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Pd(II)-catalysed *o*-aroylation of directing arenes using terminal aryl alkenes and alkynes†

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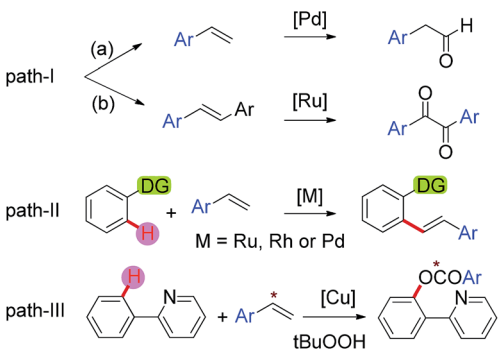
A substrate-directed Pd-catalysed *o*-aroylation strategy has been demonstrated using new aroyl surrogates *viz.* terminal aryl alkenes and alkynes in the presence of TBHP. By a subtle change in catalyst from Cu to Pd, a differential selectivity is observed. While terminal aryl alkenes/alkynes in the presence of Cu/TBHP are reported to act as *o*-aryloxy (ArCOO–) sources, the use of Pd/TBHP installs an aroyl (ArCO–) group at the *ortho* position with respect to the directing arenes.

Introduction

The development of efficient and new strategies for the construction of carbon–carbon (C–C) bonds is of immense interest to synthetic chemists. Formation of complex molecular architecture starting from simple molecules has been previously achieved *via* various classical approaches like nucleophilic additions, substitutions, Friedel–Craft type reactions, pericyclic reactions and even transition metal-catalysed cross-coupling approaches. Of late extensive investigation on transition metal-catalysed C–H bond activation strategies have greatly revolutionalised the C–C bond forming processes. The direct use of C–H bonds to generate C–C bonds is highly desirable since it has the potential to streamline synthetic schemes by shortening the number of synthetic steps and thus maintaining better atom economy of the processes. In particular, most C–H bond functionalisations processes rely on two elegant approaches *viz.* directing-group assisted C–H functionalisation[1] or cross-dehydrogenative coupling (CDC).[2]

Aryl alkenes are susceptible to undergo Wacker type oxidation to give phenylacetaldehyde[3] (Scheme 1, path-I(a)) while diarylethenes are reported to form 1,2-diketones[4] (Scheme 1, path-I(b)) using Pd and Ru catalysts respectively. In a separate study, terminal aryl alkenes are reported to introduce a vinyl moiety at the *ortho* site of ligand directed substrates using various metal catalysts such as Rh, Ru and even Pd[5] as shown in Scheme 1, path-II. Very recently our group have demonstrated a Cu(II)-catalysed *o*-benzoxylation of 2-phenylpyridine using both terminal aryl alkenes and alkynes as arylcarboxy (ArCOO–) surrogates as shown in Scheme 1, path-III.[6]

Catalyst-controlled selectivity during directed or non-directed C–C or C-heteroatom bond formation is not unprecedented in literature. In one of our recent report during the synthesis of 2-aminobenzothiazoles from 2-halothioureas, Cu preferred dehalogenative path while Pd followed C–H activation path.[7] Differential reactivity is also observed during directed *o*-functionalisation of 2-phenylpyridine with alkylbenzenes, while Pd catalyst is reported to give *o*-aroylated (ArCO–) product,[8] Cu catalyst installs an aryl carboxy (ArCOO–) group at the *ortho* site.[9] Taking cues from these literature reports on catalyst-controlled selectivities and from our recent success on transition metal catalysed *ortho* C–H functionalisations,[6,8] we thought to implement Pd catalyst during the reaction between 2-phenylbenzothiazole and terminal aryl alkenes. Now the query arises whether this catalytic condition provides *o*-vinylation as reported with catalysts like Ru, Rh and Pd or *o*-benzoxylation as has been demonstrated with Cu catalyst or all together a differential reactivity leading to a new product may be observed.



Scheme 1 Catalyst-controlled selectivity of alkenes oxidation.

