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ARTICLE

Pd-catalysed carbonylative annulation of salicylaldehydes with benzyl chlorides using *N*-formylsaccharin as a CO surrogate†

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A convenient and highly efficient Pd-catalysed carbonylative annulation of salicylaldehydes with benzyl chlorides to afford the corresponding 3-arylcoumarins in good to excellent yields has been developed. Importantly, the protocol utilizes a commercially available, low cost, solid and easy to handle *N*-formylsaccharin as an alternative to the highly toxic CO gas.

Introduction

Over the past several years, palladium-catalysed carbonylation reaction of organohalides has emerged as a powerful tool for organic synthesis both in academia and industry.[1] Thus, the reaction has found application in the synthesis of various pharmaceuticals, agrochemicals and their intermediates.[1] The success of this synthetic strategy is based on the pioneering work of Heck and Schoenberg,[2] who revealed the Pd-catalysed carbonylation of haloarenes with carbon monoxide (CO). Basically, these carbonylation reactions rely on the properties of CO to undergo insertion into carbon-palladium bond and demonstrate their high impact in the field of Pd catalysis. Generally, in carbonylation reaction CO gas is used as a reagent but its high toxicity, inflammability and difficulty in storage, handling and transportation pose serious safety concerns. In order to avoid the use of gaseous CO as a carbonylating reagent, a number of CO surrogates such as a alcohols,[3] formic acid,[4a-f] formamide,[4g-i] formates,[5a-f] including the recently reported benzene-1,3,5-triyl triformate (TFBen),[5g] formaldehyde,[6a-g] hexaketocyclohexane octahydrate ($C_6O_6.8H_2O$),[6h] $Mo(CO)_6$,[6i] biomass,[3b] and carbon dioxide[7] have been developed.

In 2013, Manabe and co-workers utilized *N*-formylsaccharin as an advantageous and efficient CO surrogate for conducting Pd-catalysed reductive carbonylation and fluorocarbonylation of aryl and alkenyl halides.[1h,j] Recently, the research group of Fleischer[1b] and our own[8] have also used *N*-formylsaccharin as a convenient CO source for alkoxycarbonylation of alkenes and azidocarbonylation of haloarenes, respectively. Owing to its easy availability in solid form, stability, ease of handling and high reactivity, *N*-formylsaccharin is more advantageous for Pd-catalysed carbonylation reactions than the other available CO surrogates,[3-7] hence we opted to use it in the present work.

Coumarins (2*H*-chromen-2-ones), 3-arylcoumarins in particular, constitute a ubiquitous class of compounds featuring in a variety of natural products, bioactive molecules and organic materials.[9] Many natural and synthetic coumarins exhibit diverse biological and pharmaceutical properties including anti-HIV-1, antibiotic, anti-inflammatory, antidiabetic, antioxidant anticancer, anticoagulant and antidepressant activities.[10] Moreover, coumarins have found applications as laser dyes,[11] organic light-emitting diodes (OLED)[12] and optical brighteners.[13] The broad application potential of coumarins has placed them among the focal points of studies in synthetic organic chemistry.

Traditionally, 3-arylcoumarins are prepared by condensation-cyclisation type reactions such as Knoevenagel condensation,[14] Wittig,[15] Pechmann,[16] and Perkin reactions[17] using phenols or aromatic carbonyl compounds. Several alternative methods involving transition metal-catalysed reactions have been developed for the synthesis of 3-arylcoumarins.[18] Among these, Pd-catalysed 3-arylation of the coumarin scaffold with aryl halides or arylbronic acid[1a,f,g,n,o,19,20] and Pd-catalysed carbonylative annulations reactions[1m,21] of 2-iodophenols (Scheme 1a)[21n] or 2-vinylphenols (Scheme 1b)[21c] are of particular importance. Coumarins have also been synthesised from salicylaldehyde and cinnamaldehyde via *N*-heterocyclic carbene catalysed unpolung reactions.[22] However, this methods is applicable to the synthesis of 3-benzylcoumarin but not suitable for the synthesis of 3-arylcoumarins. Lu and co-workers modified these methods for the synthesis of 3-arylcoumarins by replacing cinnamaldehyde with 2-chloro-2-arylacetaldehydes.[23] Although these methods have their individual advantages, they suffer from one or more drawbacks such as the use of strong acids, high temperatures, harsh reactions conditions, toxic reagents and sometimes multistep preparation of requisite starting materials. Some years

