SUPPORTING INFORMATION

Nickel(II) pincer complexes demonstrate that the remote substituent controls catalytic carbon dioxide reduction

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Photocatalysis General Information. 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 the photocatalytic experiments. Head space analysis was performed using a VICI gas tight syringe with stopcock and a custom Agilent 7890B Gas Chromatography instrument equipped with Agilent PorapakQ 6ft, 1/8 O.D. column. Quantitation of CO and CH_4 were made using an FID detector, while H2 was quantified using a TCD detector. All calibrations were done using standards purchased from BuyCalGas.com.

Photocatalysis Procedure. To a 17 mL vial was added BIH (0.005 g, 0.02 mmol), MeCN (6 ml, bulk or anhydrous), and catalyst (0.2 ml from 1 × 10 -3 M in MeCN solution). The solution was bubbled vigorously with CO2 for at least 15 minutes until the solution volume reached 1.9 ml and then 0.1 ml of degassed triethylamine or N,N,N′,N′-Tetramethyl-1,8-naphthalenediamine (proton sponge) was added to the mixture. The tube was sealed with a rubber septum and irradiated with a solar simulator. Head space samples were taken and the pressure was adjusted to atmospheric pressure by pressurizing the sample (300 μL taken from the headspace then compressed to 250 μL) then submerging the sealed gas tight syringe into diethyl ether. The syringe was open and gas was observed exiting the needle tip. The syringe was then sealed, removed from the diethyl ether solution and injected into the GC mentioned above.

Cyclic Voltammetry. C-H instruments electrochemical analyzer was used to measure the CV in the presence of Ag/AgCl as the reference electrode, Platinum as the counter electrode and Glassy carbon was the working electrode and 0.1 M n-Bu_4NPF_6 as the supporting electrolyte. All electrochemical measurements were taken in anhydrous acetonitrile (or 5% water in anhydrous acetonitrile) at a scan rate of 100 mV/s and minimum exposure to light. For each run concentration of catalyst kept constant at 1 mM. Before each measurement, the solution was degassed with Ar or CO_2 (for ~15 min). To avoid concentration changes for the electrolyte and catalyst, the desired experimental solvent volume and accurate concentrations were added to the electrolysis cell. The solvent height in the cell was marked and, the mixture was then diluted with pure acetonitrile (~2 mL). The mixture was then degassed with Ar or CO_2 until the solvent evaporated and level returned to the marked volume. During cyclic voltammetry scans, the sweep width window was set to approximately 100 mV past the second reduction wave peak. Since the catalyst is not active under dark conditions same experiments ran after exposing the catalyst and electrolyte solution to ambient fluorescent light in different time periods.

^{1}H NMR Formate Detection. Our slightly modified procedure is as follows: Upon reaction completion, 0.8 mL of the reaction solution was taken into a syringe and added to a 4 mL vial. To this 36 μL of Verkade's Triisobutyl Superbase (CAS# 331465-71-5; 2,8,9-Triisobutyl- 2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane). The mixture was sonicated for 10 minutes at room temperature. 1.16 mL of a d_3-MeCN ferrocene solution (1.19 mM concentration) was added to the mixture. The vial was thoroughly mixed, then an NMR spectrum was taken on a 500 MHz NMR or 300 MHz NMR with an extended D1-delay of 10 seconds and a minimum of 200 scans. The ratio of the formate peak (~8.7 ppm) and the ferrocene peak (~4.2 ppm, see below) were then compared to a calibration curve generated through the analysis of known concentrations of formate (0.0 mM, 0.1 mM, 1.0 mM, and 10.0 mM solutions). Through this method, the concentration of formate could be evaluated accurately through a trendline having an R^2 value of 0.997 and 0.999 (see below). All NMR spectra were evaluated with MestReNova software to ensure level baselines in the analyte region prior to integrating peaks. This method has been previously described in the literature.[1]

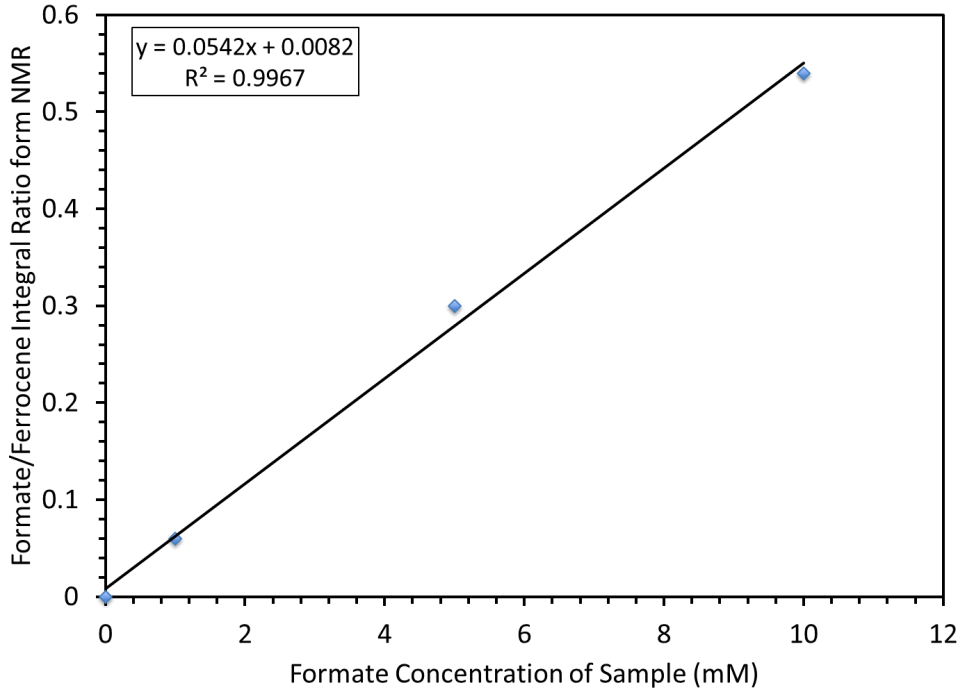

Figure S1: NMR formate calibration curve in d_3-MeCN with ferrocene as an internal standard with Verkade's base.

GC traces for photocatalytic experiments.

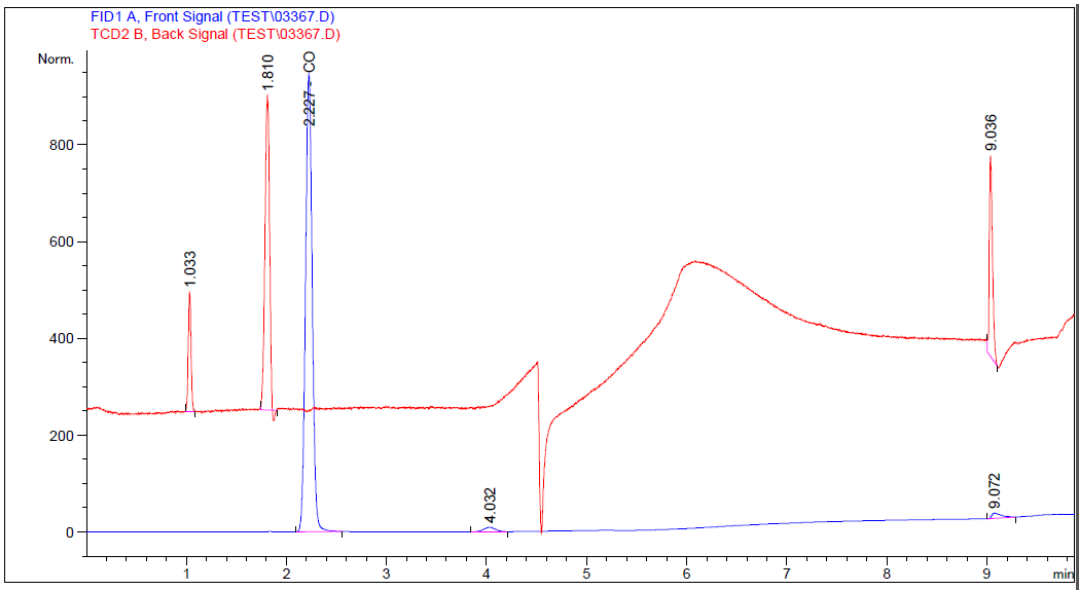

Figure S2: Example GC-trace for photocatalytic reaction with **Catalyst 3** after 5hrs. FID detector is the blue trace and can detect CO and CH_4. Only CO and H_2 is observed. The red trace is the TCD curve which can detect H_2 at ~1.0 minutes (not observed is substantial quantities). The TCD curve shows peak only as noise in the GC spectrum from the heat ramp cycle, backflush, and trace O_2. The y-axis is for the FID curve.

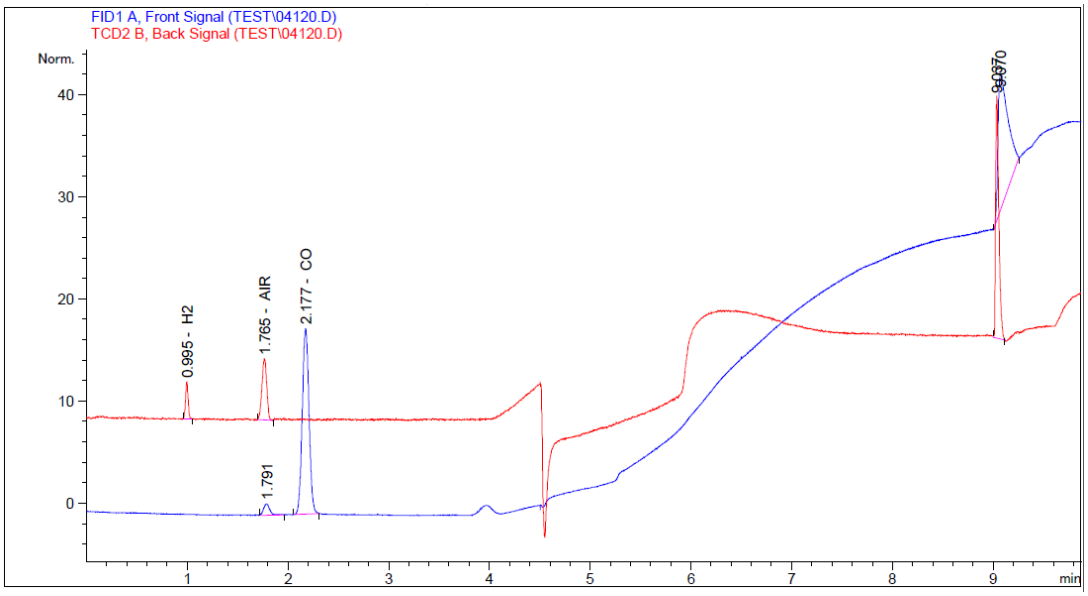

Figure S3: Example GC-trace for photocatalytic reaction with **Catalyst 4** after 5hrs. FID detector is the blue trace and can detect CO and CH_4. Only CO and H_2 is observed. The red trace is the TCD curve which can detect H2 at ~1.0 minutes (not observed is substantial quantities). The TCD curve shows peak only as noise in the GC spectrum from the heat ramp cycle, backflush, and trace O_2. The y-axis is for the FID curve.

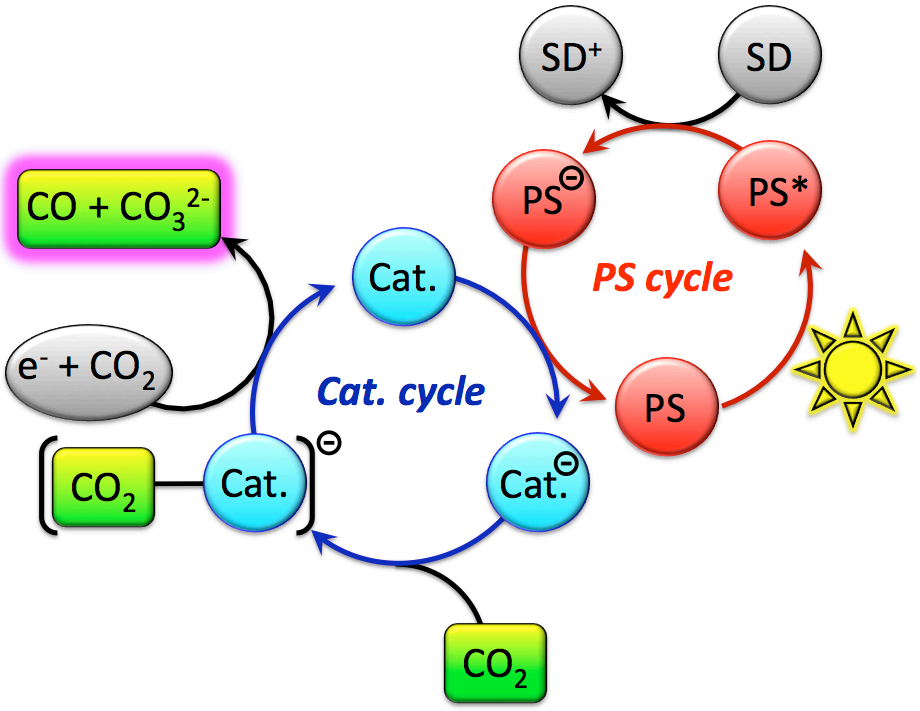

Figure S4: A generic photocatalytic cycle for the reductive disproportionation of CO_2 to CO and CO_3^{2-}.

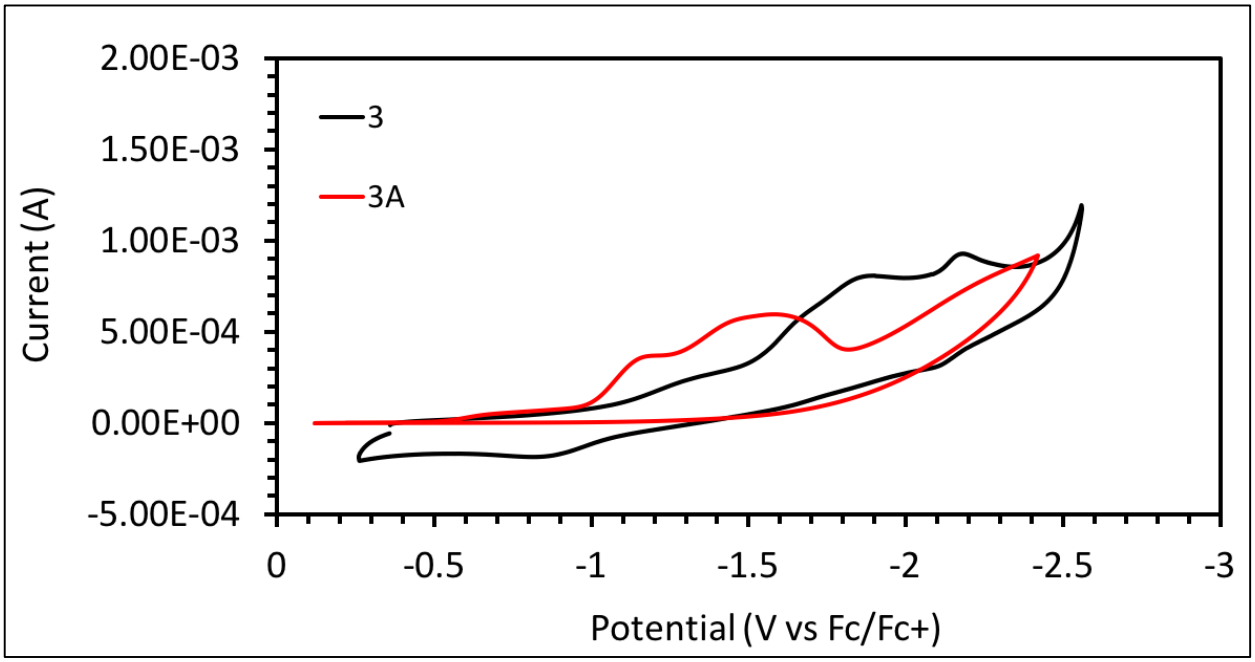

Figure S5. CV of **3** and **3A**. **3A** was prepared in situ through the addition of 1 equivalent of TfOH.

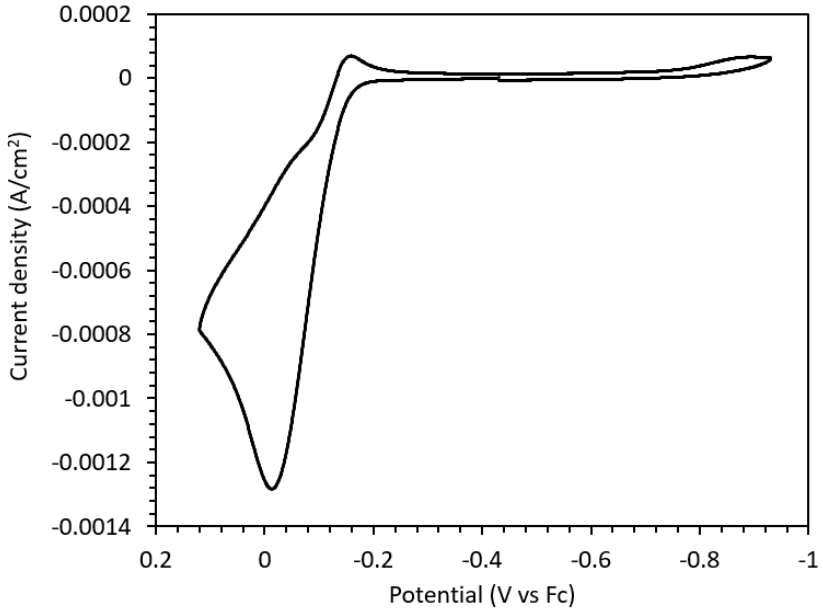

Figure S6: CV of proton sponge in MeCN under Ar atmosphere. 0.1 M Bu_4NPF_6 used as the supporting electrolyte and glassy carbon as the working electrode, and Pt is the counter and pseudo reference electrodes.

Synthetic General Methods. All syntheses were performed under inert atmosphere. All reagents were purchased from commercial sources and were used as is, except where noted. All NMR spectra were obtained on a Bruker AV360 360 MHz spectrometer and are calibrated to the residual solvent peak. IR spectra were measured on a Bruker Alpha ATR-IR spectrometer. UV-vis spectra were measured on a Perkin-Elmer Lambda 35 spectrophotometer. Air-free UV-vis samples were prepared under a nitrogen atmosphere; the spectra were measured in an air-free cuvette. Ultra-dry and air free DMSO used in the pK_a studies was produced by drying anhydrous DMSO over a column of molecular sieves and then distilling at reduced pressure. MS spectra were obtained on a Waters AutoSpec-Ultima NT spectrometer. Elemental analysis was performed by Atlantic Microlab, Inc. The carbene pre-cursor of the pincer ligand was prepared by literature procedure.[3]

Synthesis of Complex 3. 96 mg (436.9 μmol) of $Ni(dme)Cl_2$, 90.2 mg (851.0 μmol) of Na_2CO_3, and 200.5 mg (357.3 μmol) of $[^{Me}NHC\text{-}Py_{OMe}\text{-}NHC^{Me}][PF_6]_2$ were added to an oven-dried Schlenk flask. 4 mL of anhydrous DMSO were added to the flask via cannula transfer. The reaction mixture was heated at 50 °C for 14 hr and then heated at 160 °C for 1 hr. After cooling to room temperature, there is a large amount of precipitate from the reaction mixture. The solid was collected by filtration. The collected solid was sonicated in 10 mL of anhydrous methanol for 10 minutes and then filtered through a frit. The filtrate was placed at 10 °C for 12 hr. A light orange solid precipitated out and was collected by filtration. The solid was washed 3 times with 0.5 mL of cold methanol. The solid was dried under vacuum to yield a light orange solid. (36.4 mg, 29 % yield). ^{1}H-NMR (360 MHz, d_6-DMSO) δ (ppm): 3.87 (6H, s), 6.21 (2H, s), 7.38 (2H, d, J = 1.9 Hz), 7.98 (2H, d, J = 1.9 Hz). ESI-MS(+) m/z: 358.2 ($[M+HCOOH]^+$, M = $[Ni(^{Me}NHC\text{-}Py_O\text{-}NHC^{Me})]^+ = [NiON_5C_{13}H_{12}]^+$ and HCOOH is formic acid from the MS solvent). FT-IR (ATR, solid state) cm^{-1}: 3089 (w), 1639 (s), 1563 (m), 1534 (s), 1513 (s), 1481 (m), 1406 (m), 1310 (m), 1282 (m), 1237 (s), 1075 (m), 962 (m), 860 (w), 828 (w), 732 (s), 694 (m), 610 (w), 417 (m). Elem. Anal. Calcd. for $[NiClON_5C_{13}H_{12}\cdot 2H_2O]$ = (**3**·$2H_2O$): C, 40.61 %; N, 18.22 %; H, 4.19 %. Found: C, 40.29 %; N, 17.83 %; H, 4.01 %. Recrystallized **3** used for EA was the dihydrate (crystallization was done open to air) as confirmed by ^{1}H NMR.

Characterization of Complex 3.

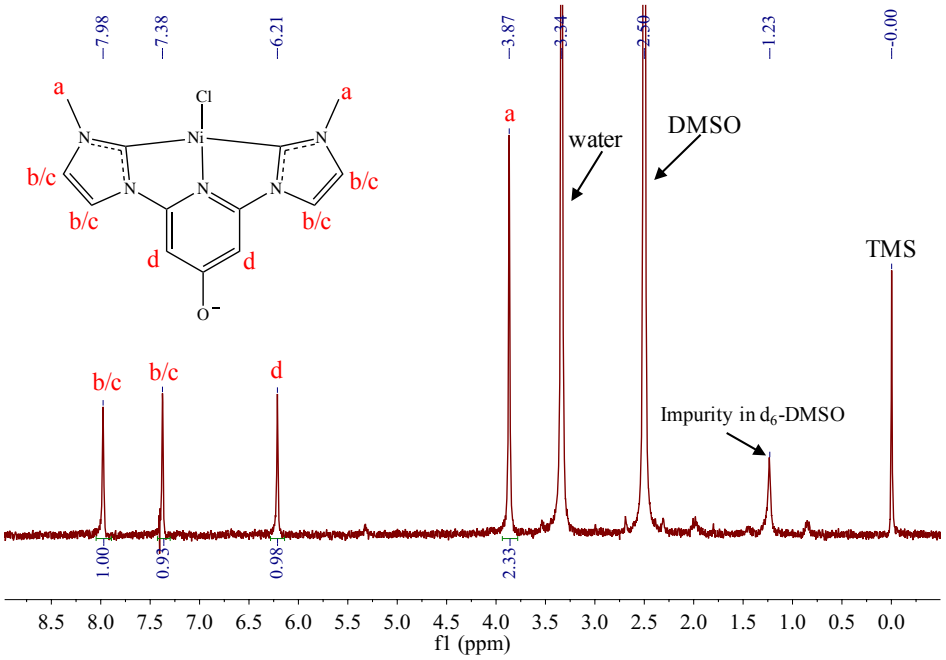

Figure S7. ^{1}H-NMR (360 MHz) spectrum of complex **3** in d_6-DMSO.

