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Site Selective Synthesis of Pentaarylpyridines *via* Multiple Suzuki–Miyaura Cross-Coupling Reactions

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Dedicated to Professor Armin de Meijere on the occasion of his 75th birthday.

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Abstract: Pentaarylpyridines were conveniently prepared in one step by pentafold Suzuki–Miyaura reactions of pentachloropyridine. Moreover, site selective reactions were performed, leading to various substituted arylpyridines. Pentaarylpyridines were studied in detail by means of DFT calculations and by optical spectroscopy.

Keywords: cross-coupling; palladium; pyridines; site selectivity; Suzuki–Miyaura reaction

Introduction

Pyridines are among the most widely studied six-membered heterocycles possessing an important role as lead compounds in various natural products,[1,2] pharmaceuticals[3] and functional materials, such as building blocks used in supramolecular chemistry[4] or ligands in transition metal catalysis.[5] As a result, the synthesis of functionalized pyridines, in particular highly substituted derivatives, has attracted much attention and a number of efficient and mild strategies for their synthesis have been developed. Examples include simple condensation reactions of carbonyl compounds,[6] thermal or metal-promoted cycloadditions[7] and new efficient multicomponent reactions, such as addition reactions with carbon-carbon multiple bonds.[8] Unfortunately, several of these methodologies are often incompatible with various functional groups or general substitution patterns, allowing only for the construction of constricted substitutions around the pyridine core. Palladium-catalyzed cross-coupling reactions may circumvent these drawbacks by successive introduction of the desired substituents on the pyridine core. During the last years, site selective cross-coupling reactions of polyhalogenated heterocycles have gained increasing interest.[9] The different distribution of the electron density of heterocycles allows the facile introduction of various substituents by palladium-catalyzed cross-coupling reactions with high selectivity.

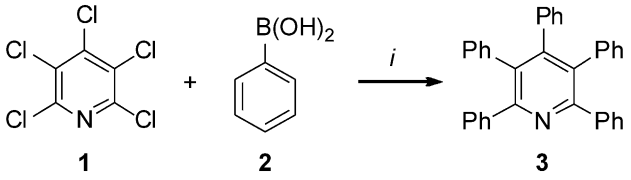
Results and Discussion

Recently, we reported the pentafold Sonogashira reaction of commercially available pentachloropyridine (**1**);[10] Reissig and co-workers recently reported that the pentafold Suzuki–Miyaura reaction of pentachloropyridine is a difficult task, due to increasing steric hindrance in the course of the reaction and due to the considerably higher electron density of position 3 as compared to position 2.[11a] Very recently, Schmitt and co-workers reported an approach to pentaarylated pyridines based on Pd-catalyzed coupling reactions of 2-chloro-3-hydroxypyridine.[11b] Despite the elegance and utility of this work, many synthetic steps were required. In fact, a site selective pentafold arylation by cross-coupling reactions of pentachloropyridine (**1**) or of another pentahalogenated pyridine derivative has, to the best of our knowledge, not been reported so

Table 1. Optimization of the synthesis of **3a**.

Entry	$PhB(OH)_2$ (equiv.)	Solvent	Temp. [°C]	Catalyst (mol%)	Base (equiv.)	GC Yield[a] [%]
1	6.0	toluene	100	$Pd(OAc)_2$ (5), SPhos (10)	KF (6)	52
2	6.0	toluene	100	$Pd(OAc)_2$ (5), Cata*XC*ium A (10)	KF (6)	9
3	6.0	toluene	100	$Pd(OAc)_2$ (5), Johnphos Cy (10)	KF (6)	2
4	6.0	toluene	100	$Pd(OAc)_2$ (5), PCy_3 (10)	KF (6)	30
5	6.0	toluene	100	$Pd(OAc)_2$ (5), XPhos (10)	KF (6)	7
6	6.0	toluene	100	$Pd(OAc)_2$ (5), Cata*CX*ium PCy_3	KF (6)	5
7	6.0	toluene	100	$Pd(OAc)_2$ (5), SPhos (10)	K_3PO_4 (6)	72
8	6.0	toluene	100	$Pd(OAc)_2$ (5), SPhos (10)	Cs_2CO_3 (6)	11
9	6.0	DMF	100	$Pd(OAc)_2$ (5), SPhos (10)	KF (6)	2
10	6.0	DMF	100	$Pd(OAc)_2$ (5), SPhos (10)	K_3PO_4 (6)	4
11	6.0	DMF	100	$Pd(OAc)_2$ (5), SPhos (10)	Cs_2CO_3 (6)	25
12	6.0	1,4-dioxane	100	$Pd(OAc)_2$ (5), SPhos (10)	KF (6)	1
13	6.0	1,4-dioxane	100	$Pd(OAc)_2$ (5), SPhos (10)	K_3PO_4 (6)	25
14	6.0	1,4 dioxane	100	$Pd(OAc)_2$ (5), SPhos (10)	Cs_2CO_3 (6)	4
15	6.0	toluene	100	$PdCl_2(CH_3CN)_2$ (5), SPhos (10)	K_3PO_4 (6)	85
16	6.0	toluene	100	$Pd(dba)_2$ (5), SPhos (10)	K_3PO_4 (9)	46
17	7.5	toluene	100	$PdCl_2(CH_3CN)_2$ (5), SPhos (10)	K_3PO_4 (6)	46
18	6.0	toluene	100	$PdCl_2(CH_3CN)_2$ (5), SPhos (10)	K_3PO_4 (7.5)	90
19	7.5	toluene	100	$PdCl_2(CH_3CN)_2$ (5), SPhos (10)	K_3PO_4 (7.5)	97[b]
20	6.0	toluene	110	$PdCl_2(CH_3CN)_2$ (4), SPhos (8)	K_3PO_4 (7.5)	36
21	6.0	toluene	110	$PdCl_2(CH_3CN)_2$ (3), SPhos (6)	K_3PO_4 (7.5)	33
22	6.0	toluene	110	$PdCl_2(CH_3CN)_2$ (2), SPhos (4)	K_3PO_4 (7.5)	23
23	6.0	toluene	110	$PdCl_2(CH_3CN)_2$ (1), SPhos (4)	K_3PO_4 (7.5)	17
24	10.0	toluene	100	$PdCl_2(CH_3CN)_2$ (5)	K_3PO_4 (10)	99[b]

[a] Hexadecane as internal GC standard was used.
[b] Isolated yield.



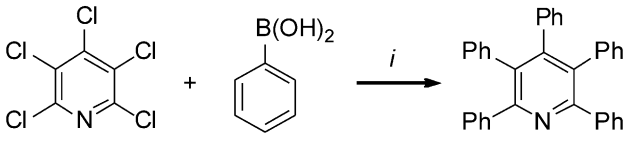
Scheme 1. Optimization of the synthesis of **3a**: *i*, **1** (1.0 equiv.), **2**, "Pd" catalyst precursor, ligand, base, solvent, 20 h.

far. Therefore, as a starting point of our studies, we developed a general catalytic system for the pentafold Suzuki–Miyaura coupling of **1** with phenylboronic acid **2a** (Scheme 1);

During the optimization (Table 1), the employment of SPhos, a biarylphosphine ligand developed by Buchwald et al.,[12] proved to be the most efficient ligand and allowed preparation of the desired product **3a** in 52% yield. In contrast, other bulky phosphine ligands, such as XPhos,[13] cyclohexyl JohnPhos[14] or Cata*CX*ium A,[15] led to low yields. Nevertheless, using SPhos, the yield could be enhanced from 52% to up to 85% when KF and $Pd(OAc)_2$ were replaced by K_3PO_4 and $PdCl_2(CH_3CN)_2$, respectively. Finally, in the presence of 7.5 equiv, of phenylboronic acid (**2a**) and K_3PO_4, an excellent yield of 97% could be achieved. During our studies related to the scope, we observed that higher yields of several products were obtained when 10.0 equiv. instead of 7.5 equiv. of boronic acid were employed. Thus, all reactions were performed in toluene at 100 °C using 1.0 equiv. of pentachloropyridine, 10.0 equiv. of boronic acid **2**, 10.0 equiv. of K_3PO_4, 5.0 mol% of $PdCl_2(CH_3CN)_2$ and 10.0 mol% of SPhos.

The reaction of **1** with various boronic acids **2**, using our optimized conditions, afforded the corresponding pentaarylpyridines **3a–m** in 42–99% yield (Scheme 2, Table 2); Products containing electron-donating as well as electron-withdrawing aryl groups could be prepared in high to quantitative yields. However, the reaction with boronic acids bearing a *para*-vinyl, *para*-fluorine or *meta*-substituent led to a significant decrease of the yield. This might be explained by side-reactions (in case of the vinyl group), electronic reasons in the case of fluorine and steric reasons in the case of *meta*-substituents.

The structure of product **3b** was independently confirmed by X-ray crystal structure analysis (Figure 1); The aryl groups attached to the pyridine moiety are twisted out of plane and oriented in a propeller-type structure. The aryl substituent located in the *para*-position [C-4–C-3–C-20–C-25 = –62.8(3)°] is more twisted out of plane than the aryl moieties located in *ortho* or *meta* positions [N-1–C-1–C-6–C-7 = –48.3(3), N-1–C-5–C-34–C-39 = –40.8(3), C-1–C-2–



1 2 3

Scheme 2. Synthesis of **3a–m**: *i*, **1** (1.0 equiv.), **2a–m** (10.0 equiv.), $PdCl_2(CH_3CN)_2$ (5.0 mol%), SPhos (10.0 mol%), K_3PO_4 (10.0 equiv.), toluene, 100 °C, 20 h.

Table 2. Synthesis of **3a–m**.

Entry	R	**3** [%][a]
a	C_6H_5	99
b	4-MeC_6H_4	93
c	4-EtC_6H_4	71
d	4-*t*-BuC_6H_4	89
e	4-(MeO)C_6H_4	99
f	4-PhC_6H_4	81
g	4-(vinyl)C_6H_4	42
h	4-FC_6H_4	46
i	4-(CF_3)C_6H_4	99
j	4-(CF_3O)C_6H_4	89
k	3-(MeO)C_6H_4	60
l	3-(NO_2)C_6H_4	57
m	2-thienyl	79

[a] Yields of isolated products.

C1-3–C-14 = −56.9(3) and C-5–C-4–C-27–C-32 = −58.2(3)°]. As a consequence, a conjugation of the π orbitals between the pyridine core and the phenyl moieties might be unlikely affecting the photophysical properties notably (*vide infra*);

With our new procedure in hand, we envisioned that **1** might also be an ideal substrate for site selective arylation of pyridine by palladium-catalyzed Suzuki–Miyaura reactions. We already reported the synthesis of 3,4,5-trichloro-2,6-diarylpyridines **4**.[16] After a more thorough optimization (Table 3) we were able to synthesize various 3,4,5-trichloro-2,6-diarylpyridines in moderate to good yield (Scheme 3, Table 4); The moderate yields of some products can be explained by difficulties in their separation from monoarylated side-product. All reactions took place selectively at positions 2 and 6 of the pyridine moiety. In contrast, an arylation of positions 3 or 4 was not observed.

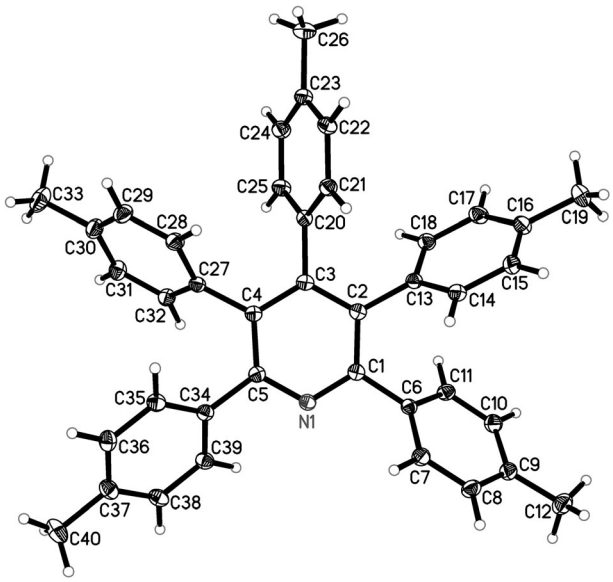


Figure 1. ORTEP plot of **3b**. Displacement ellipsoids are drawn at the 30% probability level.

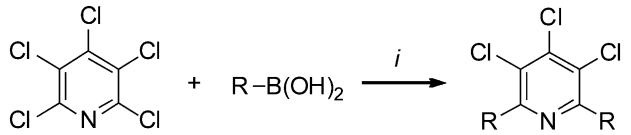
The synthesized 3,4,5-trichloro-2,6-diarylpyridines were easily converted to the corresponding pentaarylpyridines **5a–g**, containing two different aryl moieties in good to excellent yields (Scheme 4, Table 5);

In the following studies, we attempted the selective synthesis of tetraarylated pyridines using 4.5 equiv. of the appropriate boronic acid. However, in all cases we isolated inseparable mixtures of the expected 3-chloro-2,4,5,6-tetraarylpyridine **6** and of regioisomeric 4-chloro-2,3,5,6-tetraarylpyridine **7** in ratios of 4:1 up

Table 3. Optimization of the synthesis of **4a**.

Entry	Catalyst (mol%)	Base (equiv.)	Equiv. $PhB(OH)_2$	Temp. [°C]	Solvent	**4a** [%][a]
1	$Pd(PPh_3)_4$ (5)	K_3PO_4 (3.0)	2.5	100	toluene	55
2	$Pd(PPh_3)_4$ (5)	K_3PO_4 (3.0)	2.5	60	toluene	<1
3	$PdCl_2(CH_3CN)_2$ (5), $P(Cy)_3$ (10)	K_3PO_4 (3.0)	2.5	60	toluene	30
4	$PdCl_2(CH_3CN)_2$ (5), Cat*CX*ium A (10)	K_3PO_4 (3.0)	2.5	60	toluene	13
5	$Pd(PPh_3)_4$	K_3PO_4 (3.0)	2.5	100	1,4-dioxane	47
6	$Pd(PPh_3)_4$	K_3PO_4 (3.0)	2.5	80	CH_3CN	59
7	$Pd(PPh_3)_4$	K_3PO_4 (3.0)	2.5	100	DMF	54
8	$Pd(PPh_3)_4$	KF (3.0)	2.5	80	CH_3CN	24
9	$Pd(PPh_3)_4$	Cs_2CO_3 (3.0)	2.5	80	CH_3CN	<1
10	$Pd(PPh_3)_4$	K_3PO_4 (3.5)	3.0	80	CH_3CN	46

[a] Yields of isolated product.



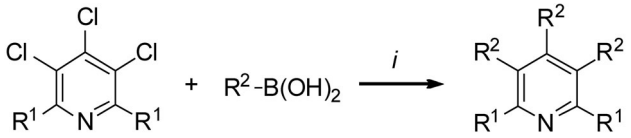
1 2 4

Scheme 3. Synthesis of **4a–h**: *i*, **1** (1.0 equiv.), **2** (3.0 equiv.) $Pd(PPh_3)_4$ (5.0 mol%), K_3PO_4 (3.5 equiv.) CH_3CN, 80 °C, 20 h.

Table 4. Synthesis of **4a–h**.

4	R	**4** [%][a]
a	C_6H_5	56
b	4-MeC_6H_4	74
c	4-EtC_6H_4	42
d	4-*t*-BuC_6H_4	42
e	4-$(MeO)C_6H_4$	59
f	3-$(MeO)C_6H_4$	71
g	3-MeC_6H_4	38
h	2-$(MeO)C_6H_4$	42

[a] Yields of isolated products



4 2 5

Scheme 4. Synthesis of **5a–g**: *i*, 4 (1.0 equiv.), 2 (6.0 equiv.), $PdCl_2(CH_3CN)_2$ (5.0 mol%), SPhos (10.0 mol%), K_3PO_4 (6.0 equiv.), toluene, 100 °C, 20 h.

Table 5. Synthesis of **5a–g**.

Entry	R^1	R^2	**5** [%][a]
a	C_6H_5	4-$(MeO)C_6H_4$	83
b	C_6H_5	4-$(CF_3)C_6H_4$	79
c	C_6H_5	4-EtC_6H_4	67
d	4-MeC_6H_4	4-$(MeO)C_6H_4$	85
e	4-EtC_6H_4	C_6H_5	92
f	4-EtC_6H_4	4-$(CF_3)C_6H_4$	96
g	4-EtC_6H_4	3-$(MeO)C_6H_4$	92

[a] Yields of isolated products.

to 5:1 (see also the Supporting Information) (Scheme 5);

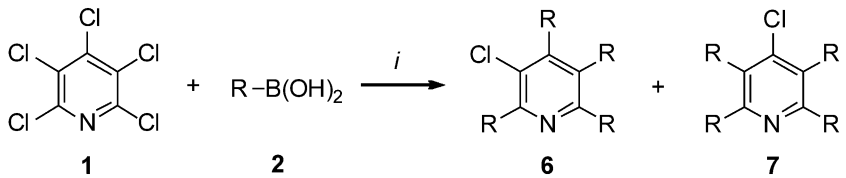
We considered that the gradual introduction of aryl substituents might influence the electronic properties of the pyridine, thus explaining the reaction pattern. NBO analysis of non-, mono- and diarylated pentachloropyridines support this hypothesis *(cf.* the Supporting Information);

In fact, substitution of one or two chlorine atoms by aryl substituents at positions 2 and 6 leads to an intense reduction of NBO charge differences on the adjacent positions 3 and 5 of the pyridine, respectively. Notably, electron-donating or electron-withdrawing groups have virtually no impact on the NBO charges (*cf.* the Supporting Information);

Therefore, we synthesized 2,3,5,6-tetrachloro-4-(4-methoxyphenyl)pyridine (**8a**) and 2,3,5,6-tetrachloro-4-[4-(trifluoromethyl)phenyl]pyridine (**8b**) by aromatic substitution[17] to circumvent the problems regarding the site selective synthesis of tetraarylated pyridines. Starting from these substrates, we were able to achieve a site selective synthesis of various pentaarylated pyridines containing two or three different aryl substituents in a two-step procedure. In general, triarylated products **9**, substituted by $R^1 = CF_3$, gave lower yields than the corresponding methoxy-substituted derivatives, due to purification problems during the column chromatography. The conditions were again thoroughly optimized (Table 6); The second step proceeded without any influence of the substituents located at position 4 and the desired pentaarylated products were isolated in up to quantitative yields in the last step (Scheme 6, Table 7);

Furthermore, starting from **8a** or **8b**, tetraarylated pyridines **11a–c**, containing two different aryl moieties, were successfully synthesized. However, these products were isolated only in moderate yields, due to the formation of lesser and higher arylated side products. Suzuki–Miyaura reactions of **11a–c** afforded pentaarylpyridines **12a–e**, containing three different aryl groups, in good to excellent yields (Scheme 7, Table 8);

Finally, we studied the complete arylation of **8a** and **8b**. Application of the reaction conditions optimized for the synthesis of **3** gave the desired pentaarylpyridines **13a–l** in good yields (Scheme 8, Table 9);



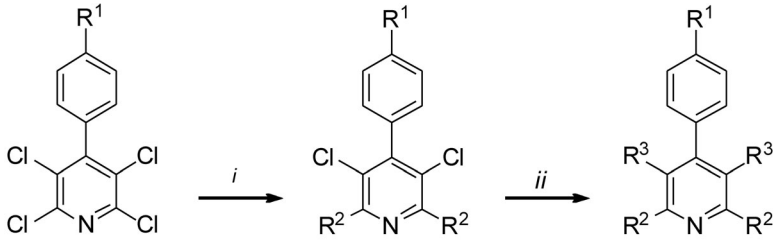
1 2 6 7

Scheme 5. Synthesis of **6** and **7** (regioisomeric mixtures); *i*: **1** (1.0 equiv.), **2** (4.5 equiv.), $PdCl_2(CH_3CN)_2$ (5.0 mol%), SPhos (10.0 mol%), K_3PO_4 (6.5 equiv.), toluene, 100 °C, 20 h.

Table 6. Optimization of the synthesis of **9d**.

Entry	Catalyst (mol%)	Base (equiv.)	Equiv. $PhB(OH)_2$	Temp. [°C]	**9d**[a] [%]
1	$Pd(PPh_3)_4$	K_3PO_4 (3.0)	3.0	100	71
2	$PdCl_2(CH_3CN)_2$ (5), SPhos (10)	K_3PO_4 (3.0)	2.5	20	<1
3	$PdCl_2(CH_3CN)_2$ (5), SPhos (10)	K_3PO_4 (3,0)	2.4	100	31
4	$PdCl_2(CH_3CN)_2$ (5), $P(Cy)_3$ (10)	K_3PO_4 (3.0)	2.5	100	53

[a] Yield of isolated product.



8a (R^1=OMe) **8b** (R^1=CF_3) **9** **10**

Scheme 6. Synthesis of **10a–h**: *i*, **8** (1.0 equiv.), **2** (2.5 equiv.), $Pd(PPh_3)_4$ (5 mol%), K_3PO_4 (3.0 equiv.), toluene, 100 °C, 20 h; *ii*, **9** (1.0 equiv.), **2** (4.0 equiv.), $PdCl_2(CH_3CN)_2$ (5 mol%), SPhos (10 mol%), K_3PO_4 (4.0 equiv.), toluene, 100 °C, 20 h.

Table 7. Synthesis of **10a–h**.

