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Article

Green and Selective Synthesis of *N*-Substituted Amides using Water Soluble Porphyrazinato Copper(II) Catalyst

Sara S. E. Ghodsinia,[a] ***Batool Akhlaghinia,****[,a] ***Elham Safaei***[b] ***and Hossein Eshghi***[a]

[a]*Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad,*
9177948974 Mashhad, Islamic Republic of Iran

[b]*Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS),*
45137-66731 Zanjan, Islamic Republic of Iran

N,N',N'',N'''-Tetrametil tetra(2,3-piridil)porfirazinato metil sulfato de cobre(II) ([Cu(2,3-tmtppa)](MeSO$_4$)$_4$) catalisou com sucesso a conversão direta de nitrilas a amidas *N*-substituídas. A síntese seletiva do tipo *one pot* de amidas *N*-substituídas a partir de nitrilas e aminas primárias foi realizada em refluxo de água. O catalisador foi recuperado e reusado no mínimo 4 vezes, mantendo a sua eficiência.

N,N',N'',N'''-Tetramethyl tetra-2,3-pyridinoporphyrazinato copper(II) methyl sulfate ([Cu(2,3-tmtppa)](MeSO$_4$)$_4$) efficiently catalyzed the direct conversion of nitriles to *N*-substituted amides. The one pot selective synthesis of the *N*-substituted amides from nitriles and primary amines was performed in refluxing H$_2$O. The catalyst was recovered and reused at least four times, maintaining its efficiency.

Keywords: [Cu(2,3-tmtppa)](MeSO$_4$)$_4$, *N*-substituted amide, nitrile, amine

Introduction

Amide bond formation is a fundamental reaction of great interest in organic and bioorganic chemistry, peptides and proteins include these bonds. Synthesis of *N*-alkyl amides has been of great interest because they are versatile synthetic intermediates used in the manufacture of several pharmacological products, polymers, detergents, lubricants and drug stabilizers, as well as key structural motifs present in numerous natural products.[1-5] Current popular synthesis strategies of amides are the reaction of amines with carboxylic acids, transamidation of amides with amines, or with the reaction of carboxylic acid derivatives such as acyl halides, anhydrides, esters and other activated species usually in the presence of coupling reagents.[6-27] Reactions promoted by coupling reagents are fundamental in organic synthesis. The majority of amide bond syntheses is merely stoichiometric, making these methods generally expensive and wasteful procedures.[28] As the society needs forward-looking environmentally acceptable technology, the development of catalytic reactions that use transition-metal complex catalysts under neutral and mild reaction conditions is particularly important. These criteria include atom efficiency, formation of little inorganic waste, and selective synthesis of desired products, encouraging an effort towards using environmentally friendly catalytic processes that will not produce such waste. The conversion of aldehydes,[29-36] oxime[34,37-46] and nitriles[47-54] constitute effective methods to access amides.[31,55-61]

A little-known reaction which yields amides is the hydrolytic amidation of nitriles with amines. A platinum and an iron catalysts were found to perform the coupling.[53,54] Nitriles can also be coupled with alcohols to form amides in the Ritter reaction. As an alternative to sulfuric acid, the Ritter reaction can be catalyzed by metal complexes such as bismuth triflate[62] and iron complexes.[63]

Our group recently reported that [Cu(2,3-tmtppa)](MeSO$_4$)$_4$ (*N,N',N'',N'''*-tetramethyl tetra-2,3-pyridinoporphyrazinato copper(II) methyl sulfate) could be used as catalyst for protection of hydroxyl and carbonyl groups.[64-66] In the course of our present study, our interesting is in using [Cu(2,3-tmtppa)](MeSO$_4$)$_4$ (Scheme 1) as a safe, environmentally benign and efficient acid catalyst in the preparation of *N*-substituted amides.

