Electronic Supplementary Information

Hydrogen Production from Formic Acid Catalyzed by a Phosphine free Manganese complex: Optimization and Mechanistic Insights.

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Content:

1. Generalities.

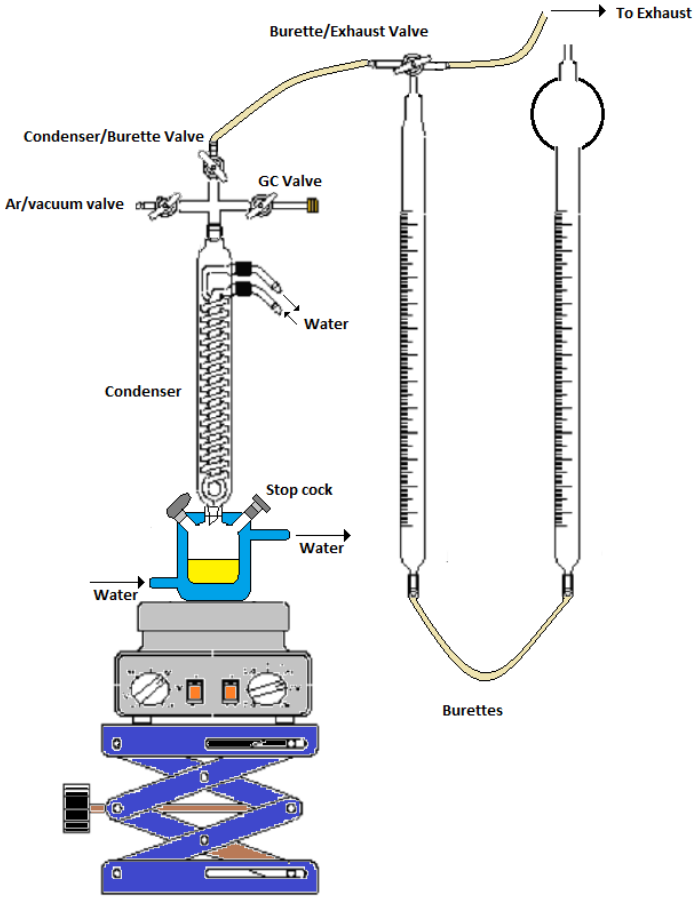
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under an inert atmosphere using standard Schlenk technique. Formic acid (99-100% purity) was purchased from BASF. Triglyme and N,N-dimethyl-n-octylamine (DMOA) were previously distilled, to get rid of eventual impurities or stabilizers. Formic acid (FA), N,N-dimethyl-n-octylamine (DMOA), triglyme and water were degassed prior to use. All organic solvents used in synthesis were collected from an SPS machine and stored under argon with drying agent (molecular sieve). All synthesized complexes were prepared under an argon atmosphere and stored under argon with light exclusion.

Thin layer chromatography - TLC - was carried out on aluminum backed hand-cut silica plates (5 cm × 10 cm, TLC Silicagel 60 F254, Merck Millipore) and visualized using ultraviolet light (wavelength: 254 nm). Column chromatography was carried out using silica (0.035-0.070 mm, Silicagel 60, Fluka Chemika). All solvents purchased from commercial sources were used without further purification techniques. **^{1}H and ^{13}C NMR spectroscopy** were carried out with a Bruker AV-300, AV-400 or f300. NMR spectrums were interpreted using MestReNova (version 8.0.1-10878). All NMR data in the experimental section are expressed as chemical shift in parts per million (ppm) relative to the residual solvent used as an internal standard for the δ scale. The multiplicity of each signal is designed by the following abbreviations; s (singlet), d (doublet), t (triplet), b (broad), m (multiplet). **Mass spectrometry** was performed on MAT 95-XP mass spectrometer using chemical ionization (CI) or electron ionization (EI). **Infrared spectrometry** was carried out with a Bruker-ALPHA FT-IR spectrometer with a spectral range of 7500 to 375 cm^{-1} (wavelength range: 1.3 to 27 mm). The solids were analyzed by ATR - Attenuated Total Reflectance - sampling method and the spectrums are exploited on OMNIC 7.3 or Origins 8.6. **Elemental analysis** was performed with a Leco TruSpec Micro CHNS. **Gas chromatography** was used to analyze the content of the gas phase with a CO quantification limit of 78 ppm. The samples were analyzed on Agilent Technologies 7890A GC system. **X-ray** structure analyses were carried out on Bruker Kappa APEX II Duo diffractometer. **pH** values were measured thanks to a 3 color indicator pH paper purchased from Carl Rooth GMBH.

2. Dehydrogenation of formic acid

General set-up used. DH of FA was carried out in a double wall 3-neck reactor connected to a thermostat. A condenser cooled by tap water was connected to the reactor and gas evolution was measured with gas burettes. Since our manganese catalysts are light sensitive in solution, the reactor and the condenser were completely covered in aluminum foil. Additionally, the window stores of the laboratory were closed and the lights were switched-off (**figure S1**).

Figure S1: Manual burette set-up for the DH off FA [a].



[a] Set-up specificities: Water heated from thermostat, condenser and reactor wrapped in aluminum foil, condenser cooled with tap water, gas released to the exhaust. Content of the gas phase analyzed by GC.

General procedure for the dehydrogenation of formic acid on manual burettes. A 3-neck double wall reactor was attached to a condenser connected to a manual burettes system. The apparatus was purged 6 times and flushed with argon for 15 minutes. Solid base was added under argon overpressure and the setup was evacuated to vacuum for 5 minutes then filed. Solvents and formic acid were added under an argon overpressure. The setup was heated to the desired temperature - thanks to the thermostat - while being flushed with argon. When the desired temperature was reached, the burette was closed to the atmosphere and the system is equilibrated for 30-60 min. The catalyst was dropped into the reactor with a mini-Teflon cup and the setup was vented to the open air in order to release the pressure in the burette. The argon/vacuum line was closed and the timer was started. After 180 minutes, a 5 mL degassed syringe was used to obtain a gas sample analyzed by gas chromatography.

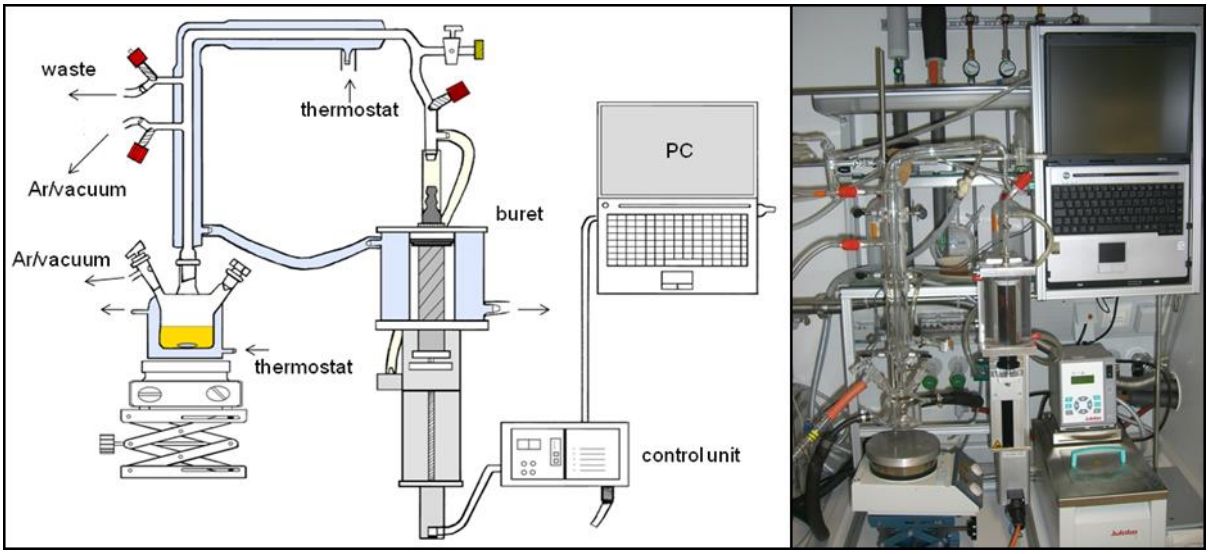
Variation for KIE experiment. The kinetic isotope effect experiments - KIE - were carried out in the same way as the "General procedure for the dehydrogenation of formic acid on manual burettes" described above. The only difference laid in the use of a smaller size reactor instead.

Variation for periodic flow experiment. The periodic flow experiment was carried out as the "General procedure for the dehydrogenation of formic acid on manual burettes" described above. Here, a GC cap connector instead of a new stopcock was installed after the catalyst addition. Formic acid portions were periodically added with a 1 mL Hamilton© syringe.

General procedure for the continuous dehydrogenation of formic acid on automatic burettes. A 3-neck double wall reactor was attached to a condenser connected to an automatic burettes system. The apparatus was purged 6 times and flushed with argon for 15 minutes. Solid base was added under argon overpressure and the setup was evacuated to vacuum for 5 minutes then refiled. Solvents and formic acid were added under an argon overpressure. The setup was heated to the desired temperature - thanks to the thermostat - while being flushed with argon. When the desired temperature was reached, the burette was closed to the atmosphere and the system was equilibrated for 30-60 min. The catalyst was dropped into the reactor with a mini-Teflon cup and the setup was vented to the open air in order to release the pressure in the burette. The timer was then started. The automatic gas burette was equipped with a pressure sensor. Evolving gas during the reaction causes a pressure increase in the closed system, which was compensated by volume increase of the burette pistons by an automatic controlling unit. The gas evolution curves were collected by use of a PC. A 5 mL degassed syringe was used to obtain a gas sample analyzed by gas chromatography.

Variation for continuous flow experiment. The continuous flow experiment on automatic burette was carried out as the "General procedure for the dehydrogenation of formic acid on automatic burettes" described above. Here, after the catalyst addition, a glass connection equipped with a GL14 adaptor and a PTFE cannula connected to a Luer-lock© 50 mL Hamilton© syringe was installed on the reactor instead of a new stop-cock. Formic acid portions were continuously added using an Infors PRECIDOR Type 8003© syringe pump.

Figure S2: Automatic burette set-up for the DH of FA.



3. Calculation of the hydrogen volume, the TON and the TOF.

Turnover number (TON):

In the gas of 1 : 1 mixtures, the gas evolution was corrected with the blank volume which corresponds to the gas evolution of the same reaction using an empty Teflon cup without any catalyst. The turnover number (TON) is calculated with the following equation:

$$\mathrm{TON} = \frac{\frac{\mathrm{V_{obs}} - \mathrm{V_{blank}}}{\mathrm{V_{m_{H_2}}} + \mathrm{V_{m_{CO_2}}}}}{\mathrm{n_{cat}}}$$

Where:

- $\mathrm{V_{obs}}$ is th gas evolution measured in the catalytic reaction.
- $\mathrm{V_{blank}}$ is the gas evolution measured in the catalytic reaction.

- $V_{m,H_2,25°C}$ and $V_{m,CO_2,25°C}$ are the molar volumes of H_2 and CO_2 respectively calculated with the Van Der Waals equation.

Calculation of H_2 molar volume:

$$V_{m\,H_2} = \frac{R \cdot T}{p} + b - \frac{a}{R \cdot T}$$

Where:

- R = 8.3145 m^3.Pa.mol^{-1}.K^{-1}
- T = 273.15 + room temperature (°C) K
- P = 101325 Pa
- a = 24.9 × 10^{-3} Pa.m^6.mol^{-2}
- b = 26.7 × 10^{-6} m^3.mol^{-1}

Calculation of CO_2 molar volume:

$$V_{m_{CO_2}} = \frac{R \cdot T}{p} + b - \frac{a}{R \cdot T}$$

Where:

- R = 8.3145 m^3.Pa.mol^{-1}.K^{-1}
- T = 273.15 + room temperature (°C) K
- P = 101325 Pa
- a = 36.5 × 10-2 Pa.m^6.mol^{-2}
- b = 42.7 × 10-6 m^3.mol^{-1}

Turnover number frequency (TOF):

The turnover number frequency (TOF) was calculated with the experimental TON value. The unit of the TON (s^{-1}, min^{-1}, h^{-1}) is linked to the temporal unit (s, min, h)

$$TOF = \frac{TON}{time}$$

4. Calculation of hydrogen volume, the TON and the TOF by ratio of H_2 : CO_2.

Some experiments showed a H_2 : CO_2 gas composition of 1:1 (**Table 1, entries 1-11; Table 2, entries 1, 7-8, 11-13**). But, for some experiments the detected gas ratio misbalanced with an excess of hydrogen (**Table 2, entries 2-6, 9-10, 14**). As we know from the monitoring experiment (**Figure 1**), the pH increased throughout the reaction reaching a value of 10. Additionally, the labelling experiments with $H^{13}COOK$ showed a signal at 161.30 ppm characteristic of the carbonate specie HCO_3^- (**Figures S25-S27**). All those information suggest that CO_2 was trapped as carbonate, due to the consumption of HCOOH leading to a pH increase, causing a misbalanced ratio. The corrected gas evolution was calculated accordingly:

- $\mathbf{V_{H_2 corrected}} = (V_{observed} - V_{blank}) \times \text{ratio } H_2 : CO_2$

  Where ratio $H_2 : CO_2 = \frac{\%V_{H_2}}{\%V_{H_2} + \%V_{CO_2}}$

Upon which, the TON has been recalculated as follow:

- $\text{TON} = \frac{\mathbf{n_{H_2 corrected}}}{n_{cat}} = \frac{\mathbf{V_{H_2 corrected}} \cdot n_{cat}}{V_{m_{H_2}}}$

A carbon dioxide liberation experiment was carried out to verify this statement.

<u>CO_2 liberation method:</u>

After the catalytic reaction was performed, the reaction mixture was cooled down to room temperature and equilibrated. Hydrochloric acid (1 M) was added dropwise to the reactor and liberated gas was measured in a manual burette. The addition was stop when no significant release was noted. Resulting gas was analyzed by GC.

Example (Table 2, entry 6, original reaction): Total gas volume produced during catalytic experiment was 266 mL (not corrected by blank volume, V_{blank} = 2.7 mL) in 3 hours. GC analysis of the gas phase points $\%V_{H2}$ = 54,88 % and $\%V_{CO2}$ = 29,77 %. After cooling the system down, HCl addition led to **77 mL** of further gas evolution analyzed by GC (confirming CO_2 in the mixture).

