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Synthesis of benzofurans from terminal alkynes and iodophenols catalyzed by recyclable palladium nanoparticles supported on *N*,*O*-dual doped hierarchical porous carbon under copper- and ligand-free conditions

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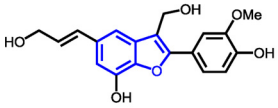
ABSTRACT

We herein report that a stable and recyclable heterogeneous catalyst, consisting of Pd nanoparticles supported on *N*,*O*-dual doped hierarchical porous carbon derived from naturally available and renewable biomass-bamboo shoots, which allows for highly efficient one-pot tandem reaction of *o*-iodophenols with terminal alkynes to synthesize biologically active 2-benzofuran derivatives under copper- and ligand-free conditions. The catalyst performed superior catalytic performance compared with the analogous Pd/C and supported on other metal oxides under otherwise identical conditions. A broad set of aryl and alkyl terminal alkynes can be effectively coupled /cyclized with various *o*-iodophenols to afford their corresponding 2-benzofurans in good to high yields with good tolerance of multiple functional groups. Moreover, the catalyst showed good stability and could be reused several times without significant loss of activity.

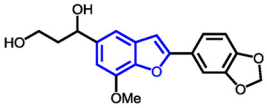
1. Introduction

Benzofuran derivatives, which structurally exist in numerous natural products and synthetic bioactive compounds, have attracted much attention in the chemical and pharmaceutical industries [1,2]. Particularly, 2-arylbenzofurans with wide distribution in nature possessing a number of biological activities and currently present in regularly prescription or potential drugs. For instance, Vibsanol [3] is used as an inhibitor for lipid peroxidation, Machicendiol [4] is used for treatment of cancer, cardiovascular disease, migraines, dementia and anxiety, and Benzbromarone [5] is a nonpurine xanthine oxidase inhibitor used for the treatment of gout.

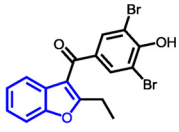
Given their immense pharmaceutical utility, the synthesis of benzofurans has been extensively explored and numerous conventional methods have been developed over the past few decades. Among all methods investigated, one-pot tandem transition-metal-catalyzed intermolecular Sonogashira cross-coupling followed by cyclization of *o*-halogenated phenols with terminal alkynes represents one of the most powerful and appealing methods owing to its convenience and environmental benefits. In this regard, a number of metal-based catalysts including Cu [6–12], Pd [13–23], Zn [24,25], and Au [26] have been employed for the transformation since the seminal work developed by Castro et al. [6] To date, the majority of those previous tandem reac-



Vibsanol



Machicendiol



Benzbromarone

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tions were prevailingly operated by soluble homogenous metal complexes, which is a particularly significant drawback for their application in pharmaceutical industry because they are expensive, cannot be recycled, and are difficult to separate from the product mixture. On the other hand, the current demand for green and sustainable transformation of organic molecules enhances the importance of heterogeneous catalysts that can facilitate the recycling of precious metals and help to prevent contamination of the products by toxic metals. Actually, there are a few heterogeneous metal-based catalysts that have been exploited for the transformation. For example, Ramon and co-workers [19] reported an impregnated Cu or Pd-Cu on magnetite catalyst for synthesis of benzofurans. Later on, a Pd catalyst supported on nanosize carbon balls was shown to be efficient catalyst for benzofurans formation by Park and co-workers [20]. Very recently, Bäckvall and co-workers [21] developed a recyclable Pd nanoparticles immobilized on siliceous mesocellular foam for efficient synthesis of benzofurans. An in-situ generation of Pd nanoparticles in porous covalent organic framework was also fabricated and showed good activity for this reaction by Banerjee and co-workers [22]. Despite such great progress, in most cases, both homogeneous and heterogeneous catalysts generally suffer from one or more drawbacks such as the use of toxic and expensive ligands, requirement of the second co-catalyst like Cu salts, limited substrate scope, and poor chemoselectivity. Therefore, it is highly desirable to develop a new heterogeneous catalytic system that is capable of performing such transformation via tandem processes under copper and ligand-free conditions.

In the course of our continuing efforts in developing green catalysis for sustainable synthesis, we have developed a highly efficient and recyclable supported Pd nanoparticles (NPs) on *N,O*-dual doped hierarchical porous carbon (Pd/*N,O*-Carbon) derived from naturally renewable biomass for chemoselective semihydrogenation and hydrosilylation of a wide range of alkynes to versatile and valuable compounds[27,28]. Intrigued by the catalytic utility of the Pd/*N,O*-Carbon, we became more interesting in the development of innovative catalytic processes that enable one-pot tandem reaction of *o*-iodophenols with terminal alkynes. Herein, we report the application of such catalyst Pd/*N,O*-Carbon for the successful tandem Sonogashira/cyclization reaction of *o*-iodophenols with terminal alkynes to construct 2-benzofuran derivatives under ligand- and copper-free conditions. The present catalytic system shows high efficiency and broad substrate scope of both *o*-iodophenols and terminal alkynes with good tolerance of functional group and can be easily recycled for successive uses without significant loss in activity and selectivity.

