

Supporting Information

**Impact of Oxidation State on Reactivity and Selectivity Differences
between Nickel(III) and Nickel(IV) Alkyl Complexes**

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I. General Procedures and Materials and Methods

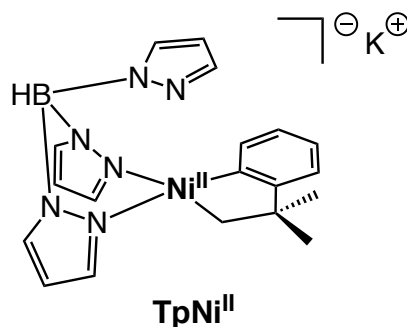
General Procedures

All experiments and manipulations were carried out under an inert nitrogen atmosphere using standard glovebox or Schlenk techniques unless otherwise indicated. NMR spectra were obtained on a Varian VNMR 700 (699.76 MHz for ^1H ; 175.95 MHz for ^{13}C), a Varian VNMR 500 (500.09 MHz for ^1H ; 470.56 MHz for ^{19}F) or a Varian VNMR 400 spectrometer (399.54 MHz for ^1H ; 128.187 for ^{11}B). ^1H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak as an internal reference. ^{19}F chemical shifts and ^{11}B chemical shifts are reported in ppm and are referenced on a unified scale, where the single primary reference is the frequency of the residual solvent peak in the ^1H NMR spectrum. Abbreviations used in the NMR data: s, singlet; ; br, broad signal. Mass spectral data were obtained on a Micromass magnetic sector mass spectrometer in electrospray ionization mode. X-ray crystallographic data were collected on a Bruker SMART APEX-I CCD-based X-ray diffractometer. Electronic spectra were collected with a Shimadzu UV-1601 UV-VIS spectrometer (190–1100 nm) with a 4 mL sealed quartz cuvette. Flash chromatography was conducted using a Biotage Isolera One system with cartridges containing high performance silica gel.

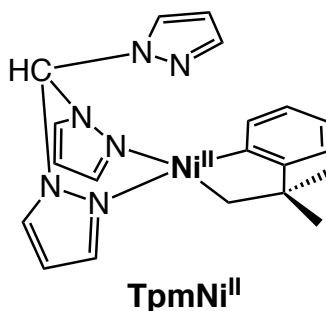
Materials and Methods

The following compounds were prepared via literature procedures: **TpNi^{II}**, $(\text{pyr})_2\text{Ni}(\text{CH}_2\text{CMe}_2\text{-o-C}_6\text{H}_4)_2$, **2-Ni^{IV+}**^{3,4}, and $(\text{PMe}_3)_2\text{NiCl}(\text{CH}_2\text{CMe}_2\text{-o-C}_6\text{H}_4)$ ⁵. Tpm was purchased from Strem. KTp was purchased from Alfa Aesar. AgBF_4 was purchased from TCI. Trifluoroacetic acid was purchased from EMD Millipore. 1,1-dimethylbenzocyclobutane was purchased from Acros. Anhydrous acetonitrile was purchased from Sigma Aldrich and used without further purification. 1,3,5-trimethoxybenzene and TMAOAc were purchased from Sigma Aldrich and dried *in vacuo*. Benzonitrile was purchased from Acros, sparged with N_2 , and used without further purification. CD_3CN and d_6 -acetone were obtained from Cambridge Isotopes Laboratories and used without further purification. Diethyl ether (EMD) and tetrahydrofuran (Fisher) were deaerated via an Ar sparge and were purified by a solvent purification system. Celite was dried for 12 h under vacuum at 100 °C. Unless otherwise noted, all glassware was dried overnight in an oven at 150 °C and cooled under an inert atmosphere before use. All commercial reagents were used without further purification/drying unless explicitly stated in the experimental section. Ambient light is from Phillips 25W fluorescent lights in the laboratory.

II. Synthesis of Ni^{II} Precursors



Synthesis of [(K)(Tp)Ni^{II}(CH₂CMe₂-*o*-C₆H₄)] (TpNi^{II}). This complex was synthesized according to a literature procedure. NMR spectral data for **TpNi^{II}** matched those reported in the literature.¹



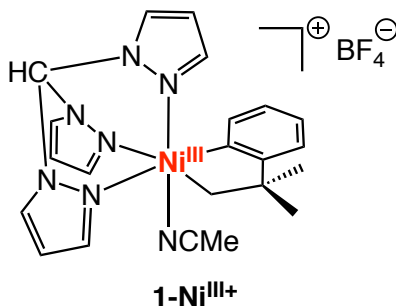
Synthesis of [(Tpm)Ni^{II}(CH₂CMe₂-*o*-C₆H₄)] (TpmNi^{II}). A solution of tris(pyrazolyl)methane (Tpm) (0.14 g, 0.65 mmol, 1.05 equiv) in Et₂O (3 mL) was added dropwise to a stirring solution of (pyr)₂Ni(CH₂CMe₂-*o*-C₆H₄)² (0.25 g, 0.62 mmol, 1.0 equiv) in Et₂O (7 mL). The resulting solution was stirred at room temperature for 16 h, during which time a yellow precipitate formed. The precipitate was collected by filtration and washed with Et₂O (3 x 5 mL). The product was then dried under vacuum and obtained as a yellow solid (230 mg, 94% yield). X-ray quality crystals were grown from a saturated solution of **TpmNi^{II}** in acetonitrile at 25 °C.

When **TpmNi^{II}** is dissolved in acetonitrile, we observe: (1) broadening of the ¹H NMR signals associated with **TpmNi^{II}**; (2) appearance of free Tpm; and (3) a new set of signals that we assign as (MeCN)₂Ni^{II}(CH₂CMe₂-*o*-C₆H₄). Drying this mixture and subsequent ¹H NMR analysis in *d*₆-acetone results in quantitative recovery of **TpmNi^{II}**.

^1H NMR (700 MHz, d_6 -acetone, 23 °C) δ 9.14 (s, 1H), 8.79 (br s, 3H), 7.84 (br s, 3H), 6.76-6.70 (multiple peaks, 2H), 6.61-6.52 (multiple peaks, 2H), 6.50 (br s, 3H), 1.36 (s, 2H), 1.34 (s, 6H).

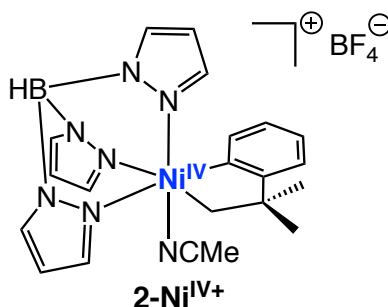
^{13}C NMR (128 MHz, d_6 -acetone, 23 °C) δ 170.6, 161.6, 144.3, 138.0, 133.4, 123.3, 122.7, 121.1, 108.0, 80.4, 48.2, 42.2, 34.9.

III. Synthesis of High-Valent Ni Complexes



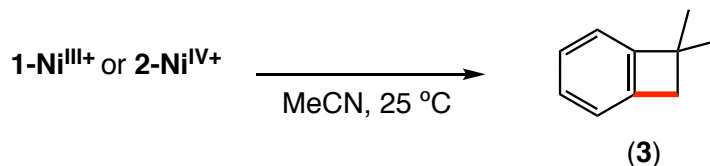
***In situ* generation of [(Tp)Ni^{III}(CH₂CMe₂-*o*-C₆H₄)(MeCN)] [BF₄] (1-Ni^{III+}).** All glassware and solvents were pre-cooled to -35 °C. A solution of **TpNi^{II}** (27.5 mg, 0.068 mmol, 1.0 equiv) in acetonitrile (3 mL) was cooled to -35 °C and then added to a vial containing AgBF₄ (13.2 mg, 0.068 mmol, 1.0 equiv). The vial was shaken and placed into the glovebox freezer (-35 °C) for 10 min. The resulting heterogeneous mixture was filtered, providing a dark red solution of **1-Ni^{III+}**. Four drops of this solution were added to 300 μ L of a 3:1 PrCN:MeCN solution. This sample was flash-frozen in a septum-capped EPR tube for EPR analysis (see p. S41).

X-ray quality crystals were grown by vapor diffusion of pentane into a saturated solution of **1-Ni^{III+}** in THF in the presence of pyridine at -35 °C.



