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REGULAR ARTICLE

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.[1–4] Palladium is one of the most widely used metals for organic transformations. However, unsupported [Pd]-nanoparticles agglomerate or sinter upon heating.[5–8] 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.[9–13]

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.[14–17] Recently, we have reported the syntheses and characterization of PdO nanoparticles impregnated on various nano-carbon supports (SWCNT, MWCNT, CNF, GO and RGO).[18,19] 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, π-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}H NMR spectra were recorded on 400 MHz spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) ($\delta_H = 0.00$ppm) or $CHCl_3$ ($\delta_H = 7.25$ ppm). ^{13}C NMR spectra were recorded on 100 MHz spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [$\delta_C = 77.00$ppm(central line of triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH_2, and 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 CH_2) and q = quartet (for CH_3). In the ^{1}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}H, ^{13}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 K_2CO_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), arylboroic acids **2** (0.5 mmol), PdO/GO nano catalyst (5 mol%), K_2CO_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 NH_4Cl solution (approximately 10 mL) was added followed by extraction with ethyl acetate. The organic layers were dried with Na_2SO_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.

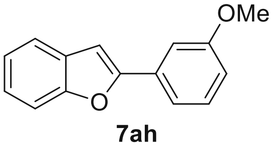
2.3 *General procedure 2 (for the synthesis of symmetrical 1,3-diynes 5)*

In an oven-dried Schlenk tube terminal alkynes **4** (0.5 mmol), Pd/GO nano catalyst (5 mol%), K_2CO_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 NH_4Cl solution (∼ 10 mL) was added fallowed by extraction with ethyl acetate. The organic layers were dried with Na_2SO_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)*

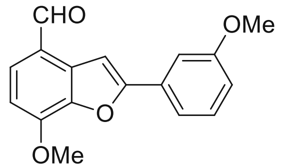
In an oven-dried Schlenk tube 2-iodophenol **6** (0.5 mmol), terminal alkyne **4** (0.5 mmol), PdO/MWCNT (5 mol%), K_2CO_3 (1 mmol) and solvent (DMSO) (1.0 mL) were added. The resulting reaction mixture was stirred at 120 °C for 24 h. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was allowed to cool to room temperature, then diluted with (10 mL) ethyl acetate and NH_4Cl (10 mL) was added fallowed by extraction with ethyl acetate. The organic layers were dried (Na_2SO_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*



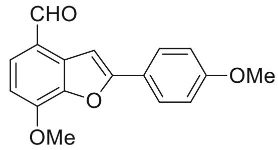
7ah

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(**4 h**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 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}C NMR ($CDCl_3$, 100 MHz): $\delta = 159.9$ (C_q), 155.7 (C_q), 154.8 (C_q), 131.7 (C_q), 129.8 (CH), 129.1 (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 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2921, 2851, 1482, 1460, 1380, 1123, 1109, 1011, 928 cm^{-1}. HR-MS (ESI$^+$) m/z calculated for $[C_{15}H_{12}O_2]^+ = [M]^+$: 224.0832; found: 224.0840.



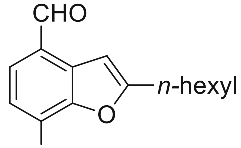
7bh

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(**6b**) = 0.50, R_f(**4 h**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 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. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.8 (C_q), 159.9 (C_q), 158.8 (C_q), 149.8 (C_q), 144.0 (C_q), 132.1 (CH), 130.9 (C_q), 129.9 (CH), 129.8 (C_q), 122.9 (C_q), 118.0 (CH), 115.5 (CH), 110.3 (CH), 106.1 (CH), 102.2 (CH), 56.4 (CH_3), 55.4 (CH_3) ppm. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2922, 2850, 1478, 1380, 1201, 1165, 1011, 920 cm^{-1}. HR-MS (ESI$^+$) m/z calculated for $[C_{17}H_{14}NaO_4]^+ = [M + Na]^+$: 305.0784; found: 305.0794.



