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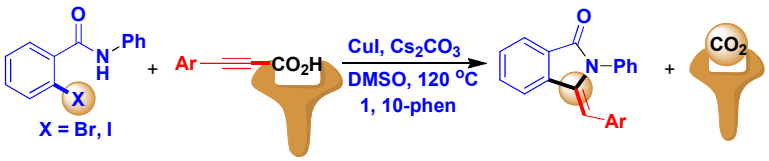

A Cu-catalysed synthesis of substituted isoindolin-1-one has been achieved via decarboxylative alkynylation–heteroannulation path.

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ARTICLE TYPE

A Cu-catalysed synthesis of substituted 3-methyleneisoindolin-1-one†

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A Cu(I)-catalysed synthesis of substituted 3-methyleneisoindolin-1-ones using alkynyl acids as alkyne source has been developed. The reaction involves decarboxylative cross-coupling of 2-halobenzamides with aryl alkynyl acids followed by 5-exo-dig heteroannulation. While reactions of 2-iodo benzamides proceeded without ligand, for 2-bromo substrates assistance of a ligand is essential.

Introduction

In modern synthetic organic chemistry, transition metal catalysed decarboxylative cross-coupling reactions using carboxylic acids have received much attention because of their ready availability and easy handling. In general, such reactions proceed via the *in situ* generation of organometallic species along with the extrusion of CO_2 as the side product. This reactive organometallic intermediate then couples with appropriate counterparts providing alternative routes to C–C or C–heteroatom bonds.[1] As one of the members of carboxylic acids, alkynyl carboxylic acids are potential candidates for cross–coupling reactions installing an alkynyl group into the substrates. Unlike aryl or vinyl carboxylic acids, decarboxylative coupling of alkynyl carboxylic acids can be initiated by a single catalytic system.[1,2] This strategy has been demonstrated by Xue group for the synthesis of diaryl alkynes via a copper catalysed decarboxylative cross–coupling of alkynyl carboxylic acids with aryl halides.[2a] Not merely restricted to the synthesis of internal alkynes, the above strategy has much more to offer by manipulation of the alkynyl group. One way to achieve this is to activate the *in situ* generated alkynyl group with a soft metal followed by an intramolecular nucleophilic attack resulting into a heterocycle. We envisaged that 2-halo benzamide with an alkynyl acid under an appropriate condition may result either 3-methylene-isoindolin-1-one via a 5-exo-dig cyclisation or substituted isoquinolin-1-one via a 6-endo-dig cyclisation.[3]

We initiated our investigation by treating 2-bromobenzamide (**1**) with phenyl propiolic acid (**a**) (1.2 equiv.) in the presence of CuI (10 mol %), Cs_2CO_3 (1.5 equiv.) in DMF solvent at 120 °C. To our delight, the reaction resulted in a selective formation of 5-exo-dig product, 3-phenylmethylene isoindolin-1-one (**1a**) in 32% yield. Herein, we report the synthesis of 3-methyleneisoindolin-1-ones involving decarboxylative cross-coupling of alkynyl carboxylic acids and 2-halo benzamides with concurrent cyclisation.

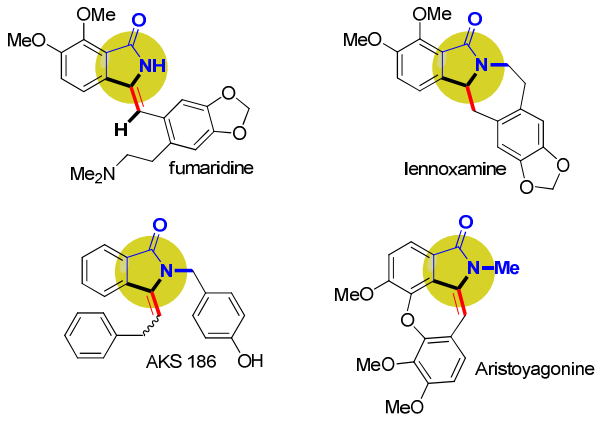

Fig. 1 Natural products and biologically active compounds containing 3-methyleneisoindolin-1-one.

