Low catalyst loading ligand-free palladium-catalyzed direct arylation of furans: an economically and environmentally attractive access to 5-arylfurans

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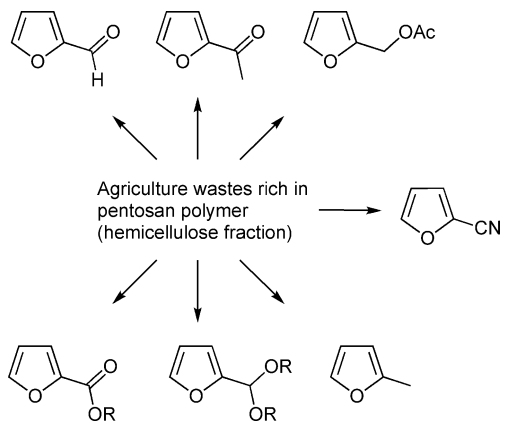
The direct 5-arylation of furans at very low catalyst loading using $Pd(OAc)_2$ as catalyst without added ligand proceed in high yields. Turnover numbers up to 10000 have been obtained for the coupling of several activated aryl bromides. A wide range of functions on the furan or aryl bromide is tolerated.

Introduction

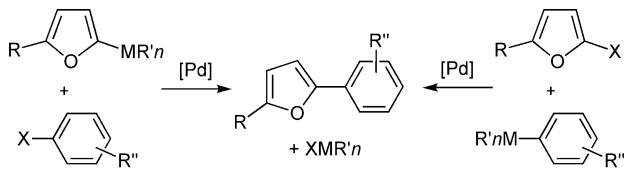
The direct use of several furan derivatives, such as furfural, 2-acetylfuran, methyl furan-2-carboxylate or furfuryl alcohol derivatives in organic synthesis is an important field for research in green chemistry, since they are obtained from agricultural wastes rich in pentosan polymers (Scheme 1).



Scheme 1 Source of some furan derivatives

Arylfurans are important building blocks in organic synthesis. Palladium catalysed Suzuki, Negishi or Stille cross-couplings are among the most important methods to prepare such arylfurans.[1] However, they require the preliminary synthesis of an organometallic derivative and provide an organometallic salt (MX) as by-product (Scheme 2).

In 1990, Ohta *et al.* reported the direct arylation of thiophenes, furans or thiazoles with aryl halides *via* a C–H bond activation in moderate to good yields using 5 mol% $Pd(PPh_3)_4$ as catalyst.[2] Since these exciting results, the palladium-catalyzed direct arylation of heteroaryl derivatives with aryl halides or triflates has proved to be a powerful method for the synthesis of arylated heteroaromatics.[3-11] This method provides a cost-effective and environmentally attractive procedure for the preparation of such compounds. The major drawback of the reported procedures is that they generally require 2-10 mol% catalyst.[3]



MR'n = $B(OH)_2$, $Sn(Bu)_3$, ZnCl, MgCl
X = Br, I

Scheme 2 Palladium-catalysed cross-couplings using organometallic derivatives

Recently, Heck and Suzuki reactions under low catalyst loading (0.1-0.01 mol%) using ligand-free catalyst $Pd(OAc)_2$ have been described by de Vries and co-workers.[12,13] They have demonstrated that, at elevated temperature, when $Pd(OAc)_2$ is employed as catalyst precursor, soluble palladium(0) colloids or nanoparticles are formed, and that the Heck or Suzuki reaction takes place *via* the interaction of the arylating agent with the palladium atoms in the outer rim of the nanoparticles. This leads to the formation of monomeric or dimeric anionic palladium complexes that undergo the usual steps of the Heck or Suzuki mechanisms.

So far, to our knowledge, all the procedures reported for the arylation *via* C–H bond activation of furans using ligand-free catalysts required 5-10 mol% catalyst,[14a,b] except one which employs only 1 mol%.[14c] Actually, such couplings under low catalyst concentration employ palladium associated to sophisticated ligands.[11d] Therefore, the discovery of more effective conditions, for the direct coupling of furan derivatives with aryl halides under low catalyst loading conditions (less than 0.1 mol%), would be a considerable advantage for industrial applications and for sustainable development.

We have already reported the direct 5-arylation of a range of thiazole or thiophene derivatives using a ligand-free palladium catalyst.[15b,c] We also described preliminary results using furan

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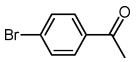
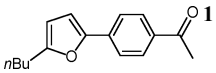
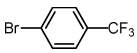
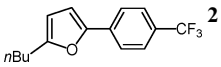
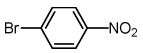
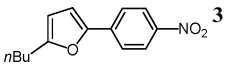
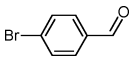
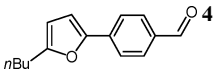
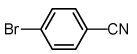
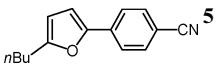
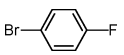
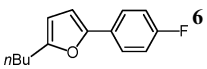
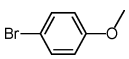
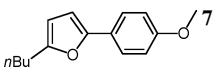
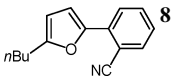
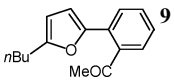
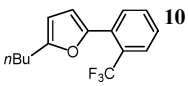
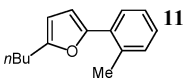
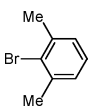
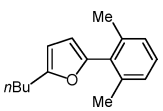
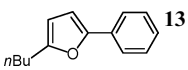
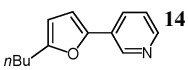
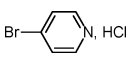
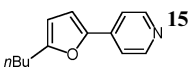
Table 1 Palladium catalysed coupling of 2-*n*-butylfuran and aryl halides (Scheme 3)[a]

Entry	Aryl halide	Substrate/Cat. ratio	Product	Conversion (%)	Yield (%)
1		10000	 **1**	100	86
2		10000	 **2**	100	90
3		10000	 **3**	100	64[b]
4		10000	 **4**	100	91
5		10000	 **5**	100	86
6		1000	 **6**	100	92
7		100	 **7**	33	12[b]
8		1000		44	18[b]
9		10000	 **8**	100	86
10		1000	 **9**	90	54[b]
11		1000	 **10**	92	90
12		100	 **11**	—	Traces
13		1000		27	16[b]
14		100	 **12**	0	—
15		1000		0	—
16		1000	 **13**	90	38[c]
17		1000	 **14**	73	70
18		1000	 **15**	93	82[d]

[a] Conditions: $Pd(OAc)_2$, 2-*n*-butylfuran (2 eq.), aryl halide (1 eq.), AcOK (2 eq.), DMAc, 150 °C, 20 h, conversion of the aryl halide determined by GC and NMR analysis, isolated yields. [b] The formation of unidentified side products was also observed. [c] The formation of an important amount of biphenyl was also observed. [d] AcOK: 3 eq.

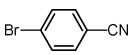
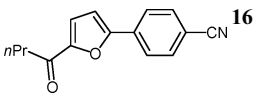
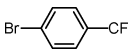
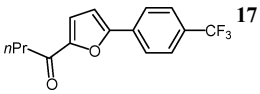
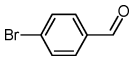
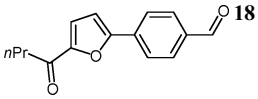
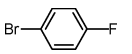
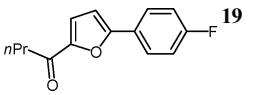
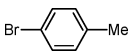
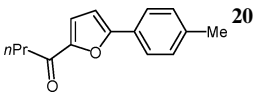
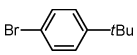
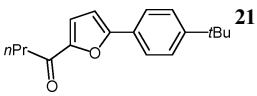
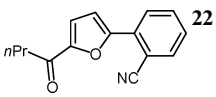
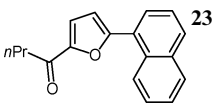
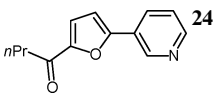
derivatives.[15a] Here, we wish to report on the reaction of a set of furans using a very wide variety of electronically and sterically diverse aryl or heteroaryl bromides at low catalyst loadings using a ligand-less palladium catalyst.

Results and discussion

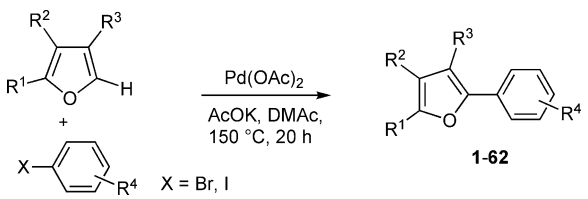
We first observed that, employing the "de Vries low catalyst loading procedure" (elevated reaction temperature, polar solvent, acetate as base, and no ligand on palladium) the coupling of 4-bromoacetophenone with 2-*n*-butylfuran using as little as 0.01 mol% $Pd(OAc)_2$ as catalyst led selectively to the 5-arylated furan **1** with complete conversion of the aryl bromide and a high isolated yield (Scheme 3, Table 1, entry 1).

Then, we studied the scope and limitations of this procedure with other *para*-substituted aryl bromides. Very high TONs of 10000 and good yields of products **2-5** were also obtained using the electron-deficient aryl bromides, 4-bromobenzotrifluoride, 4-bromobenzaldehyde, 4-bromonitrobenzene or 4-bromobenzonitrile (Table 1, entries 2-5). 4-Fluorobromobenzene reacted with 2-*n*-butylfuran and gave the expected 5-arylated furan **6** in a lower TON of 1000 but in high

Table 2 Palladium catalysed coupling of 1-(furan-2-yl)butan-1-one and aryl bromides (Scheme 3)[a]

Entry	Aryl bromide	Substrate/Cat. ratio	Product	Conversion (%)	Yield (%)
1		1000	 **16**	95	86
2		10000		28	—
3		1000	 **17**	76	70
4		10000		15	—
5		1000	 **18**	90	82
6		10000		30	24
7		1000	 **19**	78	71
8		1000	 **20**	93	84
9		1000	 **21**	48	41
10		1000	 **22**	94	87
11		1000	 **23**	90	83
12		1000	 **24**	76	70

[a] Conditions: $Pd(OAc)_2$, 1-(furan-2-yl)butan-1-one (2 eq.), aryl bromide (1 eq.), AcOK (2 eq.), DMAc, 150 °C, 20 h, conversion of the aryl bromide determined by GC and NMR analysis, isolated yields.



