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Regioselective C-2 or C-5 Direct Arylation of Pyrroles with Aryl Bromides using a Ligand-Free Palladium Catalyst

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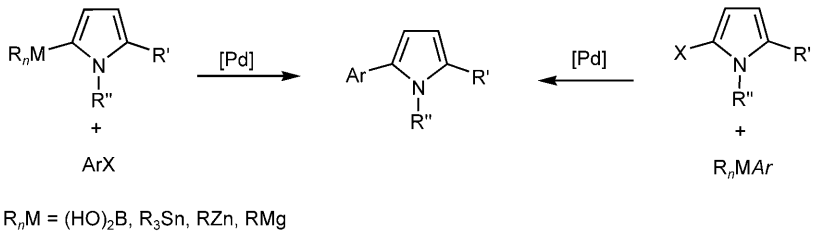
Abstract: A simple and atom-economical procedure for the regioselective C-2 or C-5 arylation of pyrroles *via* a C–H bond activation is reported. Only 0.5–0.01 mol% of commercially available and air-stable ligand-free palladium(II) acetate [$Pd(OAc)_2$] was employed as the catalyst. The presence of electron-withdrawing substituents such as formyl, acetyl or ester at the C-2 position of the pyrrole is tolerated. This environmentally attractive procedure has also been found to be tolerant to a very wide variety of functional groups on the aryl bromides such as formyl, acetyl, propionyl, ester, nitrile, nitro, fluoro, methoxy, amino or trifluoromethyl.

Keywords: aryl bromides; atom-economy; C–H bond activation; palladium; pyrroles

Introduction

Arylpyrrole derivatives continue to attract the attention of synthetic organic chemists, due to their inherent biological activity. Conventional methods for the synthesis of 2- or 5-arylpyrroles include metal-catalyzed cross-coupling reactions[1] such as Suzuki,[2] Stille,[3] Negishi[4] or Kumada[5] type reactions. They make possible either the coupling of aryl halides with organometallic derivatives of pyrroles or the coupling of halopyrroles with aryl-metal derivatives (Scheme 1). Nevertheless, these procedures require the preliminary preparation of an organometallic derivative, and produce stoichiometric amounts of metallic salts as by-products.

The direct regioselective couplings of pyrroles with aryl halides *via* C–H bond activation/functionalization would provide cost-effective and environmentally attractive accesses to arylpyrroles. The selective C-2 or C-5 arylation of heteroaromatics such as furans, thiophenes, thiazoles, oxazoles or indoles *via* a palladium-catalyzed C–H bond activation has been largely described in recent years.[6–11] On the other hand, the regioselective direct 2- or 5-arylation of pyrroles has attracted less attention. Some examples of regioselective intramolecular cyclization of pyrrole derivatives have been reported.[12] A few selective intermolecular C-2 or C-5 arylation of pyrroles *via* palladium-catalyzed C–H bond activation have also been described.[13,14] Some of these couplings employed metal pyrrolyl salts as reactants.[13] The use of such salts allows a high regiocontrol of the arylation, but produces a metallic salt as waste. Only a few results using pyrroles have been reported so far.[14] In 1992 Ohta and co-workers described the direct arylation of *N*-phenylsulfonylpyrrole using 3,6-dialkyl-2-chloropyrazines as coupling partners.[14a] In the course of these reactions, mixtures of 2- and 3-arylated pyrroles (C-2:C-3 arylation, ratios from 1:1 to 2:5) were obtained. The coupling reaction of 3-bromopyridine with pyr-



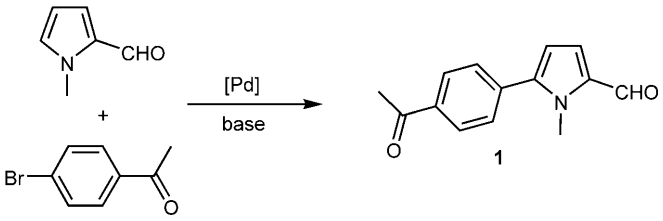
Scheme 1.

roles, using $PdCl_2(o\text{-Tol})_2$/BINAP as catalytic system, gave a mixture of 2-pyridylpyrrole and *N*-pyridylpyrrole in 46% and 21% yields, respectively.[14b] In 2006, Sames and co-workers have reported the direct arylation of a 3-acetylpyrrole using iodobenzene as coupling partner. 5 mol% of palladium associated to a carbene ligand were used as catalyst.[14c] However, again, a mixture of regioisomers was formed. 5-Phenyl-3-acetylpyrrole was obtained in 29% yield; whereas, 2-phenyl-3-acetylpyrrole and 2,5-diphenyl-3-acetylpyrrole were produced in 7% and 14% yields, respectively. This group also reported the direct 5-arylation of methyl pyrrole-2-carboxylate with iodobenzene using 5 mol% of $Pd(OAc)_2$ as catalyst.[14d] Again, the target product was obtained in a low yield of 30%. Very recently, Fagnou and co-workers have reported three examples of 5-arylation of 2-substituted pyrroles. They employed 2 mol% of $Pd(OAc)_2$, 4 mol% of air-sensitive PCy_3 and 30 mol% of pivalic acid as catalytic system.[14e] Using this procedure, the expected products were obtained in 52–69% yields. Recently, a palladium ligand-free procedure for the 2-arylation of caffeine has also been described.[15] In summary, the yields, substrate scope of both coupling partners, regioselectivities and substrate/catalyst ratios for the direct arylation of pyrroles need to be largely improved in order to provide an environmentally attractive and industrially viable procedure. Here, we wish to report on the regioselective 2- or 5-arylation of pyrrole derivatives in the presence of low loadings of a ligand-less palladium catalyst using a wide variety of aryl bromides.

Results and Discussion

We initially directed our efforts towards the palladium-catalyzed direct 5-arylation of 1-methyl-2-formylpyrrole with 4-bromoacetophenone, using the recently reported ligand-free palladium reaction conditions employed for the direct arylation of furans, thiophenes or thiazoles.[7e,8g,9e] At elevated temperature, according to de Vries,[16] when ligand-free $Pd(OAc)_2$ is employed as catalyst precursor, soluble palladium(0) colloids or nanoparticles are formed. These nanoparticles seem to produce monomeric or dimeric anionic palladium complexes that are very active catalysts. For this ligand-free procedure, low catalyst loadings have to be employed (less than 0.5 mol%). In the presence of higher palladium loadings (>1 mol%), so-called "palladium black", which is generally inactive for such catalyzed reactions, is produced more rapidly. Consequently, in the absence of stabilizing agent, the conversions of the aryl halides and the yields of coupling products are generally not increased by using a high catalyst loading (5–10 mol%).

First, we studied the coupling of 1-methyl-2-formylpyrrole with 4-bromoacetophenone using 0.01 mol% of $Pd(OAc)_2$ in DMAc in the presence of KOAc, at 150 °C for 17 h. We obtained **1** in only 27% yield (Scheme 2, Table 1, entry 1). The use of other solvents



Scheme 2.

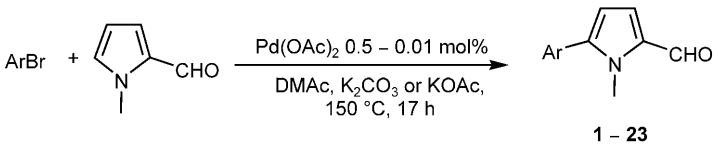
such as DMF, NMP or dioxane did not allow us to improve the yield (Table 1, entries 2–4). A similar yield of 26% was obtained using toluene (Table 1, entry 5). Then, we increased the catalyst loading to 0.05 mol% using DMAc or toluene as the solvent. A high yield of 76% of **1** was obtained using DMAc; whereas, toluene gave a very low yield of 6% (Table 1, entries 6 and 7). Toluene is apparently not a sufficiently polar solvent to stabilize relatively high concentrations of ligand-less palladium species. As expected, lower reaction temperatures of 130 or 100 °C led to lower yields (Table 1, entries 8 and 9). Then, the influence of several bases was investigated using 0.05 mol% of $Pd(OAc)_2$, DMAc, 150 °C as reaction conditions. The reactions performed with Na_2CO_3, K_2CO_3 or Cs_2CO_3 as the base gave **1** in 63–84% yields (Table 1, entries 11–13). KF was found to be an ineffective base (Table 1, entry 10). The use of NaOAc as the base led to a lower yield than KOAc: 35% yield instead of 76% yield (Table 1, entries 6 and 14). In the presence of $[PdCl(C_3H_5)]_2$ as palladium source, a lower yield of **1** was also obtained (Table 1, entry 20). For this reaction, the presence of ligands such as PPh_3 or bidentate phosphines did not enable us to increase the yields (Table 1, entries 16–19 and 21–23).