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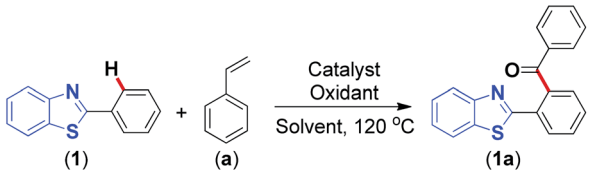
Results and discussion

With the above possibilities in mind, an initial trial reaction was performed with 2-phenylbenzothiazole (**1**) (1 equiv.) and styrene (**a**) (2.5 equiv.) in the presence of catalyst $Pd(OAc)_2$ (5 mol%) and TBHP in decane (5–6 M) (2 equiv.) in chlorobenzene at 120 °C. Surprisingly, the reaction gave a *o*-aroylated product (2-(benzo-[*d*]thiazol-2-yl)phenyl)(phenyl)methanone (**1a**) in a mere yield of 25%. This result is contrary to the previous substrate directed vinylation using Pd catalyst, of course a different combinations of oxidants are used.[5d] Synthesis of aroyl ketones *via* ligand directed *ortho* C–H functionalisation using various aroyl surrogates are well documented in literature. In recent times, a number of *o*-aroylation protocols of directing arenes have been reported between *ortho* C–H bonds with various aroyl sources *viz.* aldehydes[10] (Scheme 2, path-a), benzyl alcohols[11] (Scheme 2, path-b), alkylbenzenes[8a,12] (Scheme 2, path-c) diketones[13] (Scheme 2, path-d) and carboxylic acids[14] (Scheme 2, path-e) for the synthesis of aryl ketones. Decarboxylative *o*-aroylation protocols using a range of directing arenes have also been reported using α-keto acids as aroyl equivalents as shown in Scheme 2, path-f.[15] Very recently aryl methyl amines[16] and benzyl ethers[17] are introduced as new *o*-aroyl sources during Pd-catalysed substrate-directed processes as illustrated in Scheme 2, path-g and path-h. However, the use of terminal aryl alkenes as aroyl surrogate using Pd-catalyst substrate directed processes is not reported till date.[18]

Encouraged by this unprecedented result, a set of reactions were performed by varying reaction parameters to achieve the best possible yield of *o*-aroylated product (**1a**). Among the various Pd catalysts screened, $Pd(OAc)_2$ (Table 1, entry 1) was found to be superior (25%) over other catalysts such as $PdCl_2$ (17%), $Pd(TFA)_2$ (9%), $PdCl_2(PPh_3)_2$ (12%) as shown in Table 1, entries 1–4. An increase in the catalyst loading from 5 to 10 mol%, the product yield improved from 25% to 42% (Table 1, entry 5). Interestingly, when the oxidant quantity (TBHP in decane) was increased by two fold, the yield improved upto 57% (Table 1, entry 6). A further improvement in the yield (63%) was observed when the reaction was performed with 5 equiv. of oxidant. The use of an excess (beyond 5 equiv.) of TBHP has no substantial effect on the product yield. The nature of oxidant and their medium of storage have profound effect on the product yield. For instance, when an aqueous TBHP was used *in lieu* of a decane TBHP the yield dropped to 29% whereas aqueous H_2O_2 failed to produce the expected product (Table 1, entries 8 and 9). The reaction failed to afford any desired product either in the absence of catalyst or the oxidant. In a quest to improve the yield further various solvents *viz.* THF, DMF, DMSO, 1,4-dioxane and DCE were screened (Table 1, entries 10–14) but all were found inferior to chlorobenzene. A decrease in reaction temperature from 120 °C to 100 °C had an adverse effect on the product yield (53%). Finally, a mixture of 2-phenylbenzothiazole (**1**) (1 equiv.) and styrene (**a**) (2.5 equiv.), $Pd(OAc)_2$ (10 mol%) and TBHP in decane (5 equiv.) in chlorobenzene at 120 °C was chosen as the best optimised reaction conditions (Table 1, entry 7).