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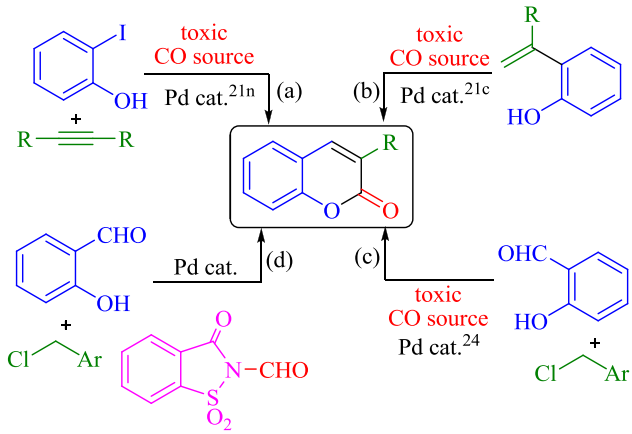
ago, Wu, Beller and co-workers have reported the same method (Scheme 1c)[24] for the synthesis of coumarins from salicylaldehydes and benzyl chlorides as the method reported herein (Scheme 1d) but their method utilizes CO gas, which is highly toxic and requires special care in handling.

In view of the above facts and our focus on the methodology development employing metal catalysis,[25] we have devised a convenient Pd-catalysed synthesis of 3-arylcoumarins from salicylaldehydes and benzyl chlorides utilizing *N*-formylsaccharin as a solid alternative to the highly hazardous CO gas (Scheme 1d).



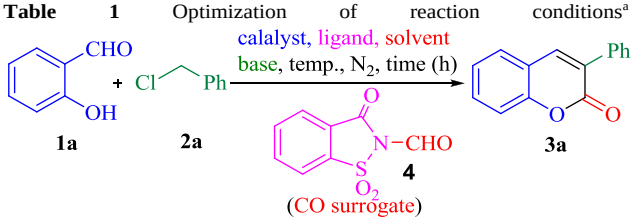
Scheme 1 Pd-catalysed carbonylative synthesis of 3-arylcoumarins.

Results and discussion

To realize our designed synthesis and optimize the reaction conditions a series of control experiments were performed with salicylaldehyde **1a** and benzyl chloride **2a** using *N*-formylsaccharin **4** as a CO surrogate and the results are summarized in Table 1. Initially, when the reaction was conducted at rt for 15 h, the desired product **3a** was not obtained (Table 1, entry 1). On conducting the reaction at 70 °C, the desired product **3a** was obtained in 61% yield (Table 1, entry 2). Thus, we optimized the temperatures and 85 °C was found to be the optimum temperature to give the maximum yield (Table 1, entries 3 and 4). Then, we optimized various Pd catalysts such as $Pd(OAc)_2$, $Pd(acac)_2$, $Pd(TFA)_2$ and $PdCl_2$, and $Pd(OAc)_2$ was found to be the best in terms of time and yield (Table 1, entry 3 vs 6-8). The optimum amount of the catalyst $Pd(OAc)_2$ was found to be 3 mol% because the yield was decreased on decreasing its amount, but was unaffected on increasing the amount to 4 mol% (Table 1, entry 3 vs 9 and 10). Next, we tested several ligands such as xantphos, PPh_3, DPPM, DPEphos, DPPE and DPPP, and xantphos was found to be the best in terms of time and yield (Table 1, entry 3 vs 11-15). A decrease in the loading of xantphos ligand from 5 mol% to 3 mol% resulted in lower yield of the product (Table 1, entry 3 vs 16), and on increasing the amount of xantphos ligand from 5 mol% to 7 mol%, the yield of the product remained unchanged (Table 1, entry 1 vs 17).

