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Nickel-Catalyzed Synthesis of *N*-(Hetero)aryl Carbamates from Cyanate Salts and Phenols Activated with Cyanuric Chloride

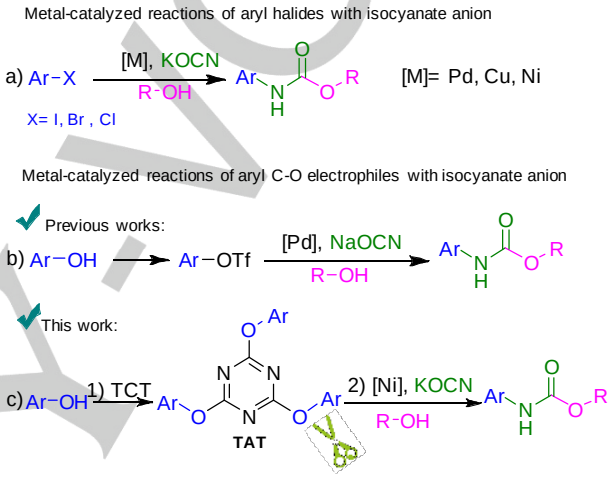
Iman Dindarloo Inaloo,*[a] Mohsen Esmaeilpour,*[a,b] Sahar Majnooni,[c] and Ali Reza Oveisi[d]

Dedication ((optional))

Abstract: A simple and efficient domino reaction has been designed and employed for the one-pot synthesis of *N*-(hetero)aryl carbamates through the reaction between alcohols and *in-situ* produced (hetero)aryl isocyanates in the presence of a nickel catalyst. The phenolic C-O bond was activated *via* the reaction of phenol with cyanuric chloride (2,4,6-trichloro-1,3,5-triazine (TCT)) as an inexpensive and readily available reagent. This strategy provides practical access to *N*-(hetero)aryl carbamates in good yields with high functional groups compatibility.

Introduction

Carbamates are the core structures of many natural and synthetic compounds with a wide range of applications in the agriculture, biological, and pharmaceutical industries.[1] However, the traditional synthetic methods for the preparation of carbamates suffer from the use of highly toxic phosgene or its derivatives.[2, 3] Recently, the synthesis of carbamates using CO_2 and CO as green carbonyl source alternatives for phosgene has been attracted great attention by researchers.[4, 5] However, these chemical transformations are performed under severe reaction conditions and need to follow strict safety guidelines.[4, 5] Since the synthesis of isocyanate *via* reacting diethyl sulfate and potassium cyanide by Wurtz in 1848, it has become one of the most popular and beneficial precursors for the synthesis of diverse organic compound specially carbamates.[6] Although the high reactivity of isocyanates is favorable for many industrial processes, however, their moisture-sensitive nature limits the scope of their applications.[7] To address the issue, the *in-situ* formation of isocyanates has been reported as the best alternative approach.[8] Hofmann,[9] Curtius,[10] Lossen,[11] and Schmidt's rearrangements have predominantly been used to generate isocyanates *in-situ* during the processes.[12] However, these reactions are limited by the availability of starting materials, harsh reaction conditions, and multiple-step synthetic procedures.[9-12] Hence, the introduction and design of new and efficient synthetic methods for straightforward access to carbamates are highly desirable.[2, 3]



Scheme 1. Metal-catalyzed reactions for the synthesis of *N*-aryl carbamates

Very recently, transition-metal catalyzed reactions of the isocyanate anion with aryl halides towards the carbamates *via* *in-situ* formation of aryl isocyanates, as reactive intermediates, have been successfully developed (Scheme 1, a).[13] Besides, activated phenolic compounds as the reactive aryl C-O electrophiles have been used as alternatives to aryl halides.[14] In recent years, the phenol derivatives have received much attention as prevailing and environmentally friendly alternatives for being used instead of aryl halides.[15] In most cases, the phenolic compounds are converted to the corresponding aryl C-O electrophiles which served as starting materials/intermediates in the metal-catalyzed reactions.[16] However, to the best of our knowledge, the literature survey showed only one report dealing with the direct conversion of aryl triflates reacted with isocyanate anion to carbamates in the presence of Pd catalyst (Scheme 1, b).[17] More recently, the *in-situ* activation of phenol derivatives with TCT towards the production of aryl-triazine ethers as the C-O electrophiles has been reported by Iranpoor *et al*.[18]

In a continuation of our previous work on the construction of C–C and C–N bonds with the cleavage of C–O bonds in the presence of nickel catalysts,[19] herein, we report the reaction of activated phenolic compounds with TCT (2,4,6-triaryloxy-1,3,5-triazine (TAT)) and cyanate anion which results in the *in-situ* formation of phenyl isocyanate in the presence of nickel catalysts followed by reacting the phenyl isocyanates with alcohol, as the nucleophile, to afford *N*-aryl carbamates (Scheme 1, c).

