Supporting information

CO_2 insertion into epoxide using cesium salt as a catalyst at ambient pressure

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Table S1. Comparison of cesium salt with single component salts/bases as catalyts for the cycloadditon of CO_2 to epoxide.

Entry	Single component salts as catalysts	Conversion (%)
1	Cs_2CO_3	97
2	KI	04
3	KBr	04
4	DMAP	100
5	TBAB	97

All reactions were conducted under identical conditions, that is 1 bar pressure for 12 h, using 0.01 mmol of the catalyst, epichlorohydrin at 120 ºC.

2. Material and characterization

All reagents and solvents employed were commercially available (Aladdin) and used without further purification. ^{1}H-NMR and ^{13}C-**NMR** spectra were recorded at ambient temperature on a Bruker 500 MHz NMR spectrometer. **X-ray photoelectron spectroscopy (XPS)** measurements were carried out on a Thermo Fisher Esca Lab 250Xi at a 01 angle of emission using a monochromatic Al Ka source (Ephoton = 1486.6 eV) with a 10 mA filament current and a 14.7 keV filament voltage source energy. Measurements were carried out in a field of 0.5 mm and a pass energy of 30 eV. In order to compensate for the charging of the sample, a charge neutralizer was used. **Scanning electron microscopy (SEM)** images were acquired with a Zeiss supra55 field emission scanning electron microscope. **Powder X-ray diffraction spectra (PXRD)** were obtained using a Bruker D8 Advance diffractometer (Cu Kα, λ = 1.5418 Å) in the 2θ range 10-80°.

3. General procedure of CO_2 coupling for the formation of cyclic carbonates

The appropriate amount of catalyst and co-catalysts (0.01 mmol) was mixed with the suitable amounts of substrates (10 mmol). The pressure was set to 1 bar after the temperature of the reaction system (autoclave) in the oil bath reached 120 °C. The reaction was stopped after the desired time, the reactor was cooled down to room temperature. Then, an aliquot of the sample was analyzed by ^{1}H and ^{13}C-NMR, using $CDCl_3$ as the solvent. Moreover, the reaction mixture was passed through column chromatography to obtain the purified isolated yield using petroleum ether/ethyl acetate mixture (3:1) as eluent. The volatile organic solvents were evaporated using the rotary, and the desired isolated cyclic carbonates were achieved with good to excellent yields.

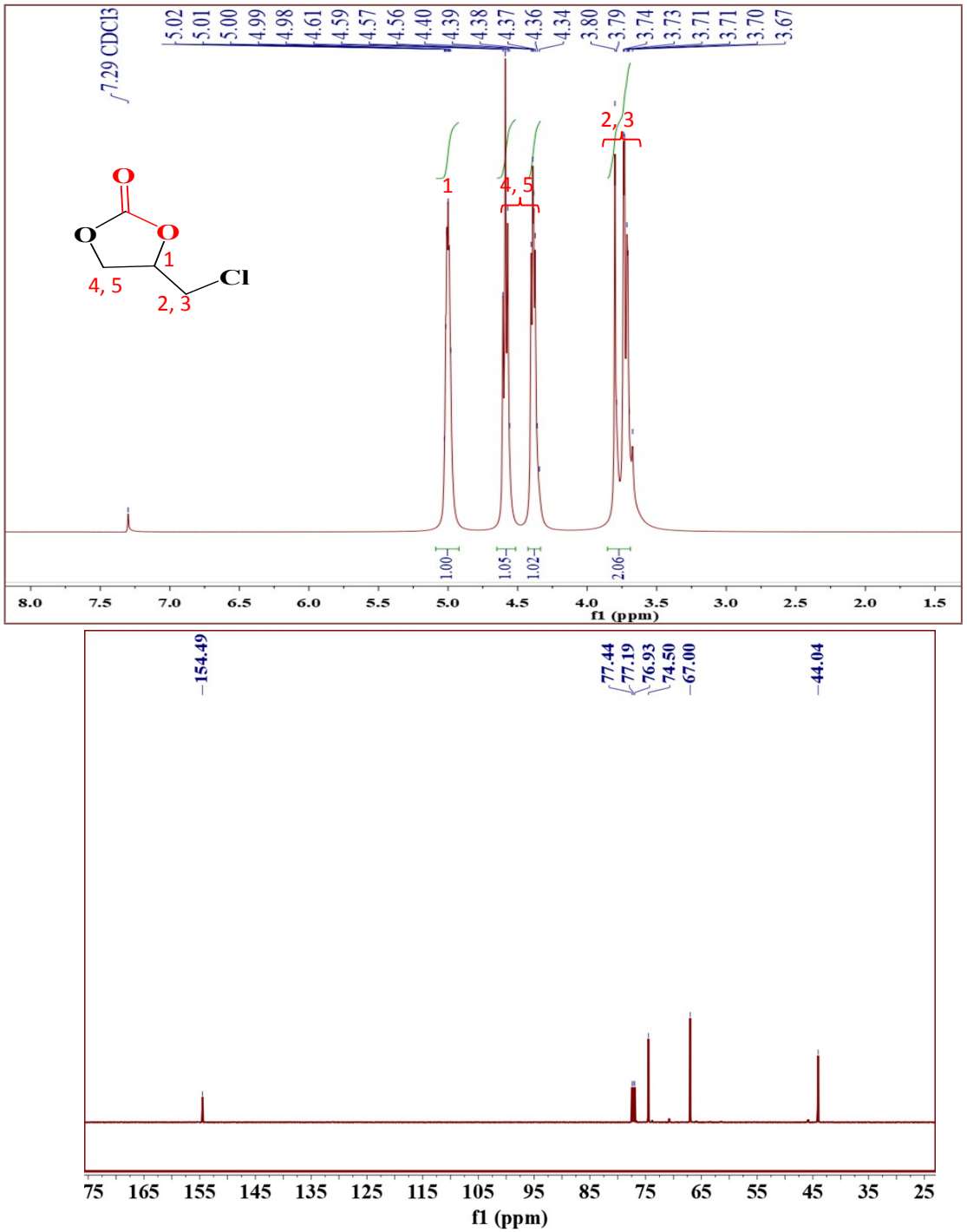


Fig. S1. ^{1}H and ^{13}C-NMR spectra of the product of epichlorohydrin using cesium carbonate and TBAB.

