

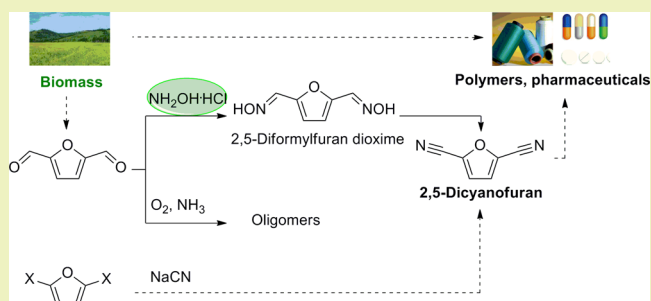
# Efficient Synthesis of 2,5-Dicyanofuran from Biomass-Derived 2,5-Diformylfuran via an Oximation–Dehydration Strategy

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## Supporting Information

**ABSTRACT:** Aromatic dinitriles show promise as a pivotal building block in polymer and pharmaceutical chemistry, and their production from biomass-based alcohols or aldehydes is highly desirable. In this work, for the first time, 2,5-dicyanofuran was efficiently synthesized from biomass-derived 2,5-diformylfuran via a two-step procedure. 2,5-Diformylfuran was first converted to 2,5-diformylfuran dioxime with 90% isolated yield in water. Hydroxylamine instead of ammonia used as nitrogen source is the key to this strategy, which avoids the polymerization reaction of intermediate aldimine. The subsequent dehydration reaction of 2,5-diformylfuran dioxime afforded 2,5-dicyanofuran in 82% isolated yield over an effective and recyclable solid acid catalyst Amberlyst-15. This approach demonstrates the feasibility of synthesis of reactive dinitriles from dialdehydes without using toxic cyanides or halides.

**KEYWORDS:** Sustainable chemistry, Aromatic dinitrile, 2,5-Diformylfuran, Hydroxylamine, Dehydration of aldoximes



## INTRODUCTION

Dinitrile is an important class of homobifunctional molecule in chemistry and biology. It serves as indispensable intermediates for the synthesis of diamine monomers,<sup>1</sup> diamidine pharmaceuticals,<sup>2</sup> and directly as monomer for the production of functional polymer materials like covalent triazine framework,<sup>3–5</sup> polybenzimidazoles<sup>6</sup> and polyamides.<sup>7</sup> Hitherto, phenyl dinitriles can be expediently derived from fossil resources through aerobic ammoxidation of hydrocarbon.<sup>8,9</sup> However, due to the challenge of activating robust C–H bond in hydrocarbon, harsh reaction conditions and complicated process are needed during their production. In addition, for the synthesis of specialty dinitriles like heteroaromatic and alkyl dinitriles, highly toxic HCN or metal cyanides are traditionally applied for nucleophilic substitutions of dihalides or the hydrocyanation of dienes,<sup>10–13</sup> and the significant amount of generated waste is a serious concern. From the viewpoint of sustainable development and green chemistry, it is desirable to convert readily available aldehydes or alcohols, especially biomass-based aldehydes or alcohols into dinitriles under mild conditions.

In the past decade, catalytic transformation of renewable biomass has received global attention, with the purpose of developing alternatives to fossil resource-derived chemicals and fuels.<sup>14–19</sup> Among the strategies for biomass valorization, the production of 5-hydroxymethylfurfural (HMF) from hexoses is a high-profile example.<sup>20–22</sup> HMF is a versatile platform for the synthesis of furan-based chemicals.<sup>21,23–27</sup> Recently, catalytic implantation of nitrogen into HMF was found as a fruitful route

to the synthesis of biomass-derived furyl diamide, diamidine, diimidate under mild conditions.<sup>28,29</sup> Even so, there are no reports on the efficacious synthesis of furyl dinitrile, which should be a promising molecule for preparation of biomass-based nitrogen-containing chemicals and materials.<sup>30,31</sup>

