Supporting Information

Halide-free ion pair organocatalyst from biobased α-hydroxy acid for cycloaddition of CO_2 to epoxide

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1. General information

Materials. O_2 was supplied by Nanjing Shangyuan Industrial Gas Factory with a purity of 99.99%. Epoxides were purchased from Alfa Aesar. DL-Mandelic acid, Glycolic acid, Lactic acid, DL-b-Phenyllactic acid, 1,8-Diazabicyclo[5.4.0]-undec-7-ene (DBU, GC, >98 %, TCI), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5 ene (MTBD, GC, >95 %, TCI), 1, 5-diazabicyclo [4,3,0]non-5-ene (DBN, GC, >98 %, TCl), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, GC, >97 %, TCI) were purchased commercially. All reagents were used without any further purification.

Characterizations. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 and 100 MHz NMR spectrometer in $CDCl_3$ 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 (^{1}H δ 7.26 for $CDCl_3$, δ 2.50 for DMSO-d_6; ^{13}C δ 77.16 for $CDCl_3$, δ 39.52 for DMSO-d_6). Conversions and selectivities of epoxides were determined by ^{1}H NMR spectroscopy.

2. Preparation of the different ion pair catalysts

2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium 2-hydroxyacetate ([DBUH][GAc]). Glycolic acid (1.901g, 25mmol, 1eq) was dissolved in methanol solution for use. A rotor was added into a 25mL round-bottled flask and 1, 8-diazadicyclic [5.4.0] undeca-7-ene (3.732mL, 25mmol, 1eq) was placed in the flask. Slowly add glycolate-methanol solution while stirring, stirring at room temperature for 5 h, the solution gradually turned into a light yellow liquid, the reaction liquid was concentrated in vacuum, the ether precipitated and washed three times, purified by column chromatography (DCM:MeOH=1:1), and vacuum dried to constant weight to obtain catalyst **[DBUH][GAc]** as a light yellow viscous liquid. Yield 87%.

2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium 2-hydroxypropanoate ([DBUH][LAc]). Lactic acid (1.654mL, 25mmol, 1eq) was dissolved in methanol solution for use. A rotor was added into a 25mL round-bottled flask, and 1, 8-diazadicyclic [5.4.0] undecan-7-ene (3.732mL, 25mmol, 1eq) was placed in the flask. Under the condition of ice bath, the lactate-methanol solution was slowly added while stirring. Stirring at room temperature for 5 h, the solution gradually turned into a light yellow liquid, the reaction liquid was concentrated in vacuum, the ether precipitated and washed three times, purified by column chromatography (DCM:MeOH=1:1), and the catalyst **[DBUH][LAc]** was obtained by vacuum drying to constant weight as a yellow viscous liquid. Yield 90%.

2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium 2-hydroxy-2-phenylacetate ([DBUH][MAc]). Dl-mandelic acid (3.804g, 25mmol, 1eq) was dissolved in methanol solution for use. A rotor was added into a 25mL round-bottled flask and 1, 8-diazadicyclic [5.4.0] undecan-7-ene (3.732mL, 25mmol, 1eq) was taken into the flask. The solution of DL-mandelic acid and methanol was slowly added while stirring. After stirring at room temperature for 5 h, the solution gradually turned into a light yellow liquid. The reaction liquid was concentrated under vacuum, precipitated by ether and washed three times, purified by column chromatography (DCM:MeOH=1:1), and then dried under vacuum to constant weight, catalyst **[DBUH][MAc]** was obtained as a yellow viscous liquid. Yield 95%.

2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium2-hydroxy-3-phenylpropanoate ([DBUH][PLAc]). D-3-phenyllactic acid (4.154g, 25mmol, 1eq) was dissolved in methanol solution for use. A rotor was added into a 25mL round-bottled flask and 1, 8-diazadicyclic [5.4.0] undecan-7-ene (3.732mL, 25mmol, 1eq) was taken into the flask. Slowly add D-3-phenyllactic acid-methanol solution while stirring, stirring at room temperature for 5 h, the solution gradually turned into a light yellow liquid, the reaction liquid was concentrated in vacuum, the ether precipitated and washed three times,

purified by column chromatography (DCM:MeOH=1:1), and the catalyst **[DBUH][PLAc]** was obtained by vacuum drying to constant weight. Yield 85%.

2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium 2-hydroxypropanoate ([DBNH][LAc]). Lactic acid (1.654mL, 25mmol, 1eq) was dissolved in methanol solution for use. A rotor was added into a 25mL round-bottled flask, and 1, 5-diazazobicyclic [4.3.0] nona-5-ene (3.09mL, 25mmol, 1eq) was placed in the flask. Under the condition of ice bath, mandelate-methanol solution was slowly added while stirring. Stirring at room temperature for 5 h, the solution gradually turned into yellow liquid, the reaction liquid was concentrated in vacuum, the ether precipitated and washed three times, purified by column chromatography (DCM:MeOH=1:1), and the catalyst **[DBNH][LAc]** was obtained by vacuum drying to constant weight. Yield 80%.

9-methyl-3,4,6,7,8,9-hexahydro-2H-pyrimido[1,2-a]pyrimidin-1-ium2-hydroxypropanoate ([MTBDH][LAc]). Lactic acid (1.654mL, 25mmol, 1eq) was dissolved in methanol solution for use. A rotor was added into a 25mL round-bottled flask and 7-methyl-1,5, 7-triazadicyclic [4.4.0] dece-5-ene (3.69mL, 25mmol, 1eq) was placed in the flask. Slowly add mandelic acid-methanol solution while stirring, stirring at room temperature for 5 h, the solution gradually turned into yellow liquid, the reaction liquid was concentrated in vacuum, the ether precipitated and washed three times, purified by column chromatography (DCM:MeOH=1:1), and the catalyst **[MTBDH][LAc]** was obtained by vacuum drying to constant weight. Yield 87%.

3,4,6,7,8,9-hexahydro-2H-pyrimido[1,2-a]pyrimidin-1-ium 2-hydroxypropanoate ([TBDH][LAc]). Lactic acid (1.654mL, 25mmol, 1eq) was dissolved in methanol solution for use. A rotor was added into a 25mL round-bottled flask and 1,5, 7-triazadicyclodecene-5-ene (3.48g, 25mmol, 1eq) was taken and placed in the flask under ice bath conditions. Slowly add mandelic acid-methanol solution while

stirring, stirring at room temperature for 5 h, the solution gradually becomes yellow liquid, the reaction liquid is concentrated in vacuum, the ether precipitation and washing three times, purification by column chromatography (DCM:MeOH=1:1), vacuum drying to constant weight to obtain catalyst **[TBDH][LAc]** as a white solid. Yield 86%.

3. Copies of ^{1}H NMR and ^{13}C NMR spectra of the ion pair catalysts

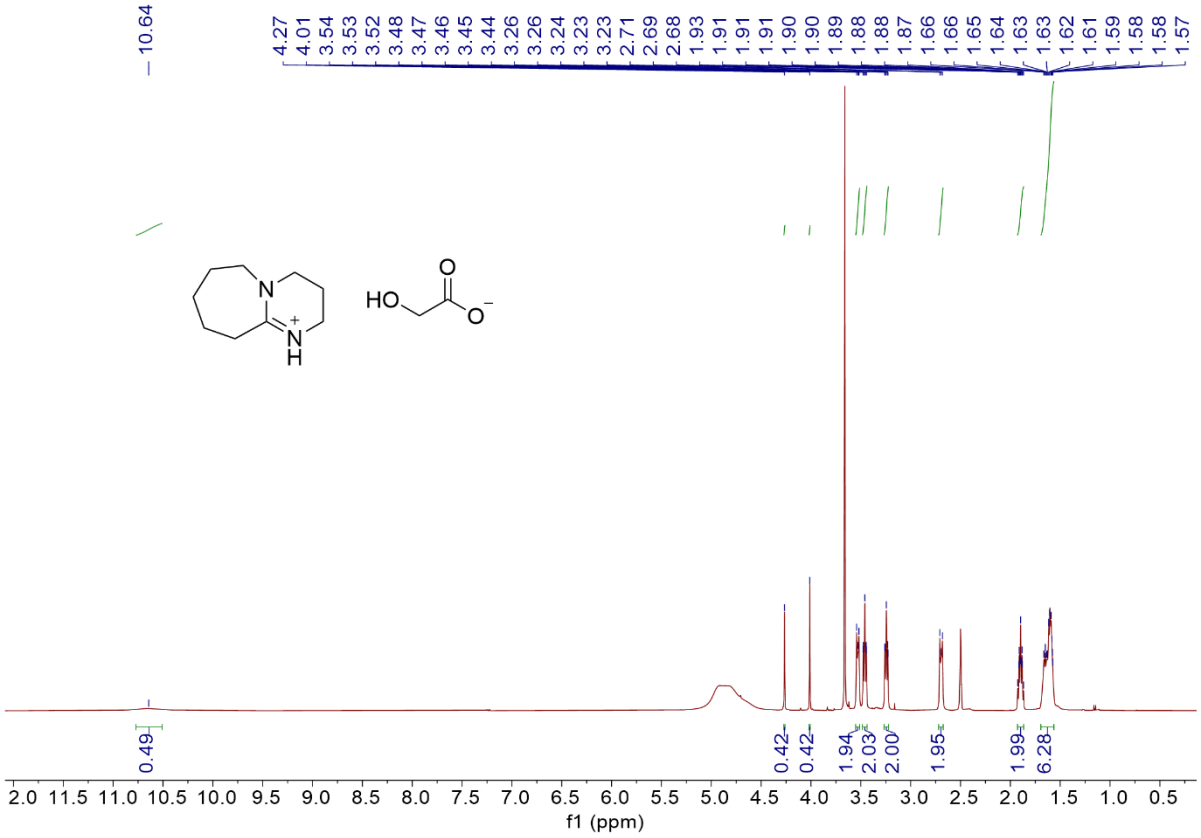

Figure S1. ^{1}H NMR Spectrum of [DBUH][GAc] (400 MHz, DMSO-d_6)

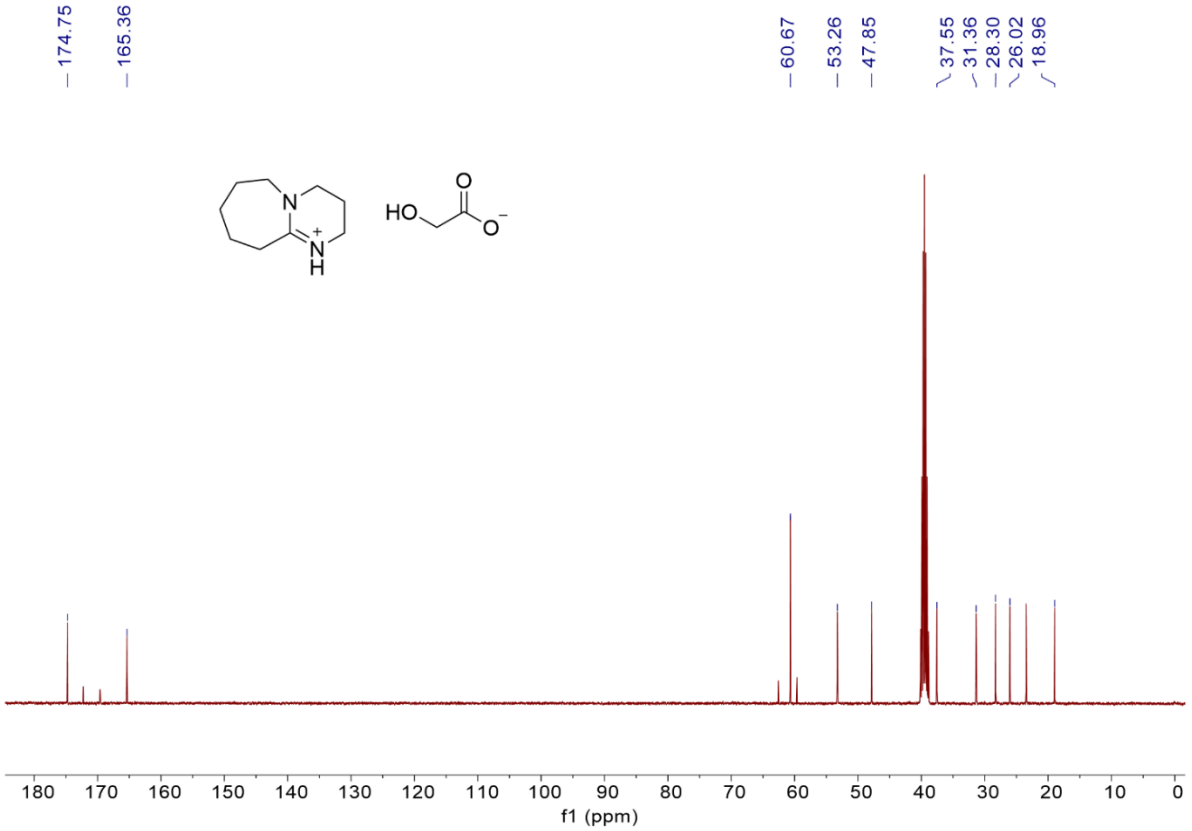

Figure S2. ^{13}C NMR Spectrum of [DBUH][GAc] (101 MHz, DMSO-d_6)

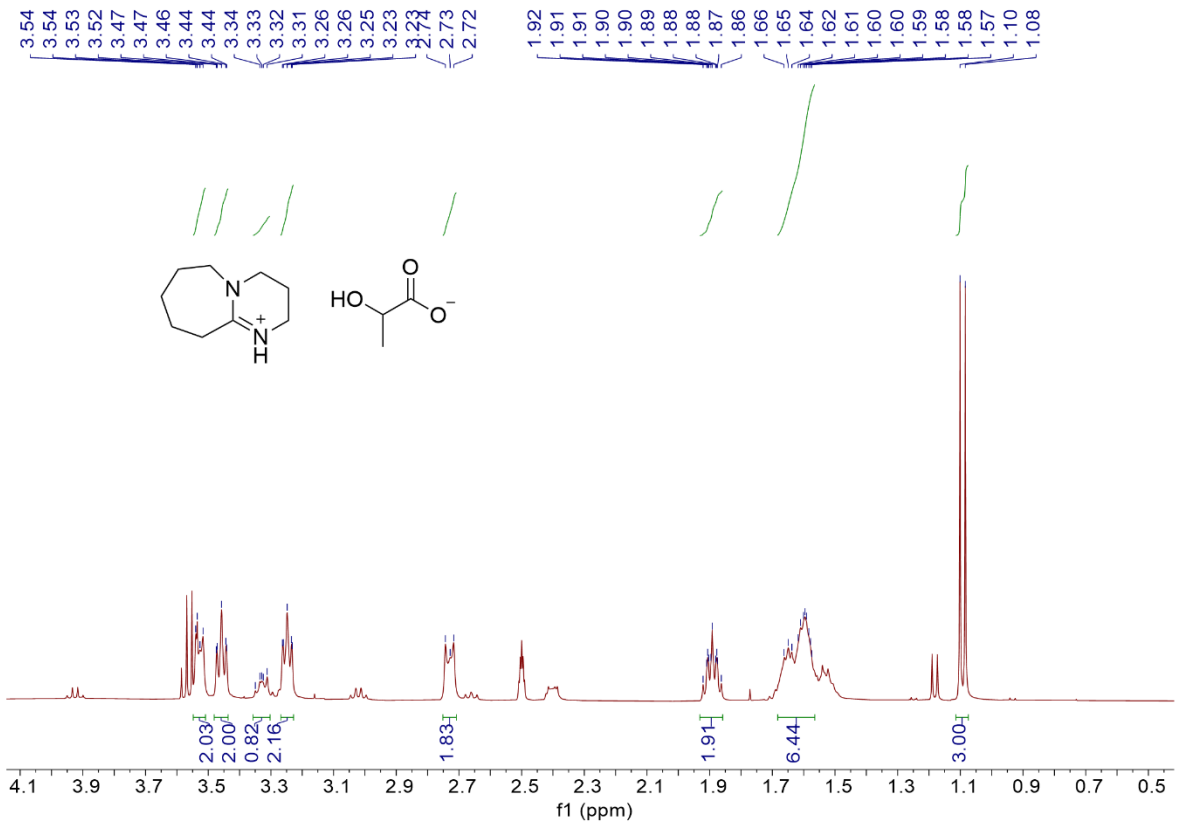

Figure S3. ^{1}H NMR Spectrum of [DBUH][LAc] (400 MHz, DMSO-d_6)

