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Photochemical CO_2 Reduction with Mononuclear and Dinuclear Rhenium Catalysts Bearing a Pendant Anthracene Chromophore

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-Supporting Information-

Table of Contents	**Page**
Materials and Characterization General Information	S3
Photocatalysis Equipment and Methods	S3
Photophysical Measurement Equipment and Methods	S3
Photocatalysis Procedure	S3
Quantum Yield Measurements	S3
Photophysical Properties of Re Complexes in Dichloromethane Solution (Table S1)	S4
Absorption and Luminescence Spectra in Dichloromethane (Figure S1)	S4
Luminescence Quenching by BIH in DMF (Figure S2)	S5
Transient Absorption Spectra of ***trans*-Re$_2$Cl$_2$** under Ar and CO$_2$ (Figure S3)	S5
Catalyst Concentration versus Absorption Plot (Figure S4)	S6
Quantum Yield Versus Catalyst Concentration (Figure S5)	S6
Photocatalytic Reaction TON, TOF, and Quantum Yield Values (Table S2)	S7
Example GC trace for a photoreaction with ***trans*-Re$_2$Cl$_2$** (Figure S6)	S8
Example ^{1}H NMR formate analysis with ferrocene (Figure S7)	S10
References	S10

Materials and Characterization. Unless otherwise noted, all synthetic manipulations were performed under N_2 atmosphere using standard Schlenk techniques or in an MBraun glovebox. Toluene was dried with a Pure Process Technology solvent purification system. Acetonitrile was distilled over CaH_2 and stored over molecular sieves before use. The rhenium precursor $Re(CO)_5Cl$ was purchased from Strem and stored in the glovebox. 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH) was prepared according to a published procedure.[1] The parent catalyst, $Re(bpy)(CO)_3Cl$,[2] and anthracene-functionalized rhenium catalysts ***cis*-Re_2Cl_2**, ***trans*-Re_2Cl_2**, and **anthryl-Re** were prepared as previously described.[3] DMF was distilled with 20% of the solvent volume forecut, and 20% of the solvent volume left in the distillation flask to ensure high purity. DMF was freshly distilled and stored in a flame-dried round bottom flask under argon before being discarded biweekly. Triethylamine (TEA) was freshly distilled prior to use. All other chemicals were reagent or ACS grade, purchased from commercial vendors, and used without further purification. ^1H and ^{13}C NMR spectra were obtained using a Bruker Advance DRX-500 spectrometer operating at 500 MHz (^1H) or 126 MHz (^{13}C). Spectra were calibrated to residual protonated solvent peaks; chemical shifts are reported in ppm.

Photocatalysis Equipment and Methods. A 150 W Sciencetech SF-150C Small Collimated Beam Solar Simulator equipped with an AM 1.5 filter was used as the light source for photocatalytic experiments. Samples were placed ~10 cm from the source; the distance at which 1 sun intensity (100 mW/cm^2) was verified with a power meter before each measurement. Headspace analysis was performed using a gas tight syringe with a stopcock and an Agilent 7890B Gas Chromatograph (GC) equipped with an Agilent Porapak Q 80-100 mesh (6 ft x 1/8 in x 2.0 mm) Ultimetal column. Quantification of CO and CH_4 was determined using a methanizer coupled to an FID detector, while H_2 was quantified using a TCD detector. All calibrations were done using standards purchased from BuyCalGas.com. Formate analysis was done according to a previously reported procedure.[4]

Photophysical Measurement Equipment and Methods. Luminescence spectra were obtained with a PTI Quanta Master spectrofluorimeter equipped with single grating monochromators and a PMT detector. Spectra were not corrected for PMT wavelength response. Transient absorption spectra and excited state lifetimes were obtained using an Applied Photophysics LKS 60 optical system with an OPOTek OPO (< 4 ns pulses) pumped by a Quantel Brilliant Laser equipped with doubling and tripling crystals. Excitation of the chromophores was typically at 420 nm using samples having an optical density of about 0.5. Samples (4 mL volume) containing the Re complex were degassed by nitrogen bubbling for 20 min immediately prior to data acquisition.

