SUPPORTING INFORMATION

Hydrogenation of CO_2 into formate using Iridium catalyst containing proton responsive imidazoline-amide ligands

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1. Experimental section

General Methods: Unless otherwise noted, chemicals were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, Loba, SD Fine and SRL Pvt. Ltd) and used without further purification. Carbon dioxide (purity 99.9%) and hydrogen (purity 99.9%) were sourced from Chemtron Science Laboratories Pvt. Ltd. All manipulations were carried out under laboratory atmosphere and all aqueous solutions were degassed by passing nitrogen prior to use. Synthesis of ligands were performed in oven-dried glassware flushed with nitrogen. However, all CO_2 hydrogenation reactions were performed in a 250 mL batch reactor (Parr Instruments, USA) flushed with nitrogen. ^{1}H NMR and ^{13}C NMR spectra were recorded in a Bruker Avanceneo 600 spectrometer using appropriate (D_2O, DMSO-d_6) solvent. Formate concentrations were determined by ^{1}H NMR analysis using sodium acetate as internal standard. The GC-mass spectrometric analysis was carried out using High Resolution Q-TOF Mass Spectrometer, equipped FID detector and capillary column (SH-Rtx-1701, length 60 meter, inner diameter 0.25 mm, film 0.25 mm). TLC inspections were performed on Silica gel 60 F254 plates. Column chromatography was performed on silica gel (60-120 mesh) using ethyl acetate/n-hexane as eluent.

Synthesis of Iridium catalysts

ImA-1: To a stirred solution of Cp*Ir$(OH_2)_3$.SO_4 (320 mg, 0.67 mmol) in water was added imidazoline-amide[1] (126 mg, 0.67 mmol**)** and the mixture was stirred at room temperature for 16 hours. Then the solution was filtered, and the filtrate was concentrated under reduced pressure to yield **ImA-1** as a bright yellow solid (374 mg, 89%).

^{1}H NMR (600 MHz, D_2O): δ (ppm) 1.34 (15H, s), 3.83 (2H, t, *J* = 10.2 Hz), 4.14 (2H, t, *J* = 10.2 Hz), 7.06 (2H, d, *J* = 7.2 Hz,), 7.19 (1H, t, *J* = 7.2 Hz), 7.38 (2H, t, *J* = 7.8 Hz).
^{13}C NMR (150 MHz, D_2O): δ (ppm) 8.1, 45.5, 52.0, 86.4, 125.6, 126.1, 129.0, 145.7, 164.6, 168.1
ESI-MS(+): *m/z* 516 [(M−H_2O−HSO_4^-) + 1].
Anal. Calc. for $C_{20}H_{28}IrN_3O_6S$: C 38.09, H 4.47, N 6.66. Found: C 37.97, H 4.51, N 6.57

ImA-2: To a stirred solution of Cp*Ir$(OH_2)_3$.SO_4 (34 mg, 0.0712 mmol) in water (15 mL) was added cyclohexyl imidazoline-amide[2] (17.3 mg, 0.0712 mmol**)** and the mixture was stirred at room temperature for 16 hours. Then the solution was filtered, and the filtrate was concentrated under reduced pressure to yield **ImA-2** as a bright yellow solid (42 mg, 92%).

^{1}H NMR (600 MHz, D_2O): δ (ppm) 1.28–1.75 (8H, m), 1.32 (15H, s), 4.17-4.20 (1H, m), 4.36-4.37 (1H, m), 7.11 (2H, d, *J* = 7.2 Hz,), 7.20 (1H, t, *J* = 7.8 Hz), 7.39 (2H, t, *J* = 8.4 Hz).
^{13}C NMR (150 MHz, D_2O): δ (ppm) 8.0, 18.9, 19.5, 25.3, 26.7, 57.9, 62.0, 86.2, 125.5, 126.1, 129.0, 145.7, 165.2, 167.3
ESI-MS(+): *m/z* 570 [(M−H_2O−HSO_4^-) + 1].
Anal. Calc. for $C_{24}H_{34}IrN_3O_6S$: C 42.09, H 5.00, N 6.14. Found: C 41.95, H 5.08, N 6.21

ImA-3: To a stirred solution of Cp*Ir$(OH_2)_3$.SO_4 (68 mg, 0.143 mmol) in water (30 mL) was added benzimidazole-amide[3] (34 mg, 0.143 mmol**)** and the mixture was stirred at room temperature for 16 hours. Then the solution was filtered, and the filtrate was concentrated under reduced pressure to yield **ImA-3** as a bright yellow solid (65 mg, 81%).

^{1}H NMR (600 MHz, D_2O): δ (ppm) 1.38 (15H, s), 7.22-7.26 (3H, m), 7.45 (2H, t, *J* = 7.8 Hz), 7.52 (2H, m), 7.72 (1H, d, *J* = 8.4 Hz), 7.85 (1H, d, *J* = 7.8 Hz).
^{13}C NMR (150 MHz, D_2O): δ (ppm) 8.3, 86.8, 114.3, 116.7, 125.1, 125.7, 126.1, 129.2, 133.5, 137.8, 145.8, 151.0, 164.2
ESI-MS(+): *m/z* 564 [(M−H_2O−HSO_4^-) + 1].
Anal. Calc. for $C_{24}H_{28}IrN_3O_6S$: C 42.47, H 4.16, N 6.19. Found: C 42.33, H 4.22, N 6.10

Experimental Procedure: CO_2 hydrogenation to formate

In a typical experiment, a 250 mL batch reactor was charged with 2M $KHCO_3$ (60 ml), iridium catalyst (26 µmol) and sealed. The vessel was purged with N_2 (3 times) and then pressurized with CO_2 followed by H_2 to the desired pressure. The temperature of the reaction mixture was increased to 50 °C. After stabilization at 50 °C under desired pressure of H_2/CO_2 (1/1) for 5 min, the reaction was started by stirring at 500 rpm. The reaction was stopped after the desided time and the reaction mixture was coled to room temperaturte. The reactor was depresurized carefully and the formate concentration was analyzed by ^{1}H NMR using sodium acetate as an internal standard.

