Domino Reactions

A Fe₃O₄@SiO₂/Schiff Base/Pd Complex as an Efficient Heterogeneous and Recyclable Nanocatalyst for One-Pot Domino Synthesis of Carbamates and Unsymmetrical Ureas

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Abstract: A palladium-catalyzed domino method for the direct synthesis of carbamates and ureas has been developed by using readily available and economical starting materials (aryl halide, carbon monoxide, sodium azide, amines and alcohols) in a one-pot approach. The domino process underwent carbonylation, Curtius rearrangement, and nucleophilic addition. This protocol provides a step-economical and highly efficient reaction to access the wide range of valuable carbamates, symmetrical and unsymmetrical ureas with high yields under remarkable mild reaction conditions that are important factors in pharmaceutical science, biochemistry and agricultural industries. Furthermore, the magnetically recoverable nanocatalyst (Fe₃O₄@SiO₂/Pd(II)) can be conveniently and swiftly recycled using external magnet and reused at least for seven times without noticeable loss of its catalytic activity.

Introduction

Carbamates and urea are of the most important and attractive structural units that are frequently present in the wide range of valuable efficacious combinations such as natural products, pharmaceuticals, cosmetics, nutraceuticals, disinfectants, and agrochemicals.[1] Nowadays due to the unique bioactive potentials of these compounds, a large number of organic compounds containing such functional groups have been developed into marketed drugs such as pimavanserin,[2] imidocarb,[3] glasdegib,[4] celiprolol,[5] cariprazine,[6] gedatolisib,[7] rivastigmine,[8] distigmine,[9] carisoprodol,[10] albendazole,[11] zafirlukast,[12] rimegepant[13] and cobicistat.[14] Figure 1 illustrates some of the mentioned compounds.

Furthermore, these compounds present very significant roles in various fields of chemical sciences including amine protecting groups specially in the peptide synthesis,[15] as directing groups in nucleoside synthesis,[16] as versatile intermediates in the manufacturing[17] and even in the synthesis of fertilizers,[18] herbicides,[19] pesticides,[20] polyurethane foams plastics,[21] synthetic rubber,[22] artificial leather,[23] fabric[24] and adhesive agents.[25]

For a long time, these compounds were principally prepared from the treatment of corresponding amines and alcohols with phosgene, isocyanate or their derivatives which isocyanates mainly have been manufactured by phosgenation of the corresponding arylamines.[26] In recent years, it is determined that
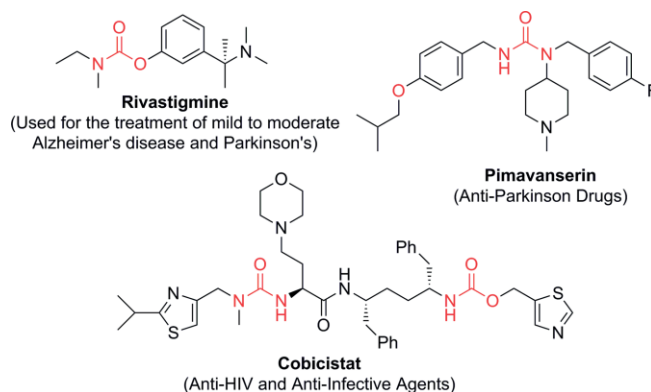

Figure 1. Important pharmaceuticals containing the carbamate or urea structures.

the phosgene is extremely toxic and hazardous substance causes serious environmental pollution and equipment corrosion.[27] Therefore, in the environment protection and social safety points of view, the development of green and eco-friendly alternative processes is highly indispensable.[28] Accordingly, there have been numerous attempts to produce carbamates and ureas with non-phosgene routes in the new millennium.[29] Of the various non-phosgene strategies, the favorable reductive or oxidative carbonylation of nitro- or amino-compounds with CO as a carbonyl source in the presence of transition metal catalysts has been attracted considerable attention.[30] A number of effective catalytic systems have also been reported for preparing carbamates and ureas via these two methods in which the transition metals such as Pd,[31] Pt,[32] Ru,[33] Rh,[34] Ir,[35] Au,[36] Cu[37] and Se are generally being applied.[38] Nonetheless, the application of these processes has been limited by low selectivity, insignificant scope and conduct-

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ing at high temperatures and pressures. Furthermore, the usage of O_2 as the common oxidant in the oxidative carbonylation of amines in these reaction conditions certainly requires rigorous safety issues.[39] It should be noted that these limitations, greatly slow down the development speed of these processes for industrial application.[39] To overcome these disadvantages, the carbonylation of azides under low CO pressure has been determined as an alternative method.[40] However, besides the usage of expensive noble metals and ligands, the organoazides as the starting material are usually not available and the preparation of them creates new challenges.[41] Although, some exquisite ways for the synthesis of azide derivatives have been developed, the traditional multi-steps methods need time-consuming and costly synthesis approaches, tedious workup, and purification of precursors as well as protection/deprotection of functional groups.[42] A general way to improve synthetic efficiency is the development of multicomponent domino reactions, which allow the formation of complex compounds starting from simple substrates.[43] Fortunately, a few successful attempts for the domino synthesis of unsymmetrical ureas by the reaction of aryl halides with sodium azide and carbon monoxide have been recently developed.[44] Nevertheless, developing the domino and one-pot process for the synthesis of carbamates and ureas from accessible and affordable materials is still highly desirable.[44]

As previously stated, the catalysts are the key enablers in most of these chemical processes.[45] Despite necessities for the recycling and reusing of so precious catalysts to develop eco-friendly and economic processes, their facile separation is one crucial proposition.[46] Recently, magnetic nanoparticles (MNPs) have been found a remarkable niche in diverse sciences especially in designing and preparing reusable catalysts.[47] They can be easily separated and collected from the reaction media with an external appropriate magnetic field.[47] Among the wide range of the magnetic nanoparticles that have been used as a substrate for catalysts, the iron oxide NPs (Fe_3O_4) have caught great attention due to their simple synthesis and functionalization, low price, good stability and high magnetic properties.[48] Additionally, to improve the properties and performance of the MNPs, the surface of them generally was coated by some shells such as silicate, carbon, ceramics and polymers.[49] Indeed, these layers can protect the core (Fe_3O_4 MNPs) from corrosion and different erosion conditions.[49]

