

## Supplementary Information for

### Charge Effects Regulate Reversible CO<sub>2</sub> Reduction Catalysis

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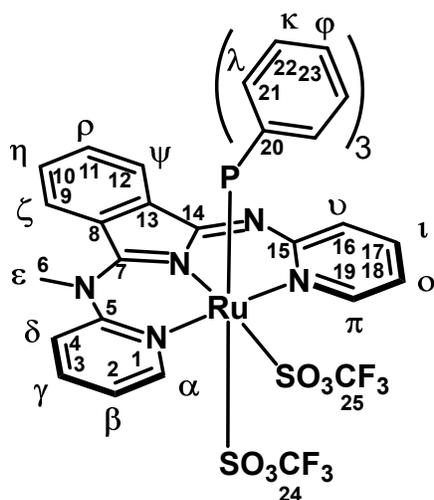
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## General Considerations:

**1, 2, 4, 5, 6, 8, and 9** were prepared according to literature procedures. Dioxane, 2-MeTHF were distilled from Na/benzophenone prior to use, and DMF, MeCN, and toluene were purified using a Glass Contour solvent purification system through percolation through a Cu catalyst, molecular sieves, and alumina. Solvents were stored over activated molecular sieves for a minimum of 48 hours prior to use. Anhydrous  $K_2CO_3$ ,  $Cs_2CO_3$ , KOtBu,  $K(N(SiMe_3)_2)$ , 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), and KOH were obtained commercially and used without further purification. Ultra-high purity  $CO_2$  and  $H_2$  were used in all experiments. All other reagents were used from commercial sources without further purification. Unless otherwise noted, all manipulations were performed under an inert nitrogen atmosphere.

NMR spectra were recorded on a Varian Vnmrs 700, Varian Vnmrs 500, or Varian MR400 spectrometer.  $^1H$ ,  $^{13}C$ ,  $^{19}F$ , and  $^{31}P$  shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference.  $^{31}P$  and  $^{19}F$  NMR spectra are referenced to a unified scale, where the single primary reference is the frequency of the residual solvent peak in the  $^1H$  NMR spectrum. Peaks not listed in the peak assignment correspond to residual solvent.<sup>1</sup> Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), septet (sp), and multiplet (m). Mass spectra were obtained on an electrospray Agilent Q-TOF mass spectrometer or a Micromass AutoSpec Ultima Magnetic Sector Mass Spectrometer electron ionization mass spectrometer. NMR spectra were processed using MestReNova version 10.0.2. For the purpose of labeling atoms for spectral assignments, hydrogen atoms are labeled with greek letters while carbon atoms are labeled with numbers.

