Supporting Information

Explorations into the Sustainable Synthesis of Cyclic and Polymeric Carbonates and Thiocarbonates from Eugenol-Derived Monomers Reactions with CO_2, COS, or CS_2

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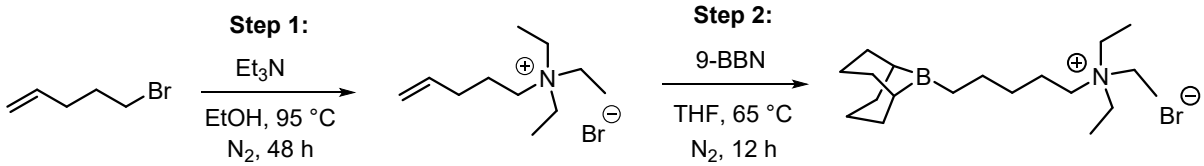
Materials and Methods:

All reactions were performed under a nitrogen or argon atmosphere using standard Schlenk line and glovebox techniques. Glassware and stainless-steel reactors were dried at 150 °C for 24 hours prior to use. Solvents were purchased from commercial sources and dried using MBraun Manual Solvent purification system packed with Alcoa F200 activated alumina desiccant. Starting materials such as eugenol, thiourea, pivaloyl chloride, *m*-CPBA, triethyl amine were purchased from Alfa Aesar, >99% carbonyl sulfide from Praxair, Catalyst (*R,R*)-*N,N*′-Bis(3,5-di-tertbutylsalicylidene)-1,2-cyclohexanediamino-chromium(III) chloride was purchase from Strem chemicals, whereas co-catalyst bis(triphenylphosphine)iminium chloride was purchased from Acros. NMR spectra were recorded on a 400 MHz Bruker spectrometer with $CDCl_3$ as an internal standard at 7.26 ppm. Infrared spectra were taken using a Bruker Tensor 27 FT-IR spectrometer and CaF_2 sample cell with 0.02 mm path length. A Malvern modular GPC apparatus with ViscoGEL I-series columns (H&L) and THF eluent was used. M_w and M_n were calculated using data from RI, Right Angle Light Scattering (RALS) and Low Angle Light Scattering (LALS) detectors calibrated against polystyrene standards. TGA analyses were performed in Mettler-Toledo TGA/ DSC 1 analyzer. DSC measurements were performed on a TA Instruments DSC 2500. Temperature and heat flow were calibrated by an indium standard. Ramp 10.00 °C/min to 25.00 °C; Isothermal for 1.0 min; Ramp 10.00 °C/min to 200.00 °C; Isothermal for 1.0 min; Ramp 10.00 °C/min to 25.00 °C; Isothermal for 1.0 min; Ramp 10.00 °C/min to 200.00 °C; Isothermal for 1.0 min; Ramp 10.00 °C/min to 25.00 °C (three cycles). The T_g was taken as the midpoint of the inflection tangent, upon the second cycle. In case of thermogravimetric analysis (TGA), the polymeric sample were heated on a TGA Q500 thermogravimetric analyzer from room temperature to 500 °C at a rate of 5 °C·min^{-1} under N_2 flow of 20 mL· min^{-1}.

Procedure for the synthesis of bifunctional organoboron catalyst.

Organoboron catalyst was synthesized by following a previously reported literature procedure.[1]

Step1: To an oven dried Schlenk flask equipped with stir bar was added a solution of triethylamine (10 mmol, 1.00 equiv) in ethanol (10 mL) was treated with 5-bromo-1-pentene (10 mmol, 1.00 equiv) under nitrogen atmosphere. Then, the reaction mixture was then heated to 95 °C for 48 h. After completion, the mixture was concentrated in vacuo to afford the crude product that was further purified by washing with ethyl acetate (3 x 10 mL). The off-white solid was isolated by vacuum filtration and was dried for 12 h in vacuo at 45 °C.



Step 2: To an oven dried Schlenk flask equipped with stir bar was added the *N,N,N*-triethylpent-4-en-1- ammonium bromide (1.3 g, 5.00 mmol, 1.00 equiv), and 9-borabicyclo[3.3.1]nonane (9-BBN) in THF (0.5 M) (10.2 mL, 5.10 mmol, 1.02 equiv) was added via cannula under nitrogen. The reaction mixture was then heated to 60 °C for 12 h, followed by concentrated in vacuo to afford the crude solid product that was further purified by washing with dry hexanes (3 x 10 mL) under nitrogen atmosphere. The white solid product was dried for 5 h in vacuo.

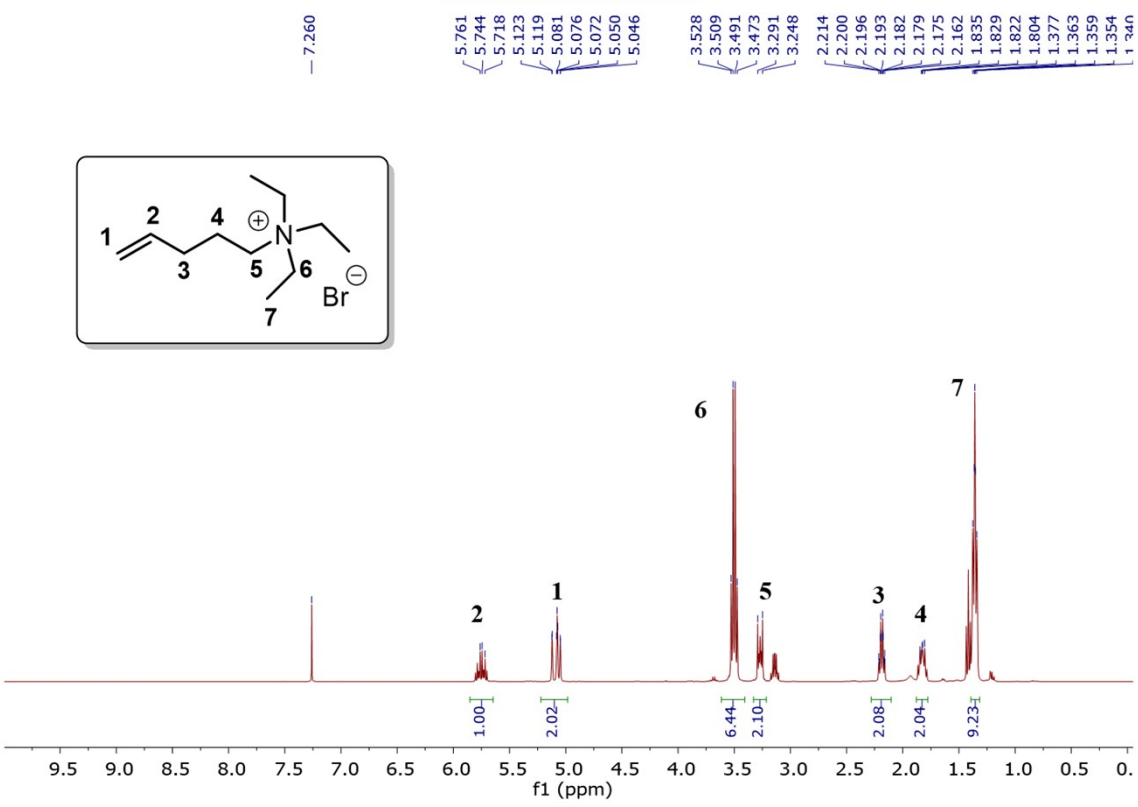


Figure S1: ^{1}H NMR of ammonium salt ($CDCl_3$, 400 MHz).

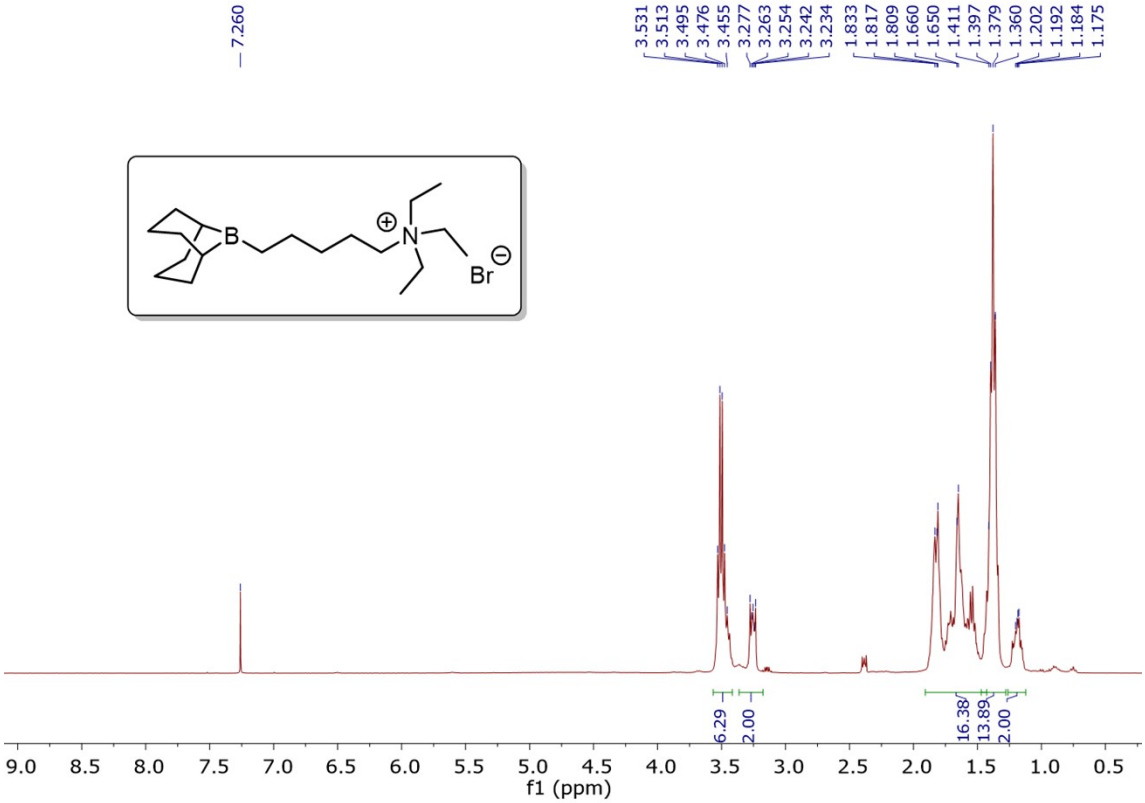
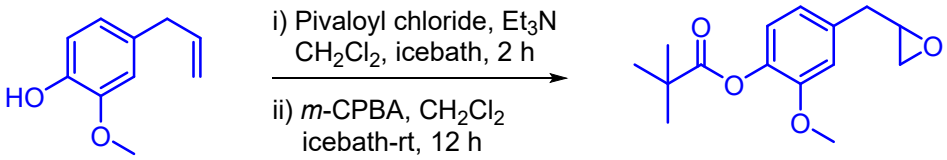


Figure S2: ^{1}H NMR of organoboron catalyst ($CDCl_3$, 400 MHz).

Procedure for the preparation of 2-Methoxy-4-(oxiran-2-ylmethyl)phenyl pivalate (monomer):



To a stirred solution of eugenol (100 mmol) in CH_2Cl_2 (100 mL) were added pivaloyl chloride (110 mmol) and triethylamine (110 mmol) under constant stirring at ice-cold temperature under N_2 and the mixture was stirred for 2 h to give an intermediate. The progress of the reaction was monitored by TLC using ethyl acetate and hexane. After completion, the mixture was washed with deionized water and dried over anhydrous $MgSO_4$. Evaporation of the solvent on a rotary evaporator gave an intermediate. Which was dissolved in CH_2Cl_2 (150 mL) and then reacted with *m*-CPBA (55%) (200 mmol) at ice-cold temperature. The stirring

was continued for 12 h, then treated with a saturated $NaHCO_3$ solution (2 x 20 mL), deionized water (2 x 20 mL). Drying anhydrous $MgSO_4$ and evaporation of the solvent on a rotary evaporator gave a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate as an eluent. The pure monomer was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 2.0 Hz, 1H), 6.82 (dd, J = 8.0, 2.0 Hz, 1H), 3.80 (s, 3 H), 3.17-3.13 (m, 1H), 2.84 (t, J = 5.2 Hz, 2 H), 2.80 (dd, J = 5.2, 4.0 Hz, 1H), 2.55 (dd, J = 5.2, 2.8 Hz, 1H), 1.36 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 151.2, 139.1, 136.0, 122.7, 121.2, 113.4, 56.1, 52.5, 46.9, 39.2, 38.8, 27.4. ESI-MS calculated for $C_{15}H_{20}O_4$ $[M+H]^+$, 265.1434; found, 265.1433.

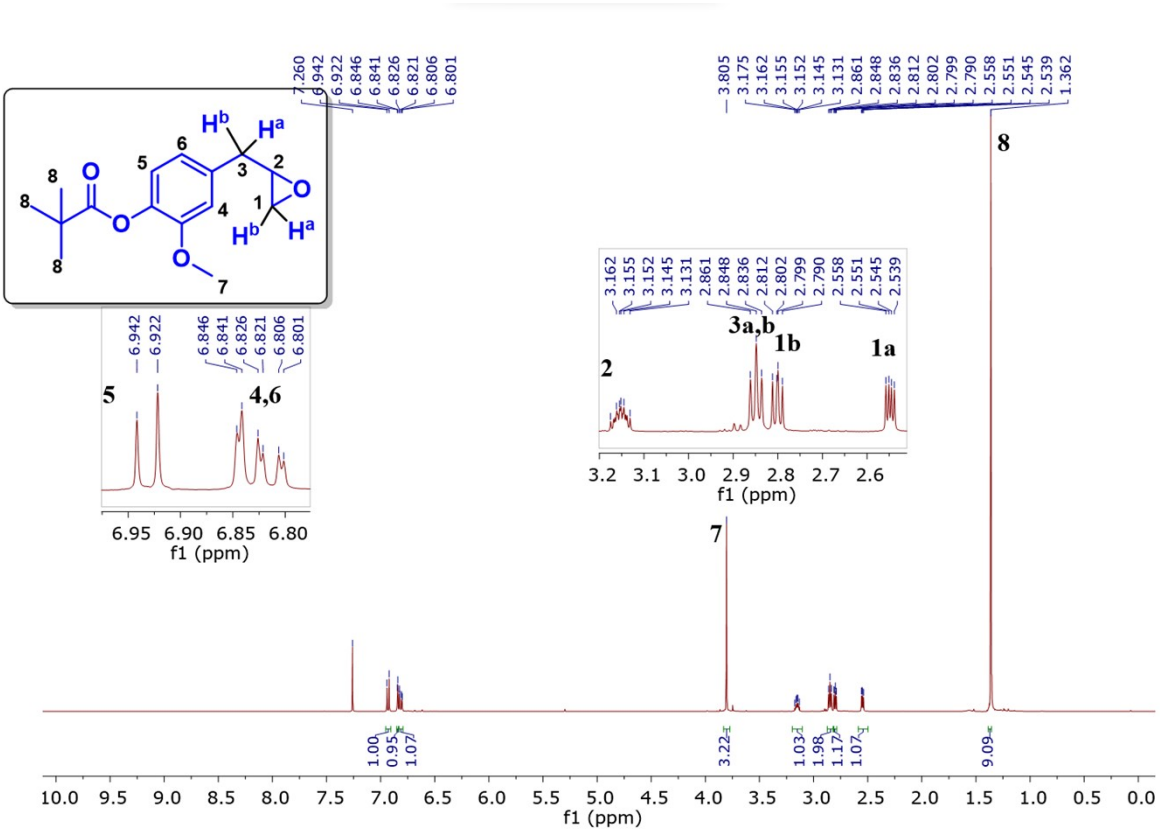


Figure S3: ^{1}H NMR of eugenol epoxide ($CDCl_3$, 400 MHz).

