Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Hydroxyethyl sulfone based reactive coalescing agents for low-VOC waterborne coatings

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1. General information

Methods: Analytical thin layer chromatography (TLC) separations were performed on Merck's silica gel 60 F_{254}-precoated aluminum sheets. Visualization was accomplished with UV light and/or aqueous potassium permanganate solution (0.1 N) stain.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained using a Bruker 400 UltraShield Spectrometer operating at 400 MHz and 100 MHz respectively. Chemical shifts for ^{1}H NMR were recorded in parts per million (ppm) downfield from proton signal of residual non-deuterated solvent (δ 7.26 ppm for $CDCl_3$ and 4.79 ppm for D_2O) as the internal signal. Coupling constants are indicated in Hertz (Hz). For ^{13}C NMR spectra, chemical shifts are reported relative to the central line of the triplet at δ 77.2 ppm for non-deuterated residuals originated from $CDCl_3$. The following abbreviations are used for spin multiplicity: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet and br=broad.

HPLC analysis was performed on Agilent 1200 series. HPLC-MS was performed on Agilent 1260 infinity equipped with Agilent 6120 quadrupole LC/MS system. Phenomenex C18 column (Gemini 5μm 110 Å, LC Column 150 x 4.60 mm) was used for the HPLC analysis. Trifluoroacetic acid (1%) in water and Trifluoroacetic acid (1%) in acetonitrile were used as mobile phase under the gradient flow (20 min) starting from 95% H_2O to 5% H_2O. 0.5 mL/min flow, 25 °C, 254 nm. Mass spectrometry was run by the electrospray ionization time-of-flight (ESI-TOF) mode on an Agilent 6210 mass spectrometer.

The particle size and MFFT of the latex were measured respectively using Malvern DLS instrument and Rhopoint instrument (operating range, -10˚C to 90˚C). For MFFT measurements, the desired temperature range has been set and waited until the instrument is ready for coating. Emulsions of latex 1, latex 2 and Poly(MMA-*co*-^{n}BA-*co*-2HEMA) latex were independently applied using 75 micron cube applicator. Film formation typically takes place in 10-15 mins and MFFT of the free latices were measured in triplicate. 2 wt% of commercial coalescing agents (BC and EEH) and HES based compounds (HES-BC and HES-EEH) were independently dispersed with latices (latex 1, latex 2 and Poly(MMA-*co*-^{n}BA-*co*-2HEMA latex). The resultant dispersion was applied using the same film applicator. When films were formed, the temperature cursor was moved on the track of the film and noted down the temperature where the film coalesced over 90% of the track width. The average values from three different measurements were taken for the figure 4.

2. **Volatility measurements in terms of percentage of weight loss**

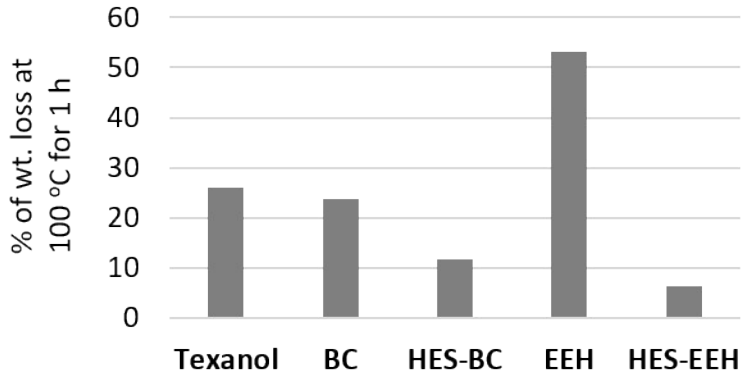


Fig. S1 Percentage of weight loss measured at 100 °C in 1h for HES based RCAs (HES-BC and HES-EEH) and commercial CAs (Texanol, BC and EEH).

3. HPLC analysis of HES-VS equilibrium reaction mixtures

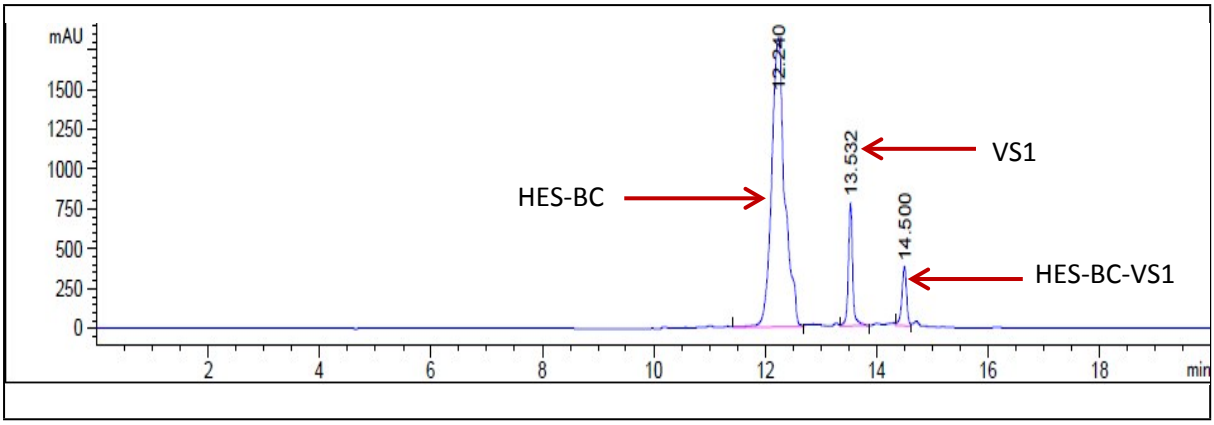


Fig. S2 HPLC spectrum of equilibrium studies of HES-BC *vs.* VS1. The formation of -VS1 and HC-BC-VS1 adduct were shoun after 15 days of drying.

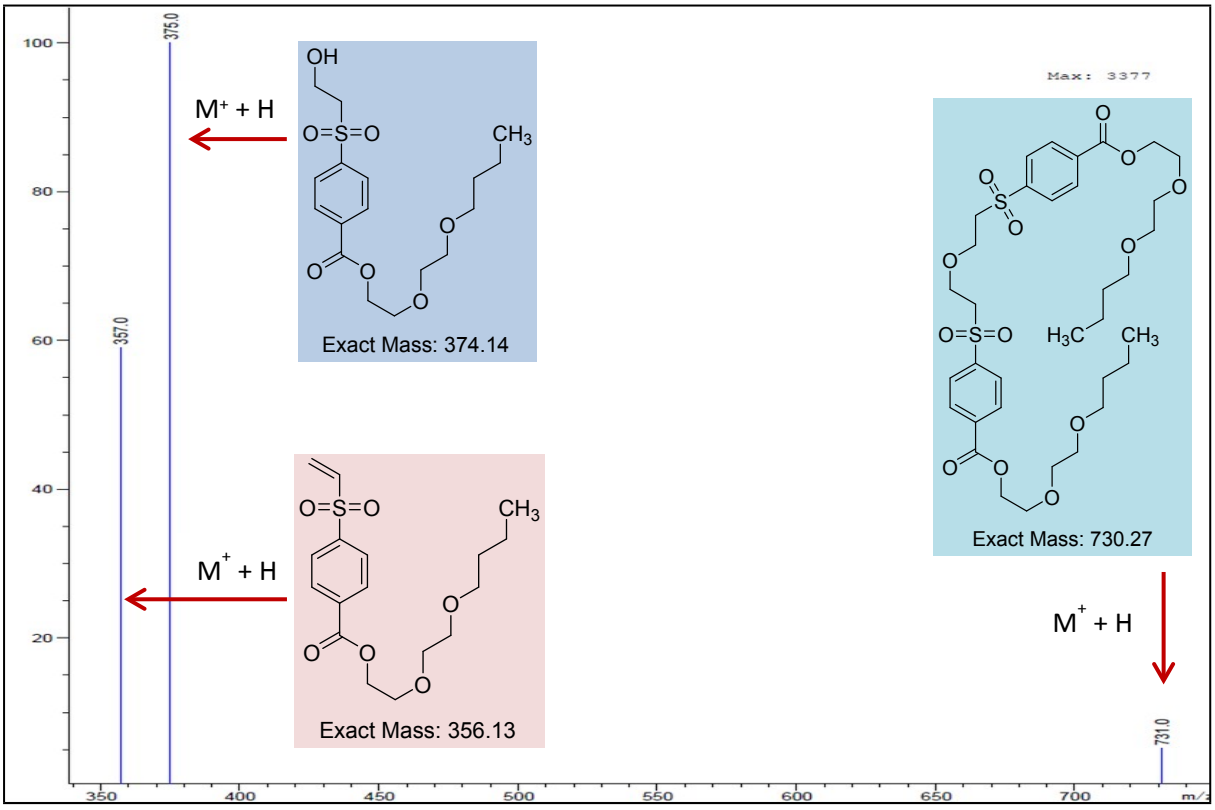


Fig. S3 Selective ion monitoring mass spectra for the identification of HES-BC, VS1 and HES-BC-VS1.

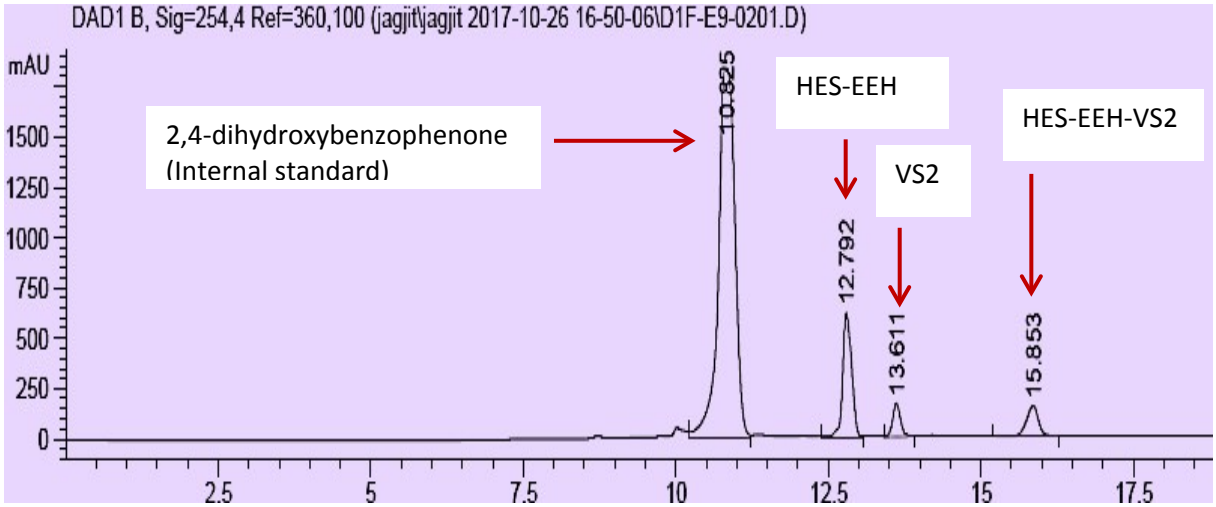


Fig. S4 HPLC spectrum of equilibrium studies of HES-EEH *vs*. VS2. The formation of VS2 and HC-EEH-VS2 adduct were shown after 15 days of drying.

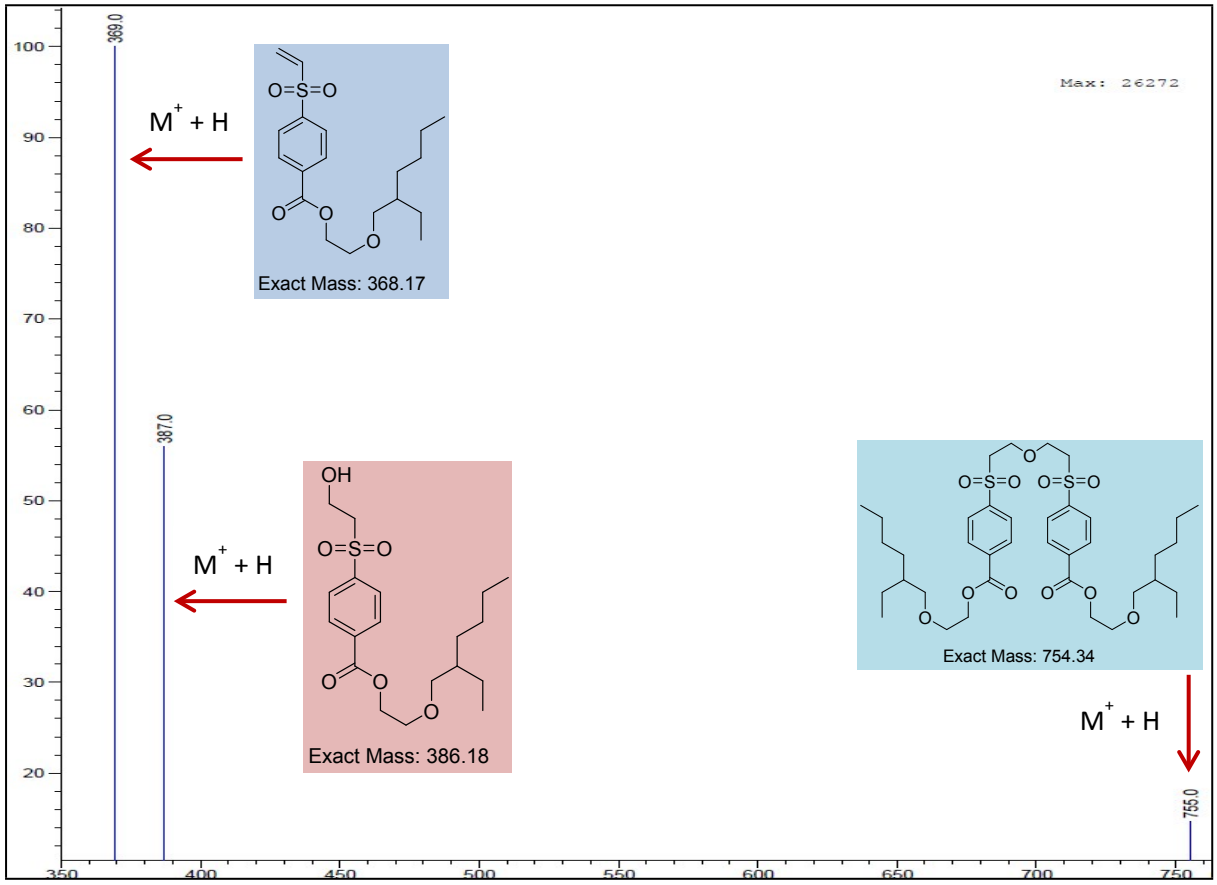


Fig. S5 Selective ion monitoring mass spectra for the identification of HES-EEH, VS2 and HES-EEH-VS2.