10	R^1	R^2	R^3	**9** [%][a]	**10** [%][a]
a	OMe	C_6H_5	4-*t*BuC_6H_4	71	85
b	OMe	C_6H_5	4-MeC_6H_4	71	84
c	OMe	4-(MeO)C_6H_4	4-$(CF_3)C_6H_4$	69	79
d	OMe	4-(MeO)C_6H_4	C_6H_5	69	91
e	OMe	4-FC_6H_4	4-MeC_6H_4	63	99
f	CF_3	C_6H_5	4-(MeO)C_6H_4	47	82
g	CF_3	C_6H_5	4-PhC_6H_4	47	73
h	CF_3	C_6H_5	4-$(CF_3)C_6H_4$	47	74

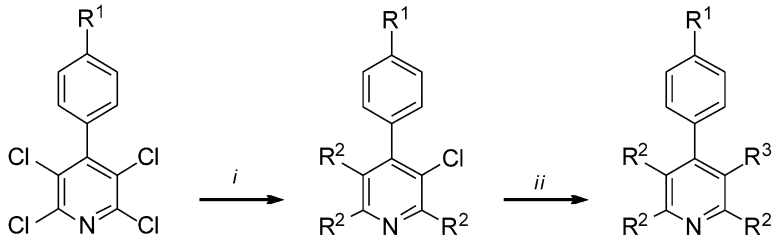
[a] Yields of isolated products.

The UV/Vis and fluorescence spectroscopic data of pentaarylpyridines **3a**, **3e** and **3i** measured in DCM are summarized in Table 10. The absorption wavelengths of **3** are in the UV region of λ_{1-4abs} = 227–316 nm and exhibit four conspicuous transitions

Table 8. Synthesis of **12a–e**.

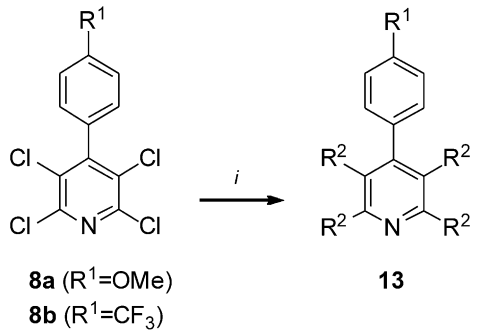
11	**12**	R^1	R^2	R^3	**11** [%][a]	**12** [%][a]
a	**a**	OMe	C_6H_5	4-*i*PrC_6H_4	54	98
b	**b**	OMe	4-MeC_6H_4	4-$(CF_3)C_6H_4$	34	93
c	**c**	CF_3	C_6H_5	4-(MeO)C_6H_4	43	77
c	**d**	CF_3	C_6H_5	4-PhC_6H_4	43	78
c	**e**	CF_3	C_6H_5	4-$(CF_3)C_6H_4$	43	89

[a] Yields of isolated products.



8a (R^1=OMe) **8b** (R^1=CF_3) **11** **12**

Scheme 7. Synthesis of **10a–h**: *i*, **8** (1.0 equiv.), **2** (3.0 equiv.), $PdCl_2(CH_3CN)_2$ (5 mol%), SPhos (10 mol%), K_3PO_4 (3.0 equiv.), toluene, 100 °C, 20 h; *ii*, **11** (1.0 equiv.), **2** (2.5 equiv.), $PdCl_2(CH_3CN)_2$ (5 mol%), SPhos (10 mol%), K_3PO_4 (2.5 equiv.), toluene, 100 °C, 20 h.



Scheme 8. Synthesis of **13a–l**: *i*, **8** (1.0 equiv.), **2** (8.0 equiv.), $PdCl_2(CH_3CN)_2$ (5 mol%), SPhos (10 mol%), K_3PO_4 (8.0 equiv.), toluene, 100 °C, 20 h.

Table 9. Synthesis of **13a–l**.

13	R^1	R^2	**13** [%][a]
a	OMe	C_6H_5	66
b	OMe	4-*t*-BuC_6H_4	62
c	OMe	4-(*i*-Pr)OC_6H_4	93
d	OMe	4-FC_6H_4	78
e	OMe	4-MeC_6H_4	61
f	OMe	4-(CF_3)C_6H_4	81
g	OMe	4-(EtO)C_6H_4	79
h	CF_3	C_6H_5	68
i	CF_3	4-MeC_6H_4	56
j	CF_3	4-(MeO)C_6H_4	68
k	CF_3	4-(PhO)C_6H_4	59
l	CF_3	3-(MeO)C_6H_4	69

[a] Yields of isolated products.

Table 10. Absorption and emission spectroscopic data of **3a**, **3e** and **3i** (CH_2Cl_2, $c = 1 \cdot 10^{-5}$ mol/L);

	3a	**3e**	**3i**
λ_{1abs} [nm]	227	228	227
log ε λ_{1abs}	4.56	4.56	4.40
λ_{2abs} [nm]	246	270	245
log ε λ_{2abs}	4.59	4.57	4.34
λ_{3abs} [nm]	276	294	272
log ε λ_{3abs}	4.52	4.55	4.18
λ_{4abs}(sh) [nm]	300	316	298
log ε λ_{4abs}(sh)	4.29	4.37	4.14
$\lambda_{5,em}$ [nm] (ϕ_{fluo}, %)[a]	369 (1)	387 (4)	369 (2)

[a] Fluorescence quantum yield was determined using naphthalene as a reference ($\phi_{fluo} = 0.23$).[15] Corrections due to molecular absorption and refractive index of DCM, used for the measurement, were incorporated in the calculations.

(λ_{1-4abs}) (Figure 2); The absorption maxima of compound **3e**, bearing electron-donating methoxy substituents, are red-shifted, which indicates a more pronounced π-electron delocalization relative to unsubstituted derivative **3a** (λ_{abs2-4}); In contrast, compound **3i**, bearing electron-withdrawing trifluoromethyl groups, caused no significant shift of the transitions. Furthermore, the position of the high-energy band located at 227–228 nm is to some extent independent of the substitution pattern and can be assigned to local π-π* transitions involving the arylpyridine core.[18] However, the lower energy transitions strongly depend on the presence of the substituent attached to the arylpyridine moiety. The emission spectra of **3** are displayed in Figure 2, also showing the same trend as observed for the absorption spectra. The fluorescence quantum yields, determined using naphthalene as reference,[19] show an emission efficiency for compound **3e** slightly higher than that of derivatives **3a** and **3i**. Anyhow, the obtained quantum yields in the range of $\varphi_{fluo} = 0.01$–0.04 are rather low indicating a weak fluorescence response (Table 10);

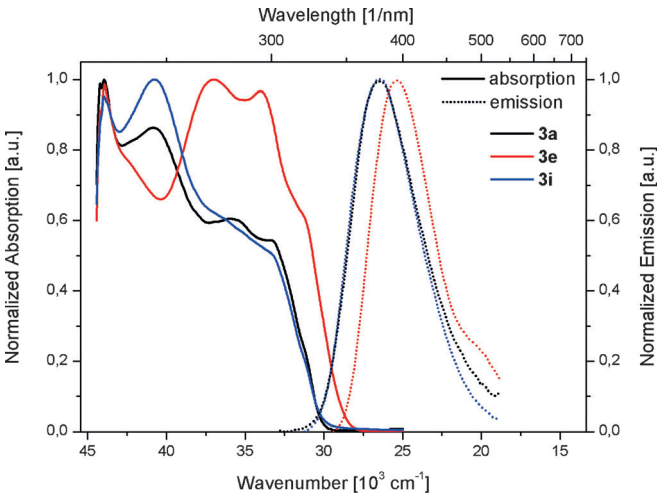


Figure 2. Normalized absorption and emission spectra of **3a**, **3e** and **3i** measured in CH_2Cl_2.

In order to clarify the differences observed in the absorption spectra of **3**, time-dependent density functional theory (TD-DFT) calculations have been performed using the B3LYP functional with a TVZP basis set and PCM solvation model as implemented in the Gaussian 09 program package.[20] Focusing on the red part of the spectrum (280–320 nm) the calculations are in good agreement with the experiment. The influence of the substitution pattern of **3** can be clearly seen by comparison of the HOMO–LUMO and HOMO–LUMO+1 energy gaps (Figure 3); In the case of compound **3e**, these gaps are decreased by about 0.3 eV relative to those of **3a** and **3i** which theoretically explains the red-shift. Inspecting the molecular orbitals, one might argue that the participation of the methoxy groups results in an increased delocalization of the HOMO (Figure 3); The visualization of the difference densities for the discussed transitions supports this view (Figure 4); During the excitation

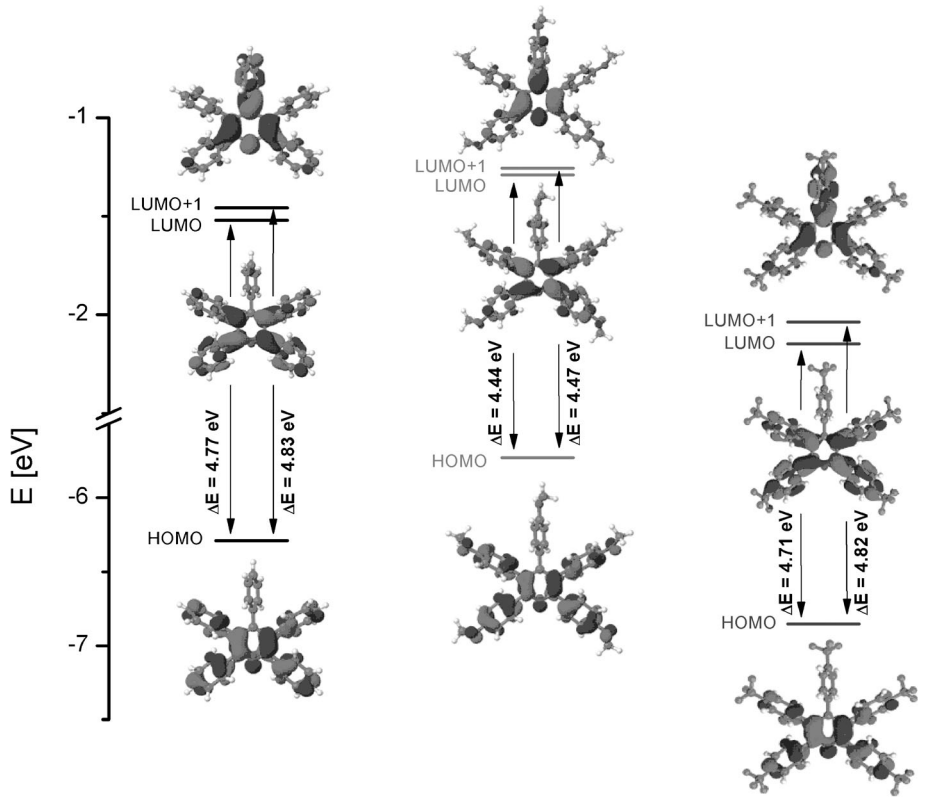


Figure 3. HOMO–LUMO and HOMO–LUMO+1 energy gaps derived from molecular orbital energies for compounds **3a**, **3e** and **3i** (from *left* to *right*);

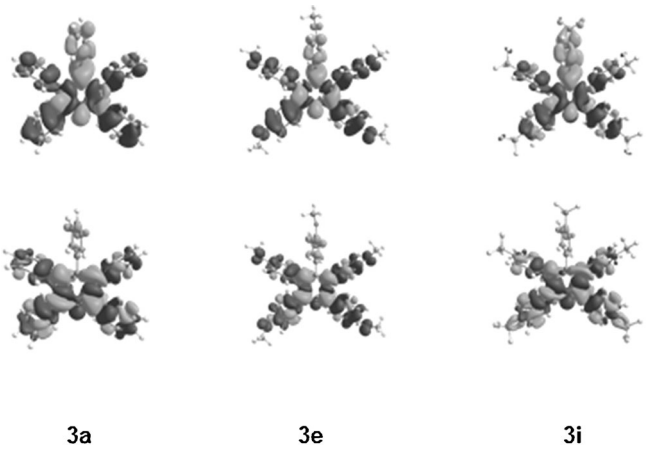


Figure 4. Difference densities for HOMO–LUMO (*bottom*) and HOMO–LUMO+1 (*top*) transitions for **3a**, **3e** and **3i** (dark gray = negative, i.e., density reduced upon excitation);

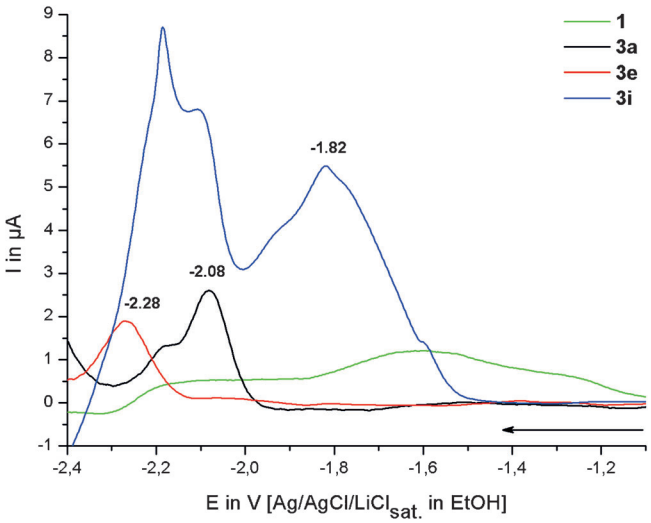


Figure 5. Reductive DPVs of **1**, **3a**, **3e** and **3i** in DMF (0.1 mol $L^{<M->1}$ $TBAPF_6$); working electrode: platinum; [Fc/Fc^+] = 0.6 V.

the electron density is shifted from the outer sphere to the inner pyridine core. This effect is much more pronounced for compound **3e** than for **3a** and **3i**.

DPV measurements were carried out to determine the electrochemical activity and the potential values of pentaaryl-substituted pyridines **3a**, **3e** and **3i**. The influence of the substitution pattern on the reduction potential is shown in Figure 5. In the case of compound **3e**, the first reduction appears at −2.28 V. In contrast, parent pentaphenylpyridine (**3a**) and trifluoromethyl-substituted pentaarylpyridine **3i** are anodically shifted, possessing potentials for the first reduction at −2.08 V and −1.82 V, respectively. Due to the shift of **3i**, two additional conspicuous poten-

tials of reduction appear at −2.11 V and −2.18 V which were not detected for **3a** and **3e**. Furthermore, no oxidations could be measured for **1** and **3a** during the anodic scan. However, in the cases of **3e** and **3i** oxidation peaks could be observed at 1.65 V and 0.70 V (not shown); The electronic influence of the *para*-substituents of products **3** on the potential can be estimated using Hammett substituent constants σ_{para}.[17] In comparison to unsubstituted **3a**, the reduction peaks of **3e** and **3i** are consistent with the position of the Hammett constants [MeO (−0.268) > H (0) > CF_3 (0.54)]. As a result, the reductions of pentaaryl-substituted pyridines bearing electron-donating substituents are cathodically shifted whereas electron-withdrawing substituents lead to an anodic shift.

Conclusions

In conclusion, we have developed the first synthesis of various substituted pentaarylpyridines by palladium-catalyzed cross-coupling reactions of pentachloropyridine (**1**); Our highly efficient catalyst system shows a very good functional group tolerance and allowed the preparation of the desired pentaarylated products in nearly quantitative yield in one step. Moreover, we developed site selective arylations using the Suzuki–Miyaura reaction. This protocol facilitates an easy access to a variety of substituted arylpyridines starting from easily available starting materials. DFT calculations were performed to verify the experimental results. Currently, further investigations on the arylation of other polychlorinated aryl compounds are underway in our laboratories.

Experimental Section

General

All reactions were carried out in oven-dried pressure tubes under an argon atmosphere (Argon 4.6) in order to simultaneously exclude oxygen and water (Schlenk techniques were applied); Solvents for reactions were dried and distilled by standard methods or purchased in extra dry quality from Sigma Aldrich. Solvents for liquid chromatography and extraction were always distilled prior to use (*n*-heptane, *n*-hexane, EtOAc, DCM); All chemicals employed, including halogenated pyridines, ligands, boronic acids and bases, were purchased from a commercial source (Sigma Aldrich, Alfa Aesar) and used without further purification.

^{1}H NMR spectroscopy: Bruker AV 300 (300 MHz) and Bruker AV 400 (400 MHz); All NMR spectra presented in this work were recorded in $CDCl_3$ solution. All chemical shifts are given in ppm. All coupling constants are indicated as *J*. References: TMS ($\delta = 0.00$ ppm) or residual $CHCl_3$ ($\delta = 7.26$ ppm) were taken as internal standard. Peak characterization: s = singlet, brs = broad singlet, d = doublet, brd = broad doublet, t = triplet, dd = doublet of doublet, q = quartet, m = multiplet. The spectra were measured with a standard number of scans (NS = 32); In case of unclear assignments all possible hydrogen atoms were stated.

^{13}C NMR spectroscopy: Bruker AV 300 (75 MHz) and Bruker AV 400 (100 MHz); All NMR spectra presented in this work were recorded in $CDCl_3$ solution. All chemical shifts are given in ppm. All coupling constants are indicated as *J*. References: TMS ($\delta = 0.00$ ppm) or residual $CHCl_3$ ($\delta = 70.00$ ppm) were taken as internal standard. Peak characterization: d = doublet, t = triplet, q = quartet. The DEPT method was used for determining the presence of primary, secondary, tertiary and quaternary carbon atoms. All spectra were measured with a standard number of scans (NS = 256); In case of unclear assignments all possible carbon atoms were stated. In some cases the number of scans was increased to 2000–8000 scans in order to detect carbon-fluorine couplings.

^{19}F NMR spectroscopy: Bruker AV 300 (282 MHz); Spectra were measured with a standard number of scans (NS = 128);

Mass spectrometry (MS): Finnigan MAT 95 XP (electron ionization EI, 70 eV); 6890 N/5973 (Agilent), 6210 Time-of-Flight LC/MS (Agilent); Gas Chromatography MS (GCMS): Agilent HP-5890 with an Agilent HP-5973 Mass Selective Detector (EI) and HP-5 capillary column using helium carrier gas. Only the measurements with an average deviation from the theoretical mass of ±2 mDa were accounted as correct. High resolution MS [HR-MS (ESI)]: Agilent 1969 A TOF. Only the measurements with an average deviation from the theoretical mass of ±2 mDa were accounted as correct.

Infrared spectroscopy (IR): Nicolet 550 FT-IR spectrometer with ATR sampling technique for solids as well as liquids. Signal characterization: w = weak, m = medium, s = strong.

UV/Vis spectroscopy (UV/Vis): Lambda 5 (PerkinElmer); Compounds were measured with solution concentrations of $1 \cdot 10^{-5}$ mol·L^{-1} in DCM. Parameters selected: Interval = 0.20 nm; Slit = 2.00 nm; Scan Speed = 240 nm min^{-1}.

Fluorescence spectroscopy: Hitachi F-4010. Compounds were measured with solution concentrations of $1 \cdot 10^{-5}$ mol·L^{-1} in DCM. Optimal excitation wavelengths of 275 nm were chosen to be appropriate. A solution of naphthalene in cyclohexane was applied as a standard for the measurement of the fluorescence quantum yields ($\varphi_{fluo} = 0.23$) (measuring inaccuracy = ±0.01); Accordingly, corrections due to molecular absorption and refractive index of DCM used for the measurement were incorporated in the calculation.

X-ray crystallography: Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F2 with the SHELXTL software package (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.); XP (Bruker AXS) was used for graphical representation. CCDC 961487 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Elemental analysis (EA): C/H/N/S – Microanalysator TruSpec CHNS (Leco);

Melting point determination (mp): Micro-Hot-Stage Galen™ III Cambridge Instruments. The melting points have not been corrected.

Thin layer chromatography (TLC): Merck Silica 60 F254 on aluminum tin foil from Macherey–Nagel. Detection with UV light at 254 nm and/or 366 nm without dipping reagent.

Column chromatography: Separation on Fluka silica gel 60 (0.063–0.200 mm, 70–320 mesh); Eluents were distilled before use.

Synthesis of 3a–m

An oven-dried, argon-flushed sealable glass tube was charged with pentachloropyridine **1** (0.2 mmol), $PdCl_2(CH_3CN)_2$ (5 mol%), SPhos (10 mol%), the appropriate boronic acid **2a–m** (2.0 mmol) and K_3PO_4 (2.0 mmol) followed by anhydrous toluene (9.6 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.

Pentaphenylpyridine (3a): Colorless solid; yield: 99%; mp 248–250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.76–6.80 (m, 2H, CH), 6.89–6.92 (m, 7H, CH), 6.94–7.01 (m, 6H, CH), 7.16–7.20 (m, 6H, CH), 7.40–7.42 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 126.2 (CH), 126.2 (CH), 126.9 (CH), 127.3 (CH), 127.3 (CH), 127.5 (CH), 130.2 (CH), 130.4 (CH), 131.3 (CH) 133.7 (C), 138.1 (C), 138.4 (C), 140.8 (C), 150.2 (C), 156.4 (C); IR (ATR): $\tilde{\nu}$ = 3101 (w), 3081 (w), 3054 (w), 3024 (w), 1599 (w), 1577 (w), 1486 (m), 1441 (m), 1393 (m), 1280 (w), 1131 (w), 1075 (m), 1024 (m), 1005 (w), 919 (m), 827 (w), 802 (m), 773 (m), 759 (m), 728 (m), 695 (s), 652 (m), 619 (m), 551 (m), 542 (m), 400 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 460 (M^+, 17), 459 (61), 458 (100), 456 (1), 380 (4), 379 (2), 378 (6), 377 (2), 352 (2), 350 (2), 302 (2), 276 (4), 230 (2), 222 (4), 220 (8), 214 (8), 201 (4), 183 (3), 178 (3), 77 (2); HR-MS (ESI): *m/z* = 460.20598, calcd. for $C_{29}H_{22}N$ ($[M+H]^+$): 460.20598; anal. calcd. for $C_{35}H_{25}N$ (459.58): C 91.47, H 5.48, N 3.05; found: C 91.46, H 5.548, N 2.968.

