Tbai/Tbhp mediated oxidative cross coupling of ketones with phenols and carboxylic acids: Direct access to benzofurans

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TBAI/TBHP-mediated oxidative cross coupling of phenols and carboxylic acids with ketones has been reported under metal-free, base free and solvent free conditions enabling environmentally benign synthesis of aryloxyketones, acyloxyketones and benzofurans. Phenoxyketones and acyloxylcarbonyl compounds were synthesized in good to high yields, where as benzofurans were synthesiszed in moderate yields. This method is operationally simple, works under mild conditions, using commercially available as well as inexpensive TBAI and an oxidant TBHP.

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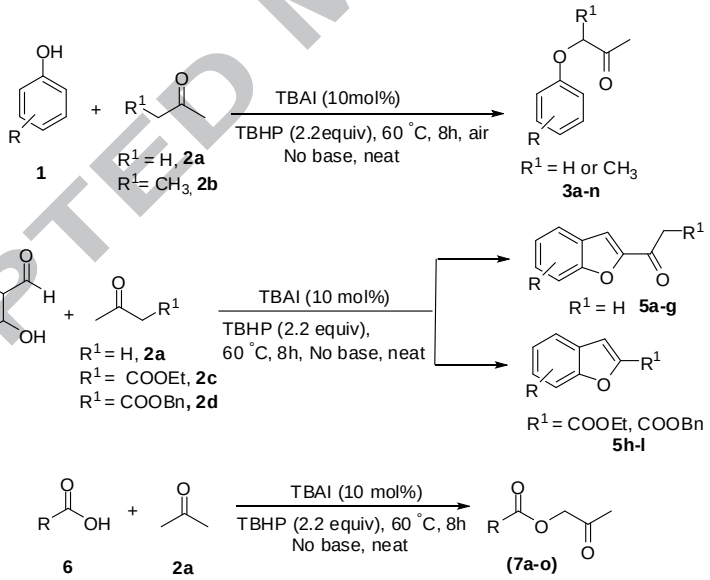

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ABSTRACT

TBAI/TBHP mediated oxidative cross coupling of phenols and carboxylic acids with ketones has been reported under metal-free, base free, solvent free conditions enabling environmentally benign synthesis of aryloxyketones, acyloxy ketones and benzofurans. Phenoxyketones and acyloxylcarbonyl compounds were synthesized in good to high yields, where as benzofurans were synthesiszed in moderate yields. This method is operationally simple, works under mild conditions, using commercially available as well as inexpensive TBAI and an oxidant TBHP.

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Introduction

There has been upsurging investigation over the past two decades on hypervalent iodine compounds as environmentally benign oxidation reagents as an alternative to rare or toxic heavy metal oxidants.[1,2] On the other hand, the stoichiometric use of hypervalent iodine reagents has been limited due to potentially explosive shock-sensitivity and poor solubility in common organic solvents.[1,2] Consequently the development of catalytic use of hypervalent iodine reactions using more expedient stoichiometric co-oxidants is needed.[3-5]

Aryloxyketones can create attractive building blocks for the synthesis of natural products, pharmaceuticals and biologically active compounds.[6] Particularly, aryloxyketones can be easily converted into quinolines by the Pfitzinger reaction.[7,8] Aryloxyketones are also used for the synthesis of substituted benzofurans.[9,10] Traditional methods for the preparation of aryloxyketones include treatment of α-halo ketones with phenols in the presence of base.[11a] Conversely the disadvantages of these methods are poor yields, use of toxic reagents and harsh reaction conditions.[11b] Hurd *et al* reported the synthesis of phenoxy acetone and 2-naphthoxy acetone by KI catalyzed reactions, the use of catalytic amount of KI has improved the yields of the products significantly.[11b]