Integrated CO_2 capture and hydrogenation to formate

In a typical experiment, a 250 mL batch reactor was charged with Water (43.3 mL) and triethyl amine (16.7 mL). The vessel was sealed purged with N_2 (3 times) and then pressurized with C O_2 (40 bar). The solution was stirred at 500 rpm for 2 hours. Then the reactor was opened, iridium catalyst ImA-1 (26 µmol) was added and sealed. The vessel was again purged with N_2 (3 times) and then pressurized with H_2 to 40 bar. The temperature of the reaction mixture was increased to 120 °C. After stabilization at 120 °C for 5 min, the reaction was started by stirring at 500 rpm. The reaction was stopped after 24 hours and the mixture was coled to room temperaturte. The reactor was depresurized carefully and the formate concentration was analyzed by ^{1}H NMR using sodium acetate as an internal standard.

Table 1: Formate formation in presence of different aqueous base.

Entry	Aq. base	Temp.(°C)	Total pressure(bar)	Formate (Molar)
1	1M NaOH	50	40	0.60
2	1M KOH	50	40	0.59
3	1M LiOH	50	40	0.67
4	1M CsOH	50	40	0.60
5	1M $NaHCO_3$	50	40	0.41
6	2M $KHCO_3$	50	40	0.68

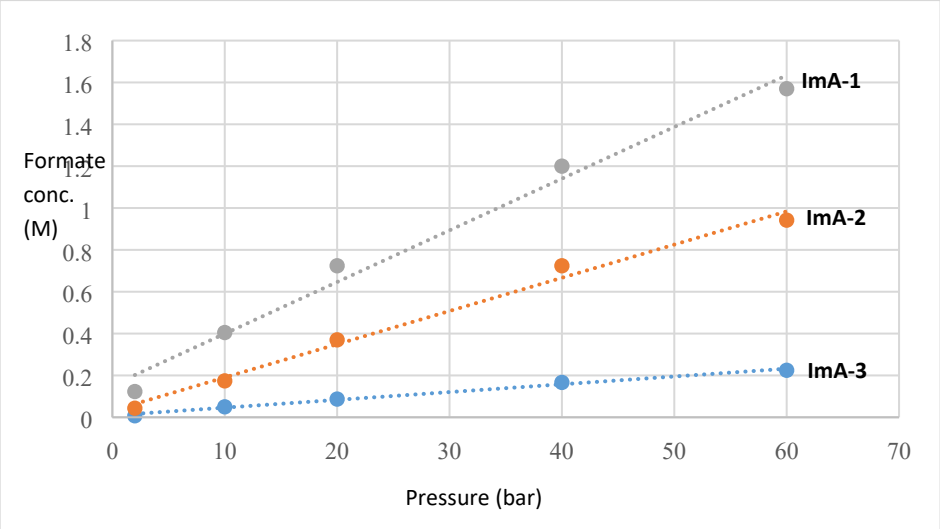
[a] Reaction conditions: Catalyst (**ImA-1**): 0.00026 M, P_{CO2} : P_{H2} = 1:1 (40 bar), temp: 50 °C, time: 6 h.

Table 2: Formate formation over time in presence of **ImA-1**, **ImA-2** and **ImA-3**

		Formate Conc (M) (**TON**)		
Sl No	**Time (h)**	**Cat. ImA-1**	**Cat. ImA-2**	**Cat. ImA-3**
1	1	0.202 (**7770**)	0.072 (**2770**)	0.050 (**1923**)
2	3	0.362 (**13923**)	0.145 (**5577**)	0.072 (**2770**)
3	6	0.500 (**19231**)	0.260 (**10000**)	0.087 (**3346**)
4	12	0.750 (**28846**)	0.492 (**18923**)	0.116 (**4462**)
5	18	0.942 (**36231**)	0.688 (**26462**)	0.145 (**5577**)
6	24	1.090 (**41923**)	0.811 (**31192**)	0.166 (**6385**)
7	36	1.304 (**50154**)	0.927 (**35654**)	0.174 (**6692**)
8	48	1.450 (**55770**)	0.992 (**38154**)	0.181 (**6962**)

Reaction conditions: Catalyst: 0.000026 M, P_{CO2} : P_{H2} = 1:1 (40 bar), temp. 50 °C,

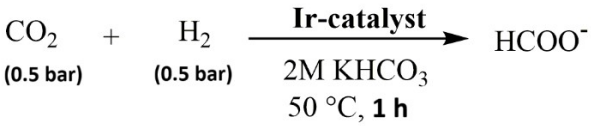
Table 3: Formate formation as a function of pressure

