Advanced Synthesis & Catalysis

DOI: 10.1002/adsc.201400659

Copper-Catalyzed Cross Dehydrogenative Coupling of *N,N*-Disubstituted Formamides and Phenols: A Direct Access to Carbamates

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Received: July 9, 2014; Revised: September 15, 2014; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201400659.

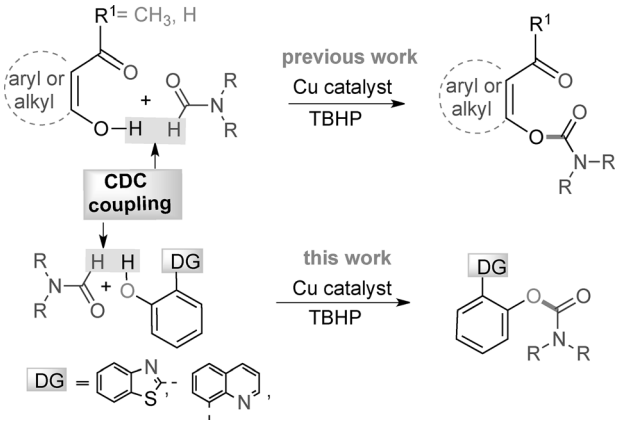
Abstract: An efficient copper-catalyzed protocol has been developed for the synthesis of carbamates from dialkylformamides and phenols possessing directing groups such as benzothiazole, quinoline and formyl at the *ortho*-position. In this chelation assisted approach, C–O bond formation takes place *via* a cross dehydrogenative coupling (CDC) between the formyl C–H of dialkylformamide and phenolic O–H in the presence of copper(II)acetate/aqueous *tert*-butyl hydroperoxide. Under identical reaction conditions, salicylic acid derivatives underwent amidation with the carboxylic group rather than formamidation of the phenolic OH. The use of a cheap and environmentally benign catalyst along with the tolerance of a wide range of functional groups makes this an easy, phosgene-free route to carbamates.

Keywords: carbamates; C–H activation; copper catalysis; cross dehyrogenative coupling

Introduction

The transition metal-catalyzed cross-coupling reactions are useful for the construction of C–C and C–heteroatom bonds.[1] However, these traditional couplings suffer from some serious drawbacks due to the use of stoichiometric organometallic reagents as well as requirements of pre-functionalized substrates. To overcome some of these problems, the direct C–H functionalization processes have emerged as viable alternatives in modern organic synthesis.[2] Two pillars on which the activation of inert C–H bonds stand are: (a) chelation assisted functionalization[3] and (b) the cross dehydrogenative coupling (CDC).[4] In particular, the CDC is an important tool employed mainly for the construction of C–C[4a,d,5] and C–N bonds.[6] However, of late the number of C–O bond forming processes is increasing. In this respect our group and others have developed several CDC protocols for C–O bond formation leading to the synthesis of various esters.[7]

Organic carbamates are useful agrochemicals, pharmaceuticals and are also present in a range of biologically active natural products.[8] In addition, carbamates play an important role as intermediates in organic synthesis and serve as a protecting group during peptide synthesis.[9] However, the general methods for their synthesis require intermediates such as chloroformates or isocyanates which, in turn, are prepared from phosgene or its derivatives.[10] Thus, a phosgene-free synthesis of carbamates is most appreciable from the environmental point of view.[11] This motive has led to the synthesis of carbamates by other methods such as (i) oxidative and reductive carbonylation of amines and nitro aromatics;[11a,c,12] (ii) reaction of amines with CO_2;[11e–i,k] (iii) metal-catalyzed cross-coupling of isocyanate with phenols; and (iv) various rearrangement reactions.[13] *N,N*-Dialkylformamides have attracted much attention because of their polygonal utility in C–H functionalizations. They are reported as surrogates of various functional groups depending upon the reaction conditions.[14] For example *N,N*-dimethylformamide (DMF) is known to act as the source of Me, CO, NMe_2, $CONMe_2$, CHO and CN groups in various synthetic protocols.[15] Among these groups, the synthetic utility of dialkylformamides as an aminocarbonyl ($CONR_2$) group is well documented in the literature. Some recent achievements include aminocarbonyl (from DMF) insertion into alkenes and alkynes,[16] synthesis of α-keto am-



Scheme 1. Methods for carbamate synthesis from phenols and formamides.

