

Supporting Information

Facile Synthesis of Polycarbonates from Biomass-Based Eugenol: Catalyst Optimization for Selective Copolymerization of CO₂ and Eugenol to Achieve Polycarbonates

Mani Sengoden^a, Gulzar A. Bhat^{b}, Tristan Roland^a, Chia-Min Hsieh^a*

and Donald J. Darensbourg^{a}*

^aDepartment of Chemistry, Texas A&M University

College Station, Texas 77843, United States

^bCentre for Interdisciplinary Research and Innovations

University of Kashmir, Srinagar Jammu and Kashmir 190006, India

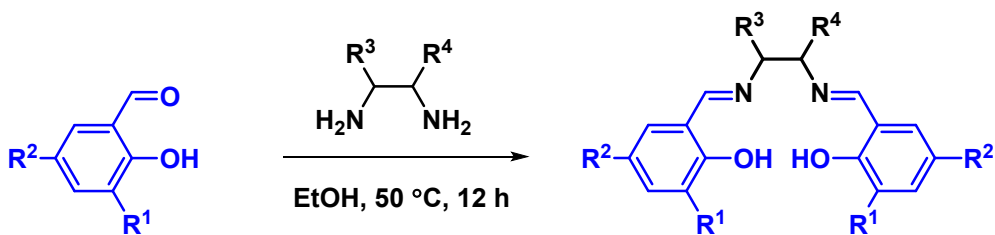
Materials and Methods:

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 salicylaldehyde, 1,2-diamines, CrCl₂, Co(OAc)₂·4H₂O, eugenol, pivaloyl chloride, 3-chloroperbenzoic acid, triethyl amine were purchased from commercial sources, Pre-catalyst (*R,R*)-*N,N'*-Bis(3,5-di-*tert*butylsalicylidene)-1,2-cyclohexanediamino-cobalt(II) and (*R,R*)-*N,N'*-Bis(3,5-di-*tert*butylsalicylidene)-1,2-cyclohexanediamino-chromium(III) chloride were purchase from Strem Chemicals, whereas co-catalyst bis(triphenylphosphine)iminium chloride and bis(triphenylphosphine)iminium trifluoroacetate were purchased from commercial sources. CO₂ was supplied from a high-pressure cylinder purchased from Praxair. NMR spectra were recorded on a 400 MHz Bruker spectrometer with CDCl₃ and DMSO-*d*₆ as an internal standard at 7.26 and 2.50 ppm, respectively. 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, the polymeric sample were heated from room temperature to 500 °C at a rate of 10 °C·min⁻¹ under N₂ flow of 20 mL· min⁻¹. 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 180.00 °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 180.00 °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. DOSY-NMR Data was collected on a 500 MHz Varian VnmrS500. Spectra were collected from 0 to 8 ppm with a 80° pulse and 2 s relaxation delay with 16 scans per fid. The DOSY pulse sequence Bipolar Pulse Pair Stimulated Echo: Dbppste in 15 increments with gradients from 71 to 1780. Dynamic light scattering measured in Malvern Zetasizer Nano ZS and sample prepared using 5 mg of polymer dispersed in 10 mL of deionized water.

General Procedure for Ligand Syntheses

Salophen ligands were synthesized in the reactions between the appropriate salicylaldehyde and 1,2-phenylenediamine (Scheme 1). A solution of 1,2-phenylenediamine (5 mmol) in absolute ethanol (10 ml) was added dropwise to salicylaldehyde (10 mmol) in absolute ethanol (40 ml) at 50 °C. The reaction mixture was stirred at 50 °C for 12 h and the solvent was evaporated under vacuum produced yellow orange powder, which was further purified by recrystallization from absolute ethanol.



Scheme 1. Synthesis of the salophen ligands.

***N,N'*-Bis-(3,5-di-*tert*-butylsalicylidene)-1,2-phenylenediamine (L1).** Orange solid (91% yield); ^1H NMR (400 MHz, CDCl_3) δ 13.40 (br s, 2H), 8.58 (s, 2H), 7.36 (d, $J = 2.4$ Hz, 2H), 7.23-7.21 (m, 2H), 7.16-7.13 (m, 4H), 1.36 (s, 18H), 1.24 (s, 18H).

***N,N'*-Bis-(3,5-di-*tert*-butylsalicylidene)-2,3-naphthalenediamine (L2).** Orange solid (88% yield); ^1H NMR (400 MHz, CDCl_3) δ 13.23 (br s, 1H), 8.77 (s, 2H), 7.87-7.84 (m, 2H), 7.59 (s, 2H), 7.49-7.46 (m, 4H), 7.28-7.27 (m, 2H), 5.30 (s, 1H), 1.45 (s, 18H), 1.34 (s, 18H).

***N,N'*-Bis-(3,5-di-*tert*-butylsalicylidene)-4,5-dichloro-1,2-phenylenediamine (L3).** Yellow solid (58% yield); ^1H NMR (400 MHz, CDCl_3) δ 13.15 (br s, 2H), 8.63 (s, 2H), 7.47 (d, $J = 2.4$ Hz, 2H), 7.34 (s, 2H), 7.22 (d, $J = 2.4$ Hz, 2H), 1.42 (s, 18H), 1.32 (s, 18H).

***N,N'*-Bis-(3-*tert*-butylsalicylidene)-1,2-phenylenediamine (L4).** Orange solid (95% yield); ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 14.03 (br s, 2H), 8.96 (s, 2H), 7.53-7.48 (m, 4H), 7.44-7.43 (m, 2H), 7.39 (d, $J = 7.6$ Hz, 2H), 6.91 (t, $J = 7.6$ Hz, 2H), 1.38 (s, 18H).

***N,N'*-Bis-(3-methoxysalicylidene)-1,2-phenylenediamine (L5).** Orange solid (97% yield); ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 12.99 (br s, 2H), 8.92 (s, 2H), 7.47-7.39 (m, 4H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.91 (t, $J = 8.0$ Hz, 2H), 3.81 (s, 6H).

***N,N'*-Bis-(3,5-di-*tert*-butylsalicylidene)-4-methyl-1,2-phenylenediamine (L6).** Orange solid (95% yield); ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.89 (s, 1H), 8.88 (s, 1H), 7.51 (dd, $J = 6.0, 2.4$ Hz, 2H), 7.45 (dd, $J = 6.0, 2.4$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.30-7.29 (m, 1H), 7.25-7.23 (m, 1H), 2.47 (s, 3H), 1.48 (s, 9H), 1.47 (s, 9H), 1.37 (s, 9H), 1.36 (s, 9H).

***N,N'*-Bis-(3,5-di-*tert*-butylsalicylidene)-4,5-dimethyl-1,2-phenylenediamine (L7).** Orange solid (93% yield); ^1H NMR (400 MHz, CDCl_3) δ 13.67 (br s, 2H), 8.66 (s, 2H), 7.43 (d, $J =$

2.8 Hz, 2 H), 7.21 (d, $J = 2.8$ Hz, 2 H), 7.03 (s, 2H), 2.33 (s, 6H), 1.44 (s, 18H), 1.32 (s, 18H).

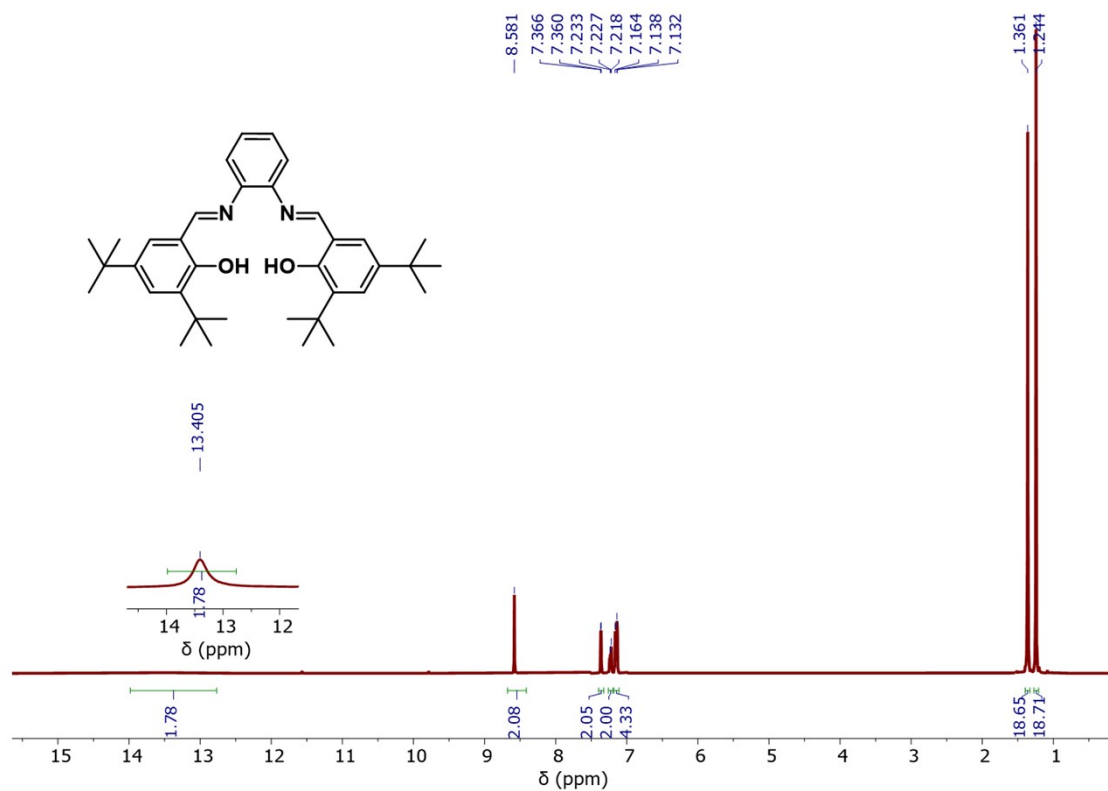


Figure S1: ^1H NMR of salphen (L1) (CDCl_3 , 400 MHz).

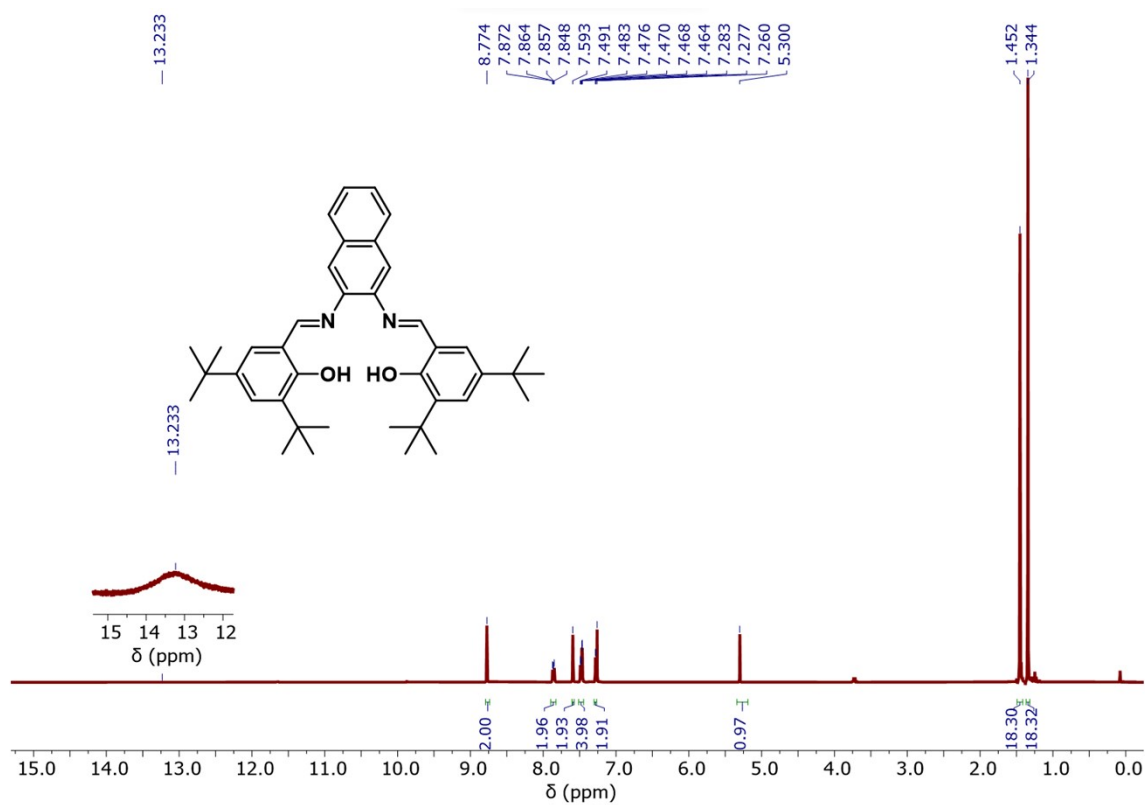


Figure S2: ^1H NMR of salophen (L2) (CDCl_3 , 400 MHz).

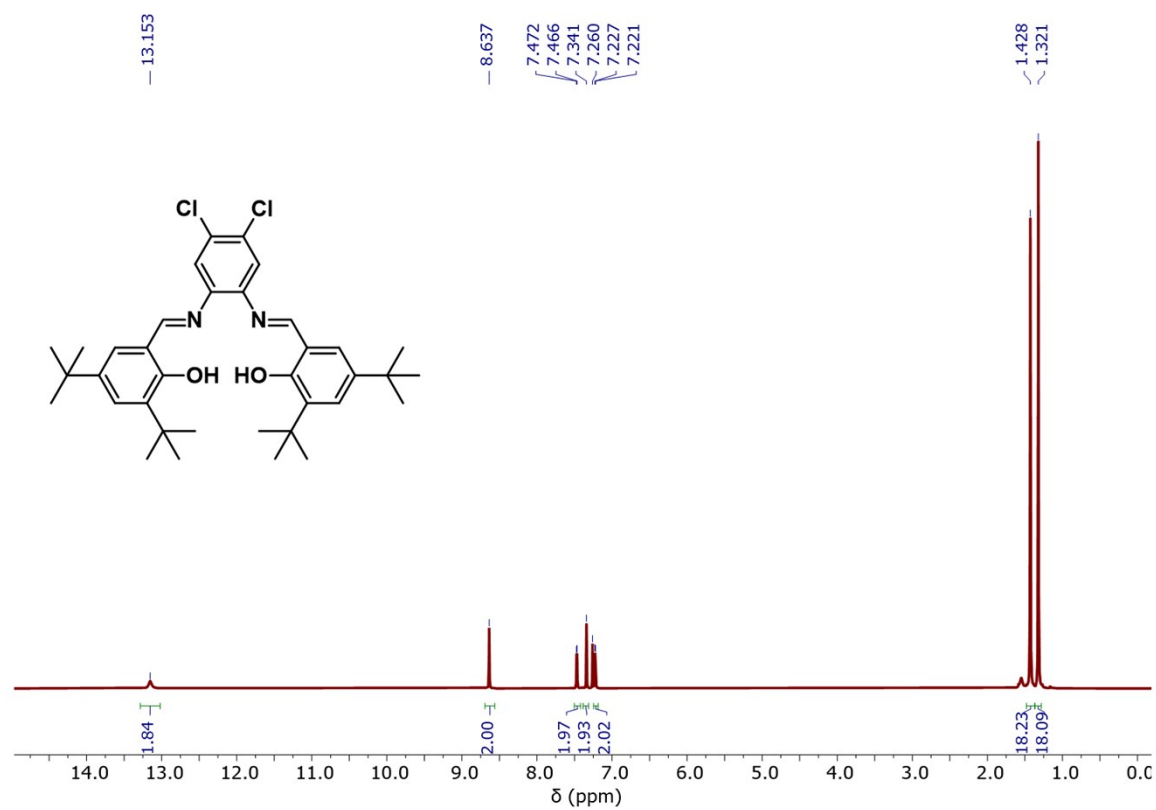


Figure S3: ^1H NMR of salophen (L3) (CDCl_3 , 400 MHz).

