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Palladium-Catalysed Direct Polyarylation of Pyrrole Derivatives

Liqin Zhao, Christian Bruneau, and Henri Doucet*[a]

The palladium-catalysed direct polyarylation of 1-methylpyrrole and 1-phenylpyrrole was studied. As the C2 and C5 positions of pyrroles are more reactive for C–H bond functionalisation than the C3 and C4 positions, the formation of 2,5-diarylpyrroles was found to proceed selectively in the presence of 3 equiv. of a variety of aryl bromides. The sequential C2 arylation followed by C5 arylation to prepare non-symmetrically substituted 2,5-diarylpyrroles was also studied. For the synthesis of such pyrroles, higher yields were obtained for the couplings with electron-deficient aryl bromides. The tetraarylation of 1-methylpyrrole was also achieved. From 4 equiv. of 3,5-bis-(trifluoromethyl)bromobenzene, the 2,3,4,5-tetraarylated pyrrole was obtained in good yield.

Introduction

The classical palladium-catalysed reactions such as Stille, Suzuki or Negishi couplings allow the formation of a wide variety of polyaryls.[1] However, for these couplings a prior synthesis of (poly)organometallic derivatives is required, which might be difficult, especially with heteroarenes. Moreover, these reactions provide a stoichiometric amount of metallic side products, from which undesired contamination could be harmful for pharmaceutical, agrochemical and related biological applications. As early as 1985, Ohta and co-workers reported that the arylations of several heteroaromatics,[2] including pyrroles, with aryl halides proceed in moderate to good yields through C–H bond activation,[3,4] using $Pd(PPh_3)_4$ as the catalyst. Since these results, the palladium-catalysed direct arylation of pyrroles with aryl halides has proved to be a very powerful method for the synthesis of a wide variety of arylated pyrroles.[5–9]

In palladium-catalysed direct arylation of pyrroles, the most reactive positions are generally the carbons C2 and C5, whereas the positions C3 and C4 display a poor reactivity (Figure 1).[3g]

In most cases, intramolecular arylations[5] or intermolecular C5-arylations of C2-substituted pyrroles have been reported.[7,8] The monoarylation at C2 of some non-substituted 1-alkylpyrroles or 1-arylpyrroles has also been described.[9] On the other hand, to our knowledge only one example of a palladium-catalysed diarylation of a pyrrole has been reported.[10] From 1-methylpyrrole and 4-(trifluoromethyl)phenyliodide, Shibahara and co-workers obtained the 2,5-diarylated 1-methylpyrrole in 79% yield by using Pd(1,10-phenanthroline)$_2$(PF_6)$_2$ (5 mol%) as the catalyst. Notably, Ackermann and co-workers have also reported an elegant regioselective 2,5-diarylation of an *N*-pyridylpyrrole and also of an *N*-pyrimidylpyrrole using a ruthenium catalyst.[11] For these reactions, the pyridyl or pyrimidyl substituent on the nitrogen atom acted as a directing group to favour the regioselective arylations at both C2 and C5 positions of the pyrrole. However, the Suzuki, Stille and Negishi coupling reactions remain the most classic methods to prepare polyarylated pyrrole derivatives.[12] For example, in 2009 Dauban and co-workers described the 2,5-diarylation of a 2,5-dibromopyrrole through Suzuki coupling.[12d]

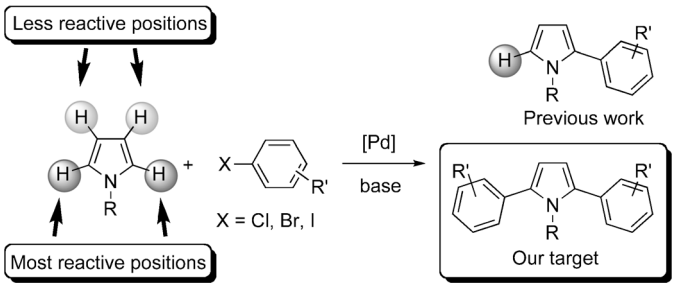

Figure 1. Regioselectivity of the arylation of pyrroles.

As only one example of a palladium-catalysed direct diarylation of pyrrole derivatives has been reported, the discovery of a procedure allowing a more general access to symmetrically or non-symmetrically substituted 2,5-diarylpyrroles is desirable.

Recently we have reported that the reaction of pyrroles with various substituents at C2 with aryl bromides using KOAc as the base, *N*,*N*-dimethylacetamide (DMAc) as the solvent and $Pd(OAc)_2$ as the catalyst led to the C5 arylated heteroaromatics in high yield.[13] We have also reported a few examples of monoarylation of 1-methylpyrrole.

Herein, starting from 1-methylpyrrole or 1-phenylpyrrole as the reactants, we report on a catalytic system based on palladium which gives access to 1) symmetrically 2,5-diarylated pyr-

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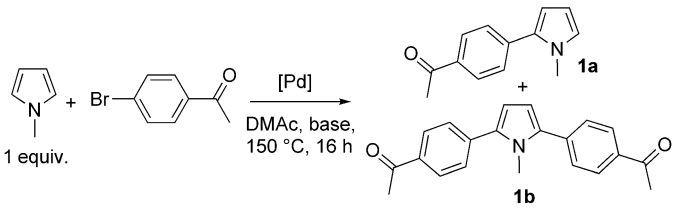
roles with a set of aryl bromides, 2) 2,3,4,5-tetraarylated pyrroles and 3) unsymmetrically 2,5-diarylated pyrroles through sequential C2 catalytic arylation followed by C5 catalytic arylation.

Results and Discussion

Firstly, we considered the reaction of 1-methylpyrrole with 4-bromoacetophenone to form the 2,5-diarylated pyrrole **1b** (Scheme 1). We observed that from 4-bromoacetophenone (2.2 equiv.) and 1-methylpyrrole (1 equiv.) with KOAc (4 equiv.)



Scheme 1. Palladium-catalysed 2,5-diarylation of 1-methylpyrrole with 4-bromoacetophenone.

as the base, DMAc as the solvent and a catalyst loading of only 0.1 mol% $Pd(OAc)_2$, the 2,5-diarylated pyrrole **1b** was obtained only in low yield because of the formation of a mixture of mono- and diarylated pyrroles **1a** and **1b** (Table 1, entry 1). The use of a higher $Pd(OAc)_2$ load (1 mol%, Table 1, entry 2) did not improve the yield. These results reveal that the concentration of active Pd species is relatively similar across these two different concentrations of $Pd(OAc)_2$. In this ligand-free procedure with relatively high palladium concentrations, so-called "palladium black" forms rapidly, which is inactive in such catalyses. Consequently, the conversions of aryl bromides and the yields of coupling products are not increased by a higher catalyst loading.