4. HES-VS equilibrium studies in triton-B solution

To acetone solution of HES-BC (10 mg, 0.027 mmol), Triton-B solution (1 mL, pH was adjusted to approx.. 10 by diluting with water) was added. The mixture was homogenized by constant stirring before transferring to a Petri dish quantitatively, and allowed to dry at 25 °C. For reliable quantification, the experiments were conducted using four Petri dishes for analysing the samples on various days (1, 4, 10 and 15 days). The contents in the Petri dish was suspended in $CDCl_3$ (1 mL) containing 2,6-difluorobenzaldehyde (3.26 mg, 0.023 mmol) as an internal standard. The mixture was filtered using a micro filter and submitted for NMR analysis. The experiments were conducted in duplicate. The graph was plotted between the concentrations of HES, VS and HES-VS adduct present against the number of days. About 61.7% of HES was found to be converted to either VS1 or HES-BC-VS1.

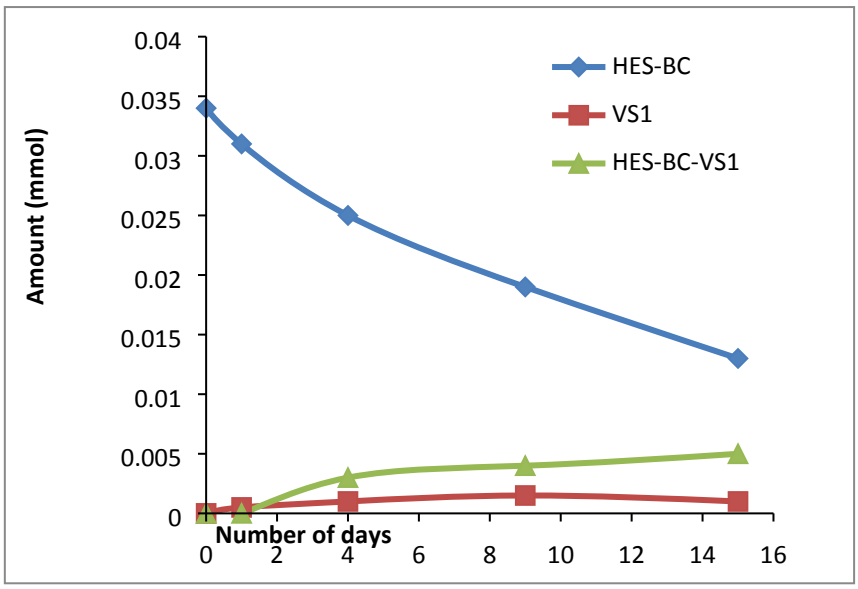
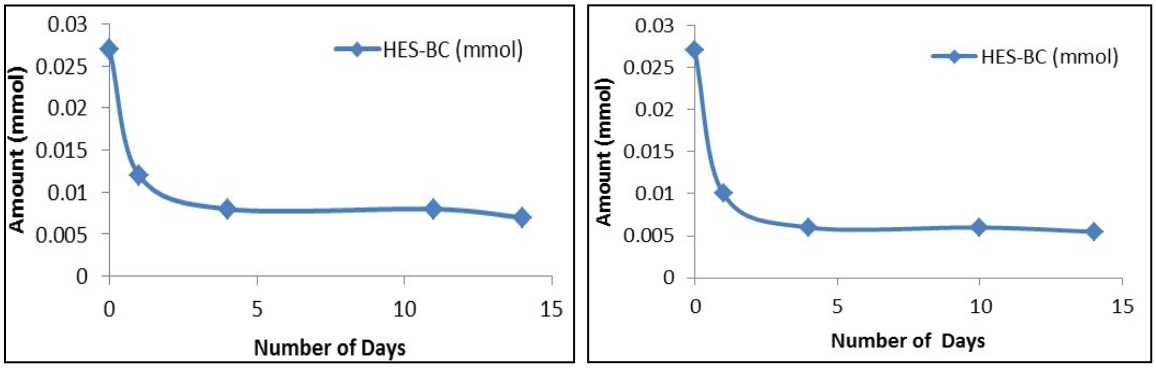


Fig. S6 Rate of consumption of HES-BC during equilibrium studies in the presence of Triton-B. 61.7% of HES was found to be converted to either VS 1 or HES-BC-VS1.

5. Reactivity of HES-BC with HEMA anf TBAEMA

HES-BC (10 mg, 0.027 mmol) was dissolved in acetone, HEMA (30 mg, 8.5 equiv.) and 1 mL of 0.1 M $NaHCO_3$ was added. The contents were stirred at room temperature for 1 h, discharged to a Petri dish and left in a fumehood for 24 hours. After drying, the content was taken in methanol and analysed by LCMS. Reactivity of HES-BC with TBAEMA (30 mg, 6.0 equiv.) was carried out in a similar manner like HEMA. The reaction progress was obtained by quantifying the unreacted HES-BC by NMR using an internal standard on various days as described in figure S6. The mass analysis of dry residue containing HEMA (Figure S7) and TBAEMA (Figure S8) are given.



(a) **(b)**

Fig. S7 Progress of reactivity of HES-BC with representative monomers, 2-hydroxyethyl methacrylate (HEMA) **(a)** and *tert*-butylaminoethyl methyacrylate (TBAEMA) **(b)**. Amount of unreacted HES was determined by NMR using an internal standard by NMR.

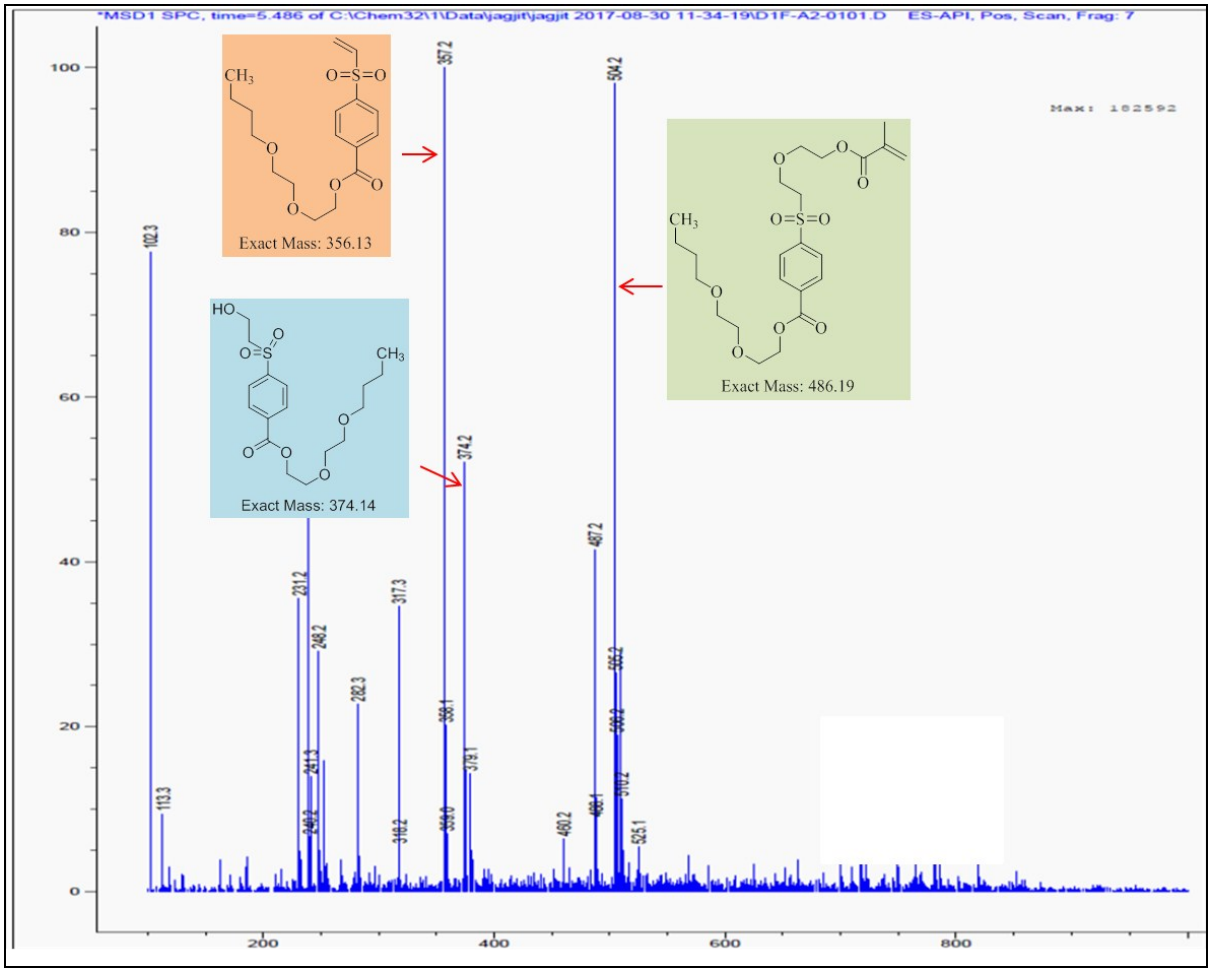


Fig. S8 Mass analysis of dry residue obtained by the dispersion of HES-BC and HEMA after 4 days.

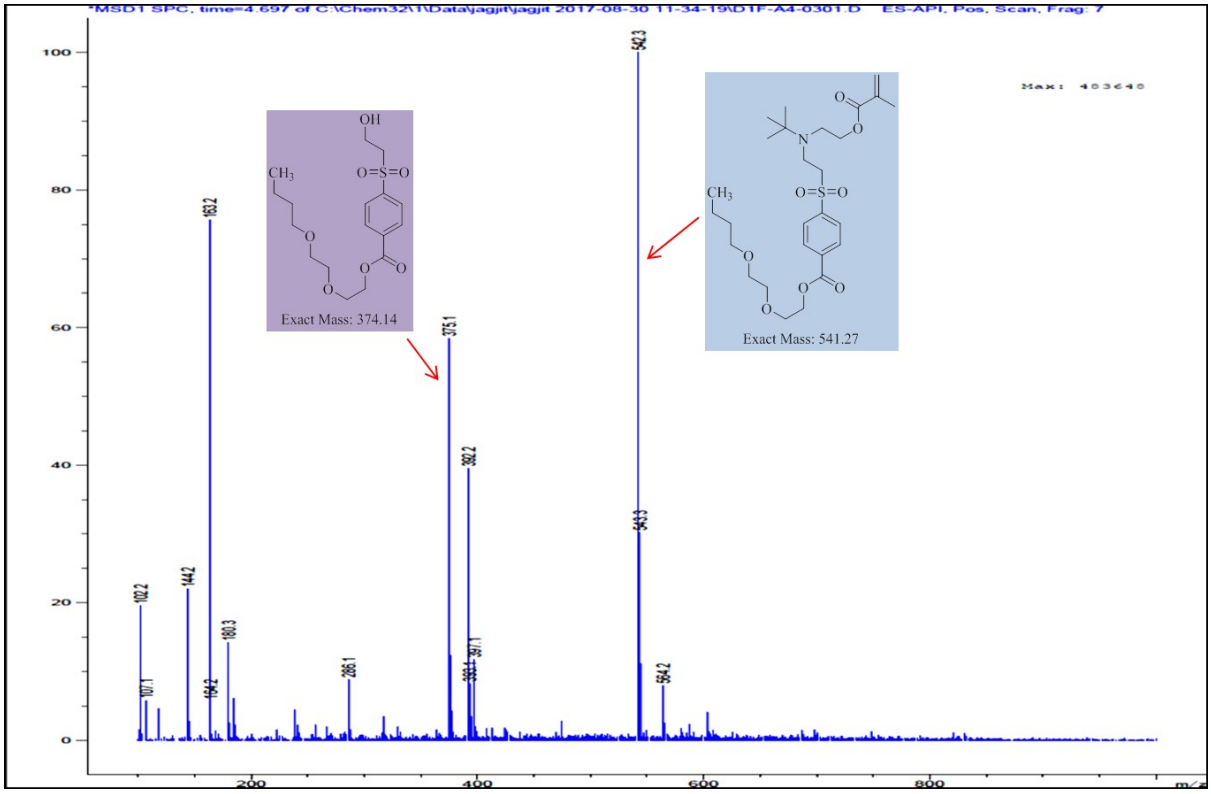


Fig. S9 Mass analysis of dry residue obtained by the dispersion of HES-BC and TBAEMA after 4 days.

