# *Supporting Information*

## Water-soluble sulfonated hyperbranched poly(arylene oxindole) catalysts as functional biomimics of cellulases

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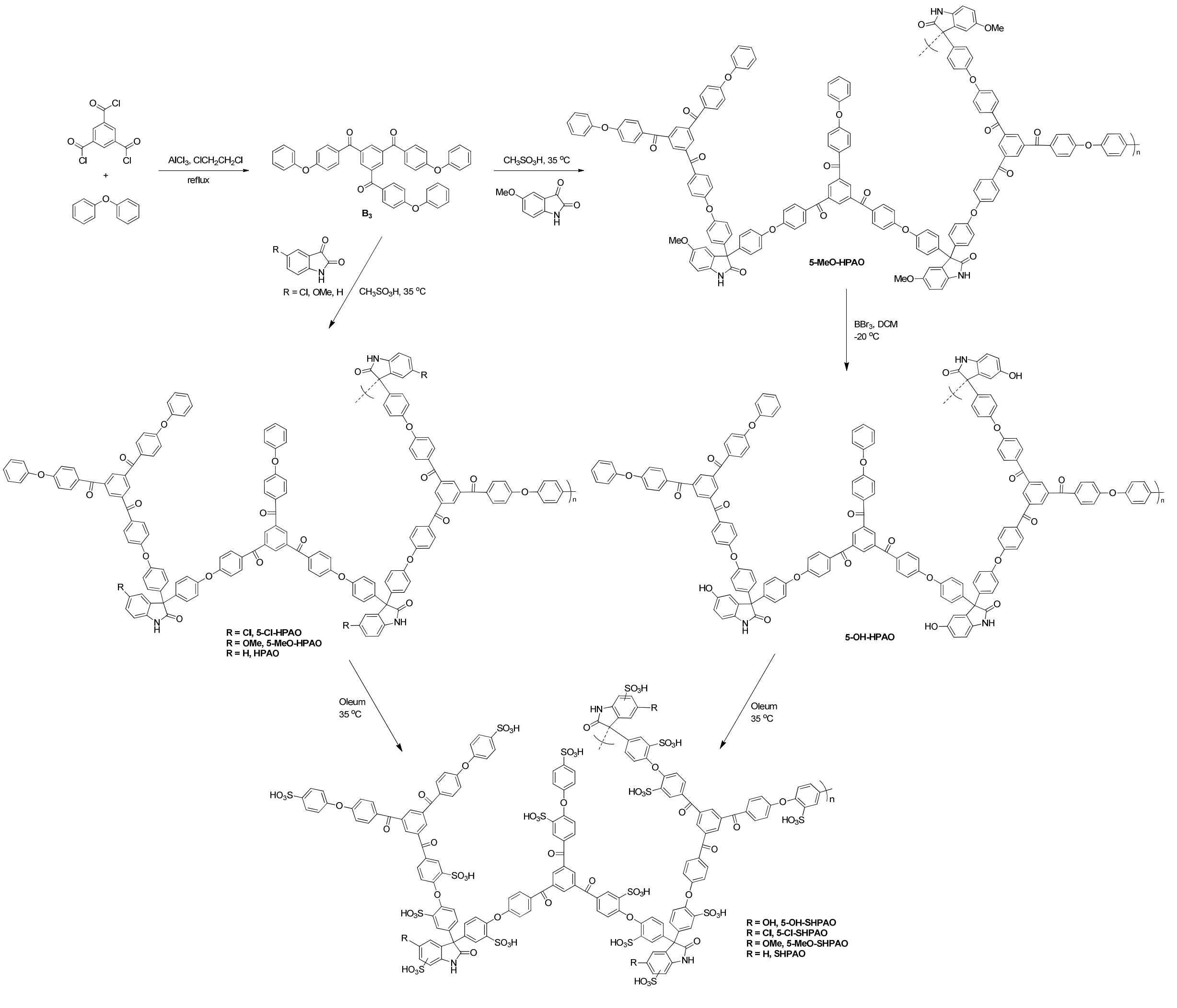
## General information

*Chemicals:* Benzene 1,3,5-tricarbonyl trichloride, diphenyl ether, isatin, 5-chloroisatin, 5-methoxyisatin, boron tribromide, oleum (20%), aluminium (III) trichloride, 1,2-dichloroethane, dichloromethane (SuperDry 99.9%), methanesulfonic acid, cellulose (Avicel® PH-101, Sigmacell 20), glucose, fructose, levoglucosan, furfural, hydroxymethylfurfural, levulinic acid, formic acid, sulfuric acid and Amberlyst 15 were purchased from Sigma-Aldrich, Acros Organics or Alfa Aesar. All chemicals were used without further purification as received. Ball-milling cellulose was used as the substrate in the acid-catalyzed hydrolysis reactions. 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.

*Methods of 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 hyperbranched polymer catalyst



**Scheme S1** Synthesis of sulfonated hyperbranched poly(arylene oxindole)s

Hyperbranched polymer acid catalyst 5-OH-SHPAO was synthesized on the basis of hyperbranched polymer 5-MeO-HPAO, followed by demethylation at low temperature (–20 $^{o}$C) with the use of BBr$_3$ and the subsequent sulfonation in fuming sulfuric acid. The synthetic route of 5-OH-SHPAO catalyst is shown in Scheme S1. The intermediate polymer 5-MeO-HPAO, as well as other hyperbranched polymers, including 5-Cl-HPAO and HPAO, was prepared according to our reported facile one-step A$_2$ + B$_3$ polycondensation strategy through superelectrophilic arylation of corresponding substituted isatin with readily synthesized B$_3$ monomer.[1,2] All these polymers were directly functionalized with sulfonic acid groups by fuming sulfuric acid treatment.

## Synthesis of 5-OH-SHPAO

The synthesis of monomer 1, 3, 5-tri-(4-phenoxybenzoyl)benzene was according to our previous publications.[1,2]

*Monomer 1, 3, 5-tri-(4-phenoxybenzoyl)benzene*: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 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 **5-MeO-HPAO***: $^1$H NMR (300 MHz, DMSO): $\delta$ = 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). $\overline{M}_n = 6.4 \times 10^3$, $\overline{M}_w / \overline{M}_n = 1.73$.

*The synthesis of Hyperbranched Polymer **5-OH-HPAO***: 1.20 g of hyperbranched polymer 5-MeO-HPAO and 60 mL of dichloromethane were added to a 100 mL of two-necked flask. The flask was purged with nitrogen and quickly sealed by a rubber stopper. Then the mixture was rapidly stirred at room temperature. After the polymer was completely dissolved in dichloromethane, 3.28 g of boron tribromide was added to the mixture over a period of 10 minutes during which time the temperature of the reaction mixture was kept around –20 $^{o}$C. Upon completion of the boron tribromide addition, the reaction mixture was then stirred overnight at temperature of –5 $^{o}$C. The reaction was quenched by pouring the mixture into 50 mL of cool water. The aqueous phase was then extracted with dichloromethane (3 × 60 mL). The combined organic layers were then washed with saturated brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to provide crude product. After purification through precipitation in methanol and drying in vacuo, 1.02 g of the desired product (*ca.* 86% yield) was obtained. $^1$H NMR (300 MHz, DMSO): $\delta$ = 10.53 (br, 1H), 9.14 (br, 1H), 8.18 (br, 3H), 7.87 (br, 6H), 7.10–7.45 (m, 18H), 6.78 (br, 1H), 6.69 (br, 2H); $^{13}$C NMR (75 MHz, DMSO): $\delta$ = 192.9, 177.8, 161.5, 161.2, 154.7, 153.9, 138.4, 137.7, 133.9, 133.2, 133.0, 132.6, 130.8, 130.6, 130.4,130.0, 124.9, 120.1, 120.0, 117.3, 117.1, 61.6. $\overline{M}_n = 6.4 \times 10^3$, $\overline{M}_w / \overline{M}_n = 1.72$.

*The synthesis of Sulfonated Hyperbranched Polymer **5-OH-SHPAO***: To a round-bottomed flask, polymer 5-MeO-HPAO (1.0 g) and 20% oleum (15 mL) were added and stirred at 35 $^{o}$C for 2 days under $N_2$. Afterwards, the solution was slowly added into ice and stirred vigorously. After dialysis against water for 7 days (Spectra / Por CE dialysis membrane; molecular weight cutoff: 3500 Da) and removal of water under reduced pressure, the brownish sulfonated product (0.91 g) was obtained. $^1$H NMR (300 MHz, DMSO): δ = 8.12–8.44 (m, 9H), 7.44–7.83 (m, 7H), 7.22 (br, 2H), 6.92 (br, 5H), 6.68 (br, 1H); $^{13}$C NMR (300 MHz, DMSO): δ = 193.1, 176.7, 159.3, 156.7, 154.2, 153.2, 152.7, 149.5, 143.3, 138.2, 137.9, 137.8, 137.4, 137.1, 136.1, 133.6, 133.3, 131.6, 129.0, 127.9, 126.4, 121.7, 121.3, 120.9, 61.5. Acid density = 3.54 mmol $H^+$/g.