2. Materials and methods

2.1. Materials

Unless otherwise noted, all reagents were purchased commercially from Sigma-Aldrich, or Aladdin and used as received without further purification. The fresh bamboo shoots were obtained from Anhui Taiping Test Centre, International Centre for Bamboo and Rattan, Anhui Province, China. The commercially available activated carbon was purchased from Fujian Xinsen Carbon Coop., Shaowu, Fujian. All operations were carried out in an argon atmosphere using glovebox and Schlenk techniques unless otherwise specified. Anhydrous tetrahydrofuran (THF), hexanes and toluene were obtained from an argon purged solvent purification system comprised of columns of activated alumina and molecular sieves. Anhydrous *N,N'*-dimethylformamide (DMF), acetonitrile (CH_3CN), dimethyl sulfoxide (DMSO) and 1,4-dioxane were purchased from Aladdin and used without further purification.

2.2. Catalyst preparation

2.2.1. Preparation of hierarchical porous carbon (N,O-carbon)

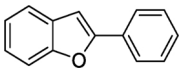
The porous heteroatom doped carbon materials were prepared in two-steps including hydrothermal treatment and carbonization process. The fresh bamboo shoots were obtained from Anhui Taiping Test Centre, International Centre for Bamboo and Rattan, Anhui Province, China. The Bamboo shoots were firstly cut into slices and dried at 70 °C for 24 h. The dried bamboo shoots (2 g) were then ground into powders and transferred in a 100 mL Teflon-inner stainless-steel autoclave coupled with 20 ml of deionized water. The autoclave was then heated to 180 °C and maintained for 6 h. The resulting brown solids were filtered, washed by distilled water thoroughly to remove any residual of soluble metal ions such as Ca^{2+} or K^+ (detected by ion chromatography), dried at room temperature under vacuum for 24 h. After that, the hydrochars were calcined at 850 °C for 4 h in N_2 flow with a heating rate of 5 °C min^{-1}. The black powder heteroatom doped porous carbons were obtained and denoted as *N,O*-Carbon.

2.2.2. Preparation of Pd nanoparticles supported on N,O-carbon

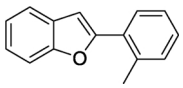
The porous heteroatom doped carbon supported Pd materials with metal loading of 2.0 wt % were prepared by ultrasound-assisted reduction method. 0.15 g of *N,O*-Carbon was dispersed in 100 mL deionized water under ultrasonic condition for 30 min. Then 3 g of 0.268 wt % of $Pd(NO_3)_2$ aqueous solution was added dropwise into the mixture and stirred vigorously for 1 h. After that, the pH value of solution was adjusted to 11 using ammonia solution. The resulting solution was put into 80 °C oil bath with subsequent addition of 0.2 mL of hydrazine solution (85%), which was further stirred vigorously for another 4 h. Finally, the product was filtered and washed with deionized water and dried at 105 °C under vacuum for 12 h. The as-prepared sample was denoted as Pd/*N,O*-Carbon and the Pd loading was determined by ICP-AES to be 1.64 wt%. For comparison, Pd NPs supported on commercial activated carbon (commercially available from Fujian Xinsen Carbon Coop., with surface area of 1580 $m^2 g^{-1}$) and other supports were prepared with the same procedure.

2.3. Typical procedure for one-pot tandem reaction between o-iodophenols and terminal alkynes

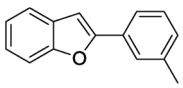
General produce: *o*-iodophenol (0.5 mmol), alkyne (1.0 mmol) and base (1.0 mmol) were added into a 10 mL dry Schlenk tube under Ar, then anhydrous DMF (5 mL) was injected into the mixture using syringe. Then the solution stirred at preheated oil bath (160 °C). The reaction was monitored by TLC and GC.The mixture was cooled down to room temperature after full conversion, then diluted with dichloromethane and washed with water three times. The organic layer was separated and washed with brine followed by drying with anhydrous Na_2SO_4. The filtrate was concentrated in vacuo to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether).



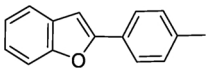
2-Phenylbenzofuran (3a): The title compound was prepared according to the general procedure. The product was obtained as white solid (92%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.2 Hz, 1 H), 7.59 (d, J = 7.3 Hz, 1 H), 7.54 (d, J = 7.8 Hz, 1 H), 7.46 (t, J = 7.6 Hz, 1 H), 7.36 (t, J = 7.4 Hz, 1 H), 7.32–7.21 (m, 1 H), 7.03 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.90, 154.87, 130.46, 129.20, 128.76, 128.52, 124.91, 124.24, 122.91, 120.88, 111.15, 101.28. These spectroscopic data matched that previously reported [29].



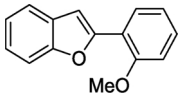
2-(*o*-Tolyl)benzofuran (3b): The title compound was prepared according to the general procedure. The product was obtained as white solid (81%) by using petroleum ether/DCM (4 : 1) as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.81 (m, 1 H), 7.61 (dd, J = 7.5, 0.8 Hz, 1 H), 7.55–7.50 (m, 1 H), 7.33–7.27 (m, 4 H), 7.24 (td, J = 7.3, 1.1 Hz, 1 H), 6.89 (d, J = 0.7 Hz, 1 H), 2.58 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.64, 154.37, 135.81, 131.24, 129.92, 129.17, 128.49, 128.14, 126.08, 124.20, 122.76, 120.89, 111.08, 105.08, 21.91. These spectroscopic data matched that previously reported [2].



