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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Microwave-assisted C-N and C-S Bond-Forming Reactions: An Efficient Three-component Domino Sequence for the Synthesis of Sulfoether-Decorated Imidazo[1,2-a]pyridines

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

An efficient and simple microwave-assisted three-component reaction for the formation of imidazo[1,2-a]pyridine derivatives in the presence of F_3CCO_2H has been described. The three-component reaction of 3-phenylpropiolaldehyde, pyridin-2-amines and thiols gives the desired products in good yields. It represents an efficient approach for the formation of C-N and C-S bonds under the microwave irradiation.

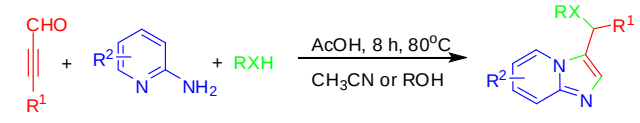
The formation of carbon-heteroatom bonds continues to be an active and challenging field of chemical research.[1] Transition metal-catalyzed reactions have emerged as a powerful methodology for the formation of carbon-heteroatom bonds over the past decades.[2] Many significant and favorable processes have been developed in this field; particularly Pd,[3] Ag,[4] Cu,[5] Au,[6] Rh[7] and Ru[8] catalyst are favorable for the formation of carbon-heteroatom bonds. However, those reactions suffer from the expensive catalyst and ligand. The cost, toxicity and environmental impact of these catalysts have hindered its further application on an industrial scale. These problems are of particular environmental and economic concern in large-scale syntheses. Therefore, the discovery of efficient processes that do not require a metal catalyst will be of great importance because such procedures provide an efficient route to avoid and solve these problems. It represents one of the most fundamental and economic strategy, and has attracted critical attention of organic chemist in recent years.[9] In spite of the utility of transformation in the preparation of complex molecules, environmental sustainability and economy remains challenging.

Microwave-assisted chemistry[10] has matured into a promising strategy for the formation of useful moleculars. It has shown tremendous advantages including simple easy work up procedure, decreased reaction time, saving energy and cost as well as providing clean products in good to excellent yields in comparison to conventional methods. Multicomponent reactions (MCRs) are very interested transformation because of their significant advantages.[11] The strategy of MCRs has been developed to enable the rapid preparation of diverse structures with an optimal number of new bonds and functionalities from readily accessible starting materials in a single operation under mild conditions.

On the other hand, imidazo[1,2-a]pyridines are recognized as an important class of heterocycles which exhibited remarkable biological activities as privileged scaffolds in drug discovery and development.[12] The core structure of imidazo[1,2-a]pyridines has been found in many drugs such as zolpidem, alpidem, zolimidine, olprinone, saripidem, necopidem[13]. Therefore, organic chemists have been making extensive efforts to prepare imidazo[1,2-a]pyridine derivatives[14] by developing novel and convenient organic transformations. Although many elegant processes have been reported to form those compounds,[15] the development of new microwave-assisted domino reations for syntesis of sulfoether-decorated imidazo[1,2-a]pyridines is still highly favorable the use of thiols and alkynes as starting materials. Our recent efforts were including the construction of imidazo[1,2-a]pyridines[16] by direct C-H functionalization or multicompoent reaction. In this context, we described a novel microwave-assisted domino reations for the formation of C-N and C-S bonds to prepare sulfoether-decorated imidazo[1,2-a]pyridine derivatives via three-component reactions of ynals, pyridin-2-amines and thiols.

Very recently, we have developed efficient three-component reaction of ynals, pyridin-2-amines and alcohol to construct functionalized imidazo[1,2-a]pyridine (Scheme 1).[16e] In our further exploration of the scope of this novel domino reaction, we employed 3-phenylpropiolaldehyde, pyridin-2-amine and 2-methyl propane-2-thiol as the substrates and surprisingly found that the desired product was obtained with lower yield in the presence of AcOH in CH_3CN at 80 °C for 8 h.

