

Electronic Supplementary Information (ESI)

A phosphine-free molecularly-defined Ni(II) complex in catalytic hydrogenation of CO₂

Ritu Bhardwaj^a and Joyanta Choudhury^{a*}

^aOrganometallics & Smart Materials Laboratory, Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal 462066, India.

E-mail: joyanta@iiserb.ac.in

I. General information

^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; DMSO-d_6 : 2.50 ppm. CO_2 (purity 99.999%) and H_2 (purity 99.999%) gases were purchased from INOX Air Products Pvt. Ltd. Single crystal X-ray diffraction measurements were performed with Bruker APEX-II CCD instrument. The Solvents utilized were dried manually. TMG and DBU was purchased from commercial suppliers and used without further purification. Deuterated solvents were purchased from CIL (Cambridge Isotope Laboratory).

II. Synthesis of the $[\text{CNCNi}]$ complex

(a) Synthesis of ligand **L**, 3,6-Di-tert-butyl-1,8-bis(3-methylimidazolium)-carbazole diiodide. The ligand **L** was prepared according to literature procedure.^{S1,S2}

^1H NMR (500 MHz, DMSO-d_6 , 298 K): δ 1.46 (s, 18H), 4.00 (s, 6H), 7.75 (s, 2H), 8.05 (d, 2H, $^3J(\text{HH})$ 3.0 Hz), 8.24 (d, $^3J(\text{HH})$ 3.0 Hz, 2H), 8.64 (s, 2H), 9.74 (s, 2H), 11.43 (s, 1H).

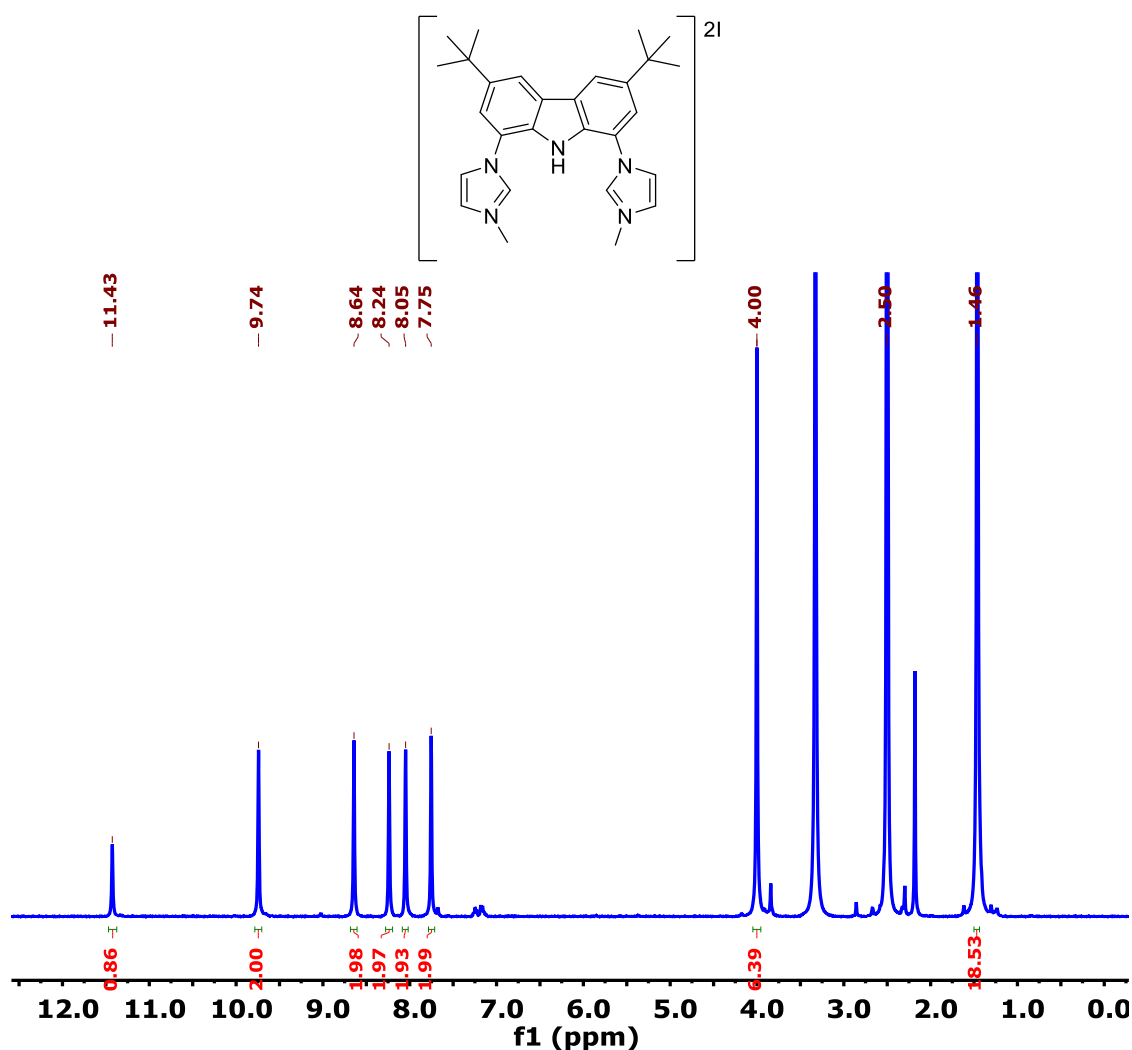
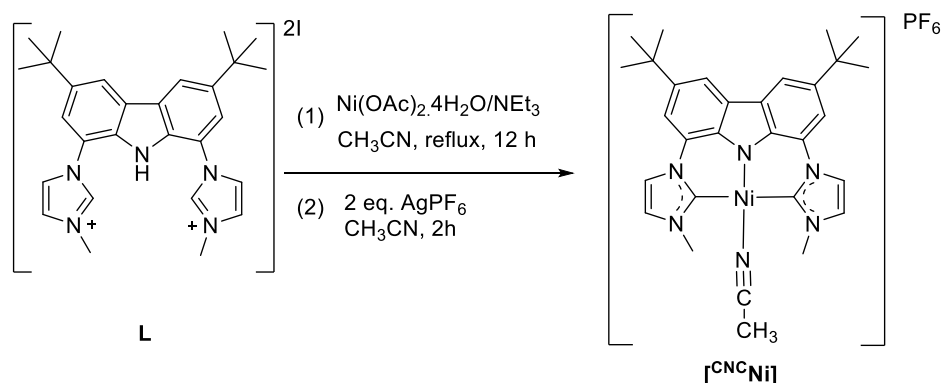


Figure S1. ^1H NMR spectrum of **L** in DMSO-d_6 .

