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## Palladium-Catalyzed Alkoxy carbonylation of Aryl halides with Phenols Employing Formic acid as the CO Source

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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An efficient palladium-catalyzed alkoxy carbonylation of aryl halides with phenols has been developed. Various aryl benzoates have been isolated in good to excellent yields with formic acid as the CO source. The reaction proceeds smoothly under mild conditions and good functional groups tolerance was observed.

### Introduction

Carboxylic ester derivative plays a very important role in a large number of organic compounds and appeared to be a key structure in many natural products, pharmaceutical compounds, and so on.<sup>1</sup> Regarding their importance, considerable efforts have been devoted to explore new synthetic methods for these kinds of compounds preparation. One of the most conventional approaches is the direct esterification of alcohols or phenols with the corresponding acid analogues.<sup>2</sup> In these procedures, disadvantages include long reaction time, harsh reaction conditions, and additive requirement limits the application of these strategies. One of the alternative protocols is palladium-catalyzed carbonylation reactions of organic halides with alcohols.<sup>3,4</sup> In the known procedures, aliphatic alcohols are more often studied than phenols with carbon monoxide as the carbonyl source.<sup>5</sup>

In recent years, the developing of CO gas-free carbonylation procedures becomes interesting. As the smell-less, flammable and highly toxic properties of CO gas limited the application of CO gas based carbonylation procedures in Lab scales. Delightly, various CO sources have been explored and applied including aldehydes,<sup>6</sup> formamides,<sup>7</sup> formates,<sup>8</sup> Mo(CO)<sub>6</sub>,<sup>9</sup> W(CO)<sub>6</sub>,<sup>10</sup> MeOH<sup>11d</sup> and etc.<sup>11</sup> More recently, Skrydstrup and co-workers developed various carbonylation procedures based on *ex-situ* generation of CO gas employing two chamber reactor.<sup>12</sup> In this regard, we recently developed a convenient palladium-catalyzed one-pot carbonylative Sonogashira and Suzuki reactions with formic acid as the CO source.<sup>13,14</sup> In our continued efforts to explore this catalytic system, herein, we wish to describe a palladium-catalyzed alkoxy carbonylation reaction of aryl halides and phenols using formic acid as the CO precursor to provide a series of aryl benzoates and their derivatives. Here it's also important to mention that Tsuji and Manabe developed palladium-

catalyzed carbonylation of aryl halides with aryl formats to produce esters in 2012 independently.<sup>8f,8i</sup> Aryl formats were applied as the sources of CO and phenols. Good yields of esters can be produced. Cacchi and co-workers applied acetic formic anhydride as the CO source for hydroxycarbonylation of aryl and vinyl halides.<sup>14a</sup> The acetic formic anhydride was produced from lithium formate and acetic anhydride, good yields of carboxylic acids have been prepared.

### Results and Discussion

At the beginning, we choose iodobenzene and phenol as the model substrates, formic acid as the CO source and acetic anhydride as the activator, Pd(OAc)<sub>2</sub> as the catalyst, PPh<sub>3</sub> as the ligand with Et<sub>3</sub>N as the base in toluene at 80°C. To our delight, phenyl benzoate was formed in 46% yield (Table 1, entry 1). Encourage by this result, we next went on our examination with different solvents (Table 1, entries 2-6). Toluene showed to be the optimal solvent. Then various bases were screened, DBU and DABCO provided the desired product in lower yields (Table 1, entries 7-8). No product was observed when K<sub>2</sub>CO<sub>3</sub> or NaOH was used as the base (Table 1, entries 9-10). Furthermore, a series of phosphine ligands were studied. For monodentate ligands, PCy<sub>3</sub> gave decreased yield (Table 1, entry 11), while XPhos gave higher yield (Table 1, entry 12). Bidentate ligands such as DPPF, DPPPe and DPPE provided similar yields compared with PPh<sub>3</sub> (Table 1, entries 13-15). 31% of yield was observed when BINAP was applied as the ligand (Table 1, entry 16). Gratifyingly, 70% yield of phenyl benzoate can be formed when using Xantphos as the ligand (Table 1, entry 17).

Table 1. Screening of reaction conditions.<sup>a</sup>

Entry	Ligand	Base	Solvent	Yield (%) <sup>b</sup>
1	PPh <sub>3</sub>	Et <sub>3</sub> N	Toluene	46
2	PPh <sub>3</sub>	Et <sub>3</sub> N	THF	35
3	PPh <sub>3</sub>	Et <sub>3</sub> N	DMAc	44

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Electronic Supplementary Information (ESI) available: [NMR spectrums]. See DOI: 10.1039/x0xx00000x