6. ^{1}H and ^{13}C NMR Spectra of all the compounds

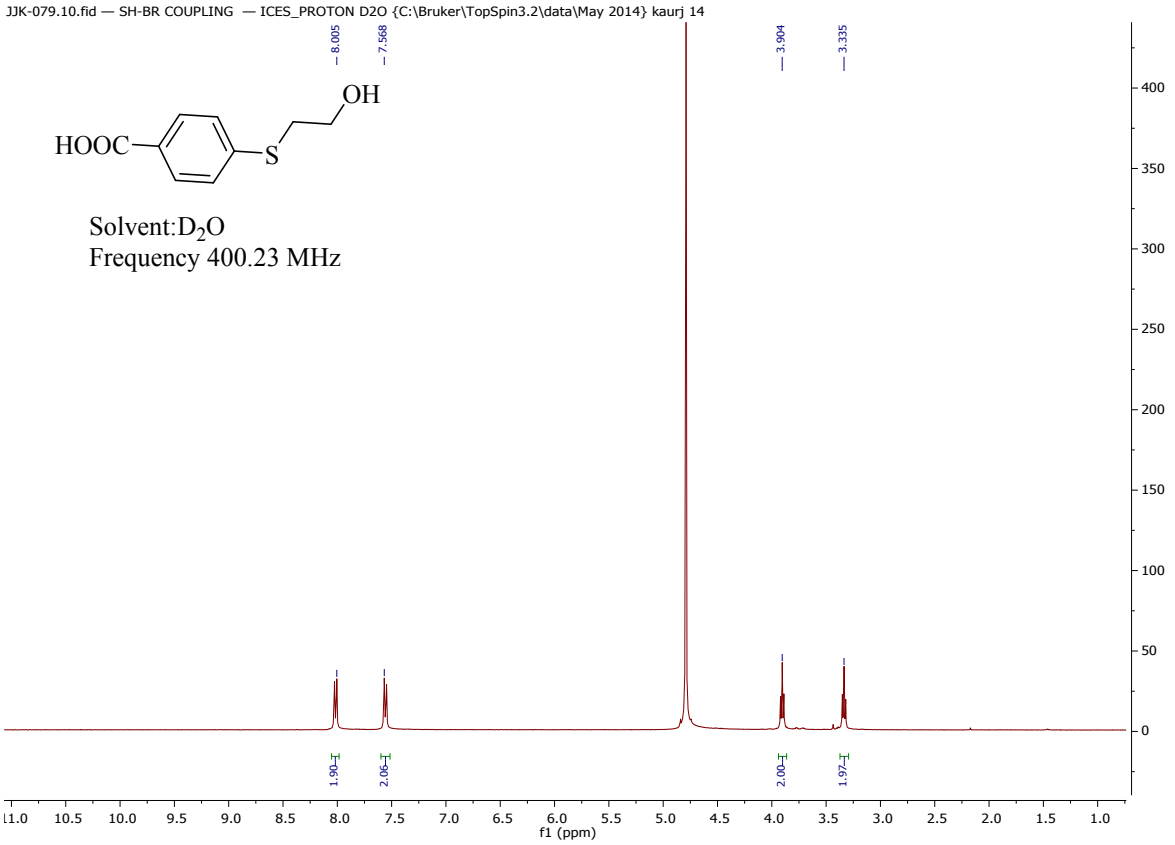


Fig. S10 ^{1}H NMR spectrum of compound **2**

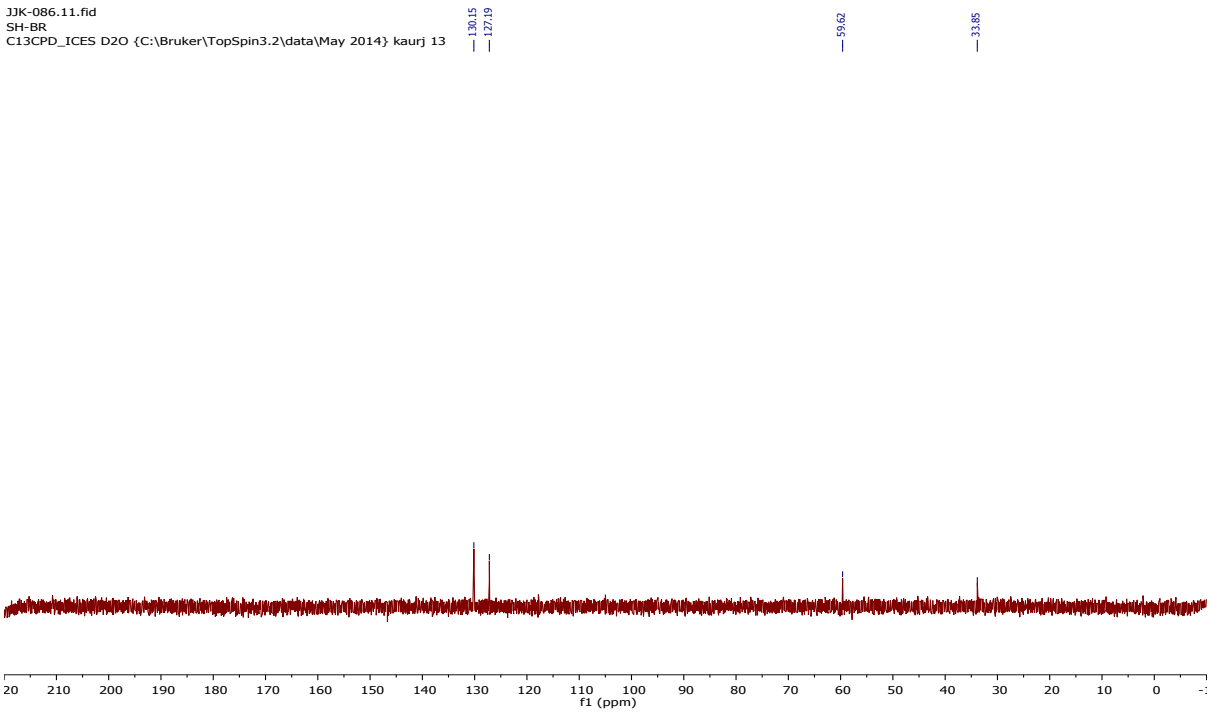


Fig. S11 ^{13}C NMR spectrum of compound **2**

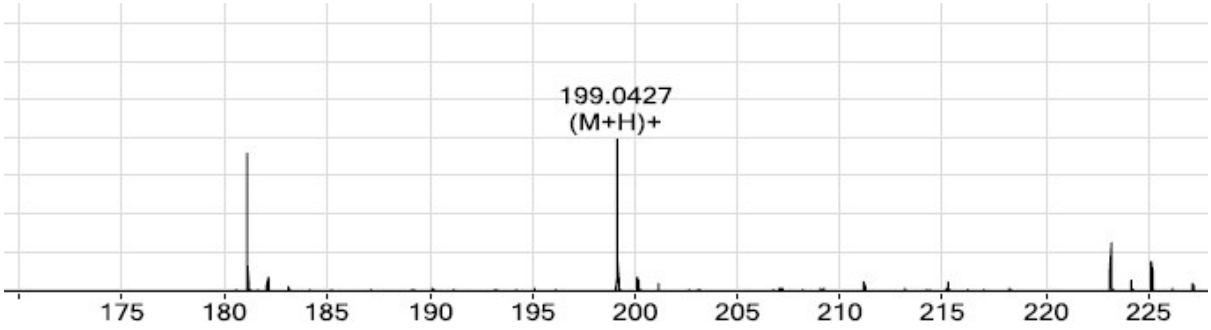


Fig. S12 ESI-Mass spectrum of compound **2**

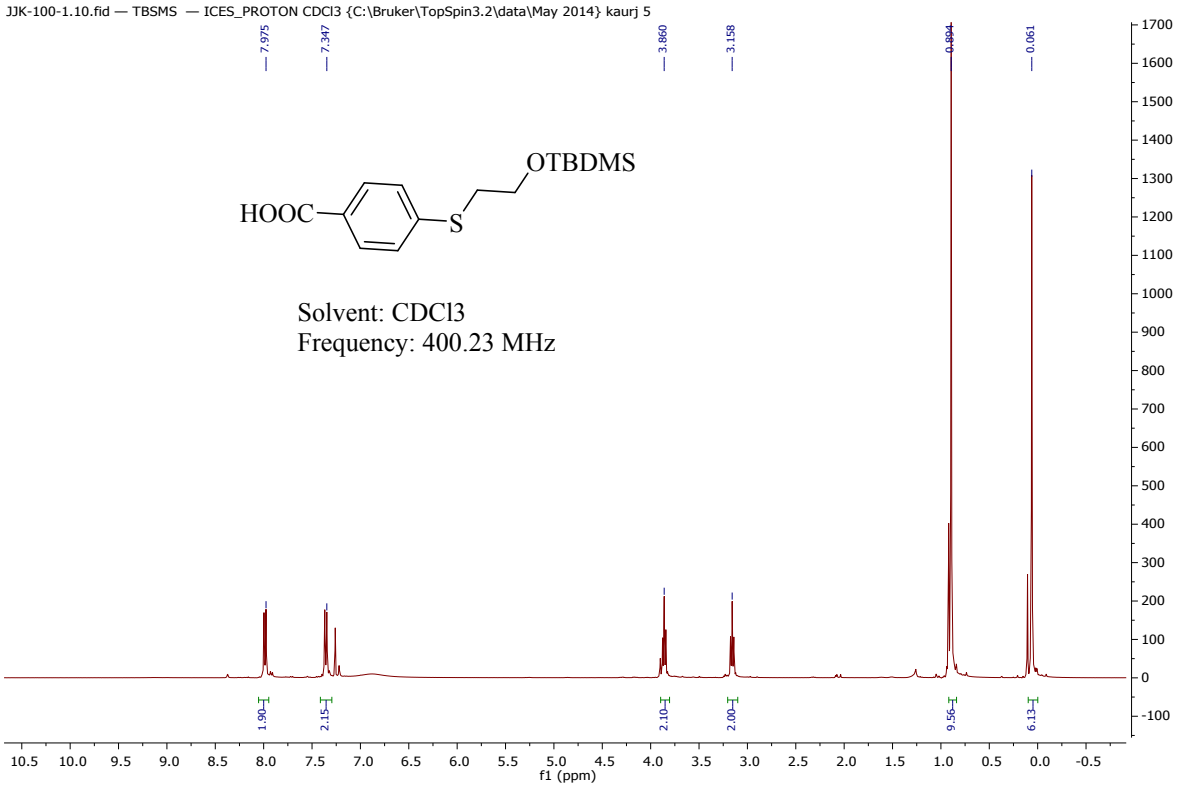


Fig. S13 ^{1}H NMR spectrum of compound **3**

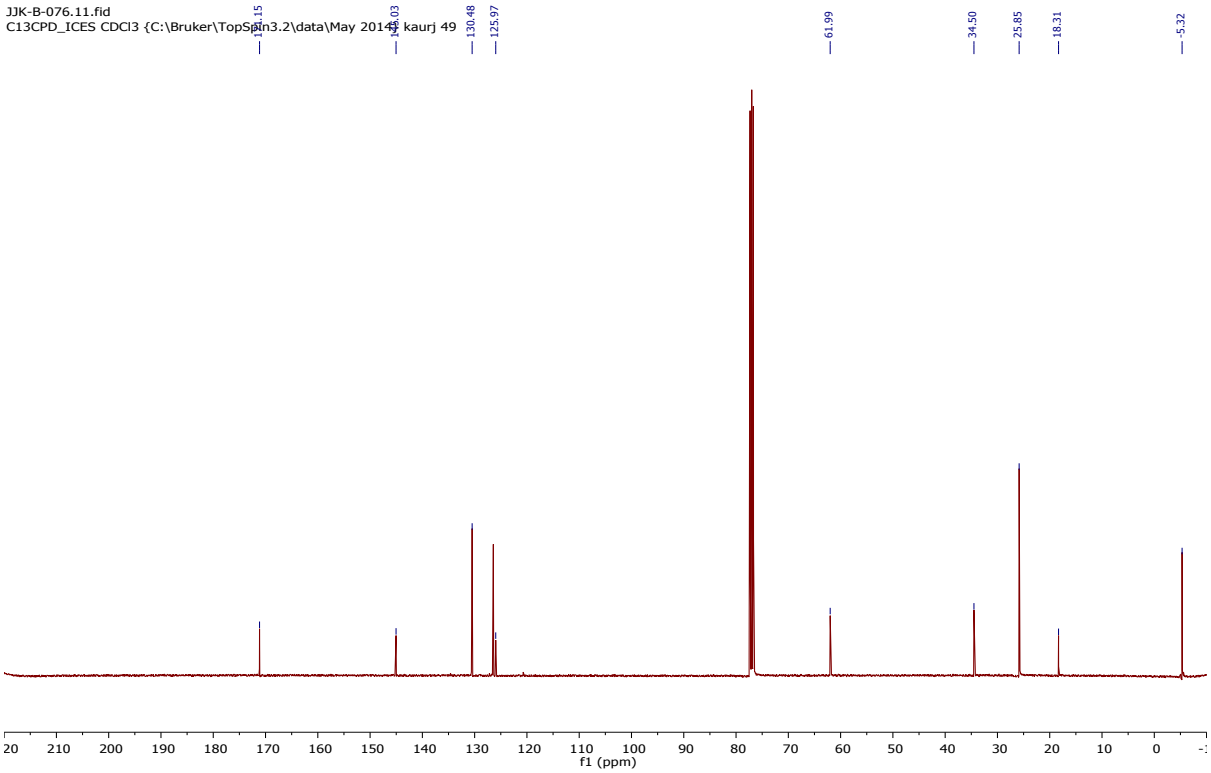


Fig. S14 ^{13}C NMR spectrum of compound **3**

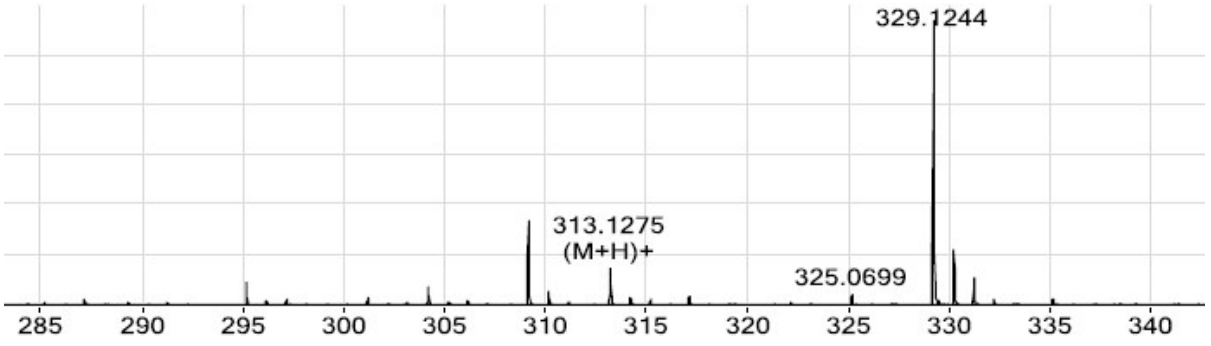