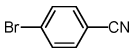
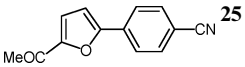
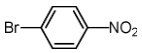
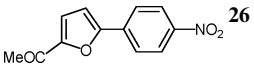
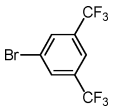
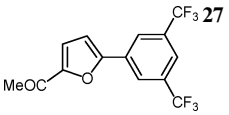
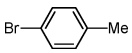
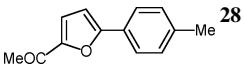
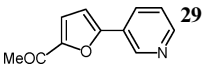
Scheme 3 Coupling of furans with aryl halides.

yield (Table 1, entry 6). On the other hand, using the electron-rich aryl bromide 4-bromoanisole, a low yield of 18% of **7** was obtained in the presence of 0.1 mol% catalyst. The formation of side-products was also observed in the course of this reaction. An increase of the catalyst loading to 1 mol% gave **7** in a lower yield of 12%, revealing that the concentration of active Pd species is relatively similar with both concentrations of $Pd(OAc)_2$ (Table 1, entries 7 and 8).

For this ligand-free procedure, under high palladium concentrations (>0.5 mol%), so-called "palladium black" forms more rapidly. This "palladium black" is generally inactive for such catalyzed reactions. Consequently, the yields of coupling products are not increased by a higher catalyst loading. With this procedure, less than 0.5 mol% catalyst should be employed.

Next, we employed *ortho*-substituted aryl bromides. 2-Bromobenzonitrile or 2-trifluoromethylbromobenzene gave **8** and **10** in high yields using 0.01 and 0.1 mol% catalyst, respectively (Table 1, entries 9 and 11). On the other hand, 2-bromoacetophenone gave **9** in only 54% isolated yield due to the formation of unidentified side-products (Table 1, entry 10). As expected, 2-bromotoluene was found to be less reactive. This congested and deactivated aryl bromide gave **11** in only 16% isolated yield when 0.1 mol% $Pd(OAc)_2$ was employed (Table 1, entry 13). Again, an increase of the catalyst loading to 1 mol% led to a lower yield of **11** (Table 1, entry 12). In the presence of highly congested 2,6-dimethylbromobenzene, no coupling product **12** was detected (Table 1, entries 14 and 15). Then, the reactivity of iodobenzene for the coupling with 2-*n*-butylfuran was examined. With this highly reactive aryl halide, the formation of a very important amount of biphenyl was observed, and the target product **13** was obtained in only 38% isolated yield (Table 2, entry 16). Therefore, for challenging substrates such as deactivated aryl bromides, aryl chlorides

Table 3 Palladium catalysed coupling of 2-acetylfuran and aryl bromides (Scheme 3)[a]

Entry	Aryl bromide	Substrate/Cat. ratio	Product	Conversion (%)	Yield (%)
1		1000	 **25**	100	86
2		10000		37	33
3		1000	 **26**	100	88
4		1000	 **27**	91	73
5		1000	 **28**	100	74[b]
6		1000	 **29**	100	80

[a] Conditions: $Pd(OAc)_2$, 2-acetylfuran (2 eq.), aryl bromide (1 eq.), AcOK (2 eq.), DMAc, 150 °C, 20 h, conversion of the aryl bromide determined by GC and NMR analysis, isolated yields. [b] The formation of unidentified side products was also observed.

or iodobenzene, palladium complexes associated to electron-rich monodentate phosphine ligands or to polydentate ligands should be employed as catalysts.[5b,11d,f]

This ligand-free procedure is not limited to aryl bromides. Heteroaryl bromides are also suitable reactants. Pyridines are π-electron deficient and, therefore, their oxidative addition to palladium is, in general, relatively easy. Using 3- or 4-bromopyridines and 2-*n*-butylfuran as reactants, **14** and **15** were obtained in high yields using only 0.1 mol% catalyst (Table 1, entries 17 and 18).

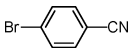
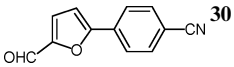
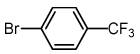
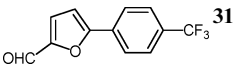
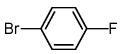
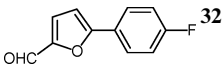
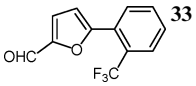
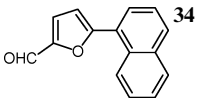
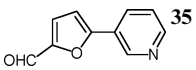
Then, we studied the scope and limitations of this low catalyst loading ligand-less procedure using a variety of furan derivatives (Tables 2-9). 1-(Furan-2-yl)butan-1-one is also a highly reactive substrate for this reaction, and several electronically and sterically diverse aryl bromides have been employed successfully. Again, the reactions are highly regioselective in favour of the 5-arylation and very small amount of side-products were detected. For example, the reaction of 4-bromobenzonitrile, 4-bromobenzaldehyde or 4-bromotoluene gave **16**, **18** and **20** in 82-86% yield using 0.1 mol% catalyst (Table 2, entries 1, 5 and 8). Using the same catalyst loading, the *ortho*-substituted aryl bromides, 2-bromobenzonitrile or 1-bromonaphthalene and the heteroaryl bromide, 3-bromopyridine also gave the 5-arylated furans **22-24** in good to high yields (Table 2, entries 10-12). On the other hand, deactivated 4-*t*-butylbromobenzene gave **21** in only 41% yield due to a partial conversion of this more challenging aryl bromide (Table 2, entry 9).

2-Acetylfuran is an inexpensive renewable bioresource; therefore, its valorisation is important. However, to our knowledge, the palladium-catalysed direct arylation of this reactant has not been reported. We observed that in the presence of the electron-deficient aryl bromides, 4-bromobenzonitrile, 4-bromonitrobenzene or 3,5-bistrifluoromethylbromobenzene, the 5-arylated furans **25-27** were obtained in 73-88% yield using 0.1 mol% catalyst (Table 3, entries 1-4). Even the slightly deactivated aryl bromide, 4-bromotoluene gave the desired compound **28** in good yield (Table 3, entry 5). 3-Bromopyridine also reacts nicely with this furan derivative to give **29** in 80% yield (Table 3, entry 6). It should be noted that small amount of side-products were also produced in the course of these reactions.

2-Formylfuran or furfural is a very cheap reagent obtained from the renewable bioresources sugar cane bagasse or corn stover. The direct arylation of this reagent, with mostly aryl iodides, has been described by McClure and co-workers using 5 mol% $PdCl_2$ associated to 10 mol% PCy_3.[11a] Fagnou and co-workers have recently reported the 5-arylation of furfural using 2 mol% $Pd(OAc)_2$ with 4 mol% PCy_3 as catalytic system.[11b] Employing our ligand-less and low catalyst loading procedure, this substrate was also found to give the 5-arylated furans in complete regioselectivity and good yields with a variety of aryl bromides (Table 4). Both *para*- and *ortho*-substituted aryl bromides have been employed using only 0.1 mol% $Pd(OAc)_2$ as catalyst and gave products **30-34** in 64-76% yields. Slightly activated aryl bromide 4-fluorobromobenzene was also found to be a suitable reactant. 3-Bromopyridine reacted with 2-formylfuran and gave target compound **35** in 73% yield. For these reactions, the formation of some side-products was also detected by GC and NMR analysis of the crude mixtures.

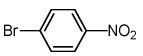
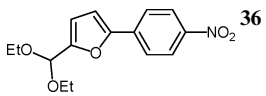
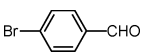
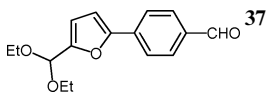
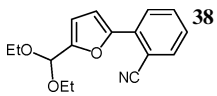
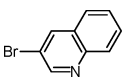
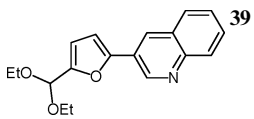
Then, we employed 2-(diethoxymethyl)furan as coupling partner (Table 5). This reactant is commercially available at an affordable cost. With this substrate, we expected to reduce the formation of side-products observed in the presence of furfural. Moreover, the direct access to protected 5-aryl-2-formylfurans might be very convenient in total synthesis. We observed that, using 4-bromonitrobenzene or 2-bromobenzonitrile, the desired 5-arylated furans **36** and **38** were obtained in good yield (Table 5, entries 1 and 3). On the other hand, in the presence of 4-bromobenzaldehyde or 3-bromoquinoline, the formation of deprotected 5-aryl-2-furaldehydes in low yield was also observed. Therefore, with these two substrates, lower yields of 70 and 69% of **37** and **39** were obtained (Table 5, entries 2 and 4). The optimization of the reaction conditions (reaction time, temperature and solvent) would certainly allow to produce the target compounds in high yields.

Table 4 Palladium catalysed coupling of 2-formylfuran and aryl bromides (Scheme 3)[a]

Entry	Aryl bromide	Product	Conversion (%)	Yield (%)
1		 **30**	100	76
2		 **31**	100	65
3		 **32**	90	64
4		 **33**	100	69
5		 **34**	100	70
6		 **35**	100	73

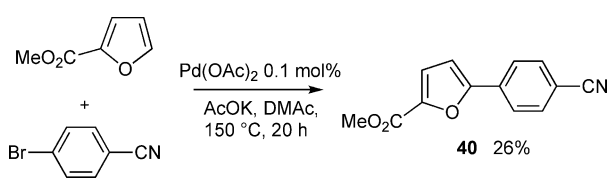
[a] Conditions: $Pd(OAc)_2$ (0.001 eq.), 2-formylfuran (2 eq.), aryl bromide (1 eq.), AcOK (2 eq.), DMAc, 150 °C, 20 h, conversion of the aryl bromide determined by GC and NMR analysis, isolated yields, the formation of unidentified side products was also observed.