4	PPh <sub>3</sub>	Et <sub>3</sub> N	DMSO	31
5	PPh <sub>3</sub>	Et <sub>3</sub> N	DCM	35
6	PPh <sub>3</sub>	Et <sub>3</sub> N	CH <sub>3</sub> CN	27
7	PPh <sub>3</sub>	DBU	Toluene	39
8	PPh <sub>3</sub>	DABCO	Toluene	17
9	PPh <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	Toluene	0
10	PPh <sub>3</sub>	NaOH	Toluene	0
11	PCy <sub>3</sub>	Et <sub>3</sub> N	Toluene	9
12	XPhos	Et <sub>3</sub> N	Toluene	59
13 <sup>c</sup>	DPPPe	Et <sub>3</sub> N	Toluene	44
14 <sup>c</sup>	DPPE	Et <sub>3</sub> N	Toluene	41
15 <sup>c</sup>	DPPF	Et <sub>3</sub> N	Toluene	44
16 <sup>c</sup>	BINAP	Et <sub>3</sub> N	Toluene	31
17 <sup>c</sup>	Xantphos	Et <sub>3</sub> N	Toluene	70

<sup>a</sup> Reaction conditions: Iodobenzene (1.0 mmol), phenol (2.0 mmol), Pd(OAc)<sub>2</sub> (3 mol%), ligand (6 mol%), base (5 equiv.), HCOOH (2.0 mmol), acetic anhydride (2.0 mmol), solvent (2 mL), 12 h. <sup>b</sup> GC yield, with dodecane as the internal standard and calculated based iodobenzene. <sup>c</sup> ligand (3 mol%). XPhos: 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl. DPPPe: 1,5-bis(diphenylphosphino)pentane. DPPE: 1,2-bis(diphenylphosphino)ethane. DPPF: 1,1'-ferrocenediyl-bis(diphenylphosphine). BINAP: (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene. Xantphos: 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

With the optimized reaction conditions in hand, we then studied various of aryl iodides with phenol (Table 2). Substrates with both electron-rich and electron-poor groups were tolerated well and provide the corresponding phenyl benzoates in moderate to good yields (Table 2, entries 2-11). Remarkably, the methyl group substituted at *ortho*-, *meta*- and *para*-position all worked well and give the desired products in good yields (Table 2, entries 2 vs. 3-4). Additionally, aryl iodides with other halide substitutions such as fluoro and chloro groups could also smoothly afforded the target products in good yields (Table 2, entries 12-17). Poly-fluoro substituted aryl iodides resulted in lower yield than mono-substitution (Table 2, entries 12-13 vs. 14). Difference from methyl group, *ortho*-chloro substitution gave similar yield as those bearing *meta*- and *para*-chloro groups (Table 2, entries 15-16 vs. 17). 57% and 61% yields of the corresponding products were generated when biphenyl and naphthalene iodides used as the substrates (Table 2, entries 18-19). Furthermore, heteroaryl groups were also investigated; 3-iodothiophene and 3-iodopyridine afford the desired products in high yields, while 49% of ester was formed from 6-iodobenzopyridine (Table 2, entries 20-22).

**Table 2.** Carbonylation reaction of aryl iodides and phenol.<sup>a</sup>

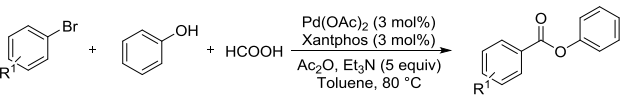
Entry	Aryl iodides	Phenyl benzoates	Yield (%) <sup>b</sup>
1			69
2			63
3			73


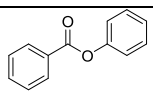

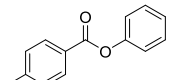
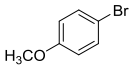
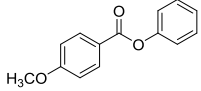
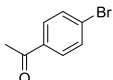
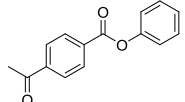
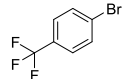
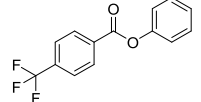
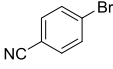
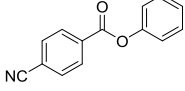

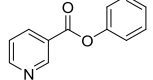
4			81
5			54
6			88
7			70
8			68
9			66
10			73
11			55
12			59
13			54
14			81
15			62
16			63
17			69
18			57
19			61
20			78
21			77
22			49

<sup>a</sup> Reaction conditions: aryl iodides (1.0 mmol), phenol (2.0 mmol), Pd(OAc)<sub>2</sub> (3 mol%), Xantphos (3 mol%), Et<sub>3</sub>N (5 equiv.), HCOOH (2.0 mmol), acetic anhydride (2.0 mmol), toluene (2 mL), 12 h. <sup>b</sup> Isolated yield.

Taking the advantages of aryl bromides compared with aryl iodides into account, various aryl bromides were tested as well. As shown in Table 3, both electron-donating and electron-deficient groups worked well and give the corresponding products in moderate to good yields (Table 3, entries 2-6). We noted that a very good yield of phenyl nicotinate was obtained by using 3-bromopyridine as the substrate under our conditions (Table 3, entry 7).

