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# COMMUNICATION

# Supported Palladium Nanoparticles-Catalyzed Synthesis of 3-Substituted 2-Quinolones from 2-Iodoanilines and Alkynes Using Oxalic Acid as C1 Source

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**Abstract:** 3-Aryl/alkyl-2-quinolones were synthesized employing microwave assisted multicomponent reaction of 2-iodoanilines, terminal alkynes and oxalic acid dihydrate ( $(CO_2H)_2.2H_2O$ ) under polystyrene supported palladium (Pd@PS) nanoparticles-catalyzed conditions. The use of a heterogeneous palladium catalyst was explored first time for 2-quinolone synthesis involving carbonylation reaction employing ( $CO_2H$ )<sub>2</sub>.2H<sub>2</sub>O as a solid and bench stable carbon monoxide (CO) source. The reaction exhibited good substrate generality for 2iodoanilines and alkynes with wide functional group tolerance and good regio-selectivity. The ligand free operation, recyclability of heterogeneous Pd@PS catalyst and use of bench stable C1 source are the invaluable merits of the protocol.

**Keywords:** Carbonylation; Quinolone ; Heterogeneous catalyst ; CO surrogate; Microwave irradiation

Palladium-catalyzed carbonylation, a versatile and indispensable tool for the synthesis of diverse carbonyl compounds, is an emerging area of research for industry and academia as well to synthesize fine chemicals, natural products, heterocycles and other valuable structural motifs.<sup>[1]</sup> Typically, carbonylation reactions utilize CO gas as the major carbonyl source,<sup>[2]</sup> but is less attractive due to its toxicity and difficulties in handling as special equipments are required to withstand the use of highly pressurized gas in the reaction. Henceforth, the use of solid and sustainable CO surrogates has garnered huge interest in recent decades.<sup>[3]</sup> Recently, several different CO acid.<sup>[4a,4b]</sup> surrogates such as formic paraformaldehyde, N-formylsaccharin,<sup>[4c]</sup> 9-methyl-9H-fluorene-9-carbonyl chloride<sup>[4d]</sup> have been described to synthesize carbonyl compounds but their application for quinolones still remain undervalued.

2-Quinolones are the versatile scaffolds present in alkaloids and synthetic molecules exhibiting broad spectrum of biological activities<sup>[5]</sup> and so far, ample

efforts have been devoted for the synthesis of variety of substituted 2-quinolones employing both traditional<sup>[6]</sup> and metal-catalyzed protocols.<sup>[7]</sup> Transition metal-catalyzed carbonylative approaches provide an alternative access to 2-quinolone synthesis. Foremost, the homogeneous palladium-catalyzed multicomponent carbonylative annulation of 2iodoaniline and terminal/internal alkynes using CO gas have emerged as a key research area for quinolones synthesis.<sup>[8]</sup> Larock and co-workers Pd-catalyzed reported the homogenous multicomponent carbonylative annulation of Nprotected 2-iodoanilines with internal or terminal alkynes using CO gas for 3/4-substituted 2quinolones, wherein, the reaction and product yields depended on the nature of protecting group.<sup>[8b]</sup> Recently, the similar approach was extended for the synthesis of 2-quinolone based heterocycles.<sup>[8c]</sup> More\_ recently, benign and abundantly available CO<sub>2</sub> gas has also been used as CO surrogate for quinolone synthesis employing transition metals like Pd,<sup>[9a]</sup>  $Ag^{[9b]}$  and Cu.<sup>[9c]</sup> Whereas, Mo(CO)<sub>6</sub> is the only bench stable CO surrogate applied in combination with homogeneous Pd catalyst for 4-quinolones synthesis under multicomponent carbonylative annulation of 2iodoanilines and terminal alkynes.[10]

Last few years we have been working in the area of exploration of (CO<sub>2</sub>H)<sub>2</sub>.2H<sub>2</sub>O as *in situ* CO, CO<sub>2</sub> and H<sub>2</sub> source and their applications in different challenging area of organic synthesis under our The conditions.<sup>[11]</sup> catalytic supported best compatibility of the support (PS) was also investigated to hold the (CO<sub>2</sub>H)<sub>2</sub>.2H<sub>2</sub>O over surface making the combination successful for better interaction with closely associated catalyst for fruitful reactions.<sup>[12]</sup> In our continuous efforts to further expand the role of bench stable (CO<sub>2</sub>H)<sub>2</sub>.2H<sub>2</sub>O as CO source, we have targeted the synthesis of 3-aryl/alkyl-2-quinolones using multicomponent reaction of 2iodoanilines, terminal alkynes and (CO<sub>2</sub>H)<sub>2</sub>.2H<sub>2</sub>O in

the presence of heterogeneous Pd@PS nanoparticles (NPs) as catalyst under microwave irradiation conditions. However, to the best of our knowledge, this is the first such report using heterogeneous palladium metal catalyst and  $(CO_2H)_2.2H_2O$  as CO source for the synthesis of 2-quinolones in a regio-selective manner.