Table 5 Palladium catalysed coupling of 2-(diethoxymethyl)furan and aryl bromides (Scheme 3)[a]

Entry	Aryl bromide	Product	Conversion (%)	Yield (%)
1		 **36**	100	78
2		 **37**	85	70[b]
3		 **38**	100	76
4		 **39**	82	69[b]

[a] Conditions: $Pd(OAc)_2$ (0.001 eq.), 2-(diethoxymethyl)furan (2 eq.), aryl bromide (1 eq.), AcOK (2 eq.), DMAc, 150 °C, 20 h, conversion of the aryl bromide determined by GC and NMR analysis, isolated yields, the formation of 5-aryl-2-formylfurans in low yields and of side-products was also observed. [b] Reaction time: 6 h.

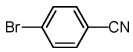
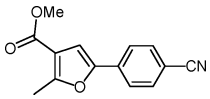
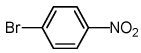
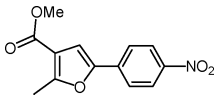
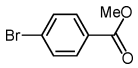
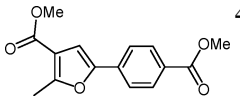
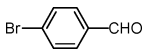
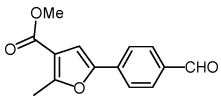
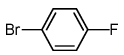
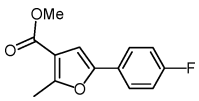
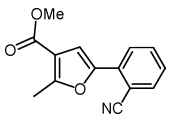
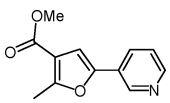
The reaction using methyl furan-2-carboxylate and 4-bromobenzonitrile also gave the desired 5-arylated methyl furan-2-carboxylate **40** (Scheme 4). However, this compound was obtained in a low yield of 26%. Due to partial decarboxylation of this furan derivative, a mixture of 5-arylated methyl furan-2-carboxylate **40**, 2-arylfuran and 2,5-diarylfuran was formed. Similar results were obtained in the presence of 4-trifluoromethylbromobenzene, 4-bromobenzaldehyde or 3-bromopyridine as coupling partners. Shorter reaction times did not allow to improve the yields.



Scheme 4 Coupling of methyl furan-2-carboxylate.

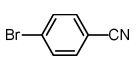
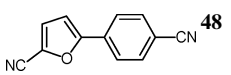
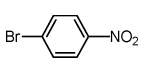
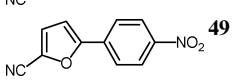
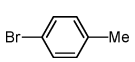
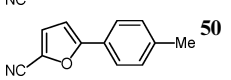
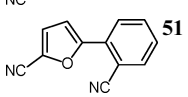
This decarboxylation side-reaction is specific for methyl furan-2-carboxylate. In the presence of methyl 2-methylfuran-3-carboxylate such decarboxylation products were not detected (Table 6). With this reactant, the expected 5-arylated furans **41-47** were produced in 65-88% yields using 0.1-0.01 mol% catalyst. The fastest reactions were observed using 2- or 4-bromobenzonitrile, and 4-bromobenzaldehyde. With these substrates, very high TONs of 8700-10000 were obtained (Table 6, entries 1, 6 and 9). 4-Bromonitrobenzene, 4-fluorobromobenzene or 3-bromopyridine also gave high yields of coupling products **42**, **45** and **47** in the presence of 0.1 mol% catalyst (Table 6, entries 2, 7 and 10).

Table 6 Palladium catalysed coupling of methyl 2-methylfuran-3-carboxylate and aryl bromides (Scheme 3)[a]

Entry	Aryl bromide	Substrate/Cat. ratio	Product	Conversion (%)	Yield (%)
1		10000	 **41**	100	88
2		1000	 **42**	91	82
3		10000		39	33
4		1000	 **43**	92	84
5		10000		43	37
6		10000	 **44**	87	79
7		1000	 **45**	91	82
8		10000		70	62
9		10000	 **46**	100	87
10		1000	 **47**	72	65
11		10000		25	—

[a] Conditions: $Pd(OAc)_2$, methyl 2-methylfuran-3-carboxylate (2 eq.), aryl bromide (1 eq.), AcOK (2 eq.), DMAc, 150 °C, 20 h, conversion of the aryl bromide determined by GC and NMR analysis, isolated yields.

Table 7 Palladium catalysed coupling of 2-cyanofuran and aryl bromides (Scheme 3)[a]

Entry	Aryl bromide	Product	Conversion (%)	Yield (%)
1		 **48**	100	64
2		 **49**	100	71
3		 **50**	—	0
4		 **51**	100	63

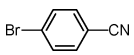
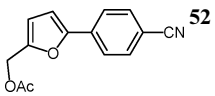
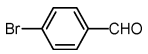
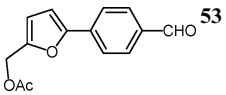
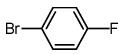
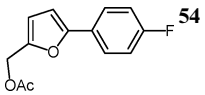
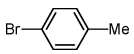
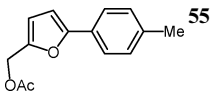
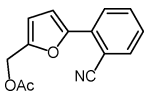
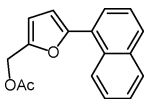
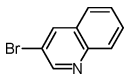
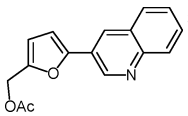
[a] Conditions: $Pd(OAc)_2$ (0.001 eq.), 2-cyanofuran (2 eq.), aryl bromide (1 eq.), AcOK (2 eq.), DMAc, 150 °C, 20 h, conversion of the aryl bromide determined by GC and NMR analysis, isolated yields, the formation of unidentified side products was also observed.

2-Cyanofuran (or 2-furonitrile), which is generally prepared from the renewable bioresource 2-formylfuran, was found to be a challenging substrate (Table 7). Only strongly activated aryl bromides were coupled successfully with this reactant. For example 2- or 4-bromobenzonitrile and 4-bromonitrobenzene gave the products **48**, **49** and **51** in 63-71% yield using 0.1 mol% catalyst (Table 7, entries 1, 2 and 4). On the other hand, employing similar reaction conditions, 4-bromotoluene was recovered unreacted (Table 7, entry 3).

Next, the reactivity of furfuryl acetate using a set of aryl bromides was studied (Table 8).

Furfuryl acetate can be prepared from furfuryl alcohol which is manufactured by the catalytic reduction of 2-formylfuran. This reactant was found to give regioselectively and in high

Table 8 Palladium catalysed coupling of furfuryl acetate and aryl bromides (Scheme 3)[a]

Entry	Aryl bromide	Subst./Cat. ratio	Product	Conversion (%)	Yield (%)
1		1000	 **52**	100	80
2		1000	 **53**	100	88
3		10000		41	36
4		1000	 **54**	94	84
5		1000	 **55**	93	81
6		1000	 **56**	100	82
7		10000		68	54
8		1000	 **57**	100	83
9		10000		8	—
10		1000	 **58**	100	83

[a] Conditions: $Pd(OAc)_2$, furfuryl acetate (2 eq.), aryl bromide (1 eq.), AcOK (2 eq.), DMAc, 150 °C, 20 h, conversion of the aryl bromide determined by GC and NMR analysis, isolated yields.

yields the desired 5-arylation compounds **52-58** using only 0.1-0.01 mol% catalyst. *Para*- or *ortho*-substituted electron-deficient aryl bromides such as 2- or 4-bromobenzonitrile or 4-bromobenzaldehyde have been employed successfully (Table 8, entries 1, 2, 3, 6 and 7). Even the slightly deactivated aryl bromide 4-bromotoluene was found to give the coupling product **55** in high yield using 0.1 mol% catalyst (Table 8, entry 5). The reaction of 3-bromoquinoline with furfuryl acetate gave **58** in 83% yield (Table 8, entry 10). For all these reactions, no formation of side-products was detected by GC analysis.

Finally, we examined the reactivity of menthofuran. This compound is naturally present in mint oil. This 2,3,4-three substituted furan was also found to be extremely reactive for the direct arylation using our ligand-less procedure (Table 9). With this substrate, the reaction of 4-bromobenzonitrile, 4-bromofluorobenzene or 2-bromobenzaldehyde gave the expected 5-arylated products **59-62** in very high yields using only 0.1-0.01 mol% catalyst.

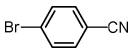
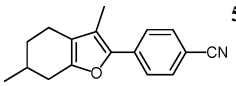
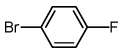
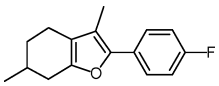
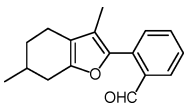
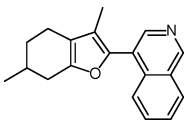
Conclusion

In summary, the "de Vries palladium ligand-free and low-catalyst loading procedure" is not limited to Heck or Suzuki reactions. The direct 5-arylation of 2-substituted furans proceeds nicely in the presence of ligand-free $Pd(OAc)_2$. With this procedure, there is no need to eliminate phosphine derivatives at the end of the reaction. Moreover, under such low catalyst concentration, palladium stabilizing agents like ammonium salts which are often employed in ligand-less palladium-catalysed reactions are needless, thus reducing the amount of waste. Substrate/catalyst ratios up to 10000 can be employed with several substrates. However, this procedure is limited to electron-deficient aryl bromides with most furan derivatives. It should be noted that a wide range of functions such as formyl, acetyl, benzoyl, ester, nitro, nitrile, fluoro or trifluoromethyl on the aryl bromide is tolerated. A variety of furan derivatives bearing several functions such as formyl, acetyl, nitrile, ester or alkyl can be employed. This reaction allows the valorisation of agriculture wastes, and the major by-products of the reactions are AcOH/KBr instead of metallic salts with classical coupling procedures, thus rendering this low catalyst loading procedure economically and environmentally attractive. Moreover, no preparation of an organometallic derivative is required, reducing the number of steps to prepare these compounds.