(b) Synthesis of $[\text{CNCNi}]$



Ligand **L** (1.00 g, 1.44 mmol) was dissolved in acetonitrile (5 mL) and heated and stirred at 60 °C. 1.48 mL of triethylamine (1.07 g, 10.6 mmol) was added to the reaction mixture, followed by addition of 0.40 g (1.61 mmol) of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$. Upon refluxing overnight and then filtering through celite a brown solution was obtained. A brown colored residue was obtained upon solvent evaporation which was washed with water.^{S3} 200 mg of the product obtained was dissolved in acetonitrile and this was followed by the addition of AgPF_6 (2 eq.) to the solution. The suspension was stirred at room temperature for 2 hours and then celite filtered. Recrystallization from acetonitrile hexane mixture afforded the $[\text{CNCNi}]$ complex (150 mg, 0.25 mmol) as a brown solid. Yield = 65 %. ^1H NMR (700 MHz, CD_3CN , 298 K, ppm): δ 1.52 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.93 (s, 3H, CH_3CN), 3.63 (s, 6H, $\text{N}-\text{CH}_3$), 7.22 (s, 2H), 7.68 (s, 2H), 7.94 (d, 2H), 8.20 (d, 2H). ^{13}C NMR (700 MHz, CD_3CN , 298 K, ppm): 156.46, 142.27, 134.60, 127.91, 127.04, 123.39, 118.26, 116.02, 111.10. HRMS (ESI, positive ion): 496.2018 (calcd 496.2006 for $[\text{C}_{28}\text{H}_{32}\text{N}_5\text{Ni}]$)

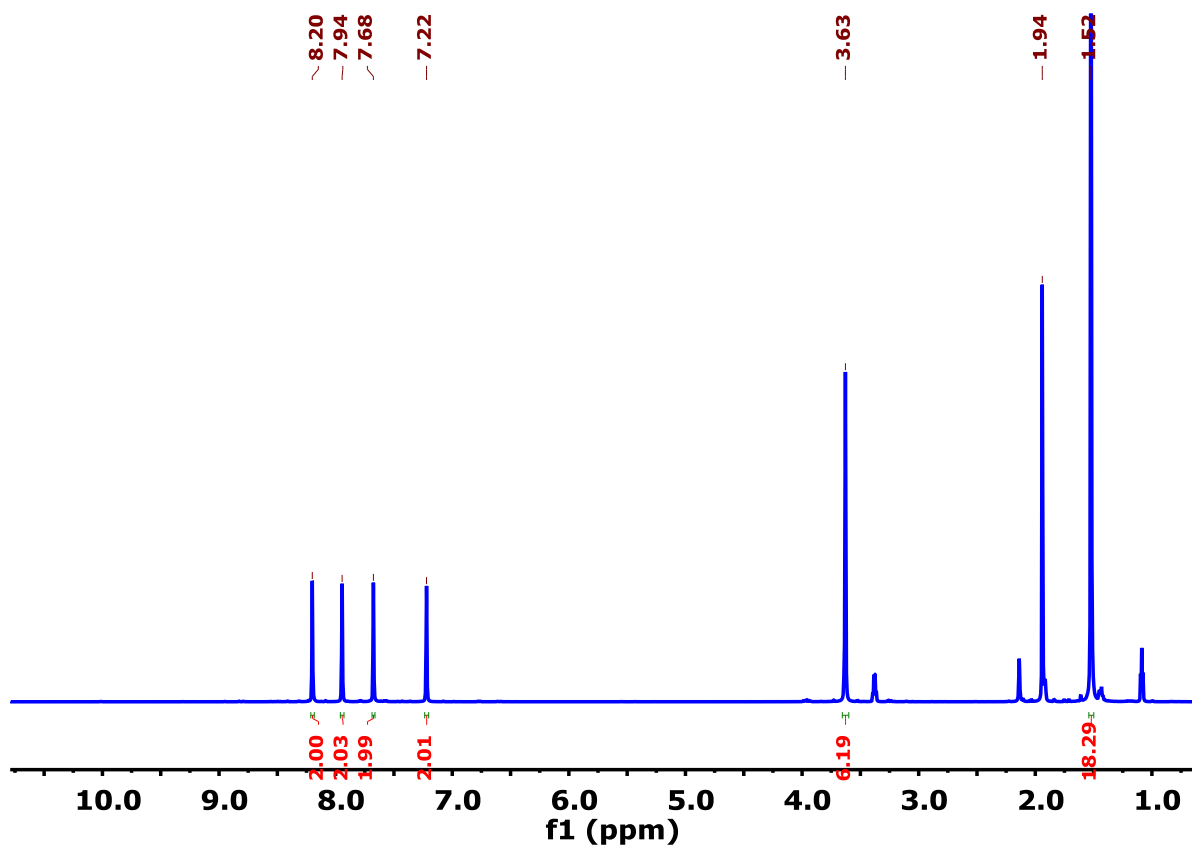


Figure S2. ^1H NMR spectrum of $[\text{CNCNi}]$ in CD_3CN .