Synthesis of [(Tp)Ni^{IV}(CH₂CMe₂-*o*-C₆H₄)(MeCN)]BF₄ (2-Ni^{IV+}). This complex was synthesized according to a literature procedure. NMR spectral data for **2-Ni^{IV+}** matched those reported in the literature.⁴

IV. Kinetic Studies of 1-Ni^{III+} and 2-Ni^{IV+}



Experimental Procedure:

Procedure for spectra recorded in the dark: In a glovebox with the lights off, **2-Ni^{IV+}** (0.0094 mmol, 1.0 equiv) was weighed into a 4 mL vial and then dissolved in CD₃CN (4.0 mL) at 25 °C. 1,3,5-trimethoxybenzene (0.0094 mmol, 1.0 equiv) was added as an NMR standard. Approximately 1 mL of the resulting solution was transferred to a screw cap NMR tube. The tube was sealed with a Teflon-lined cap and removed from the glovebox, and the initial rate of C–C bond-forming reductive elimination was determined by monitoring the appearance of product by ¹H NMR spectroscopy over 3 h at 25 °C. Yield of **3** versus time data were acquired from the integration of the ¹H NMR signals of the product 1,1-dimethylbenzocyclobutane (**3**) relative to the internal standard (1,3,5-trimethoxybenzene). Initial rate values were then obtained from the slope of a linear-fit of these data.

Complex **1-Ni^{III+}** was prepared according to the procedure outlined above in Section III, using **TpmNi^{II}** (3.9 mg, 0.0094 mmol, 1.0 equiv), AgBF₄ (1.8 mg, 0.0094 mmol, 1.0 equiv) and CD₃CN (4.0 mL). The solution containing this *in situ*-generated sample of **1-Ni^{III+}** was maintained at –35 °C, transferred to an NMR tube that was sealed with a Teflon-lined cap, removed from the glovebox, and frozen in an EtOAc/liquid nitrogen bath. The sample was transferred to the NMR spectrometer, allowed to warm to 25 °C, and then the initial rate of C–C bond-forming reductive elimination was determined by monitoring the appearance of product by ¹H NMR spectroscopy at 25 °C. Yield of **3** versus time data were acquired from the integration of the ¹H NMR signals of the product 1,1-dimethylbenzocyclobutane (**3**) relative to the internal standard (1,3,5-trimethoxybenzene). Initial rate values were then obtained from the slope of a linear-fit of these data.

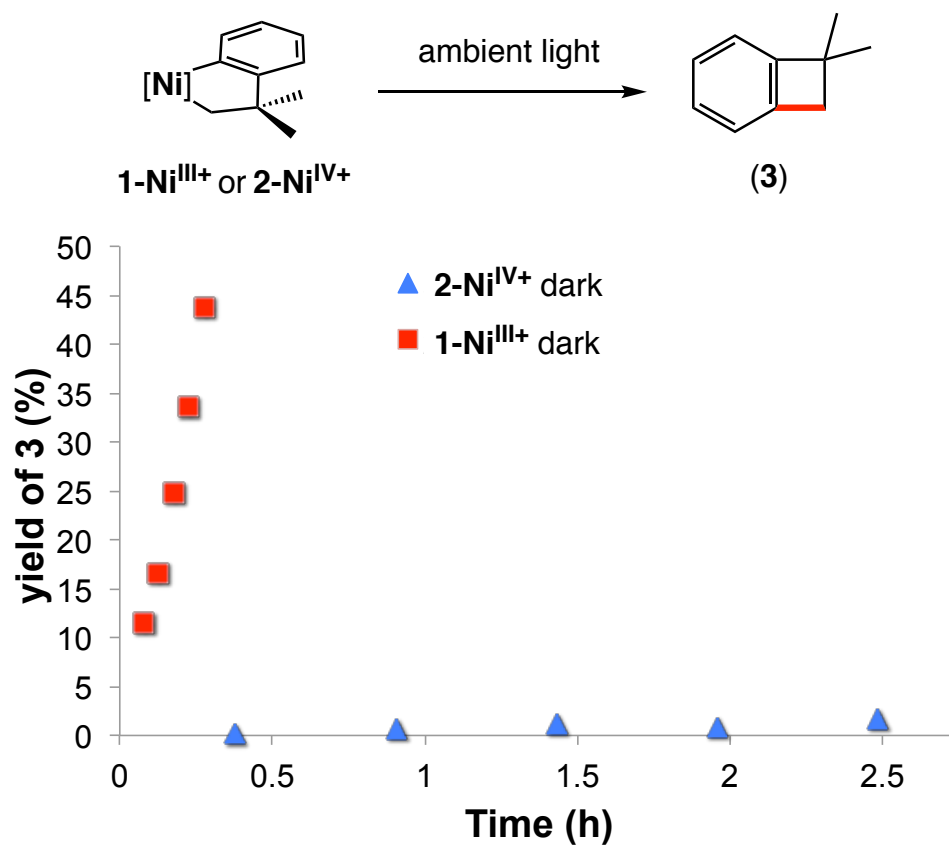


Figure S1. Plot of yield of **3** vs time for the formation of **3** from **1-Ni^{III+}** and **2-Ni^{IV+}** in the dark. Conditions: [Ni] = 0.0023 M; T = 25 °C.

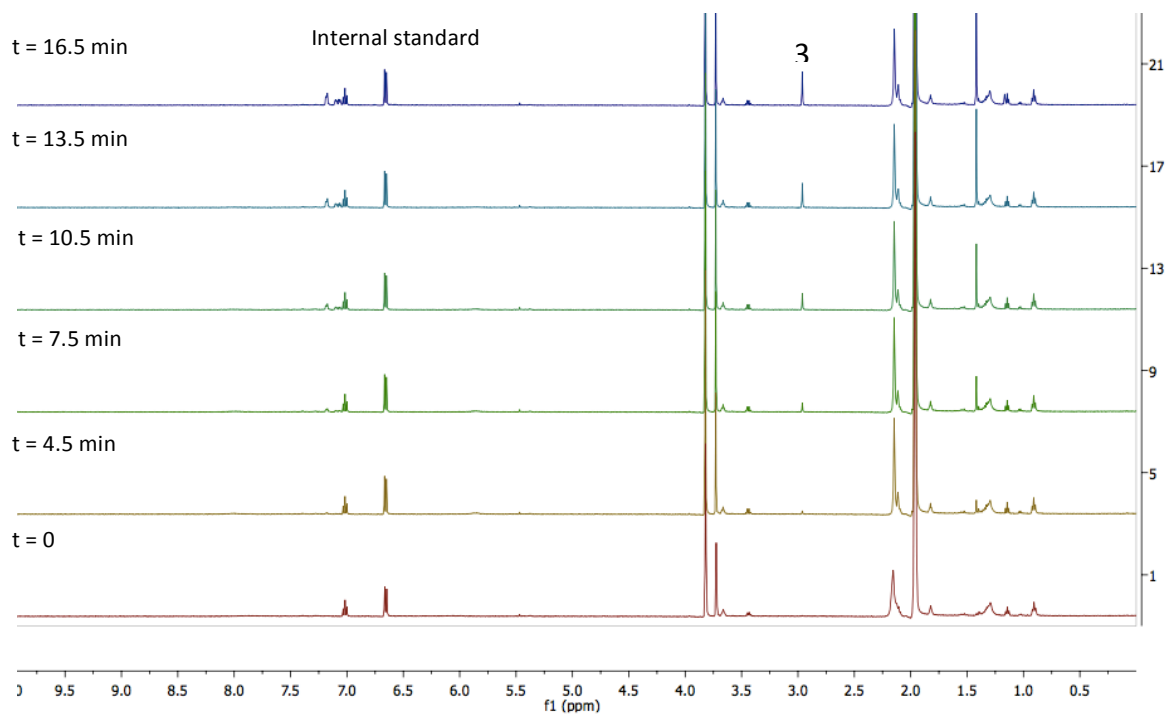


Figure S2. ^1H NMR array of C–C reductive elimination from **1-Ni^{III}** to form **3** in the dark. Conditions: $[\text{Ni}] = 0.0023$ M; $T = 25$ °C, standard = 1,2,3-trimethoxybenzene