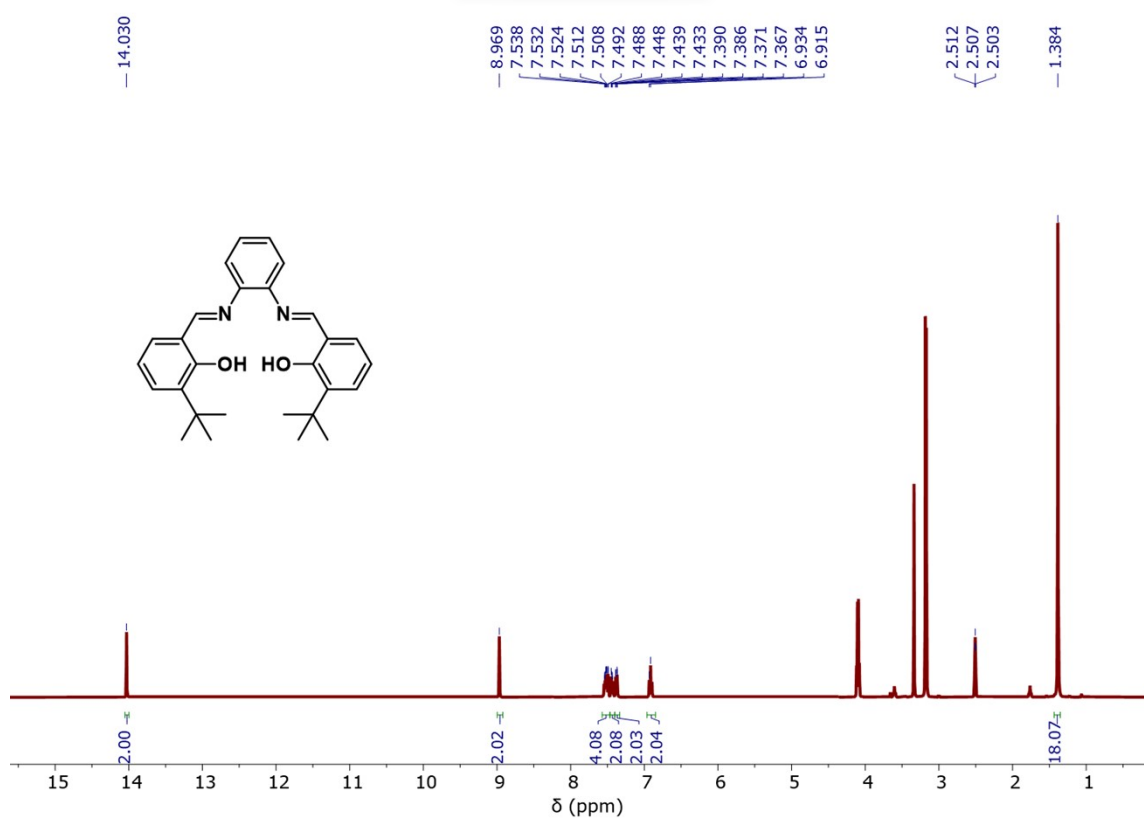


Figure S4: ^1H NMR of salophen (L4) ($\text{DMSO-}d_6$, 400 MHz).

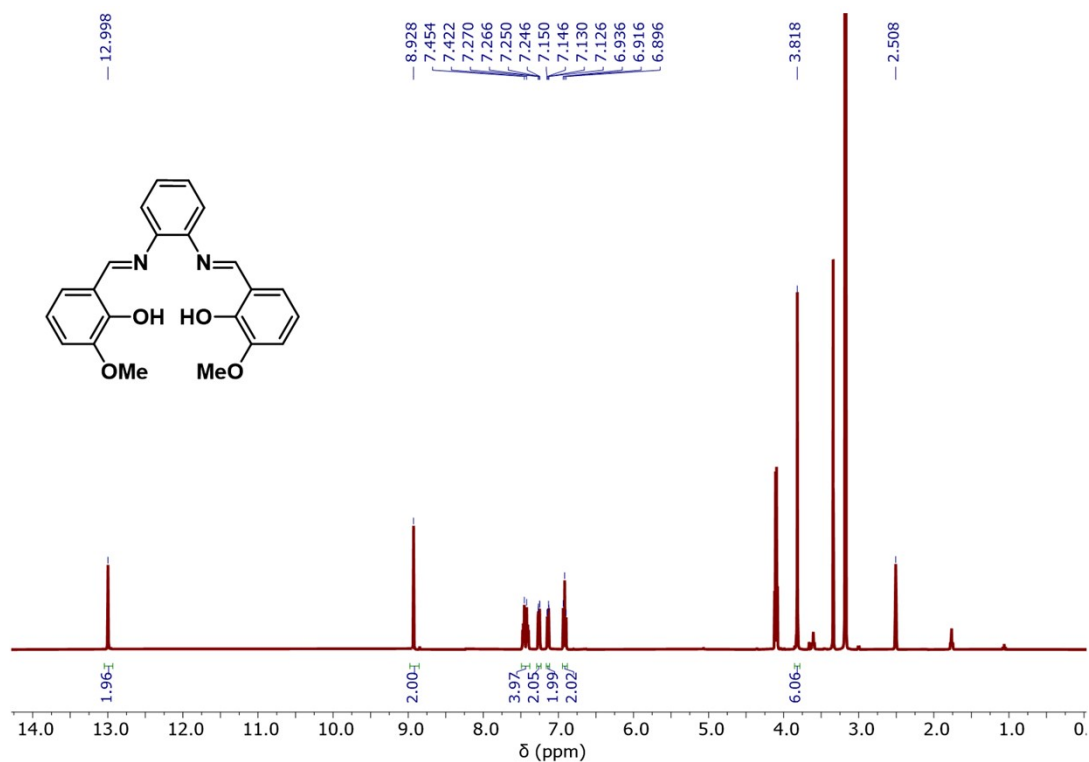


Figure S5: ^1H NMR of salophen (L5) ($\text{DMSO-}d_6$, 400 MHz).

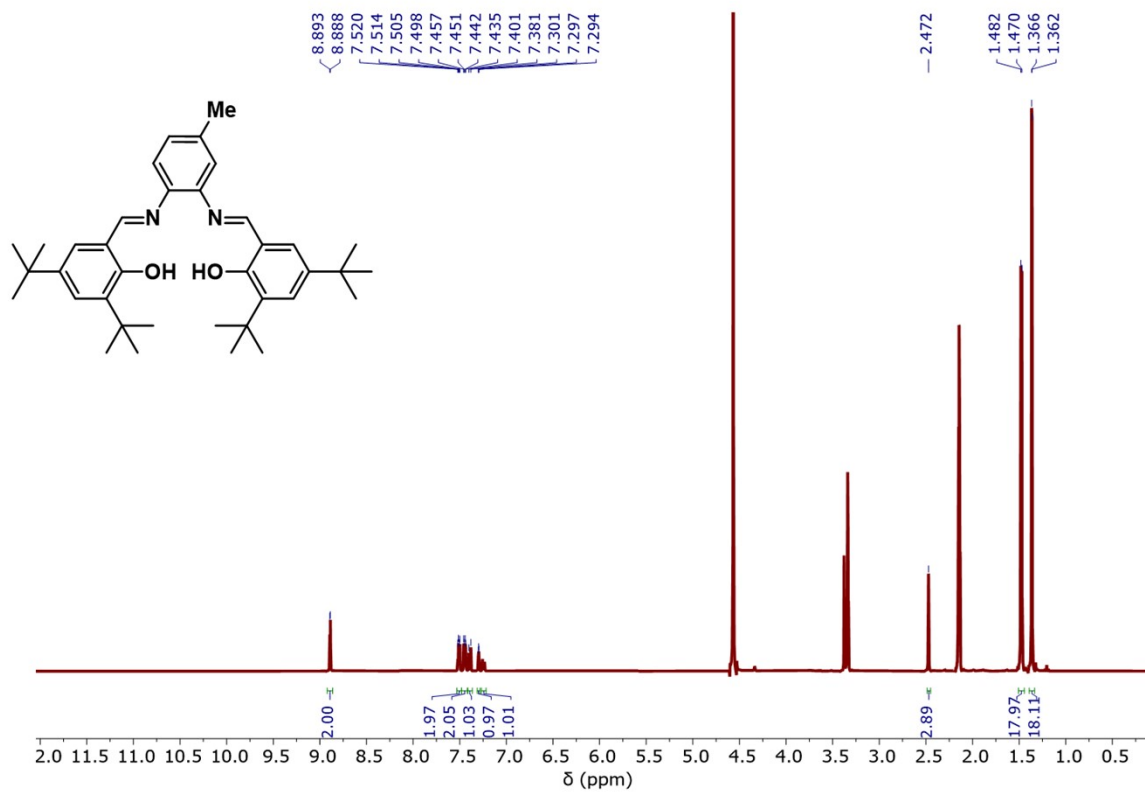


Figure S6: ^1H NMR of salophen (L6) ($\text{MeOH-}d_4$, 400 MHz).

F

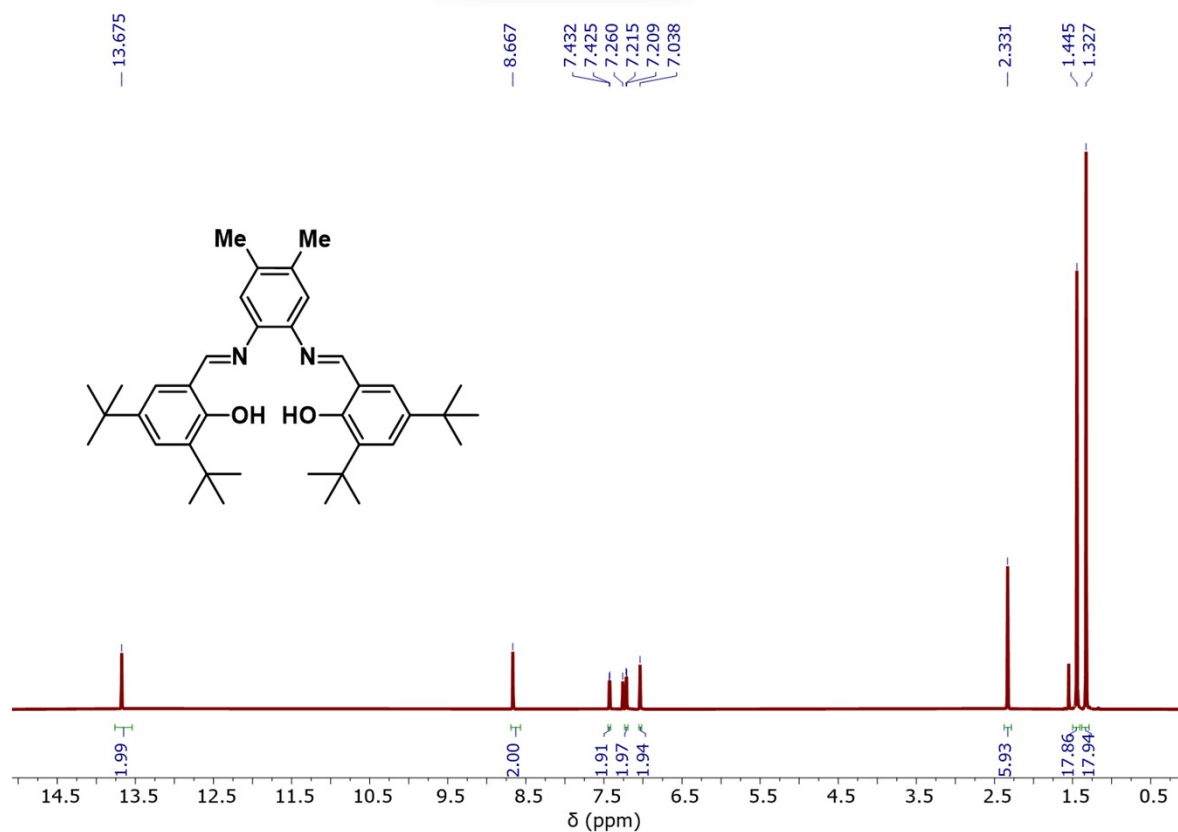


Figure S7: ¹H NMR of salophen (L7) (CDCl₃, 400 MHz).

General Procedure for Preparation of Cobalt (II) Complexes.

To a stirred solution of a ligand (1 mmol) in degassed dichloromethane (5 ml) was added a solution of cobalt(II) acetate tetrahydrate (1 mmol) in degassed absolute ethanol (20 mL) at room temperature under nitrogen. The reaction mixture immediately changes into dark red, and the flask was heated to 80 °C for 30 minutes and then cooled to room temperature. Solvent was removed by filtration in nitrogen and solids were washed with cold ethanol and dried under nitrogen flow to afford red brown solids.

Preparation of Cobalt (III) TFA Complexes

To a stirred solution of the cobalt(II) complexes (1 equiv) in dry dichloromethane in a round bottom flask wrapped in aluminium foil was added AgOOCF₃ (1 equiv). The mixture was

stirred for 1h under oxygen atmosphere, and then filtered to remove the silver byproduct. The solvent was removed in vacuo to afford as a dark red brown solid.

Characterization of Co-complex (L1)

HRMS-ESI (m/z): calculated for $C_{36}H_{46}N_2O_2Co^+$ = 597.2886; found = 597.2875.

Characterization of Co-complex (L2)

HRMS-ESI (m/z): calculated for $C_{40}H_{48}N_2O_2Co^+$ = 647.3042; found = 647.3016.

Characterization of Co-complex (L3)

HRMS-ESI (m/z): calculated for $C_{36}H_{44}Cl_2N_2O_2Co^+$ = 665.2106; found = 665.2100.

Characterization of Co-complex (L4)

HRMS-ESI (m/z): calculated for $C_{28}H_{30}N_2O_2Co^+$ = 485.1634; found = 485.1628.

Characterization of Co-complex (L5)

HRMS-ESI (m/z): calculated for $C_{22}H_{18}N_2O_4Co^+$ = 433.0593; found = 433.0588.

Characterization of Co-complex (L6)

HRMS-ESI (m/z): calculated for $C_{37}H_{48}N_2O_2Co^+$ = 611.3042; found = 611.3037.

Characterization of Co-complex (L7)

HRMS-ESI (m/z): calculated for $C_{38}H_{50}N_2O_2Co^+$ = 625.3199; found = 625.3191.

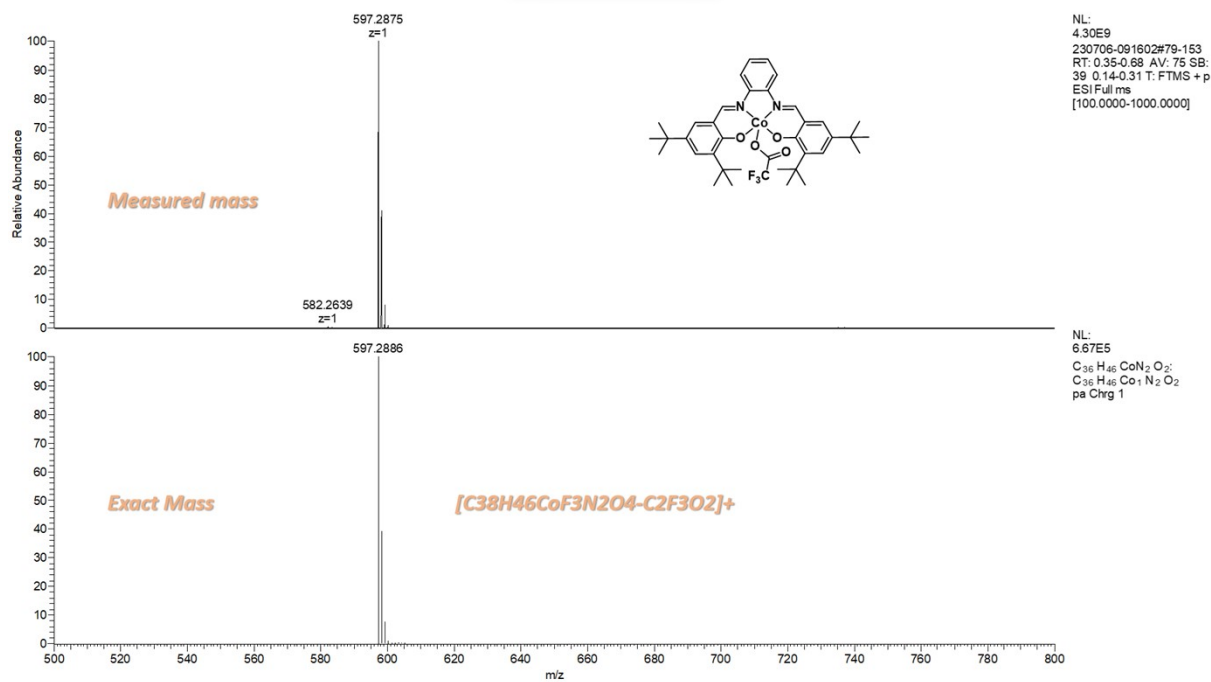


Figure S8: ESI-MS Spectrum of Co-complex (L1).