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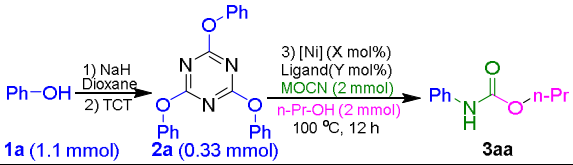
Results and Discussion

To find the proper conditions, phenol (**1a**) was selected as a model phenolic compound which initially activated by TCT to provide the corresponding 2,4,6-triphenoxy-1,3,5-triazine (**2a**). The 2,4,6-triphenyl-1,3,5-triazine (**2a**) was readily prepared according to the previously reported procedure (see the ESI).[18] Compound **2a** was then reacted with different sources of cyanate anions in the presence of various nickel catalytic systems for the *in-situ* formation of phenyl isocyanate followed by the addition of n-propanol to produce n-propyl *N*-phenylcarbamate (**3aa**) as the desired product (Table 1).

Table 1. Optimization of reaction parameters for the synthesis of propyl *N*-phenylcarbamate (**3aa**).[a]



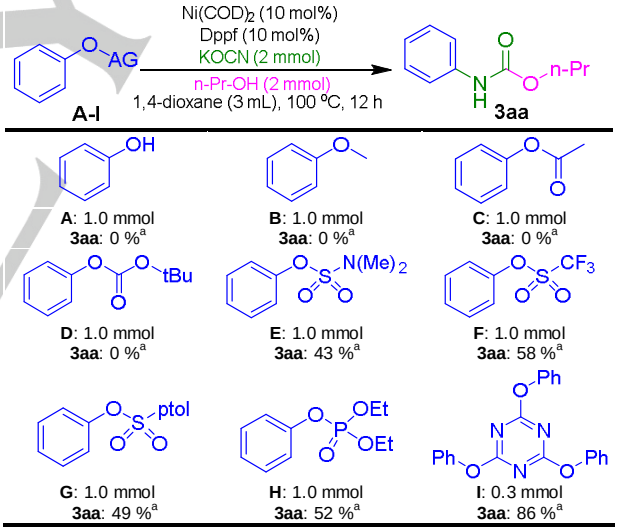
Entry	[Ni](X mol%)	Ligand(Y mol%)	MOCN	yield (%)[b]
1	$NiCl_2$ (10 mol%)	Dppf (10 mol%)	KOCN	0
2	$NiBr_2$ (10 mol%)	Dppf (10 mol%)	KOCN	0
3	$Ni(OAc)_2$ (10 mol%)	Dppf (10 mol%)	KOCN	43
4	$Ni(acac)_2$ (10 mol%)	Dppf (10 mol%)	KOCN	46
5	$Ni(COD)_2$ (10 mol%)	Dppf (10 mol%)	KOCN	86
6	--	Dppf (10 mol%)	KOCN	0
7	$Ni(COD)_2$ (10 mol%)	--	KOCN	0
8	$Ni(COD)_2$ (10 mol%)	Glyme (10 mol%)	KOCN	28
9	$Ni(COD)_2$ (10 mol%)	1,10-Phen (10 mol%)	KOCN	24
10	$Ni(COD)_2$ (10 mol%)	2,2'-Bipy (10 mol%)	KOCN	29
11	$Ni(COD)_2$ (10 mol%)	Ph_3P (10 mol%)	KOCN	30
12	$Ni(COD)_2$ (10 mol%)	PCy_3 (10 mol%)	KOCN	27
13	$Ni(COD)_2$ (10 mol%)	$P(tBu)_3$ (10 mol%)	KOCN	33
14	$Ni(COD)_2$ (10 mol%)	XantPhos (10 mol%)	KOCN	42
15	$Ni(COD)_2$ (10 mol%)	Dcype (10 mol%)	KOCN	56
16	$Ni(COD)_2$ (10 mol%)	Dppe (10 mol%)	KOCN	62
17	$Ni(COD)_2$ (10 mol%)	Dppp (10 mol%)	KOCN	68
18	$Ni(COD)_2$ (5 mol%)	Dppf (5 mol%)	KOCN	63
19	$Ni(COD)_2$ (8 mol%)	Dppf (8 mol%)	KOCN	76
20	$Ni(COD)_2$ (15 mol%)	Dppf (15 mol%)	KOCN	86
21	$Ni(COD)_2$ (8 mol%)	Dppf (15 mol%)	KOCN	73
22	$Ni(COD)_2$ (10 mol%)	Dppf (20 mol%)	KOCN	84
23	$Ni(COD)_2$ (10 mol%)	Dppf (10 mol%)	NaOCN	81
24	$Ni(COD)_2$(10 mol%)	Dppf (10 mol%)	NH_4OCN	79

