



# Organic transformations catalyzed by palladium nanoparticles on carbon nanomaterials

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**Abstract.** An efficient C–C bond coupling reactions (Suzuki–Miyaura and Glaser) catalyzed by PdO/GO nano-catalyst is presented. In addition, PdO/MWCNT nano-catalyst-mediated domino one-pot synthesis of 2-alkyl/2-aryl benzofurans has been accomplished from 2-iodophenols and terminal alkynes. The formation of benzofurans proceeds through intermolecular Sonogashira reaction followed by intramolecular nucleophilic addition of internal hydroxyl group onto the acetylenic bond. The catalyst PdO/GO has been reused successfully, with nearly no loss of activity up to 5 cycles.

**Keywords.** Graphene oxide (GO); multi-walled carbon nanotubes (MWCNT); C–C coupling reaction; benzofuran derivatives.

## 1. Introduction

From a green chemistry point of view, heterogeneous catalysis holds paramount advantages over its homogeneous counterparts such as, easy separation, reusability and stability of the catalyst. However, dispersion of the chosen catalytic material on a suitable support is still a challenge to the scientific community. This problem is even more complex in nanomaterial catalysts, due to aggregation problems. In this context, hybrid carbon materials such as graphene oxide (GO), reduced graphene oxide (RGO), multi-walled carbon nanotubes (MWCNT), single-walled carbon nanotubes (SWCNT), and carbon nanofiber (CNF) have been tested as supports.<sup>1–4</sup> Palladium is one of the most widely used metals for organic transformations. However, unsupported [Pd]-nanoparticles agglomerate or sinter upon heating.<sup>5–8</sup> Carbon-supported [Pd]-based nanoparticles proved to be highly active catalytic systems and furnished the coupling products in high yields with good selectivity. These advantageous features are attributed to the electronic, mechanical and thermal properties of the carbon support.<sup>9–13</sup>

Until now, homogenous [Pd]-catalysis has been broadly explored for organic coupling transformations. In modern organic synthesis, the development of environmentally benign organic transformations is highly desirable.<sup>14–17</sup> Recently, we have reported the syntheses and characterization of PdO nanoparticles impregnated on various nano-carbon supports (SWCNT, MWCNT, CNF, GO and RGO).<sup>18,19</sup> Also, the efficiency of these ligand-free catalysts has been demonstrated with the Heck reaction between iodoarenes and olefins. Among them, PdO/GO catalyst was found to be the best, due to a high degree of surface-bound oxygenated moieties. The combined effects of high surface area, mesoporous nature,  $\pi$ -interactions, optimum electron conductivity of GO favored the activity of PdO/GO nanohybrids, for Heck cross-coupling reactions. Encouraged by these initial results, we are reporting the extension of the scope of this versatile system for other organic coupling transformations. This communication deals with the applications of ligand-free PdO/GO, for C–C bond forming Suzuki–Miyaura and Glaser coupling reactions, respectively. In addition, ligand-free heterogeneous PdO/MWCNT-catalyzed domino one-pot synthesis of

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2-arylbenzofurans through intermolecular Sonogashira coupling followed intermolecular nucleophilic addition to the acetylenic bond, is also described.

## 2. Experimental

### 2.1 General considerations

IR spectra were recorded on a FTIR spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on 400 MHz spectrometer at 295 K in  $\text{CDCl}_3$ ; chemical shifts ( $\delta$  ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) ( $\delta_{\text{H}} = 0.00\text{ppm}$ ) or  $\text{CHCl}_3$  ( $\delta_{\text{H}} = 7.25\text{ppm}$ ).  $^{13}\text{C}$  NMR spectra were recorded on 100 MHz spectrometer at RT in  $\text{CDCl}_3$ ; chemical shifts ( $\delta$  ppm) are reported relative to  $\text{CHCl}_3$  [ $\delta_{\text{C}} = 77.00\text{ppm}$  (central line of triplet)]. In the  $^{13}\text{C}$  NMR, the nature of carbons (C, CH,  $\text{CH}_2$ , and  $\text{CH}_3$ ) was determined by recording the DEPT-135 spectra and is given in parentheses and noted as s=singlet (for C), d = doublet (for CH), t=triplet (for  $\text{CH}_2$ ) and q = quartet (for  $\text{CH}_3$ ). In the  $^1\text{H}$  NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br s. = broad singlet. The assignment of signals was confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$  CPD (carbon proton decoupled), and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded using Q-TOF multimode source. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Iodophenols, PdO on MWCNT, terminal alkynes and  $\text{K}_2\text{CO}_3$  were commercially available (local made) used without further purification.

Reactions were monitored by TLC on silica gel using a combination of petroleum ether and ethyl acetate as eluents. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 °C was used. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

### 2.2 General procedure 1 (for the synthesis of biphenyls 3)

In an oven-dried Schlenk tube iodoarenes **1** (0.25 mmol), arylboronic acids **2** (0.5 mmol), PdO/GO nano catalyst (5 mol%),  $\text{K}_2\text{CO}_3$  (0.5 mmol) and solvent (DMSO) (1.0 mL) were added. The resulting reaction mixture was stirred at 120 °C for 5–30 min. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was allowed to cool to room temperature, then diluted with (approximately 10 mL) ethyl acetate and  $\text{NH}_4\text{Cl}$  solution (approximately 10 mL) was added followed by extraction with ethyl acetate. The organic layers were dried with  $\text{Na}_2\text{SO}_4$  and concentrated in reduced vacuum. Purification of the residue by silica gel column chromatography using distilled petroleum ether/ethyl acetate as the eluent furnished the biphenyls.