## Synthesis of other polymer catalysts

*General procedure for the preparation of hyperbranched polymers:* To a round-bottomed flask both the $A_2$ monomer substituted isatin (2.26 mmol) and the $B_3$ monomer 1,3,5-tris-(4-phenoxybenzoyl)benzene (1.50 g, 2.26 mmol) were added as solids in an equimolar amount, and the appropriate amount of methanesulfonic acid (23 mL) was added. The resulting solution was stirred at 35 °C for 2 days under $N_2$. Afterwards, the solution was dropped slowly into ice water. The precipitate was collected by filtration and washed with abundant water and methanol. The solid was dissolved in dichloromethane and then it precipitated into methanol. After filtration and washing with methanol, the desired product was obtained.

The synthetic route is also provided in Scheme S1. The procedure for acidic functionalization of these synthesized hyperbranched polymers, including HPAO, 5-Cl-HPAO and 5-MeO-HPAO, is as same as that for 5-OH-HPAO.

*Hyperbranched Polymer **HPAO***: $^1$H 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). $\overline{M}_n = 10.2\times 10^3$, $\overline{M}_w / \overline{M}_n = 1.78$.

*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). Acid density = 3.66 mmol $H^+$/g.

*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 **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). Acid density = 3.63 mmol $H^+$/g.

*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). Acid density = 3.62 mmol $H^+$/g.

## Characterization of hyperbranched polymers

In the $^1$H NMR spectrum of polymer 5-MeO-HPAO, the absence of resonance signals from the starting 5-methoxyisatin as well as the occurrence of a $^{13}$C NMR signal at around 62 ppm, indicates complete integration of the $A_2$ units in the macromolecular structure during polymerization. The same changes in the $^1$H NMR spectra could also be observed in the cases of 5-Cl-SHPAO and SHPAO. The occurrence of a signal at 9.14 ppm from the OH group and the disappearance of the peak at 3.65 from –OMe in the $^1$H NMR spectrum of 5-OH-HPAO revealed that the demethylation reaction of 5-MeO-HPAO was complete. The average molecular weight $\overline{M}_n$ and polydispersity index of the resulting polymer were evaluated by GPC and found to be $6.4 \times 10^3$ and 1.72 respectively. In the $^1$H NMR spectrum of the resulting 5-OH-SHPAO polymer acid, the typical shift of the characteristic signals for the aromatic ether moieties evidences successful functionalization. Additionally, the sulfonation of the polymer upon oleum treatment is also evident from the FT-IR spectra. For instance, in the FT-IR spectrum of 5-OH-SHPAO, the appearance of two intense vibrational signals at around 1016 and 1077 cm$^{-1}$ are attributed to symmetric and asymmetric $SO_3$ stretching vibrations respectively. Additionally, the broad band appearing around 3340 cm$^{-1}$ corresponds to the OH stretch. Through elemental analysis of the sulfonated polymer, it is shown that there is an approximate 12 % sulfur content (by mass) in the polymer, revealing the presence of ca. 0.7 sulfonyl groups per aromatic group. Moreover, the acid density of the sulfonated polymer was measured by acid-base titration, and confirmed its acid density of 3.5 mmol $H^+g^{-1}$. The water content and thermal stability of 5-OH-SHPAO catalyst were evaluated by thermogravimetric analysis (TGA). The results revealed that about 19 % water content on the basis of mass was absorbed in this highly hydrophilic polymer acid, and this catalyst began to decompose when the temperature reached above 526K. The characterization of other hyperbranched polymers, such as 5-Cl-SHPAO, 5-MeO-SHPAO and SHPAO, was also conducted by the same analysis means. The average molecular weights $\overline{M}_n$ of these polymers are shown to be in the range of 6.4 × $10^3$ – 11.2 × $10^3$. The polydispersity index and acid density are measured to be around 1.8 and 3.6 mmol $H^+g^{-1}$ respectively, which show very close properties to 5-OH-SHPAO. More details can be found in Table S1.

## Sulfonic acid groups functionalization on isatin reactants

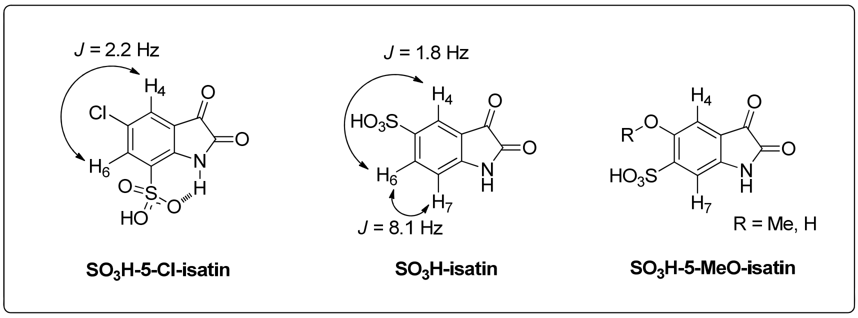


**Figure S1** J-coupling information on different sulfonated isatins.

The sulfonation of the three isatins occurs at different positions as observed by analyzing the $^1H$ NMR spectra of the sulfonated isatins through calculating J-coupling constants, and it is confirmed that the sulfonic acid group is introduced at the 5, 7, and 6 position in reactant isatin, 5-chloroisatin and 5-methoxy(hydroxyl)isatin respectively, as shown in Figure S1. In the $^1H$ NMR spectrum of $SO_3H$-5-Cl-isatin, the value of the coupling constant between two remaining hydrogens in isatin structure after sulfonation is 2.2 Hz, which is in the range of coupling constant values characteristic of meta coupling. This result implies that the sulfonic acid group substitution took place at position 7 of the isatin structure considering the fact that *meta* hydrogens could only be in position 4 and 6. In the case of $SO_3H$-isatin, both *ortho*- and *meta*- coupling occurred between hydrogens in the isatin structure with J-coupling constants of 8.1 and 1.8 Hz respectively, implying that the substitution position was at 5. For $SO_3H$-5-MeO(OH)-isatin, the absence of coupling between two hydrogens is indicative of the *para* position of the remaining hydrogens and the hydrogen at position 6 was substituted with a sulfonic acid group.

## Catalytic experiment

*Reaction procedure:* Catalytic experiments were performed in a stainless steel autoclave, equipped with a thermocouple and a magnetic stirrer. For typical runs, 80 mg of cellulose, 40 mg of polymer catalyst and 2 mL of water were loaded into a batch reactor under air and mixed by using a magnetic stirring bar. The autoclave was then heated at 165 °C for a specific time under continuous stirring. After the reaction, the reactor was removed from the heating and rapidly cooled down in an ice bath. The product mixture was sampled, the syringe filtered by a 0.45 μm PTFE membrane and submitted to analysis.

*Analysis of the catalytic reaction:* Reaction products such as glucose, fructose, HMF, furfural, levulinic acid, formic acid and levoglucosan were analyzed by high-pressure liquid chromatography (HPLC) in an Agilent 1200 Series system equipped with isocratic pump and refractive index (RI) detector on a Varian Metacarb 67H column (300 x 6.5 mm), using an aqueous solution of sulfuric acid (5 mM) at a flow rate of 0.65 mL min$^{-1}$ and a column temperature of 35 °C. Quantification of each compound was base on calibration curves obtained by analyzing standard solutions with known concentration.

*Recycling of hyperbranched polymer catalyst:* Upon completion of the reaction, the mixture was filtrated to separate the remaining cellulose from the filtrate. Then the filtrate was poured to the upper chamber of a Microsep 3K Omega centrifuge filtering tube, which is equipped with a semipermeable membrane (MW cutoff of 3000 Da). After 1 h centrifugation at 10000 rmp, the desired products were permeated into the lower reservoir while the polymer catalyst still remained in the upper chamber. The catalyst was fully recycled after an appropriate water washing and drying in vacuum.

**Table S1** The average molecular mass and acid density of polymer catalysts.

| **Catalyst** | $\overline{M}_n$ [a] | **Polydispersity Index** [a] | **Acid density (mmol H$^+$/g)** [b] |
|---|---|---|---|
| 5-OH-SHPAO | $6.4 \times 10^3$ | 1.72 | 3.54 |
| 5-MeO-SHPAO | $6.4 \times 10^3$ | 1.73 | 3.62 |
| 5-Cl-SHPAO | $11.2 \times 10^3$ | 1.76 | 3.63 |
| SHPAO | $10.2 \times 10^3$ | 1.78 | 3.66 |
| Amberlyst 15 | – | – | 2.27 |

[a] The average molecular mass (g/mol) and polydispersity index of hyperbranched polymers were measured before sulfonation treatment.

[b] The acid density of polymer catalyst was determined by acid-base titration.

