Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Fast catalytic conversion of recalcitrant cellulose into alkyl levulinates and levulinic acid in presence of soluble and recoverable sulfonated hyperbranched poly(arylene oxindole)s

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General information

Chemicals: Benzene 1,3,5-tricarbonyl trichloride, diphenyl ether, isatin, 5-chloroisatin, 5-methoxyisatin, aluminium (III) trichloride, 1,2-dichloroethane, dichloromethane, methanesulfonic acid, oleum (20%), Avicel® PH-101, α-cellulose, Sigmacell Type 20, cellobiose, sucrose, methyl α-D-glucopyranoside, methyl β-D-glucopyranoside, glucose, fructose, levoglucosan, hydroxymethylfurfural, 5-ethoxymethylfurfural, levulinic acid, methyl levulinate, ethyl levulinate, *n*-butyl levulinate, sulfuric acid, 2-naphthalenesulfonic acid and Amberlyst 15 were purchased from Sigma-Aldrich, Acros Organics or Alfa Aesar. Inulin was supplied by BENEO-Orafti. All chemicals were used without further purification as received. The ball-milling pretreatment of Avicel® PH-101 was carried out using ZrO_2 balls (mass 7.5 g; diameter 1.8 cm) for 24 h.

Catalyst characterization: The structure of the B_3 monomer and other various poly(arylene oxindole)s, before and after sulfonation, were confirmed by NMR spectra. The molecular weight of polymers was estimated by Gel permeation chromatography (GPC). NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz and Bruker AMX 400 MHz and 600 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane or the internal (NMR) solvent signal. GPC was performed with a PLgel D column (Polymer Laboratories) and THF as the eluent at 303K calibrated with linear polystyrene standards. The acid site density of the sulfonated hyperbranched poly(arylene oxindole)s was determined by back titration with a 2 M NaCl and 0.001 M NaOH solution using a Metrohm 808 Titrando antotitrator & 801 stirrer. The titration experiments were performed in duplicate and the average number for the acid capacities reported. Infrared spectra were recorded with an Alpha FTIR spectrometer (Bruker). Thermogravimetric analysis (TGA) experiments were performed by heating the polymer under flowing oxygen on a TGA Q500 (TA Instruments, Brussels, Belgium). The flow rate was 20 mL min^{-1}. After 1 h dehydration at 373 K, about 10 mg of the sample was heated at 5 K min^{-1} to 973 K.

Synthesis of polymer catalysts

The general procedures for the synthesis of 1, 3, 5-tri-(4-phenoxybenzoyl)benzene (B_3 monomer), hyperbranched poly(arylene oxindole)s and the sulfonation of hyperbranched polymers can be found in our previous reports.[1-6] A minor modification in the polymer catalysts preparation in this article is the use of 20% oleum instead of 30% oleum, in order to obtain an acid density of around 3.6 mmol H^+/g for all the polymer catalysts.

1, 3, 5-tri-(4-phenoxybenzoyl)benzene: ^1H NMR (300 MHz, $CDCl_3$): δ = 8.33 (s, 3H), 7.84 (dd, *J* = 6.9, 2.0 Hz, 6H), 7.42 (t, *J* = 7.6 Hz, 6H), 7.22 (t, *J* = 7.4 Hz, 3H), 7.11 (dd, *J* = 8.7, 1.1 Hz, 6H), 7.04 (dd, *J* = 6.9, 2.0 Hz, 6H).

*Hyperbranched Polymer **HPAO***: ^1H NMR (300 MHz, DMSO): δ = 10.84 (s, 1H), 8.01 (s, 1H), 8.18 (br, 3H), 7.87 (br, 6H), 7.70 (br, 1H), 7.44 (br, 4H), 7.09–7.26 (m, 17H). $\overline{M}_n = 10.2\times 10^3$, $\overline{M}_w / \overline{M}_n = 1.78$.

*Hyperbranched Polymer **5-MeO-HPAO***: ^{1}H NMR (300 MHz, DMSO): δ = 10.66 (br, 1H), 8.18 (br, 3H), 7.87 (br, 6H), 7.70 (br, 1H), 7.09–7.47 (m, 18H), 6.88 (br, 3H), 3.65 (s, 3H). $\overline{M}_n = 6.4 \times 10^3$, $\overline{M}_w / \overline{M}_n = 1.73$.

*Hyperbranched Polymer **5-Cl-HPAO***: ^{1}H NMR (300 MHz, DMSO): δ = 11.00 (br, 1H), 8.19 (br, 3H), 7.85 (br, 6H), 7.69 (br, 1H), 7.09–7.40 (m, 21H). $\overline{M}_n = 11.2 \times 10^3$, $\overline{M}_w / \overline{M}_n = 1.76$.

*Sulfonated Hyperbranched Polymer **SHPAO***: ^{1}H NMR (300 MHz, DMSO): δ = 10.96 (s, 1H), 8.20 (br, 3H), 7.89 (br, 6H), 7.70 (d, J = 8.3 Hz, 3H), 7.41–7.59 (m, 2H), 6.98–7.24 (m, 12H).

*Sulfonated Hyperbranched Polymer **5-MeO-SHPAO***: ^{1}H NMR (300 MHz, D_2O): δ 8.23–8.34 (m, 6H), 7.84–7.92 (m, 3H), 7.76 (br, 2H), 7.36–7.48 (m, 2H), 6.92–7.09 (m, 6H), 3.76 (s, 3H).

*Sulfonated Hyperbranched Polymer **5-Cl-SHPAO***: ^{1}H NMR (300 MHz, D_2O): δ 8.23–8.33 (m, 6H), 7.39–7.91 (m, 10H), 6.92–7.09 (m, 5H).

Table S1. The average molecular weight and acid density of the polymer catalysts.

Catalyst	$\overline{M}_n$ [a]	Polydispersity Index [a]	Acid density (mmol H^+/g) [b]
Amberlyst 15	–	–	2.27
5-MeO-SHPAO	6.4×10^3	1.73	3.62
5-Cl-SHPAO	11.2×10^3	1.76	3.63
SHPAO	10.2×10^3	1.78	3.66

[a] The average molecular weight and polydispersity index of hyperbranched polymers were measured before sulfonation treatment.
[b] The acid density of polymer catalyst was determined by acid-base titration.

Estimation of the apparent activation energy of ethyl levulinate production from cellulose in presence of 5-Cl-SHPAO

The activation energy of cellulose ethanolysis to ethyl levulinate on polymer catalyst 5-Cl-SHPAO. Halftime for reaction completion at different temperatures was recorded for plotting, as shown in Figure S1.