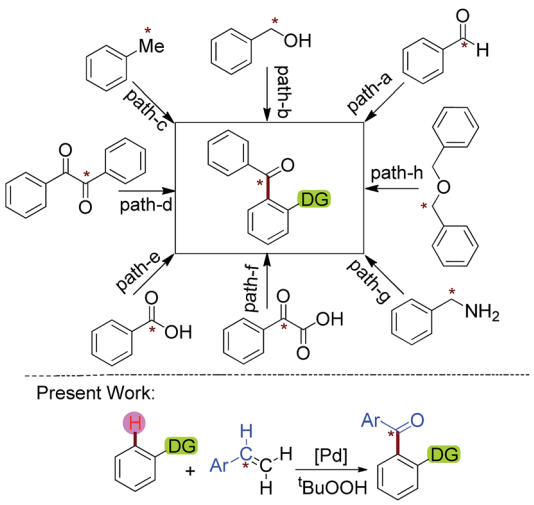
After establishing the optimised condition, the present methodology was then implemented on 2-phenylbenzothiazole (**1**) with a variety of terminal alkenes. Terminal aryl alkenes possessing both electron-donating and electron-withdrawing substituents coupled efficiently with the directing substrate (**1**). Terminal aryl alkenes having weekly activating substituent *p*-Me (**b**) efficiently reacted with (**1**) giving 61% yield of (**1b**) while strongly activating substituent *p*-OMe (**c**) provided lower yield (48%) of the corresponding product (**1c**) as shown in

Table 1 Screening of reaction conditions[a,b]



Entry	Catalyst (mol%)	Oxidant (equiv.)	Solvent	Yield (%)
1	$Pd(OAc)_2$ (5)	TBHP (2)	PhCl	25
2	$PdCl_2$ (5)	TBHP (2)	PhCl	17
3	$Pd(TFA)_2$ (5)	TBHP (2)	PhCl	9
4	$PdCl_2(PPh_3)_2$ (5)	TBHP (2)	PhCl	12
5	$Pd(OAc)_2$ (10)	TBHP (2)	PhCl	42
6	$Pd(OAc)_2$ (10)	TBHP (4)	PhCl	57
7	$Pd(OAc)_2$ (10)	TBHP (5)	PhCl	63
8	$Pd(OAc)_2$ (10)	TBHP (5)[c]	PhCl	29
9	$Pd(OAc)_2$ (10)	H_2O_2	PhCl	00
10	$Pd(OAc)_2$ (10)	TBHP (5)	THF	<9
11	$Pd(OAc)_2$ (10)	TBHP (5)	Dioxane	43
12	$Pd(OAc)_2$ (10)	TBHP (5)	DMF	27
13	$Pd(OAc)_2$ (10)	TBHP (5)	DMSO	33
14	$Pd(OAc)_2$ (10)	TBHP (5)	DCE	52

[a] Reaction conditions: 2-phenylbenzothiazole (**1**), (1 equiv., 0.5 mmol), styrene (**a**) (2.5 equiv., 1.25 mmol), and TBHP in decane (5–6 M) (5 equiv., 500 μL) in chlorobenzene (1.0 mL), 12 h. [b] Isolated yield. [c] aq. TBHP.