**Table 3.** Carbonylation reaction of aryl bromides and phenol.<sup>a</sup>

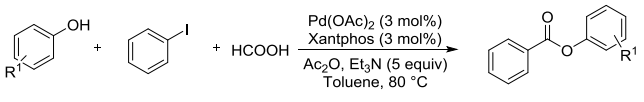


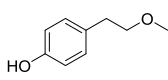
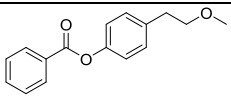
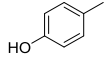
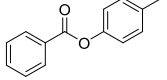
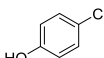
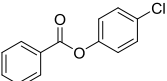
Entry	Aryl bromides	Phenyl benzoates	Yield (%) <sup>b</sup>
1			84
2			51
3			52
4			58
5			69
6			50
7			79

<sup>a</sup> Reaction conditions: aryl bromides (1.0 mmol), phenol (2.0 mmol), Pd(OAc)<sub>2</sub> (3 mol%), xantphos (3 mol%), Et<sub>3</sub>N (5 equiv), HCOOH (2.0 mmol), acetic anhydride (2.0 mmol), toluene (2 mL), 12 h. <sup>b</sup> Isolated yield.

In the case of phenols testing, moderate to good yields of the corresponding products can be successfully isolated from the tested substrates without further optimization (Table 4).

**Table 4.** Carbonylation reaction of iodobenzene and phenols.<sup>a</sup>

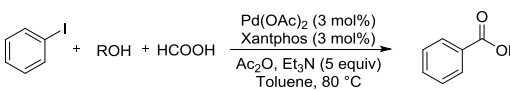


Entry	Phenols	Benzoic acid esters	Yield (%) <sup>b</sup>
1			78
2			48
3			64

<sup>a</sup> Reaction conditions: iodobenzene (1.0 mmol), phenols (2.0 mmol), Pd(OAc)<sub>2</sub> (3 mol%), xantphos (3 mol%), Et<sub>3</sub>N (5 equiv), HCOOH (2.0 mmol), acetic anhydride (2.0 mmol), toluene (2 mL), 12 h. <sup>b</sup> Isolated yield.

Then we turn our attention to aliphatic alcohols, as shown in Table 5, however, no benzoic acid esters were observed. Only benzoic acid was produced in good to excellent yields in the cases. This phenomenon can be explained that alcohols reacted with in situ formed acetic acid and release water. Then the in situ produced water reacts with acylpalladium complex to give the obtained benzoic acid.

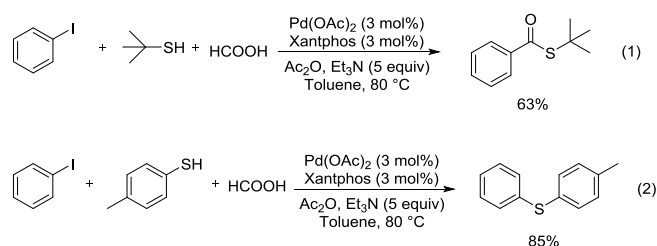
**Table 5.** Carbonylation reaction of iodobenzene and alcohols.<sup>a</sup>



Entry	Alcohols	Yield (%) <sup>b</sup>
1	Methanol	74
2	Ethanol	57
3	Propanol	78
		84 <sup>c</sup>
4	Isopropanol	63
5	Butanol	61
6	Isobutanol	64
7	<i>tert</i> -Butanol	81

<sup>a</sup> Reaction conditions: iodobenzene (1.0 mmol), alcohols (2.0 mmol), Pd(OAc)<sub>2</sub> (3 mol%), xantphos (3 mol%), Et<sub>3</sub>N (5 equiv), HCOOH (2.0 mmol), acetic anhydride (2.0 mmol), toluene (2 mL), 12 h. <sup>b</sup> Isolated yield. <sup>c</sup> propanol (5 mmol).

Aniline as a representative example of nitrogen nucleophile was tested in place of phenol but no product was detected. In the case of sulfur nucleophile, 2-methylpropane-2-thiol and 4-methylbenzenethiol were also tested. *S*-(*tert*-Butyl) benzothioate was formed in 63% yield under identical conditions (Scheme 1). However, only phenyl(*p*-tolyl)sulfane was obtained when thiophenol was utilized



**Scheme 1.** Carbonylation reaction of iodobenzene with sulfur nucleophile.

## Conclusions

In conclusion, we have developed a convenient palladium-catalyzed alkoxycarbonylation of aryl halides and phenols with formic acid as the CO precursor. This carbonylation process represents a practical protocol for the synthesis of aryl benzoates with good to excellent yields under mild reaction conditions, and a wide range of functional groups are tolerated.

