Supplementary Information

Unconventional sulfonium C-H H-bond donor catalyst in fixation of carbon dioxide

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1. General information

Materials. CO_2 was supplied by Nanjing Shangyuan Industrial Gas Factory with a purity of 99.99%. Epoxides were purchased from Alfa Aesar. Tetrahydrothiophene, tetrahydrothiopyranium, 2-bromoacetic acid, 3-bromopropionic acid, 4-bromobutyric acid, 1-bromobutane, butyric acid and anhydrous acetonitrile were purchased from Aldrich and used without further purification.

Characterizations. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 and 101 MHz NMR spectrometer in $CDCl_3$, D_2O or DMSO-d_6 as stated deuterated solvents. Chemical shifts δ are reported in parts per million (ppm) relative to a residual undeuterated solvent as an internal reference (^1H δ7.26 for $CDCl_3$, δ2.50 for DMSO-d_6, δ4.90 for D_2O; ^{13}C δ77.16 for $CDCl_3$, δ39.52 for DMSO-d_6). Conversions and selectivity of epoxides were determined by ^1H NMR spectroscopy. Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TG50 and SDT Q600 TG-DTA analyser under N_2 atmosphere. Approximately 5 mg of sample was weighed and equilibrated at 30 °C; Ramp 10 °C/min to 600 °C.

2. Experimental section

General method for synthesis of catalysts. Typical preparation procedure of tertiary sulfonium halide catalysts (**THT1-Br** and **THP1-Br**) was illustrated by tetrahydrothiophene and bromoacetic acid as an example. Tetarhydrothiophene (1.32 mL, 15 mmol) and bromo-acetic acid (2.08 g, 15 mmol) were added into 100 mL dry three-necked round bottle flask with 45 mL of anhydrous acetonitrile as the solvent. The mixture was refluxed for 3 h in 80 °C oil bath under a nitrogen atmosphere. After the reaction, the precipitate formed in acetonitrile was collected by filtration, washed with cold diethyl ether or ethyl acetate and dried under a vacuum to give **THT1-Br** as solid. The structure of **THT1-Br** was verified by ^{1}H NMR, ^{13}C NMR. Other tertiary sulfonium halide catalysts were synthesized and characterized in a similar way.

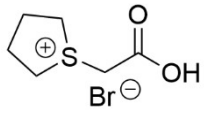
Typical preparation procedure of **THT2-Br**, **THT3-Br**, **THP2-Br**, **THP3-Br**, **THTBu-Br** was illustrated by tetrahydrothiophene and 3-bromopropionic acid as an example. Tetrahydrothiophene (1.32 mL, 15 mmol) and 3-bromopropionic acid (2.29 g, 15 mmol) were added into 100 mL dry three-necked round bottle flask with 45 mL of anhydrous acetonitrile as the solvent. The mixture was refluxed for 8 h in 80 °C oil bath under a nitrogen atmosphere. After the reaction, the excess acetonitrile was removed through rotary evaporation. The residue was dissolved with the minimum CH_3OH, the crude product was precipitated by cold diethyl ether or ethyl acetate. Then washed with diethyl ether or ethyl acetate and dried under a vacuum to give **THT2-Br** as solid. The structure of **THT2-Br** was verified by ^{1}H NMR, ^{13}C NMR. Other sulfonium halide was synthesized and characterized in a similar way.

Procedure for the synthesis of catalyst THT3-BF_4. THT3-Br (0.5 g, 1.96 mmol) was dissolved in 10 mL CH_3OH, then $NaBF_4$ (0.43 g, 4 mmol) was added into the solution, reacting for 24 h. The NaBr was precipitated and removed by filtration, the CH_3OH was removed by evaporation, the product was dried under vacuum.

General Procedure for the cycloaddition of epoxide into CO_2 to cyclic carbonate. The CCE reactions of epoxides and CO_2 were conducted in a high-pressure reactor (10 mL inner volumes). In a typical reaction, the reactor was charged with catalyst **THT3-Br** (0.0638 g, 0.25 mmol, 0.05 eq.) and styrene oxide (0.57 mL, 5 mmol, 1 eq.) successively at room temperature. The reactor was constantly purged with 0.3 MPa CO_2 to remove air for three times, and finally flushed into the reactor with 1 MPa of CO_2. After that, the reactor was heated to 100 °C and replenished the pressure of CO_2 to 1 MPa. This reaction was conducted at 100 °C for 6 h. The conversion of epoxide and yield of cyclic carbonate were determined by ^{1}H NMR analysis and obtained with supplement of 1 mol% mesitylene. The residue was purified by column chromatography with PE : EA = 5:1 as the eluent to afford the desired product.

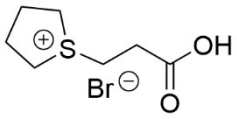
Characterization Data for Catalysts

1-(carboxymethyl)tetrahydro-1H-thiophen-1-ium bromide ***(THT1-Br)***



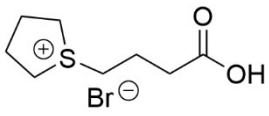
^{1}H NMR (400 MHz, Deuterium Oxide) δ 4.25 (s, 2H), 3.65 – 3.56 (m, 2H), 3.48 (dt, J = 12.2, 5.8 Hz, 2H), 2.39 – 2.20 (m, 4H). **^{13}C NMR** (101 MHz, Deuterium Oxide) δ 45.16, 43.36, 28.19. The spectral data were consistent with values reported in the literature[1].

1-(2-carboxyethyl)tetrahydro-1H-thiophen-1-ium bromide ***(THT2-Br)***



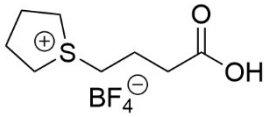
^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.61 (dt, J = 13.3, 6.5 Hz, 2H), 3.48 (dt, J = 13.1, 6.1 Hz, 2H), 3.43 (t, J = 6.8 Hz, 2H), 2.98 (td, J = 6.8, 1.1 Hz, 2H), 2.42 – 2.21 (m, 4H). **^{13}C NMR** (101 MHz, Deuterium Oxide) δ 44.32, 37.94, 29.71, 28.22. The spectral data were consistent with values reported in the literature[2].

1-(3-carboxypropyl)tetrahydro-1H-thiophen-1-ium bromide ***(THT3-Br)***



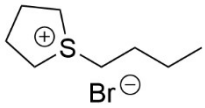
^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.57 (dt, J = 13.4, 6.6 Hz, 2H), 3.41 (dt, J = 12.4, 6.0 Hz, 2H), 3.27 – 3.20 (m, 2H), 2.59 (t, J = 7.0 Hz, 2H), 2.40 – 2.21 (m, 4H), 2.08 (p, J = 7.3 Hz, 2H). **^{13}C NMR** (101 MHz, Deuterium Oxide) δ 43.14, 41.04, 31.71, 28.18, 19.97.

1-(3-carboxypropyl)tetrahydro-1H-thiophen-1-ium tetrafluoroborate ***(THT3-BF_4)***



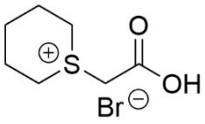
^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.60 (dd, J = 13.1, 6.5 Hz, 2H), 3.42 (dt, J = 12.3, 5.7 Hz, 2H), 3.28 – 3.20 (m, 2H), 2.65 – 2.55 (m, 2H), 2.42 – 2.22 (m, 4H), 2.10 (dq, J = 13.9, 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, Deuterium Oxide) δ 175.06, 52.35, 43.13, 41.00, 31.64, 28.18, 19.95. ^{19}F NMR (376 MHz, Deuterium Oxide) δ -150.51. The spectral data were consistent with values reported in the literature[3].

1-butyltetrahydro-1H-thiophen-1-ium bromide ***(THTBu-Br)***



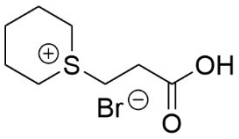
^{1}H NMR (400 MHz, Chloroform-d) δ 3.93 – 3.82 (m, 2H), 3.64 – 3.47 (m, 4H), 2.48 – 2.34 (m, 4H), 1.72 (p, J = 7.6 Hz, 2H), 1.55 – 1.42 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 44.35, 42.39, 28.93, 27.44, 21.60, 13.61. The spectral data were consistent with values reported in the literature[4].

*1-(carboxymethyl)hexahydrothiopyrylium bromide **(THP1-Br)***



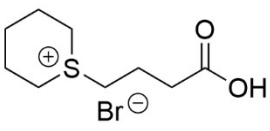
^{1}H NMR (400 MHz, Deuterium Oxide) δ 4.37 (d, J = 4.9 Hz, 1H), 3.58 – 3.49 (m, 2H), 3.26 (ddd, J = 12.8, 9.1, 3.1 Hz, 2H), 2.12 (dtt, J = 14.8, 7.3, 3.4 Hz, 2H), 1.90 (dtt, J = 15.7, 9.2, 3.4 Hz, 2H), 1.78 – 1.56 (m, 2H). **^{13}C NMR** (101 MHz, Deuterium Oxide) δ 41.65, 36.20, 22.15, 20.37. The spectral data were consistent with values reported in the literature[2].

*1-(2-carboxyethyl)hexahydrothiopyrylium bromide **(THP2-Br)***



^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.55 (t, J = 6.8 Hz, 4H), 3.23 (ddd, J = 12.7, 9.1, 3.1 Hz, 2H), 2.99 (t, J = 6.7 Hz, 2H), 2.16 (dtt, J = 14.7, 7.2, 3.3 Hz, 2H), 1.90 (dtt, J = 15.7, 9.2, 3.3 Hz, 2H), 1.80 – 1.58 (m, 2H). **^{13}C NMR** (101 MHz, Deuterium Oxide) δ 36.76, 34.48, 28.76, 22.16, 20.47.

*1-(3-carboxypropyl)hexahydrothiopyrylium bromide **(THP3-Br)***

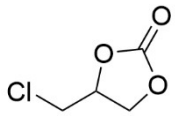


^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.56 – 3.47 (m, 2H), 3.41 – 3.34 (m, 2H), 3.17 (ddd, J = 12.9, 9.4, 3.1 Hz, 2H), 2.59 (t,

J = 7.0 Hz, 2H), 2.21 – 2.03 (m, 4H), 1.88 (dtt, J = 15.8, 9.4, 3.3 Hz, 2H), 1.80 – 1.56 (m, 2H). **^{13}C NMR** (101 MHz, Deuterium Oxide) δ 37.84, 35.92, 31.84, 22.21, 20.35, 18.77.

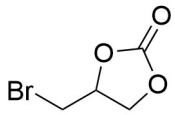
Characterization Data for Products

3-Chloropropylene carbonate



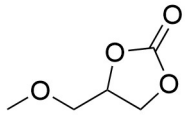
^{1}H NMR (400 MHz, Chloroform-d) δ 4.99 (ddt, J = 8.3, 5.7, 3.9 Hz, 1H), 4.55 (t, J = 8.7 Hz, 1H), 4.33 (dd, J = 8.9, 5.7 Hz, 1H), 3.80 (dd, J = 12.4, 4.3 Hz, 1H), 3.72 – 3.66 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 154.51, 74.48, 66.86, 44.18.

4-(bromomethyl)-1,3-dioxolan-2-one



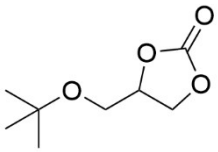
^{1}H NMR (400 MHz, Chloroform-d) δ 4.95 (dq, J = 8.2, 5.3 Hz, 1H), 4.59 (dd, J = 8.9, 8.2 Hz, 1H), 4.35 (dd, J = 8.9, 5.9 Hz, 1H), 3.58 (d, J = 5.3 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 154.24, 74.09, 68.23, 31.41.

4-(methoxymethyl)-1,3-dioxolan-2-one



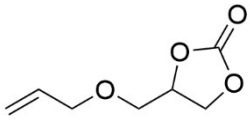
^{1}H NMR (400 MHz, Chloroform-d) δ 4.79 (ddt, J = 8.3, 6.0, 3.7 Hz, 1H), 4.47 (t, J = 8.4 Hz, 1H), 4.34 (dd, J = 8.4, 6.1 Hz, 1H), 3.62 (dd, J = 11.1, 3.6 Hz, 1H), 3.53 (dd, J = 11.1, 3.8 Hz, 1H), 3.39 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 155.07, 75.13, 71.52, 66.24, 59.68.

4-(tert-butoxymethyl)-1,3-dioxolan-2-one



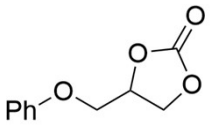
^{1}H NMR (400 MHz, Chloroform-d) δ 4.80 – 4.72 (m, 1H), 4.47 (t, J = 8.2 Hz, 1H), 4.38 (dd, J = 8.3, 5.8 Hz, 1H), 3.61 (dd, J = 10.3, 4.6 Hz, 1H), 3.53 (dd, J = 10.3, 3.6 Hz, 1H), 1.19 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 155.28, 75.26, 66.73, 61.43, 27.43.

4-((allyloxy)methyl)-1,3-dioxolan-2-one



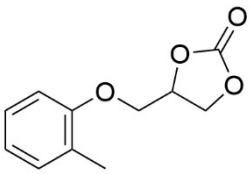
^{1}H NMR (400 MHz, Chloroform-d) δ 5.81 (ddt, J = 16.2, 11.1, 5.5 Hz, 1H), 5.27 – 5.11 (m, 2H), 4.79 (d, J = 3.2 Hz, 1H), 4.50 – 4.42 (m, 1H), 4.33 (t, J = 7.2 Hz, 1H), 4.00 (d, J = 5.7 Hz, 2H), 3.69 – 3.51 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 155.07, 133.72, 117.65, 75.19, 72.41, 68.83, 66.21.

4-(phenoxymethyl)-1,3-dioxolan-2-one



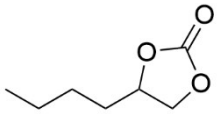
^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 (dd, J = 8.7, 7.3 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 7.8 Hz, 2H), 5.03 (d, J = 4.5 Hz, 1H), 4.66 – 4.51 (m, 2H), 4.28 – 4.13 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 157.88, 129.86, 122.18, 114.75, 67.01, 66.41.

4-((o-tolyloxy) methyl)-1,3-dioxolan-2-one



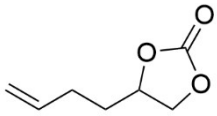
^{1}H NMR (400 MHz, Chloroform-d) δ 7.16 (t, J = 3.1 Hz, 2H), 6.93 (t, J = 6.9 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 5.09 – 5.02 (m, 1H), 4.66 – 4.55 (m, 2H), 4.26 (dd, J = 10.6, 3.6 Hz, 1H), 4.13 (dd, J = 10.6, 3.1 Hz, 1H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 155.86, 154.91, 131.21, 127.21, 127.00, 121.78, 110.92, 74.32, 67.11, 66.36, 16.09.

4-butyl-1,3-dioxane-2-one



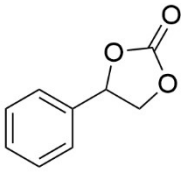
^{1}H NMR (400 MHz, Chloroform-d) δ 4.69 (qd, J = 7.5, 5.4 Hz, 1H), 4.54 – 4.48 (m, 1H), 4.05 (dd, J = 8.4, 7.2 Hz, 1H), 1.85 – 1.61 (m, 2H), 1.47 – 1.28 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 155.22, 76.82, 69.48, 33.58, 26.47, 22.29, 13.85.

4-(but-3-en-1-yl)-1,3-dioxolan-2-one



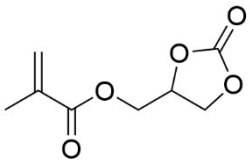
^{1}H NMR (400 MHz, Chloroform-d) δ 5.78 (ddt, J = 16.9, 10.1, 6.6 Hz, 1H), 5.14 – 4.99 (m, 2H), 4.72 (dd, J = 7.6, 5.2 Hz, 1H), 4.52 (t, J = 8.1 Hz, 1H), 4.08 (dd, J = 8.5, 7.2 Hz, 1H), 2.35 – 2.10 (m, 2H), 1.99 – 1.85 (m, 1H), 1.77 (dddd, J = 14.0, 8.7, 7.0, 5.1 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 155.08, 116.57, 76.43, 69.44, 33.17, 28.76.

4-phenyl-1,3-dioxolan-2-one



^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.22 (m, 5H), 5.57 (t, J = 8.0 Hz, 1H), 4.69 (t, J = 8.4 Hz, 1H), 4.22 (t, J = 8.2 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 154.94, 135.83, 129.66, 129.17, 125.92, 78.01, 71.17.

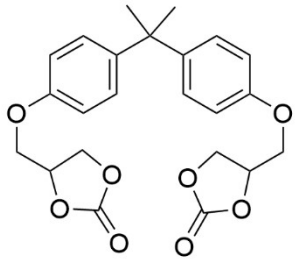
2-(Oxo-1,3-dioxalan-4-yl)methyl methacrylate



^{1}H NMR (400 MHz, Chloroform-d) δ 6.14 (t, J = 1.1 Hz, 1H), 5.64 (t, J = 1.6 Hz, 1H), 4.97 (ddt, J = 8.7, 5.6, 3.4 Hz, 1H), 4.58 (t, J = 8.6 Hz, 1H), 4.42 (dd, J = 12.6, 3.1 Hz, 1H), 4.37 – 4.28 (m, 2H), 1.94 (t, J = 1.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 166.73, 154.59, 135.23, 127.38, 73.94, 66.19, 63.54, 18.23.

4,4'-(((Propane-2,2-diylbis(4,1-phenylene))bis(oxy)bis(methylene))bis(1,3-dioxolan-2-one)



^{1}H NMR (400 MHz, Chloroform-d) δ 7.14 (d, J = 8.9 Hz, 4H), 6.80 (d, J = 8.8 Hz, 4H), 5.01 (ddt, J = 8.1, 5.9, 3.9 Hz, 2H), 4.60 (t, J = 8.4 Hz, 2H), 4.52 (dd, J = 8.5, 5.9 Hz, 2H), 4.21 (dd, J = 10.6, 4.3 Hz, 2H), 4.12 (dd, J = 10.6, 3.5 Hz, 2H), 1.63 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 155.80, 154.76, 144.50, 128.08, 114.21, 74.23, 67.07, 66.37, 41.98, 31.10.

3. References

[1] Aggarwal, V. K.; Hebach, C., Carboxylate-stabilised sulfur ylides (thetin salts) in asymmetric epoxidation for the synthesis of glycidic acids. Mechanism and implications. *Org. Biomol. Chem.* 2005, **3** (8), 1419-1427.

[2] Zhang, Y.; Hudock, M. P.; Krysiak, K.; Cao, R.; Bergan, K.; Yin, F.; Leon, A.; Oldfield, E., Activity of Sulfonium Bisphosphonates on Tumor Cell Lines. *J. Med. Chem.* 2007, **50** (24), 6067-6079.

[3] Nakamura, T.; Matsuyama, H.; Takahashi, M.; Kamigata, N., LACTONIZATION REACTIONS OF (ω-CARBOXYALKYL)SULFONIUM SALTS. *Phosphorus Sulfur.* 1992, **66** (1-4), 59-65.

[4] Aced, G.; Anklam, E.; Mockel, H. J., Separation of Sulphonium Salts by Ion Chromatography: Five- and Six-Membered Cyclic Sulphonium Salts. *J. Liq. Chromatogr. R. T.* 1987, **10** (15), 3321-3327.

4. NMR Spectra of Compounds

Copies of NMR spectra of catalysts (Figure S1 – Figure S17)