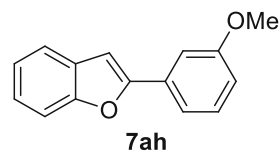
### 2.3 General procedure 2 (for the synthesis of symmetrical 1,3-diyne 5)

In an oven-dried Schlenk tube terminal alkynes **4** (0.5 mmol), Pd/GO nano catalyst (5 mol%),  $\text{K}_2\text{CO}_3$  (1 mmol) and solvent (DMSO) (1.0 mL) were added. The resulting reaction mixture was stirred at 120 °C for 2 h. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was allowed to cool to room temperature, then diluted with (~ 10 mL) ethyl acetate and  $\text{NH}_4\text{Cl}$  solution (~ 10 mL) was added followed by extraction with ethyl acetate. The organic layers were dried with  $\text{Na}_2\text{SO}_4$  and concentrated in reduced vacuum. Purification of the residue by silica gel column chromatography using distilled petroleum ether/ethyl acetate as the eluent furnished the cinnamates and stilbenes.

### 2.4 General procedure 3 (for the synthesis of benzofurans 7)

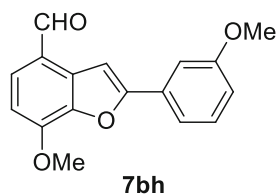
In an oven-dried Schlenk tube 2-iodophenol **6** (0.5 mmol), terminal alkyne **4** (0.5 mmol), PdO/MWCNT (5 mol%),  $\text{K}_2\text{CO}_3$  (1 mmol) and solvent (DMSO) (1.0 mL) were added. The resulting reaction mixture was stirred at 120 °C for 24 h. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was allowed to cool to room temperature, then diluted with (10 mL) ethyl acetate and  $\text{NH}_4\text{Cl}$  (10 mL) was added followed by extraction with ethyl acetate. The organic layers were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated in vacuum. Purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the benzofuran **7**.

### 2.5 Characterization data

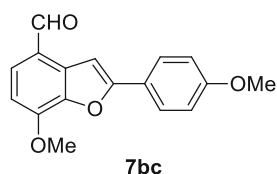


This compound was prepared according to the GP and isolated as colorless liquid 94% yield (105 mg). [TLC (petroleum ether/ethyl acetate 9:1,  $R_f$  (**6a**) = 0.50,  $R_f$  (**4h**) = 0.60, UV detection].  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.59$  (d,  $J = 7.3$  Hz, 1H), 7.53 (d,  $J = 7.3$  Hz, 1H), 7.46 (d,  $J = 8.8$  Hz, 1H), 7.42 (s, 1H), 7.36 (dd,  $J = 7.8$  and 7.8 Hz, 1H), 7.29 (dd,  $J = 8.3$  and 7.3 Hz, 1H), 7.23 (d,  $J = 7.3$  Hz, 1H), 7.03 (s, 1H), 6.91 (dd,  $J = 7.3$  and 2.0 Hz, 1H), 3.89 (s, 3H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 159.9$  ( $\text{C}_q$ ), 155.7 ( $\text{C}_q$ ), 154.8 ( $\text{C}_q$ ), 131.7 ( $\text{C}_q$ ), 129.8 (CH), 129.1 ( $\text{C}_q$ ), 124.3 (CH), 122.9 (CH), 120.9 (CH), 117.5 (CH), 114.4 (CH), 111.2 (CH), 110.1 (CH), 101.6 (CH), 55.3 ( $\text{CH}_3$ ) ppm. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2921, 2851, 1482, 1460, 1380$ ,

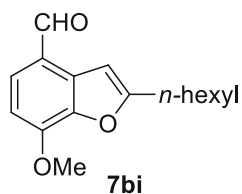
1123, 1109, 1011, 928  $\text{cm}^{-1}$ . HR-MS (ESI<sup>+</sup>)  $m/z$  calculated for  $[\text{C}_{15}\text{H}_{12}\text{O}_2]^+ = [\text{M}]^+$ : 224.0832; found: 224.0840.



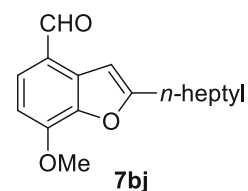
This compound was prepared according to the GP and isolated as pale yellow color viscous liquid 90% yield (127 mg). [TLC (petroleum ether/ethyl acetate 8:2,  $R_f(\mathbf{6b}) = 0.50$ ,  $R_f(\mathbf{4h}) = 0.60$ , UV detection]. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.03$  (s, 1H), 7.78 (s, 1H), 7.65 (d,  $J = 8.3$  Hz, 1H), 7.53 (d,  $J = 7.8$  Hz, 1H), 7.44 (dd,  $J = 2.4$  and 2.0 Hz, 1H), 7.36 (dd,  $J = 8.3$  and 7.8 Hz, 1H), 6.93 (dd,  $J = 8.8$  and 3.2 Hz, 1H), 6.88 (d,  $J = 8.3$  Hz, 1H), 4.11 (s, 3H), 3.88 (s, 3H) ppm. <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 190.8$  ( $\text{C}_q$ ), 159.9 ( $\text{C}_q$ ), 158.8 ( $\text{C}_q$ ), 149.8 ( $\text{C}_q$ ), 144.0 ( $\text{C}_q$ ), 132.1 (CH), 130.9 ( $\text{C}_q$ ), 129.9 (CH), 129.8 ( $\text{C}_q$ ), 122.9 ( $\text{C}_q$ ), 118.0 (CH), 115.5 (CH), 110.3 (CH), 106.1 (CH), 102.2 (CH), 56.4 ( $\text{CH}_3$ ), 55.4 ( $\text{CH}_3$ ) ppm. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2922$ , 2850, 1478, 1380, 1201, 1165, 1011, 920  $\text{cm}^{-1}$ . HR-MS (ESI<sup>+</sup>)  $m/z$  calculated for  $[\text{C}_{17}\text{H}_{14}\text{NaO}_4]^+ = [\text{M} + \text{Na}]^+$ : 305.0784; found: 305.0794.