The Pd@PS catalyst was prepared using Amberlite IRA 900 Cl- form resin as polystyrene support (PS) and Pd(OAc)<sub>2</sub> as metal precursor following reduction deposition approach (supplementary information, ESI) and well characterized by using powder X-ray diffraction (pXRD), Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and selected area electron diffraction (SAED) studies.<sup>[11,12]</sup> Under this study, the developed Pd@PS catalyst was further applied in the carbonylative annulation reaction for the synthesis of 3-substituted 2-quinolones.

To assess the optimum reaction conditions, 2iodoaniline 1a and phenylacetylene 2a were chosen as model substrates. Initially, we targeted the reaction of 1a, 2a and (CO<sub>2</sub>H)<sub>2</sub>.2H<sub>2</sub>O 3 using DBU as base in the presence of Pd@PS in PEG-400:1,4-dioxane (1:1) under MW irradiation for 1 h at 130 °C, which afforded the desired product 4a in 29% yield along with the formation of formanilide as side product in almost equal proportion, while **1a** remains unconsumed (Table 1, entry 1). The reaction in DMF gave improved product yield, but was again restricted by the formation of formanilide (Table 1, entry 2). While using Et<sub>3</sub>N as base, improved the product yield to 47% and traces of formanilide was observed in the reaction (Table 1, entry 3). Further, increasing the equivalency of Et<sub>3</sub>N and reaction time to 90 min. did not affect the reaction yield. So, increasing the catalyst loading to 5 mol% of Pd gave improved yield (Table 1, entry 4), whereas further increase in catalyst loading had marginal effect on the reaction. Then, the reaction was screened at different temperatures where reaction at 135 °C gave 4a in 75% yield (Table 1, entry 7), while raising the temperature to 140 °C led to the low product yield due to side product formation (Table 1, entry 6). The different solvents were screened to get optimal results (Table 1, entry 8-11) and as evident, DMF was found to be the most suitable solvent for the said reaction. Oxalic acid and DMF was found to be the most suitable combination for the reaction because of the highly efficient dissociation of oxalic acid in DMF was noticed. Besides assisting the dissociation of oxalic acid, DMF also has high boiling point than the decomposition temperature of oxalic acid dihydrate (>= 130 °C), rendering the reaction feasible and further optimization, easier. For both organic/inorganic bases were screened, whereas, inorganic bases were not found efficient to carry out the reaction while among all, the organic bases such as Et<sub>3</sub>N and tetrabutylammonium iodide (TBAI) were found equally efficient for the said reaction (Table 1, entry 12-23). The use of higher equivalency i.e. 3 equiv. of TBAI and longer reaction time did not

improve the reaction yield (Table 1, entry 22). But, TBAI was preferred over Et<sub>3</sub>N as broader substrate generality and synthesis of 3-substituted-2quinolones as major product with negligible quantity of 4-quinolones detected in LC-MS along with minimum by-products. Therefore, the solubility of bases is major responsible factor for the reaction as most of the screened organic bases participated well in the reaction and gave significant yields. Other palladium metal catalysts such as Pd(OAc)<sub>2</sub>. Pd/C and Pd/Al<sub>2</sub>O<sub>3</sub>were also screened in the reaction and gave the desired product 4a in 41,26 and 19% yields