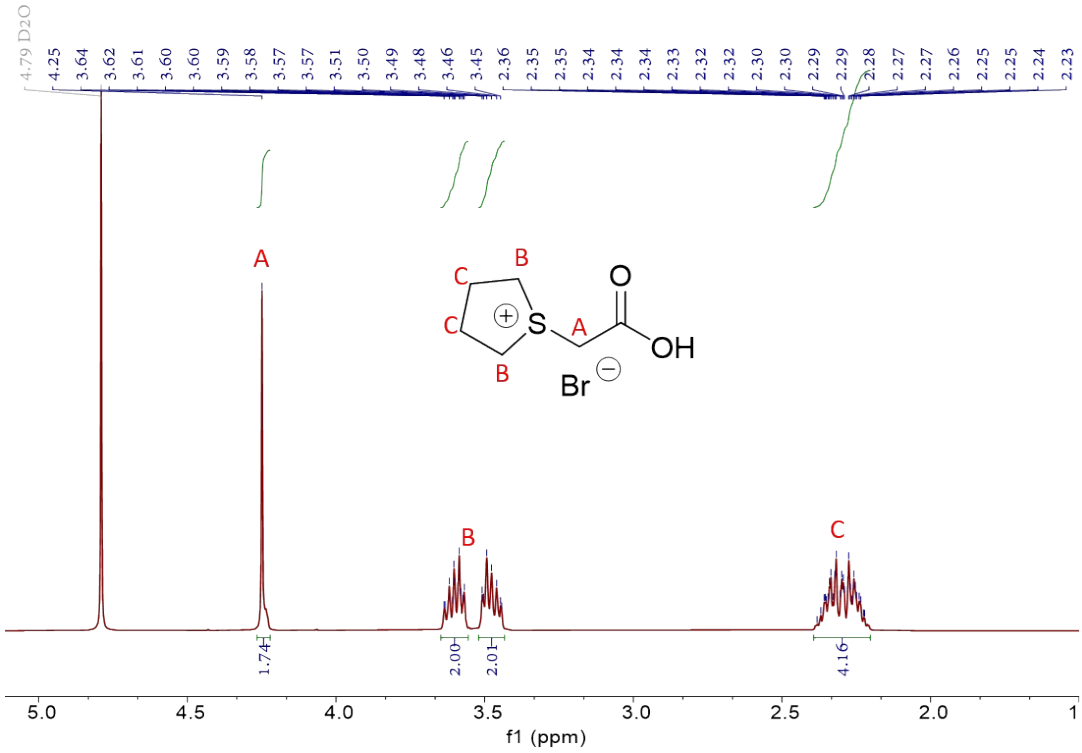


Figure S1. ^{1}H NMR spectrum (D_2O, 400 MHz) of **THT1-Br**

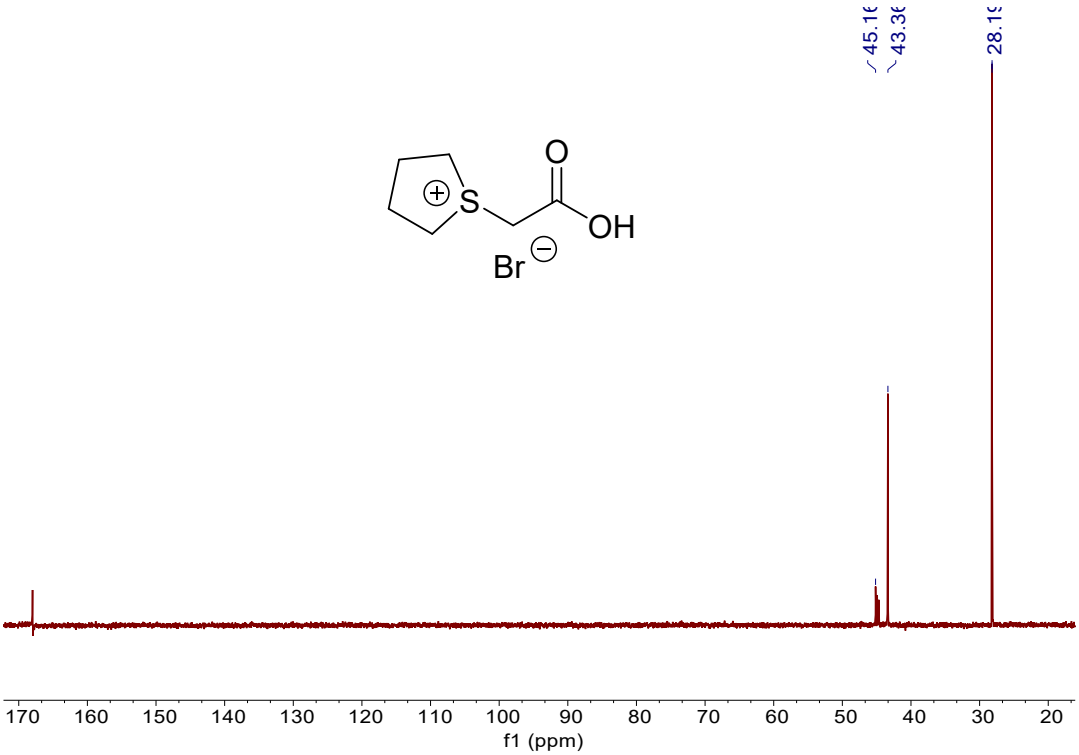


Figure S2. ^{13}C NMR spectrum (D_2O, 101 MHz) of **THT1-Br**

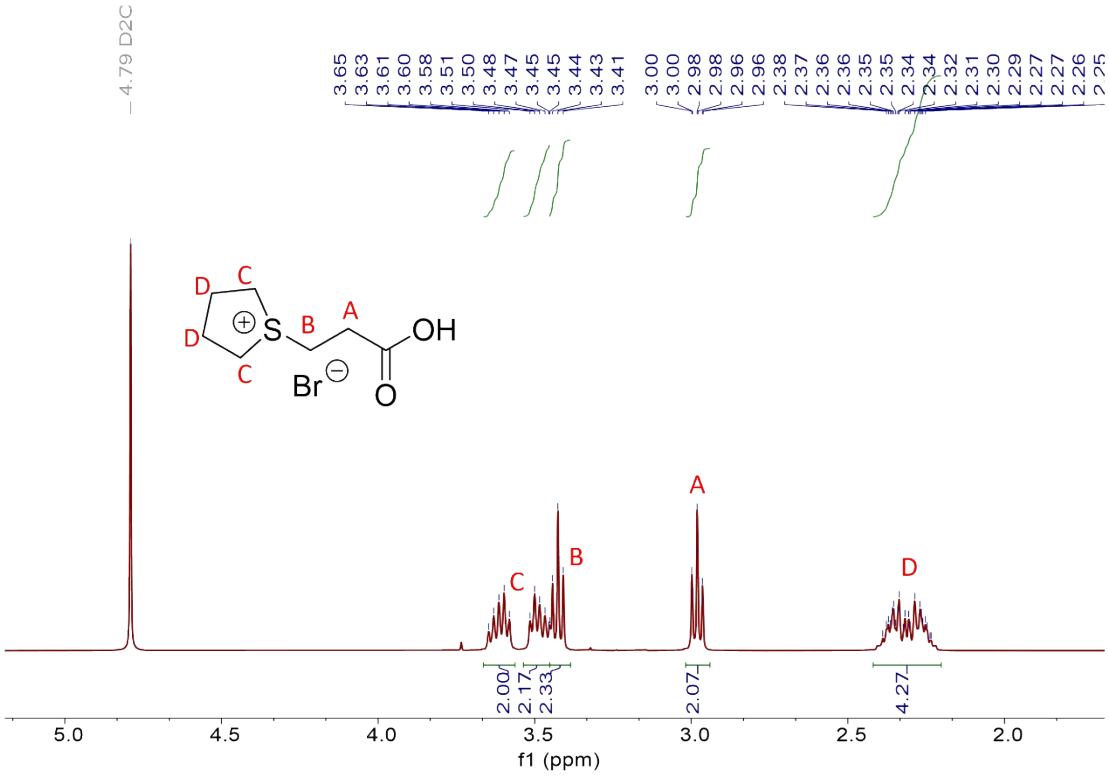


Figure S3. ^{1}H NMR spectrum (D_2O, 400 MHz) of **THT2-Br**

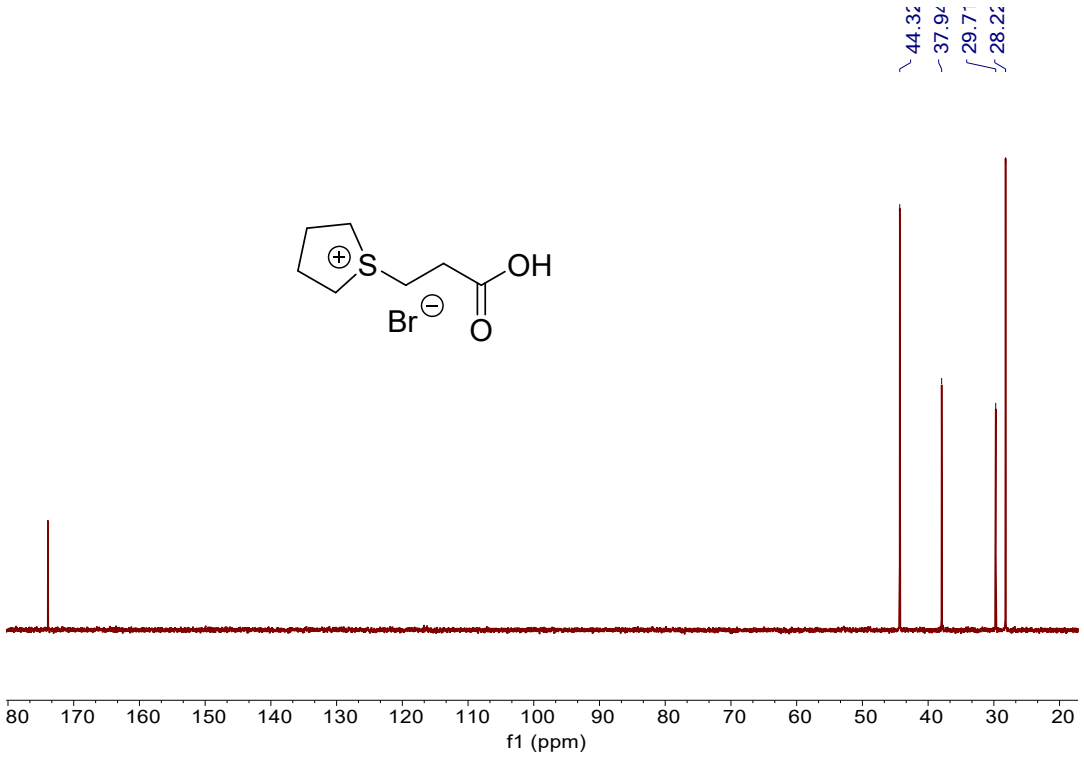


Figure S4. ^{13}C NMR spectrum (D_2O, 101 MHz) of **THT2-Br**

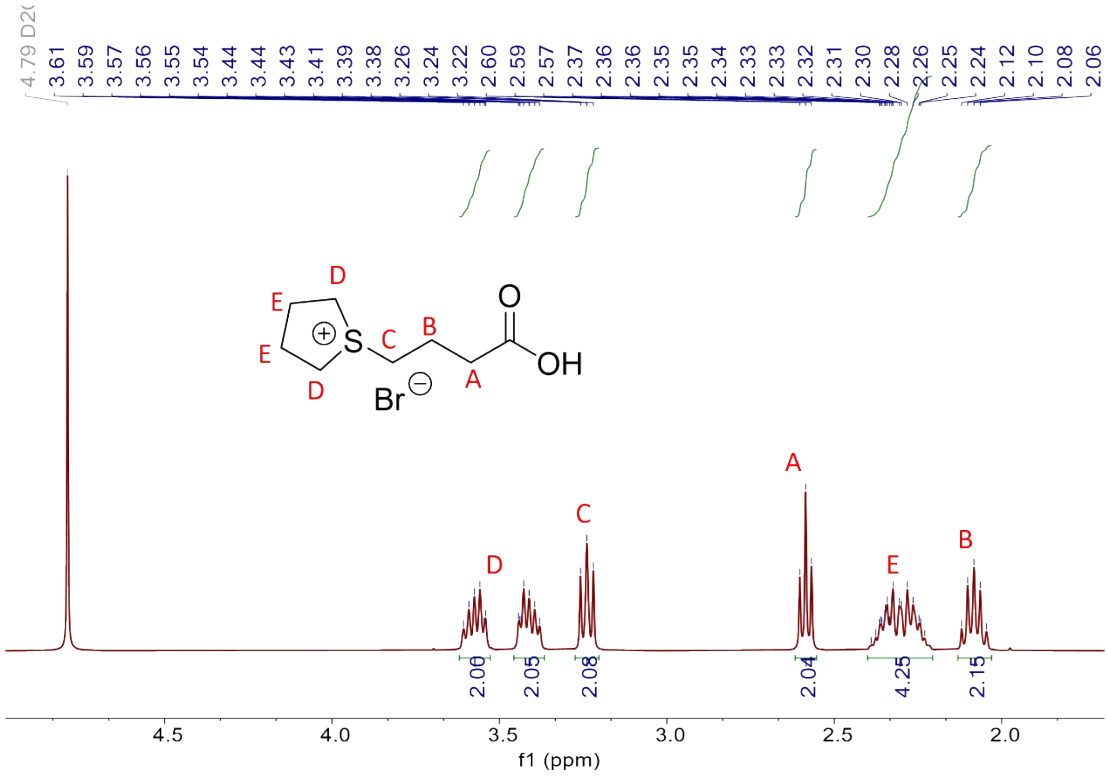


Figure S5. ^{1}H NMR spectrum (D_2O, 400 MHz) of **THT3-Br**

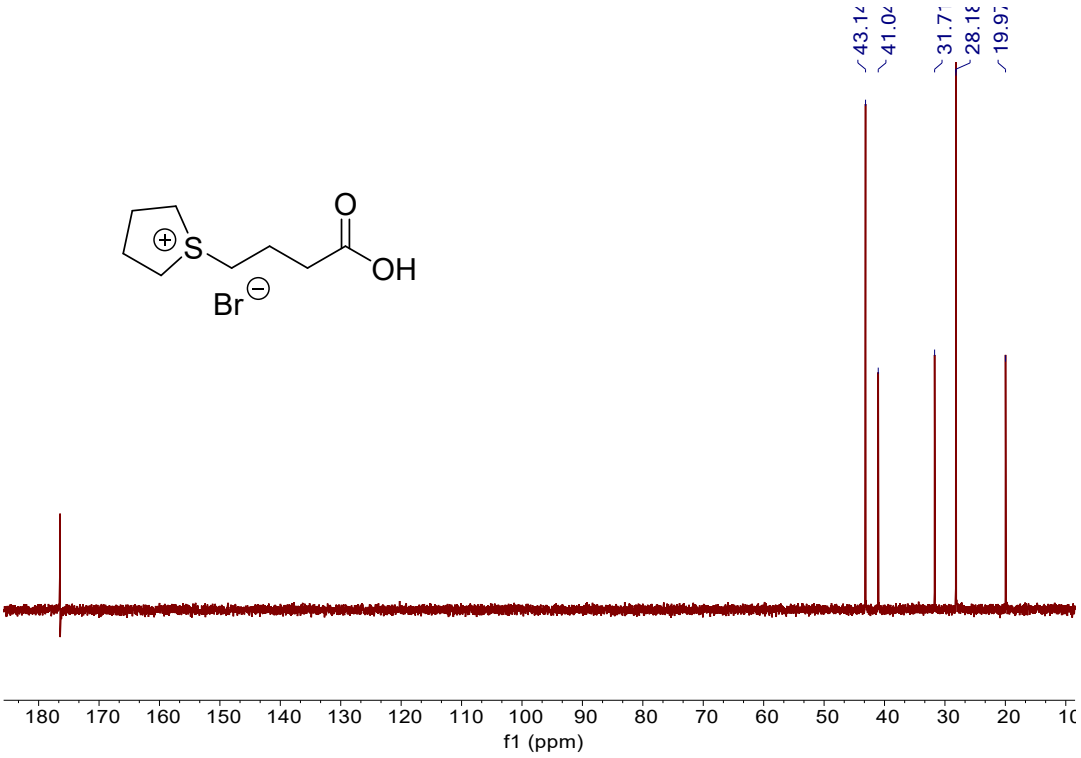


Figure S6. ^{13}C NMR spectrum (D_2O, 101 MHz) of **THT3-Br**

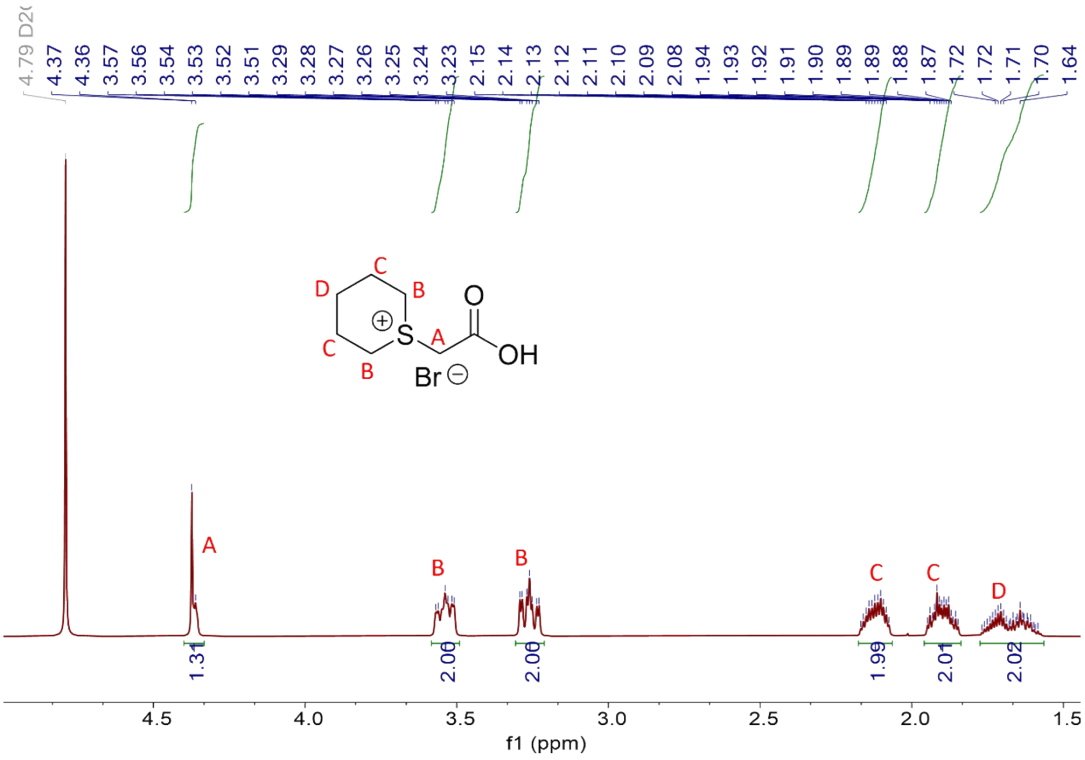


Figure S7. ^{1}H NMR spectrum (D_2O, 400 MHz) of **THP1-Br**

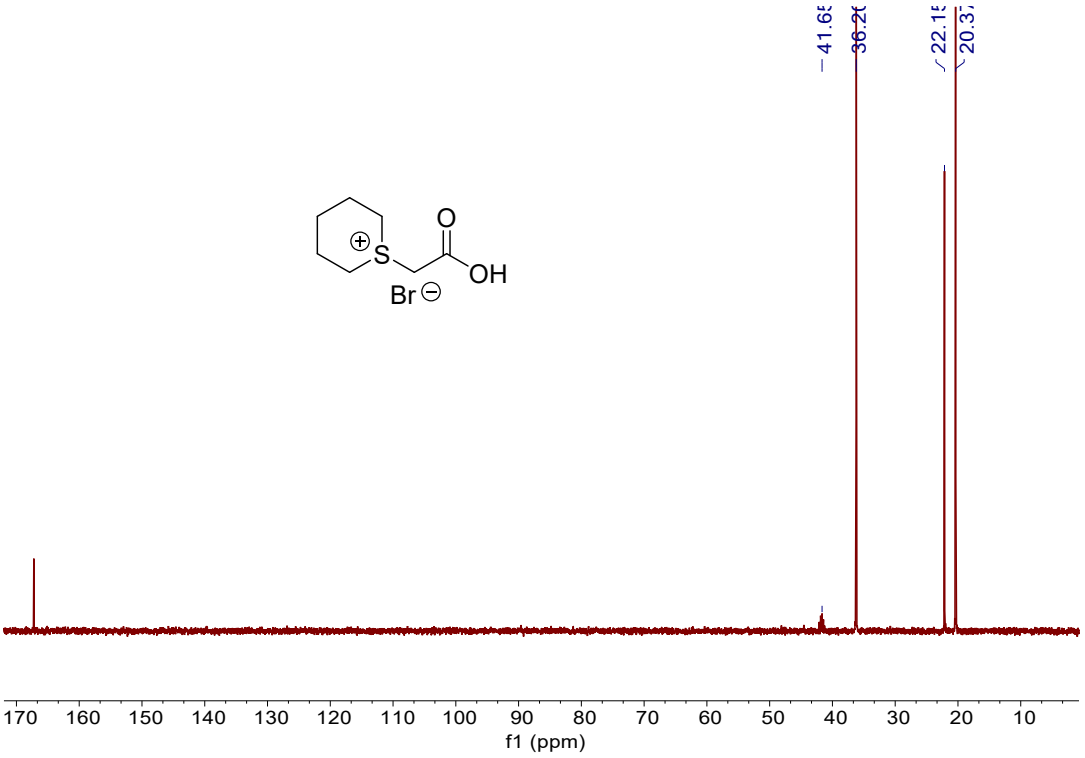


Figure S8. ^{13}C NMR spectrum (D_2O, 101 MHz) of **THP1-Br**

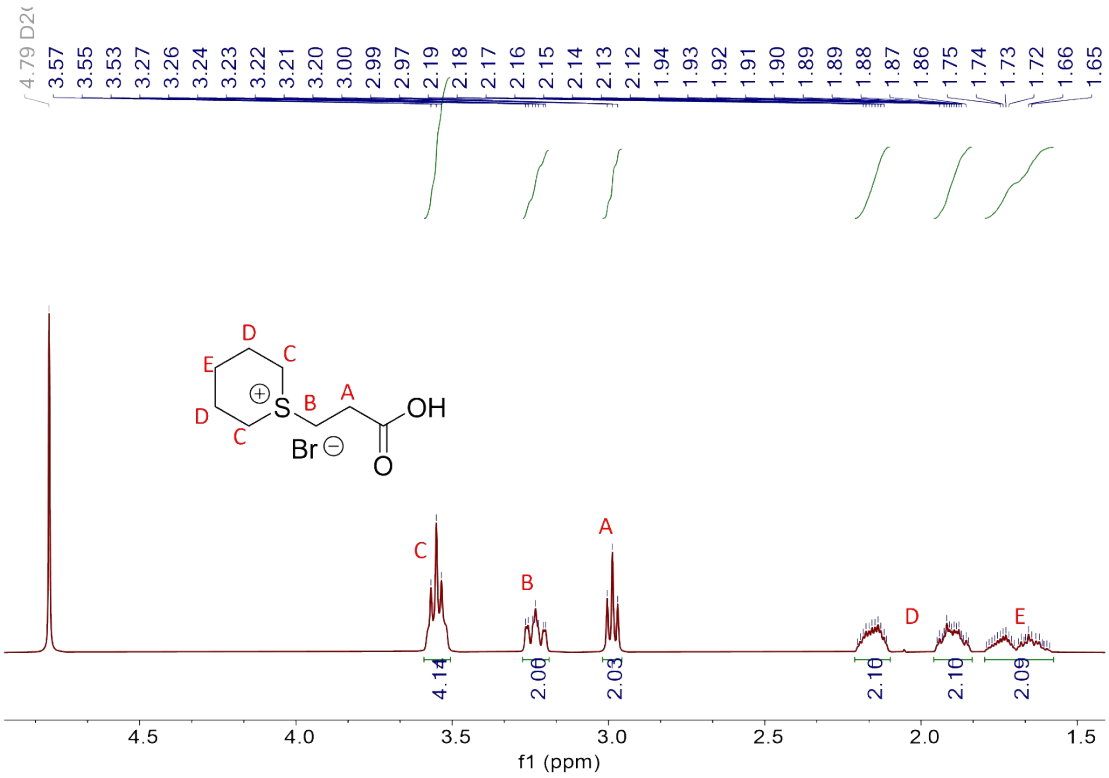


Figure S9. ^{1}H NMR spectrum (D_2O, 400 MHz) of **THP2-Br**

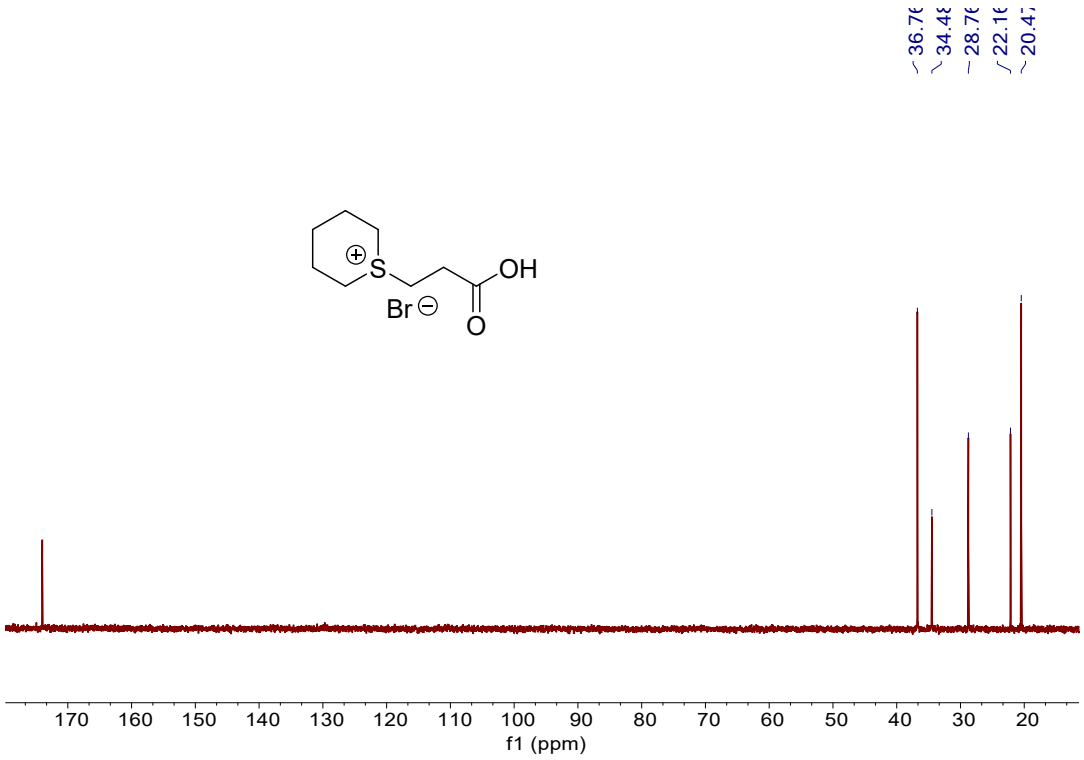


Figure S10. ^{13}C NMR spectrum (D_2O, 101 MHz) of **THP2-Br**

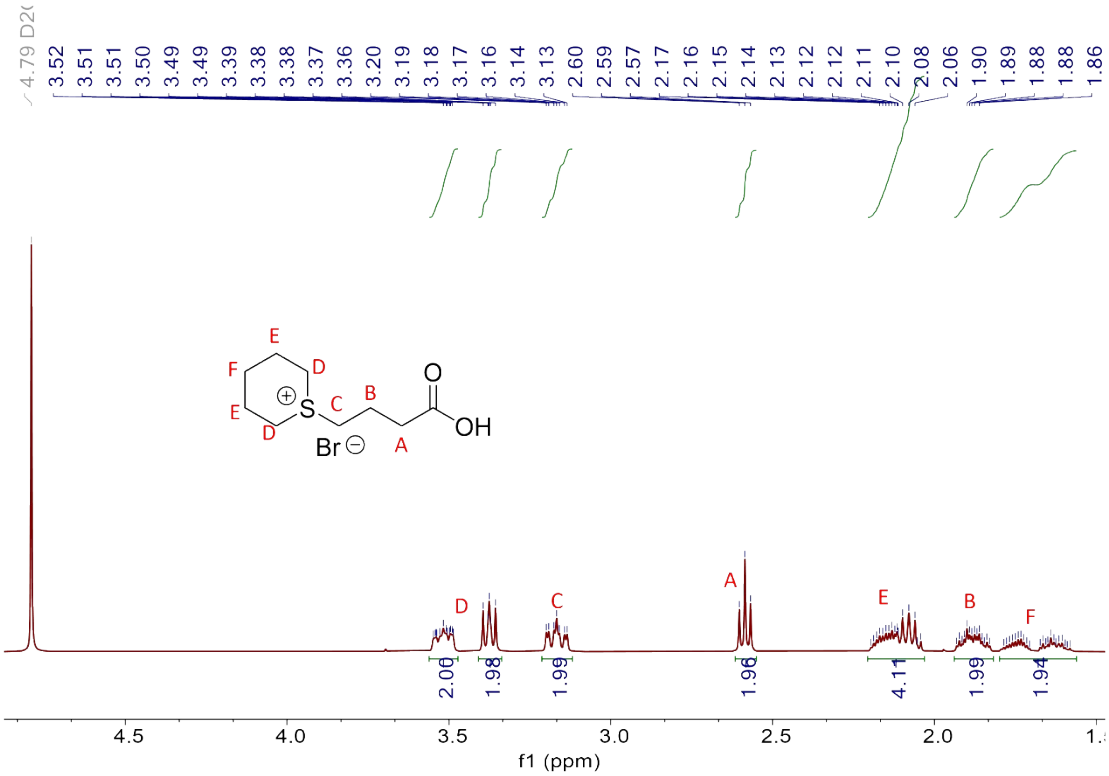


Figure S11. ^{1}H NMR spectrum (D_2O, 400 MHz) of **THP3-Br**

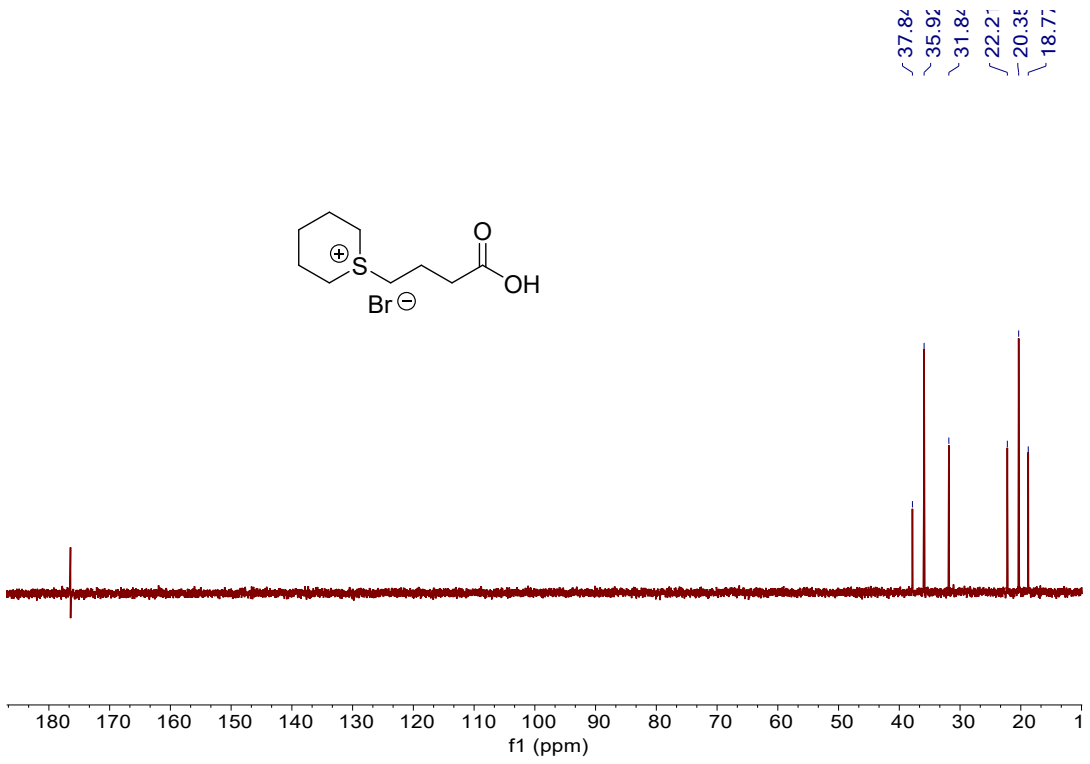


Figure S12. ^{13}C NMR spectrum (D_2O, 101 MHz) of **THP3-Br**

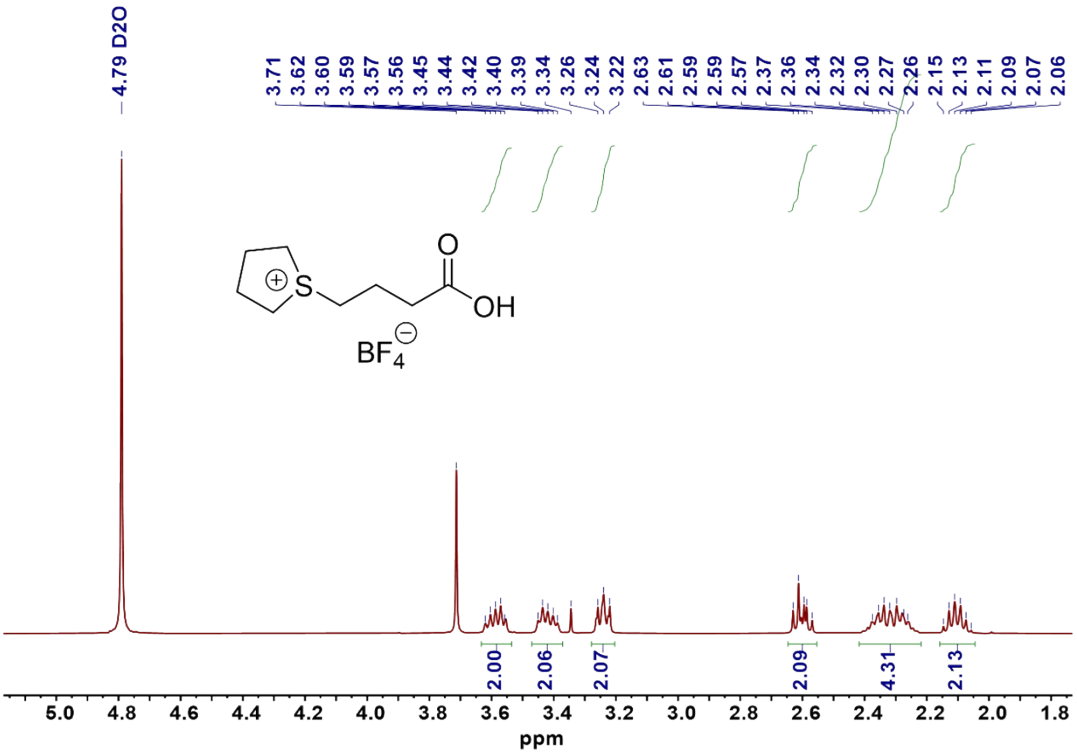


Figure S13. ^{1}H NMR spectrum (D2O, 400 MHz) of **THT3-BF_4**

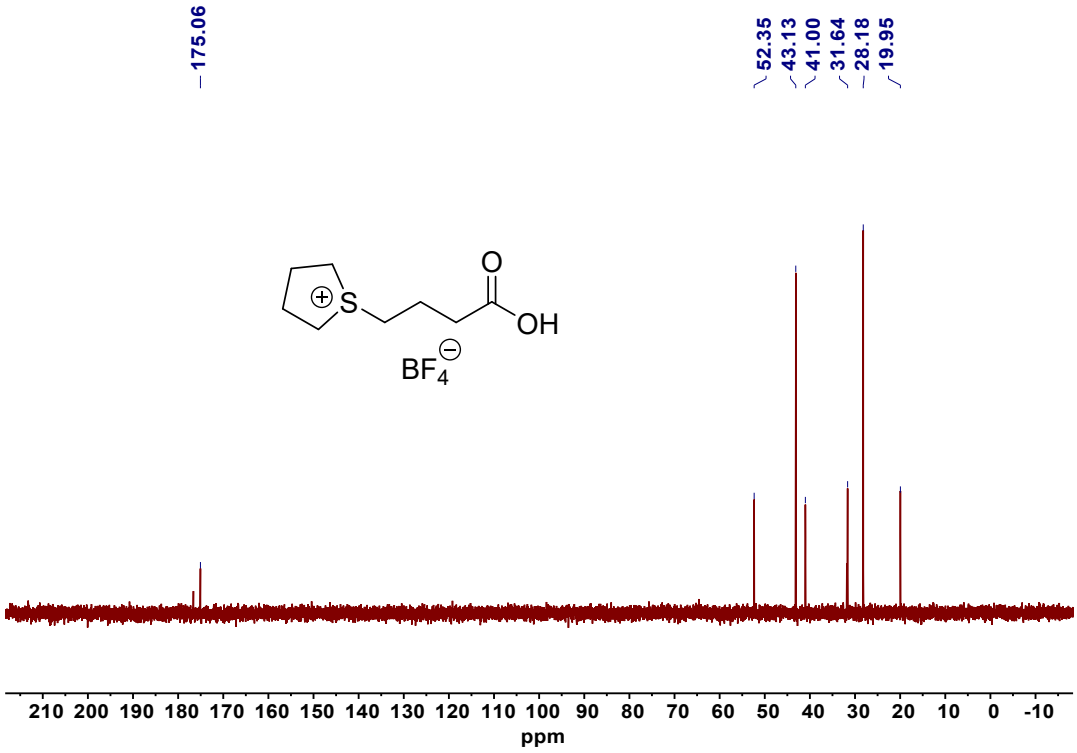


Figure S14. ^{13}C NMR spectrum (D2O, 101 MHz) of **THT3-BF_4**

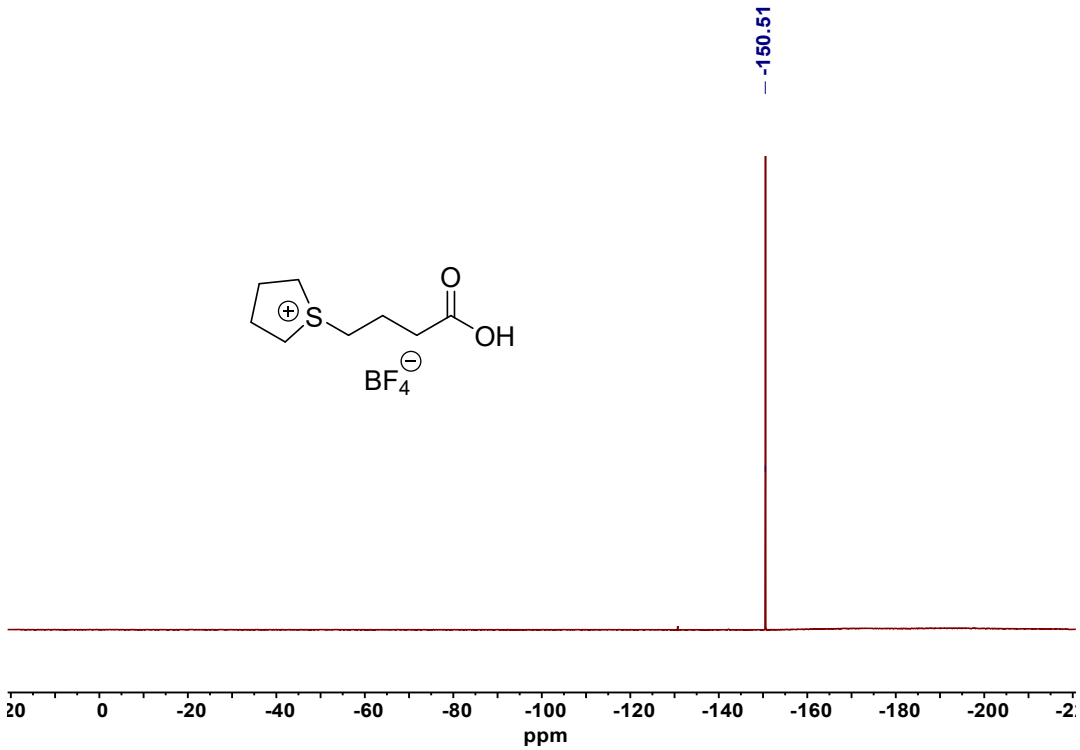


Figure S15. ^{19}F NMR spectrum (D2O, 376 MHz) of **THT3-BF_4**

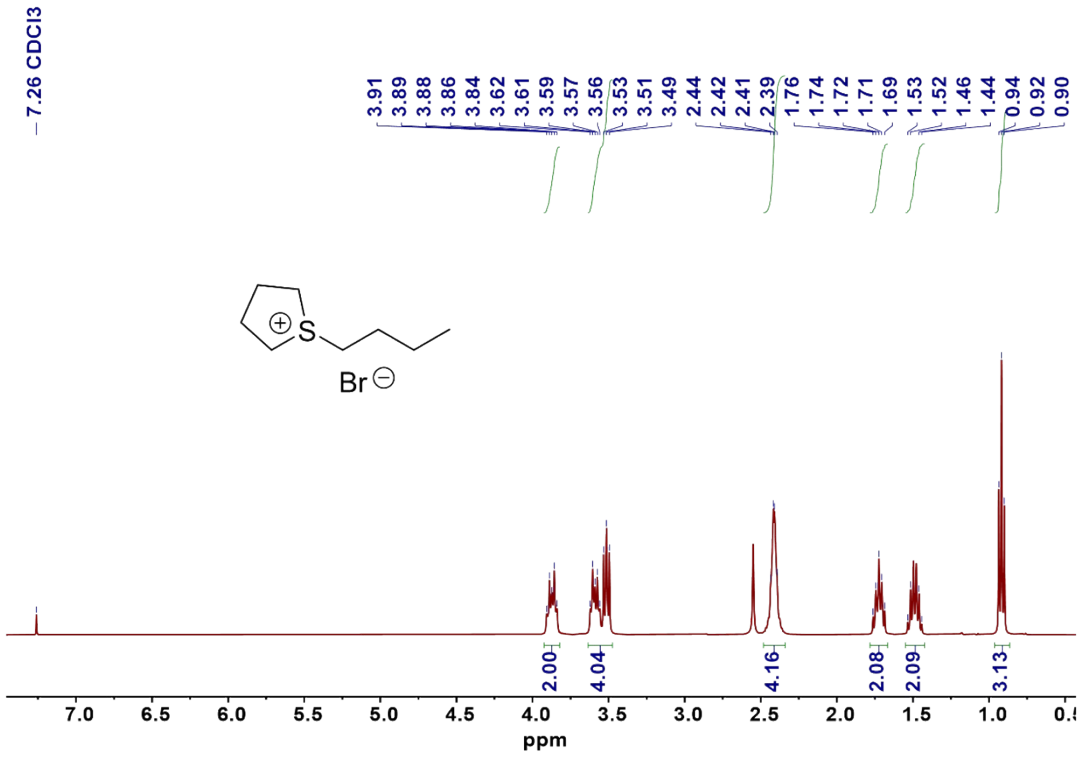


Figure S16. ^{1}H NMR spectrum (D2O, 400 MHz) of **THTBu-Br**

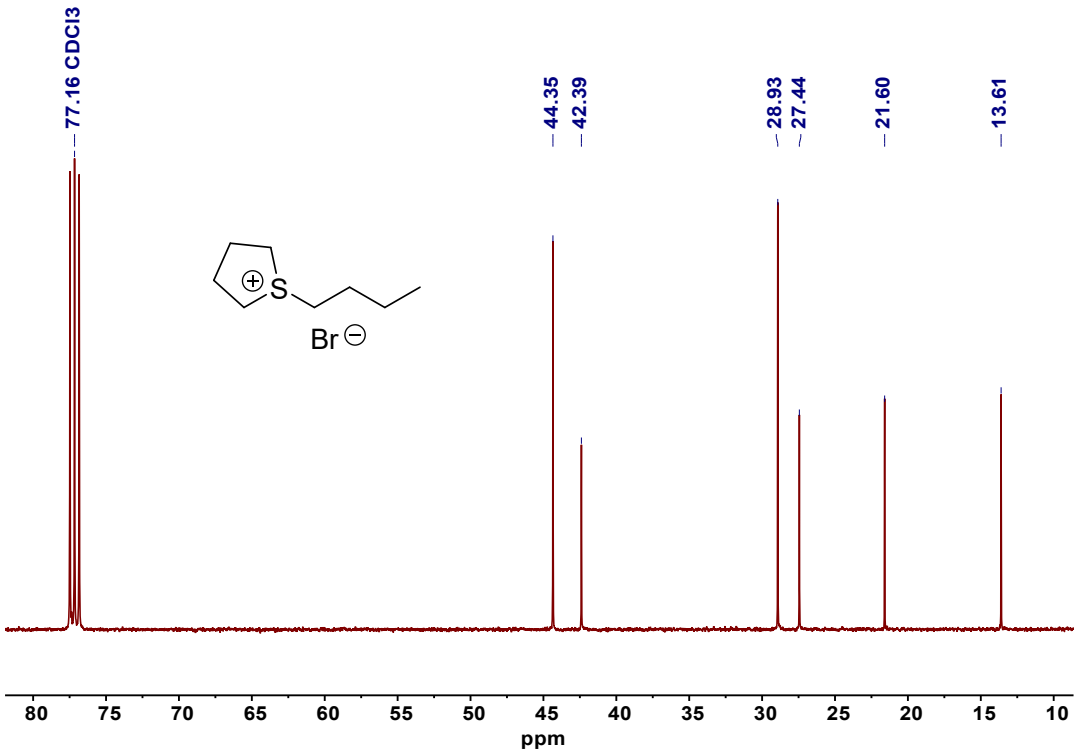


Figure S17. ^{13}C NMR spectrum (D2O, 101 MHz) of **THTBu-Br**

Copies of NMR spectra of cyclic carbonates (Figure S18 – Figure S41)

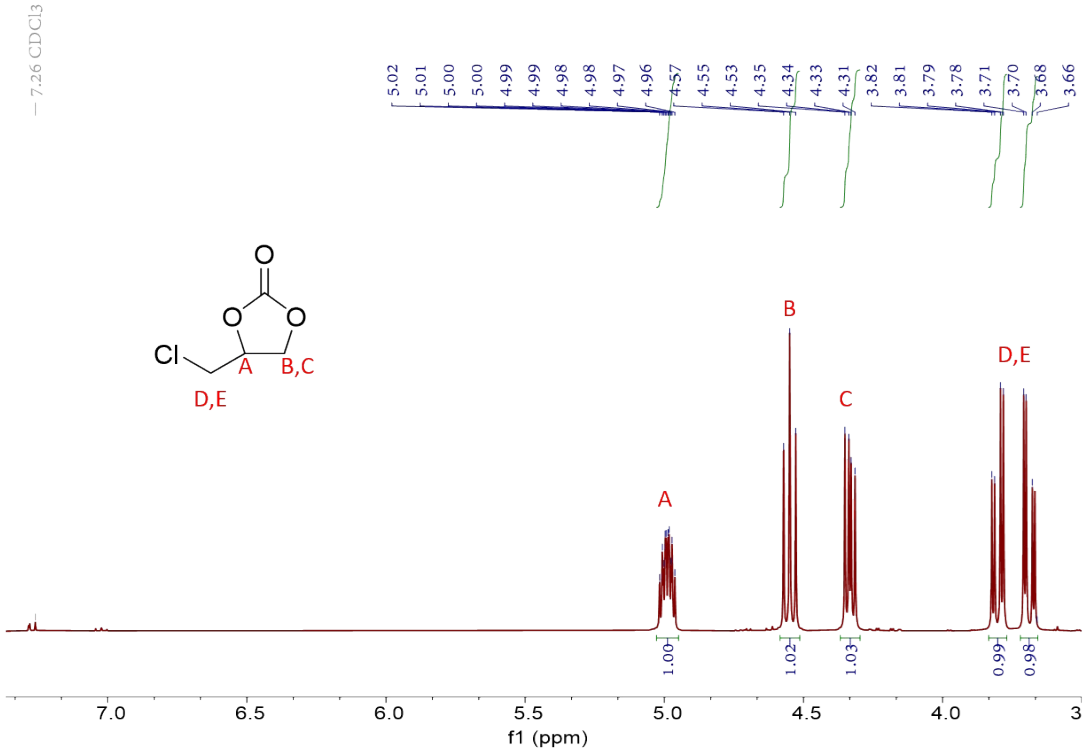


Figure S18. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 3-Chloropropylene carbonate (obtained from crude reaction mass)

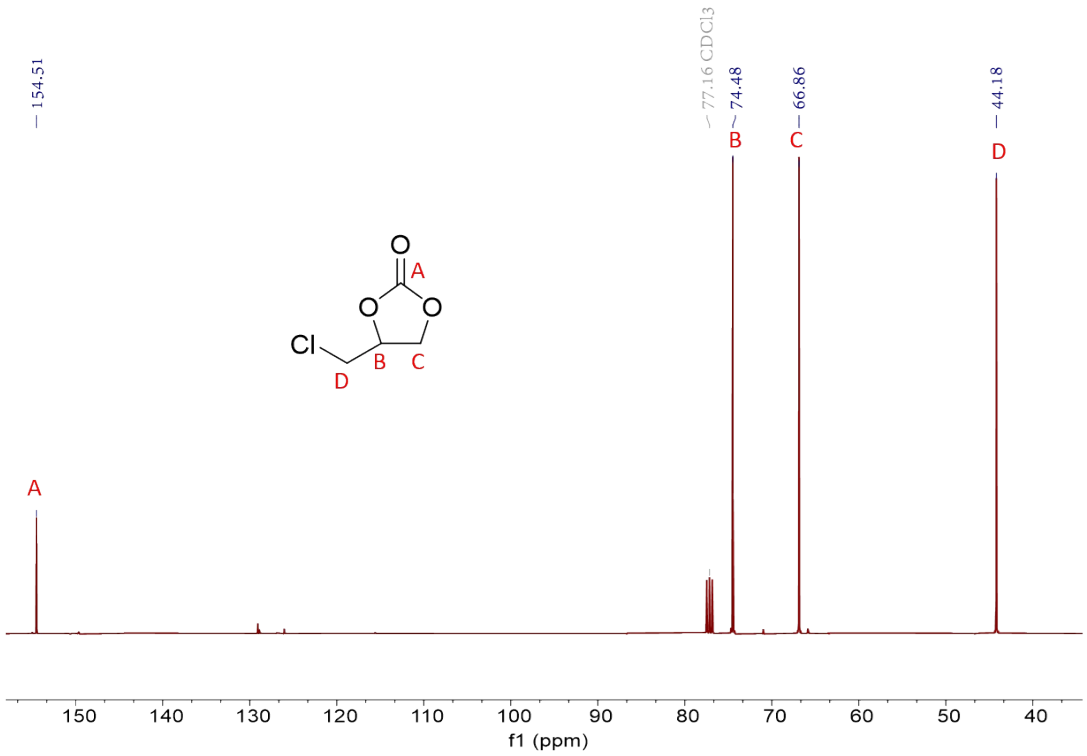


Figure S19. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 3-Chloropropylene carbonate (obtained from crude reaction mass)