Photocatalysis Procedure. To a 17 mL vial was added BIH (0.05 g, 0.24 mmol), DMF (1.8 mL), catalyst (as a 0.2 mL DMF stock solution). The solution was bubbled vigorously with CO_2 for at least 15 minutes until the solution volume reached 1.9 mL. Then, 0.1 mL of CO_2 degassed TEA was added, the tube was sealed with a rubber septum, and irradiated with a solar simulator for the indicated time. During the photolysis, headspace analysis was performed at 20, 40, 60, 120, and 240 minute time points. A 300 µL headspace sample was taken with a VICI valve syringe. The gas in the syringe was compressed to 250 µL and the tip of the syringe was submerged in a solution of diethyl ether before the valve was opened to equalize the internal pressure to atmospheric pressure prior to injecting the contents of the syringe into the GC. The entire 250 µL sample was then injected onto the GC. All experiments are average values over at least 2 reactions.

Turnover number (TON) values were calculated by dividing moles of product (carbon monoxide) by moles of catalyst in solution. Reported turnover frequency (TOF) values were determined from the fastest 20 minute time period of photocatalysis within the first 40 minutes as an estimate of the initial rate prior to significant catalyst deactivation and to account for induction periods (i.e. The TON for an initial 20 minute segment was divided by 0.33 h to obtain the reported TOF (h^{-1})).

Quantum Yield Measurements. Measurements were conducted similarly to a method previously described.[5] The number of moles of CO produced was monitored over time in 20 minute increments for the first hour and then hourly after this time period. The segment of time producing the most CO per hour was used in the calculations for quantum yield to give the maximum quantum yield observed (1 hour time point in these cases). The photon flux in the reaction was calculated by measuring the incident power density with a power meter (Coherent Field Mate with a Coherent PowerMax PM10 detector). The solar simulator spectrum was cut off with a 700 nm cutoff filter since the catalysts do not absorb light beyond 700 nm. Through this method the power density was estimated to be 57.3 mW/cm^2. The illuminated reaction area was measured to be 1.69 cm^2 which gives 96.9 mW or 9.69 x 10^{-2} J/s to the sample. The photon wavelength was taken as centered at 400 nm since each of the catalysts show a low energy transition shoulder in the UV-Vis absorption spectrum at 400 nm for an energy of 4.97 x 10^{-19} J. This gives 1.95 x 10^{17} photon per second in the reaction, which was used to calculate the quantum yield over the most productive CO generating time frame via the equation:

$$\phi_{CO} = [(\text{number of CO molecules x 2})/(\text{number of incident photons})] \text{ x } 100\%$$

$$\text{Anthracene} + e^- \leftrightharpoons (\text{Anthracene})^- \qquad E_{(AN/AN-)} = -2.25 \text{ V } vs \text{ Fc}^{+/0} \qquad (1a)$$

$$^3(\text{Anthracene}) \rightarrow \text{Anthracene} \qquad E_g^{opt} \sim 1.8 \text{ eV} \qquad (1b)$$

$$\text{BIH} \leftrightharpoons \text{BIH}^+ + e^- \qquad E_{(BIH+/BIH)} = -0.24 \text{ V } vs \text{ Fc}^{+/0} \qquad (1c)^6$$

Table S1. Photophysical properties of Re complexes in dichloromethane solution.

Complex	λ^{abs}_{max}, nm (log ε)	λ^{em}_{max}, nm		$h\overline{\omega}, cm^{-1}$	τ₀, (N_2)		TA max, nm (rel. intensity)
		λ_1	λ_2	λ_2	λ_1, ns	λ_2, μs	
anthryl-Re	252 (4.80) 296 (4.15) 366 (3.98)	570	688 764	1440	420	6 23	430 (1)
cis-Re_2Cl_2	258 (4.85) 296 (4.42) 380 (4.12)	592	700 776	1400	210	15 65	440 (1) 520 (1)
trans-Re_2Cl_2	258 (4.70) 296 (4.27) 376 (3.95)	598	698 772	1370	200	15 90	440 (1) 490 (0.95)
[(dphbpy)Re(CO)$_3$Cl]^7	384	630		---	56	---	---
Anthracene^8	340 355 375	375	670	---	6	3300	410, 440

