarylated pyridines which can be easily converted to corresponding fully arylated products in good yields.

Experimental Section

Synthesis of 4-bromo-2,3,5-trichloro-6-iodopyridine (3)

An oven-dried 100 ml Schlenk-Flask was charged with 3 ml *n*-butyllithium/hexane-Solution (2.5 M). The hexane was removed under reduced pressure and 7.5 ml of dry THF was added. The resulting solution was cooled down to –40 °C for 15 minutes and

(7.41mmol, 1.25 ml) of 2,2,6,6-Tetramethylpiperidine was slowly added. Afterwards it was allowed to warm to 0 °C (icebath) and stirred for 30 minutes at this temperature. The mixture was again cooled to -78 °C and stirred for 30 minutes at this temperature. In another Schlenk-Flask a solution of 2,3,5-trichloro-4-iodopyridine (3.73 mmol, 1.15 g) in 4 ml THF was prepared and added slowly to the LiTMP solution at -100 °C . The reaction mixture was stirred for 2 h. During this time a suspension appears. In a third Schlenk-Flask a solution of 1,2-dibromotetrachloroethane (11.24 mmol, 3.66 g = excess) in 11.5 ml THF was prepared and cooled to -78 °C. The reaction mixture was transferred into the solution of 1,2-dibromotetrachloroethane by funnel and was stirred for additional 2 hours at - 78 °C. The mixture was allowed to warm to room temperature overnight. The reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography using heptane/dichloromethane (10/1) as eluent.

4-bromo-2,3,5-trichloro-6-iodopyridine (3): colorless crystalline solid; yield: 77 % (1.118 g); mp 172 - 173 °C. **^{13}C-NMR** (62.9 MHz, $CDCl_3$): δ = 146.2 (C_{Hetar}), 138.9 (C_{Hetar}), 134.0 (C_{Hetar}), 132.7 (C_{Hetar}), 115.0 (C_{Hetar}). **MS** (EI, 70 eV): m/z (%) = 391 (M^+, 17), 389 (M^+, 65), 387 (M^+, 100), 385 (M^+, 48), 264 (12), 262 (42), 260 (65), 258 (34), 183 (12), 181 (40), 179 (38), 146 (13), 144 (21), 127 (77), 120 (12), 118 (16), 111 (17), 109 (47), 74 (23), 47 (11). **HR-MS** (EI): m/z = calcd. for C_5NBrCl_3I ($M+H^+$) 384.73189; found: 384.73204; calcd. for $C_5NBrCl_2{}^{37}ClI$ ($M+H^+$) 386.72894 found 386.72920; calcd. for $C_5N^{81}BrCl_3I$ ($M+H^+$) 386.72984; found 386.72920; calcd. for $C_5NBrCl^{37}Cl_2I$ ($M+H^+$) 388.72599; found 388.72642; calcd. for $C_5N^{81}BrCl_2{}^{37}ClI$ ($M+H^+$) 388.72689 ; found 388.72642; calcd. for $C_5N^{81}BrCl^{37}Cl_2I$ ($M+H^+$) 390.72394; found 390.72389; calcd. for $C_5NBr^{37}Cl_3I$ ($M+H^+$) 390.72304; found 390.72389. Anal. calcd. for C_5NBrCl_3I: C, 15.51; H, 3.62; found: C, 15.65; H, 3.71.

Synthesis of 4-Bromo-2,3,5-trichloro-6-arylpyridines (4a–k)

An oven-dried, argon-flushed sealable glass tube was charged with 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.3 mmol, 115.9 mg), $Pd(PPh_3)_4$ (5 mol%, 17.3 mg), the appropriate arylboronic acid (0.45 mmol) and K_3PO_4 (0.45 mmol, 95.53 mg) followed by a mixture of toluene/ water/ ethanol (6:1:1, 4 mL); The tube was sealed with a Teflon

valve and stirred at 100 °C for 19 h. The cooled reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography using heptane/dichloromethane as eluent.

4-bromo-2,3,5-trichloro-6-phenylpyridine (4a)

4a was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.3 mmol, 115.9 mg) and phenylboronic acid (0.45 mmol, 54.9 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 79 mg (78 %). mp. 111-112 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.67 - 7.69 (m, 2H, CH_{Ar}), 7.47-7.49 (m, 3H, CH_{Ar}). **^{13}C-NMR** (75.0 MHz, $CDCl_3$): δ = 154.9 ($C_{Ar/Hetar}$), 146.9 ($C_{Ar/Hetar}$), 137.0 ($C_{Ar/Hetar}$), 136.7 (C_{Ar}), 131.0 ($C_{Ar/Hetar}$), 130.7 ($C_{Ar/Hetar}$), 129.7 ($2CH_{Ar}$), 129.4 ($2CH_{Ar}$), 128.2 (CH_{Ar}). **MS** (EI, 70 eV): m/z (%) = 341 (M^+, 17), 339 (M^+, 63), 338 (M^+, 13), 337 (M^+, 100), 335 (M^+, 51), 304 (37), 303 (11), 302 (82), 300 (51), 223 (45), 222 (13), 221 (71), 186 (16), 185 (18), 160 (17), 151 (37), 150 (11), 120 (18), 118 (23), 111 (10), 110 (11), 80 (10), 51 (11). **HR-MS** (ESI): m/z = calcd. for $C_{11}H_5BrCl_3N$ ($M+H^+$) 335.87437; found: 335.87405; calcd. for $C_{11}H_5BrCl_2{}^{37}ClN$ ($M+H^+$) 337.87191; found 337.87132; calcd. for $C_{11}H_5{}^{81}BrCl_3N$ ($M+H^+$) 337.87191; found 337.87132; calcd. for $C_{11}H_5BrCl^{37}Cl_2N$ ($M+H^+$) 339.86925; found 339.86946; calcd. for $C_{11}H_5{}^{81}BrCl_2{}^{37}ClN$ ($M+H^+$) 339.86925; found 339.86946. Anal. calcd. for $C_{11}H_5BrCl_3N$: C, 39.15; H, 1.49; N, 4.15 found: C, 39.22; H, 1.60 ; N, 4.19

4-bromo-2,3,5-trichloro-6-*p*-tolylpyridine (4b)

4b was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.3 mmol, 115.9 mg) and *p*-tolylboronic acid (0.45 mmol, 61.2 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 87 mg (83 %). mp. 113 - 114 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.57 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.26 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 2.40 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 154.9 ($C_{Ar/Hetar}$), 146.8 ($C_{Ar/Hetar}$), 140.0 ($C_{Ar/Heta}$), 140.0 (C_{Ar}), 136.9 (C_{Ar}), 133.9 ($C_{Ar/Hetar}$), 130.6 ($C_{Ar/Hetar}$), 129.3 ($2CH_{Ar}$), 128.9 ($2CH_{Ar}$), 21.4 (CH_3). **MS** (EI, 70 eV): m/z (%) = 355 (M^+, 16), 354 (M^+, 13), 353 (M^+, 66), 352 (M^+, 30), 351 (M^+, 100), 350 (M^+, 29), 349 (M^+, 52), 348 (M^+, 13), 318 (15), 316 (29), 314 (19), 237 (10), 235 (17), 200 (12), 164 (20), 118 (12). **HR-MS** (ESI): m/z = calcd. for

$C_{12}H_7NBrCl_3$ ($M+H^+$) 348.88220; found: 348.88204; calcd. for $C_{12}H_7NBrCl_2{}^{37}Cl$ ($M+H^+$) 350.87925, found 350.87956; calcd. for $C_{12}H_7N^{81}BrCl_3$ ($M+H^+$) 350.88015, foud 350.87956; calcd. for $C_{12}H_7NBr^{37}Cl_2Cl$ ($M+H^+$) 352.87630, found 352.87636; calcd. for $C_{12}H_7N_{81}Br^{37}ClCl_2$ ($M+H^+$) 352.87720, found 352.87636. Anal. calcd. for $C_{12}H_7NBrCl_3$: C, 41.01; H, 2.01; N, 3.99 found: C, 41.19; H, 2.16; N, 4.09.

4-bromo-2,3,5-trichloro-6-(4-methoxyphenyl)pyridine (4c)

4c was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.3 mmol, 115.9 mg) and 4-methoxyphenylboronic acid (0.45 mmol, 68.4 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 80 mg (73 %). mp. 143 - 144 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.70 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.00 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 3.88 (s, 3H, OCH_3). **^{13}C-NMR** (75.0 MHz, $CDCl_3$): δ = 161.1 (*C*-OCH_3), 154.8 ($C_{Ar/Hetar}$), 146.9 ($C_{Ar/Hetar}$), 137.2 (C_{Ar}), 131.3 ($2CH_{Ar}$), 130.6 ($C_{Ar/Hetar}$), 130.5 ($C_{Ar/Hetar}$), 129.3 ($C_{Ar/Hetar}$), 113.9 ($2CH_{Ar}$), 55.7 (OCH_3). **MS** (EI, 70 eV): m/z (%) = 371 (M^+, 17), 370 (M^+, 8), 369 (M^+, 65), 368 (M^+, 14), 367 (M^+, 100), 365 (M^+, 52), 354 (5), 352 (7), 326 (11), 324 (16), 322 (8), 317 (5), 289 (10), 287 (6), 253 (5), 251 (7), 210 (7), 208 (11), 181 (5), 138 (7), 118 (5). **HR-MS** (ESI): m/z = calcd. for $C_{12}H_7ONBrCl_3$ ($M+H^+$) 364.87711; found: 364.87736; calcd. for $C_{12}H_7ONBrCl_2{}^{37}Cl$ ($M+H^+$) 366.87416 ; found 366.87499; calcd. for $C_{12}H_7ON^{81}BrCl_3$ ($M+H^+$) 366.87506; found 366.87499; calcd. for $C_{12}H_7ON^{81}BrCl_2{}^{37}Cl$ ($M+H^+$) 368.87211; found 368.87229; calcd. for $C_{12}H_7ONBrCl^{37}Cl_2$ ($M+H^+$) 368.87121; found 368.87229; calcd. for $C_{12}H_7ON^{81}BrCl^{37}Cl_2$ ($M+H^+$) 370.86916; found 370.86951; calcd. for $C1_2H_7ONBr^{37}Cl_3$ ($M+H^+$) 370.86826; found 370.86951. Anal. calcd. for $C_{12}H_7BrCl_3NO$: C, 39.22; H, 1.92; N, 3.81 found: C, 39.35; H, 2.01; N, 4.02.

4-bromo-2,3,5-trichloro-6-(4-fluorophenyl)pyridine (4d)

4d was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.3 mmol, 115.9 mg) and 4-fluorophenylboronic acid (0.45 mmol, 63.0 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 78 mg (73 %). mp. 148 - 149 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.67-7.74 (m, 2H, CH_{Ar}), 7.13 - 7.21 (m, 2H, CH_{Ar}). **^{13}C-NMR** (75.0 MHz, $CDCl_3$): δ = 163.5 (d, ^1J = 250.6 Hz, C_{Ar}-F), 153.8 (C_{Hetar}), 147.0 (C_{Hetar}), 137.1 (C_{Hetar}), 132.7

(d, ^4J = 3.3 Hz, C_{Ar}), 131.5 (d, ^3J = 8.5 Hz, $2CH_{Ar}$), 131.1 (C_{Hetar}), 130.6 (C_{Hetar}), 115.3 (d, ^2J = 21.9 Hz, $2CH_{Ar}$). **^{19}F-NMR** (282 MHz, $CDCl_3$): δ = -110.49. **MS** (EI, 70 eV): m/z (%) = 359 (M^+, 17), 358 (M^+, 8), 357 (M^+, 61), 356 (M^+, 12), 355 (M^+, 100), 353 (M^+, 50), 322 (20), 320 (44), 318 (26), 241 (29), 240 (8), 239 (46), 204 (10), 178 (13), 169 (22), 120 (13), 118 (16). **HR-MS** (ESI): m/z = calcd. for $C_{11}H_4NBrCl_3F$ ($M+H^+$) 352.85712, found: 352.85730; calcd. for $C_{11}H_4NBrCl_2{}^{37}ClF$ ($M+H^+$) 354.85417; found 354.85455; calcd. for $C_{11}H_4N^{81}BrCl_3F$ ($M+H^+$) 354.85508, found 354.85455; calcd. for $C_{11}H_4N^{81}BrCl_2{}^{37}ClF$ ($M+H^+$) 356.85213; found 356.85190; calcd. for $C_{11}H_4NBrCl^{37}Cl_2F$ ($M+H^+$) 356.85122; found 356.85190; calcd. for $C_{11}H_4N^{81}BrCl^{37}Cl_2F$ ($M+H^+$) 358.84918; found 358.84890; calcd. for $C_{11}H_4NBr^{37}Cl_3F$ ($M+H^+$) 358.84827; found 358.84890. Anal. calcd. for $C_{11}H_4BrCl_3FN$: C, 37.17; H, 1.13; N, 3.94 found: C, 37.14; H, 1.23; N, 4.16.