α-Acyloxycarbonyl compounds are important building blocks because of the formed products can be transformed into alfa-hydroxyketones which are present as a structural subunits in a variety of biologically active natural products and pharmaceuticals.[12,13] Traditionally, α-acyloxycarbonyl compounds have been synthesized using α-halocarbonyl compounds with carboxylic acids adopting transition metal catalyzed reactions and highly toxic heavy metal oxidants such as $Pb(OAc)_4$, $Tl(OAc)_3$ and $Mn(OAc)_3$. However the drawback of these methods was the use of toxic reagents or heavy metals.[14a,b]

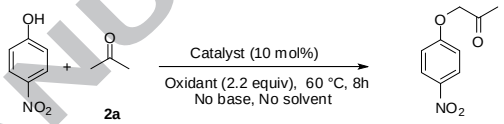
Very recently, the use of tetrabutylammonium iodide (TBAI) as catalyst in combination with the *tert*-butyl hydroperoxide(TBHP) as a powerful oxidation system has been well described by Wu *et* al.[15a] In 2014, Yu and co-workers reported the TBAI-catalyzed direct α-oxyacylation of diarylethanones with acyl peroxides[15b] In the same year, Cheng and co-workers reported the TBAI catalyzed α-acyloxylation of ketones with benzylic alcohols.[15c] Ishihara *et al* demonstrated an elegant and direct α-oxyacylation of carbonyl compounds with carboxylic acids using in situ generated ($[Bu_4N]^+[IO]^-$) ammonium hypoiodite or ($[Bu_4N]^+[IO_2]^-$) iodite catalyzed intra and intermolecular oxidative coupling reactions.[16] Xu and Nachtsheim outlined the TBAI catalyzed oxidative cross coupling of phenols and 2-aminoacetophenones.[17] In 2012, Xu and co-workers have been reported TBAI catalyzed oxidative coupling of β-ketoesters with carboxylic acids.[18] Li *et al* developed TBAI catalyzed α-oxyacylation of carbonyl compounds with toluene derivatives.[19] KI catalyzed alfa-acyloxylation of acetone with carboxylic acids has been reported by Xu and co-workers.[20] List and Bencivenni independently documented the asymmetric alfa-benzyloxylation of cyclic ketones and ketones, respectively.[21,22]

Benzofuran and their derivatives are central pharmacophores as well as privileged structures in medicinal chemistry which are found in a number of clinically used drugs. Benzofuran analogues revealed a broad spectrum of pharmacological activities by recent studies.[23] Benzofurans have been the subject of the most extensive studies and various synthetic methods were developed to access these compounds.[24-31] The majority of the reported methods for the synthesis of benzofurans could not provide satisfactory results because of the requirement of harsh conditions or difficulties in the introduction of different substituent patterns starting from readily available materials.[32] An efficient synthesis of benzofurans and their application in the preparation of natural products of the genus Calea has been reported by Cruz and Tamariz.[33]

Results and Discussion

In continuation of our efforts on TBAI/TBHP mediated oxidative cross coupling reactions,[34] as well as I_2 and KI catalyzed oxidative cross couplings,[35-41] we here in report the direct phenoxylation of acetone and butanone with diverse substituted phenols using TBAI/TBHP mediated oxidative cross coupling. This oxidative cross coupling was applied to salicylaldehydes using acetone and β-ketoesters as coupling partners to afford directly 2-acyl benzofurans and benzofuran-2-carboxylates. The method was extended to α-acyloxylation of acetone with carboxylic acids and salicylic acids as coupling partners.