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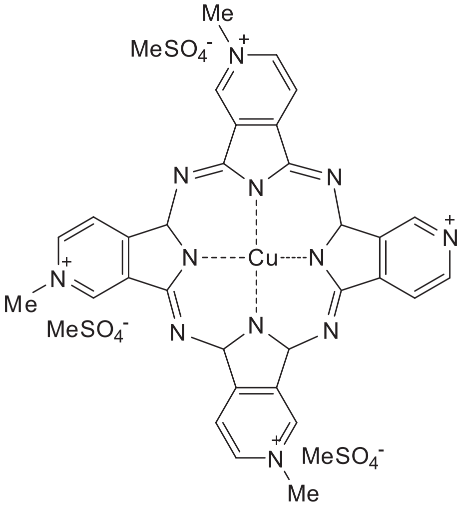
*e-mail: akhlaghinia@um.ac.ir



Scheme 1. The structure of [Cu(2,3-tmtppa)]($MeSO_4$)$_4$.

Experimental

General

The products were purified by column chromatography. The purity determinations of the products were accomplished by thin layer chromatography (TLC) on silica gel polygram STL G/UV 254 plates. The melting points of the products were determined with an Electrothermal type 9100 melting point apparatus. The Fourier transform infrared (FTIR) spectra were recorded on an Avatar 370 FTIR Therma Nicolet spectrometer. The nuclear magnetic resonance (NMR) spectra were provided on Brucker Avance 100 and 400 MHz instruments in $CDCl_3$. Elemental analyses were performed using an Elementar Vario EL V5.19.1121 and Thermofinnigan Flash EA 1112 Series instruments. Mass spectra (MS) were recorded with a Shimadzu GC-MS-QP5050 and CH7A Varianmat Bremem instruments at 70 eV. The known products were characterized by FTIR and ^{1}H NMR spectra and comparisons of their melting points (or those of the derivatives) were done with authentic samples. The catalyst was prepared and purified by the method described in the literature.[67-69]

Results and Discussion

The optimization of the reaction conditions was carried out for the reaction of phenylacetonitrile with benzylamine in the presence of [Cu(2,3-tmtppa)]($MeSO_4$)$_4$ under various reaction parameters in order to achieve the maximum chemical yield at the lowest reaction time and lowest reaction temperature. The general reaction is outlined in Scheme 2 and the representative results are shown in Table 1.

In the absence of any catalyst, there was no conversion to *N*-benzyl-2-phenylacetamide (Table 1, entries 1, 20 and 21). In solvent free condition and applying different molar ratios of phenylacetonitrile, benzylamine, [Cu(2,3-tmtppa)]$^{4+}$ was identified as a catalyst for *N*-benzyl-2-phenylacetamide formation but in prolonged reaction time and low yield (Table 1, entries 2-5). In an effort to develop better reaction conditions, different solvents were screened for the preparation of *N*-benzyl-2-phenylacetamide from the reaction of phenylacetonitrile with benzylamine in the presence of 0.5 mol% of [Cu(2,3-tmtppa)]($MeSO_4$)$_4$. No product was obtained when the reaction was performed in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), CH_2Cl_2 and Et_2O (Table 1, entries 6-9). The catalytic effect of [Cu(2,3-tmtppa)]($MeSO_4$)$_4$ was efficiently decreased in aprotic polar solvents such as DMSO and DMF because of the strong coordination of solvent with Cu^{II}. As shown in Table 1, when the reaction was performed in refluxing 1,4-dioxane and H_2O, *N*-benzyl-2-phenylacetamide was obtained in good to excellent yields. To improve amide formation, the effect of different molar ratios of phenylacetonitrile, benzylamine was examined in 1,4-dioxane and H_2O (Table 1, entries 10-19). Also, the effect of temperature was studied in 1,4-dioxane and H_2O. No conversion was observed when the reaction was carried out at room temperature (Table 1, entries 22-23). It seems that the temperature is an important factor in the preparation of *N*-benzyl-2-phenylacetamide. The best results were obtained in 1,4-dioxane, H_2O, toluene and tetrahydrofuran (THF) (Table 1, entries 10-19,25-26). Because of safety, economic and handling considerations, H_2O was chosen for further experiments. Maximum yield was observed in refluxing H_2O with a 1:2 molar ratio of phenylacetonitrile:benzylamine (Table 1, entry 18). To investigate the effect of catalyst loading, the formation of *N*-benzyl-2-phenylacetamide was carried out in refluxing H_2O in the presence of 1 mol% of catalyst. According to this study, increasing the catalyst loading did not lead to higher conversion (Table 1, entry 24). It is noteworthy that no evidence for reaction of phenylacetonitrile with water was observed in the absence of benzylamine and any tendency between phenylacetonitrile and H_2O can be prohibited (Table 1, entry 27).