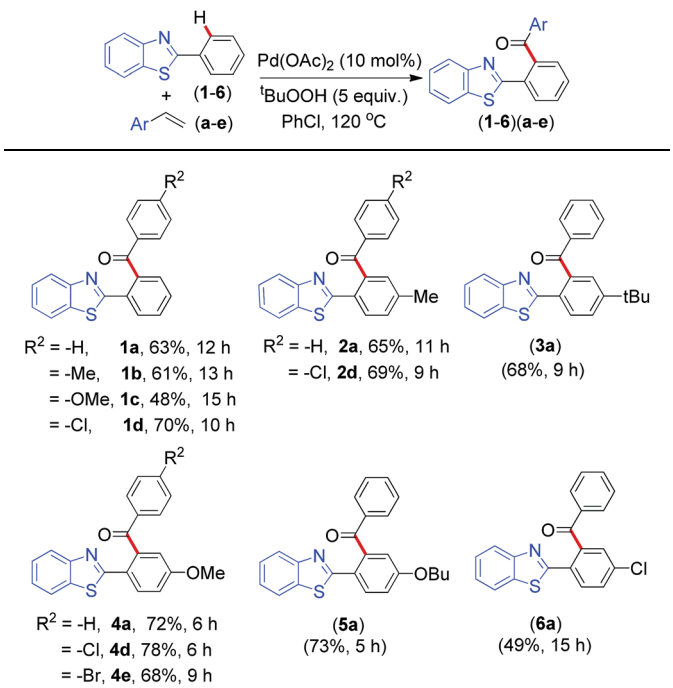


Scheme 2 Various approaches to *o*-aroylation of substrate directed arenes.

Table 2. Alkene having weekly electron withdrawing substituent *p*-Cl (**d**) showed smooth conversion with 2-phenylbenzothiazole (**1**) providing 70% yield of (**1d**). Further, this selective *o*-aroylation protocol was extended to substituted 2-phenylbenzothiazole containing both electron-donating and electron-withdrawing substituents. 2-Aryl substituted benzothiazoles with mild activating substituents in 2-phenyl ring such as *p*-Me (**2**) when treated with styrene (**a**) and *p*-Cl styrene (**d**) gave (**2a**) and (**2d**) in 65% and 69% yields respectively. Similarly, *p*-^{t}Bu (**3**) efficiently reacted with styrene (**a**) providing 68% yield of (**3a**) as shown in Table 2. Styrene containing electro-neutral –H (**a**), *p*-Cl (**d**) and *p*-Br (**e**) when treated with directing substrate (**4**) possessing a strongly electron-donating substituent *p*-OMe under the opitimised condition, all provided corresponding *o*-aroylated products (**4a**), (**4d**) and (**4e**) in good yields (Table 2). Substrate (**5**) possessing *p*-OBu group when treated with styrene (**a**), a good yield (73%) of corresponding product (**5a**) was obtained. Next, 2-phenylbenzothiazole having a weekly deactivating substituent such as *p*-Cl (**6**) when treated with styrene (**a**), a moderate yield (49%) of (**6a**) was obtained.