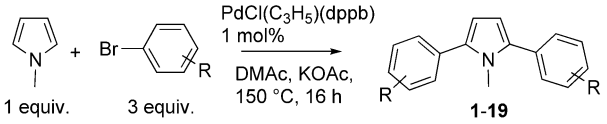
Table 1. Influence of the reaction conditions on the palladium-catalysed direct 2,5-diarylation of 1-methylpyrrole with 4-bromoacetophenone (Scheme 1).[a]

Entry	Catalyst [mol%]	4-bromoacetophenone [equiv.]	Yield of **1b** [%]
1	$Pd(OAc)_2$ (0.1)	2.2	27
2	$Pd(OAc)_2$ (1)	2.5	21
3	$PdCl(C_3H_5)(dppb)$ (1)	2.5	42
4	$PdCl(C_3H_5)(dppb)$ (1)	3	46
5	$PdCl(C_3H_5)(dppb)$ (1)	4	30

[a] 1-methylpyrrole (1 equiv.), KOAc (4 equiv.), DMAc, $T = 150\,^{\circ}C$, $t = 16$ h, isolated yields of **1b**.

Therefore, we employed $PdCl(C_3H_5)(dppb)$ [dppb = 1,4-bis(diphenylphosphino)butane] 1 mol% as the catalyst, which forms palladium black less rapidly. Moreover, we have recently demonstrated that this catalyst was among the best catalyst for the direct arylation of some thiophenes.[4b] A higher yield of 42% of **1b** was obtained if 2.5 equivalents of 4-bromoacetophenone were employed with this catalyst (Table 1, entry 3). Then, we employed a larger excess of 4-bromoacetophenone. With 3 equivalents of this aryl bromide, a yield of 46% of **1b** was obtained, whereas the use of 4 equivalents led to a lower yield of 30% (Table 1, entries 4 and 5).

Then, we examined the scope of this procedure using *para*-, *meta*- or *ortho*-substituted aryl bromides and also heteroaryl bromides (Scheme 2, Table 2). The electron-deficient *para*-sub-

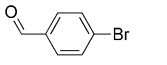
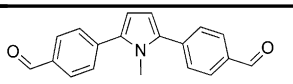
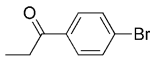
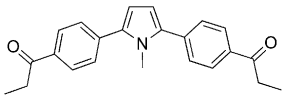
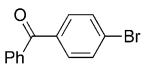
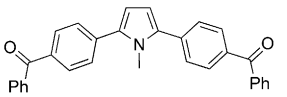
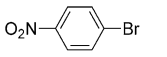
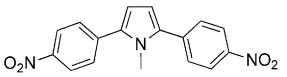
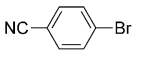
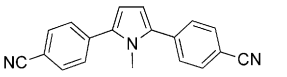
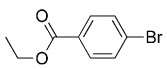
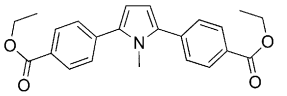
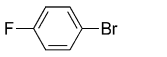
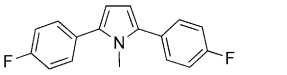
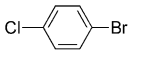
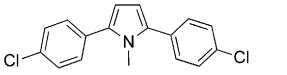
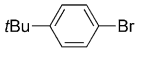
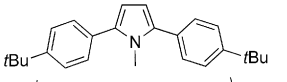
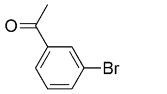
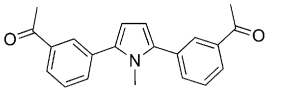
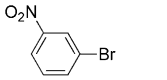
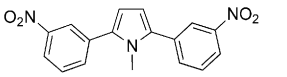
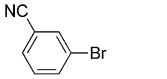
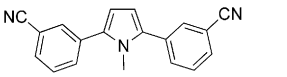
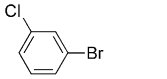
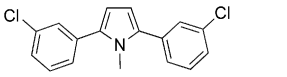
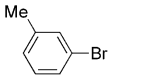
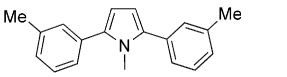
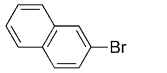
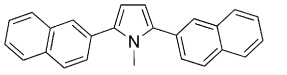
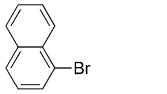
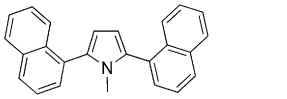
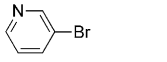
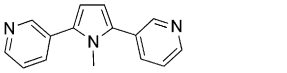
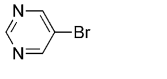
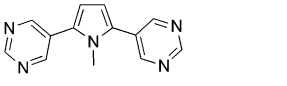


Scheme 2. Palladium-catalysed 2,5-diarylation of 1-methylpyrrole.

stituted aryl bromides, 4-bromobenzaldehyde, 4-bromopropiophenone, 4-bromobenzophenone, 4-bromonitrobenzene or 4-bromobenzonitrile reacted with 1-methylpyrrole to give the expected products **2**–**6** in 58–69% yields (Table 2, entries 1–5). A high yield of 81% of **7** was obtained with ethyl 4-bromobenzoate (Table 2, entry 6). From 4-chlorobromobenzene, **9** was obtained in 62% yield (Table 2, entry 8). In the course of this reaction no cleavage of the C–Cl bond was observed, which allows for further transformations. Surprisingly, even the electron-rich aryl bromide, 4-*tert*-butylbromobenzene was successfully coupled with 1-methylpyrrole to give **10** in 52% yield (Table 2, entry 9). A set of *meta*-substituted aryl bromides was also employed. The best yields were obtained from 3-bromoacetophenone and 3-bromonitrobenzene to give **11** and **12** in 78 and 80% yields, respectively (Table 2, entries 10 and 11). Lower yields of **13**–**15** were obtained in the presence of 3-bromobenzonitrile, 3-chlorobromobenzene and 3-bromotoluene, respectively (Table 2, entries 12–14). 1- and 2-bromonaphthalenes also gave the desired products **16** and **17** in 65 and 68% yields, respectively (Table 2, entries 15 and 16). We also employed heteroaryl bromides. The first attempt to prepare **18** from 3-bromopyridine led to a mixture of di- and triarylated pyrroles, and **18** was isolated in only 41% yield (Table 2, entry 17). However, the use of only 2.3 equivalents instead of 3 equivalents of 3-bromopyridine allowed us to obtain **18** in a higher yield of 62% (Table 2, entry 18). A more selective reaction was observed in the presence of 5-bromopyrimidine, which gave **19** in 71% yield (Table 2, entry 19).