In continuation of our research for the development and extension of the eco-friendly process as well as the introduction of recoverable catalysts in the synthesis of highly valuable organic compounds,[50] we disclose the results of our efforts to extend the effective strategy into the domino single-pot processes in which carbamates can be formed from aryl halides, sodium azide and amines or alcohols in the presence of
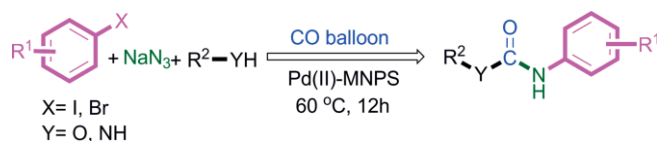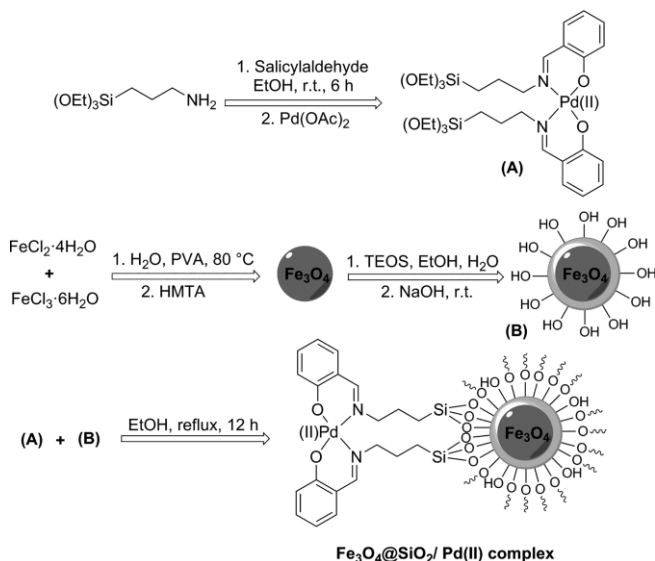

Scheme 1. Direct domino synthesis of carbamates and ureas.

$Fe_3O_4@SiO_2$/Schiff base/Pd(II) complex under mild conditions (Scheme 1).

Results and Discussion

The retrievable palladium (II) based magnetic nanocatalyst ($Fe_3O_4@SiO_2$/Pd(II)) was synthesized through the protocol had been used among recent years by our research group.[51] Scheme 2 concisely describes the synthetic procedure of the catalyst.
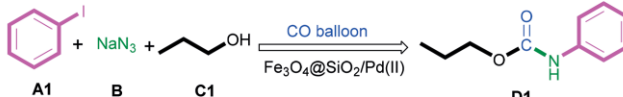

Scheme 2. Synthetic procedure of $Fe_3O_4@SiO_2$/Pd(II) complex.

After the preparation of $Fe_3O_4@SiO_2$/Pd(II), the performance and efficiency of which as the catalyst in domino synthesis of carbamates from aryl halides, sodium azide and alcohols under various conditions (including different solvents, molar ratios of reactants, amounts of catalyst, temperatures and time) were investigated. The results are summarized in Table 1 in which the reaction of phenyl iodide, sodium azide and propanol in the presence of $Fe_3O_4@SiO_2$/Pd(II) under the pressure of 1 atm of CO was selected as the model reaction.

To find the best reaction conditions, we firstly investigated the performance of model reaction in several solvents (Table 1, entries 1–11) and finally, we found that dioxane provides the best medium for the desired one-pot domino reaction. In continues, the effect of the molar ratio of reactants (phenyl iodide/ sodium azide/propanol) on the production amount of desired product was investigated (Table 1, entries 12–16). These studies showed that the model reaction presents the best performance using the molar ratio of 1:1.5:1 among phenyl iodide, sodium azide and propanol, respectively. Afterward, the activity of $Fe_3O_4@SiO_2$/Pd(II) catalyst in different amounts was studied in the model reaction (Table 1, entries 17–20). These reviews exhibited that the presence of the catalyst is necessary for reaction progress and the best result was obtained in the presence of 5 mol-% of the catalyst. Furthermore, evaluating the effect of temperature and time revealed that the highest yield will be obtained at 60 °C after 12 hours (Table 1, entries 21–29).

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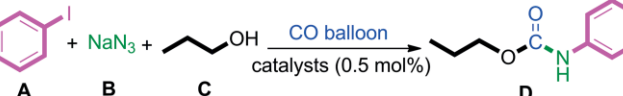Table 1. Optimization of various reaction parameters for one-pot domino synthesis of propyl phenylcarbamate (D1).

Entry	Molar ratio A1:B:C1	Solvent	Catalyst (mol %)	Temp [°C]	Time [h]	Yield (%)[a]
1	1:1.5:1	None	0.5	60	12	18
2	1:1.5:1	CH₂Cl₂	0.5	60	12	42
3	1:1.5:1	CHCl₃	0.5	60	12	36
4	1:1.5:1	DCE	0.5	60	12	48
5	1:1.5:1	MeCN	0.5	60	12	73
6	1:1.5:1	DMSO	0.5	60	12	78
7	1:1.5:1	THF	0.5	60	12	61
8	1:1.5:1	DMF	0.5	60	12	70
9	1:1.5:1	Toluene	0.5	60	12	23
10	1:1.5:1	Xylene	0.5	60	12	31
11	1:1.5:1	Dioxane	0.5	60	12	92
12	1:1:1	Dioxane	0.5	60	12	81
13	1:1.2:1	Dioxane	0.5	60	12	86
14	1:2:1	Dioxane	0.5	60	12	92
15	1:1.5:1.5	Dioxane	0.5	60	12	91
16	1:2:2	Dioxane	0.5	60	12	92
17	1:1.5:1	Dioxane	-	60	12	0
18	1:1.5:1	Dioxane	0.3	60	12	79
19	1:1.5:1	Dioxane	0.7	60	12	92
20	1:1.5:1	Dioxane	1.0	60	12	91
21	1:1.5:1	Dioxane	0.5	R.T.	12	0
22	1:1.5:1	Dioxane	0.5	40	12	18
23	1:1.5:1	Dioxane	0.5	50	12	47
24	1:1.5:1	Dioxane	0.5	70	12	89
25	1:1.5:1	Dioxane	0.5	80	12	87
26	1:1.5:1	Dioxane	0.5	60	6	64
27	1:1.5:1	Dioxane	0.5	60	9	78
28	1:1.5:1	Dioxane	0.5	60	15	90
29	1:1.5:1	Dioxane	0.5	60	24	90