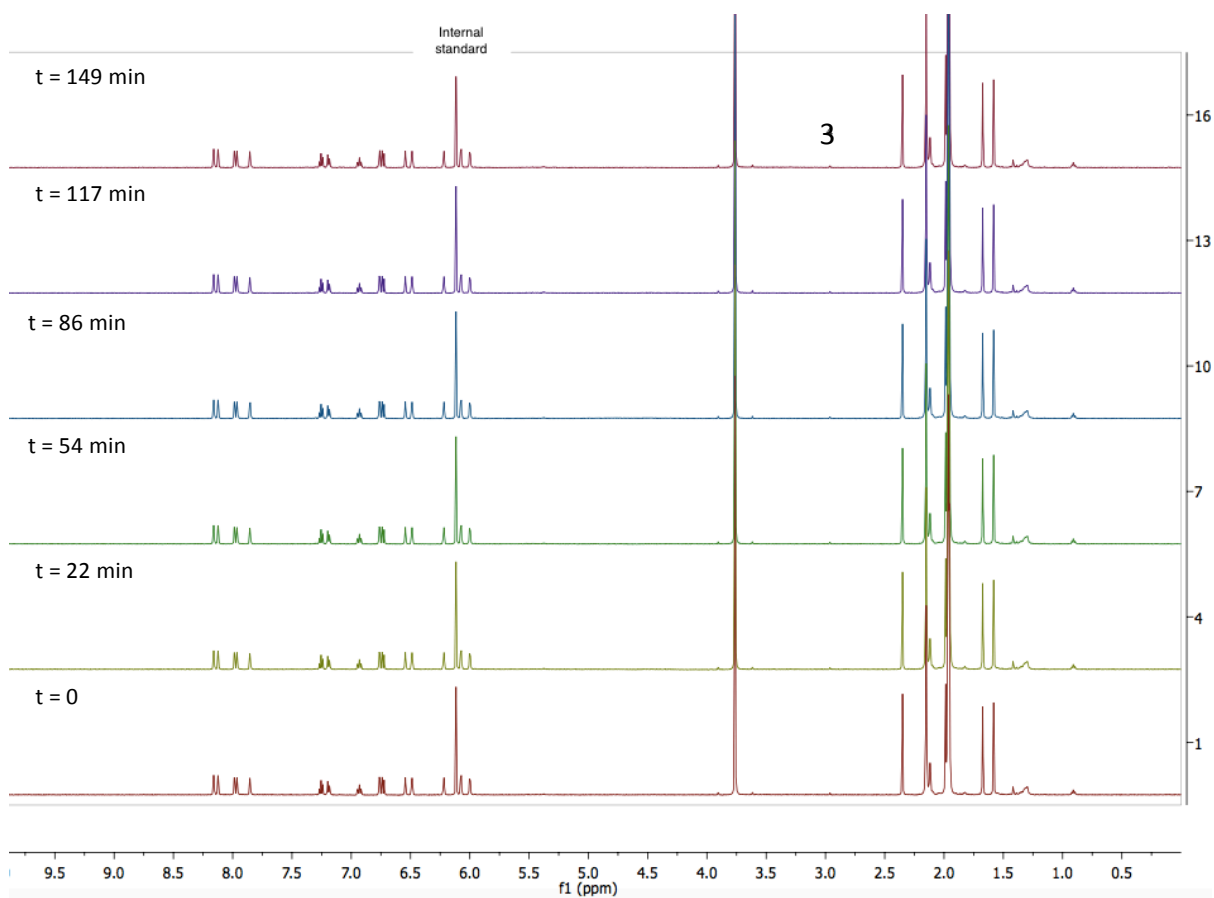


Figure S3. ¹H NMR array of C–C reductive elimination from **2-Ni^{IV+}** to form **3** in the dark. Conditions: [Ni] = 0.0023 M; T = 25 °C, standard = 1,3,5-trimethoxybenzene

Procedure for spectra recorded in the light: In a glovebox, **2-Ni^{IV+}** (0.0094 mmol, 1.0 equiv) was weighed into a 4 mL vial and then dissolved in CD₃CN (4.0 mL) at 25 °C. 1,3,5-trimethoxybenzene (0.0094 mmol, 1.0 equiv) was added as an internal ¹H NMR standard. Approximately 1 mL of the resulting solution was transferred to a screw cap NMR tube. The tube was sealed with a Teflon-lined cap and removed from the glovebox, and the initial rate of C–C bond-forming reductive elimination was determined by monitoring the appearance of product by ¹H NMR spectroscopy over 3 h at 25 °C. Each sample was placed in the NMR spectrometer, the spectrum was acquired. The sample was then removed from the spectrometer and exposed to ambient light until the next time point. Yield of **3** versus time data were acquired from the integration of the ¹H NMR signals of the product 1,1-dimethylbenzocyclobutane (**3**) relative to the internal standard (1,3,5-trimethoxybenzene). Initial rate values were then obtained from the slope of a linear-fit of these data.

The above procedure was repeated for **2-Ni^{IV+}** in MeNO₂ in the light and dark.

Complex **1-Ni^{III+}** was prepared according to the procedure outlined above in Section III, using **TpmNi^{II}** (7.9 mg, 0.0188 mmol, 1.0 equiv), AgBF₄ (3.7 mg, 0.0188 mmol, 1.0 equiv) and CD₃CN (8.0 mL). The solution containing this *in situ*-generated sample of **1-Ni^{III+}** was maintained at –35 °C, transferred to 6 different NMR tubes that were sealed with Teflon-lined caps, removed from the glovebox, and placed in an ice bath. At t = 0, the tubes were removed from the ice bath and placed into a room temperature water bath in order to regulate the temperature. The NMR tubes were left in the light until each spectrum was ready to be recorded, and one sample was used for each data point with the first sample being used as a dummy sample for locking and shimming before t = 0. The initial rate of C–C bond-forming reductive elimination was determined by monitoring the appearance of product by ¹H NMR spectroscopy at 25 °C. Yield of **3** versus time data were acquired from the integration of the ¹H NMR signals of the product 1,1-dimethylbenzocyclobutane (**3**) relative to the internal standard (1,3,5-trimethoxybenzene). Initial rate values were then obtained from the slope of a linear-fit of these data.

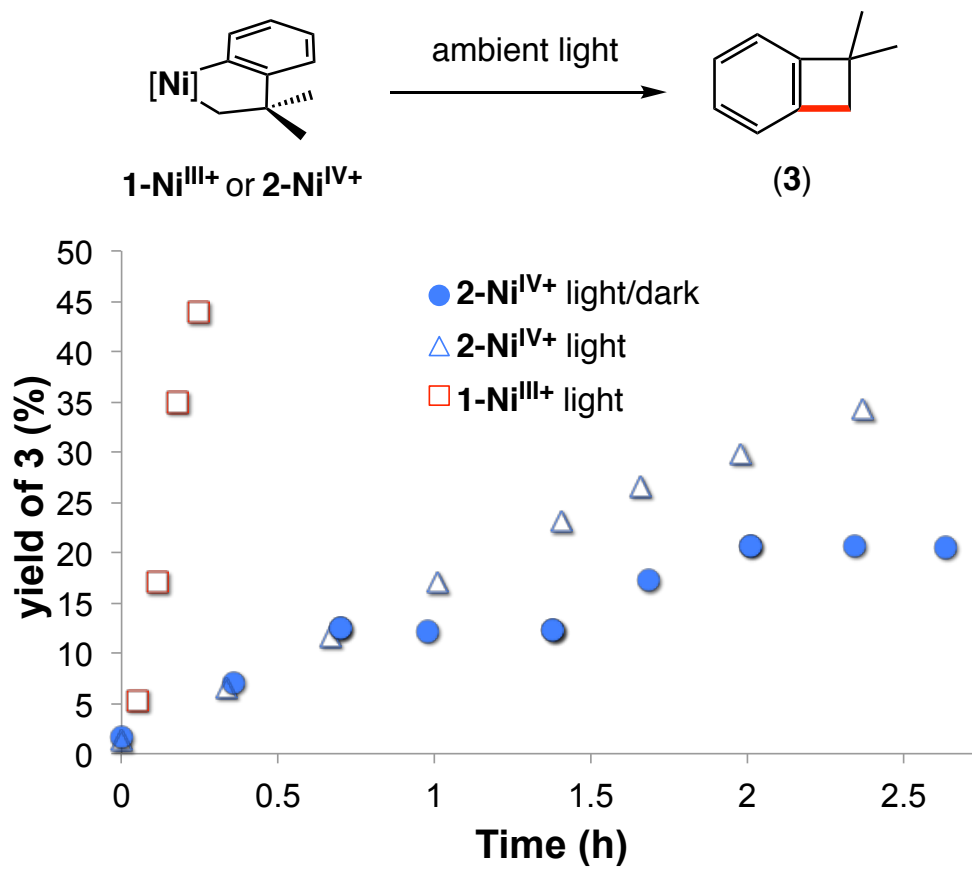


Figure S4. MeCN. Plot of yield of **3** vs time for the formation of **3** from **1-Ni^{III+}** and **2-Ni^{IV+}** in the light. Conditions: [Ni] = 0.0023 M; T = 25 °C.

