Supporting information

Conversion of Dilute CO_2 to Cyclic Carbonates at Sub-atmospheric Pressures by a Simple Indium Catalyst

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A. Experimental section

General Considerations. Unless otherwise indicated, all air- and/or water-sensitive reactions were carried out under dry nitrogen using either an M-Braun glove box or standard Schlenk line techniques. NMR spectra were recorded on Bruker Avance 300 MHz and 400 MHz spectrometers at 25 °C. ^{1}H NMR chemical shifts are reported in ppm versus residual protons in deuterated solvents as follows: δ 7.27 CDCl$_3$ and 7.16 C$_6$D$_6$, ^{13}C NMR chemical shifts are reported in ppm versus residual ^{13}C in the solvent: δ 77.2 CDCl$_3$ and 128.39 C$_6$D$_6$. Diffraction measurements for X-ray crystallography were all made using Mo-Kα radiation. Data for all complexes were collected on a Bruker APEX II DUO diffractometer equipped with TRIUMPH monochromator. In situ infrared spectroscopy was performed using an iC-15 ReactIR (Mettler-Toledo) equipped with a SiComp in-situ IR probe. The wavenumber range is 3000-650 cm^{-1} and a scan is taken every 15 sec.

Materials. Epoxides and CDCl$_3$ were degassed through a series of freeze-pump- thaw cycles and dried over CaH$_2$ before distillation. THF, toluene and C$_6$D$_6$ were degassed through a series of freeze-pump-thaw cycles and distilled from Na/benzophenone ketyl. The epoxides were purchased from Tokyo Chemical Industries (TCI) and Sigma Aldrich. All metal halides were purchased from Alfa Aesar and Sigma Aldrich and are directly used without further purifications. ^{13}CO$_2$ gas cylinder was purchased from Sigma Aldrich

Synthesis of cyclic carbonates at 1 bar. All of the synthesized cyclic carbonates have been previously reported.[1, 2] Unless otherwise stated, all cyclic carbonates, metal halides, and cocatalyst are prepared in the same way. In the glove box, a 5 ml vial was charged with a stir bar, epoxide (3.4 mmol), metal halide (0.17 mmol), cocatalyst (0.34 mmol). The mixture was stirred for 5 min and capped with a septum. The solution was taken outside the box and vented by CO$_2$ for 1 min using a balloon. After venting a new CO$_2$ balloon was added and the reaction was left stirring for a certain time at 25 °C. The reaction was then put in an ice bath for 5 min and by a syringe a crude mixture was filtered through Celite and analyzed by ^{1}H NMR (300 MHz or 400 MHz, CDCl$_3$, 25 °C). AlBr$_3$ and gallium halides are very exothermic and reagents when adding epoxide. Therefore, the epoxide and the reagents are cooled in the freezer at -30 °C before mixing them with each other.

Since the reaction is only yielding one product (cyclic carbonate) and no evaporation of epoxide is occurring, conversions can be determined by comparing the peak area of cyclic carbonate to that of remaining epoxide. For isolated yields, such as the synthesis of propylene and vinyl carbonates (Table 3 entries 1 and 4), the crude mixture was filtered through Celite and put under vacuum for 24 h to remove the remaining epoxide from the solution. The product was obtained by doing fractional distillation at least twice under vacuum and at 180 °C.

Experimental setup for low CO$_2$ pressures. For diluted CO$_2$ experiment, a high pressure vessel (230 ml head + vessel) was dried in an oven and transferred to the glovebox. The vessel was filled with **1a**, InBr$_3$, and NBu$_4$Br then sealed properly and moved outside the box. The vessel containing

the solution is separated from the reactor head by a valve. A gentle vacuum was applied to the vessel while the valve is closed. The reactor head was pressurized with N_2 and then further pressurized with CO_2 while the valve is closed. We waited 15 mins until both gases mixed properly with each other, then we opened the valve connecting the head and the vessel and we depressurized the entire reactor until 1 bar. For example to obtain 50:50 CO_2:N_2, we initially pressurized the head with N_2 at 1 bar then we further pressurized the vessel with CO_2 until 2 bars. The gases were allowed to mix and then opened the valve connecting the head to the vessel and depressurized until 1 bar. The reactions were allowed to run for 1 hr and then a sample aliquot was taken for analysis.
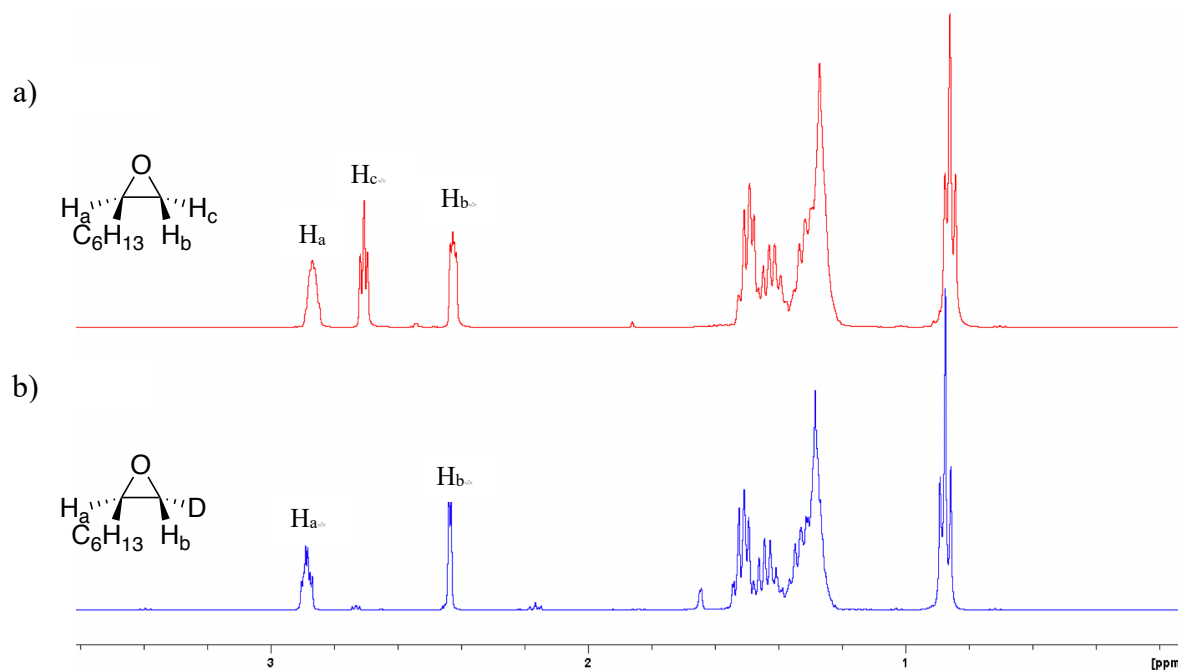
B. Synthesis of deuterated epoxide (trans 1,2-D-epoxyoctane)
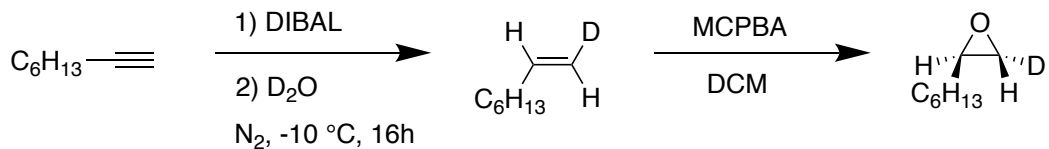
Trans-1-deuterio-1-octene: The procedure was followed according to the literature with some modifications.[3, 4] Diethylaluminium hydride in 1 M of hexane (9 ml, 0.009 mol) was added under nitrogen to 2.9 g of 1-octyne (0.027 mol) at -10 °C for 4h. The excess octyne was distilled from the reaction mixture under reduced pressure. Afterwards, D_2O was added to the reaction (4 ml, 0.18 mol) in the presence of pentane and let stir for 16 h. White precipitates formed, and the reaction mixture was filtered then with filter paper and the remaining D_2O was removed by separatory funnel. The mixture obtained was distilled and the pentane was removed by roatavap to obtain trans-1-deuterio-1-octene (0.6 g, yield: 21 %).

Trans 1,2-D-epoxyoctane: DCM was added to trans-1-deuterio-1-octene. The mixture was stirred while meta-Chloroperoxybenzoic acid (MCPBA) in DCM was added dropwise from an additional funnel. Stirring continued at room temperature for 16 h. The mixture was then filtered with suction through Celite, washed with saturated aqueous Na_2CO_3 (3*40 mL) and dried over $MgSO_4$. After filtration and concentration, the oxide was distilled to afford 0.45 g (yield: 16%).

Figure S1 compares the ^1H NMR spectra of 1,2-epoxyoctane and trans 1,2-D-epoxyoctane. It is evident that the peak at 2.7 ppm, attributed to H_c, has mostly disappeared in trans 1,2-D-epoxyoctane. This indicates that H_c is fully deuterated. In epoxides, the coupling constant in the cis vicinal proton H_b (4.32 Hz) is greater than the trans vicinal proton H_c (2.88 Hz). And the cis proton in epoxides H_b appears to be more upfield than trans proton H_c.[5] Figure S2 confirms that the the cis proton H_c in trans D-epoxyoctane is deuterated.). The ratio between the trans deuterated and fully protonated epoxides is 96:4. Similarly, the ^1H NMR of the resulting cyclic carbonic shows a ratio of 96:4 (Figure S3) which indicates that the reaction proceeds with retention in configuration.

Figure S1. ¹H NMR (400 MHz, CDCl₃, 25 °C) a) 1,2 epoxyoctane b) Trans 1,2-D-epoxyoctane.
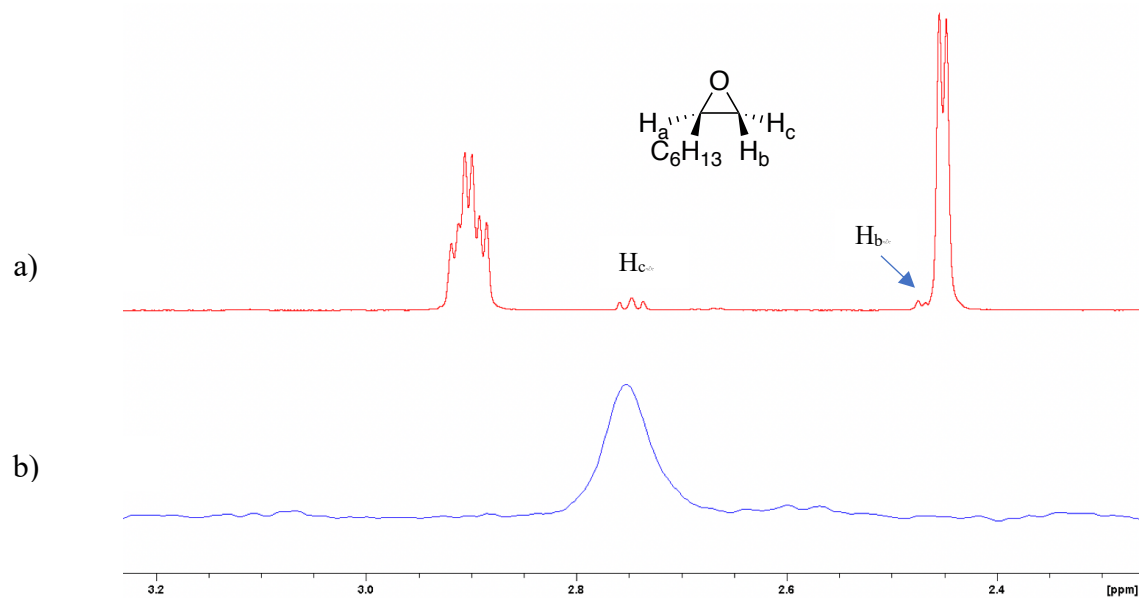
Figure S2. a) ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of trans D-epoxyoctane. b) ²H NMR (400 MHz, CDCl₃, 25 °C) of trans D-epoxyoctane.
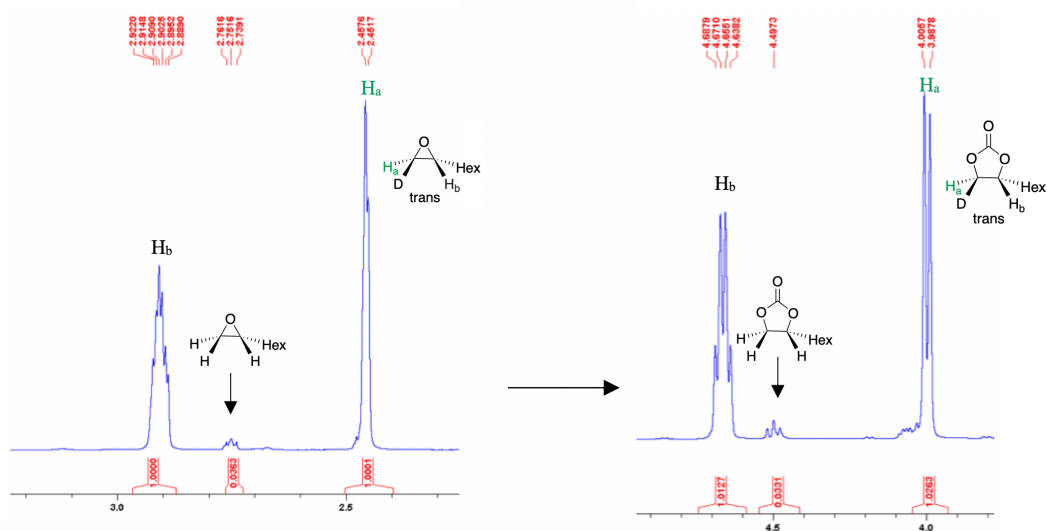
Figure S3. ^{1}H NMR spectra of deuterated epoxide and cyclic carbonate.
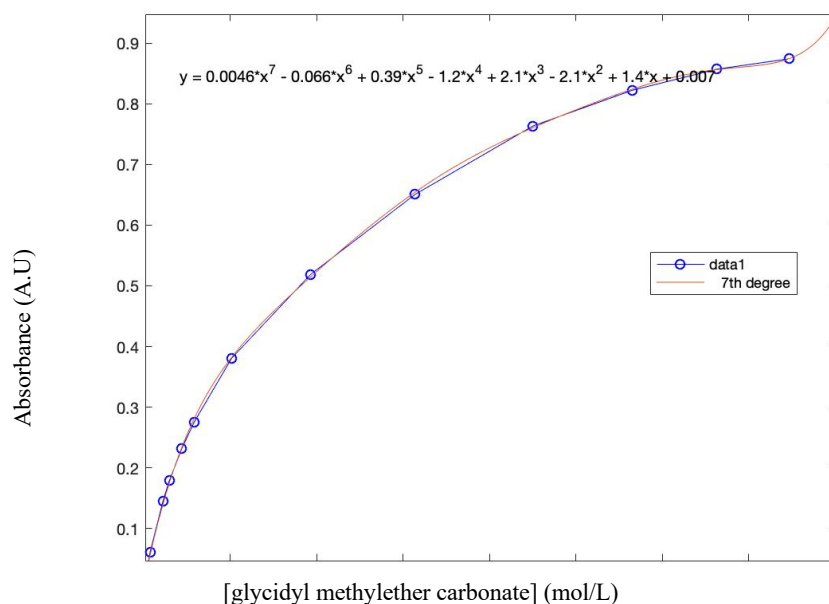
C. In situ React IR Experiments