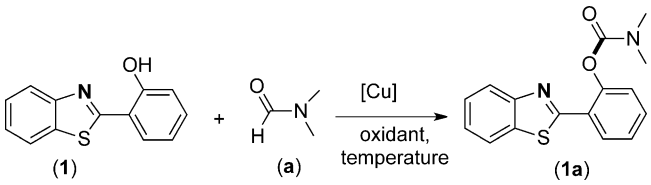
ides[7a] and direct aminocarbonylation of azoles.[17] All of the aforementioned reactions proceed *via* oxidative C–C or C–N bond formations. In the C–O bond forming segment, the use of dialkylformamides as an aminocarbonyl surrogate has been utilized for the synthesis of carbamates by reacting them with phenols and enols possessing *ortho* carbonyl directing groups.[18]

On the other hand, benzothiazole derivatives have found immense importance due to their biological and pharmaceutical activities.[19] Therefore, functionalizations of benzothiazole would provide pathways for the synthesis of intermediates that may find potential applications in various other fields.[20] This has been realized through some of our recent achievements on transition metal-catalyzed directing group-assisted (*N*-atom) functionalizations of the *ortho*-C–H bond of the 2-aryl moiety in benzothiazole.[21] Thus, we envisaged that the directing *N*-atom of benzothiazole could facilitate a metal-catalyzed aminocarbonylation of the hydroxy group present at the proximal carbon atom. Such an aminocarbonylation would lead to the formation of a hybrid benzothiazole-carbamate moiety (Scheme 1).