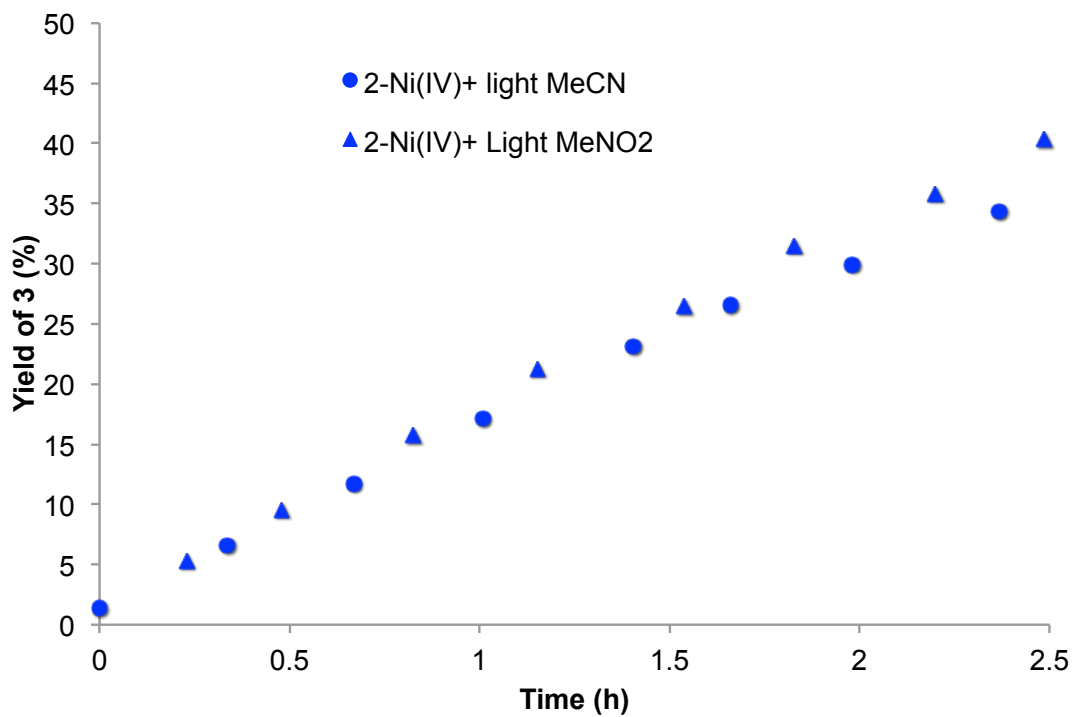


Figure S5. MeCN and MeNO₂. Plot of concentration vs time for the formation of **3** from **2-Ni^{IV+}** in the light and dark in MeCN and MeNO₂. Conditions: [Ni] = 0.0023 M; T = 25 °C. Note lines drawn for clarity, not for rates.

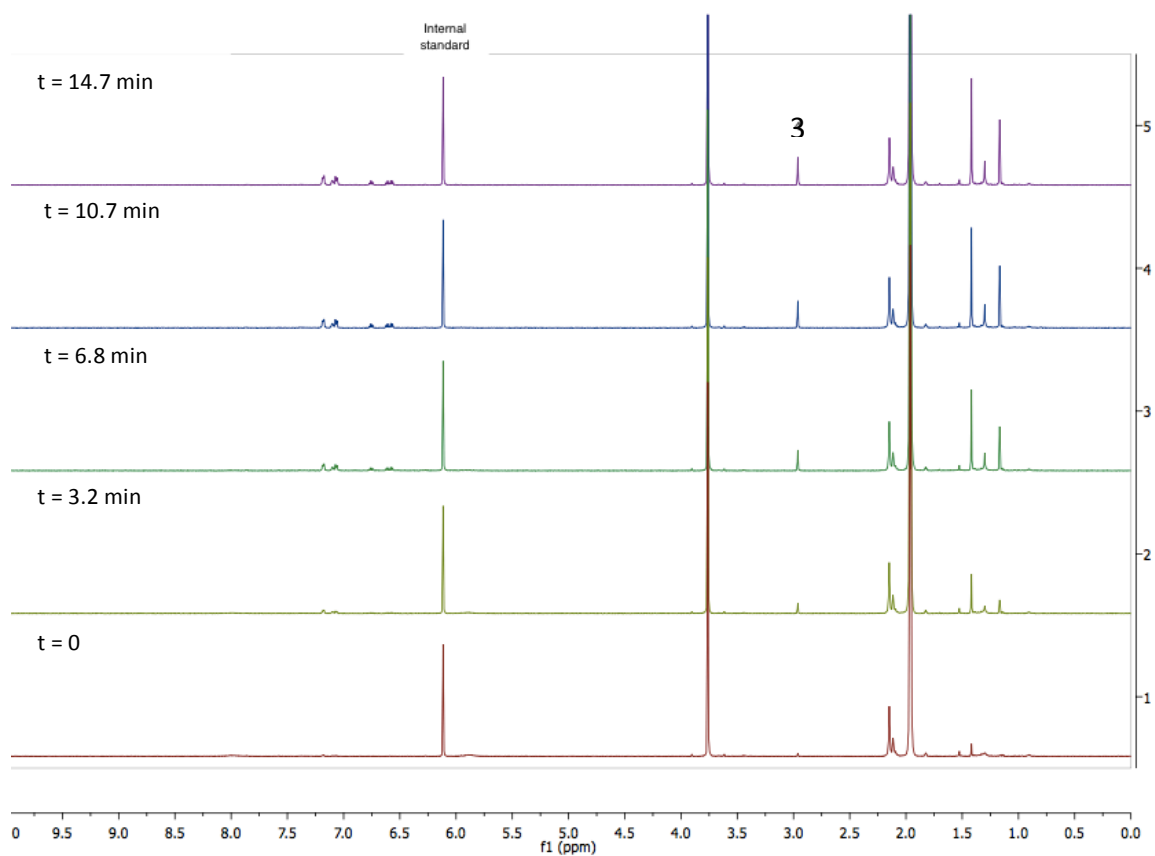


Figure S6. ^1H NMR array of C–C reductive elimination from **1-Ni^{III}** to form **3** in the light. Conditions: $[\text{Ni}] = 0.0023 \text{ M}$; $T = 25 \text{ }^\circ\text{C}$, standard = 1,3,5-trimethoxybenzene

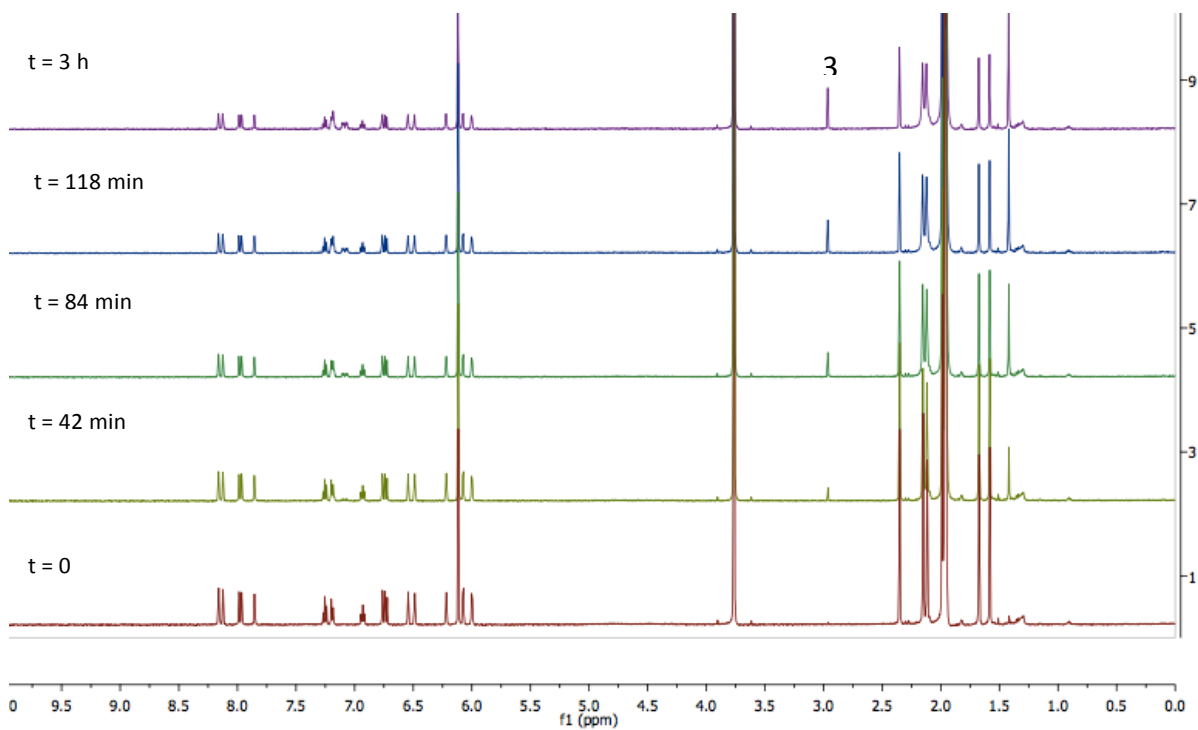


Figure S7. ¹H NMR array of C–C reductive elimination from **2-Ni^{IV+}** to form **3** in the light. Conditions: [Ni] = 0.0023 M; T = 25 °C, standard = 1,3,5-trimethoxybenzene

