

Supporting Information

Efficient autocatalytic oximation of bio-based 2,5-diformylfuran with aqueous hydroxylamine under mild conditions

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1. Experimental section

1.1 Materials

CH₂Cl₂ (99.8%), CH₃CN (99.8%), DMF (99.8%), DMSO (99.9%), MeOH (99.9%) and EtOH (99.8%) were supplied by Aladdin Chemistry Co. Ltd. and used as solvents for the tests. NaOAc (99.0%), NaOH (98.0%), NaHCO₃ (99.8%), HCl (36.0~38.0%) and AcOH (99.8%) were supplied by Aladdin Chemistry Co. Ltd. and used as catalytic additives for the tests. Hydroxylamine hydrochloride (99%, HAC) and hydroxylamine solution (50 wt.% in H₂O, HA) were also supplied by Aladdin Chemistry Co. Ltd. and used as ammonia agents for the tests. DMSO-*d*₆ (99.8 atom% D) was supplied by Sigma-Aldrich and used as deuterated solvents for NMR analysis.

2,5-diformylfuran (DFF, 99%) was synthesized in our laboratory and used as the starting materials for the tests.

1.2 Analytical method

¹H NMR and ¹³C NMR spectra in DMSO-*d*₆ were recorded on Bruker spectrometers (400 MHz AVANCE III) at 400 and 100 MHz, respectively. The structures of purified product were further confirmed on LC-MS system (SHIMADZU Ultimate 4600 series) using ESI techniques. The reaction mixture was quantitatively analyzed by HPLC (Agilent 1260 series) equipped with UV detector and ZORBAX-C18 column (150 × 4.6 mm). The column temperature was set to 35 °C, and methyl alcohol/water (10:90, v/v) was used as the mobile phase at a flow rate of 1.0 mL min⁻¹. Conversion and yield values were determined as follows based on the external standard curves adjusted by the corresponding reference reagents (R² ≥ 0.9999).

Conversion of DFF (mol%) = (1-mol of DFF residual / mole of initial DFF) × 100%.

Yield of DFFM (mol%) = (mol of DFFM residual) / (mole of initial DFF) × 100%.

Yield of DFFD (mol%) = (mol of DFFD residual) / (mole of initial DFF) × 100%

1.3 General procedure for the synthesis of DFFD

As the general procedure, solid DFF (0.5 mmol) was dissolved in 2 mL appropriate solvent (either water or organic solvents) in a 10 mL sealed reaction vessel under magnetic stirring at 600 rpm. Afterwards, the reactor

was immersed in the water of the super-grade thermostat, the temperature of which was controlled accurately in the set range of r.t.-50 °C. Then HAHC (1.2 mmol) and additives (1.2 mmol) were introduced into the reaction vessel through a charging port and the target reaction was initiated immediately. The whole mixture was then stirred for 5 min, the pH value was monitored continuously and a certain amount of samples was removed from the reaction solution at regular time interval to monitor the product evolution with time. After completion of the reaction (monitored by HPLC), DMF (5 mL) was added to the resulting mixture for homogenization and continued to stirring for another 5 min.

1.4 Isolation procedure of DFFD

After the reaction was completed, the precipitated DFFD was collected by simple filtration and then washed using water (10 mL) without further purification. Then the collected product was dried under vacuum for 12h to remove water. If white precipitate was not observed in the reaction mixture after reaction completion, the solvent was removed under reduced pressure. The remained crude mixture was purified by column chromatography (silica gel, cyclohexane/EtOAc 2:1) and white solid product was obtained.