Experimental

As a typical experiment, the reaction of 4-bromoacetophenone (0.199 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol) and AcOK (0.196 g, 2 mmol) at 150 °C during 20 h in dry DMAc (3 mL) in the presence of $Pd(OAc)_2$ complex (0.0224 mg, 0.0001 mmol) under argon affords the corresponding product 2-*n*-butyl-5-(4-acetylphenyl)furan[11d] **1** after evaporation of the solvent and filtration on silica gel (pentane/ether) in 86% (0.208 g) isolated

Table 9 Palladium catalysed coupling of menthofuran and aryl bromides (Scheme 3)[a]

Entry	Aryl halide	Subst./Cat. ratio	Product	Conversion (%)	Yield (%)
1		1000	**59** 	98	90
2		10000		90	80
3		1000	**60** 	97	88
4		10000		30	—
5		1000	**61** 	97	88
6		10000		82	74
7		1000	**62** 	99	90

[a] Conditions: $Pd(OAc)_2$, menthofuran (2 eq.), aryl bromide (1 eq.), AcOK (2 eq.), DMAc, 150 °C, 20 h, conversion of the aryl bromide determined by GC and NMR analysis, isolated yields.

yield. The conversion of 4-bromoacetophenone was determined by GC and NMR analysis of the crude mixture. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.98 (d, J = 8.6 Hz, 2 H), 7.70 (d, J = 8.6 Hz, 2 H), 6.72 (d, J = 3.2 Hz, 1 H), 6.12 (d, J = 3.2 Hz, 1 H), 2.72 (t, J = 7.4 Hz, 2 H), 2.60 (s, 3 H), 1.72 (quint., J = 7.4 Hz, 2 H), 1.45 (sext., J = 7.4 Hz, 2 H), 0.97 (t, J = 7.4 Hz, 3 H).

2-*n*-Butyl-5-(4-trifluoromethylphenyl)furan (2)

4-(Trifluoromethyl)bromobenzene (0.225 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.0224 mg, 0.0001 mmol) affords **2** in 90% (0.241 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.73 (d, J = 8.6 Hz, 2 H), 7.61 (d, J = 8.6 Hz, 2 H), 6.67 (d, J = 3.2 Hz, 1 H), 6.12 (d, J = 3.2 Hz, 1 H), 2.72 (t, J = 7.4 Hz, 2 H), 1.72 (quint., J = 7.4 Hz, 2 H), 1.45 (sext., J = 7.4 Hz, 2 H), 0.99 (t, J = 7.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 157.7, 150.6, 134.3 (q, J = 1.3 Hz), 128.2 (q, J = 32.2 Hz), 125.6 (q, J = 3.8 Hz), 124.3 (q, J = 271.6 Hz), 123.1, 107.8, 107.3, 30.1, 27.9, 22.3, 13.8. Elemental analysis: calcd (%) for $C_{15}H_{15}F_3O$ (268.27): C 67.16, H 5.64; found: C 67.41, H 5.89.

2-*n*-Butyl-5-(4-nitrophenyl)furan (3)[11d]

4-Bromonitrobenzene (0.202 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.0224 mg, 0.0001 mmol) affords **3** in 64% (0.157 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.23 (d, J = 8.6 Hz, 2 H), 7.74 (d, J = 8.6 Hz, 2 H), 6.68 (d, J = 3.2 Hz, 1 H), 6.17 (d, J = 3.2 Hz, 1 H), 2.72 (t, J = 7.4 Hz, 2 H), 1.72 (quint., J = 7.4 Hz, 2 H), 1.45 (sext., J = 7.4 Hz, 2 H), 0.99 (t, J = 7.4 Hz, 3H).

2-*n*-Butyl-5-(4-formylphenyl)furan (4)[11d]

4-Bromobenzaldehyde (0.185 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.0224 mg, 0.0001 mmol) affords **4** in 91% (0.208 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.98 (s, 1 H), 7.90 (d, J = 8.5 Hz, 2 H), 7.77 (d, J = 8.5 Hz, 2 H), 6.70 (d, J = 3.2 Hz, 1 H), 6.11 (d, J = 3.2 Hz, 1 H), 2.70 (t, J = 7.4 Hz, 2 H), 1.72 (quint., J = 7.4 Hz, 2 H), 1.45 (sext., J = 7.4 Hz, 2 H), 0.99 (t, J = 7.4 Hz, 3H).

2-*n*-Butyl-5-(4-cyanophenyl)furan (5)[11d]

4-Bromobenzonitrile (0.182 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.0224 mg, 0.0001 mmol) affords **5** in 86% (0.194 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.69 (d, J = 8.6 Hz, 2 H), 7.60 (d, J = 8.6 Hz, 2 H), 6.69 (d, J = 3.2 Hz, 1 H), 6.12 (d, J = 3.2 Hz, 1 H), 2.72 (t, J = 7.4 Hz, 2 H), 1.72 (quint., J = 7.4 Hz, 2 H), 1.45 (sext., J = 7.4 Hz, 2 H), 0.99 (t, J = 7.4 Hz, 3H).

2-*n*-Butyl-5-(4-fluorophenyl)furan (6)[11d]

4-Bromofluorobenzene (0.175 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **6** in 92% (0.201 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.61 (dd, J = 8.6 and 5.5 Hz, 2 H), 7.06 (t, J = 8.6 Hz, 2 H), 6.48 (d, J = 3.2 Hz, 1 H), 6.06 (d, J = 3.2 Hz, 1 H), 2.69 (t, J = 7.4 Hz, 2 H), 1.72 (quint., J = 7.4 Hz, 2 H), 1.45 (sext., J = 7.4 Hz, 2 H), 0.99 (t, J = 7.4 Hz, 3H).

2-*n*-Butyl-5-(4-methoxyphenyl)-furan (7)[11d]

4-Bromoanisole (0.187 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **7** in 18% (0.042 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.58 (d, J = 8.6 Hz, 2 H), 7.92 (d, J = 8.6 Hz, 2 H), 6.42 (d, J = 3.2 Hz, 1 H), 6.04 (d, J = 3.2 Hz, 1 H), 3.82 (s, 3 H), 2.69 (t, J = 7.4 Hz, 2 H), 1.72 (quint., J = 7.4 Hz, 2 H), 1.45 (sext., J = 7.4 Hz, 2 H), 0.99 (t, J = 7.4 Hz, 3H).

2-(5-*n*-Butylfuran-2-yl)benzonitrile (8)

2-Bromobenzonitrile (0.182 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.0224 mg, 0.0001 mmol) affords **8** in 86% (0.194 g) yield.

^{1}H NMR (200 MHz, CDCl): δ 7.85 (d, $J = 8.0$ Hz, 1 H), 7.68 (d, $J = 8.0$ Hz, 1 H), 7.56 (t, $J = 7.8$ Hz, 1 H), 7.32 (t, $J = 7.8$ Hz, 1 H), 7.21 (d, $J = 3.3$ Hz, 1 H), 6.16 (d, $J = 3.3$ Hz, 1 H), 2.71 (t, $J = 7.4$ Hz, 2 H), 1.70 (quint., $J = 7.4$ Hz, 2 H), 1.42 (sext., $J = 7.4$ Hz, 2 H), 0.95 (t, $J = 7.4$ Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 157.9, 147.9, 134.0, 133.5, 132.7, 126.3, 125.3, 119.1, 111.3, 107.7, 106.0, 30.0, 27.8, 22.2, 13.8. Elemental analysis: calcd (%) for $C_{15}H_{15}NO$ (225.29): C 79.97, H 6.71; found: C 79.69, H 6.96.

2-*n*-Butyl-5-(2-acetylphenyl)furan (9)

2-bromoacetophenone (0.199 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **9** in 54% (0.131 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.55 (d, $J = 7.6$ Hz, 1 H), 7.39 (m, 3 H), 6.48 (d, $J = 3.2$ Hz, 1 H), 6.09 (d, $J = 3.2$ Hz, 1 H), 2.65 (t, $J = 7.3$ Hz, 2 H), 2.27 (s, 3 H), 1.64 (quint., $J = 7.3$ Hz, 2 H), 1.38 (sext., $J = 7.3$ Hz, 2 H), 0.93 (t, $J = 7.3$ Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 204.9, 157.8, 150.3, 139.1, 130.2, 128.6, 127.3, 127.05, 127.02, 109.0, 107.2, 30.2, 29.9, 27.7, 22.2, 13.8. Elemental analysis: calcd (%) for $C_{16}H_{18}O_2$ (242.31): C 79.31, H 7.49; found: C 79.46, H 7.68.

2-*n*-Butyl-5-(2-trifluoromethylphenyl)furan (10)[11d]

2-(Trifluoromethyl)bromobenzene (0.225 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **10** in 90% (0.241 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.75 (d, $J = 8.0$ Hz, 2 H), 7.57 (t, $J = 7.6$ Hz, 1 H), 7.38 (t, $J = 7.6$ Hz, 1 H), 6.64 (d, $J = 3.2$ Hz, 1 H), 6.12 (d, $J = 3.2$ Hz, 1 H), 2.72 (t, $J = 7.3$ Hz, 2 H), 1.70 (quint., $J = 7.3$ Hz, 2 H), 1.44 (sext., $J = 7.3$ Hz, 2 H), 0.97 (t, $J = 7.3$ Hz, 3 H).

2-*n*-Butyl-5-(2-methylphenyl)furan (11)

2-Bromotoluene (0.171 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **11** in 16% (0.035 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.71 (d, $J = 8.0$ Hz, 1 H), 7.30-7.10 (m, 3 H), 6.46 (d, $J = 3.2$ Hz, 1 H), 6.11 (d, $J = 3.2$ Hz, 1 H), 2.72 (t, $J = 7.3$ Hz, 2 H), 2.51 (s, 3 H), 1.71 (quint., $J = 7.3$ Hz, 2 H), 1.42 (sext., $J = 7.3$ Hz, 2 H), 0.97 (t, $J = 7.3$ Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.9, 151.6, 134.0, 131.1, 130.5, 126.8, 126.5, 125.9, 109.2, 106.5, 30.2, 27.8, 22.3, 22.0, 13.8. Elemental analysis: calcd (%) for $C_{15}H_{18}O$ (214.30): C 84.07, H 8.47; found: C 84.01, H 8.42.

