

Supporting Information

Chromium Catalyzed Transfer Hydrogenation of CO₂ to Formate Using Isopropanol Under Ambient Pressure

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1. General procedure and materials

Complexes (**C-1** to **C-6**) were prepared using literature procedures.¹⁻³ All the manipulations were carried out using standard Schlenk and glove box techniques, unless otherwise stated. CO₂ cylinder was purchased from commercial sources and used without further purifications. Solvents were freshly distilled over suitable drying agents, and collected over 4 Å activated molecular sieves under a nitrogen atmosphere. Deuterated solvents were purchased from commercial sources and stored on 4 Å activated molecular sieves under a nitrogen atmosphere before use. The ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Bruker 500 MHz spectrometer chemical shifts reported in ppm relative to the residual deuterated solvent or the internal standard tetramethylsilane. FT-IR measurements were carried out on a Bruker Vertex, 70V PMA50 instrument. HRMS spectra were recorded using an Agilent 6500 Q-TOF spectrometer.

Caution: The reactions involve the gaseous 1 bar pressure of CO₂ and higher temperature. Hence specially designed thick walled Schlenk tubes equipped with teflon cap should be used.

2. General procedure for chromium catalyzed CO₂ transfer-hydrogenation

(a) First, a 25 ml Schlenk tube was charged with 300 µl of THF containing the required amount of catalyst (**C-1–C-6**) taken from the freshly prepared stock solution of the catalyst in THF (Table 1). Subsequently, 20 mmol NaOH solution in 3 ml distilled water was added to it. Then 2 ml isopropanol was added as hydrogen source (Table 1). The Schlenk was closed and connected to Schlenk set up where 1 bar CO₂ was purged for couple of minutes until some turbidity appears in the solution. Afterwards Schlenk was closed tightly and was heated over a pre-heated oil bath at 130 °C for 24 h. After the reaction was over, the Schlenk was allowed to cool to room temperature. Additional 2-3 ml water was added to the Schlenk for obtaining the homogeneous solution. 20 µl DMF was added as an internal standard and mixed carefully. An aliquot was taken out and dissolved in D₂O for yield determination by ¹H NMR spectroscopy.

(b) For performing reaction using 5 bar CO₂, 50 ml Teflon beaker was charged with 300 µl of THF containing the 0.04 µmol catalyst **C-3**) taken from the freshly prepared stock solution of the catalyst in THF (Table 1, entry 25). Subsequently, 20 mmol NaOH solution in 3 ml distilled water was added to it. Then 2 ml isopropanol was added as hydrogen source. Autoclave was assembled, deoxygenated and charged with 5 bar CO₂. Afterwards autoclave was heated over a pre-heated oil bath at 130 °C for 24 h. After the reaction was over, the autoclave was allowed to cool to room temperature. Additional 2-3 ml water was added for obtaining the homogeneous solution. 20 µl DMF was added as an internal standard and mixed carefully. An aliquot was taken out and dissolved in D₂O for yield determination by ¹H NMR spectroscopy.

3. General procedure for chromium catalyzed sodium bicarbonate transfer-hydrogenation.

25 ml Schlenk tube was charged with the 1.7 µmol **C-3** taken from the freshly prepared stock solution of the catalyst in THF. Subsequently, 0.5 mmol sodium bicarbonate solution in 3 ml distilled water and 2.5 mmol NaOH was added to it. Isopropanol (2 ml) was added next as

hydride source. Afterwards Schlenk was closed tightly and was heated over a pre-heated oil bath at 130 °C for 36 h. After the reaction was over, the Schlenk was allowed to cool to room temperature. Additional 1-2 ml water was added to the Schlenk for obtaining the homogeneous solution. 0.5 mmol DMF was added as an internal standard and mixed carefully. An aliquot was taken out and dissolved in D₂O for yield determination by ¹H NMR spectroscopy.

4. General procedure for chromium catalyzed inorganic carbonate transfer-hydrogenation.

25 ml Schlenk tube was charged with the 1.7 μmol C-3 taken from the freshly prepared stock solution of the catalyst in THF. Subsequently, 0.5 mmol of inorganic carbonates (Ammonium carbonate and potassium carbonate) solution in 3 ml distilled water and 2.5 mmol NaOH was added to it. Isopropanol (2 ml) was added next as hydrogen source. Afterwards Schlenk was closed tightly and was heated over a pre-heated oil bath at 130 °C for 36 h. After the reaction was over, the Schlenk was allowed to cool to room temperature. Additional 1-2 ml water was added to the Schlenk for obtaining the homogeneous solution. 0.5 mmol DMF was added as an internal standard and mixed carefully. An aliquot was taken out and dissolved in D₂O for yield determination by ¹H NMR spectroscopy.

5. (a) General procedure for the stoichiometric reactions in THF.

A 25 ml J-Young Schlenk flask was charged with the desired amount of THF solution of C-3 inside the glove box. Afterwards 5 equiv. (w.r.t. catalyst) NaOH was added while stirring. The reaction mixture was stirred for 5 min and taken out of the glove box. The reaction mixture was heated up for a specific time interval at 130 °C, and afterwards the reaction was stopped and allowed to cool at room temperature. The solvent was dried under vacuum and the obtained residue was washed with pentane to obtain a fine powder. Different reaction times gave products with different solubilities, and due to which NMR analysis was done using DMSO-d₆ and THD d₈ and the product was analyzed by ¹H, ¹³C, ³¹P NMR spectroscopy.

(b) General procedure for the stoichiometric reactions in isopropanol as solvent.

(a) A 25 ml J-Young Schlenk flask was charged with desired amount of C-3 and 2 ml isopropanol along with 0.2 ml THF for complete dissolution of catalyst inside the glove box. Afterwards 5 equiv. (w.r.t. catalyst) NaOH was added while stirring. The reaction mixture was stirred for 5 min and taken out of the glove box. The reaction mixture was heated up for 16 h at 130 °C. Afterwards the reaction was stopped and allowed to cool at room temperature. The solvent was dried under vacuum and the obtained residue was washed with pentane to obtain a fine powder. The powder obtained was dissolved in DMSO-d₆ and the product was analyzed by ¹H, and ³¹P NMR spectroscopy.

(b) A 25 ml J-Young Schlenk flask was charged with desired amount of C-3 and 2 ml isopropanol along with 0.2 ml THF for complete dissolution of catalyst inside the glove box. Afterwards 1.5 equiv. sodium isopropoxide (w.r.t. catalyst) was added while stirring. The reaction mixture was stirred for 5 min and taken out of the glove box. The reaction mixture

was heated up for 12 h at 130 °C, afterwards stopped and cool at room temperature. The solvent was dried under vacuum and analyzed by ^1H , and ^{31}P NMR spectroscopy.

6. ^1H NMR spectra of catalytic runs for CO_2 transfer hydrogenation:

Figure S1. ^1H NMR (500 MHz) in D_2O , Conditions: **C-1**, NaOH (20 mmol), $p\text{CO}_2$ (bar) = 1, 130 °C, *i*PrOH, 24 h (Table 1, entry 1).

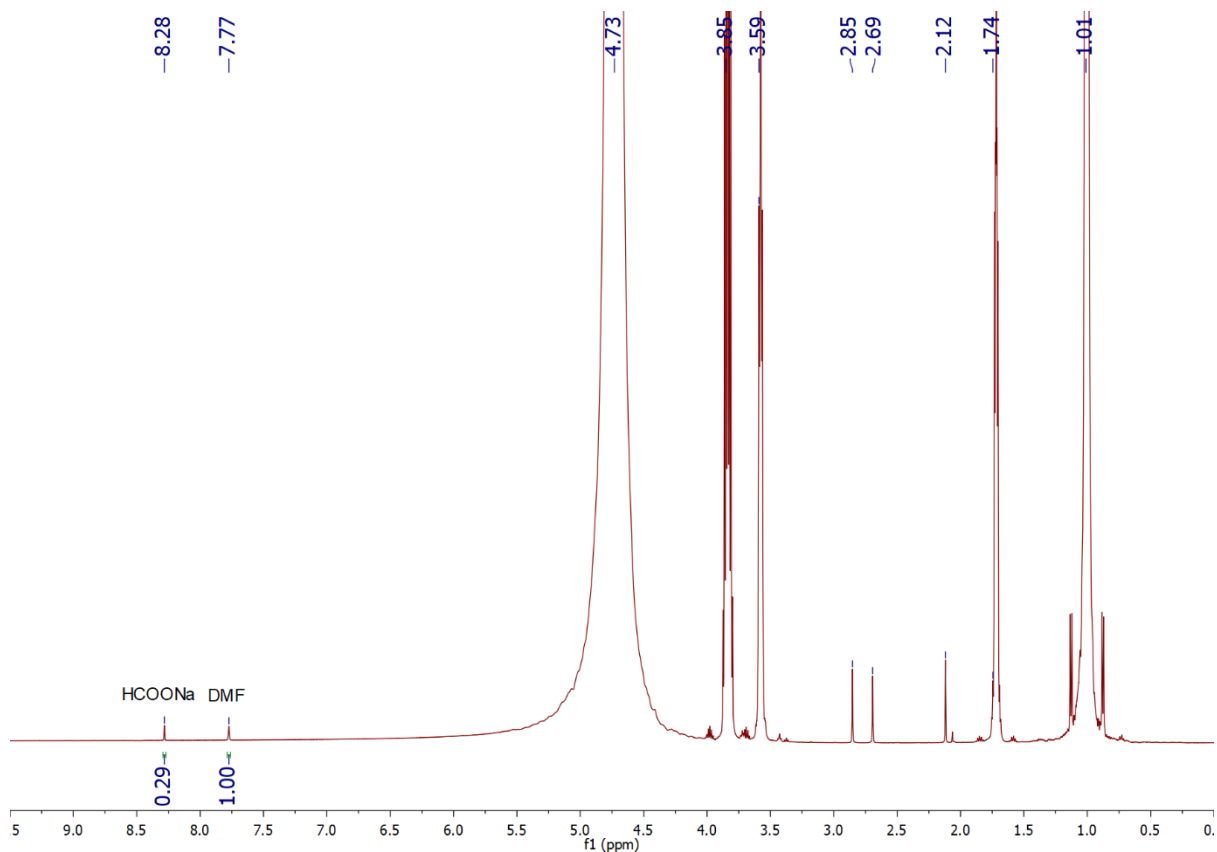


Figure S2. ^1H NMR (500 MHz) in D_2O , Conditions: **C-2**, NaOH (20 mmol), $p\text{CO}_2$ (bar) = 1, 130 °C, *i*PrOH, 24 h (Table 1, entry 2).

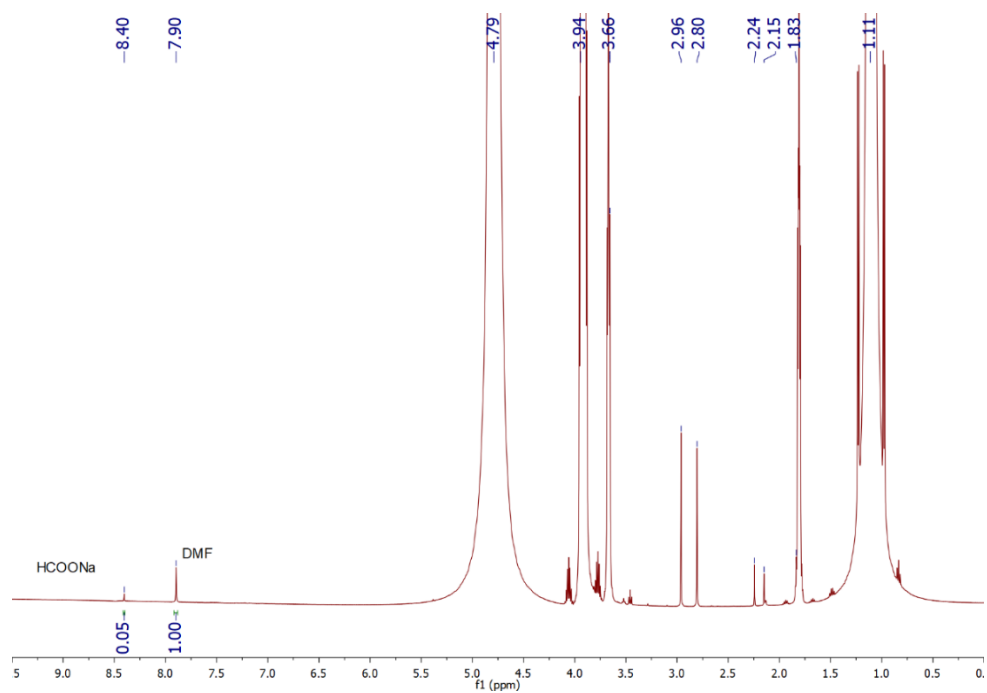


Figure S3. ¹H NMR (500 MHz) in D₂O, Conditions: C-3, NaOH (20 mmol), pCO₂ (bar) = 1, 130 °C, *i*PrOH, 24 h (Table 1, entry 3).

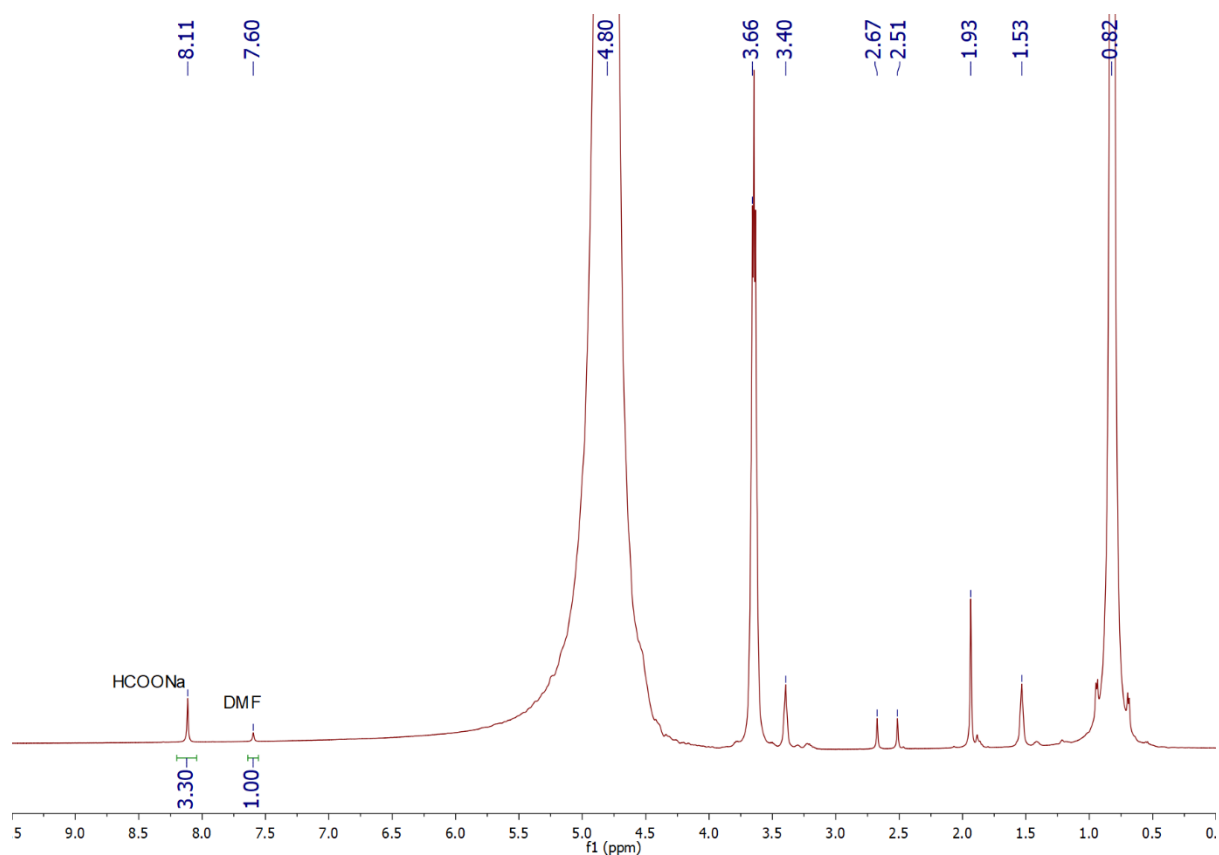


Figure S4. ¹H NMR (500 MHz) in D₂O, Conditions: C-4, NaOH (20 mmol), pCO₂ (bar) = 1, 130 °C, *i*PrOH, 24 h (Table 1, entry 4).

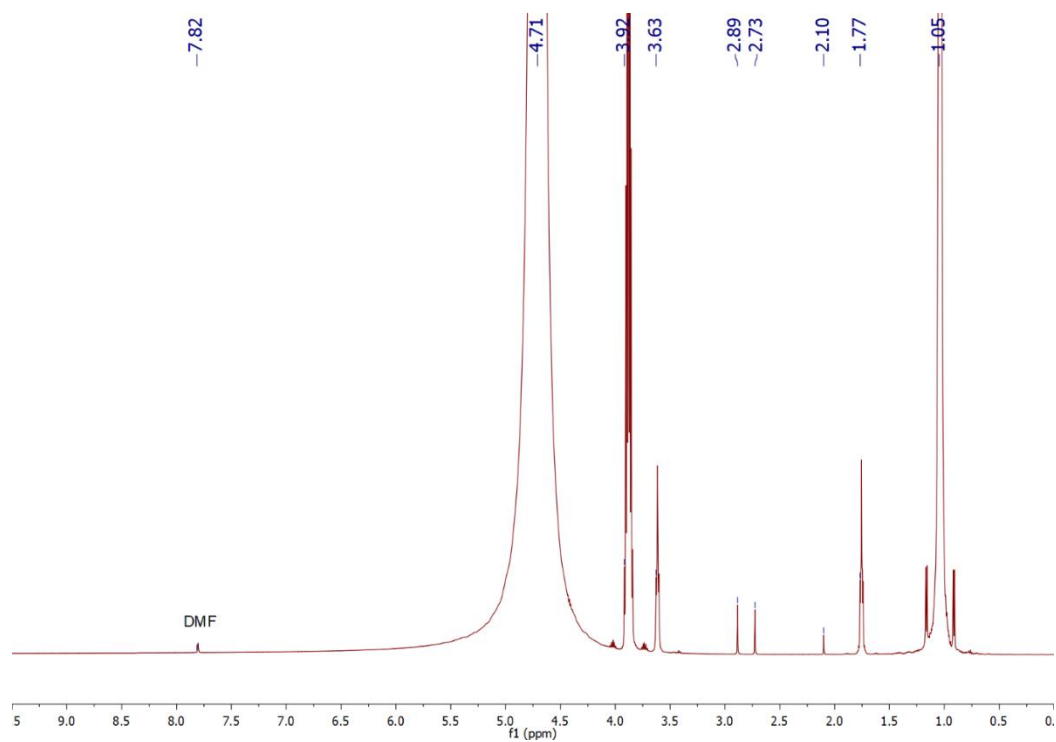


Figure S5. ¹H NMR (500 MHz) in D₂O, Conditions: NaOH (20 mmol), pCO₂ (bar) = 1, 130 °C, *i*PrOH, 24 h (Table 1, entry 5).

