Chapter 2
Palladium-Catalyzed Decarboxylative Coupling of Potassium Oxalate Monoester with Aryl and Alkenyl Halides

Abstract  Pd-catalyzed decarboxylative cross-couplings of aryl iodides, bromides, and chlorides with potassium oxalate monoesters have been discovered. This reaction is potentially useful for laboratory-scale synthesis of aryl and alkenyl esters. Pd catalyst with bidentate phosphine ligands was found as the optimal catalyst, and unlike other reported decarboxylative couplings, copper is not needed as support catalyst in this reaction. The theoretical calculation shows that the decarboxylation on Pd(II) is the rate-determining step, with a transition state where Pd(II) has a five-coordination state. The calculated energy barrier of rate-determining step is about ~30 kcal/mol, which is in accordance with the optimized reaction temperature.

2.1 Introduction

Aromatic esters are important structural elements and synthetic intermediates. Transition metal-catalyzed synthesis of aromatic esters from aryl halides has been studied mainly in the frame of Pd-catalyzed carbonylation [1, 2]. The drawback of
handling toxic CO gas and, under many circumstances, the requirement for high pressure reaction conditions often limit the scope of this reaction, especially on a laboratory scale [3]. With an inspiration of decarboxylative coupling, we noticed that we might use some carboxylate salts as d-synthon equivalent, of which the corresponding organometallics are unstable and difficult to prepare. At this juncture, we noticed that potassium oxalate monoesters may be used as an ester synthetic equivalent if this is easily accessible and stable salt can be smoothly decarboxylated in the presence of a metal catalyst. Here we report a novel, practical synthesis of aromatic esters via Pd-catalyzed decarboxylative coupling of oxalate monoester salts with aryl halides (Scheme 2.1).

This study was inspired by the recent seminal work of Goossen and coworkers [3], who discovered the decarboxylative cross-couplings of α-oxocarboxylates giving rise to ketones. Related elegant studies on decarboxylative cross-coupling reactions of aromatic carboxylates have also been reported recently by Myers [4], Forgione [5], Goossen [6], and several other groups [7–11].

2.2 Results and Discussion

2.2.1 Investigation of the Reaction Conditions

Our investigation started by examining the coupling between potassium 2-ethoxy-2-oxoacetate and bromobenzene (Table 2.1). A series of palladium salts and phosphine ligands were examined [12]. When using palladium trifluoroacetate with dppp as the catalyst and phosphine ligands, we got the best results of the reaction. Under the optimal conditions [1 mol% Pd(TFA)₂, 1.5 mol% dppp], the desired product was obtained in 85% yield. Not only aryl bromide, aryl iodide as the substrate can also have good results (entry 20). When aryl iodide was used, we found that the desired product can be obtained in 85% yield in the absence of a phosphine ligand, but for aryl chlorides (entry 21), only trace amounts of the desired product can be obtained. It should be mentioned that potassium 2-ethoxy-2-oxoacetate is a stable, crystalline salt, which can be readily made from diethyl oxalate, KOAc, and H₂O [13]. Thus, the present protocol is operationally simpler than the previous Pd-catalyzed carbonylation method (usually conducted at 100–150 °C with 1 mol % Pd catalyst [1]) because it avoids the use of toxic CO. This feature is advantageous especially for laboratory-scale synthesis.

Scheme 2.1 Decarboxylative coupling of potassium oxalate monoesters with aryl halides
The reaction is distinct from reported palladium-catalyzed decarboxylative coupling reactions, such as decarboxylative alkenylation reaction reported by Myers et al. [4] in which oxidative addition of palladium to aryl halide is not involved. It is worth mentioning that in Myers’ reaction, addition of phosphine as ligand is detrimental while phosphine ligands play a crucial role in this decarboxylative ester synthesis. Compared with the decarboxylative biaryl synthesis reported by Goossen et al. [6], which was catalyzed by a catalyst composed of copper catalyst for decarboxylation and palladium catalyst for coupling, only a palladium catalyst is used in this reaction, and the Cu catalyst is not necessary, which means both the decarboxylation and coupling took place on palladium.