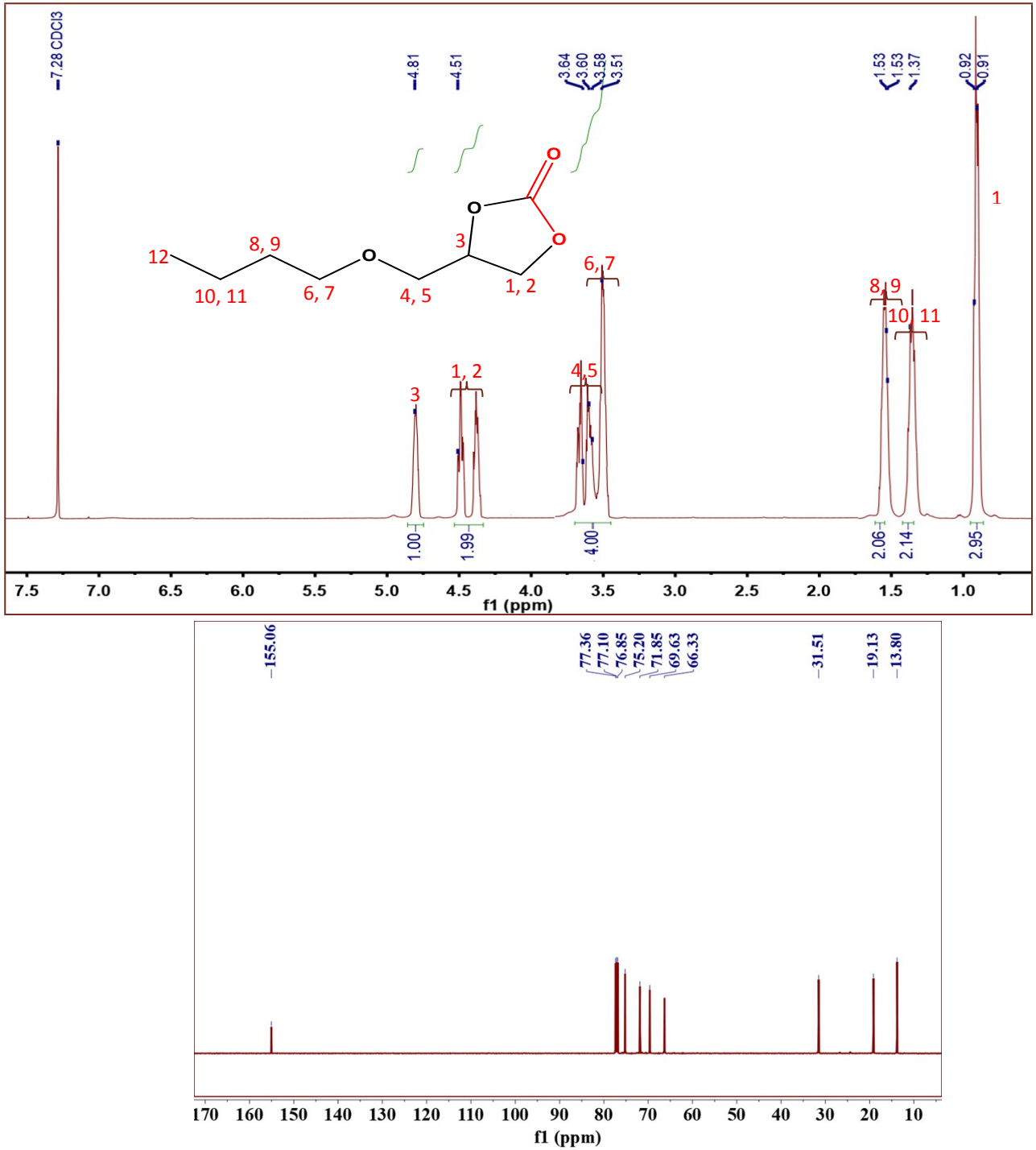


Fig. S2. ^{1}H and ^{13}C-NMR spectra of the product of butyl glycidyl ether using cesium carbonate and TBAB.

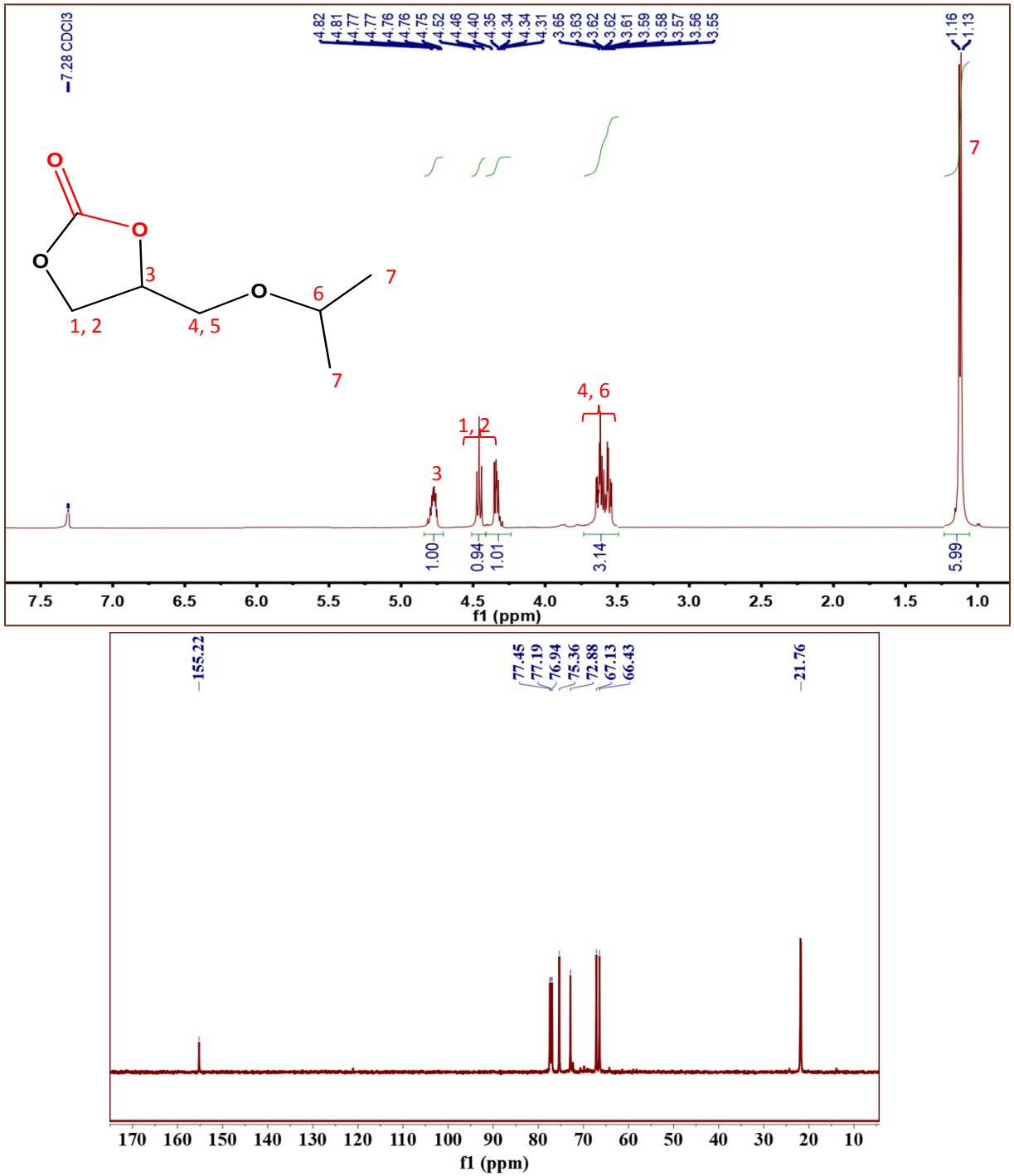


Fig. S3. ^{1}H and ^{13}C-NMR spectra of the product of glycidyl isopropyl ether using cesium carbonate and TBAB