Table1. Optimal conditions for the synthesis of *p*-nitrophenoxy acetone.[a]



1a 2a 3a

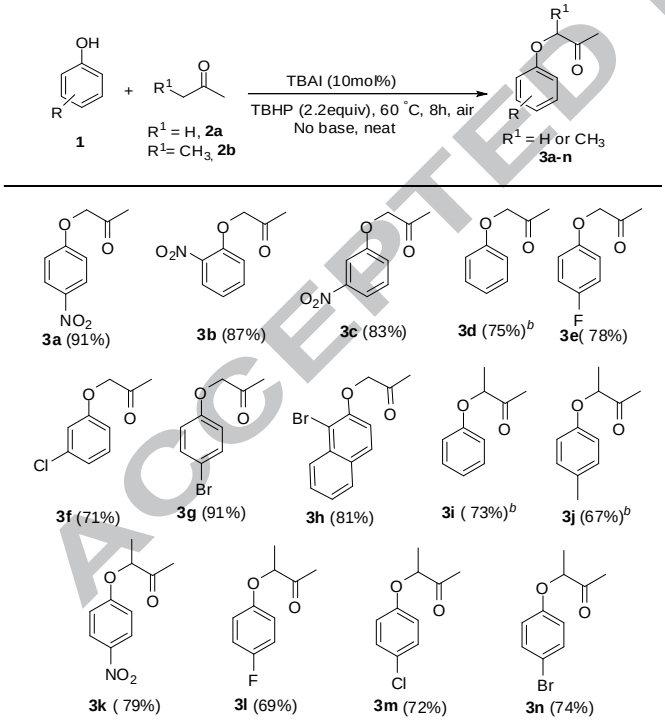
Entry	Catalyst (eq)	Oxidant (eq)	Acetone (eq)	Yield(%)[b]
1	TBAI (0.3)	TBHP (1.5)	41	45
2	TBAI (0.3)	TBHP (2.2)	41	77
3	TBAI (0.3)	TBHP (3.0)	41	69
4	TBAI (0.2)	TBHP (2.2)	41	90
5	**TBAI (0.1)**	**TBHP (2.2)**	**41**	**94 (91)[c]**
6	TBAI (0.05)	TBHP (2.2)	41	85
7	_____	TBHP (2.2)	41	NR
8	TBAI (0.1)	_____	41	NR
9	KI (0.1)	TBHP (2.2)	41	59
10	I_2 (0.1)	TBHP (2.2)	41	75
11	TBACl (0.1)	TBHP (2.2)	41	NR
12	TBABr (0.1)	TBHP (2.2)	41	NR
13	CuI (0.1)	TBHP (2.2)	41	NR
14	TBAI (0.1)	TBHP Dec (2.2)	41	86
15	TBAI (0.1)	H_2O_2 (2.2)	41	66
16	TBAI (0.1)	*m*CPBA (2.2)	41	5
17	TBAI (0.1)	TBHP (2.2)	13	59
18	TBAI (0.1)	TBHP (2.2)	6	18

[a]Reaction conditions: *p*-nitrophenol **1a** (1 equiv.), catalyst (10 mol%), **2a** acetone (3 mL, excess), oxidant (2.2 equiv.), 60°C, 8 h. [b]Yields based on GC analysis. [c]Yield based on isolated product. NR. No reaction

When 1equiv. of *p*-nitrophenol **1a**, was treated with an excess of (3mL) of acetone **2a** in the presence of 30 mol% TBAI and 1.5 equiv. of TBHP (70% solution in water) at 60 °C for 8 hours afforded **3a,** which was isolated by column chromatography in 45% yield (Table 1, entry 1). Increasing the amount of an oxidant TBHP to 2.2 equiv. raised the product **3a** yield to 77% (Table 1, entry 2). Further increase of an oxidant TBHP to 3 equiv. afforded the product **3a** only in 69% yield (Table 1, entry 3). By