## Experimental Section

Typical reaction procedure: Pd(OAc)<sub>2</sub> (3 mol %) and Xantphos (3 mol %) were transferred into an oven-dried tube which was filled with nitrogen. Toluene (2.0 mL), aryl halides (1.0 mmol), phenols (2.0 mmol) were added to the reaction tube. Then a mixture of formic acid (2.0 mmol) and acetic anhydride (2.0 mmol), which was stirred for 1.5 h at 30 °C, added dropwise to the reaction tube. After that, was added Et<sub>3</sub>N (5.0 mmol). The mixture was stirred for 12 h at 80 °C. After the reaction was complete, the reaction mixture was filtered and concentrated, column chromatography on silica gel (petroleum ether/ethyl acetate 50:1) to give the pure product.

### Phenyl benzoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.10, 150.89, 133.51, 130.09, 129.50, 129.42, 128.50, 125.81, 121.65.  
 GC-MS (EI, 70 eV): *m/z*(%)=198.0 ([M]<sup>+</sup>, 6), 198.0 (11), 105.0 (100), 77.0 (42), 51.0 (10).

### Phenyl 2-methylbenzoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.40 (m, 3H), 7.36 – 7.27 (m, 3H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.70 (s, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.74, 150.87, 141.22, 132.64, 131.89, 131.09, 129.41, 128.50, 125.85, 125.74, 121.76, 21.88.  
 GC-MS (EI, 70 eV): *m/z*(%)=212.0 ([M]<sup>+</sup>, 5), 119.0 (100), 91.0 (48), 65.0 (20).

### Phenyl 3-methylbenzoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.31 (dd, *J* = 15.4, 7.7 Hz, 4H), 7.15 (dd, *J* = 12.7, 5.3 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 2.33 (s, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.24, 150.94, 138.31, 134.26, 130.58, 129.42, 129.39, 128.38, 127.24, 125.75, 121.65, 21.19.  
 GC-MS (EI, 70 eV): *m/z*(%)=212.0 ([M]<sup>+</sup>, 7), 212.0 (11), 119.1 (100), 91.1 (43), 65.0 (15).

### Phenyl 4-methylbenzoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 3H), 2.31 (s, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.12, 150.95, 144.29, 130.11, 129.35, 129.19, 126.74, 125.68, 121.68, 21.63.  
 GC-MS (EI, 70 eV): *m/z*(%)=212.0 ([M]<sup>+</sup>, 6), 212.0 (15), 119.1 (100), 91.1 (79), 65.0 (39).

### Phenyl 4-ethylbenzoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.17, 150.98, 150.52, 130.27, 129.39, 128.05, 126.96, 125.72, 121.71, 28.98, 15.19.  
 GC-MS (EI, 70 eV): *m/z*(%)=226.0 ([M]<sup>+</sup>, 7), 226.0 (11), 133.0 (100), 105.0 (34), 77.0 (30).

### Phenyl 4-(*tert*-butyl)benzoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 1.25 (s, 9H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.04, 157.25, 150.96, 130.00, 129.35, 126.70, 125.67, 125.47, 121.69, 35.07, 31.02.  
 GC-MS (EI, 70 eV): *m/z*(%)=254.0 ([M]<sup>+</sup>, 5), 161.1 (100), 146.0 (33), 118.0 (30), 91.0 (28).

### Phenyl 4-methoxybenzoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 8.7 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.24 (dd, *J* = 12.5, 5.4 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.82, 163.82, 151.01, 132.20, 129.35, 125.63, 121.80, 121.73, 113.76, 55.41.  
 GC-MS (EI, 70 eV): *m/z*(%)=228.0 ([M]<sup>+</sup>, 8), 135.0 (100), 107.0 (20), 92.0 (32), 77.0 (36).

### Phenyl 4-acetylbenzoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.26 (dd, *J* = 13.6, 6.1 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 2.65 (s, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.43, 164.29, 150.69, 140.66, 133.29, 130.38, 129.55, 128.32, 126.12, 121.53, 26.90.  
 GC-MS (EI, 70 eV): *m/z*(%)=240.0 ([M]<sup>+</sup>, 9), 240.0 (11), 147.0 (100), 119.0 (12), 91.0 (12).

### Methyl phenyl terephthalate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J* = 8.3 Hz, 2H), 8.17 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.21 (m, 3H), 3.96 (s, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.11, 164.32, 150.71, 134.42, 133.30, 130.07, 129.66, 129.52, 126.07, 121.52, 52.46.  
 GC-MS (EI, 70 eV): *m/z*(%)=256.0 ([M]<sup>+</sup>, 9), 256.0 (10), 163.0 (100), 135.0 (11).

### Phenyl 4-(trifluoromethyl)benzoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.29 (s, 1H), 7.22 (d, *J* = 7.9 Hz, 2H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.01, 150.74, 135.03 (q, *J* = 32.33 Hz), 132.89, 130.58, 129.63, 126.25, 125.63 (q, *J* = 3.68 Hz), 123.62 (q, *J* = 273.60 Hz), 121.57.  
 GC-MS (EI, 70 eV): *m/z*(%)=266.0 ([M]<sup>+</sup>, 9), 266.0 (29), 247.0 (10), 174.0 (21), 173.0 (100), 145.0 (83).