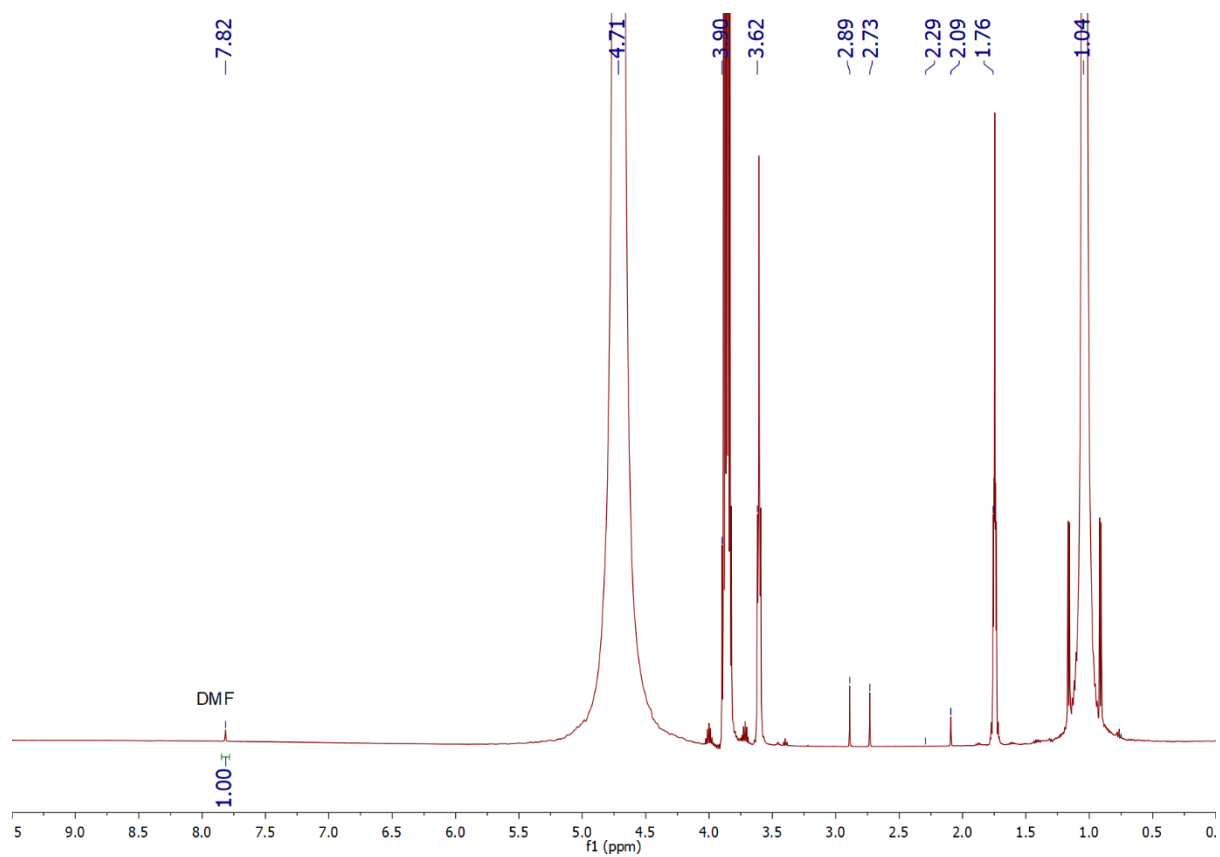


Figure S6. ¹H NMR (500 MHz) in D₂O, Conditions: C-5, NaOH (20 mmol), pCO₂ (bar) = 1, 130 °C, *i*PrOH, 24 h (Table 1, entry 6).

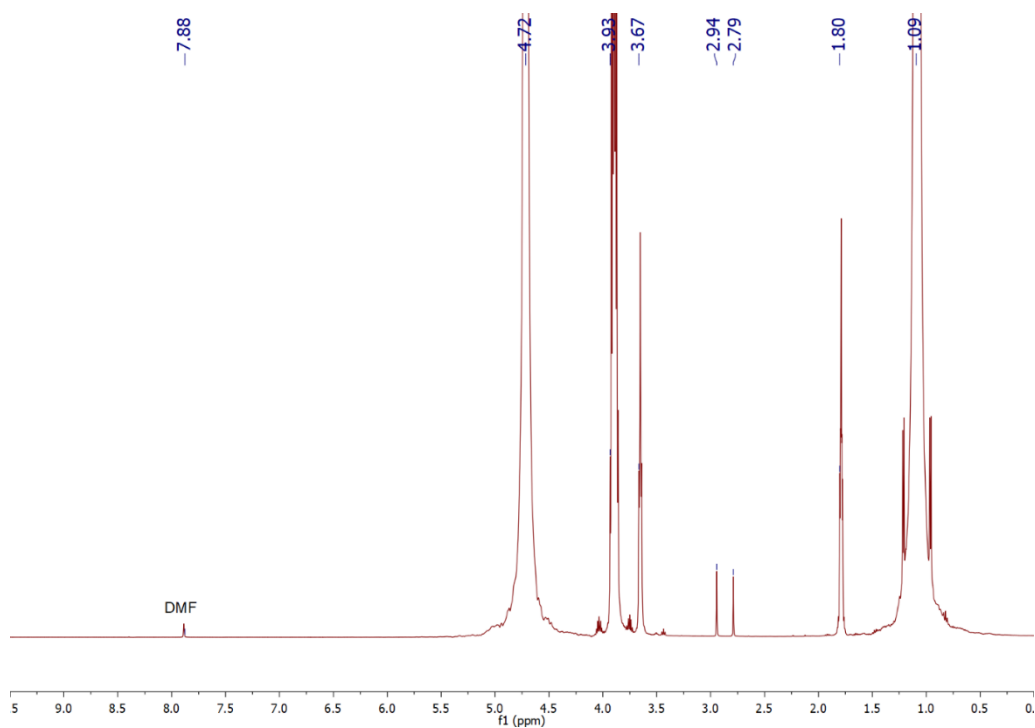


Figure S7. ^1H NMR (500 MHz) in D_2O , Conditions: **C-6**, NaOH (20 mmol), pCO_2 (bar) = 1, 130 $^\circ\text{C}$, *i*PrOH, 24 h (Table 1, entry 7).

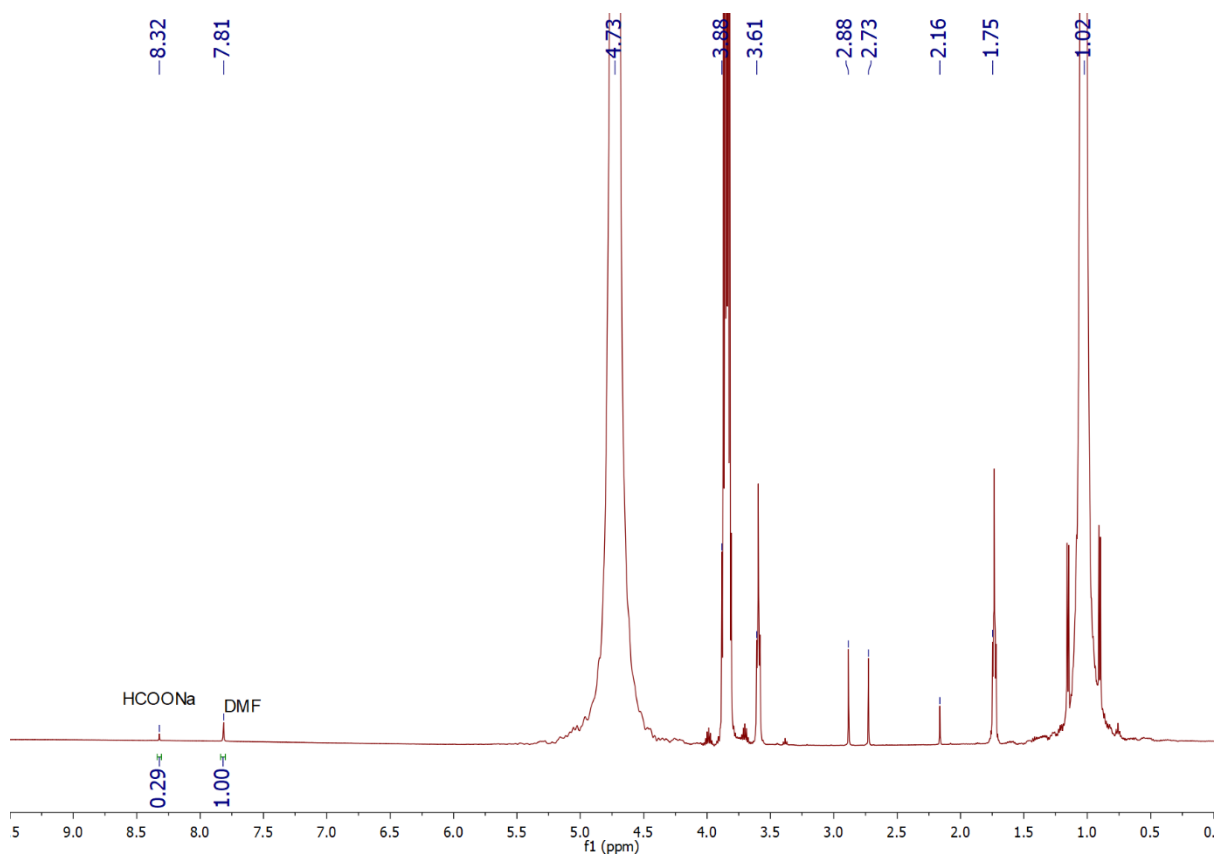


Figure S8. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, Na_2CO_3 (20 mmol), pCO_2 (bar) = 1, 130 $^\circ\text{C}$, *i*PrOH, 24 h (Table 1, entry 8).

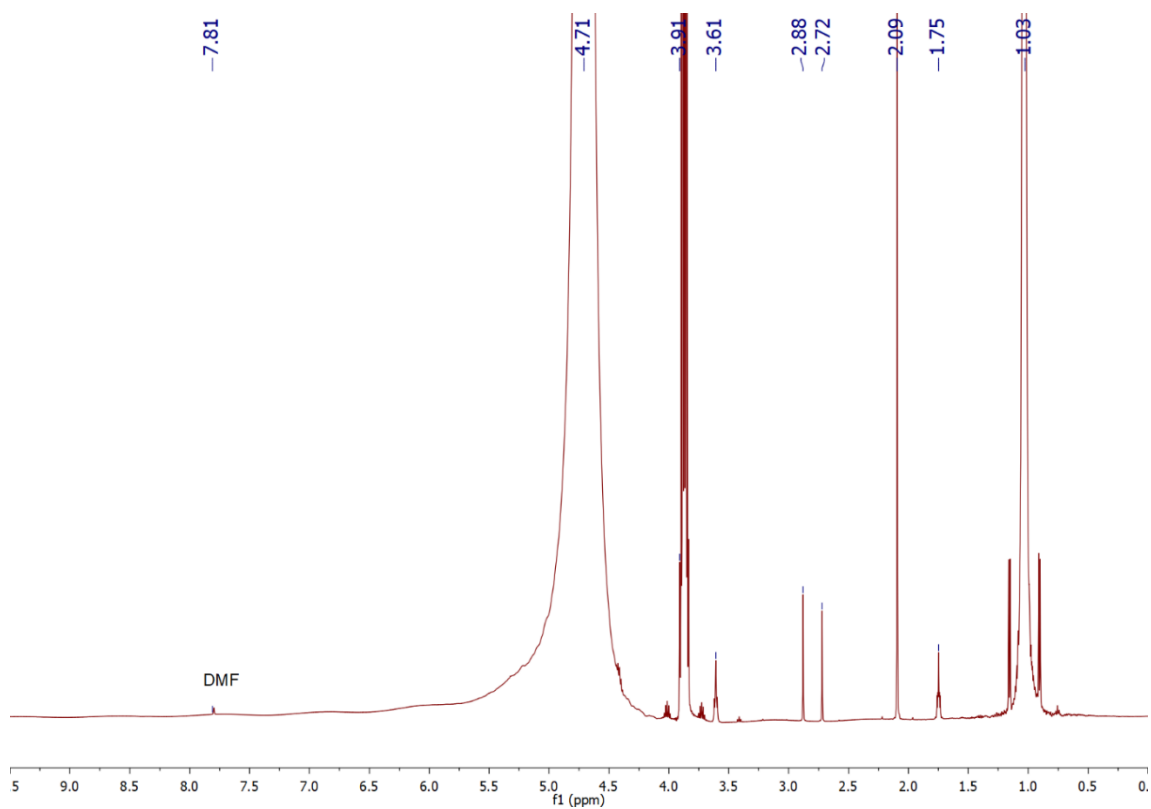


Figure S9. ¹H NMR (500 MHz) in D₂O, Conditions: C-3, K₃PO₄ (20 mmol), pCO₂ (bar) = 1, 130 °C, *i*PrOH, 24 h (Table 1, entry 9).

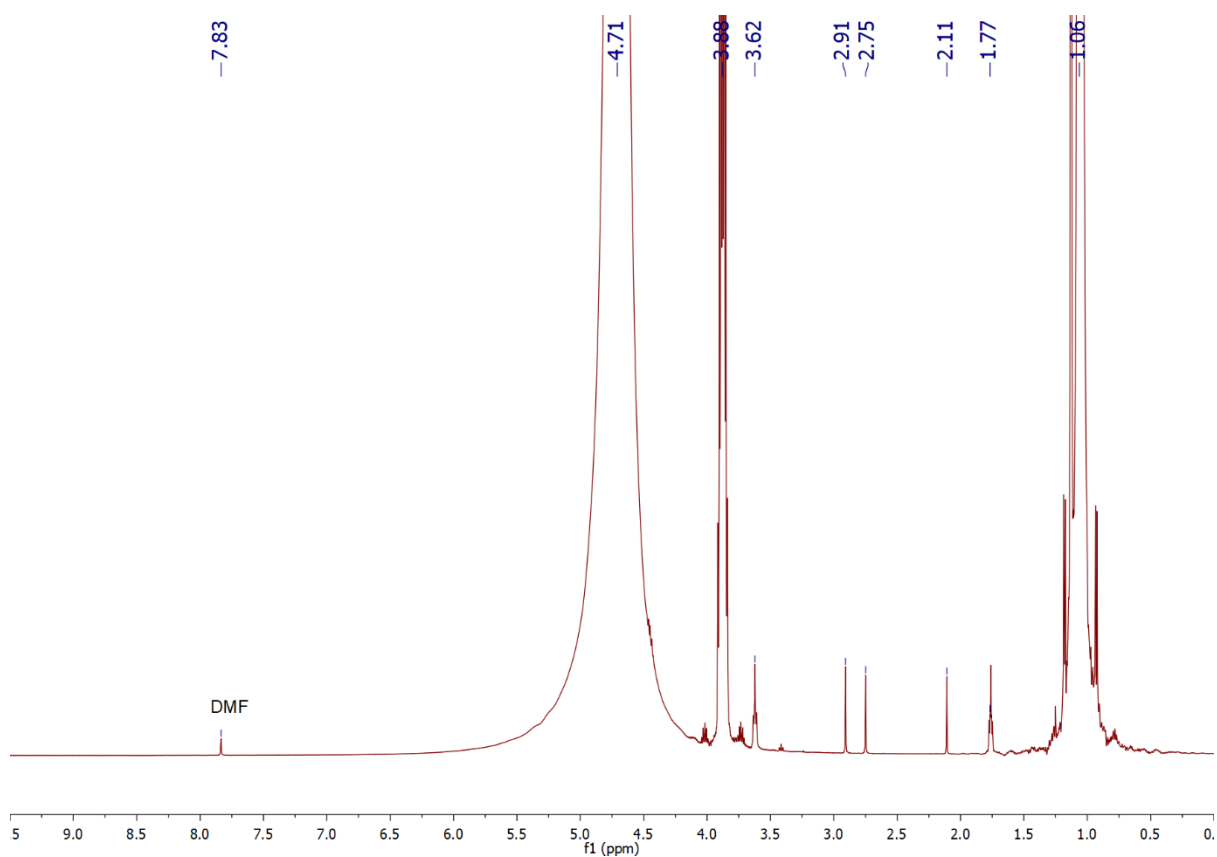


Figure S10. ¹H NMR (500 MHz) in D₂O, Conditions: C-3, *t*BuOK (20 mmol), pCO₂ (bar) = 1, 130 °C, *i*PrOH, 24 h (Table 1, entry 10).