## Temperature effect on the acid-catalyzed hydrolysis of cellulose to glucose

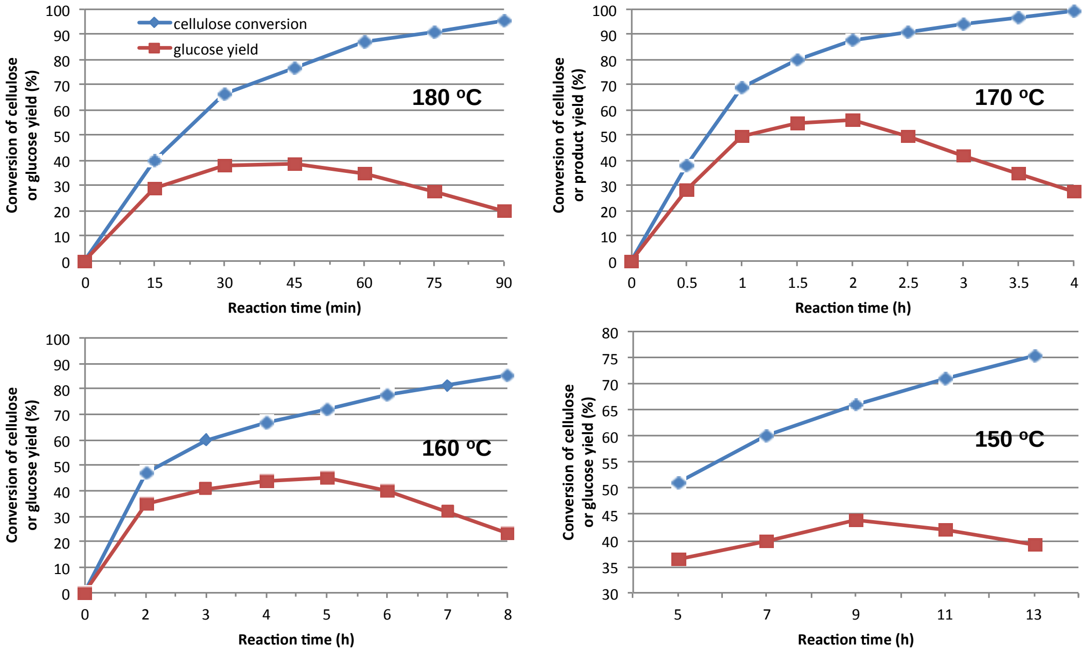
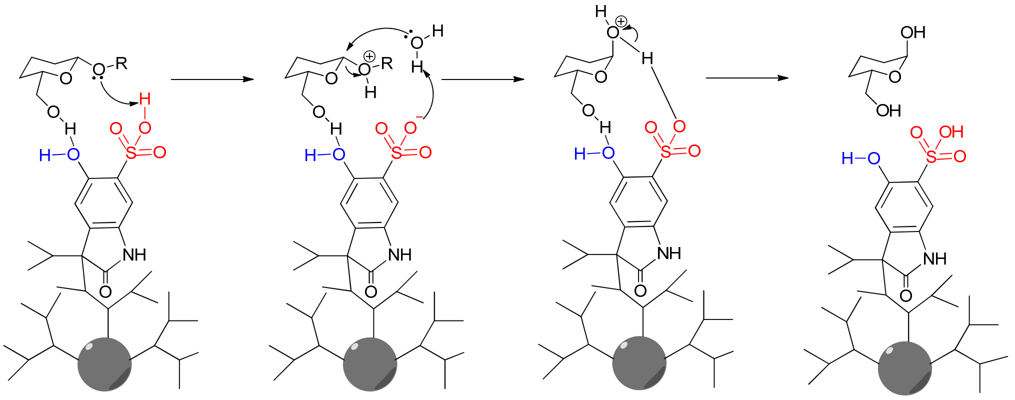


**Figure S2** Hydrolysis of cellulose into glucose at different temperature by using 5-OH-SHPAO catalyst.



**Scheme S2** Proposed stereo-inversion mechanism for acid-catalyzed hydrolysis of cellulose to glucose according to reference "J. Phys. Chem. C, 2015, 119, 20993".[3]

