

Chemoselective Ring-Opening Copolymerization of Five-Membered Cyclic Carbonates and Carbonyl Sulfide toward Poly(thioether)s

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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. Superdry propylene carbonate (99.5 %) was bought from J&K Scientifics used without further purifications. Triethyl borane (BEt₃) in tetrahydrofuran solution (1.0 mol/ L) was bought from J&K Scientific and used without further purifications. Tri-tert-butylphosphine (^tBu₃P) in toluene solution (1.0 mol/ L) were purchased from Macklin. ^tBu₃P was purified by removing the toluene in ^tBu₃P solution under vacuum firstly, and then vacuum distilling after stirring with calcium hydride overnight in nitrogen. Carbonyl sulfide (COS) (99.9 %, ACS Grade, Alfa Aesar) was purchased from the APK (Shanghai) Gas Company LTD and used as received.

Methods.

¹H, and ¹³C NMR, ¹H-¹H COSY, ¹H-¹³C HSQC, ¹H-¹³C HMBC and DOSY spectra were performed on a Bruker Advance DMX 400 MHz. Chemical shifts values for ¹H and ¹³C spectra were referenced to internal solvent resonances (to CHCl₃ at 7.26 ppm for ¹H NMR and 77.16 ppm for ¹³C NMR). The number-average molecular weight (*M_n*) and molecular weight distribution ($\mathcal{D} = M_w/M_n$) of the resultant copolymers were determined with a PL-GPC220 chromatograph (Polymer Laboratories) equipped with an HP 1100 pump from Agilent Technologies. The GPC columns were eluted with THF with 1.0 mL/min at 40°C. The sample concentration was 0.4 wt %, and the injection volume was 50 μL. Calibration was performed using monodisperse polystyrene standards. The thermal properties of samples were characterized by differential scanning calorimetry (DSC) on a TA Discovery DSC25 instrument. In DSC experiments, the samples of 3-5 mg encapsulated in an aluminum pan were first heated to 100 °C and held for 3 min to eliminate thermal history. Subsequently, the samples were cooled to -80 °C, and reheated to 100 °C to obtain DSC curves. Both the heating and cooling rates were 10 °C min⁻¹. Glass transition temperature (*T_g*) was determined from the second run.

Representative procedure for copolymerization 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 copolymerization of COS with PC described below is taken from entry 9 in Table 2 as an example. Bis(triphenylphosphine)iminium chloride (PPNCl, 0.020 g, 0.04 mmol) was firstly added into the reactor. Afterwards, propylene carbonate (PC, 0.6 ml, 7.1 mmol) and lithium chloride (LiCl, 0.003 g, 0.08 mmol), was added into the autoclave respectively. The reactor was sealed and taken out from the glove box and charged with 0.64 g COS ([COS]:[PC] = 1.5:1, molar ratio, 1.0 MPa). The copolymerization was carried out at 140 °C for 6 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 PC conversion and the molar ratio of copolymer/cyclic products by ¹H NMR spectrum. The crude product was quenched with HCl in CH₂Cl₂ (1 mol/ L). Next, the polymer was purified three times by dissolving with CH₂Cl₂ and then precipitated in methanol. The final product was dried in vacuum at 50 °C until a constant weight.

Table S1. Copolymerization of COS with PC catalyzed by PPNCl in different time ^a

Entry	Time (h)	PC conv. ^b (%)	[C1]:[C2] ^b	[P1]:[P2]:[P3] ^b	[P]:[C] ^b	M _n ^c (kDa)	Đ ^c (M _w /M _n)
1	2	17	38:62	41:57:2	61:39	3.3	1.2
2	3	40	19:81	40:36:24	49:51	4.3	1.5
3	4	76	8:92	24:13:63	76:24	7.8	1.5
4	4.5	86	0:100	14:11:75	95:5	10.1	1.6
5	6	91	50:50	14:11:75	95:5	8.2	1.6
6	8	>99	-	6:3:91	100:0	6.2	1.7
7	24	>99	-	0:0:100	100:0	4.0	1.6

^a The reactions were performed in bulk in a 10 ml autoclave, [COS]: [PC]: [PPNCl] = 300: 200: 1, 140 °C. ^b Determined by ¹H NMR spectroscopy. ^c Determined by gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards.

Table S2. Copolymerization of COS with PC catalyzed by PPNCl/ LiCl in different time ^a

Entry	Time (h)	PC conv. ^b (%)	[C1]:[C2] ^b	[P1]:[P2]:[P3] ^b	[P]:[C] ^b	M _n ^c (kDa)	Đ ^c (M _w /M _n)
1	2	34	100:0	-	0:100	-	-
2	4	52	70:30	0:0:100	14:86	2.8	1.3
3	5	97	33:67	9:3:88	92:8	14.1	1.6
4	6	97	33:67	6:3:91	92:8	11.3	1.6
5	8	>99	-	3:0:97	100:0	11.1	1.7
6	12	>99	-	3:0:97	100:0	9.4	1.6
7	24	>99	-	0:0:100	100:0	7.7	1.6

^a The reactions were performed in bulk in a 10 ml autoclave, [COS]: [PC]: [PPNCl]: [LiCl]= 300: 200: 1: 2, 140 °C. ^b Determined by ¹H NMR spectroscopy. ^c Determined by gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards.