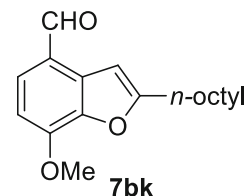
This compound was prepared according to the GP and isolated as brown color solid 91% yield (128 mg). M.p. 80–82 °C; [TLC (petroleum ether/ethyl acetate 8:2,  $R_f(\mathbf{6b}) = 0.40$ ,  $R_f(\mathbf{4h}) = 0.50$ , UV detection]. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.04$  (s, 1H), 7.87 (d,  $J = 8.8$  Hz, 1H), 7.65 (s, 1H), 7.63 (d,  $J = 8.3$  Hz, 1H), 6.97 (d,  $J = 8.8$  Hz, 1H), 6.85 (d,  $J = 8.3$  Hz, 1H), 4.12 (s, 3H), 3.86 (s, 3H) ppm. <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 190.8$  ( $\text{C}_q$ ), 160.6 ( $\text{C}_q$ ), 159.3 ( $\text{C}_q$ ), 149.6 ( $\text{C}_q$ ), 143.8 ( $\text{C}_q$ ), 131.8 (CH), 130.4 ( $\text{C}_q$ ), 127.0 (CH), 122.7 ( $\text{C}_q$ ), 122.5 ( $\text{C}_q$ ), 114.3 (CH), 105.8 (CH), 100.4 (CH), 56.4 ( $\text{CH}_3$ ), 55.4 ( $\text{CH}_3$ ) ppm. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2921$ , 2850, 1563, 1480, 1465, 1381, 1121, 1103, 1012, 928  $\text{cm}^{-1}$ . HR-MS (ESI<sup>+</sup>)  $m/z$  calculated for  $[\text{C}_{17}\text{H}_{14}\text{NaO}_4]^+ = [\text{M} + \text{Na}]^+$ : 305.0784; found: 305.0788.



This compound was prepared according to the GP and isolated as brown color viscous liquid 89% yield (116 mg). [TLC (petroleum ether/ethyl acetate 8:2,  $R_f(\mathbf{6b}) = 0.50$ ,  $R_f(\mathbf{4i}) = 0.60$ , UV detection]. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.01$  (s, 1H), 7.62 (d,  $J = 8.3$  Hz, 1H), 7.14 (s, 1H), 6.82 (d,  $J = 8.3$  Hz, 1H), 4.08 (s, 3H), 2.81 (t,  $J = 7.3$  Hz, 2H), 1.85–1.70 (m, 2H), 1.45–1.15 (m, 6H), 0.87 (t,  $J = 7.3$  Hz, 3H) ppm. <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 190.8$  ( $\text{C}_q$ ), 163.4 ( $\text{C}_q$ ), 149.4 ( $\text{C}_q$ ), 143.6 ( $\text{C}_q$ ), 131.3 (CH), 129.8 ( $\text{C}_q$ ), 122.6 ( $\text{C}_q$ ), 105.0 (CH), 102.6 (CH), 56.3 ( $\text{CH}_3$ ), 31.5 ( $\text{CH}_2$ ), 28.9 ( $\text{CH}_2$ ), 28.5 ( $\text{CH}_2$ ), 27.6 ( $\text{CH}_2$ ), 22.5 ( $\text{CH}_2$ ), 14.0 ( $\text{CH}_3$ ) ppm. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2930$ , 2843, 1560, 1481, 1456, 1375, 1187, 1160, 1009, 929  $\text{cm}^{-1}$ . HR-MS (ESI<sup>+</sup>)  $m/z$  calculated for  $[\text{C}_{16}\text{H}_{20}\text{NaO}_3]^+ = [\text{M} + \text{Na}]^+$ : 283.1305; found: 283.1308.

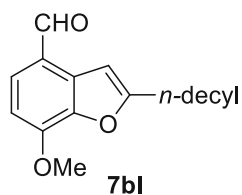


This compound was prepared according to the GP and isolated as brown color viscous liquid 86% yield (118 mg): [TLC (petroleum ether/ethyl acetate 9:1,  $R_f(\mathbf{6b}) = 0.40$ ,  $R_f(\mathbf{4j}) = 0.70$ , UV detection]. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.02$  (s, 1H), 7.63 (d,  $J = 8.3$  Hz, 1H), 7.15 (s, 1H), 6.84 (d,  $J = 8.3$  Hz, 1H), 4.09 (s, 3H), 2.83 (t,  $J = 7.8$  Hz, 2H), 1.85–1.70 (m, 2H), 1.45–1.15 (m, 8H), 0.88 (t,  $J = 7.8$  Hz, 3H) ppm. <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 190.8$  ( $\text{C}_q$ ), 163.4 ( $\text{C}_q$ ), 149.4 ( $\text{C}_q$ ), 143.7 ( $\text{C}_q$ ), 131.3 (CH), 129.9 ( $\text{C}_q$ ), 122.6 ( $\text{C}_q$ ), 105.0 (CH), 102.6 (CH), 56.3 ( $\text{CH}_3$ ), 31.7 ( $\text{CH}_2$ ), 29.1 ( $\text{CH}_2$ ), 29.0 ( $\text{CH}_2$ ), 28.5 ( $\text{CH}_2$ ), 27.6 ( $\text{CH}_2$ ), 22.6 ( $\text{CH}_2$ ), 14.0 ( $\text{CH}_3$ ) ppm. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2927$ , 2850, 1560, 1480, 1471, 1380, 1190, 1165, 1010, 926  $\text{cm}^{-1}$ . HR-MS (ESI<sup>+</sup>)  $m/z$  calculated for  $[\text{C}_{17}\text{H}_{22}\text{NaO}_3]^+ = [\text{M} + \text{Na}]^+$ : 297.1461; found: 297.1465.