Heteroaromatic nitriles were recognized as highly reactive molecules in a variety of reactions, owing to the activation of cyano group by electron-withdrawing heteroaromatic ring.<sup>32–36</sup> Furan-based nitrile is previously found to be much more reactive than the phenyl counterparts.<sup>29,32,36</sup> The addition reaction of caynofuran with nucleophilic reagent has been proved to proceed smoothly with no need of harsh catalyst like HCl or NaOMe, while it is necessary in the similar reaction of phenyl nitriles.<sup>29,32</sup> However, reactivity is a double-edged sword. Owing to the highly active yet unstable nature of cyano group adjacent to heteroaromatic ring, selective synthesis of heteroaromatic nitriles is challenging. Currently, the ammoxidation strategies applied for the transformation of HMF predominantly gave the dinitrile addition product of diamide<sup>28</sup> or diimidate,<sup>29</sup> and all failed to effectively obtain dinitrile without exception.

As a result of the recently developed catalyst systems, 2,5-diformylfuran (**1**) can now be readily synthesized from HMF or directly from carbohydrates.<sup>23,25,37,38</sup> Previously, our group reported a highly practical catalyst system consisting of

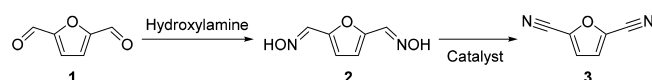
Received: October 26, 2017

Revised: January 31, 2018

Published: February 6, 2018

$\text{Cu}(\text{NO}_3)_2/\text{VOSO}_4$ , affording kilogram-scale production of **1** in our lab.<sup>23</sup> Herein, on continuance of our work on the oxidative transformation of HMF, we propose a practical strategy for the selective synthesis of 2,5-dicyanofuran (**3**) from **1** via 2,5-diformylfuran dioxime (**2**) as intermediate (Scheme 1). Key to

### Scheme 1. Synthesis of **3** from Biomass-Derived **1**



our strategy is the use of hydroxylamine, which efficiently converted both formyl groups of **1** to afford dioxime. Further dehydration of dioxime intermediate to nitrile proceeded in high selectivity over Amberlyst-15 catalyst. This is the first reported catalytic strategy for synthesizing biomass-derived furyl dinitrile.

## RESULTS AND DISCUSSION

Because 5-hydroxymethyl-furonitrile could be generated in our previous study on ammoxidation of HMF over  $\alpha\text{-MnO}_2$  or OMS-2 catalysts,<sup>28,29</sup> we investigated the possibility of **3** synthesis via catalytic ammoxidation of **1** with  $\text{NH}_3$ , and the results are shown in Table 1. GC analysis of the reaction

Table 1. Ammoxidation of **1**<sup>a</sup>

Entry	Catalyst	Conv. <sup>b</sup> (mol %)	Select. to <b>3</b> <sup>b</sup> (mol %)
1	$\alpha\text{-MnO}_2$	>99	–
2	OMS-2	>99	–

<sup>a</sup>Reaction conditions: 0.25 mmol **1** (31.0 mg), 0.25 MPa  $\text{NH}_3$ , 0.5 MPa  $\text{O}_2$ , 100 mg catalyst, 5.0 mL  $\text{CH}_3\text{CN}$ , 30 °C, 1 h. <sup>b</sup>Determined by GC.

mixture demonstrated a complete conversion of **1** under the reaction conditions, whereas showing no formation of **3** in the case of  $\alpha\text{-MnO}_2$  or OMS-2. We inferred that the main products were imine type oligomeric furan species which were confirmed by MALDI-TOF-MS analysis (Figure S1). These results suggest that **1** and corresponding diimine are very liable to go polymerization, impeding the direct ammoxidation of **1** to **3**.

Besides  $\text{NH}_3$ , hydroxylamine was widely used for implantation of nitrogen to carbonyl group.<sup>39–41</sup> Unlike the excessively reactive aldimine group generated from the condensation of aldehyde with  $\text{NH}_3$ , the oxime obtained from aldehyde and hydroxylamine is considerably stable. Moreover, aldioxime has the potential to form nitrile via dehydration.<sup>36,42–44</sup> Thus, we propose a strategy for the selective synthesis of **3** from **1** via **2** as intermediate.