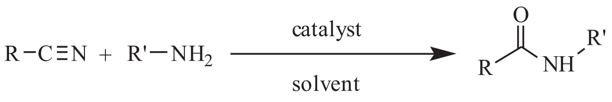
To explore the generality and scope of the *N*-substituted amides formation catalyzed by [Cu(2,3-tmtppa)]($MeSO_4$)$_4$, the optimized reaction conditions (1:2 molar ratio of nitrile:amine, 0.5 mol% catalyst, refluxing H_2O) were used for the synthesis of a series of amide derivatives (Table 2).

According to the results obtained (Table 2), *N*-substituted amides were prepared from the reaction of aromatic and aliphatic nitriles with primary aliphatic amines in the

Table 1. Synthesis of *N*-benzyl-2-phenylacetamide in the presence of 0.5 mol% of [Cu(2,3-tmtppa)]$(MeSO_4)_4$ in various solvents, different molar ratios and different temperatures

entry	Molar ratio (phenylacetonitrile:benzylamine)	Solvent	Temperature / °C	time / h	Isolated yield / %
1[a]	1/1	none	90	30	0
2	1/1	none	90	32	60
3	1/1.5	none	90	30	65
4	1/1.7	none	90	27	68
5	1/2	none	90	24	68
6	1/1	DMSO	90	24	0
7	1/1	DMF	90	24	0
8	1/1	CH_2Cl_2	reflux	24	0
9	1/1	Et_2O	reflux	24	0
10	1/1	1,4-dioxane	reflux	30	80
11	1/1.5	1,4-dioxane	reflux	25	85
12	1/1.7	1,4-dioxane	reflux	22	90
13	1/2	1,4-dioxane	reflux	20	95
14	1/2.2	1,4-dioxane	reflux	20	98
15	1/1	H_2O	reflux	23	85
16	1/1.5	H_2O	reflux	23	90
17	1/1.7	H_2O	reflux	22	95
18	1/2	H_2O	reflux	19	98
19	1/2.2	H_2O	reflux	19	97
20[a]	1/2	1,4-dioxane	reflux	20	0
21[a]	1/2	H_2O	reflux	20	0
22	1/2	1,4-dioxane	rt	20	0
23	1/2	H_2O	rt	20	0
24[b]	1/2	H_2O	reflux	19	98
25	1/2	toluene	reflux	19	98
26	1/2	THF	reflux	23	90
27	1/0	H_2O	reflux	20	0

[a]The reaction was performed in the absence of catalyst; [b]the reaction was performed in the presence of 1 mol% of catalyst.



	R		R'
1a	$C_6H_5CH_2$	**1b**	$C_6H_5CH_2$
2a	4-Cl-$C_6H_5CH_2$	**2b**	2-OMe-$C_6H_5CH_2$
3a	C_6H_5	**3b**	2-Cl-$C_6H_5CH_2$
4a	2-Pyridine	**4b**	$CH_3(CH_2)_3$
5a	3-Pyridine	**5b**	$CH_3CH_2O(CH_2)_3$
6a	4-Pyridine	**6b**	2-Furan-CH
7a	2-Thiophene	**7b**	$CH(CH_2)_5$
8a	$(CH_3)CHCH_2$		
9a	CH_3CH		

Scheme 2. Synthesis of *N*-substituted amides.