Table 2.1 Decarboxylative coupling under various conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>Pd source</th>
<th>Ligand</th>
<th>Yield %c</th>
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<tr>
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<td>Br</td>
<td>Pd(OAc)$_2$</td>
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<td>dpff</td>
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<td>7</td>
<td>Br</td>
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<td>81</td>
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<td>dppe</td>
<td>68</td>
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<td>dppp</td>
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<td>Br</td>
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<td>79</td>
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<tr>
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<td>dppp</td>
<td>80</td>
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<td>Br</td>
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<td>dppp</td>
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<tr>
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<td>I</td>
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<td>dppp</td>
<td>83</td>
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<td>21</td>
<td>Cl</td>
<td>Pd(TFA)$_2$</td>
<td>dppp</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

*Conditions 1 mol% Pd, 3 mol% monodentate ligand or 1.5 mol% bidentate ligand, aryl halide/potassium 2-ethoxy-2-oxoacetate = 1:1.5, 1.0 ml of N-methylpyrrolidone (NMP) solvent. All of the reactions were carried out at 0.5 mmol scale. b0.5 mol%. cGC yields based on PhX bold Optimal conditions

The reaction is distinct from reported palladium-catalyzed decarboxylative coupling reactions, such as decarboxylative alkenylation reaction reported by Myers et al. [4] in which oxidative addition of palladium to aryl halide is not involved. It is worth mentioning that in Myers’ reaction, addition of phosphine as ligand is detrimental while phosphine ligands play a crucial role in this decarboxylative ester synthesis. Compared with the decarboxylative biaryl synthesis reported by Goossen et al. [6], which was catalyzed by a catalyst composed of copper catalyst for decarboxylation and palladium catalyst for coupling, only a palladium catalyst is used in this reaction, and the Cu catalyst is not necessary, which means both the decarboxylation and coupling took place on palladium.
2.2.2 Exploration of the Substrate Scope

After optimizing the catalyst system, we tested the generality of the reaction with regard to both coupling partners (Table 2.2). It was found that both electron-rich and electron-poor aryl bromides can be successfully converted across a range of

Table 2.2 Decarboxylative cross-coupling with diverse aryl bromides

\[
\begin{align*}
\text{RO-} & \quad \text{CO}_2\text{K} \\
(\text{R} = \text{Me, Et}) & \quad \text{1.1-}1.5\text{ mmol}^b \\
\text{1} & \quad \text{83\%} \\
\text{2} & \quad \text{96\%} \\
\text{3} & \quad \text{92\%} \\
\text{4} & \quad \text{95\%} \\
\text{5} & \quad \text{79\%} \\
\text{6} & \quad \text{90\%} \\
\text{7} & \quad \text{89\%} \\
\text{8} & \quad \text{75\%} \\
\text{9} & \quad \text{82\%} \\
\text{10} & \quad \text{64\%} \\
\text{11} & \quad \text{67\%} \\
\text{12} & \quad \text{78\%} \\
\text{13} & \quad \text{86\%} \\
\text{14} & \quad \text{98\%} \\
\text{15} & \quad \text{52\%} \\
\text{16} & \quad \text{80\%} \\
\text{17} & \quad \text{94\%} \\
\text{18} & \quad \text{80\%} \\
\text{19} & \quad \text{82\%} \\
\text{20} & \quad \text{81\%} \\
\text{21} & \quad \text{62\%} \\
\text{22} & \quad \text{94\%} \\
\text{23} & \quad \text{81\%} \\
\text{24} & \quad \text{54\%} \\
\text{25} & \quad \text{55\%} \\
\text{26} & \quad \text{70\%} \\
\text{27} & \quad \text{77\%} \\
\text{28} & \quad \text{81\%} \\
\end{align*}
\]

\( ^a\)Isolated yields based on aryl bromides. \( ^b\)See the supporting information
functional groups [including ether (entries 4, 5, 7), thioether (entry 8), aldehyde (entry 11), ketone (entries 10, 14), amide (entry 15), nitro (entry 9), nitrile (entry 13), ester (entry 12), trifluoromethyl (entries 16, 17, 18), halogen (entries 22, 23) and heterocycle (entry 19)]. Importantly, ortho substitution can be tolerated in the transformation (entries 3, 5, 15). In addition to the ethyl esters, potassium 2-methoxy-2-oxoacetate can be used to produce methyl esters (entries 24–28). Furthermore, the method can be used to synthesize trans-acrylate derivatives in high yields from vinyl bromides (Scheme 2.2), and in a special case (Scheme 2.3), we observed cascade cross-coupling/cyclization.