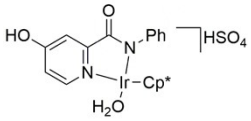
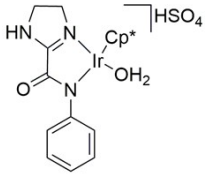


Hydrogenation of impure stream of CO_2 into formate

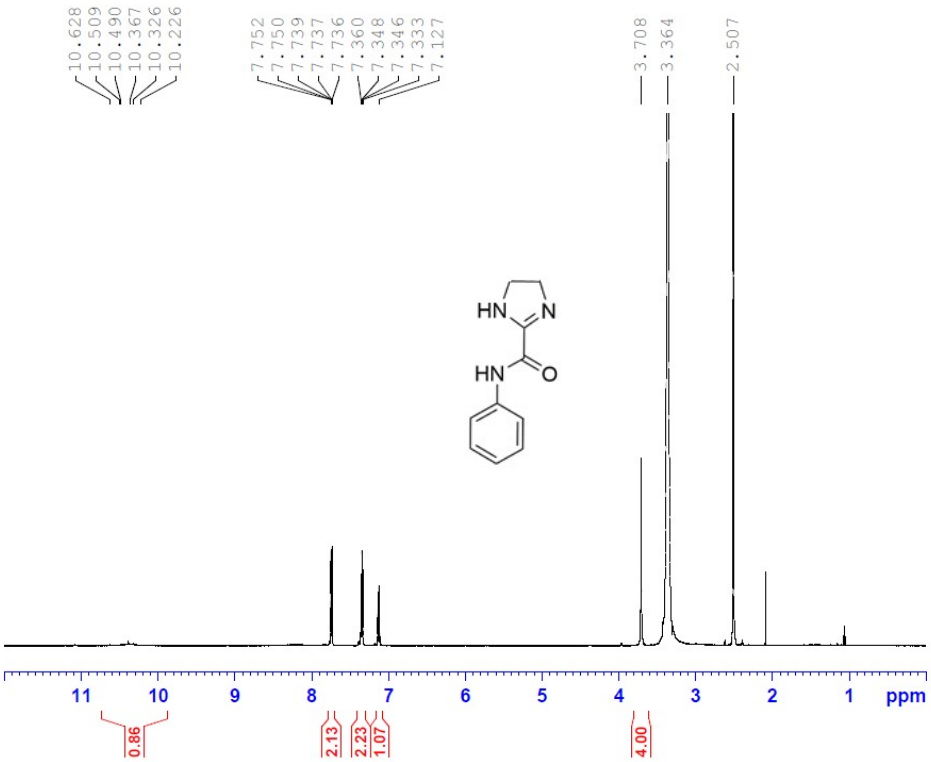
Sl No.	**Impure CO2 stream**	**Formate conc. (M)**
1	40% CO_2 + 60% methane	0.24

Hydrogenation of CO_2 into formate under reduced pressure - Comparison of catalytic activities of Imidazoline-amide ligated and picolinamide ligated Ir-catalysts.



Sl No.	**Catalyst**	**Formate Conc. (M)**	**TON**
1	 *Fujita-Himeda*	0.015	577
2	 **ImA-1**	0.014	539

3. Copies of NMR spectra of Ligands, Catalysts and Reaction mixtures

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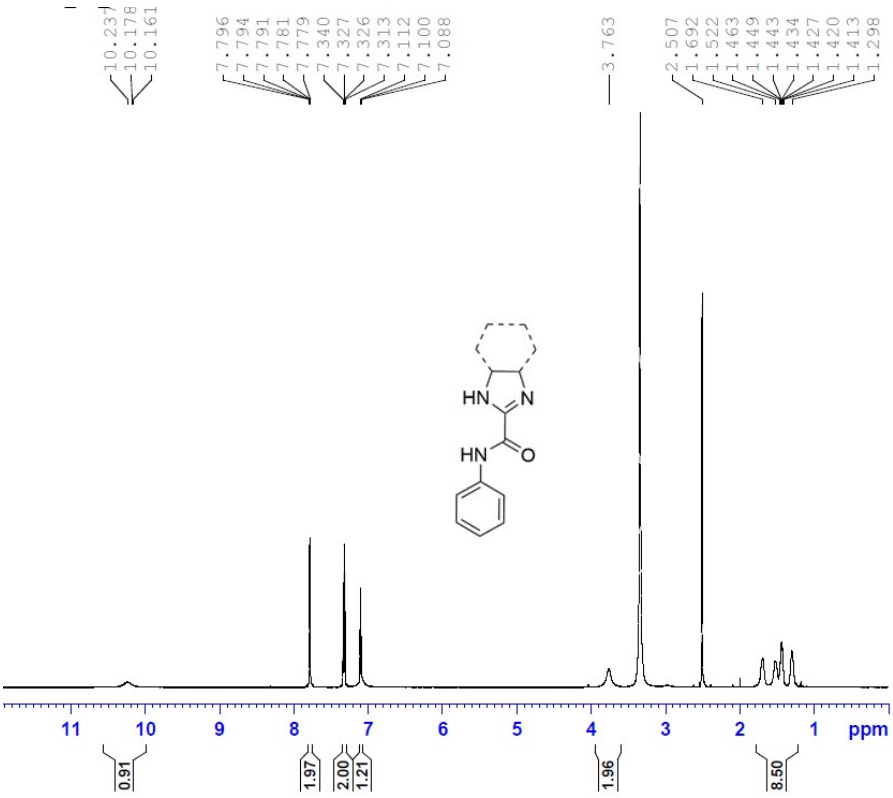