presence of [Cu(2,3-tmtppa)]$(MeSO_4)_4$ in high isolated yields. The mechanism of this transformation is unclear. On the basis of proposed mechanism in Scheme 3, the catalytic activity of [Cu(2,3-tmtppa)]$(MeSO_4)_4$ could well be attributed to the Lewis acidity of the complex. The catalytic reaction of alkyl and aryl nitriles with primary amines was achieved by refluxing aqueous solution of the corresponding nitriles, in the presence of 0.5 mol% [Cu(2,3-tmtppa)]$(MeSO_4)_4$, which initially generates the nitrile bound copper species I. This idea is supported by performing the reaction in the absence of catalyst. Without any catalyst, the reaction is not completed even after long period of time (Table 1, entries 1, 20 and 21). Nucleophilic attack of primary amines to I affords intermediate II, which upon reaction with H_2O, produces hydrolyzed product III. The formation of II and III was confirmed by the fact that nucleophilic attack of amine can be catalyzed by [Cu(2,3-tmtppa)]$(MeSO_4)_4$, according to the result obtained from Table 1, entry 27 (any tendency between nitrile compound and H_2O can be prohibited). Copper complex III produces *N*-substituted amide with concomitant loss of an ammonia molecule. Finally, the regeneration of catalyst initiates a second catalytic cycle. Nevertheless, at this time, there is no experimental evidence for I, II and III formation and action in this manner. However, further

Table 2. Synthesis of different structurally *N*-substituted amides in the presence of [Cu(2,3-tmtppa)]$(MeSO_4)_4$

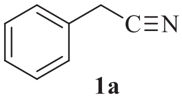
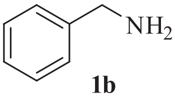
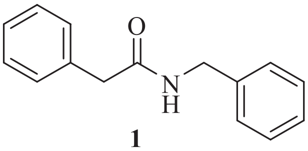
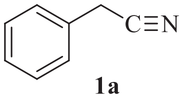
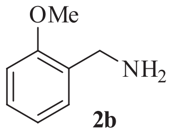
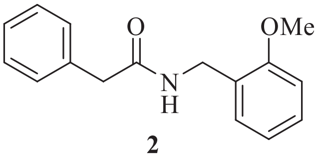
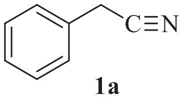
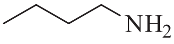
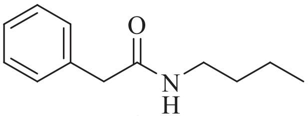
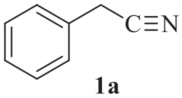
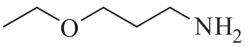
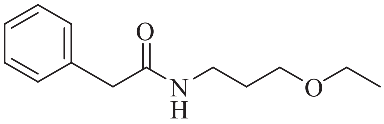
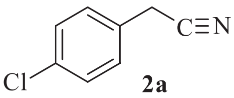
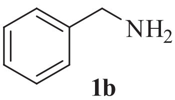
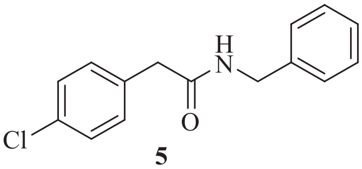
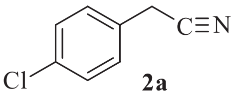
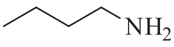
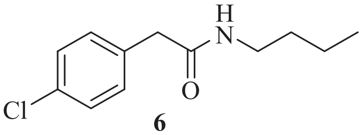
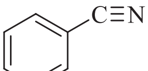
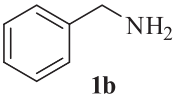
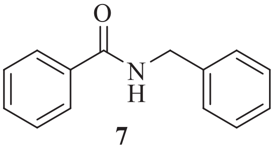
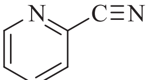
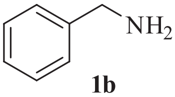
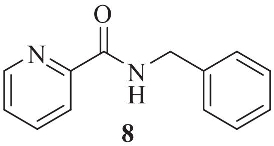
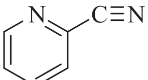
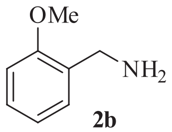
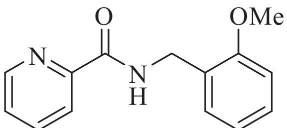
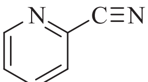
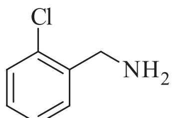
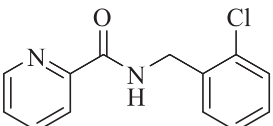
entry	Nitrile	Amine	Product	time / h	Yield / %
1	 **1a**	 **1b**	 **1**	19	98
2	 **1a**	 **2b**	 **2**	24	92
3	 **1a**	 **4b**	 **3**	15	95
4	 **1a**	 **5b**	 **4**	22	83
5	 **2a**	 **1b**	 **5**	17	90
6	 **2a**	 **4b**	 **6**	14	85
7	 **3a**	 **1b**	 **7**	24	98
8	 **4a**	 **1b**	 **8**	11	98
9	 **4a**	 **2b**	 **9**	13	92
10	 **4a**	 **3b**	 **10**	15	94