The above protocol can be applied to both aryl bromides and iodides (Table 2.1, entry 20) but not to aryl chlorides (entry 21). Use of bulky, electron-rich ligands may solve the problem, but our experiments with good Ar–Cl activation ligands such as t-Bu3P, S-Phos, DavePhos, X-Phos, and JohnPhos [14] failed to couple PhCl with potassium 2-ethoxy-2-oxoacetate. We reasoned that the use of a bulky, electron-rich ligand similar in structure to dppp might provide a solution. To our delight, dCypp proved to successfully promote the decarboxylative coupling with various aryl chlorides (Table 2.3). However, ortho substitution would inhibit the reaction due to the bulky steric hindrance of the dCypp (Table 2.3, entry 3).

### 2.2.3 Mechanistic Study

Standard density functional theory methods were used to understand the mechanism of the new decarboxylative cross-coupling reaction (Fig. 2.1) [15]. First, a Pd(0) complex was proposed to activate the aryl halide. When 1,3-diphosphinopropane was used as a model ligand, the Pd(0) complex formed a η² complex with PhBr (IN1), which should undergo oxidative addition through TS1 to produce a
Table 2.3  Decarboxylative cross-coupling with aryl chlorides

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>70%</td>
</tr>
<tr>
<td>2</td>
<td>66%</td>
</tr>
<tr>
<td>3</td>
<td>&lt; 5%</td>
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<td>4</td>
<td>73%</td>
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<td>74%</td>
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<td>92%</td>
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<td>77%</td>
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<tr>
<td>8</td>
<td>80%</td>
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<td>9</td>
<td>36%</td>
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<td>10</td>
<td>75%</td>
</tr>
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</table>

*a* Isolated yields based on aryl chlorides

Fig. 2.1  Proposed mechanism of decarboxylative cross-coupling. Reprinted with the permission from J. Am. Chem. Soc. 2009, 131, 5738. Copyright 2011 American Chemical Society
four-coordinate Pd(II) intermediate (IN2). The energy barrier for oxidative addition was +11.4 kcal/mol. IN2 then exchanged the anion to form IN3. From IN3, the decarboxylation transition state (TS2) was identified as a five-coordinate Pd(II) species [16]. In TS2, the Pd(II) coordinated to the leaving CO2 moiety through one of its oxygens and to the other carbonyl group in an \( \eta^2 \) mode. From IN3 to TS2, the free energy increased by 29.5 kcal/mol, a value whose magnitude is consistent with the experimental temperature required for the reaction (~150 °C). Thus, decarboxylation is the rate-limiting step in the catalytic cycle. The immediate product of decarboxylation was a four-coordinate acyl-Pd complex (IN4), which readily underwent reductive elimination to produce the ester product through TS3 with a low barrier of ~12 kcal/mol. In IN4, the Pd center is coordinatively saturated, preventing decarbonylation to form an inactive Pd–CO complex. This may explain why bidentate phosphine ligands are favored for the present decarboxylative cross-coupling reactions. A related phenomenon has been discussed for Pd-catalyzed carbonylation [17], where the use of bulky, electron-rich bidentate ligands has also been found to be important [2].

### 2.3 Conclusion

Pd-catalyzed decarboxylative cross-coupling of aryl iodides, bromides, and chlorides with potassium oxalate monoesters has been discovered. This reaction is potentially useful for laboratory-scale synthesis of aryl and alkenyl esters [18]. Bulky, electron-rich bidentate phosphine ligands are preferred in the reaction, whereas Cu is not needed for decarboxylation. Theoretical calculations suggest a five-coordinate Pd(II) transition state for decarboxylation with an energy barrier of ~30 kcal/mol.

### 2.4 Experimental Section and Compound Data

#### 2.4.1 General Information

All reactions were carried out in oven-dried Schlenk tubes under Argon atmosphere (purity \( \geq 99.999\% \)). The NMP solvent was bought from Alfa Aesar (sealed under argon) without further purification. All aryl halides were purchased from Alfa Aesar or Acros and used directly. All phosphine ligands were bought from Sigma-Aldrich, Strem, or Alfa Aesar and sealed under Argon. All the other reagents and solvents were bought from Sinopharm Chemical Reagent Co. Ltd or Alfa Aesar and were purified when necessary.