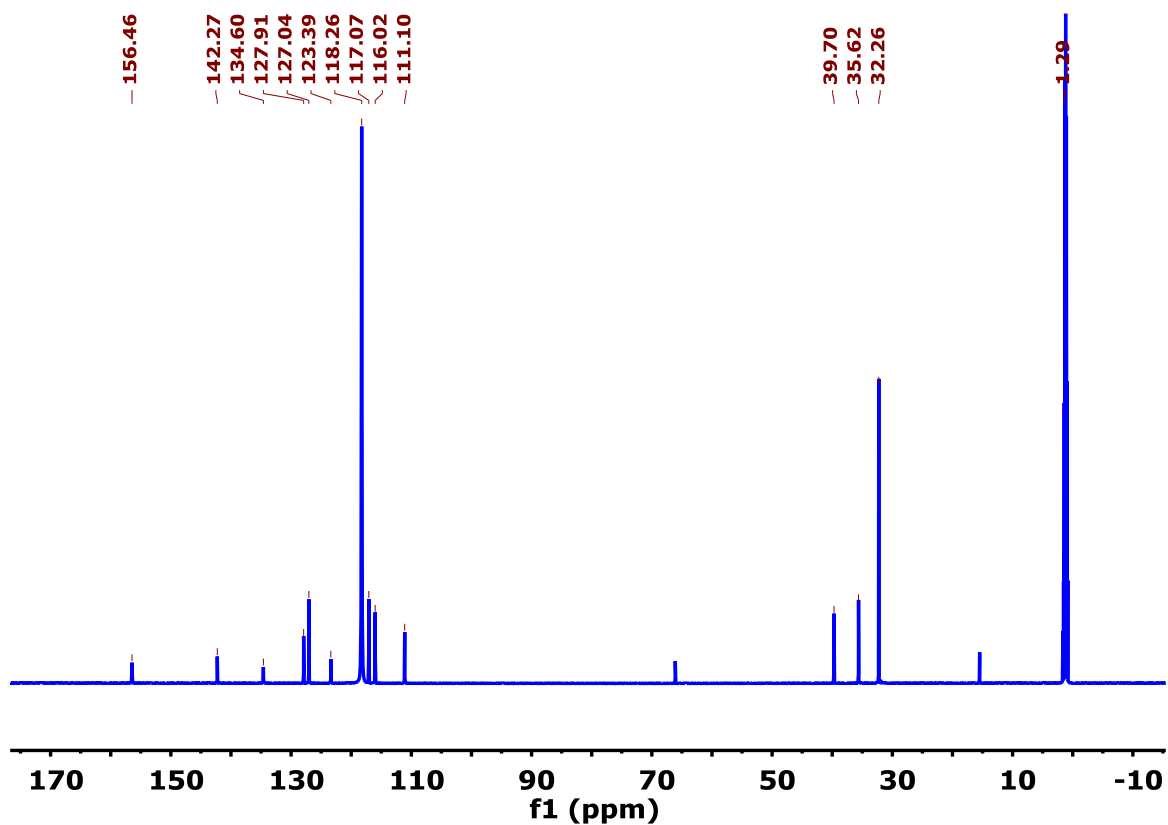


Figure S3. ^{13}C NMR spectrum of $[\text{CNCNi}]$ in CD_3CN .

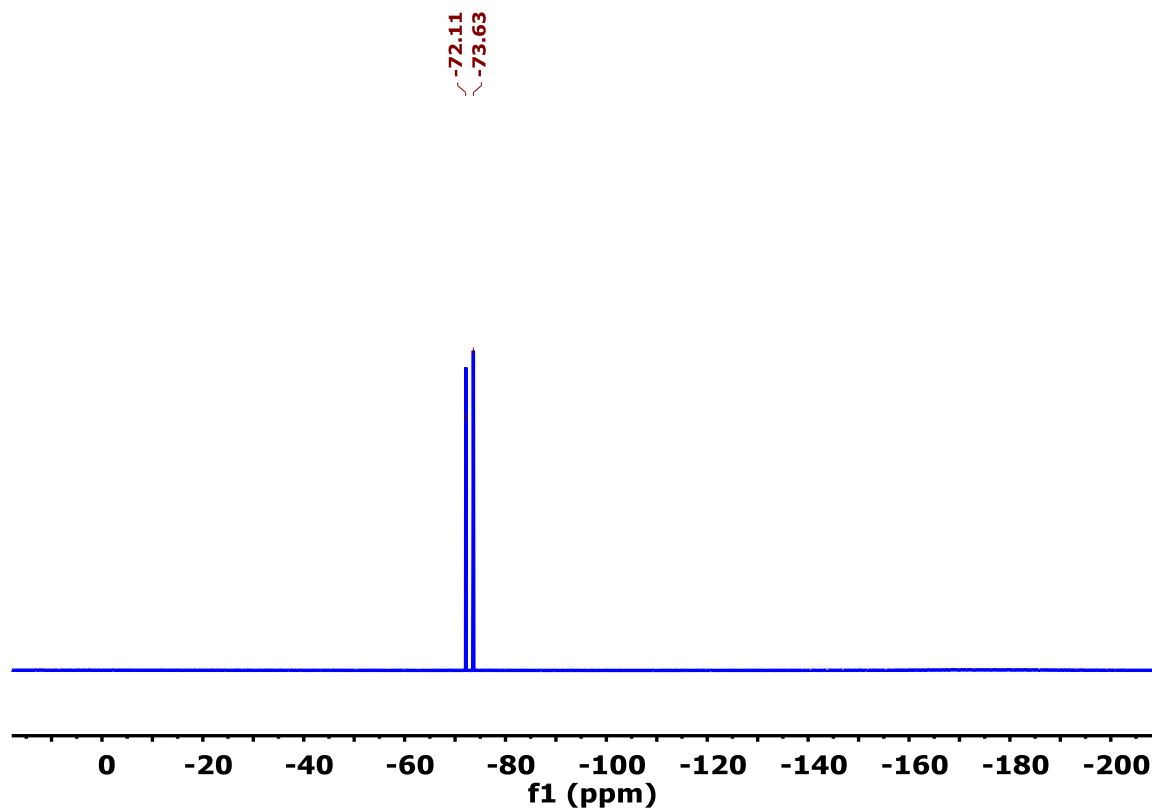


Figure S4. ^{19}F NMR spectrum of $[\text{CNCNi}]$ in CD_3CN .