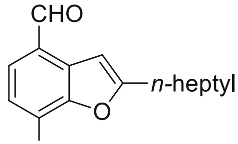
7bc

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(**6b**) = 0.40, R_f(**4 h**) = 0.50, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 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. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.8 (C_q), 160.6 (C_q), 159.3 (C_q), 149.6 (C_q), 143.8 (C_q), 131.8 (CH), 130.4 (C_q), 127.0 (CH), 122.7 (C_q), 122.5 (C_q), 114.3 (CH), 105.8 (CH), 100.4 (CH), 56.4 (CH_3), 55.4 (CH_3) ppm.IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2921, 2850, 1563, 1480, 1465, 1381, 1121, 1103, 1012, 928 cm^{-1}. HR-MS (ESI$^+$) m/z calculated for $[C_{17}H_{14}NaO_4]^+ = [M + Na]^+$: 305.0784; found: 305.0788.



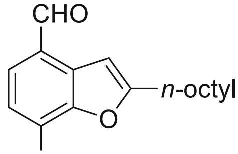
7bi

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(**6b**) = 0.50, R_f(**4i**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 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. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.8 (C_q), 163.4 (C_q), 149.4 (C_q), 143.6 (C_q), 131.3 (CH), 129.8 (C_q), 122.6 (C_q), 105.0 (CH), 102.6 (CH), 56.3 (CH_3), 31.5 (CH_2), 28.9 (CH_2), 28.5 (CH_2), 27.6 (CH_2), 22.5 (CH_2), 14.0 (CH_3) ppm. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2930, 2843, 1560, 1481, 1456, 1375, 1187, 1160, 1009, 929 cm^{-1}. HR-MS (ESI$^+$) m/z calculated for $[C_{16}H_{20}NaO_3]^+ = [M+Na]^+$: 283.1305; found: 283.1308.



7bj

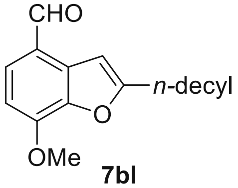
This compound was prepared according to the GP and isolated as brown color viscous liquid 86% yield (118 mg): [TLC (petroleum ether/ethyl acetate 9:1, R_f(**6b**) = 0.40, R_f(**4j**) = 0.70, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.02 (s, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.15 (s, 1H), 6.84 (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. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.8 (C_q), 163.4 (C_q), 149.4 (C_q), 143.7 (C_q), 131.3 (CH), 129.9 (C_q), 122.6 (C_q), 105.0 (CH), 102.6 (CH), 56.3 (CH_3), 31.7 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.5 (CH_2), 27.6 (CH_2),22.6 (CH_2), 14.0 (CH_3) ppm. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2927, 2850, 1560, 1480, 1471, 1380, 1190, 1165, 1010, 926 cm^{-1}. HR-MS (ESI$^+$) m/z calculated for $[C_{17}H_{22}NaO_3]^+ = [M + Na]^+$: 297.1461; found: 297.1465.



7bk

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(**6b**) = 0.50, R_f(**4 k**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 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. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.8 (C_q), 163.4 (C_q), 149.4 (C_q), 143.7 (C_q), 131.3 (CH), 129.9 (C_q), 122.6 (C_q), 105.1 (CH), 102.6 (CH), 56.3

(CH_3), 31.8 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.5 (CH_2), 27.6 (CH_2), 22.6 (CH_2), 14.1 (CH_3) ppm. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2920, 2865, 1560, 1484, 1463, 1380, 1132, 1009, 926 cm^{-1}. HR-MS (ESI$^+$) m/z calculated for $[C_{18}H_{25}O_3]^+$ = $[M + H]^+$: 289.1798; found: 289.1801.



7bl

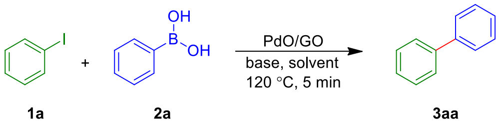
This compound was prepared according to the GP and isolated as pale yellow color liquid 90% yield (142 mg). [TLC (petroleum ether/ethyl acetate 8:2, R_f(**6b**) = 0.50, R_f(**4 l**) = 0.60, UV detection]. ^1H NMR ($CDCl_3$, 400 MHz): δ = 10.01 (s, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.14 (s, 1H), 6.83 (d, 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. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.8 (C_q), 163.4 (C_q), 149.4 (C_q), 143.7 (C_q), 131.3 (CH), 129.9 (C_q), 122.6 (C_q), 105.1 (CH), 102.6 (CH), 56.3 (CH_3), 31.9 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (2C, CH_2), 29.2 (CH_2), 28.5 (CH_2), 27.6 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2921, 2851, 1530, 1483, 1460, 1321, 1180, 1163, 1107, 1009, 920 cm^{-1}. HR-MS (ESI$^+$) m/z calculated for $[C_{20}H_{28}NaO_3]^+$ = $[M + Na]^+$: 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).[18] Thus, the reaction was explored between iodobenzene **1a** and phenylboronic acid **2a** in the presence PdO/GO of K_2CO_3 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_2CO_3 and K_3PO_4, 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 biphenyl **3aa**.[a]