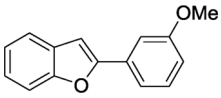
2-(*m*-Tolyl)benzofuran (3c): The title compound was prepared according to the general procedure. The product was obtained as white solid (87%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1 H), 7.58 (d, J = 7.8 Hz, 1 H), 7.51–7.46 (m, 1 H), 7.43 (d, J = 8.2 Hz, 1 H), 7.24 (t, J = 7.7 Hz, 1 H), 7.19 (td, J = 7.8, 1.4 Hz, 1 H), 7.16–7.11 (m, 1 H), 7.08 (d, J = 7.6 Hz, 1 H), 6.91 (s, 1 H), 2.34 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.09, 154.83, 138.42, 130.36, 129.36, 129.24, 128.67, 125.51, 124.14, 122.87, 122.12, 120.83, 111.11, 101.16, 21.48. These spectroscopic data matched that previously reported [2].



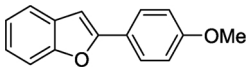
2-(*p*-Tolyl)benzofuran (3d): The title compound was prepared according to the general procedure. The product was obtained as white solid (90%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 1 H), 7.57 (d, J = 7.3 Hz, 1 H), 7.52 (d, J = 7.5 Hz, 1 H), 7.30–7.19 (m, 2 H), 6.97 (s, 1 H), 2.41 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.18, 154.76, 138.58, 129.47, 129.33, 127.74, 124.88, 123.97, 122.83, 120.72, 111.07, 100.54, 21.38. These spectroscopic data matched that previously reported [2].



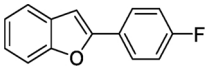
2-(2-Methoxyphenyl)benzofuran (3e): The title compound was prepared according to the general procedure. The product was obtained as white solid (87%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–8.05 (m, 1 H), 7.60 (d, J = 7.5 Hz, 1 H), 7.52 (d, J = 8.1 Hz, 1 H), 7.39–7.18 (m, 4 H), 7.09 (dd, J = 10.9, 4.2 Hz, 1 H), 7.02 (d, J = 8.3 Hz, 1 H), 4.01 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.48, 153.86, 152.14, 129.77, 129.22, 127.05, 124.08, 122.61, 121.01, 120.77, 119.36, 111.01, 110.81, 106.29, 55.45. These spectroscopic data matched that previously reported [2].



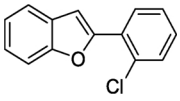
2-(3-Methoxyphenyl)benzofuran (3f): The title compound was prepared according to the general procedure. The product was obtained as colorless oil (91%) by using petroleum ether/DCM (2/1) as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.57 (m, 1 H), 7.56 – 7.51 (m, 1 H), 7.48–7.45 (m, 1 H), 7.44 – 7.41 (m, 1 H), 7.36 (t, J = 7.9 Hz, 1 H), 7.29 (td, J = 7.7 Hz, J = 1.3 Hz, 1 H), 7.24 (td, J = 7.5, 1.1 Hz, 1 H), 7.03 (d, J = 0.7 Hz, 1 H), 6.91 (ddd, J = 8.2, 2.6, 0.8 Hz, 1 H), 3.90 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.96, 155.76, 154.87, 131.79, 129.87, 129.18, 124.35, 122.97, 120.95, 117.55, 114.50, 111.20, 110.16, 101.65, 55.40. These spectroscopic data matched that previously reported [2].



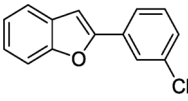
2-(4-Methoxyphenyl)benzofuran (3g): The title compound was prepared according to the general procedure. The product was obtained as white solid (90%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.8 Hz, 1 H), 7.55 (d, J = 6.6 Hz, 1 H), 7.50 (d, J = 8.0 Hz, 1 H), 7.30–7.17 (m, 1 H), 6.98 (d, J = 8.8 Hz, 1 H), 6.88 (s, 1 H), 3.86 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.97, 156.04, 154.69, 129.48, 126.41, 123.72, 123.34, 122.81, 120.55, 114.24, 110.97, 99.66, 55.36. These spectroscopic data matched that previously reported [2].



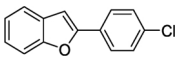
2-(4-Fluorophenyl)benzofuran (3h): The title compound was prepared according to the general procedure. The product was obtained as white solid (90%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.81 (m, 1 H), 7.60–7.56 (m, 1 H), 7.53–7.49 (m, 1 H), 7.31–7.26 (m, 1 H), 7.26–7.21 (m, 1 H), 7.18–7.11 (m, 1 H), 6.96 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.88 (d, J = 248.8 Hz), 155.01, 154.84, 129.17, 126.80, 126.76 (d, J = 8.1 Hz), 124.28, 123.01, 120.88, 115.88 (d, J = 22.0 Hz), 111.13, 100.99 (d, J = 1.4 Hz). These spectroscopic data matched that previously reported [30].