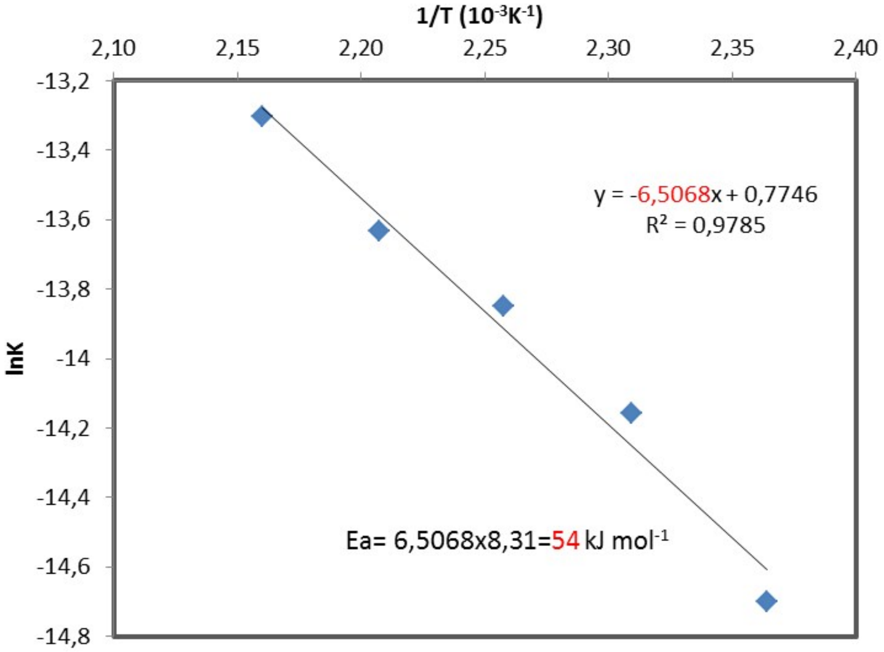


Figure S1. Arrhenius plot of ethanolysis of cellulose to ethyl levulinate on 5-Cl-SHPAO

Table 2S. Properties of selected pure cellulose powders

Type cellulose	**Pretreatment**	**Properties**		
		Particle size (μm)	**Crystallinity (CrI%)**	**DP (# units)**
Avicel PH-101	Ball-milling	57	<5	116
Avicel PH-101	None	68	79	161
Sigmacell Type 20	None	29	76	168

Reusability of 5-Cl-SHPAO catalyst

Initial 5-Cl-SHPAO catalyst (20 mg), cellulose (80 mg) and ethanol (2 mL) were used in the catalytic reaction. The reaction was carried out at 160 °C for 8 h. In each reaction, 80 mg fresh cellulose was reloaded for catalytic evaluation of the recycled catalyst. In all 5 runs under the same reaction condition, cellulose was always fully converted. The yield of EL from 1st run to 5th run is as follows: 58%, 57%, 55%, 51%, 47%. The significant drop of EL yield in the 5th run, compared with that from previous runs, is mainly due to the incomplete consumption of intermediates, such as ethyl glucoside, HMF and EMF. Small amounts of these intermediates compounds could be still detected after the 5th run of catalytic reaction.

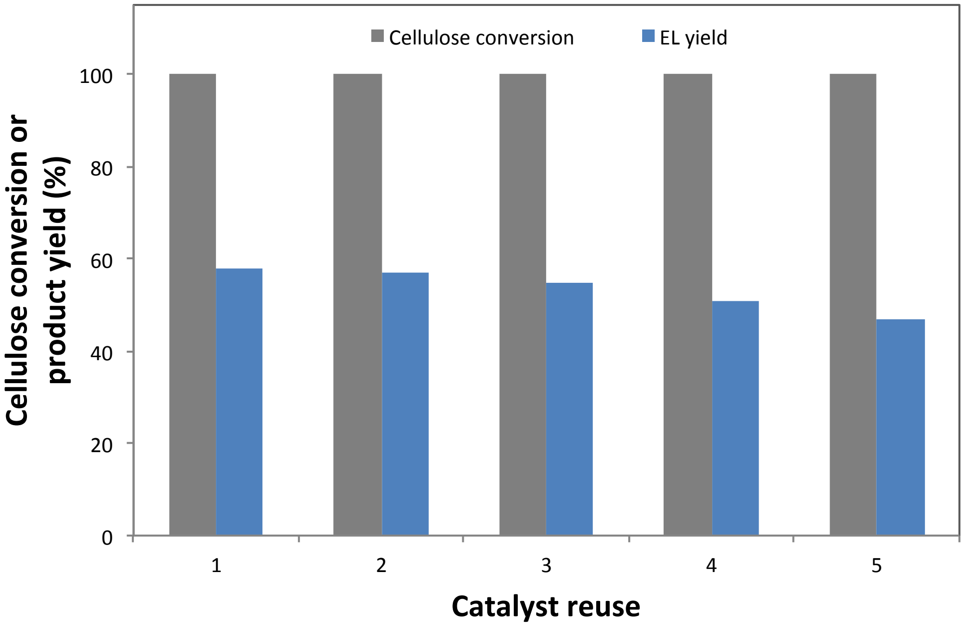


Figure S2. Reusability of 5-Cl-SHPAO in the catalytic ethanolysis of cellulose to EL.

FT-IR spectra of hyperbranched polymers

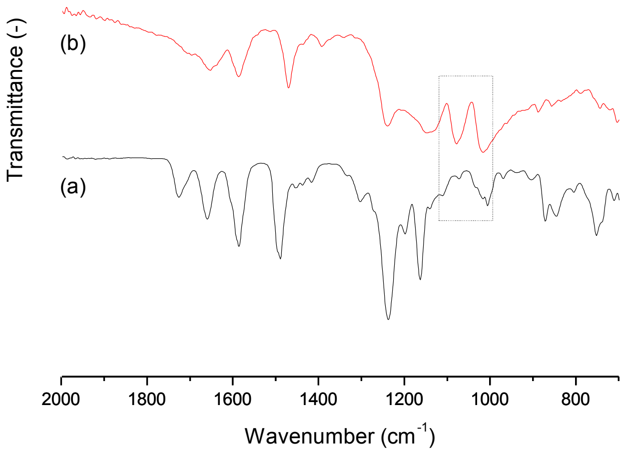


Figure S3. Comparison of FT-IR spectra of 5-MeO-HPAO before (a) and after sulfonation (b)

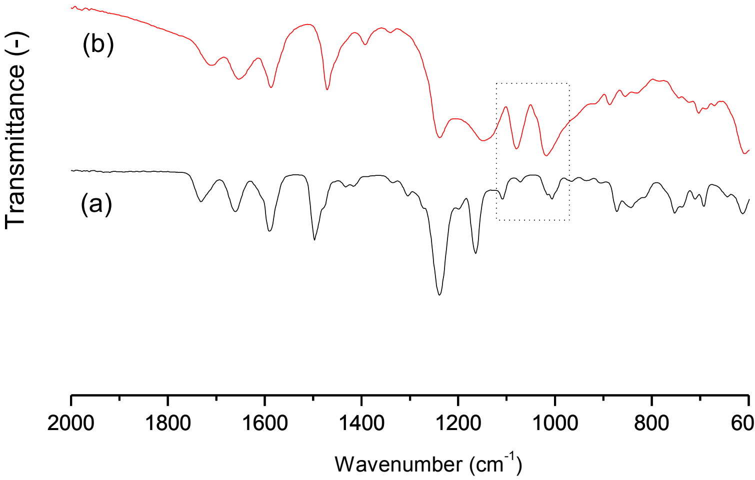


Figure S4. Comparison of FT-IR spectra of 5-Cl-HPAO before (a) and after sulfonation (b)