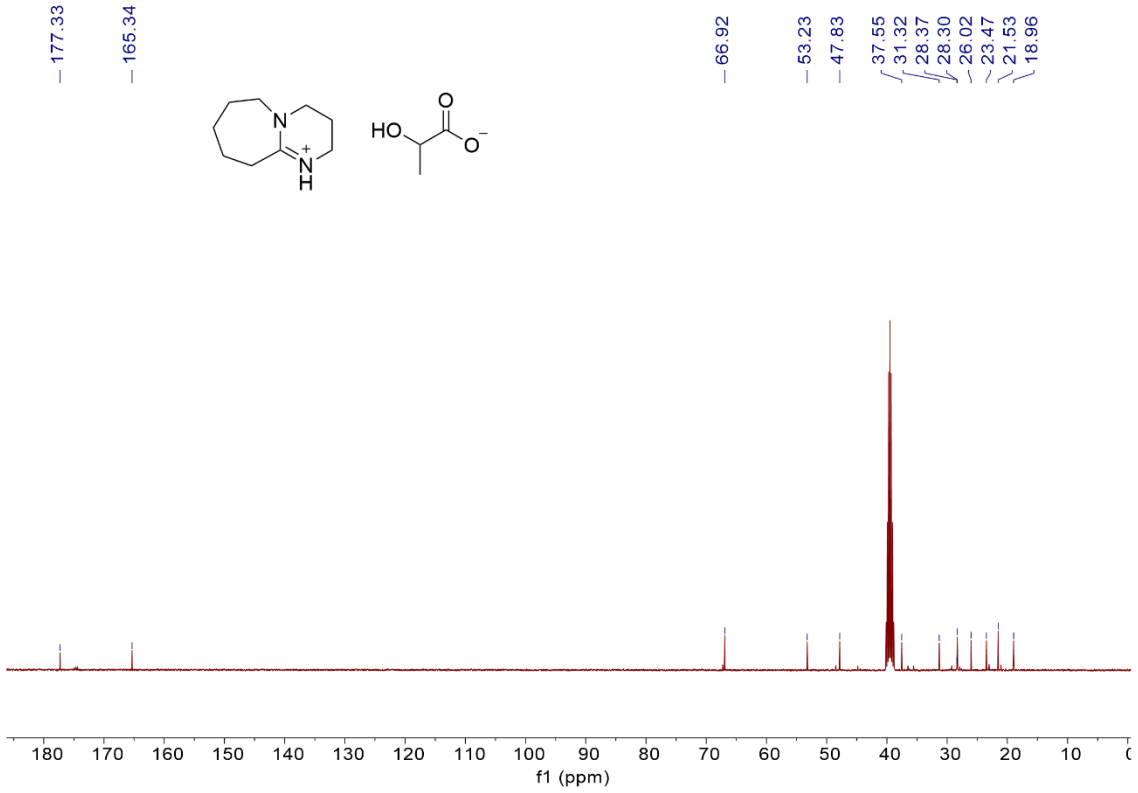

Figure S4. ^{13}C NMR Spectrum of [DBUH][LAc] (101 MHz, DMSO-d_6)

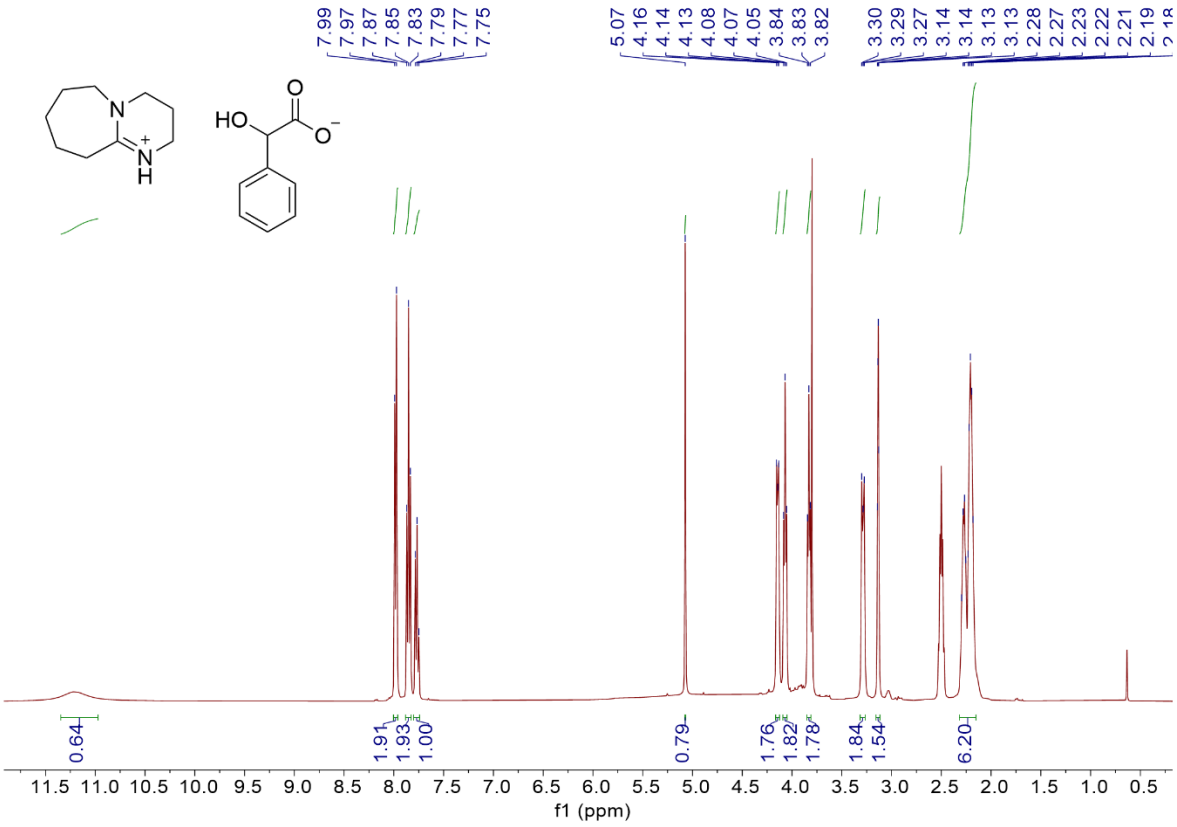

Figure S5. ^{1}H NMR Spectrum of [DBUH][MAc] (400 MHz, DMSO-d_6)

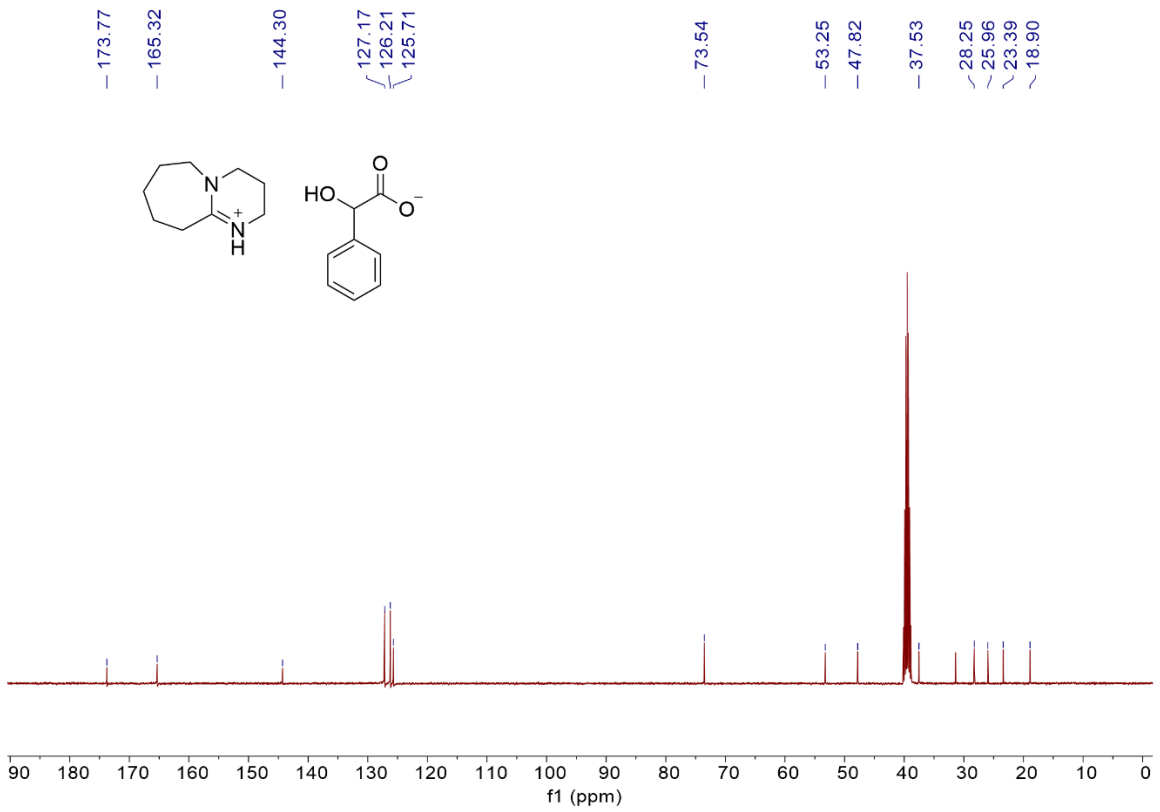

Figure S6. ^{13}C NMR Spectrum of [DBUH][MAc] (101 MHz, DMSO-d_6)

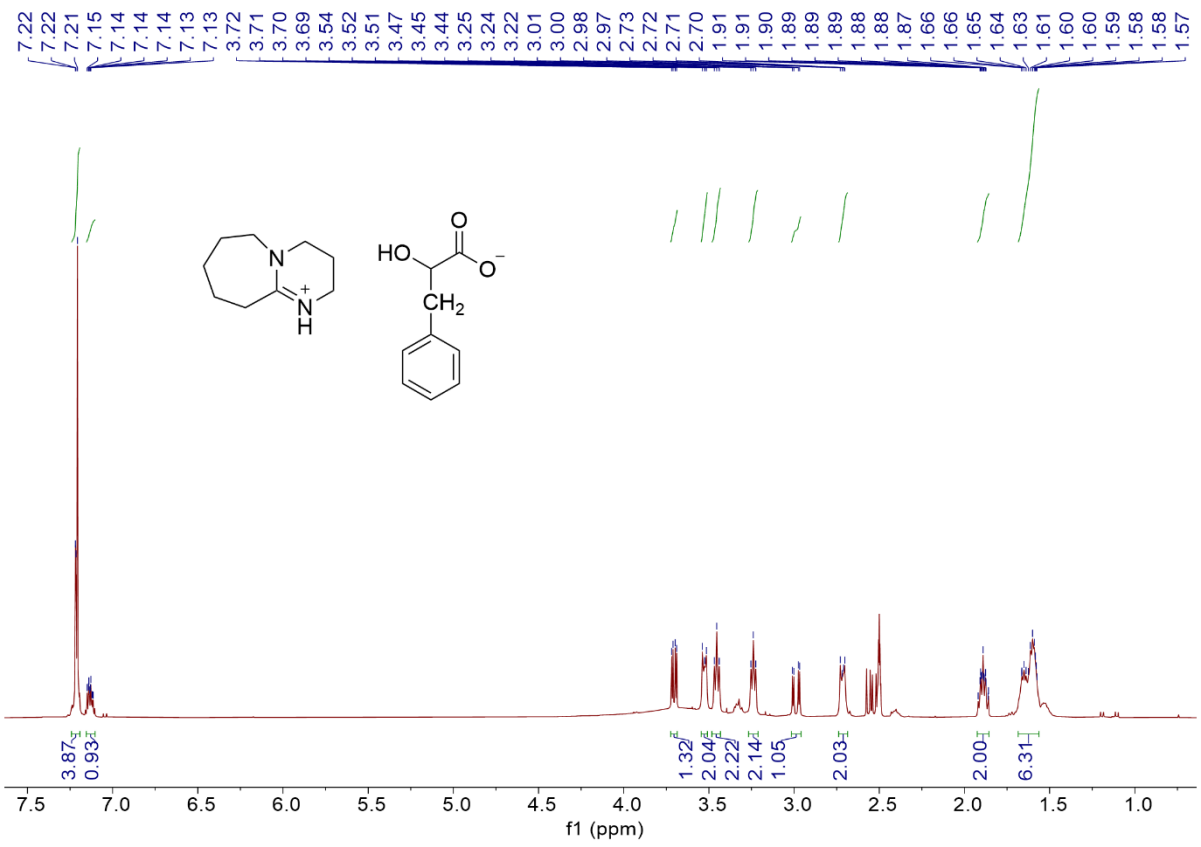

Figure S7. ^{1}H NMR Spectrum of [DBUH][PLAc] (400 MHz, DMSO-d_6)

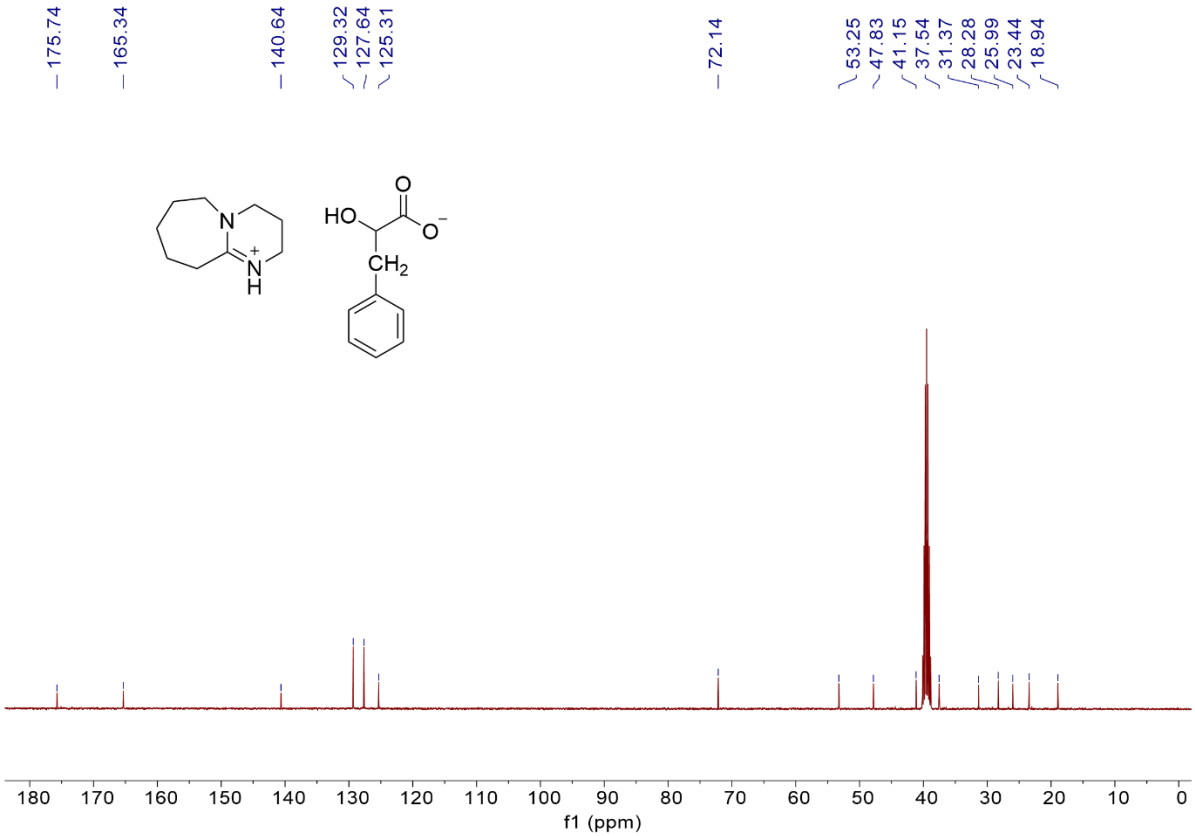

Figure S8. ^{13}C NMR Spectrum of [DBUH][PLAc] (101 MHz, DMSO-d_6)