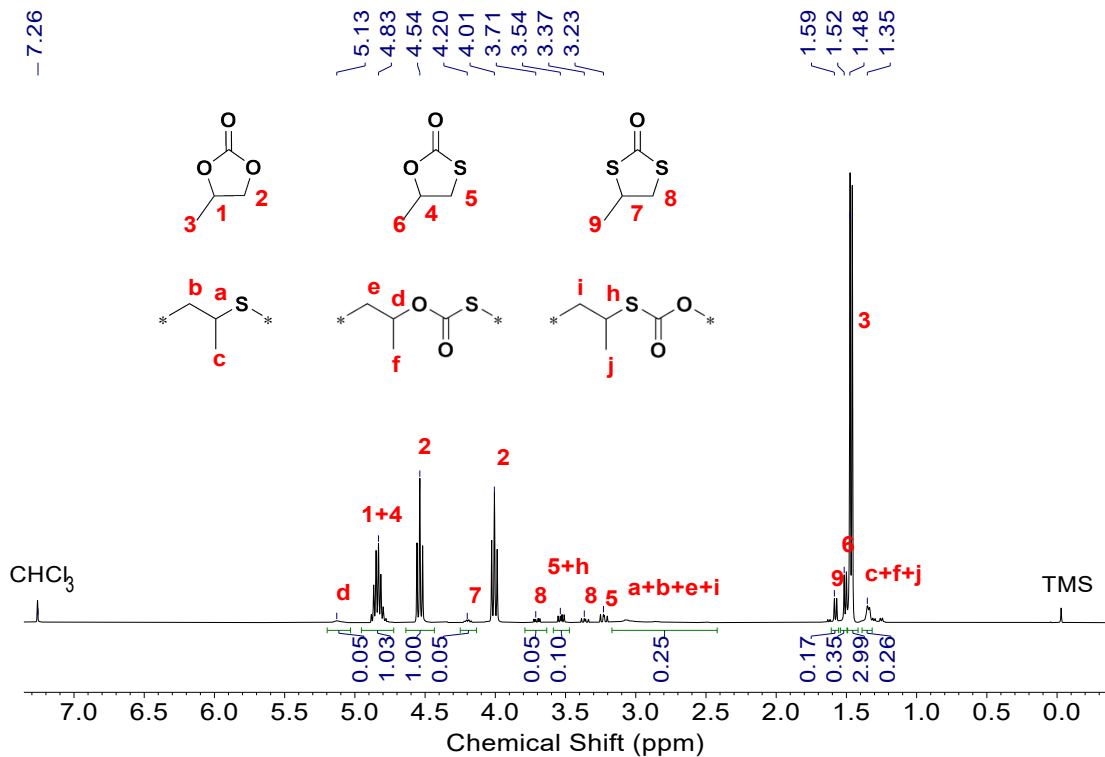
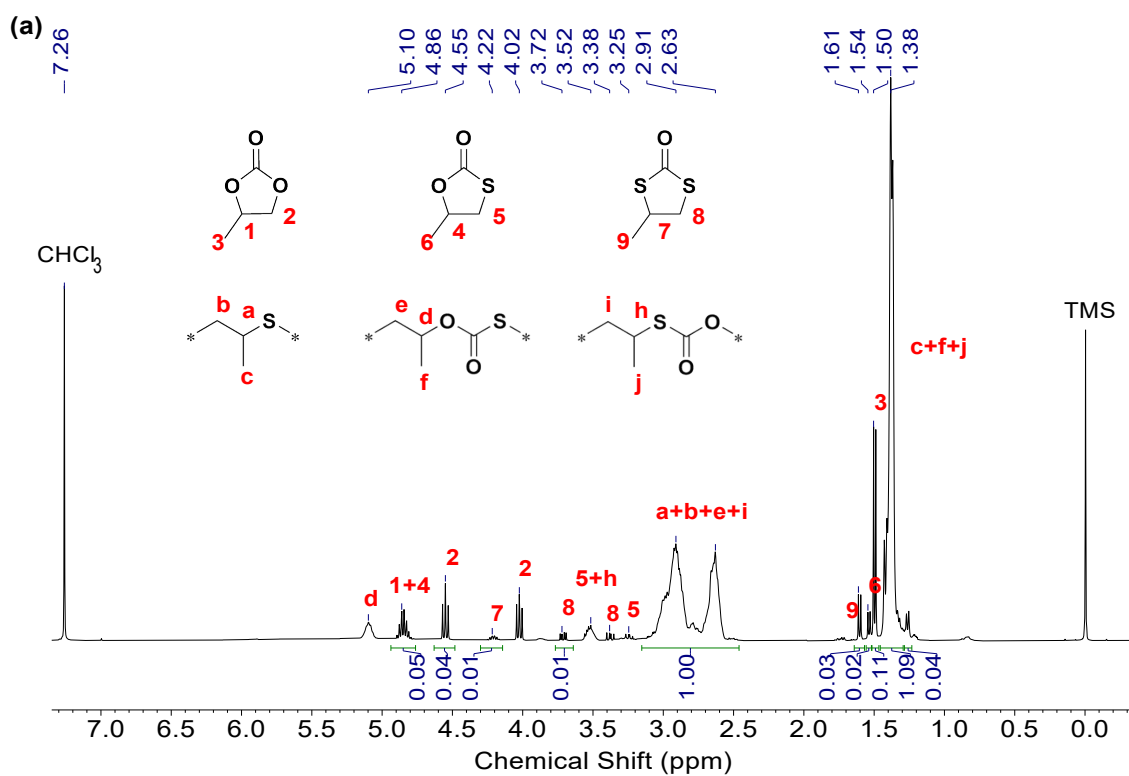
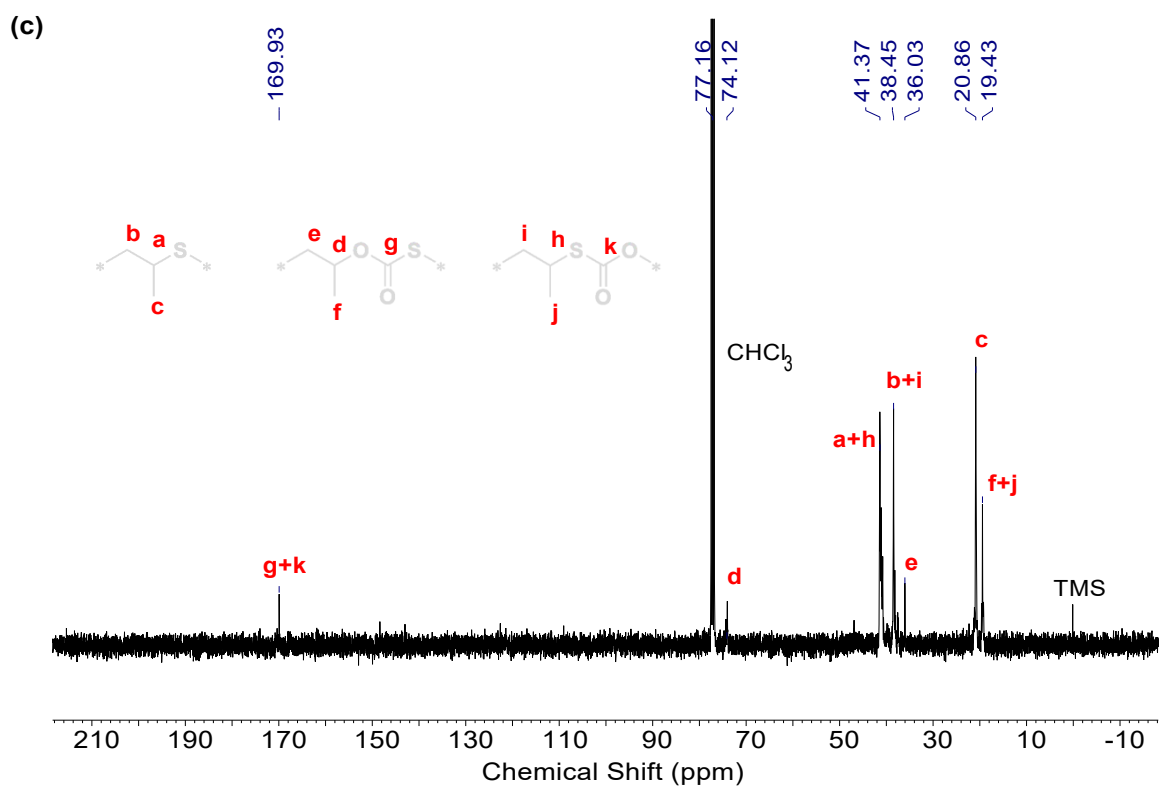
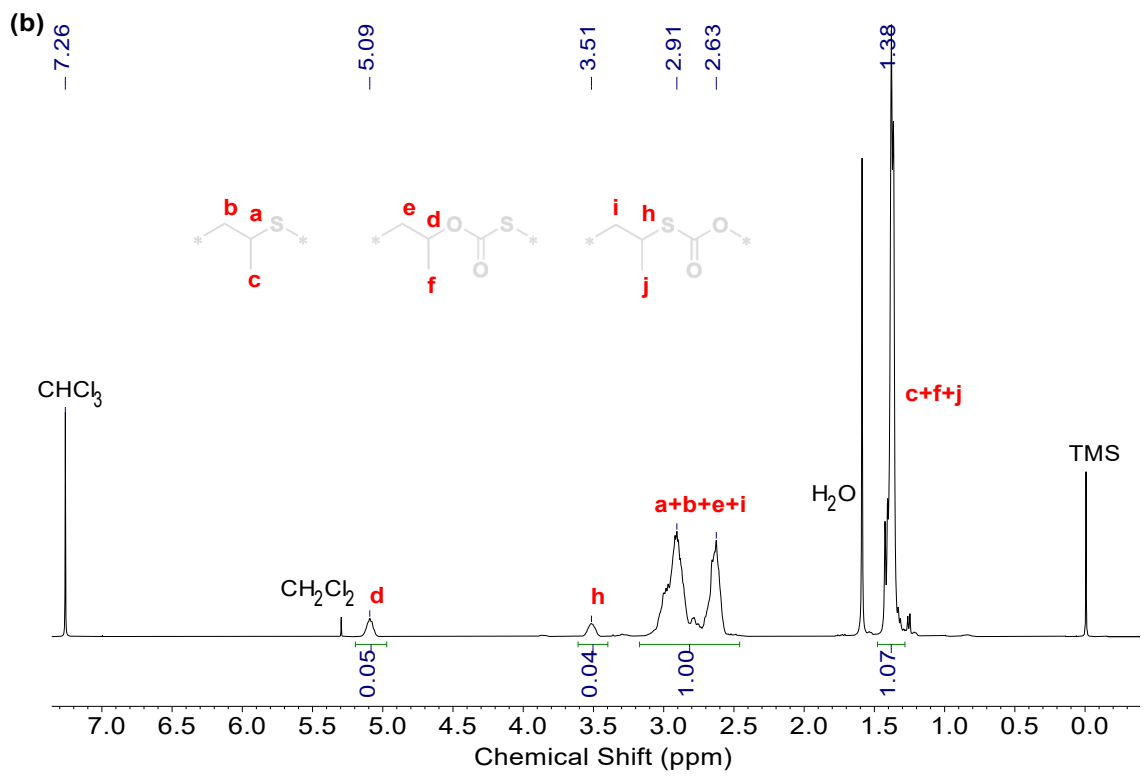
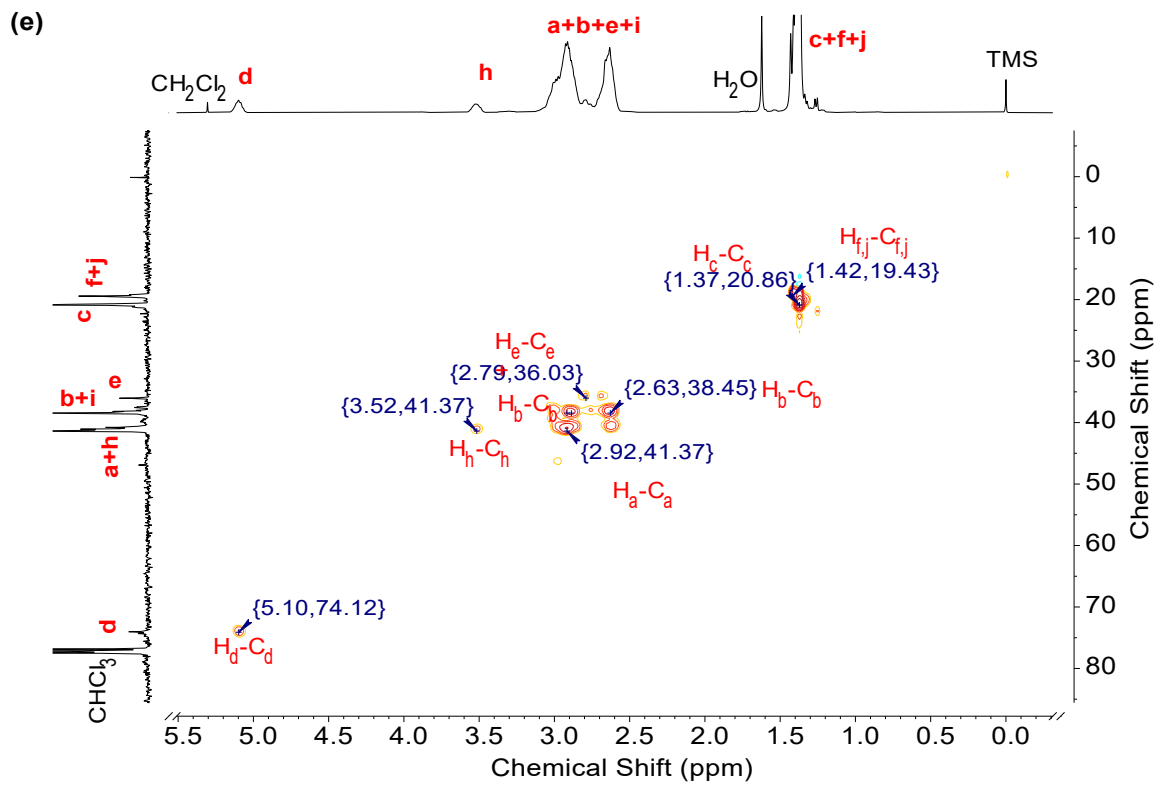
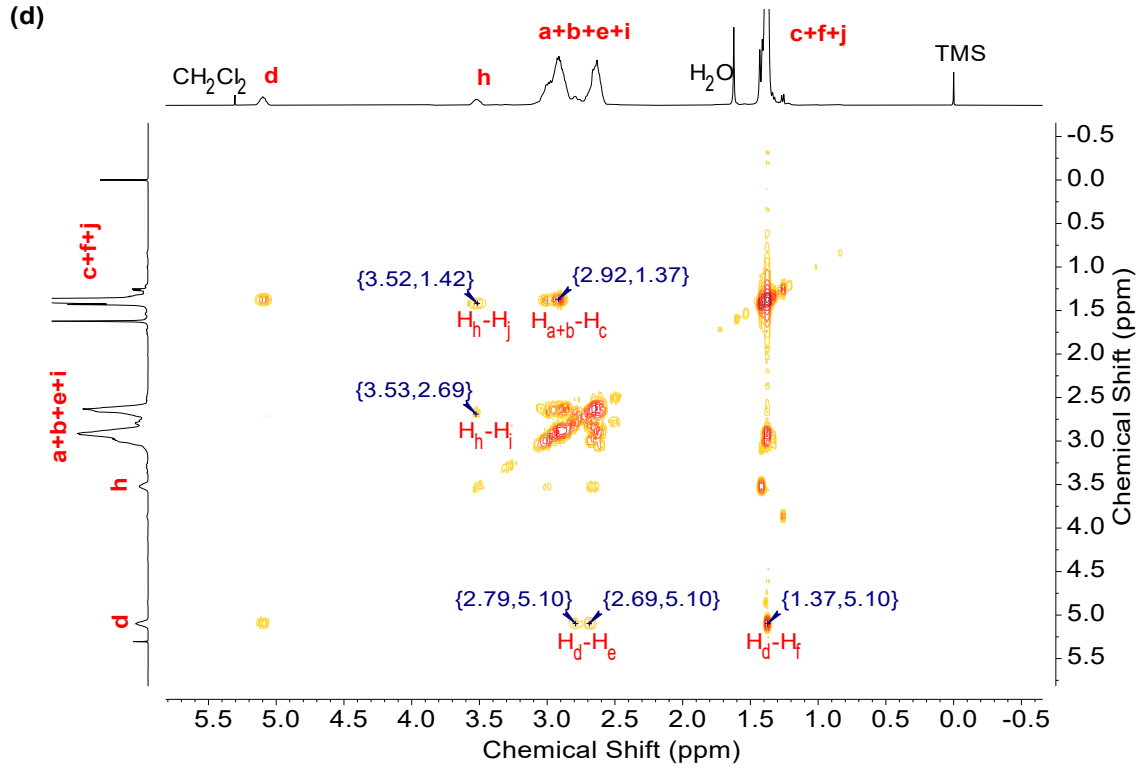


Fig. S1. ^1H NMR spectrum of the crude product of entry 1 Table 1.







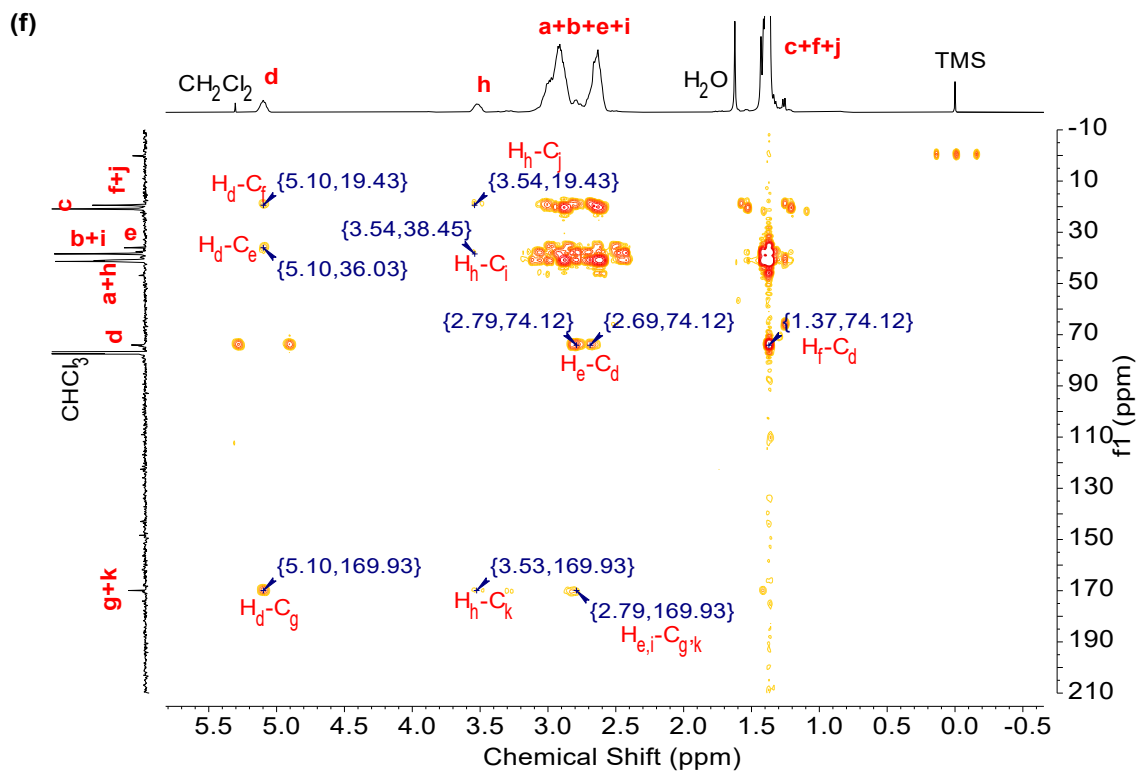


Fig. S2. (a) ^1H NMR spectrum of the crude product of entry 2 Table 1; (b) ^1H NMR spectrum of the purified product of entry 2 Table 1; (c) ^{13}C NMR spectrum of the purified product of entry 2 Table 1; (d) ^1H - ^1H COSY NMR spectrum of the purified product of entry 2 Table 1; (e) ^1H - ^{13}C HSQC NMR spectrum of the of the purified product of entry 2 Table 1; (f) ^1H - ^{13}C HMBC NMR spectrum of the of the purified product of entry 2 Table 1.