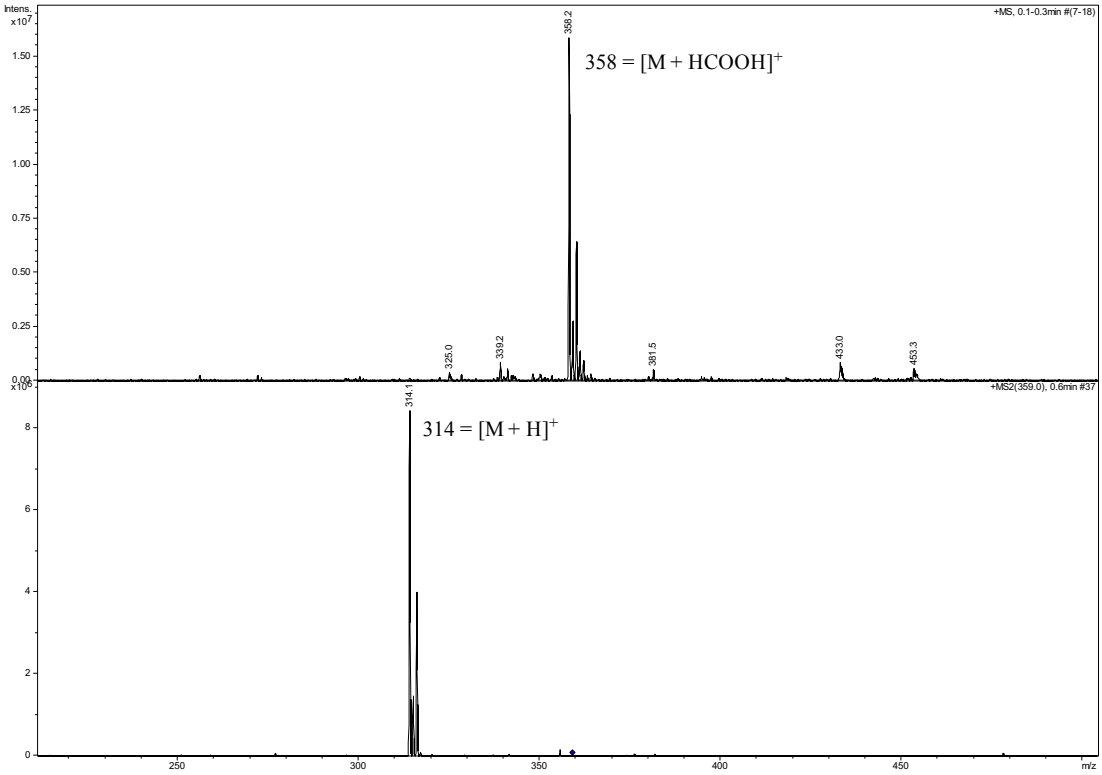

Figure S8. ESI(+)-MS of complex **3** where M is $NiON_5C_{13}H_{12}$ and HCOOH is formic acid from the MS solvent. The bottom pane is MS/MS of the peak in the top pane with m/z of 358.

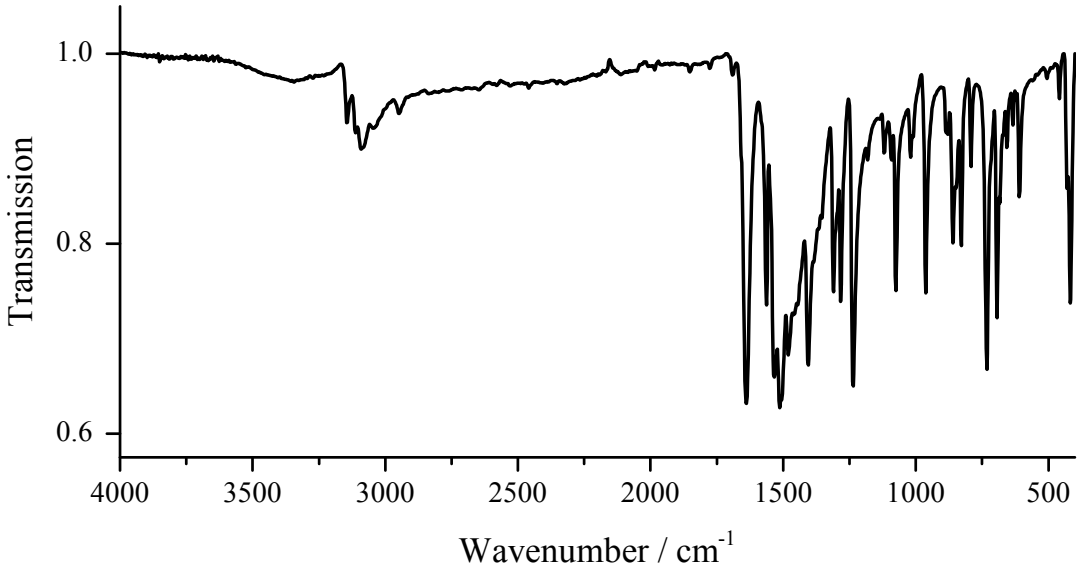

Figure S9. FT-IR (ATR) of complex **3** in the solid state.

Qualitative Tests to Confirm the Presence of a Nickel Bound Inner Sphere Chloride in 3 (vs. an Outer Sphere Chloride).

1. See Figure S10 for the ^{1}H NMR spectra from these experiments:

a. Adding a small amount (0.5 equiv) of AgOTf to complex **3** causes the peaks in the ^{1}H NMR attributed to the pincer to broaden and decrease in intensity. A precipitate is formed that is presumably AgCl. There is also a peak at ~10 ppm which suggests formation of the imidazolium salt, by reprotonating the NHC. We interpret this as a loss of stability upon removing an inner sphere Cl with silver. Removal of an outer sphere Cl would not change the ^{1}H NMR spectrum as much, if at all.

b. By adding 1 equiv of AgOTf to **3** we see similar changes to in part a), but they are more pronounced.

c. Adding AgOTf (10 eq) to **3** leads to a precipitate and a shift in all the peaks in the ^{1}H NMR. Once again, removal of an inner sphere chloride appears to have occured. Also, with excess Ag(I) present, the NMR also suggests that a silver pincer complex was formed, the location of the peaks matches that for similar NHC complexes of silver (Papish *et al. Organometallics*, **2017**, *36*, 1091) (Danopoulos *et al. Dalton Trans*. 2008, 1087). Note that the Danopoulos paper had silver(I) displacing Ni(II) to form a silver complex, as we propose here.

2. Adding CH_3CN does not lead to a change of the ^{1}H NMR spectrum in DMSO (Figure S13). This suggests that acetonitrile does not readily displace the bound halide ligand. If a water ligand was bound to Ni(II), it might be readily displaced by acetonitrile.

We believe the combined evidence above supports that **3** is [(pincer)NiCl] with an inner sphere chloride.

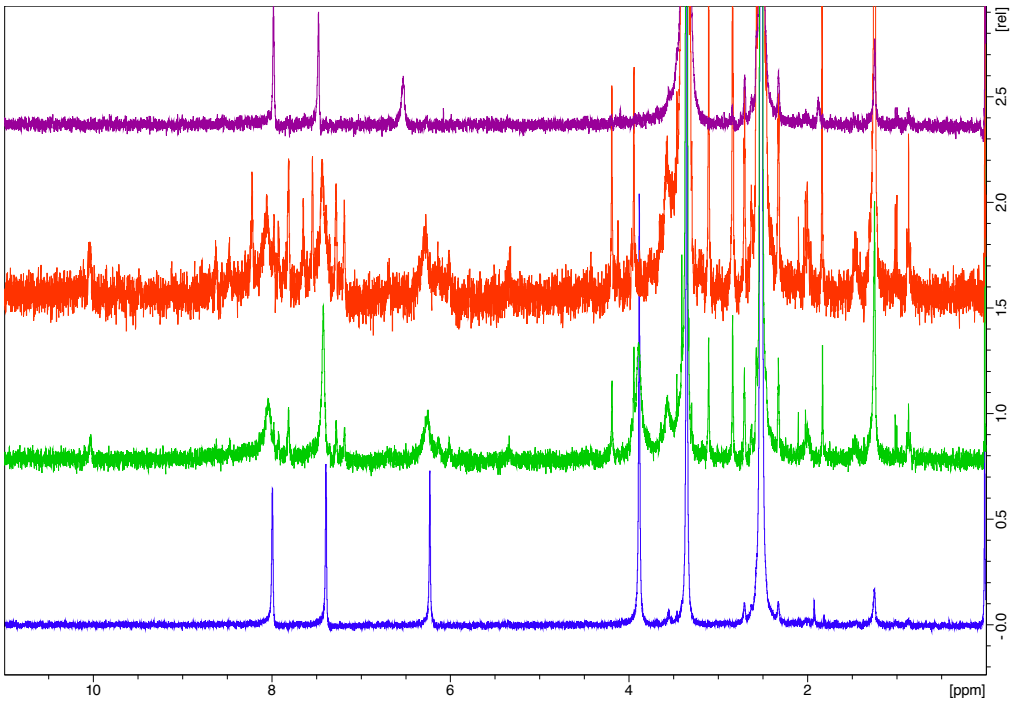

Figure S10. ^{1}H-NMR (360 MHz) spectra of complex **3** in d_6-DMSO (blue spectrum) with the addition of 0.5 equivalents of AgOTf (green spectrum), 1.0 equivalents of AgOTf (red spectrum), and 10 equivalents of AgOTf (purple spectrum).

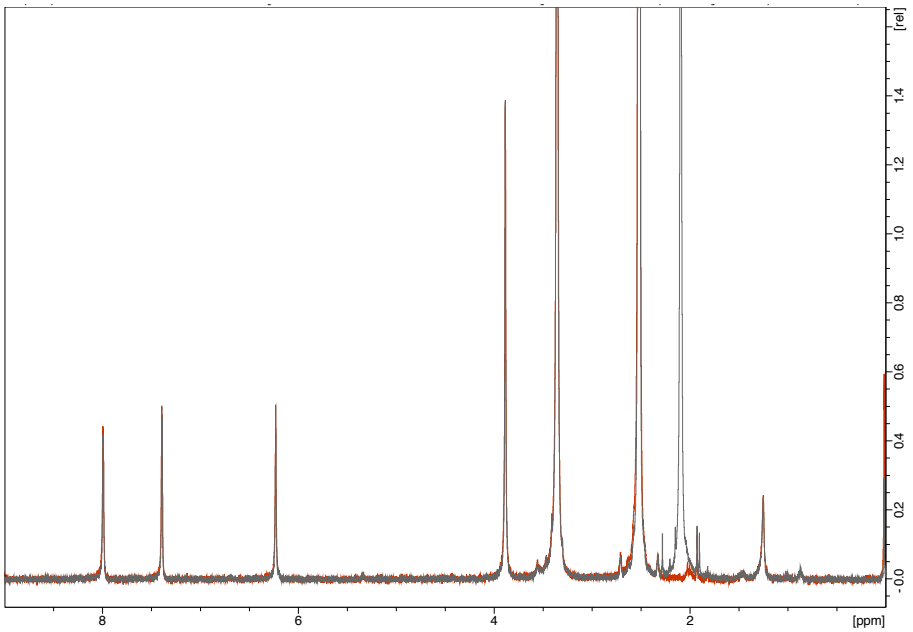

Figure S11. ^{1}H-NMR (360 MHz) spectra of complex **3** in d_6-DMSO (red spectrum) with the addition of 10 equivalents of acetonitrile (grey spectrum). The additional peak at ~2 ppm is free acetonitrile and there is no evidence of Ni(II) bound acetonitrile.

pK_a Studies of Complex 3.

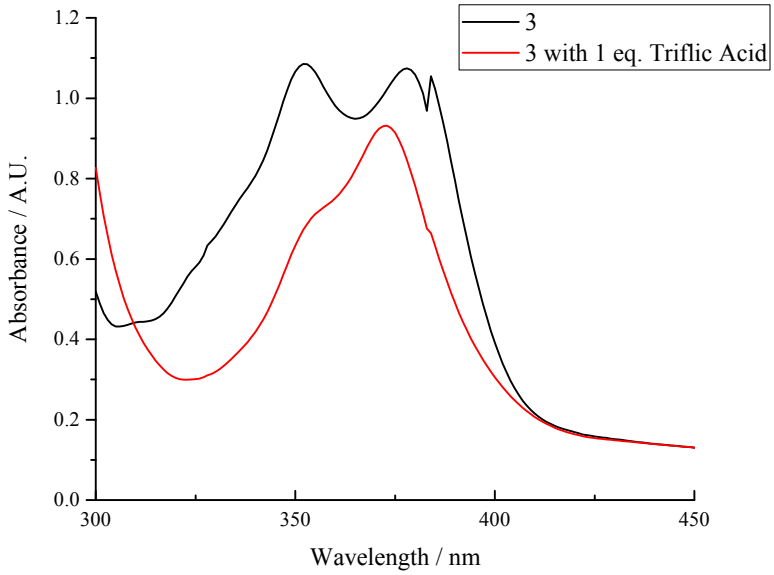

Figure S12. UV-vis spectra of complex **3** (0.26 mM) in DMSO with the addition of a 0.08 M triflic acid solution in DMSO.

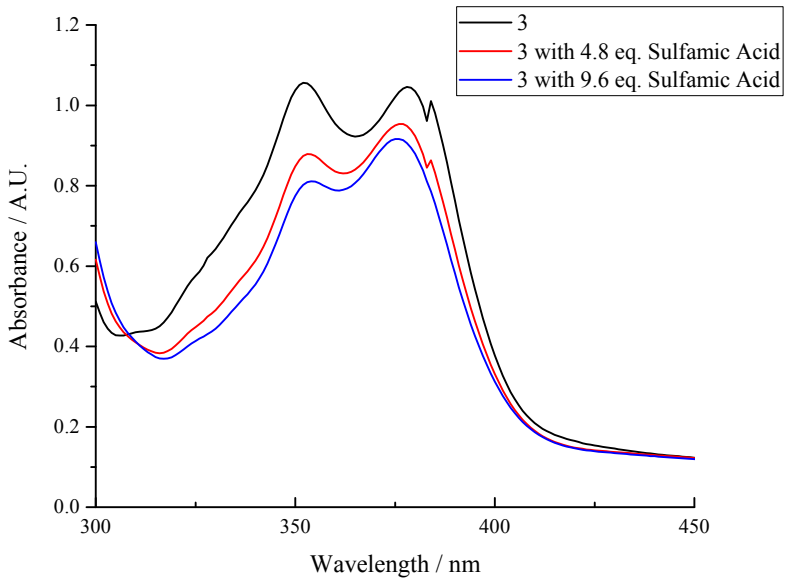

Figure S13. UV-vis spectra of complex **3** (0.26 mM) in DMSO with the addition of a 0.08 M sulfamic acid solution in DMSO.

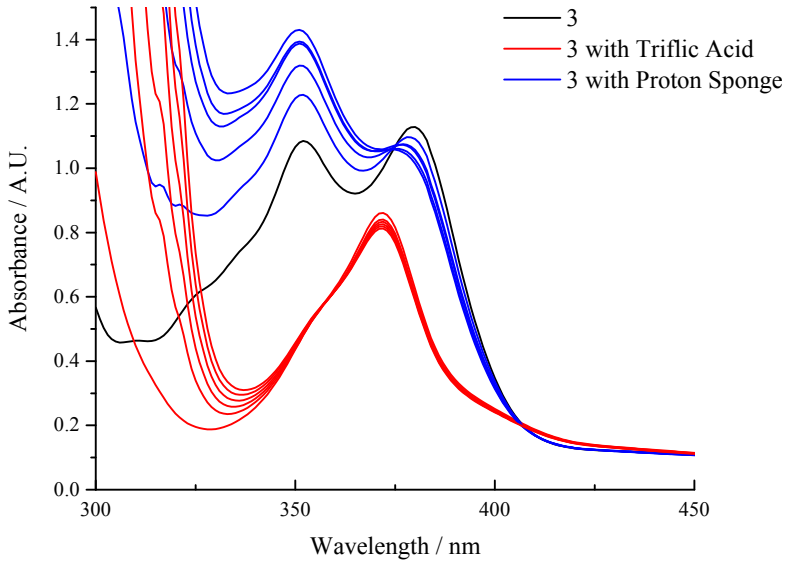

Figure S14. UV-vis spectra of complex **3** (0.28 mM) in DMSO with the alternating addition of triflic acid (1 eq., red spectra) and proton sponge (1 eq., blue spectra), showing the reversibility of the protonation and deprotonation. The increase in intensity of the peak at ~345 nm during each cycle is likely due to a slight excess of proton sponge added. (Proton sponge has a strong, broad absorption with a λ_{max} at 340 nm)

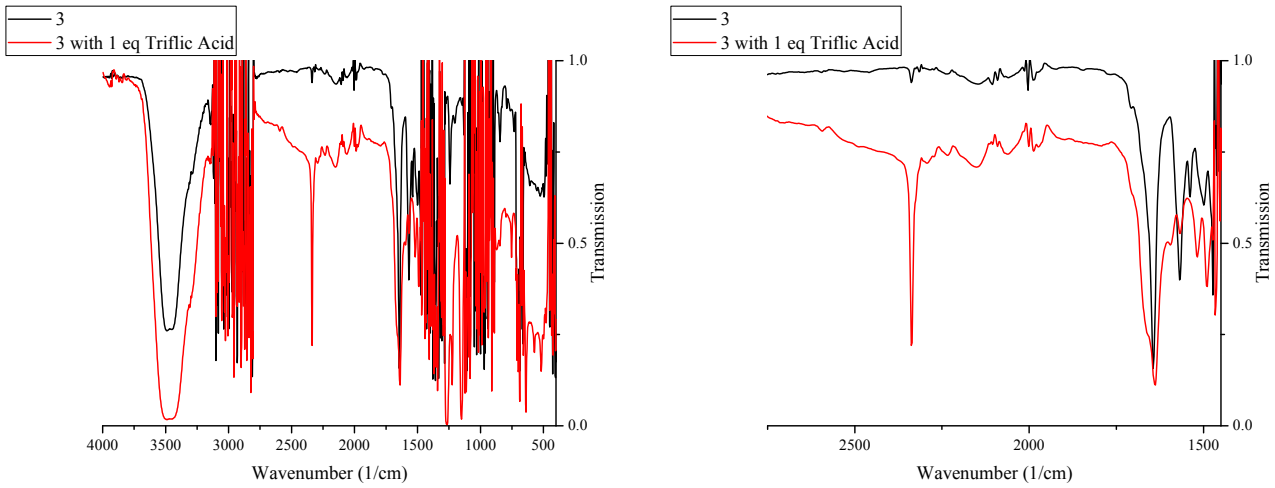

Figure S15. FT-IR spectra of complex **3** (8.3 mM) in DMSO (black spectra) with the addition of 1 equivalent of triflic acid (red spectra). The large areas of excessive noise are due to the absorptions of the solvent, DMSO (See Figure S16). The peak at 1568 cm^{-1}, assigned to the C=O stretch, decreased with the addition of triflic acid, while the peak at 1638 cm^{-1}, assigned to the C=C stretch, remained approximately unchanged.

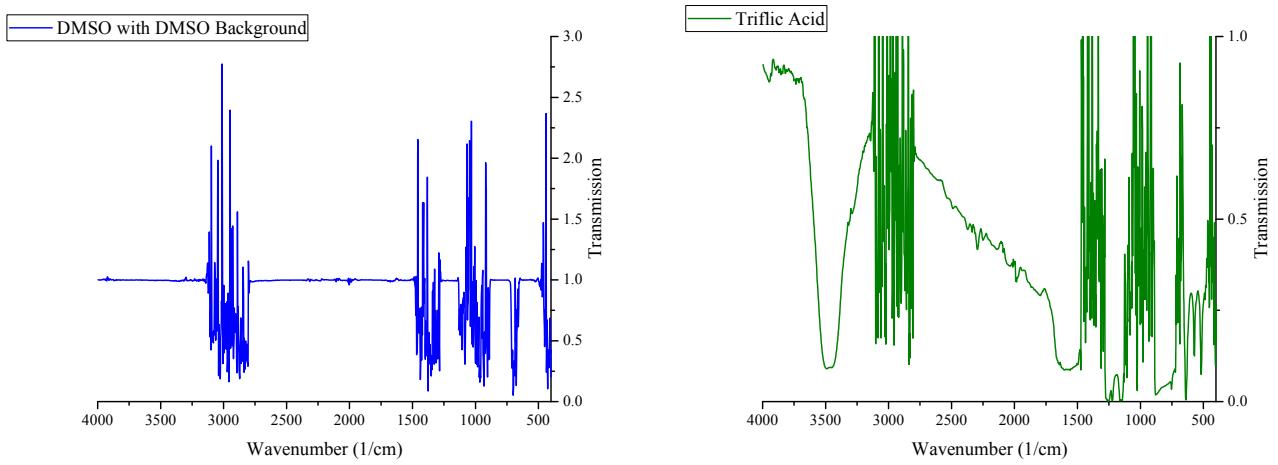

Figure S16. (Left) FT-IR spectrum of DMSO after a background of DMSO was taken. (Right) FT-IR spectrum of triflic acid in DMSO.