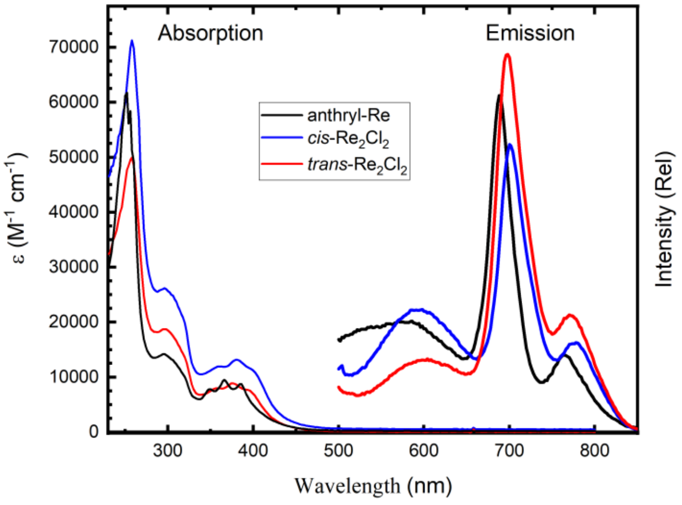


Figure S1. Absorption and luminescence spectra of anthracene containing rhenium complexes (***cis*-Re_2Cl_2**, ***trans*-Re_2Cl_2**, and **anthryl-Re**) in deoxygenated CH_2Cl_2 at room temperature.

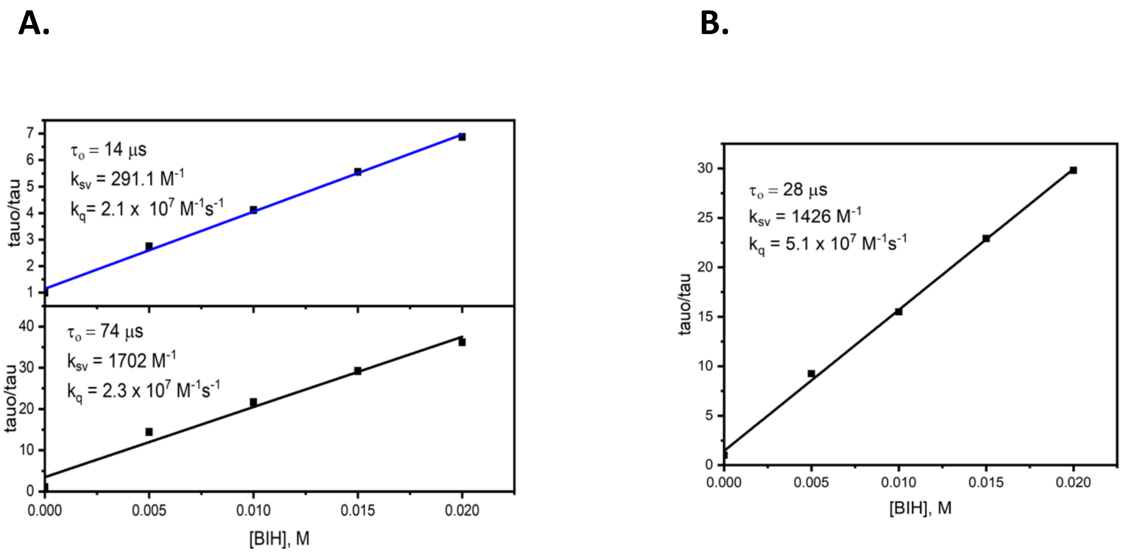


Figure S2. Stern-Volmer quenching plots of tau(0) / tau versus the concentration of BIH in DMF solution for (A) **anthryl-Re** (kq = 2.2 x 10^7 $M^{-1}s^{-1}$, average of quenching of both emission lifetime components) and (B) ***trans*-Re_2Cl_2** (k_q = 5.1 x 10^7 $M^{-1}s^{-1}$).