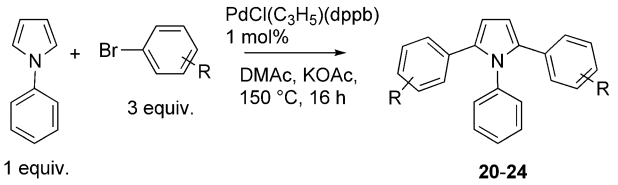
Then, arylation reactions of 1-phenylpyrrole with aryl bromides were examined (Scheme 3, Table 3). With this reactant, again only the C2 and C5 diarylated pyrroles **20**–**24** were isolated; however, in lower yield than with 1-methylpyrrole. Firstly, we studied the reactivity of two *para*-substituted aryl bromides. In the presence of 4-chlorobromobenzene or 4-bromotoluene, the products **20** and **21** were obtained in 35 and 33% yields, respectively (Table 3, entries 1 and 2). Higher yields of 54 and 52% were obtained in the presence of the *meta*-substituted aryl bromides, 3-bromobenzonitrile or 3-chlorobromo-

Table 2. Scope of the palladium-catalysed direct 2,5-diarylation of 1-methylpyrrole (Scheme 2).[a]

Entry	Aryl bromide	Product		Yield [%]
1			**2**	69
2			**3**	60
3			**4**	62
4			**5**	67
5			**6**	58
6			**7**	81
7			**8**	69
8			**9**	62
9			**10**	52
10			**11**	78
11			**12**	80
12			**13**	61
13			**14**	63
14			**15**	62
15			**16**	65
16			**17**	68
17 18			**18**	41 62[b]
19			**19**	71

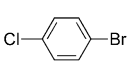
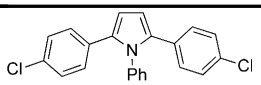
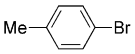
[a] $PdCl(C_3H_5)(dppb)$ (0.01 equiv.), aryl bromide (3 equiv.), 1-methylpyrrole (1 equiv.), KOAc (4 equiv.), DMAc, $T = 150\,^{\circ}C$, $t = 16$ h, isolated yields. [b] 3-bromopyridine (2.3 equiv.).

benzene, respectively (Table 3, entries 3 and 4). Finally, from 5-bromopyrimidine, **24** was formed in 51% yield.



Scheme 3. Palladium-catalysed 2,5-diarylation of 1-phenylpyrrole.

Table 3. Scope of the palladium-catalysed direct 2,5-diarylation of 1-phenylpyrrole (Scheme 3).[a]

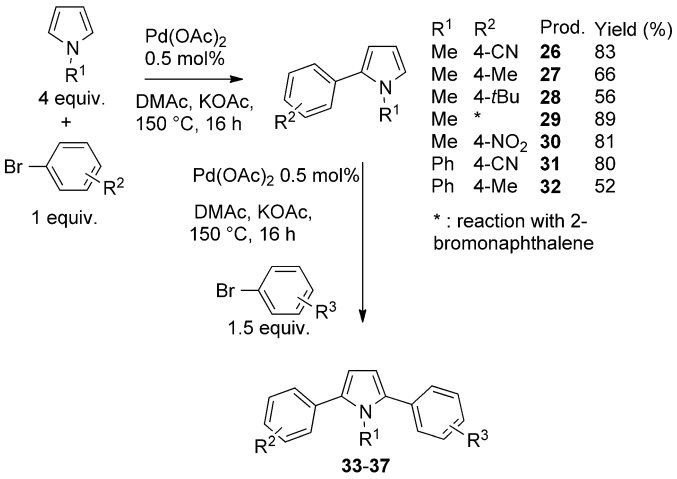
Entry	Aryl bromide	Product		Yield [%]
1			**20**	35
2			**21**	33
3			**22**	54
4			**23**	52
5			**24**	51

[a] $PdCl(C_3H_5)(dppb)$ (0.01 equiv.), aryl bromide (3 equiv.), 1-phenylpyrrole (1 equiv.), KOAc (4 equiv.), DMAc, $T = 150\,^{\circ}C$, $t = 16$ h, isolated yields.

The reactivity of 3,5-bis(trifluoromethyl)bromobenzene with 1-methylpyrrole was unusual compared to that of the other aryl bromides. The reaction of 3 equivalents of this aryl bromide with 1-methylpyrrole led to a mixture of di-, tri- and even some tetraarylated pyrroles according to GC–MS analysis. Therefore, to obtain the 2,3,4,5-tetraarylated pyrrole **25** more selectively, we employed 4 equivalents of this aryl bromide. Under these conditions, **25** was the major product with 85% selectivity and 62% yield (Scheme 4).

Scheme 4. Palladium-catalysed tetraarylation of 1-methylpyrrole.

Then, we studied the sequential C2 arylation followed by a C5 different arylation of pyrroles to prepare non-symmetrical 2,5-diarylpyrroles (Scheme 5, Table 4). The yields of the palladium-catalysed C5 direct arylations of 2-arylpyrroles were assumed to depend on the electronic properties of the aryl sub-



R^1	R^2	Prod.	Yield (%)
Me	4-CN	**26**	83
Me	4-Me	**27**	66
Me	4-*t*Bu	**28**	56
Me	*	**29**	89
Me	4-NO_2	**30**	81
Ph	4-CN	**31**	80
Ph	4-Me	**32**	52

Scheme 5. Palladium-catalysed sequential 2,5-diarylation of 1-methylpyrrole.

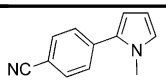
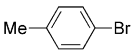
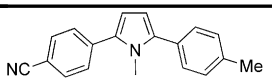
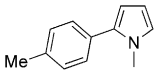
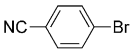
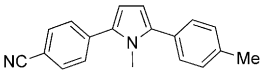
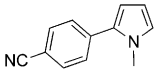
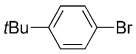
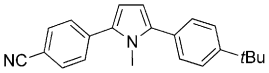
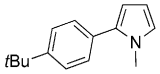
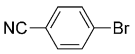
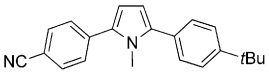
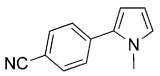
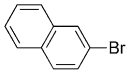
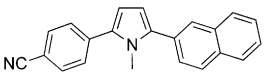
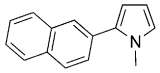
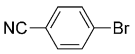
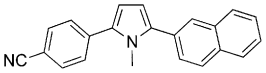
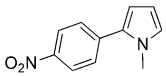
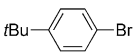
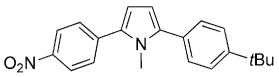
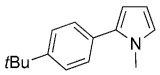
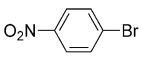
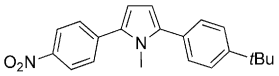
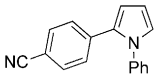
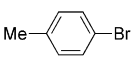
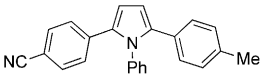
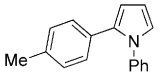
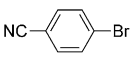
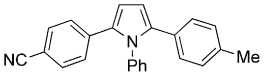
stituents both on the pyrrole and the aryl bromide. Therefore, we initially compared the reaction yields by using the two possible combinations of starting materials to prepare a specific 2,5-diarylpyrrole. For both steps we employed 0.5 mol% $Pd(OAc)_2$ as the catalyst because we previously observed that such phosphine-free conditions allows efficient direct monoarylation of some pyrrole derivatives.[13]