## TGA measurement of 5-OH-SHPAO

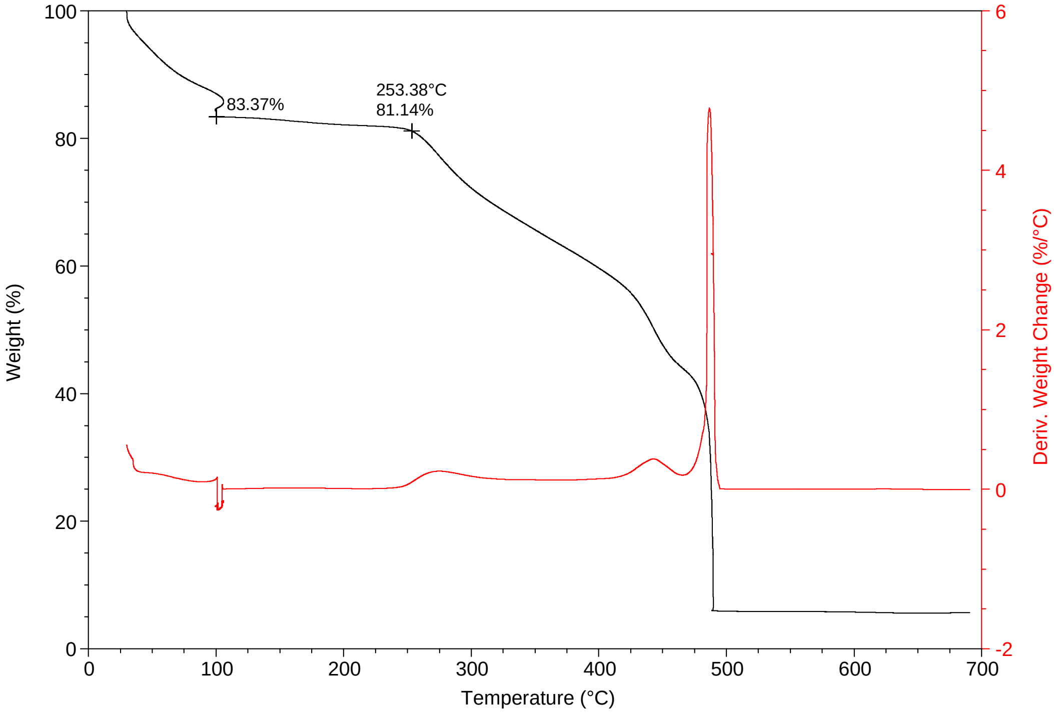


**Figure S3** TGA result of the sulfonated hyperbranched polymer 5-OH-SHPAO

## FT-IR spectra of hyperbranched polymers

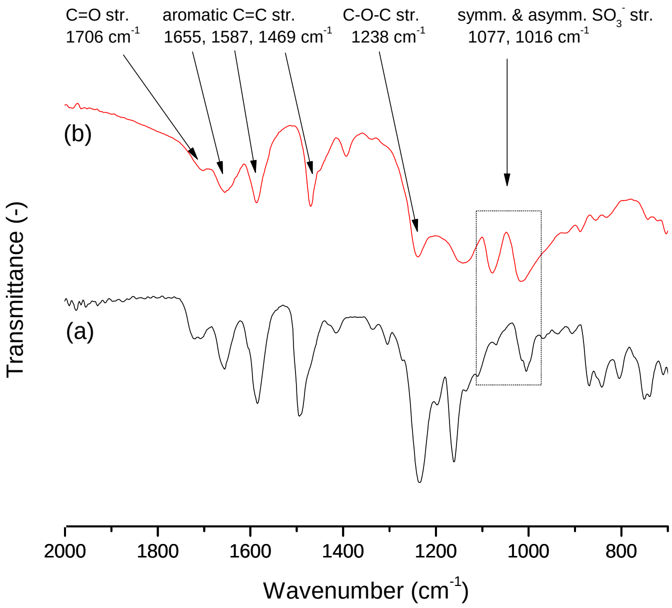


**Figure S4** Comparison of FT-IR spectra of 5-OH-HPAO before (a) and after sulfonation (b)

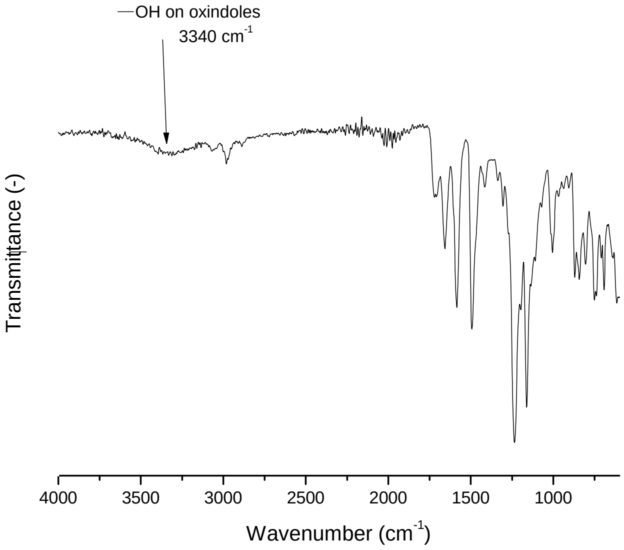


**Figure S5** FT-IR spectrum of 5-OH-HPAO

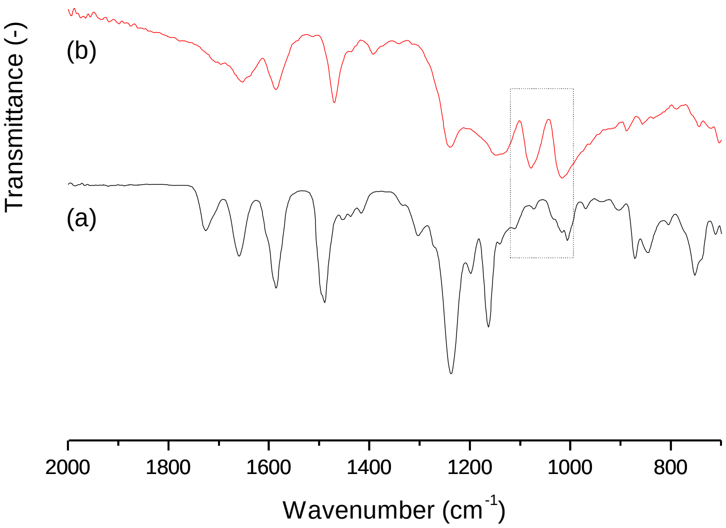


**Figure S6** Comparison of FT-IR spectra of 5-MeO-HPAO before (a) and after sulfonation (b)

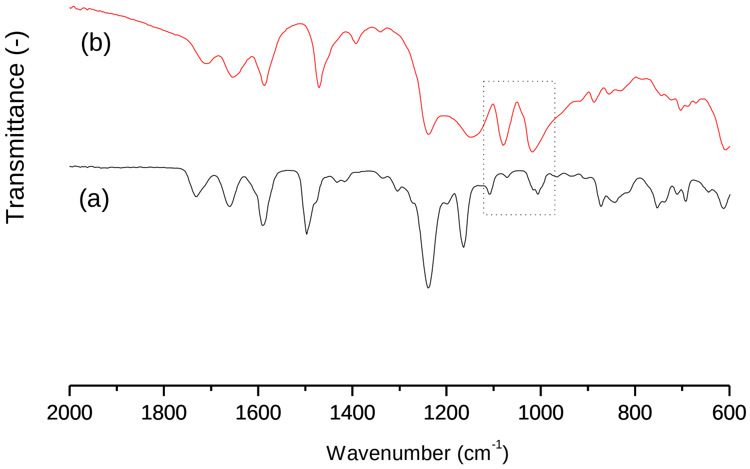


**Figure S7** Comparison of FT-IR spectra of 5-Cl-HPAO before (a) and after sulfonation (b)

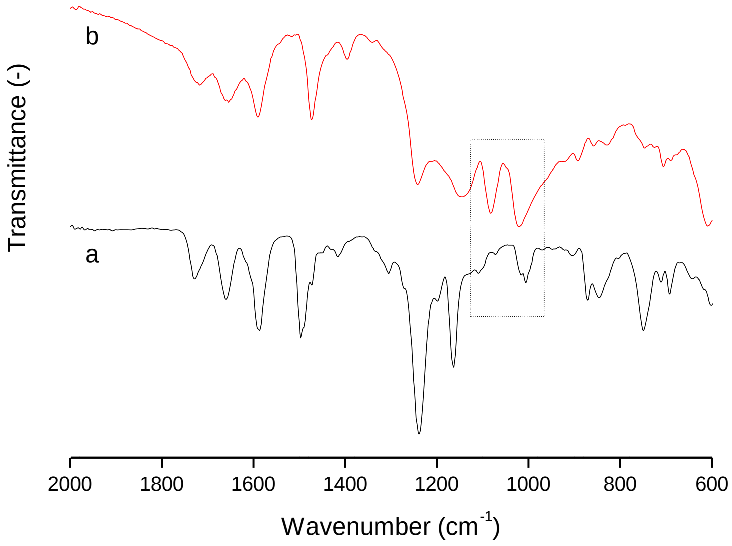


**Figure S8** Comparison of FT-IR spectra of HPAO before (a) and after sulfonation (b)

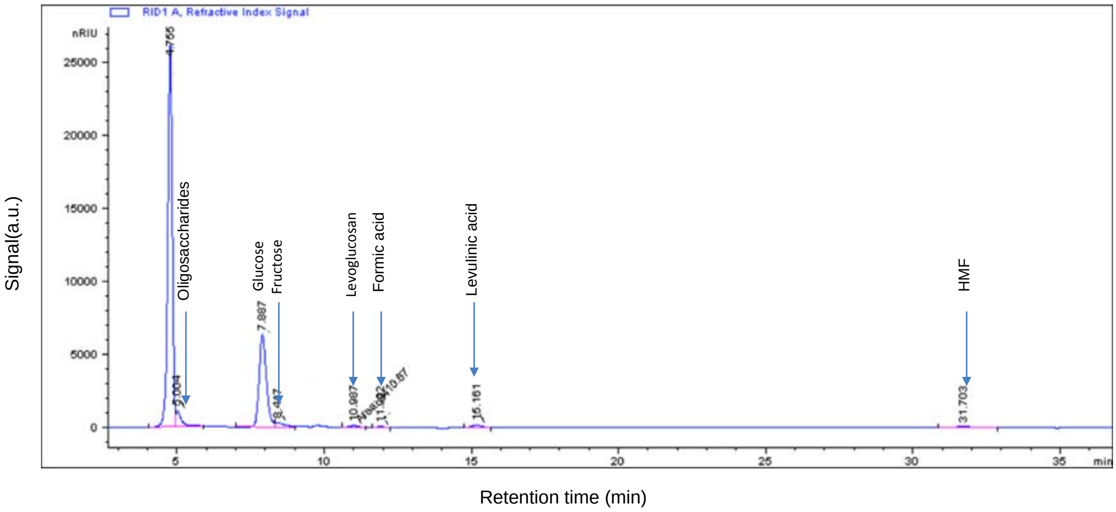


**Figure S9** Typical chromatogram of the reaction mixture obtained from the catalytic conversion of cellulose to glucose.

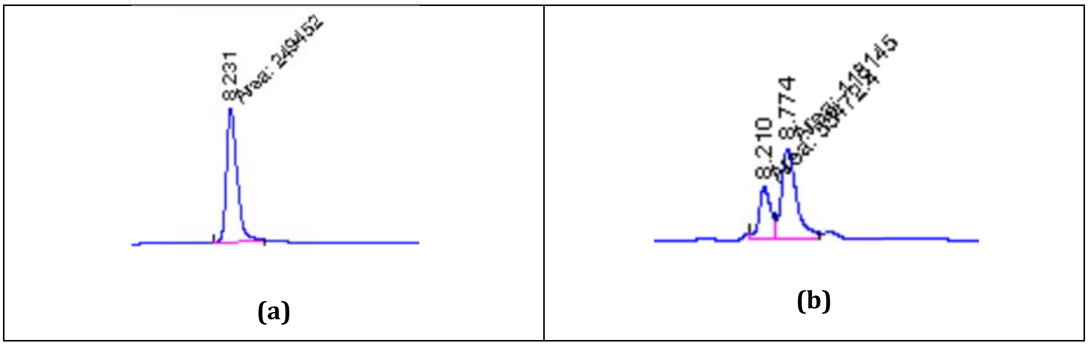
## The stereochemistry investigation

The catalytic methanolysis tests of cellobiose and maltose were carried out in methanol at 160 °C with 2.5 wt% substrate loading in the presence of 5-OH-SHPAO. The experimental results are shown in Table S2. After 0.5 h reaction, the yields of α-methylglucose and β-methylglucose from methanolysis of cellobiose were 61.2% and 28.3% respectively, exhibiting a ratio of around 2 for the two isomers. A very similar catalytic result was observed in the case of methanolysis of maltose as substrate, showing 61.7% yield of α-methylglucose and 28.6% yield of β-methylglucose. This isomer distribution actually compares well with the thermodynamic equilibrium, suggesting a fast isomerization is at play under the reaction circumstances. Therefore, the stability test of β-methylglucose in such reaction condition was carried out, showing indeed fast equilibration into the thermodynamic anomer isomer distribution, as shown in Table S2. Note that the same thermodynamic equilibrium was observed in the catalytic conversion of cellulose over sulfonated carbon by Bhaskar *et al.* in 2012.[4]

**Table S2** Methanolysis of various carbohydrates by using 5-OH-SHPAO in methanol.

| Substrate | Time (min) | Conv. (%) | Yield (%) | | |
|---|---|---|---|---|---|
| | | | α-MG | β-MG | ML |
| Cellobiose | 30 | >99 | 61.2 | 28.3 | 7.6 |
| Maltose | 30 | >99 | 61.7 | 28.6 | 6.5 |
| β-MG | 10 | 69 | 66.1 | 30.8 | 1.2 |

Reaction conditions: Substrate (40 mg), 5-OH-SHPAO (20 mg), methanol (2 mL), 160 °C. MG indicates methylglucose. ML indicates methyl levulinate.



