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COMMUNICATION

One Stone Two Birds: Cobalt Catalyzed *in situ* Generation of Isocyanate and Benzyl alcohol for the Synthesis of *N*-aryl Carbamates

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An efficient method for the synthesis of *N*-aryl carbamates from *N*-Boc protected amines has been developed. Cobalt catalyzed *in situ* generation of isocyanates from *N*-Boc protected amines and benzyl alcohols from benzyl formates has been achieved for the first time which in turn furnished the corresponding benzyl carbamates in moderate to high yields. The reaction was catalyzed by CoI_2 with tris-(4-dimethylaminophenyl)-phosphine as the ligand and Zinc powder as the reductant. The developed reaction condition was found to be compatible for aromatic amines with both electron donating and withdrawing substituents.

Introduction

Carbamates and thiocarbamates are present in various bioactive compounds such as herbicides,[1] pesticides,[1a] bactericides,[2] and antiviral agents.[3] Because of their applications in drug design and discovery, carbamates have received much attention in recent years. Carbamates have gained more importance in medicinal chemistry due to their chemical stability and their potential to enhance permeability across cellular membranes.[4] In addition, carbamates have been used as one of the protecting groups that enhance the chemical stability of amines towards acids, bases and hydrogenation.[4,5] There has been various methods reported for the preparation of carbamates. The traditional method of carbamate synthesis involves the use of highly toxic phosgene,[6a] phosgene derivatives,[6b-c] and transition metal catalysts such as palladium,[7] nickel[8] and rhodium,[9] etc. Some other common methods for the synthesis for carbamates are Hoffmann rearrangement,[10] the Curtius rearrangement,[11] the reductive carbonylation of aromatic nitro compounds,[12] the carbonylation of amines,[13] and carbon dioxide alkylation.[14] However, these methods suffer from certain limitations. There has been continuous efforts to improve the reaction pathway and for more environmentally benign route for the synthesis of carbamates and thiocarbamates.[15]

One of the most widely used precursor for the synthesis of carbamates is isocyanate group. There are various methods for the preparation of isocyanate intermediates such as Hoffmann or Curtius rearrangements, Lossen rearrangement.[16] The synthesis of carbamates via *in situ* generation of isocyanate intermediate has been furnished by different groups. Isobe and his group has reported the transformation of trichloroacetamides into the easily deprotectable carbamates via *in situ* generated isocyanate in the presence of CuCl and *n*-BuN_4Cl.[17] The synthesis of carbamates via *in situ* generation of aryl ioscyanates has been furnished through the cross-coupling of aryl boronic acids or aryl halides with potassium and sodium cyanates catalyzed by palladium or copper.[18] Kim and Lee have developed the one-pot synthesis of carbamates and thiocarbamates via *in situ* generated isocyanates which reacts with alcohols and thiols to give the corresponding carbamates and thiocarbamates.[19] Kim and co-workers have achieved a mild and efficient route for synthesis of *N*-arylcarbamates by Copper-catalyzed Chan–Lam C–N cross-coupling reactions under neutral conditions.[20] We herein report the successful synthesis of carbamates from *N*-protected anilines and benzyl formates via *in situ* generated isocyanate and benzyl alcohol intermediates. The reaction is catalyzed by inexpensive cobalt (II) iodide in the presence of tris-(4-dimethylaminophenyl)-phosphine ligand and zinc powder as reductant. Because of simple operation, mild reaction conditions, fairly good yields and use of easily available reagents, the developed protocol will be a useful method for the synthesis of *N*-aryl carbamates.

Results and Discussion

Our investigation commenced with the reaction of *N*-Boc protected aniline **1a** with benzyl formate **2a** using cobalt (II) chloride as the catalyst and tris-(4-methoxyphenyl)-phosphine as ligand in the presence of Zn powder in toluene. The reaction mixture was heated at 100 °C for 96 h. To our delight, the desired *N*-aryl carbamate **3aa** was obtained in 74% yield. In order to increase the yield of the product, various metal