[a] Reaction conditions. Step 1: phenol (1.1 mmol), NaH (1.2 mmol) in dry 1,4-dioxane (3 mL) stirred for 1h at room temperature; Step 2: TCT (0.33 mmol) was added to the reaction mixture and stirred for 10 h at 100 ℃; Step 3: Ni catalyst (X mol %), ligand (Y mol %), MOCN (2 mmol) and n-propanol (2 mmol) was added to the reaction mixture and stirred for 12h at 100 ℃.
[b] Isolated yield, an average of 3 runs.

Subsequently, to find the best catalytic system, the model reaction was tested by using 10 mol% of 1,10-bis(diphenylphosphino)ferrocene (Dppf) as the ligand and different Ni(II) catalysts (10 mol%) (Table 1, entries 1–5). Unfortunately, the model reaction did not proceed with $NiCl_2$ and $NiBr_2$ (Table 1, entries 1–2). The moderate yields of n-propyl N-phenylcarbamate (**3aa**) were observed when $Ni(OAc)_2$ and $Ni(acac)_2$ used as the catalyst (Table 1, entries 3 and 4). Fortunately, the yield of the desired product was improved to 86% in the presence of $Ni(COD)_2$ (Table 1, entry 5). The experiments showed that both Ni catalyst and ligand are necessary for the reaction (Table 1, entries 6–7). Moreover, the important effect of the ligand on the reaction efficiency was studied (Table 1, entries 8–17). As indicated in table 1, the bidentate dppf was found to be the most effective ligand for the catalytic reaction. We also examined the reaction in the presence of the different loadings of catalyst ($Ni(COD)_2$) and ligand (dppf) (Table 1, entries 5 and 18-22). As shown in table 1, 10 mol% of $Ni(COD)_2$ and 10 mol% of dppf were favorable for the proceeding reaction, providing the highest product yield of 86% (entry 5). Although the investigation of cyanate sources demonstrated that all of them were effective for this transformation, it was found that the KOCN is the best cyanate source for the formation of the desired product under these reaction conditions (Table 1, entries 23–24). Furthermore, temperature (Table S1) and reaction time (Table S2) on the model reaction were carefully investigated.

To show the versatility of the nominal catalytic system, the protocol was further checked with various derivatives of phenol-based compounds (Table 2). As shown in the table, phenol **A**, anisole **B**, phenyl acetate **C**, and *tert*-butyl phenyl carbonate **D** did not proceed with the reaction and almost remained intact. However, under identical conditions, the use of the related sulfamate, triflate, tosylate and phosphate compounds (**E-H**) successfully promoted the reaction and the obtained yields were 43%, 58%, 49%, and 52%, respectively.

Table 2. Optimization of reaction parameters for the synthesis of propyl *N*-phenylcarbamate (**3aa**).[a]



[a] Isolated yield, an average of 3 runs.