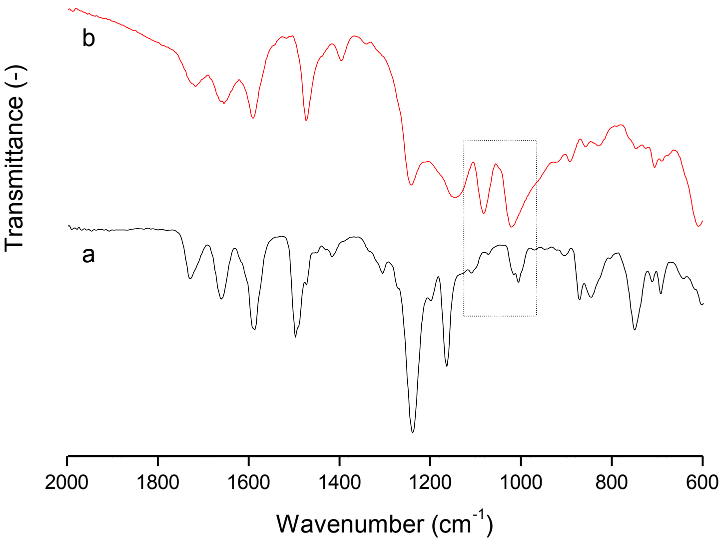


Figure S5. Comparison of FT-IR spectra of HPAO before (a) and after sulfonation (b)

Gas chromatography (GC)

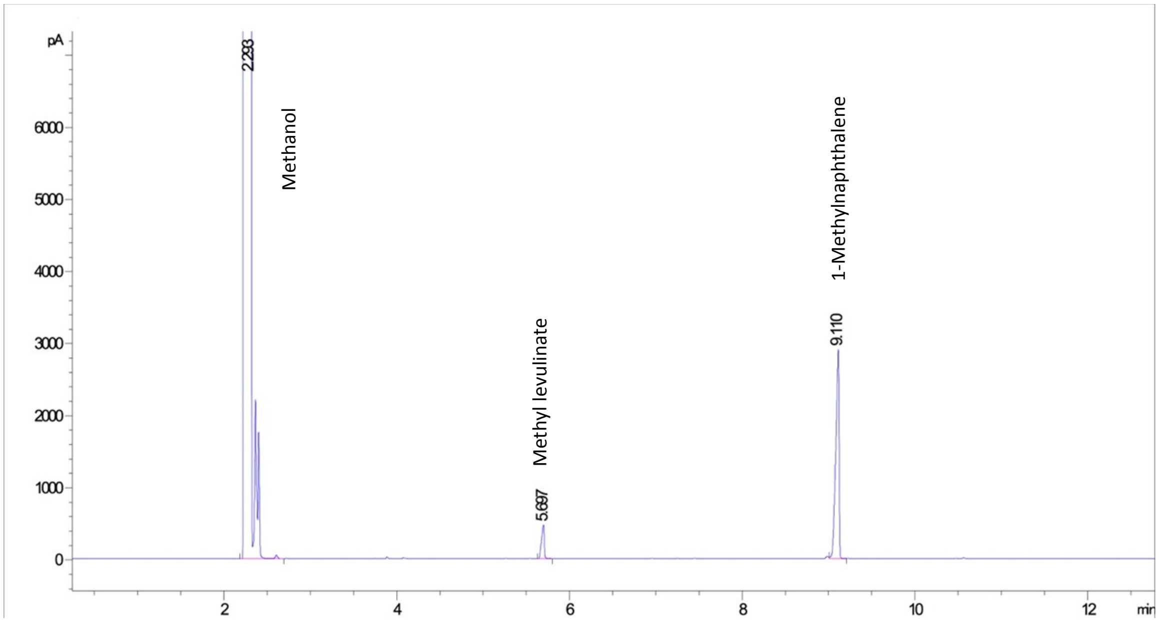


Figure S6. Typical GC chromatogram of the reaction mixture obtained from the catalytic conversion of cellulose by 5-Cl-SHPAO in methanol.

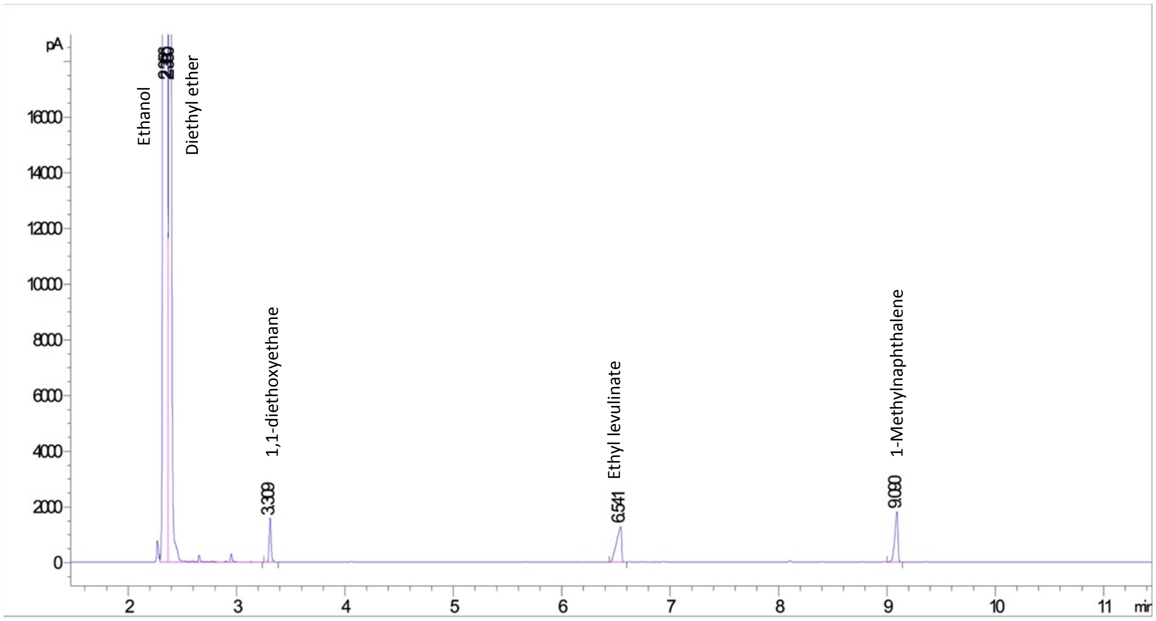


Figure S7. Typical GC chromatogram of the reaction mixture obtained from the catalytic conversion of cellulose by 5-Cl-SHPAO in ethanol.

