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Efficient and Selective Dehydration of Fructose to 5-Hydroxymethylfurfural Catalyzed by Brønsted-Acidic Ionic Liquids

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The dehydration of p-fructose and glucose has been studied with acidic ionic liquids as catalysts. A series of Brønsted-acidic ionic liquids has been synthesized and tested in the dehydration of p-fructose. The results showed that *N*-methyl-2-pyrrolidonium methyl sulfonate [NMP]⁺[CH₃SO₃]⁻ and *N*-methyl-2-pyrrolidonium hydrogen sulfate [NMP]⁺[HSO₄]⁻ have high catalytic activity. Highly efficient and selective dehydration of p-fructose to 5-hydroxymethylfurfural (HMF) was achieved in dimethyl sulfoxide (DMSO) under mild conditions. For example, a 72.3 % yield of HMF with 87.2 % selectivity were obtained for

Introduction

Renewable biomass resources are promising alternatives for the sustainable supply of chemical intermediates and liquid fuels.^[1] Particularly, fossil fuels are diminishing and contributing to global warming; therefore, catalytic biomass conversion has been an attractive hot topic in recent years.^[2-4] With the consideration of the downstream chemical processing, catalytic transformation of sugar to value-added chemicals is important in both science and commerce.^[5,6] Therefore, much effort has been devoted to the dehydration of hexoses into 5-hydroxymethylfurfural (HMF), a versatile and key intermediate both in biofuel chemistry and the petroleum industry.^[7-9] In literature, acidic catalysts have been employed for the D-fructose dehydration reaction, such as mineral acids,^[10,11] strong acid cation exchange resins,^[12-14] H-form zeolites,^[14,16] supported heteropolyacids,^[17] and metal ions.^[18,19] In addition, several reaction media, including pure water and organic solvents, and also a number of biphasic water/organic systems, have been adopted.^[20,21] However, the yields of the target product HMF were low because these catalysts may have favored the subsequent dehydration of HMF to levulinic and formic acids. Moreover, Dfructose and HMF can be oligomerized or polymerized to give the other byproducts, which also lowers the HMF yield.^[21,22]

Recently, room temperature ionic liquids (ILs) have also been employed in the dehydration of hexoses into HMF.^[8,23–27] The neutral ILs were used as reaction media in which catalysts and substrates were dissolved. For example, the IL [Emim]Cl was an effective solvent in the dehydration of p-fructose to HMF with a metal chloride as catalyst, in which a 70% yield of HMF was achieved.^[8] Moreau et al. found that [BMIm]PF₆ and [BMIm]BF₄ were suitable reaction media for the dehydration of p-fructose in the presence of Amberlyst-15.^[23] In particular, in the IL–tetrahydrofuran biphasic system, tungsten salt promoted a large2 h at 90 °C in the presence of 7.5 mol % [NMP]⁺[CH₃SO₃]⁻. The effects of the reaction temperature, time, and solvent were investigated in detail. The catalyst and solvent can be recycled for the dehydration of D-fructose. The Hammett method was used to determine the acidities of these ionic liquids, which indicated that the acidity and molecular structure have strong effects on the catalytic activity of ionic liquids. Based on the experimental results, a possible reaction mechanism for the dehydration of D-fructose is proposed.

scale continuous production protocol for HMF below 50 °C.^[24] On the other hand, Bao et al. reported that the Lewis acidic 3allyl-1-(4-sulfurylchloride butyl)-imidazolium trifluoromethanesulfonate ([ASCBI][Tf]) effectively catalyzed the dehydration of p-fructose under microwave irradiation.^[25] Moreover, special ILs, such as 1-H-3-methyl imidazolium chloride and choline chloride/citric acid, have also been used as both solvent and catalyst for the reaction, with a reported IL to p-fructose molar ratio of 12 or 5, respectively.^[26,27] However, in these reported works, the ILs mainly played a role as the solvent and were consumed in considerably large amounts. The merits and details of the ILs as single catalysts for the dehydration of p-fructose are still far from being sufficiently understood and need to be further investigated.

Very recently, Chakraborti and Roy put forward the catalytic concept of ILs based on the *O-tert*-butoxy-carbonylation of 2-naphthol catalyzed by a catalytic amount of [bmim][OAc],^[28] which revealed the unique catalytic performance of ILs. Accordingly, catalysis with a single IL has become a hot and promising research topic. As far as we know, the efficient dehydration of p-fructose with a catalytic amount of acidic ILs has not been reported until now.

