Efficient Synthesis of Biofuel Precursor with Long Carbon Chains from Fructose†

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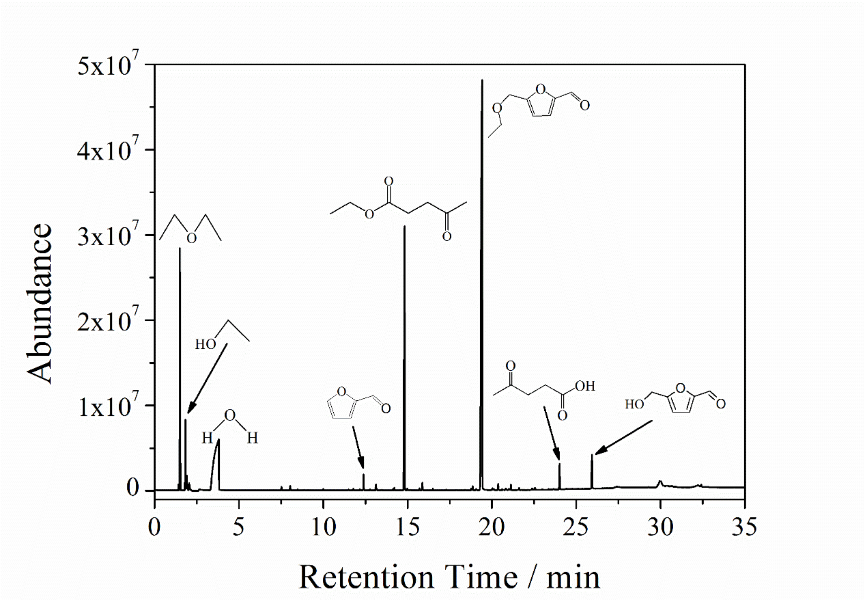

Fig. S1 Alcoholyzed products identification by GC-MS

Reaction conditions: 5 % fructose; 140 ℃; 50 mL ethanol; 1.0 h; 0.2 g $Fe_2(SO_4)_3$.

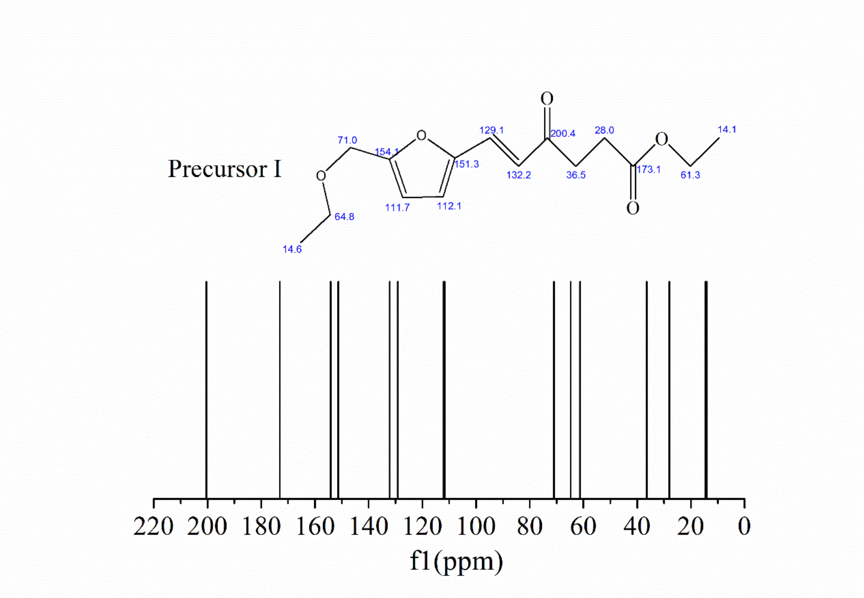

Fig. S2 Simulative ^{13}C NMR spectrum of theoretical precursor I condensed by EMF and EL at the mole ratio of 1:1.

