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Palladium-catalyzed alkoxycarbonylation of aryl halides with phenols employing formic acid as the CO source†

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An efficient palladium-catalyzed alkoxycarbonylation 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 group tolerance was observed.

Introduction

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

In recent years, the development of CO gas-free carbonylation procedures has become interesting, as the odourless, flammable and highly toxic properties of CO gas has limited the application of CO gas-based carbonylation procedures on a lab scale. Various CO sources have been explored and applied, including aldehydes,[6] formamides,[7] formates,[8] $Mo(CO)_6$,[9] $W(CO)_6$,[10] MeOH,[11d] *etc.*[11] More recently, Skrydstrup and co-workers developed various carbonylation procedures based on the *ex situ* generation of CO gas employing a two chamber reactor.[12] In this regard, we recently developed convenient palladium-catalyzed one-pot carbonylative Sonogashira and Suzuki reactions with formic acid as the CO source.[13,14] In our continued efforts to explore this catalytic system, herein, we wish to describe a palladium-catalyzed alkoxycarbonylation 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 is also important to mention that Tsuji and Manabe developed palladium-catalyzed carbonylation of aryl halides with aryl formates to produce esters independently in 2012.[8f,i] Aryl formates 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 the hydroxycarbonylation of aryl and vinyl halides.[14a] The acetic formic anhydride was produced from lithium formate and acetic anhydride, and good yields of carboxylic acids were prepared.

Results and discussion

At the beginning, we chose iodobenzene and phenol as the model substrates, formic acid as the CO source and acetic anhydride as the activator, $Pd(OAc)_2$ as the catalyst, PPh_3 as a ligand with Et_3N as a base in toluene at 80 °C. To our delight, phenyl benzoate was formed in 46% yield (Table 1, entry 1). Encouraged by this result, we next went on our examination with different solvents (Table 1, entries 2–6). Toluene was shown 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_2CO_3 or NaOH was used as the base (Table 1, entries 9–10). Furthermore, a series of phosphine ligands were studied. For monodentate ligands, PCy_3 gave a decreased yield (Table 1, entry 11), while XPhos gave a higher yield (Table 1, entry 12). Bidentate ligands, such as DPPF, DPPPe and DPPE, provided similar yields compared to PPh_3 (Table 1, entries 13–15). A 31% yield was observed when BINAP was applied as the ligand (Table 1, entry 16). Gratifyingly, a 70% yield of phenyl benzoate can be formed when using xantphos as the ligand (Table 1, entry 17).

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† Electronic supplementary information (ESI) available: NMR spectrums.
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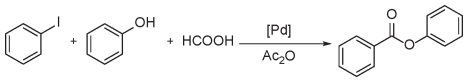
Table 1 Screening of reaction conditions[a]



Entry	Ligand	Base	Solvent	Yield[b] (%)
1	PPh_3	Et_3N	Toluene	46
2	PPh_3	Et_3N	THF	35
3	PPh_3	Et_3N	DMAc	44
4	PPh_3	Et_3N	DMSO	31
5	PPh_3	Et_3N	DCM	35
6	PPh_3	Et_3N	CH_3CN	27
7	PPh_3	DBU	Toluene	39
8	PPh_3	DABCO	Toluene	17
9	PPh_3	K_2CO_3	Toluene	0
10	PPh_3	NaOH	Toluene	0
11	PCy_3	Et_3N	Toluene	9
12	XPhos	Et_3N	Toluene	59
13[c]	DPPPe	Et_3N	Toluene	44
14[c]	DPPE	Et_3N	Toluene	41
15[c]	DPPF	Et_3N	Toluene	44
16[c]	BINAP	Et_3N	Toluene	31
17[c]	Xantphos	Et_3N	Toluene	70

[a] Reaction conditions: iodobenzene (1.0 mmol), phenol (2.0 mmol), $Pd(OAc)_2$ (3 mol%), ligand (6 mol%), base (5 equiv.), HCOOH (2.0 mmol), acetic anhydride (2.0 mmol), solvent (2 mL), 12 h. [b] GC yield, with dodecane as the internal standard and calculated based on iodobenzene. [c] 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 reactions 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, compounds with a methyl group substituted at the *ortho*-, *meta*- and *para*-position all worked well and gave 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 afford the target products in good yields (Table 2, entries 12–17). Poly-fluoro substituted aryl iodides resulted in lower yields than with mono-substitution (Table 2, entries 12–13 *vs.* 14). In a difference from the methyl group, *ortho*-chloro substitution gave a similar yield to 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 were used as the substrates (Table 2, entries 18–19). Furthermore, heteroaryl groups were also investigated; 3-iodothiophene and 3-iodopyridine afforded the desired products in high yields, while 49% of ester was formed from 6-iodobenzopyridine (Table 2, entries 20–22).