Results and Discussion

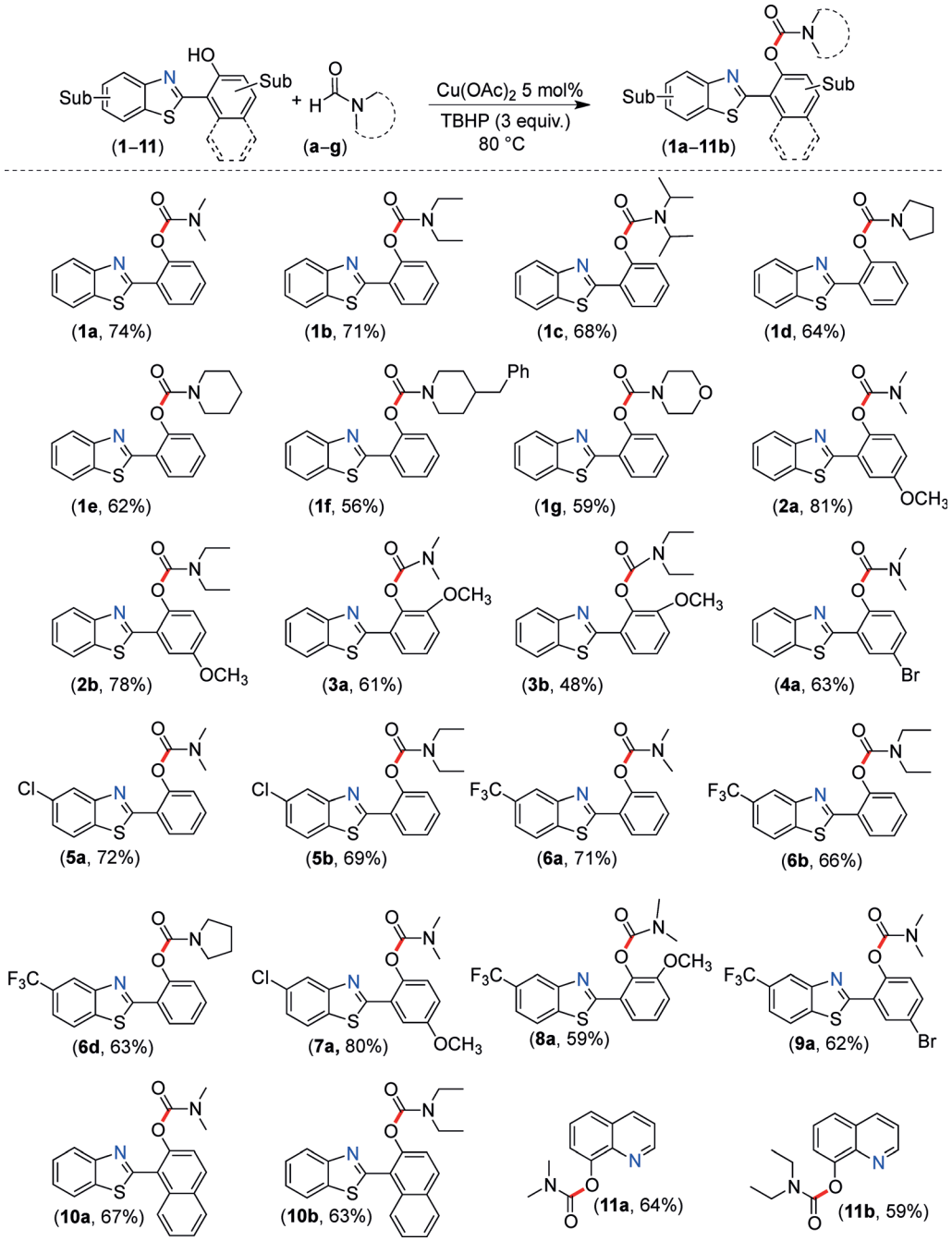
To verify our above envisaged hypothesis, 2-(benzo[*d*]thiazol-2-yl)phenol (**1**) and DMF (**a**) were reacted in the presence of copper(I) bromide (5 mol%) and TBHP in decane (2 equiv.) at 80 °C. As anticipated phenol carbamate (**1a**) was formed but in a low yield of 34% (Table 1, entry 1). To arrive at the optimized reaction conditions different salts of copper such as $CuBr_2$, CuCl, $CuCl_2$, $Cu(OAc)_2$ and $Cu(OTf)_2$ were tested among which $Cu(OAc)_2$ provided the best yield of 57% (Table 1, entries 2–6). When the catalyst loading was increased from 5 mol% to 10 mol% the yield did not improve significantly (Table 1, entry 7). The use of aqueous TBHP (70%) provided an improved yield (63%) compared to the decane solution of TBHP (Table 1, entry 8). The yield was enhanced up to 74% (Table 1, entry 9) when 3 equiv. of oxidant were used. No further improvement in the yield was observed even when the oxidant quantity was increased beyond 3 equiv. (Table 1, entry 10). The oxidant, 70% aqueous TBHP, turned out to be the best (Table 1, entry 9) compared to other peroxides such as aqueous H_2O_2, DTBP, BPO and $(NH_4)_2S_2O_8$ (Table 1, entries 11–14) screened. An increase (100 °C) or decrease (70 °C) in the reaction temperature led to a slight reduction in the yield (Table 1, entries 15 and 16). The absence of either copper catalyst or oxidant failed to produce any cross-coupled product revealing the requirement of both Cu(II) and TBHP in bringing about this transformation (Table 1, entries 17 and 18). When the reaction was carried out under metal-free conditions using tetrabutylammoni-

Table 1. Screening of the reaction conditions.[a]



Entry	Catalyst (mol%)	Oxidant (equiv.)	Temp. [°C]	Yield [%][b]
1	CuBr (5)	TBHP[c] (2)	80	34
2	$CuBr_2$ (5)	TBHP[c] (2)	80	41
3	CuCl (5)	TBHP[c] (2)	80	30
4	$CuCl_2$ (5)	TBHP[c] (2)	80	39
5	$Cu(OTf)_2$ (5)	TBHP[c] (2)	80	32
6	$Cu(OAc)_2$ (5)	TBHP[c] (2)	80	57
7	$Cu(OAc)_2$ (10)	TBHP[c] (2)	80	59
8	$Cu(OAc)_2$ (5)	TBHP[d] (2)	80	63
9	**$Cu(OAc)_2$ (5)**	**TBHP[d] (3)**	**80**	**74**
10	$Cu(OAc)_2$ (5)	TBHP[d] (4)	80	74
11	$Cu(OAc)_2$ (5)	H_2O_2[e] (3)	80	<10
12	$Cu(OAc)_2$ (5)	DTBP[f] (3)	80	<8
13	$Cu(OAc)_2$ (5)	BPO[g] (3)	80	<6
14	$Cu(OAc)_2$ (5)	$(NH_4)_2S_2O_8$ (3)	80	<3
15	$Cu(OAc)_2$ (5)	TBHP[d] (3)	100	73
16	$Cu(OAc)_2$ (5)	TBHP[d] (3)	70	70
17	none	TBHP[d] (3)	80	00
18	$Cu(OAc)_2$ (5)	none	80	00
19	TBAI (20)	TBHP[d] (3)	80	00