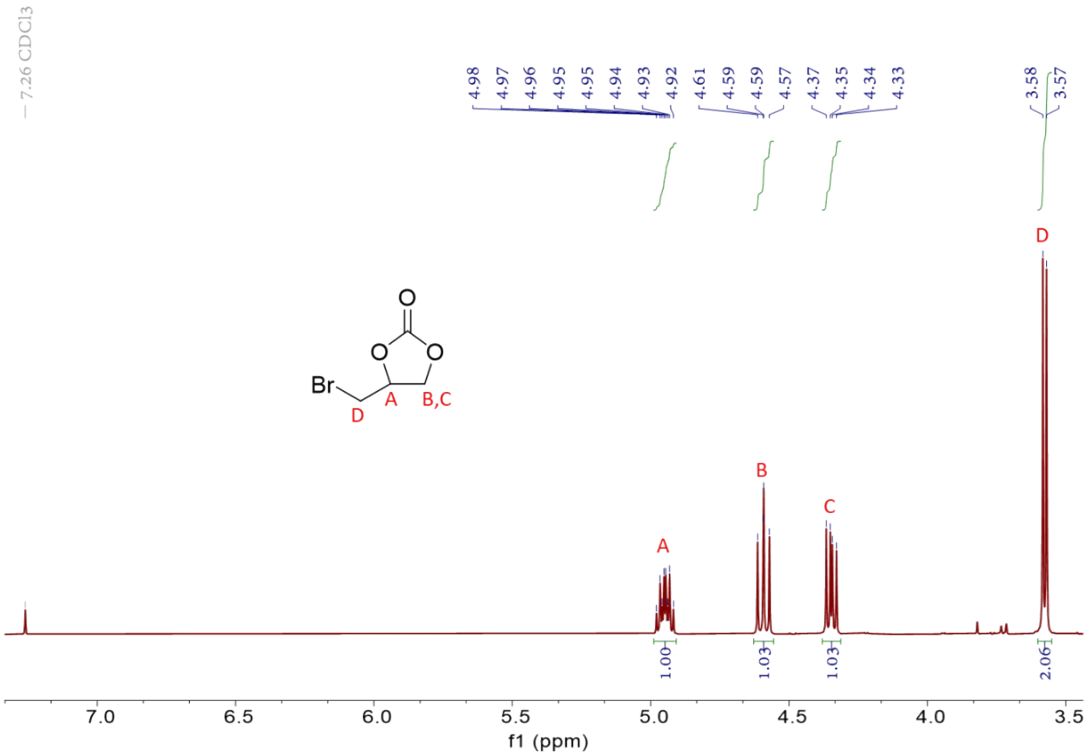


Figure S20. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4-(bromomethyl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

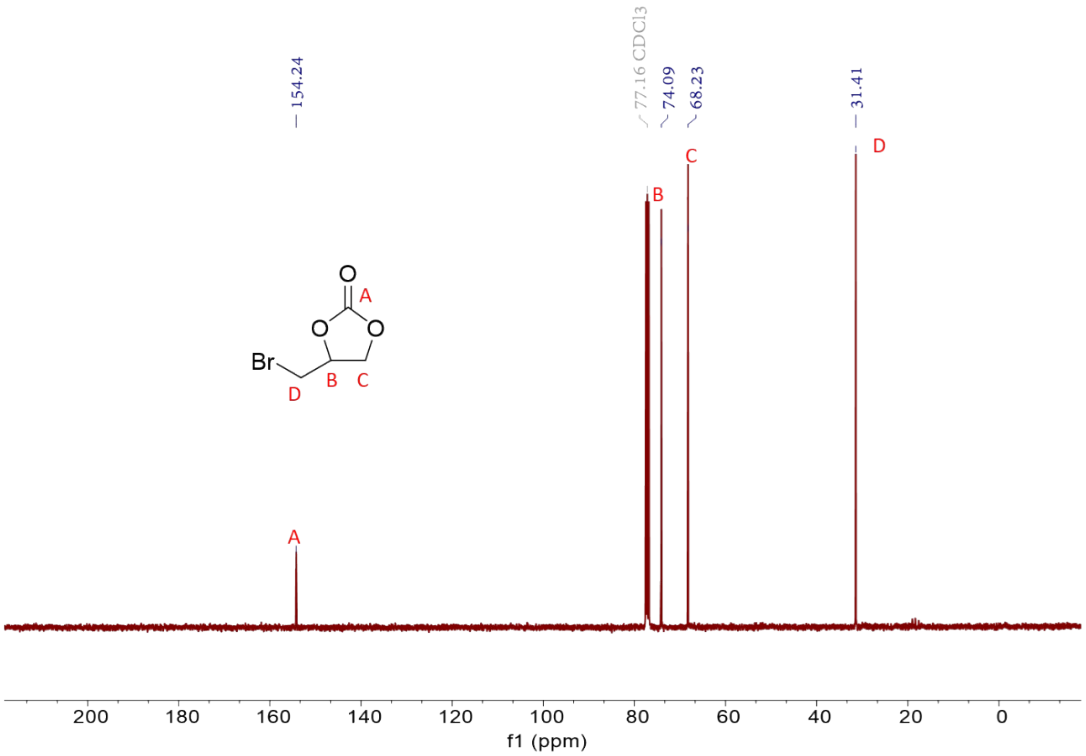


Figure S21. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 4-(bromomethyl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

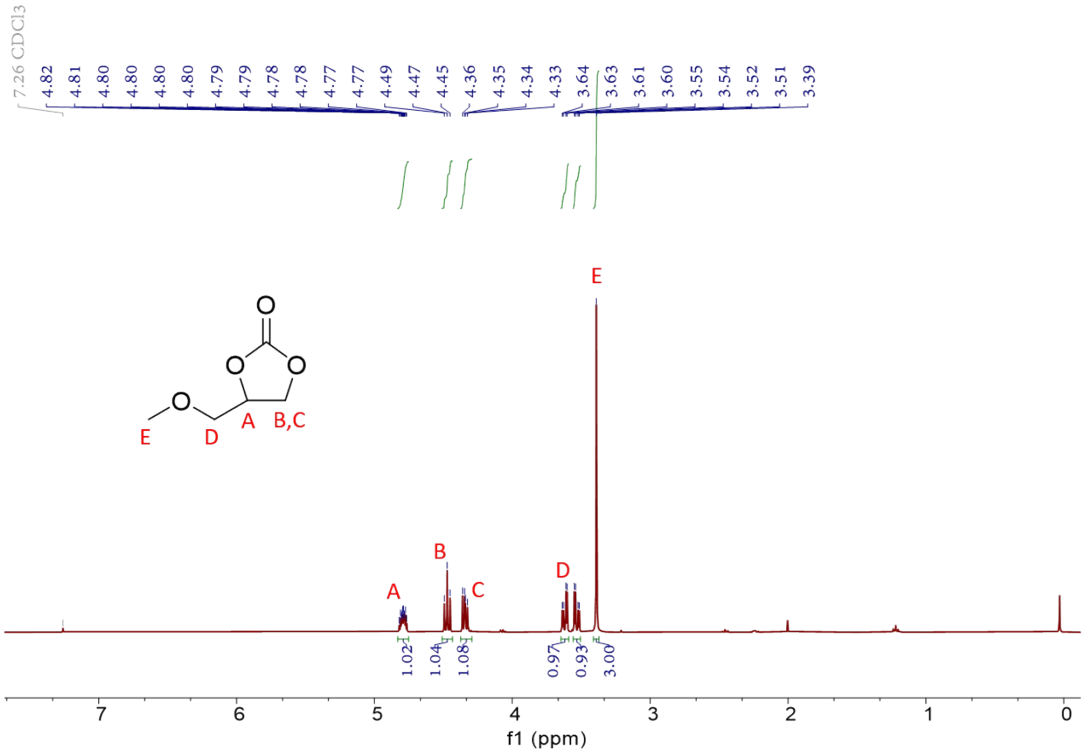


Figure S22. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4-(methoxymethyl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

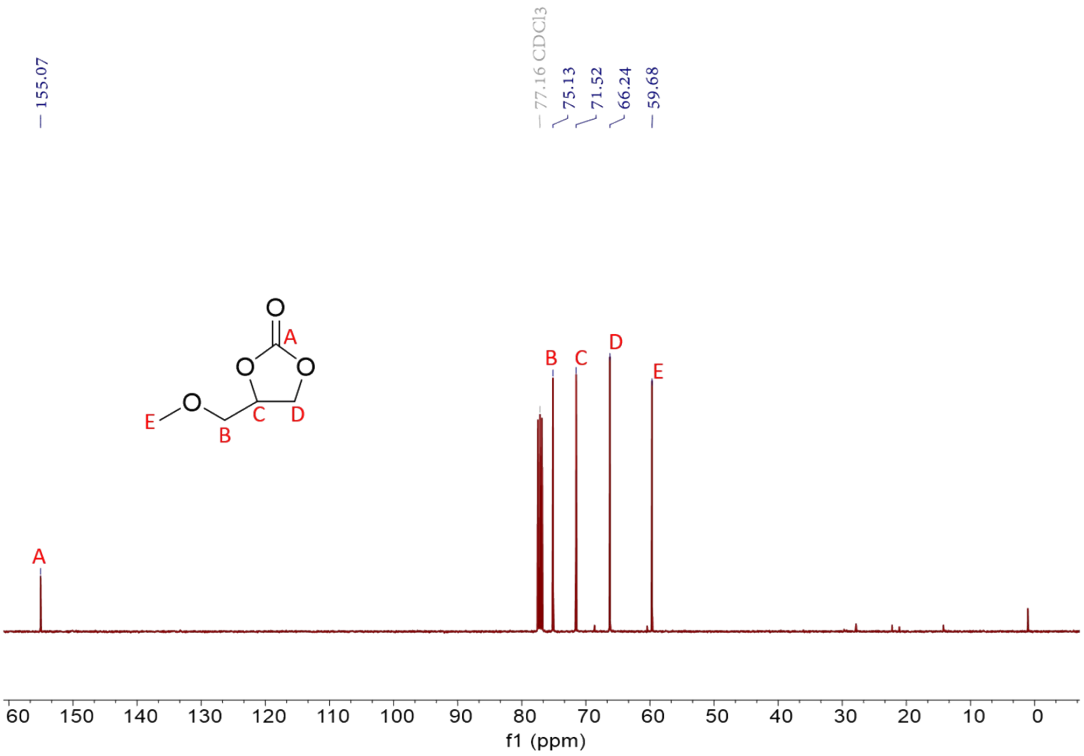


Figure S23. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 4-(methoxymethyl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

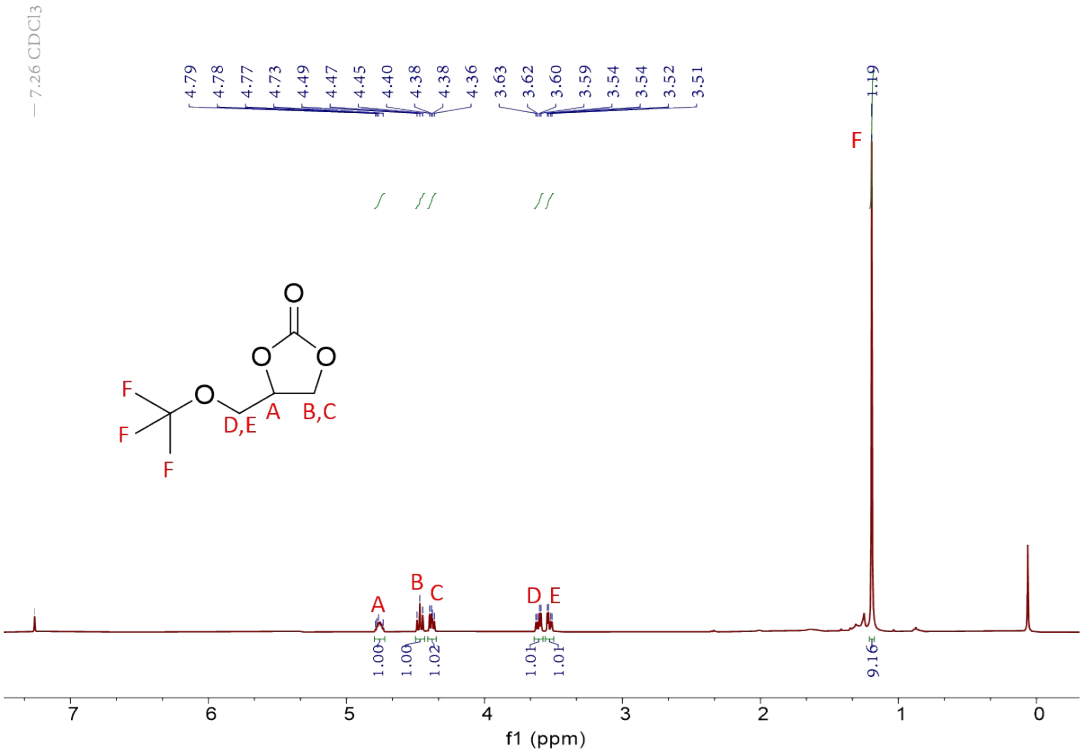


Figure S24 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4-(tert-butoxymethyl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

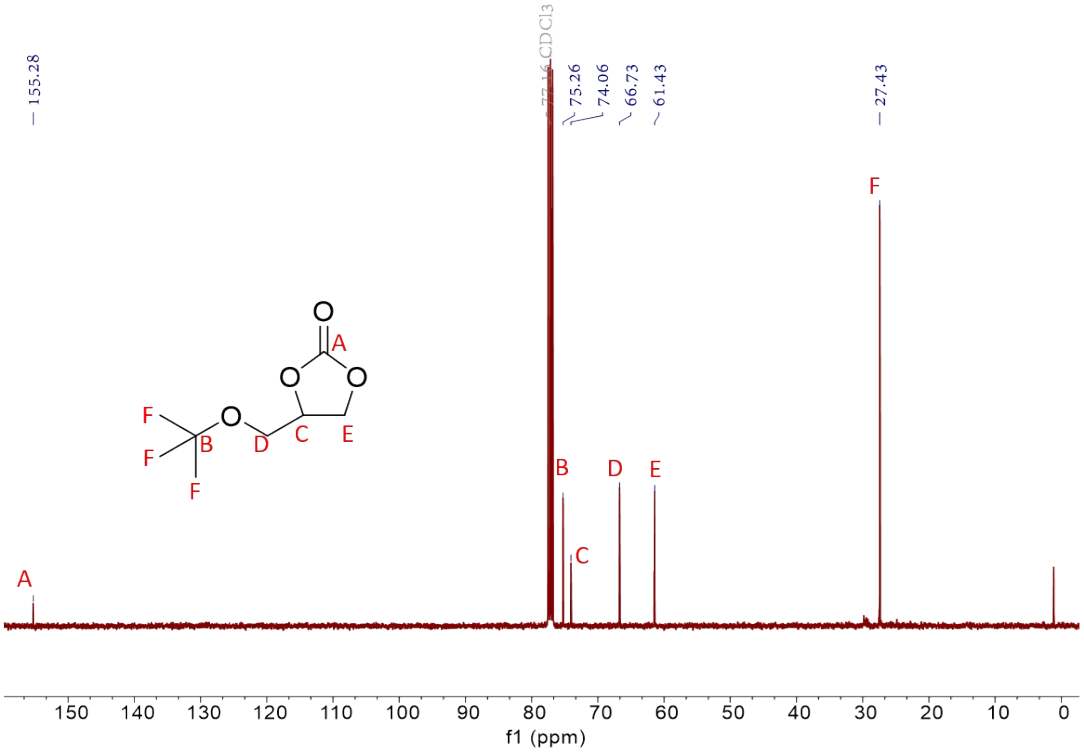


Figure S25. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 4-(tert-butoxymethyl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

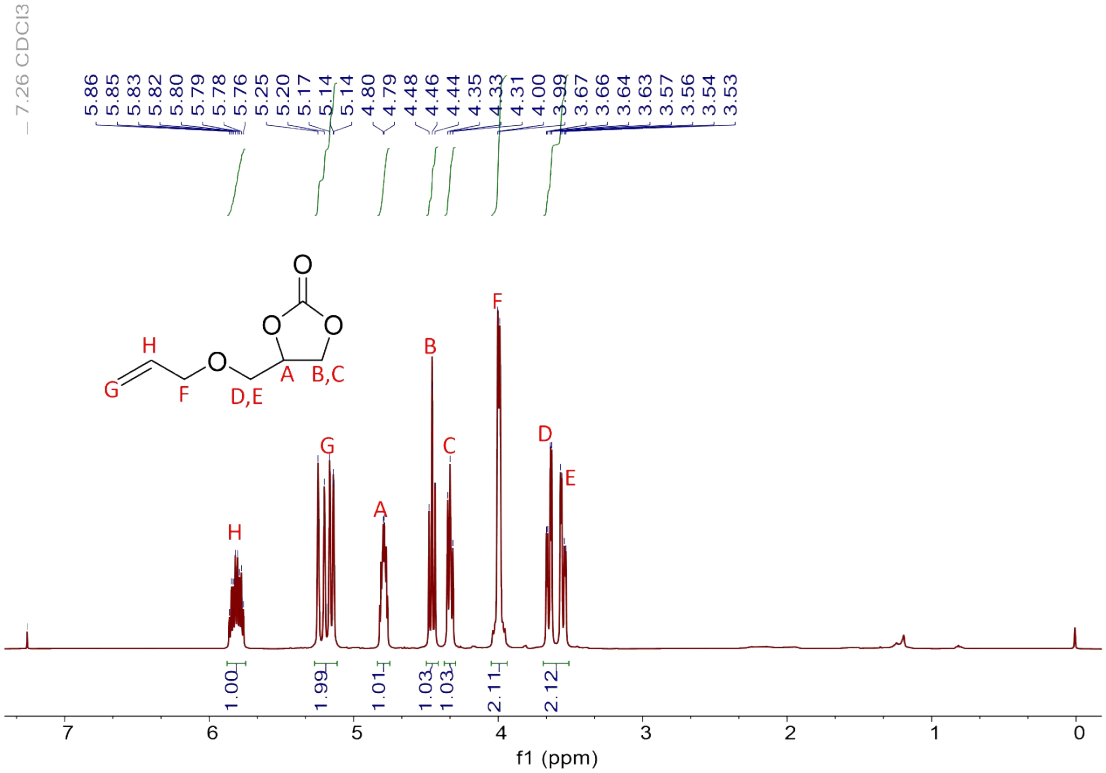


Figure S26. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4-((allyloxy)methyl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

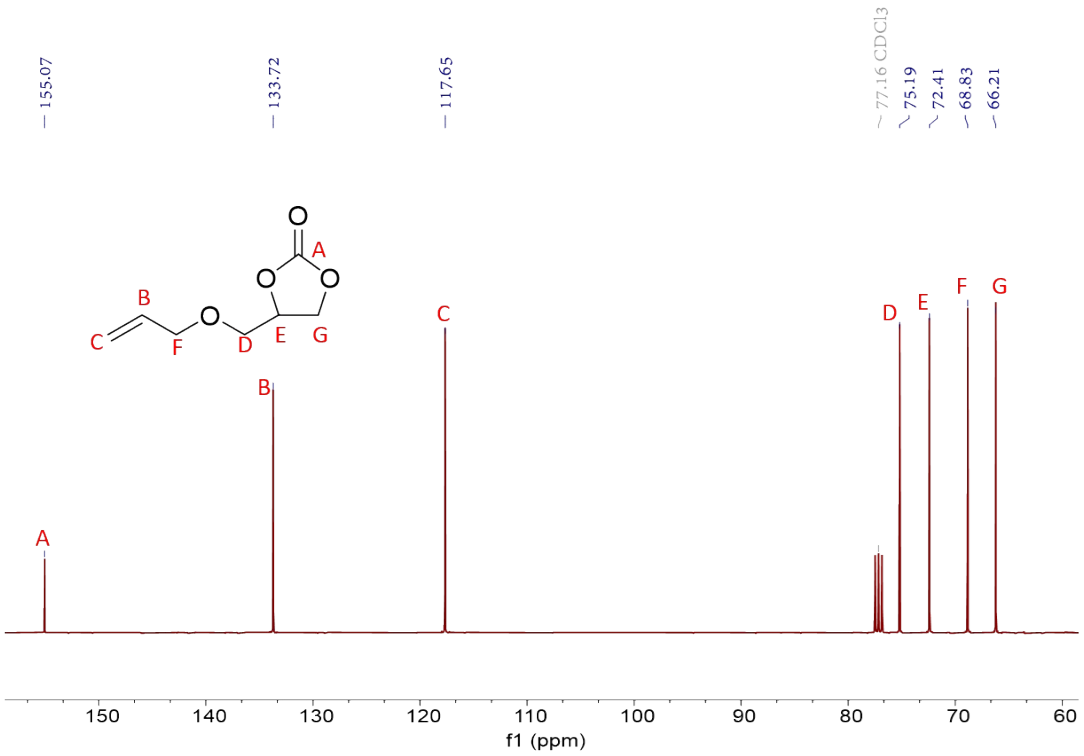


Figure S27. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 4-((allyloxy)methyl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

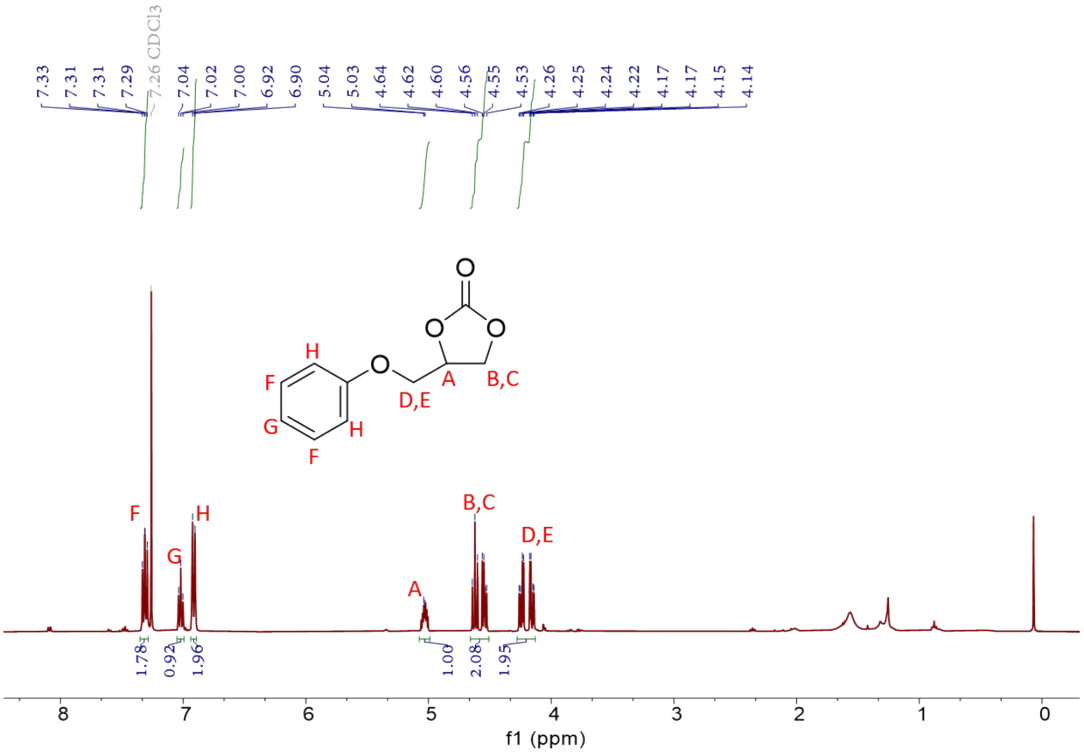


Figure S28 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4-(phenoxymethyl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

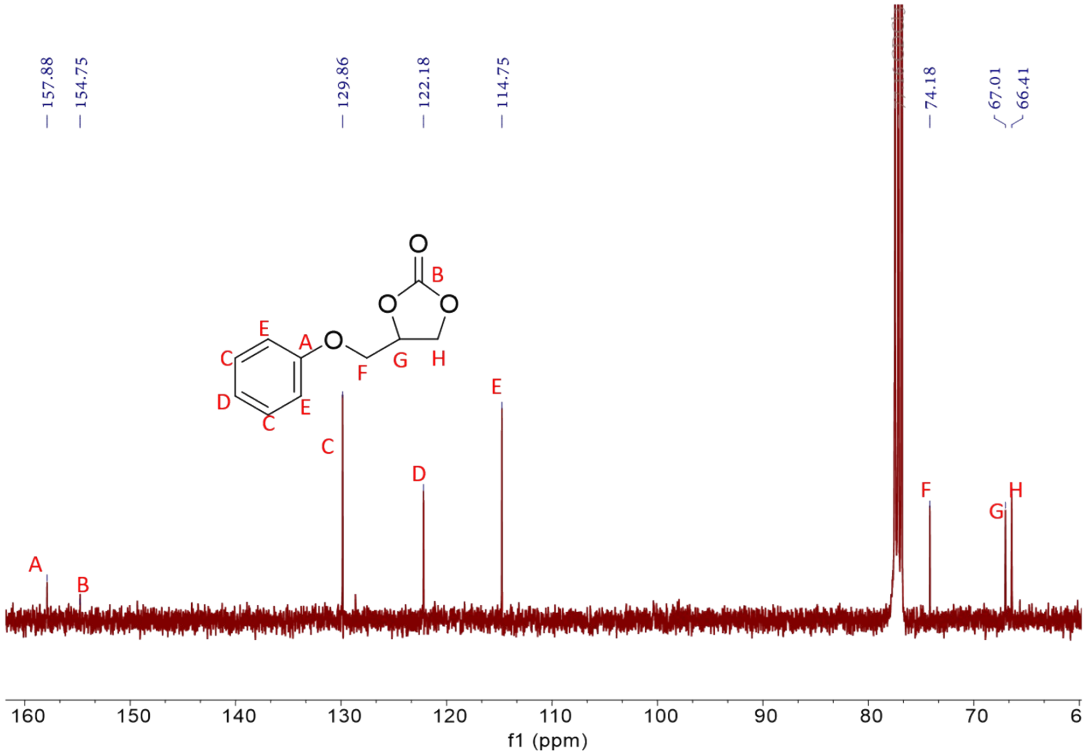


Figure S29. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 4-(phenoxymethyl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

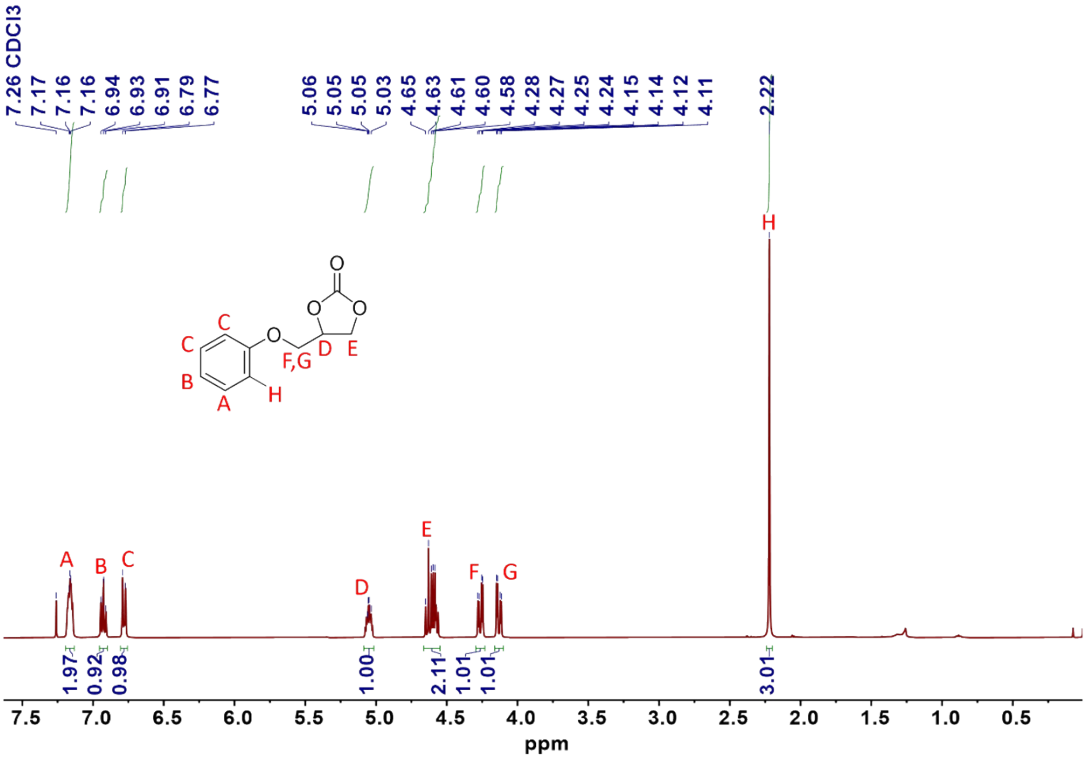


Figure S30 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4-((o-tolyloxy) methyl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

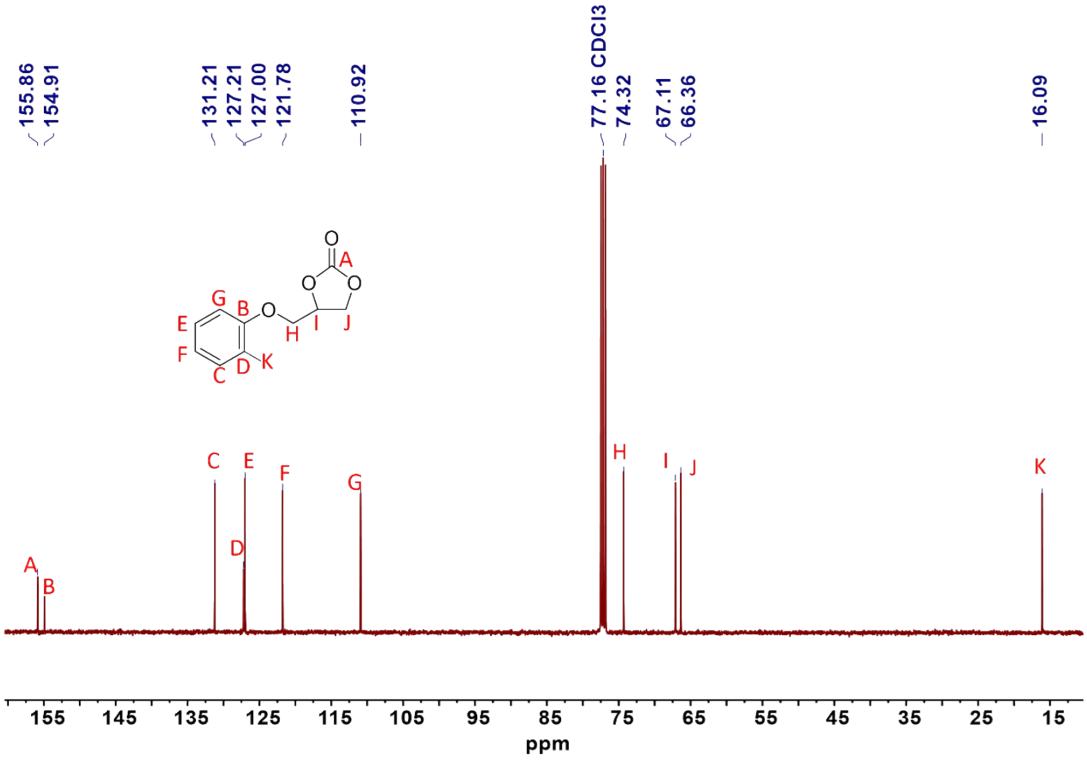


Figure S31 ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 4-((o-tolyloxy) methyl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

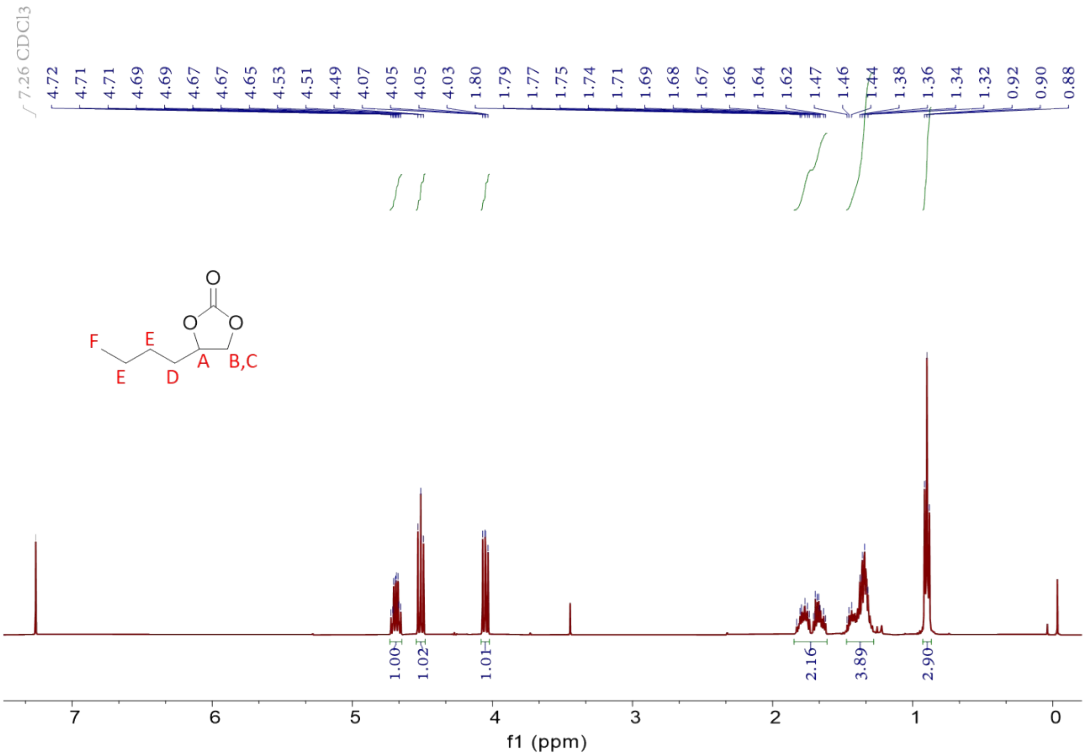


Figure S32. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4-butyl-1,3-dioxane-2-one (obtained from crude reaction mass)