**Phenyl 4-cyanobenzoate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.55, 150.51, 133.40, 132.36, 130.60, 129.63, 126.33, 121.40, 117.82, 116.97.  
 GC-MS (EI, 70 eV): *m/z*(%)=223.0 ([M]<sup>+</sup>, 6), 233.0 (33), 130.0 (100), 102.0 (51).

**Phenyl 2,4-difluorobenzoate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (dd, *J* = 15.4, 8.1 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.03 – 6.88 (m, 2H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.49 (d, *J* = 12.60 Hz), 164.76 (dd, *J* = 12.44, 33.01 Hz), 162.00 (bdd), 150.55, 134.44 (dd, *J* = 1.84, 10.66 Hz), 129.56, 126.16, 121.67, 114.64 (dd, *J* = 3.65, 9.53 Hz), 111.87 (dd, *J* = 4.05, 21.63 Hz), 105.52 (t, *J* = 25.71).  
 GC-MS (EI, 70 eV): *m/z*(%)=234.0 ([M]<sup>+</sup>, 5), 234.0 (44), 141.1 (100), 113.0 (68), 63.0 (30).

**Phenyl 2,3,4-trifluorobenzoate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 – 7.84 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 6.6 Hz, 2H), 7.09 (q, *J* = 7.4 Hz, 1H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.28 (bs), 155.80 (m), 153.37 (m), 150.77 (m), 150.38, 129.61, 126.79 (m), 126.33, 121.49, 115.85 (m), 112347 (dd, *J* = 4.05, 18.01 Hz).  
 GC-MS (EI, 70 eV): *m/z*(%)=252.0 ([M]<sup>+</sup>, 7), 252.0 (26), 159.0 (100), 131.0 (41), 81.0 (20).

**Phenyl 4-fluorobenzoate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (dd, *J* = 8.5, 5.7 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.16 (dd, *J* = 13.7, 6.3 Hz, 1H), 7.14 – 7.08 (m, 3H), 7.06 (d, *J* = 8.5 Hz, 1H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.21 (d, *J* = 255.78 Hz), 164.80, 164.12, 150.77, 132.83 (d, *J* = 9.56 Hz), 129.45, 125.91, 121.59, 115.82 (d, *J* = 22.11 Hz).  
 GC-MS (EI, 70 eV): *m/z*(%)=216.0 ([M]<sup>+</sup>, 8), 216.0 (46), 123.0 (100), 95.0 (79), 75.0 (34).

**Phenyl 4-chlorobenzoate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 – 8.10 (m, 2H), 7.48 (t, *J* = 7.1 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.33 – 7.27 (m, 1H), 7.24 – 7.17 (m, 2H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.33, 150.75, 140.11, 131.53, 129.53, 128.93, 128.01, 126.03, 121.59.  
 GC-MS (EI, 70 eV): *m/z*(%)=232.0 ([M]<sup>+</sup>, 7), 232.0 (14), 141.0 (65), 139.0 (100), 111.0 (50), 75.0 (15).

**Phenyl 3-chlorobenzoate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 – 8.05 (m, 1H), 8.00 – 7.94 (m, 1H), 7.48 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.33 (dt, *J* = 8.5, 6.5 Hz, 3H), 7.21 – 7.14 (m, 1H), 7.13 – 7.08 (m, 2H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.85, 150.63, 134.64, 133.49, 131.23, 130.06, 129.81, 129.47, 128.18, 126.01, 121.48.  
 GC-MS (EI, 70 eV): *m/z*(%)=232.0 ([M]<sup>+</sup>, 6), 232.0 (40), 139.0 (100), 141.0 (71), 111.0 (69), 75.0 (36).

**Phenyl 2-chlorobenzoate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.39 – 7.28 (m, 3H), 7.19 (dd, *J* = 15.3, 7.5 Hz, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.05, 150.65, 134.32, 133.12, 131.82, 131.29, 129.50, 129.35, 126.70, 126.07, 121.57.  
 GC-MS (EI, 70 eV): *m/z*(%)=232.0 ([M]<sup>+</sup>, 6), 232.0 (10), 141.0 (36), 139.0 (100), 111.0 (28), 75.0 (15).

**Phenyl [1,1'-biphenyl]-4-carboxylate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 – 8.15 (m, 2H), 7.71 – 7.60 (m, 2H), 7.57 (d, *J* = 6.2 Hz, 2H), 7.46 – 7.30 (m, 5H), 7.18 (d, *J* = 12.2 Hz, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.05, 150.96, 146.28, 139.82, 130.67, 129.47, 128.95, 128.28, 128.23, 127.29, 127.20, 125.86, 121.71.

GC-MS (EI, 70 eV): *m/z*(%)=274.0 ([M]<sup>+</sup>, 6), 181.0 (100), 152.0 (41).