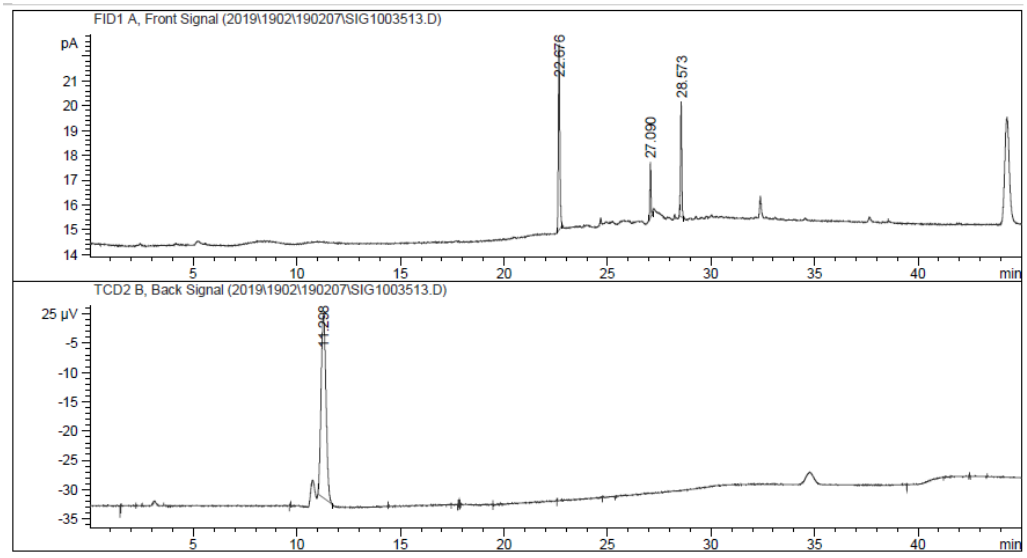
- $\mathbf{V_{H_2 corrected}} = (V_{observed} - V_{blank}) \times \text{ratio } H_2 : CO_2 = \mathbf{171\ mL}$

  Where ratio $H_2 : CO_2 = \frac{\%V_{H_2}}{\%V_{H_2} + \%V_{CO_2}} = \mathbf{0,65}$
- Thus, 266 - 171 = 95 mL of CO_2, according to $\mathbf{V_{H_2 corrected}}$ we are missing 171 - 96 = **75 mL** of CO_2.

Recalculation with GC percentage and recalculations based on liberated CO_2 seemed to be in agreement. The predicted $V_{CO_2 trapped}$ (76 mL) matched the experimental $V_{CO_2 trapped}$ (77 mL).

5. Typical GC chromatogram.

Figure S3: Blank chromatogram for the DH of FA [a].

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Signal 2: TCD2 B, Back Signal

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 14.700            -          -          -         CO
 26.900            -          -          -         CH4
 34.800            -          -          -         CO2

Totals :                                0.00000
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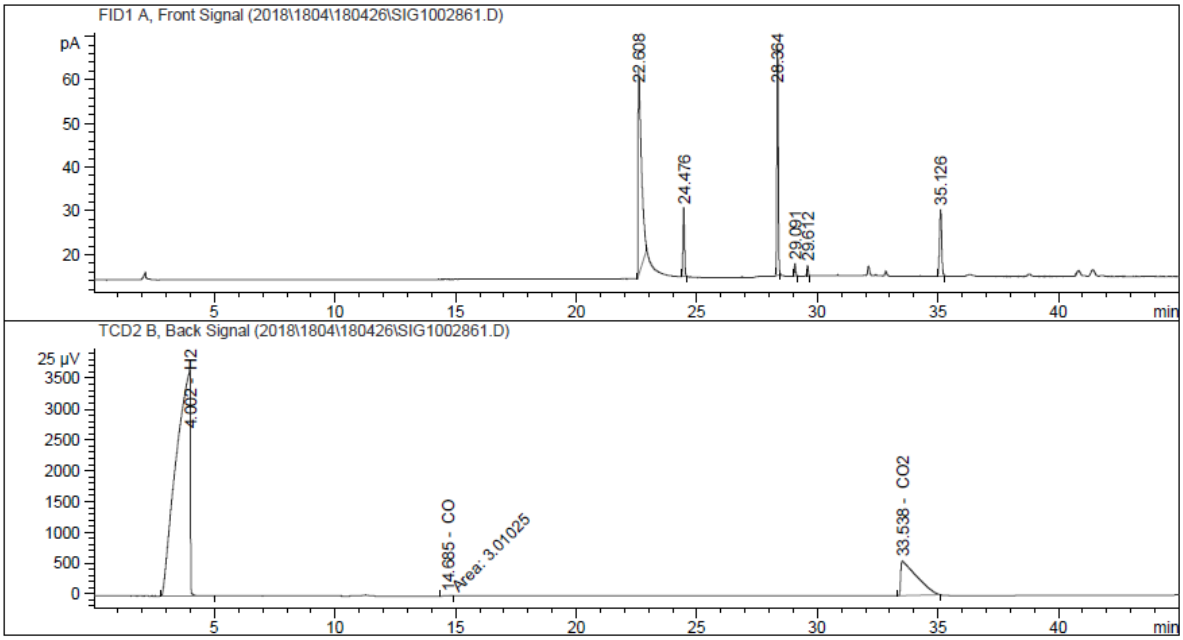
[a] Reaction conditions: HCOOK (32 mmol), HCOOH (5 mmol), H_2O (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes). HCOOH injected with a syringe pump (factor: 0.1; speed: 0.09 mL·min^{-1}). Light exclusion, gas evolution monitored with manual burettes and content of the gas phase analyzed by GC.

Figure S4: Typical GC chromatogram for the DH of FA [a].

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Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A, Front Signal


Signal 2: TCD2 B, Back Signal

RetTime  Type     Area      Amt/Area    Amount    Grp   Name
 [min]          [25 µV*s]               [% Vol.]
-------|------|----------|----------|----------|--|------------------
  4.002 BB     1.48562e5  3.18433e-4   47.30695    H2
 14.685 MM        3.01025 1.91357e-3 5.76034e-3    CO
 26.900             -          -          -        CH4
 33.538 BB     2.56769e4  1.84985e-3   47.49850    CO2
-------|------|----------|----------|----------|--|------------------
Totals :                                94.81121
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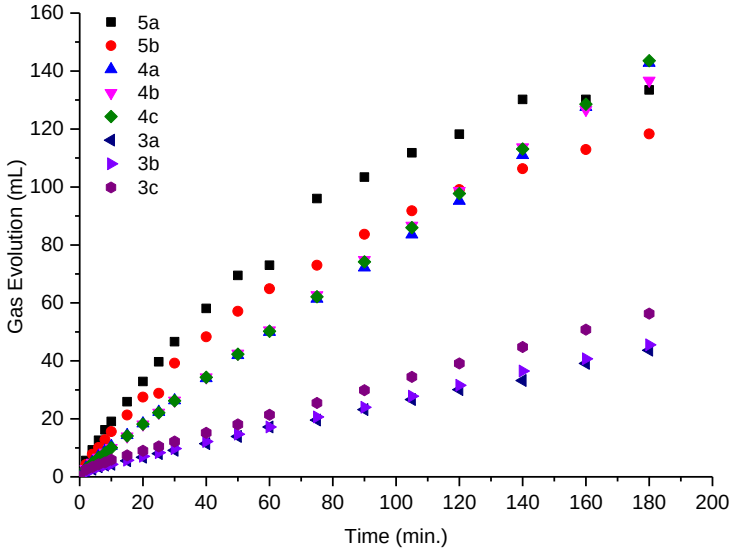
[a] Reaction conditions: HCOOK (32 mmol), HCOOH (5 mmol), Mn(pyridine-imidazoline)$(CO)_3Br$ (0.050 mmol), H_2O (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes). HCOOH injected with a syringe pump (factor: 0.1; speed: 0.09 mL·min^{-1}). Light exclusion, gas evolution monitored with manual burettes and content of the gas phase analyzed by GC.

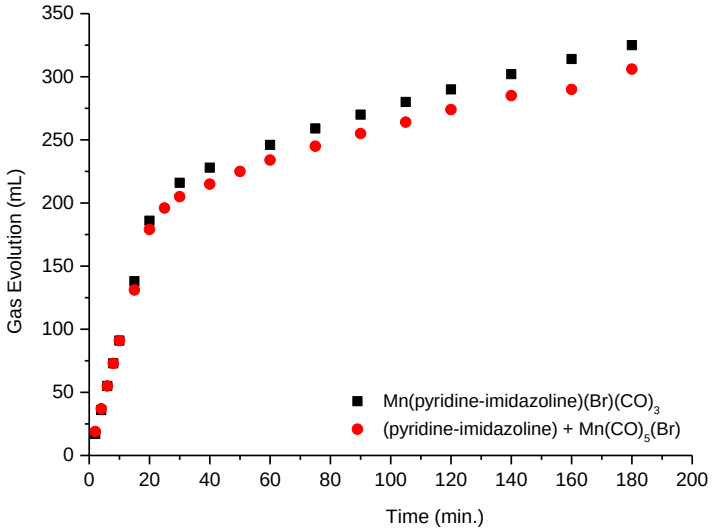
6. Gas evolution plots:

Figure S5: Best working catalysts [a].



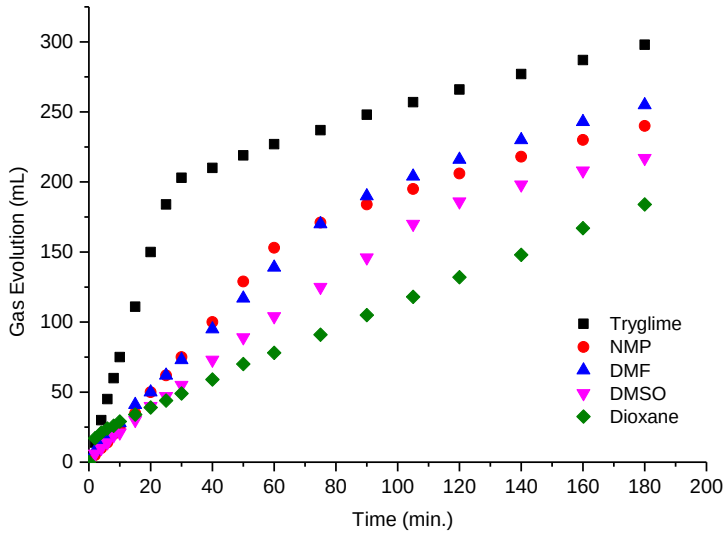
[a] Reaction conditions: HCOOH (37 mmol), KOH (40 mmol), $Mn(L)(CO)_3Br$ (0.005 mmol), H_2O (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes), light exclusion. Gas evolution monitored with manual burettes and content of the gas phase analyzed by GC.

Figure S6: *In-situ* system [a].



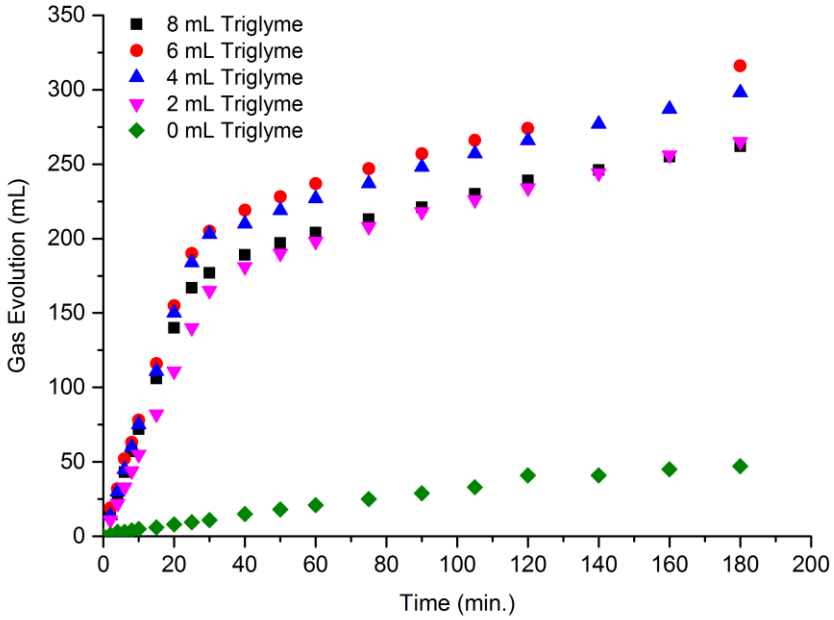
[a] Reaction conditions for the black plot: HCOOH (5 mmol), HCOOK (32 mmol), Mn(pyridine-imidazoline)$(CO)_3Br$ (0.05 mmol), H_2O (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes), light exclusion. Reaction conditions for the red plot: HCOOH (5 mmol), HCOOK (37 mmol), $Mn(CO)_5Br$ (0.05 mmol), 2-(4,5-dihydro-1H-imidazol-2-yl)pyridine (0.05 mmol), H_2O (9 mL), triglyme (4 mL),), t_{set} (92.5°C), time (180 minutes), light exclusion. Gas evolution monitored with manual burettes and content of the gas phase analyzed by GC.

Figure S7: Organic solvent variation [a].



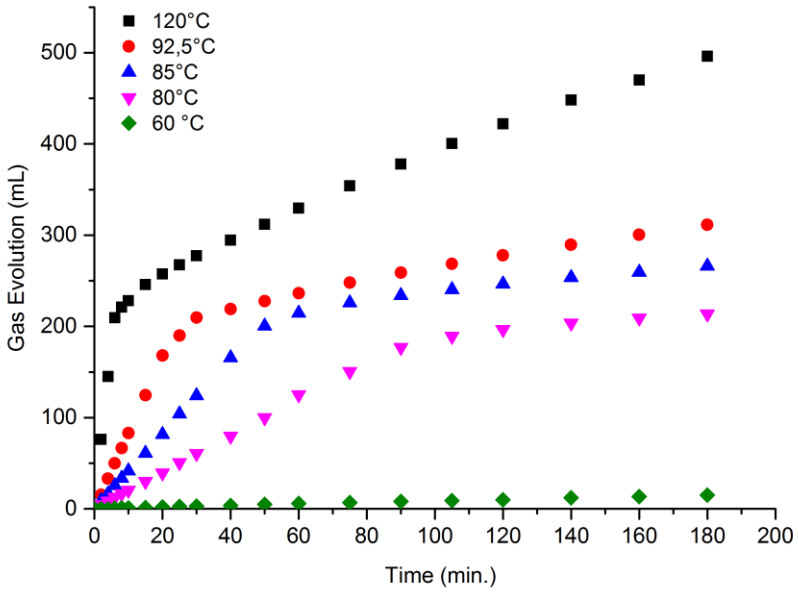
[a] Reaction conditions: HCOOH (5 mmol), HCOOK (32 mmol) , Mn(pyridine-imidazoline)$(CO)_3$Br (0.05 mmol), H_2O (9 mL), organic solvent (4 mL), t_{set} (92.5°C), time (180 minutes), light exclusion. Gas evolution monitored with manual burettes and content of the gas phase analyzed by GC.