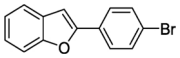
2-(2-Chlorophenyl)benzofuran (3i): The title compound was prepared according to the general procedure. The product was obtained as colorless oil (77%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 7.9, 1.7 Hz, 1 H), 7.65 (d, J = 7.6 Hz, 1 H), 7.56–7.49 (m, 3 H), 7.41–7.23 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.17, 151.95, 131.34, 130.91, 129.08 (2 C), 128.99 (2 C), 126.99, 124.92, 123.00, 121.50, 111.09, 107.39. These spectroscopic data matched that previously reported [4].



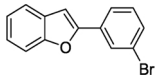
2-(3-Chlorophenyl)benzofuran (3j): The title compound was prepared according to the general procedure. The product was obtained as white solid (84%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (t, J = 1.7 Hz, 1 H), 7.71 (dt, J = 7.6, 1.4 Hz, 1 H), 7.61–7.56 (m, 1 H), 7.51 (dd, J = 8.2, 0.7 Hz, 1 H), 7.35 (t, J = 7.8 Hz, 1 H), 7.33 – 7.27 (m, 2 H), 7.26–7.20 (m, 1 H), 7.02 (d, J = 0.8 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.93, 154.31, 134.84, 132.16, 130.03, 128.90, 128.40, 124.88, 124.75, 123.12, 122.92, 121.12, 111.24, 102.36. These spectroscopic data matched that previously reported [4].



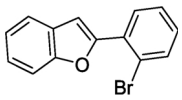
2-(4-Chlorophenyl)benzofuran (3k): The title compound was prepared according to the general procedure. The product was obtained as white solid (87%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.70 (m, 2 H), 7.51 (dd, J = 4.4, 3.9 Hz, 1 H), 7.44 (d, J = 8.1 Hz, 1 H), 7.37–7.32 (m, 2 H), 7.25–7.20 (m, 1 H), 7.18–7.14 (m, 1 H), 6.94 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.89, 154.77, 134.30, 129.05, 129.03, 128.98, 126.12, 124.55, 123.09, 120.99, 111.19, 101.74. These spectroscopic data matched that previously reported [23].



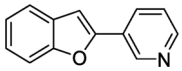
2-(4-Bromophenyl)benzofuran (3l): The title compound was prepared according to the general procedure. The product was obtained as white solid (87%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 1 H), 7.61–7.55 (m, 2 H), 7.52 (d, J = 8.0 Hz, 1 H), 7.33–7.28 (m, 1 H), 7.25–7.21 (m, 1 H), 7.03 (d, J = 0.7 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.89, 154.77, 131.96, 129.39, 129.03, 126.36, 124.60, 123.10, 122.49, 121.01, 111.20, 101.84. These spectroscopic data matched that previously reported [31].



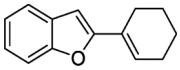
2-(3-Bromophenyl)benzofuran (3m): The title compound was prepared according to the general procedure. The product was obtained as white solid (83%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (t, J = 1.7 Hz, 1 H), 7.67 (d, J = 7.8 Hz, 1 H), 7.49 (d, J = 7.7 Hz, 1 H), 7.43 (d, J = 8.2 Hz, 1 H), 7.37 (dd, J = 7.9, 0.8 Hz, 1 H), 7.24–7.18 (m, 2 H), 7.15 (t, J = 7.4 Hz, 1 H), 6.93 (s, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.92, 154.13, 132.39, 131.30, 130.27, 128.87, 127.76, 124.75, 123.35, 123.11, 122.94, 121.11, 111.24, 102.38. These spectroscopic data matched that previously reported [31].



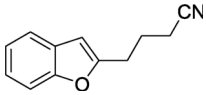
2-(2-Bromophenyl)benzofuran (3n): The title compound was prepared according to the general procedure. The product was obtained as colorless oil (65%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 7.9, 1.7 Hz, 1 H), 7.63 (dd, J = 8.0, 1.2 Hz, 1 H), 7.59 – 7.53 (m, 1 H), 7.48 – 7.43 (m, 2 H), 7.35 (dt, J = 7.9, 2.6 Hz, 1 H), 7.28 – 7.22 (m, 1 H), 7.21 – 7.09 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.29, 153.12, 134.26, 131.02, 129.81, 129.40, 128.80, 127.48, 124.84, 122.97, 121.45, 120.76, 111.11, 107.02. These spectroscopic data matched that previously reported [31].



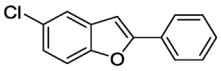
3-(Benzofuran-2-yl)pyridine (3o): The title compound was prepared according to the general procedure. The product was obtained as white solid (81%) by using DCM/EA (3/1) as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, J = 1.6 Hz, 1 H), 8.59 (dd, J = 4.9, 1.3 Hz, 1 H), 8.26 – 8.18 (m, 1 H), 7.63 (d, J = 7.8 Hz, 1 H), 7.56 (d, J = 8.2 Hz, 1 H), 7.47 (dd, J = 8.0, 5.0 Hz, 1 H), 7.38 – 7.32 (m, 1 H), 7.30 – 7.27 (m, 1 H), 7.17 (d, J = 0.6 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.18, 152.21, 147.71, 145.06, 132.96, 128.61, 127.26, 125.28, 124.10, 123.42, 121.36, 111.39, 103.43. These spectroscopic data matched that previously reported [2].



