Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Iridium–NHC-Based Catalyst for Ambient Pressure Storage and Low Temperature Release of H_2 via CO_2/HCO_2H Couple

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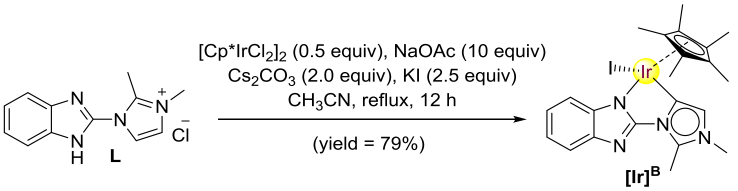
I. General information

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AVANCE III 400 and 500 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 – $CDCl_3$: δ = 7.26 ppm for ^1H spectra, 77.16 ppm for $^{13}C\{^1H\}$ spectra; DMSO-d_6: δ = 2.50 ppm for ^1H spectra, 39.50 ppm for $^{13}C\{^1H\}$ spectra; D_2O: δ = 4.79 ppm for ^1H spectra; CD_3CN: 1.94 ppm for ^1H spectra. All coupling constants (*J*) are expressed in hertz (Hz) and only given for ^1H–^1H couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), bs (broad singlet). ESI mass spectrometry was performed on a Bruker microTOF QII spectrometer. Single crystal X-ray diffraction measurements were performed with Bruker APEX-II CCD instrument. Dry solvents and reagents were obtained from commercial suppliers and used without further purification. Deuterated solvents were purchased from Sigma Aldrich. CO_2 (purity 99.999%) and H_2 (purity 99.999%) gases were purchased from INOX Air Products Pvt. Ltd. Catalyst **[Ir]^A** was synthesized following a procedure reported earlier by our group.[S1] 2-chloro-1-H-benzimidazole was purchased from Sigma Aldrich. 1,2-dimethyl-1H-imidazole was purchased from Spectrochem.

II. Synthesis of [Ir]^B



Scheme S1 Synthesis of **[Ir]^B**.

(a) Step I: Preparation of the ligand precursor 3-(1H-benzo[d]imidazol-2-yl)-1,2-dimethyl-1H-imidazol-3-ium chloride, L. Ligand **L** was synthesized by stirring neat reaction of 2-chloro-1-H-benzimidazole (1 mmol) and 1,2-dimethyl-1H-imidazole (3 mmol) in a pressure tube at 135 °C for 8 h. After the end of the reaction, the residue was washed with dry THF three times followed by washing with chloroform. The resulting off-white powder was isolated and dried in vacuum. Yield: 150 mg (60 %). ^1H NMR (400 MHz, DMSO-d_6): δ 14.10 (bs, 1H), 8.30 (d, *J* = 2.1 Hz, 1H), 7.95 (d, *J* = 2.1 Hz, 1H), 7.70 (dd, *J* = 5.9, 3.3 Hz, 2H), 7.35 (dd, *J* = 6.0, 3.2 Hz, 2H), 3.91 (s, 3H), 2.96 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6) δ 146.44, 141.19, 123.50, 123.39, 120.38, 35.28, 11.71 ppm (*few peaks due to quaternary carbons were not observed!*). LRMS (positive ion): 213.1 (calcd 213.1 for $[C_{12}H_{13}N_4]^+$)

(b) Step II: Preparation of the complex [Ir]^B. A mixture of the ligand precursor **L** (42.5 mg, 0.125 mmol), $[IrCp^*Cl_2]_2$ (50 mg, 0.063 mmol), CH_3COONa (102.53 mg, 1.25 mmol), Cs_2CO_3 (102.3 mg, 0.314 mmol) and KI (52 mg, 0.314 mmol) was refluxed in CH_3CN (20 mL) for 12 h. After cooling to room temperature, the reaction mixture was filtered through Celite and all volatiles were removed under reduced pressure. Complex **[Ir]^B** was obtained as a brown-red solid by precipitation from CH_2Cl_2/Et_2O. Yield: 66.3 mg (79%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.66 – 7.64 (d, *J* = 8 Hz, 1H, CH_{Benz}), 7.36 – 7.34 (d, *J* = 8 Hz, 1H, CH_{Benz}), 7.14 – 7.11 (m, 2H, CH_{Benz}), 6.56 (s, 1H, CH_{imid}), 3.73 (s, 3H, CH_{methyl}), 3.24 (s, 3H, CH_{methyl}), 1.95 (s, 15H, $(CH_3)_5Cp^*$)) ppm (see Fig. S1). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 155.64 (Ir-$C_{imidazole}$), 145.94, 141.04, 139.21, 138.19, 121.38, 120.47, 120.11, 118.60, 114.17, 88.74 $(CH_3)_5Cp^*$), 34.06 (N-$CH_{3imidazole}$), 10.73 $(CH_3)_5Cp^*$), 10.57 (C-$CH_{3imidazole}$) ppm (see Fig. S2). HRMS (ESI, positive ion): 539.1782 (calcd 539.1782 for $[C_{22}H_{26}N_4Ir]^+$) (see Fig. S3).

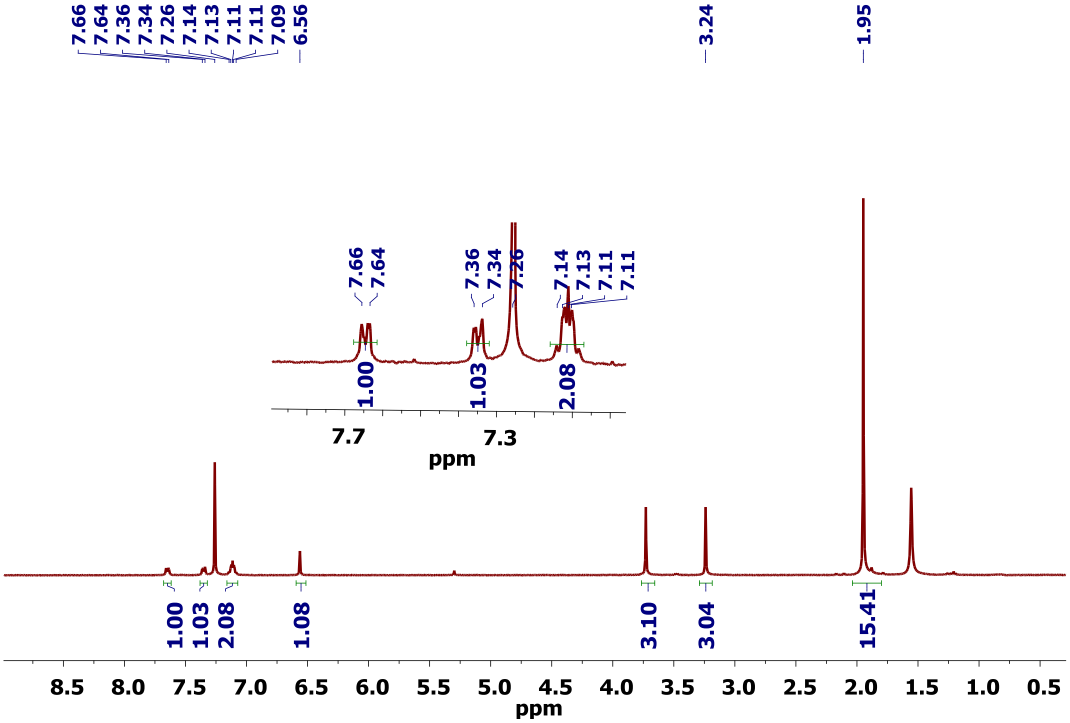


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **[Ir]^{B}**.

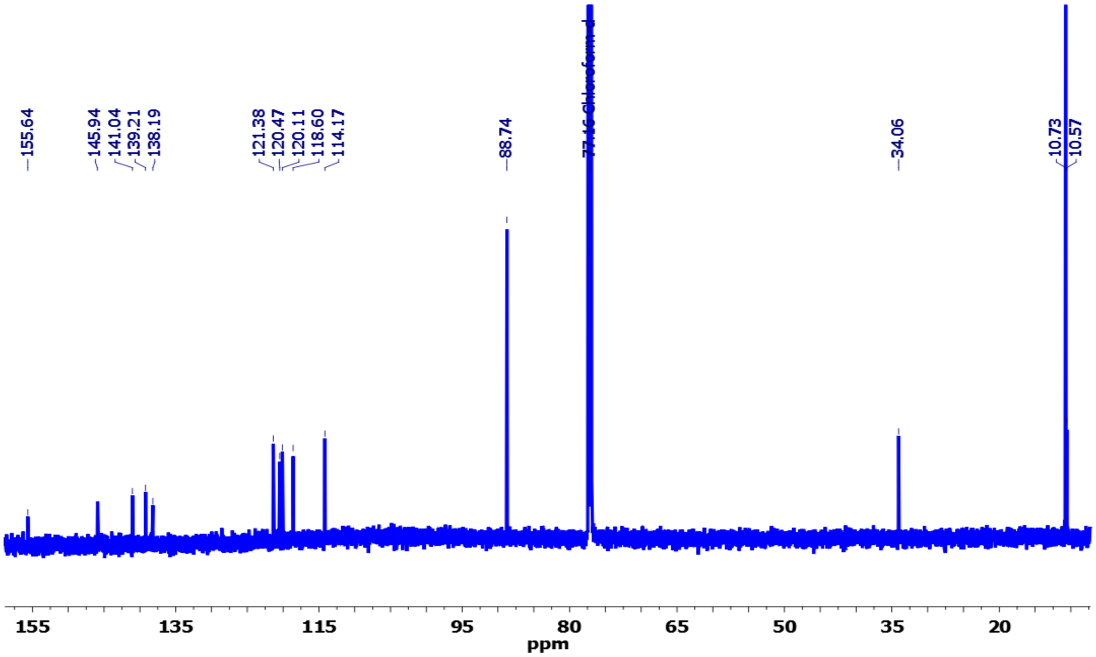


Fig. S2 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of **[Ir]^{B}**.