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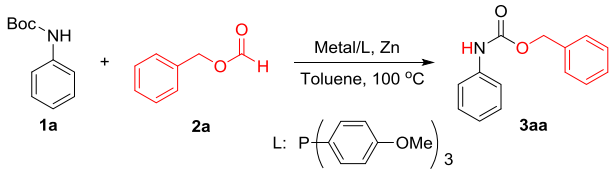
catalysts were screened (Table 1). $CoBr_2$ gave the product **3aa** in reduced yield (Table 1, entry 2). Gratifyingly, the desired carbamate was afforded in 80% yield when CoI_2 was used (Table 1, entry 3). $Co(acac)_2$ resulted into diminished yield (Table 1, entry 4). The *N*-Boc protected aniline **1a** was not completely consumed even after extending the reaction time as indicated when $CoCl_2$, $CoBr_2$ and $Co(acac)_2$ were used. Other cobalt catalysts such as CoF_3, $Co(OAc)_2$, $CoCO_3$, $Co(SCN)_2$ and $Co_3(PO_4)_2.8H_2O$ were not suitable for the present reaction as the reaction either did not occur or the product was formed only in trace amount (Table 1, entries 5-9). This result shows that the most ideal metal catalyst for the present transformation is CoI_2.

Table 1. Optimization of metal catalysts[a]

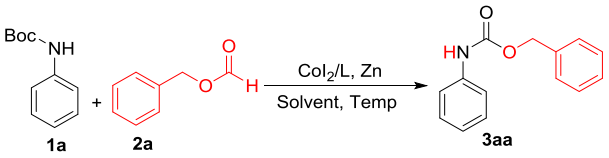


Entry	Metal	Time (h)	Yield (%)[b]
1	$CoCl_2$	96	74
2	$CoBr_2$	108	59
3	CoI_2	48	80
4	$Co(acac)_2$	108	55
5	CoF_3	72	NR
6	$Co(OAc)_2$	72	Trace
7	$CoCO_3$	72	NR
8	$Co(SCN)_2$	72	NR
9	$Co_3(PO_4)_2.8H_2O$	72	Trace

[a]*Reaction conditions:* Cobalt salt (10 mol%), ligand (24 mol%) and Zn powder (0.6 mmol) were stirred in toluene (1 mL) for 30 minutes at room temperature (rt) under Ar. *N*-Boc protected aniline **1a** (0.2 mmol), benzyl formate **2a** (0.6 mmol) and toluene (1 mL) were added to the above mixture. The reaction mixture was stirred under argon atmosphere at 100 °C. The reaction was monitored by TLC. [b]Isolated yields.

Further optimization of the reaction conditions was performed by screening various ligands and solvents (Table 2). When the reaction was carried out in the absence of ligand, the product was obtained in poor yield indicating that a ligand is required for the synthesis of *N*-aryl carbamate under the present catalytic system (Table 2, entry 1). Diphosphine ligands such as dppp, dppe could not increase the reaction yield (Table 2, entries 2 and 3). Improvement in the yield to 89% was observed on using monophosphine ligand tricyclohexyl phosphine (Table 2, entry 4). Other ligands such as dppm, dppb, PPh_3, 1,10-Phenanthroline, (±)-BINAP, tris-(3,5-dimethylphenyl)-phosphine and tri-(furan-2-yl)-phosphine were found unsuitable for the present transformation. There was either no reaction or the product was formed in low yield or trace amount. Gratifyingly, highest yield was observed when the more electron rich tris-(4-dimethylaminophenyl)-phosphine was used as the ligand (Table 2, entry 6). No improvement in the reaction yield was observed on screening different solvents such as 1,4-dioxane, DCE, THF, DMF, DMSO and CH_3CN indicating that toluene is the optimal solvent for the present reaction. Surprisingly, on increasing the reaction temperature to 120 °C, the reaction was completed in just 24 h with 92% yield (Table 2, entry 9). The reaction yield was reduced when the equivalent of zinc was lowered and no reaction took place in the absence of zinc indicating the importance of zinc in the present protocol. The reaction did not occur when Mn (3 equiv) was used instead of Zn under the same reaction conditions (See Table S1 in Supporting Information for detailed optimization study).