[a] Isolated yield.

To illustrate the merit of the Fe₃O₄@SiO₂/Pd(II) catalyst in the proposed research, the model reaction was carefully examined with using a series of transition metal catalysts and the results are listed in Table 2.

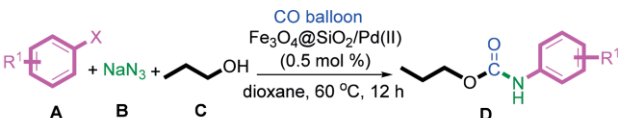Table 2. The screening of catalysts reactivity on one-pot domino synthesis of propyl phenylcarbamate (D1).[a]

Entry	Catalyst	Yield [%][b]
1	Cu(OAc)₂	trace
2	Ni(OAc)₂	trace
3	Co(OAc)₂	trace
4	PdCl₂	17
5	Pd₂dba₃	21
6	Pd(OAc)₂	26
7	Pd(acac)₂	13
8	Fe₃O₄	0
9	Fe₃O₄@SiO₂	0
10	Fe₃O₄@SiO₂/Pd(II)	92
11	Schiff base/Pd(II) complex	91

[a] Reaction conditions: phenyl iodide (1 mmol), sodium azide (1.5 mmol), propanol (1 mmol) and catalyst (0.5 mol-%) in dioxane (3 mL) and under CO pressure (1 atm) at 60 °C for 12 h. [b] Isolated yield.

These results showed the superiority of presented magnetic nanocatalyst (Fe₃O₄@SiO₂/Pd(II)) and efficiency rather than other tested transition metal catalysts in the model reaction (Table 2, entries 1–10). Additionally, it can be observed that the better results did not obtain either using other palladium sources as the homogeneous catalysts in the model reaction (Table 2, entries 4–7) or evenusing Schiff base/Pd(II) complex as homogeneous catalyst under the optimized reaction conditions (Table 2, entry 11). It should be noted that the use of Fe₃O₄ or Fe₃O₄@SiO₂ as catalyst did not result in the preparation of the desired product (Table 2, entries 8–9).

To further explore the scope and limitations of the one-pot domino synthesis of carbamates, a variety of aryl halide substrates were examined in the reaction with propanol and sodium azide under the optimized reaction conditions (Table 3).

Table 3. The substrates scope of the aryl halides in the one-pot domino synthesis of carbamates.[a]

D1
X: I, 92%[b]
X: Br, 89%[b]

D2
X: I, 93%[b]
X: Br, 90%[b]

D3
X: I, 92%[b]
X: Br, 88%[b]

D4
X: I, 90%[b]
X: Br, 86%[b]

D5
X: I, 93%[b]
X: Br, 88%[b]

D6
X: I, 89%[b]
X: Br, 85%[b]

D7
X: I, 94%[b]
X: Br, 91%[b]

D8
X: I, 93%[b]
X: Br, 89%[b]

D9
X: I, 87%[b]
X: Br, 83%[b]

D10
X: I, 86%[b]
X: Br, 81%[b]

D11
X: I, 88%[b]
X: Br, 85%[b]

D12
X: I, 84%[b]
X: Br, 80%[b]