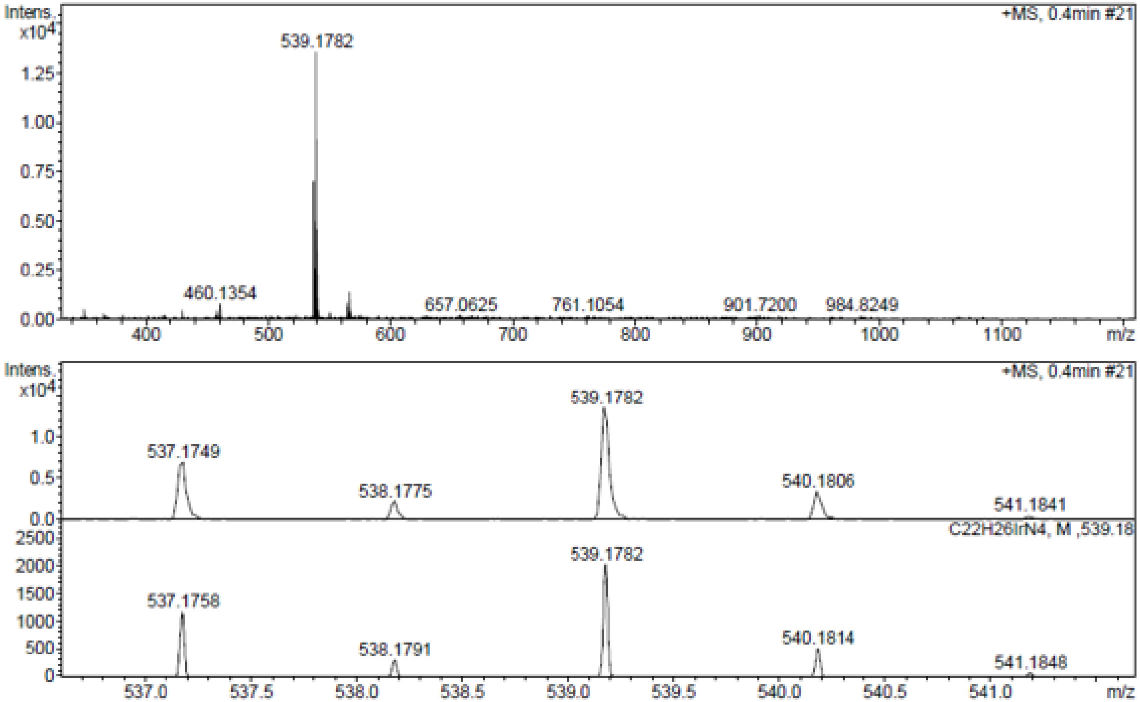


Fig. S3 ESI-MS spectrum of **[Ir]^B**.

III. General procedure for catalytic CO_2-hydrogenation

A 50 mL round-bottom flask was charged with aqueous solution (20 mL) of base (1 M KOH) and the catalyst **[Ir]^A** or **[Ir]^B** (0.002 mmol, from a stock solution in CH_3CN). This mixture was bubbled with CO_2 gas filled in a rubber balloon (volume ≈ 1 L) for 1 h at ambient temperature. After that H_2(g) and CO_2(g) were bubbled simultaneously for 1 h at 30 °C keeping the flask in a temperature-controlled oil-bath. The rate of bubbling for both the gases was maintained at ≈70 mL/min. An aliquot (500 µL) of the reaction mixture was withdrawn and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt, $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$ (5.01 mg, 0.0229 mmol) was added to the aliquot as an internal reference. ^1H NMR spectrum was recorded using D_2O as a locking solvent taken inside a sealed capillary. Corresponding TON and TOF values were obtained from the concentration of the product formate which was calculated from the integration values of the formate peak ($\underline{H}COO^-$) at 8.46 ppm and the internal standard peak at 2.92 ppm ($(CH_3)_3SiCH_2CH_2C\underline{H_2}SO_3Na$).

IV. General procedure for optimization of catalytic CO_2-hydrogenation

A 50 mL round-bottom flask was charged with aqueous solution (20 mL) of base (1 M or 2 M) and the catalyst **[Ir]^A** or **[Ir]^B** (0.002, 0.0015, 0.001, or 0.0008 mmol from a stock solution in CH_3CN). This mixture was bubbled with CO_2 gas filled in a rubber balloon (volume ≈ 1 L) for 1 h at ambient temperature. After that H_2(g) and CO_2(g) were bubbled simultaneously for 1 h at 30 °C keeping the flask in a temperature-controlled oil-bath. The rate of bubbling for both the gases was maintained at ≈70 mL/min. An aliquot (500 µL) of the reaction mixture was withdrawn and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt, $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$ (5.01 mg, 0.0229 mmol) was added to the aliquot as an internal reference. ^1H NMR spectrum was recorded using D_2O as a locking solvent taken inside a sealed capillary.

Corresponding TON and TOF values were obtained from the concentration of the product formate which was calculated from the integration values of the formate peak ($\underline{H}COO^-$) at 8.46 ppm and the internal standard peak at 2.92 ppm ($(CH_3)_3SiCH_2CH_2C\underline{H}_2SO_3Na$). The results are shown in Table S1. A representative calculation is given here. For entry 1 in Table S1, the resulting ^{1}H NMR spectrum (Fig. S4) provided the concentration of formate as 0.033 mmol present in 20 mL of reaction solution as shown below.

mmol of formate in 500 µL aliquot = (mmol of internal standard) × [(integral of formate peak/no. of corresponding proton)/(integral of internal standard/no. of corresponding proton)] = 0.0229 × [(0.037/1) / (2.000/2)] = 0.0008473. Hence, mmol of formate in 20 mL of reaction solution = 0.0008473 × 20 mL/500 µL = 0.033892

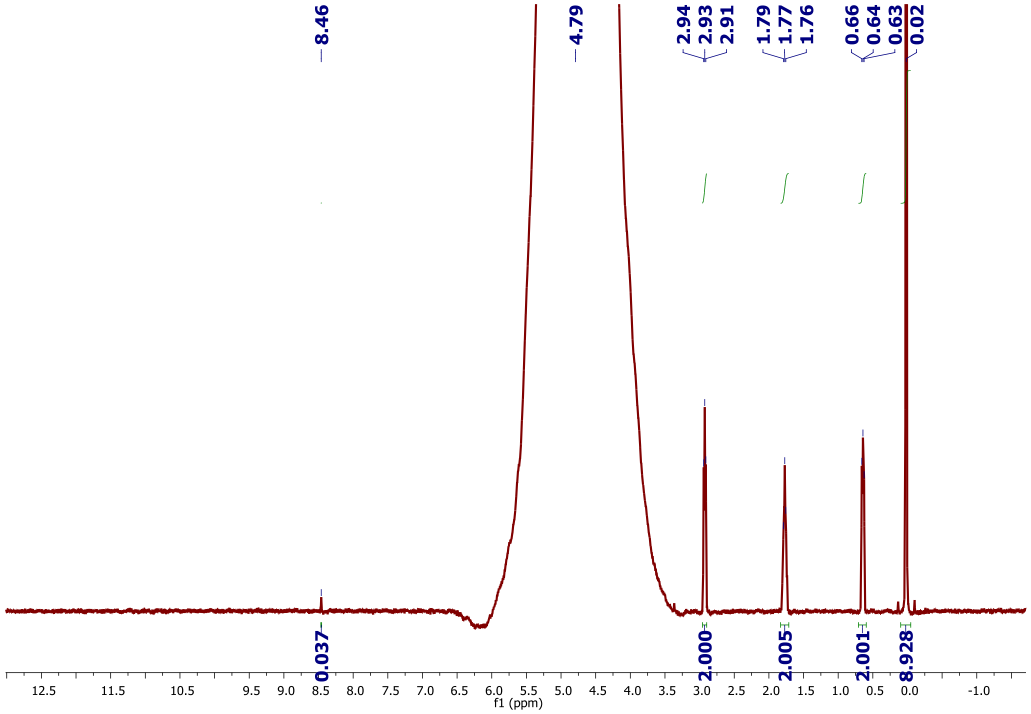


Fig. S4 A representative ^{1}H NMR spectrum of a reaction solution for hydrogenation (Entry 1, Table S1).

Table S1 Optimization table for catalytic CO_2-hydrogenation.

Entry	Catalyst (µmol)	Base (M)	Formate (µmol)	TOF (h^{-1})
1	**[Ir]**^{A}/2.0	1.0 M KOH	34	17
2	**[Ir]**^{B}/2.0	1.0 M KOH	87	44
3	**[Ir]**^{B}/1.5	1.0 M KOH	79	53
4	**[Ir]**^{B}/1.1	1.0 M KOH	61	56
5	**[Ir]**^{B}/0.8	1.0 M KOH	47	58
6	**[Ir]**^{B}/0.8	2.0 M KOH	44	55
7	**[Ir]**^{B}/0.8	1.0 M K_2CO_3	47	58
8	**[Ir]**^{B}/0.8	2.0 M K_2CO_3	44	55
9	**[Ir]**^{B}/0.8	1.0 M $KHCO_3$	31	39
10	**[Ir]**^{B}/0.8	2.0 M $KHCO_3$	29	37
Note: The TOF values were based on average of 3 runs. TOF was calculated after 1 h of reaction.				

V. General procedure of catalytic dehydrogenation

A 5 mL round-bottom flask was loaded with the catalyst (0.0005 mmol). It was degassed three times with argon and then connected to a standard water displacement apparatus using a graduated cylinder to measure volume of the generated gas. The apparatus contained a 5 M NaOH solution as CO_2-trap. Thus when the gaseous product(s) formed in the reaction were passed through the trap, CO_2(g) was dissolved, and the volume of CO_2-free other gas(es) was measured by the graduated cylinder. The reaction was performed by charging a 5:2 (w/w) HCO_2H/NEt_3 azeotrope mixture (1.5 mL) into the flask and stirring the mixture vigorously at the specified temperature. After that, the volume of gas collected was noted. It was found that only H_2 gas was present in the product after the CO_2 gas was trapped (see below for detailed analysis). The TON and TOF values of the catalyst was calculated from the volume of the collected gas, as proposed earlier by Tanaka *et al.*[S2] and Xiao *et al.*[S3]

The volume of 1 mole H_2(g) was calculated using van der Waals equation: $(P+\frac{n^2a}{V^2})(V-nb) = nRT$

Substituting respective values of constants involved in above equation we get:

V (H_2(g), 25 °C, 1 atm) = 24.49 L·for 1 mol of H_2(g).