In this work, the dehydration of D-fructose to HMF using catalytic amounts of Brønsted-acidic ILs (molar ratio of IL to D-

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fructose of 0.075 or 0.1) has been investigated in water and organic solvents. Various acidic ILs, including 1-methylimidazolium hydrogen sulfate ([MIM]⁺[HSO₄]⁻), *N*-methyl-2-pyrrolidonium hydrogen sulfate ([NMP]⁺ [HSO₄]⁻), 1-methylimidazolium methyl sulfonate ([MIM]⁺[CH₃SO₃]⁻), and *N*-methyl-2-pyrrolidonium methyl sulfonate ([NMP]⁺[CH₃SO₃]⁻) were synthesized and employed as catalysts for the reaction. Here, the ILs [NMP]⁺[CH₃SO₃]⁻ and [NMP]⁺[HSO₄]⁻ showed the highest catalytic activities in the dehydration of D-fructose; [NMP]⁺-[CH₃SO₃]⁻ also exhibited superior selectivity for HMF.

Results and Discussion

Basic characterizations of Brønsted-acidic ILs

The preparation procedures of the ILs are similar to those reported in previous literature.^[29–31] The detailed synthesis conditions are described in the experimental section. [MIM]⁺[HSO₄]⁻ and [NMP]⁺[HSO₄]⁻ are colorless and light yellow liquid at room temperature, respectively. The fresh [NMP]⁺[CH₃SO₃]⁻ is a viscous liquid at room temperature; however, it solidifies after several days. [MIM]⁺[CH₃SO₃]⁻ is a white solid at room temperature.

Hammett acidity of Brønsted-acidic ILs

As the dehydration of D-fructose is closely associated with the acidity of the catalyst, [32] Hammett acidity function of the different ILs was investigated in methanol solution. Based on the protocol given by Gilbert et al.,^[33] the acidities of these Brønsted-acidic ILs were characterized using UV/Vis spectroscopy with *p*-nitroaniline as the indicator and molecular probe. Therein, the ILs and 4-nitroaniline were dissolved in methanol with concentrations of $3.0 \times 10^{-2} \text{ mol L}^{-1}$ and $7.5 \times 10^{-5} \text{ mol L}^{-1}$, respectively. Then, the solutions were mixed for 2 h with magnetic stirring, and then their UV spectra were recorded with a PerkinElmer Lambda 900 UV/Vis spectrometer. The experimental data are summarized in Figure 1 and Table 1. There was a noticeable change in the absorption curve of *p*-nitroaniline in methanol in the wavelength region from 350 to 400 nm upon the addition of the acidic ILs (Figure 1); moreover, compared to the addition of [MIM]⁺-based ILs, the change in absorbance was more obvious when [NMP]+-based ILs were added to the p-nitroaniline solution. Correspondingly, the protonic acidity of [NMP]⁺-based ILs is stronger than that of [MIM]⁺-based ILs.

In Table 1, the Hammett acidity function (H₀) can be expressed as the equation $H_0 = pK_a(ln) + log([ln]/[lnH^+])$, where $pK_a(ln)$ is the pK_a value of the *p*-nitroaniline indicator solution (about 0.99), [ln] and [lnH⁺] are the molar concentrations of the protonated and unprotonated forms of *p*-nitroaniline indicator, respectively. Based on the UV spectra of Figure 1, the quantitative data of H_0 values were obtained. The corresponding H_0 values of [MIM]⁺[CH₃SO₃]⁻, [NMP]⁺[HSO₄]⁻, and [NMP]⁺-[CH₃SO₃]⁻ were 3.03, 1.69, and 1.84, respectively (Table 1). These results indicated that the acidity of [NMP]⁺[HSO₄]⁻ was the strongest among these ILs examined, and the acidity of [NMP]⁺[HSO₄]⁻.



Figure 1. The UV/Vis spectra according to the Hammett method (the amplified peaks are presented at the top right corner). Concentrations: 3.0×10^{-2} mol L⁻¹ of ILs and 7.5×10^{-5} mol L⁻¹ *p*-nitroaniline in methanol.