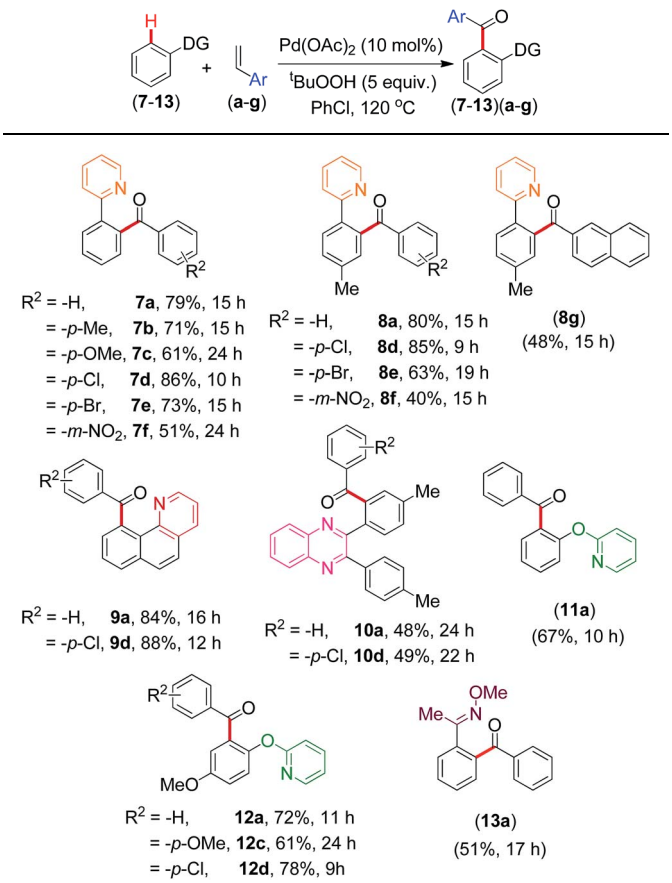
After successfully achieving *o*-aroylation of benzothiazoles (Table 2) using terminal alkenes as aroyl surrogates the protocol was then extended to other substrate directed arenes. At first, commonly investigated N-directed arene, 2-phenyl pyridine (**7**) when reacted with styrene (**a**) under the identical condition, a good yield (79%) of (**7a**) was obtained after 15 h. As demonstrated in Table 3, styrenes bearing both activated substituents such as *p*-Me (**b**), *p*-OMe (**c**) and deactivated substituents *p*-Cl (**d**), *p*-Br (**e**) and *m*-NO_2 (**f**) when treated with 2-phenyl pyridine (**7**), all provided modest to good yields of their corresponding *o*-aroylated products (**7b–7f**) respectively. Similarly, *p*-methyl-2-phenylpyridine (**8**) also reacted with styrene (**a**) and substituted styrenes such as *p*-Cl (**d**), *p*-Br (**e**), *m*-NO_2 (**f**) and even 2-napthylstyrene (**g**) providing their desired *o*-aroylated products (**8a**), (**8d**), (**8e**), (**8f**) and (**8g**) as shown in Table 3. Use of styrenes (**a**) and (**d**) as *o*-aroyl equivalents have been demonstrated through successful aroylation of benzoquinoline (**9**) giving products (**9a**) and (**9d**) respectively as shown in Table 3. This strategy was found to be successful with another directing arene 2,3-diphenylquinoxaline containing *p*-Me substituent (**10**) at its 2,3-aryl rings providing their desired *o*-aroylated products (**10a**) and (**10d**) respectively when treated with styrene (**a**) and its *p*-Cl derivative (**d**). Interestingly, arenes possessing removable directing groups such as 2-aroyloxypyridine (**11–12**) and acetophenone *O*-methyl oxime (**13**) were successfully *o*-aroylated under the present optimised conditions. 2-Aroyloxypyridine containing electron neutral –H (**11**) and *p*-OMe (**12**) substituents

Table 2 Scope of *o*-aroylation of 2-arylbezthiazoles with terminal alkenes[a,b]



[a] Reaction conditions: 2-arylbenzothiazole (**1–6**), (0.5 mmol), alkenes (**a–e**) (1.25 mmol), and TBHP in decane (5–6 M) (500 μL) in chlorobenzene (1.0 mL), 120 °C, 5–15 h. [b] Yields of isolated product.

Table 3 Scope of directing arenes for *o*-aroylation with terminal alkenes[a,b]

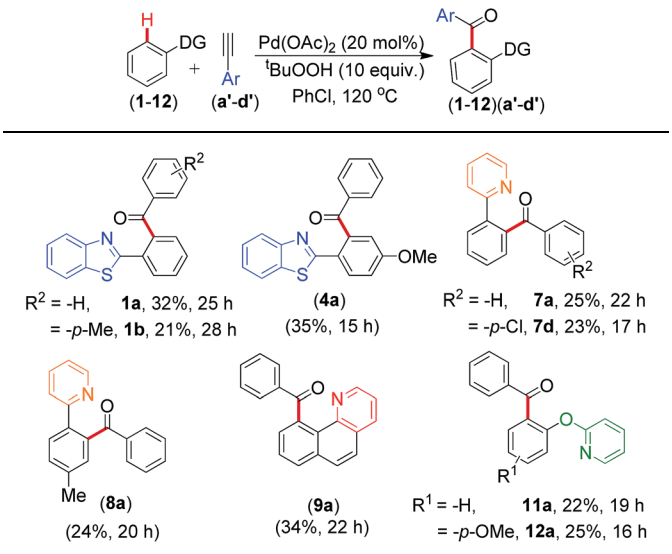


[a] Reaction conditions: directing arenes (**7–13**), (0.5 mmol), alkenes (**a–g**) (1.25 mmol), and TBHP in decane (5–6 M) (500 μL) in chlorobenzene (1.0 mL), 120 °C, 9–24 h. [b] Yields of isolated product.

reacted with styrene derivatives (**a**), (**c**) and (**d**) providing their corresponding *o*-aroylated products (**11a**), (**12a**), (**12c–d**) respectively. Similarly, acetophenone *O*-methyl ketoxime (**13**) when reacted with styrene (**1**) gave decent yield of the *o*-aroylated product (**13a**).