decreasing the catalyst loading to 20 mol% and using 2.2 equiv. of an oxidant increased the product **3a** yield to 90%. Further decrease of catalyst loading to 10 mol% and fixing an oxidant 2.2 equiv. increased the product **3a** yield up to 94% GC yield and we could isolate the product **3a** in 91% yield based on column chromatography (Table 1, entries 4 and 5). When only 5 mol% of catalyst is used with 2.2 equiv. of TBHP, the product **3a** yield was decreased to 85% (Table 1, entry 6). When the blank experiments were conducted without using catalyst, only with an oxidant the reaction did not proceeded and similarly in absence of an oxidant using only TBAI, the reaction was unsuccessful (Table 1, entries 7 and 8). These experiments suggests that the present oxidative cross coupling is effective with the use of catalyst TBAI and an oxidant TBHP combination. Change of catalyst from TBAI to KI and I_2 lowered the product yield **3a** to 59% and 75% respectively (Table 1, entries 9 and 10). When other tetrabutylammonium halides such as TBACl and TBABr were used there was no product formation (Table 1, entries 11 and 12). Cu catalyzed phenoxylation was not successful when CuI is used as a catalyst (Table 1, entry 13). The absence of water in an oxidant TBHP (TBHP in decane) did not improve the product yield of **3a** when compare to standard reaction conditions (Table 1, entries 14 and 5). By changing an oxidant from TBHP to H_2O_2 or *m*-CPBA furnished the coupled product **3a** in lower to very low yields 66% and 5% respectively (Table 1, entries 15 and 16). Lowering the amount of acetone from 41 equiv. to 13 equiv. or 6 equiv. decreased the product yield **3a** to 59% and 18% (Table 1 entries 17 and 18).

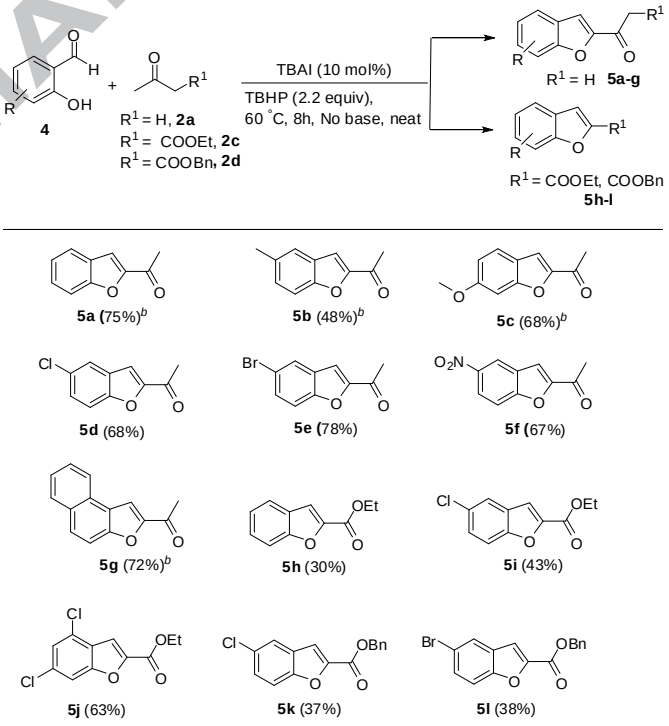
Table 2. Substrate scope of phenols in oxidative cross coupling



[a]Reaction conditions: Phenol (1 equiv.), TBAI (10 mol%), Ketone **2a** or **2b** (excess), TBHP (2.2 equiv.), 60 °C, 8 h. Numbers in parentheses are the isolated yields of the products. [b]Reactions performed under stoichiometric use of TBAI.