General preparation of IR sample: In the glove box, a vial was charged with stir bar, epoxide, InBr$_3$ and NBu$_4$Br. The IR probe was attached to a 16 ml vial using a septum cap. Toluene was added to the vial via syringe and a blank was taken. The vial was then vented with CO$_2$ using a balloon for 5 min. After saturation of CO$_2$ a mixture of epoxide, InBr$_3$ and NBu$_4$Br is added to the vial via a syringe and stirred at 1000 rpm and at 25 °C. 3D plots are of absorbance vs. wavenumber vs. time (snapshot of the IR spectra at every 15 seconds) are obtained (Figure S4). From this figure, a clear and sharp band is formed at 1802 cm^{-1} that is attributed to the carbonyl stretching band of the cyclic carbonate product.
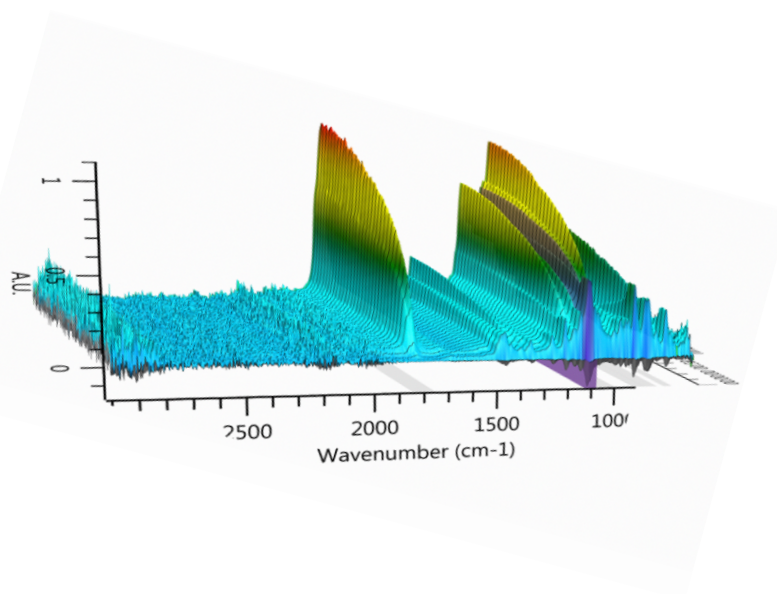
Figure S4. a) *In situ* IR spectroscopy 3D spectrum of coupling neat epoxide and CO_2. Carbonyl signal of cyclic carbonate grows at 1802 cm^{-1}.

The absorbance was converted to concentration using a calibration curve. The calibration curve obtained is not a straight line, because we are using extremely high concentrated solutions of epoxides. The equation of the curve was determined using MATLAB R2018b software (Figure S5). The best fit curve (red curve) has a seventh-degree polynomial equation, which overlaps perfectly with the blue calibration plot that has been obtained by preparing 12 different stock solutions of glycidyl methyl ether carbonate **2a** (0.010 to 3.7 M in toluene).

Plot — y-axis: Absorbance (A.U); x-axis: [glycidyl methylether carbonate] (mol/L).

Equation on plot: $y = 0.0046 \cdot x^7 - 0.066 \cdot x^6 + 0.39 \cdot x^5 - 1.2 \cdot x^4 + 2.1 \cdot x^3 - 2.1 \cdot x^2 + 1.4 \cdot x + 0.007$

Legend: data1; 7th degree

Figure S5. Blue: calibration curve prepared from different cyclic carbonates **2a** concentrations from 0.010 to 3.7 M in toluene. Red: simulated plot.

(a) (a) Inhibition in initial rates when [InBr$_3$] exceeds [NBu$_4$Br]

Table S1. Varying [InBr$_3$] while keeping [NBu$_4$Br] constant.

Entry	[InBr$_3$] (M)	[NBu$_4$Br] (M)	[InBr$_3$]/[NBu$_4$Br]	ν_o (mol·L^{-1}.h^{-1})
1	0.025	0.1	0.25	0.21 ± 0.02
2	0.050	0.1	0.5	0.59 ± 0.02
3	0.067	0.1	0.67	0.89 ± 0.01
4	0.10	0.1	1.0	0.84 ± 0.02
5	0.15	0.1	1.5	0.39 ± 0.04
6	0.20	0.1	2.0	0.23 ± 0.03

Reaction conditions; **1a** = 0.34 g/ml in toluene; P(CO$_2$) = 1 bar; T= 25 °C. Errors are calculated using the standard deviation of three trials in excel.
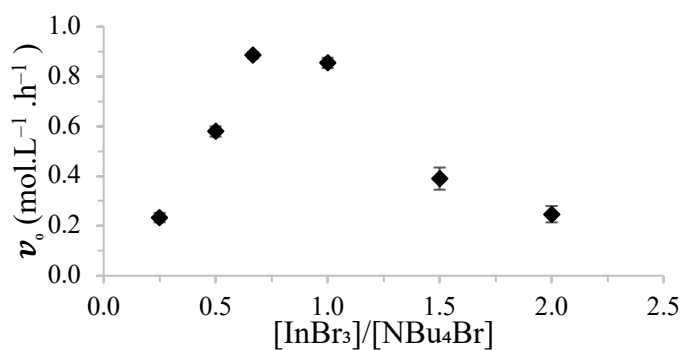
**Plot 1. 1a** = 0.34 g/ml in toluene; P(CO$_2$) = 1 bar; T= 25 °C. Errors are calculated using the standard deviation of three trials in excel.

(b) (b) Reaction order with respect to $[InBr_3]$

The order of indium bromide has been determined using Variable Time Normalization Analysis (VTNA).[6, 7]   Three reaction profiles have been obtained using different $InBr_3$ concentrations (0.025, 0.050 and 0.10 M) and at constant NBu_4Br and epoxide **1a** concentrations. By normalizing the time axis by multiplying the time with $[InBr_3]$ raised to the correct reaction order, the reaction profiles will overlap with each other. Four different orders have been plotted (Figure S6). The reaction profiles overlap with each other when they are raised to power one.
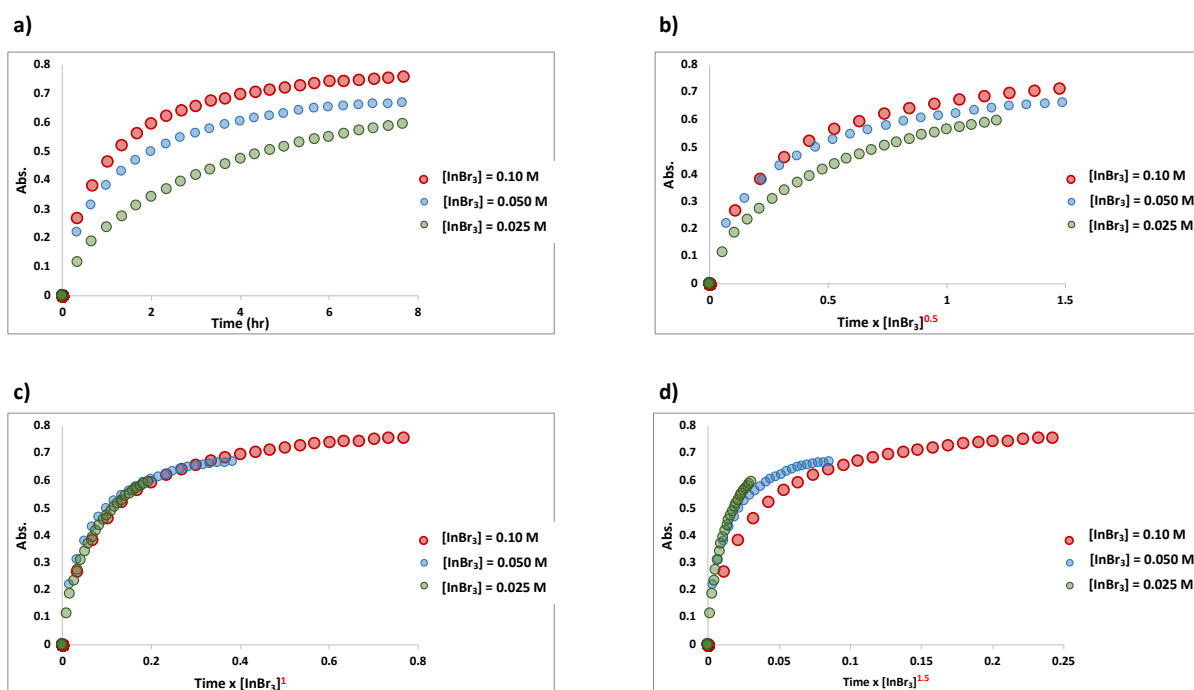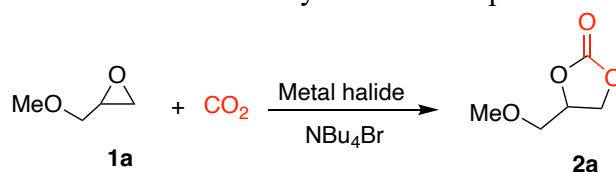
Figure S6. a) Reaction profile when raised to power zero. b) Reaction profile when raised to power 0.5. c) Reaction profile when raised to power 1. d) Reaction profile when raised to power 1.5 Reaction conditions: $[NBu_4Br]$ = 0.1M; Epoxide **1a** = 0.34 g/ml in toluene; $P(CO_2)$ = 1 bar; T= 25 °C.