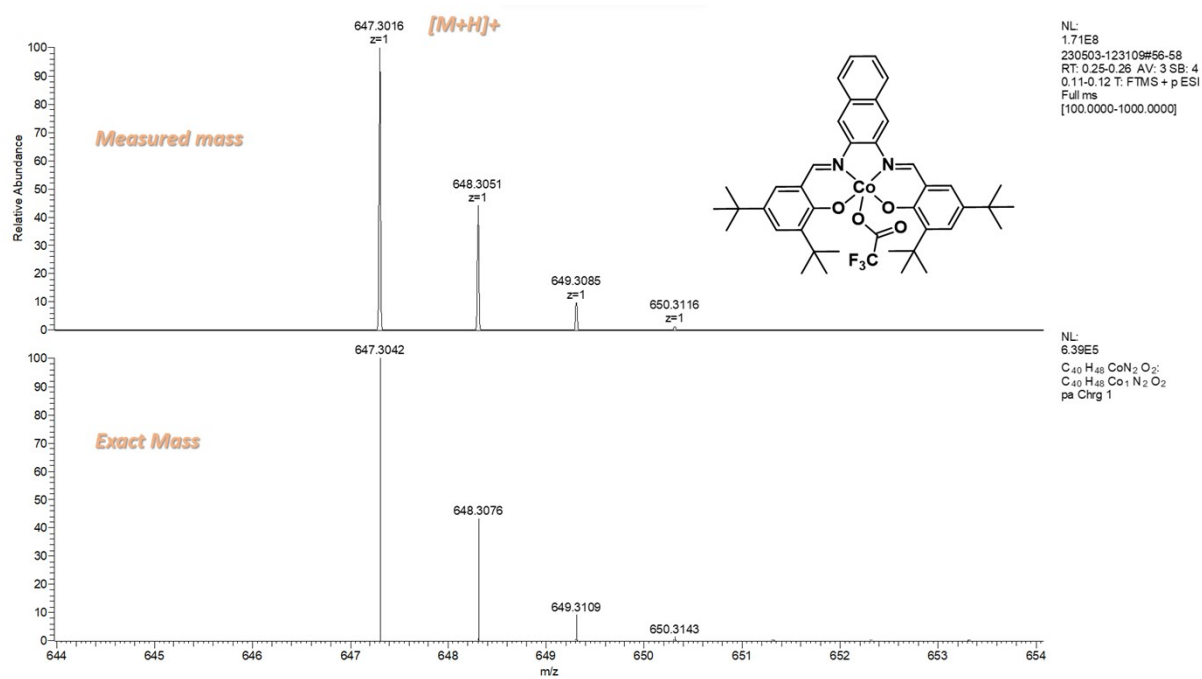


Figure S9: ESI-MS Spectrum of Co-complex (L2).

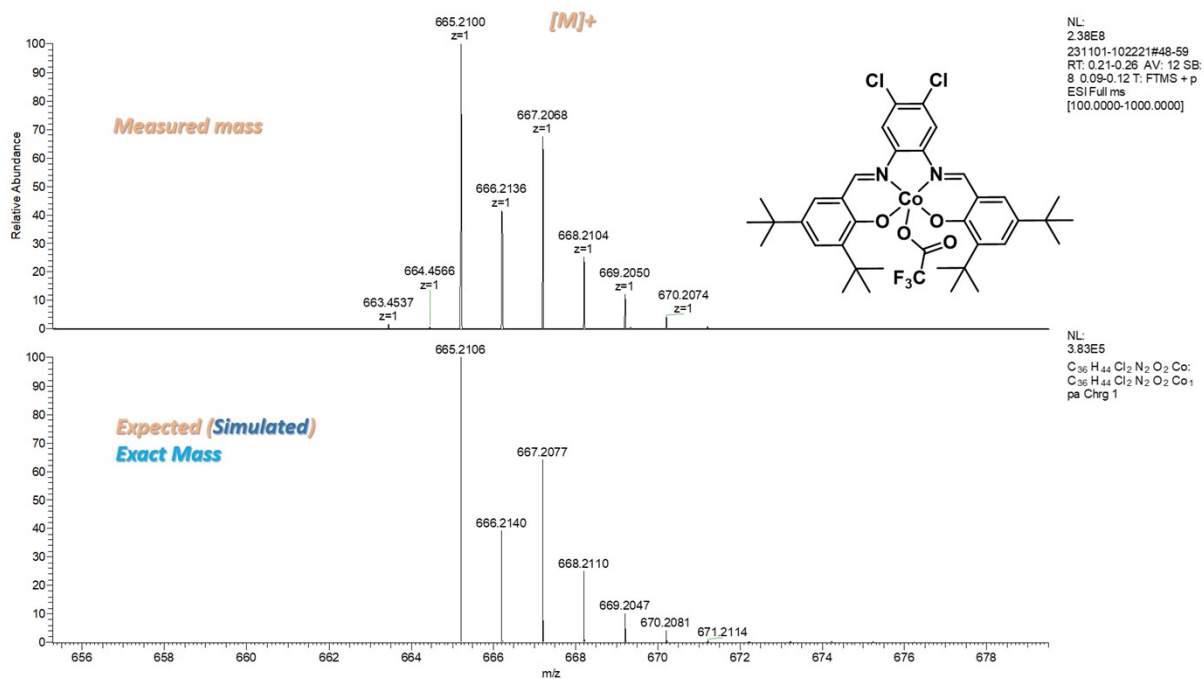


Figure S10: ESI-MS Spectrum of Co-complex (L3).

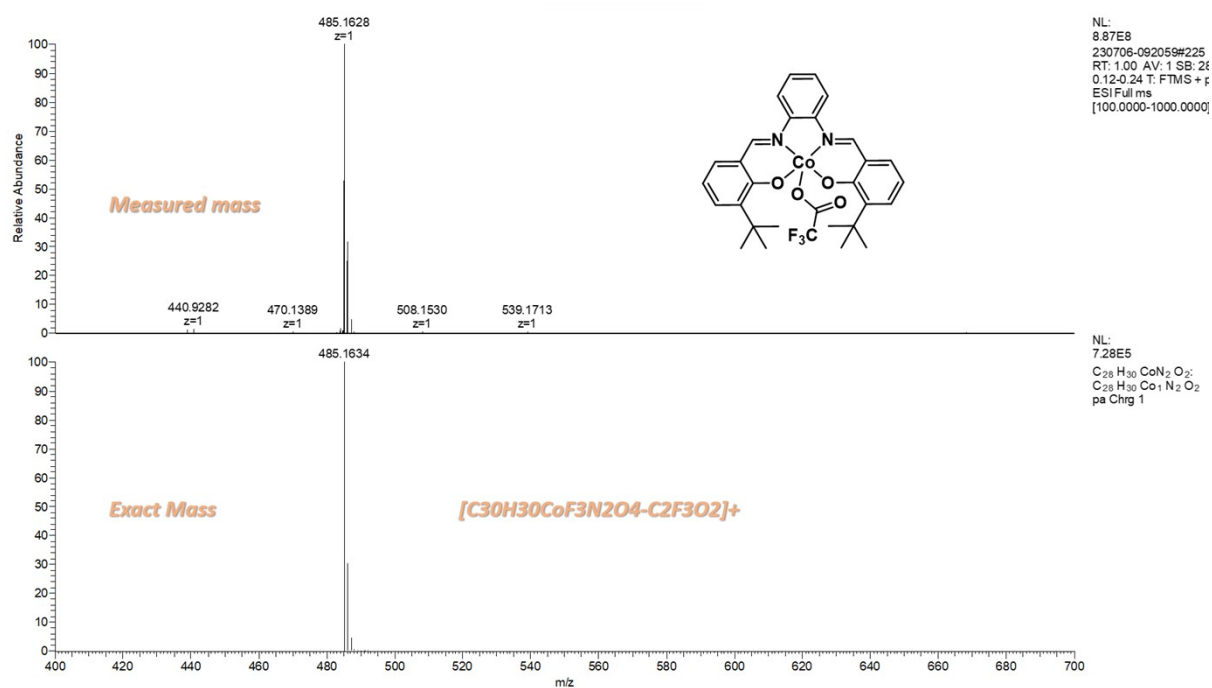


Figure S11: ESI-MS Spectrum of Co-complex (L4).

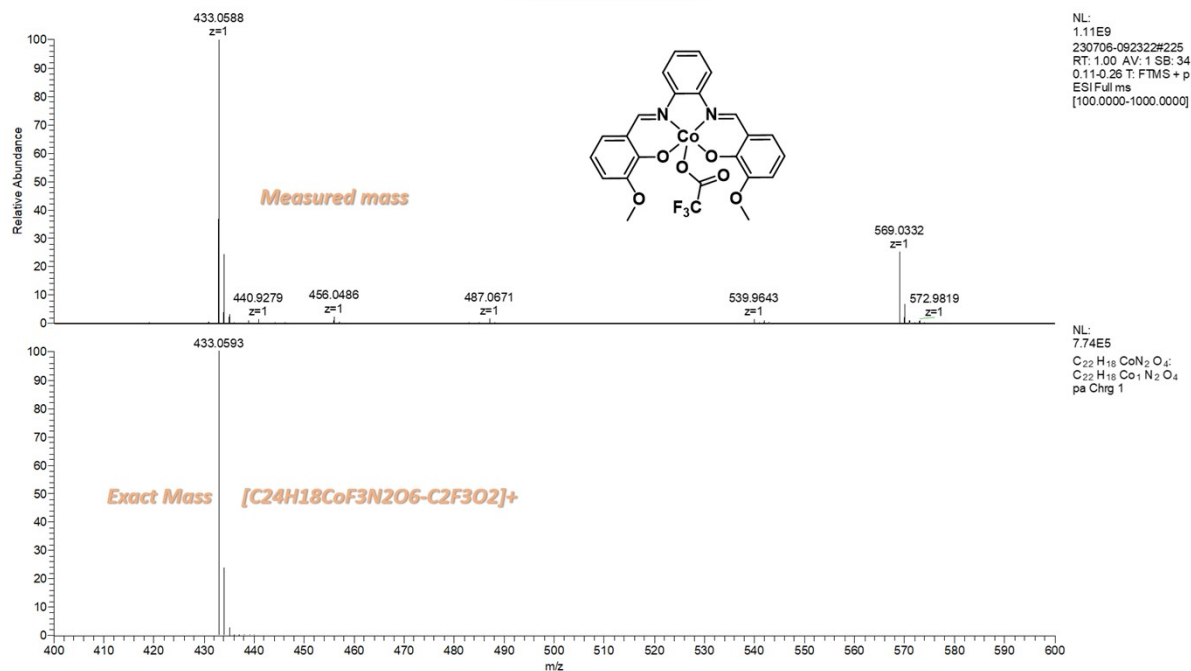


Figure S12: ESI-MS Spectrum of Co-complex (L5).

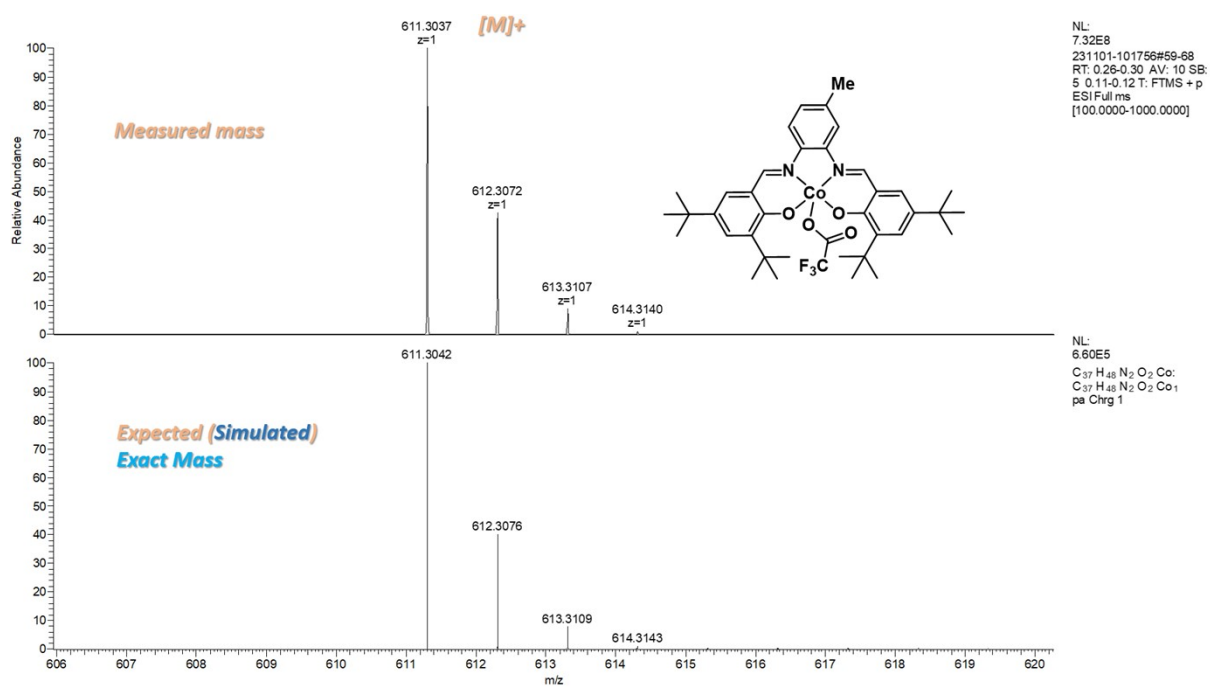


Figure S13: ESI-MS Spectrum of Co-complex (L6).

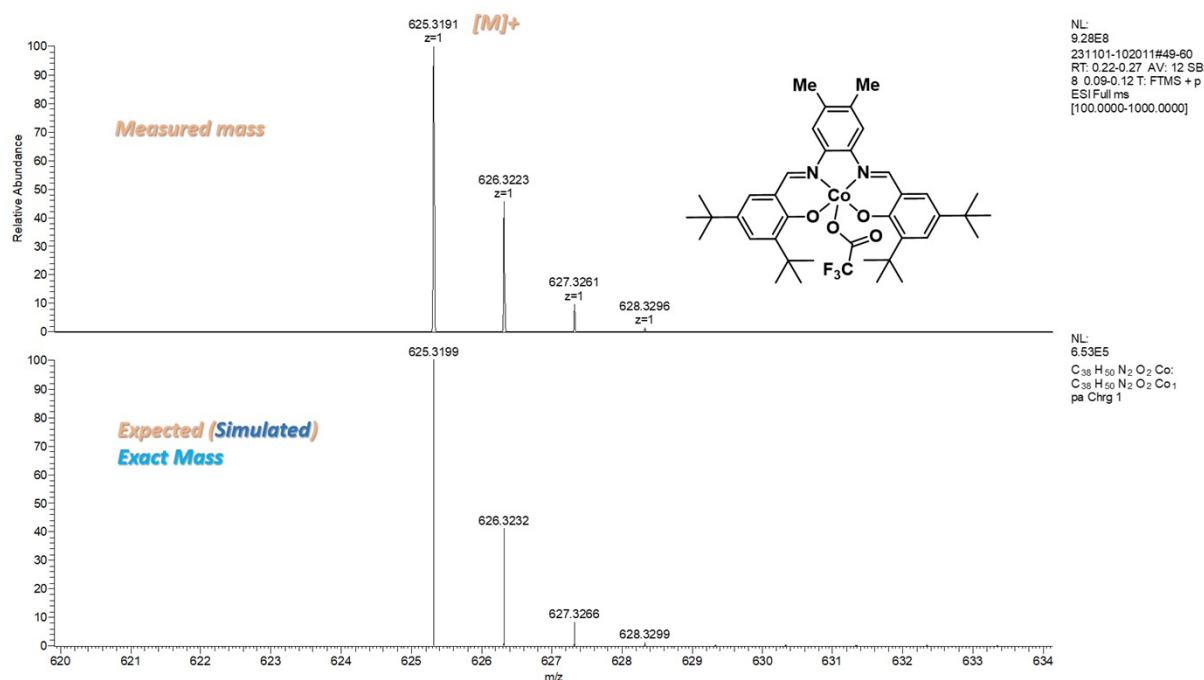


Figure S14: ESI-MS Spectrum of Co-complex (L7).