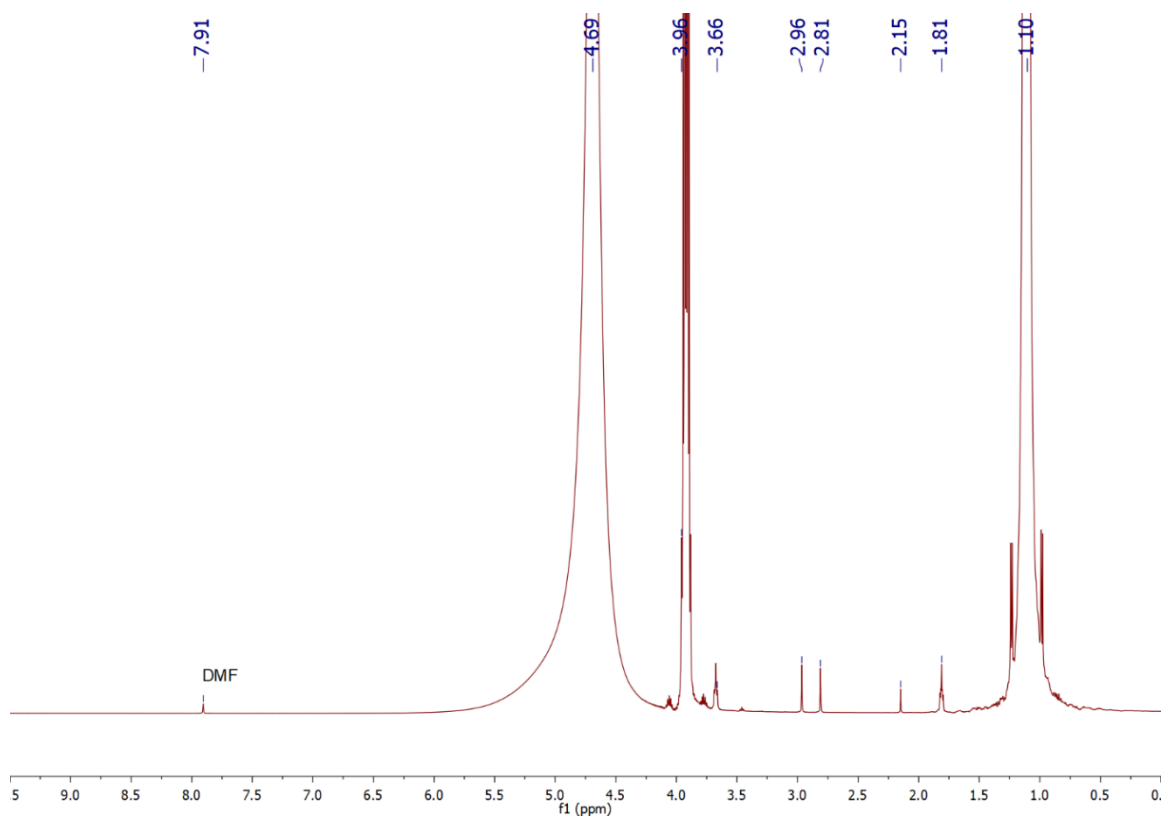


Figure S11. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, DBU (20 mmol), $p\text{CO}_2$ (bar) = 1, 130°C , *i*PrOH, 24 h (Table 1, entry 11).

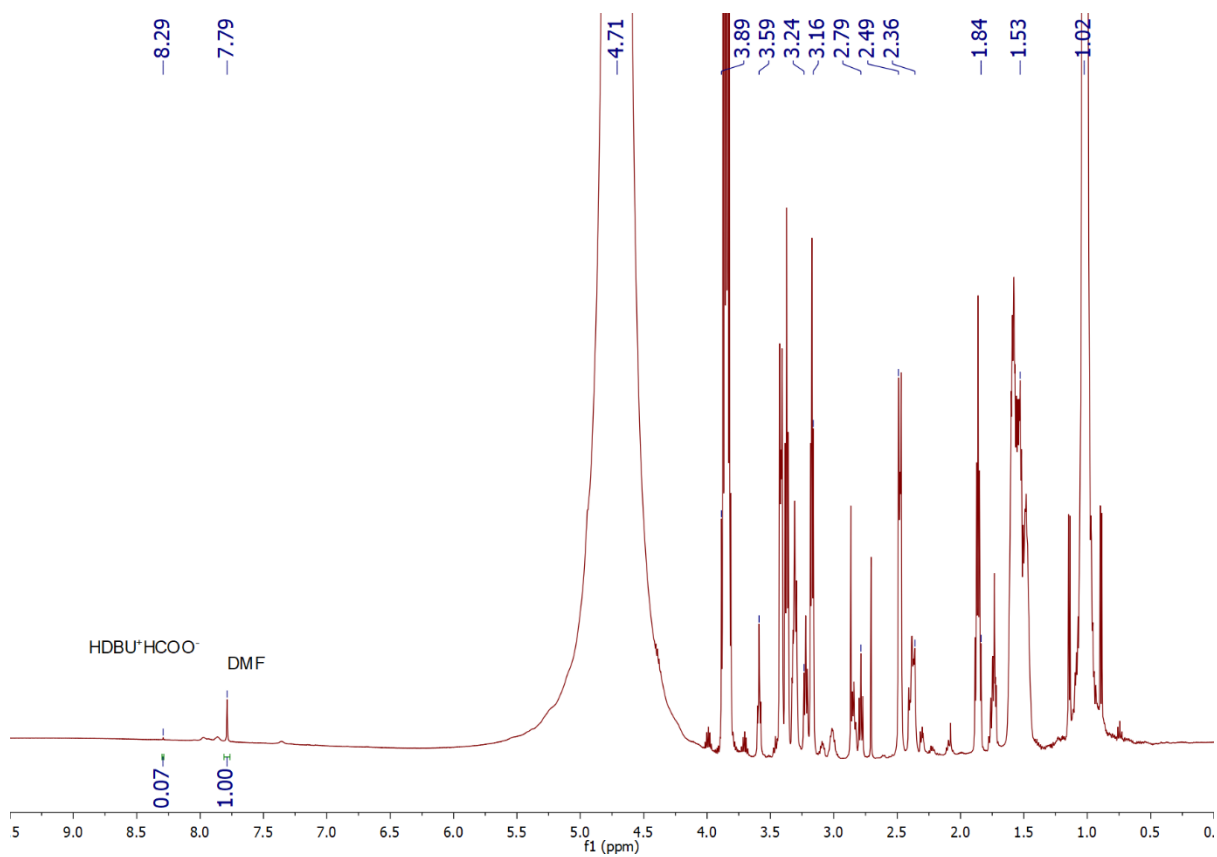


Figure S12. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, Et_3N (20 mmol), pCO_2 (bar) = 1, $130\text{ }^\circ\text{C}$, *i*PrOH, 24 h (Table 1, entry 12).

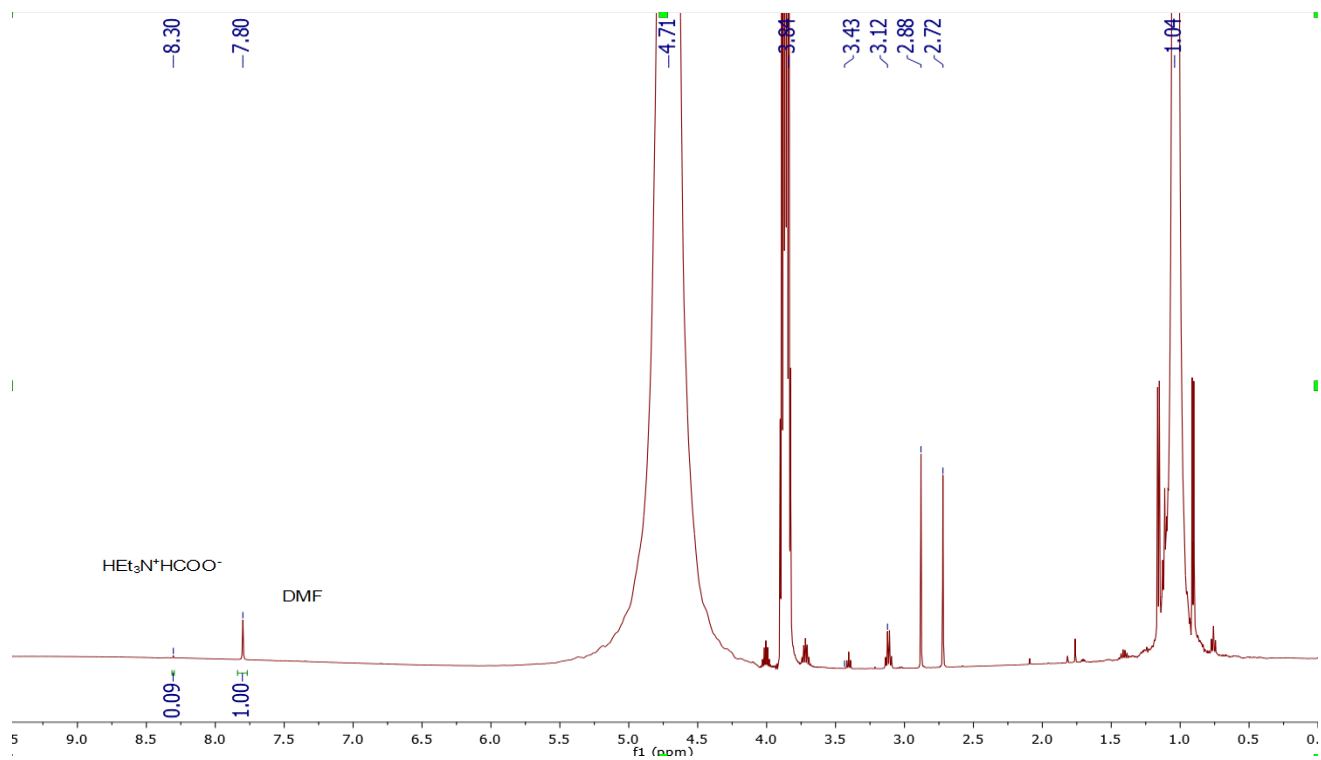


Figure S13. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, KOH (20 mmol), pCO_2 (bar) = 1, $130\text{ }^\circ\text{C}$, *i*PrOH, 24 h (Table 1, entry 13).

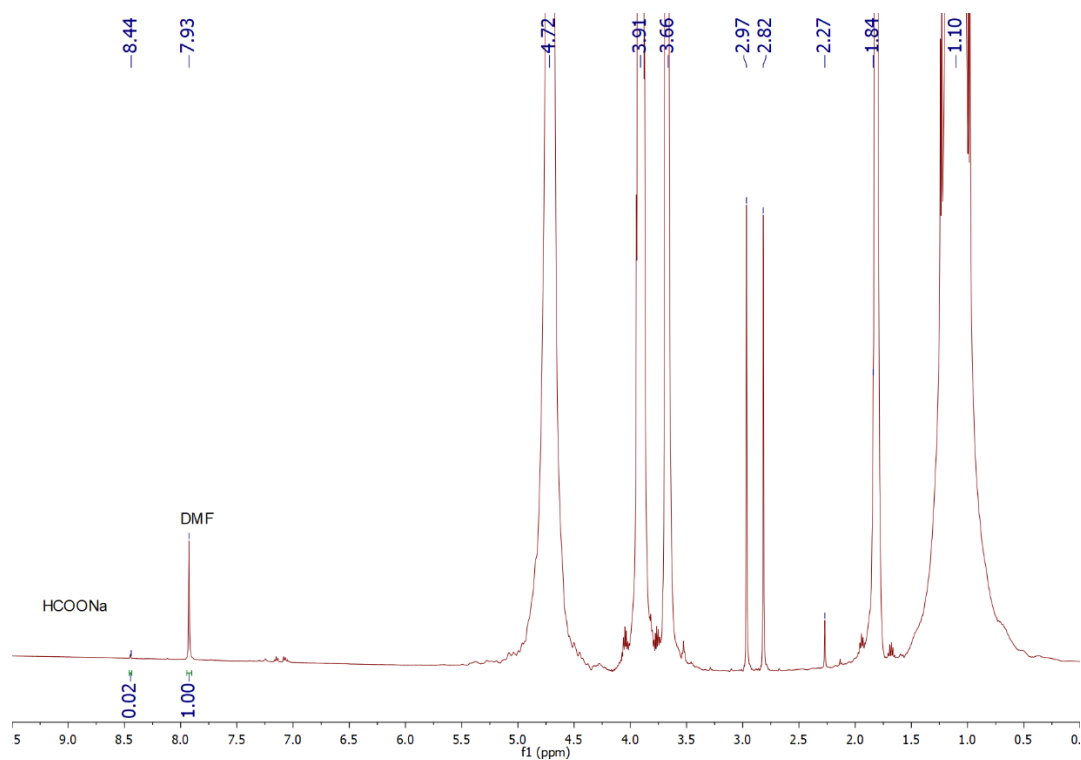


Figure S14. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, NaOH (20 mmol), pCO_2 (bar) = 1, 130 $^\circ\text{C}$, MeOH, 24 h (Table 1, entry 14).

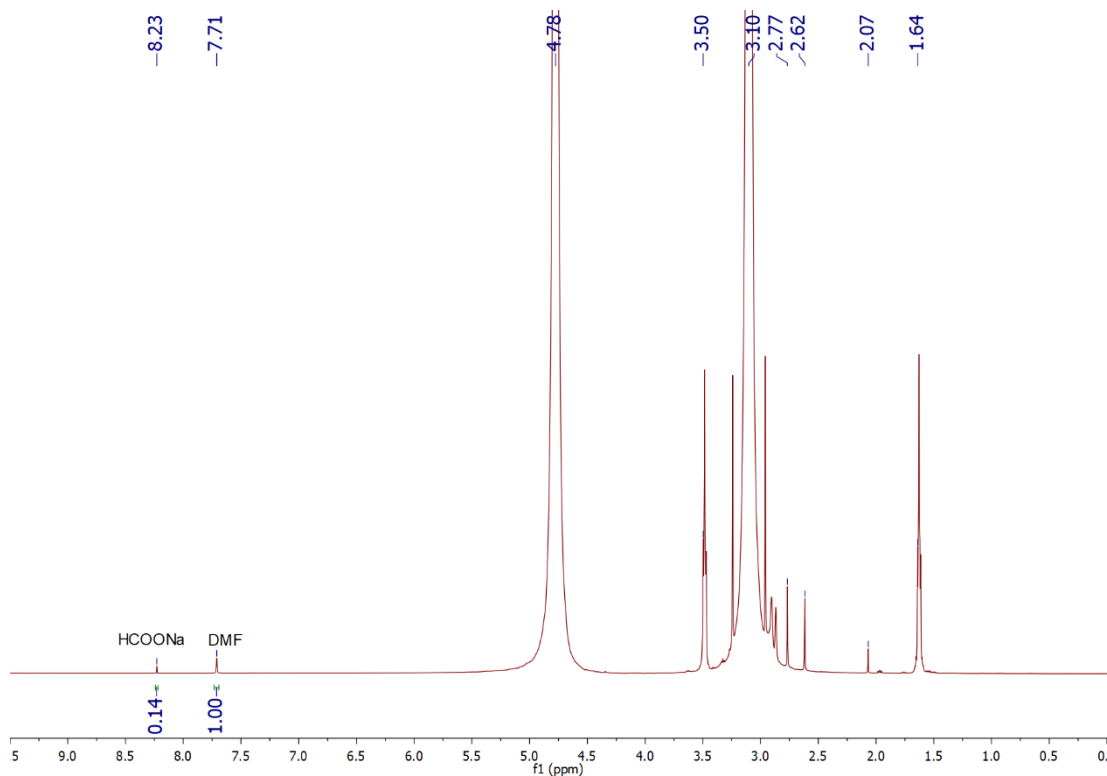


Figure S15. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, NaOH (20 mmol), pCO_2 (bar) = 1, 130 $^\circ\text{C}$, EtOH, 24 h (Table 1, entry 15).

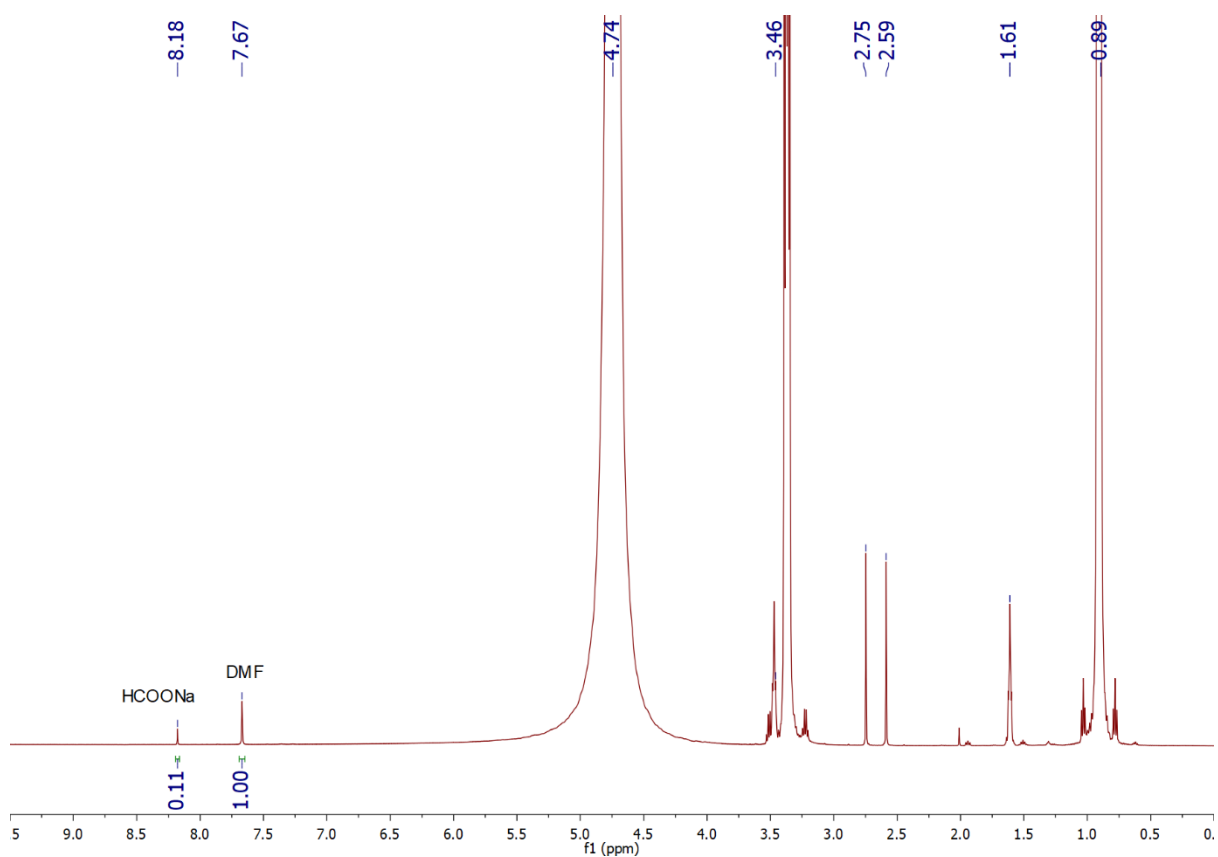


Figure S16. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, NaOH (20 mmol), $p\text{CO}_2$ (bar) = 1, 130°C , 1,4 BuOH, 24 h (Table 1, entry 16).

