Supporting Information

Fast and efficient upgrading of levulinic acid into long-chain alkyl levulinates fuel additives with tungsten salt catalyst at low temperature

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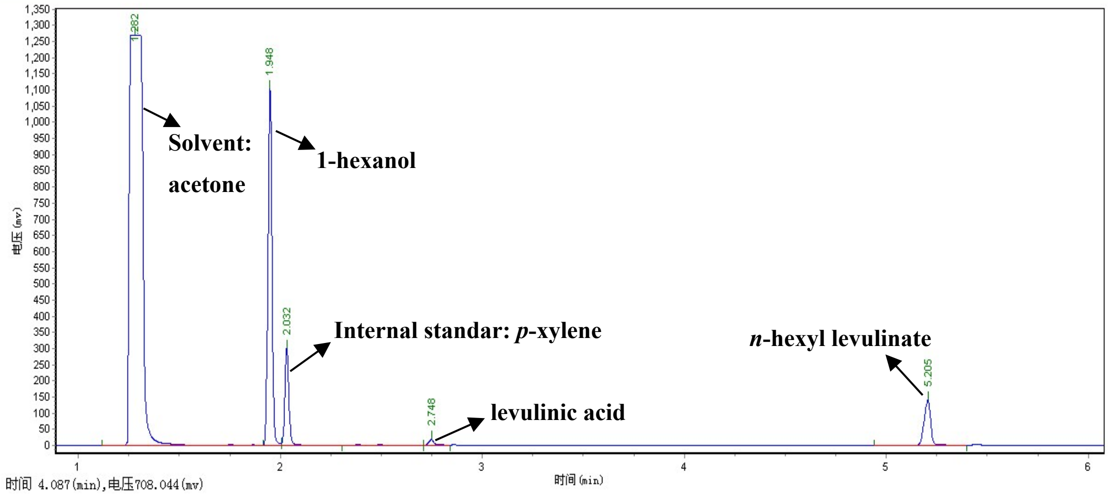


Fig. S1 Representative GC chromatogram for the esterification of LA and 1-hexanol.

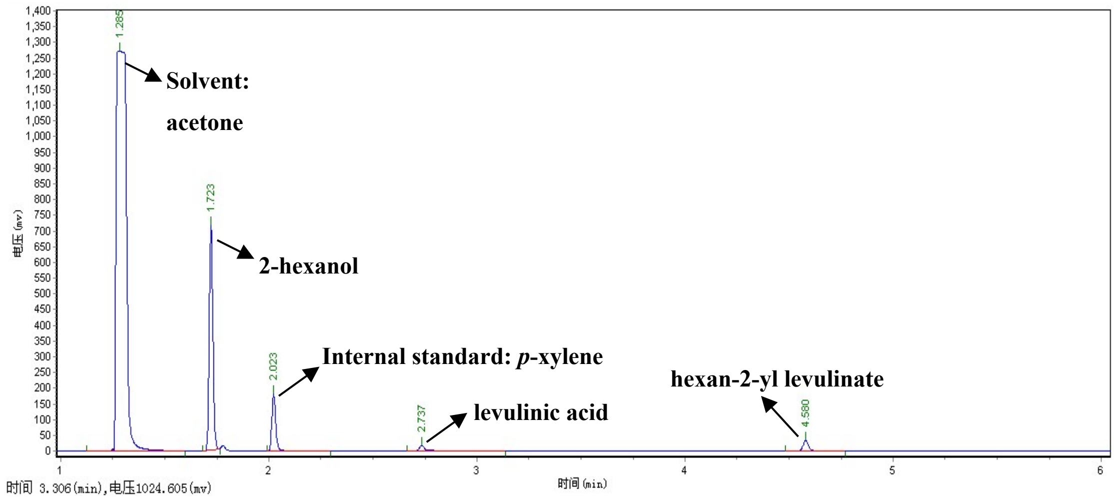


Fig. S2 Representative GC chromatogram for the esterification of LA and 2-hexanol.

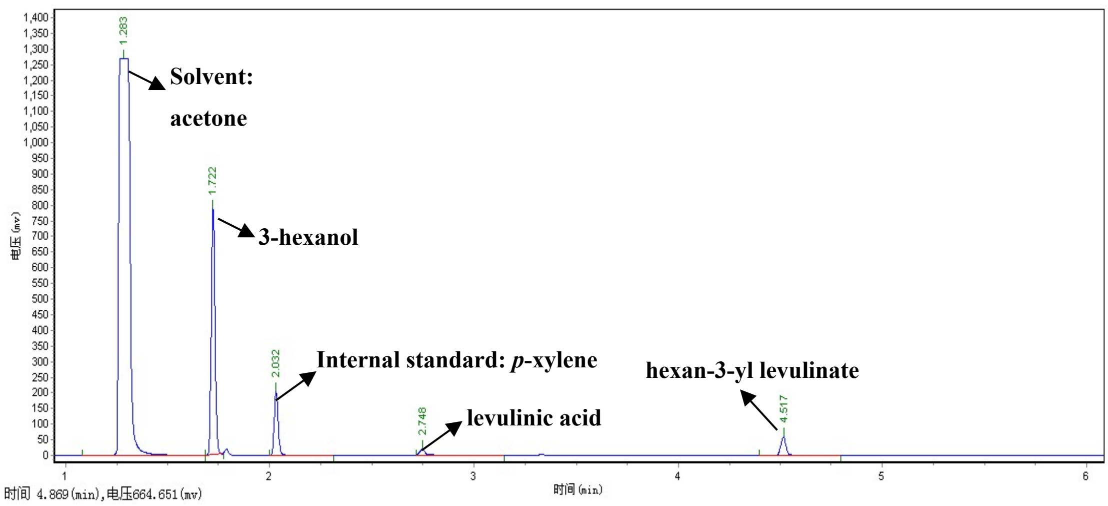


Fig. S3 Representative GC chromatogram for the esterification of LA and 3-hexanol.