For the first reaction step (Scheme 5, top), the electron-deficient aryl bromides, 4-bromobenzonitrile and 4-bromonitrobenzene, gave the C2 monoarylated products **26**, **30** and **31** very selectively. The C2,C5 diarylated pyrroles were only produced as traces. A high yield of **29** was also obtained from 2-bromonaphthalene. On the other hand, the reactions with 4-bromotoluene and 4-*tert*-butylbromobenzene surprisingly gave mixtures of mono- and diarylated pyrroles (mono-/diarylation ratio of 75:25), although we employed a 1:4 ratio of aryl bromide and pyrrole derivative. The second arylation step of pyrroles appeared to be favoured by the presence of electron-donating groups on the aryl substituent of 2-arylpyrroles.

For the C5 arylation step, we observed that the reaction of 4-bromotoluene with **26** gave **33** in 52% yield, whereas the reaction of 4-bromobenzonitrile with **27** led to **33** in 71% yield (Table 4, entries 1 and 2). Product **34** was also obtained in much higher yield by coupling of 4-bromobenzonitrile with **28** than by using 4-*tert*-butylbromobenzene and **26** (Table 4, entries 3 and 4). On the other hand, very similar yields in **35** were obtained by both reaction pathways (Table 4, entries 5 and 6). For the synthesis of **36** and **37**, again the best yields were obtained by using the most electron-deficient aryl bromide in the second step (Table 4, entries 7–10). In summary, for the synthesis of non-symmetrical 2,5-diarylpyrroles, high yields were obtained for both reaction steps with electron-deficient aryl bromides. On the other hand, with electron-rich aryl bromides, moderate yields were obtained because of the formation of some 2,5-diarylpyrroles in the reaction with 1-methylpyrrole or the poor reactivity of the aryl bromides in the C5 arylation of some 2-arylpyrroles.

Finally, the 4,4′-diheteroarylation of 4,4′-dibromobiphenyl was studied (Scheme 6). From 1-methylpyrrole (3 equiv.) and 4,4′-dibromobiphenyl (1 equiv.) in the presence of 1 mol% $PdCl(C_3H_5)$(dppb), the desired product **38** was produced in 81% yield (Scheme 6).

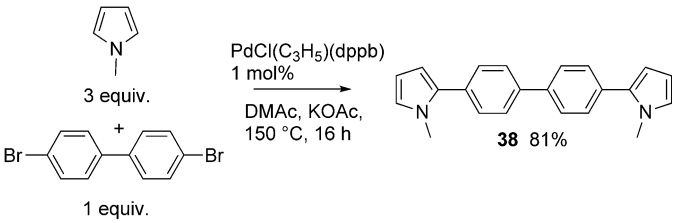
Table 4. Scope of the palladium-catalysed direct sequential 2,5-diarylation of 1-methyl- or 1-phenyl-2-arylpyrroles (Scheme 5).[a]

Entry	Pyrrole		Aryl bromide	Product		Yield [%]
1		**26**			**33**	52
2		**27**			**33**	71
3		**26**			**34**	32
4		**28**			**34**	74
5		**26**			**35**	87
6		**29**			**35**	90
7		**30**			**36**	42
8		**28**			**36**	80
9		**31**			**37**	55
10		**32**			**37**	86

[a] $Pd(OAc)_2$ (0.005 equiv.), aryl bromide (1.5 equiv.), 1-methyl- or 1-phenyl-2-arylpyrrole (1 equiv.), KOAc (2 equiv.), DMAc, $T = 150\,^{\circ}C$, $t = 16$ h, isolated yields.

Conclusions

We have demonstrated that the palladium-catalysed direct diarylation at C2 and C5 of 1-methylpyrrole or 1-phenylpyrrole using $PdCl(C_3H_5)$(dppb) [dppb = 1,4-bis(diphenylphosphino)butane]



Scheme 6. Palladium-catalysed arylation of 1-methylpyrrole with 4,4′-dibromobiphenyl.

1 mol% as the catalyst and KOAc as the base proceeds with electron-poor and some electron-rich aryl bromides. A variety of substituents on the aryl bromide such as ester, acetyl, formyl, propionyl, benzoyl, nitro, nitrile, chloro, fluoro or *tert*-butyl is tolerated. The sequential C2 arylation of 1-methylpyrrole or 1-phenylpyrrole followed by C5 arylation reveals that electron-deficient aryl bromides should be employed preferably. Notably, from 3,5-bis(trifluoromethyl)bromobenzene and 1-methylpyrrole, the 2,3,4,5-tetrarylated product was formed in good yield. To our knowledge, this is the first example of a catalysed direct tetraarylation of a pyrrole. Moreover, these arylations were performed with only 0.5–1 mol% of air-stable catalysts. The major by-products of these reactions are a base associated to HBr, and the method does not require the initial preparation of a requisite (poly)organometallic compound, thus reducing the number of reaction steps. For these reasons, this process gives an economically viable and environmentally attractive access to polyarylated pyrrole derivatives.

Experimental Section

DMAc (*N*,*N*-dimethylacetamide) (99%) was purchased from Acros. KOAc (99%), $[Pd(C_3H_5)Cl]_2$ (56.5%) and dppb [1,4-bis(diphenylphosphino)butane] (98%) were purchased from Alfa Aesar. These compounds were not purified before use.

Preparation of the $PdCl(C_3H_5)$(dppb) catalyst:[14] An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere was charged with $[Pd(C_3H_5)Cl]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). Anhydrous dichloromethane (10 mL) was added and the solution was stirred at RT for 20 min. The solvent was removed in vacuum. The yellow powder was used without purification. ^{31}P NMR (81 MHz, $CDCl_3$): $\delta =$ 19.3 ppm (s).

General procedure for syntheses of 1–24: As a typical experiment, reaction of the aryl bromide (3 mmol), 1-methylpyrrole (0.081 g, 1 mmol) or 1-phenylpyrrole (0.143 g, 1 mmol), and KOAc (0.392 g, 4 mmol) at 150 °C during 16 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) under argon afforded the corresponding diarylation product after extraction with dichloromethane, evaporation and filtration on silica gel.

