Supporting Information

Molecular design of sulfonated hyperbranched poly(arylene oxindole)s for efficient cellulose conversion to levulinic acid

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General information

For polymer synthesis experiments, all reagents were used as received unless otherwise stated. Starting materials such as benzene-1,3,5-tricarbonyl trichloride, diphenyl ether, isatin, 5-fluoroisatin, 5-chloroisatin, 5-bromoisatin, 5-methoxyisatin, 5,7-dichloroisatin, methanesulfonic acid, trifluoromethanesulfonic acid, methyl iodide, 1,3-diiodopropane, oleum (20%, 30% and 60% SO_3), terephthaloyl chloride, monochlorobenzene, methanol, diethyl ether, dimethylformamide, dichloromethane, hydrochloric acid (36.5%), aluminium (III) trichloride, sodium hydroxide, magnesium sulfate and potassium carbonate were purchased from Sigma-Aldrich, Acros Organics or Alfa Aesar. 5-Bromoisatin was purified through recrystallization in dichloromethane before use.

The structures 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. Thermogravimetric analysis (TGA) experiments were performed by means of 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.

For catalytic experiments, carbohydrate substrates like cellulose (Avicel® PH-101), cellobiose, sucrose, fructose, xylose and furfural were supplied by Sigma-Aldrich. Glucose, 1,6-anhydro-β-D-glucopyranose, 5-hydroxymethylfurfural and levulinic acid were purchase from Acros Organics. Orafti® inulin was supplied by BENEO-Orafti. All chemicals were used without further purification as received. Ball-milling treated cellulose was used as 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. Reaction products

such as levulinic acid, formic acid, glucose, fructose, HMF, furfural 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 0.7 mL min^{-1} and a column temperature of 35 ^{o}C. Quantification of each compound was base on calibration curves obtained by analyzing standard solutions with known concentration. For the case of calculating response factor of LA, 8 different LA concentrations from 0.06696 g/L to 20.088 g/L were employed to acquire the corresponding area value from 5906 to 1776301. Then the linear trendline with high accuracy can be obtained. The general gradient was calculated to be 88422, which represents the sensitive factor of LA. The same procedure is for the calculation of other products. The sensitive factors for glucose, fructose, formic acid, HMF, furfural are 111623, 114243,48986, 147746, 135464 respectively. For instance, 48.4% yield of LA in the study corresponds to a concentration of 6.636 g/L in the reaction mixture.

Synthesis of hyperbranched polymers with various substituents

The general procedure for synthesis of hyperbranched poly(arylene oxindole)s is provided in the experimental section of the article.

Hyperbranched polymer ***5-Br-HPAOs***: 1.82 g product, *ca.* 91% yield. ^{1}H NMR (300 MHz, DMSO): δ = 10.98 (br, 1H), 8.17 (br, 3H), 7.84 (br, 6H), 7.67 (br, 1H), 7.07–7.44 (m, 21H); ^{13}C NMR (75 MHz, DMSO): δ = 192.9, 177.5, 161.6, 161.1, 154.7, 154.1, 140.7, 137.6, 135.2, 133.3, 132.7, 130.8, 130.6, 130.4, 130.0, 128.5, 124.9, 120.2, 117.4, 117.1, 114.0, 112.3, 61.5. $\overline{M}_n$ = 10.1 × 10^3, $\overline{M}_w$ / $\overline{M}_n$ = 1.78.

Sulfonated hyperbranched polymer ***5-Br-SHPAOs***: 1.20 g product. ^{1}H NMR (300 MHz, D_2O): δ 8.23–8.34 (m, 6H), 7.66–7.91 (m, 8H), 7.39 (br, 2H), 6.93–7.09 (m, 5H); ^{13}C NMR (100 MHz, D_2O): δ = 195.8, 179.5, 158.7, 158.1, 155.2, 152.7, 138.8, 137.7, 137.5, 136.2, 135.9, 135.6, 135.3, 134.9, 134.4, 133.7, 133.3, 132.9, 131.6, 131.2, 130.9, 130.8, 128.3, 127.2, 126.2, 122.9, 122.3, 120.8, 120.2, 115.6, 61.8.

Hyperbranched polymer ***5-Cl-HPAOs***: 1.79 g product, *ca.* 94% yield. ^{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); ^{13}C NMR (75 MHz, DMSO): δ = 192.9, 177.7, 161.5, 161.1, 154.7, 154.1, 149.1, 140.3, 137.7, 137.6,

133.3,132.7, 132.4, 130.8, 130.6, 130.0, 129.7, 126.3, 124.9, 120.2, 118.7, 117.4, 117.1, 111.8, 61.5. $\overline{M}_n$ = 11.2 × 10^3, $\overline{M}_w$ / $\overline{M}_n$ = 1.76.

Sulfonated hyperbranched polymer ***5-Cl-SHPAOs***: 1.14 g product. ^{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); ^{13}C NMR (75 MHz, D_2O): δ = 190.7, 177.8, 174.4, 152.9, 150.0, 133.7, 132.5, 132.4, 130.4, 130.3, 130.1, 129.7, 129.6, 129.2, 128.5, 127.7, 126.4, 126.0, 125.8, 125.6, 123.7, 123.4, 123.1, 121.0, 117.7, 117.1, 117.0, 115.6, 115.0, 94.8, 56.6.

Hyperbranched polymer ***5-F-HPAOs***: 1.65 g product, *ca.* 88% yield. ^{1}H NMR (300 MHz, DMSO): δ = 10.9 (br, 1H), 8.20 (br, 3H), 7.85–7.91 (m, 6H), 7.65 (br, 1H), 7.08–7.45 (m, 20H); ^{13}C NMR (75 MHz, DMSO): δ = 192.9, 177.9, 161.6, 161.1, 156.6, 154.7, 154.1, 137.7,134.5, 133.2, 132.7, 130.8, 130.6, 130.4, 130.0, 124.9, 120.2, 120.0, 117.3, 117.1, 111.1, 61.7. $\overline{M}_n$ = 12.1 × 10^3, $\overline{M}_w$ / $\overline{M}_n$ = 1.81.

Sulfonated hyperbranched polymer ***5-F-SHPAOs***: 1.20 g product. ^{1}H NMR (300 MHz, D_2O): δ 8.22–8.34 (m, 6H), 7.83–7.91 (m, 4H), 7.75 (br, 2H), 7.31–7.39 (m, 4H), 6.91–7.09 (m, 6H); ^{13}C NMR (75 MHz, D_2O): δ = 195.9, 179.9, 158.7, 158.0, 155.2, 152.6, 138.8, 137.7, 137.5, 136.3, 135.7, 134.9, 134.4, 133.7, 132.8, 131.6, 131.3, 130.9, 130.8, 126.2, 122.9, 122.2, 120.8, 62.1.

Hyperbranched polymer ***5-MeO-HPAOs***: 1.70 g product, *ca.* 90% yield. ^{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); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.7, 162.4, 161.9, 155.2, 138.5, 137.8, 133.5, 132.6, 131.0, 130.7, 130.2, 124.9, 120.4, 120.2, 117.6, 117.3, 62.4, 55.8. $\overline{M}_n$ = 6.4 × 10^3, $\overline{M}_w$ / $\overline{M}_n$ = 1.73.

Sulfonated hyperbranched polymer ***5-MeO-SHPAOs***: 1.04 g product. ^{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);

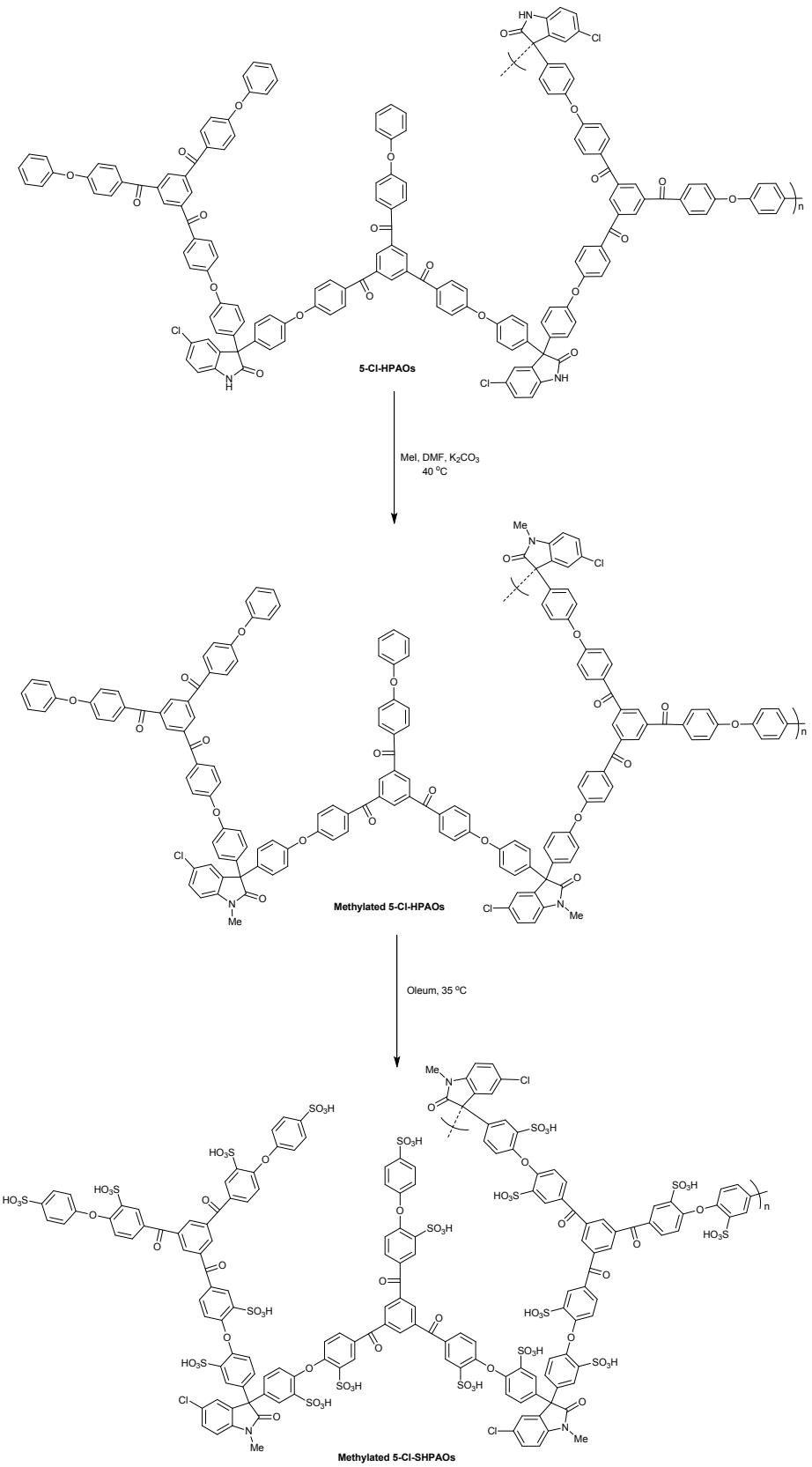
Hyperbranched polymer ***5,7-Cl$_2$-HPAOs***: 1.84 g product, *ca.* 93% yield. ^{1}H NMR (300 MHz, DMSO): δ = 11.5 (br, 1H), 8.20 (br, 3H), 7.84–7.91 (m, 6H), 7.65 (br, 1H), 7.07–7.47 (m, 20H); ^{13}C NMR (75 MHz, DMSO): δ = 192.9, 177.6, 161.5, 161.0, 154.7, 154.3, 138.4, 137.7, 137.0, 135.8, 133.2, 132.7, 130.8, 130.6, 130.4, 130.0, 126.9, 125.0, 120.1, 117.5, 117.1, 115.3, 62.3. $\overline{M}_n$ = 20.6 × 10^3, $\overline{M}_w$ / $\overline{M}_n$ = 1.89.

Sulfonated hyperbranched polymer ***5,7-Cl$_2$-SHPAOs***: 1.30 g product. ^{1}H NMR (300 MHz, D_2O): δ 8.22–8.31 (m, 6H), 7.73–7.90 (m, 6H), 7.27–7.37 (m, 3H), 6.90–7.08 (m, 5H); ^{13}C NMR (75 MHz, D_2O): δ = 195.9, 180.0, 158.9, 158.7, 155.2, 152.8, 149.1, 138.9, 137.6, 135.7, 134.4, 133.7, 131.5, 131.0, 130.8, 126.2, 120.8, 62.1.

Synthesis of methylated 5-Cl-SHPAOs

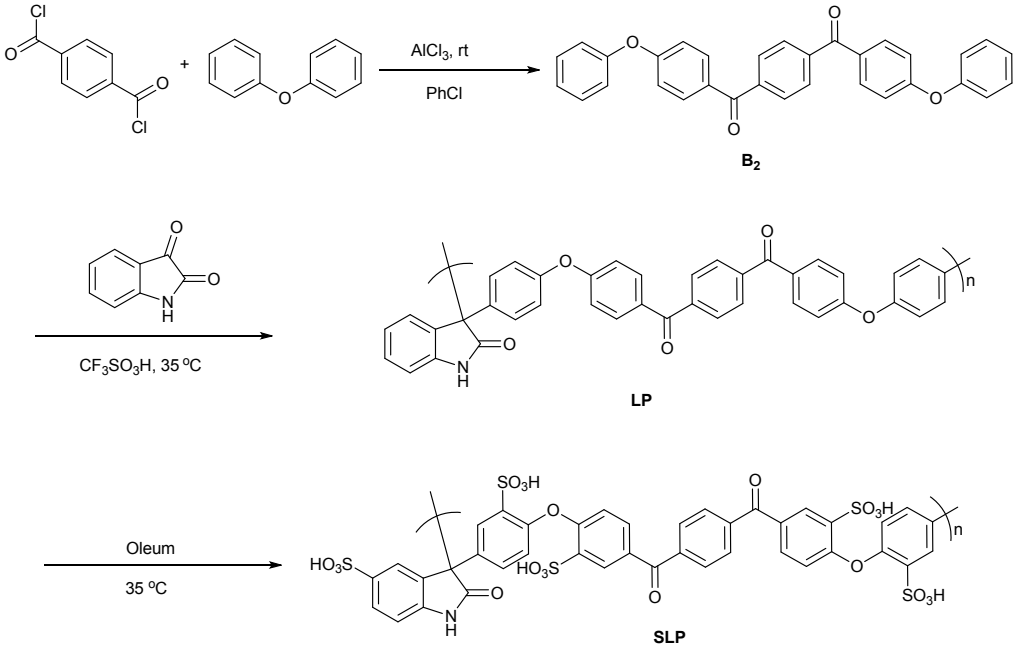
Synthesis of ***methylated 5-Cl-HPAOs****:* To a solution of hyperbranched polymer 5-Cl-HPAOs (0.6 g) and K_2CO_3 (0.20 g, 1.45 mmol) in 10 mL DMF, methyl iodide (0.21 g, 1.45 mmol) was dropwise added at room temperature. Then the reaction mixture was stirred at room temperature overnight. The reaction was quenched by an addition of 40 mL water to the reaction mixture. The aqueous phase was 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 a viscous liquid. After precipitation in methanol, 0.56 g (*ca.* 92%) of the desired product was obtained. ^{1}H NMR (300 MHz, DMSO): δ 8.20 (br, 3H), 7.86–7.88 (br, 6H), 7.69 (br, 1H), 7.08–7.43 (m, 21H), 3.21 (s, 3H); ^{13}C NMR (75 MHz, DMSO): δ = 192.9, 175.8, 161.5, 161.1, 154.7, 154.1, 141.7, 137.7, 137.3, 133.2, 132.6, 130.8, 130.6, 130.4, 130.0, 129.7, 128.7, 127.0, 125.5, 124.9, 120.1, 120.0, 118.6, 117.4, 117.1, 111.0, 60.9, 28.6, 26.7. $\overline{M}_n$ = 12.0 × 10^3, $\overline{M}_w$ / $\overline{M}_n$ = 1.77.

Synthesis of ***methylated 5-Cl-SHPAOs****:* To a round-bottomed flask, polymer methylated 5-Cl-HPAOs (0.5 g) and 30% oleum (12 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, a brownish sulfonated product (0.4 g) was obtained. ^{1}H NMR (300 MHz, D_2O): δ 8.21–8.31 (m, 5H), 7.81–7.89 (m, 4H), 7.50–7.70 (m, 4H), 7.32 (br, 2H), 6.89–7.07 (m, 5H), 3.66 (s, 2H), 3.27 (s, 1H); ^{13}C NMR (75 MHz, D_2O): δ = 195.9, 179.7, 158.8, 158.2, 158.1, 155.3, 152.7, 138.9, 137.6, 135.7, 135.4, 135.0, 134.5, 133.8, 133.0, 131.6, 131.3, 131.0, 130.8, 128.5, 126.3, 122.9, 122.3, 120.9, 110.7, 62.1, 60.6, 30.8, 27.1.



