

Electronic Supplementary Information (ESI)

An all-aqueous and phosphine-free integrated amine-assisted CO₂ capture and catalytic conversion to formic acid

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I. Materials and methods

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on Bruker AVANCE III 400 500 and 700 MHz NMR spectrometers at 25 °C unless mentioned otherwise. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal reference as applicable D_2O : $\delta = 4.79$ ppm for ^1H spectra; CD_3CN : 1.94 ppm for ^1H spectra. CO_2 (purity 99.999%) and H_2 (purity 99.999%) gases were purchased from INOX Air Products Pvt. Ltd. $[\text{Ir}]^{\text{imd}}$ was synthesized following a procedure reported earlier by our group. PEHA, TMG, DBU, DABCO, L-Lysine, MEA and PMDTA were purchased from commercial suppliers and used without further purification. Analytical grade THF, >99.9%, standard was obtained from Sigma Aldrich. Deuterated solvents were purchased from CIL (Cambridge Isotope Laboratory).

II. CO_2 capture by various amine solutions

In a 25 ml round-bottom flask, 1g amine was dissolved in 3 ml water. A CO_2 filled balloon was sequestered to the round-bottom flask using a take-off. The aqueous amine solution was stirred for 1 hour at room temperature. The amount of CO_2 captured was analysed by gravimetry.

1. PEHA with CO_2 in water

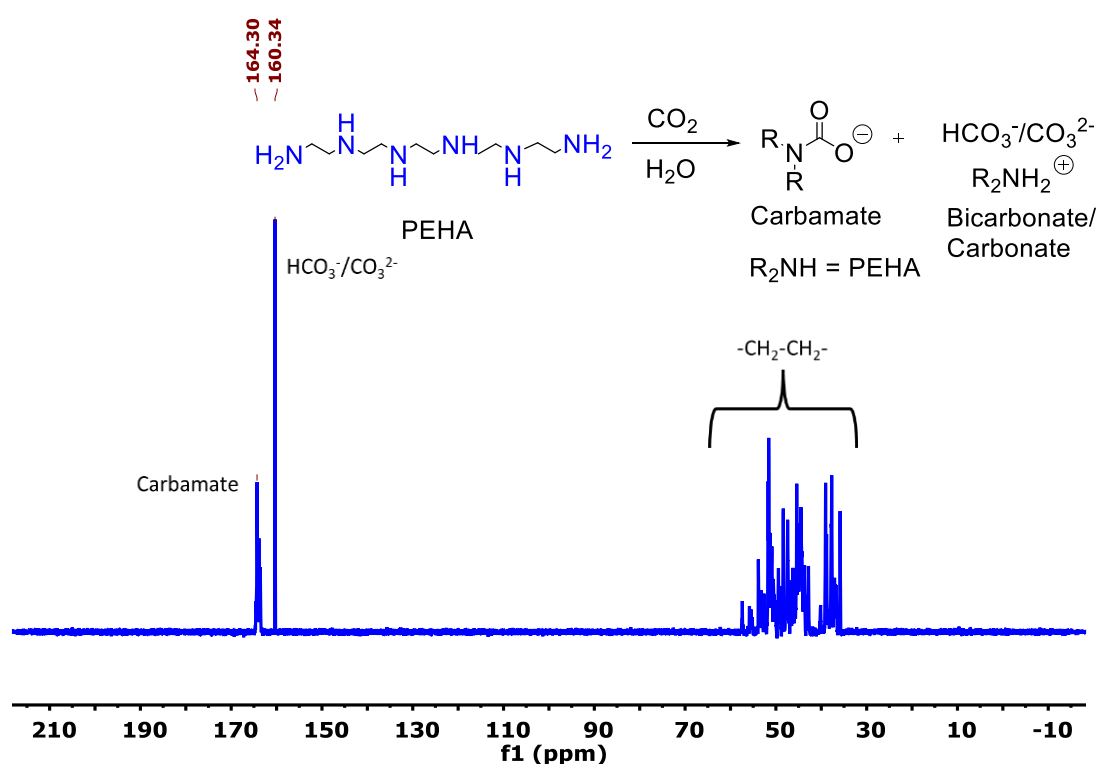


Figure. S1. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of PEHA- CO_2 - H_2O in D_2O .

2. TMG with CO₂ in water

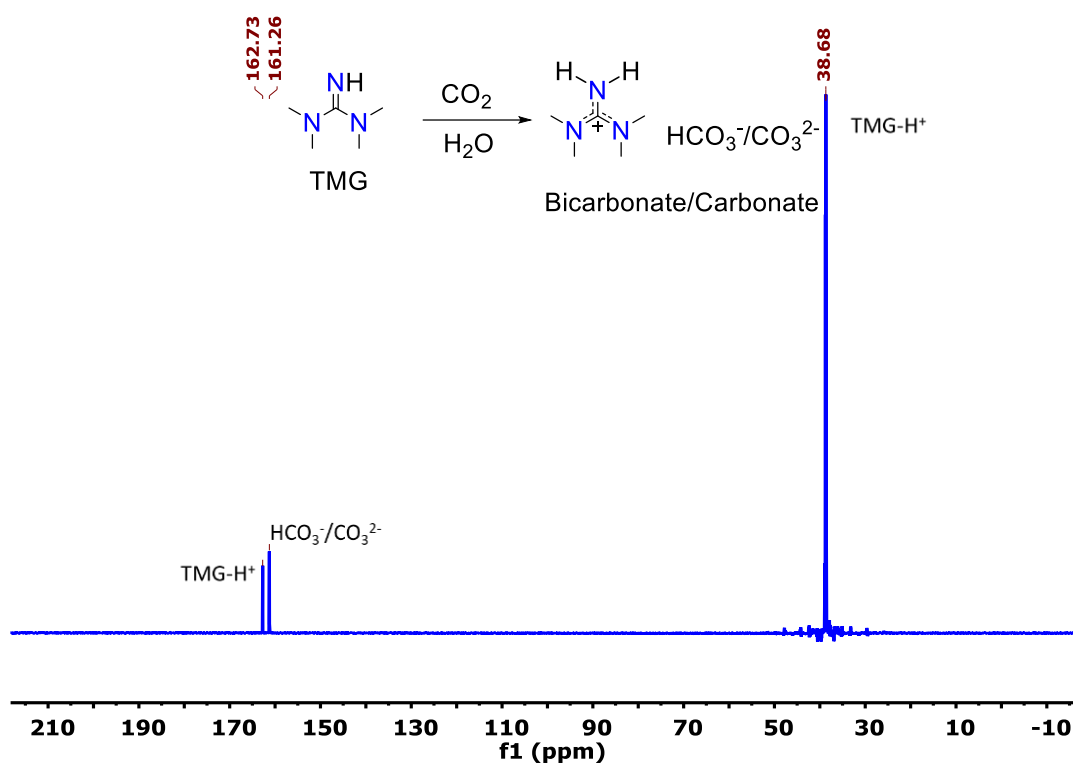


Figure. S2. ¹³C{¹H} NMR spectrum of TMG-CO₂-H₂O in D₂O.

3. MEA with CO₂ in water

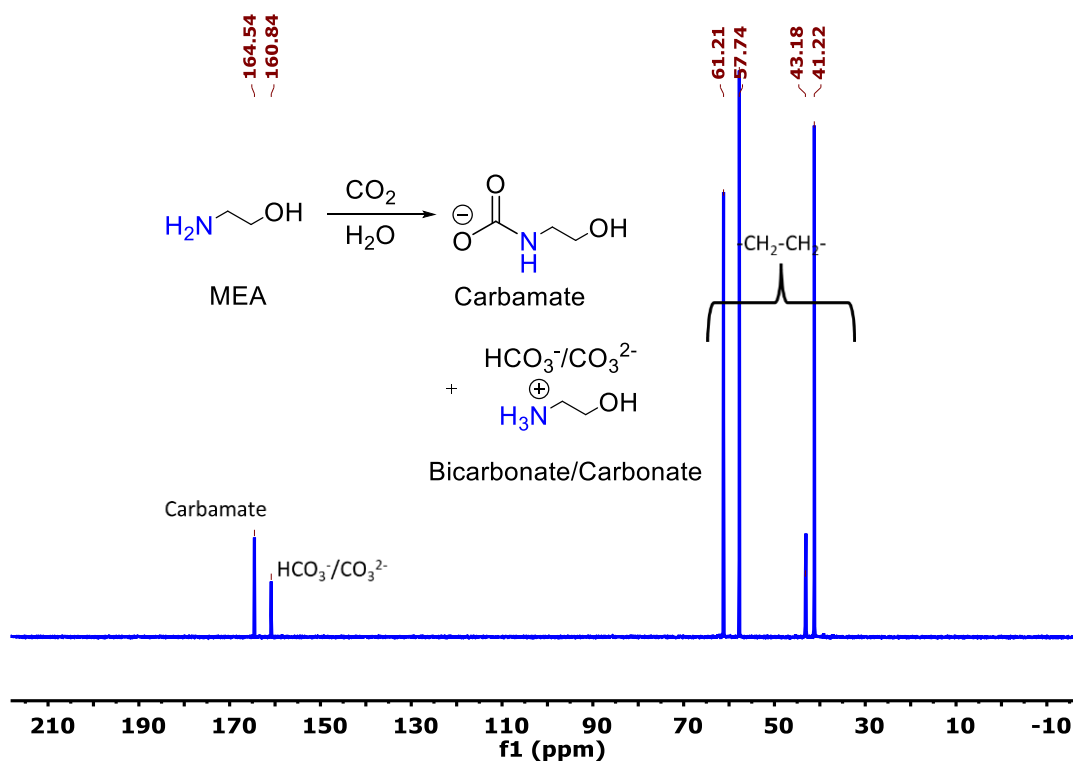


Figure. S3. ¹³C{¹H} NMR spectrum of MEA-CO₂-H₂O in D₂O.

4. L-Lysine with CO₂ in water

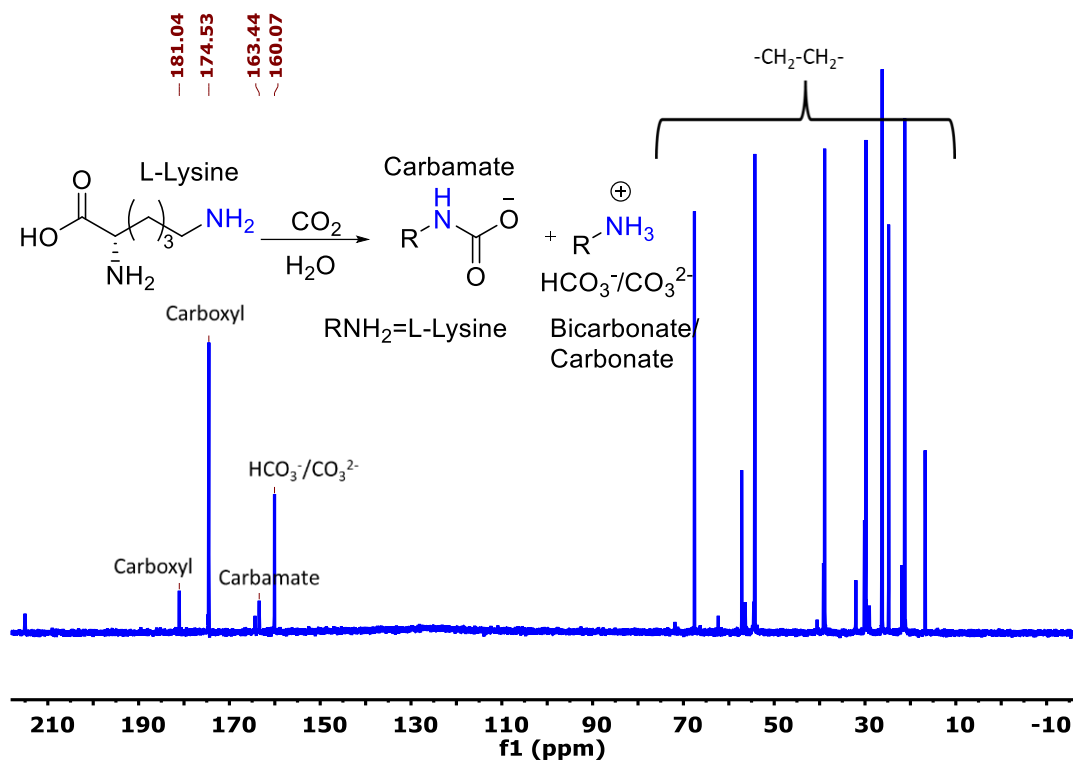


Figure. S4. ¹³C{¹H} NMR spectrum of L-lysine-CO₂-H₂O in D₂O.

