Chemical recycling of CO_2-based polycarbonates to sulfur-containing polymers

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Experiment

General details

Unless otherwise specified, all syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under nitrogen atmosphere or in a nitrogen-filled glovebox. Triethyl borane (BEt_3) in tetrahydrofuran solution (1.0 mol/L) was bought from J&K Scientific and used without further purifications. 1,3-Diisopropyl-2-thiourea (TU-1) was purchased from Sigma Aldrich and sublimeed before use. 1-cyclohexyl-3-phenylthiourea (TU-2) were synthesized according to literature.[1] Carbonyl sulfide (COS) (99.9 %, ACS Grade, Alfa Aesar) was purchased from the APK (Shanghai) Gas Company LTD and used as received.

1 Lu, A.; Wang, Z.; Zhou, Z.; Chen, J.; Wang, Q., Application of "Hydrogen Bonding Interaction" in new drug development: design, synthesis, antiviral activity, and SARs of thiourea derivatives. *J. Agric. Food Chem.* **2015**, *63*, 1378-1384.

Methods.

^1H, and ^{13}C NMR spectra were performed on a Bruker Advance DMX 400 MHz. Chemical shifts values for ^1H and ^{13}C spectra were referenced to internal solvent resonances (to $CHCl_3$ at 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). The number-average molecular weight (M_n) and molecular weight distribution ($Đ = M_w/M_n$) of the resultant copolymers were measured by GPC at 40 °C using a Waters 1515 isocratic pump, a model 2414 differential refractometer GPC instrument with tetrahydrofuran (THF) as the mobile phase and Waters Styragel HR3, HR4 and HR5 7.8×300mm columns. The flow rate of THF was 1.0 mL/min. Linear polystyrene polymers with narrow molar mass distributions were used as standards to calibrate the apparatus. Differential scanning calorimetry (DSC) was taken on a DSCQ200 equipped with a liquid nitrogen cooling system. Approximately 3–5 mg of samples were placed in aluminum pans. The cooling and heating rates were 10 °C/min. Thermogravimetric analysis (TGA) was performed on a Q600-SDT thermogravimetric analyzer (TA Instruments Co., Ltd., New Castle, DE, United States).

Representative procedure for polymerization reactions.

A 10mL autoclave with magnetic stirrer was dried in an oven at 110 °C overnight, then immediately placed into the glove box chamber. After keeping under vacuum for 1-2 h, the reaction vessel was put into the glove box under nitrogen atmosphere. The polymerization of COS with PPC described below is taken from entry 2 in Table 1 as an example. PPC (0.102 g, 1 mmol [-PO-*alt*-CO_2-] repeating unit) was firstly added into the reactor and dissolved in 0.5 mL of THF (2M of repeating unit). Afterwards, Potassium tert-butoxide (KO^tBu, 1.1 mg, 0.01 mmol) was added into the autoclave. The reactor was sealed and taken out from the glove box and charged with 0.8 Mpa of COS. The copolymerization was carried out at 140 °C for 4 h. At the end of the polymerization, the autoclave was cooled in ice-water bath and return to room temperature. The gas was slowly released. A spot of crude product was taken

for the determination of PPC conversion and the molar ratio of polymer/cyclic products by ^{1}H NMR spectrum. The crude product was quenched with HCl in CH_2Cl_2 (1 mol/L). Next, the polymer was purified three times by dissolving with CH_2Cl_2 and then precipitated in methanol. The final product was dried in vacuum at 40 °C until a constant weight.

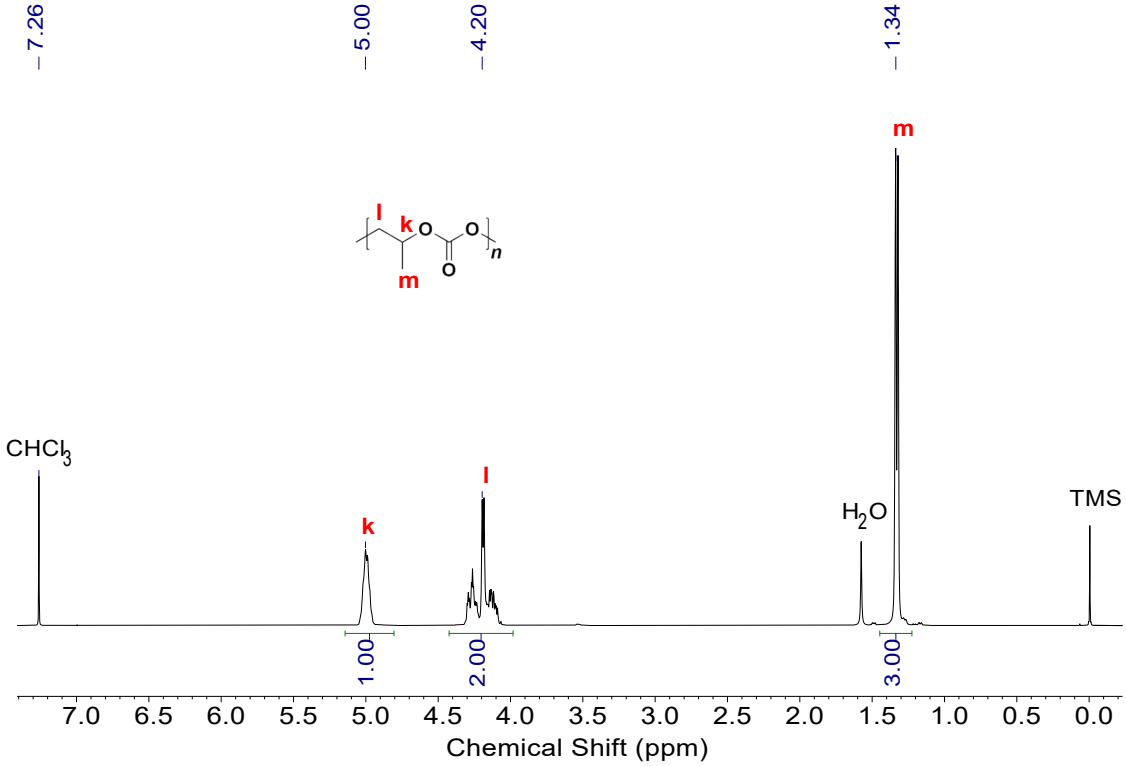
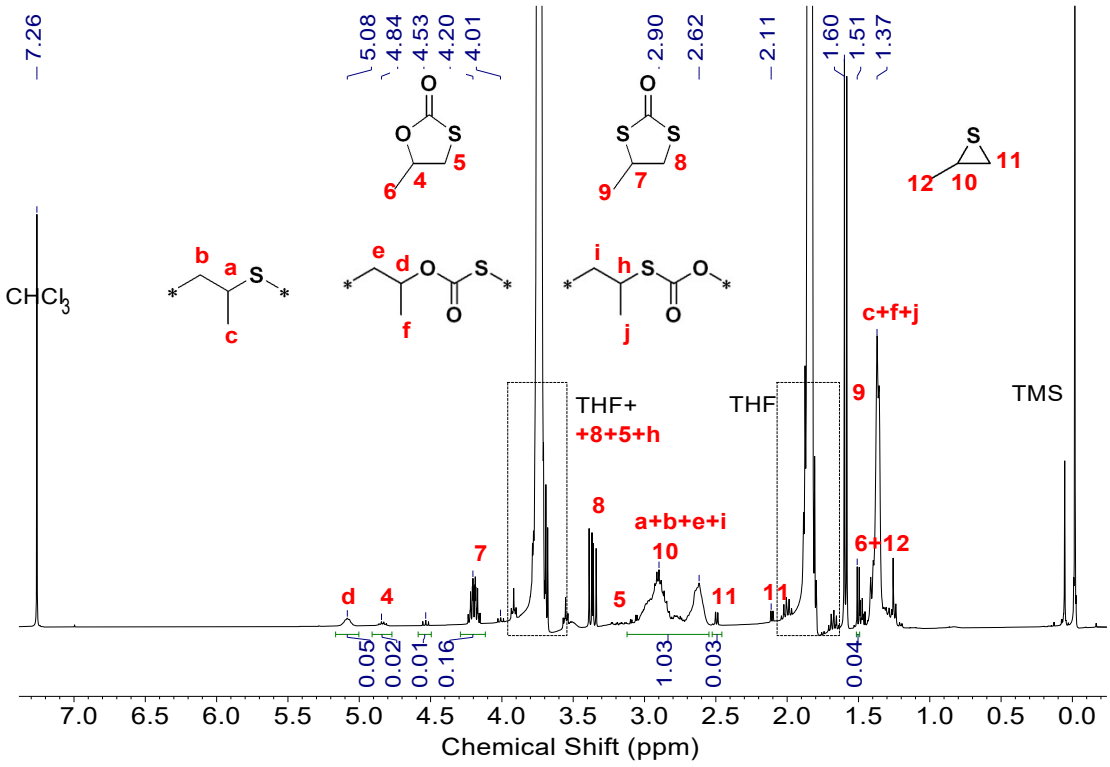


Fig. S1. ^{1}H NMR spectrum of the crude product of entry 1 Table 1.