Table 2. Screening of different Ligands and solvents[a]



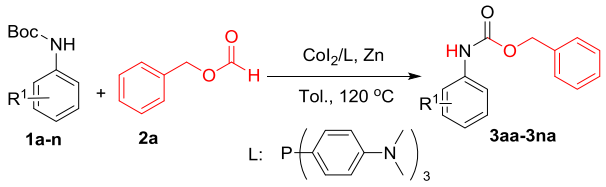
Entry	Ligand	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	-	Toluene	100	72	39
2	dppp	Toluene	100	48	53
3	dppe	Toluene	100	72	71
4	$P(Cy)_3$	Toluene	100	72	89
5	tris-(4-methoxyphenyl)-phosphine	Toluene	100	48	80
6	**tris-(4-dimethylaminophenyl)-phosphine**	**Toluene**	**100**	**72**	**93**
7	tris-(4-dimethylaminophenyl)-phosphine	DCE	100	72	trace
8	tris-(4-dimethylaminophenyl)-phosphine	DMF	100	48	62
9	tris-(4-dimethylaminophenyl)-phosphine	Toluene	120	24	92
10[c]	tris-(4-dimethylaminophenyl)-phosphine	Toluene	120	48	NR

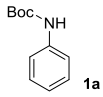
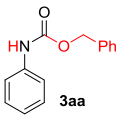
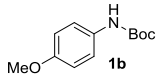
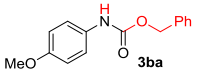
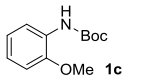
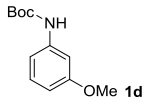
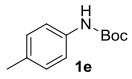
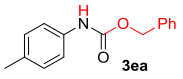
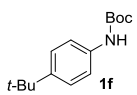
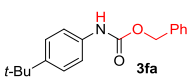
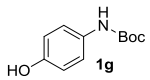
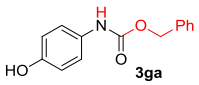
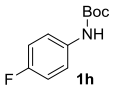
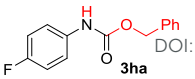
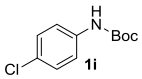
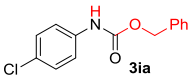
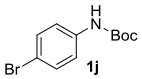
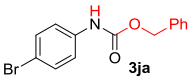
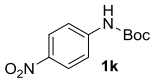
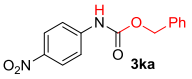
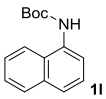
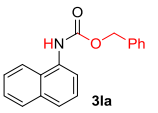
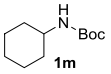
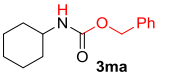
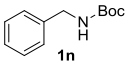
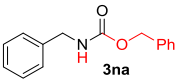
[a]*Reaction conditions:* CoI_2 (10 mol%), monophosphine ligands (24 mol%) or diphosphine ligands (12 mol%) and Zn powder were stirred in solvent (1 mL) for 30 minutes at rt under Ar. *N*-Boc protected aniline **1a** (0.2 mmol), benzyl formate **2a** (0.6 mmol) and 1 mL solvent were added. The reaction mixture was stirred under argon atmosphere at 100 °C or 120 °C. The reaction was monitored by TLC. [b]Isolated yields. [c]Reaction was carried out in absence of Zn.

After obtaining the optimized reaction conditions, the substrate scope of the developed catalytic system was analyzed with respect to the aromatic amines (Table 3). The substrates gave the desired products in different time

intervals. Aromatic amines with electron donating substituents **1b-f** performed well under the present reaction conditions and afforded the corresponding benzyl carbamates **3ba-fa** in 82-90% yields (Table 3, entries 2-6). The results indicate that the size or the position of the substituents does not have much influence on the reactivity of the substrates. Unfortunately, Boc-protected 4-aminophenol **1g** resulted into diminished yield (Table 3, entry 7). The present catalytic system were found to be compatible for electron withdrawing halogen substituted aromatic amines as they participated well in the reaction. The desired products were obtained in 60-94% yields (Table 3, entries 8-10). Nitro substituted amine **1k** also gave the corresponding carbamate **3ka** in 80% (Table 3, entry 11). The developed protocol was also found to be applicable to naphthalen-1-amine **1l** and the product **3la** was obtained in 72% yield (Table 4, entry 12). Boc-protected aliphatic substrate **1m** delivered the desired carbamate in 82% (Table 3, entry 13). Boc-protected benzylamine **1n** also participated in the reaction and provided the expected product **3na** in 54% yield (Table 3, entry 14).