2. Characterization of products

2.1 HPLC analysis of isolated DFFD

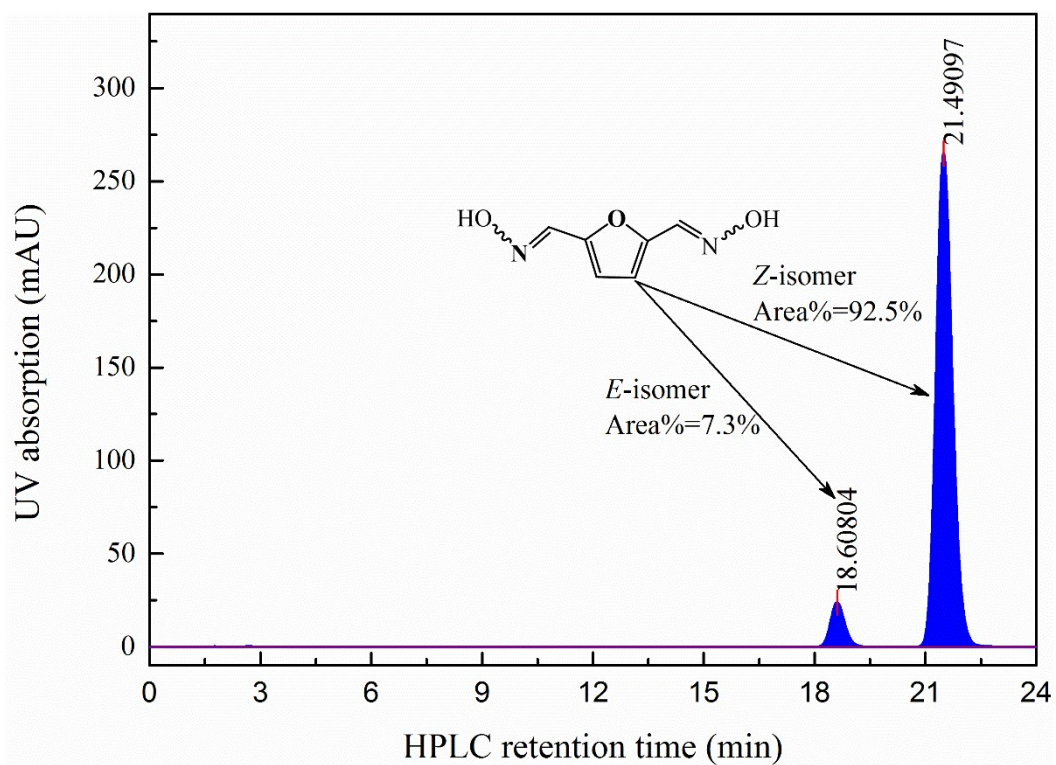


Figure S1. HPLC spectrum of the isolated 2,5-Diformylfuran dioxime (DFFD) by filtration on gram scale. *E/Z* ratio was determined by ^1H NMR from crude mixtures.¹

2.2 NMR analysis of DFFD

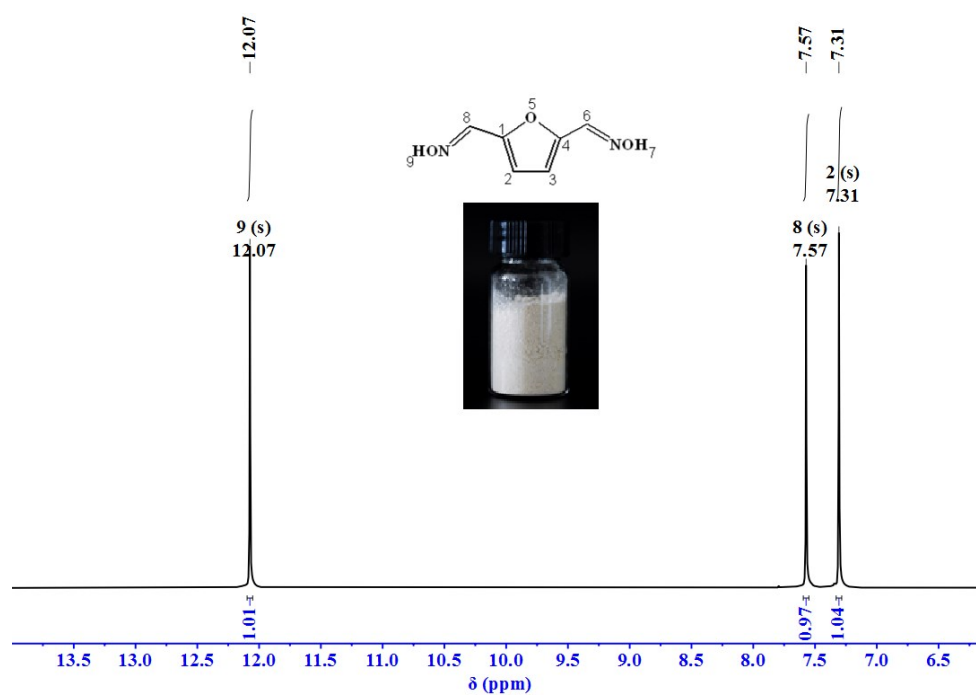


Figure S2. ^1H NMR spectra of purified 2,5-Diformylfuran dioxime (DFFD), *E*-isomer in $\text{DMSO-}d_6$.