Substituted 3-methyleneisoindolin-1-ones are medicinally important heterocyclic scaffold prevalent in many natural products and pharmaceuticals.[4] Apart from their significant biological profile; they also find applications in material chemistry.[5] Some of the natural products and biologically active molecules having 3-methyleneisoindolin-1-one as the core unit are shown in Figure 1. Due to the myriad of applications of this important motif there has been development of numerous synthetic protocols for their synthesis. The traditional methods for the synthesis of 3-methyleneisoindolin-1-one include Horner-Wadsworth-Emmons type of condensation,[6] addition/dehydration of phthalimides,[7] 5-exo-dig cyclisation of preformed 2-alkynylbenzamides[3a,b,c,8] and base triggered addition to benzonitriles.[9] However, they are associated with poor regioselectivity in case of unsymmetrical substrates or require number of additional synthetic steps. These shortcomings stimulated the emergence of transition metal catalysed reactions such as Heck-Suzuki-Miyaura domino reactions involving ynamides (path a, Scheme 1),[10] Sonagashira coupling-

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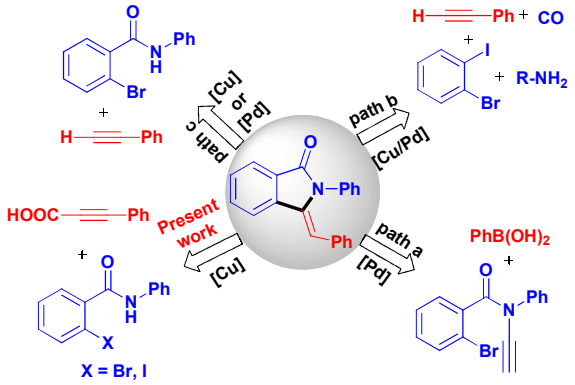
carbonylation-hydroamination of *ortho* dihalo arenes (path b, Scheme 1)[11] and Ullmann coupling-hydroamination of *ortho* halo benzamides (path c, Scheme 1).[12] Apart from the cross-coupling strategies, recently You *et al*. developed a Cu mediated approach to 3-methylene isoindolin-1-one that proceeds via tandem oxidative cross-coupling between (Csp^2–H) of arenes with terminal alkynes followed by an intramolecular annulation.[13] In the latter two cross-coupling strategies (path b and c, Scheme 1), terminal alkynes have been utilised for the initial alkynylation purpose. However, the use of their acid derivatives to serve as alkyne surrogates via decarboxylative C–C bond formation for the synthesis of 3-methylene isoindolin-1-one is the first precedence of its kind.[14] The use of alkynyl carboxylic acids as alternatives to terminal alkynes are advantageous because of their superior reactivity and ready availability.[15] They are less susceptible to homocoupling; thereby suppressing the competing diyne byproduct in Sonogashira reaction.[16]

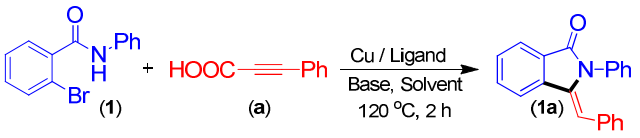


Scheme 1. Various approaches for synthesis of 3-methyleneisoindolin-1-one.