Table 3. Substrate scope of aromatic amines[a]

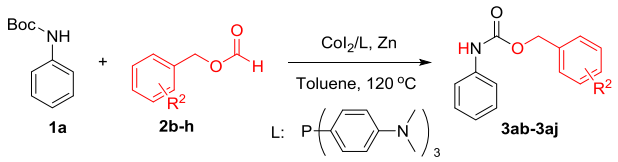


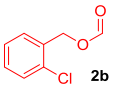
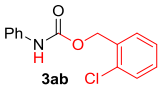
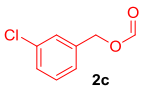
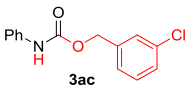
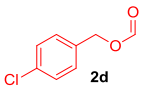
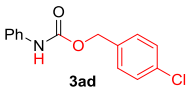
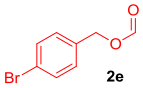
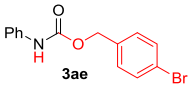
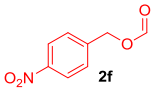
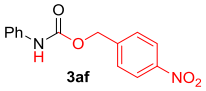
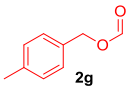
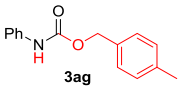
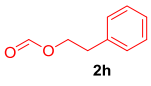
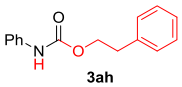
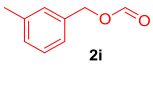
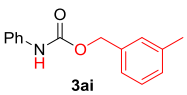
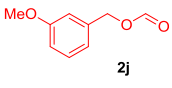
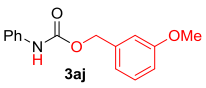
Entry	Substrate	Product	Time (h)	Yield (%)[b]
1	 1a	 3aa	24	92
2	 1b	 3ba	48	90
3	 1c	 3ca	24	86
4	 1d	 3da	40	86
5	 1e	 3ea	48	82
6	 1f	 3fa	24	83
7	 1g	 3ga	48	41
8	 1h	 3ha	38	94
9	 1i	 3ia	48	89
10	 1j	 3ja	48	60
11	 1k	 3ka	72	80
12	 1l	 3la	48	72
13	 1m	 3ma	48	82
14	 1n	 3na	72	54

[a]*Reaction conditions:* CoI_2 (10 mol%) , ligand (24 mol%) and Zn powder (0.6 mmol) were stirred in toluene (1 mL) for 30 minutes at rt under Ar. *N*-Boc protected amines **1a-1n** (0.2 mmol), benzyl formate **2a** (0.6 mmol) and 1 mL toluene were added. The reaction mixture was stirred under argon atmosphere at 120 °C. The reaction was monitored by TLC. [b]Isolated yields.

The present investigation was further extended by examining the scope of different benzyl formates **2b-j** under the developed reaction condition (Table 4). The efficiency of benzyl formate with electron withdrawing chloro group at *meta*-position was found to be less as compared to those at *ortho*- and *para*-positions (Table 4, entries 1-3). On the other hand, benzyl formate with bromo-group at *para*-position **2e** displayed good reactivity furnishing the expected product **3ae** in 79% yield (Table 4, entry 4). Electron withdrawing nitro group substituted benzyl formate **2f** also performed well in the present protocol giving the product **3af** with 87% yield (Table 4, entry 5). The present protocol was found to be amenable for substrate with electron donating methyl group **2g** with fair yield (Table 4, entry 6). Phenethyl formate **2h** also participated under the present protocol and gave the desired product **3ah** in 62% yield (Table 4, entry 7). Unfortunately, the product **3ai** was obtained only in trace amount along with complex mixture when *m*-methyl benzyl formate **2i** was used (Table 4, entry 8). The reason for this observation is obscure. When *m*-methoxy benzyl formate **2j** was used, the desired product **3aj** was obtained in 87% yield (Table 4, entry 9).