Fig. S15 ESI-Mass spectrum of compound **3**

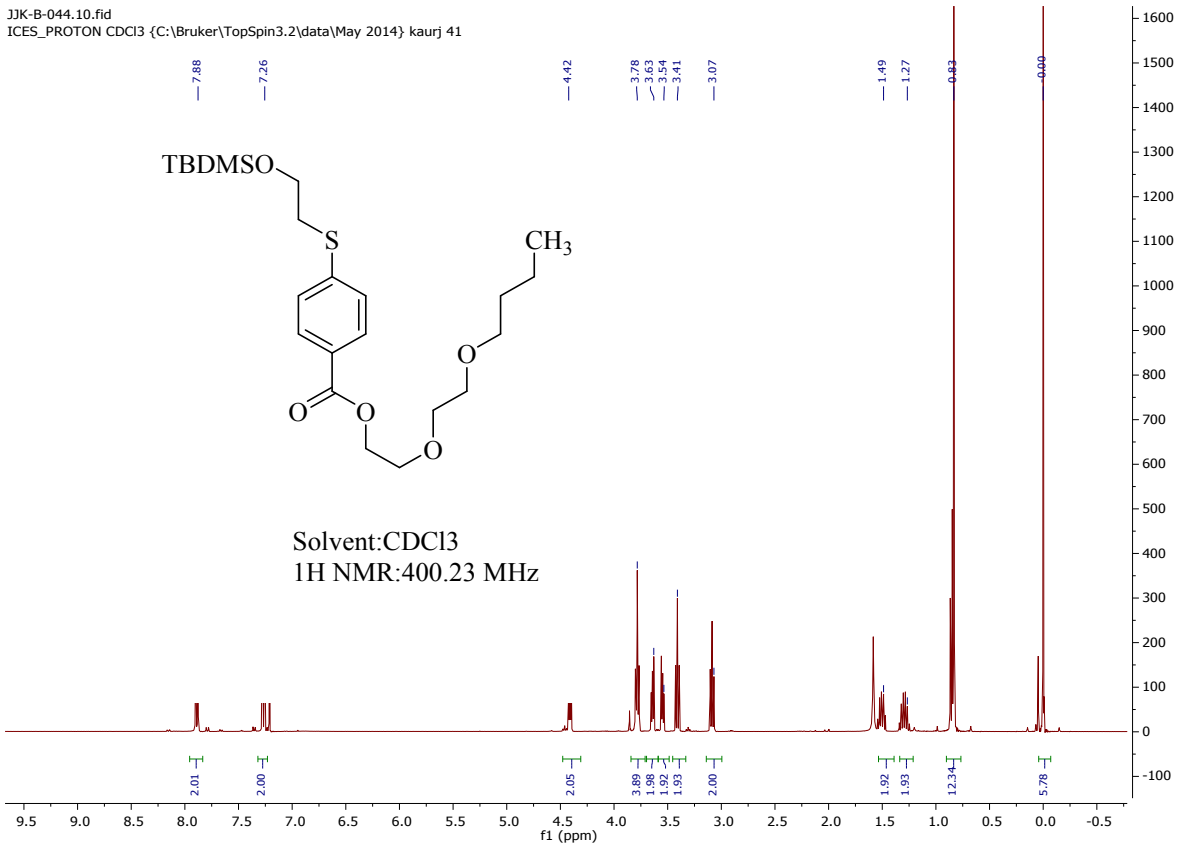


Fig. S16 ^{1}H NMR spectrum of compound **4a**

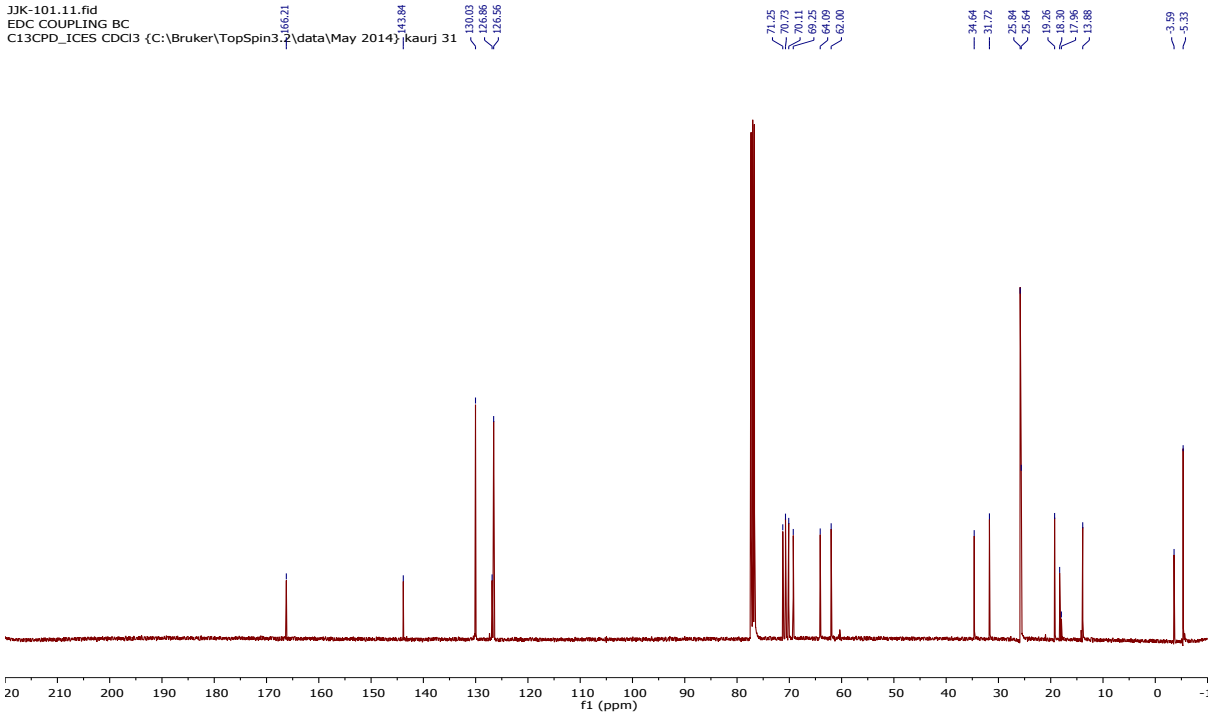


Fig. S17 ^{13}C NMR spectrum of compound **4a**

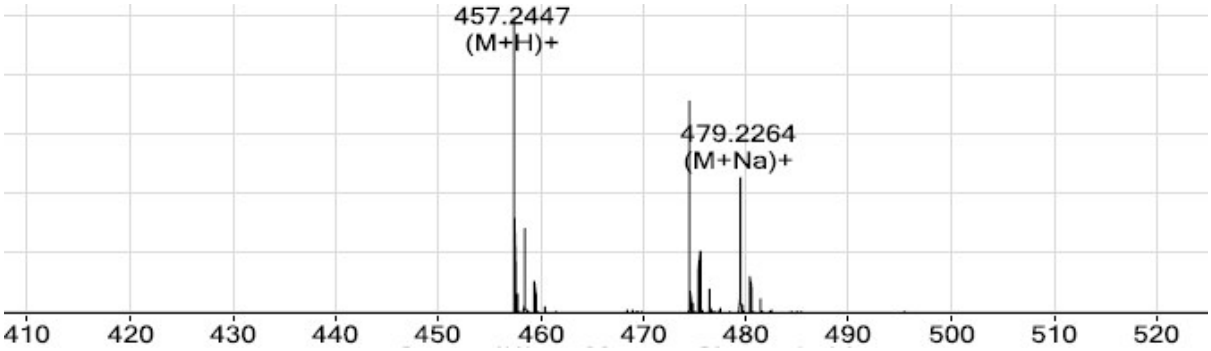


Fig. S18 ESI-Mass spectrum of compound **4a**

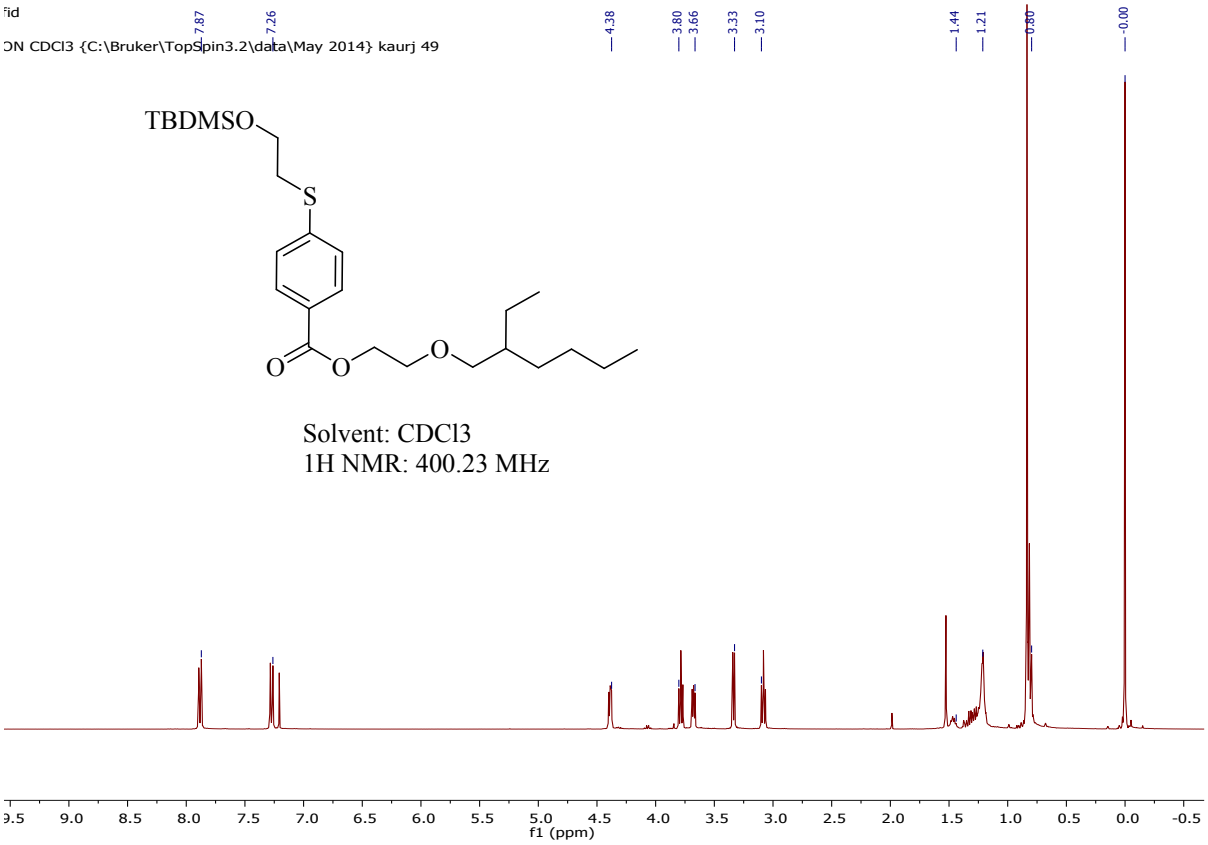


Fig. S19 ^{1}H NMR spectrum of compound **4b**

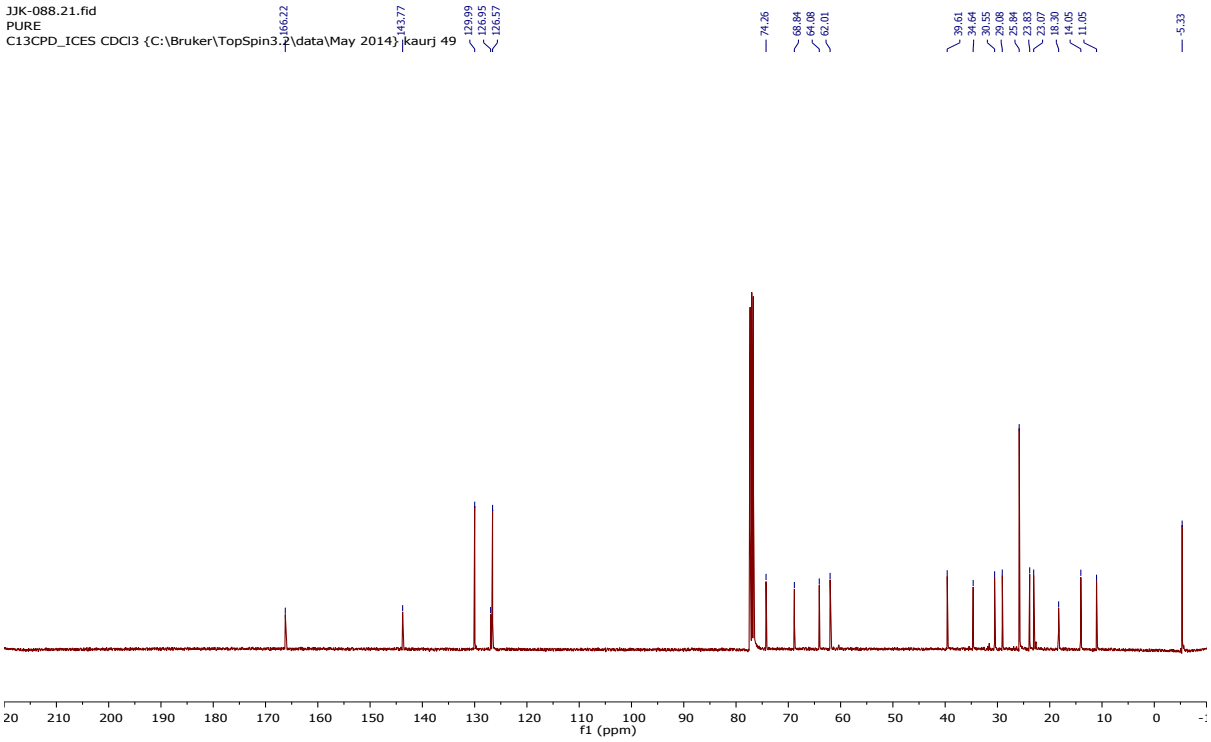


Fig. S20 ^{13}C NMR spectrum of compound **4b**

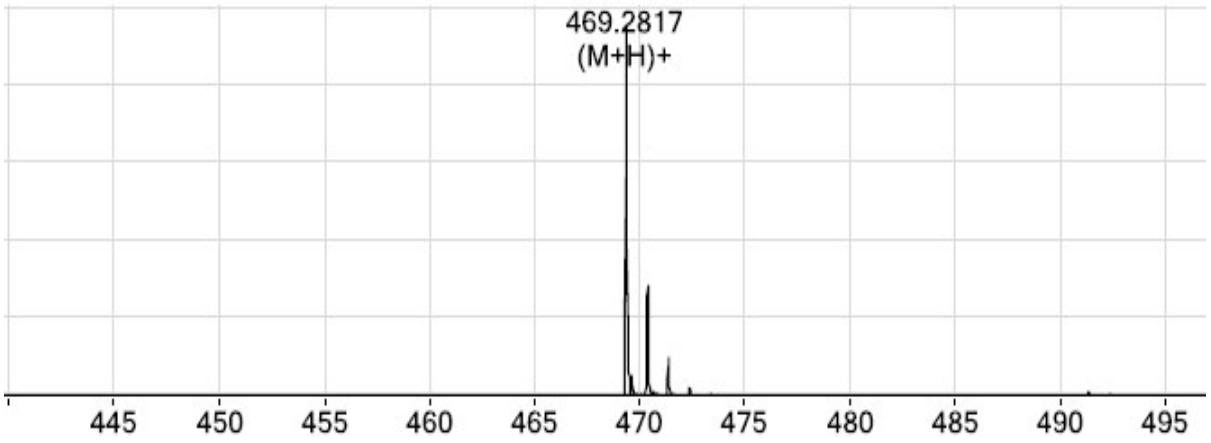