[a] Reaction conditions: aryl halides (1 mmol), sodium azide (1.5 mmol), propanol (1 mmol) and catalyst (0.5 mol-%, 0.02 g) in dioxane (3 mL) and under CO pressure (1 atm) at 60 °C for 12 h. [b] Isolated yield.
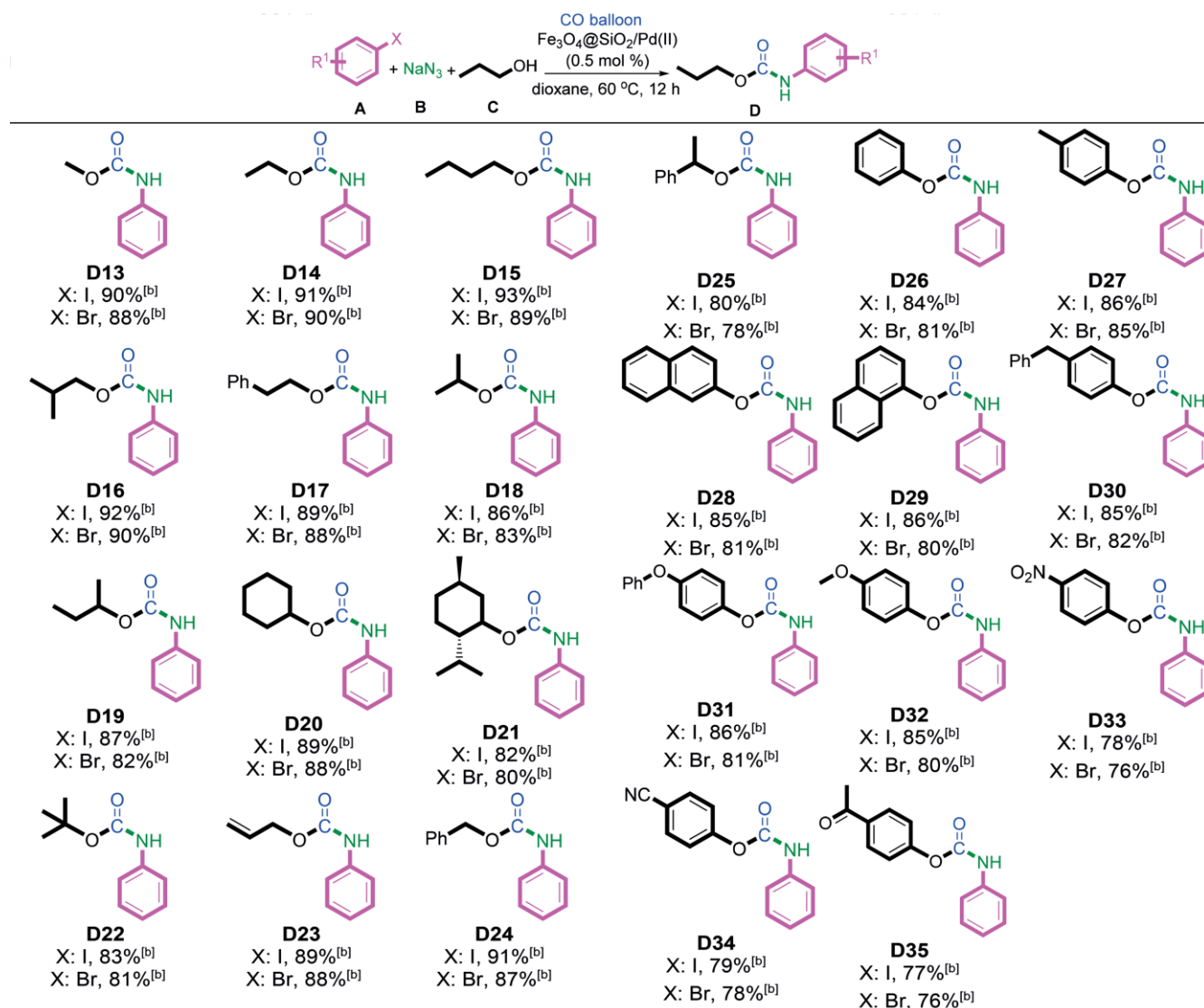
As shown in Table 3, a series of substituted aryl and heterocyclic halides (iodides and bromides) were successfully applied to this reaction and produced the desired carbamates in good to excellent yields (Table 3, entries D1–D12).

Fortunately, both electron-donating groups (Table 3, entries D1–D8) and electron-withdrawing groups (Table 3, entries D9–D11) tolerate the reaction conditions very well. Additionally, the steric effect of aryl halide substituents did not significantly affect the reaction yields (Table 3, entries D2–D6). However, the substrates with electron-withdrawing groups gave somehow lower yields in comparison with those bearing electron-donating groups. Moreover, both 3-iodothiophene and 3-bromothiophene as the heterocyclic halides have very admirable tolerance against the reaction conditions and prepared the desired carbamate in very satisfactory yield (Table 3, entry D12). It should be noted that different aryl iodides tolerate these reaction conditions slightly better than the bromides.

To assess and define the scope of this methodology, the capability of a library of aliphatic and aromatic alcohols was studied in the one-pot domino synthesis of carbamates under the optimized reaction conditions (Table 4).

As shown in Table 4, the primary, secondary and tertiary aliphatic alcohols can properly take part in the reaction (Table 4, entries D13–D17). Unfortunately, when the alcohols that suffer from strict hindrance were served as nucleophile in the reactions, the steric effects decreased the efficiency and afforded the desired carbamates in lower yields (Table 4, entries D21, D22 and D25). On the other hand, when L-(–)-menthol is used as a chiral substrate, the related carbamate was obtained without any changes in the configuration of stereo centers in high yield (Table 4, entry D21). Moreover, the allylic and benzylic alcohols performed effectively in this one-put domino reaction resulting in the corresponding carbamates in notable yields (Table 4, entries D23–D25). It was pleasing to observe that the

Table 4. The substrates scope of the aryl halides in the one-pot domino synthesis of carbamates.[a]

D13
X: I, 90%[b]
X: Br, 88%[b]

D14
X: I, 91%[b]
X: Br, 90%[b]

D15
X: I, 93%[b]
X: Br, 89%[b]

D25
X: I, 80%[b]
X: Br, 78%[b]

D26
X: I, 84%[b]
X: Br, 81%[b]

D27
X: I, 86%[b]
X: Br, 85%[b]

D16
X: I, 92%[b]
X: Br, 90%[b]

D17
X: I, 89%[b]
X: Br, 88%[b]

D18
X: I, 86%[b]
X: Br, 83%[b]

D28
X: I, 85%[b]
X: Br, 81%[b]

D29
X: I, 86%[b]
X: Br, 80%[b]

D30
X: I, 85%[b]
X: Br, 82%[b]

D19
X: I, 87%[b]
X: Br, 82%[b]

D20
X: I, 89%[b]
X: Br, 88%[b]

D21
X: I, 82%[b]
X: Br, 80%[b]

D31
X: I, 86%[b]
X: Br, 81%[b]

D32
X: I, 85%[b]
X: Br, 80%[b]

D33
X: I, 78%[b]
X: Br, 76%[b]

D22
X: I, 83%[b]
X: Br, 81%[b]

D23
X: I, 89%[b]
X: Br, 88%[b]

D24
X: I, 91%[b]
X: Br, 87%[b]