2,5-Bis(4-acetylphenyl)-1-methylpyrrole 1b: From 4-bromoacetophenone (0.597 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **1** was obtained in 46% (0.146 g) yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.95$ (d, $J = 7.8$ Hz, 4H), 7.50 (d, $J = 7.8$ Hz, 4H), 6.39 (s, 2H), 3.61 (s, 3H), 2.56 ppm (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 197.5$, 137.5, 137.3, 135.3, 128.7, 128.2, 110.7, 35.0, 26.6 ppm. Elemental analysis: calcd (%) for $C_{21}H_{19}NO_2$ (317.38): C 79.47, H 6.03, N 4.41; found: C 79.69, H 6.09, N 4.31.

2,5-Bis(4-formylphenyl)-1-methylpyrrole 2: From 4-bromobenzaldehyde (0.555 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **2** was obtained in 69% (0.200 g) yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 9.96$ (s, 2H), 7.87 (d, $J = 7.0$ Hz, 4H), 7.57 (d, $J = 7.0$ Hz, 4H), 6.43 (s, 2H), 3.63 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 191.6$, 138.7, 137.6, 134.7, 130.1, 128.6, 111.4, 35.2 ppm. Elemental analysis: calcd (%) for $C_{19}H_{15}NO_2$ (289.33): C 78.87, H 5.23, N 4.84; found: C 78.96, H 5.35, N 4.89.

2,5-Bis(4-propionylphenyl)-1-methylpyrrole 3: From 4-bromopropiophenone (0.639 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **3** was obtained in 60% (0.207 g) yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.96$ (d, $J = 7.0$ Hz, 4H), 7.50 (d, $J = 7.0$ Hz, 4H), 6.38 (s, 2H), 3.61 (s, 3H), 2.96 (q, $J = 7.5$ Hz, 4H), 1.19 ppm (t, $J =$ 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 200.2$, 137.4, 137.3, 135.1, 128.4, 128.3, 110.6, 34.9, 31.7, 8.3 ppm. Elemental analysis: calcd (%) for $C_{23}H_{23}NO_2$ (345.43): C 79.97, H 6.71, N 4.05; found: C 80.11, H 6.64, N 3.89.

{4-[5-(4-Benzoyl-phenyl)-1-methylpyrrol-2-yl]-phenyl}-phenylmethanone 4: From 4-bromobenzophenone (0.783 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **4** was obtained in 62% (0.273 g) yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.83$ (d, $J =$ 7.6 Hz, 4H), 7.78 (d, $J = 7.6$ Hz, 4H), 7.60–7.50 (m, 6H), 7.44 (t, $J =$ 7.6 Hz, 4H), 6.42 (s, 2H), 3.67 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 196.1$, 137.7, 137.3, 137.1, 135.7, 132.4, 130.6, 130.0, 128.3, 128.0, 110.7, 35.0 ppm. Elemental analysis: calcd (%) for $C_{31}H_{23}NO_2$ (441.52): C 84.33, H 5.25, 3.17; found: C 84.21, H 5.01, N 3.28.

2,5-Bis(4-nitrophenyl)-1-methylpyrrole 5:[15] From 4-bromonitrobenzene (0.606 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **5** was obtained in 67% (0.216 g) yield.

2,5-Bis(4-cyanophenyl)-1-methylpyrrole 6:[5g] From 4-bromobenzonitrile (0.546 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **6** was obtained in 58% (0.164 g) yield.

2,5-Bis(ethyl 4-benzoate)-1-methylpyrrole 7: From ethyl 4-bromobenzoate (0.687 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **7** was obtained in 81% (0.305 g) yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.03$ (d, $J = 7.0$ Hz, 4H), 7.47 (d, $J = 7.0$ Hz, 4H), 6.37 (s, 2H), 4.33 (q, $J = 7.5$ Hz, 4H), 3.59 (s, 3H), 1.34 ppm (t, $J = 7.5$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 166.4$, 137.3, 137.2, 129.8, 128.7, 128.1, 110.4, 61.0, 34.9, 14.4 ppm. Elemental analysis: calcd (%) for $C_{23}H_{23}NO_4$ (377.43): C 73.19, H 6.14, N 3.71; found: C 73.04, H 6.10, N 3.88.

2,5-Bis(4-fluorophenyl)-1-methylpyrrole 8: From 4-fluorobromobenzene (0.525 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **8** was obtained in 69% (0.186 g) yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.34$ (dd, $J = 8.6$, 5.4 Hz, 4H), 7.04 (t, $J = 8.6$ Hz, 4H), 6.19 (s, 2H), 3.47 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta =$ 162.0 (d, $J = 246.8$ Hz), 135.7, 130.4 (d, $J = 8.0$ Hz), 129.6, 115.4 (d, $J = 21.5$ Hz), 108.6, 33.9 ppm. Elemental analysis: calcd (%) for $C_{17}H_{13}F_2N$ (269.29): C 75.82, H 4.87, N 5.20; found: C 75.90, H 4.74, N 5.39.

2,5-Bis(4-chlorophenyl)-1-methylpyrrole 9: From 4-bromochlorobenzene (0.574 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **9** was obtained in 62% (0.187 g) yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.30$ (s, 8H), 6.22 (s, 2H), 3.48 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 136.1$, 132.9, 131.8, 129.9, 128.7, 109.2,

34.3 ppm. Elemental analysis: calcd (%) for $C_{17}H_{13}Cl_2N$ (302.20): C 67.57, H 4.34, N 4.63; found: C 67.47, H 4.30, N 4.50.

2,5-Bis(4-*tert*-butylphenyl)-1-methylpyrrole 10: From 4-*tert*-butylbromobenzene (0.639 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **10** was obtained in 52% (0.179 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.36 (d, J = 7.0 Hz, 4H), 7.33 (d, J = 7.0 Hz, 4H), 6.21 (s, 2H), 3.54 (s, 3H), 1.29 ppm (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 149.7, 136.6, 130.8, 128.4, 125.3, 108.3, 34.6, 34.3, 31.4 ppm. Elemental analysis: calcd (%) for $C_{25}H_{31}N$ (345.52): C 86.90, H 9.04, N 4.05; found: C 86.98, H 9.18, N 4.23.