General Synthetic Procedure for Chromium Complexes

Salophen ligand (1.0 equiv) and chromium(II) chloride (1.1 equiv) were dissolved in THF and stirred under argon at room temperature for 24 h. The reaction mixture then was exposed to air and stirred for an additional 24 h. After the reaction mixture was poured into diethyl ether, the organic layer was washed with saturated aqueous ammonium chloride and followed by brine. The ether layer dried with anhydrous sodium sulphate and filtrated. The solvent was removed under vacuo, yielding a red powder.

Characterization of Cr-complex (L1)

HRMS-ESI (m/z): calculated for C₃₆H₄₆N₂O₂Cr⁺ = 590.2959; found = 590.2946.

Characterization of Cr-complex (L2)

HRMS-ESI (m/z): calculated for C₄₀H₄₈N₂O₂Cr⁺ = 640.3115; found = 640.3103.

Characterization of Cr-complex (L3)

HRMS-ESI (m/z): calculated for $C_{36}H_{44}ClN_2O_2Cr^+$ = 658.2179; found = 658.2172.

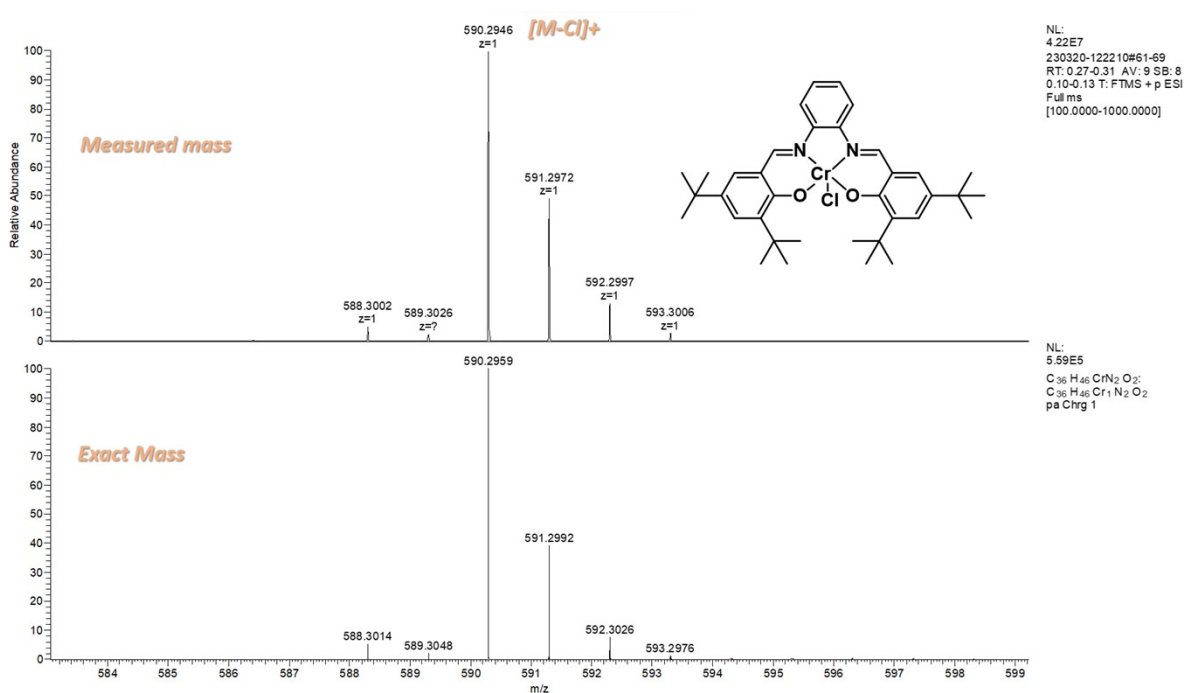


Figure S15: ESI-MS Spectrum of Cr-complex (L1).

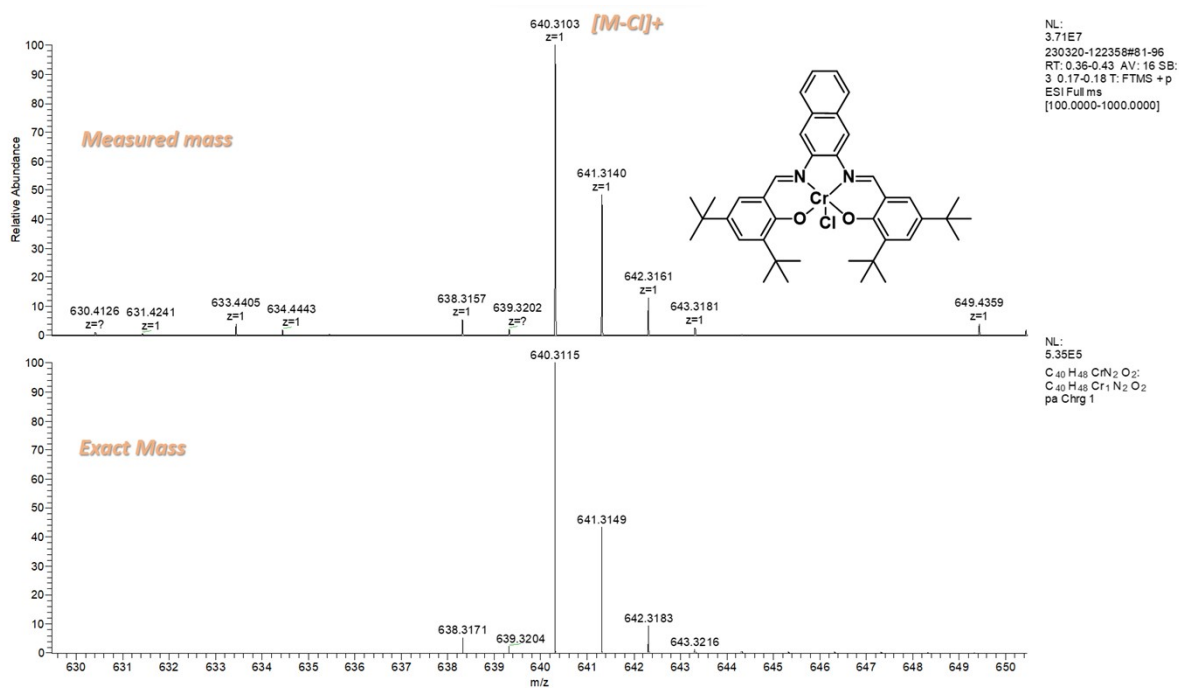


Figure S16: ESI-MS Spectrum of Cr-complex (L2).

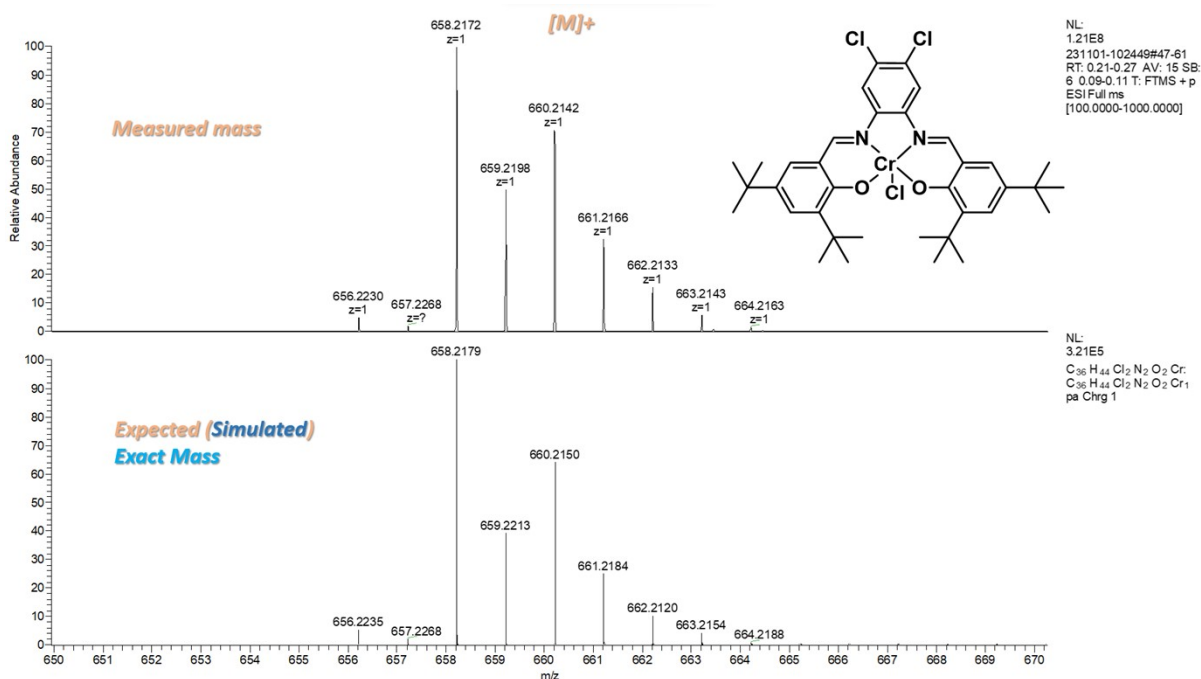
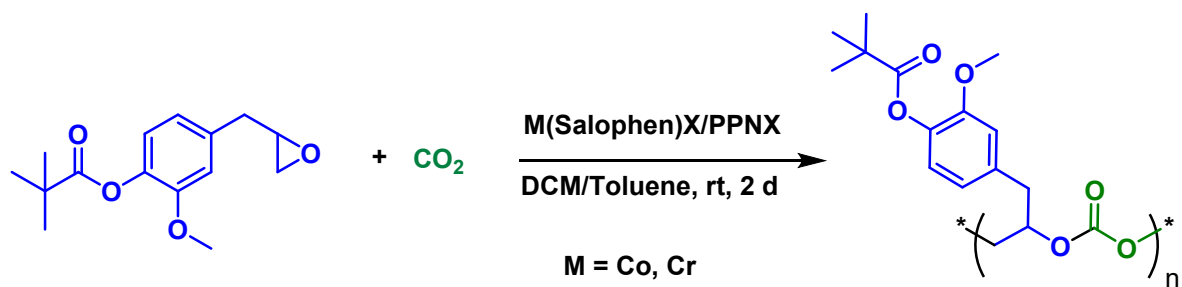


Figure S17: ESI-MS Spectrum of Cr-complex (L3).

Procedure for Copolymerization of Eugenol Epoxide (EuO) with CO₂:

In a glovebox, the catalyst, co-catalyst, eugenol epoxide, and 0.8 mL solvent (CH₂Cl₂: toluene, 1:1 v/v) were placed in a predried 15 mL stainless steel reactor in an argon atmosphere. All reactions were performed on the scale of 0.0068 mmol of catalyst, using ratios of 1/1/X for catalyst/cocatalyst/monomer where the molar ratio of eugenol epoxide was varied with different experiments. The reactor was pressurized to 0.5-3.0 MPa by CO₂, then the reaction mixture was stirred at room temperature for the allotted time. Then excess CO₂ was vented, a small amount of the resultant mixture was removed from the reactor for ¹H NMR analysis to determine the conversion. The polymeric material was purified by precipitation in methanol. Initial precipitation was performed by adding dropwise to acidic methanolic solution (4 drops of conc. HCl/50 mL MeOH), followed by two precipitations in methanol. The resulted polymer was subsequently dried in under vacuum before further characterization.



Scheme S2. Copolymerization of eugenol epoxide (EuO) with CO_2 .

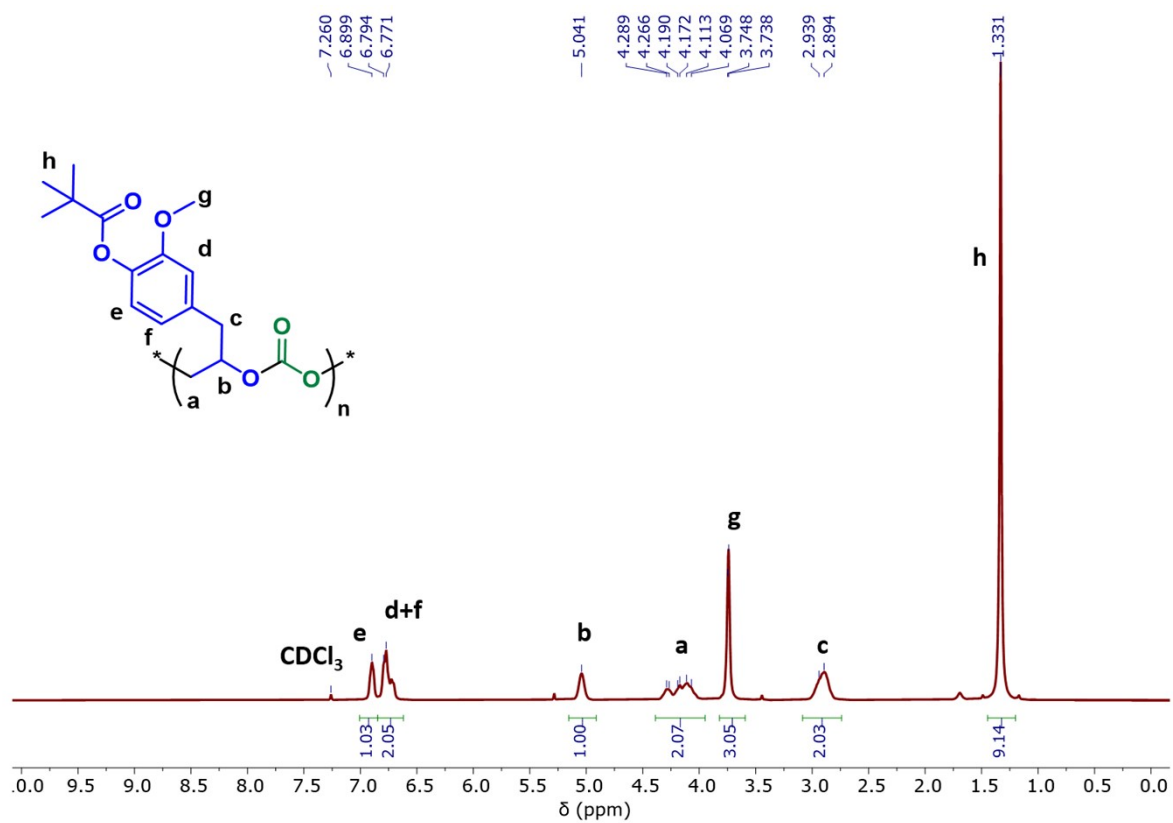


Figure S18: ^1H NMR of polycarbonate of EuO with CO_2 (CDCl_3 , 400 MHz).

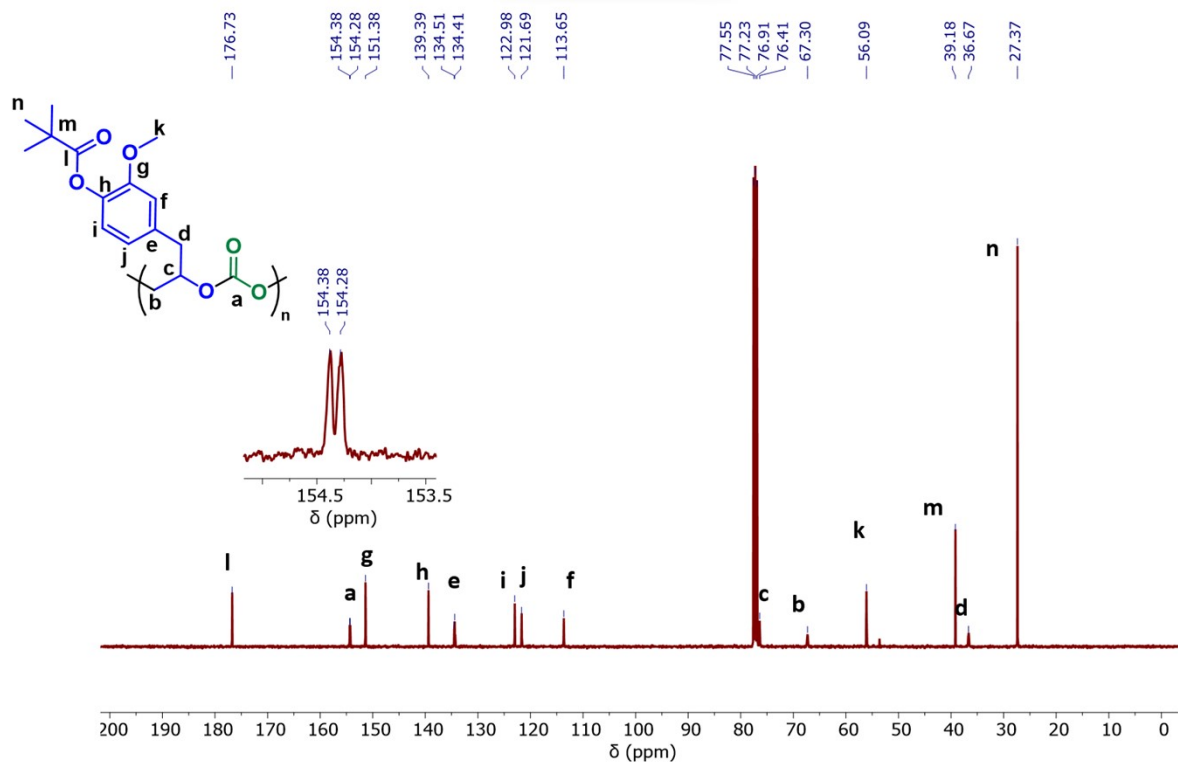


Figure S19: ^{13}C NMR of polycarbonate of EuO with CO_2 (CDCl_3 , 100 MHz).