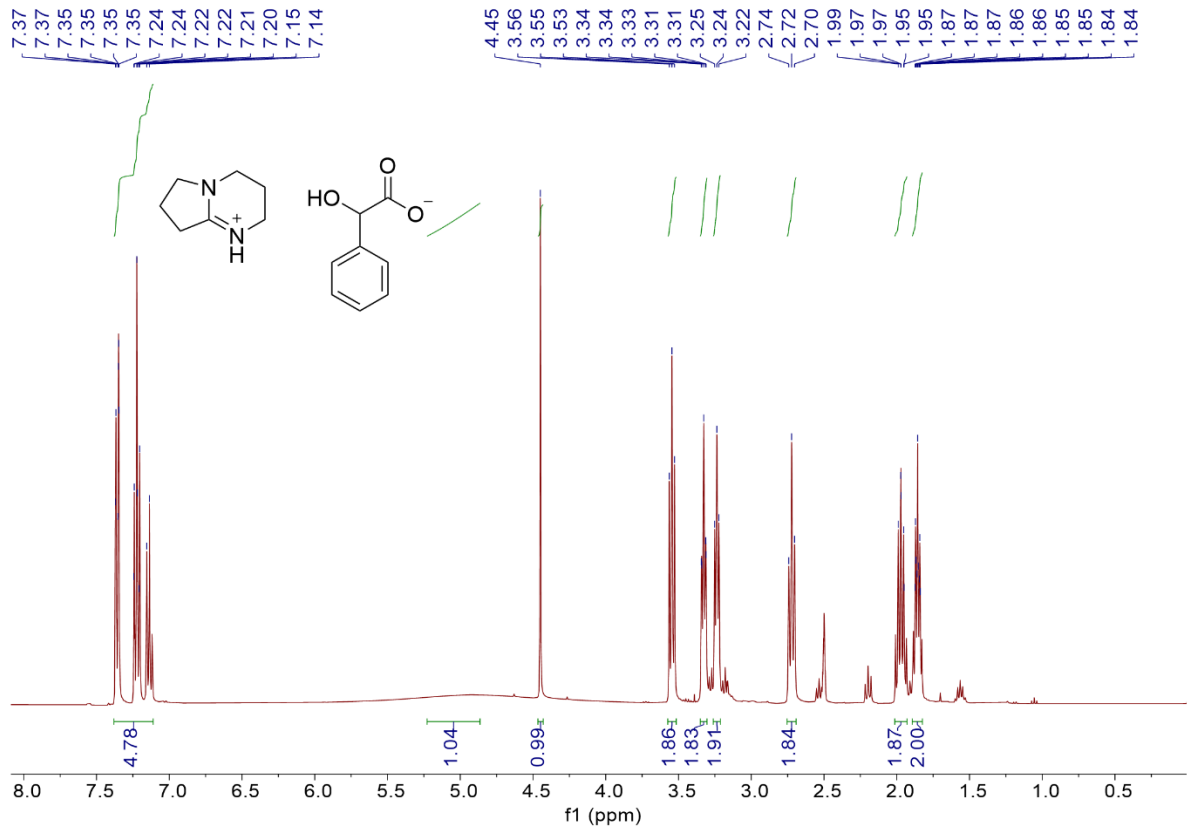

Figure S9. ^{1}H NMR Spectrum of [DBNH][MAc] (400 MHz, DMSO-d_6)

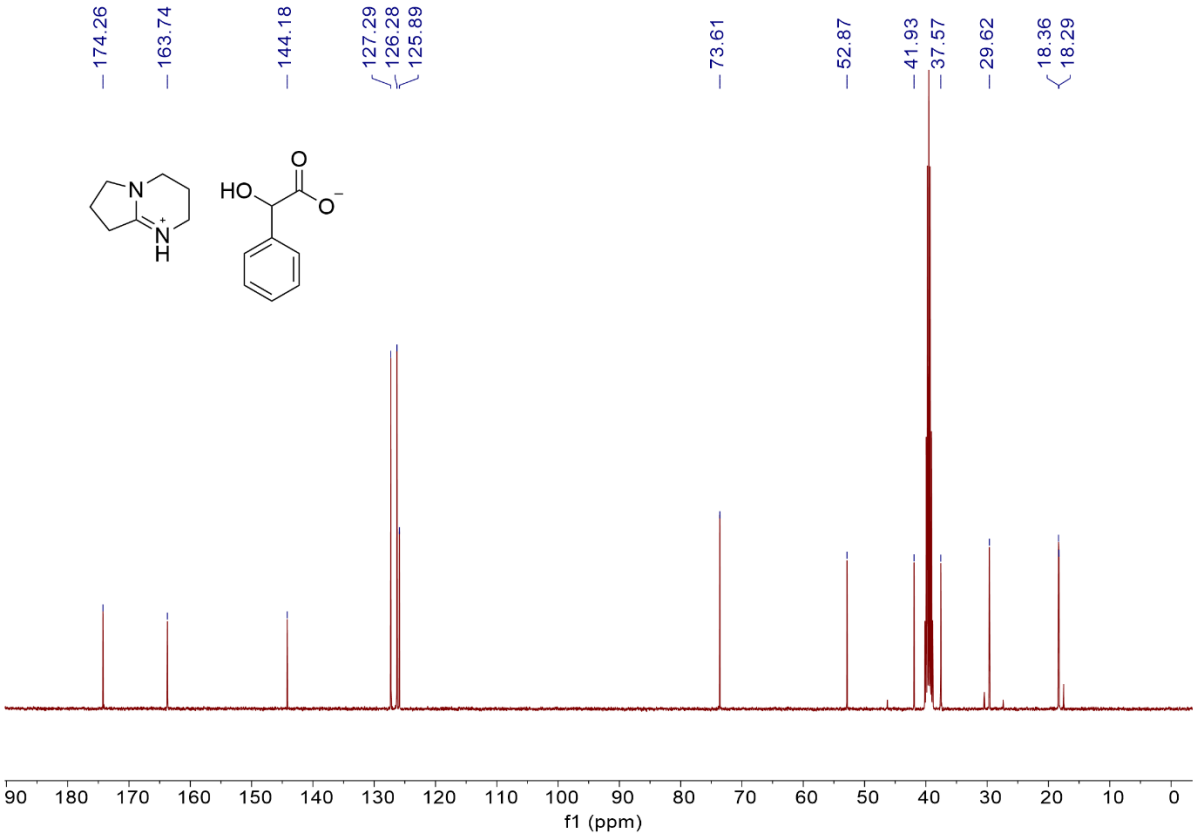

Figure S10. ^{13}C NMR Spectrum of [DBNH][MAc] (101 MHz, DMSO-d_6)

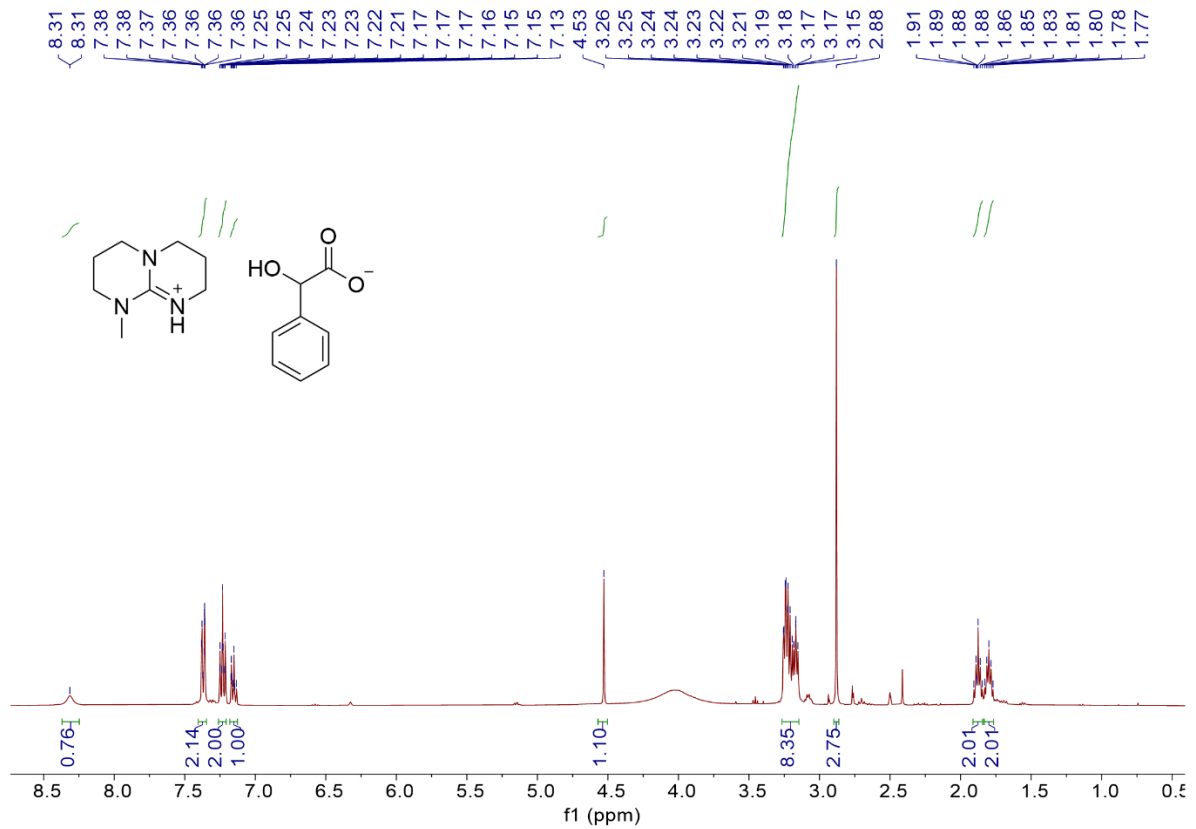

Figure S11. ^{1}H NMR Spectrum of [MTBDH][MAc] (400 MHz, DMSO-d_6)

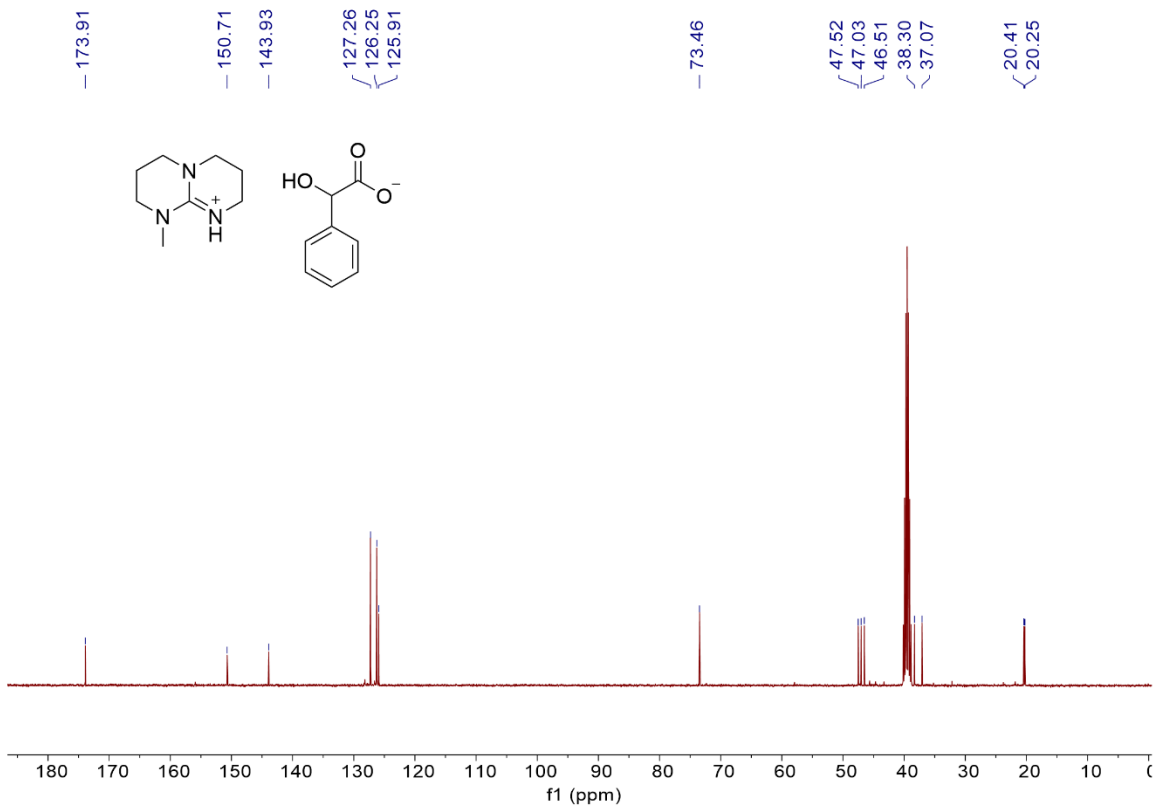

Figure S12. ^{13}C NMR Spectrum of [MTBDH][MAc] (101 MHz, DMSO-d_6)

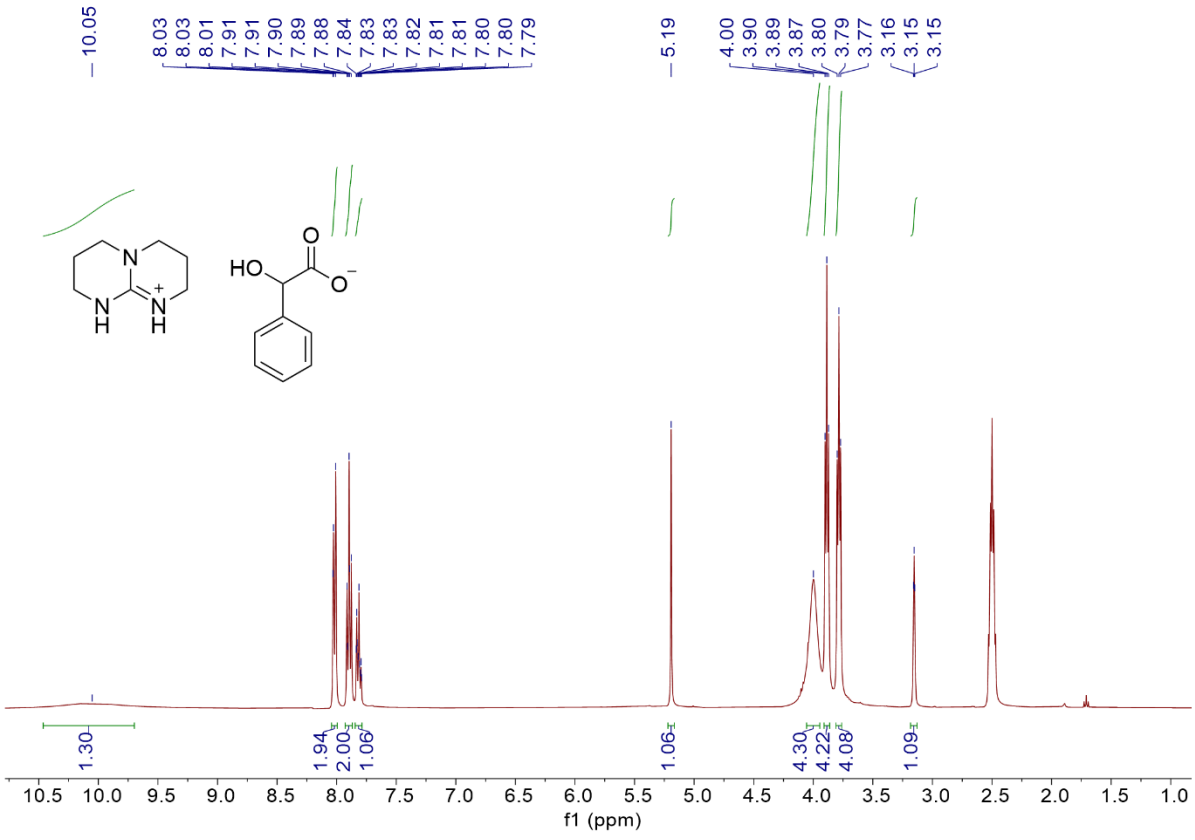

Figure S13. ^{1}H NMR Spectrum of [TBDH][MAc] (400 MHz, DMSO-d_6)

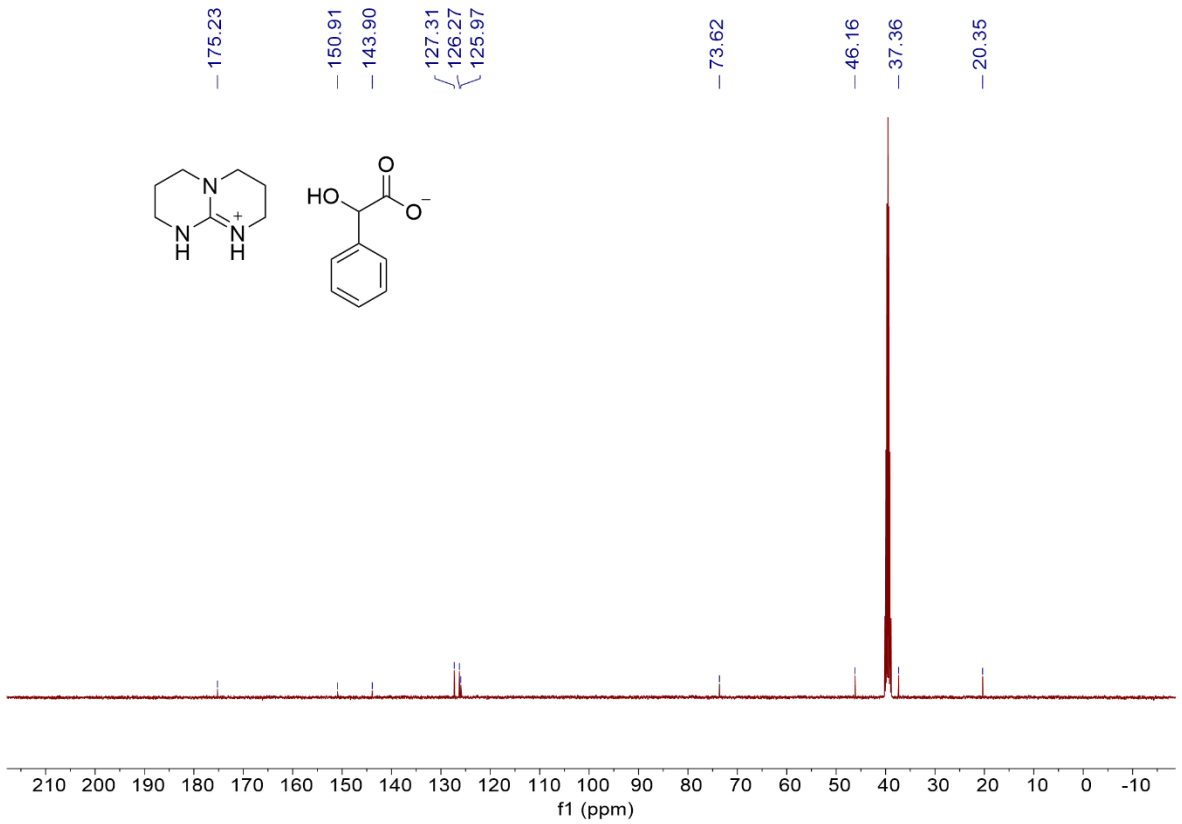

Figure S14. ^{13}C NMR Spectrum of [TBDH][MAc] (101 MHz, DMSO-d_6)

4. General procedure for the cycloaddition of CO_2 into epoxide (CCE)

The internal epoxide (10.0 mmol) and catalyst [DBUH][MAc] (76 mg, 0.25 mmol, 2.5mol%) were placed in a dry 10 mL stainless steel reactor containing a magnetic stir bar, the reactor was constantly purged with 1 MPa CO2 to remove air and finally maintain the pressure at 1.0 MPa. The reaction mixture was heated to 120 °C and stirred for 12 h. Then the reactor was cooled down to room temperature and slowly depressurized to ≤ 0.1 MPa. The conversions of epoxides were determined by 1H NMR spectra with CDCl3 as a solvent, and the selectivity of cyclic carbonates were determined with 1,3,5-Trimethoxybenzene as the internal standard. before it was sampled for 1H NMR spectra measurements. The reaction mixture was filtered over silica gel (SiO2) with petroleum ether: ethyl acetate = 10:1–1:1 to afford the corresponding cyclic carbonate.