Entry	Base	Solvent	Yield **3aa**(%)[b]
1	K_2CO_3	DMSO	90
2	K_2CO_3	DMF	78
3	K_2CO_3	DMA	55
4	K_2CO_3	toluene	43
5	K_2CO_3	1,4-dioxane	70
6	K_2CO_3	THF	64
7	K_2CO_3	acetonitrile	50
8	Na_2CO_3	DMSO	72
9	K_3PO_4	DMSO	65

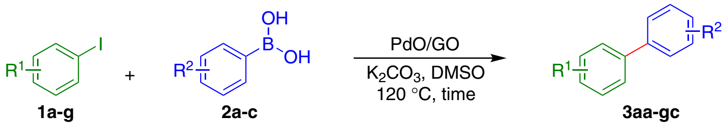
[a] Reaction Conditions: aryl iodides **1a** (0.25 mmol), aryl boronic acid **2a** (0.5 mmol), PdO/GO (5 mol%), K_2CO_3 (0.5 mmol) and DMSO (1 mL) at 120 °C. [b] Isolated yields of product **3aa**.

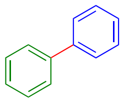
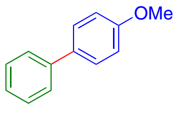
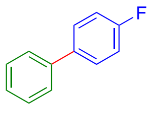
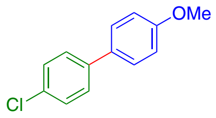
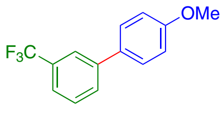
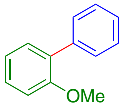
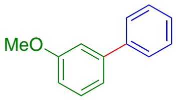
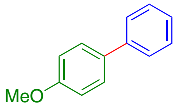
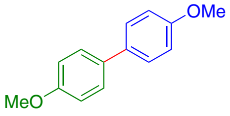
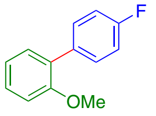
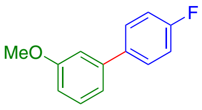
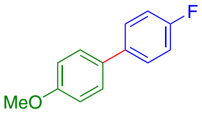
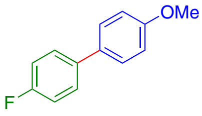
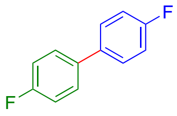
Gratifyingly, the reaction was found to be amenable and afforded the corresponding biaryls **3aa-gc**, in very good to excellent yields (Table 2). Interestingly, the reaction was successful with simple iodobenzene **1a** and also with different functional (CF_3, F, Me and OMe) groups on aromatic ring **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,[18] 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 π-conjugated

Table 2. Synthesis of biphenyls **3aa-gc** with aryl iodides **1a-g** and arylboronic acids **2a-c**.[a,b]



 **3aa** (5 min, 90%)	 **3ab** (5 min, 90%)	 **3ac** (5 min, 90%)	 **3ba** (10 min, 85%)	 **3cb** (5 min, 91%)
 **3da** (10 min, 91%)	 **3ea** (60 min, 90%)	 **3fa** (10 min, 88%)	 **3fb** (10 min, 94%)	 **3dc** (10 min, 86%)
 **3ec** (30 min, 81%)	 **3fc** (5 min, 94%)	 **3gb** (10 min, 80%)	 **3gc** (5 min, 85%)	

[a]Reaction Conditions: iodobenzene **1a-g** (0.25 mmol), arylboronic acid **2a-c** (0.5 mmol), PdO/GO (5 mol%), K_2CO_3 (0.5 mmol) and DMSO (1 mL) at 120 °C. [b]Isolated yields of product **3aa-gc**.