Then, we examined the scope and limitations of this ligand-less palladium procedure using a wide variety of aryl bromides (Scheme 3, Table 2 and Table 3). In the presence of *para*-substituted electron-deficient aryl bromides such as 4-bromobenzaldehyde, 4-bromopropiophenone, 4-bromobenzonitrile or 4-trifluoromethylbromobenzene, the expected compounds **2**, **3**, **5** and **7** were obtained in good yields using only 0.1 mol% catalyst. Even poorly activated 4-fluorobromobenzene gave a good yield of **8** using 0.1 mol% catalyst (Table 2, entry 12). For these reactions KOAc was employed as the base. It should be noted that in the presence of 4-bromopropiophenone, 4-trifluoromethylbromobenzene or 4-fluorobromobenzene, the use of K_2CO_3 as the base gave low con-

Table 1. Pd-catalyzed direct arylation of 1-methyl-2-formylpyrrole (Scheme 2).[a]

Entry	Catalyst	Ratio Substrate/Catalyst	Base	Solvent	Temp. [°C]	Yield. [%]
1	$Pd(OAc)_2$	10,000	KOAc	DMAc	150	27
2	$Pd(OAc)_2$	10,000	KOAc	DMF	150	0
3	$Pd(OAc)_2$	10,000	KOAc	NMP	150	2
4	$Pd(OAc)_2$	10,000	KOAc	dioxane	150	0
5	$Pd(OAc)_2$	10,000	KOAc	toluene	150	26
6	$Pd(OAc)_2$	2000	KOAc	DMAc	150	76
7	$Pd(OAc)_2$	2000	KOAc	toluene	150	6
8	$Pd(OAc)_2$	10,000	KOAc	DMAc	130	8
9	$Pd(OAc)_2$	10,000	KOAc	DMAc	100	3
10	$Pd(OAc)_2$	2000	KF	DMAc	150	0
11	$Pd(OAc)_2$	2000	Cs_2CO_3	DMAc	150	83
12	$Pd(OAc)_2$	2000	Na_2CO_3	DMAc	150	63
13	$Pd(OAc)_2$	2000	K_2CO_3	DMAc	150	84
14	$Pd(OAc)_2$	2000	NaOAc	DMAc	150	35
15	$Pd(OAc)_2$	1000	KOAc	DMAc	150	100 (90)
16	$Pd(OAc)_2$/2 PPh_3	2000	K_2CO_3	DMAc	150	36
17	$Pd(OAc)_2$/DPPB	2000	K_2CO_3	DMAc	150	61
18	$Pd(OAc)_2$/DPPE	2000	K_2CO_3	DMAc	150	64
19	$Pd(OAc)_2$/DPPM	2000	K_2CO_3	DMAc	150	67
20	$[Pd(C_3H_5)Cl]_2$	2000	K_2CO_3	DMAc	150	61
21	$[Pd(C_3H_5)Cl]_2$/4 PPh_3	2000	K_2CO_3	DMAc	150	16
22	$[Pd(C_3H_5)Cl]_2$/2 DPPB	2000	K_2CO_3	DMAc	150	3
23	$[Pd(C_3H_5)Cl]_2$/2 DPPE	2000	K_2CO_3	DMAc	150	38

[a] *Conditions:* 4-bromoacetophenone (1 mmol), 1-methyl-2-formylpyrrole (2 mmol), base (2 mmol), solvent (3 mL), 17 h, GC and NMR yields, yield in parenthesis is isolated.



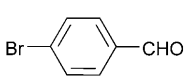
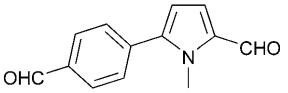
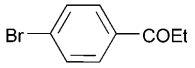
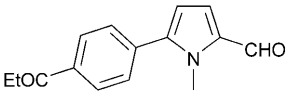
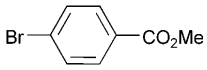
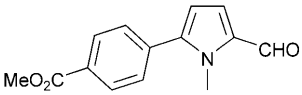
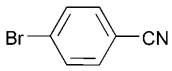
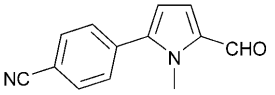
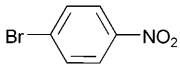
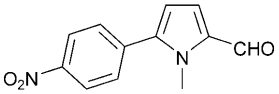
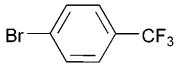
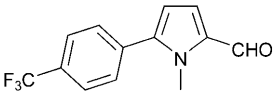
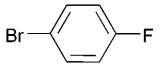
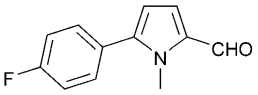
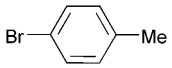
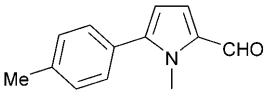
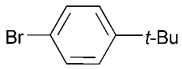
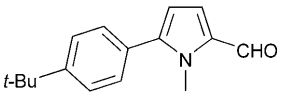
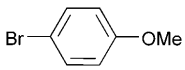
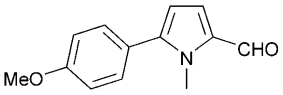
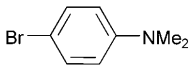
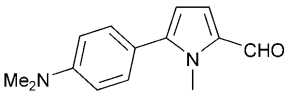
Scheme 3.

versions of these aryl bromides (Table 2, entries 4, 11 and 13). With deactivated aryl bromides, the oxidative addition to palladium is generally slower. We obtained satisfactory results using 4-bromotoluene or 4-bromoanisole, but on the other hand, with 4-*tert*-butylbromobenzene or 4-bromo-*N*,*N*-dimethylaniline, moderate yields of **10** and **12** were obtained using KOAc as the base (Table 2, entries 14–25). Surprisingly, with these deactivated aryl bromides good yields were generally obtained using K_2CO_3 as the base and 0.5 mol% catalyst (Table 2, entries 17 and 23).

These results reveal that, as expected, the stability of the palladium active species largely depends on the palladium concentration. However, it also depends on the nature of the base. In general, when 0.1 mol% catalyst was employed, the use of KOAc as the base gave higher conversions of the aryl bromides than with K_2CO_3. Under such low palladium concentrations, the aggregation of palladium into "palladium black" seems to be relatively slow. On the other hand, when 0.5 mol% of catalyst was employed, the use of K_2CO_3 generally led to similar or higher yields than KOAc, especially for the reactions performed with deactivated aryl bromides. We believe that K_2CO_3 is a more suitable base for stabilizing ligandless palladium species; whereas, KOAc associated to palladium gives less stable but more active palladium species.

Next, we studied the reactivity of *meta*- or *ortho*-substituted aryl bromides and also heteroaryl bromides with 1-methyl-2-formylpyrrole (Table 3). The *meta*-substituted aryl bromides, 3-bromobenzaldehyde, 3-bromobenzonitrile or 2-bromonaphthalene, using KOAc as the base, gave satisfactory results using only 0.5–0.1 mol% of catalyst (Table 3, entries 1–6). *ortho*-Substituents on the aryl bromides generally have a more important effect on the reactions rates and yields, for most palladium-catalyzed reactions, due to their steric and/or coordination properties. However, good yields of coupling products

Table 2. Pd-catalyzed direct arylation of 1-methyl-2-formylpyrrole using *para*-substituted aryl bromides (Scheme 3).[a]

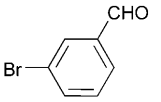
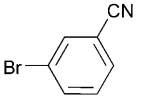
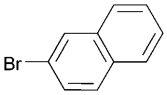
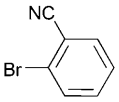
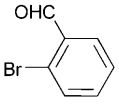
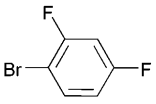
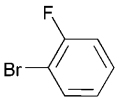
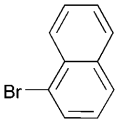
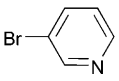
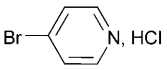
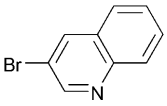
Entry	Aryl Bromide	Major Product		Base	Ratio Substrate/Catalyst	Yield [%]
1			**2**	KOAc	1000	88 (80)
2				KOAc	10,000	30
3			**3**	KOAc	1000	91 (81)
4				K_2CO_3	200	30
5			**4**	KOAc	200	77 (70)
6				KOAc	1000	42
7			**5**	KOAc	1000	90 (81)
8				KOAc	10,000	14
9			**6**	KOAc	1000	68 (61)
10			**7**	KOAc	1000	93 (84)
11				K_2CO_3	1000	31
12			**8**	KOAc	1000	92 (84)
13				K_2CO_3	1000	19
14			**9**	KOAc	1000	88 (81)
15				K_2CO_3	1000	80
16			**10**	KOAc	200	10
17				K_2CO_3	200	81 (73)
18				KOAc	1000	50
19				K_2CO_3	1000	43
20			**11**	KOAc	200	66
21				K_2CO_3	200	83 (74)
22			**12**	KOAc	200	33
23				K_2CO_3	200	79 (71)
24				KOAc	1000	15
25				K_2CO_3	1000	43

[a] *Conditions:* $Pd(OAc)_2$, aryl bromide (1 mmol), 1-methyl-2-formylpyrrole (2 mmol), K_2CO_3 or KOAc (2 mmol), DMAc (3 mL), 150 °C, 17 h, GC and NMR yields, yields in parenthesis are isolated.