2-*n*-Butyl-5-phenylfuran (13)[4]

Iodobenzene (0.204 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **13** in 38% (0.076 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.67-7.19 (m, 5 H), 6.58 (d, $J = 3.2$ Hz, 1 H), 6.09 (d, $J = 3.2$ Hz, 1 H), 2.72 (t, $J = 7.3$ Hz, 2 H), 1.64 (quint., $J = 7.3$ Hz, 2 H), 1.32 (sext., $J = 7.3$ Hz, 2 H), 0.97 (t, $J = 7.3$ Hz, 3 H).

2-*n*-Butyl-5-(3-pyridyl)furan (14)[11d]

3-Bromopyridine (0.158 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **14** in 70% (0.141 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.88 (m, 1 H), 8.49 (m, 1 H), 7.85 (d, $J = 7.4$ Hz, 1 H), 7.25 (m, 1 H), 6.62 (d, $J = 3.2$ Hz, 1 H), 6.07 (d, $J = 3.2$ Hz, 1 H), 2.68 (t, $J = 7.4$ Hz, 2 H), 1.67 (quint., $J = 7.4$ Hz, 2 H), 1.42 (m, 2 H), 0.91 (t, $J = 7.4$ Hz, 3 H).

2-*n*-Butyl-5-(4-pyridyl)furan (15)

4-Bromopyridine hydrochloride (0.194 g, 1 mmol), 2-*n*-butylfuran (0.248 g, 2 mmol), AcOK (0.294 g, 3 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **15** in 82% (0.165 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.58 (d, $J = 4.8$ Hz, 2 H), 7.48 (d, $J = 4.8$ Hz, 2 H), 6.79 (d, $J = 3.2$ Hz, 1 H), 6.14 (d, $J = 3.2$ Hz, 1 H), 2.71 (t, $J = 7.4$ Hz, 2 H), 1.67 (quint., $J = 7.4$ Hz, 2 H), 1.42 (m, 2 H), 0.97 (t, $J = 7.4$ Hz, 3 H).^{13}C NMR (50 MHz, $CDCl_3$): δ 158.0, 150.4, 149.7, 138.1, 117.6, 110.2, 107.9, 30.4, 28.8, 22.8, 14.2. Elemental analysis: calcd (%) for $C_{13}H_{15}NO$ (201.26): C 77.58, H 7.51; found: C 77.62, H 7.47.

1-[5-(4-Cyanophenyl)furan-2-yl]butan-1-one (16)

4-Bromobenzonitrile (0.182 g, 1 mmol), 1-(furan-2-yl)butan-1-one (0.276 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **16** in 86% (0.206 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.89 (d, $J = 8.6$ Hz, 2 H), 7.72 (d, $J = 8.6$ Hz, 2 H), 7.28 (d, $J = 3.2$ Hz, 1 H), 6.93 (d, $J = 3.2$ Hz, 1 H), 2.87 (t, $J = 7.4$ Hz, 2 H), 1.82 (m, 2 H), 1.03 (t, $J = 7.4$ Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 189.7, 155.2, 153.2, 133.7, 133.1, 125.5, 119.1, 118.9, 112.5, 110.3, 40.8, 18.2, 14.3. Elemental analysis: calcd (%) for $C_{15}H_{13}NO_2$ (239.27): C 75.30, H 5.48; found: C 75.42, H 5.54.

1-[5-(4-Trifluoromethylphenyl)furan-2-yl]butan-1-one (17)

4-(Trifluoromethyl)bromobenzene (0.225 g, 1 mmol), 1-(furan-2-yl)butan-1-one (0.276 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **17** in 70% (0.198 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.90 (d, $J = 8.6$ Hz, 2 H), 7.69 (d, $J = 8.6$ Hz, 2 H), 7.28 (d, $J = 3.2$ Hz, 1 H), 6.89 (d, $J = 3.2$ Hz, 1 H), 2.88 (t, $J = 7.4$ Hz, 2 H), 1.81 (m, 2 H), 1.04 (t, $J = 7.4$ Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 189.2, 155.2, 152.2, 133.3, 130.3 (q, $J = 32.7$ Hz), 125.6 (q, $J = 3.8$ Hz), 124.7, 123.3 (q, $J = 272.3$ hz), 119.6, 108.7, 40.2, 17.0, 13.6. Elemental analysis: calcd (%) for $C_{15}H_{13}F_3O_2$ (282.26): C 63.83, H 4.64; found: C 63.98, H 4.70.

1-[5-(4-Formylphenyl)furan-2-yl]butan-1-one (18)

4-Bromobenzaldehyde (0.185 g, 1 mmol), 1-(furan-2-yl)butan-1-one (0.276 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **18** in 82% (0.199 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.94 (s, 1 H), 7.90-7.80 (m, 4 H), 7.21 (d, J = 3.2 Hz, 1 H), 6.89 (d, J = 3.2 Hz, 1 H), 2.80 (t, J = 7.4 Hz, 2 H), 1.72 (m, 2 H), 0.97 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 191.7, 189.6, 155.8, 153.0, 136.4, 134.9, 130.6, 125.5, 119.3, 110.3, 40.7, 18.2, 14.2. Elemental analysis: calcd (%) for $C_{15}H_{14}O_3$ (242.27): C 74.36, H 5.82; found: C 74.42, H 5.72.

1-[5-(4-Fluorophenyl)furan-2-yl]butan-1-one (19)

4-Bromofluorobenzene (0.175 g, 1 mmol), 1-f(uran-2-yl)butan-1-one (0.276 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **19** in 71% (0.165 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.79 (dd, J = 8.7 and 5.3 Hz, 2 H), 7.27 (d, J = 3.2 Hz, 1 H), 7.14 (d, J = 8.7 Hz, 2 H), 6.73 (d, J = 3.2 Hz, 1 H), 2.85 (t, J = 7.4 Hz, 2 H), 1.82 (m, 2 H), 1.03 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 189.7, 163.7 (d, J = 250.0 Hz), 156.9, 152.3, 127.2 (d, J = 8.3 Hz), 126.2, 119.6, 116.5 (d, J = 22.1 Hz), 107.4, 40.8, 18.4, 14.4. Elemental analysis: calcd (%) for $C_{14}H_{13}FO_2$ (232.25): C 72.40, H 5.64; found: C 72.49, H 5.78.

1-[5-(4-Methylphenyl)furan-2-yl]butan-1-one (20)

4-Bromotoluene (0.171 g, 1 mmol), 1-(furan-2-yl)butan-1-one (0.276 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **20** in 84% (0.192 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.70 (d, J = 8.6 Hz, 2 H), 7.30-7.20 (m, 3 H), 6.73 (d, J = 3.2 Hz, 1 H), 2.87 (t, J = 7.4 Hz, 2 H), 2.41 (s, 3 H), 1.82 (m, 2 H), 1.04 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 189.7, 158.2, 152.1, 139.7, 130.0, 127.2, 125.3, 119.6, 107.1, 40.7, 21.8, 18.5, 14.4. Elemental analysis: calcd (%) for $C_{15}H_{16}O_2$ (228.29): C 78.92, H 7.06; found: C 78.97, H 7.14.

1-[5-(4-*t*-Butylphenyl)furan-2-yl]butan-1-one (21)

4-*t*-Butylbromobenzene (0.213 g, 1 mmol), 1-(furan-2-yl)butan-1-one (0.276 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **21** in 41% (0.111 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.74 (d, J = 8.6 Hz, 2 H), 7.47 (d, J = 8.6 Hz, 2 H), 7.27 (d, J = 3.2 Hz, 1 H), 6.74 (d, J = 3.2 Hz, 1 H), 2.87 (t, J = 7.4 Hz, 2 H), 1.82 (m, 2 H), 1.38 (s, 9 H), 1.04 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 189.7, 158.1, 152.9, 152.1, 127.2, 126.2, 125.2, 119.6, 107.2, 40.8, 35.3, 31.6, 18.5, 14.4. Elemental analysis: calcd (%) for $C_{18}H_{22}O_2$ (270.37): C 79.96, H 8.20; found: C 80.12, H 8.17.

1-[5-(2-Cyanophenyl)furan-2-yl]butan-1-one (22)

2-Bromobenzonitrile (0.182 g, 1 mmol), 1-(furan-2-yl)butan-1-one (0.276 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **22** in 87% (0.209 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.96 (d, J = 8.6 Hz, 1 H), 7.70 (d, J = 8.6 Hz, 1 H), 7.64 (t, J = 7.6 Hz, 1 H), 7.41 (t, J = 7.6 Hz, 1 H), 7.31 (d, J = 3.2 Hz, 1 H), 7.25 (d, J = 3.2 Hz, 1 H), 2.87 (t, J = 7.4 Hz, 2 H), 1.77 (m, 2 H), 0.98 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 189.2, 152.1, 152.0, 134.1, 132.8, 131.3, 128.5, 126.6, 118.1, 118.0, 111.6, 107.6, 40.1, 17.4, 13.5. Elemental analysis: calcd (%) for $C_{15}H_{13}NO_2$ (239.27): C 75.30, H 5.48; found: C 75.30, H 5.60.

1-[5-(Naphthalen-1-yl)furan-2-yl]butan-1-one (23)

1-Bromonaphthalene (0.207 g, 1 mmol), 1-(furan-2-yl)butan-1-one (0.276 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **23** in 83% (0.219 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.44 (d, J = 8.6 Hz, 1 H), 8.00-7.80 (m, 3 H), 7.70-7.50 (m, 3 H), 7.37 (d, J = 3.2 Hz, 1 H), 6.86 (d, J = 3.2 Hz, 1 H), 2.92 (t, J = 7.4 Hz, 2 H), 1.88 (m, 2 H), 1.07 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 189.1, 156.8, 152.0, 133.6, 129.9, 129.7, 128.4, 126.9, 126.8, 126.7, 125.9, 124.9, 124.7, 118.2, 111.2, 40.1, 17.7, 13.7. Elemental analysis: calcd (%) for $C_{18}H_{16}O_2$ (264.32): C 81.79, H 6.10; found: C 81.90, H 6.21.