[a] *Reaction conditions:* 2-(benzo[*d*]thiazol-2-yl)phenol (0.5 mmol), formamide (1 mL), at 80 °C for 10 h.
[b] Isolated yield.
[c] 5–6 M decane solution.
[d] 70% aqueous solution.
[e] 50% aqueous solution.
[f] Di-*tert*-butyl peroxide.
[g] Benzoyl peroxide.



Scheme 2. Oxidative coupling of phenols with formamides. *Reaction conditions:* phenols (**1**–**11**) (0.5 mmol), formamides (**a**–**g**) (1 mL), $Cu(OAc)_2$ (0.05 mmol), TBHP (3 equiv.), 80 °C, for 8–12 h. Yields of isolated pure products given.

um iodide (TBAI) as the catalyst and TBHP as the oxidant the desired carbamate did not form at all (Table 1, entry 19). No further improvement in the product yield was observed even when a standard reaction was performed under an inert (nitrogen) atmosphere. Hence, it was found that the use of 5 mol% of $Cu(OAc)_2$ in the presence of aqueous TBHP (3 equiv.) at 80 °C were the best conditions for the conversion of (**1**) to (**1a**).

With this optimized conditions in hand, we further investigated the scope of this transformation with different formamides and phenols possessing *N*-directing groups (Scheme 2). Initially various formamides (**a–g**) were reacted with 2-(benzo[*d*]thiazol-2-yl)phenol (**1**) and it was found that both acyclic (**a–c**) and cyclic (**d–g**) formamides coupled well with (**1**) giving the corresponding carbamates in moderate to good yields (Scheme 2, **1a–c** and **1d–g**). However, cyclic formamides (**d–g**) gave marginally lower yields compared

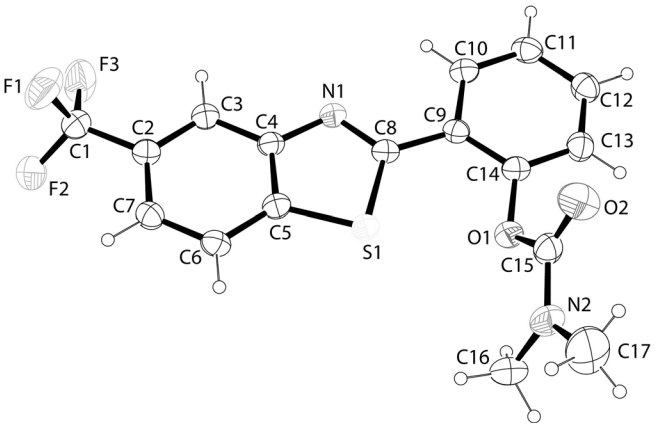
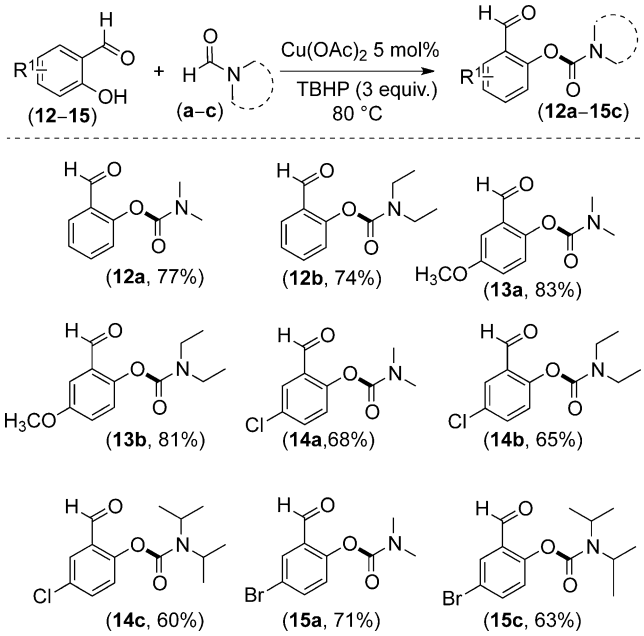