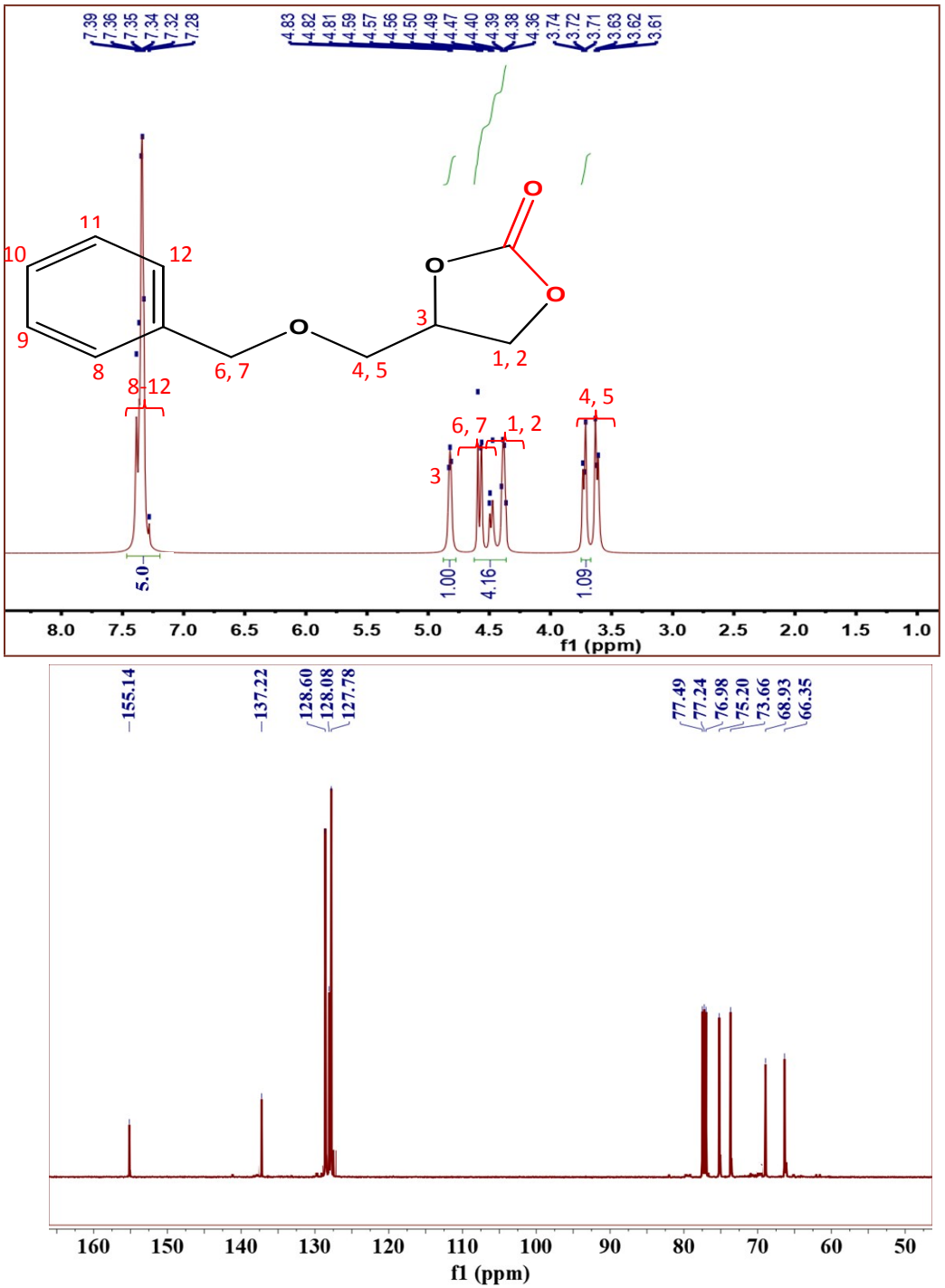


Fig. S4. ^{1}H and ^{13}C-NMR spectra product of the benzyl glycidyl ether using cesium carbonate and TBAB