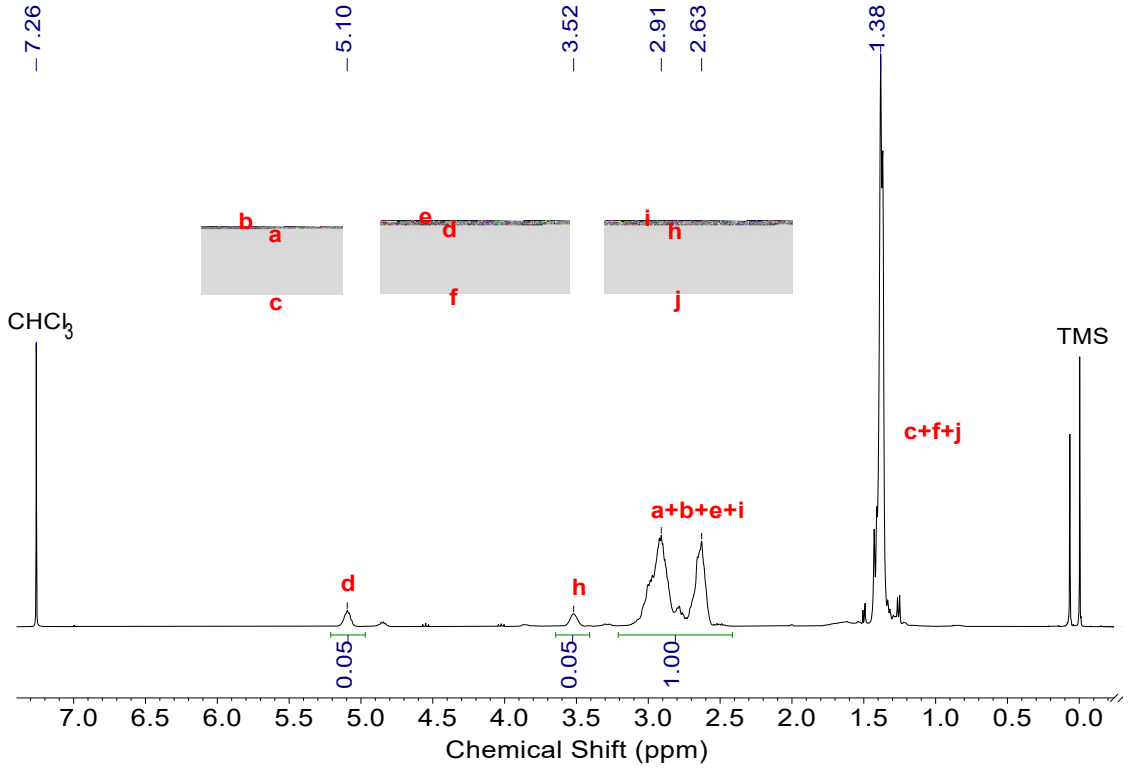
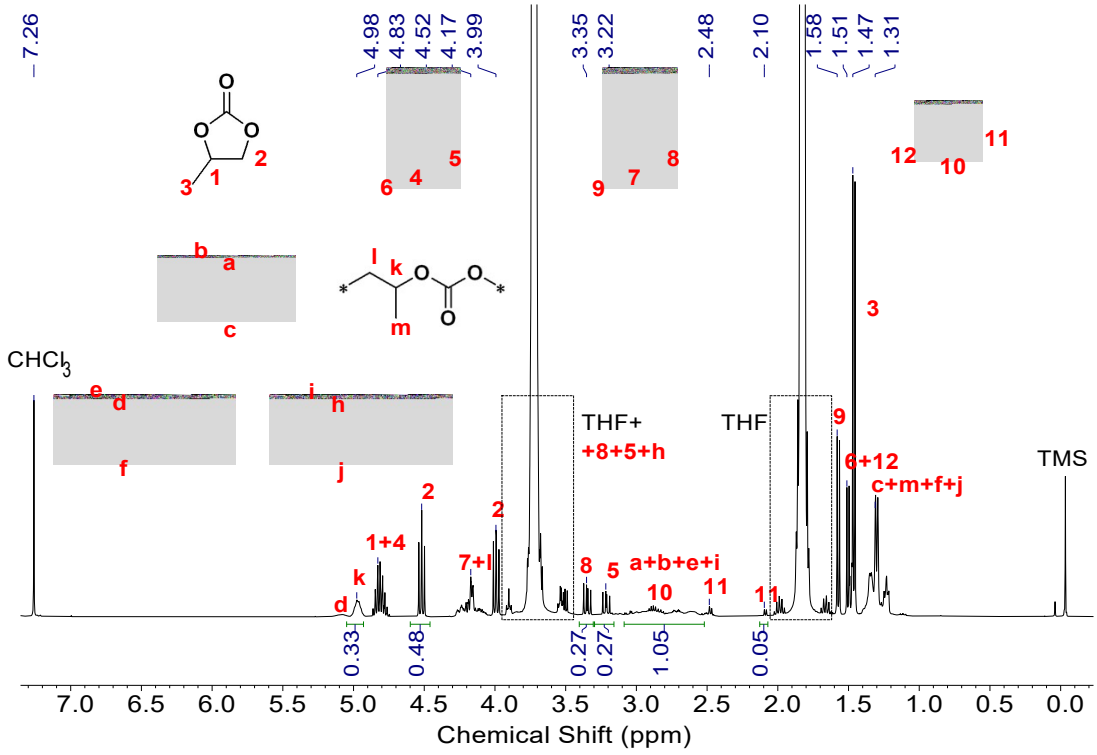


Fig. S2. ^{1}H NMR spectrum of (a) the crude product and (b) the purified product of entry 2 Table 1;



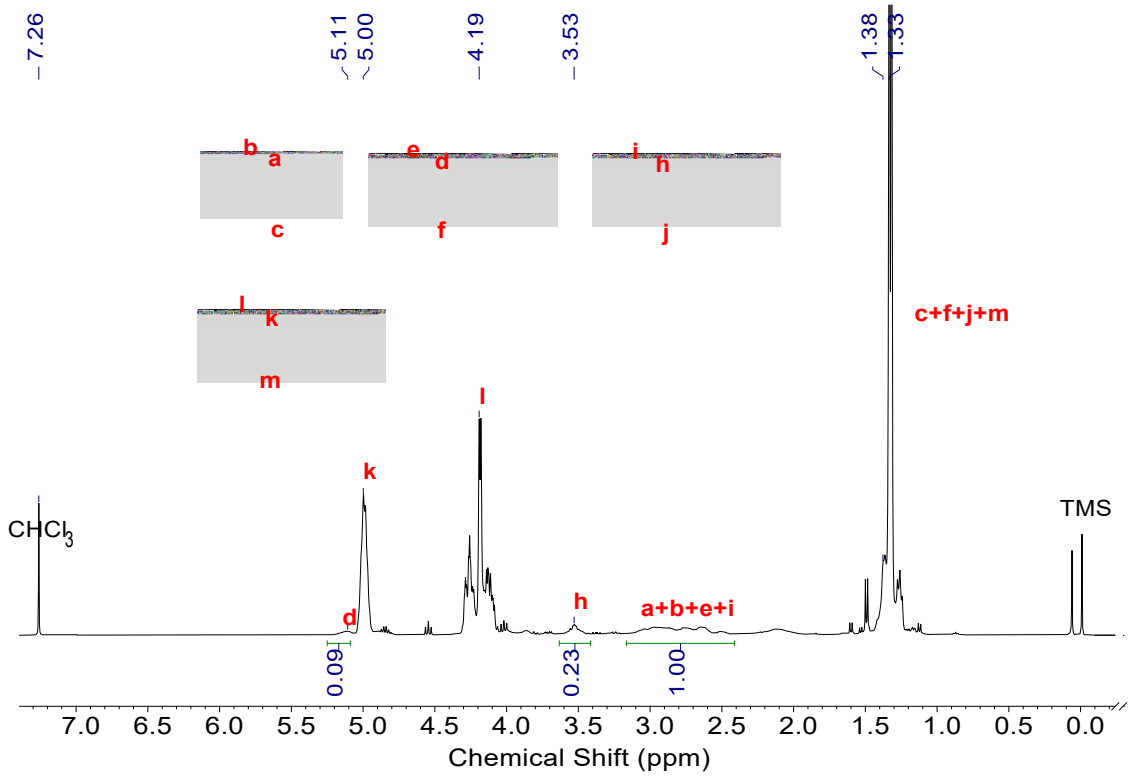
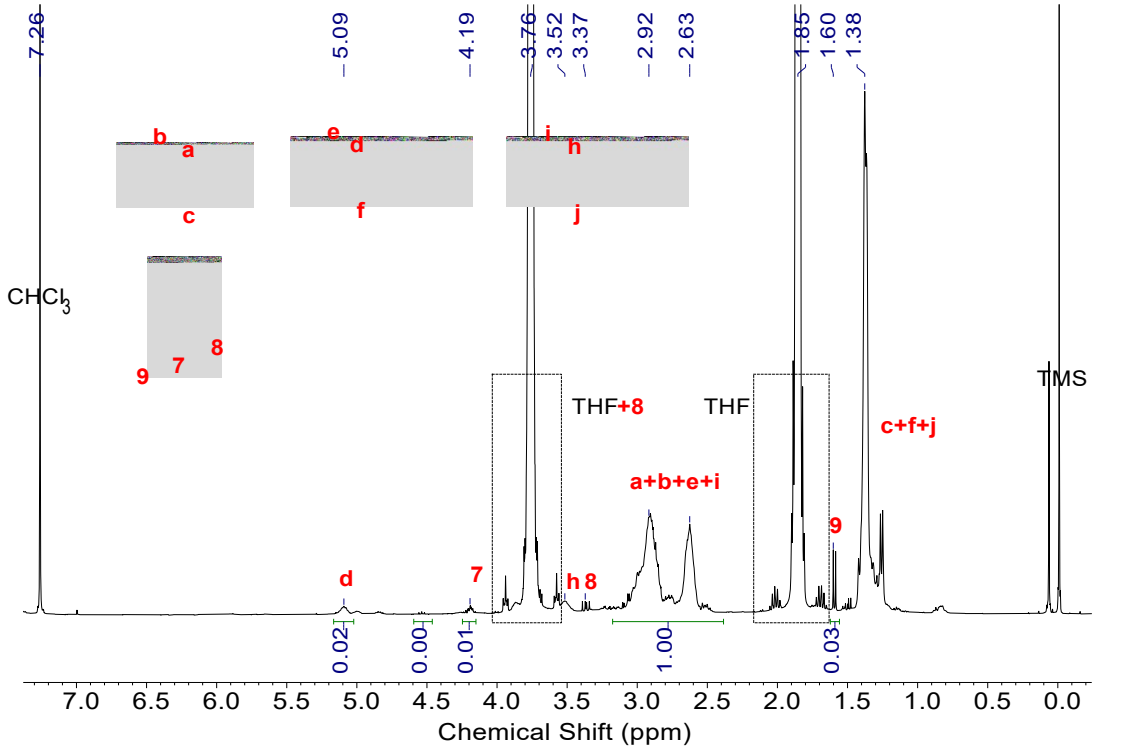


Fig. S3. ^{1}H NMR spectrum of (a) the crude product and (b) the purified product of entry 3 Table 1.