1-[5-(3-Pyridyl)-furan-2-yl]butan-1-one (24)

3-Bromopyridine (0.158 g, 1 mmol), 1-(furan-2-yl)butan-1-one (0.276 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **24** in 70% (0.151 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.02 (m, 1 H), 8.59 (m, 1 H), 8.07 (d, J = 8.0 Hz, 1 H), 7.40 (m, 1 H), 7.27 (d, J = 3.2 Hz, 1 H), 6.87 (d, J = 3.2 Hz, 1 H), 2.85 (t, J = 7.4 Hz, 2 H), 1.80 (m, 2 H), 1.01 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 188.7, 153.7, 151.9, 149.1, 145.7, 131.3, 125.0, 123.1, 118.1, 107.9, 39.8, 17.2, 13.3. Elemental analysis: calcd (%) for $C_{13}H_{13}NO_2$ (215.25): C 72.54, H 6.09; found: C 75.32, H 6.14.

4-(5-Acetylfuran-2-yl)benzonitrile (25)

4-Bromobenzonitrile (0.182 g, 1 mmol), 2-acetylfuran (0.220 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **25** in 86% (0.182 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.90 (d, J = 8.6 Hz, 2 H), 7.68 (d, J = 8.6 Hz, 2 H), 7.23 (d, J = 3.2 Hz, 1 H), 6.87 (d, J = 3.2 Hz, 1 H), 2.54 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 186.8, 166.4, 153.1, 133.6, 133.1, 126.8, 118.6, 116.9, 112.6, 110.4, 27.0. Elemental analysis: calcd (%) for $C_{13}H_9NO_2$ (211.22): C 73.92, H 4.29; found: C 73.81, H 4.41.

1-[5-(4-Nitrophenyl)furan-2-yl]ethanone (26)[16]

4-Bromonitrobenzene (0.202 g, 1 mmol), 2-acetylfuran (0.220 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **26** in 88% (0.204 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.28 (d, J = 8.6 Hz, 2 H), 7.92 (d, J = 8.6 Hz, 2 H), 7.30 (d, J = 3.2 Hz, 1 H), 6.97 (d, J = 3.2 Hz, 1 H), 2.54 (s, 3 H).

1-[5-(3,5-Bistrifluoromethylphenyl)furan-2-yl]ethanone (27)[17]

3,5-Bistrifluoromethylbromobenzene (0.293 g, 1 mmol), 2-acetylfuran (0.220 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **27** in 73% (0.235 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.21 (s, 2 H), 7.82 (s, 1 H), 7.30 (d, $J = 3.2$ Hz, 1 H), 6.97 (d, $J = 3.2$ Hz, 1 H), 2.54 (s, 3 H).

1-(5-*p*-Tolylfuran-2-yl)ethanone (28)

4-Bromotoluene (0.171 g, 1 mmol), 2-acetylfuran (0.220 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **28** in 74% (0.148 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.70 (d, $J = 8.4$ Hz, 2 H), 7.27 (d, $J = 8.4$ Hz, 2 H), 7.23 (d, $J = 3.2$ Hz, 1 H), 6.74 (d, $J = 3.2$ Hz, 1 H), 2.54 (s, 3 H), 2.41 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 186.7, 158.4, 152.1, 139.9, 130.0, 127.1, 125.4, 120.1, 107.2, 26.4, 21.9. Elemental analysis: calcd (%) for $C_{13}H_{12}O_2$ (200.23): C 77.98, H 6.04; found: C 78.04, H 6.07.

1-[5-(Pyridin-3-yl)furan-2-yl]ethanone (29)[18]

3-Bromopyridine (0.158 g, 1 mmol), 2-acetylfuran (0.220 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **29** in 80% (0.150 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.20 (m, 2 H), 7.83 (m, 1 H), 7.30 (d, $J = 3.2$ Hz, 1 H), 7.25 (m, 1 H), 6.95 (d, $J = 3.2$ Hz, 1 H), 2.56 (s, 3 H).

4-(5-Formylfuran-2-yl)benzonitrile (30)[11a]

4-Bromobenzonitrile (0.182 g, 1 mmol), 2-formylfuran (0.192 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **30** in 76% (0.150 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.72 (s, 1 H), 7.93 (d, $J = 8.6$ Hz, 2 H), 7.75 (d, $J = 8.6$ Hz, 2 H), 7.37 (d, $J = 3.2$ Hz, 1 H), 7.00 (d, $J = 3.2$ Hz, 1 H).

5-(4-Trifluoromethylphenyl)furan-2-carbaldehyde (31)[1e]

4-(Trifluoromethyl)bromobenzene (0.225 g, 1 mmol), 2-formylfuran (0.192 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **31** in 65% (0.156 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.70 (s, 1 H), 7.93 (d, $J = 8.6$ Hz, 2 H), 7.70 (d, $J = 8.6$ Hz, 2 H), 7.35 (d, $J = 3.2$ Hz, 1 H), 6.94 (d, $J = 3.2$ Hz, 1 H).

5-(4-Fluorophenyl)furan-2-carbaldehyde (32)[1d]

4-Bromofluorobenzene (0.175 g, 1 mmol), 2-formylfuran (0.192 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **32** in 64% (0.122 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.59 (s, 1 H), 7.85 (dd, $J = 8.6$ and 5.0 Hz, 2 H), 7.34 (d, $J = 3.2$ Hz, 1 H), 7.15 (t, $J = 8.6$ Hz, 2 H), 6.80 (d, $J = 3.2$ Hz, 1 H).

5-(2-Trifluoromethylphenyl)furan-2-carbaldehyde (33)[19]

2-(Trifluoromethyl)bromobenzene (0.225 g, 1 mmol), 2-formylfuran (0.192 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **33** in 69% (0.166 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.73 (s, 1 H), 7.85 (d, $J = 8.6$ Hz, 1 H), 7.75 (d, $J = 8.6$ Hz, 1 H), 7.62 (t, $J = 7.8$ Hz, 1 H), 7.52 (t, $J = 7.8$ Hz, 1 H), 7.34 (d, $J = 3.2$ Hz, 1 H), 6.90 (d, $J = 3.2$ Hz, 1 H).

5-(Naphthalen-1-yl)furan-2-carbaldehyde (34)[20]

1-Bromonaphthalene (0.207 g, 1 mmol), 2-formylfuran (0.192 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **34** in 70% (0.156 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.76 (s, 1 H), 8.42 (d, $J = 8.6$ Hz, 1 H), 8.00-7.80 (m, 3 H), 7.70-7.50 (m, 3 H), 7.45 (d, $J = 3.2$ Hz, 1 H), 6.905 (d, $J = 3.2$ Hz, 1 H).

5-(3-Pyridyl)furan-2-carbaldehyde (35)[1e]

3-Bromopyridine (0.158 g, 1 mmol), 2-formylfuran (0.192 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **35** in 73% (0.127 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.71 (s, 1 H), 9.06 (m, 1 H), 8.65 (d, $J = 5.0$ Hz, 1 H), 8.14 (d, $J = 8.0$ Hz, 1 H), 7.42 (dd, $J = 8.0$ and 5.0 Hz, 1 H), 7.39 (d, $J = 3.2$ Hz, 1 H), 6.96 (d, $J = 3.2$ Hz, 1 H).

2-(Diethoxymethyl)-5-(4-nitrophenyl)furan (36)

4-Bromonitrobenzene (0.202 g, 1 mmol), 2-(diethoxymethyl)-furan (0.340 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **36** in 78% (0.227 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.23 (d, $J = 8.2$ Hz, 2 H), 7.78 (d, $J = 8.2$ Hz, 2 H), 6.85 (d, $J = 3.2$ Hz, 1 H), 6.56 (d, $J = 3.2$ Hz, 1 H), 5.58 (s, 1 H), 3.63 (m, 4 H), 1.22 (t, $J = 7.5$ Hz, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.2, 151.8, 146.7, 136.7, 124.6, 124.4, 111.4, 109.9, 96.6, 62.0, 15.4. Elemental analysis: calcd (%) for $C_{15}H_{17}NO_5$ (291.30): C 61.85, H 5.88; found: C 61.80, H 5.71.

2-(Diethoxymethyl)-5-(4-formylphenyl)furan (37)

4-Bromobenzaldehyde (0.185 g, 1 mmol), 2-(diethoxymethyl)-furan (0.340 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **37** in 70% (0.192 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.99 (s, 1 H), 7.89 (d, $J = 8.2$ Hz, 2 H), 7.82 (d, $J = 8.2$ Hz, 2 H), 6.81 (d, $J = 3.2$ Hz, 1 H), 6.56 (d, $J = 3.2$ Hz, 1 H), 5.61 (s, 1 H), 3.63 (m, 4 H), 1.22 (t, $J = 7.5$ Hz, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 192.0, 153.6, 152.7, 136.3, 135.3, 130.7, 124.4, 111.0, 109.0, 96.7, 61.9, 15.6. Elemental analysis: calcd (%) for $C_{16}H_{18}O_4$ (274.31): C 70.06, H 6.61; found: C 70.10, H 6.69.