5. DBU with CO₂ in water

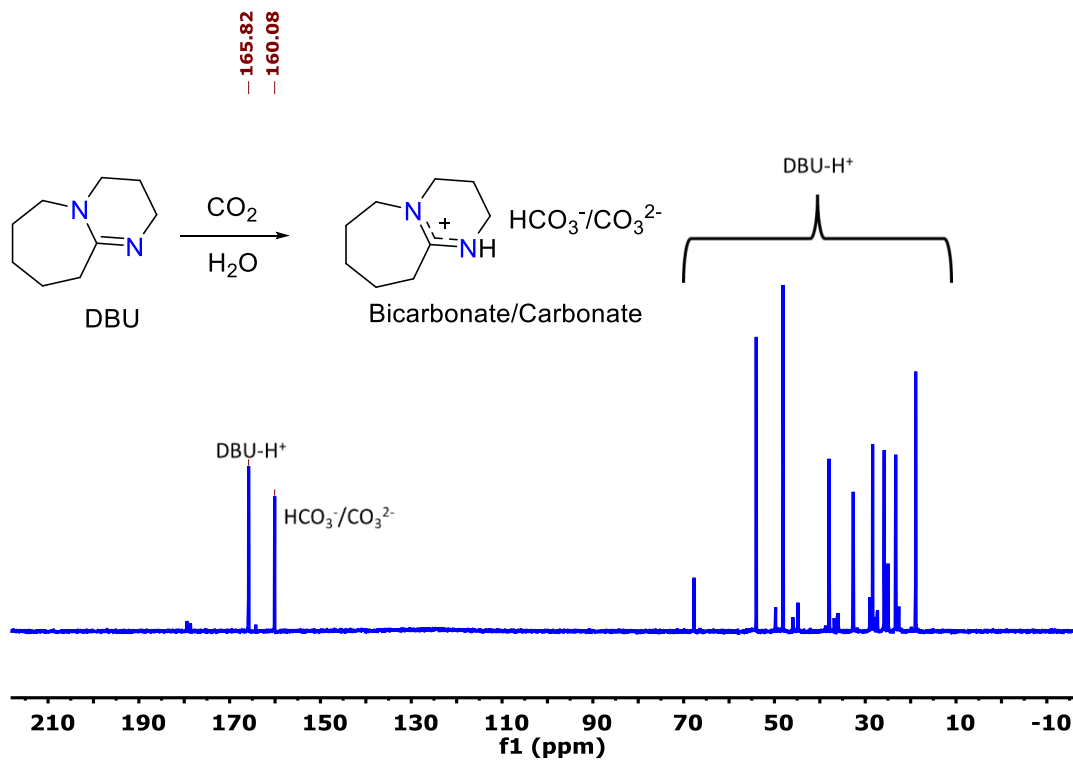


Figure. S5. ¹³C{¹H} NMR spectrum of DBU-CO₂-H₂O in D₂O.

6. DABCO with CO₂ in water

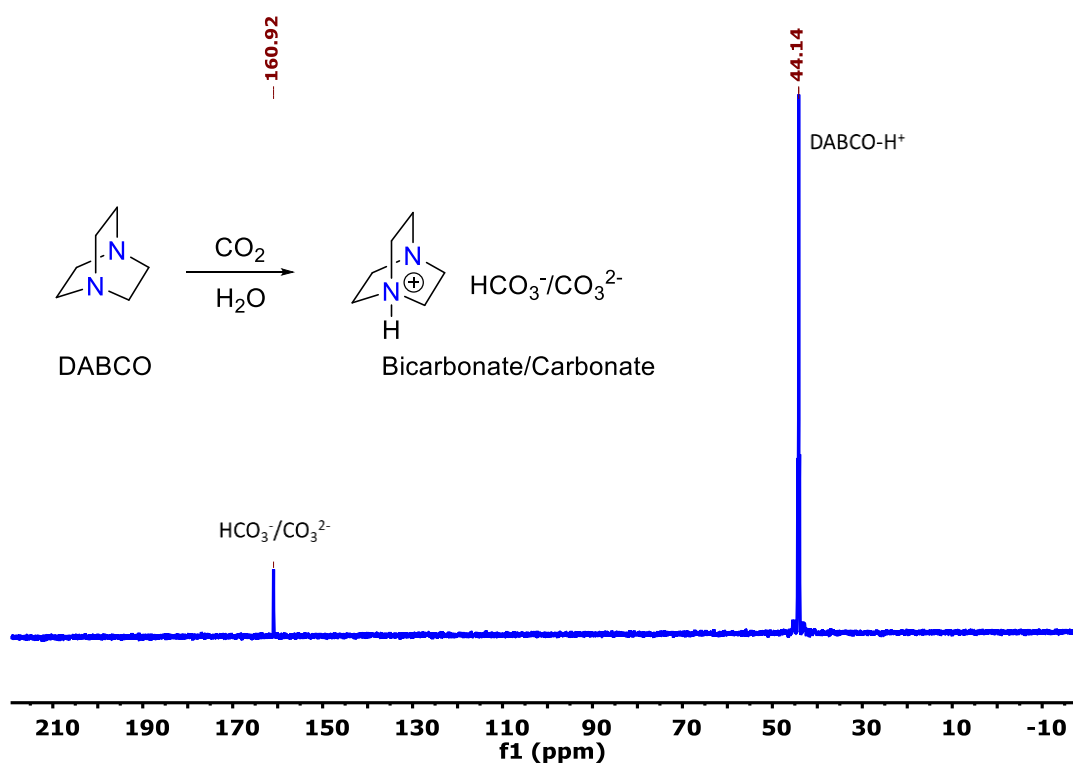


Figure. S6. ¹³C{¹H} NMR spectrum of DABCO-CO₂-H₂O in D₂O.

7. PMDTA with CO₂ in water

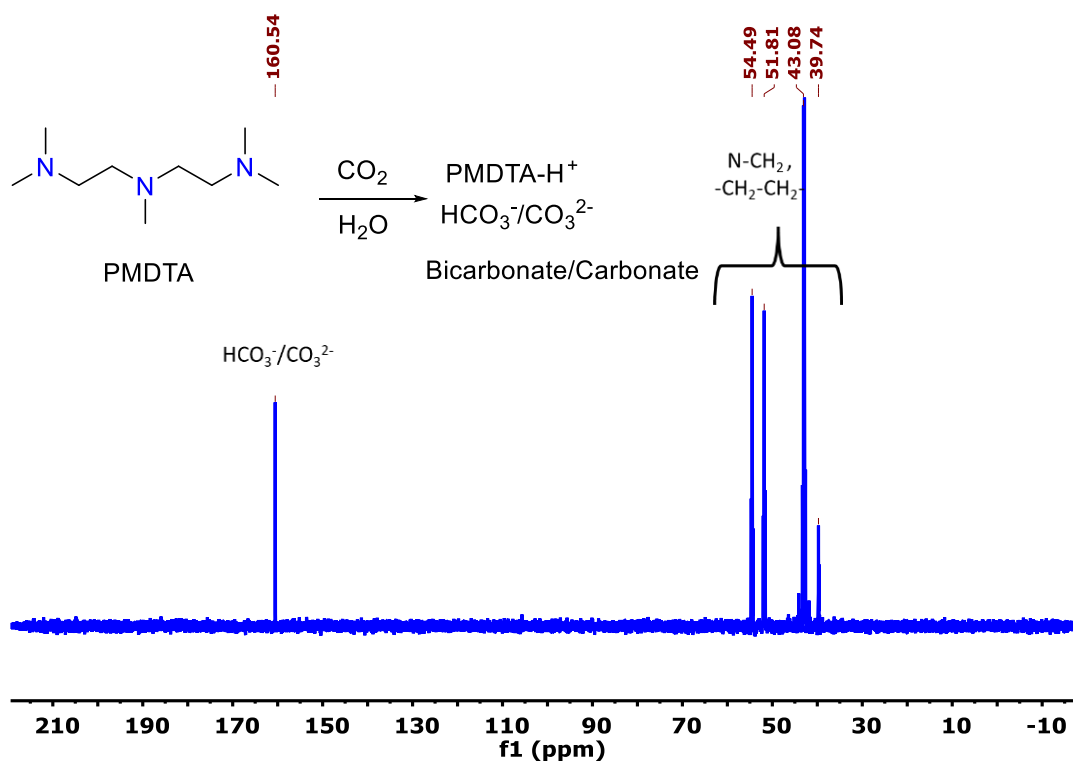


Figure. S7. ¹³C{¹H} NMR spectrum of PMDTA-CO₂-H₂O in D₂O.

III. Hydrogenation of captured CO₂ to formate

Upon completion of CO₂ capture in aqueous amine solutions, the solutions were subjected to hydrogenation. The CO₂ loaded solution, catalyst [Ir]^{imd} and water were added to the 25 ml pressure reactor. The reactor was then pressurized to the desired H₂ pressure (50 bar) and stirred at 120 °C for the desired reaction time. The reactor was then cooled to room temperature. The reaction vessel was then opened and a known amount of internal standard imidazole was added. The reaction mixture was then analysed by ¹H and ¹³C NMR spectroscopy using D₂O as the deuterated solvent. Yield of product was determined by ¹H NMR spectroscopy.

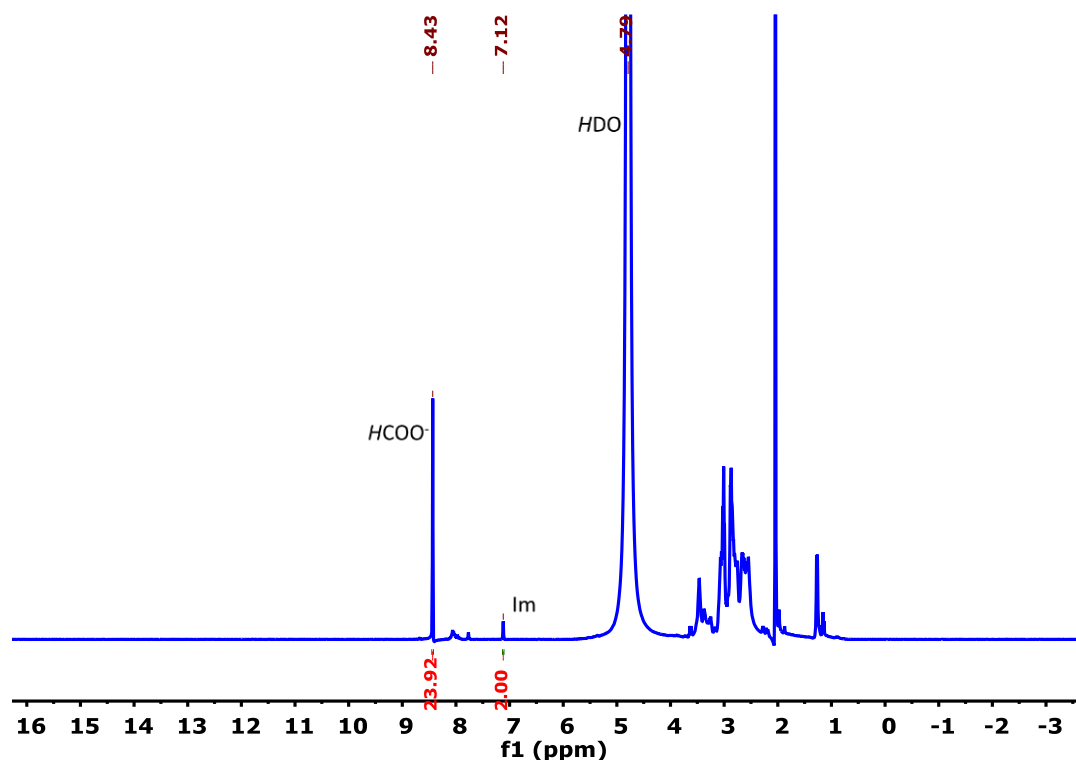


Figure S8. ¹H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO₂ captured product from PEHA in D₂O. Imidazole added as internal standard.