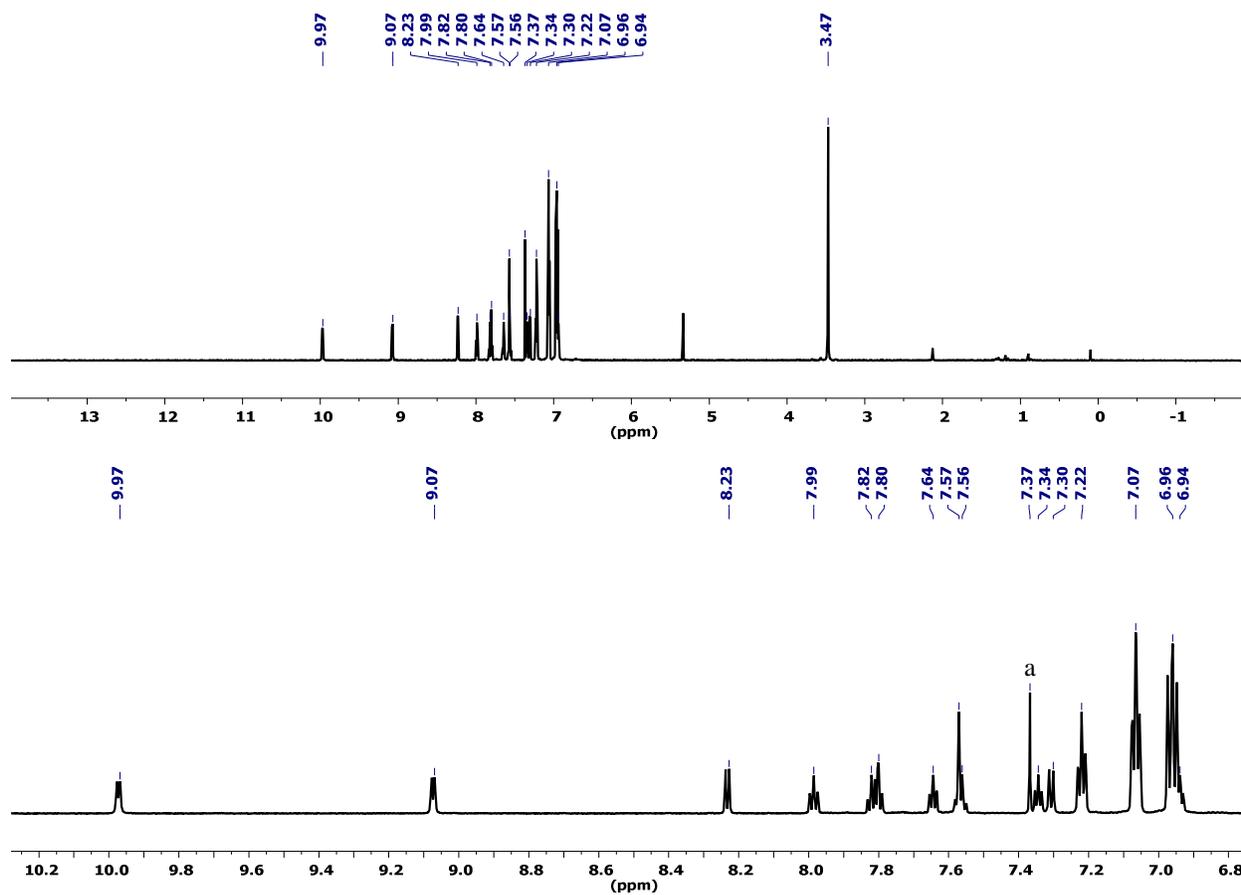
## Preparation of 3



### Ru(BPI<sup>Me</sup>)PPh<sub>3</sub>OTf<sub>2</sub> (3):

Ru(BPI)(PPh<sub>3</sub>)<sub>2</sub>Cl (**2**, 0.103 mmol, 100 mg) was dissolved in 0.5 mL DCM and 10 equiv. MeOTf (1.03 mmol, 116  $\mu$ L) added. The solution was allowed to stand for 16 hours, then the reaction solution cooled to -80  $^{\circ}$ C for 1 hour to precipitate the product. The solvent was decanted and the crystals washed with pentane to give the product (52.4 mg) as large, blue crystals (52%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>): 9.97 ( $\alpha$ , 1H, (d,  $J_{1H-1H}$ =5.6)), 9.07 ( $\pi$ , 1H, (d,  $J_{1H-1H}$ =5.9)), 8.23 ( $\psi$ , 1H, (d,  $J_{1H-1H}$ =7.3)), 7.99 ( $\gamma$ , 1H, (t,  $J_{1H-1H}$ =8.1)), 7.82 ( $\iota$ , 1H, (t,  $J_{1H-1H}$ =7.4)), 7.80 ( $\nu$ , 1H, (d,  $J_{1H-1H}$ =6.1)), 7.64 ( $\rho$ , 1H, (t,  $J_{1H-1H}$ =7.7)), 7.57 ( $\zeta$ , 1H, (d,  $J_{1H-1H}$ =6.7)), 7.56 ( $\eta$ , 1H, m (overlap)), 7.34 ( $\beta$ , 1H, (t,  $J_{1H-1H}$ =6.6)), 7.30 ( $\delta$ , 1H, (d,  $J_{1H-1H}$ =8.4)), 7.22 ( $\phi$ , 3H, (t,  $J_{1H-1H}$ =7.4)), 7.07 ( $\kappa$ , 6H, (t,  $J_{1H-1H}$ =6.8)), 6.96 ( $\lambda$ , 6H, (dd,  $J$ =8.2, 9.1)), 6.94 ( $\omicron$ , 1H, (t,  $J_{1H-1H}$ =6.1)), 3.47 ( $\epsilon$ , 3H, s). <sup>13</sup>C-NMR: 163.74 (7), 157.19 (19), 157.16 (1), 154.60 (15), 152.88 (5), 146.93 (14), 140.84 (13), 138.44 (3), 137.43 (17), 134.34 (8), 132.88 (21 (d,  $J_{13C-31P}$ =42)), 131.61 (20 (d,  $J_{13C-31P}$ =196)), 131.28 (11), 131.11 (10), 130.43 (16), 129.80 (23 (d,  $J_{13C-31P}$ =14)), 128.25 (trace benzene), 128.03 (22 (d,  $J_{13C-31P}$ =49)), 123.67 (12), 122.67 (9), 121.07 (18), 119.41 (2), 118.83 (24, 25) 114.23 (4), 42.19 (6). <sup>31</sup>P-NMR: 59.10. <sup>19</sup>F-NMR: -79.15, -79.26. HRMS (ESI<sup>+</sup>): 826.0803 (M-OTf: 826.0807). Note: Shorter reaction time gives incomplete conversion, longer reaction time decomposes product.

Fig. S1. <sup>1</sup>H NMR Spectrum, Aromatic Region Detail:



a: Trace benzene

Fig. S2.  $^{13}\text{C}$  NMR Spectrum, Aromatic Region Detail:

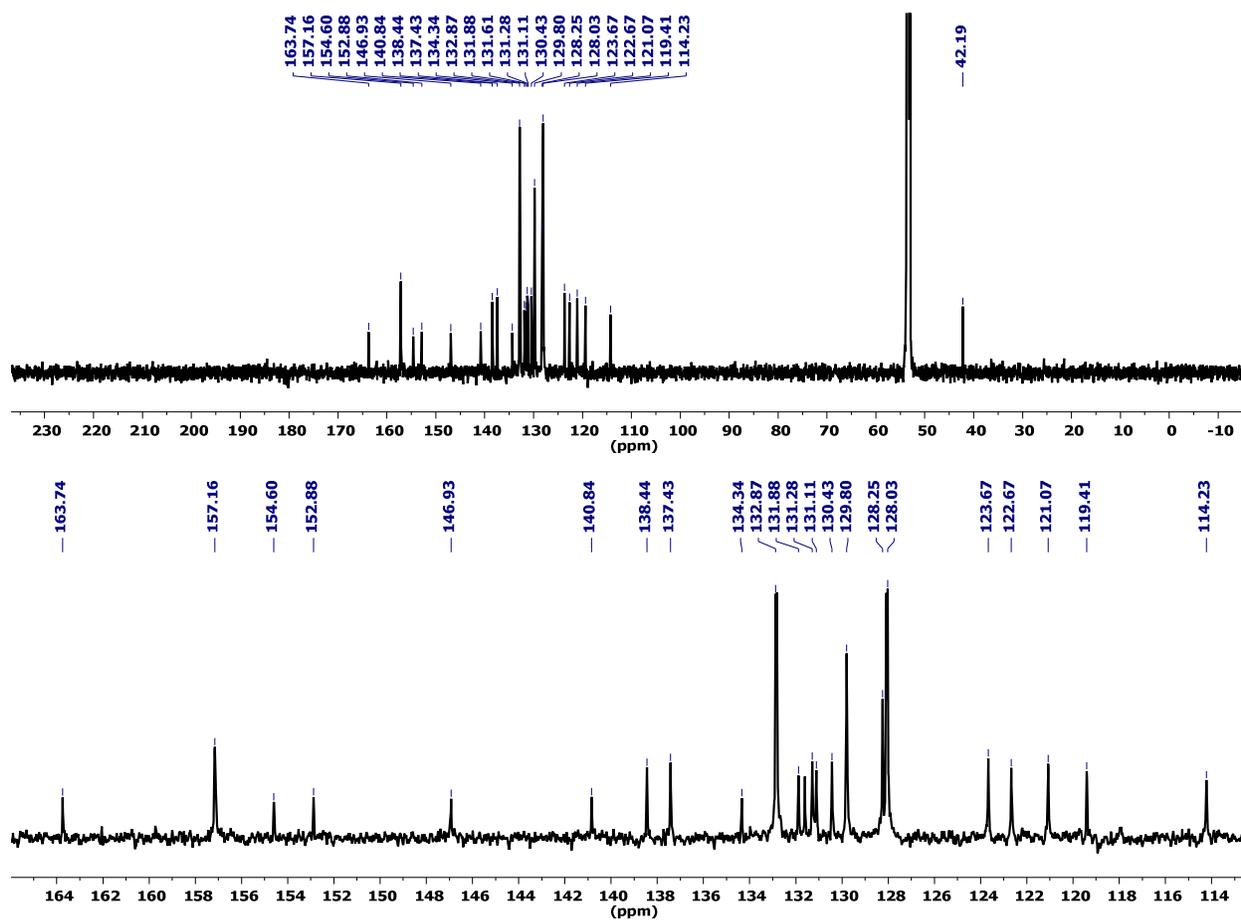


Fig. S3.  $^{31}\text{P}$  NMR Spectrum:

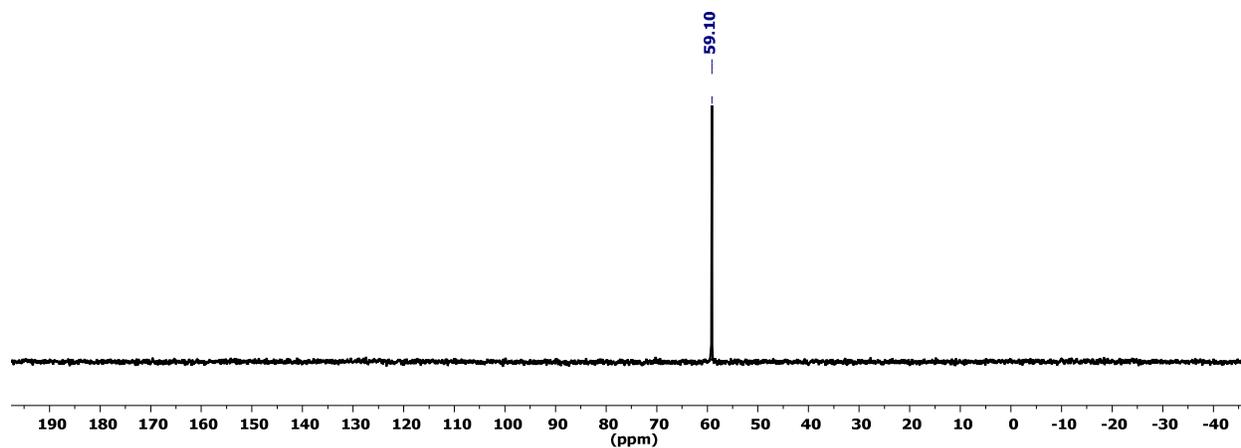


Fig. S4.  $^{19}\text{F}$  NMR Spectrum,  $\text{CF}_3$  Region Detail:

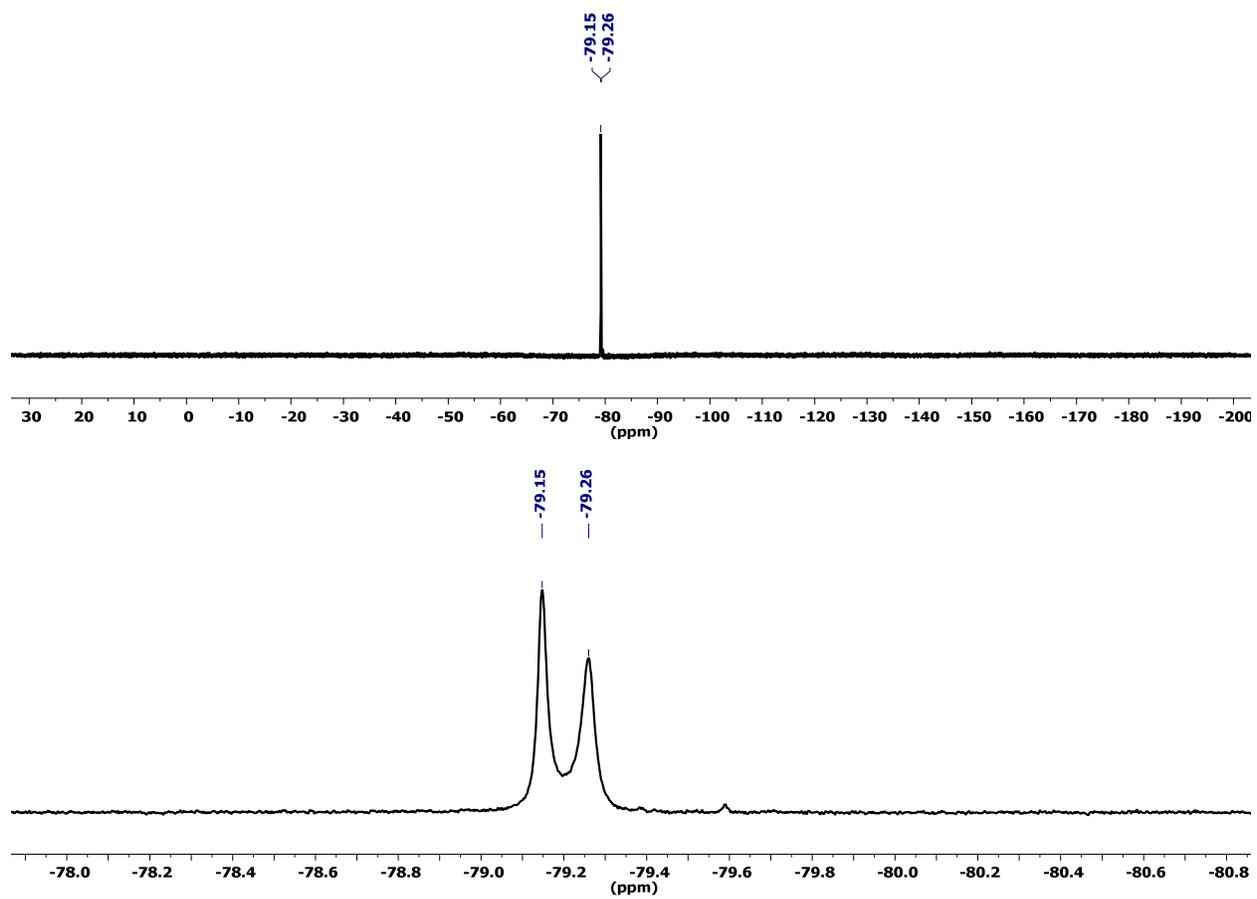


Fig. S5.  $^1\text{H}$ -gCOSY Spectrum:

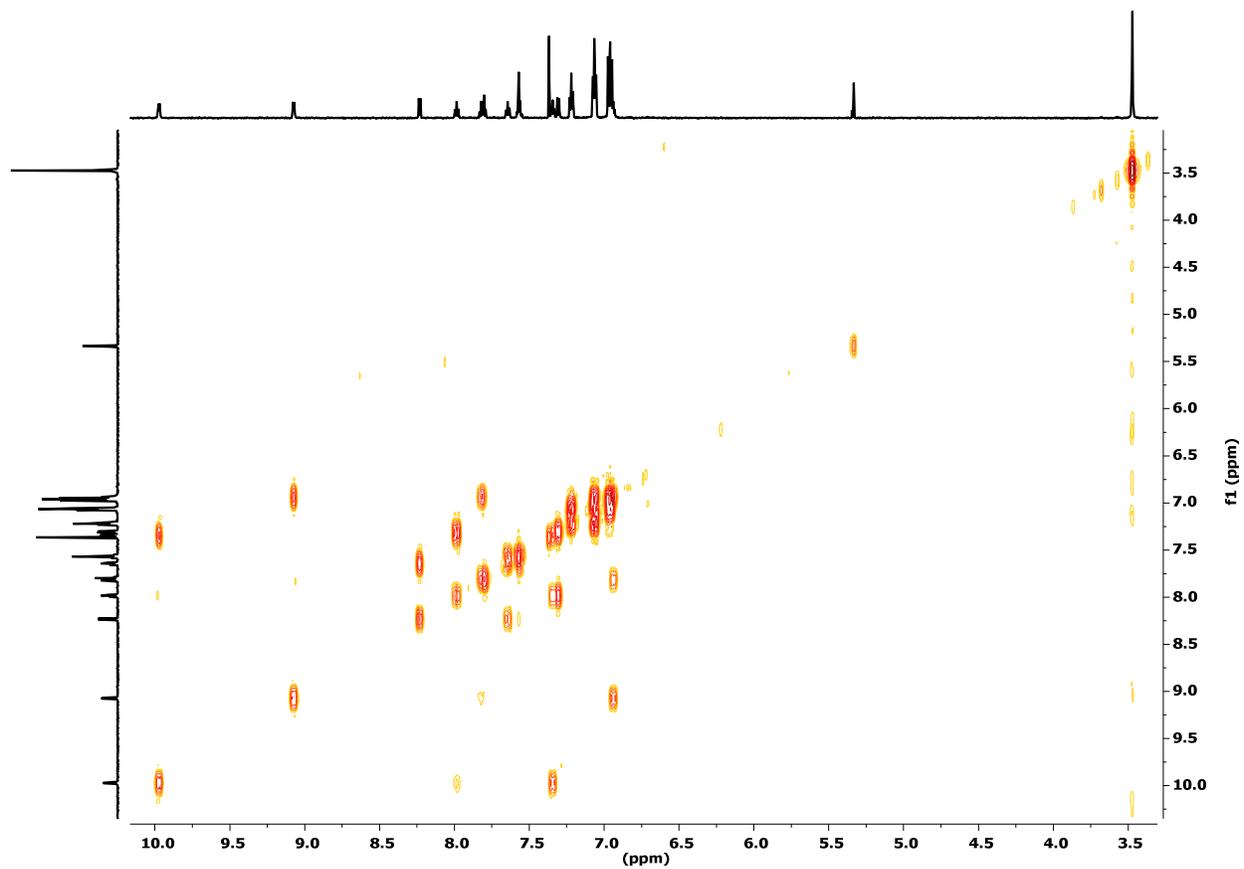


Fig. S6.  $^1\text{H}$ - $^{13}\text{C}$  gHSQCAD Spectrum:

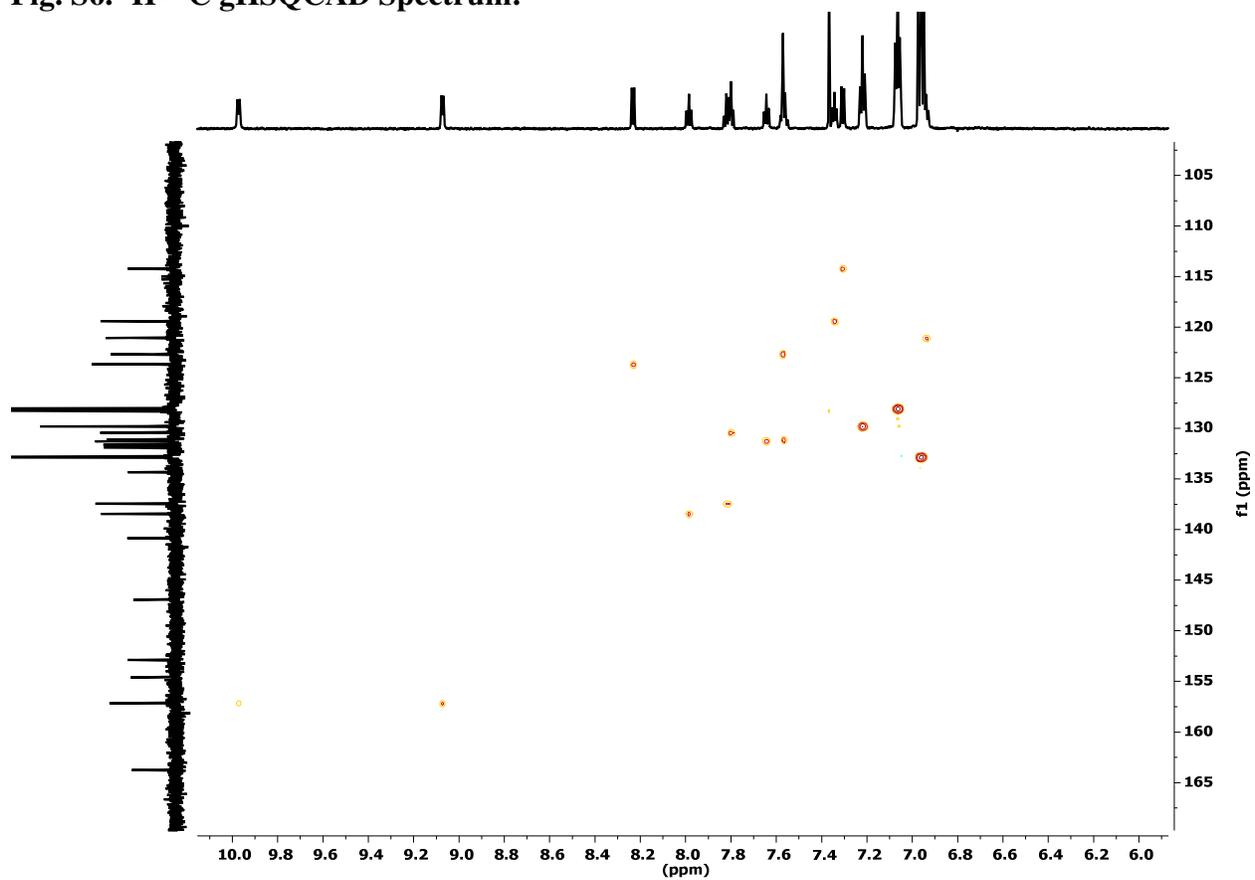


Fig. S7.  $^1\text{H}$ - $^{13}\text{C}$  gHMBCAD Spectrum:

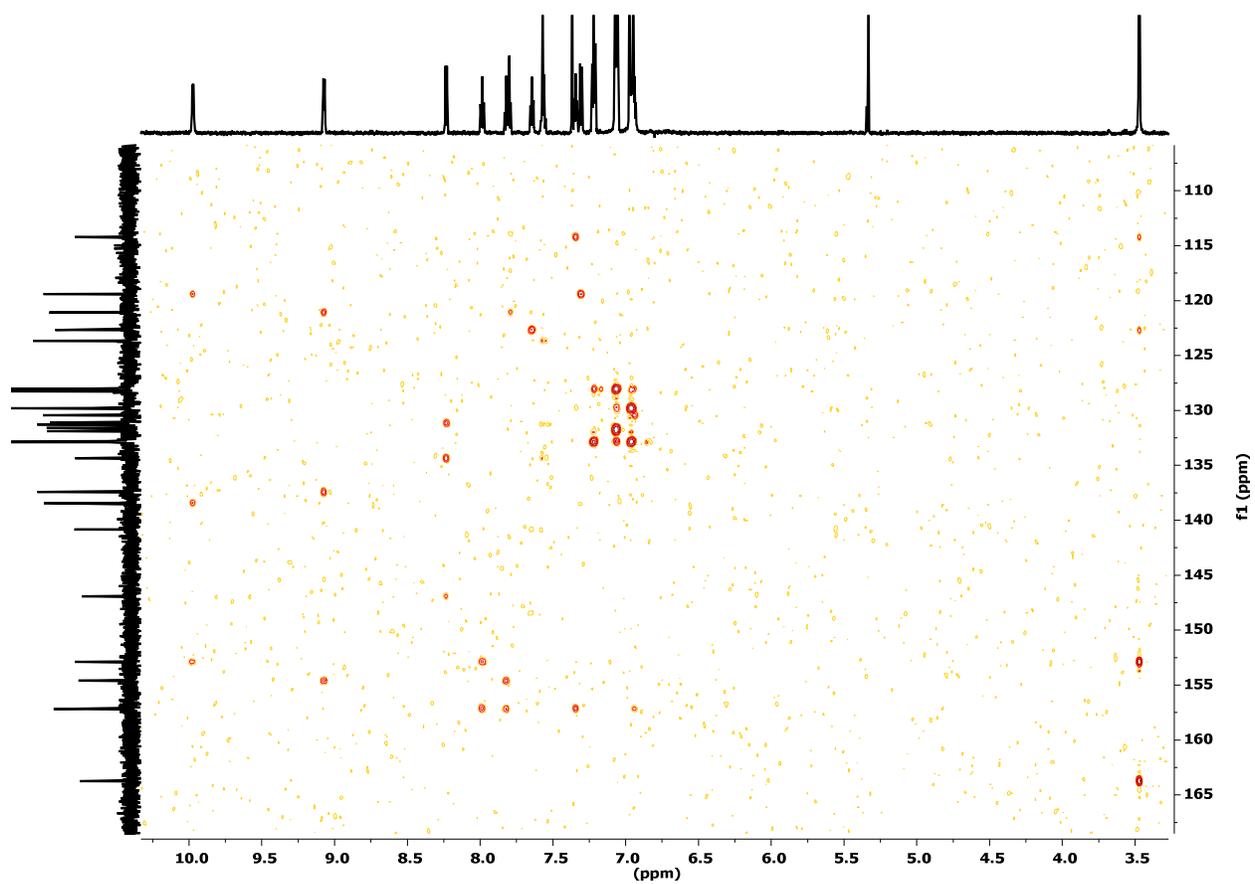


Fig. S8.  $^{19}\text{F}$ - $^{13}\text{C}$  CRISIS2-gHSQC Spectrum:

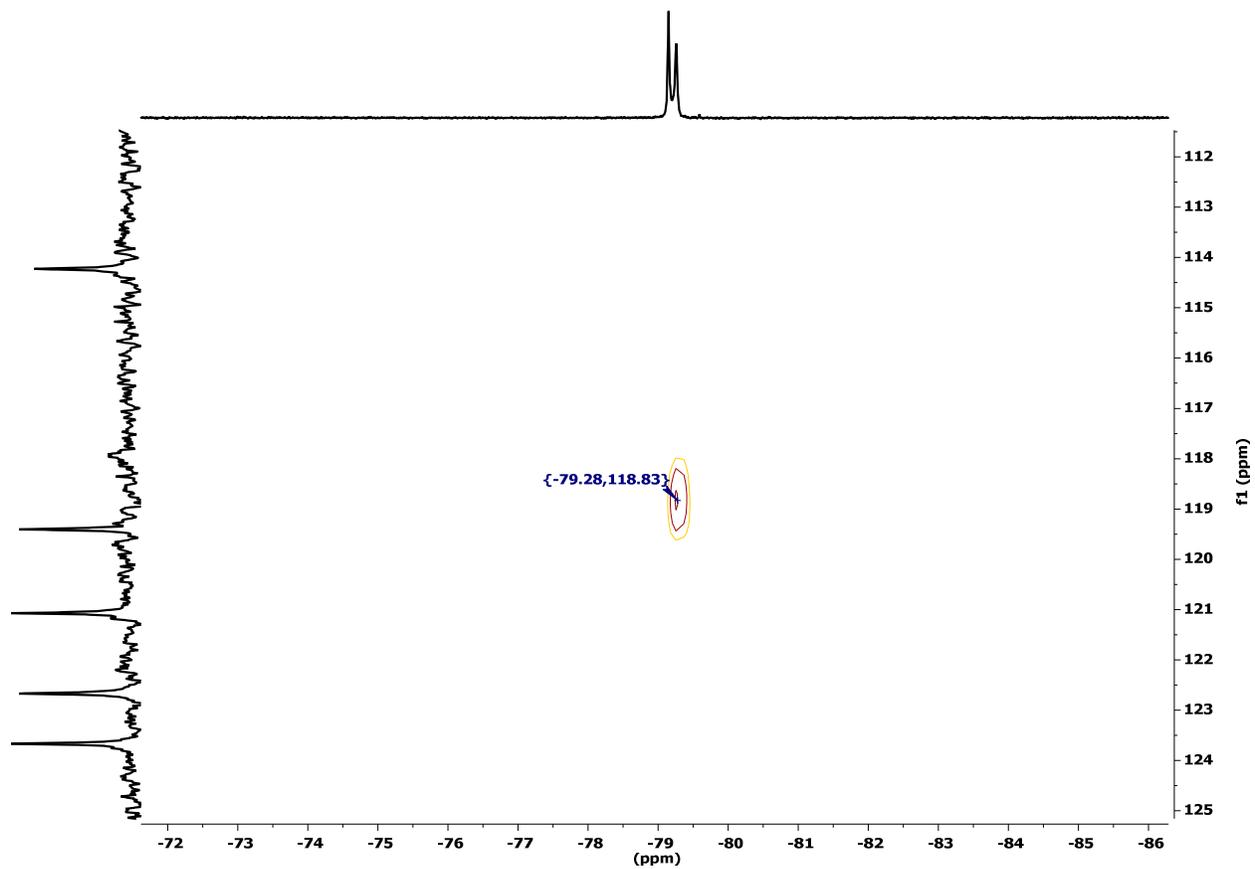
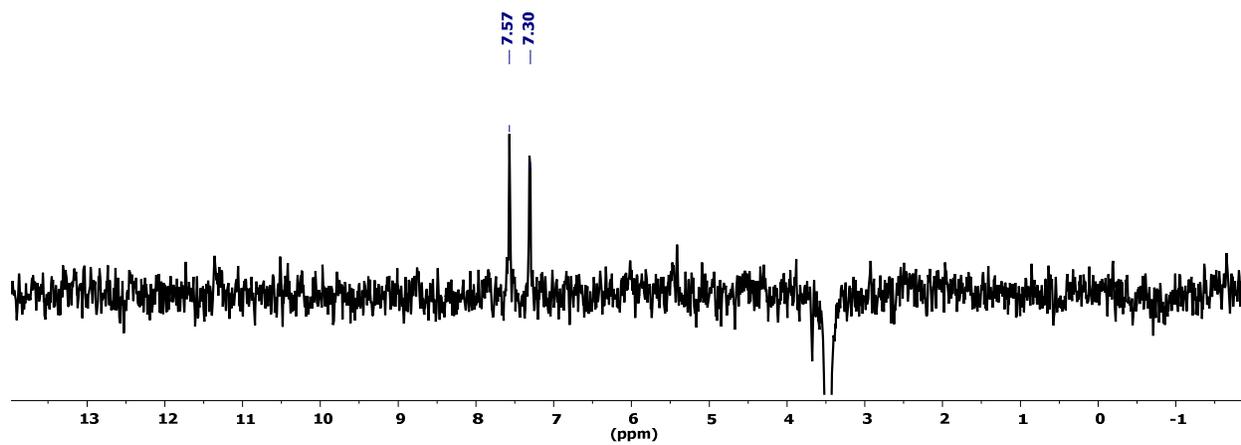


Fig. S9.  $^1\text{H}$ -ROESY-1D Spectrum (irradiation at  $-\text{CH}_3$  ( $\epsilon$ ) resonance):



## General Protocols for CO<sub>2</sub> Hydrogenation and Formate Dehydrogenation

### Description of apparatus for pressurized reactions:

All reactions were run in 300 or 130 mL stainless steel Parr reactors equipped with a pressure gauge, burst disc, and inlet/outlet needle valve. Small-scale reactions were conducted in 8 mL scintillation vials that were loaded into an aluminum block machined to hold seven vials and fit into a 300 mL Parr reactor. Large-scale reactions were conducted in a c.a. 130 mL volume glass liner loaded into either a 130 mL or 300 mL Parr reactor. To exclude air from the reactions, the volume contained in the connection between the tank and the reactor was purged with ultra-high-purity reactant gas (CO<sub>2</sub> or H<sub>2</sub>) 10 times at 100 psi.