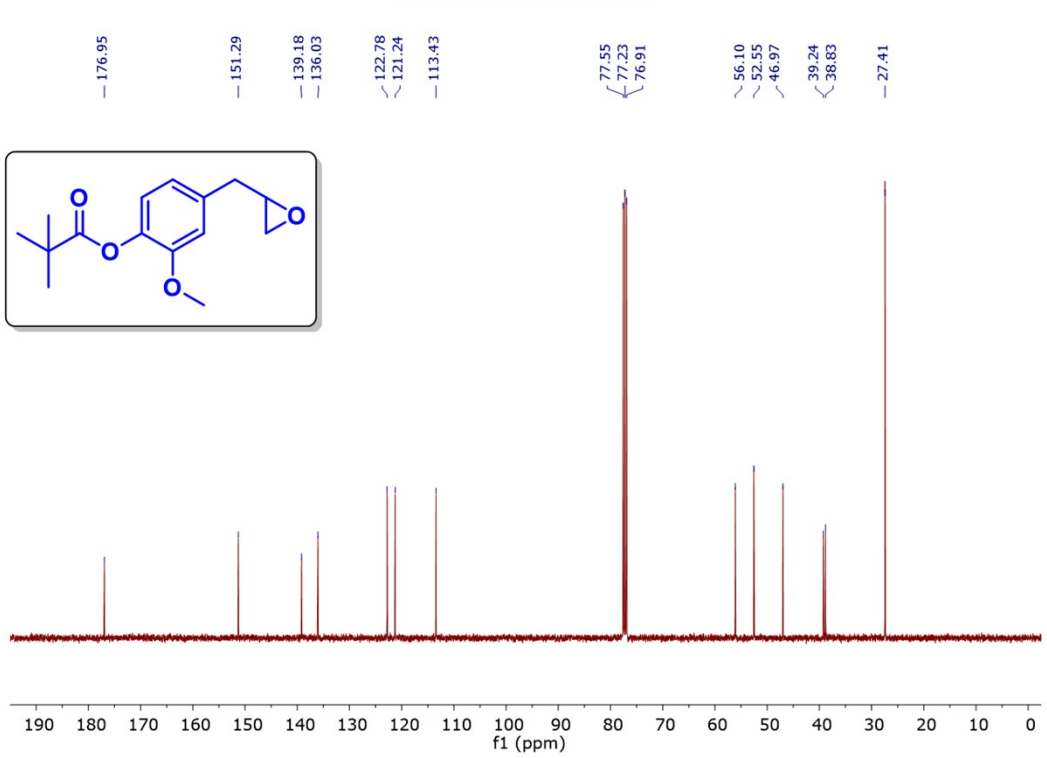


Figure S4: ^{13}C NMR of eugenol epoxide ($CDCl_3$, 100 MHz).

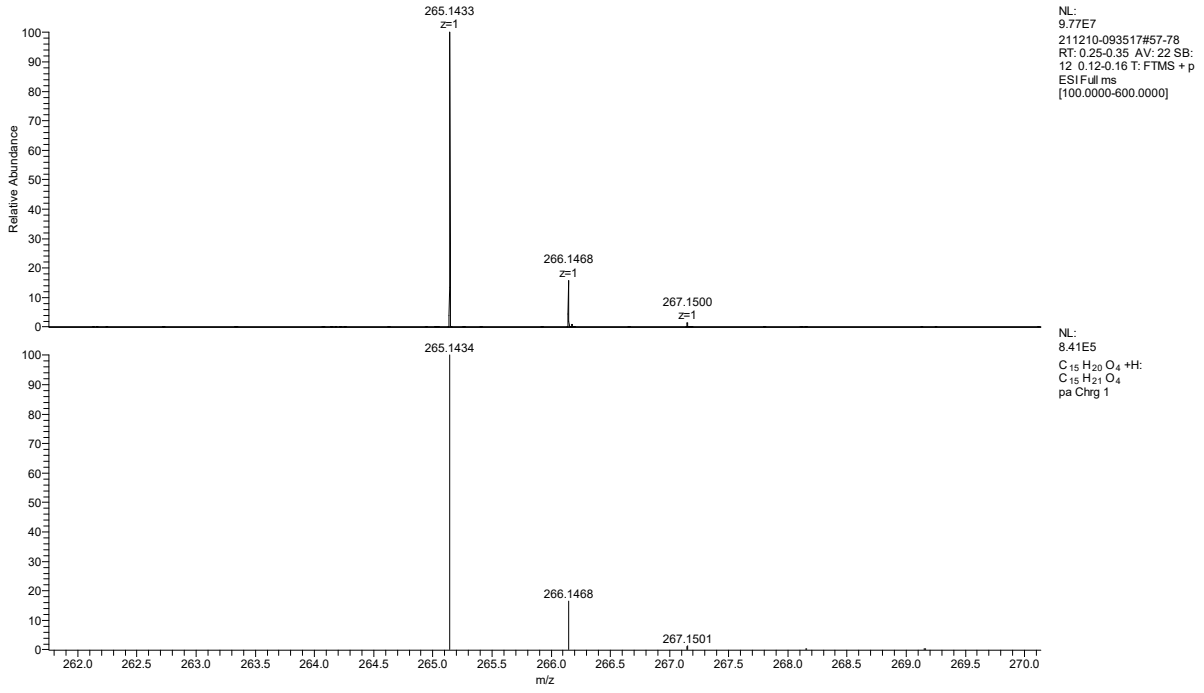


Figure S5: ESI-MS Spectrum of eugenol epoxide.

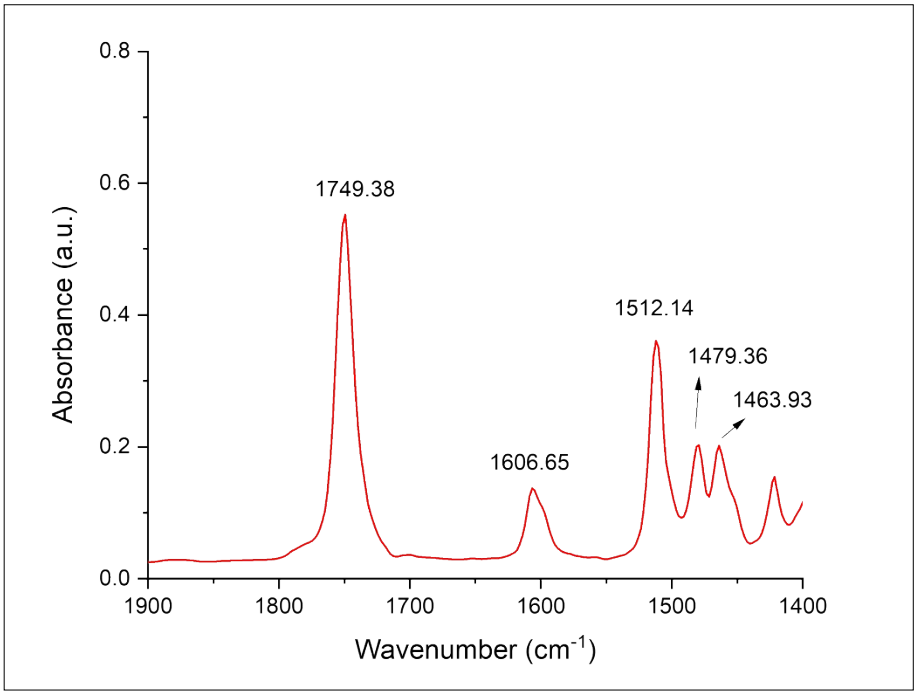
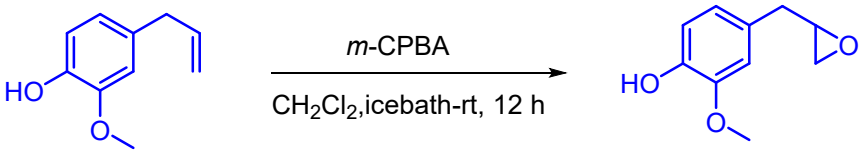


Figure S6. ATR FT-IR spectrum of eugenol epoxide

Procedure for the preparation of 2-Methoxy-4-(oxiran-2-ylmethyl)phenol:



To a stirred solution of eugenol (100 mmol) in CH_2Cl_2 (100 mL) was added *m*-CPBA (55%) (200 mmol) at ice-cold temperature for 30 min. The stirring was continued for 12 h, then treated with a saturated $NaHCO_3$ solution (2 x 20 mL), deionized water (2 x 20 mL). Drying anhydrous $MgSO_4$ and evaporation of the solvent on a rotary evaporator gave a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate as an eluent. The pure monomer was obtained as a red liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 1.6 Hz, 1H), 6.74 (dd, J = 8.0, 2.0 Hz, 1H), 5.57 (s, 1H), 3.88 (s, 3 H), 3.15-3.10 (m, 1H), 2.81-2.78 (m, 3H), 2.54 (dd, J = 5.2, 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 144.5, 129.1, 121.7, 114.5, 111.7, 56.0, 52.8, 46.9, 38.4. APCI-MS calculated for $C_{15}H_{20}O_4$ $[M-H]^-$, 179.0703; found, 179.0703.

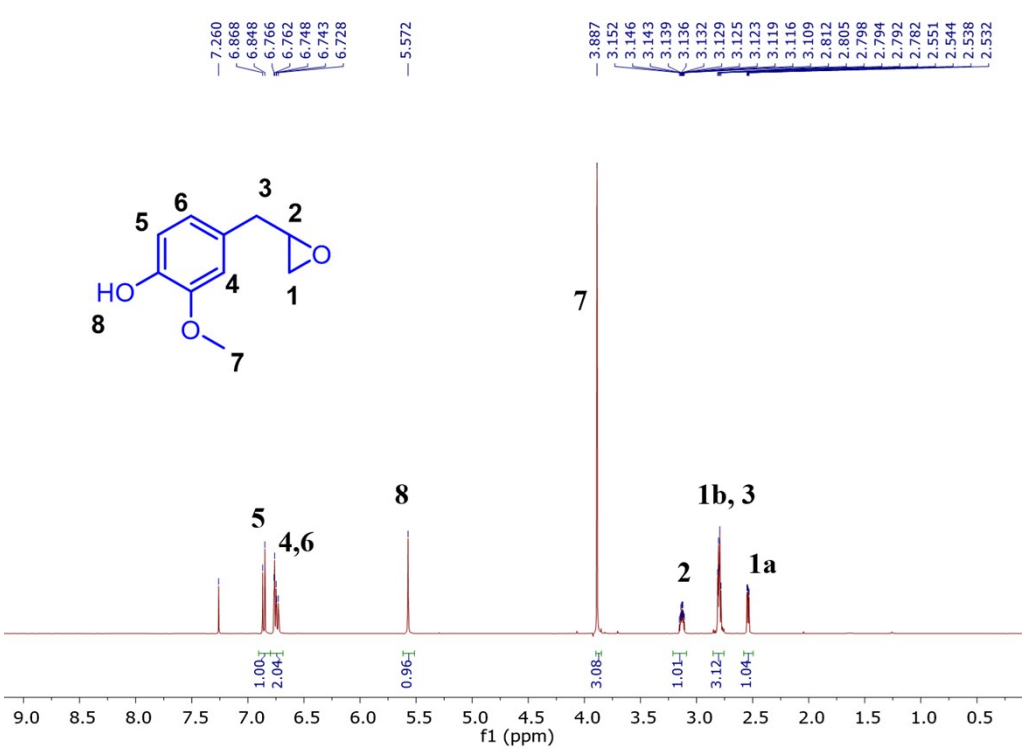


Figure S7: ^{1}H NMR of eugenol epoxide ($CDCl_3$, 400 MHz).

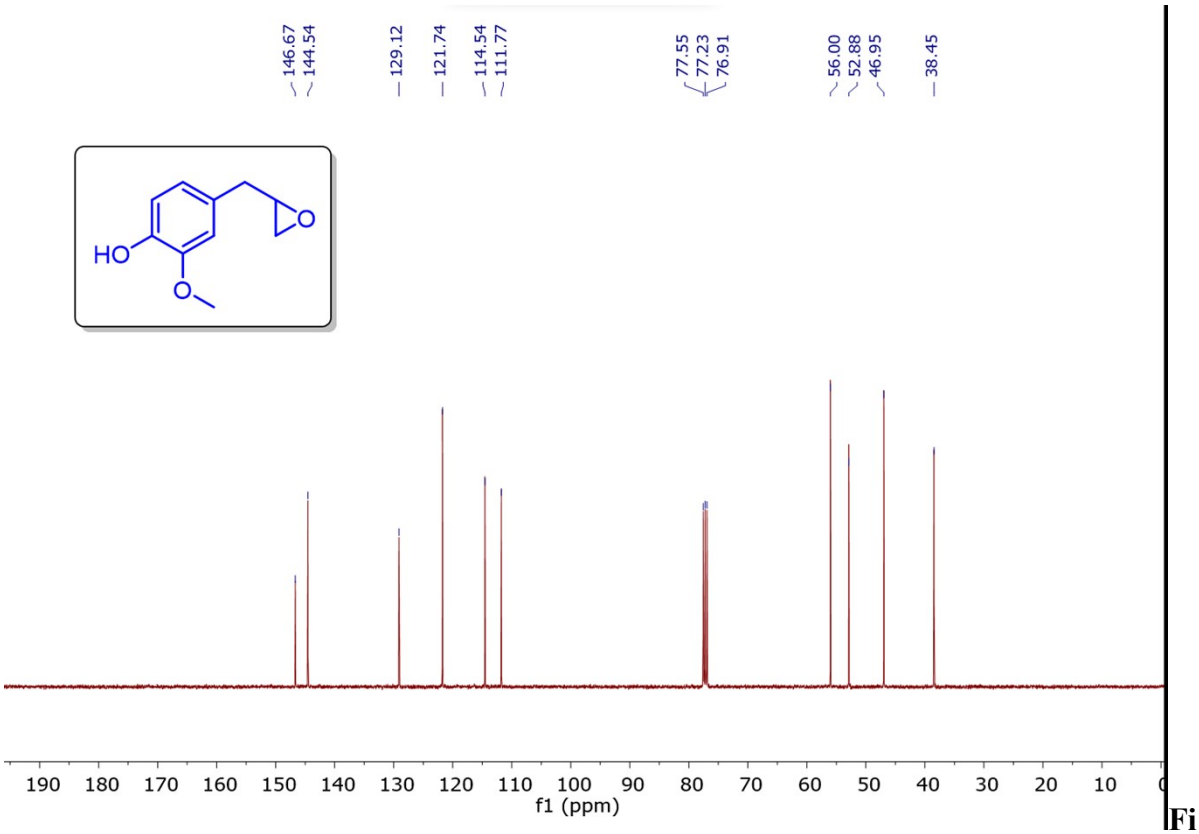


Figure S8: ^{13}C NMR of eugenol epoxide ($CDCl_3$, 100 MHz).