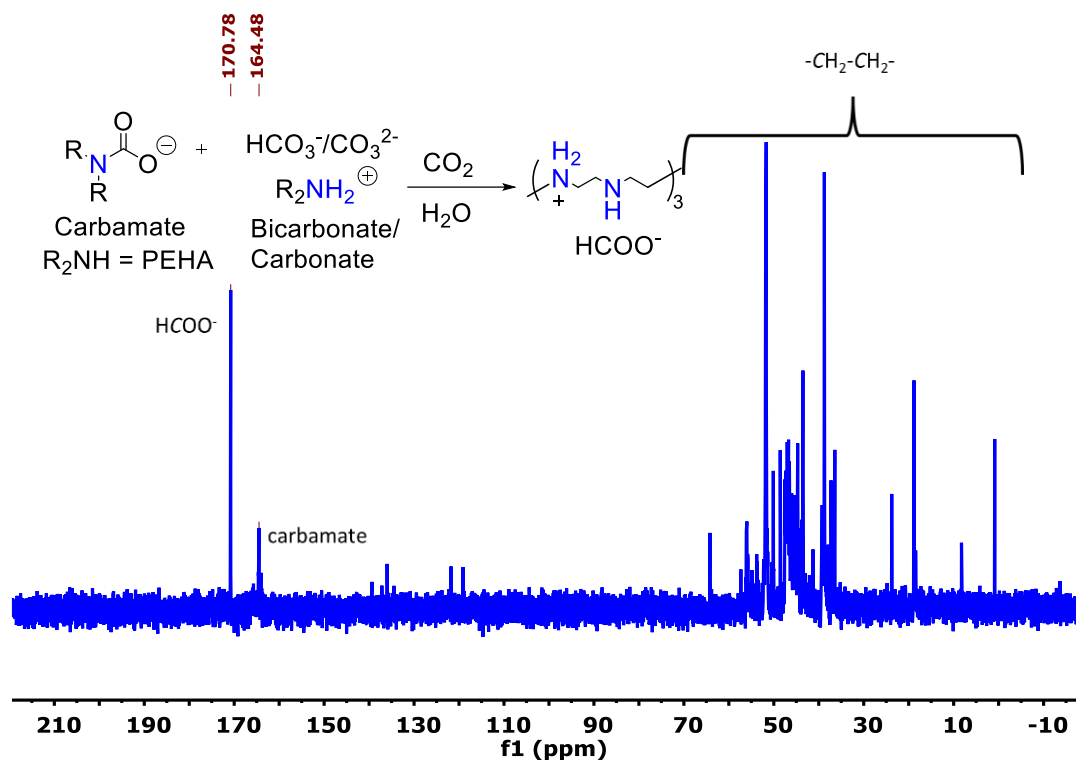


Figure. S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture obtained after the hydrogenation of CO₂ captured product from PEHA in D₂O.

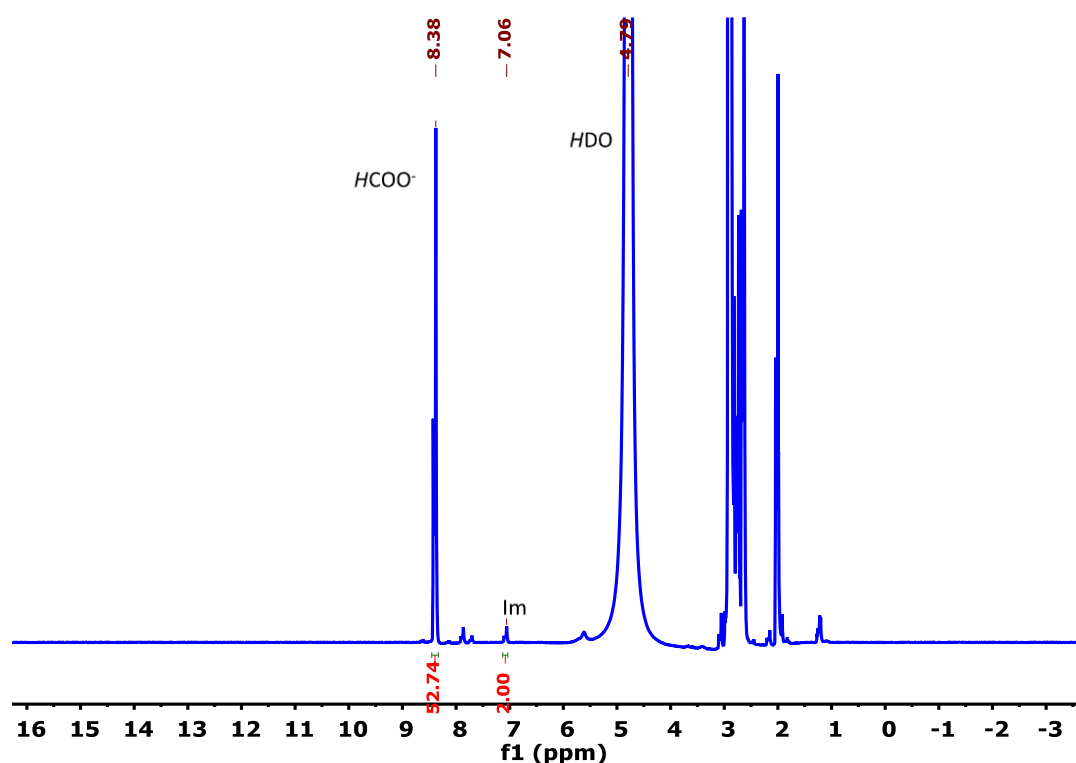


Figure. S10. ^1H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO₂ captured product from TMG in D₂O. Imidazole added as internal standard.

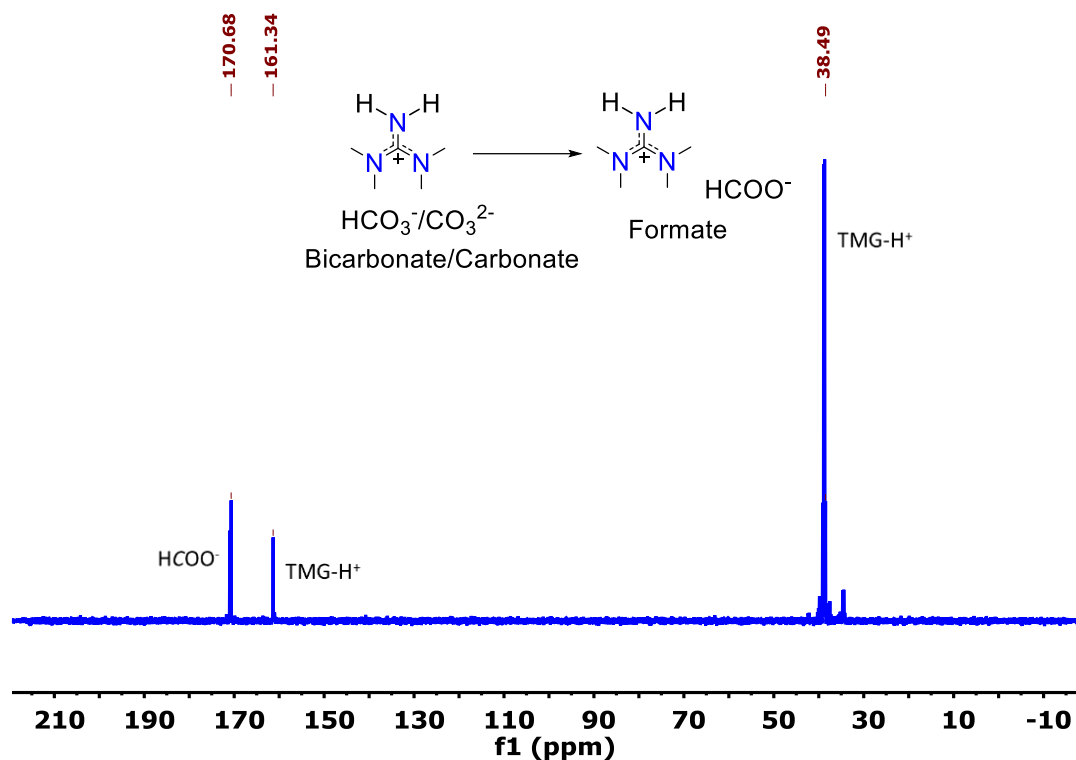


Figure. S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 captured product from TMG in D_2O .

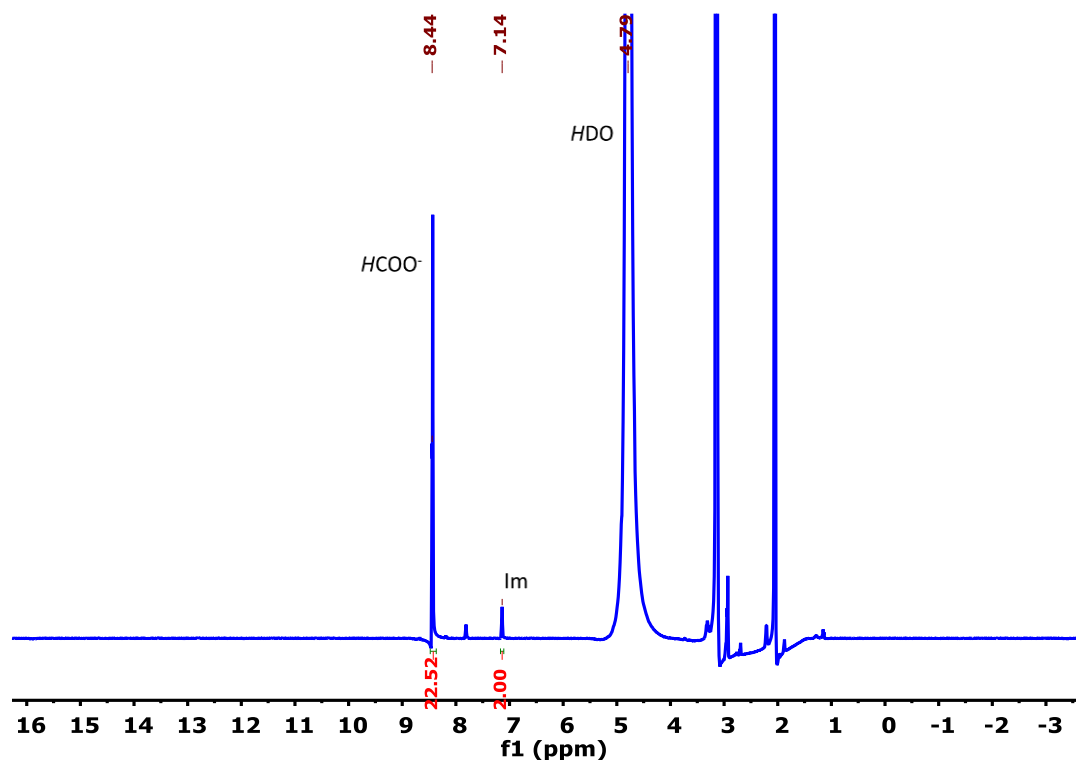


Figure. S12. ^1H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 captured product from DABCO in D_2O . Imidazole added as internal standard.