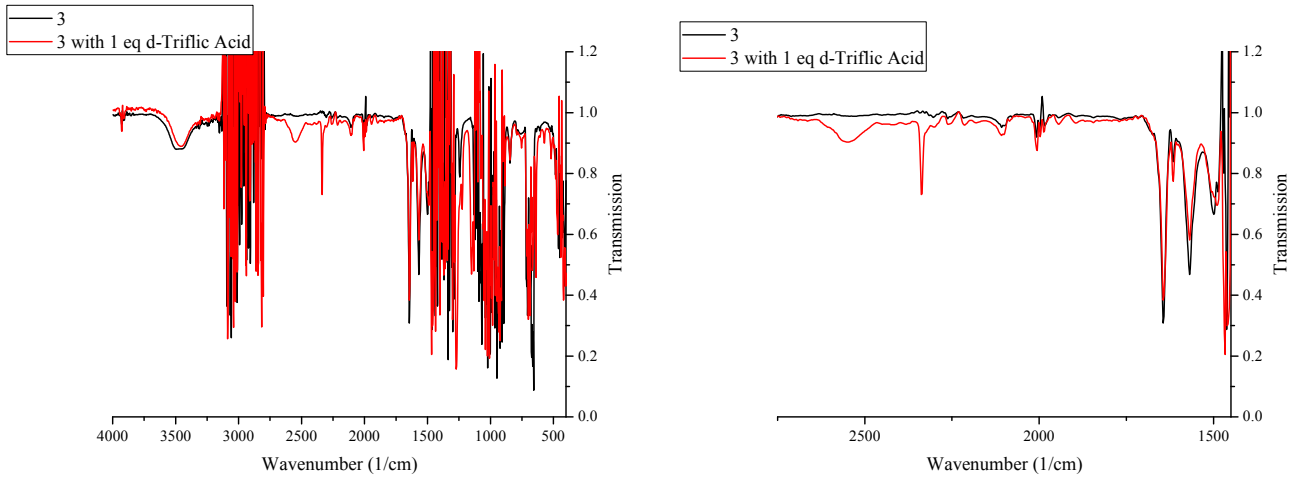

Figure S17. FT-IR spectra of complex **3** (5.5 mM) in DMSO (black spectra) with the addition of 1 equivalent of deuterated-triflic acid (red spectra). The large areas of excessive noise are due to the absorptions of the solvent, DMSO (see Figure S16). The peak at 2556 cm^{-1} is the OD stretch. The peak at 1568 cm^{-1} also decreased.

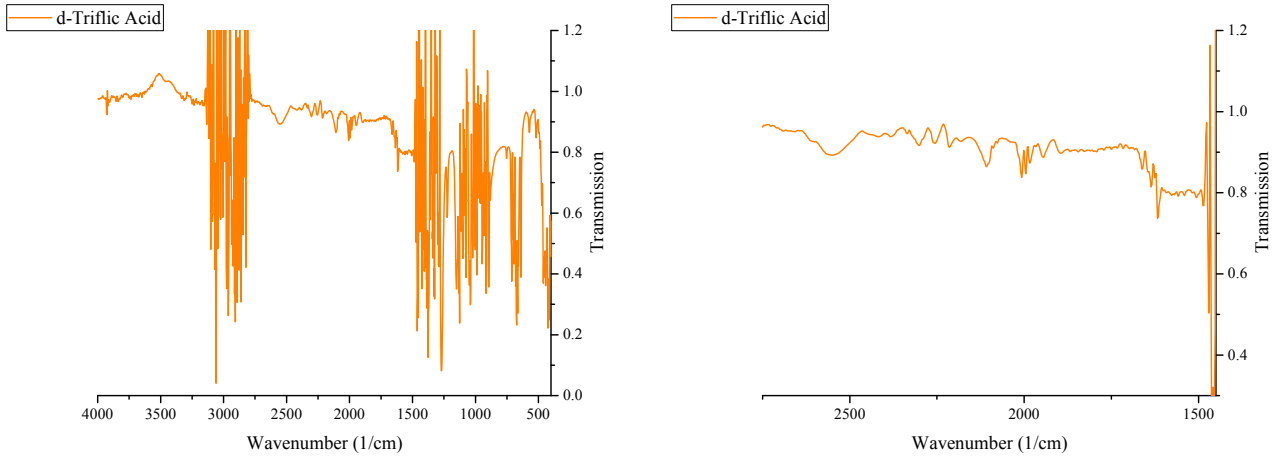

Figure S18. FT-IR spectrum of d-triflic acid in DMSO.

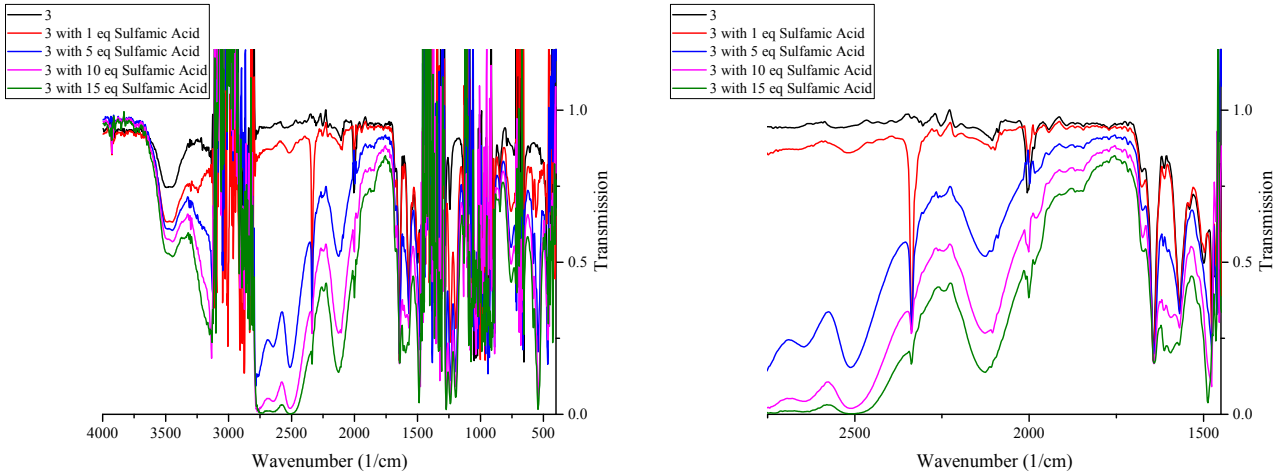

Figure S19. FT-IR spectra of complex **3** (6.5 mM) in DMSO (black spectra) with the addition of multiple equivalents of sulfamic acid. The large areas of excessive noise are due to the absorptions of the solvent, DMSO (See Figure S16). Unfortunately, sulfamic acid has large absorptions in the IR (see Figure S20), so any change in the peak at 1568 cm^{-1} is obscured.

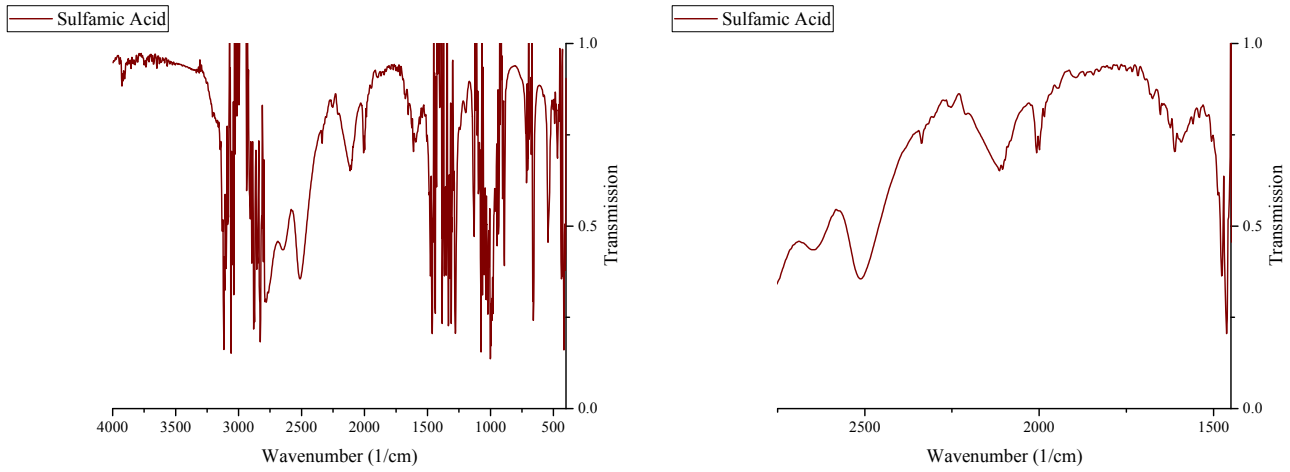

Figure S20. FT-IR spectrum of sulfamic acid in DMSO.

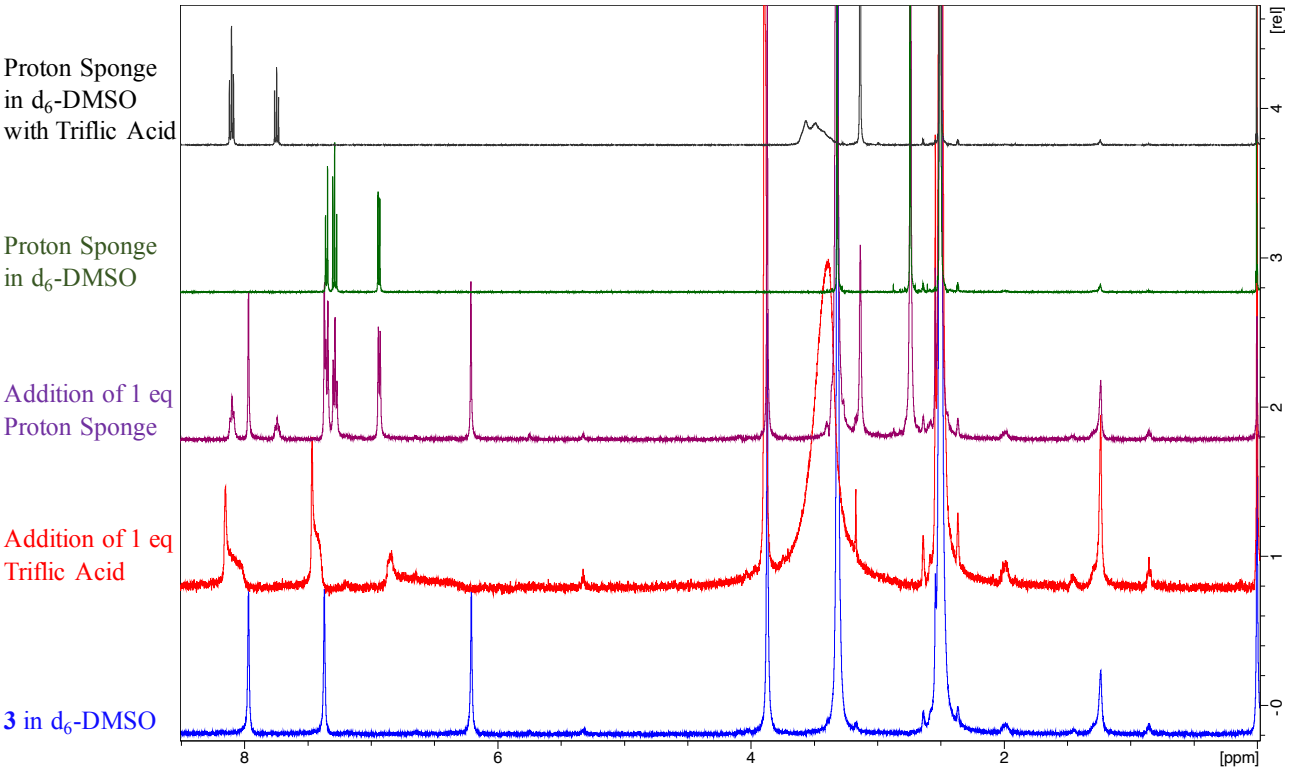

Figure S21a. ^{1}H-NMR spectra of a solution of complex **3** in d_6-DMSO (blue spectrum) with the addition of 1 equivalent of triflic acid (red spectrum), followed by the addition of 1 equivalent of proton sponge (violet spectrum). The NMR spectra of proton sponge (green spectrum) and proton sponge with the addition of triflic acid (black spectrum) in d_6-DMSO are also shown.

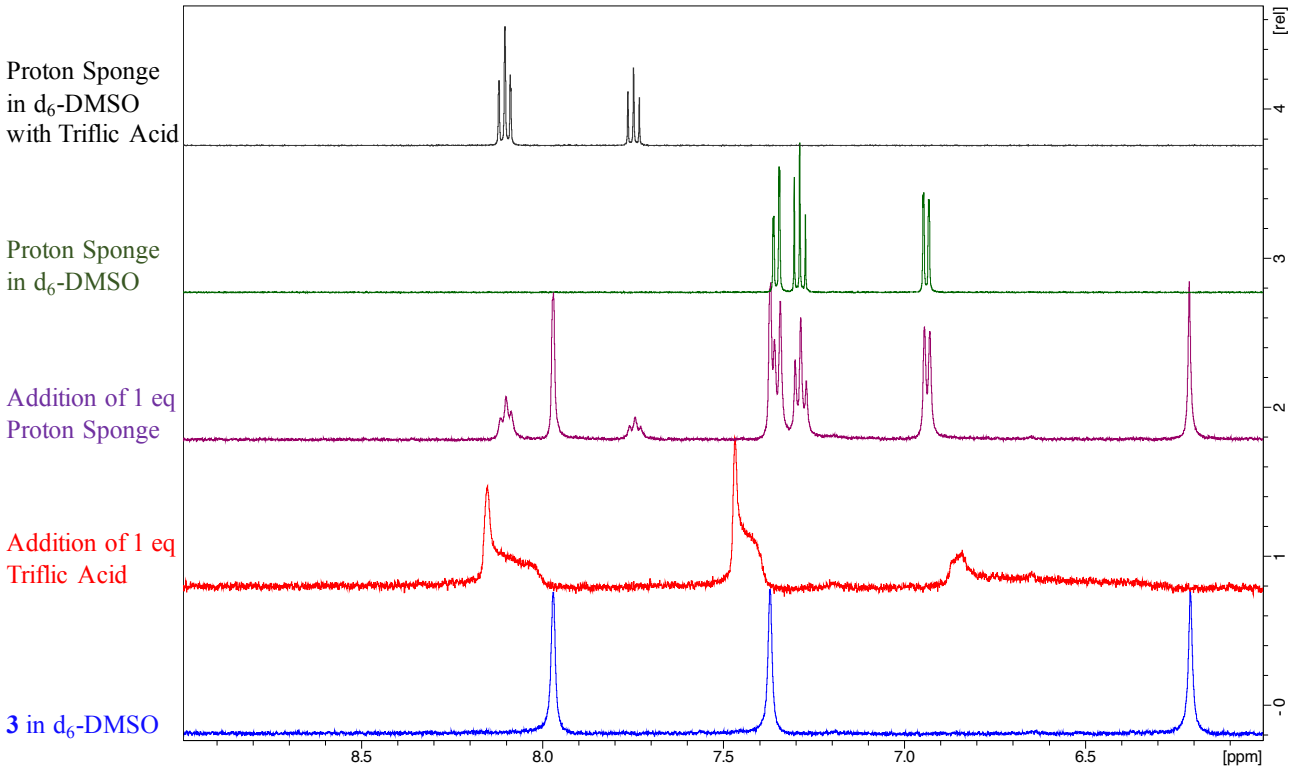

Figure S21b. The aromatic region of the ^{1}H-NMR spectra shown in Figure S21a. Upon the addition of acid (blue spectrum to red spectrum), all of the peaks shift downfield, with the proton of the pyridinol ring shifting the most (6.21 ppm to 6.98 ppm). This is consistent with the proton's environment changing from an alkene in the quinoidal deprotonated form to aromatic in the pyridinol protonated form. With the addition of base to the solution (red spectrum to violet spectrum), the peaks shift back to the original chemical shifts of the deprotonated complex **3**; this demonstrates the reversibility of the protonation and deprotonation.

Isolation and Characterization of Complex 3A.

To a solution of complex **3** (5.8 mg, 17 µmol) in DMSO (2.0 mL), 1 equivalent of triflic acid was added. The solution immediately changed from light orange to light yellow. After sitting undisturbed for 48 hr, a bright yellow solid had precipitated out of the solution. The solid was collected by filtration and washed 3 times with 0.5 mL of dichloromethane. <1 mg of the solid was recovered. The characterization data of the solid follow.

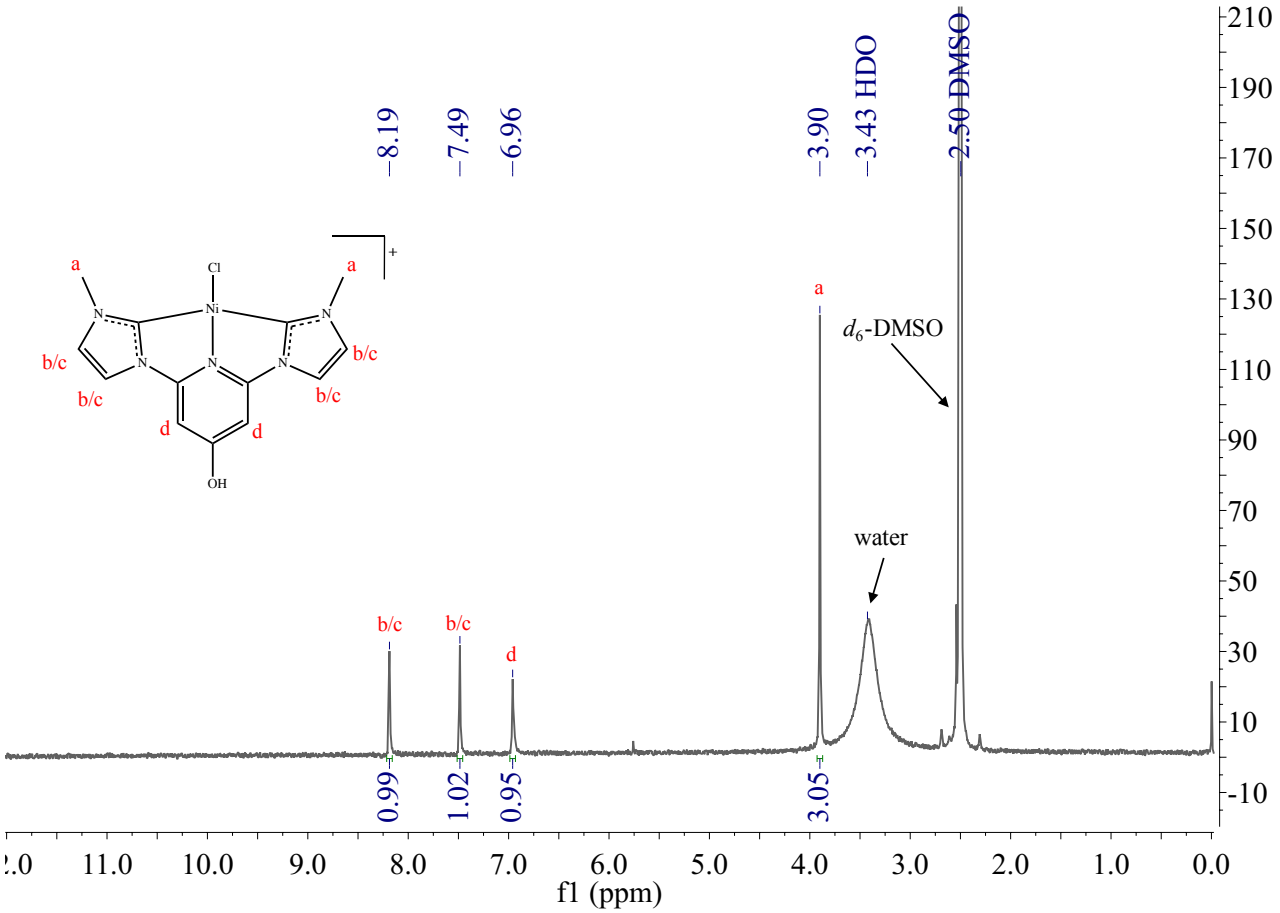

Figure S22. ^{1}H-NMR (360 MHz) spectrum of complex **3A** in d_6-DMSO.

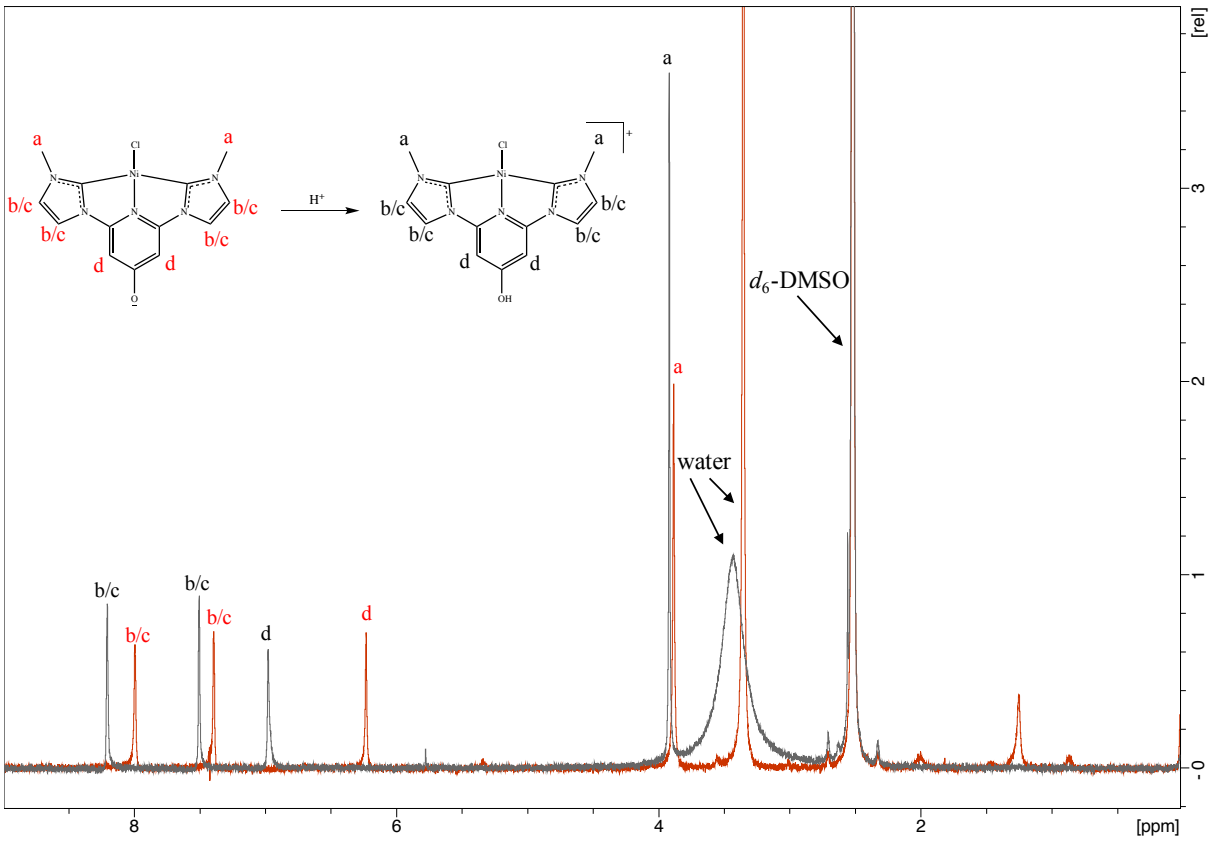

Figure S23. Overlayed ^{1}H-NMR spectra of complexes **3** (crimson spectrum) and **3A** (grey spectrum) in d_6-DMSO. As observed with the in situ-generated protonated complex **3A** (Figure S21), all of the proton peaks of complex **3A** are shifted downfield relative to complex **3**. The largest shift is the pyridinol proton (labeled "d"). The residual water peak in the solvent has also broadened significantly in the spectrum of **3A**. This is commonly observed with compounds containing a hydroxyl group.