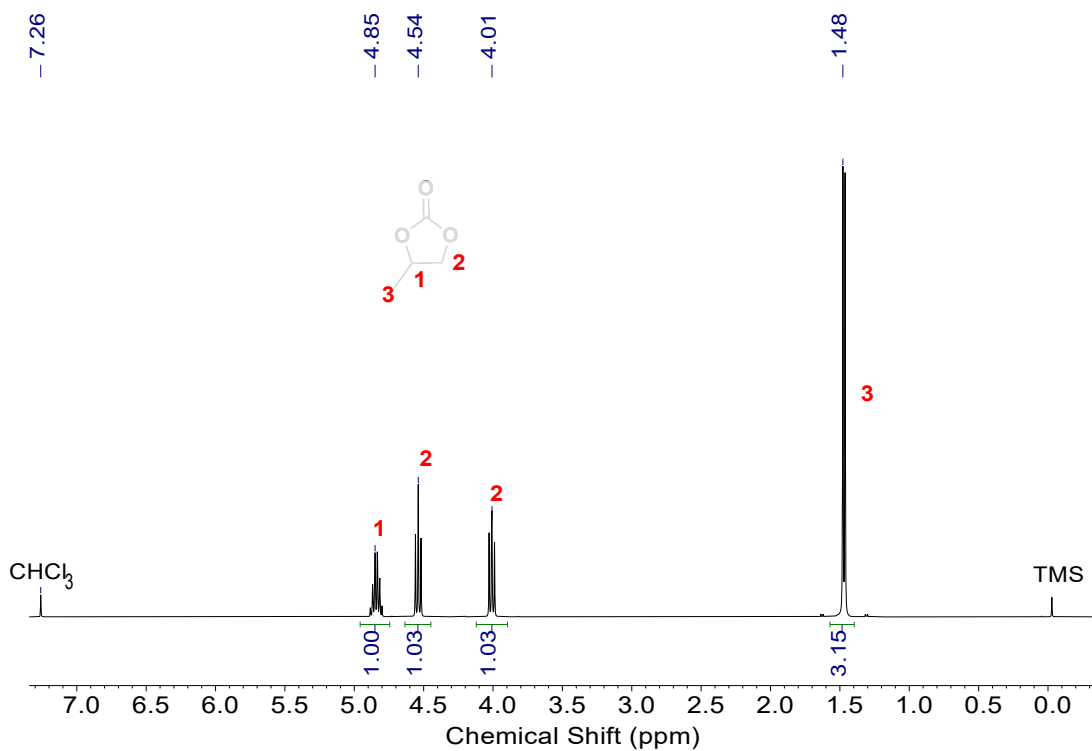


Fig. S3. ^1H NMR spectrum of the crude product of entry 3 Table 1.

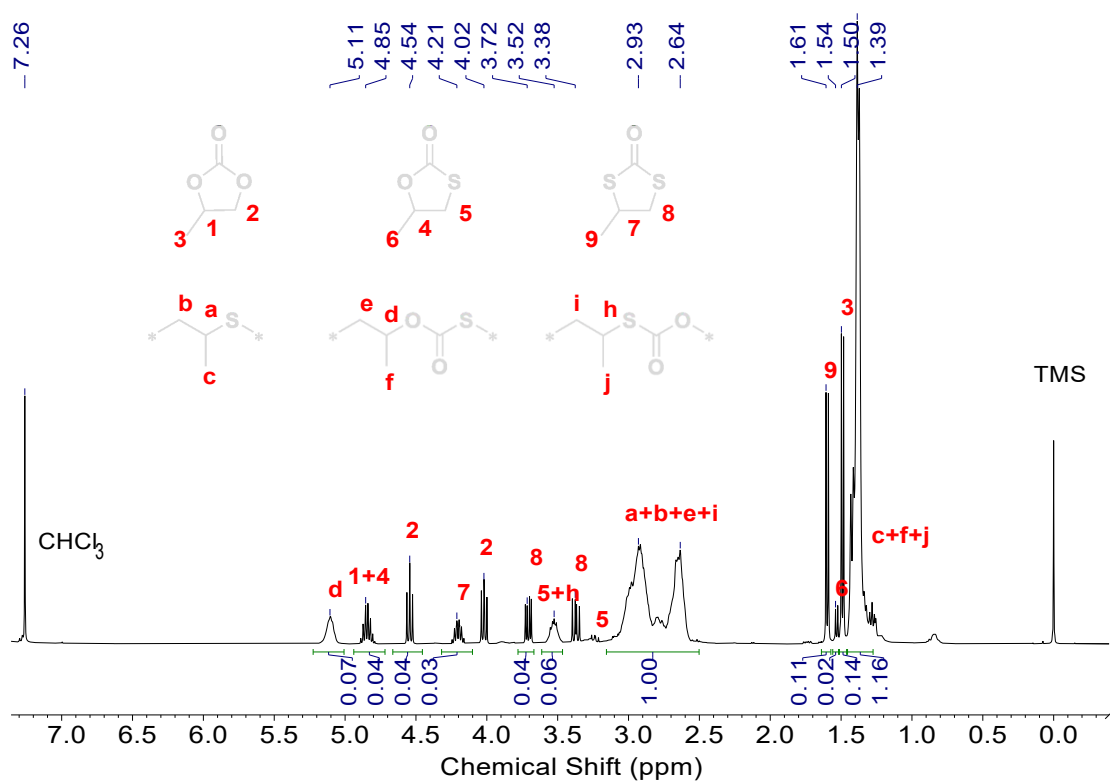


Fig. S4. ^1H NMR spectrum of the crude product of entry 4 Table 1.

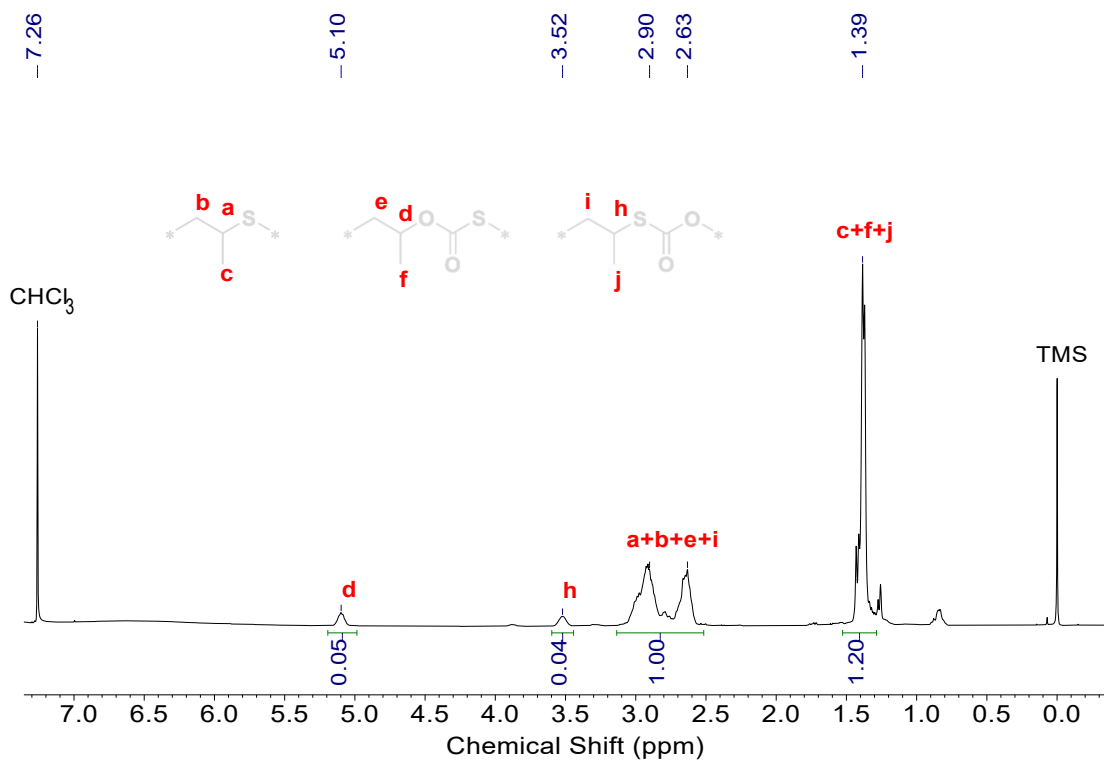


Fig. S5. ^1H NMR spectrum of the crude product of entry 5 Table 1.

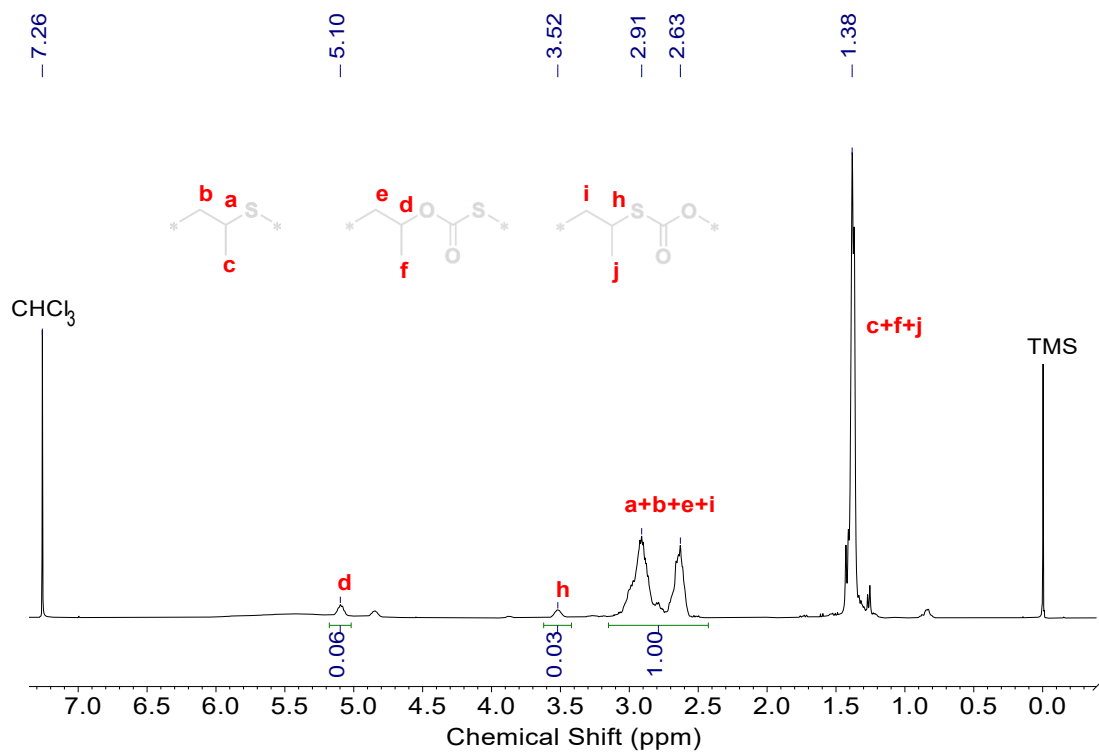


Fig. S6. ¹H NMR spectrum of the crude product of entry 6 Table 1.

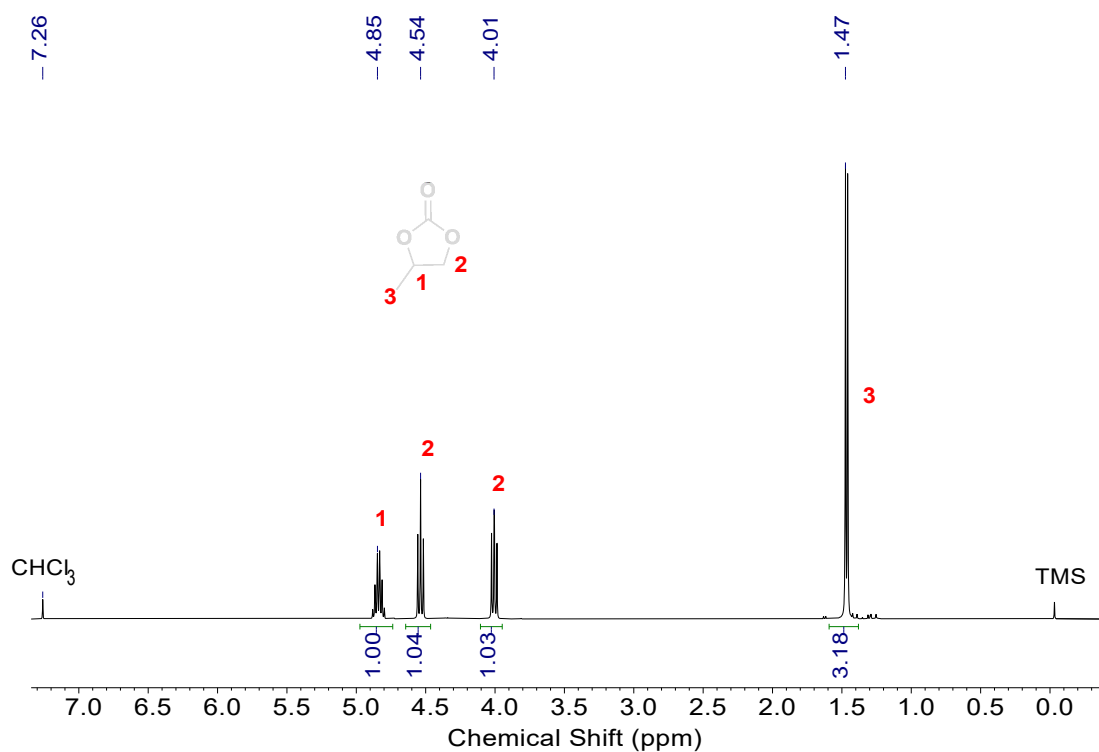


Fig. S7. ¹H NMR spectrum of the crude product of entry 7 Table 1.