Previous work:



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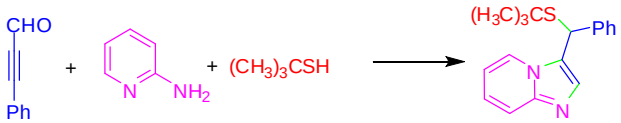

Scheme 1. Synthesis of imidazo[1,2-a]pyridines

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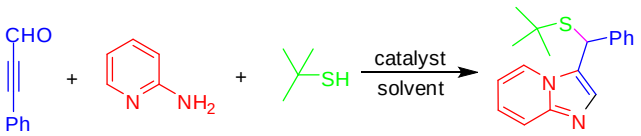
Table 1. Optimization of Reaction Conditions[a]



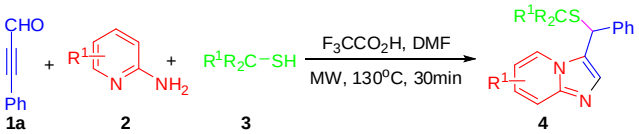
1a **2a** **3a** **4a**

Entry	Catalyst	Thermal/MW	Solvent	t	Yield(%)[b]
1	AcOH	80℃	CH_3CN	24h	10
2	AcOH	120℃(MW)	DMF	30min	39
3	$PhCO_2H$	120℃(MW)	DMF	30min	22
4	TsOH	120℃(MW)	DMF	30min	46
5	F_3CCO_2H	120℃(MW)	DMF	30min	83
6	HCl	120℃(MW)	DMF	30min	45
7	H_2SO_4	120℃(MW)	DMF	30min	17
8	F_3CCO_2H	100℃(MW)	DMF	30min	69
9	F_3CCO_2H	130℃(MW)	DMF	30min	84
10	F_3CCO_2H	150℃(MW)	DMF	30min	76
11	F_3CCO_2H	130℃(MW)	DMSO	30min	80
12	F_3CCO_2H	130℃(MW)	Toluene	30min	34
13	F_3CCO_2H	130℃(MW)	DMA	30min	79
14	F_3CCO_2H	130℃(MW)	dioxane	30min	36
15	F_3CCO_2H	130℃(MW)	DMF	20min	72
16	F_3CCO_2H	130℃(MW)	DMF	50min	82

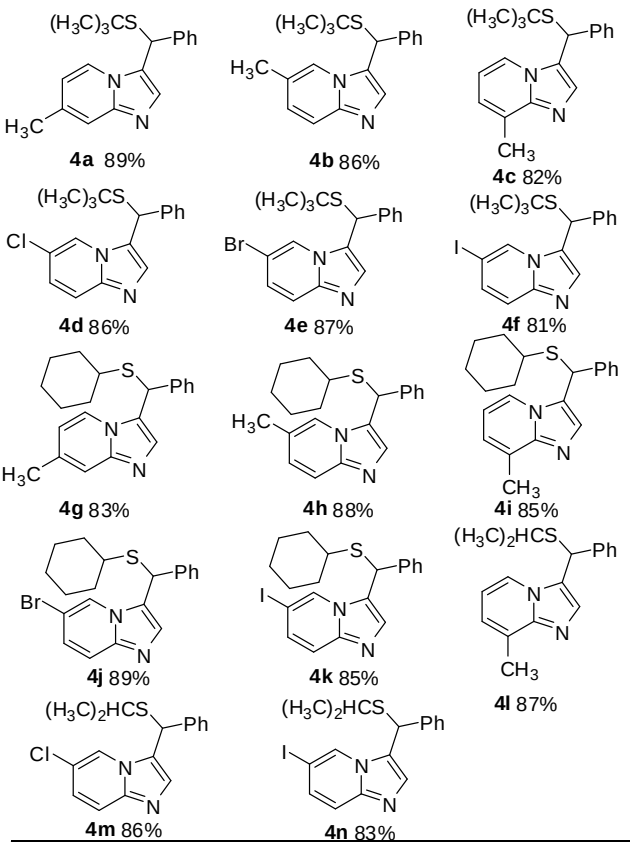
[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), **3a** (1.2 mmol), catalyst (2.0 mol %); solvent (3.0 mL), under microwave 500 W. ; [b]GC-yield.