Fig. S21 ESI-Mass spectrum of compound **4b**

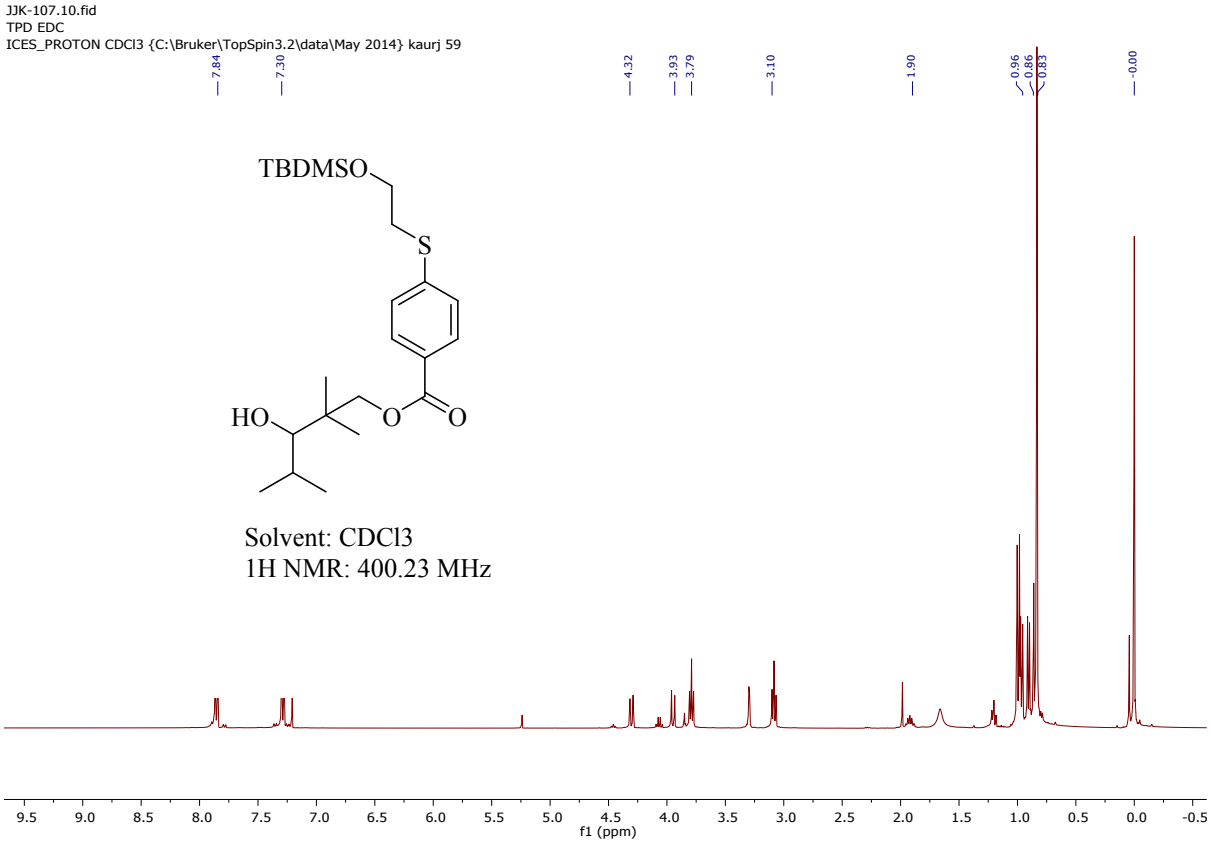


Fig. S22 ^{1}H NMR spectrum of compound **4c**

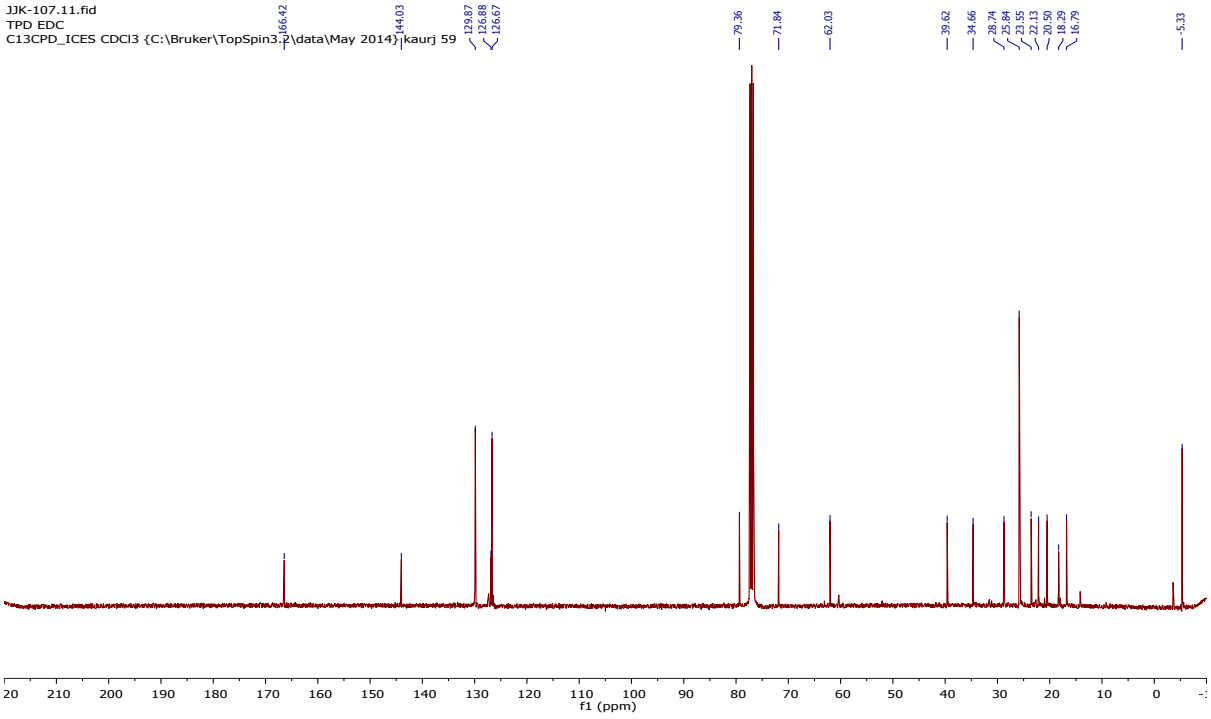


Fig. S23 ^{13}C NMR spectrum of compound **4c**

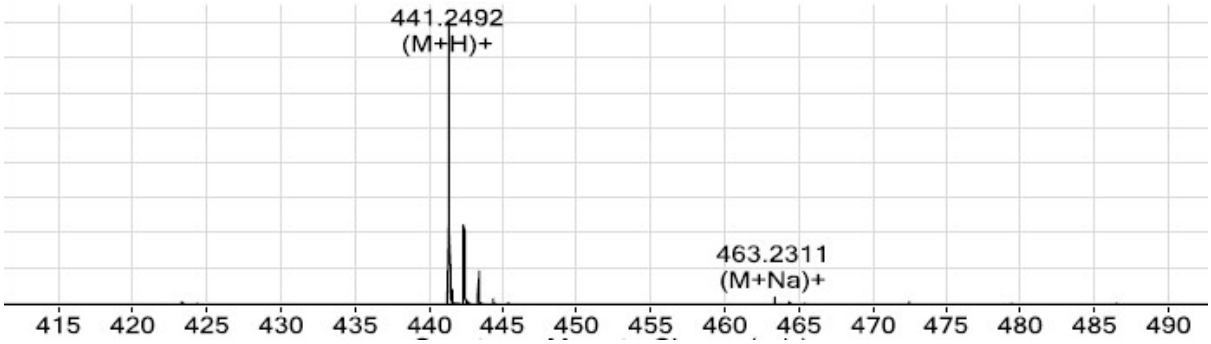


Fig. S24 ESI-Mass spectrum of compound **4c**

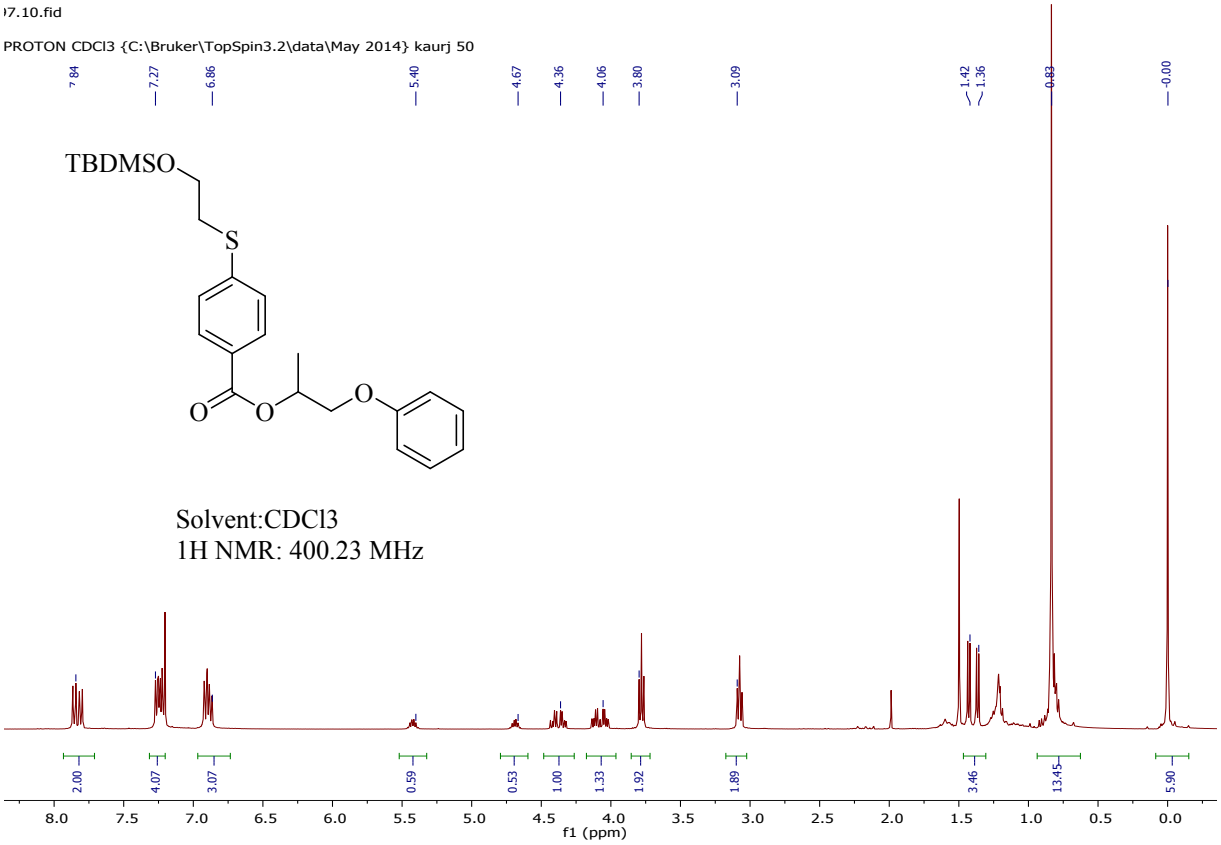


Fig. S25 ^{1}H NMR spectrum of compound **4d**

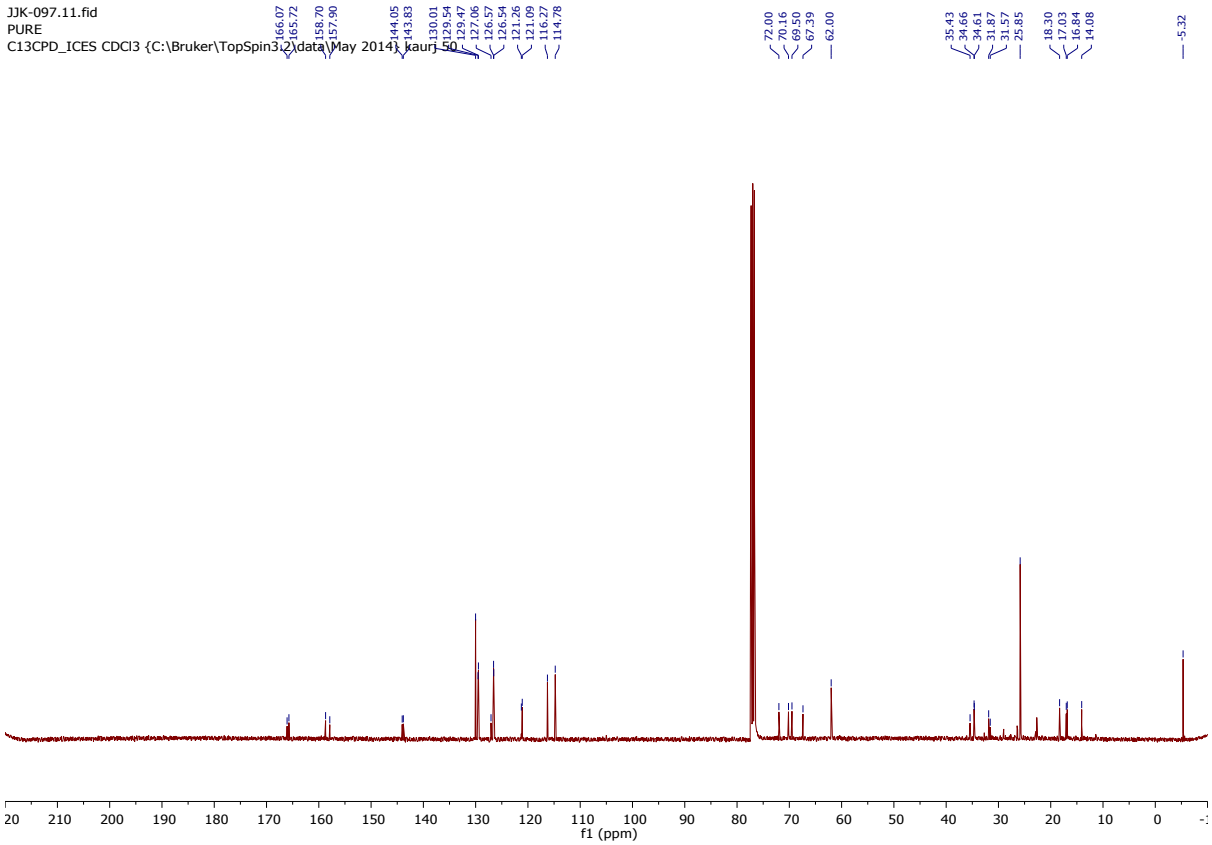


Fig. S26 ^{13}C NMR spectrum of compound **4d**

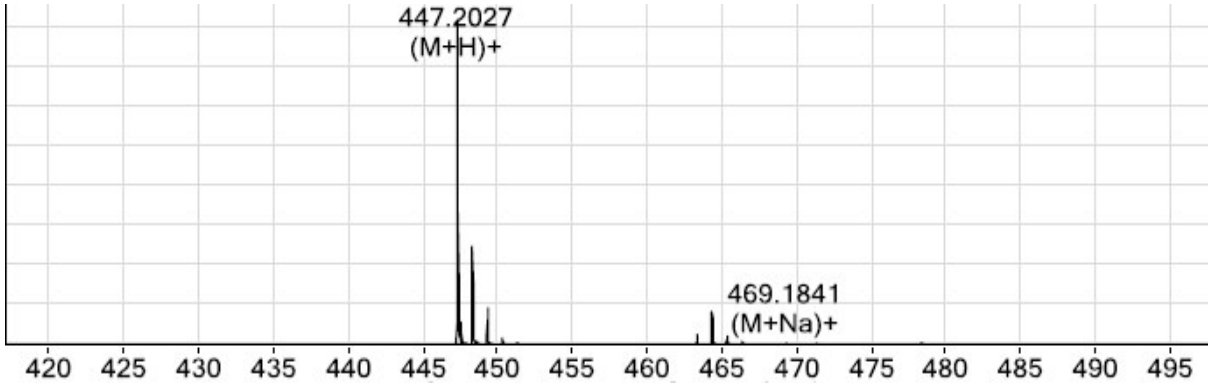