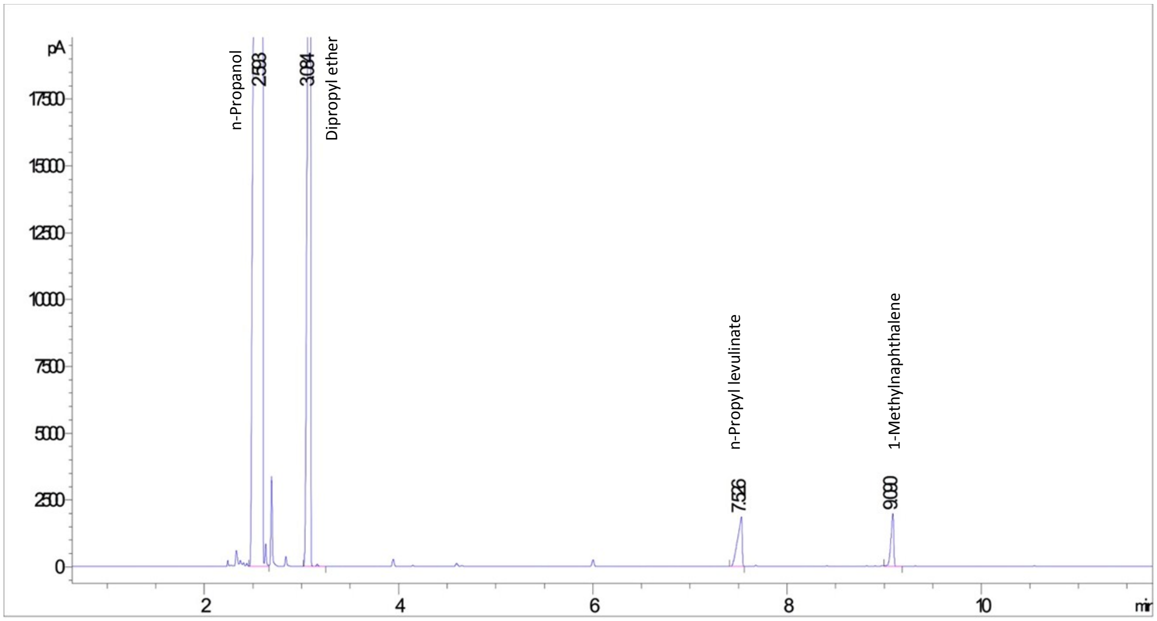


Figure S8. Typical GC chromatogram of the reaction mixture obtained from the catalytic conversion of cellulose by 5-Cl-SHPAO in n-propanol.

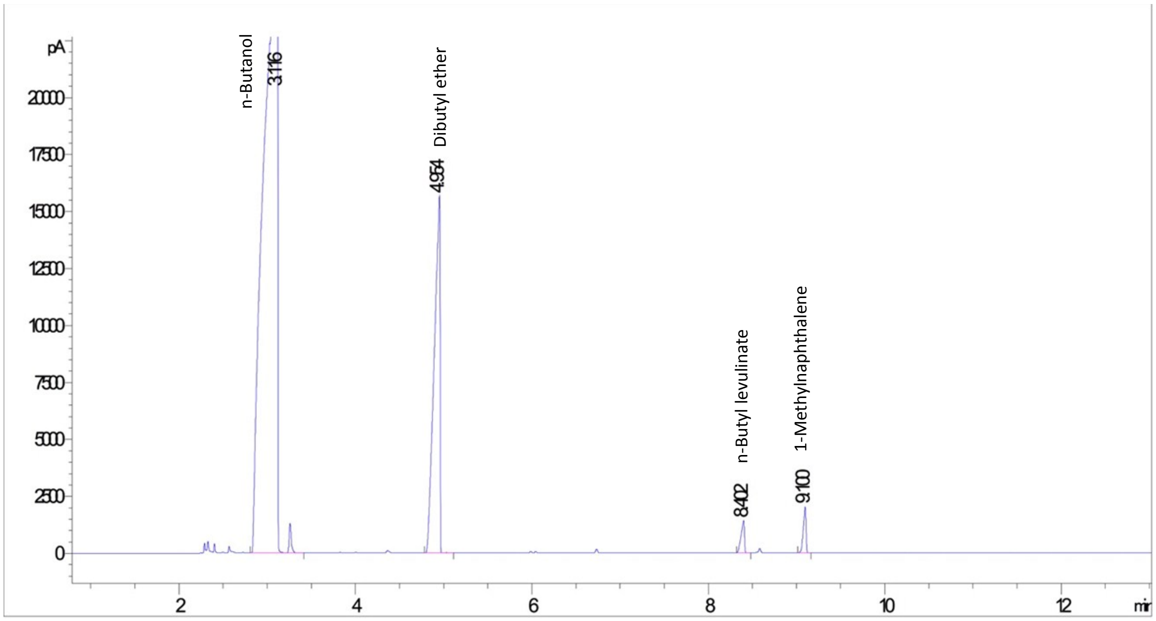


Figure S9. Typical GC chromatogram of the reaction mixture obtained from the catalytic conversion of cellulose by 5-Cl-SHPAO in n-butanol.

High performance liquid chromatography (HPLC)

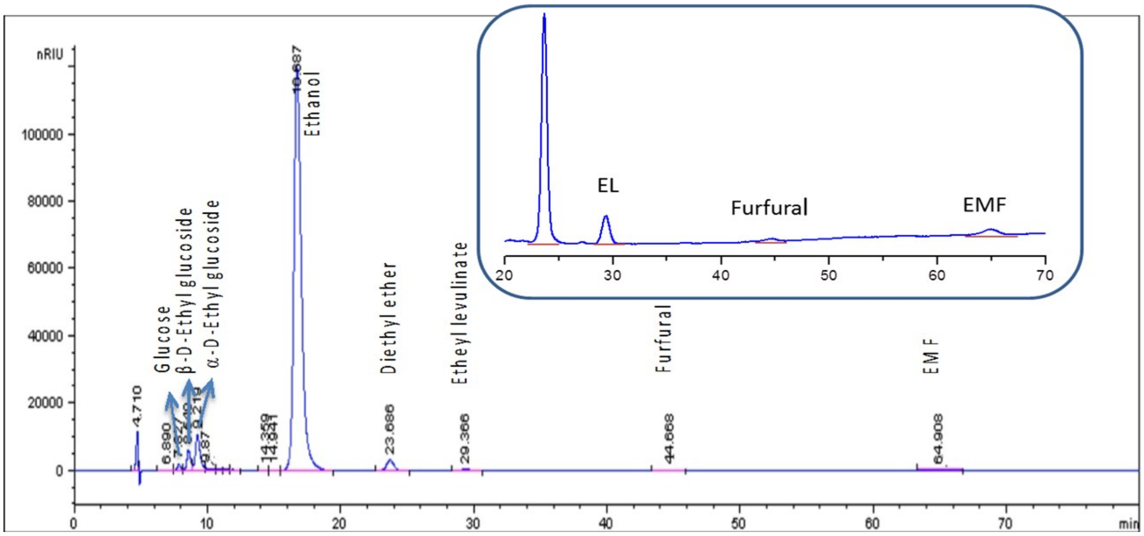
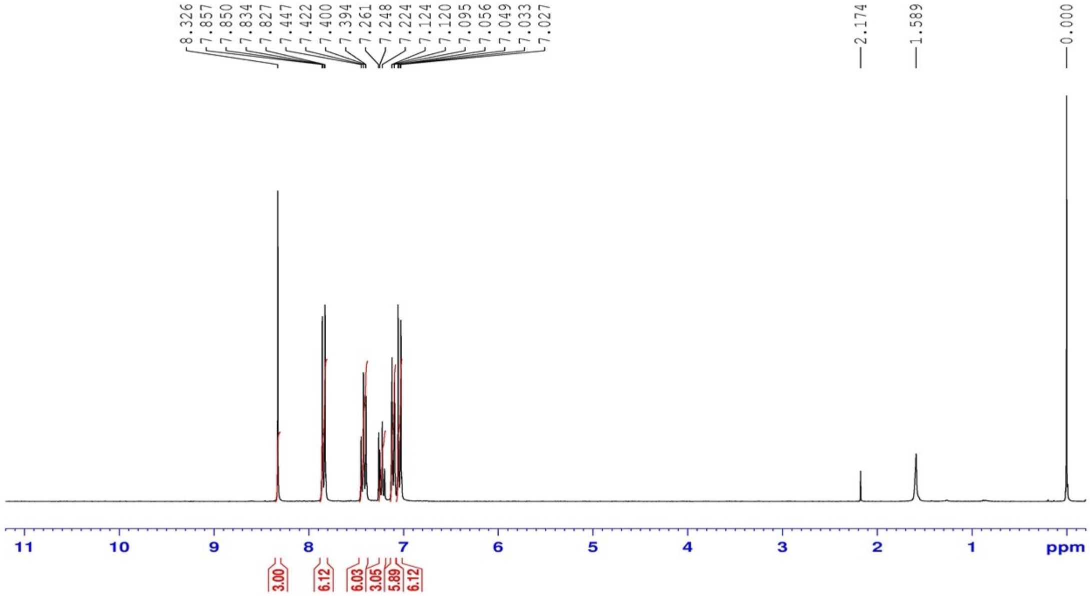