5. Copies of ^{1}H NMR and ^{13}C NMR spectra of cyclic carbonates

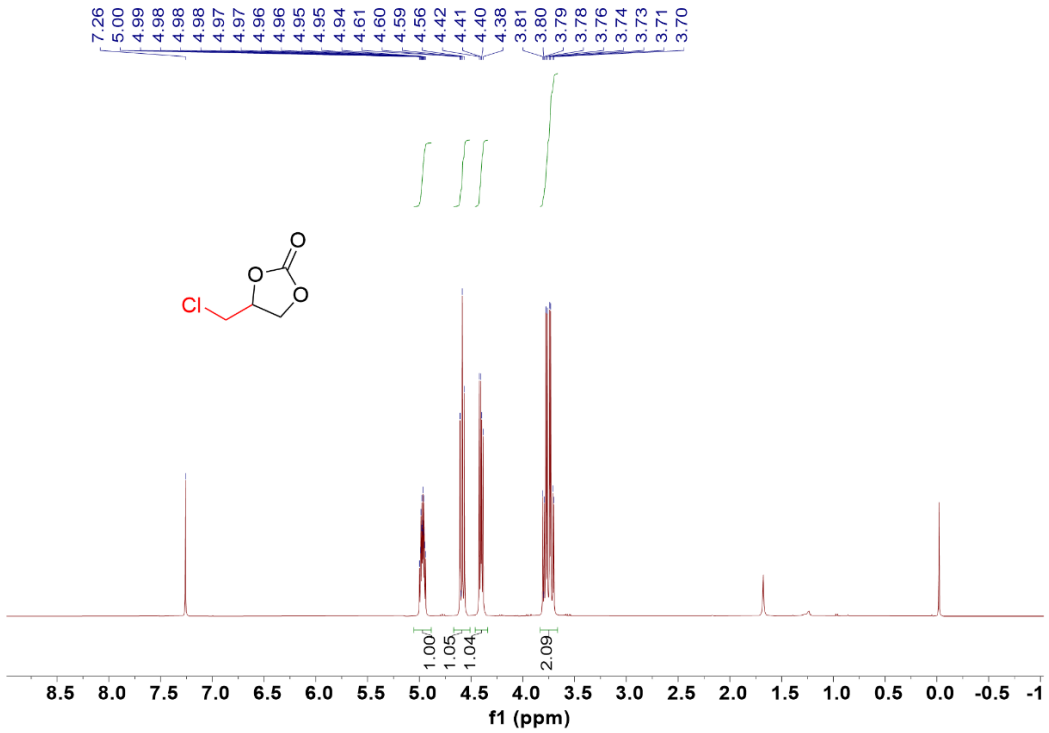

Figure S15. ^{1}H NMR Spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (400 MHz, $CDCl_3$)

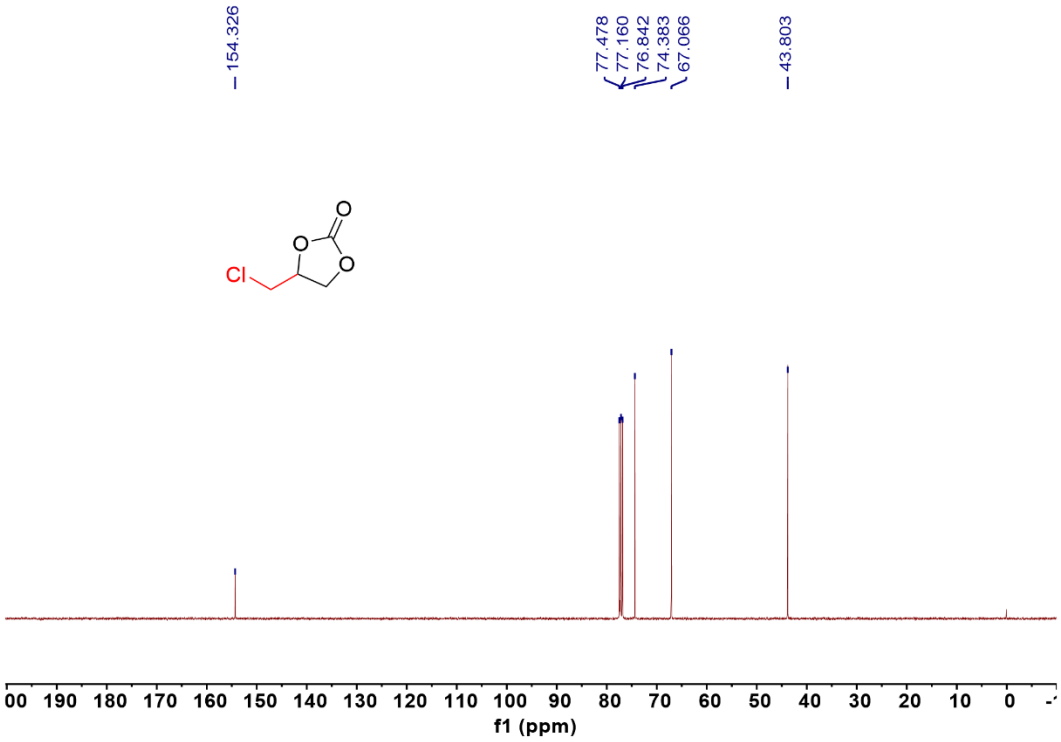

Figure S16. ^{13}C NMR Spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (101 MHz, $CDCl_3$)

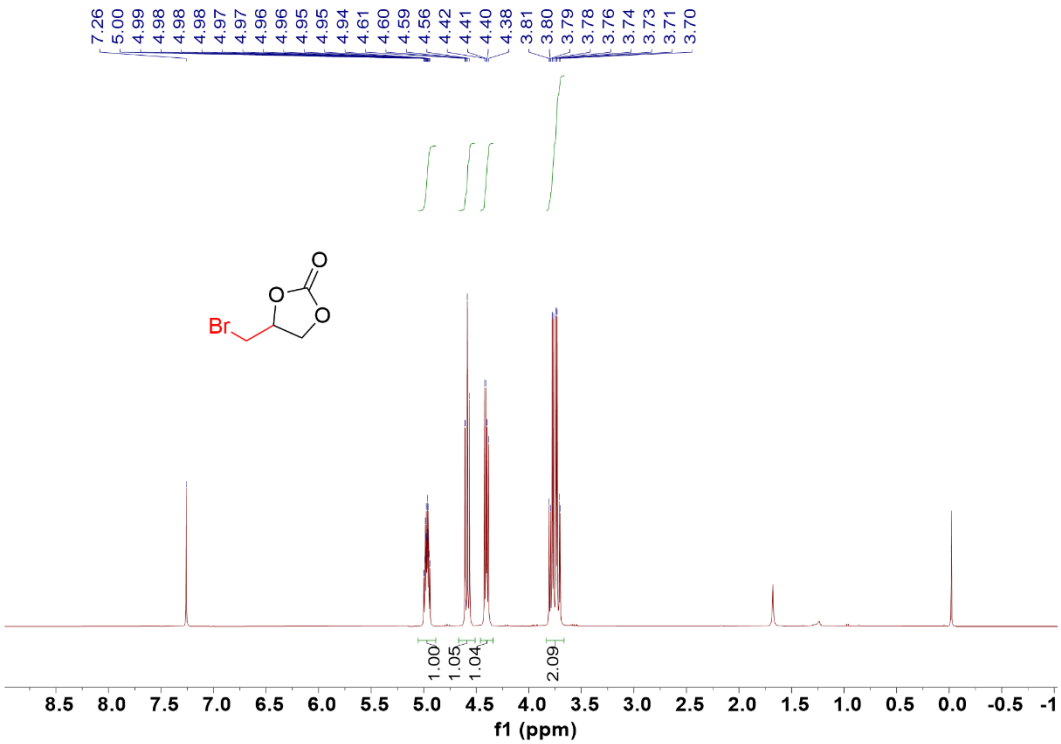

Figure S17. ^{1}H NMR Spectrum of 4-(bromomethyl)-1,3-dioxolan-2-one (400 MHz, $CDCl_3$)

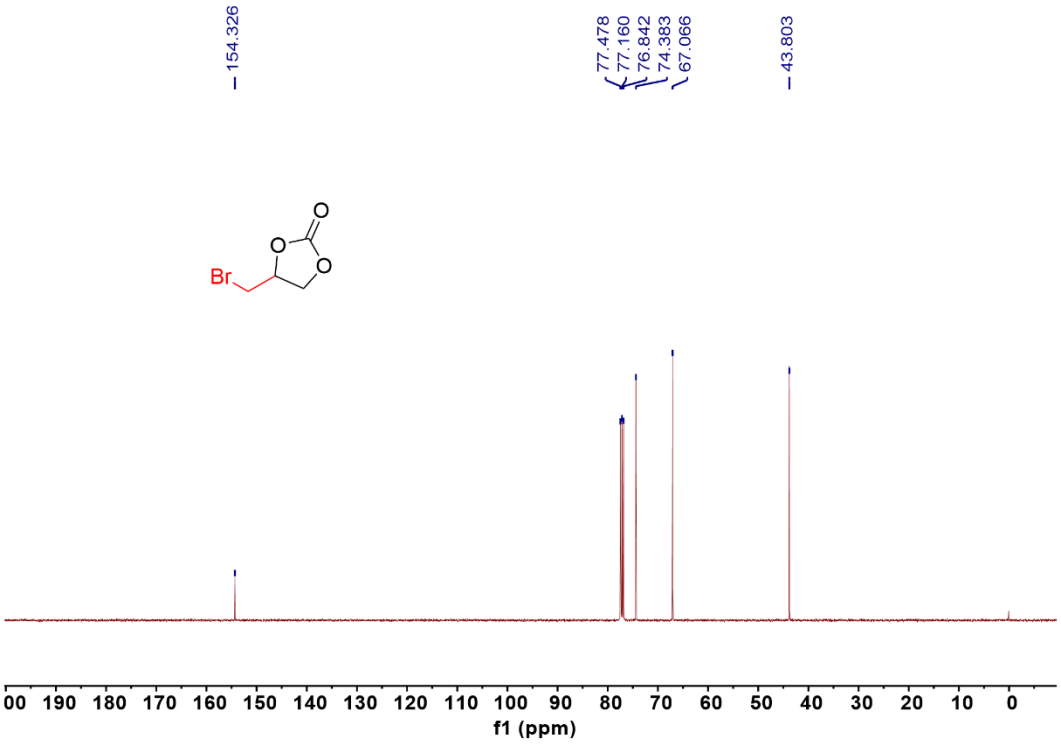

Figure S18. ^{13}C NMR Spectrum of 4-(bromomethyl)-1,3-dioxolan-2-one (101 MHz, $CDCl_3$)

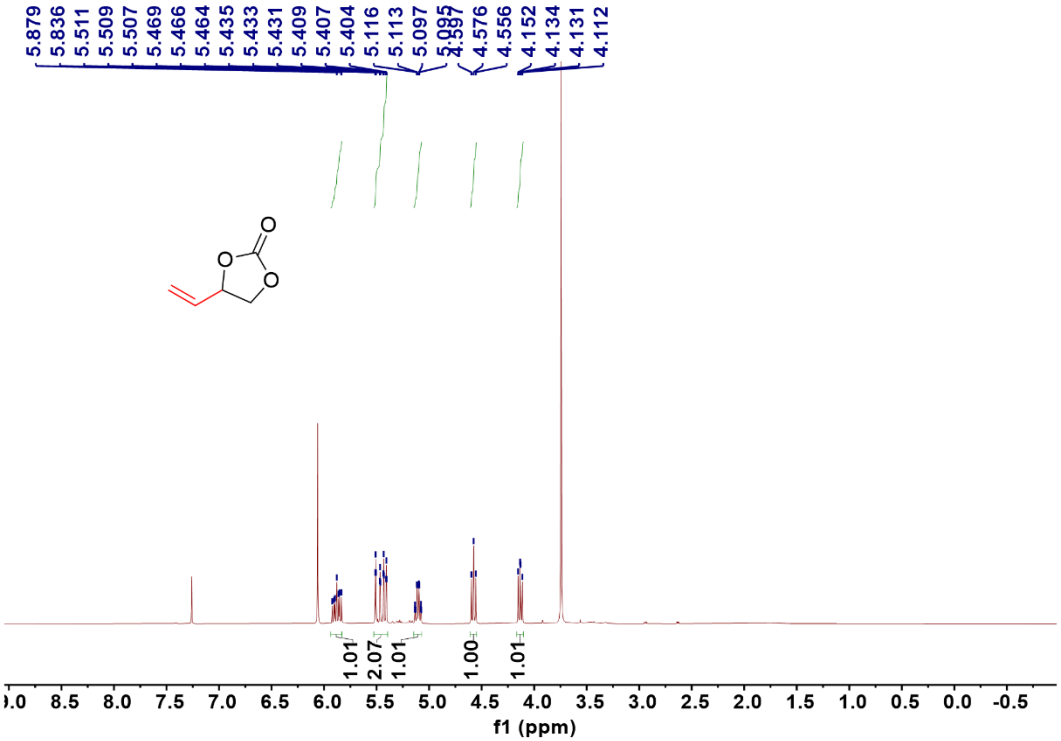

Figure S19. ^{1}H NMR Spectrum of 4-vinyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$)

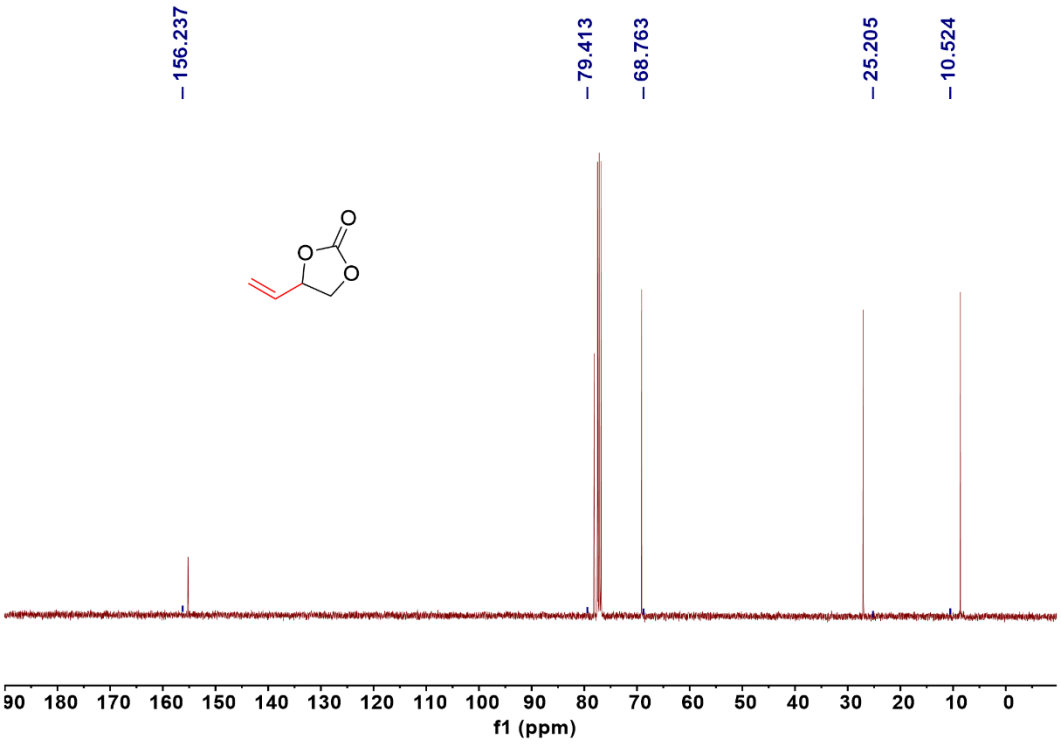

Figure S20. ^{13}C NMR Spectrum of 4-butyl-1,3-dioxolan-2-one (101 MHz, $CDCl_3$)