Table 1. Hammett function values of various ILs.							
lonic liquid	Absorbance	[ln] [%] ^[a]	[InH ⁺] [%] ^[b]	$H_0^{[c]}$			
none	1.13	100	0	-			
[MIM] ⁺ [HSO ₄] ⁻	1.13	100	0	-			
[MIM] ⁺ [CH ₃ SO ₃] ⁻	1.12	99.1	0.9	3.03			
[NMP] ⁺ [HSO ₄] ⁻	0.94	83.2	16.8	1.69			
$[NMP]^+[CH_3SO_3]^-$	0.99	87.6	12.4	1.84			
[a] [In] represents the molar concentration of the 4-nitroaniline indicator. [b] [InH ⁺] represents the molar concentration of the protonated 4-nitroa- niline. [c] $H_0 = pK_a(ln) + log([ln]/[lnH+]), pK_a = 0.99;$ solvent: methanol; $c(ln) = 7.5 \times 10^{-5} \text{ mol L}^{-1}; c(sample) = 3.0 \times 10^{-2} \text{ mol L}^{-1};$ temperature =							

Dehydration of D-fructose to HMF catalyzed by Brønstedacidic ILs

25 °C.

The dehydration of D-fructose was carried out in a 100 mL flask with a condenser under a nitrogen atmosphere. After the reaction, the mixture was decanted into a volumetric flask using H_2O or ethanol as diluter, and then analyzed by HPLC equipped with UV and refractive index detectors. In a typical dehydration reaction, D-fructose loses three water molecules to produce HMF in the presence of Brønsted-acidic ILs (Scheme 1).

In Table 2, the dehydration results of p-fructose with different ILs as catalysts are summarized. $[NMP]^+$ -based ILs showed better catalytic performance than $[MIM]^+$ -based ILs; moreover, the ILs containing $[CH_3SO_3]^-$ ion exhibited better selectivity than those containing $[HSO_4]^-$ under the same conditions.



Scheme 1. Reaction process for the dehydration of D-fructose.

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Table 2. Dehydration of D-fructose catalyzed by the acidic ILs. ^[a]							
Entry	Catalysts	Solvent	Yield [%] ^[b]	Selectivity [%] ^[b]			
1	[NMP] ⁺ [HSO ₄] ⁻	DMSO	69.4	70.4			
2	[MIM] ⁺ [HSO₄] [−]	DMSO	23.6	51.6			
3	[NMP] ⁺ [CH₃SO₃] [−]	DMSO	72.3	87.2			
4	$[MIM]^+[CH_3SO_3]^-$	DMSO	25.1	63.1			
5	none	DMSO	3.2	68.1			
6	[NMP] ⁺ [HSO ₄] ⁻	H₂O	2.4	-			
7	$[NMP]^+[CH_3SO_3]^-$	H_2O	2.7	-			
[a] The reaction of D-fructose was performed on a 1.0 g scale, in the presence of acidic IL (7.5 mol%) under nitrogen atmosphere, in solvent (12 mL); reaction time = 2 h, temperature = 90 °C. [b] Yield and selectivity of HMF were obtained by HPLC analysis.							

Yields of 69.4% or 72.3% HMF were obtained in dimethylsulfoxide (DMSO) when 7.5 mol% [NMP]⁺[HSO₄]⁻ or [NMP]⁺-[CH₃SO₃]⁻ were employed in the reaction, respectively (Table 2, entries 1 and 3). On the other hand, using [MIM]⁺[HSO₄]⁻ or $[MIM]^+[CH_3SO_3]^-$ as a catalyst, only 23.6% or 25.1% yields were obtained, respectively (Table 2, entries 2 and 4). In selectivity, 87.2% and 70.4% of HMF in the presence of [NMP]+-based ILs were also satisfying. For comparison, a blank experiment was carried out in the absence of any IL, and the HMF yield was 3.2% (Table 2, entry 5). Furthermore, the dehydration reactions of p-fructose in pure water in the presence of [NMP]⁺[HSO₄]⁻ or [NMP]⁺[CH₃SO₃]⁻ were also carried out, and the yields of HMF were 2.4% and 2.7%, respectively (Table 2, entries 6 and 7). These results indicated that [NMP]⁺[CH₃SO₃]⁻ was the most efficient catalyst for the dehydration of D-fructose to HMF in all four acidic ILs.