Figure 1. ORTEP view of **6a**.[25]

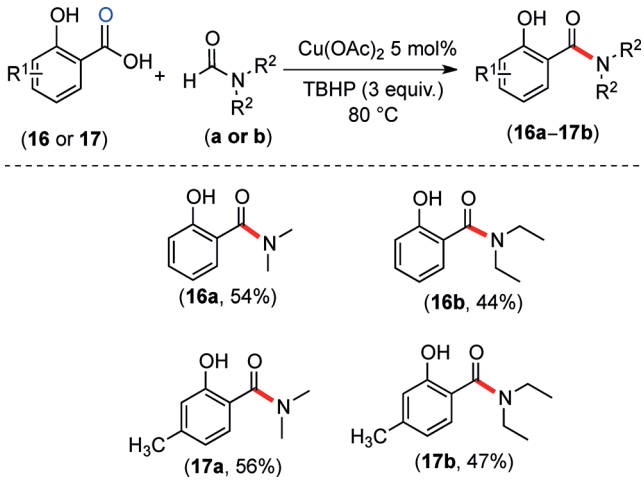
to acyclic ones (**a–c**). Further, the effect of substituents on the phenol moiety was investigated by reacting them with various formamides and the results are summarized in Scheme 2. Phenol rings bearing electron-donating groups such as *p*-MeO (**2**) underwent efficient coupling with *N*,*N*-dimethylformamide (**a**) and *N*,*N*-diethylformamide (**b**) affording carbamates (**2a**) and (**2b**) in 81% and 78% yields, respectively. However, yields of the product (**3a**) and (**3b**) dropped to 61% and 48% when the MeO group is present *ortho* to the OH (**3**), which could be due to the *ortho* steric hindrance. The phenol ring bearing a moderately electron-withdrawing group such as *p*-Br (**4**) when reacted with DMF provided its carbamate (**4a**) in slightly lower yield (63%) compared to the electron-donating counterpart (**2a**). Relative to the electron-neutral (H) analogue (**1**) the presence of the moderately electron-withdrawing group Cl (**5**) and the strongly electron-withdrawing group CF_3 (**6**) on the aryl ring of benzothiazole moiety had negligible influence on the product yields (Scheme 2, **5a**, **b**, **6a, b** and **6d**). The structure of the product (**6a**) was further confirmed by single X-ray crystallography (Figure 1). Syntheses of different carbamates (**7a**), (**8a**) and (**9a**) from their respective coupling partners reveal the versatility of this protocol. This methodology is also equally applicable for the synthesis of β-naphthyl carbamates (**10a**) and (**10b**) by reacting 1-(benzo[*d*]thiazol-2-yl) naphthalen-2-ol (**10**) with formamides (**a**) and (**b**). Beside benzothiazoles, the *N*-atom in 8-hydroxyquinoline (**11**) provided similar chelation assistance towards *O*-formamidation giving products (**11a**) and (**11b**) when treated with the respective formamides (**a**) and (**b**) under otherwise identical reaction conditions. When 2-(benzo[*d*]thiazol-2-yl)phenol (**1**) and 8-hydroxyquinoline (**11**) were reacted with *N*-methylformamide or an arylformamide such as the monoaryl (*N*-methyl-*N*-phenylformamide) and diaryl (*N*,*N*-diphenylformamide) species in all cases the reaction failed to provide any carbamates. It may be mentioned here that traditionally the phenolic OH group is protected as its ether, ester, silyl ether, acetate etc. which require harsh reaction conditions as well as expensive and toxic chemicals.[9a] Compared to these, the present phenolic OH protection *via* carbamate formation using simple formamides may find useful applications in organic synthesis.