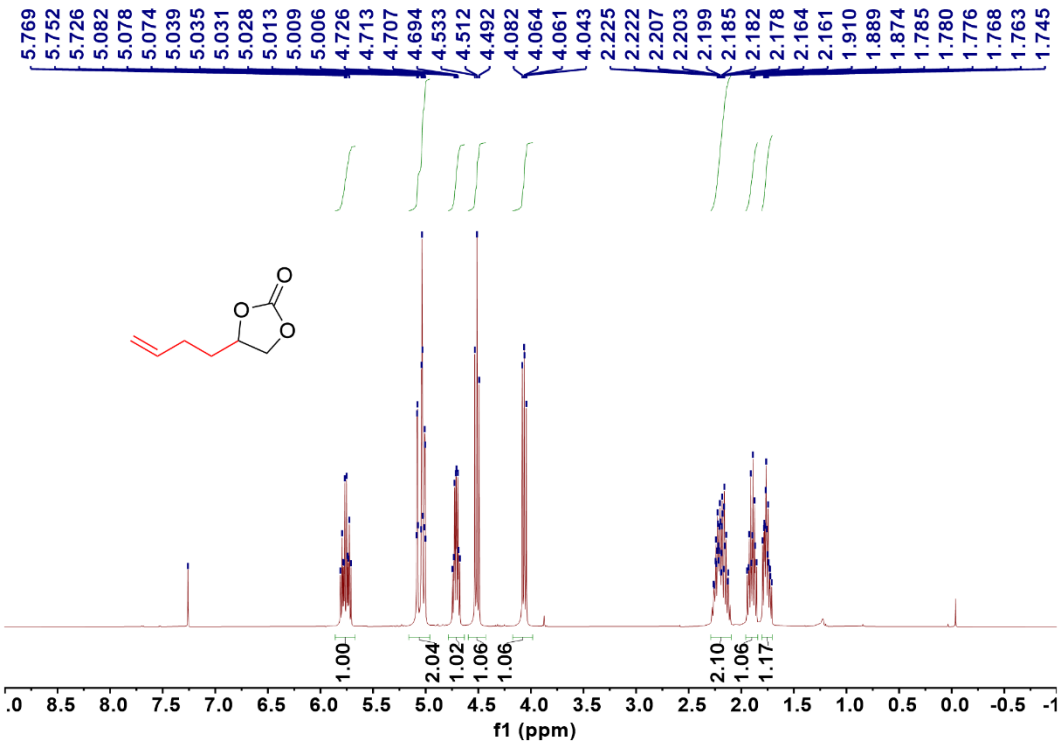

Figure S21. ^{1}H NMR Spectrum of 4-(but-3-en-1-yl)-1,3-dioxolan-2-one (400 MHz, $CDCl_3$)

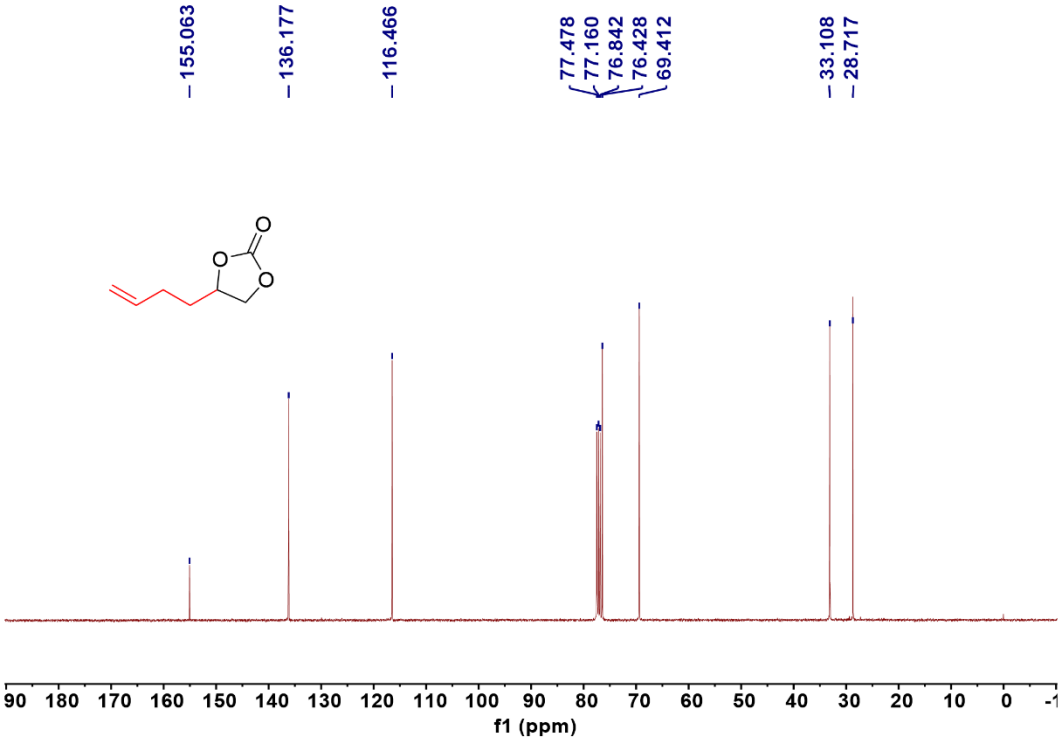

Figure S22. ^{13}C NMR Spectrum of 4-(but-3-en-1-yl)-1,3-dioxolan-2-one (101 MHz, $CDCl_3$)

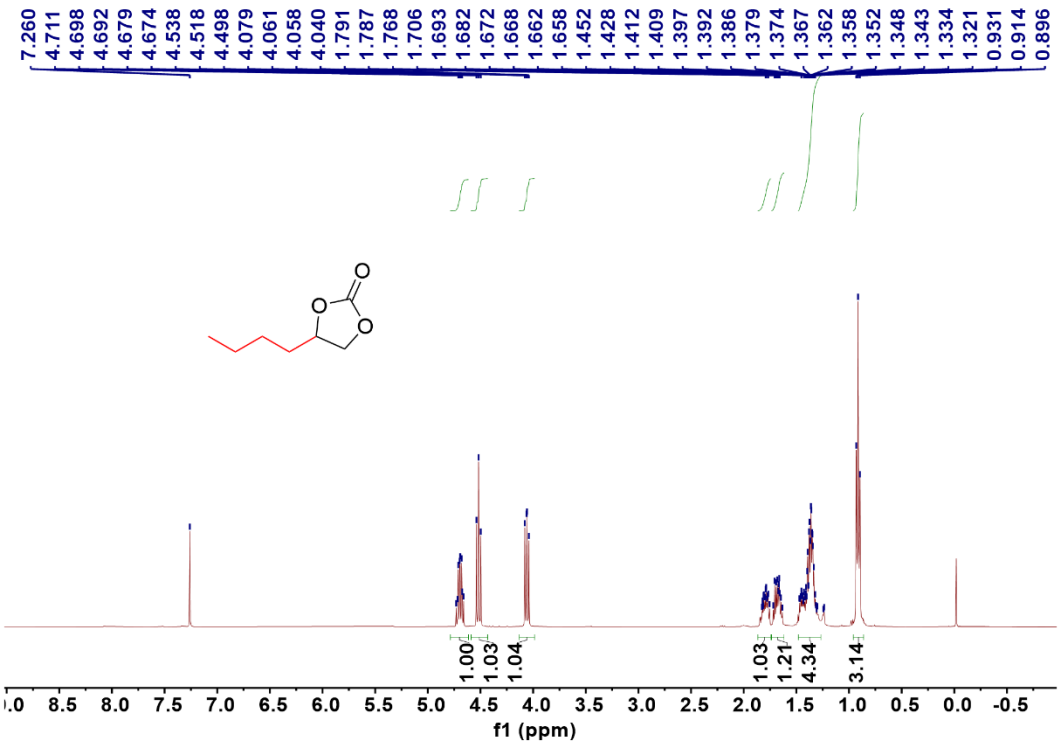

Figure S23. ^{1}H NMR Spectrum of 4-butyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$)

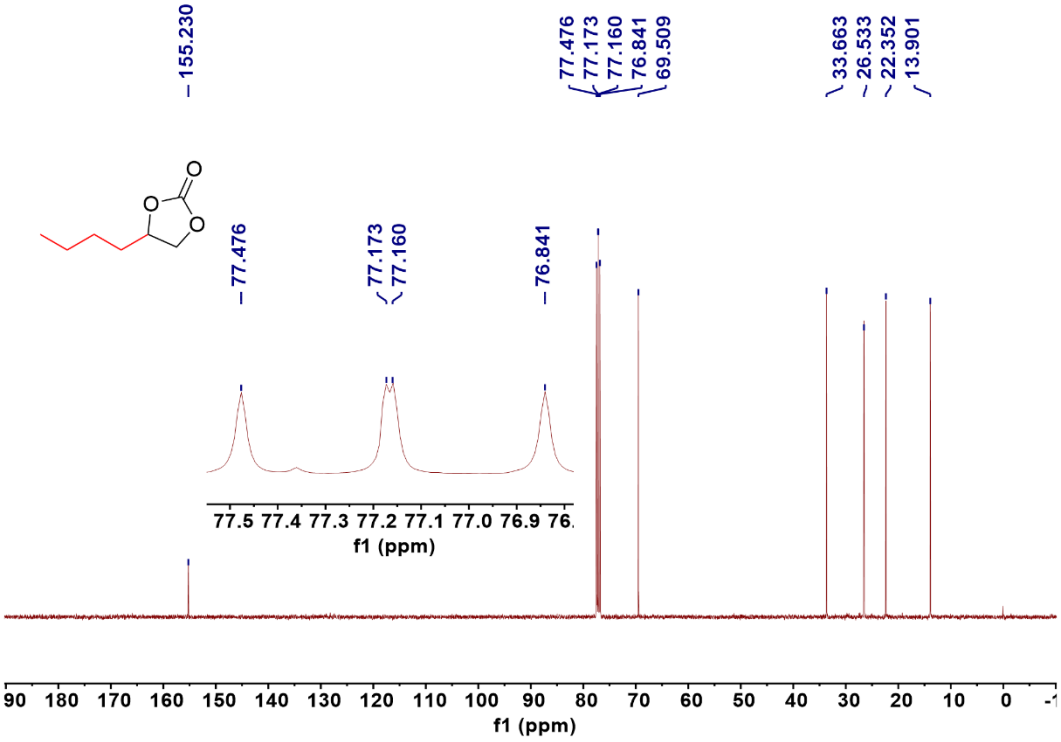

Figure S24. ^{13}C NMR Spectrum of 4-butyl-1,3-dioxolan-2-one (101 MHz, $CDCl_3$)

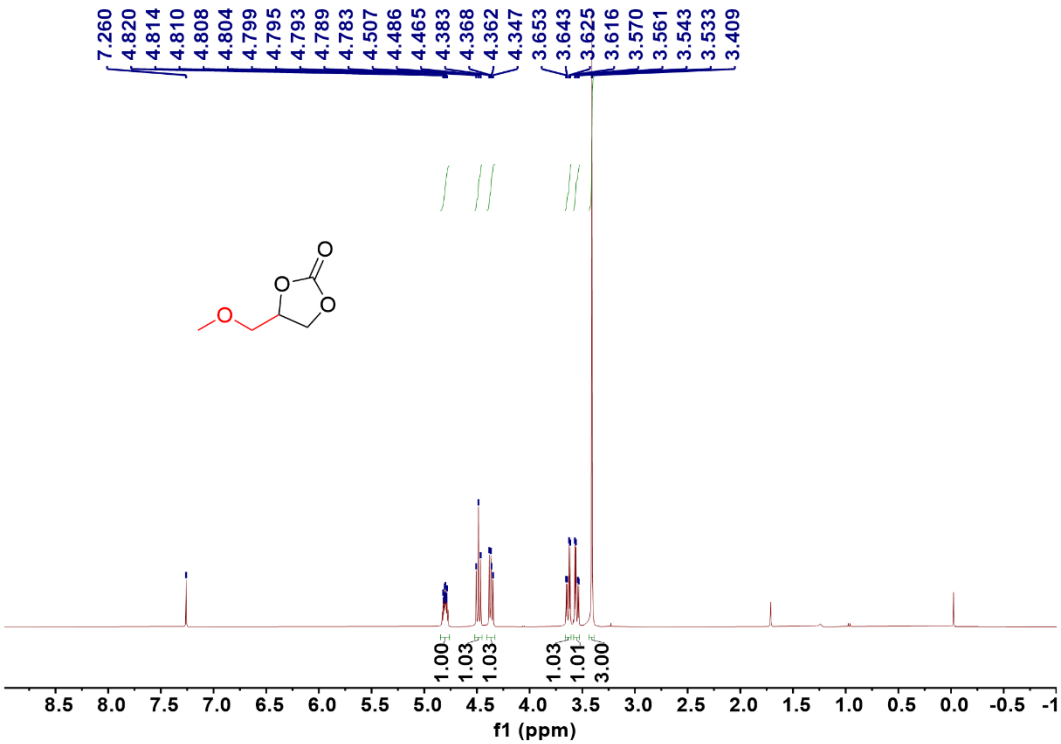

Figure S25. ^{1}H NMR Spectrum of 4-(methoxymethyl)-1,3-dioxolan-2-one (400 MHz, $CDCl_3$)

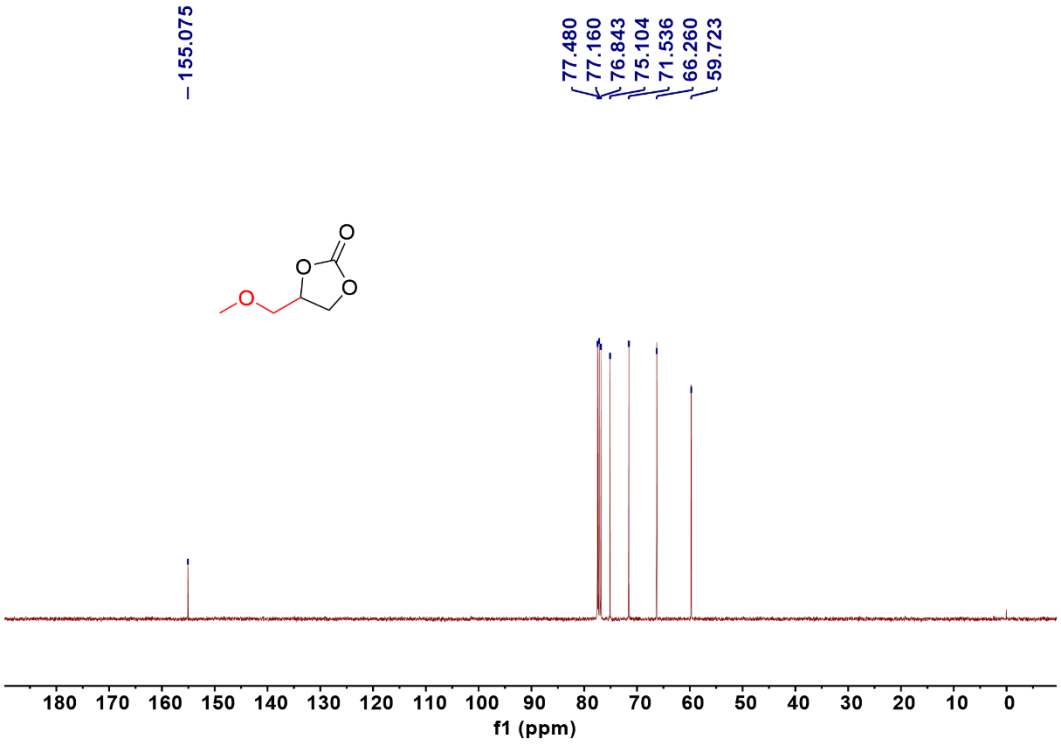

Figure S26. ^{13}C NMR Spectrum of 4-(methoxymethyl)-1,3-dioxolan-2-one (101 MHz, $CDCl_3$)