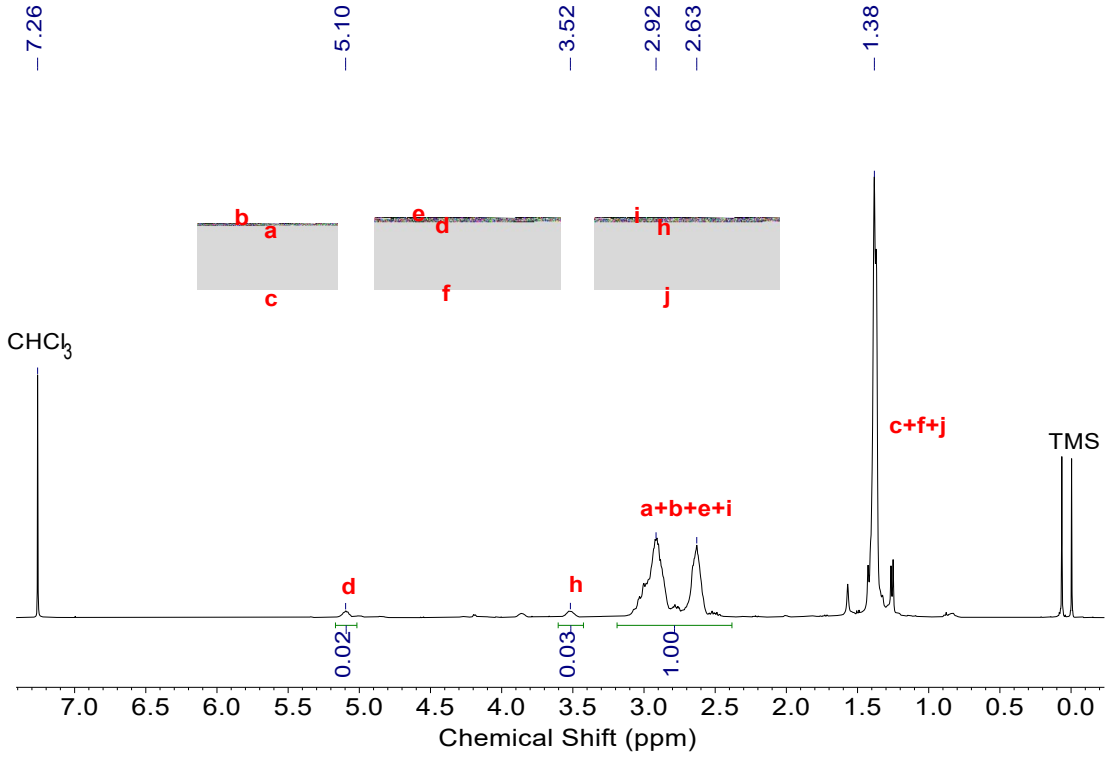
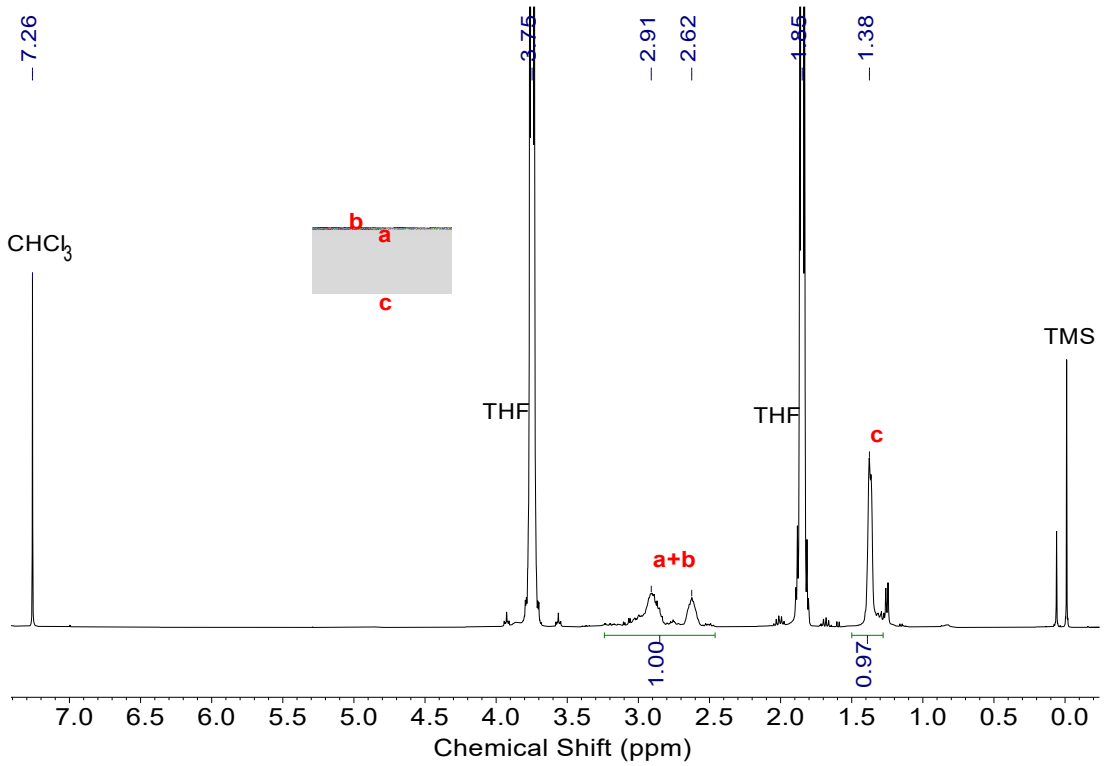


Fig. S4. ^{1}H NMR spectrum of (a) the crude product and (b) the purified product of entry 4 Table 1.



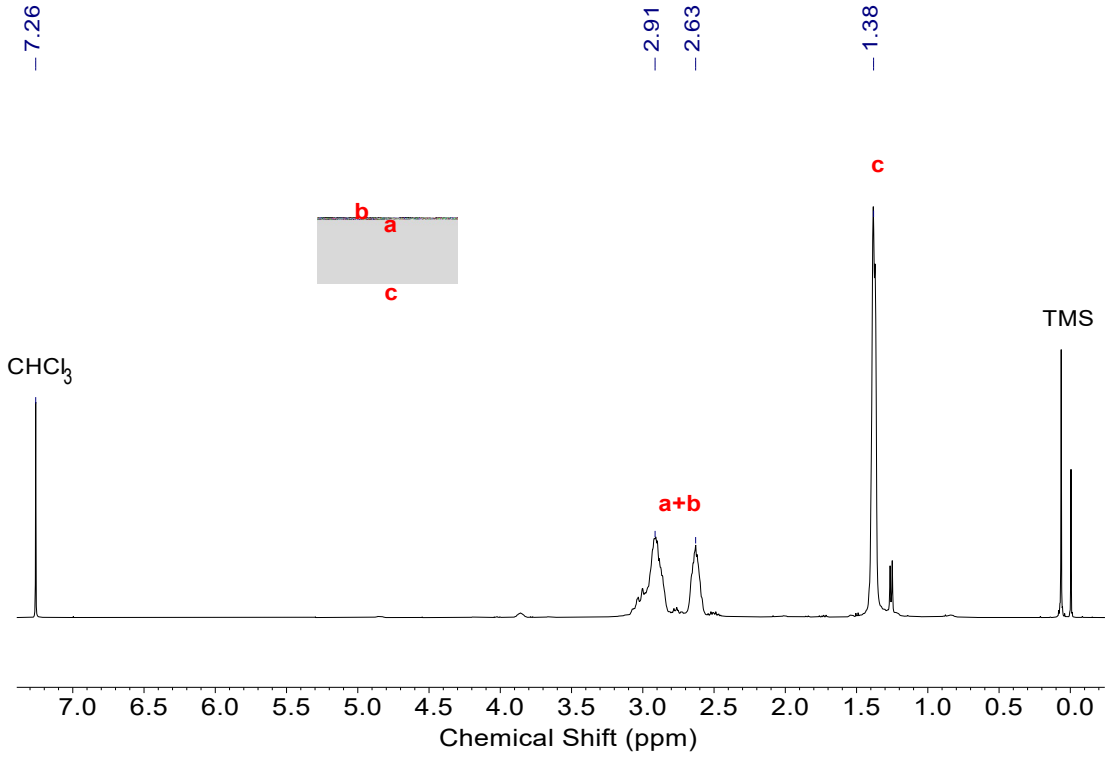
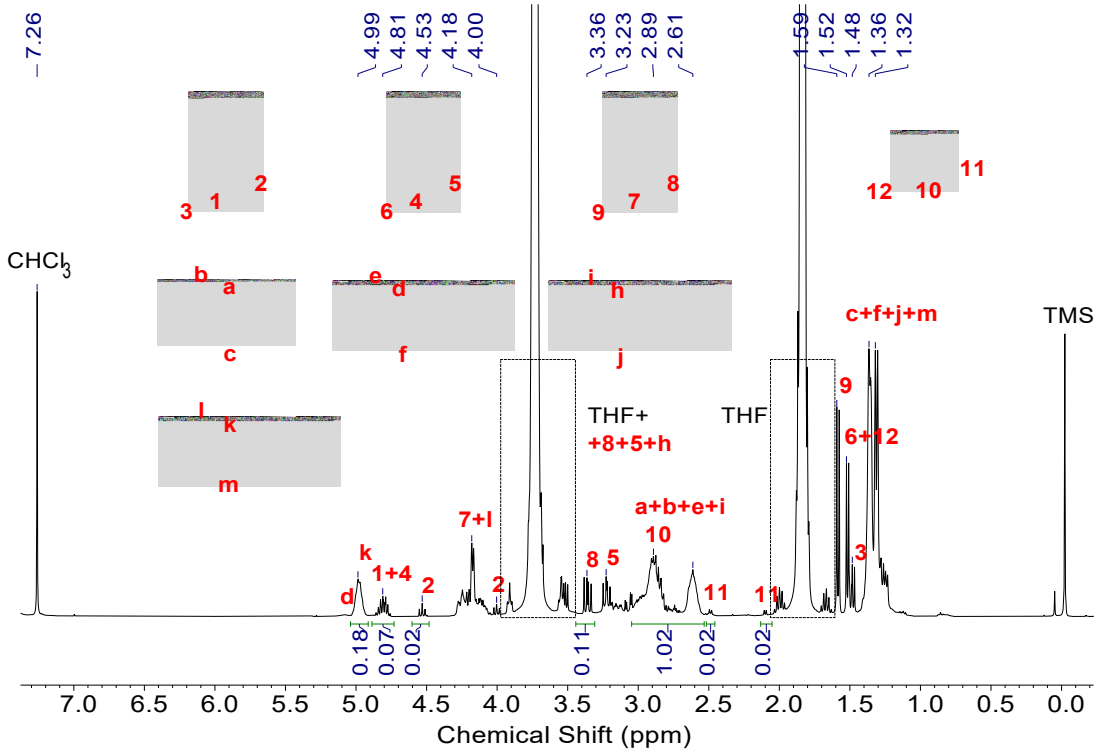