16, 17 or **20** were obtained in the presence of 2-bromobenzonitrile, 2-bromobenzaldehyde or 1-bromonaphthalene (Table 3, entries 7, 8 and 13). These reactions were performed using only 0.1 mol% of catalyst. 2-Fluorobromobenzene or 2,4-difluorobromobenzene were found to be slightly less reactive substrates. With these reactants, 0.5 mol% of catalyst had to be employed. Under this palladium concentration, K_2CO_3 used as the base gave higher yields than KOAc (Table 3, entries 9–12). Then, we examined the reactivity of a few heteroaryl bromides. Palladium chemistry involving heterocycles has its unique characteristics stemming from the heterocycle's inherently different structural and electronic properties in comparison to the corresponding carbocyclic aryl compound. Pyridines or quinolines are π-electron deficient heterocycles. Therefore, their reactivity is quite similar to that of the electron-deficient aryl bromides. As expected, using 3- or 4-bromopyridines, or 3-bromoquinoline, the coupling products **21**–**23** were obtained in high yields using only 0.5–0.1 mol% of catalyst and KOAc as the base (Table 3, entries 14–19).

1-Methyl-2-acetylpyrrole was also found to be a reactive coupling partner. Using the $Pd(OAc)_2$ ligandless procedure, this pyrrole gave the 5-arylation products in high regioselectivities and yields (Scheme 4, table 4). Again, the electron-deficient aryl bromides such as 4-trifluoromethylbromobenzene, 4-bromobenzonitrile or 4-fluorobromobenzene gave satisfactory results using 0.5–0.1 mol% of catalyst and KOAc as

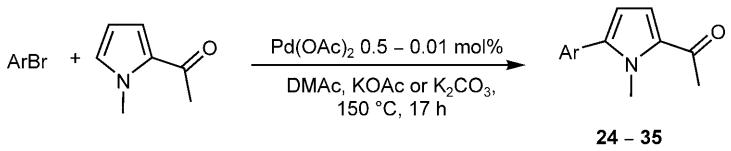
Table 3. Pd-catalyzed direct arylation of 1-methyl-2-formylpyrrole using *meta*-, or *ortho*-substituted aryl bromides and heteroaryl bromides (Scheme 3).[a]

Entry	Aryl Bromide	Major Product	Base	Substrate/Catalyst Ratio	Yield [%]
1		**13**	KOAc	200	67 (60)
2			K_2CO_3	200	66
3		**14**	KOAc	200	90 (82)
4			KOAc	1000	77
5		**15**	KOAc	1000	91 (82)
6			KOAc	10,000	46
7		**16**	KOAc	1000	85 (79)
8		**17**	KOAc	1000	78 (69)
9		**18**	KOAc	200	52
10			K_2CO_3	200	63 (54)
11		**19**	KOAc	200	63
12			K_2CO_3	200	75 (69)
13		**20**	KOAc	1000	84 (77)
14		**21**	KOAc	1000	88 (80)
15			KOAc	10,000	25
16		**22**	KOAc	200	79 (70)[b]
17			KOAc	1000	40[b]
18		**23**	KOAc	1000	86 (78)
19			KOAc	10,000	40

[a] *Conditions:* $Pd(OAc)_2$, aryl bromide (1 mmol), 1-methyl-2-formylpyrrole (2 mmol), K_2CO_3 or KOAc (2 mmol), DMAc (3 mL), 150 °C, 17 h, GC and NMR yields, yields in parenthesis are isolated.

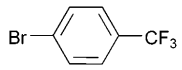
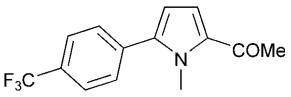
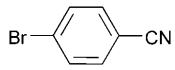
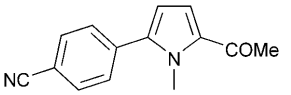
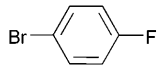
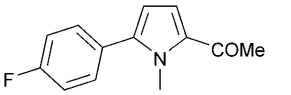
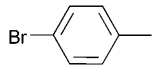
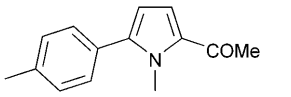
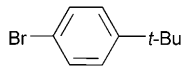
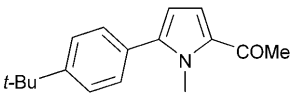
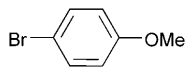
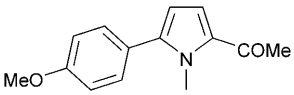
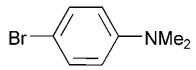
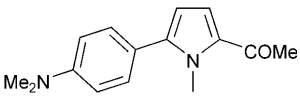
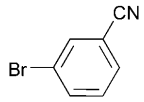
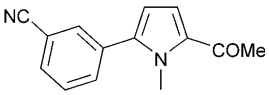
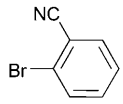
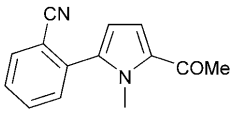
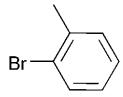
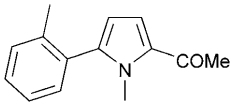
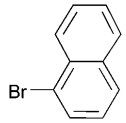
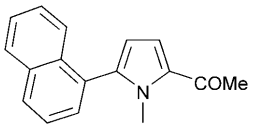
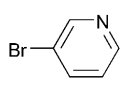
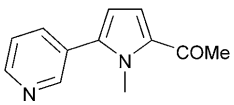
[b] KOAc: 3 mmol.

the base (Table 4, entries 1–8). As expected, in the presence of deactivated aryl bromides, using KOAc as the base and 0.5 mol% catalyst, quite low conversions were generally obtained (Table 4, entries 9, 11, 13 and 17). On the other hand, in the presence of K_2CO_3 as the base, 4-bromotoluene, 4-*tert*-butylbromobenzene, 4-bromoanisole or 4-*N*,*N*-dimethylaminobromobenzene gave the desired coupling products **27**–**30** in 73–82% yields (Table 4, entries 10, 12, 15 and 18). The sterically congested and deactivated aryl bromide, 2-bromotoluene was found to be less reactive. The best yield was obtained using 0.5 mol% of catalyst and KOAc as the base (Table 4, entries 22 and 23). With this challenging substrate, the use of palladium associated to phosphine ligands would certainly give higher yields.[14e] 1-Bromonaphthalene or 3-bromopyridine have also been reacted with 1-methyl-2-acetylpyrrole. These substrates, in the presence of KOAc as the base, gave **34** and **35** in high yields and high TONs (Table 4, entries 24–31).

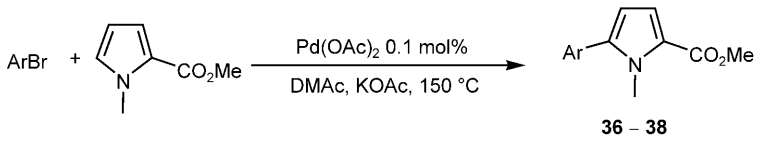


Scheme 4.