Figure S8: Triglyme quantities variations [a].



[a] Reaction conditions: HCOOH (5 mmol), HCOOK (32 mmol) , Mn(pyridine-imidazoline)$(CO)_3$Br (0.05 mmol), H_2O (9 mL), organic solvent (4 mL), t_{set} (92.5°C), time (180 minutes), light exclusion. Gas evolution monitored with manual burettes and content of the gas phase analyzed by GC.

Figure S9: Temperature variations [a].



[a] Reaction conditions: HCOOH (5 mmol), HCOOK (32 mmol) , Mn(pyridine-imidazoline)$(CO)_3$Br (0.05 mmol), H_2O (9 mL), organic solvent (4 mL), time (180 minutes)., light exclusion. Gas evolution monitored with manual burettes and content of the gas phase analyzed by GC. CO content in between 113 ppm (quantification limit) and 3078 ppm.

Figure S10: CO amount for various experimental conditions.

Table 1: Tested Catalysts for the FA dehydrogenation [a].

Entry	Cat.	$H_2 + CO_2$(mL) [b]	TON (3 h.)	TOF (h^{-1})	CO (ppm) [c]
1	1	4.1	17	6	2632
2	2a	12	50	17	93
3	2b	4.7	19	6	not detected
4	3a	37	151	50	527
5	3b	43	175	58	<78
6	3c	54	220	73	<78
7	4a	138	564	188	<78
8	4b	134	549	183	193
9	4c	141	577	192	536
10	5a	136	556	185	213
11	5b	116	473	158	303

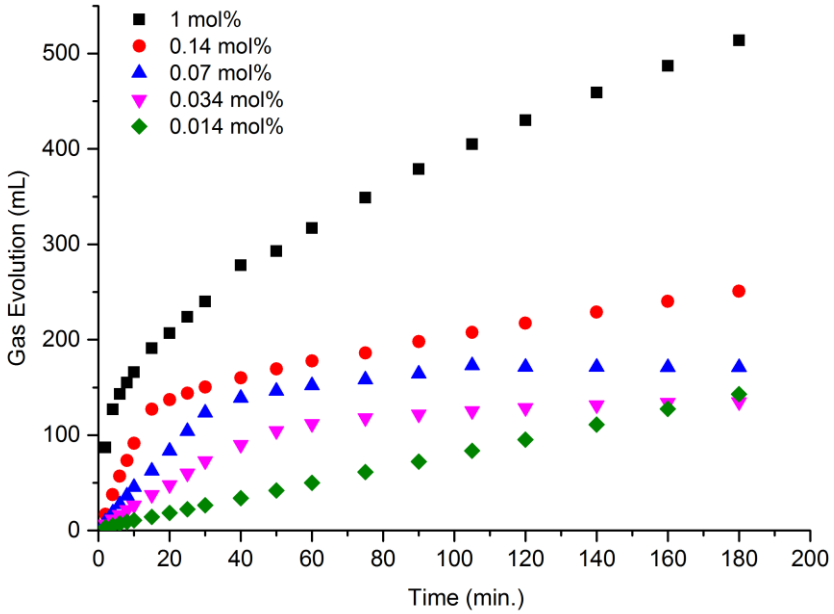
[a]Reaction conditions: HCOOH (37 mmol), KOH (40 mmol), Mn catalyst (0.005 mmol), H_2O (9 mL), triglyme (4 mL), T_{set} (92.5°C), [b] time (180 min), light exclusion. Gas evolution monitored with manual burettes, corrected by blank volume (2.7 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio H_2 : CO_2 in all cases 1:1; [c]CO content in between 78 ppm (quantification limit) and 2632 ppm.

Table 2: Investigation for the FA dehydrogenation [a].

Entry	Loading (µmol)	Base	Co-solvent	T (°C)	$H_2 + CO_2$ (mL)[c,e]	[d] CO (ppm)
1[a]	5	KOH	Triglyme	92.5	138	<78
2[a]	12.5	KOH	Triglyme	92.5	175	332
3[a]	25	KOH	Triglyme	92.5	223	735
4[a]	50	KOH	Triglyme	92.5	337	1 195
5[a]	370	KOH	Triglyme	92.5	721	2 287
6[b]	50	HCOOK	Triglyme	92.5	373	1 065
7[b]	50	HCOOK	DMSO	92.5	214	3 908
8[b]	50	HCOOK	Dioxane	92.5	181	<78
9[b]	50	KCOOK	NMP	92.5	12	259
10[b]	50	KCOOK	DMF	92.5	306	1 177
11[b]	50	KCOOK	Triglyme	60	12	113
12[b]	50	KCOOK	Triglyme	80	211	254
13[b]	50	KCOOK	Triglyme	85	263	207
14[b]	50	KCOOK	Triglyme	120	622	3 078

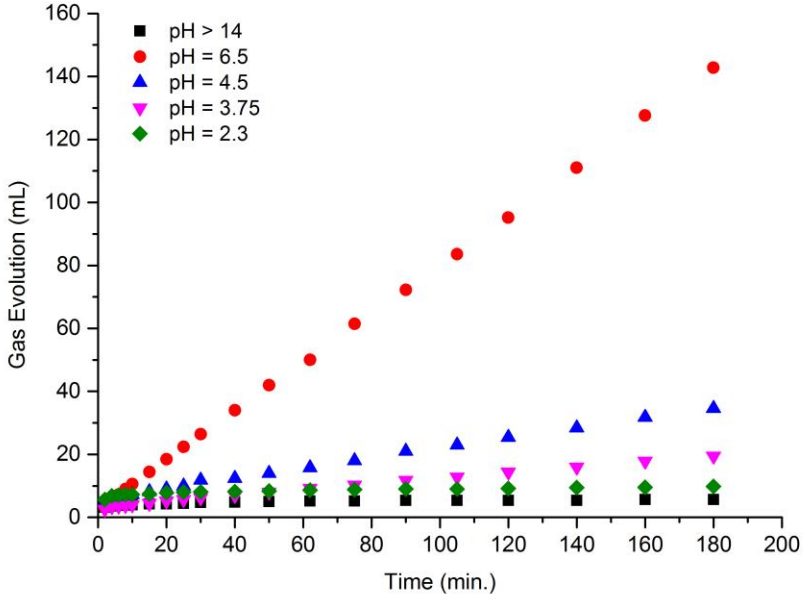
[a]Reaction conditions: HCOOH (37 mmol), KOH (40 mmol), [Mn(imidazoline-pyridine)$(CO)_3$Br], H_2O (9 mL), triglyme (4 mL). [b]Reaction conditions: HCOOH (5 mmol), HCOOK (32 mmol), [Mn(imidazoline-pyridine)$(CO)_2$Br] (50 µmol), H_2O (9 mL), Solvent (4 mL). [c]time (180 min), light exclusion. Gas evolution monitored with manual burettes, corrected by blank volume (2.7 mL). Content of the gas phase analyzed by GC, ratio H_2 : CO_2 in all cases 1:1. [d] CO content in between 78 ppm (quantification limit) and 3908 ppm. Experiments were performed at least twice (except entries 5, 7-10) with reproducibility differences between 0.7 and 9.3 % except entry 2 (21%). [e]TONs, TOFs and conversions calculated based on ratio of H_2 : CO_2 between 1.3 : 1 to 2.4 : 1 (entries 2 - 6, 9 - 10, 14) (Supporting Information section 4: "Calculation of hydrogen volume, the TON and the TOF by ratio of H_2 : CO_2").

Figure S11: Catalytic loading [a].



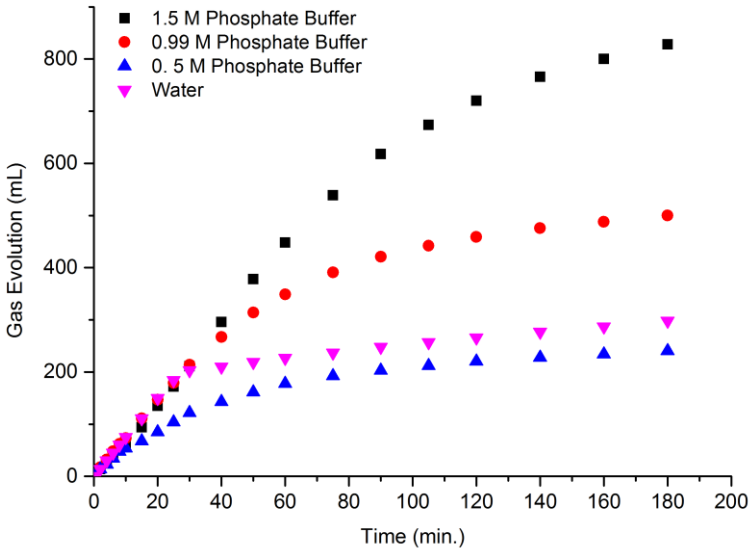
[a] Reaction conditions: HCOOH (37 mmol), KOH (40 mmol), H2O (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes), light exclusion. Gas evolution monitored with manual burettes and content of the gas phase analyzed by GC.

Figure S12: Dependence in activity and initial pH by variating the KOH equivalents [a].



[a] Reaction conditions: HCOOH (37 mmol), KOH (respectively 0 mmol, 7.4 mmol, 18.5 mmol, 40 mmol and 55.6 mmol), H_2O (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes), light exclusion. Gas evolution monitored with manual burettes and content of the gas phase analyzed by GC.

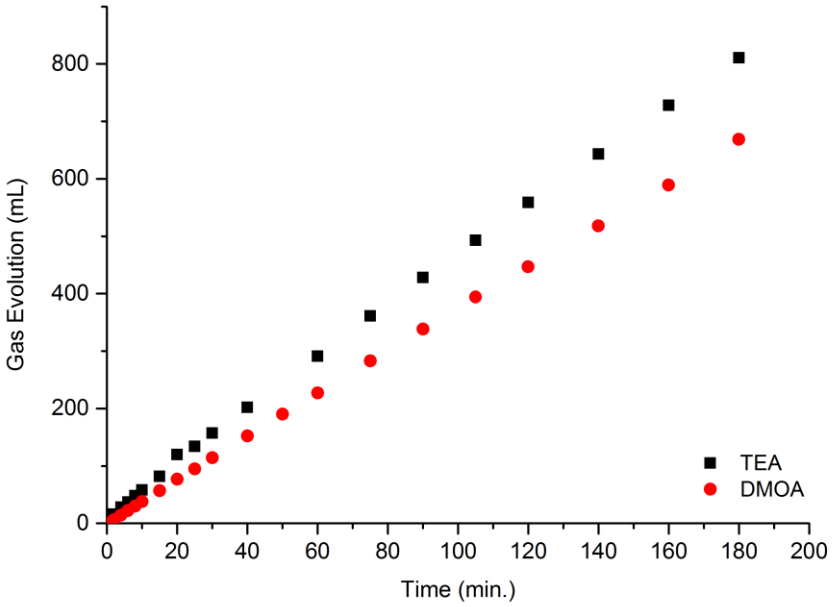
Figure S13: Applications of aqueous phosphates buffers [a].



Entry	Buffer Strength (mol.L^{-1})	Conversion[b]	TON[b]	TOF[b]	pH $_{0\ min.}$	pH $_{180\ min.}$
1	None	19%	142	47	5.5	10
2	0.5	15%	113	38	5.75	10
3	0.99	28%	204	68	6	9
4	1.5	46%	338	113	5.5	8.5

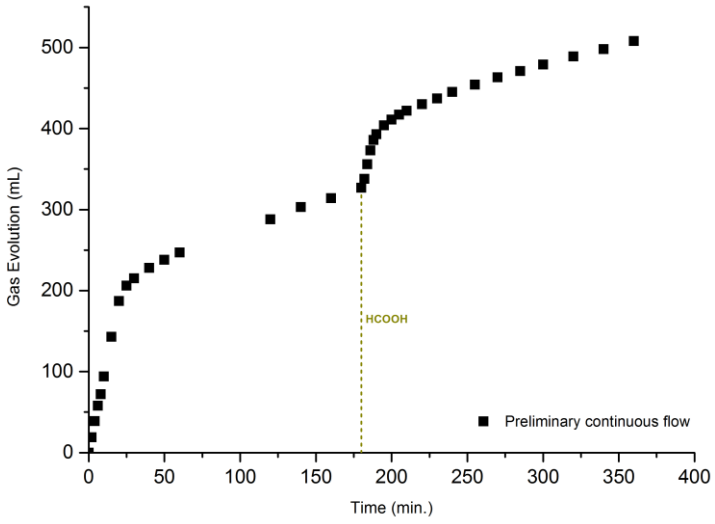
[a] Reaction conditions: HCOOH (5 mmol), HCOOK (32 mmol) , Mn(pyridine-imidazoline)$(CO)_3$Br (0.05 mmol), phosphate buffer (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes)., light exclusion. Gas evolution monitored with manual burettes and content of the gas phase analyzed by GC. [b] Experimental volumes were corrected by blank volumes; TONs, TOFs and conversions calculated based on ratio H_2 : CO_2 of 1,4 : 1 (entries 1-2).

Figure S14: Organic bases [a].



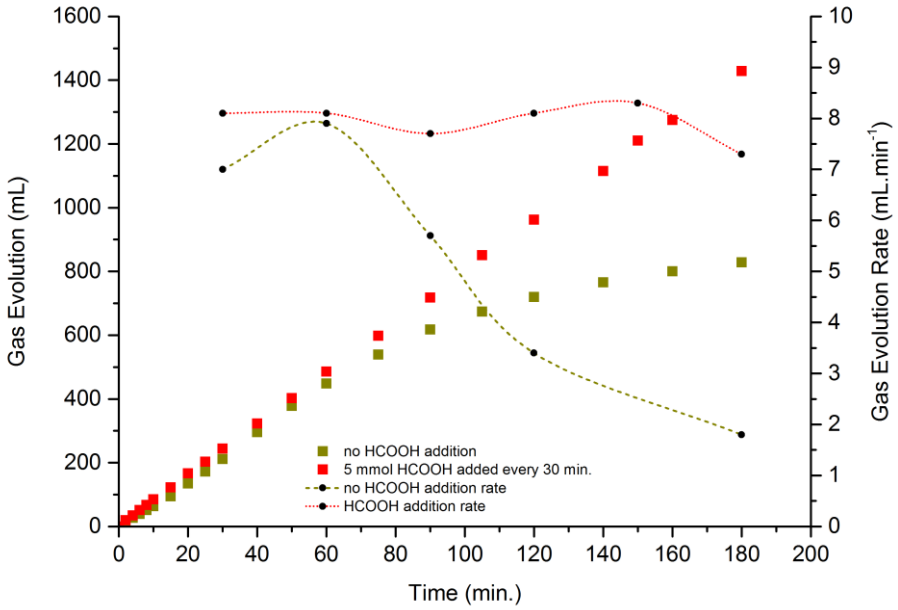
[a] Reaction conditions: HCOOH (37 mmol), Mn(pyridine-imidazoline)$(CO)_3$Br (0.05 mmol), Organic Base (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes), light exclusion. Gas evolution monitored with manual burettes and content of the gas phase analyzed by GC.