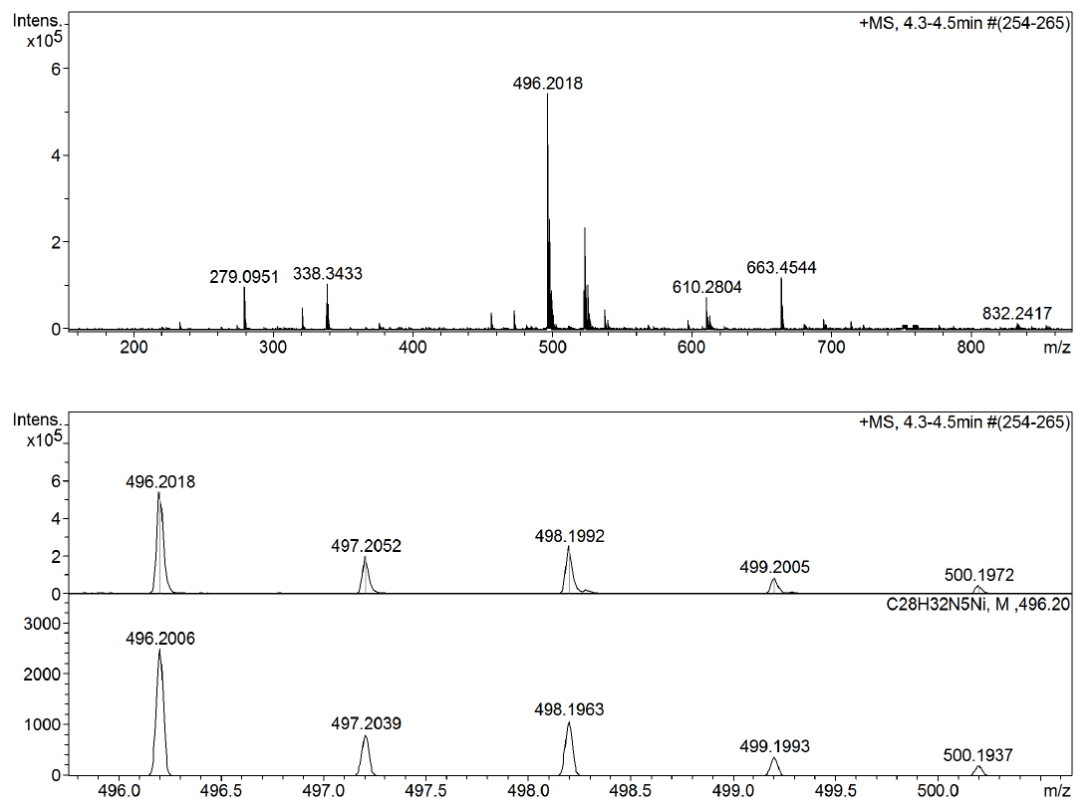


Figure S5. ESI-MS (positive mode) spectrum of $[\text{CNCNi}]$, 496.2018 (calcd 496.2006 for $[\text{C}_{28}\text{H}_{32}\text{N}_5\text{Ni}^+]$)

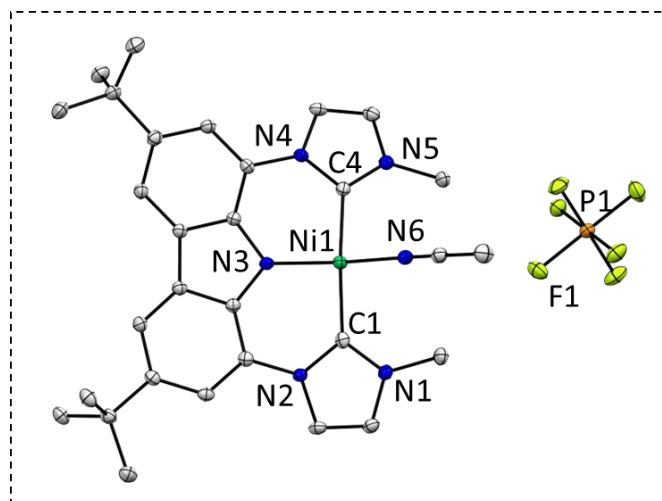


Figure S6. Molecular structure of $[\text{CNCNi}]$ catalyst (50% probability level). Selected bond lengths (\AA) and bond angles ($^\circ$): Ni1-C1 = 1.936, Ni1-C4 = 1.943, Ni1-N3 = 1.832, Ni1-N6 = 1.868, C1-Ni1-N3 = 90.94, C4-Ni1-N3 = 90.95, C4-Ni1-C1 = 161.226 (H-atoms and one free CH_3CN molecule are omitted for clarity. The asymmetric unit consists of two identical molecules).

Table S1 Crystal data and structure refinement for $[\text{CNCNi}]$.

Identification code	F1
Empirical formula	$\text{C}_{62}\text{H}_{73}\text{F}_{12}\text{N}_{13}\text{Ni}_2\text{P}_2$
Formula weight	1407.69
Temperature/K	140.0
Crystal system	monoclinic
Space group	$\text{P2}_1/\text{n}$
$a/\text{\AA}$	21.7635(11)
$b/\text{\AA}$	13.5055(7)
$c/\text{\AA}$	22.7364(12)
$\alpha/^\circ$	90
$\beta/^\circ$	108.365(2)
$\gamma/^\circ$	90
Volume/ \AA^3	6342.5(6)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.474
μ/mm^{-1}	0.731
F(000)	2920.0
Crystal size/ mm^3	$0.17 \times 0.05 \times 0.04$
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073$)
2Θ range for data collection/ $^\circ$	4.346 to 60.308
Index ranges	$-30 \leq h \leq 30, -19 \leq k \leq 19, -32 \leq l \leq 30$
Reflections collected	104927
Independent reflections	18689 [$R_{\text{int}} = 0.1326, R_{\text{sigma}} = 0.1053$]

Data/restraints/parameters 18689/0/839
Goodness-of-fit on F² 1.011
Final R indexes [I>=2σ (I)] R₁ = 0.0563, wR₂ = 0.1162
Final R indexes [all data] R₁ = 0.1238, wR₂ = 0.1439
Largest diff. peak/hole / e Å⁻³ 0.60/-0.44

III. Hydrogenation of CO₂ to formate

Nickel catalyst, base, additive in acetonitrile 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 sodium trimethylsilylpropanesulfonate (DSS) 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.