2,5-Bis(3-acetylphenyl)-1-methylpyrrole 11: From 3-bromoacetophenone (0.597 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **11** was obtained in 78% (0.247 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.99 (s, 2H), 7.83 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 6.31 (s, 2H), 3.55 (s, 3H), 2.58 ppm (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 198.0, 137.4, 136.4, 133.8, 133.1, 128.9, 128.4, 126.8, 109.5, 34.3, 26.7 ppm. Elemental analysis: calcd (%) for $C_{21}H_{19}NO_2$ (317.38): C 79.47, H 6.03, N 4.41; found: C 79.35, H 6.11, N 4.65.

2,5-Bis(3-nitrophenyl)-1-methylpyrrole 12: From 3-bromonitrobenzene (0.606 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **12** was obtained in 80% (0.258 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.27 (s, 2H), 8.12 (d, J = 7.9 Hz, 2H), 7.74 (d, J = 7.9 Hz, 2H), 7.55 (t, J = 7.5 Hz, 2H), 6.39 (s, 2H), 3.61 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 148.5, 135.7, 134.5, 134.2, 129.6, 123.1, 121.8, 110.7, 34.5 ppm. Elemental analysis: calcd (%) for $C_{17}H_{13}N_3O_4$ (323.30): C 63.15, H 4.05, N 13.00; found: C 63.31, H 4.14, N 12.89.

2,5-Bis(3-cyanophenyl)-1-methylpyrrole 13: From 3-bromobenzonitrile (0.546 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **13** was obtained in 61% (0.172 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.67 (s, 2H), 7.62 (d, J = 7.9 Hz, 2H), 7.52 (d, J = 7.9 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 6.31 (s, 2H), 3.53 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 135.6, 134.3, 132.7, 131.8, 130.5, 129.5, 118.6, 113.0, 110.5, 34.4 ppm. Elemental analysis: calcd (%) for $C_{19}H_{13}N_3$ (283.33): C 80.54, H 4.62, N 14.83; found: C 80.68, H 4.78, N 14.99.

2,5-Bis(3-chlorophenyl)-1-methylpyrrole 14: From 3-bromochlorobenzene (0.574 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **14** was obtained in 63% (0.190 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.36 (s, 2H), 7.30–7.22 (m, 4H), 7.19 (t, J = 7.5 Hz, 2H), 6.24 (s, 2H), 3.51 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 136.0, 135.0, 134.4, 129.8, 128.6, 127.0, 126.7, 109.6, 34.4 ppm. Elemental analysis: calcd (%) for $C_{17}H_{13}Cl_2N$ (302.20): C 67.57, H 4.34, N 4.63; found: C 67.69, H 4.48, N 4.82.

2,5-Bis(*m*-tolyl)-1-methylpyrrole 15: From 3-bromotoluene (0.513 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **15** was obtained in 62% (0.162 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.30–7.15 (m, 6H), 7.05 (d, J = 7.8 Hz, 2H), 6.22 (s, 2H), 3.51 (s, 3H), 2.33 ppm (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 138.0, 136.9, 133.6, 129.5, 128.3, 127.6, 125.8, 108.6, 34.3, 21.5 ppm. Elemental analysis: calcd (%) for $C_{19}H_{19}N$ (261.36): C 87.31, H 7.33, N 5.36; found: C 87.47, H 7.14, N 5.47.

1-Methyl-2,5-dinaphthalen-2-ylpyrrole 16: From 2-bromonaphthalene (0.621 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **16** was obtained in 65% (0.216 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.88 (s, 2H), 7.85–7.80 (m, 6H), 7.60 (d, J = 7.8 Hz, 2H), 7.45–7.40 (m, 4H), 6.41 (s, 2H), 3.69 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 137.3, 133.5, 132.3, 130.9, 128.0, 127.9, 127.7, 127.1, 127.0, 126.4, 125.9, 109.5, 34.7 ppm. Elemental analysis: calcd (%) for $C_{25}H_{19}N$ (333.43): C 90.06, H 5.74, N 4.20; found: C 90.11, H 5.60, N 4.11.

1-Methyl-2,5-dinaphthalen-1-ylpyrrole 17:[16] From 1-bromonaphthalene (0.621 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **17** was obtained in 68% (0.227 g) yield.

2,5-Bis(pyridin-3-yl)-1-methylpyrrole 18: From 3-bromopyridine (0.363 g, 2.3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **18** was obtained in 62% (0.146 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.69 (s, 2H), 8.50 (d, J = 4.9 Hz, 2H), 7.70 (d, J = 7.7 Hz, 2H), 7.30 (dd, J = 7.7, 4.9 Hz, 2H), 6.34 (s, 2H), 3.56 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 149.5, 148.2, 135.7, 134.0, 129.1, 123.4, 110.2, 34.1 ppm. Elemental analysis: calcd (%) for $C_{15}H_{13}N_3$ (235.28): C 76.57, H 5.57, N 17.86; found: C 76.69, H 5.40, N 17.69.

2,5-Bis(pyrimidin-5-yl)-1-methylpyrrole 19: From 5-bromopyrimidine (0.477 g, 3 mmol) and 1-methylpyrrole (0.081 g, 1 mmol), **19** was obtained in 71% (0.168 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.12 (s, 2H), 8.80 (s, 4H), 6.44 (s, 2H), 3.60 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.2, 155.8, 131.1, 127.1, 111.5, 34.0 ppm. Elemental analysis: calcd (%) for $C_{13}H_{11}N_5$ (237.26): C 65.81, H 4.67, N 29.52; found: C 65.79, H 4.79, N 29.68.

2,5-Bis(4-chlorophenyl)-1-phenylpyrrole 20: From 4-bromochlorobenzene (0.574 g, 3 mmol) and 1-phenylpyrrole (0.143 g, 1 mmol), **20** was obtained in 35% (0.127 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.25–7.15 (m, 5H), 7.07 (d, J = 7.9 Hz, 4H), 6.89 (d, J = 7.9 Hz, 4H), 6.39 ppm (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 138.5, 134.9, 132.3, 131.5, 129.8, 129.1, 128.8, 128.2, 127.7, 110.3 ppm. Elemental analysis: calcd (%) for $C_{22}H_{15}Cl_2N$ (364.27): C 72.54, H 4.15, N 3.85; found: C 72.39, H 4.07, N 4.02.

2,5-Bis(4-methylphenyl)-1-phenylpyrrole 21: From 4-bromotoluene (0.513 g, 3 mmol) and 1-phenylpyrrole (0.143 g, 1 mmol), **21** was obtained in 33% (0.107 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.17–7.10 (m, 3H), 7.00–6.92 (m, 2H), 6.90–6.80 (m, 8H), 6.35 (s, 2H), 2.18 ppm (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 139.2, 135.8, 135.7, 130.5, 129.0, 128.7, 128.6, 128.5, 127.1, 109.5, 21.1 ppm. Elemental analysis: calcd (%) for $C_{24}H_{21}N$ (323.43): C 89.12, H 6.54, N 4.33; found: C 89.20, H 6.68, N 4.25.