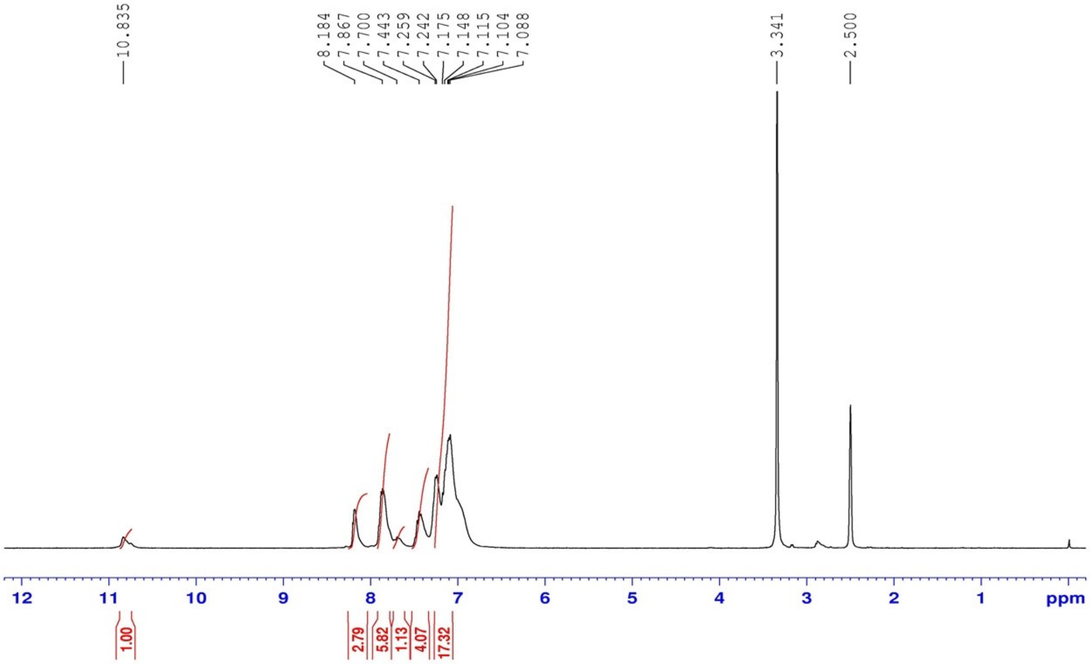
Figure S10. Typical HPLC chromatogram of the reaction mixture obtained from the catalytic conversion of cellulose by 5-Cl-SHPAO.