After these observations, we screened several solvents and found that DMF was the best among DMSO, DMF, THF, toluene and CH_3CN (Table 1, entry 3 vs 18-21). Then, bases Na_2CO_3, K_2CO_3, Cs_2CO_3, Et_3N and DABCO were optimized and Na_2CO_3 was found to

Table 1 Optimization of reaction conditions[a]



Entry	Catalyst (mol%)	Lingand (mol%)	Solvents (mL)	base (mmol)	Temp. (°C)	Time (h)	Yield (%)[b]
1	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	rt	15	n.d.
2	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	70	10	61
3	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	87
4	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	100	10	87
5	–	–	DMSO	–	85	24	n.d.
6	$Pd(acac)_2$	Xantphos	DMSO	Na_2CO_3	85	15	59
7	$Pd(TFA)_2$	Xantphos	DMSO	Na_2CO_3	85	15	45
8	$PdCl_2$	Xantphos	DMSO	Na_2CO_3	85	15	54
9	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	56[c]
10	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	87[d]
11	$Pd(OAc)_2$	PPh_3	DMSO	Na_2CO_3	85	15	51
12	$Pd(OAc)_2$	DPPM	DMSO	Na_2CO_3	85	15	60
13	$Pd(OAc)_2$	DPEphos	DMSO	Na_2CO_3	85	15	75
14	$Pd(OAc)_2$	DPPE	DMSO	Na_2CO_3	85	15	40
15	$Pd(OAc)_2$	DPPP	DMSO	Na_2CO_3	85	15	59
16	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	60[e]
17	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	18	87[f]
18	$Pd(OAc)_2$	Xantphos	DMF	Na_2CO_3	85	10	76
19	$Pd(OAc)_2$	Xantphos	THF	Na_2CO_3	85	10	75
20	$Pd(OAc)_2$	Xantphos	Toluene	Na_2CO_3	85	10	60
21	$Pd(OAc)_2$	Xantphos	CH_3CN	Na_2CO_3	85	10	52
22	$Pd(OAc)_2$	Xantphos	DMSO	K_2CO_3	85	10	81
23	$Pd(OAc)_2$	Xantphos	DMSO	Cs_2CO_3	85	10	77
24	$Pd(OAc)_2$	Xantphos	DMSO	NEt_3	85	10	64
25	$Pd(OAc)_2$	Xantphos	DMSO	DABCO	85	10	58
26	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	24[g]
27	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	35[h]
28	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	21[i]
29	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	42[j]
30	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	31[k]
31	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	33[l]
32	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	n.d.[m]
33	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	53[n]
34	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	67[o]
35	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	56[p]
36	$Pd(OAc)_2$	Xantphos	DMSO	Na_2CO_3	85	10	48[q]