For the past few years our group has developed various CDC reactions using metals as well as metal-free conditions.[7f–k,21] During one of the investigations, we have demonstrated the oxidative coupling of alkylbenzenes with salicylaldehydes which formed phenol esters without affecting the formyl group.[7i] Inspired by this result, we envisaged a similar cross dehydrogenative coupling of formamide and salicylaldehyde. Thus, when salicylaldehyde (**12**) and DMF (**a**) were reacted under the above optimized conditions 2-formylphenyl carbamate was obtained in 77% isolated yield. Gratifyingly, similar to our previous report on esterfication,[7i] herein as well the oxidation sensitive formyl group remained unaffected under the reaction conditions which can be transformed into other useful functionality if desired. Coincidentally, while the work was under progress the group of Wang and Chang[22a] independently reported a similar *O*-formamidation of salicylaldehyde; the only difference being the use of copper(I) chloride instead of $Cu(II)(OAc)_2$ and a different stoichiometry of TBHP. The same group has also demonstrated an Fe-catalyzed selective C–O bond formation *via* α C–H bond functionalization of cyclic ethers in the presence of a labile formyl group.[22b] Thus, the present methodology using Cu(II) was demonstrated only with a limited number of substrates. Salicylaldehyde (**12**) when treated with formamides (**a**) and (**b**) resulted in the formation of carbamates (**12a**) and (**12b**) in good yields (Scheme 3). The reaction of methoxy-substituted salicylaldehyde (**13**) led to the formation of expected carbamates (**13a**) and (**13b**) in better yields compared to unsubstituted salicylaldehyde (**12**) when coupled with formamides (**a**) and (**b**) respectively (Scheme 3). Salicylaldehydes bearing halogen substituents such as Cl (**14**) and Br (**15**) afforded slightly lower yields compared to the unsubstituted salicylaldehyde (**12**) when treated with various dialkylformamides (**a**), (**b**) and (**c**) as shown in Scheme 3.

During our earlier substrate directed *O*-aroylation, both formyl (CHO) and acetyl ($COCH_3$) served as excellent directing groups while the carboxy (COOH) group was completely ineffective.[7i] So curiosity arose whether *O*-formamidation can be achieved with carboxy (COOH) as the directing group in salicylic acid? Salicylic acid (**16**) bearing a COOH directing group at the *ortho* position when treated with DMF (**a**) gave an amide (**16a**) rather than the expected phenol carbamate (Scheme 4). The structure of the product (**16a**) has been confirmed by single X-ray crystallogra-



Scheme 3. Synthesis of carbamates from salicylaldehydes. *Reaction conditions:* salicylaldehydes (**12**–**15**) (1.0 equiv.), formamide (**a**–**c**) (1 mL), $Cu(OAc)_2$ (0.05 mmol), TBHP (3 equiv.), 80 °C for 3 h. Yields of isolated pure products given.



Scheme 4. Oxidative coupling of salicylic acids with formamides. *Reaction conditions:* salicylic acids (**16** or **17**) (1.0 equiv.), formamide (**a** or **b**) (1 mL), $Cu(OAc)_2$ (0.05 mmol), TBHP (3 equiv.), 80 °C for 6 h. Yields of isolated pure products given.

phy (Figure 2). This is not a singular exception; salicylic acid (**16**) with the other formamide (**b**) and methyl-substituted salicylic acid (**17**) with formamides (**a**) and (**b**) also yielded amides (**16b**), (**17a**) and (**17b**) as the major products. A similar amidation of benzoic acid with formamide has been reported under identical conditions.[23] Thus this reaction might be proceeding *via* a radical path as has been proposed in the literature.[23]