**Table 1**. Optimization studies of reaction conditions for 3aryl/alkyl-2-quinolones synthesis<sup>a</sup>

-		-				لسباب
L 1a	+ NH <sub>2</sub> 2a	+ (COOH) <sub>2</sub> .21	H <sub>2</sub> O Pd@PS, Base Solvent, MW Temp, 1 h	e → ↓ 4a	y-C≈O	Q
Entry	Catalyst (mol% of Pd)	Solvent	Base (Equiv.)	Temp. (°C)	Yield (%) <sup>b</sup>	
1	Pd@PS (3)	PEG-400:Dioxa	ne DBU (2)	130	29	$\cup$
2	Pd@PS (3)	DMF	DBU (2)	130	40	()
3	Pd@PS (3)	DMF	Et <sub>3</sub> N (2)	130	47	U,
4	Pd@PS (5)	DMF	Et <sub>3</sub> N (2)	130	58	
5	Pd@PS (5)	DMF	Et <sub>3</sub> N (2)	120	23	
6	Pd@PS (5)	DMF	Et <sub>3</sub> N (2)	140	62	
7	Pd@PS (5)	DMF	Et <sub>3</sub> N (2)	135	75	
8	Pd@PS (5)	PEG-400	Et <sub>3</sub> N (2)	135	traces	
9	Pd@PS (5)	1,4-Dioxane	Et <sub>3</sub> N (2)	135	nd	U
10	Pd@PS (5)	NMP	Et <sub>3</sub> N (2)	135	33	
11	Pd@PS (5)	DMA	Et <sub>3</sub> N (2)	135	26	>
12	Pd@PS (5)	DMF	K <sub>2</sub> CO <sub>3</sub> (2)	135	traces	
13	Pd@PS (5)	DMF	$Cs_2CO_3(2)$	135	traces	
14	Pd@PS (5)	DMF	Et <sub>2</sub> NH (2)	135	54	77
15	Pd@PS (5)	DMF	DMAP (2)	135	42	$\cup$
16	Pd@PS (5)	DMF	DABCO (2)	135	45	1
17	Pd@PS (5)	DMF	Et <sub>3</sub> N:DMAP (2:0.1)	135	67	V
18	Pd@PS (5)	DMF	Ру (2)	135	39	<u>+</u>
19	Pd@PS (5)	DMF	TBAF.3H <sub>2</sub> O (2)	135	66	
20	Pd@PS (5)	DMF	TBAB (2)	135	27	
21	Pd@PS (5)	DMF	TBAI (2)	135	73	1
22	Pd@PS (5)	DMF	TBAI (3)	135	74	Y
23	Pd@PS (5)	DMF	TBACI (2)	135	32	()
24	Pd(OAc) <sub>2</sub> (5)	DMF	TBAI (2)	135	41	
25	Pd/C (5)	DMF	TBAI (2)	135	26	()
26	Pd/Al <sub>2</sub> O <sub>3</sub> (5)	DMF	TBAI (2)	135	19	
27		DMF	TBAI (2)	135	nd	
28	Pd@PS (5)	DMF		135	nd	

<sup>[a]</sup>Reaction conditions: 1a (50 mg, 0.228 mmol), 2a (62.5  $\mu$ L, 0.57 mmol), oxalic acid dihydrate (114.91 mg, 0.912 mmol), Pd catalyst (as mentioned above), base (as mentioned above), solvent (1 mL), under MW irradiations for 1 h; <sup>b</sup>Isolated yields.

respectively but reaction proceeded with poor selectivity for **4a** (Table 1, entry 24, 25,26). To establish the role of Pd@PS catalyst, the reaction in absence of Pd@PS catalyst was carried out wherein 4a was not formed (Table 1, entry 27). Also, the reaction was not feasible in absence of TBAI (Table 1, entry 28). The optimal equivalency of phenylacetylene and oxalic acid dihydrate to obtain maximum product yield was also screened (Table S1, ESI). Finally, the reaction stated in Table 1, entry 21 was found to be the optimal condition wherein 2iodoaniline (1 equiv.), phenylacetylene (2.5 equiv.), equiv.), Pd@PS (5 TBAI (2 mol%) and (CO<sub>2</sub>H)<sub>2</sub>.2H<sub>2</sub>O (4 equiv.) in DMF at 135 °C gave the highest yield (73%) of regio-selective product 4a. The application of various other CO surrogates has also been screened so as to compare the efficiency of all C1 sources under the optimized reaction conditions (Table S2, ESI). The study established (CO<sub>2</sub>H)<sub>2</sub>.2H<sub>2</sub>O as most efficient C1 source in presence of heterogeneous Pd@PS catalyst for the synthesis of 3-substituted-2-quinolones (Table S2).

Further, the versatility of the reaction was determined with variety of substrates (Table 2). The reaction was feasible with various substituted 2-iodoaniline derivatives. All 4-Cl, 5-Cl, 4-Br, 4-F, 4-CH<sub>3</sub>, 4-COOCH<sub>3</sub>, 4-CN substituted 2-iodoanilines participated well in the reaction with phenylacetylene or 4-ethynyltoluene to give corresponding 2-quinolones derivatives **4b-j** in good to moderate yields. We have also subjected 2-bromoaniline and 2-chloroaniline under the same catalytic conditions. However, in case of 2-bromoaniline we ended up with complex reaction mixture while no reaction occurred with 2-chloroaniline.