This compound was prepared according to the GP and isolated as brown color viscous liquid 90% yield (129 mg): [TLC (petroleum ether/ethyl acetate 8:2,  $R_f(\mathbf{6b}) = 0.50$ ,  $R_f(\mathbf{4k}) = 0.60$ , UV detection]. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.01$  (s, 1H), 7.62 (d,  $J = 8.3$  Hz, 1H), 7.14 (s, 1H), 6.83 (d,  $J = 8.3$  Hz, 1H), 4.08 (s, 3H), 2.81 (t,  $J = 7.3$  Hz, 2H), 1.85–1.70 (m, 2H), 1.45–1.15 (m, 10H), 0.87 (t,  $J = 7.3$  Hz, 3H) ppm. <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 190.8$  ( $\text{C}_q$ ), 163.4 ( $\text{C}_q$ ), 149.4 ( $\text{C}_q$ ), 143.7 ( $\text{C}_q$ ), 131.3 (CH), 129.9 ( $\text{C}_q$ ), 122.6 ( $\text{C}_q$ ), 105.1 (CH), 102.6 (CH), 56.3

(CH<sub>3</sub>), 31.8 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 28.5 (CH<sub>2</sub>), 27.6 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>) ppm. IR (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{\max}$  = 2920, 2865, 1560, 1484, 1463, 1380, 1132, 1009, 926 cm<sup>-1</sup>. HR-MS (ESI<sup>+</sup>) m/z calculated for [C<sub>18</sub>H<sub>25</sub>O<sub>3</sub>]<sup>+</sup> = [M + H]<sup>+</sup>: 289.1798; found: 289.1801.



This compound was prepared according to the GP and isolated as pale yellow color liquid 90% yield (142 mg). [TLC (petroleum ether/ethyl acetate 8:2, R<sub>f</sub>(**6b**) = 0.50, R<sub>f</sub>(**4l**) = 0.60, UV detection]. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 10.01 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.14 (s, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 4.08 (s, 3H), 2.82 (t, *J* = 7.3 Hz, 2H), 1.85–1.70 (m, 2H), 1.45–1.15 (m, 14H), 0.87 (t, *J* = 7.3 Hz, 3H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 190.8 (C<sub>q</sub>), 163.4 (C<sub>q</sub>), 149.4 (C<sub>q</sub>), 143.7 (C<sub>q</sub>), 131.3 (CH), 129.9 (C<sub>q</sub>), 122.6 (C<sub>q</sub>), 105.1 (CH), 102.6 (CH), 56.3 (CH<sub>3</sub>), 31.9 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.3 (2C, CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 28.5 (CH<sub>2</sub>), 27.6 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>) ppm. IR (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{\max}$  = 2921, 2851, 1530, 1483, 1460, 1321, 1180, 1163, 1107, 1009, 920 cm<sup>-1</sup>. HR-MS (ESI<sup>+</sup>) m/z calculated for [C<sub>20</sub>H<sub>28</sub>NaO<sub>3</sub>]<sup>+</sup> = [M + Na]<sup>+</sup>: 339.1931; found: 339.1930.

### 3. Results and Discussion

The first part of the report deals with the optimization of conditions for Suzuki–Miyaura coupling. Recently, we reported that PdO/GO shows the best activity for Heck coupling, where it showed the best efficacy, turn over number (TON) and turn over frequency (TOF).<sup>18</sup> Thus, the reaction was explored between iodobenzene **1a** and phenylboronic acid **2a** in the presence PdO/GO of K<sub>2</sub>CO<sub>3</sub> base in DMSO as solvent at 120 °C. Interestingly, the reaction was quite successful and furnished the biaryl product **3aa**, in excellent yield (Table 1, entry 1). On the other hand, the reaction was found to be inferior with the other solvents, such as DMF, DMA, toluene, 1,4-dioxane, THF and acetonitrile (Table 1, entries 2–7). Also, the reaction gave fair to good yields of the product **3aa** with the bases Na<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub>, respectively (Table 1, entries 8 to 9).

Table 1 summarizes the optimization conditions of the present study. With these optimized conditions in hand, to extend the scope and generality of the method, the Suzuki–Miyaura coupling was explored between various iodoarenes **1a–g** and arylboronic acids **2a–c**.

**Table 1.** Optimization studies for the formation of biaryl **3aa**.<sup>a</sup>

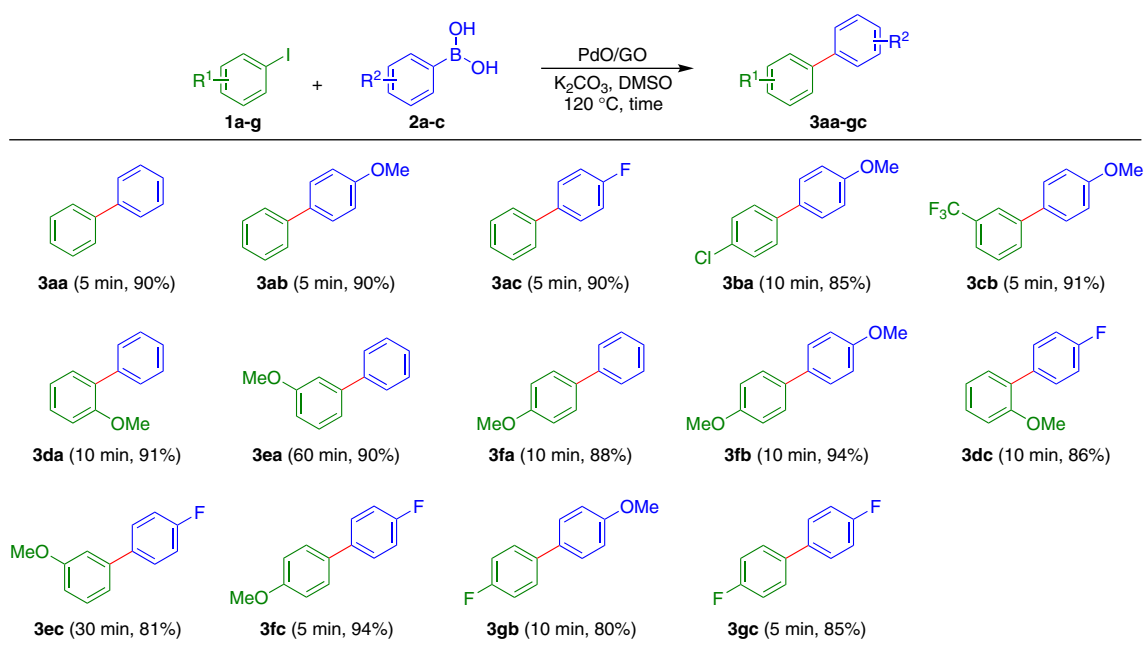
Entry	Base	Solvent	Yield <b>3aa</b> (%) <sup>b</sup>
1	K <sub>2</sub> CO <sub>3</sub>	DMSO	90
2	K <sub>2</sub> CO <sub>3</sub>	DMF	78
3	K <sub>2</sub> CO <sub>3</sub>	DMA	55
4	K <sub>2</sub> CO <sub>3</sub>	toluene	43
5	K <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	70
6	K <sub>2</sub> CO <sub>3</sub>	THF	64
7	K <sub>2</sub> CO <sub>3</sub>	acetonitrile	50
8	Na <sub>2</sub> CO <sub>3</sub>	DMSO	72
9	K <sub>3</sub> PO <sub>4</sub>	DMSO	65