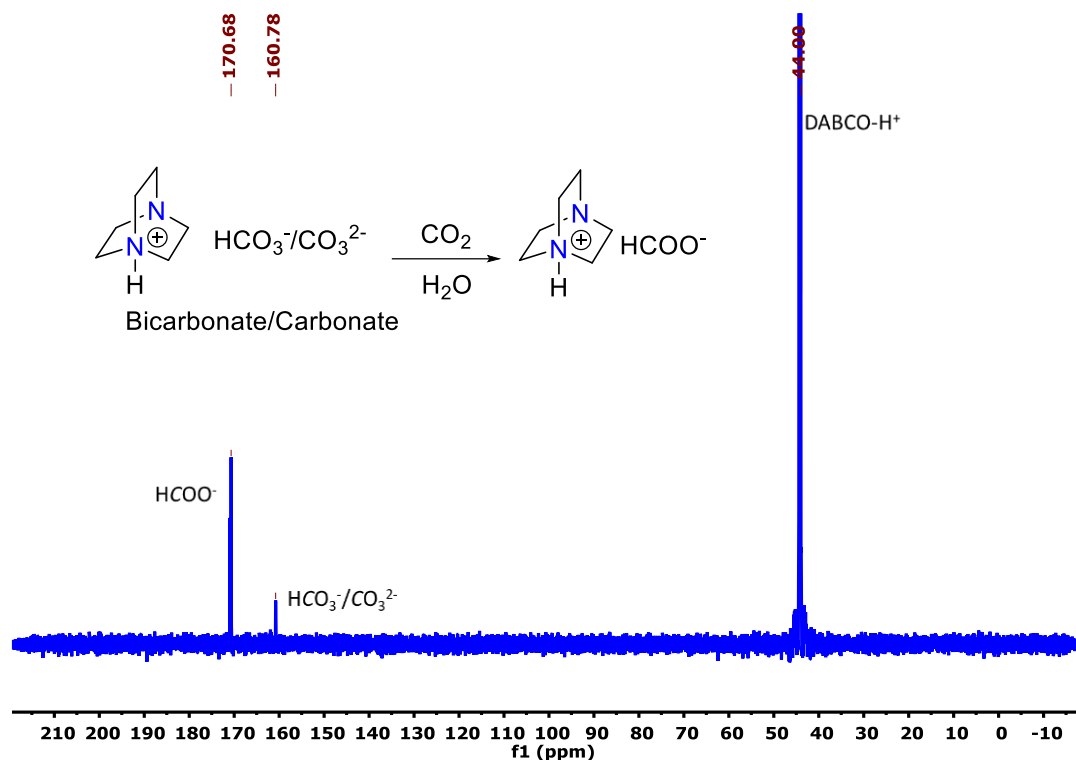


Figure. S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 captured product from DABCO in D_2O .

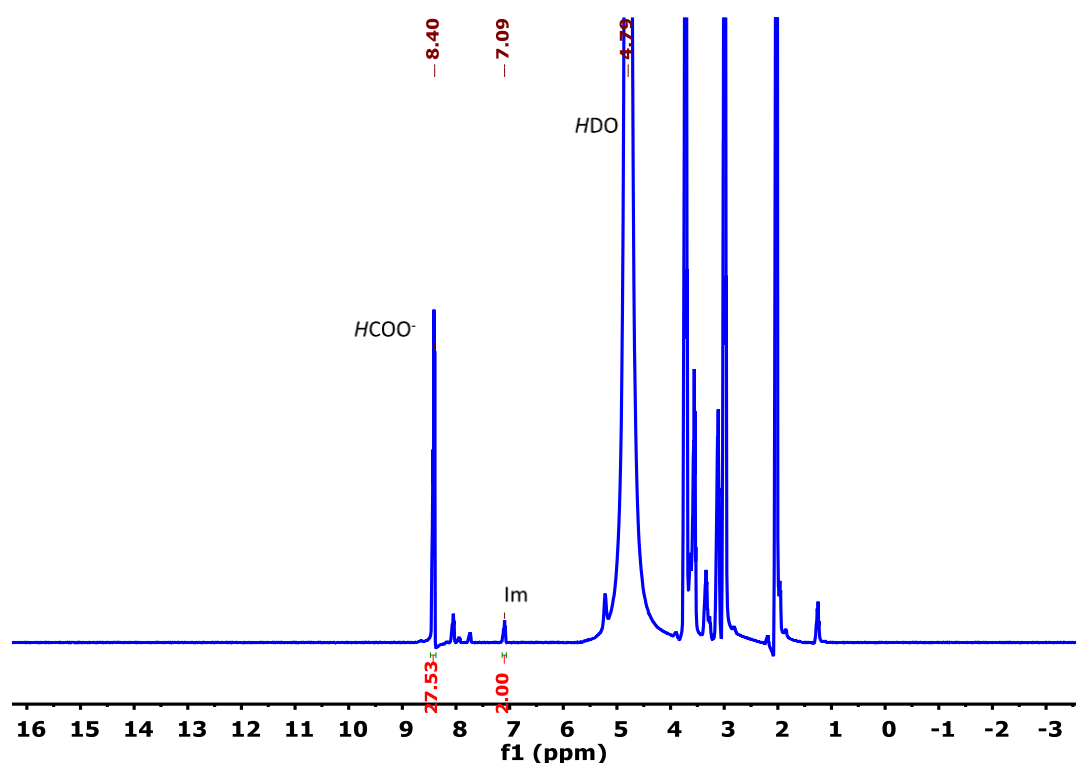


Figure. S14. ^1H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 captured product from MEA in D_2O . Imidazole added as internal standard.

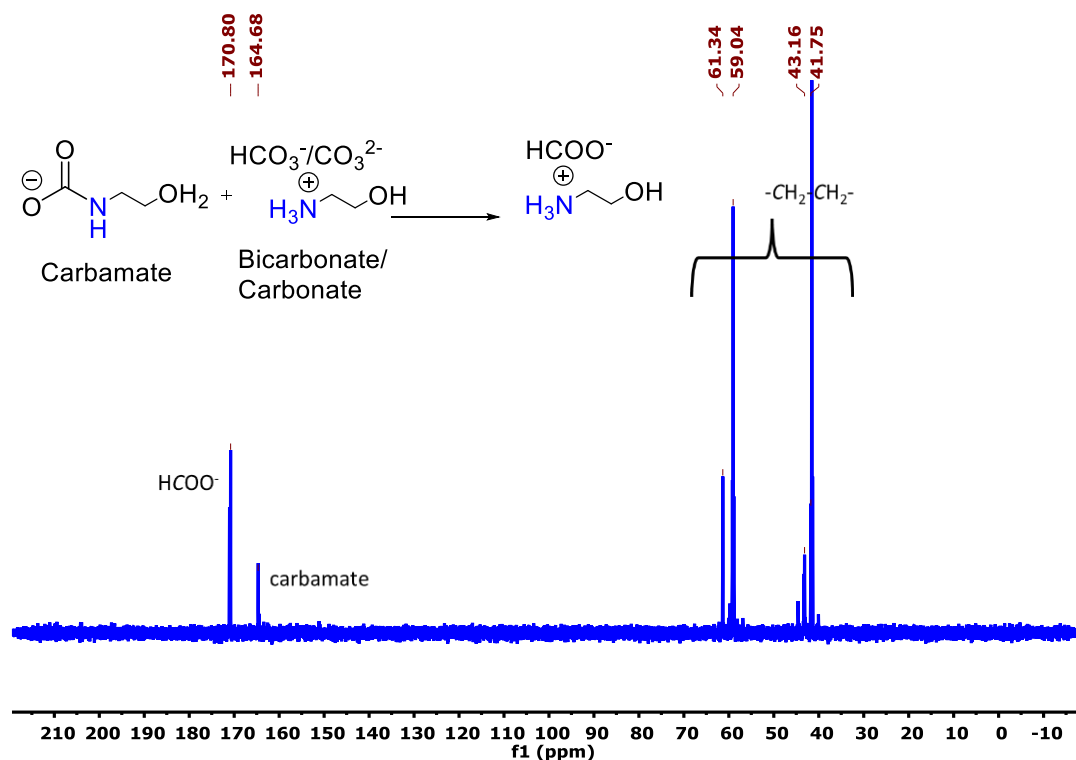


Figure. S15. ¹³C{¹H} NMR spectrum of the reaction mixture obtained after the hydrogenation of CO₂ captured product from MEA in D₂O.

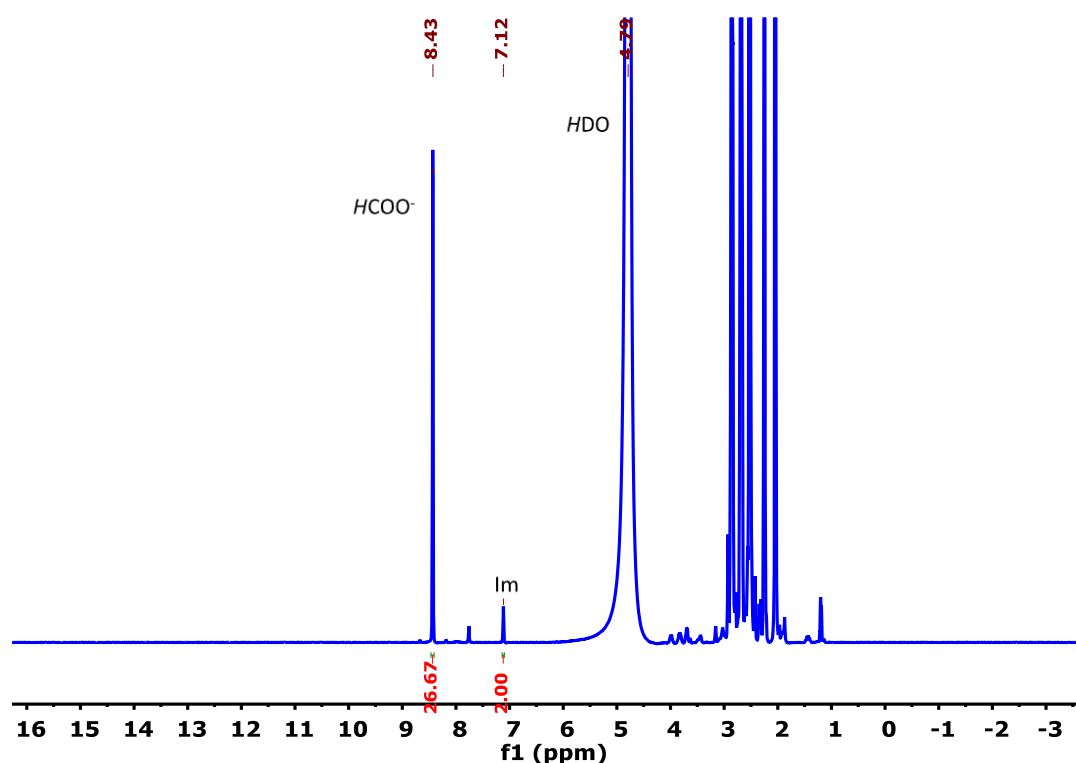


Figure. S16. ¹H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO₂ captured product from PMDTA in D₂O. Imidazole added as internal standard.