Fig. S5 ^{1}H NMR spectrum of (a) the crude product and (b) the purified product of entry 5 Table 1.



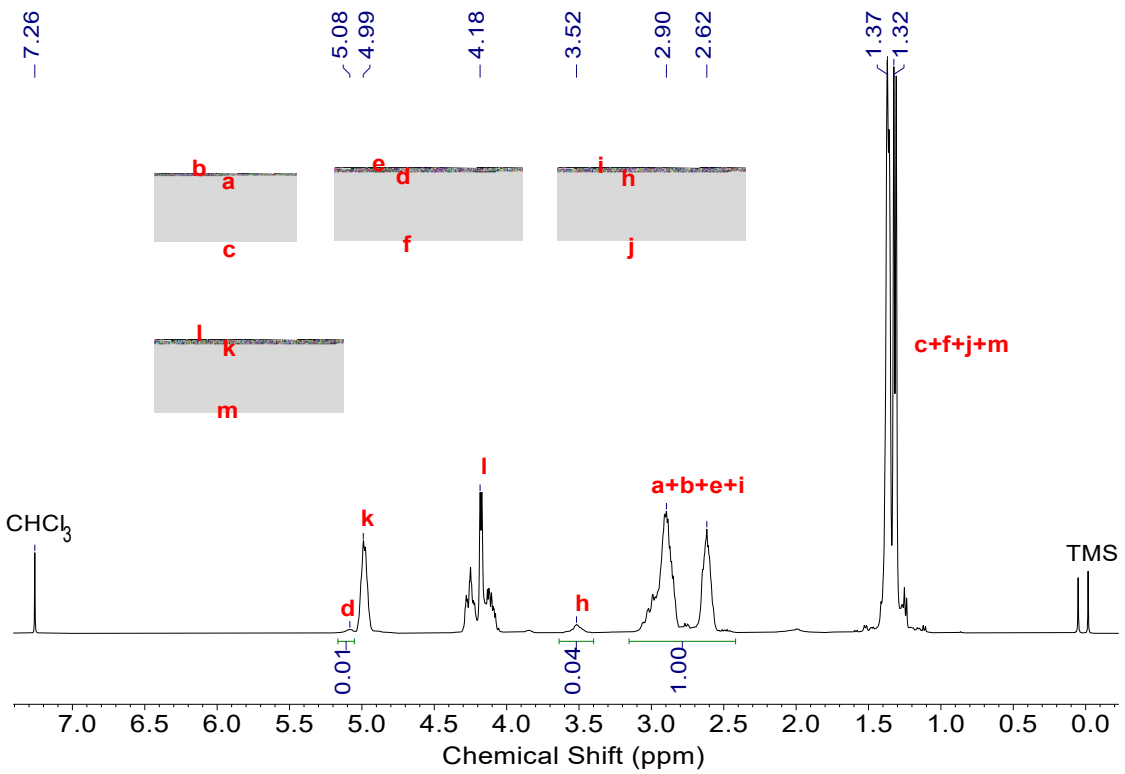
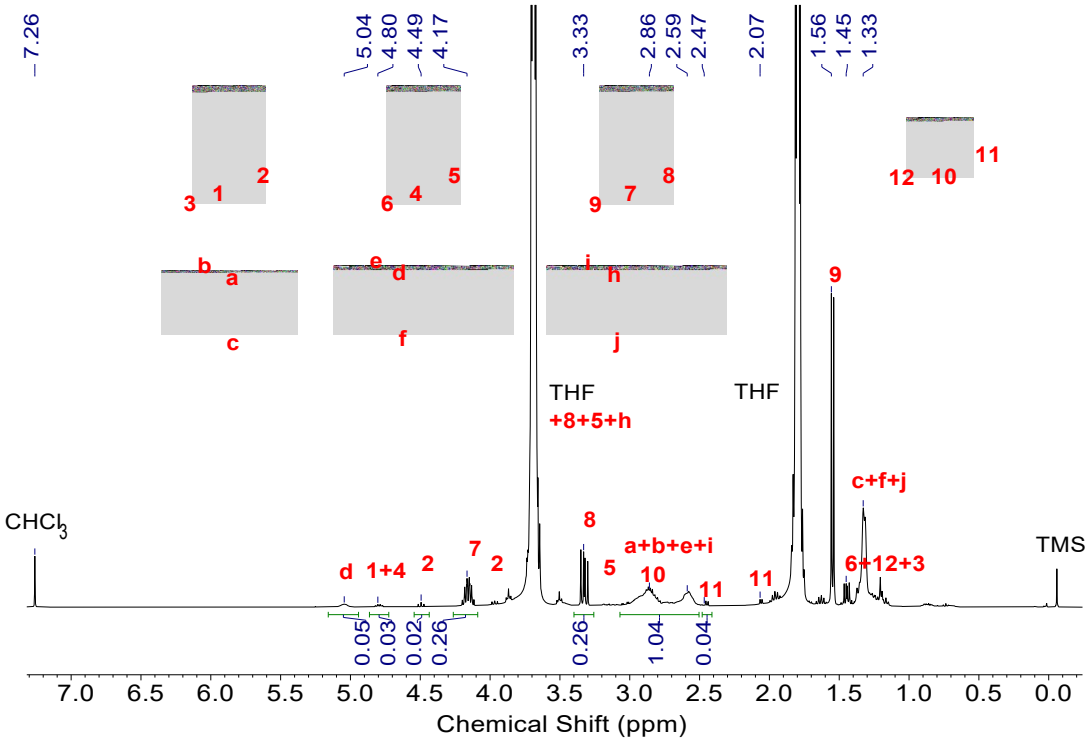


Fig. S6. ^{1}H NMR spectrum of (a) the crude product and (b) the purified product of entry 6 Table 1.