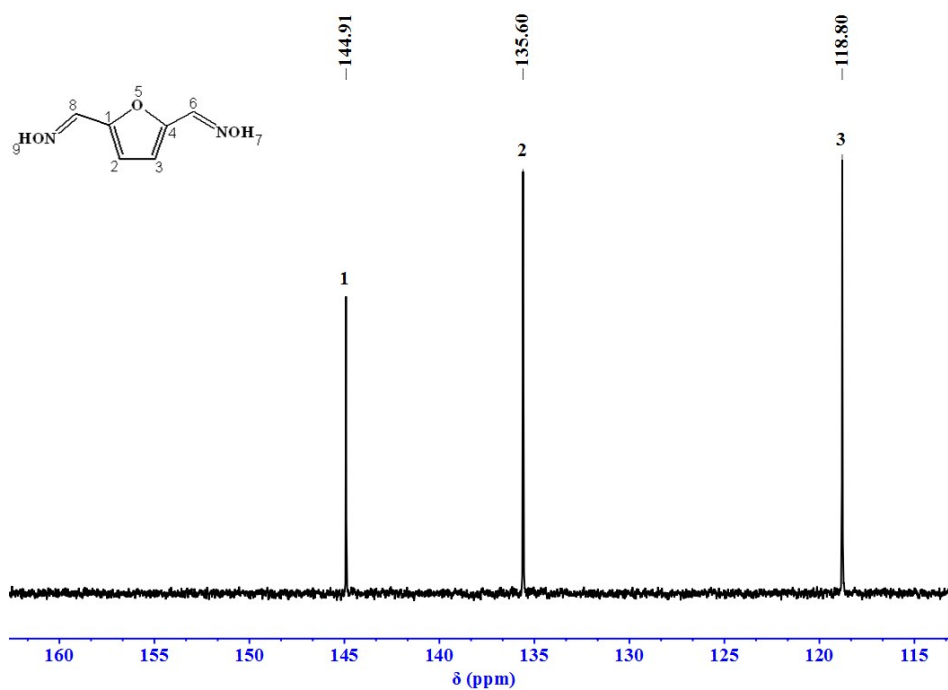


Figure S3. ^{13}C NMR spectra of purified 2,5-Diformylfuran dioxime (DFFD), *E*-isomer in $\text{DMSO-}d_6$.