(c) (c) Reaction order with respect to [NBu$_4$Br]

Three reaction profiles have been obtained using different NBu$_4$Br concentrations (0.025, 0.050 and 0.10 M) and at constant InBr$_3$ and epoxide concentrations. By normalizing the time axis by multiplying the time with [NBu$_4$Br] raised to the correct reaction order, the reaction profiles will overlap with each other. Four different orders have been plotted (Figure S7). The reaction profiles overlap with each other when they are raised to power one.
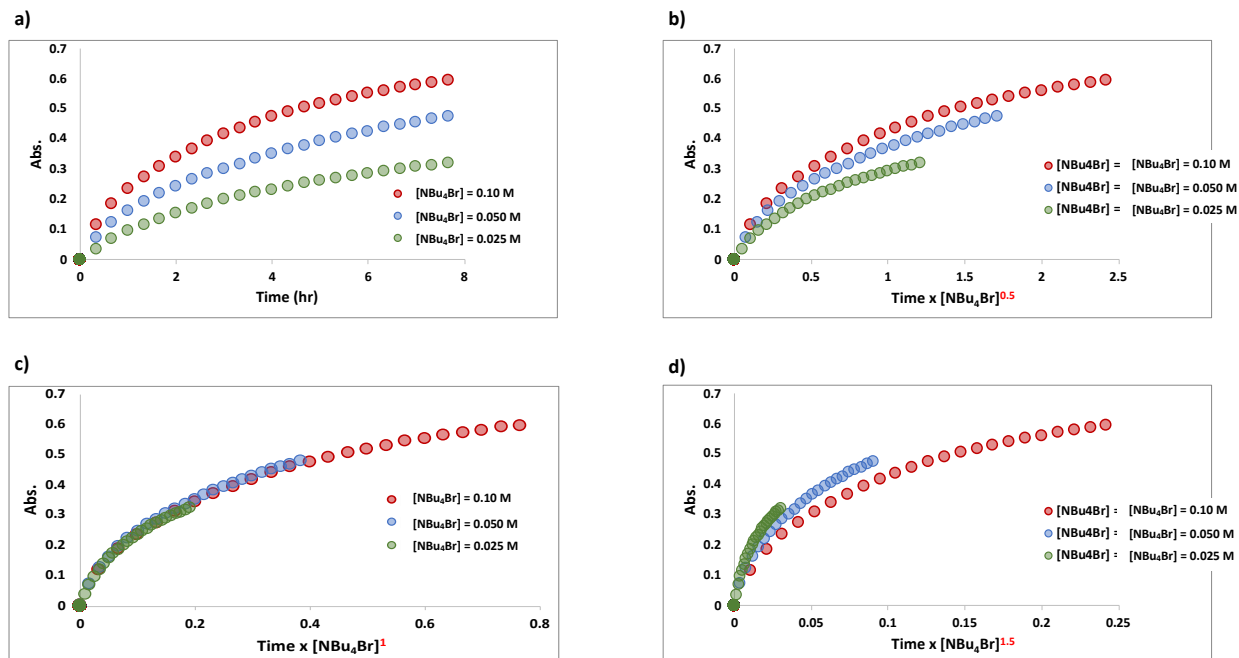
Figure S7. a) Reaction profile when raised to power zero. b) Reaction profile when raised to power 0.5. c) Reaction profile when raised to power 1. d) Reaction profile when raised to power 1.5 Reaction conditions: [InBr$_3$] = 0.025M; **1a** = 0.34 g/ml in toluene; P(CO$_2$) = 1 bar; T= 25 °C.

D. Catalyst deactivation/product inhibition

The robustness of the catalyst was checked using reaction progress kinetic analysis (RPKA) protocols with some modification.[8] Stock solutions of **1a** were prepared in concentrations of 0.34 and 0.20 g/ml in toluene. Initial concentrations of $InBr_3$, NBu_4Br, and CO_2 are the same and remain constant throughout the reaction. By "time-shifting" the profile of experiment 2 toward the profile of experiment 1, we observe and overlap of the two profiles indicating no catalyst poisoning or product inhibition (Figure S8).

	Experiment 1	Experiment 2
1a in toluene (g/ml)	0.34	0.20
$[InBr_3]$ (M)	0.10	0.10
$[NBu_4Br]$ (M)	0.20	0.20

(a)   b)
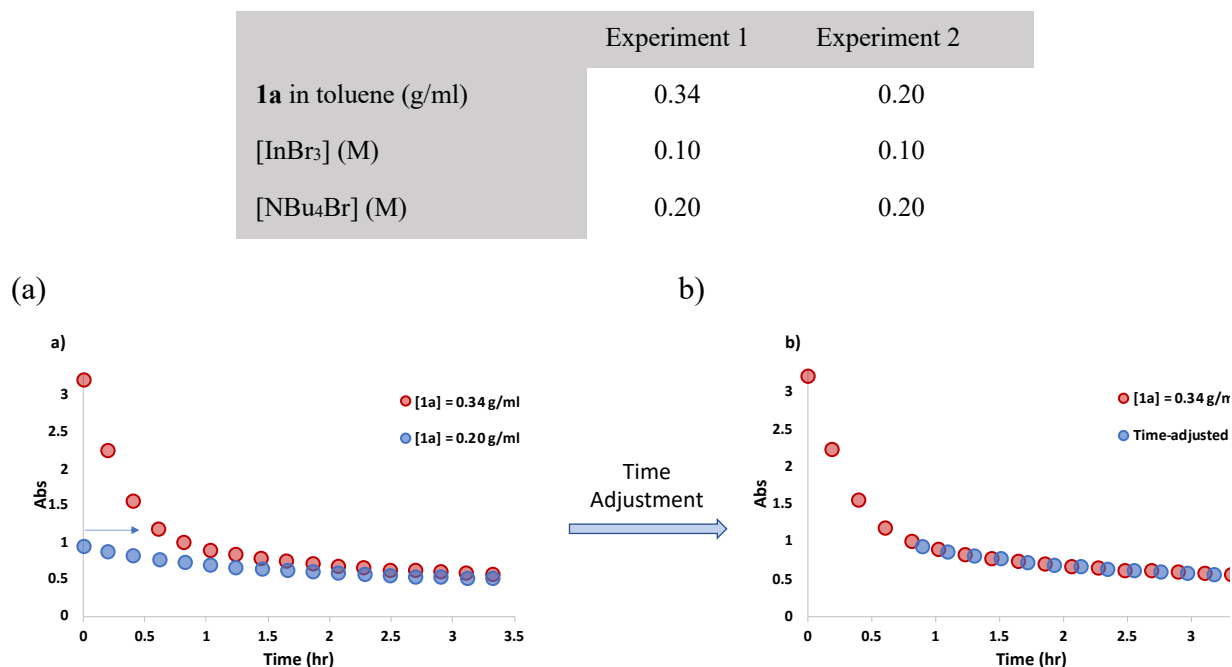
Figure S8. a) Reaction profiles at two different starting points; In Black profile, the mass addition of epoxide **1a** is 0.34 g/ml in toluene. In the orange profile, **1a** is 0.20 g/ml in toluene. b) Time adjusting the orange profile to overlap with the black profile. Reaction conditions: $P(CO_2) = 1$ bar; $T = 25 °C$ in toluene.

E. Relationship between $[InBr_3]$ and the intensity of carbonate IR signals

Equimolar solutions of $InBr_3$ and NBu_4Br in 0.21 g/ml propylene oxide **1b** were prepared in a 16 ml vial and a blank solution was recorded. Afterwards, fixed amount of CO_2 (0.6 mmol) was added to the solution via a balloon (Figure S9). The maximum intensity of the signals assigned to the carbonate intermediate species at 1610 and 1305 cm^{-1} have been plotted versus $[InBr_3]$ which revealed a linear relationship between the initial concentration of $InBr_3$ and the concentration of carbonate (Figures S10 and 11). Also, the maximum intensity of the signals at 1610 and 1305 cm^{-1} versus [epoxide] has been plotted. The plot revealed no relationship between **[1b]** and maximum intensities (Figure S12 and 13). The concentration of intermediate is dependent on $[InBr_3]$. So, one should expect increase in the maximum intensity of the intermediate by increasing $[InBr_3]$. Since

there is excess of epoxide in solution (compared to indium) there should be no increase in maximum intensity of the intermediate by increasing **[1b]**. Also, if two indium centers are involved in the intermediate, then we should not see a linear correlation between $[InBr_3]$ and [intermediate].
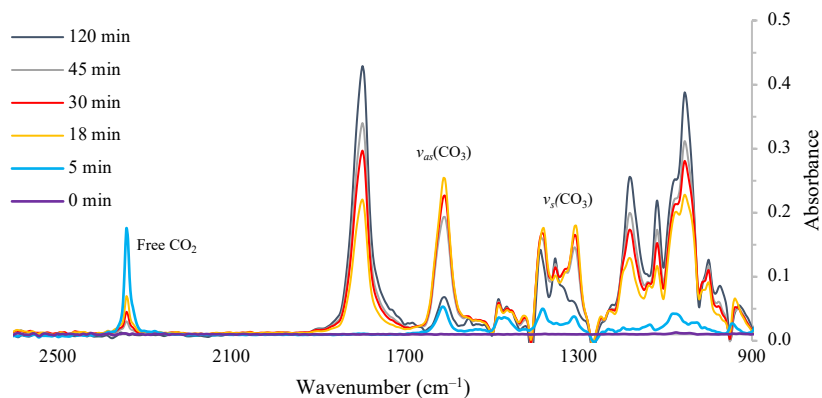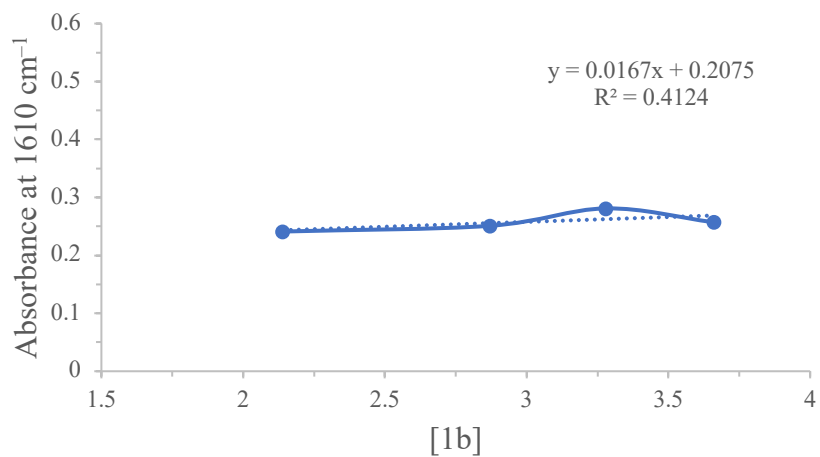

Figure S9. Absorbance vs wavenumber (cm^{-1}) IR spectroscopy spectra from 0-120 min. Reaction conditions: **1b** = 0.21 g/ml in DCM, $[InBr_3]$ = 0.37 M, $[NBu_4Br]$ = 0.37 M at $P(CO_2)$ = 1 bar and T = 25 °C.
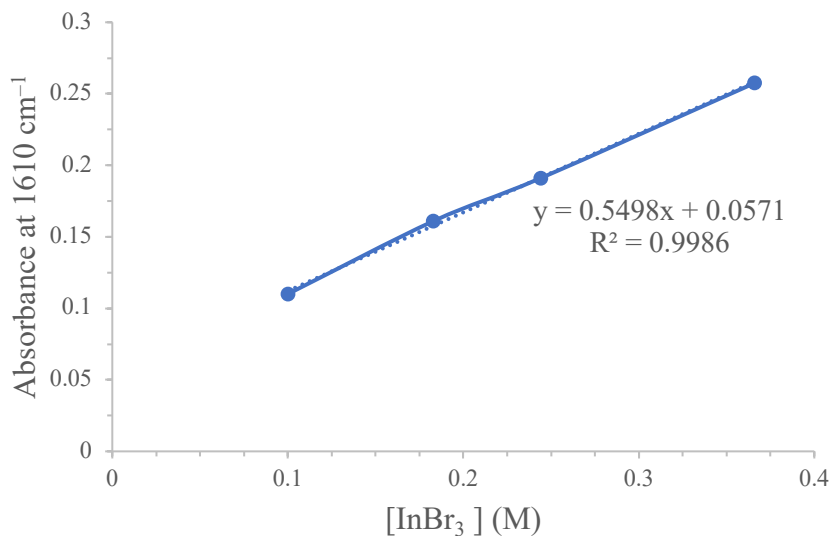
Figure S10. Intensity of carbonate absorption at 1610 cm^{-1} versus the initial concentration of $InBr_3$
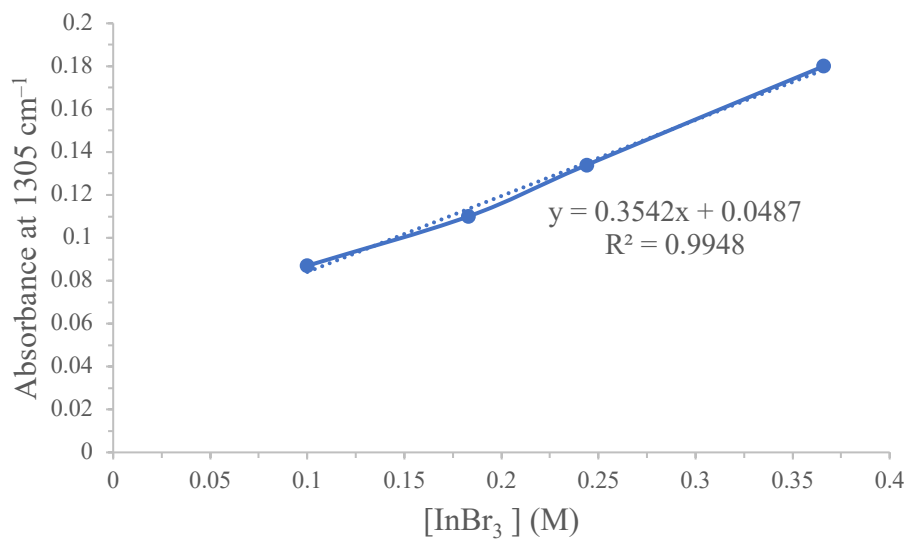
**Figure S11.** Intensity of carbonate absorption at 1305 cm^{-1} versus the initial concentration of InBr$_3$