Alkynylation of sp^2 and sp^3 C–H bonds using terminal alkynes by metal catalysed cross coupling reactions are well investigated.[19,20] Specially, phenylacetylenes are used as *o*-alkenylated partner in the chelation assisted C–H activation process.[20c] Besides terminal alkenes, terminal alkynes are found to be the efficient source of carboxy group under Cu/TBHP system.[6] So in next approach, we wish to see if phenyl acetylene can act as a benzoxy source (PhCOO–) or it will be a source of aroyl group (PhCO–) similar to styrene as discussed above. Thus when (**1**) and phenyl acetylene (**a′**) were reacted under the identical conditions to that of styrene (**a**), surprisingly *o*-aroylated product (**1a**) was again obtained but in a poor yield of 25%. Hence, further optimisation reactions were performed to get an improved yield. Even by increasing the catalyst quantity 20 mol% and TBHP (10 equiv.), the yield did not improve beyond 32%. Thus high catalytic loading (20 mol%) condition was chosen and applied for all aryl acetylenes towards substrate directed *o*-aroylation. Subsequently substrate 2-phenyl benzothiazole (**1**) when treated with *p*-Cl phenyl acetylene (**d′**) under the modified optimised condition, gave (**1d**) in 35% yield. Other directed arenes such as 2-phenylpyridine derivatives (**7**) and (**8**), benzoquinoline (**9**), 2-aroyloxypyridines (**11**) and (**12**) when treated with various terminal alkynes (**a′**) and (**d′**), yielded their corresponding aroylated products in the range of 21–35% only as shown in Table 4. Alkynes provided much lower yields than alkenes because of possible homo-coupling which make the aroyl sources unavailable for further *o*-aroylation reactions.

Table 4 Scope of substrate directed arenes for *o*-aroylation with terminal alkynes[a,b]

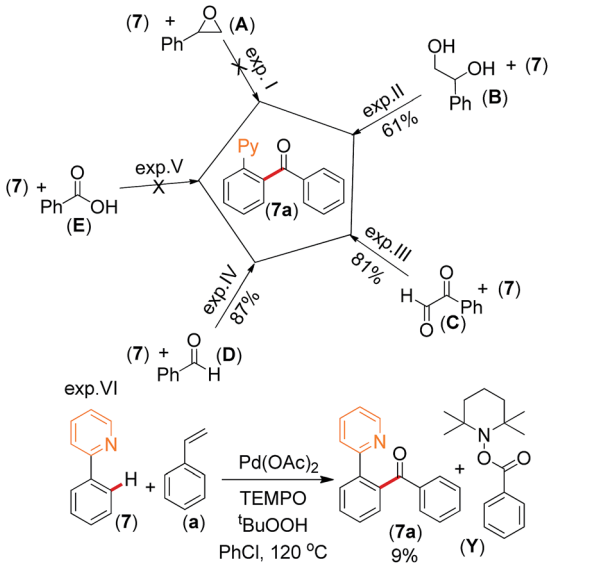


[a] Reaction conditions: directing arenes (**1–12**), (0.5 mmol), alkynes (**a′–d′**) (1.25 mmol), and TBHP in decane (5–6 M) (500 μL) in chlorobenzene (1.0 mL), 120 °C, 15–28 h. [b] Yields of isolated product.