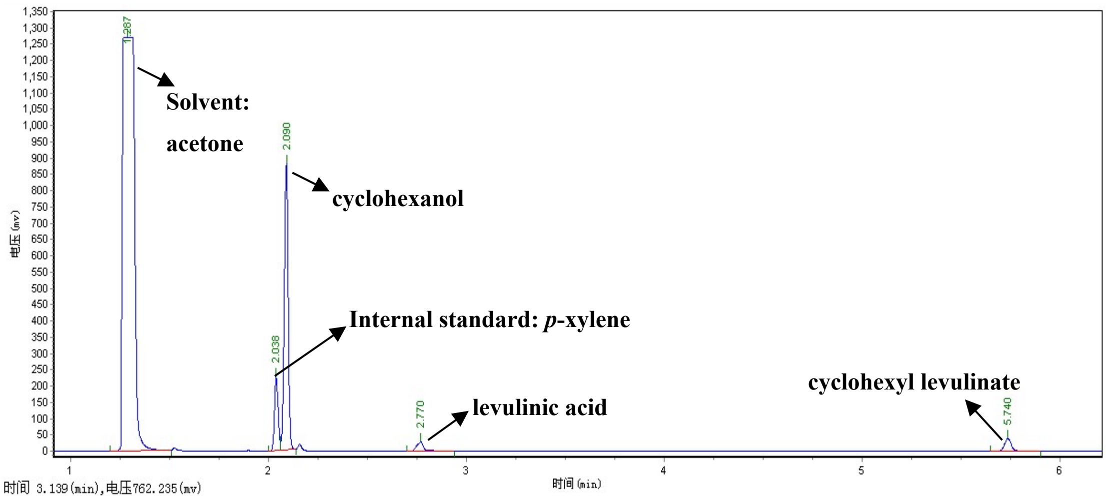


Fig. S4 Representative GC chromatogram for the esterification of LA and cyclohexanol.

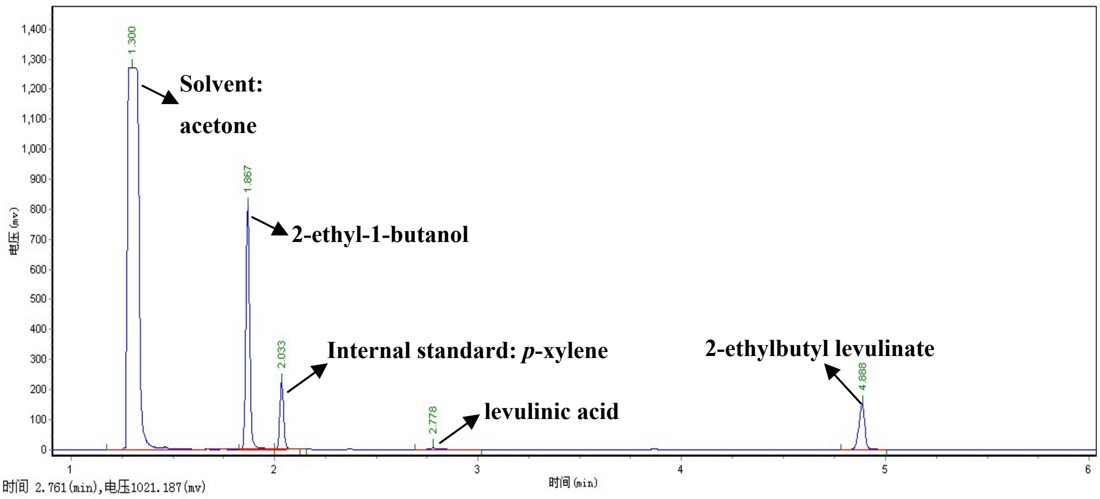


Fig. S5 Representative GC chromatogram for the esterification of LA and 2-ethyl-1-butanol.

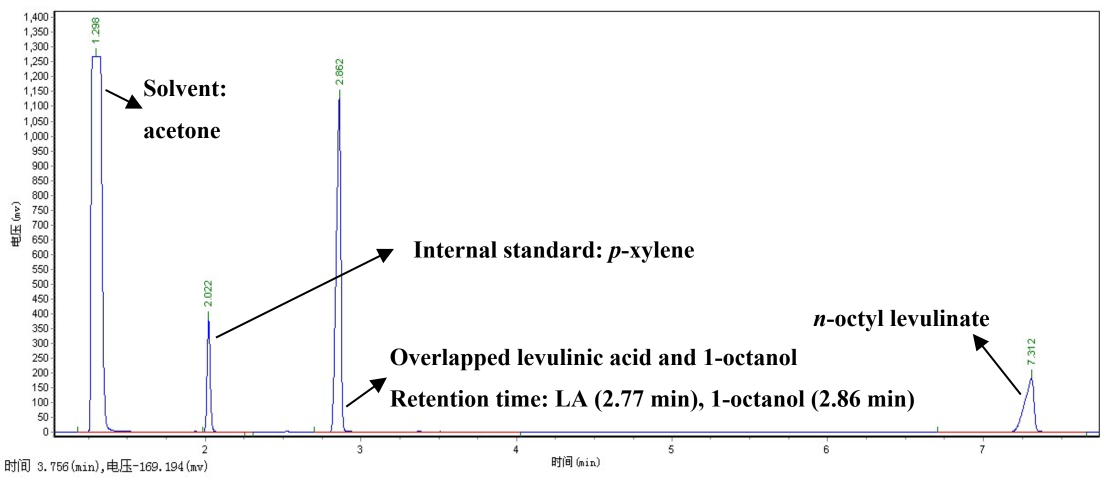


Fig. S6 Representative GC chromatogram for the esterification of LA and 1-octanol.