Initially, 3-phenylpropiolaldehyde **1a**, pyridin-2-amine **2a** and 2-methylpropane-2-thiol **3a** were chosen as model substrates to screen the catalysts and determine suitable reaction conditions for the MCRs. The results are summarized in Table 1. The desired product **4a** was formed in 10% yield in the presence of AcOH in DMF at 80 °C for 24 h(Table 1, entry 1). Interestingly, the expected product 3-(tert-butylthio(phenyl)methyl) imidazo[1,2-a]pyridine **4a** was obtained in 39% yield (Table 1, entry 2) under microwave irradiation condition at 120°C in the presence of AcOH for 30min. Encouraged by the result that microwave irradiation could promote the reaction, other catalyst, such as $PhCO_2H$, TsOH, F_3CCO_2H, HCl, and H_2SO_4, were next to examined (entries 3-7, Table 1). To our delight, the product **4a** was formed in 83% yield in the presence of F_3CCO_2H under microwave heating condition. The results indicated that $PhCO_2H$, TsOH, HCl or H_2SO_4 could catalyze the transformation for yielding the product in moderate yields. It was interestingly found that the three-component reaction was highly sensitive to temperature variations (Table 1, entries 8-10). When the reaction carried out decreasing the reaction temperature from 120 °C to 100°C, the corresponding product **4a** was obtained in 69% yield. Furthermore, the effects of solvents were surveyed (Table 1, entries 11-14). The results clearly indicated that best result presented when DMF was used as solvent. An increase of reaction time was studied and the same efficiency was obtained after 50 min of microwaves activation, while the decrease of reaction time lead to lower yield (Table 1, entries 15-16).

Table 2. Microwave-assisted Synthesis of Imidazo[1,2-a]pyridines [a]



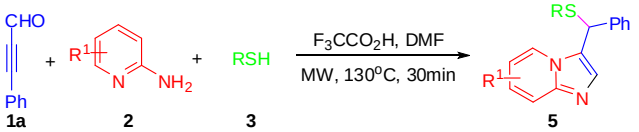
1a **2** **3** **4**



[a] Isolated yields

Under the optimized reaction conditions, we evaluated the scope of this novel transformation synthesis of sulfoether-decorated imidazo[1,2-a]pyridines. The results are summarized in Table 2. First, **1a** and **3a** fixed as substrates to test various substituted pyridin-2-amines. As shown in Table 2, a variety of substituted pyridin-2-amine derivatives were effective substrates for this transformation and the corresponding products (**4a**-**4f**) were obtained in good yields in all the cases. To our delight, the sensitive functionalized groups on the pyridine ring, such as Cl, Br and I, were also tolerated to afford the corresponding in good yields. Subsequently, cyclohexanethiol (**3b**) and propane-2-thiol (**3c**) were also employed for this transformation. The resulsts also indicated that all of the reactions proceeded smoothly under the optimized conditions and provided the thioether-decorated imidazo[1,2-a]pyridine derivatives (**4g**-**4n**) in good yields.

Table 3. F_3CCO_2H-catalyzed synthesis of imidazo[1,2-a]pyridines[a]



1a **2** **3** **5**

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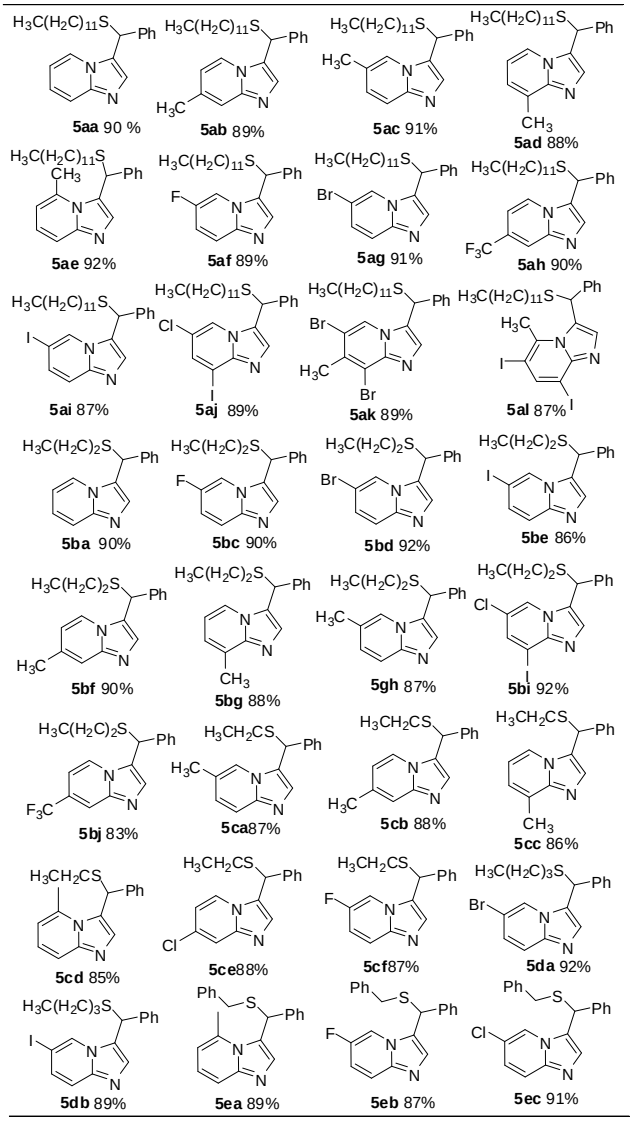
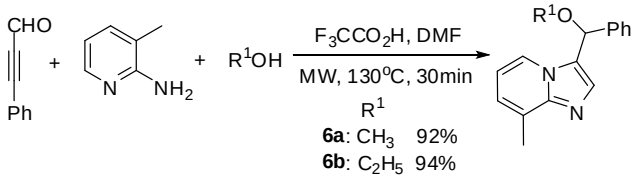