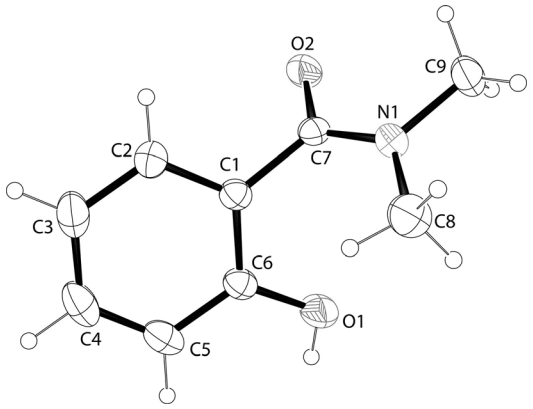
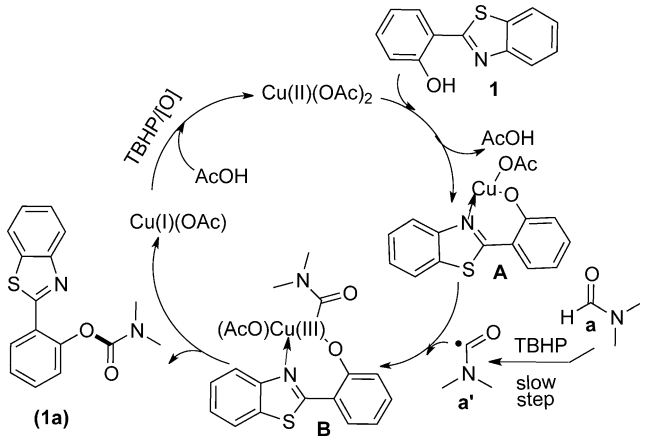


Figure 2. ORTEP view of **16a**.[26]

So far as the mechanism of *O*-formamidation with other directing groups is concerned, the complex forming ability of 2-(benzo[*d*]thiazol-2-yl)phenol and salicylaldehyde through co-ordination with Cu metal could be one of the crucial factors. Furthermore, reaction of simple phenols with formamides failed to produce the target phenol carbamates; thus suggesting the involvement of an adjacent directing group. The reaction between 2-(benzo[*d*]thiazol-2-yl)phenol (**1**) and DMF (**a**) in the presence of a radical scavenger such as TEMPO [2,2,6,6-tetramethylpipridine 1-oxyl] resulted in the formation of carbamate (**1a**) in $<5\%$ yield indicating a radical path for the reaction.[22a] Surprisingly, when the reaction was performed in the presence of another radical scavenger such as 1,4-cyclohexadine there was no retardation of the reaction rate and the yield remained unaltered. A significant kinetic isotope effect ($K_H/K_D \sim 3.2$) was observed in the reaction between 4-methoxy-2-(5-(trifluoromethyl)benzo[*d*]thiazol-2-yl)phenol with DMF-d_7 demonstrating that sp^2 C–H bond cleavage of formamide is possibly the slow step in the reaction. Based on literature precedents and our experimental observations, a radical mechanism for this transformation is predicted that involves formation of an aminoacyl radical (**a′**) as the crucial step.[7a,17,24] A six-membered copper complex (**A**) is formed *via* the chelation of Cu(II) with (**1**) through *N*-binding of benzothiazole and *O*-binding of phenolic group. Simultaneously, a butoxy radical generated by the dissociation of TBHP abstracts a hydrogen atom from the DMF to produce an aminoacyl radical (**a′**). This aminoacyl radical (**a′**) reacts with complex (**A**) to form a Cu(III) intermediate (**B**). Reductive elimination of intermediate (**B**) results in the formation of desired carbamate (**1a**) and releasing a Cu(I) species, which is reoxidized to Cu(II) in the medium for a further catalytic cycle (Scheme 5). A similar mechanism is likely to operate for the other directing groups as well.



Scheme 5. Proposed reaction mechanism.

Conclusions

In conclusion, we have developed an efficient synthesis of phenol carbamates from dialkylformamides and phenols possessing benzothiazole, quinoline and formyl directing groups at their *ortho*-positions. This directing group-assisted cross dehydrogenative coupling (CDC) occurs between the formyl C–H bond of dialkylformamides and the phenolic O–H bond in the presence of the Cu(II) catalyst and oxidant aqueous TBHP. However, an exception was observed for salicylic acid derivatives which gave *o*-hydroxy amides. A plausible radical mechanism has been proposed for the reaction. The use of a cheap and environmentally benign catalyst and tolerance of a range of functional groups makes this an alternative phosgene-free route to phenol carbamates.