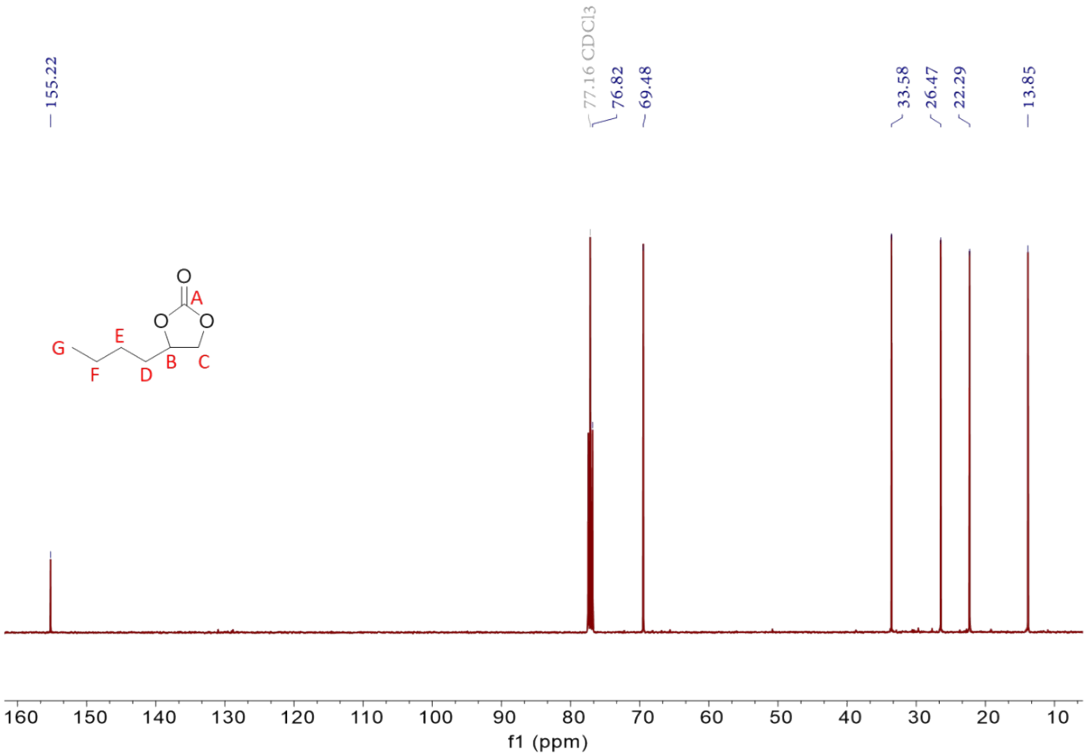


Figure S33. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 4-butyl-1,3-dioxane-2-one (obtained from crude reaction mass)

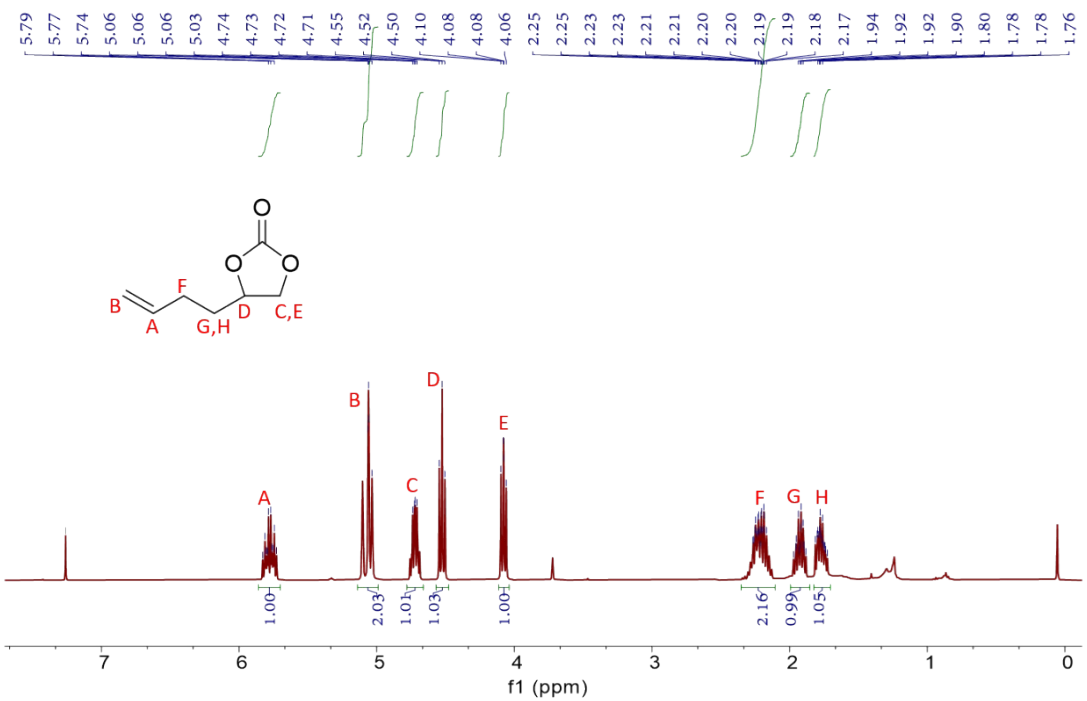


Figure S34. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of cyclic carbonate 4-(but-3-en-1-yl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

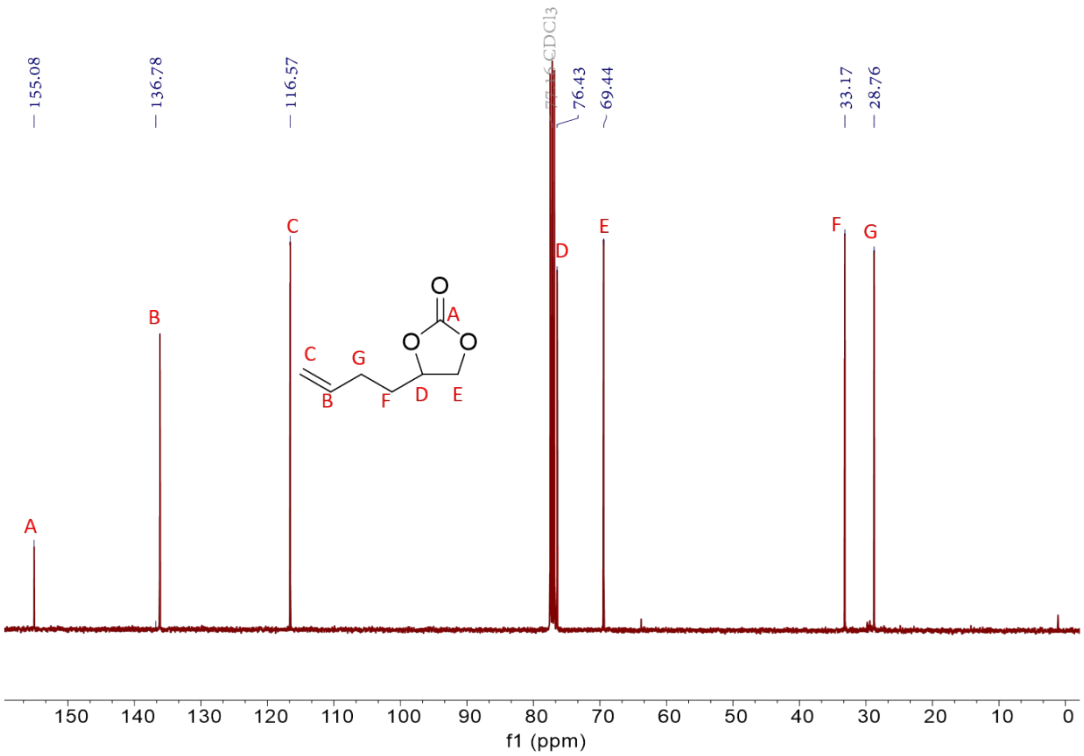


Figure S35. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 4-(but-3-en-1-yl)-1,3-dioxolan-2-one (obtained from crude reaction mass)

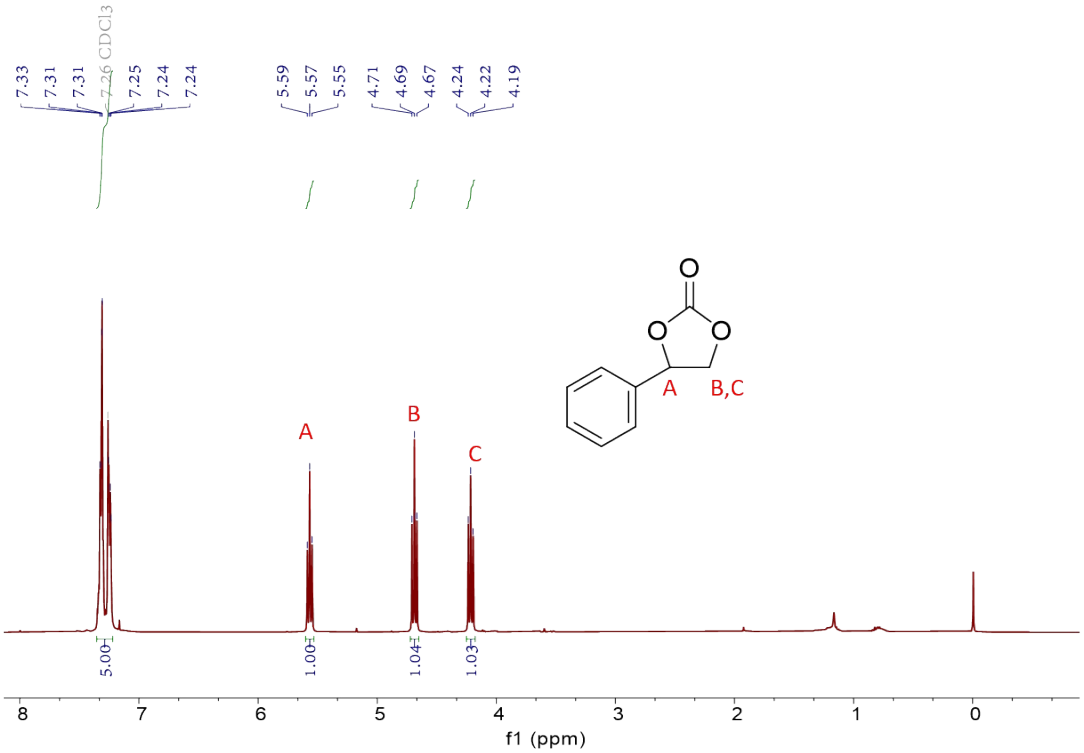


Figure S36. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4-phenyl-1,3-dioxolan-2-one (obtained from crude reaction mass)

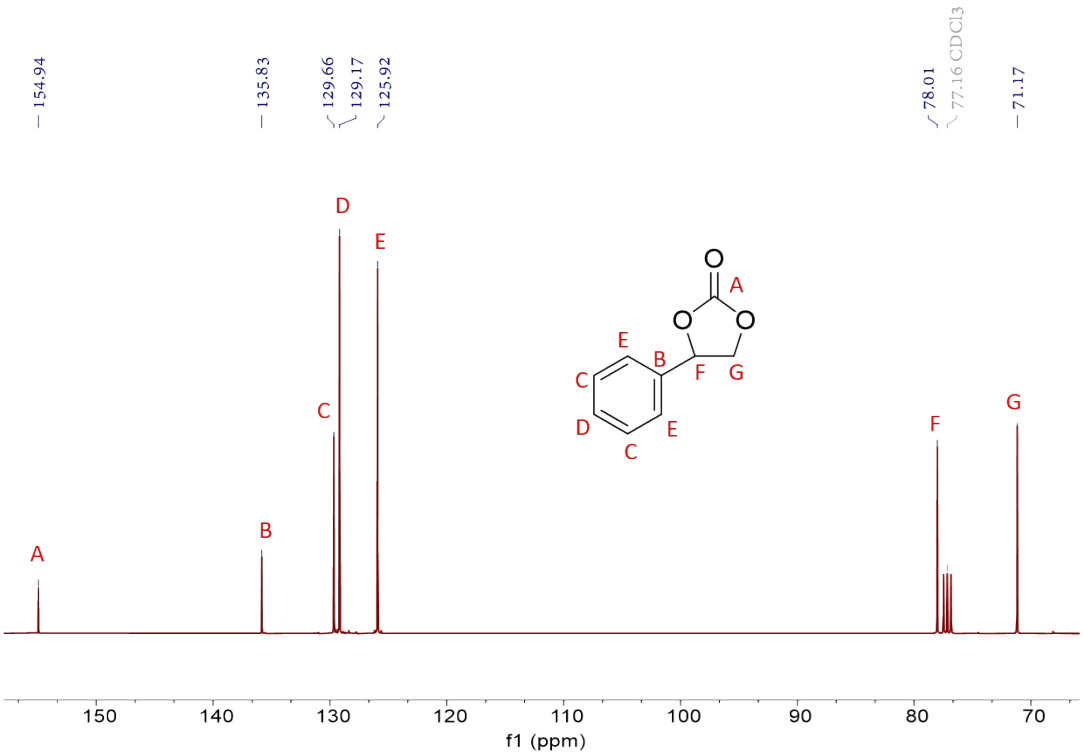


Figure S37. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 4-phenyl-1,3-dioxolan-2-one (obtained from crude reaction mass)

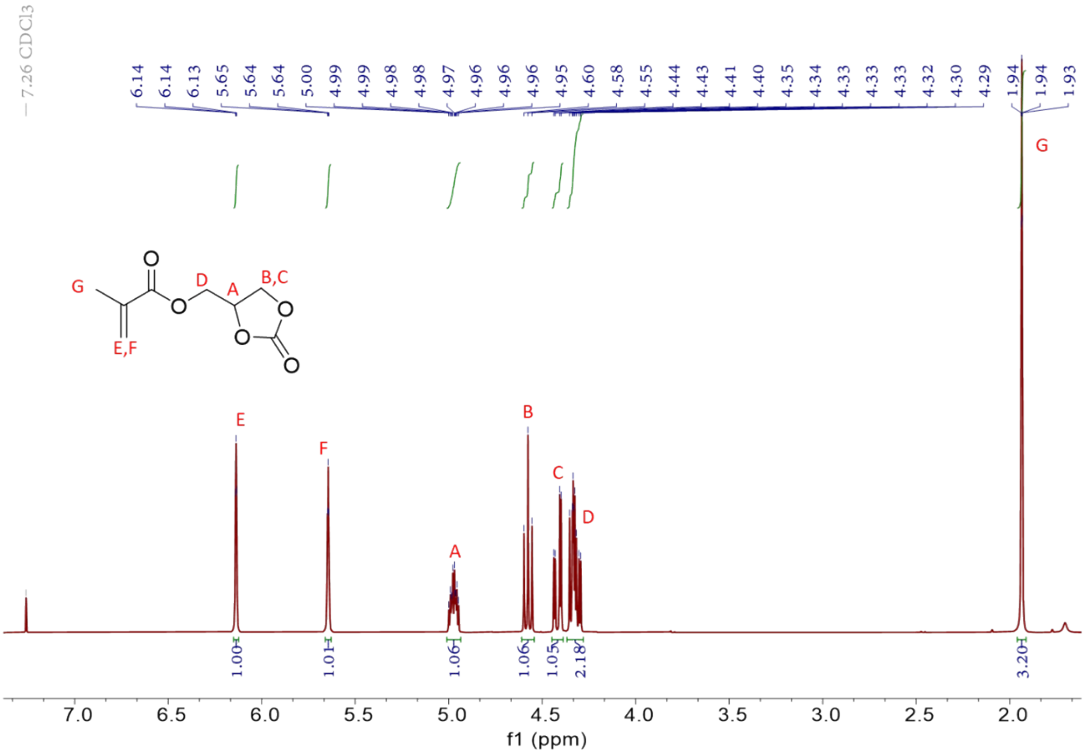


Figure S38. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 2-(Oxo-1,3-dioxalan-4-yl)methyl methacrylate (obtained from crude reaction mass)

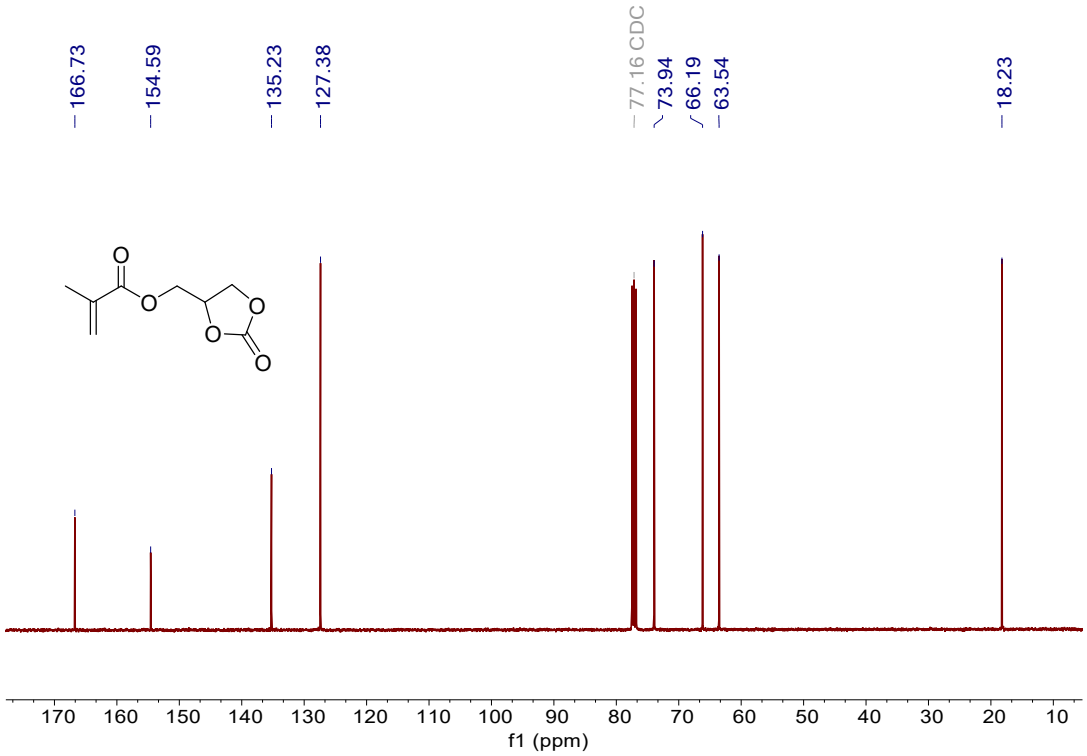


Figure S39. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 2-(Oxo-1,3-dioxalan-4-yl)methyl methacrylate (obtained from crude reaction mass)

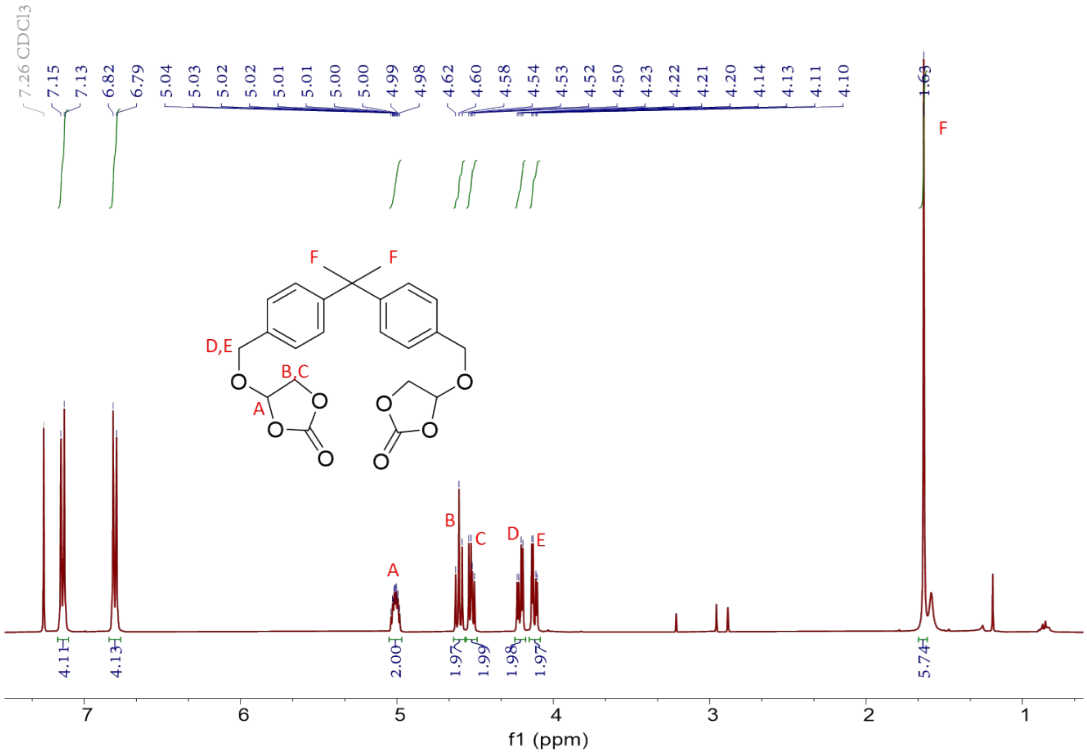


Figure S40. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 4,4'-(((Propane-2,2-diylbis(4,1-phenylene))bis(oxy)bis(methylene))bis(1,3-dioxolan-2-one) (obtained from crude reaction mass)

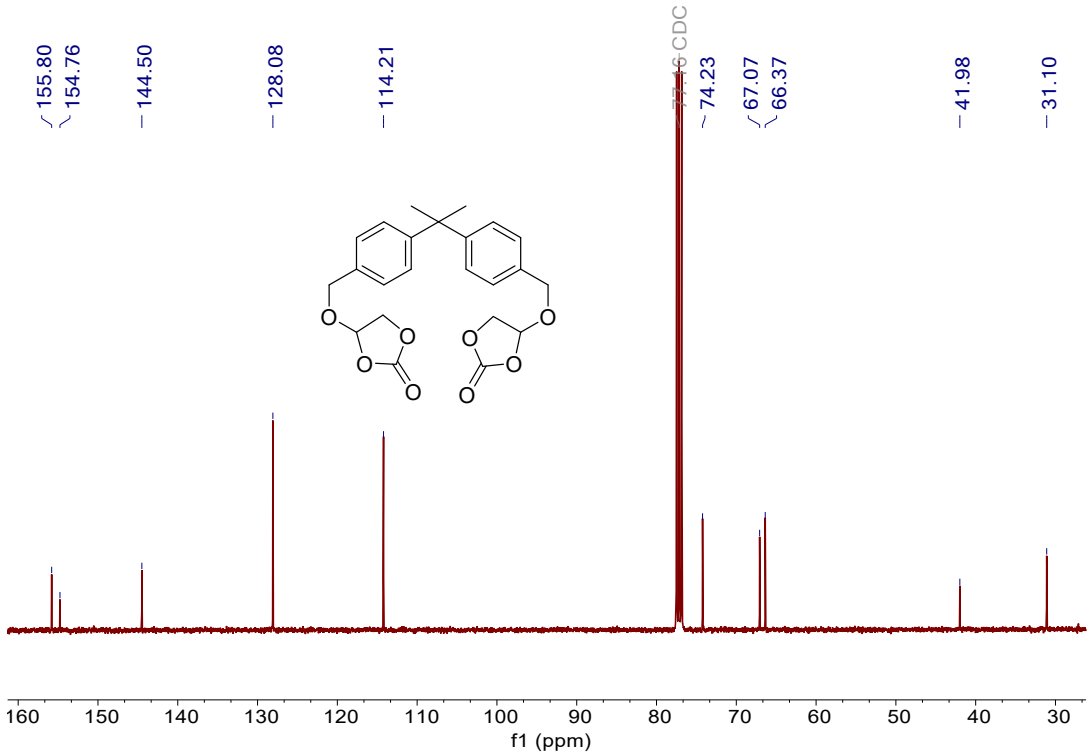


Figure S41. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of 4,4'-(((Propane-2,2-diylbis(4,1-phenylene))bis(oxy)bis(methylene))bis(1,3-dioxolan-2-one) (obtained from crude reaction mass)