Figure S15: Preliminary continuous flow experiment [a].



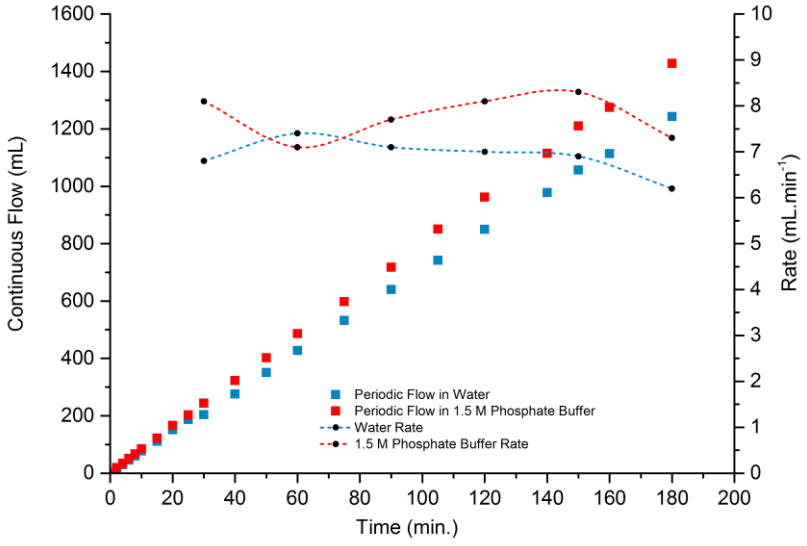
[a] Reaction conditions: HCOOH (37 mmol), Mn(pyridine-imidazoline)$(CO)_3$Br (0.05 mmol), water (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes), light exclusion. HCOOH (5 mmol) added via Hamilton© syringe. Gas evolution monitored with manual burettes and content of the gas phase analyzed by GC.

Figure S16: Periodic dosage of formic acid in 1.5 M phosphate buffer [a].



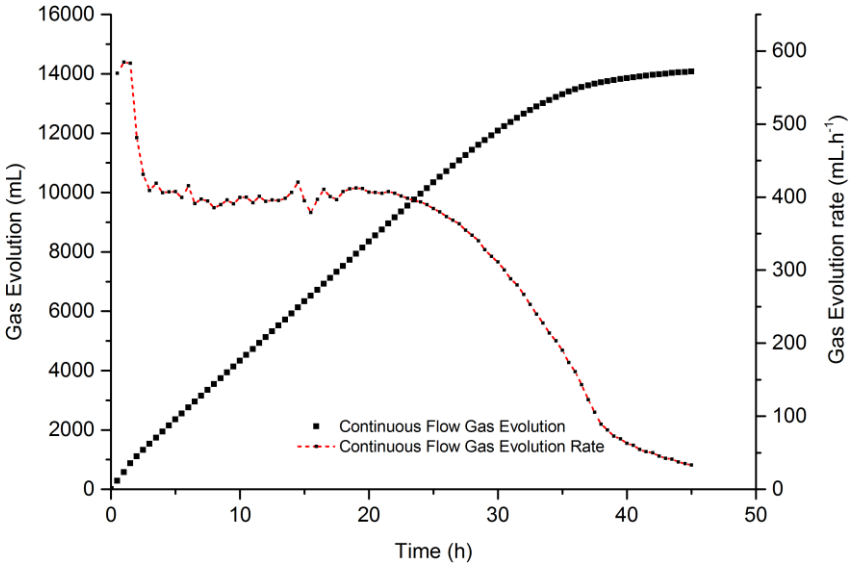
[a] Reaction conditions for the red plot: HCOOH (37 mmol), Mn(pyridine-imidazoline)$(CO)_3$Br (0.05 mmol), 1.5 M aqueous phosphate buffer (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes), light exclusion. HCOOH (5 mmol) added via Hamilton© syringe every 30 minutes. Reaction conditions for the dark yellow plot: HCOOH (37 mmol), Mn(pyridine-imidazoline)$(CO)_3$Br (0.05 mmol), 1.5 M aqueous phosphate buffer (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes), light exclusion. Gas evolution monitored with manual burettes and content of the gas phase analyzed by GC. Rate calculated as follow: $\Delta V/\Delta t$ with t = 30 min. CO content: <78 ppm (red) and 175 ppm (green).

Figure S17: Periodic dosage of formic acid in water [a].



[a] Reaction conditions for the red plot: HCOOH (37 mmol), Mn(pyridine-imidazoline)$(CO)_3$Br (0.05 mmol), 1.5 M aqueous phosphate buffer (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes), light exclusion. HCOOH (5 mmol) added via Hamilton© syringe every 30 minutes. Reaction conditions for the deep blue plot: HCOOH (37 mmol), Mn(pyridine-imidazoline)$(CO)_3$Br (0.05 mmol), water (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes), light exclusion. HCOOH (5 mmol) added via Hamilton© syringe every 30 minutes. Gas evolution monitored with manual burettes and content of the gas phase analyzed by GC. Rate calculated as follow: ΔV/ Δt with t = 30 min. CO content: <78 ppm (red) and 141 ppm (blue).

Figure S18: Continuous dosage of formic acid in water, activity [a].



[a] Reaction conditions: HCOOH (5 mmol), HCOOK (32 mmol), Mn(pyridine-imidazoline)$(CO)_3$Br (0.05 mmol), water (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (87 hours), HCOOH (392 mmol) added via an Infors Precidor Type 8003© syringe pump using a 50 mL Luer-lock© Hamilton© syringe connected to the reactor via a GL14 valve and a PTFE cannula. Rate of the addition: 0.007 mL·min^{-1}. Light exclusion, Gas evolution monitored with automatic burettes and content of the gas phase analyzed by GC. Ending pH, evaluated using pH paper, was 3.5. Rate calculated as follow: ΔV/ Δt with t = 30 min. CO content: 857 ppm.

7. Crystal structures.

Procedure for the crystallization for Mn(pyridine-imidazoline)$(CO)_3$(OOCH): DMSO (4 mL), water (9 mL), HCOOH (0.19 mL) and HCOOK (2.7 g) were loaded into a 50 mL Schlenk flask previously flushed. Mn(pyridine-imidazoline)$(CO)_3$Br (50 µmol) was introduced in the mixture and the set-up was heated at 92.5°C for 60 minutes under exclusion of light. The solution was cooled down and was extracted with 3 portions DCM (3 mL). The organic phase was placed into a Schlenk flask and overlayered with n-heptane. The liquid diffusion crystallization mixture was put in the freezer at - 32 °C. Crystals were obtained and analyzed by X-Ray diffraction and NMR (in DMSO-d^6).

Procedure for crystallization for Mn(pyridine-imidazoline)$(CO)_3$Br: A small spatula head of complex was dissolved in a GC vial with 1 mL acetone. The vial was placed in a larger vial containing 7 mL of diethylether. The flask was closed, covered in aluminum foil and placed in the fridge for a week.

X-ray crystal structure analysis of Mn(pyridine-imidazoline)(CO)$_3$(OOCH): and Mn(pyridine-imidazoline)(CO)$_3$Br: Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by direct methods (SHELXS-97: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2014: Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3.). XP (Bruker AXS) was used for graphical representations. CCDC 1922221 and 1922222 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Crystal data of Mn(pyridine-imidazoline)(CO)$_3$(OOCH): (CCDC 1922221): $C_{12}H_{10}MnN_3O_5$, M = 331.17, triclinic, space group $P\bar{1}$, a = 7.5940(14), b = 8.5623(16), c = 13.088(3) Å, α = 97.266(3), β = 95.849(3), γ = 95.577(3)°, V = 834.5(3) Å^3, T = 150(2) K, Z = 2, 33103 reflections measured, 4438 independent reflections (R_{int} = 0.0251), final R values ($I > 2\sigma(I)$): R_1 = 0.0346, wR_2 = 0.1035, final R values (all data): R_1 = 0.0384, wR_2 = 0.1074, 194 parameters. Contributions of co-crystallized solvent molecules were removed from the diffraction data with PLATON/SQUEEZE (Spek, A. L. *Acta Cryst.* **2015**, *C71*, 9).

Crystal data of Mn(pyridine-imidazoline)(CO)$_3$Br (CCDC 1922222): $C_{11}H_9BrMnN_3O_3$, M = 366.06, monoclinic, space group $P2_1/n$, a = 7.9845(13), b = 12.118(2), c = 14.112(2) Å, β = 100.181(3)°, V = 1344.0(4) Å^3, T = 150(2) K, Z = 4, 34275 reflections measured, 3248 independent reflections (R_{int} = 0.0292), final R values ($I > 2\sigma(I)$): R_1 = 0.0201, wR_2 = 0.0507, final R values (all data): R_1 = 0.0239, wR_2 = 0.0525, 176 parameters.

Figure S19: ORTEP representation of Mn(pyridine-imidazoline)(CO)$_3$(OOCH). Displacement ellipsoids correspond to 30% probability.

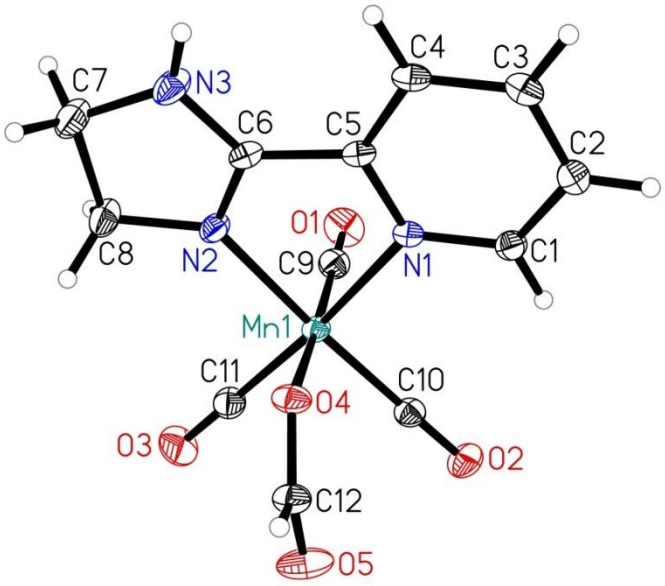


Figure S20: ORTEP representation of Mn(pyridine-imidazoline)$(CO)_3$Br. Displacement ellipsoids correspond to 30% probability.

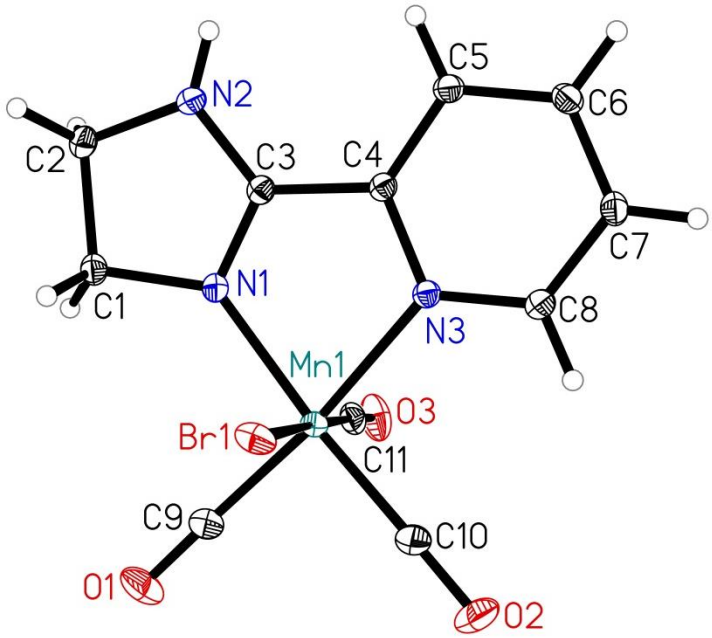
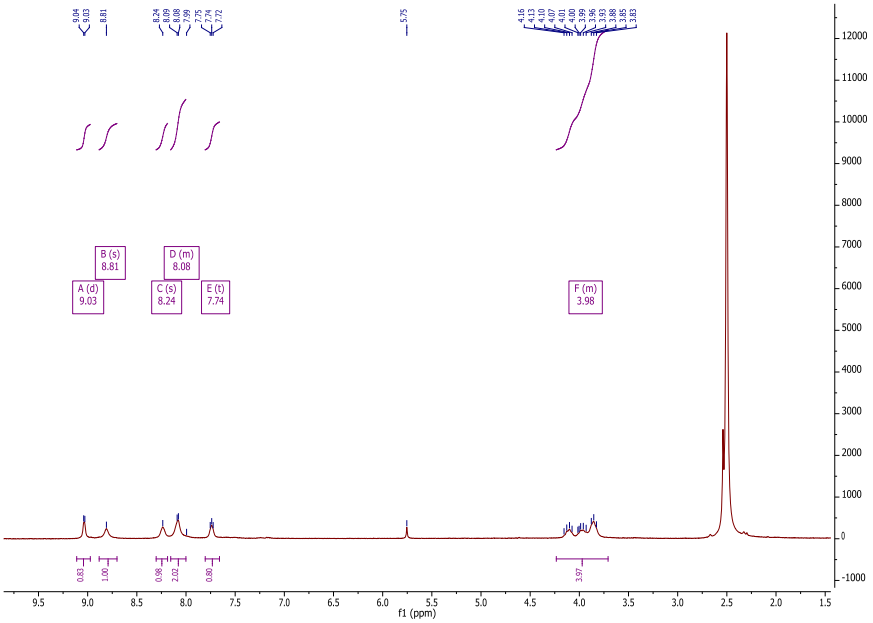
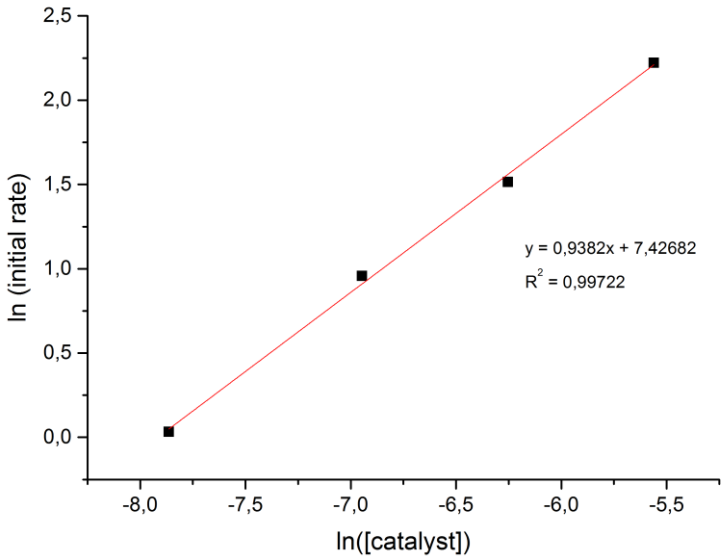


Figure S21: NMR of the formate complex crystal [a].