Table 4. Synthesis of carbamate using different Benzyl formates[a]

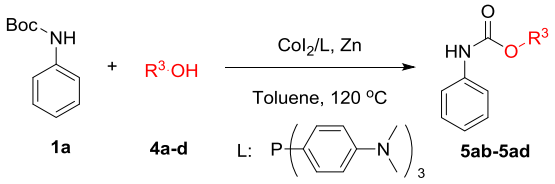


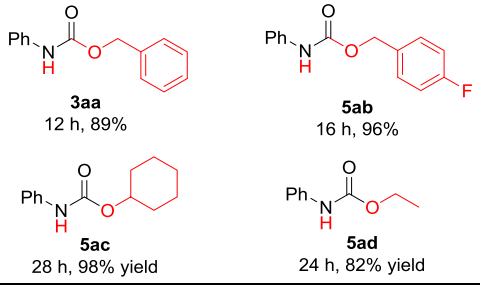
Entry	Benzyl formate	Product	Time (h)	Yield (%)[b]
1	 2b	 3ab	12	64
2	 2c	 3ac	24	38
3	 2d	 3ad	24	65
4	 2e	 3ae	40	79
5	 2f	 3af	40	87
6	 2g	 3ag	36	62
7	 2h	 3ah	24	62
8	 2i	 3ai	12	Trace
9	 2j	 3aj	18	87

[a]*Reaction conditions:* CoI_2 (10 mol%) , ligand (24 mol%) and Zn powder (0.6 mmol) were stirred in toluene (1 mL) for 30 minutes at rt under Ar. *N*-Boc protected aniline **1a** (0.2 mmol), benzyl formate **2b**-**2j** (0.6 mmol) and 1 mL toluene were added. The reaction mixture was stirred under argon atmosphere at 120 °C. The reaction was monitored by TLC. [b]Isolated yields.

To further investigate the scope of the developed catalytic system, alcohols were used instead of benzyl formate as reaction partner under the present reaction conditions (Table 5). Benzyl alcohol **4a** gave the desired carbamate **3aa** in good yield. Gratifyingly, when *p*-fluorobenzyl alcohol **4b** was used, the desired carbamate **5ab** was furnished in excellent yield. To our delight, aliphatic alcohols cyclohexanol **4c** and ethanol **4d** also participated in the present reaction giving the desired carbamates **5ac** and **5ad** in 98% and 82% yields respectively. This observation furthers broadens the substrate scope of the present catalytic system.

Table 5. Synthesis of carbamate using alcohol[a,b]



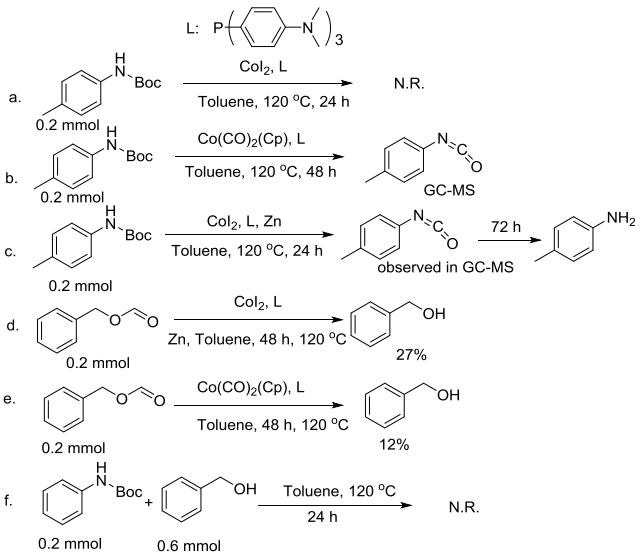


[a]*Reaction conditions*: CoI_2 (10 mol%) , ligand (24 mol%) and Zn powder (0.6 mmol) were stirred in toluene (1 mL) for 30 minutes at rt under Ar. *N*-Boc protected aniline **1a** (0.2 mmol), alcohols **4a-4d** (0.6 mmol) and 1 mL toluene were added. The reaction mixture was stirred under argon atmosphere at 120 °C for the indicated time. The reaction was monitored by TLC. [b]Isolated yields.