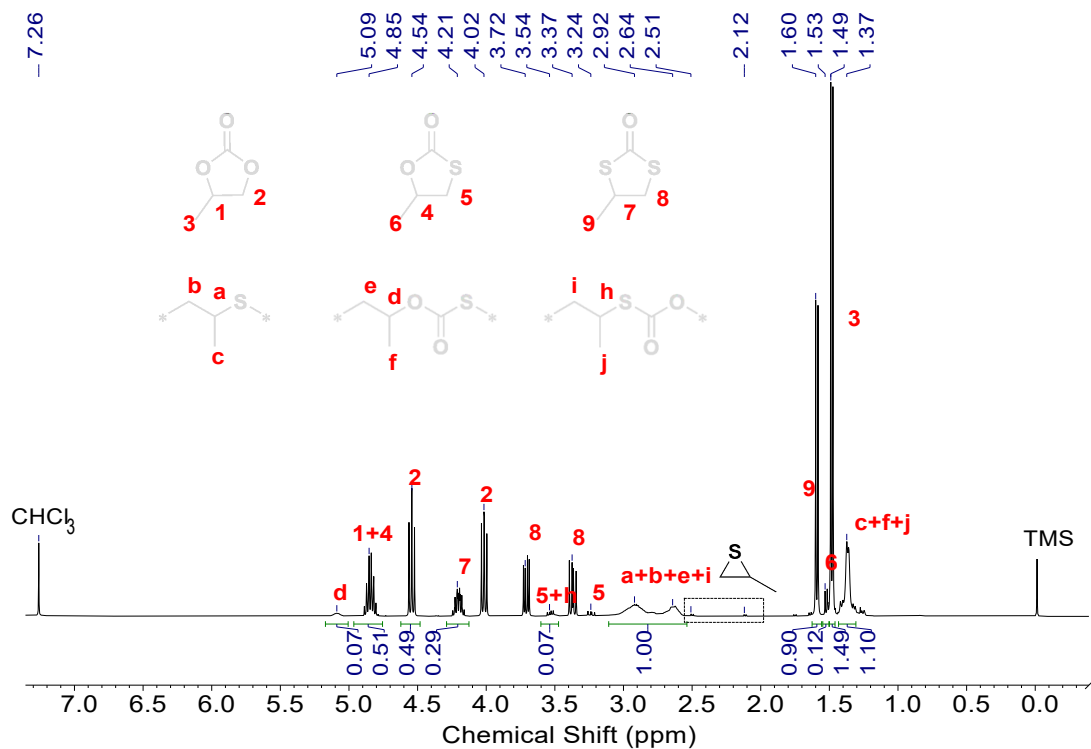


Fig. S8. ¹H NMR spectrum of the crude product of entry 8 Table 1.

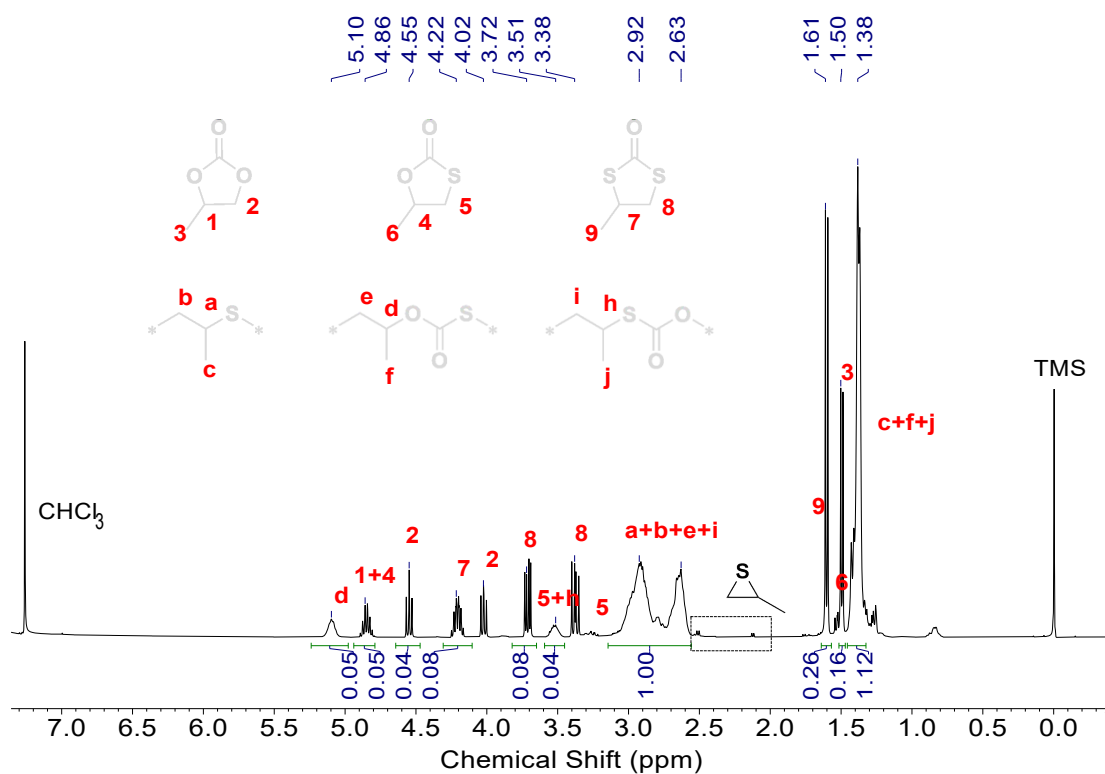


Fig. S9. ¹H NMR spectrum of the crude product of entry 9 Table 1.

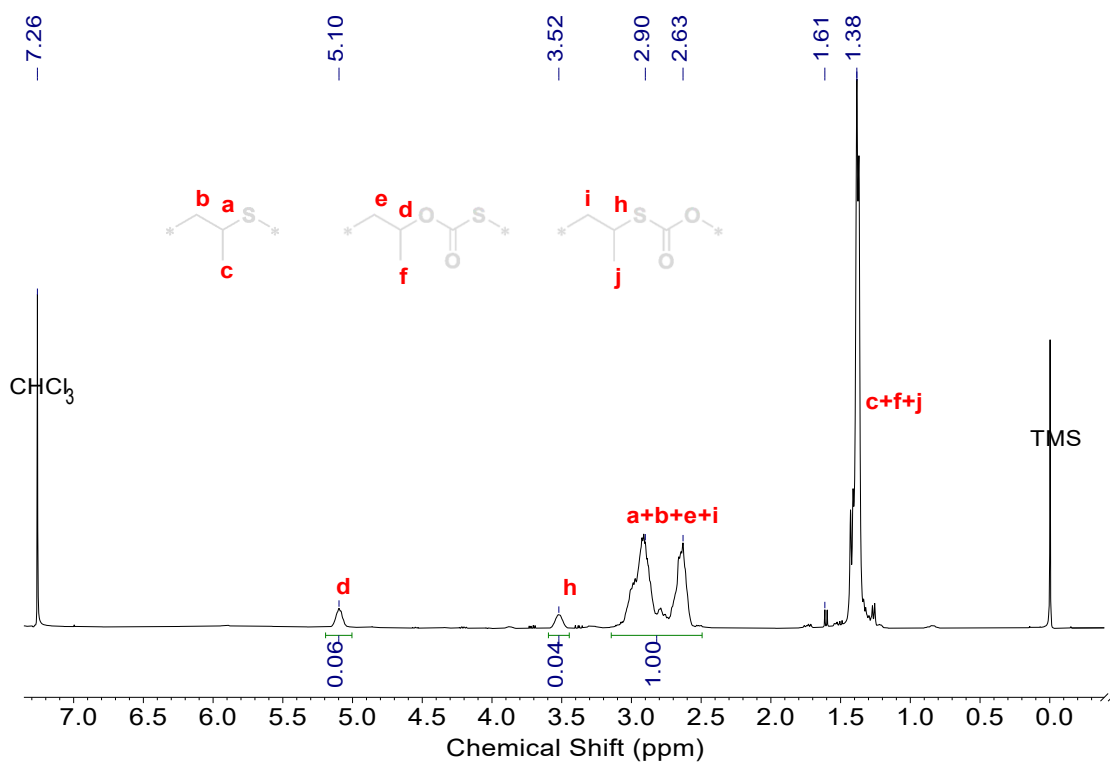


Fig. S10. ^1H NMR spectrum of the crude product of entry 10 Table 1.

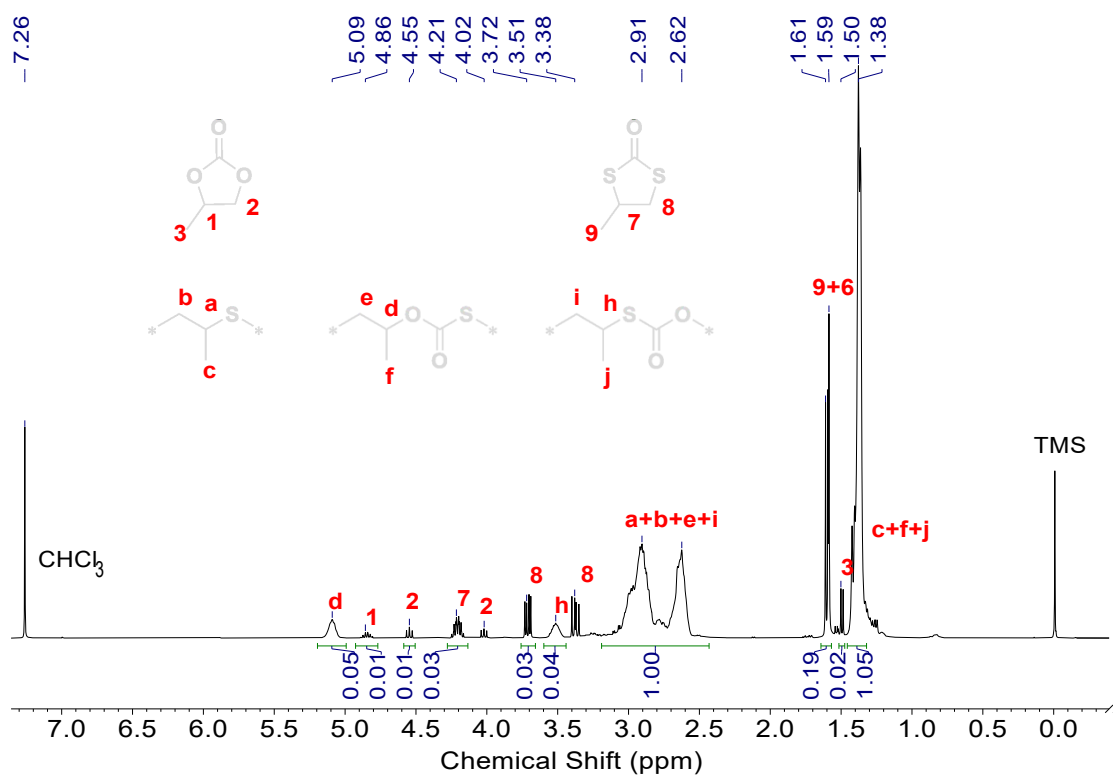
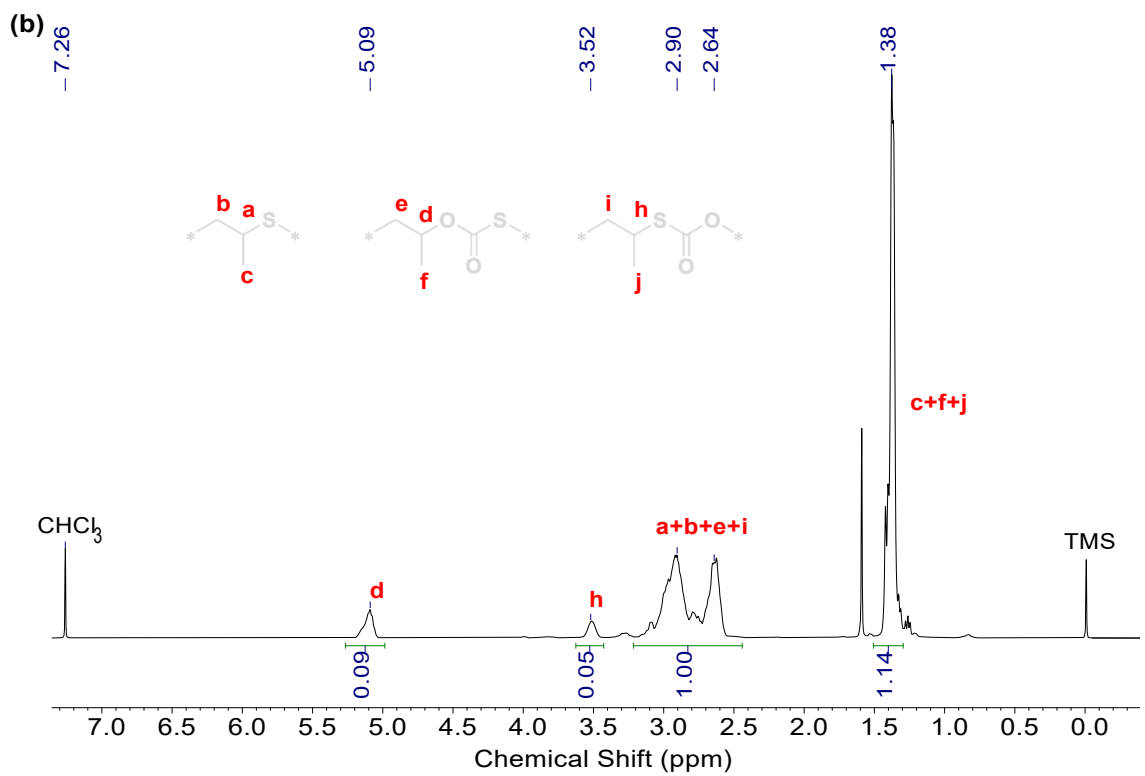
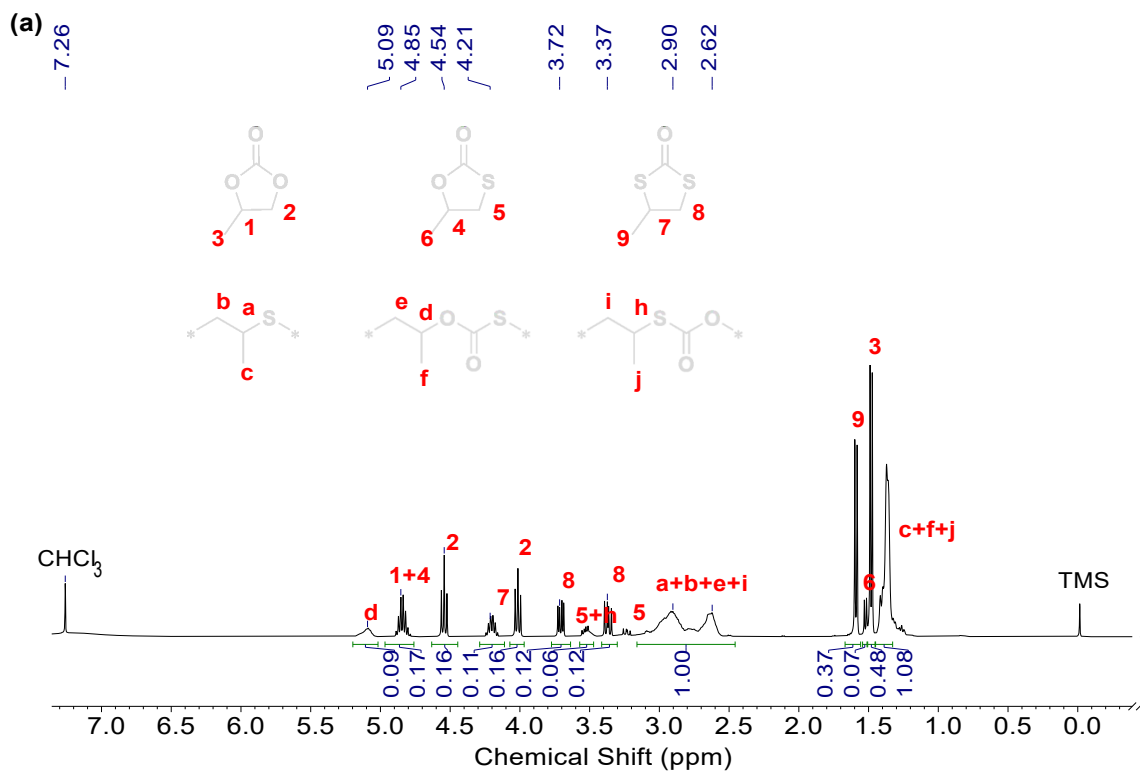