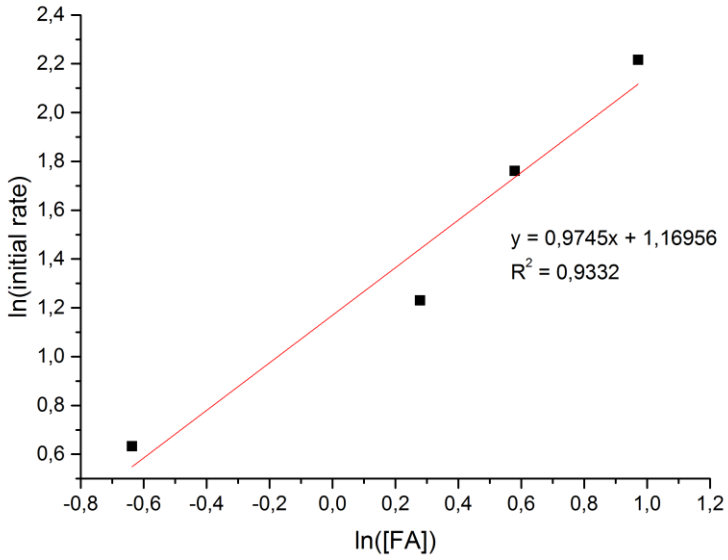
8. Mechanistic elucidation.

Figure S22: Reaction order in manganese catalyst [a].



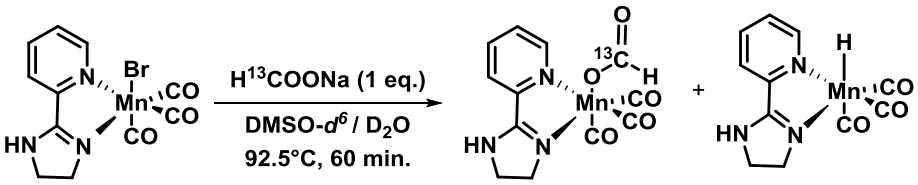
[a] Reaction conditions: HCOOK (32 mmol), HCOOH (5 mmol), Mn(pyridine-imidazoline)$(CO)_3$Br (respectively 5, 12.5, 25 and 50 µmol), H_2O (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes). Kinetics calculations carried on with values measured at t = 6 minutes. Gas evolution measured with manual burette and gas mixture analyzed by GC.

Figure S23: Reaction order in HCOOH/HCOOK [a].



[a] Reaction conditions: HCOOH and HCOOK (Respectively 1 and 6.4, 2.5 and 16, 3.4 and 21.6, 5 and 32 mmol), HCOOH (5 mmol), Mn(pyridine-imidazoline)$(CO)_3$Br (50 µmol), H_2O (9 mL), triglyme (4 mL), t_{set} (92.5°C), time (180 minutes). Kinetics calculations carried on with values measured at t = 6 minutes. Gas evolution measured with manual burette and gas mixture analyzed by GC.

Procedure for the labelling experiment:



A 5 mL Schlenk flask equipped with a stir bar was flushed 6 times. $H^{13}COONa$ (82 µmol, 5 mg, 1 eq.) in D_2O (0.6 mL) and Mn(pyridine-imidazoline)$(CO)_3Br$ (82 µmol, 30 mg, 1 eq.) in DMSO-d^6 (0.25 mL) were charged into the flask under a positive pressure of Ar. The stop cock was changed for a rubber septum and the reaction mixture was stirred at 90°C for 60 minutes. A GC sample was collected through the septum and analyzed. The mixture was filtered with a PTFE cannula equipped with a filter pad and directly transferred into a J. Young NMR tube. The content of the Schlenk was washed with D_2O (0.3 mL) and DMSO-d^6 (0.05 mL). The sample was analyzed by NMR spectroscopy right away. All the following NMR spectrums were calibrated on the signal of the residual DMSO (2.50 ppm for ^1H and 39.52 ppm in ^{13}C).

Figure S24: Crude, ^1H NMR:

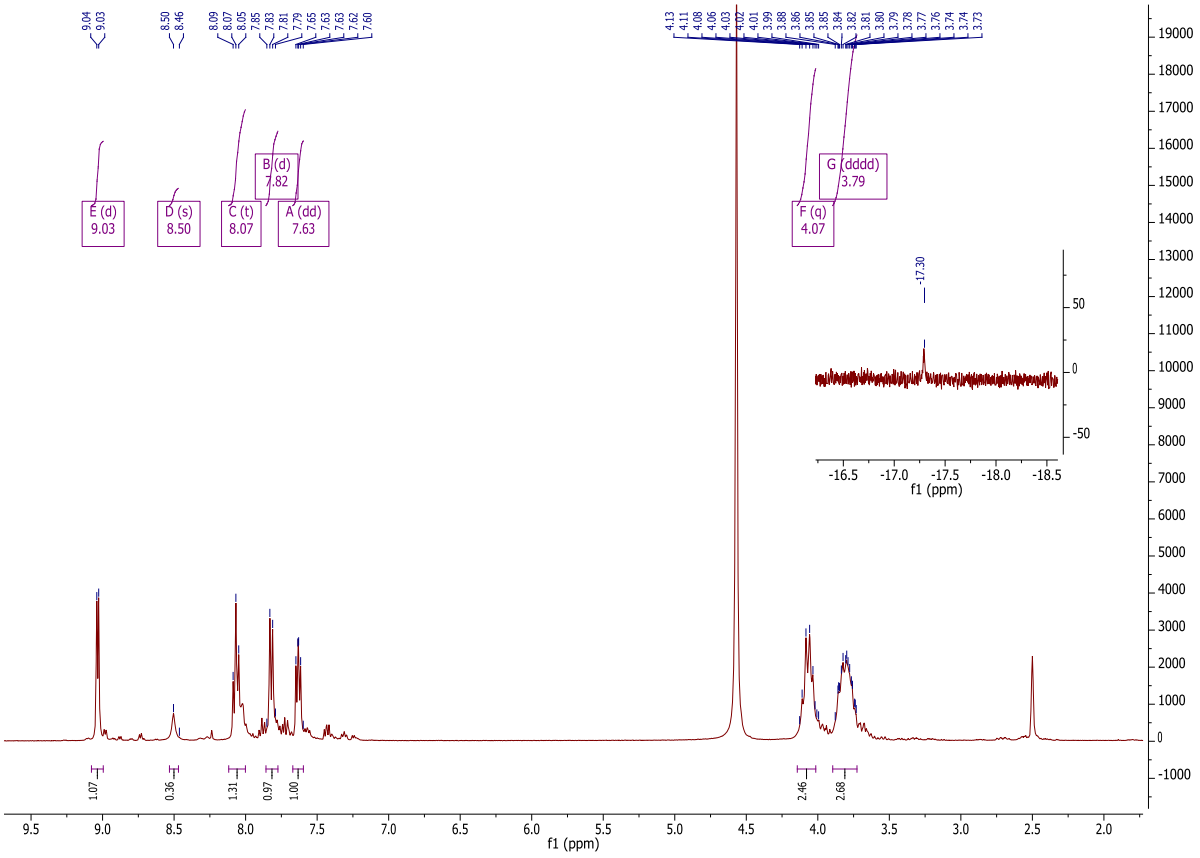


Figure S25: Crude and $H^{13}COOK$, Stacked ^{1}H NMR.

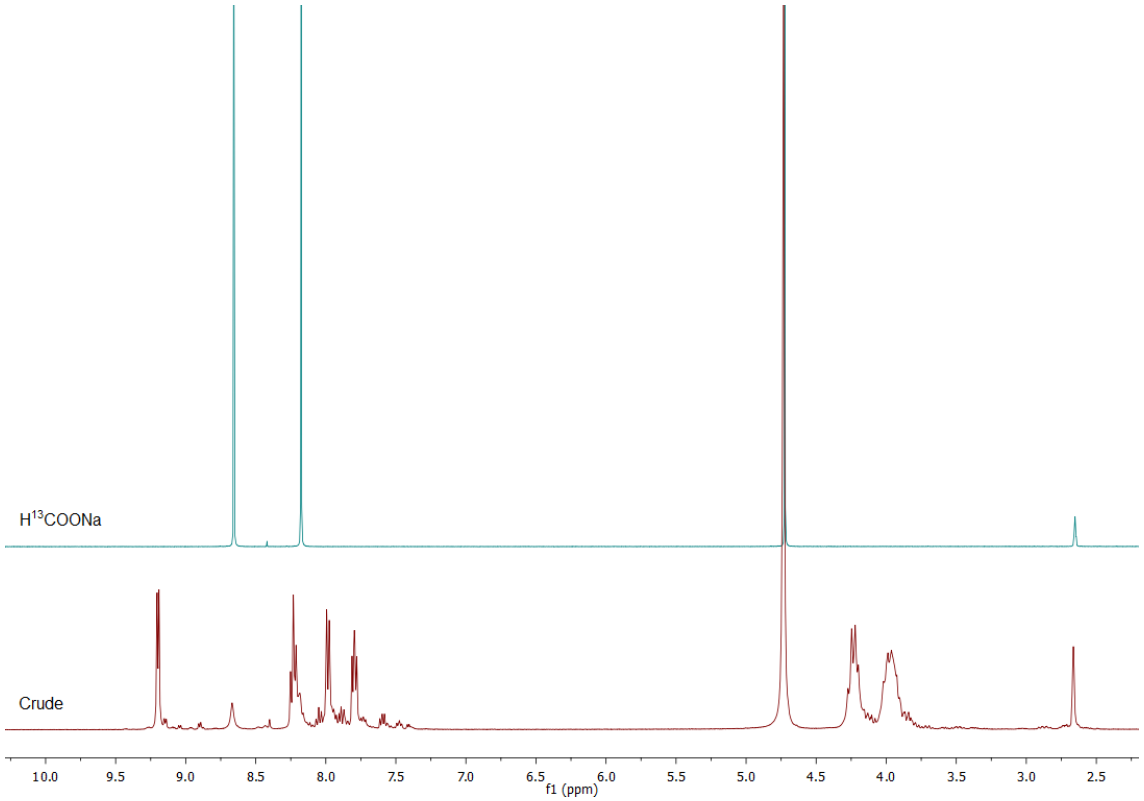


Figure S26: Crude ^{13}C NMR.

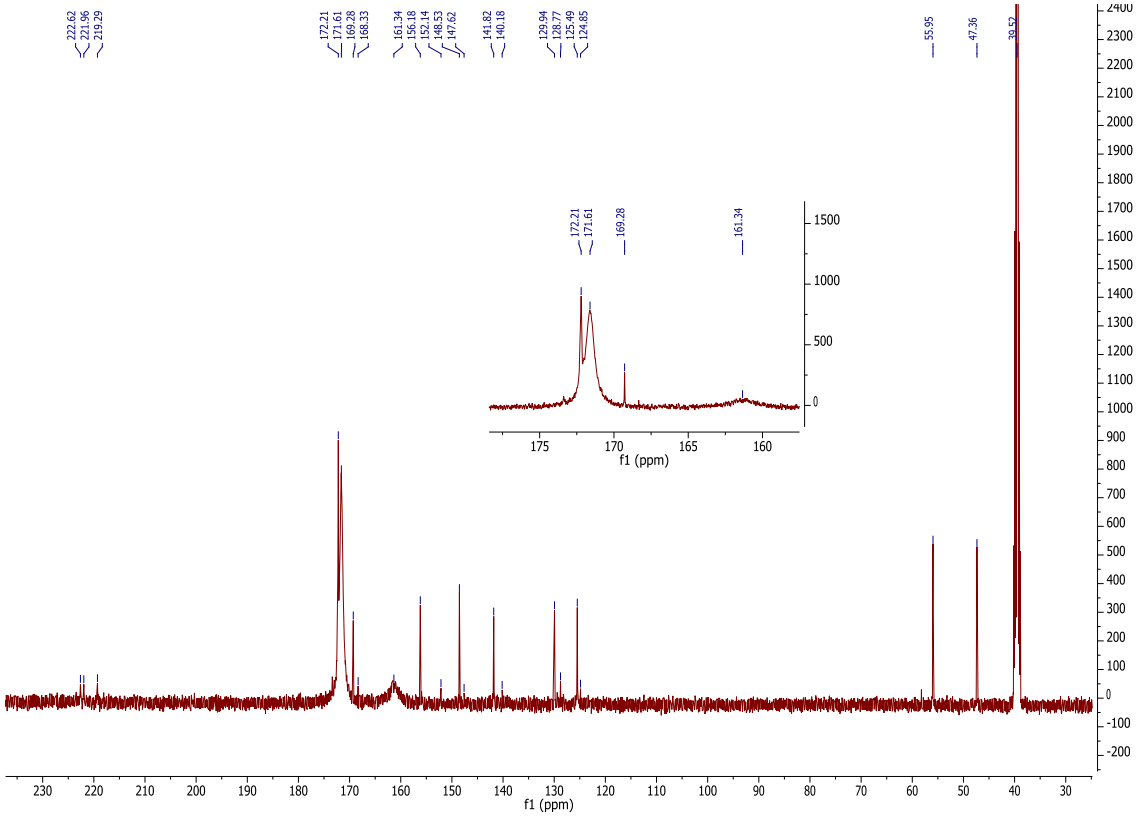


Figure S27: Crude ^{13}C no dec. NMR.