2,3,4,5,6-Pentakis(4-tolyl)pyridine (3b): Colorless solid; yield: 99%; mp 253 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.15 (s, 3H, CH_3), 2.20 (s, 6H, CH_3), 2.28 (s, 6H, CH_3), 6.63 (d, 2H, ^3J = 8.3 Hz, CH), 6.72–6.83 (m, 10H, CH), 6.98 (d, 4H, ^3J = 7.9 Hz, CH), 7.30 (d, 4H, ^3J = 7.9 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1, 21.2, 21.2 (CH_3), 127.6, 128.1, 128.1, 130.1, 130.3, 131.1 (CH), 133.4, 135.3, 135.3, 135.4, 135.6, 136.8, 156.0 (C); IR (ATR): $\tilde{\nu}$ = 3025 (w), 2918 (w), 2863 (w), 1531 (w), 1501 (w), 1387 (m), 1183 (w), 1112 (w), 1021 (w), 913 (w), 813 (s), 735 (s), 652 (w), 554 (m), 526 (s), 491 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 528 (M^+, 100), 420 (2), 406 (2), 265 (2), 235 (3), 226 (3); HR-MS (ESI): *m/z* = 530.28469, calcd. for $C_{40}H_{36}N$ ($[M+H]^+$): 530.28423; anal. calcd. for $C_{40}H_{35}N$ (529.71): C 90.70, H 6.66; found: C 90.82, H 7.024.

2,3,4,5,6-Pentakis(4-ethylphenyl)pyridine (3c): Colorless solid; yield: 71%; mp 166 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (t, 3H, ^3J = 7.6 Hz, CH_3), 1.12 (t, 6H, ^3J = 7.6 Hz, CH_3), 1.20 (t, 6H, ^3J = 7.6 Hz, CH_3), 2.44 (q, 2H, ^3J = 7.6 Hz, CH_2), 2.50 (q, 4H, ^3J = 7.6 Hz, CH_2), 2.60 (q, 4H, ^3J = 7.6 Hz, CH_2), 6.65 (d, 2H, ^3J = 8.3 Hz, CH), 6.74 (d, 2H, ^3J = 8.3 Hz, CH), 6.79–6.85 (m, 8H, CH), 7.01 (d, 4H, ^3J = 8.4 Hz, CH), 7.35 (d, 4H, ^3J = 8.3 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4, 15.5, 15.6 (CH_3), 28.5, 28.5, 28.6 (CH_2), 126.3, 126.8, 126.9, 130.3, 130.5, 131.3 (CH), 133.4, 135.8, 136.1, 138.7, 141.8, 141.9, 143.1, 150.5, 156.0 (C); IR (ATR): $\tilde{\nu}$ = 3024 (w), 2962 (s), 2928 (m), 1531 (m), 1501 (m), 1454 (m), 1388 (m), 1185 (m), 1116 (m), 1020 (m), 847 (s), 825 (s), 746 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 599 (M^+, 76), 598 (100), 582 (5), 570 (4), 535 (2), 287 (11); HR-MS (ESI): *m/z* = 600.36294, calcd. for $C_{45}H_{45}N$ ($[M+H]^+$): 600.36248; anal. calcd. for $C_{45}H_{45}N$ (599.85): C 90.10, H 7.56, N 2.34; found: C 89.90, H 7.55, N 2.44.

Pentakis(4-*tert*-butylphenyl)pyridine (3d): Colorless solid; yield: 89%; mp 340–342 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (s, 9H, $CH_{3\ t\text{-Bu}}$), 1.17 (s, 18H, $CH_{3\ t\text{-Bu}}$), 1.24 (s, 9H, $CH_{3\ t\text{-Bu}}$), 6.60–6.63 (m, 2H, CH), 6.76–6.80 (m, 4H, CH), 6.84–6.88 (m, 2H, CH), 6.95–6.99 (m, 4H, CH), 7.13–7.17 (m, 4H, CH), 7.32–7.36 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.1 ($CH_{3\ t\text{-Bu}}$), 31.2 ($CH_{3\ t\text{-Bu}}$), 31.3 ($CH_{3\ t\text{-Bu}}$), 34.1 ($C_{\ t\text{-Bu}}$), 34.2 ($C_{\ t\text{-Bu}}$), 34.4 ($C_{\ t\text{-Bu}}$), 123.4 (CH), 123.9 (CH), 124.2 (CH), 129.8 (CH), 130.0 (CH), 130.9 (CH), 133.5 (C), 135.5 (C), 135.8 (C), 148.5 (C), 148.7 (C), 149.8 (C), 149.8 (C), 149.8 (C), 155.8 (C); IR (ATR): $\tilde{\nu}$ = 3053 (w), 2961 (s), 2902 (m), 2865 (m), 1610 (m), 1568 (w), 1531 (w), 1497 (m), 1460 (m), 1388 (m), 1361 (m), 1270 (m), 1201 (m), 1137 (m), 1107 (m), 1017 (m), 1002 (w), 970 (w), 922 (w), 851 (s), 832 (s), 815 (s), 779 (m), 758 (w), 736 (w), 675 (m), 638 (m), 626 (m), 597 (w), 580 (m), 547 (m), 481 (w), 445 (w), 445 (w), 407 (w), 386 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 740 (M^+, 42), 739 (100), 738 (97), 737 (13), 736 (8), 725 (4), 722 (9), 708 (3), 707 (2), 706 (3), 682 (5), 668 (3), 666 (5), 652 (4), 650 (3), 626 (4), 540 (3), 414 (3), 391 (2), 366 (2), 362 (3), 355 (10), 352 (5), 341 (4), 338 (5), 281 (4), 206 (6), 57 (15), 44 (31), 43 (6); HR-MS (ESI): *m/z* = 740.51898, calcd. for $C_{55}H_{66}N$ ($[M+H]^+$): 740.51834; anal. calcd. for $C_{55}H_{65}N$ (740.11): C 89.26, H 8.85, N 1.89; found: C 89.61, H 8.488, N 1.647.

2,3,4,5,6-Pentakis(4-methoxyphenyl)pyridine (3e): Slightly yellow solid; yield: 124 mg (99%); mp 240 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 3H, OCH_3), 3.70, 3.74 (s, 6H, OCH_3), 6.49 (d, 2H, ^3J = 8.9 Hz, CH), 6.58 (d, 4H, ^3J = 8.9 Hz, CH), 6.66 (d, 2H, ^3J = 8.7 Hz, CH), 6.72 (d, 4H, ^3J = 8.8 Hz, CH), 6.80 (d, 4H, ^3J = 8.7 Hz, CH), 7.36 (d, 4H, ^3J = 8.9 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.9, 54.9, 55.1 (OCH_3), 112.5, 112.9, 112.9 (CH), 130.8, 131.2 (C), 131.4, 131.5, 132.3 (CH), 132.7, 133.8, 150.2, 155.7, 157.4, 157.6, 158.7 (C); IR (ATR): $\tilde{\nu}$ = 2960 (w), 2935 (w), 2836 (w), 1607 (m), 1514 (m), 1388 (m), 1286 (m), 1242 (s), 1030 (s), 830 (s), 542 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 609 (M^+, 100), 564 (4), 550 (2), 262 (2), 238 (3), 223 (8), 195 (4); HR-MS (ESI): *m/z* = 610.25978, calcd. for $C_{40}H_{35}NO_5$ ($[M+H]^+$): 610.2588.

Penta(biphenyl-4-yl)pyridine (3f): Slightly yellow solid; yield: 81%; mp 341–343 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.81–6.86 (m, 2H, CH), 6.98–6.99 (m, 3H, CH), 7.18–7.51 (m, 40H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 125.7 (CH), 126.1 (CH), 126.3 (CH), 126.7 (CH), 126.8 (CH), 127.6 (CH), 127.2 (CH), 127.2 (CH), 128.3 (CH), 128.6 (CH), 128.6 (CH), 128.6 (CH), 130.7 (CH), 130.9 (CH), 131.7 (CH), 133.5 (C), 137.0 (C), 137.3 (C), 138.7 (C), 138.8 (C), 139.4 (C), 140.1 (C), 140.3 (C), 140.3 (C), 140.6 (C), 155.1 (C), 156.0 (C); IR (ATR): $\tilde{\nu}$ = 3401 (w), 3055 (w), 3027

(m), 1597 (m), 1524 (m), 1484 (m), 1382 (m), 1261 (w), 1177 (m), 1113 (m), 1075 (m), 1006 (m), 825 (m), 764 (m), 745 (m), 732 (m), 693 (s), 572 (m), 496 (m), 458 (w), 404 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 840 (M^+, 6), 839 (12), 838 (10), 432 (3), 308 (9), 276 (15), 250 (28), 225 (17), 212 (14), 211 (100), 209 (41), 208 (9), 207 (24), 196 (9), 195 (4), 194 (3), 183 (11), 182 (56), 181 (30), 180 (5), 166 (7), 165 (6), 153 (17), 152 (39), 151 (12), 150 (9), 139 (19), 138 (15), 119 (11), 98 (12), 97 (6), 91 (13), 69 (14), 66 (15), 65 (10), 55 (10), 44 (37), 43 (16), 41 (14), 39 (12); HR-MS (ESI): *m/z* = 840.3637, calcd. for $C_{65}H_{46}N$ ($[M+H]^+$): 840.3625; anal. calcd. for $C_{65}H_{45}N$ (840.06): C 92.93, H 5.40, N 1.67; found: C 92.83, H 5.555, N 1.484.

Pentakis(4-vinylphenyl)pyridine (3g): Colorless solid; yield: 42%; mp 376–378 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.12 (dd, $^3J_{H,H,cis}$ = 10.9 Hz, $^2J_{H,H,gem}$ = 1.0 Hz, 1H, CH=H-H_{cis} and CH=CH-H_{gem}), 5.15 (dd, $^3J_{H,H,cis}$ = 11.3 Hz, $^2J_{H,H,gem}$ = 0.8 Hz, 2H, CH=CH-H_{cis} and CH=CH-H_{gem}), 5.19 (dd, $^3J_{H,H,cis}$ = 10.7 Hz, $^2J_{H,H,gem}$ = 1.0 Hz, 2H, CH=H-H_{cis} and CH=H-H_{gem}), 5.57 (dd, $^3J_{H,H,trans}$ = 17.2 Hz, $^2J_{H,H,gem}$ = 1.0 Hz, 1H, CH=CH-H_{trans} and CH=CH-H_{gem}), 5.62 (dd, $^3J_{H,H,trans}$ = 17.2 Hz, $^2J_{H,H,gem}$ = 1.0 Hz, 2H, CH=CH-H_{trans} and CH=CH-H_{gem}), 5.68 (dd, $^3J_{H,H,trans}$ = 17.2 Hz, $^2J_{H,H,gem}$ = 1.0 Hz, 2H, CH=CH-H_{trans} and CH=CH-H_{gem}), 6.50 (dd, $^3J_{H,H,trans}$ = 17.9 Hz, $^3J_{H,H,cis}$ = 11.1 Hz, 1H, CH_2=CH_{trans} and CH_2=CH_{cis}), 6.55 (dd, $^3J_{H,H,trans}$ = 18.3 Hz, $^3J_{H,H,cis}$ = 11.1 Hz, 2H, CH_2=CH_{trans} and CH_2=CH_{cis}), 6.63 (dd, $^3J_{H,H,trans}$ = 18.3 Hz, $^3J_{H,H,cis}$ = 11.1 Hz, 2H, CH_2=CH_{trans} and CH_2=CH_{cis}), 6.69–6.71 (m, 2H, CH), 6.83–6.85 (m, 4H, CH), 6.98–6.99 (m, 2H, CH), 7.05–7.07 (m, 4H, CH), 7.20–7.22 (m, 4H, CH), 7.34–7.37 (m, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.5 (CH_2), 113.5 (CH_2), 113.9 (CH_2), 125.1 (CH), 125.5 (CH), 125.5 (CH), 130.4 (CH), 130.6 (CH), 131.4 (CH), 133.1 (C), 135.3 (C), 135.4 (C), 136.5 (CH), 136.5 (CH), 136.6 (C), 136.6 (CH), 137.5 (C), 137.9 (C), 140.3 (C), 149.9 (C), 156.0 (C); IR (ATR): $\tilde{\nu}$ = 3083 (w), 3059 (w), 3033 (w), 2973 (w), 2851 (w), 1626 (m), 1606 (w), 1528 (m), 1498 (w), 1401 (w), 1386 (s), 1272 (m), 1247 (w), 1131 (w), 1116 (m), 1030 (w), 1015 (m), 992 (s), 953 (w), 905 (s), 830 (s), 777 (m), 732 (m), 694 (m), 667 (m), 621 (m), 545 (m), 486 (m), 393 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 590 (M^+, 39), 589 (91), 588 (100), 484 (3), 252 (2), 245 (2), 181 (3), 169 (3), 139 (3), 135 (3), 125 (5), 123 (4), 119 (3), 111 (7), 109 (6), 97 (11), 95 (8), 85 (8), 84 (4), 83 (11), 82 (4), 81 (9), 71 (11), 69 (16), 57 (18), 55 (13), 44 (10), 43 (11), 39 (4); HR-MS (EI, 70 eV): *m/z* = 589.274025, calcd. for $C_{45}H_{35}N$: 589.27640; anal. calcd. for $C_{45}H_{35}N$ (589.77): C 91.64, H 5.98, N 2.37; found: C 91.73, H 5.996, N, 2.163.

Pentakis(4-fluorophenyl)pyridine (3h): Colorless solid; yield: 46%; mp 286–288 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.66–6.92 (m, 16H, CH), 7.29–7.36 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 114.5 (d, $^2J_{C,F}$ = 21.7 Hz, CH), 114.7 (d, $^2J_{C,F}$ = 21.1 Hz, CH), 114.9 (d, $^2J_{C,F}$ = 21.9 Hz, CH), 131.7 (d, $^3J_{C,F}$ = 8.0 Hz, CH), 131.8 (d, $^3J_{C,F}$ = 8.4 Hz, CH), 132.6 (d, $^3J_{C,F}$ = 7.6 Hz, CH), 132.8 (C), 133.5 (d, $^4J_{C,F}$ = 4.0 Hz, CH), 133.8 (d, $^4J_{C,F}$ = 4.0 Hz, CH), 136.3 (d, $^4J_{C,F}$ = 3.3 Hz, CH), 149.7 (C), 155.8 (C), 161.2 (d, $^1J_{C,F}$ = 247.4 Hz, CF), 161.4 (d, $^1J_{C,F}$ = 246.8 Hz, CF), 162.2 (d, $^1J_{C,F}$ = 248.0 Hz, CF); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −113.6 (F), −114.3 (F), −114.4 (F); IR (ATR): $\tilde{\nu}$ = 3080 (w), 1596 (m), 1539 (m), 1501 (s), 1413 (m), 1389 (m), 1299 (w), 1218 (s), 1156 (s), 1125 (w), 1096 (m), 1014 (m), 960 (w), 849 (m), 831 (s), 813 (s), 756 (m), 727 (w), 680 (m), 648 (m), 618 (m), 552 (m), 525 (s), 502 (m), 467 (w), 387 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 550 (M^+, 17), 549 (68), 548 (100), 452 (6), 450 (3), 432 (2), 431 (2), 411 (1), 332 (2), 330 (4), 312 (1), 254 (2), 253 (2), 247 (5), 244 (3), 243 (3), 234 (4), 215 (2), 214 (7), 213 (2), 212 (3), 207 (2), 194 (3), 193 (2), 188 (2), 168 (1), 32 (1); HR-MS (ESI): *m/z* = 550.15851, calcd. for $C_{35}H_{21}F_5N$ ($[M+H]^+$): 550.15887.

2,3,4,5,6-Pentakis[4-(trifluormethyl)phenyl]pyridine (3i): Colorless solid; yield: 77%; mp 282 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.89 (d, 4H, ^3J = 7.9 Hz, CH), 7.02 (d, 2H, ^3J = 8.0 Hz, CH), 7.28 (d, 2H, ^3J = 8.3 Hz, CH), 7.35 (d, 4H, ^3J = 8.3 Hz, CH), 7.45–7.52 (m, 8H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.6 (q, ^1J = 272 Hz, CF_3), 123.7 (q, ^1J = 272 Hz, CF_3), 124.0 (q, ^1J = 124.0 CF_3), 124.7 (q, ^4J = 3.7 Hz, CH), 125.0 (q ^4J = 3.7 Hz, CH), 125.1 (q, ^4J = 3.7 Hz, CH), 129.7 (q, ^2J = 33.4 Hz, C_{Ar}), 129.7 (q, ^2J = 32.9 Hz, C_{Ar}), 130.4, 130.4, 131.3 (CH), 133.0, 140.4, 140.7, 143.0 149.3, 156.0 (C); IR (ATR): $\tilde{\nu}$ = 1617 (w), 1535 (w), 1407 (w), 1320 (s), 1160 (m), 1120 (s), 1106 (s), 1064 (s), 1017 (m), 846 (m), 829 (m), 609 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 798 (M^+, 100), 780 (6), 688 (4), 111 (2), 97 (2); HR-MS (ESI): *m/z* = 800.14218, calcd. for $C_{40}H_{20}F_{15}N$ ($[M+H]^+$): 800.1429; anal. calcd. for $C_{40}H_{20}F_{15}N$ (799.57): C 60.23, H 2.52, N 1.75; found: C 60.23, H 2.379, N 1.914.

Pentakis[4-(trifluoromethoxy)phenyl]pyridine (3j): Colorless solid; yield: 89%; mp 164–166 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.73–6.76 (m, 2H, CH), 6.84–6.94 (m, 10H, CH), 7.04–7.07 (m, 4H, CH), 7.37–7.40 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.3 (CH), 120.8 (CH), 120.3 (q, $^1J_{C,F}$ = 258.6 Hz, CF_3), 120.3 (q, $^1J_{C,F}$ = 258.5 Hz, CF_3), 120.3 (q, $^1J_{C,F}$ = 258.4 Hz, CF_3), 120.4 (CH), 131.4 (CH), 131.5 (CH), 132.3 (CH), 132.7 (C), 135.8 (C), 136.1 (C), 138.3 (C), 147.9 (q, $^3J_{C,F}$ = 2.2 Hz, C), 148.1 (q, $^3J_{C,F}$ = 2.1 Hz, C), 148.9 (q, $^3J_{C,F}$ = 2.2 Hz, C), 149.4 (C), 155.7 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −57.5 (CF_3), −57.8 (CF_3), −58.0 (CF_3); IR (ATR): $\tilde{\nu}$ = 1609 (w), 1533 (w), 1511 (m), 1394 (w), 1251 (s), 1203 (s), 1147 (s), 1017 (m), 1005 (m), 921 (m), 845 (m), 807 (m), 762 (w), 657 (m), 635 (m), 613 (w), 520 (m), 475 (w), 383 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 880 (M^+, 20), 879 (65), 878 (100), 794 (3), 355 (2), 281 (2), 221 (2), 147 (2), 111 (2), 97 (4), 95 (3), 85 (3), 84 (2), 83 (4), 81 (3), 71 (5), 70 (3), 69 (7), 67 (2), 63 (2), 57 (8), 56 (3), 55 (5), 45 (2), 44 (5), 43 (6), 42 (2), 41 (5), 40 (2); HR-MS (ESI): *m/z* = 878.100825, calcd. for $C_{40}H_{19}F_{15}NO_5$: 878.10182; anal. calcd. for $C_{40}H_{20}F_{15}NO_5$ (879.57): C 54.62, H 2.29, N 1.59; found: C 54.67, H 2.358, N 1.647.

2,3,4,5,6-Pentakis(3-methoxyphenyl)pyridin (3k): Yellow oil; yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.48 (s, 3H, OCH_3), 3.50 (s, 6H, OCH_3), 3.60 (s, 6H, OCH_3), 6.38–6.61 (m, 9H, CH), 6.75–6.79 (m, 2H, CH), 6.85–6.98 (m, 5H, CH), 7.06–7.15 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.1, 55.1 (OCH_3), 112.8, 114.1, 114.9, 115.6, 116.3, 122.7, 123.0, 123.8, 128.0, 128.4, 128.5 (CH), 133.4, 139.2, 139.6, 141.9, 149.9, 156.0, 158.4, 158.7, 158.8 (C); IR (ATR): $\tilde{\nu}$ = 2936 (w), 2832 (w), 1577 (s), 1531 (m), 1423 (m), 1385 (m), 1284 (m), 1236 (s), 1160 (m), 1040 (s), 858 (m), 735 (s), 701 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%) = 609 (M^+, 79), 608 (100), 592 (5), 578 (4), 564 (2), 536 (7), 502 (3); HR-MS (EI, 70 eV): *m/z* = 609.250275, calcd. for $C_{40}H_{35}O_5N$: 609.25097.

Pentakis(3-nitrophenyl)pyridine (3l): Colorless solid; yield: 57%; mp 237–239 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.46 (m, 8H, CH), 7.67–7.72 (m, 3H, CH), 7.83 (brs, 2H, CH), 7.89–7.92 (m, 1H, CH), 7.97–8.00 (m, 2H, CH), 8.13–8.16 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 122.9 (CH), 123.0 (CH), 123.6 (CH), 125.1 (CH), 125.4 (CH), 125.5 (CH), 129.3 (CH), 129.4 (CH), 129.7 (CH), 129.9 (CH), 135.7 (CH), 135.7 (CH), 132.7 (C), 137.5 (C), 137.8 (C), 140.2 (C), 147.5 (C), 147.9 (C), 148.0 (C), 149.0 (C), 155.7 (C); IR (ATR): $\tilde{\nu}$ = 3083 (w), 2924 (w), 2865 (w), 1521 (s), 1436 (w), 1394 (w), 1344 (s), 1276 (w), 1147 (w), 1082 (m), 1001 (w), 900 (m), 868 (m), 836 (w), 806 (m), 785 (w), 759 (w), 736 (m), 711 (m), 687 (s), 619 (w), 537 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 685 (M^+, 6), 684 (16), 683 (9), 667 (2), 655 (2), 654 (5), 637 (7), 591 (5), 342 (4), 281 (5), 267 (3), 220 (3), 219 (6), 208 (4), 207 (13), 193 (6), 183 (5), 181 (5), 152 (5), 151 (5), 149 (4), 143 (3), 135 (9), 131 (6), 125 (10), 123 (8), 121 (7), 119 (9), 111 (15), 109 (12), 97 (22), 95 (16), 91 (11), 85 (15), 83 (22), 81 (18), 71 (22), 70 (13), 69 (42), 67 (15), 66 (23), 65 (16), 57 (36), 55 (31), 45 (10), 44 (100), 43 (43), 41 (26), 40 (13), 39 (17); HR-MS (ESI): *m/z* = 685.13137, calcd. for $C_{35}H_{21}N_6O_{10}$ ($[M+H]^+$): 685.13055.