Results and Discussion

Encouraged by the initial success, further optimisations were carried out to attain an improved yield of the product (**1a**). Several reports revealed that for substrates undergoing metal catalysed cross-coupling reactions involving bromo substituent, assistance of a ligand often facilitates the process.[17] Furthermore, an orthogonal selectivity has been demonstrated during a ligand assisted Cu-catalysed reaction.[17f,i] A ligand functions by inhibiting the aggregation of the metal and improve the solubility of the catalyst/co-catalyst; thereby resulting in better catalytic activity of the metal. Taking cues from the aforementioned reports, when the coupling between 2-bromobenzamide (**1**) (1 equiv.) and phenyl propiolic acid (**a**) (1.2 equiv.) was performed in the presence of ligand 1,10-phenanthroline (10 mol%), CuI (10 mol%), Cs_2CO_3 (1.5 equiv.) the product (**1a**) was obtained in an improved yield of 59% (entry 2, Table 1). During the catalyst screening CuI was found to be superior over all other Cu(I) and Cu(II) salts such as CuBr, CuCl, $Cu(OAc)_2$, $CuCl_2$, $CuBr_2$ tested (entries 3–7, Table 1). Replacement of base Cs_2CO_3 with other inorganic bases such as K_2CO_3, K_3PO_4 resulted in lower yields (entries 8 and 9, Table 1). The use of organic base like NEt_3 was found to be almost ineffective in bringing about the transformation (entry 10, Table 1). Other ligands such as diethylmalonate (DEM), L-proline, tetramethylethylenediamine (TMEDA), dimethylethylenediamine (DMEDA) tested were found to be inferior to 1,10-phenanthroline (entries 11–14, Table 1). Further, improvement in the yield (69%) was observed when the reaction was performed in DMSO instead of DMF (entry 15, Table 1). Other solvents such as 1,4-dioxane, 1,2-dichloroethane (DCE) and *N*-methyl-2-pyrrolidone (NMP) were found to be unsuitable for this transformation (entries 16–18, Table 1). Thus, CuI (10 mol%), 1,10-phen (10 mol%), Cs_2CO_3 (1.5 equiv.) in DMSO solvent at 120°C was found to be the optimal condition and rest of the reactions were performed under exactly identical conditions.

Table 1 Optimisation of reaction conditions[a]



Entry	Catalyst (mol %)	Base (equiv.)	Ligand (mol %)	Solvent	Yield (%)[b]
1	CuI (10)	Cs_2CO_3 (1.5)	-	DMF	32
2	CuI (10)	Cs_2CO_3 (1.5)	1,10-phen (10)	DMF	59
3	CuBr (10)	Cs_2CO_3 (1.5)	1,10-phen (10)	DMF	51
4	CuCl (10)	Cs_2CO_3 (1.5)	1,10-phen (10)	DMF	43
5	$Cu(OAc)_2$ (10)	Cs_2CO_3 (1.5)	1,10-phen (10)	DMF	38
6	$CuCl_2$ (10)	Cs_2CO_3 (1.5)	1,10-phen (10)	DMF	40
7	$CuBr_2$(10)	Cs_2CO_3 (1.5)	1,10-phen (10)	DMF	49
8	CuI (10)	K_2CO_3(1.5)	1,10-phen (10)	DMF	53
9	CuI (10)	K_3PO_4(1.5)	1,10-phen (10)	DMF	41
10	CuI (10)	NEt_3 (1.5)	1,10-phen (10)	DMF	<5
11	CuI (10)	Cs_2CO_3 (1.5)	DEM (10)	DMF	35
12	CuI (10)	Cs_2CO_3 (1.5)	L-proline (10)	DMF	54
13	CuI (10)	Cs_2CO_3 (1.5)	TMEDA (10)	DMF	39
14	CuI (10)	Cs_2CO_3 (1.5)	DMEDA (10)	DMF	46
15	**CuI (10)**	**Cs_2CO_3 (1.5)**	**1,10-phen (10)**	**DMSO**	**69**
16	CuI (10)	Cs_2CO_3 (1.5)	1,10-phen (10)	1,4-dioxane	42
17	CuI (10)	Cs_2CO_3 (1.5)	1,10-phen (10)	NMP	49
18	CuI (10)	Cs_2CO_3 (1.5)	1,10-phen (10)	DCE	53

[a]Reactions were monitored by TLC. [b]Isolated yield.