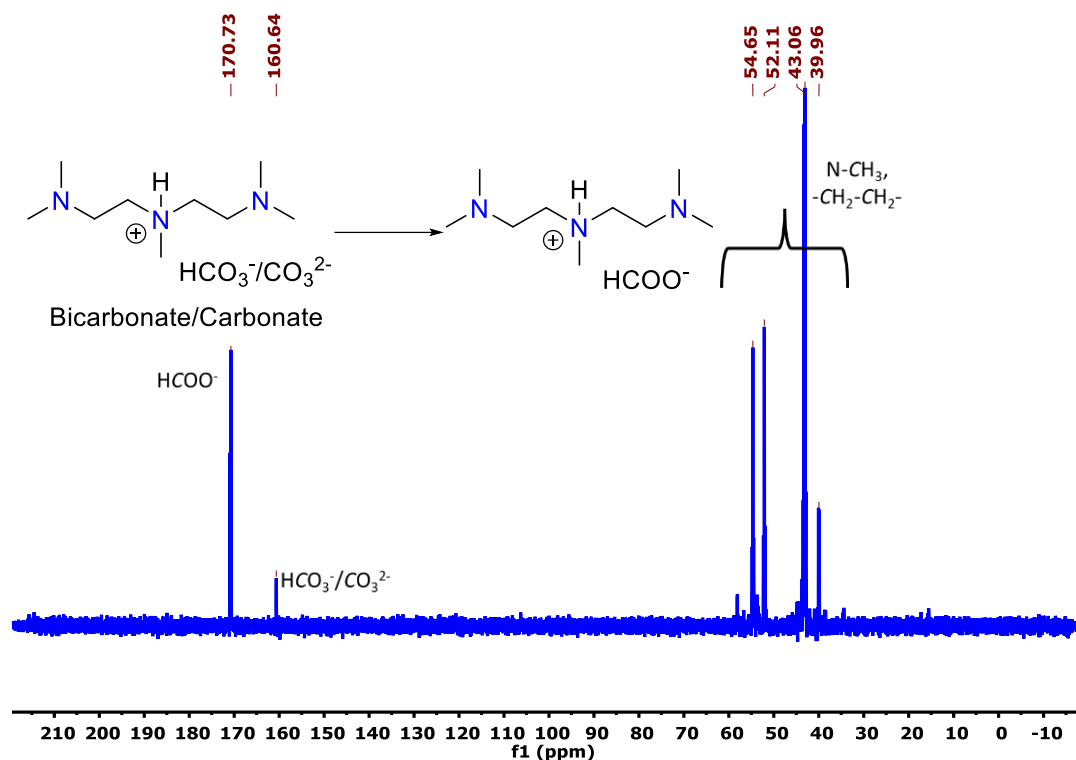


Figure. S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 captured product from PMDTA in D_2O .

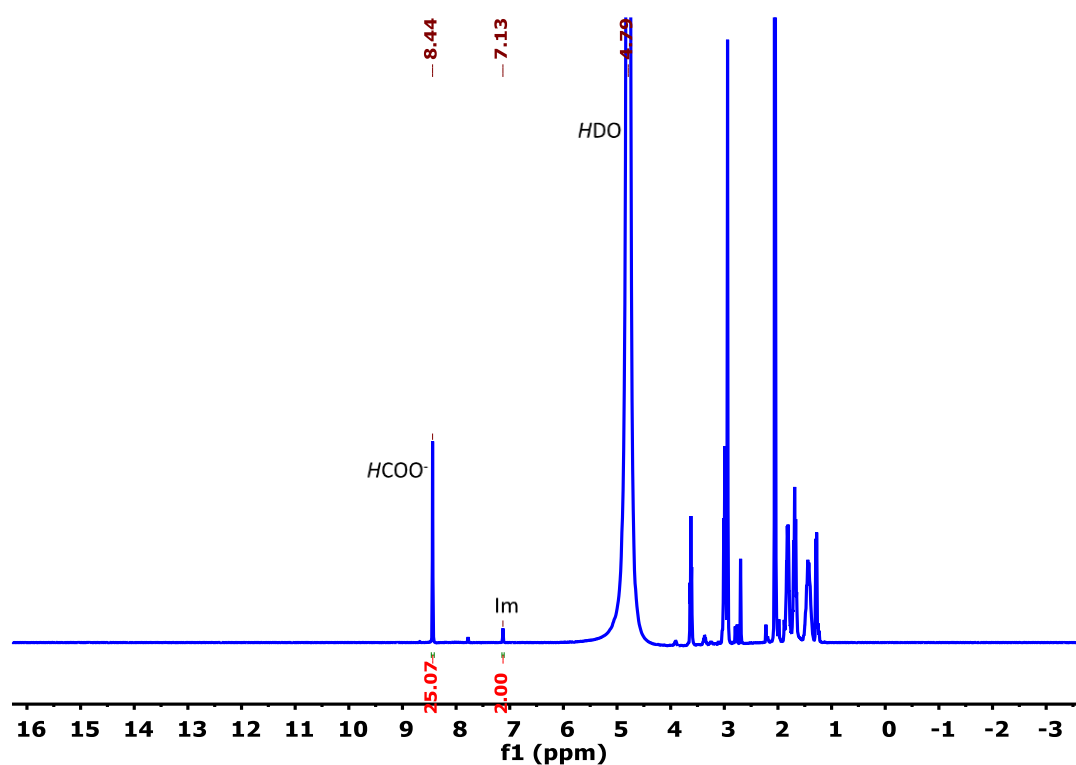


Figure. S18. ^1H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 captured product from L-Lysine in D_2O . Imidazole added as internal standard.

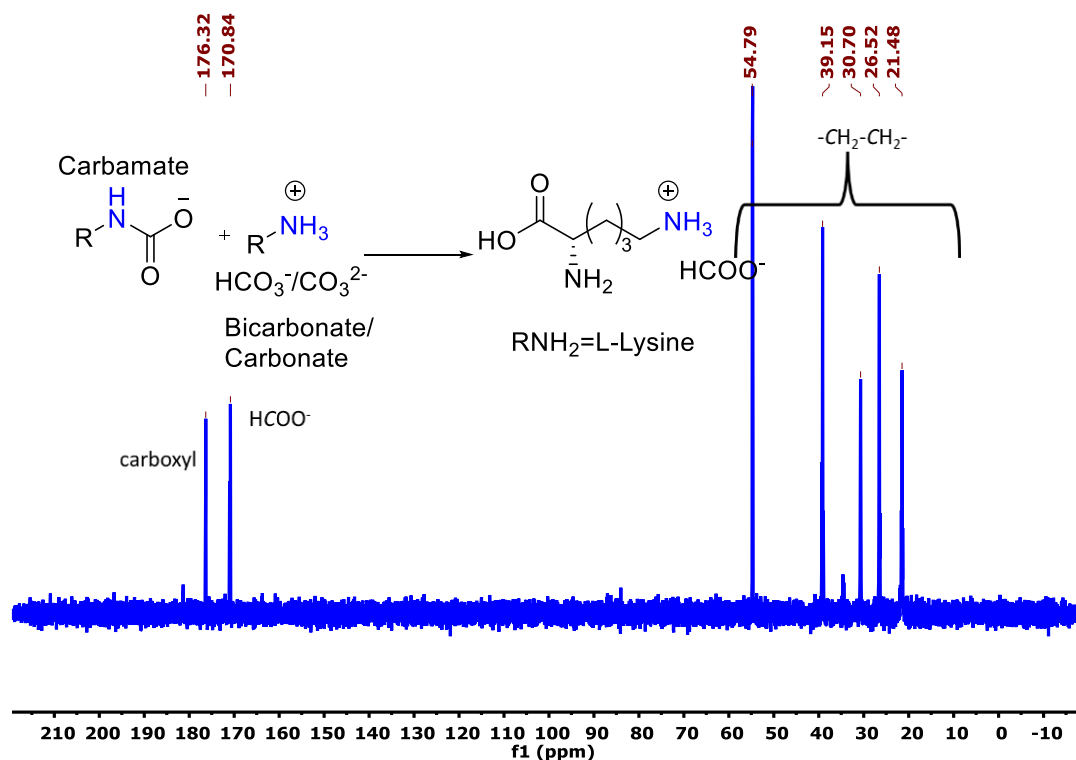


Figure. S19. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 captured product from L-Lysine in D_2O .

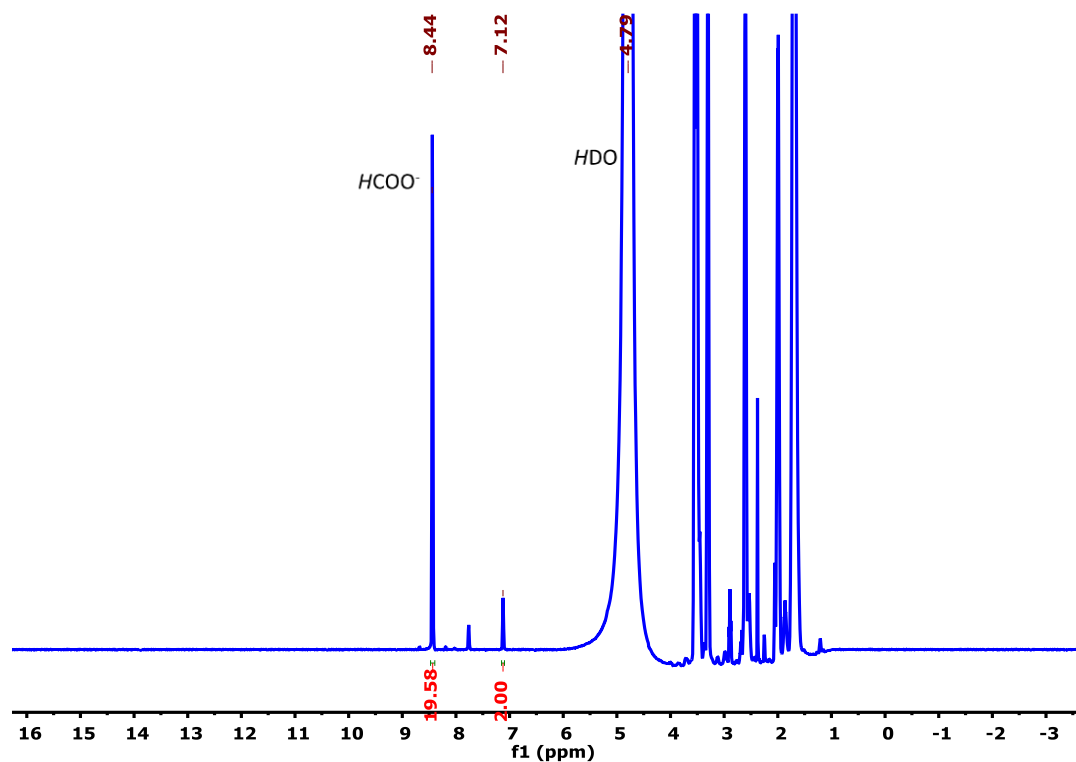


Figure. S20. ^1H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 captured product from DBU in D_2O . Imidazole added as internal standard.