2,3,4,5,6-Penta(thiophen-2-yl)pyridine (3m): Dark yellow solid; 79%; mp 300–302 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.60 (dd, 1H, ^3J = 3.6 Hz, ^4J = 1.3 Hz, CH), 6.63 (dd, 2H, ^3J = 3.9 Hz, ^4J = 1.2 Hz, CH), 6.70 (dd, 1H, ^3J = 5.2 Hz, ^3J = 3.6 Hz, CH), 6.87–6.89 (m, 4H, CH), 6.96 (dd, 2H, ^3J = 5.1 Hz, ^3J = 3.4 Hz, CH), 7.11 (dd, 1H, ^3J = 4.9 Hz, ^4J = 1.2 Hz, CH), 7.33 (dd, 2H, ^3J = 5.1 Hz, ^4J = 1.2 Hz, CH), 7.35 (dd, 2H, ^3J = 5.1 Hz, ^4J = 1.2 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 124.5 (C), 125.8, 126.6, 127.1, 127.3, 127.7, 128.4, 128.9, 129.2, 129.4 (CH), 137.1, 138.2, 144.3, 147.9, 151.0 (C); IR (ATR): $\tilde{\nu}$ = 3097 (w), 3067 (w), 1509 (m), 1426 (m), 1381 (m), 1215 (m), 1108 (m), 1063 (m), 1037 (m), 846 (m), 755 (m), 696 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%) = 489 (M^+, 100), 456 (12), 444 (4), 422 (4), 411 (3), 371 (2), 228 (3), 205 (3), 190 (5); HR-MS (ESI): *m/z* = 489.989, calcd. for $C_{25}H_{15}NS_5$ ($[M+H]^+$): 489.988; anal. calcd. for $C_{25}H_{15}NS_5$ (489.72): C 61.31, H 3.09, N 2.86, S 32.74; found: C 60.89, H 3.127, N 2.817, S 32.93.

Synthesis of 3,4,5-Trichloro-2,6-diarylpyridines 4a–h

An oven-dried and argon-flushed pressure tube was charged with pentachloropyridine **1** (1.0 equiv.), $Pd(PPh_3)_4$ (5.0 mol%), the appropriate boronic acid (3.0 equiv.) and K_3PO_4 (3.5 equiv.) followed by anhydrous CH_3CN (3.5 mL); The tube was sealed with a Teflon valve and the reaction mixture was stirred at 80 °C for 20 h. The cooled reaction mixture was diluted with water and extracted with DCM. The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated under vacuum. The residue was purified by column chromatography.

3,4,5-Trichloro-2,6-diphenylpyridine (4a): Colorless solid; yield: 56%; mp 159–161 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.48 (m, 6H, CH), 7.64–7.70 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.2 (CH), 128.8 (C), 129.3 (CH), 129.7 (CH), 136.3 (C), 144.1 (C), 155.0 (C); IR (ATR): $\tilde{\nu}$ = 3026 (w), 2920 (m), 2851 (m), 1729 (m), 1600 (w), 1514 (m), 1486 (m), 1446 (m), 1355 (m), 1287 (m), 1072 (m), 816 (m), 750 (s), 686 (s), 662 (m), 631 (m), 617 (m), 542 (w), 483 (m), 456 (w), 401 cm^{-1} (w);; MS (EI, 70 eV): *m/z* (%) = 335 (M^+, 66), 334 (16), 333 (68), 302 (11), 301 (12), 300 (66), 299 (20), 298 (100), 263 (13), 228 (15), 227 (30), 200 (4), 160 (25), 149 (11), 114 (8), 77 (6); HR-MS (EI, 70 eV): m/z = 332.98725, calcd. for $C_{17}H_{10}Cl_3N$: 332.98733; anal. calcd. for $C_{17}H_{10}Cl_3N$ (334.63): C 61.02, H 3.01, N 4.19; found: C 61.35, H 3.237, N 3.889.

3,4,5-Trichloro-2,6-(*para*-tolyl)pyridine (4b): Colorless solid; yield: 74%; mp 139–141 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 6H, CH_3), 7.26–7.29 (m, 4H, CH), 7.65 (d, 4H, ^3J = 8.1 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 127.7 (C), 128.8, 129.4 (CH), 135.0, 139.3, 142.8, 155.1 (C); IR (ATR): $\tilde{\nu}$ = 3033 (w), 2919 (m), 2854 (m), 1612 (m), 1493 (s), 1368 (s), 1300 (m), 1272 (m), 1184 (m), 1089 (m), 1019 (m), 958 (m), 880 (m), 819 (s), 776 (s), 674 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%) = 361 (M^+, 100), 326 (78), 291 (9), 275 (3), 255 (8), 240 (9); HR-MS (EI, 70 eV): *m/z* = 361.018050, calcd for $C_{19}H_{14}Cl_3N$: 361.01863; anal. calcd. for $C_{19}H_{14}Cl_3N$ (362.68): C 62.92, H 3.89, N 3.86; found: C 62.97, H 3.943, N 3.705.

3,4,5-Trichloro-2,6-bis(4-ethylphenyl)pyridine (4c): Colorless solid; yield: 42%; mp 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, ^{3}JH-H = 7.7 Hz, 6H, CH_3), 2.71 (q, ^3J = 7.7 Hz, 4H, CH_2), 7.28 (d, ^3J = 8.5 Hz, 4H, CH), 7.67 (d, ^3J = 8.5 Hz, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.3 (CH_3), 28.7 (CH_2), 127.5 (CH), 127.7 (C), 129.5 (CH), 135.2 (C), 142.7 (C), 145.5 (C), 155.2 (C); IR (ATR): $\tilde{\nu}$ = 3032 (w), 2966 (m), 2919 (m), 2879 (w), 1900 (w), 1611 (m), 1492 (m), 1457 (m), 1367 (s), 1186 (m), 1099 (m), 1018 (m), 977 (w), 836 (s), 818 (s), 779 (m), 755 (m), 665 (m), 624 (m), 585 (m), 529 (m), 490 (m), 475 (m), 428 (w), 401 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 391 (M^+, 97), 390 (52), 389 (100), 388 (32), 378 (16), 377 (12), 376 (48), 375 (12), 374 (54), 361 (9), 360 (6), 180 (11), 179 (14), 173 (7), 144 (4), 138 (4), 120 (4), 105 (4), 77 (5); HR-MS (ESI): *m/z* = 390.05771, calcd. for $C_{21}H_{19}Cl_3N$ ($[M+H]^+$): 390.05776.

3,4,5-Trichloro-2,6-bis(4-*tert*-butylphenyl)pyridine (4d): Colorless solid; yield: 42%; mp 134–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 18H, CH_3 *t*-Bu), 7.46 (d, ^3J = 8.6 Hz, 4H, CH), 7.68 (d, ^3J = 8.6 Hz, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2 (CH_3 *t*-Bu), 34.8 (C *t*-Bu), 125.0 (CH), 127.7 (C), 129.2 (CH), 135.0 (C), 124.8 (C), 152.3 (C), 155.1 (C); IR (ATR): $\tilde{\nu}$ = 2961 (s), 2866 (m), 1610 (m), 1527 (m), 1493 (m), 1369 (s), 1267 (m), 1161 (m), 1087 (m), 1017 (m), 967 (w), 881 (w), 839 (s), 813 (s), 771 (m), 736 (w), 719 (s), 633 (m), 561 (m), 540 (s), 467 (m), 397 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 447 (M^+, 30), 446 (10), 445 (30), 434 (33), 433 (26), 432 (97), 431 (26), 430 (100), 416 (6), 414 (6), 376 (4), 374 (5), 208 (10), 207 (9), 194 (5), 179 (16), 57 (17), 41 (12); HR-MS (ESI): *m/z* = 446.12064, calcd. for $C_{25}H_{27}Cl_3N$ ($[M+H]^+$): 446.12036.

3,4,5-Trichloro-2,6-(4-methoxyphenyl)pyridine (4e): Colorless solid; yield: 59%; mp 195–196 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 6H, OCH_3), 6.95 (d, 4H, ^3J = 8.9 Hz, CH), 7.47 (d, 4H, ^3J = 8.9 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 114.1, 127.6 (CH), 129.5, 133.3, 144.6, 146.3, 158.6 (C); IR (ATR): $\tilde{\nu}$ = 2957 (w), 2914 (w), 2839 (w), 1604 (m), 1498 (m), 1326 (w), 1274 (m), 1245 (m), 1039 (m), 820 (s), 681 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 393 (M^+, 100), 358 (12), 343 (12), 315 (4), 308 (5), 272 (4); HR-MS (EI, 70 eV): *m/z* = 393.007989, calcd. for $C_{19}H_{14}Cl_3NO_2$: 393.00846.

3,4,5-Trichloro-2,6-(3-methoxyphenyl)pyridine (4f): Colorless solid; yield: 71%; mp 122–123 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 6H, OCH_3), 6.90 (ddd, 2H, ^3J = 8.1 Hz, ^4J = 2.6 Hz, ^4J = 1.1 Hz, CH), 7.16 (dd, 2H, ^4J = 2.4 Hz, ^4J = 1.7 Hz, CH), 7.21 (ddd, 2H, ^3J = 7.7 Hz, ^4J = 1.5 Hz, ^4J = 1.3 Hz, CH), 7.29 (dd, 2H, ^3J = 7.9 Hz, ^3J = 7.9 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3 (CH_3), 114.9, 115.0, 121.8 (CH), 128.3 (C), 129.1 (CH), 138.9, 143.0, 155.0, 159.2 (C); IR (ATR): $\tilde{\nu}$ = 3060 (w), 3004 (w), 2936 (w), 2834 (w), 1596 (m), 1529 (w), 1486 (m), 1374 (m), 1310 (m), 1232 (s), 1031 (s), 774 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%) = 393 (M^+, 67), 365 (28), 334 (3), 321 (3), 284 (4), 272 (4); HR-MS (ESI): *m/z* = 394.01641, calcd. for $C_{19}H_{15}Cl_3NO_2$ ($[M+H]^+$): 394.01629.

3,4,5-Trichloro-2,6-di-m-tolylpyridine (4g): Colorless solid; yield: 38%); mp 82–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 6H, CH_3), 7.22–7.25 (m, 2H, CH), 7.31–7.36 (m, 2H, CH), 7.49–7.51 (m, 4H, CH); ^{13}C NMR (100 MHz, CDCl3): δ = 21.4 (CH_3), 126.5 (CH), 127.9 (CH), 128.1 (C), 129.6 (CH), 129.6 (C), 130.0 (CH), 137.7 (C), 137.9 (C), 155.8 (C); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2918 (w), 1606 (w), 1586 (m), 1512 (m), 1485 (m), 1366 (s), 1271 (w), 1143 (m), 1100 (m), 969 (m), 877 (w), 773 (m), 755 (m), 701 (s), 642 (w), 610 (m), 563 (m), 523 (m), 511 (w), 492 (m), 429 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 363 (M^+, 76), 362 (22), 361 (77), 330 (12), 329 (15), 328 (67), 327 (23), 326 (100), 291 (10), 290 (8), 240 (11), 180 (11), 139 (16), 138 (8), 91 (7), 89 (5); HR-MS (ESI): *m/z* = 362.02678, calcd. for $C_{19}H_{15}Cl_3N$ ($[M+H]^+$): 362.02646.

3,4,5-Trichloro-2,6-bis(2-methoxyphenyl)pyridine (4h): Colorless solid; yield: 29%; mp 191–193 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 6H, MeO), 6.94–7.04 (m, 4H, CH), 7.30–7.42 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.5 (MeO), 111.0 (CH), 120.6 (CH), 127.5 (CH), 130.3 (C), 130.4 (C), 130.5 (CH), 141.2 (C), 154.1 (C), 156.7 (C); IR (ATR): $\tilde{\nu}$ = 2930 (w), 2831 (w), 1600 (m), 1582 (m), 1491 (m), 1460 (m), 1161 (m), 1113 (m), 1092 (m), 1020 (m), 821 (m), 793 (s), 758 (s), 705 (m), 655 (m), 552 (m), 512 (m), 488 (w), 466 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 395 (M^+, 5), 394 (3), 362 (12), 361 (14), 360 (65), 359 (22), 358 (100), 328 (5), 308 (19), 243 (4), 227 (4), 214 (3), 154 (3), 147 (4), 139 (4), 125 (3); HR-MS (ESI): *m/z* = 394.0167, calcd. for $C_{19}H_{15}Cl_3NO_2$ ($[M+H]^+$): 394.0163; anal. calcd. for $C_{19}H_{14}Cl_3NO_2$ (394.67): C 57.82, H 3.58, N 3.55; found: C 57.85, H 3.700, N, 3.789.

Synthesis of Pentaarylpyridines 5a–g Starting from 4

An oven-dried and argon-flushed pressure tube was charged with the appropriate 3,4,5-trichloro-2,6-diarylpyridines **4** (1.0 equiv.), $PdCl_2(CH_3CN)_2$ (5.0 mol%), SPhos (10.0 mol%), boronic acid (6.0 equiv.) and K_3PO_4 (6.0 equiv.) followed by anhydrous toluene (3.0 mL); The tube was sealed with a Teflon valve and the reaction mixture was stirred at 100 °C for 20 h. The cooled reaction mixture was diluted with water and extracted with DCM. The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated under vacuum. The residue was purified by column chromatography.

2,6-Diphenyl-3,4,5-tris(4-methoxyphenyl)pyridine (5a): Colorless solid; yield: 83%; mp 219–221 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3H, MeO), 3.67 (s, 6H, MeO), 6.47–6.56 (m, 6H, CH), 6.64–6.67 (m, 2H, CH), 6.75–6.78 (m, 4H, CH), 7.15–7.18 (m, 6H, CH), 7.36–7.39 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.9 (MeO), 55.0 (MeO), 112.6 (CH), 112.9 (CH), 127.1 (CH), 127.5 (CH), 130.2 (CH), 130.6 (C), 130.8 (C), 131.6 (CH), 132.3 (CH), 133.6 (C), 141.1 (C), 150.3 (C), 156.4 (C), 157.6 (C), 157.7 (C); IR (ATR): $\tilde{\nu}$ = 3000 (w), 2933 (w), 2836 (w), 1883 (w), 1606 (m), 1509 (m), 1491 (m), 1461 (m), 1443 (w), 1388 (m), 1285 (m), 1242 (s), 1175 (m), 1075 (w), 1030 (m), 917 (w), 831 (m), 796 (m), 777 (w), 750 (m), 695 (s), 658 (m), 633 (m), 559 (m), 538 (m), 410 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 550 (M^+, 29), 549 (97), 548 (100), 534 (7), 490 (6), 431 (4), 259 (8), 250 (5), 239 (13), 238 (15), 235 (8), 234 (7), 229 (11), 227 (8), 222 (18), 221 (14), 214 (21), 213 (16), 208 (21), 182 (13), 181 (4), 177 (5), 157 (8); HR-MS (ESI): *m/z* = 550.23808, calcd. for $C_{38}H_{32}NO_3$ ($[M+H]^+$): 550.23767; anal. calcd. for $C_{38}H_{31}NO_3$ (549.66): C 83.03, H 5.68, N 2.55; found: C 83.27, H 5.526, N 2.115.

2,6-Diphenyl-3,4,5-tris(4-(trifluoromethyl)phenyl)pyridine (5b): Colorless solid; yield: 79%; mp 305–307 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.86–6.89 (m, 2H, CH), 6.98–7.01 (m, 4H, CH), 7.16–7.35 (m, 16H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.6 (q, $^1J_{C,F}$ = 271.6 Hz, CF_3), 123.7 (q, $^1J_{C,F}$ = 271.6 Hz, CF_3), 124.5 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 124.7 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 127.8 (CH), 128.0 (CH), 129.0 (q, $^2J_{C,F}$ = 32.6 Hz, C), 129.3 (q, $^2J_{C,F}$ = 32.6 Hz, C), 130.1 (CH), 130.5 (CH), 131.4 (CH), 132.1 (C), 139.7 (C), 141.1 (C), 141.6 (C), 148.5 (C), 157.2 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −62.3 (CF_3), −62.4 (CF_3); IR (ATR): $\tilde{\nu}$ = 1617 (m), 1538 (w), 1410 (w), 1392 (w), 1320 (s), 1162 (m), 1108 (s), 1067 (m), 1017 (m), 850 (m), 778 (m), 695 (m), 677 (m), 662 (w), 642 (m), 635 (m), 608 (w), 499 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 664 (M^+, 15), 663 (58), 662 (100), 644 (5), 276 (2), 255 (2), 245 (2), 242 (2), 227 (3), 226 (3); HR-MS (ESI): *m/z* = 664.16814, calcd. for $C_{38}H_{23}F_9N$ ($[M+H]^+$): 664.16813.

3,4,5-Tris(*para*-tolyl)-2,6-phenylpyridine (5c): Colorless solid; yield: 67%; mp 184–185 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (t, 3H, ^3J = 7.5 Hz, CH_3), 1.12 (t, 6H, ^3J = 7.5 Hz, CH_3), 2.41–2.54 (m, 6H, CH_2), 6.67 (d, 2H, ^3J = 8.1 Hz, CH) 6.75–6.85 (m, 10H, CH), 7.16–7.21 (m, 6H, CH), 7.42–7.45 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4, 15.5 (CH_3), 28.4 (CH_2), 126.3, 126.7, 127.1, 127.4, 130.2, 130.4, 131.2 (CH), 133.8, 135.5, 135.7, 141.1, 141.8, 142.0, 150.6, 156.1 (C); IR (ATP): $\tilde{\nu}$ = 2958 (m), 2922 (m), 2852 (m), 1491 (w), 1446 (w), 1389 (m), 1183 (w), 1115 (w), 1059 (w), 1021 (w), 914 (w), 825 (m), 775 (m), 694 (s), 659 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 543 (M^+, 69), 542 (100), 526 (6), 514 (6), 484 (2); HR-MS (ESI): *m/z* = 544.3002, calcd. for $C_{41}H_{38}N$ ($[M+H]^+$): 544.29988.

3,4,5-Tris(4-methoxyphenyl)-2,6-di(*para*-tolyl)pyridine (5d): Slightly yellow solid; yield: 85%; mp 203 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 6H, CH_3), 3.66 (s, 3H, OCH_3), 3.70 (s, 6H, OCH_3), 6.50 (d, 2H, ^3J = 8.9 Hz, CH), 6.57 (d, 4H, ^3J = 8.9 Hz, CH), 6.66 (d, 2H, ^3J = 8.9 Hz, CH), 6.80 (d, 4H, ^3J = 8.9 Hz, CH), 7.00 (d, 4H, ^3J = 8.1 Hz, CH), 7.30 (d, 4H, ^3J = 8.1 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH_3), 54.9, 55.0 (OCH_3), 112.5, 112.9, 128.2, 130.1 (CH), 130.8, 131.1 (C), 131.6, 132.3 (CH), 133.1, 136.8, 150.2, 156.1, 157.5, 157.7 (C); IR (ATR): $\tilde{\nu}$ = 2917 (w), 2835 (w), 1608 (m), 1514 (m), 1386 (m), 1287 (m), 1244 (s), 1174 (s), 1032 (m), 826 (m), 809 (m), 756 (m), 728 (m), 558 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 577 (M^+, 85), 576 (100), 532

(6), 489 (2), 337 (2), 289 (4); HR-MS (ESI): m/z = 578.26951, calcd. for $C_{40}H_{36}NO_3$ ($[M+H]^+$) 578.26897.

2,6-Bis(4-ethylphenyl)-3,4,5-triphenylpyridine (5e): Colorless solid; yield: 92%; mp 223–225 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{H,H}$ = 7.7 Hz, 6H, CH_3), 2.58 (q, $^3J_{H,H}$ = 7.8 Hz, 4H, CH_2), 6.76–6.79 (m, 2H, CH), 6.89–6.95 (m, 7H, CH), 6.99–7.02 (m, 10H, CH), 7.33–7.36 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3 (CH_3), 28.5 (CH_2), 126.0 (CH), 126.1 (CH), 126.9 (CH), 127.0 (CH), 127.3 (CH), 130.2 (CH), 130.4 (CH), 131.3 (CH), 133.2 (C), 138.2 (C), 138.3 (C), 138.6 (C), 143.2 (C), 150.2 (C), 156.1 (C); IR (ATR): $\tilde{\nu}$ = 3032 (w), 2958 (m), 2926 (w), 2866 (m), 1889 (w), 1531 (m), 1509 (w), 1413 (w), 1391 (m), 1279 (w), 1186 (w), 1022 (m), 1007 (m), 845 (m), 820 (m), 739 (s), 711 (s), 697 (s), 658 (m), 629 (m), 594 (m), 559 (m), 526 (m), 488 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 516 (M^+, 20), 515 (65), 514 (100), 486 (6), 393 (2), 227 (1), 226 (1), 220 (5), 214 (2), 213 (2), 189 (2); HR-MS (ESI): m/z = 516.2686, calcd. for $C_{39}H_{34}N$ ($[M+H]^+$): 516.26858; anal. calcd. for $C_{39}H_{33}N$ (515.69): C 90.83, H 6.45, N 2.72; found: C 90.93, H 6.141, N 2.389.