Figure S12. Intensity of carbonate absorption at 1610 cm^{-1} versus the initial concentration of propylene oxide.
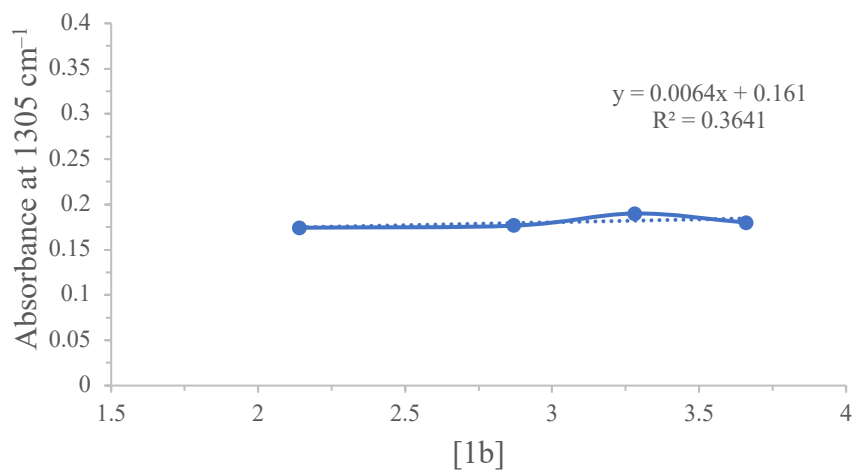
Figure S13. Intensity of carbonate absorption at 1305 cm^{-1} versus the initial concentration of propylene oxide.

F. *In situ* IR spectroscopy using tetra butyl ammonium azide

IR samples are prepared similar to the ones reported earlier. Initially, a blank spectrum was recorded for an empty vial at T= 25 °C. Next, via a syringe NBu_4N_3 dissolved in DCM was added to the vial and an immediate band at 2000 cm^{-1} has appeared (Figure S14a). After the stabilization of the band at 2000 cm^{-1}, $InBr_3$ dissolved in DCM was added to the solution (Figure S14c). Then **1a** epoxide was added followed by CO_2 (Figure S14c and d). In a different experiment, **1a** was added to a solution of NBu_4N_3 in DCM (Figure S14b). We observe a small band at 2080 cm^{-1} which indicates a minimal formation of ring-opened epoxide by an azide anion. *Caution: extra care must be implemented when adding NBu₄N₃ to DCM solution. There is a possibility that diazidomethane may form which is an explosive chemical.*[9]
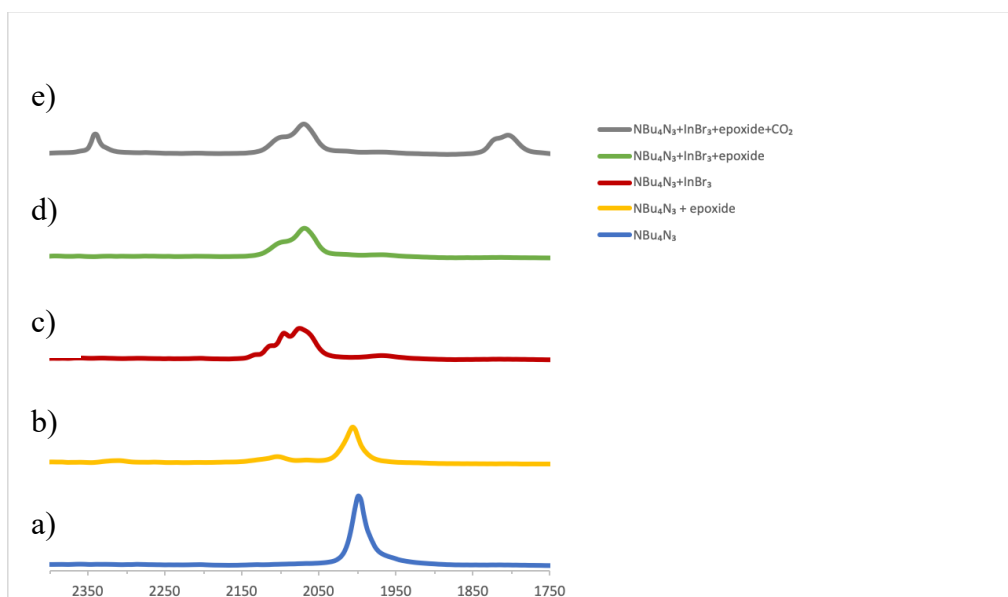
Figure S14. Infrared spectra illustrating the different binding modes of azide anion. Infrared spectra illustrating the different binding modes of azide anion at T = 25 °C. a) NBu_4N_3 in DCM. b) NBu_4N_3 and **1a**. Note: this has been done in a separate experiment c) 1:1 NBu_4N_3:$InBr_3$ in DCM. d) 1:1 NBu_4N_3:$InBr_3$, **1a**, and DCM. e) 1:1 NBu_4N_3:$InBr_3$, **1a**, CO_2 in DCM.

G. Crystal structure of indium tetra-bromide anion:

[NBu$_4$][InBr$_4$] crystals have been successfully isolated when a concentrated solution of toluene was put in the freezer in the presence of epoxide (Figure S15). The structure has been previously characterized and reported.[10, 11]
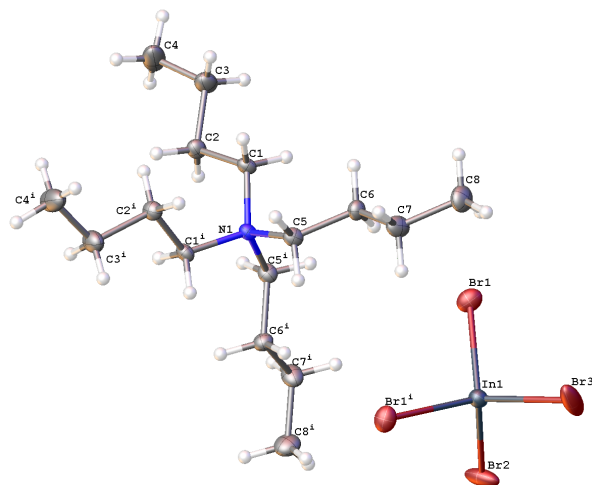

Figure S15. Molecular structure of [NBu$_4$][InBr$_4$]. Thermal ellipsoids are drawn at 50% of the probability level. Selected bond lengths (Å) and angles (deg): In1-Br1 2.479(2), N1-C1 1.5421(11), Br1-In-Br3 110.1(1).

H. Reactivity towards Et$_3$PO

Reactivity towards Et$_3$PO as scale for Lewis acidity

The Gutmann−Beckett method[12, 13] involves the addition of the Lewis base triethylphosphine oxide (OPEt$_3$) to a Lewis acid to form an adduct of interest in situ. The shift of the free OPEt$_3$ is measured for each sample by the addition of a capillary containing a solution of free OPEt$_3$ to the NMR tube. The chemical shift of the phosphorus nucleus to a lower field is an indication of Lewis acidity (Figure S16).
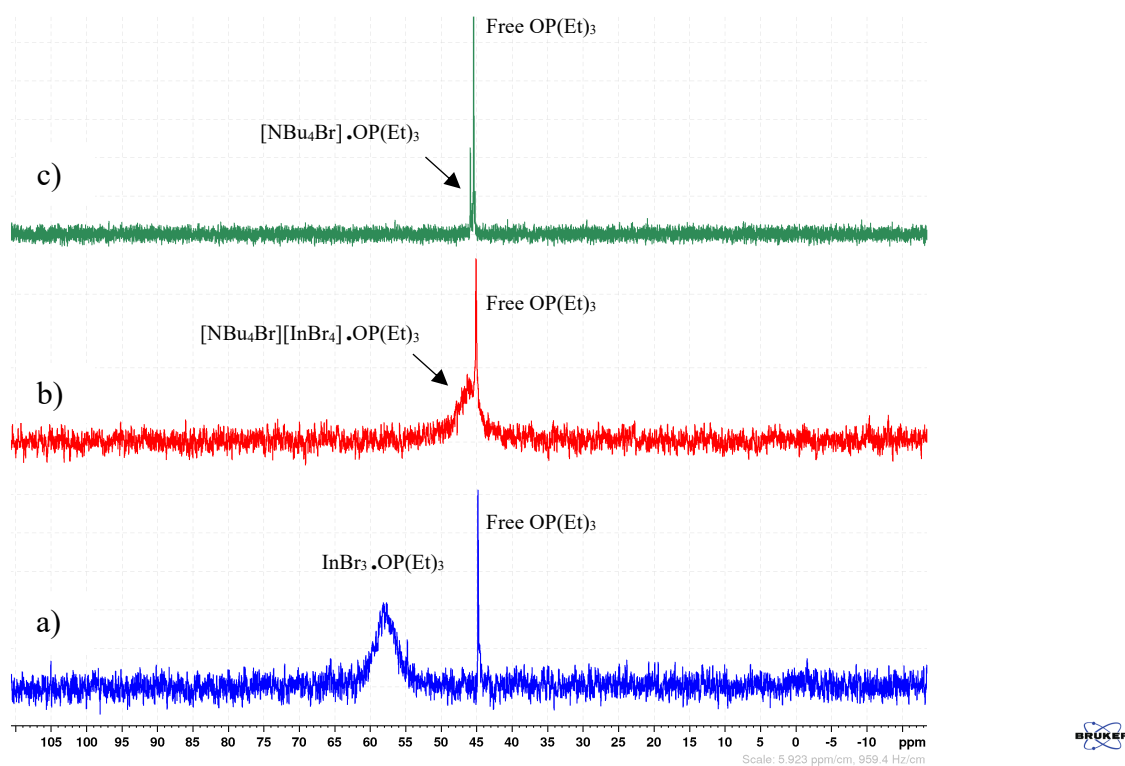
Figure S16. ^{31}P$\{^1$H$\}$ NMR spectrum of 20mM solutions of a) InBr$_3$ b) [NBu$_4$Br][InBr$_4$] and c) [NBu$_4$Br] prepared with 17mM standard solution of OP(Et)$_3$ in C$_6$H$_6$ (0.8mL, 0.8equiv.). A sealed capillary tube containing 20mM solution of OP(Et)$_3$ was inserted into NMR samples to serve as an internal standard. Spectra are calibrated to the peak of "free" OP(Et)$_3$ from the internal standard at 45ppm.