Table 4. Pd-catalyzed direct 5-arylation of 1-methyl-2-acetylpyrrole (Scheme 4).[a]

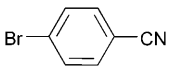
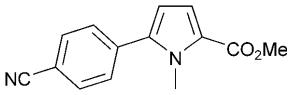
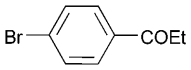
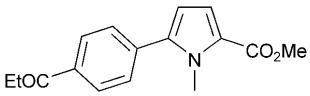
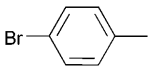
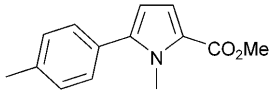
Entry	Aryl Bromide	Major Product		Base	Substrate/Catalyst Ratio	Yield [%]
1			**24**	KOAc	200	74 (66)
2				KOAc	1000	53
3				K_2CO_3	200	74
4				K_2CO_3	1000	20
5			**25**	KOAc	200	92 (81)
6				KOAc	1000	77
7			**26**	KOAc	1000	93 (80)
8				K_2CO_3	1000	20
9			**27**	KOAc	200	12
10				K_2CO_3	200	82 (73)
11			**28**	KOAc	200	21
12				K_2CO_3	200	94 (82)
13			**29**	KOAc	200	56
14				KOAc	1000	53
15				K_2CO_3	200	88 (80)
16				K_2CO_3	1000	23
17			**30**	KOAc	200	12
18				K_2CO_3	200	82 (74)
19			**31**	KOAc	1000	92 (83)
20				KOAc	10,000	11
21			**32**	KOAc	1000	77 (70)
22			**33**	KOAc	200	42 (37)
23				K_2CO_3	200	26
24			**34**	KOAc	200	89 (80)
25				KOAc	1000	85
26				KOAc	10,000	71
27				K_2CO_3	200	85
28			**35**	KOAc	200	92 (84)
29				KOAc	1000	74
30				K_2CO_3	200	89
31				K_2CO_3	1000	49

[a] *Conditions:* $Pd(OAc)_2$, aryl bromide (1 mmol), 1-methyl-2-acetylpyrrole (2 mmol), K_2CO_3 or KOAc (2 mmol), DMAc (3 mL), 150 °C, 17 h, GC and NMR yields, yields in parenthesis are isolated.



Scheme 5.

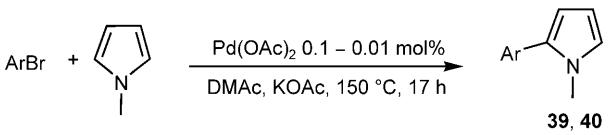
Table 5. Pd-catalyzed direct 5-arylation of methyl 1-methyl-2-pyrrolecarboxylate (Scheme 5).[a]

Entry	Aryl Bromide	Major Product		Yield [%]
1			**36**	92 (83)
2			**37**	87 (80)[b]
3			**38**	60 (52)[b]

[a] *Conditions:* $Pd(OAc)_2$ (0.001 mmol), aryl bromide (1 mmol), methyl 1-methyl-2-pyrrolecarboxylate (2 mmol), KOAc (2 mmol), DMAc (3 mL), 150 °C, 5 h, GC and NMR yields, yields in parenthesis are isolated.
[b] Reaction time 2 h.

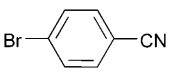
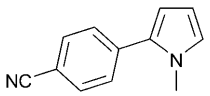
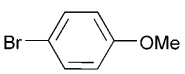
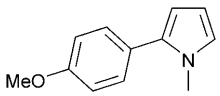
We initially obtained quite disappointing results using methyl 1-methyl-2-pyrrolecarboxylate as reactant (Scheme 5, Table 5). With this substrate, when the reactions were stopped after 17 h, mixtures of the expected 5-arylated pyrroles **36–38** and 2-arylpyrroles arising from decarboxylation were obtained. Up to 50% of these decarboxylated pyrroles could be formed. However, the GC analysis of the reactions mixtures at 1 h, 2 h and 5 h revealed that this decarboxylation process was relatively slow, as compared to the palladium-catalyzed 5-arylation rate. When the reactions were stopped after 2 h or 5 h, the target products **36–38** were obtained in moderate to high yields, and only a minor amount of 1-methyl-2-arylpyrroles was detected. It should be noted that all these reactions were performed using only 0.1 mol% of catalyst.

This procedure is not limited to the use of 2-substituted pyrroles. We observed that the selective 2-arylation of 1-methylpyrrole also proceeded nicely (Scheme 6, Table 6). However, in the course of this reaction, the formation of 2,5-diarylpyrroles was possible. In order to reduce the amount of these 2,5-diarylpyrroles, we employed four equivalents of this coupling partner. Using these reaction conditions, we observed that the 2-arylation of 1-methylpyrrole with 4-bromobenzonitrile was very fast. This reaction proceeds nicely to give **39** in 80% yield using only 0.01 mol% of catalyst (Table 6, entry 1). Moreover, only trace amounts of the diarylated pyrrole side-product were detected by GC and GC/MS analysis. As expected, with the more challenging 4-bromoani-



Scheme 6.

Table 6. Pd-catalyzed direct 2-arylation of 1-methylpyrrole (Scheme 6).[a]

Entry	Aryl Bromide	Major Product		Substrate/Catalyst Ratio	Yield [%]
1			**39**	10000	91 (80)
2			**40**	1000	78 (70)

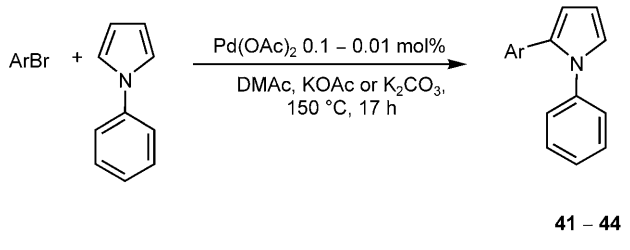
[a] *Conditions:* $Pd(OAc)_2$, aryl bromide (1 mmol), 1-methylpyrrole (4 mmol), KOAc (2 mmol), DMAc (3 mL), 150 °C, 17 h, GC and NMR yields, yields in parenthesis are isolated.

sole, the reaction was slower. In order to obtain a good conversion of this aryl bromide, we had to employ 0.1 mol% of catalyst (Table 6, entry 2). With this substrate, approximately 18% of the diarylated pyrrole was also produced.

Quite similar results were obtained using 1-phenylpyrrole (Scheme 7, Table 7). Electron-deficient aryl bromides were reacted using only 0.01 mol% of catalyst, whereas electron-excessive ones required 0.1 mol% of $Pd(OAc)_2$. In all cases, good yields of 2-aryl-1-phenylpyrroles **41**–**44** were obtained, and only small amounts of diarylpyrroles were formed.

As position C-5 of compounds **39**–**44** is very reactive towards palladium-catalyzed direct arylation, it should allow the synthesis of unsymmetrically substituted 2,5-diarylpyrroles. As expected, using **39** and 3-bromopyridine as coupling partners, **45** was obtained in 72% yield (Scheme 8). This successive arylation method should allow the synthesis of a very wide variety of 2,5-diarylpyrroles in only two steps.

Finally, we studied the regioselectivity of the direct arylation of 1-methylindole with 4-bromoacetophenone using our ligand-less palladium procedure. Sames and co-worker had observed that for the reaction of 1-methylindole with 4-iodoacetophenone, using 0.5 mol% of $Pd(OAc)_2$ associated to 2 mol% of PPh_3 as catalyst, the 2-arylated indole was selectively obtained in 52% yield.[11a] Using our reaction conditions, 4-bromoacetophenone, which is less expensive than 4-iodoacetophenone, regioselectively led to the 2-arylated indole **46** in 78% yield (Scheme 9). This reaction was performed using only 0.1 mol% of $Pd(OAc)_2$ as catalyst.

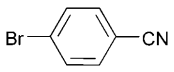
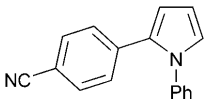
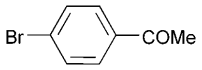
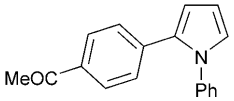
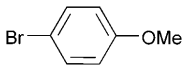
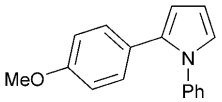
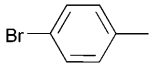
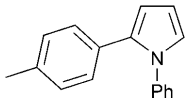


Scheme 7.

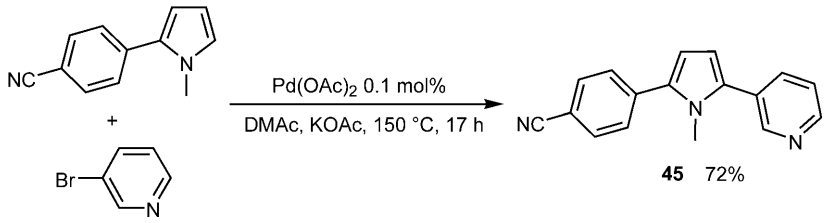
Conclusions

In summary, we report here an atom-economical method for the direct regioselective C-2 or C-5 arylation of pyrroles. This procedure employs a low catalyst loading of a commercially available, ligand-less

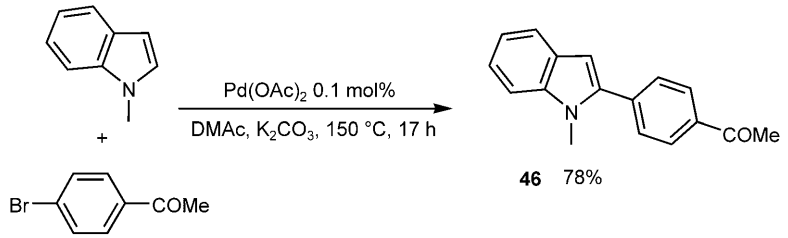
Table 7. Pd-catalyzed direct 2-arylation of 1-phenylpyrrole (Scheme 7).[a]

Entry	Aryl Bromide	Major Product		Substrate/Catalyst Ratio	Yield [%]
1			**41**	10,000	92 (78)
2			**42**	10,000	94 (80)
3			**43**	1000	87 (70)
4			**44**	1000	92 (73)

[a] *Conditions:* $Pd(OAc)_2$, aryl bromide (1 mmol), 1-phenylpyrrole (4 mmol), KOAc (2 mmol), DMAc (3 mL), 150 °C, 17 h, GC and NMR yields, yields in parenthesis are isolated.