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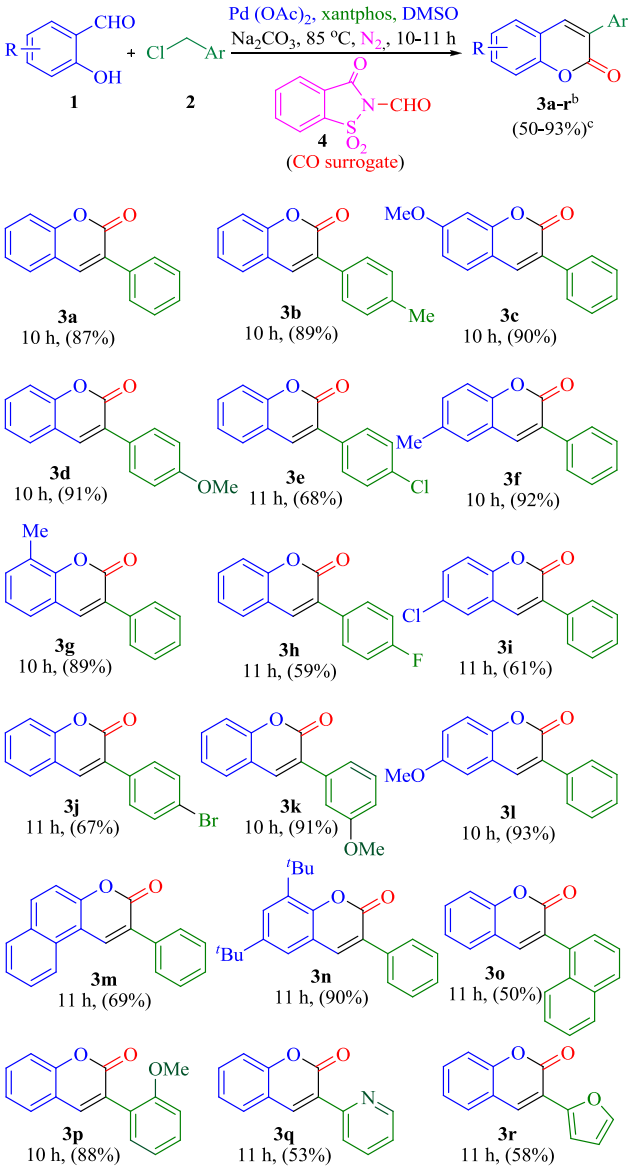
[a] Reaction conditions: salicylaldehyde (**1a**, 1 mmol), benzyl chloride (**2a**, 1 mmol), *N*-formylsaccharin **4** as a CO surrogate (2.5 mmol), ligand (5 mol%), Pd-catalyst (3 mol%), base (3 mmol), solvent (3 mL), N_2 atmosphere, at rt-100 °C for 10-24 h. [b] Isolated yield of 3**a**; n.d.= not detected.[c] 2 mol% of $Pd(OAc)_2$.[d] 4 mol% of $Pd(OAc)_2$. [e] 3 mol% of xantphos.[f] 7 mol% of xantphos.[g] 2.5 mmol of formic acid was used instead of **4**. [h] 2.5 mmol of phenyl formate was used instead of **4**. [i] 2.5 mmol of DMF was used instead of **4**. [j] 2.5 mmol of benzene-1,3,5-triyl triformate (TFBen) was used instead of **4**. [k] 2.5 mmol of hexaketocyclohexane octahydrate ($C_6O_6.H_2O$) was used instead of **4**. [l] 2.5 mmol of $Mo(CO)_6$ was used instead of **4**. [m] In the absence of **4**. [n] Benzyl iodide was used instead of **2a**. [o] Benzyl bromide was used instead of **2a**. [p] Benzyl tosylate was used instead of **2a**. [q] Benzyl carbonate was used instead of **2a**.

work most efficiently in terms of yield (Table 1, entry 3 vs 22-25). The feasibility of this reaction was also tested using other CO surrogates such as formic acid, phenyl formate, DMF, TFBen, $C_6O_6.H_2O$ and $Mo(CO)_6$ but none of these was found as effective as *N*-formylsaccharin (Table 1, entry 3 vs 26-31). A controlled experiment showed that the product **3a** was not formed in the absence of *N*-formylsaccharin as the CO surrogate (Table 1, entry 32). The release of CO from *N*-formylaccharin under the present reaction conditions could also be easily detected with a chemical spot detector containing $PdCl_2$, which goes black on exposure to CO. It was found that the best yield (87%) of **3a** was obtained with 2.5 equiv of the *N*-formylsaccharin as the CO surrogate (Table 1, entry 3). When other benzyl sources such as benzyl iodide, benzyl bromide, benzyl tosylate and benzyl carbonate were used in the place of benzyl chloride, the yield of **3a** was considerably decreased (Table 1, entry 3 vs 33-36). Thus, the synthesis of coumarin **3a** was conducted employing the optimized reaction conditions with **1a** (1 mmol), **2a** (1 mmol), $Pd(OAc)_2$ (3 mol%), xantphos (5 mol%), *N*-formylsaccharin (2.5 mmol) and Na_2CO_3 (3 mmol) in DMSO (3 mL) at 85 °C under stirring to afford 87% yield of the desired product (Table1, entry 3).

Encouraged by the above studies, we explored the generality and scope of the reaction by using diverse salicylaldehydes **1** and a variety of benzyl chlorides **2** under the optimized conditions and results are summarized in Table 2. The results show that both electron-withdrawing and -donating groups could be tolerated in salicylaldehydes **1** as well as benzyl chlorides **2** as they reacted to give good to excellent yields of the desired products **3**. A variety of functional groups such as Me, OMe, tertiary butyl, Br, Cl, and F are compatible with the present protocol. However, salicylaldehydes **1** or benzyl chlorides **2** with an electron-donating group afforded slightly higher yields (Table 2, entries **3b**, **3c**, **3d**, **3f, 3g**, **3k**, **3l** and **3p**) as compared to those bearing an electron-withdrawing group (Table 2, entries **3e**, **3h**, **3i** and **3j**). The present carbonylative annulation method also works well with 2-hydroxy-1-naphthaldehyde, 3,5-di-tertiary butyl salicylaldehyde, and 1-chloromethylnaphthalene (Table 2, entries **3m**–**o**). Moreover, the reaction is also satisfactorily applicable to chloromethylheteroarenes (Table 2, entries **3q** and **3r**). The exclusive formation of products **3a-r** (Table 2) demonstrates the high regioseletivity of the present carbonylative annulation reactions.

