A NHC-Involved, Cascade, Metal-Free, and Three-Component Synthesis of 2,3-Diarylated Fully Substituted Furans under Solvent-Free Conditions

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Abstract: An efficient synthesis of 2,3-diarylated fully substituted furans was performed through the sequential reactions of Knoevenagel reaction, Stetter reaction catalyzed by NHC, and intramolecular cyclization under solvent-free conditions. The protocol has the advantages of easy workup, high yields, and an environmental benign procedure compared with the reported methods.

Key words: NHC, fully substituted furans, umpolung, solvent-free synthesis, multicomponent reaction

Multisubstituted furans are one of the most important classes of heterocyclic compounds. They not only have great significance in medicinal, agricultural, and material chemistry, but also act as useful and versatile building blocks in organic synthesis.[1–4] Therefore, the development of new synthetic approaches to synthesize multisubstituted furans represents an important area of research in organic chemistry.[5–7] The direct construction of the furan ring system using some specific substrates have been designed and well applied,[8] such as cyclocondensation of 1,4-dicarbonyl compounds (Paal–Knorr synthesis),[9] Feist–Bénary synthesis[10] and transition-metal-catalyzed cycloisomerization of alkynyl or allenyl substrates.[11] In addition, transition-metal-catalyzed coupling reactions and related transformations are also effective methods to yield highly functionalized furans.[12] However, most of the synthetic protocols reported have many drawbacks, including prolonged reaction time, drastic reaction conditions, tedious workup, low yields, poor tolerance of functional groups, and the use of organic solvent or expensive catalysts. Interestingly, because furans of the type **5** are key synthetic intermediates,[13] the synthesis of these furan derivatives has attracted considerable attention. So far, there are a few reports on the syntheses of tetrasubstituted furans with two aryl groups and an amino, a cyano, or an ester,[14] for example, the direct conversion from β,β-dicyanoketone, the transformation from benzoin (or α-bromodiarylethanone) and malononitrile, the cascade Stetter–γ-ketonitrile cyclization reaction of aromatic aldehydes with acylidenemalononitriles, the multistep synthesis from deoxybenzoin. However, the difficulty to prepare the starting material, such as crossed benzoin, α-bromodiarylethanone, and deoxybenzoin, makes these methods not suitable for the diversity-oriented synthesis of 2,3-diarylated fully substituted furans. Therefore, a strong demand remains to develop an efficient approach to synthesize these important fully substituted furans.

In the recent years there have been a continuously growing number of successful and novel applications of N-heterocyclic carbenes (NHC) as organocatalysts and reagents for an expanding set of reactions.[15,16] Knoevenagel condensation between aryl aldehyde and malononitrile may afford arylmethylidenemalononitriles efficiently.[17] We envisioned that the umpolung addition between aryl aldehyde and arylmethylidenemalononitriles catalyzed by NHC (Stetter reaction) could give the key intermediate β,β-dicyanoketone to synthesize the furans of the type **5**. The diversity of products could be adjusted effectively by varying the types of aryl aldehyde used. The diversity-generating potential of multicomponent reactions (MCR) has been recognized, and their utility in preparing libraries to screen for functional molecules is well appreciated.[18] Besides, progress in the field of solvent-free reactions is gaining more and more significance because of their high efficiency, operational simplicity, and environmentally benign processes. So far, many organic reactions have been reported to proceed under solvent-free conditions.[19]

As a continuation of our work on the multicomponent synthesis of a heterocyclic-compound library with high diversity,[20] we herein shall report that a N-heterocyclic carbenes (NHC) involved, highly efficient, multicomponent synthesis of 2,3-diarylated fully substituted furans **5** from aromatic aldehydes **1**, **3** and malononitrile (or ethyl cyanoacetate) **2** (Scheme 1).

In order to determine the optimal reaction conditions, the multicomponent reaction was first studied with benzaldehyde and malononitrile as model reactants. Firstly, the solvent effect on the reaction was investigated using EtOH, THF, and DMF at room temperature (Table 1, entries 1–3). In EtOH as well as in THF, only 68% of product **5**[21] could be isolated (entries 1 and 2), whereas a yield of 57% could be obtained in DMF (Table 1, entry 3). Thus, the results showed that reaction under solvent-free conditions gave the expected product in the highest yield (Table 1, entry 4). So we used solvent-free conditions to