Scheme 8.



Scheme 9.

and air-stable palladium source. Therefore, there is no need to eliminate phosphine derivatives at the end of the reaction. Under such low catalyst concentrations, palladium stabilizing agents such as ammonium salts are useless, thus reducing the amount of wastes. Moreover, both electron-excessive and electron-deficient aryl bromides can be employed. In the presence of electron-deficient aryl bromides, K_2CO_3 should be employed as the base in some cases; whereas, with electron-poor aryl bromides, KOAc should be preferred. This catalytic system has proven to be tolerant to a variety of functional groups such as ester, formyl, acetyl, nitrile, nitro, fluoro, methoxy, amino, or trifluoromethyl on the aryl bromide. This reaction can be performed using as little as 0.1–0.01 mol% of catalyst with several substrates. Finally, this procedure is environmentally attractive as the major by-products are AcOK or K_2CO_3 associated to HBr instead of metallic salts using more classical coupling procedures.

Experimental Section

General Remarks

All chemical reactants and palladium complexes were obtained from commercial sources and used with out further purification. DMAc analytical grade (99%) was not distilled before use. K_2CO_3 or KOAc (99+%) were employed. All reactions were run under argon using vacuum lines in Schlenk tubes in oven-dried glassware. ^1H (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in $CDCl_3$ solutions. Chemical shifts (δ) are reported in ppm relative to $CDCl_3$. Flash chromatographies were performed on silica gel (230–400 mesh).

General Procedure

In a typical experiment, the aryl bromide (1 mmol), pyrrole derivative (2 mmol) and KOAc or K_2CO_3 (2 mmol, see Tables) were introduced in a Schlenk tube, equipped with a magnetic stirring bar. The $Pd(OAc)_2$ (see Tables) and DMAc (3 mL) were added, and the Schlenk tube purged several times with argon. The Schlenk tube was placed in a pre-heated oil bath at 150 °C and reactants were allowed to stir for 17 h. Then, the reaction mixture was analyzed by gas chromatography to determine the conversion of the aryl bromide. The solvent was removed by heating the reaction vessel under vacuum and the residue was charged directly onto a silica gel column. The products were eluted, using an appropriate ratio of diethyl ether and pentane.

5-(4-Acetylphenyl)-1-methyl-2-formylpyrrole (1): The reaction of 4-bromoacetophenone (0.200 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **1**; isolated yield: 0.205 g (90%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 9.60$ (s, 1H), 8.05 (d, $J = 8.2$ Hz, 2H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.00 (d, $J = 4.0$ Hz, 1H), 6.38 (d, $J = 4.0$ Hz, 1H), 3.95 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 196.4$, 178.8, 141.7, 135.6, 134.5, 132.6, 128.2, 127.6, 123.4, 110.4, 33.5, 25.7; anal. calcd. for $C_{14}H_{13}NO_2$: C 73.99, H 5.77; found: C 73.87, H 5.71.

5-(4-Formylphenyl)-1-methyl-2-formylpyrrole (2): The reaction of 4-bromobenzaldehyde (0.187 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **2**; isolated yield: 0.171 g (80%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 10.07$ (s, 1H), 9.63 (s, 1H), 7.97 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.00 (d, $J = 4.1$ Hz, 1H), 6.40 (d, $J = 4.1$ Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 191.4$, 179.9, 142.4, 136.9, 135.9, 133.8, 129.9, 129.6, 124.3, 111.6, 34.6; anal. calcd. for $C_{13}H_{11}NO_2$: C 73.22, H 5.20; found: C 73.30, H 5.41.

5-(4-Propionylphenyl)-1-methyl-2-formylpyrrole (3): The reaction of 4-bromopropiophenone (0.214 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **3**; isolated yield: 0.195 g (81%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 9.60$ (s, 1H), 8.05 (d, $J = 8.2$ Hz, 2H), 7.52 (d, $J = 8.2$ Hz, 2H), 7.00 (d, $J = 4.0$ Hz, 1H), 6.37 (d, $J = 4.0$ Hz, 1H), 3.95 (s, 3H), 3.03 (q, $J = 7.6$ Hz, 2H), 1.25 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 196.4$, 179.7, 136.4, 135.2, 133.4, 129.1, 128.1, 124.2, 121.9, 111.2, 34.4, 31.7, 8.1; anal. calcd. for $C_{15}H_{15}NO_2$: C 74.67, H 6.27; found: C 74.80, H 6.47.

Methyl 4-(5-formyl-1-methylpyrrol-2-yl)-benzoate (4): The reaction of methyl 4-bromobenzoate (0.216 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **4**; isolated yield: 0.170 g (70%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 9.61$ (s, 1H), 8.13 (d, $J = 8.2$ Hz, 2H), 7.51 (d, $J = 8.2$ Hz, 2H), 7.00 (d, $J = 4.0$ Hz, 1H), 6.38 (d, $J = 4.0$ Hz, 1H), 3.96 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 179.8$, 166.5, 142.8, 135.5, 133.6, 130.0, 129.9, 129.0, 124.4, 111.3, 52.3, 34.5; anal. calcd. for $C_{14}H_{13}NO_3$: C 69.12, H 5.39; found: C 69.21, H 5.27.

4-(5-Formyl-1-methylpyrrol-2-yl)-benzonitrile (5): The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **5**; isolated yield: 0.171 g (81%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.61 (s, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.00 (d, J = 4.1 Hz, 1H), 6.37 (d, J = 4.1 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 179.9, 141.6, 135.5, 133.8, 132.4, 129.6, 124.2, 118.3, 112.1, 111.6, 34.5; anal. calcd. for $C_{13}H_{10}N_2O$: C 74.27, H 4.79; found: C 73.98, H 4.61.

5-(4-Nitrophenyl)-1-methyl-2-formylpyrrole (6): The reaction of 4-bromonitrobenzene (0.202 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **6**; isolated yield: 0.140 g (61%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.62 (s, 1H), 8.32 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.01 (d, J = 4.1 Hz, 1H), 6.41 (d, J = 4.1 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 179.6, 147.4, 141.2, 137.4, 134.0, 129.2, 123.8, 123.4, 111.4, 34.1; anal. calcd. for $C_{12}H_{10}N_2O_3$: C 62.60, H 4.38; found: C 62.47, H 4.45.

5-(4-Trifluoromethylphenyl)-1-methyl-2-formylpyrrole (7): The reaction of 4-trifluoromethylbromobenzene (0.225 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **7**; isolated yield: 0.213 g (84%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.64 (s, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 4.1 Hz, 1H), 6.38 (d, J = 4.1 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 179.8, 134.7, 133.5, 131.1, 129.5, 129.3 (q, J = 32.5 Hz), 125.6 (m), 125.5 (q, J = 272.5 Hz), 124.3, 111.3, 34.4; anal. calcd. for $C_{13}H_{10}F_3NO$: C 61.66, H 3.98; found: C 61.90, H 4.14.

5-(4-Fluorophenyl)-1-methyl-2-formylpyrrole (8): The reaction of 4-bromofluorobenzene (0.175 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **8**; isolated yield: 0.171 g (84%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.59 (s, 1H), 7.42 (dd, J = 8.5 and 5.9 Hz, 2H), 7.17 (t, J = 8.5 Hz, 2H), 7.00 (d, J = 3.8 Hz, 1H), 6.29 (d, J = 3.8 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 179.5, 162.8 (d, J = 249.1 Hz), 143.0, 132.9, 131.0 (d, J = 8.2 Hz), 127.1 (m), 124.3, 115.8 (d, J = 21.8 Hz), 110.0, 34.1; anal. calcd. for $C_{12}H_{10}FNO$: C 70.93, H 4.96; found: C 70.89, H 4.78.