\(^1\)H-NMR, \(^13\)C-NMR spectra were recorded on a Bruker Advance 400 spectrometer at ambient temperature in CDCl\(_3\) unless otherwise noted. Data for
NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for 13C-NMR are reported in terms of chemical shift (δ ppm). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. MS analysis was performed on Finnigan LCQ advantage Max Series MS System. Elementary Analysis was carried out on Elementar Vario EL III elemental analyzer. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200–300 mesh).

2.4.2 Experimental Procedure

General procedure A: the synthesis of aromatic esters from aryl bromides

Palladium(II) trifluoroacetate (0.01 mmol), 1,3-bis(diphenylphosphino)-propane (0.015 mmol), appointed amount of ethyl (or methyl) potassium oxalate (1.1–1.5 mmol, see Page S8-16 for detailed quantities) and the aryl bromide (1.00 mmol) (if solid) were placed in an oven-dried 20 ml Schlenk tube. The reaction vessel was evacuated and filled with argon for three times. Then aryl bromide (1.00 mmol) (if liquid) and NMP (2 ml) were added with a syringe under a counter flow of argon. The vessel was sealed, connected to the Schlenk line which was full with argon and stirred at 150 ± 5 °C for the appointed time. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with diethyl ether (20 ml). It was then filtered through a short silica column to remove the deposition. The organic layers were washed with water (20 ml × 3), and then with brine, dried over Na2SO4, and filtered. The solvents were removed. Purification of the residue by column chromatography (silica gel, ethyl acetate/hexane gradient) yielded the corresponding aryl ester.

General procedure B: the synthesis of aromatic esters from aryl chlorides

Palladium(II) trifluoroacetate (0.03 mmol), appointed amount of ethyl potassium oxalate and the aryl chloride (1.00 mmol) (if solid) were placed in an oven-dried 20 ml Schlenk tube. The reaction vessel was evacuated and filled with argon for three times. Aryl chloride (1.00 mmol) (if liquid), 1,3-bis(dicyclohexylphosphino)propane (0.06 mmol, 108 μl1) (as a solution, 250 mg in 2 ml NMP) and NMP (2 ml) were added with a syringe under a counter flow of argon, the vessel was sealed, connected to the Schlenk line which was full with argon and stirred at 150 ± 5 °C for the appointed time. Upon completion of the reaction, the mixture was cooled to room temperature, diluted with diethyl ether (20 ml) and filtered

11,3-bis(dicyclohexylphosphino)propane was bought from Sigma-Aldrich as a colorless oil (250 mg Package), and 2 ml NMP was directly added to the bottle to dissolve it before use.
through a short silica column to remove the deposition. The organic layers were washed with water (20 ml × 3) and then with brine, dried over Na₂SO₄, and filtered. The solvents were removed. Purification of the residue by column chromatography (silica gel, ethyl acetate/hexane gradient) yielded the corresponding aryl ester.

### 2.4.3 Characterization of the Products

**Compound name** benzoic acid ethyl ester

Colorless liquid (125 mg, 83% yield). 1H-NMR (400 MHz, CDCl₃): δ 1.40 (t, 3H, J = 7.2 Hz), 4.38 (q, 2H, J = 7.1 Hz), 7.41–7.46 (m, 2H), 7.52–7.57 (m, 1H), 8.03–8.06 (m, 2H). 13C-NMR (100 MHz, CDCl₃, δ ppm): 14.3, 60.9, 128.3, 129.5, 130.6, 132.8, 166.6.

**Compound name** Benzo [1,3] dioxole-5-carboxylic acid ethyl ester

Yellow liquid (173 mg, 89% yield). Spectral data matched literature description (Ref. Lee, A. S.; Wu, C.C.; Lin, L.S.; Hsu, H.F. Synthesis. 2004, 4, 568). 1H-NMR (400 MHz, CDCl₃): δ 1.37 (t, 3H, J = 7.0 Hz), 4.33 (q, 2H, J = 7.2 Hz), 6.02 (s, 2H), 6.82 (d, 1H, J = 8.4 Hz), 7.46 (d, 1H, J = 1.6 Hz), 7.65 (dd, 1H, J₁ = 1.6 Hz, J₂ = 8.0 Hz). 13C-NMR (100 MHz, CDCl₃, δ ppm): 14.4, 60.9, 101.8, 107.9, 109.5, 124.6, 125.3, 147.7, 151.5, 166.0.