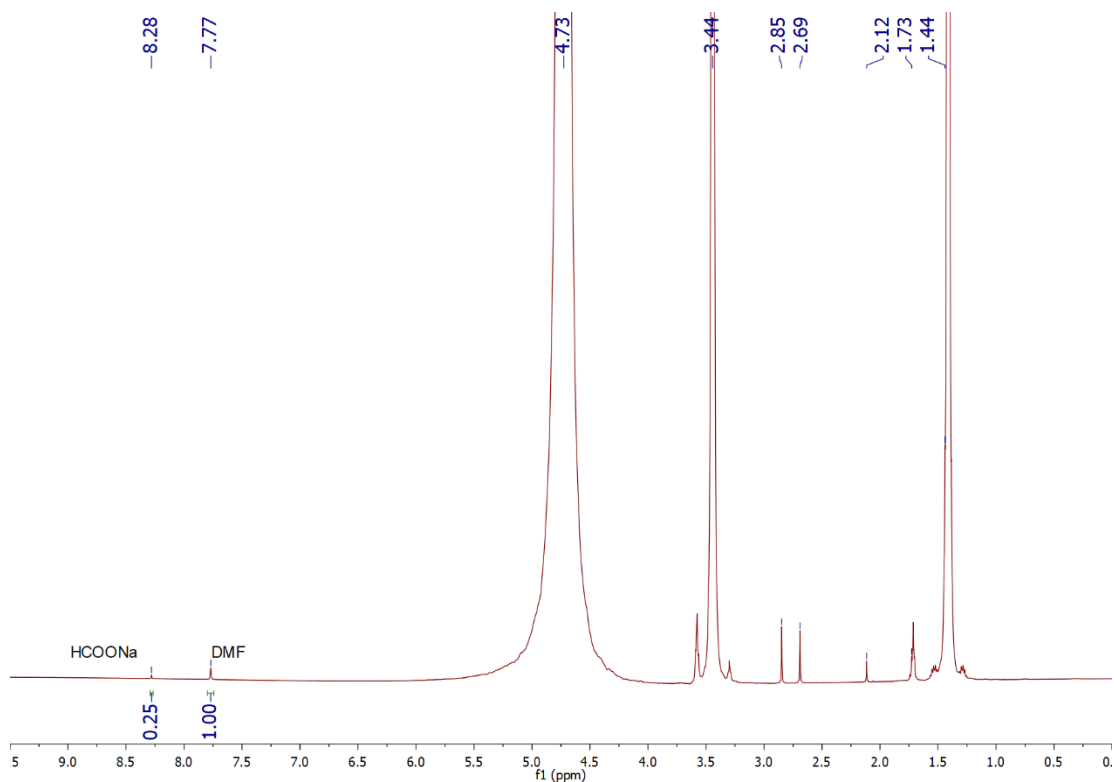


Figure S17. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, NaOH (20 mmol), $p\text{CO}_2$ (bar) = 1, 130°C , N_2H_4 , 24 h (Table 1, entry 17).

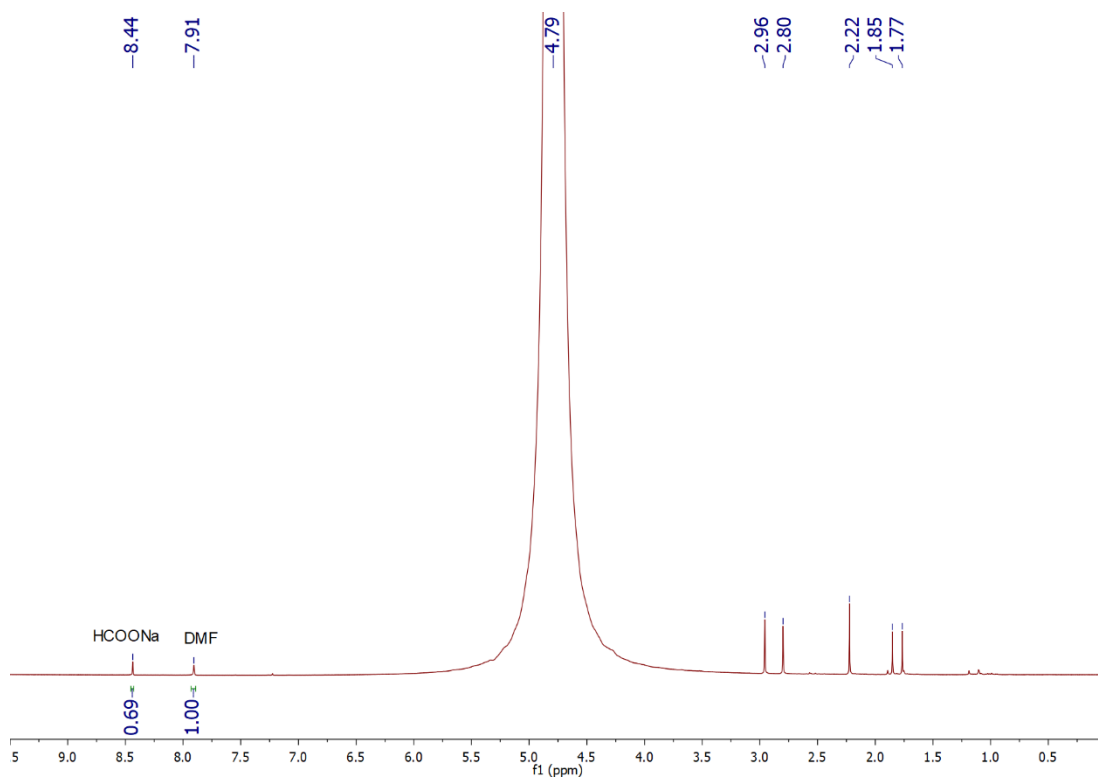


Figure S18. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, NaOH (20 mmol), $p\text{CO}_2$ (bar) = 1, 130°C , Glycerol, 24 h (Table 1, entry 18).

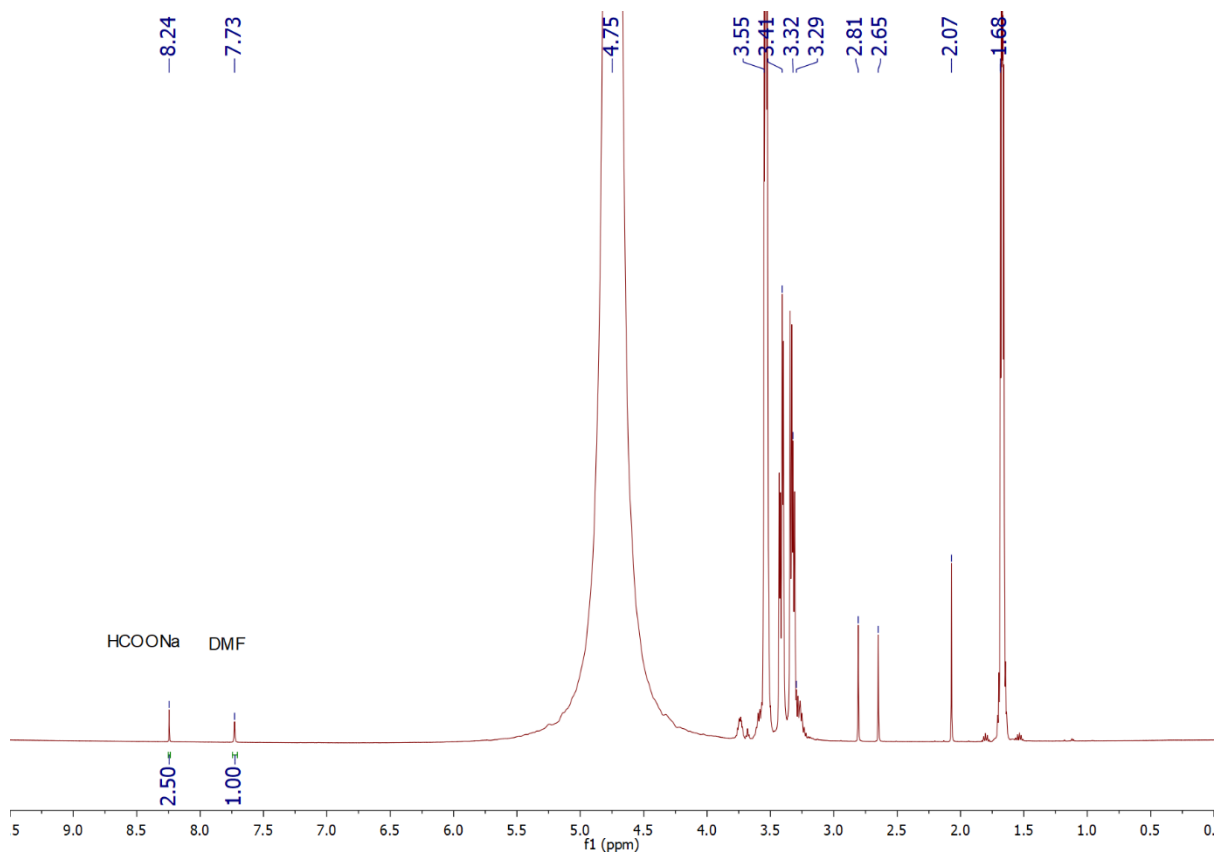


Figure S19. ¹H NMR (500 MHz) in D₂O, Conditions: **C-3**, NaOH (20 mmol), pCO₂ (bar) = 1, 130 °C, No hydride source, 24 h (Table 1, entry 19).

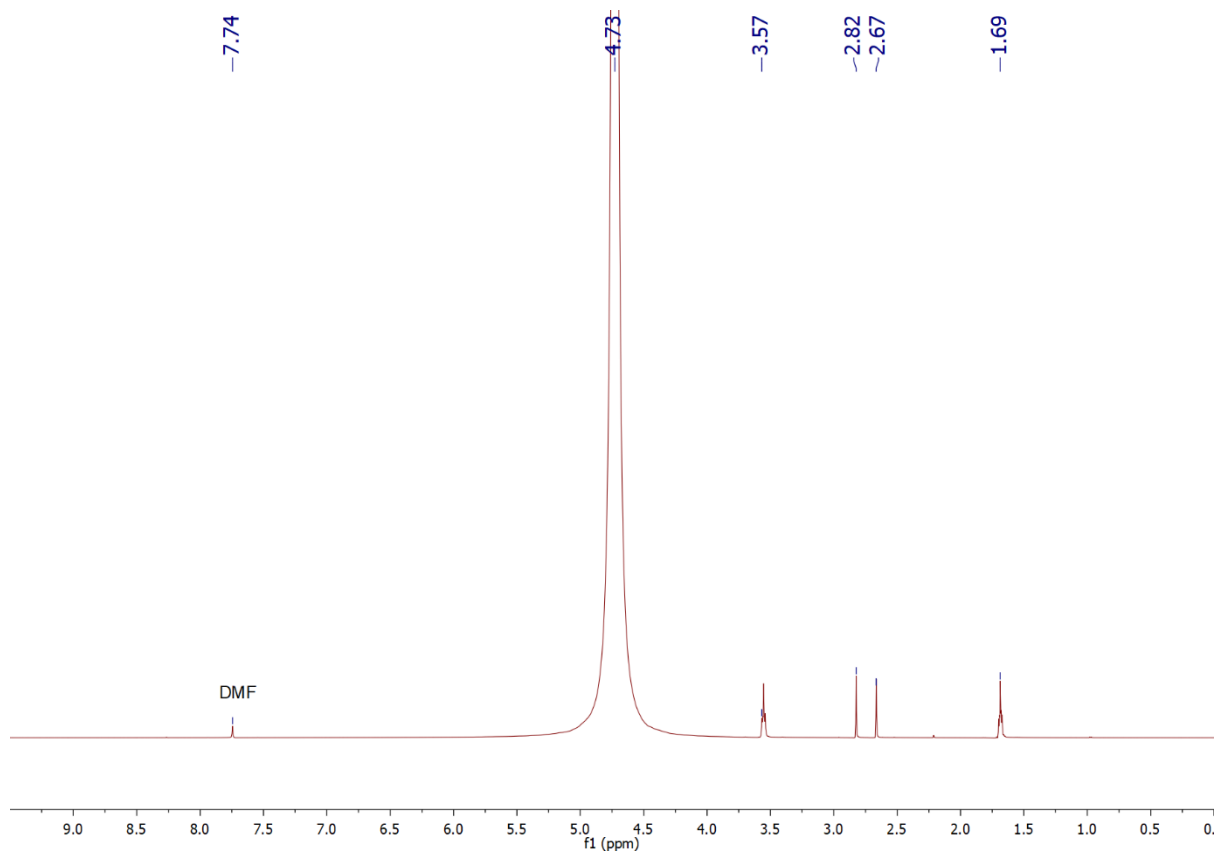


Figure S20. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, NaOH (20 mmol), pCO_2 (bar) = 1, 130°C , only *i*PrOH, 24 h (Table 1, entry 20).

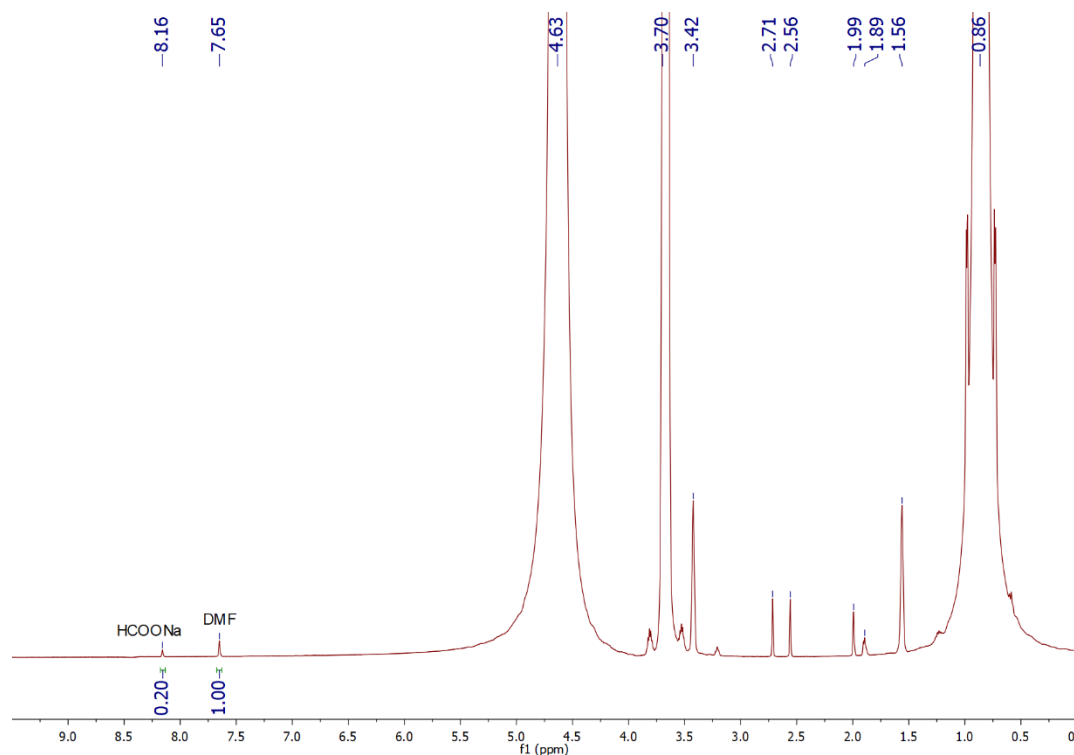


Figure S21. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, NaOH (20 mmol), pCO_2 (bar) = 1, 130°C , *i*PrOH, only water as solvent, 24 h (Table 1, entry 21).