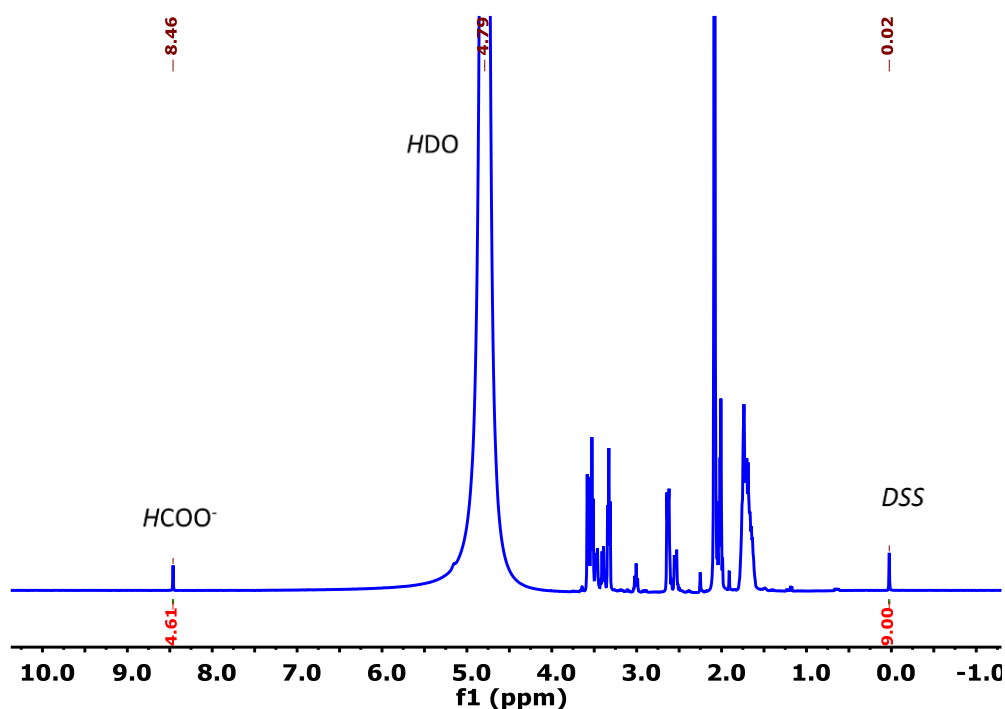


Figure S7. ¹H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO₂ using [^{CNC}Ni] cat. (4.5 μmol) and DBU (6.7 mmol) without adding any Lewis acid additive recorded in D₂O. DSS (0.091 mmol, 20 mg) added as internal standard.

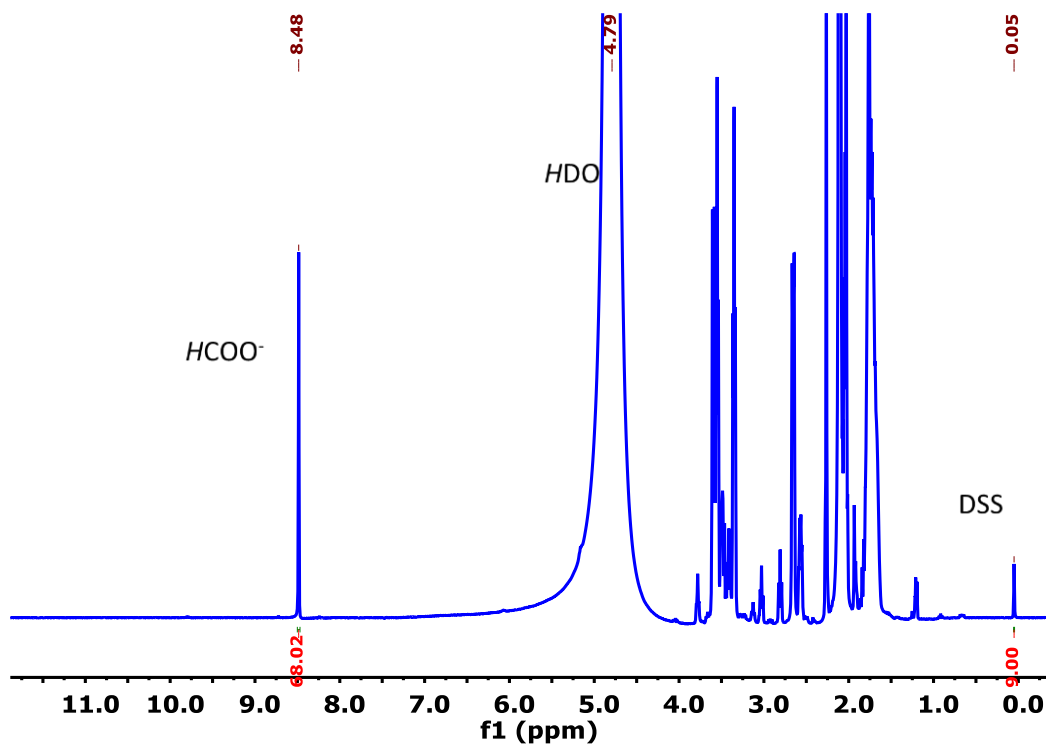


Figure S8. ^1H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 using $[\text{C}^{\text{NC}}\text{Ni}]$ cat. ($4.5\ \mu\text{mol}$) and DBU ($6.7\ \text{mmol}$) with $\text{Zn}(\text{OAc})_2$ ($1.5\ \text{mmol}$) additive recorded in D_2O . DSS ($0.091\ \text{mmol}$, $20\ \text{mg}$) added as internal standard.