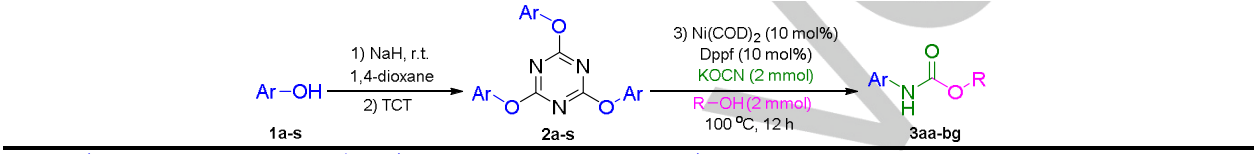
Interestingly, when compound 2,4,6-triphenyl-1,3,5-triazine (**I**) was used as the starting material, the increase in the product yield up to 86% was observed. The data confirm the benefits of using the TAT as the phenol-based electrophile respect to the others for the preparation of *N*-aryl carbamates (Table 2).

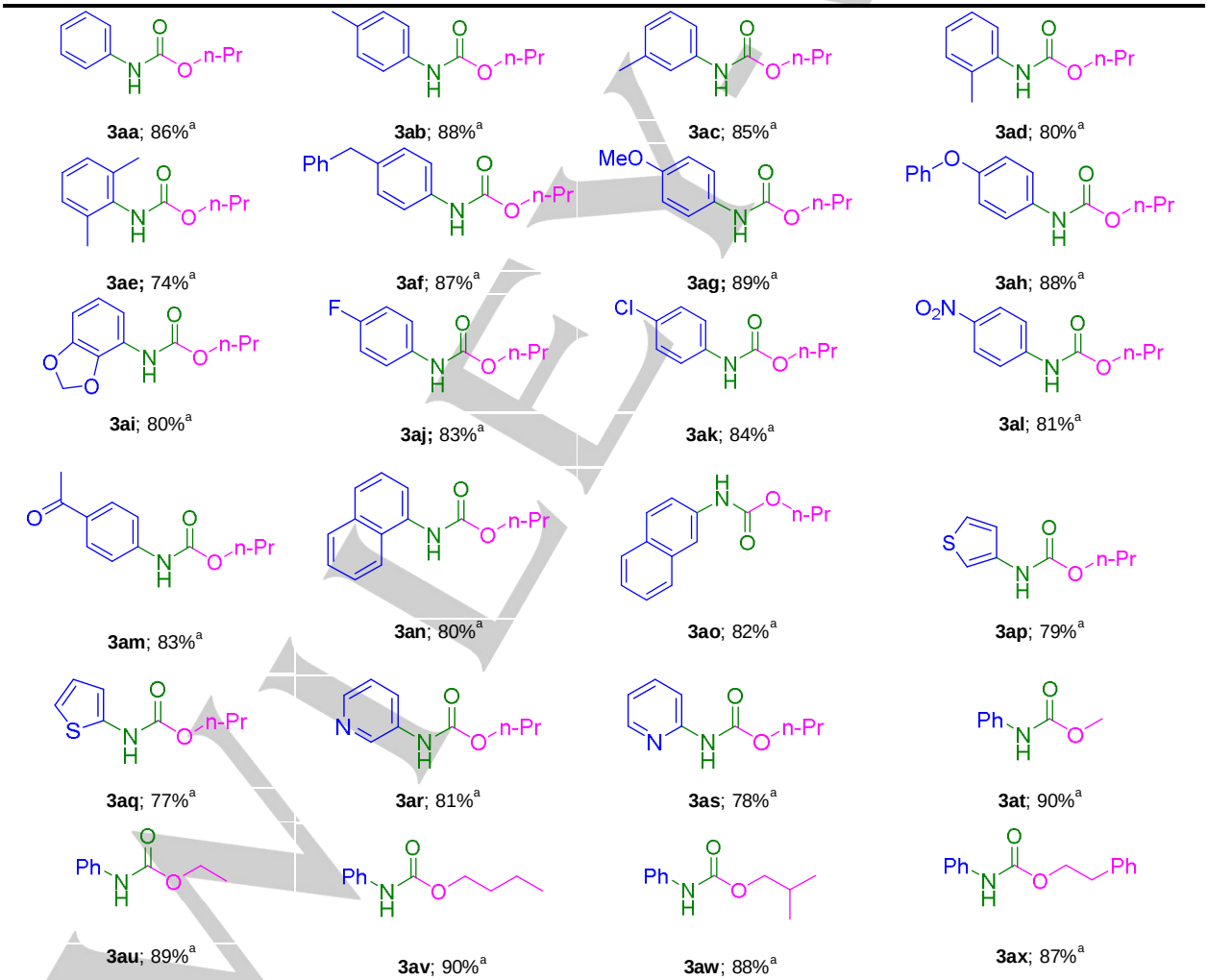
Having established efficient conditions for the *in-situ* preparation of aryl isocyanate from the activated aryl alcohol toward carbamate formation, we next explored the substrate scope of the present protocol with different varieties of TAT substrates and alcohols (Table 3).