TON was calculated as follows:

TON = (V_{exp} (H_2(g), 25 °C, 1 atm)/24.49)/n_{cat} where V_{exp} is the volume (in L) of H_2(g) determined in the experiment and n_{cat} is the number of moles of catalyst used in the experiment. The turnover frequency, TOF (h^{-1}) = TON/ time (h).

VI. General procedure for optimization of catalytic dehydrogenation

The above procedure was used for optimization studies. A 5 mL round-bottom flask was loaded with the catalyst (0.0005 mmol). It was degassed three times with argon and then connected to a standard water displacement apparatus using a graduated cylinder to measure volume of the generated gas. The apparatus contained a 5 M NaOH solution as CO_2-trap. Thus when the gaseous product(s) formed in the reaction were passed through the trap, CO_2(g) was dissolved, and the volume of CO_2-free other gas(es) was measured by the graduated cylinder. The reaction was performed by charging the substrate (1.5 mL) (as mentioned in the Table S2) into the flask and stirring the mixture vigorously at the specified temperature (45 °C, 90 °C). After that, the volume of gas collected was noted. It was found that only H_2 gas was present in the product after the CO_2 gas was trapped (see below for detailed analysis). The TON and TOF values of the catalyst was calculated from the volume of the collected gas.

Table S2 Optimization table for catalytic HCO_2H-dehydrogenation.

Catalyst	**Solvent/Substrate**	**T (°C)**	**TOF (h^{-1})**
[Ir]^A	5:2 (w/w) HCO_2H/NEt_3	45	200
[Ir]^B	5:2 (w/w) HCO_2H/NEt_3	45	1200
[Ir]^B	5:2 (w/w) HCO_2H/NEt_3	90	58000
[Ir]^B	1 M 1:1 (w/w) HCO_2H/HCO_2Na	90	59000

Note: Formation of CO as a by-product was not detected by $^{13}C\{^1H\}$ NMR spectroscopy. The TOF values were based on average of 3 runs. TOF was determined after 2 min of reaction.

VII. Control reaction of catalyst **[Ir]^B** and H_2 in CD_3CN followed by reaction with CO_2 gas

A 5 mm J young NMR tube was charged with a CD_3CN-solution of complex **[Ir]^B** (0.00375 mmol taken from a stock solution in CD_3CN). ^{1}H NMR spectrum of this solution was recorded (Fig. S5a,b,c-i). Next, to this solution was added 1 M KOH/D_2O (50 µL from a stock solution in D_2O). The solution was bubbled with H_2 gas from a balloon for 30 min at ambient temperature. Then ^{1}H NMR spectrum of the reaction mixture was recorded (Fig. S5a,b,c-ii). To the above reaction mixture, H_2 and CO_2 were bubbled simultaneously for next 30, 60, 90 min with occasional shaking. ^{1}H NMR spectra of this reaction mixture were recorded (Figs. S5a,b,c-iii-iv-v). The generation of the Ir–H peak at −14.84 ppm was confirmed from the Fig. S5c. This was accompanied with some changes in the aromatic region corresponding to the ligand backbone. On application of CO_2(g), free formate peak was observed at 8.43 ppm. No intermediate could be detected.

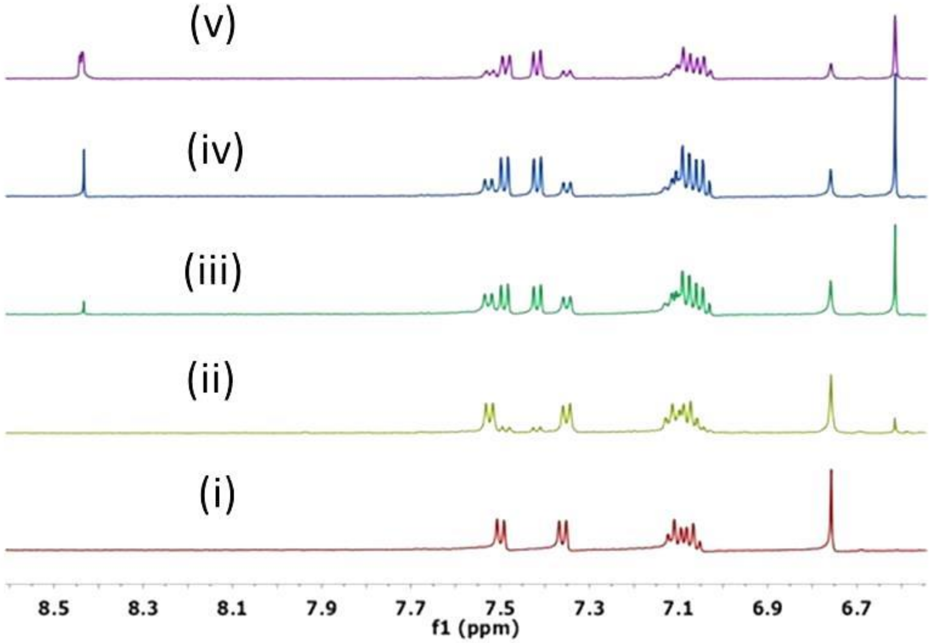


Fig. S5a ^{1}H NMR spectrum **(aromatic region)** of a control reaction of catalyst **[Ir]^B** and H_2 in CD_3CN followed by reaction with CO_2 gas. (i) free catalyst; (ii) catalyst + H_2; (iii) catalyst + H_2 + CO_2 (30 min); (iv) catalyst + H_2 + CO_2 (60 min); (v) catalyst + H_2 + CO_2 (90 min).

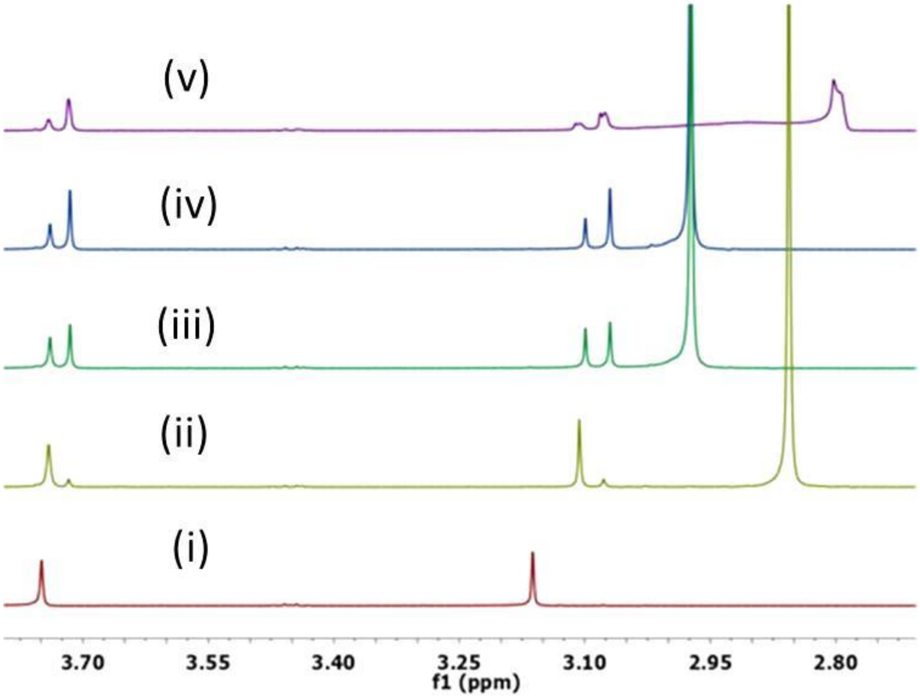


Fig. S5b ^{1}H NMR spectrum **(2.8 to 4.0 ppm region)** of a control reaction of catalyst **[Ir]^B** and H_2 in CD_3CN followed by reaction with CO_2 gas. (i) free catalyst; (ii) catalyst + H_2; (iii) catalyst + H_2 + CO_2 (30 min); (iv) catalyst + H_2 + CO_2 (60 min); (v) catalyst + H_2 + CO_2 (90 min).

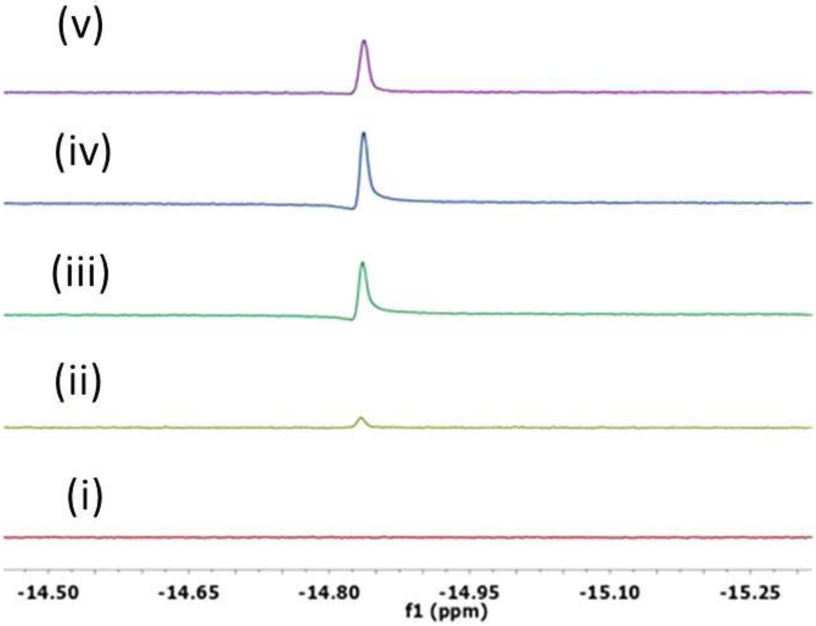


Fig. S5c ^{1}H NMR spectrum **(upfield region)** of a control reaction of catalyst **[Ir]^B** and H_2 in CD_3CN followed by reaction with CO_2 gas. (i) free catalyst; (ii) catalyst + H_2; (iii) catalyst + H_2 + CO_2 (30 min); (iv) catalyst + H_2 + CO_2 (60 min); (v) catalyst + H_2 + CO_2 (90 min).