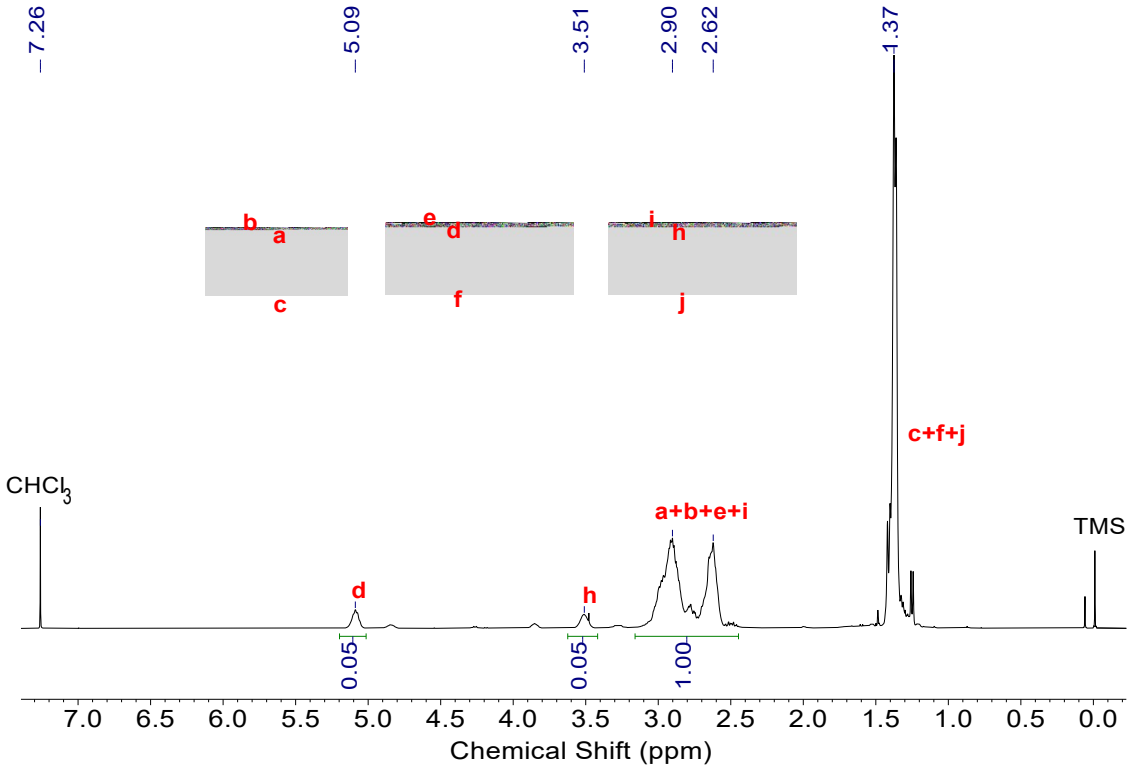
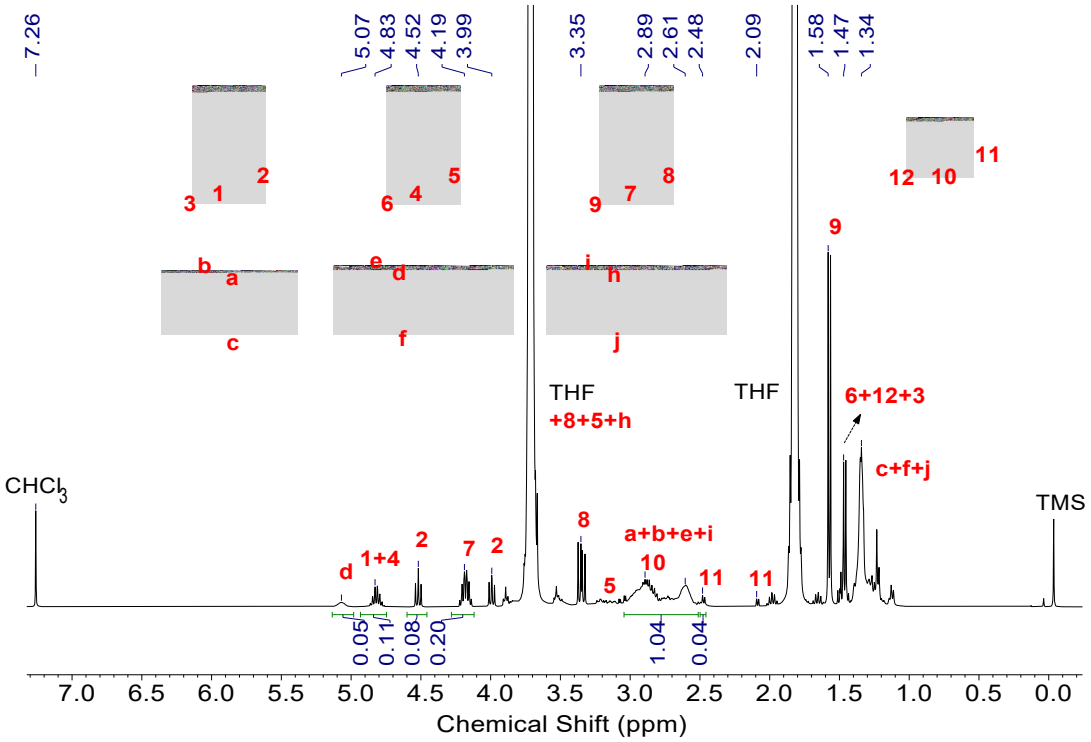


Fig. S7. ^{1}H NMR spectrum of (a) the crude product and (b) the purified product of entry 1 Table 2.



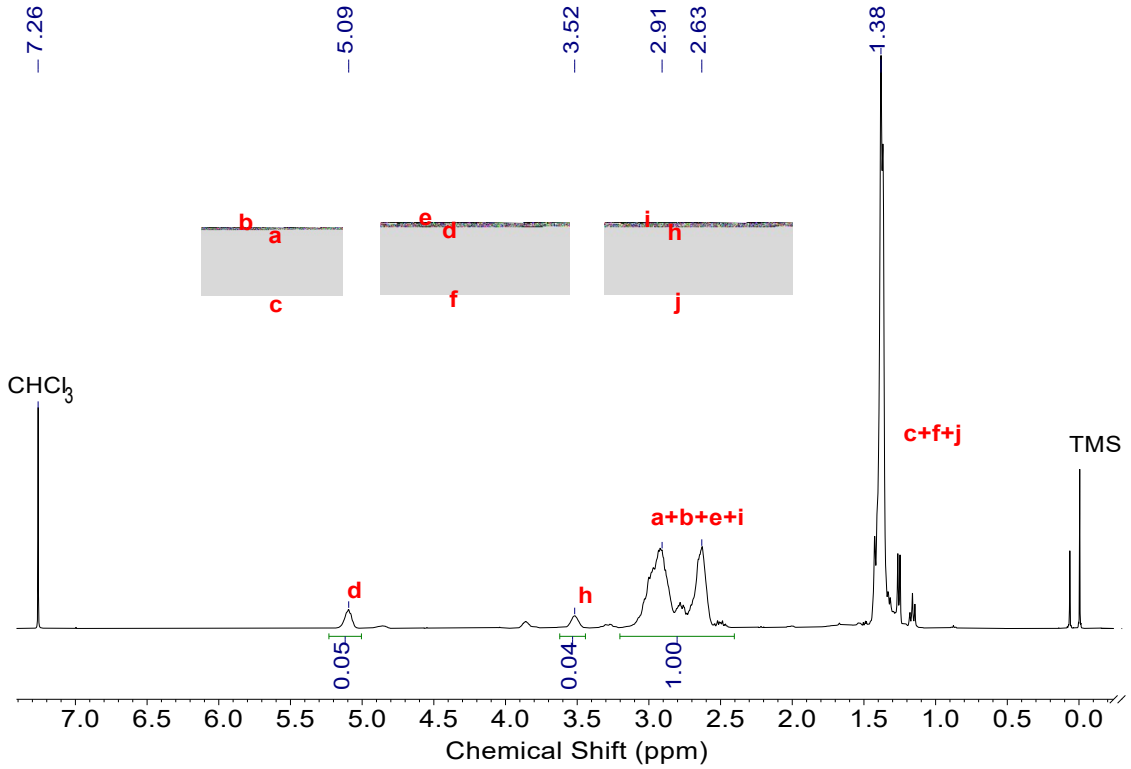
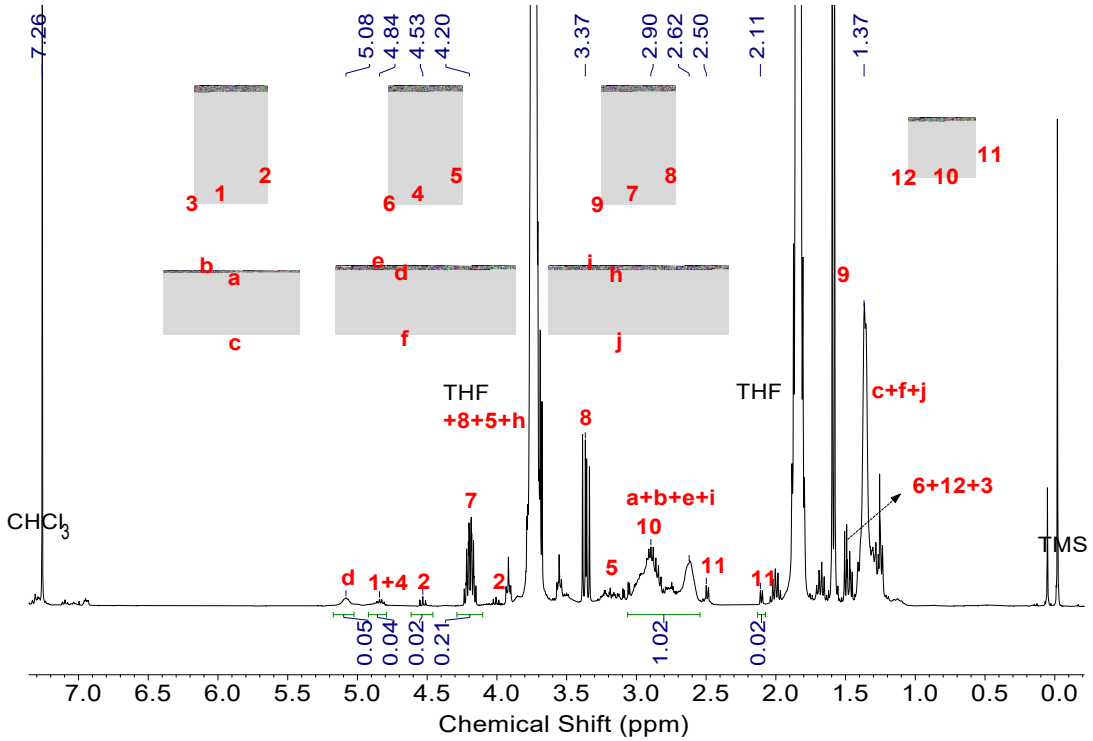


Fig. S8. ^{1}H NMR spectrum of (a) the crude product and (b) the purified product of entry 2 Table 2.