<sup>a</sup>Reaction Conditions: aryl iodides **1a** (0.25 mmol), aryl boronic acid **2a** (0.5 mmol), PdO/GO (5 mol%), K<sub>2</sub>CO<sub>3</sub> (0.5 mmol) and DMSO (1 mL) at 120 °C. <sup>b</sup>Isolated yields of product **3aa**.

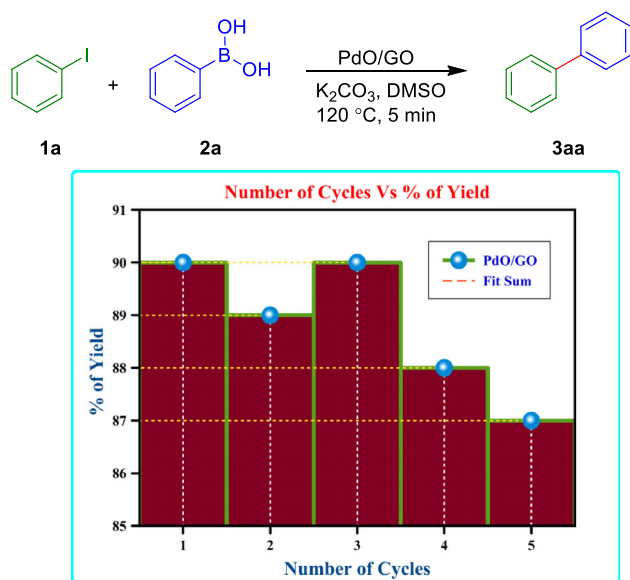
Gratifyingly, the reaction was found to be amenable and afforded the corresponding biaryls **3aa–gc**, in very good to excellent yields (Table 2). Interestingly, the reaction was successful with simple iodobenzene **1a** and also with different functional (CF<sub>3</sub>, F, Me and OMe) groups on aromatic ring **1b–g** (Table 2). Notably, the reaction was also amenable with simple arylboronic acid **2a** as well as electron-rich **2b** and electron deficient **2c** aromatic moieties (Table 2). However, in an analogy to our previous report,<sup>18</sup> the reaction with bromoarenes did not show progress. This may due to the fact the iodoarenes are relatively more reactive than that of bromo ones.

It is worth noting that the catalyst retains its activity, which is evident with nearly no loss of activity until the fifth cycle (Figure 1). This was done by recovering the catalyst by centrifugation and washing with ethyl acetate and acetone followed by drying in a hot air oven at 60 °C for 12 h. The recovered PdO/GO catalyst was then subjected to the next catalytic cycle. The marginal loss of activity after the fifth cycle (< 3%) may be due to loss of some amount of the catalyst during the recovery of PdO/GO. The catalyst was recycled five times without appreciable change in the product **3aa** yield under the established conditions at 120 °C. Thus, based on the above results it was confirmed that PdO/GO catalyst is stable enough and can be reused.

After successful synthesis of biaryls using Suzuki–Miyaura coupling, we attempted Glaser coupling. Symmetrical 1,3-diynes comprise an important class of compounds used for the accomplishment of  $\pi$ -conjugated

**Table 2.** Synthesis of biphenyls **3aa-gc** with aryl iodides **1a-g** and arylboronic acids **2a-c**.<sup>a,b</sup>

<sup>a</sup>Reaction Conditions: iodobenzene **1a-g** (0.25 mmol), arylboronic acid **2a-c** (0.5 mmol), PdO/GO (5 mol%), K<sub>2</sub>CO<sub>3</sub> (0.5 mmol) and DMSO (1 mL) at 120 °C. <sup>b</sup>Isolated yields of product **3aa-gc**.

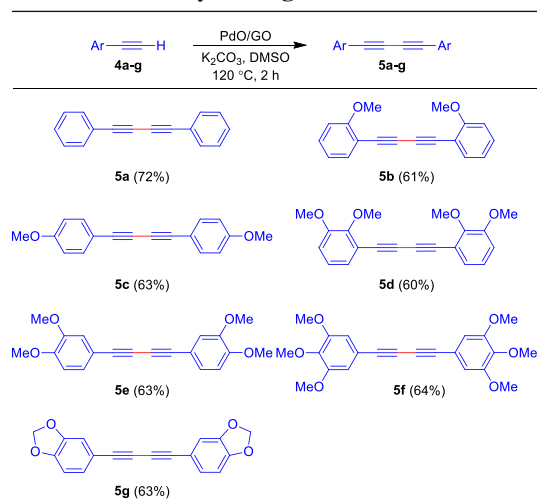
**Figure 1.** Recyclability of the catalyst in Suzuki reaction.

polymeric materials, supramolecular structures, natural products and pharmaceuticals.<sup>20–25</sup>