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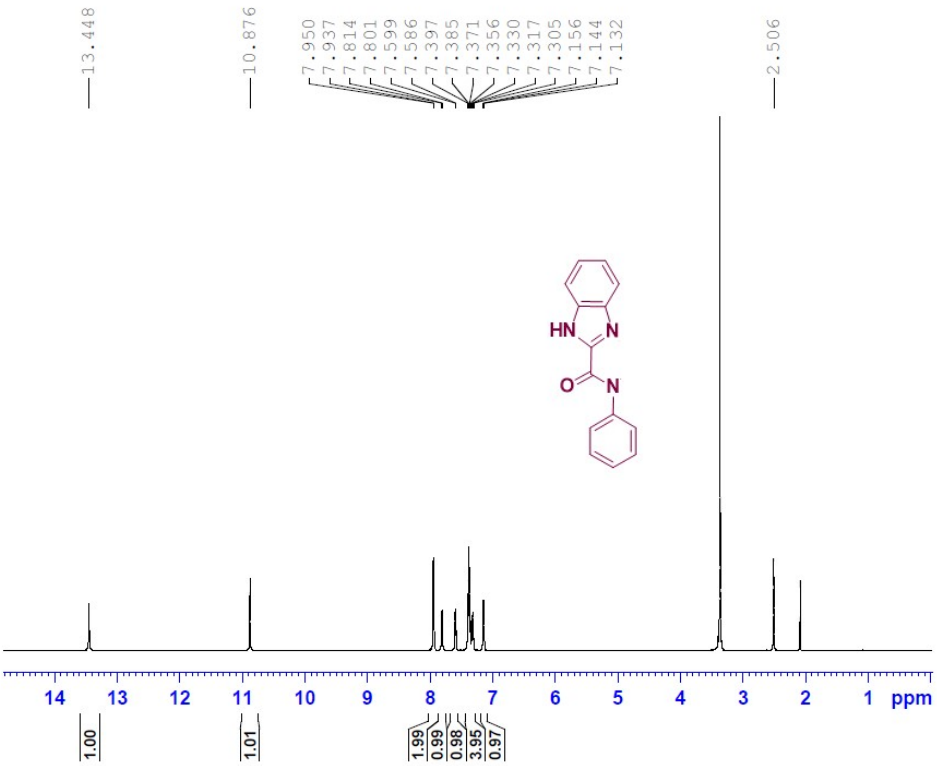


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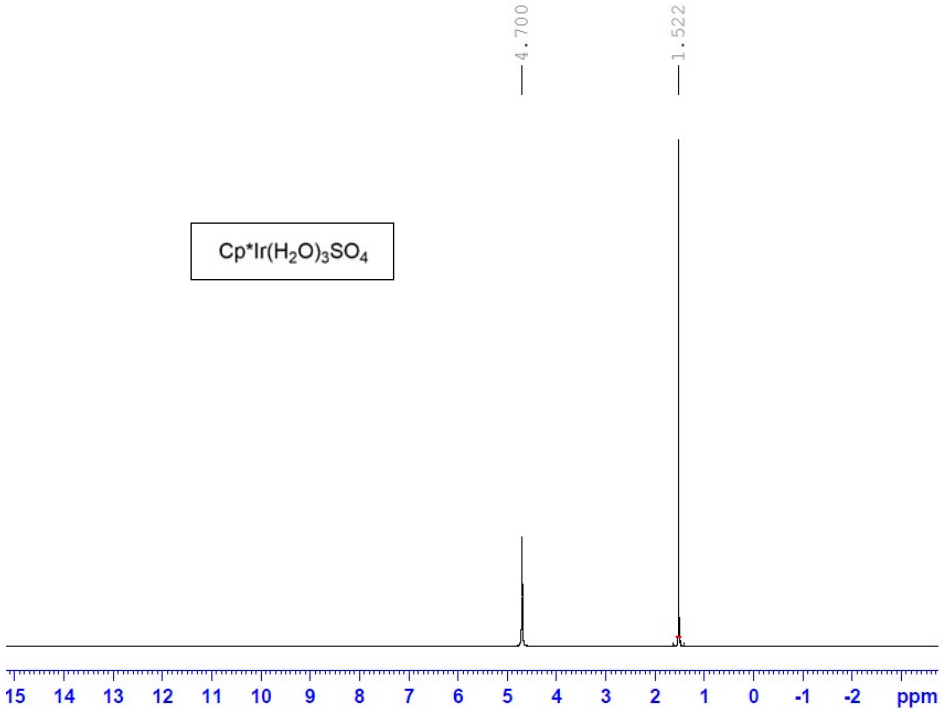