Effect of reaction time and temperature for the dehydration of $\ensuremath{\,{\mbox{\tiny D}}}$ -fructose

The effect of reaction time in the dehydration of p-fructose catalyzed by $[NMP]^+[CH_3SO_3]^-$ is shown in Figure 2. It was found that the yield of HMF increased gradually and the selectivity was maintained during the reaction from 0.5 h to 2.0 h. When the time was extended to 2.5 h and longer, the yield and selectivity of HMF decreased, which indicated that the conversion to byproducts was probably more rapid than the generation of HMF. The effect of temperature is presented in Figure 3. The yield of HMF increased slowly and the selectivity hardly changed from 40 °C to 90 °C. However, the HMF yield decreased gradually when the temperature was further elevated to the higher range. These results showed that the optimal temperature was 90 °C in the acidic IL-catalyzed dehydration of p-fructose.

Effect of solvent in the dehydration of D-fructose

Different solvents, including protic (ethanol) and aprotic ones (*N*, *N*-dimethyl acetamide, acetonitrile, carbon tetrachloride, and DMSO), were employed in the dehydration of p-fructose for 2 h at 85 °C (Table 3). Here, 20.5 % conversion or 69.4 % conversion with *N*, *N*-dimethylacetamide or DMSO as a solvent



Figure 2. Effect of reaction time on the dehydration of D-fructose.



Figure 3. Effect of temperature on the dehydration of D-fructose.

was superior to 5.9% conversion or 4.2% conversion with ethanol or acetonitrile as a solvent. When carbon tetrachloride was used as a solvent, due to the limited solubility of D-fructose, the dehydration reaction hardly occurred. It was concluded that aprotic and polar solvents are more suitable for this reaction system, which can be attributed to their ability to solubilize and differentiate the structures. However, DMSO is also a

Table 3. Dehydration of D-fructose in the different solvents. ^[a]						
Entry	Solvent	Yield [%] ^[b]	Selectivity [%] ^[b]			
1	ethanol	5.9	63.5			
2	acetonitrile	4.2	67.3			
3	dimethylacetamide(DMAc)	20.5	75.1			
4	dimethylsulfoxide (DMSO)	69.4	87.8			
5	carbon tetrachloride	0.3	-			
[a] The reaction of D-fructose was performed on a 1.0 g scale, in the presence of $[NMP]^+[CH_3SO_3]^-$ (7.5 mol%) under nitrogen atmosphere, in solvent (12 mL); reaction time = 2 h, temperature = 85 °C. [b] Yield and selectivity of HMF were obtained by HPLC analysis.						

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favorable solvent for the dehydration of D-fructose to HMF due to its ability to prevent the formation of byproducts, such as levulinic acid and humins.

Investigations on the recycling of catalyst and solvent

The recycling of catalyst and the reuse of solvent were examined. The investigations were performed at 90 °C for 2 h in the presence of [NMP]⁺[CH₃SO₃]⁻ (10.0 mol%). After the dehydration reaction, the mixture was first distilled under reduced pressure. Pure DMSO was collected and the remaining mixture was extracted with ethyl acetate (10 mL \times 4) after water (0.5 g) was added, similar to other procedures in the literature.^[27] D-Fructose and [NMP]⁺[CH₃SO₃]⁻ were found to be insoluble in ethyl acetate; thus, the total amount of extracted HMF in the combined ethyl acetate layers was accounted as the isolated yield of HMF. The obtained mixture after extraction was heated at 75 °C for 12 h in a vacuum oven to remove water and residual ethyl acetate. It was then used directly in the next run by adding the distilled DMSO and an equal amount of D-fructose. The yield of HMF was essentially maintained for the former three recycled reactions (Figure 4), which showed that the cat-



Figure 4. Recycling of the catalyst system in the dehydration of D-fructose (the reaction condition was similar to that of Table 2, entry 3).

alyst retained very high activity for the dehydration of D-fructose. Furthermore, the yield of HMF only decreased slightly (about 3.0%) after being recycled five times. All these results indicated that the catalyst $[NMP]^+[CH_3SO_3]^-$ was efficiently recycled in the D-fructose dehydration.