Scheme S1. Synthesis of methylated sulfonated 5-Cl-SHPAOs

Synthesis of linear polymer catalyst



Scheme S2. Synthesis of sulfonated linear poly(arylene oxindole)s

*Synthesis of 1,4-phenylenebis((4-phenoxyphenyl)methanone) (**B_2 monomer**)*: To 100 mL of chlorobenzene in a two-necked flask was added terephthaloyl chloride (2.0 g, 9.9 mmol) and diphenyl ether (13.6 g, 39.6 mmol). The reaction mixture was stirred at room temperature for a while to dissolve the solid starting materials, and then cooled to 0 °C in an ice bath. Subsequently, anhydrous aluminium chloride (8.1 g, 29.7 mmol) was slowly added to the stirring solution. After the addition, the mixture was allowed to reach room temperature and stirred overnight. When the reaction was completed, the reaction mixture was poured into icy cold 10% HCl solution (30 mL). The solution was then neutralized with the addition of 10% NaOH and transferred to an extraction funnel. The aqueous layer was washed with CH_2Cl_2 (3 × 80 mL). The combined organic fractions were then washed with brine (1 × 80 mL), dried with Na_2SO_4 and concentrated in vacuo to afford the crude products. The crude products were purified through crystallization in chlorobenzene, and gave 3.3 g (ca. 71% yield) of desired pure product with white color. ^{1}H NMR (300 MHz, DMSO): δ = 7.85 (d, *J* = 6.9 Hz, 8H), 7.48 (t, *J* = 7.8 Hz, 4H), 7.27 (t, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 4H), 7.11 (d, *J* = 8.4 Hz, 4H).

*Synthesis of linear polymer (**LP**)*: To a round-bottomed flask both the A_2 monomer isatin (0.33 g, 2.24 mmol) and the B_2 monomer 1,4-phenylenebis((4-phenoxyphenyl)methanone) (1.06 g, 2.24 mmol) were added as solids in an equimolar amount, and the appropriate amount of trifluoromethanesulfonic acid (22 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 after washed with abundant water and methanol. The solid was dissolved into dichloromethane and then precipitated in methanol. After filtration and washed with methanol, a white solid (1.20 g, *ca.* 86%) was obtained. ^{1}H NMR (300 MHz, DMSO): δ = 10.84 (br, 1H), 7.77 (br, 8H), 7.23 (br, 6H), 6.98–7.07 (br, 10H). $\overline{M}_n$ = 10.9 × 10^3, $\overline{M}_w$ / $\overline{M}_n$ = 1.67.

*Synthesis of sulfonated linear polymer (**SLP**)*: To a round-bottomed flask, linear polymer (1.0 g) and 30% oleum (15 mL) were added and stirred at 35 °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, a light brownish sulfonated product (0.9 g) was obtained. ^{1}H NMR (300 MHz, D_2O): δ = 8.23 (s, 2H), 8.01 (s, 1H), 7.74–7.83 (m, 9H), 7.40 (d, *J* = 8.4 Hz, 3H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, D_2O): δ = 197.5, 180.0, 158.7, 152.8, 140.2, 139.4, 138.1, 136.2, 135.4, 134.9, 134.6, 133.5, 132.7, 131.2, 130.0, 128.3, 125.9, 124.7, 123.0, 120.1, 61.7.

Synthesis of hyperbranched polymer catalysts with no substituents

The standard sulfonated hyperbranched poly(arylene oxindole)s were synthesized by the following reported procedure.[1,2,3] The variation in the average molecular weight of polymers was achieved by tuning the reaction time, from 6 hours to 2 days, or reaction temperature, from 35 to 50 °C. In addition, the hyperbranched polymers with low molecular weight, such as the polymer with $\overline{M}_n$ equal to 6300, 4000, and 2700, were obtained through fractional precipitation in methanol.

Table S1. Catalytic hydrolysis of cellulose into levulinic acid by various SHPAOs with different molecular weight and acid density

Entry	$\overline{M}_n$	Polydispersity index	Acid density (mmol H^+/g)	LA yield (%)
1	20.2×10^3	1.72	3.6	31
2	20.2×10^3	1.72	4.4	33
3	12.9×10^3	1.64	3.4	32
4	12.9×10^3	1.64	4.7	33
5	6.3×10^3	1.12	4.5	32
6	6.3×10^3	1.12	4.8	31
7	4.0×10^3	1.10	4.1	33
8	4.0×10^3	1.10	4.6	33
9	2.7×10^3	1.10	4.7	30
10	2.7×10^3	1.10	4.1	32

[a]Reaction conditions: 0.17 mmol H^+ in added catalyst, 40 mg of celllulose, 2 ml of H_2O, 165 ^oC, 5 h.

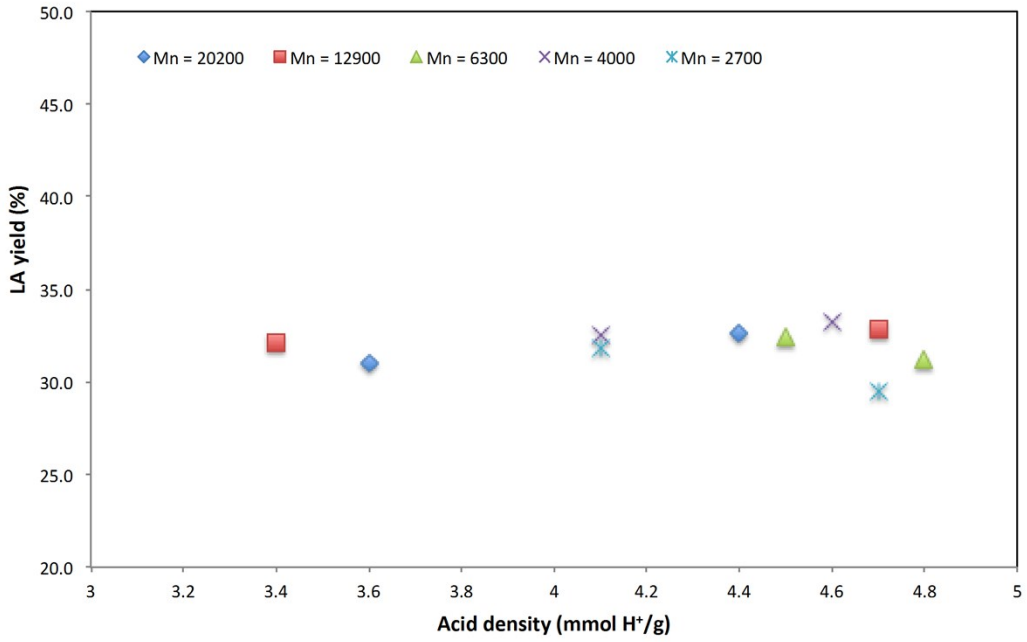


Figure S1. The effect of molecular weight and acid density of sulfonated hyperbranched polymer SHPAOs on the catalytic hydrolysis of cellulose into LA

Synthesis of small sulfonic acids

General procedure for the synthesis of sulfonated isatins ***SO_3H-5-Cl-Isatin****:* To a round-bottomed flask, 1.0 g of A_2 monomer (isatin with different substituent) and 5 mL of oleum (30%) were added. Under nitrogen atmosphere, the reaction mixture was stirred at 35 ^oC for 1 day. Afterwards, the reaction flask was kept in an ice bath for 20 min, and some amount of orange solid was crystallized during that period. The desired orange solid was then collected through filtration and washed with some icy water to remove the remaining sulfuric acid. After drying *in vacuo*, the desired product was obtained as a solid.

SO_3H-5-Cl-Isatin*:* 0.30 g orange product, *ca.* 21% yield. mp: 166 ^oC; ^1H NMR (300 MHz, DMSO): δ = 9.79 (br, s, 1H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.56 (dd, *J* = 2.2, 0.6 Hz, 1H); ^{13}C NMR (75 MHz, DMSO): δ = 182.4, 158.3, 144.3, 133.5, 132.7, 126.4, 124.6, 120.2.

SO_3H-Isatin*:* 0.34 g orange product, *ca.* 22% yield. ^1H NMR (300 MHz, DMSO): δ = 11.27 (br, s, 1H), 7.81 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.60 (d, *J* = 1.8 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H).

SO_3H-5-MeO-Isatin*:* 0.28 g dark red product, *ca.* 19% yield. mp: 204 ^oC; ^1H NMR (300 MHz, DMSO): δ = 10.99 (br, s, 1H), 7.29 (s, 1H), 7.08 (s, 1H), 3.73 (s, 3H).

Synthesis of sulfonated B_3 monomer ***SO_3H-B_3****:* To a round-bottomed flask, 0.6 g of B_3 monomer and 5 mL of oleum (30%) were added. Under nitrogen atmosphere, the reaction mixture was stirred at 35 ^oC for 1 day. Afterwards, the reaction mixture was poured into ice water. The diluted solution was then neutralized by saturated barium dichloride solution. The precipitated $BaSO_4$, formed during neutralization, was separated from aqueous solution by means of centrifugation. The neutralization process lasted until the time point when no precipitate was formed with adding a drop of barium dichloride solution into the reaction mixture. After complete removal of the remaining sulfuric acid, the solution was collected and dried at reduced pressure, affording 1.0 g of desired product as a brown viscous liquid. ^1H NMR (300 MHz, D_2O): δ = 8.55–8.64 (m, 6H), 7.97–8.23 (m, 5H), 7.71 (br, 2H), 7.16–7.41 (m, 4H).

The recycling and reuse of sulfonated hyperbranched polymers

Upon completion of the catalytic reaction, the reaction mixture was treated with a simple filtration to remove the remaining cellulose or the formed humin, and then the filtrate was transferred to the upper chamber of a Microsep 3K Omega centrifuge filtering tube, which

contains a semipermeable membrane with a molecular weight cutoff of 3000 Da. The filtering tube was centrifuged at 10000 rmp for 2 h, forcing the desired products into the lower reservoir. The polymer catalyst was kept in the retentate placed in the upper sample reservoir. After washing with hot distilled water and drying in vacuum, the polymer catalyst was recovered.

The recycled 5-Cl-SHPAOs catalyst was fully loaded into a new reactor with 40 mg fresh cellulose and 2 mL H_2O. Following the standard procedure of hydrolysis cellulose at 165 ^oC for 5 h, 48 % LA yield with >99% cellulose conversion was obtained.

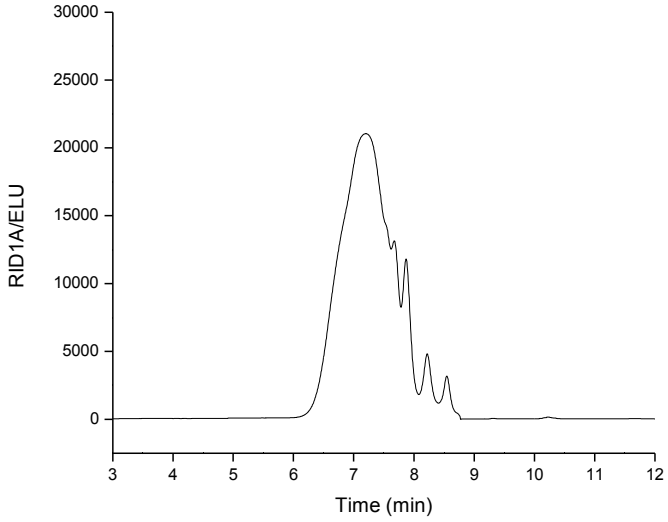


Figure S2. A representative GPC measurement result for the hyperbranched poly(arylene oxindole)s (The figure shows the result from 5-Cl-SHPAOs).

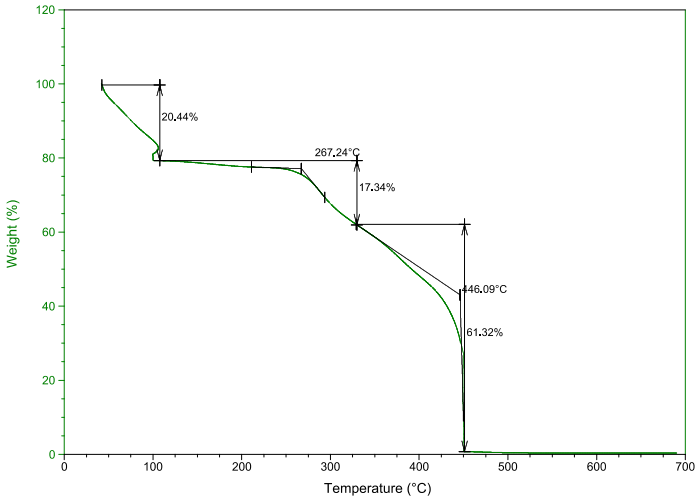


Figure S3. TGA result of the sulfonated hyperbranched polymer 5-Cl-SHPAOs

FT-IR spectra of hyperbranched polymers

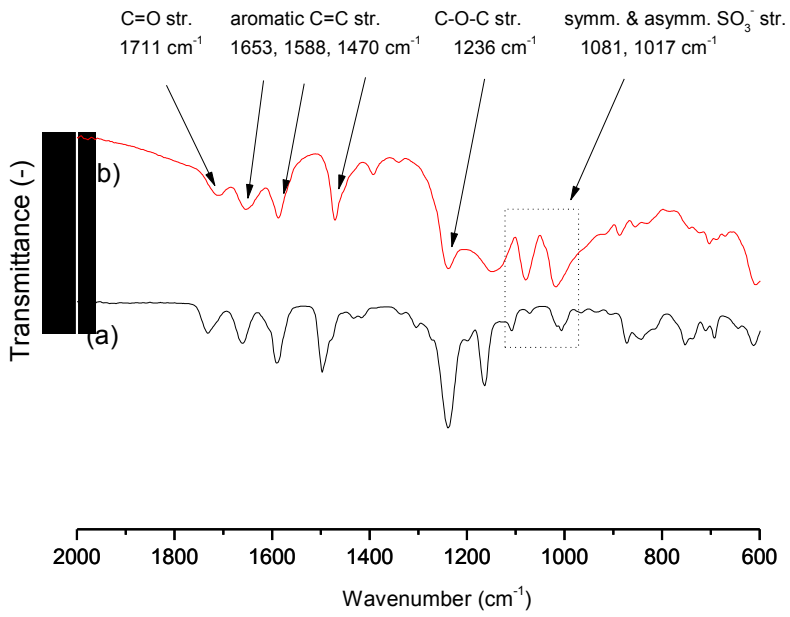


Figure S4. Comparison of FT-IR spectra of 5-Cl-HPAOs before (a) and after sulfonation (b)

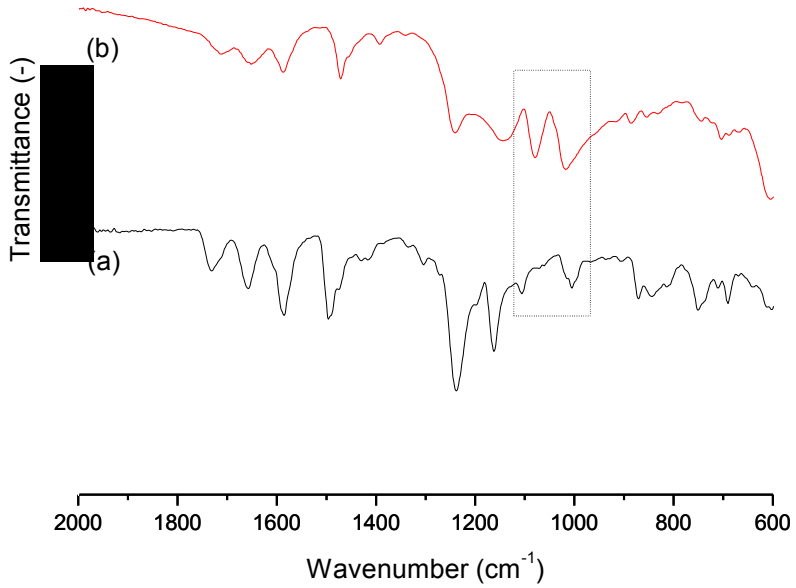


Figure S5. Comparison of FT-IR spectra of 5-Br-HPAOs before (a) and after sulfonation (b)