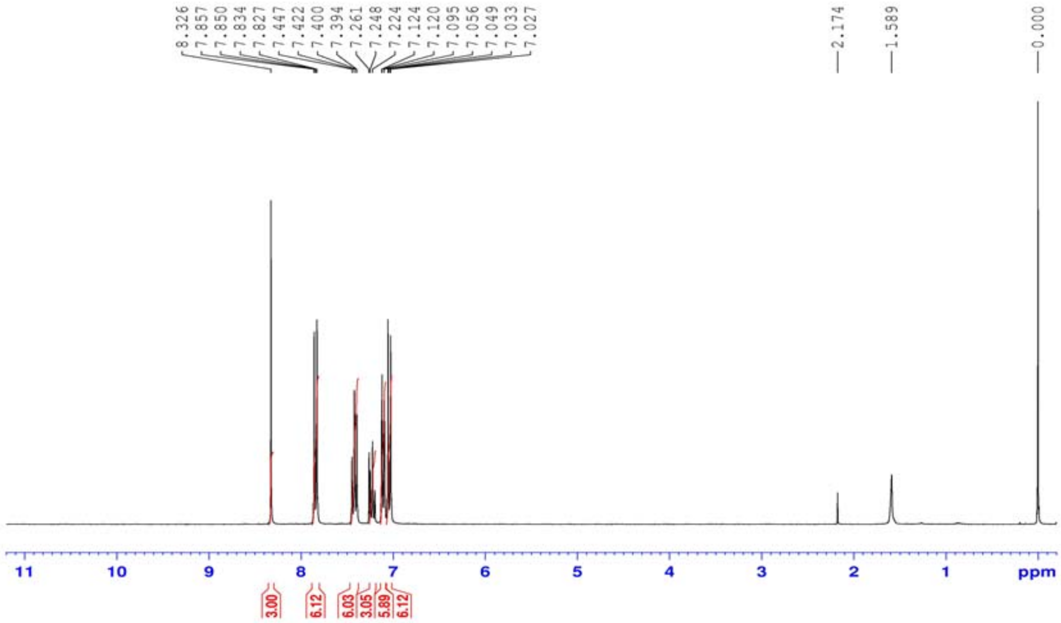
(a)

(b)

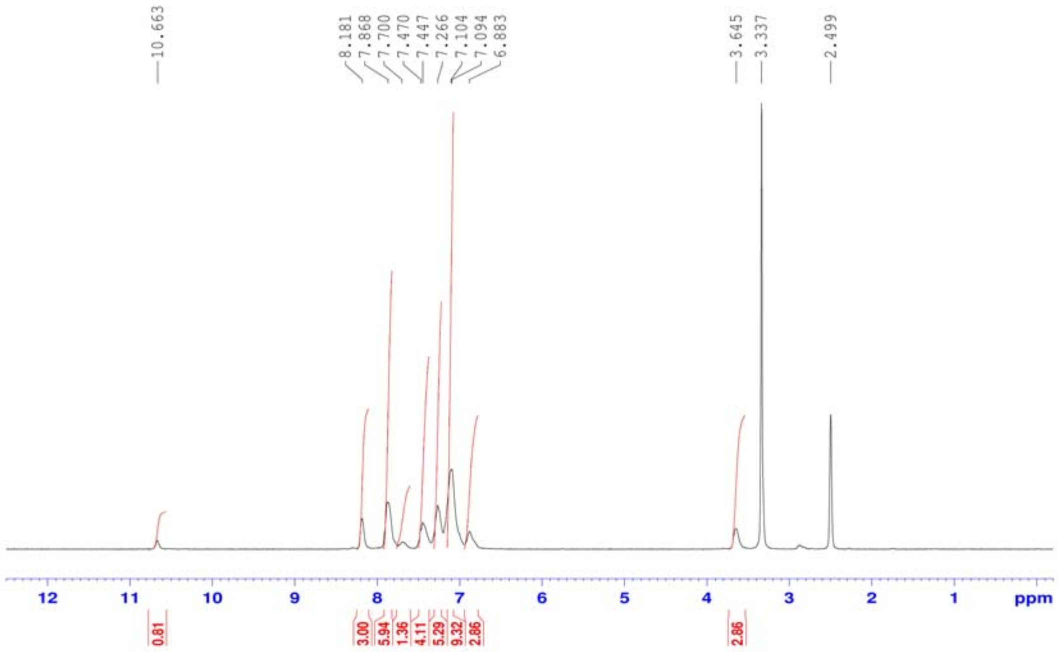
**Figure S10** The chromatogram results before (a) and after reaction (b) from the test of isomerization of β-methylglucose.