2-(Diethoxymethyl)-5-(2-cyanophenyl)furan (38)

2-Bromobenzonitrile (0.182 g, 1 mmol), 2-(diethoxymethyl)-furan (0.340 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **38** in 76% (0.206 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.90 (d, $J = 8.2$ Hz, 1 H), 7.67 (d, $J = 8.2$ Hz, 1 H), 7.60 (t, $J = 7.8$ Hz, 1 H), 7.32 (t, $J = 7.8$ Hz, 1 H), 7.28 (d, $J = 3.2$ Hz, 1 H), 6.58 (d, $J = 3.2$ Hz, 1 H), 5.61 (s, 1 H), 3.63 (m, 4 H), 1.22 (t, $J = 7.5$ Hz, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 153.2, 149.7, 134.7, 134.4, 133.3, 127.6, 126.4, 112.7, 111.4, 111.0, 107.2, 96.6, 61.9, 15.6. Elemental analysis: calcd (%) for $C_{16}H_{17}NO_3$ (271.31): C 70.83, H 6.32; found: C 70.89, H 6.40.

2-(Diethoxymethyl)-5-(quinolin-3-yl)furan (39)

3-Bromoquinoline (0.208 g, 1 mmol), 2-(diethoxymethyl)furan (0.340 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **39** in 69% (0.205 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.22 (s, 1 H), 8.42 (s, 1 H), 8.10 (d, $J = 8.5$ Hz, 1 H), 7.86 (d, $J = 8.5$ Hz, 1 H), 7.70 (t, $J = 7.5$ Hz, 1 H), 7.56 (t, $J = 7.5$ Hz, 1 H), 6.86 (d, $J = 3.2$ Hz, 1 H), 6.59 (d, $J = 3.2$ Hz, 1 H), 5.65 (s, 1 H), 3.70 (m, 4 H), 1.30 (t, $J = 7.5$ Hz, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 153.1, 151.5, 147.4, 132.3, 131.0, 129.7, 129.6, 129.0, 128.4, 128.1, 127.6, 110.8, 107.6, 96.7, 61.9, 15.6. Elemental analysis: calcd (%) for $C_{18}H_{19}NO_3$ (297.35): C 72.71, H 6.44; found: C 72.59, H 6.54.

Methyl 5-(4-cyanophenyl)furan-2-carboxylate (40)

4-Bromobenzonitrile (0.182 g, 1 mmol), methyl furan-2-carboxylate (0.252 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **40** in 26% (0.059 g) yield. This compound was contaminated with some side products.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.90 (d, $J = 8.5$ Hz, 2 H), 7.73 (d, $J = 8.5$ Hz, 2 H), 7.29 (d, $J = 3.7$ Hz, 1 H), 6.91 (d, $J = 3.7$ Hz, 1 H), 3.95 (s, 3 H).

Methyl 2-methyl-5-(4-cyanophenyl)furan-3-carboxylate (41)

4-Bromobenzonitrile (0.182 g, 1 mmol), methyl 2-methylfuran-3-carboxylate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.0224 mg, 0.0001 mmol) affords **41** in 88% (0.212 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.66 (m, 4 H), 7.03 (s, 1 H), 3.85 (s, 3 H), 2.65 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.8, 160.1, 149.6, 133.7, 132.5, 123.7, 118.7, 115.7, 110.5, 108.6, 51.5, 13.9. Elemental analysis: calcd (%) for $C_{14}H_{11}NO_3$ (241.24): C 69.70, H 4.60; found: C 69.53, H 4.55.

Methyl 5-(4-nitrophenyl)-2-methylfuran-3-carboxylate (42)

4-Bromonitrobenzene (0.202 g, 1 mmol), methyl 2-methylfuran-3-carboxylate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **42** in 82% (0.214 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.25 (d, $J = 8.5$ Hz, 2 H), 7.77 (d, $J = 8.5$ Hz, 2 H), 7.13 (s, 1 H), 3.88 (s, 3 H), 2.70 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.8, 160.7, 148.5, 145.6, 135.7, 124.4, 123.8, 116.8, 109.6, 51.7, 14.1. Elemental analysis: calcd (%) for $C_{13}H_{11}NO_5$ (261.23): C 59.77, H 4.24; found: C 59.60, H 4.32.

Methyl 5-(4-methoxycarbonylphenyl)-2methylfuran-3-carboxylate (43)

Methyl 4-bromobenzoate (0.215 g, 1 mmol), methyl 2-methylfuran-3-carboxylate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **43** in 84% (0.230 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.05 (d, $J = 8.5$ Hz, 2 H), 7.68 (d, $J = 8.5$ Hz, 2 H), 7.01 (s, 1 H), 3.93 (s, 3 H), 3.86 (s, 3 H), 2.67 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.1, 164.5, 160.1, 151.1, 134.3, 130.5, 129.2, 115.9, 108.1, 52.5, 51.9, 14.4. Elemental analysis: calcd (%) for $C_{15}H_{14}O_5$ (274.27): C 65.69, H 5.15; found: C 65.62, H 5.31.

Methyl 5-(4-formylphenyl)-2-methylfuran-3-carboxylate (44)

4-Bromobenzaldehyde (0.185 g, 1 mmol), methyl 2-methylfuran-3-carboxylate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.0224 mg, 0.0001 mmol) affords **44** in 79% (0.193 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.97 (s, 1 H), 7.88 (d, $J = 8.6$ Hz, 2 H), 7.75 (d, $J = 8.6$ Hz, 2 H), 7.06 (s, 1 H), 3.85 (s, 3 H), 2.66 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 191.4, 164.0, 160.1, 150.3, 135.2, 135.1, 130.3, 123.7, 115.7, 108.6, 51.4, 14.0. Elemental analysis: calcd (%) for $C_{14}H_{12}O_4$ (244.24): C 68.85, H 4.95; found: C 68.97, H 4.99.

Methyl 5-(4-fluorophenyl)-2-methylfuran-3-carboxylate (45)

4-Bromofluorobenzene (0.175 g, 1 mmol), methyl 2-methylfuran-3-carboxylate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **45** in 82% (0.192 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.61 (dd, $J = 8.6$ and 5.0 Hz, 2 H), 7.08 (t, $J = 8.6$ Hz, 2 H), 6.81 (s, 1 H), 3.88 (s, 3 H), 2.65 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.8, 162.8 (d, $J = 247.0$ Hz), 159.1, 151.3, 128.7, 125.8 (d, $J = 8.3$ Hz), 116.1 (d, $J = 22.1$ Hz), 115.5, 105.4, 51.8, 14.2. Elemental analysis: calcd (%) for $C_{13}H_{11}FO_3$ (234.22): C 66.66, H 4.73; found: C 66.54, H 4.71.

Methyl 5-(2-cyanophenyl)-2-methylfuran-3-carboxylate (46)

2-Bromobenzonitrile (0.182 g, 1 mmol), methyl 2-methylfuran-3-carboxylate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.0224 mg, 0.0001 mmol) affords **46** in 87% (0.210 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.82 (d, $J = 8.0$ Hz, 1 H), 7.70-7.20 (m, 4 H), 3.87 (s, 3 H), 2.70 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.3, 160.5, 147.9, 134.6, 133.4, 132.7, 127.9, 126.2, 119.0, 116.1, 111.2, 107.2, 51.9, 14.2. Elemental analysis: calcd (%) for $C_{14}H_{11}NO_3$ (241.24): C 69.70, H 4.60; found: C 69.78, H 4.51.

Methyl 5-(3-pyridyl)-2-methylfuran-3-carboxylate (47)

3-Bromopyridine (0.158 g, 1 mmol), methyl 2-methylfuran-3-carboxylate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **47** in 65% (0.141 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.92 (m, 1 H), 8.52 (m, 1 H), 7.92 (d, $J = 8.1$ Hz, 1 H), 7.35 (dd, $J = 8.1$ and 4.8 Hz, 1 H), 6.93 (s, 1 H), 3.87 (s, 3 H), 2.66 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.5, 160.2, 148.3, 145.1, 140.6, 131.4, 124.1, 115.7, 111.5, 107.6, 54.0, 14.3. Elemental analysis: calcd (%) for $C_{12}H_{11}NO_3$ (217.22): C 66.35, H 5.10; found: C 66.48, H 5.14.

5-(4-Cyanophenyl)furan-2-carbonitrile (48)[21]

4-Bromobenzonitrile (0.182 g, 1 mmol), 2-cyanofuran (0.186 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **48** in 64% (0.124 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.80 (d, J = 8.2 Hz, 2 H), 7.70 (d, J = 8.2 Hz, 2 H), 7.20 (d, J = 3.2 Hz, 1 H), 6.88 (d, J = 3.2 Hz, 1 H).

5-(4-Nitrophenyl)furan-2-carbonitrile (49)[22]

4-Bromonitrobenzene (0.202 g, 1 mmol), 2-cyanofuran (0.186 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **49** in 71% (0.152 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.32 (d, J = 8.2 Hz, 2 H), 7.83 (d, J = 8.2 Hz, 2 H), 7.24 (d, J = 3.2 Hz, 1 H), 6.94 (d, J = 3.2 Hz, 1 H).

5-(2-Cyanophenyl)furan-2-carbonitrile (51)

2-Bromobenzonitrile (0.182 g, 1 mmol), 2-cyanofuran (0.186 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **51** in 63% (0.122 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.95 (d, J = 8.2 Hz, 1 H), 7.75-7.50 (m, 2 H), 7.44 (t, J = 7.8 Hz, 1 H), 7.40 (d, J = 3.2 Hz, 1 H), 7.27 (d, J = 3.2 Hz, 1 H).^{13}C NMR (50 MHz, $CDCl_3$): δ 154.3, 134.8, 133.6, 131.3, 129.8, 127.4, 126.6, 124.4, 118.6, 111.7, 111.5, 106.6. Elemental analysis: calcd (%) for $C_{12}H_6N_2O$ (194.19): C 74.22, H 3.11; found: C 74.10, H 3.04.

5-(4-Cyanophenyl)furfurylacetate (52)

4-Bromobenzonitrile (0.182 g, 1 mmol), furfurylacetate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **52** in 80% (0.193 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.75 (d, J = 8.6 Hz, 2 H), 7.65 (d, J = 8.6 Hz, 2 H), 6.78 (d, J = 3.2 Hz, 1 H), 6.54 (d, J = 3.2 Hz, 1 H), 5.12 (s, 2 H), 2.11 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.9, 152.8, 151.1, 134.6, 133.0, 124.5, 119.3, 113.5, 111.0, 109.4, 58.4, 21.3. Elemental analysis: calcd (%) for $C_{14}H_{11}NO_3$ (241.24): C 69.70, H 4.60; found: C 69.78, H 4.74.