Dehydration of glucose catalyzed by Brønsted-acidic ILs

The dehydration of glucose was investigated using [NMP]⁺-based acidic ILs and mineral acid under similar reaction conditions. In Table 4 the yield of HMF was



in the presence of acidic IL or mineral acid (10.0 mol%) under a nitrogen atmosphere, in solvent (12 mL); reaction time = 2 h, temperature = 90 °C. [b] Yield and selectivity of HMF were obtained by HPLC analysis.

3.0% or 2.4% in DMSO solvent when $[NMP]^+[CH_3SO_3]^-$ or $[NMP]^+[HSO_4]^-$ was employed as a catalyst (entries 1 and 2). Moreover, a 1.4% or 21.2% yield of HMF was obtained in the presence of 10.0 mol% sulfuric acid or hydrochloric acid (entries 3 and 4). Compared to the results on the dehydration of p-fructose, these data indicate that the catalytic efficiency of acidic ILs is closely related to the reaction substrate. The difference between the dehydration of p-fructose and glucose is helpful to understand the dehydration mechanism of hexoses in the presence of $[NMP]^+$ -based acidic ILs, which shows that the ketose is more easily dehydrated than aldose in this catalytic system.

Mechanism of the D-fructose dehydration by acidic ILs

From the above experimental results, it can be shown that the dehydration of D-fructose to HMF catalyzed by the acidic ILs is a very complex process. In general, the efficiency in the D-fructose dehydration is closely related to the acidity of the catalyst. However, the product selectivity can be affected by numerous factors, such as the structure effect and solvent effect. Thus, the cyclic furan and enediol intermediates were proposed to account for the mechanism of the dehydration of D-fructose.^[34,35]

 $[NMP]^+[HSO_4]^-$ and $[NMP]^+[CH_3SO_3]^-$ have higher acidity and exhibit better activity compared to $[MIM]^+$ -based acidic ILs. The acidity of $[MIM]^+[HSO_4]^-$ and $[MIM]^+[CH_3SO_3]^-$ are very weak; accordingly, their catalytic performances are rather poor in the reaction. In our catalytic system, the conversion of Dfructose was likely sensitive to the structure of the ionic liquid. As shown in Scheme 2, the first and third water molecules can be lost directly under appropriate protonic acidity; nevertheless, the loss of the second water molecule is selective and





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needs the help of a chemical force, which has been testified by an NMR study.^[36] Here, when $[NMP]^+[CH_3SO_3]^-$ was employed as a catalyst, the IL may have interacted with p-fructose or the intermediate through hydrogen bonding and nucleophilic effect, owing to the existence of a carbonyl group and protonated nitrous cation, which led to the production of HMF with high selectivity. Indeed, in the dehydration of glucose, the yield of HMF was relatively low due to the difficulty in forming a penta-ringed structure. Further investigations on the capture of the intermediates are underway.

Conclusions

Efficient synthesis of HMF from D-fructose dehydration has been achieved using small amounts of acidic ILs as catalysts under mild conditions. [NMP]⁺[CH₃SO₃]⁻ showed very high catalytic activity and selectivity in the dehydration of D-fructose, and a 72.3% HMF yield and 87.2% selectivity were obtained when it was employed as a catalyst at 90°C after 2 h. Compared to pure water and other solvents, DMSO was a better reaction medium and exhibited superior performance in the dehydration of D-fructose and glucose. The effects of reaction time and reaction temperature were investigated in detail. The catalyst and solvent can be recycled for the dehydration of Dfructose. The relationship between the characteristics of ILs and the catalytic activity was discussed according to the Hammett acidity function and the experimental results. Furthermore, a possible mechanism for the dehydration of D-fructose was proposed.

Experimental Section

Reagents

N-methyl-2-pyrrolidone, 1-methylimidazole, H₂SO₄, CH₃SO₃H, D-fructose, and glucose were analytical grade. The anhydrous DMSO was purified by distillation. The pure water was prepared by the Ultrapure Water System (electrical resistivity = 10–16 m Ω cm). The HMF used as the standard sample was purchased from Alfa Aesar.