The generality as well as substrate scope of the reaction was studied by various substituted phenols of both electron withdrawing and electron donating groups. The substrates containing electron withdrawing groups at *para*, *ortho*, *meta* nitrophenols afforded higher yields **3a** in 91%, **3b** in 87% and **3c** in 83% yields (Table 2 entries **3a-3c**). Where as simple phenol provided very low conversion, but increasing the TBAI to stoichiometric amount the product was isolated in 75% yield. The halogen substituted phenols (4-fluoro, 3-chloro and 4-bromo phenols) furnished the corresponding products **3e** in 78%, **3f** in 71% and **3g** in 91% yields. When the substrate scope was explored from phenols to fused aromatic system, which is 1-bromo-2-naphthol the coupled product **3h** was obtained in 81% yield. When butanone is used as a coupling partner with simple phenol and 4-methyl phenol in presence of catalytic amount of TBAI, the yields of the corresponding coupling products **3i** and **3j** were lowered, however by using the stoichiometric amount of TBAI the yields of the **3i** and **3j** were increased to 73% and 67% respectively. The 4-nitro phenol with butanone afforded **3k** in good yield (79%). Whereas halogen substituted phenols such as 4-fluoro, 4-chloro and 4-bromo phenols afforded the yields of the corresponding coupling products **3l** in 69%, **3m** in 72% and **3n** in 74% which were increased gradually. No regioisomers were observed with butanone. Consequently, having an electron withdrawing groups on phenol ring/aromatic ring, are more beneficial to the reaction, than having an electron donating groups.

Table 3. Substrate scope of salicylaldehydes in oxidative cross coupling



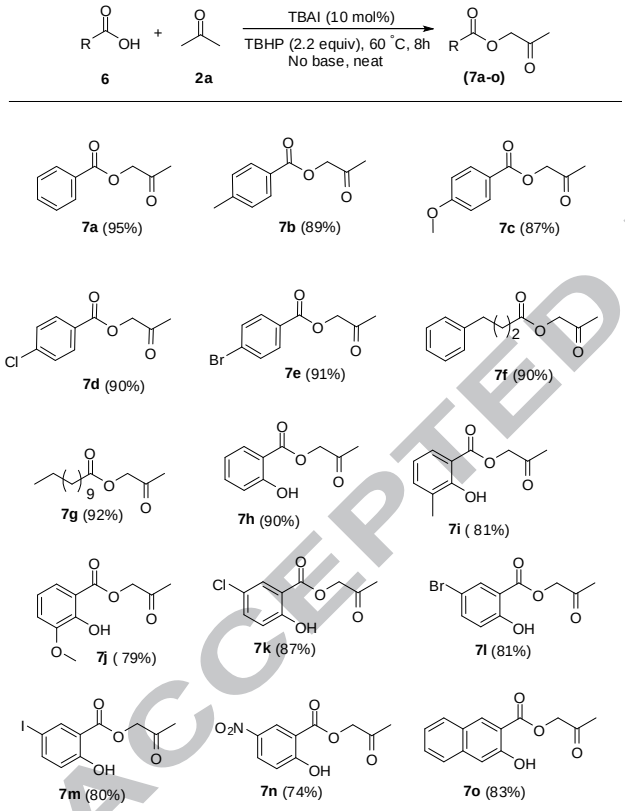
[a]Reaction conditions: Salicylaldehyde (1 equiv.), TBAI (10 mol%), Acetone **2a** (excess) or EAA **2c** (excess) or Benzylacetoacetate **2d** (excess), TBHP (2.2 equiv.), 60 °C, 8 h. Numbers in parentheses are the isolated yields of the products. [b]Reactions performed under stoichiometric use of TBAI.

When salicylaldehyde was treated with acetone under the standard reaction conditions (10 mol% TBAI, 2.2 eq TBHP, 60 °C, 8h) to our serendipity, only 2-acetylbenzofuran was obtained (Table 3, entry **5a**). The phenoxylation of OH group of the salicylaldehyde followed by a possible cyclodehydration furnished the 2-substituted benzofurans. To study the generality and substrate scope of the reaction, several experiments were conducted with various substituted salicylaldehydes having electron donating as well as electron withdrawing groups. Simple salicylaldehyde was given lower yield under catalytic conditions,

however the yield of 2-acetylbenzofuran **5a** was improved to 75% by using stoichiometric use of TBAI. The electron rich systems **5b** and **5c** were also obtained in poor yields by using catalytic amount of TBAI, which were improved from moderate to good yields while using stoichiometric amount of TBAI. All the substrates having electron withdrawing groups worked well under catalytic conditions and provided corresponding benzofuran derivatives in good yeilds (**5d-5f)**.