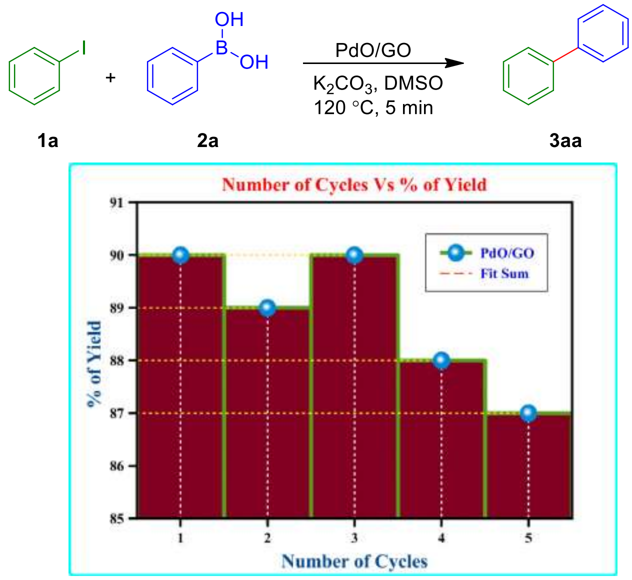


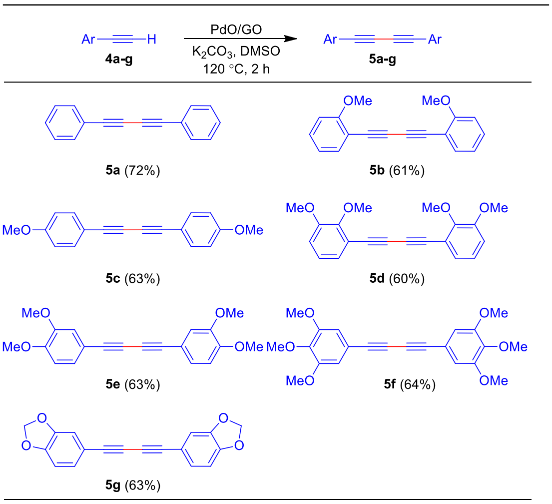
Figure 1. Recyclability of the catalyst in Suzuki reaction.

polymeric materials, supramolecular structures, natural products and pharmaceuticals.[20–25]

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.[26,27] Subsequently, Eglinton[28] and Hay[29,30] 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,[32,33] Pd-Ag,[34] Pd,[25,35] Ni,[36] Au,[37,38] 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).

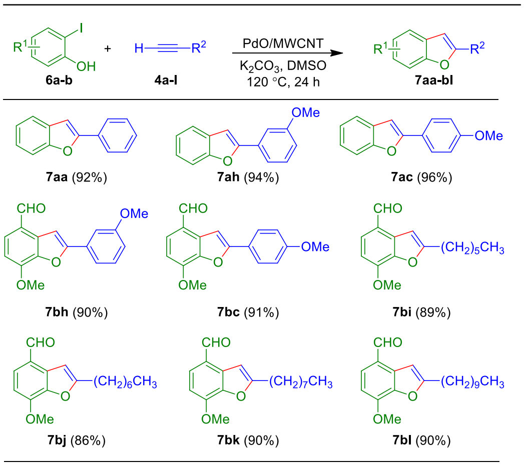
To further demonstrate the applicability of PdO/GO catalyst, one-pot synthesis of benzofurans was tested. Benzofurans are ubiquitous oxygen-containing heterocyclic motifs that constitute many natural products, pharmaceuticals, biologically important compounds and organic materials. In this context, many synthetic strategies have been established for their synthesis. Notably, transition metal-catalyzed (Pd,[39–47] Rh,[48] Ru,[48–52] Ir,[53] Au[54] and Cu[55–57]) 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**.[a,b]



[a] Reaction Conditions: aryl alkynes **4a-g** (0.5 mmol), PdO/GO (5 mol%), K_2CO_3 (0.10 mmol) and DMSO (1 mL) at 120 °C. [b] Isolated yields of product **5a-g**.

Table 4. Synthesis of benzofurans **7aa-bl** from 2-iodophenols **6a-b** and aryl alkynes **4a-l**.[a,b]



[a] Reaction Conditions: Iodophenol **6a-b** (0.5 mmol), arylalkyne **4a-i** (0.5 mmol), PdO/MWCNT (5 mol%), K_2CO_3 (1 mmol) and DMSO (1 mL) at 120 °C. [b] 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)

^{1}H, ^{13}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.

Acknowledgements

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