## $^1$H NMR and $^{13}$C NMR Spectra

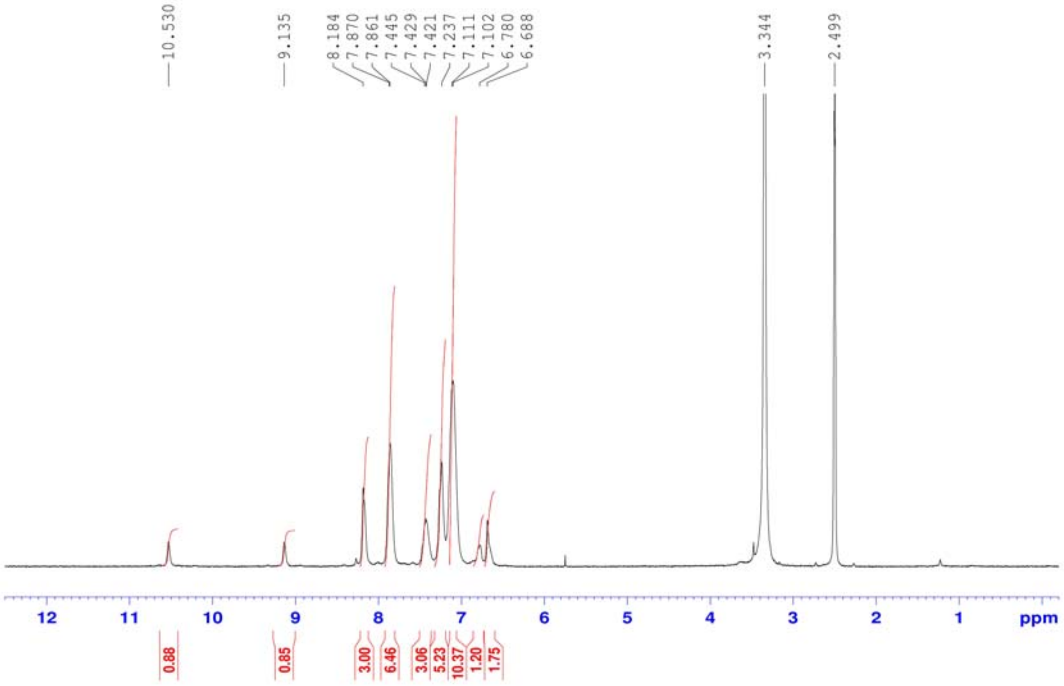
### $B_3$ monomer



### 5-MeO-HPAO



**5-OH-HPAO**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3.344
2.499
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10
9
8
7
6
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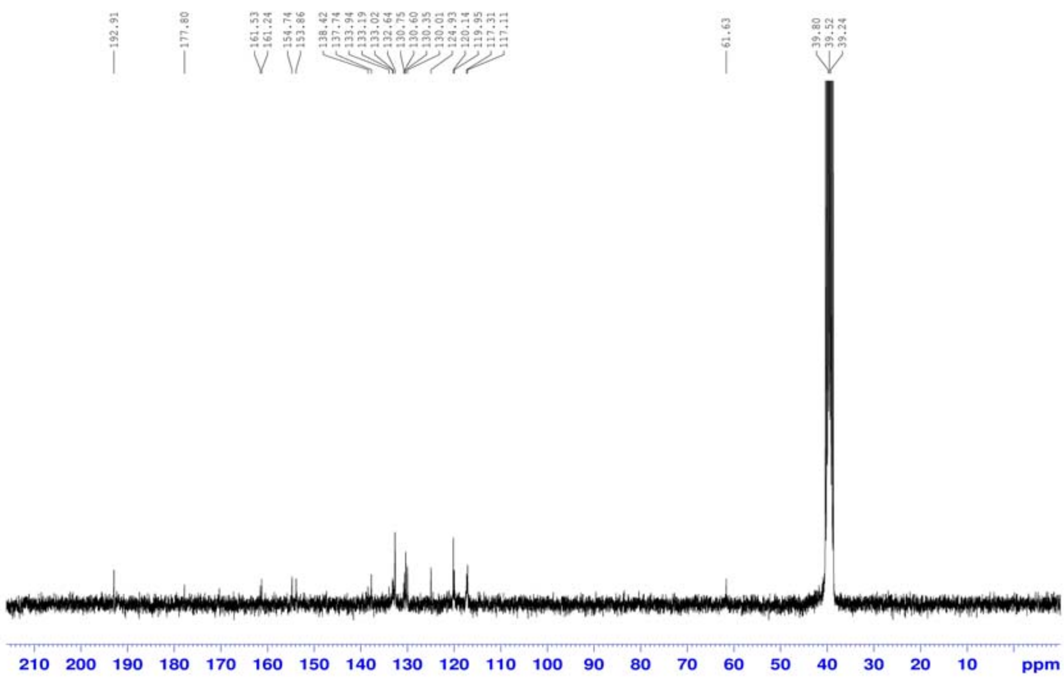
1.75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39.24
210
200
190
180
170
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100
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50
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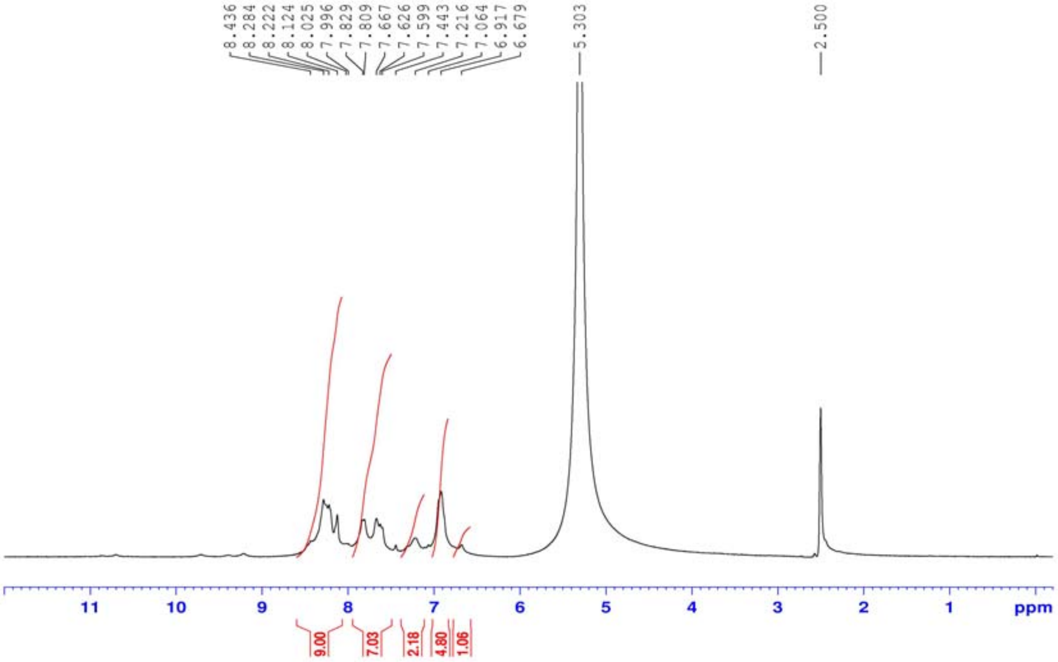
30
20
10
ppm

**5-OH-SHPAO**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6.917
6.679
5.303
2.500
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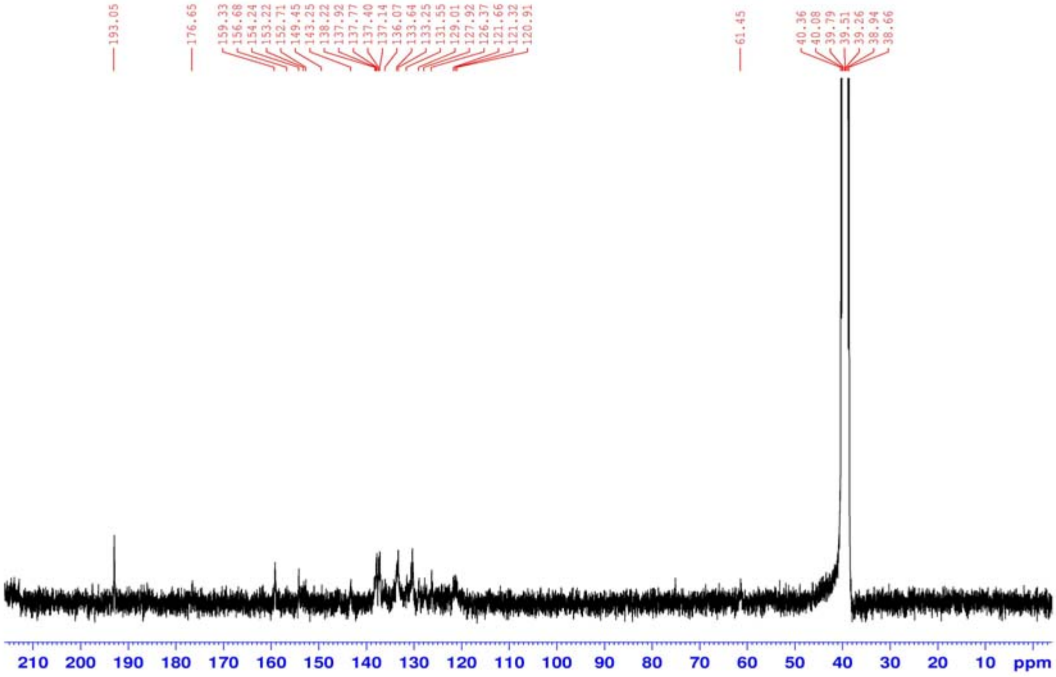
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137.14
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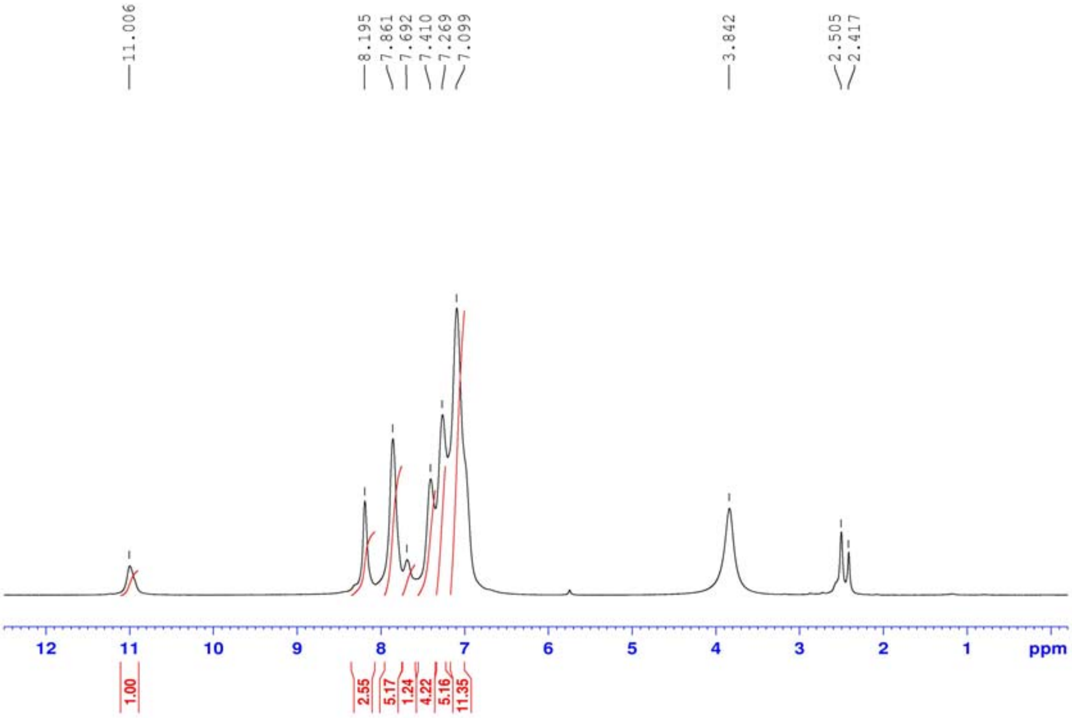
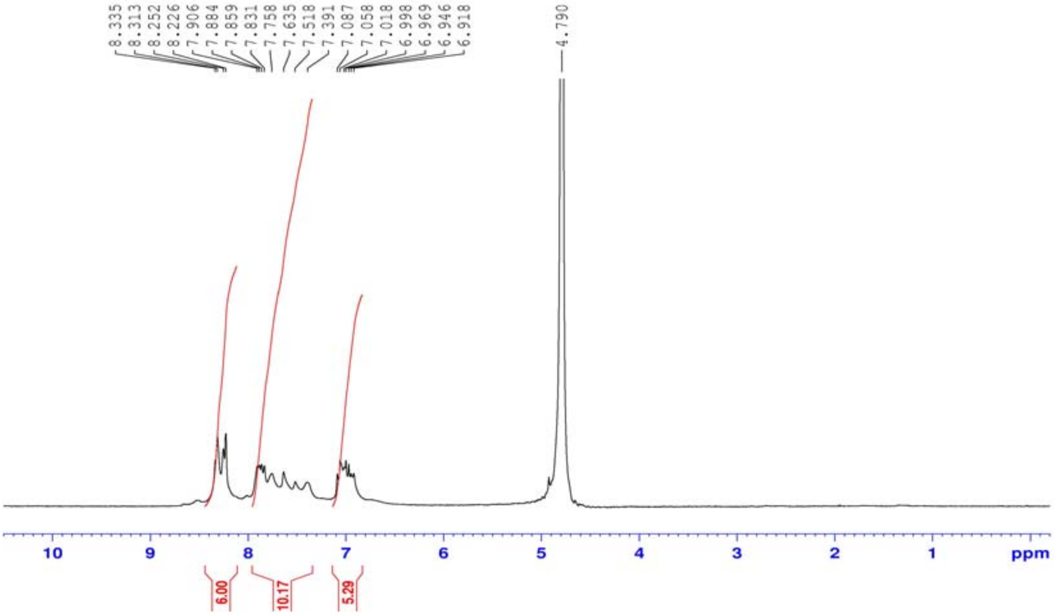
129.01
127.92
126.37
121.66
121.32
120.91
61.45
40.36
40.08
39.79
39.51
39.26
38.94
38.66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