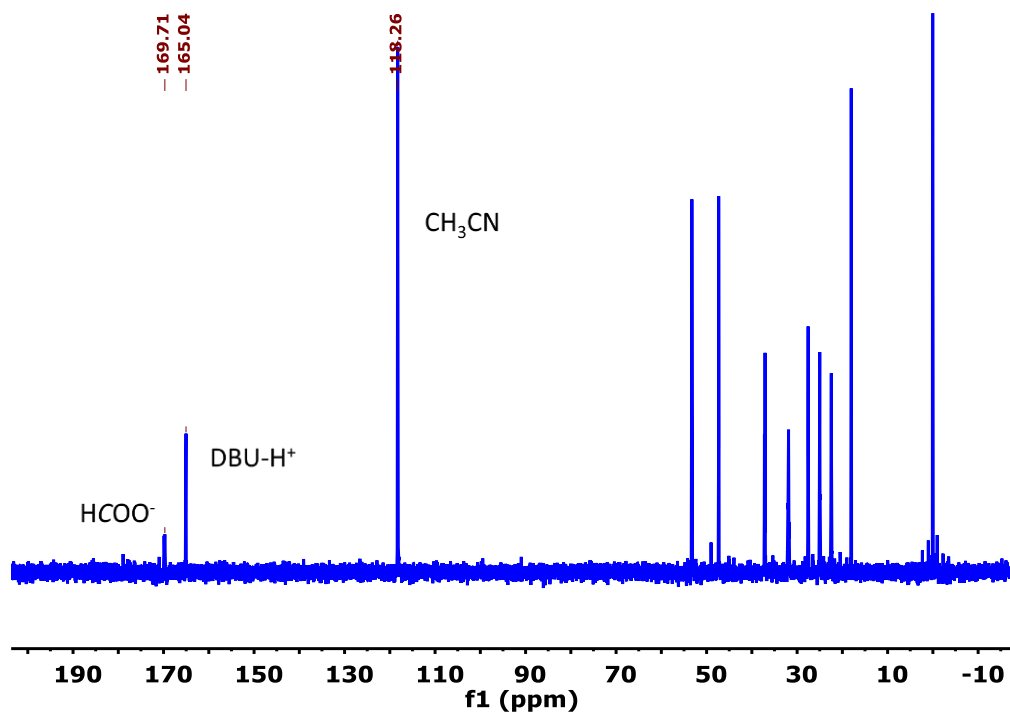


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture obtained after the hydrogenation of CO_2 using $[\text{C}^{\text{NC}}\text{Ni}]$ cat. ($4.5\ \mu\text{mol}$) and DBU ($6.7\ \text{mmol}$) with $\text{Zn}(\text{OAc})_2$ ($1.5\ \text{mmol}$) additive recorded in D_2O . DSS ($0.091\ \text{mmol}$, $20\ \text{mg}$) added as internal standard.

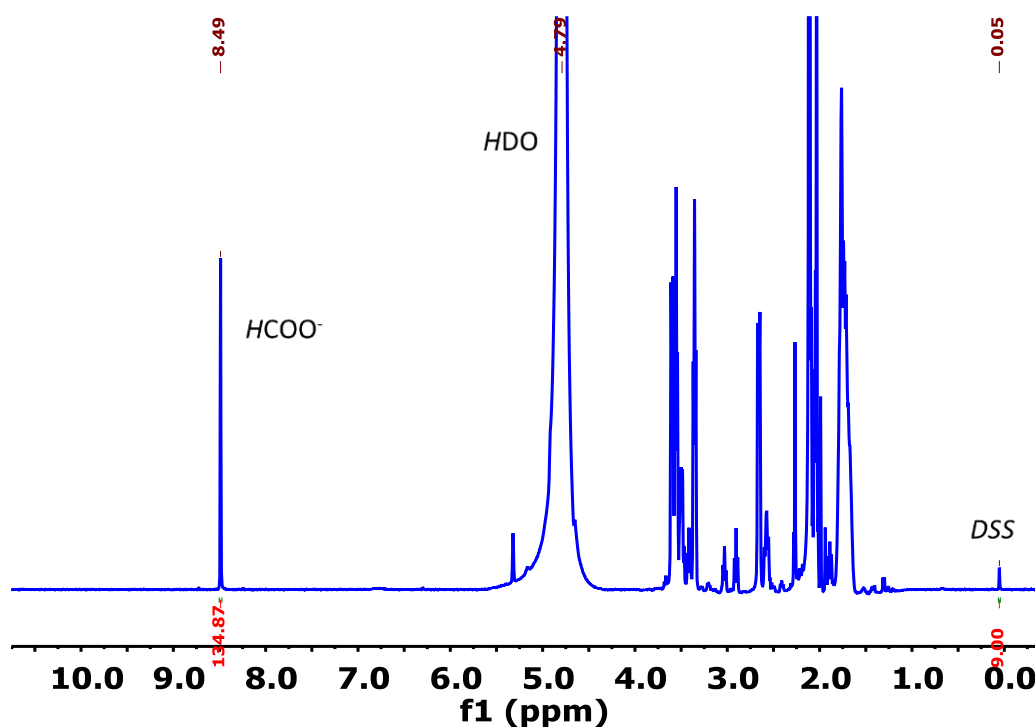


Figure S10. ¹H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO₂ using [CNCNi] cat. (4.5 μmol) and DBU (13.4 mmol) with Zn(OAc)₂ (1.5 mmol) additive recorded in D₂O. DSS (0.091 mmol, 20 mg) added as internal standard.