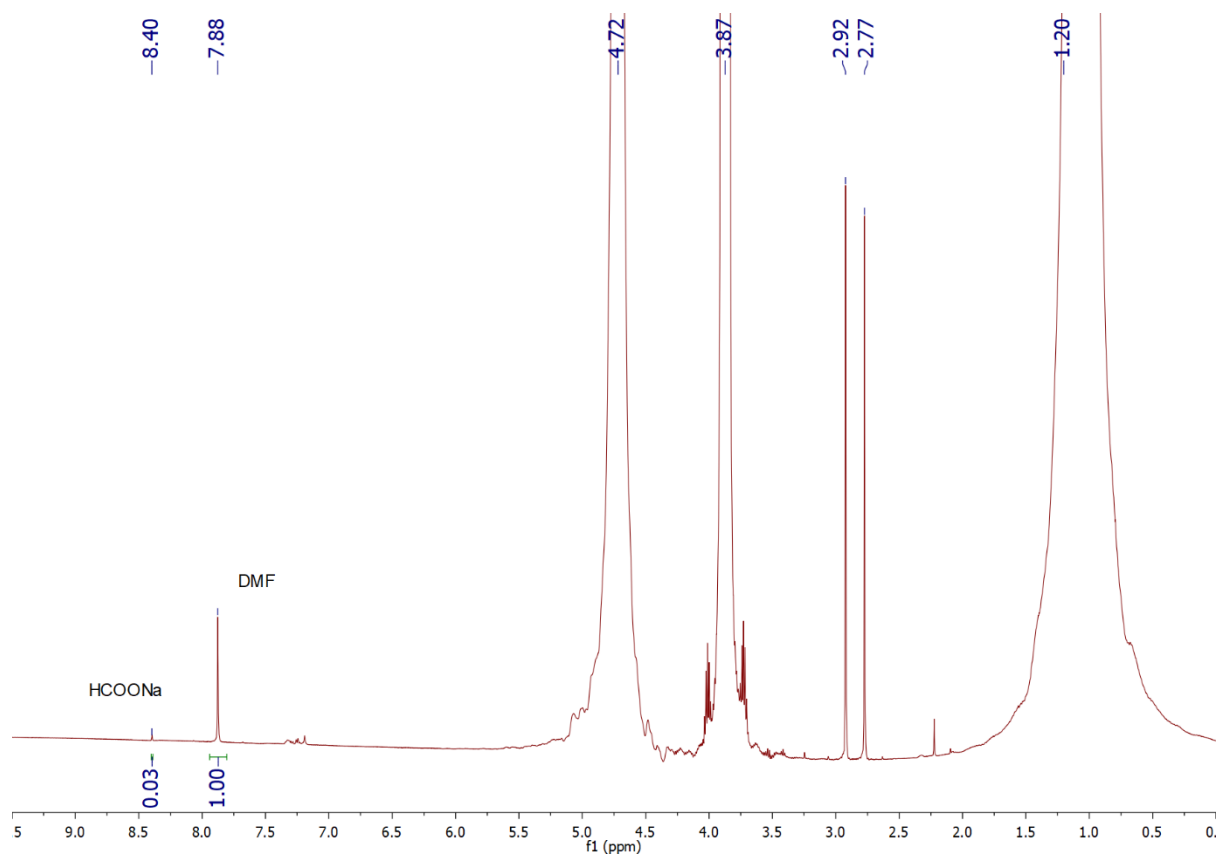


Figure S22. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, Me_3NO 0.1 mmol, NaOH (20 mmol), pCO_2 (bar) = 1, 130°C , *i*PrOH, 24 h (Table 1, entry 22).

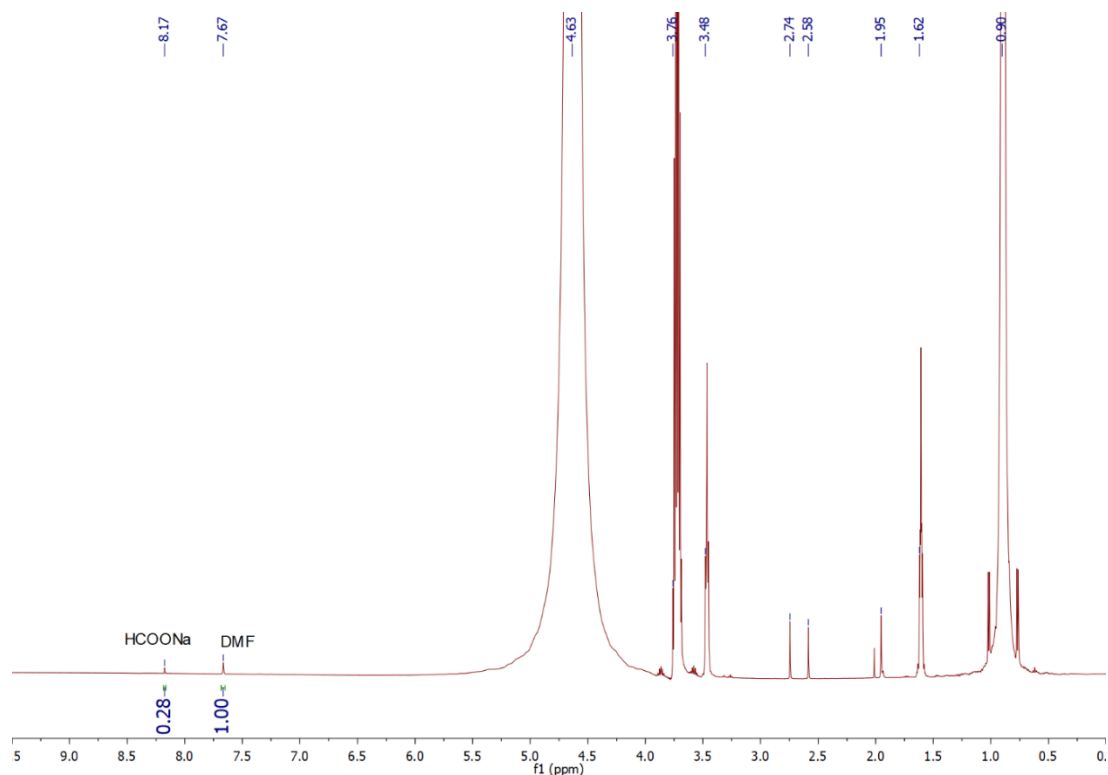


Figure S23. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, NaOH (2 mmol), pCO_2 (bar) = 1, 130°C , *i*PrOH, 24 h (Table 1, entry 23).

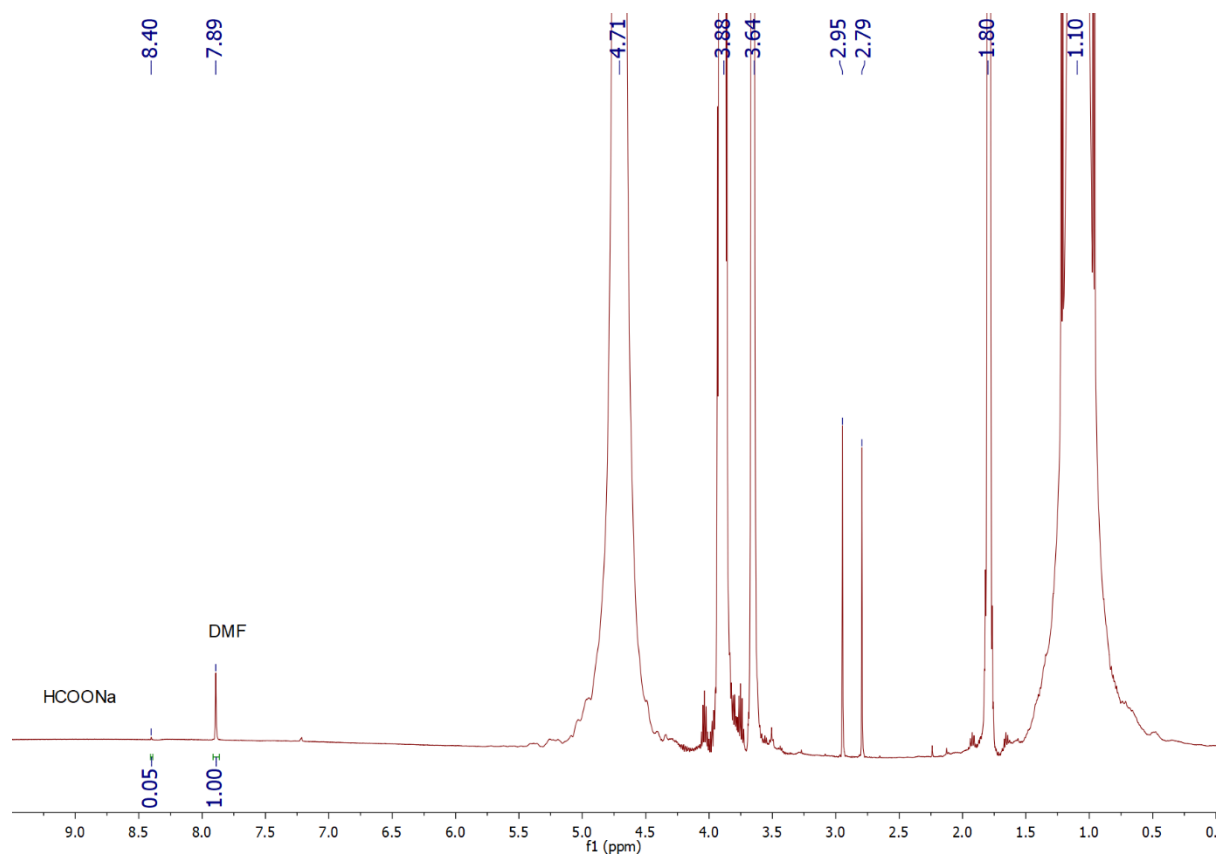


Figure S24. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, NaOH (20 mmol), pCO_2 (bar) = 1, 150°C , *i*PrOH, 24 h (Table 1, entry 24).

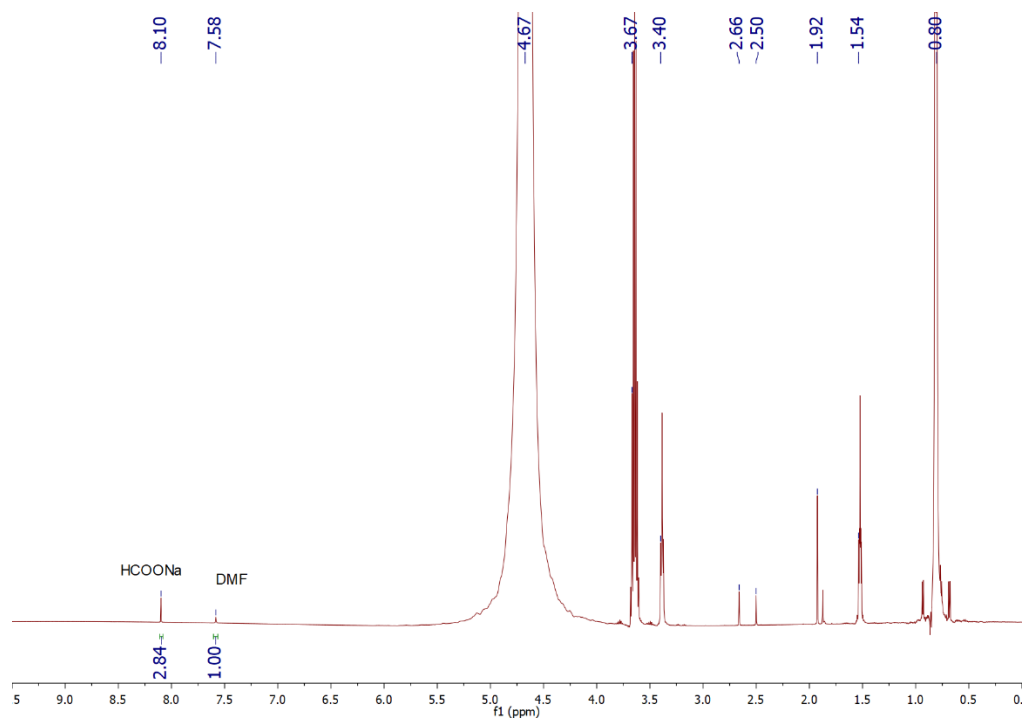
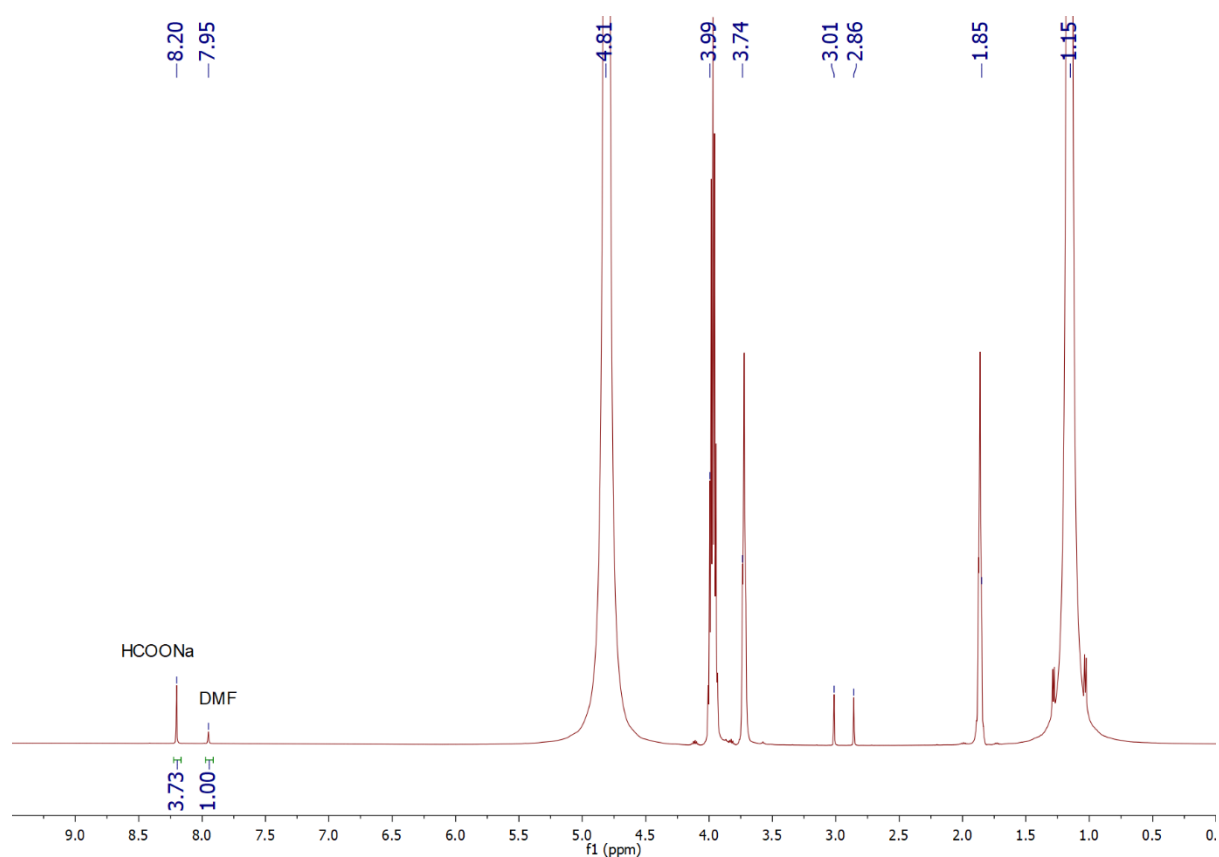
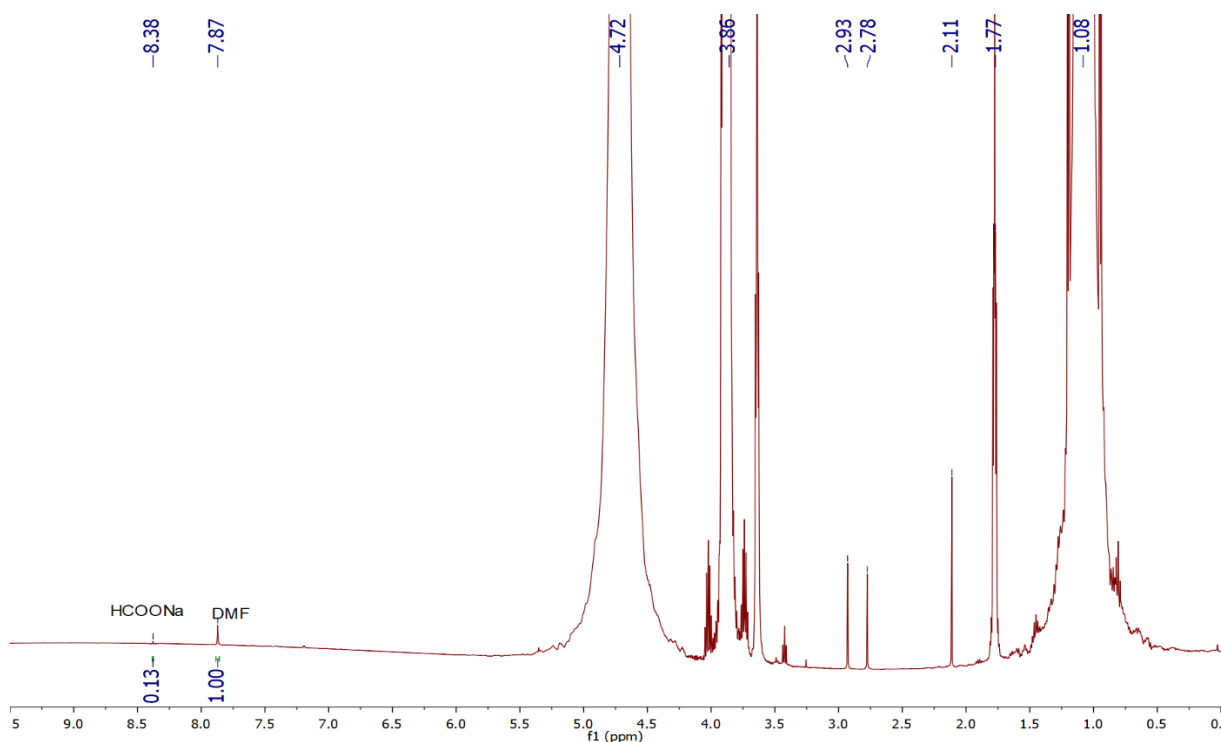


Figure S25. ^1H NMR (500 MHz) in D_2O , Conditions: **C-3**, NaOH (20 mmol), pCO_2 (bar) = 5, 130°C , *i*PrOH, 24 h (Table 1, entry 25).