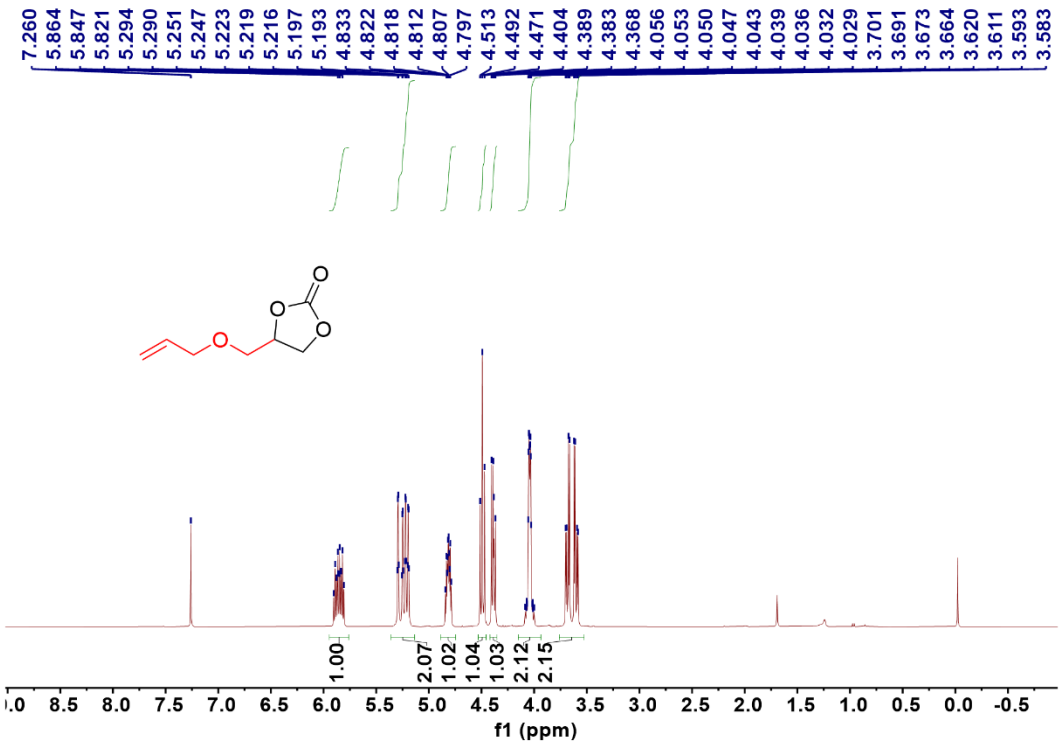

Figure S27. ^{1}H NMR Spectrum of 4-((allyloxy)methyl)-1,3-dioxolan-2-one (400 MHz, $CDCl_3$)

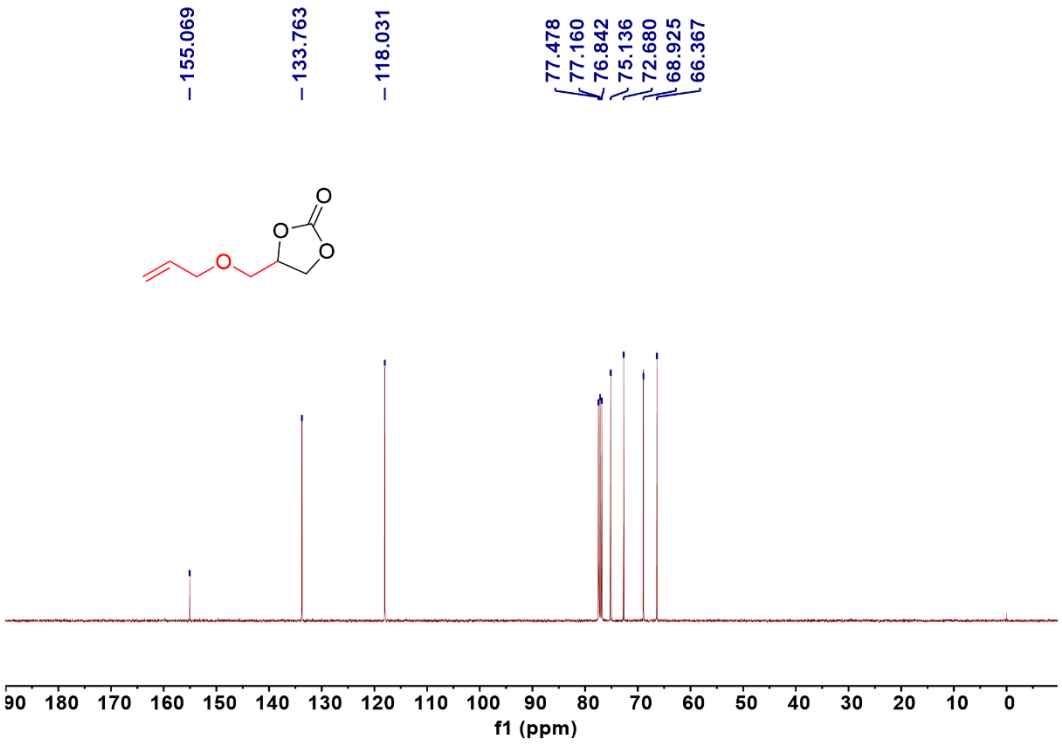

Figure S28. ^{13}C NMR Spectrum of 4-((allyloxy)methyl)-1,3-dioxolan-2-one (101 MHz, $CDCl_3$)

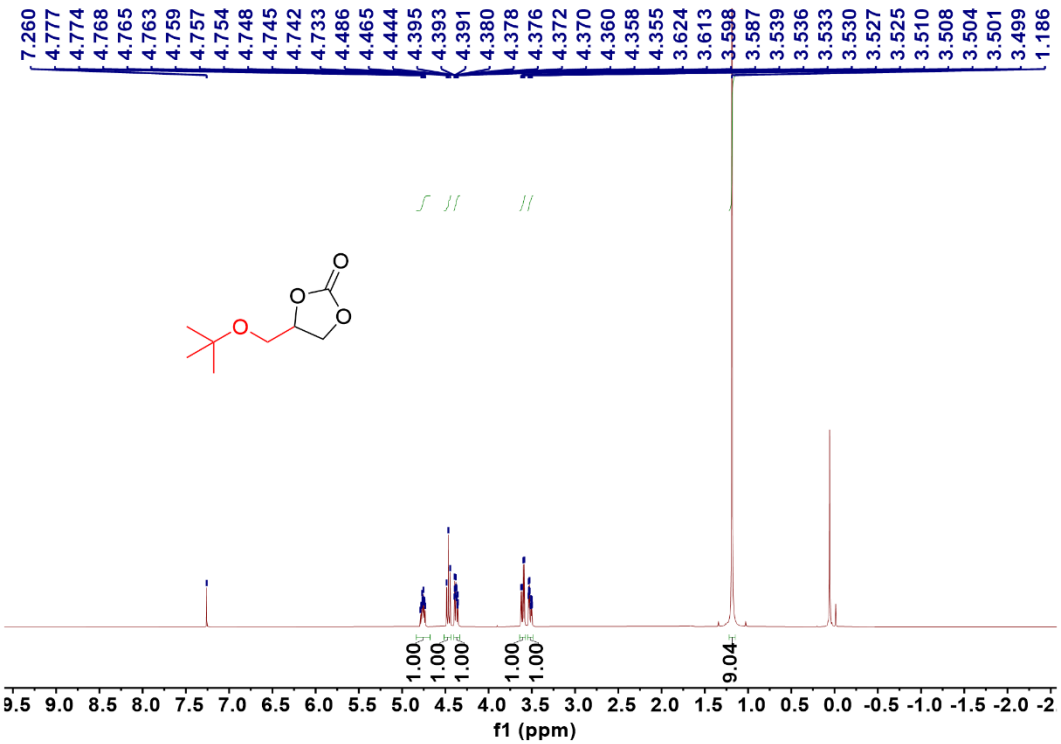

Figure S29. ^{1}H NMR Spectrum of 4-(*tert*-butoxymethyl)-1,3-dioxolan-2-one (400 MHz, $CDCl_3$)

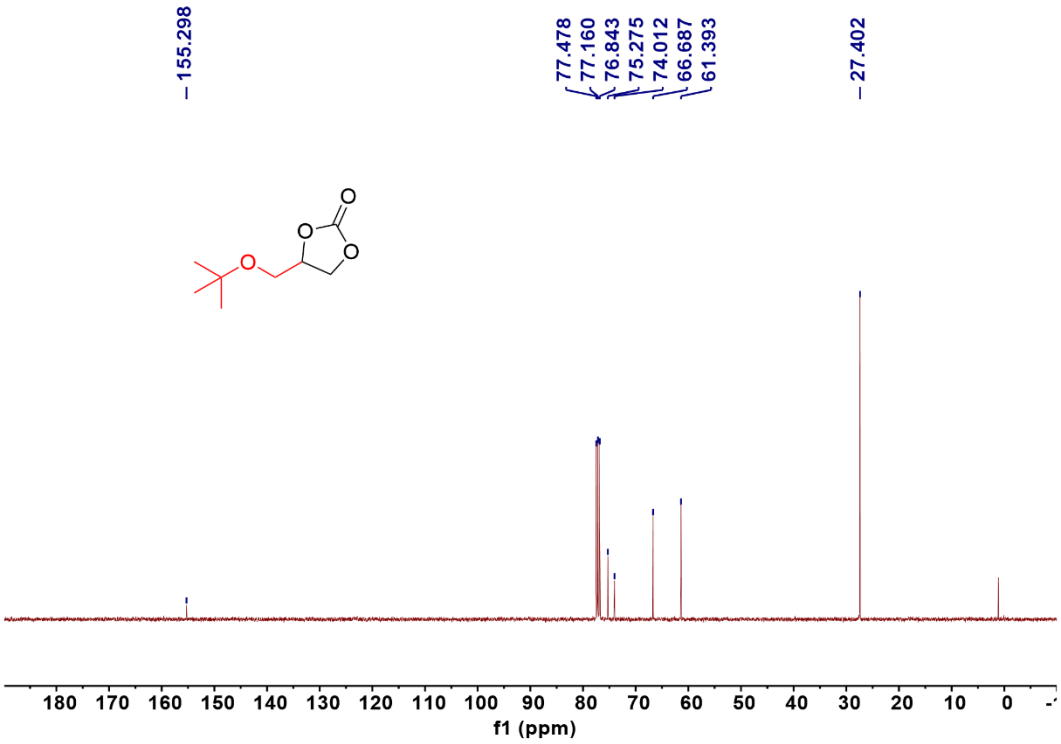

Figure S30. ^{13}C NMR Spectrum of 4-(*tert*-butoxymethyl)-1,3-dioxolan-2-one (101 MHz, $CDCl_3$)

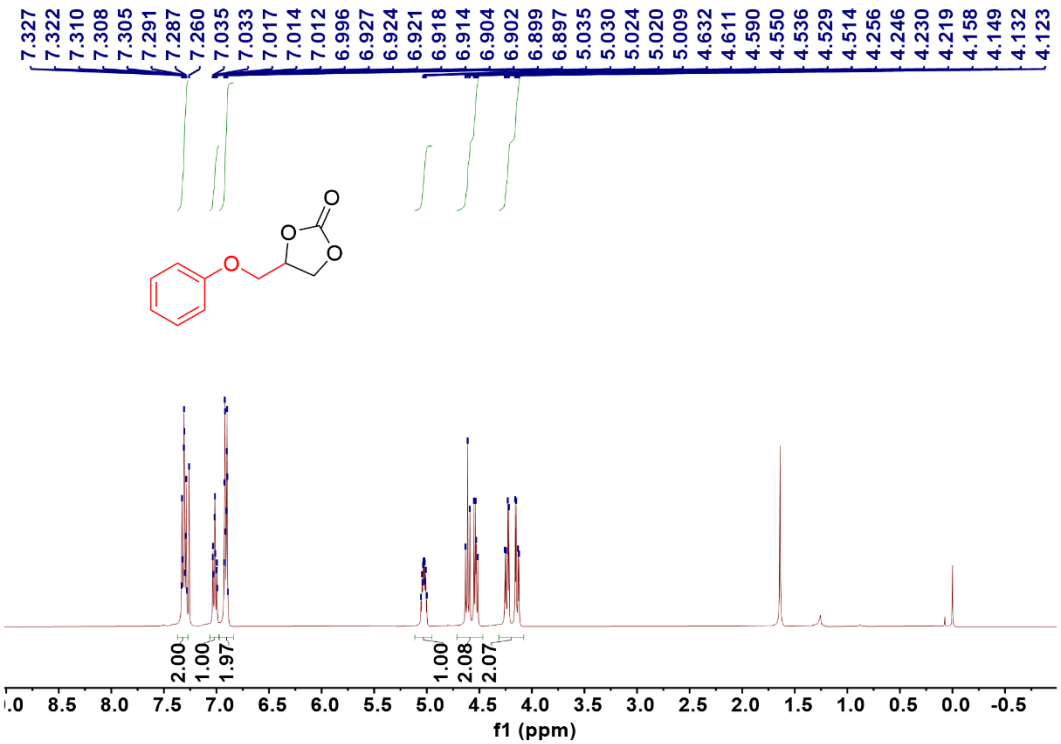

Figure S31. ^{1}H NMR Spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one (400 MHz, $CDCl_3$)

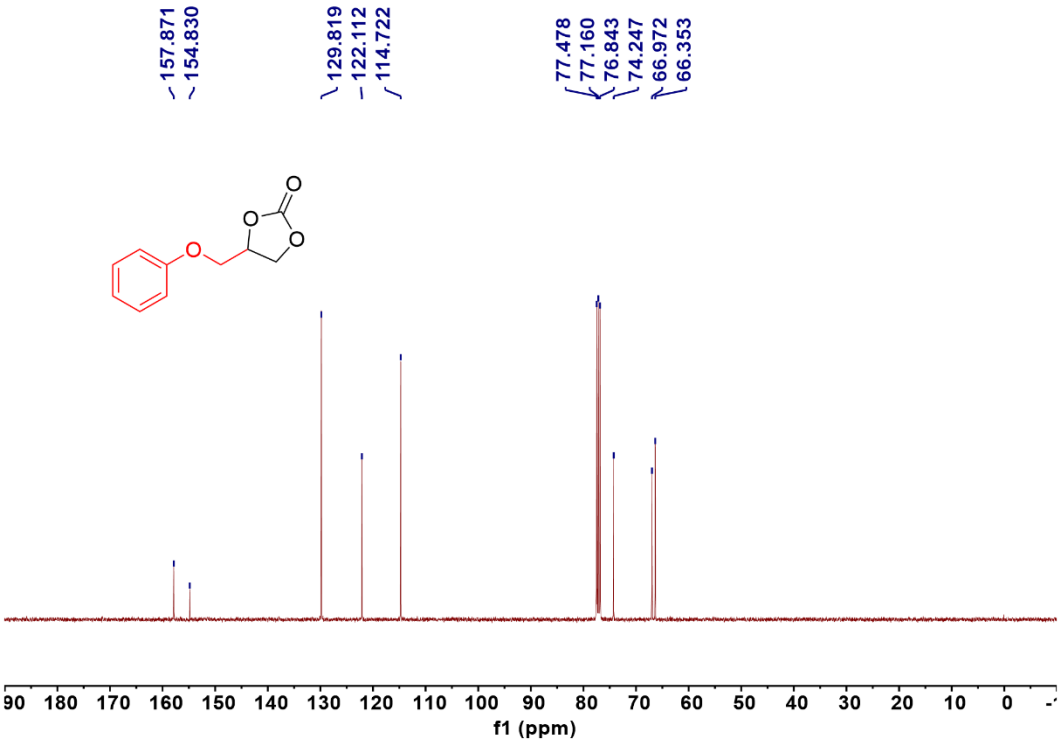

Figure S32. ^{13}C NMR Spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one (101 MHz, $CDCl_3$)