4-bromo-2,3,5-trichloro-6-(3-methoxyphenyl)pyridine (4e)

4e was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.3 mmol, 115.9 mg) and 3-methoxyphenylboronic acid (0.45 mmol, 68.4 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 85 mg (77 %). mp. 128 - 129 °C. **^{1}H-NMR** (250 MHz, $CDCl_3$): δ = 7.40 (pt, ^3J = 7.9 Hz, 1H, CH_{Ar}), 7.25 (ddd, ^3J = 6.67 Hz, ^4J = 1.6 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 7.18 (dd, ^4J = 2.6 Hz, ^4J = 1.6 Hz, 1H, CH_{Ar}), 7.02 (ddd, ^3J = 8.2 Hz, ^4J = 2.6 Hz, ^4J = 1.0 Hz, 1H, CH_{Ar}), 3.87 (s, 3H, OCH_3). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 159.3 (*C*-OCH_3), 154.8 ($C_{Ar/Hetar}$), 146.9 ($C_{Ar/Hetar}$), 137.9 (C_{Ar}), 137.0 ($C_{Ar/Hetar}$), 131.1 ($C_{Ar/Hetar}$), 130.8 ($C_{Ar/Hetar}$), 129.3 (CH_{Ar}), 121.7 (CH_{Ar}), 115.5 (CH_{Ar}), 114.8 (CH_{Ar}), 55.4 (OCH_3). **MS** (EI, 70 eV): m/z (%) = 371 (M^+, 18), 370 (M^+, 19), 369 (M^+, 65), 368 (M^+, 61), 367 (M^+, 100), 366 (M^+, 79), 365 (M^+, 51), 364 (M^+, 37), 341, 340 (14), 339 (15), 338 (23), 337 (20), 336 (13), 302 (18), 300 (12), 289 (10), 223 (10), 221 (15), 210 (13), 208 (18), 138 (10), 118 (10). **HR-MS** (ESI): m/z = calcd. for $C_{12}H_7ONBrCl_3$ ($M+H^+$) 364.87711, found: 364.87699; calcd. for $C_{12}H_7ONBrCl_2{}^{37}Cl$ ($M+H^+$) 366.87416; found 366.87451; calcd. for $C_{12}H_7ON^{81}BrCl_3$ ($M+H^+$) 366.87506, found 366.87451; calcd. for $C_{12}H_7ON^{81}BrCl_2{}^{37}Cl$ ($M+H^+$) 368.87211; found 368.87179; calcd. for $C_{12}H_7ONBrCl^{37}Cl_2$ ($M+H^+$) 368.87121; found 368.87179; calcd. for $C_{12}H_7ON^{81}BrCl^{37}Cl_2$ ($M+H^+$) 370.86916, found 370.86922; calcd. for $C_{12}H_7ONBr^{37}Cl_3$

($M+H^+$) 370.86826; found 370.86922. Anal. calcd. for $C_{12}H_7BrCl_3NO$: C, 39.22; H, 1.92; N, 3.81 found: C, 39.40; H, 2.03; N, 3.99.

4-bromo-2,3,5-trichloro-6-(thiophen-2-yl)pyridine (4f)

4f was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.3 mmol, 115.9 mg) and 2-thienylboronic acid (0.45 mmol, 57.6 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 83 mg (81 %). mp. 98 - 99 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 8.08 (dd, ^4J = 3.0 Hz, ^4J = 1.3 Hz, 1H, CH_{Hetar}), 7.69 (dd, ^3J = 5.1 Hz, ^4J = 1.3 Hz, 1H, CH_{Hetar}), 7.40 (dd, ^3J = 5.1 Hz, ^4J = 3.0 Hz, 1H, CH_{Hetar}). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 149.5 (C_{Hetar}), 146.6(C_{Hetar}), 137.4(C_{Hetar}), 137.1(C_{Hetar}), 130.2(C_{Hetar}), 129.7(C_{Hetar}), 128.8 (CH_{Hetar}), 128.7(CH_{Hetar}), 125.2(CH_{Hetar}). **MS** (EI, 70 eV): m/z (%) = 347 (M^+, 19), 346 (M^+, 9), 345 (M^+, 70), 344 (M^+, 15), 343 (M^+, 100), 341 (M^+, 49), 310 (19), 308 (40), 306 (24), 229 (13), 227 (19), 157 (12), 118 (12), 45 (12). **HR-MS** (ESI): m/z = calcd. for $C_9H_3NBrCl_3S$ ($M+H^+$) 340.82297; found 340.82284; calcd. for $C_9H_3N^{81}BrCl_3S$ ($M+H^+$) 342.82092; found 342.82059; calcd. for $C_9H_3NBrCl_2{}^{37}ClS$ ($M+H^+$) 342.82002; found 342.82059; calcd. for $C_9H_3N^{81}BrCl_2{}^{37}ClS$ ($M+H^+$) 344.81797; found 344.81780; calcd. for $C_9H_3NBrCl^{37}Cl_2S$ ($M+H^+$) 344.81707; found 344.81780; calcd. for $C_9H_3N^{81}BrCl^{37}Cl_2S$ ($M+H^+$) 346.81502; found 346.81466; calcd. for $C_9H_3NBr^{37}Cl_3S$ ($M+H^+$) 346.81412; found 346.81466. Anal. calcd. for $C_9H_3BrCl_3NS$: C, 31.47; H, 0.88; N, 4.08 found: C, 31.60; H, 1.20; N, 4.29.

4-bromo-2,3,5-trichloro-6-(3-nitrophenyl)pyridine (4g)

4g was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.3 mmol, 115.9 mg) and 3-nitrophenylboronic acid (0.45 mmol, 75.1 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 89 mg (78 %). mp. 166 - 167 °C. **^{1}H-NMR** (250 MHz, $CDCl_3$): δ = 8.60 (pt, ^4J = 1.7 Hz, 1H, CH_{Ar}), 8.34 (ddd, ^3J = 8.3 Hz, ^4J = 2.3 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 8.05 (ddd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, ^4J = 1.1 Hz, 1H, CH_{Ar}), 7.68 (pt, ^3J = 8.0 Hz, 1H, CH_{Ar}). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 152.0 ($C_{Ar/Hetar}$), 148.0 ($C_{Ar/Hetar}$), 147.5 (C_{Ar}), 138.0 (C_{Ar}), 137.5 ($C_{Ar/Hetar}$), 135.4 (CH_{Ar}), 132.4 ($C_{Ar/Hetar}$), 130.9 ($C_{Ar/Hetar}$), 129.4 (CH_{Ar}), 124.7 (CH_{Ar}), 124.5 (CH_{Ar}). **MS** (EI, 70 eV): m/z (%) = 386 (M^+, 19), 385 (M^+, 10), 384 (M^+, 66), 383 (M^+, 14), 382 (M^+, 100), 380 (M^+,

54), 340 (12), 338 (46), 337 (10), 336 (70), 334 (35), 324 (10), 301 (16), 299 (10), 257 (27), 255 (26), 220 (15), 187 (11), 185 (32), 118 (11). **HR-MS** (ESI): m/z = calcd. for $C_{11}H_4O_2N_2BrCl_3$ ($M+H^+$) 379.85162; found: 379.85154; calcd. for $C_{11}H_4O_2N_2BrCl_2{}^{37}Cl$ ($M+H^+$) 381.84867; found 381.84911; calcd. for $C_{11}H_4O_2N_2{}^{81}BrCl_3$ ($M+H^+$) 381.84958; found 381.84911; calcd. for $C_{11}H_4O_2N_2BrCl^{37}Cl_2$ ($M+H^+$) 383.84572; found 383.84618; calcd. for $C_{11}H_4O_2N_2{}^{81}BrCl_2{}^{37}Cl$ ($M+H^+$) 383.84663; found 383.84618; calcd. for $C_{11}H_4O_2N_2Br{}^{37}Cl_3$ ($M+H^+$) 385.81277, found 385.84350; calcd. for $C_{11}H_4O_2N_2{}^{81}BrCl^{37}Cl_2$ ($M+H^+$) 385.84368; found 385.84350. Anal. calcd. for $C_{11}H_4BrCl_3N_2O_2$: C, 34.55; H, 1.05; N, 7.33 found: C, 34.36; H, 1.15; N, 7.19.

4-bromo-2,3,5-trichloro-6-(4-(trifluoromethyl)phenyl)pyridine (4h)

4h was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.3 mmol, 115.9 mg) and 4-(trifluoromethyl)phenylboronic acid (0.45 mmol, 85.5 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 73 mg (60 %). mp. 123 - 124 °C. **^{1}H-NMR** (250 MHz, $CDCl_3$): δ = 7.82 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 7.75 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 153.3 ($C_{Ar/Hetar}$), 147.3 ($C_{Ar/Hetar}$), 140.0 (q, ^5J = 1.1 Hz, C_{Ar}), 137.3 ($C_{Ar/Hetar}$), 132.0 ($C_{Ar/Hetar}$), 131.6 (q, ^2J = 32.7 Hz, (C_{Ar}), 130.9 ($C_{Ar/Hetar}$), 129.8 ($2CH_{Ar}$), 125.3 (q, ^3J = 3.7 Hz, $2CH_{Ar}$), 123.8 (q, ^1J = 272.8 Hz, CF_3). **^{19}F-NMR** (235 MHz, $CDCl_3$): δ = - 62.89 ($ArCF_3$). **MS** (EI, 70 eV): m/z (%) = 409 (M^+, 17), 408 (M^+, 9), 407 (M^+, 63), 406 (M^+, 14), 405 (M^+, 100), 404 (M^+, 7), 403 (M^+, 53), 386 (8), 372 (33), 371 (10), 370 (74), 368 (47), 291 (41), 290 (14), 289 (64), 257 (12), 255 (18), 254 (19), 253 (13), 228 (19), 219 (24), 218 (14), 200 (11), 193 (14), 185 (12), 169 (11), 155 (17), 153 (18), 145 (11), 123 (12), 122 (11), 121 (10), 75 (17), 74 (10), 69 (18). **HR-MS** (EI): m/z = calcd. for $C_{12}H_4NBrCl_3F_3$ $[M]^+$: 402.85393; found: 402.85369; calcd. for $C_{12}H_4NBrCl_2{}^{37}ClF_3$: 404.85098; found 404.85134; calcd. for $C_{12}H_4N^{81}BrCl_2{}^{37}ClF_3$: 406.84893; found 406.84873. Anal. calcd. for $C_{12}H_4BrCl_3F_3N$: C 35.55, H 0.99, N 3.45; found: C 35.75, H 1.03 , N 3.36.