D34
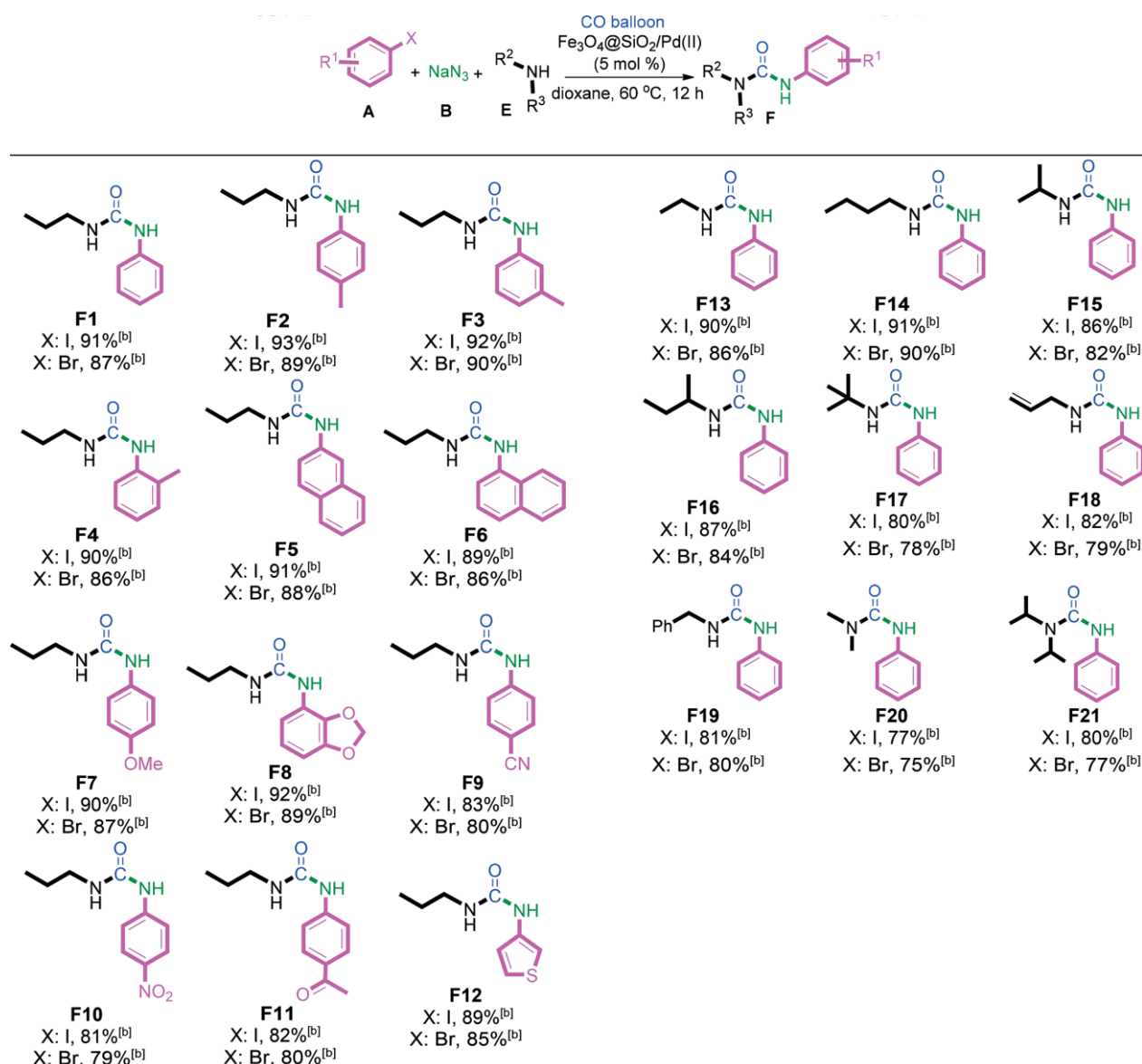X: I, 79%[b]
X: Br, 78%[b]

D35
X: I, 77%[b]
X: Br, 76%[b]

[a] Reaction conditions: aryl halides (1 mmol), sodium azide (1.5 mmol), alcohols (1 mmol) and catalyst (0.5 mol-%, 0.02 g) in dioxane (3 mL) and under CO pressure (1 atm) at 60 °C for 12 h. [b] Isolated yield.

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bout aromatic alcohols containing electron-donating groups and electron-withdrawing groups on the aryl rings can be applied in this reaction to afford the desired carbamates in good yields (Table 4, entries D26–D35). It is noteworthy to explain that the efficiencies of the electron-deficient substrates were slightly lower than those bearing electron-rich substrates because they deactivate the nucleophilicity of hydroxyl group via inductive and resonance effect (Table 4, entries D33–D35).

After studying this process getting delightful results, we decided to determine the practical efficiency, range and generality of this methodology by using in the synthesis of unsymmetrical ureas. Therefore, various aromatic and aliphatic amines were investigated under the optimized reaction conditions for the preparation of symmetrical and unsymmetrical ureas and the results are summarized in Table 5.

Fortunately, a similar stupendous phenomenon was also observed for the one-pot domino synthesis of symmetrical and unsymmetrical ureas. Similarly, the treatment of aryl and heterocyclic halides (iodides and bromides) with propylamine presented the expected ureas in good to excellent yields (Table 5, entries F1–F12). However, the use of aryl halides containing the electron-deficient substitutions presents somewhat lower yields (Table 5, entries F9–F12). Additionally, it was found that primary and secondary aliphatic amines give the desired ureas in good to excellent yields (Table 5, entries F13–F23). As expected, the lower yield was beholden for secondary amines, which suffers from steric hindrance (Table 5, entries F20–F23). Moreover, the allyl and benzylamines presented the corresponding products in excellent yields (Table 5, entries F18–F19). Unfortunately, when aromatics amines were subjected to this

Table 5. The substrates scope of the amines and aryl halides in the one-pot domino synthesis of ureas.[a]

[a] Reaction conditions: aryl halides (1 mmol), sodium azide (1.5 mmol), amines (1 mmol) and catalyst (0.5 mol-%, 0.02 g) in dioxane (3 mL) and under CO pressure (1 atm) at 60 °C for 12 h. [b] Isolated yield.