5-(4-Methylphenyl)-1-methyl-2-formylpyrrole (9): The reaction of 4-bromotoluene (0.171 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **9**; isolated yield: 0.162 g (81%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.59 (s, 1H), 7.34 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 4.1 Hz, 1H), 6.30 (d, J = 4.1 Hz, 1H), 3.94 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 179.3, 144.3, 138.5, 132.7, 129.2, 126.9, 128.0, 124.4, 110.4, 34.2, 21.2; anal. calcd. for $C_{13}H_{13}NO$: C 78.36, H 6.58; found: C 78.39, H 6.68.

5-(4-*tert*-Butylphenyl)-1-methyl-2-formylpyrrole (10): The reaction of 4-*tert*-butylbromobenzene (0.213 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and K_2CO_3 (0.278 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **10**; isolated yield: 0.176 g (73%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.59 (s, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H), 7.00 (d, J = 4.1 Hz, 1H), 6.32 (d, J = 4.1 Hz, 1H), 3.97 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 179.4, 151.7, 144.4, 132.8, 128.8, 126.0, 125.5, 124.5, 110.6, 34.7, 34.4, 31.2; anal. calcd. for $C_{16}H_{19}NO$: C 79.63, H 7.94; found: C 79.47, H 7.88.

5-(4-Methoxylphenyl)-1-methyl-2-formylpyrrole (11): The reaction of 4-bromoanisole (0.187 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and K_2CO_3 (0.278 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **11**; isolated yield: 0.159 g (74%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.56 (s, 1H), 7.36 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 8.3 Hz, 2H), 6.99 (d, J = 4.1 Hz, 1H), 6.27 (d, J = 4.1 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 179.2, 159.7, 144.1, 132.6, 130.3, 124.4, 123.2, 113.2, 110.2, 55.2, 34.1; anal. calcd. for $C_{13}H_{13}NO_2$: C 72.54, H 6.09; found: C 72.37, H 6.01.

5-(4-Dimethylaminophenyl)-1-methyl-2-formylpyrrole (12):[17] The reaction of 4-bromo-*N*,*N*-dimethylaniline (0.200 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and K_2CO_3 (0.278 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **12**; isolated yield: 0.162 g (71%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.54 (s, 1H), 7.32 (d, J = 8.3 Hz, 2H), 6.97 (d, J = 4.1 Hz, 1H), 6.79 (d, J = 8.3 Hz, 2H), 6.26 (d, J = 4.1 Hz, 1H), 3.96 (s, 3H), 3.04 (s, 6H).

5-(3-Formylphenyl)-1-methyl-2-formylpyrrole (13): The reaction of 3-bromobenzaldehyde (0.187 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **13**; isolated yield: 0.128 g (60%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.07 (s, 1H), 9.61 (s, 1H), 7.98–7.90 (m, 3H), 7.70–7.60 (m, 1H), 7.00 (d, J = 4.1 Hz, 1H), 6.36 (d, J = 4.1 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 191.4, 179.9, 142.4, 136.7, 134.8, 133.4, 132.2, 130.1, 129.8, 129.5, 124.4, 111.2, 34.4; anal. calcd. for $C_{13}H_{11}NO_2$: C 73.22, H 5.20; found: C 73.41, H 5.37.

3-(5-Formyl-1-methylpyrrol-2-yl)-benzonitrile (14): The reaction of 3-bromobenzonitrile (0.182 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **14**; isolated yield: 0.172 g (82%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.61 (s, 1H), 7.80–7.60 (m, 4H), 6.99 (d, J = 4.1 Hz, 1H), 6.33 (d, J = 4.1 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 180.0, 141.2, 133.5, 133.3, 132.5, 132.4, 131.9, 129.6, 124.2, 118.1, 113.2, 111.3, 34.4; anal. calcd. for $C_{13}H_{10}N_2O$: C 74.27, H 4.79; found: C 74.44, H 4.62.

1-Methyl-5-naphthalen-2-ylpyrrole-2-carbaldehyde (15): The reaction of 2-bromonaphthalene (0.207 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **15**; isolated yield: 0.193 g (82%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.65 (s, 1H), 8.00–7.90 (m, 4H), 7.62–7.40 (m, 3H), 7.05 (d, J = 4.1 Hz, 1H), 6.44 (d, J = 4.1 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 179.5, 144.1, 133.0, 132.9, 132.8, 128.5, 128.3, 128.2, 128.1, 127.7, 126.8, 126.7, 126.5, 124.5, 111.0, 34.4; anal. calcd. for $C_{16}H_{13}NO$: C 81.68, H 5.57; found: C 81.77, H 5.41.

2-(5-Formyl-1-methylpyrrol-2-yl)-benzonitrile (16): The reaction of 2-bromobenzonitrile (0.182 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **16**; isolated yield: 0.166 g (79%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.65$ (s, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 4.1$ Hz, 1H), 6.46 (d, $J = 4.1$ Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 180.0$, 138.9, 134.5, 133.5, 133.3, 132.6, 131.0, 129.1, 123.8, 117.5, 113.3, 112.3, 34.1; anal. calcd. for $C_{13}H_{10}N_2O$: C 74.27, H 4.79; found: C 74.40, H 4.60.

5-(2-Formylphenyl)-1-methylpyrrole-2-carbaldehyde (17): The reaction of 2-bromobenzaldehyde (0.187 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **17**; isolated yield: 0.147 g (69%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.88$ (s, 1H), 9.64 (s, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.70–7.45 (m, 2H), 7.42 (d, $J = 8.0$ Hz, 1H), 7.03 (d, $J = 4.1$ Hz, 1H), 6.30 (d, $J = 4.1$ Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 191.0$, 179.9, 139.0, 135.2, 133.9, 133.8, 133.1, 131.5, 129.6, 128.4, 123.8, 113.1, 34.0; anal. calcd. for $C_{13}H_{11}NO_2$: C 73.22, H 5.20; found: C 73.40, H 5.34.

5-(2,4-Difluorophenyl)-1-methylpyrrole-2-carbaldehyde (18): The reaction of 1-bromo-2,4-difluorobenzene (0.193 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and K_2CO_3 (0.278 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **18**; isolated yield: 0.120 g (54%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.61$ (s, 1H), 7.45–7.15 (m, 1H), 7.10–6.95 (m, 3H), 6.30 (d, $J = 4.1$ Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 179.7$, 165.2 (d, $J = 252.4$ Hz), 165.1 (d, $J = 250.4$ Hz), 137.0, 133.1, 132.9 (dd, $J = 9.6$ and 4.2 Hz), 123.9, 115.3 (d, $J = 15.5$ Hz), 111.9 (dd, $J = 11.7$ and 3.5 Hz), 111.7, 104.0 (dd, $J = 26.8$ and 25.6 Hz), 34.0; anal. calcd. for $C_{12}H_9F_2NO$: C 65.16, H 4.10; found: C 65.00, H 4.24.

5-(2-Fluorophenyl)-1-methylpyrrole-2-carbaldehyde (19): The reaction of 2-bromofluorobenzene (0.175 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and K_2CO_3 (0.278 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **19**; isolated yield: 0.140 g (69%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.62$ (s, 1H), 7.60–7.10 (m, 4H), 7.02 (d, $J = 4.1$ Hz, 1H), 6.33 (d, $J = 4.1$ Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 179.7$, 159.7 (d, $J = 249.0$ Hz), 138.1, 133.0, 132.0, 131.1 (d, $J = 8.3$ Hz), 124.4, 124.1, 119.0 (d, $J = 15.3$ Hz), 116.1 (d, $J = 22.0$ Hz), 111.7, 34.1; anal. calcd. for $C_{12}H_{10}FNO$: C 70.93, H 4.96; found: C 71.04, H 4.87.

1-Methyl-5-naphthalen-1-ylpyrrole-2-carbaldehyde (20): The reaction of 1-bromonaphthalene (0.207 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **20**; isolated yield: 0.181 g (77%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.70$ (s, 1H), 8.03–7.95 (m, 2H), 7.65–7.40 (m, 5H), 7.12 (d, $J = 4.1$ Hz, 1H), 6.40 (d, $J = 4.1$ Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 179.4$, 142.3, 133.4, 132.4, 132.2, 129.4, 128.5, 128.3, 128.2, 126.8, 126.2, 125.3, 125.0, 124.1, 111.9, 33.9; anal. calcd. for $C_{16}H_{13}NO$: C 81.68, H 5.57; found: C 81.58, H 5.70.

1-Methyl-5-pyridin-3-ylpyrrole-2-carbaldehyde (21):[18] The reaction of 3-bromopyridine (0.158 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **21**; isolated yield: 0.149 g (80%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.78$ (s, 1H), 8.70 (m, 2H), 7.72 (d, $J = 7.5$ Hz, 1H), 7.40 (dd, $J = 7.5$ and 4.2 Hz, 1H), 6.98 (d, $J = 3.9$ Hz, 1H), 6.33 (d, $J = 3.9$ Hz, 1H), 3.87 (s, 3H).