4-bromo-2,3,5-trichloro-6-(2-methoxyphenyl)pyridine (4i)

4i was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.3 mmol, 115.9 mg) and 2-methoxyphenylboronic acid (0.45 mmol, 68.4 mg) and was purified via column chromatography (heptane/dichloromethane). Pink

solid; yield: 94 mg (86 %). mp. 123 - 124 °C. **^{1}H-NMR** (250 MHz, $CDCl_3$): δ = 7.37-7.48 (m, 1H, CH_{Ar}), 7.27 (dd, ^{3}J = 7.0 Hz, ^{4}J = 2.1 Hz, 1H, CH_{Ar}), 6.97-7.09 (m, 2H, CH_{Ar}), 3.81 (s, 3H, OCH_3). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 156.6 (*C*-OCH_3), 153.9 ($C_{Ar/Hetar}$), 146.6 ($C_{Ar/Hetar}$), 135.9 ($C_{Ar/Hetar}$), 133.0 ($C_{Ar/Hetar}$), 131.1 (CH), 131.0 ($C_{Ar/Hetar}$), 130.1 (CH), 126.5 (C_{Ar}), 120.7 (CH_{Ar}), 111.0 (CH_{Ar}), 55.5 (OCH_3). **MS** (EI, 70 eV): m/z (%) = 369 (M^+, 15), 367 (M^+, 23), 365 (M^+, 12), 334 (46), 333 (15), 332 (100), 331 (13), 330 (64), 317 (10), 304 (21), 302 (21), 273 (11), 271 (12), 253 (37), 252 (12), 251 (57), 225 (11), 223 (27), 222 (10), 221 (22), 216 (16), 210 (15), 208 (20), 201 (11), 188 (11), 187 (13), 185 (12), 151 (15), 147 (12), 138 (18), 120 (14), 118 (20), 111 (11), 63 (12), 62 (6), 39 (8). **HR-MS** (EI): m/z = calcd. for $C_{12}H_7ONBrCl_3$ $[M]^+$: 364.87711; found: 364.87695; calcd. for $C_{12}H_7ONBrCl_2{}^{37}Cl$: 366.87416; found 366.87456; calcd. for $C_{12}H_7ON\ {}^{81}BrCl_2{}^{37}Cl$: 368.87211; found 368.87198. Anal. calcd. for $C_{12}H_7BrCl_3NO$: C 39.22, H 1.92, N 3.81; found: C 39.52, H 2.45, N 3.46.

4-bromo-2,3,5-trichloro-6-(4-cyanophenyl)pyridine (4j)

4j was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.3 mmol, 115.9 mg) and 4-cyanophenylboronic acid (0.45 mmol, 66.1 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 64 mg (60 %). mp. 195 - 196 °C. **^{1}H-NMR** (250 MHz, $CDCl_3$): δ = 7.74-7.84 (m, 4H, CH_{Ar}). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 152.6 ($C_{Ar/Hetar}$), 147.4 ($C_{Ar/Hetar}$), 140.7 ($C_{Ar/Hetar}$), 137.5 ($C_{Ar/Hetar}$), 132.3 ($C_{Ar/Hetar}$), 132.0 ($2CH_{Ar}$), 130.9 ($C_{Ar/Hetar}$), 130.2 ($2CH_{Ar}$), 118.2 (C≡N), 113.5 (C_{Ar}). **MS** (EI, 70 eV): m/z (%) = 366 (M^+, 17), 365 (M^+, 9), 364 (M^+, 64), 363 (M^+, 14), 362 (M^+, 100), 361 (M^+, 8), 360 (M^+, 52), 329 (36), 328 (12), 327 (79), 325 (50), 248 (39), 247 (13), 246 (61), 212 (10), 211 (20), 210 (21), 187 (10), 185 (28), 176 (38), 163 (10), 155 (14), 153 (15), 150 (12), 124 (12), 123 (19) 122 (11), 120 (34), 118 (49), 110 (10), 99 (15), 92 (12), 76 (10), 75 (19), 74 (12). **HR-MS** (EI): m/z = calcd. for $C_{12}H_4N_2BrCl_3$ $[M]^+$: 359.86180; found: 359.86197; calcd. for $C_{12}H_4N_2{}^{81}BrCl_3$: 361.85975; found 361.85963; calcd. for $C_{12}H_4N_2\ {}^{81}BrCl_2{}^{37}Cl$: 363.85680; found 363.85706; calcd. for $C_{12}H_4N_2{}^{81}BrCl^{37}Cl_2$: 365.85385; found 365.85453. Anal. calcd. for $C_{12}H_4BrCl_3N_2$: C 39.77, H 1.11, N 7.73; found: C 40.24, H 1.36, N 7.39.

4-bromo-2,3,5-trichloro-6-(4-chlorophenyl)pyridine (4k)

4k was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.3 mmol, 115.9 mg) and 4-chlorophenylboronic acid (0.45 mmol, 70.4 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 77 mg (69 %). mp. 161 - 162 °C. **^{1}H-NMR** (250 MHz, $CDCl_3$): δ = 7.65 (d, ^{3}J = 8.56 Hz, 2H, CH_{Ar}), 7.46 (d, ^{3}J = 8.56 Hz, 2H, CH_{Ar}). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 153.6 ($C_{Ar/Hetar}$), 147.1 ($C_{Ar/Hetar}$), 137.2 ($C_{Ar/Hetar}$), 136.0 (C_{Ar}), 135.0 ($C_{Ar/Hetar}$), 131.3 ($C_{Ar/Hetar}$), 130.8 ($2CH_{Ar}$), 130.7 (C_{Ar}), 128.5 ($2CH_{Ar}$). **MS** (EI, 70 eV): m/z (%) = 377 (M^+, 6), 375 (M^+, 32), 374 (M^+, 10), 373 (M^+, 83), 372 (M^+, 13), 371 (M^+, 100), 370 (M^+, 6), 369 (M^+, 45), 338 (31), 336 (49), 334 (26), 259 (17), 257 (54), 256 (10), 255 (57), 222 (10), 221 (10), 220 (15), 219 (12), 196 (12), 194 (12), 187 (14), 185 (41), 169 (11), 168 (15), 155 (12), 153 (12), 150 (12), 123 (14), 120 (25), 118 (33), 111 (13), 110 (12), 109 (10), 99 (12), 98 (17), 97 (20), 85 (10), 75 (20), 74 (14), 50 (10). **HR-MS** (EI): m/z = calcd. for $C_{11}H_4NBrCl_4$ $[M]^+$: 368.82757; found: 368.82764; calcd. for $C_{11}H_4NBrCl_3{}^{37}Cl$: 370.82462; found 370.82506; calcd. for $C_{11}H_4N{}^{81}BrCl_3{}^{37}Cl$: 372.82258; found 372.82230; calcd. for $C_{11}H_4N{}^{81}BrCl_2{}^{37}Cl_2$: 374.81963; found 374.81961. Anal. calcd. for $C_{11}H_4BrCl_4N$: C 35.53, H 1.08, N 3.77; found: C 35.67, H 1.18, N 3.76.

Synthesis of 4,6-diaryl-2,3,5-trichloropyridines (5a–h)

An oven-dried, argon-flushed sealable glass tube was charged with 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.26 mmol, 100 mg), $Pd(OAc)_2$ (5 mol%, 2.9 mg), PCy_3 (10 mol%, 7.24 mg), the appropriate arylboronic acid (0.55 mmol) and K_3PO_4 (0.55 mmol, 115.12 mg) followed by a mixture of toluene/water/*n*-butanol (6:1:1, 4 mL). The tube was sealed with a Teflon valve and stirred at 100 °C for 19 h. The cooled reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography using heptane/dichloromethane as eluent.

2,3,5-trichloro-4,6-di-*p*-tolylpyridine (5a):

5a was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.26 mmol, 100 mg) and *p*-tolylboronic acid (0.55 mmol, 74.8 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 76 mg (81 %). mp. 121 - 122 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.65 (d,

^3J = 8.2 Hz, 2H, CH_{Ar}), 7.35 (d, ^3J = 8.0 Hz, 2H, CH_{Ar}), 7.29 (d, ^3J = 8.0 Hz, 2H, CH_{Ar}), 7.19(d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 2.46 (s, 3H, CH_3), 2.43 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 154.9 ($C_{Ar/Hetar}$), 150.9 ($C_{Ar/Hetar}$), 147.1($C_{Ar/Hetar}$), 139.5 ($C_{Ar/Hetar}$), 139.1 ($C_{Ar/Hetar}$), 134.1 ($C_{Ar/Hetar}$), 133.0 ($C_{Ar/Hetar}$), 129.4 ($4CH_{Ar}$), 129.0 ($2C_{Ar/Hetar}$), 128.8 ($2CH_{Ar}$), 128.3($2CH_{Ar}$), 21.5 (CH_3), 21.4 (CH_3). **MS** (EI, 70 eV): m/z (%) = 366 (M^+, 7), 365 (M^+, 34), 364 (M^+, 24), 363 (M^+, 97), 362 (M^+, 33), 361 (M^+, 100), 360 (M^+, 13), 328 (32), 327 (11), 326 (50), 255 (9), 254 (11), 241 (7), 240 (14), 91 (8). **HR-MS** (ESI): m/z = calcd. for $C_{19}H_{14}Cl_3N$ ($M+H^+$) 361.01863, found: 361.01827. Anal. calcd. for $C_{19}H_{14}Cl_3N$: C, 62.92; H, 3.89; N, 3.86 found: C, 62.89; H, 3.82; N, 3.95.

2,3,5-trichloro-4,6-bis(4-chlorophenyl)pyridine (5b)

5b was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.26 mmol, 100 mg) and 4-chlorophenylboronic acid (0.55 mmol, 86.0 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 80 mg (77 %). mp. 143 - 144 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.70 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.53 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 7.46 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.23 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 153.7 ($C_{Ar/Hetar}$), 149.9 ($C_{Ar/Hetar}$), 147.5 ($C_{Ar/Hetar}$), 135.8 ($C_{Ar/Hetar}$), 135.4 ($C_{Ar/Hetar}$), 135.0 ($C_{Ar/Hetar}$), 133.8 ($C_{Ar/Hetar}$), 130.9 ($2CH_{Ar}$), 129.9 ($2CH_{Ar}$), 129.5 ($C_{Ar/Hetar}$), 129.2 ($2CH_{Ar}$), 128.7 ($C_{Ar/Hetar}$), 128.5 ($2CH_{Ar}$). **MS** (EI, 70 eV): m/z (%) = 407 (M^+, 21), 406 (M^+, 12), 405 (M^+, 65), 404 (M^+, 19), 403 (M^+, 100), 402 (M^+, 13), 401 (M^+, 63), 370 (26), 369 (11), 368 (54), 366 (42), 333 (14), 331 (15), 297 (15), 296 (15), 295 (21), 263 (12), 261 (38), 225 (22), 196 (15), 194 (22), 185 (13), 184 (15), 149 (18), 148 (27), 135 (11), 130 (24), 99 (15), 75 (14). **HR-MS** (ESI): m/z = calcd. for $C_{17}H_8Cl_5N$ ($M+H^+$) 401.91721, found: 401.91763; calcd. for $C_{17}H_8\,Cl_4{}^{35}ClN$: 403.91436, found: 403.9144; calcd. for $C_{17}H_8\,Cl_3{}^{35}Cl_2N$: 405.91156; found 405.91234. Anal. calcd. for $C_{17}H_8Cl_5N$: C, 50.60; H, 2.00; N, 3.47 found: C, 50.74; H, 2.28; N, 3.54.

2,3,5-trichloro-4,6-bis(4-methoxyphenyl)pyridine (5c)

5c was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.26 mmol, 100 mg) and 4-methoxyphenylboronic acid (0.55 mmol, 83.6 mg) and was purified via column chromatography (heptane/dichloromethane).

White solid; yield: 55 mg (54 %). mp. 122 - 123 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.74 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 7.23 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 7.06 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 6.99 (d, ^{3}J = 8.9 Hz, 2H, CH_{Ar}), 3.89 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 160.5 (*C*-OCH_3), 160.0 (*C*-OCH_3), 154.4 ($C_{Ar/Hetar}$), 150.6 ($C_{Ar/Hetar}$), 147.1($C_{Ar/Hetar}$), 131.1 ($2CH_{Ar}$), 129.9 ($2CH_{Ar}$), 129.4 ($C_{Ar/Hetar}$), 129.0 ($C_{Ar/Hetar}$), 128.9 ($C_{Ar/Hetar}$), 128.1 ($C_{Ar/Hetar}$), 114.0 ($2CH_{Ar}$), 113.5($2CH_{Ar}$), 55.35 (OCH_3), 55.27 (OCH_3). **MS** (EI, 70 eV): m/z (%) = 398 (M^+, 7), 397 (M^+, 32), 396 (M^+, 21), 395 (M^+, 96), 394 (M^+, 22), 393 (M^+, 100), 352 (8), 350 (8), 315 (7), 272 (7), 237 (8), 202 (8), 201 (13), 197 (9), 196 (11), 176 (7), 175 (11), 124 (7), 123 (7). **HR-MS** (EI): m/z = calcd. for $C_{19}H_{14}O_2NCl_3$ $[M]^+$: 393.00846; found: 393.00705; calcd. for $C_{19}H_{14}O_2NCl_2{}^{37}Cl$: 395.00551; found 395.00537; calcd. for $C_{19}H_{14}O_2NCl{}^{37}Cl_2$: 397.00256; found 397.00288. Anal. calcd. for $C_{19}H_{14}Cl_3NO_2$: C 57.82, H 3.58, N 3.55; found: C 58.08, H 3.69, N 3.49.