**Phenyl 2-naphthoate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.81 (s, 1H), 8.22 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.61 (dt, *J* = 14.9, 7.0 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.28, 151.00, 135.74, 132.43, 131.85, 129.46, 129.42, 128.55, 128.32, 127.77, 126.77, 126.71, 125.85, 125.39, 121.72.  
 GC-MS (EI, 70 eV): *m/z*(%)=248.0 ([M]<sup>+</sup>, 7), 248.0 (21), 155.0 (100), 127.0 (80).

**Phenyl thiophene-3-carboxylate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 2.1 Hz, 1H), 7.66 (d, *J* = 5.1 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 4.6, 3.4 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 2H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.00, 150.63, 133.96, 132.84, 130.12, 129.42, 128.52, 128.17, 126.32, 125.83, 121.65.  
 GC-MS (EI, 70 eV): *m/z*(%)=204.0 ([M]<sup>+</sup>, 5), 204.0 (30), 111.0 (100), 83.0 (26).

**Phenyl nicotinate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.40 (s, 1H), 8.85 (d, *J* = 4.7 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.39 (m, 3H), 7.32 – 7.17 (m, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.60, 153.52, 150.92, 150.35, 137.71, 129.47, 126.12, 125.60, 123.47, 121.39.  
 GC-MS (EI, 70 eV): *m/z*(%)=199.0 ([M]<sup>+</sup>, 6), 199.0 (47), 106.0 (100), 78.0 (66), 51.0 (32).

**Phenyl quinoline-6-carboxylate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.06 (d, *J* = 3.6 Hz, 1H), 8.79 (s, 1H), 8.47 (d, *J* = 8.8 Hz, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 8.27 (d, *J* = 8.8 Hz, 1H), 7.54 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.30 (dd, *J* = 17.1, 7.8 Hz, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.56, 152.36, 150.82, 149.68, 137.97, 131.79, 129.60, 129.56, 129.46, 127.73, 127.47, 126.08, 122.01, 121.61.  
 GC-MS (EI, 70 eV): *m/z*(%)=249.0 ([M]<sup>+</sup>, 8), 249.0 (10), 156.0 (100), 128.0 (42), 101.0 (12).

**4-(2-Methoxyethyl)phenyl benzoate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 – 8.18 (m, 2H), 7.63 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 3.62 (t, *J* = 7.0 Hz, 2H), 3.37 (s, 3H), 2.91 (t, *J* = 7.0 Hz, 2H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.17, 149.26, 136.58, 133.45, 130.06, 129.77, 129.54, 128.46, 121.44, 73.40, 58.58, 35.54.  
 GC-MS (EI, 70 eV): *m/z*(%)=256.0 ([M]<sup>+</sup>, 6), 256.0 (13), 105.0 (100), 77.0 (34).

***p*-Tolyl benzoate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 – 8.18 (m, 2H), 7.63 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.36, 148.68, 135.49, 133.47, 130.12, 129.97, 129.66, 128.51, 121.34, 20.88.  
 GC-MS (EI, 70 eV): *m/z*(%)=212.0 ([M]<sup>+</sup>, 4), 212.0 (24), 105.0 (100), 77.0 (49), 51.0 (10).

**4-Chlorophenyl benzoate.**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (d, *J* = 7.9 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.82, 149.34, 133.70, 131.15, 130.10, 129.44, 129.09, 128.55, 123.03.  
 GC-MS (EI, 70 eV): *m/z*(%)=232.0 ([M]<sup>+</sup>, 5), 232.0 (26), 105.0 (100), 77.0 (68), 51.0 (28).

**Benzoic acid**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 13.03 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.68, 133.80, 130.19, 129.30, 128.44.  
GC-MS (EI, 70 eV):  $m/z(\%)$ =122.0 ([M]<sup>+</sup>, 4), 122.0 (94), 105.0 (100), 77.0 (79), 51.0 (31).

#### S-(tert-Butyl) benzothioate

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J$  = 7.2 Hz, 2H), 7.52 (t,  $J$  = 7.4 Hz, 1H), 7.40 (t,  $J$  = 7.7 Hz, 2H), 1.58 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.81, 138.23, 132.86, 128.40, 126.90, 48.09, 29.96.

GC-MS (EI, 70 eV):  $m/z(\%)$ =194.0 ([M]<sup>+</sup>, 8), 194.0 (33), 138.0 (46), 105.0 (100), 77.0 (49), 57.1 (30).

#### Phenyl(p-tolyl)sulfane

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J$  = 8.0 Hz, 2H), 7.26 (d,  $J$  = 4.4 Hz, 4H), 7.14 (s, 1H), 7.12 (d,  $J$  = 6.5 Hz, 2H), 2.34 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.58, 137.10, 132.25, 131.25, 130.04, 129.75, 129.02, 126.38, 21.11.

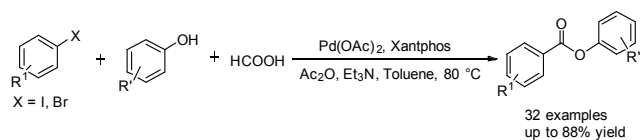
GC-MS (EI, 70 eV):  $m/z(\%)$ =200.0 ([M]<sup>+</sup>, 12), 201.0 (18), 200.0 (100), 199.0 (36), 185.0 (46), 184.0 (45), 91.0 (26).