### General conditions for CO<sub>2</sub> hydrogenation reactions:

Base (0.400 mmol), 1 mL solvent, and **1-9** (dispensed as a 2.0 mM stock solution in matching solvent) were combined in 8 mL scintillation vials equipped with a stirbar and topped with an open-top septum screwcap with inner PTFE liner. The septum was pierced with a 0.25 inch, 27 gauge needle, and the vials loaded into a stainless steel reactor and CO<sub>2</sub> and H<sub>2</sub> were added to the headspace to obtain the desired gas partial pressures. The reactor was then heated to the desired temperature in a large, machined aluminum heating block for the desired reaction time with stirring at 660 rpm. At the end of the reaction the reactor was cooled in an ice bath until the internal temperature dropped below 25 °C (as measured through changes in the internal pressure, ca. 10 min), and slowly vented to atmospheric pressure and analyzed for formate content.

### General conditions for small-scale formate dehydrogenation reactions:

**1-9** (dispensed as a 2.0 mM stock solution in DMF) were combined with DBU (0.400 mmol) and formic acid (0.400 mmol) in 1 mL DMF in 8 mL scintillation vials equipped with a stirbar and topped with an open-top septum screwcap with inner PTFE liner. The septum was pierced with a 0.25 inch, 27 gauge needle, and the vials loaded into an aluminum heating block and heated in the glovebox as open systems for the desired reaction time and with 660 rpm stirring to permit continuous release of CO<sub>2</sub>/H<sub>2</sub> gas. At the end of the reaction the vials were cooled to room temperature and analyzed for formate content. Control reactions were carried out in the absence of catalyst to measure the rate of the background formate decomposition reaction, allowing for determination of the turnover number.

### Formate Quantification:

<sup>1</sup>H-NMR spectroscopy was used to quantify formate in the reaction mixtures. With DBU as base and DMF as the solvent for CO<sub>2</sub> hydrogenation and in all FA dehydrogenation experiments, 0.400 mmol PhSiMe<sub>3</sub> internal standard was added to the reaction mixture, the mixture vortexed for 10 seconds at 2000 rpm, and then the homogeneous solution sampled for <sup>1</sup>H-NMR in DMSO-d<sub>6</sub>. With all other solvents and bases, solvent and other volatiles were removed from the reaction mixture under vacuum. The resulting solid was dissolved in D<sub>2</sub>O along with 0.400 mmol sodium acetate internal standard to afford a homogeneous solution for <sup>1</sup>H NMR integration. NMR acquisition parameters: d1=40 seconds, total interpulse delay: 45 seconds.

## Optimization of CO<sub>2</sub> Hydrogenation Reaction Conditions Using **4**

### *Solvent and Base Optimization*

Conditions and set-up for optimization reactions were similar to those used for the “small-scale CO<sub>2</sub> hydrogenation” experiments. Base (0.400 mmol), 1 mL solvent, and 0.0625mol% **4** (dispensed as a 4 mM stock solution in DMF) were combined under N<sub>2</sub> in 8 mL scintillation vials equipped with a stirbar and topped with an open-top septum screwcap with inner PTFE liner. The septum was pierced with a 0.25 inch, 27 gauge needle, and the vials loaded into a stainless steel Parr reactor and CO<sub>2</sub> (6 atm) and H<sub>2</sub> (35 atm) were added to the headspace. The reactor was then heated to 80 °C in a large, machined aluminum heating block for 16 hours with stirring at 600 rpm. At the end of the reaction the reactor was allowed to cool in an ice bath, and slowly vented to atmospheric pressure and analyzed for formate content.

**Fig. S10. Solvent and base optimization:**

Solvent	K <sub>2</sub> CO <sub>3</sub>	KO <sup>t</sup> Bu	K(N(SiMe <sub>3</sub> ) <sub>2</sub> )	Cs <sub>2</sub> CO <sub>3</sub>	KOH	DBU	NEt <sub>3</sub>
<b>Dioxane</b>							
TON	136	150	8	9.6	3.2	138	73.6
<b>DMF</b>							
TON	--	--	--	1424	--	1216	--
<b>MeCN</b>							
TON	539	68.8	510	512	14.4	877	17.6
<b>2-MeTHF</b>							
TON	104	163	8	240	6.4	606	1.6
<b>Toluene</b>							
TON	0	52.8	3.2	28.8	4.8	253	1.6
<b><i>o</i>-dichlorobenzene</b>							
TON	214	448	6.4	62.4	4.8	642	0
<b>DMF (air)</b>							
TON	92.8	722	258	54.4	114	1090	4.8
<b>NEt<sub>3</sub></b>							
TON	43.2	92.8	261	40	--	483	3.2

### *Reaction Temperature Optimization*

Cs<sub>2</sub>CO<sub>3</sub> base (0.400 mmol), 1 mL solvent, and 0.0625mol% **4** (dispensed as a 4 mM stock solution in DMF) were combined under N<sub>2</sub> in 8 mL scintillation vials equipped with a stirbar and topped with an open-top septum screwcap with inner PTFE liner. The septum was pierced with a 0.25 inch, 27 gauge needle, and the vials loaded into a stainless steel Parr reactor and CO<sub>2</sub> (6 atm) and H<sub>2</sub> (35 atm) were added to the headspace. The reactor was then heated in a large, machined aluminum heating block for 1 or 16 hours, dependent on experiment, with stirring at 600 rpm. At the end of the reaction the reactor was allowed to cool in an ice bath, and slowly vented to atmospheric pressure and analyzed for formate content.

**Fig. S11. Temperature optimization:**

Entry	Temperature (°C)	Time (hr)	TON (avg)
1	80	1	411
2	80	16	1420
3	120	1	1370
4	120	16	2330
5	150	1	2460
6	150	16	2710
7	180	1	2860
8	180	16	3190

*Catalyst Loading Optimization*

Cs<sub>2</sub>CO<sub>3</sub> base (0.400 mmol), 1 mL DMF, and varied amounts of **4** (dispensed as a 4 mM stock solution in DMF) were combined under N<sub>2</sub> in 8 mL scintillation vials equipped with a stirbar and topped with an open-top septum screwcap with inner PTFE liner. The septum was pierced with a 0.25 inch, 27 gauge needle, and the vials loaded into a stainless steel reactor and CO<sub>2</sub> (6 atm) and H<sub>2</sub> (35 atm) were added to the headspace. The reactor was then heated to 80 °C in a large, machined aluminum heating block, with stirring at 600 rpm. At the end of the reaction the reactor was allowed to cool in an ice bath, and slowly vented to atmospheric pressure and analyzed for formate content.