^1H NMR Spectra of hyperbranched polymer catalysts

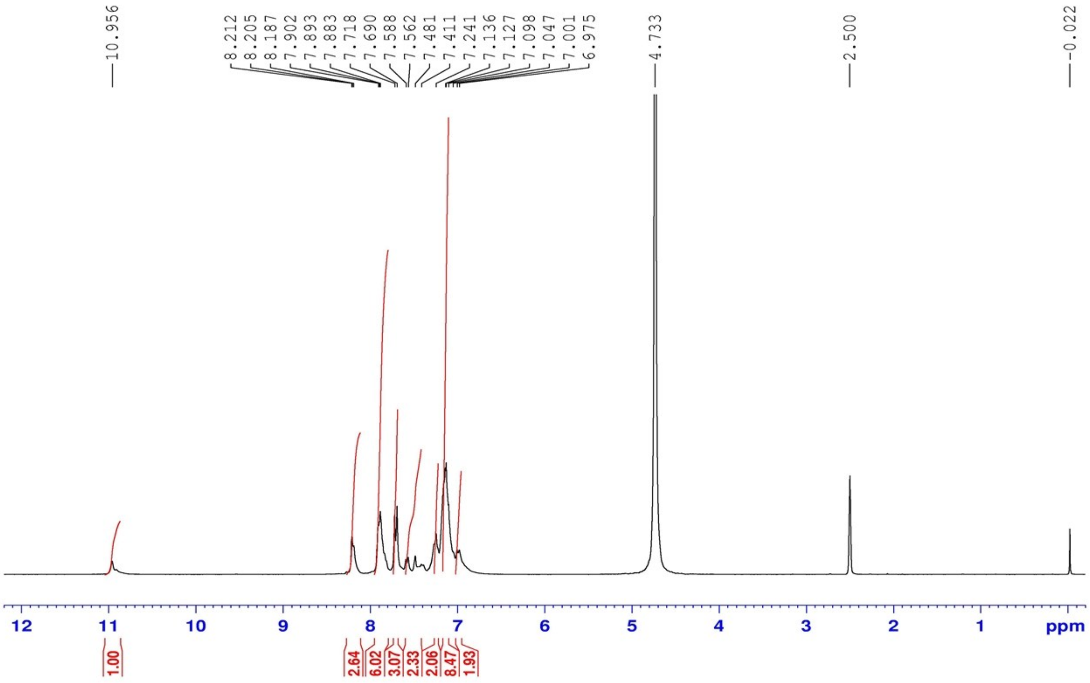
B_3 monomer



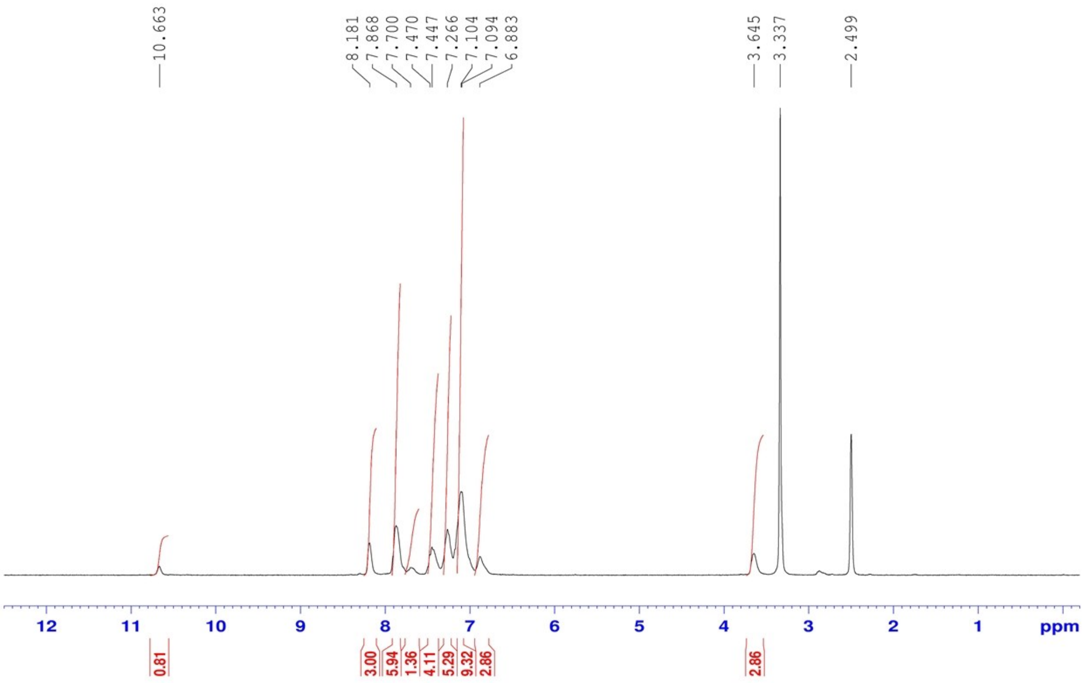
HPAO



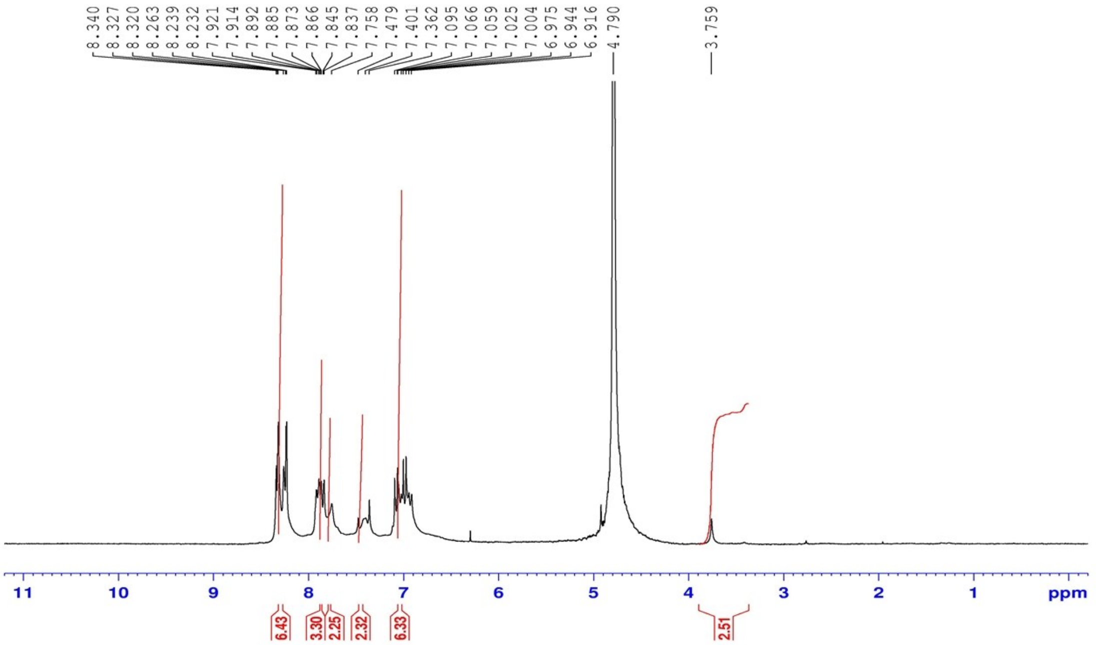
SHPAO