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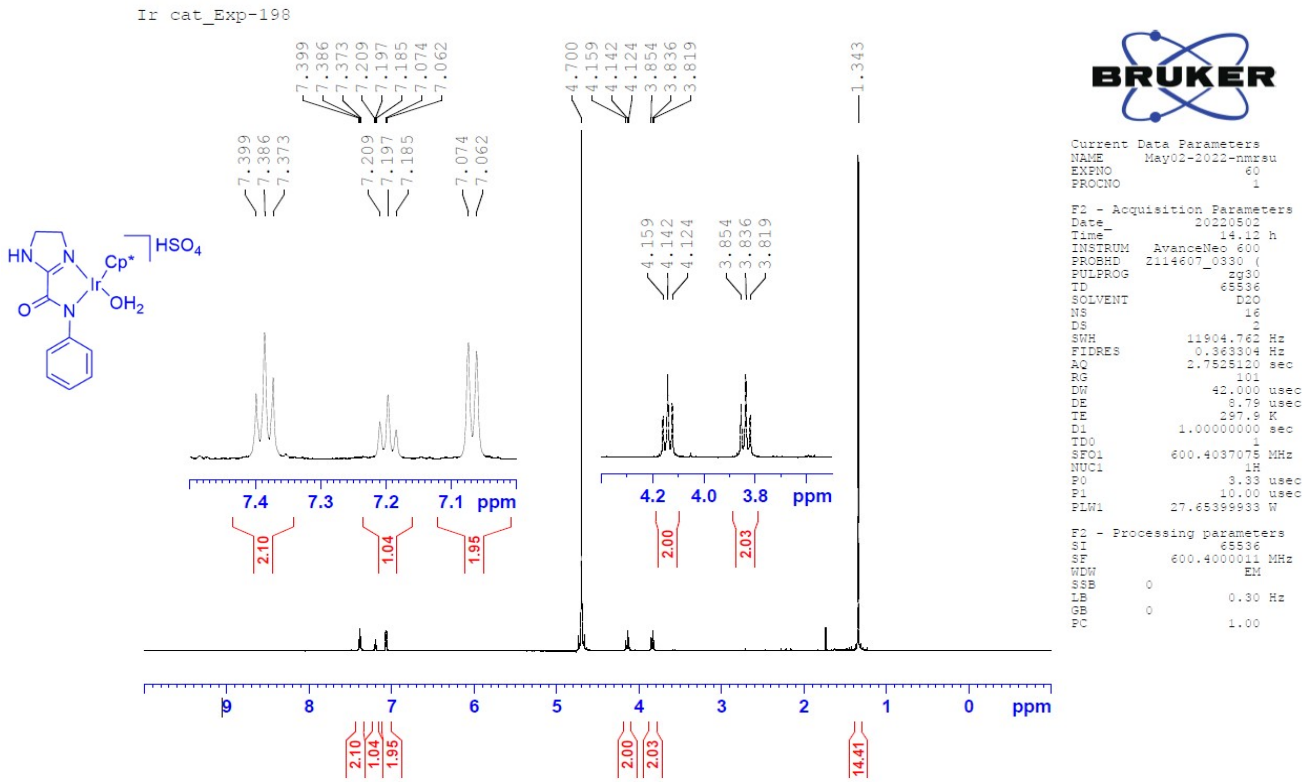


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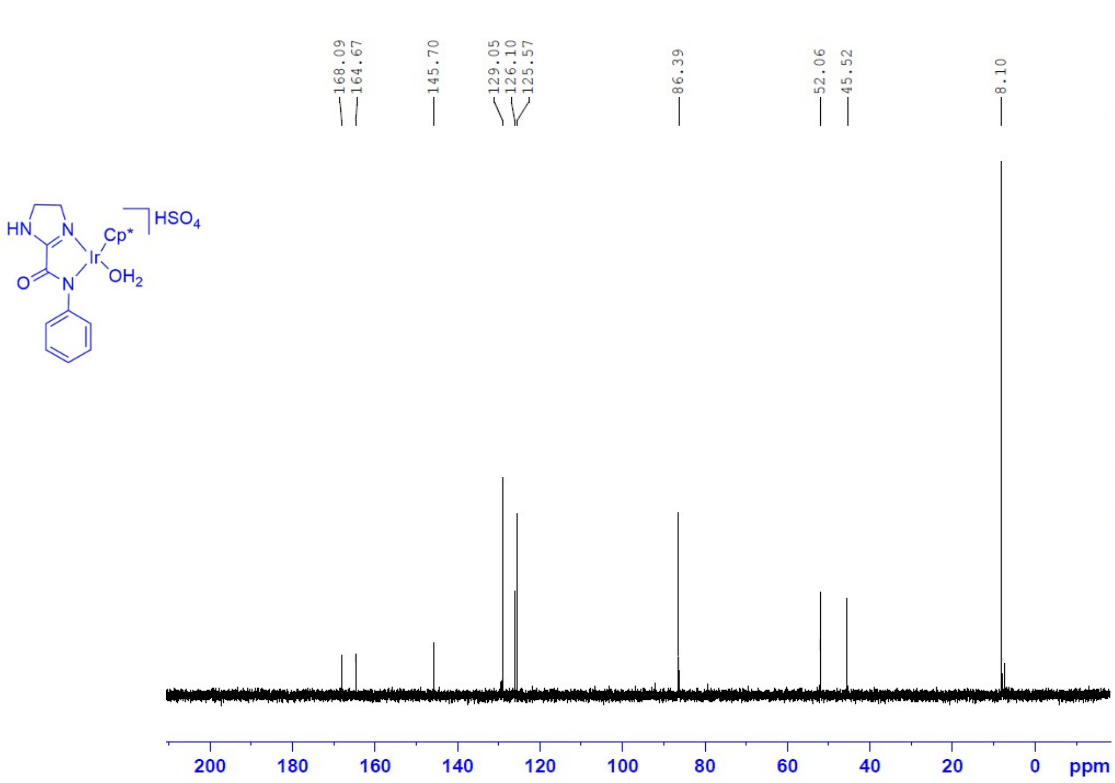