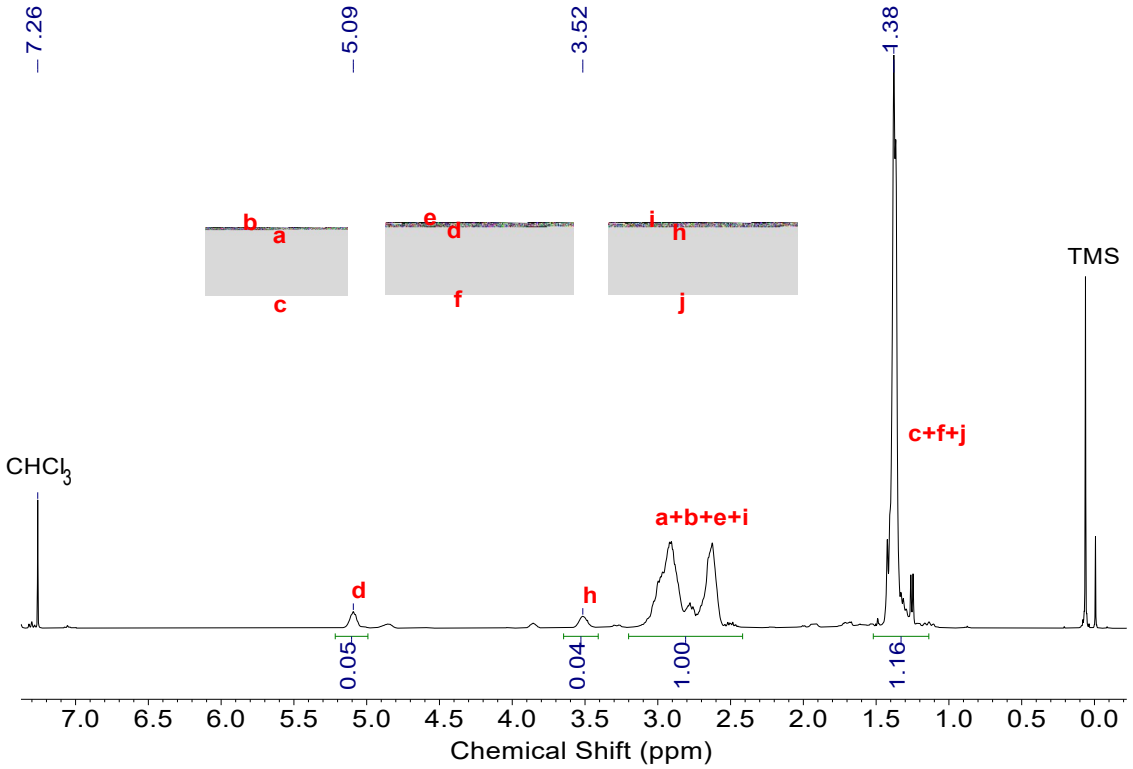


Fig. S9. ^{1}H NMR spectrum of (a) the crude product and (b) the purified product of entry 3 Table 2.

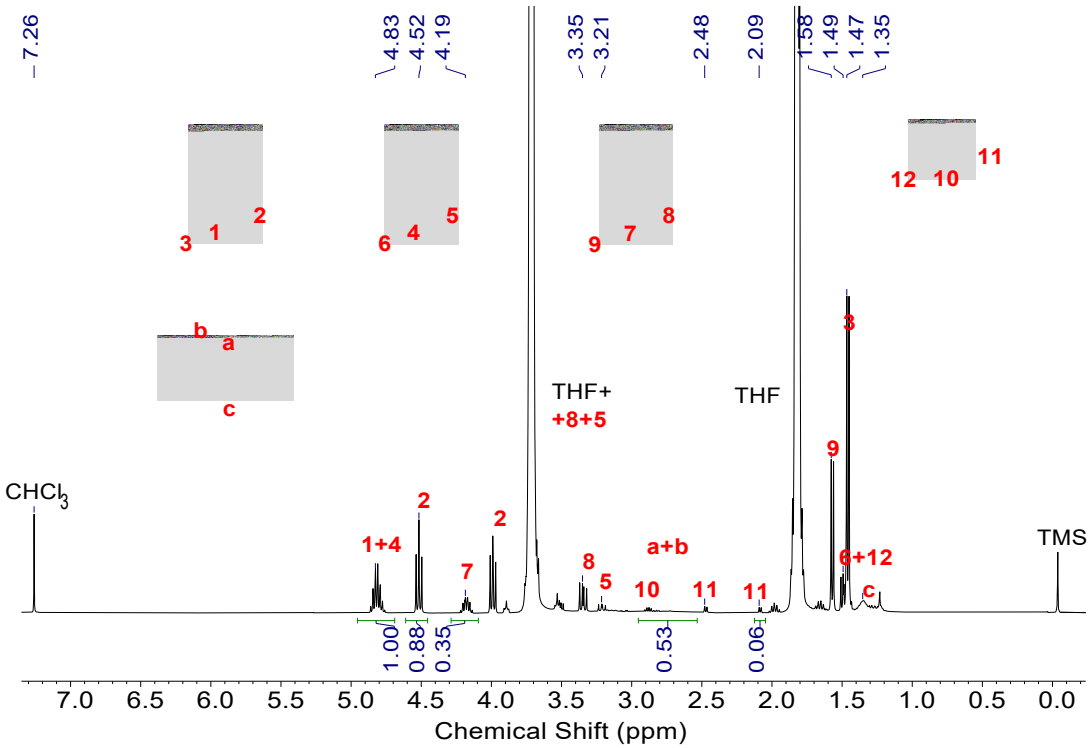


Fig. S10. ^{1}H NMR spectrum of the crude product of entry 4 Table 2.

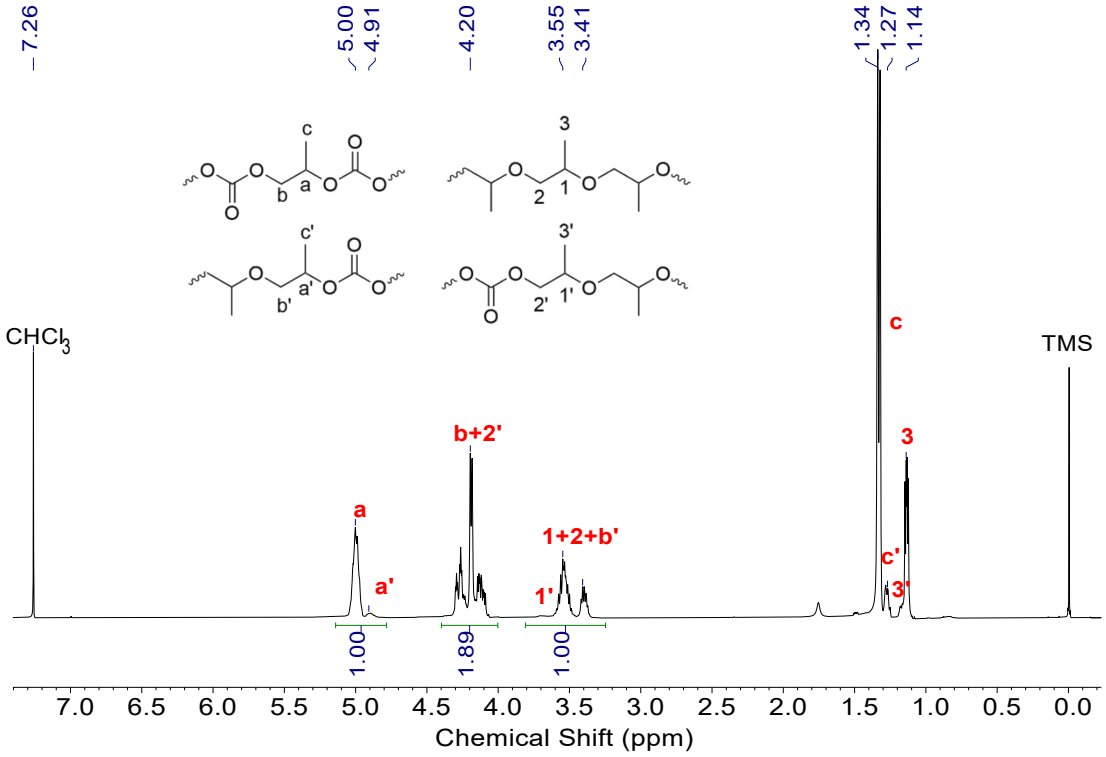
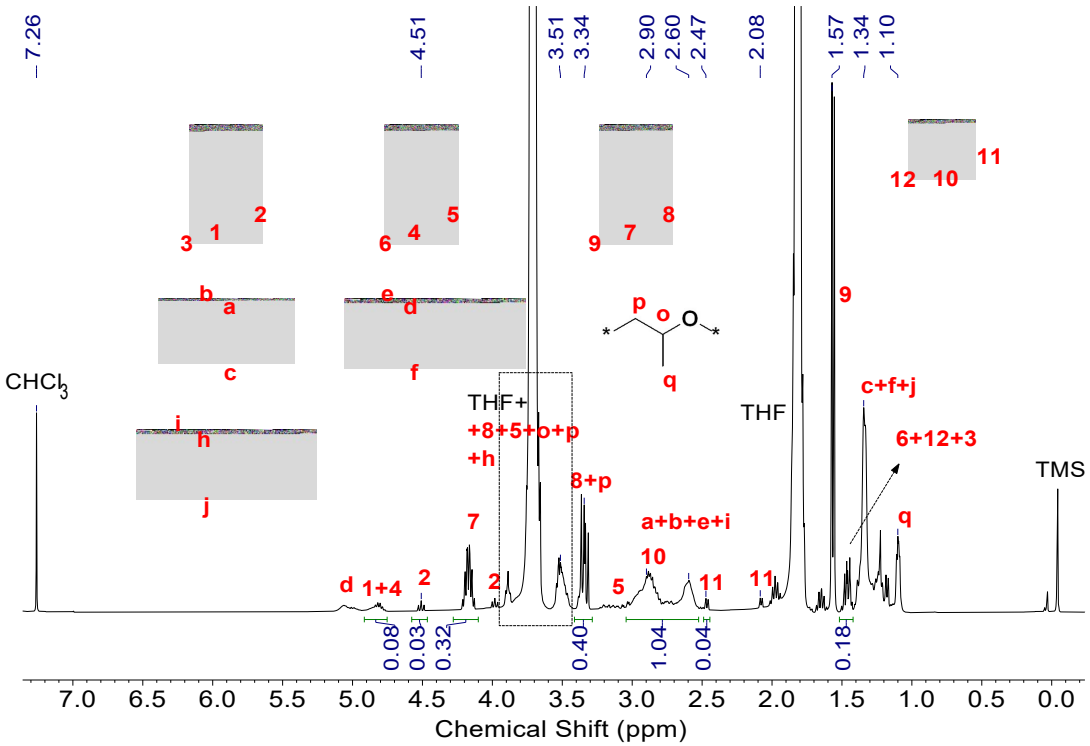


Fig. S11 ^{1}H NMR spectrum of the crude product of entry 1 Table 3.