**Compound name** 4-methylthiobenzoic acid ethyl ester

Yellow acicular solid (147 mg, 75% yield). Spectral data matched literature description (Ref. Lu, X.; Rodriguez, M.; Gu, W.; Silverman, R. B. Bioorg. Med. Chem. 2003, 11, 4423). 1H-NMR (400 MHz, CDCl₃): δ 1.38 (t, 3H, J = 7.2 Hz), 2.51 (s, 3H), 4.35 (q, 2H, J = 7.1 Hz), 7.24 (d, 2H, J = 8.40 Hz), 7.93 (d, 2H, J = 8.8 Hz). 13C-NMR (100 MHz, CDCl₃, δ ppm): 14.4, 14.9, 60.9, 125.0, 126.7, 129.9, 145.3, 166.6.
**Compound name** 4-(trifluoromethyl)benzoic acid ethyl ester

![4-(trifluoromethyl)benzoic acid ethyl ester](image)

colorless liquid (175 mg, 80% yield). Spectral data matched literature description (Ref. Bromilow, J.; Brownlee, R.; Craik, D. J.; Sadek, M.; Taft, R. W. J. Org. Chem. 1980, 45, 2429). 1H-NMR (400 MHz, CDCl3): δ 1.42 (t, 3H, \(J = 7.2\) Hz), 4.41 (q, 2H, \(J = 7.1\) Hz), 7.69 (d, 2H, \(J = 8.4\) Hz), 8.15 (dd, 2H, \(J_1 = 0.4\) Hz, \(J_2 = 8.8\) Hz). 13C-NMR (100 MHz, CDCl3, δ ppm): 14.3, 61.6, 123.8 (q, \(J = 271\) Hz), 125.4 (q, \(J = 3.5\) Hz), 130.0, 133.8, 134.4 (q, \(J = 32.4\) Hz), 165.4.

**Compound name** 4-trifluoromethoxy-benzoic acid ethyl ester

![4-trifluoromethoxy-benzoic acid ethyl ester](image)

colorless liquid (187 mg, 80% yield). 1H-NMR (400 MHz, CDCl3): δ 1.40 (t, 3H, \(J = 7.2\) Hz), 4.39 (q, 2H, \(J = 7.1\) Hz), 7.26 (d, 2H, \(J = 8.8\) Hz), 8.09 (d, 2H, \(J = 8.4\) Hz). 13C-NMR (100 MHz, CDCl3, δ ppm): 14.3, 61.4, 120.4 (q, \(J = 257\) Hz), 120.3, 129.0, 131.6, 152.6, 165.5.

**Compound name** 3-pyridinecarboxylic acid ethyl ester

![3-pyridinecarboxylic acid ethyl ester](image)

colorless liquid (124 mg, 82% yield). 1H-NMR (400 MHz, CDCl3): δ 1.42 (t, 3H, \(J = 7.0\) Hz), 4.42 (q, 2H, \(J = 7.1\) Hz), 7.39 (m, 1H), 8.31 (m, 1H), 8.78 (m, 1H), 9.23 (d, 1H, \(J = 2.0\) Hz). 13C-NMR (100 MHz, CDCl3, δ ppm): 14.2, 61.3, 123.2, 126.3, 136.9, 150.8, 153.2, 165.1.

**Compound name** naphthalene-1-carboxylic acid ethyl ester

![naphthalene-1-carboxylic acid ethyl ester](image)

yellow liquid (124 mg, 62% yield). 1H-NMR (400 MHz, CDCl3): δ 1.44 (t, 3H, \(J = 7.2\) Hz), 4.46 (q, 2H, \(J = 7.2\) Hz), 7.44–7.52 (m, 2H), 7.57–7.61 (m, 1H), 7.83–7.87 (d, 1H, \(J = 8.4\) Hz), 7.96–7.98 (d, 1H, \(J = 8.4\) Hz), 8.16–8.18 (dd, 1H, \(J_1 = 7.2\) Hz, \(J_2 = 1.2\) Hz), 8.91–8.93 (d, 1H, \(J = 8.4\) Hz). 13C-NMR (100 MHz, CDCl3, δ ppm): 14.4, 61.1, 124.5, 125.9, 126.2, 127.6, 127.7, 128.6, 130.1, 131.4, 133.2, 133.9, 167.6.
Compound name 4-acetylbenzoic acid ethyl ester