5. Thermogravimetric analysis of catalysts (Figure S42 – Figure S48)

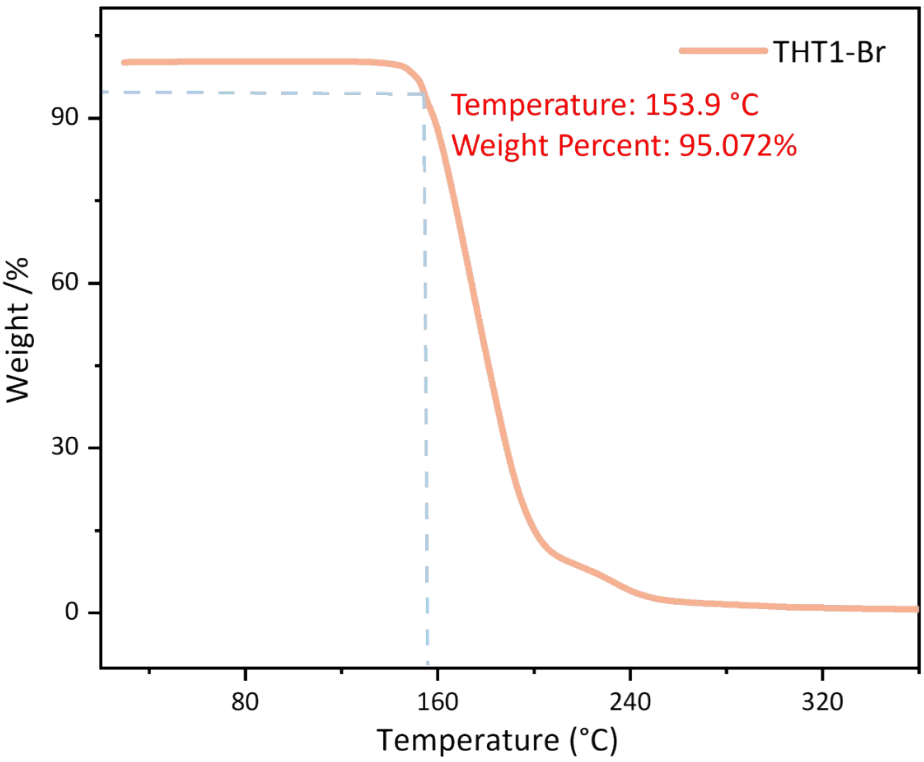


Figure S42. Thermogravimetric analysis of catalyst **THT1-Br**

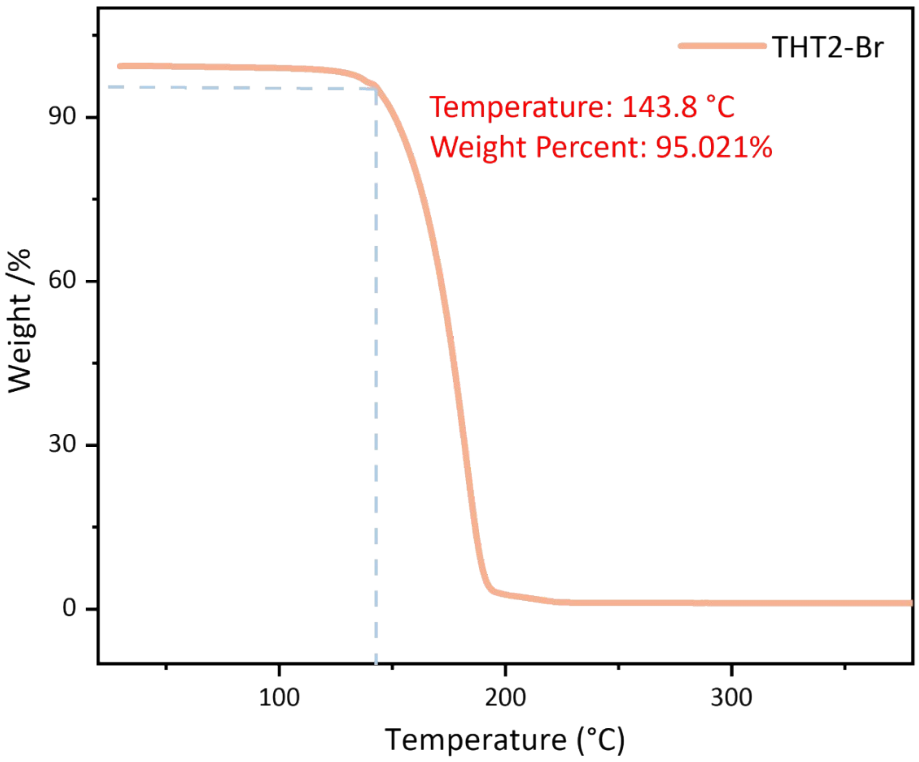


Figure S43. Thermogravimetric analysis of catalyst **THT2-Br**

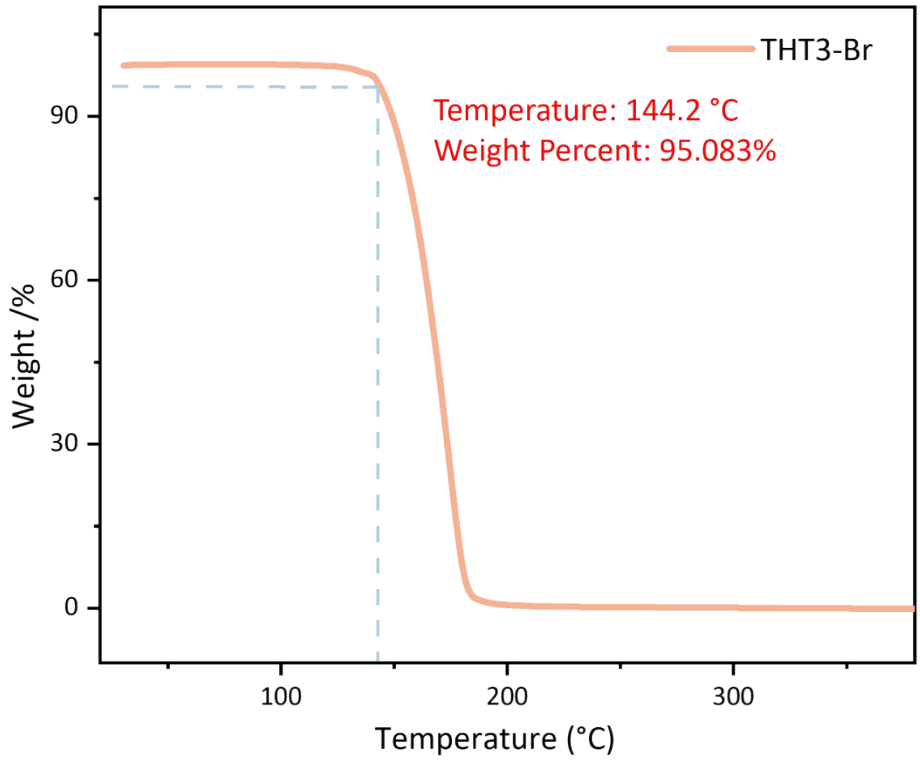


Figure S44. Thermogravimetric analysis of catalyst **THT3-Br**

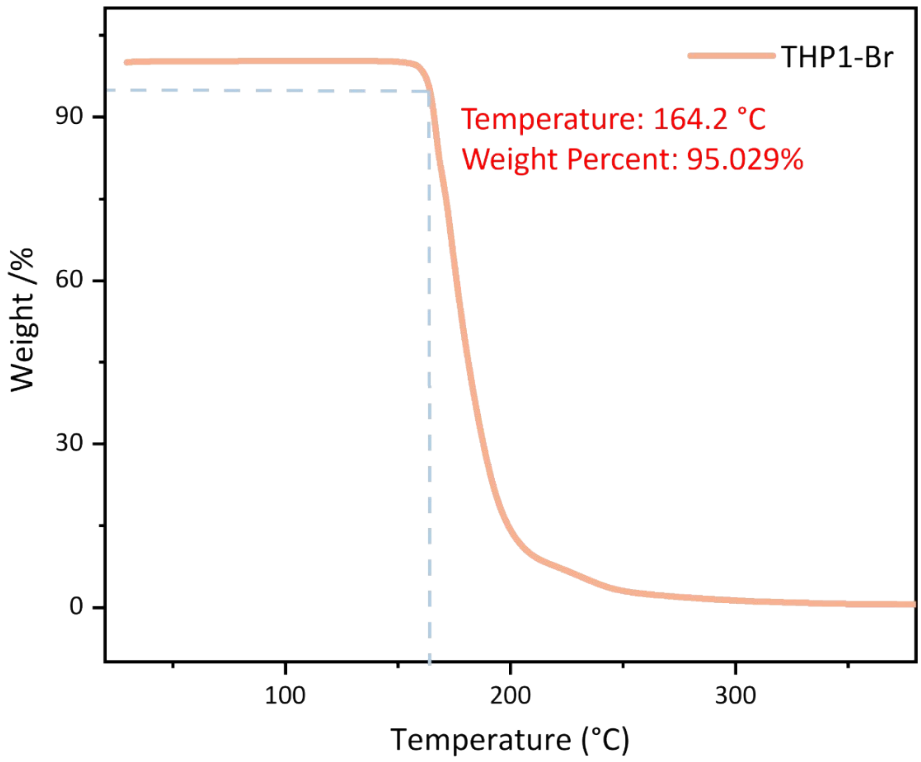


Figure S45. Thermogravimetric analysis of catalyst **THP1-Br**

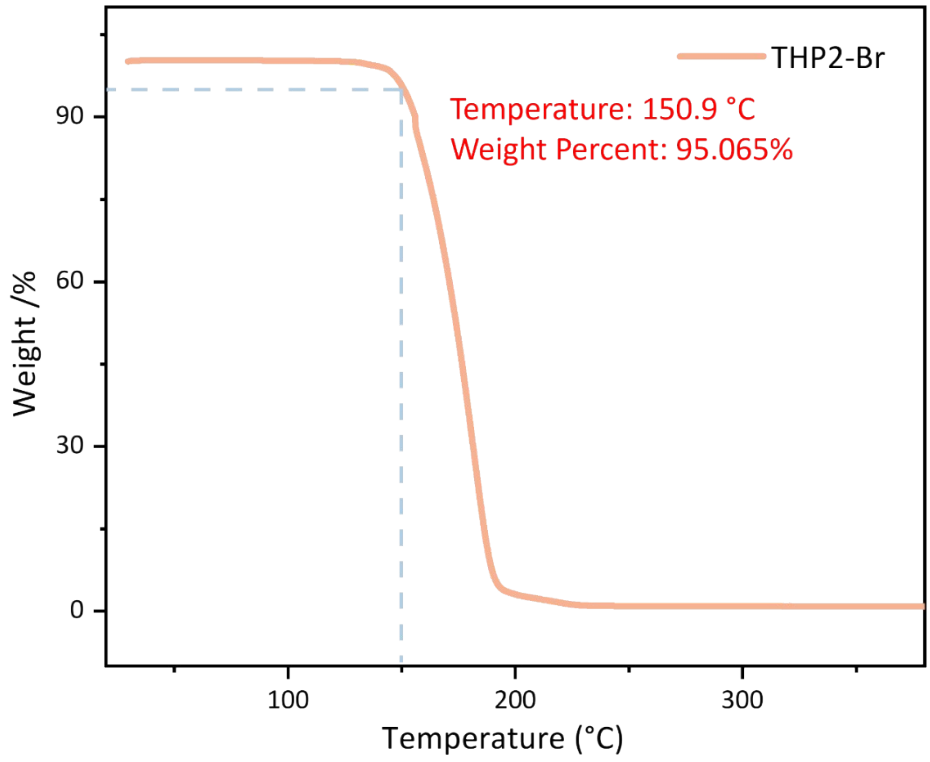


Figure S46. Thermogravimetric analysis of catalyst **THP2-Br**

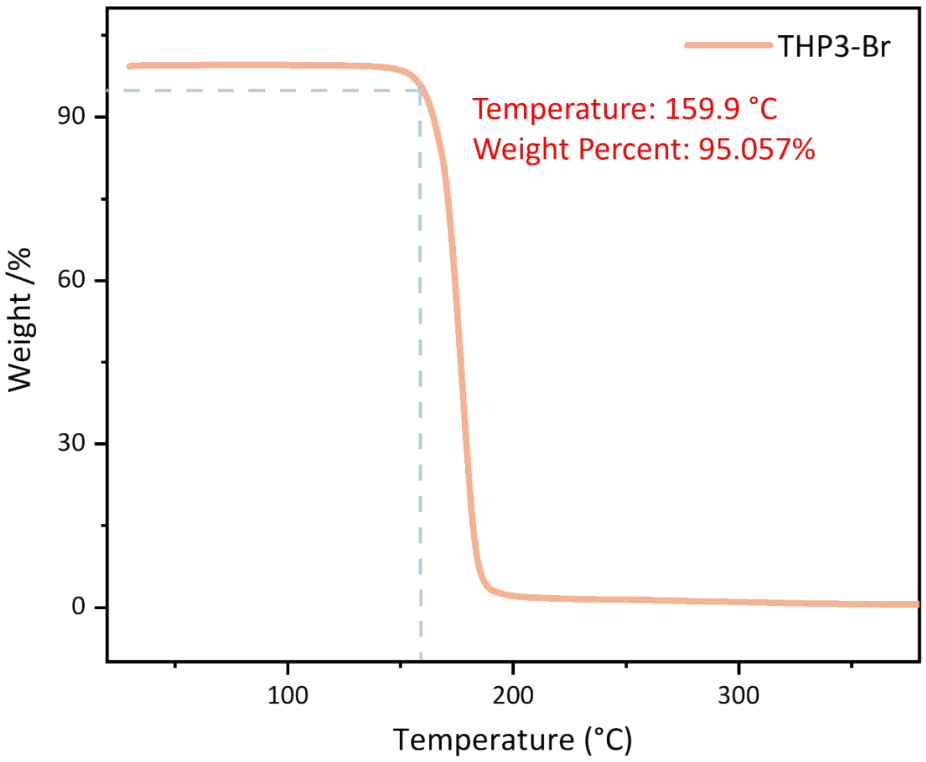


Figure S47. Thermogravimetric analysis of catalyst **THP3-Br**

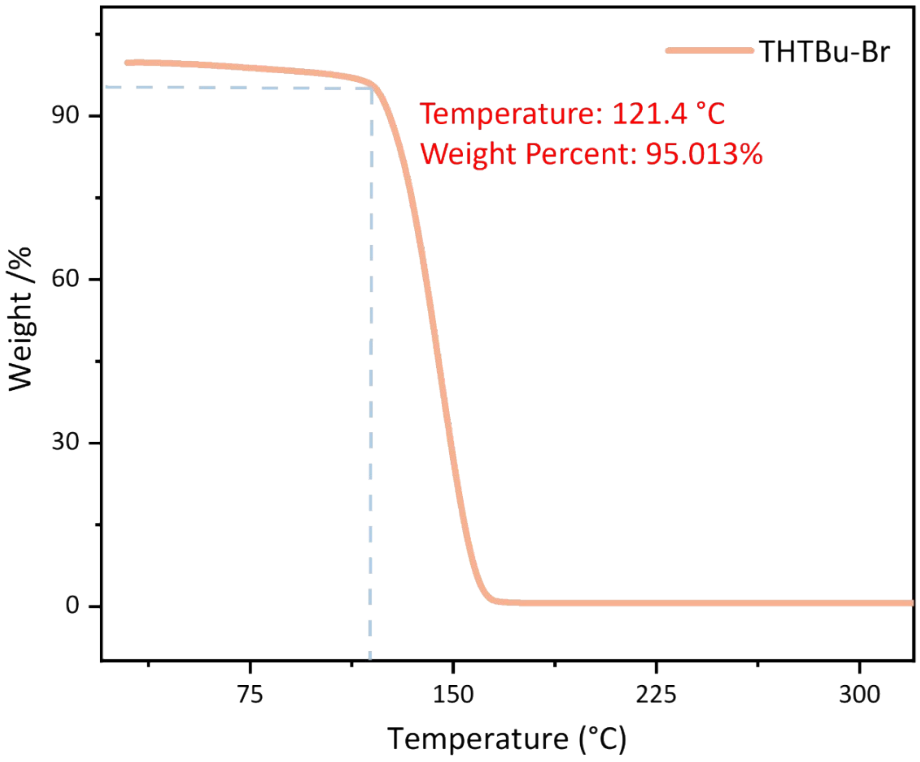


Figure S48. Thermogravimetric analysis of catalyst **THTBu-Br**

6. NMR Titration of catalyst and styrene oxide (SO) (Figure S49 – Figure S52)

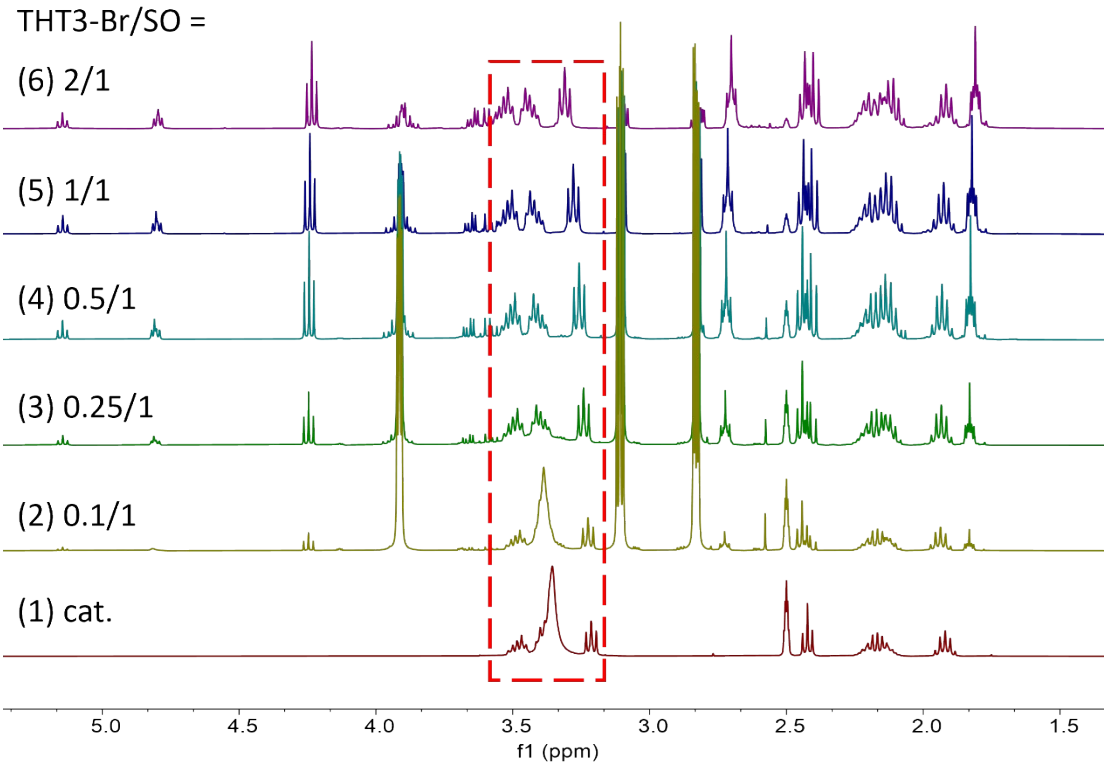


Figure S49. Full scale of ^{1}H NMR titration in DMSO-d_6: catalyst THT3-Br / SO ratios (1) 1/0, (2) 0.1/1, (3) 0.25/1, (4) 0.5/1, (5) 1/1, (6) 2/1.

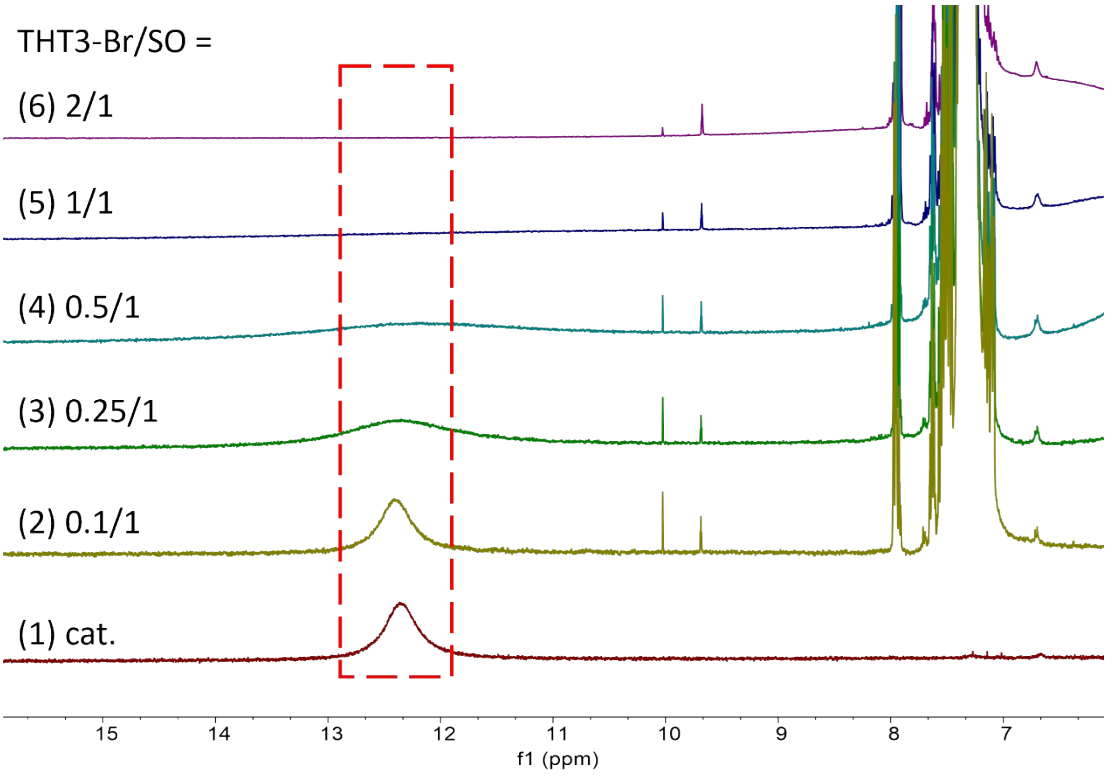


Figure S50. The proton of carboxylic acid ^{1}H NMR titration in DMSO-d_6: catalyst THT3-Br / SO ratios (1) 1/0, (2) 0.1/1, (3) 0.25/1, (4) 0.5/1, (5) 1/1, (6) 2/1.

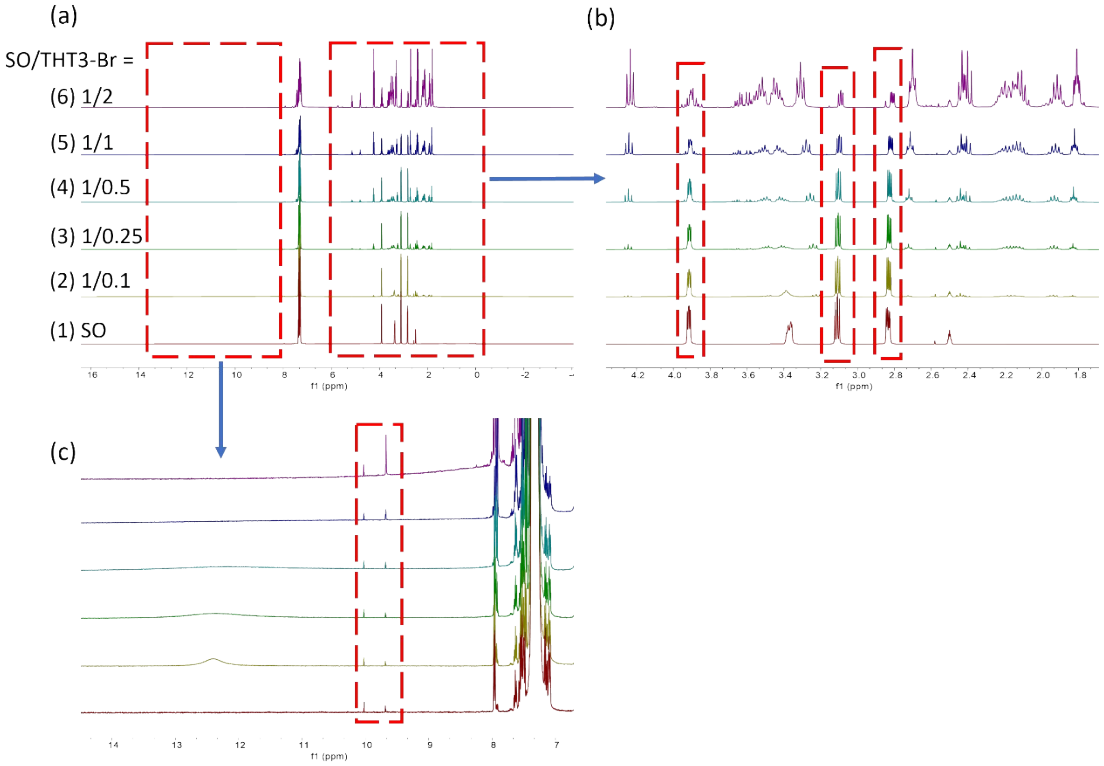


Figure S51 (a) Full scale of ^{1}H NMR titration in DMSO-d_6: catalyst THT3-Br / SO ratios (1) 0/1, (2) 0.1/1, (3) 0.25/1, (4) 0.5/1, (5) 1/1, (6) 2/1.; (b) The chemical shift of methylene and methine proton of styrene oxide; (c) Scale of the chemical shift 7-14 ppm.

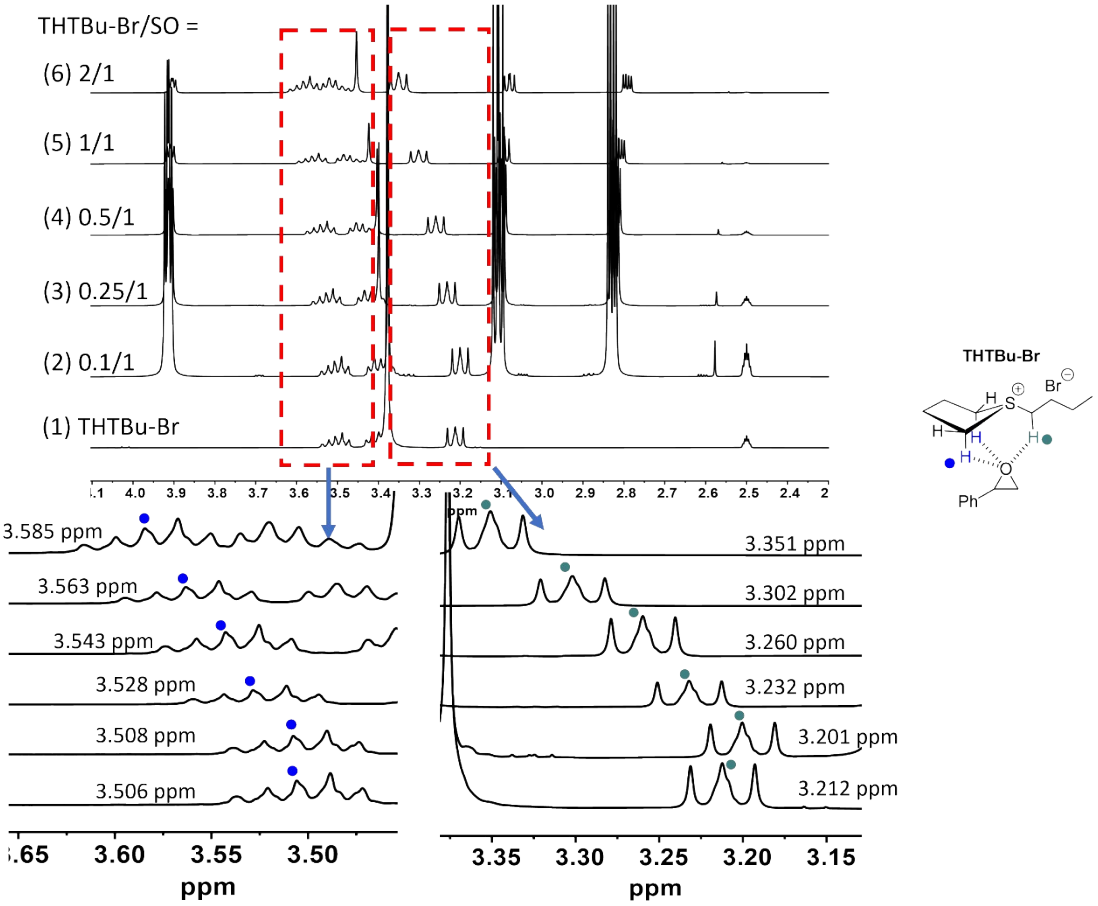


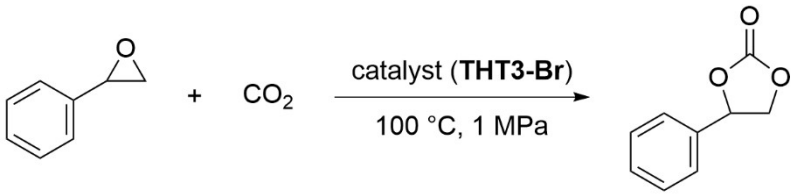
Figure S52 Full scale of ^{1}H NMR titration in DMSO-d_6: catalyst THTBu-Br / SO ratios (1) 1/0, (2) 0.1/1, (3) 0.25/1, (4) 0.5/1, (5) 1/1, (6) 2/1.

7. Supporting Tables (Page S41)

Table S1 Thermogravimetric Analysis of Catalysts

Entry	Catalyst	$T_{d5\%}$ /%	Temp. /°C
1	**THT1-Br**	95.072	153.9
2	**THT2-Br**	95.021	143.8
3	**THT3-Br**	95.083	144.2
4	**THP1-Br**	95.029	164.2
5	**THP2-Br**	95.065	150.9
6	**THP3-Br**	95.057	159.9
7	**THTBu-Br**	95.013	121.4

Table S2. Kinetic of catalyst **THT3-Br** for the synthesis of cyclic carbonate from styrene oxide (SO) and carbon dioxide. [a]



Entry	Time [h]	Conv. [b] [%]	Selec. [b] [%]
1	10	99	96
2	8	94	95
3	6	94	93
4	4	69	100
5	2	45	>99
6	1	23	>99
7	0.5	6	>99

[a] Conditions: temperature 100 °C, 5 mmol (0.57 mL) of styrene epoxide, 5 mol% catalyst loading of catalyst, CO_2 (1 MPa). [b] Determined by ^{1}H NMR with 1 mol% mesitylene as the internal standard.

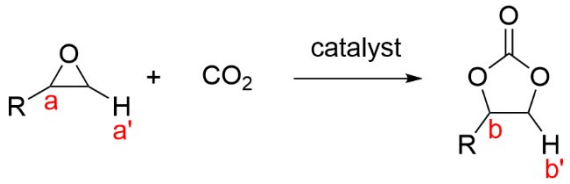
8. Copies and analysis of the ^{1}H NMR spectra of crude products (reaction mixture) of the CCE reactions (Figure S53 – Figure S91)

The CCE reaction mixture was cooled in ice before it was sampled for ^{1}H NMR measurements. The crude mixture of cyclic carbonate products was sampled of W_m mg, and then the W_i mg of internal standard mesitylene was added. Using 0.5 mL $CDCl_3$ or DMSO-d_6 to dissolve the mixture for ^{1}H NMR measurements. The integral values (I) of epoxides, cyclic carbonates and mesitylene (around 6.70 ppm) in ^{1}H NMR spectra were observed as I_e, I_c, and I_i. The molecular weights of cyclic carbonates are $M_{w,c}$, and mesitylene is $M_{w,i}$ (120.192 g/mol). The purity of mesitylene is P_i. The integral of proton in aromatic ring is I_{Ph}. The conversion (Conv.) and the selectivity were calculated from equation S1 (**eq. S1**) and equation S2 (**eq. S2**), respectively. Bisphenol A diglycidyl ether used DMF as solvent, the selectivity was calculated from equation S3 (**eq. S3**).

$$Conversion\ (\%) = \frac{I_c}{I_c + I_e} (eq. S1)$$

$$Selectivity\ of\ cyclic\ carbonate\ (\%) = \frac{3 \times W_i \times I_c \times M_{w,c} \times P_i}{M_{w,i} \times I_i \times W_m \times Conv.} (eq. S2)$$

$$Selectivity\ of\ cyclic\ carbonate\ (\%) = \frac{2 \times I_c}{I_{Ph} \times Conv.} (eq. S3)$$



Scheme S1. Cycloadditions of CO_2 into epoxides for cyclic carbonates

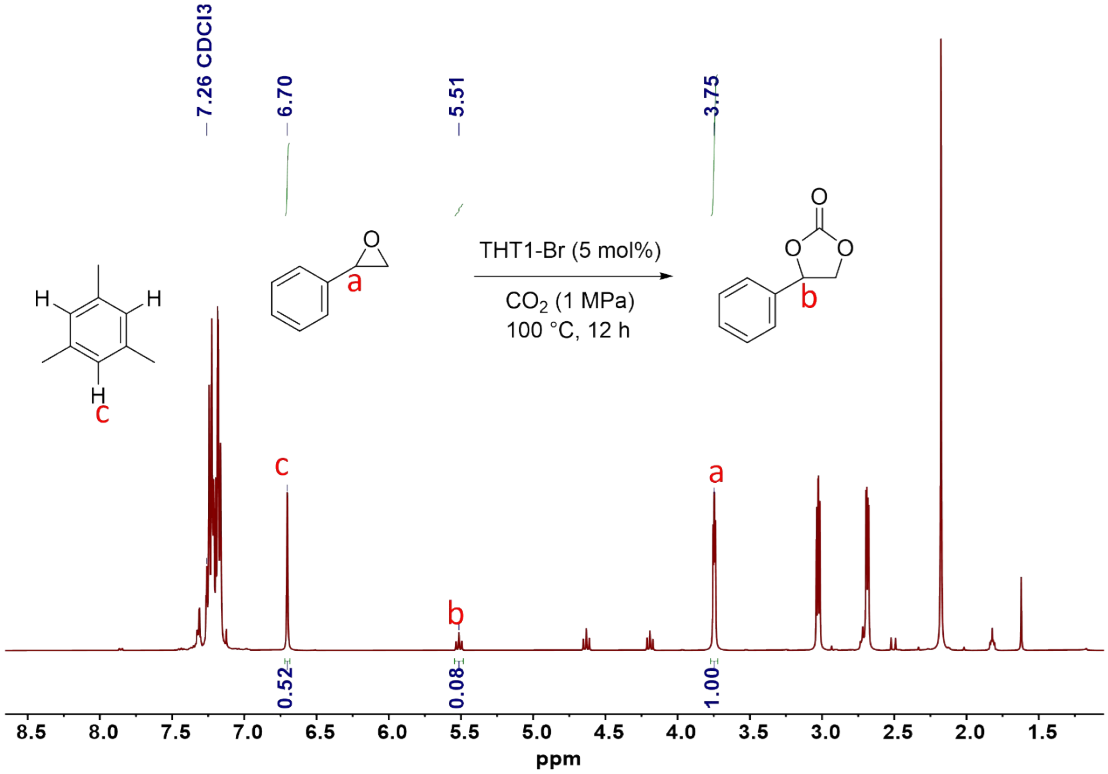


Figure S53. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THT1-Br (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, 58.1 mg crude mixture, 9.3 mg mesitylene (Table 1, entry 1). Conversion, 7%; selectivity, >99%.

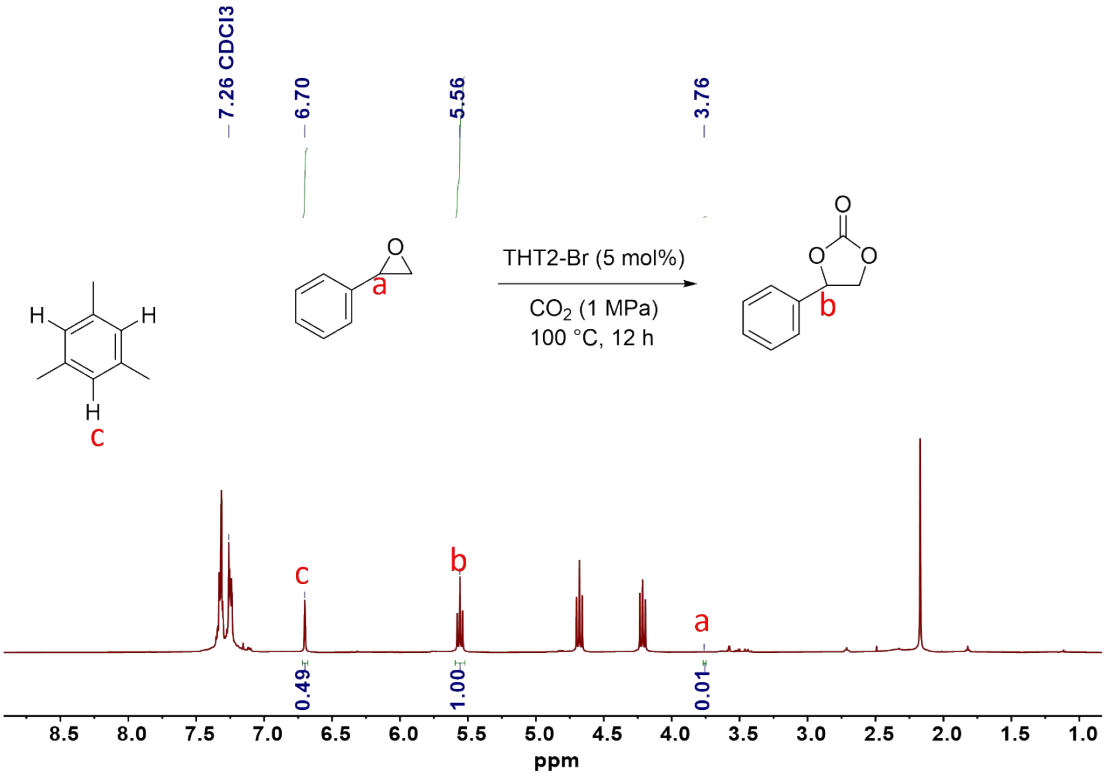


Figure S54. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THT2-Br (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, 82.5 mg crude mixture, 8.8 mg mesitylene (Table 1, entry 2). Conversion, >99%; selectivity, 88%.

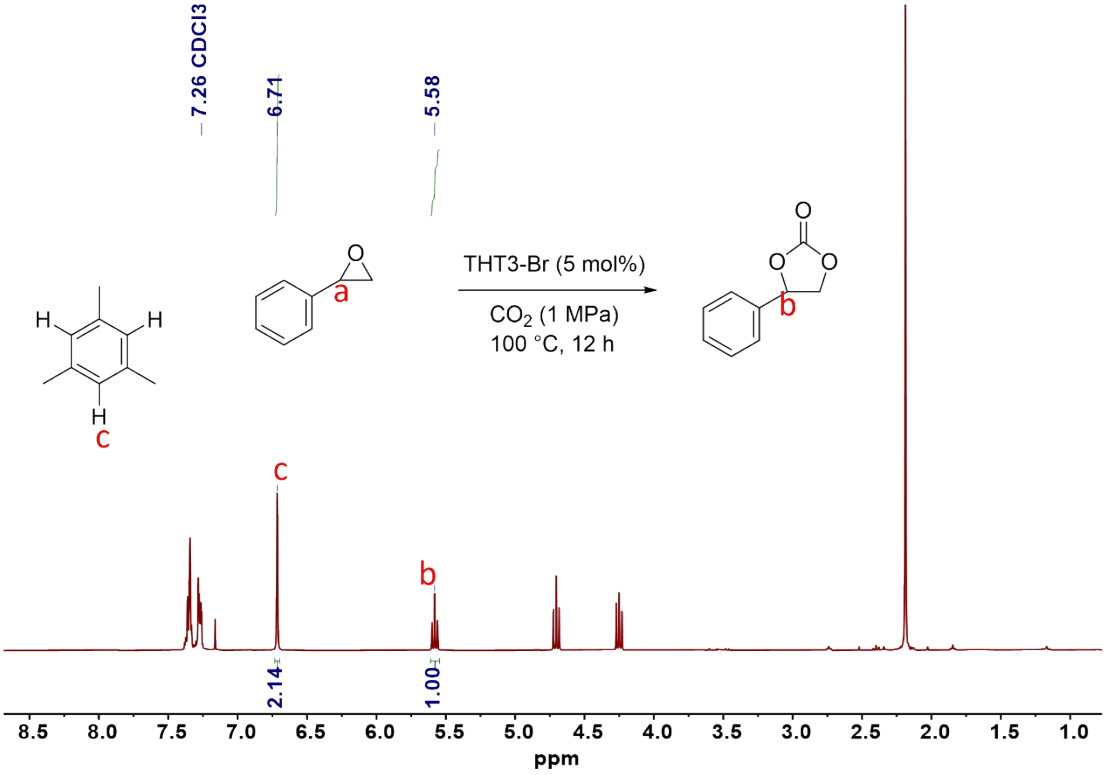


Figure S55. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, 11.9 mg crude mixture, 7.1 mg mesitylene (Table 1, entry 3). Conversion, >99%; selectivity, >99%.

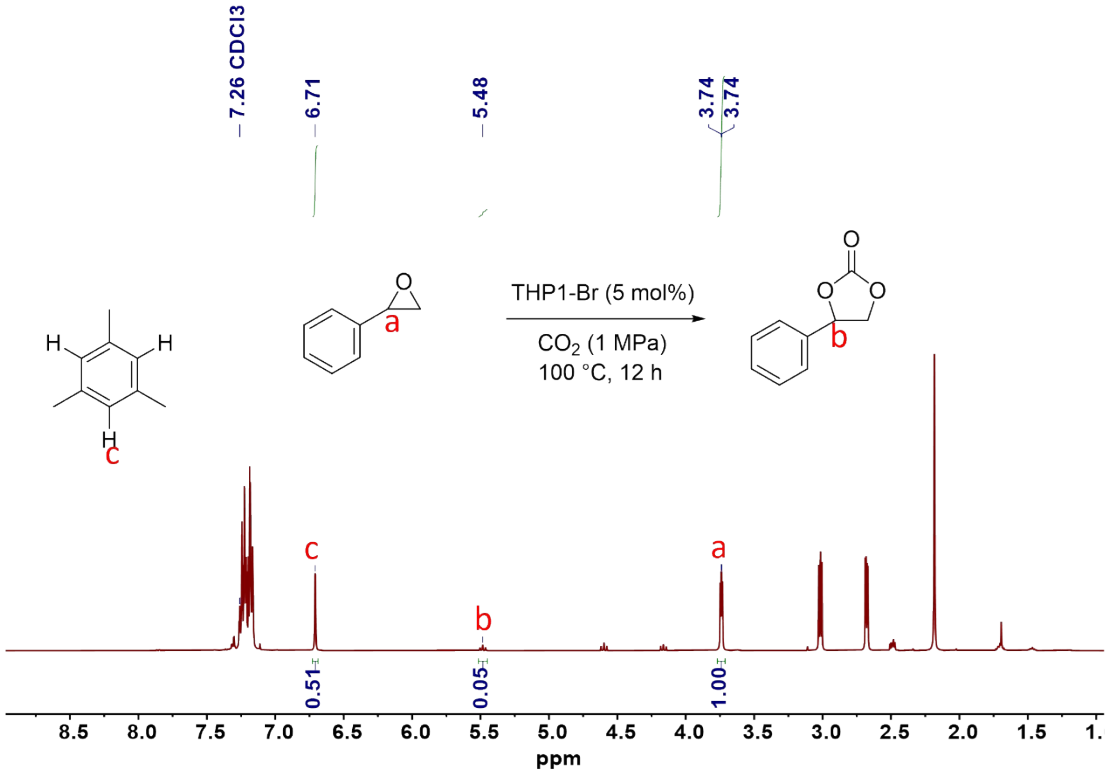


Figure S56. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THP1-Br (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, 87.6 mg crude mixture, 13.9 mg mesitylene (Table 1, entry 4). Conversion, 5%; selectivity, >99%.

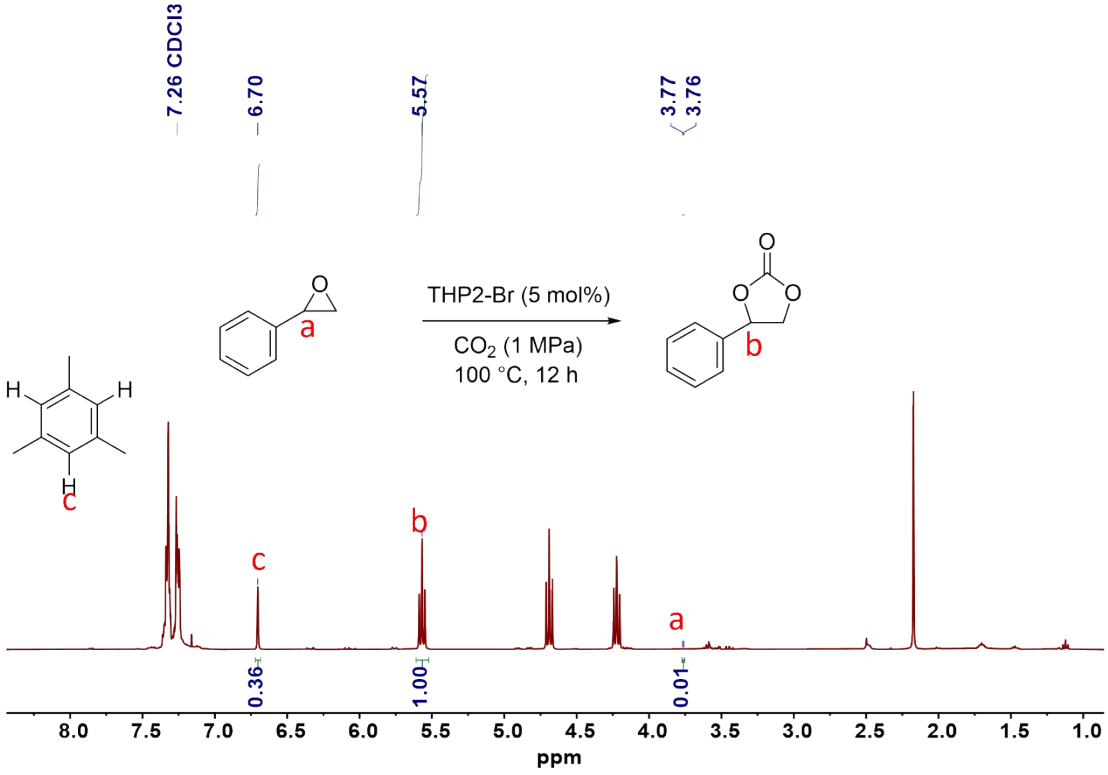


Figure S57. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THP2-Br (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, 63.9 mg crude mixture, 5.2 mg mesitylene (Table 1, entry 5). Conversion, >99%; selectivity, 92%.