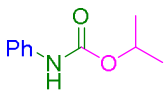
At first, we screened the reaction of different phenol substrates and found that phenol containing both electron-donating and

withdrawing groups provided the carbamate product in good to excellent yields (Table 3, compounds **3aa-am**). However, substitution at *ortho*-position in the phenols showed a reduced yield of the desired carbamates due to the diminished yield of the aryl isocyanate (Table 3, compounds **3ad-ae**). Besides, the naphthalic alcohols could also provide the corresponding carbamates in good yields (Table 3, compounds **3an**-**ao**). Interestingly, heteroaryl alcohols were employed and carbamate products obtained in satisfactory yields (Table 3, compounds **3ap**-**as**). Next, we sought the possibility of applying other alcohols as nucleophiles on the synthesis of carbamates under the optimized reaction conditions. Intestinally, the aliphatic, allylic, and benzylic alcohols generally performed well in this transformation towards the production of the desired carbamates in good to excellent yields (Table, compounds **3at**-**bf**). The sterically hindered substrates such as L-(-)-menthol and *tert*-butyl alcohol gave corresponding products in slightly lower yields (Table 3, compounds **3bb**-**bc**). In the synthesis of carbamates from aryl isocyanates, the aromatic alcohols could not react similarly to the aliphatic alcohols which might be due to their lower nucleophilicity. On the other hand, the increase in the amount of aryl isocyanate in the reaction media could lead to the formation of isocyanurate as a side product.

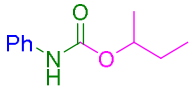
Table 4. Activation of the C–O bond in aryl-alcohols using TCT reagent for the Ni-catalyzed synthesis of *N*-aryl carbamates.[a]



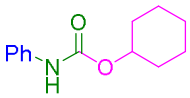




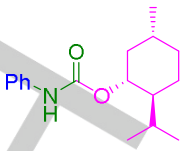
3ay; 83%[a]



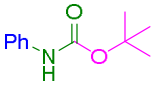
3az; 82%[a]



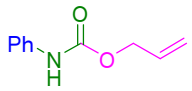
3ba; 85%[a]



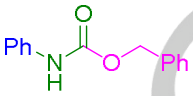
3bb; 64%[a]



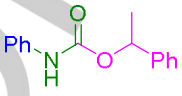
3bc; 66%[a]



3bd; 82%[a]



3be; 81%[a]



3bf; 73%[a]

[a] Isolated yield, an average of 3 runs.

To understand the stability of the [Ni(COD)(dppf)] catalytic system [20] during the reaction condition, as a case study, we examined ^{31}P-NMR spectroscopy of the complex 1 before and after increasing temperature up to 100 °C at different times under N_2 atmosphere.

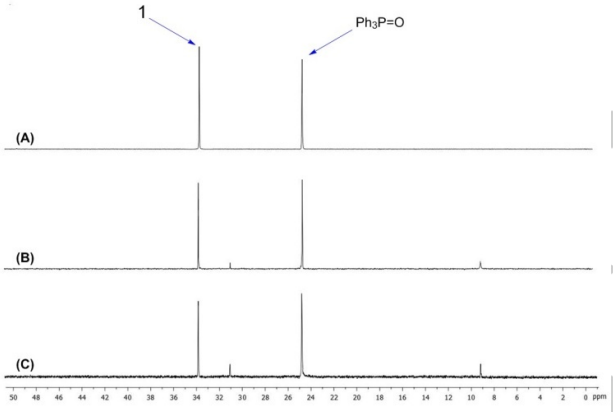
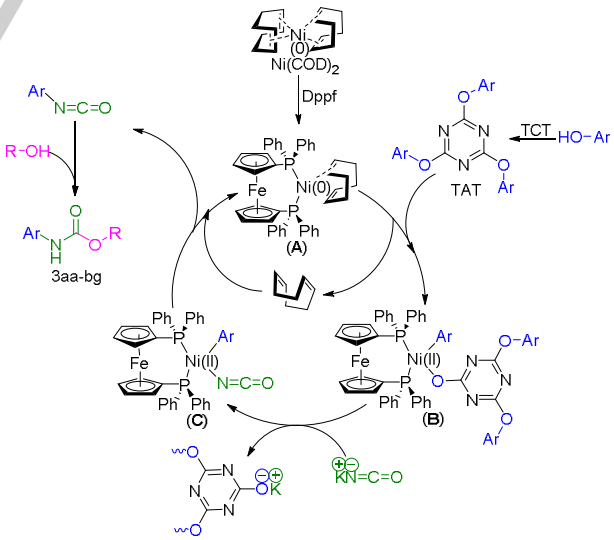