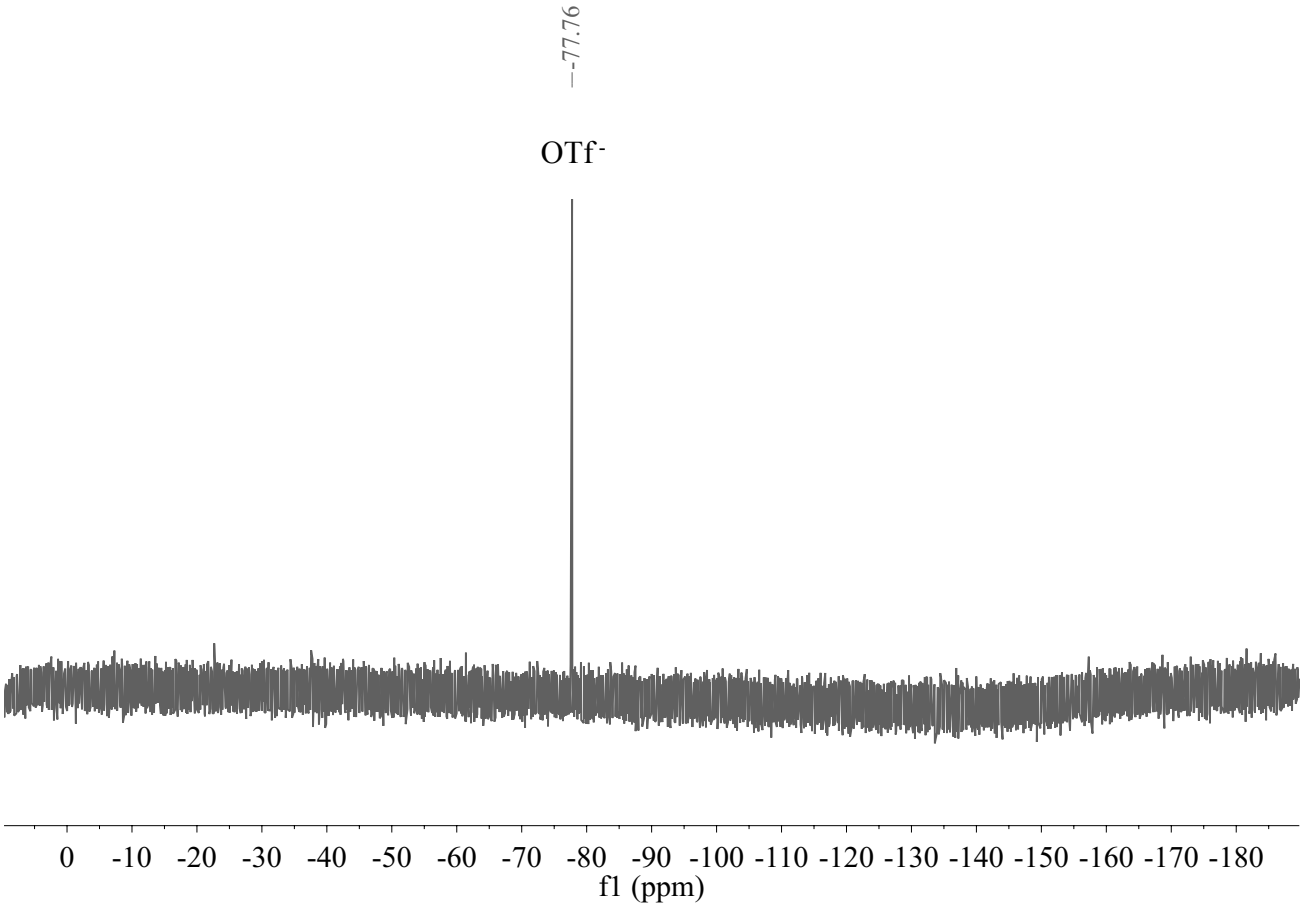

Figure S24. ^{19}F-NMR (338.8 MHz) spectrum of complex **3A** in d_6-DMSO.

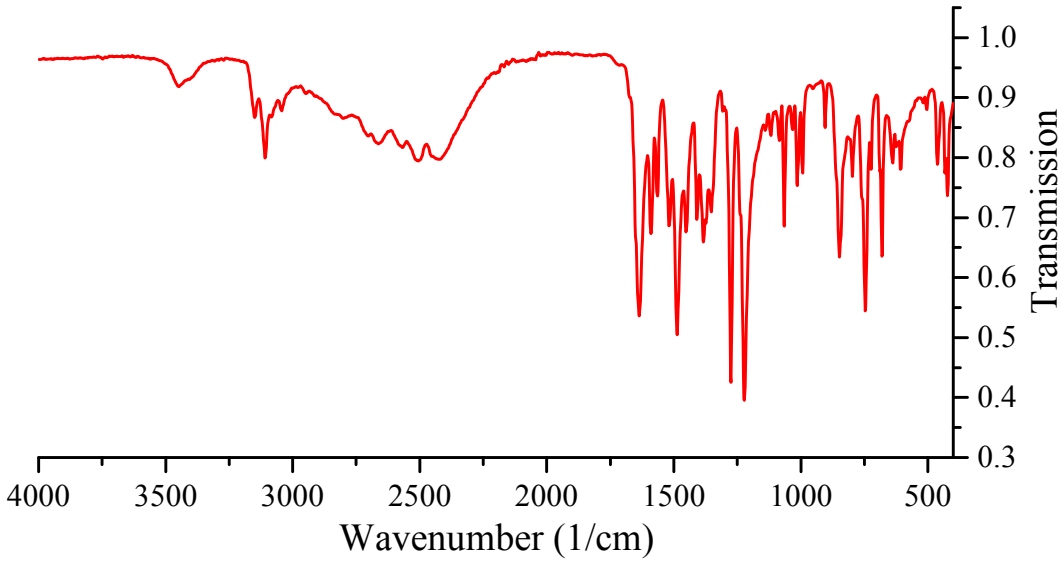

Figure S25. FT-IR (ATR) spectrum of complex **3A** in the solid state.

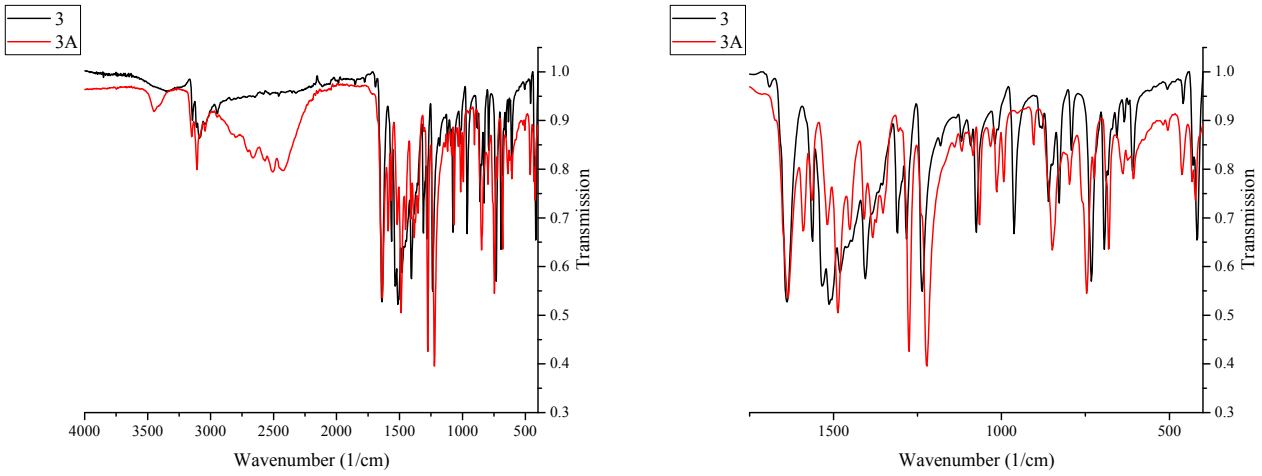

Figure S26. FT-IR (ATR) spectra of complexes **3** (black spectrum) and **3A** (red spectrum) in the solid state. The peak at 1568 cm^{-1}, assigned to the C=O stretch, is diminished in **3A** compared to **3**. The peak at 1638 cm^{-1}, assigned to the C=C stretch, remains constant in both spectra. A new peak at 3455 cm^{-1} appears in the spectrum of **3A**, corresponding to the OH stretch. The broad peaks from ~2300 cm^{-1} to ~3000 cm^{-1} in the spectrum of **3A** are probably due to the triflate counterion.

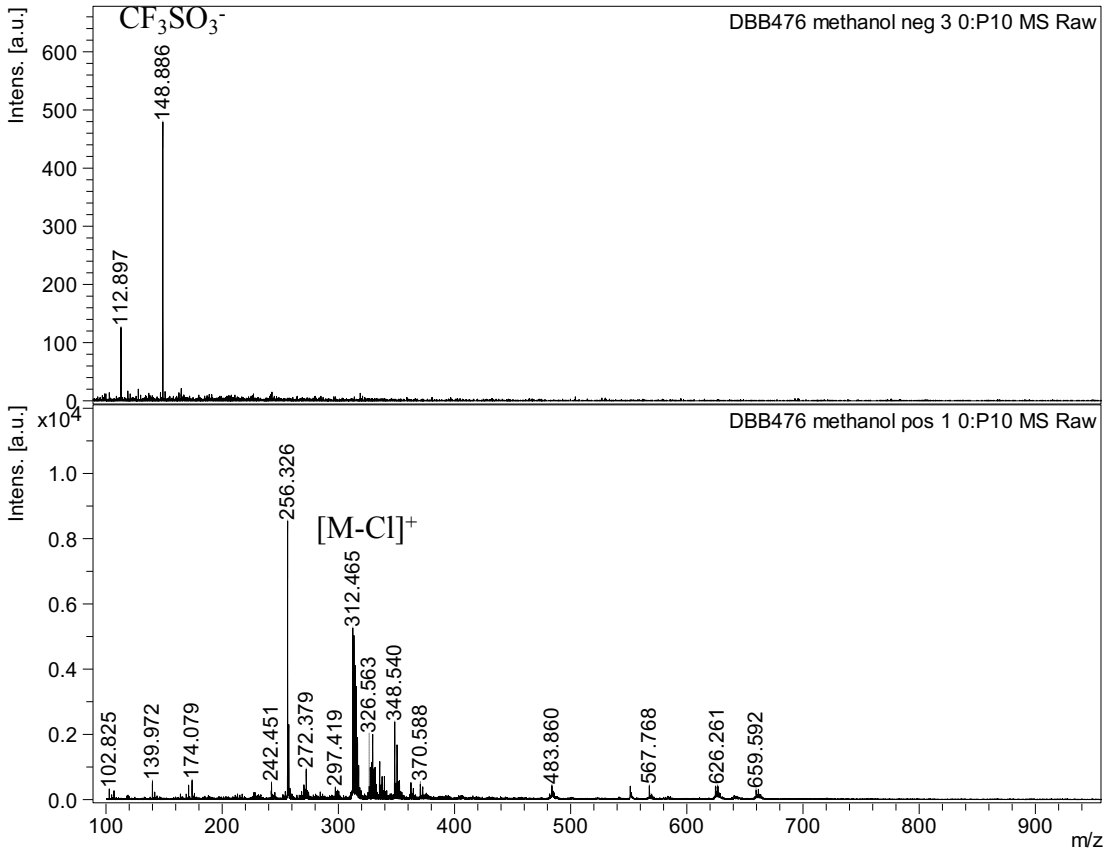

Figure S27a. MALDI-MS spectrum of complex **3A**. (Top) Spectrum in negative mode. $[CF_3SO_3]$- is the triflate counterion. (Bottom) Spectrum in positive mode. M is $NiClON_5C_{13}H_{12}$.

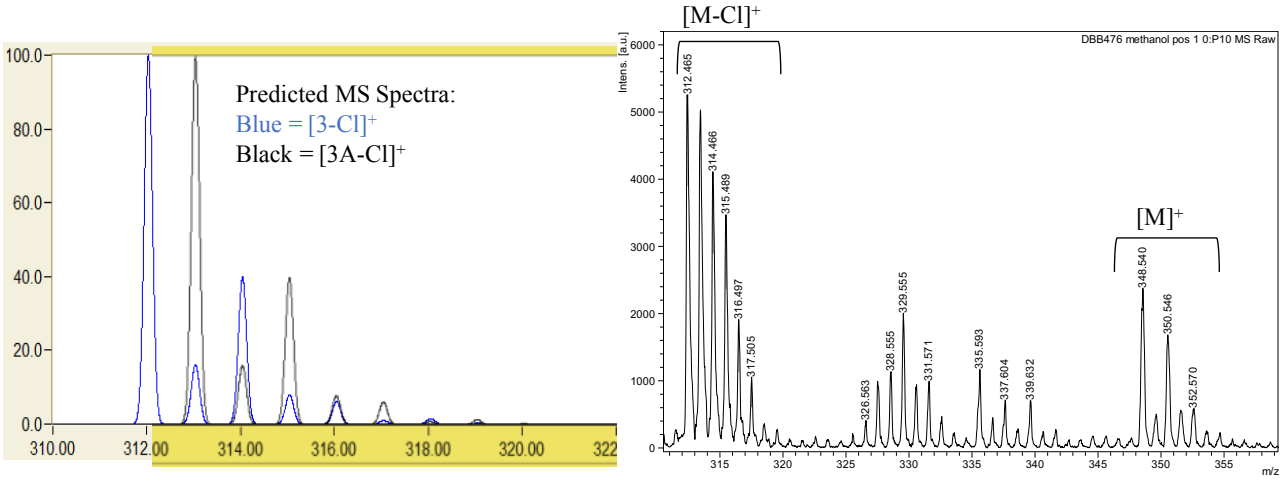

Figure S27b. MALDI-MS spectrum of complex **3A**. (Left) Predicted isotopic pattern of a 50:50 mix of **3** and **3A**, with a chloride lost. (Right) MALDI-MS spectrum of **3A**. The $[M\text{-}Cl]^+$ peak corresponds to a ~1:1 ratio of **3** to **3A**, which matches the predicted pattern on the right. Deprotonation of **3A** to yield **3** could occur in the solvent of the MS.

Summary of Data from pK_a Studies.

All of the data presented above are consistent with a reversible protonation of complex **3** upon the addition of triflic acid. The UV-vis spectra reversibly switch back-and-forth upon successive additions of triflic acid and proton sponge. In the IR spectra, the peak at 1568 cm^{-1}, assigned to the C=O stretch (corroborated by computations, vide infra), decreases in intensity with the addition of triflic acid, both in situ and in the isolated complex **3A**. In the ^{1}H-NMR spectra, the peaks all shift downfield with the addition of triflic acid to complex **3**, with the pyridinol proton being the most affected. These changes in the chemical shifts in the ^{1}H-NMR are reversible, as observed with the successive additions of triflic acid and proton sponge.

Computational Methods

All computations were carried out using the Gaussian 09[4] implementation of B3LYP[5, 6] or PBEPBE[7, 8] (with auto-fitting functions)[9, 10]. The basis set for nickel was the Hay and Wadt basis set (BS) and effective core potential (ECP) combination (LANL2DZ)[11, 12] as modified by Couty and Hall[13] where the two outermost p functions have been replaced by a (41) split of the optimized nickel 4p function. The basis set for chlorine was the [LANL2DZ(d,p)][11, 12, 14] basis set (BS) and effective core potential (ECP) combination. The 6-31G(d')[15, 16] basis sets were used for all other atoms. Spherical harmonic d functions were used throughout, *i.e.*, there are 5 angular basis functions per d function. This basis set combination is referred to as BS1. All geometries were fully optimized with corresponding analytical frequency computations to ensure a zeroth-order saddle-point was achieved. Solvent optimizations utilized the IEF-PCM solvation model with UAKS radii and parameters consistent with either acetonitrile or DMSO (for determination of pK_a only) as the solvent. The free energy of a proton in DMSO (–280.0 kcal mol^{-1}) was determined using the following equation:

$$G_{H^+}^{soln} = G_{H^+}^{gas} + G_{H^+}^{solv}$$

where $G_{H^+}^{gas}$ is the gas-phase free energy of a proton (–6.28 kcal mol^{-1}),[17] $G_{H^+}^{solv}$ is the recommended free energy of solvation of a proton in DMSO (–273.7 kcal mol^{-1}),[18] and $G_{H^+}^{soln}$ is the solution free energy of a proton.

Results

Complex **3** contains a monoanionic pincer that could be formally represented as a phenoxide. Computations with no geometry constraints result in a bonding pattern that is more consistent with a quinonidal resonance form, which contains more C–O double bond character and places the formal negative charge on the N_{py} atom. The C–O bond length is significantly shorter in **3** compared to **3A** (1.25 vs 1.33 Å), indicating that there is increased double-bond character between carbon and oxygen. Reduction events and deprotonation of any species results in increase in negative charge on O, N_{py}, and Ni. One-electron reduction from **3A** to **3A^0** or **3** to **3**$^-$ results in a gain of a full –1 charge. These reduction events lead to a significant increase in negative charge for the Cl. Other atoms (Ni, N_{py}, C, and O) also have increases their negative charge. Dechlorination (**3A^0** to **5A** or **3**$^-$ to **5**) results in a significant loss in negative charge for Ni and a small increase in negative charge on N_{py}. Dechlorination results in no change in charge for oxygen (**3A^0** to **5A**) or a decrease in negative charge (**3**$^-$ to **5**). Dechlorination from **3A^0** to **5A** results in a loss of a full –1 charge from the complex. However, since the charge of Cl in **3A^0** is ~–0.79, there is a net loss of ~0.21 units of negative charge from all other atoms in **3A^0** upon production of **5A**.

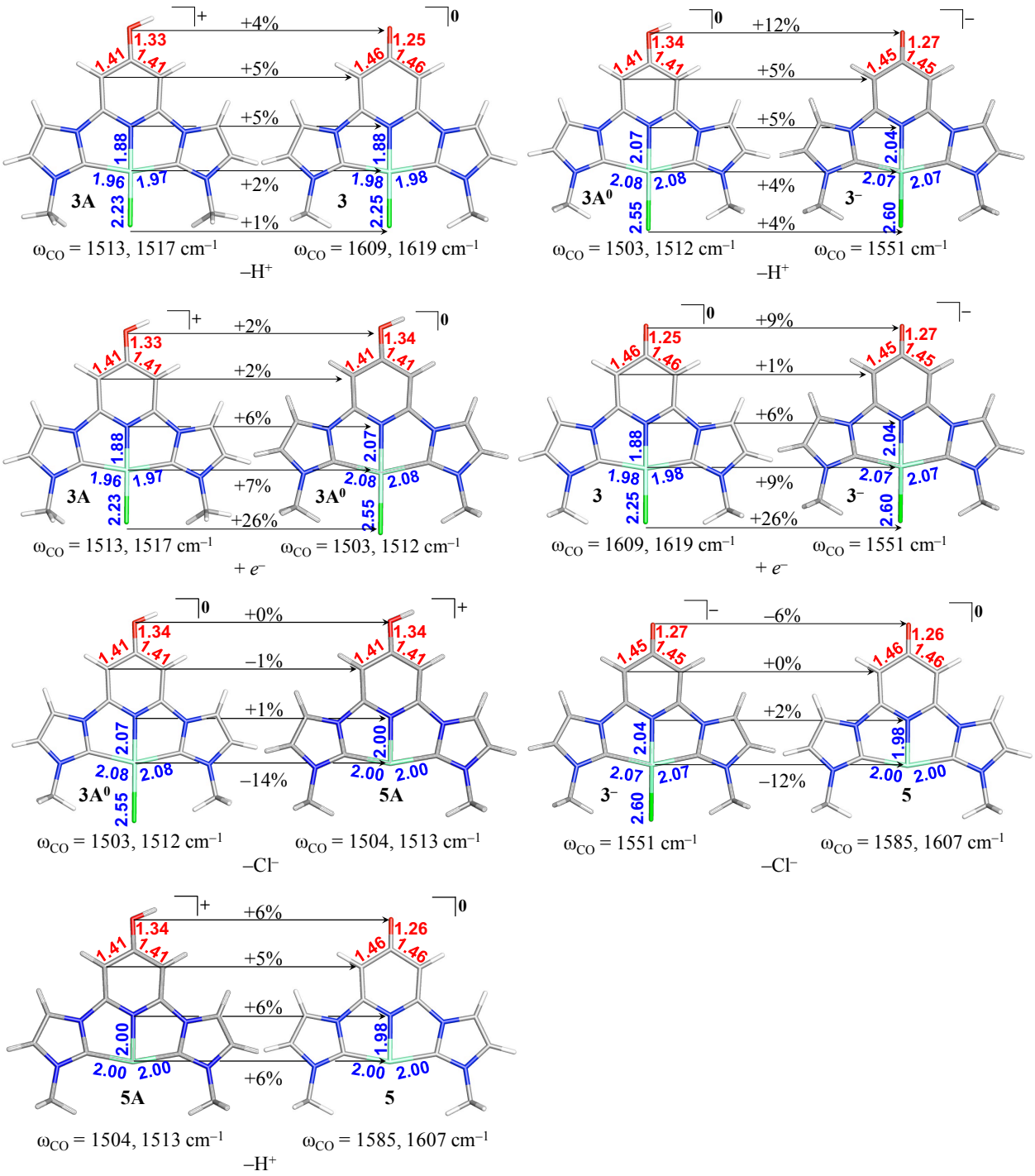

Figure S28: Changes in select bond lengths (Å), ω_{CO} (cm^{-1}), and percent change in negative charge, % (as measured by change in NAO charges for protonation, reduction, or chloride dissociation events) with PCM-B3LYP/BS1. Percentages reflect the changes in negative charge for the designated atoms.