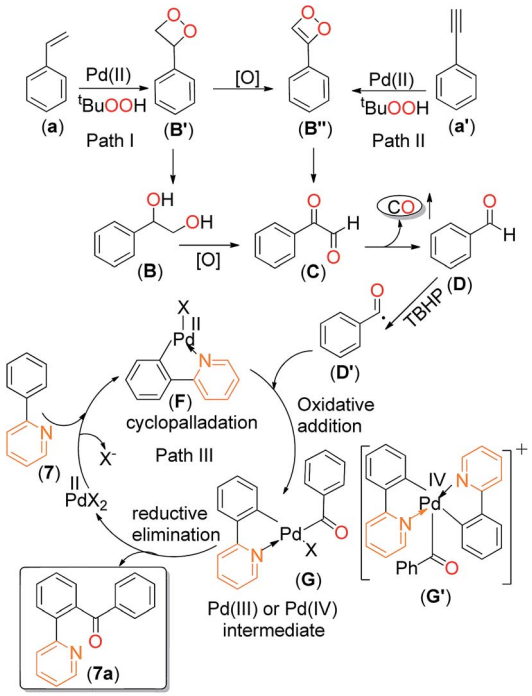
Several control reactions were carried out to illustrate a plausible mechanistic path for this Pd-catalysed aroylation. Styrene in the presence of oxidant TBHP may form styrene oxide (**A**) or 1-phenyl-1,2-ethane diol (**B**) in the medium. To ascertain which one of this (**A** or **B**) intermediate is involved, both were reacted separately with 2-phenylpyridine (**7**) under otherwise identical conditions. In the former case (Scheme 3, experiment I) no desired product was obtained whereas the later (Scheme 3, experiment II) provided 61% yield of the desired product (**7a**) suggesting (**B**) as one of the possible active intermediates in the reaction. Analysis of the crude reaction mixture between styrene, TBHP and Pd after one hour divulged the presence of phenylglyoxal (**C**), benzaldehdye (**D**) and benzoic acid (**E**) in the medium.

Therefore (**C**), (**D**) and (**E**) are other possible intermediates (in addition to (**B**)) which may lead to *o*-aroylation of (**7**), an observation consistent with our recent result.[6,20] To confirm the other possible active intermediates, 2-phenylpyridine (**7**) was treated separately with (**C**), (**D**) and (**E**) under identical conditions. While reaction with (**C**) (Scheme 3, experiment III) and (**D**) (Scheme 3, experiment IV) provided product (**7a**) in 81% and 87% yields respectively, benzoic acid (**E**) (Scheme 3, experiment V) failed to give any trace of (**7a**). A possible pathway for the formation of phenylglyoxal (**C**), benzaldehyde (**D**), benzoic acid (**E**) (except (**B**)) from styrene has been recently demonstrated by us.[6,21] To deduce the nature of the reaction a standard reaction was carried out in the presence of a radical quencher, TEMPO. Detection of TEMPO-ester (**Y**) along with substantial drop in product yield (9%) of (**7a**) suggests the radical nature of the reaction (Scheme 3, experiment VI). In fact all the active intermediates (**B**), (**C**) and (**D**) are capable of generating aroyl radical under the reaction conditions toward *o*-aroylation.

Based on results obtained from controlled experiments and recent literature,[6,22,23] a plausible mechanism has been proposed for this transformation as shown in Scheme 4. In



Scheme 3 Various control experiments with 2-phenylpyridine (**7**).



Scheme 4 Plausible mechanism for *o*-aroylation.