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reaction, the corresponding ureas obtained in lower yields in comparison to the aliphatic amines can be attributed to the low nucleophilicity of aromatic amines (Table 5, entries F24–F28). Moreover, the presence of an electron-withdrawing substituent on the benzene ring of aniline gave more reduction in yield of the desired product (Table 5, entries F27–F28). Furthermore, when *N*-methyl aniline was treated by diphenylamine, the corresponding urea derivatives were isolated in moderate yields, which were probably due to steric effects and low nucleophilicity of these compared with primary amines (Table 5, entries F29–F30). These results indicate that the nucleophilicity of alcohols or amines is an essential requirement for the efficient formation of carbamates and ureas.

The durability and recyclability of the catalysts are so essential from both ecological and economic points of view. To verify these issues, the perfect magnetic separation and recycling of the magnetic $Fe_3O_4@SiO_2/Pd(II)$ nanocatalyst were investigated. As it can be seen in Figure 2, this catalyst can be completely dispersed in the reaction media and also, it can be easily collected and recovered from the reaction mixture using an external magnetic field.
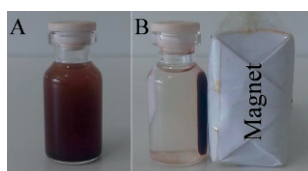

Figure 2. Photo images of magnetic field-response of the $Fe_3O_4@SiO_2$/Schiff base of Pd(II) nanoparticles before the application of a magnetic field (A) and under the magnetic field (B).

Furthermore, to determine the reusability of the catalyst after completing the model reaction, the catalyst was completely separated from the reaction mixture by using an external magnet, washed with hot ethanol, dried thoroughly under vacuum and reused in the next cycle of model reaction. As it is exhibited in Figure 3, this process was repeated for seven consecutive cycles and no considerable losing in catalytic activity was observed.
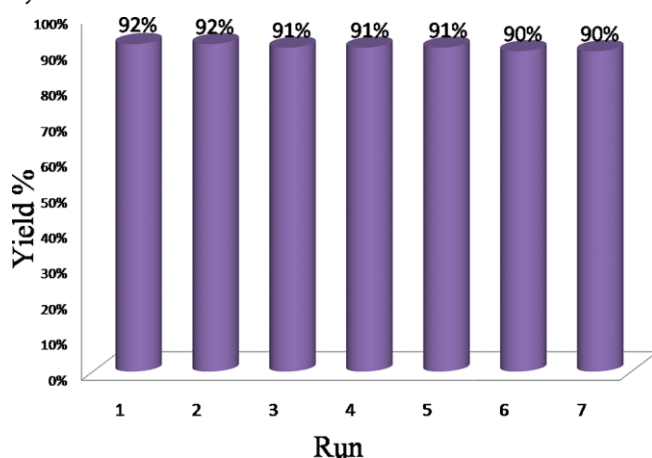

Figure 3. Reuse of the catalyst for the one-pot domino synthesis of *O*-propyl phenylcarbamate (**D1**).

Moreover, to confirm the stability of the catalyst, the recycled catalyst after the last cycle was characterized by FT-IR, XRD and

FE-SEM (Figure 4). Both fresh and reused catalysts have almost similar IR spectrum in which the peaks at 1100, 1618, 2973 and 3414 are related to Si–O–Si, C=N, C–H and O–H groups, respectively. The degree of crystallinity and phase investigation of the reused catalyst was performed by powder X-ray diffraction (XRD) in which the consistency in the position of peaks shows that the crystalline structure of the magnetite was essentially maintained. Besides, the FE-SEM image of the recovered catalyst after the seventh run demonstrates that nanocatalyst keeps its spherical shape with insignificant agglomeration.
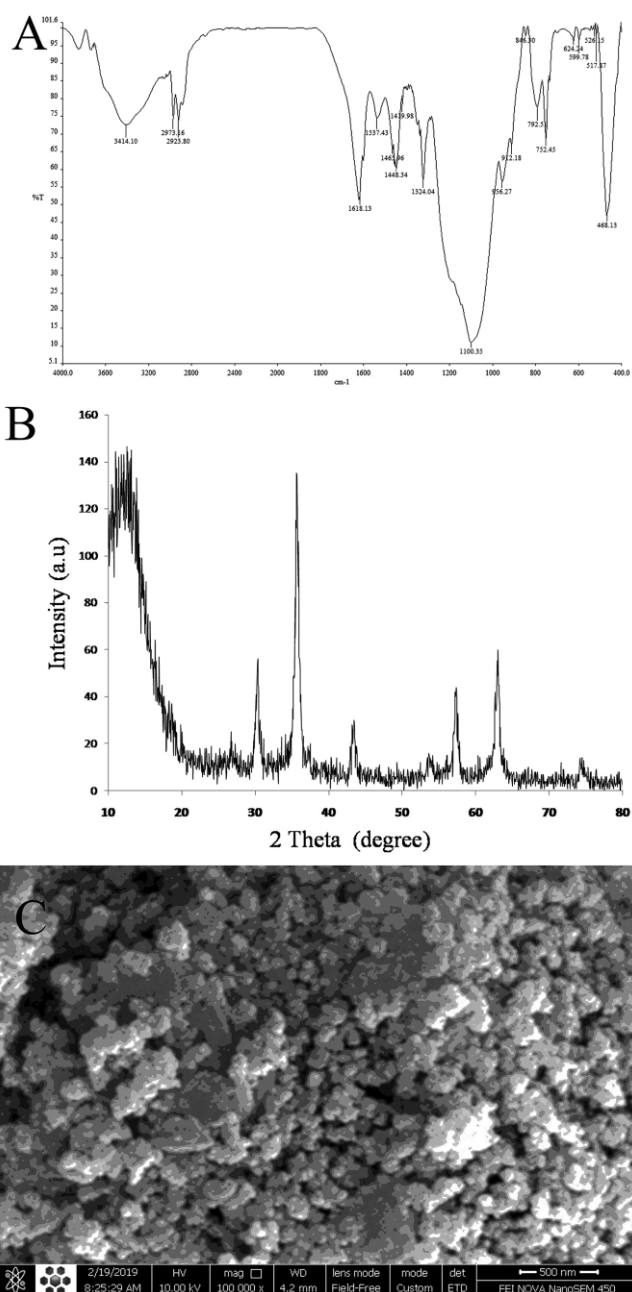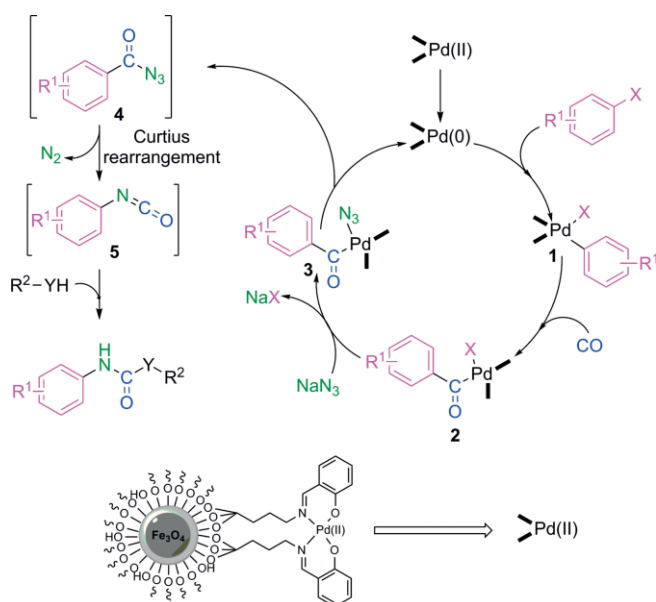