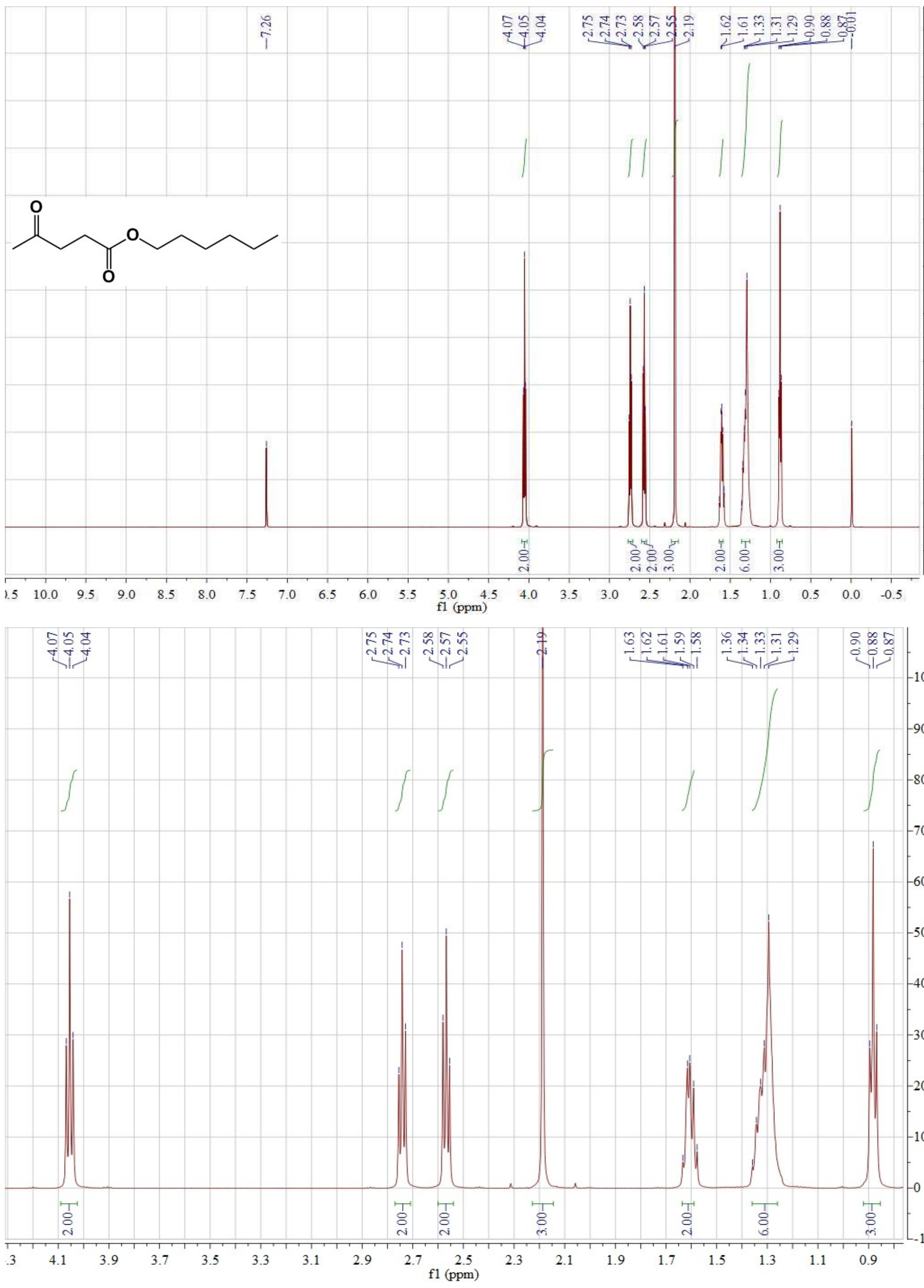


Fig. S7 ^{1}H NMR spectra of *n*-hexyl levulinate.

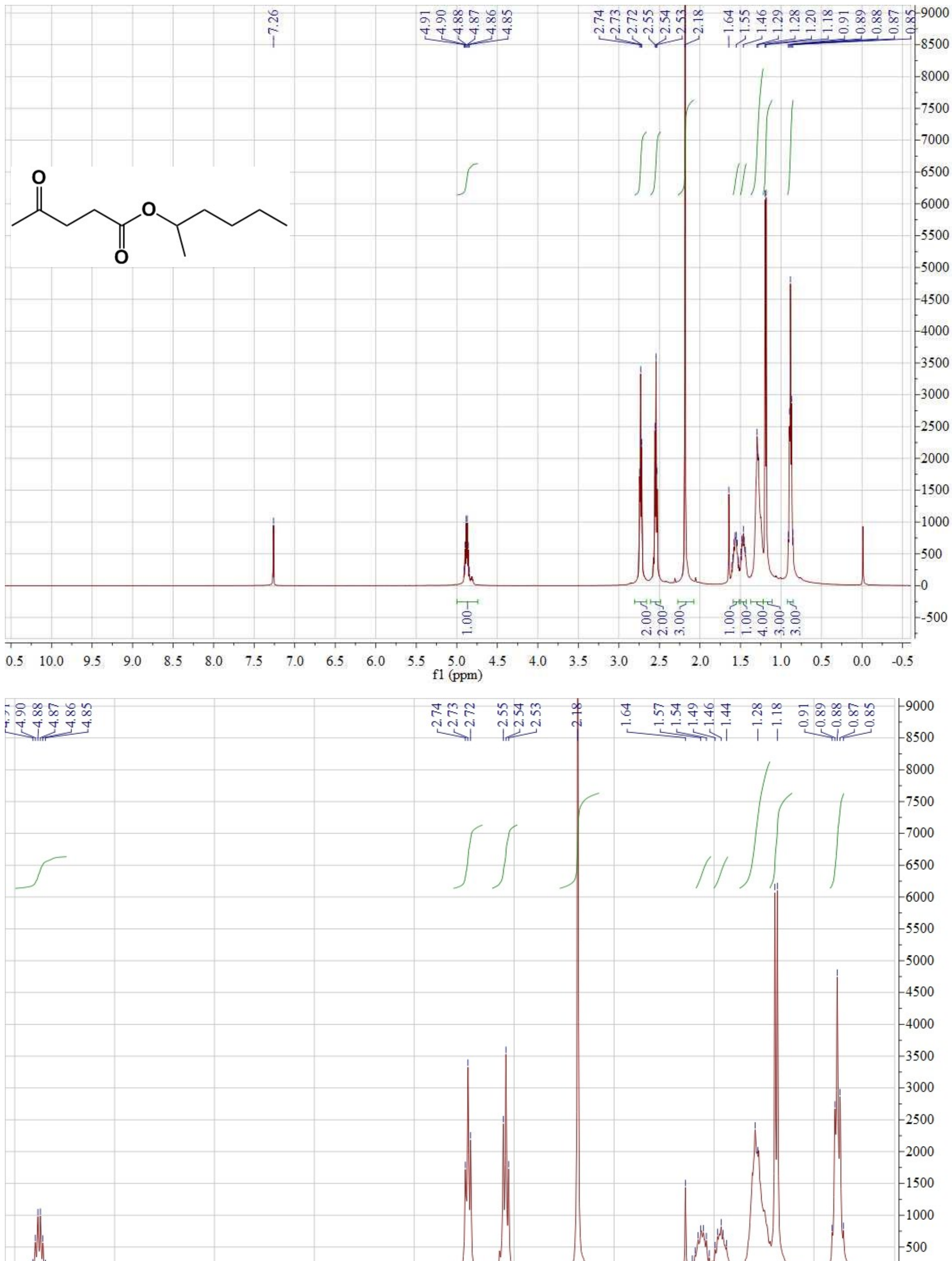


Fig. S8 ^{1}H NMR spectra of hexan-2-yl levulinate.