The condensation of **1** and hydroxylamine to **2** was conducted in a round-bottom flask within an oil bath, and the results are shown in Table 2. Complete conversions of **1** were observed in all cases of reaction condition within 2 h. However, target product **2** was formed with only 52% selectivity when no alkali additive was added (Table 2, entry 1). Intriguingly, the selectivity of **2** could be tuned greatly by alkali additives. Alkali additives such as  $\text{Na}_2\text{CO}_3$ , pyridine and  $\text{Et}_3\text{N}$  gave improved selectivity of **2** to 75%, 59% and 74%, respectively (Table 2, entries 4–6). This might result from the

Table 2. Oximation of **1** to **2**<sup>a</sup>

Entry	Additive	Solvent	Conv. <sup>b</sup> (mol %)	Select. <sup>b</sup> (mol %)
1	–	$\text{H}_2\text{O}$	>99	52
2 <sup>c</sup>	–	$\text{H}_2\text{O}$	69	87
3 <sup>d</sup>	–	$\text{H}_2\text{O}$	83	91
4	$\text{Na}_2\text{CO}_3$	$\text{H}_2\text{O}$	>99	75
5	Pyridine	$\text{H}_2\text{O}$	>99	59
6	$\text{Et}_3\text{N}$	$\text{H}_2\text{O}$	>99	74
7	NaOAc	$\text{H}_2\text{O}$	>99	95 (90)
8	NaOAc	DMF	>99	18
9	NaOAc	EtOH	>99	42
10 <sup>e</sup>	NaOAc	$\text{H}_2\text{O}$	81	95
11 <sup>f</sup>	NaOAc	$\text{H}_2\text{O}$	>99	95 (91)

<sup>a</sup>Reaction conditions: 1.0 mmol **1** (124 mg), 2.6 mmol  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , 2.6 mmol additive, 10.0 mL solvent, reflux (in 110 °C oil bath), 2 h.

<sup>b</sup>Determined by HPLC. <sup>c</sup>2.6 mmol  $\text{NH}_2\text{OH}$  in 50 wt % aqueous solution substituting for  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . <sup>d</sup>5.2 mmol  $\text{NH}_2\text{OH}$  in 50 wt % aqueous solution. <sup>e</sup>0.5 h. <sup>f</sup>6 h. The data in parentheses were isolated yields.

promoting role of alkali additives on the release of hydroxylamine hydrochloride to hydroxylamine smoothly. Remarkably, the addition of NaOAc with moderate basicity gave selectivity of **2** as high as 95% (Table 2, entry 7). These results indicate that modest alkaline environment is essential to the production of **2**. The conversion of **1** achieved 81% after 0.5 h with a 95% selectivity of **2** (Table 2, entry 10). The selectivity of **2** was maintained even prolonging the reaction time to 6 h (Table 2, entry 11). After the reaction was complete, **2** could be easily separated from the reaction mixture by simple filtration and recrystallization. Hydroxylamine in water solution has a significant advantage over hydroxylamine hydrochloride because no HOAc or NaCl is produced in oximation of **1** and hydroxylamine. When equivalent hydroxylamine in 50 wt % aqueous solution was used, decreased conversion and selectivity of **2** were observed (Table 2, entry 2), which might result from the rapid decomposition of hydroxylamine under the reaction conditions. In order to counteract the decomposition portion, the amount of hydroxylamine was increased. As a result, conversion of **1** and selectivity of **2** increased to 83% and 91%, respectively (Table 2, entry 3). When DMF or EtOH was used as solvent instead of  $\text{H}_2\text{O}$ , release of hydroxylamine hydrochloride to hydroxylamine should be impeded, and this resulted in sharply reduced selectivity of **2** (Table 2, entries 8, 9).

Next, we studied the catalytic dehydration of **2** to **3**. It has been reported that various metal oxides with different acid–base properties could catalyze the dehydration of aldioximes to nitriles.<sup>36</sup> Noritaka Mizuno et al. reported that the dehydration of aldioximes proceeded efficiently in the presence of catalysts with a suitable acidity.<sup>44</sup> As shown in Table 3, we screened a variety of solid catalysts to gain the best catalytic performance. In comparison with metal oxide catalysts, Amberlyst-15 showed better catalytic activity for dehydration of **2** (Table 3, entries 2–9). We further examined homogeneous sulfonic acid and carboxylic acid. In the case of methanesulfonic acid as catalyst (Table 3, entry 11), conversion of **2** reached to 99% with 87% selectivity of **3**. *p*-Toluenesulfonic acid gave 99% conversion of **2** and 89% selectivity of **3** (Table 3, entry 12). By contrast,