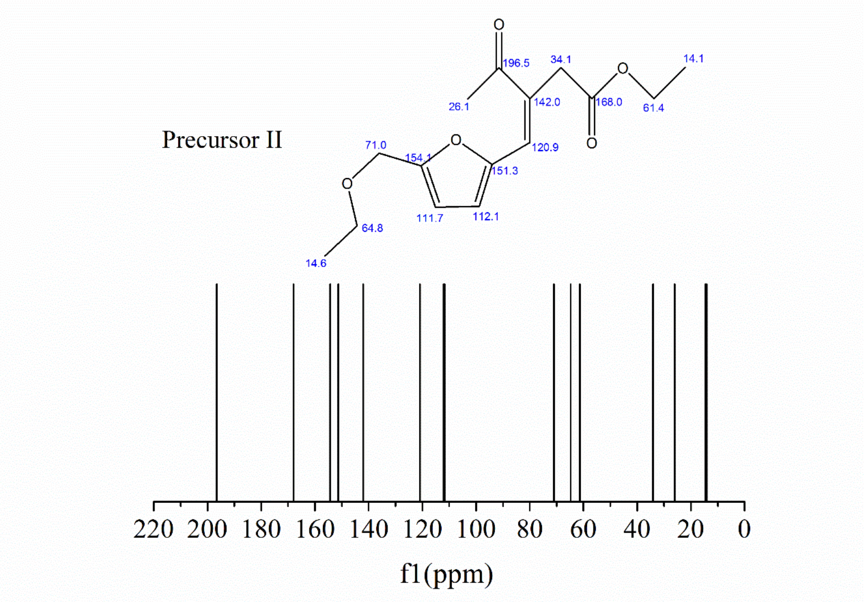

Fig. S3 Simulative ^{13}C NMR spectrum of theoretical precursor II condensed by EMF and EL at the mole ratio of 1:1.

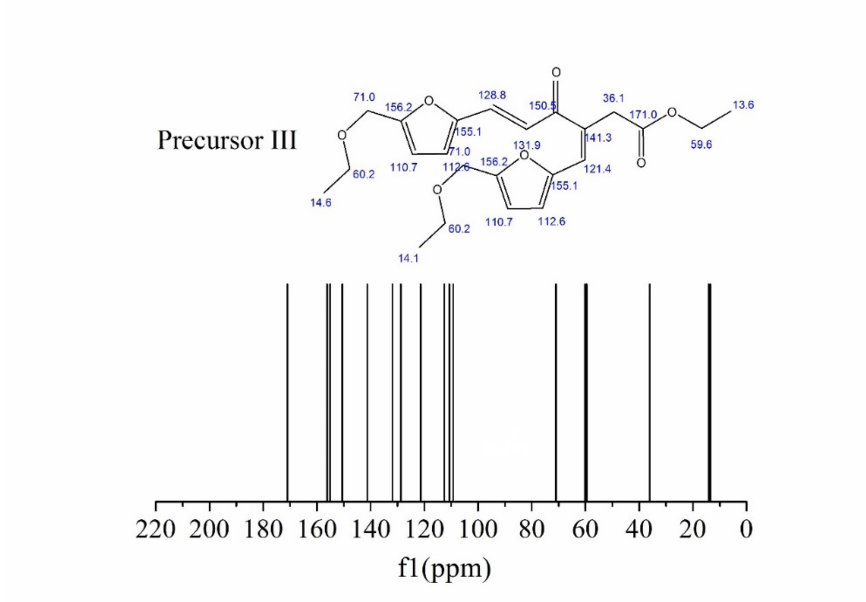

Fig. S4 Simulative ^{13}C NMR spectrum of theoretical precursor III condensed by EMF and EL at the mole ratio of 2:1