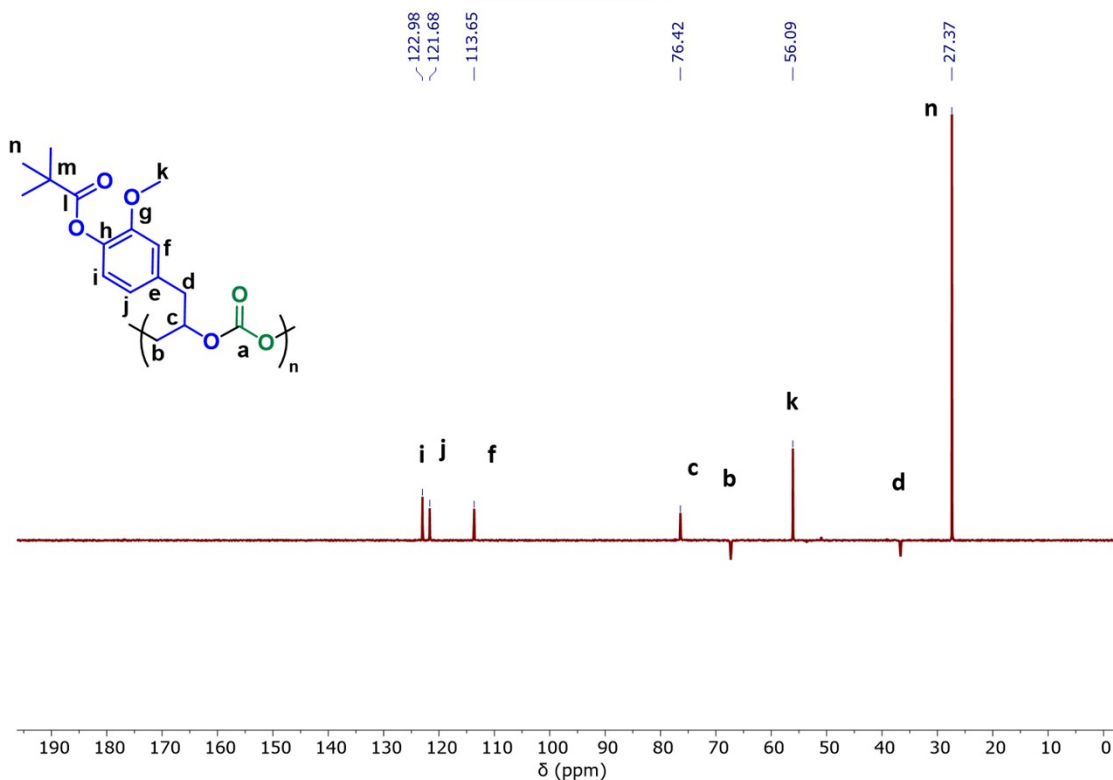


Figure S20: ^{13}C (DEPT-135) NMR of polycarbonate of EuO with CO_2 (CDCl_3 , 100 MHz).

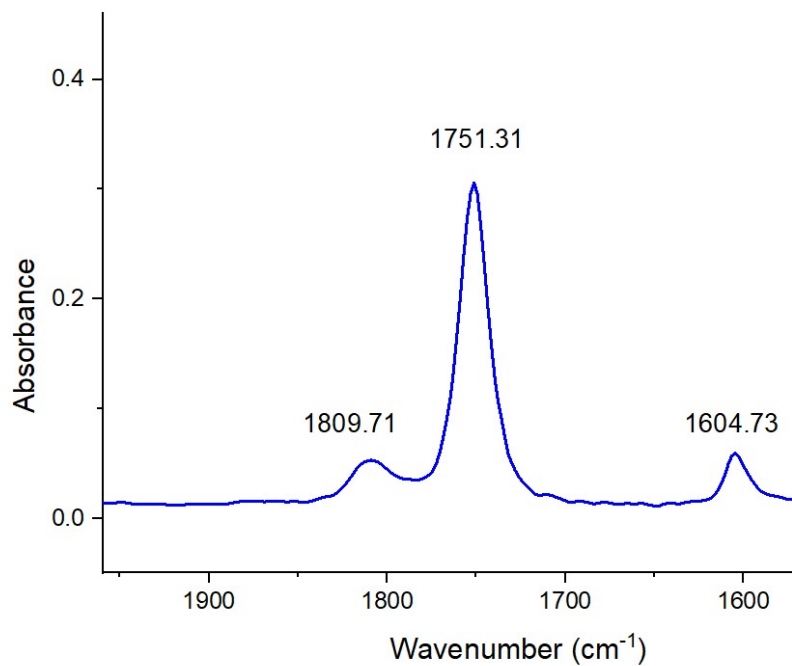


Figure S21: Reaction mixture ATR FT-IR spectrum of eugenol with CO₂ in CH₂Cl₂.

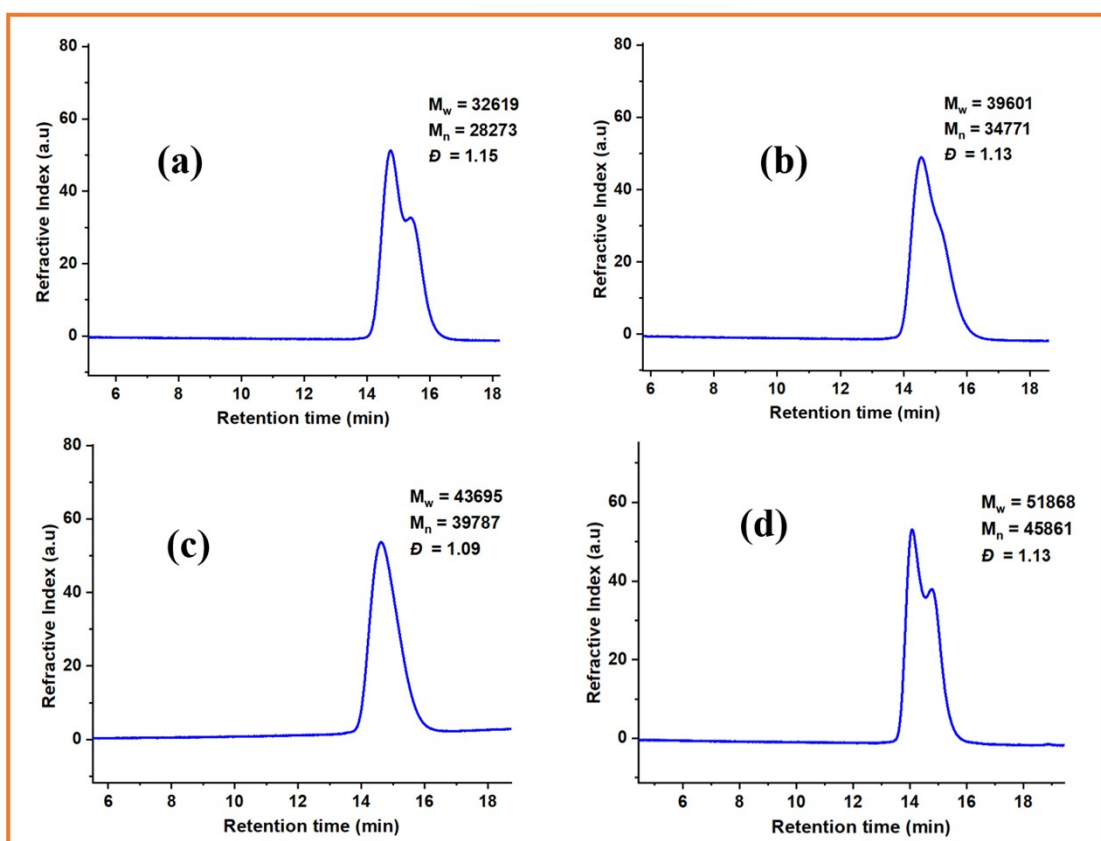


Figure S22. GPC traces for polycarbonates under different at CO₂ pressure. (a) 5 bar; (b) 10 bar; (c) 15 bar; (d) 30 bar CO₂

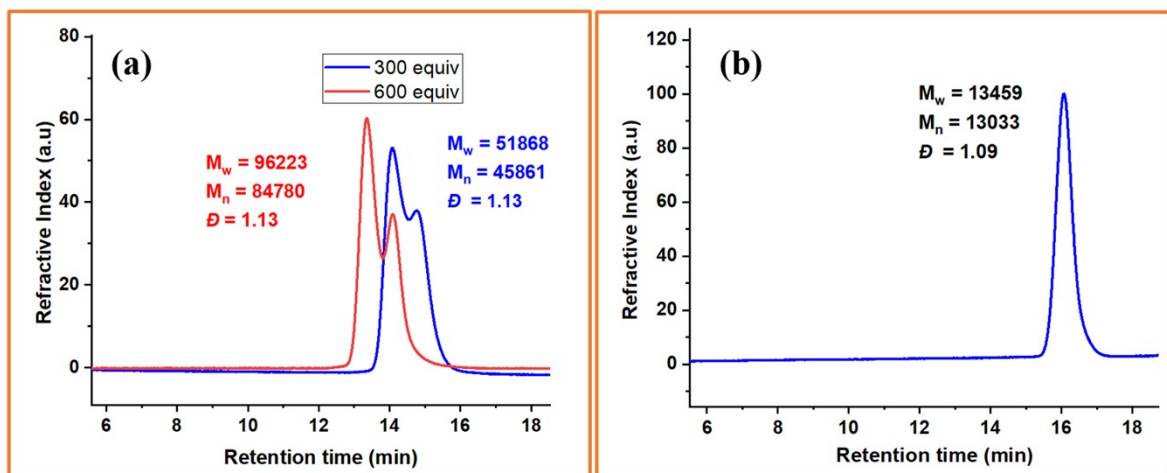


Figure S23. (a) GPC traces for copolymer synthesized by using 300 and 600 equivalent of eugenol epoxide with CO₂. (b) Copolymerization performed using ratios of 1/1/300/5 for catalyst/co-catalyst/EuO/CTA respectively (1,2-propanediol used as a CTA).

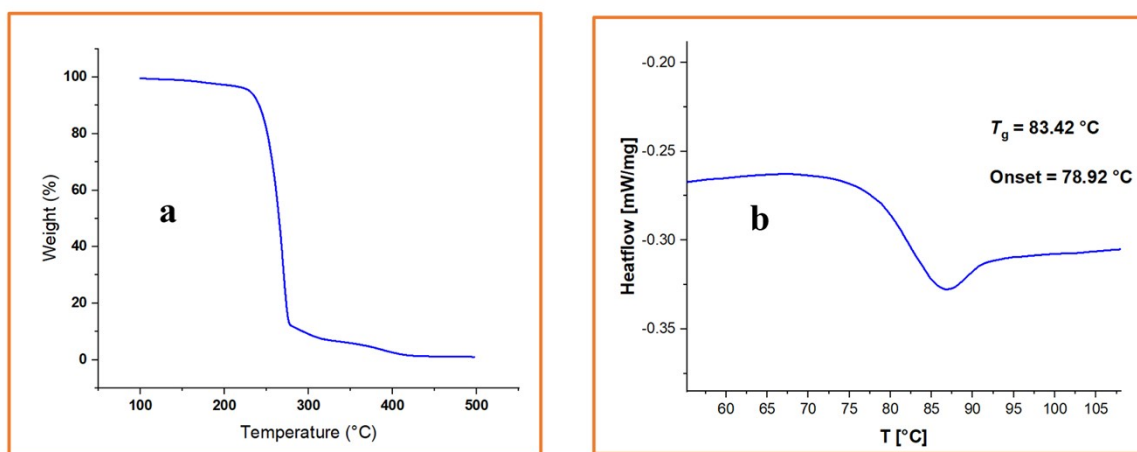


Figure S24. (a) TGA and (b) DSC curves for the polycarbonate of EuO with CO₂.

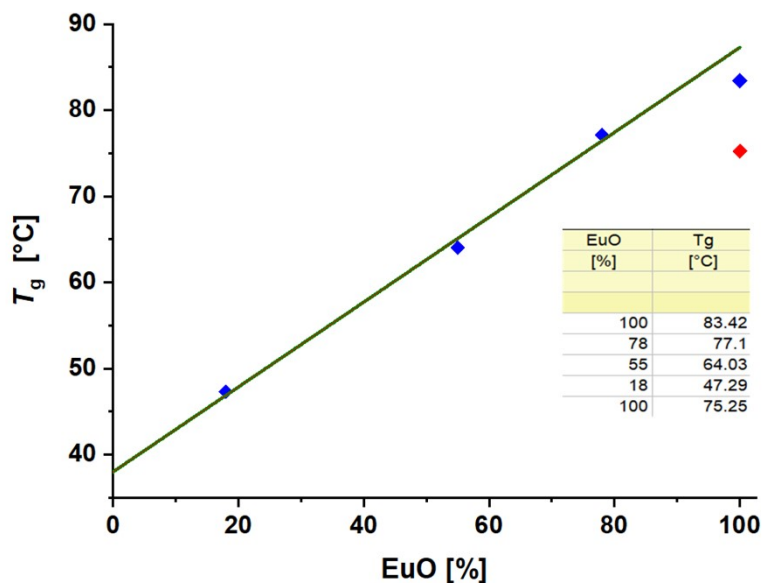
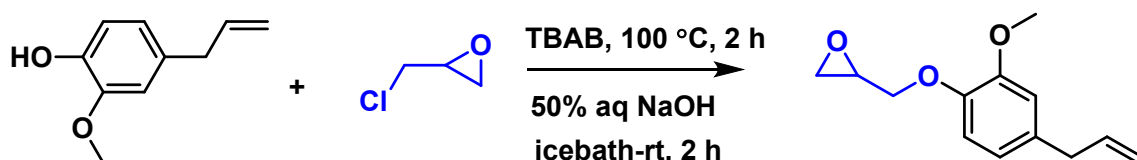


Figure S25. Comparison of T_g for the polycarbonate having different EuO (%). Red square corresponds to polymonothiocarbonate of EuO.

Procedure for Synthesis of Eugenol Glycidyl Ether (EGE):

Eugenol (10 mmol), epichlorohydrin (50 mmol) and tetrabutylammonium bromide (1 mmol) were poured in a round bottom flask and stirred for 2 h at 100 °C. The reaction mixture then cooled down to room temperature and a solution of 50% aqueous NaOH (50 mmol) were added dropwise to the mixture at ice-cold temperature and stirred for additional 2 h. upon completion, the mixture was diluted with water (50 mL) and extracted using ethyl acetate (3 x 20 mL). The organic layer was finally dried with $MgSO_4$, and solvent was the solvent was removed under vacuum produced yellow orange liquid, which was further purified by flash column using ethyl acetate-hexane gave corresponding monomer as a colorless solid with 68% yield.



Scheme S3. Synthesis of Eugenol Glycidyl Ether (EGE).