**Fig. S12. Catalyst loading optimization:**

Catalyst Loading (mol%)	1	0.5	0.25	0.125	0.0625	0.03125	0.0156
TON	182	374	700	1272	1424	979	544

*Pressure Optimization*

Cs<sub>2</sub>CO<sub>3</sub> base (0.400 mmol), 1 mL DMF, and 0.0625 mol% **4** (dispensed as a 4 mM stock solution in DMF) were combined under N<sub>2</sub> in 8 mL scintillation vials equipped with a stirbar and topped with an open-top septum screwcap with inner PTFE liner. The septum was pierced with a 0.25 inch, 27 gauge needle, and the vials loaded into a stainless steel Parr reactor and CO<sub>2</sub> (6 atm for variable H<sub>2</sub> experiments) and H<sub>2</sub> (28 atm for variable CO<sub>2</sub> experiments) were added to the headspace. The reactor was then heated to 80 °C in a large, machined aluminum heating block for 16 hours, with stirring at 600 rpm. At the end of the reaction the reactor was allowed to cool in an ice bath, and slowly vented to atmospheric pressure and analyzed for formate content.

**Fig. S13. Pressure optimization:**

Entry	CO <sub>2</sub> Pressure (atm)	H <sub>2</sub> Pressure (atm)	TON
1	0	28	12.8
2	6	28	957
3	27	28	883
4	41	28	590
5	6	28	883
6	6	39	1277
7	6	50	1298

**Activity of 1-9 in CO<sub>2</sub> Hydrogenation and Formate Dehydrogenation****Fig. S14. Comparison of 1-9:**

Catalyst	CO <sub>2</sub> Hydrogenation (TON)		FA Dehydrogenation (TON)	
	3h, 0.005 %	18h, 0.001 %	3h, 0.005 %	18h, 0.001 %
1	5.4(2) x 10 <sup>3</sup>	2.9(2) x 10 <sup>4</sup>	5.8(4) x 10 <sup>3</sup>	3.7(2) x 10 <sup>3</sup>
2	2.32(2) x 10 <sup>3</sup>	1.45(5) x 10 <sup>4</sup>	7.63(8) x 10 <sup>3</sup>	5.5(1) x 10 <sup>3</sup>
3	8.4(3) x 10 <sup>3</sup>	4.5(1) x 10 <sup>4</sup>	1.38(2) x 10 <sup>4</sup>	6.0(4) x 10 <sup>3</sup>
4	1.03(1) x 10 <sup>4</sup>	5.3(2) x 10 <sup>4</sup>	2.1(5) x 10 <sup>3</sup>	5.8(2) x 10 <sup>3</sup>
5	7.4(7) x 10 <sup>3</sup>	3.4(4) x 10 <sup>4</sup>	1.62(4) x 10 <sup>4</sup>	1.14(7) x 10 <sup>4</sup>
6	1.16(5) x 10 <sup>4</sup>	5.6(5) x 10 <sup>4</sup>	1.71(1) x 10 <sup>4</sup>	1.56(2) x 10 <sup>4</sup>
7	9.1(3) x 10 <sup>3</sup>	4.7(3) x 10 <sup>4</sup>	1.60(5) x 10 <sup>4</sup>	1.21(2) x 10 <sup>4</sup>
8	7.0(3) x 10 <sup>3</sup>	6.1(1) x 10 <sup>4</sup>	1.5(1) x 10 <sup>4</sup>	1.23(1) x 10 <sup>4</sup>
9	3.4(1) x 10 <sup>3</sup>	3.4(2) x 10 <sup>4</sup>	2.5(2) x 10 <sup>3</sup>	3.95(5) x 10 <sup>3</sup>

Note: Reactions were performed in triplicate with all catalysts except 4, for which single data points are used.

**Effect of Alterations to Reactant Initial Concentrations on TON with 1-3****Fig. S15. CO<sub>2</sub> Hydrogenation (3 hours, 0.005 % [Ru])**

Catalyst	standard TON	altered conditions (% change in TON)				
		-H <sub>2</sub> <sup>a</sup>	-CO <sub>2</sub> <sup>b</sup>	+ FA <sup>c</sup>	+ DBU <sup>d</sup>	+ HDBU <sup>+</sup> e
4	5.4(2) x 10 <sup>3</sup>	34	86	66	101	64
5	2.32(2) x 10 <sup>3</sup>	65	132	56	166	47
6	8.4(3) x 10 <sup>3</sup>	49	122	124	95	81

a) Reaction performed with 35 atm H<sub>2</sub> rather than 70 atm H<sub>2</sub>. b) Reaction performed with 3.5 atm CO<sub>2</sub> rather than 7 atm CO<sub>2</sub>. c) Reaction performed in the presence of 0.2 mmol (0.5 equiv. vs. DBU) tetrabutylammonium formate. d) Reaction performed in the presence of 0.6 mmol

DBU rather than 0.4 mmol DBU. e) Reaction performed in the presence of 0.2 mmol (0.5 equiv. vs. DBU) of a 1:1 mixture of DBU and trifluoroacetic acid (generating HDBU<sup>+</sup>/TFA<sup>-</sup>).

**Fig. S16. FA Dehydrogenation (3 hours, 0.005% [Ru]):**

Catalyst	standard TON	altered conditions (% change in TON)				
		-H <sub>2</sub> <sup>a</sup>	-CO <sub>2</sub> <sup>b</sup>	+ FA <sup>-c</sup>	+ DBU <sup>d</sup>	+ HDBU <sup>+e</sup>
<b>4</b>	5.8(4) x 10 <sup>3</sup>	78	12	103	94	90
<b>5</b>	7.63(8) x 10 <sup>3</sup>	81	8	86	99	90
<b>6</b>	1.38(2) x 10 <sup>4</sup>	83	13	73	79	93

a) Reaction performed with 7 atm H<sub>2</sub> rather than 0 atm H<sub>2</sub>. b) Reaction performed with 7 atm CO<sub>2</sub> rather than 0 atm CO<sub>2</sub>. c) Reaction performed in the presence of 0.2 mmol (0.5 equiv. vs. DBU) tetrabutylammonium formate. d) Reaction performed in the presence of 0.6 mmol DBU rather than 0.4 mmol DBU. e) Reaction performed in the presence of 0.2 mmol (0.5 equiv. vs. DBU) of a 1:1 mixture of DBU and trifluoroacetic acid (generating HDBU<sup>+</sup>/TFA<sup>-</sup>).