When salicylaldehyde was treated with β-ketoesters, it reacted well and afforded the benzofuran carboxylates. The salicylaldehyde, 5-chloro-2-hydroxy benzaldehyde and 2,4-dichloro-6-hydroxy benzaldehyde, were reacted with ethyl acetoacetate and furnished the corresponding benzofuran carboxylate ethyl esters **5h** in 30%, **5i** in 43% and **5j** in 63% yields. While 5-chloro-2-hydroxy benzaldehyde, and 5-bromo-2-hydroxy benzaldehyde reacted with benzylacetoacetate afforded the corresponding benzofuran carboxylate benzyl esters **5k** and **5l** in lower yields (37% and 38% Table 3, entries **5h-5l**).

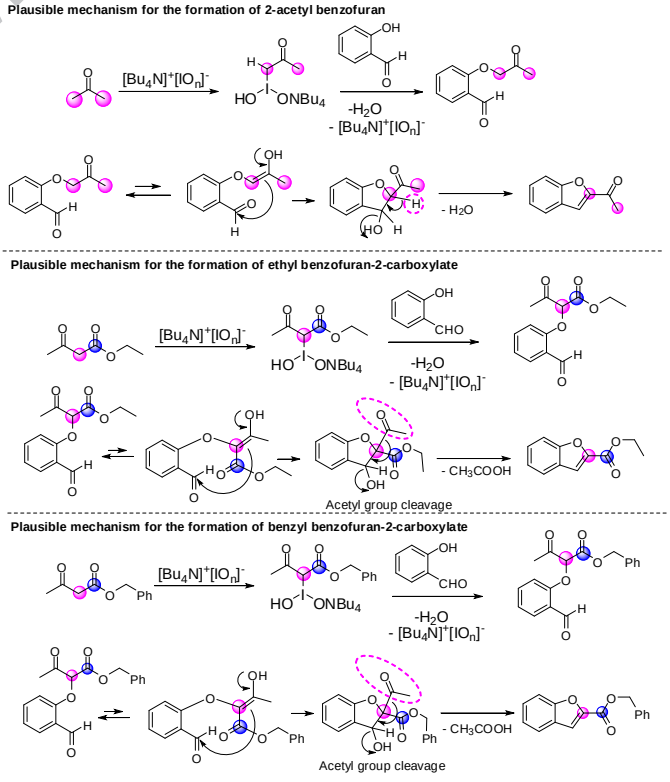
Table 4. Substrate scope of carboxylic acids/salicylic acids in oxidative cross coupling



[a]Reaction conditions: Carboxylic acid (1 equiv.), TBAI (10 mol%), Acetone **2a** (excess), TBHP (2.2 equiv.), 60 °C, 8 h. Numbers in parentheses are the isolated yields of the products.