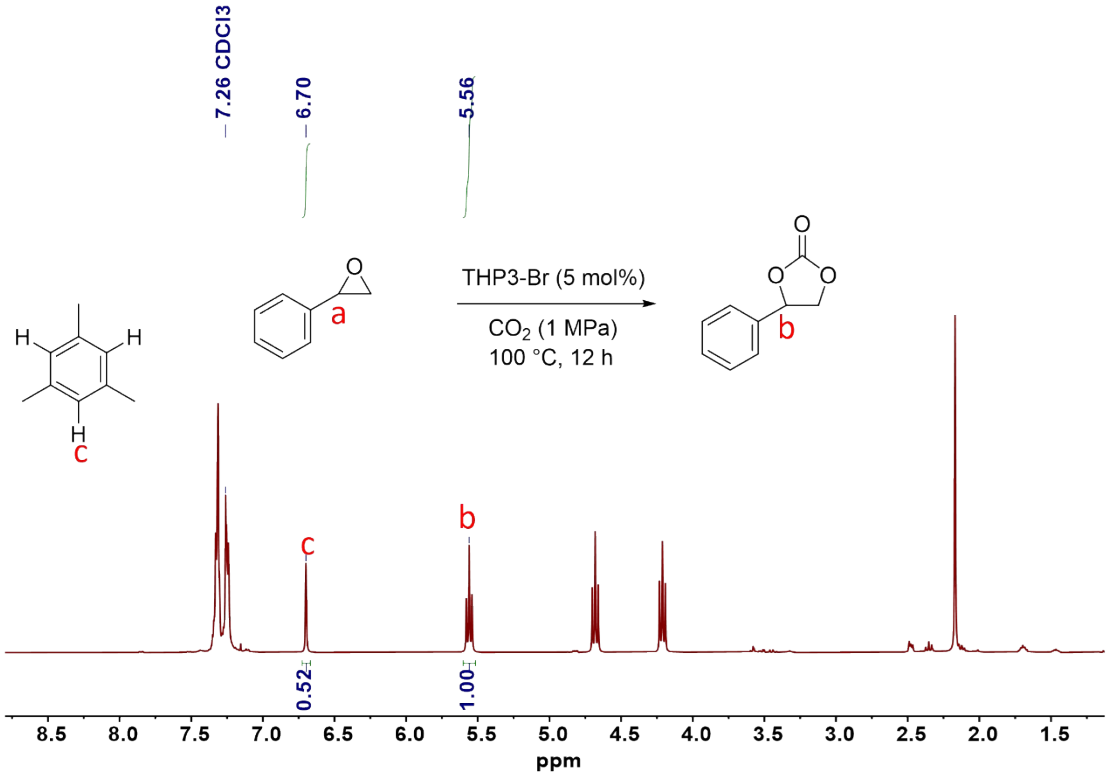


Figure S58. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THP3-Br (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, 78.8 mg crude mixture, 9.7 mg mesitylene (Table 1, entry 6). Conversion, >99%; selectivity, 96%.

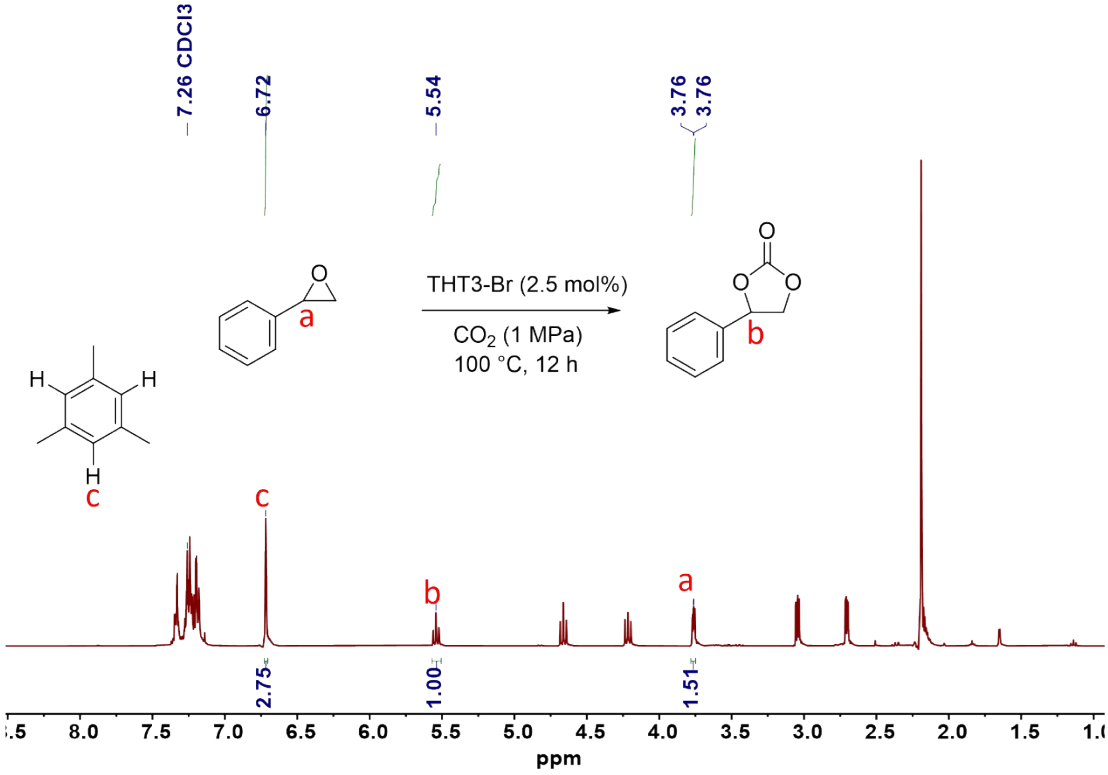


Figure S59. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THT3-Br (2.5 mol%), CO_2 (1 MPa), 12 h, 100 °C, 52.9 mg crude mixture, 16.8 mg mesitylene (Table 1, entry 7). Conversion, 40%; selectivity, >99%.

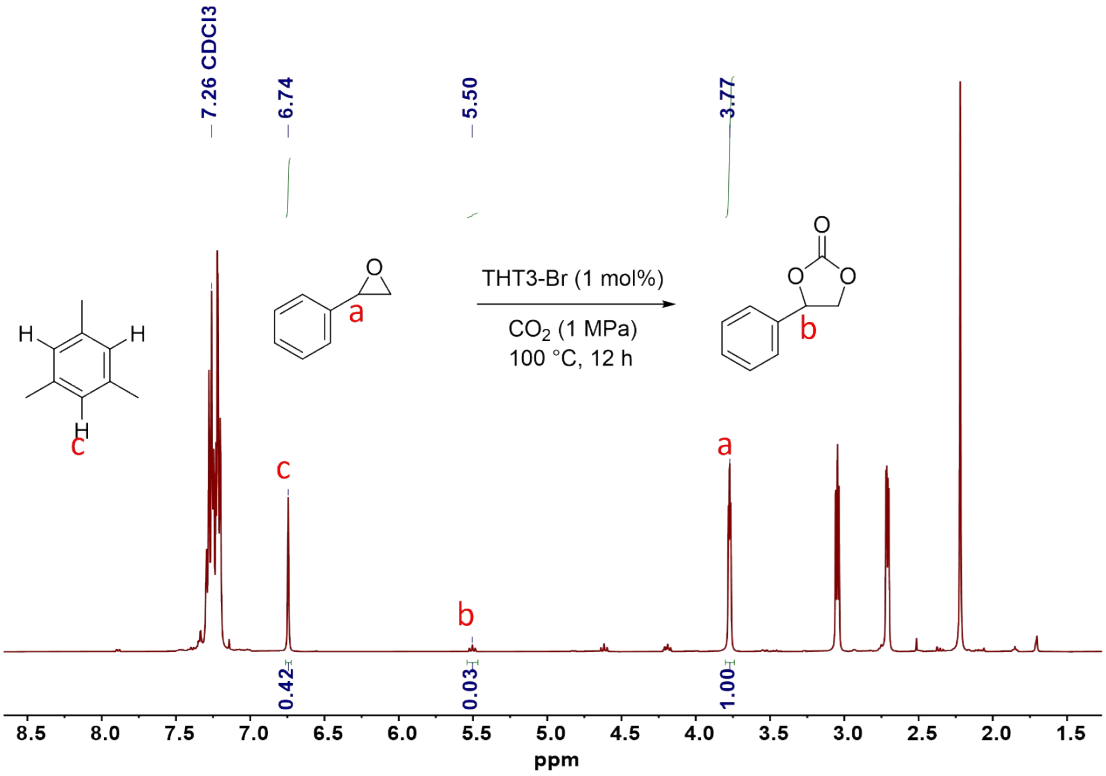


Figure S60. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THT3-Br (1 mol%), CO_2 (1 MPa), 12 h, 100 °C, 86.2 mg crude mixture, 12 mg mesitylene (Table 1, entry 8). Conversion, 3%; selectivity, >99%.

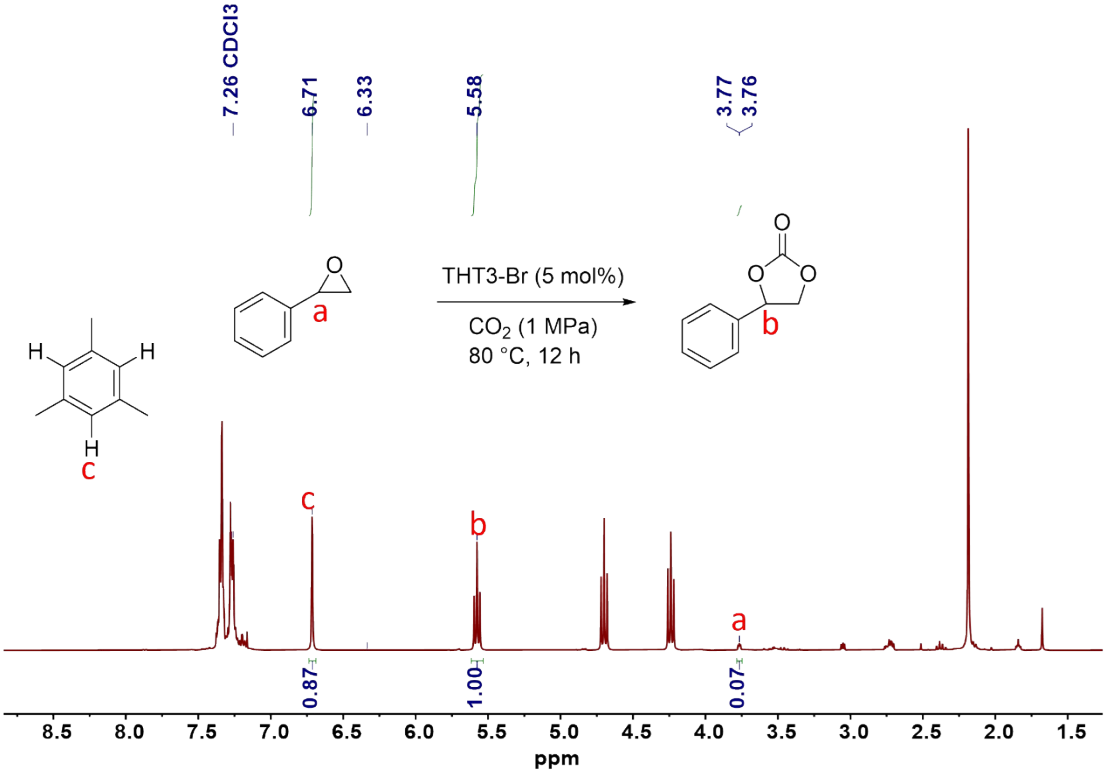


Figure S61. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 12 h, 80 °C, 52.9 mg crude mixture, 9.7 mg mesitylene (Table 1, entry 9). Conversion, 93%; selectivity, 91%.

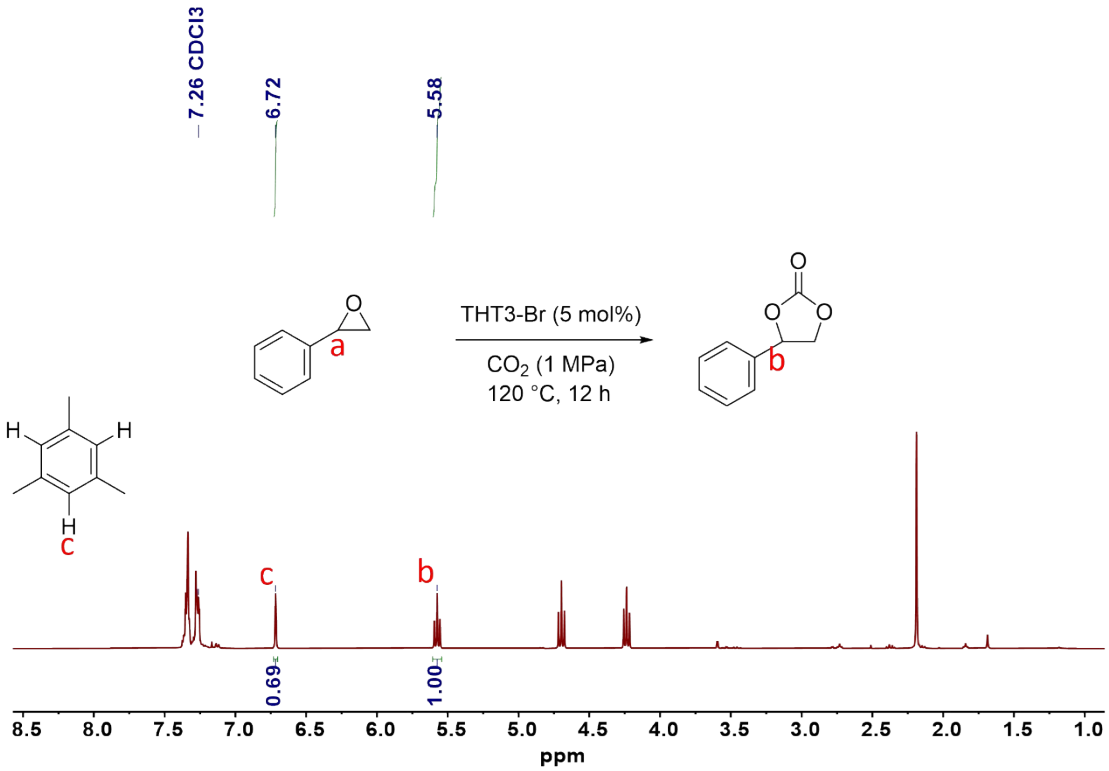


Figure S62. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 12 h, 120 °C, 60.2 mg crude mixture, 9.1 mg mesitylene (Table 1, entry 10). Conversion, >99%; selectivity, 89%.

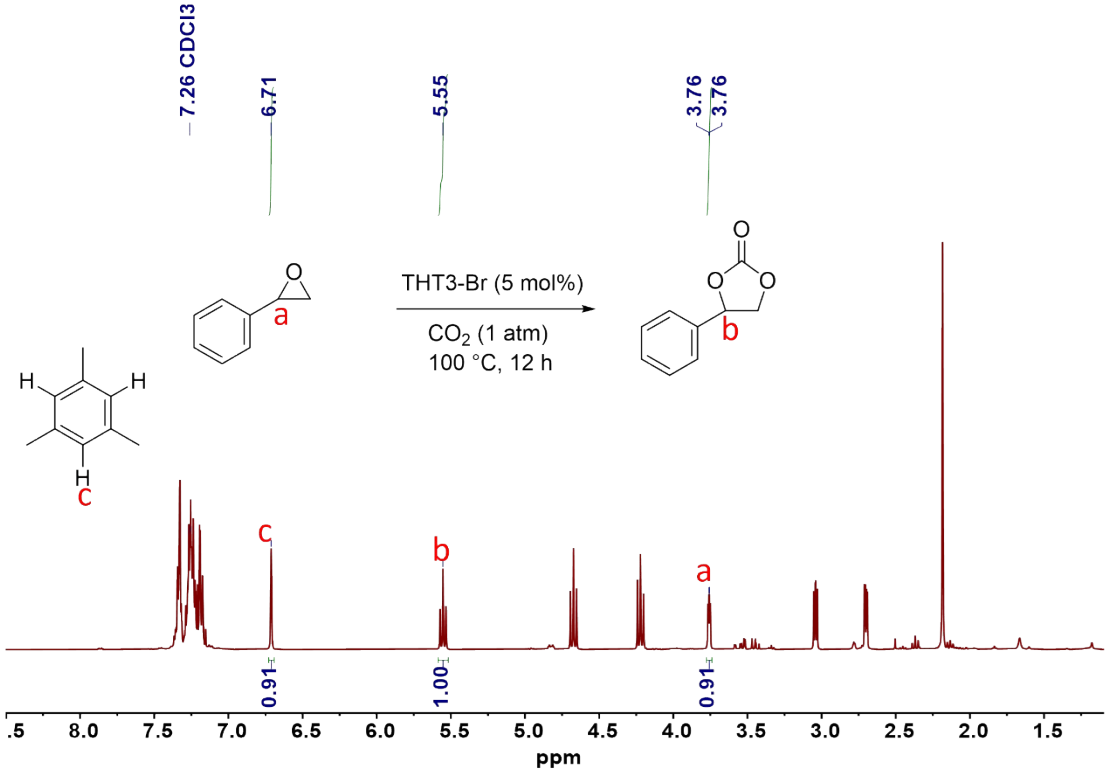


Figure S63. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 atm), 12 h, 100 °C, 52.5 mg crude mixture, 5.8 mg mesitylene (Table 1, entry 11). Conversion, 52%; selectivity, 94%.

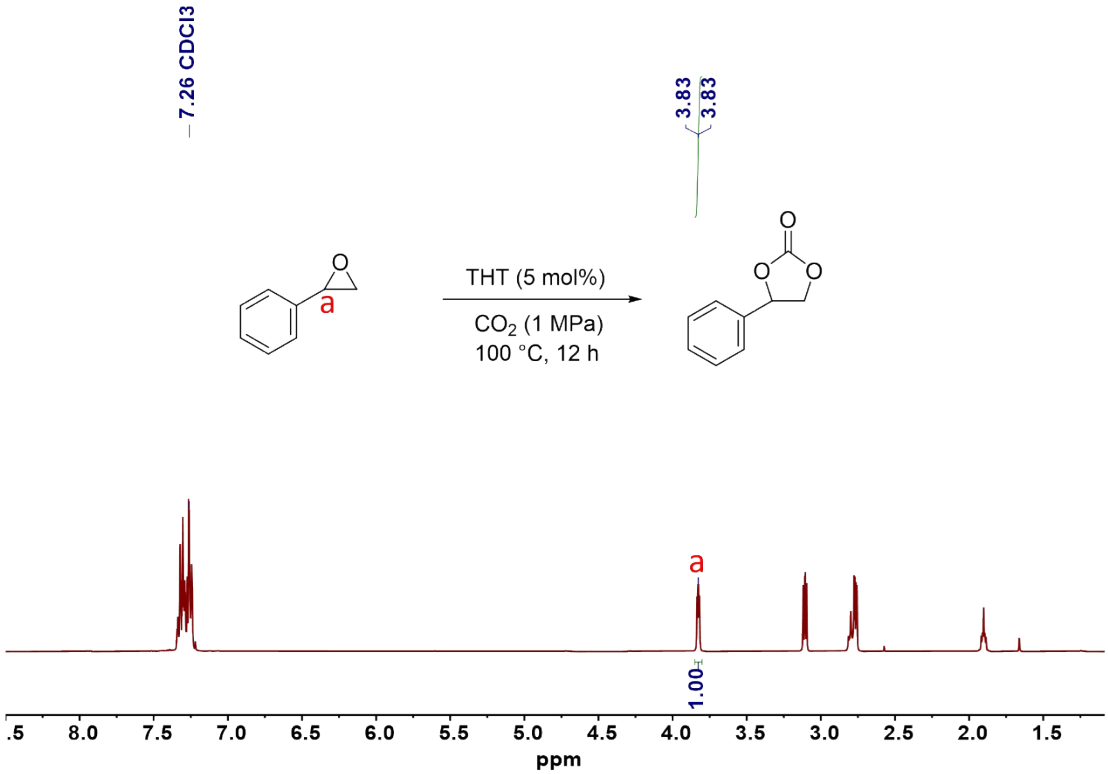


Figure S64. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THT (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, (Table 1, entry 12). Conversion, 0%; selectivity, -.

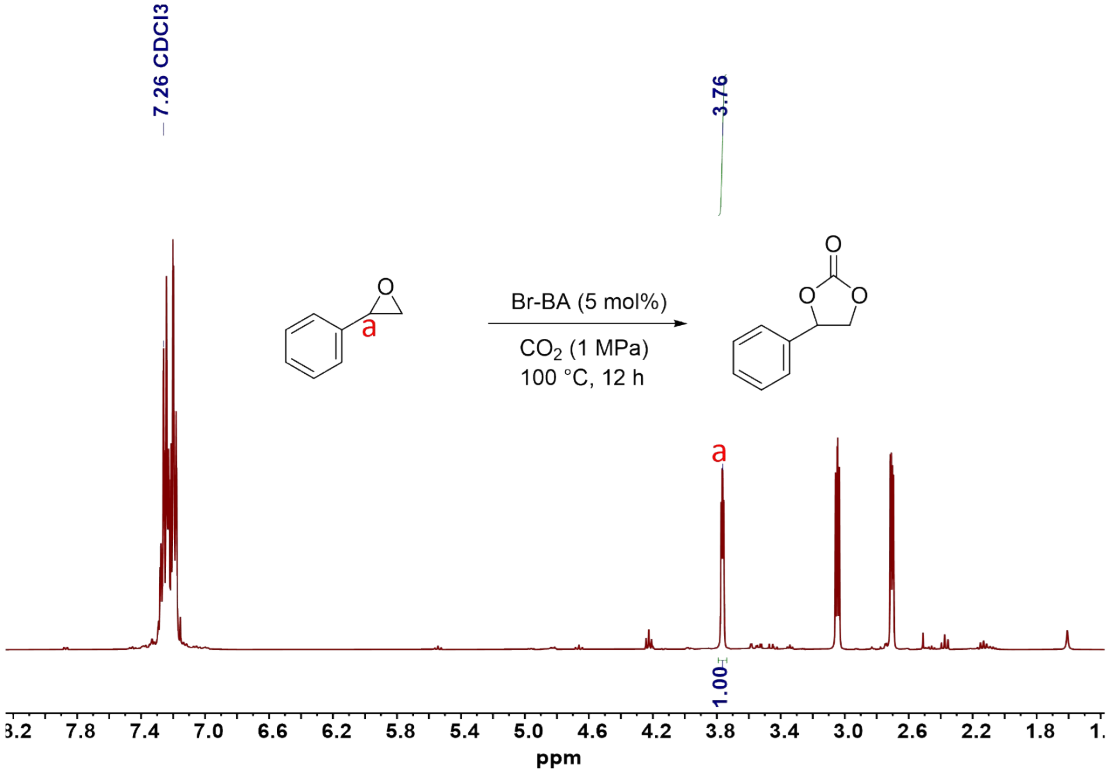


Figure S65. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), Br-BA (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, (Table 1, entry 13). Conversion, 0%; selectivity, -.

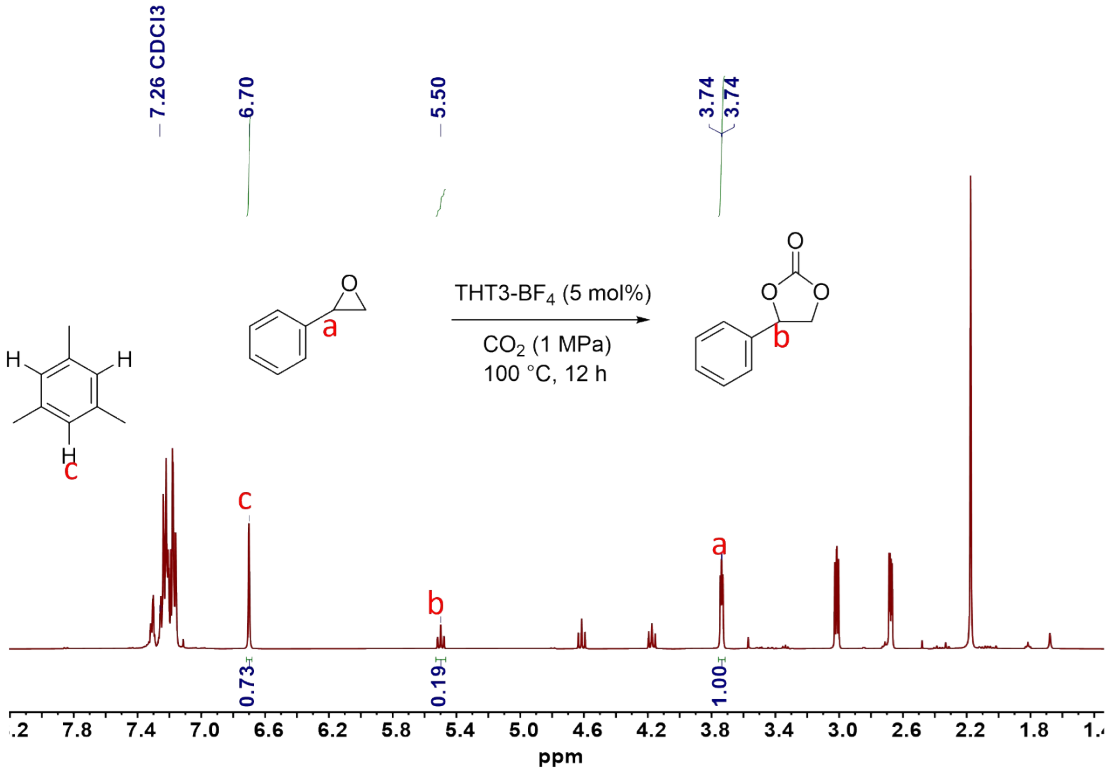


Figure S66. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), THT3-BF_4 (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, 76.9 mg crude mixture, 13.6 mg mesitylene (Table 1, entry 14). Conversion, 16%; selectivity, >99%.

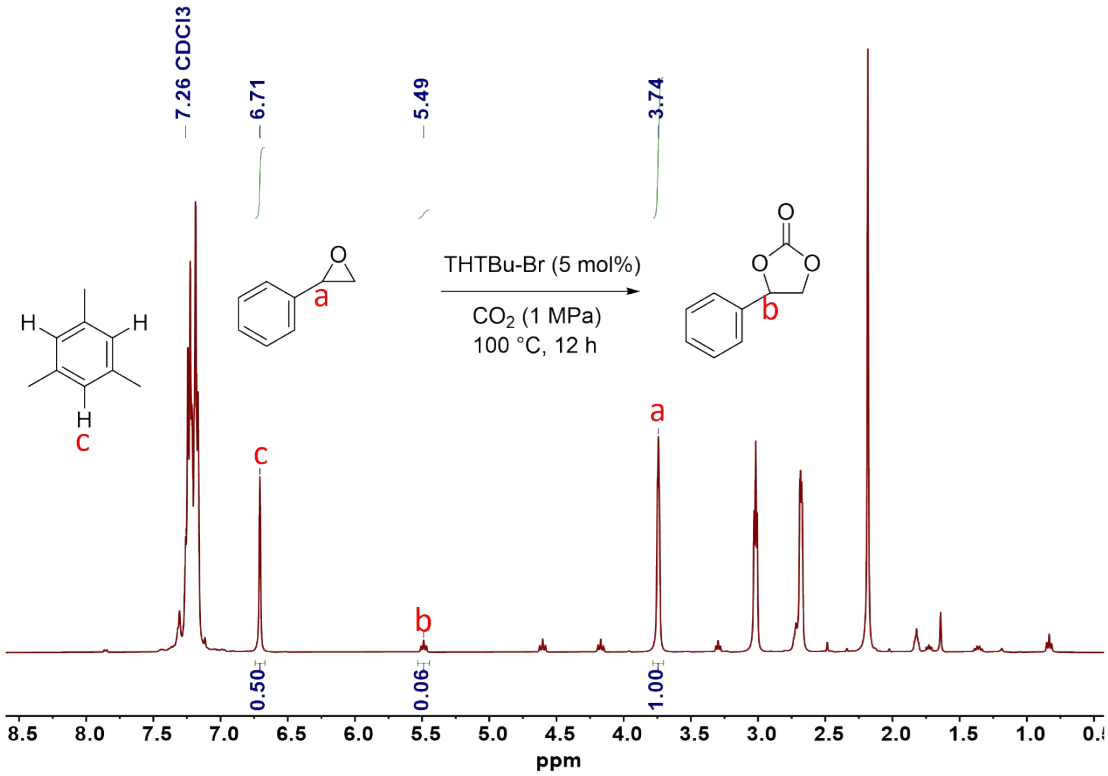


Figure S67. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), THTBu-Br (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, 86.1 mg crude mixture, 12.7 mg mesitylene (Table 1, entry 15). Conversion, 6%; selectivity, >99%.

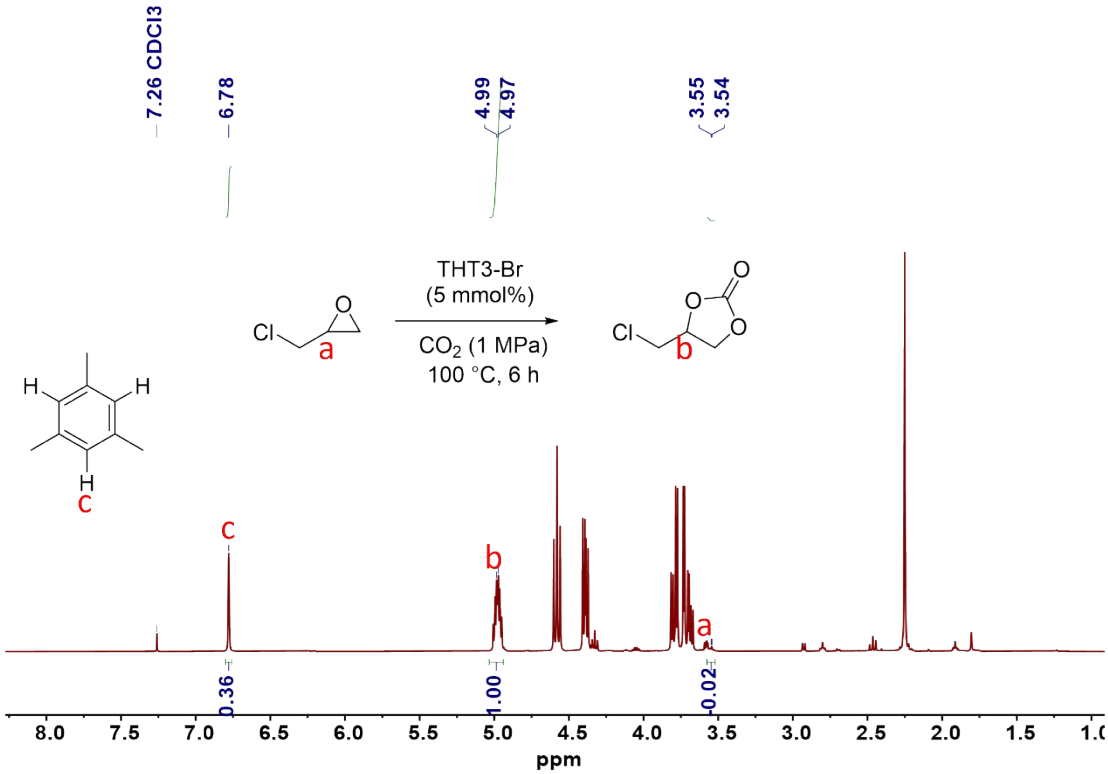


Figure S68. ^{1}H NMR Spectrum of crude CCE reaction mixture of epichlorohydrin (400 MHz, $CDCl_3$). Epichlorohydrin (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 6 h, 100 °C, 62.3 mg crude mixture, 6.1 mg mesitylene (Table 2, entry 1). Conversion, 98%; selectivity, 92%.

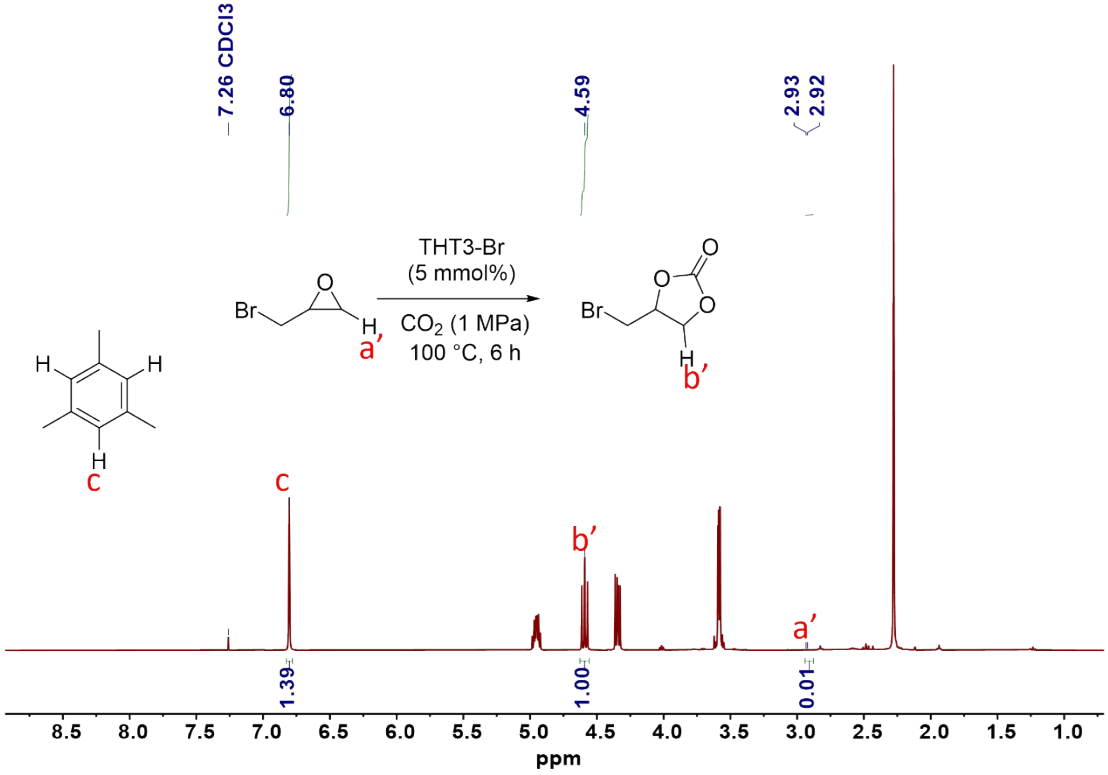


Figure S69. ^{1}H NMR Spectrum of crude CCE reaction mixture of 1-bromo-2,3-epoxypropane (400 MHz, $CDCl_3$). 1-Bromo-2,3-epoxypropane (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 6 h,

100 °C, 62.9 mg crude mixture, 18.3 mg mesitylene (Table 2, entry 2). Conversion, 99%; selectivity, 94%.