Table 3. Dehydration of 2 to 3<sup>a</sup>

Entry	Catalyst	Conv. <sup>b</sup> (mol %)	Select. <sup>b</sup> (mol %)
1	—	9	—
2	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	22	82
3	MoO <sub>3</sub>	67	78
4	WO <sub>3</sub>	63	78
5	Nb <sub>2</sub> O <sub>5</sub>	43	60
6	CeO <sub>2</sub>	64	89
7	$\alpha$ -MnO <sub>2</sub>	57	60
8	MgO	88	93
9	Amberlyst-15	89	98
10 <sup>c</sup>	Amberlyst-15	96	95
11	Methanesulfonic acid	>99	87
12	<i>p</i> -Toluenesulfonic acid	>99	89
13	Acetic acid	74	85
14 <sup>d</sup>	Amberlyst-15	83	88
15 <sup>e</sup>	Amberlyst-15	85	87

<sup>a</sup>Reaction conditions: 1.0 mmol 2 (154.0 mg), 30 mg catalyst, 8.0 mL CH<sub>3</sub>CN, reflux (in 120 °C oil bath), 3 h. <sup>b</sup>Determined by HPLC. <sup>c</sup>6 h. <sup>d</sup>Toluene as solvent. <sup>e</sup>Toluene as solvent, conducted in a Dean–Stark instrument.

when using acetic acid as catalyst, conversion of 2 and selectivity of 3 reduced to 74% and 85%, respectively (Table 3, entry 13). The above results indicated that acid strength of catalysts was a key parameter to achieve high activity and selectivity in dehydration of 2. Above all, this is the first report of using Amberlyst-15 as efficient catalyst for dehydration of oximes compounds. A 95% selectivity of 3 at 96% conversion was obtained upon prolonging the reaction time to 6 h (Table 3, entry 10). The crude product of 3 was purified by crystallization with *n*-hexane. The water generated in the dehydration reaction reacted with acetonitrile to form acetamide, which can be removed from the product by crystallization (Table S1, Figure S4–5).

Moreover, to avoid the hydrolysis of acetonitrile we performed the dehydration reaction as an azeotropic distillation using toluene as the solvent. In comparison with the results using CH<sub>3</sub>CN as solvent, conversion of 2 reduced to 83% with decreased selectivity of 88% to 3 (Table 3, entry 14). This indicated that toluene was not the optimal solvent for the dehydration of 2. The dehydration reaction was also performed in a Dean–Stark instrument to inspect the efficiency of azeotropic distillation. 85% Conversion of 2 and 87% selectivity of 3 were attained, indicating that the promoting effect of azeotropic distillation with toluene is not obvious.

As the reusability of heterogeneous catalyst was a key attribute for practical applications, the recyclability of Amberlyst-15 catalyst in the dehydration reaction of oximes was confirmed. The catalyst was centrifuged and fully washed with *N,N*-dimethylformamide and acetonitrile after each cycle. After dried at 80 °C under vacuum, the catalyst was directly used for the next run. As shown in Figure 1, there was no obvious decrease in the conversion of 2 and selectivity of 3 in the first 4 consecutive runs. There was a slight decrease in the selectivity of 3 in the fifth and sixth runs. This illustrated the catalyst was stable under the reaction conditions.

Further studies concerning the stability of 3 under the reaction conditions were employed. Following the evolution of

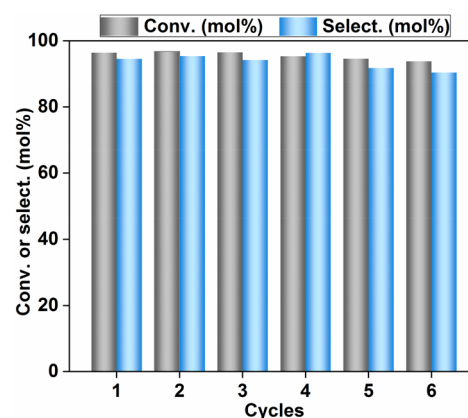


Figure 1. Cycle experiments of the dehydration of 2. Reaction conditions: 1.0 mmol 2 (154 mg), 30 mg Amberlyst-15, 8.0 mL CH<sub>3</sub>CN, reflux (in 120 °C oil bath), 6 h.

the time course, partly dehydrated product 5-cyano-furaldehyde oxime (4) was detected, and Figure 2 shows the kinetic curves.