Figure 4. (a) FT-IR spectrum, (b) XRD pattern, and (c) TEM images of the catalyst after the seventh run.

Additionally, fresh and recovered catalysts after the last run were investigated by inductively coupled plasma (ICP) analysis to determine the amount of palladium leaching. Accordingly,

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the amount of loaded palladium on the fresh catalyst was measured to be 0.26 mmol/g. Propitiously, the ICP analysis after the seventh run showed just 0.9 % palladium leaching.

Moreover, to determine the responsibility of palladium moiety for carrying out the one-pot domino synthesis of carbamate, the hot filtration test was performed. When the reaction time of model reaction reached half time of reaction quenching, the catalyst nanoparticles were gathered from the reaction mixture by an external magnetic field and the residue was allowed to be stirred under the reaction conditions. The monitoring of reaction mixture by TLC did not show any considerable progress. These results showed that only a few species of palladium were leached into the reaction medium and the main responsible species to catalyze such one-pot domino synthesis of carbamates is the magnetic $Fe_3O_4@SiO_2$/Pd(II) nanoparticles. All of these data confirmed the high stability and reusability of the catalyst under these reaction conditions.

Although the detailed mechanism of this one-pot domino reaction is still unclear, the plausible mechanistic approach to explain the formation and rearrangement of the products is depicted in Scheme 3 based on obtained evidences as well as the reported researches in the literature.[44,52] Initially, the process begins with the reduction of the $Fe_3O_4@SiO_2$/Pd(II) with carbon monoxide, sodium azide, alcohol or amine to an active $Fe_3O_4@SiO_2$/Pd(0) species. Subsequently, the catalytic cycle starts with the oxidative addition of Pd(0) to give the intermediate complex **1**. Then, the intermediate complex **2** was obtained with coordination and insertion of carbon monoxide by the intermediate complex **1**. The anion exchange of intermediate complex **2** with sodium azide produces the intermediate **3** followed by reductive elimination step to give Pd(0) and aroylazide **4**. Moreover, the regenerated catalytic active Pd(0) is ready to simultaneously take part in catalyst cycle. The produced aroylazide **4** underwent Curtius rearrangement catalyzed by palladium to form the corresponding isocyanate intermediate **5** with the loss of the molecular nitrogen (N_2). Finally, the ureas or carbamates as final products obtained immediately by the nucleophilic attack of amines or alcohols to the aryl isocyanates **5** had been already activated by the Pd-catalyst as a Lewis acid.

Conclusions

In summary, we have presented an attractive and convenient one-pot domino route for the formation of valuable carbamates and ureas from readily available and economical starting materials. The $Fe_3O_4@SiO_2$/Schiff base/Pd(II) complex has been introduced as an effective magnetic nanocatalyst for the successful domino synthesis of such compounds from aryl halide, sodium azide, amines or alcohols under atmospheric carbon monoxide conditions. Other key features of this reaction are the simple workup, high yields and broad substrate scopes with high functional group tolerance. Furthermore, this magnetic nanocatalyst is very stable under the reaction conditions and could be rapidly and completely recovered and reused for seven cycles without any decrease in the catalytic activity. It is worth noting that this methodology provides a green, facile and highly efficient approach for the synthesis of beneficial compounds without the formation of harmful and corrosive wastes or by-products makes this procedure a promising alternative to the traditional procedures in the various industries particularly in the pharmaceutical industry, cosmetics industry and agriculture industry.

Experimental Section

General: All chemicals were purchased from Merck, Flucka and Aldrich Chemicals in high purity and were used without further purification. The products were characterized by the comparison of their spectral and physical data such as FT-IR, NMR, CHNS and melting point with available literature data. The overall progress of reactions and also the purities of reaction products were checked by TLC on silica gel polygram SILG/UV254 plates. Fourier transform infrared (FTIR) spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with Bruker Avance DPX 250 MHz instruments with Me_4Si or solvent resonance as the internal standard. ^1H 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. The elemental analyses (C, H, N) were performed using a Thermo Finnigan Flash EA-1112 CHNSO rapid elemental analyzer. Pd loading and leaching test was carried out with an Inductively Coupled Plasma (ICP) analyzer (Varian, vista-pro). X-ray diffraction (XRD) of the samples was also studied using a Bruker AXS D8-advance XRD using a Philips powder diffractometer type PW 1373 goniometer with the scanning rate of 2° min^{-1} in the 2θ range from 0° to 90°. Field emission scanning electron microscopy (FE-SEM) was performed using a Hitachi S-4160. Dynamic light scattering was done on a Horiba-LB550.