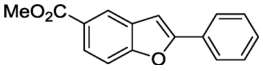
2-(Cyclohex-1-en-1-yl)benzofuran (3p): The title compound was prepared according to the general procedure. The product was obtained as colorless oil (75%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, J = 7.5 Hz, 1 H), 7.42 (d, J = 8.1 Hz, 1 H), 7.24–7.20 (m, 1 H), 7.19–7.15 (m, 1 H), 6.62 (td, J = 4.1, 2.4 Hz, 1 H), 6.50 (s, 1 H), 2.39 (dtd, J = 6.3, 4.2, 2.1 Hz, 2 H), 2.30–2.25 (m, 2 H), 1.83–1.76 (m, 2 H), 1.73–1.67 (m, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.48, 154.41, 129.16, 127.16, 126.09, 123.77, 122.45, 120.52, 110.69, 100.02, 25.40, 24.92, 22.33, 22.11. These spectroscopic data matched that previously reported [32].



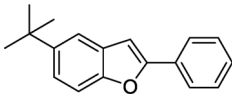
4-(Benzofuran-2-yl)butanenitrile (3q): The title compound was prepared according to the general procedure. The product was obtained as yellow oil (57%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.40 (m, 1 H), 7.36–7.32 (m, 1 H), 7.19–7.08 (m, 2 H), 6.40 (d, J = 0.8 Hz, 1 H), 2.88 (t, J = 7.2 Hz, 2 H), 2.34 (t, J = 7.1 Hz, 2 H), 2.04 (p, J = 7.1 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.19, 154.78, 128.49, 123.65, 122.68, 120.46, 119.08, 110.82, 103.41, 27.08, 23.62, 16.42. These spectroscopic data matched that previously reported [33].



5-Chloro-2-phenylbenzofuran (3r): The title compound was prepared according to the general procedure. The product was obtained as white solid (90%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, J = 7.4 Hz, 2 H), 7.55 (d, J = 1.8 Hz, 1 H), 7.48–7.42 (m, 3 H), 7.38 (t, J = 7.4 Hz, 1 H), 7.24 (dd, J = 8.7, 2.0 Hz, 1 H), 6.96 (s, 1 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.38, 153.24, 130.56, 129.95, 128.98, 128.84, 128.47, 125.04, 124.38, 120.40, 112.10, 100.78. These spectroscopic data matched that previously reported [33].

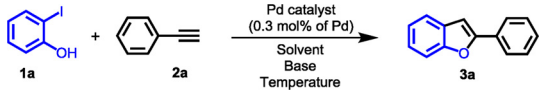


Methyl 2-phenylbenzofuran-5-carboxylate (3s): The title compound was prepared according to the general procedure. The product was obtained as white solid (73%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 1.6 Hz, 1 H), 8.02 (dd, J = 8.6, 1.7 Hz, 1 H), 7.89–7.85 (m, 2 H), 7.54 (d, J = 8.6 Hz, 1 H), 7.50–7.44 (m, 2 H), 7.41–7.36 (m, 1 H), 7.07 (s, 1 H), 3.95 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.31, 157.43, 157.40, 129.90, 129.26, 129.05, 128.90, 126.07, 125.34, 125.09, 123.32, 111.02, 101.53, 52.13. These spectroscopic data matched that previously reported [34].



5-(*tert*-Butyl)-2-phenylbenzofuran (3t): The title compound was prepared according to the general procedure. The product was obtained

Table 1
Reaction condition optimization.[a]



Entry	Base	Solvent	Temperature /°C	Reaction time /h	Conversion /%[b]	Selectivity /%[b]
1	K_2CO_3	DMF	160	3	100	60
2	Na_2CO_3	DMF	160	5	100	40
3	Cs_2CO_3	DMF	160	10	90	94
4	KOH	DMF	160	4.5	100	89
5	K_3PO_4	DMF	160	8	100 (92)[c]	96
6	NaO*t*Bu	DMF	160	3.5	0	–
7	NEt_3	DMF	160	5	64	25
8	DBU	DMF	160	5.5	100	0
9	K_3PO_4	CH_3CN	160	5	0	–
10	K_3PO_4	Toluene	160	6.5	100	66
11	K_3PO_4	DMSO	160	5	100	71
12	K_3PO_4	DMF	150	8	100	94
13	K_3PO_4	DMF	140	11	100	98
14	K_3PO_4	DMF	120	8	0	–
15	K_3PO_4	DMF	100	8	0	–

[a] Reaction conditions: *o*-iodophenol (0.5 mmol), phenylacetylene (1.0 mmol), Pd/*N*,*O*-Carbon (10 mg, 0.3 mol% of Pd), solvent (5 mL) under argon atmosphere.
[b] Determined by GC-FID using dodecane as the internal standard.
[c] Isolated yield.