VIII. NMR spectral studies to show the presence of bicarbonate (HCO_3^-) in a control reaction solution

A mixture of catalyst **[Ir]**^{B} (0.002 mmol) and aqueous solution (20 mL) of KOH (0.1 M) was taken in a 50 mL round-bottom flask. 3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt, $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$ (5.01 mg, 0.0229 mmol) was added as a reference. This solution was vigorously stirred and bubbled with CO_2 at 303 K for 1 h. An aliquot (0.5 mL) was withdrawn and ^1H NMR spectrum was recorded using D_2O in a sealed capillary as a locking solvent (Fig. S6a). No formate peak was observed at 8.46 ppm. Importantly, the peak at 2.24 ppm indicated the presence of bicarbonate ($\underline{H}CO_3^-$) in the solution. This was further confirmed by $^{13}C\{^1H\}$ NMR spectroscopy using one drop of CH_3OH as a reference (δ 49.50 ppm) where the peak corresponding to ($H\underline{C}O_3^-$) was observed at 160.74 ppm (Fig. S6b). The ^1H and $^{13}C\{^1H\}$ NMR chemical shifts for bicarbonate anion, HCO_3^-, were matched with the reported values.[S4]

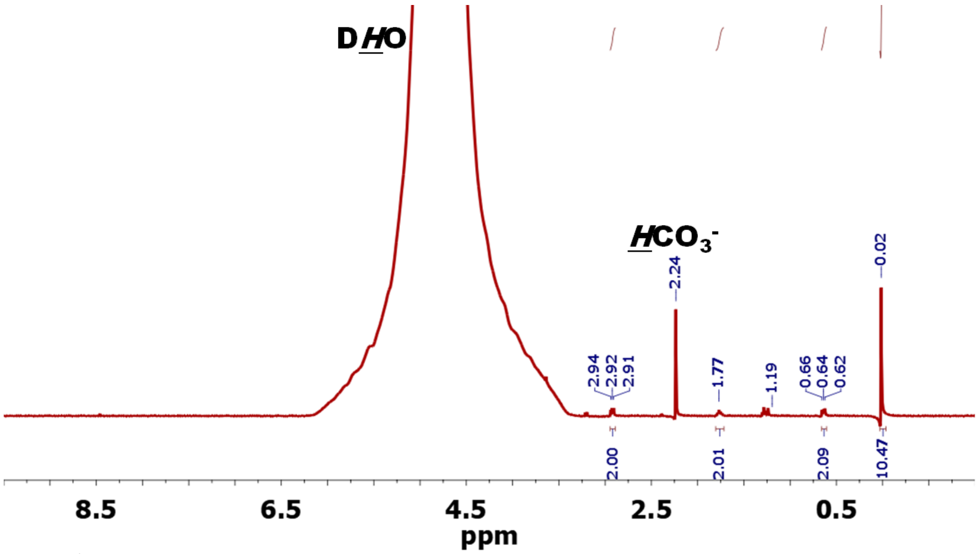


Fig. S6a ^1H NMR spectrum of a reaction solution showing the presence of bicarbonate.

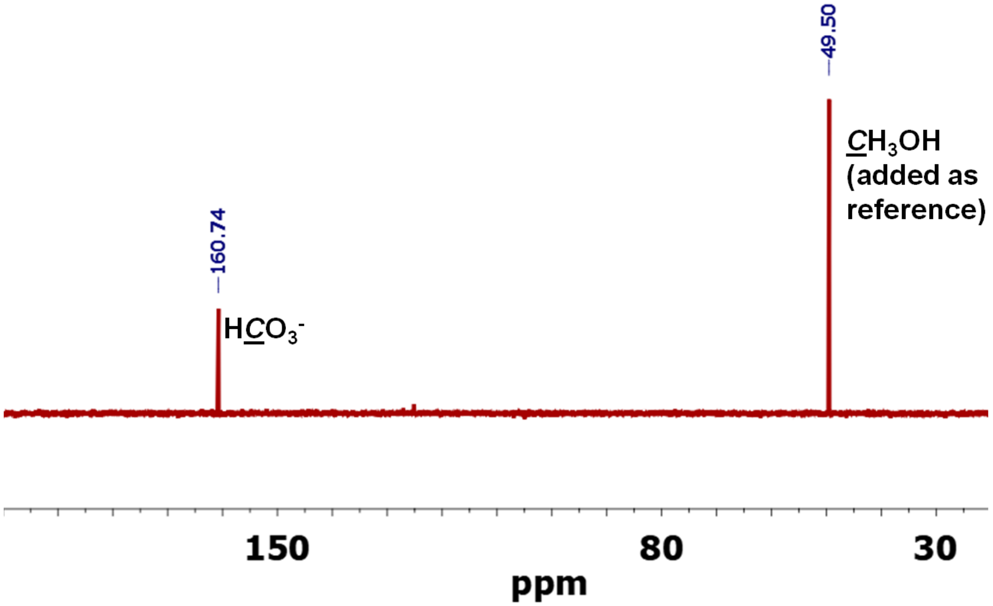


Fig. S6b $^{13}C\{^1H\}$ NMR spectrum of a reaction solution showing the presence of bicarbonate.

IX. Control reaction of catalyst **[Ir]^{A}** and H_2 in 1 M KOH/D_2O followed by reaction with $KHCO_3$

A 5 mm J young NMR tube was charged with a CD_3CN-solution of complex **[Ir]^{A}** (0.00375 mmol, taken from a stock solution in CD_3CN). To this solution was added 1 M KOH/D_2O (50 µL from a stock solution in D_2O). ^{1}H NMR spectrum of this solution was recorded (Fig. S7a,b,c-i). Then this solution was bubbled with H_2 gas from a balloon for 1 h at ambient temperature. Then ^{1}H NMR spectrum of the reaction mixture was recorded (Fig. S7a,b,c-ii). To the above reaction mixture, a D_2O-solution of $KHCO_3$ (0.0037 mmol taken from a stock solution in D_2O) was added, and the mixture was occasionally shaken. After 2 h and 3 h duration, ^{1}H NMR spectra of this reaction mixture were recorded (Figs. S7a,b,c-iii, iv). Generation of formate peak was observed at 8.40 ppm on addition of bicarbonate.

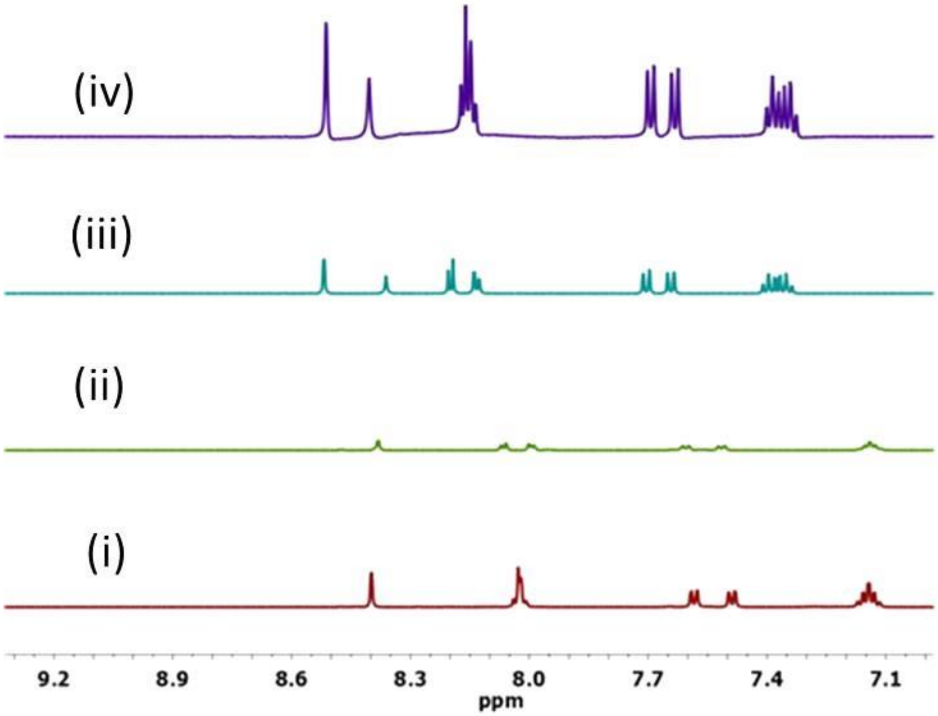


Fig. S7a ^{1}H NMR spectrum **(aromatic region)** of a control reaction of catalyst **[Ir]^{A}** and H_2 in CD_3CN followed by reaction with $KHCO_3$. (i) free catalyst; (ii) catalyst + H_2; (iii) catalyst + H_2 + $KHCO_3$ (2 h); (iv) catalyst + H_2 + $KHCO_3$ (3 h).