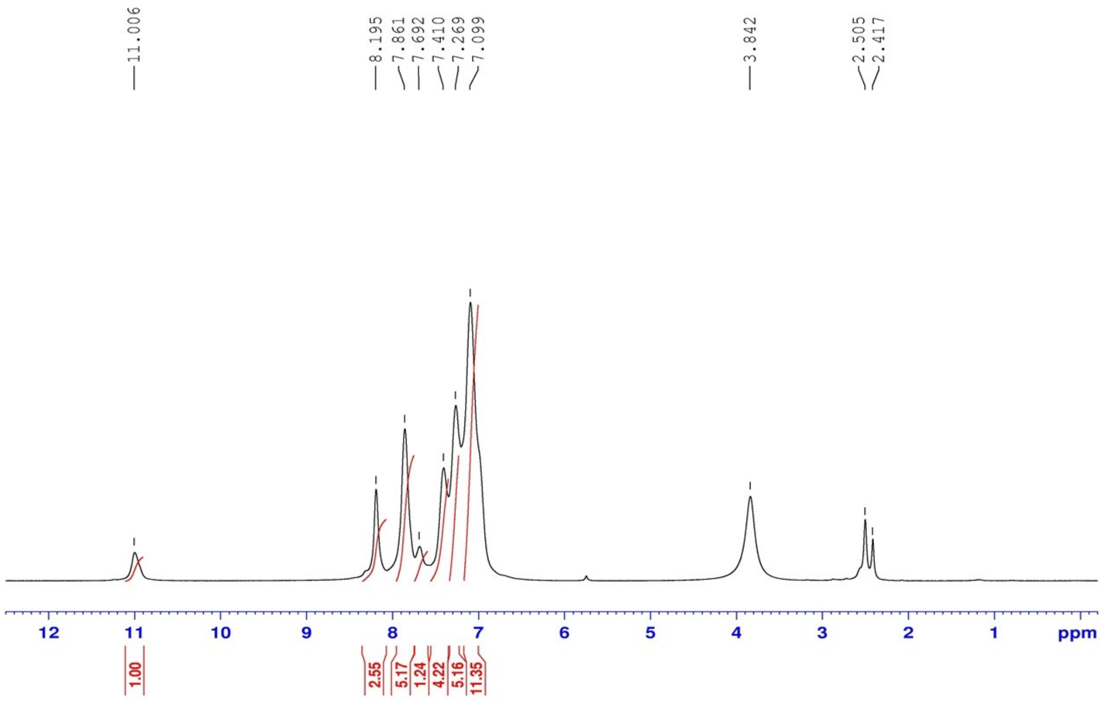
5-MeO-HPAO



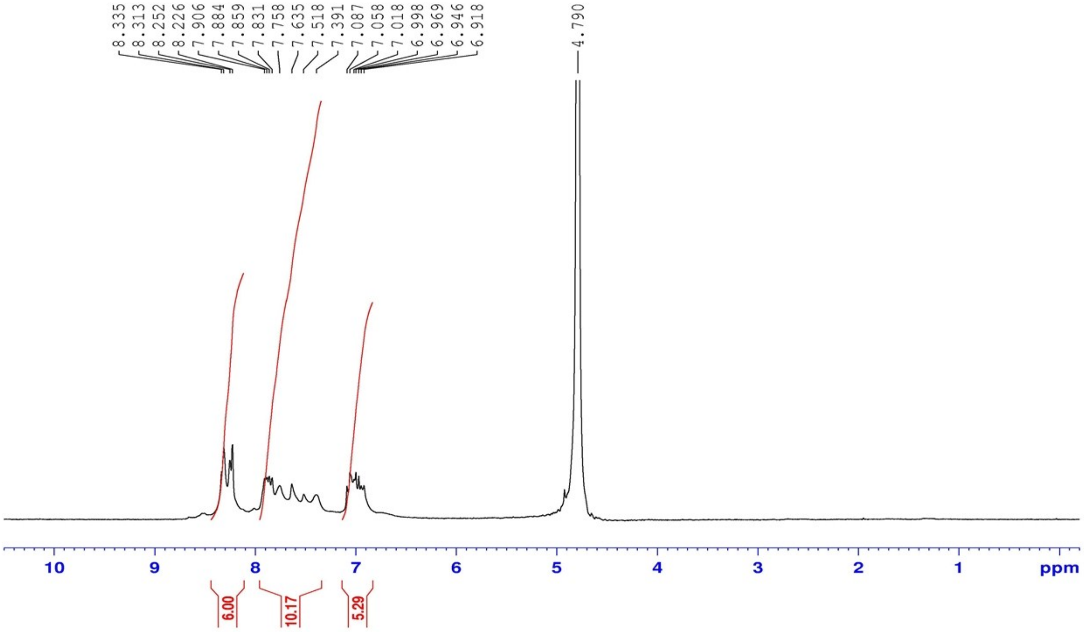
5-MeO-SHPAO



5-Cl-HPAO



5-Cl-SHPAO



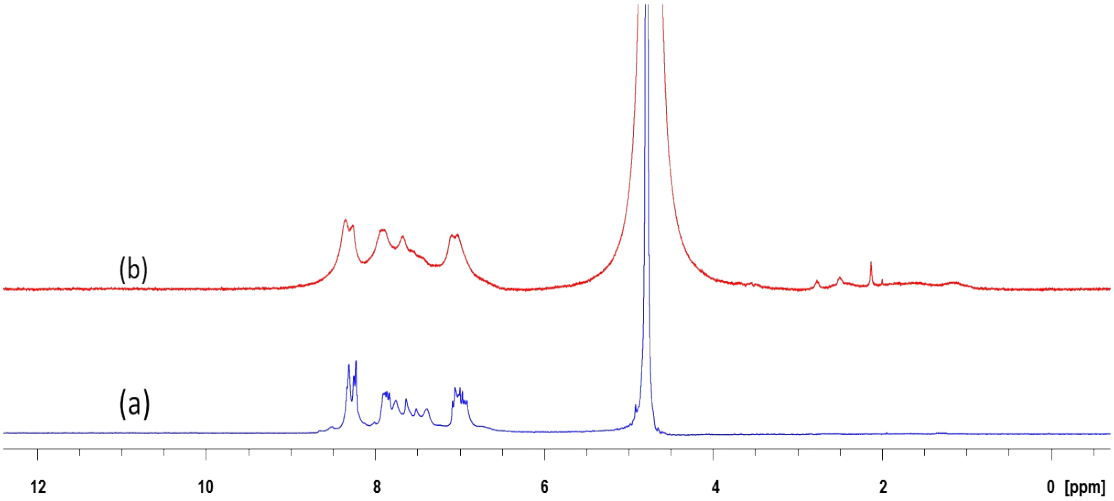
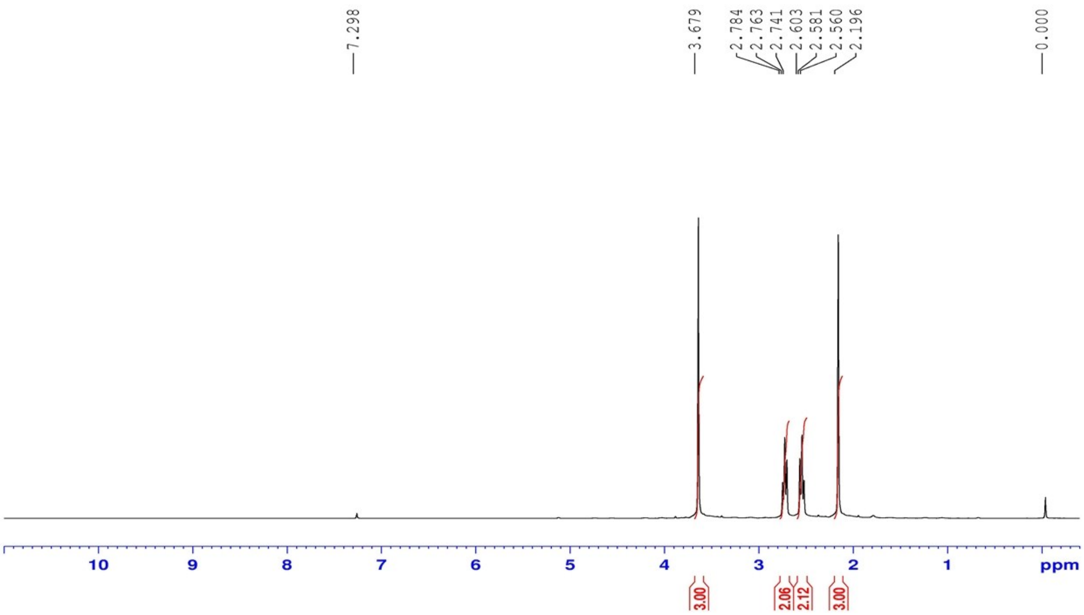