2,5-Bis(3-cyanophenyl)-1-phenylpyrrole 22: From 3-bromobenzonitrile (0.546 g, 3 mmol) and 1-phenylpyrrole (0.143 g, 1 mmol), **22** was obtained in 54% (0.186 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.40–7.10 (m, 10H), 6.97–6.90 (m, 3H), 6.48 ppm (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 137.7, 134.3, 134.0, 132.6, 131.8, 129.9, 129.5, 128.8, 128.6, 128.5, 118.6, 112.4, 111.4 ppm. Elemental analysis: calcd (%) for $C_{24}H_{15}N_3$ (345.40): C 83.46, H 4.38, N 12.17; found: C 83.61, H 4.17, N 12.35.

2,5-Bis(3-chlorophenyl)-1-phenylpyrrole 23: From 3-bromochlorobenzene (0.574 g, 3 mmol) and 1-phenylpyrrole (0.143 g, 1 mmol), **23** was obtained in 52% (0.189 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.25–7.15 (m, 3H), 7.05–6.90 (m, 8H), 6.77 (d, J = 7.9 Hz, 2H), 6.42 ppm (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 138.3, 134.8, 134.7, 133.8, 129.1, 129.0, 128.8, 128.5, 127.9, 126.7, 126.4, 110.7 ppm. Elemental analysis: calcd (%) for $C_{22}H_{15}Cl_2N$ (364.27): C 72.54, H 4.15, N 3.85; found: C 72.66, H 4.25, N 3.64.

2,5-Bis(pyrimidin-5-yl)-1-phenylpyrrole 24: From 5-bromopyrimidine (0.477 g, 3 mmol) and 1-phenylpyrrole (0.143 g, 1 mmol), **24** was obtained in 51% (0.152 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.93 (s, 2H), 8.35 (s, 4H), 7.40–7.28 (m, 3H), 7.03 (d, J = 7.8 Hz, 2H), 6.62 ppm (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 156.5, 155.4, 137.0, 130.7, 130.1, 129.3, 128.6, 126.8, 112.1 ppm. Ele-

mental analysis: calcd (%) for $C_{18}H_{13}N_5$ (299.33): C 72.23, H 4.38, N 23.40; found: C 72.31, H 4.24, N 23.19.

2,3,4,5-Tetrakis-(3,5-bis-trifluoromethylphenyl)-1-methylpyrrole 25: The reaction of 3,5-bis-(trifluoromethyl)bromobenzene (1.172 g, 4 mmol), 1-methylpyrrole (0.081 g, 1 mmol) and KOAc (0.392 g, 4 mmol) at 150 °C during 16 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) under argon affords after extraction with dichloromethane, evaporation and filtration on silica gel the tetraarylation product **25** in 62% (0.576) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.84 (s, 2H), 7.11 (s, 4H), 7.56 (s, 2H), 7.26 (s, 4H), 3.46 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 135.1, 132.7, 132.6 (q, J = 33.9 Hz), 131.9 (q, J = 33.5 Hz), 131.3, 130.9 (m), 130.2 (m), 122.6 (q, J = 272.7 Hz), 122.5 (q, J = 272.7 Hz), 122.4 (m), 121.8, 120.5 (m), 33.8 ppm. Elemental analysis: calcd (%) for $C_{37}H_{15}F_{24}N$ (929.48): C 47.81, H 1.63, N 1.51; found: C 47.99, H 1.97, N 1.36.

General procedure for the synthesis of 26–32: As a typical experiment, the reaction of the aryl bromide (1 mmol), 1-methylpyrrole (0.324 g, 4 mmol) or 1-phenylpyrrole (0.572 g, 4 mmol), and KOAc (0.196 g, 2 mmol) at 150 °C during 16 h in DMAc (3 mL) in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) under argon afforded the corresponding arylation product after extraction with dichloromethane, evaporation and filtration on silica gel.

4-(1-Methylpyrrol-2-yl)-benzonitrile 26:[13] From 4-bromobenzonitrile (0.182 g, 1 mmol) and 1-methylpyrrole (0.324 g, 4 mmol), **26** was obtained in 83% (0.151 g) yield.

1-Methyl-2-*p*-tolylpyrrole 27:[17] From 4-bromotoluene (0.171 g, 1 mmol) and 1-methylpyrrole (0.324 g, 4 mmol), **27** was obtained in 66% (0.113 g) yield.

2-(4-*tert*-Butylphenyl)-1-methylpyrrole 28: From 4-*tert*-butylbromobenzene (0.213 g, 1 mmol) and 1-methylpyrrole (0.324 g, 4 mmol), **28** was obtained in 56% (0.119 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.33 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 6.61 (s, 1H), 6.15–6.06 (m, 2H), 3.57 (s, 3H), 1.27 ppm (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 149.7, 134.6, 130.5, 128.4, 125.3, 123.3, 108.4, 107.7, 35.1, 34.6, 31.4 ppm. Elemental analysis: calcd (%) for $C_{15}H_{19}N$ (213.32): C 84.46, H 8.98, N 6.57; found: C 84.5, H 8.79, N 6.40.

1-Methyl-2-naphthalen-2-ylpyrrole 29: From 2-bromonaphthalene (0.207 g, 1 mmol) and 1-methylpyrrole (0.324 g, 4 mmol), **29** was obtained in 89% (0.184 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.07–8.00 (m, 4H), 7.77 (d, J = 7.8 Hz, 1H), 7.71–7.62 (m, 2H), 6.94 (m, 1H), 6.61 (m, 1H), 6.50 (m, 1H), 3.86 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 134.6, 133.5, 132.2, 130.8, 128.0, 127.9, 127.7, 127.2, 127.0, 126.4, 125.9, 124.0, 109.2, 108.0, 35.3 ppm. Elemental analysis: calcd (%) for $C_{15}H_{13}N$ (207.27): C 86.92, H 6.32, N 6.76; found: C 86.99, H 6.24, N 6.64.

1-Methyl-2-(4-nitrophenyl)-pyrrole 30:[17] From 4-bromonitrobenzene (0.202 g, 1 mmol) and 1-methylpyrrole (0.324 g, 4 mmol), **30** was obtained in 81% (0.164 g) yield.

4-(1-Phenylpyrrol-2-yl)-benzonitrile 31:[13] From 4-bromobenzonitrile (0.182 g, 1 mmol) and 1-phenylpyrrole (0.536 g, 4 mmol), **31** was obtained in 80% (0.195 g) yield.