Fig. S11. ^1H NMR spectrum of the crude product of entry 11 Table 1.



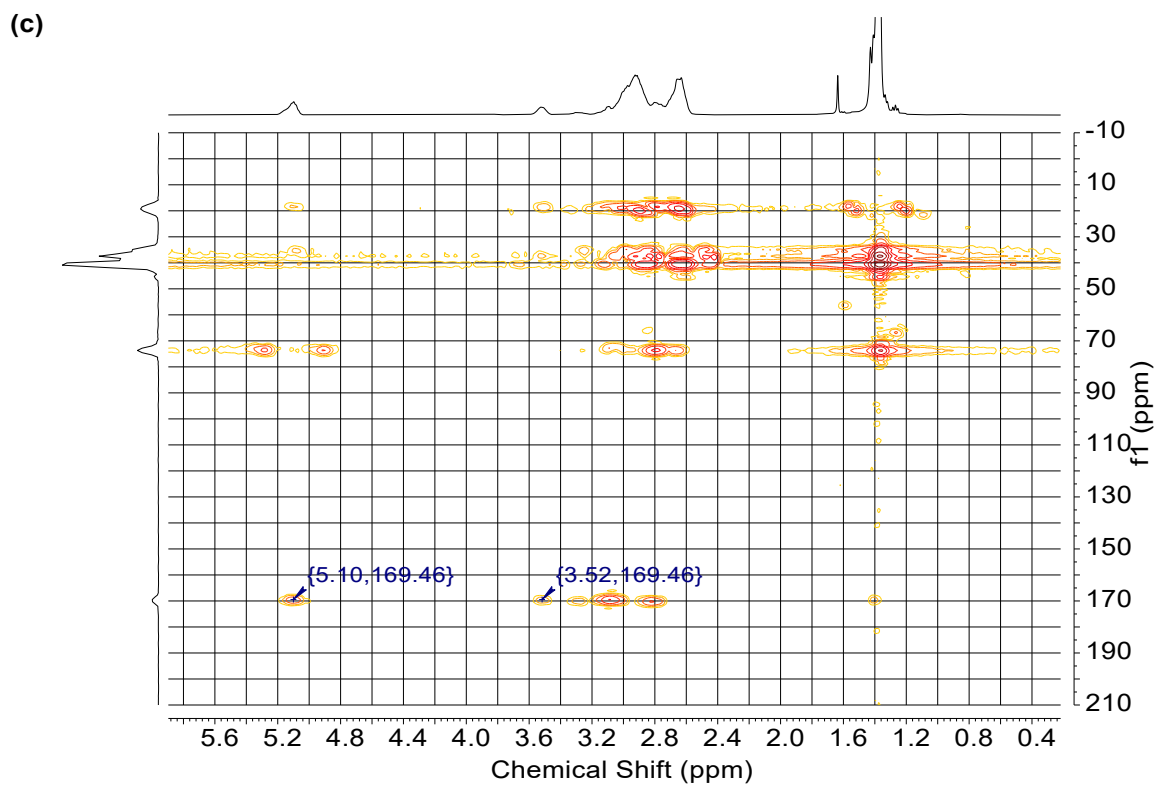


Fig. S12. (a) ^1H NMR spectrum of the crude product of entry 1 Table 2; (b) ^1H NMR spectrum of the purified product of entry 1 Table 2; (c) ^1H - ^{13}C HMBC NMR spectrum of the of the purified product of entry 1 Table 2.

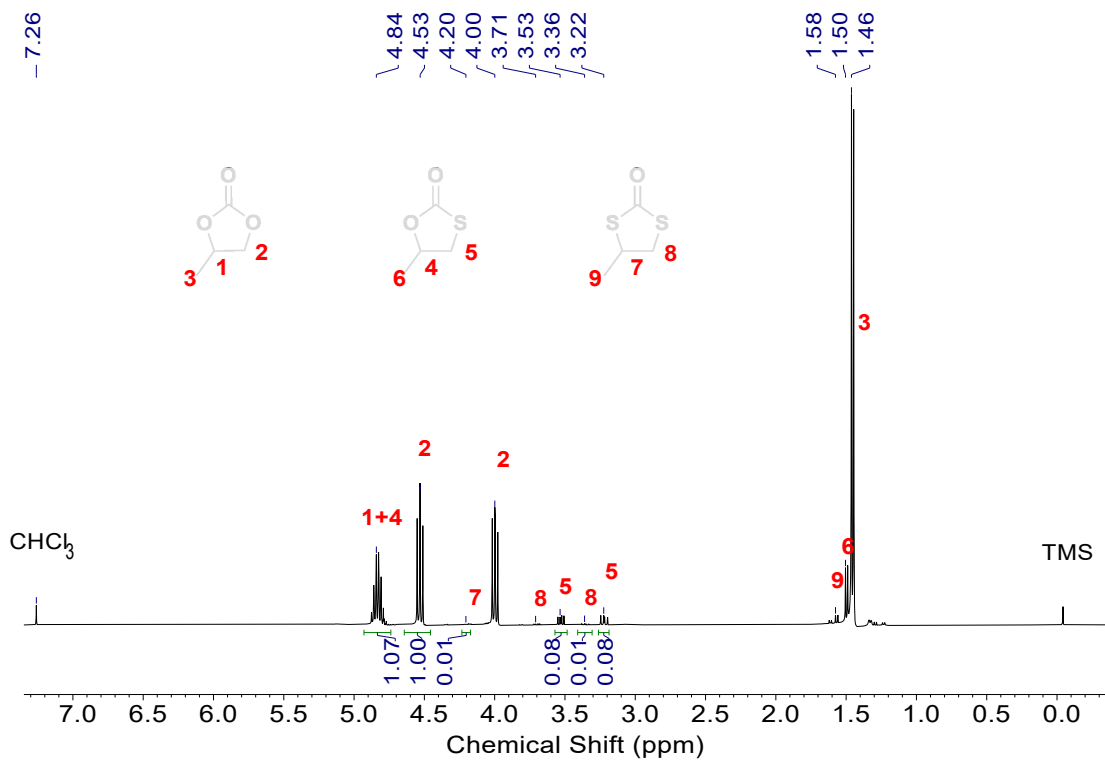


Fig. S13. ^1H NMR spectrum of the crude product of entry 2 Table 2.

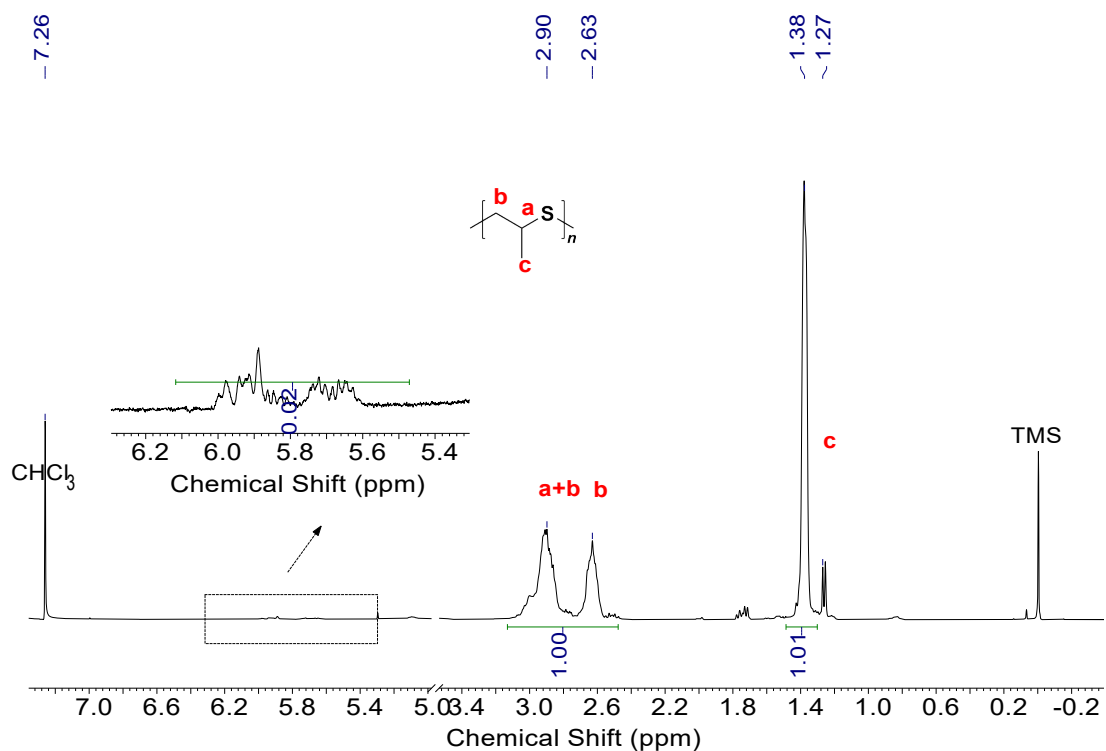


Fig. S14. ¹H NMR spectrum of the crude product of entry 3 Table 2.

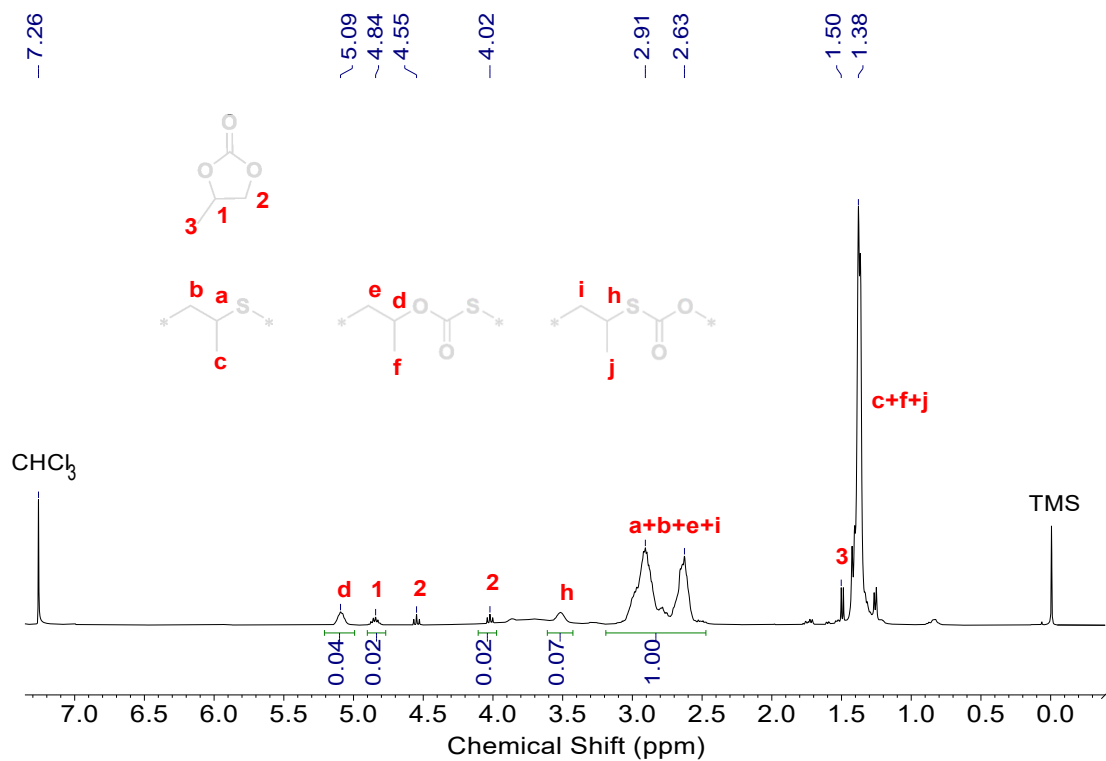


Fig. S15. ¹H NMR spectrum of the crude product of entry 4 Table 2.