Synthesis procedure and characterization data of ILs

[NMP]⁺[CH₃SO₃][−] was synthesized using the following procedure: *N*-methyl-2-pyrrolidone (9.9 g, 0.1 mol) was added to a 50 mL flask with magnetic stirring. Then, methyl sulfonic acid (9.6 g, 0.1 mol) was dropped slowly into the flask over approximately 30 min in an ice bath. The reaction was kept stirring for another 4 h at room temperature. The mixture was washed with ethyl acetate three times and dried at 90°C under vacuum. ¹H NMR ([D₆]DMSO): δ = 8.568 (s, 1 H), 3.270–3.298 (t, 2 H, *J*=7.1 Hz), 2.672 (s, 3 H), 2.458–2.464 (d, 3 H, *J*=2.2 Hz), 2.144–2.177(t, 2 H, *J*=8.1 Hz) 1.861–1.906 ppm (quint, 2 H, *J*=7.6 Hz). ESI-MS: *m/z* 99.8 [NMP]⁺, 94.8 [CH₃SO₃][−].

The preparation of ionic liquid $[MIM]^+[CH_3SO_3]^-$ was similar to that of $[NMP]^+[CH_3SO_3]^-$. ¹H NMR (DMSO-*d*6, 500 MHz): 9.037 (s, 1 H), 7.646–7.675 (d, 2 H, J = 14.5 Hz), 3.851 (s, 3 H), 3.390 (s, 1 H), 2.328 (s, 3 H). ESI-MS: *m/z* 83.2 [MIM]⁺, 95.1 [CH₃SO₃]⁻.

[NMP]⁺[HSO₄]⁻ was obtained by mixing *N*-methyl-2-pyrrolidone (9.9 g, 0.1 mol) with concentrated sulfuric acid (9.6 g, 0.1 mol) at 0– 5 °C and stirring for 4 h at room temperature. The liquid was then washed with ethyl acetate (3×10 mL) and dried at 80 °C in vacuo. The ionic liquid was obtained in quantitative yield. ¹H NMR ([D₆]DMSO): δ = 3.266–3.294 (t, 2 H, *J* = 7.2 Hz), 2.665 (s, 3 H), 2.143– 2.175 (t, 2 H, *J* = 8.1 Hz), 1.840–1.900 ppm (quint, 2 H, *J* = 7.6 Hz). ESI-MS: *m/z* (+) 99.9 [NMP]⁺, 96.8 [HSO₄]⁻.

The preparation of the ionic liquid $[MIM]^+[HSO_4]^-$ was similar to that of $[NMP]^+[HSO4]^-$. ¹H NMR (DMSO-*d*6, 500 MHz): 9.011 (s, 1 H), 7.626–7.675 (d, 2 H, J=25.1 Hz), 3.846 (s, 3 H); ESI-MS: *m/z* 83.2 [MIM]⁺, 97.0 [HSO₄]⁻.

Reaction conditions for the dehydration of D-fructose

All the dehydration reaction experiments were performed in a 100 mL flask equipped with magnetic stirring and a condenser. Typical procedure for dehydration of p-fructose is as follows: a solution of p-fructose (1.0 g, 5.6 mmol), acidic ILs (7.5 mol%), and solvent (12 mL) were charged into the flask. The atmosphere inside was replaced with nitrogen before the flask was airproofed. Under stirring, the flask was preheated to 90 °C with an oil bath and then remained for 2 h under a nitrogen atmosphere. After the reaction, the mixture was decanted to a volumetric flask with pure H₂O or ethanol as diluter, and then analyzed by an HPLC equipped with UV and refractive index detectors.

Typical separation procedure for HMF

After the dehydration of p-fructose, the reaction mixture was transferred into a flask and was distilled under reduced pressure. The remaining mixture was extracted with ethyl acetate (10 mL×4) after water (0.5 g) was added, and then the organic phase was collected. After drying with anhydrous sodium sulfate, the organic layer was distilled under reduced pressure to obtain pure HMF as the main product. The purity was more than 95% from HPLC analysis. ¹H NMR spectrum ([D6]DMSO): 3.396–3.483 (d, 1H, J=7.078), 4.483 (s, 2H), 6.580–6.586 (d, 1H, J=3.417) 7.466–7.473 (d, 1H, J=3.417), 9.522 (s, 1H); ¹³C NMR spectrum ([D6]DMSO): δ 56.524, 56.650, 110.385, 152.413, 162.805, 178.667. The GC/MS and HPLC spectra of reaction products and detailed HPLC measurement conditions are contained in the Supporting Information.

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