## Acknowledgements

The authors thank the financial supports from NSFC (21472174), education department of Zhejiang Province (Y201432060) and Zhejiang Sci-Tech University (1206838-Y; 14062015-Y). X.-F. Wu appreciates the general support from Matthias Beller in LIKAT.

**Keywords:** Palladium catalyst • alkoxycarbonylation • CO free • aryl halides • aryl benzoate

- [1] a) J. Otera, *Esterification: Methods, Reactions and Applications*, Wiley VCH, Weinheim, 2003; b) K. Bauer, D. Garbe, H. Sturburg, *Common Fragrance and Flavor Materials: Preparation and Uses*, 4th ed. Wiley-VCH, Weinheim, 2001; c) M. A. Ogliaruso, J. F. Wolfe, *The Chemistry of Carboxylic Acids and Esters*, (Ed.: S. Patai), Interscience, London, 1991.
- [2] a) A. R. Katritzky, C. O. Meth-Cohn, W. R. Charles, *Comprehensive Organic Functional Group Transformations*, Cambridge University Press, Cambridge, 1995, Vol. 5; b) T. W. Green, P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 3rd ed. John Wiley and Sons, New York, 1999; c) R. C. Larock, *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, 2nd ed. John Wiley & Sons, New York, 1999.
- [3] a) A. Brennfürer, H. Neumann, M. Beller, *Angew. Chem., Int. Ed.* 2009, **48**, 4114-4133; b) X.-F. Wu, H. Neumann, *ChemCatChem* 2012, **4**, 447-458; c) Q. Liu, H. Zhang, A. Lei, *Angew. Chem. Int. Ed.* 2011, **50**, 10788-10799; d) B. Liu, F. Hu, B.-F. Shi, *ACS Catal.*, 2015, **5**, 1863-1881.
- [4] For selected recent examples, see: a) Y. Zhao, L. Jin, P. Li, A. Lei, *J. Am. Chem. Soc.* 2008, **130**, 9429-9433; b) H. Zhang, R. Shi, P. Gan, C. Liu, A. Ding, Q. Wang, A. Lei, *Angew. Chem. Int. Ed.* 2012, **51**, 5204-5207; c) W. Li, C. Liu, H. Zhang, K. Ye, G. Zhang, W. Zhang, Z. Duan, S. You, A. Lei, *Angew. Chem. Int. Ed.* 2014, **53**, 2443-2446; d) L. Wang, Y. Wang, C. Liu, A. Lei, *Angew. Chem. Int. Ed.* 2014, **53**, 5657-5661; e) W. Li, Z. Duan, X. Zhang, H. Zhang, M. Wang, R. Jiang, H. Zeng, C. Liu, A. Lei, *Angew. Chem. Int. Ed.* 2015, **54**, 1893-1896; f) P. Xie, Y. Xie, B. Qian, H. Zhou, C. Xia, H. Huang, *J. Am. Chem. Soc.* 2012, **134**, 9902-9905.
- [5] For selected examples of carbonylation of aryl halides in which also phenols have been used as nucleophiles see: a) H.-U. Blaser, M. Diggelmann, H. Meier, F. Naud, E. Scheppach, A. Schnyder, M. Studer, *J. Org. Chem.* 2003, **68**, 3725-3728; b) C. Ramesh, Y. Kubota, M. Miwa, Y. Sugi, *Synthesis* 2002, 2171-2173; c) Z. Liu, R. C. Larock, *Org. Lett.* 2004, **6**, 99-102; d) D. A. Watson, X. Fan, S. L. Buchwald, *J. Org. Chem.* 2008, **73**, 7096-7101; e) X.-F. Wu, H. Neumann, *ChemCatChem* 2012, **2**, 509-513; f) X.-F. Wu, H. Neumann, M. Beller, *Chem. Eur. J.* 2012, **18**, 3831-3835; g) E. Akpinar, M. Kus, M. U. Cuncu, E. Karakus, L. Artok, *Org. Lett.* 2011, **13**, 748-751; h) M. A. Mercadante, N. E. Leadbeater, *Org. Biomol. Chem.* 2011, **9**, 6575-6578; i) D. C. Reeves, S. Rodriguez, H. Lee, N. Haddad, D. Krishnamurthy, C. H. Senanayake, *Org. Lett.* 2011, **13**, 2495-2497.
- [6] a) T. Morimoto, K. Fuji, K. Tsutsumi, K. Kakiuchi, *J. Am. Chem. Soc.* 2002, **124**, 3806-3807; b) T. Shibata, N. Tashida, K. Takagi, *Org. Lett.* 2002, **4**, 1619-1621; c) T. Morimoto, K. Yamasaki, A. Hirano, K. Tsutsumi, N. Kagawa, K. Kakiuchi, Y. Harada, Y. Fukumoto, N. Chatani, T. Nishioka, *Org. Lett.* 2009, **11**, 1777-1780; d) W. Li, X.-F. Wu; *J. Org. Chem.* 2014, **79**, 10410-10416; e) K. Natte, A. Dumrath, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* 2014, **53**, 10090-10094.