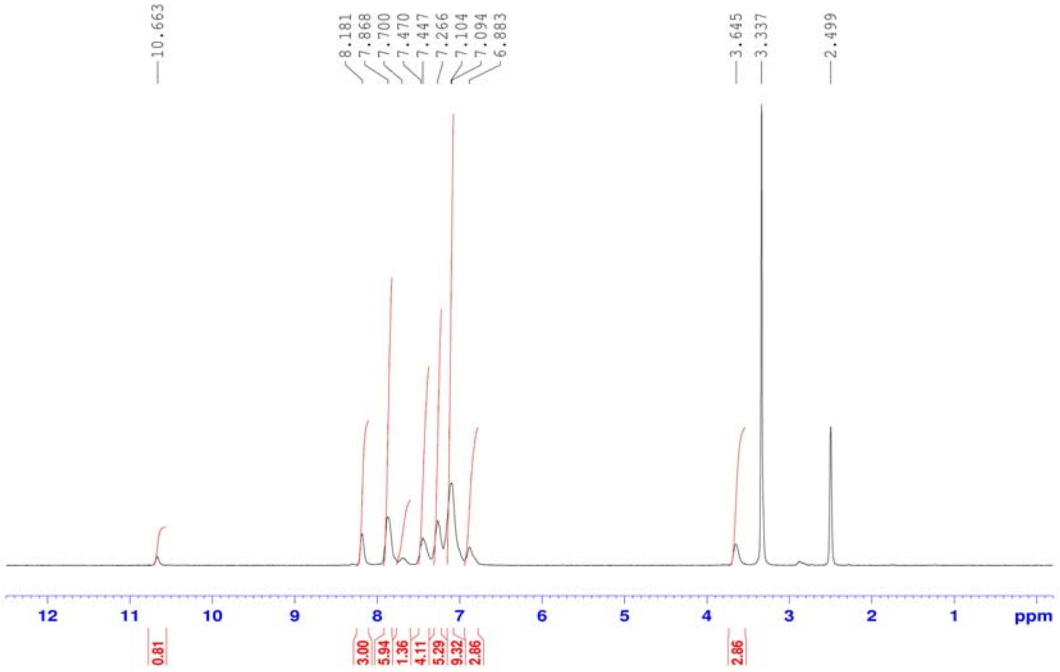
**5-Cl-HPAO**



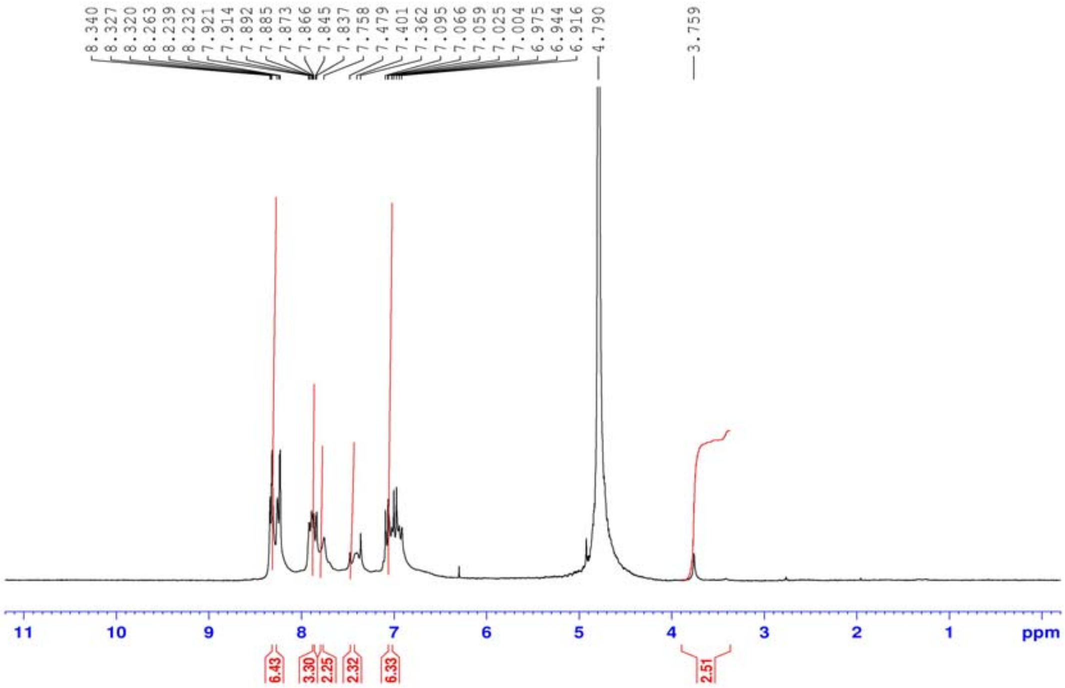
**5-Cl-SHPAO**



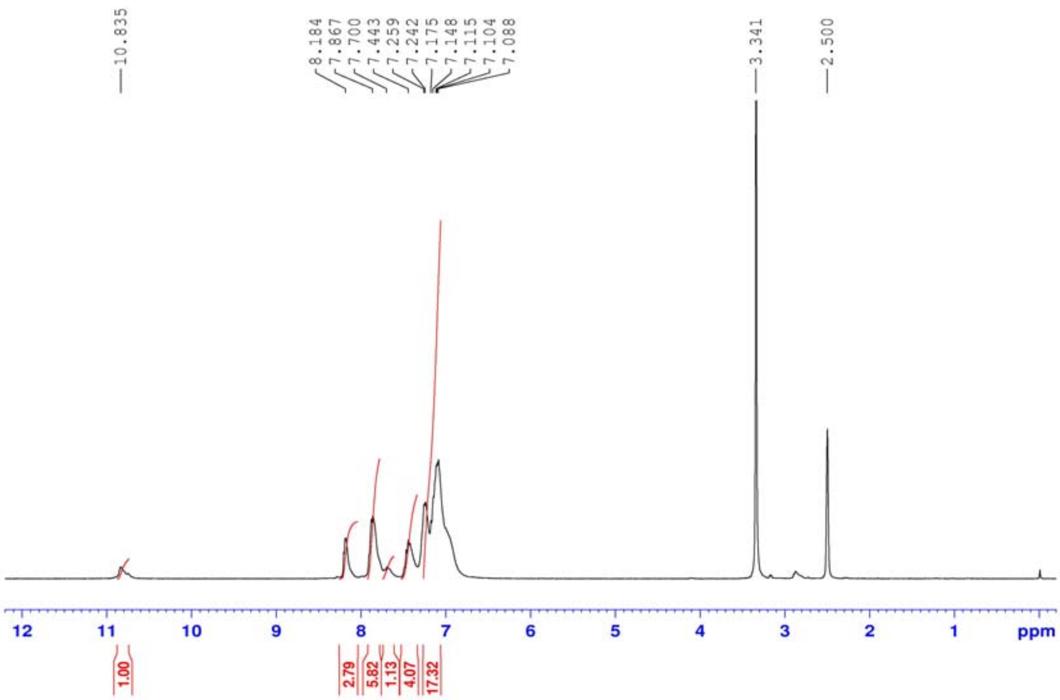
**5-MeO-HPAO**



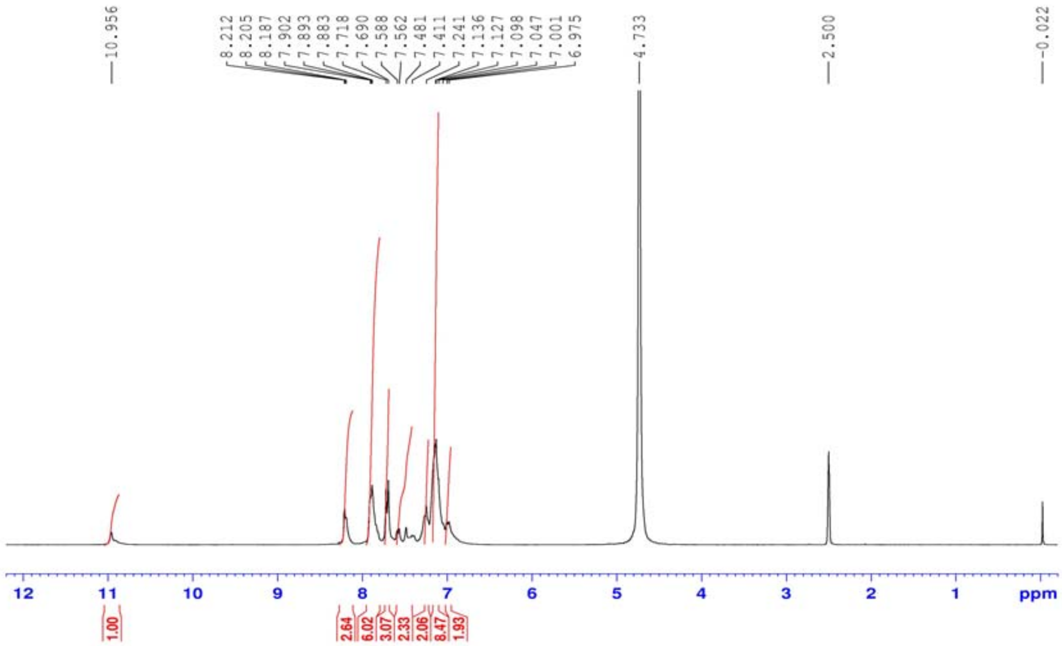
**5-MeO-SHPAO**



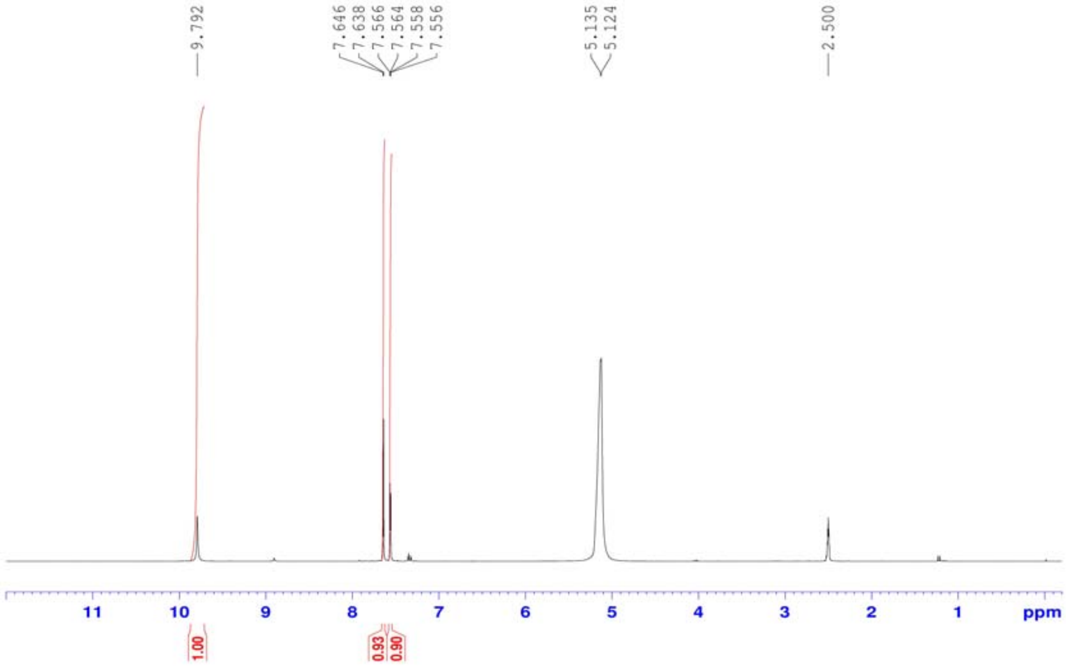
**HPAO**


10.835
8.184
7.867
7.700
7.443
7.259
7.242
7.175
7.148
7.115
7.104
7.088
3.341
2.500
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.79
5.82
1.13
4.07
17.32