After establishing the optimised conditions, the substrate scope for this decarboxylation-heteroannulation methodology was explored. A variety of substituted 3–arylmethylene isoindolin-1-ones has been synthesised as shown in Scheme 2. At first, the effect of substituents present on the *N*-aryl ring of benzamide was examined by reacting them with phenyl propiolic acid (**a**). The *N*-aryl ring of amide bearing electron-donating groups such as 3-Me (**2**), 3,4-diMe (**3**), 4-OMe (**4**) yielded their respective products (**2a**), (**3a**) and (**4a**) in 62%, 78% and 66% respectively (Scheme 2). While benzamides derived from aryl amines possessing moderately electron-withdrawing groups such as 4-Cl (**5**), 4-Br (**6**), 4-F (**7**) provided their corresponding isoindolin-1-one (**5a**), (**6a**) and (7**a**) in 72%, 73% and 76% yields respectively (Scheme 2). A comparison between two sets of substrates one possessing electron-donating groups and other electron-withdrawing groups shows that yields are marginally better with the latter set with the lone exception being 3,4-diMe substrate (**3**). The structure of the product (**5a**) has been confirmed by X-ray crystallography.

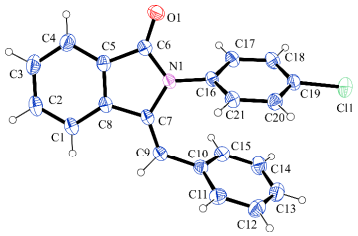
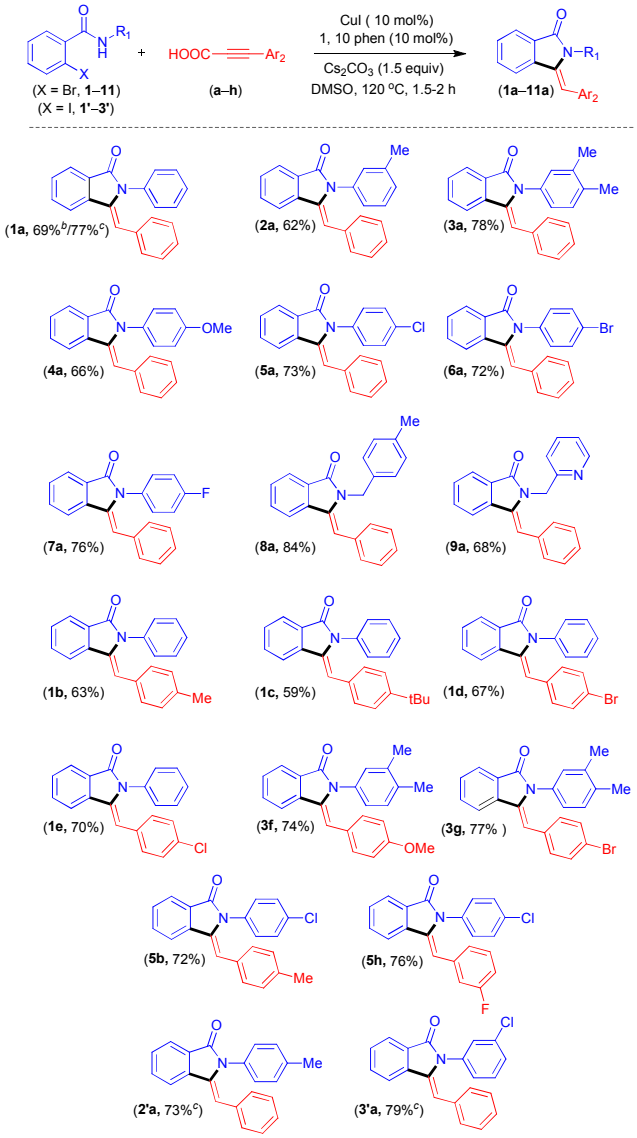


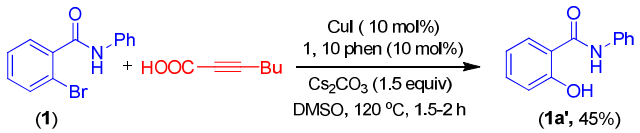
Fig. 2 ORTEP view of compound (**5a**).