7. ^1H NMR Spectra of catalytic runs for sodium bicarbonate transfer-hydrogenation:

Figure S26. ^1H NMR (500 MHz) in D_2O , Conditions: NaHCO_3 0.5 mmol, NaOH (2.5 mmol), **C-3**, *i*PrOH, 130 $^\circ\text{C}$, 36 h.



8. ^1H NMR Spectra of Catalytic Runs for Ammonium and potassium carbonate transfer-hydrogenation:

Figure S27. ^1H NMR (500 MHz) in D_2O , Conditions: $(\text{NH}_4)_2\text{CO}_3$ 0.5 mmol, NaOH (2.5 mmol), **C-3**, *i*PrOH, 130 $^\circ\text{C}$, 36 h.

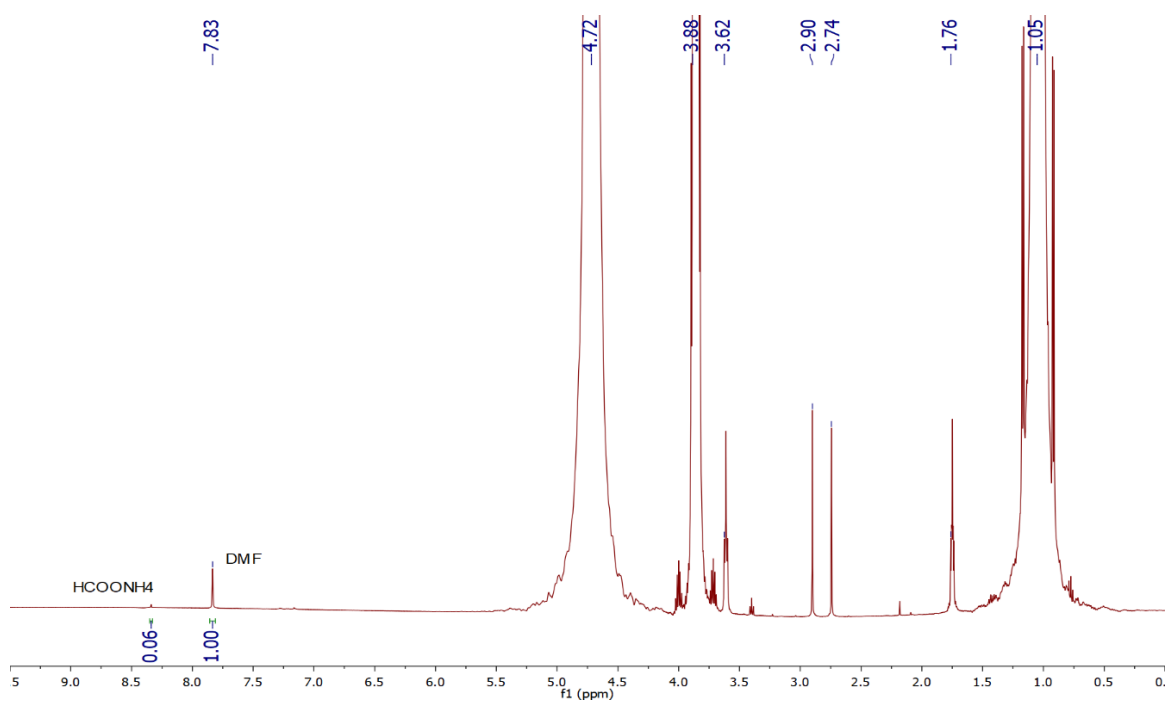
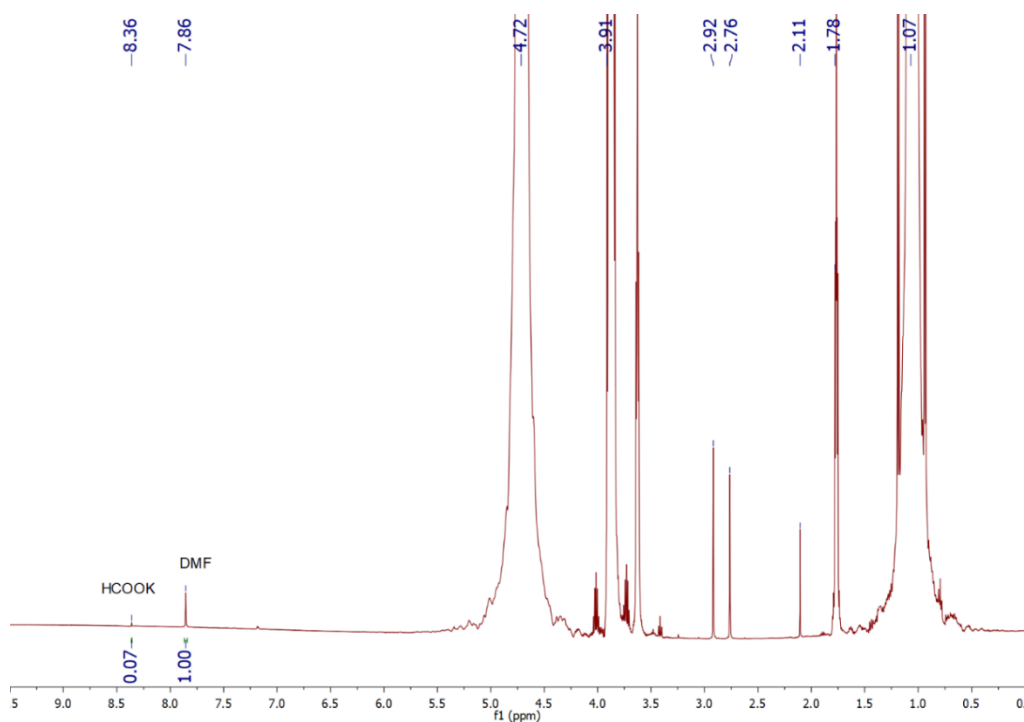
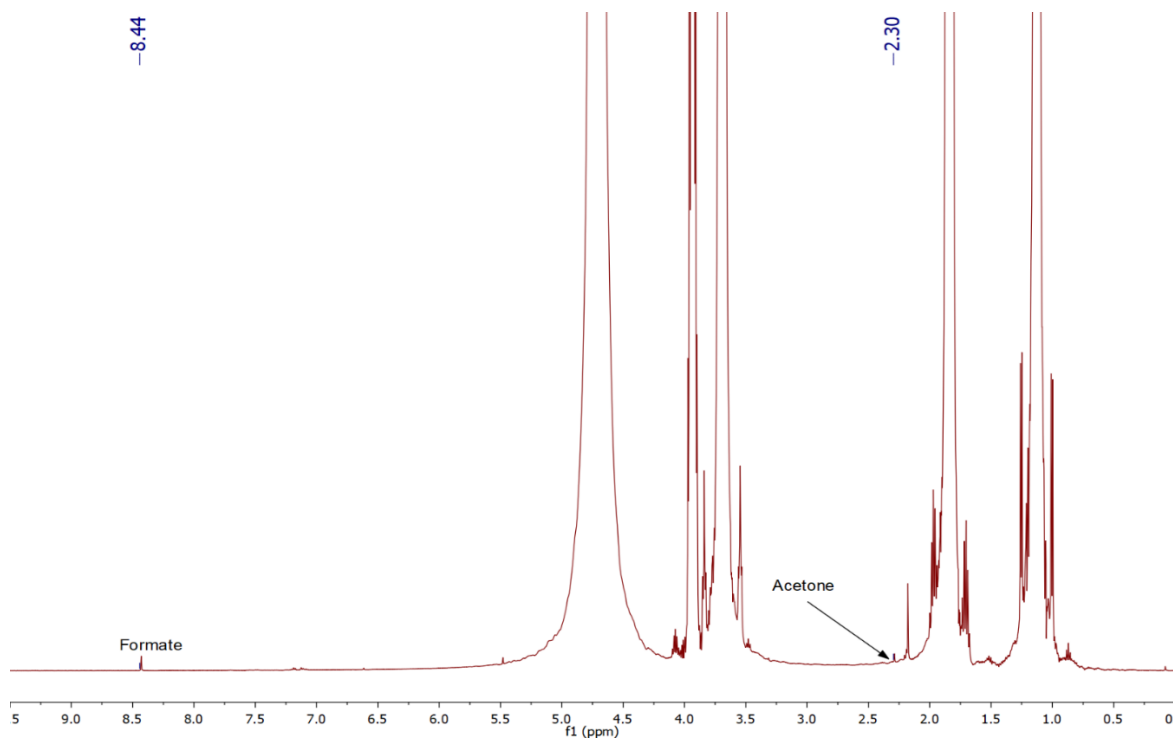


Figure S28. ^1H NMR (500 MHz) in D_2O , Conditions: K_2CO_3 (0.5 mmol), NaOH (2.5 mmol), **C-3**, *i*PrOH, 130 °C, 24 h.



9. Acetone Detection: The benchmark reaction was performed overnight under optimized conditions and after the completion of reaction, Schlenk was cooled to 0 °C for 1 hour then allow to come to room temperature. Afterwards an aliquot was taken out and subjected for NMR analysis in D_2O .

Figure S29. ^1H NMR (500 MHz) in D_2O , for acetone detection.



10. Mechanistic Experiments:

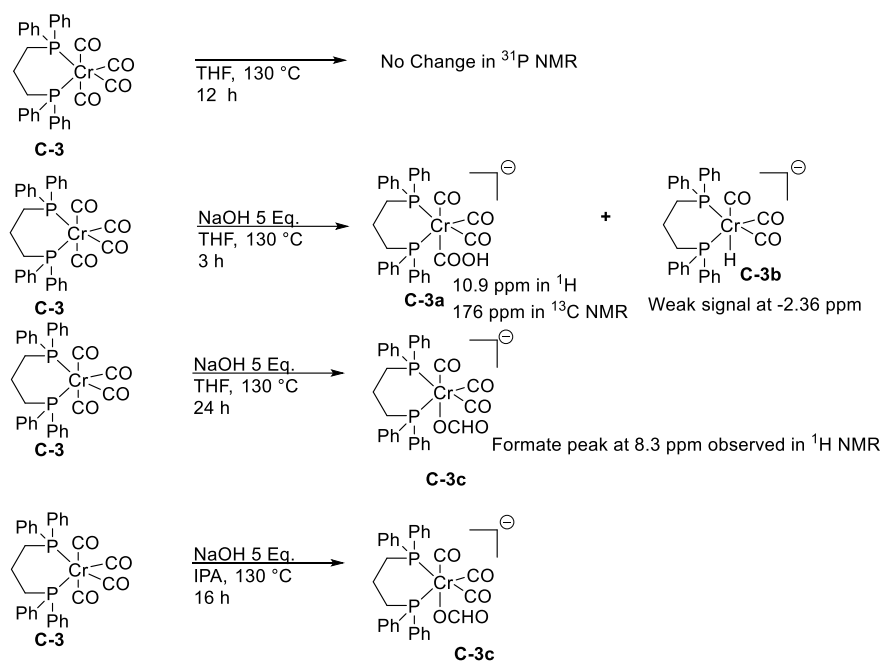


Figure S30 Scheme for mechanistic experiments.

Figure S31 ^{31}P NMR (203 MHz) in CDCl_3 for **C-3** after overnight heating in THF at 130°C .

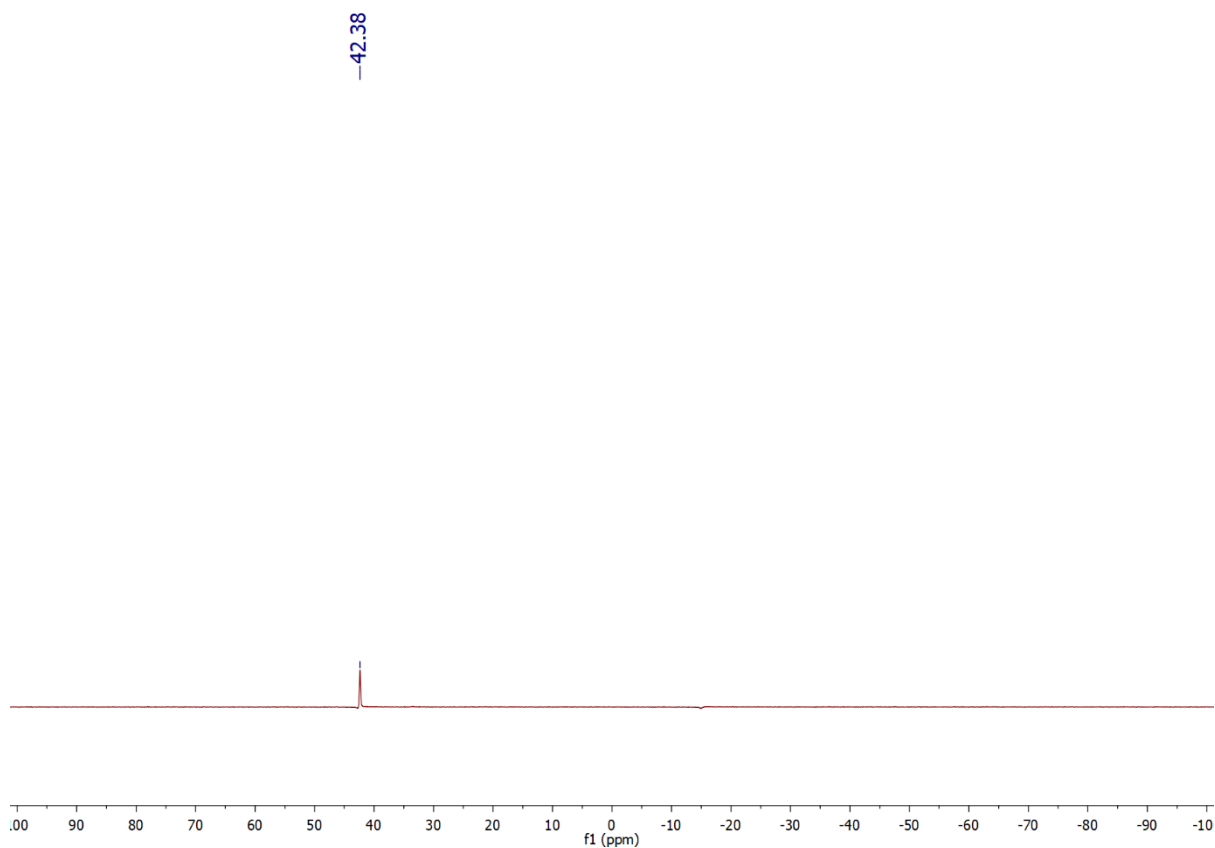


Figure S32 ^1H NMR (500 MHz) in THF d_8 after 3 h of heating in presence of 5 equiv. NaOH.

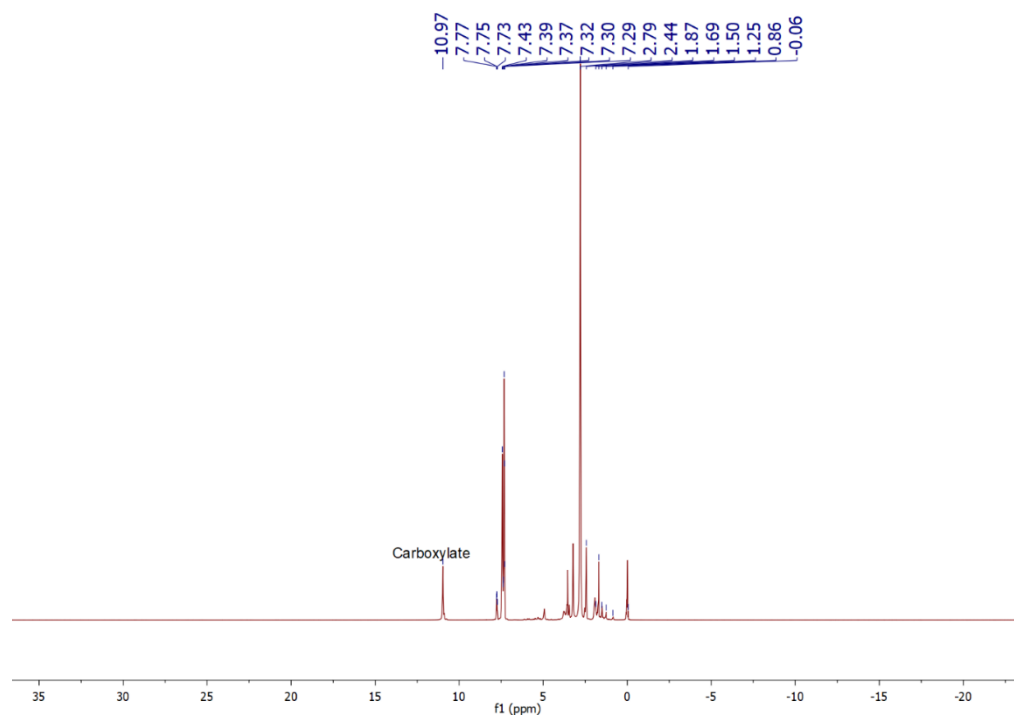


Figure S33 ^1H NMR (500 MHz) in DMSO- d_6 after 3 h of heating in presence of 5 equiv. NaOH in THF.