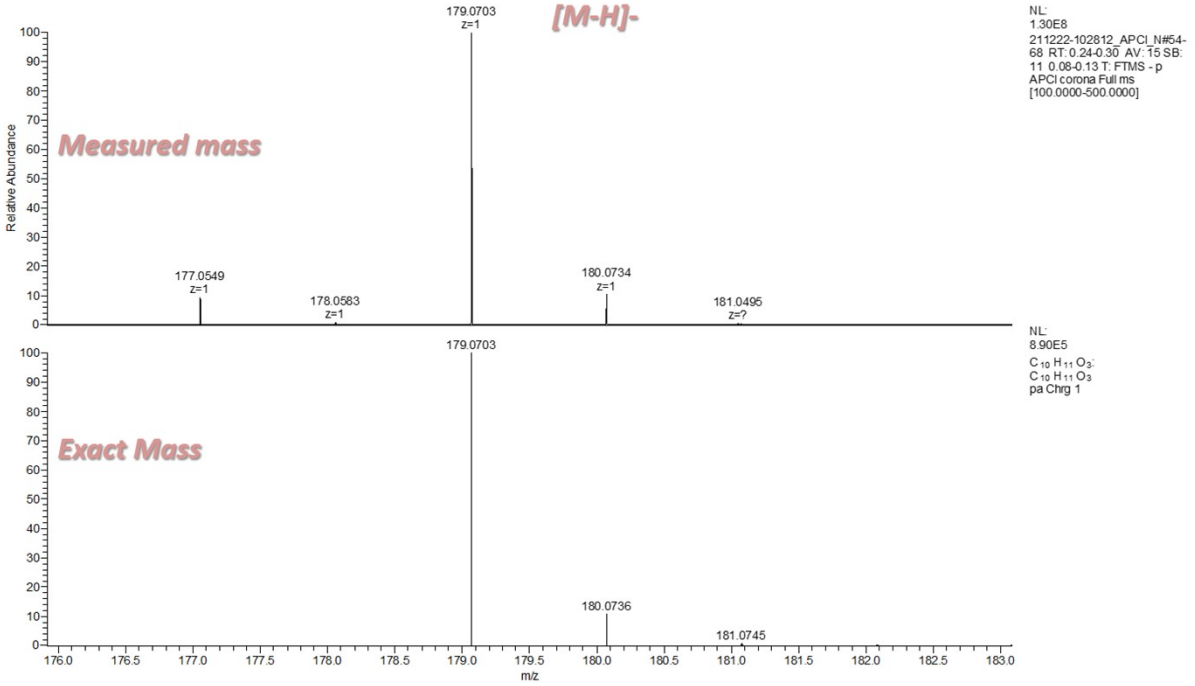


Figure S9: ESI-MS Spectrum of eugenol epoxide.

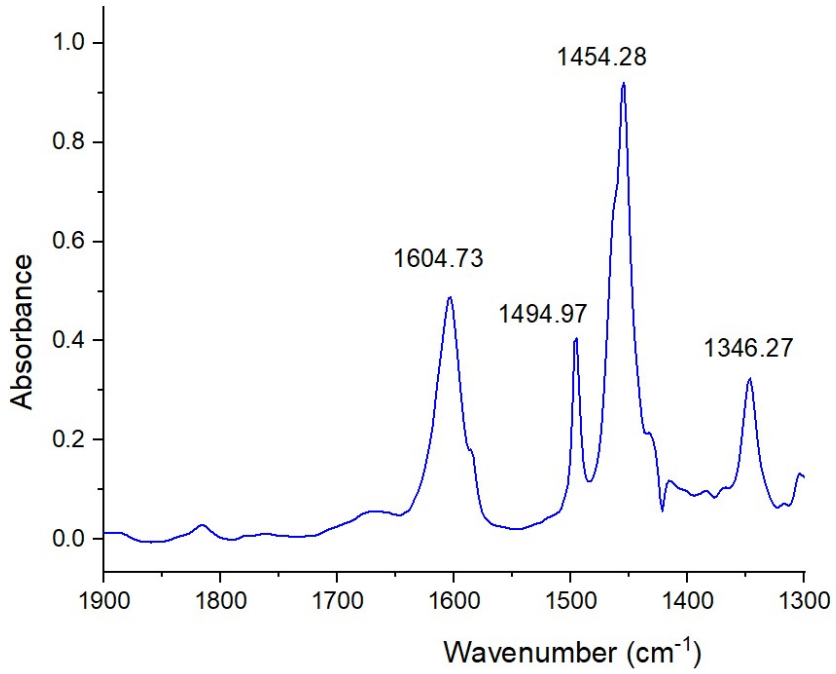


Figure S10. ATR FT-IR spectrum of eugenol epoxide

Procedure for the cyclic carbonate formation:

In a glovebox, a mixture of catalyst, co-catalyst, monomer, and 0.8 mL solvent (CH_2Cl_2: toluene, 1:1 v/v) were placed in a 15 mL stainless steel reactor vessel under an argon atmosphere. The reaction was performed using 1/1/250 equivalents of catalyst/co-catalyst/monomer where catalyst is used in the scale of 4 mg. The reactor was pressurized to 3 MPa by CO_2 and heated the desired temperature. The reaction mixture was stirred for 24 h, then the autoclave was cooled room temperature and excess CO_2 vented. Conversion of cyclic carbonate was determined by ^{1}H NMR analysis. The residue was purified by silica gel column chromatography using ethyl acetate and hexanes as eluents to give the cyclic carbonate as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 1.6 Hz, 1H), 6.82 (dd, J = 8.0, 2.0 Hz, 1H), 4.95-4.88 (m, 1H), 4.44 (t, J = 8.0 Hz, 1 H), 4.16 (dd, J = 8.4, 6.8 Hz, 1H), 3.80 (s, 3H), 3.13 (dd, J = 14.4, 6.4 Hz, 1H), 2.97 (dd, J = 14.4, 6.4 Hz, 1H), 1.35 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 154.9, 151.7, 139.9, 132.6, 123.3, 121.5, 113.6, 76.8, 68.6, 56.2, 39.6, 39.2, 27.3. ESI-MS calculated for $C_{16}H_{20}O_6$ $[M+H]^+$, 309.1325; found, 309.1333.

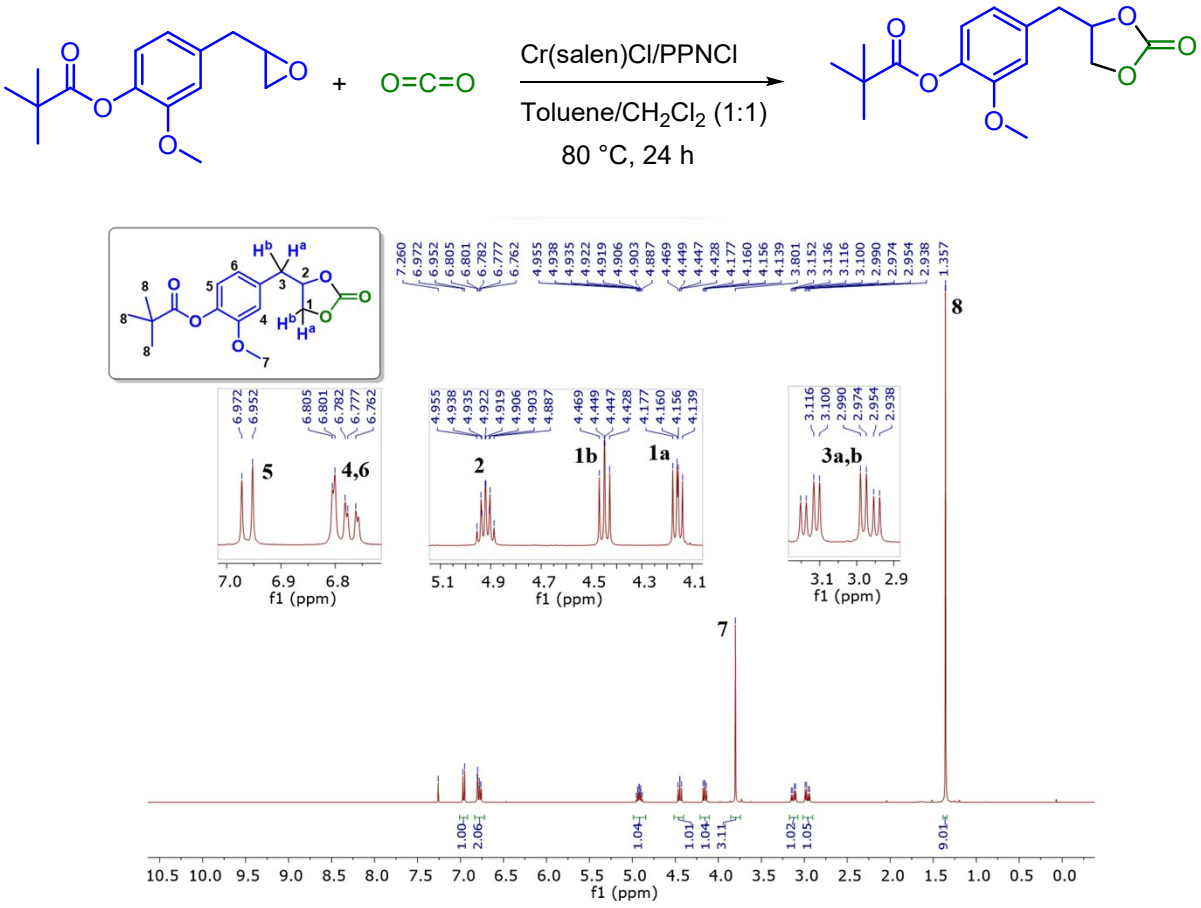


Figure S11. ^{1}H NMR of cyclic carbonate ($CDCl_3$, 400 MHz).

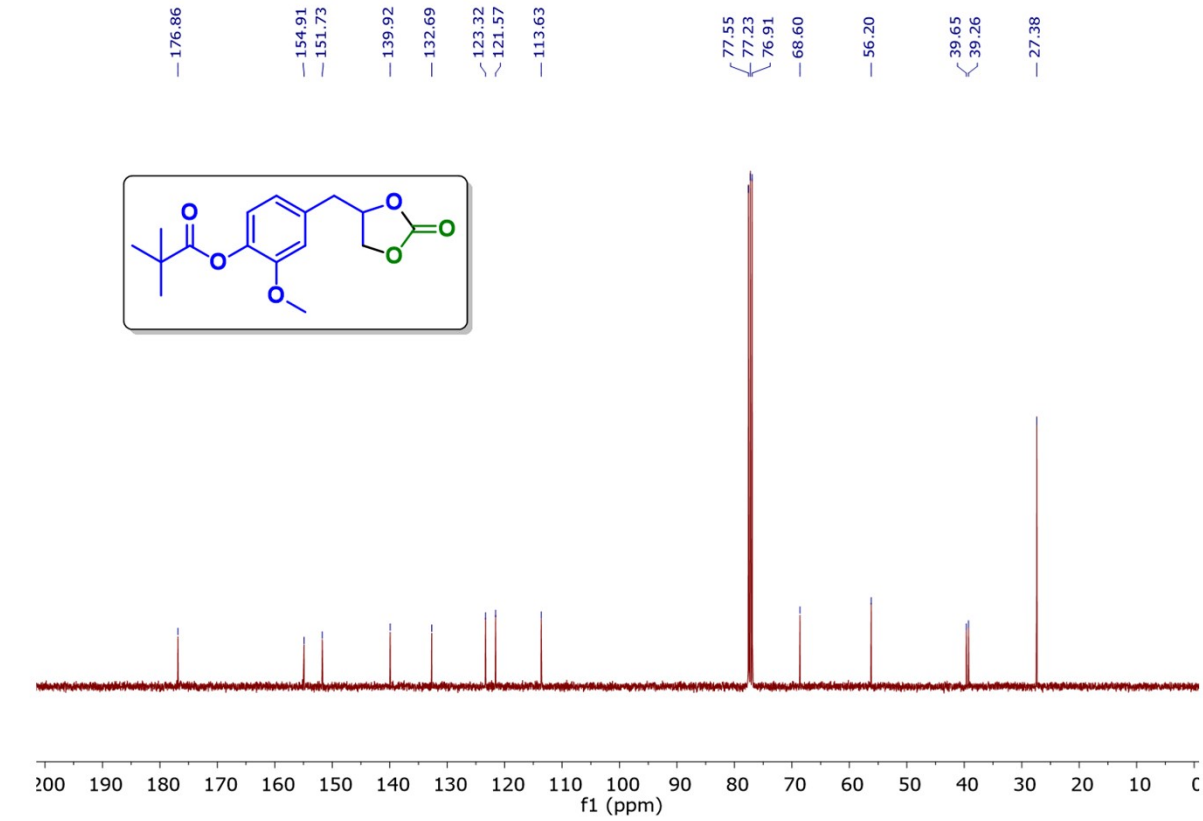


Figure S12. ^{13}C NMR of cyclic carbonate ($CDCl_3$, 100 MHz).

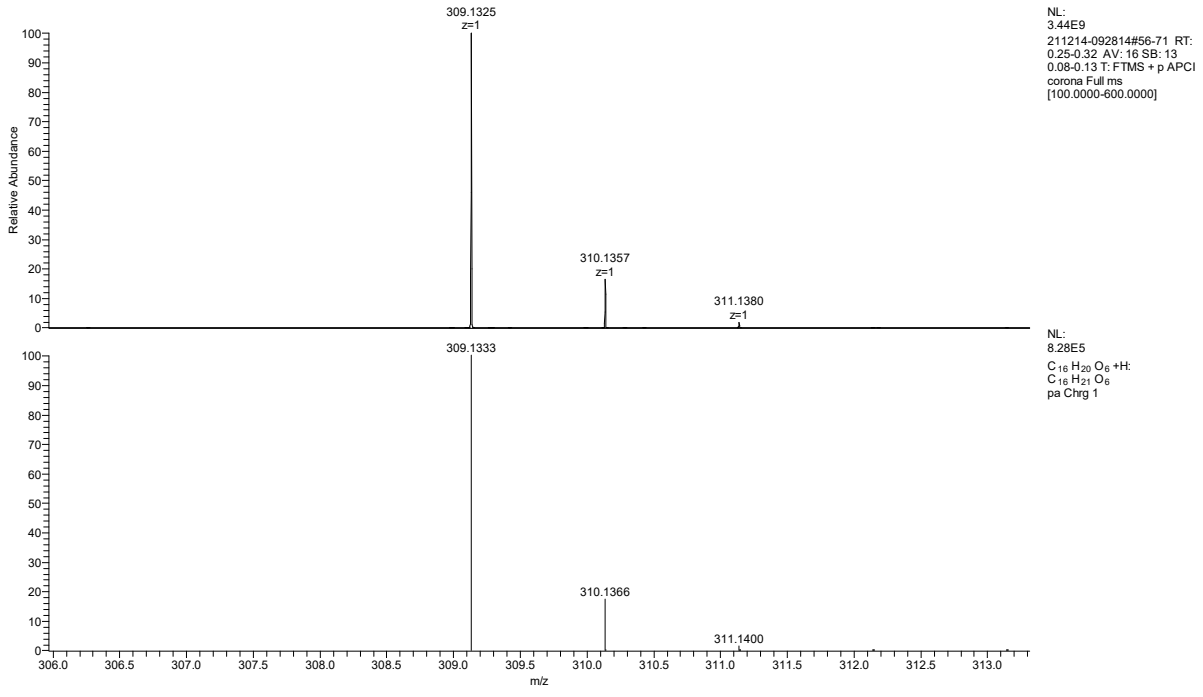


Figure S13. ESI-MS Spectrum of cyclic carbonate.

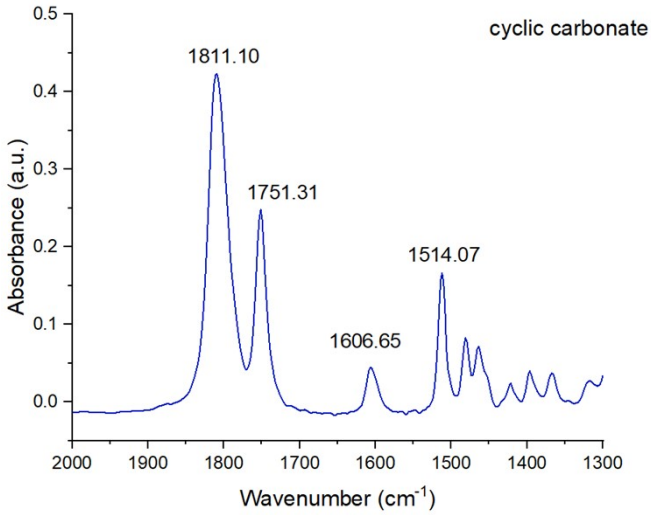
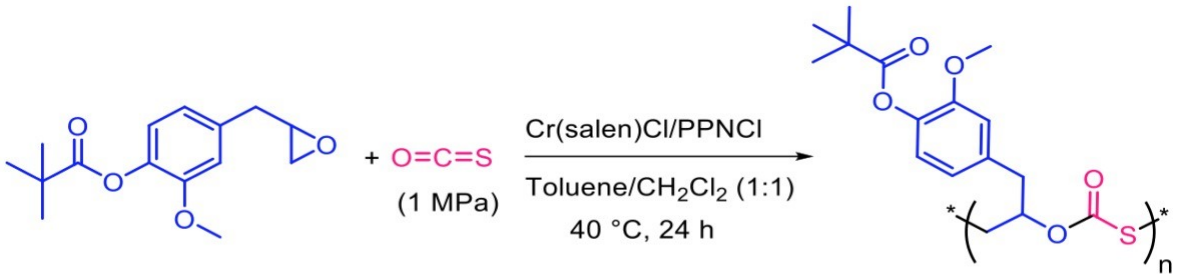


Figure S14. ATR FT-IR spectrum of cyclic carbonate.