[a] Isolated yields

Encouraged by the successful syntheses of substituted imidazo[1,2-a]pyridines, our attention turned to the possibility of synthesizing functionalized imidazo[1,2-a]pyridine derivatives by using primary thiols in this reaction under the optimized conditions. And the results are shown in Table 3. Dodecane-1-thiol (**3d**) was firstly examined. Various substituted pyridin-2-amines reacted well with **1a**, **3d** and led to the desired product **5aa**–**5al** in good to high yields. Furthermore, multisubstituted pyridin-2-amine, such as 5-chloro-3-iodopyridin-2-amine, 3,5-dibromo-4-methylpyridin-2-amine or 3,5-diiodo-6-methylpyridin-2-amine reacted with **1a** and **3d** smoothly under the optimized conditions. Other commercially available aliphatic primary thiols, such as, propane-1-thiol(**3e**), ethanethiol (**3f**), butane-1-thiol (**3g**), and phenylmethanethiol (**3f**), were also tested. We were pleased to find that substituted thiols as substrates were also tolerated in the reaction and provided the desired imidazo[1,2-a]pyridines **5ba**–**5ec** in good to excellent yields. To our delight, substituted thiols reacted with **1a** and multisubstituted or electron-poor groups substituted (CF_3) pyridin-2-amines smoothly and afforded the desired product in good yields. It is worth pointing out that multi-halogen-substituted pyridin-2-amines could also be achieved upon carrying out the experiment under the optimized conditions. The results clearly indicated that this strategy can be extended to a variety of substituted thiols to form functionalized imidazo[1,2-a]pyridine derivatives. Notably, the sole products were detected in the reaction, which was indicated that this one pot transformation was regioselective and chemoselective.

To our delight, other nucleophiles, such as CH_3OH and C_2H_5OH, were also performed very vell and affored the corresponding products in 95% and 86% yields respectively (Scheme 2).



Scheme 2. MCRs of **1a**, **2a** and ethanol for the synthesis of imidazo[1,2-a]pyridines

In summary, we have reported an efficient microwave-assisted three-component reactions synthesis of sulfoether-decorated imidazo[1,2-a]pyridines. This procedure offers easy access to highly functionalized imidazo[1,2-a]pyridines which are useful structural motif in pharmaceuticals and natural compounds. This transformation provides a convenient strategy for the formation of C-N and C-S bonds to prepare sulfoether-decorated imidazo[1,2-a]pyridines. This methodology has several advantages: 1) it does not require expensive substrates or catalysts; 2) it decrease reaction time, saves energy and cost as well as provides clean products in good to excellent yields; 3) it has provided a wide range of substrates. Further studies and applications of metal-free multicomponent reactions are ongoing in our laboratory.

Acknowledgements

This research was financially Supported by National Natural Science Foundation of China (21302023) and the Project of Department of Education of Guangdong Province (2013KJCX0111)

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† Electronic Supplementary Information (ESI) available: Experimental Protocols and NMR Spectra for products **4aa**-**4eg**. See DOI: 10.1039/b000000x/

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