Fig. S27 ESI-Mass spectrum of compound **4d**

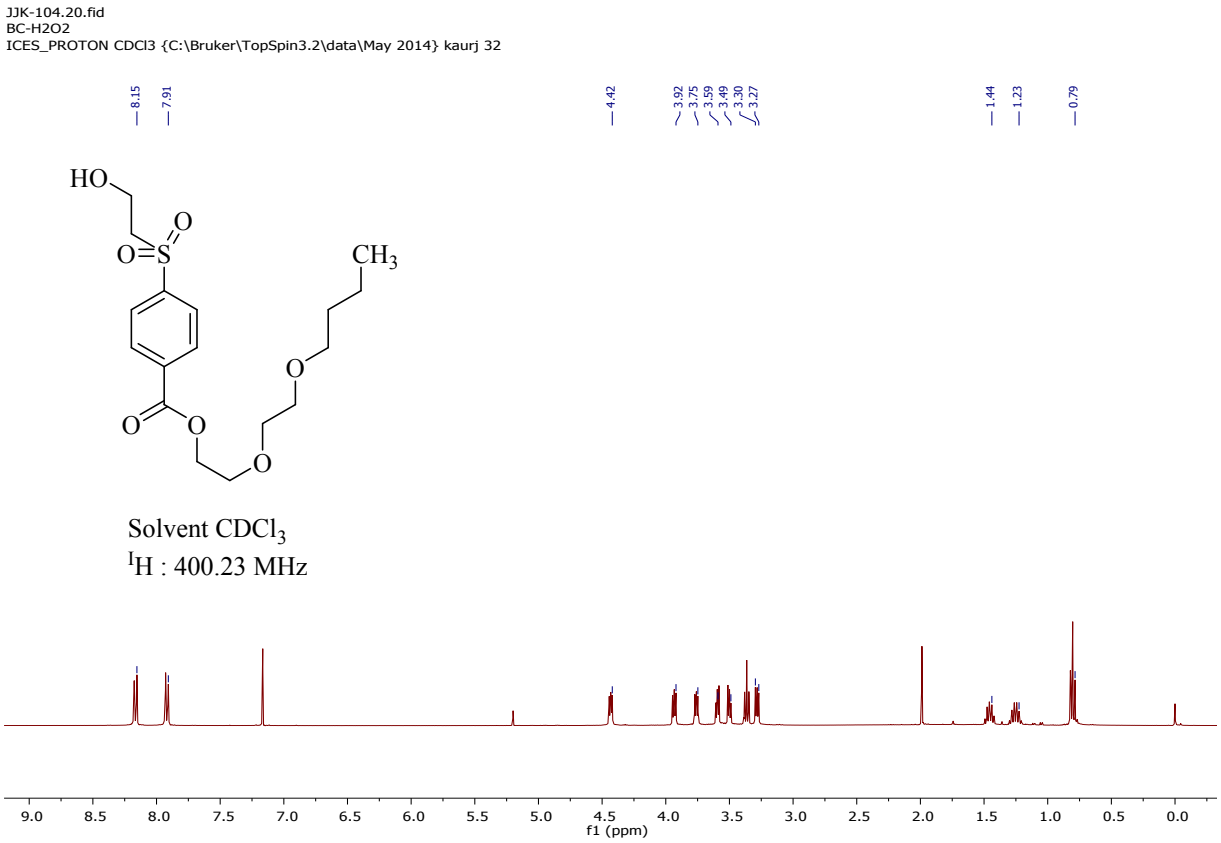


Fig. S28. ^{1}H NMR spectrum of **HES-BC**

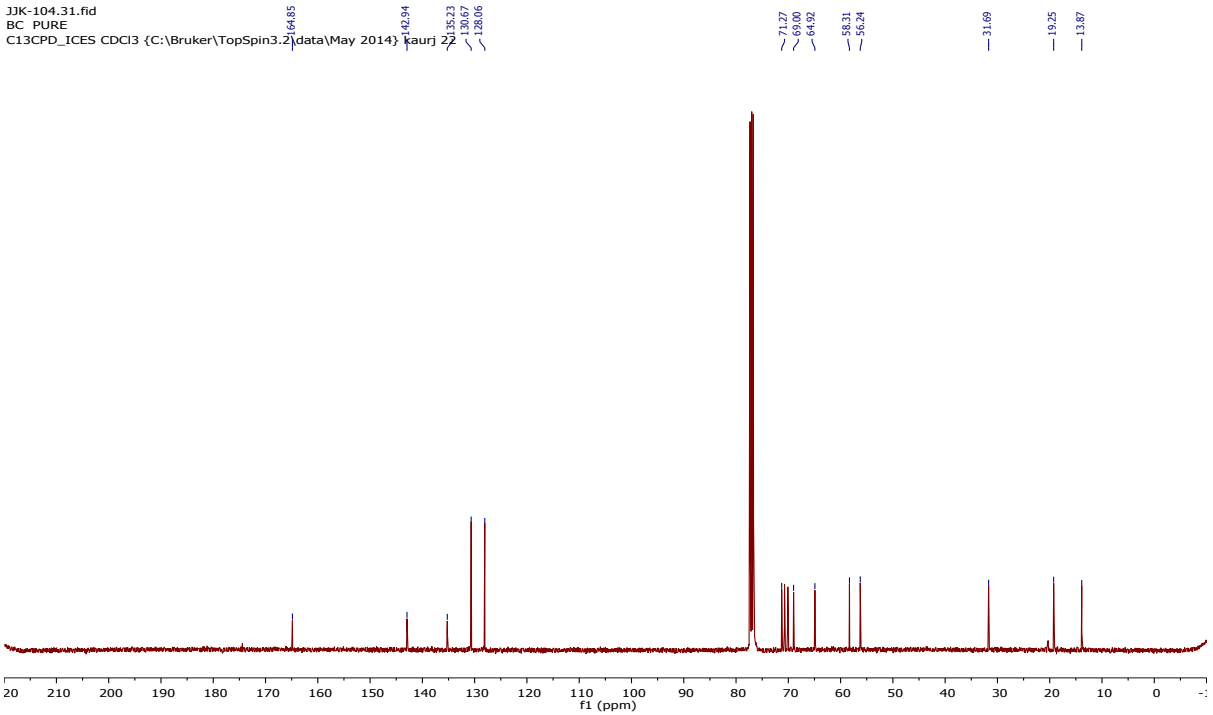


Fig. S29 ^{13}C NMR spectrum of **HES-BC**

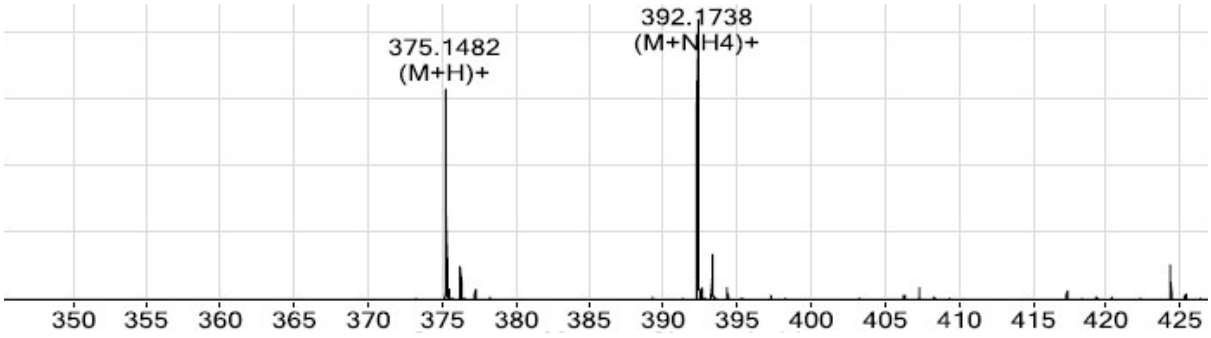


Fig. S30 ESI-Mass spectrum of **HES-BC**.

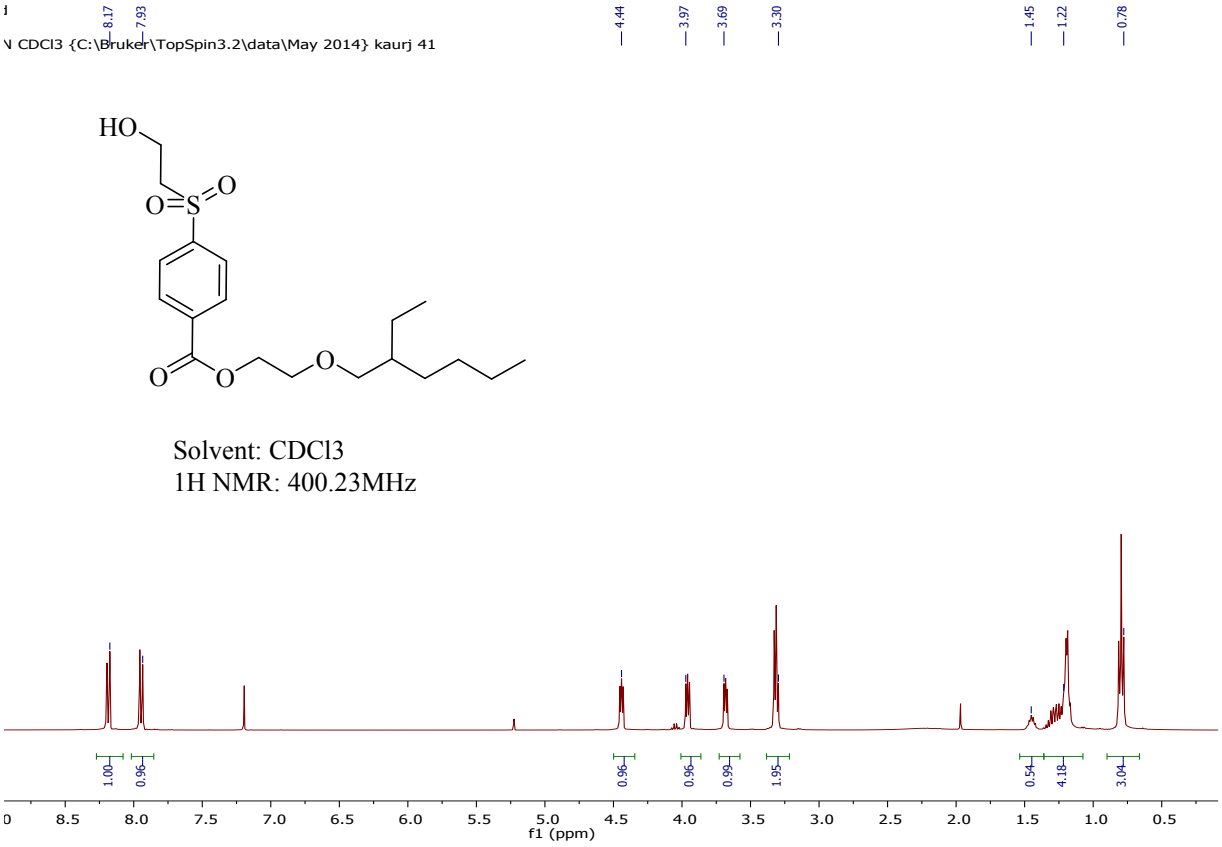


Fig. S31 ^{1}H NMR spectrum of **HES-EEH**

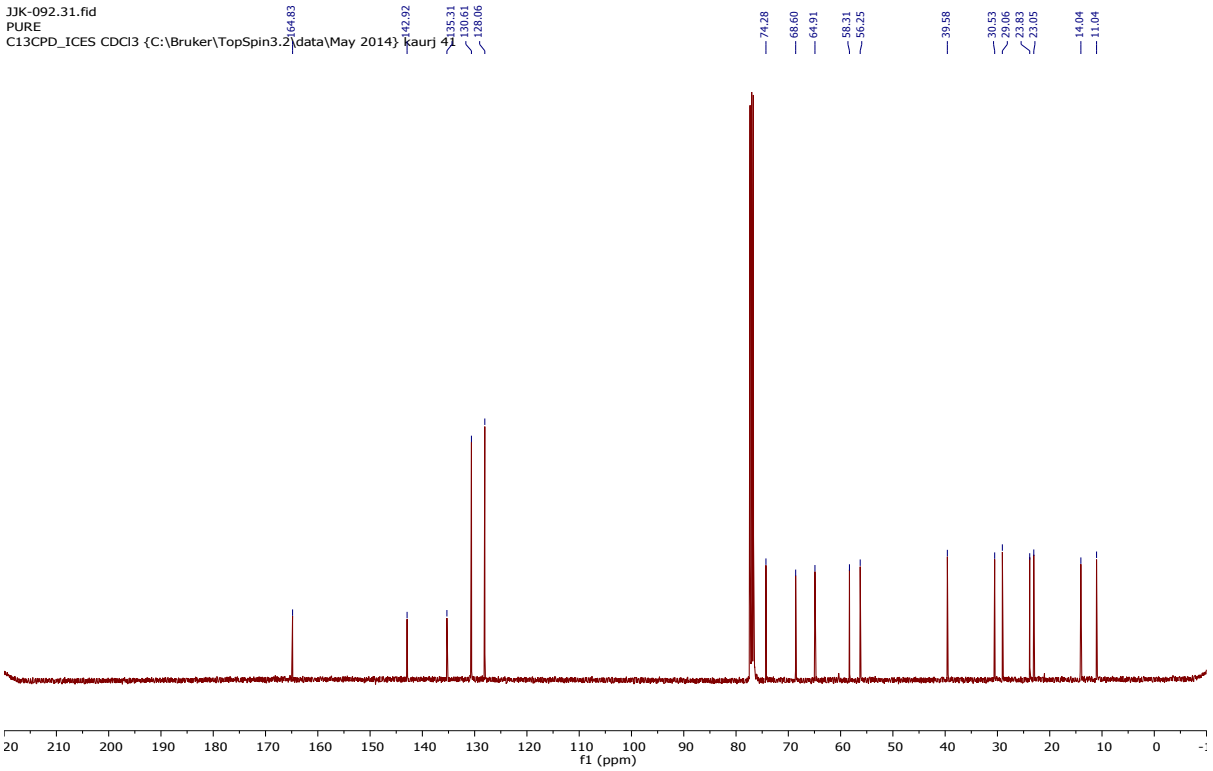


Fig. S32 ^{13}C NMR spectrum of **HES-EEH**

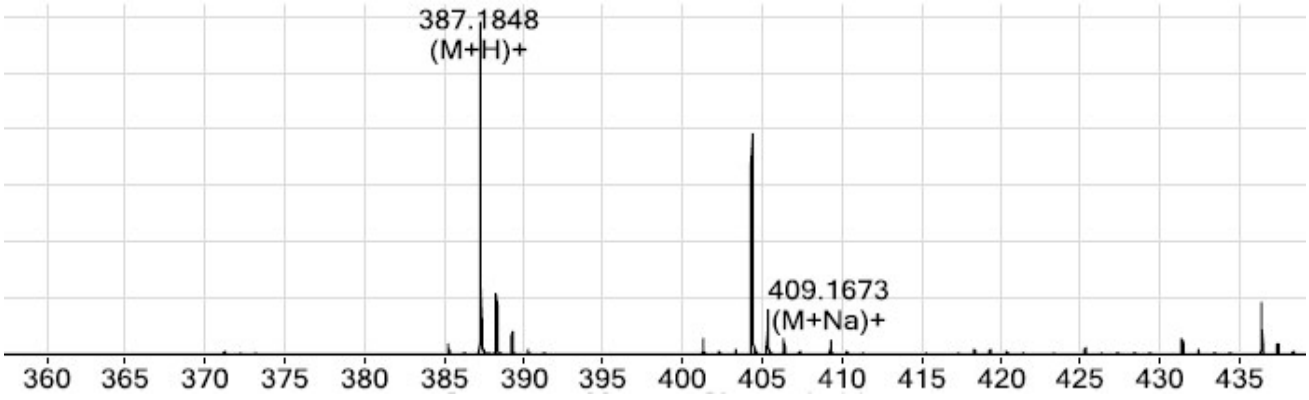


Fig. S33 ESI-Mass spectrum of **HES-EEH**.