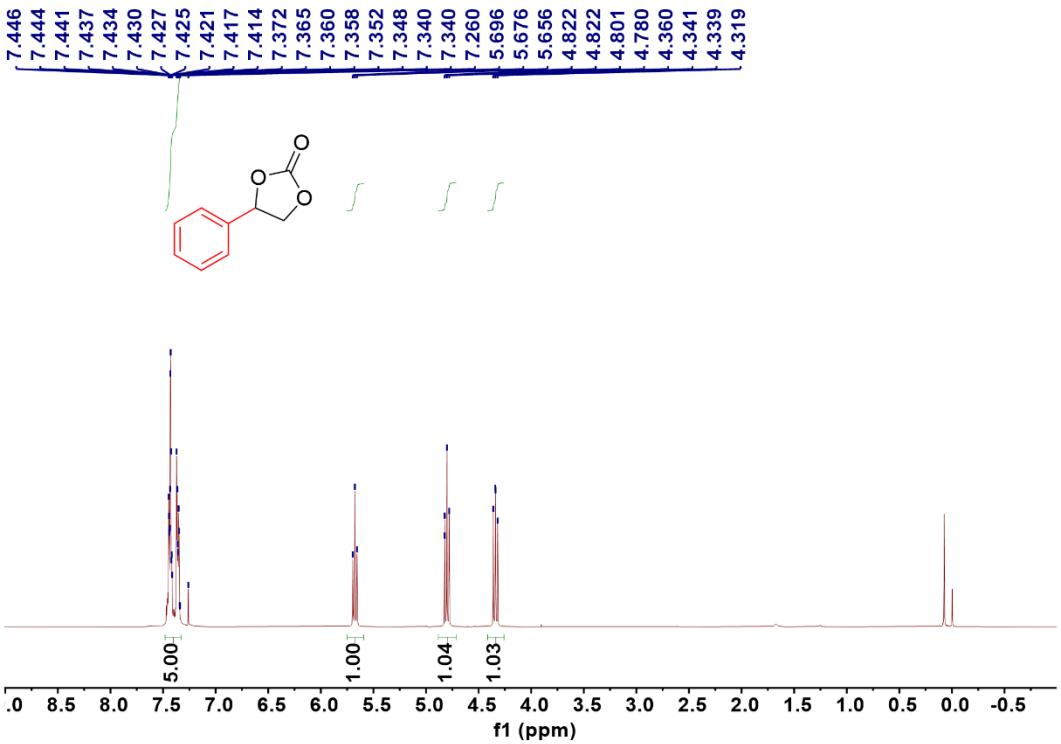

Figure S33. ^{1}H NMR Spectrum of 4-phenyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$)

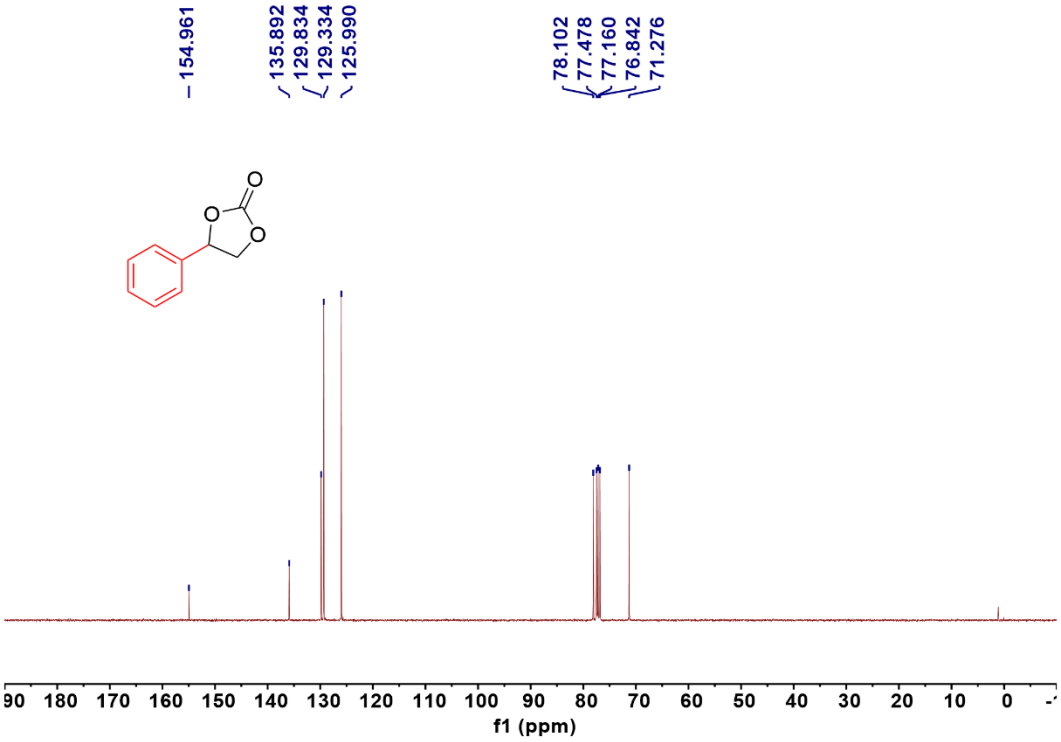

Figure S34. ^{13}C NMR Spectrum of 4-phenyl-1,3-dioxolan-2-one (101 MHz, $CDCl_3$)

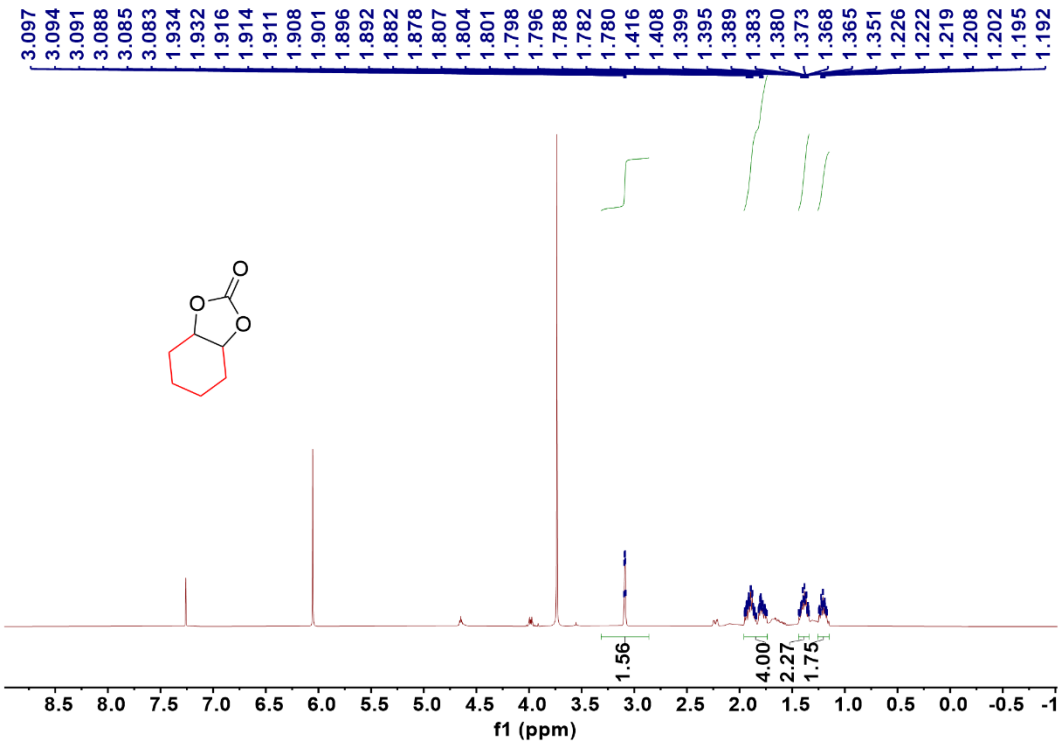

Figure S35. ^{1}H NMR Spectrum of hexahydrobenzo[d]-1,3-dioxolan-2-one (400 MHz, $CDCl_3$)

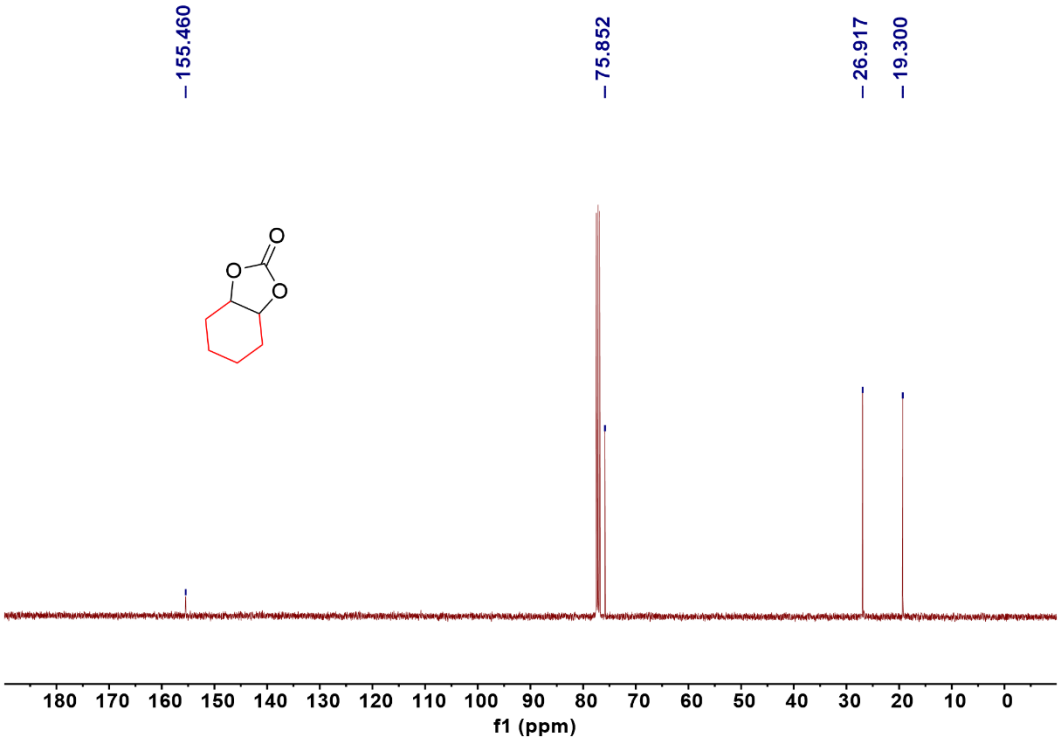

Figure S36. ^{13}C NMR Spectrum of hexahydrobenzo[d]-1,3-dioxolan-2-one (101 MHz, $CDCl_3$)

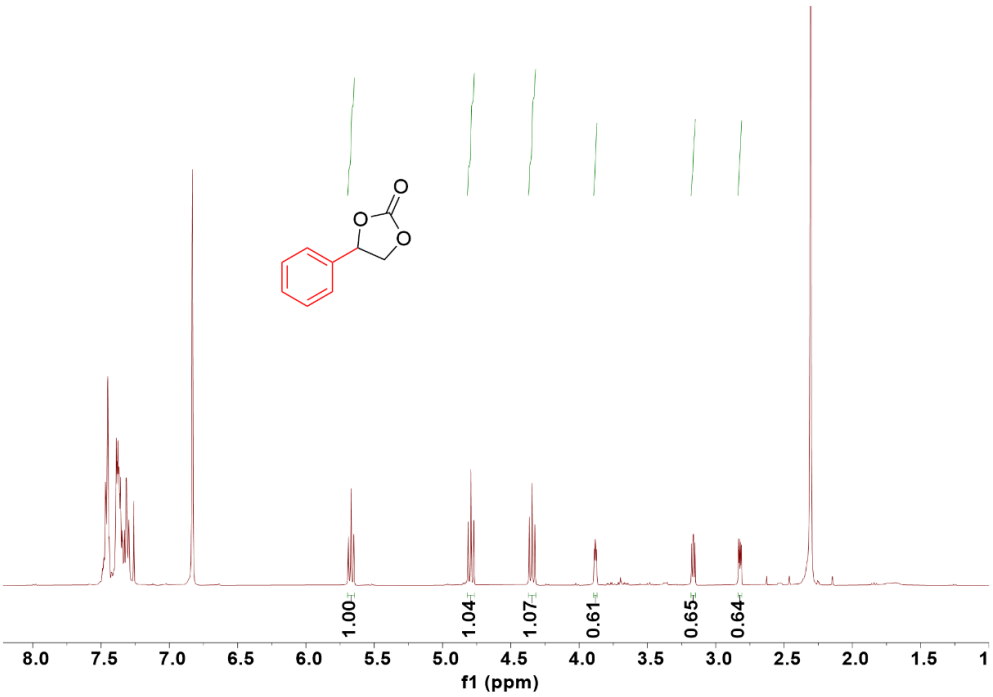

Figure S37. ^{1}H NMR Spectrum of 4-phenyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$) catalyst:[DBUH][Pac]

6. C spectrum of intermediate

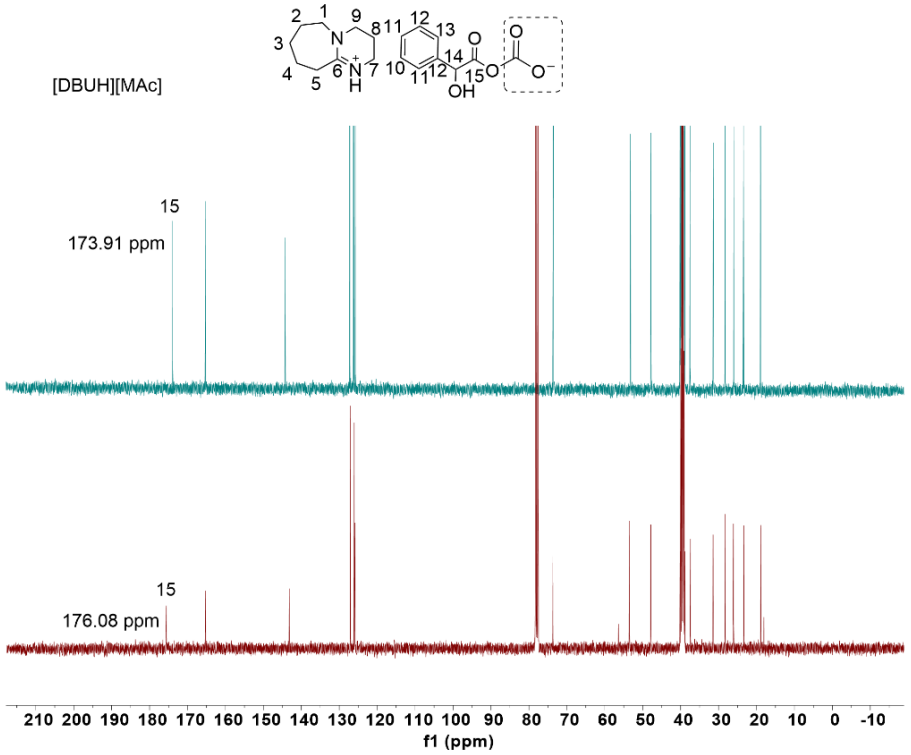

Figure S38. ^{13}C spectra (DMSO-d6) of [DBUH][MAc] during the absorption of CO_2 (b), Pure [DBUH][MAc] (a), CO_2 (1 Mpa), Catalyst[DBUH][MAc]

7. Supplementary data

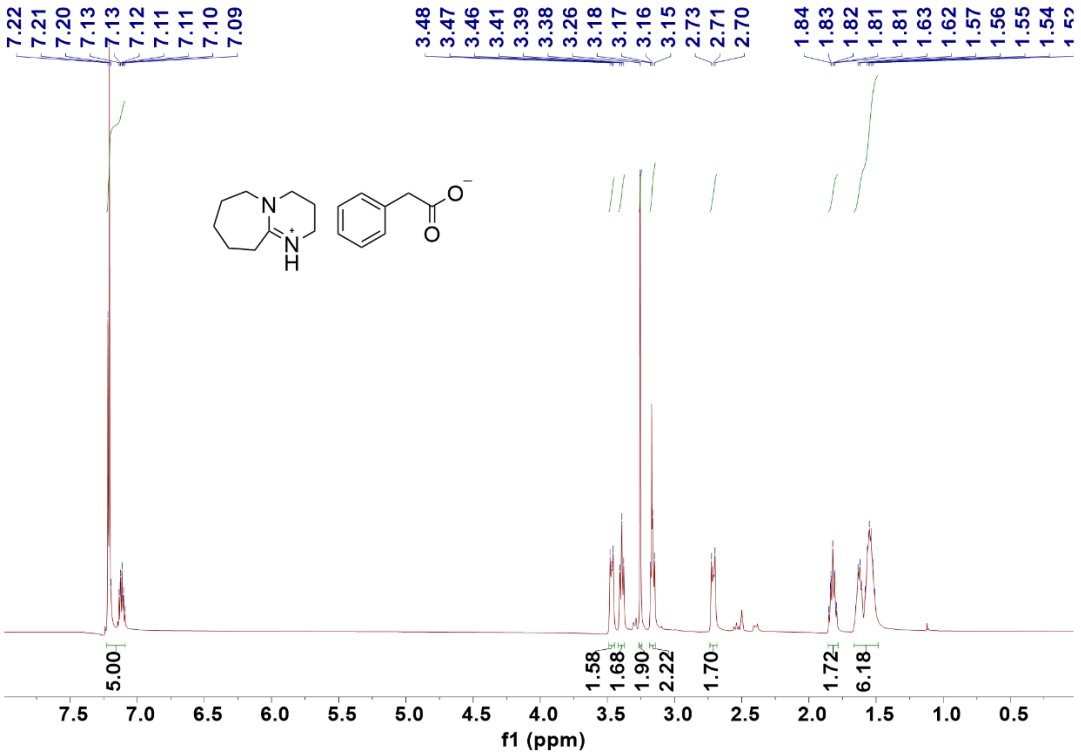

Figure S39. ^{1}H NMR Spectrum of [DBUH][PAc] (400 MHz, DMSO-d_6)

