Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Elucidating the Origins of Enhanced CO_2 Reduction in Manganese Electrocatalysts Bearing Pendant Hydrogen-Bond Donors

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Experimental Methods:

General Procedures. All electrochemical experiments and bulk electrolyses were performed under air free conditions, unless noted otherwise. Manganese complexes were handled under a red light at all times except during weighing. For all electrochemical experiments, the electrolyte was bubbled with the desired gas (argon or CO_2) for 15 minutes prior to taking a background scan to ensure a featureless background from 0 to -2.2 V vs Ag/AgCl. After adding the desired complex, the electrolyte was bubbled for 5 more minutes before collecting experimental data. Complexes were loaded at a concentration of 1 mM for both voltammetry and bulk electrolyses. The total volume of electrolyte used for these experiments was 10 mL for voltammetry and 20 mL for bulk electrolysis. Bulk electrolytes were operated for ~4 hours, and the headspace was analyzed by GC approximately every 20 minutes. Voltammograms were referenced to ferrocene/ferrocenium at the end of the experiment and then later converted to vs. SCE by adding 380 mV. Elemental microanalyses were performed at Robertson Microlit Laboratories (Ledgewood, NJ).

Materials. Tetrabutylammonium perchlorate (TBAP) was synthesized by the dropwise addition of concentrated perchloric acid into an equimolar solution of tetrabutylammonium bromide in water. The precipitated TBAP was collected, recrystallized three times from ethyl acetate/hexanes, and dried under reduced pressure (<0.1 Torr) for several hours over P_2O_5. Manganese pentacarbonyl bromide (Strem) and 2,2'-bipyridine (Sigma-Aldrich) were used as received. Acetonitrile was degassed and passed through two columns of activated alumina prior to use. Electrolyte solutions were prepared by dissolving TBAP in acetonitrile and passing the solution through a column of activated alumina in a fritted Schlenk filter directly into a Schlenk flask. The electrolyte was stored under an inert atmosphere and degassed immediately before performing any experiments. A 3 mm glassy carbon disk working electrode and a Ag/AgCl reference electrode (BASi Models MF-2012 and MF-2052, respectively) were used in all electrochemical experiments. A platinum mesh (~1 cm^2) connected to a platinum wire was used as the counter electrode in all electrochemical experiments. A 15 mL three-neck round-bottom flask was used as the electrochemical cell for voltammetry and a 25 mL three-neck round-bottom flask was used for bulk electrolysis. The working and reference electrodes were secured using "mini" No. 7 Ace-threaded adaptors from Ace-glass. The counter electrode was threaded through a septum, which was the fitted onto one neck of the cell.

2-chloro-5-iodopyridine (97%, Sigma-Aldrich), 2-chloro-4-iodopyridine (Apollo Scientific), anhydrous DMF (99.8%, Sigma-Aldrich), anhydrous DME (99.5%, Sigma-Aldrich), 2-methoxyphenylboronic acid (97%, Frontier Scientific), tetrakis(triphenylphosphine)palladium(0) (99.9+%, Strem), triphenylphoshphine (99%, Sigma-Aldrich) and manganese pentacarbonyl bromide (min. 98%, Strem) were all used as received. THF, DCM, Et_2O, and MeCN were all passed through two columns of activated alumina prior to use.

General procedure for the Suzuki cross-coupling of pyridyl iodides with 2-methoxyphenylboronic acid. A 500 mL round-bottom Schlenk flask was charged 2-chloro-4-iodopyridine (1.0 equiv.), 2-methoxyphenylboronic acid (1.0 equiv.), Na_2CO_3 (3.0 equiv.), and a PTFE coated stir bar. The flask was brought into a glove box and charge with $Pd(PPh_3)_4$ (5 mol%) and sealed with a septum. The

flask was brought out of the glove box and subjected to three cycles of vacuum/N_2 backfill, leaving the flask under a positive N_2 pressure on the last cycle. Degassed, anhydrous DME (0.14 M) was added to the reaction via a syringe through the septum followed by degassed Millipore H_2O (One quarter the volume of DME) by the same method. The reaction was heated to reflux in a preset oil bath. After 12 hours of reflux, a small sample of the reaction was analyzed by mass spectrometry to ensure consumption of 2-chloro-4-iodopyridine and formation of product. The reaction was concentrated under reduced pressure, dissolved in ethyl acetate, and washed with water three times in a separatory funnel in order to remove inorganic salts. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude mixture was chromatographed on silica gel using a gradient of 10-30% ethyl acetate in hexanes.

General procedure for the Stille cross-coupling of pyridyl chlorides with 2-(tributylstannyl)pyridine. The synthetic procedure was modified from the literature. Two dry 100 mL pear shaped flasks were charged with 2-chloro-4-(2-methoxyphenyl)pyridine and 2-(tributylstannyl)pyridine, respectively. Each flask was placed under vacuum for 10 minutes and backfilled with N_2. Each flask was charged with anhydrous DMF and further degassed by evacuated/backfilled with N_2 three times. A 500 mL round-bottom Schlenk flask was charged with PPh_3, brought into the glove box, charged with $Pd(PPh_3)_4$, fitted with a septum, and removed from the glove box. A dry 25 mL Schlenk flask was charged with CuI and a PTFE coated stirbar. The solution of 2-chloro-4-(2-methoxyphenyl)pyridine was cannula transferred to the Schlenk flask containing the CuI via syringe. The resulting two solutions were allowed to stir at room temperature for 20 minutes before the CuI/2-(tributylstannyl)pyridine solution was transferred to the 2-chloro-4-(2-methoxyphenyl)pyridine solution. The reaction was then heated to 125 ^oC under argon. After 16 hours, a small quantity of the reaction was analyzed by mass-spec. Disappearance of the 2-chloro-4-(2-methoxyphenyl)pyridine indicated complete conversion, however appearance of desired product could not be determined because it has the same mass as PPh_3. The reaction was quenched by stirring with NH_4OH/THF until two individual layers had formed (~12 hours). The layers were separated and the aqueous layer was extracted with THF three times. The organic extracts were dried over Na_2SO_4, filtered, and concentrated. The crude was chromatographed on silica gel using a gradient of 10-30% ethyl acetate and 1% trimethylamine in hexanes.

General procedure for the ligation of substituted 2,2'-bipyridine ligands to $BrMn(CO)_5$. A 100 mL Schlenk flask was equipped with a stir bar and dried in an over at 100 ^oC for no less than 1 hour. The flask was removed from the oven, equipped with a septum, and allowed to cool to room temperature under vacuum. The flask was moved to the dark room and charged with substituted 2,2'-bipyridine, $BrMn(CO)_5$, and 50 mL Et_2O. The resulting solution was bubble degassed for 15 minutes with argon and afterward was left under a positive atmosphere of argon. The flask was then placed in an oil that had been preset for 35 ^oC and allowed to reflux for approximately 2 hours. Over the course of the reaction the solution became increasingly cloudy as product precipitates out of solution. Once the reaction is considered done, it is removed from the oil bath and allowed to cool to room temperature. The reaction mixture is then filtered through a piece of filter paper. The residue is washed three times with Et_2O to remove any unreacted ligand or $BrMn(CO)_5$. The powder is allowed to air dry briefly until it can

be easily scraped off the filter paper and collected into an amber vial. The powder is then dried under vacuum to remove Et_2O before spectroscopic characterization and electrochemical experiments. Yield: 72%; ^{1}H NMR (DMSO, 500 MHz, 303 K): δ = 9.19, 8.65, 8.23, 7.72 ppm; 13C NMR (DMSO, 500 MHz, 303 K): δ = 154.98, 153.32, 139.14, 126.71, 123.12; ATR-FTIR: 2019, 1940, and 1945 cm^{-1}.

Instrumentation. Electrochemical measurements were performed on a Model CHI 760D electrochemical workstation (CH Instruments, Austin, TX). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE spectrometer (500 MHz for ^{1}H nuclei and 125 MHz for ^{13}C nuclei). Chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane and are referenced to the solvent residual peak. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Model 730 FT-IR spectrometer for gas samples and Nicolet Model 6700 FT-IR spectrometer equipped with a single-reflection diamond ATR attachment for solid samples. Ultraviolet-visible (UV-vis) spectra were recorded on a Hewlett-Packard Model 8453 spectrophotometer. X-ray diffraction (XRD) data were collected with a Bruker Photon 100 CMOS detector using Cu Kα radiation (**1**) or a Bruker Apex II CCD detector using Mo Kα radiation (**2**). CO production was analyzed using a Model HP 5980 GC system with a TCD analyzer and analog integrator. An Agilent Model CP7538 molecular sieve column was used to separate CO from CO_2 at a column head pressure of 12 psi, an oven temperature of 70 ^{o}C, an injection temperature of 200 ^{o}C, and a detector temperature of 250 ^{o}C.

Preparation of 6L-OH. *6'-(2-Hydroxyphenyl)-2,2'-bipyridine.* Yield: 71%; 1 H NMR (DMSO, 500 MHz, 303 K): δ = 13.99 (s, 1H), 8.78 (d, 1H), 8.30 (dd, 2H), 8.17 (q, 2H), 8.07 (m, 2H), 7.54 66 (m, 1H), 7.35 (t, 1H), 6.97 (m, 2H); 13C NMR (DMSO, 500 MHz, 303 K): δ = 158.73, 156.47, 153.84, 152.69, 149.83, 139.42, 137.76, 131.42, 127.52, 124.60, 120.52, 120.34, 119.36, 119.00, 117.75.

Preparation of 6L-OMe. *6'-(2-Methoxyphenyl)-2,2'-bipyridine.* Yield: 65%; 1 H NMR (DMSO, 500 MHz, 303 K): δ = 8.70 (d, 1H), 8.48 (d, 1H), 8.31 (dd, 1H), 7.94 (m, 4H), 7.45 (m, 2H), 7.18 (d, 1H), 7.12 (td, 1H), 3.08 (s, 3H); 13C NMR (DMSO, 500 MHz, 303 K): δ = 156.93, 155.44, 154.88, 154.57, 149.18, 137.22, 137.01, 130.76, 130.20, 128.16, 124.99, 124.06, 120.69, 120.49, 118.47, 111.99, 55.62.

Preparation of 4L-OH. 4'-(2-Hydroxyphenyl)-2,2'-bipyridine (4L−OH). Yield: 49%; 1 H NMR (DMSO, 500 MHz, 303 K): δ = 9.86 (s, 1H), 8.69 (d, 1H), 8.64 (s, 1H), 8.43 (d, 1H), 7.96 (td, 1H), 7.65 (dd, 1H), 7.45 (m, 2H), 7.01 (d, 1H), 6.96 (t, 1H); 13C NMR (DMSO, 500 MHz, 303 93 K): δ = 155.40, 155.01, 154.74, 149.20, 149.05, 147.04, 137.21, 130.11, 130.00, 124.81, 124.04, 120.48, 120.43, 119.69, 116.36.

Preparation of 4L-OMe. 4'-(2-Methoxyphenyl)-2,2'-bipyridine. Yield: 72%; 1 H NMR (DMSO, 500 MHz, 303 K): δ = 8.70 (m, 2H), 8.48(m, 2H), 7.97 (td, 1H), 7.58 (m, 1H), 7.46 (m, 3H), 7.16 (m, 3H) 3.82 (s, 3H); 13C NMR (DMSO, 500 MHz, 303 K): δ = 156.26, 155.27, 155.12, 149.26, 149.06, 146.78, 137.25, 130.43, 130.14, 127.01, 124.39, 124.13, 121.01, 120.60, 120.53, 112.02, 55.67.

Preparation of 4L-OH. 4'-(2-Hydroxyphenyl)-2,2'-bipyridine. Yield: 49%; 1 H NMR (DMSO, 500 MHz, 303 K): δ = 9.86 (s, 1H), 8.69 (d, 1H), 8.64 (s, 1H), 8.43 (d, 1H), 7.96 (td, 1H), 7.65 (dd, 1H), 7.45 (m, 2H), 7.01 (d, 1H), 6.96 (t, 1H); 13C NMR (DMSO, 500 MHz, 303 93 K): δ = 155.40, 155.01, 154.74, 149.20, 149.05, 147.04, 137.21, 130.11, 130.00, 124.81, 124.04, 120.48, 120.43, 119.69, 116.36.

Preparation of 5L-OMe. 5'-(2-Methoxyphenyl)-2,2'-bipyridine. Yield: 52%; 1 H NMR (DMSO, 500 MHz, 303 K): δ = 8.81 (d, 1H), 8.70 (d, 1H), 8.43 (dd, 2H), 8.06 (d, 1H), 7.96 (s, 1H), 7.45 (m, 3H), 7.18 (d, 1H), 7.09 (td, 1H), 3.82 (s, 3H); 13C NMR (DMSO, 500 MHz, 303 K): δ = 156.34, 155.07, 153.48, 149.29, 137.57, 137.24, 133.97, 130.29, 129.84, 125.95, 124.05, 121.00, 120.32, 119.73, 111.88, 55.60.

Preparation of 5L-OH. 5'-(2-Hydroxyphenyl)-2,2'-bipyridine. Yield: 40%; 1 H NMR (DMSO, 500 MHz, 303 K): δ = 9.85 (s, 1H), 8.87 (d, 1H), 8.70 (d, 1H), 8.43 (d, 2H), 8.12 (dd, 1H), 7.96 (td, 1H), 7.46 (t, 1H), 7.41 (d, 1H), 7.25 (dd, 1H), 7.01 (d,1H), 6.94 (t, 1H); 13C NMR (DMSO, 500 MHz, 303 K): δ = 155.70, 155.18, 153.68, 149.79, 149.67, 137.80, 137.74, 134.90, 130.66, 130.00, 124.49, 124.47, 120,80, 120.22, 116.67

Preparation of 6-OH. An aliquot of $MnBr(CO)_5$ (49.8 mg, 0.181 mmol) was added to 6-(2-hydroxyphenyl)-bpy (45 mg, 0.181 mmol) that had been dissolved in 15 mL of degassed Et_2O. The resulting orange solution was heated to reflux for 2 hours under argon, then allowed to cool to room temperature before filtration. The solid was filtered and washed with cold Et_2O and dried *in vacuo* to afford 69.6 mg (82% yield) of orange product. The following were observed for the mixture of atropisomers (hydroxyphenyl adduct parallel and antiparallel to the axial plane): IR νCO (ATR, cm^{-1}): 2019 (s), 1920 (br). 1 H NMR (DMSO-d6, 500 MHz): δ 9.99−9.92 (1H, s), 9.34−9.12. (1 H, m), 8.90−8.56 (2 H, m), 8.45−8.16 (2 H, m), 7.91−7.55 (2 H, m) 7.52−7.20 (2 H, m) 7.18−6.92 (2 H, m). 13C NMR (DMSO-d6, 125 MHz): δ 224.29, 222.86, 221.42, 221.35, 217.50, 216.27, 162.79, 162.48, 157.53, 156.95, 156.47, 155.45, 155.43, 154.97, 153.34, 153.28, 139.49, 139.43, 139.36, 138.41, 131.58, 131.52, 131.43, 130.90, 130.12, 128.79, 126.85, 126.33, 124.00, 123.94, 121.98, 121.81, 119.32, 118.84, 116.79, 115.87. Anal. Found: C, 48.80; H, 2.52; N, 5.91. Calcd: C, 48.85; H, 2.59; N, 6.00

Preparation of 6-OMe. An aliquot of $MnBr(CO)_5$ (171.8 mg, 0.625 mmol) was added to 6-(2-methoxyphenyl)-bpy (164 mg, 0.625 mmol) that had been dissolved in 30 mL Et_2O. The resulting orange solution was heated to reflux for 2 hours under argon, the allowed to cool to room temperature before filtration. The solid was filtered and washed with cold Et_2O and dried *in vacuo* to afford 296 mg (98% yield) of orange product. The following were observed for the mixture of atropisomers (methoxyphenyl adduct parallel and antiparallel to the axial plane): IR νCO (ATR, cm^{-1}): 2021 (s), 1934 (s), 1882 (s). 1 H NMR (DMSO-d6, 500 MHz): δ 9.25−9.20 (1 H, m), 8.75−8.50 (2 H, m), 8.37−8.15 (2 H, m), 7.84−7.45 (3 H, m), 7.45− 7.10 (3 H, m), 3.87−3.72 (3 H, s). 13C NMR (DMSO-d6, 125 MHz): δ 224.71, 223.19, 221.92, 218.29, 216.87, 162.71, 162.52, 157.89, 157.41, 157.02, 156.13, 153.99, 153.98, 140.19, 132.60, 131.99, 131.82, 131.38, 129.26, 127.53, 124.77, 122.83, 121.54, 111.98, 57.16, 56.10. Anal. Found: C, 49.93; H, 2.81; N, 5.74. Calcd: C, 49.92; H, 2.93; N, 5.82.