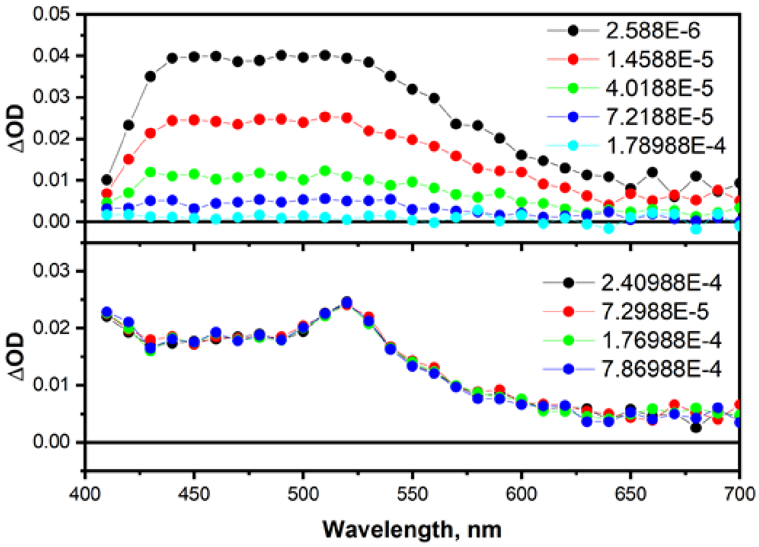


Figure S3. Transient absorption spectra at specified times after pulsed laser excitation (λ_{ex} = 355 nm) of ***trans*-Re_2Cl_2** in DMF under Ar purge (top) and ***trans*-Re_2Cl_2** with BIH (0.01 M) under CO_2 purge (bottom). No reaction of the one-electron reduced ***trans*-Re_2Cl_2** complex with CO_2 is evident in the first 800 μs following excitation.

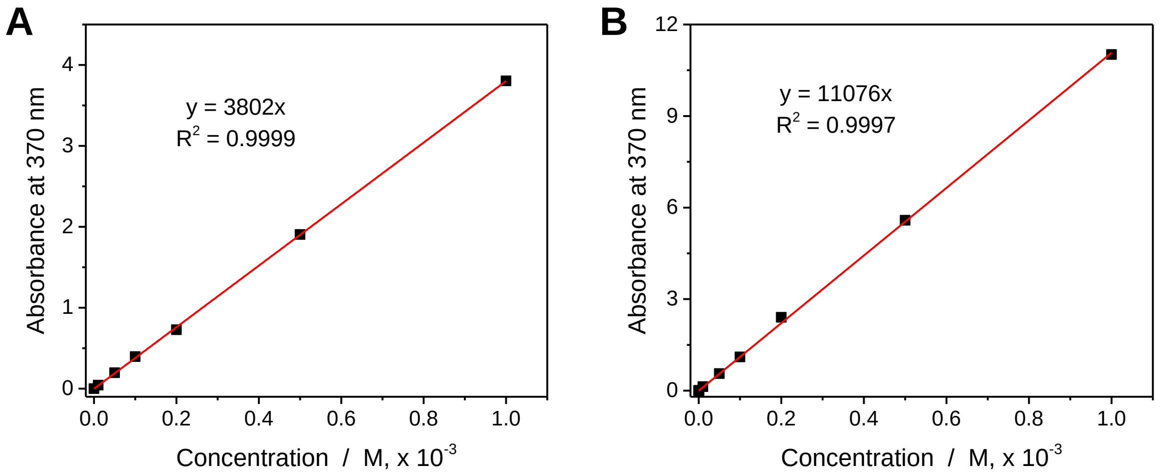


Figure S4. Plots of absorbance at 370 nm as a function of concentration in DMF solution for A) Re(bpy)(CO)$_3$Cl and B) **anthryl-Re**.