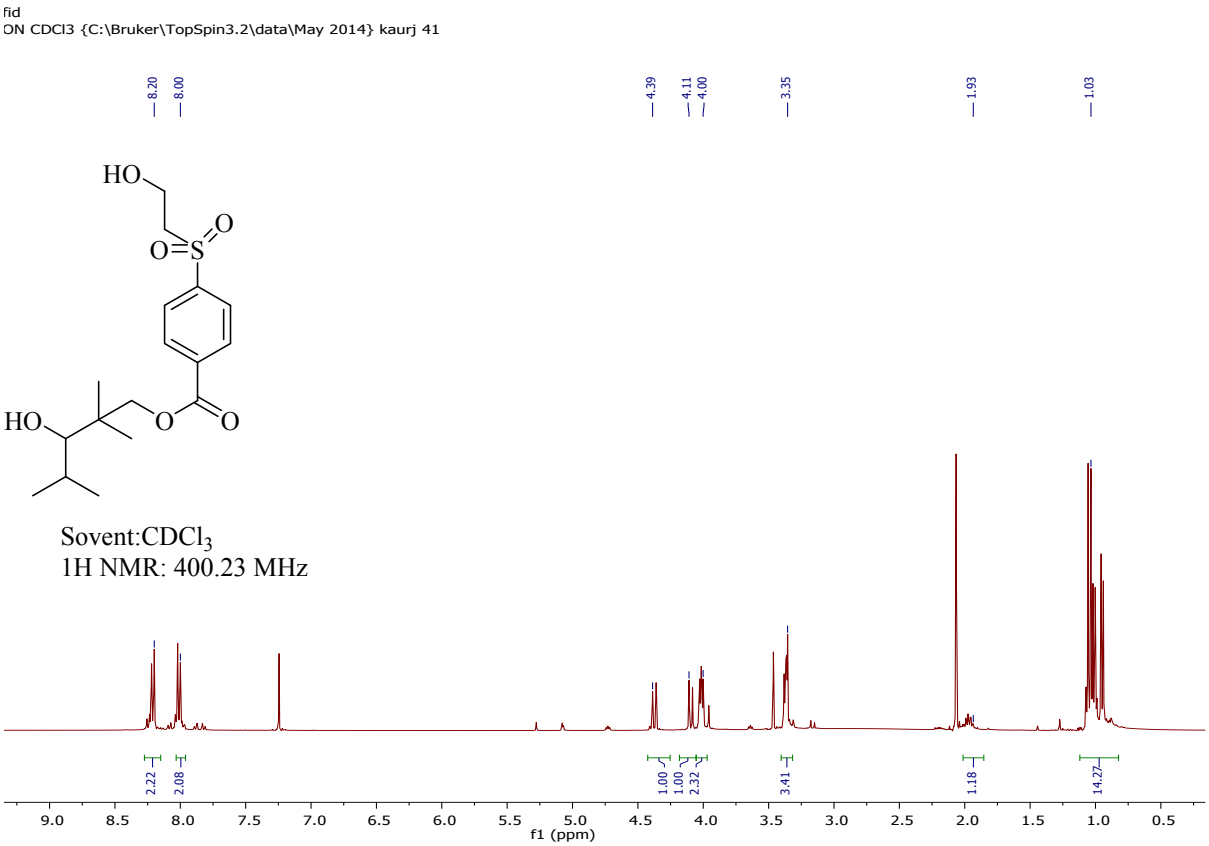


Fig. S34 ^{1H} NMR spectrum of **HES-TPD**

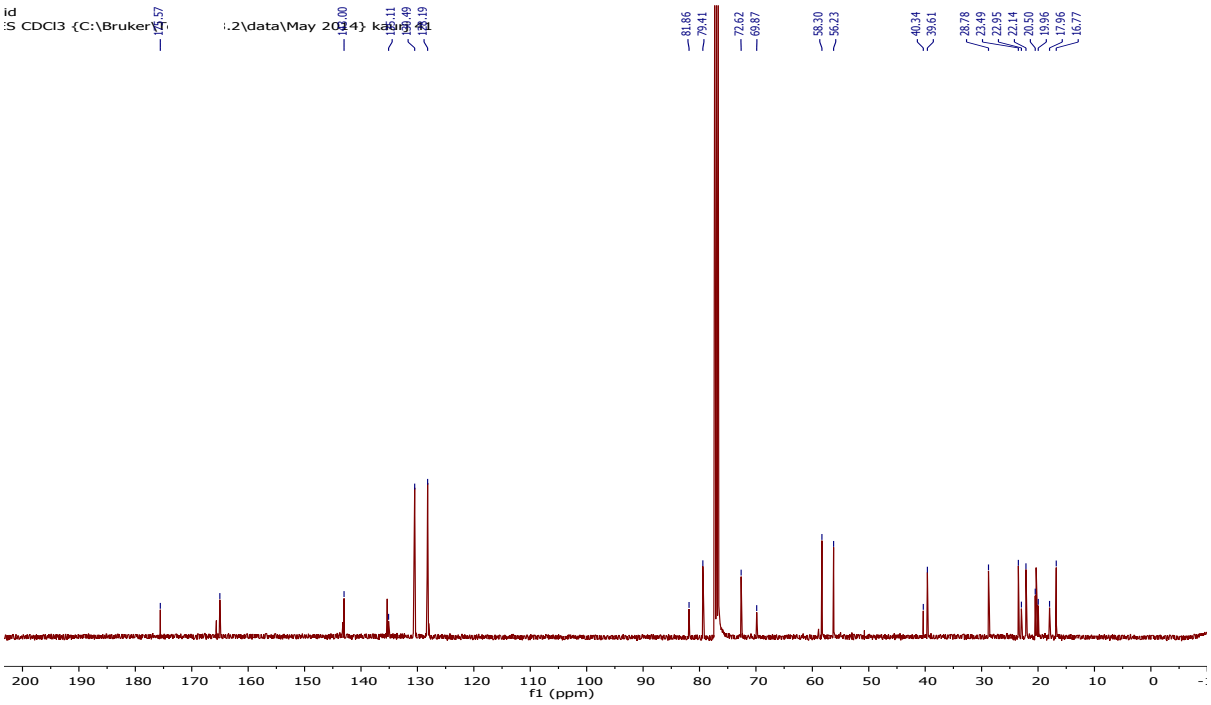


Fig. S35 ^{13}C NMR spectrum of **HES-TPD**

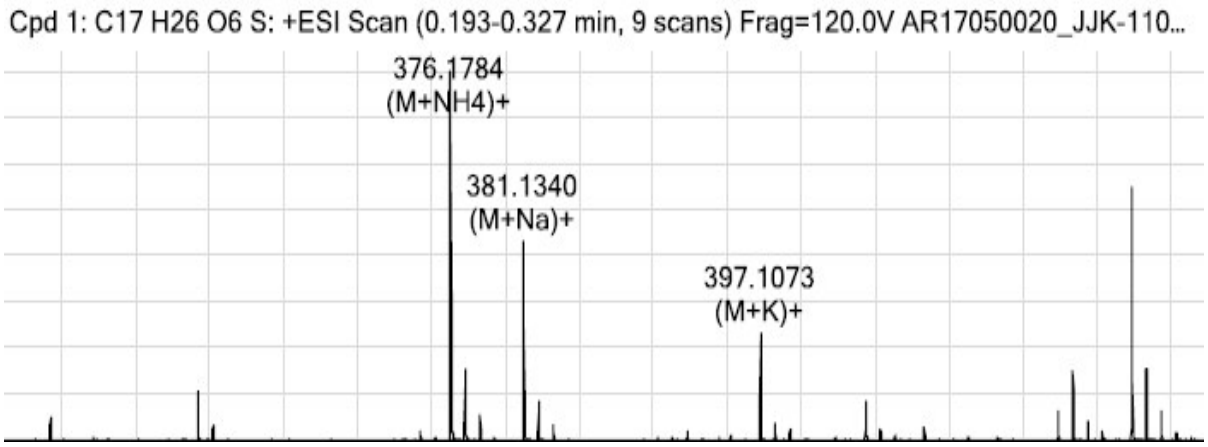


Fig. S36 ESI-Mass spectrum of **HES-TPD**

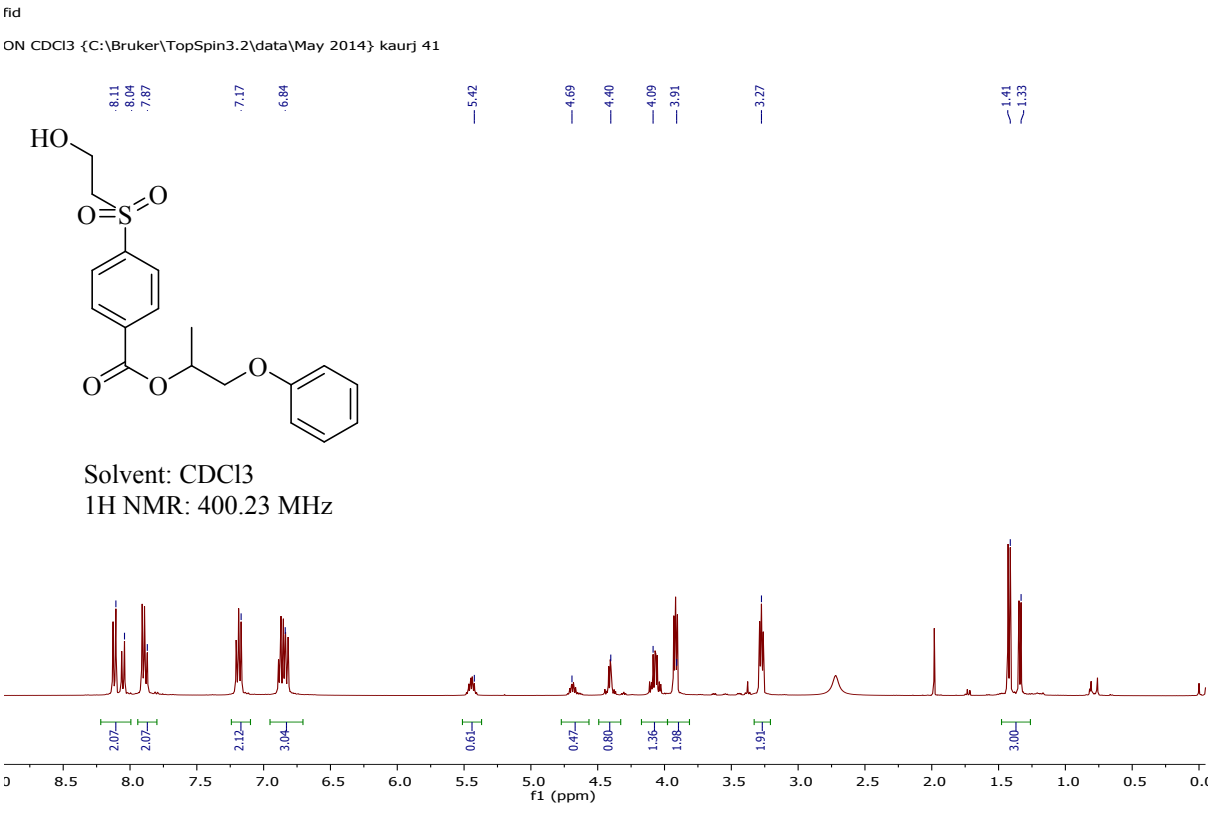


Fig. S37 ^{1}H NMR spectrum of **HES-PPH**

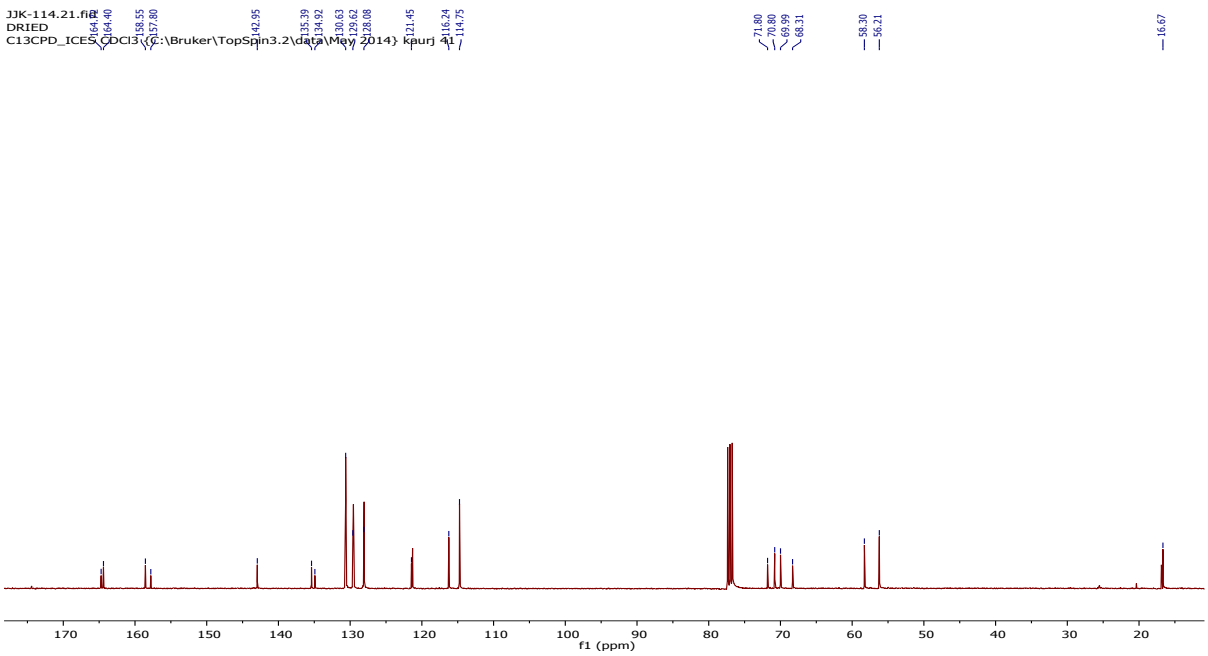


Fig. S38 ^{13}C NMR spectrum of **HES-PPH**

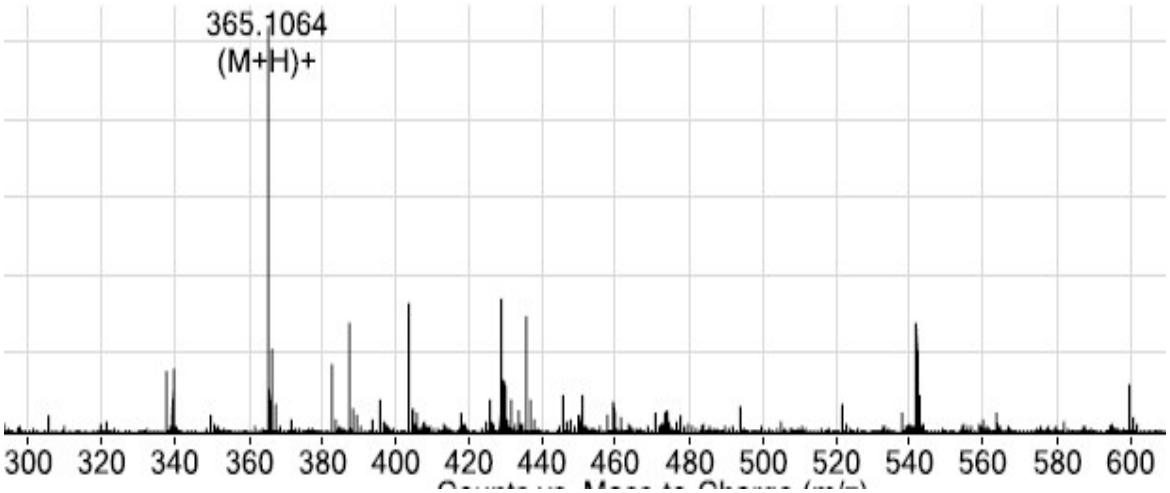
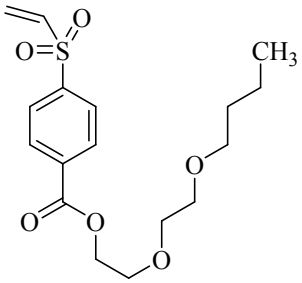