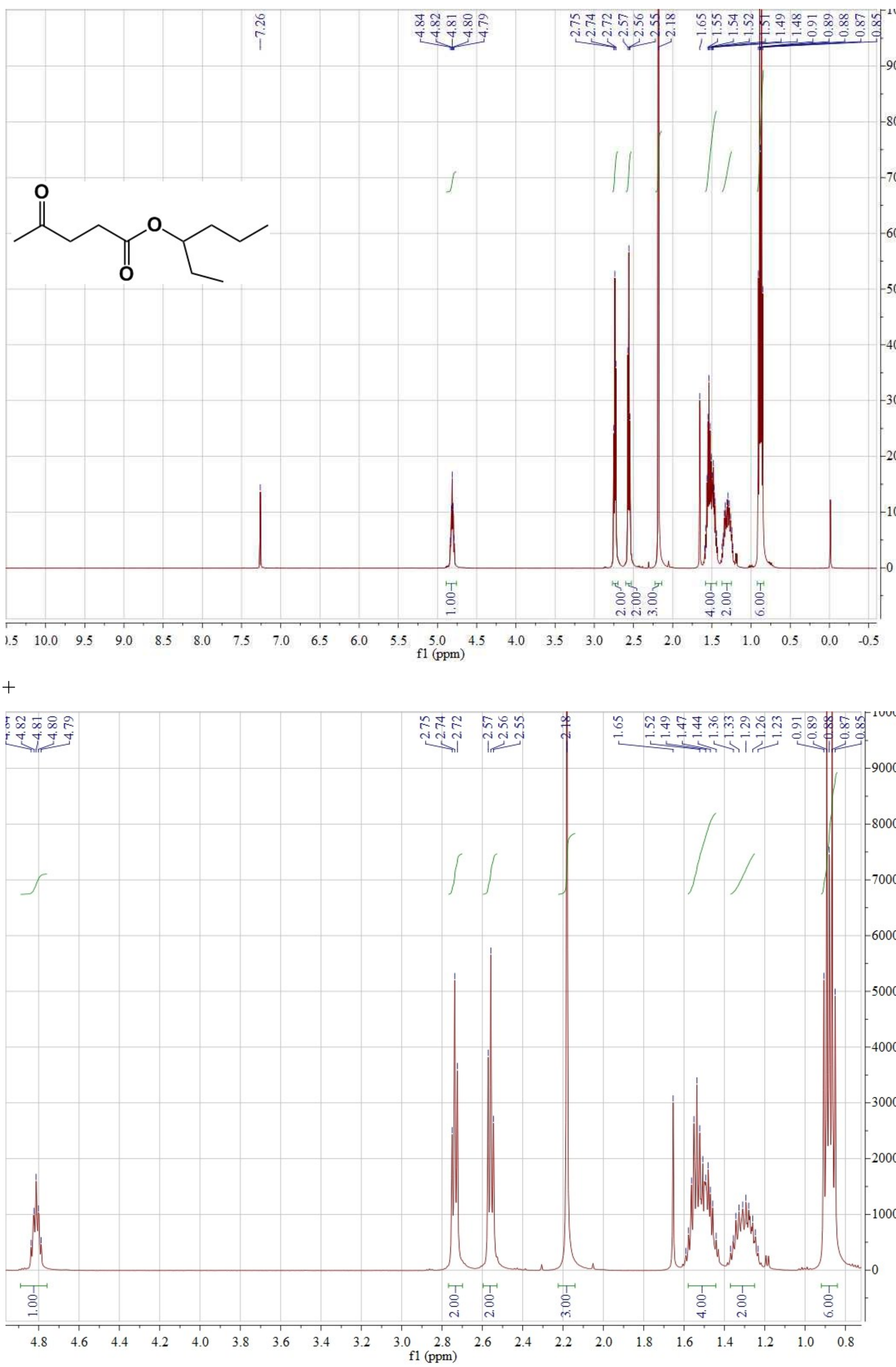


Fig. S9 ^{1}H NMR spectra of hexan-3-yl levulinate.