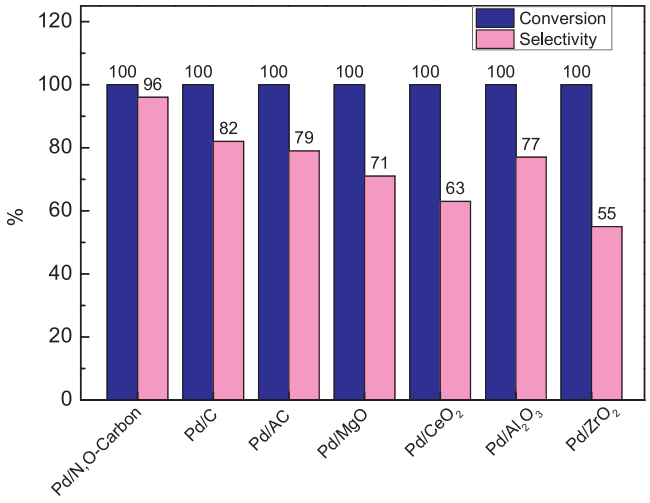
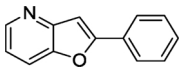


Fig. 1. Comparison of catalytic performance for one-pot tandem reaction of o-iodophenol and phenylacetylene with various supported catalysts.
Reaction conditions: *o*-iodophenol (0.5 mmol), phenylacetylene (1.0 mmol), catalyst (10 mg, 0.3 mol% of Pd), DMF (5 mL), 8 h under argon atmosphere. Determined by GC-FID using dodecane as the internal standard.

as white solid (82%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.3 Hz, 2 H), 7.63 (d, J = 1.8 Hz, 1 H), 7.52–7.45 (m, 3 H), 7.42–7.35 (m, 2 H), 7.03 (s, 1 H), 1.44 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.01, 153.13, 145.95, 130.67, 128.89, 128.73, 128.34, 124.83, 122.23, 117.07, 110.43, 101.48, 34.70, 31.84. These spectroscopic data matched that previously reported [23].



2-Phenylfuro [3,2-*b*] pyridine (3u): The title compound was prepared according to the general procedure. The product was obtained as white solid (79%) by using petroleum ether as the column eluent on silica gel. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, J = 4.8 Hz, 1 H), 7.90 (d, J = 7.5 Hz, 2 H), 7.77 (d, J = 8.2 Hz, 1 H), 7.48 (t, J = 7.4 Hz, 2 H), 7.41 (t, J = 7.4 Hz, 1 H), 7.24–7.18 (m, 2 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.69, 148.90, 148.00, 145.84, 129.62, 129.57, 128.89, 125.30, 118.74, 117.87, 102.30. These spectroscopic data matched that previously reported [29].

2.4. Characterization

The X-ray diff ;raction (XRD) patterns of all the catalysts were obtained on a Bruker D8 Advance X-ray diff ;raction diff ;ractometer equipped with Cu Ka radiation (λ = 1.5147 Å). The morphology of catalysts was examined by a H-7600 transmission electron microscopy (TEM), a Tecnai G2 F30 high-resolution TEM (HRTEM) and a FEI Tecnai G2 F20 scanning transmission electron microscopy (STEM). Nitrogen adsorption–desorption data were obtained on a Micromeritics ASAP 2020 static volumetric sorption analyzer. The specific surface area of the samples was calculated by the Brunauer-Emmet-Teller (BET) method. The micropore volume was calculated by t-plot method. The pore size distributions were determined by non-local density functional theory (NLDFT). The X-ray photoelectron spectroscopy (XPS) data was collected on an ESCALAB 250Xi (Thermo Scientific, UK) instrument equipped with a monochromatized Al Ka line source. All the binding energies obtained were calibrated based on the C 1 s peak at 284.8 eV. The elemental composition analysis of the catalysts was conducted on Vario El elemental analyzer. Ion Chromatography was conducted on a Thermo Scientific Dionex ICS-5000 equipped with CS-12 column with methanesulfonic acid (20 mM) as an eluent. Raman spectra were obtained on a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer system using a 532 nm wavelength laser at room temperature. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted on a PerkinElmer Optima 5300 DV instrument. Gas chromatography analysis was performed on an Agilent HP-7890 instrument with a flame ionization detector (FID) and an HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thicknesses) using helium as the carrier gas. Gas chromatography-mass spectrometry analysis was carried out on an Agilent HP-7890 instrument with an Agilent HP-5975 with triple-axis detector and HP-5 capillary column using helium carrier gas. NMR spectra were from a Bruker DRX-400, or DRX-600, instrument and calibrated using residual non-deuterated solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; C_6D_6: δ_H = 7.16 ppm, δ_C = 128.06 ppm) as an internal reference.