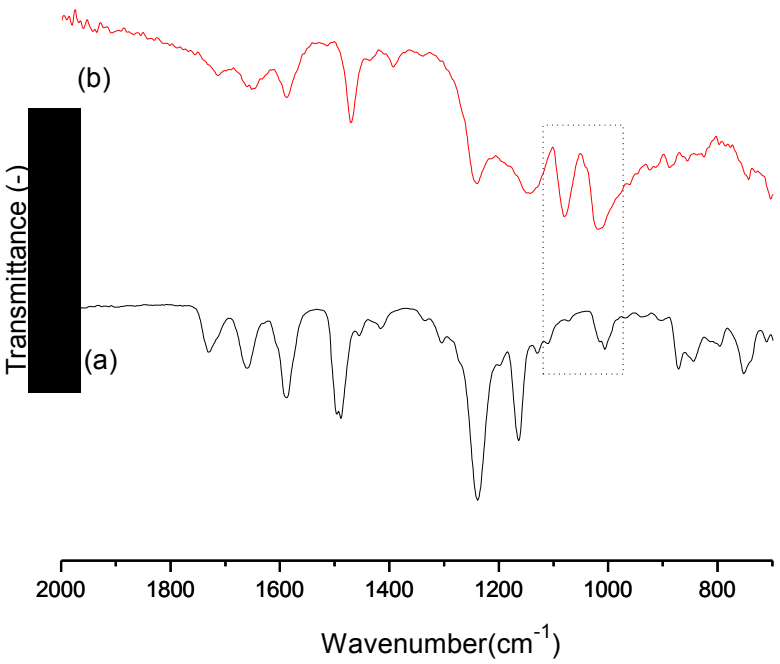


Figure S6. Comparison of FT-IR spectra of 5-F-HPAOs before (a) and after sulfonation (b)

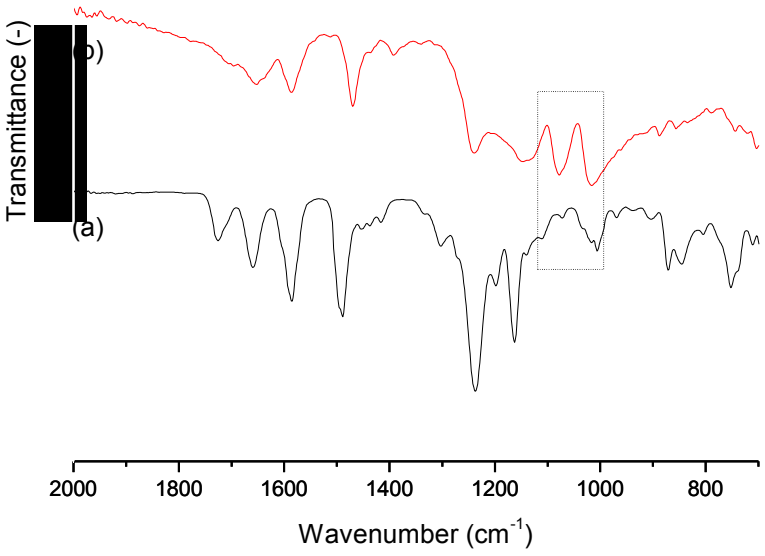


Figure S7. Comparison of FT-IR spectra of 5-MeO-HPAOs before (a) and after sulfonation (b)

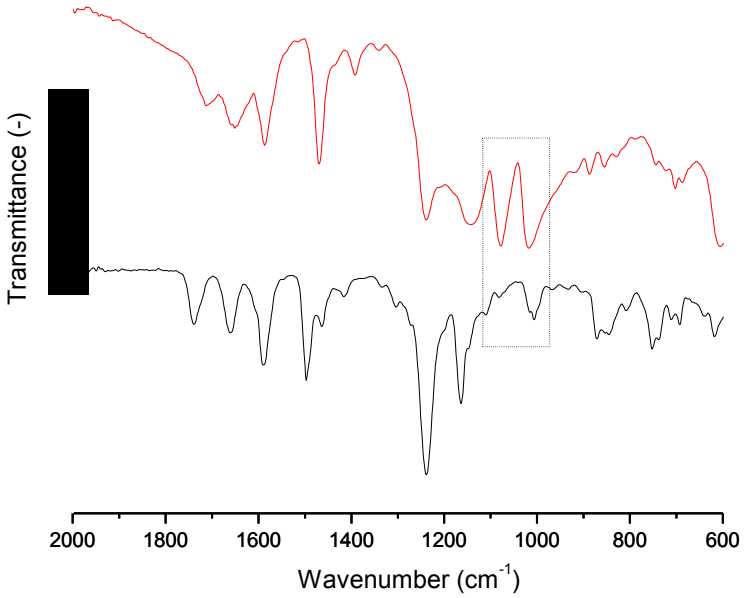


Figure S8. Comparison of FT-IR spectra of 5,7-Cl_2-HPAOs before (a) and after sulfonation (b)

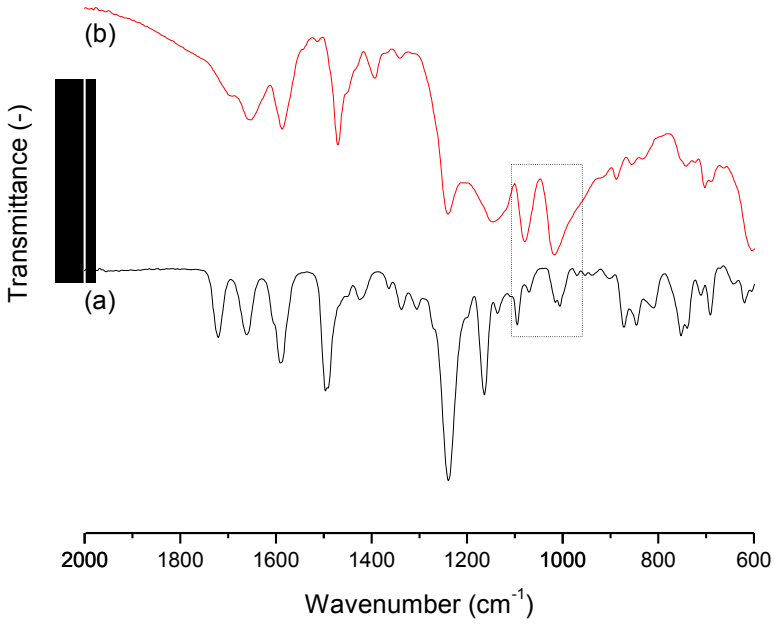


Figure S9. Comparison of FT-IR spectra of methylated 5-Cl-HPAOs before (a) and after sulfonation (b)

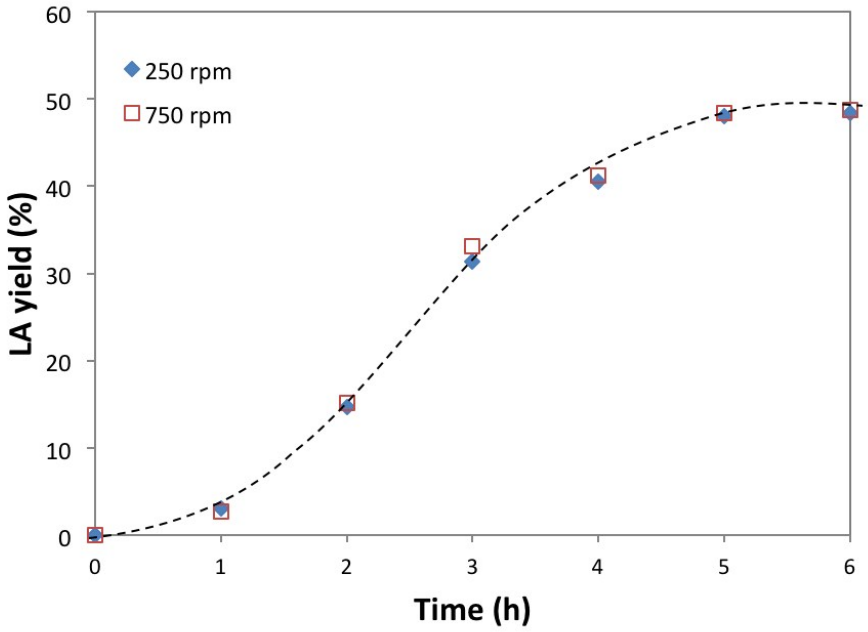


Figure S10. The effect of stirring rates on the catalytic hydrolysis of cellulose to LA by 5-Cl-SHPAOs. Reaction conditions: 0.17 mmol H^+ in added catalyst, 40 mg of celllulose, 2 ml of H_2O, 165 ^oC.

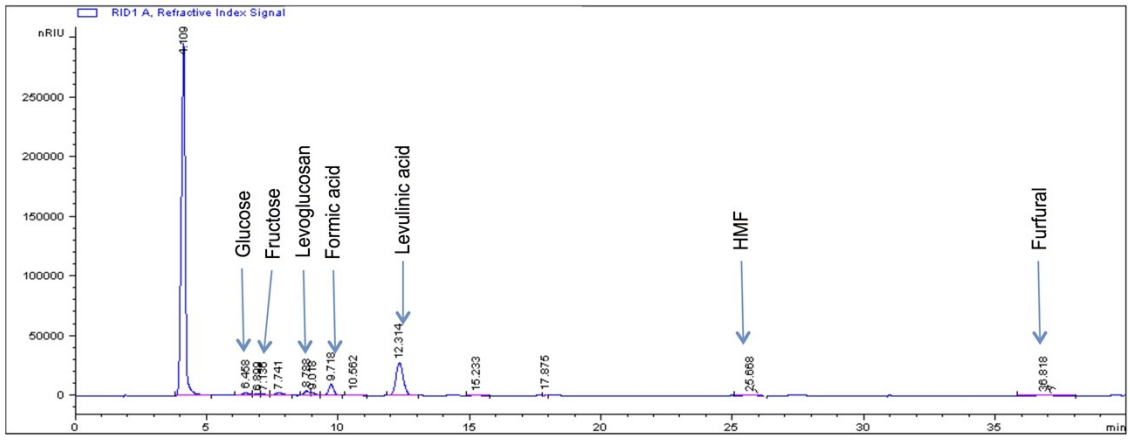
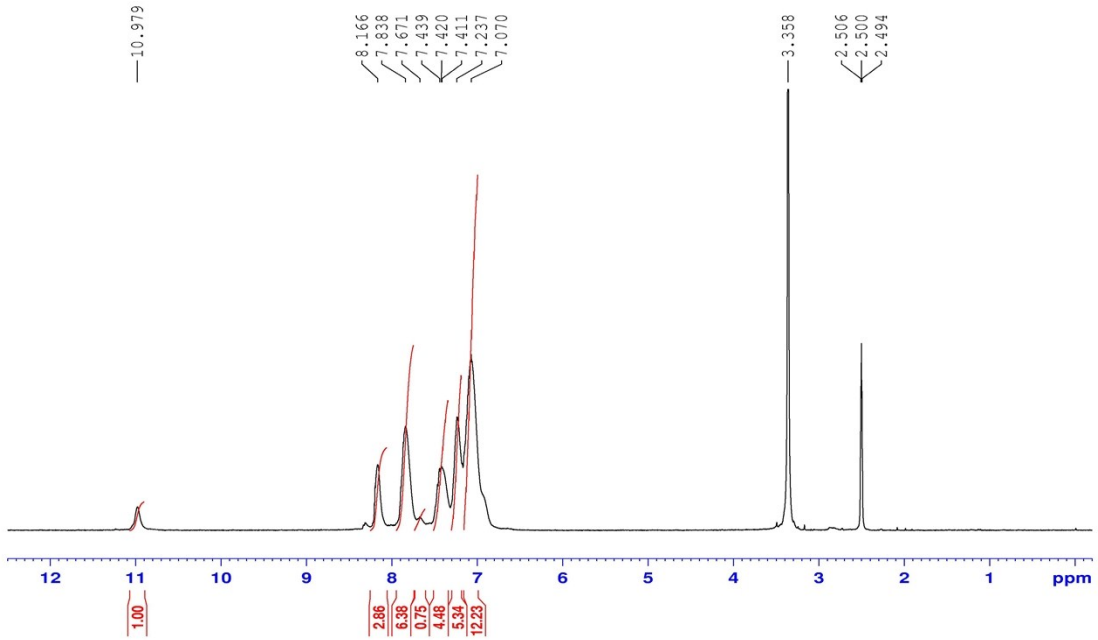
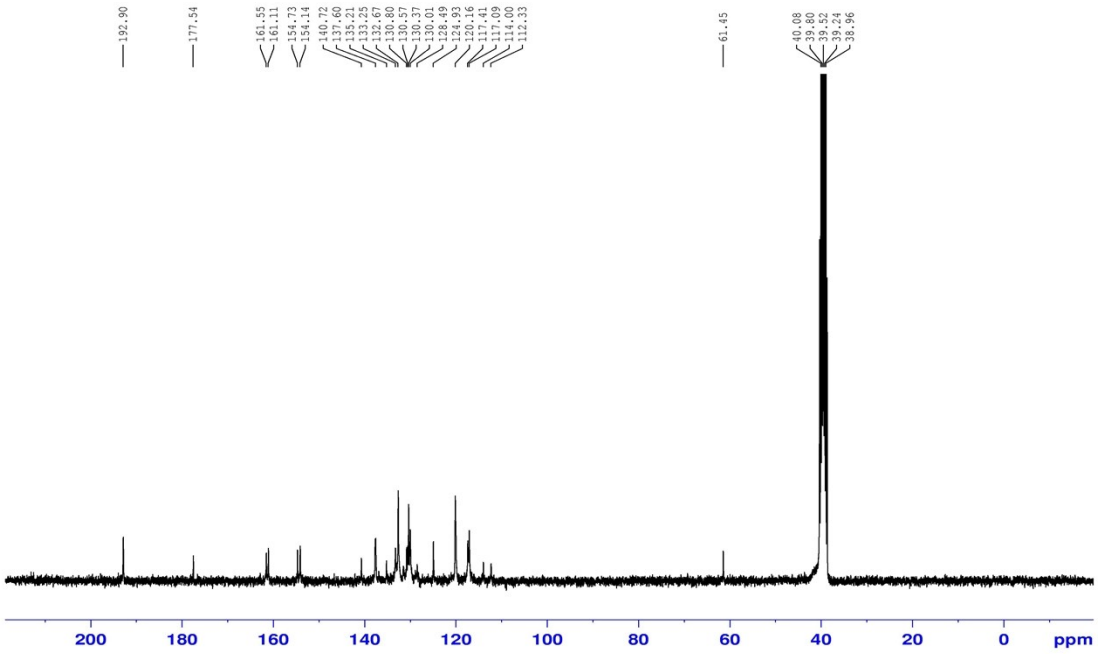


Figure S11. Typical result from HPLC measurement of the reaction mixture after catalytic conversion of cellulose to LA by 5-Cl-SHPAOs.