Procedure for the synthesis of polymer with protected eugenol:

In a glovebox, the catalyst, co-catalyst, monomer, and 0.8 mL solvent (CH_2Cl_2: toluene, 1:1 v/v) were placed in a 15 mL stainless steel reactor vessel. All reactions were performed on the scale of 4.0 mg of catalyst, using ratios of 1/1/X for catalyst/cocatalyst/monomer where X = 250, 500, and 750 equivalents. The reactor was pressurized to 1.0 MPa by COS and heated the desired temperature. The reaction mixture was stirred for 24 h, then the autoclave was cooled room temperature and excess COS vented. The polymer was obtained after removing the solvent under reduced pressure and conversion was determined by ^{1}H NMR analysis. Initial recrystallization was performed by adding dropwise to acidic methanolic solution (4 drops of conc. HCl/50 mL MeOH), followed by two recrystallizations in neutral methanol. The polymer was subsequently dried in vacuum oven.



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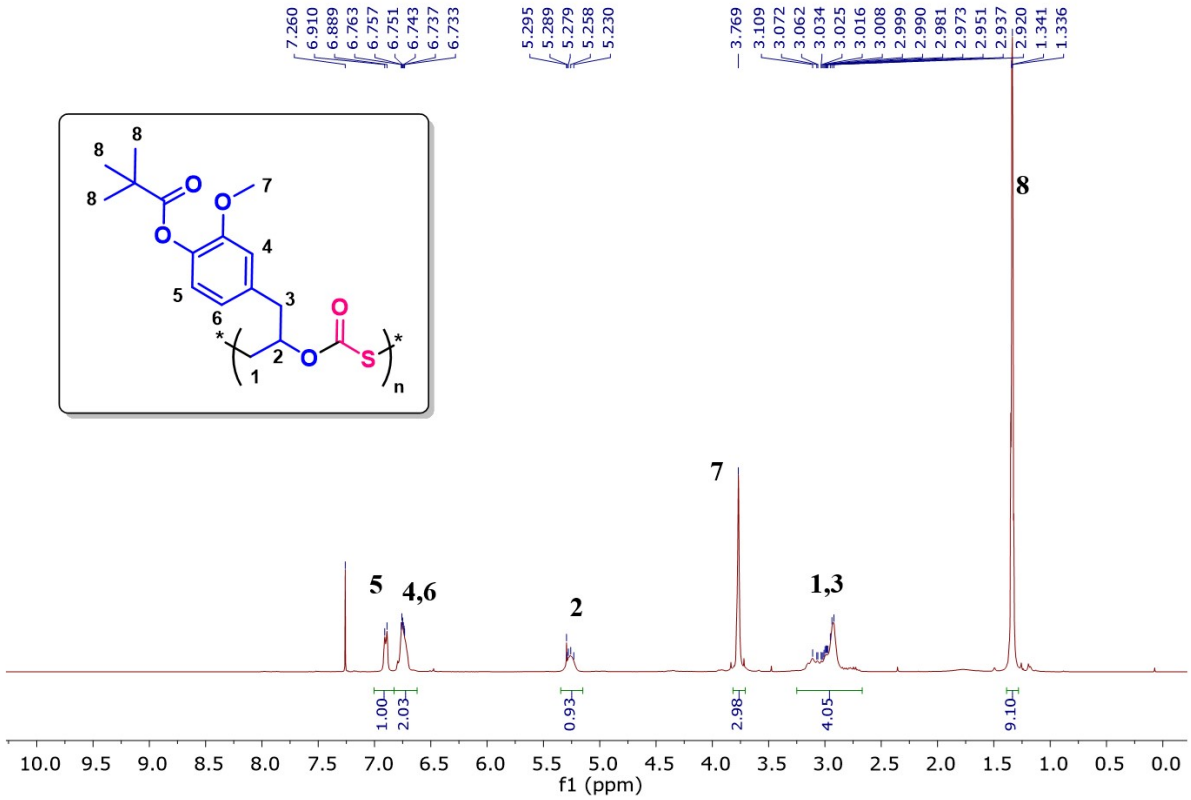


Figure S15: ^{1}H NMR of polymonothiocarbonate ($CDCl_3$, 400 MHz).

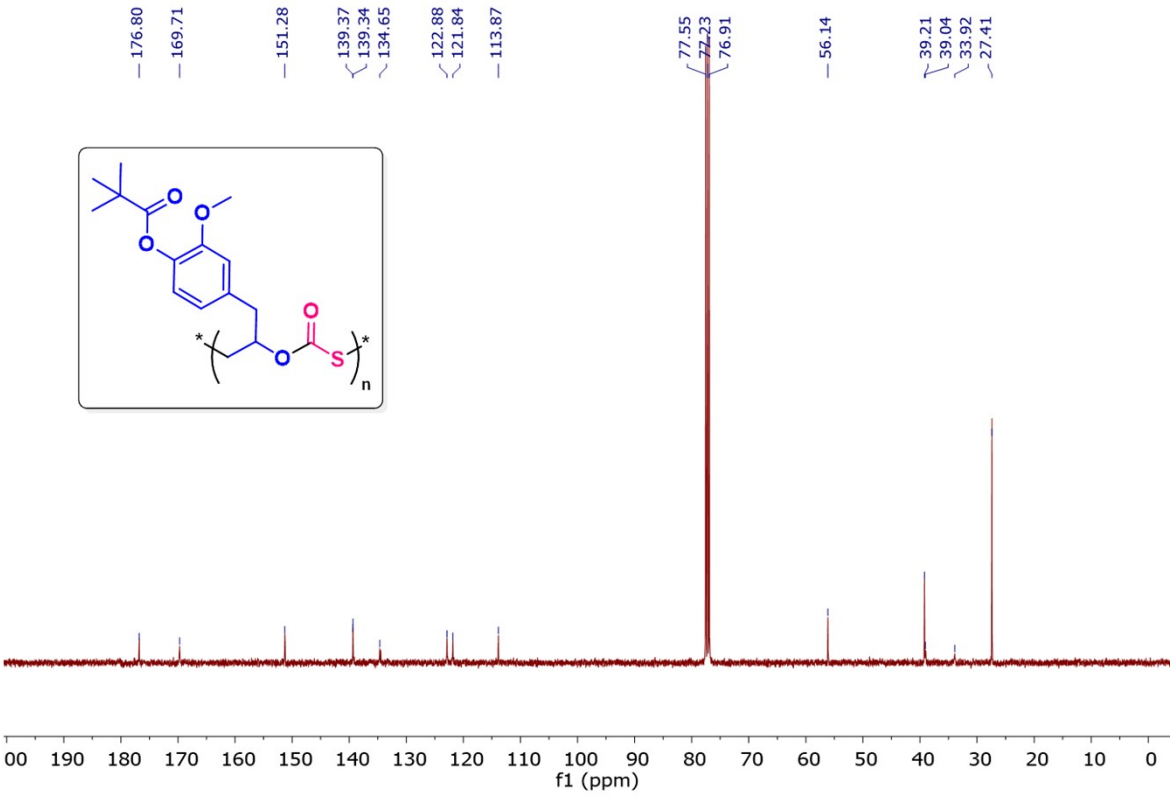


Figure S16: ^{13}C NMR of polymonothiocarbonate ($CDCl_3$, 100 MHz).

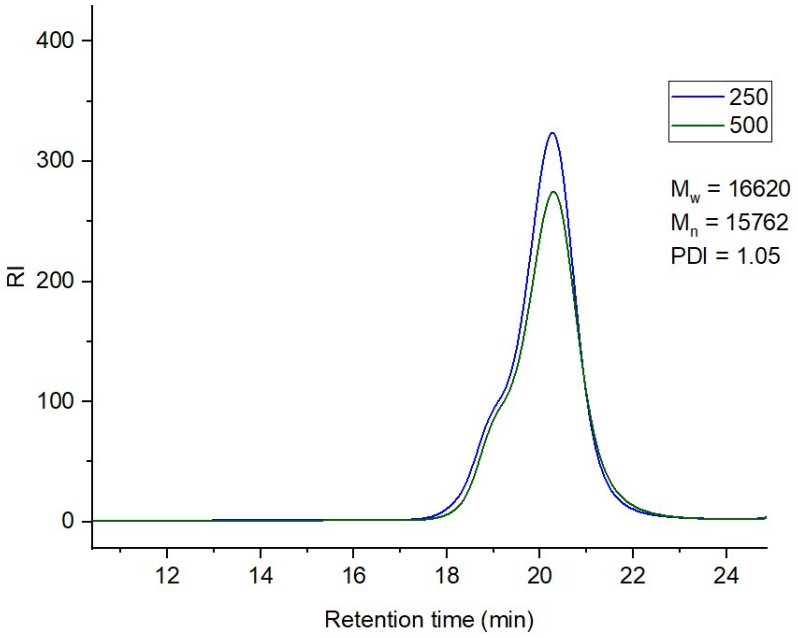


Figure S17: GPC traces for copolymer synthesized by using 250 and 500 equivalent of eugenol epoxide with COS.

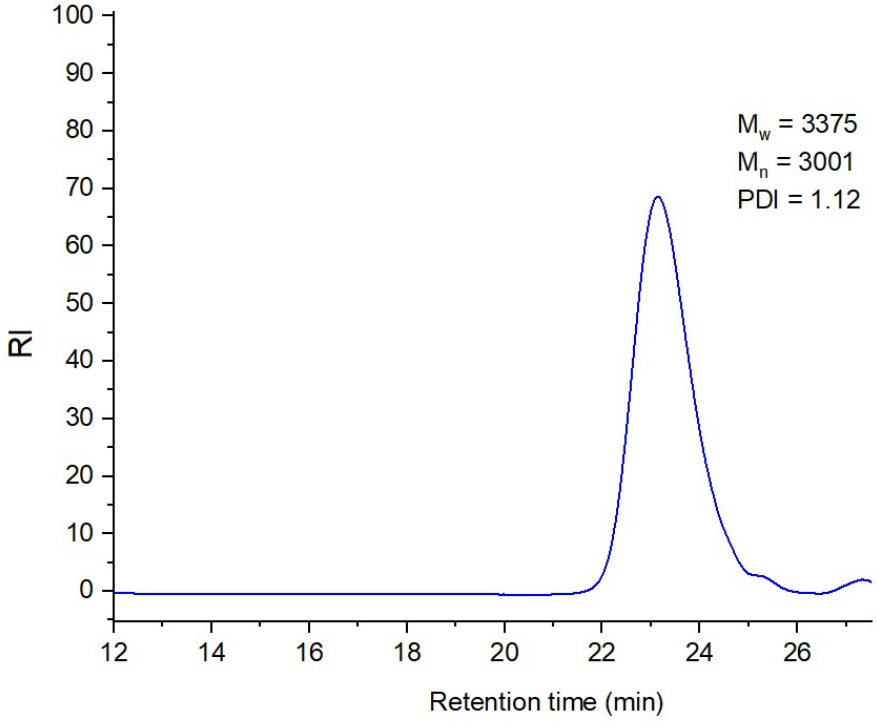


Figure S18: GPC traces for copolymer synthesized by using 250 equivalent of eugenol epoxide at 1 bar of COS pressure.

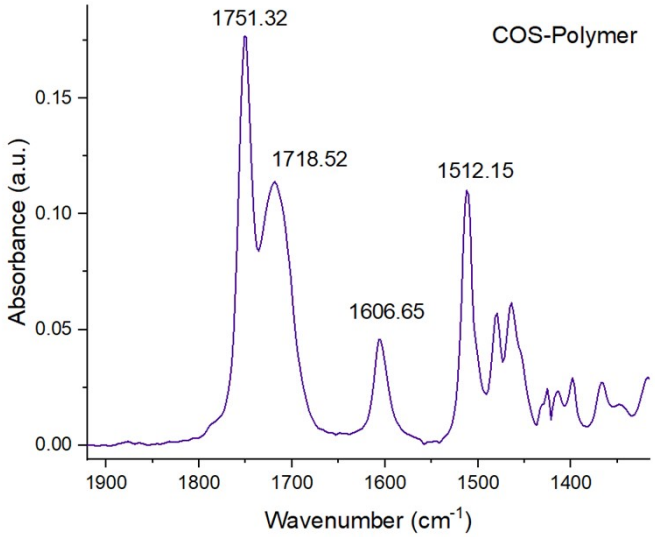


Figure S19. ATR FT-IR spectrum of polymonothiocarbonate polymer.

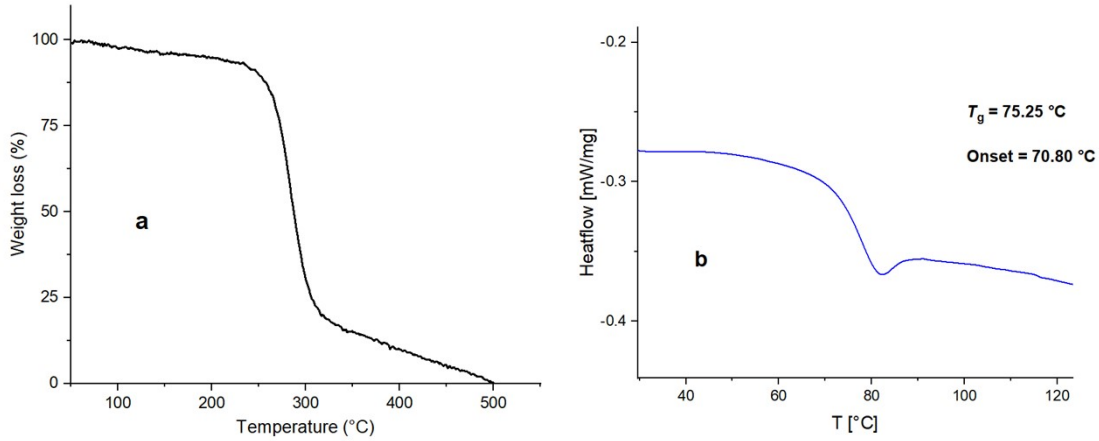
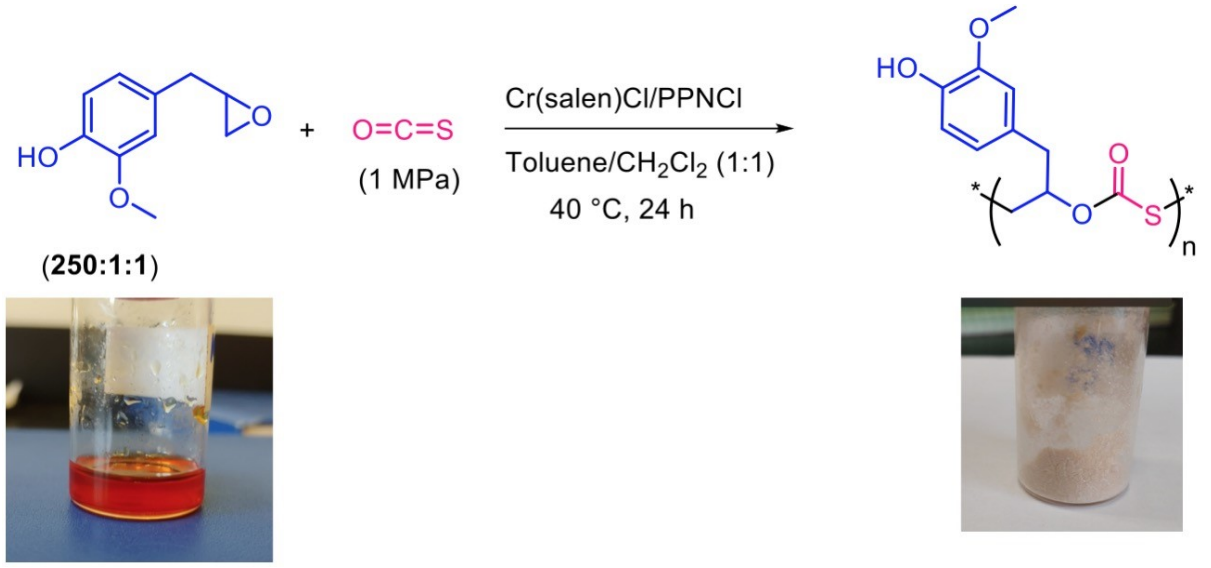


Figure S 20. (a) TGA and (b) DSC curves for the polymonothiocarbonate copolymer.