path-I, styrene possibly form a four-membered dioxetane intermediate (**B′**) by the action of Pd/TBHP. The ring opening of the intermediate (**B′**) may give 1-phenyl-1,2-ethanediol (**B**), which readily oxidised to give phenylglyoxal (**C**) under the oxidative reaction condition. Alternatively, cyclic intermediate (**B′**) may undergo oxidation to generate another cyclic intermediate (**B″**) which may also be directly obtained from phenylacetylene (**a′**) (Scheme 4, path II). Formation of intermediate (**B″**) from (**B′**) has been reported by Jiao *et al.*[24] The ring fragmentation of intermediate (**B″**), may provide phenylglyoxal (**C**). Intermediate (**C**) in presence of TBHP leads to the formation of benzyldehyde (**D**) with the extrusion of CO. Further benzaldehyde (**D**) in presence of TBHP leads to the formation of benzoyl radical (**D′**). In path-III, cyclopalladation of the directing arene (**7**) leads to the formation of Pd–substrate complex (**F**). In the next step, the oxidative addition of *in situ* generated benzoyl radical (**D′**) to Pd–substrate complex (**F**) leads to the formation of a Pd(IV)[22] or a dimeric Pd(III)[25] intermediate (**G**). During the course of this reaction, the formations of the cationic Pd(IV) intermediate (**G′**) has been detected by the ESI/MS analysis of reaction aliquot (see ESI†). Finally, a reductive elimination of the Pd from (**G**) leads to C–C bond formation to afford *o*-aroylated product (**7a**) along with the regeneration of the Pd(II) catalyst for the next cycle.

Conclusions

We have developed a new, efficient Pd-catalysed directing group assisted aroylation of arenes using terminal alkenes and alkynes as the new aroyl surrogate. Based on the detection of reaction intermediates and taking cues from the literature a radical mechanism has been proposed. This strategy have been implemented to a wide range of ligand directed substrates and afforded modest to good yields. This strategy showed a good tolerance of functional groups. Differential selectivities of Cu and Pd have been demonstrated; while Cu/TBHP combination installs an *o*-aryloxy (ArCOO–) the use of Pd/TBHP incorporate an *o*-aroyl (ArCO–) group using both alkenes and alkynes.

General procedure for the synthesis of (2-(benzo[*d*]thiazol-2-yl)phenyl)(phenyl)methanone (**1a**) from 2-phenylbenzo[*d*]thiazole (**1**) and styrene (**a**)

An oven-dried flask was charged with 2-phenylbenzo[*d*]thiazole (**1**), (0.5 mmol, 0.105 g), styrene (**a**) (1.25 mmol, 0.13 g), $Pd(OAc)_2$ (10 mol%, 0.011 g), TBHP in decane (5–6 M) (500 μL) in chlorobenzene (1 mL). The flask was fitted to a condenser and the resultant reaction mixture was stirred in a preheated oil bath at 120 °C for 12 h. After stipulated time, the reaction mixture was cooled down to room temperature and diluted with ethyl acetate (1 × 10 mL). This diluted reaction mixture passed through a celite bed and subsequently washed with additional (2 × 10 mL) ethyl acetate. The combined organic layer then washed with 10% aq. saturated solution of $NaHCO_3$ (2 × 5 mL) followed by water (2 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was further purified by silica gel column chromatography using (hexane/ethylacetate = 19 : 1) as eluent to yield pure [2-(benzo[*d*]thiazol-2-yl)phenyl](phenyl)methanone (**1a**, 0.198 g, 63%) as a gummy material.

General procedure for the synthesis of phenyl(2-(pyridin-2-yl)phenyl)methanone (**7a**) from 2-phenylpyridine (**7**) and phenylacetylene (**a′**)

An oven-dried flask was charged with phenyl acetylene (**a′**), (0.125 mmol, 0.128 g), 2-phenylpyridine (**1**), (0.5 mmol, 0.078 g), $Pd(OAc)_2$ (20 mol%, 0.022 g), TBHP in decane (5–6 M) (1.0 mL) in chlorobenzene (1 mL). The flask was fitted to a condenser and the resultant reaction mixture was stirred in a preheated oil bath at 120 °C for 25 h. After stipulated time, the reaction mixture was cooled down to room temperature and diluted with ethyl acetate (1 × 10 mL). This diluted reaction mixture passed through a celite bed and subsequently washed with additional (2 × 10 mL) ethyl acetate. The combined organic layer then washed with 10% aq. saturated solution of $NaHCO_3$ (2 × 5 mL) followed by water (2 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was further purified by silica gel column chromatography using (hexane/ethylacetate = 9 : 1) as eluent to yield pure phenyl(2-(pyridin-2-yl)phenyl)methanone (**7a**, 0.083 g, 32%) as brown solid.

Acknowledgements

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