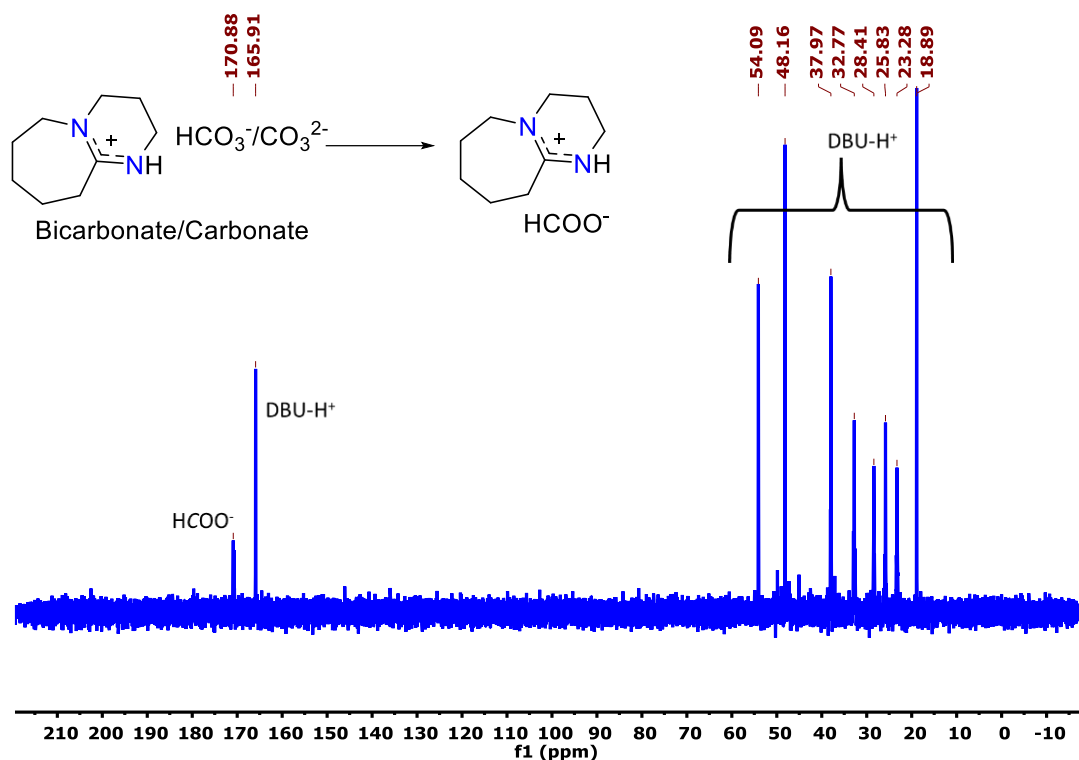


Figure. S21. ¹³C{¹H} NMR spectrum of the reaction mixture obtained after the hydrogenation of CO₂ captured product from DBU in D₂O.

IV. In-situ capture and conversion of CO₂ to formate

Catalyst [Ir]^{imd}, TMG and water were added to the 25 ml pressure reactor. The reactor was then pressurized to the desired CO₂/H₂ pressure and stirred at 120 °C for the desired reaction time. The reactor was then cooled to room temperature. The reaction vessel was then opened and a known amount of internal standard imidazole was added. The reaction mixture was then analysed by ¹H and ¹³C NMR spectroscopy using D₂O as the deuterated solvent. Yield of product was determined by ¹H NMR spectroscopy.

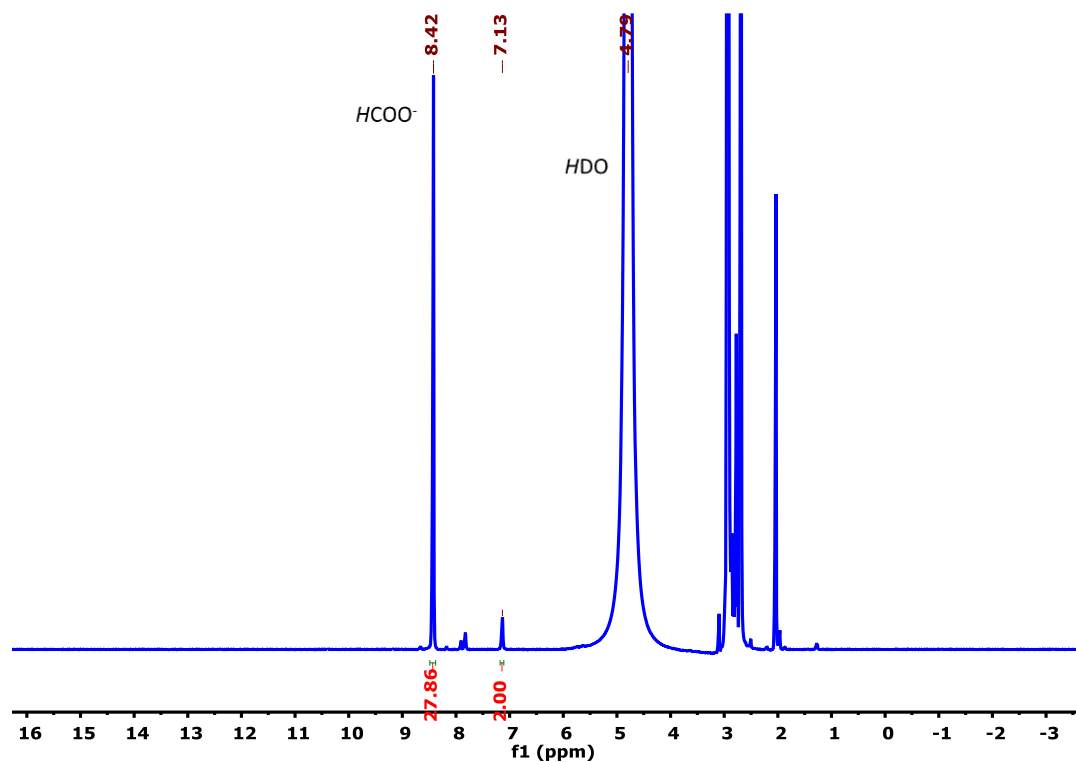


Figure. S22. ^1H NMR spectrum of the reaction mixture obtained after the in-situ hydrogenation of CO_2 using TMG in D_2O . Imidazole added as internal standard.

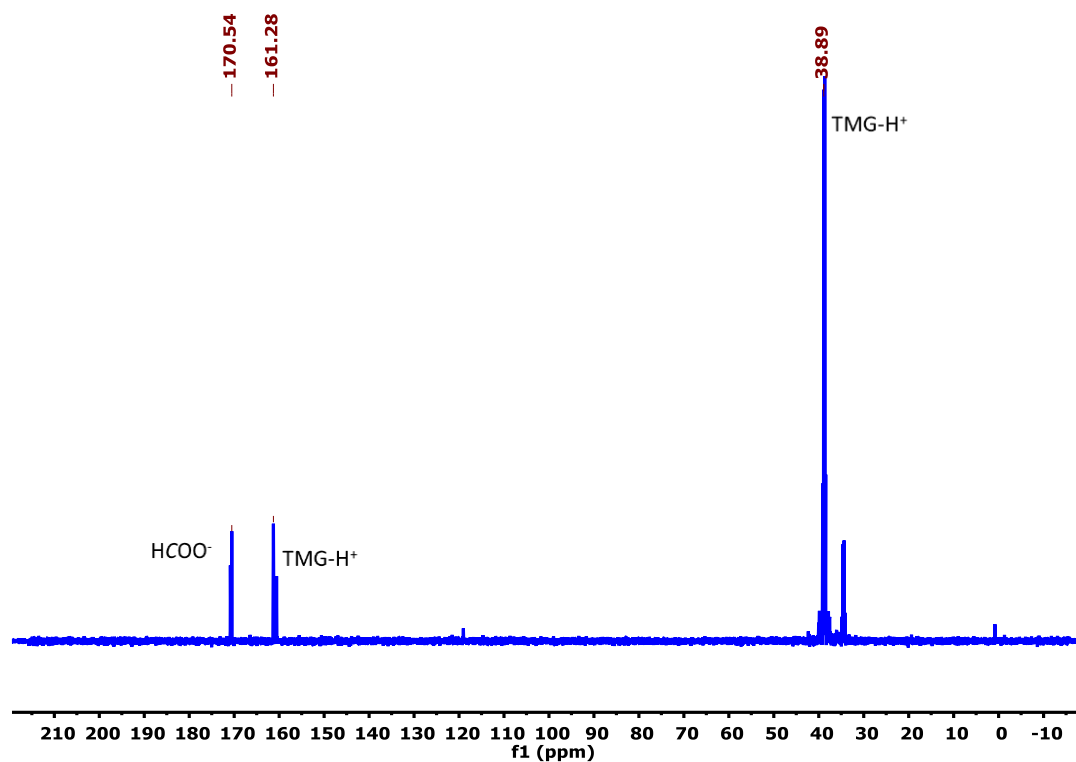


Figure. S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture obtained after the in-situ hydrogenation of CO_2 using TMG in D_2O .

V. CO₂ capture from atmospheric air and catalytic conversion to formate

TMG (0.9 g, 7.9 mmol) was dissolved in water (8 mL) in a 25 mL Schlenk tube. 50 mL/min of ambient air was bubbled through the Schlenk tube using a needle for 72 h. THF was added as a standard to the solution, and the mixture was analyzed by ¹³C NMR with decoupled-NOE, relaxation delay = 25s (rd > 25 s did not change the integration), pulse angle = 45°, scans = 1000 and acquisition time = 1.36 s.

Upon completion of CO₂ capture from air, the solution was subjected to the catalytic hydrogenation protocol. The CO₂ loaded solution, catalyst [Ir]^{imd} and water were added to the 25 mL pressure reactor. The reactor was then pressurized to the desired H₂ pressure (50 bar) and stirred at 120 °C for the desired reaction time. The reactor was then cooled to room temperature. The reaction vessel was then opened and a known amount of internal standard imidazole was added. The reaction mixture was then analysed by ¹H and ¹³C NMR spectroscopy using D₂O as the deuterated solvent. Yield of formate product was determined by ¹H NMR spectroscopy.

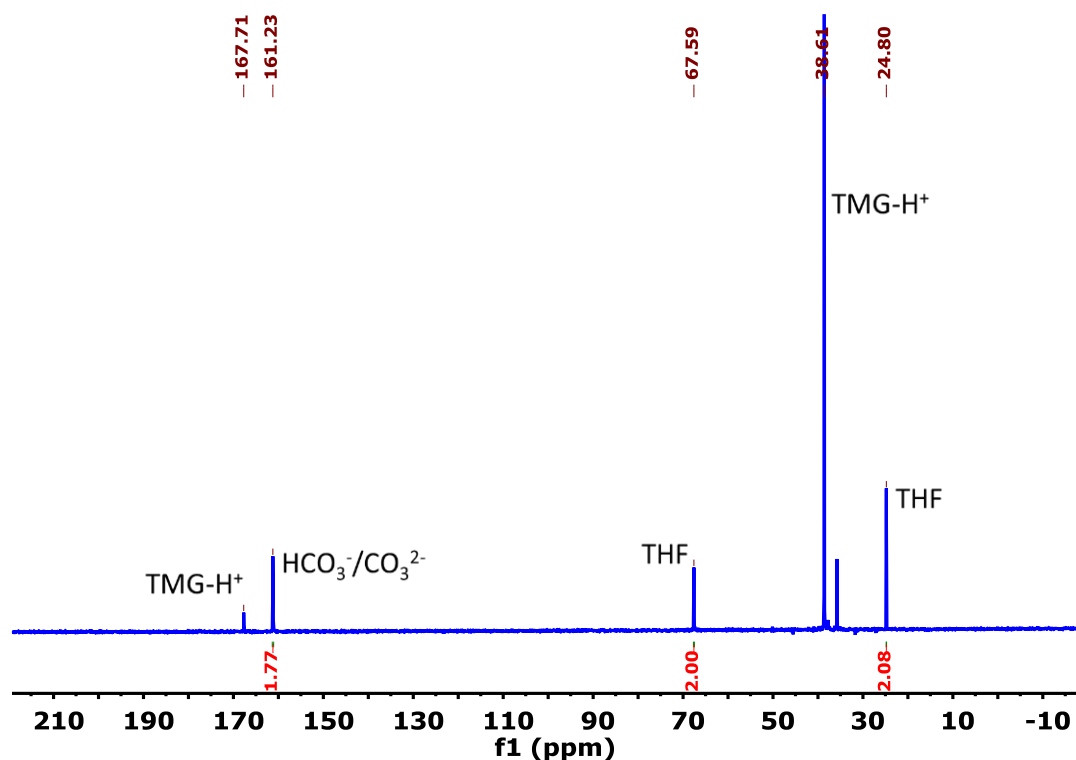


Figure. S24. ¹³C{¹H} NMR spectrum of CO₂ captured from air using aqueous TMG in D₂O.