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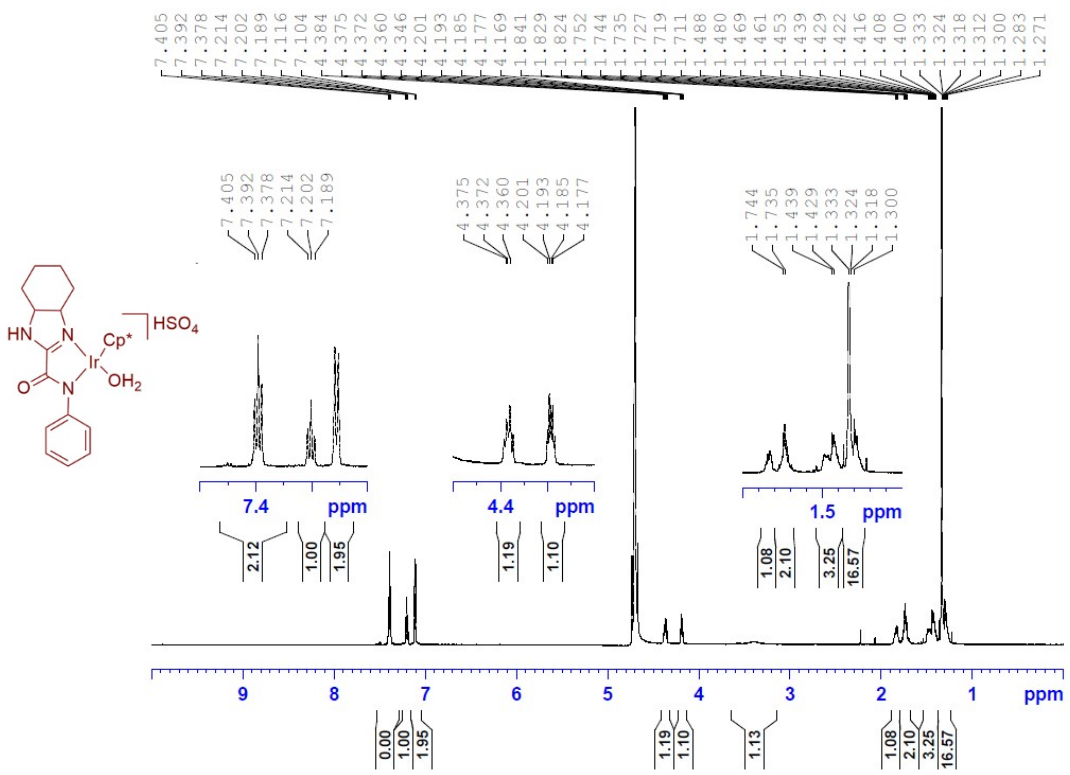

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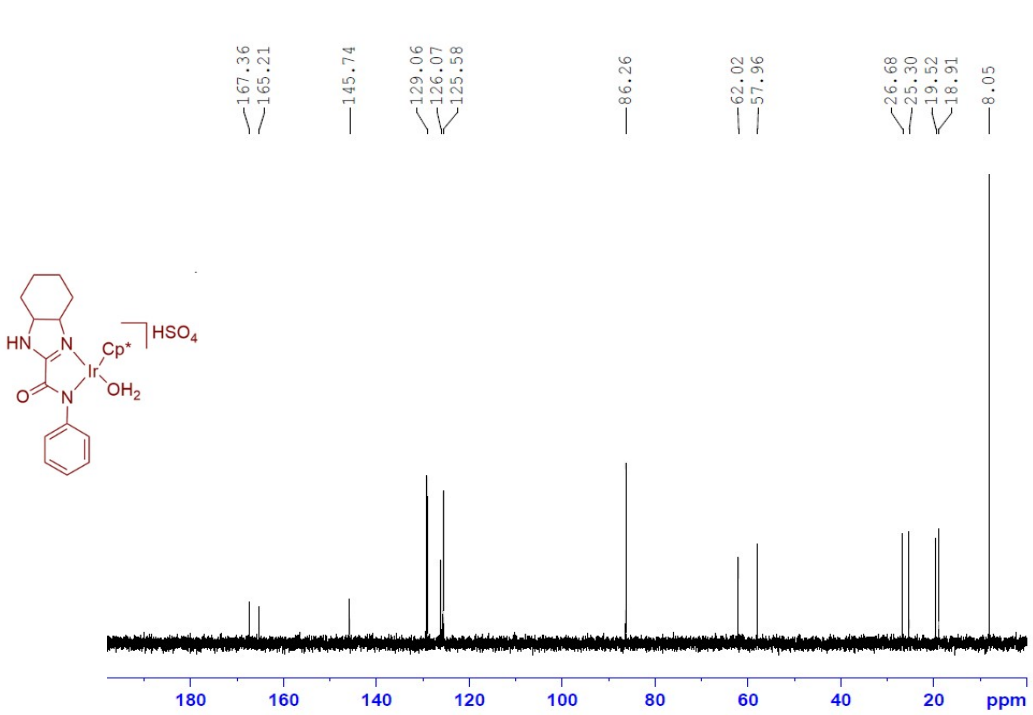