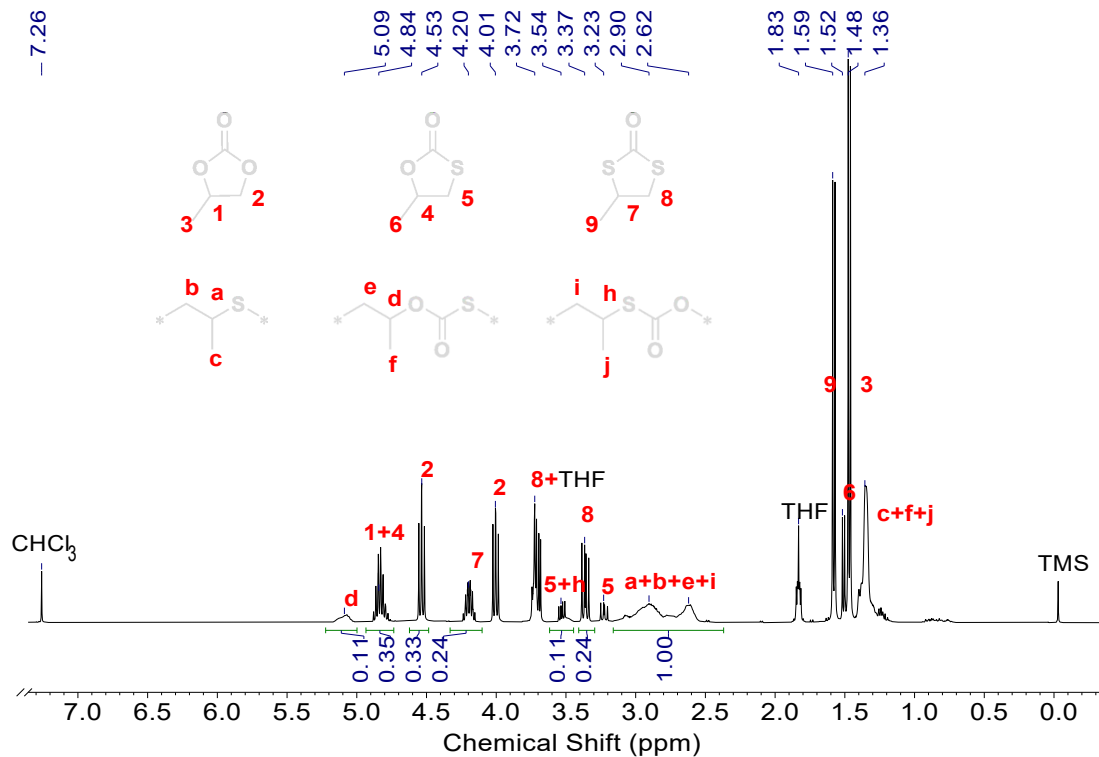


Fig. S16. ^1H NMR spectrum of the crude product of entry 5 Table 2.

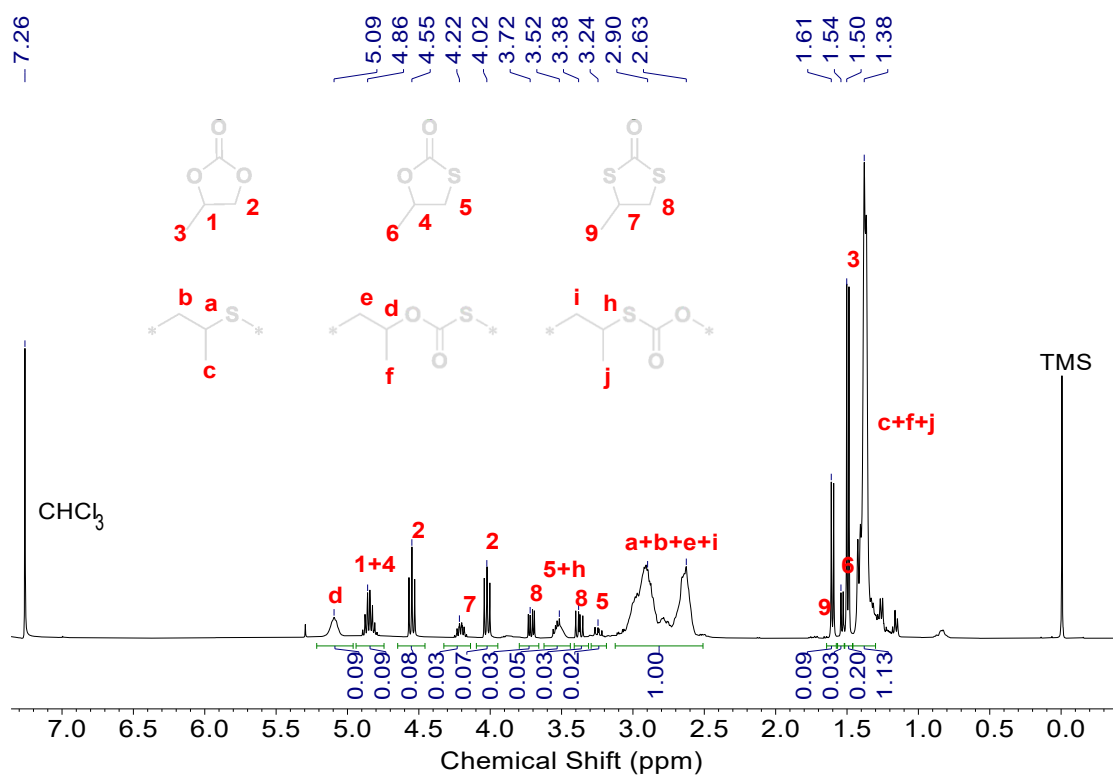


Fig. S17. ^1H NMR spectrum of the crude product of entry 6 Table 2.

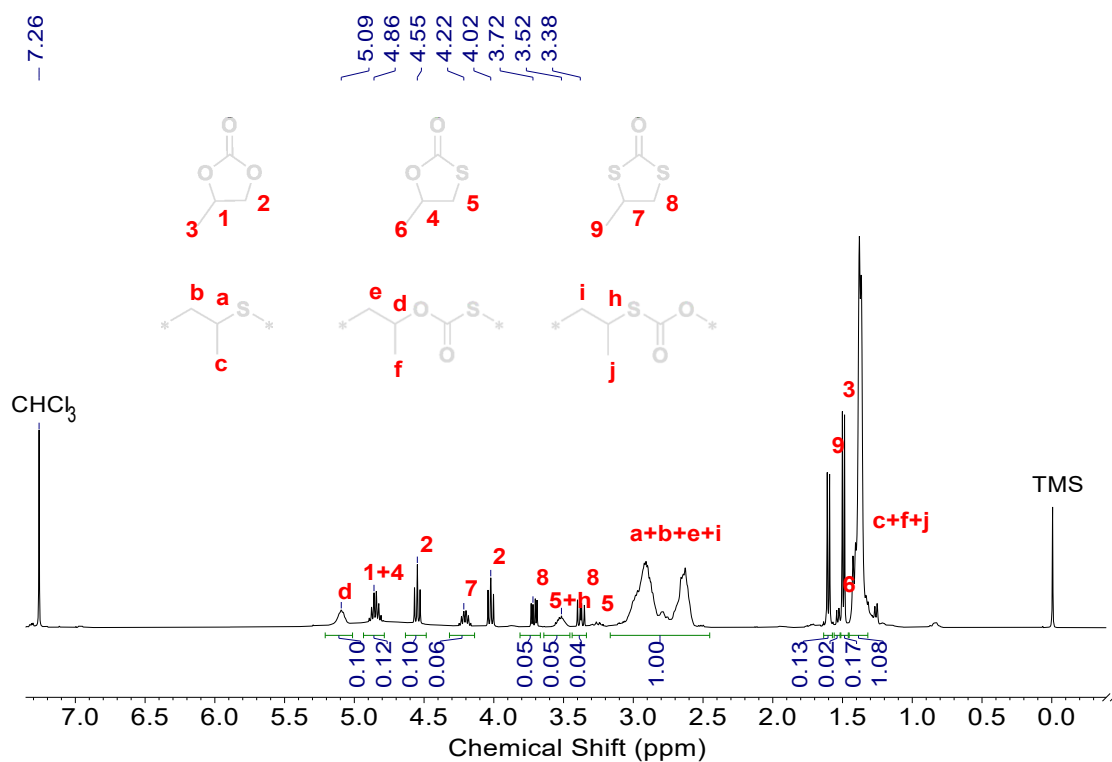


Fig. S18. ^1H NMR spectrum of the crude product of entry 7 Table 2.

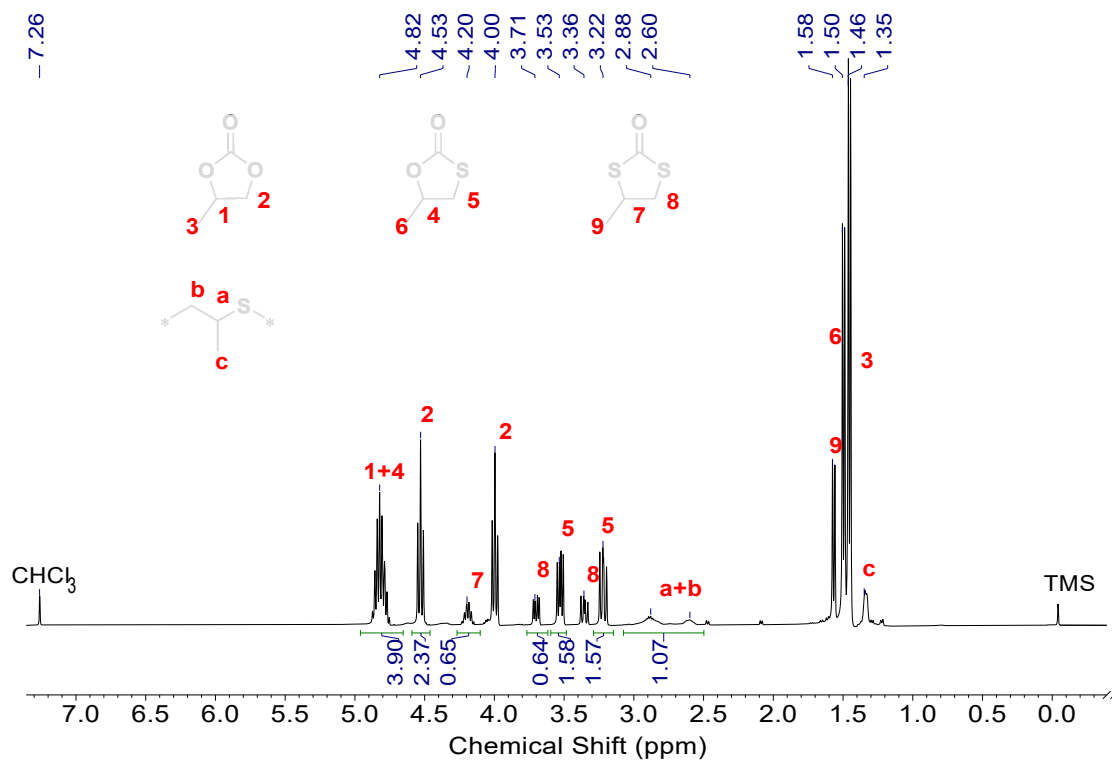


Fig. S19. ^1H NMR spectrum of the crude product of entry 8 Table 2.