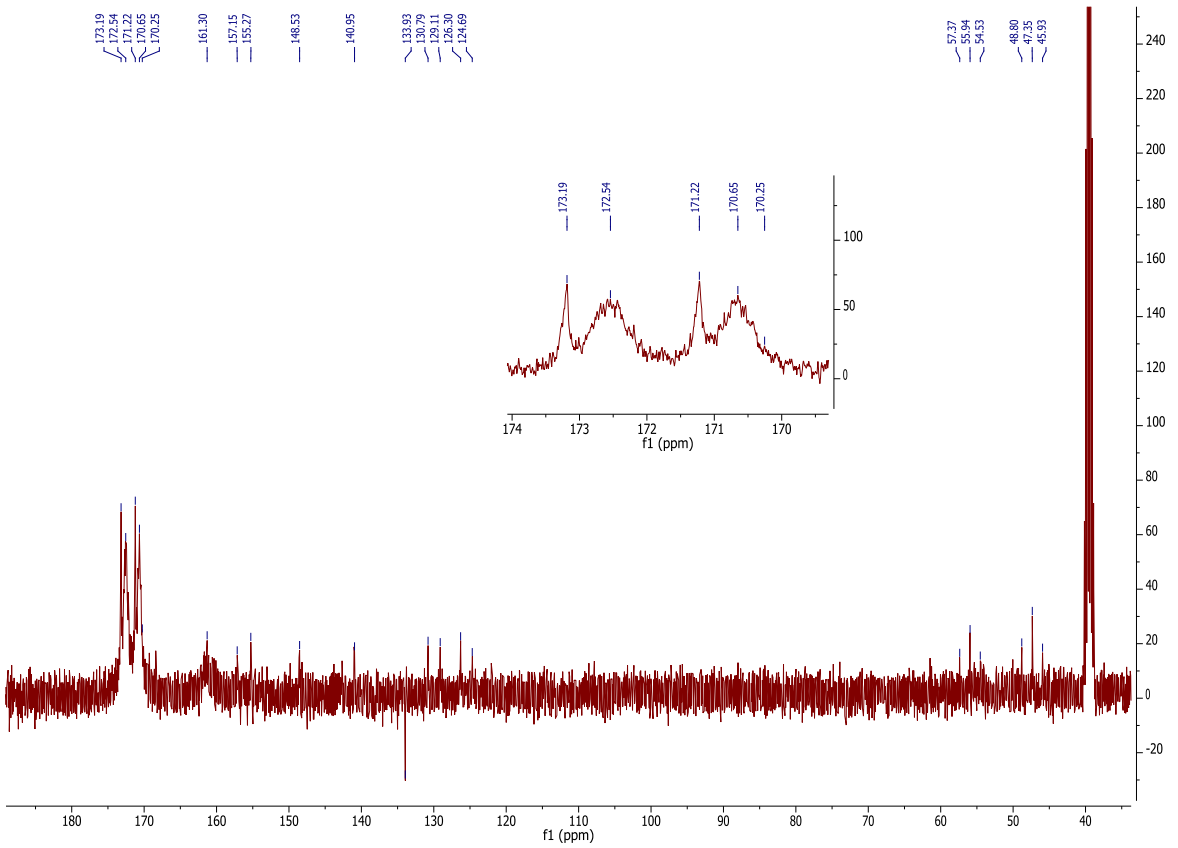


Figure S28: Crude and H^{13}COOK, Stacked ^{13}C NMR.

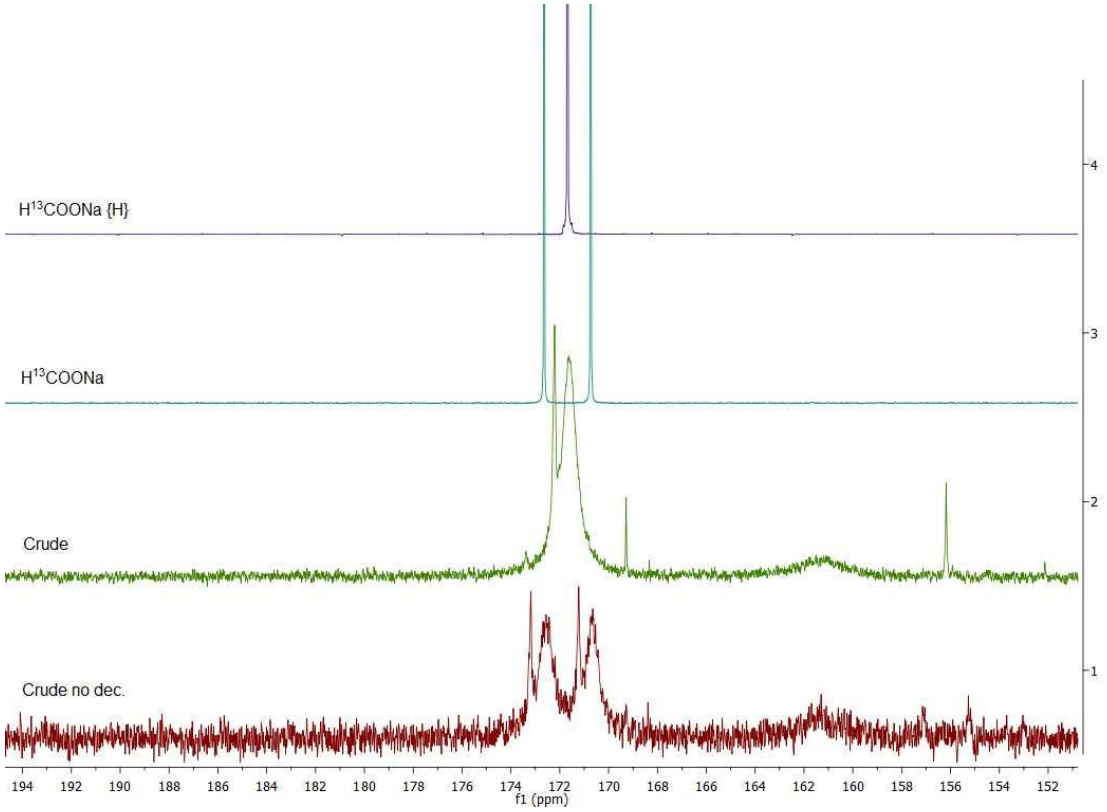


Figure S29: Crude, ^{1}H - ^{13}C no dec. HMQC NMR (formyl region).

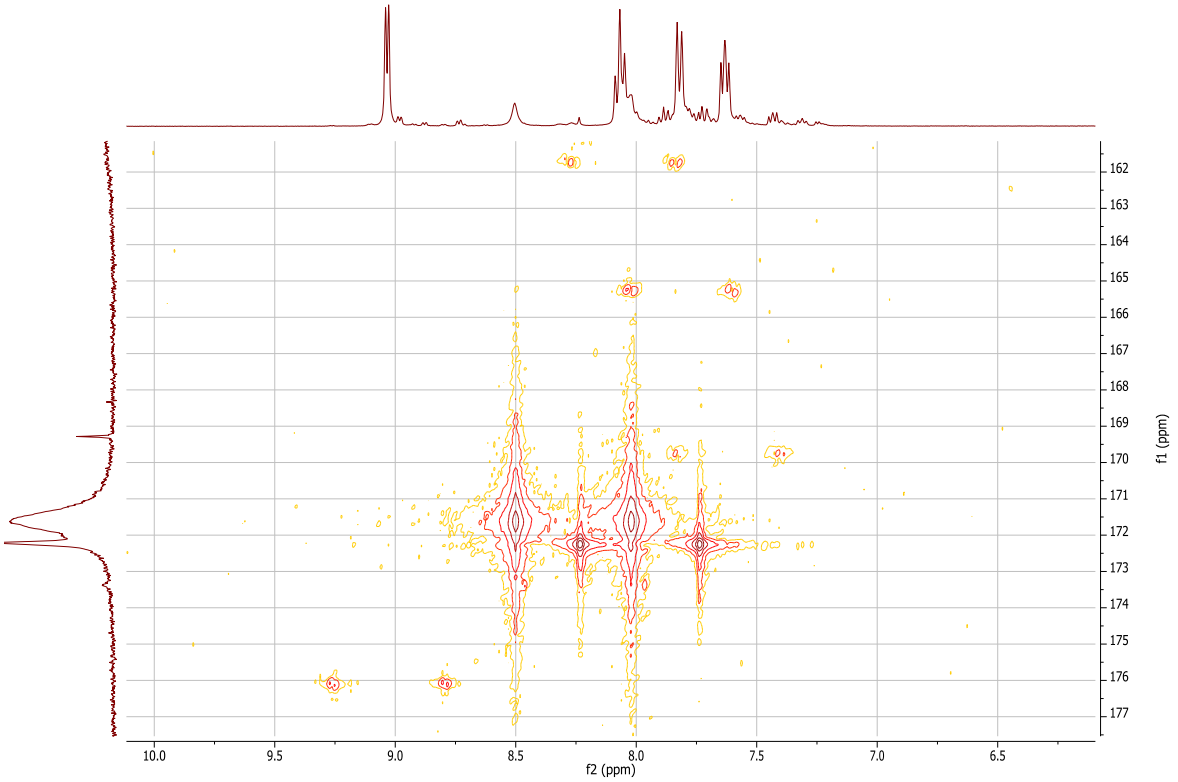


Figure S30: Crude, ^{1}H - ^{13}C HSQC NMR.

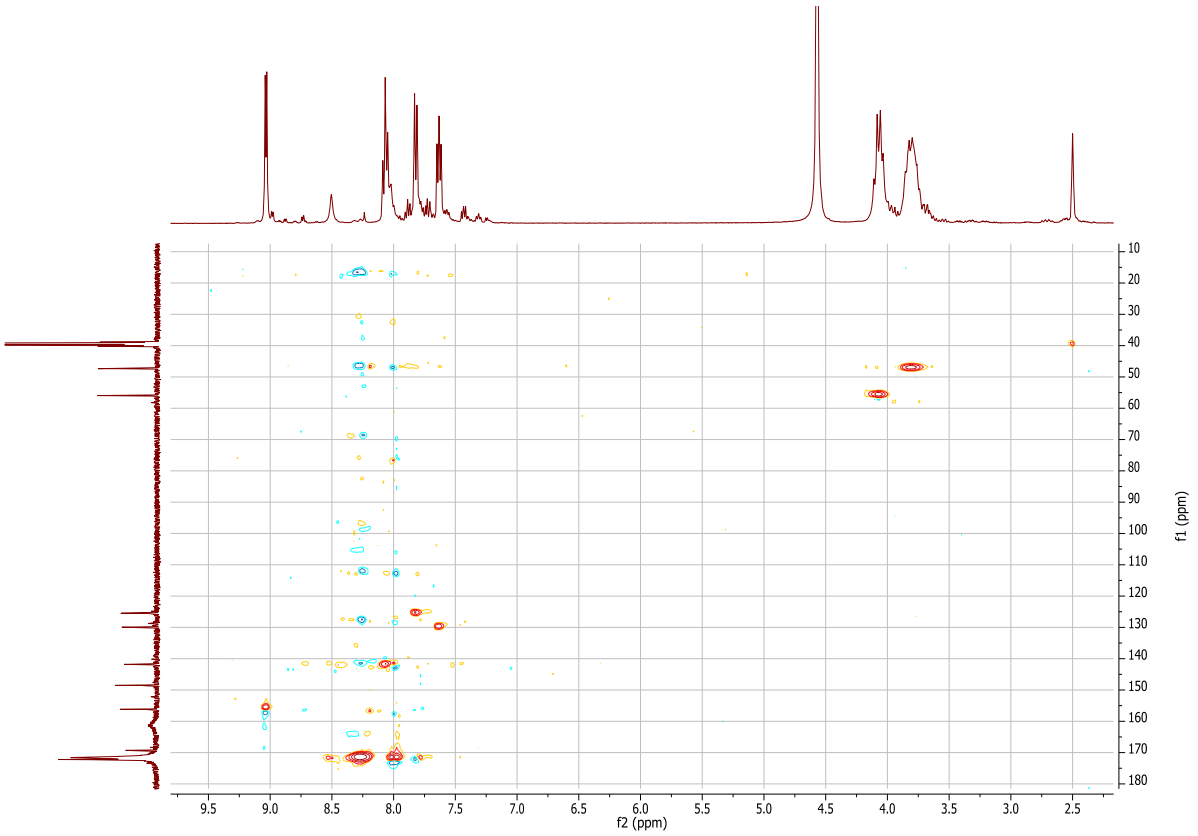
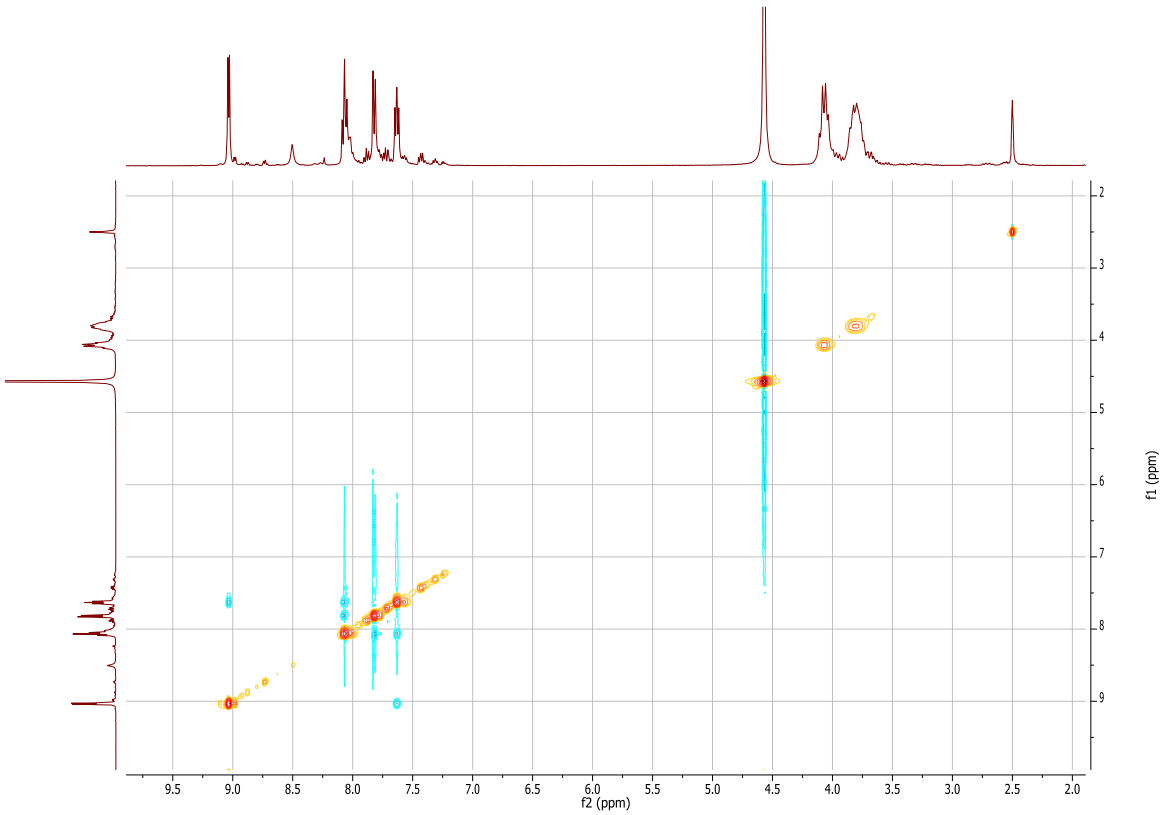
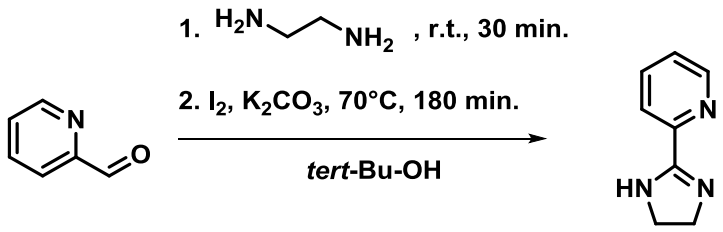


Figure S31: Crude, ^{1}H - ^{1}H NOESY NMR.