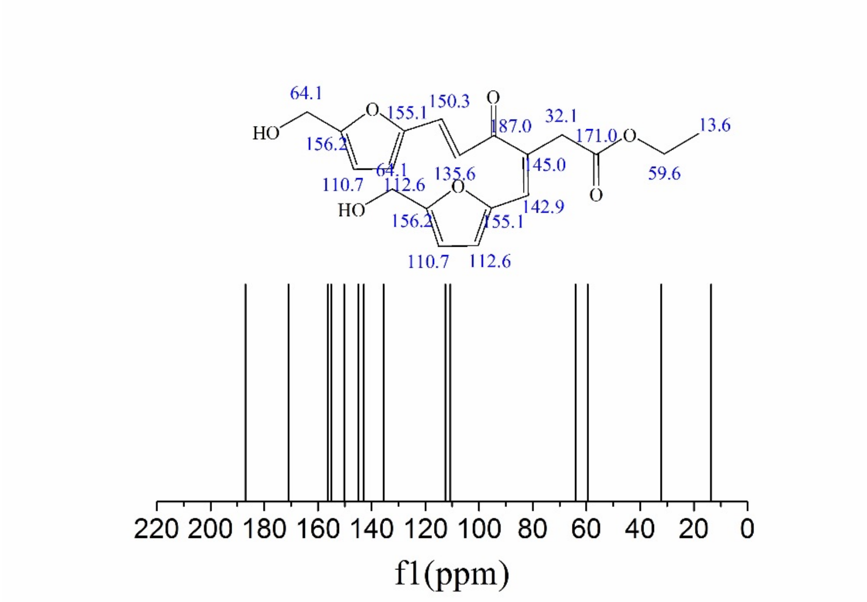

Fig. S5 Simulative ^{13}C NMR spectrum of theoretical precursor condensed by 5-HMF and EL at the mole ratio of 2:1.

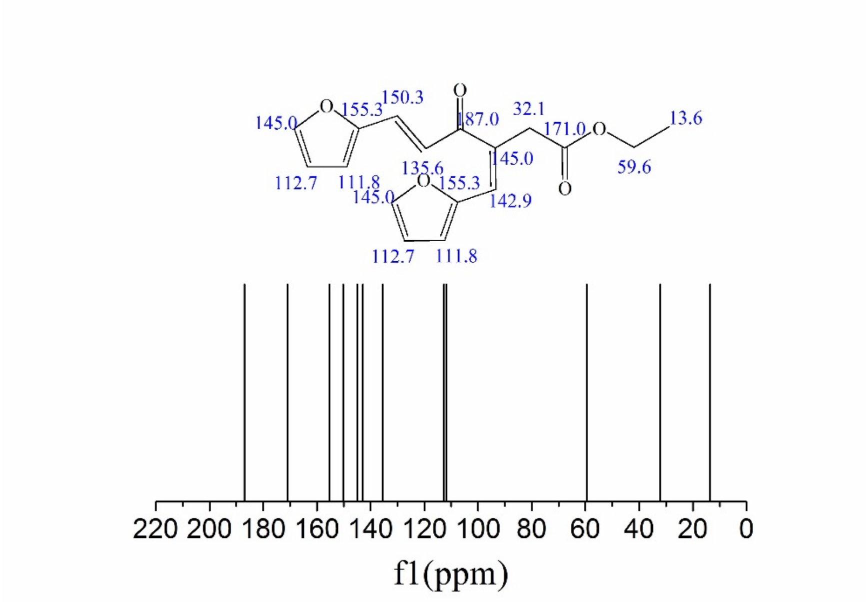

Fig. S6 Simulative ^{13}C NMR spectrum of theoretical precursor condensed by FA and EL at the mole ratio of 2:1.