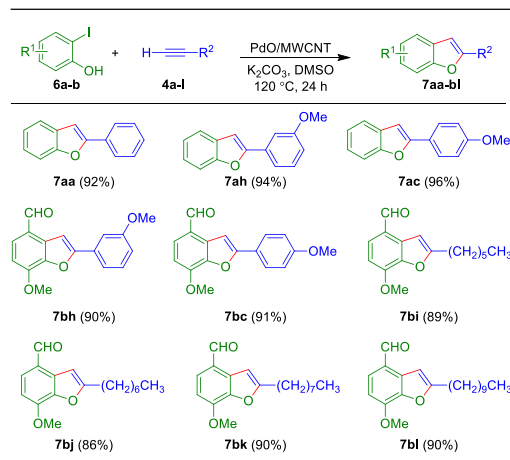
The first synthesis of symmetric 1,3-diynes through homo-coupling of terminal alkynes was reported by Carl Glaser in 1869 in the presence of Cu(I) salt and oxygen in air.<sup>26,27</sup> Subsequently, Eglington<sup>28</sup> and Hay<sup>29,30</sup> modified the method to improve the versatility of the method. Thereafter, some interesting [Cu]-catalyzed approaches

have been developed. Though Glaser coupling was well established under [Cu]-catalysis, there are a few reports by using other transition-metal-catalysts, such as Pd-Cu,<sup>32,33</sup> Pd-Ag,<sup>34</sup> Pd,<sup>25,35</sup> Ni,<sup>36</sup> Au,<sup>37,38</sup> etc. Herein, we intended to check the applicability of present PdO/GO catalyst for Glaser coupling. Therefore, the reaction was performed with terminal acetylenes **4a-g** under established reactions of Suzuki–Miyaura coupling. As seen from Table 3, the reaction was quite successful and furnished the Glaser coupling products **5a-g**, in fair to good yields (Table 3).

To further demonstrate the applicability of PdO/GO catalyst, one-pot synthesis of benzofurans was tested. Benzofurans are ubiquitous oxygen-containing heterocyclic motifs that constitute many natural products, pharmaceuticals, biologically important compounds and organic materials. In this context, many synthetic strategies have been established for their synthesis. Notably, transition metal-catalyzed (Pd,<sup>39–47</sup> Rh,<sup>48</sup> Ru,<sup>48–52</sup> Ir,<sup>53</sup> Au<sup>54</sup> and Cu<sup>55–57</sup>) annulations proved to be powerful strategies for the synthesis of benzofurans. With this background, PdO/GO catalyst was employed for the one-pot synthesis of 2-substituted benzofurans starting from 2-iodophenol **6a** and terminal acetylene **4a**, under standard conditions. However, the reaction furnished the simple Glaser product through homo-coupling and PdO/MWCNT catalyst is the best catalyst and furnished the benzofuran **7aa**, in excellent yield (Table 4).

**Table 3.** Synthesis of Symmetrical 1,3-diynes **5a-g** from terminal alkynes **4a-g**.<sup>a,b</sup>

<sup>a</sup>Reaction Conditions: aryl alkynes **4a-g** (0.5 mmol), PdO/GO (5 mol%), K<sub>2</sub>CO<sub>3</sub> (0.10 mmol) and DMSO (1 mL) at 120 °C. <sup>b</sup>Isolated yields of product **5a-g**.

**Table 4.** Synthesis of benzofurans **7aa-bl** from 2-iodophenols **6a-b** and aryl alkynes **4a-l**.<sup>a,b</sup>

<sup>a</sup>Reaction Conditions: Iodophenol **6a-b** (0.5 mmol), arylalkyne **4a-l** (0.5 mmol), PdO/MWCNT (5 mol%), K<sub>2</sub>CO<sub>3</sub> (1 mmol) and DMSO (1 mL) at 120 °C. <sup>b</sup>Isolated yields of product **7aa-bl**.

These conditions were applied to other systems as well. As anticipated, the protocol was quite successful and furnished the 2-substituted benzofurans **7ah-bl**, in very good to excellent yields (Table 4). Notably, the reaction was compatible with aryl as well as alkyl terminal acetylenes. Significantly, the reaction was tolerable to the aldehyde functionality on the aromatic ring of iodophenol.

## 4. Conclusions

In summary, an efficient PdO/GO nano-catalyst catalyzed Suzuki–Miyaura and Glaser coupling reactions have been demonstrated, for the synthesis of biaryls and 1,3-diynes. Also, domino one-pot synthesis of 2-alkyl/2-aryl benzofurans has been accomplished starting from 2-iodophenols and terminal alkynes, in the presence of PdO/MWCNT nano-catalyst. The formation of benzofurans proceeds through intermolecular Sonogashira reaction followed by intramolecular nucleophilic addition of internal hydroxyl group onto the acetylene bond. Catalyst retains its activity even after 5 cycles.

## Supplementary Information (SI)

<sup>1</sup>H, <sup>13</sup>C NMR spectras of all isolated products, XRD pattern, SEM images of as-synthesized catalysts are given. Supplementary Information is available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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## References

- Lin J, Mei T, Lv M, Zhang C A, Zhao Z and Wang X 2014 Size-controlled PdO/graphene oxides and their reduction products with high catalytic activity *RSC Adv.* **4** 29563
- Wang X, Chen W and Yan L 2014 Three-dimensional reduced graphene oxide architecture embedded palladium nanoparticles as highly active catalyst for the Suzuki–Miyaura coupling reaction *Mater. Chem. Phys.* **148** 103
- Schaetz A, Zeltner M and Stark W J 2012 Carbon modifications and surfaces for catalytic organic transformations *ACS Catal.* **2** 1267
- Nakhate A V and Yadav G D 2016 Palladium nanoparticles supported carbon based graphene oxide monolith as catalyst for sonogashira coupling and hydrogenation of nitrobenzene and alkenes *ChemistrySelect.* **1** 3954
- Li H, Johansson Seechurn C C and Colacot T J 2012 Development of preformed Pd catalysts for cross-coupling reactions, beyond the 2010 Nobel Prize *ACS Catal.* **2** 1147
- Zhou J, Li X and Sun H J 2010 An efficient and recyclable water-soluble cyclopalladated complex for aqueous Suzuki reactions under aerial conditions *Organomet. Chem.* **695** 297
- Reetz M T and de Vries J G 2004 Ligand-free Heck reactions using low Pd-loading *Chem. Commun.* 1559
- Kumbhar A, Kamble S, Mane A, Jha R and Salunkhe R 2013 Modified zeolite immobilized palladium for ligand-free Suzuki–Miyaura cross-coupling reaction *J. Organomet. Chem.* **738** 29