2,3,5-trichloro-4,6-bis(4-cyanophenyl)pyridine (5d)

5d was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.26 mmol, 100 mg) and 4-cyanophenylboronic acid (0.55 mmol, 80.8 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 65 mg (66 %). mp. 232 - 233 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.88-7.84 (m, 4H, $4CH_{Ar}$), 7.79 (d, ^{3}J = 8.3 Hz, 2H, CH_{Ar}), 7.43 (d, ^{3}J = 8.4 Hz, 2H, CH_{Ar}). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 152.9 ($C_{Ar/Hetar}$), 149.3 ($C_{Ar/Hetar}$), 148.1 ($C_{Ar/Hetar}$), 140.5 ($C_{Ar/Hetar}$), 139.5 ($C_{Ar/Hetar}$), 132.7 ($2CH_{Ar}$), 132.0 ($2CH_{Ar}$), 130.3 ($2CH_{Ar}$), 130.0 ($C_{Ar/Hetar}$), 129.4 ($2CH_{Ar}$), 128.3 ($C_{Ar/Hetar}$), 118.2 (C≡N), 118.0 (C≡N), 113.6 (C_{Ar}), 113.4(C_{Ar}). **MS** (EI, 70 eV): m/z (%) = 388 (M^+, 6), 387 (M^+, 31), 386 (M^+, 19), 385 (M^+, 93), 384 (M^+, 22), 383 (M^+, 95), 352 (12), 351 (14), 350 (63), 349 (22), 348 (100), 313 (15), 286 (15), 278 (25), 277 (49), 252 (17), 251 (19), 250 (22), 224 (12), 187 (15), 185 (35), 176 (10), 175 (11), 174 (11), 161 (14), 156 (15), 150 (11), 143 (12), 138 (12), 126 (10), 125 (13), 112 (11), 102 (11), 100 (10), 99 (15), 76 (11), 75 (18). **HR-MS** (EI): m/z = calcd. for $C_{19}H_8N_3Cl_3$ $[M]^+$: 382.97783; found: 382.97752; calcd. for $C_{19}H_8N_3Cl_2{}^{37}Cl$: 384.97488; found 384.97485; calcd. for $C_{19}H_8N_3Cl{}^{37}Cl_2$: 386.97193; found 386.97304. Anal. calcd. for $C_{19}H_8Cl_3N_3$: C 59.33, H 2.10, N 10.92; found: C 59.36, H 2.44, N 10.50.

2,3,5-trichloro-4,6-bis(3,5-dimethylphenyl)pyridine (5e)

5e was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.26 mmol, 100 mg) and 3,5-dimethylphenylboronic acid (0.55 mmol, 82.5 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 72 mg (72 %). mp. 120 - 121 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.31 (s, 2H, CH_{Ar}), 7.13 (s, 1H, CH_{Ar}), 7.10 (s, 1H, CH_{Ar}), 6.89 (s, 2H, CH_{Ar}), 2.41 (s, 6H, $2CH_3$), 2.39 (s, 6H, $2CH_3$). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 155.3 ($C_{Ar/Hetar}$), 151.2 ($C_{Ar/Hetar}$), 147.0 ($C_{Ar/Hetar}$), 138.3 ($2C_{Ar/Hetar}$), 137.7 ($2C_{Ar/Hetar}$), 136.9 ($C_{Ar/Hetar}$), 135.8 ($C_{Ar/Hetar}$), 131.0 (CH_{Ar}), 130.7 (CH_{Ar}), 129.0 ($C_{Ar/Hetar}$), 128.9 ($C_{Ar/Hetar}$), 127.1 ($2CH_{Ar}$), 125.8 ($2CH_{Ar}$), 21.4 ($2CH_3$), 21.3 ($2CH_3$). **MS** (EI, 70 eV): m/z (%) = 394 (M^+, 7), 393 (M^+, 32), 392 (M^+, 25), 391 (M^+, 96), 390 (M^+, 35), 389 (M^+, 100), 388 (M^+, 12), 356 (38), 355 (15), 354 (59), 268 (13), 169 (12), 152 (11), 151 (9), 133 (17), 77 (10). **HR-MS** (EI): m/z = calcd. for $C_{21}H_{18}NCl_3$ $[M]^+$: 389.04993; found: 389.04979; calcd. for $C_{21}H_{18}NCl_2{}^{37}Cl$: 391.04698; found 391.04716; calcd. for $C_{21}H_{18}NCl^{37}Cl_2$: 393.04403; found 393.04448. Anal. calcd. for $C_{21}H_{18}Cl_3N$: C 64.55, H 4.64, N 3.58; found: C 64.34, H 4.58, N 3.38.

2,3,5-trichloro-4,6-bis(4-ethylphenyl)pyridine (5f)

5f was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.26 mmol, 100 mg) and 4-ethylphenylboronic acid (0.55 mmol, 82.5 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 59 mg (58 %). mp. 93 - 94 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.68 (d, ^{3}J = 8.1 Hz, 2H, CH_{Ar}), 7.37 (d, ^{3}J = 8.1 Hz, 2H, CH_{Ar}), 7.32 (d, ^{3}J = 8.1 Hz, 2H, CH_{Ar}), 7.21 (d, ^{3}J = 8.1 Hz, 2H, CH_{Ar}), 2.81-2.69 (m, 4H, $2CH_2CH_3$), 1.33 (t, ^{3}J = 6.7 Hz, 3H, CH_2CH_3), 1.29 (t, ^{3}J = 6.7 Hz, 3H, CH_2CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 154.9 ($C_{Ar/Hetar}$), 150.9 ($C_{Ar/Hetar}$), 147.1 ($C_{Ar/Hetar}$), 145.7 ($C_{Ar/Hetar}$), 145.1 ($C_{Ar/Hetar}$), 134.4 ($C_{Ar/Hetar}$), 133.1 ($C_{Ar/Hetar}$), 129.5 (2CH), 129.0 ($C_{Ar/Hetar}$), 128.9 ($C_{Ar/Hetar}$), 128.3 ($2CH_{Ar}$), 128.1 ($2CH_{Ar}$), 127.7 ($2CH_{Ar}$), 28.7 (CH_2CH_3), 28.6 (CH_2CH_3), 15.4 (CH_2CH_3), 15.1(CH_2CH_3). **MS** (EI, 70 eV): m/z (%) = 394 (M^+, 8), 393 (M^+, 32), 392 (M^+, 31), 391 (M^+, 99), 390 (M^+, 49), 389 (M^+, 100), 388 (28), 378 (20), 377 (13), 376 (58), 375 (16), 374 (61), 253 (10), 240 (9), 188 (11), 187 (11), 181 (13), 180 (36), 179 (40), 144 (10), 127 (12), 126 (11), 119 (12), 105

(14). **HR-MS** (EI): m/z = calcd. for $C_{21}H_{18}NCl_3$ $[M]^+$: 389.04993; found: 389.04880; calcd. for $C_{21}H_{18}NCl_2{}^{37}Cl$: 391.04698; found 391.04634; calcd. for $C_{21}H_{18}NCl^{37}Cl_2$: 393.04403; found 393.04394. Anal. calcd. for $C_{21}H_{18}Cl_3N$: C 64.55, H 4.64, N 3.58; found: C 65.00, H 4.99, N 3.30.

2,3,5-trichloro-4,6-bis(3-chlorophenyl)pyridine (5g)

5g was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.26 mmol, 100 mg) and 3-chlorophenylboronic acid (0.55 mmol, 86.0 mg) and was purified via column chromatography (heptane/dichloromethane). Oil colorless; yield: 35 mg (34 %). *Rf* (10 % ethyl acetate/ heptan) = 0.52. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.73 (d, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.63 (pdt, ^3J = 6.8, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.50-7.46 (m, 2H, CH_{Ar}), 7.35-7.45 (m, 2H, CH_{Ar}), 7.27-7.31 (m, 1H, CH_{Ar}), 7.14 - 7.21 (m, 1H, CH_{Ar}). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 153.5 ($C_{Ar/Hetar}$), 149.6 ($C_{Ar/Hetar}$), 147.6 ($C_{Ar/Hetar}$), 138.2 ($C_{Ar/Hetar}$), 137.0 ($C_{Ar/Hetar}$), 134.8 ($C_{Ar/Hetar}$), 134.2 ($C_{Ar/Hetar}$), 130.2 (CH_{Ar}), 129.7 ($C_{Ar/Hetar}$), 129.6 (CH_{Ar}), 129.6 (CH_{Ar}), 129.5 (CH_{Ar}), 129.5 (CH_{Ar}), 128.8 ($C_{Ar/Hetar}$), 128.5 (CH_{Ar}), 127.7 (CH_{Ar}), 126.6 (CH_{Ar}). **MS** (EI, 70 eV): m/z (%) = 407 (M^+, 21), 406 (M^+, 12), 405 (M^+, 65), 404 (M^+, 19), 403 (M^+, 100), 402 (M^+, 12), 401 (M^+, 62), 370 (35), 369 (15), 368 (72), 367 (13), 366 (56), 333 (15), 331 (15), 298 (11), 297 (18), 296 (16), 295 (23), 263 (12), 261 (40), 225 (25), 200 (10), 196 (15), 194 (21), 185 (12), 184 (12), 166 (13), 165 (12), 149 (20), 148 (29), 135 (10), 130 (13), 123 (10), 117 (10), 111 (10), 99 (17), 75 (18). **HR-MS** (EI): m/z = calcd. for $C_{17}H_8NCl_5$ $[M]^+$: 400.90939; found: 400.90909; calcd. for $C_{17}H_8NCl_4{}^{37}Cl$: 402.90644; found 402.90615; calcd. for $C_{17}H_8NCl_3{}^{37}Cl_2$: 404.90349; found 404.90354. Anal. calcd. for $C_{17}H_8Cl_5N$: C 50.60, H 2.00, N 3.47; found: C 50.97, H 2.48, N 3.07.

2,3,5-trichloro-4,6-bis(4-(trifluoromethyl)phenyl)pyridine (5h)

5h was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.26 mmol, 100 mg) and 4-(trifluoromethyl)phenylboronic acid (0.55 mmol, 104.5 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 43 mg (35 %). mp. 156 - 157 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.88 (d, ^3J = 8.3 Hz, 2H, CH_{Ar}), 7.83 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.76 (d, ^3J = 8.3 Hz, 2H, CH_{Ar}), 7.44 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 153.6 ($C_{Ar/Hetar}$), 149.7 ($C_{Ar/Hetar}$), 147.9 ($C_{Ar/Hetar}$), 139.9 ($C_{Ar/Hetar}$), 138.8 ($C_{Ar/Hetar}$), 131.5 (q, ^2J = 32.7 Hz, 2C_{Ar}), 130.0 (2CH_{Ar}), 129.9 (C_{Ar}),

129.0 ($2CH_{Ar}$), 128.6 (C_{Ar}), 125.9 (q, ^3J = 3.7 Hz, $2CH_{Ar}$), 125.3 (q, ^3J = 3.7 Hz, $2CH_{Ar}$), 123.9 (q, ^1J = 272.3 Hz, CF_3), 123.8 (q, ^1J = 272.3 Hz, CF_3). **^{19}F-NMR** (282 MHz, $CDCl_3$): δ = -62.83 ($ArCF_3$), -62.85 ($ArCF_3$). **MS** (EI, 70 eV): m/z (%) = 473 (M^+, 27), 472 (M^+, 18), 471 (M^+, 83), 470 (M^+, 19), 469 (M^+, 85), 452 (12), 450 (13), 438 (11), 437 (14), 436 (66), 435 (22), 434 (100), 400 (10), 364 (10), 363 (14), 344 (13), 329 (12), 295 (21), 294 (12), 228 (18), 193 (13), 145 (12), 75 (11), 69 (18). **HR-MS** (EI): m/z = calcd. for $C_{19}H_8NCl_3F_6$ $[M]^+$: 468.96210; found: 468.96243; calcd. for $C_{19}H_8NCl_2{}^{37}ClF_6$: 470.95915; found 470.95954; calcd. for $C_{19}H_8NCl^{37}Cl_2F_6$: 472.95620; found 472.95697. Anal. calcd. for $C_{19}H_8Cl_3F_6N$: C 48.49, H 1.71, N 2.98; found: C 48.43, H 1.98, N 2.82.