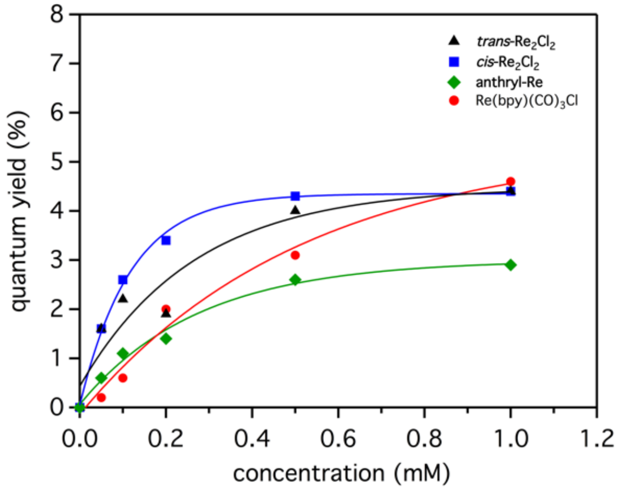
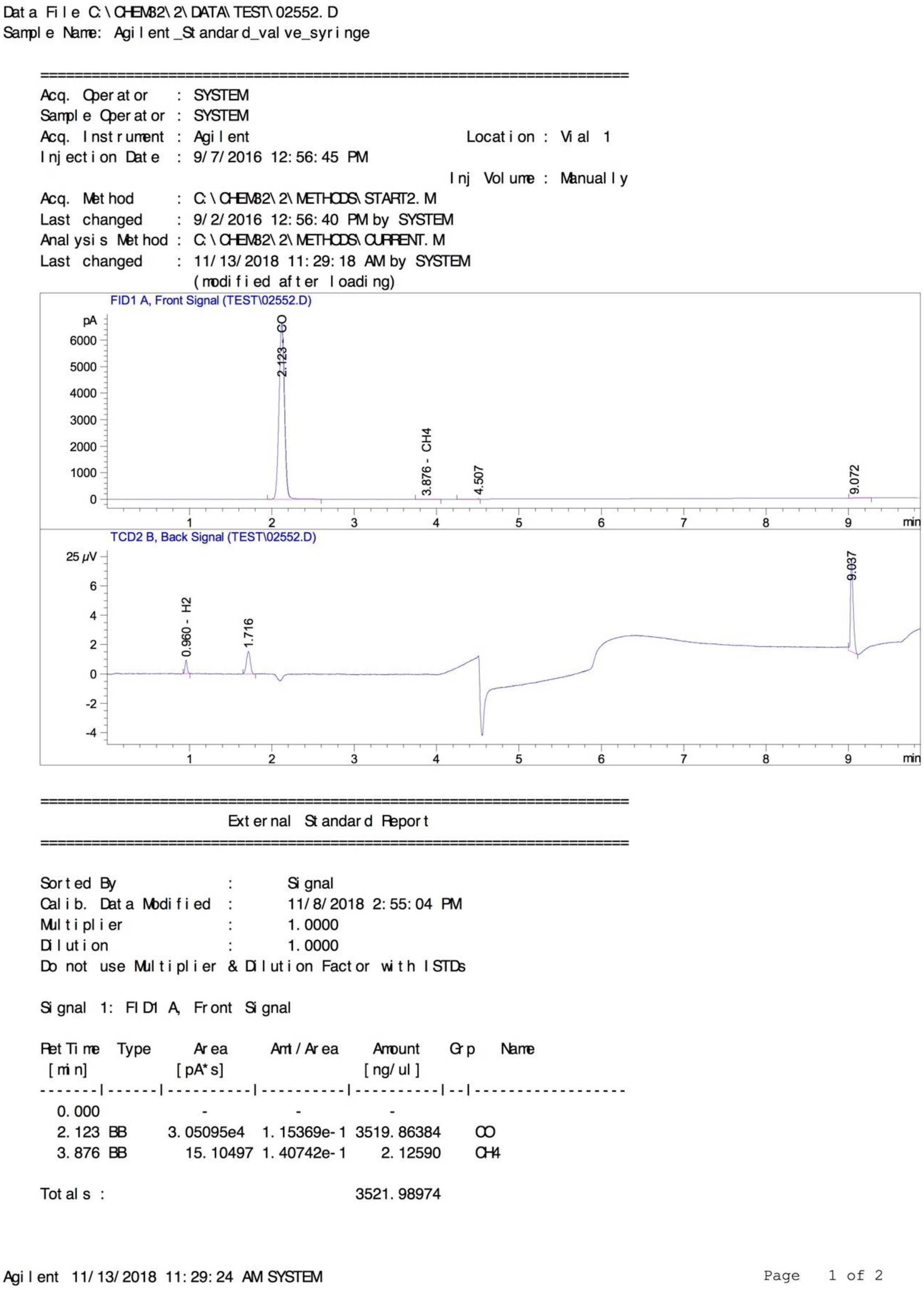