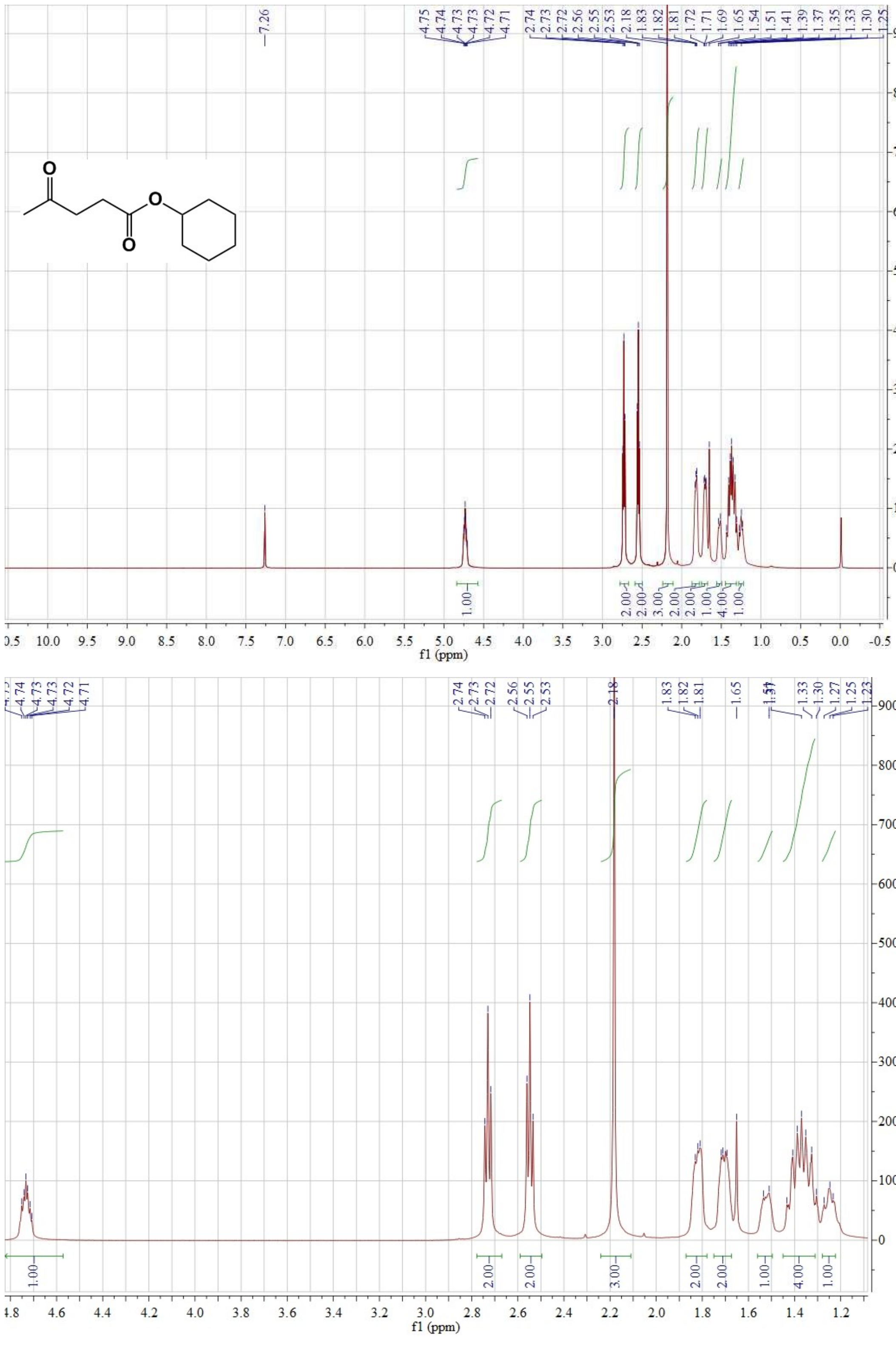
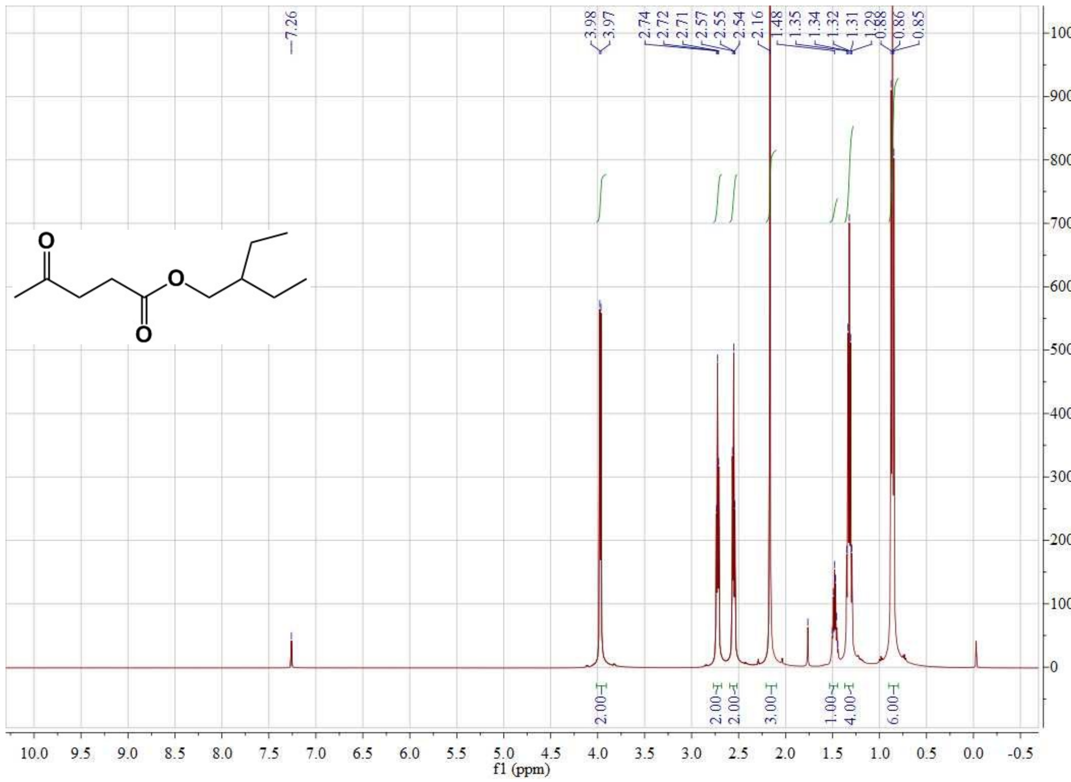


Fig. S10 ^{1}H NMR spectra of cyclohexyl levulinate.



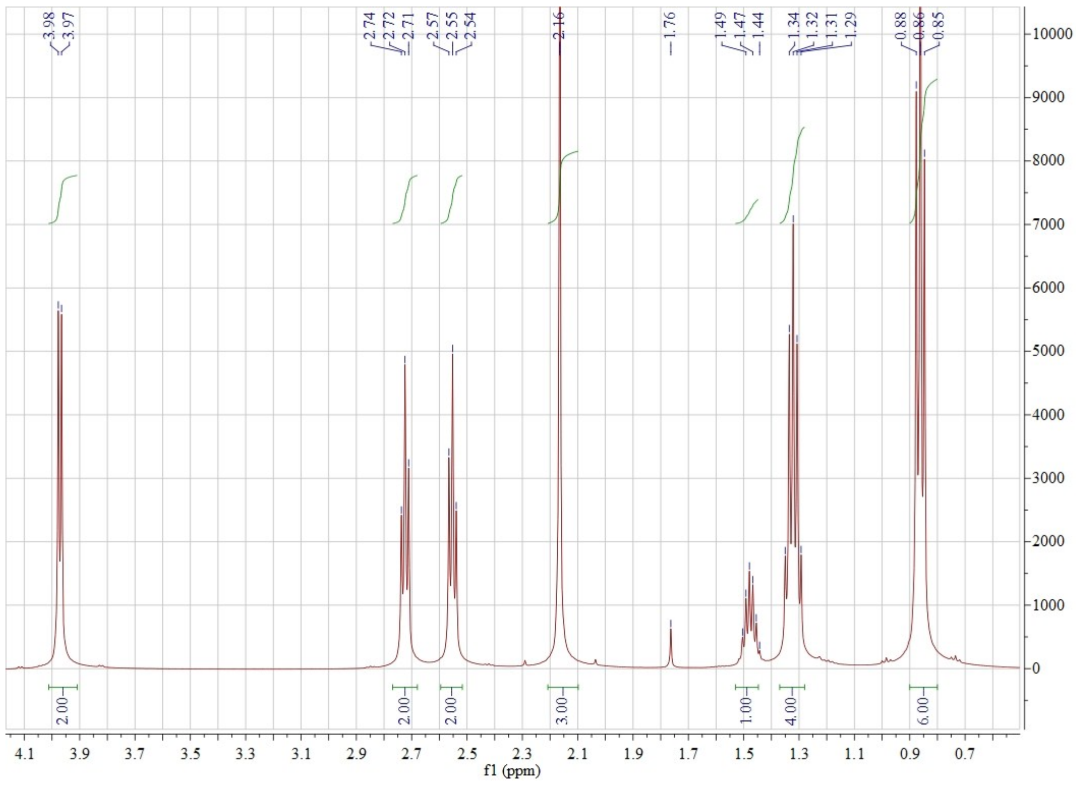


Fig. S11 ^{1}H NMR spectra of 2-ethylbutyl levulinate.