H. Variable temperature (VT) ^{1}H NMR spectra

VT ^{13}C{^{1}H} NMR spectroscopy experiments. A mixture of 0.34 M InBr$_3$, 0.34 M NBu$_4$Br, and 3.4 mmol of **1a** in CDCl$_3$ is prepared inside the glovebox and put inside J-young tube. The tube was closed properly and removed outside the box. The tube was attached to a Schlenk line, put under liquid N$_2$, and then vacuum was applied. ^{13}CO$_2$ cylinder attached to the Schlenk line gently supplied the J-young tube with gas. The frozen tube was taken immediately for ^{13}C{H} NMR spectroscopy analysis using 400 MHz Bruker instrument in CDCl$_3$ (Figure S17). All ^{13}C-spectra are normalized to CDCl$_3$ signal (77 ppm).
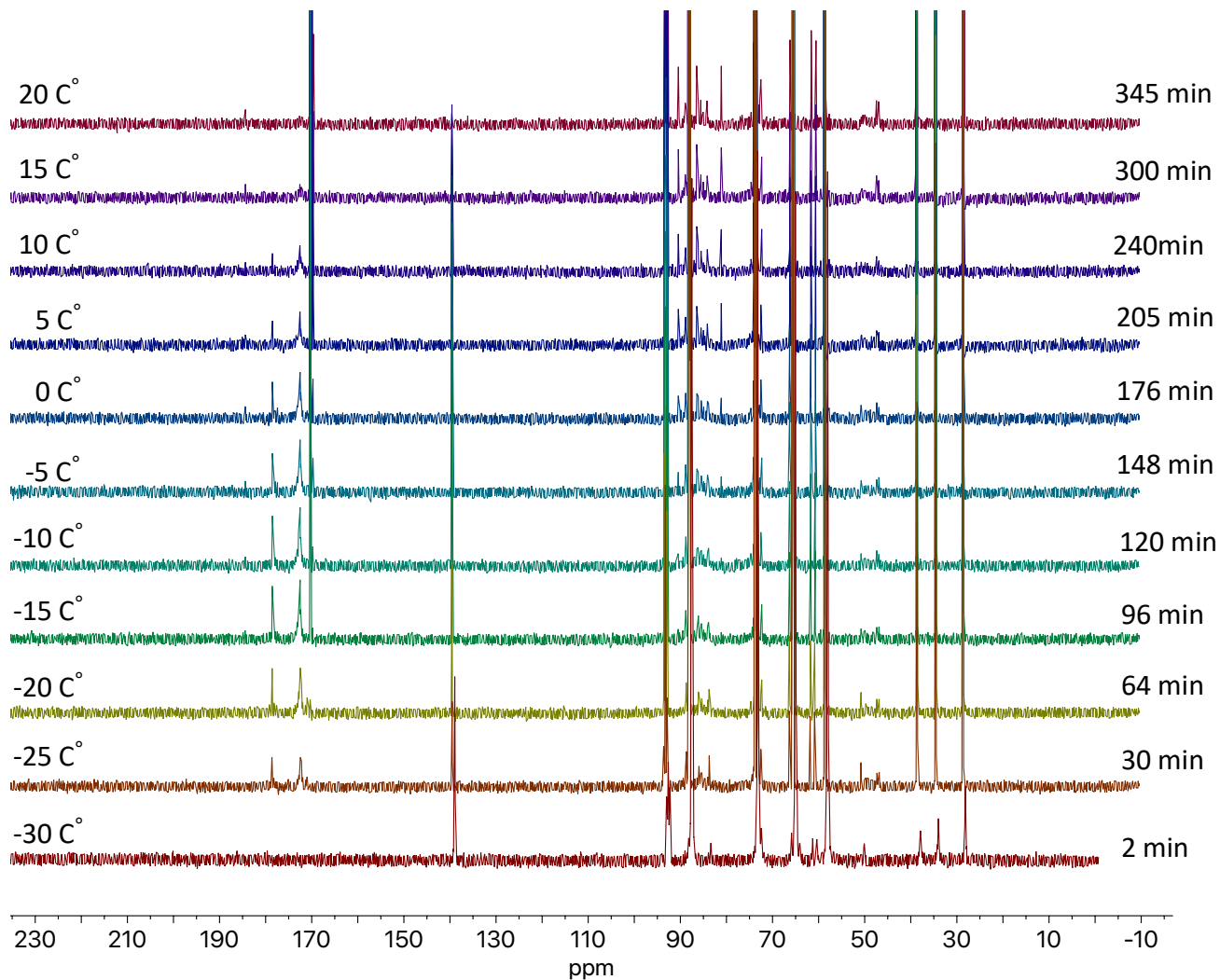

Figure S17. Variable temperature (VT) ^{1}H NMR spectra (400 MHz, CDCl$_3$, -30 to 20 °C). CDCl$_3$ is taken as a reference. **2a** = 3.4 mmol, InBr$_3$ = 0.34 mmol, NBu$_4$Br = 0.34 mmol in ^{13}CO$_2$.

I. Comparison of InBr₃/NBu₄Br with other homogeneous systems that are active at diluted CO₂ pressures.

Table S2.

| Entry	Lewis Acid (LA)	Co-Cat.	Epoxide	Epox:LA:CO-Cat.	CO_2 pressure (bar)	Temp. (°C)	Time (h)	Conversion (%)	Reference
1	InBr₃	NBu₄Br	GME	100:5:10	0.5	20	1	45	-
2	ScCl₃	NBu₄Br	EPH	100:1:2	0.5	22	5	41	14
3	YCl₃	NBu₄Br	EPH	100:1:2	0.5	22	5	39	14
4	ZrCl₄	NBu₄Br	EPH	100:1:2	0.5	22	5	37	14
5	TaCl₅	NBu₄Br	EPH	100:1:2	0.5	22	5	8	14
6	NbCl₅	NBu₄Br	EPH	100:1:2	0.5	22	5	15	14
7	ZnBr₂	[Bmim][Br]/ K₂CO₃	SO	100:5:5	0.5	50	18	89	15
8	-	[AITMG][Br]	AGE	100:10	0.15	100	48	99	16
9	Co(acac)₂	NBu₄I	HO	100:0.5:2.5	0.1	70	4	92	17

Epoxides abbreviation, GME: glycidyl methyl ether; EPH: epichlorohydrin; SO: styrene oxide; AGE: allyl glycidyl ether; HO: 1,2 hexene oxide.
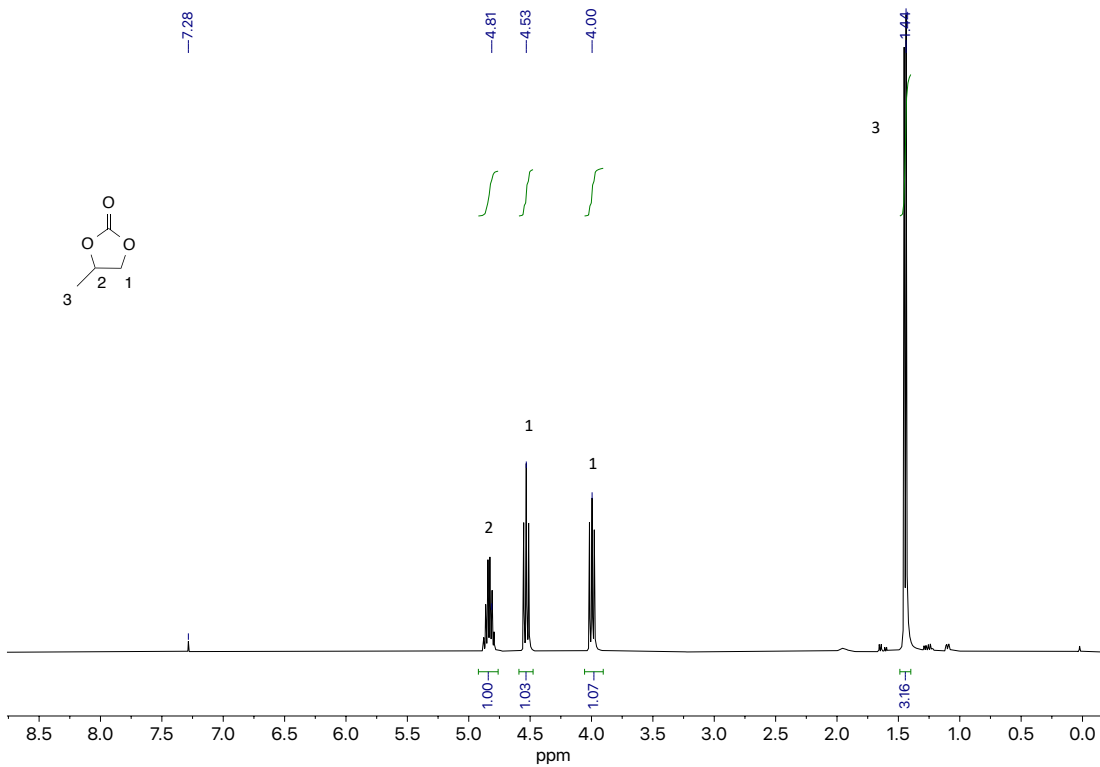

[AITMG][Br]   [Bmim][Br]   Co(acac')₂
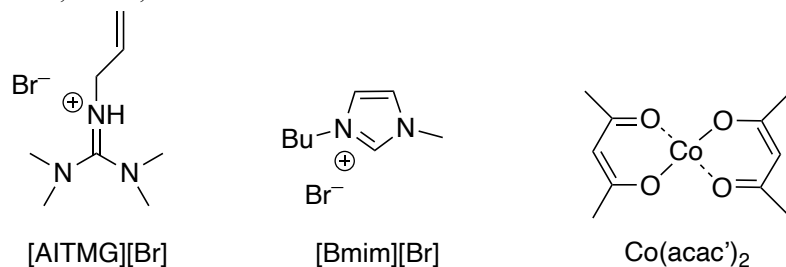
Figure S18. Homogeneous catalysts that are active for CO_2/epoxide cycloaddition at diluted pressures (Table S2 entries 7-9).

