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Communication and Perspective

Synthesis of bis(amino)furans from biomass based 5-hydroxymethyl furfural

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ABSTRACT

In this study we report a new reaction pathway in which the hydroxyl and the aldehyde groups of 5-hydroxymethyl furfural were aminated respectively. Hydroxyl group was aminated via Ritter reaction followed by direct reductive amination of aldehyde group. For the Ritter reaction of 5-hydroxymethyl furfural, mixture of trifluoromethane sulfonic acid and phosphoric anhydride showed good performance and the intermediate *N*-acyl-5-aminomethyl furfural with the highest yield of 89.1% was obtained. Optimization of direct reductive amination of 2,5-bis(aminomethyl) furan was conducted and a yield of 45.7% was achieved. This study presents a simple way for preparing bis(amino)furans from renewable biomass based 5-hydroxymethyl furfural, which enriches the biorefinery concept from biomass.

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1 As an important platform chemical derived from biomass,
2 5-hydroxymethyl furfural (HMF) is attracting increasing atten-
3 tion owing to the unique chemical structure containing both
4 hydroxyl and aldehyde groups. It can be converted to a vari-
5 ety of value-added furan compounds such as 2,5-dimethylfuran
6 (DMF), 2,5-diformylfuran (DFF), 2,5-furandimethanol (FDM), 2,5-
7 furandicarboxylic acid (FDCA), 5-chloromethylfurfural (CMF), and
8 5-acetoxymethylfurfural (AMF) [1–6]. Moreover, HMF has attracted
9 attention in the synthesis of polymers as it contains similar struc-
10 ture as aromatics. It is reported that HMF has been used for the
11 production of special phenolic resins with phenol [7].

12 Amines, especially primary amines and di-amines, are impor-
13 tant intermediates in chemical industry for polymerization reac-
14 tions [8,9]. As a new type of 2,5-disubstituted furan derivative,
15 2,5-bis(aminomethyl)furan (BAF) is considered as a monomer for
16 polymers such as polyamides and polyurethanes [10–12]. Gener-
17 ally, various types of amines are assembled with the reduction
18 of aldehyde amine compounds [13,14]. BAF can be generated by
19 the further reduction of DFF, which is obtained via direct pro-
20 cesses from carbohydrates or HMF [15]. Thomas et al. described
21 a two-step pathway for preparing BAF from DFF in the presence of
22 Raney-Ni catalyst with a yield of 76% [16]. Most recently, Le et al.

23 claimed the direct reductive amination of DFF to BAF with Raney-
24 Ni catalysts under mild conditions and the yield of BAF is 42.6%.
25 However, by-products of secondary, tertiary and polymeric amine
26 species were generated due to the condensation of the reactive di-
27 aldehyde and di-amines groups [17].

28 In this study, we describe a new reaction pathway in which the
29 hydroxyl and the aldehyde groups of HMF were aminated succes-
30 sively (Scheme 1). N atoms were introduced into HMF in two steps
31 separately, during which the hydroxylmethyl group was converted
32 to amide group by Ritter reaction followed by the reductive ami-
33 nation of the aldehyde group to primary amine. Subsequently, BAF
34 was obtained by simple hydrolysis. Le et al. represented the se-
35 lective oxidation of HMF into DFF over VO²⁺ and Cu²⁺ ions im-
36 mobilized on sulfonated carbon catalysts, providing a DFF yield of
37 98%, but the preparation of the catalyst was complicated and high
38 pressure was required [2,17]. In the process of DFF to BAF, by-
39 products such as secondary, tertiary and polymeric amine species
40 affected BAF production. In this study, a special reaction pathway
41 was proposed, which got rid of the formation of DFF and thus,
42 the generation of polymers in further reductive amination was
43 avoided.

44 5-Hydroxymethyl furfural, trifluoromethane sulfonic acid,
45 Raney-Ni were purchased from Aladdin Chemical Reagent (Shang-
46 hai, China). All other chemicals were supplied by Sinopharm
47 Chemical Reagent Co. Ltd. (Shanghai, China) and used without
48 further purification.