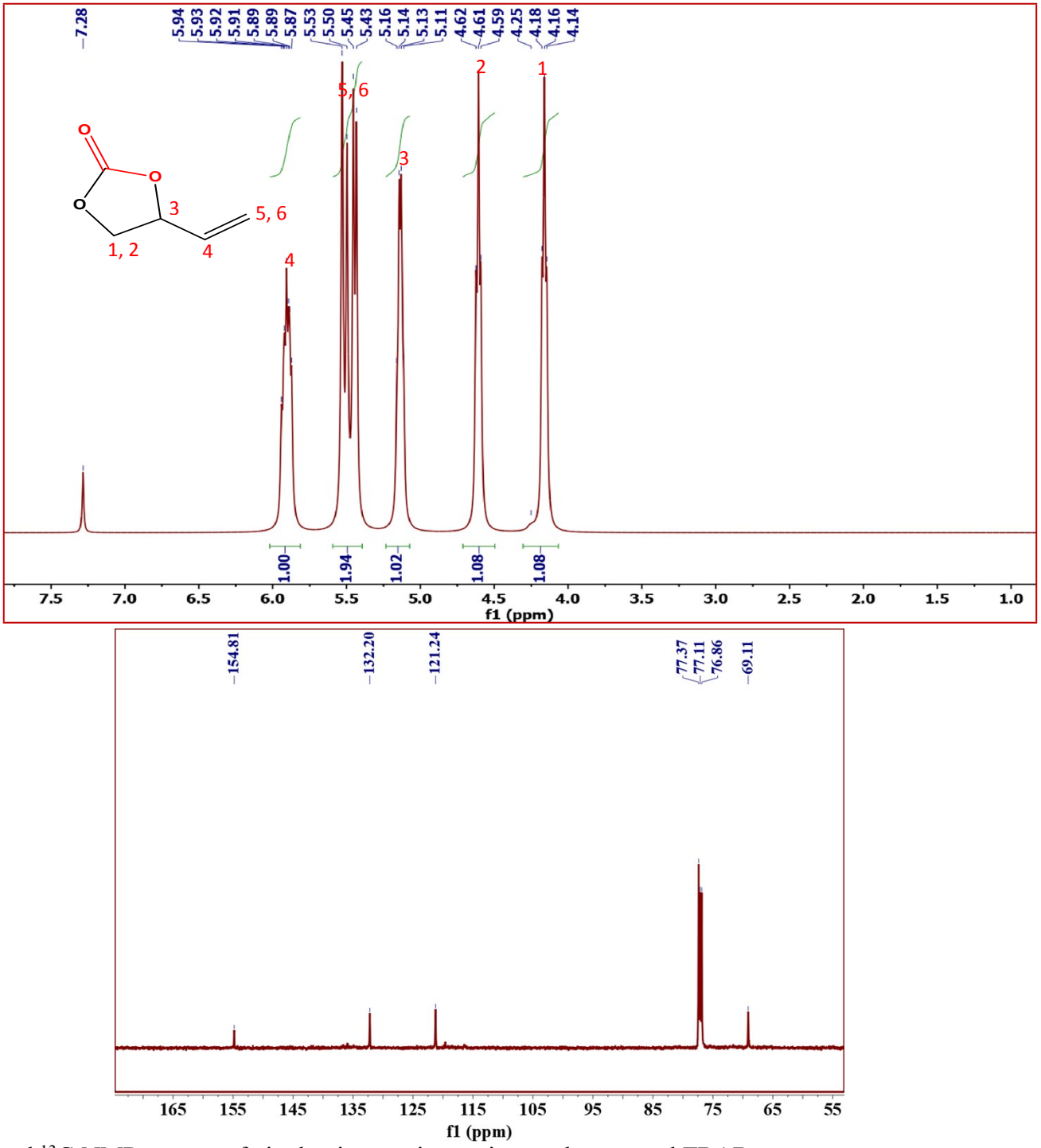


Fig. S5. ^{1}H and ^{13}C-NMR spectra of vinyl oxirane using cesium carbonate and TBAB

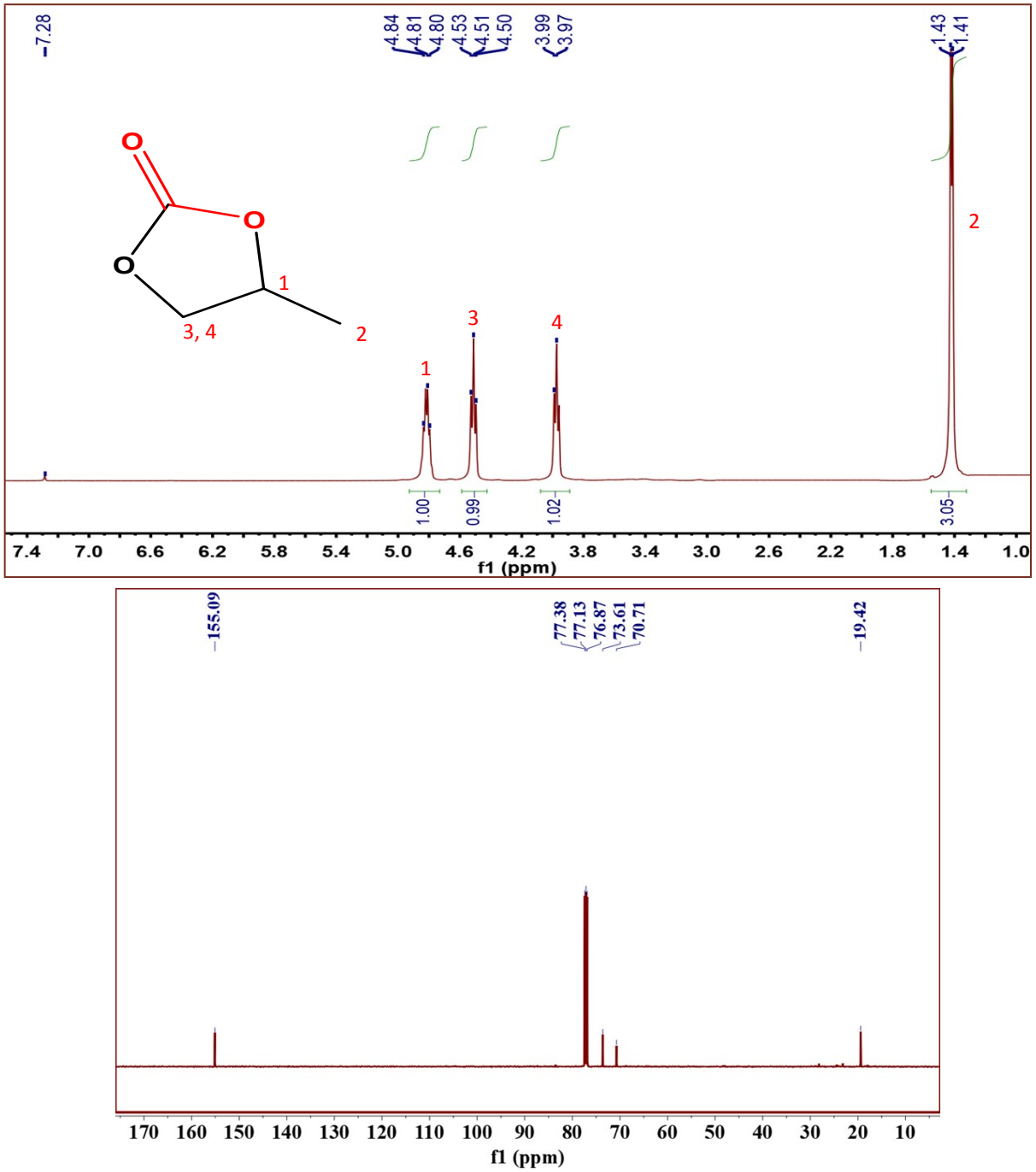


Fig. S6. ^{1}H and ^{13}C -NMR spectra of propylene oxide using cesium carbonate and TBAB.