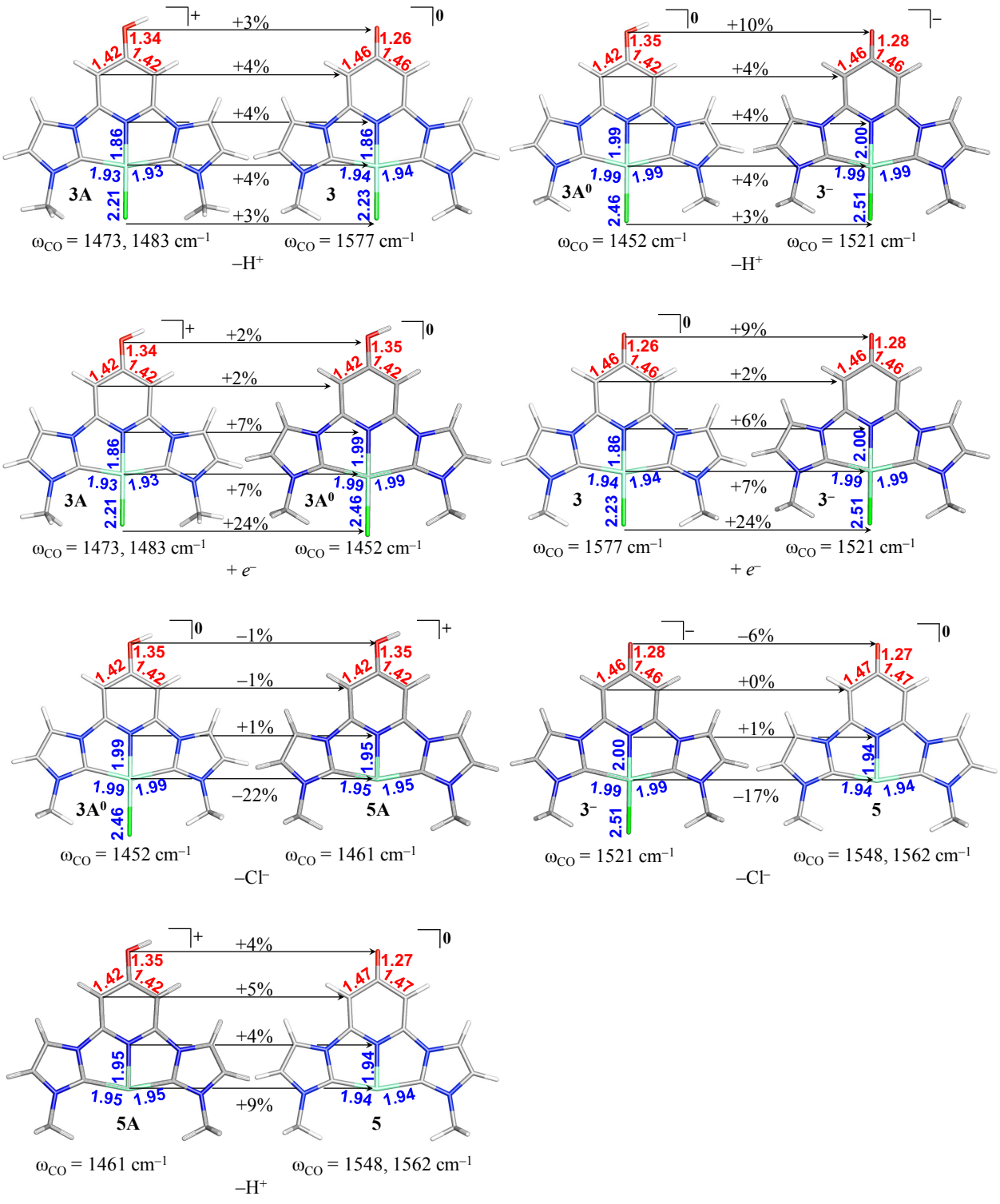

Figure S29: Changes in select bond lengths (Å), ω_{CO} (cm^{-1}), and percent change in negative charge, % (as measured by change in NAO charges for protonation, reduction, or chloride dissociation events) with PCM-PBEPBE-auto/BS1. Percentages reflect the changes in negative charge for the designated atoms.

For the reaction **3A** ⇌ **3** + H^+, ΔG_{rxn} is determined from:

$$\Delta G_{rxn} = (G_{\mathbf{3}} + G_{H^+}) - (G_{\mathbf{3A}})$$

Using the relationship between ΔG and the equilibrium constant, *K*:

$$K = e^{(-\Delta G_{rxn}/RT)}$$

where R = 1.9858775 x 10^{-3} kcal K^{-1} mol^{-1} and T = 298.15 K, the pK_a of **3A** in DMSO is computed to be 3.9.

Carbonyl Stretching Frequencies

Table S1 provides the computed ω_{CO} for **3**, **3A**, and select carbonyl containing compounds from the literature. Including PCM solvation consistently shifts the computed ω_{CO} to lower energy. The computed ω_{CO} of **3** and **3A** are significantly lower in energy compared to other compounds containing the C=O moiety, but the shift to lower a lower energy in a solvent field is consistent throughout. Computed ω_{CO} correlates quite well with experimental ν_{CO} using either B3LYP/BS1 or PCM-B3LYP/BS1 (Figure S30). Results for complex **3A** (which is a monocation) are not included in the plot in Figure S30. We can speculate that ion-pairing effects will significantly alter the observed stretching frequency and no attempt has been made to model those effects in the computations.

Table S1: ω_{CO} and ν_{CO} of **3**, **3A**, and select carbonyl containing compounds (in cm^{-1})[19, 20]

Compound	ω_{CO}^{gas}		ω_{CO}^{MeCN}		ν_{CO}^{Expt}
3	1695(1)	1722(919)	1619(804)	1619(859)	1513
3A	1529(86)		1517(341)	1517(338)	1609
3^{-}	n.d.		1551(1218)		n.d.
3A^{0}	n.d.		1503(175)	1512(247)	n.d.
acetone	1822(163)		1772(336)		1731
cyclobutanone	1889(284)		1827(562)		1775
cyclopentanone	1844(226)		1787(446)		1750
cyclohexanone	1819(202)		1763(441)		1715
anthrone	1742(194)		1690(510)	1646(239)	1662
2,5-cyclohexadiene-1,4-dione	1756(365)		1716(1092)		1669

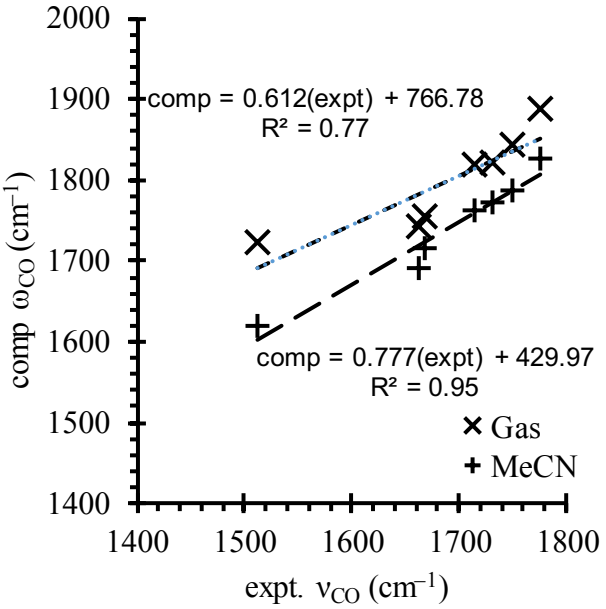

Figure S30: Computed ω_{CO} vs experimental ν_{CO} for neutral carbonyl containing compounds.[19, 20]

Generation of Catalyst and Binding CO_2

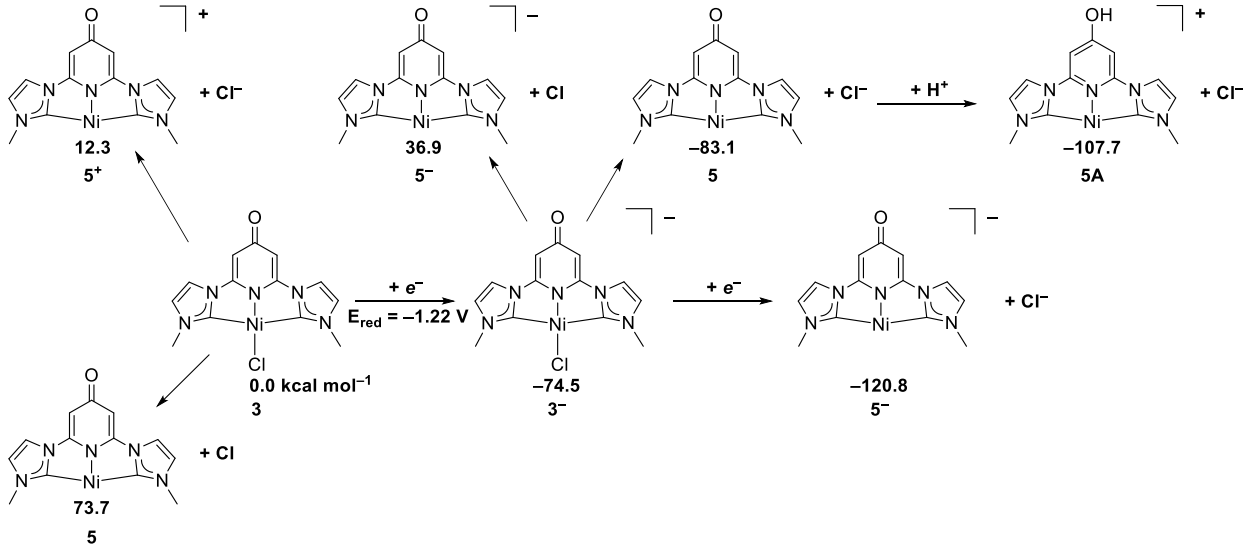

Figure S31: Possible electrochemical events with **3** for generation of species responsible for catalysis in acetonitrile (PCM-B3LYP/BS1). Reduction potential is reported vs NHE in acetonitrile.

For one-step reactions involving **3** and **5**, protonation of the O atom is the most favored. In the presence of TfOH acid, some nickel chlorides are known to exchange the chloride ligand for a triflate; this reaction (Figure S32) is nearly thermoneutral. However, simple dissociation of the chloride ligand to form $\mathbf{5}^{+}$ is relatively endergonic (ΔG_{rxn} = 11.4 kcal mol^{-1}), the exchange could also proceed through an associative mechanism (not studied here). Upon formation of the nickel triflate complex, two such complexes can dimerize forming a bond between the O atom of one complex and the nickel atom of a neighboring complex releasing a triflate counterion in the process. This dimerization is exergonic (ΔG = –10.7 kcal mol^{-1}) and, based on the thermodynamics, could lead to a polymerization sequence. This could be one explanation for the observed cloudiness of some reaction solutions.

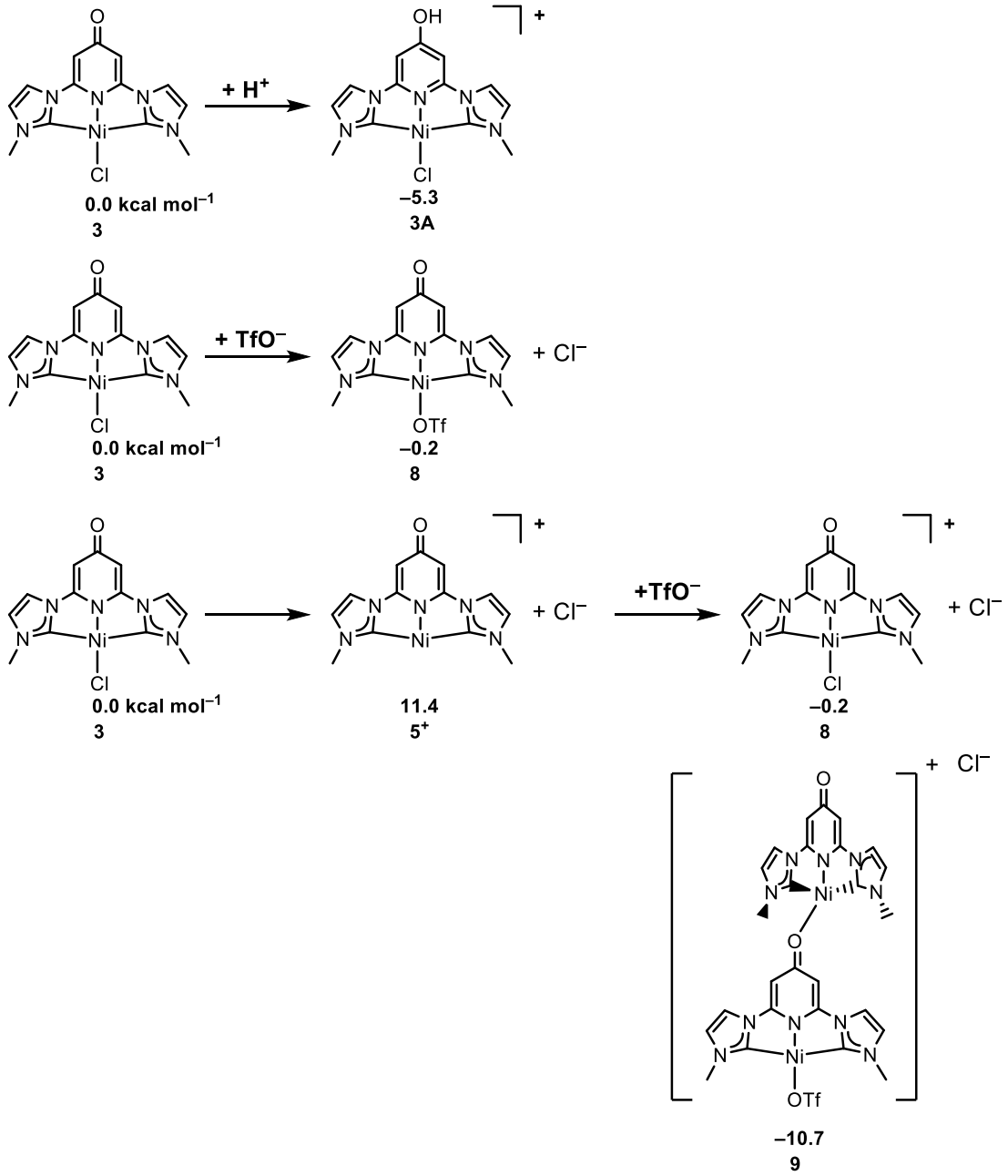

Figure S32: Possible reactions of **3** and **5** with triflate in DMSO (PCM-B3LYP/BS1).

CO_2 binds to complex **5** to produce complex **6**. Attempts to locate bound CO_2 structures with coordinatively unsaturated complex **5A** were unsuccessful. Structure **6A** has an unbound CO_2; the Ni-C_{CO_2} distance is 3.32 Å, and the OCO bond angle is nearly linear (179.3°). In the case of the neutral catalyst, CO_2 does bind to nickel through the carbon atom (Ni-C_{CO_2} 2.04 Å) and is free energy for binding CO_2 is endergonic by 10.2 kcal mol^{-1}. Inspection of the total spin density on the CO_2 atoms in **7** and **6A** shows that there is a slight net β spin in **7** (–0.0616) and a slight net α spin in **6A** (0.0005) while the Ni has a large α spin in both cases (~0.94).

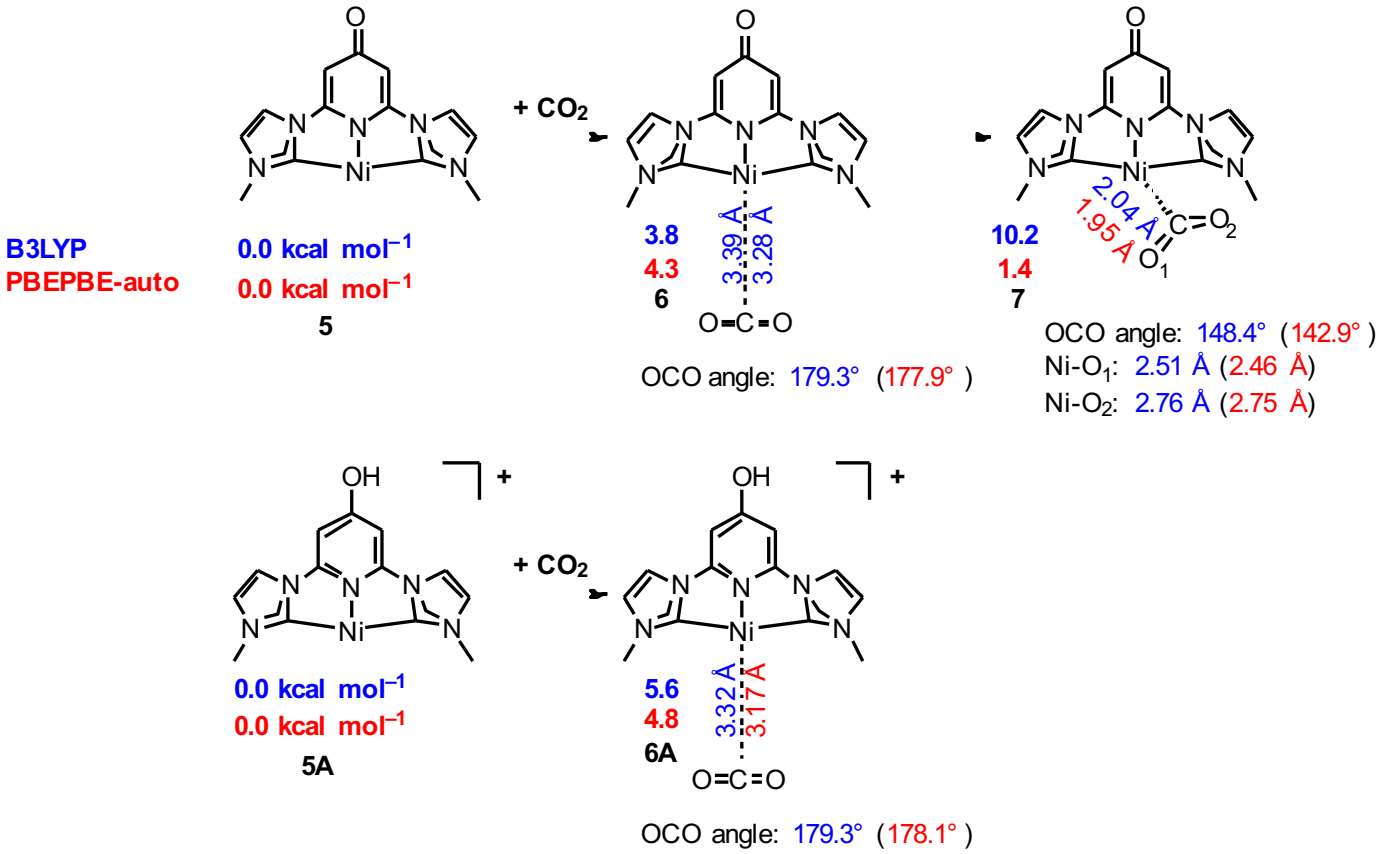

Figure S33: Relative energy (kcal mol^{-1}) of binding of CO_2 to the neutral vs. protonated proposed catalyst (PCM-B3LYP/BS1).

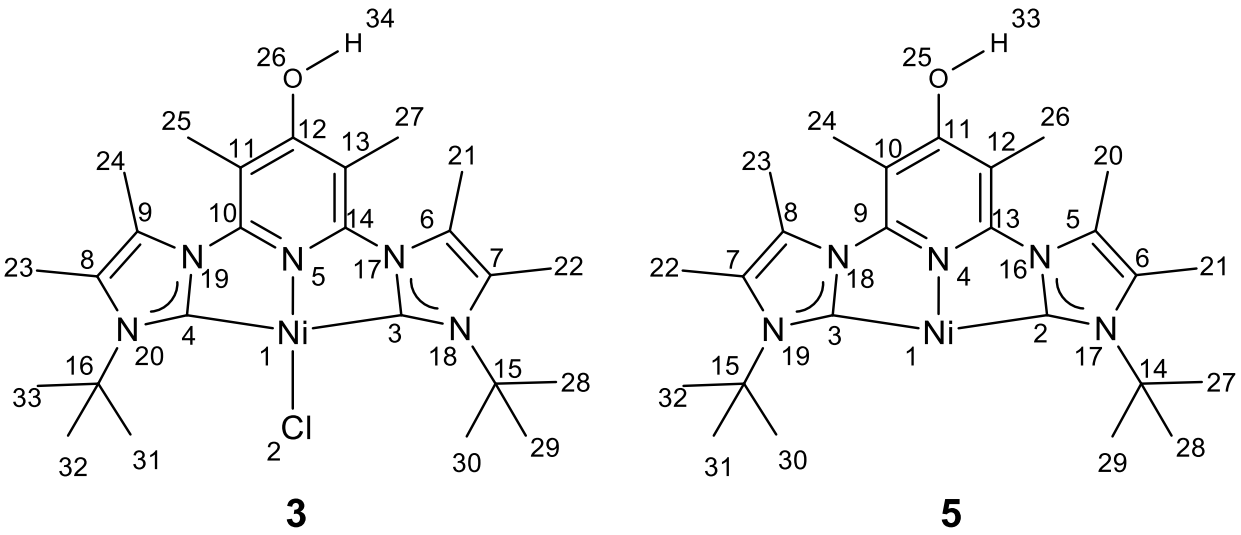

Figure S34: Numbering scheme used for **3**, **5**, and their derivatives; when deprotonated, atoms 34 (in **3**) and 33 (in **5**) are removed. Addition of CO_2 simply adds to the end of the numbering.