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Nomenclature

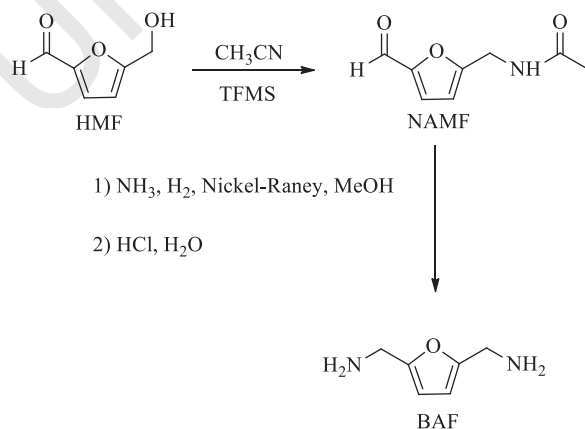
Abbreviations

HMF	5-Hydroxymethyl furfural
NAMF	N-Acyl-5-aminomethyl furfural
NBAF	N-Acyl-2,5-bis(aminomethyl)furan
BAF	2,5-bis(Aminomethyl)furan
DFF	2,5-Diformylfuran
OMBF	5,5'-Oxydimethylenebis (2-furfural)
MHP	5-Methyl-2-hydroxypyridine
TFMS	Trifluoromethane sulfonic acid

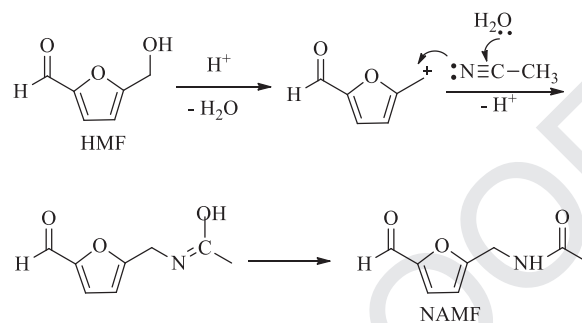
49 In a typical reaction, trifluoromethane sulfonic acid (0.45 g) was
50 added dropwise to HMF (1 g, 1.62 mmol) in 20 mL acetonitrile,
51 and kept at 100 °C. The solution was neutralized with sodium bi-
52 carbonate after 3 h and then 10 mL deionized water was added.
53 Then the product was extracted by 20 mL chloroform for five
54 times. The organic phase was evaporated at 45 °C under vacu-
55 um and the obtained NAMF raw product was dried with sodium
56 sulfate. The raw product was then purified by silica gel column
57 (CHCl₃:CH₃COOCH₂CH₃ = 2:1) to give NAMF as a brown oil.

58 The NAMF raw product was dissolved in methanol to make
59 a 30 wt.% solution. The experiments were performed in a 50 mL
60 cylindrical stainless steel high-pressure reactor (PARR 4848, in-
61 strument company, USA). In a typical reductive amination reac-
62 tion, the reactor was loaded with NAMF solution (20 mL), Raney-
63 Ni (0.05 g), ammonia (5 mL), and then hydrogen was introduced
64 for several times to remove air. Thereafter, hydrogen was charged
65 into the reactor with a pressure of 15 bar (at room temperature).
66 After cooling down, the gaseous phase was released, and the cat-
67 alyst was removed with centrifugation from the solution, whilst
68 the supernatant is collected. Hydrochloric acid was added into the
69 supernatant to hydrolyze NBAF, and then BAF·HCl was obtained.
70 Subsequently, the pH of the solution was adjusted to 13 with
71 40 wt.% sodium hydroxide solution to give BAF, which was then ex-
72 tracted with 20 mL ethyl acetate for five times. The organic phase
73 was evaporated under vacuum and dried over sodium sulfate. The
74 product was distilled under vacuum and BAF as colorless liquid
75 was obtained with high purity at 115–120 °C.