J. NMR spectra of unpurified cyclic carbonates

2a
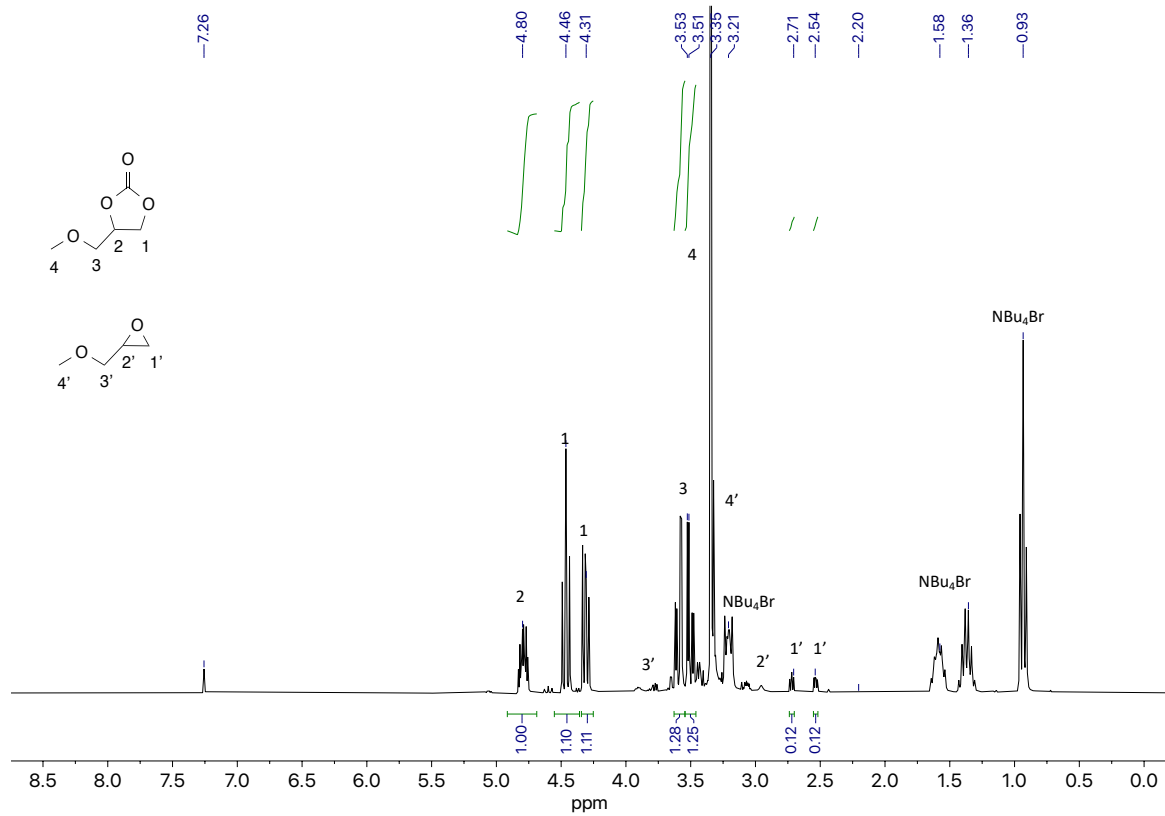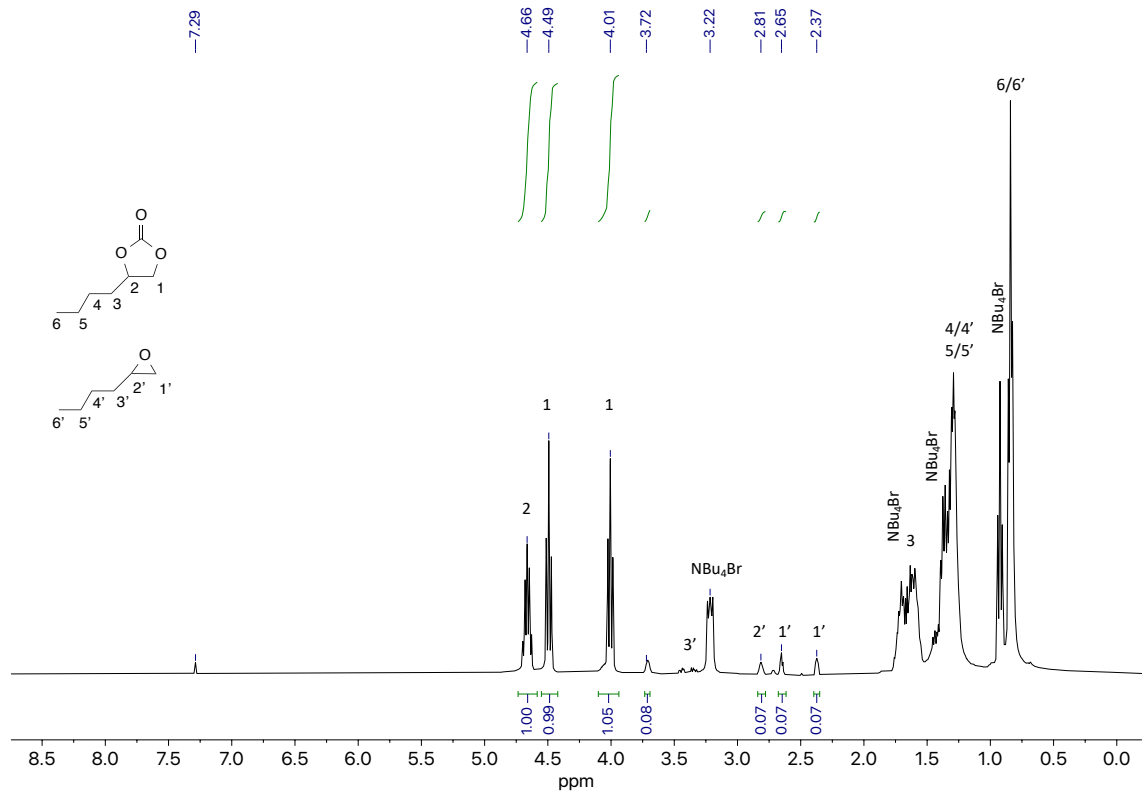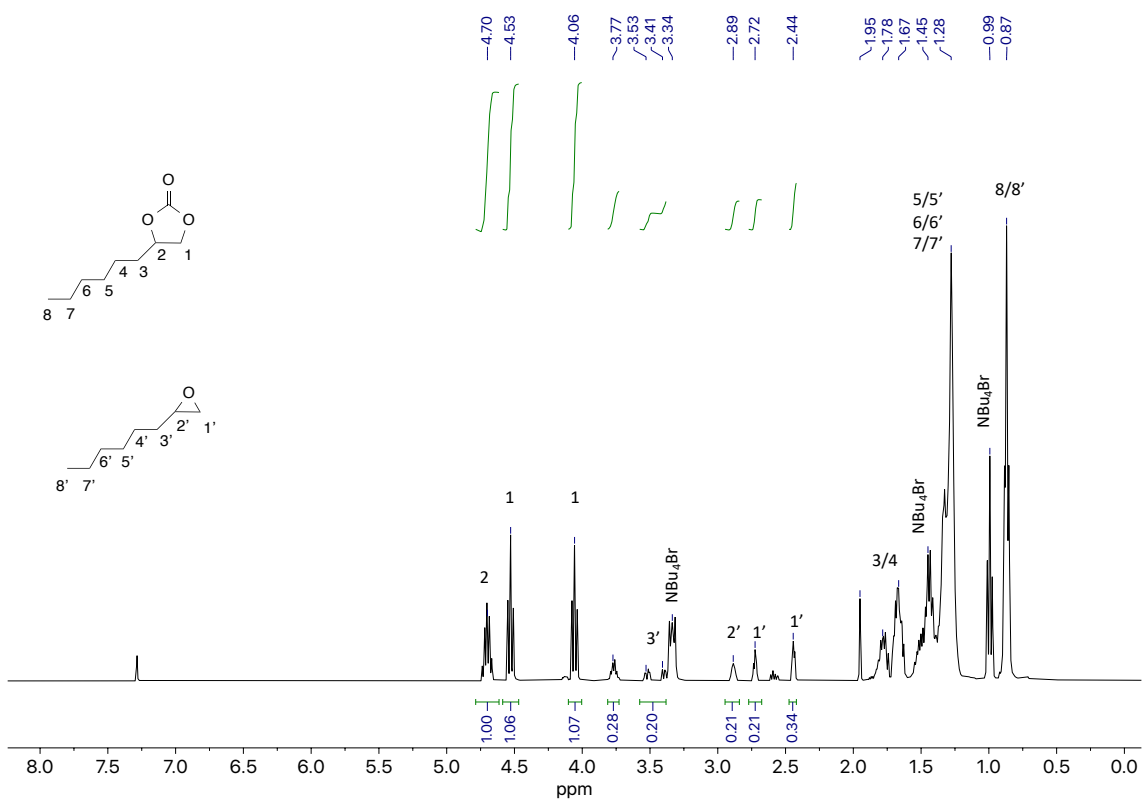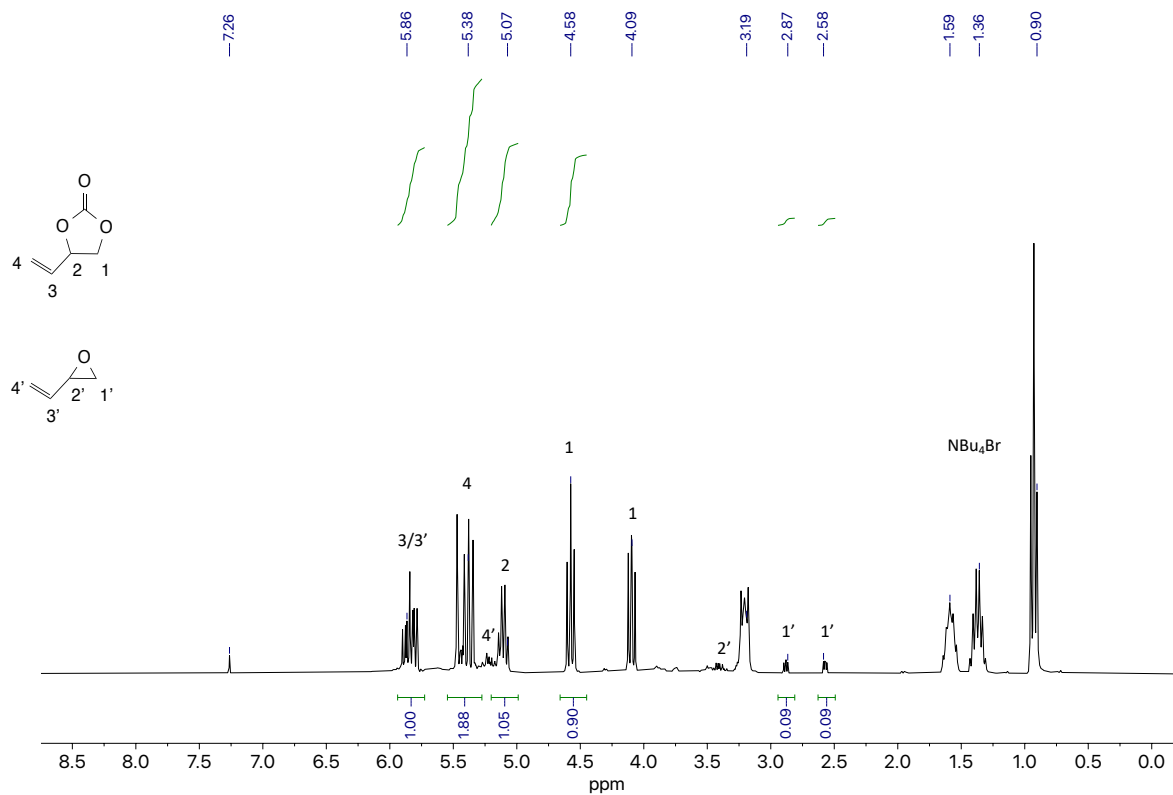