Procedure for the synthesis of polymer with unprotected eugenol:

In a glovebox, the catalyst, co-catalyst, monomer, and 0.8 mL solvent (CH_2Cl_2: toluene, 1:1 v/v) were placed in a 15 mL stainless steel reactor vessel. All reactions were performed on the scale of 4.0 mg of catalyst, using ratios of 1/1/X for catalyst/cocatalyst/monomer where X = 250, 500, and 750 equivalents. The reactor was pressurized to 1.0 MPa by COS and heated the desired temperature. The reaction mixture was stirred for 24 h, then the autoclave was cooled room temperature and excess COS vented. The polymer was obtained after removing the solvent under reduced pressure and conversion was determined by ^{1}H NMR analysis. Initial

recrystallization was performed by adding dropwise to acidic methanolic solution (4 drops of conc. HCl/50 mL MeOH), followed by two recrystallizations in neutral methanol. The polymer was subsequently dried in vacuum oven.



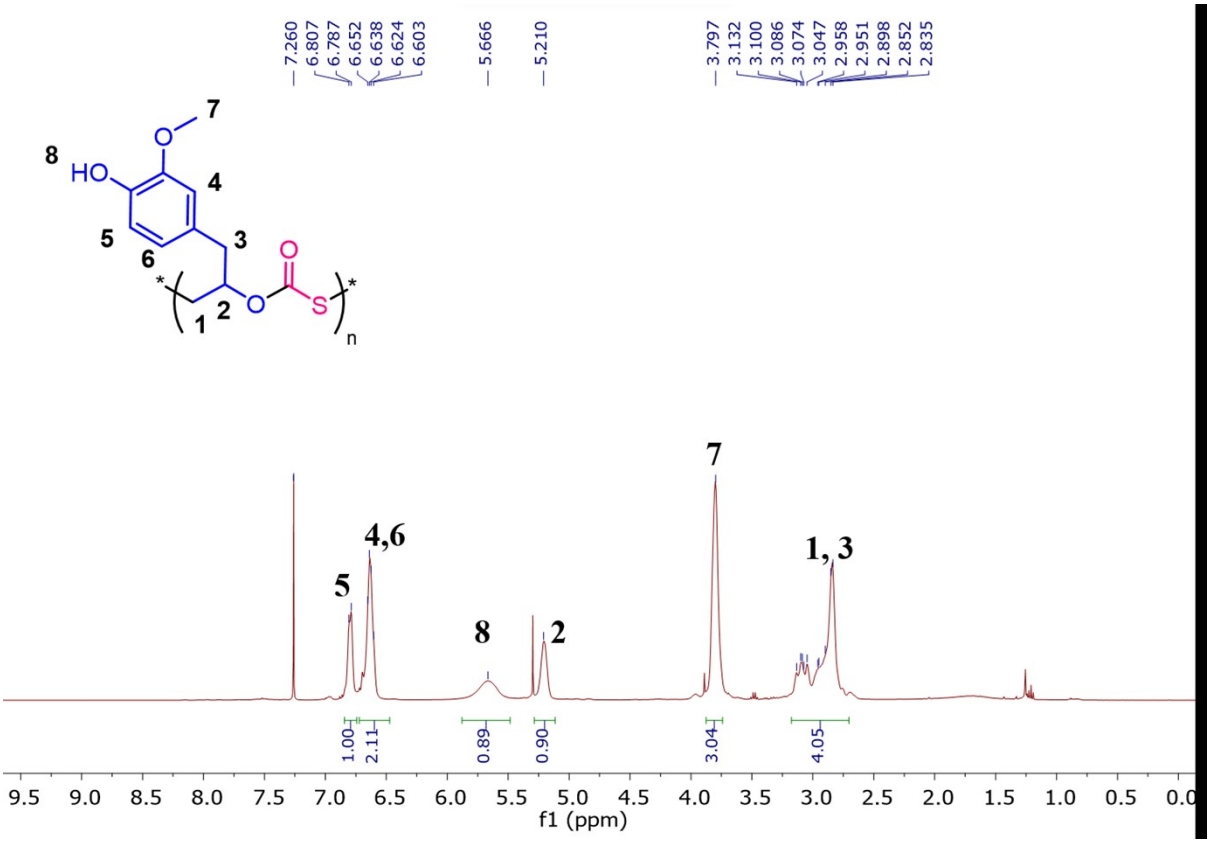


Figure S21: ^{1}H NMR of polymonothiocarbonate ($CDCl_3$, 400 MHz).

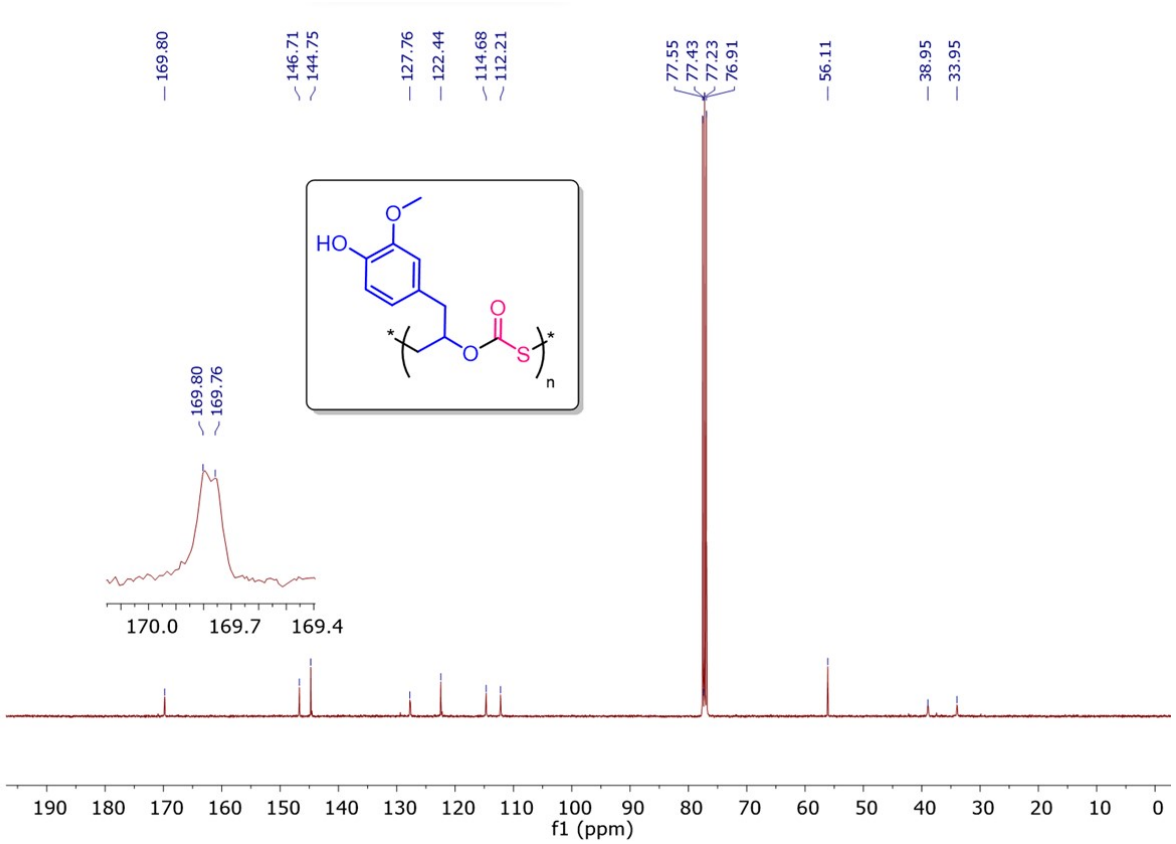


Figure S22: ^{13}C NMR of polymonothiocarbonate copolymer ($CDCl_3$, 100 MHz).

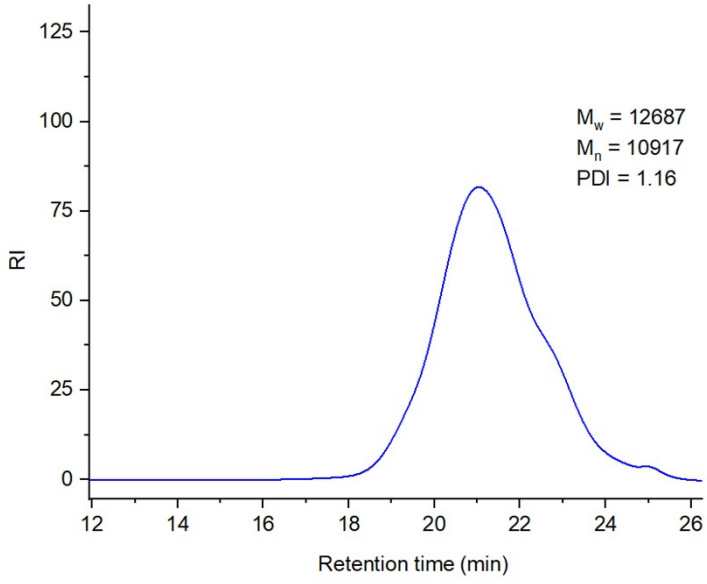


Figure S23: GPC traces for copolymer synthesized by using eugenol epoxide with COS.

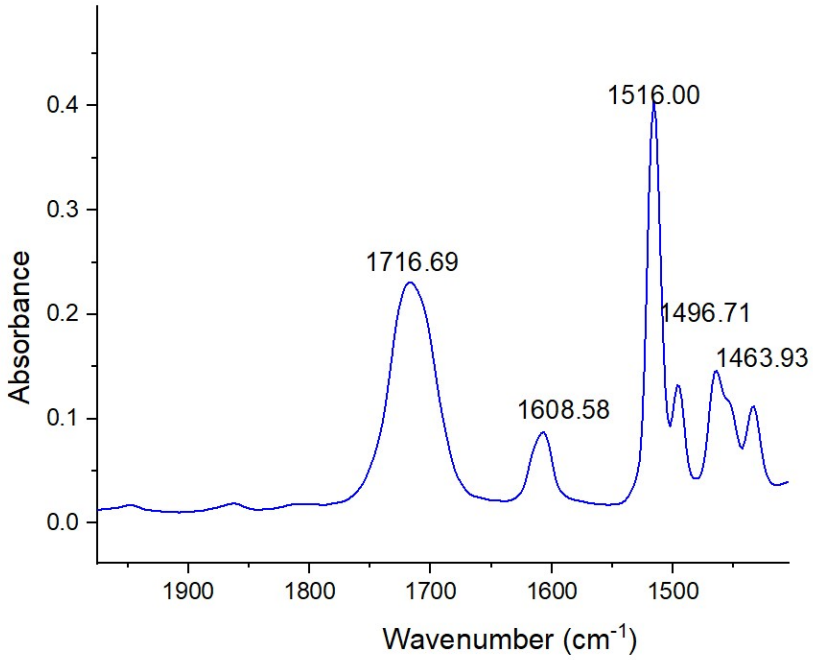


Figure S24. ATR FT-IR spectrum of polymonothiocarbonate copolymer.

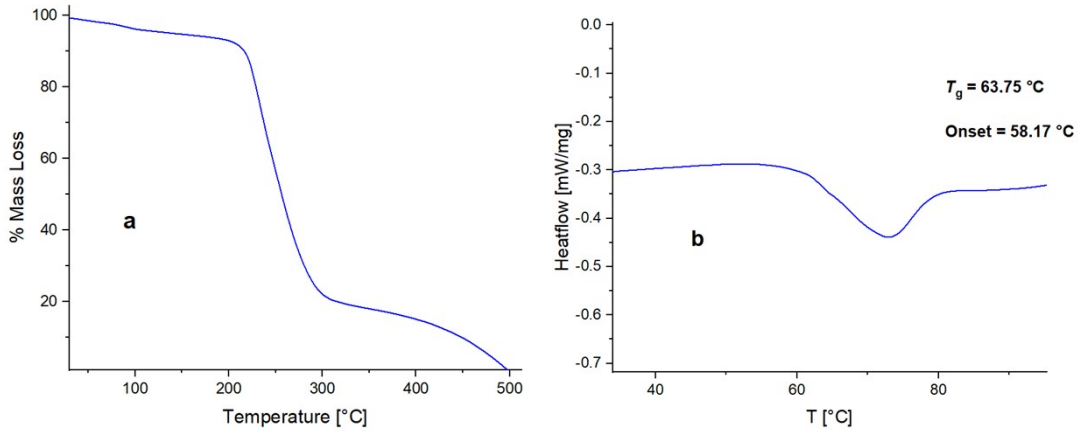


Figure S25. (a) TGA and (b) DSC curves for the polymonothiocarbonate copolymer.

Procedure for the cyclic thiocarbonate formation.

In a glovebox, a mixture of catalyst, co-catalyst, monomer, and 0.8 mL solvent (CH_2Cl_2: toluene, 1:1 v/v) were placed in a 15 mL stainless steel reactor vessel under an argon atmosphere. The reaction was performed using 1/1/250 equivalents of catalyst/co-catalyst/monomer where catalyst is used in the scale of 4 mg. The reactor was pressurized to 1 MPa by COS and heated the desired temperature. The reaction mixture was stirred for 24 h, then the autoclave was cooled room temperature and excess COS vented. The residue was purified by silica gel column chromatography using ethyl acetate and hexanes as eluents to give the cyclic thiocarbonate as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 7.6 Hz, 1H), 6.80-6.77 (m, 2H), 4.88-4.84 (m, 1H), 3.80 (s, 3H), 3.42 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.32 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.21 (dd, *J* = 14.0, 6.0 Hz, 1H), 3.01 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.36 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 172.5, 151.6, 139.8, 133.6, 123.2, 121.6, 113.6, 81.2, 56.2, 39.8, 39.2, 35.8, 27.4. ESI-MS calculated for $C_{16}H_{20}O_5S$ $[M+H]^+$, 325.1104; found, 325.1102.