Instead of an aryl group when a benzyl substituent is attached to the *N*-atom of the benzamide (**8**), the product (**8a**) was obtained in good yield (84%). However, with analogous picolinamide (**9**) there was substantial drop in the yield (68%). The variation of substituents in aryl alkynyl acids were scrutinised by reacting them with benzamide (**1**). Aryl propiolic acids possessing electron-donating groups such as 4-Me (**b**), 4-^{t}Bu (**c**) and electron-withdrawing groups such as 4-Br (**d**), 4-Cl (**e**) underwent facile reactions with (**1**) affording their respective products (**1b**), (**1c**), (**1d**) and (**1e**) in moderate yields as shown in Scheme 2.



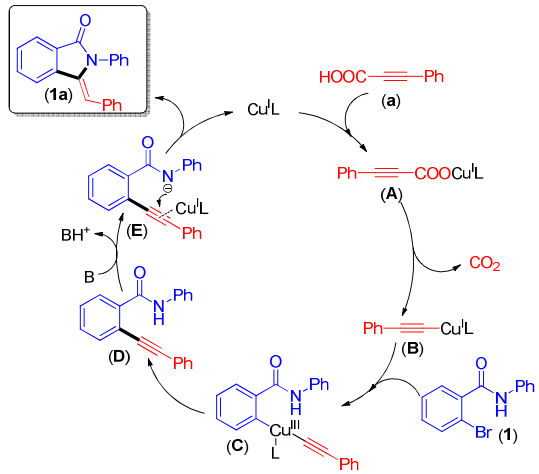
Scheme 2 Substrate scope of substituted 3-arylmethylene isoindolin-1-ones. [a]Yields of isolated pure products are reported. [b]X = Br. [c]X = I.

From the trends in products yield it is evident that no significant electronic effect of substituents present in aryl propiolic acids could be ascertained. An attempt was made to find out whether some combination of substituents present in *N*-aryl ring of the benzamides and aryl ring of alkynyl acids (based on their electronic effects) could be the most suitable for this transformation. With this motive two independent reactions were carried out with benzamide containing electron-donating 3,4-diMe group in the *N*-aryl ring (**3**) with aryl alkynyl acids bearing electron-donating 4-OMe group (**f**) and having electron-withdrawing 4-Br group (**g**). Another set of reactions were performed with benzamide possessing electron withdrawing 4-Cl group (**5**) with aryl alkynyl acids bearing electron-donating group 4-Me (**b**) and having electron-withdrawing 3-F group (**h**). However, judging by the yield pattern of products (**3f**), (**3g**), (**5b**) and (**5h**) obtained from the aforementioned combinations, again no correlation between yields and substituent effect could be arrived (Scheme 2). To check the efficacy of this transformation with aliphatic alkynyl acid a reaction was performed between 2-bromobenzamide (**1**) and 2-butynoic acid. The reaction failed to give the desired isoindolin-1-one product, instead hydroxylation *ortho* to amide (**1a′**) moiety was observed under the reaction condition (Scheme 3). Similar hydroxylation of *o*-haloanilides and *o*-halo benzamides has been observed during Cu catalysed reaction in an aqueous medium.[18] Due to lesser reactivity of bromo group towards oxidative addition with aliphatic alkyne species the hydroxylation path is preferred and the possible hydroxyl source is from the water present in the commercial grade DMSO.



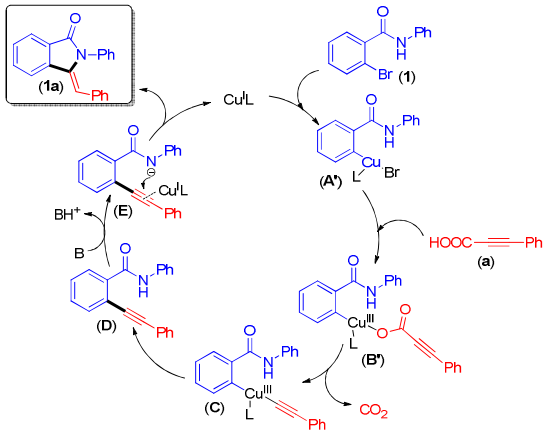
Scheme 3. Competative hydroxylation of 2-bromobenzamide.