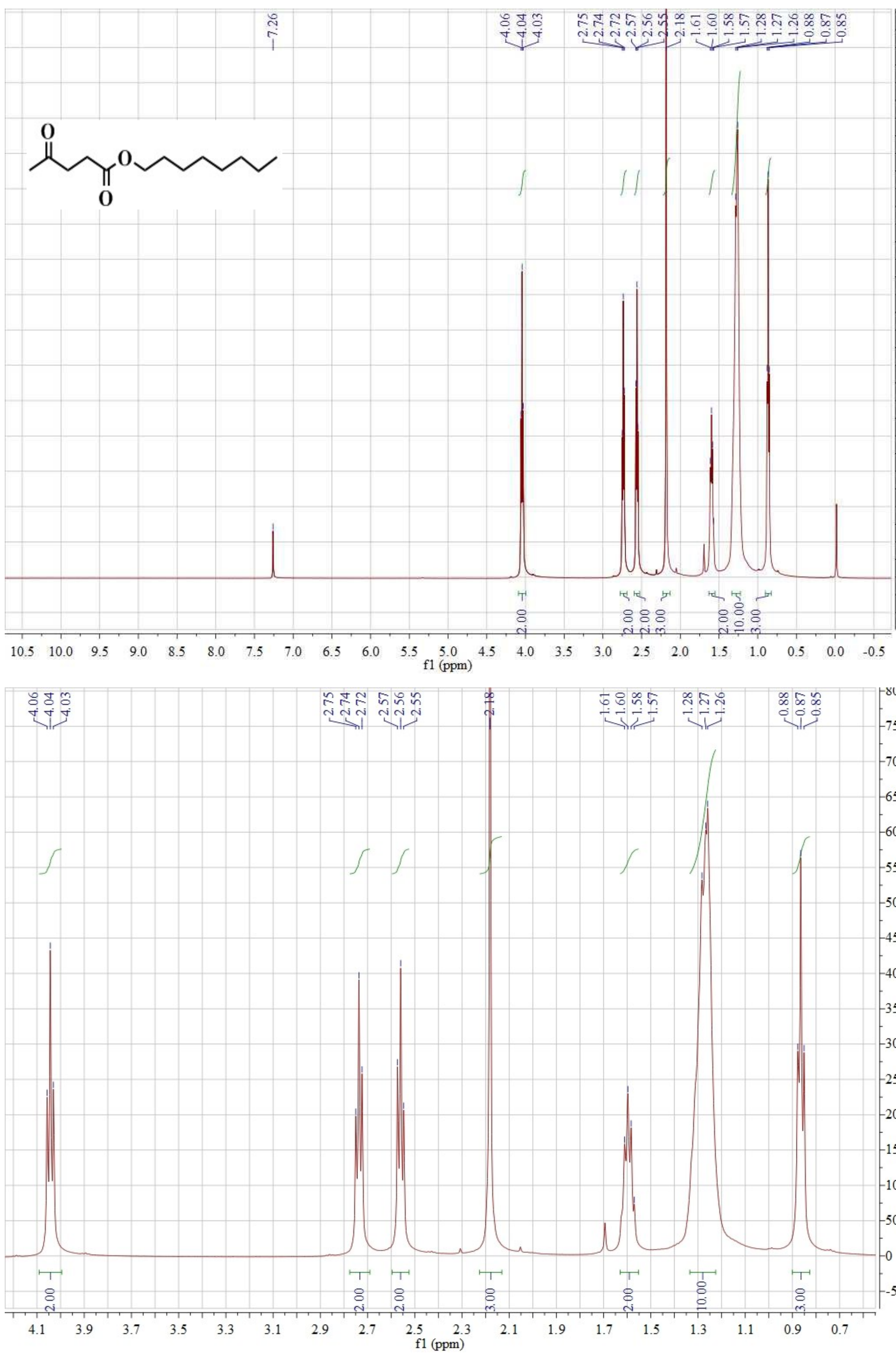


Fig. S12 ^{1}H NMR spectra of *n*-octyl levulinate

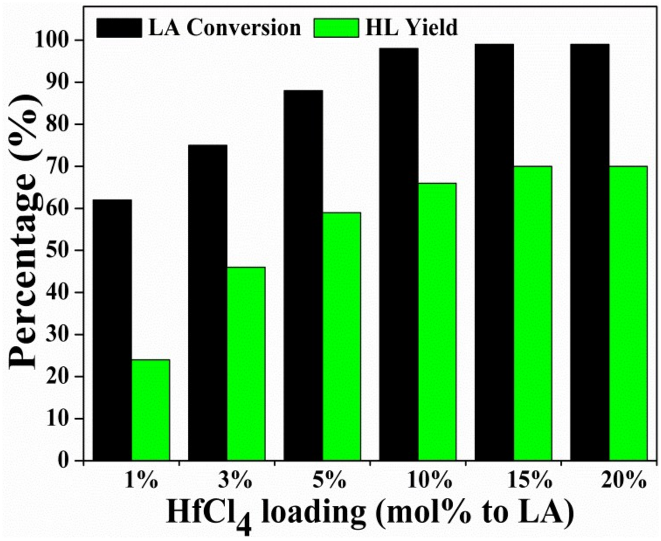


Fig. S13 Effect of $HfCl_4$ loading on the synthesis of HL by the esterification of LA and 1-hexanol. Conditions: 1 mmol LA, 5 mmol 1-hexanol, 50 °C, 30 min. The amount of $HfCl_4$ was 0.01, 0.03, 0.05, 0.1, 0.15 and 0.2 mmol, respectively.