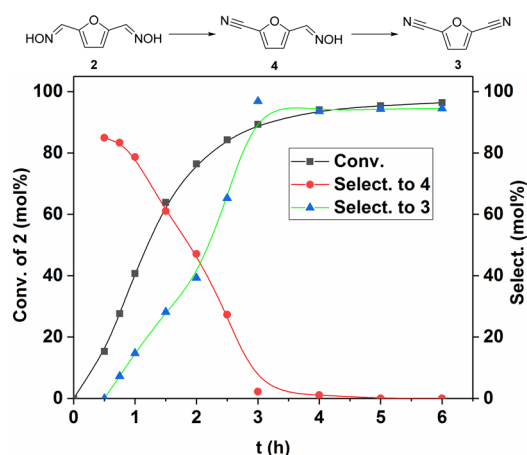


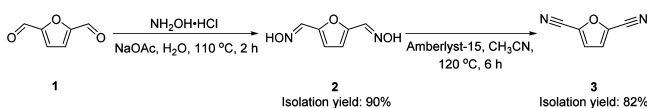
Figure 2. Time course of the dehydration of 2 to 3 over Amberlyst-15. Reaction conditions: 1.0 mmol 2 (154 mg), 30 mg Amberlyst-15, 8.0 mL CH<sub>3</sub>CN, reflux (in 120 °C oil bath).

Initially, 2 was converted to 4 with a maximum of ca. 85% selectivity. As the reaction was further prolonged, 4 was decreased accompanied by the sustained increase of target product 3. At 3 h, only trace amount of 4 was detected while the conversion of 2 was 95%. Afterward the conversion of 2 kept increasing without accumulation of 4. This indicates that dehydration of 4 proceeds smoothly over Amberlyst-15. The selectivity toward 3 was still more than 90% even after prolonging the reaction time to 6 h. The undesired pathway of hydration reaction of 3 to amide was effectively avoided using Amberlyst-15 as dehydration catalyst.

The synthetic utility of our strategy was examined under scale-up conditions. We performed gram-scale reactions as shown in Scheme 2, and isolation yields of 2 and 3 were 90% and 82%, respectively.

## CONCLUSION

In summary, we reported a novel method for the selective synthesis of 2,5-dicyanofuran (3) from 2,5-diformylfuran (1) via 2,5-diformylfuran dioxime (2) as intermediate. 1 could be converted to 2 with 90% isolated yield in the presence of

Scheme 2. Gram-Scale Synthesis of 3 from 1<sup>a</sup>

<sup>a</sup>81 mmol 1 (10.0 g), 210 mmol NH<sub>2</sub>OH·HCl, 210 mmol NaOAc, 120 mL H<sub>2</sub>O, reflux (in 110 °C oil bath), 2 h; 73 mmol 2 (11.2 g), 650 mg Amberlyst-15, 120 mL CH<sub>3</sub>CN, reflux (in 120 °C oil bath), 6 h.

NaOAc in water. Key to this approach is the use of hydroxylamine as nitrogen source. Side reactions such as polymerization of intermediate aldimine can be avoided effectively. An 82% isolated yield 3 was obtained during the subsequent dehydration reaction of 2 catalyzed by solid acid Amberlyst-15. This work provides a practical strategy to obtain versatile dinitriles 3 from biomass resources.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b03913.

Experimental details including reaction procedures and product analysis, and additional results (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (project 21233008, 21703236, 21790331), the Strategic Priority Research Program of Chinese Academy of Sciences (No. XDB17020300), the Outstanding Young Scientist Foundation, Chinese Academy of Sciences (CAS) and the Dalian Young Star of Science and Technology Project (No. 2016RQ027).

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