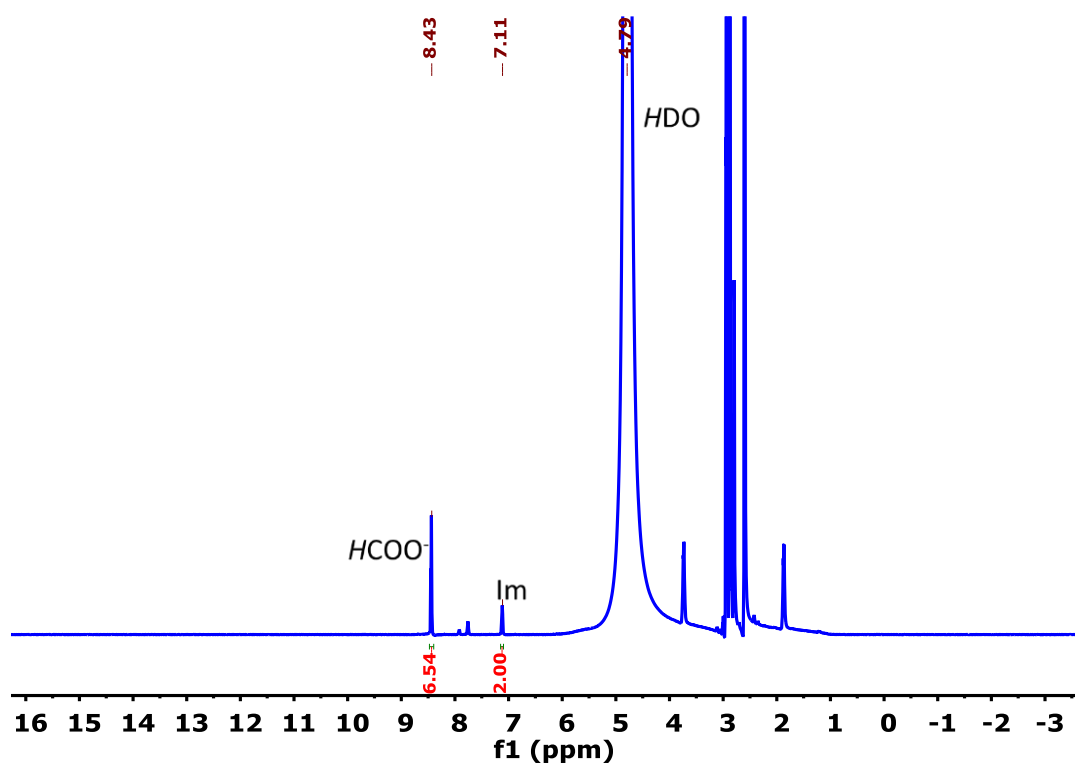


Figure. S25. ^1H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 captured product from air using TMG in D_2O . Imidazole added as internal standard.

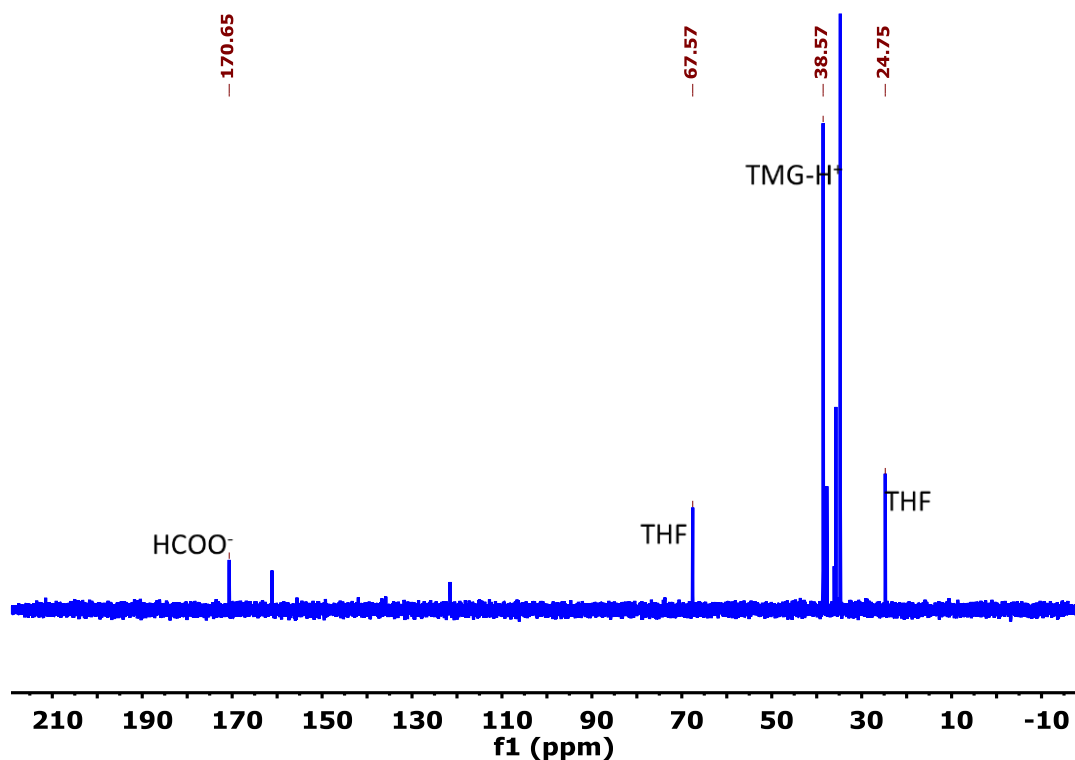


Figure. S26. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 captured product from air using TMG in D_2O .

VI. Characterization of catalyst and amine-adduct after the completion of the catalytic hydrogenation reaction (as described in Section III, using TMG as the amine)

1. Catalyst characterization

Upon completion of the catalytic hydrogenation reaction (as described in Section III, using TMG as the amine), 10 mL dichloromethane (DCM) was added to the aqueous reaction mixture. This was followed by a solvent extraction for the catalyst. The DCM layer was concentrated and subjected to ^1H NMR spectroscopy and mass spectrometry analysis. The analysis indicated that the catalyst backbone (the bound Cp^* and the benzimidazole-NHC ligands) remained intact.

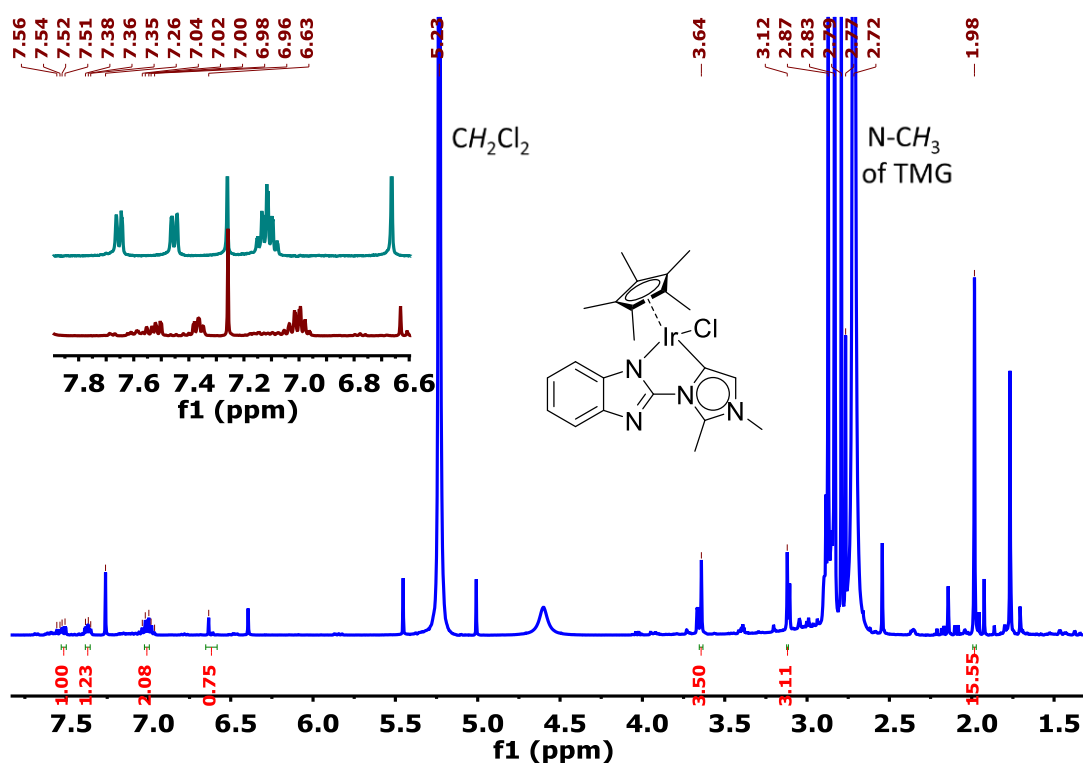


Figure. S27. ^1H NMR spectrum of the catalyst after completion of reaction in CDCl_3 . The inset shows the comparison of the aromatic region with the original catalyst.

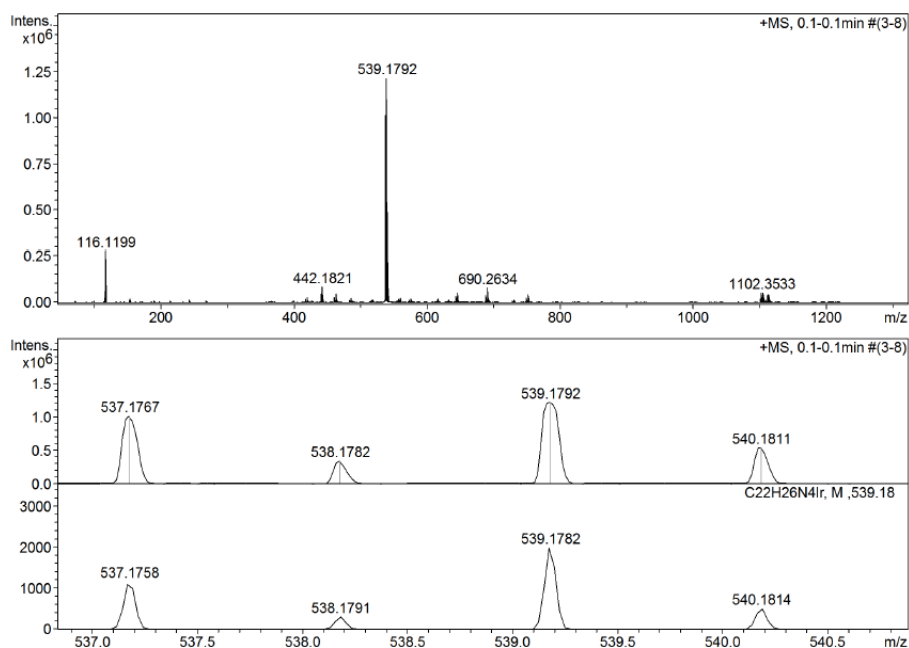


Figure. S28. ESI-MS (positive mode) spectrum of the catalyst after the completion of the reaction. HRMS (ESI, positive ion) $[M-Cl]^+ = 539.1792$ (calcd for $[C_{22}H_{26}N_4Ir]^+ = 539.1782$)

2. Amine-adduct characterization

The amine base TMG stabilized the formic acid product generated upon completion of the reaction by forming an acid-base adduct. This was confirmed through integration analysis of the corresponding peaks in the 1H NMR spectrum of the reaction mixture. An authentic equimolar mixture of HCOOH and TMG in water was also subjected to 1H NMR spectroscopy to support the analysis.