Figure 1. Partial ^{31}P NMR of complex 1([Ni(COD)(dppf)]) in toluene-*d8* at different times. Sample conditions: before heating at 100 °C (A), after 2 hours (B) and after 5 h(C). Ph_3PO is an internal standard.

As shown in figure 1A, the mixture of complex 1 and Ph_3PO (as an internal standard) at room temperature presented two peaks in ~25 ppm and ~34 ppm. These two peaks were also observed in ^{31}P NMR of the mixture after 2 hours at 100 °C, along with two small peaks in around ~9 ppm and ~31 ppm (Figure 1B). This spectral pattern was further clearly observed in ^{31}P NMR spectrum after 5 hours at 100 °C (Figure 1C). Based on this finding and the above-mentioned results, complex 1 was stable enough to drive the reaction to the desired product. The results are consistent well with previously reported stability studies of the complex (**A**).[20-21] It has been reported that a series of comproportionation and disproportionation events can occur during the organic transformations.[20]

It should be noted that the modulation of the ligand sphere at Ni centers affect the oxidation state and reactivity of the elementary catalytic steps.[21] In accordance with the previously reported Ni-catalytic systems,[22] the plausible mechanism for this protocol is proposed as illustrated in Scheme 2.

It is known that the $Ni(COD)_2$ catalyst in the presence of dppf ligand forms the Ni-complex (**A**) due to the high steric demand of the dppf ligand. Subsequently, the oxidative addition of TAT electrophile to the Ni-complex (**A**) led to the formation of Ni(II)-complex (**B**) as an intermediate. The next step involves rapid coordination/ligand exchange of the intermediate (**B**) by a cyanate ion to form the intermediate (**C**). This intermediate through a reductive elimination process results in the formation of (hetero)aryl isocyanate and regenerating the Ni-complex (**A**). It should be noted that the C-O bond cleavage takes place selectively at aryl C-O [18, 22] and no product with respect to the cleavage of the triazine C-O was observed. Finally, the alcohol can attack to the *in-situ* produced (hetero)aryl isocyanate to afford the corresponding carbamate. Moreover, the regenerated Ni-complex (**A**) is ready to concurrently take part in the next cycle.



Scheme 2. Proposed mechanism for nickel-catalyzed synthesis of *N*-(hetero)aryl carbamates from potassium isocyanate and activated phenol with TCT.

Conclusions

In summary, we have designed and developed an efficient domino strategy for the one-pot conversion of phenolic compounds to their corresponding *N*-aryl carbamates. The aryl isocyanate intermediates are *in-situ* formed from the nickel-catalyzed coupling of cyanate anions with electrophilic TAT reagents *via* C-O activation. Triaryloxytriazine is used as an alternative for the aryl halides for the carbamate synthesis. Notably, the method allows the one-pot preparation of electrophilic TAT reagents from the cheap and accessible (hetero)aryl alcohols in the presence of TCT without the need of the isolation and purification process. The features of this method such as the broad substrate scope and the use of green and inexpensive starting materials make it a viable strategy for the industrial and pharmaceutical applications. We believe that the method would open a new avenue for the synthesis of various organic compounds from alcohols and phenols as starting materials.