Figure S5. Plot of quantum yield versus catalyst concentration. *Conditions*: DMF containing 5% triethylamine, 10 mM BIH; irradiated with a solar simulator (AM 1.5 filter, 100 mW/cm^2).

Table S2. Photocatalytic reaction TON, TOF, and quantum yield values.

Complex	**concentration (mM)**	**max. TON (CO)**	**max. TOF (h^{-1})**	**max. ϕ (%)**
anthryl-Re	0.05	34	43	0.6
anthryl-Re	0.1	38	43	1.1
anthryl-Re	0.2	20	30	1.4
anthryl-Re	0.5	16	18	2.6
anthryl-Re	1.0	12	12	2.9
cis-Re_2Cl_2	0.05	95	128	1.6
cis-Re_2Cl_2	0.1	78	105	2.6
cis-Re_2Cl_2	0.2	52	71	3.4
cis-Re_2Cl_2	0.5	31	37	4.3
cis-Re_2Cl_2	1.0	17	20	4.4
trans-Re_2Cl_2	0.000001	40000	2500	---
trans-Re_2Cl_2	0.05	105	158	1.6
trans-Re_2Cl_2	0.1	63	92	2.2
trans-Re_2Cl_2	0.2	28	38	1.9
trans-Re_2Cl_2	0.5	27	30	4.0
trans-Re_2Cl_2	1.0	16	15	4.4
Re(bpy)$(CO)_3$Cl	0.05	16	17	0.2
Re(bpy)$(CO)_3$Cl	0.1	21	23	0.6
Re(bpy)$(CO)_3$Cl	0.2	43	30	2.0
Re(bpy)$(CO)_3$Cl	0.5	24	21	3.1
Re(bpy)$(CO)_3$Cl	1.0	19	16	4.6



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Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A, Front Signal

RetTime  Type    Area       Amt/Area     Amount    Grp   Name
 [min]         [pA*s]                   [ng/ul]
-------|------|----------|----------|----------|--|------------------
  0.000          -           -          -
  2.123 BB   3.05095e4  1.15369e-1 3519.86384     CO
  3.876 BB    15.10497  1.40742e-1    2.12590     CH4

Totals :                             3521.98974

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Figure S6. Example GC trace for a photoreaction with ***trans*-Re_2Cl_2** at 0.1 mM concentration. The FID trace (top) shows CO at 2.12 minutes retention time and only trace other products (CH_4 RT = 3.88 min, back flush at 4.5 minutes, followed by a column bake). The TCD trace shows only trace reactivity (H_2 at 0.96 min and O_2/N_2 at 1.72 min) and is a zoomed in y-axis range with the tallest peak at the top of the spectrum. (Continued on next page).