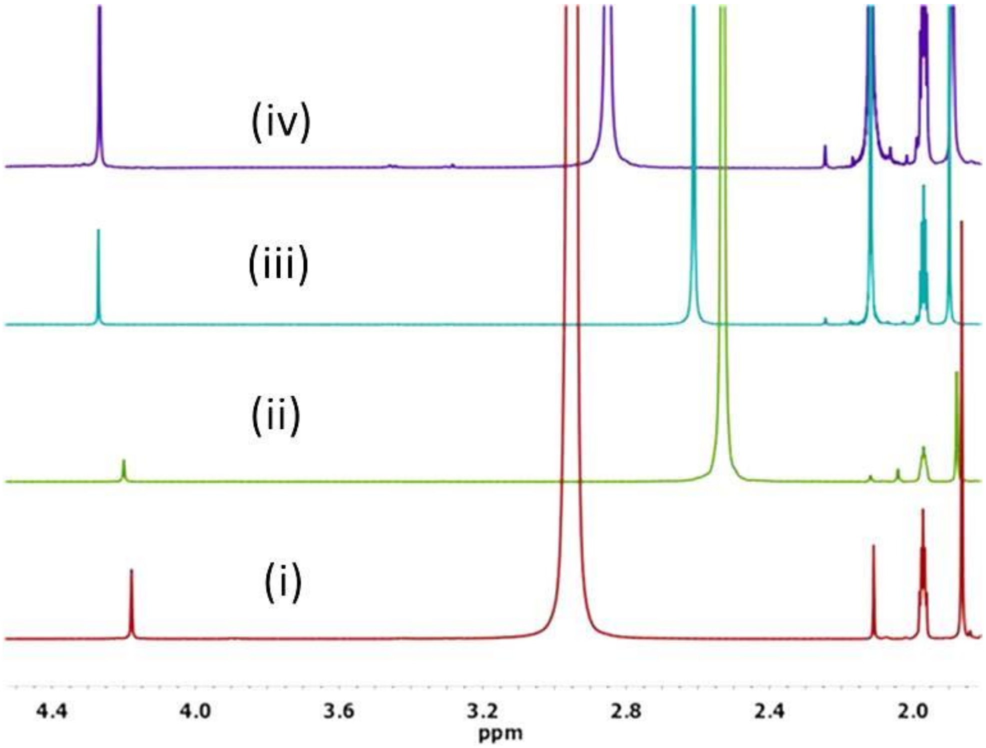


Fig. S7b ^{1}H NMR spectrum **(1.5 to 4.5 ppm region)** of a control reaction of catalyst **[Ir]^A** and H_2 in CD_3CN followed by reaction with $KHCO_3$. (i) free catalyst; (ii) catalyst + H_2; (iii) catalyst + H_2 + $KHCO_3$ (2 h); (iv) catalyst + H_2 + $KHCO_3$ (3 h).

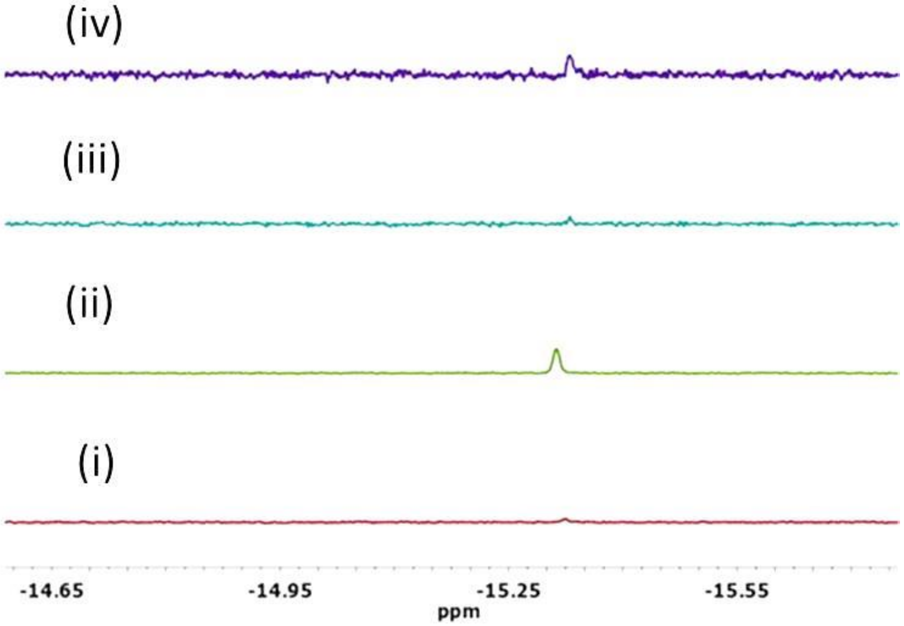


Fig. S7c ^{1}H NMR spectrum **(upfield region)** of a control reaction of catalyst **[Ir]^A** and H_2 in CD_3CN followed by reaction with $KHCO_3$. (i) free catalyst; (ii) catalyst + H_2; (iii) catalyst + H_2 + $KHCO_3$ (2 h); (iv) catalyst + H_2 + $KHCO_3$ (3 h).

X. NMR spectroscopic analysis of the gas products generated in the dehydrogenation catalysis

(a) Analysis of H_2

In a 5 mL round-bottom flask, catalyst **[Ir]^B** (0.0005 mmol) and 1.5 mL HCOOH/NEt_3 (5:2, w/w) azeotrope were added. The resulting mixture was stirred at 50°C for 1 h. The evolved gas was allowed to pass through a 5 M NaOH solution (which was used as CO_2-trap in water displacement setup as described earlier). The gas collected finally was bubbled through CD_3CN (0.6 mL) kept in an NMR tube. After that, ^{1}H NMR spectrum of this solution was recorded (Fig. S8). The peak observed at 4.57 ppm was due to dihydrogen (H_2) dissolved in the solvent as per the literature reported value.[S5]

(b) Analysis of CO_2

In a 5 mL round-bottom flask, catalyst **[Ir]^B** (0.0005 mmol) and 1.5 mL HCOOH/NEt_3 (5:2, v/v) azeotrope were added. The resulting mixture was stirred at 50°C. The evolved gas was bubbled to a 5 M NaOH/D_2O solution (0.6 mL) kept in an NMR tube. After that $^{13}C\{^1H\}$ NMR spectrum of the solution was recorded (Fig. S9). One drop of CH_3OH was added as reference (49.50 ppm). The peak observed at 168.93 ppm was due to $\underline{C}O_3^{2-}$ in D_2O as per the literature reported value.[S4]

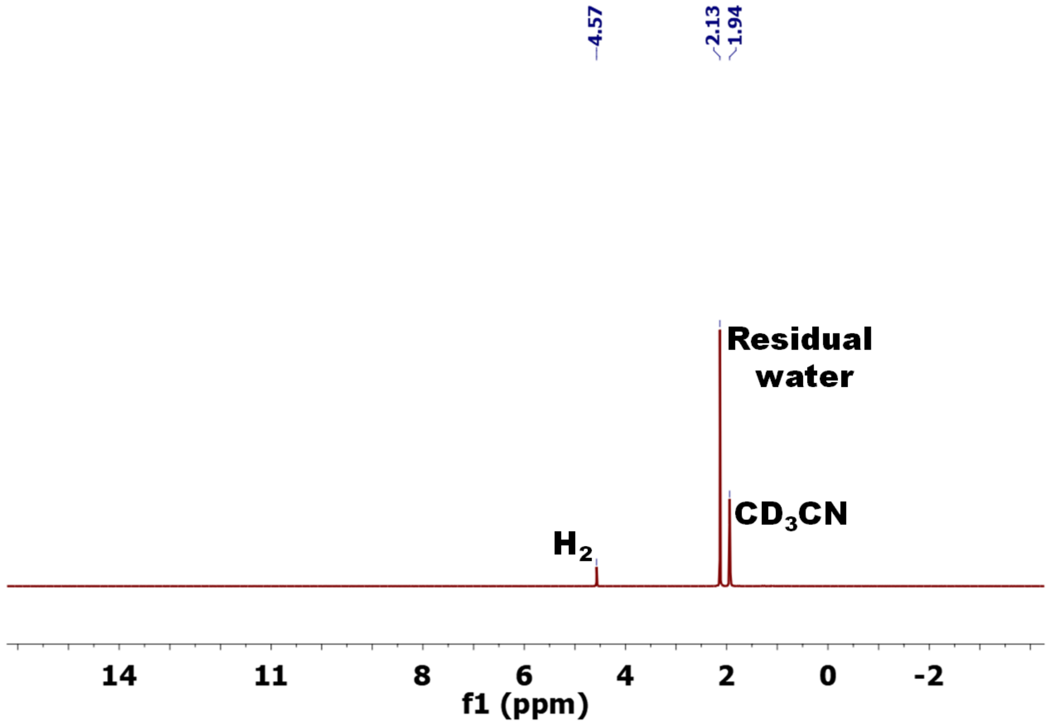


Fig. S8 ^{1}H NMR spectroscopic characterization of H_2 gas from the HCO_2H-dehydrogenation catalysis.

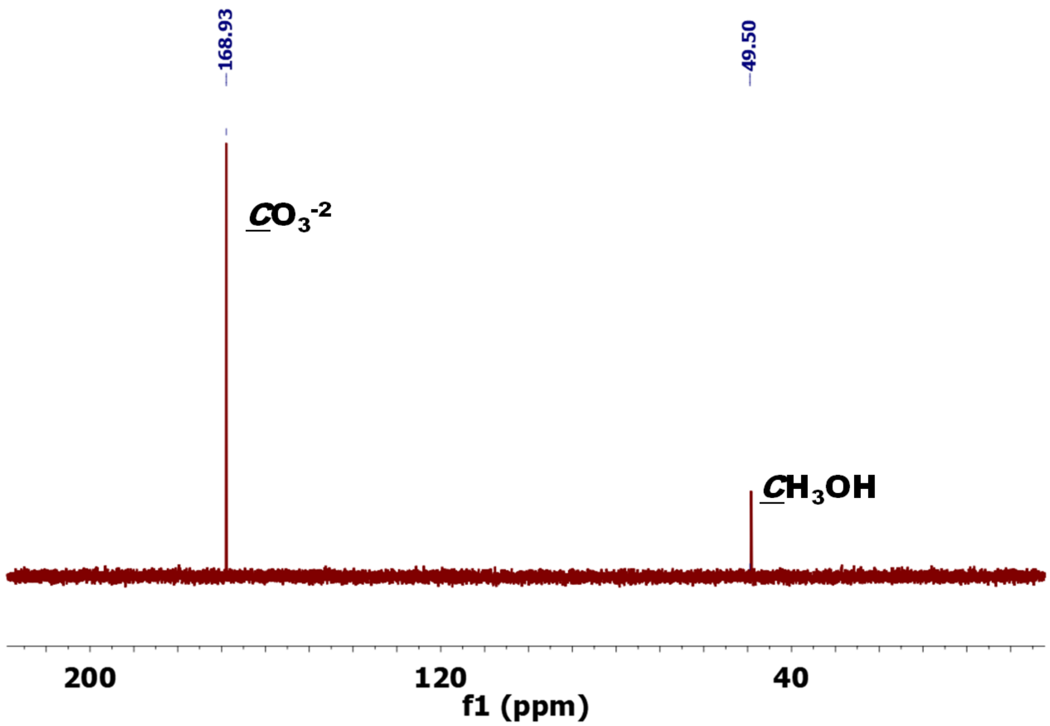


Fig. S9 $^{13}C\{^1H\}$ NMR spectroscopic characterization of CO_2 gas (in the form of trapped carbonate, CO_3^{2-}) from the HCO_2H-dehydrogenation catalysis.