5-(4-Formylphenyl)furfurylacetate (53)

4-Bromobenzaldehyde (0.185 g, 1 mmol), furfurylacetate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **53** in 88% (0.215 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.99 (s, 1 H), 7.90 (d, J = 8.6 Hz, 2 H), 7.81 (d, J = 8.6 Hz, 2 H), 6.81 (d, J = 3.2 Hz, 1 H), 6.54 (d, J = 3.2 Hz, 1 H), 5.13 (s, 2 H), 2.11 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 191.9, 171.0, 153.5, 151.0, 136.1, 135.5, 130.7, 124.5, 113.6, 109.3, 58.5, 21.3. Elemental analysis: calcd (%) for $C_{14}H_{12}O_4$ (244.24): C 68.85, H 4.95; found: C 68.98, H 4.77.

5-(4-Fluorophenyl)furfurylacetate (54)

4-Bromofluorobenzene (0.175 g, 1 mmol), furfurylacetate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **54** in 84% (0.197 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.67 (dd, J = 8.6 and 5.2 Hz, 2 H), 7.10 (t, J = 8.6 Hz, 2 H), 6.57 (d, J = 3.2 Hz, 1 H), 6.50 (d, J = 3.2 Hz, 1 H), 5.12 (s, 2 H), 2.12 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.1, 163.0 (d, J = 247 Hz), 154.2, 149.3, 128.7, 126.2 (d, J = 8.1 Hz), 116.1 (d, J = 21.9 Hz), 113.2, 105.9, 58.6, 21.4. Elemental analysis: calcd (%) for $C_{13}H_{11}FO_3$ (234.22): C 66.66, H 4.73; found: C 66.79, H 4.78.

5-(*p*-Tolyl)furfurylacetate (55)

4-Bromotoluene (0.171 g, 1 mmol), furfurylacetate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **55** in 81% (0.186 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.61 (d, J = 8.4 Hz, 2 H), 7.22 (d, J = 8.4 Hz, 2 H), 6.58 (d, J = 3.2 Hz, 1 H), 6.50 (d, J = 3.2 Hz, 1 H), 5.13 (s, 2 H), 2.40 (s, 3 H), 2.13 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.2, 155.3, 148.9, 138.0, 129.8, 128.2, 124.3, 113.2, 105.5, 58.7, 21.7, 21.4. Elemental analysis: calcd (%) for $C_{14}H_{14}O_3$ (230.26): C 73.03, H 6.13; found: C 73.17, H 6.04.

5-(2-Cyanophenyl)furfurylacetate (56)

2-Bromobenzonitrile (0.182 g, 1 mmol), furfurylacetate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **56** in 82% (0.198 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.91 (d, J = 8.6 Hz, 1 H), 7.70 (d, J = 8.6 Hz, 1 H), 7.62 (t, J = 7.8 Hz, 1 H), 7.35 (t, J = 7.8 Hz, 1 H), 7.28 (d, J = 3.2 Hz, 1 H), 6.57 (d, J = 3.2 Hz, 1 H), 5.14 (s, 2 H), 2.12 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.9, 150.7, 150.6, 134.6, 133.4, 133.2, 127.8, 126.5, 119.2, 113.4, 111.7, 107.4, 58.3, 21.3. Elemental analysis: calcd (%) for $C_{14}H_{11}NO_3$ (241.24): C 69.70, H 4.60; found: C 69.79, H 4.57.

5-(Naphthalen-1-yl)furfurylacetate (57)

1-Bromonaphthalene (0.207 g, 1 mmol), furfurylacetate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **57** in 83% (0.221 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.46 (d, J = 8.5 Hz, 1 H), 8.00-7.75 (m, 3 H), 7.65-7.45 (m, 3 H), 6.74 (d, J = 3.2 Hz, 1 H), 6.64 (d, J = 3.2 Hz, 1 H), 5.23 (s, 2 H), 2.16 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.2, 154.5, 149.7, 134.4, 130.7, 129.3, 129.0, 128.8, 127.1, 126.8, 126.4, 125.8, 125.7, 112.9, 110.6, 58.8, 21.4. Elemental analysis: calcd (%) for $C_{17}H_{14}O_3$ (266.29): C 76.68, H 5.30; found: C 76.80, H 5.17.

5-(Quinolin-3-yl)furfurylacetate (58)

3-Bromoquinoline (0.208 g, 1 mmol), furfurylacetate (0.280 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **58** in 83% (0.222 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.14 (s, 1 H), 8.23 (s, 1 H), 8.04 (d, J = 8.6 Hz, 1 H), 7.76 (d, J = 8.6 Hz, 1 H), 7.63 (t, J = 7.8 Hz, 1 H), 7.47 (t, J = 7.8 Hz, 1 H), 6.78 (d, J = 3.2 Hz, 1 H), 6.54 (d, J = 3.2 Hz, 1 H), 5.12 (s, 2 H), 2.09 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.0, 152.3, 150.5, 147.5, 147.3, 129.8, 129.7, 129.6, 128.4, 128.2, 127.6, 123.9, 113.4, 107.9, 58.4, 21.3. Elemental analysis: calcd (%) for $C_{16}H_{13}NO_3$ (267.28): C 71.90, H 4.90; found: C 72.07, H 5.01.

4-(3,6-Dimethyl-4,5,6,7-tetrahydrobenzofuran-2-yl)benzonitrile (59)

4-Bromobenzonitrile (0.182 g, 1 mmol), menthofuran (0.300 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **59** in 90% (0.226 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.66 (d, $J = 8.6$ Hz, 2 H), 7.60 (d, $J = 8.6$ Hz, 2 H), 2.76 (m, 1 H), 2.50-2.20 (m, 3 H), 2.19 (s, 3 H), 2.00-1.80 (m, 2 H), 1.50-1.30 (m, 1 H), 1.12 (d, $J = 7.5$ Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.1, 144.4, 135.9, 131.0, 123.9, 120.4, 119.6, 119.0, 107.6, 31.0, 30.7, 29.2, 21.1, 19.5, 9.9. Elemental analysis: calcd (%) for $C_{17}H_{17}NO$ (251.32): C 81.24, H 6.82; found: C 81.30, H 6.78.

2-(4-Fluorophenyl)-3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (60)

4-Bromofluorobenzene (0.175 g, 1 mmol), menthofuran (0.300 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **60** in 88% (0.215 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.58 (dd, $J = 8.6$ and 5.3 Hz, 2 H), 7.10 (t, $J = 8.6$ Hz, 2 H), 2.76 (m, 1 H), 2.50-2.20 (m, 3 H), 2.16 (s, 3 H), 2.00-1.80 (m, 2 H), 1.50-1.30 (m, 1 H), 1.13 (d, $J = 7.5$ Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 162.9 (d, $J = 245.5$ Hz), 149.7, 146.3, 129.1, 129.0, 127.0 (d, $J = 7.8$ Hz), 120.1, 116.0 (d, $J = 21.5$ Hz), 31.8, 31.7, 30.1, 21.9, 20.5, 10.1. Elemental analysis: calcd (%) for $C_{16}H_{17}FO$ (244.30): C 78.66, H 7.01; found: C 78.74, H 6.97.

2-(3,6-Dimethyl-4,5,6,7-tetrahydrobenzofuran-2-yl)benzaldehyde (61)

2-Bromobenzaldehyde (0.185 g, 1 mmol), menthofuran (0.300 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **61** in 88% (0.224 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 10.06 (s, 1 H), 7.98 (dd, $J = 7.8$ and 0.9 Hz, 1 H), 7.60 (t, $J = 7.5$ Hz, 1 H), 7.51 (d, $J = 7.8$ Hz, 1 H), 7.40 (t, $J = 7.5$ Hz, 1 H), 2.78 (m, 1 H), 2.50-2.20 (m, 3 H), 2.00 (s, 3 H), 2.00-1.80 (m, 2 H), 1.50-1.30 (m, 1 H), 1.10 (d, $J = 7.5$ Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 193.1, 152.1, 144.4, 135.0, 133.8, 133.7, 130.0, 127.9, 127.8, 120.5, 120.0, 31.8, 31.5, 30.0, 21.9, 20.5, 9.7. Elemental analysis: calcd (%) for $C_{17}H_{18}O_2$ (254.32): C 80.28, H 7.13; found: C 80.35, H 7.30.

4-(3,6-Dimethyl-4,5,6,7-tetrahydrobenzofuran-2-yl)isoquinoline (62)

4-Bromoisoquinoline (0.208 g, 1 mmol), menthofuran (0.300 g, 2 mmol), AcOK (0.196 g, 2 mmol) and $Pd(OAc)_2$ (0.224 mg, 0.001 mmol) affords **62** in 90% (0.250 g) yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ 9.20 (s, 1 H), 8.56 (s, 1 H), 8.15 (d, $J = 8.5$ Hz, 1 H), 7.99 (d, $J = 8.5$ Hz, 1 H), 7.71 (t, $J = 7.8$ Hz, 1 H), 7.60 (t, $J = 7.8$ Hz, 1 H), 2.80 (m, 1 H), 2.50-2.20 (m, 3 H), 2.04 (s, 3 H), 2.00-1.80 (m, 2 H), 1.50-1.30 (m, 1 H), 1.13 (d, $J = 7.5$ Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 152.2, 151.6, 144.4, 143.5, 134.6, 131.0, 129.0, 128.2, 127.7, 126.0, 123.6, 119.7, 119.6, 31.9, 31.7, 30.1, 22.0, 20.6, 9.8. Elemental analysis: calcd (%) for $C_{19}H_{19}NO$ (277.36): C 82.28, H 6.90; found: C 82.39, H 6.74.

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