76 The raw products from reaction were identified by Shimadzu
77 GCMS-QP2010SE instrument with Rtx-5MS column (length 30 m,
78 inner diameter 0.20 mm, film thickness 0.33 μm) and electron im-
79 pact ionization (EI), with a 25 μA emission current and electron
80 energy of 70 eV. Carrier gas was He with an elution rate of
81 1.00 mL/min and a split ratio of 5:1. Samples were injected (1 μL)
82 from the auto sampler and the temperature program was as fol-
83 lows: initial oven temperature was set to 40 °C for 1 min, and



Scheme 1. Synthetic pathway for preparing BAF from HMF.



Scheme 2. Reaction mechanism for the conversion of HMF to NAMF by Ritter reaction.

then heated to 280 °C at 10 °C/min and held at 280 °C for 1 min. 84
Quantitation by GC-MS was carried out using internal standards. 85
Determination of the products (by-products) was performed us- 86
ing full scan mode. Characteristic ions with the highest abundance 87
were selected as the quantitative ion peak and product/by-product 88
were identified and quantified. Typically, NAMF, OMBF and BAF 89
were calculate as follows: 90

$$\text{NAMF yield (wt.\%)} = \frac{\text{the weight of NAMF}}{\text{initial weight of HMF}} \times 100 \%$$

$$\text{NAMF yield (mol.\%)} = \frac{\text{mole of NAMF}}{\text{initial mole of HMF}} \times 100 \%$$

$$\text{OMBF yield (wt.\%)} = \frac{\text{the weight of OMBF}}{\text{initial weight of HMF}} \times 100 \%$$

$$\text{BAF yield (wt.\%)} = \frac{\text{the weight of BAF}}{\text{initial weight of NAMF}} \times 100 \%$$

$$\text{BAF yield (mol.\%)} = \frac{\text{mole of BAF}}{\text{initial mole of NAMF}} \times 100 \%$$

In Ritter reaction, nitriles were converted to *N*-alkyl amides 95
with alkylation agents such as isobutylene and alcohols [18,19]. 96
The aldehyde group of HMF can be directly converted to pri- 97
mary amines by reductive amination. However, the hydroxylmethyl 98
group could be acylated instead of direct reductive amination [20]. 99
In the presence of strong acids, HMF carbocation could be gener- 100
ated and attacked by nitrogen atom in nitrile (Scheme 2). Primary 101
amine was obtained with further hydrolysis reaction unless a final 102
product is reached, as primary amine is much more unstable than 103
N-acyl-5-aminomethyl group [21]. Herein, the Ritter reaction not 104
only introduces the N atom into hydroxyl group of HMF, but also 105
the primary amino protector via the amide group generated during 106
the reaction. 107

Considering that acetonitrile is the simplest nitrile molecule, 108
it was applied as the solvent in this study. Strong acids such as 109
sulfonic acid, trifluoromethane sulfonic acid (CHF₃O₃S), and espe- 110
cially, a mixture of CHF₃O₃S and phosphoric anhydride, were pre- 111
ferred. HMF and acetonitrile solution were mixed and maintained 112
at 100 °C for 3 h in the presence of CHF₃O₃S and the highest yield 113
of NAMF of 89.1 wt.% (67.2 mol.%) was obtained (Table 1). We ob- 114
served that the yield of NAMF increased with the increase of acid 115
loading (Table 1, Entries 1–5). 5,5'-Oxydimethylenebis (2-furfural) 116
(OMBF) as the main by-product has been detected in the reaction, 117
and the yield decreased with the increase of acid content. How- 118
ever, it dropped down once the CHF₃O₃S content was as high as 119
6.7 mmol (Table 1, Entry 5), probably due to that more undesired 120
by-products such as soluble polymers and insoluble humins were 121
formed [22]. 122

For different catalysts, the conversion increased with increas- 123
ing acid strength (Table 1, Entries 4, 7, 10). When the mixture of 124
two acids (CHF₃O₃S or H₂SO₄ and P₂O₅) was applied, the yield of 125

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