Control experiments

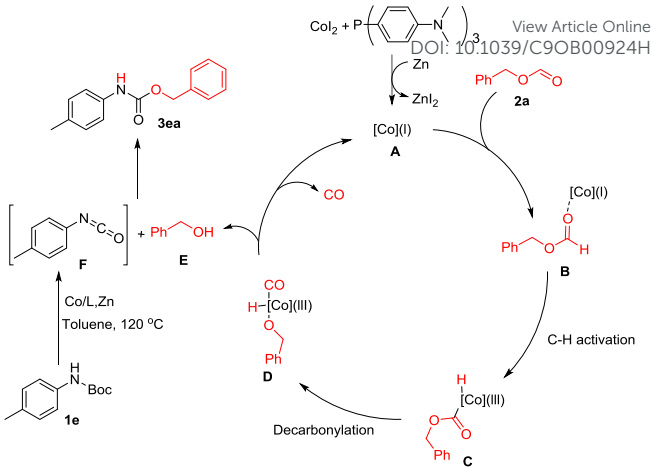
In order to get more information about the reaction intermediates for the developed reaction protocol, we carried out some control experiments (Scheme 1). No reaction took place when *N*-Boc protected aryl amine **1e** was subjected to the catalytic system in the absence of Zn (equation a). Generation of isocyanate intermediate was observed from the GC-MS analysis when *N*-Boc protected amine **1e** was subjected to the reaction using Co(I) catalyst $Co(CO)_2(Cp)$ with the phosphine ligand in toluene at 120 °C for 48 h (equation b). These observations indicate that *in situ* generation of isocyanate is involved in the reaction pathway and it is catalyzed by Co(I). Formation of the isocyanate was observed in GC-MS under the optimized reaction conditions after 24 h of reaction time which was converted into the corresponding amine after 72 h which may have been caused by the generated ZnI_2 (equation c). This further supports the involvement of *in situ* generation of isocyanate intermediate in the reaction. Conversion of benzyl formate **2a** to benzyl alcohol was obtained under the standard reaction conditions and also by using Co(I) catalyst (equations d and e). The benzyl alcohol was afforded only in trace amount on using only CoI_2 or ZnI_2 or in the absence of catalyst. No reaction took place when the unprotected aniline was subjected to react with benzyl formate under the developed reaction conditions. This observation shows that the carbonyl in the carbamate is from the Boc-protecting group. No reaction occurred when the reaction between **1a** and benzyl alcohol was carried out in absence of cobalt catalyst (equation f). The overall results led

us to conclude that there is reduction of Co(II) to Co(I) which catalyzes the *in situ* generation of both isocyanate and benzyl alcohol in the catalytic cycle. The application of less expensive alcohols for the transcarbamation of *N*-Boc protected amines via *in situ* generated isocyanate has been reported earlier.[19, 22] Although alcohols could also react under the developed reaction conditions, we used benzyl formates because our main focus was to investigate the application of the catalytic system in the *in situ* generation of isocyanate from *N*-Boc protected amines and benzyl alcohol from benzyl formate and their subsequent reactions (See Scheme S1 in Supporting Information for detailed control experiments).



Scheme 1. Control experiments to identify the reaction intermediates

Based on the results of the control experiments, we have hypothesized a plausible reaction pathway for the present reaction under the newly developed protocol (Scheme 2). The catalytic cycle commenced with the combination of CoI_2, tris-(4-dimethylaminophenyl)-phosphine and Zinc forming the reduced cobalt complex **A**. Next, complex **A** combines with benzyl formate **2a** to give intermediate **B** which underwent C-H activation to give complex **C**.[21] Decarbonylation of **C** resulted into **D** that gives rise to benzyl alcohol **E** by releasing a molecule of CO. Then, benzyl alcohol **E** combines with the isocyanate **F** generated *in situ* from **1e** under the catalytic system to give the final product **3ea**.



Scheme 2. Plausible mechanism for the synthesis of benzyl carbamate **3ea**

Conclusions

In summary, we have developed a low valent cobalt catalyst generated from CoI_2, a monophosphine ligand and zinc powder for the preparation of *N*-aryl carbamates from *N*-protected amines and benzyl formates via *in situ* generation of isocyanate and benzyl alcohol as intermediates. For the first time, benzyl formates were successfully used for the synthesis of carbamates (up to 92% yield). The developed catalytic system was compatible for *N*-Boc protected amines with both electron donating and withdrawing groups giving the corresponding *N*-aryl carbamates in up to 94% yield.

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Conflicts of interest

There are no conflicts to declare.

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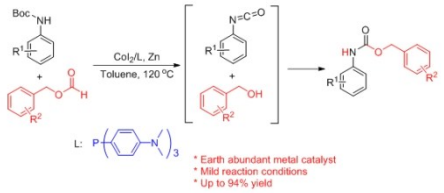

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