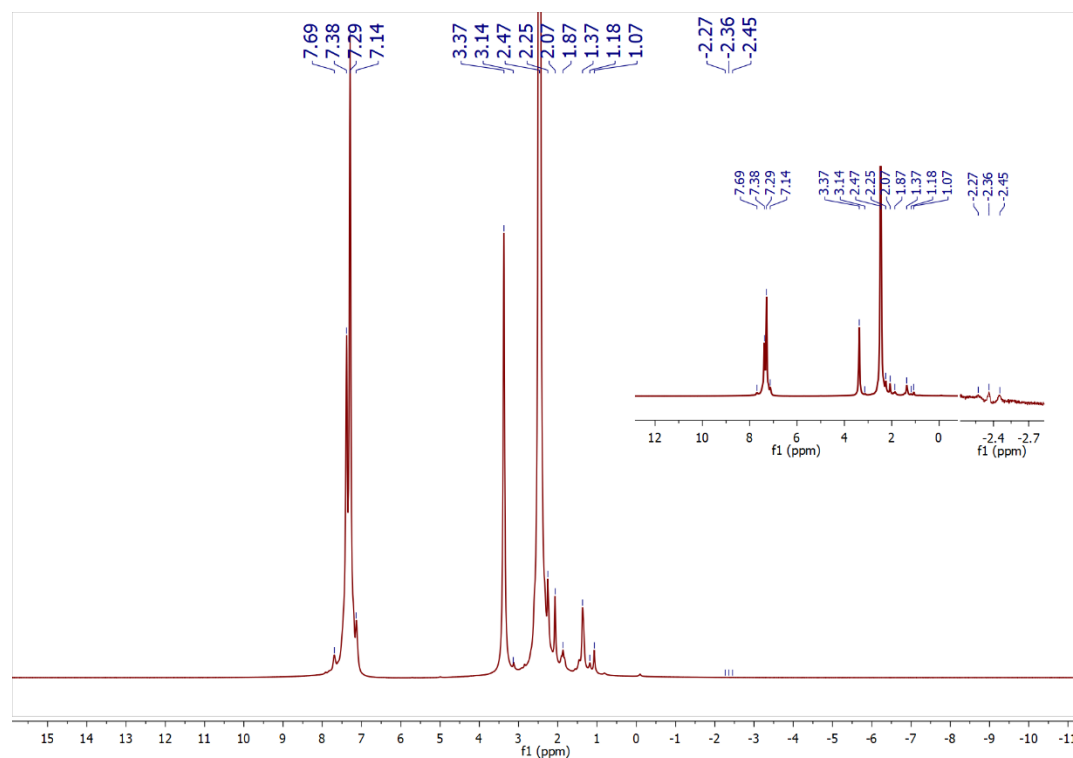


Figure S34 ^1H NMR (500 MHz) in DMSO- d_6 after 3 h of heating in presence of 5 equiv. NaOH in THF enlarged between -1.5 ppm to -10 ppm.

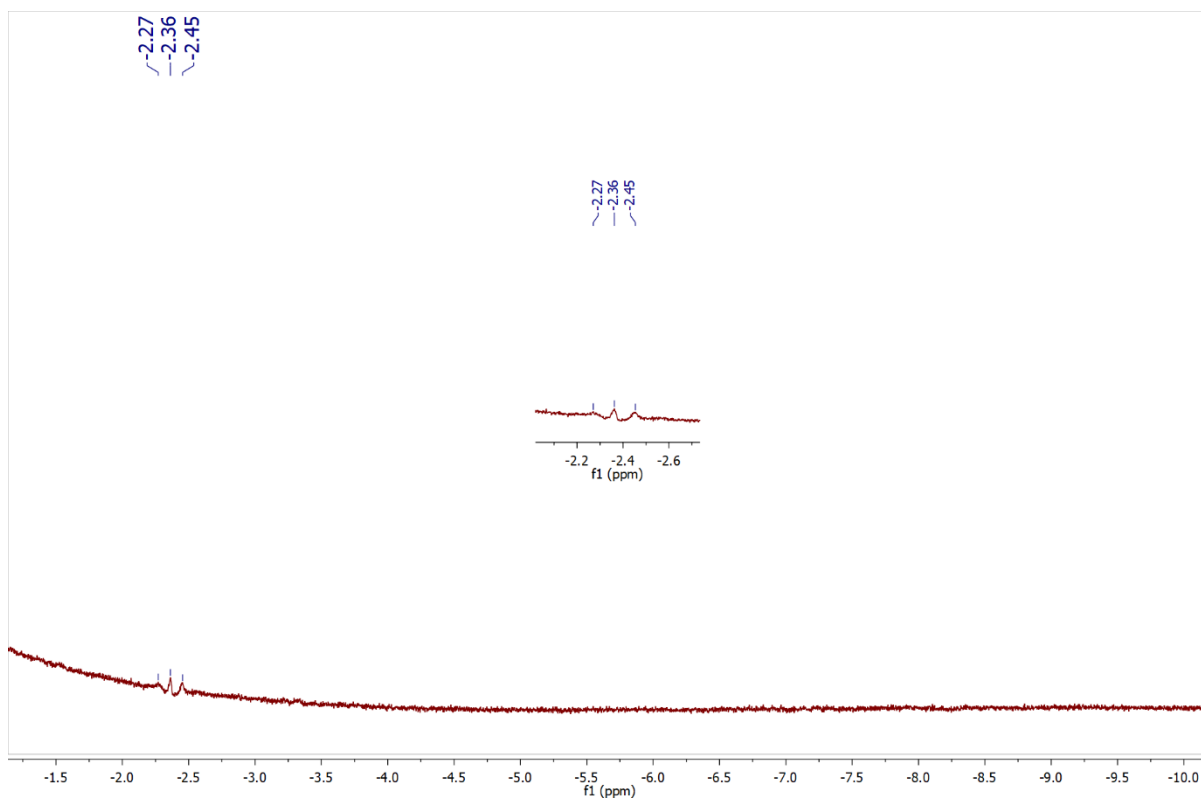


Figure S35 ^{13}C NMR (126 MHz) in THF d_8 after 3 h of heating of **C-3** in presence of 5 equiv. NaOH in THF.

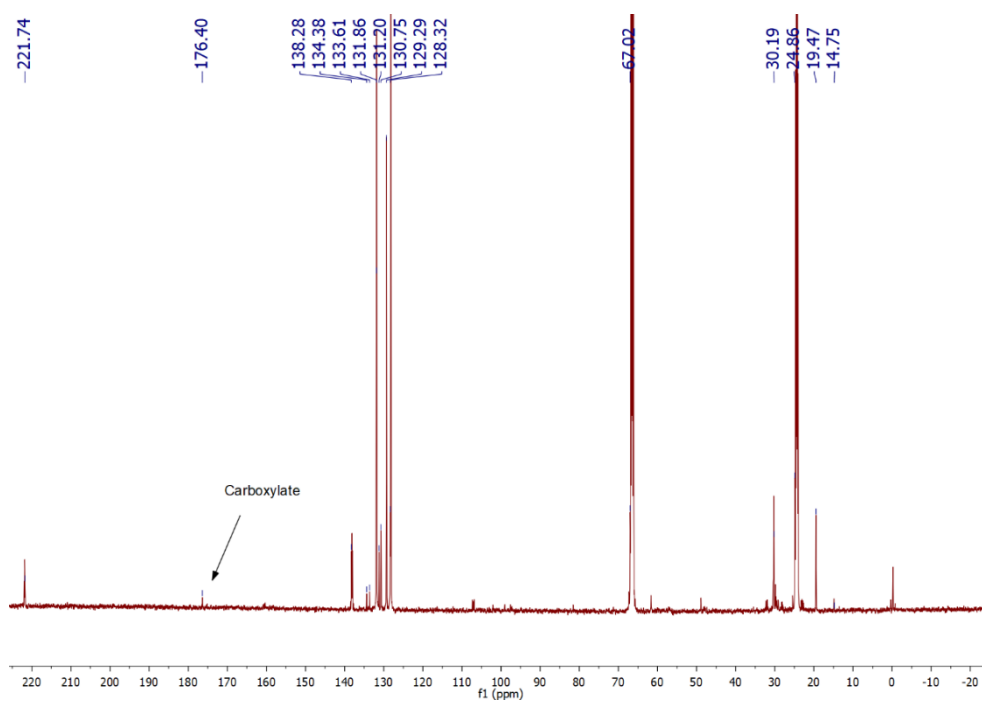


Figure S36 IR spectra after 3 h of heating **C-3** in the presence of 5 equiv. NaOH in THF.

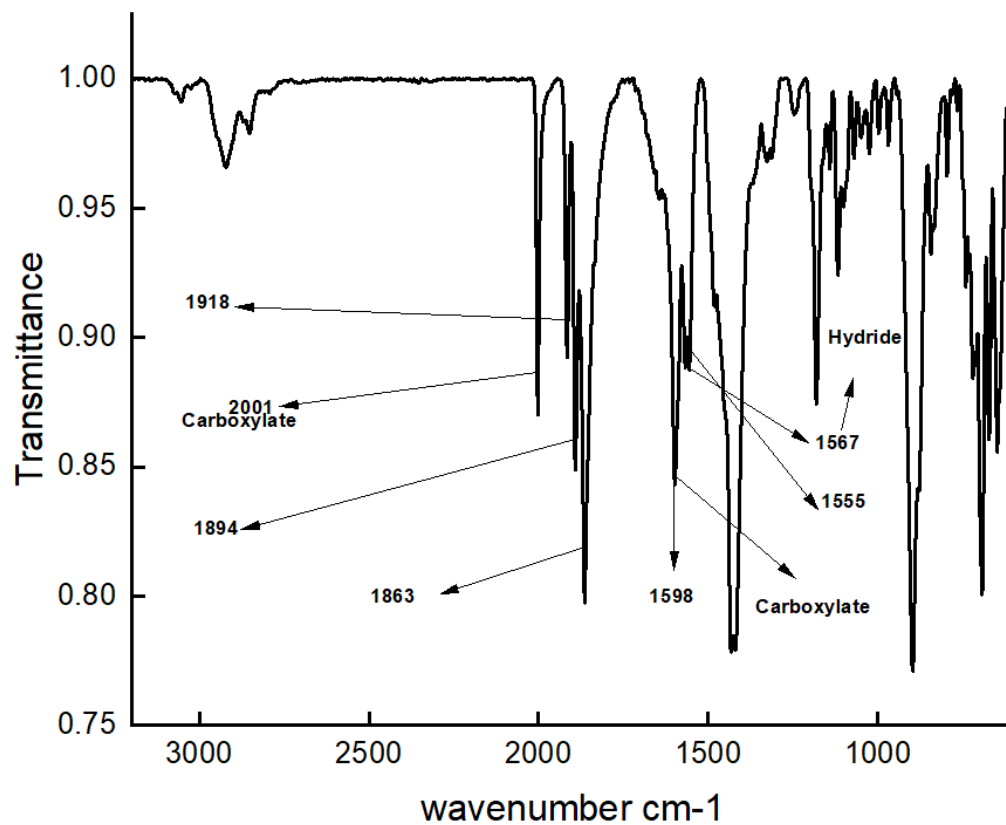


Figure S37 Zoomed IR spectra after 3 h of **C-3** heating in presence of 5 equiv. NaOH in THF.

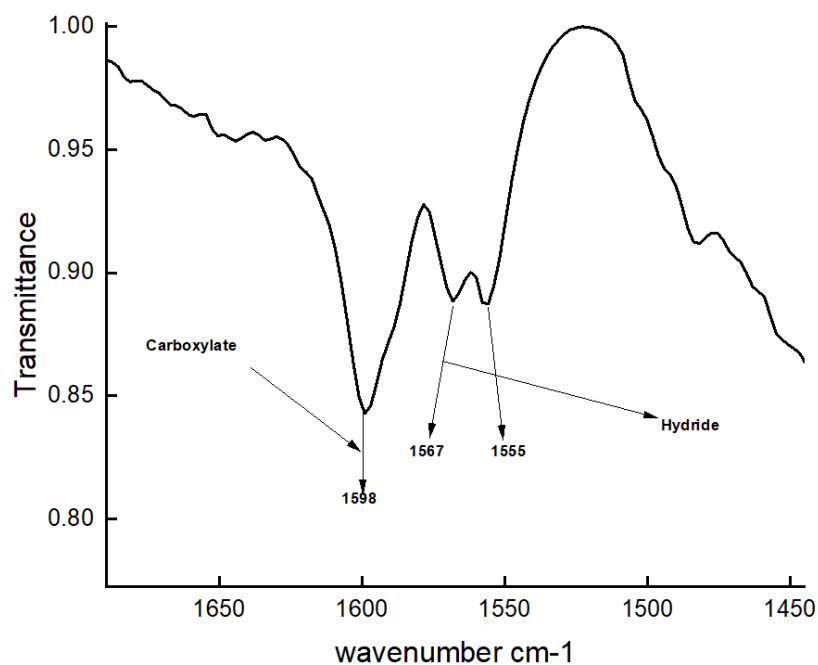


Figure S38 Simulated IR spectra for hydride intermediate **C-3b**.

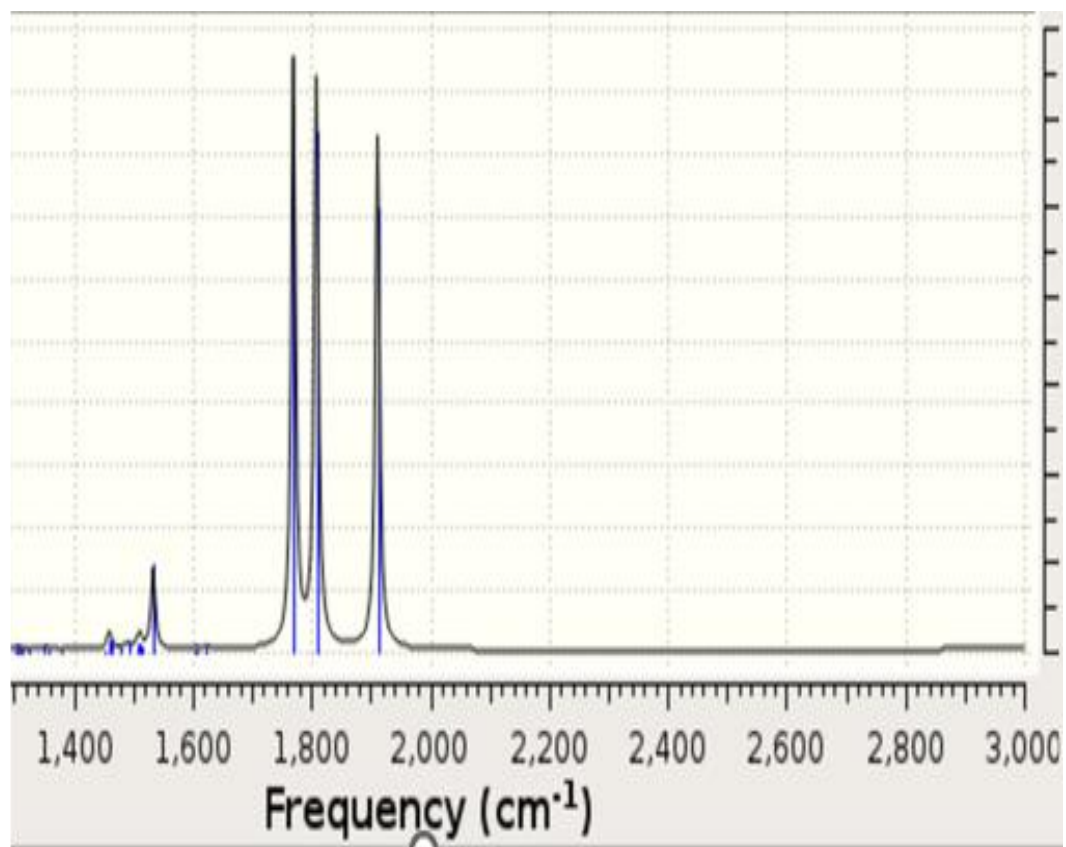


Figure S39 HRMS data of the reaction mixture taken after 3 h heating of **C-3** in presence of 5 equiv. NaOH in THF.