### Closed System, Cycled H<sub>2</sub> Storage

DBU (11.2 mmol, 1.67 mL) and **6** (0.05%, 5.6 μmol, 5.6 mg) were dissolved in 14 mL DMF in a glass-lined, 300 mL stainless steel Parr reactor along with a PTFE stirbar. The reactor was then charged to 7 atm CO<sub>2</sub> / 70 atm H<sub>2</sub> and stirred at 660 rpm at 120 °C for one hour (*H<sub>2</sub> storage*). At the end of this time the reactor was cooled in a stirred water bath to 30 °C (10 min.), and pressure inside the reactor vented through an oil bubbler. After venting for 15 minutes, the reactor was heated to 120 °C for one hour (*H<sub>2</sub> release*). In this time, evolved gas was collected and measured in a 600 mL gas buret submerged in 10 liters of pH 1.0 water (acidified to lower CO<sub>2</sub> solubility). Thermal gas expansion in the headspace was measured to be 103 mL (from 30 °C to 120 °C), and this volume was subtracted from the collected gas volume to accurately measure the molar quantity of CO<sub>2</sub>:H<sub>2</sub> evolved during FA dehydrogenation. At the end of this time, the reactor was cooled to 25 °C in a water bath, charged with 7 atm CO<sub>2</sub> / 70 atm H<sub>2</sub>, and stirred at 660 rpm at 120 °C to begin a new H<sub>2</sub> storage cycle. During the sixth cycle, the evolved gas was analyzed by GC-TCD: 46.9% CO<sub>2</sub>, 43.2% H<sub>2</sub>, and no CO (detection limit: 0.01%; >99.99% selectivity for H<sub>2</sub>/CO<sub>2</sub> vs. H<sub>2</sub>O/CO). Six cycles were performed. An additional set of reactions were performed as described above, but at 0.1% **3** and using only 30 minute reaction times for CO<sub>2</sub> hydrogenation and FA dehydrogenation.

**Fig. S17. Cycled H<sub>2</sub> Storage**

Cycle	1h, 0.05% <b>6</b>		30 min, 0.1% <b>6</b>	
	Gas Evolved (mL)	% Yield (vs. DBU)	Gas Evolved (mL)	% Yield (vs. DBU)
1	622	113%	707	129%
2	547	99%	647	117%
3	497	90%	692	125%
4	422	76%	547	99%
5	277	50%	557	101%
6	347	63%	522	94%

### Generation of High Pressure Gas Through Formic Acid Dehydrogenation

Formic acid (160 mmol, 6.000 mL), DBU (7.47 mmol, 1.117 mL), and **6** (0.004%, 6.0 mg, 5.9  $\mu$ mol) were dissolved in DMF (120 mL) with a PTFE stirbar in a 150 mL glass-lined stainless steel reactor under nitrogen at ambient pressure. The headspace volume was approximately 40 mL. The reactor was sealed and heated to 120 °C for three hours, at which time the pressure had increased to 190 atm. The evolved gas was measured using a gas buret, showing that the reaction evolved 7275 mL gas (94% vs. starting formic acid, 247,000 turnovers). The reactor's safety burst disc pressure, 210 atm, limited our ability to investigate catalysis at higher pressures. A sample of the evolved gas was analyzed by GC-TCD: 13.90% CO<sub>2</sub>, 56.06% H<sub>2</sub>, and 0.032% CO (99.94% selectivity for H<sub>2</sub>/CO<sub>2</sub> vs. H<sub>2</sub>O/CO). The analyzed sample was enriched in H<sub>2</sub> because the pressure of evolved gas liquified the generated CO<sub>2</sub>.

### Mercury Poisoning Experiment with **6**

DBU (0.400 mmol), 1 mL DMF, 0.0053 mol% **6**, and 1-2 drops of Hg<sup>0</sup> were combined under N<sub>2</sub> in 8 mL scintillation vials equipped with a stirbar and topped with an open-top septum screwcap with inner PTFE liner. The septum was pierced with a 0.25 inch, 27 gauge needle, and the vials loaded into a stainless steel Parr reactor and CO<sub>2</sub> (6 atm) and H<sub>2</sub> (35 atm) were added to the headspace. The reactor was then heated to 80 °C in a large, machined aluminum heating block for 2 hours, with stirring at 600 rpm. At the end of the reaction the reactor was allowed to cool in an ice bath, and slowly vented to atmospheric pressure and analyzed for formate content. Formate was quantified by first evaporating DMF solvent from vials in vacuum chamber; then 6 mL DMSO, 1 mL D<sub>2</sub>O, and benzaldehyde (0.400 mmol) internal standard were added to each reaction and stirred at 900 rpm for 30 minutes before collecting <sup>1</sup>H NMR. Without Hg(0), the average turnover number through three runs was 1.34(2) x 10<sup>3</sup>. With Hg(0), the observed turnover number in one run was 1220.

### Long Duration CO<sub>2</sub> Hydrogenation:

DBU (0.400 mmol), 1 mL DMF, and **4** or **6** (dispensed as a 5 mM stock solution in DMF) were combined under N<sub>2</sub> in 8 mL scintillation vials equipped with a stirbar and topped with an open-top septum screwcap with inner PTFE liner. Identical vials were prepared within the same experiment for error estimation. The septum was pierced with a 0.25 inch, 27 gauge needle, and the vials loaded into a stainless steel reactor and CO<sub>2</sub> (6 atm) and H<sub>2</sub> (35 atm) were added to the

headspace. The reactor was then heated to 80 °C in a large, machined aluminum heating block for 7 days, with stirring at 600 rpm. At the end of the reaction the reactor was allowed to cool in an ice bath, and slowly vented to atmospheric pressure and analyzed for formate content. Formate was quantified by first evaporating DMF solvent from vials in vacuum chamber; then 6 mL DMSO, 1 mL D<sub>2</sub>O, and benzaldehyde (0.400 mmol) internal standard were added to each reaction and stirred at 900 rpm for 30 minutes before collecting <sup>1</sup>H NMR.

**Fig. S18. Long Duration CO<sub>2</sub> Storage**

Catalyst	Loading (mol%)	Loading (μmol)	Base	TON
<b>6</b>	0.0053	2.12 x 10 <sup>-2</sup>	DBU	2.5(1) x 10 <sup>4</sup>
<b>4</b>	0.0053	2.12 x 10 <sup>-2</sup>	DBU	2.3(1) x 10 <sup>4</sup>
--	--	--	DBU	3.84 x 10 <sup>2</sup>
<b>6</b>	0.0018	7.07 x 10 <sup>-3</sup>	DBU	6.51(7) x 10 <sup>4</sup>
<b>4</b>	0.0018	7.07 x 10 <sup>-3</sup>	DBU	5.84(9) x 10 <sup>4</sup>
<b>6</b>	0.0018	7.07 x 10 <sup>-3</sup>	--	4.48 x 10 <sup>2</sup>
<b>6*</b>	0.00009	3.50 x 10 <sup>-3</sup>	DBU	2.03(4) x 10 <sup>5</sup>
<b>4*</b>	0.00009	3.50 x 10 <sup>-3</sup>	DBU	2.01(2) x 10 <sup>5</sup>
<b>--*</b>	--	--	DBU	8.49 x 10 <sup>4</sup>

\* Run with  $P(\text{CO}_2:\text{H}_2) = 6:70$  atm

### References

(1) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, 29, 2176.