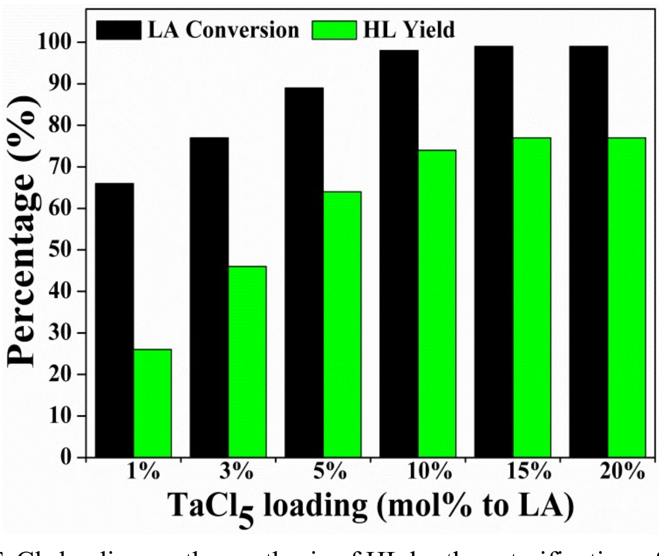


Fig. S14 Effect of $TaCl_5$ loading on the synthesis of HL by the esterification of LA and 1-hexanol. Conditions: 1 mmol LA, 5 mmol 1-hexanol, 50 °C, 30 min. The amount of $TaCl_5$ was 0.01, 0.03, 0.05, 0.1, 0.15 and 0.2 mmol, respectively.

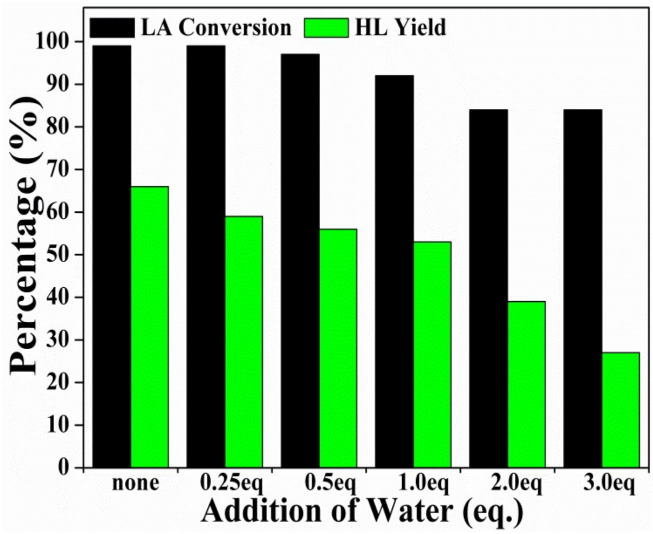


Fig. S15 Effect of initial addition of water on the synthesis of HL by the esterification of LA and 1-hexanol in the presence of $HfCl_4$. Conditions: 1 mmol LA, 5 mmol 1-hexanol, 0.1 mmol $HfCl_4$, 50 °C, 30 min. The amount of added water was 0.25 eq, 0.5 eq, 1.0 eq, 2.0 eq and 3.0 eq to the theoretical amount of in-situ formed water by complete esterification.

Table S1 Determination of the combustion calorimetry of various levulinate esters.[a]

Levulinate ester	Combustion equation	$\Delta_f H^\theta_m$ of ester (kJ/mol)	$\Delta_c H^\theta_m$ of ester (kJ/mol)
n-Methyl levulinate	$C_6H_{10}O_3(l)+7O_2(g) \rightarrow 6CO_2(g)+5H_2O(l)$	-524.55[b]	-3265.45
n-Ethyl levulinate	$C_7H_{12}O_3(l)+8.5O_2(g) \rightarrow 7CO_2(g)+6H_2O(l)$	-545.19[b]	-3924.11
n-Propyl levulinate	$C_8H_{14}O_3(l)+10O_2(g) \rightarrow 8CO_2(g)+7H_2O(l)$	-565.83[b]	-4582.77
n-Butyl levulinate	$C_9H_{16}O_3(l)+11.5O_2(g) \rightarrow 9CO_2(g)+8H_2O(l)$	-586.47[b]	-5241.43
n-Pentyl levulinate	$C_{10}H_{18}O_3(l)+13O_2(g) \rightarrow 10CO_2(g)+9H_2O(l)$	-607.11[b]	-5900.09
n-Hexyl levulinate	$C_{11}H_{20}O_3(l)+14.5O_2(g) \rightarrow 11CO_2(g)+10H_2O(l)$	-628[c]	-6558.5
n-Octyl levulinate	$C_{13}H_{24}O_3(l)+17.5O_2(g) \rightarrow 13CO_2(g)+12H_2O(l)$	-670[c]	-7875.1

[a] The calculation of combustion calorimetry of various levulinate esters is according to the reference 44 in the paper. For example, $\Delta_c H^\theta_m$ (methyl levulinate)=6$\Delta_f H^\theta_m$ (CO_2)+5$\Delta_f H^\theta_m$ (H_2O)-$\Delta_f H^\theta_m$ (methyl levulinate). The values of $\Delta_f H^\theta_m$ (CO_2) and $\Delta_f H^\theta_m$ (H_2O) are -393.5 and -285.8 kJ/mol, respectively.

[b] These values are checked on a website (https://www.chemeo.com).

[c] These values are estimated based on that the increase of each methylene group leads to an increment of about 21 kJ/mol according to the data counted from methyl levulinate to pentyl levulinate.

Table S2 Determination of the lower heating values of *n*-hexyl and *n*-octyl levulinates.

Levulinate ester	$\Delta_c H^\theta_m$ of ester (kJ/mol)	Lower heating value (MJ/L)
n-Ethyl levulinate	-3924.11	24.8[a]
n-Butyl levulinate	-5241.43	27.1[a]
n-Hexyl levulinate	-6558.5	29.4[b]
n-Octyl levulinate	-7875.1	31.7[b]

[a] These data are according to the reference 22 in this paper.

[b] A preliminary standard curve of lower heating value as a function of $\Delta_c H^\theta_m$ is established by the parameters of *n*-ethyl and *n*-butyl levulinates. The curve can be expressed in an equation that is y=-572.7478x+10280.0361, where y and x represent $\Delta_c H^\theta_m$ and lower heating value, respectively. The lower heating values of *n*-hexyl and *n*-octyl levulinates are estimated by the above standard curve.

Table S3 Representative works on the synthesis of LA and levulinate esters from biomass with metal salt catalysts.