 Table 2. Substrate scope for the regio-selective synthesis of 3-aryl/alkyl-2-quinolones<sup>a</sup>



<sup>[a]</sup>Reaction conditions: 2-iodoaniline derivatives (1 equiv.), terminal alkyne (2.5 equiv.), oxalic acid dihydrate (4 equiv.), TBAI (2 equiv.) and Pd@PS (5 mol% of Pd) in 1 mL of DMF under MWI for 1 h at 135 °C; Isolated yields.

The effect of functional groups present on aromatic alkynes for the synthesis of 2-quinolones was also studied in detail. The reaction of 2-iodoaniline with 3-ethynyland 2-ethynyltoluene gave the corresponding products 4k-l in 63 and 47% yields. The relatively lower yield of **4** can be attributed to the steric hindrance at the ortho position of alkyne. The reaction of 2-iodoaniline with 4-tertbutylphenylacetylene gave the corresponding product **4m** in 64% yield. The 4-OCH<sub>3</sub>/ $C_2H_5$  substituted alkynes also participated in the reaction to give 4n-o in 58 and 56% yield respectively. The halogen substituted aromatic alkynes were found reactive to procure corresponding 2-quinolones 4p-r in good yields. The aromatic alkynes comprising electron withdrawing functional groups such as -CF<sub>3</sub> and -CN were also screened to give products 4s-t in moderate yields. The 3-alkyl-2-quinolones **4u-v** were prepared in moderate yields using corresponding alicyclin alkynes that is 1-ethynylcyclohexene and 1ethynylcyclohexane. The aliphatic alkynes also participated well in the reaction to afford 4w-x in 54-57% yields (Table 2). The formanilide 5a was obtained up to 10% yield as side product in case of aliphatic alkynes. Moreover, the formation of 4substituted regio-isomer for **4b-x** was not detected.

The molecular structure of **4a** was also confirmed using X-ray crystallography (Figure 1).



**Figure 1.** The molecular structure of **4a** determined by X-ray crystallography.<sup>[13]</sup>

A set of control experiments was performed to elucidate the reaction pathway. Wherein, the reaction of 6 under the standard conditions didn't give the desired product 4a which effectively ruled out the possibility of Sonogashira coupling and subsequent carbonylative annulation reaction (Scheme 1, entry 'a'). As per literature reports,  $(CO_2H)_2.2H_2O$  is known to decompose into CO and CO<sub>2</sub>, hence, to discover the fate of CO<sub>2</sub> molecule, we performed the reaction of 1a and 2a with CO<sub>2</sub> (dry ice) under standard conditions and obtained the final product 4a in 34% yield which led to the conclusion that CO and CO<sub>2</sub> both can participate in the carbonylation reaction under this condition (Scheme 1, entry 'b'). Similarly, reaction of 1a was also performed with 1-octyne (2x)using CO<sub>2</sub> (dry ice) to procure 4x in 31% yields (Scheme 1, entry 'c'). The reaction of 7 with 2aunder optimized conditions gave the product 4a in 54% yield but the formation of 8 was not detected (Scheme 1, entry 'd'). Likewise, when 9 was treated with 2a under standard reaction conditions gave 4a in

traces but the formation of **10** was not observed (Scheme 1, entry 'e'). This implies that

Scheme 1. Set of control experiments to understand the reaction mechanism



deprotection of compound 7 and 9 might have occurred before it participated in the reaction. Whereas, the reaction of 7 with 2a in absence of  $(CO_2H)_2.2H_2O$  and under standard reaction conditions gave 4a in traces (5-7% yield).

Based on the control experiments and literature reports, we propose the possible reaction mechanism, wherein, both CO and  $CO_2$  (decomposition products of (CO<sub>2</sub>H)<sub>2</sub>.2H<sub>2</sub>O) participates in the reaction as carbonyl source (Scheme 2). Also, the insertion of alkyne bond to Pd-C bond is preferred over CO insertion and is a decisive point in the course of reaction for 3-substituted 2-quinolones synthesis. The Pd@PS undergoes oxidative addition with 2iodoaniline (I) to procure arylpalladium intermediate (II). The insertion of alkyne to intermediate (II) results in the formation of vinylpalladium intermediate (III). However, the intermediate (III) might follow two pathways, 'a' or 'b'. In pathway 'a', the interaction of CO with palladium metal afforded intermediate (IV) which follows insertion reaction to give acylpalladium intermediate (V).Further, the nucleophilic attack of amine moiety on the carbonyl of acylpalladium intermediate afforded the desired product 4 (3-substituted 2-quinolones). On the other hand, based on the experiment (Scheme 1, 'f'), However, the intermediate (III) might follow two pathways, 'a' or 'b'. In pathway 'a', the interaction of CO with palladium metal afforded intermediate (IV) follows insertion which reaction to give acylpalladium intermediate (V). Further, the reaction