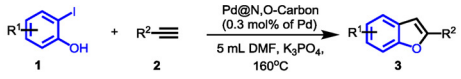
3. Results and discussion

From the outset, the reaction of *o*-iodophenol (**1a**) with phenylacetylene (**2a**) was chosen as benchmark reaction to assess whether the catalyst Pd/*N*,*O*-Carbon could enable one-pot sequential Sonogashira-cyclization under ligand- and copper-free conditions. The reaction was initially performed in the presence of 0.3 mol% (10 mg) of Pd@*N*,*O*-Carbon, K_2CO_3 in DMF at 160 °C. We pleased to observe that the reaction proceeded efficiently and **1a** was completely converted to the target product 2-phenylbenzofuran **3a** in 60% selectivity (Table 1, entry 1). Encouraged by this result, we decided to further optimize the conditions to improve the reaction efficiency and a set of factors including bases, solvents and reaction temperature were subsequently screened. Selected results are compiled in Table 1. Firstly, the reaction was performed with various bases such as Na_2CO_3, K_2CO_3, Cs_2CO_3, K_3PO_4, NaO^{t}Bu, KOH, DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene), and TEA (triethylamine). Under otherwise identical conditions, K_3PO_4 with 2 equivalents with respect to **1a** was found to be the best choice to give superior catalytic performance in terms of both activity and selectivity (full conversion with up to 96% selectivity) among all bases investigated (entries 2–8) (see Table S1 in the Supporting information). Other bases showed either lower reactivity or poorer selectivity or both. Subsequently, the reaction was conducted at varying temperatures (from 100 to 160 °C). An increase of reaction temperature considerably enhances the reaction rate without affecting the selectivity to **3a**, whereas the reaction completely shut down when the reaction temperature was below 130 °C even with extending the reaction times (entries 12–15). Next, the reaction was performed in various organic solvents including DMF, DMSO, toluene, and CH_3CN (entries 9–12). Among all solvents screened, DMF was found to be the best choice for the selective formation of **3a** in high efficiency. Further investigation showed that excess of **2a** (at least 2 equivalents with respect to **1a**) is required to achieve **3a** in high yield with excellent selectivity (see Table S2 in Supporting information).

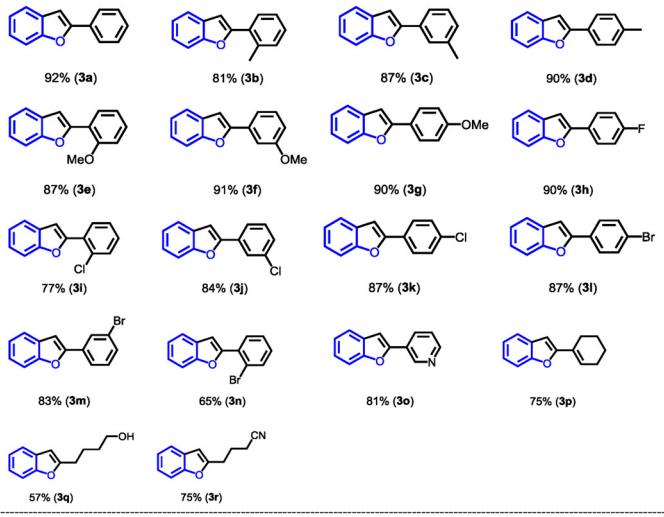
For comparison, commercially available Pd/C (10 wt% of Pd) and the catalysts prepared from commonly used activated carbon (AC with surface area of 1580 $m^2 g^{-1}$) and other supports such as Al_2O_3, TiO_2, CeO_2 and ZrO_2 with roughly equal Pd loading and same preparation procedure were employed for the reaction under otherwise identical conditions (Fig. 1). In most cases, those catalysts gave roughly equal reaction efficiency but with considerably lower selectivity to **3a**. In sharp contrast, the reaction efficiency and chemoselectivity to **3a** of the commercial Pd/C without any heteroatom-doping was significantly lower than that of Pd/*N*,*O*-Carbon under identical conditions, indicating the intrinsic nature of *N*,*O*-dual-doped hierarchical porous carbon played a crucial role in catalysis (see Table S4, Figs. S1 & S2 in the Supporting information). The reaction proceed slowly with either the bare support *N*,*O*-Carbon as catalyst or no catalyst, while only dehalogenated product phenol was produced with 23% conversion of **1a**. Such results demonstrate the essential role of the catalyst in this tandem reaction. Token together, the optimized reaction conditions involve K_3PO_4 as the base, DMF as the solvent, in the presence of 0.3 mol% of the catalyst Pd/*N*,*O*-Carbon at 160 °C reaction temperature.

Having identified the optimal reaction conditions, we next investigated the substrate scope to explore the versatility of this ligand- and copper-free Pd-catalyzed one-pot tandem reaction protocol (Table 2). In general, the catalyst Pd/*N*,*O*-Carbon enabled the one-pot tandem reaction of a diverse array of terminal alkynes with **1a**, providing the corresponding 2-benzofuran derivatives in moderate to high yields. Aryl alkynes bearing either electron-rich or electron-poor groups

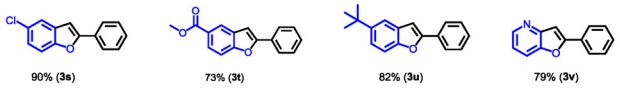
Table 2
Substrate scopes.[a]



a) Scope of terminal alkynes



b) Scope of *o*-iodophenols



[a]Reaction conditions: *o*-iodophenol (0.5 mmol), alkyne (1.0 mmol), Pd/N,O-Carbon (10 mg, 0.3 mol% of Pd), K_3PO_4 (1.0 mmol), DMF (5 mL), 160°C under argon atmosphere, 8-12 h. All yields are isolated ones.