Procedure for “light/dark” experiment: In a glovebox, **2-Ni^{IV}** (2.7 mg, 0.0047 mmol, 1.0 equiv) was weighed into a 4 mL vial and then dissolved in CD₃CN (2.0 mL) at 25 °C. 1,3,5-trimethoxybenzene (0.0047 mmol, 1.0 equiv) was added as a ¹H NMR standard. Approximately 1 mL of the resulting solution was transferred to a screw cap NMR tube. The tube was sealed with a Teflon-lined cap and removed from the glovebox, and the initial rate of C–C bond-forming reductive elimination was determined by monitoring the appearance of product by ¹H NMR spectroscopy over 3 h at 22°C. The sample was placed in the NMR spectrometer, the spectrum was acquired, and the sample was removed from the spectrometer and exposed to ambient light until the next time point (*light phase*) or kept in the spectrometer until the next time point (*dark phase*). Spectra were acquired approximately 20 min apart with 40 min between each phase of light or dark. Yield of **3** versus time data were acquired from the integration of the ¹H NMR signals of the product 1,1-dimethylbenzocyclobutane **3** relative to the internal standard (1,3,5-trimethoxybenzene).

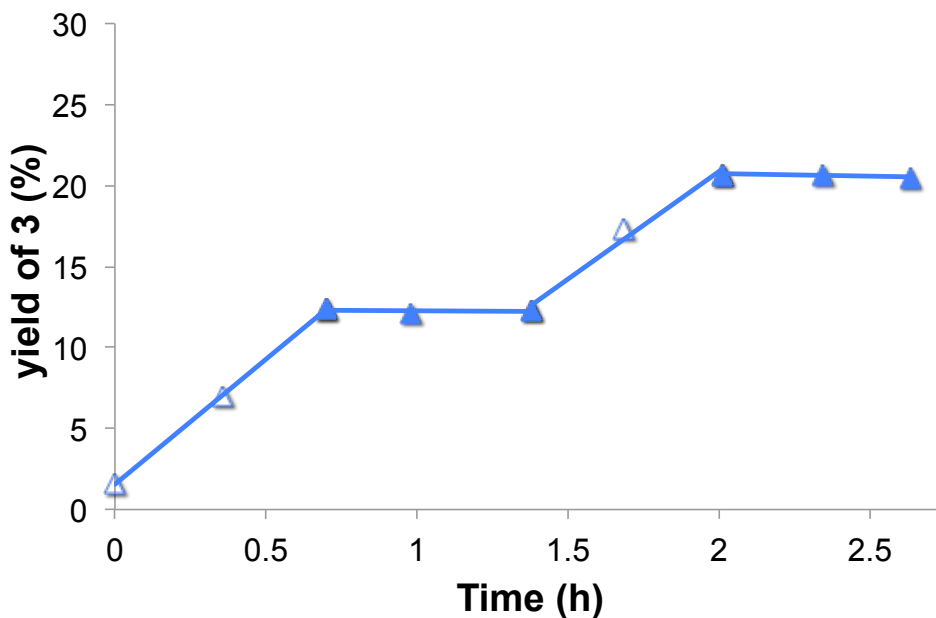
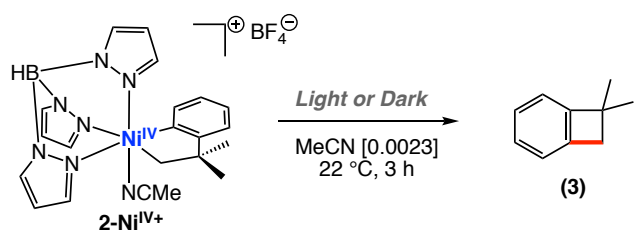


Figure S8. Plot of yield vs time for the formation of **3** from **2-Ni^{IV}** in the light and dark (alternating phases). Conditions: [Ni] = 0.0023 M; T = 25 °C. Note: lines drawn for clarity, not for rates.

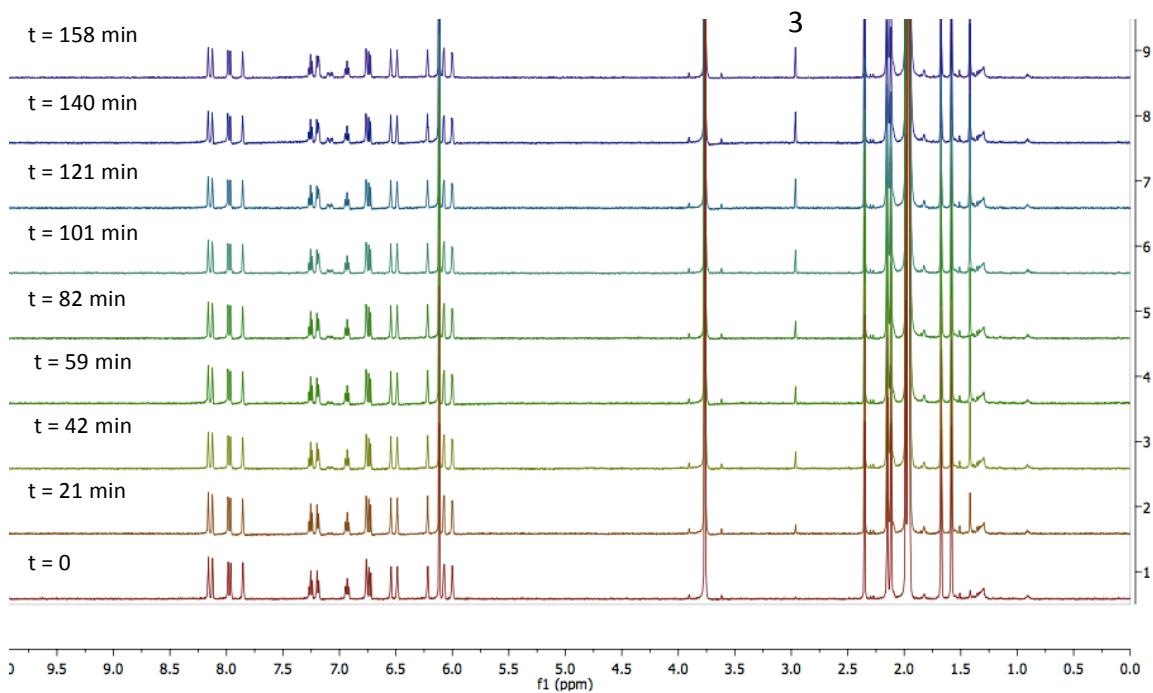
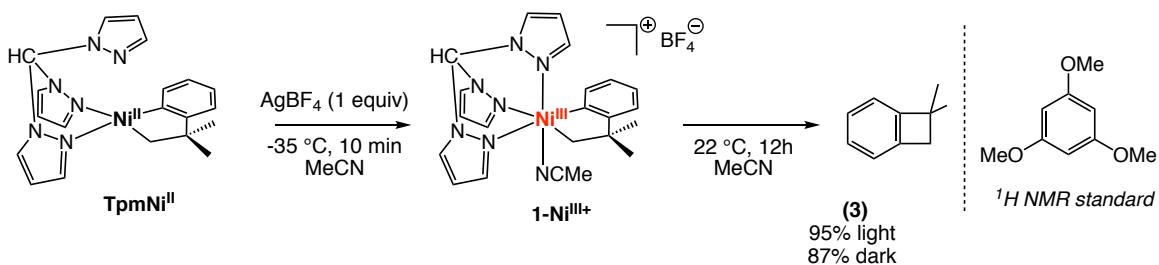


Figure S9. ¹H NMR array of C–C reductive elimination from **2-Ni^{IV+}** to form **3** in the light and dark (alternating phases). Conditions: [Ni] = 0.0023 M; T = 25 °C, standard = 1,3,5-trimethoxybenzene

V. Reactivity Studies of 1-Ni^{III+} and 2-Ni^{IV+}

C–C Coupling from 1-Ni^{III+}



Experimental Procedure: A solution of **TpmNi^{II}** (4.0 mg, 0.0094 mmol, 1.0 equiv) and trimethoxybenzene (1.0 equiv) in CD_3CN (2.0 mL) was added to a vial containing AgBF_4 (1.8 mg, 0.0094 mmol, 1.0 equiv). The solution immediately turned dark red and Ag^0 formation was observed. The vial was placed inside a $-35\text{ }^\circ\text{C}$ freezer. After 10 min, the solution was filtered through a pad of Celite (that was pre-cooled to $-35\text{ }^\circ\text{C}$). The Celite was washed with CD_3CN until the total volume was 4.0 mL. Approximately 1 mL of the resulting orange solution was transferred to each of 4 screw cap NMR tubes. The tubes were sealed with Teflon-lined caps and removed from the glovebox. Two tubes were kept in the light and two were wrapped in aluminum foil. The reactions were kept at room temperature for 12 h. The solutions were then analyzed by ^1H NMR spectroscopy to determine the yield of 1,1-dimethylbenzocyclobutane (which represents an average of two runs). The yield of **3** was 95% in the light and 87% in the dark.