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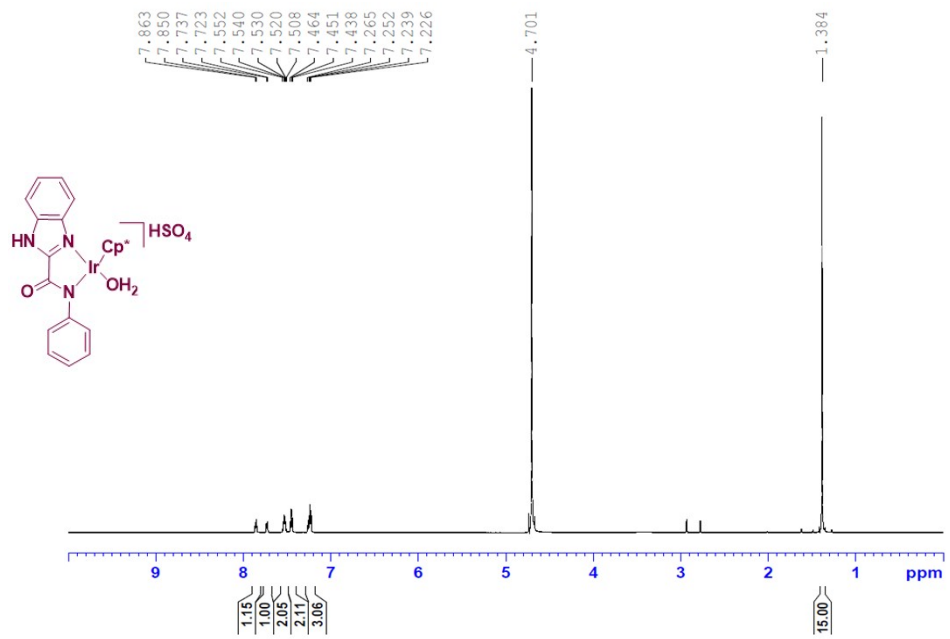

BRUKER

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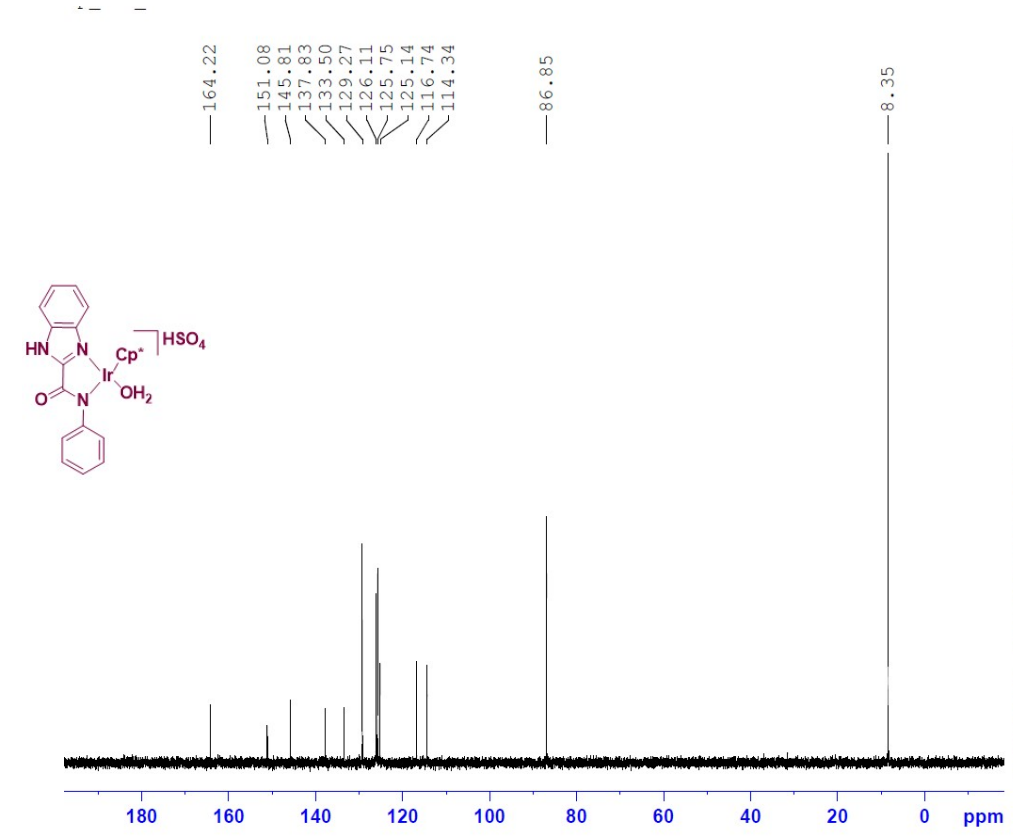