Synthesis of asymmetric 4,6-diaryl-2,3,5-trichloropyridines (6a–c)

An oven-dried, argon-flushed sealable glass tube was charged with 4-bromo-2,3,5-trichloro-6-*p*-tolylpyridine **4b** (0.29 mmol, 100 mg), $Pd(PPh_3)_4$ (5 mol%, 16.5 mg), the appropriate arylboronic acid (0.43 mmol) and K_3PO_4 (0.43 mmol, 91 mg) followed by a mixture of toluene/water/*n*-butanol (6:1:1, 4 mL); The tube was sealed with a Teflon valve and stirred at 100 °C for 20 h. The cooled reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography using heptane/ethyl acetate as eluent.

2,3,5-trichloro-4-(4-cyanophenyl)-6-*p*-tolylpyridine (6a)

6a was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-*p*-tolylpyridine **4b** (0.29 mmol, 100 mg) and 4-cyanophenylboronic acid (0.43 mmol, 63.2 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 53 mg (50 %). mp. 191 - 192 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.85 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.65 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.43 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.30 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 2.43 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 155.3 ($C_{Ar/Hetar}$), 148.8 ($C_{Ar/Hetar}$), 147.5 ($C_{Ar/Hetar}$), 140.2 ($C_{Ar/Hetar}$), 139.9 ($C_{Ar/Hetar}$), 133.5 ($C_{Ar/Hetar}$), 132.6 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 129.4 ($2CH_{Ar}$), 128.9 ($2CH_{Ar}$), 128.0 ($C_{Ar/Hetar}$), 122,2 ($C_{Ar/Hetar}$), 118.2 (C≡N), 113.3 ($C_{Ar/Hetar}$), 21.4 (CH_3). **MS** (EI, 70 eV): m/z (%) = 377 (M^+, 7), 376 (M^+, 31), 375 (M^+, 24), 374 (M^+, 96), 373 (M^+, 34), 372 (M^+, 100), 371 (14), 339 (29), 338 (12), 337 (45), 301 (10), 266 (19), 265 (24), 240 (10), 238 (10), 185 (11), 150 (10), 133 (15), 91 (18).

HR-MS (EI): m/z = calcd. for $C_{19}H_{11}N_2Cl_3$ $[M]^+$: 371.99823; found: 371.99710; calcd. for $C_{19}H_{11}N_2Cl_2{}^{37}Cl$: 373.99528; found 373.99417; calcd. for $C_{19}H_{81}N_2Cl^{37}Cl_2$: 375.99233; found 375.99208. Anal. calcd. for $C_{19}H_{11}Cl_3N_2$: C 61.07, H 2.97, N 7.50; found: C 61.33, H 3.24, N 7.34.

2,3,5-trichloro-4-(3-nitrophenyl)-6-*p*-tolylpyridine (6b)

6b was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-*p*-tolylpyridine **4b** (0.29 mmol, 100 mg) and 3-nitrophenylboronic acid (0.43 mmol, 71.8 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 62 mg (55 %). mp. 113 - 114 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 8.38 (ddd, ^3J = 8.2 Hz, ^4J = 2.3 Hz, ^4J = 1.2 Hz, 1H, CH_{Ar}), 8.22 (pt, ^4J = 1.8 Hz, 1H, CH_{Ar}), 7.75 (pt, ^3J = 7.9 Hz, 1H, CH_{Ar}), 7.67-7.63 (m, 3H, CH_{Ar}), 7.30 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 2.43 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 155.5 ($C_{Ar/Hetar}$), 148.4($C_{Ar/Hetar}$), 148.1 ($C_{Ar/Hetar}$), 147.5 ($C_{Ar/Hetar}$), 139.9 ($C_{Ar/Hetar}$), 137.1 ($C_{Ar/Hetar}$), 134.7 (CH_{Ar}), 133.5 ($C_{Ar/Hetar}$), 129.9 (CH_{Ar}), 129.4 (CH_{Ar}), 128.9 (CH_{Ar}), 128.5 ($C_{Ar/Hetar}$), 128.3 ($C_{Ar/Hetar}$), 124.1 (CH_{Ar}), 123.9 (CH_{Ar}), 21.4 (CH_3). **MS** (EI, 70 eV): m/z (%) = 397 (M^+, 6), 396 (M^+, 33), 395 (M^+, 20), 394 (M^+, 97), 393 (M^+, 24), 392 (M^+, 100), 348 (25), 346 (26), 311 (13), 276 (19), 275 (13), 274 (10), 261 (10), 241 (18), 240 (30), 238 (20), 214 (11), 213 (16), 155 (14), 138 (13), 120 (27), 106 (17), 91 (17). **HR-MS** (ESI): m/z = calcd. for $C_{18}H_{11}Cl_3N_2O_2$ ($[M+H]^+$): 392.99589, found: 392.99597, calcd. for $C_{18}H_{11}Cl_2{}^{37}ClN_2O_2$: 394.99315, found 394.99326, calcd. for $C_{18}H_{11}Cl^{37}Cl_2N_2O_2$: 396.99061, found 396.99107. Anal. calcd. for $C_{18}H_{11}Cl_3N_2O_2$: C 54.92, H 2.82, N 7.12; found: C 55.04, H 3.27, N 6.86.

2,3,5-trichloro-4-(3-methoxyphenyl)-6-*p*-tolylpyridine (6c)

6c was synthesized according to general procedure using 4-bromo-2,3,5-trichloro-6-*p*-tolylpyridine **4b** (0.29 mmol, 100 mg) and 3-methoxyphenylboronic acid (0.43 mmol, 65.3 mg) and was purified via column chromatography (heptane/dichloromethane). Colorless viscous oil; yield: 51 mg (48 %). Rf = 0.73 (Heptan/ EA 4:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.66 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.45 (dd, ^3J = 7.96 Hz, ^3J = 7.96 Hz, 1H, CH_{Ar}), 7.29 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.03 (ddd, ^3J = 8.4 Hz, ^4J = 2.6 Hz, ^5J = 0.9 Hz, 1H, CH_{Ar}), 6.83-6.88 (m, 1H, CH_{Ar}), 6.82 (dd, ^4J = 2.6 Hz, ^4J = 1.7 Hz, 1H, CH_{Ar}), 3.87 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3), **^{13}C-NMR** (75 MHz,

$CDCl_3$): δ = 159.7 (*C*-OCH_3), 154.9 ($C_{Ar/Hetar}$), 150.7 ($C_{Ar/Hetar}$), 147.1 ($C_{Ar/Hetar}$), 139.5 ($C_{Ar/Hetar}$), 137.0 ($C_{Ar/Hetar}$), 134.0 ($C_{Ar/Hetar}$), 129.9 ($2CH_{Ar}$), 129.4 ($2CH_{Ar}$), 128.8 (CH_{Ar}), 128.8 ($2C_{Ar/Hetar}$), 120.5 (CH_{Ar}), 114.5 (CH_{Ar}), 114.0 (CH_{Ar}), 55.3 (OCH_3), 21.4 (CH_3). **MS** (EI, 70 eV): m/z (%) = 382 (M^+, 7), 381 (M^+, 33), 380 (M^+, 32), 379 (M^+, 100), 378 (M^+, 57), 377 (M^+, 99), 376 (37), 350 (5), 349 (9), 348 (8), 347 (9), 312 (6), 264 (7), 228 (9), 227 (9), 91 (5), 63 (5), 39 (5). **HR-MS (ESI)**: m/z = calcd. for $C_{19}H_{14}Cl_3NO$ ($M+H^+$) 378.02137; found 378.02176; calcd. for $C_{19}H_{14}Cl_2{}^{37}ClNO$ ($M+H^+$) 380.01864; found 380.01903; calcd. for $C_{19}H_{14}Cl^{37}Cl_2NO$ ($M+H^+$) 382.01611; found 382.01658; calcd. for $C_{19}H_{14}Cl_3NO$ ($M+Na^+$) 400.00332; found 400.00353; calcd. for $C_{19}H_{14}Cl_2{}^{37}ClNO$ ($M+H^+$) 402.00059; found 402.00064. Anal. calcd. for $C_{19}H_{14}Cl_3NO$: C 60.26, H 3.73, N 3.70; found: C 60.04, H 3.57 , N 3.86.

Synthesis of Triarylpyridines from 3 (mixtures 7/8)

An oven-dried, argon-flushed sealable glass tube was charged with 4-bromo-2,3,5-trichloro-6-iodopyridine **3** (0.26 mmol, 100 mg), $Pd(OAc)_2$ (5 mol%, 2.9 mg), PCy_3 (10 mol%, 7.24 mg) or SPhos (10 mol%, 10.6 mg), the appropriate arylboronic acid (2.5-4.5 equivalent) and K_3PO_4 (0.77 mmol, 164.45 mg) followed by a mixture of toluene/water/buthanol (6:1:1, 4 mL); The tube was sealed with a Teflon valve and stirred at 100 °C or 70 °C for 19 h. The cooled reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography affording isomeric mixtures of 3,5-dichloro-2,4,6-tri-*p*-tolylpyridine **7** and 3-chloro-2,4,5,6-tetrakis-*p*-tolylpyridine **8** which could not be separated preparatively by column chromatography. The products were confirmed by GC-MS und HR-MS data.

Synthesis of asymmetric 2,4,6-triaryl-3,5-dichloropyridines (9a–d)

An oven-dried, argon-flushed sealable glass tube was charged with 2,3,5-trichloro-4,6-di-*p*-tolylpyridine **5a** (0.28 mmol, 100 mg), $Pd(PPh_3)_4$ (5 mol%, 16 mg), the appropriate arylboronic acid (0.33 mmol) and K_3PO_4 (0.33 mmol, 70.3 mg) followed by anhydrous toluene (3 mL); The tube was sealed with a Teflon valve and stirred at 100 °C for 20 h. The cooled reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuum.

The residue was purified by column chromatography using heptane/dichloromethane as eluent.