- [7] a) S. Ko, H. Han, S. Chang, *Org. Lett.* 2003, **5**, 2687-2690; b) K. Hosoi, K. Nozaki, T. Hiyama, *Org. Lett.* 2002, **4**, 2849-2851.
- [8] a) H. Li, H. Neumann, M. Beller, X.-F. Wu, *Angew. Chem. Int. Ed.* 2014, **53**, 3183-3186; b) T. Ueda, H. Konishi, K. Manabe, *Org. Lett.* 2012, **14**, 4722-4725; c) T. Ueda, H. Konishi, K. Manabe, *Angew. Chem. Int. Ed.* 2013, **52**, 8611-8615; d) T. Ueda, H. Konishi, K. Manabe, *Org. Lett.* 2012, **14**, 5370-5373; e) T. Ueda, H. Konishi, K. Manabe, *Tetrahedron Lett.* 2012, **53**, 5171-5175; f) T. Ueda, H. Konishi, K. Manabe, *Org. Lett.* 2012, **14**, 3100-3103; g) S. Ko, C. Lee, M.-G. Choi, Y. Na, S. Chang, *J. Org. Chem.* 2003, **68**, 1607-1610; h) Y. Katafuchi, T. Fujihara, T. Iwai, J. Terao, Y. Tsuji, *Adv. Synth. Catal.* 2011, **353**, 475-482; i) T. Fujihara, T. Hosoki, Y. Katafuchi, T. Iwai, J. Terao, Y. Tsuji, *Chem. Comm.* 2012, **48**, 8012-8014.
- [9] For an excellent review on this using  $\text{Mo}(\text{CO})_6$  as CO source, see: L. R. Odell, F. Russo, M. Larhed, *Synlett* 2012, 685-698; selected examples see: b) Y. Wan, M. Alterman, M. Larhed, A. Hallberg, *J. Org. Chem.* 2002, **67**, 6232-6235; c) J. Wannberg, M. Larhed, *J. Org. Chem.* 2003, **68**, 5750-5753.
- [10] a) O. Lagerlund, M. Larhed, *J. Comb. Chem.* 2006, **8**, 4-6; b) X. Wu, J. K. Ekegren, M. Larhed, *Organometallics* 2006, **25**, 1434-1439; c) M. Iizuka and Y. Kondo, *Eur. J. Org. Chem.* 2007, 5180-5182; d) P. Appukkuttan, L. Axelsson, E. V. der Eycken, M. Larhed, *Tetrahedron Lett.* 2008, **49**, 5625-5628; e) A. Wieckowska, R. Fransson, L. R. Odell, M. Larhed, *J. Org. Chem.* 2011, **76**, 978-981.
- [11] a) T. Morimoto, K. Kakiuchi, *Angew. Chem. Int. Ed.* 2004, **43**, 5580-5588; b) L. Wu, Q. Liu, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* 2014, **53**, 6310-6320; c) P. Gautam, B. M. Bhanage, *Catal. Sci. Technol.*, 2015, **5**, 4663-4702; d) B. Sam, B. Breit, M. J. Krische, *Angew. Chem. Int. Ed.* 2015, **54**, 3267-3274.
- [12] a) K. T. Neumann, S. R. Laursen, A. T. Lindhardt, B. Bang-Andersen, T. Skrydstrup, *Org. Lett.* 2014, **16**, 2216-2219; b) C. Brancour, T. Fukuyama, Y. Mukai, T. Skrydstrup, I. Ryu, *Org. Lett.* 2013, **15**, 2794-2797.
- [13] a) X. Qi, L.-B. Jiang, C.-L. Li, R. Li, X.-F. Wu, *Chem. Asian J.* 2015, **10**, 1870-1873; b) X. Qi, L.-B. Jiang, H.-P. Li, X.-F. Wu, *Chem. Eur. J.* 2015, **21**, 17650-17656.
- [14] a) S. Cacchi, G. Fabrizi, A. Goggiani, *Org. Lett.* 2003, **5**, 4269-4272; b) S. Cacchi, G. Fabrizi, A. Goggiani, *J. Comb. Chem.* 2004, **6**, 692-694; c) S. Korsager, R. H. Taaning, T. Skrydstrup, *J. Am. Chem. Soc.* 2013, **135**, 2891-2894; d) J. Hou, J.-H. Xie, Q.-L. Zhou, *Angew. Chem. Int. Ed.* 2015, **54**, 6302-6305.



An efficient palladium-catalyzed alkoxy carbonylation of aryl halides with phenols has been developed. Various aryl benzoates have been isolated in good to excellent yields with formic acid as the CO source. The reaction proceeds smoothly under mild conditions and good functional groups tolerance was observed