white solid (123 mg, 64% yield). Spectral data matched literature description (Ref. Cai, C.; Rivera, N. R.; Balsells, J.; Sidler, R. R.; McWilliams, J. C.; Shultz, C. S.; Sun, Y. Org. Lett. 2006, 8, 5161). 1H-NMR (400 MHz, CDCl3): δ 1.42 (t, 3H, J = 7.0 Hz), 2.64 (s, 3H), 4.41 (q, 2H, J = 7.0 Hz), 8.01 (m, 2H), 8.12 (m, 2H). 13C-NMR (100 MHz, CDCl3, δ ppm): 14.4, 26.9, 61.5, 128.2, 129.8, 134.4, 140.2, 165.8, 197.6.

Compound name 4-cyanobenzoic acid ethyl ester

yellow solid (150 mg, 86% yield). 1H-NMR (400 MHz, CDCl3): δ 1.42 (t, 3H, J = 7.2 Hz), 4.42 (q, 2H, J = 7.2 Hz), 7.74 (d, 2H, J = 8.0 Hz), 8.14 (d, 2H, J = 8.0 Hz). 13C-NMR (100 MHz, CDCl3, δ ppm): 14.3, 61.9, 116.4, 118.0, 130.1, 132.2, 134.4, 165.0.

Compound name 4-ethoxycarbonylbenzophenone

eyellow oil (249 mg, 98% yield). Spectral data matched literature description (Ref. Duplais, C.; Bures, F.; Sapountzis, I.; Korn, T. J.; Cahiez, G.; Knochel, P. Angew. Chem. 2004, 116, 3028; Angew. Chem, Int. Ed. 2004, 43, 2968). 1H-NMR (400 MHz, CDCl3): δ 1.42 (t, 3H, J = 7.2 Hz), 4.42 (q, 2H, J = 7.2 Hz), 7.48–7.52 (m, 2H), 7.59–7.64 (m, 1H), 7.72–7.73 (m, 2H), 7.80–7.81 (m, 4H), 8.14–8.17 (m, 2H). 13C-NMR (100 MHz, CDCl3, δ ppm): 14.4, 61.5, 128.5, 129.5, 129.8, 130.2, 133.0, 133.7, 137.1, 141.3, 165.9, 196.1.

Compound name 3-methylidene-3H-isobenzofuran-1-one

white solid (45 mg, 31% yield). Spectral data matched literature description (Ref. Yamamoto, H.; Pandey, G.; Asai, Y.; Nakano, M.; Kinoshita, A.; Namba, K.; Imagawa, H.; Nishizawa, M. Org. Lett. 2007, 9, 4029) 1H-NMR (400 MHz, CDCl3): δ 5.23 (dd, 2H, J1 = 3.2 Hz, J2 = 4.0), 7.55–7.62 (m, 1H), 7.72–7.73 (m,
2H), 7.90–7.92 (m, 1H). 13C-NMR (100 MHz, CDCl3, δ ppm): 91.3, 120.7, 125.2, 125.4, 130.5, 134.5, 139.1, 151.9, 166.9.

**Compound name** 2-acetylamino benzoic acid ethyl ester

![Chemical structure](https://www.chemistryworld.org/images/structure.png)

pale yellow solid (108 mg, 52% yield). 1H-NMR (400 MHz, CDCl3): δ 1.42 (t, 3H, J = 7.0 Hz), 2.24 (s, 3H), 4.38 (q, 2H, J = 7.2 Hz), 7.05–7.09 (m, 1H), 7.51–7.56 (m, 1H), 8.03–8.05 (m, 1H), 8.69–8.71 (m, 1H), 11.09 (s, br, 1H).

13C-NMR (100 MHz, CDCl3, δ ppm): 14.3, 25.6, 61.5, 115.2, 120.4, 122.4, 130.8, 134.6, 141.7, 168.4, 169.1.

**References**

12. Cu co-catalyst was used in the beginning but our experiments quickly revealed that the use of Pd only is sufficient for the present system.


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Shang, R.
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