General Procedure for the Preparation of Fe_3O_4 Nanoparticles:[51] The naked Fe_3O_4 nanoparticles were prepared according to the improved chemical coprecipitation method as previously reported. To the solution of 1.3 g $FeCl_3 \cdot 6H_2O$ (4.8 mmol) in deionized water (15 mL), added a mixture of polyvinyl alcohol (PVA 15000)

Scheme 3. The plausible mechanism for the one-pot domino synthesis of carbamates and ureas.

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(1.0 g), as the surfactant, and 0.9 g FeCl$_2$·4H$_2$O (4.5 mmol) in deionized water (15 mL). The resultant solution was stirred with mechanical stirring for 30 min at 80 °C. In the next step, hexamethylenetetramine (HMTA) (1.0 mol/L) was added dropwise with vigorous stirring to produce a black solid product and also the reaction media reaches pH 10. Next, the black mixture was heated for 2 hours at 60 °C. Finally, the synthesized Fe$_3$O$_4$ nanoparticles were separated magnetically and washed with ethanol three times and dried at 80 °C for 10 hours.

General Procedure for the Preparation of Fe$_3$O$_4$@SiO$_2$ Coreshell:[51] For the preparation of Fe$_3$O$_4$@SiO$_2$ core-shell, Fe$_3$O$_4$ (0.5 g, 2.1 mmol) was dispersed in a solution of ethanol (50 mL), deionized water (5.0 mL) and tetraethoxysilane (TEOS) (0.2 mL), followed by the addition of 5.0 mL of NaOH (10 wt.-%) under vigorous stirring. This mixture was left to be stirred for 30 min at room temperature. Then, the product Fe$_3$O$_4$@SiO$_2$ was separated by an external magnet, washed three times with a solution of deionized water and ethanol and dried at 80 °C for 10 hours.

General Procedure for Preparation of the Ligand:[51] A solution of the stoichiometric amount of salicylaldehyde (1.0 mmol, 0.122 g) in ethanol (25 mL) was added dropwise to the 3-aminopropyl (triethoxy) silane (1.0 mmol, 0.176 g) in 25 mL of ethanol. Then, the mixture was stirred at room temperature for 6 hours. The resulting salen ligand, as the bright yellow precipitate, was separated by filtration, washed with ethanol (5.0 mL) and dried in vacuo. The final crude was recrystallized from ethanol to obtain the pure product in 98 % yield (0.271 g).

General Procedure for Preparation of the Pd(II) Complex:[51] Pd(OAc)$_2$ (0.224 g, 1.0 mmol) was added to the solution of synthesized ligand (0.651 g, 2.0 mmol) in ethanol (25 mL). Then, the obtained mixture was allowed to proceed in reflux conditions. After the completion of complex formation, the resulted product was filtered and washed with ethanol. Finally, the Pd(II) complex was purified by recrystallization from ethanol.

General Procedure for Preparation of the Pd(II) Complex Supported on Superparamagnetic Fe$_3$O$_4$@SiO$_2$ Nanoparticles:[51] Fe$_3$O$_4$@SiO$_2$ (2.0 g) was firstly added to the solution of Pd(II) complex (1.0 mmol) in ethanol (10 mL) and the resultant was stirred under reflux condition for 12 hours. Then, hot ethanol and water were added to the mixture. Next, the nanocatalyst Fe$_3$O$_4$@SiO$_2$/Pd(II) complex was separated by an external magnet and dried at 80 °C for 6 hours.

General Procedure for the One-pot Domino Synthesis of Carbamates (D1–D35): The 10 mL round-bottomed flask was charged with aryl halide (1.0 mmol), sodium azide (0.1 g, 1.5 mmol), alcohols (1.0 mmol), Fe$_3$O$_4$@SiO$_2$/Pd(II) (0.028 g, 0.5 mol-%) and dioxane (3 mL). The flask was evacuated and back-filled with CO. The mixture was heated to 60 °C and stirred for 12 hours under CO atmosphere. After the completion of the reaction, the reaction mixture was cooled down to room temperature and diluted with water (15 mL). Subsequently, the catalyst was separated by using an external magnetic field, washed with hot ethanol, dried, and reused for sequential runs under the same reaction conditions. Then, the mixture was extracted with ethyl acetate (2 × 10 mL) and the organic layer was dried with anhydrous Na$_2$SO$_4$. The resulting solution was evaporated under vacuum to give the crude product. Finally, the obtained crude product was purified by recrystallization from the diethyl ether.

General Procedure for the One-pot Domino Synthesis of Unsymmetrical Ureas (F1–F30): A 10 mL round-bottomed flask was charged with aryl halide (1.0 mmol), sodium azide (0.1 g, 1.5 mmol),

amine (1.0 mmol), Fe$_3$O$_4$@SiO$_2$/Pd(II) (0.028 g, 0.5 mol-%) and dioxane (3 mL). The flask was evacuated and back-filled with CO. The mixture was heated to 60 °C and stirred for 12 hours under CO atmosphere using balloon set up. After the completion of the reaction, it was cooled down to room temperature and diluted with water (15 mL). Subsequently, the catalyst was separated using an external magnetic field, washed with hot ethanol, dried, and reused for the next runs under the same reaction conditions. Then, the mixture was extracted with ethyl acetate (2 × 10 mL). The organic layer was dried with anhydrous Na$_2$SO$_4$ and resulting solution was evaporated under vacuum to give the crude product. Finally, the product was obtained by the recrystallization of final crude using the diethyl ether.

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