1-Methyl-5-pyridin-4-ylpyrrole-2-carbaldehyde (22): The reaction of 4-bromopyridine hydrochloride (0.194 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.294 g, 3 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **22**; isolated yield: 0.130 g (70%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.62$ (s, 1H), 8.70 (d, $J = 6.0$ Hz, 2H), 7.34 (d, $J = 6.5$ Hz, 2H), 6.99 (d, $J = 3.9$ Hz, 1H), 6.40 (d, $J = 3.9$ Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 179.9$, 150.1, 140.7, 138.6, 133.9, 124.1, 123.2, 111.5, 34.4; anal. calcd. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; found: C, 70.80; H, 5.57.

1-Methyl-5-quinolin-3-ylpyrrole-2-carbaldehyde (23): The reaction of 3-bromoquinoline (0.208 g, 1 mmol), 1-methyl-2-formylpyrrole (0.219 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **23**; isolated yield: 0.184 g (78%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.62$ (s, 1H), 8.98 (s, 1H), 8.19 (s, 1H), 8.16 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.77 (t, $J = 7.8$ Hz, 1H), 7.60 (t, $J = 7.8$ Hz, 1H), 7.03 (d, $J = 4.1$ Hz, 1H), 6.42 (d, $J = 4.1$ Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 179.9$, 150.3, 147.6, 140.5, 135.8, 133.7, 130.4, 129.4, 128.0, 127.5, 127.3, 124.4, 124.3, 111.7, 34.5; anal. calcd. for $C_{15}H_{12}N_2O$: C 76.25 H 5.12; found: C 76.40, H 5.23.

5-(4-Trifluoromethylphenyl)-1-methyl-2-acetylpyrrole (24): The reaction of 4-trifluoromethylbromobenzene (0.225 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.247 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **24**; isolated yield: 0.176 g (66%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.71$ (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.04 (d, $J = 4.1$ Hz, 1H), 6.27 (d, $J = 4.1$ Hz, 1H), 3.80 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 188.8$, 141.0, 135.3, 132.5, 130.4 (q, $J = 32.5$ Hz), 129.5, 125.7 (q, $J = 272.5$ Hz), 125.5 (q, $J = 3.8$ Hz), 119.6, 109.9, 35.2, 27.4; anal. calcd. for $C_{14}H_{12}F_3NO$: C 62.92, H 4.53; found: C 62.87, H 4.65.

4-(5-Acetyl-1-methylpyrrol-2-yl)-benzonitrile (25): The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.247 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **25**; isolated yield: 0.182 g (81%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.62$ (d, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 6.94 (d, $J = 4.1$ Hz, 1H), 6.20 (d, $J = 4.1$ Hz, 1H), 3.78 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 188.2$, 139.9, 135.6, 132.4, 131.8, 129.2, 119.2, 118.0, 111.0, 109.9, 34.8, 26.9; anal. calcd. for $C_{14}H_{12}N_2O$: C 74.98, H 5.39; found: C 74.90, H 5.54.

5-(4-Fluorophenyl)-1-methyl-2-acetylpyrrole (26): The reaction of 4-bromofluorobenzene (0.175 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.247 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **26**; isolated yield: 0.174 g (80%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.38$ (dd, $J = 8.5$ and

5.9 Hz, 2H), 7.14 (t, J=8.5 Hz, 2H), 7.02 (d, J=4.1 Hz, 1H), 6.18 (d, J=4.1 Hz, 1H), 3.85 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=188.5, 164.3 (d, J=248.5 Hz), 141.7, 131.9, 131.1 (d, J=8.2 Hz), 127.8 (m), 119.6, 115.7 (d, J=21.7 Hz), 109.2, 35.0, 27.3; anal. calcd. for $C_{13}H_{12}FNO$: C 71.87, H 5.57; found: C 71.89, H 5.60.

5-(4-Tolyl)-1-methyl-2-acetylpyrrole (27): The reaction of 4-bromotoluene (0.171 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.247 g, 2 mmol) and K_2CO_3 (0.278 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **27**; isolated yield: 0.156 g (73%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.40–7.20 (m, 4H), 7.06 (d, J=4.1 Hz, 1H), 6.22 (d, J=4.1 Hz, 1H), 3.92 (s, 3H), 2.50 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=187.9, 142.6, 137.8, 131.3, 128.8, 128.7, 128.4, 119.3, 108.7, 34.7, 26.9, 20.9; anal. calcd. for $C_{14}H_{15}NO$: C 78.84, H 7.09; found: C 78.80, H 7.14.

5-(4-*tert*-Butylphenyl)-1-methyl-2-acetylpyrrole (28): The reaction of 4-*tert*-butylbromobenzene (0.213 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.247 g, 2 mmol) and K_2CO_3 (0.278 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **28**; isolated yield: 0.209 g (82%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.50 (d, J=8.0 Hz, 2H), 7.37 (d, J=8.0 Hz, 2H), 7.06 (d, J=4.1 Hz, 1H), 6.23 (d, J=4.1 Hz, 1H), 3.93 (s, 3H), 2.50 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=188.2, 151.2, 142.9, 131.9, 128.8, 128.6, 125.3, 119.6, 109.0, 35.1, 35.0, 31.1, 27.2; anal. calcd. for $C_{17}H_{21}NO$: C 79.96, H 8.29; found: C 79.84, H 8.24.

5-(4-Methoxyphenyl)-1-methyl-2-acetylpyrrole (29): The reaction of 4-bromoanisole (0.187 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.247 g, 2 mmol) and K_2CO_3 (0.278 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **29**; isolated yield: 0.183 g (80%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.34 (d, J=8.3 Hz, 2H), 7.04 (d, J=4.1 Hz, 1H), 7.00 (d, J=8.3 Hz, 2H), 6.19 (d, J=4.1 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=188.0, 159.3, 142.5, 131.3, 130.0, 123.7, 119.4, 113.7, 108.6, 55.0, 34.8, 26.9; anal. calcd. for $C_{14}H_{15}NO_2$: C 73.34, H 6.59; found: C 73.39, H 6.47.

5-(4-Dimethylaminophenyl)-1-methyl-2-acetylpyrrole (30): The reaction of 4-bromo-*N*,*N*-dimethylaniline (0.200 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.247 g, 2 mmol) and K_2CO_3 (0.278 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **30**; isolated yield: 0.179 g (74%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.50 (d, J=8.3 Hz, 2H), 7.36 (d, J=8.3 Hz, 2H), 7.06 (d, J=4.1 Hz, 1H), 6.23 (d, J=4.1 Hz, 1H), 3.93 (s, 3H), 2.50 (s, 3H), 1.38 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=187.5, 149.8, 143.5, 130.9, 129.7, 119.5, 118.7, 111.5, 106.1, 39.9, 34.7, 26.8; anal. calcd. for $C_{15}H_{18}N_2O$: C 74.35, H 7.49; found: C 74.30, H 7.43.

3-(5-Acetyl-1-methylpyrrol-2-yl)-benzonitrile (31): The reaction of 3-bromobenzonitrile (0.182 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.247 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **31**; isolated yield: 0.186 g (83%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.75–7.55 (m, 4H), 7.01 (d, J=4.1 Hz, 1H), 6.23 (d, J=4.1 Hz, 1H), 3.85 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=188.6, 139.7, 133.2, 132.9, 132.4, 132.3, 131.4, 129.3, 119.4, 118.1, 112.8, 109.9, 35.0, 27.3; anal. calcd. for $C_{14}H_{12}N_2O$: C 74.98, H 5.39; found: C 75.04, H 5.47.

2-(5-Acetyl-1-methylpyrrol-2-yl)-benzonitrile (32): The reaction of 2-bromobenzonitrile (0.182 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.247 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **32**; isolated yield: 0.157 g (70%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.76 (d, J=7.8 Hz, 1H), 7.64 (t, J=7.5 Hz, 1H), 7.51 (t, J=7.5 Hz, 1H), 7.44 (d, J=8.0 Hz, 1H), 7.04 (d, J=4.1 Hz, 1H), 6.35 (d, J=4.1 Hz, 1H), 3.80 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=188.6, 137.5, 135.1, 133.3, 132.4, 132.2, 131.0, 128.7, 119.1, 117.3, 113.3, 110.8, 34.8, 27.3; anal. calcd. for $C_{14}H_{12}N_2O$: C 74.98, H 5.39; found: C 74.84, H 5.60.