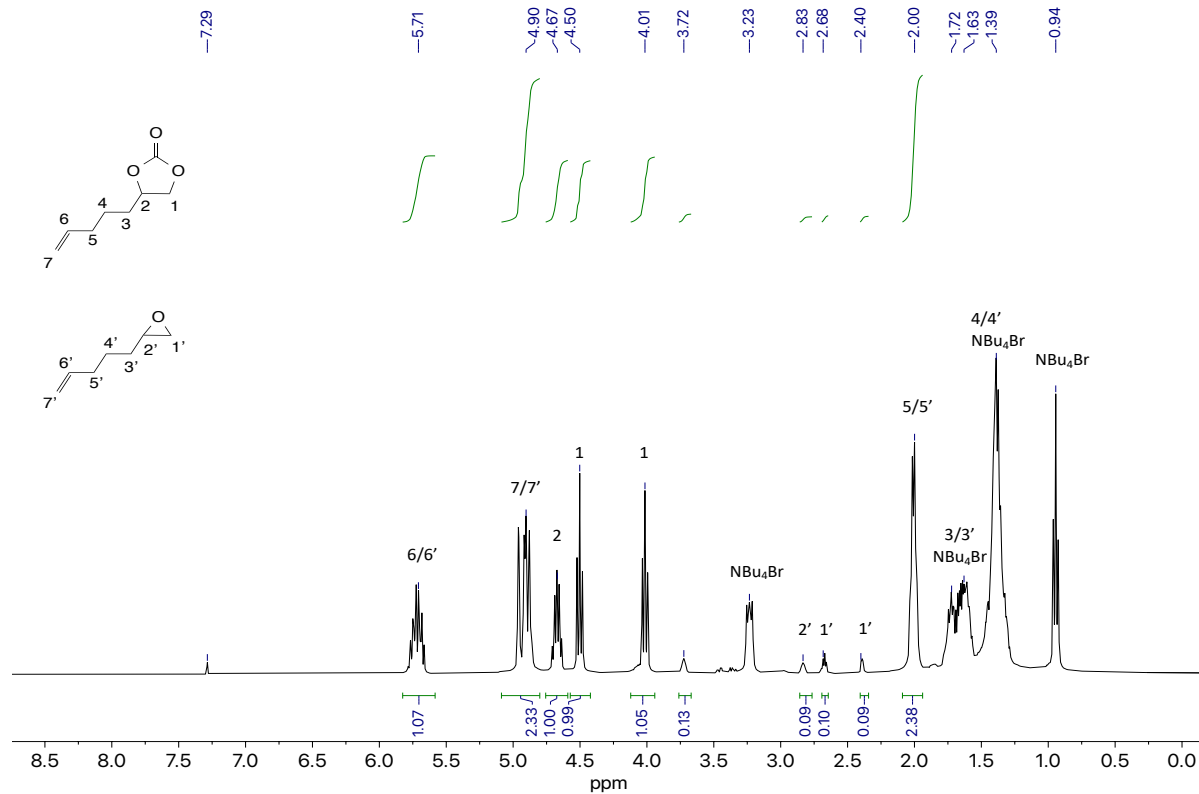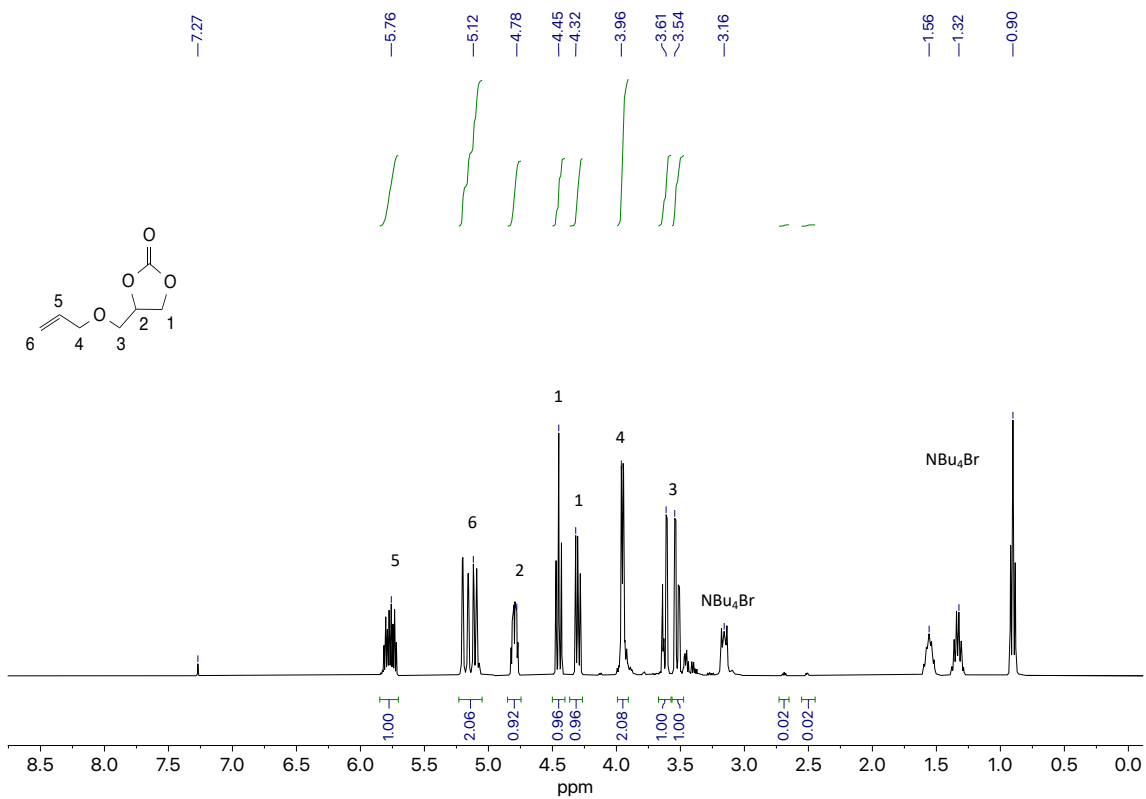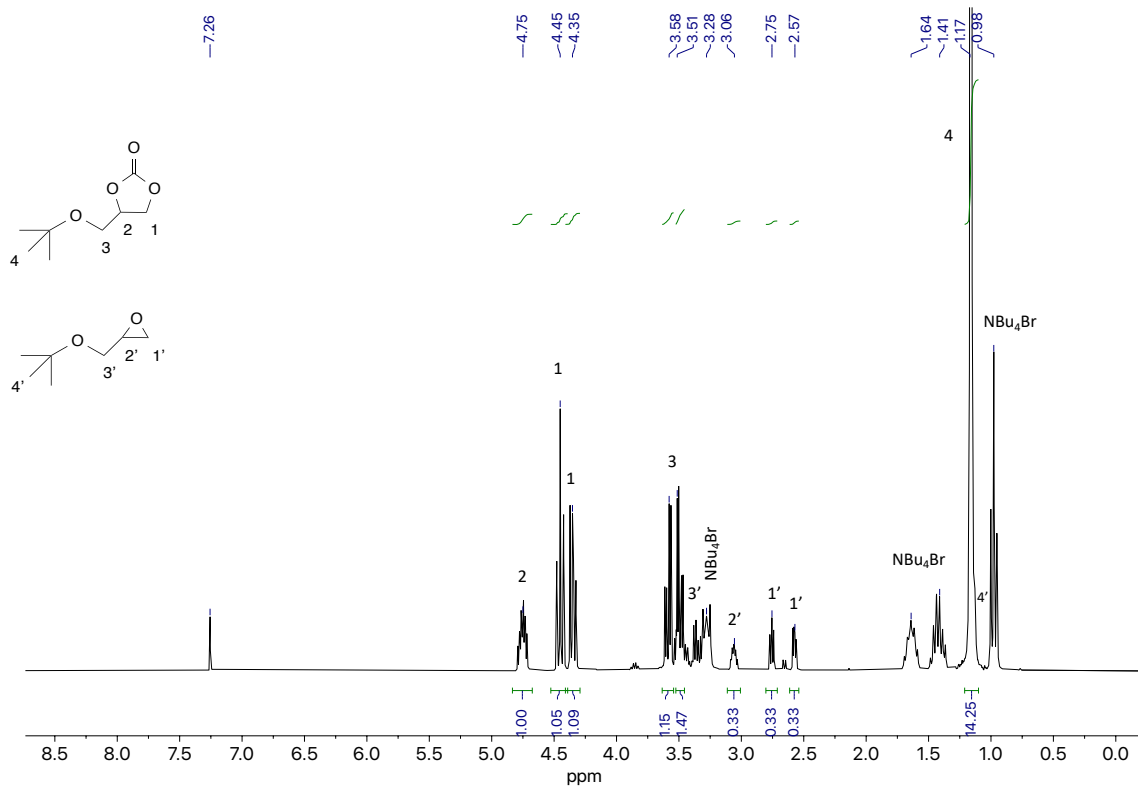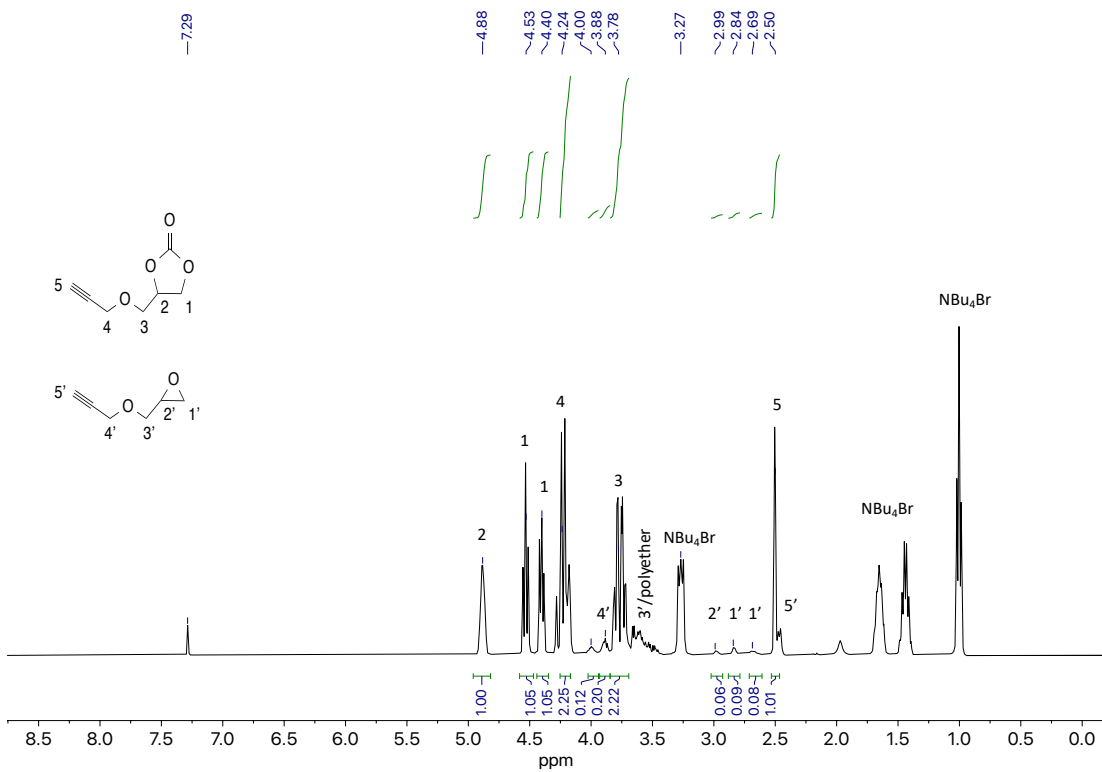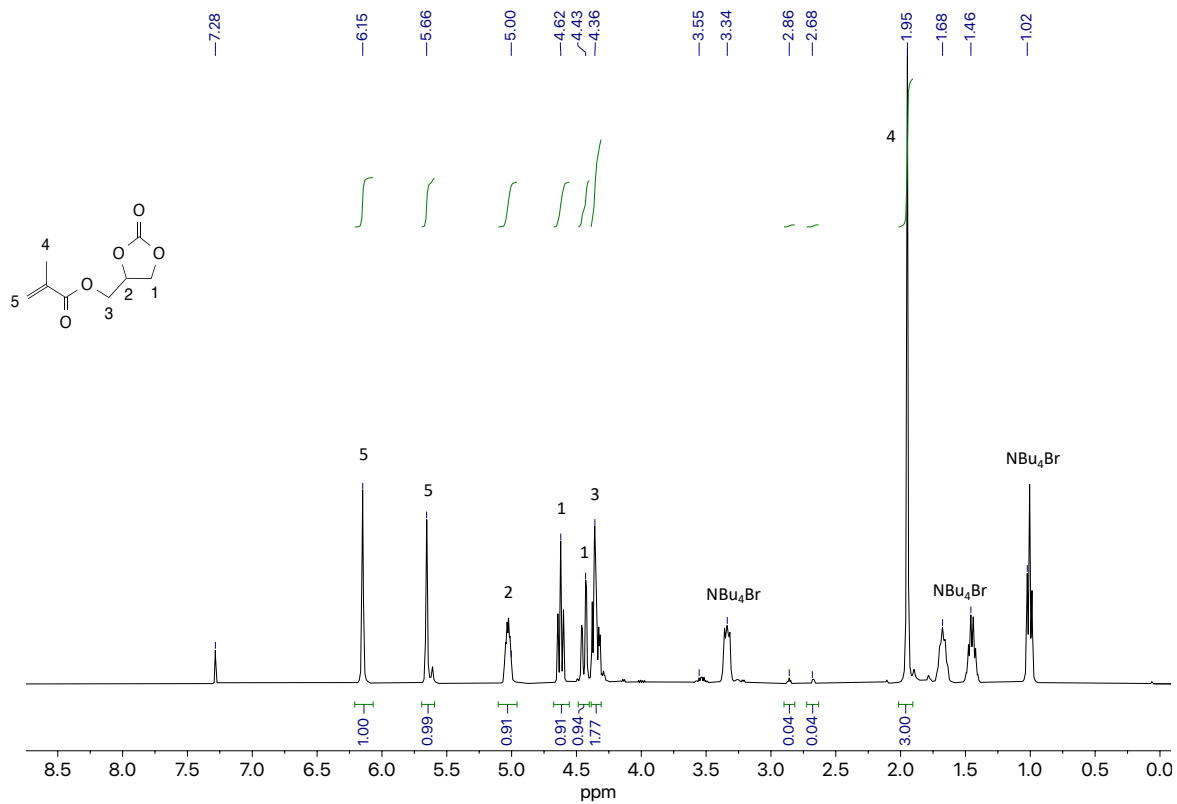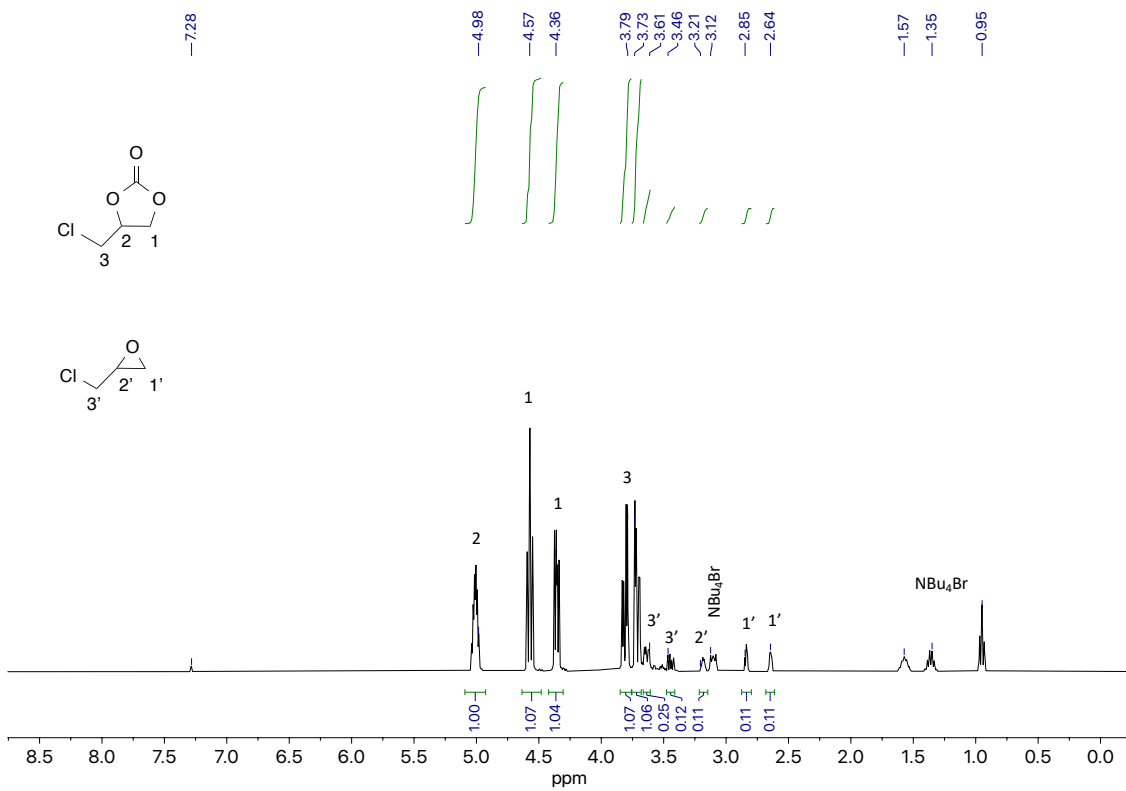
2b