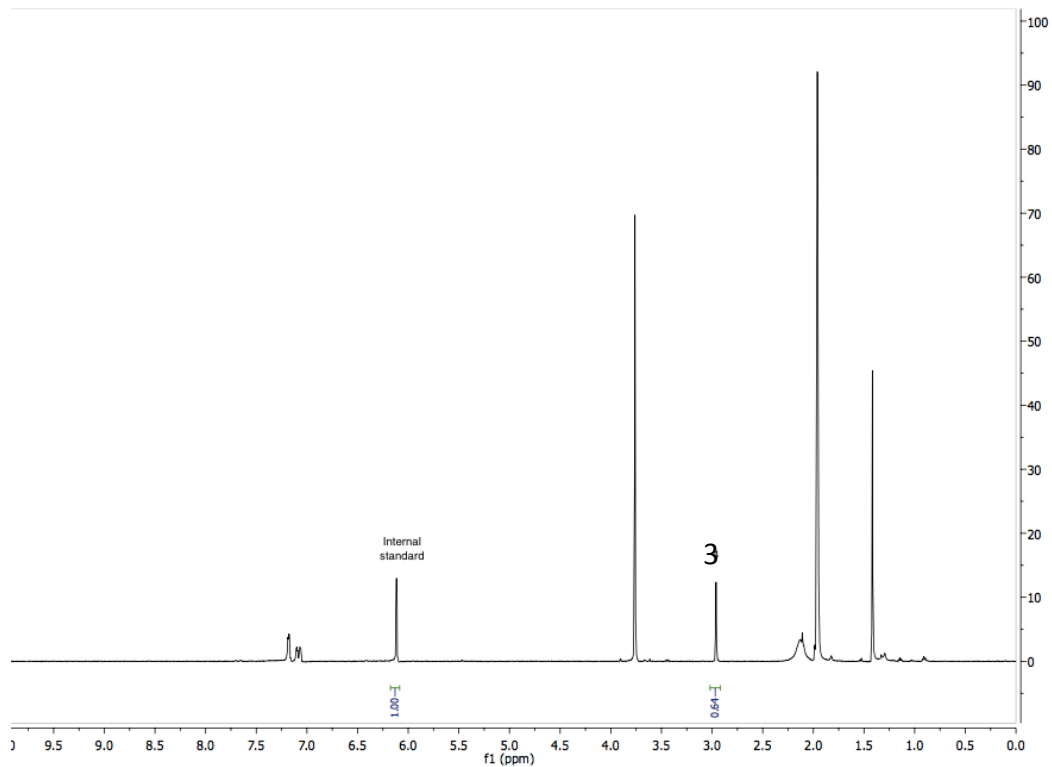


Figure S10. ^1H NMR spectrum of the crude reaction mixture of $1\text{-Ni}^{\text{III}+}$ at 22 °C for 12 h in the light. Standard = 1,3,5-trimethoxybenzene

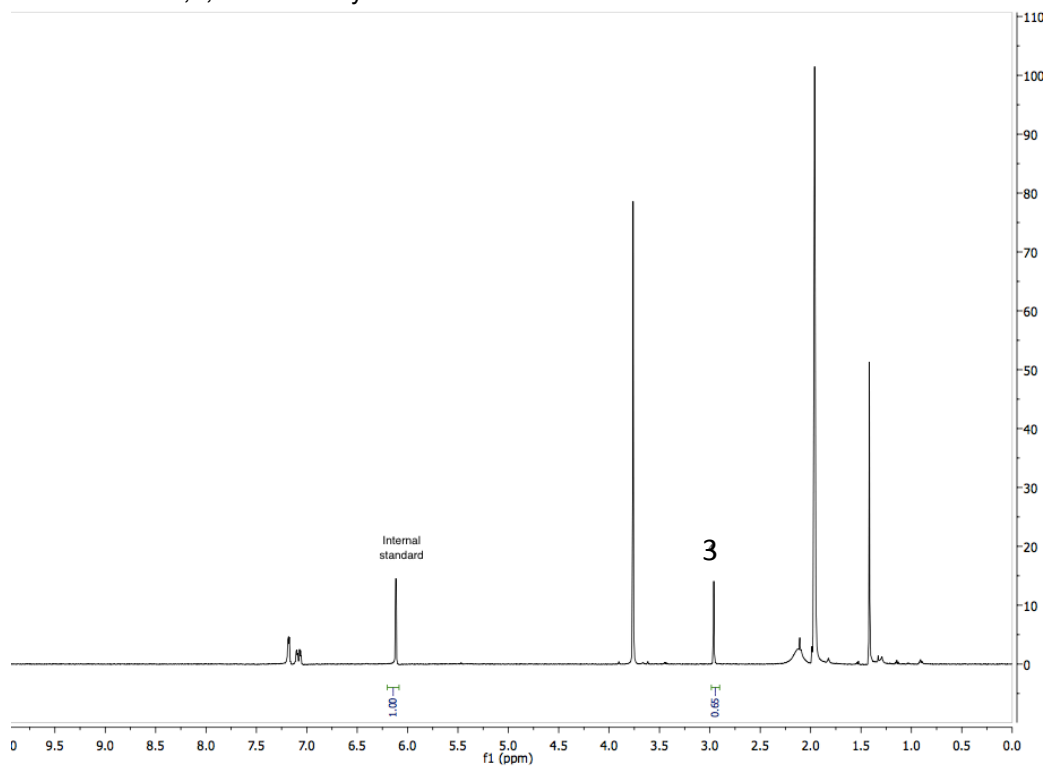
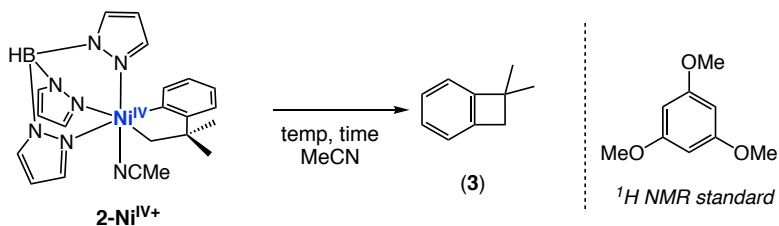


Figure S11. ^1H NMR spectrum of the crude reaction mixture of $1\text{-Ni}^{\text{III}+}$ at 22 °C for 12 h in the dark. Standard = 1,3,5-trimethoxybenzene

C–C Coupling from Ni^{IV} Complex 2-Ni^{IV+}



Entry	Complex	Temp (°C)	Time (h)	Yield (%) Light	Yield (%) Dark
1	2-Ni ^{IV+}	22	12	65	<5
2	2-Ni ^{IV+}	50	6	43	<5
3	2-Ni ^{IV+}	70	3	30	10

Experimental Procedure: A 20 mL vial was charged with **2-Ni^{IV+}** (5.4 mg, 0.0094 mmol, 1.0 equiv), 1,3,5-trimethoxybenzene (1.0 equiv) as a ¹H NMR standard, and CD₃CN (4.0 mL). Approximately 1 mL of the resulting orange solution was transferred to each of four screw cap NMR tubes. The tubes were sealed with Teflon-lined caps and removed from the glovebox. Two tubes were kept in the light and two were wrapped in aluminum foil. The reactions were maintained at the appropriate temperature for the times indicated in the table above. The solutions were then analyzed by ¹H NMR spectroscopy to determine the yield of **3** (the yields reported above represent an average of at least two runs).