Preparation of 5-OH. The same procedure used for the preparation of 6L-OH was used for the preparation of 5L-OH, except using 5-(2-hydroxyphenyl)-bpy. Yield: 56%; 1 H NMR (DMSO, 500 MHz, 303 K): δ = 9.37 (s, 1H), 9.20 (d, 1H), 8.69 (t, 2H), 8.39 (d, 1H), 7.79 (t, 1H), 7.72 (t, 1H), 7.62 (d, 1H), 7.52 (t, 1H), 7.26 (d, 1H), 7.17 (t, 1H) 3.88 (s, 3H) 13C 94 NMR (DMSO, 500 MHz, 303 K): δ = 156.19, 154.90, 153.35, 153.12, 152.65, 139.14, 138.96, 135.93, 130.97, 130.26, 126.56, 123.46, 123.12, 122.63, 121.27, 112.18, 55.67; ATR-FTIR: 2019, 1938, 1909 cm^{-1}

Preparation of 5-OMe. The same procedure used for the preparation of 6L-OMe was used for the preparation of 5L-OMe, except using 5-(2-methoxyphenyl)-bpy. Yield: 56%; 1 H NMR (DMSO, 500 MHz, 303 K): δ = 9.37 (s, 1H), 9.20 (d, 1H), 8.69 (t, 2H), 8.39 (d, 1H), 7.79 (t, 1H), 7.72 (t, 1H), 7.62 (d, 1H), 7.52 (t, 1H), 7.26 (d, 1H), 7.17 (t, 1H) 3.88 (s, 3H) 13C 94 NMR (DMSO, 500 MHz, 303 K): δ = 156.19, 154.90, 153.35, 153.12, 152.65, 139.14, 138.96, 135.93, 130.97, 130.26, 126.56, 123.46, 123.12, 122.63, 121.27, 112.18, 55.67; ATR-FTIR: 2019, 1938, 1909 cm^{-1}

Preparation of 4-OH. The same procedure used for the preparation of 6L-OH was used for the preparation of 4L-OH. Yield: 49%; 1 H NMR (DMSO, 500 MHz, 303 K): δ = 9.86 (s, 1H), 8.69 (d, 1H), 8.64 (s, 1H), 8.43 (d, 1H), 7.96 (td, 1H), 7.65 (dd, 1H), 7.45 (m, 2H), 7.01 (d, 1H), 6.96 (t, 1H); 13C NMR (DMSO, 500 MHz, 303 93 K): δ = 155.40, 155.01, 154.74, 149.20, 149.05, 147.04, 137.21, 130.11, 130.00, 124.81, 124.04, 120.48, 120.43, 119.69, 116.36

Preparation of 4-OMe. The same procedure used for the preparation of 6L-OMe was used for the preparation of 4L-OMe. Yield: 66%; 1 H NMR (DMSO, 500 MHz, 303 K): δ = 9.18 (dd, 2H), 8.75 (s, 2H), 8.22 (t, 1H), 7.90 (t, 1H), 7.73 (t, 1H), 7.63 (d, 1H), 7.53 (t, 1H), 7.25 (d, 1H), 7.16 (t, 1H), 3.88 (s, 3H); 13C NMR (DMSO, 500 MHz, 303 K): δ = 156.24, 155.04, 154.80, 153.19, 152.53, 148.40, 138.96, 131.30, 130.40, 126.72, 126.56, 124.77, 123.17, 122.95, 120.82, 111.83, 55.51; ATRFTIR: 2023, 1919 cm^{-1}

NMR and IR Characterizations of Complexes Studied

6-OMe

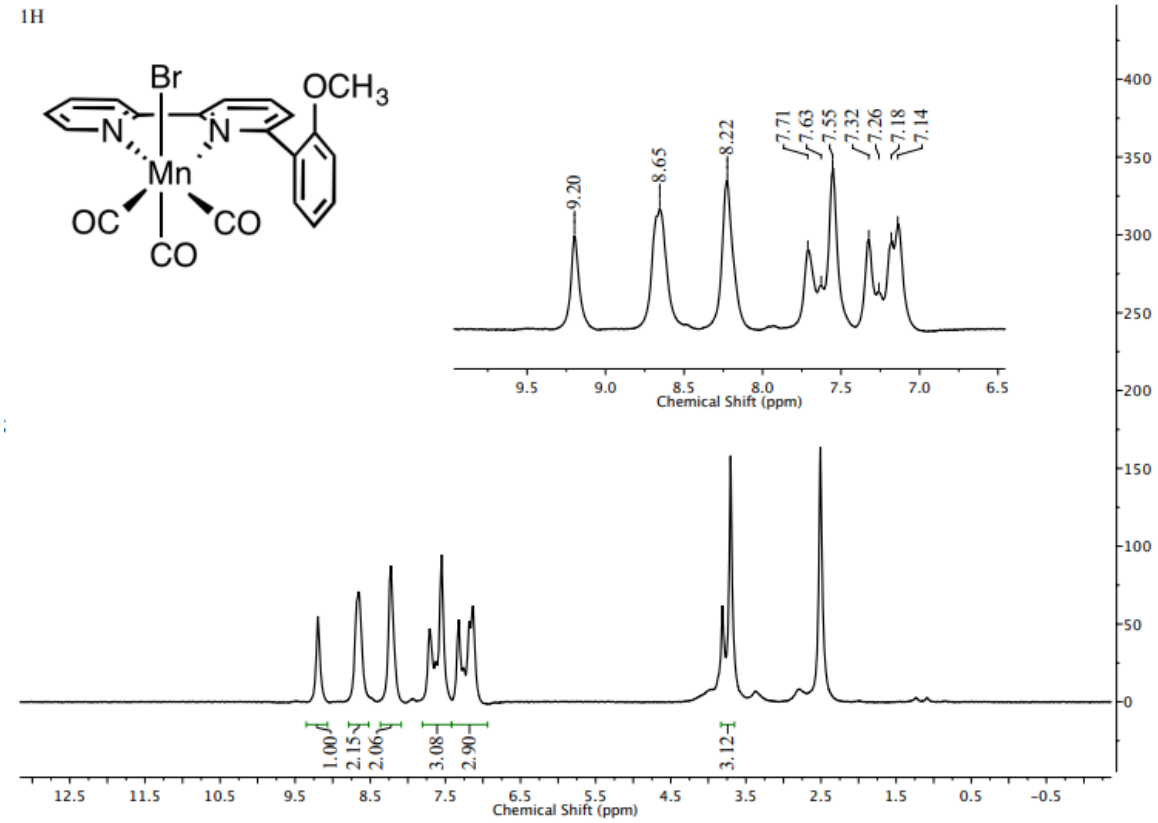


Figure S1

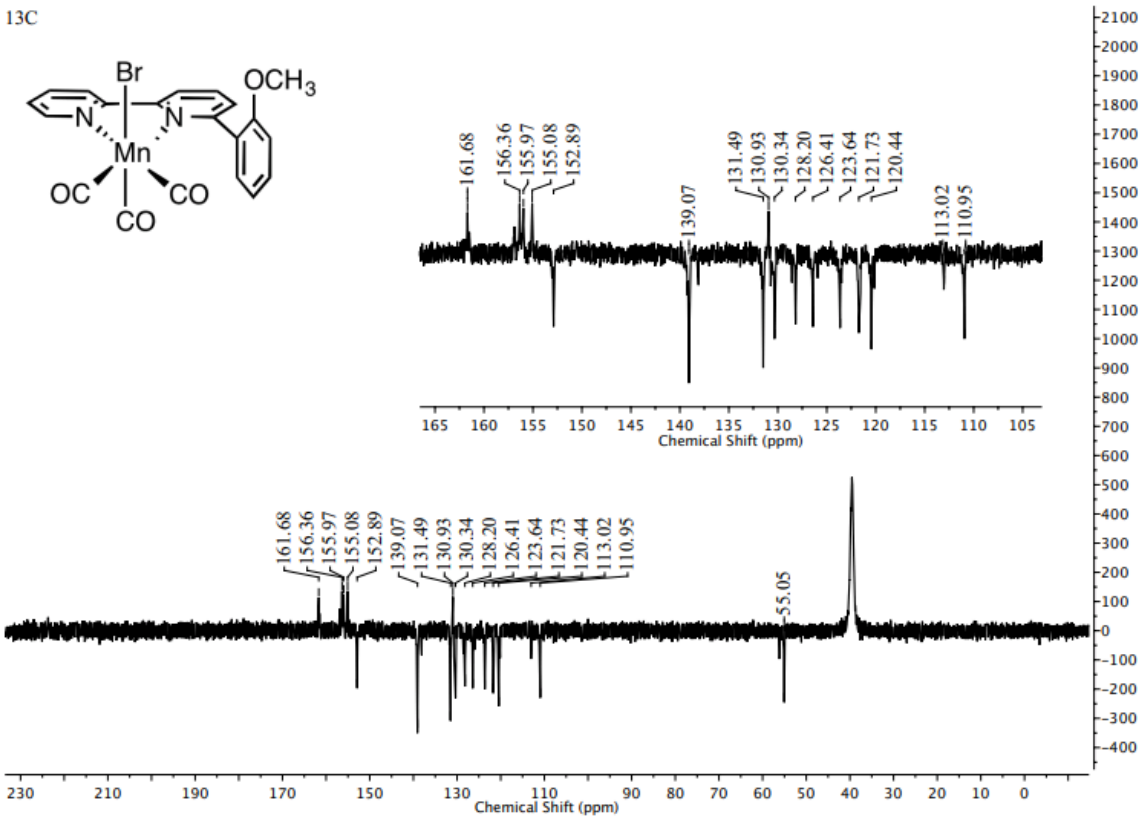


Figure S2

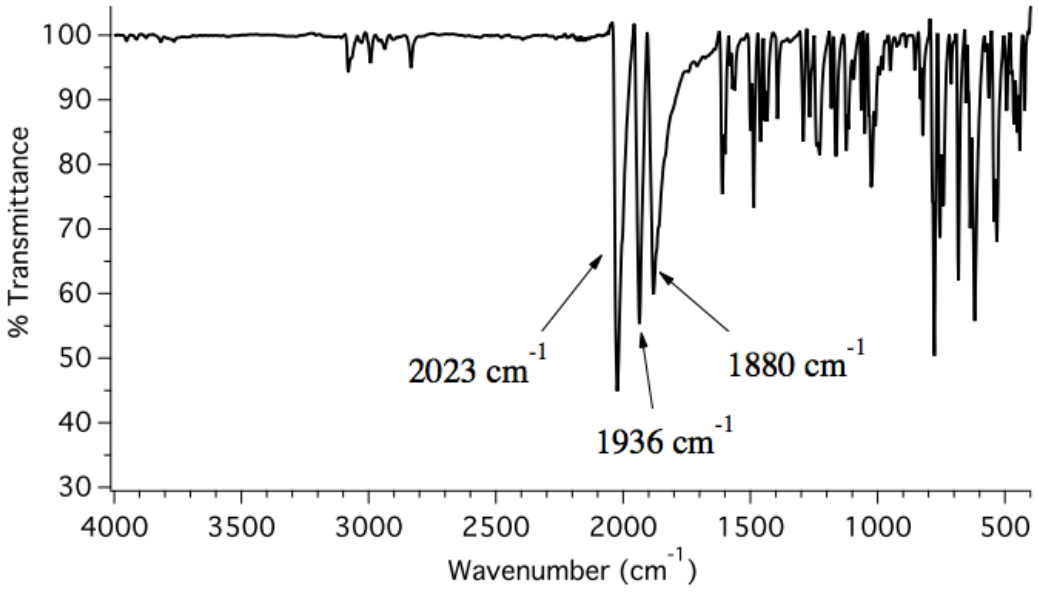


Figure S3

6-OH

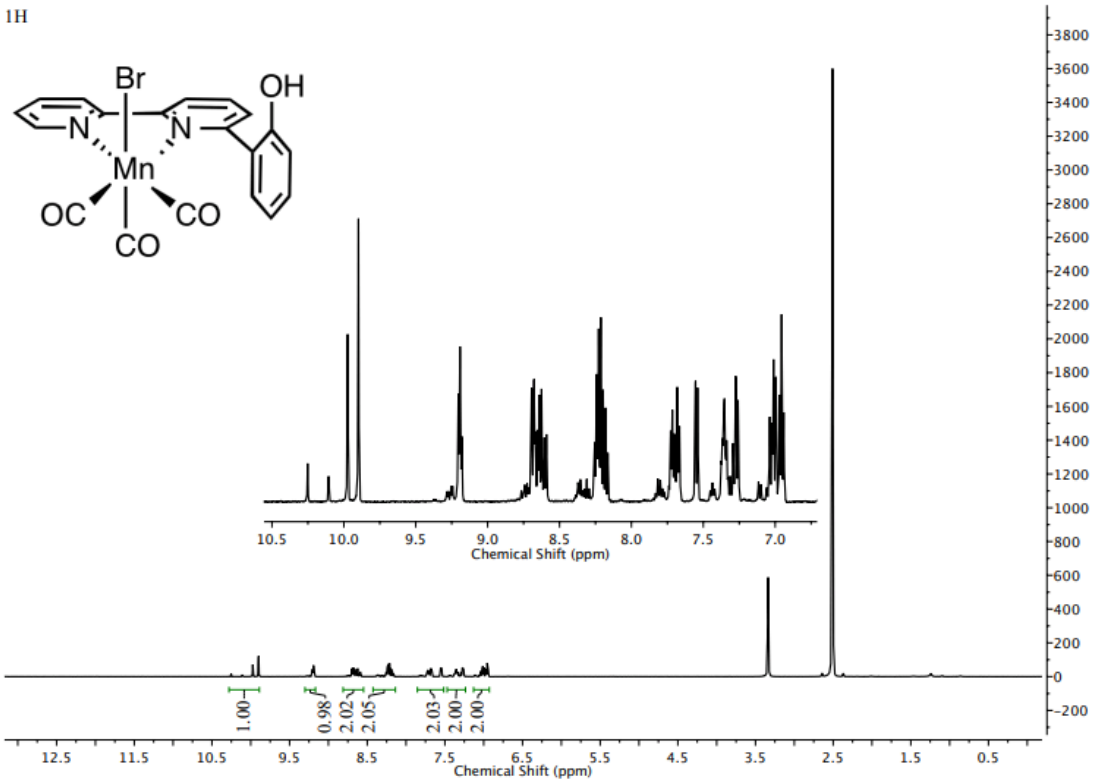
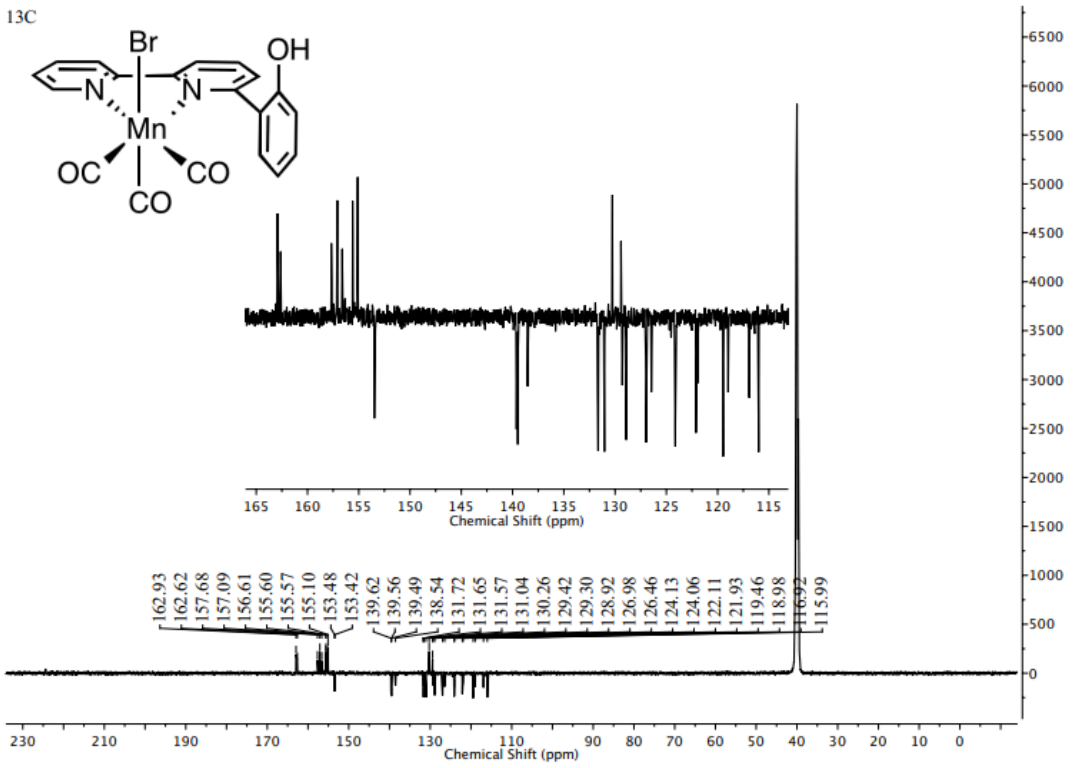


Figure S4



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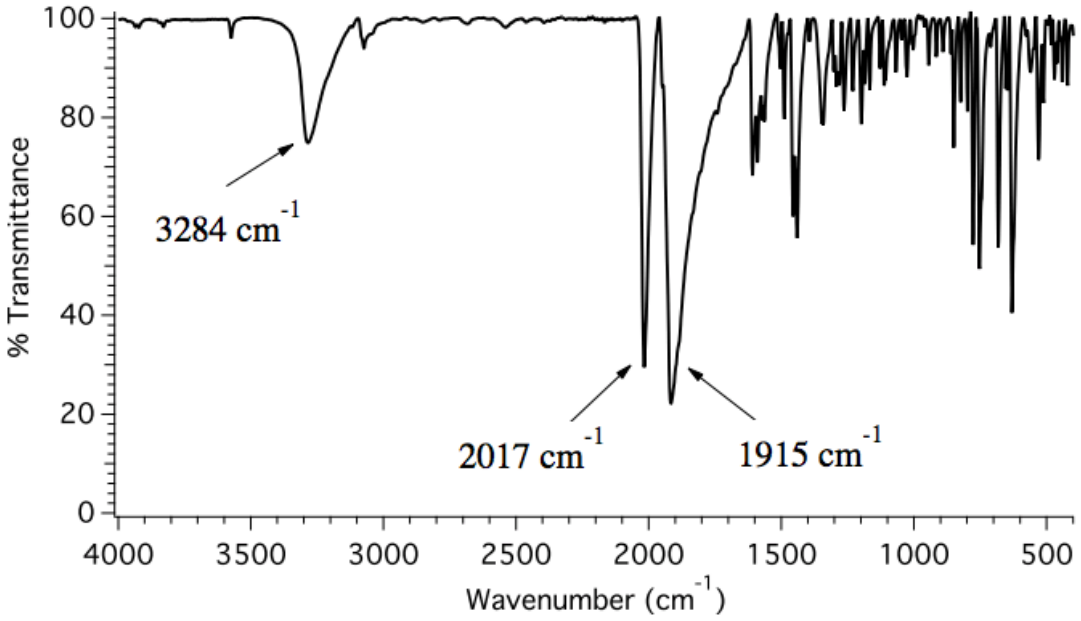
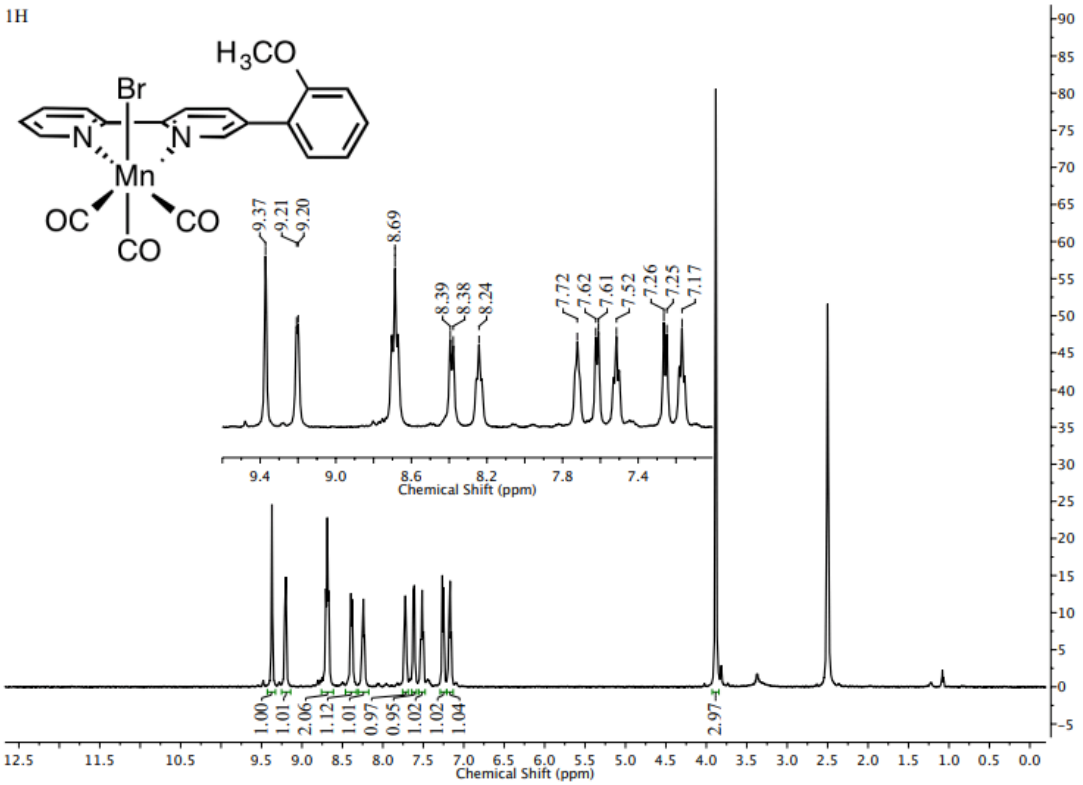