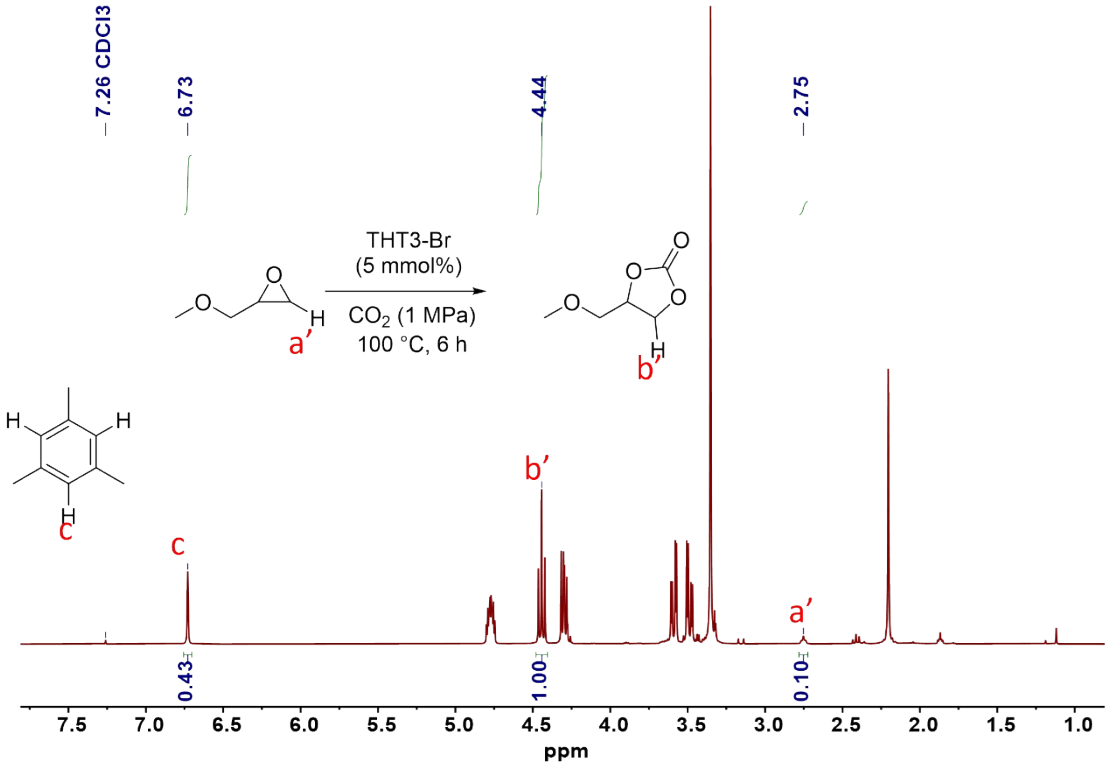


Figure S70. ^{1}H NMR Spectrum of crude CCE reaction mixture of glycidyl methyl ether (400 MHz, $CDCl_3$). Glycidyl methyl ether (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 6 h, 100 °C, 128.5 mg crude mixture, 15.5 mg mesitylene (Table 2, entry 3). Conversion, 91%; selectivity, >99%.

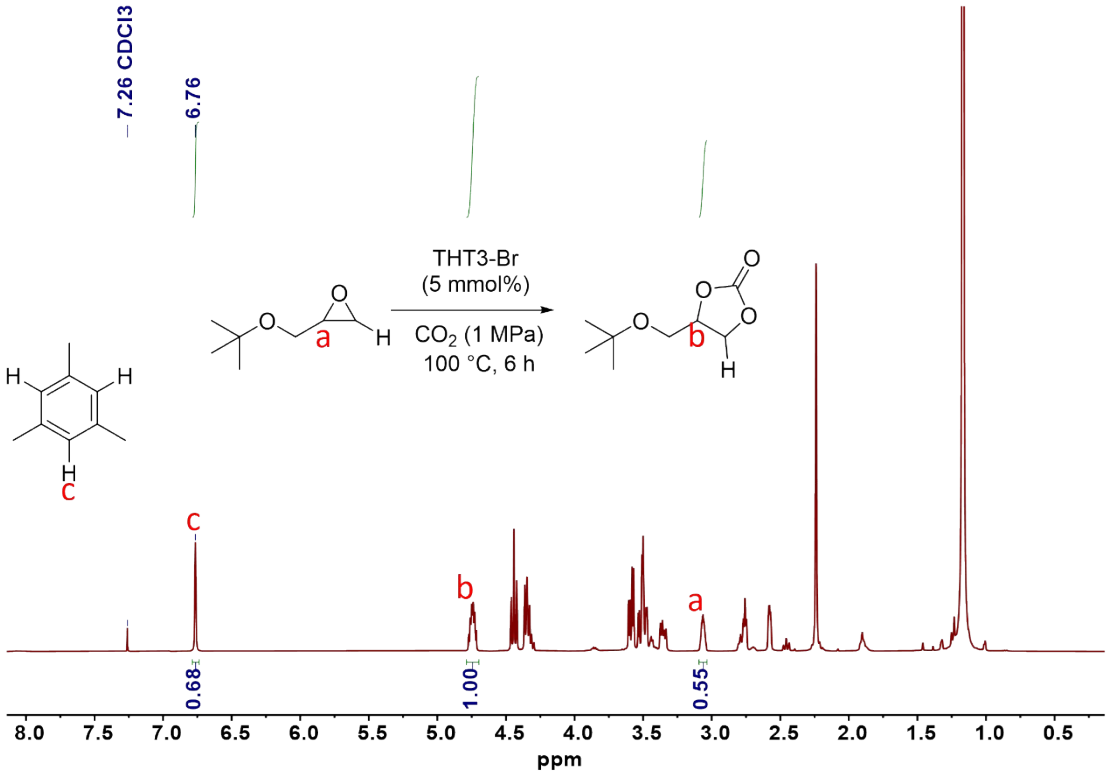


Figure S71. ^{1}H NMR Spectrum of crude CCE reaction mixture of *tert*-butyl glycidyl ether (400 MHz, $CDCl_3$). *tert*-Butyl glycidyl ether (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 6 h, 100 °C, 67.1 mg crude mixture, 7.5 mg mesitylene (Table 2, entry 4). Conversion, 65%; selectivity, >99%.

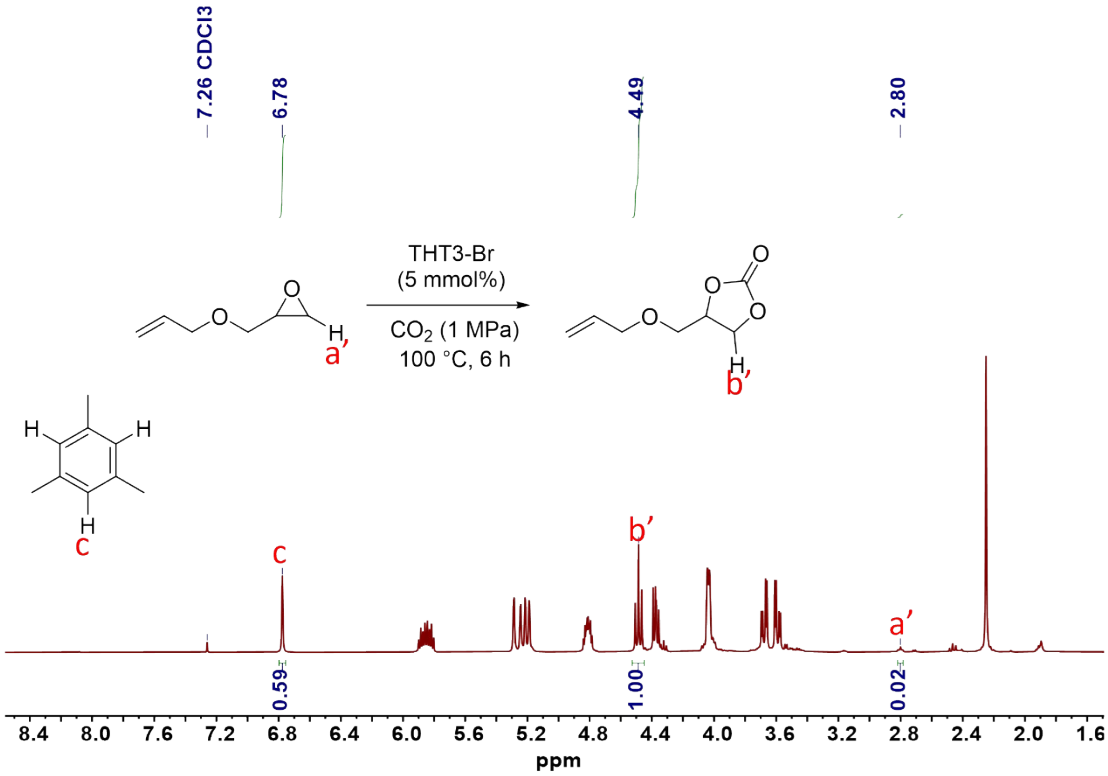


Figure S72. ^{1}H NMR Spectrum of crude CCE reaction mixture of allyl glycidyl ether (400 MHz, $CDCl_3$). Allyl glycidyl ether (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 6 h, 100 °C, 52.1 mg crude mixture, 7.0 mg mesitylene (Table 2, entry 5). Conversion, 98%; selectivity, 90%.

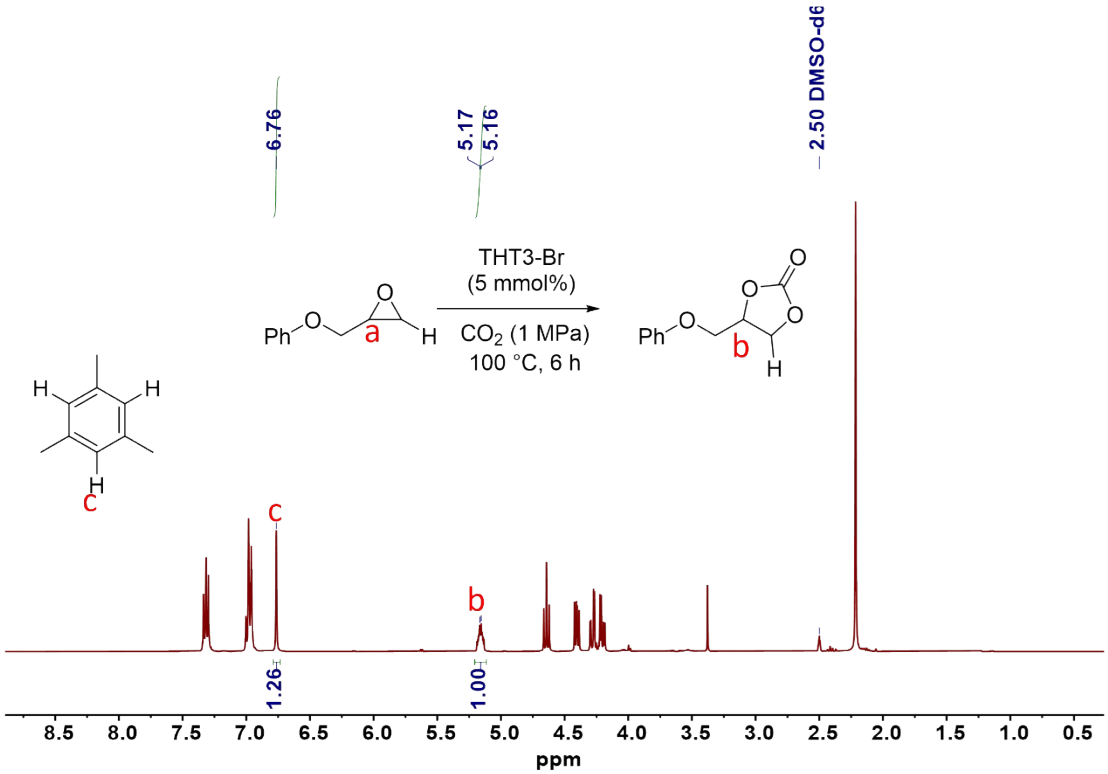


Figure S73. ^{1}H NMR Spectrum of crude CCE reaction mixture of glycidyl phenyl ether (400 MHz, DMSO-d_6). Glycidyl phenyl ether (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 6 h, 100 °C, 65.1 mg crude mixture, 15.4 mg mesitylene (Table 2, entry 6). Conversion, >99%; selectivity, 90%.

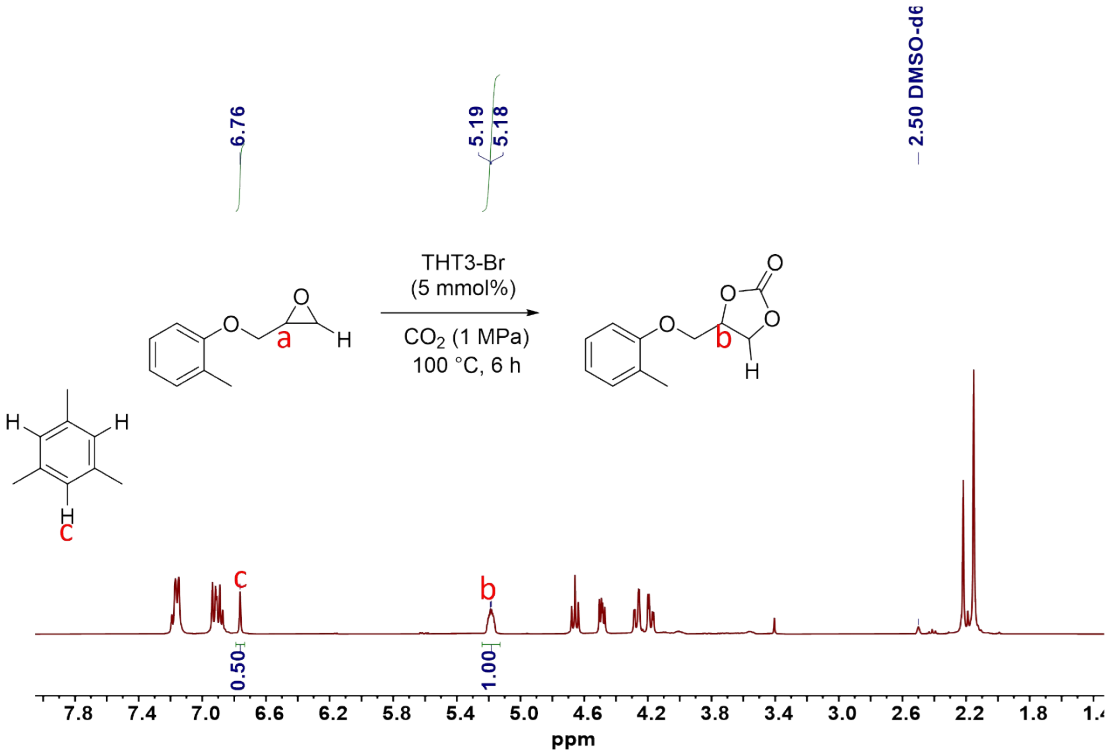


Figure S74. ^{1}H NMR Spectrum of crude CCE reaction mixture of 2-((*o*-tolyloxy)methyl)oxirane (400 MHz, DMSO-d_6). 2-((*o*-Tolyloxy)methyl)oxirane (5 mmol), THT3-Br (5 mol%), CO_2 (1

MPa), 6 h, 100 °C, 121.9 mg crude mixture, 11.7 mg mesitylene (Table 2, entry 7). Conversion, >99%; selectivity, 99%.

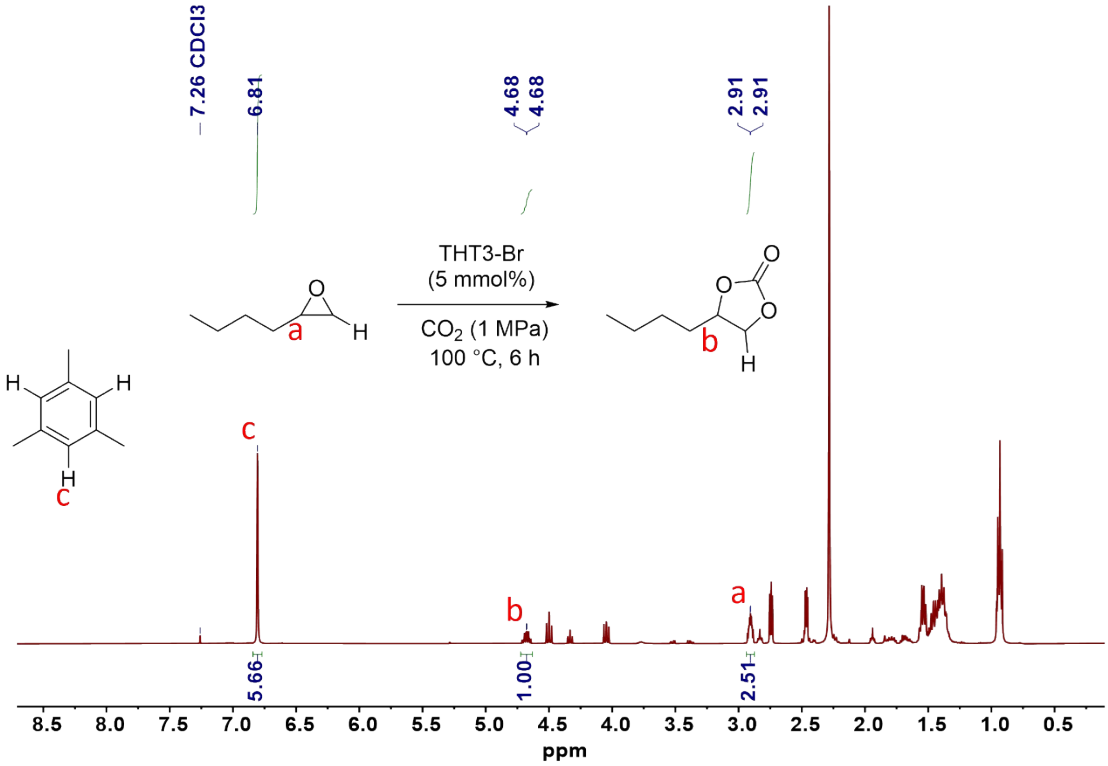


Figure S75. ^{1}H NMR Spectrum of crude CCE reaction mixture of 1,2-epoxyhexane (400 MHz, $CDCl_3$). 1,2-Epoxyhexane (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 6 h, 100 °C, 54.1 mg crude mixture, 25.4 mg mesitylene (Table 2, entry 8). Conversion, 28%; selectivity, >99%.

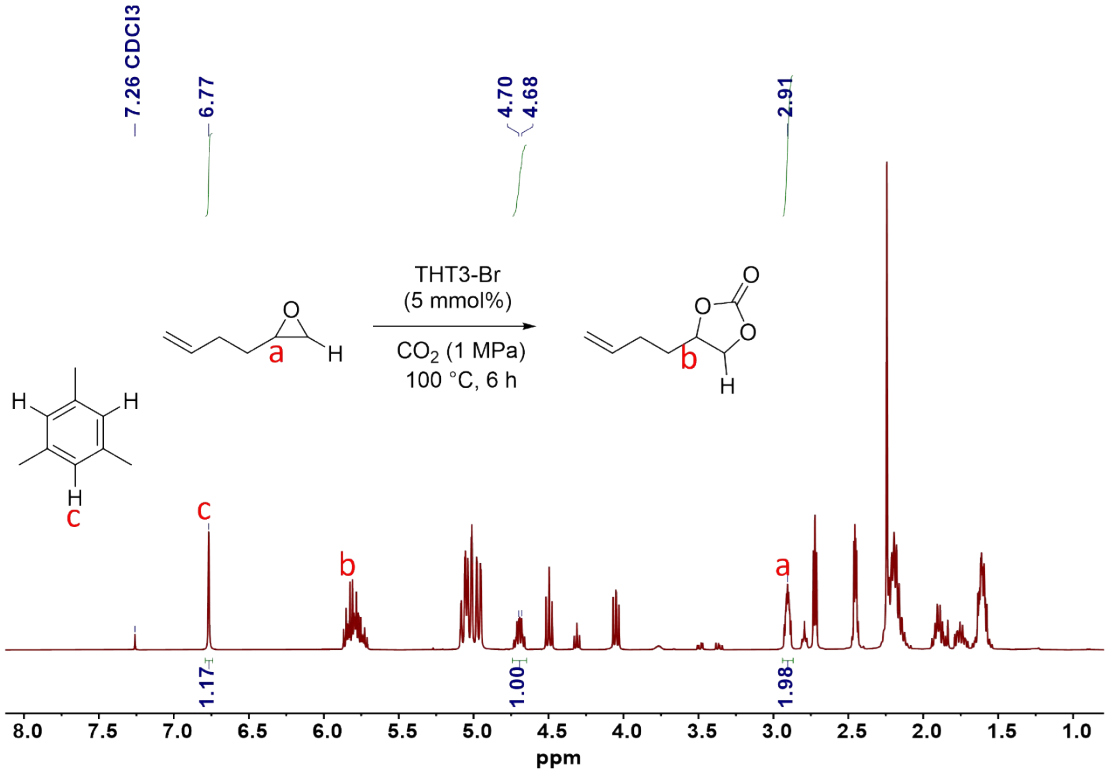


Figure S76. ^{1}H NMR Spectrum of crude CCE reaction mixture of 2-(but-3-en-1-yl)oxirane (400 MHz, $CDCl_3$). 2-(But-3-en-1-yl)oxirane (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 6 h, 100 °C, 83.6 mg crude mixture, 10.1 mg mesitylene (Table 2, entry 9). Conversion, 33%; selectivity, >99%.

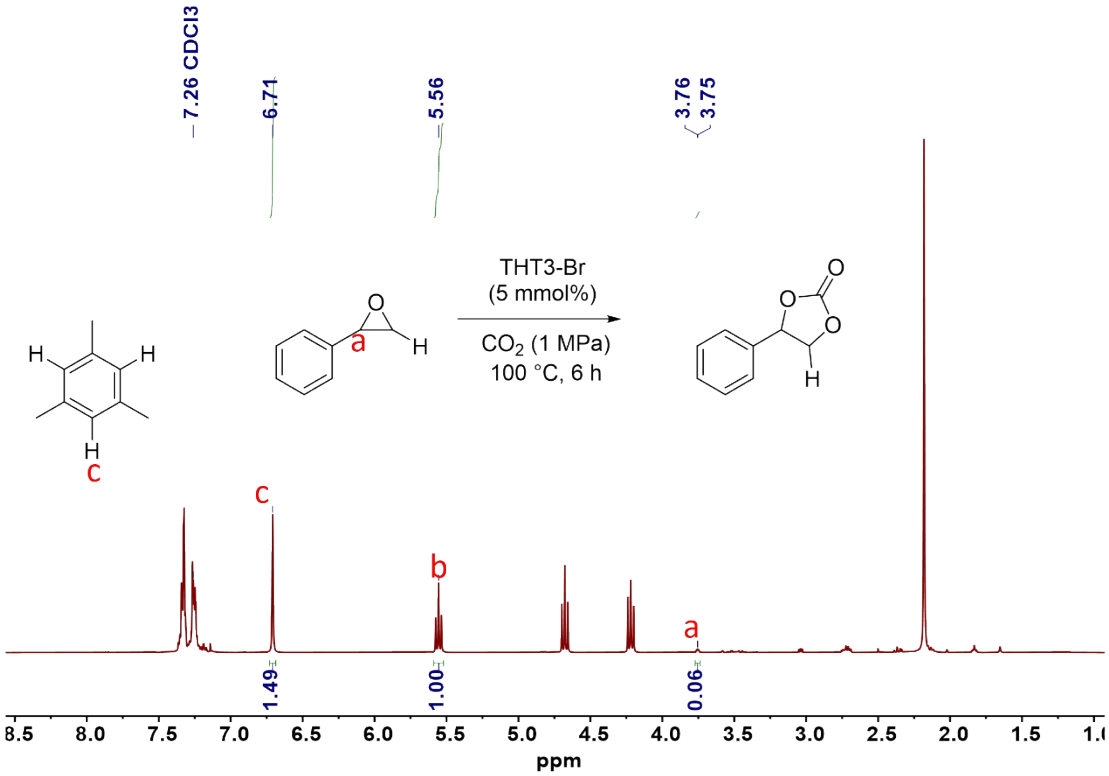


Figure S77. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 6 h, 100 °C, 56.2 mg crude mixture, 18.3 mg mesitylene (Table 2, entry 10). Conversion, 94%; selectivity, 93%.

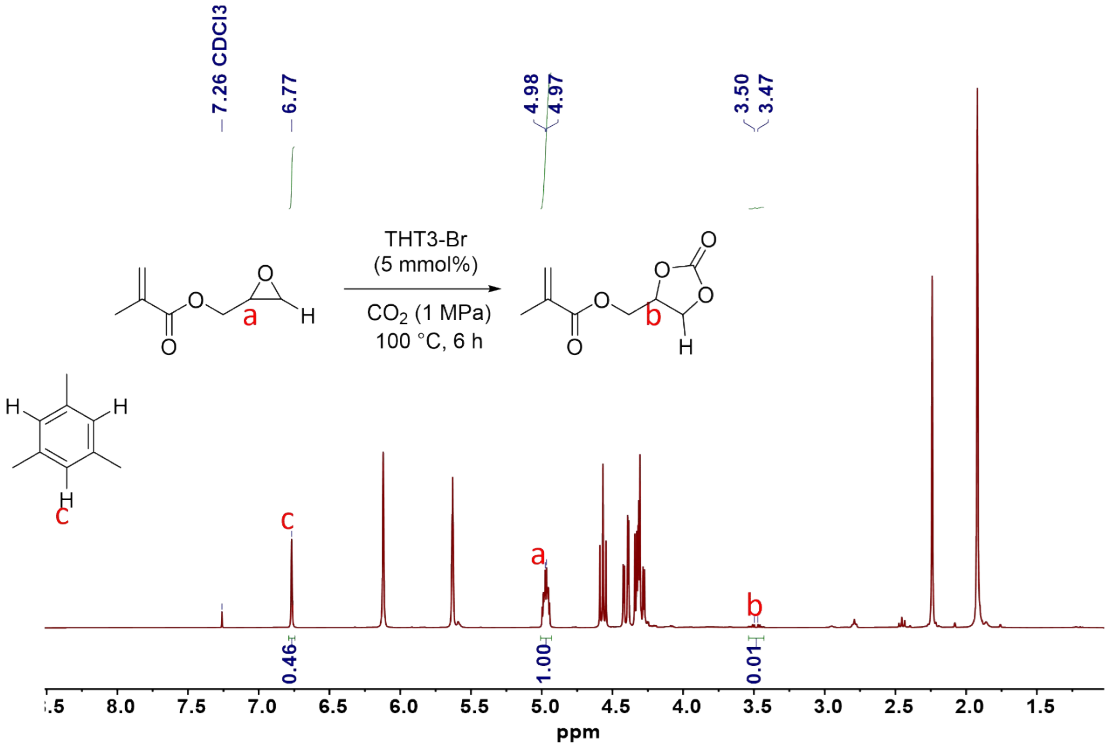


Figure S78. ^{1}H NMR Spectrum of crude CCE reaction mixture of glycidyl methacrylate (400 MHz, $CDCl_3$). Glycidyl methacrylate (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 6 h, 100 °C, 62.2 mg crude mixture, 5.7 mg mesitylene (Table 2, entry 11). Conversion, 99%; selectivity, 92%.

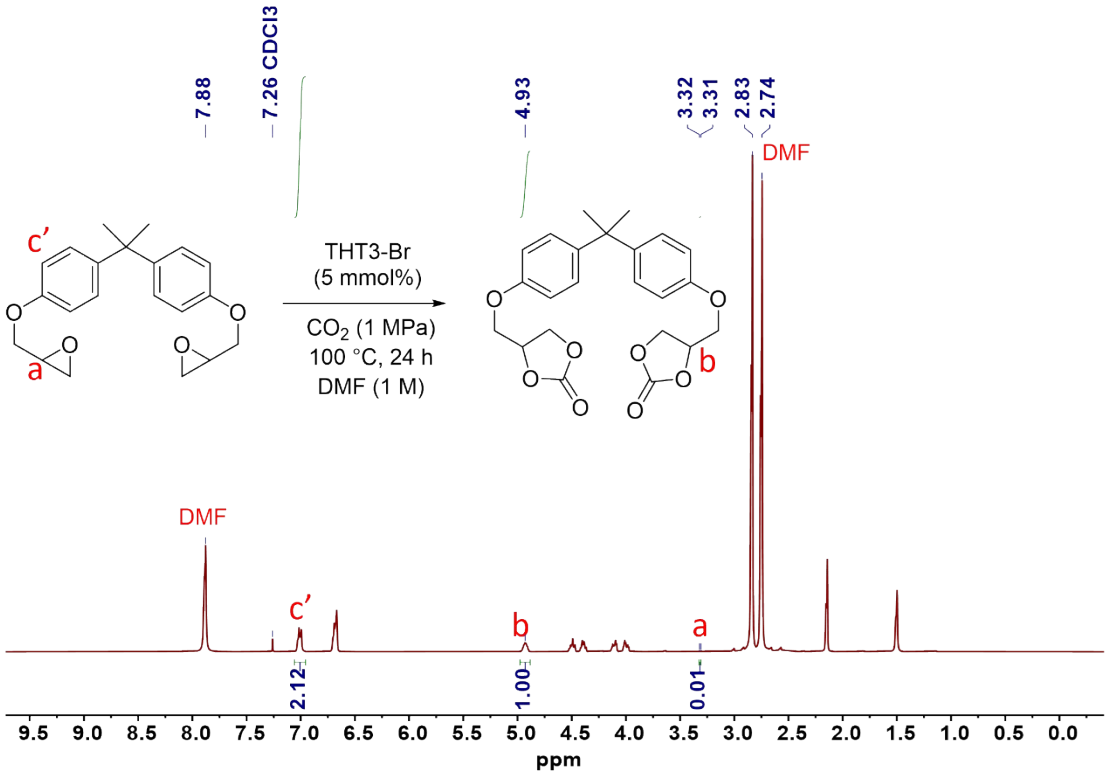


Figure S79. ^{1}H NMR Spectrum of crude CCE reaction mixture of bisphenol A diglycidyl ether (400 MHz, $CDCl_3$). Bisphenol A diglycidyl ether (1 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 24 h, 100 °C, DMF (1 M), (Table 2, entry 12). Conversion, 99%; selectivity, 95%.

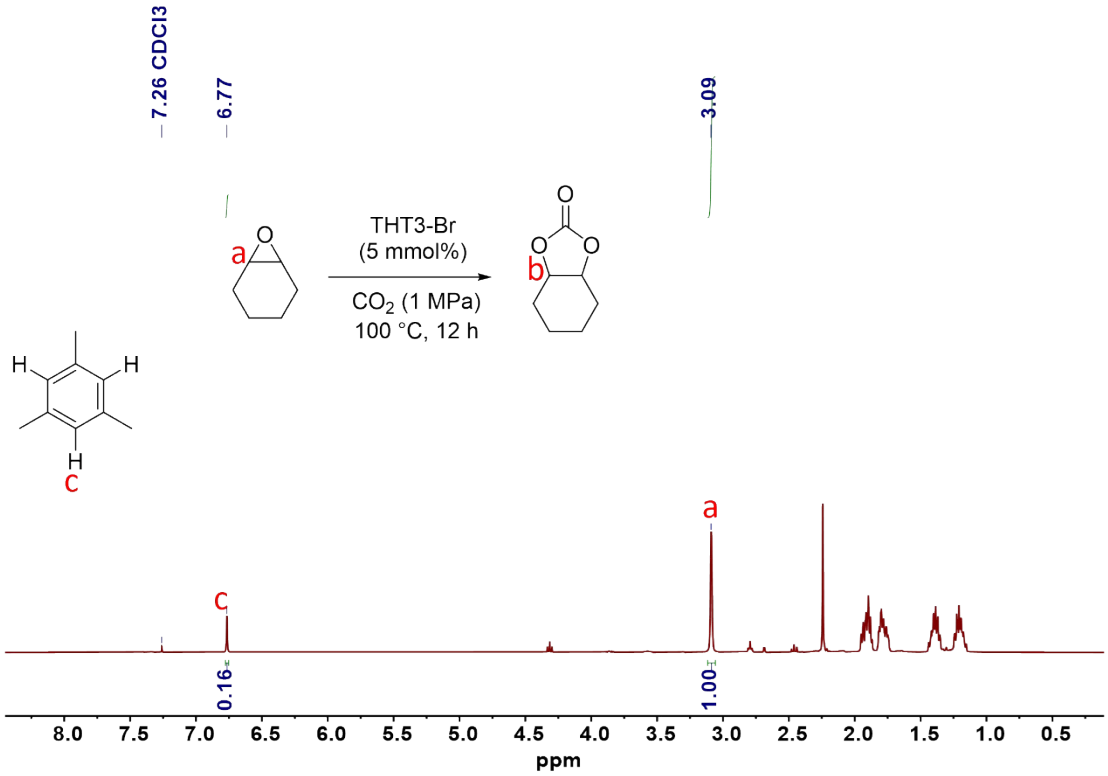


Figure S80. ^{1}H NMR Spectrum of crude CCE reaction mixture of cyclohexene oxide (400 MHz, $CDCl_3$). Cyclohexene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, DMF (1 M), 56.2 mg crude mixture, 18.3 mg mesitylene (Table 2, entry 13). Conversion, 0%; selectivity, -.

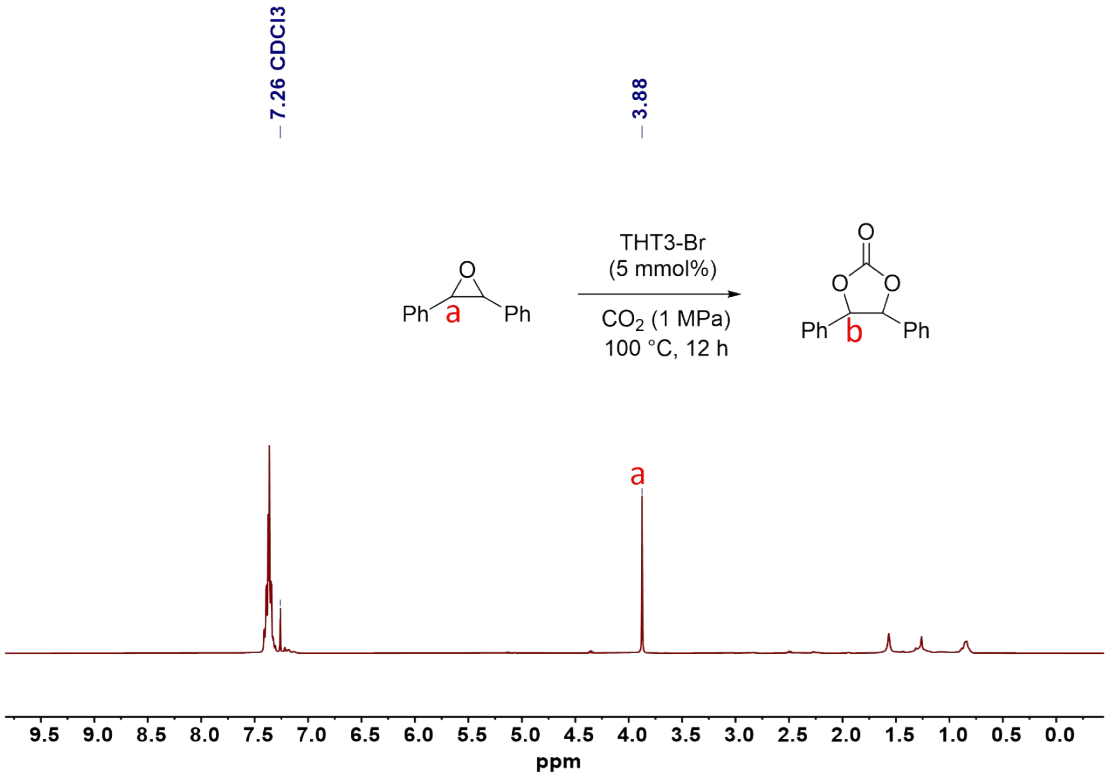


Figure S81. ^{1}H NMR Spectrum of crude CCE reaction mixture of *trans*-stilbene oxide (400 MHz, $CDCl_3$). *trans*-Stilbene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 12 h, 100 °C,

DMF (1 M), 56.2 mg crude mixture, 18.3 mg mesitylene (Table 2, entry 14). Conversion, 0%; selectivity, -.