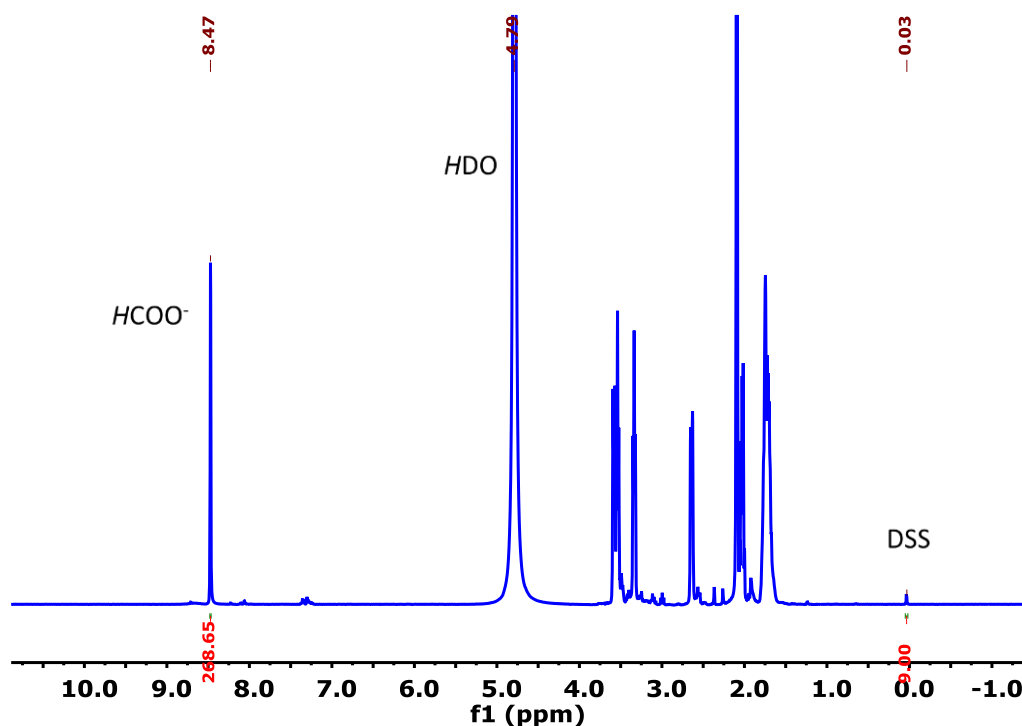


Figure S11. ¹H NMR spectrum of the reaction mixture obtained after the hydrogenation of CO₂ using [CNCNi] cat. (4.5 μmol) and DBU (26.8 mmol) with Zn(OAc)₂ (1.5 mmol) additive recorded in D₂O. DSS (0.091 mmol, 20 mg) added as internal standard.

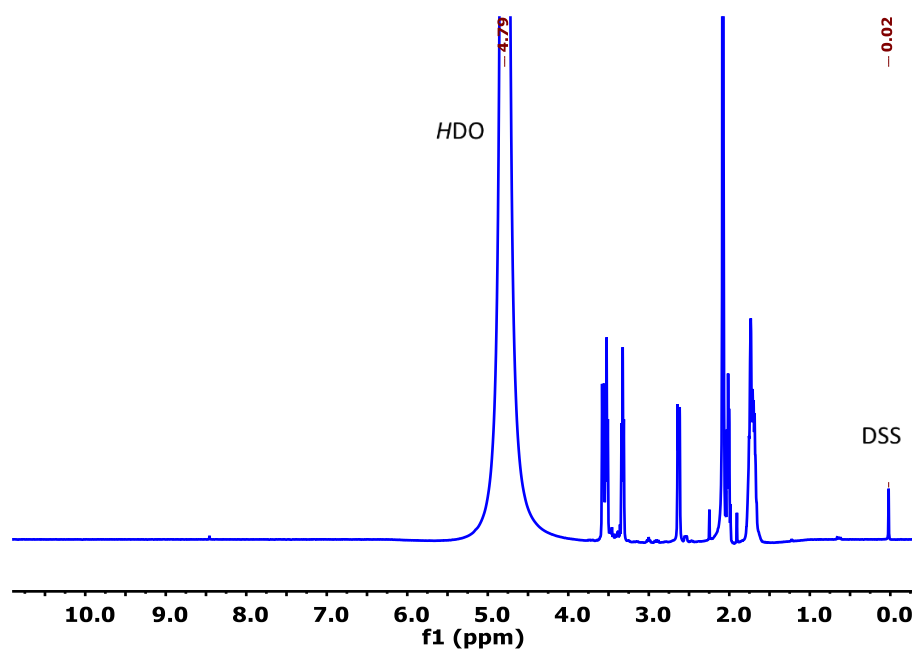


Figure S12. ^1H NMR spectrum of the reaction mixture obtained after the in-situ hydrogenation of CO_2 in the absence of $[\text{CNCNi}]$ cat. ($4.5 \mu\text{mol}$) using DBU (6.7 mmol) with $\text{Zn}(\text{OAc})_2$ (1.5 mmol) additive recorded in D_2O . DSS (0.091 mmol , 20 mg) added as internal standard.