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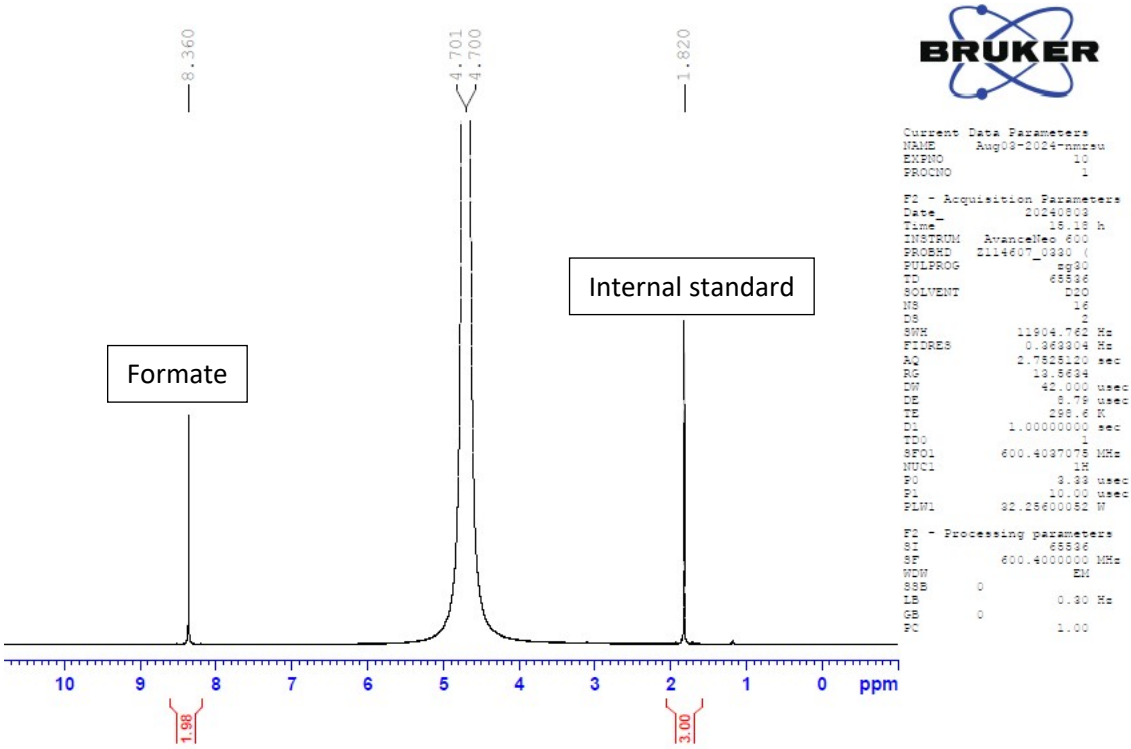
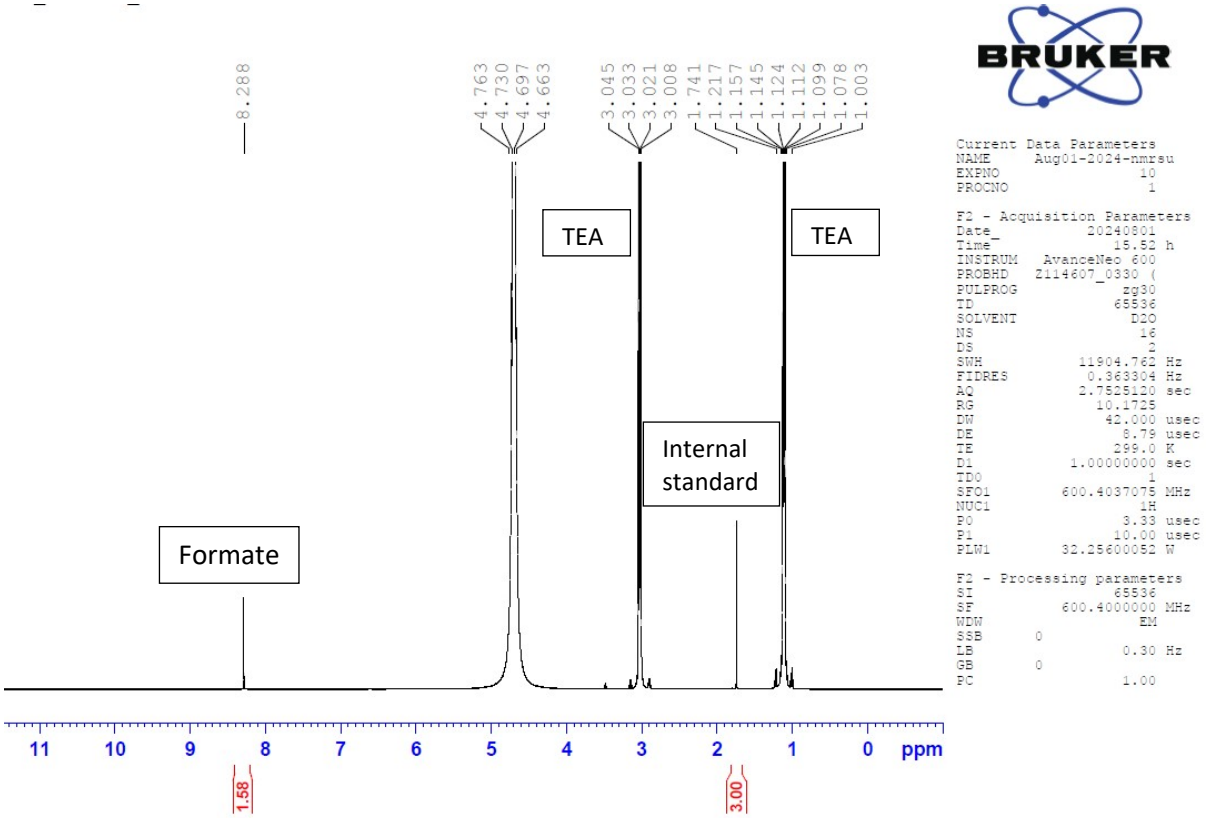
1. Reaction mixture of CO_2 hydrogenation to formate



2. Reaction mixture of integrated CO_2 capture with triethylamine and hydrogenation to formate



4. References

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