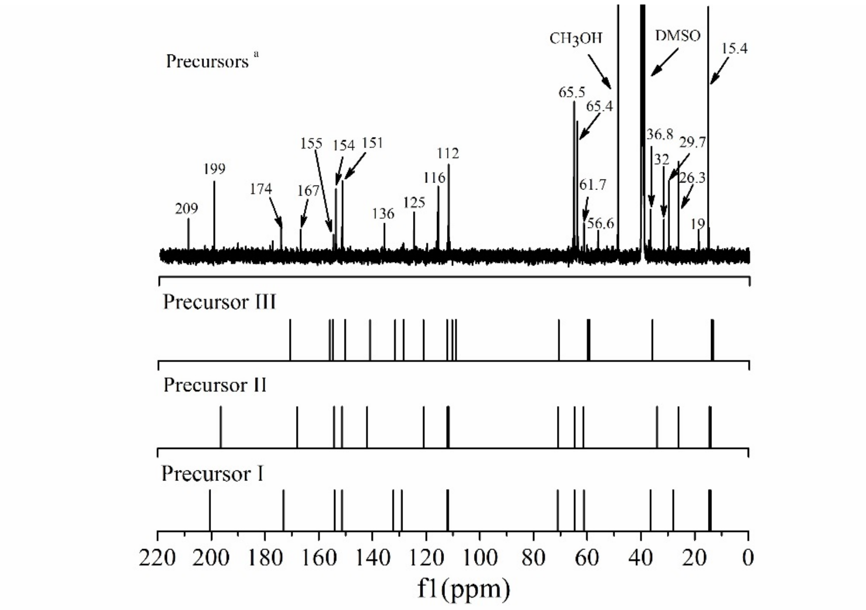

Fig. S7 ^{13}C NMR comparison of precursor ^{a} with theoretical precursors

δ = 199 ppm are attributed to the carbon of ketone group in precursor I and II; δ = 174 ppm is attributed to the carbon of ester group in precursor I; δ = 167 ppm is attributed to the carbon of ester group in precursor II; δ = 155, 154 ppm are attributed to the carbons of furan ring in precursor III; δ = 151 ppm is attributed to the carbon of furan ring in precursor I and II; δ = 136 ppm is attributed to the carbon of olefinic bond in precursor I; δ = 125 ppm is attributed to the carbon of olefinic bond in precursor III; δ = 112 ppm is attributed to the carbon of furan ring in II and III; δ = 65.4, 65.5 and 61.7 ppm are attributed to the carbons of oxethyl; δ = 36.8 and 32 ppm is attributed to the alkyl carbon of precursor III; δ = 29.7 and 26.3 ppm are attributed to I and II respectively.

Because of not the only cross condensation in this system, FA and 5-HMF could also be condensed with EL and LA respectively under NaOH.[1, 2] Therefore, the chemical shifts like δ = 136, 125, 116, 56.6 and 19 ppm are attributed to the other condensation products (Fig. S5 and S6).

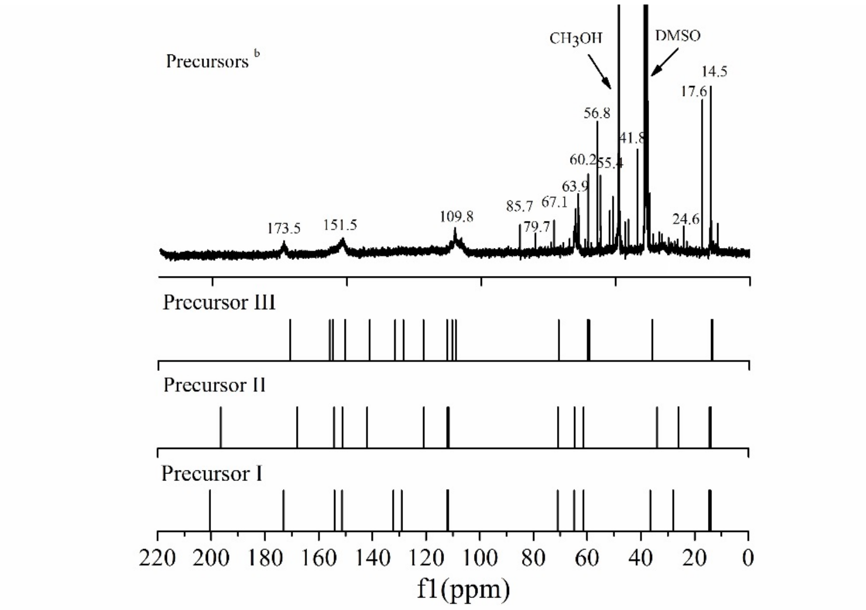

Fig. S8 ^{13}C NMR comparison of precursor ^{b} with theoretical precursors

According to previous investigation,[1] δ = 173.5, 151.5 and 109.8 ppm are attributed to the polymer formed by self-Michael additions. At the same time, these three chemical shifts are probably attributed to the precursor III either. δ= 67.1, 63.9 and 14.5 are attributed to the precursor III. Due to the complex condensation at the mole ratio of 1.9 over base catalyst, the chemical shifts without the scope of precursor I, II and III are attributed to the other undefined condensation products.

References:

1. A. S. Amarasekara, T. B. Singh, E. Larkin, M. A. Hasan and H. J. Fan, *Industrial Crops and Products*, 2015, **65**, 546-549.
2. L. Faba, E. Diaz and S. Ordonez, *ChemSusChem*, 2014, **7**, 2816-2820.