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 note that a very good yield of phenyl nicotinate was obtained by using 3-bromopyridine as the substrate under our conditions (Table 3, entry 7).

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

Then, we turned 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 these cases. This phenomenon can be explained by the alcohols reacting with the *in situ* formed acetic acid and releasing water. Then, the *in situ* produced water reacts with the acylpalladium complex to give the obtained benzoic acid.

Aniline, as a representative example of a nitrogen nucleophile, was tested in place of phenol, but no product was detected. For the cases of a 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.

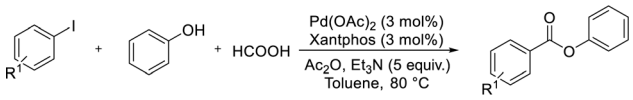
Conclusions

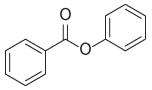
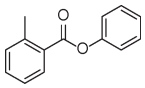
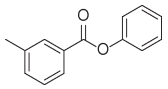
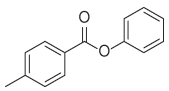
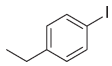
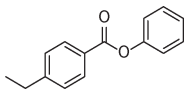
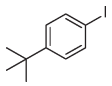
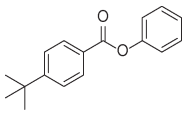
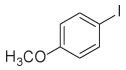
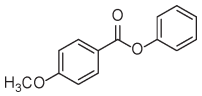
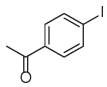
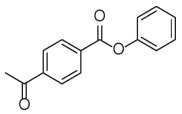
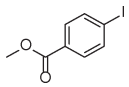
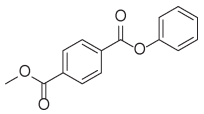
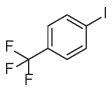
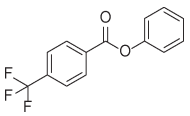
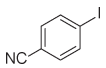
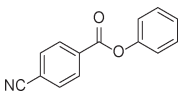
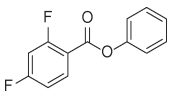
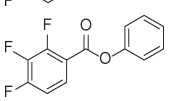
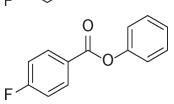
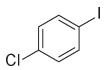
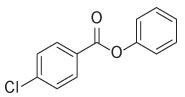
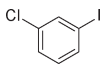
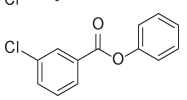
In conclusion, we have developed a convenient palladium-catalyzed alkoxycarbonylation of aryl halides and phenols with formic acid as the CO precursor. This carbonylation process represents a practical protocol for the synthesis of aryl benzoates with good to excellent yields under mild reaction conditions,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

Experimental section

Typical reaction procedure: $Pd(OAc)_2$ (3 mol%) and xantphos (3 mol%) were transferred into an oven-dried tube which was

Table 2 Carbonylation reaction of aryl iodides and phenol[a]



Entry	Aryl iodides	Phenyl benzoates	Yield[b] (%)
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

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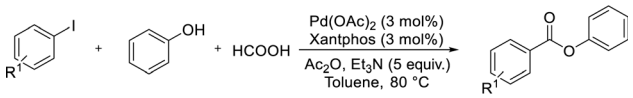
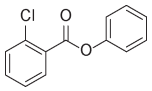
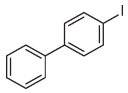
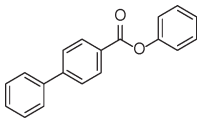
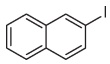
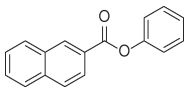
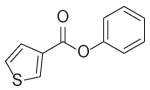
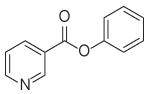
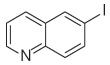
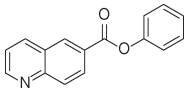


Entry	Aryl iodides	Phenyl benzoates	Yield[b] (%)
17			69
18			57
19			61
20			78
21			77
22			49

[a] Reaction conditions: aryl iodides (1.0 mmol), phenol (2.0 mmol), $Pd(OAc)_2$ (3 mol%), xantphos (3 mol%), Et_3N (5 equiv.), HCOOH (2.0 mmol), acetic anhydride (2.0 mmol), toluene (2 mL), 12 h. [b] Isolated yield.

filled with nitrogen. Toluene (2.0 mL), aryl halides (1.0 mmol), and 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, was added dropwise to the reaction tube. After that, Et_3N (5.0 mmol) was added. The mixture was stirred for 12 h at 80 °C. After the reaction was complete, the reaction mixture was filtered and concentrated, and column chromatography on silica gel (petroleum ether/ethyl acetate 50 : 1) was carried out to give the pure product.