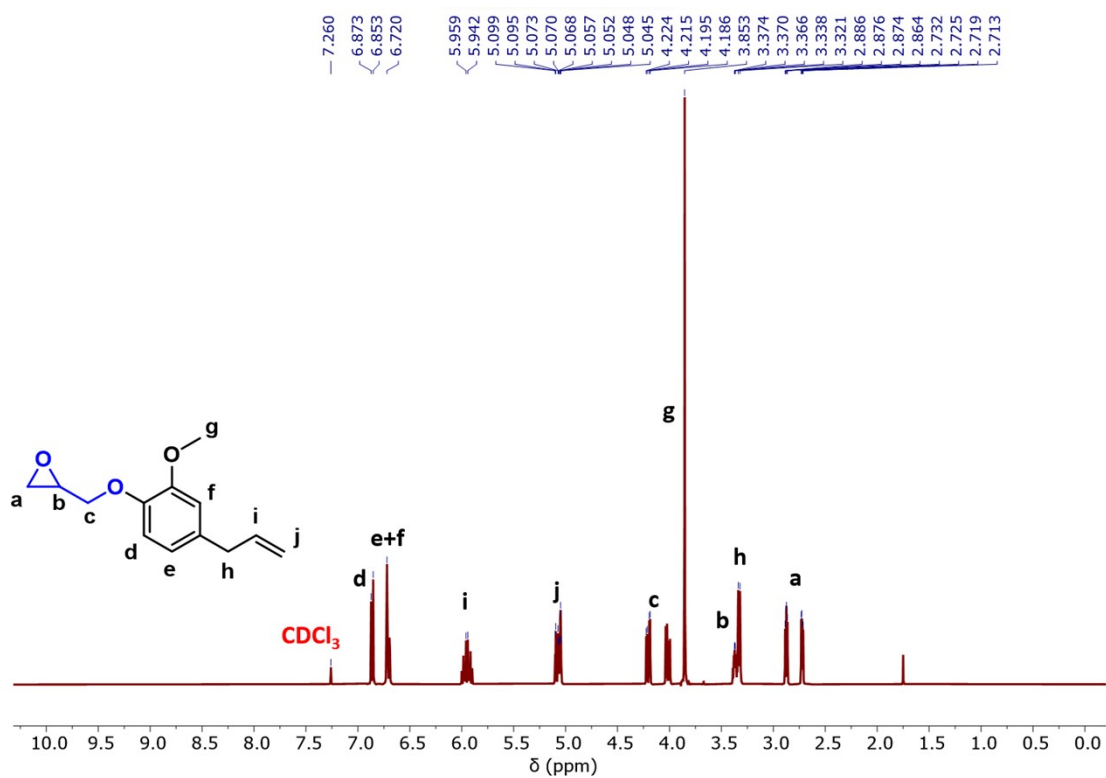


Figure S26: ¹H NMR of EGE (CDCl₃, 400 MHz).

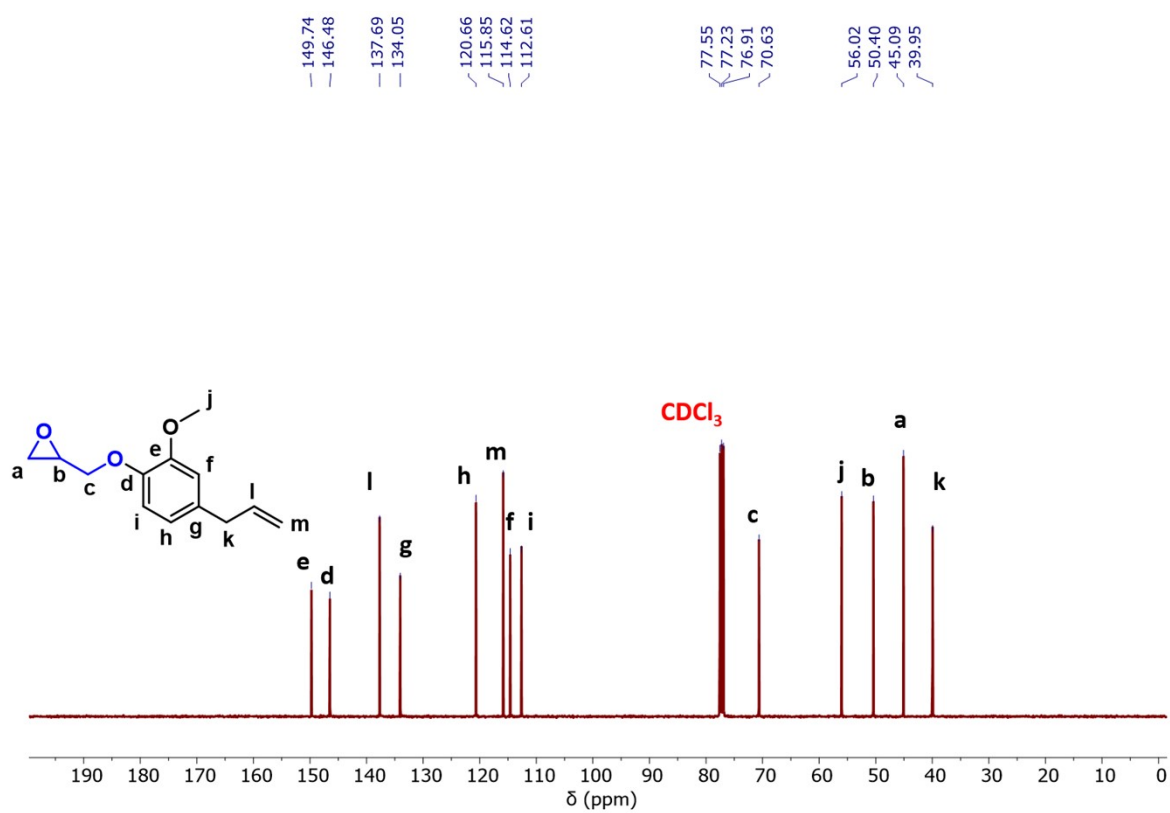


Figure S27: ¹³C NMR of EGE (CDCl₃, 100 MHz).

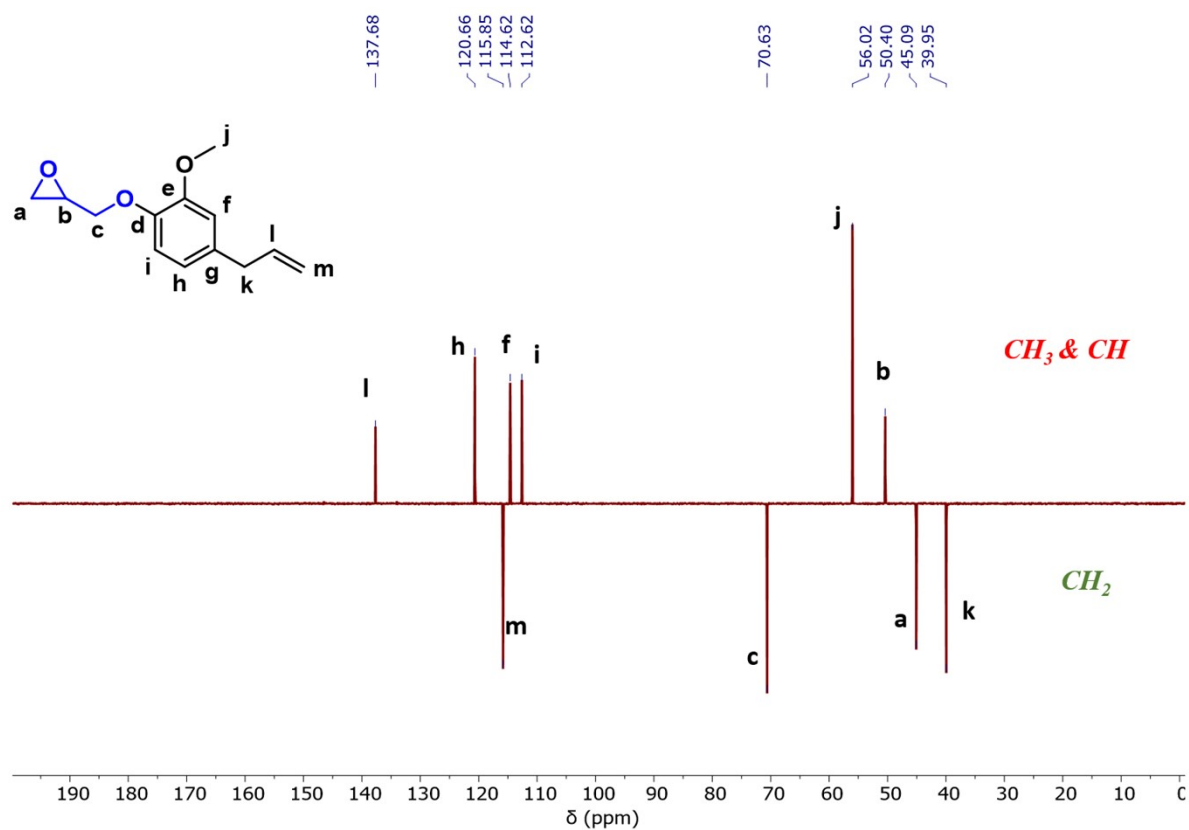


Figure S28: ¹³C (DEPT-135) NMR of EGE (CDCl₃, 100 MHz).

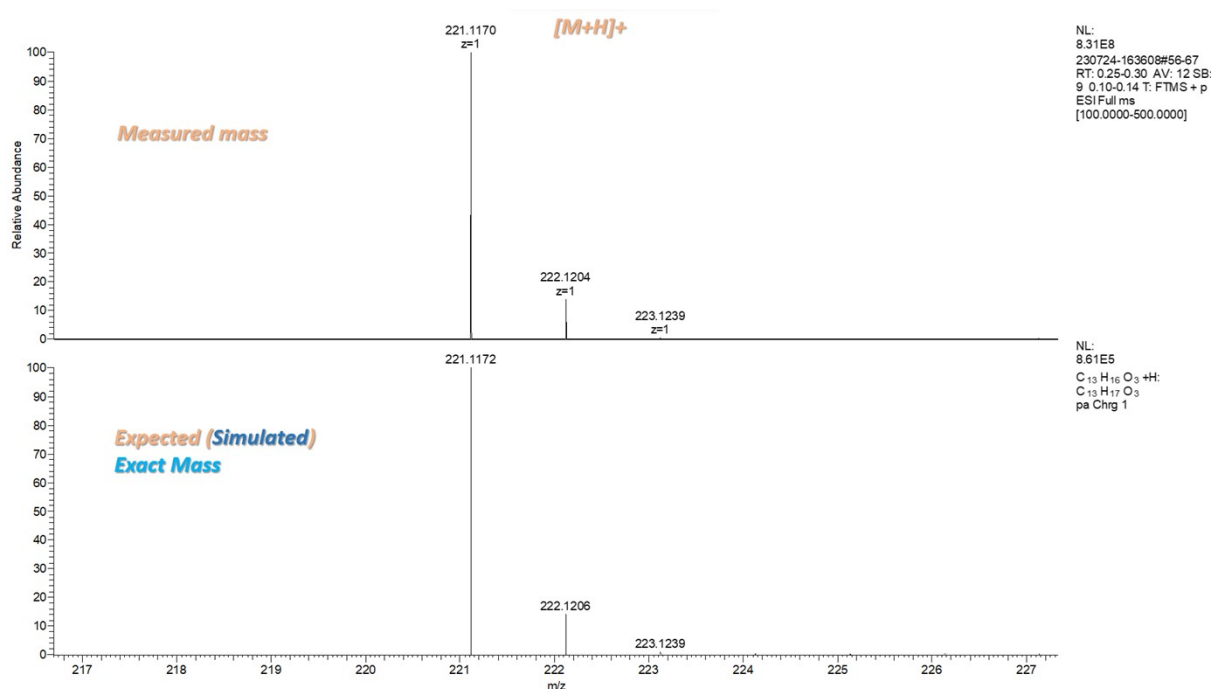
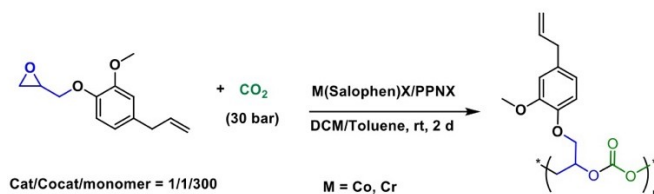


Figure S29: ESI-MS Spectrum of EGE.

Procedure for Copolymerization of Eugenol Glycidyl Ether (EGE) with CO₂:

In a glovebox, the catalyst, co-catalyst, eugenol glycidyl ether, and 0.8 mL solvent (CH₂Cl₂: toluene, 1:1 v/v) were placed in a pre-dried 15 mL stainless steel reactor in an argon atmosphere. All reactions were performed on the scale of 0.0068 mmol of catalyst, using ratios of 1/1/300 for catalyst/cocatalyst/monomer. The reactor was pressurized to 3.0 MPa by CO₂, then the reaction mixture was stirred at room temperature for the allotted time. Then excess CO₂ was vented, a small amount of the resultant mixture was removed from the reactor for ¹H NMR analysis to determine the conversion. The polymeric material was purified by precipitation in acidic methanol. The resulted polymer was subsequently dried in under vacuum before further characterization.

Table S1. Summary of Copolymerization of eugenol glycidyl ether (EGE) with CO₂ to form cyclic or polymeric products catalysed by M(Salophen)X/PPNX (M = Co, Cr ; X = Cl, CF₃CO₂) (**1-10**) catalysts at ambient temperature and 3MPa CO₂ pressure.



Entry	Catalyst	Co-catalyst	Conv. (%)	Selectivity		Carbonate linkages	M_n [kg mol ⁻¹]	\bar{D}
				Poly	Cyclic			
1	1	PPNCl	100	-	100	-	-	-
2	2	PPNTFA	41	-	41	-	-	-
3	3	PPNCl	100	-	100	-	-	-
4	4	PPNCl	-	-	-	Not done	-	-
5	5	PPNTFA	68	26	42	-	-	-
6	6	PPNTFA	71	28	43	99	7.8	1.54
7	7	PPNTFA	-	-	-	Not done	-	-
8	8	PPNTFA	38	-	38	-	-	-
9	9	PPNTFA	89	59	30	99	26.8	1.23
10	10	PPNTFA	74	25	49	-	-	-

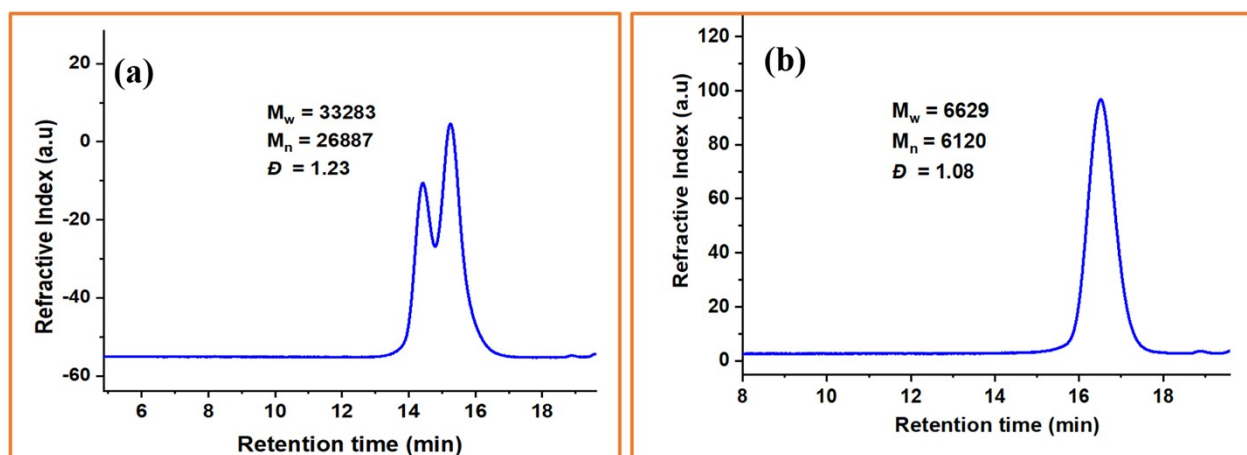


Figure S34. (a) GPC traces for copolymer synthesized by using 300 equivalent of eugenol glycidyl ether with CO₂. (b) Copolymerization performed using ratios of 1/1/300/5 for catalyst/co-catalyst/EGE/CTA respectively (Terephthalic acid used as a CTA).

Procedure for block polymerization of eugenol epoxide (EuO), eugenol glycidyl ether (EGE) with CO₂:

In a glovebox, a predried 50 mL stainless steel reactor equipped with a magnetic stirrer, catalyst, co-catalyst, EuO, and 6 mL solvent (CH₂Cl₂: toluene, 1:1 v/v) in an argon atmosphere using ratios of 1/1/300 for catalyst/cocatalyst/monomer and pressurized with CO₂ to 30 bar. After complete conversion EuO, the eugenol glycidyl ether (300 equiv) was added. The reactor was again recharged with 3.0 MPa of CO₂. Then excess CO₂ was released after 48 h. The crude polymer was dissolved in dichloromethane and purified by precipitation in methanol. The initial precipitation was in acidic methanol followed by two precipitations in neutral methanol, then the pure polymer was dried under vacuum.