may follow a minor pathway, wherein, the amine group of intermediate (III) may be formylated and which in turn interacts with Pd metal to generate intermediate (VI). The final annulation step leads to the formation of desired product (4) and regeneration of the catalyst (Scheme 2).

**Scheme 2.** The plausible mechanism of Pd@PS-catalyzed multicomponent carbonylative annulation for 2-quinolone synthesis



Moreover, in pathway 'b', the  $CO_2$  generated from  $(CO_2H)_2.2H_2O$  interacts with amine moiety of vinylpalladium intermediate (III) to afford (VII) which in presence of base gave intermediate (VIII) which is also supported by control experiments (Scheme 1, 'b and c'). The intermediate (VIII) afforded the final product (4) following the nucleophilic attack of vinyl group at the carbon of isocyanate group and regenerate the Pd@PS.

Moreover, the Pd@PS was recycled up to fourtimes with no substantial loss of activity (ESI). The ICP-AES analysis of reaction mixture was performed for 2<sup>nd</sup> and 4<sup>th</sup> cycle but no significant Pd metal leaching (<0.01 ppm) was detected (ESI). The TEM studies of Pd@PS after 4th cycle showed notable increase in Pd NPs size which might be the potential cause of loss of catalytic activity (ESI). Besides, the heterogeneity of Pd@PS in the reaction was established using the mercury poisoning test which gave 4a in traces only (ESI). To see that the solution phase Pd is not responsible for the reaction, we have removed Pd@PS through hot filtration from reaction mixture after 0.5 h and the reaction mixture further continue for another 0.5 h, but no progress in reactivity was noticed (ESI).

In conclusion, we have developed a multicomponent approach involving 2-iodoaniline derivatives, terminal alkynes, and  $(CO_2H)_2.2H_2O$  as bench stable CO source under microwave irradiation for the synthesis of regio-selective 3-substituted 2-quinolones. The detailed mechanistic evaluation established the role of CO itself and CO<sub>2</sub> as CO

source in the reaction. The use of recyclable heterogeneous catalyst, bench stable CO surrogate, microwave irradiations, easy handling of reaction and regio-selectivity of products are the major highpoints of the protocol.

# **Experimental Section**

#### Typical Experimental procedures for the synthesis of 2quinolones

2-Iodoaniline **1a** (50 mg, 0.228 mmol), oxalic acid dihydrate (114.66 mg, 0.91 mmol), tetrabutylammonium iodide (168.43 mg, 0.456 mmol), Pd@PS (256 mg, 5 mol% of Pd) were taken in 1.5 mL DMF in a MW tube. Then, phenylacetylene (62.60  $\mu$ L, 0.57 mmol) was added to the reaction mixture. The resultant reaction mixture was treated under MW irradiation at 135 °C, 60 W for 1 h. The reaction was monitored by TLC. The reaction mixture was cooled to ambient temperature and quenched with water and then extracted using ethyl acetate (4X5 mL). The resulting organic layer was treated with anhy. Na<sub>2</sub>SO<sub>4</sub> and dried under reduced pressure. The corresponding 3-phenylquinolin-2(1*H*)-one **4a** was obtained in 37 mg, 73% yield as off white solid after purification by column chromatography on silica gel (60-120 mesh) using Hexane:EtOAc (75:25) as eluent.

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- [13] CCDC 1855656 includes supplementary crystallographic data for crystal structure **4a** of this manuscript. The data can be procured free of charge from the Cambridge crystallographic data centre via <u>www.ccdc.cam.ac.uk/data\_request/cif</u>. Also, further information about the crystal structure is given is supporting info

#### Supported Palladium Nanoparticles-Catalyzed Synthesis of 3-Substituted 2-Quinolones from 2-Iodoanilines and Alkynes Using Oxalic Acid as C1 Source

Adv. Synth. Catal. Year, Volume, Page - Page

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