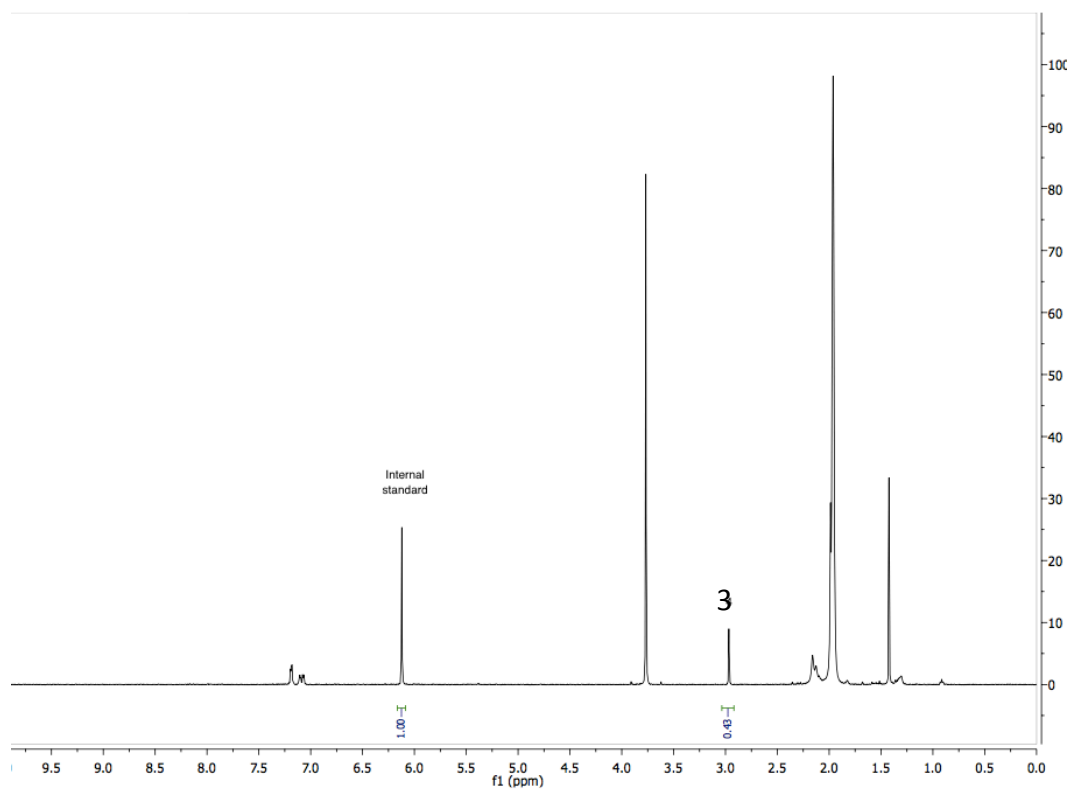


Figure S12. ^1H NMR spectrum of the crude reaction mixture of $2\text{-Ni}^{\text{IV}+}$ at 22 °C for 12 h in the light. Standard = 1,3,5-trimethoxybenzene

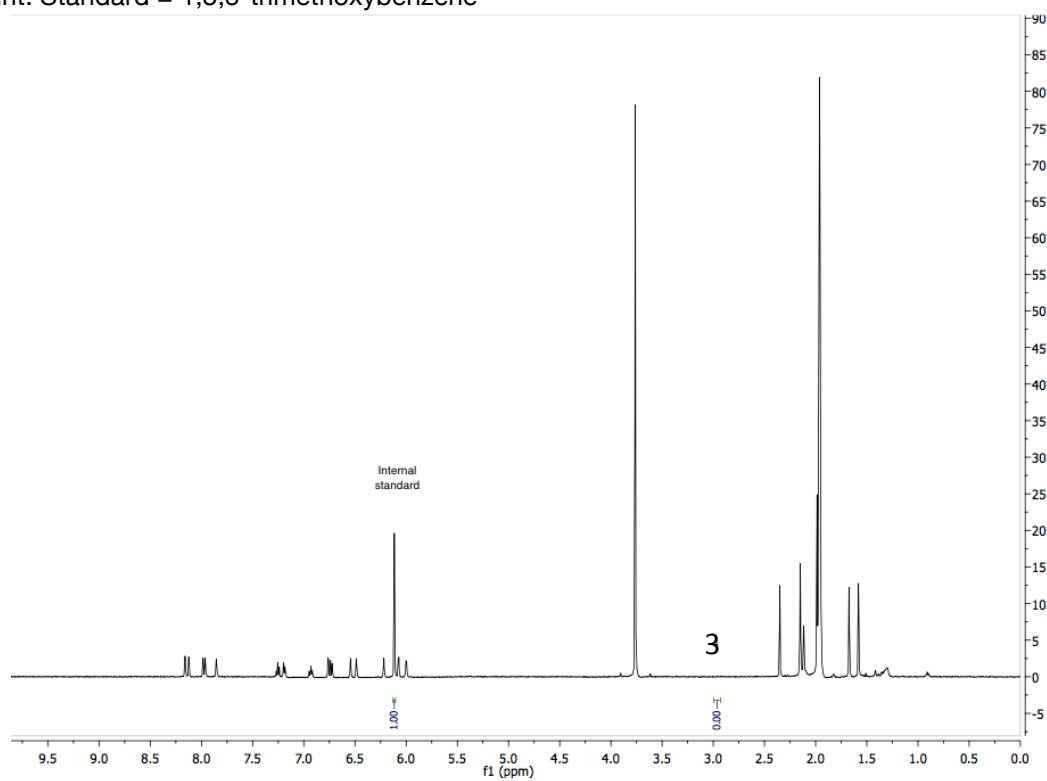


Figure S13. ^1H NMR spectrum of the crude reaction mixture of $2\text{-Ni}^{\text{IV}+}$ at 22 °C for 12 h in the dark. Standard = 1,3,5-trimethoxybenzene

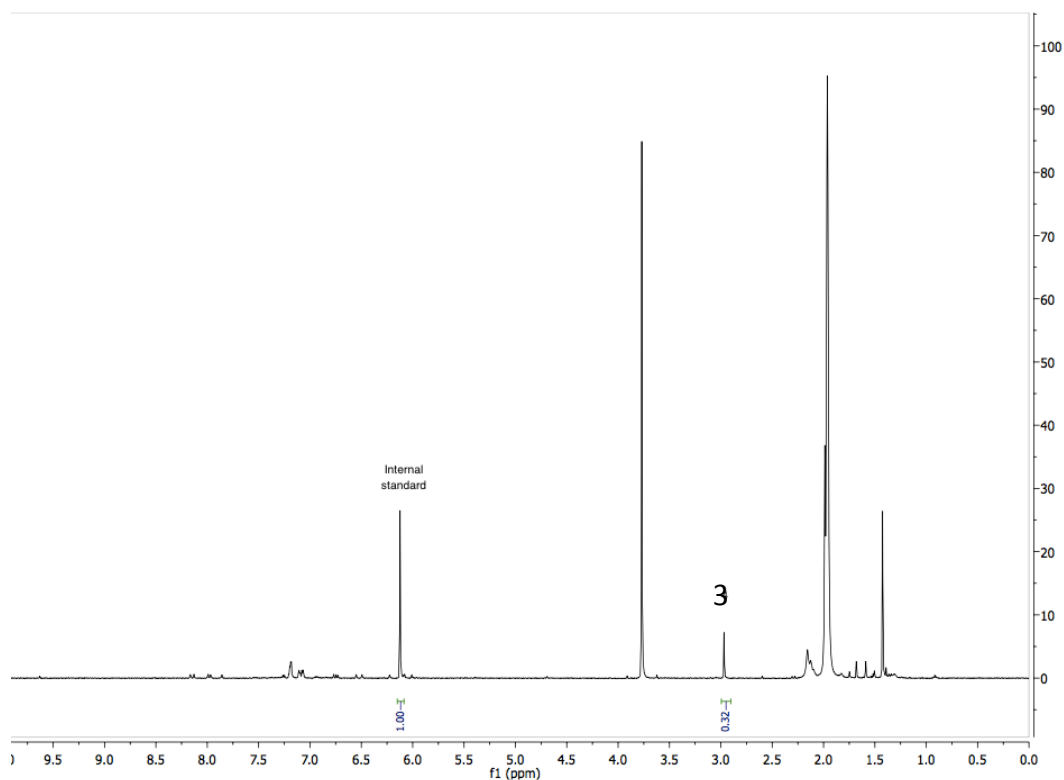


Figure S14. ^1H NMR spectrum of the crude reaction mixture of $2\text{-Ni}^{\text{IV}+}$ at $50\text{ }^\circ\text{C}$ for 6 h in the light. Standard = 1,3,5-trimethoxybenzene