XI. ^1H NMR spectroscopic analysis of the aliquots withdrawn from ongoing hydrogenation and dehydrogenation reactions with catalyst [Ir]^B

(a) Hydrogenation case: A typical CO_2-hydrogenation reaction was performed using catalyst **[Ir]^B** (0.002 mmol) in 0.1 M aqueous KOH (5 mL) as per the procedure described above. After 30 min of bubbling with H_2(g) and CO_2(g), the reaction was stopped and the mixture was extracted with dichloromethane (DCM) to obtain an orange coloured solution. This solution was dried under vacuum and the residue was dissolved in CD_3CN to record ^1H NMR spectrum (Fig. S10a). This NMR spectrum was compared with a known ^1H NMR spectrum of an unused sample of complex **[Ir]^B** in CD_3CN (Fig. S10b). The analysis suggested that the catalyst **[Ir]^B** remained as its amido-bound (benzimidazolato) form.

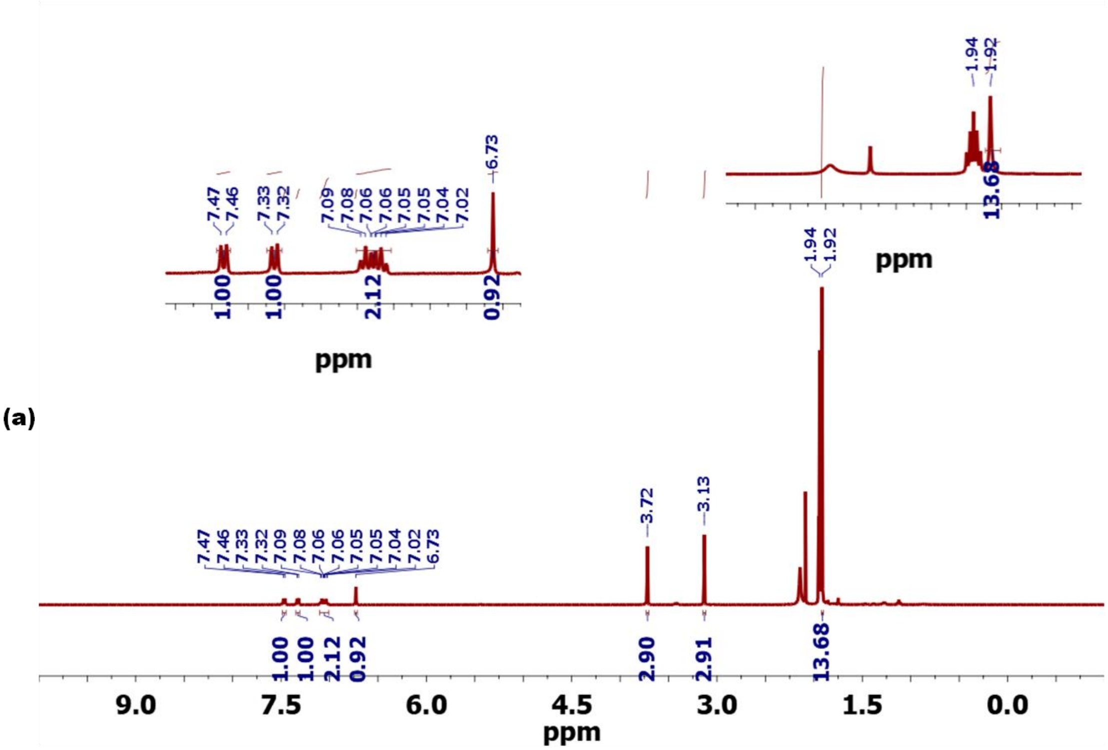


Fig. S10a ^{1}H NMR spectrum (CD_3CN) of a reaction solution for CO_2-hydrogenation with **[Ir]$^{\mathbf{B}}$**.

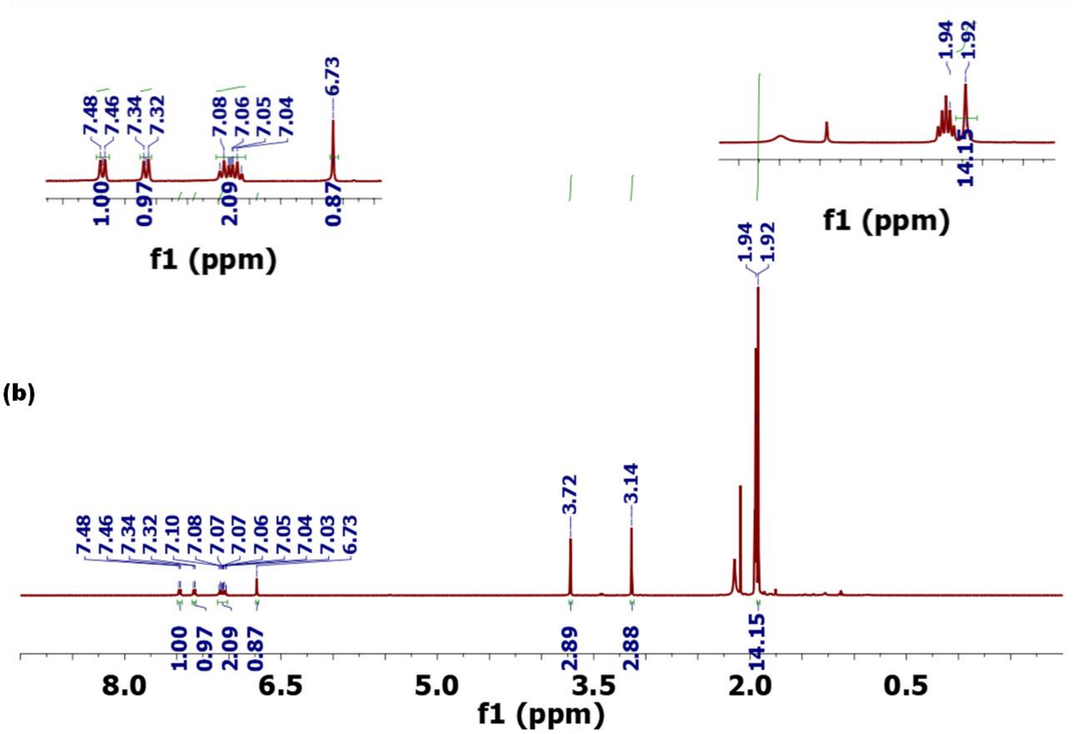


Fig. S10b ^{1}H NMR spectrum (CD_3CN) of an unused sample of **[Ir]$^{\mathbf{B}}$**.

(b) Dehydrogenation case: Similarly, control ^{1}H NMR spectrum of catalyst **[Ir]^B** was recorded in CDCl$_3$ (Fig. S11a). A typical dehydrogenation reaction was performed with catalyst **[Ir]^B** (0.004 mmol) in 1 mL of HCO$_2$H/NEt$_3$ (5:2, w/w) azeotrope at 30°C for 5 min. Evolution of gas bubbles could be observed inside the reaction flask. An aliquot (250 µL) was withdrawn from the reaction mixture and was analyzed by ^{1}H NMR spectroscopy in CDCl$_3$ (Fig. S11b). The analysis suggested that there are changes in the chemical shift values of the ligand backbone protons along with appearance of new peaks at 8.37 ppm and 7.82 ppm which might be due to $\underline{H}CO_2^-$ counter-ion^{S6} and the N$\underline{H}$ proton of the imino-bound ligand. These changes indicated that the catalyst **[Ir]^B** existed as its imino-bound form under the dehydrogenation reaction conditions via protonation of the basic amido nitrogen of the benzimidazolato ligand.