3,5-dichloro-2-(4-methoxyphenyl)-4,6-di-*p*-tolylpyridine (9a)

9a was synthesized according to general procedure using 2,3,5-trichloro-4,6-di-*p*-tolylpyridine **5a** (0.28 mmol, 100 mg) and 4-methoxyphenylboronic acid (0.33 mmol, 50.1 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 68 mg (57 %). mp. 137 - 138 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.79 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 7.70 (d, ^{3}J = 8.1 Hz, 2H, CH_{Ar}), 7.36 (d, ^{3}J = 7.9 Hz, 2H, CH_{Ar}), 7.30-7.23 (m, 4H, CH_{Ar}), 6.99 (d, ^{3}J = 8.8 Hz, 2H, CH_{Ar}), 3.87 (s, 3H, OCH_3), 2.47 (s, 3H, CH_3), 2.42 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 160.1 (*C*-OCH_3), 154.6 ($C_{Ar/Hetar}$), 154.2 ($C_{Ar/Hetar}$), 149.4 ($C_{Ar/Hetar}$), 138.8 ($C_{Ar/Hetar}$), 138.5 ($C_{Ar/Hetar}$), 135.6 ($C_{Ar/Hetar}$), 133.8 ($C_{Ar/Hetar}$), 131.1 (2CH), 130.8 ($C_{Ar/Hetar}$), 129.5 ($2CH_{Ar}$), 129.3 ($2CH_{Ar}$), 128.7 ($2CH_{Ar}$), 128.6 ($2CH_{Ar}$), 128.3 ($C_{Ar/Hetar}$), 128.2 ($C_{Ar/Hetar}$), 113.4 ($2CH_{Ar}$), 55.3 (OCH_3), 21.5 (CH_3), 21.4 (CH_3). **MS** (EI, 70 eV): m/z (%) = 437 (M^+, 11), 436 (M^+, 17), 435 (M^+, 66), 434 (M^+, 28), 433 (M^+, 100), 400 (7), 399 (5), 398 (18), 202 (4). **HR-MS** (ESI): m/z = calcd. for $C_{26}H_{21}Cl_2NO$ ($[M+H]^+$): 434.1073, found: 434.10737, calcd. for $C_{26}H_{21}Cl^{37}ClN_2O$: 436.10493, found 436.10496, calcd. for $C_{26}H_{21}{}^{37}Cl_2N_2O$: 438.1033, found 438.10339. Anal. calcd. for $C_{26}H_{21}Cl_2NO$: C 71.89, H 4.87, N 3.22; found: C 71.67, H 5.03, N 2.96.

3,5-dichloro-2-(2-methoxyphenyl)-4,6-di-*p*-tolylpyridine (9b)

9b was synthesized according to general procedure using 2,3,5-trichloro-4,6-di-*p*-tolylpyridine **5a** (0.28 mmol, 100 mg) and 2-methoxyphenylboronic acid (0.33 mmol, 50.1 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 59 mg (49 %). mp. 106 - 107 °C.**^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.69 (d, ^{3}J = 8.1 Hz, 2H, CH_{Ar}), 7.41 (d, ^{3}J = 7.4 Hz, 2H, CH_{Ar}), 7.35 (d, ^{3}J = 8.1 Hz, 2H, CH_{Ar}), 7.28 (m, 4H, CH_{Ar}), 7.10-7.07 (m, 1H, CH_{Ar}), 7.00 (d, ^{3}J = 8.7 Hz, 1H, CH_{Ar}), 3.85 (s, 3H, OCH_3), 2.46 (s, 3H, CH_3), 2.41 (s, 3H, CH_3). **13C-NMR** (75 MHz, $CDCl_3$): δ = 156.9 (*C*-OCH_3), 154.8 ($2C_{Ar/Hetar}$), 153.8 ($C_{Ar/Hetar}$), 148.3 ($C_{Ar/Hetar}$), 138.6 ($C_{Ar/Hetar}$), 138.5 ($C_{Ar/Hetar}$), 135.6 ($C_{Ar/Hetar}$), 133.5 ($C_{Ar/Hetar}$), 130.6 (CH_{Ar}), 130.2 (CH_{Ar}), 129.6 ($2CH_{Ar}$), 129.2 ($2CH_{Ar}$), 128.8 ($2CH_{Ar}$), 128.7 ($2CH_{Ar}$), 128.1 ($2C_{Ar/Hetar}$), 120.6 (CH_{Ar}), 110.9 (CH_{Ar}), 55.6 (OCH_3), 21.4 (CH_3), 21.3 (CH_3).

MS (EI, 70 eV): m/z (%) = 435 (M^+, 13), 434 (M^+, 11), 433 (M^+, 20), 432 (8), 401 (19), 400 (76), 399 (61), 398 (100), 368 (16), 363 (13), 215 (8), 202 (8), 158 (9). **HR-MS** (EI): m/z = calcd. for $C_{26}H_{21}ONCl_2$ $[M]^+$: 433.09947; found: 433.09878; calcd. for $C_{26}H_{21}ONCl^{37}Cl$: 435.09652; found 435.09638. Anal. calcd. for $C_{26}H_{21}Cl_2NO$: C 71.89, H 4.87, N 3.22; found: C 71.78, H 4.83, N 3.00.

3,5-dichloro-2-(4-fluorophenyl)-4,6-di-*p*-tolylpyridine (9c)

9c was synthesized according to general procedure using 2,3,5-trichloro-4,6-di-*p*-tolylpyridine **5a** (0.28 mmol, 100 mg) and 4-fluorophenylboronic acid (0.33 mmol, 46.2 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 44 mg (38 %). mp. 152 - 153 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.81 (dd, ^3J = 8.9 Hz, ^4J = 2.27 Hz, 2H, CH_{Ar}), 7.70 (d, ^3J = 8.2 Hz, 2H CH_{Ar}), 7.37 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 7.30 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 7.25 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.16 (pt, ^3J = 8.8 Hz, 2H, CH_{Ar}), 2.47 (s, 3H, CH_3), 2.43 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 163.1 (d, ^1J = 249.8 Hz, (C_{Ar}-F)), 154.9 ($C_{Ar/Hetar}$), 153.6 ($C_{Ar/Hetar}$), 149.5 ($C_{Ar/Hetar}$), 138.9 ($C_{Ar/Hetar}$), 138.6 ($C_{Ar/Hetar}$), 135.3 ($C_{Ar/Hetar}$), 134.4 (d, ^4J = 3.66 Hz, C_{Ar}), 133.5 ($C_{Ar/Hetar}$), 131.7 (d, ^3J = 8.24 Hz, 2CH), 129.5 ($2CH_{Ar}$), 129.3 ($2CH_{Ar}$), 128.8 ($C_{Ar/Hetar}$), 128.7 ($2CH_{Ar}$), 128.5 ($2CH_{Ar}$), 128.4 ($C_{Ar/Hetar}$), 115.0 (d, ^2J = 22.0 Hz, $2CH_{Ar}$), 21.4 (CH_3), 21.4 (CH_3). **^{19}F-NMR** (282 MHz, $CDCl_3$): δ = -112.42. **MS** (EI, 70 eV): m/z (%) = 425 (M^+, 13), 424 (M^+, 18), 423 (M^+, 76), 422 (M^+, 33), 421 (M^+, 100), 406 (6), 388 (22), 387 (17), 386 (69), 350 (6), 234 (6), 233 (8). **HR-MS** (EI): m/z = calcd. for $C_{25}H_{18}NCl_2F$ $[M]^+$: 421.07948; found: 421.07922; calcd. for $C_{25}H_{18}NCl^{37}ClF$: 423.07653; found 423.07657. Anal. calcd. for $C_{25}H_{18}Cl_2FN$: C 71.10, H 4.30, N 3.32; found: C 71.26, H 4.19, N 3.25.

3,5-dichloro-2-(4-chlorophenyl)-4,6-di-*p*-tolylpyridine (9d)

9d was synthesized according to general procedure using 2,3,5-trichloro-4,6-di-*p*-tolylpyridine **5a** (0.28 mmol, 100 mg) and 4-chlorophenylboronic acid (0.33 mmol, 51.6 mg) and was purified via column chromatography (heptane/dichloromethane). White solid; yield: 60 mg (50 %). mp. 163 - 164 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.76 (d, ^3J = 9.1 Hz, 2H, CH_{Ar}), 7.70 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.45 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.37 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 7.30 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 7.25 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 2.47 (s, 3H, CH_3), 2.43 (s, 3H, CH_3). **^{13}C-NMR**

(75 MHz, $CDCl_3$): δ = 154.9 ($C_{Ar/Hetar}$), 153.4 ($C_{Ar/Hetar}$), 149.6 ($C_{Ar/Hetar}$), 139.0 ($C_{Ar/Hetar}$), 138.7 ($C_{Ar/Hetar}$), 136.7 ($C_{Ar/Hetar}$), 135.3 ($C_{Ar/Hetar}$), 134.9 ($C_{Ar/Hetar}$), 133.4 ($C_{Ar/Hetar}$), 131.1 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 129.3 ($2CH_{Ar}$), 129.0 ($C_{Ar/Hetar}$), 128.8 ($2CH_{Ar}$), 128.5 ($2CH_{Ar}$), 128.4 ($C_{Ar/Hetar}$), 128.2 ($2CH_{Ar}$), 21.5 (CH_3), 21.4 (CH_3). **MS** (EI, 70 eV): m/z (%) = 442 (M^+, 8), 441 (M^+, 30), 440 (M^+, 26), 439 (M^+, 100), 438 (M^+, 31), 437 (M^+, 99), 406 (6), 405 (9), 404 (35), 403 (15), 402 (56), 215 (6.34), 213 (8), 158 (5). **HR-MS** (EI): m/z = calcd. for $C_{25}H_{18}NCl_3$ $[M]^+$: 437.04993; found: 437.04960; calcd. for $C_{25}H_{18}NCl_2{}^{37}Cl$: 439.04698; found 439.04679. Anal. calcd. for $C_{25}H_{18}Cl_3N$: C 68.43, H 4.13, N 3.19; found: C 68.42, H 4.11, N 3.18.

Synthesis of asymmetric 2,4,6-triaryl-3,5-dichloropyridines (10a–c)

An oven-dried, argon-flushed sealable glass tube was charged with 2,3,5-trichloro-4-(4-cyanophenyl)-6-*p*-tolylpyridine **6a** (0.27 mmol, 100 mg), $Pd(PPh_3)_4$ (5 mol%, 15.5 mg), the appropriate arylboronic acid (0.32 mmol) and K_3PO_4 (0.32 mmol, 68.4 mg) followed by anhydrous toluene (3 mL); The tube was sealed with a Teflon valve and stirred at 100 °C for 20 h. The cooled reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography using heptane/ethyl acetate as eluent.

3,5-dichloro-2-(4-methoxyphenyl)-4-(4-cyanophenyl)-6-*p*-tolylpyridine (10a)

10a was synthesized according to general procedure using 2,3,5-trichloro-4-(4-cyanophenyl)-6-*p*-tolylpyridine **6a** (0.27 mmol, 100 mg) and 4-methoxyphenylboronic acid (0.32 mmol, 48.6 mg) and was purified via column chromatography (heptane/ ethyl acetate). White solid; yield: 75 mg (63 %). mp. 187 - 188 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.84 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.79 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.70 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.48 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.30 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 7.00 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 3.87 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 160.6 (*C*-OCH_3), 155.2 ($C_{Ar/Hetar}$), 154.8 ($C_{Ar/Hetar}$), 147.7 ($C_{Ar/Hetar}$), 141.4 ($C_{Ar/Hetar}$), 139.5 ($C_{Ar/Hetar}$), 135.2 ($C_{Ar/Hetar}$), 132.7 (2CH), 131.4 (2CH), 130.4 ($C_{Ar/Hetar}$), 130.1 ($2CH_{Ar}$), 129.7 ($2CH_{Ar}$), 129.0 ($2CH_{Ar}$), 127.5 ($C_{Ar/Hetar}$), 127.4 ($C_{Ar/Hetar}$), 118.7 (C≡N), 113.7 ($2CH_{Ar}$), 112.9 ($C_{Ar/Hetar}$), 55.6 (OCH_3), 21.6 (CH_3). **MS** (EI, 70 eV): m/z (%) = 448 (M^+, 12), 447 (M^+, 19), 446 (M^+, 67), 445 (M^+, 31) 444

(M^+, 100), 409 (16), 393 (5), 366 (6), 330 (7), 329 (7), 316 (5), 240 (8), 222 (6), 214 (9). **HR-MS** (EI): m/z = calcd. for $C_{26}H_{18}ON_2Cl_2$ $[M]^+$: 444.07907; found: 444.07896; calcd. for $C_{26}H_{18}ON_2Cl^{37}Cl$: 446.07612; found 446.07673. Anal. calcd. for $C_{26}H_{18}Cl_2N_2O$: C 70.12, H 4.07, N 6.29; found: C 69.91, H 4.20, N 6.49.