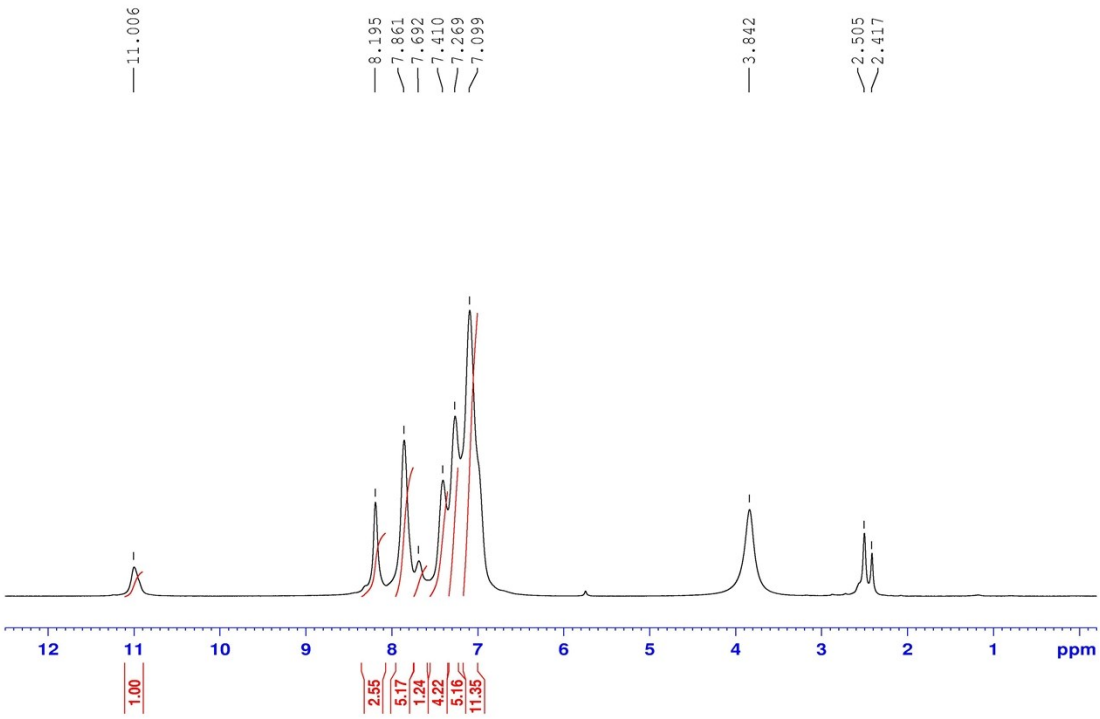
^{1}H NMR and ^{13}C NMR Spectra

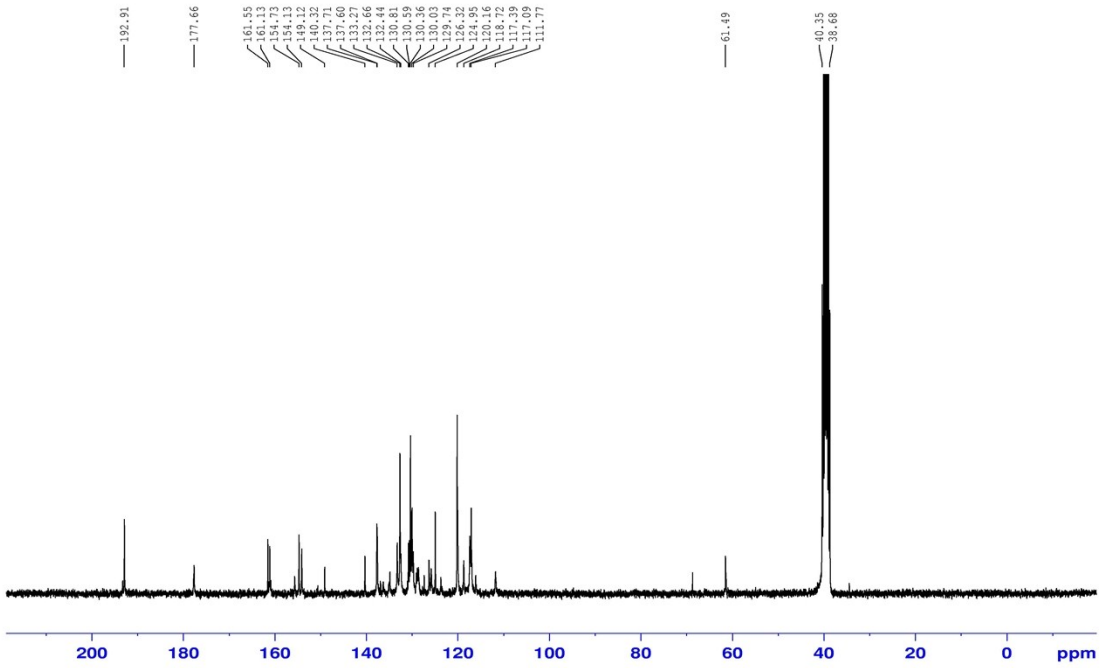
5-Br-HPAOs



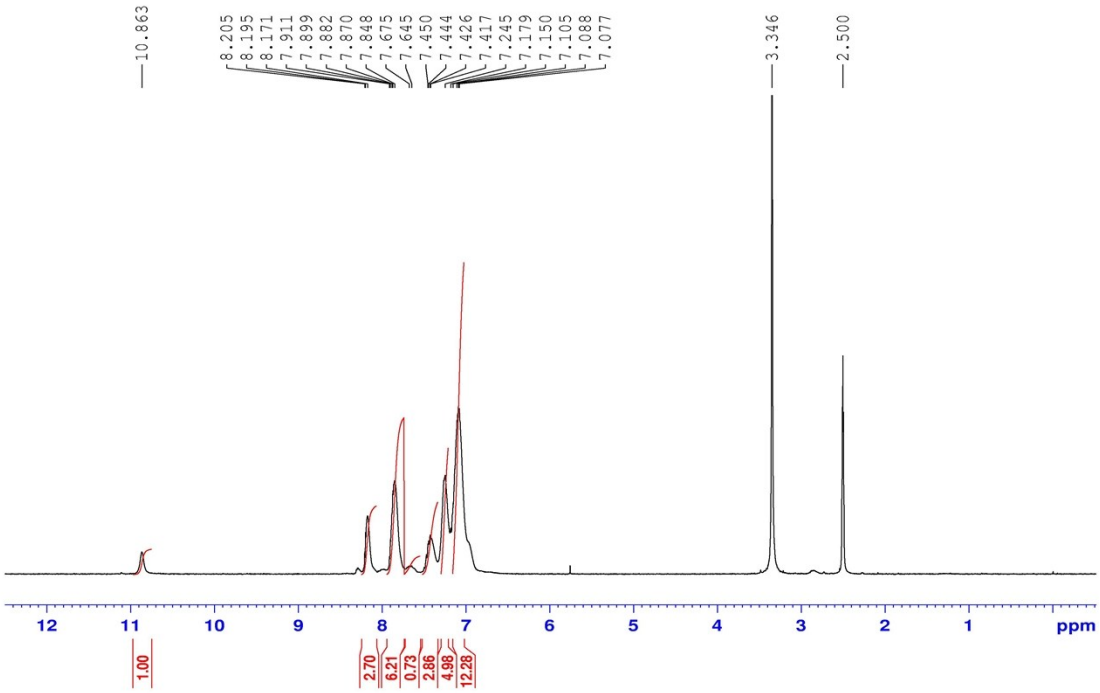


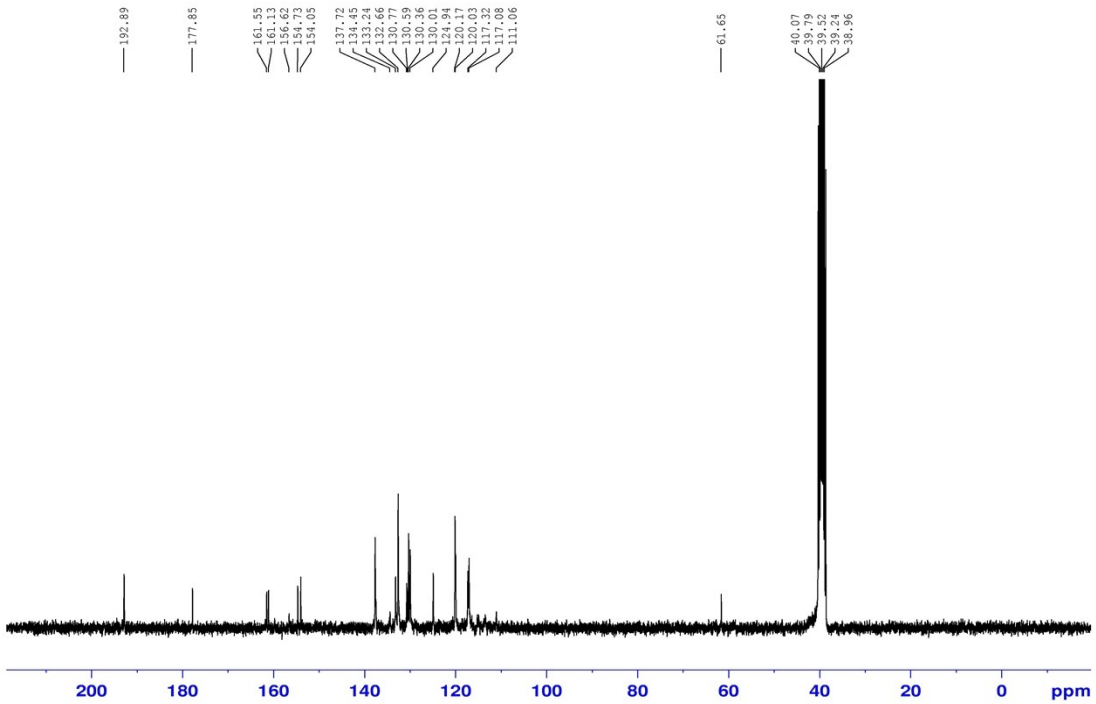
5-Cl-HPAOs


11.006
8.195
7.861
7.692
7.410
7.269
7.099
3.842
2.505
2.417
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.55
5.17
1.24
4.22
5.16
11.35

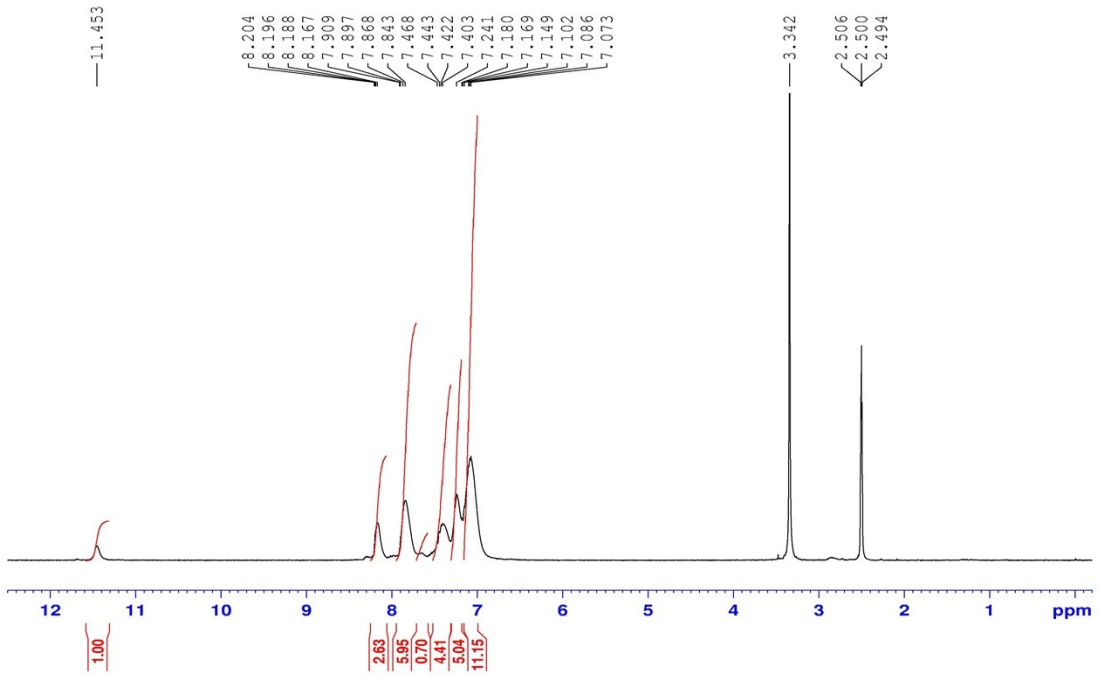

192.91
177.66
161.55
161.13
154.73
154.13
149.12
140.32
137.71
137.60
137.27
132.66
132.44
130.81
130.59
130.36
130.03
129.74
126.32
124.95
120.16
118.72
117.39
117.09
111.77
61.49
40.35
38.68
200
180
160
140
120
100
80
60
40
20
0
ppm

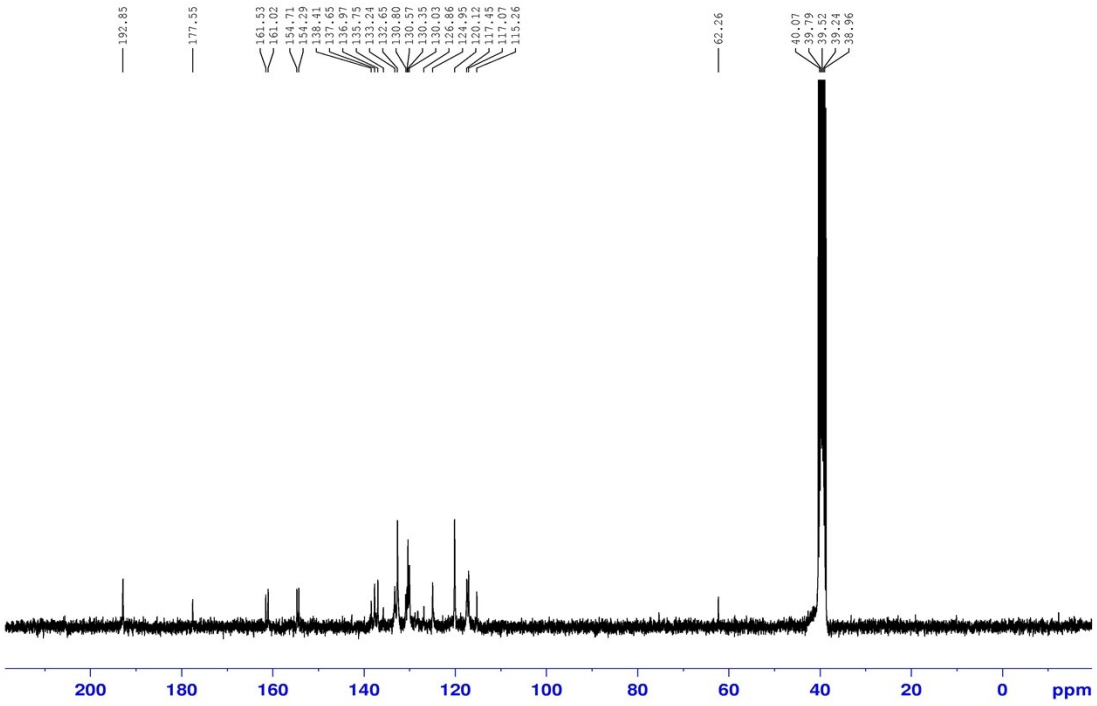
5-F-HPAOs


10.863
8.205
8.195
8.171
7.911
7.899
7.882
7.870
7.848
7.675
7.645
7.450
7.444
7.426
7.417
7.245
7.179
7.150
7.105
7.088
7.077
3.346
2.500
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.70
6.21
0.73
2.86
4.98
12.28

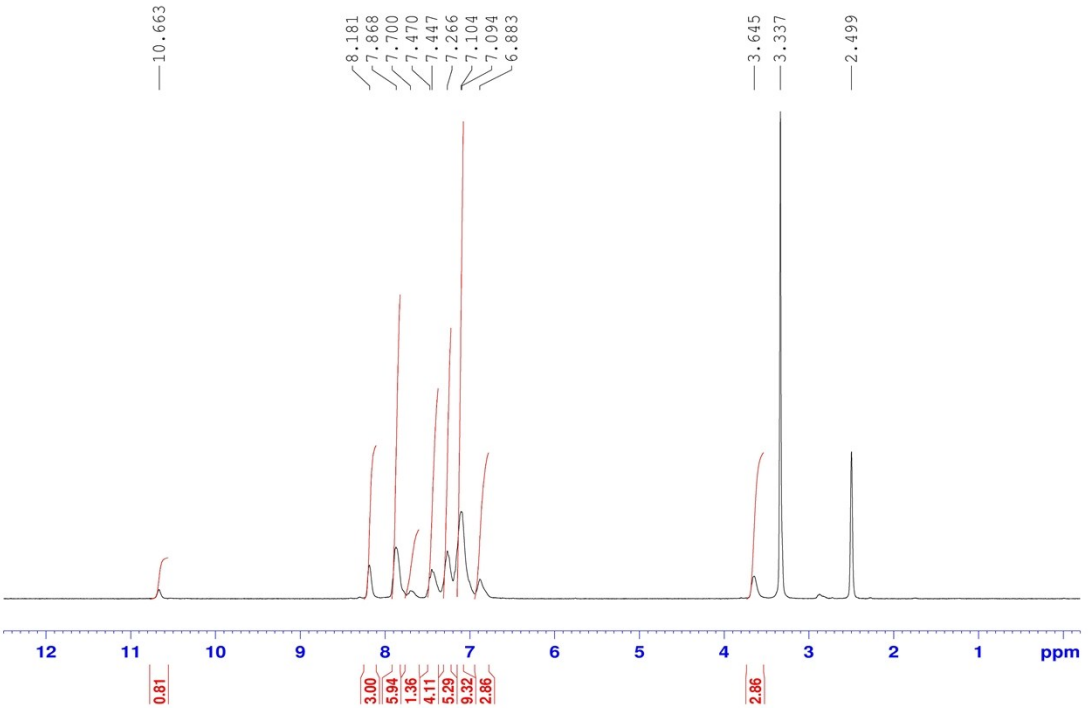

192.89
177.85
161.55
161.13
156.62
154.73
154.05
137.72
134.45
133.24
132.66
130.77
130.59
130.36
130.01
124.94
120.17
120.03
117.32
117.08
111.06
61.65
40.07
39.79
39.52
39.24
38.96
200
180
160
140
120
100
80
60
40
20
0
ppm