Table S2: NAO charges (B3LYP/BS1) for the complexes studied

Atom	Element	3A	3	$3A^0$	3^-	Atom	5A	5	Atom		6A	Atom	6	7
1	Ni	0.3260	0.3059	0.2538	0.2116	1	0.3975	0.3334	1	Ni	0.3783	1	0.3178	0.4096
2	Cl	–0.5306	–0.5443	–0.7886	–0.8060	-	-	-	-	-	-	-	-	-
3	C	0.2615	0.2479	0.1358	0.1281	2	0.1191	0.1132	2	C	0.1221	2	0.1161	0.1604
4	C	0.2638	0.2479	0.1351	0.1281	3	0.1183	0.1132	3	C	0.1217	3	0.1157	0.1604
5	N	–0.4713	–0.5197	–0.5357	–0.5830	4	–0.5440	–0.6005	4	N	–0.5434	4	–0.6005	–0.5936
6	C	–0.0648	–0.0645	–0.0764	–0.0764	5	–0.0693	–0.0699	5	C	–0.0689	5	–0.0697	–0.0658
7	C	–0.0605	–0.0692	–0.0754	–0.0830	6	–0.0732	–0.0813	6	C	–0.0729	6	–0.0809	–0.0760
8	C	–0.0596	–0.0692	–0.0756	–0.0830	7	–0.0733	–0.0813	7	C	–0.0729	7	–0.0809	–0.0760
9	C	–0.0661	–0.0645	–0.0762	–0.0764	8	–0.0690	–0.0699	8	C	–0.0689	8	–0.0696	–0.0658
10	C	0.4575	0.4197	0.4439	0.4164	9	0.4461	0.4129	9	C	0.4463	9	0.4130	0.4165
11	C	–0.3420	–0.3895	–0.3580	–0.4041	10	–0.3526	–0.4042	10	C	–0.3521	10	–0.4037	–0.3958
12	C	0.4232	0.4418	0.3997	0.4244	11	0.4045	0.4287	11	C	0.4048	11	0.4288	0.4344
13	C	–0.3595	–0.3895	–0.3749	–0.4041	12	–0.3698	–0.4042	12	C	–0.3693	12	–0.4038	–0.3958
14	C	0.4626	0.4197	0.4480	0.4164	13	0.4504	0.4129	13	C	0.4507	13	0.4130	0.4165
15	C	–0.4793	–0.4813	–0.4800	–0.4791	14	–0.4786	–0.4780	14	C	–0.4786	14	–0.4778	–0.4793
16	C	–0.4777	–0.4813	–0.4800	–0.4791	15	–0.4785	–0.4780	15	C	–0.4785	15	–0.4777	–0.4793
17	N	–0.3854	–0.3830	–0.4006	–0.3975	16	–0.3968	–0.3930	16	N	–0.3961	16	–0.3925	–0.3863
18	N	–0.3587	–0.3634	–0.3770	–0.3809	17	–0.3704	–0.3746	17	N	–0.3704	17	–0.3746	–0.3665
19	N	–0.3842	–0.3830	–0.4003	–0.3975	18	–0.3965	–0.3930	18	N	–0.3959	18	–0.3925	–0.3863
20	N	–0.3592	–0.3634	–0.3771	–0.3809	19	–0.3705	–0.3746	19	N	–0.3705	19	–0.3746	–0.3665
21	H	0.2859	0.2817	0.2746	0.2717	20	0.2784	0.2746	20	H	0.2786	20	0.2748	0.2777
22	H	0.2825	0.2779	0.2725	0.2688	21	0.2759	0.2716	21	H	0.2761	21	0.2718	0.2747
23	H	0.2824	0.2779	0.2724	0.2688	22	0.2758	0.2716	22	H	0.2760	22	0.2717	0.2747
24	H	0.2861	0.2817	0.2750	0.2717	23	0.2787	0.2746	23	H	0.2789	23	0.2748	0.2777
25	H	0.3015	0.2715	0.2868	0.2600	24	0.2909	0.2606	24	H	0.2909	24	0.2607	0.2645
26	O	–0.6858	–0.7289	–0.7024	–0.8180	25	–0.6987	–0.7583	25	O	–0.6986	25	–0.7580	–0.7453
27	H	0.3005	0.2715	0.2856	0.2600	26	0.2898	0.2606	26	H	0.2900	26	0.2607	0.2645
28	H	0.2599	0.2561	0.2511	0.2492	27	0.2564	0.2538	27	H	0.2562	27	0.2544	0.2554
29	H	0.2592	0.2561	0.2513	0.2502	28	0.2564	0.2537	28	H	0.2570	28	0.2536	0.2570
30	H	0.2682	0.2627	0.2622	0.2621	29	0.2609	0.2590	29	H	0.2602	29	0.2577	0.2612
31	H	0.2667	0.2627	0.2622	0.2621	30	0.2608	0.2590	30	H	0.2602	30	0.2577	0.2612
32	H	0.2589	0.2561	0.2512	0.2502	31	0.2563	0.2537	31	H	0.2569	31	0.2536	0.2570
33	H	0.2620	0.2561	0.2510	0.2492	32	0.2563	0.2538	32	H	0.2560	32	0.2544	0.2554
34	H	0.5763	-	0.5661	-	33	0.5685	-	33	H	0.5687	-	-	-
									34	O	–0.5257	33	–0.5199	–0.5876
									35	C	1.0533	34	1.0540	0.8595
									36	O	–0.5201	35	–0.5273	–0.5729

Table S3: NAO charges (PBEPBE-auto/BS1) for the complexes studied

Atom	Element	3A	3	$3A^0$	3^-	Atom	5A	5	Atom		6A	Atom	6	7
1	Ni	0.1908	0.1530	0.1162	0.0794	1	0.3312	0.2450	1	Ni	0.2995	1	0.2185	0.2638
2	Cl	–0.4628	–0.4894	–0.7013	–0.7331	–			–	–	–	–		
3	C	0.2531	0.2396	0.1287	0.1158	2	0.1014	0.0964	2	C	0.1080	2	0.1025	0.1780
4	C	0.2527	0.2396	0.1283	0.1158	3	0.1009	0.0964	3	C	0.1075	3	0.1022	0.1780
5	N	–0.4252	–0.4663	–0.4914	–0.5301	4	–0.4975	–0.5423	4	N	–0.4955	4	–0.5414	–0.5299
6	C	–0.0803	–0.0834	–0.0946	–0.0945	5	–0.0837	–0.0850	5	C	–0.0832	5	–0.0844	–0.0786
7	C	–0.0721	–0.0806	–0.0887	–0.0969	6	–0.0849	–0.0937	6	C	–0.0842	6	–0.0930	–0.0859
8	C	–0.0723	–0.0806	–0.0889	–0.0969	7	–0.0850	–0.0937	7	C	–0.0843	7	–0.0930	–0.0859
9	C	–0.0800	–0.0834	–0.0941	–0.0945	8	–0.0833	–0.0850	8	C	–0.0828	8	–0.0844	–0.0786
10	C	0.4253	0.3882	0.4114	0.3847	9	0.4159	0.3822	9	C	0.4169	9	0.3829	0.3892
11	C	–0.3401	–0.3826	–0.3582	–0.4002	10	–0.3524	–0.3976	10	C	–0.3515	10	–0.3969	–0.3822
12	C	0.3829	0.3927	0.3566	0.3767	11	0.3684	0.3830	11	C	0.3693	11	0.3837	0.3944
13	C	–0.3572	–0.3826	–0.3749	–0.4002	12	–0.3695	–0.3976	12	C	–0.3688	12	–0.3967	–0.3822
14	C	0.4293	0.3882	0.4147	0.3847	13	0.4196	0.3822	13	C	0.4207	13	0.3829	0.3892
15	C	–0.5180	–0.5168	–0.5189	–0.5184	14	–0.5187	–0.5180	14	C	–0.5186	14	–0.5177	–0.5198
16	C	–0.5180	–0.5168	–0.5188	–0.5184	15	–0.5186	–0.5180	15	C	–0.5186	15	–0.5177	–0.5198
17	N	–0.3583	–0.3557	–0.3716	–0.3707	16	–0.3687	–0.3664	16	N	–0.3678	16	–0.3654	–0.3592
18	N	–0.3358	–0.3417	–0.3544	–0.3579	17	–0.3456	–0.3504	17	N	–0.3452	17	–0.3500	–0.3403
19	N	–0.3580	–0.3557	–0.3714	–0.3707	18	–0.3685	–0.3664	18	N	–0.3676	18	–0.3654	–0.3592
20	N	–0.3359	–0.3417	–0.3544	–0.3579	19	–0.3457	–0.3504	19	N	–0.3452	19	–0.3500	–0.3403
21	H	0.2965	0.2918	0.2849	0.2816	20	0.2894	0.2853	20	H	0.2897	20	0.2856	0.2901
22	H	0.2932	0.2883	0.2825	0.2786	21	0.2869	0.2824	21	H	0.2872	21	0.2827	0.2871
23	H	0.2931	0.2883	0.2825	0.2786	22	0.2868	0.2824	22	H	0.2871	22	0.2827	0.2871
24	H	0.2967	0.2918	0.2853	0.2816	23	0.2897	0.2853	23	H	0.2900	23	0.2857	0.2901
25	H	0.3124	0.2834	0.2973	0.2712	24	0.3024	0.2731	24	H	0.3027	24	0.2734	0.2805
26	O	–0.6544	–0.6851	–0.6742	–0.7703	25	–0.6668	–0.7093	25	O	–0.6662	25	–0.7080	–0.6824
27	H	0.3114	0.2834	0.2963	0.2712	26	0.3013	0.2731	26	H	0.3016	26	0.2735	0.2805
28	H	0.2759	0.2691	0.2633	0.2610	27	0.2700	0.2671	27	H	0.2698	27	0.2679	0.2706
29	H	0.2719	0.2723	0.2651	0.2628	28	0.2700	0.2670	28	H	0.2709	28	0.2670	0.2706
30	H	0.2784	0.2758	0.2734	0.2715	29	0.2718	0.2694	29	H	0.2707	29	0.2678	0.2712
31	H	0.2783	0.2758	0.2732	0.2715	30	0.2716	0.2694	30	H	0.2707	30	0.2679	0.2712
32	H	0.2720	0.2723	0.2652	0.2628	31	0.2700	0.2670	31	H	0.2708	31	0.2669	0.2706
33	H	0.2756	0.2691	0.2635	0.1307	32	0.2699	0.2671	32	H	0.2697	32	0.2680	0.2706
34	H	0.5790	–	0.5674	–	33	0.5717	–	33	H	0.5721	–		
									34	O	–0.4865	33	–0.4805	–0.5643
									35	C	0.9714	34	0.9714	0.7309
									36	O	–0.4804	35	–0.4886	–0.5552

Table S4: B3LYP/BS1 spin densities at nickel and (if present) C_{CO_2} and O_{CO_2} for **5**, **5A**, **6**, **6A**, and **7**.

Atom # 6/7 *or* **6A**	**Element**	**5**	**5A**	**6**	**6A**	**7**
1	Ni	0.9385	0.9461	0.9359	0.9445	0.9430
33 *or* 34	O	-	-	0.0000	0.0019	0.0151
34 *or* 35	C	-	-	–0.0006	–0.0012	–0.0451
35 *or* 36	O	-	-	0.0023	–0.0003	–0.0316
Sum of spin densities for [CO_2] unit:				0.0018	0.0005	–0.0616

Table S5: PBEPBE-auto/BS1 spin densities at nickel and (if present) C_{CO_2} and O_{CO_2} for **5**, **5A**, **6**, **6A**, and **7**.

Atom # 6/7 *or* **6A**	**Element**	**5**	**5A**	**6**	**6A**	**7**
1	Ni	0.8707	0.8827	0.8672	0.8802	0.6660
33 *or* 34	O			0.0002	0.0032	0.1117
34 *or* 35	C			0.0010	–0.0006	0.0276
35 *or* 36	O			0.0035	–0.0003	0.0117
Sum of spin densities for [CO_2] unit:				0.0047	0.0023	0.1510

Table S6: B3LYP/BS1 NAO charges of (if present) nickel, C_{CO_2}, and O_{CO_2} for **5**, **5A**, **6**, **6A**, **7**, and CO_2.

Atom 6/7 *or* **6A**	**Element**	**5**	**5A**	**6**	**6A**	**7**	**CO_2**
1	Ni	0.3334	0.3975	0.3178	0.3783	0.4096	-
33 *or* 34	O	-	-	–0.5199	–0.5257	–0.5876	–0.52593
34 *or* 35	C	-	-	1.0540	1.0533	0.8595	1.05186
35 *or* 36	O	-	-	–0.5273	–0.5201	–0.5729	–0.52593
Sum of charges for [CO_2] unit:				0.0068	0.0074	–0.3009	0.0

Table S7: PBEPBE-auto/BS1 NAO charges of (if present) nickel, C_{CO_2}, and O_{CO_2} for **5**, **5A**, **6**, **6A**, **7**, and CO_2.

Atom 6/7 *or* **6A**	**Element**	**5**	**5A**	**6**	**6A**	**7**	**CO_2**
1	Ni	0.2450	0.3312	0.2185	0.2995	0.2638	-
33 *or* 34	O	–	–	–0.4805	–0.4865	–0.5643	–0.4878
34 *or* 35	C	–	–	0.9714	0.9714	0.7309	0.9755
35 *or* 36	O	–	–	–0.4886	–0.4804	–0.5552	–0.4878
Sum of charges for [CO_2] unit:				0.0022	0.0045	–0.3886	0.0

Table S8: Raw energies in Hartrees (PCM-B3LYP/BS1)

	E_{el}	E_0	G
H+_acetonitrile			–0.42466
co2_acetonitrile	–188.58267	–188.57118	–188.59189
cl_acetonitrile	–14.90267	–14.90267	–14.91835
cl–_acetonitrile	–15.15318	–15.15319	–15.16821
3_acetonitrile	–1035.95238	–1035.71061	–1035.76062
3-_acetonitrile	–1036.06789	–1035.82905	–1035.87929
3A_acetonitrile	–1036.41927	–1036.16687	–1036.21459
3A(0)_acetonitrile	–1036.54140	–1036.29197	–1036.34312
5+_acetonitrile	–1020.76797	–1020.52776	–1020.57277
5_acetonitrile	–1020.91664	–1020.67822	–1020.72478
5-_acetonitrile	–1020.97573	–1020.73853	–1020.78349
5A_acetonitrile	–1021.39124	–1021.14226	–1021.18863
6_acetonitrile	–1209.49932	–1209.24890	–1209.30047
6A_acetonitrile	–1209.97760	–1209.71656	–1209.77161
acetone_acetonitrile	–193.16062	–193.07773	–193.10601
butone_acetonitrile	–231.23676	–231.14868	–231.17694
pentone_acetonitrile	–270.57814	–270.45844	–270.48681
hexone_acetonitrile	–309.88953	–309.74048	–309.77154
anthrone_acetonitrile	–614.75983	–614.56501	–614.60149
benzodione_acetonitrile	–381.45814	–381.37446	–381.40504
H+_dmso			–0.44618
3_dmso	–1035.95292	–1035.71120	–1035.76118
3A_dmso	–1036.42032	–1036.16802	–1036.21576
3_gas	–1035.90805	–1035.66292	–1035.70936
3A_gas	–1036.31211	–1036.05398	–1036.10110
acetone_gas	–193.15057	–193.06671	–193.09449
butone_gas	–231.22233	–231.13135	–231.16001
pentone_gas	–270.56560	–270.44397	–270.47237
hexone_gas	–309.87680	–309.72577	–309.75682
anthrone_gas	–614.73933	–614.54054	–614.57698
benzodione_gas	–381.44114	–381.35589	–381.38641

Table S9: Raw energies in Hartrees (PCM-PBEPBE-auto/BS1)

	E_{el}	E_0	G
H+_acetonitrile			–0.42466
co2_acetonitrile	–188.39583	–188.38465	–188.40540
cl_acetonitrile	–14.89619	–14.89619	–14.91186
cl–_acetonitrile	–15.14425	–15.14426	–15.15928
3_acetonitrile	–1034.97189	–1034.73708	–1034.78493
3-_acetonitrile	–1035.07878	–1034.84685	–1034.89695
3A_acetonitrile	–1035.43623	–1035.19137	–1035.23906
3A(0)_acetonitrile	–1035.55090	–1035.30887	–1035.35881
5+_acetonitrile	–1019.78994	–1019.55706	–1019.60268
5_acetonitrile	–1019.93454	–1019.70299	–1019.74969
5-_acetonitrile	–1020.01741	–1019.78738	–1019.83269
5A_acetonitrile	–1020.40567	–1020.16402	–1020.21049
6_acetonitrile	–1208.34542	–1208.10147	–1208.15283
6A_acetonitrile	–1208.80712	–1208.55371	–1208.60825

Molecular Coordinates:

co2_acetonitrile_b3lyp

O	0.000000	0.000000	1.166216
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	-1.166216

el energy= -188.582672536
zpe= -188.571180
th energy= -188.568537
th enthalpy= -188.567593
free energy= -188.591892

3_acetonitrile_b3lyp

Ni	0.000000	0.000000	0.928455
Cl	0.000000	0.000000	3.176952
C	0.000000	1.953203	0.612534
C	0.000000	-1.953203	0.612534
N	0.000000	0.000000	-0.946925
C	0.000000	3.607816	-0.967578
C	0.000000	4.187104	0.261315
C	0.000000	-4.187104	0.261315
C	0.000000	-3.607816	-0.967578
C	0.000000	-1.161040	-1.638943
C	0.000000	-1.231293	-3.005864
C	0.000000	0.000000	-3.784995
C	0.000000	1.231293	-3.005864
C	0.000000	1.161040	-1.638943
C	0.000000	3.442034	2.646432
C	0.000000	-3.442034	2.646432
N	0.000000	2.242705	-0.733199
N	0.000000	3.164353	1.207906
N	0.000000	-2.242705	-0.733199
N	0.000000	-3.164353	1.207906
H	0.000000	4.034926	-1.964619
H	0.000000	5.231821	0.555172
H	0.000000	-5.231821	0.555172
H	0.000000	-4.034926	-1.964619
H	0.000000	-2.190456	-3.527652
O	0.000000	0.000000	-5.039395
H	0.000000	2.190456	-3.527652
H	-0.897495	4.023167	2.902367
H	0.897495	4.023167	2.902367
H	0.000000	2.495530	3.186376
H	0.000000	-2.495530	3.186376
H	0.897495	-4.023167	2.902367
H	-0.897495	-4.023167	2.902367

el energy= -1035.95238143
zpe= -1035.710610
th energy= -1035.691516
th enthalpy= -1035.690572
free energy= -1035.760618

3-_acetonitrile_b3lyp

Ni	-1.049813	0.033130	0.000000
Cl	-3.511343	-0.795596	0.000000
C	-0.596714	0.163066	2.013653
C	-0.596714	0.163066	-2.013653
N	0.992462	-0.068843	0.000000
C	1.061480	0.050700	3.605335
C	-0.126624	0.202252	4.246863
C	-0.126624	0.202252	-4.246863
C	1.061480	0.050700	-3.605335
C	1.668336	-0.066444	-1.152172
C	3.043554	-0.116740	-1.229974
C	3.808301	-0.159630	0.000000
C	3.043554	-0.116740	1.229974
C	1.668336	-0.066444	1.152172
C	-2.529403	0.460798	3.563167
C	-2.529403	0.460798	-3.563167
N	0.764072	0.027116	2.249739
N	-1.112079	0.267372	3.264427
N	0.764072	0.027116	-2.249739
N	-1.112079	0.267372	-3.264427
H	2.071310	-0.043385	3.988847
H	-0.359659	0.269821	5.304639
H	-0.359659	0.269821	-5.304639
H	2.071310	-0.043385	-3.988847
H	3.576451	-0.111396	-2.182641
O	5.079681	-0.210772	0.000000
H	3.576451	-0.111396	2.182641
H	-2.677750	1.429609	4.062570
H	-2.885367	-0.344346	4.222293
H	-3.086158	0.438171	2.621791
H	-3.086158	0.438171	-2.621791
H	-2.885367	-0.344346	-4.222293
H	-2.677750	1.429609	-4.062570

el energy= -1036.06789399
zpe= -1035.829053
th energy= -1035.809224
th enthalpy= -1035.808280
free energy= -1035.879294

3A_acetonitrile_b3lyp

Ni	-0.032365	-0.952711	-0.005039
Cl	-0.112625	-3.175875	0.117590
C	1.921359	-0.702898	-0.022471
C	-1.961386	-0.581652	-0.019751
N	0.027303	0.930398	-0.019321

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C     3.632870  0.823307 -0.013213
C     4.164087 -0.425862 -0.035182
C    -4.182866 -0.173824 -0.035378
C    -3.578812  1.042399 -0.019501
C    -1.114023  1.638073 -0.005147
C    -1.136053  3.018210  0.015527
C     0.111953  3.680102  0.025667
C     1.315932  2.942584  0.017968
C     1.208665  1.564309 -0.002781
C     3.320734 -2.788127 -0.045259
C    -3.474901 -2.584224 -0.042291
N     2.257630  0.636208 -0.007266
N     3.106951 -1.336768 -0.044887
N    -2.217331  0.774208 -0.011165
N    -3.181973 -1.145916 -0.038120
H     4.096919  1.804108 -0.008525
H     5.197420 -0.757602 -0.050981
H    -5.233996 -0.443656 -0.049000
H    -3.983744  2.049065 -0.017805
H    -2.067689  3.589047  0.026606
O     0.088864  5.011997  0.045387
H     2.286507  3.447720  0.030619
H     3.330302 -3.164160  0.987706
H     4.288679 -2.990696 -0.521274
H     2.515280 -3.270137 -0.604399
H    -2.862726 -3.080698 -0.801659
H    -4.539573 -2.710513 -0.274795
H    -3.255789 -3.013324  0.944181
H     1.024932  5.389355  0.054476
    el energy= -1036.41927291
          zpe= -1036.166873
    th energy= -1036.147924
  th enthalpy= -1036.146980
  free energy= -1036.214593

3A(0)_acetonitrile_b3lyp
Ni   -0.027752 -1.086900  0.001591
Cl   -0.084272 -3.637905 -0.089085
C     2.007963 -0.667185  0.018779
C    -2.041351 -0.572334  0.016403
N     0.020901  0.982791 -0.011409
C     3.628175  0.976274  0.003372
C     4.249207 -0.230053  0.022241
C    -4.259689 -0.031767  0.024020
C    -3.583161  1.144473  0.005294
C    -1.117820  1.670810 -0.009613
C    -1.158866  3.058056 -0.012776
C     0.083970  3.725729 -0.015557
C     1.293972  3.001541 -0.012192
C     1.189048  1.615562 -0.009173
C     3.539449 -2.636821  0.058186
C    -3.662094 -2.469224  0.056362
N     2.265354  0.700031  0.001232
N     3.251130 -1.203426  0.031014
N    -2.234848  0.805085  0.000494
N    -3.308046 -1.050581  0.030176
H     4.027308  1.984639 -0.009282
H     5.304098 -0.485467  0.029924
H    -5.325327 -0.237767  0.033382
H    -3.934871  2.170418 -0.005547
H    -2.089561  3.628986 -0.011422
O     0.053480  5.067670 -0.018895
H     2.255595  3.522088 -0.010251
H     4.097920 -2.885750  0.972402
H     4.141834 -2.909797 -0.820506
H     2.590839 -3.178543  0.041595
H    -2.739228 -3.053851  0.037204
H    -4.278317 -2.713125 -0.821262
H    -4.229419 -2.693324  0.971554
H     0.986727  5.440053 -0.019369
    el energy= -1036.54140132
          zpe= -1036.291973
    th energy= -1036.271795
  th enthalpy= -1036.270850
  free energy= -1036.343119