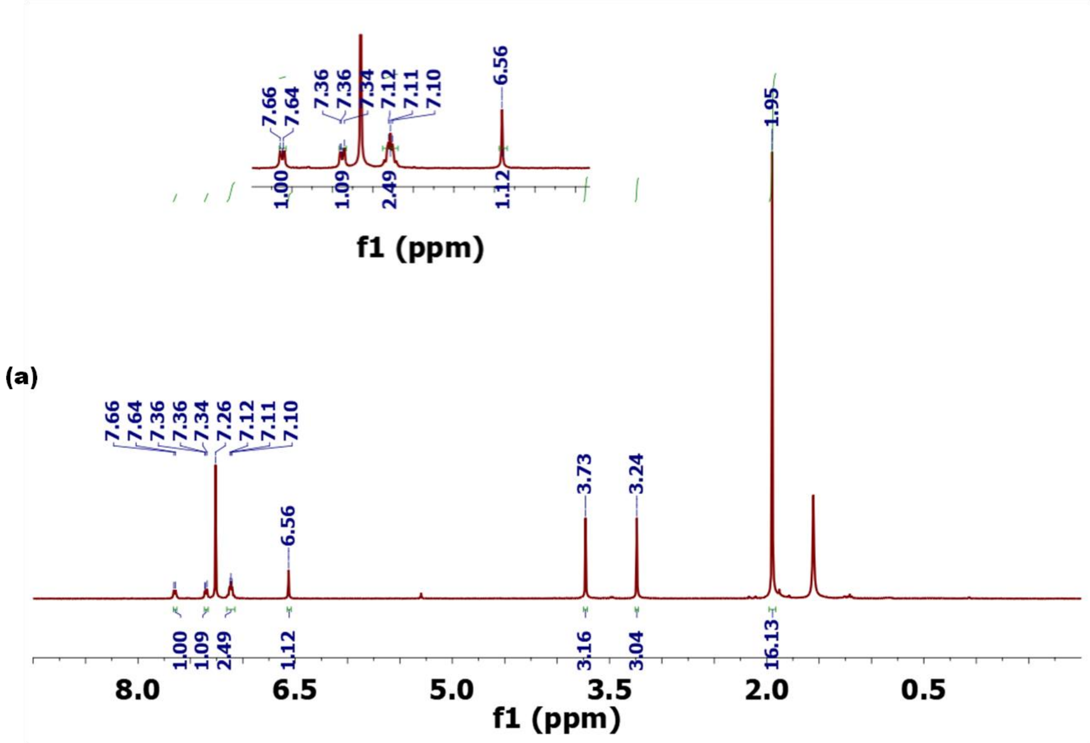
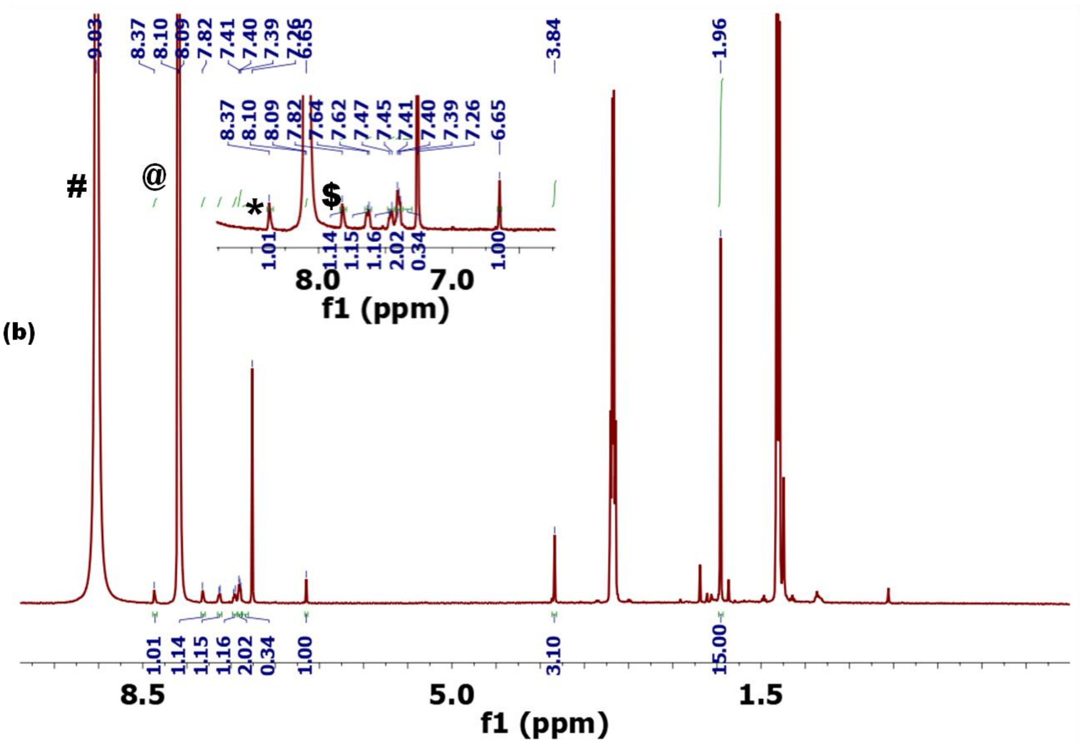


Fig. S11a ^{1}H NMR spectrum (CDCl$_3$) of an unused sample of **[Ir]^B**.



Free $HCOO\underline{H}$, **@** Free $\underline{H}COOH$, * $\underline{H}COO^{-}$ counter-ion, **\$** N$\underline{H}$ of the complex

Fig. S11b. ^{1}H NMR spectrum ($CDCl_3$) of a reaction solution for HCO_2H-dehydrogenation with **[Ir]**^{B}.

XII. DFT-calculated LUMO energies of the conjugate hydride acceptors '[Cp*Ir(*a*NHC$_{pyridinylidene}$–N$_{benzimidazolato}$)]$^{+}$' and '[Cp*Ir(*a*NHC$_{imidazolylidene}$–N$_{benzimidazolato}$)]$^{+}$', derived from [Ir]^{A} and [Ir]^{B} respectively

The geometries of the conjugate hydride acceptors namely, '[Cp*Ir(*a*NHC$_{pyridinylidene}$–N$_{benzimidazolato}$)]$^{+}$' fragment derived from **[Ir]**^{A}, and '[Cp*Ir(*a*NHC$_{imidazolylidene}$–N$_{benzimidazolato}$)]$^{+}$' fragment derived from **[Ir]**^{B} were optimized with the nonlocal hybrid Becke three-parameter Lee-Yang-Parr (B3LYP) exchange-correlation functional[S7] with the 6-310G(d) basis set for H,C,O and N atoms and LANL2DZ for iridium atom in vacuum phase. Calculations were performed with Gaussian 09[S8] using Gaussview[S9] to generate structures. All values were converted to eV from the reported Hartree energies. The results are shown in Fig. S12 (left: for **[Ir]**^{A}-derived fragment; right: for **[Ir]**^{B}-derived fragment). The XYZ coordinates have been shown in Table S3 (for '[Cp*Ir(*a*NHC$_{pyridinylidene}$–N$_{benzimidazolato}$)]$^{+}$' and Table S4 (for [Cp*Ir(*a*NHC$_{imidazolylidene}$–N$_{benzimidazolato}$)]$^{+}$).

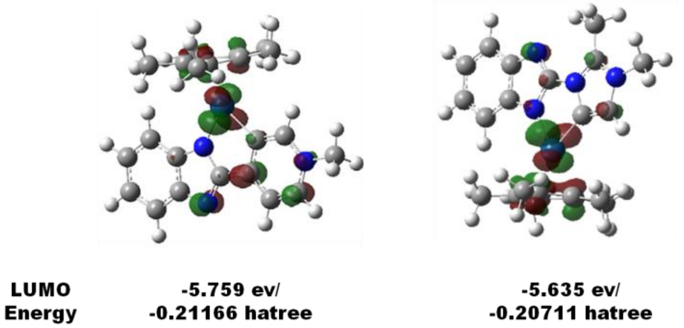


Fig. S12 DFT-calculated LUMO energies of the conjugate hydride acceptors '[Cp*Ir(aNHC$_{pyridinylidene}$–N$_{benzimidazolato}$)]$^{+}$' (left) and '[Cp*Ir(aNHC$_{imidazolylidene}$–N$_{benzimidazolato}$)]$^{+}$' (right), derived from **[Ir]**^{A} and **[Ir]**^{B} respectively.

Table S3 XYZ coordinates of the optimized structure for '[Cp*Ir(*a*NHC$_{\text{pyridinylidene}}$–N$_{\text{benzimidazolato}}$)]$^{+}$'.

C	-3.57300	-0.20200	-0.00100
H	-3.27900	-1.24500	-0.00100
C	-4.91800	0.16700	-0.00100
H	-5.67900	-0.60800	-0.00100
C	-5.31800	1.52000	-0.00000
H	-6.37700	1.75700	-0.00000
C	-4.38100	2.54700	-0.00000
H	-4.67500	3.59100	0.00000
C	-3.02600	2.19300	0.00000
C	-2.62700	0.82300	-0.00000
C	-0.90200	2.17200	0.00000
C	0.50900	2.45100	0.00000
C	1.06100	3.73800	0.00100
H	0.42400	4.61500	0.00100
C	2.43200	3.86700	0.00100
H	2.93700	4.82600	0.00100
C	2.69200	1.50800	-0.00000
H	3.42400	0.71200	-0.00100
C	1.32600	1.28300	-0.00000
C	4.69400	2.95700	-0.00200
H	5.18200	1.98300	0.00900
H	4.99400	3.52000	0.88500
H	4.99400	3.50000	-0.90200
C	-0.33600	-2.60200	0.70600
C	1.00800	-2.20300	1.15500
C	1.85400	-2.07100	0.00000
C	1.00800	-2.20400	-1.15400
C	-0.33600	-2.60300	-0.70500
C	-1.44800	-2.98900	-1.63200
H	-2.40300	-3.08400	-1.11100
H	-1.22500	-3.96000	-2.09500
H	-1.57500	-2.26200	-2.43900
C	-1.44700	-2.98700	1.63400
H	-1.57300	-2.25900	2.44100
H	-1.22500	-3.95700	2.09800
H	-2.40200	-3.08200	1.11400
C	1.44400	-2.16300	2.58700
H	0.65300	-1.77700	3.23500

H	2.33000	-1.53900	2.72400
H	1.69200	-3.17700	2.93100
C	3.34600	-1.92400	-0.00000
H	3.70400	-1.39800	-0.89000
H	3.81900	-2.91500	0.00100
H	3.70400	-1.39700	0.88900
C	1.44300	-2.16600	-2.58600
H	2.33000	-1.54300	-2.72400
H	0.65200	-1.77800	-3.23500
H	1.68800	-3.18000	-2.93000
N	-1.23600	0.82000	-0.00000
N	-1.91300	3.01300	0.00000
N	3.23000	2.76800	0.00000
Ir	0.26400	-0.49600	-0.00000

Table S4 XYZ coordinates of the optimized structure for ‘[Cp*Ir(aNHC$_{\text{imidazolylidene}}$–N$_{\text{benzimidazolato}}$)]$^{+}$’.