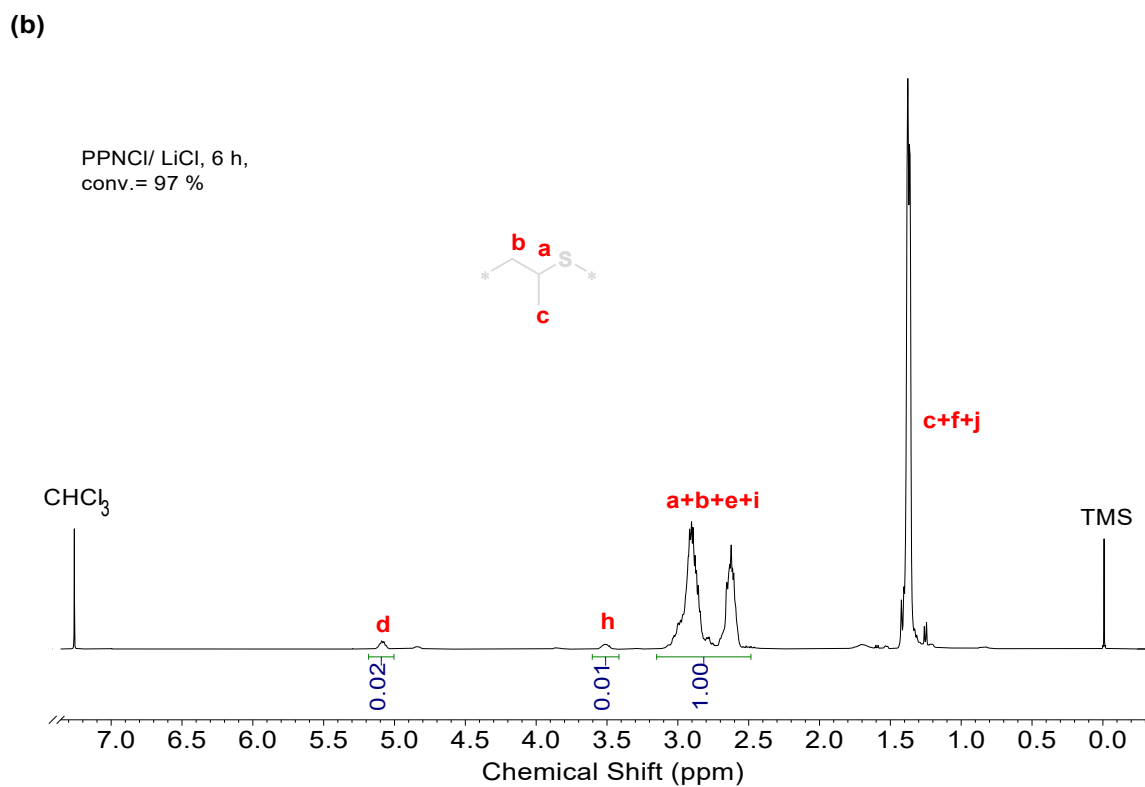
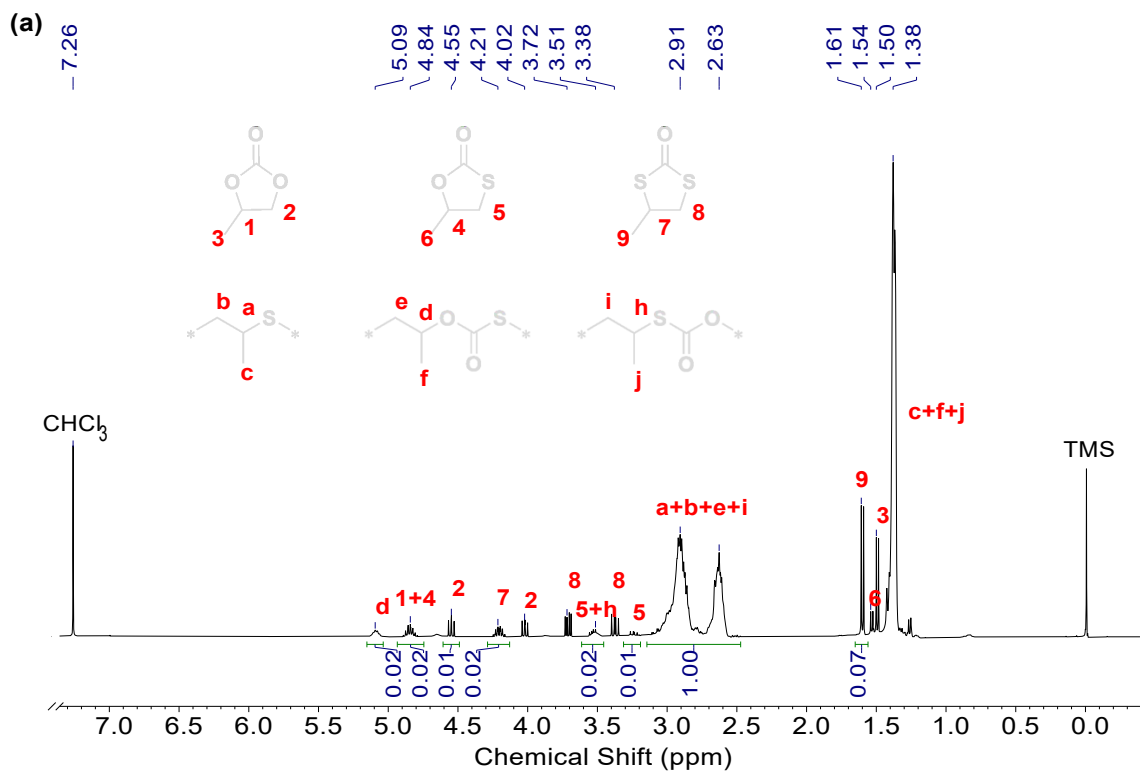


Fig. S20. ¹H NMR spectrum of the crude product of entry 9 Table 2.

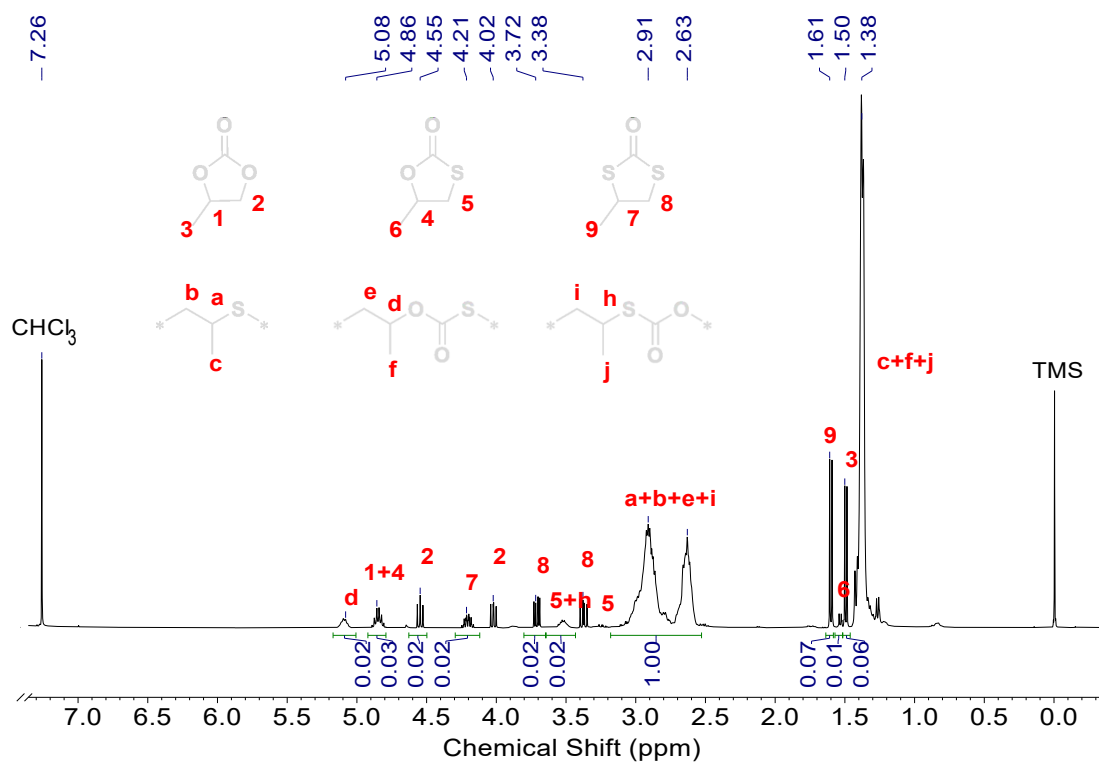


Fig. S21. ¹H NMR spectrum of the crude product of entry 10 Table 2.

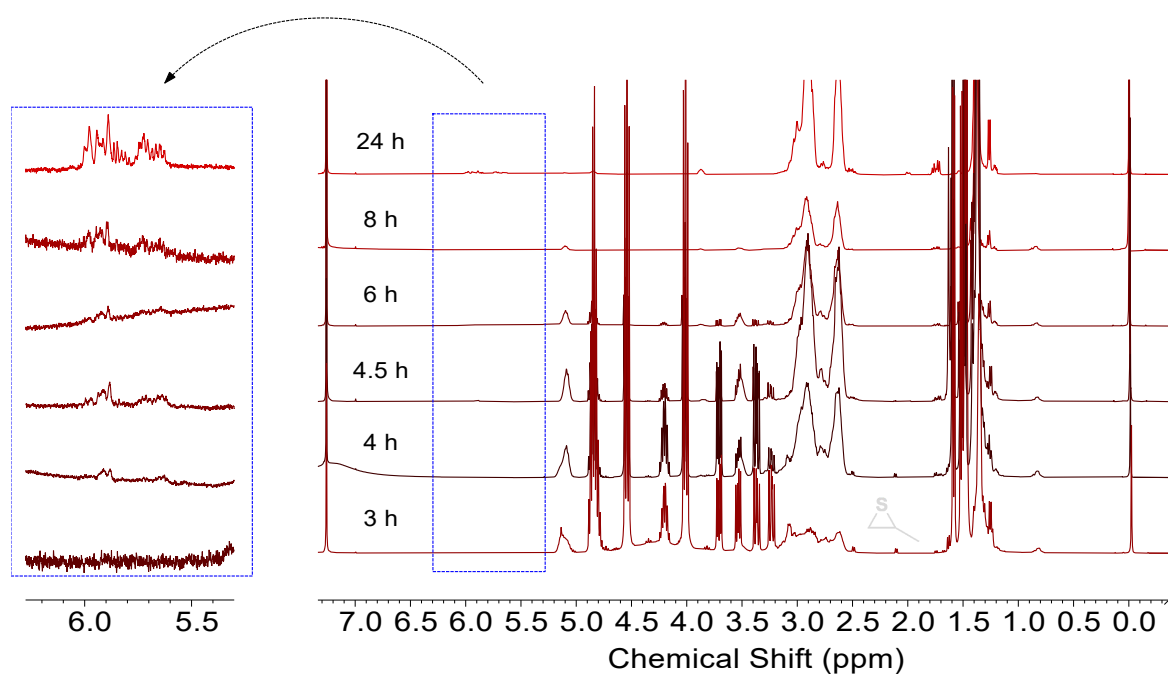


Fig. S22. ¹H NMR spectrum of the crude product obtained by PPNCI at different time (Table S1).

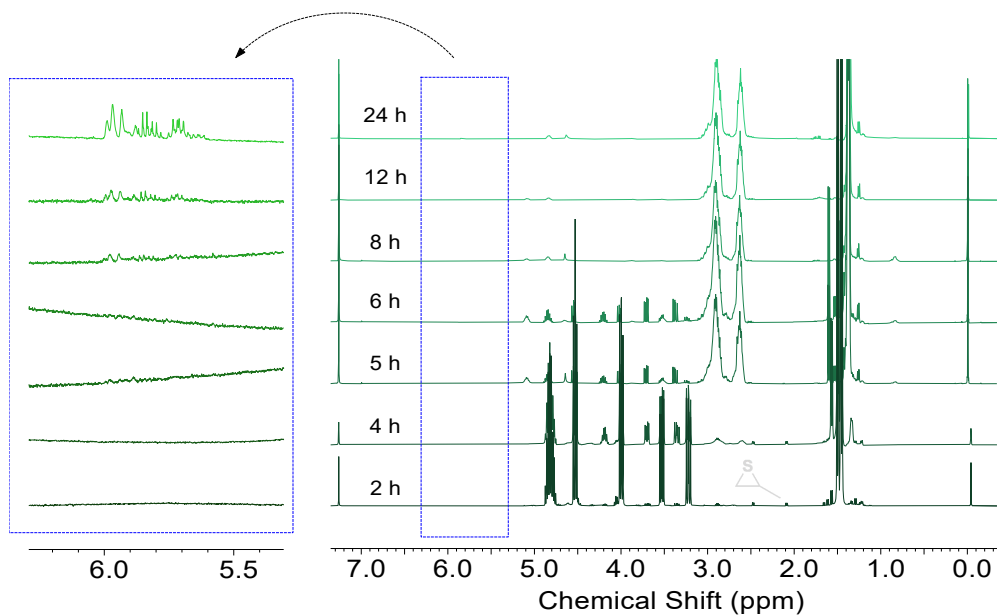


Fig. S23. ^1H NMR spectrum of the crude product obtained by PPNCI/ LiCl at different time (Table S2).

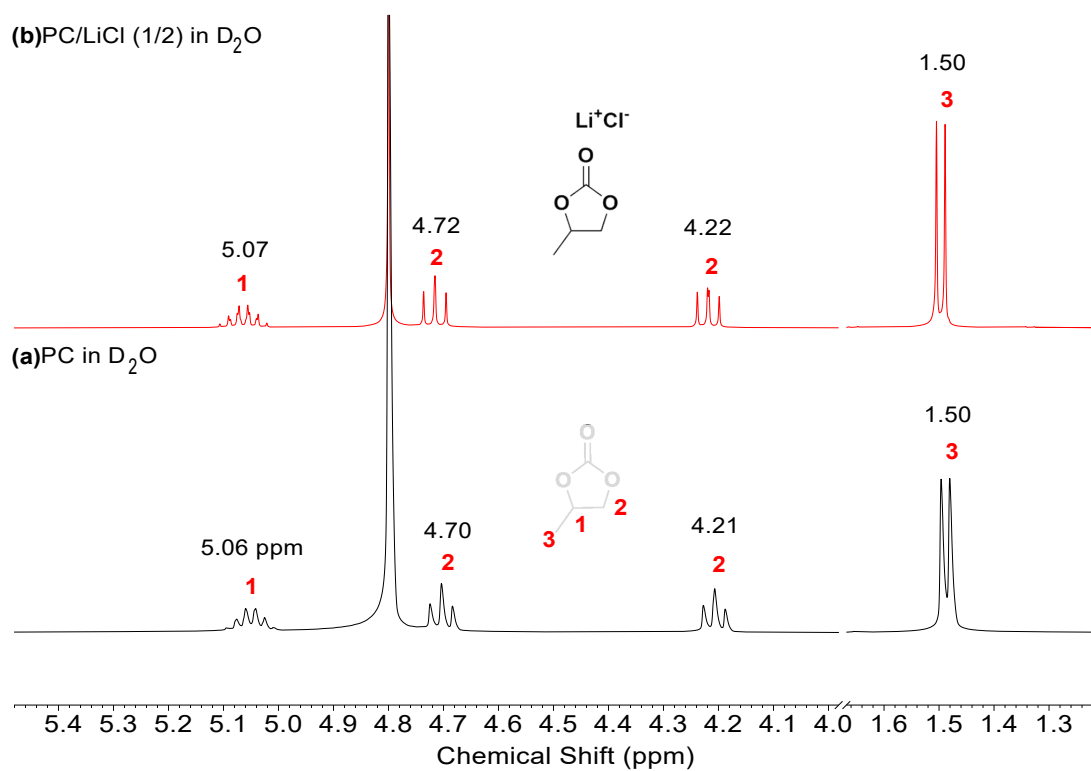


Fig. S24. ^1H NMR spectrum of (a) PC and (b) PC/LiCl (1/2) in D_2O at rt.