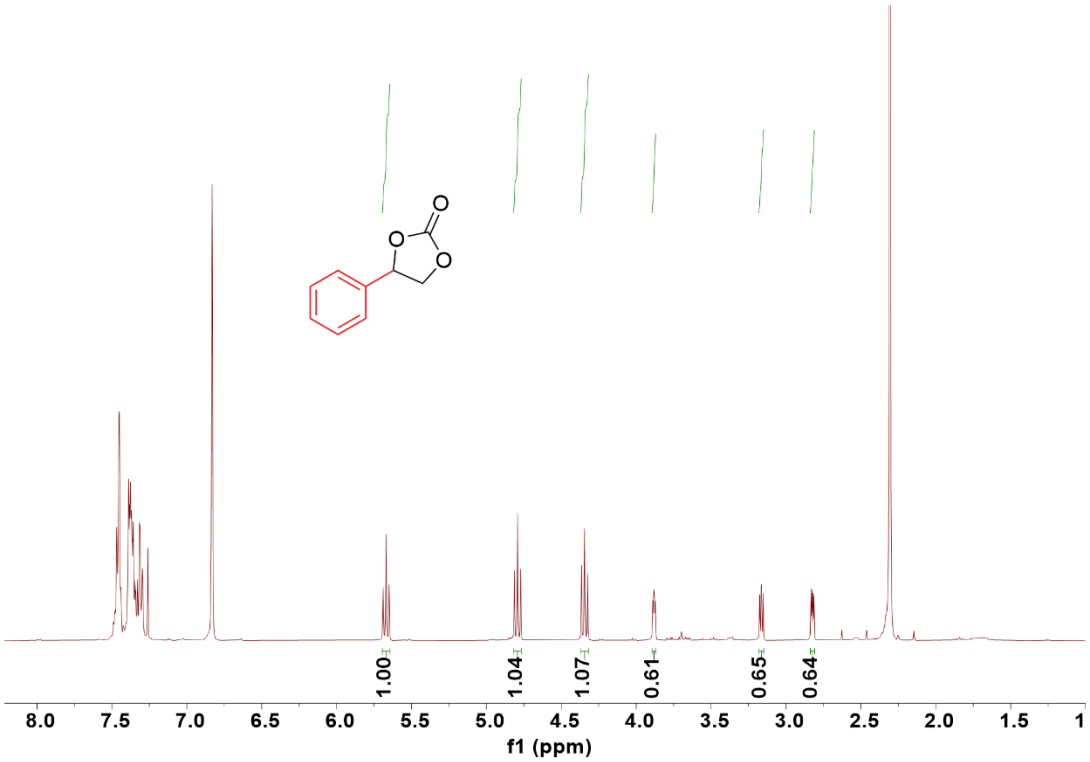

Figure S40.^{1}H NMR Spectrum of 4-phenyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$) [DBUH][PAc]

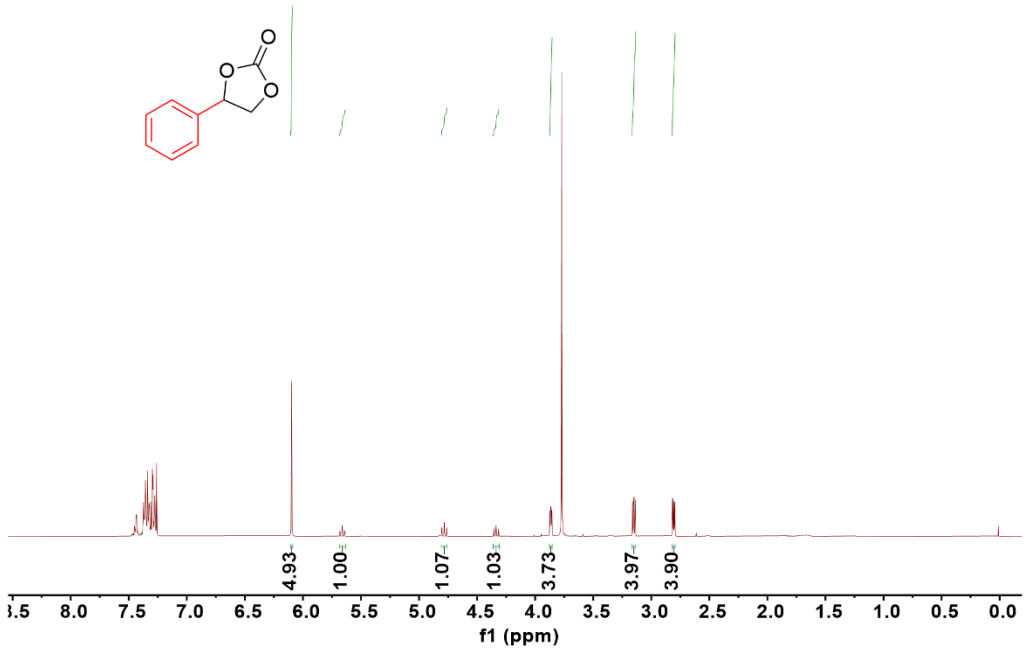

Figure S41.^{1}H NMR Spectrum of 4-phenyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$) [DBU]

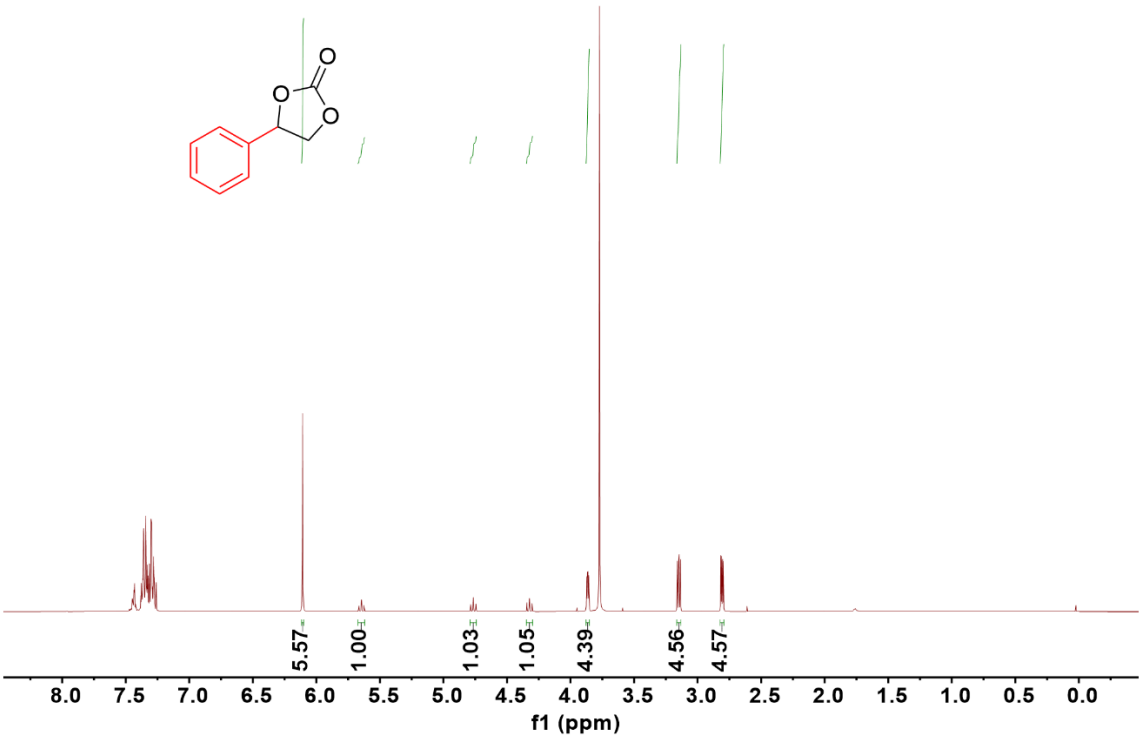

Figure S42.^{1}H NMR Spectrum of 4-phenyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$) [MAc]

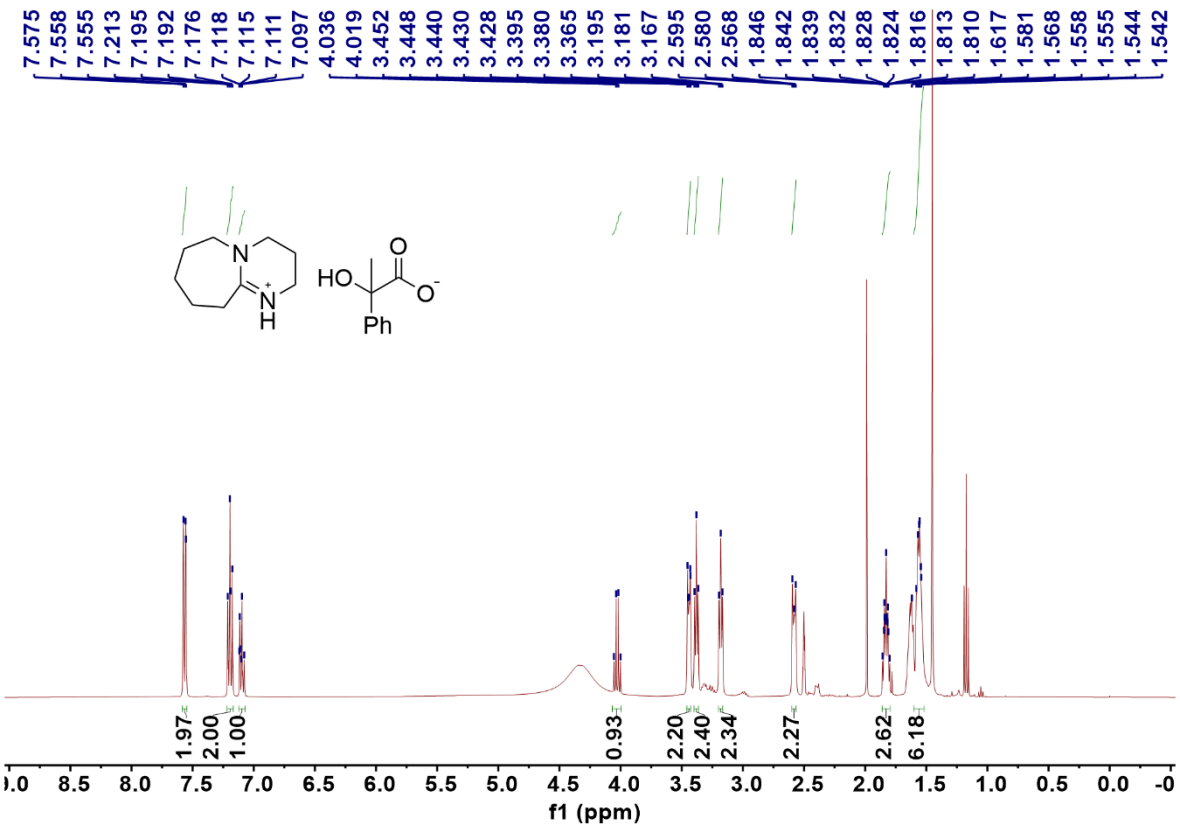

Figure S43. ^{1}H NMR Spectrum of [DBUH][ALc] (400 MHz, DMSO-d_6)

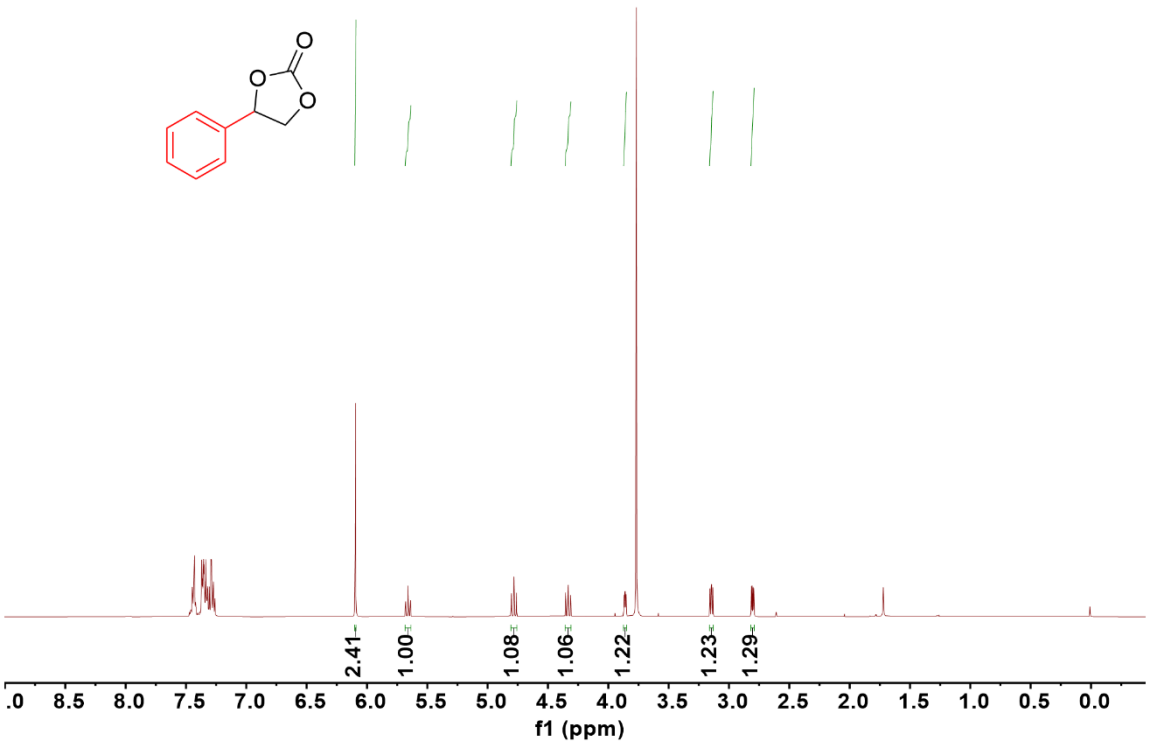

Figure S44.^{1}H NMR Spectrum of 4-phenyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$) [DBUH][ALc]

Amplification experiment:

In order to verify the possibility of industrial application of catalyst [DBUH][MAc] in catalyzing the synthesis of five-member cyclic carbonates from epoxides and CO_2, we carried out scale-up experiments with 100 g oxidized styrene as epoxy substrate under optimal reaction conditions. As shown in Figure S45, 23% SC nuclear magnetic yield was obtained with [DBUH][MAc] as catalyst at laboratory scale. Therefore, it is not suitable for industrialization.

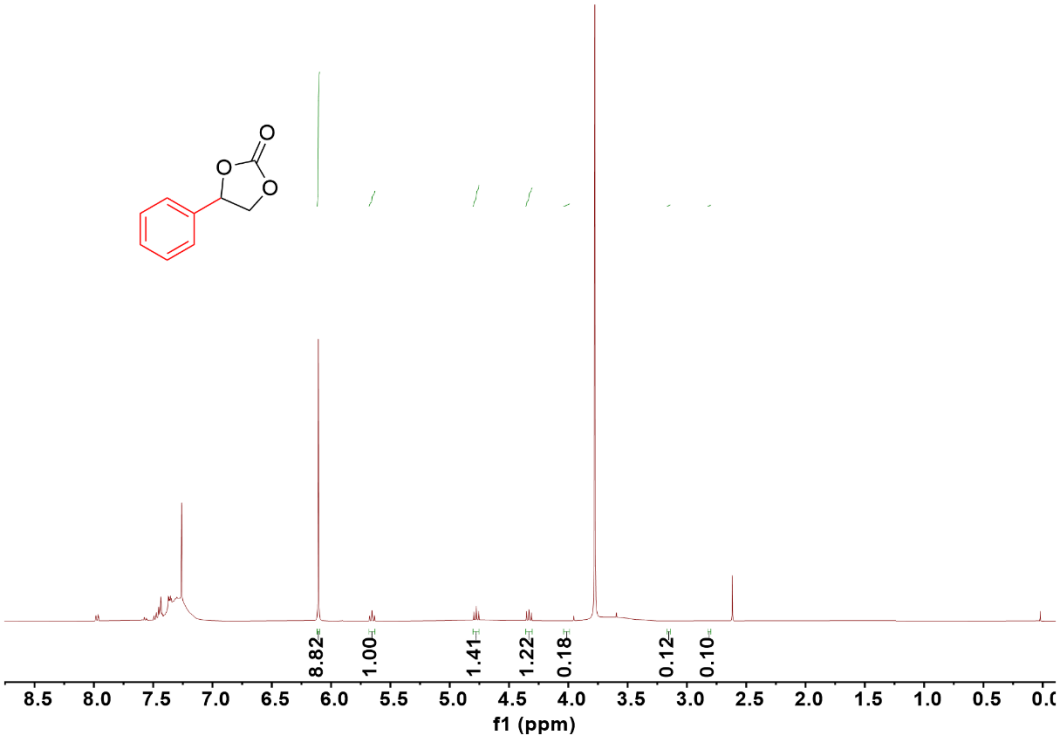

Figure S45.^{1}H NMR Spectrum of 4-phenyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$) [DBUH][MAc]