9. Moussa S, Siamaki A R, Gupton B F and El-Shall M S 2012 Pd-Partially reduced graphene oxide catalysts (Pd/PRGO): Laser synthesis of Pd nanoparticles supported on PRGO nanosheets for carbon-carbon cross coupling reactions *ACS Catal.* **2** 145
10. Rao C N R, Sood A K, Subrahmanyam K S and Govindaraj A 2009 Graphene: the new two-dimensional nanomaterial *Angew. Chem. Int. Edit.* **48** 7752
11. Novoselov K S, Jiang Z, Zhang Y, Morozov S V, Stormer H L, Zeitler U, Maan J C, Boebinger G S, Kim P and Geim A K 2007 Room-temperature quantum hall effect in graphene *Science* **315** 1379
12. Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M L, Grigorieva I V, Dubonos S V and Firsov A A 2005 Two-dimensional gas of massless Dirac fermions in grapheme *Nature* **438** 197
13. Duan H, Li M, Zhang G, Gallagher J R, Huang Z, Sun Y and Lei A 2015 Single-site palladium(II) catalyst for oxidative heck reaction: catalytic performance and kinetic investigations *ACS Catal.* **5** 3752
14. Zhou P X, Ye Y Y, Liu C, Zhao L B, Hou J Y, Chen D Q and Xu P F 2015 Palladium-Catalyzed Acylation/Alkenylation of Aryl Iodide: A Domino Approach Based on the Catellani-Lautens Reaction *ACS Catal.* **5** 4927
15. Larhed M and Hallberg A 2001 Microwave-assisted high-speed chemistry: a new technique in drug discovery *Drug Discov. Today* **6** 406
16. Yar M S and Ansari Z H 2009 Synthesis and in vivo diuretic activity of biphenyl benzothiazole-2-carboxamide derivatives *Acta Pol. Pharm.* **66** 387
17. Williams D A and Lemke T L 2002 *Foye's Principles of Medical Chemistry* 15th edn. (Philadelphia: Lippincott Williams & Wilkins) p. 533
18. Narayana B L, Mahendar L, Ghosal P, Satyanarayana G and Subrahmanyam Ch 2017 Nano-sized recyclable PdO supported carbon nanostructures for heck reaction: influence of carbon materials *ChemistrySelect.* **2** 2703
19. Narayana B L, Mukri B D, Ghosal P and Subrahmanyam Ch 2016 Mn Ion substituted CeO<sub>2</sub> nano spheres for low temperature CO oxidation: the promoting effect of Mn ions *ChemistrySelect.* **1** 3150
20. Nicolaou K C, Petasis N A and Zipkin R E 1982 The endiandric acid cascade. Electrocyclizations in organic synthesis. 4. Biomimetic approach to endiandric acids A-G. Total synthesis and thermal studies *J. Am. Chem. Soc.* **104** 5560
21. Zhou L, Zhan H Y and Jiang H F 2007 An efficient and practical process for Pd/Cu cocatalyzed homocoupling reaction of terminal alkynes using sodium percarbonate as a dual reagent in aqueous media *Chin. J. Chem.* **25** 1413
22. Siemsen P, Livingston R C and Diederich F 2000 Acetylenic coupling: a powerful tool in molecular construction *Angew. Chem. Int. Edit.* **39** 2632
23. Zhang L Y and Wang L 2008 Immobilized palladium on organic-inorganic hybrid materials: a novel and reusable catalyst for the copper-free sonogashira coupling reaction *Chin. J. Chem.* **26** 1601
24. Tour J M 1996 Conjugated macromolecules of precise length and constitution. Organic synthesis for the construction of nanoarchitectures *Chem. Rev.* **96** 537
25. Yin L and Liebscher 2007 Carbon-carbon coupling reactions catalyzed by heterogeneous palladium catalysts *J. Chem. Rev.* **107** 133
26. Glaser C 1869 Beiträge zur Kenntniss des Acetenylbenzols *Ber. Dtsch. Chem. Ges.* **2** 422
27. Glaser C 1870 Untersuchungen über einige Derivate der Zimmtsäure *Ann. Chem. Pharm.* **154** 137
28. Eglinton G and Galbraith R 1959 Macrocyclic acetylenic compounds. Part I. Cyclotetradeca-1 :3-diyne and related compounds *J. Chem. Soc.* **0** 889
29. Hay A S 1960 Communications-oxidative coupling of acetylenes *J. Org. Chem.* **25** 1275
30. Hay A S 1962 Oxidative coupling of acetylenes *J. Org. Chem.* **27** 3320
31. Merkul E, Urselmann D and Muller T 2011 Consecutive one-pot Sonogashira-Glaser coupling sequence - direct preparation of symmetrical diynes by sequential Pd/Cu catalysis *Eur. J. Org. Chem.* **2** 238
32. Lei A, Srivastava M and Zhang X 2002 Transmetalation of palladium enolate and its application in palladium-catalyzed homocoupling of alkynes: a room-temperature, highly efficient route to make diynes *J. Org. Chem.* **67** 1969
33. Li J H, Liang Y and Xie Y X 2005 Efficient palladium-catalyzed homocoupling reaction and Sonogashira cross-coupling reaction of terminal alkynes under aerobic conditions *J. Org. Chem.* **70** 4393
34. Guo M, Chen B, Lv M, Zhou X, Wen Y and Shen X 2016 The homocoupling reaction of aromatic terminal alkynes by a highly active palladium(II)/AgNO<sub>3</sub> cocatalyst in aqueous media under aerobic conditions *Molecules* **21** 606
35. Rossi R, Carpita A and Bigelli C 1985 A palladium-promoted route to 3-alkyl-4-(1-alkynyl)-hexa-1,5-dyn-3-enes and/or 1,3-diynes *Tetrahedron Lett.* **26** 523
36. Yin W, He C, Chen M, Zhang H and Lei A 2009 Nickel-catalyzed oxidative coupling reactions of two different terminal alkynes using O<sub>2</sub> as the oxidant at room temperature: facile syntheses of unsymmetric 1,3-diynes *Org. Lett.* **11** 709
37. Leyva-Perez A, Domenech A, Al-Resayes S I and Corma A 2012 Gold redox catalytic cycles for the oxidative coupling of alkynes *ACS Catal.* **2** 121
38. Zhu M, Ning M, Fu J W, Xu C and Zou G L 2012 Gold-catalyzed homocoupling reaction of terminal alkynes to 1,3-diynes *Bull. Korean Chem. Soc.* **33** 1325
39. Kuram M R, Bhanuchandra M and Sahoo A K 2013 Direct access to benzo[b]furans through palladium-catalyzed oxidative annulation of phenols and unactivated internal alkynes *Angew. Chem. Int. Edit.* **52** 4607
40. Castro C E, Gaughan E J and Owsley D C 1966 Indoles, benzofurans, phthalides, and tolanes via copper(I) acetylides *J. Org. Chem.* **31** 4071
41. Arcadi A, Marinelli F and Cacchi S 1986 Palladium-catalyzed reaction of 2-hydroxyaryl and hydroxyheteroaryl halides with 1-alkynes: an improved route to the benzo [b] furan ring system *Synthesis* **9** 749