Ir	-0.72000	-0.02700	-0.00100
N	1.19700	-0.61000	-0.00000
N	1.24000	3.78800	-0.01500
N	1.64600	1.67500	-0.00100
N	3.41300	0.00300	-0.00200
C	0.23800	1.77200	-0.00200
C	2.16900	0.37100	-0.00200
C	1.95400	-1.78900	0.00100
C	-2.86300	0.56400	-0.00000
C	-2.56500	-0.24000	-1.15500
C	-2.22700	-1.59900	-0.70400
C	1.59100	-3.13400	0.00200
H	0.55100	-3.44000	0.00200
C	-2.22600	-1.59700	0.70900
C	0.01400	3.12300	-0.00800
H	-0.90700	3.68400	-0.01300
C	2.23900	2.88200	-0.00700
C	3.70000	3.16500	-0.00400
H	4.24900	2.22200	0.03300
H	3.97800	3.77600	0.86300
H	3.99500	3.70900	-0.90900
C	2.62100	-4.07700	0.00200

H	2.37200	-5.13400	0.00300
C	-3.42300	1.95600	-0.00200
H	-3.11400	2.51400	-0.89000
H	-3.11200	2.51700	0.88400
H	-4.51900	1.92200	-0.00100
C	4.34000	-2.34500	0.00100
H	5.38000	-2.03700	0.00000
C	3.31800	-1.39500	-0.00000
C	-2.56400	-0.23600	1.15600
C	3.97300	-3.69100	0.00200
H	4.74300	-4.45500	0.00200
C	-2.73900	0.17000	2.58600
H	-3.74600	-0.10100	2.93200
H	-2.62100	1.24900	2.71500
H	-2.01800	-0.33100	3.23700
C	1.41600	5.24000	0.02200
H	2.28000	5.52400	-0.58100
H	1.55900	5.58500	1.05000
H	0.52500	5.71000	-0.39700
C	-1.99300	-2.75400	1.63200
H	-1.36100	-2.47500	2.48000
H	-1.52100	-3.59600	1.12300
H	-2.95200	-3.10500	2.03700
C	-1.99600	-2.75900	-1.62400
H	-1.52200	-3.59900	-1.11300
H	-1.36700	-2.48200	-2.47500
H	-2.95600	-3.11200	-2.02500
C	-2.74200	0.16300	-2.58600
H	-3.75000	-0.10800	-2.92900
H	-2.02300	-0.34100	-3.23600
H	-2.62300	1.24100	-2.71800

XIII. Determination of activation energy for the catalytic hydrogenation

A 50 mL round-bottom flask was charged with an aqueous solution (20 mL) of base (1 M KOH), catalyst **[Ir]**^{B} (0.002 mmol taken from a stock solution in CH_3CN), and (3-(trimethylsilyl)-1-propanesulfonate) sodium salt (5.01 mg, 0.0229 mmol) (as internal NMR reference). This mixture was bubbled with CO_2(g) from a balloon for 1 h at room temperature. After that, H_2(g) and CO_2(g) were bubbled simultaneously at different temperatures (303 K; 323 K, 333 K, 343 K). The rate of bubbling of both the gases was maintained at ≈70 mL/min. Aliquots were withdrawn at different time intervals and ^{1}H NMR spectra were recorded using D_2O as locking solvent kept inside a sealed capillary. TON values were calculated from the amount of formate produced as described earlier. The results were shown in Fig. S13. The activation energy was found to be 17.5 kcal/mol.

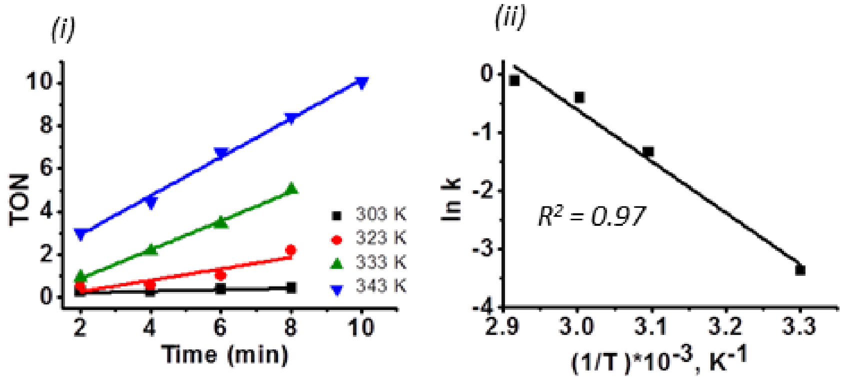


Fig. S13 Rate (i) and Arrhenius plot (ii) for hydrogenation. The equation: $\ln(k) = \ln(A) - E_a/R\ (1/T)$ was used to obtained the activation energy, where k = rate constant, A = pre-exponential factor, E_a = activation energy, R = gas constant, T = absolute temperature, K. From the graph, the following parameters were obtained: Intercept = 25.97 (sd. error = 2.92); Slope = -8856 (sd. error = 949)

XIV. Determination of activation energy for the catalytic dehydrogenation

A 5 mL round-bottom flask was loaded with the catalyst **[Ir]**^{B} (0.0005 mmol taken from a stock solution in CH_3CN). It was degassed three times with argon and then connected to a standard water displacement apparatus using a graduated cylinder to measure volume of the generated gas. The apparatus contained a 5 M NaOH solution as CO_2-trap. Thus when the gaseous product(s) formed in the reaction were passed through the trap, CO_2(g) was dissolved, and the volume of CO_2-free other gas(es) was measured by the graduated cylinder. The reaction was performed by charging a 5:2 (w/w) HCO_2H/NEt_3 azeotrope mixture (1.5 mL) into the flask and stirring the mixture vigorously at different temperatures (318 K, 333 K, 343 K, 353 K). After that, the volume of gas collected at different time intervals was noted. The TON values of the catalyst were calculated as described above. The results were shown in Fig. S14. The activation energy was found to be 11.6 kcal/mol.

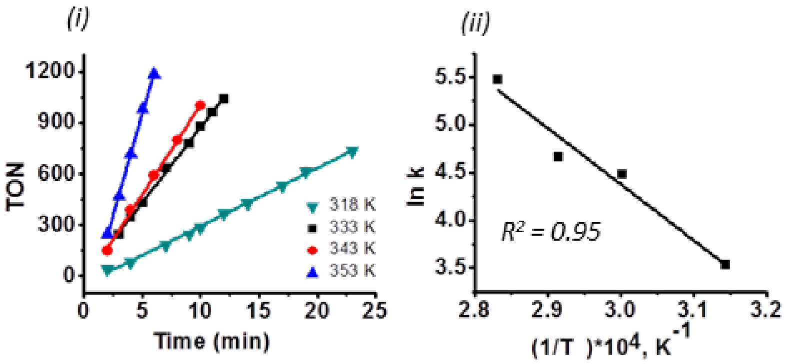


Fig. S14 Rate (i) and Arrhenius plots (ii) for dehydrogenation. The equation: ln(k) = ln(A) – E_a/R (1/T) was used to obtained the activation energy, where k = rate constant, A = pre-exponential factor, E_a = activation energy, R = gas constant, T = absolute temperature, K. From the graph, the following parameters were obtained: Intercept = 21.97 (sd. error = 2.46); Slope = -5862 (sd. error = 828)

XV. Dehydrogenation catalysis with 4.5 mL of substrate

A 10 mL round-bottom flask was loaded with the catalyst **[Ir]**^{B} (0.0005 mmol taken from a stock solution in CH_3CN). It was degassed three times with argon and then connected to a standard water displacement apparatus using a graduated cylinder to measure volume of the generated gas. The apparatus contained a 5 M NaOH solution as CO_2-trap. Thus when the gaseous product(s) formed in the reaction were passed through the trap, CO_2(g) was dissolved, and the volume of CO_2-free other gas(es) was measured by the graduated cylinder. The reaction was performed by charging a 5:2 (w/w) HCO_2H/NEt_3 azeotrope mixture (4.5 mL) into the flask and stirring the mixture vigorously at 363 K. After that, the volume of gas collected at different time intervals was noted. The TON values of the catalyst were calculated as described above.

XVI. Dehydrogenation catalysis with recharging of substrate

A 10 mL round-bottom flask was loaded with the catalyst **[Ir]**^{B} (0.0005 mmol taken from a stock solution in CH_3CN). It was degassed three times with argon and then connected to a standard water displacement apparatus using a graduated cylinder to measure volume of the generated gas. The apparatus contained a 5 M NaOH solution as CO_2-trap. Thus when the gaseous product(s) formed in the reaction were passed through the trap, CO_2(g) was dissolved, and the volume of CO_2-free other gas(es) was measured by the graduated cylinder. The reaction was performed by charging a 5:2 (w/w) HCO_2H/NEt_3 azeotrope mixture (1.5 mL) into the flask initially and stirring the mixture vigorously at 363 K. After each interval of 2 min the recharging with freshly made 1.5 mL of 5:2 (w/w) HCO_2H/NEt_3 was done upto 8 min. The volume of gas collected at 2 min time intervals was noted. The TON values of the catalyst were calculated as described earlier.

XVII. Dehydrogenation catalysis at different pH

A 50 mL round-bottom flask was loaded with the catalyst **[Ir]**^{B} (0.0005 mmol taken from a stock solution in CH_3CN). It was degassed three times with argon and then connected to a standard water displacement apparatus using a graduated cylinder to measure volume of the generated gas. The apparatus contained a 5 M NaOH solution as CO_2-trap. Thus when the gaseous product(s) formed in the reaction were passed through the trap, CO_2(g) was dissolved, and the volume of CO_2-free other gas(es) was measured by the graduated cylinder. The reaction was performed by charging 1 M (1:1) $HCO_2H/HCOONa$ (20 mL) substrate of different pH (1.7, 2.1, 3.8, 4.1, 4.4, 4.8, 5.6) into the flask and stirring the mixture vigorously at 363 K. After that, the volume of gas collected after 2 min was noted. The TON values of the catalyst were calculated as described earlier.

XVIII. References

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