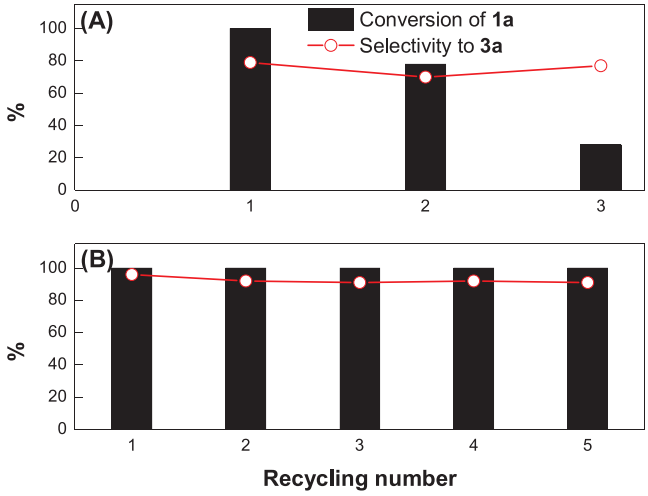


Fig. 2. Recycling experiments for the catalyst (A) Pd/AC and (B) Pd/N,*O*-Carbon.

were effectively transformed, and substituents in the *para*-, *meta*-, and *ortho*- positions of the aryl ring are compatible with the reaction conditions. However, substrates with *ortho*- substituents (**2b** and **2e**) appeared to be less reactive than their *para*- or *meta*-substituted analogues, possibly due to the steric effect. Halogen-substituted aryl alkynes (**2h-n**) underwent the reaction in moderate to high yields, and dehalogenation products were not observed. Heteroaromatic alkyne, 2-3-ethynylpyridine (**2o**) proceeded smoothly to deliver the corresponding 2-benzofurans products (**3o**) in 81% yield. Besides, not only terminal aryl alkynes but also terminal alkyl alkynes (**2p-r**) even with bearing functional groups e.g. −OH, −CN are also suitable substrates and underwent the sequential Sonogashira/cyclization tandem reaction under the optimized conditions to afford the product in 57–75%yields. It appears that the present catalytic system has a broad substrate scope as well as functional group tolerance for the terminal alkynes.

Subsequently, we further explore the compatibility of various substituted *o*-iodophenols for the tandem catalysis. Several substituted groups such as −Cl, ester, -^{t}Bu on the para-position of *o*-iodophenols all gave high yields to the corresponding 2-benzofuran derivatives (**3s-v**). Surprisingly, 2-iodopyridin-3-ol (**1v**) also worked well for the tandem catalysis and afforded the desired product in 79% yield.

Durability/recyclability of a catalyst is critical for practical applications. To test the durability of Pd/*N*,*O*-Carbon, the catalyst was recollected, washed, and dried after completion of a tandem catalysis experiment for subsequent cycles. As shown in Fig. 2(B). The activity and selectivity remained with negligible changes after five recycling experiments, demonstrating the high durability of this catalyst. The heterogeneity of Pd/*N*,*O*-Carbon was further confirmed by several experiments. We carried out the tandem catalysis of phenylacetylene (**2a**) with *o*-iodophenol (**1a**) and removed the catalyst from the reaction mixture by filtration at approximately 40% conversion of **1a**. After removal of the Pd/*N*,*O*-Carbon, the filtrate was again held at 160 °C for continuing reaction. In this case, no significant increase in conversion was observed, indicating that leached Pd species from the catalyst (if any) are not responsible for the observed activity. It was confirmed by ICP-AES analyses that the amounts of Pd that leached into the supernatant after the first run were not detectable (below the detection limit). These tests rule out the role of any leached Pd nanoparticles or other Pd-species in catalyzing one-pot tandem reaction. However, the Pd/AC catalyst without any heteroatom-doping, which exhibited considerably slower reaction rate and lower selectivity as discussed above, displayed a drastic decrease in activity in the second successive recycle uses (Fig. 2(A)), indicating the vital roles of *N*,*O*-dual-doped hierarchical porous carbon for the strong stability in catalysis.

4. Conclusions

In summary, we have developed a highly efficient and robust heterogeneous supported Pd NPs on *N*,*O*-dual-doped hierarchical porous carbon for one-pot tandem reaction of *o*-iodophenols with terminal alkynes. The catalyst enabled the sequential intermolecular Sonogashira cross-coupling followed by cyclization of *o*-iodophenols with terminal alkynes to synthesize a range of 2-benzofuran derivatives under copper- and ligand-free conditions. A broad set of terminal alkynes and *o*-iodophenols could be efficiently transformed with good functional groups tolerance. The catalyst also demonstrates strong stability, can be easily recovered for successive uses. The process represents a green methodology for synthesizing biologically valuable heterocyclic compounds.

Acknowledgements

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2018.04.036.

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