Catalyst	Feedstock	Main product	General conditions	Reference
$CrCl_3$	cellulose, glucose	LA	180—200 °C, 180 min	S1
$AlCl_3$	cellulose, glucose	LA	180—200 °C, 180 min	S1
$FeCl_3$	cellulose, glucose	LA	180—200 °C, 180 min	S1
$CuCl_2$	cellulose, glucose	LA	180—200 °C, 180 min	S1
$CrCl_3$+HCl	glucose, fructose	LA	140 °C, 180 min	S2
$GaCl_3$	corncob	LA	180 °C, 60 min	S3
WCl_6	corncob	LA	180 °C, 60 min	S3
$SnCl_4$	corncob	LA	180 °C, 60 min	S3
$FeCl_3$	glucose	LA	140 °C, 240 min	S4
$ZrOCl_2$	agarose	LA+5-HMF	140 °C, 60 min	S5
$ZrCl_4$	agarose	LA+5-HMF	140 °C, 60 min	S5
$ZnBr_2$+HCl	glucose	LA	90 °C, 6 min (microwave)	S6
$InCl_3$	glucose	LA+5-HMF	180—210 °C, 60 min	S7
$FeCl_3$	cellulose	LA	195 °C, 240 min	S8
$CrCl_3$	cellulose	LA	195 °C, 240 min	S8
$CrCl_3$	LA+methanol	ML	110 °C, 10 min (microwave)	S9
$SnCl_4$	LA+methanol	ML	110 °C, 10 min (microwave)	S9
$FeCl_3$	LA+methanol	ML	110 °C, 10 min (microwave)	S9
$Fe_2(SO_4)_3$	LA+methanol	ML	110 °C, 10 min (microwave)	S9
$AlCl_3$	LA+methanol	ML	110 °C, 10 min (microwave)	S9
$Al_2(SO_4)_3$	LA+methanol	ML	110 °C, 10 min (microwave)	S9
$CuCl_2$	5-HMF+ethanol	EL	160 °C, 5 min (microwave)	S10
$FeCl_3$	5-HMF+ethanol	EL	160 °C, 5 min (microwave)	S10
$AlCl_3$	5-HMF+ethanol	EL	160 °C, 5 min (microwave)	S10
$SnCl_4$	5-HMF+ethanol	EL	160 °C, 5 min (microwave)	S10
$Fe_2(SO_4)_3$	LA+methanol/ethanol/ propanol/butanol	ML/EL/ PL/BL	60 °C, 240 min	S11
$Al(OTf)_3$+ H_2SO_4	glucose/fructose +ethanol	EL	180 °C, 120 min	S12
$Al_2(SO_4)_3$	cassava+ethanol	EL	200 °C, 720 min	S13

References:

[S1] L. Peng, L. Lin, J. Zhang, J. Zhuang, B. Zhang and Y. Gong, Catalytic Conversion of Cellulose to Levulinic Acid by Metal Chlorides, Molecules, 2010, 15, 5258-5272.

[S2] V. Choudhary, S. H. Mushrif, C. Ho, A.Anderko, V. Nikolakis, N. S. Marinkovic, A. I. Frenkel, S. I. Sandler and D. G. Vlachos, Insights into the Interplay of Lewis and Brønsted Acid Catalysts in Glucose and Fructose Conversion to 5-(Hydroxymethyl)furfural and Levulinic Acid in Aqueous Media, J. Am. Chem. Soc., 2013, 135, 3997-4006.

[S3] P. Zhao, C. Zhou, J. Li, S. Xu and C. Hu, Synergistic Effect of Different Species in Stannic

Chloride Solution on the Production of Levulinic Acid from Biomass, ACS Sustainable Chem. Eng., 2019, 7, 5176-5183.

[S4] Y. Jiang, L. Yang, C. M. Bohn, G. Li, D. Han, N. S. Mosier, J. T. Miller, H. I. Kenttamäa and M. M. Abu-Omar, Speciation and kinetic study of iron promoted sugar conversion to 5-hydroxymethylfurfural (HMF) and levulinic acid (LA), Org. Chem. Front., 2015, 2, 1388-1396.

[S5] X. He, J. Ma, K. Wang, Z. Xu and S. Jia, Catalytic Synthesis of 5-Hydroxymethylfurfural and Levulinic Acid from Agarose with $ZrOCl_2$ as Catalyst, Biomass Chem. Eng., 2019, 53, 15-20.

[S6] V. B. Kumar, I. N. Pulidindia and A. Gedanken, Synergistic catalytic effect of the $ZnBr_2$–HCl system for levulinic acid production using, microwave irradiation, RSC Adv., 2015, 5, 11043-11048.

[S7] Y. Shen, J. Sun, Y. Yi, B. Wang, F. Xu and R. Sun, 5-Hydroxymethylfurfural and levulinic acid derived from monosaccharides dehydration promoted by $InCl_3$ in aqueous medium, J. Mol. Catal. A, 2014, 394, 114-120.

[S8] C. Chiappe, M. J. R. Douton, A. Mezzetta, L. Guazzelli, C. S. Pomelli, G. Assanelli and A. R. Angelis, Exploring and exploiting different catalytic systems for the direct conversion of cellulose into levulinic acid, New J. Chem., 2018, 42, 1845-1852.

[S9] Y. Huang, T. Yang, B. Cai, X. Chang and H. Pan, Highly efficient metal salt catalyst for the esterification of biomass derived levulinic acid under microwave irradiation, RSC Adv., 2016, 6, 2106-2111.

[S10] S. Quereshi, E. Ahmad, K. K. Pant and S. Dutta, Insights into the metal salt catalyzed ethyl levulinate synthesis frombiorenewable feedstocks, Catal. Today, 2017, 291, 187-194.

[S11] F. P. Martins, F. A. Rodrigues and M. J. Silva, $Fe_2(SO_4)_3$-Catalyzed Levulinic Acid Esterification: Production of Fuel Bioadditives, Energies, 2018, 11, 1263.

[S12] J. Dai, L. Peng and H. Li, Intensified ethyl levulinate production from cellulose using a combination of low loading H_2SO_4 and $Al(OTf)_3$, Catal. Commun., 2018, 103, 116-119.

[S13] J. Tan, Q. Liu, L. Chen, T. Wang, L. Ma and G. Chen, Efficient production of ethyl levulinate from cassava over $Al_2(SO_4)_3$ catalyst in ethanol–water system, J. Energy Chem., 2017, 26, 115-120.