2.3 MS analysis of DFFD and DFFM

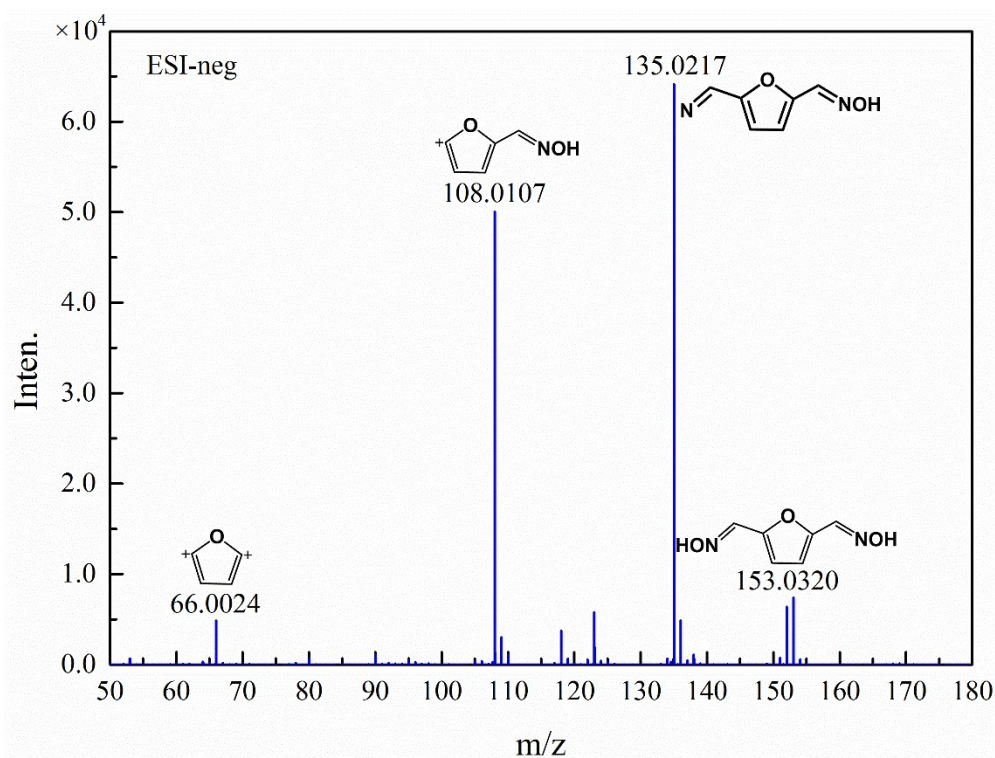


Figure S4. Mass spectra of purified 2,5-Diformylfuran dioxime (DFFD), *E*- and *Z*-isomers.

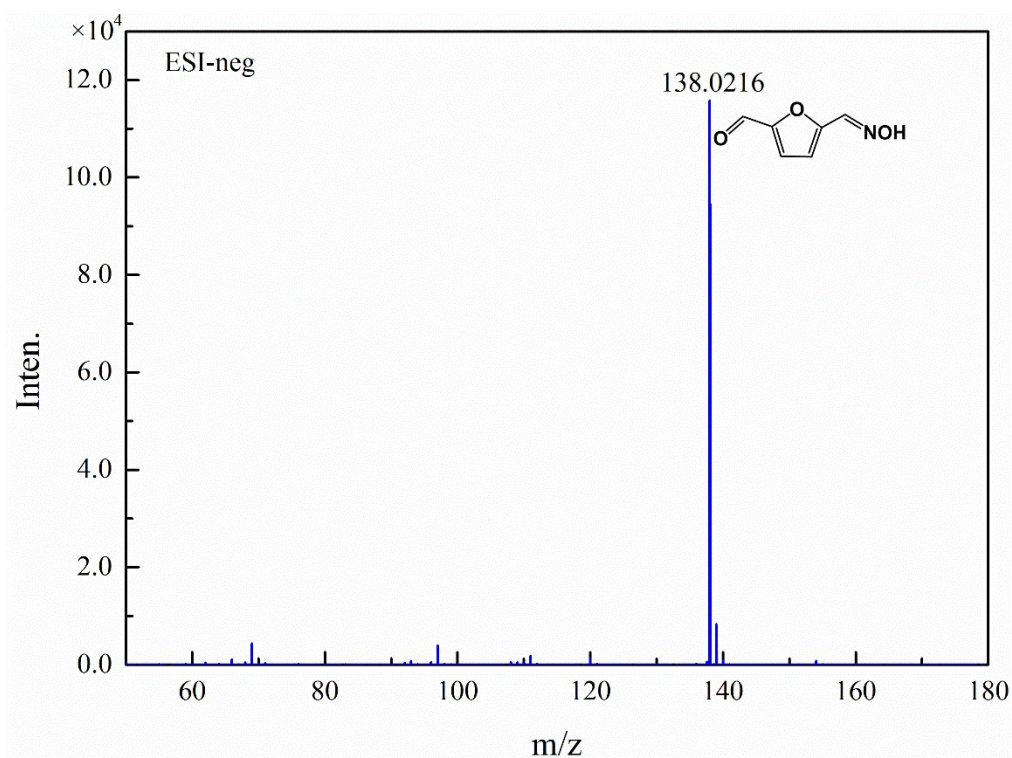


Figure S5. Mass spectra of purified 2,5-diformylfuran monooxime (DFFM), *E*- and *Z*-isomers.

3. Reference

- 1 (a) D. K. Kölmel and E. T. Kool, *Chemical reviews*, 2017, **117**, 10358; (b) L. Zborovsky, A. Kostenko, D. Bravo-Zhivotovskii and Y. Apeloig, *Angewandte Chemie International Edition*, 2019, **58**, 14524; (c) M. Balaz, Z. Kudlickova, M. Vilkova, J. Imrich, L. Balazova and N. Daneu, *Molecules (Basel, Switzerland)*, 2019, **24**; (d) S. Nsikabaka, W. Harb and M. F. Ruiz-López, *Journal of Molecular Structure: THEOCHEM*, 2006, **764**, 161; (e) A. G. Smith, P. A. Tasker and D. J. White, *Coordination Chemistry Reviews*, 2003, **241**, 61.