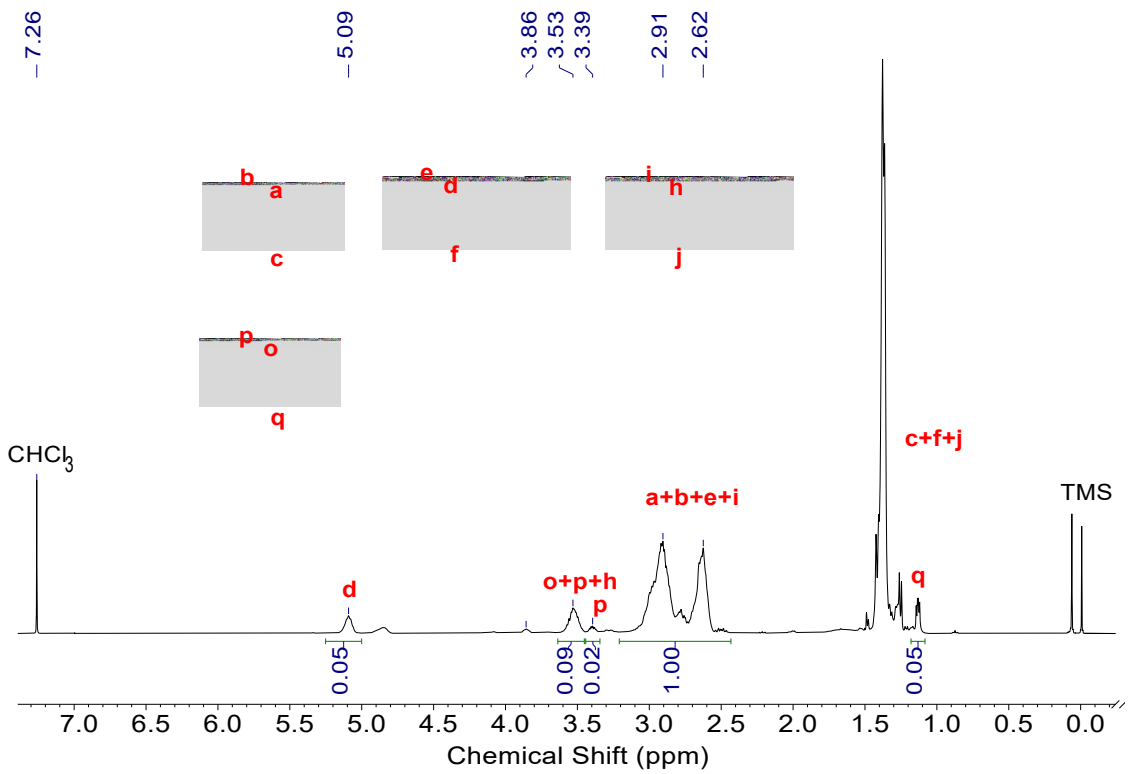
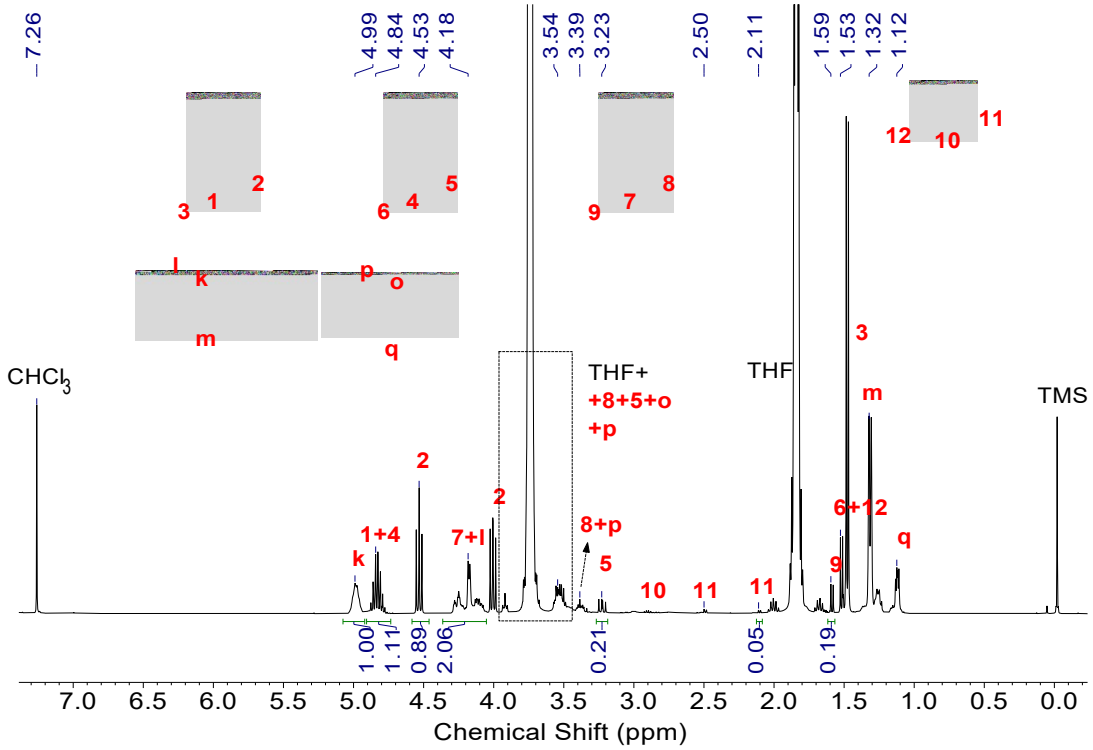


Fig. S12. ^{1}H NMR spectrum of (a) the crude product and (b) the purified product of entry 2 Table 3.



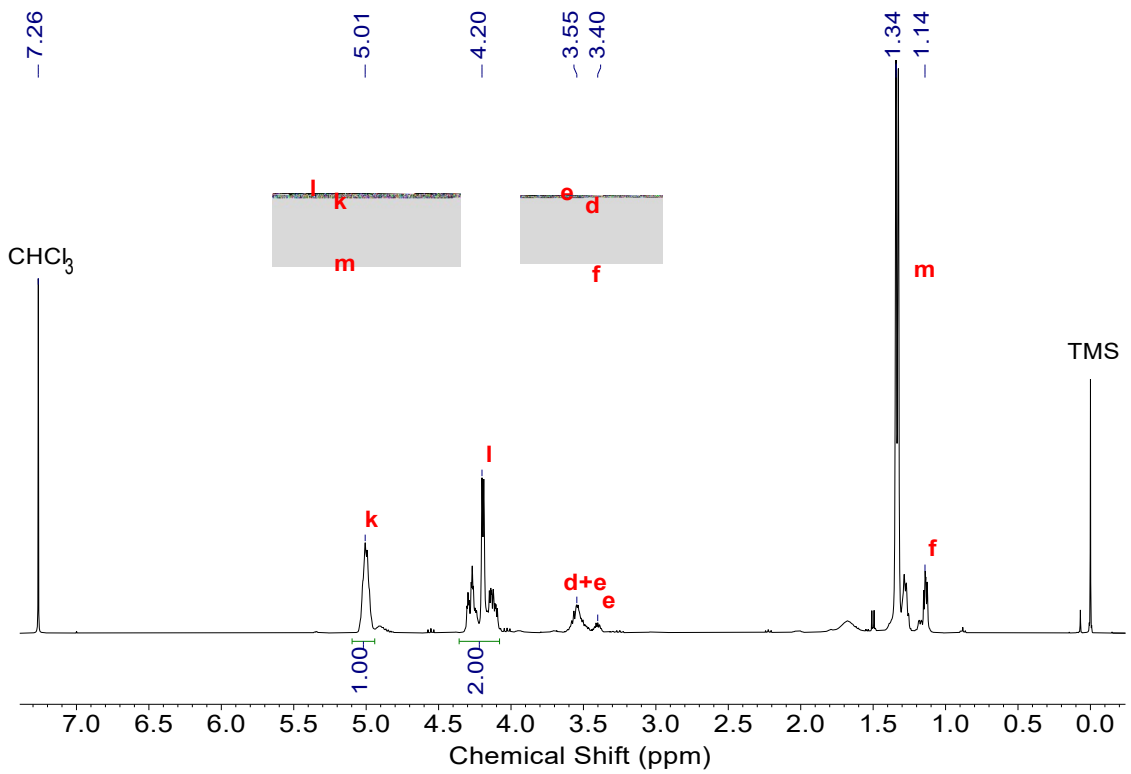


Fig. S13. ^{1}H NMR spectrum of (a) the crude product and (b) the purified product of entry 3 Table 3.