Experimental Section

General experimental:

Chemicals were obtained from Sigma-Aldrich and Merck. Column chromatography was performed using silica gel from Macherey-Nagel (60 M, 0.04–0.063 mm). The products were characterized by spectral and physical data such as NMR, FT-IR, MS, CHNS and melting point. Melting points were recorded by Electrothermal 9100. Fourier transforms infrared (FTIR) spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance DPX 250MHz instruments with Me_4Si or solvent resonance as the internal standard. ^{1}H NMR spectroscopic data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q= quartet, quint = quintet, sext = sextet, sept = septet, br. = broad, m = multiplet), coupling constants (Hz), and integration. ^{31}P NMR spectra were recorded on a Bruker Avance DRX 400 MHz. The mass spectra were recorded on a Shimadzu GC-MS QP 1000 EX instrument. The C, H, N and S elemental analyses were carried out by using a Thermofinigan Flash EA-1112 CHNSO rapid elemental analyzer. Determination of the purity of the substrate and monitoring of the reaction were accomplished by thin-layer chromatography (TLC) on a silica-gel polygram SILG/UV 254 plates.

General Procedure for the activation of the C–O bond in aryl-alcohols using TCT reagent for the synthesis of *N*-aryl carbamates (3aa-3bf):

In a flask, NaH (1.2 mmol) was added to a stirring mixture of phenol (1.1 mmol) in dry 1,4-dioxane (3 mL) at room temperature and stirred for 1h. Then, TCT (0.33 mmol) was added and the mixture was stirred for 10 h at 100 °C which delivered TAT in good yield. Then, the reaction was cooled down to room temperature and $Ni(COD)_2$ (10 mol%) and dppf (10 mol%) were weighed and added in a glove box. Then, the potassium cyanate (2 mmol) and alcohol (2 mmol) was added; the mixture was stirred at 100 ℃ for 12 h under nitrogen atmosphere. The reaction was monitored by TLC. After completion of the reaction, ethyl acetate (3×10 mL) was added and the mixture was filtered. The organic phase was washed with water (2×10 mL) and dried over anhydrous Na_2SO_4. The solvent (EtOAc) was removed under reduced pressure and the product was purified by column chromatography on silica gel (petroleum ether and ethyl acetate, 8:2) and characterized. The isolated pure products were obtained in excellent to moderate yields.

Propyl phenylcarbamate(3aa):White crystal (0.1541 gr, 86% yield); mp: 50-51℃. IR (KBr); 3317 (s), 3138 (m), 3058 (m), 3019 (vw), 2985 (s), 2974 (s), 1704 (vs), 1597 (s), 1544 (s), 1447 (s), 1376 (m), 1317 (vs), 1304 (m), 1238 (vs), 1177 (m), 1159 (w), 1121 (s), 1080 (m), 1054 (s), 1027 (m), 995 (vw), 966 (w), 905 (s), 855 (vw), 845 (vw), 823 (w), 761 (s), 747 (s), 690 (s), 508 (m) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$):δ= 7.26 (m, 4H), 6.97 (m, 1H), 6.64 (s, br, 1H, NH), 4.05 (t, J = 7.5 Hz, 2H), 1.62 (sext, J = 7.5 Hz, 2H), 0.90 (t, J = 7.5 Hz, 3H) ppm. ^{13}C-NMR (63 MHz, $CDCl_3$):δ =153.74, 137.98, 129.01, 123.30, 118.63, 66.83, 22.26, 10.34 ppm. MS Calcd*m/z* 179.22, Found 179. Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82%. Found: C, 66.97; H, 7.32; N, 7.86%.

The data for all the other prepared carbamates can be found in the SupportingInformation.

Acknowledgments

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Keywords: Carbamate • C-O bond activation • Phenol • Nickel catalyst • Aryl isocyanate • Cyanuric Chloride.

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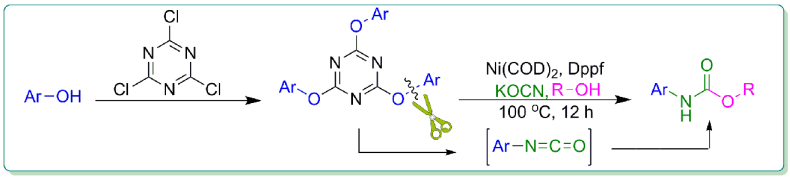

In this work, a simple and efficient domino reaction has been designed and used for the synthesis of *N*-(hetero)aryl carbamates by the *in-situ* formation of (hetero)aryl isocyanates and their reaction with alcohols in the presence of a nickel catalyst. The C-O bond was activated through the reaction of phenol with cyanuric chloride. This strategy provides a practical access to *N*-(hetero)aryl carbamates in good yields with high functional groups compatibility.