Phenyl benzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 6), 198.0 (11), 105.0 (100), 77.0 (42), 51.0 (10).

Phenyl 2-methylbenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 5), 119.0 (100), 91.0 (48), 65.0 (20).

Phenyl 3-methylbenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 7), 212.0 (11), 119.1 (100), 91.1 (43), 65.0 (15).

Phenyl 4-methylbenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

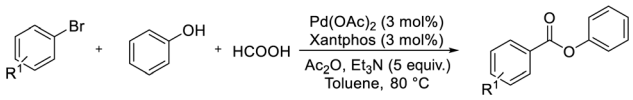
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.12, 150.95, 144.29, 130.11, 129.35, 129.19, 126.74, 125.68, 121.68, 21.63.

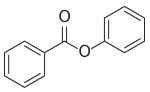
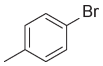
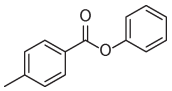
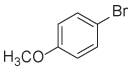
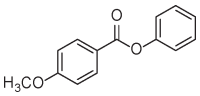
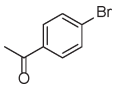
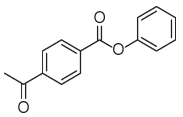
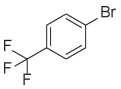
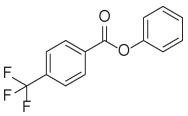
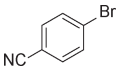
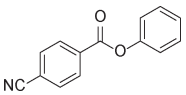
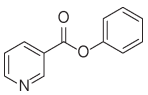
GC-MS (EI, 70 eV): m/z(%) = 212.0 ([M]+, 6), 212.0 (15), 119.1 (100), 91.1 (79), 65.0 (39).

Phenyl 4-ethylbenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

Table 3 Carbonylation reaction of aryl bromides and phenol[a]



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

[a] Reaction conditions: aryl bromides (1.0 mmol), phenol (2.0 mmol), $Pd(OAc)_2$ (3 mol%), xantphos (3 mol%), Et_3N (5 equiv.), HCOOH (2.0 mmol), acetic anhydride (2.0 mmol), toluene (2 mL), 12 h. [b] Isolated yield.

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 7), 226.0 (11), 133.0 (100), 105.0 (34), 77.0 (30).

Phenyl 4-(*tert*-butyl)benzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 5), 161.1 (100), 146.0 (33), 118.0 (30), 91.0 (28).

Phenyl 4-methoxybenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 8), 135.0 (100), 107.0 (20), 92.0 (32), 77.0 (36).

Phenyl 4-acetylbenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 9), 240.0 (11), 147.0 (100), 119.0 (12), 91.0 (12).

Methyl phenyl terephthalate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

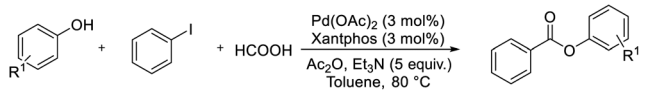
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.11, 164.32, 150.71, 134.42, 133.30, 130.07, 129.66, 129.52, 126.07, 121.52, 52.46.

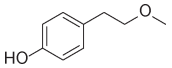
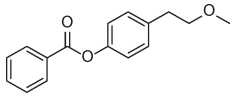
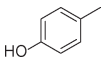
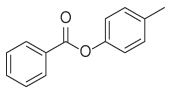
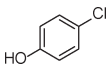
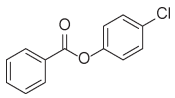
GC-MS (EI, 70 eV): *m*/*z*(%) = 256.0 ([M]+, 9), 256.0 (10), 163.0 (100), 135.0 (11).

Phenyl 4-(trifluoromethyl)benzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

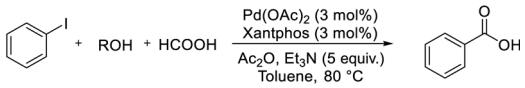
Table 4 Carbonylation reaction of iodobenzene and phenols[a]



Entry	Phenols	Benzoic acid esters	Yield[b] (%)
1			78
2			48
3			64

[a] Reaction conditions: iodobenzene (1.0 mmol), phenols (2.0 mmol), $Pd(OAc)_2$ (3 mol%), xantphos (3 mol%), Et_3N (5 equiv.), HCOOH (2.0 mmol), acetic anhydride (2.0 mmol), toluene (2 mL), 12 h. [b] Isolated yield.