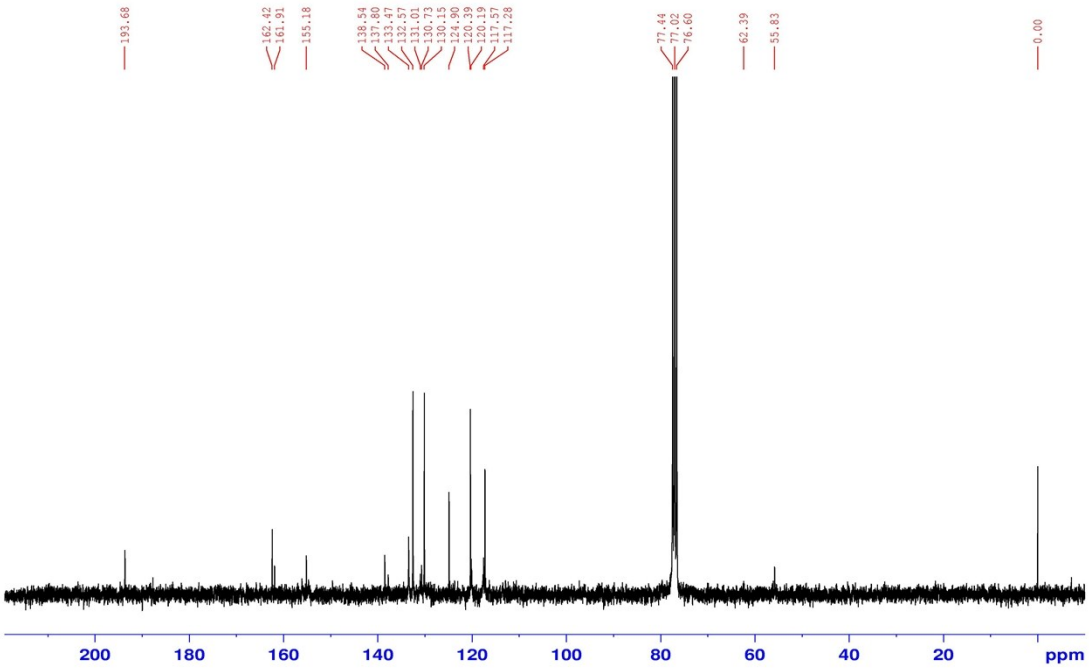
5,7-Cl_2-HPAOs


11.453
8.204
8.196
8.188
8.167
7.909
7.897
7.868
7.843
7.468
7.443
7.422
7.403
7.241
7.180
7.169
7.149
7.102
7.086
7.073
3.342
2.506
2.500
2.494
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.63
5.95
0.70
4.41
5.04
11.15

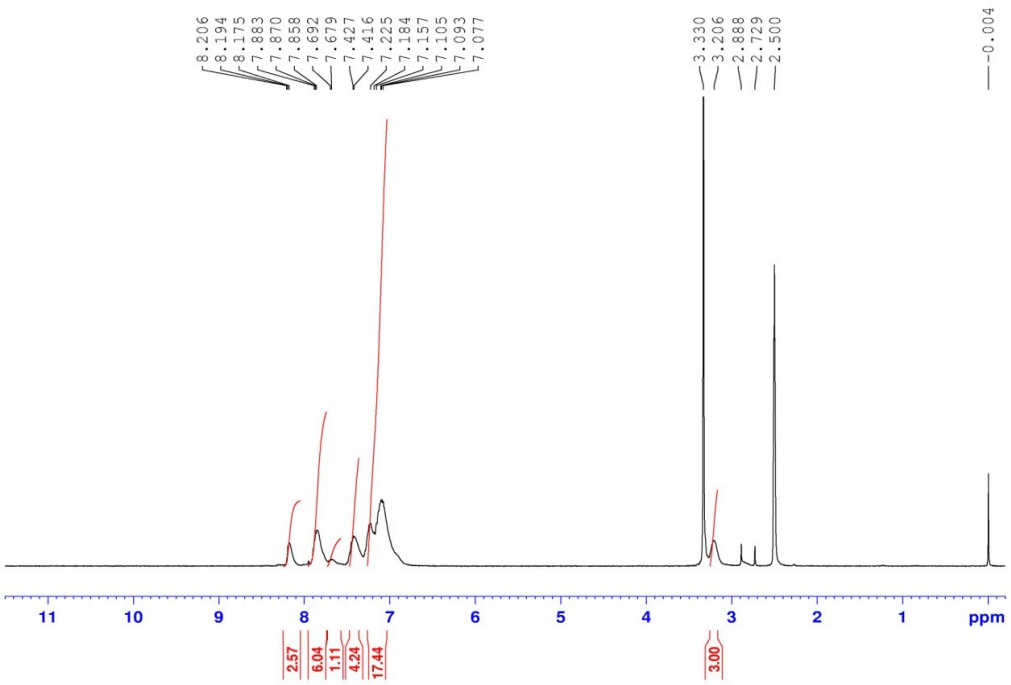

192.85
177.55
161.53
161.02
154.71
154.29
138.41
137.65
136.97
135.75
133.24
132.65
130.80
130.57
130.35
130.03
126.86
124.95
120.12
117.45
117.07
115.26
62.26
40.07
39.79
39.52
39.24
38.96
200
180
160
140
120
100
80
60
40
20
0
ppm

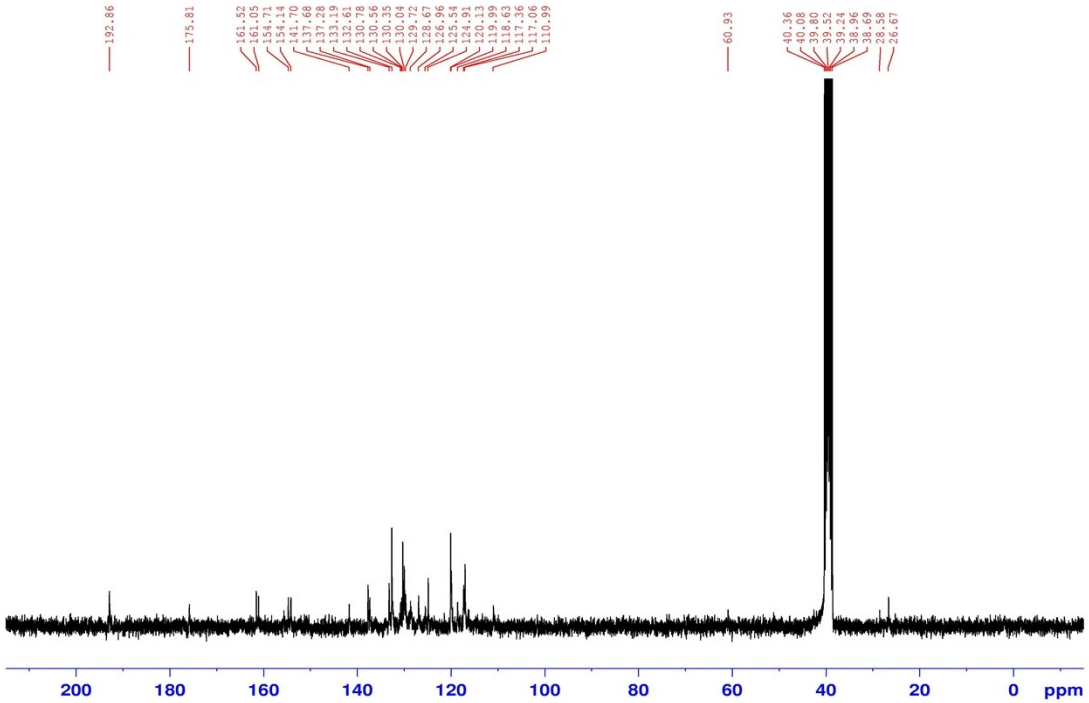
5-MeO-HPAOs


10.663
8.181
7.868
7.700
7.470
7.447
7.266
7.104
7.094
6.883
3.645
3.337
2.499
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.81
3.00
5.94
1.36
4.11
5.29
9.32
2.86
2.86

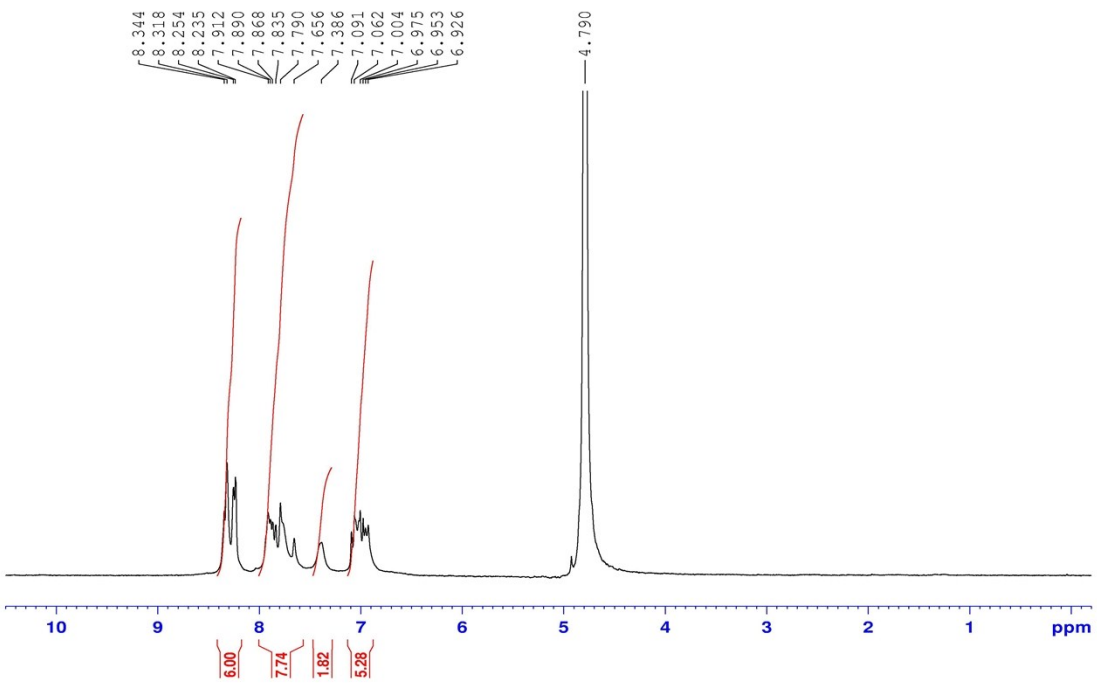

193.68
162.42
161.91
155.18
138.54
137.80
133.47
132.57
131.01
130.73
130.15
124.90
120.39
120.19
117.57
117.28
77.44
77.02
76.60
62.39
55.83
0.00
200
180
160
140
120
100
80
60
40
20
ppm

Methylated 5-Cl-HPAOs





5-Br-SHPAOs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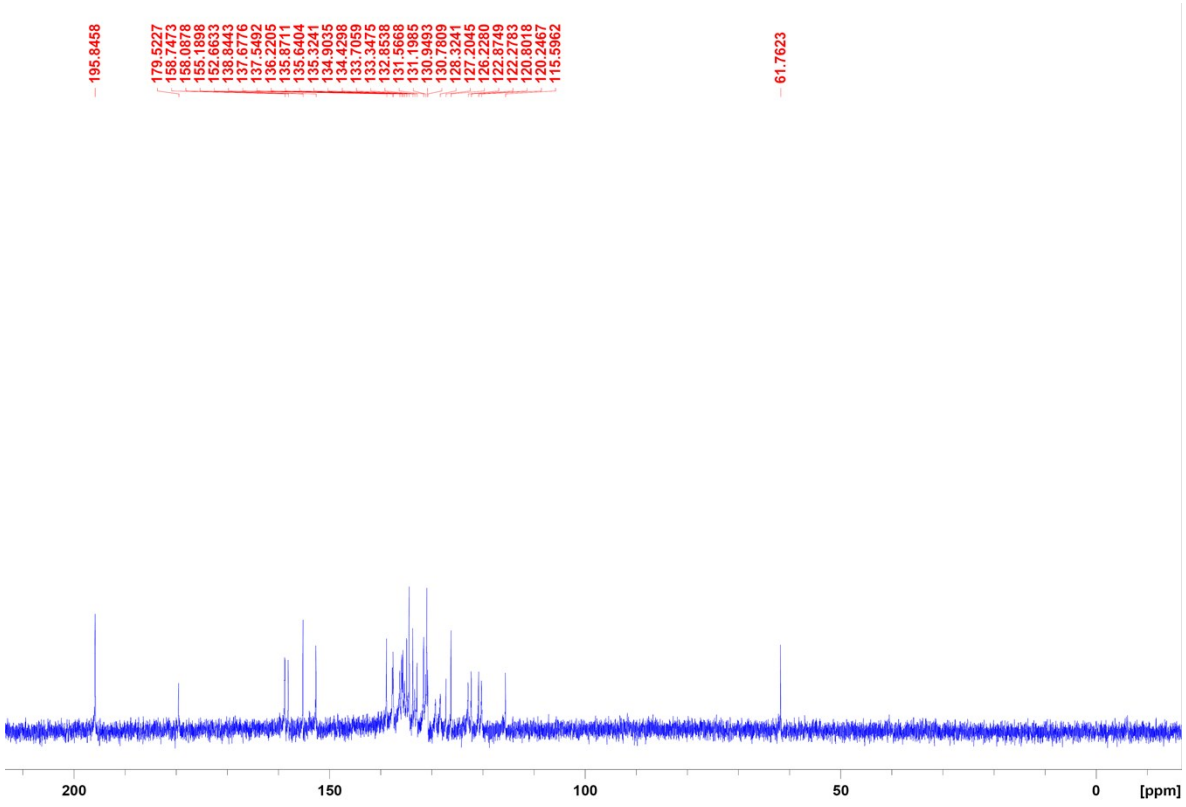
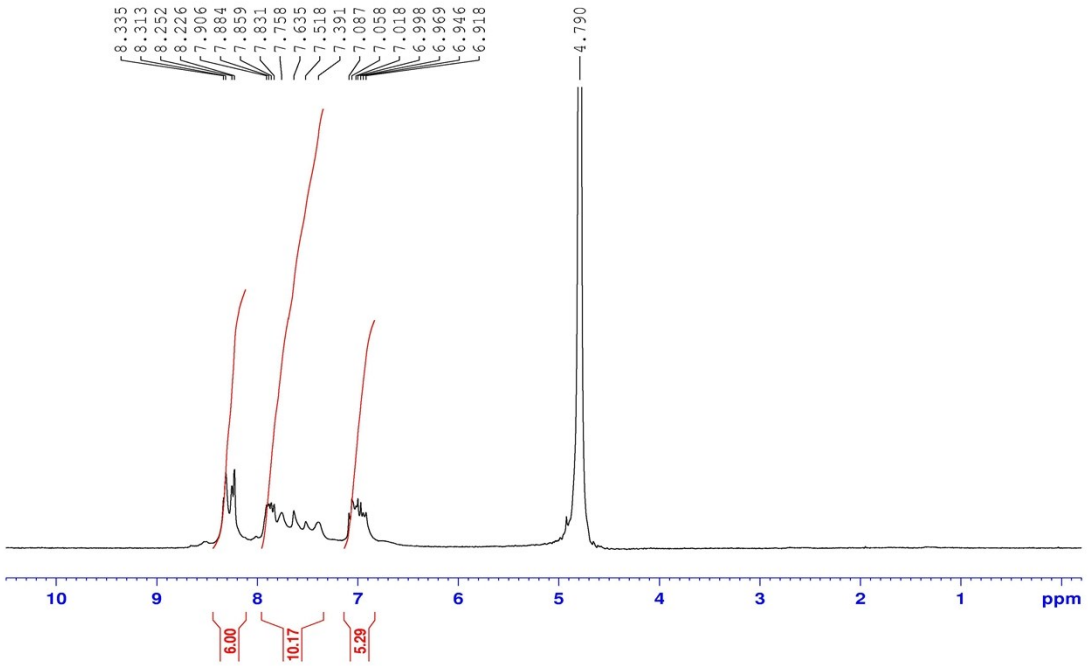
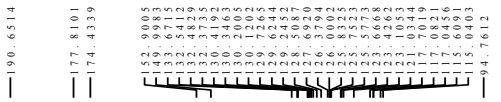
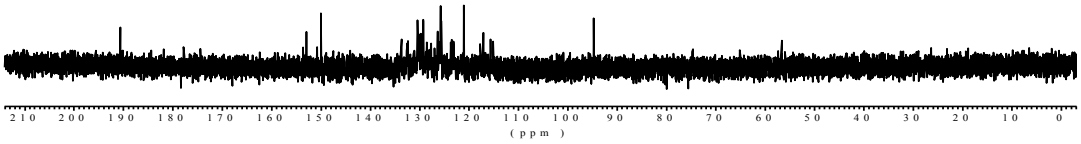
8.318
8.254
8.235
7.912
7.890
7.868
7.835
7.790
7.656
7.386
7.091
7.062
7.004
6.975
6.953
6.926
4.790
10
9
8
7
6
5
4
3
2
1
ppm
6.00
7.74
1.82
5.28