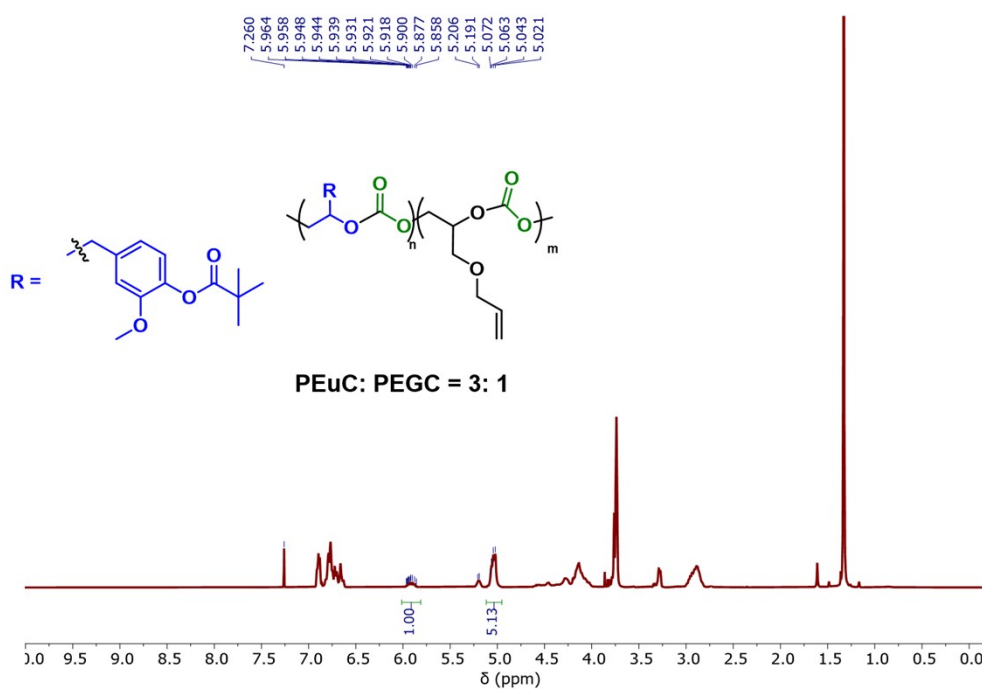


Figure S35. ^1H NMR of block polycarbonate derived from EuO, EGE with CO_2 (CDCl_3 , 400 MHz).

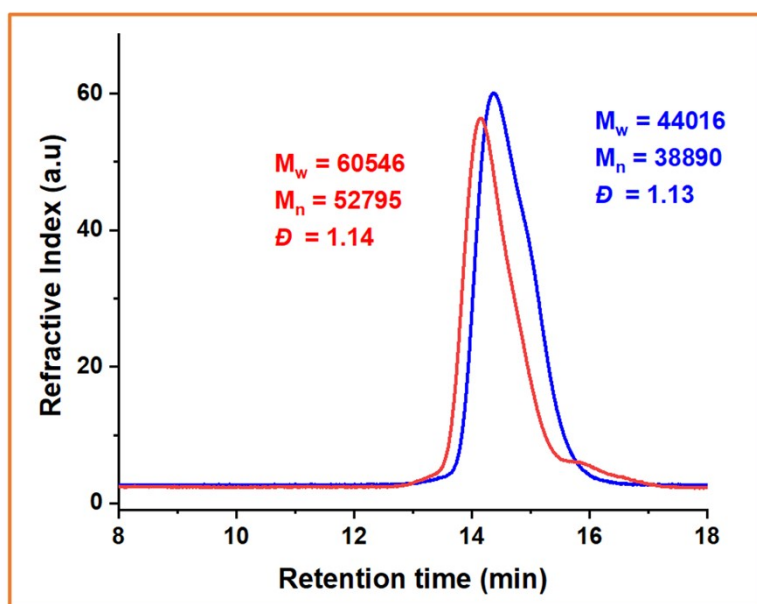


Figure S36. GPC traces for block copolymer synthesized by using EuO, EGE with CO_2 .

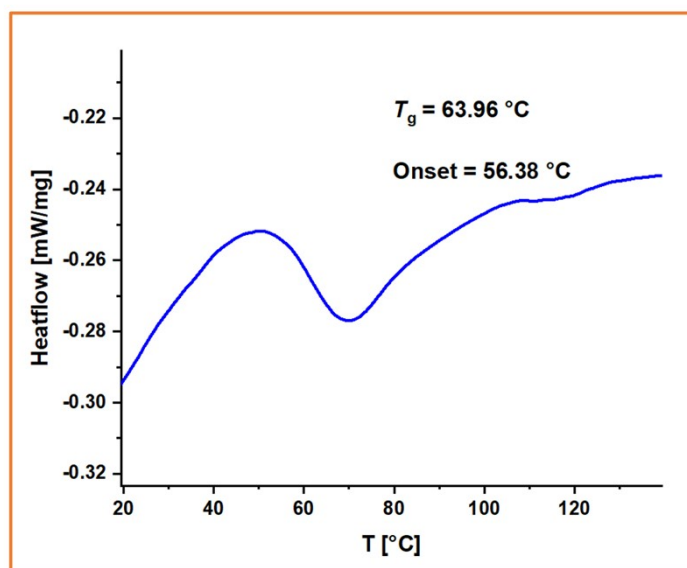


Figure S37. DSC curves for the block polycarbonate of EuO, EGE with CO₂.

Procedure for triblock polycarbonate of eugenol epoxide (EuO), eugenol glycidyl ether (EGE) with CO₂:

In a glovebox, a predried 15 mL stainless steel reactor equipped with a magnetic stirrer, catalyst, co-catalyst, EuO, terephthalic acid and 0.8 mL solvent (CH₂Cl₂: toluene, 1:1 v/v) in an argon atmosphere using ratios of 1/1/300/3 for catalyst/cocatalyst/monomer/CTA and pressurized with CO₂ to 3.0 MPa. Upon complete conversion of EuO, the EGE (300 equiv) was added. The reactor was again recharged with 3.0 MPa of CO₂. Then excess CO₂ was released after 48 h. The curde polymer was dissolved in dichloromethane and purified by precipitation in methanol. The initial precipitation was in acidic methanol followed by two precipitations in neutral methanol, then the pure polymer was dried under vacuum.

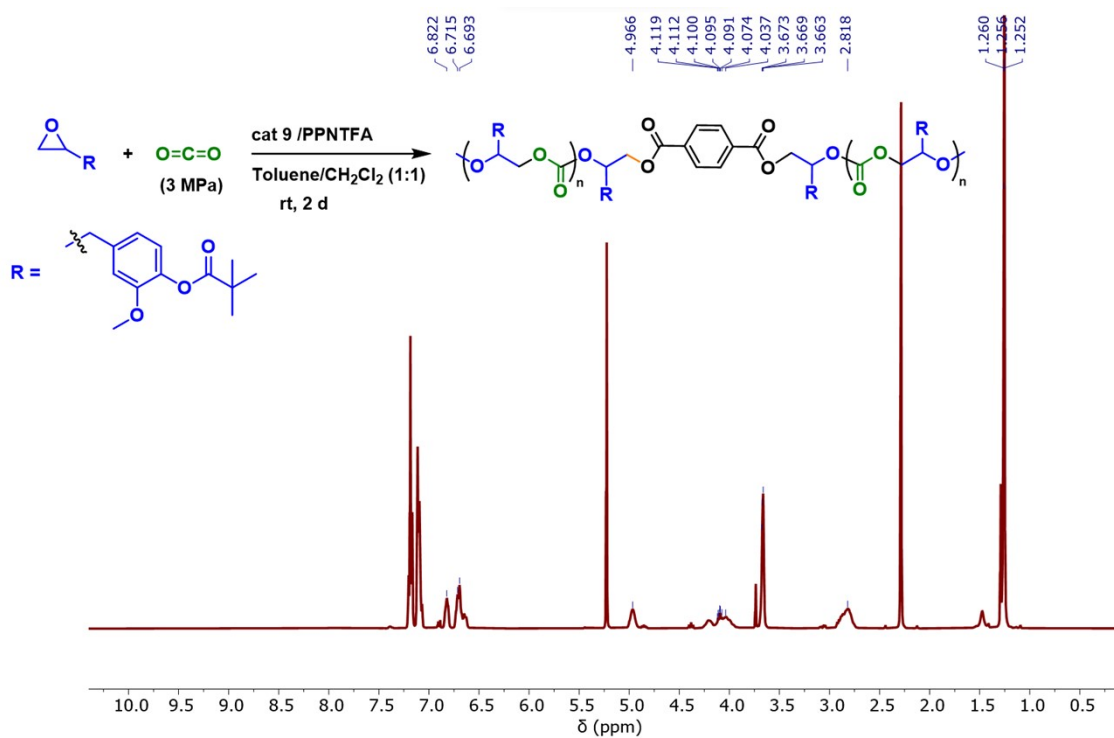


Figure S38. Reaction mixture ^1H NMR of polycarbonate derived from EuO with CO_2 (CDCl_3 , 400 MHz).

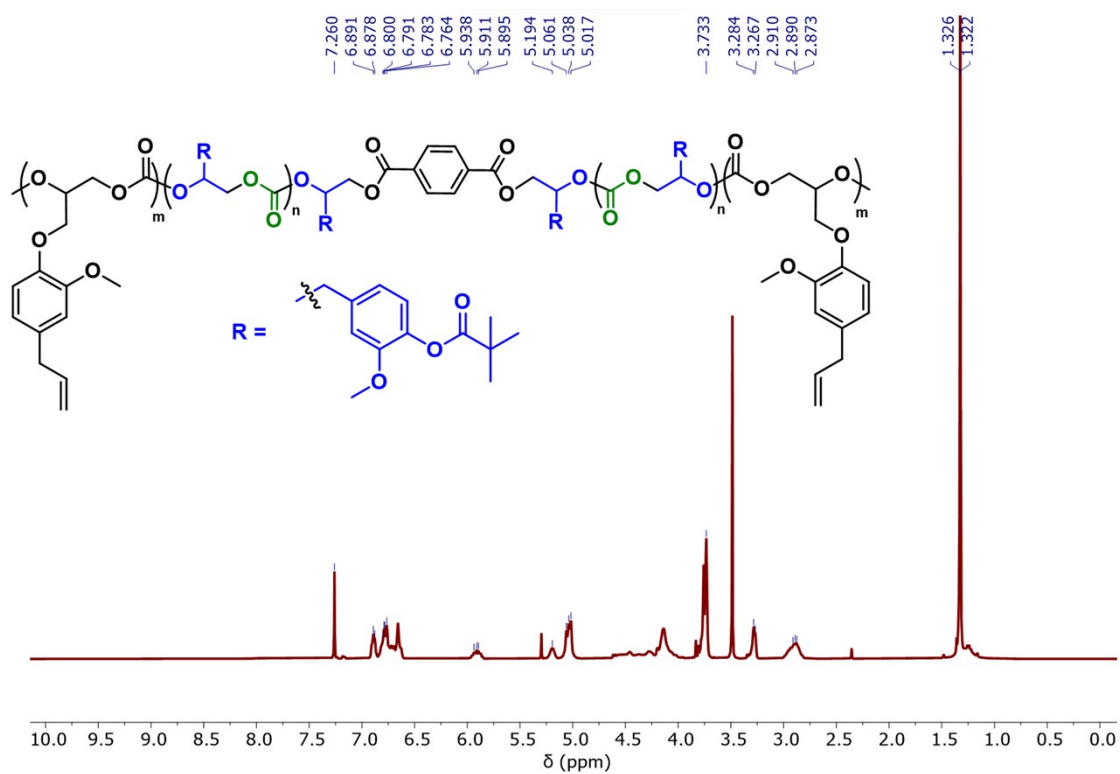


Figure S39. ^1H NMR of triblock polycarbonate derived from EuO, EGE with CO_2 (CDCl_3 , 400 MHz).

Procedure for Click reaction and salt preparation of polymer:

To an oven dried Schlenk flask equipped with magnetic stir bar was added a solution of block polymer in THF (10 mL) were added 5 equivalent of mercaptoacetic acid to alkene and AIBN (5 mol%) under nitrogen atmosphere. Then, the reaction mixture was stirred at 68 °C for 24 h. Evaporation of solvent in vacuo to afford the crude product. Then excess thioglycolic acid was removed by washing with diethyl ether then the pure polymer was dried under vacuum. The polymer was dissolved in THF and aqueous ammonia (2 equiv) was added dropwise under constant N₂ flow and stirring at room temperature resulted the immediate precipitation of amphiphilic polymer.

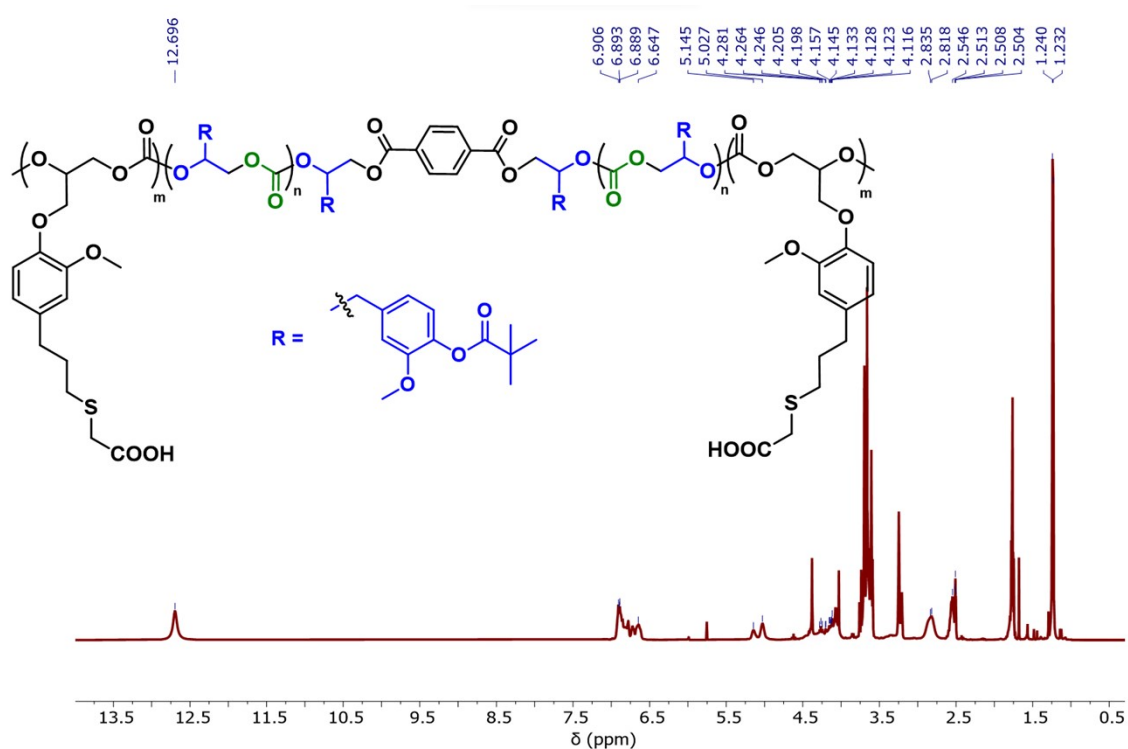


Figure S40. ¹H NMR of thio-click triblock polycarbonate (DMSO-d₆, 400 MHz).