3,5-dichloro-2-(4-chlorophenyl)-4-(4-cyanophenyl)-6-*p*-tolylpyridine (10b)

10b was synthesized according to general procedure using 2,3,5-trichloro-4-(4-cyanophenyl)-6-*p*-tolylpyridine **6a** (0.27 mmol, 100 mg) and 4-chlorophenylboronic acid (0.32 mmol, 50.0 mg) and was purified via column chromatography (heptane/ ethyl acetate). White solid; yield: 92 mg (77 %). mp. 164 - 165 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.85 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 7.76 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.69 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.48 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 7.45 (d, ^3J = 8.6 Hz, 2H, CH_{Ar}), 7.30 (d, ^3J = 8.0 Hz, 2H, CH_{Ar}), 2.43 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 155.3 ($C_{Ar/Hetar}$), 153.7 ($C_{Ar/Hetar}$), 147.6 ($C_{Ar/Hetar}$), 140.8 ($C_{Ar/Hetar}$), 139.4 ($C_{Ar/Hetar}$), 136.1 ($C_{Ar/Hetar}$), 135.3 ($C_{Ar/Hetar}$), 134.7 ($C_{Ar/Hetar}$), 132.5 ($2CH_{Ar}$), 130.9 ($2CH_{Ar}$), 129.7 ($2CH_{Ar}$), 129.4 ($2CH_{Ar}$), 128.8 ($2CH_{Ar}$), 128.3 ($2CH_{Ar}$), 128.0 (C_{Ar}), 127.4 (C_{Ar}), 118,3 (C≡N), 112.9 (C_{Ar}), 21.4 (CH_3). **MS** (EI, 70 eV): m/z (%) = 453 (M^+, 8), 452 (M^+, 34), 451 (M^+, 29), 450 (M^+, 99), 449 (M^+, 35), 448 (M^+, 100), 447 (8), 416 (11), 415 (36), 414 (18), 413 (55), 377 (11), 342 (9), 341 (9), 261 (19), 241 (11), 240 (20), 238 (11), 225 (21), 171 (10), 170 (13), 157 (14), 91 (12). **HR-MS** (EI): m/z = calcd. for $C_{25}H_{15}N_2Cl_3$ $[M]^+$: 448.02953; found: 448.02876; calcd. for $C_{25}H_{15}N_2Cl_2{}^{37}Cl$: 450.02658; found 450.02618; calcd. for $C_{25}H_{15}N_2Cl^{37}Cl_2$: 452.02363; found 452.02238. Anal. calcd. for $C_{25}H_{15}Cl_3N_2$: C 66.76, H 3.36, N 6.23; found: C 66.90, H 3.41 , N 6.09.

3,5-dichloro-2-(4-(trifluoromethyl)phenyl)-4-(4-cyanophenyl)-6-*p*-tolylpyridine (10c):

10c was synthesized according to general procedure using 2,3,5-trichloro-4-(4-cyanophenyl)-6-*p*-tolylpyridine **6a** (0.27 mmol, 100 mg) and 4-(trifluoromethyl)phenylboronic acid (0.32 mmol, 60.8 mg) and was purified via column chromatography (heptane/ ethyl acetate). White solid; yield: 79 mg (61 %). mp. 187 - 188 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.92 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.86 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 7.75 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.70 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.50 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 7.31 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 2.44 (s, 3H, CH_3). **^{13}C-**

NMR (75 MHz, $CDCl_3$): δ = 155.5 ($C_{Ar/Hetar}$), 153.5 ($C_{Ar/Hetar}$), 147.8 ($C_{Ar/Hetar}$), 141.2 ($C_{Ar/Hetar}$), 140.6 ($C_{Ar/Hetar}$), 139.6 ($C_{Ar/Hetar}$), 134.6 ($C_{Ar/Hetar}$), 132.6 ($2CH_{Ar}$), 131.1 (q, ^2J = 32.5 Hz, C_{Ar}), 130.0 ($2CH_{Ar}$), 129.8 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 128.9 ($2CH_{Ar}$), 128.6 ($C_{Ar/Hetar}$), 127.6 ($C_{Ar/Hetar}$), 125.1 (q, ^3J = 3.85 Hz, $2CH_{Ar}$), 123.9 (q, ^1J = 272.35 Hz, CF_3), 118.3 (C≡N), 113.0 (C_{Ar}), 21.4 (CH_3). **^{19}F-NMR** (282 MHz, $CDCl_3$): δ = -62.73 ($ArCF_3$). **MS** (EI, 70 eV): m/z (%) = 486 (M^+, 13), 485 (M^+, 19), 484 (M^+, 68), 483 (M^+, 35), 482 (M^+, 100), 481 (14), 449 (19), 448 (16), 447 (52), 295 (6), 240 (6). **HR-MS** (ESI): m/z = calcd. for $C_{26}H_{15}Cl_2F_3N_2$ ($[M+H]^+$): 483.06371, found: 483.06374, calcd. for $C_{26}H_{15}Cl^{37}ClF_3N_2$: 485.06132, found 485.06241. Anal. calcd. for $C_{26}H_{15}Cl_2F_3N_2$: C 64.61, H 3.13, N 5.80; found: C 64.45, H 3.07, N 5.47.

Synthesis of pentaarylpyridines (11a–b)

An oven-dried, argon-flushed sealable glass tube was charged with 3,5-dichloro-2-(4-methoxyphenyl)-4,6-di-*p*-tolylpyridine **9a** (0.23 mmol, 100 mg), $PdCl_2(CH_3CN)_2$ (5 mol%, 3.0 mg), SPhos (10 mol%, 9.5 mg), the appropriate arylboronic acid (0.92 mmol) and K_3PO_4 (0.92 mmol, 195.5 mg) followed by anhydrous toluene (3 mL); The tube was sealed with a Teflon valve and stirred at 100 °C for 20 h. The cooled reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography using heptane/dichloromethane as eluent.

2-(4-methoxyphenyl)-3,5-diphenyl-4,6-di-*p*-tolylpyridine (11a)

11a was synthesized according to general procedure using 3,5-dichloro-2-(4-methoxyphenyl)-4,6-di-*p*-tolylpyridine **9a** (0.23 mmol, 100 mg) and phenylboronic acid (0.92 mmol, 112.2 mg) and was purified via column chromatography (heptane/ dichloromethane). White solid; yield: 118 mg (99 %). mp. 242 - 243 °C.**^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.37 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 7.33 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.06 - 6.99 (m, 8H, CH_{Ar}), 6.97–6.89 (m, 4H, CH_{Ar}), 6.75-6.70 (m, 4H, CH_{Ar}), 6.65 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 3.77 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3), 2.14 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 158.9 ($C_{Ar/Hetar}$), 156.1 ($C_{Ar/Hetar}$), 155.7 ($C_{Ar/Hetar}$), 150.2 ($C_{Ar/Hetar}$), 138.9 ($C_{Ar/Hetar}$), 138.9 ($C_{Ar/Hetar}$), 138.2 ($C_{Ar/Hetar}$), 136.9 ($C_{Ar/Hetar}$), 135.5 ($C_{Ar/Hetar}$), 135.2 ($C_{Ar/Hetar}$), 133.5 ($C_{Ar/Hetar}$),133.1 ($C_{Ar/Hetar}$), 133.1 ($C_{Ar/Hetar}$), 131.6 ($2CH_{Ar}$), 131.3 ($2CH_{Ar}$), 130.3 ($2CH_{Ar}$), 130.1 ($2CH_{Ar}$), 128.2 ($2CH_{Ar}$), 127.6 ($2CH_{Ar}$),

127.4 ($2CH_{Ar}$), 127.3 ($2CH_{Ar}$), 126.0 ($2CH_{Ar}$), 125.9 ($2CH_{Ar}$), 112.9 ($2CH_{Ar}$), 55.1 (OCH_3), 21.2 (CH_3), 21.1 (CH_3). **MS** (EI, 70 eV): m/z (%) = 518 (M^+, 21), 517 (71), 516 (100), 472 (10), 236 (7), 220 (5), 213 (6), 207 (8), 201 (7), 191 (6), 189 (7), 165 (6). **HR-MS** (ESI): m/z = calcd. for $C_{38}H_{31}NO$ ($[M+H]^+$): 518.24784, found: 518.24755. Anal. calcd. for $C_{38}H_{31}NO$: C 88.17, H 6.04, N 2.71; found: C 87.81, H 5.94, N 2.52.

3,5-bis(4-*tert*-butylphenyl)-2-(4-methoxyphenyl)-4,6-di-*p*-tolylpyridine (11b)

11b was synthesized according to general procedure using 3,5-dichloro-2-(4-methoxyphenyl)-4,6-di-*p*-tolylpyridine **9a** (0.23 mmol, 100 mg) and 4-*tert*-butylphenylboronic acid (0.92 mmol, 163.8 mg) and was purified via column chromatography (heptane/ dichloromethane). White solid; yield: 116 mg (80 %). mp. 237 - 238 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.36 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.32 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 7.03 (dd, ^3J = 8.5 Hz, ^3J = 8.4 Hz, 4H, CH_{Ar}), 6.97 (d, ^3J = 8.0 Hz, 2H CH_{Ar}), 6.81 (d, ^3J = 7.9 Hz, 4H, CH_{Ar}), 6.70 (d, ^3J = 8.7 Hz, 4H, CH_{Ar}), 6.60 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 3.77 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 1.22 (s, 18H, CH_3 $_{t\text{-Bu}}$). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 158.7 ($C_{Ar/Hetar}$), 155.8 ($C_{Ar/Hetar}$), 155.5 ($C_{Ar/Hetar}$), 150.4 ($C_{Ar/Hetar}$), 148.9 ($C_{Ar/Hetar}$), 148.9 ($C_{Ar/Hetar}$), 136.7 ($C_{Ar/Hetar}$), 135.9 ($C_{Ar/Hetar}$), 135.8 ($C_{Ar/Hetar}$), 135.4 ($C_{Ar/Hetar}$), 135.1 ($C_{Ar/Hetar}$), 133.1 ($C_{Ar/Hetar}$), 133.1 ($C_{Ar/Hetar}$), 131.6 ($2CH_{Ar}$), 130.9 ($4CH_{Ar}$), 130.4 ($2CH_{Ar}$), 130.2 ($2CH_{Ar}$), 128.1 ($2CH_{Ar}$), 127.3 ($2CH_{Ar}$), 124.2 ($2CH_{Ar}$), 124.1 ($2CH_{Ar}$), 112.7 ($2CH_{Ar}$), 55.1 (OCH_3), 34.3 2($C_{t\text{Bu}}$), 31.3 2(CH_3 $_{t\text{Bu}}$), 21.2 (CH_3), 20.9 (CH_3). **MS** (EI, 70 eV): m/z (%) = 630 (32), 629 (M^+, 88), 628 (100), 614 (7), 613 (7), 612 (12), 572 (9), 556 (8), 528 (3), 281 (5), 231 (7), 219 (6), 181 (12), 169 (11), 131 (16), 119 (14), 91 (18), 78 (6), 69 (50), 57 (9), 44 (20), 43 (6), 41 (13), 40 (44), 39 (10). **HR-MS** (ESI): m/z = calcd. for $C_{46}H_{47}NO$ ($[M+H]^+$): 630.37304 found: 630.37286. Anal. calcd. for $C_{46}H_{47}NO$: C 87.72, H 7.52, N 2.22; found: C 87.52, H 7.50, N 2.15.

Synthesis of pentaarylpyridines (12a–b)

An oven-dried, argon-flushed sealable glass tube was charged with 2,3,5-trichloro-4-(4-cyanophenyl)-6-*p*-tolylpyridine **6a** (0.23 mmol, 85 mg), $PdCl_2(CH_3CN)_2$ (5 mol%, 3.0 mg), SPhos (10 mol%, 9.4 mg), the appropriate arylboronic acid (1.37 mmol) and K_3PO_4 (1.37 mmol, 291 mg) followed by anhydrous toluene (4 mL); The tube was sealed with a Teflon valve and stirred at 100 °C for 20 h. The cooled reaction mixture

was diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography using heptane/dichloromethane as eluent.