195.8458
179.5227
158.7473
158.0878
155.1898
152.6633
138.8443
137.6776
137.5492
136.2205
135.8711
135.6404
135.3241
134.9035
134.4298
133.7059
133.3475
132.8538
131.5668
131.1985
130.9493
130.7809
128.3241
127.2045
126.2280
122.8749
122.2783
120.8018
120.2467
115.5962
61.7623
200
150
100
50
0
[ppm]

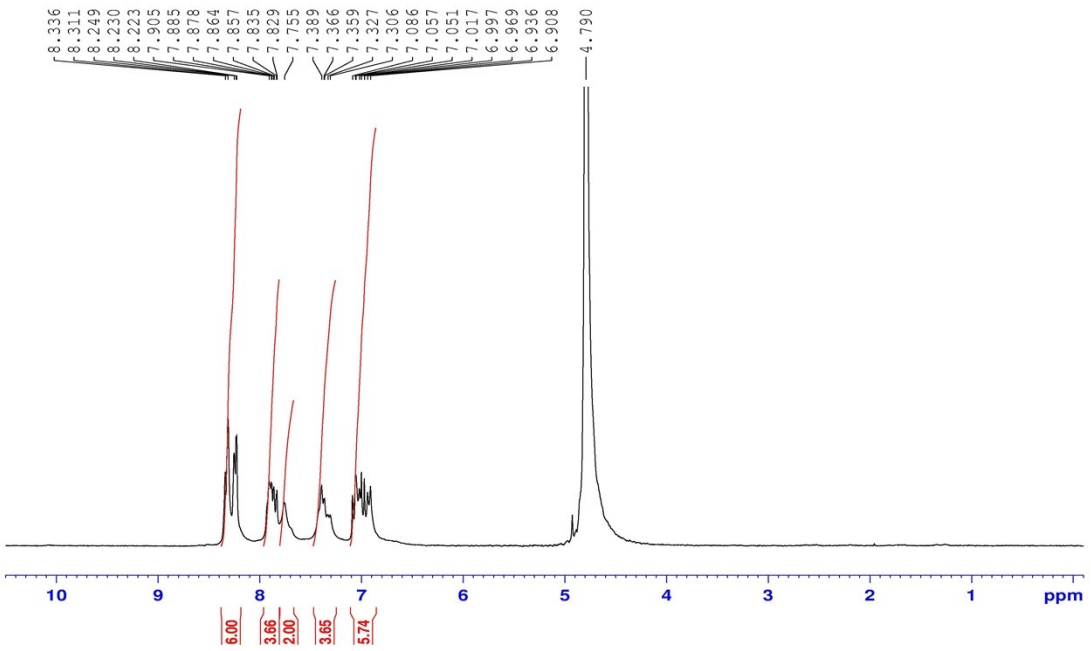
5-Cl-SHPAOs


8.335
8.313
8.252
8.226
7.906
7.884
7.859
7.831
7.758
7.635
7.518
7.391
7.087
7.058
7.018
6.998
6.969
6.946
6.918
4.790
10
9
8
7
6
5
4
3
2
1
ppm
6.00
10.17
5.29


190.6514
177.8101
174.4339
152.9005
149.9983
133.6715
132.5412
132.4429
132.2135
132.1192
130.3463
130.2005
130.1202
129.7265
129.6444
129.2452
128.5087
127.6920
126.3794
126.0902
125.8255
125.7523
125.5773
123.6668
123.4262
123.1053
121.1034
117.7019
117.0821
117.0456
115.6091
115.0403
94.7612
56.6458


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

5-F-SHPAOs


8.336
8.311
8.249
8.230
8.223
7.905
7.885
7.878
7.864
7.857
7.835
7.829
7.755
7.389
7.366
7.359
7.327
7.306
7.086
7.057
7.051
7.017
6.997
6.969
6.936
6.908
4.790
10
9
8
7
6
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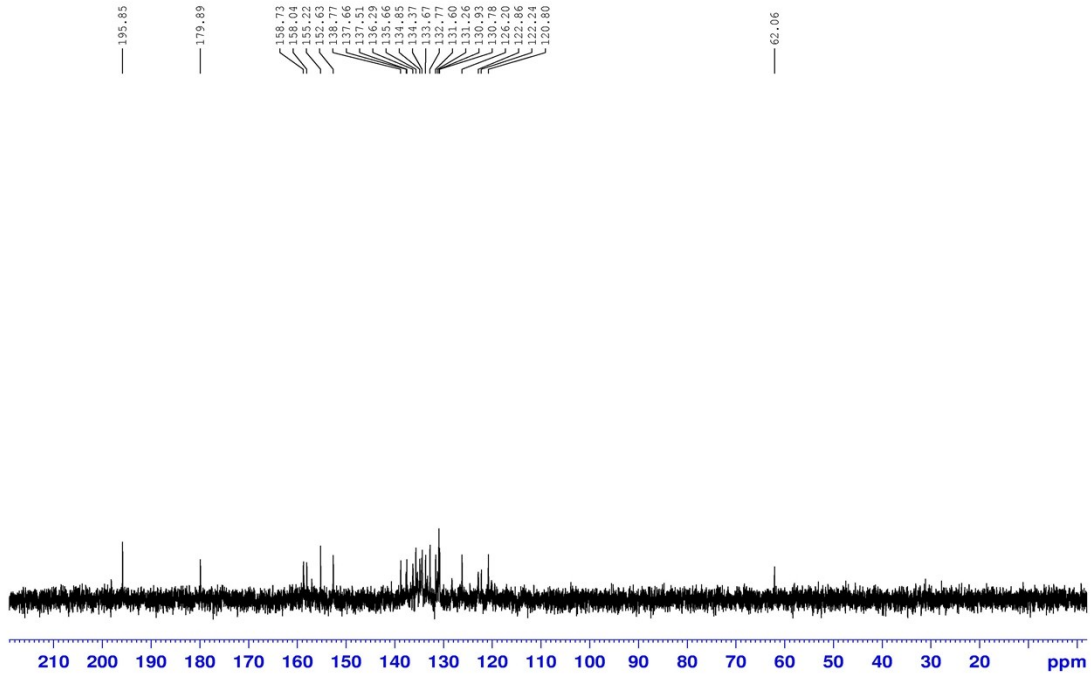
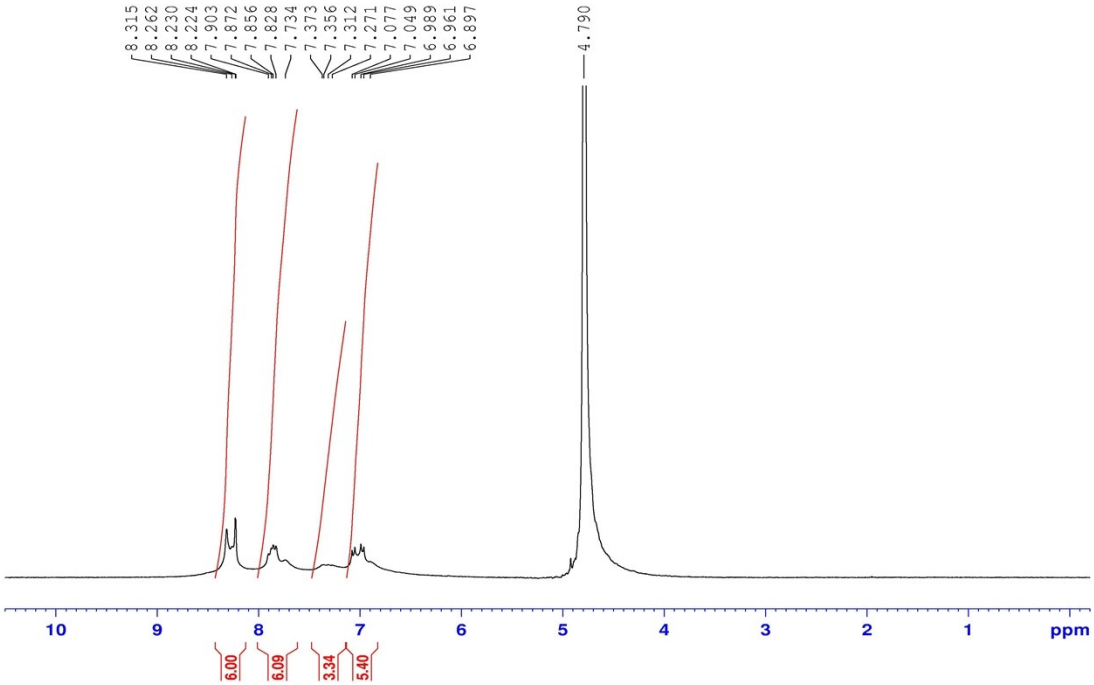
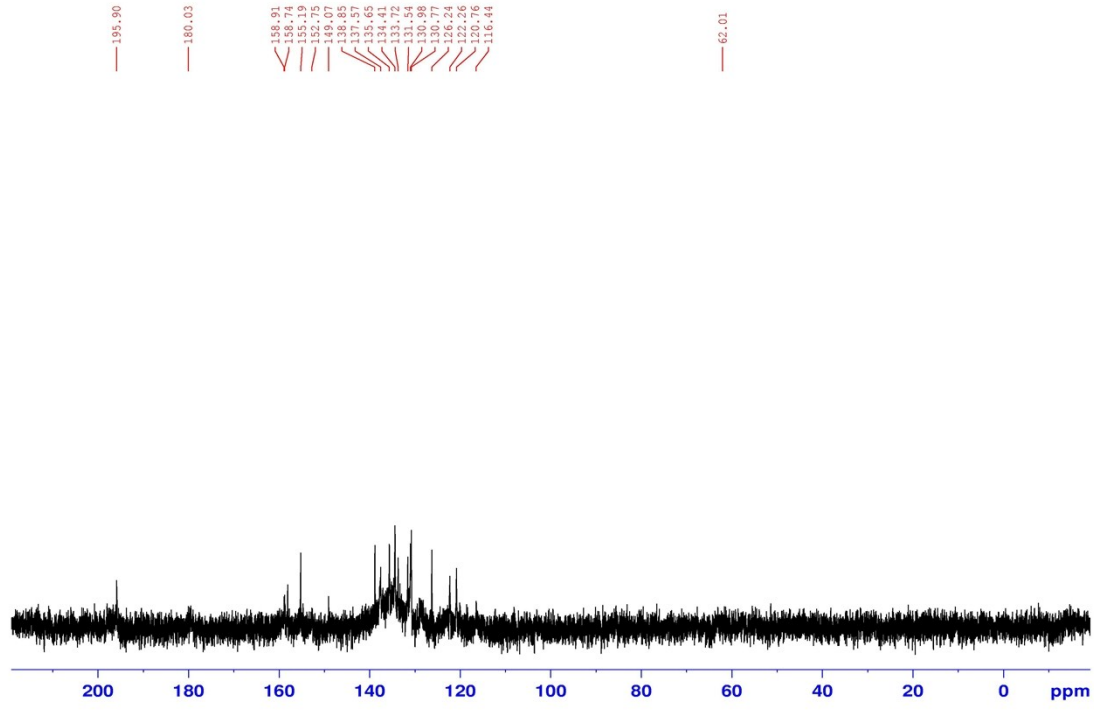
ppm
6.00
3.66
2.00
3.65
5.74

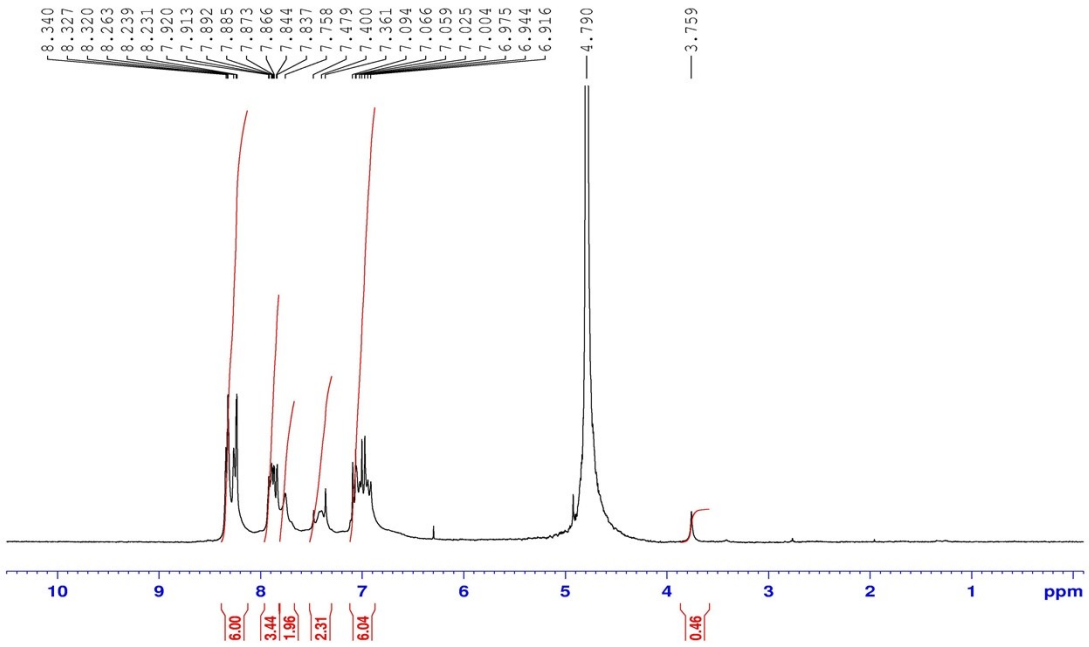

195.85
179.89
158.73
158.04
155.22
152.63
138.77
137.66
137.51
136.29
135.66
134.85
134.37
133.67
132.77
131.60
131.26
130.93
130.78
126.20
122.86
122.24
120.80
62.06
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