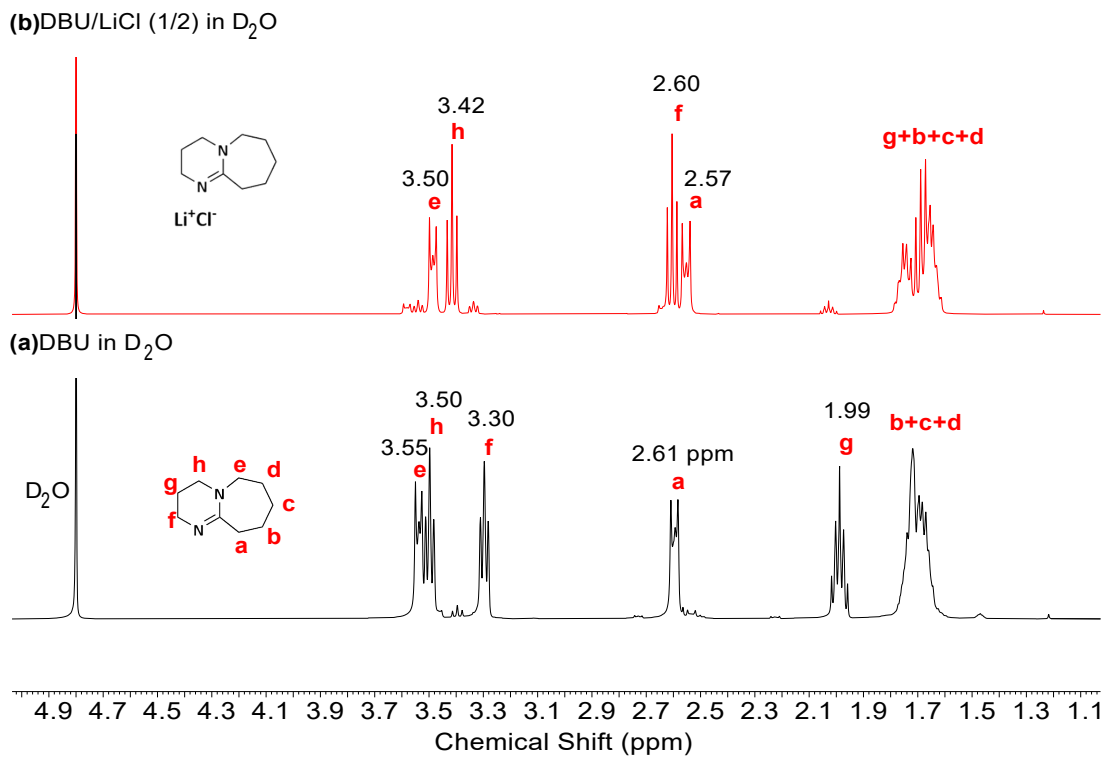


Fig. S25. ¹H NMR spectrum of (a) DBU and (b) DBU/LiCl (1/2) in D₂O at rt.

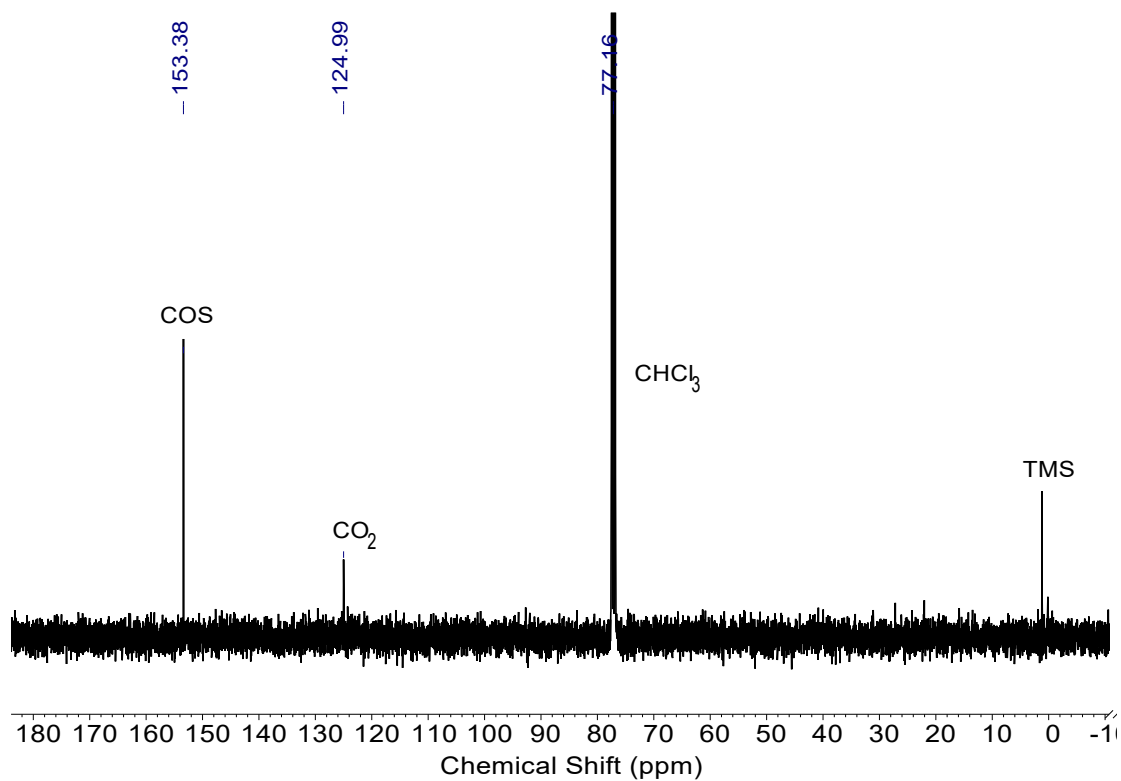
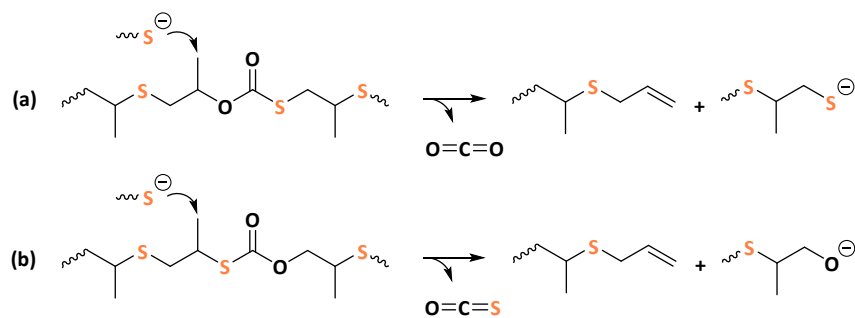
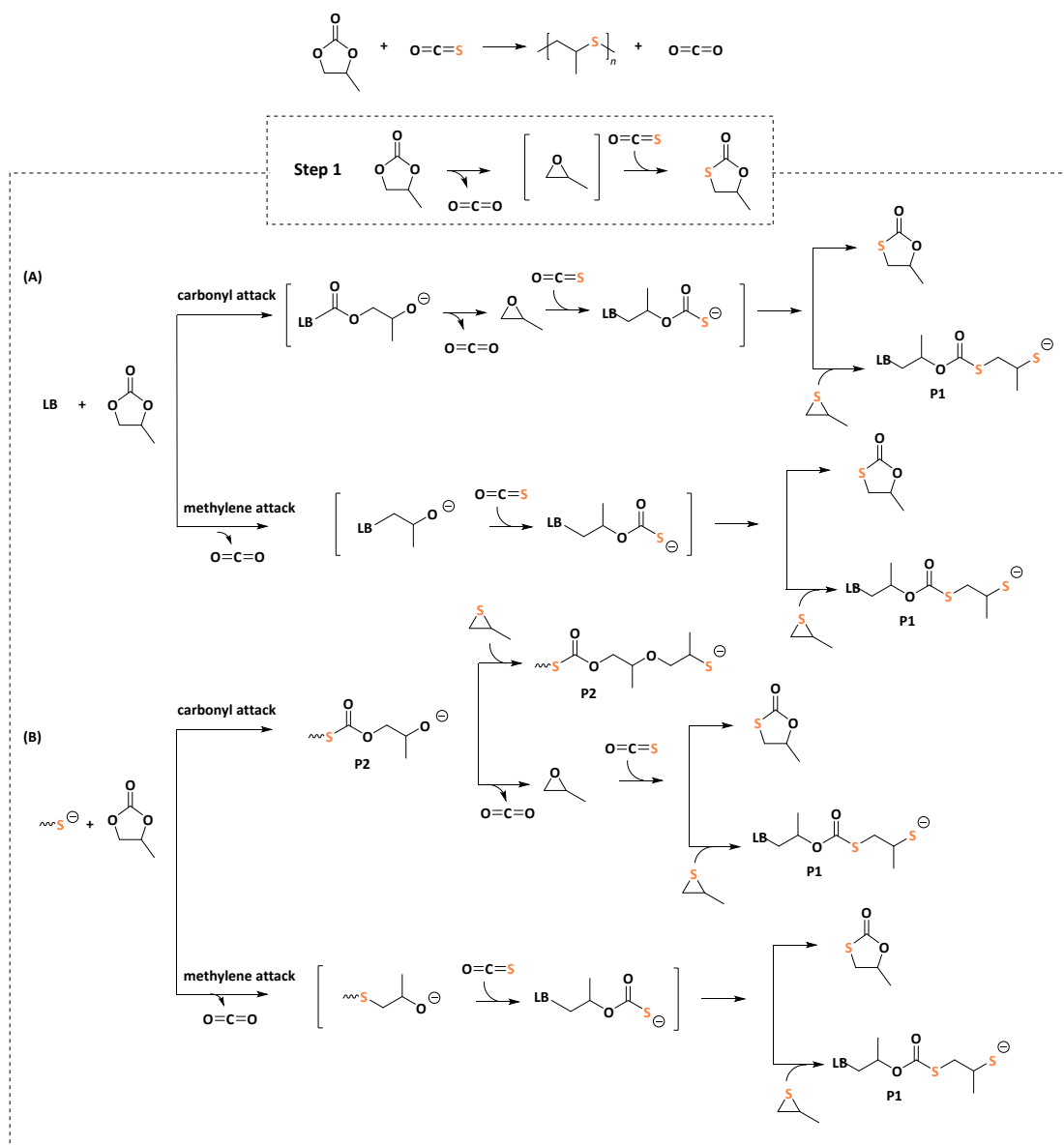
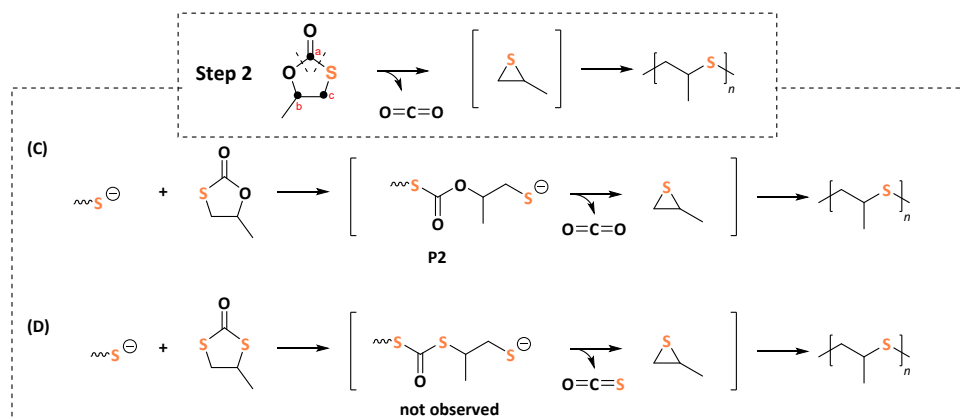


Fig. S26. ¹³C NMR spectra in CDCl₃ of COS and CO₂ released from polymerization of entry 4 Table 2.



Scheme S1. The thiocarbonate bonds are broken to lower the copolymer molar mass and reduce the thiocarbonate content.





Scheme S2. Plausible mechanism of COS/PC copolymerization. Chemoselective is mainly manifested in the ring-opening site of the cyclic thiocarbonates C1. Previous studies had shown that the free energies of the process of ring opening at the position a (Scheme 1) followed by the C-S bond cleavage was the lowest. (*J. Am. Chem. Soc.*, 2019, 141, 5490-5496.)