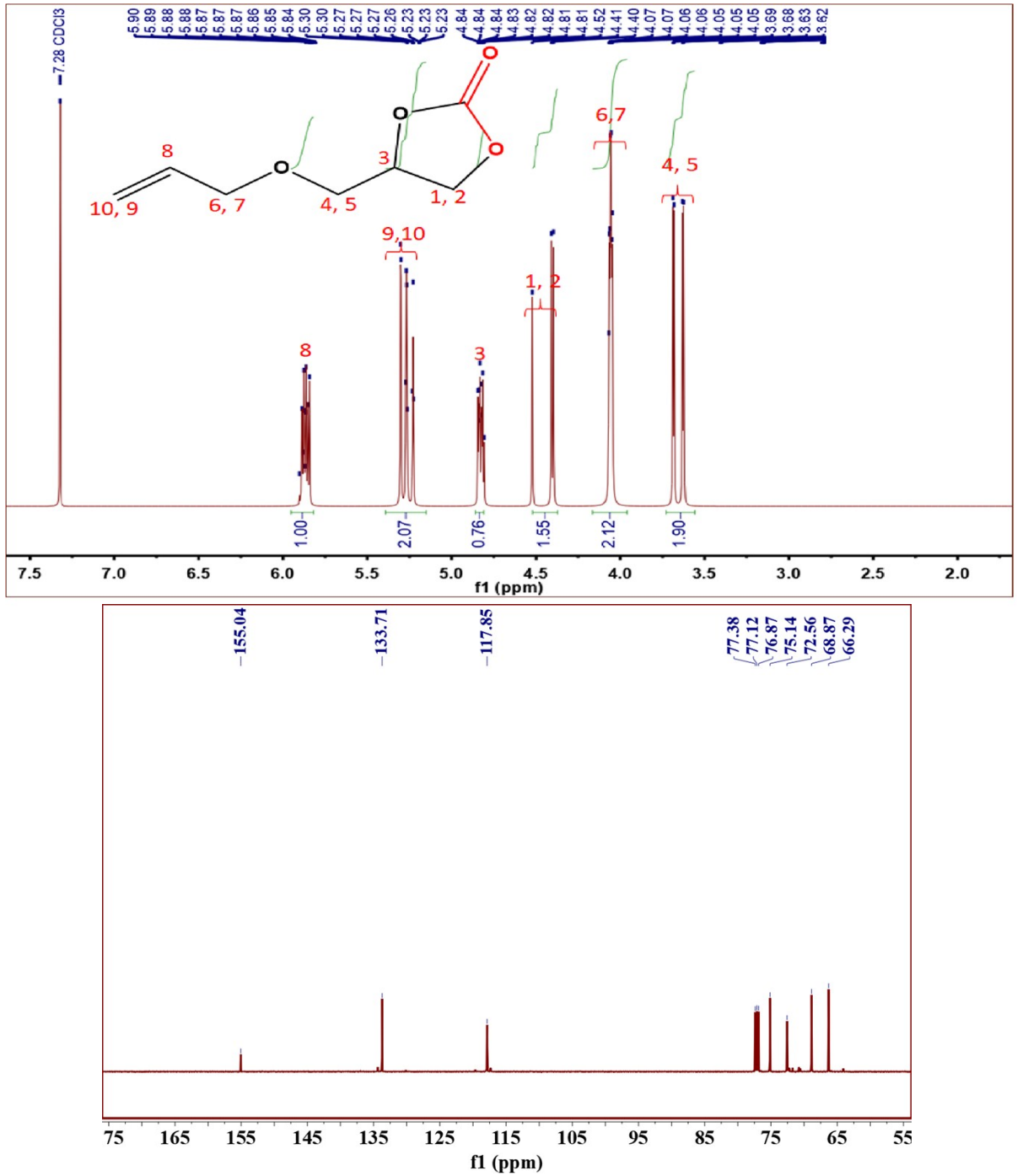


Fig. S7. ^{1}H and ^{13}C-NMR spectra of allyl glycidyl ether using cesium carbonate and TBAB.

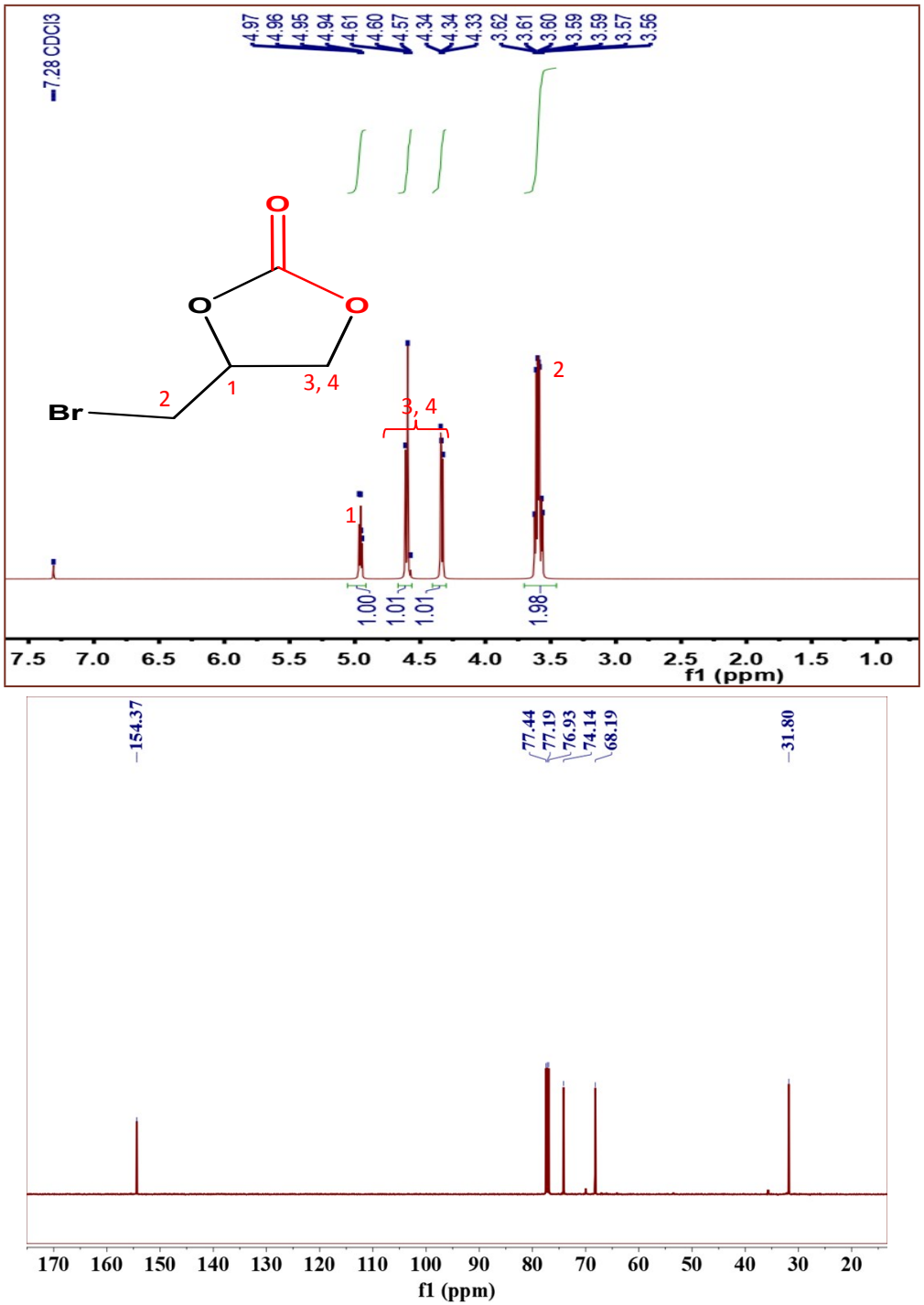


Fig. S8. ^{1}H and ^{13}C-NMR spectra of epibromohydrin using cesium carbonate and TBAB.