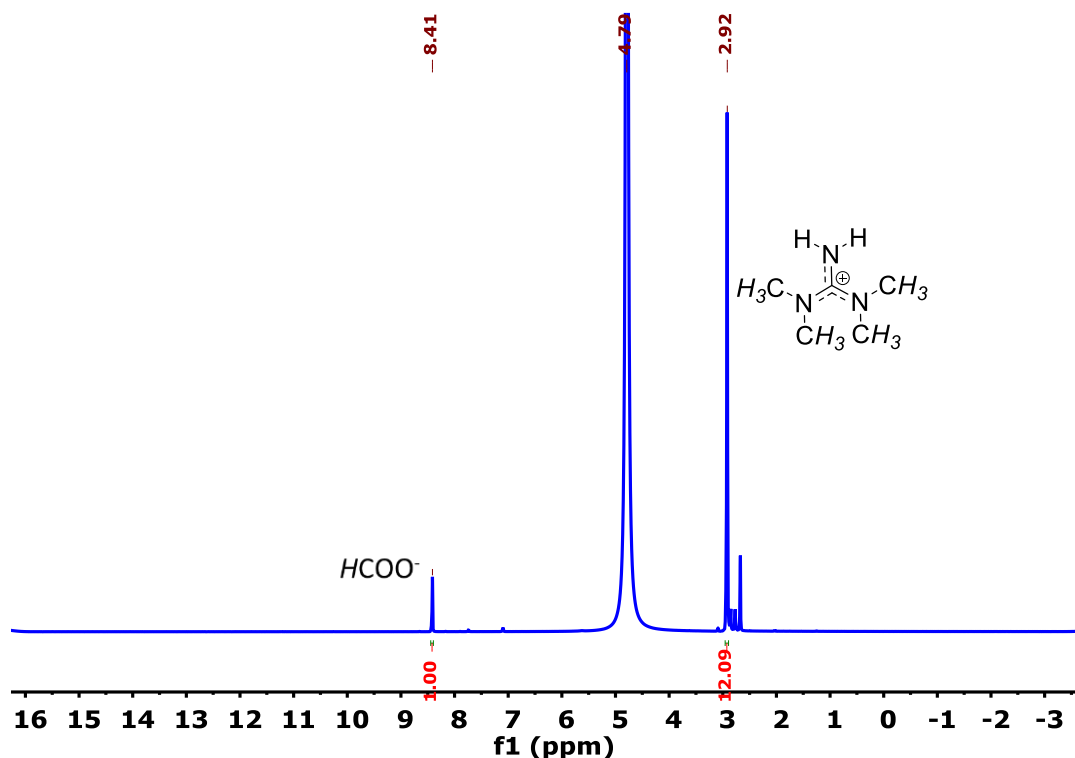


Figure. S29. 1H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 captured product from TMG in D_2O .

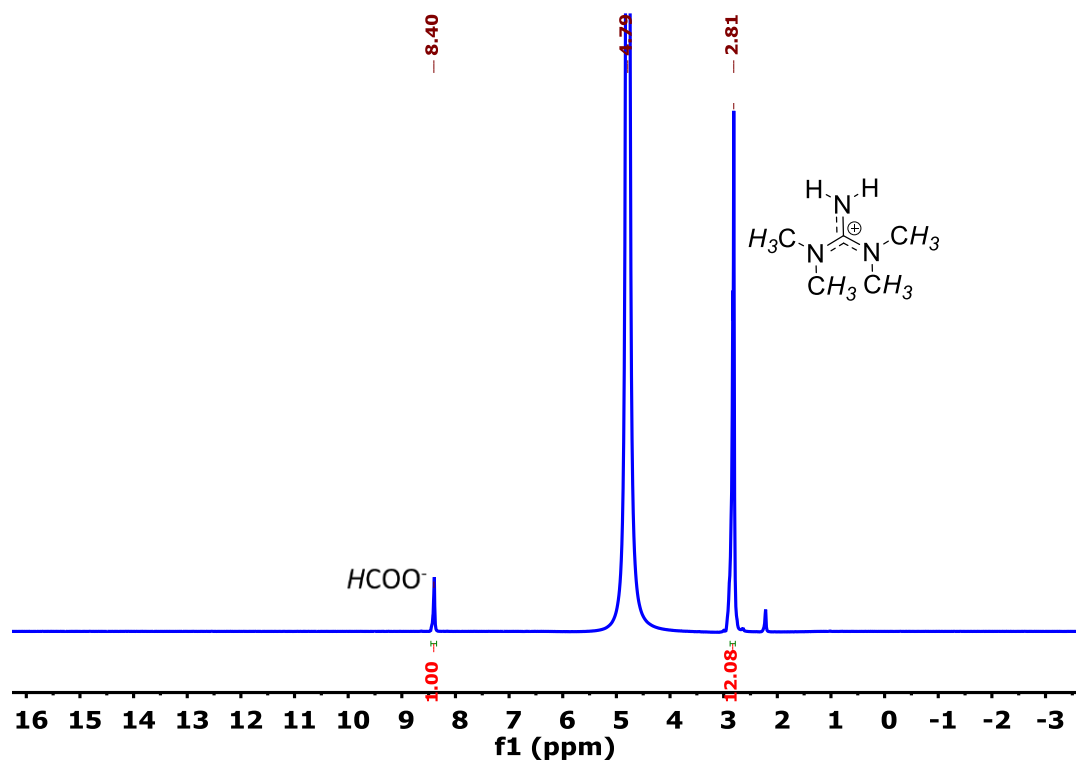


Figure. S30. ^1H NMR spectrum of a sample of authentic equimolar HCOOH and TMG in D_2O .

VII. An amine-free high-pressure CO_2 hydrogenation reaction

Catalyst $[\text{Ir}]^{\text{imd}}$ ($4.3 \mu\text{mol}$) and water (10 ml) were added to a 25 mL pressure reactor. The reactor was then pressurized to the desired CO_2/H_2 pressure (10 bar CO_2 : 40 bar H_2) and then the reaction mixture was stirred at $120 \text{ }^\circ\text{C}$ for 4 h. The reactor was then cooled to room temperature and was opened. A known amount of internal standard imidazole was added. The reaction mixture was then analysed by ^1H NMR spectroscopy using D_2O as the deuterated solvent. Formation of formate product was not observed.

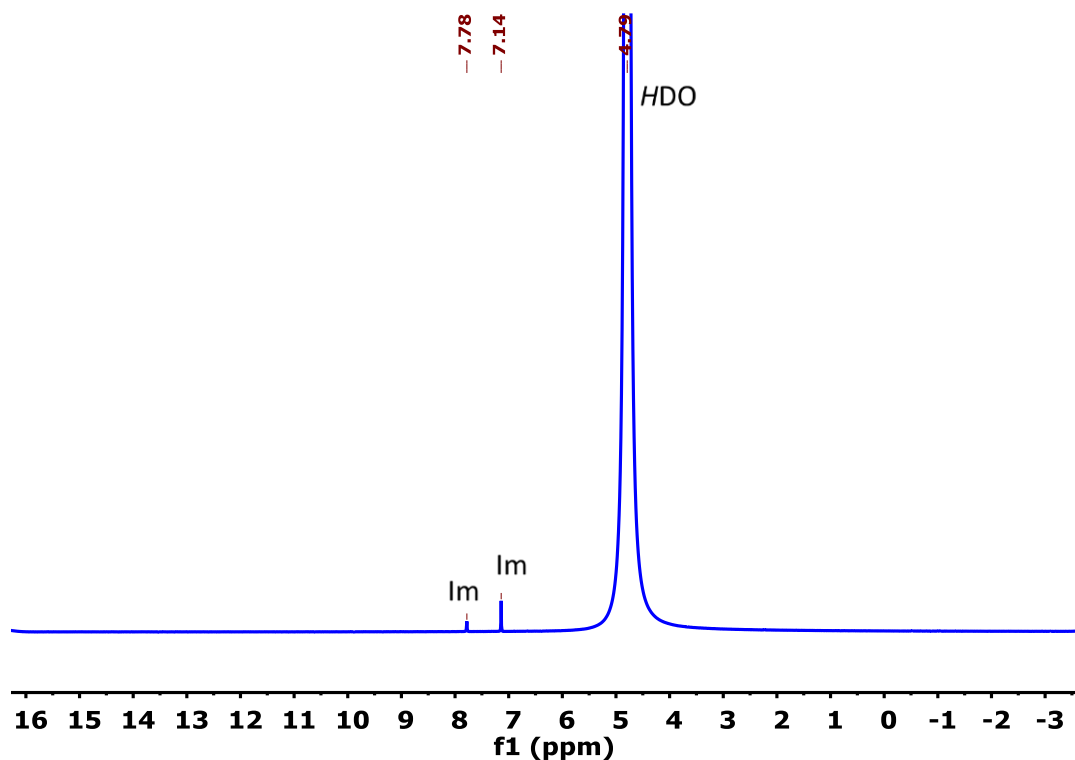


Figure. S31. ^1H NMR spectrum of the reaction mixture obtained after the in-situ hydrogenation of CO_2 in amine-free conditions in D_2O . Imidazole added as internal standard.

VIII. Plausible catalytic reaction mechanism

The plausible catalytic cycle for the present CO_2 -hydrogenation reaction is proposed (Fig. S32). After the halide dissociation from the catalyst $[\text{Ir}]^{\text{imd}}$ in water, the active species cleaves H_2 to generate Ir-H under the basic conditions (amine-water system). The proton (from H_2) might be abstracted by the basic medium. The Ir-H species then delivers its hydride ligand to the substrate present in the reaction mixture, to produce Ir-formato species, which dissociates formate stabilized as the amine-adduct and regenerates the active catalyst.

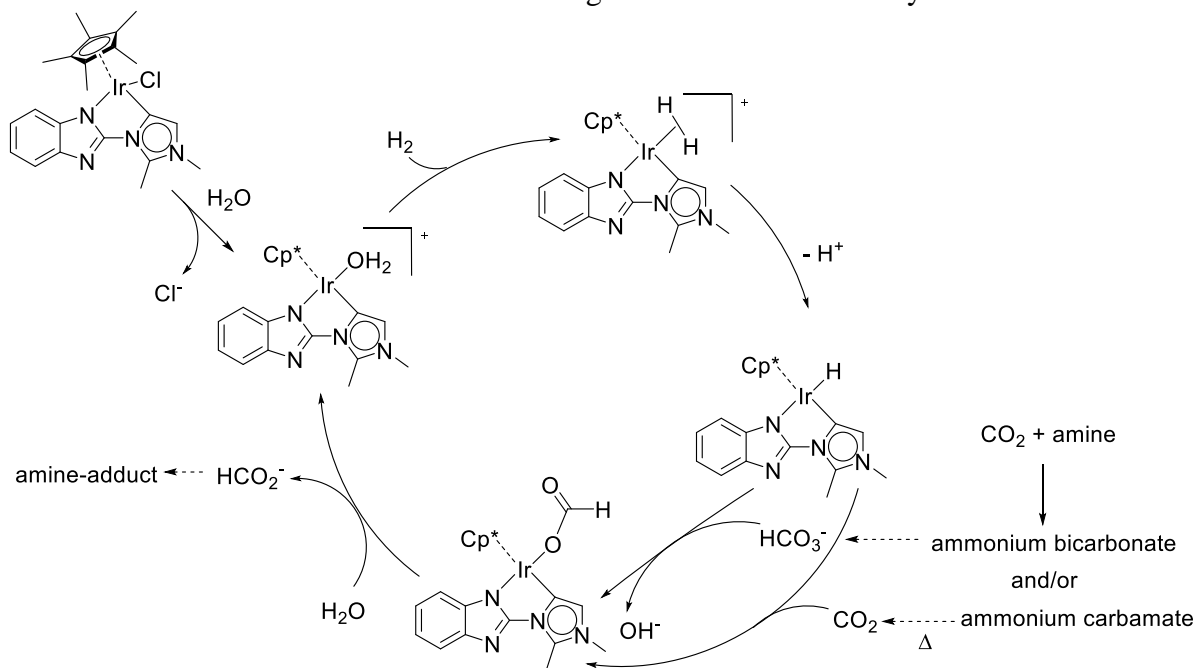


Figure. S32. Plausible catalytic cycle for the amine-assisted CO_2 -hydrogenation reaction with $[\text{Ir}]^{\text{imd}}$ catalyst.