9. Synthesis of the ligands and Mn complexes.

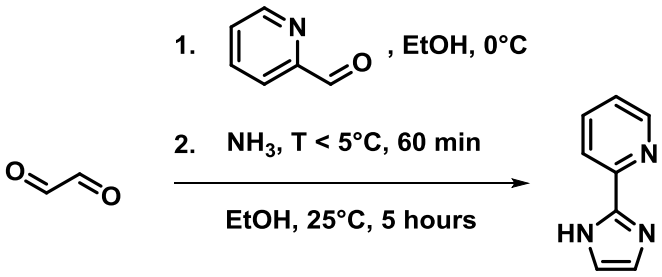
2-(4,5-dihydro-1H-imidazol-2-yl)pyridine :



Procedure adapted from literature[1]. A 100 mL three neck round bottom flask equipped with two stop cocks and an Allhin condenser - equipped with argon entry and bubbler- was dried with a 640°C heat gun under vacuum. The glassware was put under positive argon flow and charged with *tert*-butanol (30 mL) and 2-pyridinecarboxaldehyde (0.40 mL, 4 mmol, 1 eq.). Ethylene diamine (0.30 mL, 4.4 mmol, 1.1 eq.) was added dropwise and the mixture was stirred at room temperature for 30 minutes. Iodine (762 mg, 6 mmol, 1.5 eq.) and K_2CO_3 (1.07 g, 8 mmol, 2 eq.) were added in two portions and the setup was heated to 70°C for 3 hours. The reaction was quenched with aqueous saturated sodium sulfite solution (40 mL). The organic phase was recovered and the aqueous phase was

extracted with 3 X 30 mL ethyl acetate. The combined organic layers were washed with an aqueous saturated sodium chloride (40 mL), dried with Na_2SO_4 and concentrated under vacuum to afford a yellowish solid. Column chromatography purification with ethyl acetate : triethylamine (99 : 1, R_f=0.15) then ethyl acetate : Methanol : triethylamine (89.5 : 9.5 : 1, R_f=0.24) afforded a light yellow solid (515 mg, 3.5 mmol, 88% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.56 (ddd, *J* = 0.95, 1.77, 4.90 Hz, 1H), 8.13 (dt, *J* = 1.09, 1.09, 7.94 Hz, 1H), 7.75 (td, *J* = 1.75, 7.73, 7.77 Hz, 1H), 7.34 (ddd, *J* = 1.23, 4.85, 7.56 Hz, 1H), 3.83(s, 4H).

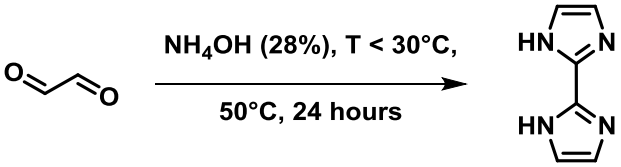
2-(1H-imidazol-2-yl)pyridine :



Procedure adapted from two existing literatures sources[2,3]. 2-pyridinecarboxaldehyde (4.76 mL, 50 mmol, 1 eq.) and ethanol (10 mL) were charged into a two neck round bottom flask and cooled down to 0°C with an ice bath. Simultaneously, Glyoxal (40% Glyoxal solution in H_2O, 7.23 mL, 1.26 eq.) was charged in a three neck round bottom - flask equipped with an argon/vacuum entry, a thermometer and a stop cock - and cooled down to 0°C. After 10 minutes of stirring, the 2-pyridinecarboxaldehyde/ethanol solution was added to the glyoxal/ethanol solution. The mixture was stirred until the internal temperature reached 0°C. Simultaneously, ammonia (7M solution in methanol, 114 mL, 800 mmol, 16 eq.) was cooled down to 0°C. Then, the cooled ammonia solution was added to the reaction mixture by taking extra caution of keeping the internal temperature bellow 5°C. After the addition, the solution was stirred at 0°C for 60 minutes. The ice bath was removed and the reaction mixture was stirred for 5 hours at room temperature monitored by TLC. The solution turns from deep yellow (0 to 60 min.) to orange/yellow (60 min.) to deep orange (2 hours 40 min.) to brown (3 hours) to dark brown (3 hours 45 min.). After 6 hours, the reaction was stopped and the mixture was transferred to a single coil round bottom flask and most of the volatiles solvents were removed under vacuum. The resulting mixture was poured into 50 mL Et_2O. Aqueous solution of saturated NaCl (10 mL) CH_2Cl_2 (10 mL) were added in order to get rid of an emulsion. The aqueous phase was extracted with 3 X 50 mL Et_2O. The combined organic layers were dried with Na_2SO_4 and filtered. The crude mixture was concentrated under vacuum to afford 5.74 g of deep

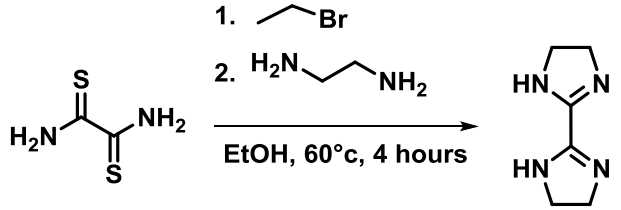
brown oil which was additionally dried on the high vacuum line overnight. The crude product was purified by flash chromatography using ethyl acetate (99%) and triethylamine (1%) to neutralize the acidity of the silica. 2-(1H-imidazol-2-yl)pyridine was obtained as a light brown solid (R_f in EA = 0.35, 4.06 g, 28 mmol, 56% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.51 (ddd, *J* = 0.95, 1.74, 4.89 Hz, 1H), 8.20 (dt, *J* = 1.09, 1.09, 7.97 Hz, 1H), 7.78 (td, *J* = 1.74, 7.53, 7.98 Hz, 1H), 7.25 (ddd, *J* = 1.20, 4.89, 7.54 Hz, 1H) , 7.19(s, 2H).

1H,1'H-2,2'-biimidazole :



This procedure was adapted from literature precedence [4]. Glyoxal (40% in water, 20 mL, 174 mmol, 1 eq.) was charged into a three neck round bottom flask - equipped with a thermometer, a condenser and a stop cock - and cooled to 0°C. NH_4OH (28%, 37 mL, 276 mmol, 1.6 eq.) was added dropwise through an addition funnel (50 mL) with a rate of roughly 1 drop.sec^{-1}. At the start of the addition, the solution turns to bright yellow, then deep yellow, then deep orange, then to red/brown. Special care was carried out throughout the addition to avoid internal temperature to rise above 30°C. Once done, the reaction mixture was heated to 50°C for 24 hours. The resulting black precipitated was filtered with suction filtration and dried under vacuum for 24 hours at room temperature. NMR analysis showed some water trace so the mixture was heated 24 hours at 50°C. NMR analysis confirmed the successfully obtained 1H,1'H-2,2'-biimidazole (898 mg, 5 mml, 2% yield). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 12.67 (bs, 2H), 7.13 (bs, 2H), 7.01 (bs, 2H).

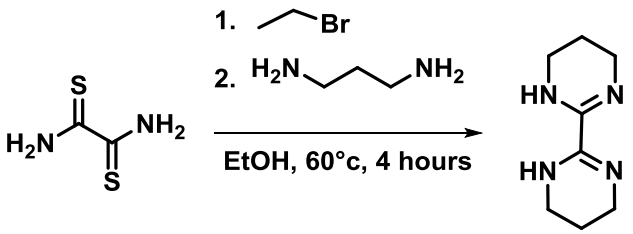
4,4',5,5'-tetrahydro-1H,1'H-2,2'-biimidazole:



This procedure was adapted from literature precedence [5]. A 50 mL three neck round bottom flask was equipped with a condenser (bubbler, argon/vacuum entry), a stop cock and an argon/vacuum

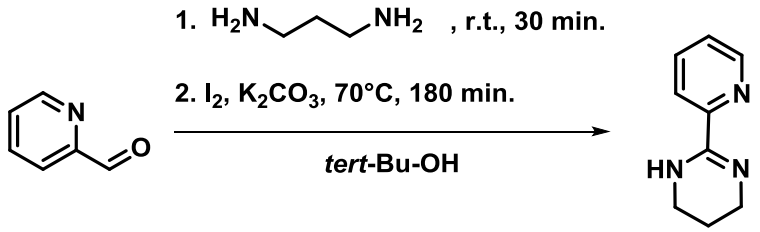
line. The apparatus was dried under vacuum with a 650°C heat gun and cooled to room temperature. Dithiooxamide (2 g, 16.6 mmol, 1 eq.) and ethanol (10 mL) were charged in the setup and bromoethane (3 mL, 40.2 mmol, 2.42 eq.) was added dropwise (deep red solution). The reaction mixture was then heated to 60°C and stirred for 4 hours. Ethylene diamine (7.5 mL, 112.2 mmol, 6.75 eq.) was added dropwise over 60 minutes (the solution turns from light brown to deep yellow). When the addition was over, the reaction medium was heated at 80°C for 20 minutes. The solution was then cooled down using an ice bath and the mixture was stirred 45 min. at 0°C. Filtration afforded a white solid which was dried overnight under vacuum. The resulting grey solid showed satisfying purity on NMR (1.77g, 12.81 mmol, 77% yield). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 6.66 (bs, 2H), 3.50 (bs, 8H).

1,1',4,4',5,5',6,6'-octahydro-2,2'-bipyrimidine:



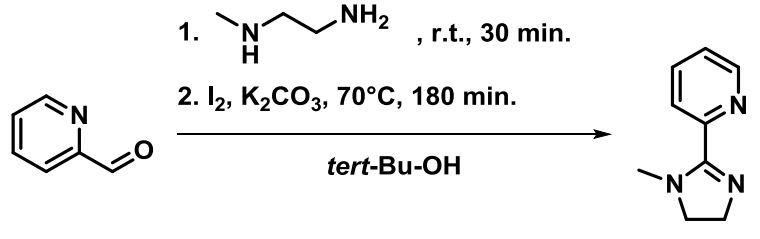
This procedure was adapted from literature precedence[5]. A 50 mL three neck round bottom flask was equipped with a condenser (bubbler, argon/vacuum entry), a stop cock and an argon/vacuum line. The apparatus was dried under vacuum with a 650°C heat gun and cooled to room temperature. Dithiooxamide (2 g, 16.6 mmol, 1 eq.) and ethanol (10 mL) were charged in the setup and bromoethane (3 mL, 40.2 mmol, 2.42 eq.) was added dropwise (deep red/orange solution). The reaction mixture was then heated to 60°C and stirred for 4 hours. Ethylene diamine (7.5 mL, 112.2 mmol, 6.75 eq.) was added dropwise over 60 minutes (the solution turns from light brown to deep yellow). When the addition was over, the reaction medium was heated at 80°C for 20 minutes and turned into a white creamy color. The solution was then cooled down using an ice bath and the mixture was stirred 45 min. at 0°C. The white solid was filtered and washed with ethanol to afford 1,1',4,4',5,5',6,6'-octahydro-2,2'-bipyrimidine (3.66g, 20 mmol, 100% yield) as a grey solid. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 5.09 (bs, 2H), 2.73 (t, J = 6.84, 6.84 Hz, 8H), 1.60 (p, J = 6.84, 6.84, 6.85, 6.85 Hz, 4H).

2-(pyridin-2-yl)-1,4,5,6-tetrahydropyrimidine:



This procedure was adapted from literature precedence[1]. A three neck round bottom flask equipped with two stop cocks and an allhin condenser - equipped with argon entry and bubbler- was dried with a 640°C heat gun under vacuum. The glassware was put under positive argon flow and charged with *tert*-butanol (30 mL) and 2-pyridinecarboxaldehyde (0.19 mL, 2 mmol, 1 eq.). Propylene diamine (0.18 mL, 2 mmol, 1.1 eq.) was added dropwise at 0°C. The reaction is stirred 40 minutes at room temperature. Iodine (762 mg, 6 mmol, 1.5 eq.) and K_2CO_3 (1.07 g, 8 mmol, 2 eq.) were added to the reaction medium at 0°C and the setup is heated to 70°C for 3 hours. The reaction was quenched with an aqueous saturated sodium sulfite solution (20 mL). The organic phase was recovered and the aqueous phase was extracted with 3 X 50 mL ethyl acetate. The combined organic layers were washed with aqueous saturated sodium chloride, dried with Na_2SO_4 and concentrated under vacuum to afford a yellow oil (190 mg, 1.17 mmol, 59% yield). NMR analysis showed a good quality product thus, no further purification was attempted. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.53 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.08 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.83 (ddd, *J* = 8.0, 7.5, 1.8 Hz, 1H), 7.44 (ddd, *J* = 7.5, 4.8, 1.3 Hz, 1H), 3.44 – 3.33 (m, 4H), 1.75 – 1.65 (m, 2H).

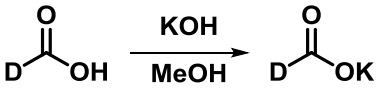
2-(1-methyl-4,5-dihydro-1H-imidazol-2-yl)pyridine:



This procedure was adapted from literature precedence[1]. A 100 mL three neck round bottom flask equipped with two stop cocks and an allhin condenser - equipped with argon entry and bubbler- was dried with a 640°C heat gun under vacuum. The glassware was put under positive argon flow and charged with *tert*-butanol (30 mL) and 2-pyridinecarboxaldehyde (0.10 mL, 1 mmol, 1 eq.). N-

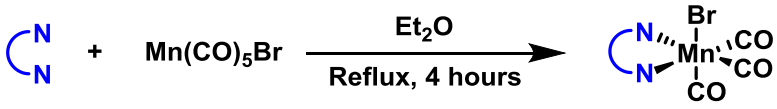
methylene diamine (0.96 mL, 1.1 mmol, 1.1 eq.) was added dropwise and the mixture is stirred at room temperature for 45 minutes. Iodine (254 mg, 1.5 mmol, 1.5 eq.) was added to the mixture (color change from deep yellow to orange) and then K_2CO_3 (1.07 g, 8 mmol, 2 eq.) was added too (color change from orange to brown). The mixture was heated to 70°C and stirred for 3 hours. After 5 minutes, the solution turned to deep orange and after 10 minutes, the color was whitish. With time, the color evolved to deeper white. The reaction was quenched with aqueous solution of saturated sodium sulfite (40 mL). The organic phase was recovered and the aqueous phase was extracted with 3 X 30 mL ethyl acetate. The combined organic layers were washed with aqueous saturated sodium chloride (40 mL), dried with Na_2SO_4 and concentrated under vacuum to afford a yellowish solid which was additionally dried under vacuum overnight (278 mg of crude product). Purification by flash column chromatography afforded 2-(1-methyl-4,5-dihydro-1H-imidazol-2-yl)pyridine as a dark brown oil (89 mg, 0.5 mmol, 50% yield). Column chromatography purification with ethyl acetate : hexanes : triethylamine (49.5 : 49.5 : 1, R_f=0) then methanol : dichloromethane : triethylamine (4.5 : 94.5 : 1, R_f=0.19) affords a light yellow solid (515 mg, 3.5 mmol, 88% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.63 (bd, *J* = 5.30, 1H), 7.91 (bd, *J* = 7.88 Hz, 1H), 7.77 (td, *J* = 1.72, 7.77, 7.81 Hz, 1H), 7.34 (ddd, *J* = 1.08, 4.85, 7.59 Hz, 1H), 3.91 (t, *J* = 10.06, 10.06 Hz, 2H), 3.54 (t, *J* = 10.18, 10. 18 Hz, 2H), 3.08 (s, 3H).