2,3,5-tris(4-methoxyphenyl)-4-(4-cyanophenyl)-6-*p*-tolylpyridine (12a)

12a was synthesized according to general procedure using 2,3,5-trichloro-4-(4-cyanophenyl)-6-*p*-tolylpyridine **6a** (0.23 mmol, 85 mg) and 4-methoxyphenylboronic acid (1.37 mmol, 208.2 mg) and was purified via column chromatography (heptane/ dichloromethane). White solid; yield: 124 mg (93 %). mp. 228 - 229 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.28 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 7.23 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.18 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 6.93 (d, ^3J = 8.0 Hz, 2H, CH_{Ar}), 6.80 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 6.70–6.63 (m, 6H, CH_{Ar}), 6.50 (dd, ^3J = 8.8, ^4J = 3.7 Hz, 4H, CH_{Ar}), 3.69 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 2.21 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 159.0 (*C*-OCH_3), 158.1 (*C*-OCH_3), 158.1 (*C*-OCH_3), 156.5 ($C_{Ar/Hetar}$), 156.0 ($C_{Ar/Hetar}$), 148.6 ($C_{Ar/Hetar}$), 144.2 ($C_{Ar/Hetar}$), 137.8 ($C_{Ar/Hetar}$), 137.2 ($C_{Ar/Hetar}$), 133.1 ($C_{Ar/Hetar}$), 132.2 (4CH_{Ar}), 131.9 ($C_{Ar/Hetar}$), 131.9 ($C_{Ar/Hetar}$), 131.5 (2CH_{Ar}), 131.2 (2CH_{Ar}), 130.9 (2CH_{Ar}), 130.2 ($C_{Ar/Hetar}$), 130.2 ($C_{Ar/Hetar}$), 130.1 (2CH_{Ar}), 128.3 (2CH_{Ar}), 118.9 (C≡N), 113.3 (2CH_{Ar}), 113.2 (2CH_{Ar}), 113.0 (2CH_{Ar}), 109.8 ($C_{Ar/Hetar}$), 55.2 (O*C*H_3), 55.0 (2O*C*H_3), 21.2 (CH_3). **MS** (EI, 70 eV): m/z (%) = 590 (7), 589 (26), 588 (M^+, 84), 587 (100), 543 (8), 294 (33), 253 (7), 234 (7), 233 (6), 223 (6), 218 (8), 207 (14), 201 (7), 152 (6), 73 (11). **HR-MS** (ESI): m/z = calcd. for $C_{40}H_{32}N_2O_3$ ($[M+H]^+$): 589.24857, found: 589.24799. Anal. calcd. for $C_{40}H_{32}N_2O_3$: C 81.61, H 5.48, N 4.76; found: C 81.22, H 5.49 , N 4.48.

2,3,5-tris(4-*tert*-butylphenyl)-4-(4-cyanophenyl)-6-*p*-tolylpyridine (12b)

12b was synthesized according to general procedure using 2,3,5-trichloro-4-(4-cyanophenyl)-6-*p*-tolylpyridine **6a** (0.23 mmol, 85 mg) and 4-*tert*-butylphenylboronic acid (1.37 mmol, 243.9 mg) and was purified via column chromatography (heptane/ dichloromethane). White solid; yield: 114 mg (75 %). mp. 256 - 257 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.33 (d, ^3J = 8.4 Hz, 4H, CH_{Ar}), 7.23-7.16 (m, 4H, CH_{Ar}), 7.07-6.97 (m, 6H, CH_{Ar}), 6.89 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 6.78 (dd, ^3J = 8.5 Hz, ^3J = 8.5 Hz, 4H, CH_{Ar}), 2.30 (s, 3H, CH_3), 1.27 (s, 9H, CH_3 *t*-Bu), 1.22 (s, 9H, CH_3 *t*-Bu), 1.22 (s, 9H, CH_3 *t*-Bu). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 156.5 ($C_{Ar/Hetar}$), 156.2 ($C_{Ar/Hetar}$), 150.2

($C_{Ar/Hetar}$), 149.7 ($C_{Ar/Hetar}$), 149.7 ($C_{Ar/Hetar}$), 148.2 ($C_{Ar/Hetar}$), 144.1 ($C_{Ar/Hetar}$), 137.7 ($C_{Ar/Hetar}$), 137.6 ($C_{Ar/Hetar}$), 137.1 ($C_{Ar/Hetar}$), 134.9 ($C_{Ar/Hetar}$), 134.9 ($C_{Ar/Hetar}$), 132.6 ($C_{Ar/Hetar}$), 132.5 ($C_{Ar/Hetar}$), 131.3 ($2CH_{Ar}$), 130.8 ($2CH_{Ar}$), 130.8 ($2CH_{Ar}$), 130.5 ($2CH_{Ar}$), 130.1 ($2CH_{Ar}$), 129.8 ($2CH_{Ar}$), 128.2 ($2CH_{Ar}$), 124.6 ($2CH_{Ar}$), 124.5 ($2CH_{Ar}$), 124.3 ($2CH_{Ar}$), 118.9 (C≡N), 109.6 (C_{Ar}), 34.4 (C *t*-Bu), 34.4 (C *t*-Bu), 34.3 (C *t*-Bu), 31.2 ($6CH_3$ *t*-Bu), 31.2 ($3CH_3$ *t*-Bu), 21.2 (CH_3). **MS** (EI, 70 eV): m/z (%) = 666 (M^+, 63), 665 (100), 651 (5), 609 (7), 593 (5), 579 (6), 554 (5), 553 (9), 551 (11), 318 (23), 207 (6), 57 (59), 41(16). **HR-MS** (ESI): m/z = calcd. for $C_{49}H_{50}N_2$ ($[M+H]^+$): 667.40468, found: 667.40437. Anal. calcd. for $C_{49}H_{50}N_2$: C 88.24, H 7.56, N 4.20; found: C 88.17, H 7.27 , N 3.89

Synthesis of pentaarylpyridines (13a–b)

An oven-dried, argon-flushed sealable glass tube was charged with the appropriate tri-arylated pyridine **10a** or **10b** (0.22 mmol, 100 mg), $PdCl_2(CH_3CN)_2$ (5 mol%, 2.9 mg), SPhos (10 mol%, 9.22 mg), the appropriate arylboronic acid (0.99 mmol) and K_3PO_4 (0.99 mmol, 191 mg) followed by anhydrous toluene (3 mL); The tube was sealed with a Teflon valve and stirred at 100 °C for 20 h. The cooled reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by column chromatography using heptane/ethyl acetate as eluent.

2-**(4-methoxyphenyl)-3,5-diphenyl-4-(4-cyanophenyl)-6-*p*-tolylpyridine (13a)**

13a was synthesized according to general procedure using 3,5-dichloro-2-(4-methoxyphenyl)-4-(4-cyanophenyl)-6-*p*-tolylpyridine **10a** (0.22 mmol, 100 mg), and phenylboronic acid (0.99 mmol, 120.7 mg) and was purified via column chromatography (heptane/ ethyl acetate). White solid; yield: 107 mg (90 %). mp. 261 - 262 °C. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 7.38 (d,^3J = 8.9 Hz, 2H, CH_{Ar}), 7.33 (d,^3J = 8.2 Hz, 2H, CH_{Ar}), 7.23 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 7.08–7.04 (m, 6H, CH_{Ar}), 7.01 (d, ^3J = 8.4 Hz, 2H, CH_{Ar}), 6.94–6.84 (m, 6H, CH_{Ar}), 6.73 (d, ^3J = 8.9 Hz, 2H, CH_{Ar}), 3.77 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 159.1 (*C*-OCH_3), 156.4 ($C_{Ar/Hetar}$), 155.9 ($C_{Ar/Hetar}$), 148.3 ($C_{Ar/Hetar}$), 143.8 ($C_{Ar/Hetar}$), 138.0 ($C_{Ar/Hetar}$), 137.9 ($C_{Ar/Hetar}$), 137.5 ($C_{Ar/Hetar}$), 137.4 ($C_{Ar/Hetar}$), 132.9 ($C_{Ar/Hetar}$), 132.3 ($C_{Ar/Hetar}$), 132.3 ($C_{Ar/Hetar}$), 131.5 ($2CH_{Ar}$), 131.1 ($2CH_{Ar}$), 131.1 ($2CH_{Ar}$), 130.8

($2CH_{Ar}$), 130.1 ($2CH_{Ar}$), 128.3 ($2CH_{Ar}$), 127.8 ($2CH_{Ar}$), 127.8 ($2CH_{Ar}$), 126.7 ($2CH_{Ar}$), 126.6 ($2CH_{Ar}$), 118.7 (C≡N), 113.0 ($2CH_{Ar}$), 109.9 (C_{Ar}), 55.1 (OCH_3), 21.2 (CH_3). **MS** (EI, 70 eV): m/z (%) = 529 (21), 528 (M^+, 71), 527 (100), 484 (8), 483 (12), 264 (8), 165 (5). **HR-MS** (ESI): m/z = calcd. for $C_{38}H_{28}N_2O$ ($[M+H]^+$): 529.22744, found: 529.22698. Anal. calcd. for $C_{38}H_{28}N_2O$: C 86.34, H 5.34, N 5.30; found: C 86.12, H 5.29, N 5.14.

2-(4-chlorophenyl)-3,5-bis(4-methoxyphenyl)-4-(4-cyanophenyl)-6-*p*-tolylpyridine (13b)

13b was synthesized according to general procedure using 3,5-dichloro-2-(4-chlorophenyl)-4-(4-cyanophenyl)-6-*p*-tolylpyridine **10b** (0.22 mmol, 100 mg), and 4-methoxyphenylboronic acid (0.99 mmol, 150.4 mg) and was purified via column chromatography (heptane/ ethyl acetate). White solid; yield: 66 mg (50 %). mp. 246 - 247 °C. **^{1}H-NMR** (250 MHz, $CDCl_3$): δ = 7.35 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.30 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.27 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.18 (d, ^3J = 8.7 Hz, 2H, CH_{Ar}), 7.03 (d, ^3J = 7.9 Hz, 2H, CH_{Ar}), 6.89 (d, ^3J = 8.5 Hz, 2H, CH_{Ar}), 6.75 (dd, ^3J = 8.8 Hz, ^3J = 8.8 Hz, 4H, CH_{Ar}), 6.59 (dd, ^3J = 8.8 Hz, ^3J = 8.9 Hz, 4H, CH_{Ar}), 3.73 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 158.3 (*C*-OCH_3), 158.2 ($C_{Ar/Hetar}$), 156.8 ($C_{Ar/Hetar}$), 155.3 ($C_{Ar/Hetar}$), 148.8 ($C_{Ar/Hetar}$), 143.9 ($C_{Ar/Hetar}$), 139.1 ($C_{Ar/Hetar}$), 137.5 ($C_{Ar/Hetar}$), 137.4 ($C_{Ar/Hetar}$), 133.6 ($C_{Ar/Hetar}$), 132.8 ($C_{Ar/Hetar}$), 132.4 ($C_{Ar/Hetar}$), 132.1 ($4CH_{Ar}$), 131.5 ($2CH_{Ar}$), 131.2 ($2CH_{Ar}$), 130.9 ($2CH_{Ar}$), 129.9 ($2CH_{Ar}$), 129.9 (C_{Ar}), 129.6 (C_{Ar}), 128.4($2CH_{Ar}$), 127.8 ($2CH_{Ar}$), 118.8 (C≡N), 113.4 ($2CH_{Ar}$), 113.3 ($2CH_{Ar}$), 110.0 (C_{Ar}), 55.0 ($2OCH_3$), 21.2 (CH_3). **MS** (EI, 70 eV): m/z (%) = 595 (M^+, 11), 594 (M^+, 32), 593 (M^+, 58), 592 (M^+, 84), 591 (100), 547 (11), 297 (7), 296 (11), 227 (5), 220 (5), 207 (7), 199 (6), 190 (13), 178 (6), 164 (5), 163 (6). **HR-MS** (ESI): m/z = calcd. for $C_{39}H_{29}ClN_2O_2$ ($[M+H]^+$): 593.19903, found: 593.199, calcd. for $C_{39}H_{29}{}^{37}ClN_2O_2$: 595.19825, found 595.19807. Anal. calcd. for $C_{39}H_{29}ClN_2O_2$: C 78.98, H 4.93, N 4.72; found: C 78.78, H 4.59, N 4.84.

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