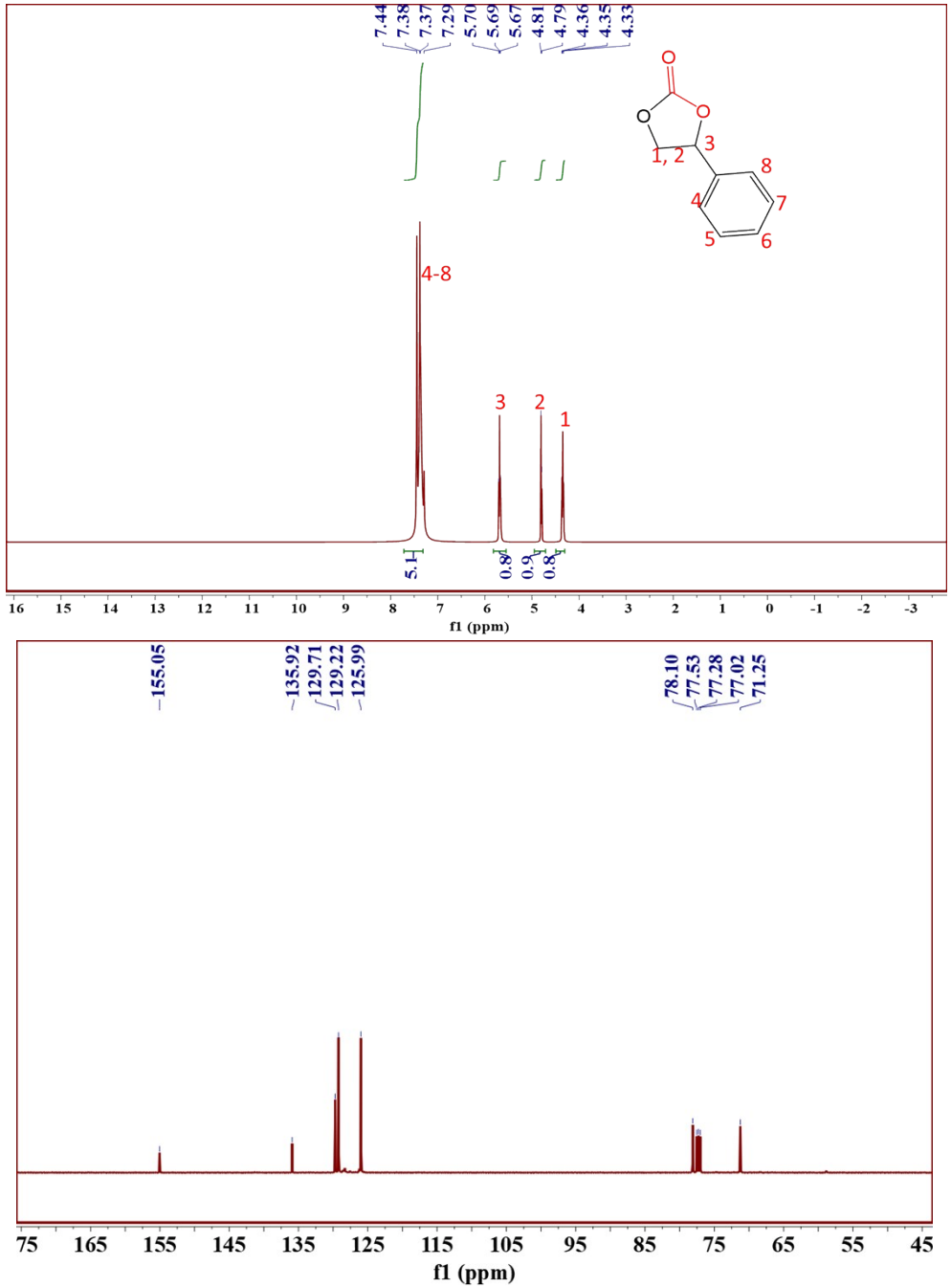
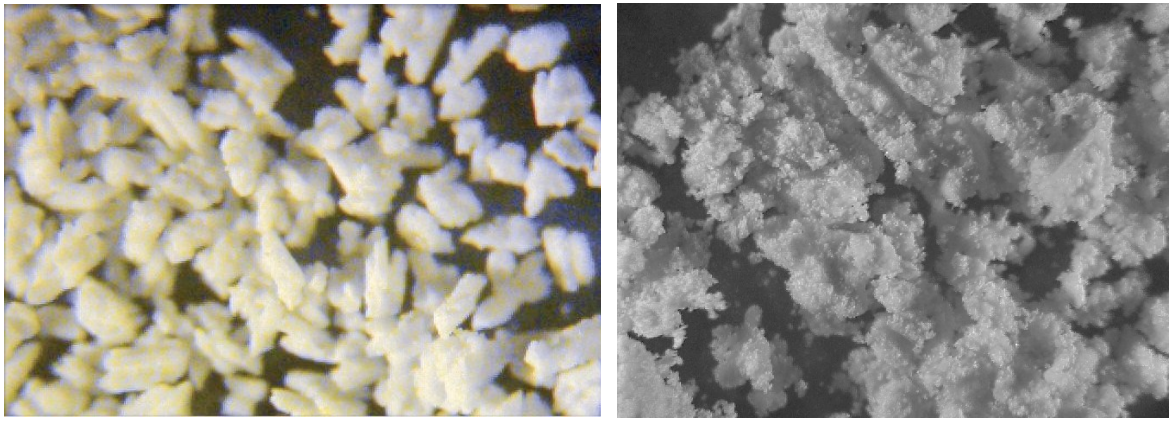


Fig. S9. ^{1}H and ^{13}C-NMR spectra of styrene oxide using cesium carbonate and TBAB.



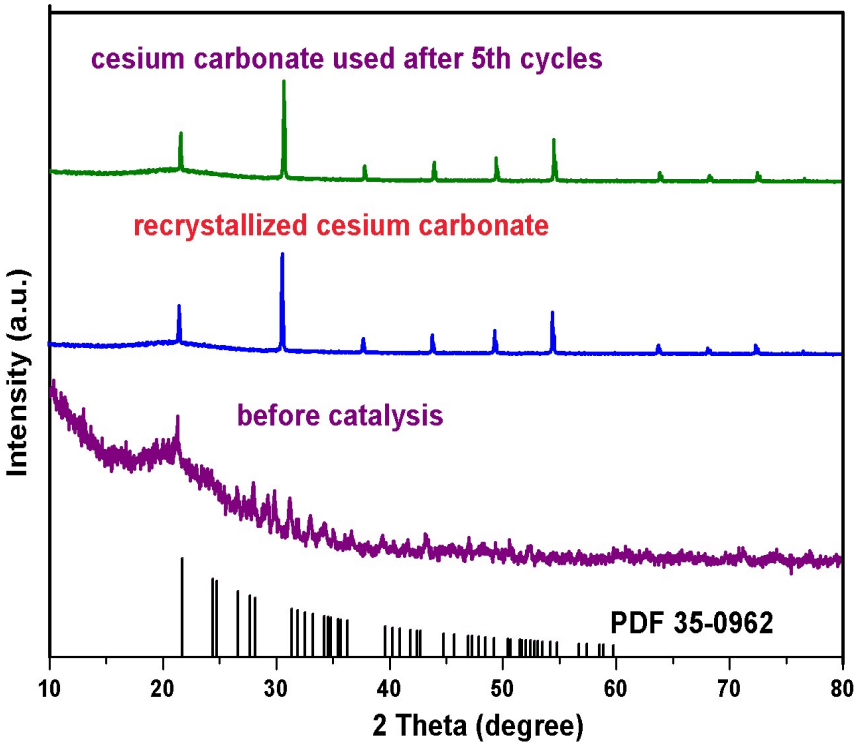


Fig. S10. Microscopic view of the cesium carbonate before (left) and after (right) the reaction.