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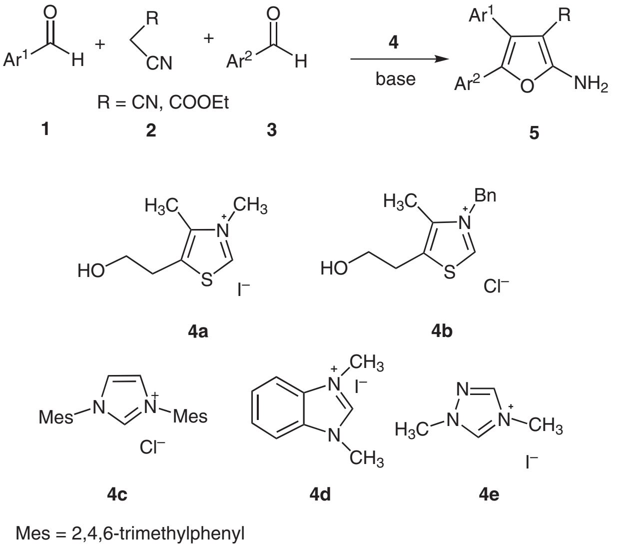
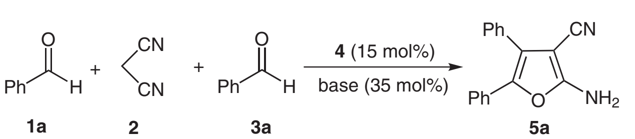


Scheme 1 Synthesis of substituted furans **5** catalyzed by different N-heterocyclic carbenes

Table 1 Optimization of Reaction Conditions for the Formation of Representative Compound **5a**[a,b]



Entry	Base	Solvent	Temp (°C)	Yield (%)[c]
1	DBU	EtOH	r.t.	68
2	DBU	THF	r.t.	68
3	DBU	DMF	r.t.	57
4	DBU	solvent-free	r.t.	72
5	DBU	solvent-free	40	75
6	DBU	solvent-free	50	82
7	DBU	solvent-free	55	90
8	DBU	solvent-free	60	84
9	Et_3N	solvent-free	55	75
10	Cs_2CO_3	solvent-free	55	65

[a] For the experimental procedure, see ref. 21.
[b] All entries were performed in 1 h.
[c] Isolated yield.

synthesize the target compound throughout the present study.

Next, in order to accelerate the reaction rate and enhance the yield, the aforementioned reaction was carried out under solvent-free conditions from room temperature to 55 °C (Table 1, entries 4–7). The yield of **5a**[22] was improved from 72% to 90%. However, when the temperature reached 60 °C, the reaction became complex, and the desired product was isolated in lower yield (Table 1, entry 8). Therefore, the temperature of 55 °C was chosen to synthesize the substitued furans.

To further examine the practical base for the synthesis, the effect of base was investigated under solvent-free conditions at 55 °C (Table 1, entries 9 and 10). To our delight, the precatalyst **4a** with DBU gave the desired product in the yield of 90% (Table 1, entry 7). Further study showed that the optimal loading for the precatalyst **4a** was 15 mol%. Besides, other types of NHC precursors, such as **4b–e** were applied to the three-component reaction at the loading of 15 mol%, and **4a** was found to be most effective. Therefore, all of the following experiments were conducted in the presence of 15 mol% of the precatalyst **4a** and 35 mol% of DBU.

In order to study the substrate scope and general validity of the protocol, the reactions of other substrates were next investigated (Table 2). When **1** and **3** were the same aromatic aldehydes, the yield of furans were found to be good to excellent, and the highest yield of **5** was 90% (Table 2, **5a**). The similar result was obtained when the different aromatic aldehydes were added. The effect of electronic nature of substituents on the aromatic ring did not show strongly obvious difference in terms of yields. This protocol can be applied not only to aromatic aldehydes either with electron-withdrawing groups (such as a halogen) or electron-donating groups (such as a methyl group) but also heteroaromatic aldehydes with moderate to excellent yields under the same conditions, which highlighted the wide scope of this condensation. However, when the aliphatic aldehyde was applied to this reaction, no expected product was obtained. In order to check the versatility of the methodology, another active methylene compound such as ethyl cyanoacetate was used instead of malononitrile. To our delight, the reaction under the above-optimized conditions gave the corresponding products in moderate to good yields (Table 2, entries 14 and 15).