On the basis of the above observations and the literature precedents,[1b,h,j,8,21m,24] we propose a plausible mechanism for the formation of 3-arylcoumarins **3** as depicted in Scheme 2. According to the previously reported mechanism, palladium acetate is reduced to Pd^0 catalyst, which undergoes oxidative addition with benzyl chloride **2** to generate aromatic organopalladium species **5**.[24] *N*-formylsaccharin is decomposed to CO with Na_2CO_3, which reacts with aromatic organopalladium species **5** to form acylpalladium complex **6**. The nucleophilic reaction of salicylaldehyde **1** with acylpalladium complex **6**

Table 2 Substrate scope for the synthesis of 3-arylcoumarins from salicylaldehydes and benzyl chlorides[a]



[a] Reaction conditions: salicylaldehyde **1a** (1 mmol), benzyl chloride **2** (1 mmol), *N*-formylsaccharin as a CO surrogate (2.5 mmol), xantphos (5 mol%), $Pd(OAc)_2$ (3 mol%), Na_2CO_3 (3 mmol), DMSO (3 mL), N_2 atmosphere, at 85 °C for 10-11 h. (See the ESI for a general procedure and characterization of the products **3**). [b] All compounds are known and were characterized by comparison of their spectral data with those reported in the literature.[23,24,26] Yields of the pure isolated products **3** are reported.

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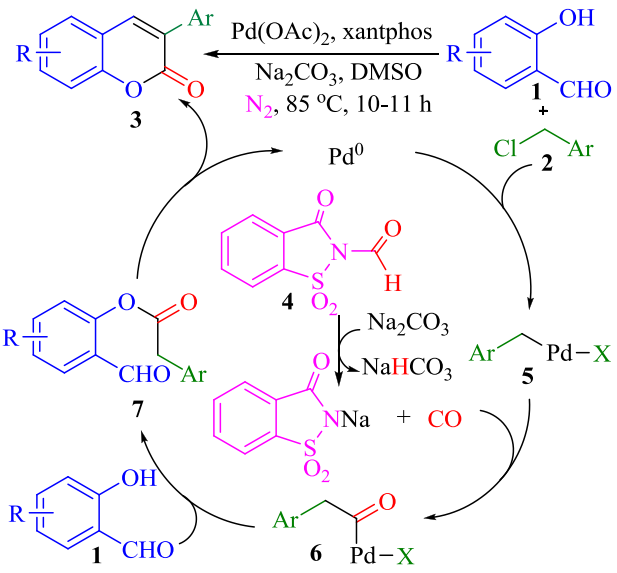
eliminates 2-formylphenyl phenylacetate **7**, which in situ undergoes the intramolecular condensation[27] to afford the desired 3-arylcoumarins **3**.



Scheme 2 A plausible mechanism for the formation of 3-arylcoumarins.

Conclusions

In conclusion, we have developed a novel and highly efficient one-pot Pd-catalysed carbonylative cyclisation of salicylaldehydes with benzyl chlorides to afford 3-arylcoumarins using *N*-formylsaccharin as a CO surrogate. The protocol offers a superior alternative to access 3-arylcoumarins, mainly because it utilizes a solid, readily available, and easy to handle *N*-formylsaccharin as the CO source in the present carbonylative annulation reaction.

Conflicts of interest

There are no conflicts of interest to declare.

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Graphical Abstract

Pd-catalysed carbonylative annulation of salicylaldehydes with benzyl chlorides using *N*-formylsaccharin as a CO surrogate

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A highly efficient synthesis of 3-arylcoumarins by Pd-catalysed carbonylative cyclisation of salicylaldehydes with benzyl chlorides using *N*-formylsaccharin as a CO source is developed.