2,6-Bis(4-ethylphenyl)-3,4,5-tris[4-(trifluoromethyl)phenyl]pyridine (5f): Colorless solid; yield: 96%; mp 207–208 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{H,H}$ = 7.7 Hz, 6H, CH_3), 2.59 (q, $^3J_{H,H}$ = 7.6 Hz, 4H, CH_2), 6.85–6.88 (m, 2H, CH), 7.00–7.04 (m, 8H, CH), 7.22–7.31 (m, 10H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2 (CH_3), 28.5 (CH_2), 123.7 (q, $^1J_{C,F}$ = 274.1 Hz, CF_3), 123.8 (q, $^1J_{C,F}$ = 272.0 Hz, CF_3), 124.4 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 124.7 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 128.9 (q, $^2J_{C,F}$ = 33.3 Hz, C), 129.1 (q, $^2J_{C,F}$ = 32.9 Hz, C), 130.1 (CH), 130.6 (CH), 131.5 (CH), 131.6 (C), 137.2 (C), 141.3 (C), 141.9 (C), 144.2 (C), 148.5 (C), 157.1 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −62.2 (CF_3), −62.4 (CF_3); IR (ATR): $\tilde{\nu}$ = 2967 (w), 1616 (m), 1534 (w), 1407 (w), 1321 (s), 1164 (m), 1108 (s), 1065 (s), 1017 (m), 857 (m), 827 (m), 794 (w), 768 (w), 755 (w), 704 (w), 635 (w), 610 (m), 593 (m), 550 (w), 475 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 720 (M^+, 15), 719 (57), 718 (100), 703 (5), 277 (3), 276 (13), 275 (16), 207 (33), 197 (4), 183 (7), 165 (6), 133 (4), 109 (3), 108 (4), 107 (3), 97 (4), 96 (4), 91 (7), 78 (4), 73 (6), 69 (7), 57 (7), 45 (7), 44 (7), 43 (8), 41 (5); HR-MS (EI, 70 eV): m/z = 718.21443, calcd. for $C_{42}H_{29}NF_9$: 718.21508; anal. calcd. for $C_{42}H_{30}F_9N$ (719.68): C 70.09, H 4.20, N 1.95; found: C 70.52, H 3.940, N 1.594.

2,6-Bis(4-ethylphenyl)-3,4,5-tris(3-methoxyphenyl)pyridine (5g): Colorless oil; yield: 92%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{H,H}$ = 7.7 Hz, 6H, CH_3), 2.61 (q, $^3J_{H,H}$ = 7.6 Hz, 4H, CH_2), 3.45 (brs, 3H, MeO), 3.47 (s, 6H, MeO), 6.35–6.59 (m, 9H, CH), 6.83–7.00 (m, 3H, CH), 7.00–7.03 (m, 4H, CH), 7.34–7.37 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3 (CH_3), 28.5 (CH_2), 55.0 (MeO), 55.0 (MeO), 112.8 (CH), 115.5 (CH), 116.4 (CH), 123.0 (CH), 124.0 (CH), 127.0 (CH), 127.9 (CH), 128.3 (CH), 130.0 (CH), 130.0 (CH), 132.8 (C), 138.1 (C), 139.5 (C), 139.8 (C), 143.3 (C), 149.6 (C), 156.2 (C), 158.4 (C), 158.7 (C); IR (ATR): $\tilde{\nu}$ = 2961 (w), 2931 (m), 2871 (w), 2832 (w), 1906 (w), 1598 (s), 1578 (s), 1531 (m), 1489 (m), 1451 (m), 1387 (m), 1315 (m), 1284 (m), 1234 (m), 1215 (s), 1180 (m), 1122 (w), 1048 (s), 1022 (m), 995 (m), 838 (s), 816 (m), 781 (m), 727 (s), 696 (m), 633 (w), 563 (w), 471 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 606 (M^+, 23), 605 (75), 604 (100), 603 (5), 590 (5), 588 (6), 287 (2), 226 (1), 97 (1), 85 (2), 73 (4), 71 (2), 60 (5), 57 (2), 44 (9), 43 (5), 41 (2); HR-MS (ESI): m/z = 606.30033, calcd. for $C_{42}H_{40}NO_3$ ($[M+H]^+$): 606.30027.

Synthesis of Tetraarylpyridines from 1 (Regioisomeric Mixtures 6/7)

An oven-dried and argon-flushed pressure tube was charged with pentachloropyridine **1** (1 equiv.), $PdCl_2(CH_3CN)_2$ (5.0 mol%), SPhos (10.0 mol%), boronic acid (4.5 equiv.) and K_3PO_4 (6.5 equiv.) followed by anhydrous toluene (7.0 mL); The tube was sealed with a Teflon valve and the reaction mixture was stirred at 100 °C for 20 h. The cooled reaction mixture was diluted with water and extracted with DCM. The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated under vacuum. The residue was purified by column chromatography affording isomeric mixtures of 5-chloro-2,3,4,6-tetraaryl-substituted pyridines **6** and 4-chloro-2,3,5,6-tetraaryl-substituted pyridines **7** which could not be separated preparatively by column chromatography. The products were confirmed by GC-MS und HR-MS data. A detailed analysis of the NMR spectra (^{1}H, ^{13}C NMR) could not be performed due to several overlapping signals. The ratio of regioisomers was determined by inverse gated-decoupling ^{13}C NMR spectroscopy (^{13}C igd).

Synthesis of 3,5-Dichloro-2,4,6-triarylpyridines 9a–k

An oven-dried and argon-flushed pressure tube was charged with 2,3,5,6-tetrachloro-4-(4-(aryl)pyridine **8a** or **8b** (1.0 equiv.), $Pd(PPh_3)_4$ (5.0 mol%), the appropriate boronic acid (3.0 equiv.) and K_3PO_4 (3.0 equiv.) followed by anhydrous toluene (4.0 mL); The tube was sealed with a Teflon valve and the reaction mixture was stirred at 100 °C for 20 h. The cooled reaction mixture was diluted with water and extracted with DCM. The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated under vacuum. The residue was purified by column chromatography.

3,5-Dichloro-2,6-diphenyl-4-[4-(trifluoromethyl)phenyl]-pyridine (9a): Colorless solid; yield: 47%; mp 162–164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.50 (m, 8H, CH), 7.74–7.81 (m, 6H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 124.1 (q, $^1J_{C,F}$ = 272.6 Hz, CF_3), 125.7 (q, $^3J_{C,F}$ = 4.0 Hz, CH), 128.1 (CH), 128.2 (C), 129.1 (CH), 129.3 (CH), 129.5 (CH), 130.8 (q, $^2J_{C,F}$ = 32.4 Hz, C), 137.8 (C), 139.9 (C), 148.0 (C), 155.0 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −62.2 (CF_3); IR (ATR): $\tilde{\nu}$ = 3054 (w), 1935 (w), 1615 (w), 1541 (w), 1523 (w), 1493 (m), 1365 (m), 1323 (s), 1169 (m), 1158 (s), 1128 (s), 1083 (m), 1066 (m), 1037 (w), 1019 (m), 960 (w), 870 (w), 849 (m), 775 (w), 757 (m), 744 (w), 691 (s), 677 (m), 658 (m), 640 (m), 623 (w), 562 (m), 528 (m), 479 (w), 403 (w), 383 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 444 (M^+, 33), 443 (100), 426 (5), 410 (33), 409 (27), 408 (96), 406 (5), 372 (13), 332 (7), 270 (18), 227 (6), 204 (9), 200 (7), 152 (5), 151 (7), 51 (4); HR-MS (EI, 70 eV): m/z = 443.04483, calcd. for $C_{24}H_{14}Cl_2F_3N$: 443.04499, m/z = 445.04232, calcd. for $C_{24}H_{14}Cl^{37}ClF_3N$: 445.04204; anal. calcd. for $C_{24}H_{14}Cl_2F_3N$ (444.28): C 64.88, H 3.18, N 3.15; found: C 65.07, H 3.005, N 3.070.

3,5-Dichloro-2,6-di-*para*-tolyl-4-[4-(trifluoromethyl)phenyl]pyridine (9b): Colorless solid; yield: 41%; mp 124–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 6H, CH_3),

7.26 (d, ^3J=7.3 Hz, 4H, CH), 7.46 (d, $^3J_{H,H}$=8.0 Hz, 2H, CH), 7.67 (d, ^3J=8.0 Hz, 4H, CH), 7.78 (d, $^3J_{H,H}$=8.1 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.4 (CH_3), 124.1 (q, $^1J_{C,F}$=273.2 Hz, CF_3), 125.6 (q, $^3J_{C,F}$=3.8 Hz, CH), 126.8 (C), 127.8 (C), 128.7 (CH), 129.3 (CH), 129.5 (CH), 130.8 (q, $^2J_{C-F}$=32.7 Hz, C), 135.1 (C), 139.1 (C), 147.9 (C), 154.9 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−62.2 (CF_3); IR (ATR): $\tilde{\nu}$=3053 (w), 3034 (w), 2919 (m), 2858 (w), 1908 (w), 1613 (m), 1543 (w), 1507 (m), 1408 (m), 1367 (m), 1324 (s), 1186 (m), 1159 (m), 1120 (s), 1108 (s), 1083 (m), 1066 (s), 1019 (m), 908 (w), 876 (m), 851 (m), 821 (s), 776 (m), 752 (m), 674 (m), 663 (m), 618 (m), 525 (m), 490 (m), 377 (m); MS (EI, 70 eV): *m/z* (%)=472 (M^+, 30), 471 (100), 438 (20), 437 (15), 436 (49), 402 (4), 386 (4), 346 (2), 284 (6), 283 (7), 262 (3), 240 (4), 235 (9), 213 (5), 200 (3), 158 (3), 157 (6), 151 (4), 115 (5), 91 (6), 65 (4); HR-MS (ESI): *m/z*=472.08485, calcd. for $C_{26}H_{19}Cl_2F_3N$ ($[M+H]^+$): 472.08412; anal. calcd. for $C_{26}H_{18}Cl_2F_3N$ (472.33): C 66.11, H 3.84, N 2.97; found: C 66.06, H 3.955, N 3.149.

3,5-Dichloro-2,6-bis(3-methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]pyridine (9c): Colorless solid; yield: 52%; mp 165–166 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.84 (s, 6H, MeO), 6.98 (ddd, $^3J_{H,H}$=7.7 Hz, $^4J_{H,H}$=2.7 Hz, $^4J_{H,H}$=2.2 Hz, 2H, CH), 7.28–7.40 (m, 6H, CH), 7.47 (brd, $^3J_{H,H}$=7.6 Hz, 2H, CH), 7.79 (brd, $^3J_{H,H}$=7.7 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.4 (MeO), 114.8 (CH), 115.2 (CH), 122.0 (CH), 124.1 (q, $^1J_{C,F}$=272.2 Hz, CF_3), 125.7 (q, $^3J_{C,F}$=4.0 Hz, CH), 128.3 (C), 129.1 (CH), 129.3 (CH), 130.9 (q, $^2J_{C,F}$=33.1 Hz, C), 130.1 (C), 139.8 (C), 148.1 (C), 154.8 (C), 159.3 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−62.2 (CF_3); IR (ATR): $\tilde{\nu}$=3002 (w), 2928 (w), 2834 (m), 1596 (m), 1579 (m), 1489 (m), 1407 (w), 1358 (m), 1321 (s), 1287 (m), 1275 (m), 1253 (m), 1229 (s), 1161 (s), 1119 (s), 1109 (s), 995 (m), 933 (m), 846 (m), 776 (s), 754 (m), 705 (s), 691 (m), 658 (m), 562 (m), 509 (w), 446 (w), 382 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%)=504 (M^+, 84), 503 (80), 502 (100), 476 (12), 475 (21), 474 (22), 473 (27), 472 (7), 430 (4), 395 (4), 346 (5), 251 (12), 207 (6), 163 (5), 145 (7), 137 (3), 63 (3); HR-MS (EI, 70 eV): *m/z*=503.06484, calcd. for $C_{26}H_{18}Cl_2F_3NO_2$: 503.06612, *m/z*=505.06218, calcd. for $C_{26}H_{18}Cl^{37}ClF_3NO_2$: 505.06317.

3,5-Dichloro-2,6-bis[4-(trifluoromethyl)phenyl]-4-(4-methoxyphenyl)pyridine (9d): Colorless solid; yield: 71%; mp 164–166 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.90 (s, 3H, OCH_3), 7.07 (d, 2H, ^3J=8.9 Hz, CH), 7.31 (d, 2H, ^3J=8.9 Hz, CH), 7.43–7.51 (m, 6H, CH_{Ph}), 7.78–7.81 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.2 (OCH_3), 113.9, 128.6 (CH), 128.6 (C), 128.8 (CH), 129.1 (C), 129.6, 130.1 (CH), 138.3, 149.1, 154.8, 159.7 (C); IR (ATR): $\tilde{\nu}$=3026 (w), 2918 (w), 2836 (w), 1613 (w), 1514 (m), 1358 (m), 1250 (m), 1027 (m), 892 (m), 762 (m), 692 (s), 569 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%)=405 (M^+, 100), 390 (8), 370 (61), 355 (5), 327 (13), 291 (12); HR-MS (EI, 70 eV): *m/z*=405.06800, calcd. for $C_{24}H_{17}Cl_2NO$: 405.06817; anal. calcd. for $C_{24}H_{17}Cl_2NO$ (406.30): C 70.95, H 4.22, N 3.45; found: C 71.02, H 4.123, N 3.467.

3,5-Dichloro-2,4,6-(4-methoxyphenyl)pyridine (9e): Colorless solid; yield: 69%; mp 136–138 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.86 (s, 6H, OCH_3), 3.89 (s, 3H, OCH_3), 6.99 (d, 4H, ^3J=8.8 Hz, CH), 7.06 (d, 2H, ^3J=8.8 Hz, CH), 7.28 (d, 2H, ^3J=8.8 Hz, CH), 7.78 (d, 4H, ^3J=8.8 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.2, 55.3 (OCH_3), 113.3, 113.9 (CH), 128.3, 128.9 (C), 130.1 (CH), 130.8 (C), 131.7 (CH), 149.1, 154.2, 159.6, 160.1 (C); IR (ATR): $\tilde{\nu}$=2930 (w), 2835 (w), 1606 (m), 1502 (s), 1457 (m), 1364 (m), 1290 (m), 1247 (s), 1173 (s), 1028 (s), 826 (s), 783 (m), 551 (m), 535 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%)=465 (M^+, 100), 430 (10), 414 (6), 387 (3), 372 (2), 262 (3); HR-MS (EI, 70 eV): *m/z*=465.08910, calcd, for $C_{26}H_{21}Cl_2NO_3$: 465.08930; anal. calcd. for $C_{26}H_{21}Cl_2NO_3$ (466.36): C 66.96, H 4.54, N 3.00; found: C 67.02, H 4.503, N 3.107.

3,5-Dichloro-4-(4-methoxyphenyl)-2,6-bis(4-vinylphenyl)-pyridine (9f): Colorless solid; yield: 45%; mp 95–97 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.90 (s, 3H, OCH_3), 5.33 (dd, 2H, ^2J=0.9 Hz, ^3J=10.9 Hz, HC=CH_2), 5.84 (dd, 2H, ^2J=0.8 Hz, ^3J=17.6 Hz, HC=CH_2), 6.79 (dd, 2H, ^3J=17.6 Hz, ^3J=10.7 Hz, HC=CH_2), 7.07 (d, 2H, ^3J=8.8 Hz, CH), 7.30 (d, 2H, ^3J=8.8 Hz, CH), 7.52 (d, 4H, ^3J=8.3 Hz, CH), 7.80 (d, 4H ^3J=8.3 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.2, (OCH_3), 113.9 (CH_{vinyl}), 114.8 (CH_2), 125.8 (CH), 128.6, 128.9 (C), 129.9, 130.1, 136.4 (CH), 137.6, 138.1, 149.2, 154.3, 159.7 (C); IR (ATR): $\tilde{\nu}$=2954 (w), 2917 (w), 2834 (w), 1607 (m), 1500 (s), 1361 (s), 1246 (s), 1177 (m), 1039 (m), 987 (m), 907 (m), 830 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%)=447 (M^+, 100), 422 (28), 407 (4), 379 (7), 343 (4), 315 (3); HR-MS (ESI): *m/z*=458.10801, calcd. for $C_{28}H_{22}Cl_2NO$ ($[M+H]^+$): 458.1073; anal. calcd. for $C_{28}H_{21}Cl_2NO$ (458.38): C 73.37, H 4.62, N 3.06; found: C 72.99, H 4.807, N 2.935.

3,5-Dichloro-2,6-bis[4-(trifluoromethyl)phenyl]-4-(4-methoxyphenyl)pyridine (9g): Colorless solid; yield: 40%; mp 119–121 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.90 (s, 3H, OCH_3), 7.08 (d, 2H, ^3J=8.8 Hz, CH), 7.30 (d, 2H, ^3J=8.8 Hz, CH), 7.74 (d, 4H, ^3J=8.3 Hz, CH), 7.90 (d, 4H, ^3J=8.3 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.3 (OCH_3), 114.1 (CH), 124.0 (q, ^1J=272.3 Hz, CF_3), 125.1 (q, ^3J=3.7 Hz CH), 127.9, 129.9 (C), 130.0, 130.1 (CH), 131.0 (q, ^2J=32.9 Hz, C-CF_3), 141.4, 149.8, 153.7, 160.0 (C); IR (ATR): $\tilde{\nu}$=2918 (w), 1611 (m), 1506 (m), 1366 (m), 1322 (s), 1252 (m), 1163 (m), 1106 (s), 1065 (s), 1016 (s), 829 (m), 705 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%)=541 (M^+, 100), 526 (8), 522 (8), 506 (40), 463 (12), 428 (5); HR-MS (ESI): *m/z*=542.05092, calcd. for $C_{26}H_{16}Cl_2F_6NO$ ($[M+H]^+$): 542.05077.

3,5-Dichloro-2,6-bis(4-isopropylphenyl)-4-(4-methoxyphenyl)pyridine (9h): Colorless solid; yield: 69%; mp 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.31 (d, 12H, ^3J=6.9 Hz, CH_3), 2.99 (sept, 2H, ^3J=6.9 Hz, $CH_{i\text{-}Pr}$), 3.89 (s, 3H, OCH_3), 7.06–7.09 (m, 2H, CH), 7.29–7.35 (m, 6H, CH), 7.74–7.77 (m, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=23.8 (CH_3), 33.9 ($CH_{i\text{-}Pr}$), 55.1 (OCH_3), 113.8, 126.0 (CH), 128.6, 128.7 (C), 129.5, 130.1 (CH), 135.8, 148.9, 149.5, 154.6, 159.5 (C); IR (ATR): $\tilde{\nu}$=2957 (m), 2868 (w), 2835 (w), 1609 (m), 1500 (s), 1460 (m), 1361 (s), 1290 (m), 1246 (s), 1018 (m), 828 (s), 731 (m), 657 (m), 557 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%)=489 (M^+, 100), 474 (73), 458 (6), 432 (4), 230 (23), 215 (4), 158 (4); HR-MS (EI, 70 eV): *m/z*=489.16144, calcd. for $C_{30}H_{29}Cl_2NO$: 489.16207; anal. calcd. for $C_{30}H_{29}Cl_2NO$ (490.46): C 73.47, H 5.96, N 2.86; found: C 73.25, H 5.90, N 2.75.

3,5-Dichloro-2,6-bis(4-fluorophenyl)-4-(4-methoxyphenyl)pyridine (9i): Colorless solid; yield: 63%; mp 224–226 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.86 (s, 3H, OCH_3), 7.01–7.06 (m, 2H, CH), 7.08–7.16 (m, 4H, CH), 7.22–7.27

(m, 2H, CH), 7.71–7.78 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.2 (OCH_3), 113.9 (CH), 115.0 (d, $^2J_{C,F}$= 21.8 Hz, CH), 128.3, 129.1 (C), 130.0 (CH), 131.5 (d, $^3J_{C,F}$= 8.3 Hz, CH), 134.1 (d, $^4J_{C,F}$=3.2 Hz, C), 149.4, 153.7, 159. 7 (C), 163.1 (d, $^1J_{C,F}$=249.0 Hz, CF); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−111.7 (s, 2F, CF); IR (ATR): $\tilde{\nu}$=3004 (w), 2939 (w), 2838 (w), 1603 (m), 1504 (s), 1359 (m), 1292 (m), 1230 (s), 1156 (s), 834 (s), 529 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%)=441 (M^+, 100), 406 (34), 363 (10), 327 (8), 207 (14); HR-MS (EI, 70 eV): *m/z*=441.04912, calcd. for $C_{24}H_{15}Cl_2F_2NO$: 441.04933; anal. calcd. for $C_{24}H_{15}Cl_2F_2NO$ (442.28): C 65.17, H 3.42, N 3.17; found: C 65.20, H 3.56, N 3.19.

3,5-Dichloro-2,6-di(*meta*-tolyl)-4-(4-methoxyphenyl)pyridine (9j): Colorless solid; yield: 47%; mp 130–132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.40 (s, 6H, CH_3), 3.87 (s, 3H, OCH_3), 7.01–7.06 (m, 2H, CH), 7.20–7.36 (m, 6H, CH), 7.52–7.54 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 21.4 (CH_3), 55.2 (OCH_3), 113.8, 126.6, 127.8 (CH), 128.6, 129.0 (C), 129.6, 130.1 (CH), 137.7, 138.2, 148.9, 155.0, 159.6 (C); IR (ATR): $\tilde{\nu}$=3040 (w), 2921 (w), 2830 (w), 1605 (m), 1507 (s), 1356 (s), 1285 (m), 1243 (s), 1178 (m), 1022 (m), 790 (s), 774 (s), 698 (s), 586 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%)=433 (M^+, 100), 398 (66), 355 (8), 202 (10), 152 (9); HR-MS (EI, 70 eV): *m/z*=433.09915, calcd. for $C_{26}H_{21}Cl_2NO$: 433.09947; anal. calcd. for $C_{26}H_{21}Cl_2NO$ (434.36): C 71.89, H 4.87, N 3.22; found: C 71.81, H 5.13, N 3.22.