1-Phenyl-2-*p*-tolylpyrrole 32:[13] From 4-bromotoluene (0.171 g, 1 mmol) and 1-phenylpyrrole (0.536 g, 4 mmol), **32** was obtained in 52% (0.121 g) yield.

General procedure for the synthesis of 33–37: As a typical experiment, the reaction of the aryl bromide (1.5 mmol), pyrrole derivative (1 mmol) and KOAc (0.196 g, 2 mmol) at 150 °C during 16 h in DMAc (3 mL) in the presence of $PdOAc)_2$ (1.12 mg, 0.005 mmol) under argon afforded the corresponding arylation product after extraction with dichloromethane, evaporation and filtration on silica gel.

4-(1-Methyl-5-*p*-tolylpyrrol-2-yl)-benzonitrile 33: From 4-bromobenzonitrile (0.273 g, 1.5 mmol) and 1-methyl-2-*p*-tolylpyrrole **27** (0.171 g, 1 mmol), **33** was obtained in 71% (0.223 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.61 (d, J = 7.8 Hz, 2H), 7.49 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 6.36 (d, J = 3.7 Hz, 1H), 6.24 (d, J = 3.7 Hz, 1H), 3.55 (s, 3H), 2.34 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 139.2, 137.9, 137.3, 134.7, 132.3, 130.0, 129.3, 128.8, 128.3, 119.1, 110.8, 109.5, 109.1, 34.6, 21.2 ppm. Elemental analysis: calcd (%) for $C_{19}H_{16}N_2$ (272.34): C 83.79, H 5.92, N 10.29; found: C 83.97, H 5.99, N 10.36.

4-[5-(4-*tert*-Butylphenyl)-1-methylpyrrol-2-yl]-benzonitrile 34: From 4-bromobenzonitrile (0.273 g, 1.5 mmol) and 2-(4-*tert*-butylphenyl)-1-methylpyrrole **28** (0.213 g, 1 mmol), **34** was obtained in 74% (0.232 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.61 (d, J = 7.8 Hz, 2H), 7.49 (d, J = 7.8 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 6.36 (d, J = 3.7 Hz, 1H), 6.24 (d, J = 3.7 Hz, 1H), 3.56 (s, 3H), 1.29 ppm (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 150.5, 139.2, 137.9, 134.6, 132.3, 130.0, 128.6, 128.2, 125.5, 119.1, 110.8, 109.5, 109.2, 34.7, 31.3 ppm. Elemental analysis: calcd (%) for $C_{22}H_{22}N_2$ (314.42): C 84.04, H 7.05, N 8.91; found: C 83.89, H 7.18, N 8.67.

4-(1-Methyl-5-naphthalen-2-ylpyrrol-2-yl)-benzonitrile 35: From 4-bromobenzonitrile (0.273 g, 1.5 mmol) and 1-methyl-2-naphthalen-2-ylpyrrole **29** (0.207 g, 1 mmol), **35** was obtained in 90% (0.277 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.89–7.78 (m, 4H), 7.63 (d, J = 7.8 Hz, 2H), 7.55–7.50 (m, 3H), 7.50–7.40 (m, 2H), 6.41 (d, J = 3.7 Hz, 1H), 6.39 (d, J = 3.7 Hz, 1H), 3.63 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 139.2, 137.8, 135.3, 133.4, 132.5, 132.4, 130.2, 128.4, 128.2, 128.0, 127.7, 127.5, 126.9, 126.6, 126.2, 119.1, 111.1, 110.0, 109.7, 34.9 ppm. Elemental analysis: calcd (%) for $C_{22}H_{16}N_2$ (308.38): C 85.69, H 5.23, N 9.08; found: C 85.88, H 5.41, 8.98.

2-(4-*tert*-Butylphenyl)-1-methyl-5-(4-nitrophenyl)-pyrrole 36: From 4-bromonitrobenzene (0.303 g, 1.5 mmol) and 2-(4-*tert*-butylphenyl)-1-methylpyrrole **28** (0.213 g, 1 mmol), **36** was obtained in 80% (0.267 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.18 (d, J = 7.8 Hz, 2H), 7.52 (d, J = 7.8 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 6.42 (d, J = 3.7 Hz, 1H), 6.26 (d, J = 3.7 Hz, 1H), 3.58 (s, 3H), 1.29 ppm (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 150.6, 145.8, 139.9, 139.8, 134.4, 129.8, 128.6, 127.9, 125.5, 124.0, 111.6, 109.5, 34.8, 34.7, 31.3 ppm. Elemental analysis: calcd (%) for $C_{21}H_{22}N_2O_2$ (334.41): C 75.42, H 6.63, N 8.38; found: C 75.58, H 6.54, N 8.24.

4-(1-Phenyl-5-p-tolylpyrrol-2-yl)-benzonitrile 37: From 4-bromobenzonitrile (0.273 g, 1.5 mmol) and 1-phenyl-2-*p*-tolyl-1-pyrrole **32** (0.233 g, 1 mmol), **37** was obtained in 86% (0.287 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.34 (d, J = 7.8 Hz, 2H), 7.25–7.15 (m, 3H), 7.02 (d, J = 7.8 Hz, 2H), 7.00–6.96 (m, 2H), 6.92 (d, J = 7.8 Hz, 2H), 6.86 (d, J = 7.8 Hz, 2H), 6.52 (d, J = 3.7 Hz, 1H), 6.86 (d, J = 3.7 Hz, 1H), 2.21 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 138.6, 137.9, 137.7, 136.6, 133.3, 131.7, 129.7, 129.1, 128.8, 128.7, 128.6, 128.2, 127.8, 119.1, 111.9, 110.3, 109.0, 21.1 ppm. Elemental analysis: calcd (%) for $C_{24}H_{18}N_2$ (334.41): C 86.20, H 5.43, N 8.38; found: C 86.01, H 5.59, N 8.40.

4,4′-Bis(1-methylpyrrol-2-yl)-biphenyl 38: From 4,4′-dibromobiphenyl (0.312 g, 1 mmol), 1-methylpyrrole (0.243 g, 3 mmol) and KOAc (0.392 g, 4 mmol) at 150 °C during 16 h in DMAc (3 mL) in the presence of $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol), **38** was obtained in 81% (0.253 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta =$ 7.59 (d, $J = 8.2$ Hz, 4H), 7.42 (d, $J = 8.2$ Hz, 4H), 6.67 (m, 2H), 6.22 (m, 2H), 6.16 (m, 2H), 3.65 ppm (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 138.9$, 134.2, 132.3, 128.9, 126.9, 123.9, 108.9, 107.9, 35.2 ppm. Elemental analysis: calcd (%) for $C_{22}H_{20}N_2$ (312.41): C 84.58, H 6.45, N 8.97; found: C 84.69, H 6.69, N 8.79.

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