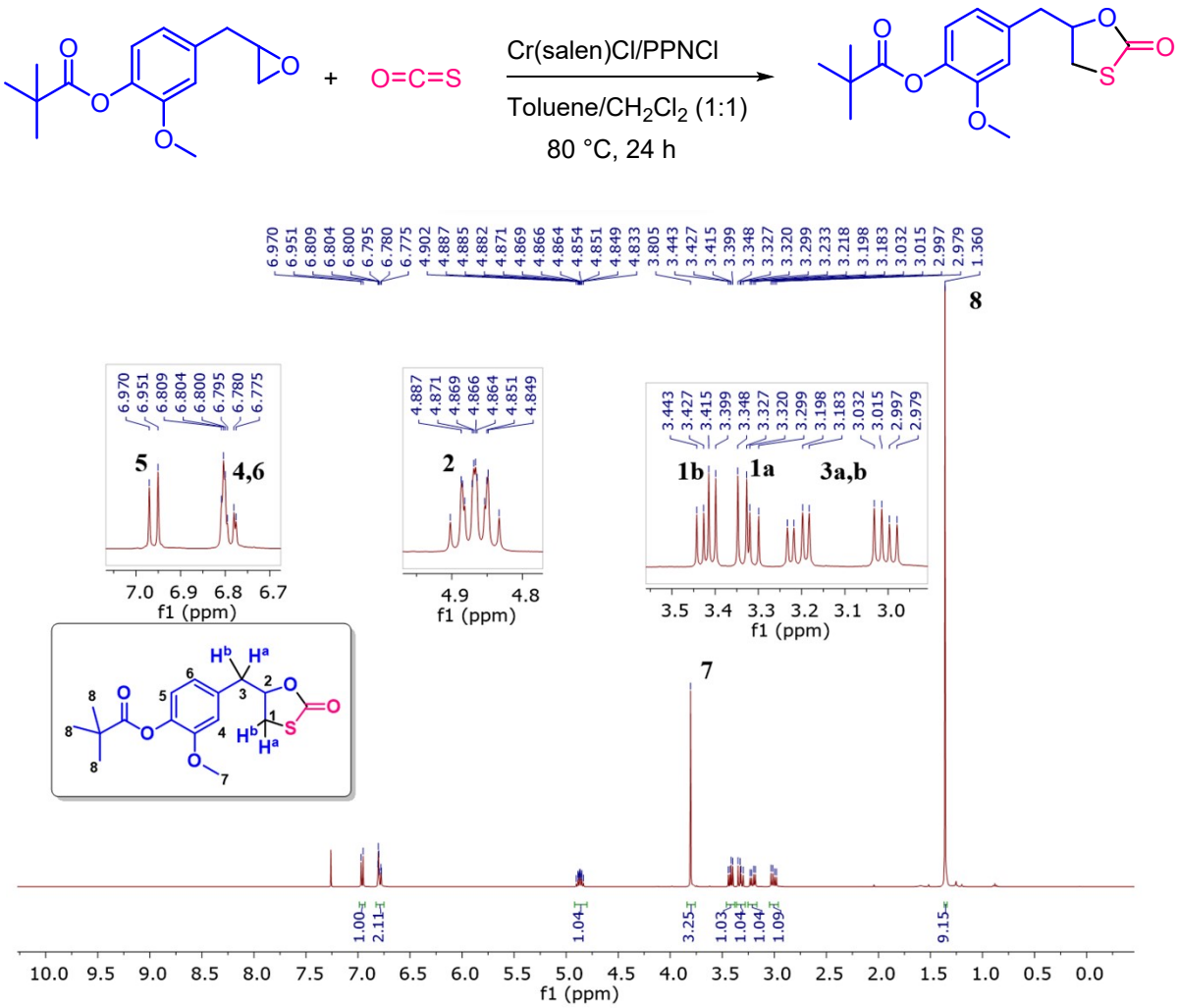


Figure S26: ^{1}H NMR of cyclic thiocarbonate ($CDCl_3$, 400 MHz).

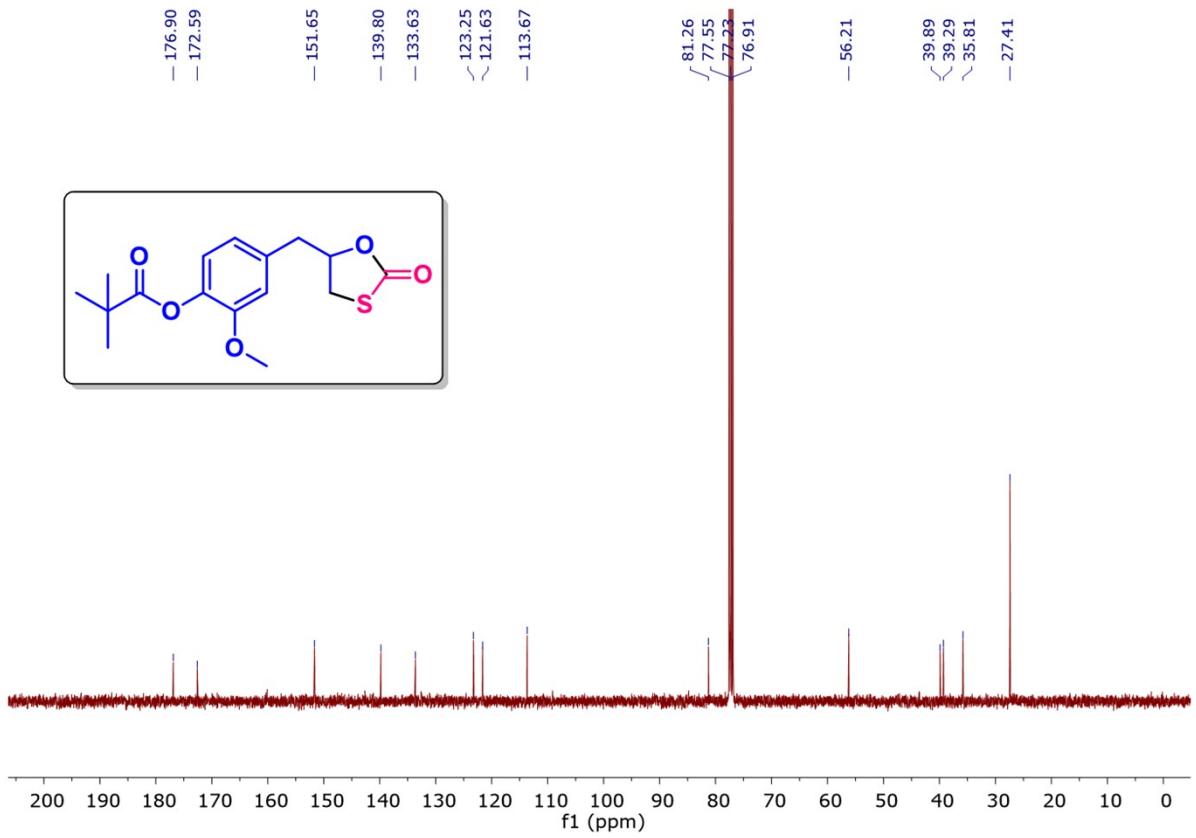


Figure S27: ^{13}C NMR of cyclic thiocarbonate ($CDCl_3$, 100 MHz).

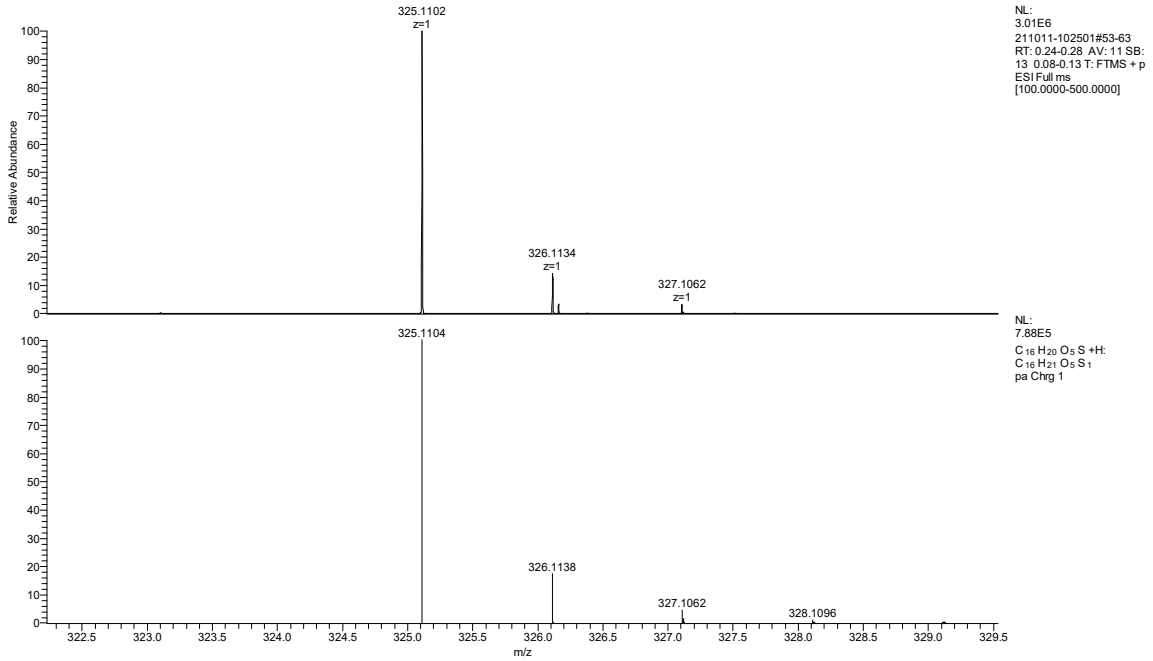


Figure S28: ESI-MS Spectrum of cyclic thiocarbonate.

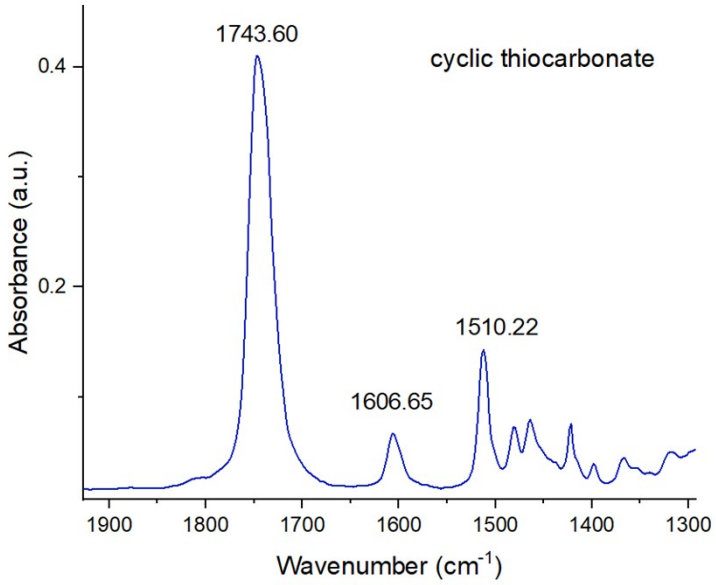
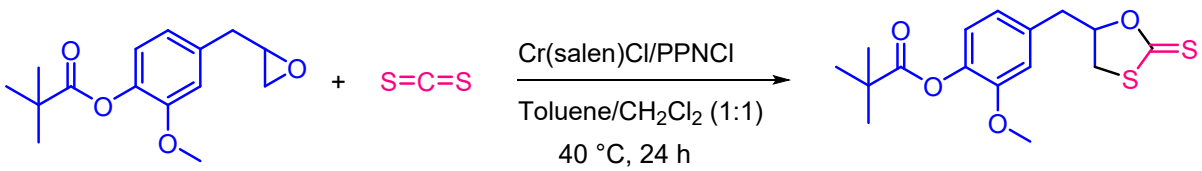


Figure S29. ATR FT-IR spectrum of cyclic thiocarbonate

Procedure for the cyclic dithiocarbonate formation.

In a glovebox, a mixture of catalyst, co-catalyst, monomer, and 0.8 mL solvent (CH_2Cl_2: toluene, 1:1 v/v) were placed in a 15 mL stainless steel reactor vessel under an argon atmosphere. The reaction was performed using 1/1/250/250 equivalents of catalyst/co-catalyst/monomer/CS_2 where catalyst is used in the scale of 4 mg. The reaction mixture was stirred for 24 h, then the autoclave was cooled room temperature and excess COS vented. The residue was purified by silica gel column chromatography using ethyl acetate and hexanes as eluents to give the cyclic dithiocarbonate as a pale-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, J = 8.0 Hz, 1H), 6.83 (s, 1H), 6.80 (d, J = 7.6 Hz, 1H), 5.34-5.27 (m, 1H), 3.80 (s, 3H), 3.52 (dd, J = 11.2, 6.8 Hz, 1H), 3.43 (dd, J = 11.2, 6.4 Hz, 1H), 3.30 (dd, J = 14.0, 6.0 Hz, 1H), 3.12 (dd, J = 14.0, 6.0 Hz, 1H), 1.36 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.8, 176.8, 151.6, 139.8, 133.3, 123.2, 121.6, 113.7, 91.1, 56.2, 39.3, 39.2, 38.6, 27.3. ESI-MS calculated for $C_{16}H_{20}O_4S_2$ $[M+H]^+$, 341.0876; found, 341.0876.



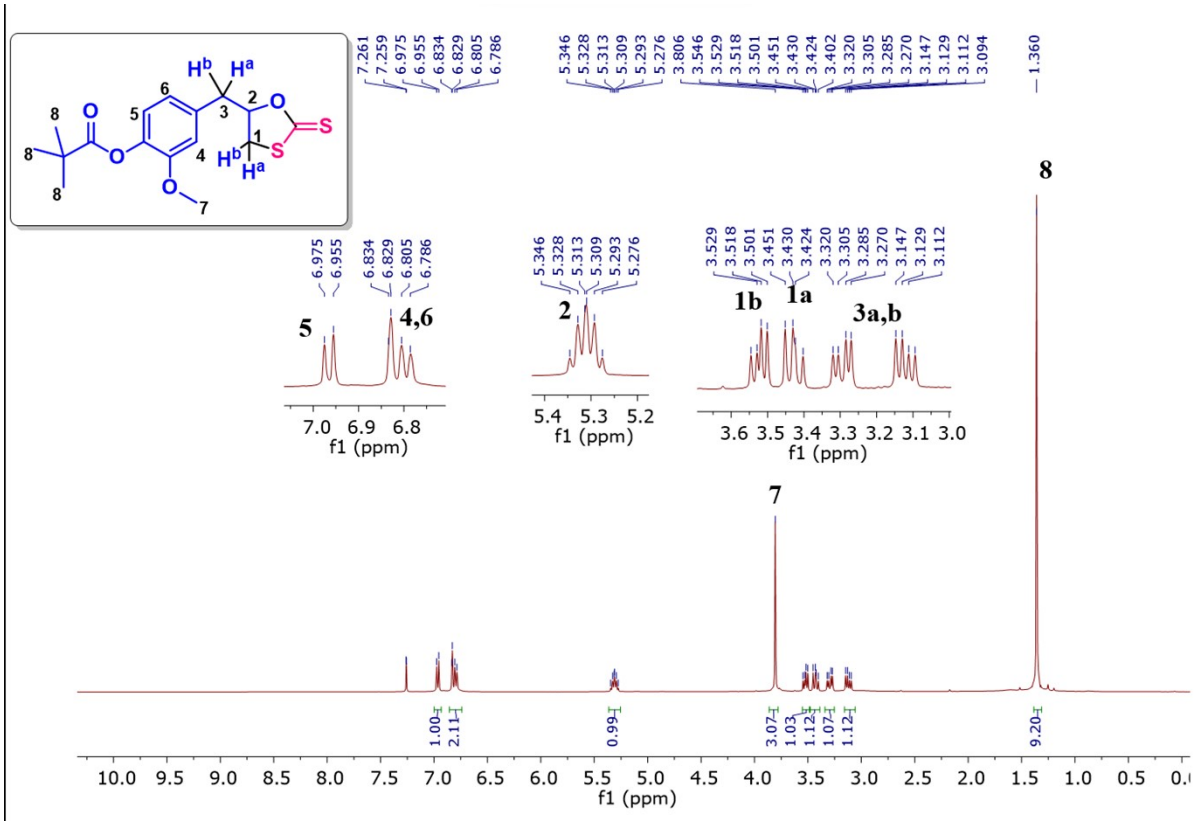


Figure S30: ^{1}H NMR of cyclic dithiocarbonate ($CDCl_3$, 400 MHz).