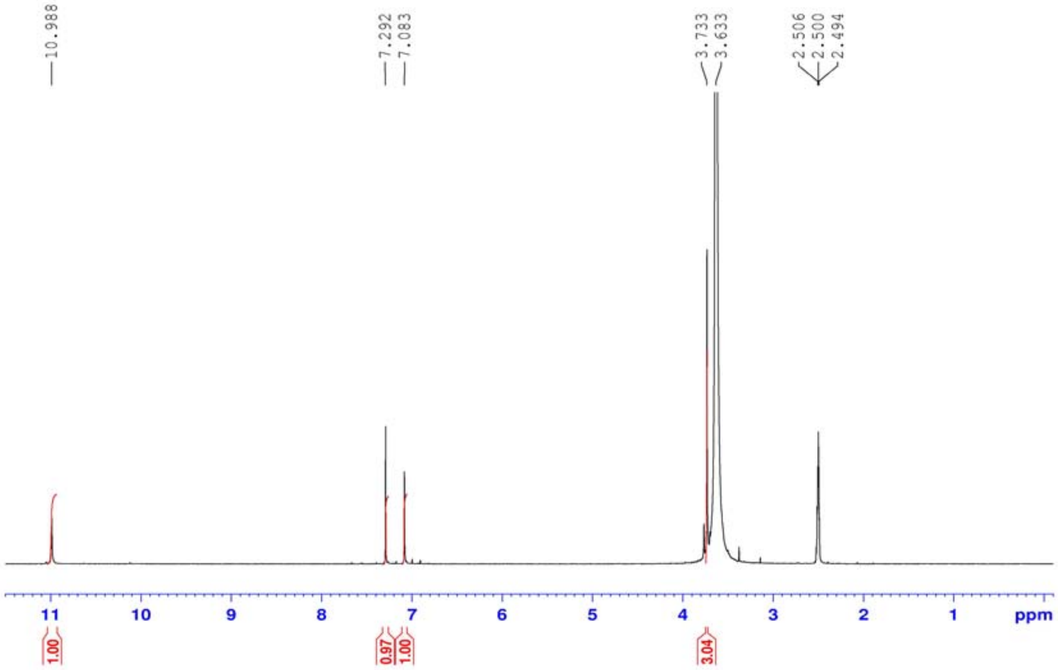
**SHPAO**


10.956
8.212
8.205
8.187
7.902
7.893
7.883
7.718
7.690
7.588
7.562
7.481
7.411
7.241
7.136
7.127
7.098
7.047
7.001
6.975
4.733
2.500
-0.022
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.64
6.02
3.07
2.33
2.06
8.47
1.93

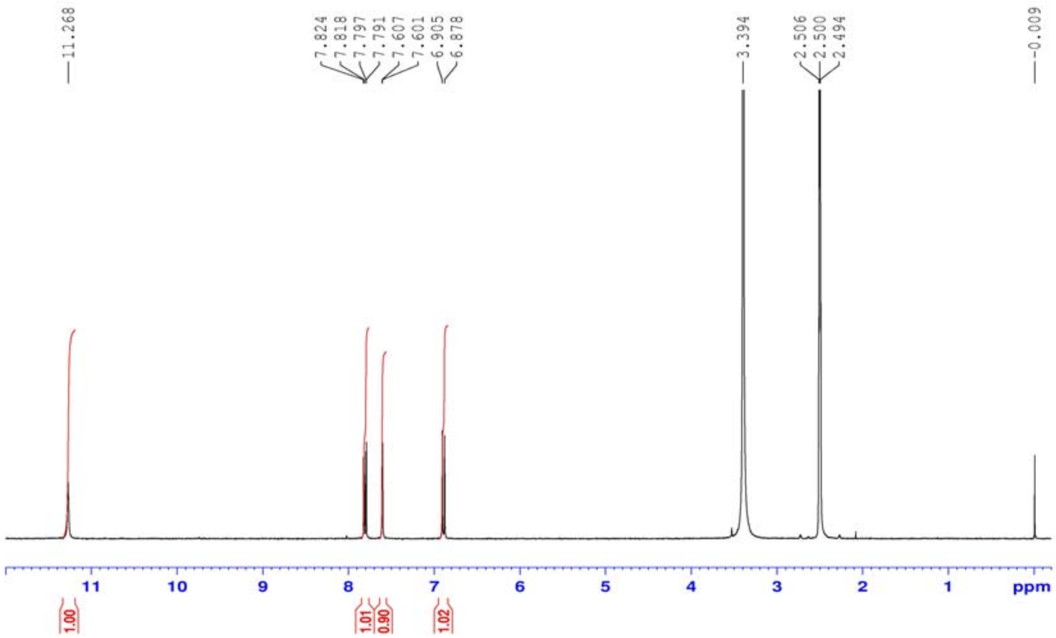
**$SO_3H$-5-Cl-isatin**



**$SO_3H$-5-MeO-isatin**



**SO$_3$H-isatin**



## References

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