5,7-Cl_2-SHPAOs





5-MeO-SHPAOs


8.340
8.327
8.320
8.263
8.239
8.231
7.920
7.913
7.892
7.885
7.873
7.866
7.844
7.837
7.758
7.479
7.400
7.361
7.094
7.066
7.059
7.025
7.004
6.975
6.944
6.916
4.790
3.759
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4
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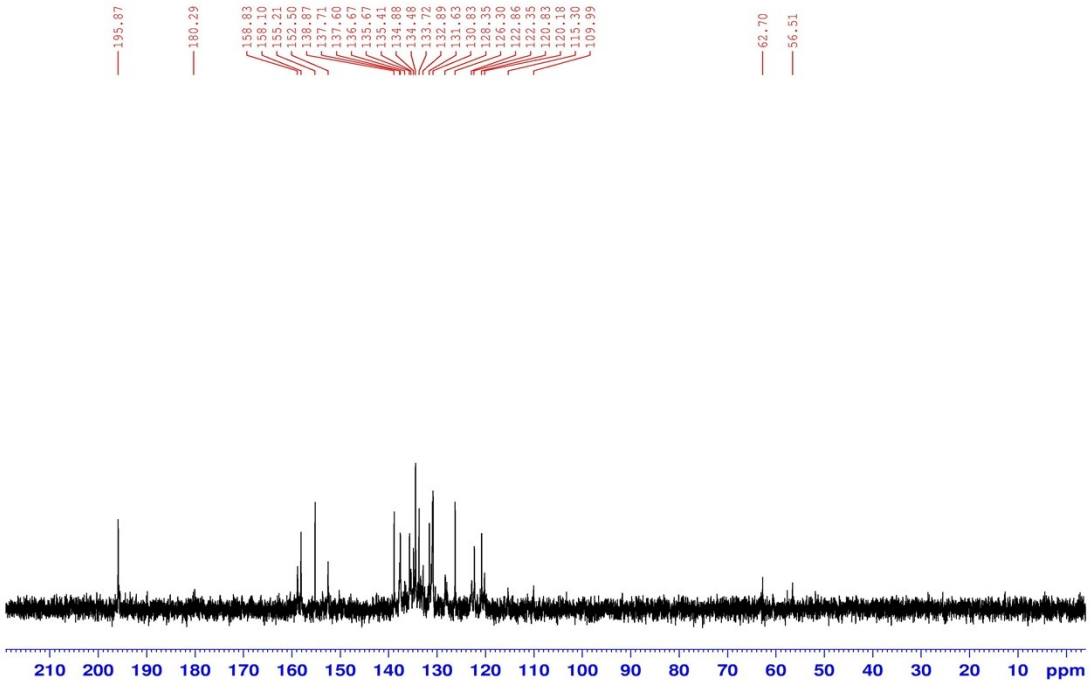
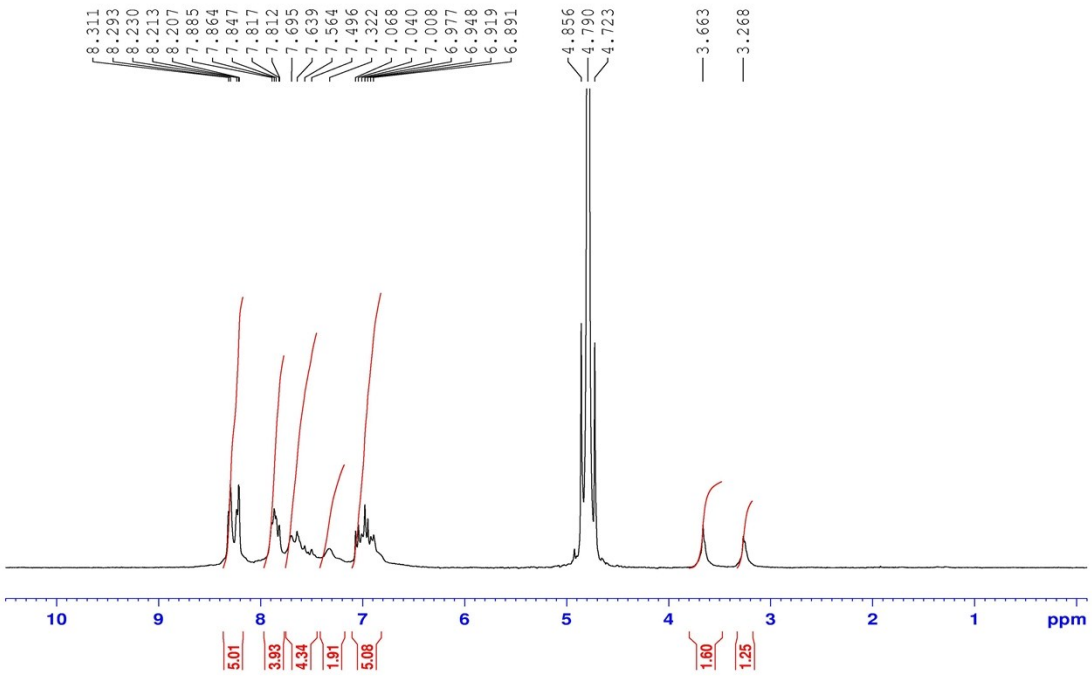
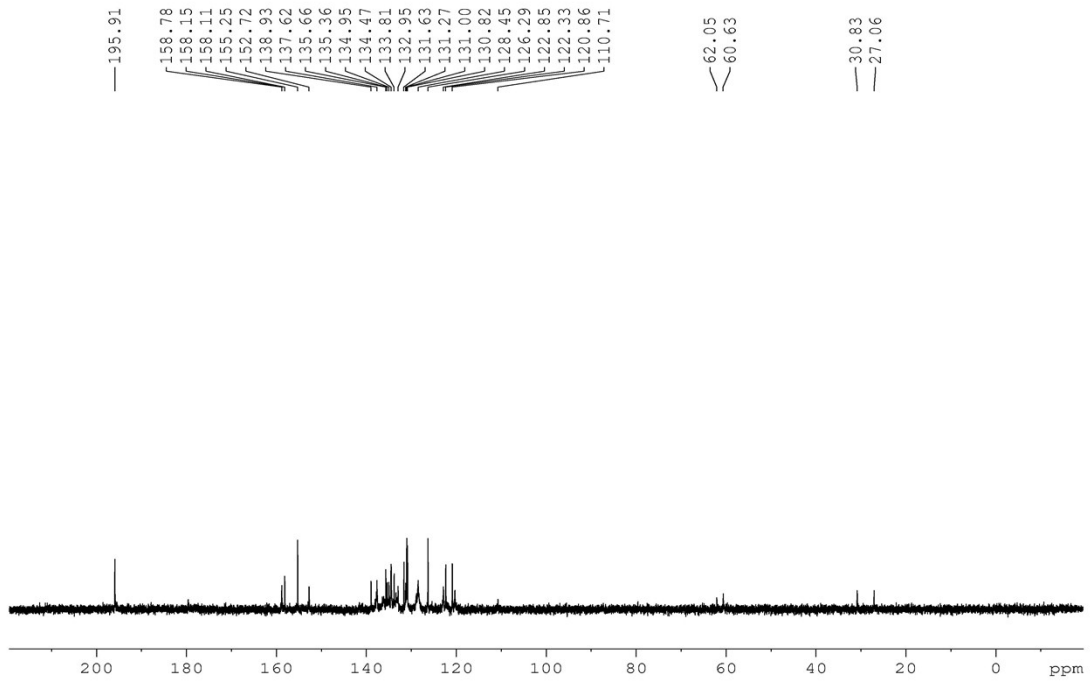
6.00
3.44
1.96
2.31
6.04
0.46

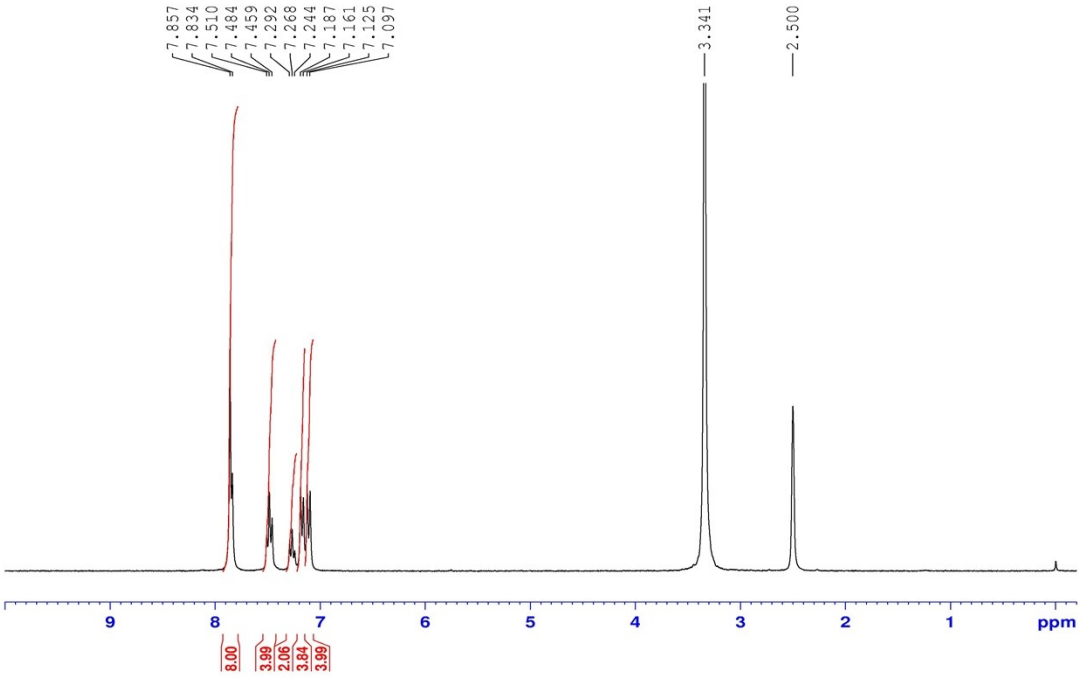

195.87
180.29
158.83
158.10
155.21
152.50
138.87
137.71
137.60
136.67
135.67
135.41
134.88
134.48
133.72
132.89
131.63
130.83
128.35
126.30
122.86
122.35
120.83
120.18
115.30
109.99
62.70
56.51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Methylated 5-Cl-SHPAOs

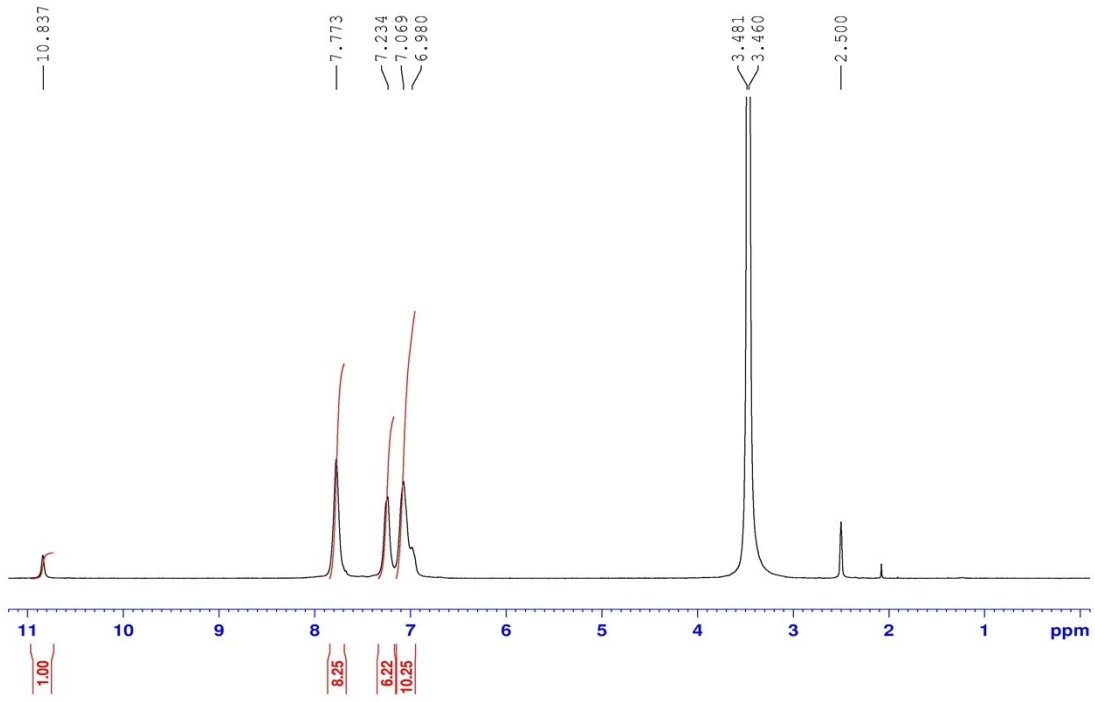




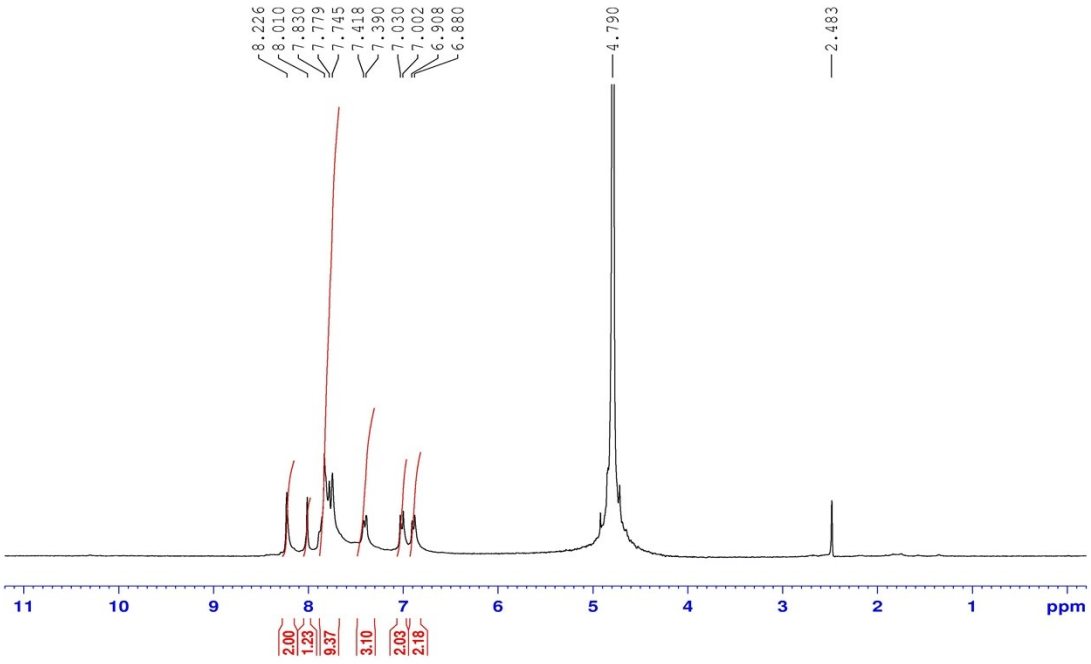
B_2 Monomer

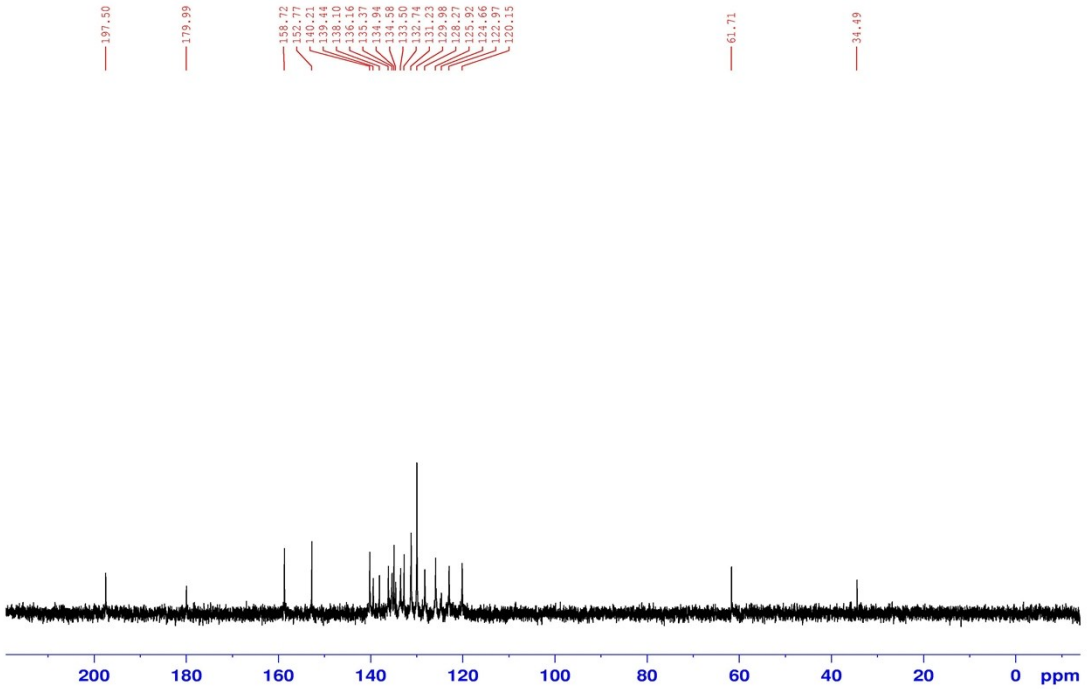


Linear polymer

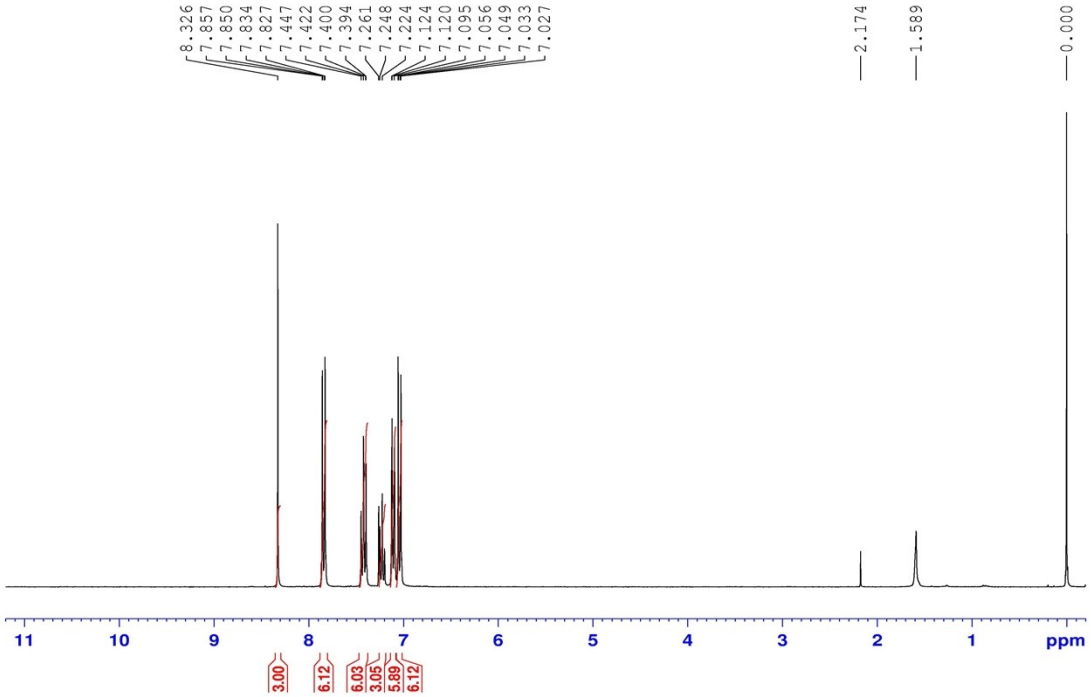


Sulfonated linear polymer (SLP)