After successful accomplishment of the present transformation with 2-bromo benzamides next we turned our attention towards more reactive 2-iodo benzamides. The reaction of 2-iodo benzamide (**1′**) with phenyl propiolic acid (**a**) under previous optimised conditions provided 3-phenylmethylene isoindolin-1-one (**1a**) in 77% isolated yield. Interestingly, the same reaction when performed in the absence of ligand 1,10-phen, proceeded smoothly virtually unaffecting the yield and reaction time. This illustrates the higher reactivity of C–I bond compared to C–Br bond towards decarboxylative C–C bond formation. Further, this ligand free condition was then applied for the reaction of 2-iodo benzamides (**2′**) and (**3′**) with phenyl propiolic acid (**a**) which provided their corresponding isoindolin-1-one products (**2′a**) and (**3′a**) in 73% and 79% yields respectively. The trend in the yields obtained from 2-iodo precursors without the involvement of ligand was found to be identical to that of 2-bromo benzamides with assistance of ligand.



Scheme 4. Plausible mechanism for the formation of 3-methyleneisoindolin-1-one.

Based on the literature reports,[19,2a,2e,14] a plausible mechanism for the formation of 3-phenylmethyleneisoindolin-1-one is outlined in Scheme 4. Initially a Cu(I) intermediate (**A**) is formed with phenyl propiolic acid (**a**). This Cu(I) species via a decarboxylative path gives Cu-alkynylide species (**B**) which undergoes oxidative addition with 2-bromobenzamide (**1**) to produce Cu(III) intermediate (**C**). Reductive elimination of Cu from (**C**) gives the *ortho*-alkynylated product (**D**). Deprotonation of the amide N–H of the intermediate (**D**) and subsequent hydroamination[20] of C–C triple bond promoted by co-ordination of Cu(I) with the alkynyl group results in the formation of 3-phenylmethyleneisoindolin-1-one (**1a**) via the intermediacy of (**E**) along with regeneration of Cu(I). The formation of intermediate species (**A**), (**B**), (**C**) and (**D**) have been detected by the ESI/MS analysis of reaction aliquot which support the proposed mechanism in Scheme 4 (see Supporting Information [SI]).



Scheme 5. Plausible mechanism for the formation of 3-methyleneisoindolin-1-one.

However an alternative mechanism involving initial oxidative addition of Cu(I) with 2-halobenzamide to give intermediate (**A′**) as proposed in Scheme 5 cannot be completely ruled out. Intermediate (**A′**) couples with phenylpropiolic acid (**a**) to give intermediate (**B′**). Loss of CO_2 from intermediate (**B′**) would give intermediate (**C**) which eventually lead to the formation of desired product (**1a**) as shown in Scheme 4.

Conclusion

In conclusion, we have developed a Cu(I)-catalysed synthesis of substituted 3-methyleneisoindolin-1-ones involving decarboxylative cross-coupling of 2-halobenzamides with aryl alkynyl acids followed by 5-exo-dig heteroannulation. In this transformation alkynyl acids have been utilised to generate alkyne intermediate for the synthesis of this important heterocycle scaffold. While reactions of 2-iodo benzamides proceeded without ligand, for 2-bromo subtrates the assistance of a ligand is essential.

General procedure for the synthesis of (*Z*)-3-benzylidene-2-phenylisoindolin-1-one (1a)

To a solution of 2-bromobenzamide (**1**) (138 mg, 0.5 mmol) in DMSO (2 mL) was added CuI (9.5 mg, 0.05 mmol), 1,10-phen (9 mg, 0.05 mmol), Cs_2CO_3 (245 mg, 0.75 mmol), phenyl propiolic acid (**a**) (87.6 mg, 0.6 mmol) and the resultant mixture was stirred in a preheated oil bath at 120 ^{o}C for 2 h. The reaction mixture was then cooled to room temperature, admixed with water (5 mL) and the product was extracted with ethyl acetate (2 x 20 mL). The organic phase was dried over anhydrous sodium sulphate and concentrated in vacuo. The crude product was purified over a column of silica gel and eluted with (19:1 hexane / ethyl acetate to give (*Z*)-3-benzylidene-2-phenylisoindolin-1-one (**1a**) (102.5 mg, 69% yield).

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