Fig. S39 ESI-Mass spectrum of **HES-PPH**

10.fid
ON CDCl3 {C:\Bruker\TopSpin3.2\data\May 2014} kaurj 41



Solvent:CDCl3
1H NMR: 400.23 MHz

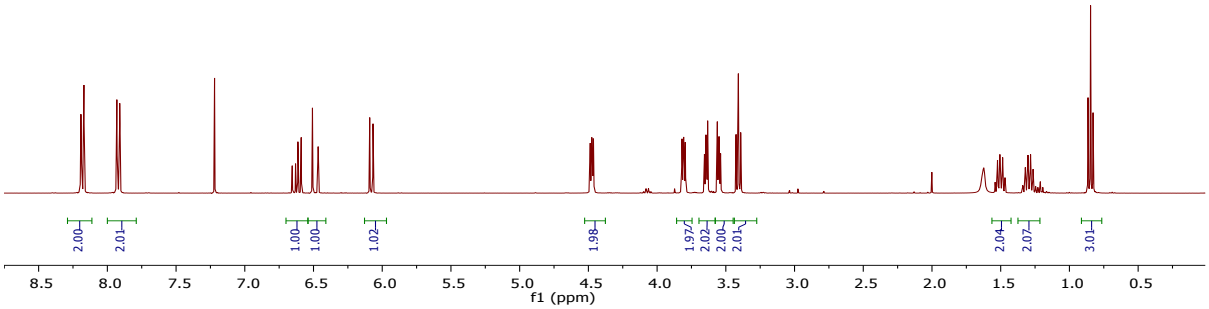


Fig. S40 [1]H NMR spectrum of **VS1**

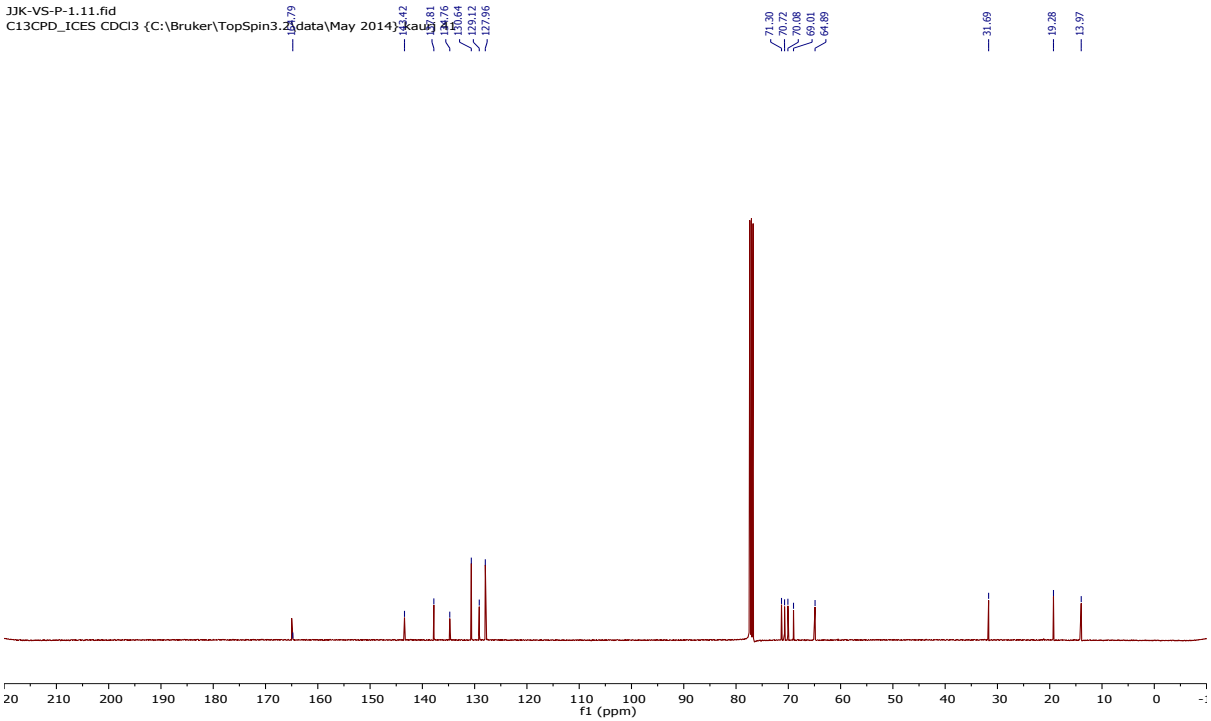


Fig. S41 [13]C NMR spectrum of **VS1**

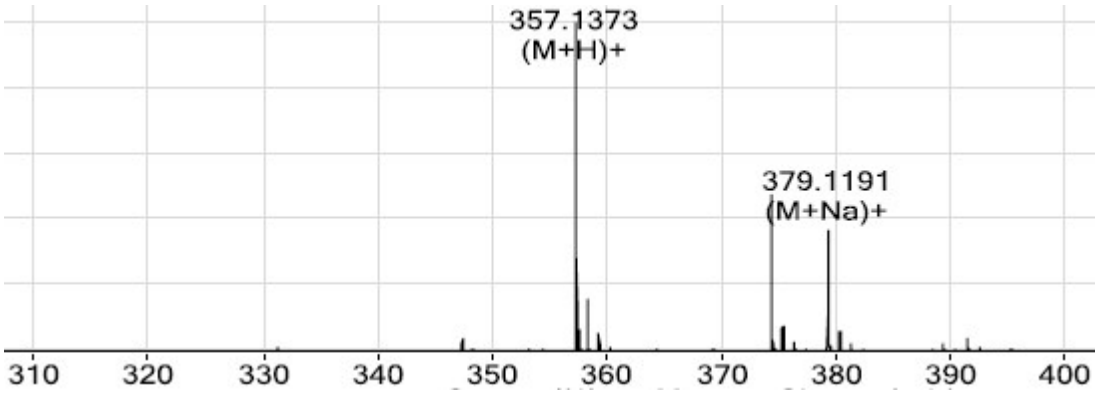


Fig. S42 ESI-Mass spectrum of **VS1**

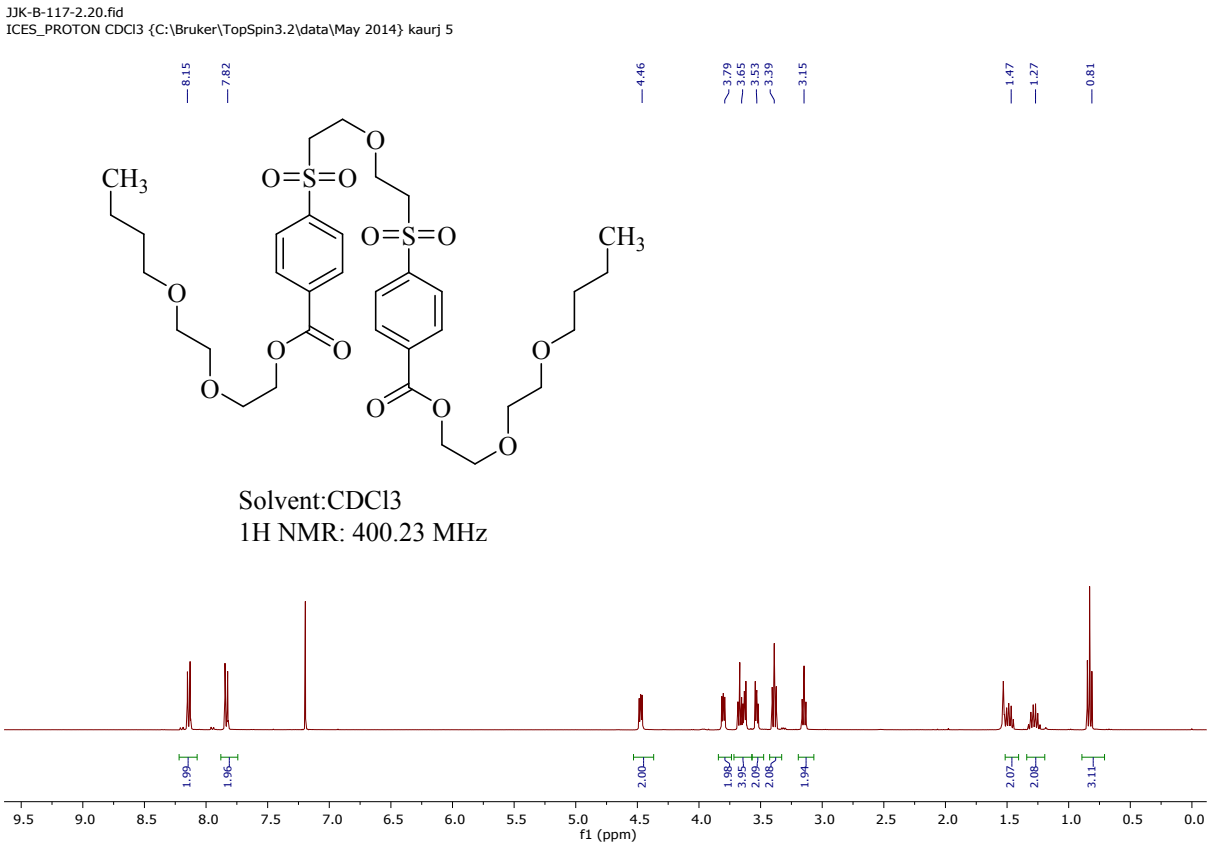


Fig. S43 ^{1}H NMR spectrum of **HES-BC-VS1**

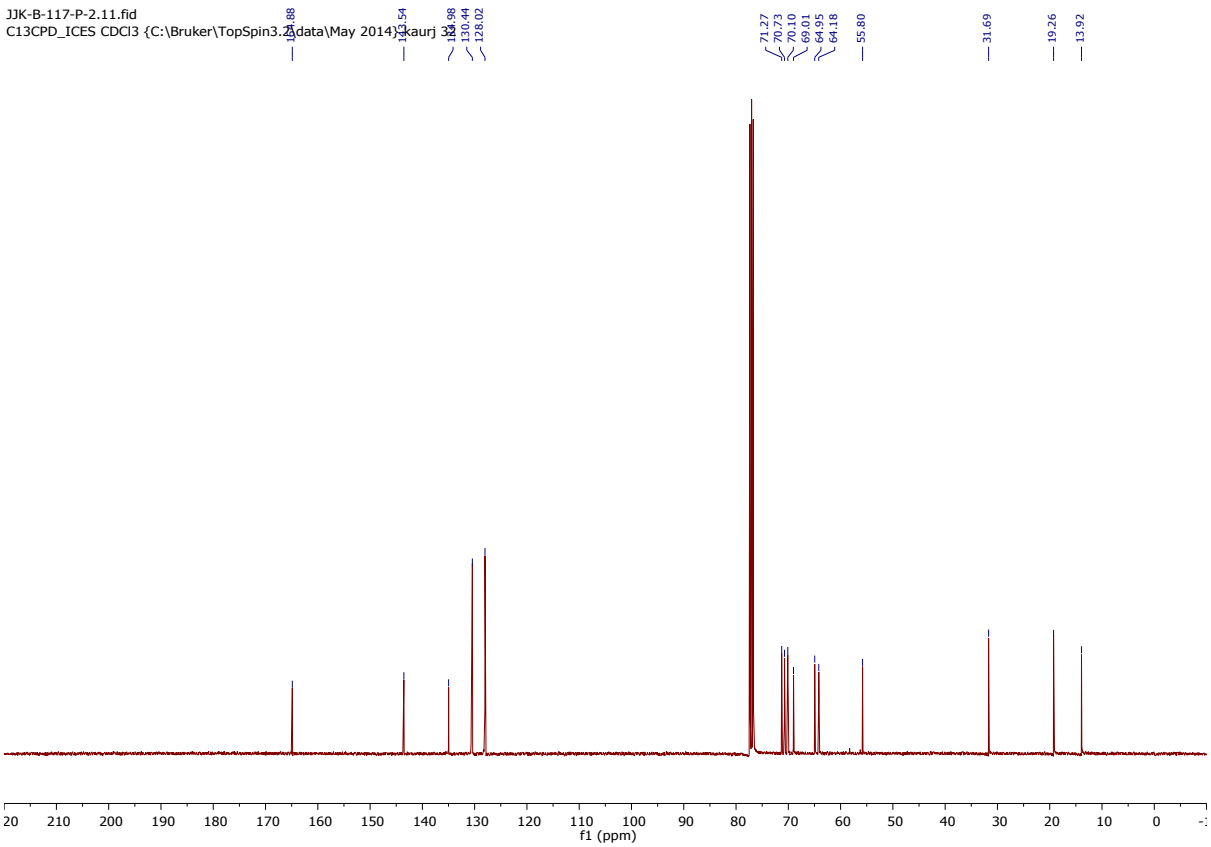


Fig. S44 ^{13}C NMR spectrum of **HES-BC-VS1**

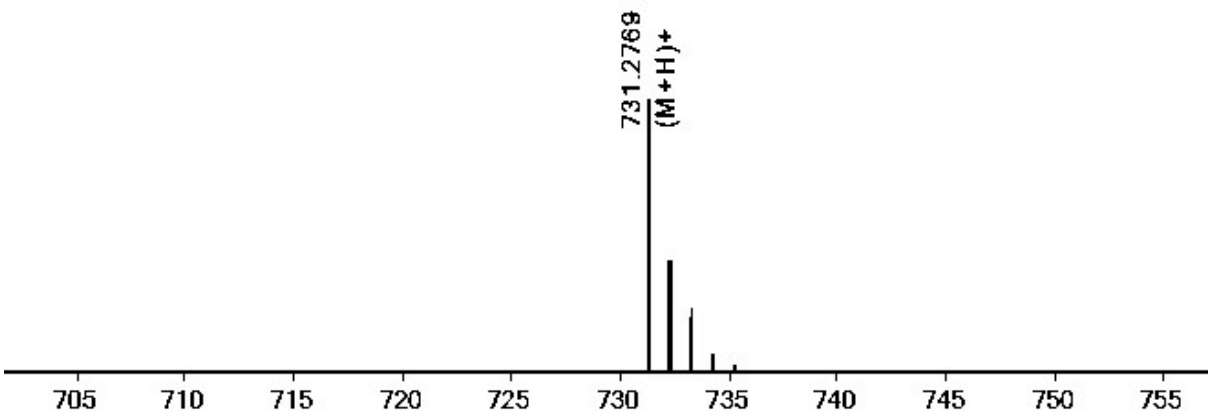


Fig. S45 ESI-Mass spectrum of **HES-BC-VS1**