5+_acetonitrile_b3lyp
Ni    0.000007 -1.200005 -0.000025
C    -1.920243 -0.924299 -0.000006
C     1.920255 -0.924306 -0.000008
N    -0.000007  0.640131  0.000012
C    -3.621585  0.584611 -0.000004
C    -4.154180 -0.668502  0.000029
C     4.154178 -0.668468  0.000133
C     3.621565  0.584635 -0.000079
C     1.172146  1.325154  0.000013
C     1.236935  2.688746 -0.000001
C    -0.000011  3.465906  0.000001
C    -1.236889  2.688768  0.000013
C    -1.172219  1.325173  0.000014
C    -3.247229 -3.030067  0.000015
C     3.247267 -3.030049 -0.000012
N    -2.246440  0.406532  0.000010
N    -3.093874 -1.573662 -0.000010
N     2.246416  0.406529  0.000000
N     3.093884 -1.573647 -0.000020
H    -4.089753  1.563541 -0.000013
H    -5.187706 -1.000592  0.000048
```

```
H     5.187710 -1.000541  0.000240
H     4.089720  1.563572 -0.000150
H     2.194875  3.213444 -0.000013
O    -0.000021  4.716489 -0.000004
H    -2.194817  3.213341  0.000013
H    -3.798156 -3.341141 -0.898828
H    -3.797675 -3.341171  0.899144
H    -2.247990 -3.482494 -0.000261
H     2.248036 -3.482494 -0.000346
H     3.797672 -3.341154  0.899141
H     3.798246 -3.341103 -0.898829
    el energy= -1020.76796941
          zpe= -1020.527757
    th energy= -1020.510704
  th enthalpy= -1020.509760
  free energy= -1020.572766

5_acetonitrile_b3lyp
Ni   -0.000003 -1.317367  0.000509
C     1.965675 -0.971147  0.000183
C    -1.965672 -0.971156  0.000186
N     0.000006  0.662325 -0.003542
C     3.603669  0.637326 -0.001349
C     4.207807 -0.581171 -0.000282
C    -4.207803 -0.581163 -0.000315
C    -3.603653  0.637328 -0.001383
C    -1.158958  1.327120 -0.001597
C    -1.238292  2.699524  0.000507
C    -0.000012  3.471327  0.001060
C     1.238257  2.699526  0.000499
C     1.158993  1.327123 -0.001610
C     3.437863 -2.978060  0.001026
C    -3.437875 -2.978058  0.001071
N     2.239493  0.390757 -0.001167
N     3.194768 -1.537126  0.000675
N    -2.239481  0.390749 -0.001164
N    -3.194769 -1.537125  0.000687
H     4.019722  1.638965 -0.002274
H     5.258204 -0.853705 -0.000109
H    -5.258201 -0.853691 -0.000160
H    -4.019705  1.638967 -0.002328
H    -2.190237  3.233886  0.002313
O     0.000004  4.732071  0.002804
H     2.190202  3.233915  0.002285
H     4.011824 -3.260521  0.895483
H     4.001837 -3.262953 -0.899034
H     2.468667 -3.489943  0.007071
H    -2.468683 -3.489949  0.007154
H    -4.001828 -3.262966 -0.898998
H    -4.011862 -3.260491  0.895520
    el energy= -1020.91663574
          zpe= -1020.678220
    th energy= -1020.660769
  th enthalpy= -1020.659824
  free energy= -1020.724780

5-_acetonitrile_b3lyp
Ni    0.000004 -1.263304 -0.064355
C    -1.884408 -0.951657 -0.061114
C     1.884414 -0.951650 -0.061121
N    -0.000005  0.704913  0.455177
C    -3.580211  0.591667  0.247881
C    -4.145300 -0.640324  0.137382
C     4.145309 -0.640296  0.137294
C     3.580199  0.591677  0.247927
C     1.153042  1.346014  0.192370
C     1.228427  2.695363 -0.089256
C    -0.000007  3.458646 -0.178249
C    -1.228441  2.695360 -0.089263
C    -1.153062  1.346011  0.192367
C    -3.316372 -2.989045 -0.212675
C     3.316389 -2.989040 -0.212629
N    -2.210220  0.398981  0.146203
N    -3.111223 -1.555184 -0.044179
N     2.210218  0.398987  0.146204
N     3.111232 -1.555175 -0.044167
H    -4.025586  1.568384  0.402790
H    -5.185892 -0.945894  0.172698
H     5.185907 -0.945852  0.172546
H     4.025570  1.568389  0.402881
H     2.176715  3.191446 -0.306663
O    -0.000015  4.714739 -0.413510
H    -2.176645  3.191409 -0.306641
H    -4.128649 -3.166151 -0.932643
H    -3.576139 -3.459345  0.747647
H    -2.382543 -3.423151 -0.588956
H     2.382555 -3.423162 -0.588878
H     3.576183 -3.459322  0.747695
H     4.128649 -3.166154 -0.932613
    el energy= -1020.97572540
          zpe= -1020.738532
    th energy= -1020.721271
  th enthalpy= -1020.720327
  free energy= -1020.783485

5A_acetonitrile_b3lyp
Ni   -0.011657 -1.357530  0.000598
C     1.956377 -1.016015  0.000037
```

```
C    -1.974737 -0.988184  0.000161
N     0.002366  0.639709 -0.001833
C     3.605234  0.591019 -0.001384
C     4.199412 -0.630407 -0.000973
C    -4.212245 -0.571932 -0.001021
C    -3.601131  0.641203 -0.001334
C    -1.154329  1.294297 -0.000820
C    -1.216754  2.679195  0.000393
C     0.021039  3.363037  0.000782
C     1.248259  2.662338  0.000239
C     1.166764  1.276403 -0.000921
C     3.419887 -3.025390  0.001265
C    -3.465796 -2.977385  0.001152
N     2.237115  0.348935 -0.000824
N     3.180672 -1.582815 -0.000152
N    -2.236639  0.380300 -0.000664
N    -3.206803 -1.538248 -0.000195
H     4.027137  1.590570 -0.002243
H     5.248361 -0.909256 -0.001256
H    -5.264945 -0.836250 -0.001391
H    -4.008863  1.646650 -0.002165
H    -2.154606  3.238797  0.001324
O    -0.031499  4.702002  0.002076
H     2.199797  3.201662  0.001038
H     3.985046 -3.307835  0.901210
H     3.992031 -3.308196 -0.894111
H     2.449180 -3.534376 -0.002399
H    -2.502193 -3.499701 -0.002767
H    -4.041954 -3.252300 -0.894108
H    -4.034580 -3.252203  0.901175
H     0.895134  5.093012  0.002560
    el energy= -1021.39123726
          zpe= -1021.142259
    th energy= -1021.124606
  th enthalpy= -1021.123662
  free energy= -1021.188628

6_acetonitrile_b3lyp
Ni    0.000012 -0.999471 -0.328444
C    -1.990106 -0.625466 -0.298533
C     1.990102 -0.625447 -0.298524
N    -0.000008  0.981931 -0.127394
C    -3.609525  0.982038 -0.146685
C    -4.221274 -0.224915 -0.287297
C     4.221264 -0.224882 -0.287349
C     3.609512  0.982068 -0.146730
C     1.159432  1.645192 -0.043186
C     1.238000  3.005047  0.123746
C    -0.000020  3.772991  0.215842
C    -1.238033  3.005036  0.123752
C    -1.159453  1.645182 -0.043189
C    -3.466374 -2.613569 -0.555015
C     3.466357 -2.613553 -0.554990
N    -2.247222  0.724600 -0.154473
N    -3.215397 -1.183501 -0.374759
N     2.247209  0.724622 -0.154477
N     3.215392 -1.183478 -0.374761
H    -4.018100  1.981539 -0.043617
H    -5.273077 -0.488620 -0.332085
H     5.273068 -0.488582 -0.332156
H     4.018084  1.981572 -0.043681
H     2.190796  3.533813  0.190626
O    -0.000024  5.022011  0.366484
H    -2.190834  3.533793  0.190641
H    -3.879782 -2.798321 -1.557261
H    -4.181390 -2.958308  0.205149
H    -2.517114 -3.147721 -0.438725
H     2.517118 -3.147708 -0.438564
H     4.181472 -2.958256  0.205097
H     3.879642 -2.798342 -1.557280
O    -0.000034 -3.304876  0.666786
C     0.000039 -2.258854  1.278311
O     0.000113 -1.693895  2.337782
    el energy= -1209.49932409
          zpe= -1209.248895
    th energy= -1209.227678
  th enthalpy= -1209.226734
  free energy= -1209.300473

6A_acetonitrile_b3lyp
Ni   -0.053619 -0.863971 -0.485723
C    -1.990042 -0.374583 -0.417807
C     1.933389 -0.658783 -0.404054
N     0.086745  1.089044 -0.087125
C    -3.508417  1.328093 -0.109646
C    -4.195754  0.180544 -0.345723
C     4.195655 -0.428170 -0.315920
C     3.679546  0.807354 -0.086737
C     1.290552  1.638776  0.034101
C     1.459936  2.989734  0.294387
C     0.279031  3.757016  0.423000
C    -0.998872  3.168251  0.289516
C    -1.024599  1.804876  0.028217
C    -3.604990 -2.222122 -0.817624
C     3.266634 -2.721348 -0.788597
N    -2.163477  0.982695 -0.154627
N    -3.254458 -0.832295 -0.526888
N     2.299211  0.659576 -0.141524
```

```
N     3.119297 -1.294610 -0.503031
H    -3.851581  2.338717  0.085455
H    -5.263126 -0.008924 -0.399369
H     5.224823 -0.769997 -0.361278
H     4.163382  1.758487  0.109447
H     2.438074  3.464214  0.398408
O     0.436671  5.063809  0.673759
H    -1.905583  3.771865  0.388193
H    -4.066513 -2.291803 -1.813544
H    -4.311939 -2.589240 -0.060133
H    -2.688042 -2.822189 -0.789646
H     2.271886 -3.181050 -0.765169
H     3.907969 -3.184658 -0.025446
H     3.719432 -2.860969 -1.781152
H    -0.456197  5.520885  0.748955
O    -0.266307 -4.024502  0.621726
C    -0.294382 -3.418554  1.619214
O    -0.322689 -2.825747  2.622506
    el energy= -1209.97759516
          zpe= -1209.716564
    th energy= -1209.694473
  th enthalpy= -1209.693528
  free energy= -1209.771605

acetone_acetonitrile_b3lyp
C     0.000000  0.000000  0.182607
O     0.000000  0.000000  1.404301
C     0.000000  1.289041 -0.613976
C     0.000000 -1.289041 -0.613976
H     0.000000  2.154396  0.058201
H     0.883554  1.326150 -1.269683
H    -0.883554  1.326150 -1.269683
H     0.000000 -2.154396  0.058201
H    -0.883554 -1.326150 -1.269683
H     0.883554 -1.326150 -1.269683
    el energy= -193.160622141
          zpe= -193.077727
    th energy= -193.072286
  th enthalpy= -193.071342
  free energy= -193.106006

butone_acetonitrile_b3lyp
C     0.073156  0.668359  0.000000
O     0.339047  1.849721  0.000000
C    -0.118920 -0.371265  1.108680
C    -0.118920 -0.371265 -1.108680
H     0.677622 -0.399146  1.868182
H    -1.086074 -0.243267  1.622696
H    -1.086074 -0.243267 -1.622696
H     0.677622 -0.399146 -1.868182
C    -0.118920 -1.473682  0.000000
H     0.807384 -2.082596  0.000000
H    -1.001241 -2.143227  0.000000
    el energy= -231.236760269
          zpe= -231.148679
    th energy= -231.143732
  th enthalpy= -231.142788
  free energy= -231.176937

pentone_acetonitrile_b3lyp
C     0.000000  0.000000  0.920917
O     0.000000  0.000000  2.139262
C     0.000000  1.241485  0.031488
C     0.000000 -1.241485  0.031488
H    -0.693129  2.005600  0.412712
H     1.018725  1.669111  0.084495
H     0.693129 -2.005600  0.412712
H    -1.018725 -1.669111  0.084495
C    -0.301582  0.712696 -1.382520
C     0.301582 -0.712696 -1.382520
H    -1.391175  0.656030 -1.534893
H     0.112994  1.349323 -2.175918
H     1.391175 -0.656030 -1.534893
H    -0.112994 -1.349323 -2.175918
    el energy= -270.578137343
          zpe= -270.458435
    th energy= -270.452882
  th enthalpy= -270.451938
  free energy= -270.486807

hexone_acetonitrile_b3lyp
C     1.174747 -0.000078 -0.000119
O     2.397556  0.000061  0.000745
C     0.361443  1.235359 -0.350400
C     0.361392 -1.235826  0.349160
H     0.959583  2.131300 -0.127117
H     0.212238  1.216682 -1.447498
H     0.959337 -2.131547  0.124392
H     0.213181 -1.218530  1.446419
C    -0.999946  1.237675  0.366407
H    -0.818873  1.255341  1.452838
H    -1.543773  2.163854  0.129416
C    -1.857708  0.000132  0.000771
C    -1.000528 -1.237285 -0.366524
H    -2.516113 -0.238064  0.847555
H    -2.517704  0.238257 -0.844790
H    -0.820361 -1.254105 -1.453119
H    -1.544358 -2.163536 -0.129819
```

```
    el energy= -309.889533606
          zpe= -309.740480
    th energy= -309.733767
  th enthalpy= -309.732823
  free energy= -309.771539

anthrone_acetonitrile_b3lyp
C     0.000000  2.490356  1.230961
H     0.000000  2.455627  2.319670
C     0.000000  1.272512  0.521266
C     0.000000  0.000000  1.287495
C     0.000000  1.276228 -0.887255
C     0.000000  0.000000 -1.685261
C     0.000000  2.510953 -1.557201
H     0.000000  2.521917 -2.648982
C     0.000000  3.710955 -0.849362
H     0.000000  4.658628 -1.390715
C     0.000000  3.703741  0.555246
H     0.000000  4.642612  1.110438
C     0.000000 -1.272512  0.521266
C     0.000000 -1.276228 -0.887255
C     0.000000 -2.510953 -1.557201
H     0.000000 -2.521917 -2.648982
C     0.000000 -3.710955 -0.849362
H     0.000000 -4.658628 -1.390715
C     0.000000 -3.703741  0.555246
H     0.000000 -4.642612  1.110438
C     0.000000 -2.490356  1.230961
H     0.000000 -2.455627  2.319670
O     0.000000  0.000000  2.523299
H    -0.886885  0.000000 -2.372233
H     0.886885  0.000000 -2.372233
    el energy= -614.759830455
          zpe= -614.565013
    th energy= -614.554275
  th enthalpy= -614.553330
  free energy= -614.601489

benzodione_acetonitrile_b3lyp
C    -0.672588  1.271743 -0.000001
C    -1.439984  0.000000  0.000001
C     0.672588  1.271743 -0.000003
C     1.439984  0.000000 -0.000001
C    -0.672588 -1.271743  0.000003
C     0.672588 -1.271743  0.000001
O    -2.668090  0.000000  0.000002
O     2.668090  0.000000 -0.000002
H    -1.261675  2.194825 -0.000002
H     1.261675  2.194825 -0.000005
H    -1.261675 -2.194825  0.000005
H     1.261675 -2.194825  0.000002
    el energy= -381.458136728
          zpe= -381.374464
    th energy= -381.368208
  th enthalpy= -381.367264
  free energy= -381.405035

3_dmso_b3lyp
Ni    0.000000  0.000000  0.928705
Cl    0.000000  0.000000  3.177321
C     0.000000  1.953455  0.612586
C     0.000000 -1.953455  0.612586
N     0.000000  0.000000 -0.946176
C     0.000000  3.607993 -0.967796
C     0.000000  4.187938  0.260658
C     0.000000 -4.187938  0.260658
C     0.000000 -3.607993 -0.967796
C     0.000000 -1.161095 -1.638534
C     0.000000 -1.231547 -3.005282
C     0.000000  0.000000 -3.784034
C     0.000000  1.231547 -3.005282
C     0.000000  1.161095 -1.638534
C     0.000000  3.443491  2.645320
C     0.000000 -3.443491  2.645320
N     0.000000  2.242981 -0.733023
N     0.000000  3.165086  1.207100
N     0.000000 -2.242981 -0.733023
N     0.000000 -3.165086  1.207100
H     0.000000  4.034703 -1.965100
H     0.000000  5.232772  0.554492
H     0.000000 -5.232772  0.554492
H     0.000000 -4.034703 -1.965100
H     0.000000 -2.190585 -3.527522
O     0.000000  0.000000 -5.038603
H     0.000000  2.190585 -3.527522
H    -0.897597  4.024814  2.900690
H     0.897597  4.024814  2.900690
H     0.000000  2.497146  3.185531
H     0.000000 -2.497146  3.185531
H     0.897597 -4.024814  2.900690
H    -0.897597 -4.024814  2.900690
    el energy= -1035.95292494
          zpe= -1035.711196
    th energy= -1035.692099
  th enthalpy= -1035.691155
  free energy= -1035.761180

3A_dmso_b3lyp
```

```
Ni   -0.032336 -0.952793 -0.005041
Cl   -0.112525 -3.176402  0.117906
C     1.921514 -0.702840 -0.022511
C    -1.961542 -0.581700 -0.019740
N     0.027334  0.930276 -0.019283
C     3.632796  0.823611 -0.013113
C     4.164260 -0.425463 -0.035182
C    -4.183054 -0.173509 -0.035437
C    -3.578730  1.042579 -0.019523
C    -1.113983  1.637915 -0.005140
C    -1.136096  3.017993  0.015529
C     0.111882  3.679958  0.025676
C     1.316003  2.942580  0.017996
C     1.208659  1.564324 -0.002756
C     3.321493 -2.787812 -0.045603
C    -3.475741 -2.583935 -0.042494
N     2.257640  0.636259 -0.007247
N     3.107253 -1.336535 -0.044972
N    -2.217339  0.774124 -0.011167
N    -3.182287 -1.145759 -0.038158
H     4.096557  1.804656 -0.008355
H     5.197688 -0.757122 -0.051050
H    -5.234286 -0.443222 -0.049143
H    -3.983366  2.049459 -0.017843
H    -2.067980  3.588674  0.026576
O     0.088614  5.011789  0.045412
H     2.286672  3.447872  0.030640
H     3.330899 -3.164100  0.987338
H     4.289759 -2.989882 -0.521310
H     2.516442 -3.269970 -0.605254
H    -2.863906 -3.080545 -0.802100
H    -4.540563 -2.709660 -0.274918
H    -3.256814 -3.013257  0.943982
H     1.025331  5.389063  0.054456
    el energy= -1036.42032234
          zpe= -1036.168024
    th energy= -1036.149070
  th enthalpy= -1036.148126
  free energy= -1036.215756

3_gas_b3lyp
Ni    0.000000  0.000000  0.921802
Cl    0.000000  0.000000  3.145808
C     0.000000  1.939681  0.609375
C     0.000000 -1.939681  0.609375
N     0.000000  0.000000 -0.952517
C     0.000000  3.607582 -0.948782
C     0.000000  4.177012  0.285397
C     0.000000 -4.177012  0.285397
C     0.000000 -3.607582 -0.948782
C     0.000000 -1.161345 -1.650395
C     0.000000 -1.235753 -3.010952
C     0.000000  0.000000 -3.807963
C     0.000000  1.235753 -3.010952
C     0.000000  1.161345 -1.650395
C     0.000000  3.382445  2.664603
C     0.000000 -3.382445  2.664603
N     0.000000  2.242245 -0.731494
N     0.000000  3.145513  1.220621
N     0.000000 -2.242245 -0.731494
N     0.000000 -3.145513  1.220621
H     0.000000  4.044527 -1.935771
H     0.000000  5.215346  0.583987
H     0.000000 -5.215346  0.583987
H     0.000000 -4.044527 -1.935771
H     0.000000 -2.181469 -3.543820
O     0.000000  0.000000 -5.041536
H     0.000000  2.181469 -3.543820
H    -0.894558  3.951381  2.941364
H     0.894558  3.951381  2.941364
H     0.000000  2.417337  3.172762
H     0.000000 -2.417337  3.172762
H     0.894558 -3.951381  2.941364
H    -0.894558 -3.951381  2.941364
    el energy= -1035.90805367
          zpe= -1035.662918
    th energy= -1035.644284
  th enthalpy= -1035.643340
  free energy= -1035.709361

3A_gas_b3lyp
Ni   -0.008303 -0.955264  0.000058
Cl   -0.025159 -3.136918  0.000885
C     1.932517 -0.665849  0.000103
C    -1.943597 -0.634889 -0.000315
N     0.007701  0.935794 -0.000331
C     3.618743  0.893693 -0.000631
C     4.168938 -0.345572 -0.000721
C    -4.174373 -0.278654 -0.000469
C    -3.604166  0.951633 -0.000527
C    -1.153525  1.611710 -0.000225
C    -1.204325  2.993121  0.000116
C     0.026143  3.681337  0.000427
C     1.247345  2.976673  0.000373
C     1.175806  1.591255 -0.000029
C     3.369197 -2.725659 -0.000023
C    -3.413769 -2.671320  0.000093
N     2.243699  0.686819 -0.000158
```