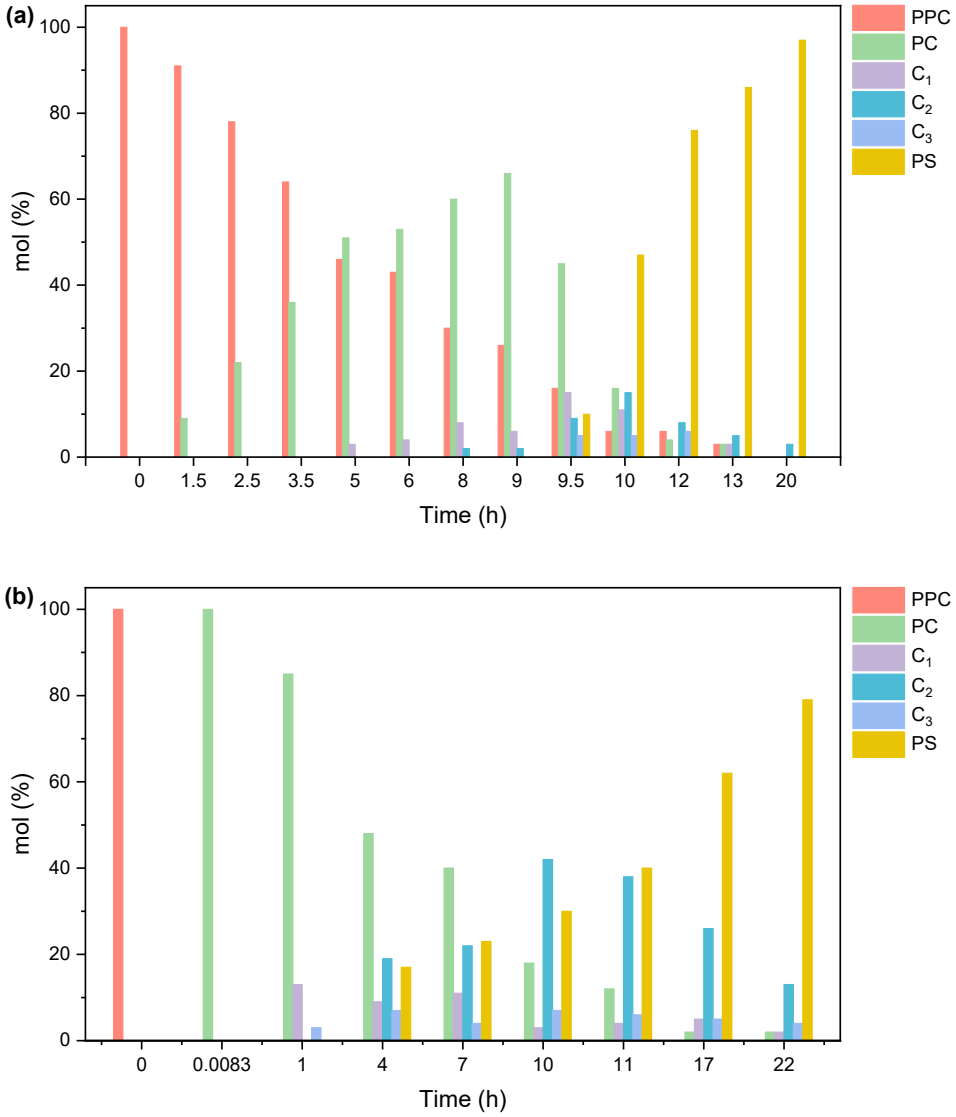


Fig. S14 The content of multiple components varied with time in the transformation process of PPC to PS catalyzed by (a) DBU and (b) KO^{t}Bu in THF (1.0 M) at 140 °C, [PPC repeating unit]:[LB] = 100:1.

Table S1 Thermal properties of PPC and **PS**.

entry	Samples	**P$_3$** (%)	T_g (°C) [a]	$T_{d,\,5\%}$ (°C) [b]	$T_{d,\,max}$ (°C) [b]
1	PPC	-	39	185	209
2	PS	100	-38	222	279
3	PS	85	-33	208	279

[a] Determined by DSC. [b] Determined by TGA, $T_{d,\,5\%}$ is the temperature at 5% weight loss, $T_{d,\,max}$ is the temperature at the maximum decomposition rate.

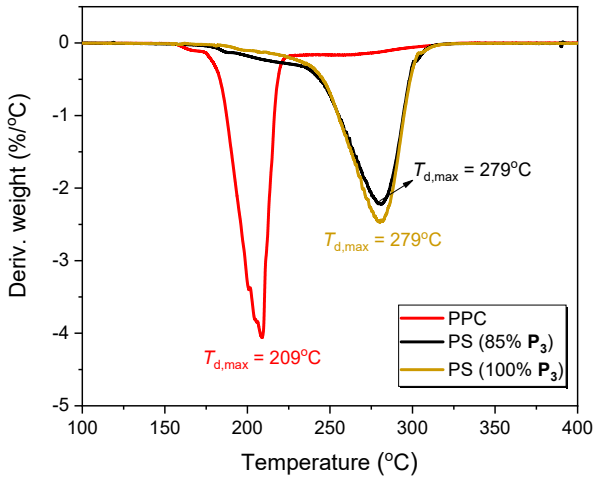


Fig. S15 DTG curves of representative PPC (F_{CO_2} > 99%) and **PS** ($\mathbf{P_3}$ = 85 and 100%).

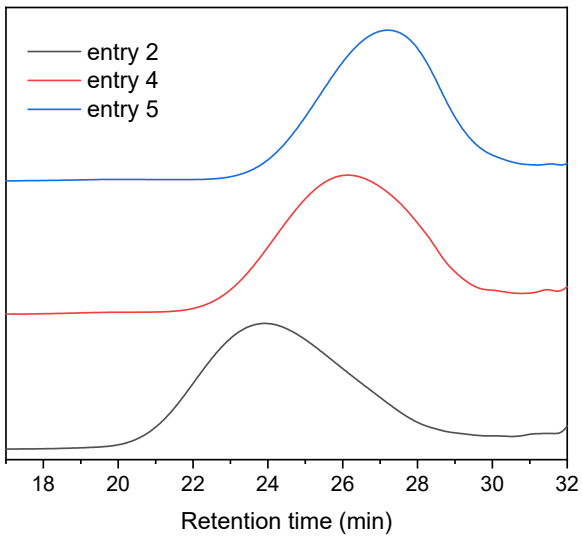
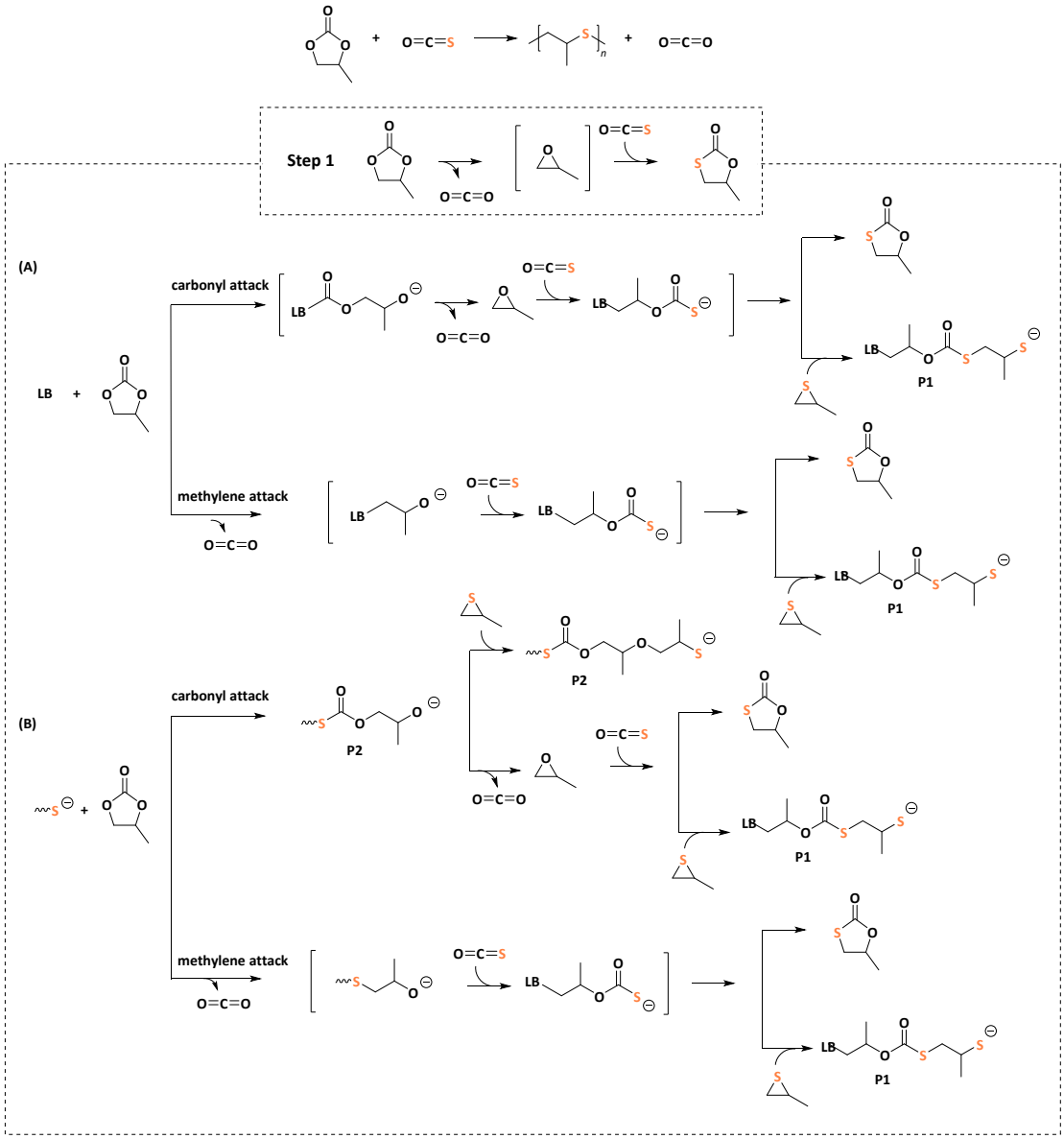


Fig. S16 GPC curves of the generated poly(thioether)s in entries 2, 4 and 5 in Table 1.



Scheme S1. Plausible mechanism for the incorporation of thiocarbonate into **PS**.