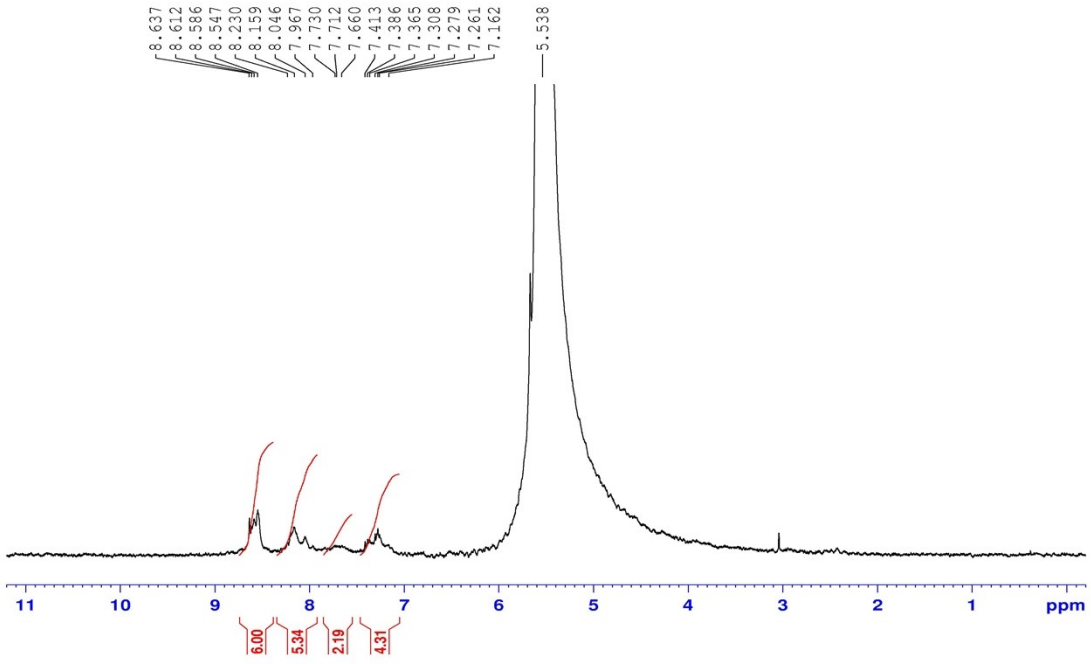




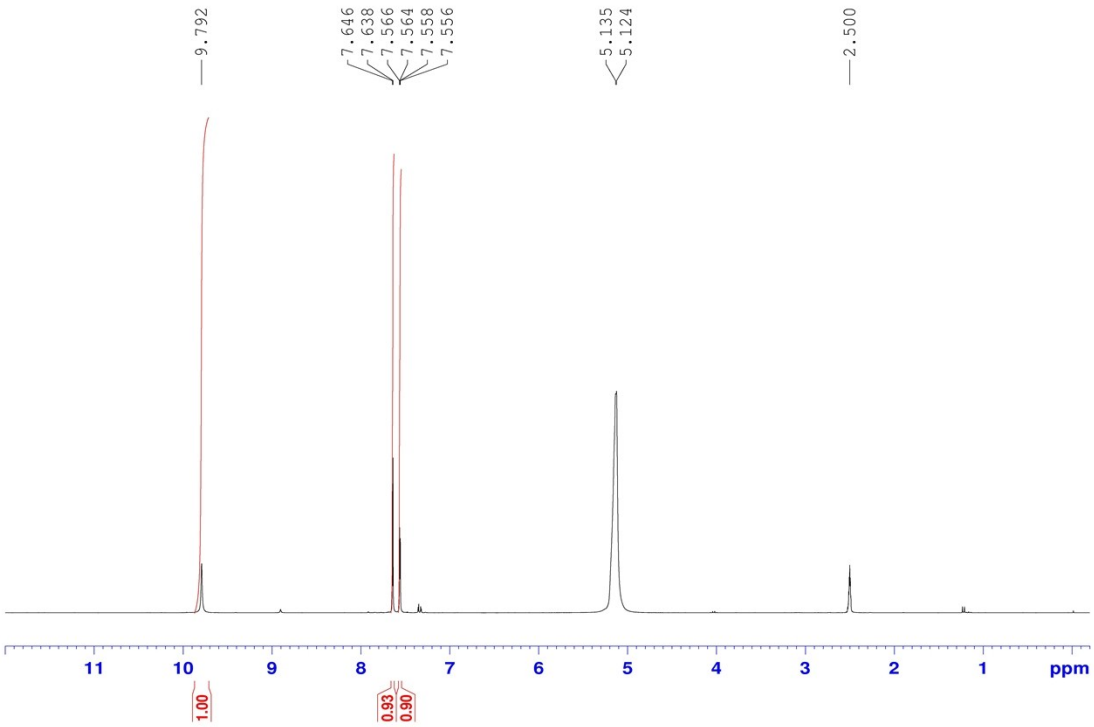
B_3 monomer

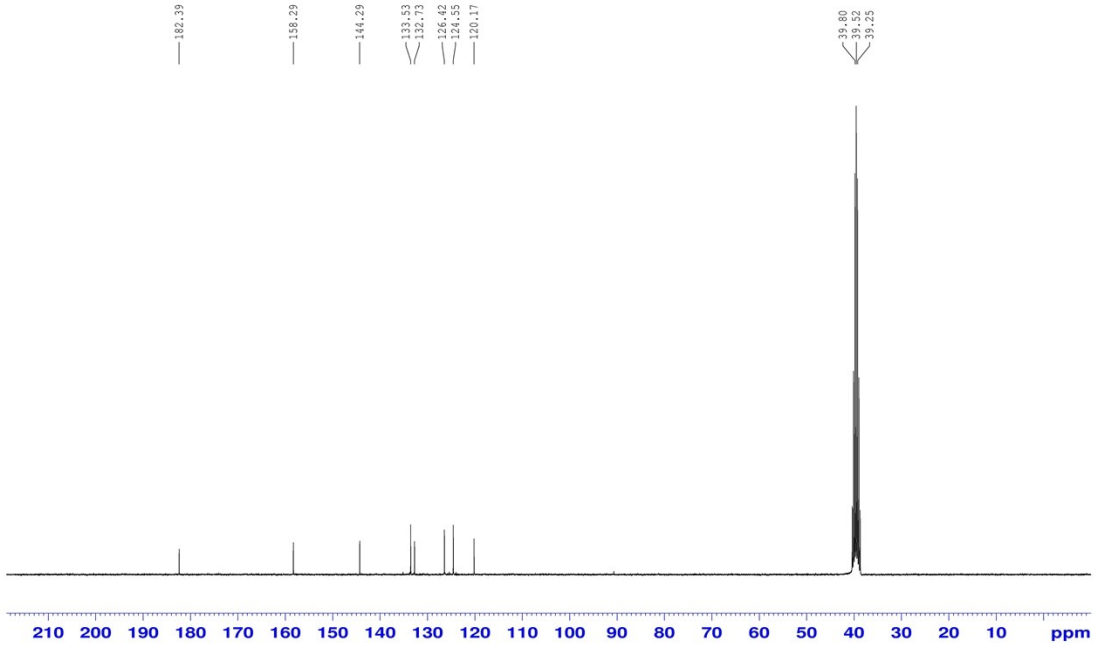


SO_3H-B_3

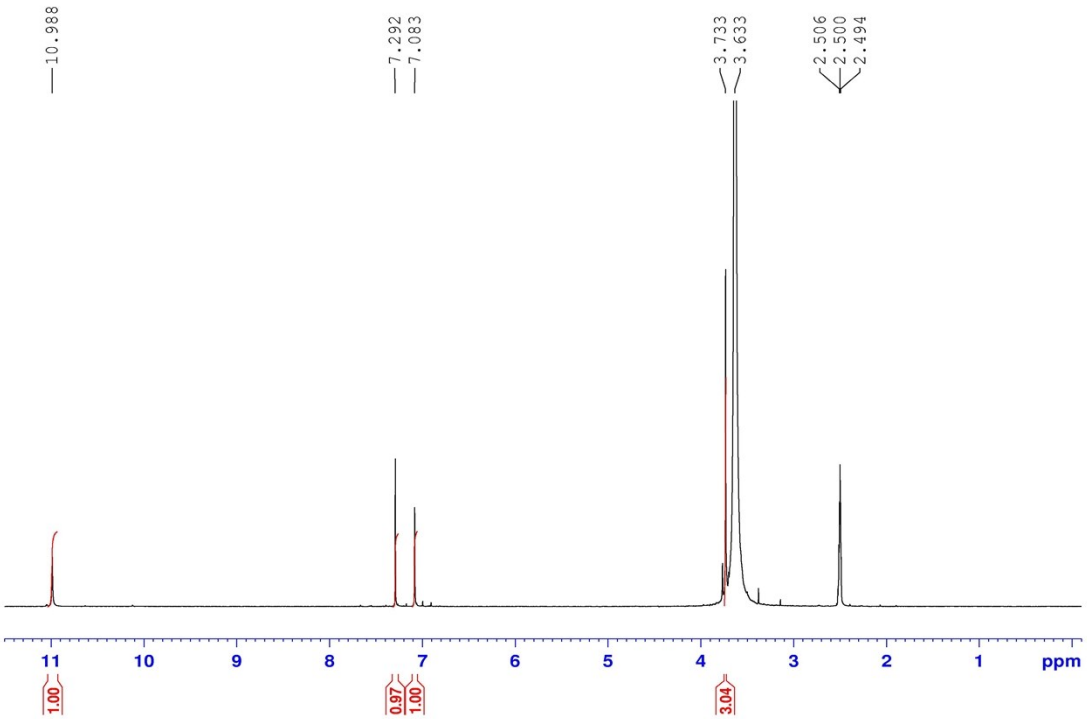


SO_3H-5-Cl-Isatin

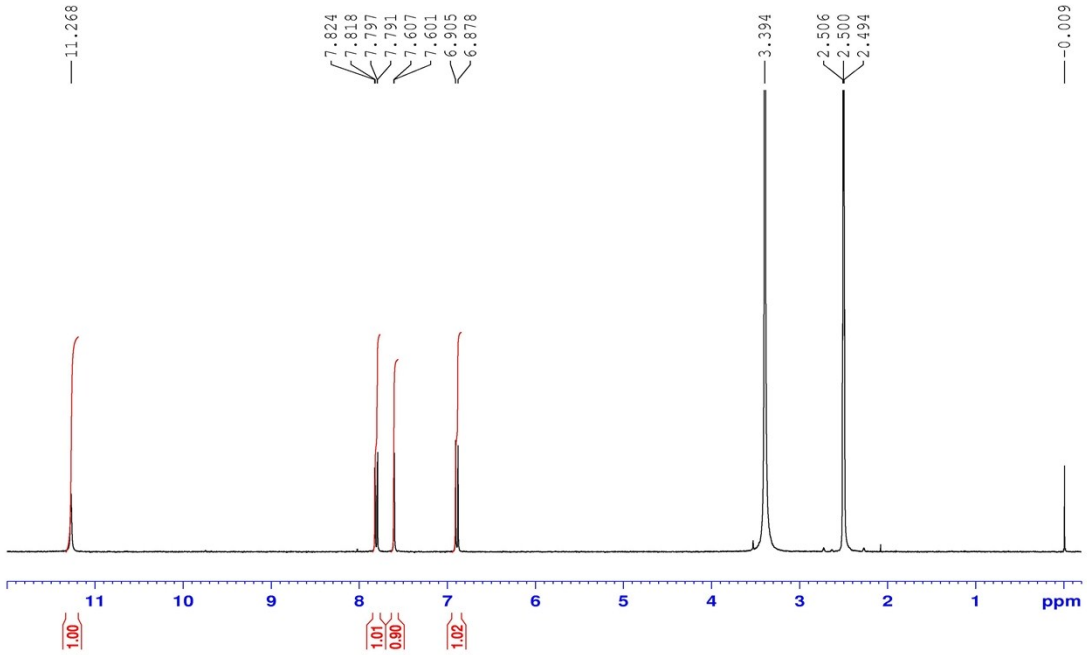




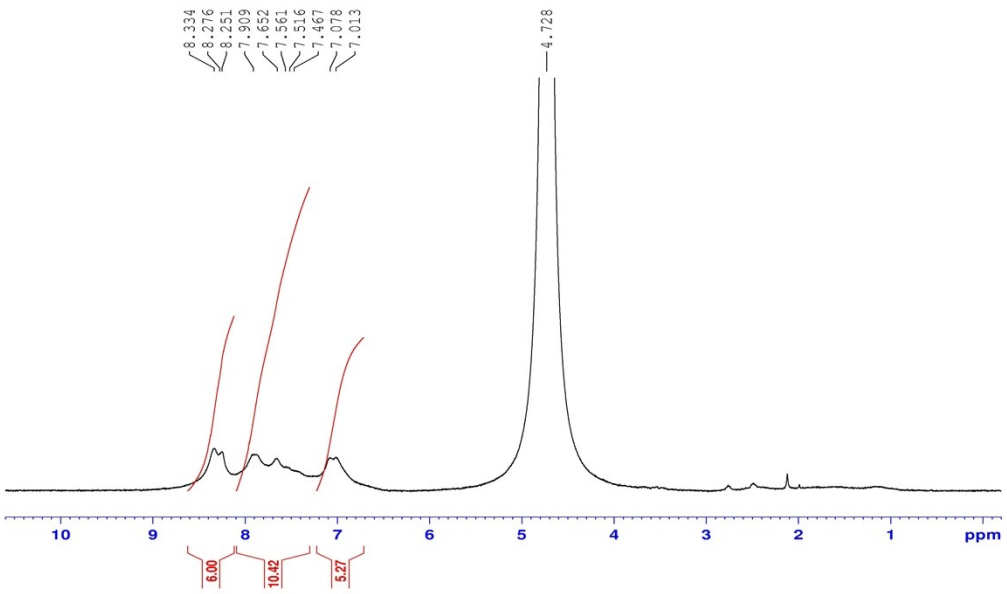
SO_3H-5-MeO-Isatin



SO_3H-Isatin



^{1}H NMR of recycled 5-Cl-SHPAOs



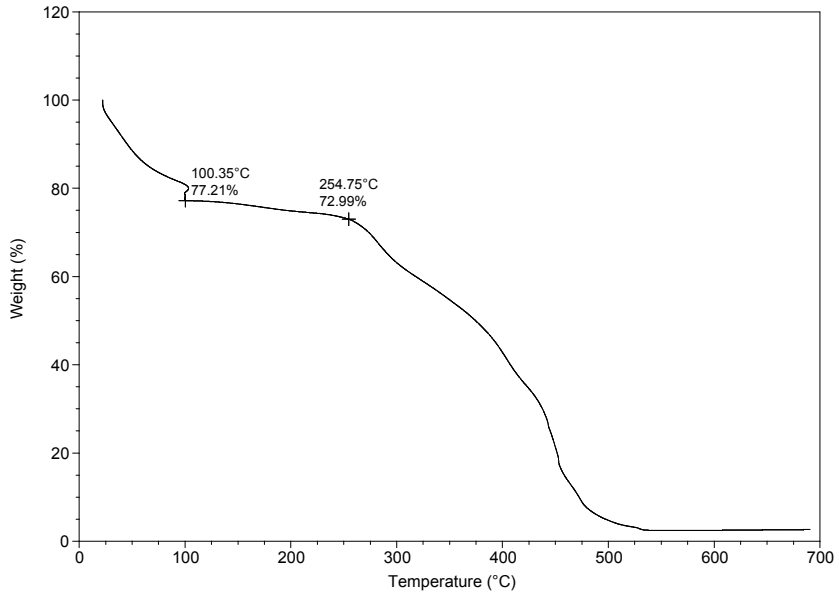


Figure S12. TGA result of the recovered 5-Cl-SHPAOs catalyst after third recycling cycle

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