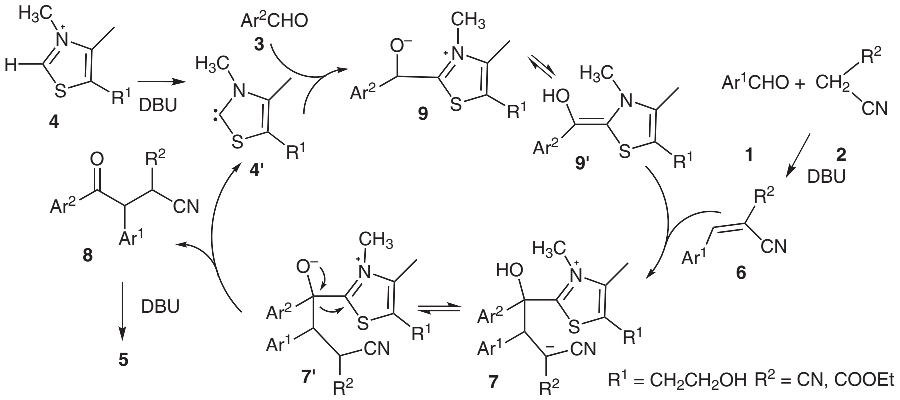
According to the literature, the detailed mechanism of the multicomponent reactions is still unclear, so we propose a plausible reaction mechanism, which is illustrated in Scheme 2. In the initial step, Knoevenagel condensation between aryl aldehyde and malononitrile under basic conditions gave intermediate **6**. Intermolecular Stetter reactions between aryl aldehyde **3** and **6** catalyzed by NHC then furnished the intermediate **8**, followed by intramolecular cyclization to give **5** under the effect of base. To confirm that this is a NHC-involved reaction some control reactions were performed. When DBU was used as the single catalyst, the reaction gave the intermediate (arylmethylidenemalononitriles) only. If the NHC precursor was applied to the reaction merely, trace amount of the same intermediate was also obtained. The facts provided the evidence in support of the proposed pathway.

In summary, we have provided a NHC-involved, efficient, and three-component route using inexpensive starting materials to the synthesis of a series of 2,3-diarylated fully substituted furans under solvent-free conditions. The experimental simplicity, high yields, short reaction time,

Table 2 Multicomponent Reactions of Aryl Aldehydes and Propanedinitrile for the Synthesis of Substituted Furans **5a–o**[a]

Entry	Ar^1	Ar^2	R	Time (h)	Product	Yield (%)[b]
1	Ph	Ph	CN	1	**5a**	90
2	$3-MeOC_6H_4$	Ph	CN	2.5	**5b**	78
3	$4-FC_6H_4$	$4-FC_6H_4$	CN	2	**5c**	87
4	$3,4-Cl_2C_6H_3$	Ph	CN	2.5	**5d**	81
5	$3-ClC_6H_4$	$3-ClC_6H_4$	CN	3	**5e**	85
6	$4-ClC_6H_4$	$4-ClC_6H_4$	CN	2	**5f**	84
7	$4-MeC_6H_4$	$4-ClC_6H_4$	CN	2.5	**5g**	82
8	$3,4-Cl_2C_6H_3$	$3,4-Cl_2C_6H_3$	CN	3	**5h**	80
9	$2-FC_6H_4$	$2-FC_6H_4$	CN	2.5	**5i**	79
10	Ph	$3-FC_6H_4$	CN	4	**5j**	78
11	$3-FC_6H_4$	$3-FC_6H_4$	CN	3	**5k**	86
12	$3-MeOC_6H_4$	$3-MeOC_6H_4$	CN	5	**5l**	82
13	$4-BrC_6H_4$	$4-BrC_6H_4$	CN	3.5	**5m**	84
14	$4-ClC_6H_4$	$4-BrC_6H_4$	COOEt	3.5	**5n**	82
15	$4-ClC_6H_4$	thiophene-2-yl	COOEt	5	**5o**	74

[a] All products have been characterized by HRMS spectrometry, ^1H NMR, ^{13}C NMR, and IR spectroscopy.
[b] Isolated yield.



Scheme 2 A plausible mechanism for multicomponent catalyzed by **4a**

eco-friendly, and the simple workup procedure make the procedure attractive to synthesize a variety of 2,3-diarylated fully substituted furans.

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(21) **General Procedure for the Synthesis of 5**
Aryl aldehyde **1** (1 mmol), DBU (0.35 mmol), and malononitrile **2** (1 mmol) were triturated together in an agate mortar with a pestle for 5 min. Then the mixture was kept at 55 °C for a certain time (monitored by TLC). After addition of another aryl aldehyde (1 mmol), sulfamethiazole salt

(0.15 mmol) was added and mixed thoroughly by grinding at 55 °C. The reaction mixture was mixed by grinding every half an hour with a pestle and mortar during 1–5 h reaction time (monitored by TLC). The resultant mixture was cooled to r.t., purified through column chromatography using acetone and PE (1:5) as the eluent, to give pure product **5a**–**o**.

(22) **Characterization Data of Representative Compounds 5a**
Yield 90%, white solid, mp 205–206 °C (reported 204–206 °C). IR (KBr): ν_{max} = 3467, 3443, 2216, 1653, 1455, 1067, 763, 694 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.17–7.27 (m, 5 H, ArH), 7.38–7.47 (m, 5 H, ArH). 7.75 (s, 2 H, NH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.5, 136.6, 131.2, 129.4, 129.0, 128.8, 128.6, 128.3, 126.9, 124.2, 121.8, 115.5, 69.2 ppm. ESI-HRMS: *m/z* calcd for $C_{17}H_{11}N_2O$ [M – H]$^-$: 259.0871; found: 259.0871.