The generality of the acyloxylation reaction of the carboxylic acids and salicylic acids was investigated with both electron donating as well as electron withdrawing groups. Simple benzoic acid has given the coupling product **7a** in excellent yield (95%) compare to electron donating substrates **7b** and **7c** (89% and 87% yields). The halogenated substrates **7d** and **7e** were afforded in slightly more yields (90 % and 91%) than electron donating substrates **7b** and **7c**. When an electron withdrawing groups were introduced on benzoic acid (Table 4, entries **7d** and **7e)**, the yields of the corresponding cross coupling products were little higher than an electron donating groups having on benzoic acid (Table 4, entries **7b** and **7c**). As a result, having an electron withdrawing groups on benzoic acid is relatively more beneficial to the reaction, than having an electron donating groups on benzoic acid. Further exploration of acyloxylation to aliphatic carboxylic acids also worked smoothly and afforded the coupling products in very good yields **7f** in 90% and **7g** in 92% (Table 4 entries **7a-7g**). Simple salicylic acid has given the coupling product in excellent yield (**7h,** 90%) compare to electron donating groups such as 2-hydroxy-3-methyl benzoic acid (**7i,** 81%) and 2-hydroxy 3-methoxy benzoic acid (**7j,** 79%). The halogenated substrates **7k, 7l** and **7m** were afforded in 87%, 81% and 80% yields respectively. Among the substrates having electron withdrawing groups on salicylic acids only the substrate having 4-chloro has shown higher yield than the other electron withdrawing groups (Table 4, entry **7k**). There is not much variation in the yields of the substrates having either electron donating or withdrawing groups on salicylic acids (Table 4 entries **7i-7n**). An electron withdrawing nitro substrate **7n** was obtained in 74% yield. Fused ring aromatic system, 3-hydroxy-2-naphthoic acid has given good yield (**7o,** 83%) (Table 4 entries **7h-7o**). When salicylic acids were used, we have not observed any aryloxyketones as it is known that the carboxylic acid functionality is more reactive than phenolic hydroxy functionality. It is also supported by the ^{1}H and ^{13}C NMR data of the corresponding coupling products of the acyloxyketones but not aryloxyketones (Table 4 entries **7h-7o**).

Scheme 1. The plausible mechanism for the formation of 2-substituted benzofurans.



Ishihara and co-workers conducted several control experiments and found that initially TBAI reacts with TBHP and generates $[Bu_4N]^+[IO_n]^-$ in situ which is the active iodine species called ammonium hypoiodite (n=1) or iodite (n=2).[16] Naik and co-workers reported a mechanism for the formation of 2-acetyl benzofurans from salicylaldehyde and chloroacetone in presence of a strong base potassium *tert*-butoxide.[42] Based on these observations, we have proposed here a plausible reaction mechanism for the formation of 2-substituted benzofurans as

shown in Scheme 1. The active iodine species reacts with ketone or beta-keto ester and forms an intermediate. Then the hydroxy functionality of the salicylaldehyde reacts with an intermediate and gives the corresponding O-C cross coupled product. Further more, these O-C cross coupled products enolizes and migrates the double bond of enol, to the carbonyl carbon of the salicylaldehyde and leads to the formation of 2,3-disubstituted dihydrofurans. By elimination of water or acetic acid from 2,3-disubstituted dihydrofurans leads to the formation of 2-acetyl benzofuran, benzofuran-2-carboxylate ethyl esters and benzofuran 2- carboxylate benzyl esters (Scheme 1).

Conclusion

In conclusion, we have demonstrated TBAI/TBHP mediated oxidative cross coupling of phenols and carboxylic acids with ketones under metal-free, base free and solvent free conditions towards environmentally benign synthesis of aryloxyketones, acyloxyketones and benzofurans. It is noteworthy to have operationally simple method, under mild conditions, use of commercially available and cheaper catalyst (TBAI) as well as an oxidant (TBHP). This method avoids the use of hazardous reagents, toxic metals and metal oxidants. Furthermore, investigations on the reaction mechanism and to expand the scope of these reactions are underway in our laboratory.

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Supplementary Material

Supplementary data (experimental procedures, analytical data, ^{1}H and ^{13}C NMR spectra) associated with this article can be found, in the online version, at http://dx.doi.org/

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HEIGHLIGHTS

- Demonstrated TBAI/TBHP mediated C-O bond forming oxidative cross coupling reactions.
- Synthesis of aryloxyketones, α-acyloxy ketones and benzofurans has been achieved.
- The present method works under metal-free, base free and solvent free conditions.
- The present method works under mild conditions and utilizes inexpensive TBAI and TBHP reagents.
- This method avoids the use of hazardous reagents, toxic metals and metal oxidants.

TBAI/TBHP mediated oxidative cross coupling of ketones with phenols and carboxylic acids: Direct access to benzofurans

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Graphical Abstract