Table 2. continuation

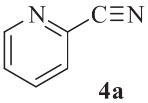
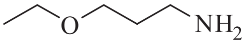
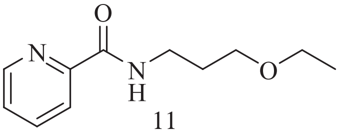
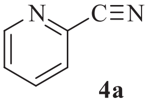
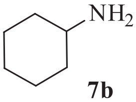
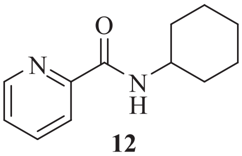
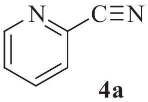
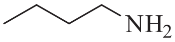
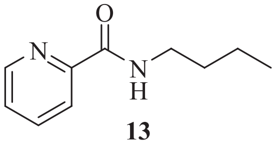
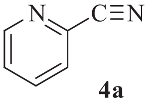
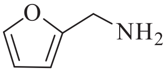
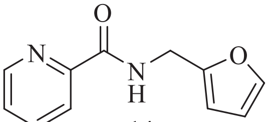
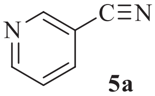
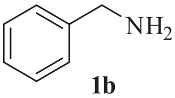
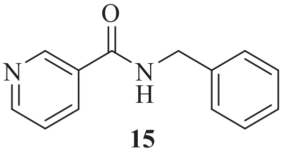
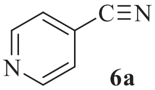
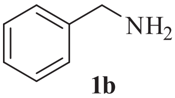
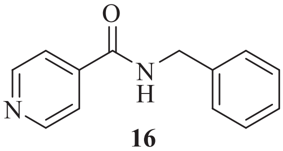
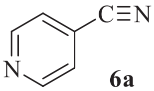
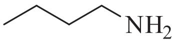
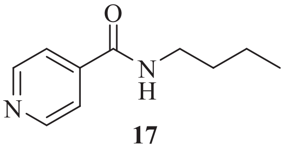
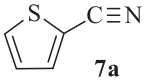
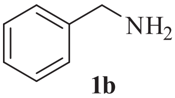
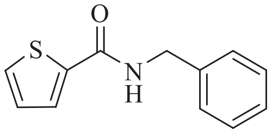
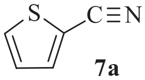
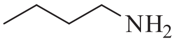
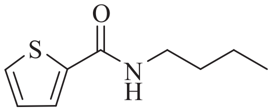