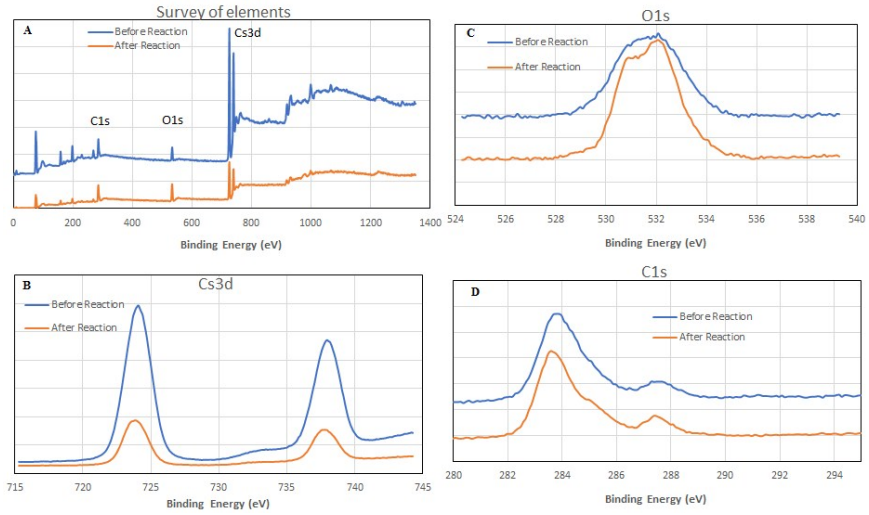


Fig. S12 XPS of Cs_2CO_3 before (blue) and after (orange) the catalytic reaction.

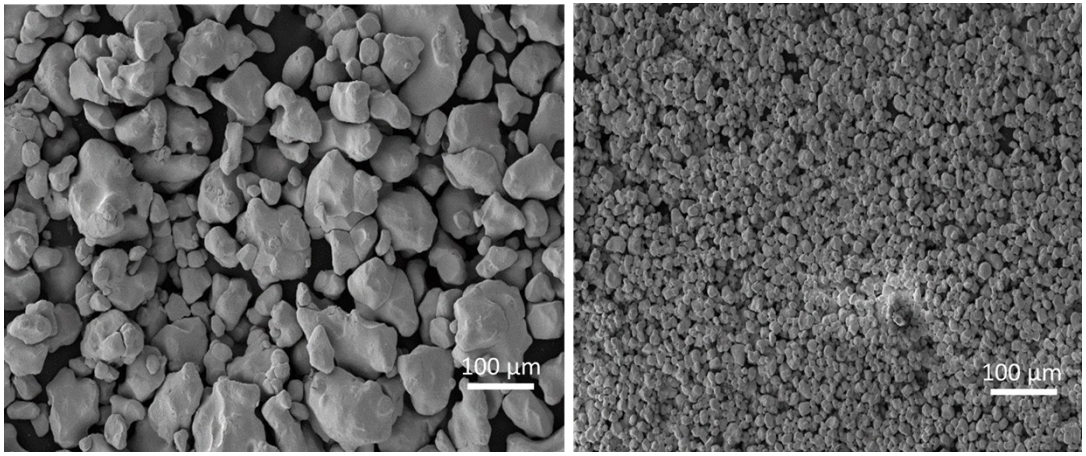


Fig. S13. SEM images of Cs_2CO_3 before (left) and after (right) performing the catalytic reaction.

8. ICP- MS (Inductively Coupled Mass Spectrometry)

Table S2. ICP-MS results, mixture of cesium carbonate and epichlorohydrin.

ICP	Results
After first cycle	0.34 mg/L
After fifth cycle	0.16 mg/L

9. Cesium carbonate activity compared to inorganic salts (CsCl, $CsNO_3$, K_2NO_3, Na_2NO_3)

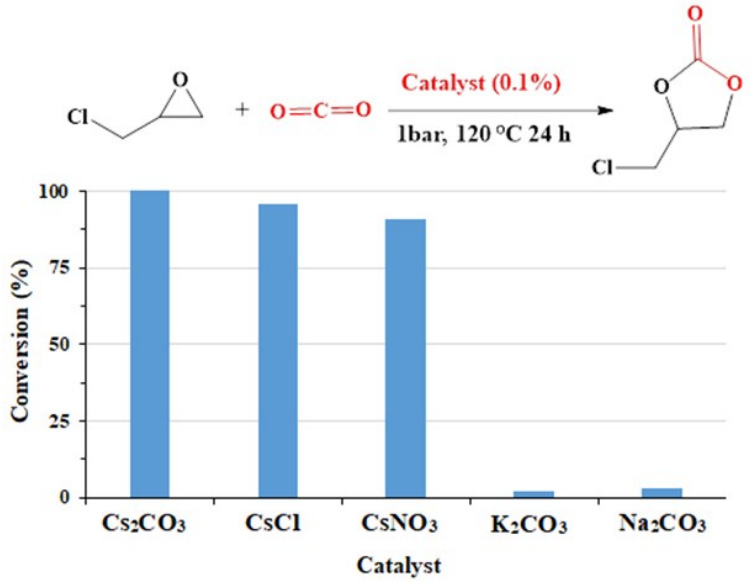
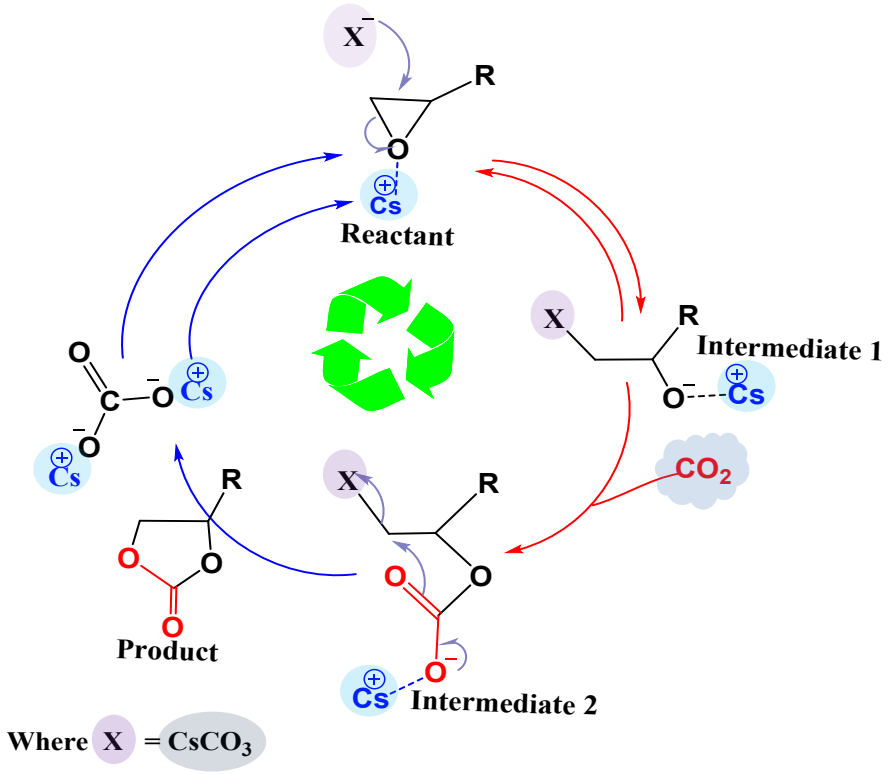


Fig. S14. Different alkali metal salts catalysing the CO_2 insertion into epichlorohydrin.