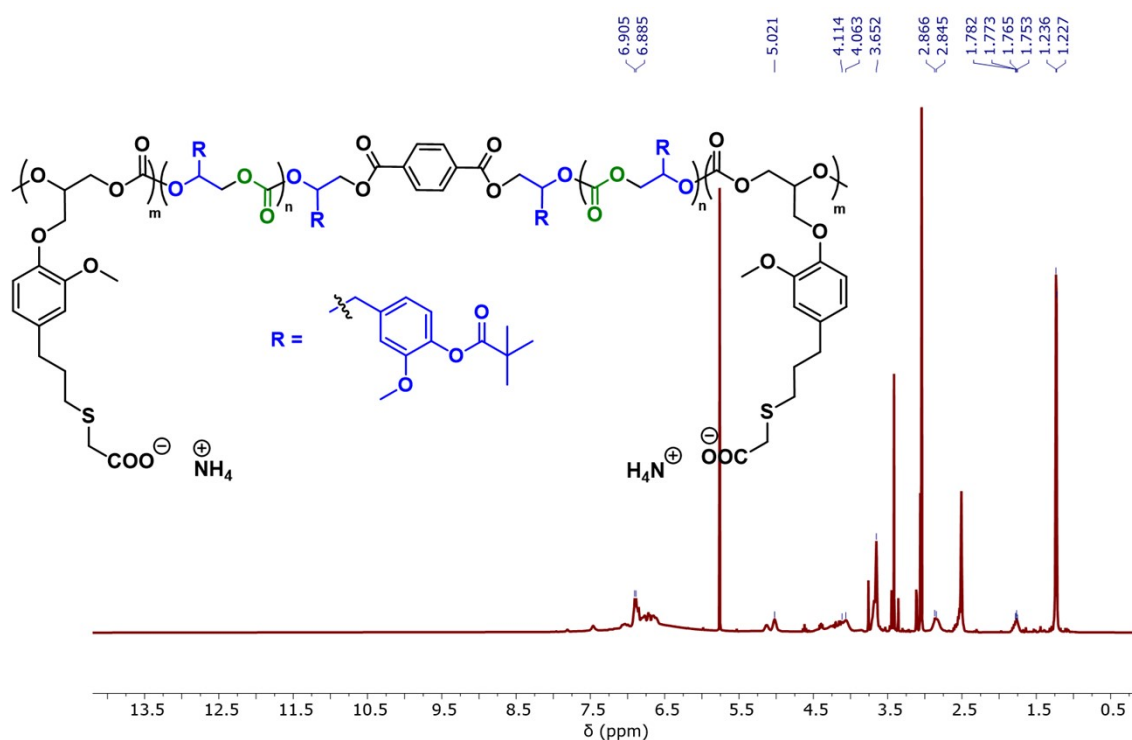


Figure S41. ¹H NMR of thio-click triblock polycarbonate ammonium salt (DMSO-d₆, 400 MHz).

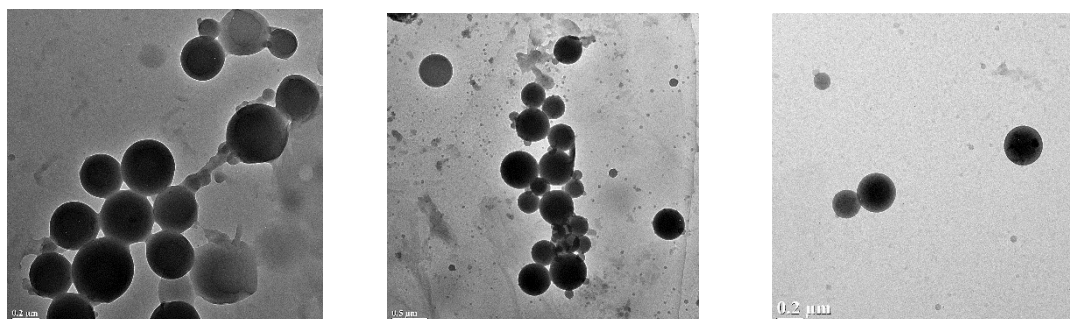


Figure S42. TEM images of micelles at different areas showing the spherical morphology.

Kinetic Experiment procedure:

In a glovebox, the catalyst, co-catalyst, and 2 M solution of eugenol epoxide (CH₂Cl₂: toluene, 1:1 v/v) were placed in a predried 15 mL stainless steel reactor in an argon atmosphere. All reactions were performed on the scale of 0.0068 mmol of catalyst, using ratios of 1/1/300 for catalyst/cocatalyst/monomer. The reactor was pressurized to 3.0 MPa by CO₂, then the reaction mixture was stirred at room temperature for the allotted time. Then excess CO₂ was vented,

reactor transferred to a glovebox and a small amount of the resultant mixture was removed from the reactor for ^1H NMR analysis to determine the conversion.

Table S2. Comparison of reactivity using Co-catalyst. Catalyst derived using dichloro phenylenediamine (a), phenylenediamine (b), dimethyl phenylenediamine (c).

Entry	Time (h)	(a) diCl			(b) Ph			(c) diMe		
		EuO (M)	PEuC (M)	CEuC (M)	EuO (M)	PEuC (M)	CEuC (M)	EuO (M)	PEuC (M)	CEuC (M)
1	2.5	1.910	0	0.09	1.774	0.136	0.09	1.556	0.324	0.12
2	5.0	1.794	0.086	0.12	1.49	0.348	0.162	1.066	0.804	0.13
3	7.5	1.678	0.16	0.162	1.184	0.644	0.172	0.702	1.138	0.16
4	10.0	1.570	0.252	0.178	0.936	0.894	0.17	0.474	1.364	0.162
5	24.0	1.084	0.68	0.236	0.22	1.57	0.21	0.156	1.666	0.178

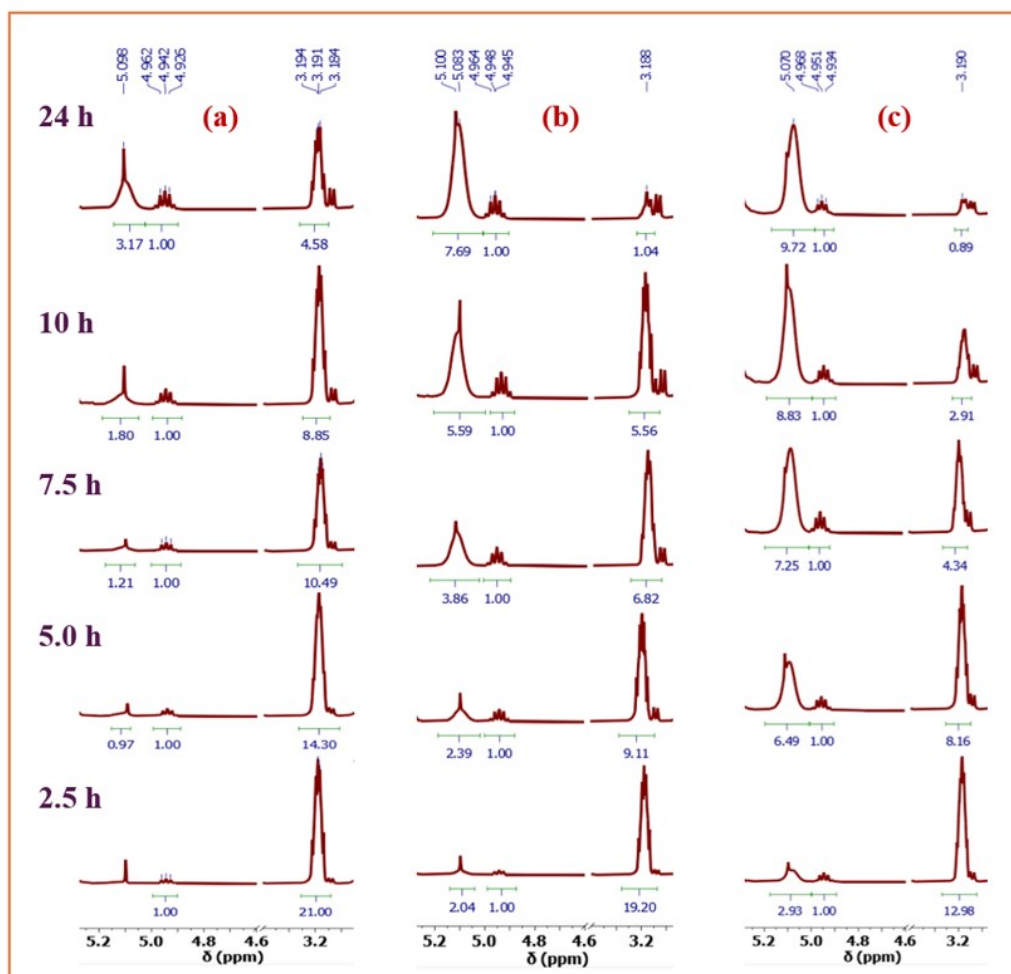


Figure S43. ^1H NMR of reaction mixture employing different Co-catalyst. Dichloro phenylenediamine (a), phenylenediamine (b), dimethyl phenylenediamine (c).

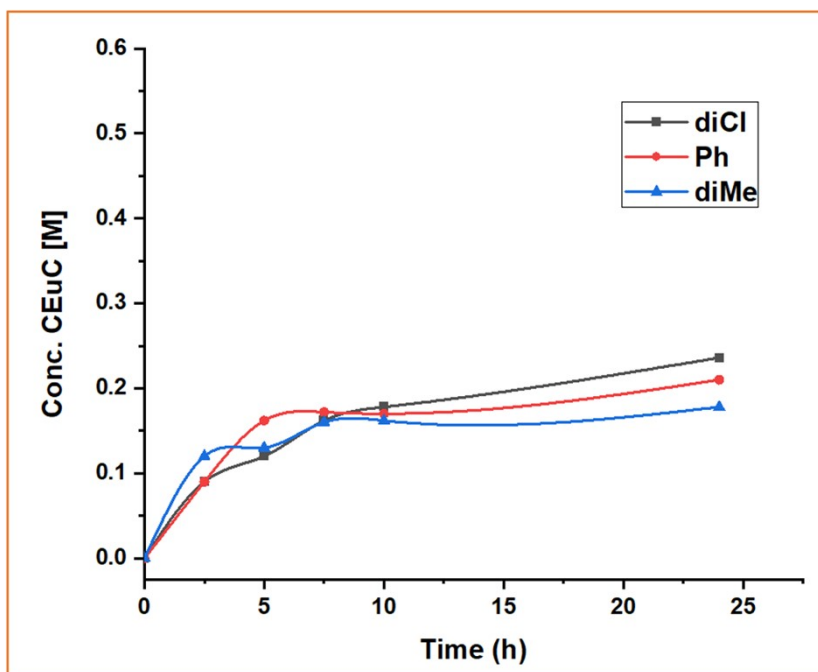


Figure S44. Concentration of cyclic carbonate Vs Time plot using Catalyst derived using dichloro phenylenediamine, phenylenediamine, and dimethyl phenylenediamine.

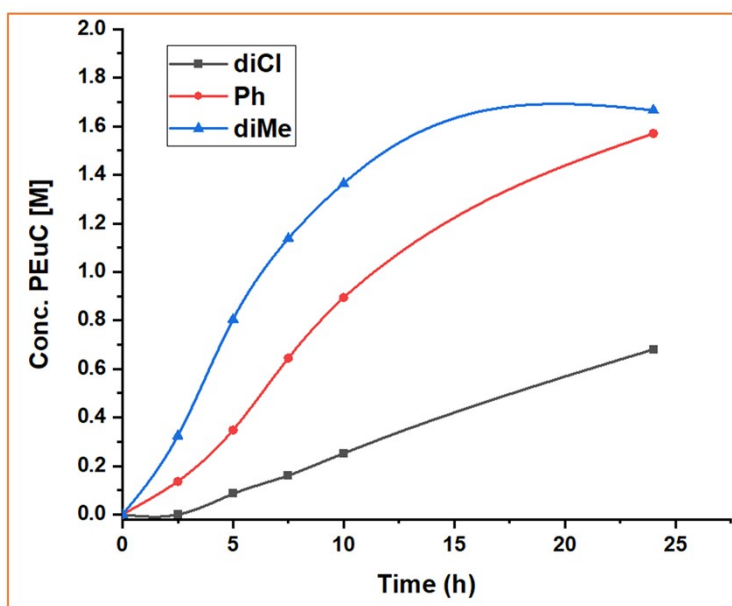


Figure S45. Concentration of poly carbonate Vs Time plot using Catalyst derived using dichloro phenylenediamine, phenylenediamine, and dimethyl phenylenediamine.

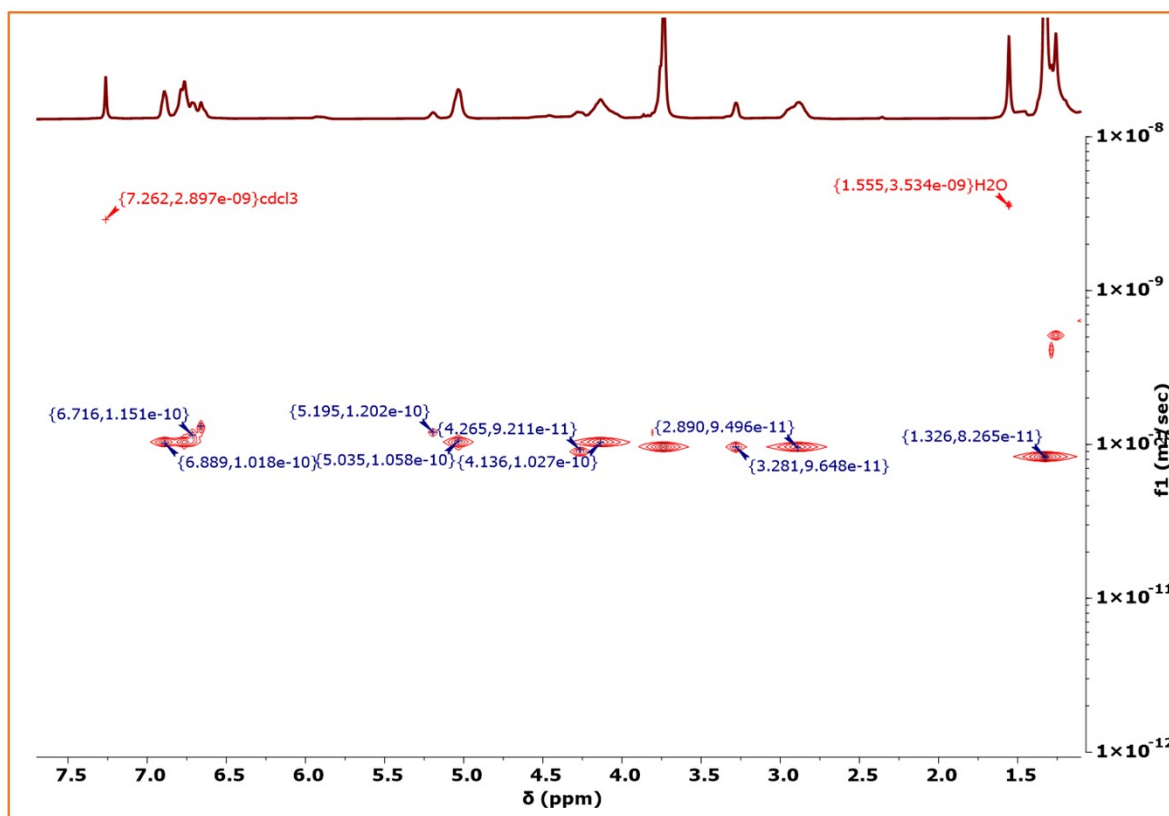


Figure S46. DOSY NMR spectra of diblock polymer. (CDCl_3 , 500 MHz). The ^1H NMR spectrum exhibited signals corresponding to the PEuC block ($\delta = 6.89, 5.03, 4.13, 2.89$ and 1.32 ppm) and PEGC block ($\delta = 6.71, 5.19, 4.26,$ and 3.28 ppm). The ^1H NMR signals of the PEuC and PEGC blocks exhibited the same diffusion coefficient, $D = 1.017 \times 10^{-10} \text{ m}^2/\text{s}$.

Table S3. DOSY NMR data of block polycarbonate derived from EuO, EGE with CO_2

Peak	Freq/ppm	D/($10^{-10} \text{ m}^2/\text{s}$)
1	6.889	1.018
2	6.716	1.151
3	5.195	1.202
4	5.035	1.058
5	4.265	0.921
6	4.136	1.027
7	3.281	0.964
8	2.890	0.949
9	1.326	0.826

Table S3. Comparison of reactivity using Co-catalyst. Catalyst derived using dichloro phenylenediamine (a), phenylenediamine (b), dimethyl phenylenediamine (c).

Entry	Time (h)	(a)			(b)			(c)		
		Conv. (%)	PEuC (%)	CEuC (%)	Conv. (%)	PEuC (%)	CEuC (%)	Conv. (%)	PEuC (%)	CEuC (%)
1	2.5	4.5	-	4.5	11.3	6.8	4.5	22.2	16.2	6.0
2	5.0	10.3	4.3	6	25.5	17.4	8.1	46.7	40.2	6.5
3	7.5	16.1	8.0	8.1	40.8	32.2	8.6	64.9	56.9	8.0
4	10.0	21.5	12.6	8.9	53.2	44.7	8.5	76.3	68.2	8.1
5	24.0	45.8	34.0	11.8	89.0	78.5	10.5	92.2	83.3	8.9