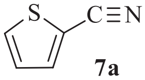
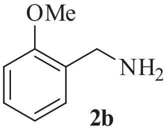
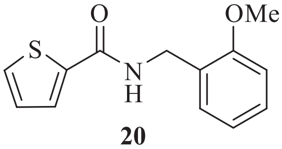
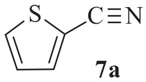
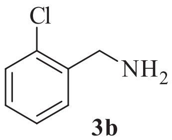
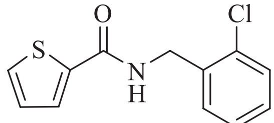
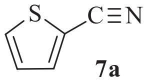
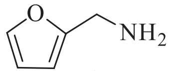
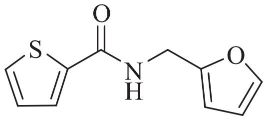
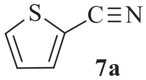
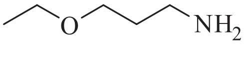
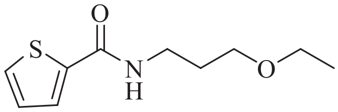
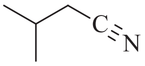
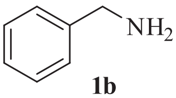
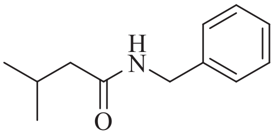
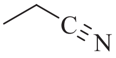
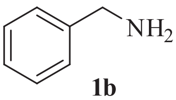
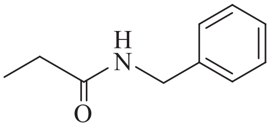
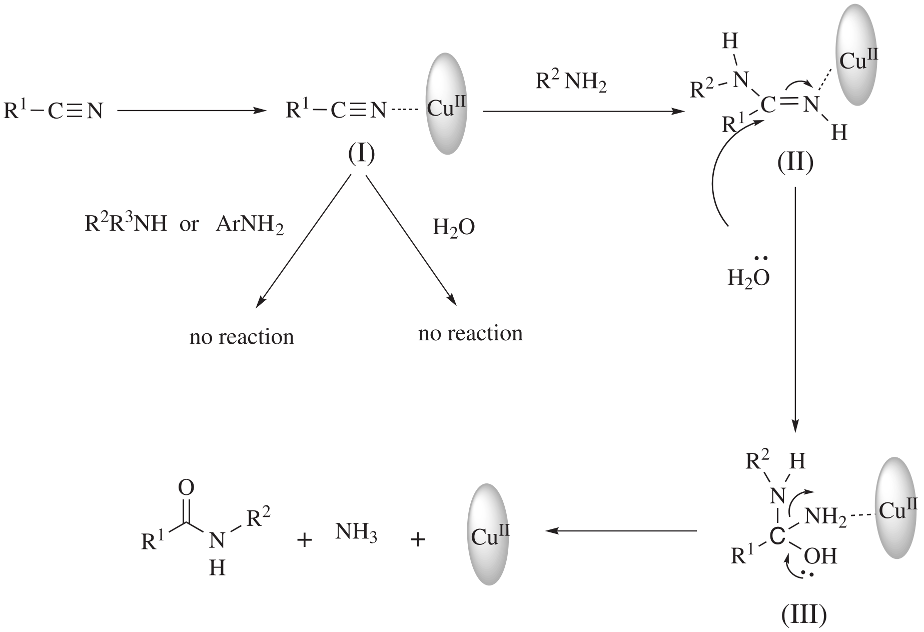
entry	Nitrile	Amine	Product	time / h	Yield / %
11	 **4a**	 **5b**	 11	16	90
12	 **4a**	 **7b**	 **12**	19	90
13	 **4a**	 **4b**	 **13**	14	92
14	 **4a**	 **6b**	 **14**	17	91
15	 **5a**	 **1b**	 **15**	16	92
16	 **6a**	 **1b**	 **16**	15	90
17	 **6a**	 **4b**	 **17**	18	96
18	 **7a**	 **1b**	 **18**	10	97
19	 **7a**	 **4b**	 **19**	15	98
20	 **7a**	 **2b**	 **20**	12	97