Experimental Section

Typical Procedure for the Synthesis of 2-(Benzo[*d*]-thiazol-2-yl)phenyl Dimethylcarbamate (1a)

An oven-dried round-bottom flask was charged with 2-(benzo[*d*]thiazol-2-yl)phenol (0.5 mmol, 114 mg), $Cu(OAc)_2$ (0.025 mmol, 4.5 mg), 70% aqueous TBHP (1.5 mmol, 215 μL), and DMF as formamide source (1 mL), and the mixture was stirred in a preheated oil bath at 80 °C for 10 h. After cooling to room temperature, the reaction mixture was admixed with water (5 mL) and the product extracted with ethyl acetate (2×10 mL). The organic layer was dried over anhydrous Na_2SO_4 and solvent removed under vacuum. The crude product so obtained was purified over a short column of silica gel (ethyl acetate/hexane, 1:9) to afford 2-(benzo[*d*]thiazol-2-yl)phenyl dimethylcarbamate (**1a**); yield: 110 mg (74%).

Typical Procedure for the Synthesis of 2-Formylphenyl Dimethylcarbamate (12a)

An oven-dried round-bottom flask was charged with salicylaldehyde (122 mg, 1 mmol), $Cu(OAc)_2$ (0.050 mmol, 9.0 mg), 70% aqueous TBHP (3 mmol, 430 μL), and DMF as formamide source (1 mL) and the mixture was stirred in a preheated oil bath at 80 °C for 3 h. After cooling to room temperature, the reaction mixture was admixed with water (5 mL) and the product extracted with ethyl acetate (2×10 mL). The organic layer was dried over anhydrous Na_2SO_4 and solvent removed under vacuum. The crude product so obtained was purified over a short column of silicagel (ethyl acetate/hexane, 2:8) to afford corresponding 2-formylphenyl dimethylcarbamate (**12a**); yield: 149 mg (77%).

Typical Procedure for the Synthesis of 2-Hydroxy-*N,N*-dimethylbenzamide (16a)

An oven-dried round-bottom flask was charged with salicylic acid (138 mg, 1 mmol), $Cu(OAc)_2$ (0.05 mmol, 9.0 mg), 70% aqueous TBHP (3 mmol, 430 μL), and DMF as formamide source (1 mL), and the mixture was stirred in a preheated oil bath at 80 °C for 6 h. After cooling to room temperature, the reaction mixture was admixed with water (5 mL) and the product extracted with ethyl acetate (2×10 mL). The ethyl acetate layer was washed with 5% sodium bicarbonate solution (2×2 mL). Organic layer was dried over anhydrous Na_2SO_4 and solvent removed under vacuum. The crude product so obtained was purified over a short column of silica gel (ethyl acetate/hexane, 3:7) to afford 2-hydroxy-*N,N*-dimethylbenzamide (**16a**); yield: 89 mg, 54%.

Acknowledgements

B.K.P. acknowledges the support of this research by the Department of Science and Technology (DST), New Delhi (SR/S1/OC-79/2009), and the Council of Scientific and Industrial Research (CSIR) (02(0096)/12/EMR-II). WA, SKR, SG, AB thank CSIR for fellowships.

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[25] CCDC 997031 (**6a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[26] CCDC 997032 (**16a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. See also the Supporting Information.

Copper-Catalyzed Cross Dehydrogenative Coupling of *N,N*-Disubstituted Formamides and Phenols: A Direct Access to Carbamates

Adv. Synth. Catal. **2015**, *357*, 1 – 9

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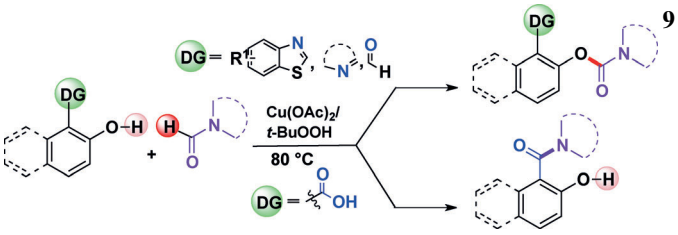

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