```
N     3.128429 -1.275630 -0.000291
N    -2.233125  0.721788 -0.000492
N    -3.149151 -1.225692 -0.000339
H     4.076547  1.871350 -0.001155
H     5.204676 -0.654064 -0.001077
H    -5.214944 -0.570361 -0.000566
H    -4.043518  1.937805 -0.000980
H    -2.132047  3.553519  0.000206
O    -0.045409  5.015746  0.000818
H     2.199456  3.498472  0.000709
H     3.939431 -2.992806  0.895280
H     3.938866 -2.993233 -0.895550
H     2.406872 -3.237033  0.000441
H    -2.460268 -3.198763 -0.000108
H    -3.988484 -2.929538 -0.894975
H    -3.987828 -2.929127  0.895703
H     0.832216  5.426382  0.001111
    el energy= -1036.31211395
          zpe= -1036.053977
    th energy= -1036.035212
  th enthalpy= -1036.034267
  free energy= -1036.101102

acetone_gas_b3lyp
C     0.000000  0.000000  0.187483
O     0.000000  0.000000  1.399982
C     0.000000  1.293781 -0.614695
C     0.000000 -1.293781 -0.614695
H     0.000000  2.151272  0.063568
H     0.881647  1.341443 -1.268888
H    -0.881647  1.341443 -1.268888
H     0.000000 -2.151272  0.063568
H    -0.881647 -1.341443 -1.268888
H     0.881647 -1.341443 -1.268888
    el energy= -193.150571229
          zpe= -193.066706
    th energy= -193.061298
  th enthalpy= -193.060354
  free energy= -193.094491

butone_gas_b3lyp
C     0.045139  0.681077  0.000000
O     0.200666  1.871109  0.000000
C    -0.070954 -0.381541  1.111712
C    -0.070954 -0.381541 -1.111712
H     0.762974 -0.391187  1.824231
H    -1.005316 -0.296727  1.681760
H    -1.005316 -0.296727 -1.681760
H     0.762974 -0.391187 -1.824231
C    -0.070954 -1.477960  0.000000
H     0.830993 -2.097785  0.000000
H    -0.945295 -2.135468  0.000000
    el energy= -231.222325629
          zpe= -231.131349
    th energy= -231.126380
  th enthalpy= -231.125435
  free energy= -231.160008

pentone_gas_b3lyp
C     0.000000  0.000000  0.930099
O     0.000000  0.000000  2.138023
C     0.000000  1.245046  0.029859
C     0.000000 -1.245046  0.029859
H    -0.696884  2.001690  0.406799
H     1.008296  1.684437  0.083207
H     0.696884 -2.001690  0.406799
H    -1.008296 -1.684437  0.083207
C    -0.299358  0.713818 -1.382391
C     0.299358 -0.713818 -1.382391
H    -1.386031  0.659604 -1.538614
H     0.111455  1.344733 -2.178584
H     1.386031 -0.659604 -1.538614
H    -0.111455 -1.344733 -2.178584
    el energy= -270.565599537
          zpe= -270.443970
    th energy= -270.438423
  th enthalpy= -270.437479
  free energy= -270.472371

hexone_gas_b3lyp
C     1.182686 -0.000014 -0.000045
O     2.395170  0.000019  0.000257
C     0.359963  1.239369 -0.350682
C     0.359951 -1.239543  0.350205
H     0.957951  2.129061 -0.121852
H     0.210981  1.235309 -1.443337
H     0.957869 -2.129114  0.120676
H     0.211485 -1.236121  1.442923
C    -0.999900  1.237360  0.367191
H    -0.818905  1.253297  1.451383
H    -1.547908  2.160758  0.141126
C    -1.857394  0.000094  0.000224
C    -1.000184 -1.237252 -0.367118
H    -2.517759 -0.238720  0.844437
H    -2.517988  0.239045 -0.843774
H    -0.819617 -1.253135 -1.451384
H    -1.548195 -2.160609 -0.140905
    el energy= -309.876801849
```

```
          zpe= -309.725772
    th energy= -309.719074
  th enthalpy= -309.718129
  free energy= -309.756824

anthrone_gas_b3lyp
C     0.000000  2.486630  1.230063
H     0.000000  2.435940  2.315519
C     0.000000  1.274233  0.517616
C     0.000000  0.000000  1.290400
C     0.000000  1.281829 -0.887894
C     0.000000  0.000000 -1.687552
C     0.000000  2.515194 -1.556092
H     0.000000  2.531205 -2.645571
C     0.000000  3.713350 -0.845514
H     0.000000  4.659628 -1.383304
C     0.000000  3.701364  0.556628
H     0.000000  4.636526  1.112559
C     0.000000 -1.274233  0.517616
C     0.000000 -1.281829 -0.887894
C     0.000000 -2.515194 -1.556092
H     0.000000 -2.531205 -2.645571
C     0.000000 -3.713350 -0.845514
H     0.000000 -4.659628 -1.383304
C     0.000000 -3.701364  0.556628
H     0.000000 -4.636526  1.112559
C     0.000000 -2.486630  1.230063
H     0.000000 -2.435940  2.315519
O     0.000000  0.000000  2.516236
H    -0.871516  0.000000 -2.361533
H     0.871516  0.000000 -2.361533
    el energy= -614.739325107
          zpe= -614.540536
    th energy= -614.529849
  th enthalpy= -614.528905
  free energy= -614.576976

benzodione_gas_b3lyp
C    -0.672203  1.269698 -0.000001
C    -1.447632  0.000000  0.000001
C     0.672203  1.269698 -0.000003
C     1.447632  0.000000 -0.000001
C    -0.672203 -1.269698  0.000003
C     0.672203 -1.269698  0.000001
O    -2.669544  0.000000  0.000002
O     2.669544  0.000000 -0.000002
H    -1.261542  2.184381 -0.000002
H     1.261542  2.184381 -0.000005
H    -1.261542 -2.184381  0.000005
H     1.261542 -2.184381  0.000002
    el energy= -381.441139217
          zpe= -381.355886
    th energy= -381.349651
  th enthalpy= -381.348707
  free energy= -381.386407

co2_acetonitrile_pbepbe
O     0.000000  0.000000  1.177529
C     0.000000  0.000000  0.000000
O     0.000000  0.000000 -1.177529
    el energy= -188.395830364
          zpe= -188.384654
    th energy= -188.381985
  th enthalpy= -188.381040
  free energy= -188.405395

3_acetonitrile_pbepbe
Ni   -0.904387  0.000780  0.000000
Cl   -3.125975 -0.121812  0.000000
C    -0.611413  0.016993  1.912986
C    -0.611413  0.016993 -1.912986
N     0.955933  0.018589  0.000000
C     0.936623  0.020652  3.613253
C    -0.317187  0.039313  4.164773
C    -0.317187  0.039313 -4.164773
C     0.936623  0.020652 -3.613253
C     1.653446  0.002563 -1.168041
C     3.028486 -0.017837 -1.236187
C     3.812043 -0.027369  0.000000
C     3.028486 -0.017837  1.236187
C     1.653446  0.002563  1.168041
C    -2.690474  0.051872  3.346122
C    -2.690474  0.051872 -3.346122
N     0.735316  0.008314  2.241732
N    -1.241566  0.038956  3.119472
N     0.735316  0.008314 -2.241732
N    -1.241566  0.038956 -3.119472
H     1.931071  0.020367  4.067824
H    -0.639561  0.056895  5.209926
H    -0.639561  0.056895 -5.209926
H     1.931071  0.020367 -4.067824
H     3.552912 -0.030371 -2.204736
O     5.075100 -0.046149  0.000000
H     3.552912 -0.030371  2.204736
H    -2.866055  0.258540  4.418173
H    -3.125110 -0.929938  3.077426
H    -3.156491  0.838401  2.727219
H    -3.156491  0.838401 -2.727219
```

```
H    -3.125110 -0.929938 -3.077426
H    -2.866055  0.258540 -4.418173
    el energy= -1034.97188849
          zpe= -1034.737082
    th energy= -1034.717888
  th enthalpy= -1034.716944
  free energy= -1034.784926

3-_acetonitrile_pbepbe
Ni    1.000465 -0.029102  0.000000
Cl    3.339262  0.888500  0.000000
C     0.604852 -0.199846  1.939058
C     0.604852 -0.199846 -1.939058
N    -0.983570  0.177073  0.000000
C    -0.992186  0.000081  3.606775
C     0.225729 -0.189420  4.203804
C     0.225729 -0.189420 -4.203804
C    -0.992186  0.000081 -3.606775
C    -1.669313  0.106906 -1.160415
C    -3.052498  0.088822 -1.234541
C    -3.825494  0.115001  0.000000
C    -3.052498  0.088822  1.234541
C    -1.669313  0.106906  1.160415
C     2.589564 -0.556711  3.424354
C     2.589564 -0.556711 -3.424354
N    -0.749882 -0.002234  2.238467
N     1.170288 -0.303813  3.183526
N    -0.749882 -0.002234 -2.238467
N     1.170288 -0.303813 -3.183526
H    -1.988793  0.145165  4.032062
H     0.501965 -0.252264  5.260461
H     0.501965 -0.252264 -5.260461
H    -1.988793  0.145165 -4.032062
H    -3.584942  0.027382 -2.196600
O    -5.104528  0.116297  0.000000
H    -3.584942  0.027382  2.196600
H     2.725445 -1.556809  3.884040
H     2.998087  0.216456  4.105453
H     3.115369 -0.511357  2.455983
H     3.115369 -0.511357 -2.455983
H     2.998087  0.216456 -4.105453
H     2.725445 -1.556809 -3.884040
    el energy= -1035.07878236
          zpe= -1034.846845
    th energy= -1034.826731
  th enthalpy= -1034.825786
  free energy= -1034.896949

3A_acetonitrile_pbepbe
Ni   -0.024898 -0.932476 -0.002061
Cl   -0.075572 -3.138539  0.123617
C     1.893544 -0.690561 -0.017168
C    -1.928977 -0.597594 -0.017180
N     0.020449  0.930711 -0.017504
C     3.631899  0.822852 -0.017922
C     4.149967 -0.443470 -0.037526
C    -4.170680 -0.242024 -0.038809
C    -3.591819  0.997836 -0.021572
C    -1.131660  1.640616 -0.003941
C    -1.161690  3.027364  0.015049
C     0.087124  3.702490  0.024461
C     1.300606  2.967332  0.017229
C     1.204486  1.582124 -0.002096
C     3.276049 -2.799258 -0.056315
C    -3.411248 -2.637321 -0.049365
N     2.253493  0.652369 -0.006916
N     3.082183 -1.344542 -0.038769
N    -2.223544  0.760988 -0.009572
N    -3.147831 -1.193632 -0.037771
H     4.111117  1.806125 -0.015464
H     5.187243 -0.791392 -0.054214
H    -5.223536 -0.539479 -0.055395
H    -4.022311  2.003418 -0.021438
H    -2.107460  3.593559  0.025571
O     0.053678  5.040416  0.042815
H     2.277986  3.480602  0.029105
H     2.978361 -3.230657  0.918408
H     4.347726 -2.996986 -0.243823
H     2.661260 -3.244971 -0.858044
H    -2.807111 -3.117227 -0.839219
H    -4.488480 -2.784773 -0.250727
H    -3.147761 -3.075621  0.932204
H     1.006556  5.414995  0.051369
    el energy= -1035.43623259
          zpe= -1035.191372
    th energy= -1035.172064
  th enthalpy= -1035.171120
  free energy= -1035.239056

3A(0)_acetonitrile_pbepbe
Ni   -0.020708 -1.028533  0.028564
Cl   -0.045766 -3.304697 -0.890750
C     1.921002 -0.671709  0.206859
C    -1.949783 -0.605526  0.202087
N     0.012989  0.948870 -0.163358
C     3.622083  0.894564 -0.011729
C     4.190679 -0.335587  0.177130
C    -4.206478 -0.190772  0.179569
```

```
C    -3.595732  1.019465 -0.006525
C    -1.139441  1.644489 -0.099681
C    -1.184647  3.036764 -0.083436
C     0.059951  3.717788 -0.102073
C     1.279310  2.994232 -0.082785
C     1.187773  1.602727 -0.099860
C     3.365194 -2.682974  0.561496
C    -3.462420 -2.567225  0.550564
N     2.246563  0.679350  0.000798
N     3.151605 -1.259611  0.302824
N    -2.228727  0.756437  0.001235
N    -3.199856 -1.150811  0.299225
H     4.068543  1.880907 -0.165084
H     5.241686 -0.634594  0.233764
H    -5.267096 -0.453266  0.238094
H    -4.007664  2.021603 -0.154093
H    -2.129036  3.601986 -0.036950
O     0.019905  5.066527 -0.097625
H     2.247791  3.520622 -0.034694
H     3.829123 -2.820746  1.559253
H     4.033342 -3.106825 -0.214600
H     2.386155 -3.189219  0.524558
H    -2.500870 -3.106134  0.514877
H    -4.141895 -2.965085 -0.229440
H    -3.933753 -2.693801  1.546320
H     0.969337  5.434050 -0.092802
    el energy= -1035.55090490
          zpe= -1035.308869
    th energy= -1035.288564
  th enthalpy= -1035.287620
  free energy= -1035.358810

5+_acetonitrile_pbepbe
Ni    0.000000  1.183539 -0.000018
C     1.894460  0.919347 -0.000003
C    -1.894460  0.919347 -0.000006
N     0.000000 -0.644370  0.000016
C     3.628846 -0.568490 -0.000016
C     4.142678  0.703563  0.000055
C    -4.142678  0.703562  0.000233
C    -3.628846 -0.568491 -0.000160
C    -1.179384 -1.336088  0.000017
C    -1.239658 -2.708334 -0.000004
C     0.000000 -3.490709  0.000003
C     1.239659 -2.708334  0.000017
C     1.179384 -1.336088  0.000018
C     3.189978  3.052933 -0.000007
C    -3.189979  3.052932 -0.000043
N     2.249160 -0.413318  0.000011
N     3.066482  1.593439 -0.000011
N    -2.249160 -0.413318 -0.000007
N    -3.066482  1.593439 -0.000025
H     4.116610 -1.547761 -0.000038
H     5.178491  1.056923  0.000093
H    -5.178491  1.056922  0.000428
H    -4.116610 -1.547762 -0.000300
H    -2.208804 -3.232916 -0.000027
O     0.000000 -4.750010 -0.000005
H     2.208803 -3.232917  0.000016
H     3.738827  3.377750 -0.906182
H     3.738438  3.377782  0.906394
H     2.173082  3.487710 -0.000233
H    -2.173084  3.487710 -0.000364
H    -3.738361  3.377792  0.906400
H    -3.738907  3.377738 -0.906175
    el energy= -1019.78993514
          zpe= -1019.557061
    th energy= -1019.539463
  th enthalpy= -1019.538519
  free energy= -1019.602684

5_acetonitrile_pbepbe
Ni    0.000000 -1.271559 -0.000048
C    -1.917263 -0.965459 -0.000136
C     1.917263 -0.965459 -0.000138
N     0.000000  0.670939  0.002178
C    -3.608876  0.606071  0.000791
C    -4.181423 -0.639491  0.000107
C     4.181423 -0.639492  0.000115
C     3.608876  0.606071  0.000792
C     1.167484  1.343816  0.000917
C     1.243157  2.723397 -0.000393
C     0.000000  3.500481 -0.001046
C    -1.243156  2.723397 -0.000391
C    -1.167484  1.343816  0.000918
C    -3.338362 -3.017555 -0.000786
C     3.338361 -3.017555 -0.000792
N    -2.237102  0.397124  0.000699
N    -3.141653 -1.569093 -0.000467
N     2.237102  0.397124  0.000697
N     3.141652 -1.569093 -0.000469
H    -4.055592  1.604121  0.001300
H    -5.232177 -0.943547 -0.000038
H     5.232177 -0.943548 -0.000024
H     4.055593  1.604121  0.001302
H     2.204684  3.260029 -0.001319
O     0.000000  4.768539 -0.001414
H    -2.204683  3.260029 -0.001316
```

```
H    -3.905367 -3.321458 -0.903422
H    -3.898412 -3.323012  0.905690
H    -2.343513 -3.499089 -0.004993
H     2.343512 -3.499089 -0.005014
H     3.898399 -3.323017  0.905690
H     3.905378 -3.321456 -0.903421
    el energy= -1019.93454069
          zpe= -1019.702991
    th energy= -1019.685177
  th enthalpy= -1019.684233
  free energy= -1019.749694

5-_acetonitrile_pbepbe
Ni    0.000000 -1.244963  0.054766
C     1.869312 -0.953557  0.067965
C    -1.869313 -0.953556  0.067965
N     0.000000  0.693001 -0.447704
C     3.591396  0.582859 -0.231441
C     4.146834 -0.666750 -0.130236
C    -4.146829 -0.666757 -0.130308
C    -3.591399  0.582866 -0.231381
C    -1.160473  1.351784 -0.185146
C    -1.232029  2.711324  0.084193
C     0.000001  3.483220  0.165311
C     1.232031  2.711325  0.084187
C     1.160473  1.351783 -0.185144
C     3.282120 -3.012004  0.204733
C    -3.282122 -3.012001  0.204750
N     2.216967  0.404556 -0.132879
N     3.103093 -1.573671  0.043346
N    -2.216968  0.404557 -0.132876
N    -3.103094 -1.573669  0.043350
H     4.051325  1.563613 -0.379358
H     5.192949 -0.984134 -0.167331
H    -5.192940 -0.984147 -0.167462
H    -4.051331  1.563627 -0.379246
H    -2.189452  3.211198  0.300920
O     0.000001  4.748735  0.392250
H     2.189455  3.211200  0.300907
H     4.121685 -3.210745  0.900545
H     3.495411 -3.494490 -0.771119
H     2.341716 -3.424225  0.617936
H    -2.341729 -3.424217  0.617985
H    -3.495383 -3.494494 -0.771104
H    -4.121707 -3.210738  0.900539
    el energy= -1020.01740779
          zpe= -1019.787379
    th energy= -1019.769657
  th enthalpy= -1019.768713
  free energy= -1019.832692

5A_acetonitrile_pbepbe
Ni   -0.011964 -1.308149  0.000175
C     1.910119 -1.011682  0.000069
C    -1.929328 -0.982408  0.000100
N     0.002633  0.642928 -0.000554
C     3.610934  0.558987 -0.000422
C     4.174350 -0.688991 -0.000523
C    -4.188428 -0.626706 -0.000477
C    -3.606548  0.612882 -0.000449
C    -1.161444  1.310053 -0.000212
C    -1.221124  2.700638  0.000165
C     0.022677  3.389145  0.000264
C     1.254876  2.682038  0.000116
C     1.175571  1.290770 -0.000252
C     3.324461 -3.065283  0.000502
C    -3.373190 -3.015322  0.000444
N     2.235819  0.353449 -0.000202
N     3.129949 -1.615564 -0.000114
N    -2.234801  0.387157 -0.000151
N    -3.157869 -1.568525 -0.000136
H     4.062878  1.555072 -0.000692
H     5.223825 -0.998558 -0.000783
H    -5.242330 -0.920834 -0.000715
H    -4.043392  1.615701 -0.000752
H    -2.168883  3.262465  0.000452
O    -0.031699  4.733201  0.000625
H     2.216631  3.223118  0.000365
H     3.886407 -3.367936  0.906714
H     3.890224 -3.368074 -0.903268
H     2.329022 -3.545608 -0.001547
H    -2.384721 -3.509843 -0.001824
H    -3.943357 -3.310024 -0.903228
H    -3.939185 -3.310043  0.906748
H     0.913786  5.116290  0.000765
    el energy= -1020.40567113
          zpe= -1020.164020
    th energy= -1020.146036
  th enthalpy= -1020.145092
  free energy= -1020.210486

6_acetonitrile_pbepbe
Ni    0.000008 -0.911787 -0.233621
C    -1.945425 -0.584742 -0.219183
C     1.945440 -0.584682 -0.219209
N    -0.000021  1.036617 -0.224876
C    -3.613523  0.997327 -0.167466
C    -4.195330 -0.239695 -0.259539
```

```
C     4.195333 -0.239550 -0.259576
C     3.613479  0.997452 -0.167505
C     1.167784  1.701050 -0.069661
C     1.242554  3.059659  0.145898
C    -0.000065  3.833285  0.241578
C    -1.242660  3.059619  0.145898
C    -1.167848  1.701015 -0.069673
C    -3.396983 -2.622244 -0.391780
C     3.397072 -2.622134 -0.391714
N    -2.244634  0.771292 -0.146149
N    -3.165455 -1.179993 -0.289182
N     2.244598  0.771363 -0.146151
N     3.165491 -1.179887 -0.289174
H    -4.048203  1.999990 -0.124687
H    -5.247366 -0.535701 -0.310628
H     5.247378 -0.535520 -0.310671
H     4.048119  2.000132 -0.124742
H     2.205183  3.582348  0.261247
O    -0.000085  5.083767  0.421290
H    -2.205306  3.582276  0.261255
H    -3.968563 -2.838758 -1.316137
H    -3.973598 -2.969500  0.488744
H    -2.420657 -3.133834 -0.425421
H     2.420761 -3.133752 -0.425398
H     3.973640 -2.969354  0.488855
H     3.968716 -2.838647 -1.316031
O     0.000116 -3.352324  0.096369
C     0.000061 -2.454797  0.954354
O     0.000033 -2.259538  2.160993
    el energy= -1208.34541969
          zpe= -1208.101472
    th energy= -1208.080178
  th enthalpy= -1208.079234
  free energy= -1208.152831

6A_acetonitrile_pbepbe
Ni    0.016508 -0.854219 -0.480000
C    -1.907934 -0.574257 -0.414105
C     1.933119 -0.525786 -0.407943
N    -0.008172  1.064425 -0.115754
C    -3.616060  0.962192 -0.132927
C    -4.173292 -0.268729 -0.355544
C     4.189886 -0.164414 -0.341235
C     3.601402  1.052912 -0.123788
C     1.152709  1.725488  0.004584
C     1.205340  3.092704  0.259315
C    -0.041989  3.763011  0.387135
C    -1.271043  3.061315  0.260601
C    -1.184444  1.694261  0.003605
C    -3.310846 -2.601156 -0.789594
C     3.387194 -2.518979 -0.770529
N    -2.239901  0.767136 -0.170169
N    -3.124315 -1.175229 -0.519440
N     2.230820  0.823715 -0.166053
N     3.164401 -1.096981 -0.507093
H    -4.073114  1.939158  0.049316
H    -5.221110 -0.579334 -0.409015
H     5.245283 -0.449147 -0.389574
H     4.033159  2.041486  0.057674
H     2.150139  3.650432  0.360610
O     0.007282  5.084316  0.631846
H    -2.235483  3.588140  0.361132
H    -3.699929 -2.745220 -1.817868
H    -4.029691 -3.023823 -0.060182
H    -2.331773 -3.103238 -0.683613
H     2.419012 -3.043549 -0.673719
H     4.107515 -2.922711 -0.031860
H     3.790946 -2.656945 -1.793944
H    -0.939475  5.458291  0.703170
O     0.039613 -3.916118  0.794288
C     0.014581 -3.160500  1.700003
O    -0.010553 -2.436353  2.628865
    el energy= -1208.80712189
          zpe= -1208.553709
    th energy= -1208.531334
  th enthalpy= -1208.530390
  free energy= -1208.608249
```

Table S10. Photocatalysis in the absence and presence of Hg over time.

Time (hours)	TON without Hg	TON with Hg
0	0	0
0.33	0.9	0.9
0.66	1.8	2.1
1	2.3	2.6*
2	4.7	4.7
4	8.7	9.1
5	10.3	10.4
6	10.4	10.4

*Indicates the time at which >3000 equiv. of Hg was added to the reaction. Addition of Hg is recommended to be done after the active catalysts has had time to form. See *Journal of Molecular Catalysis A: Chemical* **2003**, *198*, 317-341 for further discussion. No appreciable rate difference is observed in the presence of Hg.

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