Table 2. continuation

entry	Nitrile	Amine	Product	time / h	Yield / %
21	 **7a**	 **3b**	 **21**	13	95
22	 **7a**	 **6b**	 **22**	15	93
23	 **7a**	 **5b**	 **23**	17	95
24	 **8a**	 **1b**	 **24**	24	73
25	 **9a**	 **1b**	 **25**	23	78



Scheme 3. A proposed mechanism for the formation of *N*-substituted amides.

mechanistic studies are required to confirm this mechanism. The catalytic activity of $[Cu(2,3\text{-tmtppa})](MeSO_4)_4$ was examined for the reaction of alkyl and aryl nitriles with secondary amines and aryl amines. Surprisingly, even after long period of time, secondary amines and aryl amines remain intact in the reaction medium.

[Cu(2,3-tmtppa)](MeSO$_4$)$_4$ acts as a recyclable catalyst for one pot amide formation from various nitriles and primary amines in refluxing H$_2$O, which provides a new and green catalytic system for *N*-substituted amide synthesis. The catalyst can be easily recovered from the reaction mixture by extraction of organic compounds (3 × 5 mL CH$_2$Cl$_2$). The aqueous layer was evaporated and the catalyst was washed with CH$_2$Cl$_2$ three times to remove the products followed by drying in air at room temperature. Using this treatment, the recyclabilty of the catalsyt was evaluated for the reaction of phenylacetonitrile with benzyl amine (Table 3). The recovered catalyst was reused at least four times without any decrease in the yield of the *N*-benzyl-2-phenylacetamide. The 5th run gave 95% conversion after 19 h, but complete conversion and similar yield was obtained after 25 h.

Table 3. Reaction of phenylacetonitrile with benzylamine in the presence of reused catalyst

entry	time / h	Conversion / %	Isolated yield / %
1	19	100	98
2	19	100	98
3	19	100	95
4	19	100	97
5[a]	25/19	100/95	95
6[a]	25/19	100/95	96

[a]The second numbers in the third column correspond to yields after 19 h.

The results obtained (Table 2) clearly demonstrate that this method is inapplicable to synthesis of primary and *N,N*-disubstituted amides. The catalytic activity of [Cu(2,3-tmtppa)](MeSO$_4$)$_4$ in this reaction is selective.

In our experiments, the completion of the reaction was confirmed by the disappearance of the nitrile on TLC followed by the disappearance of CN stretching frequency at 2230 cm^{-1} in the FTIR spectra. Also, absorption bands at 1677-1612 and 3396-3284 cm^{-1} due to carbonyl and NH group of *N*-substituted amide in FTIR spectra confirmed the amide formation. In the ^{1}H NMR spectrum, the NH proton of *N*-substituted amide showed a downfield shift as compared to the NH$_2$ protons of amine. In the ^{13}C NMR spectrum, a signal at 173-161 ppm is assigned to the quaternary carbonyl carbon. The structure of all products was further confirmed by mass spectroscopy and CHN analysis.

Conclusions

In this study, our group not only investigated another catalytic activity of [Cu(2,3-tmtppa)](MeSO$_4$)$_4$ in organic synthesis, but also introduced an efficient, clean, convenient, practical and selective synthesis of *N*-substituted amides from the reaction of alkyl and aryl nitriles with amines in green solvent.

This process is attractive in comparison with the conventional methods because this method offers several advantages: (*i*) the reaction proceeds smoothly and selectively with a wide range of amides (aliphatic and aromatic *N*-substituted); (*ii*) the catalyst is stable and reusable that offers easy handling and simple work-up; (*iii*) this method has satisfactory yields of a variety of amides;[49] (*iv*) in contrast to the previously reported catalytic systems, which proceeded by hydration of nitrile to the primary amide and subsequent transamidation with amine, in the present method, amides are produced by direct reaction of nitriles with amines; (*v*) in comparison with the previous methods, nitriles are storage-stable and less corrosive substrates.

Supplementary Information

Supplementary data and spectra of the synthesized compounds are available free of charge at http://jbcs.sbq.org.br as PDF file.

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