Deuterated potassium formate:



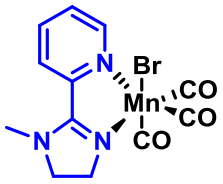
In a 25 mL round-bottom flask, KOH (1 eq., 53 mmol, 2.97 g) is dissolved in MeOH (10 mL). DCOOH (1 eq., 53 mmol, 2 mL) is added dropwise and the reaction mixture is stirred for 4 hours at room temperature. The solvent was evaporated on the high vacuum line and the solid is dried overnight under vacuum. A white solid is obtained (3.26 g, 38.5 mmol, 72 % yield). **^{1}H NMR** (300 MHz, D_2O) δ 8.44 (s, 1H, residual non-deuterated HCOOK). **^{13}C NMR** (75 MHz, D_2O) δ 170.27 (t, *J* = 30.53 Hz, 30.23 Hz, 1C).

General procedure for Mn complex synthesis:



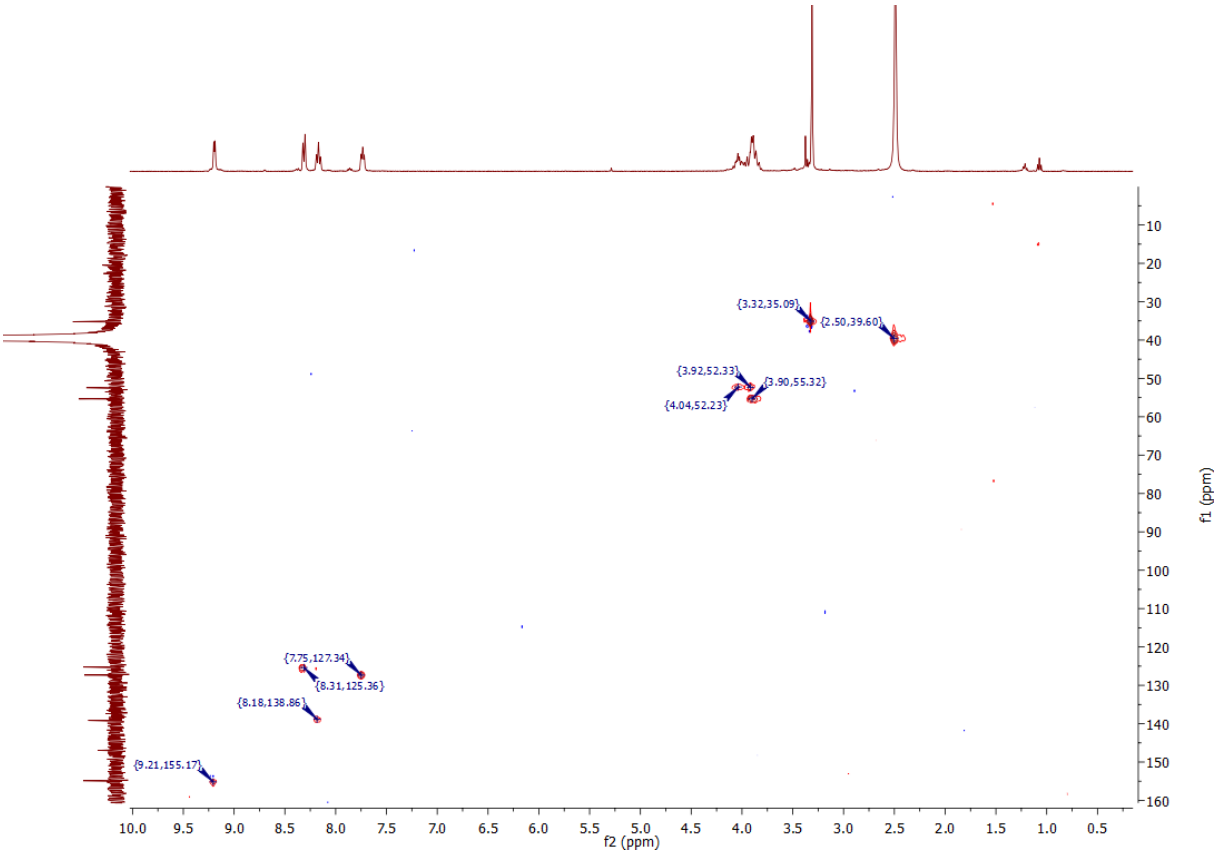
Procedure adapted from existing literature[6]. A three neck round bottom flask (50 mL or 100 mL) was equipped with an argon/vacuum entry line, an allhin condenser (equipped with an argon/vacuum line and an oil bubbler) and a stop cock. The setup was dried under vacuum with a 640°C heat gun for 5 to 10 minutes. Then, the glassware was cooled down to room temperature while being under vacuum. The set-up was put under a positive pressure of argon and charged with $Mn(CO)_5Br$, Et_2O and the corresponding ligand (added as a solid or loaded as an oil). Aluminum foil was wrapped around the glassware (round bottom flask and condenser) to avoid light exposure. In addition, the window stores of the lab were closed and the lights were turned off. The reaction mixture was heated to reflux in diethylether for 4 hour. In every case, a solid was recovered, filtered and washed with Et_2O to afford the corresponding manganese complex. All catalysts were stored under argon in the absence of light.

(2-(1-methyl-4,5-dihydro-1H-imidazol-2-yl)pyridine)Mn(CO)$_3$Br :



^{1}H NMR (300 MHz, Acetonitrile-d_3) δ 9.92 (bd, *J* = 5.20 Hz, 1H), 8.16 (bd, *J* = 7.78 Hz, 1H), 8.06 (bt, *J* = 7.69, 7.69 Hz, 1H), 7.61 (bt, *J* = 6.35, 6.35 Hz, 1H), 3.23 – 3.73 (m, 4H), 3.30 (s, 3H). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.20 (d, *J* = 5.1 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.18 (t, *J* = 7.8 Hz, 1H), 7.74 (dd, *J* = 7.6, 5.3 Hz, 1H), 4.17 – 3.76 (m, 4H), 3.35 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.49, 154.91, 147.01, 139.21, 127.36, 125.28, 55.38, 52.46, 35.26, CO resonance not detected. **CI-MS**: m/z = 300 $[M\text{-}Br]^+$. **IR (ATR)**: 2012 (CO), 1904 (b, CO) cm^{-1}. **EA** calculated: C, 37.92; H, 2.92; N, 11.06. Found: C, 37.83; H, 2.67; N, 10.83.

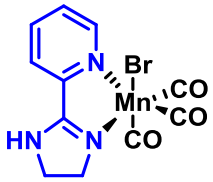
^{1}H - ^{13}C HSQC spectrum for (2-(1-methyl-4,5-dihydro-1H-imidazol-2-yl)pyridine)Mn(CO)$_3$Br :



(2,2'-bipyridine)Mn(CO)$_3$Br :

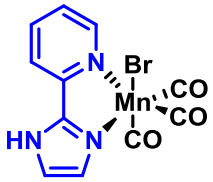
Complex reported in literature precedence [6]. **^{1}H NMR** (300 MHz, Acetonitrile-d_3) δ 9.22 (d, *J* = 5.1 Hz, 2H), 8.34 (d, *J* = 8.0 Hz, 2H), 8.11 (td, *J* = 7.9, 1.6 Hz, 2H), 7.61 (t, *J* = 6.4 Hz, 2H).

(2-(4,5-dihydro-1H-imidazol-2-yl)pyridine)Mn(CO)$_3$Br :



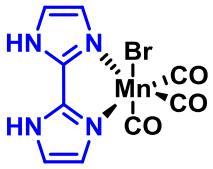
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.14 (d, *J* = 5.2 Hz, 1H), 8.71 (s, 1H), 8.28 – 8.14 (m, 2H), 8.11 – 8.04 (m, 1H), 7.80 – 7.70 (m, 1H), 4.22 – 3.82 (m, 4H). **^{13}C NMR** (101 MHz, DMSO) δ 260.24, 251.23, 165.51, 154.33, 147.03, 139.34, 132.00, 127.63, 124.06, 54.21, 45.40. **CI-MS**: m/z = 286 $[M\text{-}Br]^+$. **IR (ATR)**: 3252 (N-H), 2016 (CO), 1898 (b, CO) cm^{-1}.

(2-(1H-imidazol-2-yl)pyridine)Mn(CO)$_3$Br :



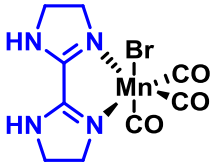
^{1}H NMR (300 MHz, DMSO-d_6) δ 14.11 (bs, 1H), 9.06 (bd, *J* = 5.2 Hz, 1H), 8.17 (bd, *J* = 5.7 Hz, 2H), 7.74 – 7.68 (bm, 1H), 7.60 (bd, *J* = 8.6 Hz, 2H). **^{13}C NMR** (75 MHz, DMSO) δ 154.37, 147.76, 146.38, 139.85, 131.32, 125.63, 122.39, 120.77, 40.84, 40.57, 40.29, 40.01, 39.74, 39.46, 39.18, CO resonance not detected. **IR (ATR)**: 3079 (N-H), 2024 (CO), 1910 (b, CO) cm^{-1}. **CI-MS**: m/z = 307 $[M\text{-}2\ CO]^+$.

(2-(1H-imidazol-2-yl)pyridine)Mn(CO)$_3$Br :



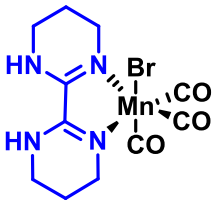
^{1}H NMR (300 MHz, DMSO-d_6) δ 12.92 (s, 2H), 7.81 – 6.79 (m, 4H). **^{13}C NMR** (75 MHz, DMSO) δ 138.48, 130.37, 120.47, CO resonance not detected. **CI-MS**: m/z = 269 $[M\text{-}3\ CO]^+$. **IR (ATR)**: 3180 (N-H), 2027 (CO), 1902 (b, CO) cm^{-1}.

(4,4',5,5'-tetrahydro-1H,1'H-2,2'-biimidazole)Mn(CO)$_3$Br :



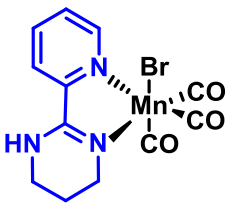
^{1}H NMR (300 MHz, DMSO-d_6) δ 7.89 (s, 1H), 4.16 – 3.65 (m, 8H). **^{13}C NMR** (75 MHz, DMSO) δ 158.63, 53.93, 46.22, CO resonance not detected. **CI-MS**: m/z = 277 $[M\text{-}Br]^+$. **IR (ATR)**: 3232 (N-H), 2017 (CO), 1906 (CO).

(1,1',4,4',5,5',6,6'-octahydro-2,2'-bipyrimidine)Mn(CO)$_3$Br :



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.89 (s, 2H), 4.18 – 3.59 (m, 12H). **^{13}C NMR** (75 MHz, DMSO) δ 158.63, 53.92, 46.22, CO resonance not detected. **IR (ATR)**: 3234 (N-H) 2019 (CO), 1901 (b, CO) cm^{-1}. **EI-MS**: m/z = 389 $[M]^+$.

(2-(pyridin-2-yl)-1,4,5,6-tetrahydropyrimidine)Mn(CO)$_3$Br :

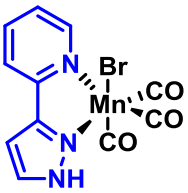


^{1}H NMR (400 MHz, DMSO-d_6) δ 9.10 (d, *J* = 5.3 Hz, 1H), 8.65 – 8.57 (m, 1H), 8.24 – 8.11 (m, 2H), 7.70 (ddd, *J* = 7.3, 5.4, 2.1 Hz, 1H), 3.81 (p, *J* = 5.3, 4.5 Hz, 2H), 3.49 – 3.28 (m, 3H), 2.06 – 1.85 (m, 2H). **^{13}C NMR** (101 MHz, DMSO) δ 154.92, 153.58, 152.07, 138.94, 126.98, 121.92, 49.78, 37.57, 21.00, CO resonance not detected. **MS-ES**: m/z = 381. **IR (ATR)**: 3307 (N-H) 2016 (CO), 1899 (b, CO) cm^{-1}.

(2,2'-biquinoline)Mn(CO)$_3$Br :

^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.99 (d, J = 9.0 Hz, 2H), 8.55 (d, J = 8.6 Hz, 2H), 8.34 (d, J = 8.4 Hz, 2H), 8.03 (dd, J = 9.3, 4.9 Hz, 4H), 7.84 – 7.72 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 159.10, 150.43, 140.48, 132.60, 129.62, 129.37, 129.33, 125.56, 119.71. **EI-MS**: m/z = 291 $[M\text{-}3CO]^+$**. IR (ATR)**: 2019 (CO), 1901 (b, CO) cm^{-1}.

(2-(1H-pyrazol-3-yl)pyridine)Mn(CO)$_3$Br :



^{1}H NMR (400 MHz, DMSO-d_6) δ 14.62 (s, 1H), 9.06 (dt, *J* = 5.5, 1.1 Hz, 1H), 8.21 (d, *J* = 2.7 Hz, 1H), 8.19 (t, *J* = 1.1 Hz, 1H), 8.13 (td, *J* = 7.7, 1.5 Hz, 1H), 7.56 (ddd, *J* = 7.3, 5.5, 1.5 Hz, 1H), 7.29 (d, *J* = 2.7 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 153.45, 151.31, 150.94, 139.22, 135.00, 124.82, 121.84, 104.40, CO resonance not detected. **EI-MS:** m/z = 307 [M-2CO]+. **IR (ATR)**: 3149 (N-H), 2030 (CO), 1909 (b, CO) cm^{-1}.

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