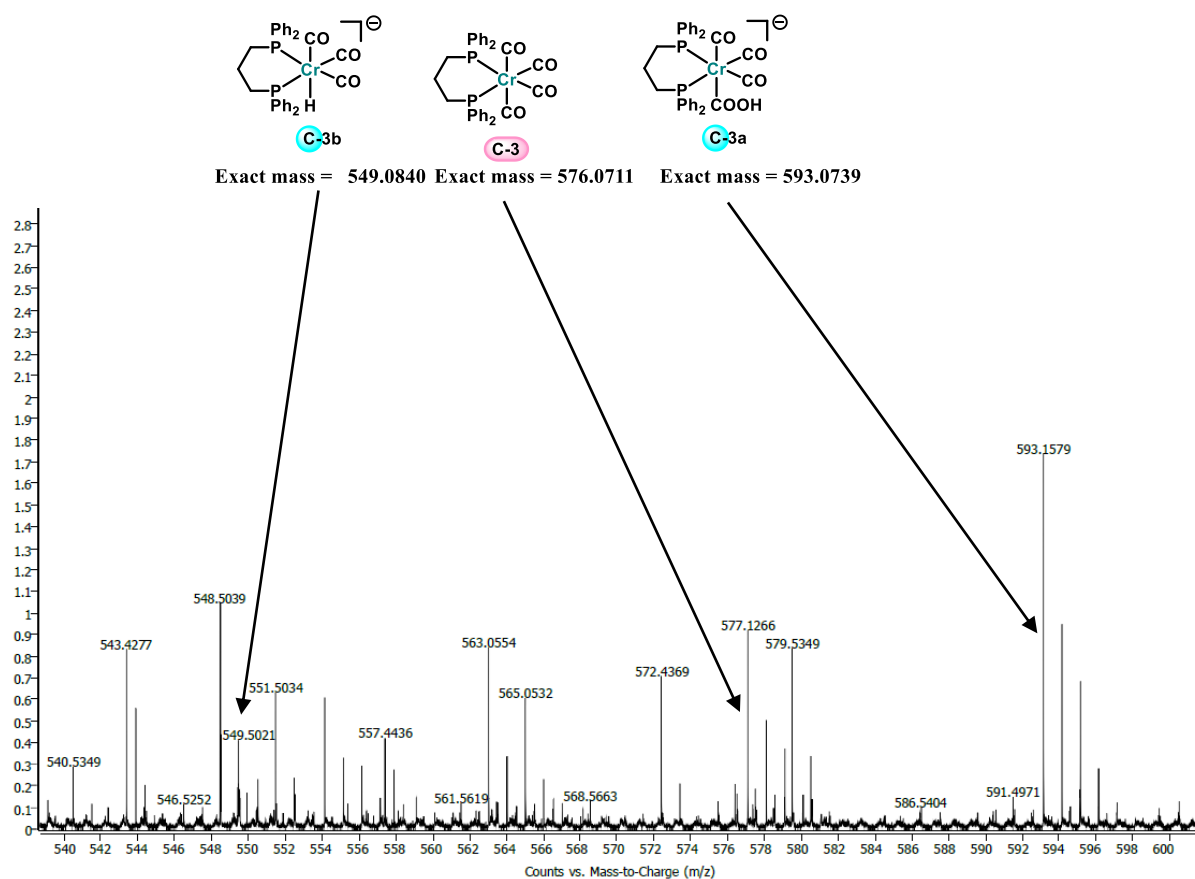


Figure S40 ^{31}P NMR (203 MHz) in THF d-8 of reaction mixture heated **C-3** for 3 h in presence of 5 equiv. NaOH

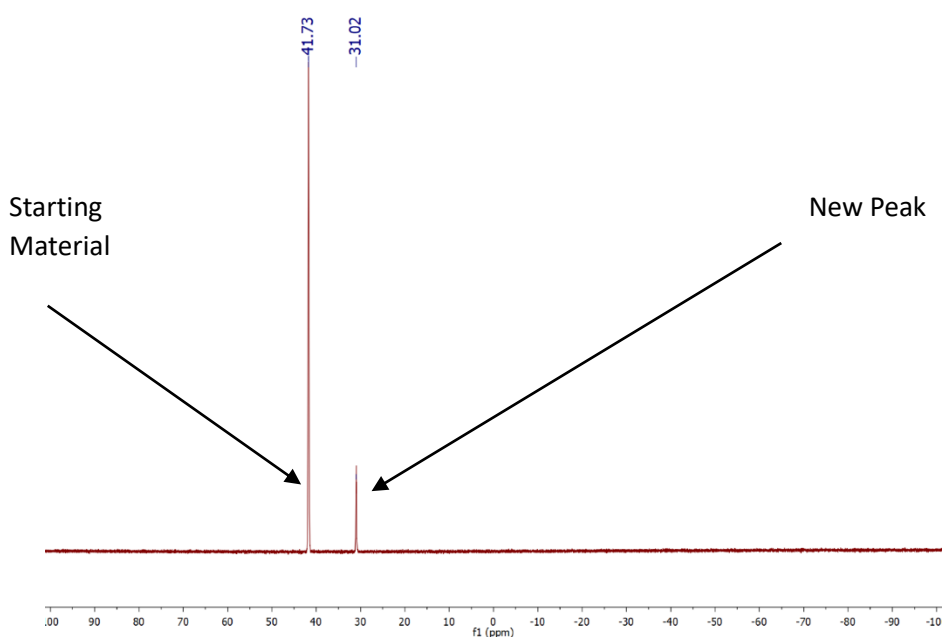


Figure S41 ^1H NMR (500 MHz) in DMSO-d₆ of **C-3** reaction mixture heated for 24 h in THF.

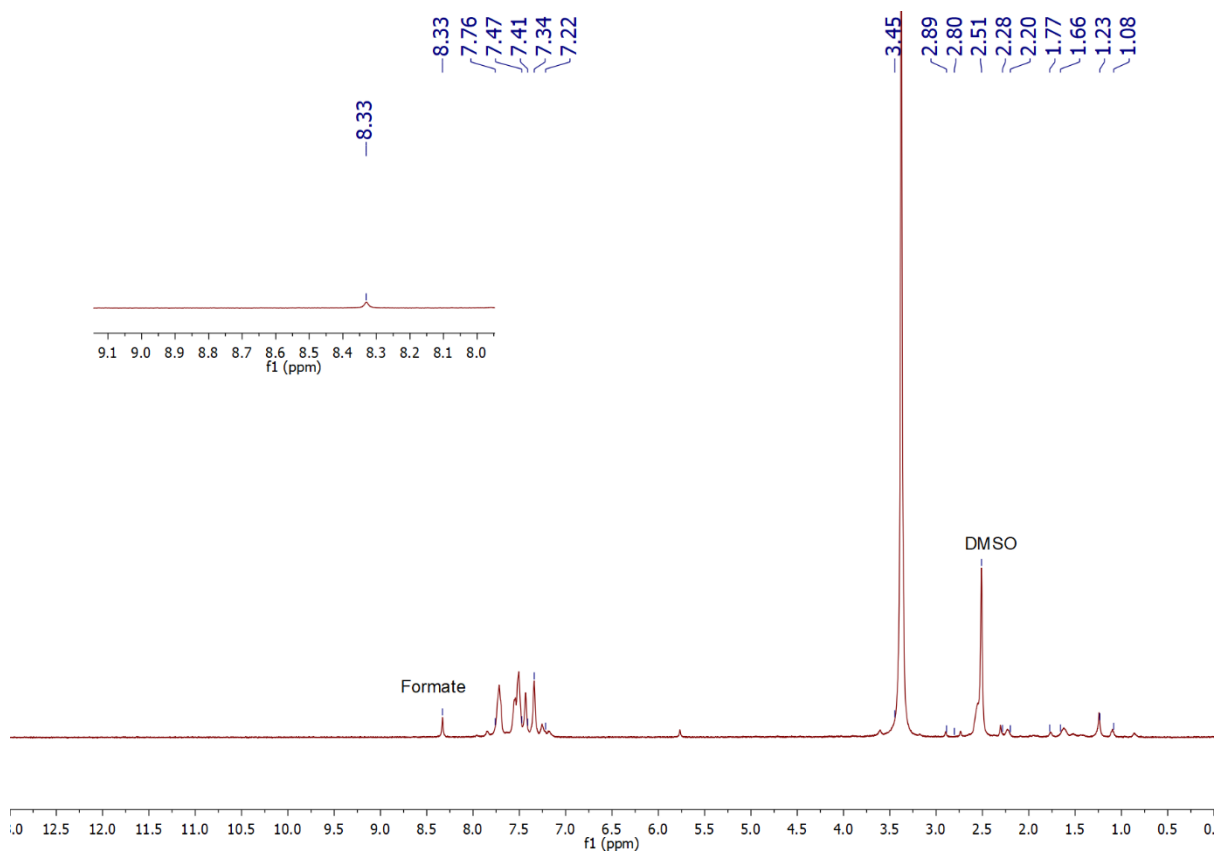


Figure S42 ^{31}P NMR (203 MHz) in DMSO- d_6 of the **C-3** reaction mixture heated for 24 h in THF.

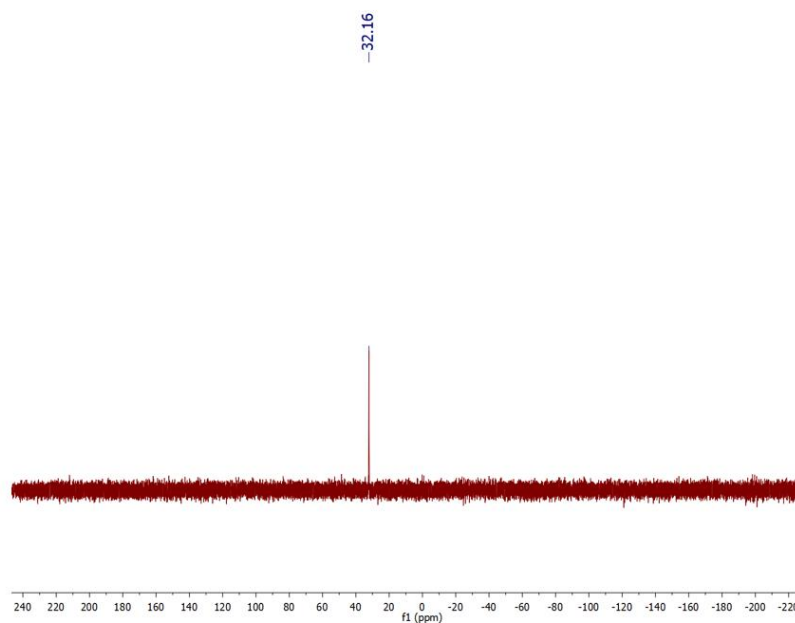


Figure S43 IR spectra of **C-3** reaction mixture heated for 24 h in THF.

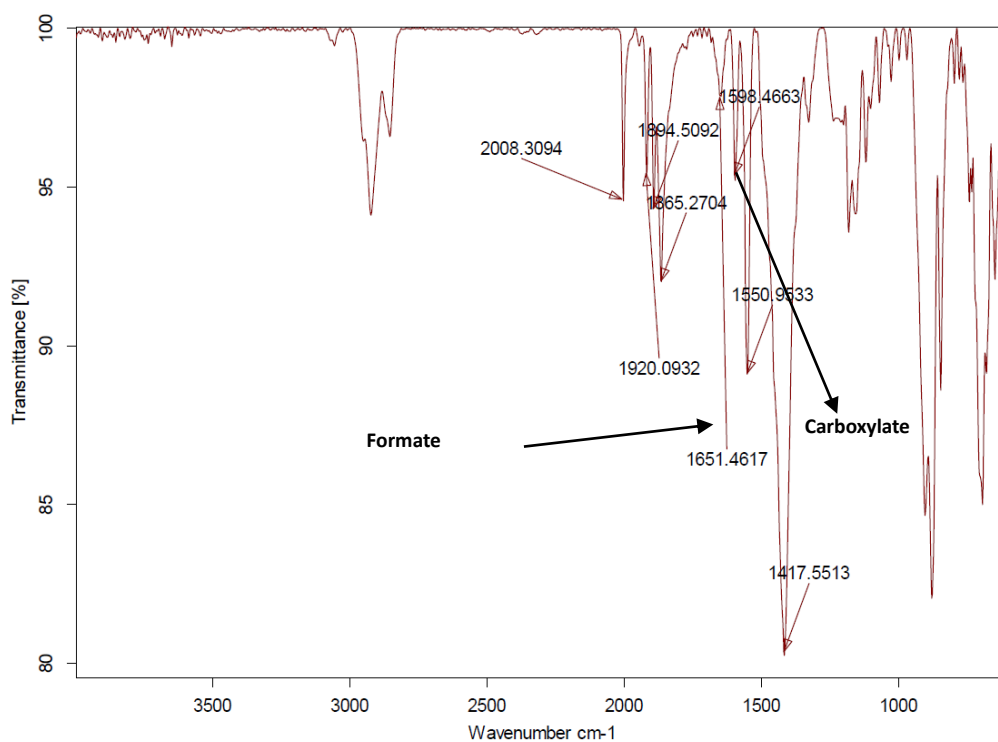


Figure S44 ^1H NMR (500 MHz) in DMSO- d_6 of **C-3** reaction mixture heated for 16 h in *i*PrOH in the presence of 5 equiv. NaOH base.

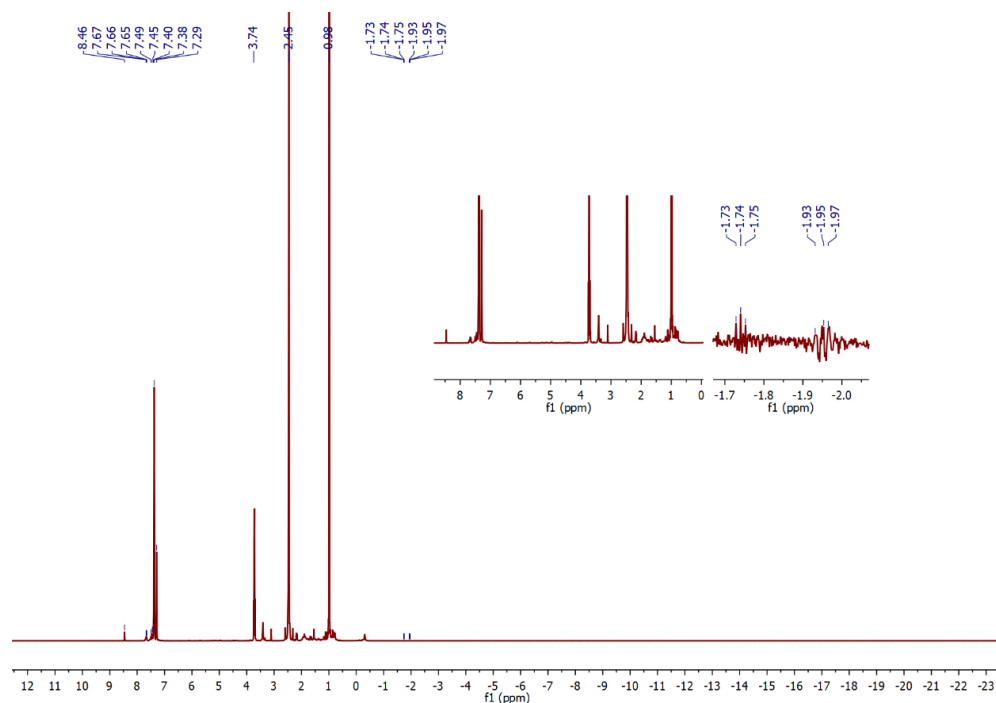


Figure S45 ^{31}P NMR (203 MHz) in DMSO d_6 of **C-3** reaction mixture heated for 16 h in *i*PrOH in the presence of 5 equiv. NaOH base.

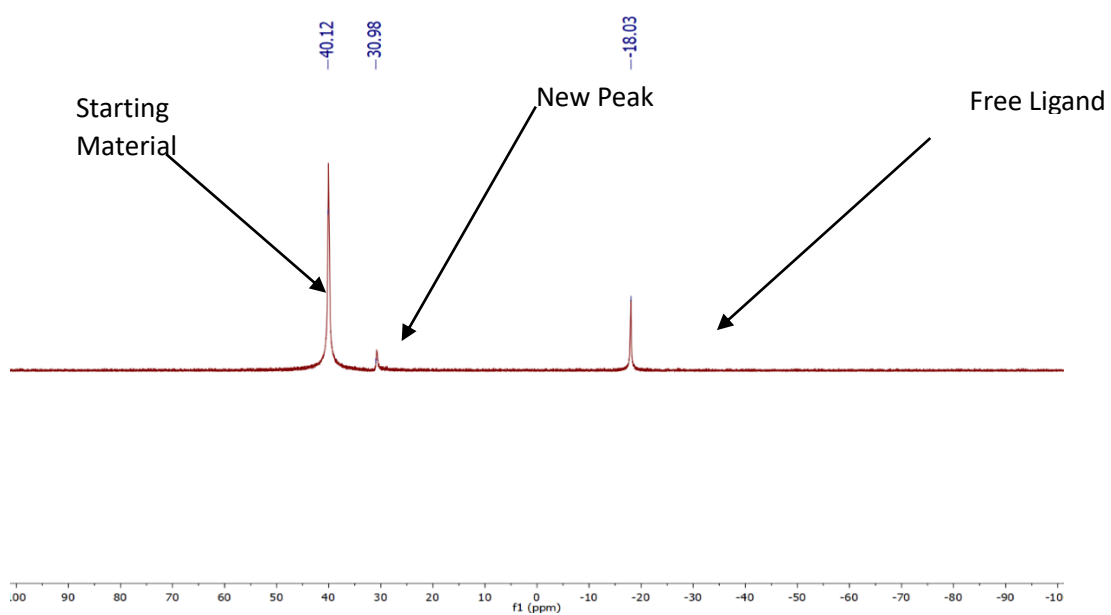
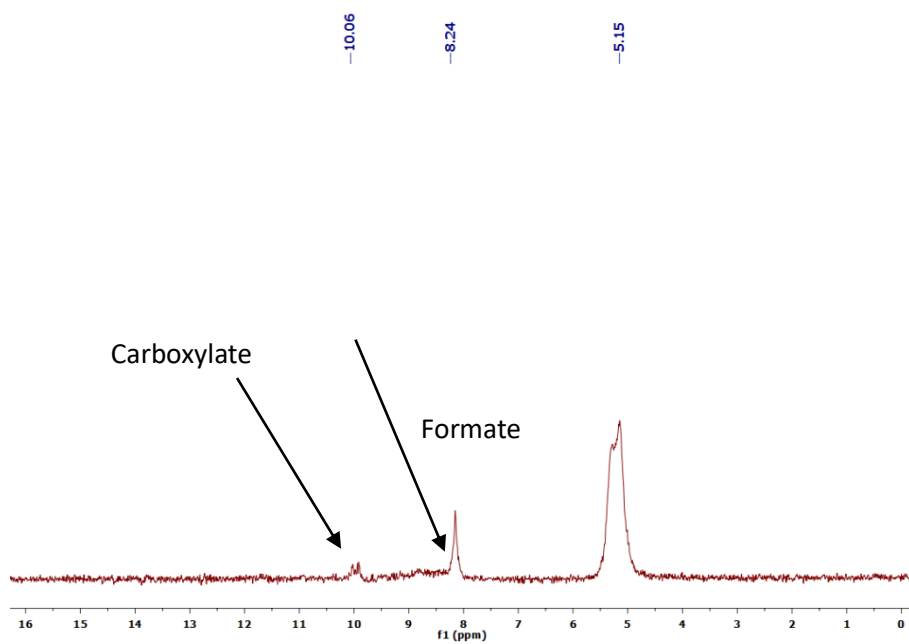


Figure S46 ^2H NMR of **C-3** reaction mixture heated for 24 h in THF in presence of 5 eq. NaOD in D_2O solution at 130 °C.



11. References:

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