3,5-Dichloro-2,6-bis(4-isopropoxyphenyl)-4-(4-methoxyphenyl)pyridine (9k): Colorless solid; yield: 71%; mp 173–175 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.37 (d, 12H, ^3J= 6.0 Hz, CH_3), 3.87 (s, 3H, OCH_3), 4.61 (sept, 2H, ^3J= 6.0 Hz, $CH_{i\text{-}Pr}$), 6.94–6.99 (m, 4H, CH), 7.02–7.07 (m, 2H, CH), 7.25–7.30 (m, 2H, CH), 7.74–7.79 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.9 (CH_3), 55.1 (OCH_3), 69.7 ($CH_{i\text{-}Pr}$), 113.8, 114.9 (CH), 128.0, 128.9 (C), 130.0 (CH), 130.4 (C), 131.0 (CH), 149.0, 154.1, 158.4, 159.5 (C); IR (ATR): $\tilde{\nu}$=2974 (w), 2934 (w), 2831 (w), 1607 (m), 1500 (s), 1363 (m), 1291 (m), 1247 (s), 1104 (s), 1040 (m), 950 (m), 830 (s), 785 (m), 638 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%)=521 (M^+, 37), 437 (100), 402 (15), 219 (8), 43 (17); HR-MS (EI, 70 eV): *m/z*=521.15137, calcd. for $C_{30}H_{29}Cl_2NO_3$: 521.15190; anal. calcd. for $C_{30}H_{29}Cl_2NO_3$ (522.46): C 68.97, H 5.59, N 2.68; found: C 68.83, H 5.76, N 2.64.

Synthesis of Pentaarylpyridines 10a–h Starting from 9

An oven-dried and argon-flushed pressure tube was charged with 3,5-dichloro-2,4,6-triarylpyridine **9** (1.0 equiv.), $PdCl_2(CH_3CN)_2$ (5.0 mol%), SPhos (10.0 mol%), boronic acid (4.0 equiv.) and K_3PO_4 (4.0 equiv.) followed by anhydrous toluene (3.5 mL); The tube was sealed with a Teflon valve and the reaction mixture was stirred at 100 °C for 20 h. The cooled reaction mixture was diluted with water and extracted with DCM. The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated under vacuum. The residue was purified by column chromatography.

3,5-Bis(4-*tert*-butylphenyl)-4-(4-methoxyphenyl)-2,6-diphenyl)pyridine (10a): Colorless solid; yield: 85%; mp 231–232 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.22 (s, 18H, CH_3), 3.64 (s, 3H, OCH_3), 6.47 (d, 2H, ^3J=8.9 Hz, CH), 6.67 (d, 2H, ^3J=8.9 Hz, CH), 6.82 (d, 4H, ^3J=8.3 Hz, CH), 7.04 (d, 4H, ^3J=8.3 Hz, CH), 7.15–7.20 (m, 6H, CH), 7.40–7.44 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.2 (CH_3), 34.3 ($C_{t\text{-}Bu}$), 55.0 (OCH_3), 112.3, 124.2, 127.1, 127.3, 130.2 (CH), 130.6 (C), 130.9, 131.7 (CH), 133.9, 135.5, 141.1, 149.0, 150.0, 156.2, 157.6 (C); IR (ATR): $\tilde{\nu}$=2956 (m), 2903 (w), 2864 (w), 2832 (w), 1610 (m), 1510 (m), 1387 (m), 1248 (s), 1172 (m), 1107 (m), 1022 (w), 828 (m), 779 (m), 699 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%)=601 (M^+, 91), 600 (100), 586 (9), 544 (11), 530 (6), 488 (6); HR-MS (ESI): *m/z*=602.34224, calcd. for $C_{44}H_{44}NO$ ($[M+H]^+$): 602.34174; anal. calcd. for $C_{44}H_{43}NO$ (601.82): C 87.81, H 7.20, N 2.33; found: C 87.47, H 7.082, N 2.279.

4-(4-Methoxyphenyl)-2,6-diphenyl-3,5-di-*para*-tolylpyridine (10b): Colorless solid; yield: 84%; mp 238–239 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.17 (s, 6H, CH_3), 3.63 (s, 3H, OCH_3), 6.47 (d, 2H, ^3J=8.9 Hz, CH), 6.66 (d, 2H, ^3J= 8.9 Hz, CH), 6.74–6.81 (m, 8H, CH), 7.15–7.17 (m, 6H, CH), 7.37–7.40 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.1 (CH_3), 54.0 (OCH_3), 112.4, 127.1, 127.4, 128.1, 130.2 (CH), 130.6 (C), 131.1, 131.5 (CH), 133.9, 135.5, 135.5, 141.1, 150.0, 156.3, 157.6 (C); IR (ATR): $\tilde{\nu}$=2919 (m), 2850 (w), 1606 (w), 1508 (m), 1389 (m), 1288 (m), 1243 (m), 1172 (m), 1028 (m), 915 (w), 816 (m), 776 (m), 695 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%)=517 (M^+, 73), 516 (100), 472 (7), 408 (1), 259 (1), 220 (7); HR-MS (ESI): *m/z*=518.24876, calcd for $C_{38}H_{32}NO$ 518.24784.

3,5-Bis[4-(trifluoromethyl)phenyl]-2,4,6-tris(4-methoxyphenyl)pyridine (10c): Colorless solid; yield: 79%; mp 203 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.66 (s, 3H, OCH_3), 3.77 (s, 6H, OCH_3), 6.50 (d, 2H, ^3J=8.9 Hz, CH), 6.60 (d, 2H, ^3J=8.9 Hz, CH), 6.73 (d, 4H, ^3J=8.9 Hz, CH), 7.03 (d, 4H, ^3J=8.9 Hz, CH), 7.28–7.35 (m, 8H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.0, 55.1 (OCH_3), 112.9, 113.1 (CH), 124.1 (d, ^1J=272 Hz, CF_3), 124.5 (d, ^3J=4.2 Hz, CH), 128.3 (d, ^2J=32.2 Hz, *C*-CF_3), 129.3 (C), 131.3, 131.5, 131.6 (CH), 131.9, 132.6, 142.7, 149.8, 156.3, 158.1, 159.2 (C); IR (ATR): $\tilde{\nu}$=1606 (w), 1503 (w), 1321 (s), 1248 (m), 1160 (m), 1106 (s), 1065 (s), 1016 (m), 833 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%)=685(M^+, 95), 684 (100), 666 (4), 640 (8), 597 (2), 343 (3), 276 (2); HR-MS (ESI): *m/z*=686.21244, calcd for $C_{40}H_{30}F_6NO_3$ ($[M+H]^+$): 686.21244.

2,4,6-Tris(4-methoxyphenyl)-3,5-diphenylpyridine (10d): Colorless solid; yield: 91%; mp 92–94 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.62 (s, 3H, OCH_3), 3.76 (s, 6H, OCH_3), 6.47 (d, 2H, ^3J=8.9 Hz, CH), 6.66 (d, 2H, ^3J= 8.9 Hz, CH), 6.72 (d, 4H, ^3J=8.9 Hz, CH), 6.91–6.94 (m, 4H, CH), 7.03–7.05 (m, 6H, CH), 7.37 (d, 4H, ^3J=8.9 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=54.9, 55.1 (OCH_3), 112.4, 112.9, 126.0, 127.5 (CH), 130.5 (C), 131.3, 131.5 (CH), 133.1, 133.4, 138.9, 150.0, 155.6, 157.6, 158.8 (C); IR (ATR): $\tilde{\nu}$=2932 (w), 2834 (w), 1604 (m), 1503 (m), 1389 (m), 1290 (m), 1241 (s), 1173 (s), 1027 (m), 907 (w), 832 (m), 764 (m), 698 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%)=549 (M^+, 77), 548 (100), 504 (7), 461 (2), 354 (2), 275 (11), 251 (10), 239 (10); HR-MS (ESI): m/z=550.23797, calcd for $C_{38}H_{32}NO_3$ ($[M+H]^+$): 550.23767.

2,6-Bis(4-fluorophenyl)-4-(4-methoxyphenyl)-3,5-di-*para*-tolyl-pyridine (10e): Colorless solid; yield: 99%; mp 234–236 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.18 (s, 6H, CH_3), 3.63 (s, 3H, OCH_3), 6.44–6.48 (m, 2H, CH), 6.61–6.66 (m,

2H, CH), 6.70–6.74 (m, 4H, CH), 6.80–6.88 (m, 8H, CH), 7.30–7.37 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (CH_3), 54.9 (OCH_3), 112.4 (CH), 114.4 (d, $^2J_{C,F}$ = 21.2 Hz, CH), 128.3 (CH), 130.3 (C), 131.0, 131.4 (CH), 131.8 (d, $^3J_{C,F}$ = 7.8 Hz, CH), 134.0, 135.1, 135.8 (C), 136.9 (d, $^4J_{C,F}$ = 3.2 Hz, C), 150.4, 155.2, 157.6 (C), 162.1 (d, $^1J_{C,F}$ = 246.6 Hz, CF); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −114.4 (s, 2F, CF); IR (ATR): $\tilde{\nu}$ = 2923 (w), 1596 (m), 1498 (s), 1389 (m), 1287 (m), 1220 (s), 1155 (s), 1038 (m), 834 (m), 806 (s), 524 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%) = 552 (M^+, 100), 167 (20), 149 (51), 107 (13), 97 (14), 84 (15), 71 (23), 66 (11), 57 (32), 43 (18); HR-MS (EI, 70 eV): *m/z* = 552.21339, calcd. for $C_{38}H_{28}F_2NO$: 552.21335; anal. calcd. for $C_{38}H_{29}F_2NO$ (553.64): C 82.44, H 5.28, N 2.53; found: C 82.54, H 5.34, N 2.43.

3,5-Bis(4-methoxyphenyl)-2,6-diphenyl-4-[4-(trifluoromethyl)phenyl]pyridine (10f): Colorless solid; yield: 82%; mp 279–281 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 6H, MeO), 6.53–6.58 (m, 4H, CH), 6.72–6.78 (m, 4H, CH), 6.90 (brd, $^3J_{H,H}$ = 8.2 Hz, 2H, CH), 7.18–7.24 (m, 8H, CH), 7.38–7.44 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.9 (MeO), 113.1 (CH), 124.0 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 124.1 (q, $^1J_{C,F}$ = 272.8 Hz, CF_3), 127.3 (CH), 127.6 (CH), 128.2 (q, $^2J_{C,F}$ = 32.4 Hz, C), 130.0 (C), 130.1 (CH), 130.8 (CH), 132.2 (CH), 133.0 (C), 140.6 (C), 142.5 (C), 149.1 (C), 156.6 (C), 158.0 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −62.1 (CF_3); IR (ATR): $\tilde{\nu}$ = 3040 (w), 3001 (w), 2955 (w), 2835 (w), 1609 (m), 1576 (w), 1533 (m), 1510 (s), 1388 (m), 1319 (s), 1289 (m), 1245 (s), 1175 (m), 1158 (s), 1106 (s), 1065 (m), 1034 (m), 1019 (m), 919 (w), 850 (m), 825 (m), 756 (m), 697 (s), 555 (m), 537 (m), 440 (m), 386 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%)) = 588 (M^+, 23), 587 (80), 586 (100), 542 (11), 498 (3), 294 (2), 242 (4), 236 (3), 227 (3), 221 (6), 214 (7), 207 (8), 201 (5), 165 (5), 163 (2); HR-MS (EI, 70 eV): *m/z* = 586.19874, calcd. for $C_{38}H_{27}F_3NO_2$: 586.19884; anal. calcd. for $C_{38}H_{28}F_3NO_2$ (587.21): C 77.67, H 4.80, N 2.38; found: C 77.49, H 4.658, N 2.089.

3,5-Di(biphenyl-4-yl)-2,6-diphenyl-4-[4-(trifluoromethyl)-phenyl]pyridine (10g): Colorless solid; yield: 73%; mp 281–283 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.97–7.03 (m, 6H, CH), 7.23–7.56 (m, 26H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 124.0 (q, $^1J_{C,F}$ = 273.4 Hz, CF_3), 124.1 (q, $^3J_{C,F}$ = 4.0 Hz, CH), 126.1 (CH), 126.7 (CH), 127.3 (CH), 127.5 (CH), 127.6 (CH), 128.6 (CH), 130.1 (q, $^2J_{C,F}$ = 32.4 Hz, C), 130.2 (CH), 130.8 (CH), 131.6 (CH), 133.0 (C), 136.8 (C), 139.0 (C), 140.2 (C), 140.4 (C), 142.1 (C), 148.8 (C), 156.6 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −62.2 (CF_3); IR (ATR): $\tilde{\nu}$ = 3081 (w), 3030 (w), 1615 (w), 1599 (w), 1487 (m), 1389 (m), 1318 (s), 1155 (m), 1123 (m), 1066 (m), 1019 (m), 1065 (m), 847 (m), 759 (s), 734 (m), 694 (s), 660 (m), 638 (w), 618 (m), 573 (w), 538 (w), 522 (w), 485 (w), 399 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 680 (M^+, 26), 679 (82), 678 (100), 340 (2), 281 (2), 207 (2), 169 (2), 147 (12), 115 (2), 111 (2), 101 (2), 97 (3), 95 (2), 83 (4), 82 (4), 81 (2), 78 (6), 75 (23), 73 (9), 69 (12), 66 (16), 63 (7), 60 (11), 57 (8), 56 (3), 55 (7), 44 (35), 43 (15), 40 (12), 39 (8); HR-MS (ESI): *m/z* = 680.25619, calcd. for $C_{48}H_{33}NF_3$ ($[M+H]^+$): 680.25596.

2,6-Diphenyl-3,4,5-tris[4-(trifluoromethyl)phenyl]pyridine (10h): Colorless solid; yield: 70 mg (74%); mp 303–305 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82 (brd, $^3J_{H,H}$ = 8.3 Hz, 2H, CH), 6.94 (brd, $^3J_{H,H}$ = 8.3 Hz, 4H, CH), 7.12–7.29 (m, 16H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.7 (q, $^1J_{C,F}$ = 271.9 Hz, CF_3), 123.8 (q, $^1J_{C,F}$ = 273.1 Hz, CF_3), 124.5 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 124.7 (q, $^3J_{C,F}$ = 4.0 Hz, CH), 127.9 (CH), 128.1 (CH), 129.0 (q, $^2J_{C,F}$ = 32.4 Hz, C), 129.2 (q, $^2J_{C,F}$ = 32.4 Hz, C), 130.1 (CH), 130.5 (CH), 131.4 (CH), 132.1 (C), 139.6 (C), 141.1 (C), 141.6 (C), 148.6 (C), 157.2 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −62.3 (CF_3), −62.4 (CF_3); IR (ATR): $\tilde{\nu}$ = 3063 (w), 3035 (w), 1615 (m), 1576 (w), 1537 (m), 1410 (m), 1393 (w), 1320 (s), 1161 (m), 1107 (m), 1066 (S), 1017 (m), 916 (w), 850 (m), 831 (m), 779 (m), 758 (w), 695 (m), 662 (w), 608 (m), 465 (m), 394 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 664 (M^+, 15), 663 (57), 662 (100), 645 (2), 644 (5), 420 (2), 350 (1), 322 (5), 287 (2), 276 (1), 254 (3), 242 (2), 226 (3), 220 (4); HR-MS (EI, 70 eV): *m/z* = 662.15249, calcd. for $C_{38}H_{21}F_9N$: 662.15248; anal. calcd. for $C_{38}H_{22}F_9N$ (663.57): C 68.78, H 3.34, N 2.11; found: C 68.71, H 3.058, N 2.106.

Synthesis of 3-Chloro-2,4,5,6-tetraarylpyridines 11a–h Starting from 8a and 8b

An oven-dried and argon-flushed pressure tube was charged with 2,3,5,6-tetrachloro-4-arylpyridine **8a** or **8b** (1.0 equiv.), $PdCl_2(CH_3CN)_2$ (5.0 mol%), SPhos (10.0 mol%), boronic acid (3.0 equiv.) and K_3PO_4 (3.0 equiv.), followed by anhydrous toluene (3.5 mL). The tube was sealed with a Teflon valve and the reaction mixture was stirred at 100 °C for 20 h. Afterwards, the cooled reaction mixture was diluted with water and extracted with DCM. The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated under vacuum. The residue was purified by column chromatography.

3-Chloro-2,5,6-triphenyl-4-[4-(trifluoromethyl)phenyl]pyridine (11a): Colorless solid; yield: 43%; mp 164–166 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.83–6.86 (m, 2H, CH), 6.98–7.05 (m, 3H, CH), 7.13–7.34 (m, 7H, CH), 7.44–7.52 (m, 5H, CH), 7.84–7.87 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 124.1 (q, $^1J_{C,F}$ = 272.6 Hz, CF_3), 124.7 (q, $^3J_{C,F}$ = 4.0 Hz, CH), 127.1 (CH), 127.7 (CH), 127.8 (CH), 127.8 (CH), 128.0 (CH), 128.8 (CH), 129.6 (q, $^2J_{C,F}$ = 32.7 Hz, C), 129.7 (CH), 129.9 (CH), 130.1 (CH), 130.8 (CH), 135.0 (C), 136.9 (C), 138.8 (C), 139.6 (C), 140.9 (C), 148.5 (C), 155.8 (C), 155.8 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −62.1 (CF_3); IR (ATR): $\tilde{\nu}$ = 3056 (w), 3031 (w), 2927 (w), 1617 (w), 1543 (m), 1520 (w), 1491 (w), 1441 (w), 1395 (m), 1352 (w), 1319 (s), 1165 (m), 1128 (s), 1107 (m), 1067 (m), 1038 (w), 1020 (m), 957 (w), 926 (w), 847 (s), 786 (m), 758 (m), 750 (m), 697 (s), 664 (m), 651 (m), 624 (w), 600 (m), 561 (m), 533 (m), 461 (w), 433 (w), 403 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 486 (M^+, 47), 485 (61), 484 (100), 448 (10), 378 (4), 276 (8), 201 (5), 189 (6), 182 (6), 175 (2), 138 (2), 77 (3); HR-MS (ESI): *m/z* = 486.12291, calcd. for $C_{30}H_{20}ClF_3N$ ($[M+H]^+$): 486.12309; anal. calcd. for $C_{30}H_{19}ClF_3N$ (485.93): C 74.15, H 3.94, N 2.88; found: C 74.16, H 4.150, N 2.717.

3-Chloro-2,5,6-tri-*para*-tolyl-4-[4-(trifluoromethyl)phenyl]pyridine (11b): Colorless solid; yield: 49%; mp 129–131 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 6.69–6.72 (m, 2H, CH), 6.80–6.83 (m, 2H, CH), 6.94–6.96 (m, 2H, CH), 7.17–7.22 (m, 4H, CH), 7.28 (brd, $^3J_{H,H}$ = 8.0 Hz, 2H, CH), 7.48 (brd, $^3J_{H,H}$ = 7.8 Hz, 2H, CH), 7.73–7.77 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (CH_3), 21.2 (CH_3), 21.4 (CH_3),

124.1 (q, $^{1}J_{C,F}$=271.8 Hz, CF_3), 124.7 (q, $^{3}J_{C,F}$=3.9 Hz, CH), 127.3 (C), 128.3 (CH), 128.5 (CH), 128.6 (CH), 129.4 (q, $^{2}J_{C,F}$=33.1 Hz, C), 129.6 (CH), 129.8 (CH), 130.0 (CH), 130.6 (CH), 134.0 (C), 134.6 (C), 136.0 (C), 136.6 (C), 136.9 (C), 137.5 (C), 138.7 (C), 141.2 (C), 148.4 (C), 155.4 (C), 155.6 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−62.1 (CF_3); IR (ATR): $\tilde{\nu}$=3028 (w), 2923 (w), 2861 (w), 1907 (w), 1615 (w), 1503 (w), 1351 (m), 1319 (s), 1185 (m), 1165 (m), 1130 (s), 1107 (s), 1066 (s), 1019 (m), 956 (w), 878 (w), 849 (m), 830 (m), 813 (m), 795 (m), 754 (m), 730 (m), 720 (m), 680 (w), 650 (w), 633 (w), 537 (m), 526 (m), 480 (m), 448 (m), 407 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%)=528 (M^+, 46), 527 (66), 526 (100), 508 (2), 490 (5), 476 (3), 344 (1), 255 (2), 245 (2), 243 (2), 240 (2), 222 (3), 214 (3), 202 (5), 201 (3), 196 (6), 188 (5), 181 (2), 165 (2), 116 (2); HR-MS (ESI): *m/z*=528.17098, calcd. for $C_{33}H_{26}ClF_3N$ ($[M+H]^+$): 528.17004; anal. calcd. for $C_{33}H_{25}ClF_3N$ (528.01): C 75.07, H 4.77, N 2.65; found: C 74.86, H 4.744, N 2.425.