42. Larock R C, Yum E K, Doty M J and Sham K K C 1995 Synthesis of aromatic heterocycles via palladium-catalyzed annulation of internal alkynes *J. Org. Chem.* **60** 3270
43. Sanz R, Castroviejo M P, Fernandez Y and Fananas F J 2005 A new and efficient synthesis of 4-functionalized benzo[b]furans from 2,3-dihalophenols *J. Org. Chem.* **70** 6548
44. Gill G S, Grobelny D W, Chaplin J H and Flynn B L 2008 An efficient synthesis and substitution of 3-aryl-2-bromobenzo[b]furans *J. Org. Chem.* **73** 1131
45. Akai N, Uchida N and Konakahara T 2008 Facile and efficient synthesis of polyfunctionalized benzofurans: three-component coupling reactions from an alkynylsilane, an o-hydroxybenzaldehyde derivative, and a secondary amine by a Cu(I)–Cu(II) cooperative catalytic system *Tetrahedron Lett.* **49** 3437
46. Wang J R and Manabe K 2010 Hydroxyterphenylphosphine-palladium catalyst for benzo[b]furan synthesis from 2-chlorophenols. Bifunctional ligand strategy for cross-coupling of chloroarenes. *J. Org. Chem.* **75** 5340
47. Wang R, Mo S, Lu Y and Shen Z 2011 Domino Sonogashira coupling/cyclization reaction catalyzed by copper and ppb levels of palladium: a concise route to indoles and benzo[b]furans *Adv. Synth. Catal.* **353** 713
48. Zhou Z, Liu G, Shen Y and Lu X 2014 Synthesis of benzofurans via ruthenium-catalyzed redox-neutral C–H functionalization and reaction with alkynes under mild conditions *Org. Chem. Front.* **1** 1161
49. Yeh C H, Chen W C, Gandeepan P, Hong Y C, Shih C H and Cheng C H 2014 Rh(III)-catalyzed dual directing group assisted sterically hindered C–H bond activation: a unique route to meta and ortho substituted benzofurans *Org. Biomol. Chem.* **12** 9105
50. Lee D H, Kwon K H and Yi C S, 2012 Dehydrative C–H alkylation and alkenylation of phenols with alcohols: expedient synthesis for substituted phenols and benzofurans *J. Am. Chem. Soc.* **134** 7325
51. Thirunavukkarasu V S, Donati M and Ackermann L 2012 Hydroxyl-directed ruthenium-catalyzed C–H bond functionalization: versatile access to fluorescent pyrans *Org. Lett.* **14** 3416
52. Mochida S, Shimizu M, Hirano K, Satoh T and Miura M 2010 Synthesis of naphtho[1,8-bc]pyran derivatives and related compounds through hydroxy group directed C–H bond cleavage under rhodium catalysis *Chem. Asian J.* **5** 847
53. Tsuchikama K, Hashimoto Y K, Endo K and Shibata T 2009 Iridium-catalyzed selective synthesis of 4-substituted benzofurans and indoles via directed cyclodehydration *Adv. Synth. Catal.* **351** 2850
54. Liao J, Guo P and Chen Q 2016 Au-catalyzed synthesis of benzofurans from phenols and alkynes using molecular oxygen *Catal. Commun.* **77** 22
55. Bonnamour J, Piedrafita M and Bolm C 2010 Iron and copper salts in the synthesis of benzo[b]furans *Adv. Synth. Catal.* **352** 1577
56. Zhu R, Wei J and Shi Z 2013 Benzofuran synthesis via copper-mediated oxidative annulation of phenols and unactivated internal alkynes *Chem. Sci.* **4** 3706
57. Zeng W, Wu W, Jiang H, Huang L, Sun Y, Chen Z and Li X 2013 Facile synthesis of benzofurans via copper-catalyzed aerobic oxidative cyclization of phenols and alkynes *Chem. Commun.* **49** 6611