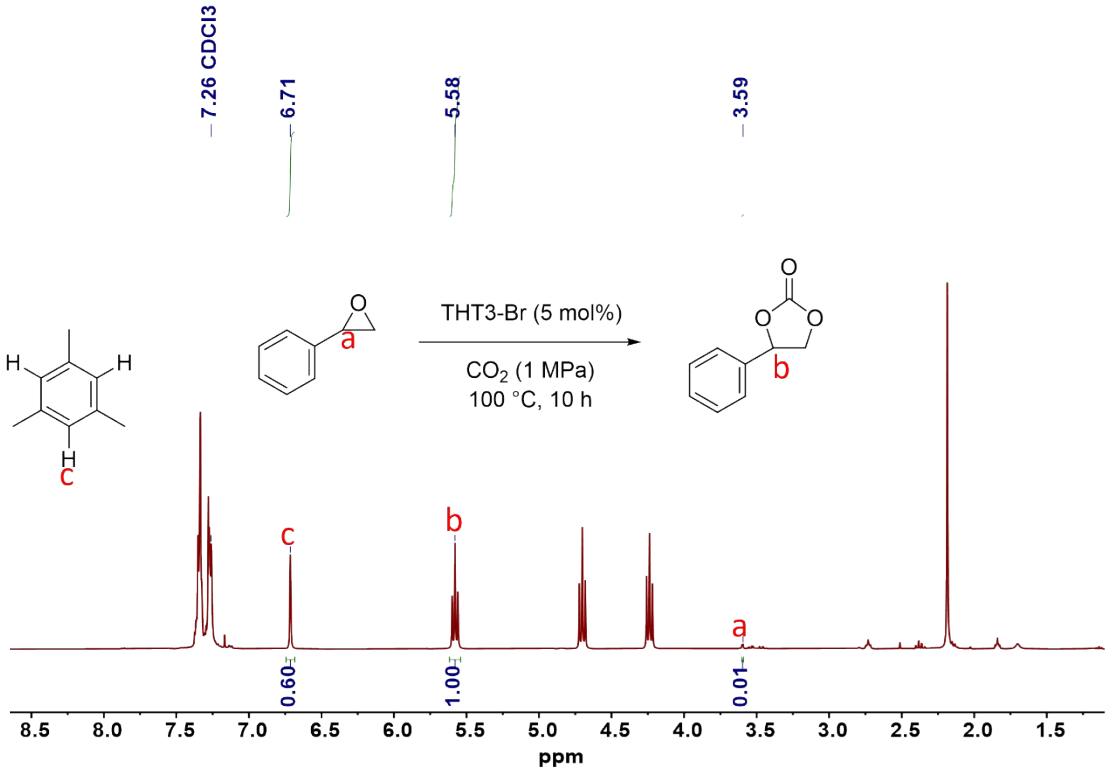


Figure S82. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 10 h, 100 °C, 56.9 mg crude mixture, 8.1 mg mesitylene (Table S2, entry 1). Conversion, 99%; selectivity, 96%.

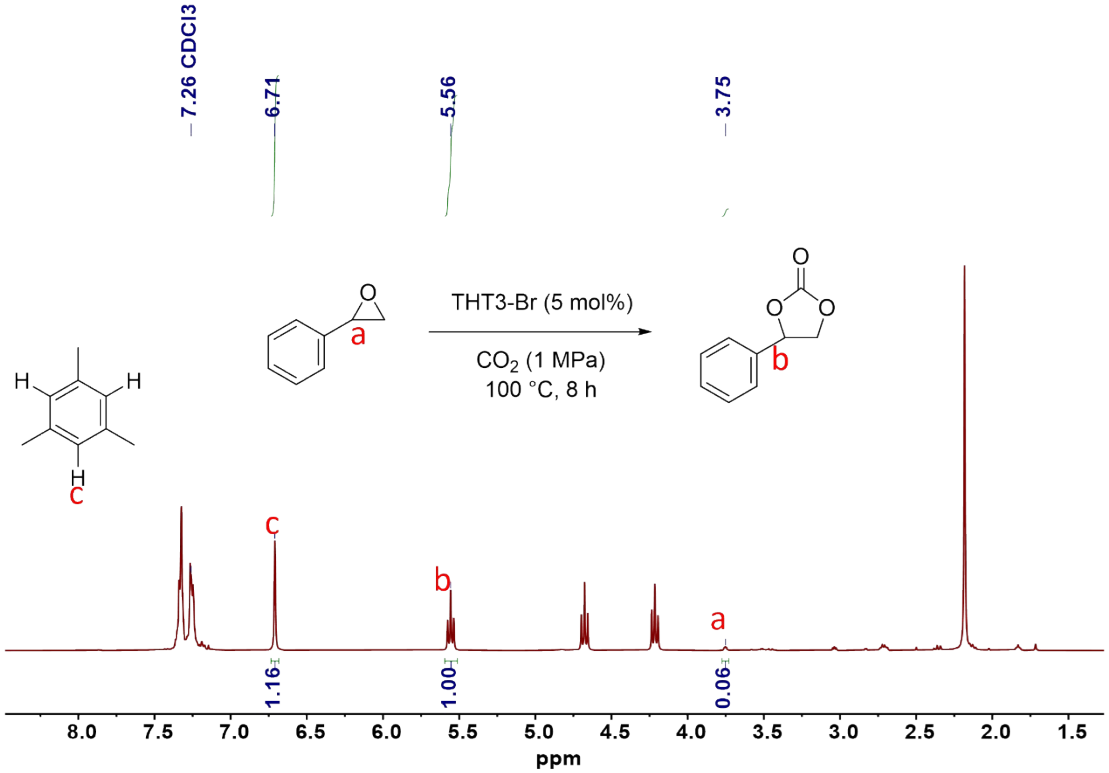


Figure S83. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 8 h, 100 °C, 76.5 mg crude mixture, 19.8 mg mesitylene (Table S2, entry 2). Conversion, 94%; selectivity, 95%.

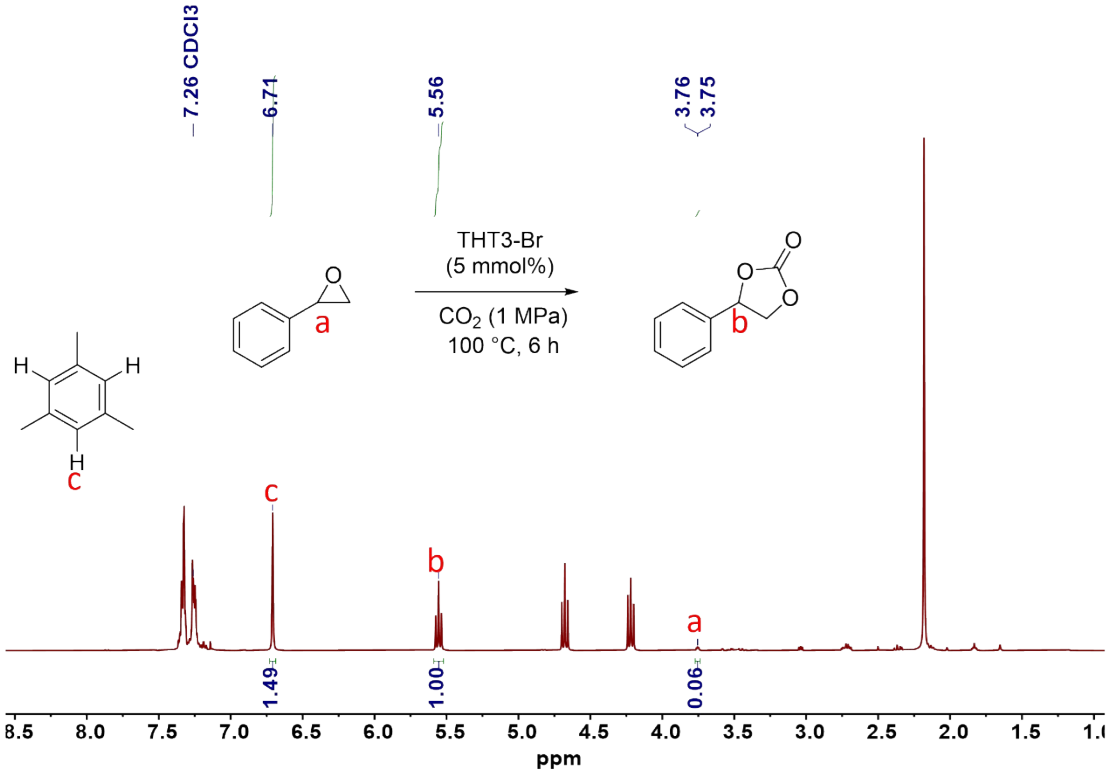


Figure S84. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 6 h, 100 °C, 56.2 mg crude mixture, 18.3 mg mesitylene (Table S2, entry 3). Conversion, 94%; selectivity, 93%.

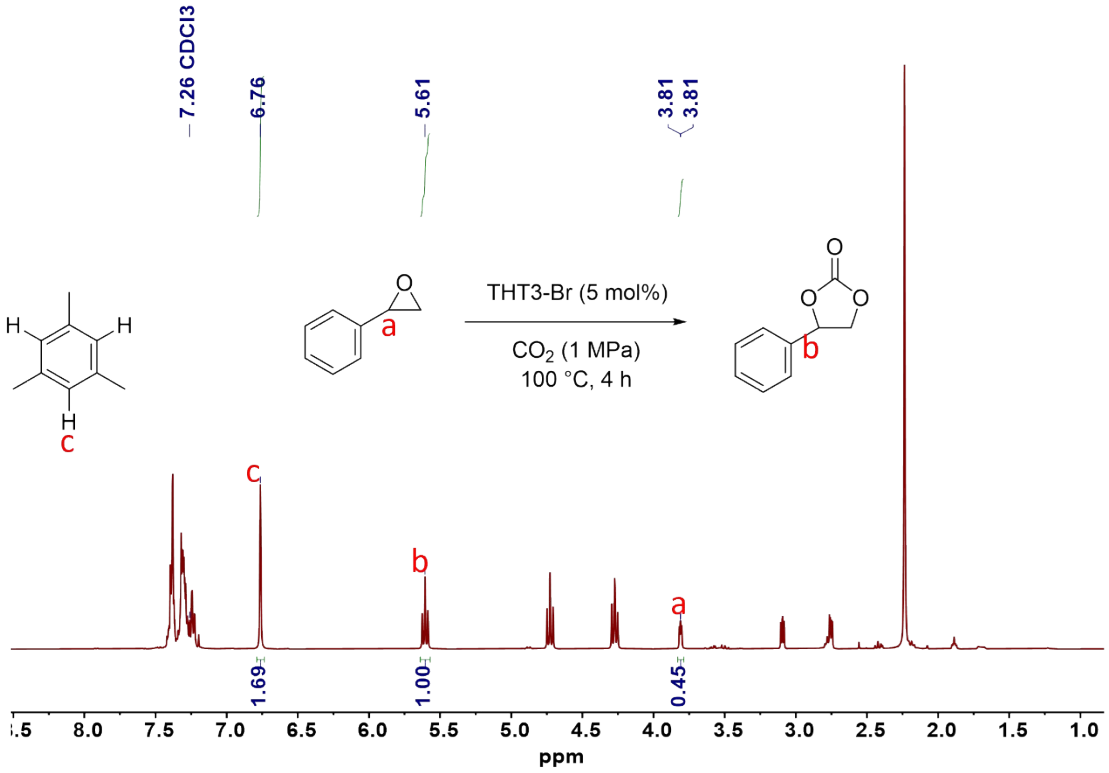


Figure S85. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 4 h, 100 °C, 57.9 mg crude mixture, 16.8 mg mesitylene (Table S2, entry 4). Conversion, 69%; selectivity, 100%.

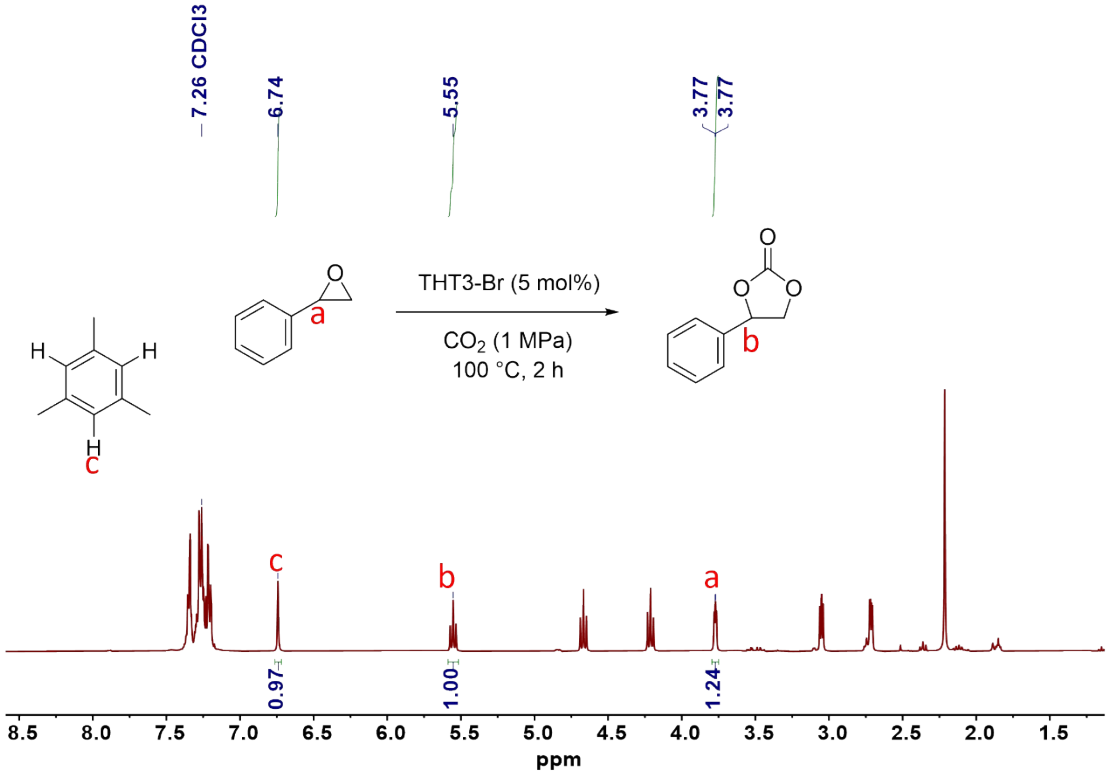


Figure S86. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 2 h, 100 °C, 136.7 mg crude mixture, 15 mg mesitylene (Table S2, entry 5). Conversion, 45%; selectivity, >99%.

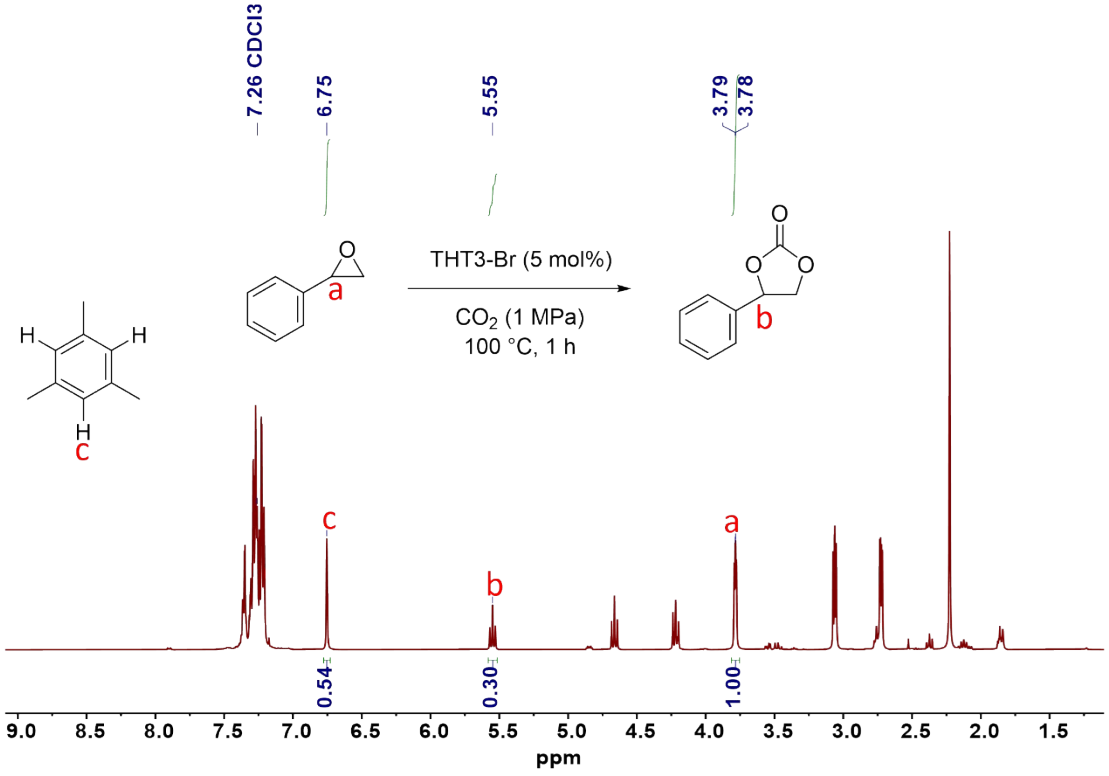


Figure S87. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 1 h, 100 °C, 105 mg crude mixture, 11.9 mg mesitylene (Table S2, entry 6). Conversion, 23%; selectivity, >99%.

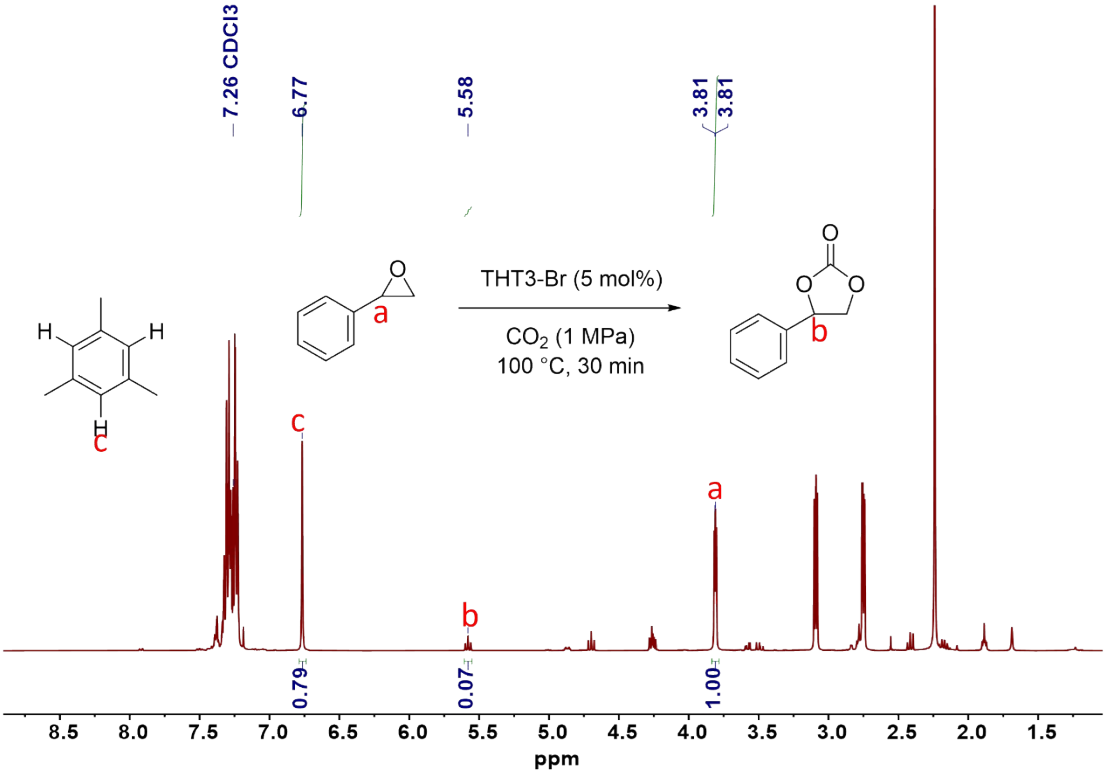


Figure S88. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 30 min, 100 °C, 55.2 mg crude mixture, 12.5 mg mesitylene (Table S2, entry 7). Conversion, 6%; selectivity, >99%.

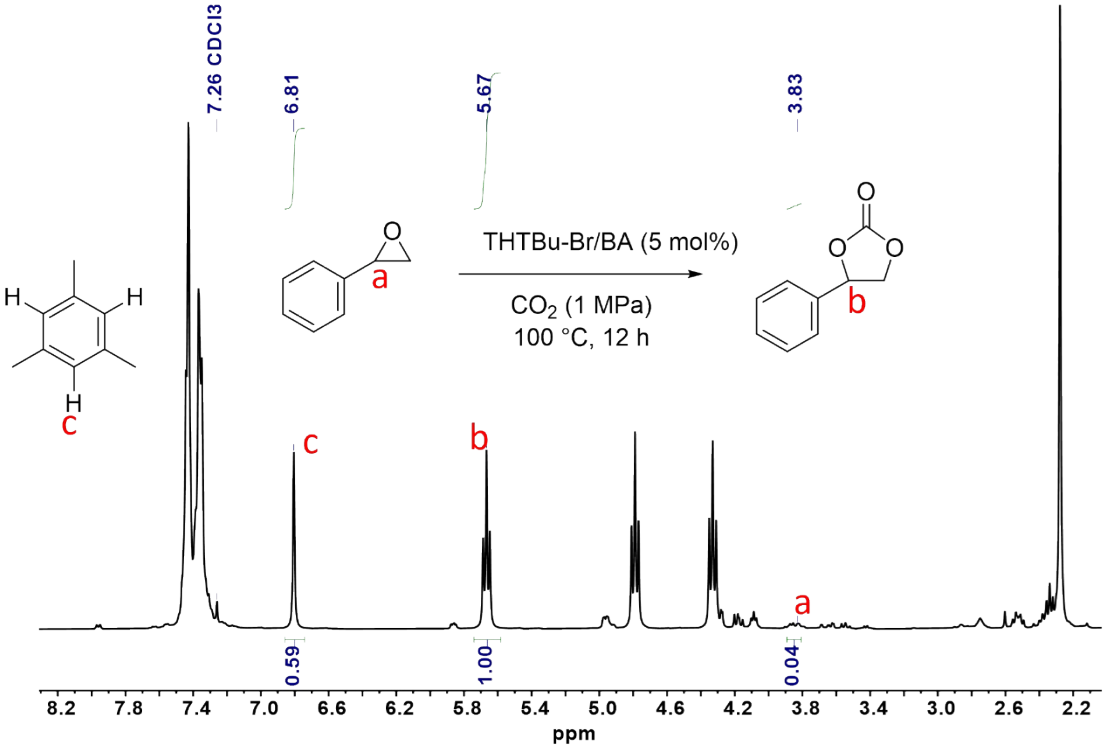


Figure S89. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), THTBu-Br (5 mol%), BA (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, 61.3 mg crude mixture, 6.9 mg mesitylene (Table 1, entry 17). Conversion, 96%; selectivity, 79%.

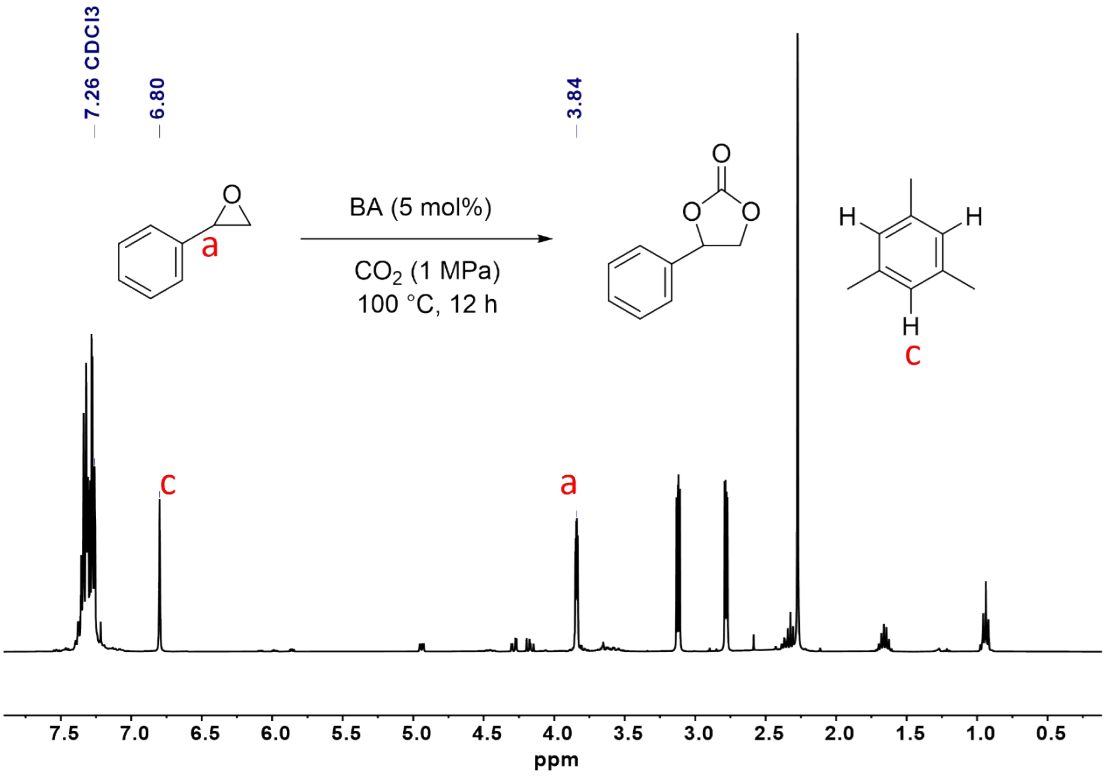


Figure S90. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, $CDCl_3$). Styrene oxide (5 mmol), BA (5 mol%), CO_2 (1 MPa), 12 h, 100 °C, 61.1 mg crude mixture, 9.3 mg mesitylene (Table 1, entry 16). Conversion: -; selectivity: -.

Take table 1, entry 9 for an example to analyze the by-products. In the ^{1}H NMR spectrum (Figure S91), there existed some peaks of diol[5, 6] by-product and polyether[7, 8] by-product at 3.3–3.6 ppm, and their presence led to the moderated selectivity of CCE reactions. The high nucleophilicity of Br^- were able to directly attack the epoxides for diol with traces of moisture or polyether (with next epoxide) by-products.

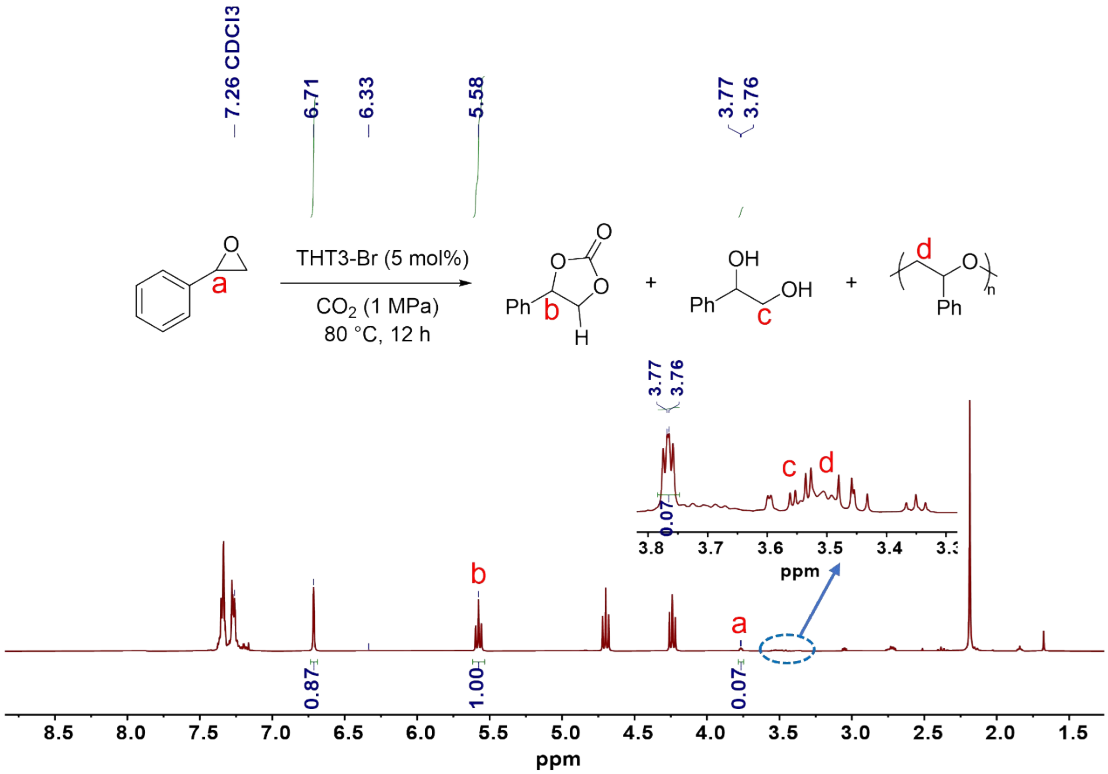


Figure S91. ^{1}H NMR Spectrum of crude CCE reaction mixture of styrene oxide (400 MHz, CDCl3). Styrene oxide (5 mmol), THT3-Br (5 mol%), CO_2 (1 MPa), 12 h, 80 °C, 52.9 mg crude mixture, 9.7 mg mesitylene (Table 1, entry 9). Conversion, 93%; selectivity, 91%.

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9. Reaction parameters of CCE reactions (Figure S92)

The effect of catalyst loading on the reaction rate was investigated, the kinetic about catalyst was plotted (Figure S92 (a)). It was carried out under 100 °C, 1 – 5 mol% catalyst loading, 10 h, no solvent. According to previous kinetic and activation enthalpy and entropy study, which were reported by Abdul Rehman *et al.*[9, 10], a first-order dependence reaction kinetics graph with a slope of 0.4885 In [SO] verse time was plotted at 5 mol% **THT3-Br**, 100 °C, 1 MPa CO_2, 10 h, no solvent (Figure S92(b)). The double logarithmic plot between k_{obs} and catalyst concentration was drawn. It is obvious that the reaction rate relies on catalyst concentration in the first order from 87 – 439 mM **THT3-Br** (Figure S92(c)). In addition, the influence of temperature on the reaction rate was studied by preforming experiments at range of 80 – 120 °C, 5 mol% **THT3-Br** (Figure S92(d)). Due to these experiments were carried out under bulk, the Arrhenius plot between In (k_{obs}) vs. 1/T was not desired, the activation energy was estimated at E_a = 37.8 KJ·mol^{-1} in the presence of catalyst **THT3-Br** (Figure S92(e)). Further, the enthalpy ($\Delta H^{\ddagger}$ = 34.76 KJ·mol^{-1}) and entropy ($\Delta S^{\ddagger}$ = -132.17 KJ·mol^{-1}) were obtained using Eyring equation (Figure S92(f)).

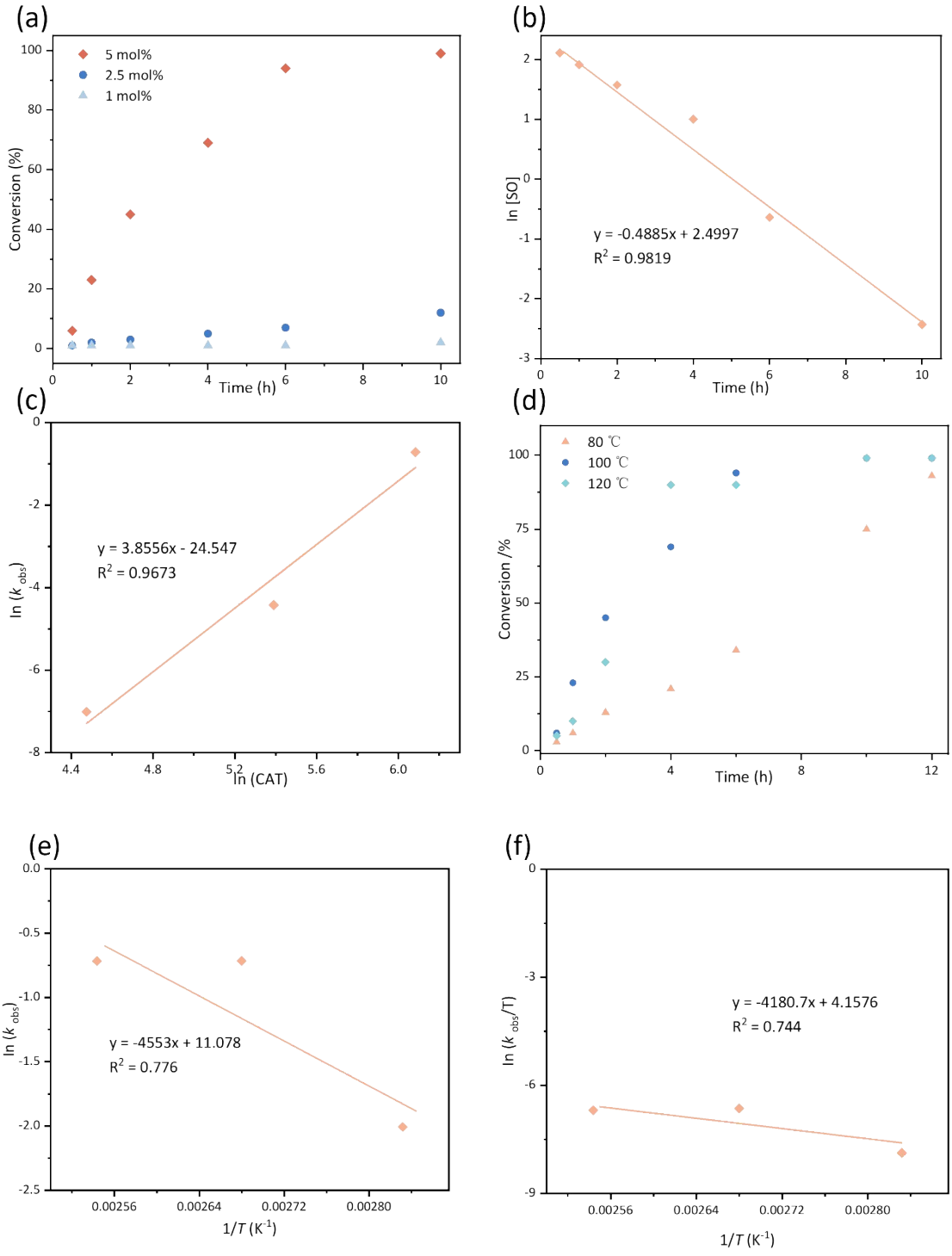

Figure S92. (a) Effect of the catalyst loading on the conversion of styrene oxide (**SO**). Reaction conditions: 1, 2.5, and 5 mol% of **THT3-Br**, 100 °C, 1 MPa CO_2, 10 h. (b) First order plot of ln [SO] versus time. Reaction conditions: 5 mol% **THT3-Br**, 100 °C, 1 MPa CO_2, 10 h. (c) Double plot between k_{obs} and catalyst **THT3-Br** concentration. Reaction conditions: 87 – 439 mM **THT3-Br**, 100 °C, 1 MPa CO_2, 10 h. (d) Influence of the reaction temperature on the conversion of **SO** in the presence of catalyst **THT3-Br**. (e) Arrhenius plots for activation energy estimation

in the presence of catalyst **THT3-Br**. (f) Eyring plots for activation enthalpy and entropy estimation in the presence of catalyst **THT3-Br**. Reaction conditions: 5 mol% **THT3-Br**, 80 – 120 °C (T = 353.15 - 393.15 K), 1 MPa.

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