2c

2d

2e

2f

2g

2h

2i

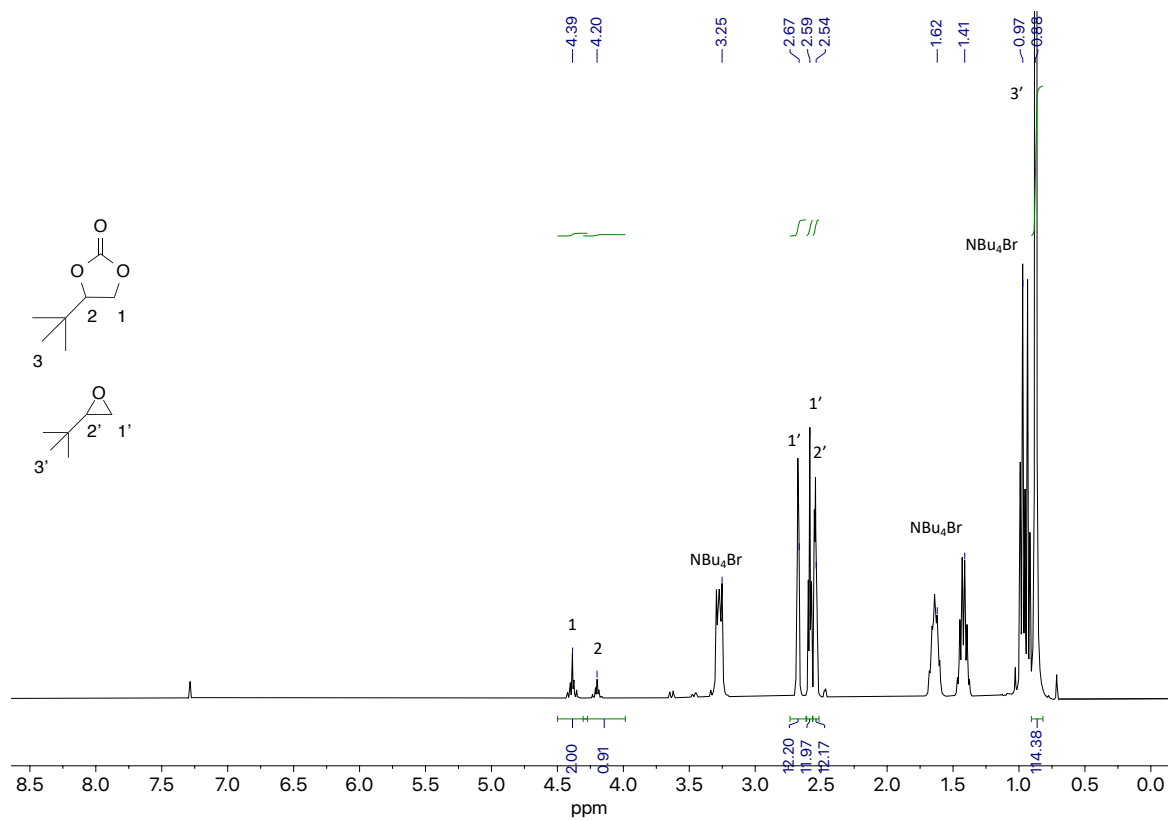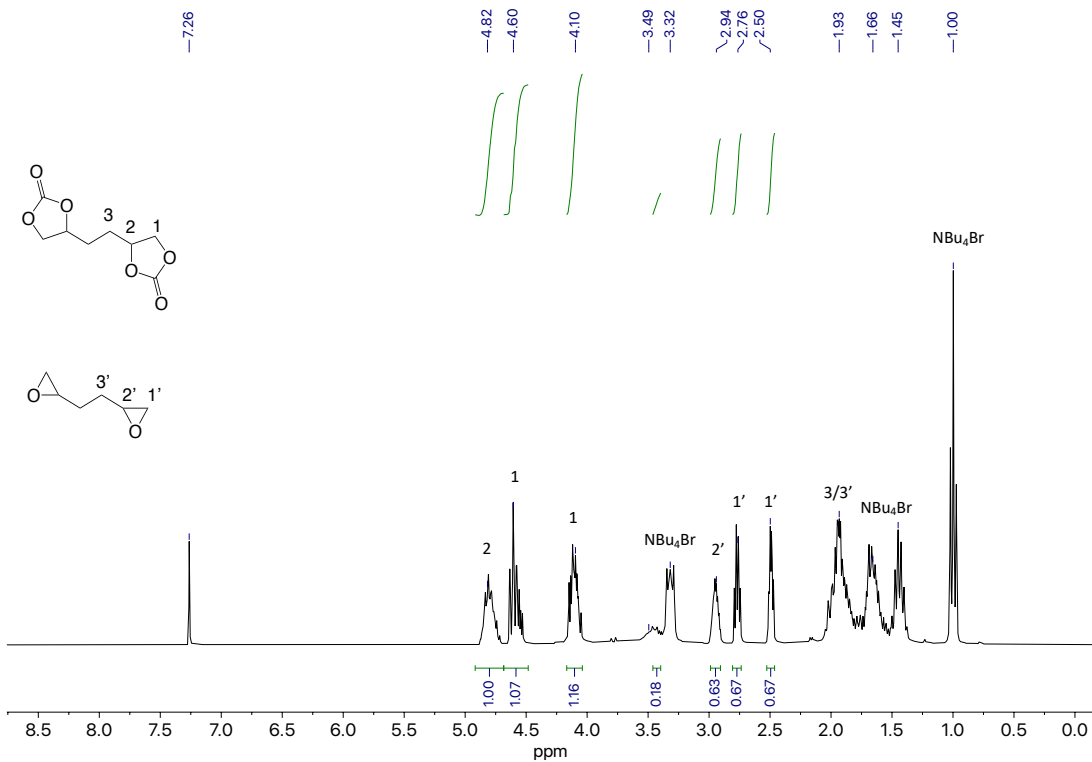**2j**

2k
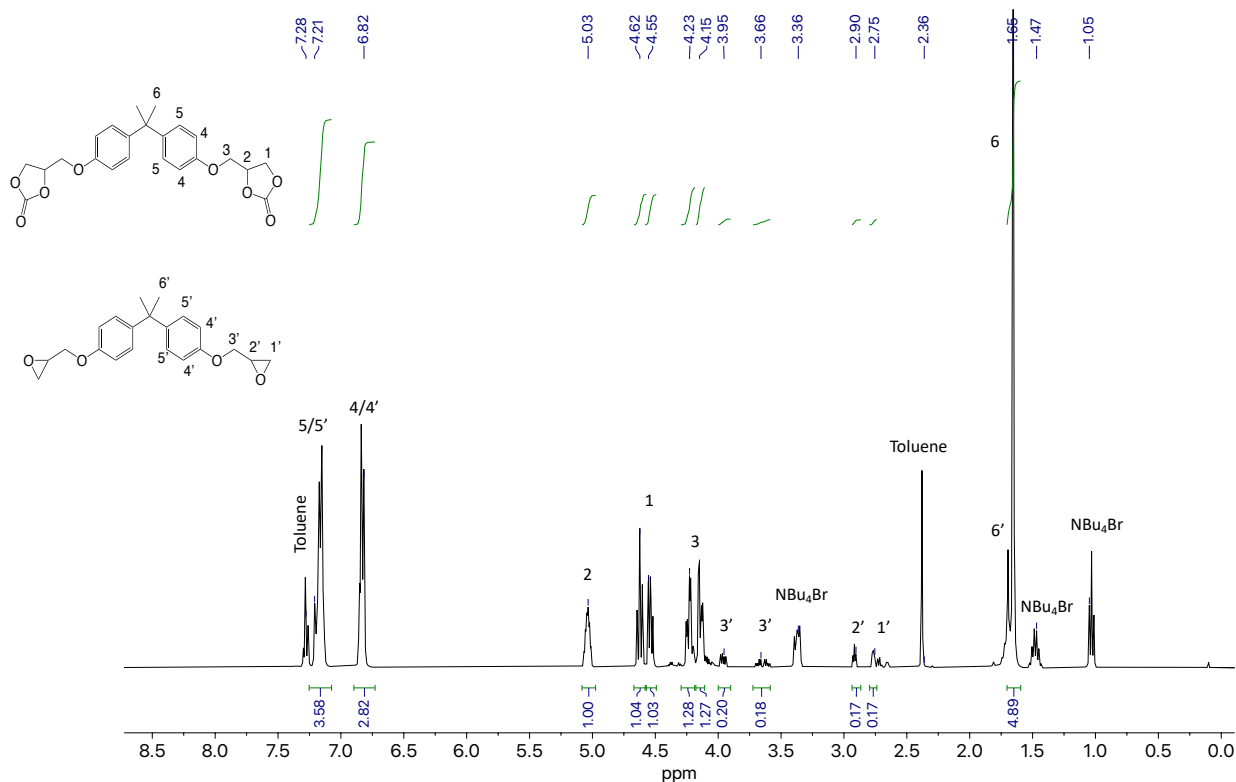
2m

2n

2l

2o

2p

2q
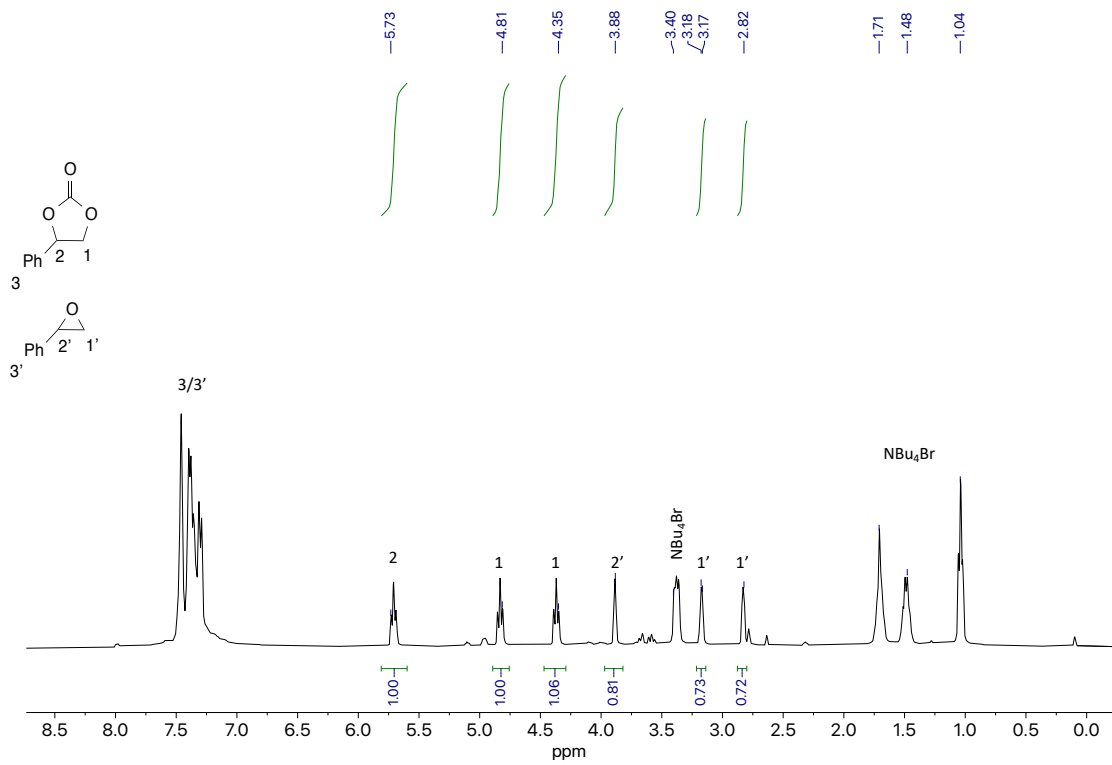
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