3-Chloro-2,5,6-tris(4-methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]pyridine (11c): Colorless solid; yield: 53%; mp 97–99 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.68 (s, 3H, MeO), 3.73 (s, 3H, MeO), 3.85 (s, 3H, MeO), 6.54–6.59 (m, 2H, CH), 6.67–6.75 (m, 4H, CH), 6.97–7.02 (m, 2H, CH), 7.19 (brd, $^{3}J_{H,H}$=8.2 Hz, 2H, CH), 7.25–7.28 (m, 2H, CH), 7.50 (brd, $^{3}J_{H,H}$=8.2 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.0 (MeO), 55.1 (MeO), 55.3 (MeO), 113.1 (CH), 113.4 (CH), 124.1 (q, $^{1}J_{C,F}$=274.1 Hz, CF_3), 124.7 (q, $^{3}J_{C,F}$=3.9 Hz, CH), 126.9 (C), 129.4 (C), 129.4 (q, $^{2}J_{C,F}$=33.0 Hz, C), 130.0 (CH), 131.1 (CH), 131.3 (CH), 131.9 (CH), 131.9 (CH), 132.2 (C), 133.8 (C), 141.3 (C), 148.6 (C), 154.9 (C), 155.3 (C), 158.3 (C), 159.2 (C), 156.0 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−62.1 (CF_3); IR (ATR): $\tilde{\nu}$=3063 (w), 3003 (w), 2957 (w), 2935 (w), 2911 (w), 2837 (w), 1607 (m), 1578 (w), 1543 (w), 1515 (s), 1461 (m), 1393 (m), 1321 (s), 1288 (m), 1245 (s), 1174 (s), 1123 (s), 1108 (s), 1067 (s), 1023 (s), 911 (w), 826 (s), 802 (m), 780 (w), 732 (m), 649 (w), 636 (w), 609 (w), 551 (m), 537 (m), 407 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%)=576 (M^+, 62), 575 (93), 574 (100), 560 (5), 530 (3), 453 (3), 288 (6), 252 (4), 245 (4), 223 (3), 212 (3), 210 (2), 191 (5), 187 (3), 186 (3), 177 (3), 169 (7), 73 (2); HR-MS (ESI): *m/z*=576.15513, calcd. for $C_{33}H_{26}ClF_3NO_3$ ($[M+H]^+$): 576.15478.

3-Chloro-2,5,6-tris(3-methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]pyridine (11d): Colorless solid; yield: 38%; mp 130–132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.50 (s, 3H, MeO), 3.57 (s, 3H, MeO), 3.86 (s, 3H, MeO), 6.39 (dd, $^{4}J_{H,H}$=2.6 Hz, $^{4}J_{H,H}$=2.4 Hz, 1H, CH), 6.46 (ddd, $^{3}J_{H,H}$=7.5 Hz, $^{4}J_{H,H}$=1.8 Hz, $^{4}J_{H,H}$=1.1 Hz, 1H, CH), 6.59 (ddd, $^{3}J_{H,H}$=8.3 Hz, $^{4}J_{H,H}$=2.7 Hz, $^{4}J_{H,H}$=1.1 Hz, 1H, CH), 6.74 (ddd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=2.7 Hz, $^{4}J_{H,H}$=1.2 Hz, 1H, CH), 6.86 (dd, $^{4}J_{H,H}$=2.7 Hz, $^{4}J_{H,H}$=2.1 Hz, 1H, CH), 6.91–7.00 (m, 3H, CH), 7.08 (dd, $^{3}J_{H,H}$=7.7 Hz, $^{3}J_{H,H}$=8.0 Hz, 1H, CH), 7.23–7.25 (m, 2H, CH), 7.36–7.44 (m, 3H, CH), 7.51 (d, $^{3}J_{H,H}$=8.0 Hz, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.0 (MeO), 55.1 (MeO), 55.3 (MeO), 113.1 (CH), 114.3 (CH), 114.5 (CH), 114.8 (CH), 115.2 (CH), 116.3 (CH), 122.1 (CH), 122.4 (CH), 123.4 (CH), 124.0 (q, $^{1}J_{C,F}$=273.4 Hz, CF_3), 124.8 (q, $^{3}J_{C,F}$=3.8 Hz, CH), 127.8 (C), 128.7 (CH), 128.9 (CH), 129.0 (CH), 129.6 (q, $^{2}J_{C,F}$=32.5 Hz, C), 130.0 (CH), 134.9 (C), 138.1 (C), 139.9 (C), 140.7 (C), 140.8 (C), 148.4 (C), 155.4 (C), 155.6 (C), 158.9 (C), 159.0 (C), 159.2 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−62.2 (CF_3); IR (ATR): $\tilde{\nu}$=2994 (w), 2959 (w), 2835 (w), 1581 (m), 1547 (m), 1513 (w), 1490 (m), 1460 (m), 1424 (m), 1350 (w), 1326 (s), 1289 (m), 1234 (m), 1171 (m), 1133 (w), 1118 (s), 1108 (s), 1069 (m), 1042 (s), 1027 (m), 992 (w), 942 (w), 873 (m), 842 (m), 786 (s), 755 (m), 702 (s), 602 (m), 560 (m), 524 (w), 486 (w), 454 (w), 432 (w), 409 (w), 382 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%)=576 (M^+, 54), 575 (76), 574 (100), 546 (5), 545 (7), 544 (6), 530 (4), 421 (2), 420 (2), 262 (3), 254 (3), 225 (2), 215 (3), 207 (4), 198 (2), 191 (3), 183 (4), 176 (6), 175 (4), 163 (3); HR-MS (ESI): *m/z*=576.15573, calcd. for $C_{33}H_{26}ClF_3NO_3$ ($[M+H]^+$): 576.15478; anal. calcd. for $C_{33}H_{25}ClF_3NO_3$ (576.00): C 68.81, H 4.37, N 2.43; found: C 68.42; H 4.606, N 2.164.

3-Chloro-4-(4-methoxyphenyl)-2,5,6-triphenylpyridine (11e): Colorless solid; yield: 54%; mp 206–208 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.74 (s, 3H, OCH_3), 6.73–6.78 (m, 2H, CH), 6.85–6.87 (m, 2H, CH), 6.98–7.03 (m, 5H, CH), 7.14–7.16 (m, 3H, CH), 7.28–7.31 (m, 2H, CH), 7.39–7.50 (m, 3H, CH), 7.85–7.88 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.0 (OCH_3), 113.1, 126.6, 127.5, 127.6 (CH), 127.9, 128.5 (CH), 128.7, 129.3 (C), 129.7, 129.9, 130.9, 131.0 (CH), 135.5, 137.6, 139.2, 140.0, 149.6, 155.5, 155.6, 158.7 (C); IR (ATR): $\tilde{\nu}$=3029 (w), 2924 (w), 2851 (w), 1608 (m), 1507 (m), 1396 (m), 1357 (m), 1289 (m), 1244 (s), 1172 (m), 1149 (m), 1030 (m), 838 (m), 743 (m), 695 (s), 562 (m), 537 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%)=446 (M^+, 33), 400 (19), 369 (91), 317 (100), 287 (67), 220 (22), 205 (71); HR-MS (ESI): m/z=448.14655, calcd. for $C_{30}H_{23}ClNO$ ($[M+H]^+$): 448.14627.

3-Chloro-4-(4-methoxyphenyl)-2,5,6-tri-*para*-tolylpyridine (11f): Colorless solid; yield: 34%; mp 142–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.19, (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 6.71–6.77 (m, 4H, CH), 6.81–6.83 (m, 2H, CH), 7.17–7.21 (m, 2H, CH), 7.25–7.28 (m, 2H, CH), 7.74–7.77 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.1 (CH_3), 21.3 (CH_3), 55.0 (OCH_3), 113.1, 128.2, 128.3, 128.5, 129.6 (CH), 129.7 (C), 129.8, 130.8, 130.9 (CH), 134.7, 135.1, 136.0, 136.4, 137.1, 137.3, 138.3, 149.5, 155.2, 155.4, 158.5 (C); IR (ATR): $\tilde{\nu}$=3026 (w), 2918 (w), 2856 (w), 1610 (m), 1499 (m), 1391 (m), 1347 (m), 1293 (m), 1244 (s), 1183 (m), 1034 (m), 813 (s), 532 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%)=488 (M^+, 61), 167 (26), 149 (75), 111 (24), 97 (36), 83 (38), 71 (64), 57 (100), 43 (85); HR-MS (EI, 70 eV): *m/z*=488.17753, calcd. for $C_{33}H_{27}ClNO$: 488.17757.

3-Chloro-2,5,6-tris(4-fluorophenyl)-4-(4-methoxyphenyl)-pyridine (11g): Colorless solid; yield: 62%; mp 181–183 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.75 (s, 3H, OCH_3), 6.73–6.79 (m, 6H, CH), 6.81–6.89 (m, 2H, CH), 6.92–6.97 (m, 2H, CH), 7.11–7.18 (m, 2H, CH), 7.21–7.21 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.1 (OCH_3), 113.3 (CH), 114.7 (d, $^{2}J_{C,F}$=21.6 Hz, CH), 114.9 (d, $^{2}J_{C,F}$=21.6 Hz, CH), 115.0 (d, $^{2}J_{C,F}$=21.6 Hz, CH), 128.8, 129.0 (C), 130.7 (CH), 131.6 (d, $^{3}J_{C,F}$=8.1 Hz, CH), 132.5 (d, $^{3}J_{C,F}$=8.1 Hz, CH), 133.3 (d, $^{4}J_{C,F}$=3.7 Hz, C), 134.5 (C), 134.9 (d, $^{4}J_{C,F}$=3.7 Hz, C), 135.7 (d, $^{4}J_{C,F}$=3.1 Hz, C), 150.0, 154.5, 154.8, 158.8 (C), 161.5 (d, $^{1}J_{C,F}$=247.3 Hz, CF), 162.3 (d, $^{1}J_{C,F}$=248.1 Hz, CF), 163.0 (d, $^{1}J_{C,F}$=248.1 Hz, CF); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−112.1 (s, 1F, CF), −113.3 (s, 1F, CF), −114.0 (s, 1F, CF); IR (ATR): $\tilde{\nu}$=2922 (w), 2841 (w), 1601 (m), 1498 (s), 1391 (m), 1290 (m), 1218 (s), 1157 (s), 1033 (m), 831 (s), 752 (m), 539 (s); MS (EI, 70 eV): *m/z* (%)=500 (M^+, 90), 223 (19), 179 (18), 160 (18), 149 (23), 112 (61), 109 (19), 105

(80), 97 (48), 83 (63), 77 (28), 69 (60), 57 (100), 43 (84); HR-MS (ESI): $m/z = 502.1185$, calcd. for $C_{30}H_{20}ClF_3NO$ ($[M+H]^+$): 502.118.

3-Chloro-2,4,5,6-tetrakis(4-methoxyphenyl)pyridine (11h): Slightly Yellow solid; yield: 40%; mp 171–173 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.62$, (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.48–6.53 (m, 2H, CH), 6.60–6.64 (m, 2H, CH), 6.66–6.72 (m, 4H, CH), 6.88–6.95 (m, 4H, CH), 7.16–7.21 (m, 2H, CH), 7.75–7.80 (m, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 54.9$, 55.0, 55.1, 55.2 (OCH_3), 113.0, 113.1 (CH), 113.2 (CH), 127.9, 129.8, 130.2 (C), 130.8, 131.1, 131.2 (CH), 131.8 (C), 132.1 (CH), 132.7, 134.4, 149.7, 154.7, 155.0, 158.0, 158.5, 159.0, 159.8 (C); IR (ATR): $\tilde{\nu} = 2920$ (m), 2849 (w), 1718 (w), 1607 (m), 1497 (m), 1461 (m), 1395 (m), 1289 (m), 1243 (s), 1173 (s), 1030 (s), 828 (s), 801 (s), 728 (m), 546 cm^{-1} (s); MS (EI, 70 eV): m/z (%) = 537 (M^+, 100), 539 (16), 313 (15), 149 (14), 99 (23), 85 (14), 71 (24), 57 (39); HR-MS (EI, 70 eV): $m/z = 537.16831$, calcd. for $C_{33}H_{28}ClNO_4$: 537.17014.

Synthesis of Pentaarylpyridines 12a–e Starting from 11

An oven-dried and argon-flushed pressure tube was charged with 3-chloro-2,4,5,6-tetraarylpyridine **11** (1.0 equiv.), $PdCl_2(CH_3CN)_2$ (5.0 mol%), SPhos (10.0 mol%), boronic acid (2.5 equiv.) and K_3PO_4 (2.5 equiv.) followed by anhydrous toluene (3.0 mL). The tube was sealed with a Teflon valve and the reaction mixture was stirred at 100 °C for 20 h. The cooled reaction mixture was diluted with water and extracted with DCM. The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated under vacuum. The residue was purified by column chromatography.

3-(4-Isopropylphenyl)-4-(4-methoxyphenyl)-2,5,6-triphenyl-pyridine (12a): Slightly yellow solid; yield: 98%; mp 189–191 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.12$ (d, 6H, $^3J = 6.9$ Hz, CH_3), 2.74 (sept, 1H, $^3J = 6.9$ Hz, $CH_{i\text{-}Pr}$), 3.61 (s, 3H, OCH_3), 6.42–6.47 (m, 2H, CH), 6.63–6.67 (m, 2H, CH), 6.76–6.79 (m, 2H, CH), 6.84–6.92 (m, 4H, CH), 6.98–7.02 (m, 3H, CH), 7.13–7.18 (m, 6H, CH), 7.35–7.42 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 23.8$ (CH_3), 33.5 ($CH_{i\text{-}Pr}$), 54.9 (OCH_3), 112.3, 125.4, 126.0 (CH), 127.1 (CH), 127.3 (CH), 127.4, 130.1, 130.2 (CH), 130.4 (C), 131.1, 131.3, 131.6, 133.8, 134.0, 135.7, 138.6, 141.0, 146.7, 149.8, 156.2, 156.4, 157.6 (C); IR (ATR): $\tilde{\nu} = 2956$ (w), 2923 (w), 2852 (w), 1731 (w), 1607 (w), 1510 (m), 1387 (m), 1244 (s), 1174 (m), 1028 (m), 835 (m), 753 (m), 693 (s), 671 (s), 564 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 530 (M^+, 92), 281 (15), 155 (100), 127 (43), 111 (23), 97 (40), 85 (51), 71 (90), 57 (98), 43 (57); HR-MS (ESI): $m/z = 532.2641$, calcd. for $C_{39}H_{34}NO$ ($[M+H]^+$): 532.26349.

4-(4-Methoxyphenyl)-5-[4-(trifluoromethyl)phenyl]-2,3,6-tri-*para*-tolylpyridine (12b): Colorless solid; yield: 93%; mp 188–190 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.19$, (s, 3H, CH_3), 2.27 (s, 6H, CH_3), 3.63 (s, 3H, OCH_3), 6.44–6.48 (m, 2H, CH), 6.58–6.63 (m, 2H, CH), 6.74–6.83 (m, 4H, CH), 6.95–7.01 (m, 6H, CH), 7.21–7.30 (m, 6H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.1$ (CH_3), 21.2 (CH_3), 54.9 (OCH_3), 112.6 (CH), 124.1 (q, $^1J_{C,F} = 271.9$ Hz, CF_3), 124.3 (q, $^3J_{C,F} = 3.7$ Hz, CH), 128.2 (CH), 128.3 (CH), 130.1(CH), 131.0, 131.4, 131.6 (CH), 132.1, 133.5, 135.3, 135.6, 137.0, 137.2, 137.5, 137.9, 143.0, 149.8, 155.8, 156.8, 157.8 (C); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -61.9$ (s, 3F, CF_3); IR (ATR): $\tilde{\nu} = 2921$ (w), 2853 (w), 1611 (m), 1501 (m), 1387 (m), 1320 (s), 1291 (m), 1246 (s), 1163 (s), 1123 (s), 1065 (s), 1015 (m), 817 (s), 666 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 598 (M^+, 100), 454 (12), 149 (16), 111 (19), 97 (28), 91 (18), 83 (25), 71 (38), 57 (54), 43 (26); HR-MS (EI, 70 eV): $m/z = 598.23489$, calcd. for $C_{40}H_{31}Cl_2F_3NO$: 598.23523.

3-(4-Methoxyphenyl)-2,5,6-triphenyl-4-[4-(trifluoromethyl)phenyl]pyridine (12c): Colorless solid; yield: 77%; mp 236–238 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.67$ (s, 3H, MeO), 6.54–6.57 (m, 2H, CH), 6.71–6.79 (m, 2H, CH), 6.85–6.91 (m, 4H, CH), 6.99–7.02 (m, 3H, CH), 7.15–7.22 (m, 8H, CH), 7.38–7.42 (m, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.0$ (MeO), 113.1 (CH), 123.9 (q, $^3J_{C,F} = 4.0$ Hz, CH), 124.0 (q, $^2J_{C,F} = 272.8$ Hz, CF_3), 126.6 (CH), 127.4 (CH), 127.5 (CH), 127.5 (CH), 127.5 (CH), 127.6 (CH), 128.2 (q, $^2J_{C,F} = 32.6$ Hz, C), 129.9 (C), 130.2 (CH), 130.2 (CH), 130.7 (CH), 131.1 (CH), 132.2 (CH), 133.0 (C), 133.4 (C), 137.9 (C), 140.4 (C), 140.6 (C), 142.3 (C), 149.0 (C), 156.3 (C), 156.8 (C), 158.1 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): $\delta = -62.1$ (CF_3); IR (ATR): $\tilde{\nu} = 3044$ (w), 3016 (w), 2970 (w), 2843 (w), 1605 (m), 1531 (m), 1458 (m), 1391 (m), 1326 (s), 1247 (m), 1159 (m), 1123 (s), 1067 (s), 1029 (m), 910 (w), 791 (w), 756 (m), 698 (m), 655 (m), 559 (m), 537 (m), 428 (w), 404 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 558 (M^+, 20), 557 (73), 556 (100), 512 (14), 281 (2), 278 (2), 268 (3), 256 (2), 254 (2), 249 (3), 241 (4), 233 (4), 220 (14), 214 (8), 208 (4), 194 (5), 168 (3), 157 (3), 77 (2); HR-MS (EI, 70 eV): $m/z = 556.18833$, calcd. for $C_{37}H_{25}F_3NO$: 556.18828.

3-(Biphenyl-4-yl)-2,5,6-triphenyl-4-[4-(trifluoromethyl)-phenyl]pyridine (12d): Colorless solid; yield: 78%; mp 227–229 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.87$–6.90 (m, 2H, CH), 6.92–6.96 (m, 4H, CH), 7.00–7.04 (m, 3H, CH), 7.17–7.23 (m, 7H, CH), 7.26–7.31 (m, 3H, CH), 7.35–7.50 (m, 8H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 124.0$ (q, $^1J_{C,F} = 272.6$ Hz, CF_3), 124.0 (q, $^3J_{C,F} = 3.6$ Hz, CH), 126.2 (CH), 126.6 (CH), 126.8 (CH), 127.3 (CH), 127.5 (CH), 127.5 (C), 127.6 (CH), 127.6 (CH), 127.6 (CH), 128.4 (q, $^2J_{C,F} = 32.2$ Hz, C), 128.7 (CH), 130.2 (CH), 130.2 (CH), 130.8 (CH), 131.2 (CH), 131.6 (CH), 132.9 (C), 133.4 (C), 136.9 (C), 137.9 (C), 139.0 (C), 140.3 (C), 140.5 (C), 142.1 (C), 148.8 (C), 156.6 (C), 156.7 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): $\delta = -62.1$ (CF_3); IR (ATR): $\tilde{\nu} = 3081$ (w), 3051 (w), 3028 (w), 1617 (w), 1530 (w), 1388 (m), 1324 (s), 1166 (m), 1118 (m), 1067 (m), 1020 (w), 850 (m), 761 (m), 752 (m), 736 (m), 696 (s), 677 (m), 660 (m), 627 (w), 597 (w), 569 (w), 458 (w), 400 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 604 (M^+, 23), 603 (73), 602 (100), 524 (2), 404 (3), 377 (2), 354 (3), 352 (2), 345 (2), 301 (3), 292 (12), 291 (4), 281 (4), 264 (5), 259 (4), 252 (19), 250 (3), 245 (6), 227 (7), 226 (4), 208 (7), 207 (6), 191 (3), 176 (3), 163 (2), 149 (2), 146 (3), 118 (4); HR-MS (ESI): $m/z = 604.225$, calcd. for $C_{42}H_{29}F_3N$ ($[M+H]^+$): 604.22466; anal. calcd. for $C_{42}H_{28}F_3N$ (603.67): C 83.56, H 4.68, N 2.32; found: C 83.30, H 4.83, N 1.966.

2,3,6-Triphenyl-4,5-bis[4-(trifluoromethyl)phenyl]pyridine (12e): Colorless solid; yield: 89%; mp 236–238 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.86$–6.90 (m, 4H, CH), 6.99–7.06 (m, 5H, CH), 7.16–7.28 (m, 10H, CH), 7.33–7.40 (m, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 123.6$ (q, $^1J_{C,F} = 272.7$ Hz, CF_3), 124.1 (q, $^1J_{C,F} = 272.6$ Hz, CF_3), 124.2 (q, $^3J_{C,F} = 3.9$ Hz, CH), 124.6 (q, $^3J_{C,F} = 3.9$ Hz, CH), 126.8 (CH),

127.6 (CH), 127.7 (CH), 127.7 (CH), 127.8 (CH), 127.8 (CH), 128.7 (q, $^2J_{C,F}$=32.7 Hz, C), 128.8 (q, $^2J_{C,F}$=32.7 Hz, C), 130.1 (CH), 130.1 (CH), 130.6 (CH), 131.1 (CH), 131.5 (CH), 131.9 (C), 133.5 (C), 137.5 (C), 140.0 (C), 140.2 (C), 141.6 (C), 142.0 (C), 148.7 (C), 156.6 (C), 157.3 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−62.1 (CF_3), −62.3 (CF_3); IR (ATR): $\tilde{\nu}$=3085 (w), 3057 (w), 3033 (w), 1617 (m), 1534 (m), 1494 (w), 1392 (m), 1321 (s), 1165 (m), 1108 (m), 1067 (s), 1020 (m), 850 (m), 754 (m), 698 (s), 659 (m), 596 (w), 551 (w), 462 (w), 397 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%)=596 (M^+, 16), 595 (61), 594 (100), 576 (4), 448 (2), 276 (2), 242 (1), 226 (2), 221 (3), 220 (3), 214 (2); HR-MS (ESI): *m/z*=596.18118, calcd. for $C_{37}H_{24}F_6N$ ($[M+H]^+$): 596.18075; anal. calcd. for $C_{37}H_{23}F_6N$ (595.58): C 74.62, H 3.89, N 2.35; found: C 74.23, H 3.609, N 2.192.