Figure S6

5-OMe



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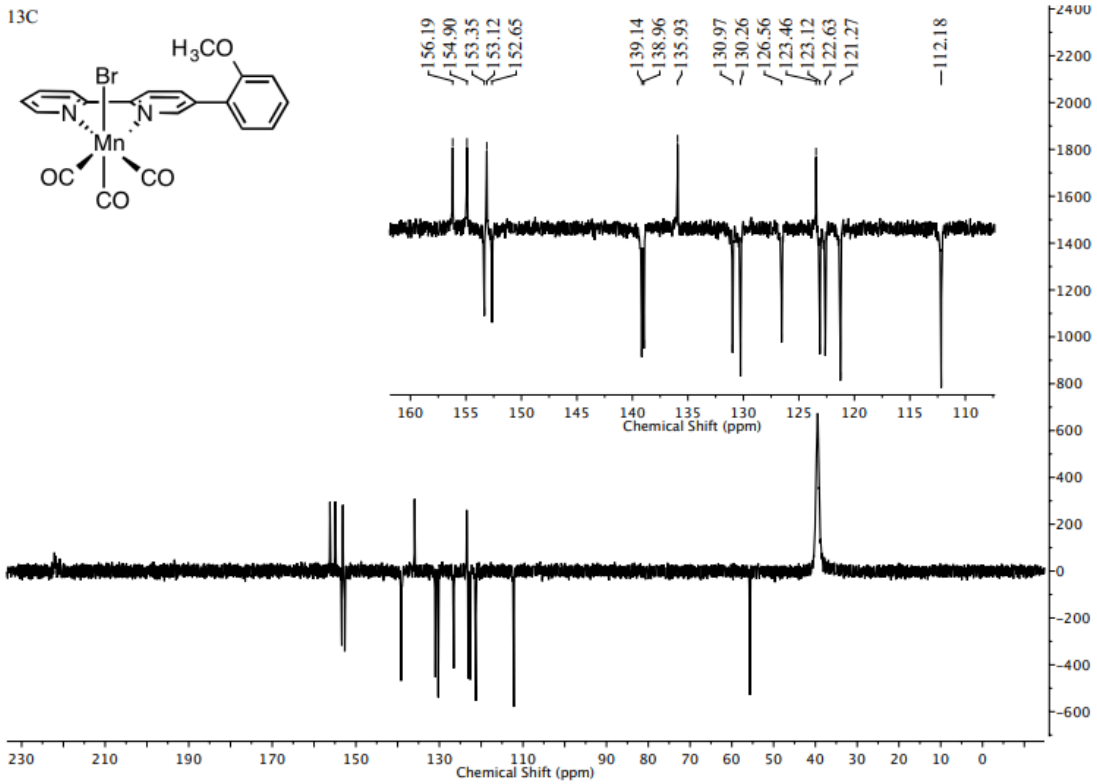


Figure S8

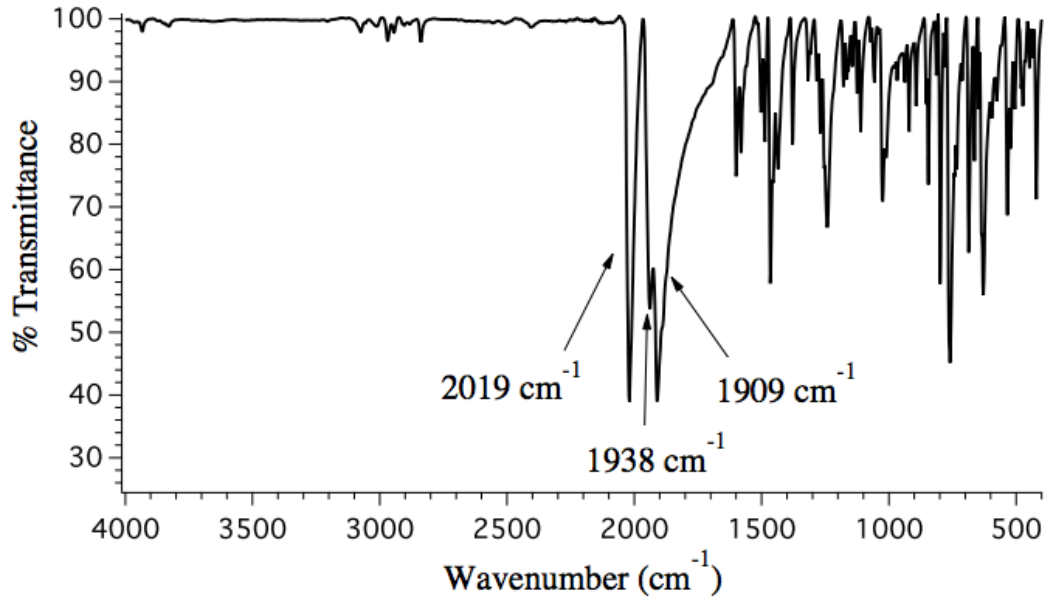


Figure S9

5-OH

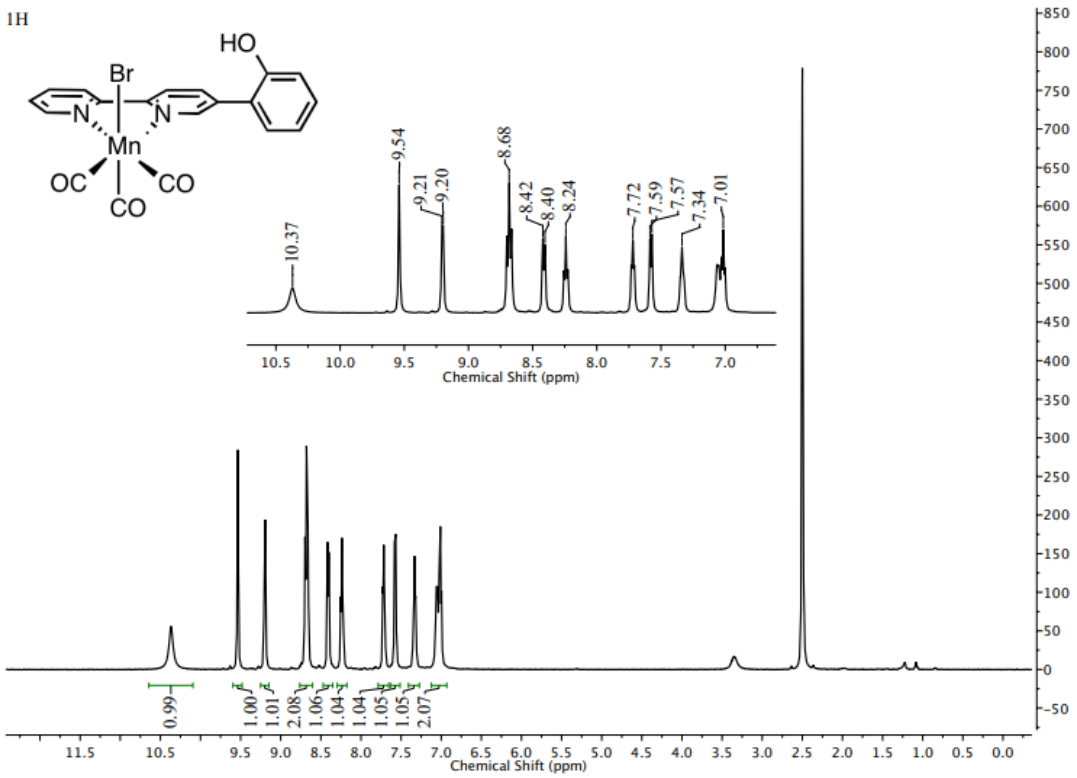


Figure S10

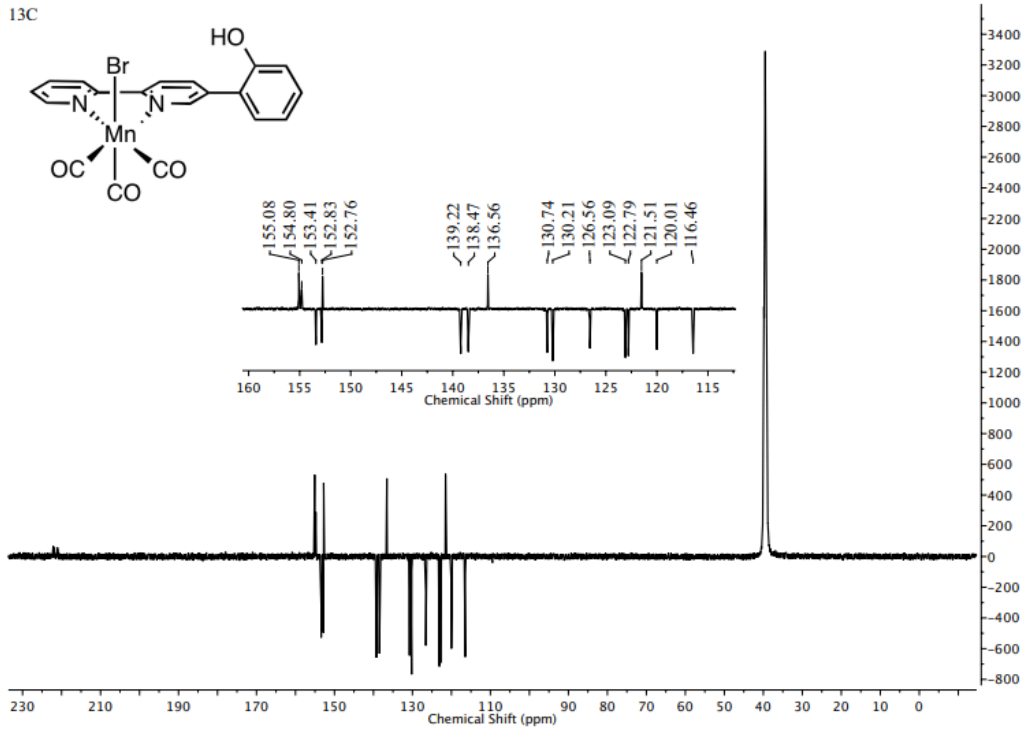


Figure S11

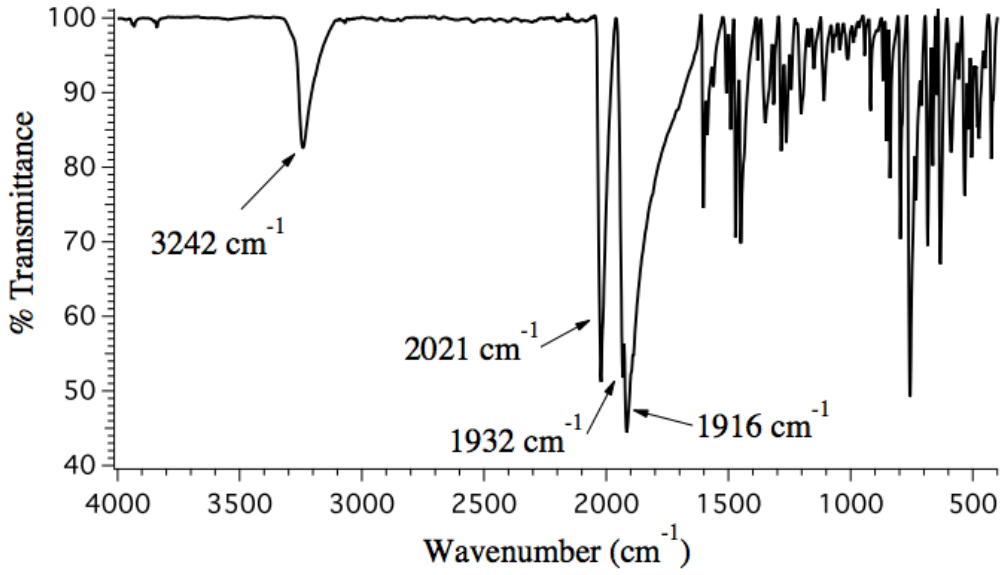


Figure S12

4-OMe

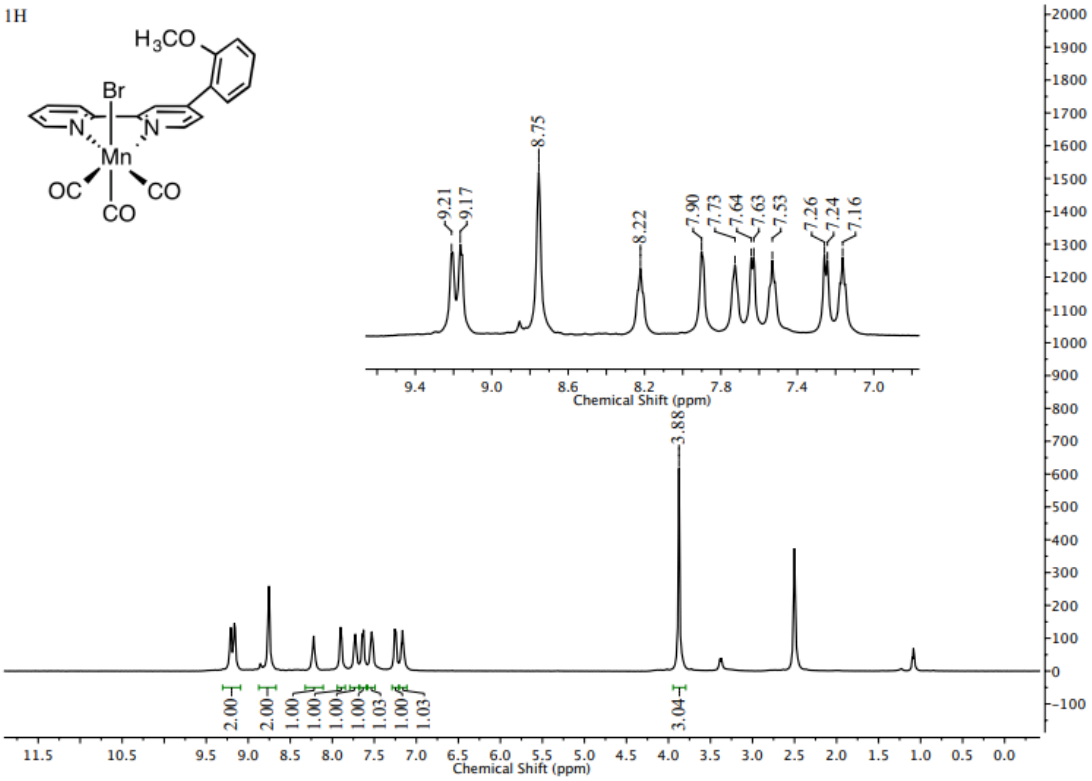
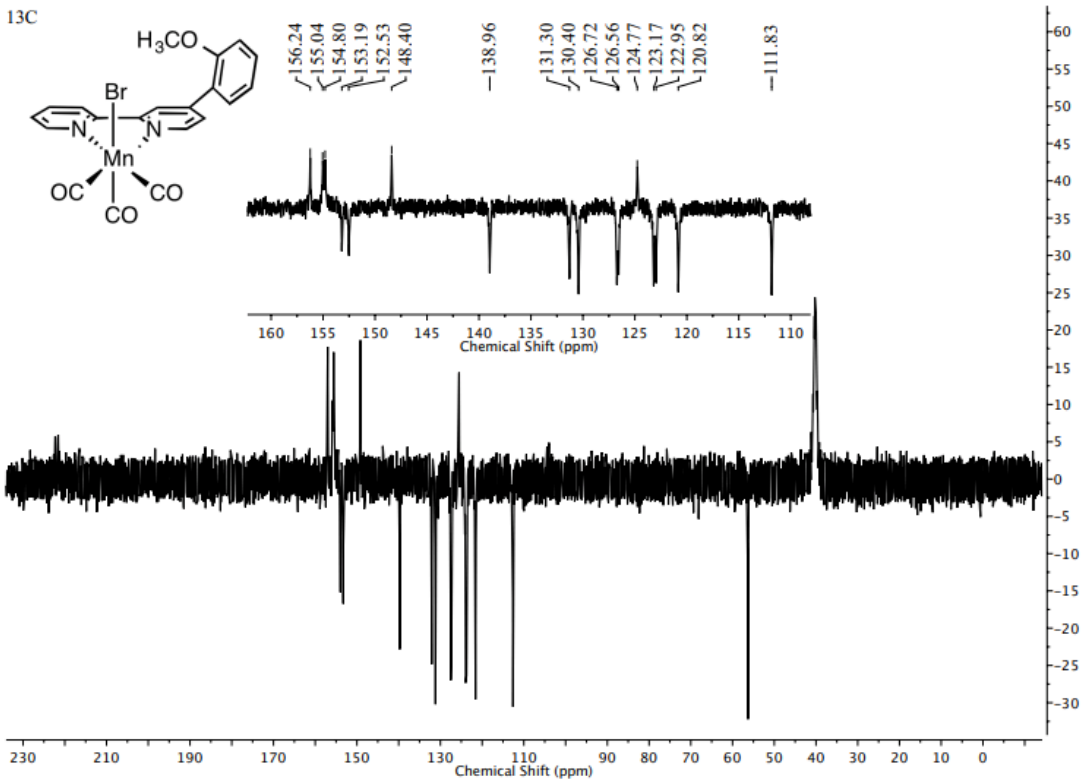