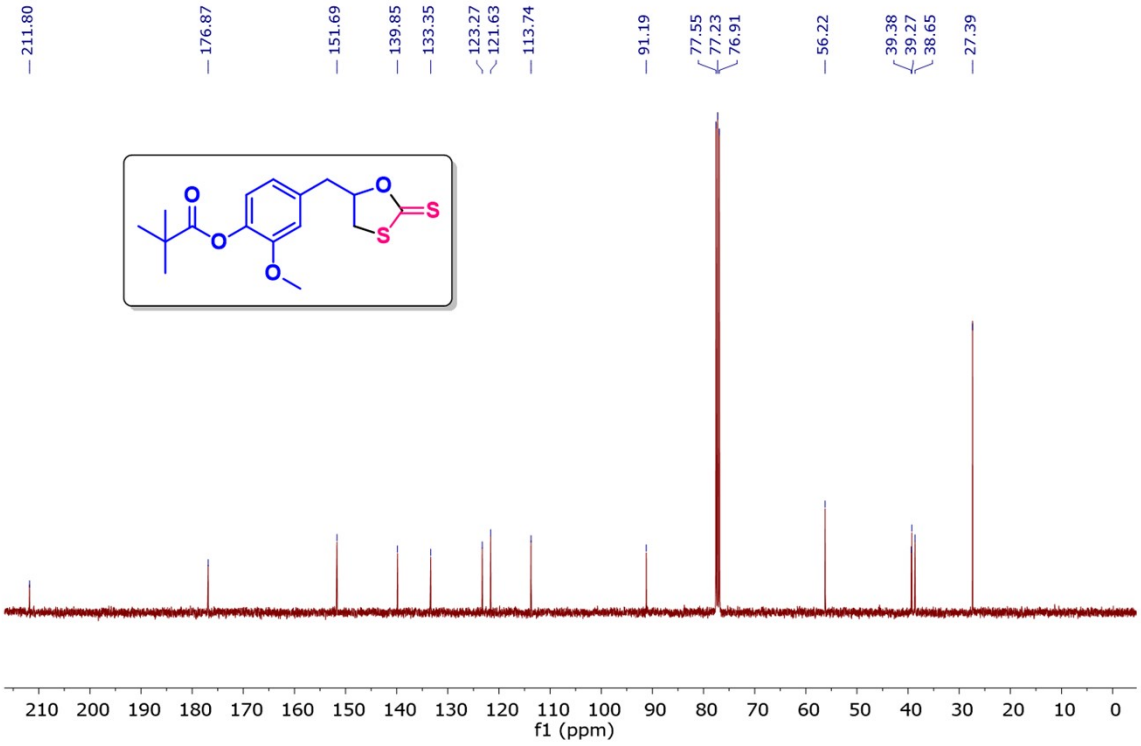


Figure S31: ^{13}C NMR of cyclic dithiocarbonate ($CDCl_3$, 100 MHz).

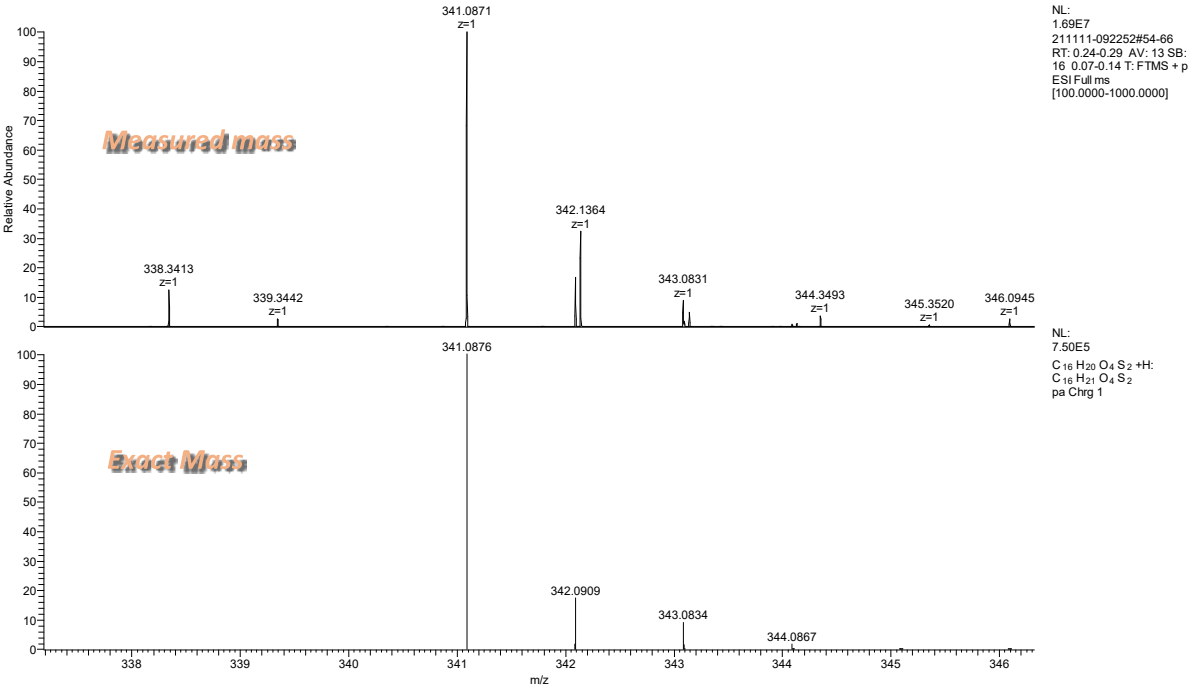


Figure S32: ESI-MS Spectrum of cyclic dithiocarbonate.

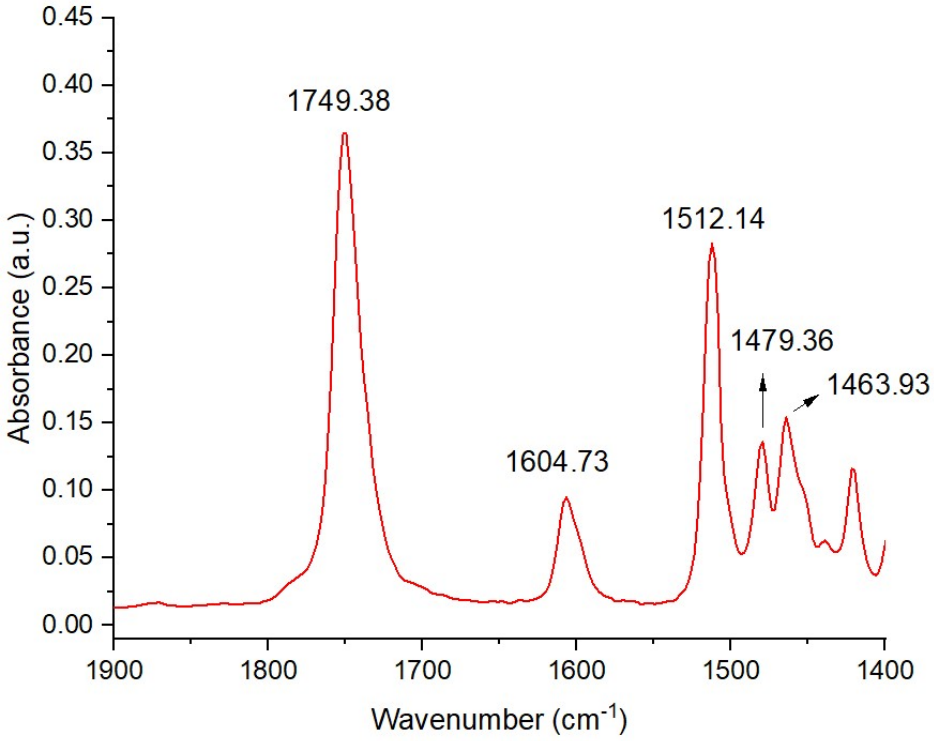
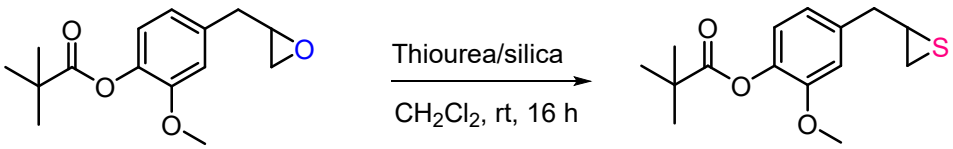


Figure S33. ATR FT-IR spectrum of cyclic dithiocarbonate.

Procedure for the preparation of 2-Methoxy-4-(thiiran-2-ylmethyl)phenyl pivalate (monomer):



To a stirred solution of eugenol epoxide (10 mmol) in CH_2Cl_2 (100 mL) were added thiourea (20 mmol) and silicagel (3 g). The progress of the reaction was monitored by TLC using ethyl acetate and hexane. After completion, the mixture was filtered and evaporation of the solvent on a rotary evaporator gave a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate as an eluent. The pure monomer was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 7.6 Hz, 1H), 6.85-6.81 (m, 2H), 3.80 (s, 3 H), 3.11-3.07 (m, 1H), 2.99 (dd, *J* = 14.4, 6.0 Hz, 1 H), 2.88 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.56 (dd, *J* = 6.0, 1.2 Hz, 1H), 2.28 (dd, *J* = 6.0, 1.2 Hz, 1H), 1.36 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 151.2, 139.1, 138.0, 122.7, 120.8, 113.0, 56.0, 42.6, 39.2, 35.9, 27.4, 25.8. ESI-MS calculated for $C_{15}H_{20}O_3S$ $[M+H]^+$, 281.11206; found, 281.1200.

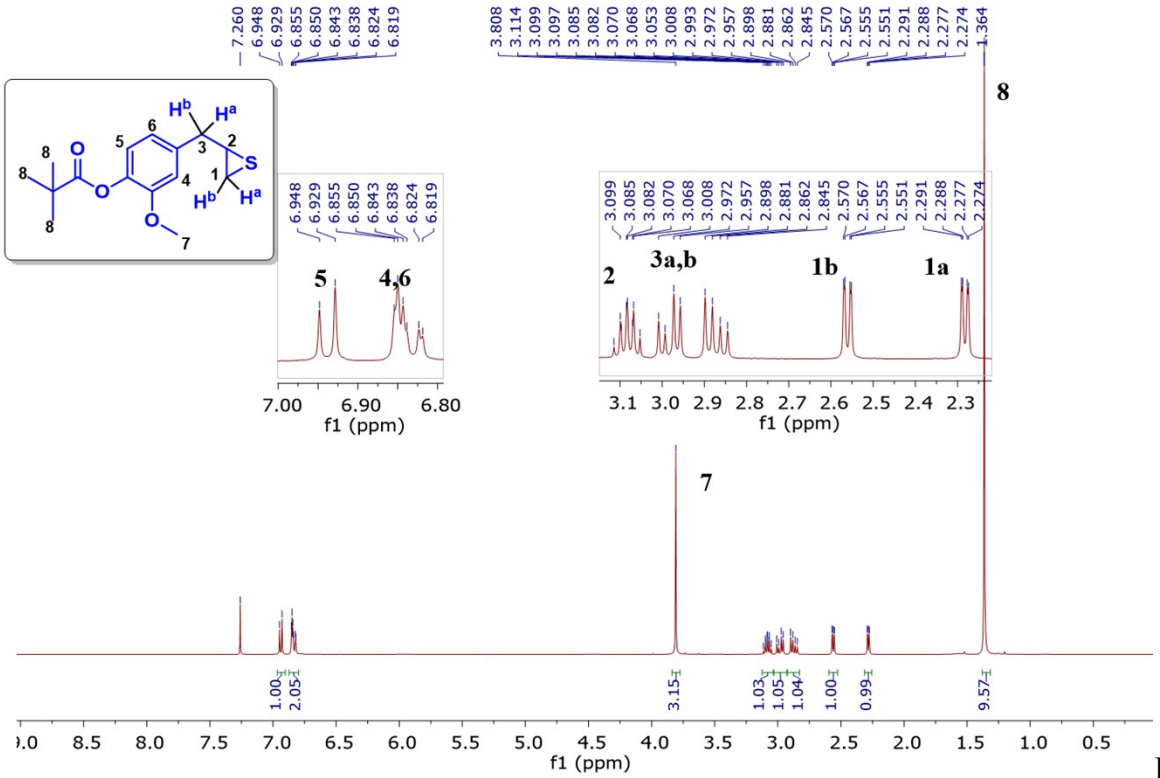


Figure S34: ^{1}H NMR of eugenol thiirane ($CDCl_3$, 400 MHz).

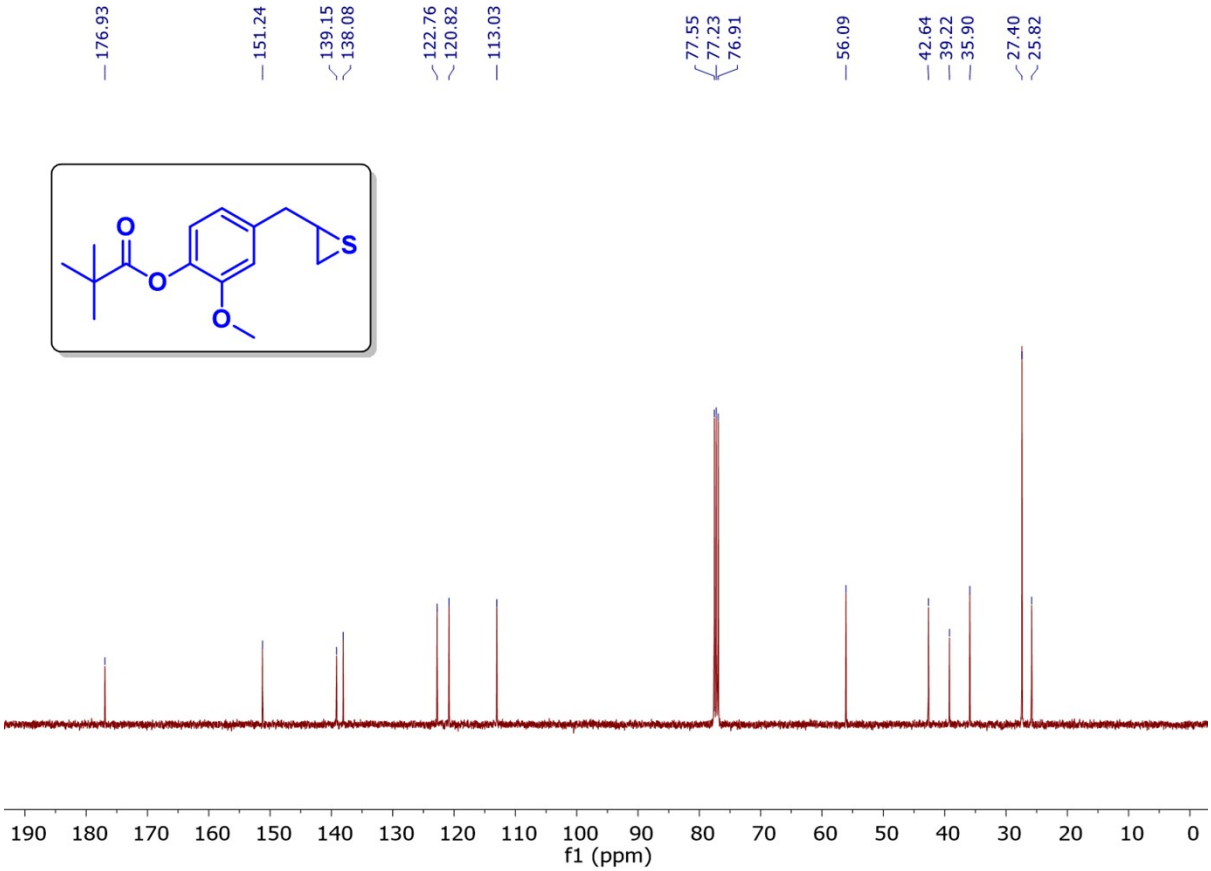


Figure S35: ^{13}C NMR of eugenol thiirane ($CDCl_3$, 100 MHz).