Table 5 Carbonylation reaction of iodobenzene and alcohols[a]



Entry	Alcohols	Yield[b] (%)
1	Methanol	74
2	Ethanol	57
3	Propanol	78
		84[c]
4	Isopropanol	63
5	Butanol	61
6	Isobutanol	64
7	*tert*-Butanol	81

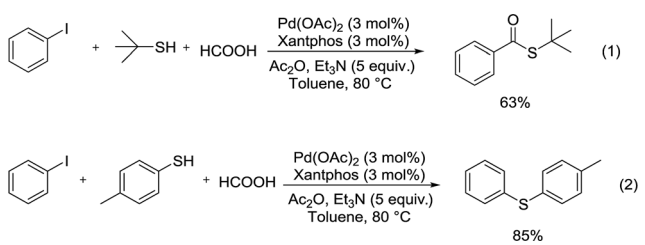
[a] Reaction conditions: iodobenzene (1.0 mmol), alcohols (2.0 mmol), $Pd(OAc)_2$ (3 mol%), xantphos (3 mol%), Et_3N (5 equiv.), HCOOH (2.0 mmol), acetic anhydride (2.0 mmol), toluene (2 mL), 12 h. [b] Isolated yield. [c] Propanol (5 mmol).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 9), 266.0 (29), 247.0 (10), 174.0 (21), 173.0 (100), 145.0 (83).

Phenyl 4-cyanobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).



Scheme 1 Carbonylation reactions of iodobenzene with sulfur nucleophiles.

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 6), 233.0 (33), 130.0 (100), 102.0 (51).

Phenyl 2,4-difluorobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 5), 234.0 (44), 141.1 (100), 113.0 (68), 63.0 (30).

Phenyl 2,3,4-trifluorobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 7), 252.0 (26), 159.0 (100), 131.0 (41), 81.0 (20).

Phenyl 4-fluorobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 8), 216.0 (46), 123.0 (100), 95.0 (79), 75.0 (34).

Phenyl 4-chlorobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 7), 232.0 (14), 141.0 (65), 139.0 (100), 111.0 (50), 75.0 (15).

Phenyl 3-chlorobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 6), 232.0 (40), 139.0 (100), 141.0 (71), 111.0 (69), 75.0 (36).

Phenyl 2-chlorobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 6), 232.0 (10), 141.0 (36), 139.0 (100), 111.0 (28), 75.0 (15).

Phenyl [1,1′-biphenyl]-4-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 6), 181.0 (100), 152.0 (41).

Phenyl 2-naphthoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 7), 248.0 (21), 155.0 (100), 127.0 (80).

Phenyl thiophene-3-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 5), 204.0 (30), 111.0 (100), 83.0 (26).

Phenyl nicotinate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 6), 199.0 (47), 106.0 (100), 78.0 (66), 51.0 (32).

Phenyl quinoline-6-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 8), 249.0 (10), 156.0 (100), 128.0 (42), 101.0 (12).

4-(2-Methoxyethyl)phenyl benzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 6), 256.0 (13), 105.0 (100), 77.0 (34).

p-Tolyl benzoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 4), 212.0 (24), 105.0 (100), 77.0 (49), 51.0 (10).

4-Chlorophenyl benzoate.

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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]+, 5), 232.0 (26), 105.0 (100), 77.0 (68), 51.0 (28).

Benzoic acid

^{1}H NMR (400 MHz, $CDCl_3$) 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}C NMR (101 MHz, $CDCl_3$) δ 172.68, 133.80, 130.19, 129.30, 128.44.

GC-MS (EI, 70 eV): *m*/*z*(%) = 122.0 ([M]+, 4), 122.0 (94), 105.0 (100), 77.0 (79), 51.0 (31).

***S*-(*tert*-Butyl) benzothioate**

^{1}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (101 MHz, $CDCl_3$) δ 192.81, 138.23, 132.86, 128.40, 126.90, 48.09, 29.96.

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

Phenyl(*p*-tolyl)sulfane

^{1}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (101 MHz, $CDCl_3$) δ 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]+, 12), 201.0 (18), 200.0 (100), 199.0 (36), 185.0 (46), 184.0 (45), 91.0 (26).

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