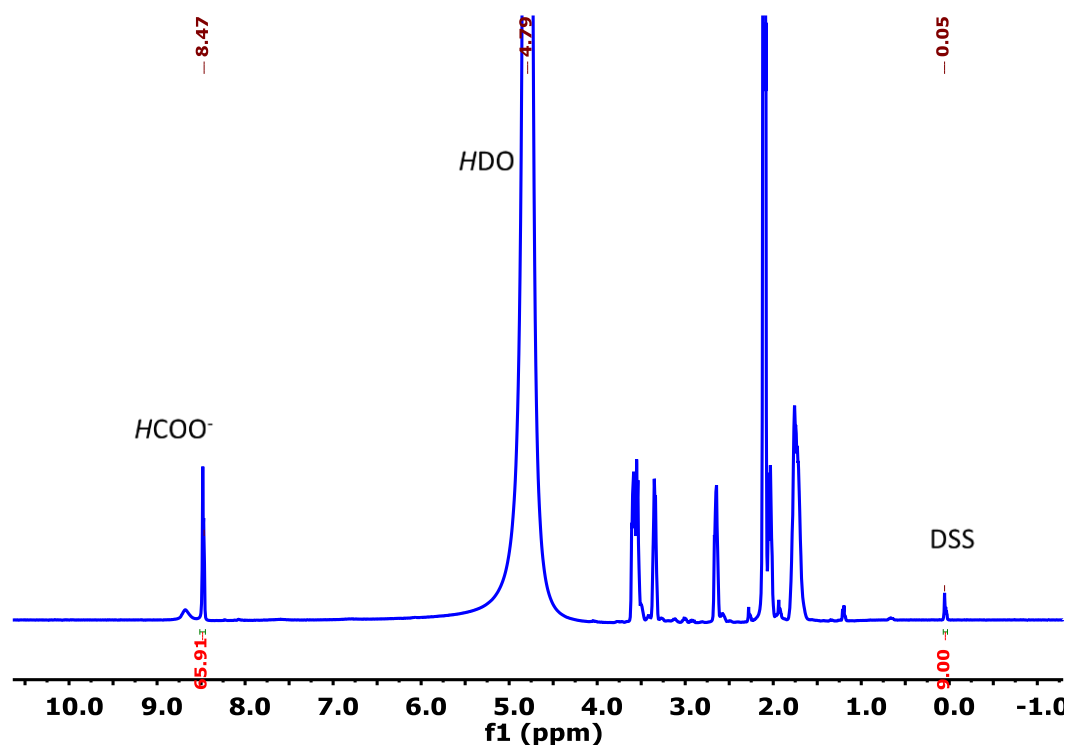


Figure S13. ^1H NMR spectrum of the reaction mixture obtained after the in-situ hydrogenation of CO_2 using $[\text{CNCNi}]$ cat. ($4.5 \mu\text{mol}$) and DBU (6.7 mmol) with ZnCl_2 (1.5 mmol) additive recorded in D_2O . DSS (0.091 mmol , 20 mg) added as internal standard.

IV. Plausible catalytic cycle

A plausible catalytic reaction mechanism is proposed based on previous literature reports (Fig S14).^{S4, S5} CH₃CN dissociation from the [CNCNi] complex and H₂ cleavage in the presence of base, DBU will result in the formation of the Ni-H species. The Ni-H species will then react with CO₂ to afford the Ni-formate species. The formate then dissociates and the base stabilized adduct, [DBUH⁺][HCOO⁻] is obtained as the product.

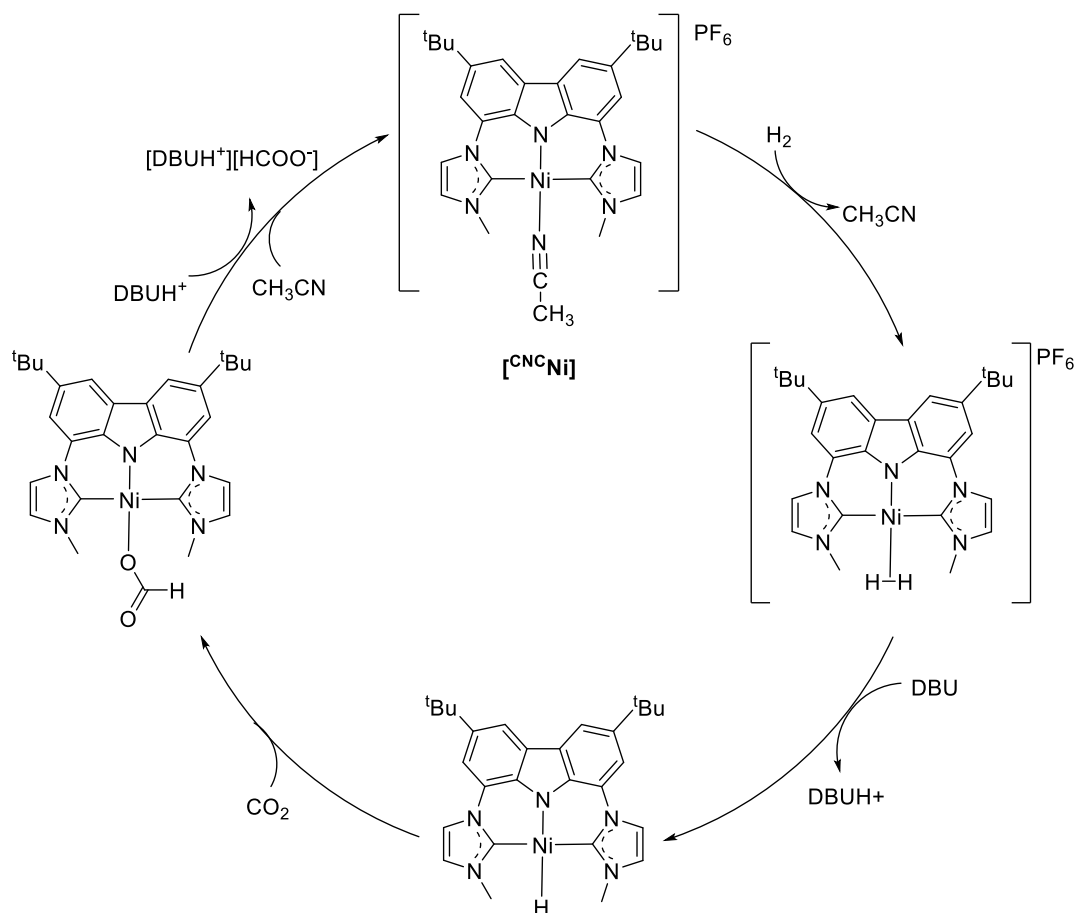


Figure S14. Plausible catalytic cycle for the CO₂ hydrogenation reaction using [CNCNi].

V. References

- S1. N. Sinha, B. Pfund, C. Wegeberg, A. Prescimone and O. S. Wenger, *J. Am. Chem. Soc.*, 2022, **144**, 9859-9873.
- S2. M. Moser, B. Wucher, D. Kunz and F. Rominger, *Organometallics*, 2007, **26**, 1024-1030.
- S3. T.-Y. Lee, Y.-J. Lin, Y.-Z. Chang, L.-S. Huang, B.-T. Ko and J.-H. Huang, *Organometallics*, 2017, **36**, 291-297.
- S4. S. Enthaler, A. Brück, A. Kammer, H. Junge, E. Irran and S. Gülak, *ChemCatChem*, 2015, **7**, 65-69.
- S5. S. A. Burgess, A. J. Kendall, D. R. Tyler, J. C. Linehan and A. M. Appel, *ACS Catal.*, 2017, **7**, 3089-3096.