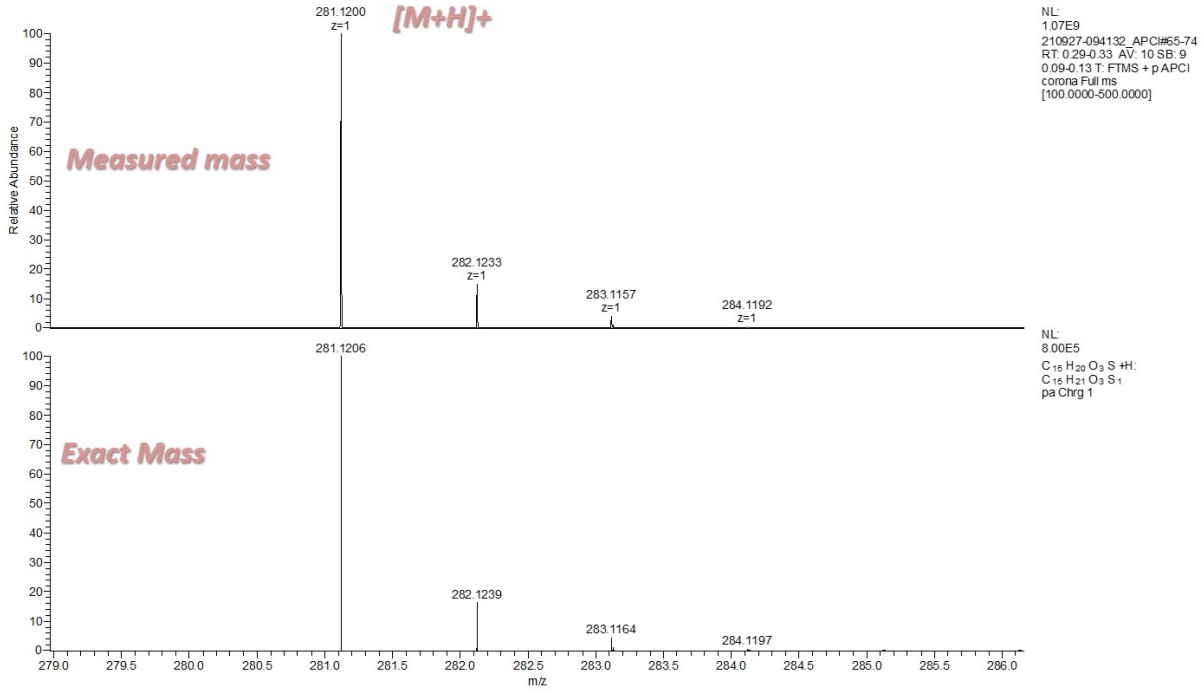


Figure S36: ESI-MS Spectrum of eugenol thiirane.

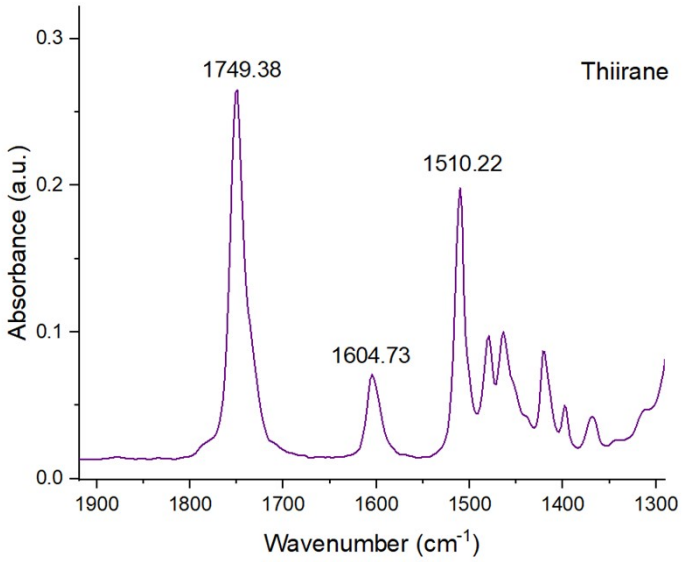


Figure S37. ATR FT-IR spectrum of eugenol thiirane.

Procedure for the synthesis of polythioether.

In a glovebox, the monomer, boron trifluoride etherate ($BF_3{\cdot}OEt_2$) and 0.8 mL solvent (CH_2Cl_2: toluene, 1:1 v/v) were placed in a 15 mL stainless steel reactor vessel. Reactions were performed on the scale of 4.0 mg of catalyst, using ratios of 1/250 for catalyst/monomer equivalents. The reactor was pressurized to 3.0 MPa by CO_2 and continued stirring at room

temperature for 24 h, then the autoclave was cooled room temperature. The polymer was obtained after removing the solvent under reduced pressure. Further purified by short path silica gel column using dichloromethane as an eluent.

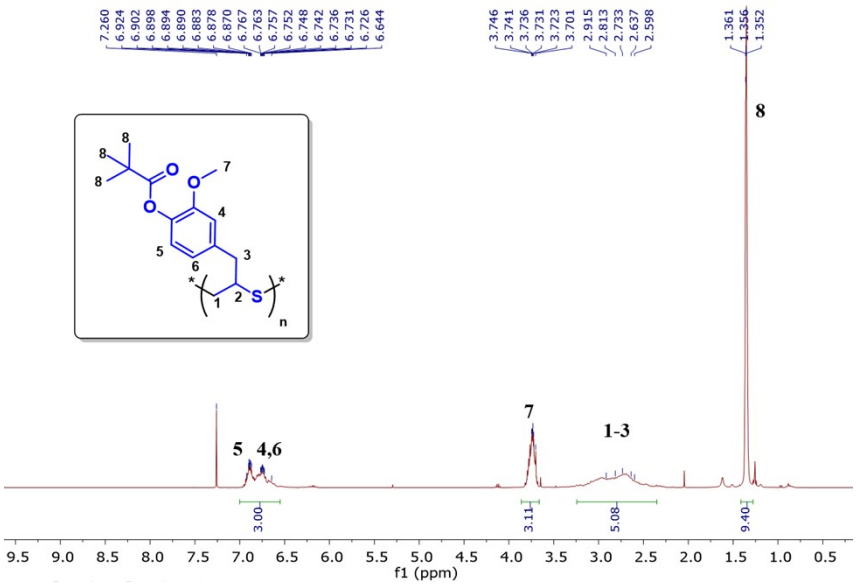


Figure S38: ^{1}H NMR of polythioether ($CDCl_3$, 400 MHz).

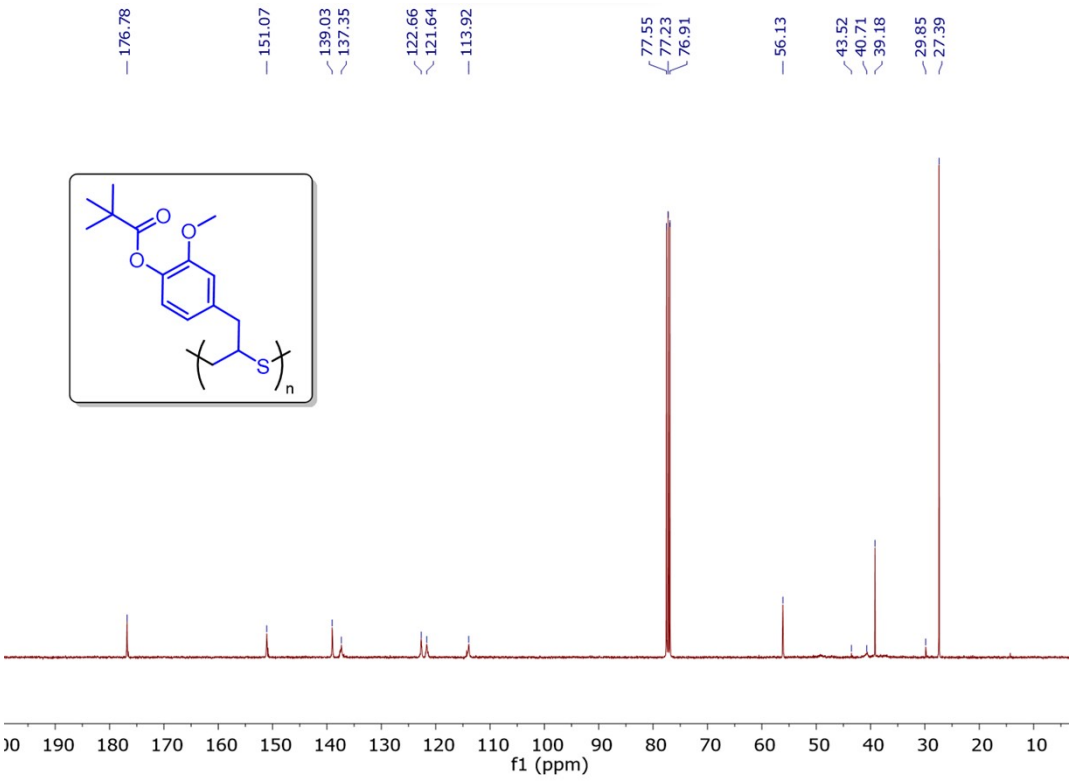


Figure S39: ^{13}C NMR of polythioether ($CDCl_3$, 100 MHz).

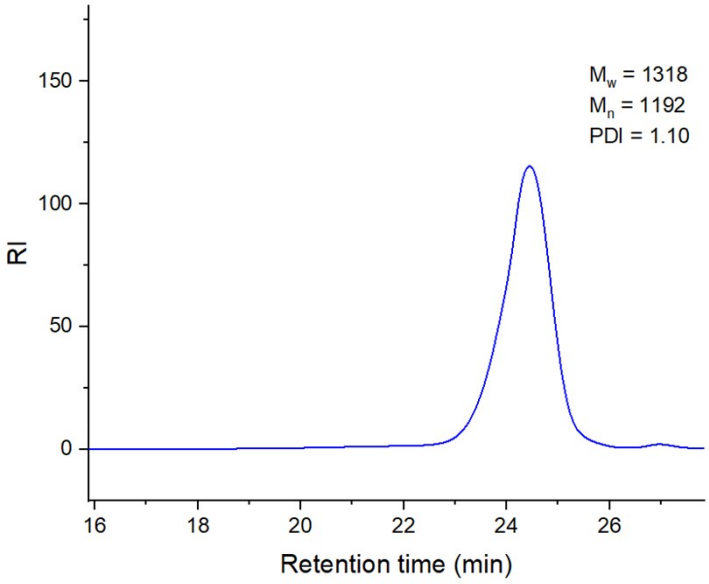


Figure S40: GPC trace of polythioether.

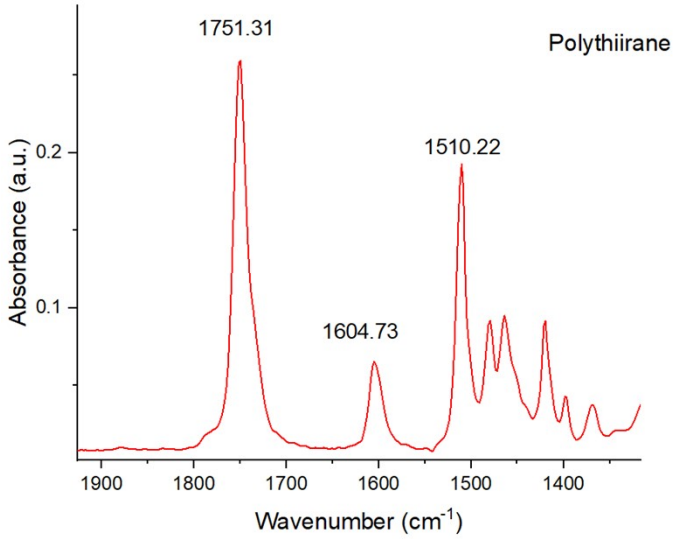


Figure S41. ATR FT-IR spectrum of polythioether.

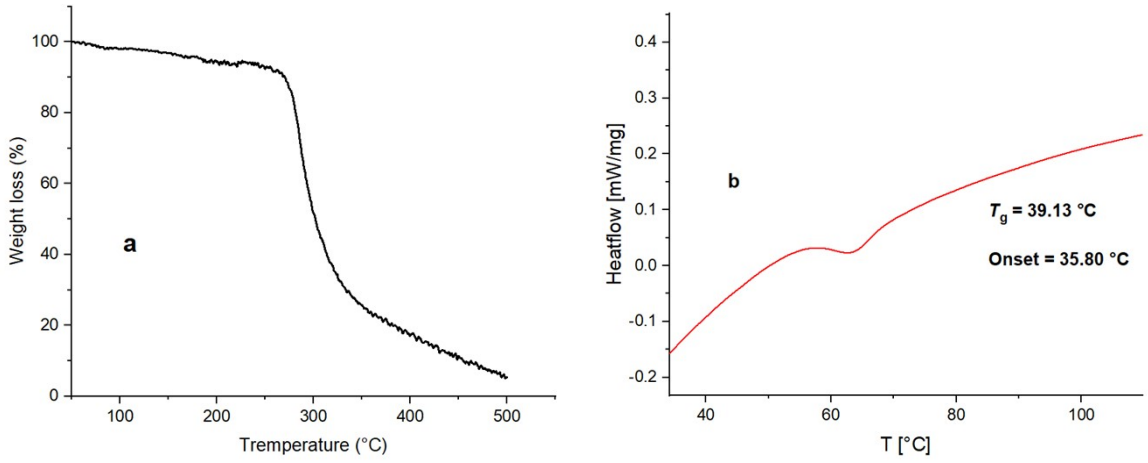


Figure S42. (a) TGA and (b) DSC curves for the polythioether

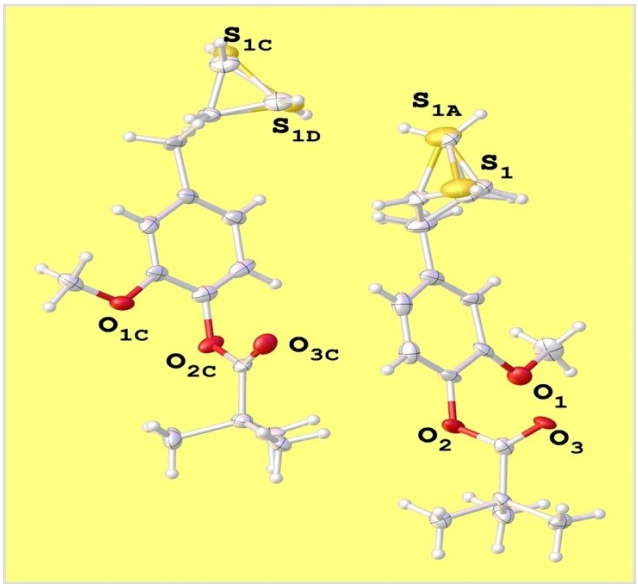


Figure 43. X-ray crystal structure of the thiirane eugenol.

Table S1. Crystallographic data and refinement details for the crystal structure of eugenol based monomers and their cyclic products.

Compound	**Eugenol epoxide**	**Eugenol thiirane**	**Cyclic Carbonate**	**Cyclic thiocarbonate**
Empirical formula	$C_{15}H_{20}O4$	$C_{15}H_{20}O_3S$	$C_{16}H_{20}O_6$	$C_{16}H_{20}O_5S$
CCDC number	**2143469**	**2143470**	**2143471**	**2143472**
FW	264.31	280.37	308.32	324.38
Temp, [K]	110	110	110	110
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca*	$Pca2_1$	*P1211*	$P2_1/n$
a, [Å]	16.3085(4)	21.6035(6)	10.8206(5)	13.9329(5)
b, [Å]	7.9252(4)	7.9904(2)	6.2424(3)	6.1434(2)
c, [Å]	21.3840(6)	16.8357(5)	12.0066(5)	19.2618(7)
α, [°]	90	90	90	90
β, [°]	90	90	109.921(1)	96.736(2)
γ, [°]	90	90	90	90
V, [Å^3]	2763.84	2906.20	762.48(6)	1637.34(2)
Z	8	8	2	4
D(calcd), [Mg/cm^3]	1.270	1.282	1.343	1.316
μ [mm^{-1}]	0.746	0.224	0.859	1.940
GOF	1.073	1.070	1.057	1.070
R1(I_0>2σ(I_0))	0.0719	0.055	0.0308	0.0353
wR2 (all data)	0.1962	0.1629	0.0802	0.0962

References

1. Yang, G.-W.; Zhang, Y.-Y.; Xie, R.; G.-P. Wu, *J. Am. Chem. Soc.* **2020**, *142*, 12245.