Figure S13



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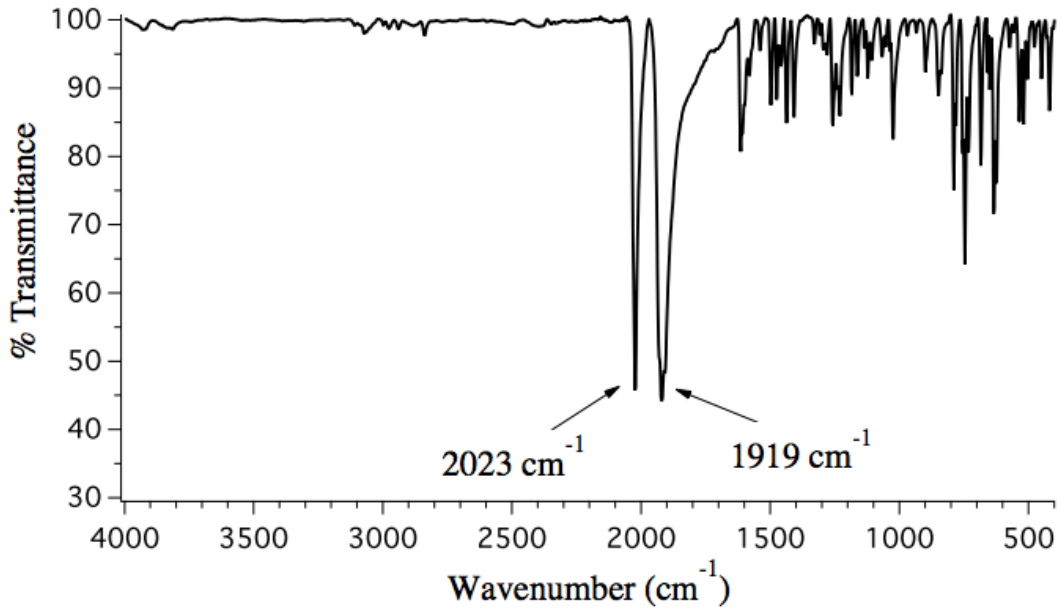
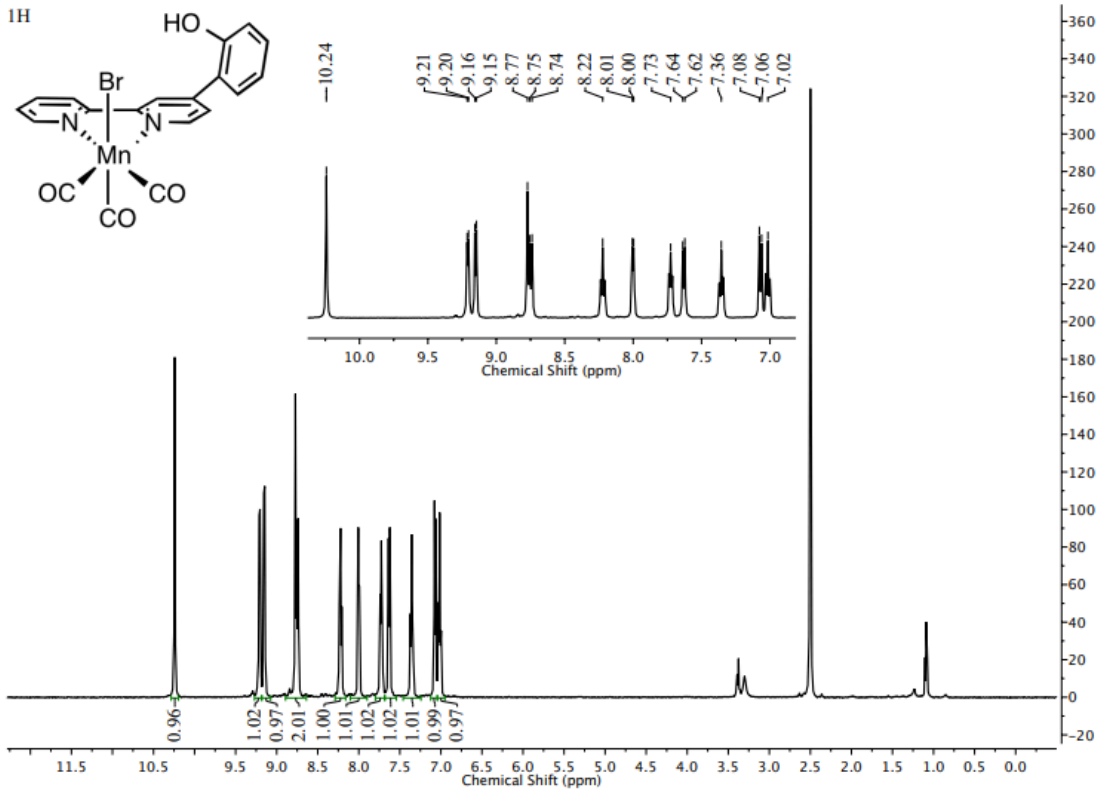


Figure S15

4-OH



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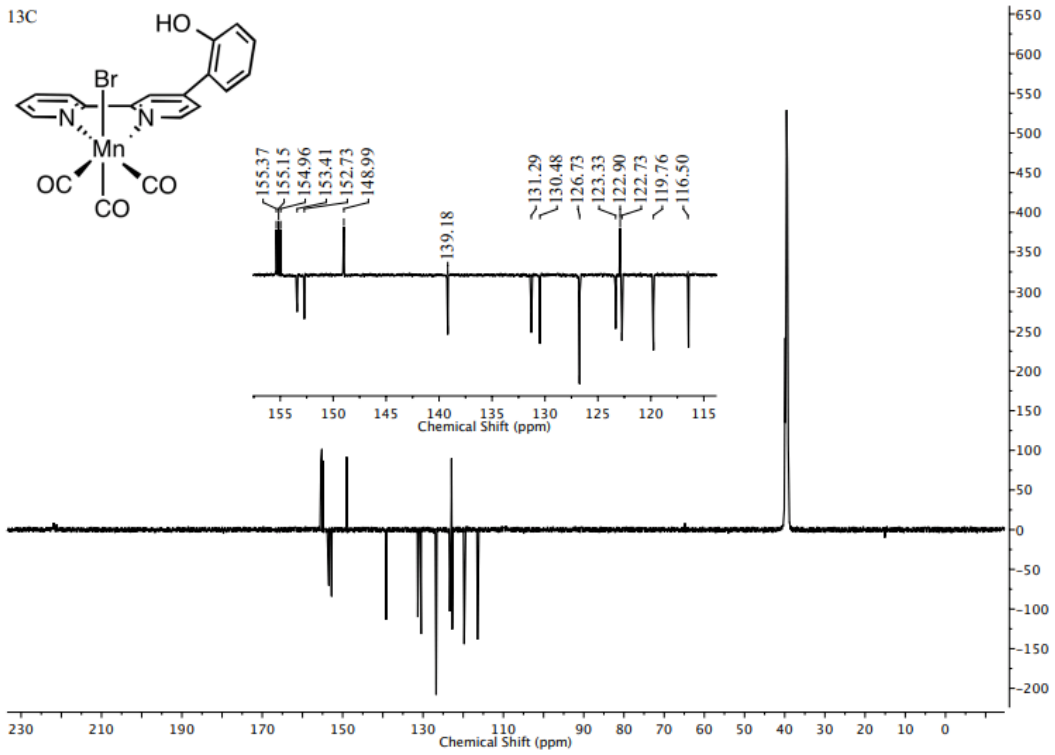


Figure S17

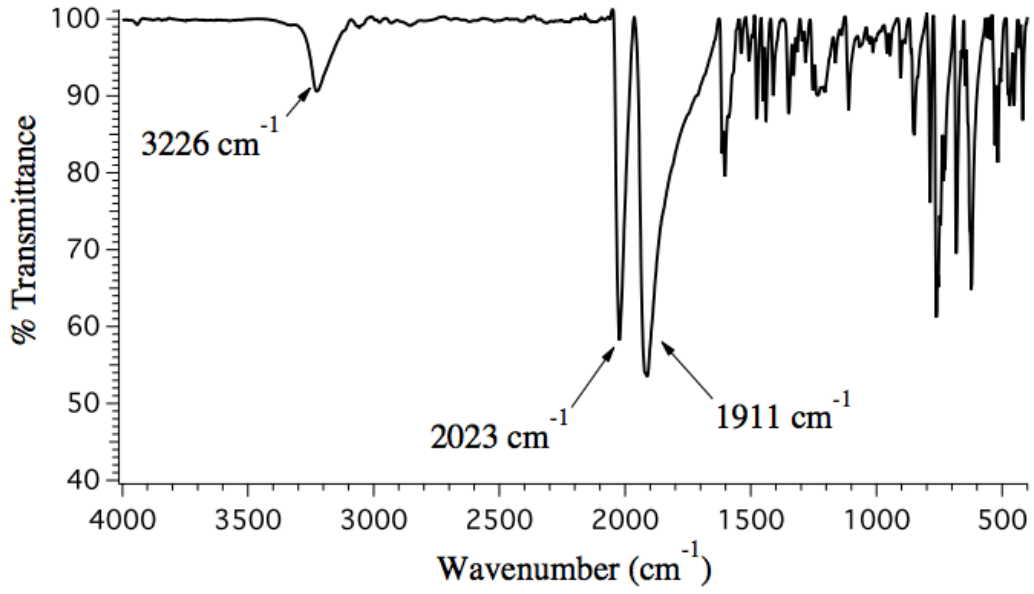
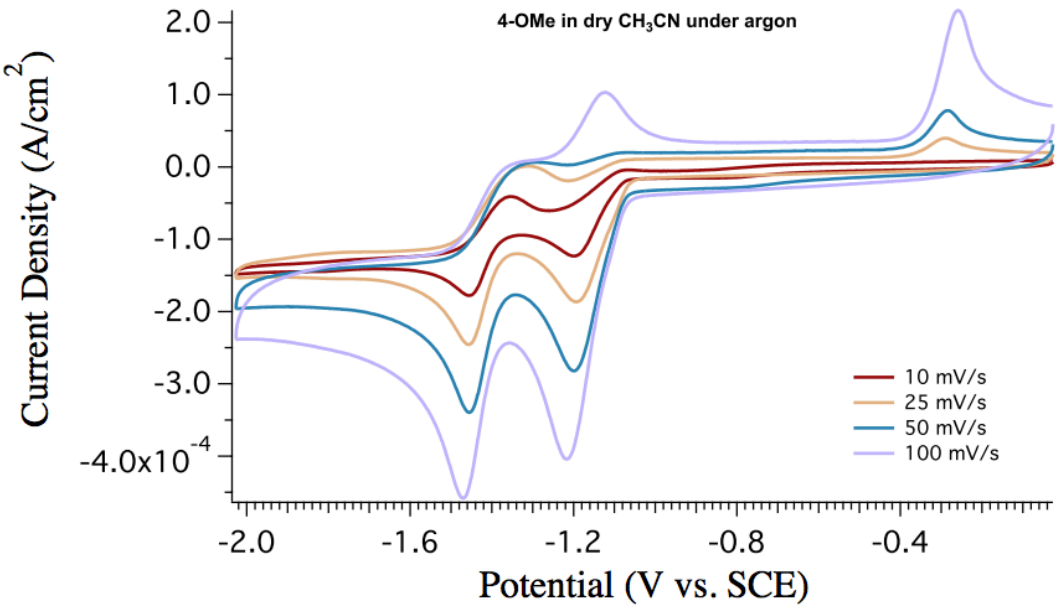


Figure S18

Cyclic Voltammetry Data of Complexes Studied with Scan Rate Dependence

4-OMe

4-OMe in dry CH_3CN under argon:



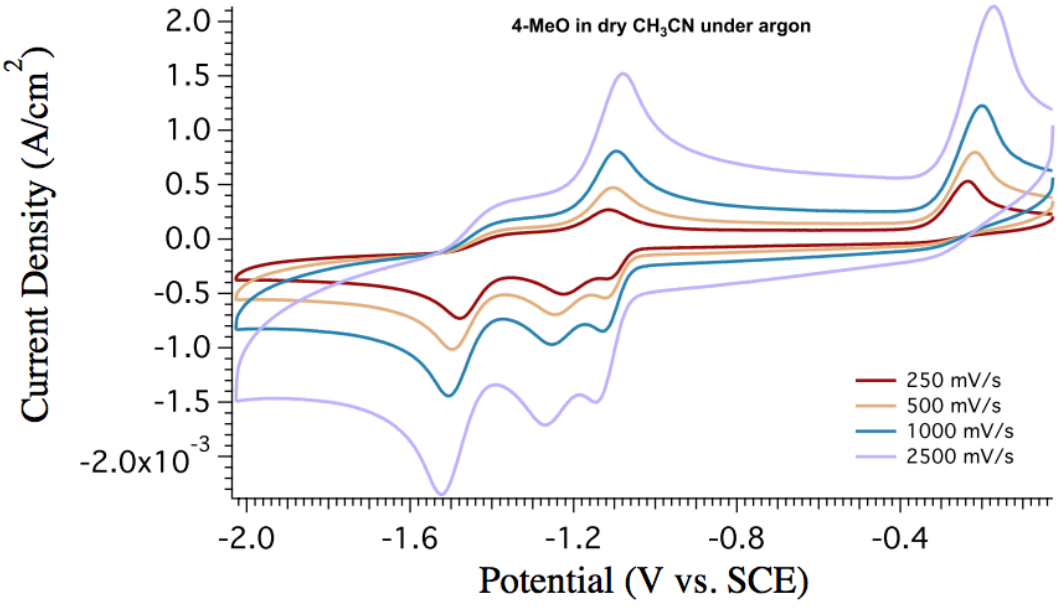


Figure S19

4-OMe in CH_3CN with 5% H_2O under argon:

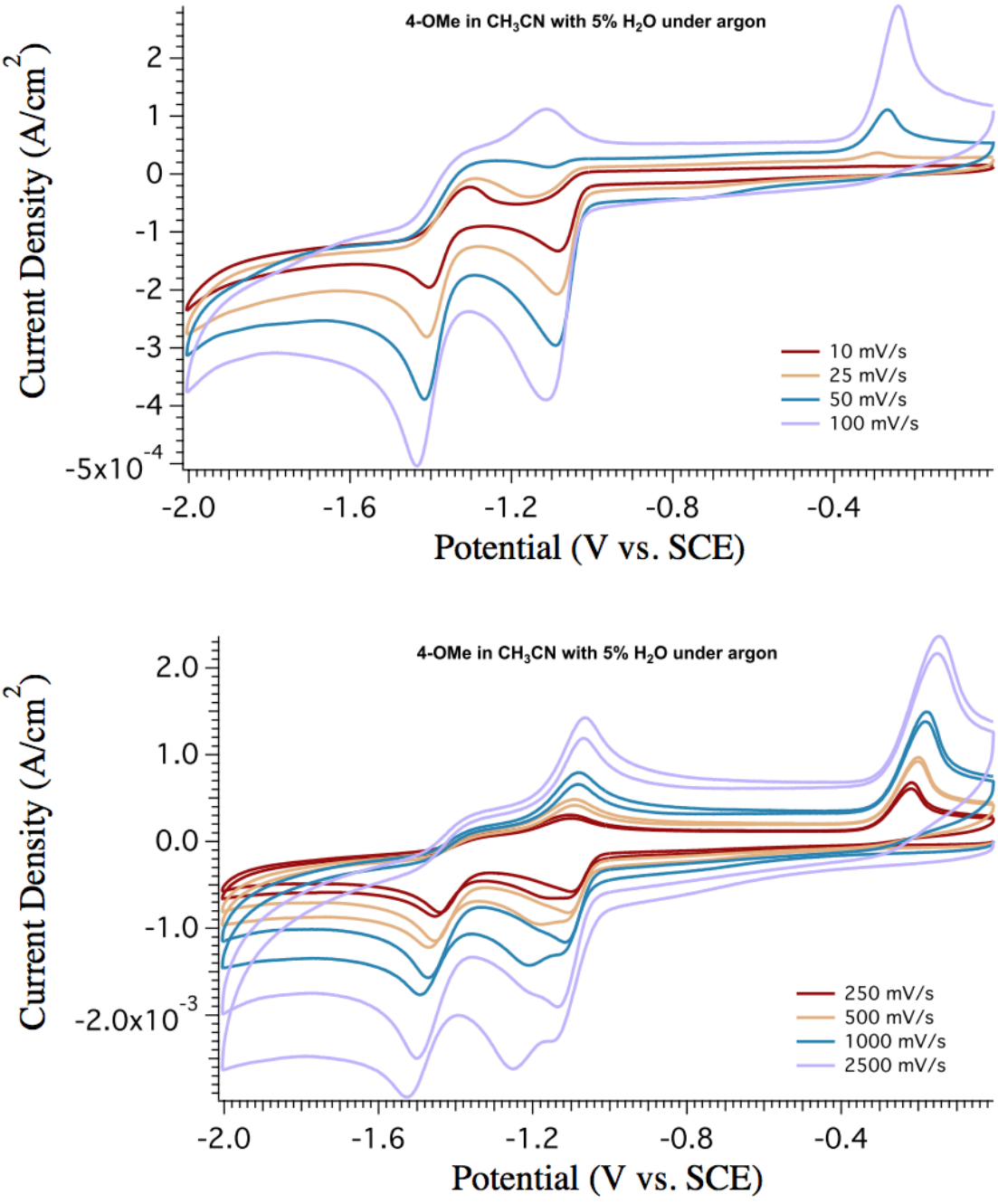


Figure S20

4-OMe in CH_3CN with 5% H_2O under CO_2:

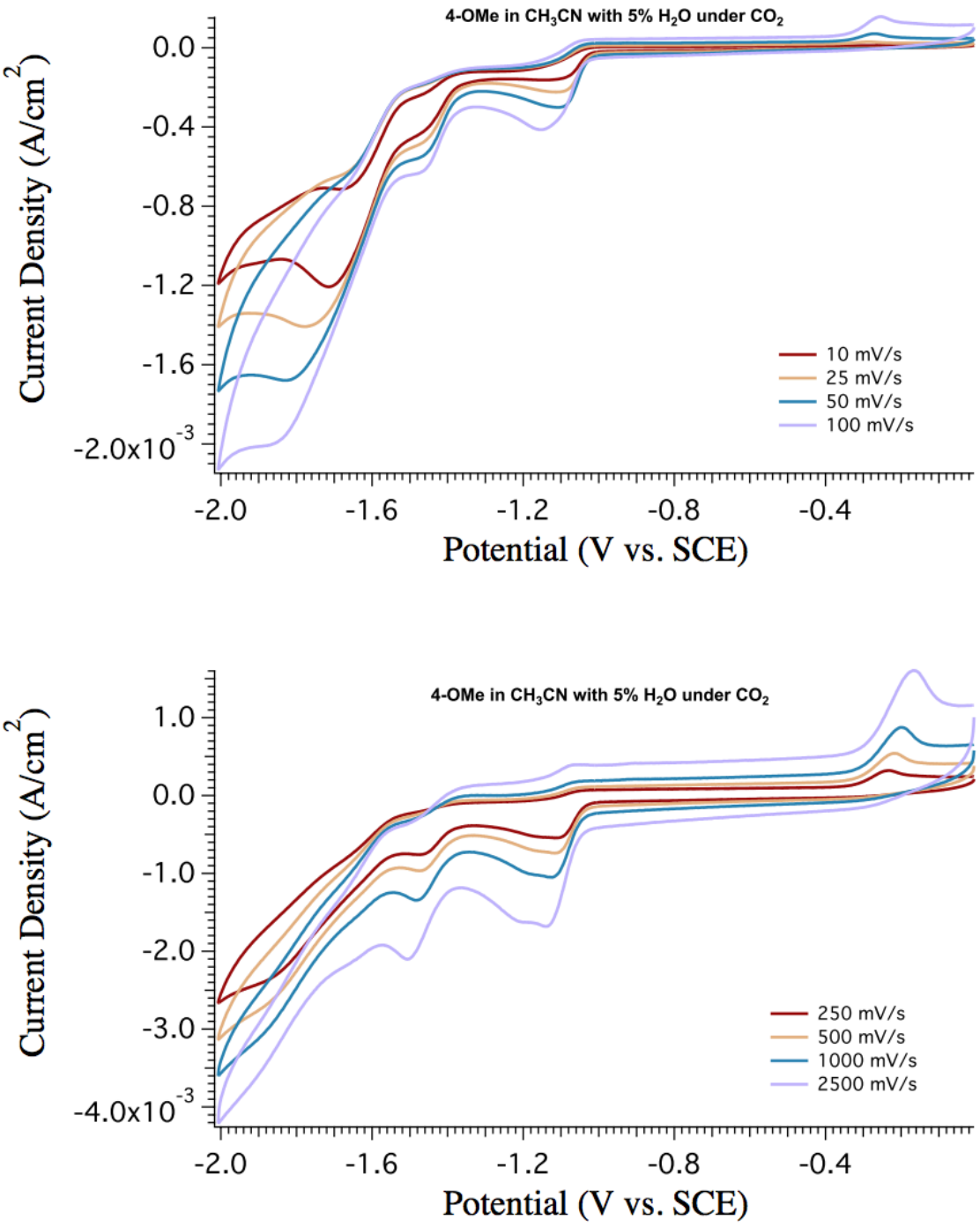
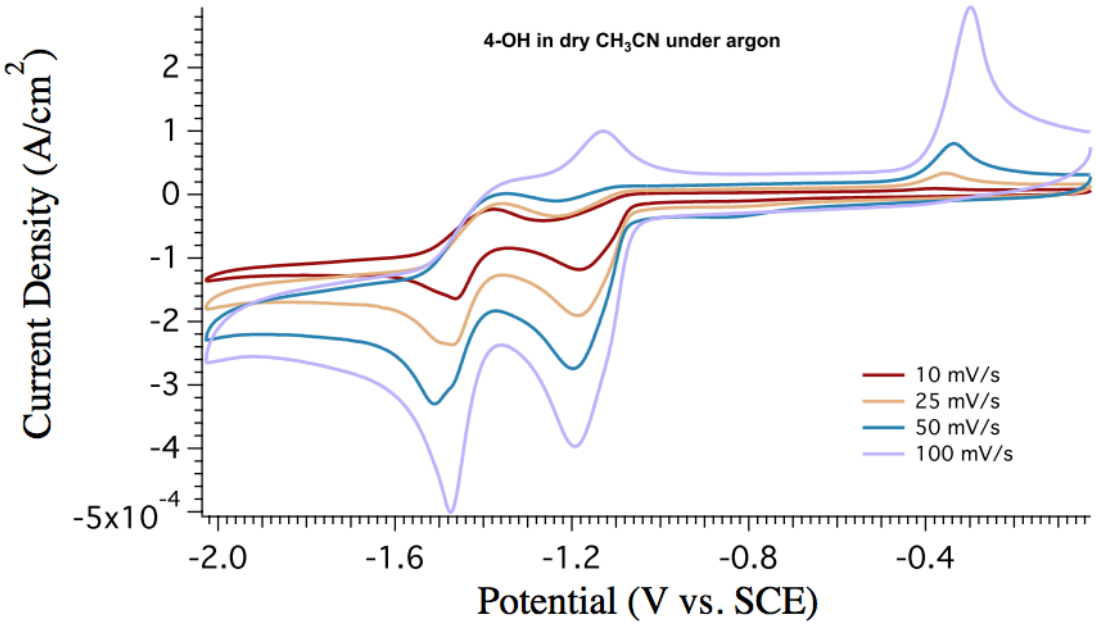


Figure S21

4-OH

4-OH in dry CH_3CN under argon:



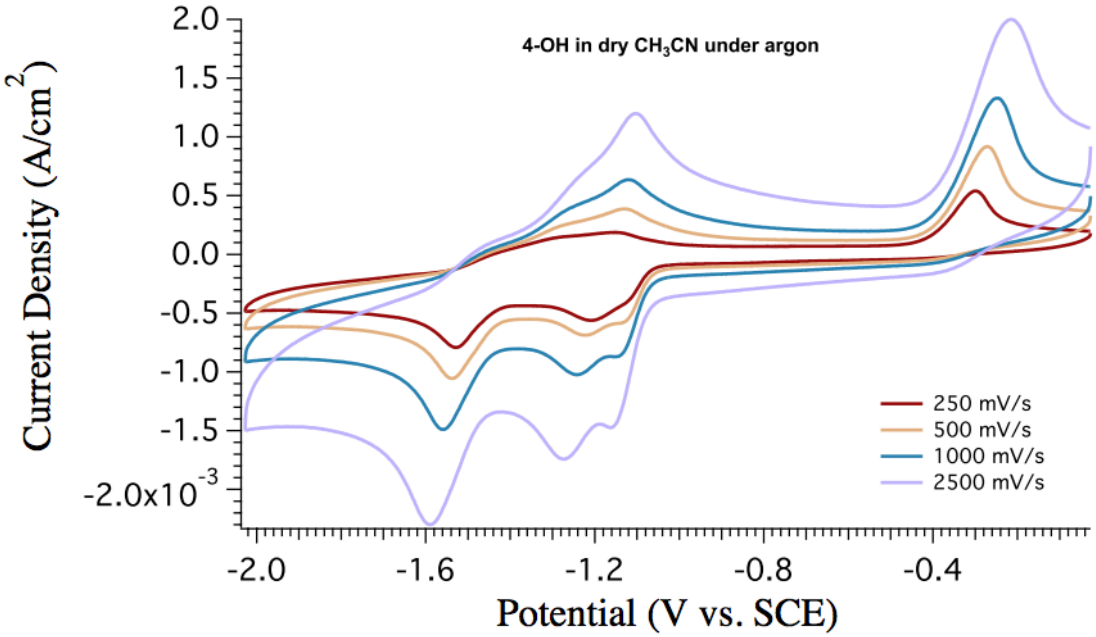


Figure S22

4-OH in CH_3CN with 5% H_2O under argon:

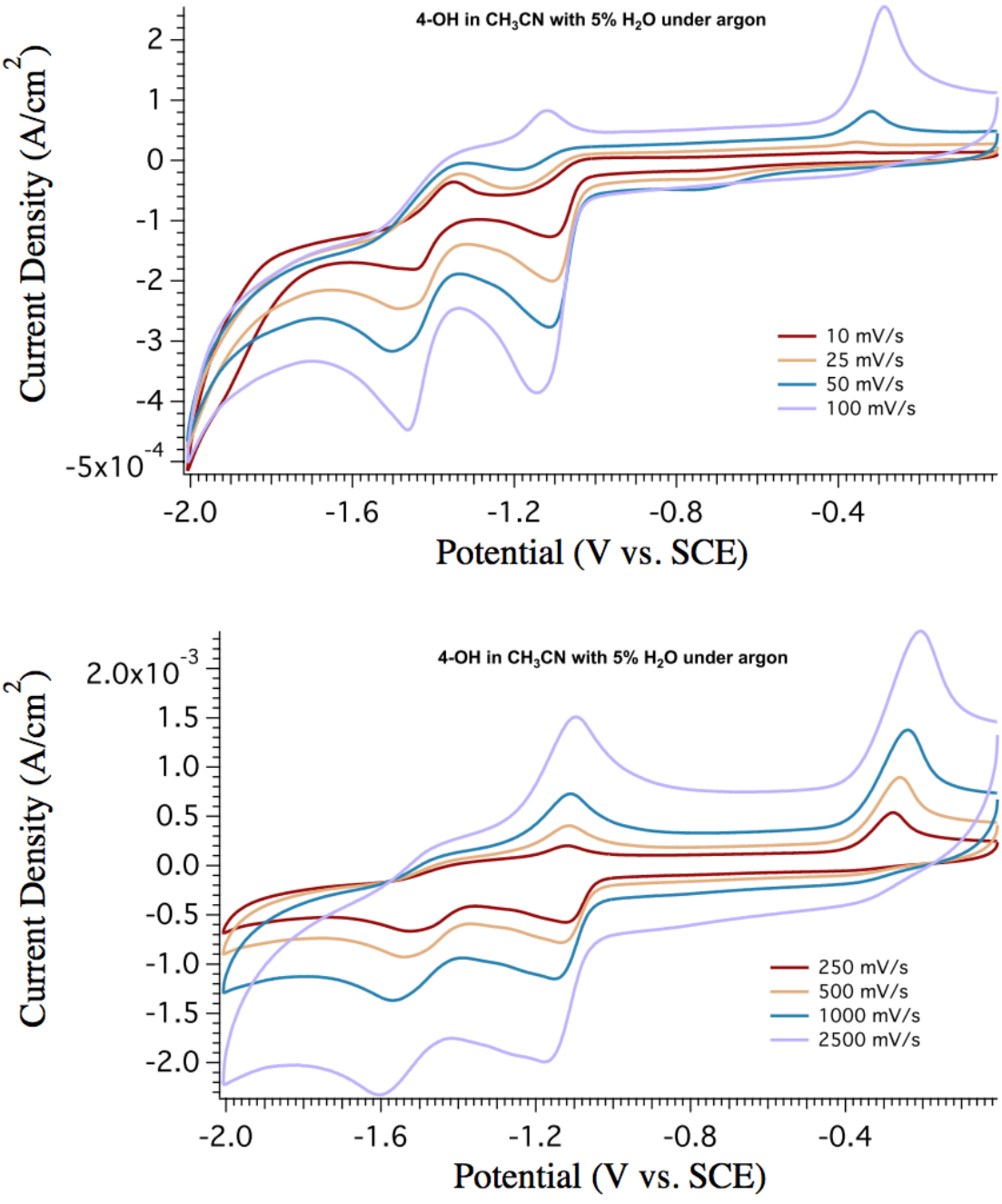


Figure S23

4-OH in CH_3CN with 5% H_2O under CO_2:

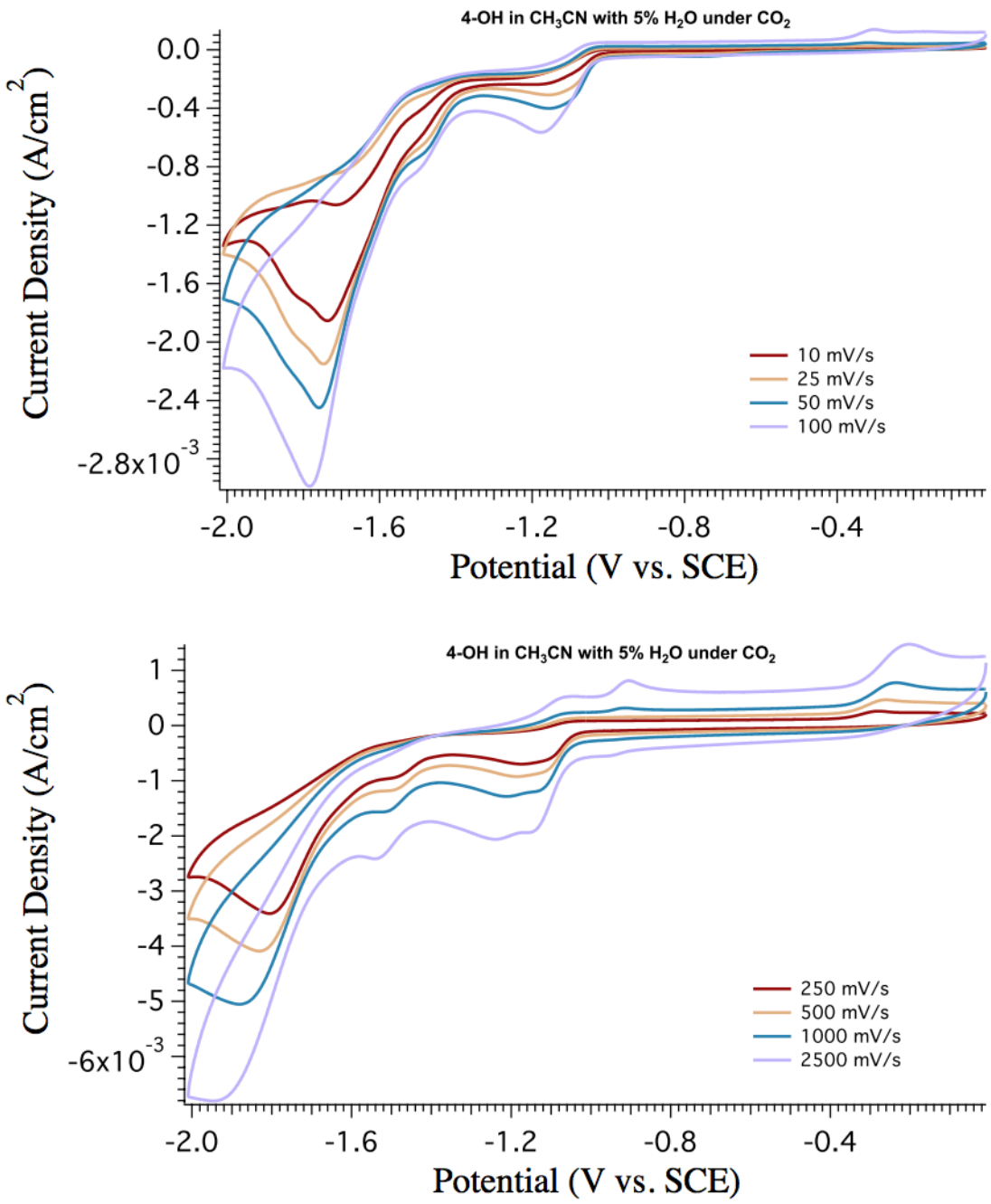


Figure S24

4-OH in dry CH_3CN under CO_2:

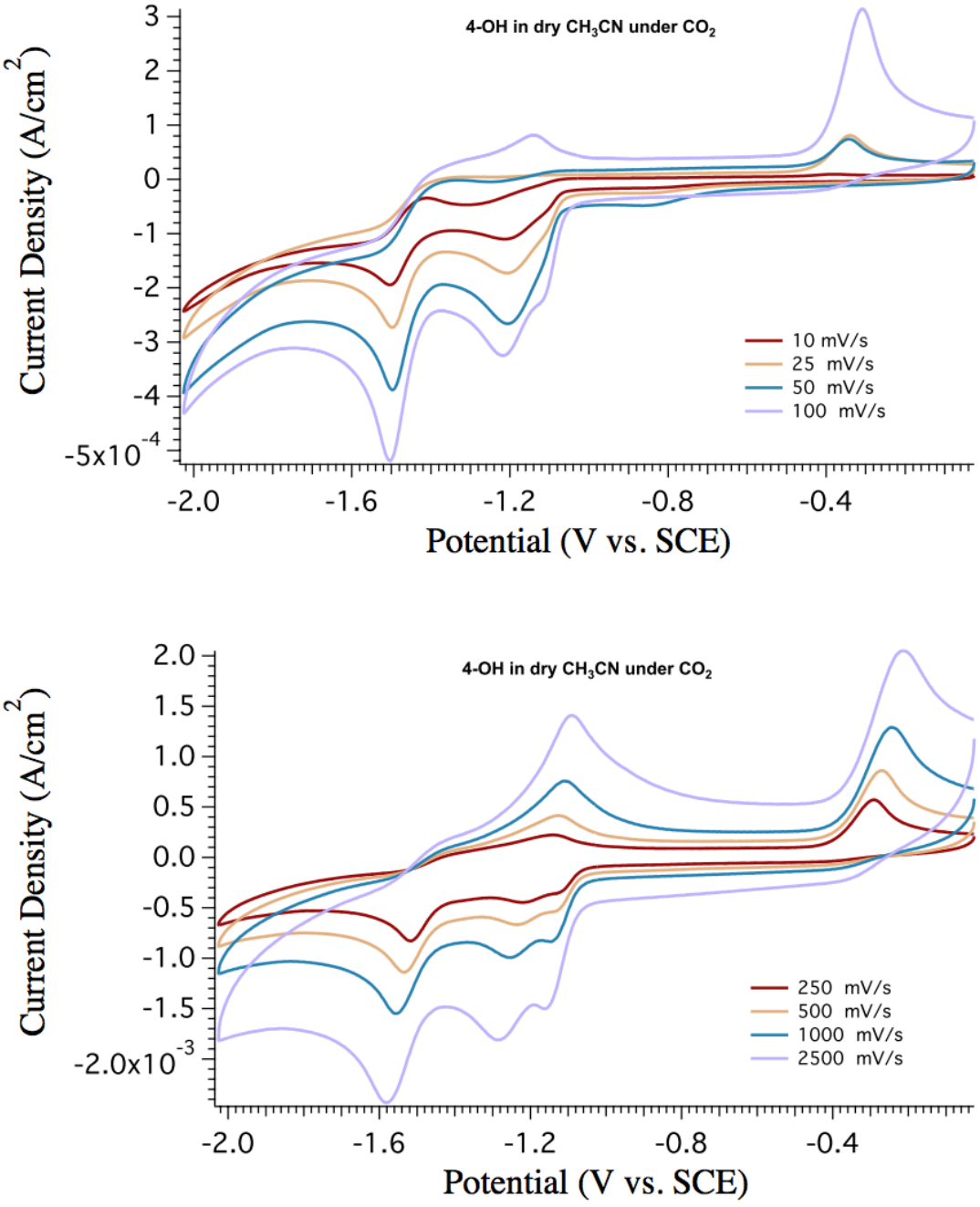


Figure S25

5-OMe

5-OMe in dry CH_3CN under argon:

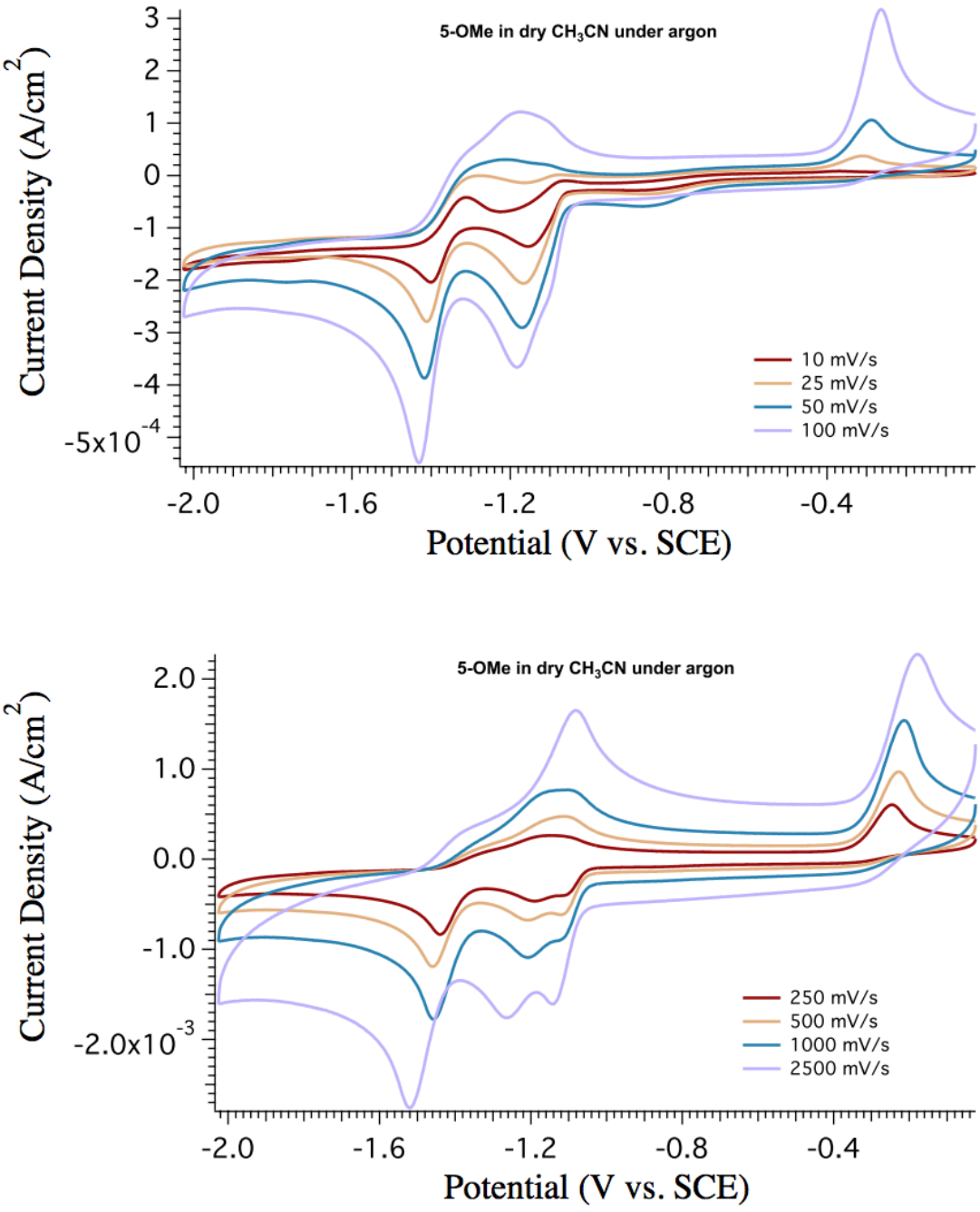


Figure S26

5-OMe in CH_3CN with 5% H_2O under argon:

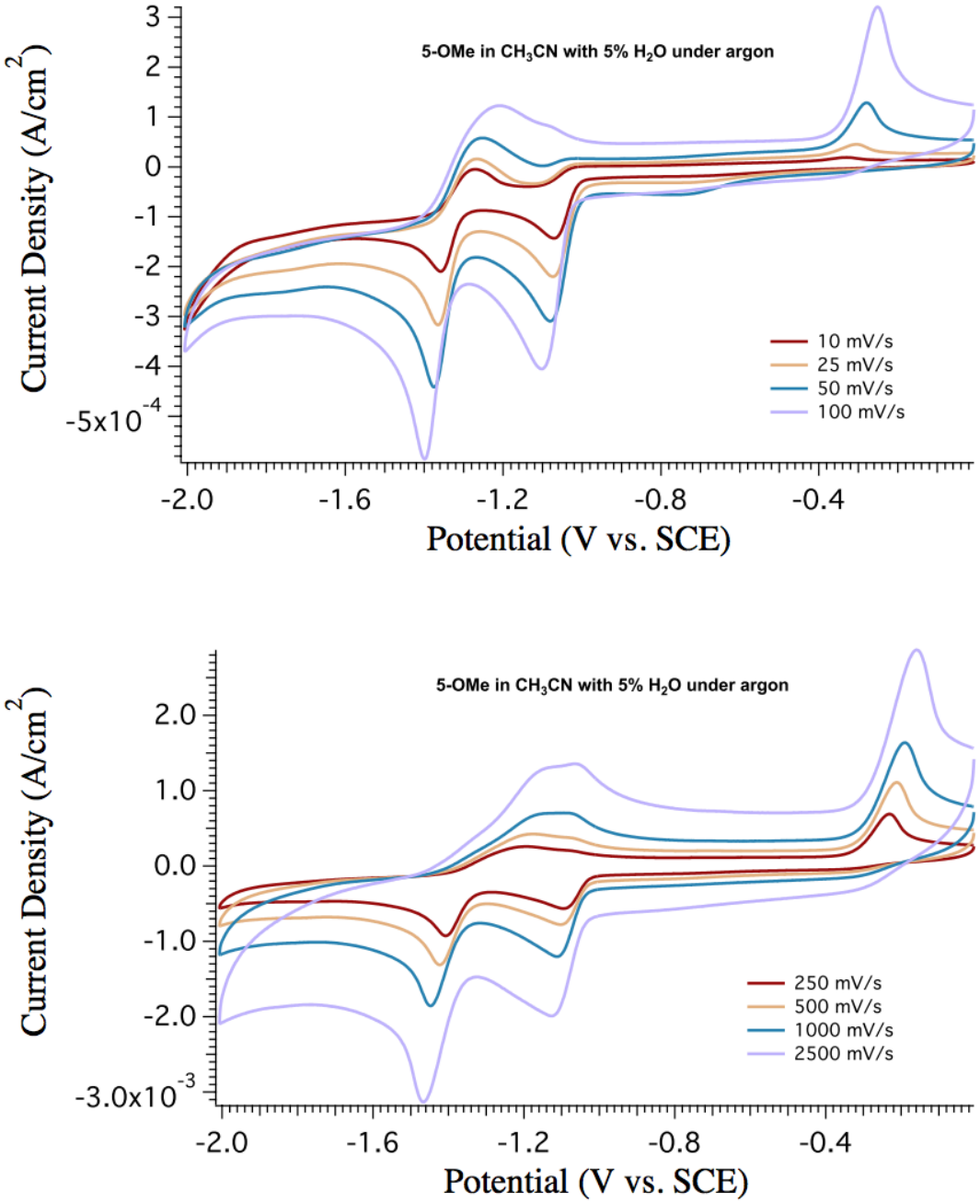


Figure S27

5-OMe in CH_3CN with 5% H_2O under CO_2:

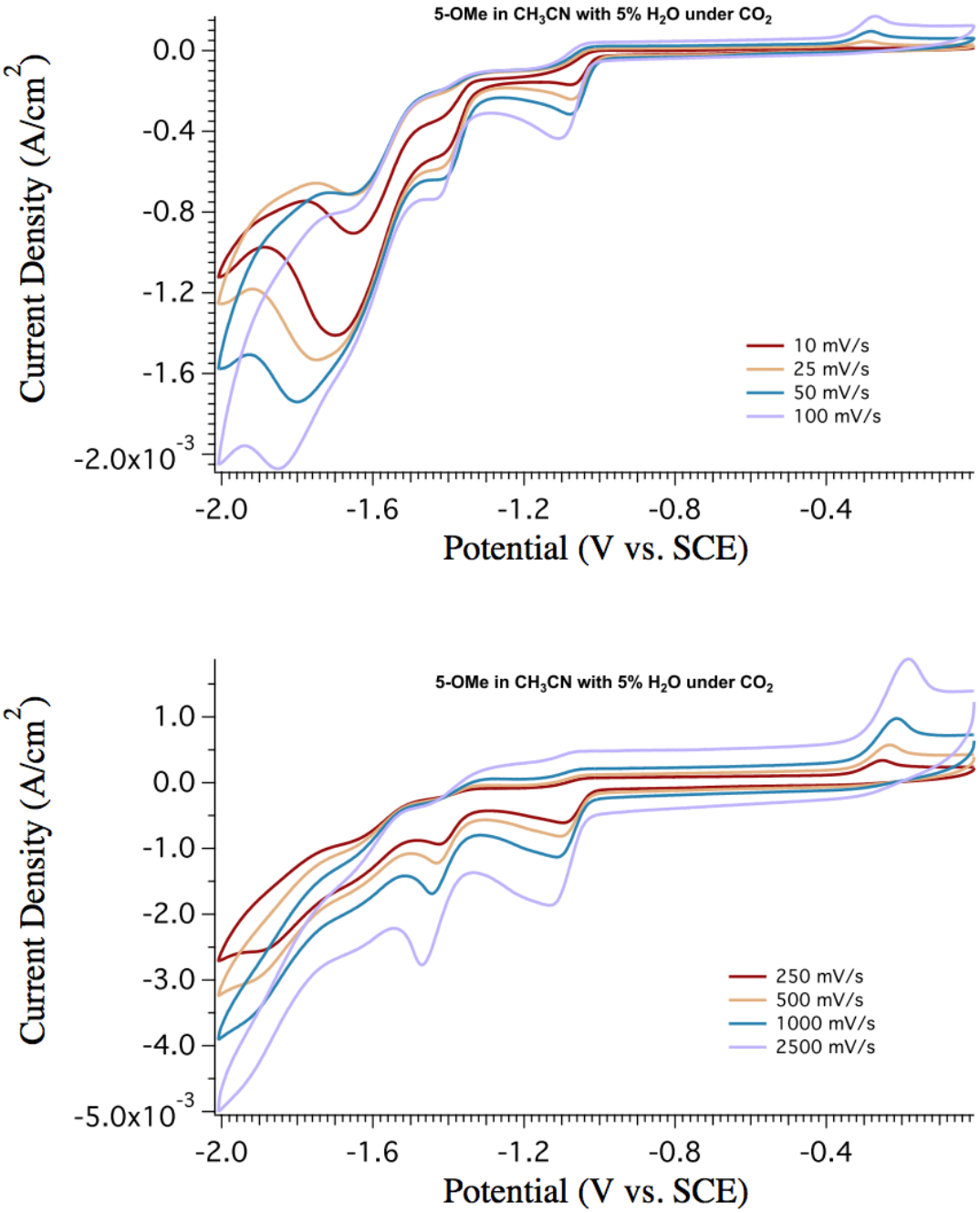


Figure S28

5-OH

5-OH in dry CH_3CN under argon:

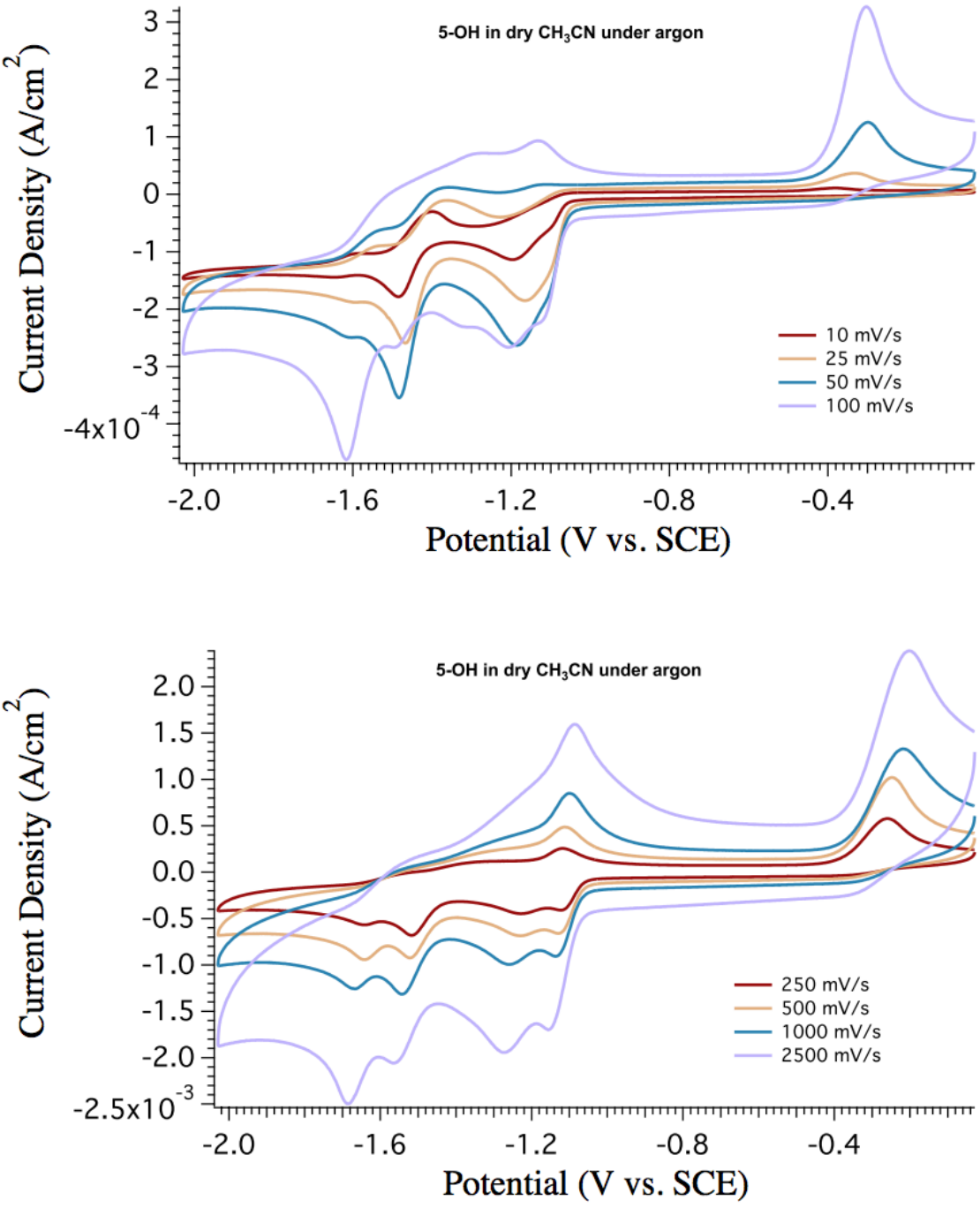


Figure S29

5-OH in CH_3CN with 5% H_2O under argon:

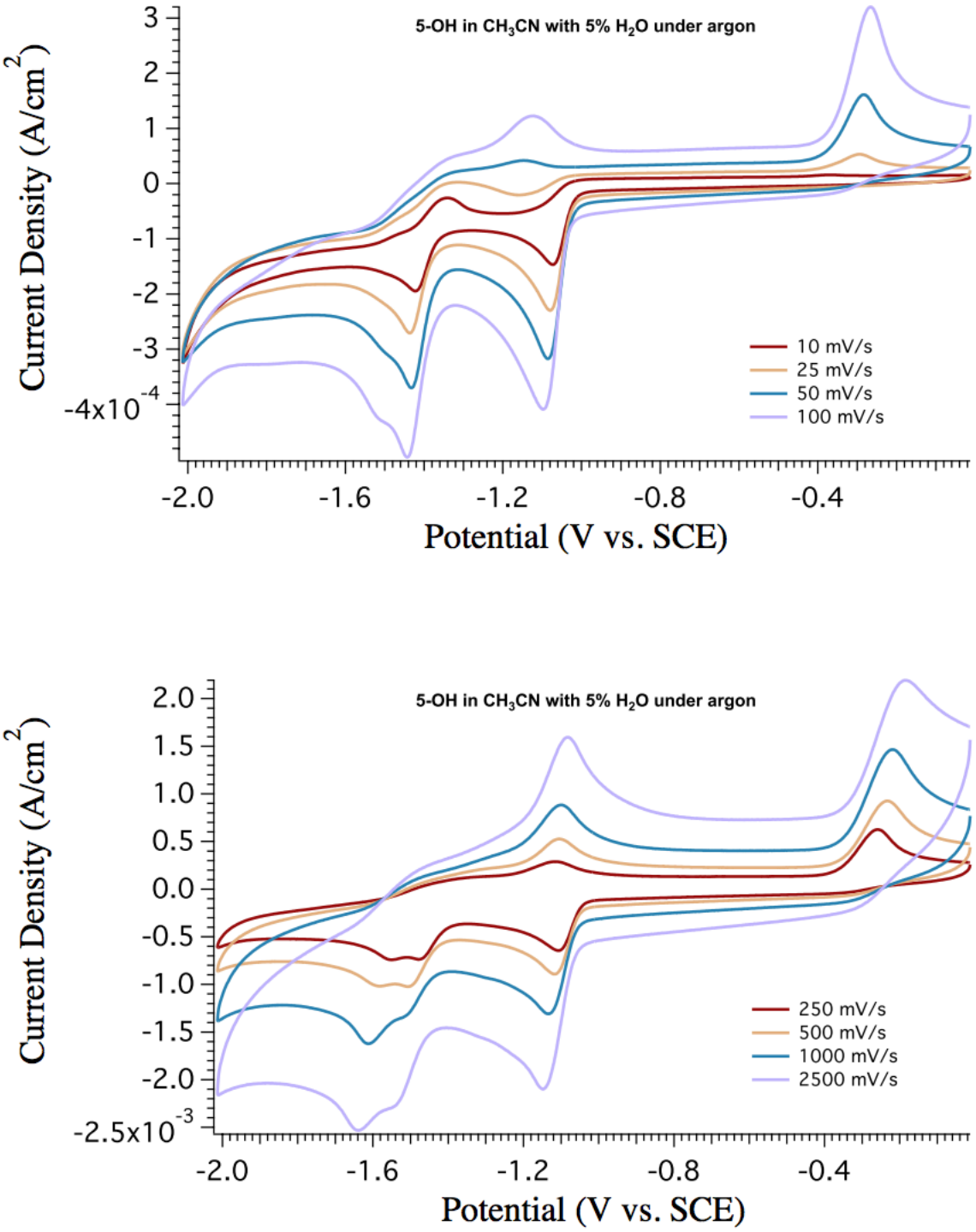


Figure S30

5-OH in CH_3CN with 5% H_2O under CO_2:

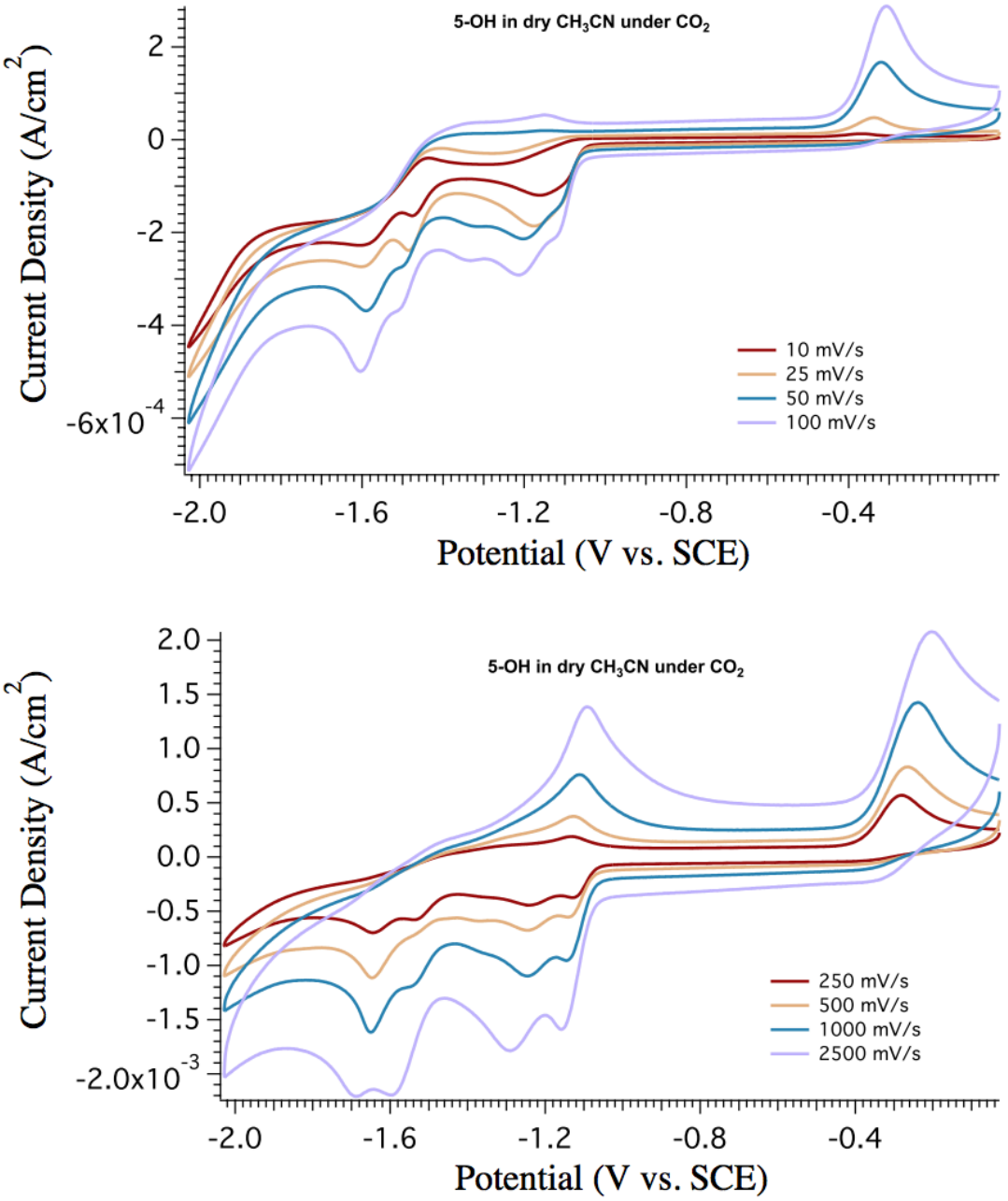


Figure S31

5-OH in dry CH_3CN under CO_2:

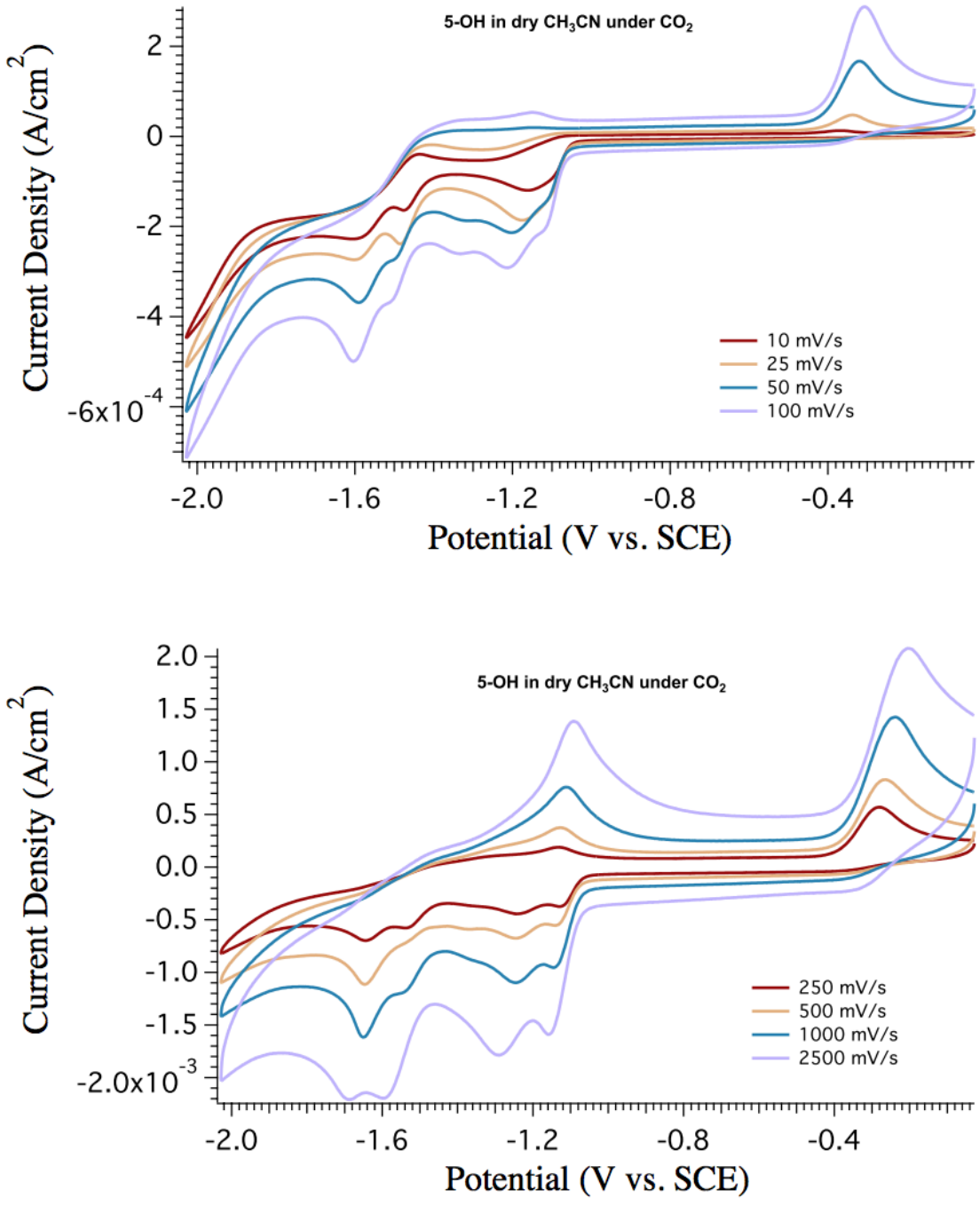


Figure S32

6-OMe

6-OMe in dry CH_3CN under argon:

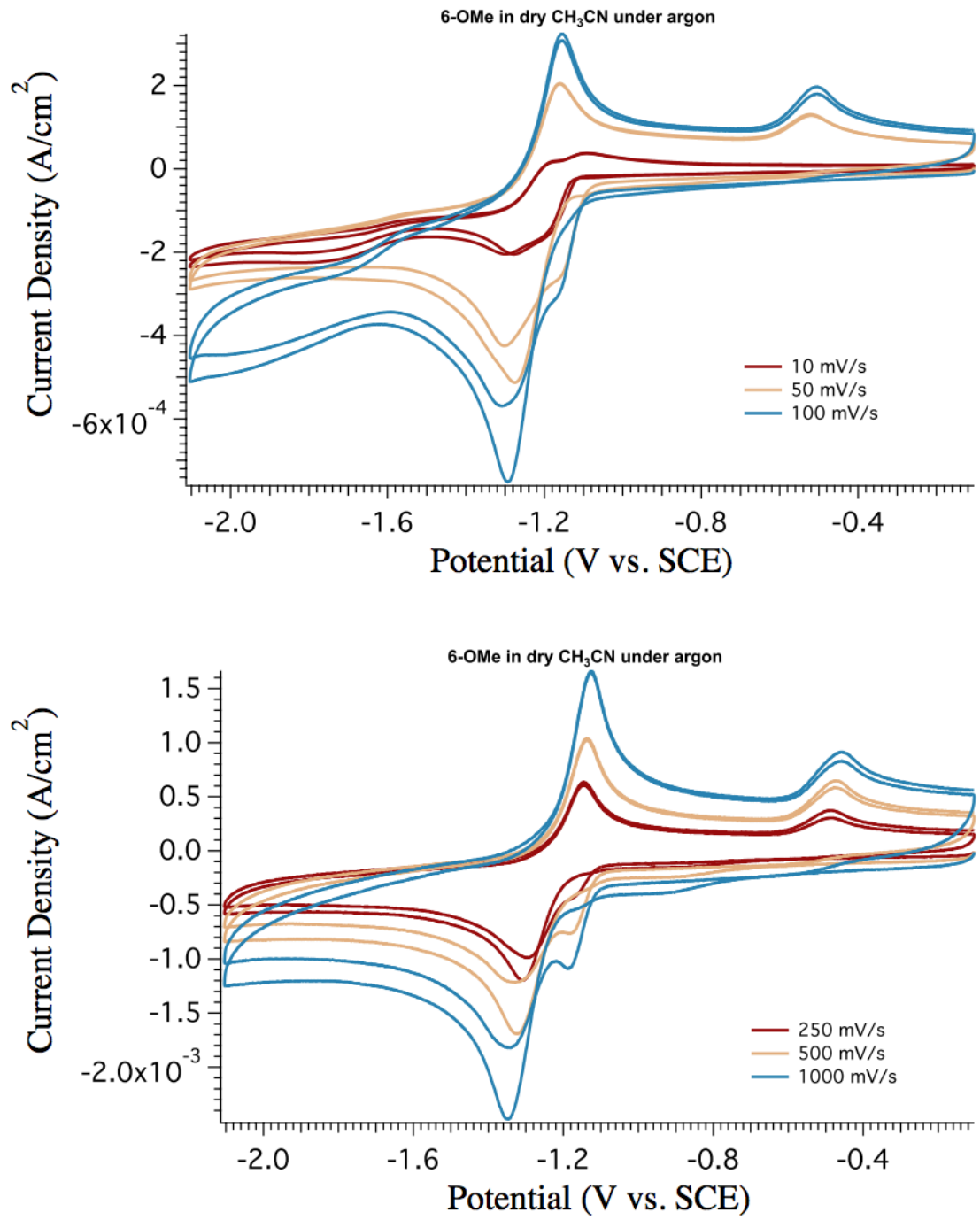


Figure S33

6-OMe in CH_3CN with 5% H_2O under argon:

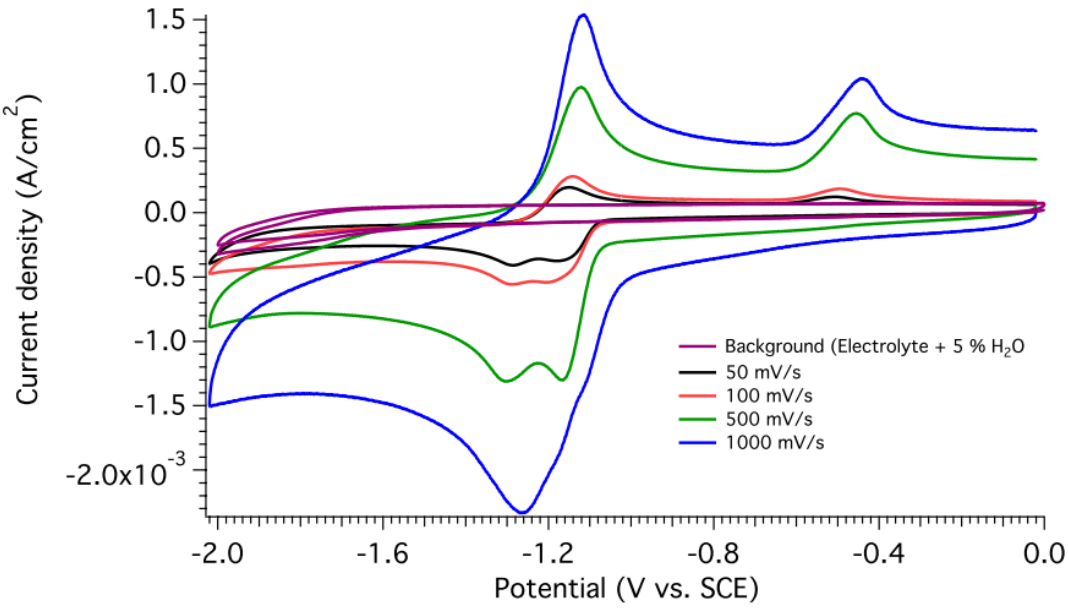


Figure S34

6-OH

6-OH in CH_3CN with 5% H_2O under argon:

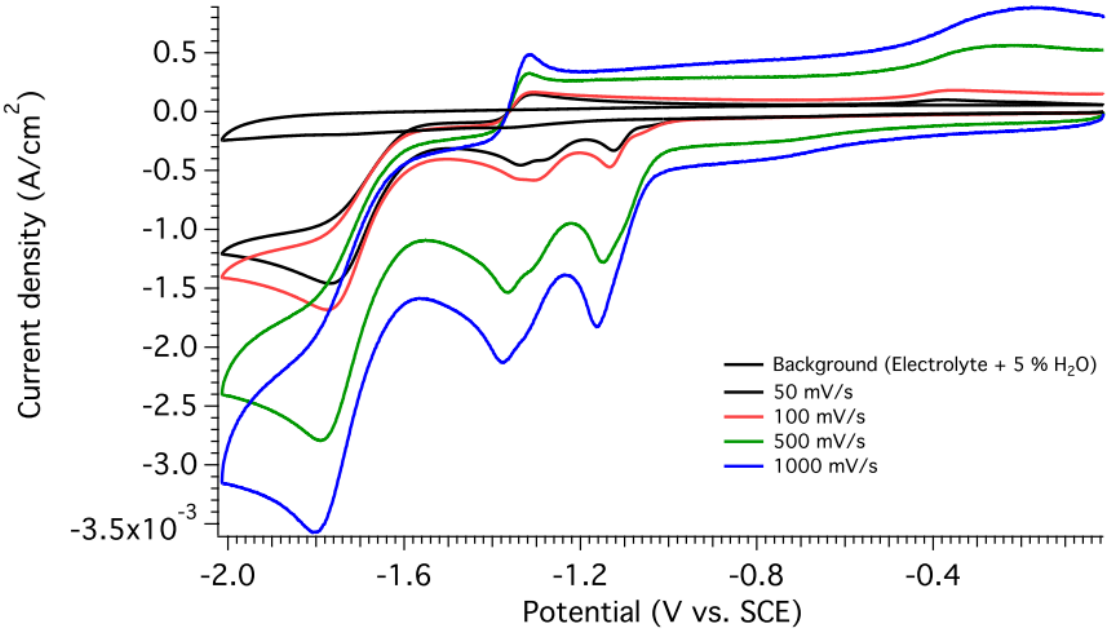


Figure S35

6-OH in dry CH_3CN under CO_2:

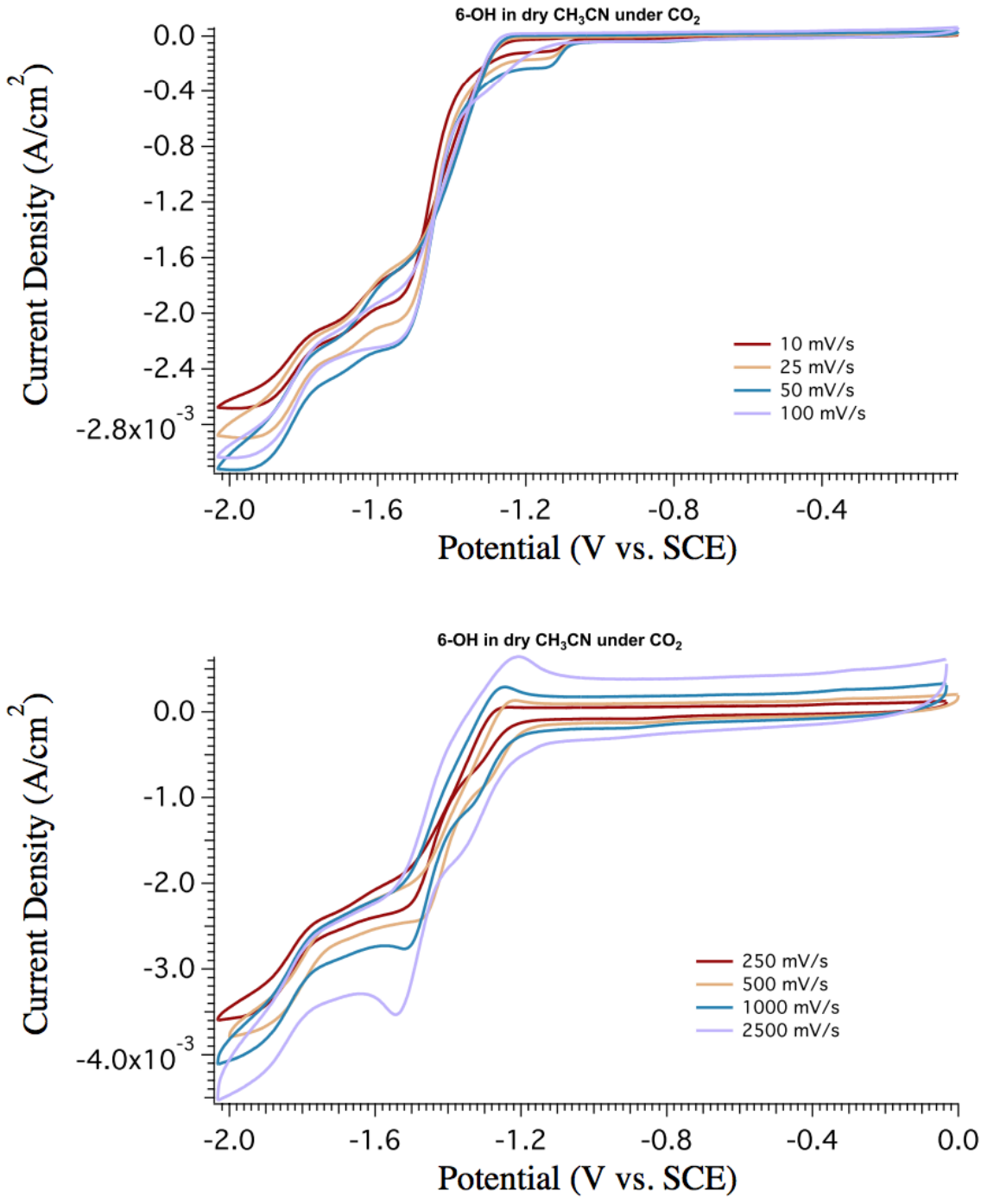


Figure S36

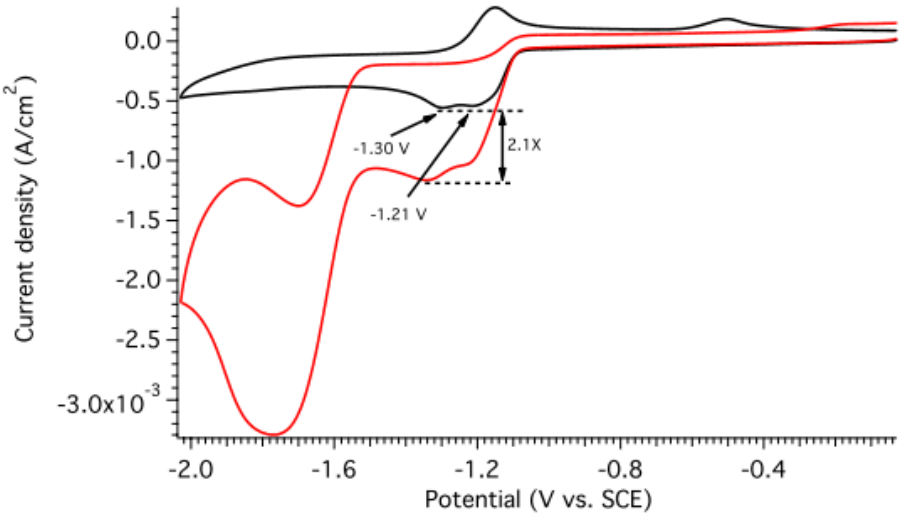


Figure S37. Cyclic voltammogram of 6-OMe under argon (black trace) and CO_2 (red trace) at 100 mV/s in wet electrolyte.

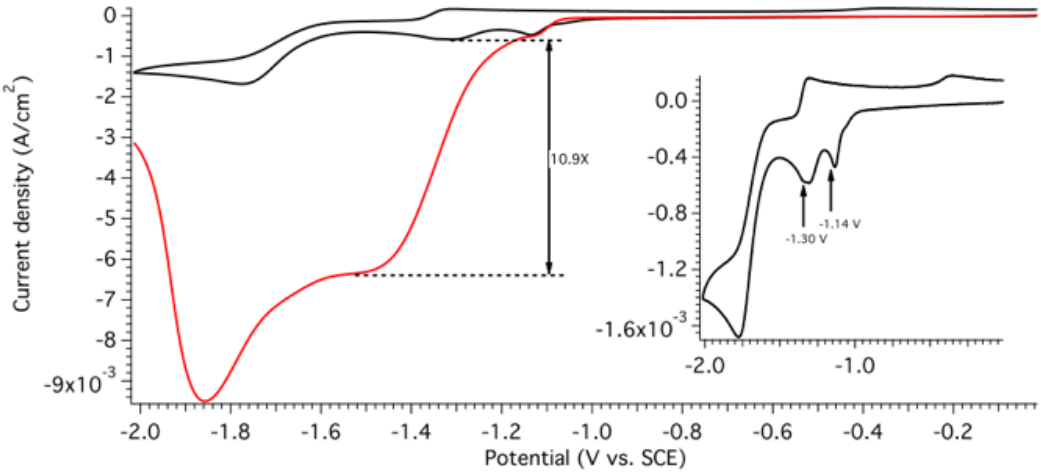


Figure S38. Cyclic voltammogram of 6-OH under argon (black trace) and CO_2 (red trace) at 100 mV/s in wet electrolyte. Inset shows the black trace in greater detail.

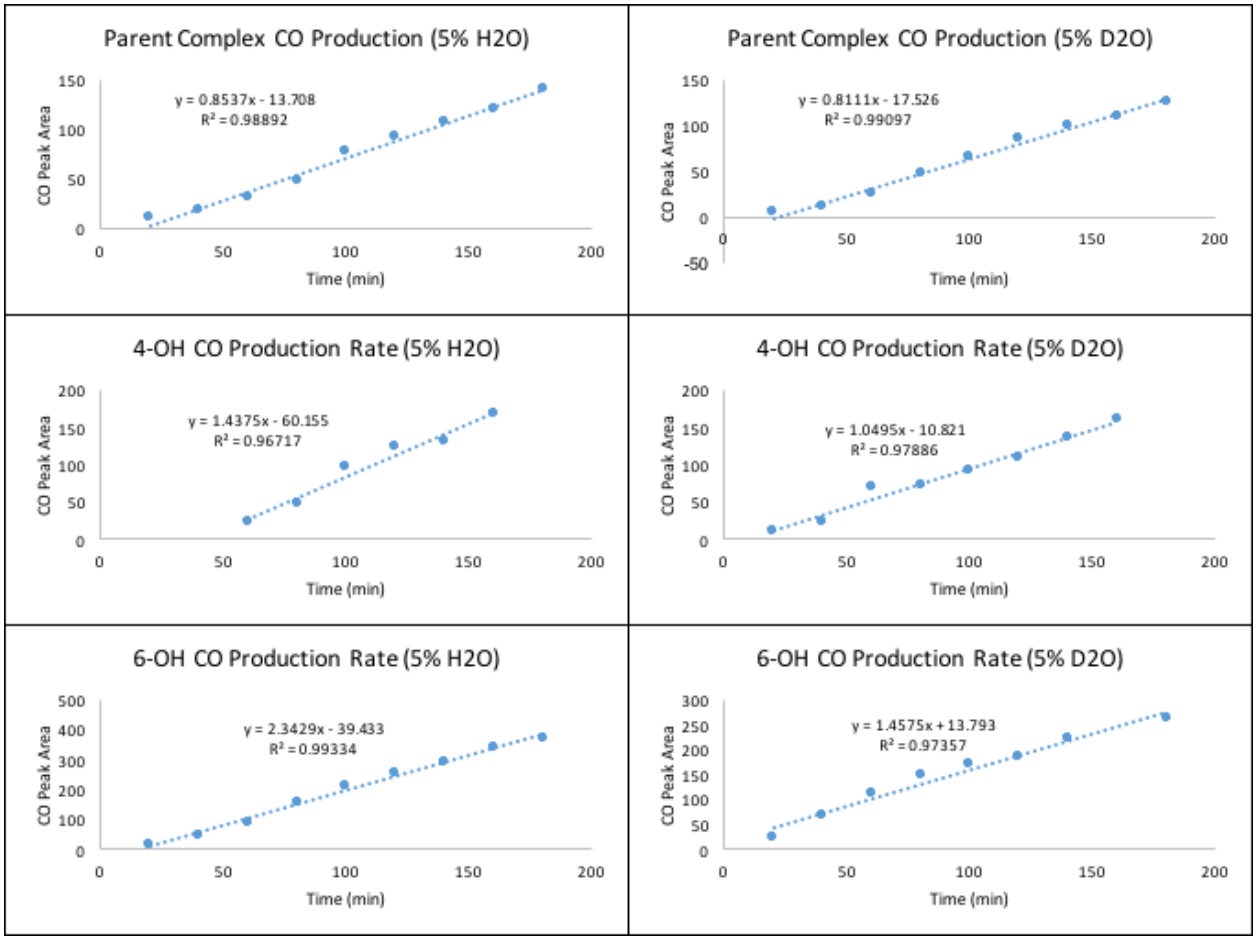


Figure S39. CO production rates of the parent complex, 4-OH, and 6-OH under 5% H_2O or 5% D_2O.

F.E. of Complexes Above:

Parent Complex (5% H_2O): 76.4%
Parent Complex (5% D_2O): 53.2%

4-OH Complex (5% H_2O): 57.3%
4-OH Complex (5% D_2O): 54.6%

6-OH Complex (5% H_2O): 77.6%
6-OH Complex (5% D_2O): 43.8%

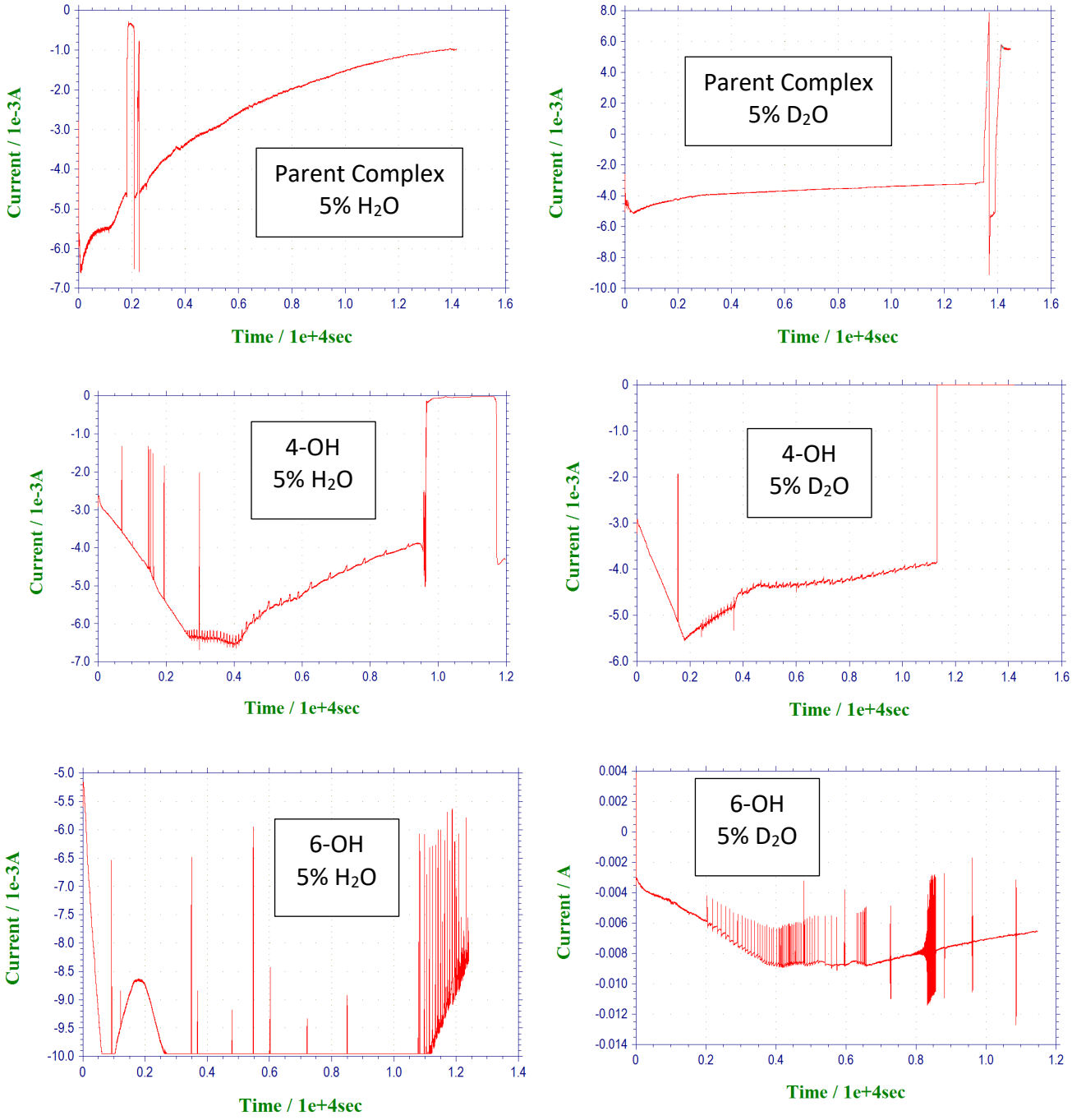


Figure S40. Current vs. time traces for the 3 complexes in 5% H_2O or 5% D_2O

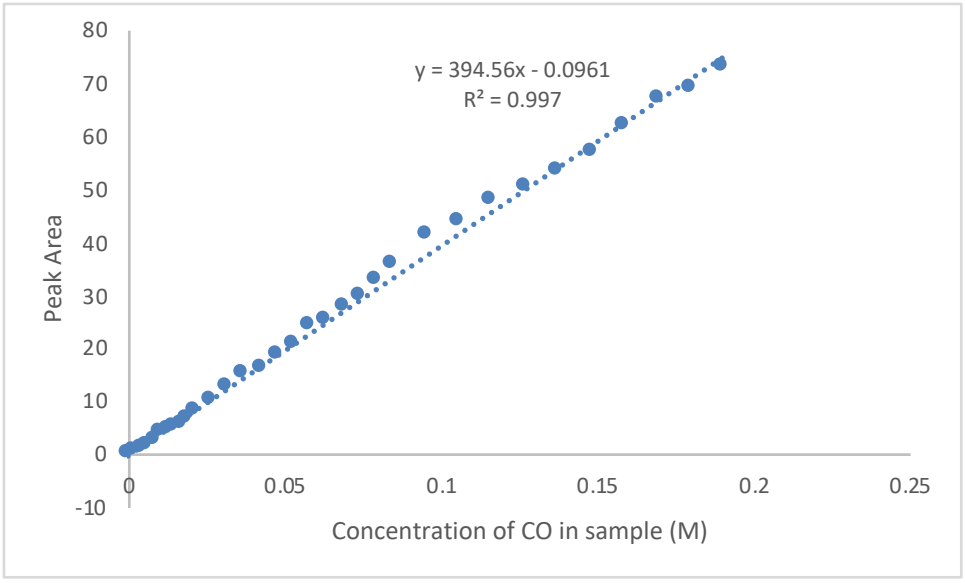


Figure S41. Calibration curve of CO quantification.