Synthesis of Pentaarylpyridines 13a–l Starting from 8

An oven-dried and argon-flushed pressure tube was charged with 2,3,5,6-tetrachloro-4-arylpyridine **8a** or **8b** (1.0 equiv.), $PdCl_2(CH_3CN)_2$ (5.0 mol%), SPhos (10.0 mol%), boronic acid (8.0 equiv.) and K_3PO_4 (8.0 equiv.) followed by anhydrous toluene (6 mL); The tube was sealed with a Teflon valve and the reaction mixture was stirred at 100 °C for 20 h. The cooled reaction mixture was diluted with water and extracted with DCM. The combined organic layers were dried (Na2SO4), filtered and the filtrate was concentrated under vacuum. The residue was purified by column chromatography.

4-(4-Methoxyphenyl)-2,3,5,6-tetraphenylpyridine (13a): Colorless solid; yield: 66%; mp 221 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.64 (s, 3H, OCH_3), 6.45 (d, 2H, ^3J=8.9 Hz, CH), 6.69 (d, 2H, ^3J=8.9 Hz, CH), 6.91–6.94 (m, 4H, CH), 7.01–7.06 (m, 6H, CH), 7.17–7.21 (m, 6H, CH), 7.39–7.43 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=54.9 (OCH_3), 112.5, 126.1, 127.2, 127.4, 127.4, 130.2 (CH), 130.3 (C), 131.3, 131.5 (CH), 134.0, 138.5, 140.8, 150.0, 156.4, 157.7 (C); IR (ATR): $\tilde{\nu}$=3056 (w), 2917 (m), 2869 (m), 1608 (w), 1510 (m), 1392 (m), 1290 (w), 1244 (s), 1179 (m), 1107 (s), 1029 (m), 756 (m), 697 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%)=489 (M^+, 66), 488 (100), 444 (13), 365 (3), 245 (2), 228 (2); HR-MS (EI, 70 eV): *m/z*=488.20078, calcd for $C_{36}H_{26}NO$: 488.20089.

2,3,5,6-Tetrakis(4-*tert*-butylphenyl)-4-(4-methoxyphenyl)-pyridine (13b): Colorless solid; yield: 62%; mp 266–267 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.22 (s, 18H, CH_3), 1.26 (s, 18H, CH_3), 3.64 (s, 3H, OCH_3), 6.47 (d, 2H, ^3J=8.9 Hz, CH), 6.69. (d, 2H, ^3J=8.9 Hz, CH), 6.80 (d, 4H, ^3J=8.3 Hz, CH), 7.02 (d, 4H, ^3J=8.3 Hz, CH), 7.16 (d, 4H, ^3J=8.7 Hz CH), 7.31 (d, 4H, ^3J=8.7 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.2, 31.2 (CH_3), 34.3, 34.4 ($C_{t\text{-Bu}}$), 55.0 (OCH_3), 112.3, 124.1, 124.2, 129.8, (CH), 130.8 (C), 131.0, 131.7 (CH), 133.6, 135.8, 138.2, 148.8, 149.7, 156.2, 157.5 (C); IR (ATR): $\tilde{\nu}$=2953 (m), 2902 (m), 2866 (m), 1609 (w), 1984 (m), 1460 (m), 1388 (m), 1362 (m), 1241 (s), 1176 (s), 1109 (m), 1016 (m), 827 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%)=713 (M^+, 100), 696 (5), 615 (27), 580 (42), 566 (5), 502 (4), 342 (5); HR-MS (ESI): *m/z*=714.46724, calcd for ($[M+H]^+$) $C_{52}H_{60}NO$: 714.46694.

2,3,5,6-Tetrakis(4-isopropoxyphenyl)-4-(4-methoxyphenyl)-pyridine (13c): Colorless solid; yield: 93%; mp 181–183 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.25 (d, 12H, ^3J=6.1 Hz, CH_3), 1.30 (d, 12H, ^3J=6.1 Hz, CH_3), 3.65 (s, 3H, OCH_3), 4.42 (sept, 2H, ^3J=6.1 Hz, *CH*-CH_3), 4.50 (sept, 2H, ^3J=6.1 Hz, *CH*-CH_3), 6.48 (d, 2H, ^3J=8.8 Hz, CH), 6.57 (d, 4H, ^3J=8.5 Hz, CH), 6.65 (d, 2H, ^3J=8.8 Hz, CH), 6.69 (d, 4H, ^3J=8.8 Hz, CH), 6.76 (d, 4H, ^3J=8.8 Hz, CH), 7.34 (d, 4H, ^3J=8.8 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.9, 22.0 (CH_3), 54.9 (OCH_3), 69.6, 69.8 (OCH), 112.4, 114.7, 115.4, (CH), 130.9, 131.2 (C), 131.5, 131.6 (CH), 131.6 (C), 132.4 (CH), 132.9, 155.6, 155.9, 157.1, 157.5 (C); IR (ATR): $\tilde{\nu}$=2974 (m), 2931 (w), 2836 (w), 1605 (m), 1510 (m), 1383 (m), 1284 (m), 1239 (s), 1179 (s), 1105 (s), 953 (s), 832 (s); MS (EI, 70 eV): *m/z* (%)=721 (M^+, 100), 678 (17), 636 (10), 617 (11), 552 (20), 508 (3); HR-MS (ESI): *m/z*=744.36595, calcd for $C_{48}H_{51}NO_5Na$ ($[M+Na]^+$): 744.36594.

2,3,5,6-Tetrakis(4-fluorophenyl)-4-(4-methoxyphenyl)pyridine (13d): Colorless solid; yield: 78%; mp 252–254 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.65 (s, 3H, OCH_3), 6.47–6.51 (m, 2H, CH), 6.58–6.61 (m, 2H, CH), 6.70–6.75 (m, 4H, CH), 6.78–6.83 (m, 4H, CH), 6.84–6.90 (m, 4H, CH), 7.29–7.34 (m, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=54.9 (OCH_3), 112.8 (CH), 114.6 (d, $^2J_{C,F}$=21.1 Hz, CH), 114.7 (d, $^2J_{C,F}$=21.9 Hz, CH), 129.6 (C), 131.3 (CH), 131.8 (d, $^3J_{C,F}$=8.2 Hz, CH), 132.7 (d, $^3J_{C,F}$=7.8 Hz, CH), 133.1 (C), 134.1 (d, $^4J_{C,F}$=3.6 Hz, C), 136.4 (d, $^4J_{C,F}$=2.8 Hz, C), 150.5, 155.6, 157.9 (C), 161.3 (d, $^1J_{C,F}$=246.7 Hz, CF), 162.2 (d, $^1J_{C,F}$=247.6 Hz, CF); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−113.8 (s, 2F, CF), −114.8 (s, 2F, CF); IR (ATR): $\tilde{\nu}$=2932 (w), 2832 (w), 1603 (m), 1510 (s), 1389 (m), 1247 (s), 1220 (s), 1156 (s), 1040 (m), 815 (s), 533 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%)=560 (M^+, 100), 516 (12), 244 (4), 183 (4); HR-MS (EI, 70 eV): *m/z*=560.16315, calcd. for $C_{36}H_{22}F_4NO$: 560.16320; anal. calcd. for $C_{36}H_{23}F_4NO$ (561.57): C 77.0, H 4.13, N 2.49; found: C 77.25, H 4.48, N 2.51.

4-(4-Methoxyphenyl)-2,3,5,6-tetra-*para*-tolylpyridine (13e): Colorless solid; yield: 61%; mp 234–236 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.18 (s, 6H, CH_3), 2.26 (s, 6H, CH_3), 3.63 (s, 3H, OCH_3), 6.42–6.47 (m, 2H, CH), 6.60–6.64 (m, 2H, CH), 6.71–6.75 (m, 4H, CH), 6.79–6.81 (m, 4H, CH), 6.94–6.97 (m, 4H, CH), 7.25–7.29 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.1, 21.2 (CH_3), 54.9 (OCH_3), 112.3, 128.1, 130.1 (CH), 130.7 (C), 131.1, 131.5 (CH), 133.6, 135.4, 136.9, 155.8, 157.5 (C); IR (ATR): $\tilde{\nu}$=3025 (w), 2918 (w), 1611 (m), 1499 (m), 1242 (s), 1171 (m), 1049 (m), 808 (s), 748 (m), 521 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%)=544 (M^+, 100), 529 (5), 500 (7), 234 (4), 227 (4), 220 (4), 69 (10), 44 (7); HR-MS (EI, 70 eV): *m/z*=544.26318, calcd. for $C_{40}H_{34}NO$: 544.26349; anal. calcd. for $C_{40}H_{35}NO$ (545.71): C 88.04, H 6.46, N 2.57; found: C 88.26, H 6.48, N 2.45.

4-(4-Methoxyphenyl)-2,3,5,6-tetrakis[4-(trifluoromethyl)-phenyl]pyridine (13f): Colorless solid; yield: 81%; mp 240–242 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.65 (s, 3H, OCH_3), 6.47–6.52 (m, 2H, CH), 6.56–6.61 (m, 2H, CH), 7.00 (d, 4H, ^3J=8.1 Hz, CH), 7.32 (d, 4H, ^3J=8.1 Hz, CH), 7.41–7.47 (m, 8H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=55.0 (OCH_3), 113.1 (CH), 123.8 (q, $^1J_{C,F}$=272.3 Hz, CF_3), 123.9 (q, $^1J_{C,F}$=272.1 Hz, CF_3), 124.8 (q, $^3J_{C,F}$=3.8 Hz, CH), 128.3 (CH), 129.5 (q, $^2J_{C,F}$=32.9 Hz, C), 130.3, 131.2, 131.4 (CH), 133.5, 141.4, 143.4, 150.5, 155.7, 158.4 (C); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.1 (s, 3F, CF_3), −62.2 (s, 3F, CF_3); IR (ATR): $\tilde{\nu}$=2936 (w), 1616 (m), 1516 (m), 1321 (s), 1163 (s), 1106 (s), 1065 (s), 1015 (s), 853 (s), 833 (s), 669 (m); MS

(EI, 70 eV): *m/z* (%) = 760 (M^+, 100), 742 (5), 716 (10), 381 (5); HR-MS (EI, 70 eV): *m/z* = 760.14943, calcd. for $C_{40}H_{22}F_{12}NO$: 760.15043; anal. calcd. for $C_{40}H_{23}F_{12}NO$ (761.60): C 63.08, H 3.04, N 1.84; found: C 63.34, H 3.36, N 1.85.

2,3,5,6-Tetrakis(4-ethoxyphenyl)-4-(4-methoxyphenyl)pyridine (13g): Colorless solid; yield: 79%; mp 231–233 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30–1.37 (m, 12H, CH_3), 3.63 (s, 3H, OCH_3), 3.88 (q, 4H, ^3J = 7.0 Hz, CH_2), 3.96 (q, 4H, ^3J = 7.0 Hz, CH_2), 6.44–6.48 (m, 2H, CH), 6.51–6.56 (m, 4H, CH), 6.59–6.64 (m, 2H, CH), 6.65–6.70 (m, 4H, CH), 6.72–6.76 (m, 4H, CH), 7.29–7.34 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7, 14.8 (CH_3), 54.9 (OCH_3), 63.0, 63.1 (CH_2), 112.4, 113.4, 113.5 (CH), 130.8, 131.0 (C), 131.4, 131.5, 132.3 (CH), 132.8, 155.6, 157.0, 157.4, 158.1 (C); IR (ATR): $\tilde{\nu}$ = 2979 (w), 2923 (w), 1605 (m), 1514 (m), 1388 (m), 1239 (s), 1172 (s), 1112 (s), 1040 (s), 824 (s), 655 (m), 553 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%) = 665 (M^+, 100), 636 (8), 575 (11), 99 (14), 44 (10); HR-MS (EI, 70 eV): *m/z* = 665.31230, calcd. for $C_{44}H_{43}NO_5$: 665.31357; anal. calcd. for $C_{44}H_{43}NO_5$ (665.82): C 79.37, H 6.51, N 2.10; found: C 78.89, H 6.86, N 2.09.

2,3,5,6-Tetraphenyl-4-[4-(trifluoromethyl)phenyl]pyridine (13h): Colorless solid; yield: 68%; mp 237–239 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.85–6.91 (m, 6H, CH), 6.99–7.03 (m, 6H, CH), 7.15–7.19 (m, 8H, CH), 7.38–7.41 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.9 (q, $^3J_{C,F}$ = 4.0 Hz, CH), 123.9 (q, $^1J_{C,F}$ = 272.6 Hz, CF_3), 126.6 (CH), 127.5 (CH), 127.5 (CH), 127.6 (CH), 128.3 (q, $^2J_{C,F}$ = 32.7 Hz, C), 130.2 (CH), 130.7 (CH), 131.1 (CH), 133.3 (C), 137.8 (C), 140.5 (C), 142.1 (C), 148.7 (C), 156.6 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −62.2 (CF_3); IR (ATR): $\tilde{\nu}$ = 3056 (w), 1600 (w), 1533 (w), 1493 (w), 1442 (w), 1315 (m), 1167 (m), 1135 (m), 1106 (m), 1065 (m), 1019 (w), 846 (m), 755 (m), 697 (s), 656 (m), 626 (m), 598 (w), 532 (w), 487 (m), 431 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 528 (M^+, 16), 527 (62), 526 (100), 448 (3), 380 (2), 276 (3), 253 (3), 219 (4), 213 (3), 207 (4), 189 (4), 176 (3), 151 (2); HR-MS (ESI): *m/z* = 528.19391, calcd. for $C_{36}H_{25}F_3N$ ($[M+H]^+$): 528.19336.

2,3,5,6-Tetra-*para*-tolyl-4-[4-(trifluoromethyl)phenyl]pyridine (13i): Colorless solid; yield: 56%; mp 208–210 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19 (s, 6H, CH_3), 2.27 (s, 6H, CH_3), 6.72–6.75 (m, 4H, CH), 6.79–6.82 (m, 4H, CH), 6.86–6.89 (m, 2H, CH), 6.97–6.99 (m, 4H, CH), 7.17–7.20 (m, 2H, CH), 7.29–7.32 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (CH_3), 21.2 (CH_3), 123.8 (q, $^3J_{C,F}$ = 4.0 Hz, CH), 124.1 (q, $^1J_{C,F}$ = 272.3 Hz, CF_3), 128.1 (q, $^2J_{C,F}$ = 33.7 Hz, C), 128.2 (CH), 128.3 (CH), 130.1 (CH), 130.8 (CH), 131.0 (CH), 132.8 (C), 135.0 (C), 136.0 (C), 137.1 (C), 137.9 (C), 142.6 (C), 148.8 (C), 156.2 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −62.0 (CF_3); IR (ATR): $\tilde{\nu}$ = 2919 (w), 1614 (w), 1532 (w), 1389 (m), 1350 (w), 1322 (s), 1184 (m), 1164 (m), 1127 (m), 1107 (s), 1067 (s), 1034 (m), 1019 (m), 850 (m), 830 (m), 811 (m), 757 (m), 734 (m), 669 (m), 652 (m), 637 (w), 572 (m), 553 (w), 523 (w), 494 (w), 443 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 584 (M^+, 18), 583 (67), 582 (100), 460 (1), 363 (1), 292 (1), 282 (4), 281 (2), 276 (2), 262 (2), 256 (2), 241 (2), 234 (2), 228 (3), 226 (3), 207 (3), 189 (3); HR-MS (ESI): *m/z* = 584.25614, calcd. for $C_{40}H_{33}F_3N$ ($[M+H]^+$): 584.25596.

2,3,5,6-Tetrakis(4-methoxyphenyl)-4-[4-(trifluoromethyl)-phenyl]pyridine (13j): Colorless solid; yield: 68%; mp 191–193 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68 (s, 6H, MeO), 3.75 (s, 6H, MeO), 6.53–6.58 (m, 4H, CH), 6.69–6.76 (m, 8H, CH), 6.85–6.88 (m, 2H, CH), 7.19–7.22 (m, 2H, CH), 7.31–7.37 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.0 (MeO), 55.1 (MeO), 113.0 (CH), 113.2 (CH), 123.9 (q, $^3J_{C,F}$ = 3.8 Hz, CH), 124.1 (q, $^1J_{C,F}$ = 271.2 Hz, CF_3), 128.0 (q, $^2J_{C,F}$ = 32.2 Hz, C), 130.4 (C), 130.7 (CH), 131.5 (CH), 132.1 (C), 132.2 (CH), 133.3 (C), 142.7 (C), 149.1 (C), 155.9 (C), 158.0 (C), 159.0 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −62.1 (CF_3); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2999 (w), 2931 (m), 2834 (w), 1742 (m), 1604 (w), 1509 (m), 1440 (m), 1322 (m), 1245 (s), 1174 (s), 1023 (s), 962 (w), 840 (m), 824 (m), 805 (m), 765 (w), 668 (m), 648 (m), 630 (m), 541 (m), 389 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 648 (M^+, 34), 647 (100), 646 (99), 603 (4), 602 (9), 324 (49), 299 (5), 293 (6), 274 (5), 272 (7), 269 (5), 249 (4), 248 (7), 245 (8), 228 (11), 214 (9), 213 (9), 200 (8), 156 (6); HR-MS (ESI): *m/z* = 648.23596, calcd. for $C_{40}H_{33}F_3NO_4$ ($[M+H]^+$): 648.23562.

2,3,5,6-Tetrakis(4-phenoxyphenyl)-4-[4-(trifluoromethyl)-phenyl]pyridine (13k): Colorless solid; yield: 59%; mp 227–229 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.62–6.81 (m, 16H, CH), 6.86–7.04 (m, 10H, CH), 7.15–7.27 (m, 10H, CH), 7.33–7.38 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 117.7 (CH), 118.2 (CH), 118.8 (CH), 119.2 (CH), 123.1 (CH), 123.4 (CH), 124.0 (q, $^3J_{C,F}$ = 4.1 Hz, CH), 124.1 (q, $^1J_{C,F}$ = 272.6 Hz, CF_3), 128.5 (q, $^2J_{C,F}$ = 32.6 Hz, C), 129.6 (CH), 129.7 (CH), 130.8 (CH), 131.5 (CH), 131.7 (CH), 132.5 (CH), 132.5 (C), 133.1 (C), 135.3 (C), 142.3 (C), 149.3 (C), 155.6 (C), 156.0 (C), 156.8 (C), 157.0 (C), 157.2 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −62.1 (CF_3); IR (ATR): $\tilde{\nu}$ = 3042 (m), 1883 (w), 1608 (m), 1586 (m), 1508 (s), 1488 (s), 1418 (w), 1390 (m), 1324 (m), 1286 (w), 1233 (s), 1198 (m), 1120 (m), 1108 (m), 1068 (m), 1014 (w), 913 (w), 869 (m), 812 (m), 765 (m), 691 (s), 633 (w), 553 (m), 496 (s), 408 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 896 (M^+, 47), 895 (100), 894 (66), 800 (2), 448 (3), 445 (2), 401 (2), 368 (5), 240 (3), 207 (2), 44 (1), 36 (2); HR-MS (ESI): *m/z* = 896.29854, calcd. for $C_{60}H_{41}F_3NO_4$ ($[M+H]^+$): 896.29822.

2,3,5,6-Tetrakis(3-methoxyphenyl)-4-[4-(trifluoromethyl)-phenyl]pyridine (13l): Slightly yellow oil; yield: 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.55 (s, 6H, MeO), 3.65 (s, 6H, MeO), 6.48–6.50 (m, 2H, CH), 6.54–6.57 (m, 2H, CH), 6.65 (ddd, $^3J_{H,H}$ = 8.1 Hz, $^3J_{H,H}$ = 2.8 Hz, $^3J_{H,H}$ = 0.9 Hz, 2H, CH), 6.65 (ddd, $^3J_{H,H}$ = 7.9 Hz, $^3J_{H,H}$ = 2.8 Hz, $^3J_{H,H}$ = 1.1 Hz, 2H, CH), 7.00–7.03 (m, 6H, CH), 7.10–7.23 (m, 4H, CH), 7.29–7.31 (m 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.0 (MeO), 55.0 (MeO), 112.8 (CH), 114.2 (CH), 115.0 (CH), 116.6 (CH), 121.7 (CH), 123.8 (CH), 124.0 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 124.1 (q, $^1J_{C,F}$ = 273.0 Hz, CF_3), 128.5 (q, $^2J_{C,F}$ = 33.7 Hz, C), 128.6 (CH), 128.7 (CH), 130.6 (CH), 133.2 (C), 139.1 (C), 141.6 (C), 142.2 (C), 148.6 (C), 156.2 (C), 158.8 (C), 158.9 (C); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −62.2 (CF_3); IR (ATR): $\tilde{\nu}$ = 3001 (w), 2937 (w), 2834 (w), 1598 (m), 1578 (s), 1534 (m), 1489 (w), 1453 (w), 1425 (m), 1407 (m), 1386 (m), 1322 (s), 1285 (m), 1238 (m), 1160 (m), 1119 (w), 1041 (s), 995 (w), 951 (w), 879 (m), 838 (m), 780 (s), 756 (m), 725 (m), 702 (s), 673 (w), 603 (w), 554 (m), 480 (w), 432 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 648 (M^+, 20), 647 (68), 646 (100), 631 (3), 630 (4), 588 (2), 111 (1), 97 (2), 95 (1), 83 (2), 81 (1), 71 (1), 70 (1), 69 (2), 57 (2), 55 (2), 44 (2), 43 (3); HR-MS (ESI): *m/z* = 648.23568, calcd. for $C_{40}H_{33}F_3NO_4$ ($[M+H]^+$): 648.23562.

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