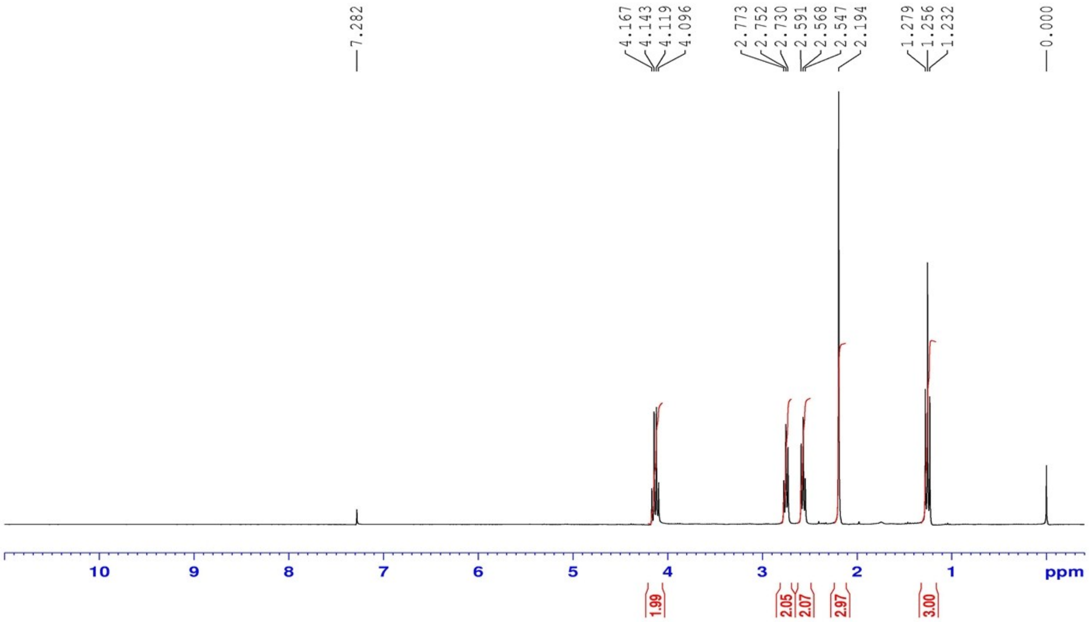
Figure 11S. The comparison of ^{1}H NMR spectrum from fresh 5-Cl-SHPAO (a) and recycled 5-Cl-SHPAO (b).

^{1}H NMR Spectra of alkyl levulinate products

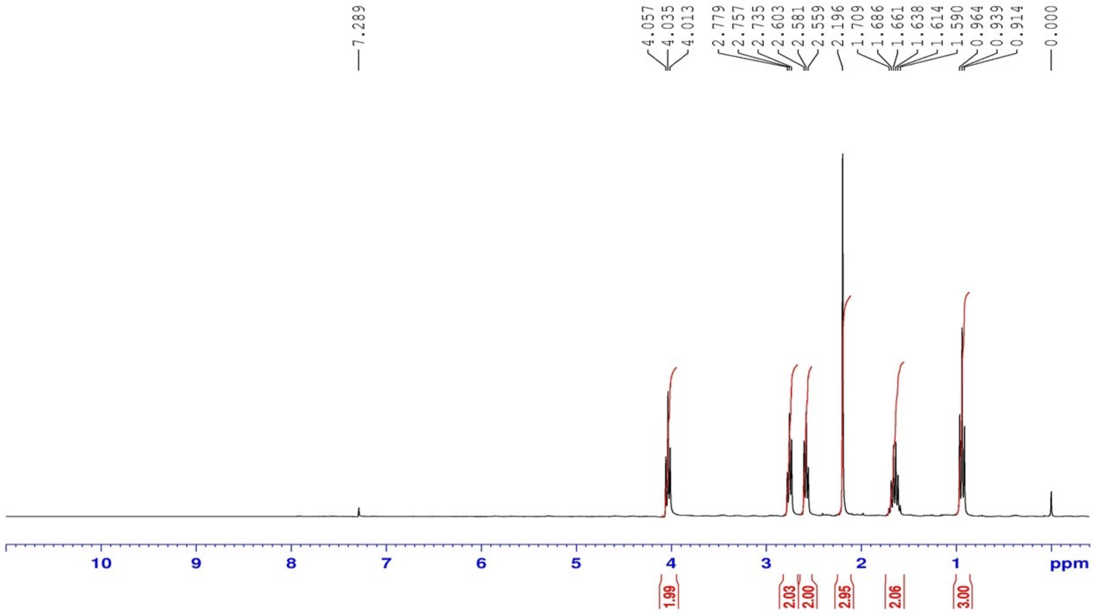
Methyl levulinate: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68 (s, 3H), 2.76 (t, *J* = 6.4 Hz, 2H), 2.58 (t, *J* = 6.6 Hz, 2H), 2.20 (s, 3H).



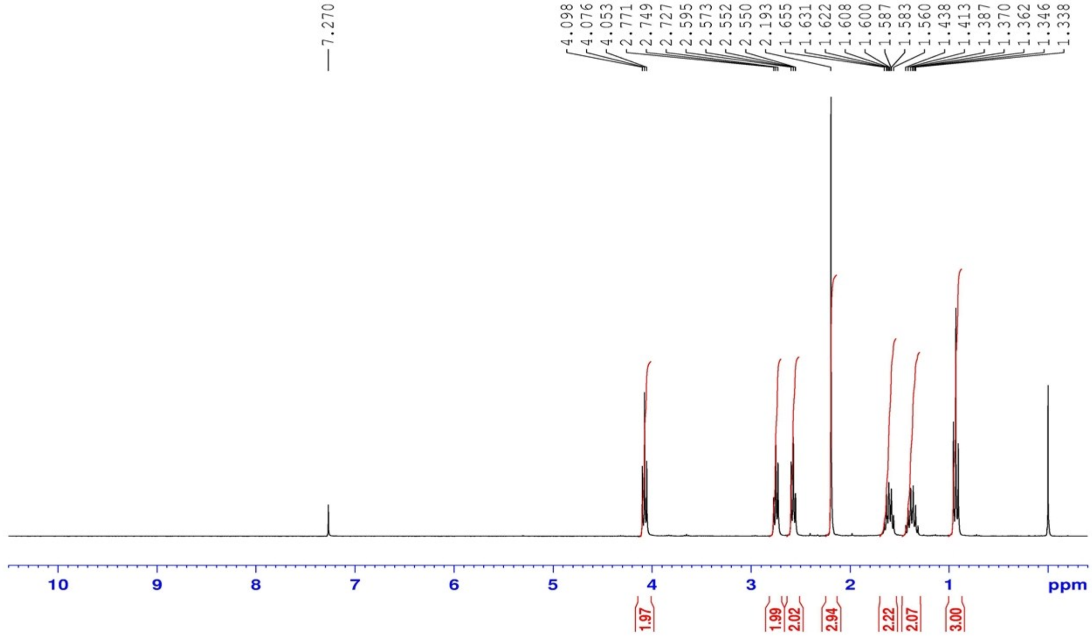
Ethyl levulinate: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.13 (q, *J* = 7.2 Hz, 2H), 2.75 (t, *J* = 6.3 Hz, 2H), 2.57 (t, *J* = 6.3 Hz, 2H), 2.19 (s, 3H), 1.26 (t, *J* = 6.9 Hz, 3H).



***n*-Propyl levulinate**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.04 (t, *J* = 6.6 Hz, 2H), 2.76 (t, *J* = 6.6 Hz, 2H), 2.58 (t, *J* = 6.6 Hz, 2H), 2.20 (s, 3H), 1.65 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H).



***n*-Butyl levulinate**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.08 (t, *J* = 6.6 Hz, 2H), 2.75 (t, *J* = 6.4 Hz, 2H), 2.57 (t, *J* = 6.6 Hz, 2H), 2.19 (s, 3H), 1.60 (m, 2H), 1.37 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).



References

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