5-(2-Tolyl)-1-methyl-2-acetylpyrrole (33): The reaction of 2-bromotoluene (0.171 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.247 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **33**; isolated yield: 0.079 g (37%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.50–7.20 (m, 4H), 7.06 (d, J=4.1 Hz, 1H), 6.12 (d, J=4.1 Hz, 1H), 3.67 (s, 3H), 2.50 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=188.4, 142.1, 138.0, 131.6, 130.9, 130.7, 130.1, 128.9, 125.7, 119.4, 109.1, 34.4, 27.2, 19.8; anal. calcd. for $C_{14}H_{15}NO$: C 78.84, H 7.09; found: C 78.89, H 7.01.

1-(1-Methyl-5-naphthalen-1-ylpyrrol-2-yl)-ethanone (34): The reaction of 1-bromonaphthalene (0.207 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.247 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **34**; isolated yield: 0.199 g (80%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.00–7.83 (m, 2H), 7.65–7.40 (m, 5H), 7.17 (d, J=4.1 Hz, 1H), 6.32 (d, J=4.1 Hz, 1H), 3.70 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=188.4, 140.8, 133.4, 132.5, 131.3, 129.5, 129.2, 128.6, 128.3, 126.7, 126.1, 125.5, 125.0, 119.4, 110.4, 34.7, 27.2; anal. calcd. for $C_{17}H_{15}NO$: C 81.90, H 6.06; found: C 82.04, H 6.00.

1-(1-Methyl-5-pyridin-3-ylpyrrol-2-yl)-ethanone (35):[19] The reaction of 3-bromopyridine (0.158 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.247 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) affords the corresponding product **35**; isolated yield: 0.168 g (84%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.65 (m, 2H), 7.70 (d, J=7.2 Hz, 1H), 7.38 (dd, J=7.2 and 4.2 Hz, 1H), 7.03 (d, J=4.2 Hz, 1H), 6.26 (d, J=4.2 Hz, 1H), 3.87 (s, 3H), 2.47 (s, 3H).

Methyl 5-(4-cyanophenyl)-1-methylpyrrole-2-carboxylate (36): The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), methyl 1-methyl-2-pyrrolecarboxylate (0.278 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **36**; isolated yield: 0.200 g (83%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.65 (d, J=8.0 Hz, 2H), 7.44 (d, J=8.0 Hz, 2H), 6.95 (d, J=4.1 Hz, 1H), 6.20 (d, J=4.1 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=161.5, 139.1, 136.4, 132.2, 129.4, 124.7, 118.4, 117.6, 111.3, 110.2, 51.1, 34.4; anal. calcd. for $C_{14}H_{12}N_2O_2$: C 69.99, H 5.03; found: C 70.11, H 4.87.

Methyl 1-methyl-5-(4-propionylphenyl)-pyrrole-2-carboxylate (37): The reaction of 4-bromopropiophenone (0.214 g, 1 mmol), methyl 1-methyl-2-pyrrolecarboxylate (0.278 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$

(0.22 mg, 0.001 mmol) affords the corresponding product **37**; isolated yield: 0.217 g (80%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.3 Hz, 2H), 7.03 (d, J = 4.1 Hz, 1H), 6.27 (d, J = 4.1 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 3.03 (q, J = 7.5 Hz, 2H), 1.25 (t, J = 7.5 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 199.9, 161.6, 140.2, 136.3, 135.9, 129.1, 128.1, 124.2, 117.7, 109.8, 51.0, 34.5, 31.7, 8.1; anal. calcd. for $C_{16}H_{17}N_2O_3$: C 70.83, H 6.32; found: C 70.68, H 6.40.

Methyl 1-methyl-5-*p*-tolylpyrrole-2-carboxylate (38): The reaction of 4-bromotoluene (0.171 g, 1 mmol), methyl 1-methyl-2-pyrrolecarboxylate (0.278 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **38**; isolated yield: 0.120 g (52%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.35–7.10 (m, 4H), 7.04 (d, J = 4.1 Hz, 1H), 6.20 (d, J = 4.1 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 161.7, 141.6, 137.7, 129.0, 128.9, 128.8, 122.9, 117.7, 108.7, 50.8, 34.1, 21.0; anal. calcd. for $C_{14}H_{15}NO_2$: C 73.34, H 6.59; found: C 73.10, H 6.62.

2-(4-Cyanophenyl)-1-methylpyrrole (39):[20] The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 1-methylpyrrole (0.324 g, 4 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.022 mg, 0.0001 mmol) affords the corresponding product **39**; isolated yield: 0.146 g (80%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 6.81 (m, 1H), 6.37 (m, 1H), 6.26 (m, 1H), 3.74 (s, 3H).

2-(4-Methoxyphenyl)-1-methylpyrrole (40):[21] The reaction of 4-bromoanisole (0.187 g, 1 mmol), 1-methylpyrrole (0.324 g, 4 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **40**; isolated yield: 0.131 g (70%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.37 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 6.75 (m, 1H), 6.23 (m, 2H), 3.89 (s, 3H), 3.68 (s, 3H).

2-(4-Cyanophenyl)-1-phenylpyrrole (41): The reaction of 4-bromobenzonitrile (0.182 g, 1 mmol), 1-phenylpyrrole (0.536 g, 4 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.022 mg, 0.0001 mmol) affords the corresponding product **41**; isolated yield: 0.191 g (78%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.49 (d, J = 8.0 Hz, 2H), 7.45–7.35 (m, 3H), 7.30–7.15 (m, 4H), 7.02 (m, 1H), 6.60 (m, 1H), 6.43 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.7, 137.1, 131.8, 131.6, 129.2, 127.8, 127.2, 126.3, 125.6, 118.9, 112.6, 109.8, 109.1; anal. calcd. for $C_{17}H_{12}N_2$: C 83.58, H 4.95; found: C 83.47, H 5.10.

2-(4-Acetylphenyl)-1-phenylpyrrole (42): The reaction of 4-bromoacetophenone (0.199 g, 1 mmol), 1-phenylpyrrole (0.536 g, 4 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.022 mg, 0.0001 mmol) affords the corresponding product **42**; isolated yield: 0.209 g (80%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.0 Hz, 2H), 7.40–7.25 (m, 3H), 7.25–7.15 (m, 4H), 7.00 (m, 1H), 6.60 (m, 1H), 6.43 (m, 1H), 2.57 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 197.2, 140.1, 137.3, 134.3, 132.3, 129.0, 128.1, 127.4, 126.8, 125.7, 125.5, 112.1, 109.6; anal. calcd. for $C_{18}H_{15}NO$: C 82.73, H 5.79; found: C 82.80, H 5.89.

2-(4-Methoxyphenyl)-1-phenylpyrrole (43):[22] The reaction of 4-bromoanisole (0.187 g, 1 mmol), 1-phenylpyrrole (0.536 g, 4 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **43**; isolated yield: (0.175 g (70%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.50–7.15 (m, 5H), 7.10 (d, J = 8.4 Hz, 2H), 6.95 (m, 1H), 6.81 (d, J = 8.4 Hz, 2H), 6.40 (m, 2H), 3.81 (s, 3H).

2-(4-Methylphenyl)-1-phenylpyrrole (44):[22] The reaction of 4-bromotoluene (0.171 g, 1 mmol), 1-phenylpyrrole (0.536 g, 4 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **44**; isolated yield: 0.170 g (73%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.50–6.90 (m, 10H), 6.52–6.35 (m, 2H), 2.35 (s, 3H).

2-(4-Cyanophenyl)-5-(3-pyridyl)-1-methylpyrrole (45): The reaction of 3-bromopyridine (0.158 g, 1 mmol), 2-(4-cyanophenyl)-1-methylpyrrole **39** (0.364 g, 2 mmol) and KOAc (0.196 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **45**; isolated yield: 0.187 g (72%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.75 (m, 1H), 8.58 (m, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.71(d, J=8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.38 (m, 1H), 6.44 (m, 1H), 6.40 (m, 1H), 3.64 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 149.4, 148.3, 137.6, 135.9, 135.7, 135.0, 132.3, 128.5, 123.6, 118.9, 111.0, 110.4, 110.1, 34.5; anal. calcd. for $C_{17}H_{13}N_3$: C 78.74, H 5.05; found: C 78.80, H 5.14.

2-(4-Acetylphenyl)-1-methylindole (46):[11a] The reaction of 4-bromoacetophenone (0.200 g, 1 mmol), 1-methylindole (0.262 g, 2 mmol) and K_2CO_3 (0.278 g, 2 mmol) with $Pd(OAc)_2$ (0.22 mg, 0.001 mmol) affords the corresponding product **46**; isolated yield: 0.195 g (78%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.3 Hz, 2H), 7.80–7.60 (m, 3H), 7.50–7.10 (m, 3H), 6.69 (s, 1H), 3.85 (s, 3H), 2.70 (s, 3H).

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