10. Proposed catalytic mechanism



Scheme S1. Proposed catalytic mechanism for cyclic carbonate syntheses.

11. Catalytic recyclability

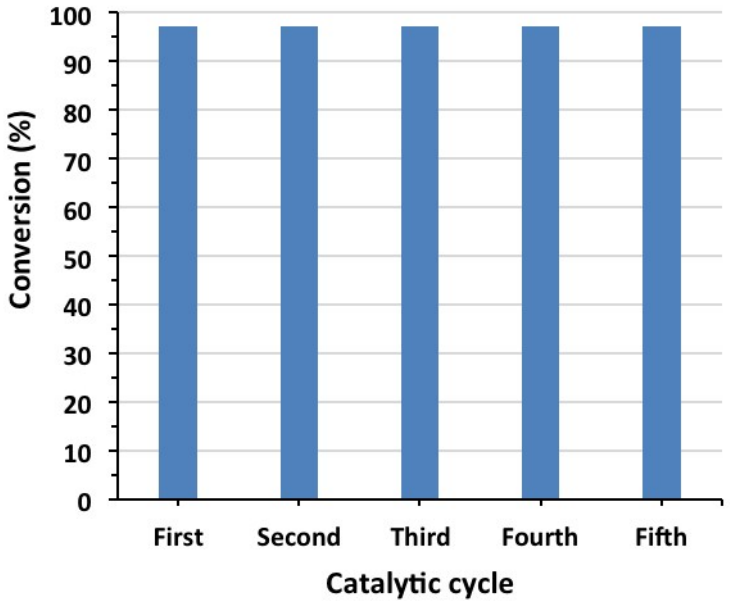


Fig. S15. Use of recovered cesium carbonate catalyst for five successive cycles for the cycloaddition of CO_2 to epichlorohydrin.

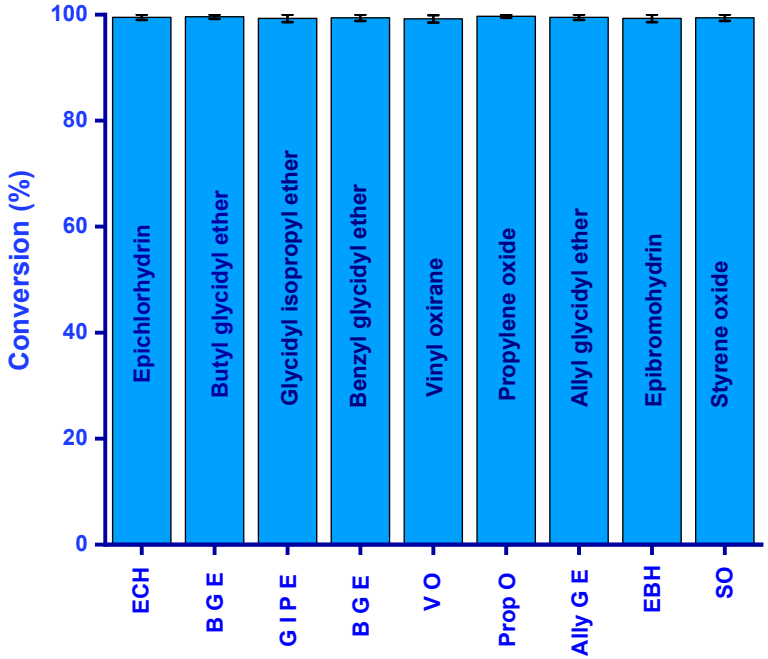
12. Table S3. Comparison of cesium salts with the previously reported catalytic systems (involving salts) for the cycloadditon of CO_2 to epoxides.

Catalytic system (Catalyst/Cocatalyst)	Catalyst (mol%)	Substrate	Amount of substrate (mmol)	Pressure (atm)	Temp. (°C)	Conversion / yield (%)	TON	Reference
Cs_2CO_3	0.1	ECH [c]	10.0	1.0	120	100	1,000	This work
Cs_2CO_3	0.01	ECH	100	1.0	120	72/ 96 [g]	72,000	This work
$CsNO_3$	0.1	ECH	10.0	1.0	120	91/100 [g]	910	This work
CsCl	0.1	ECH	10.0	1.0	120	96/100 [g]	960	This work
Cs_2CO_3	0.1	PO [d]	10.0	1.0	120	99	990	This work
Zn	0.0009	1, 2 EH[#]	-	17	120	-	310,000	1
Zn	0.0004	PO [d]	-	17	120	96/-	240,000	2
Co	0.0005	ECH	-	1	120	>99/-	200,000	3
$ZnCl_2$/BMImBr [a]	0.21	EO [e]	-	15	110	95/-	-	4
Bis(triphenylphosphine)immium salt	100	ECH	3.50	5.0	100	-	853	5
$Re(CO)_5Cl$	0.1	ECH	-	60	110	75/-	710	6
Betaine hydro iodide	2.5	PO	10.0	80	140	-/98	-	7
Zn-complex /TBAB [b]	100	CMO [f]	214	50	130	-/86.2	-	8
MOF-8924 /nBu_4NBr	0.32	EO	6.87	1.0	80	78/44	-	9
Salen–Cu(II) @MIL-101(Cr)/ Bu_4NBr	7.2	PO	25.0	1.0	25	-/87.8	-	10
NH_2-MIL-101(Al)/ TBAB	0.17	PO	105	18	120	-/96	130	11
Mg−Al mixed Oxide	0.8	PO	4.00	5.0	120	96/88	-	12
NaI/PPh_3/PhOH	2.0	PO	45.0	40	120	-/96	-	13

[a] 1-butyl-3-methylimidazole bromide, [b] Tetrabutylammonium bromide, [c] Epichlorohydrin, [d] Propylene oxide, [e] 2-ethyloxirane, [f] 2-(chloromethyl) oxirane, [#] 1, 2 epoxyhexane and [g] percentage conversion after 48 hours of reaction time.

13. Standard deviation for all epoxides screened in this study to point out the consistency of the results

A



B

Substrate	Conversions (%)	Standard Deviation
Epichlorohydrin	99.5	± 0.5
Butyl glycidyl ether	99.6	± 0.4
Glycidyl isopropyl ether	99.3	± 0.7
Benzyl Glycidyl ether	99.4	± 0.6
Vinyl oxirane	99.2	± 0.7
Propylene	99.7	± 0.3
Allyl glycidyl ether	99.5	± 0.5
Epibromohydrin	99.3	± 0.7
Styrene oxide	99.4	± 0.6

Fig. S16. Presentation of the standard deviation values as vertical bar lines in the columns of the conversion (%) for different reaction substrates under the optimized set of reaction conditions (A); Numerical values of the standard deviation of the conversion (%) for the different substrates under the optimized set of reaction conditions (B).

References

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