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    -------|------|----------|----------|----------|--|------------------
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      0.960 BB       1.66333 2.65015e-4 4.40806e-4     H2
      1.610              -          -          -       AIR

    Totals :                             4.40806e-4


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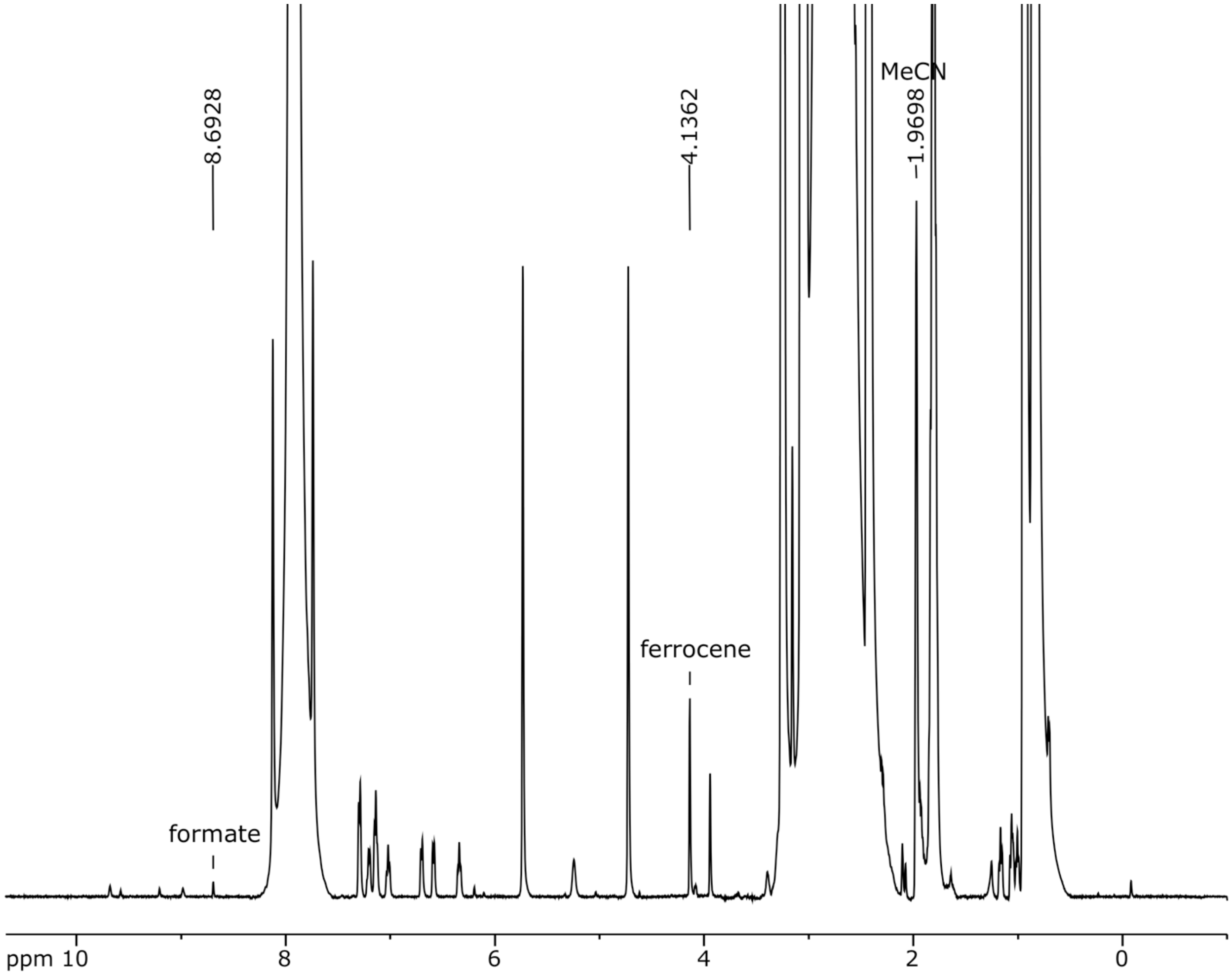

Figure S7. Example ^{1}H NMR formate analysis with ferrocene as an internal standard at 4.18 ppm and formate as an analyte at 8.63 ppm. This example is for a photoreaction with ***trans*-Re$_2$Cl$_2$** at 0.1 mM concentration. The ratio of the peaks is 20:1, which is 7 TON of formate for this catalytic reaction.

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