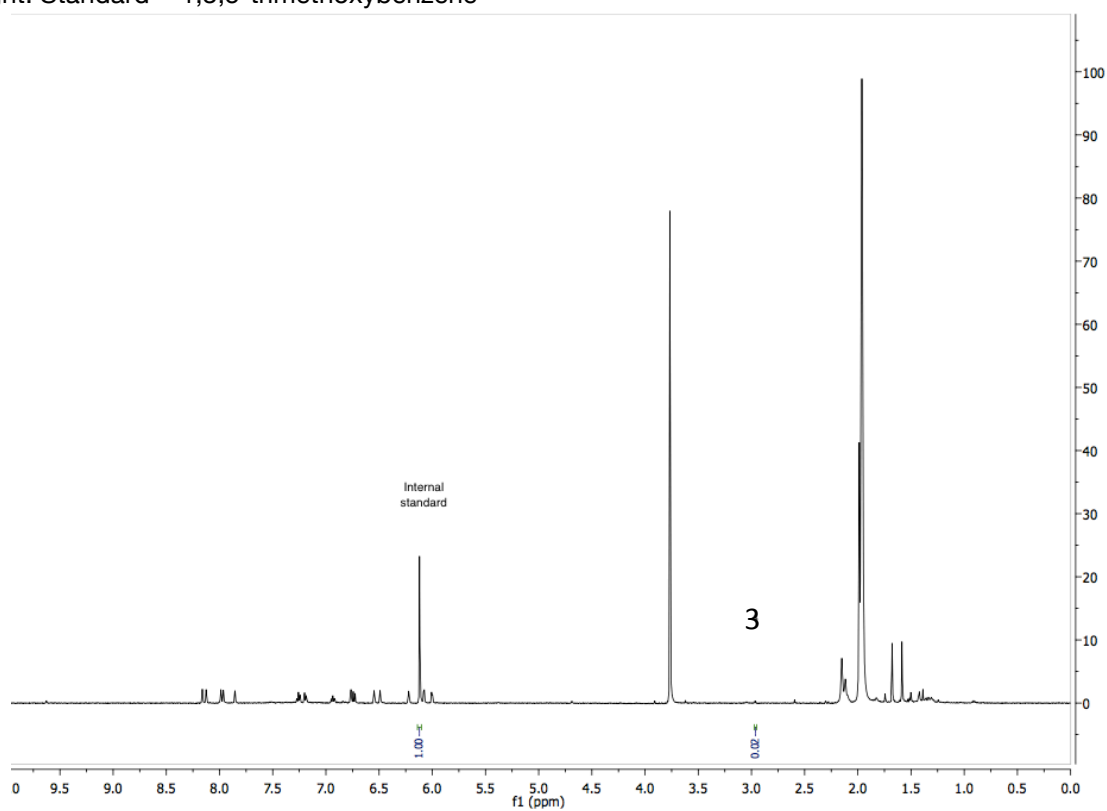


Figure S15. ^1H NMR spectrum of the crude reaction mixture of $2\text{-Ni}^{\text{IV}+}$ at $50\text{ }^\circ\text{C}$ for 6 h in the dark. Standard = 1,3,5-trimethoxybenzene

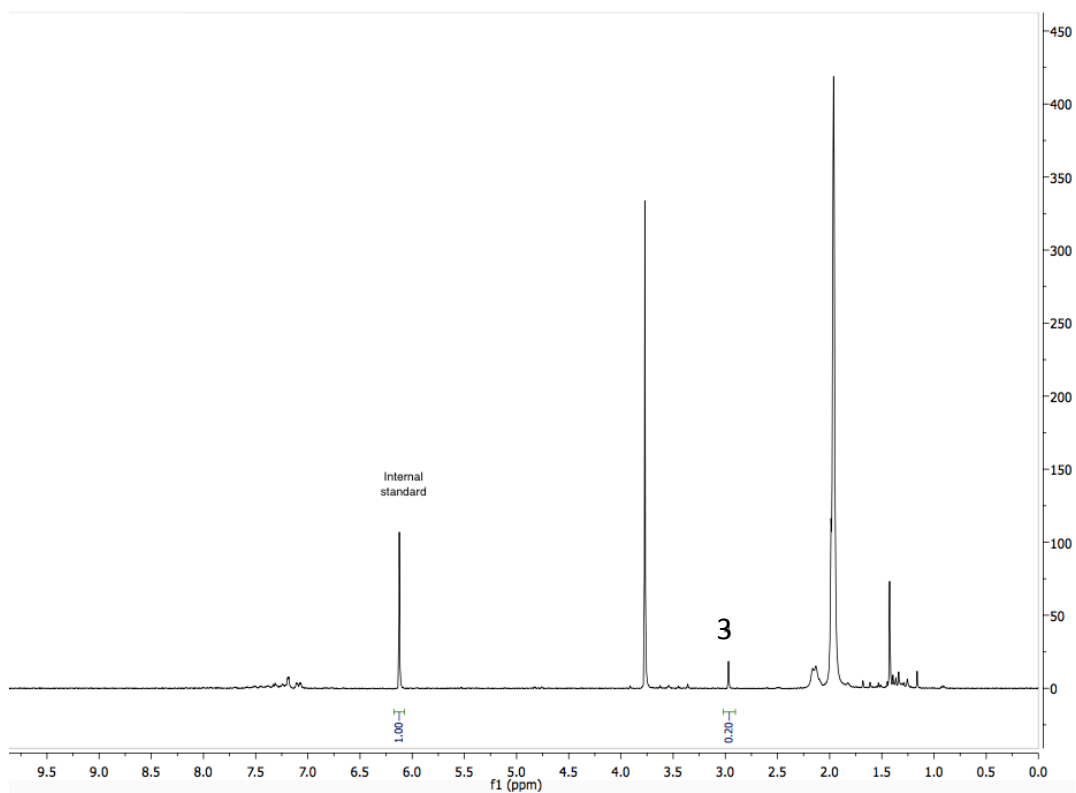


Figure S16. ^1H NMR spectrum of the crude reaction mixture of $2\text{-Ni}^{\text{IV}+}$ at $70\text{ }^\circ\text{C}$ for 3 h in the light. Standard = 1,3,5-trimethoxybenzene

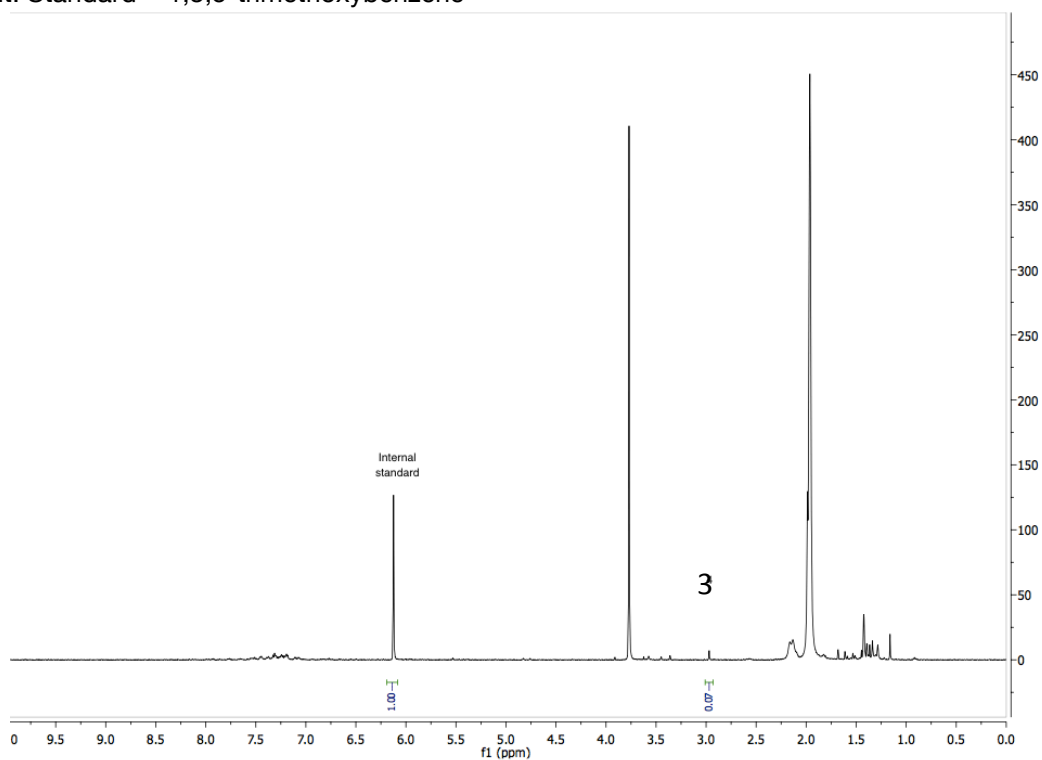
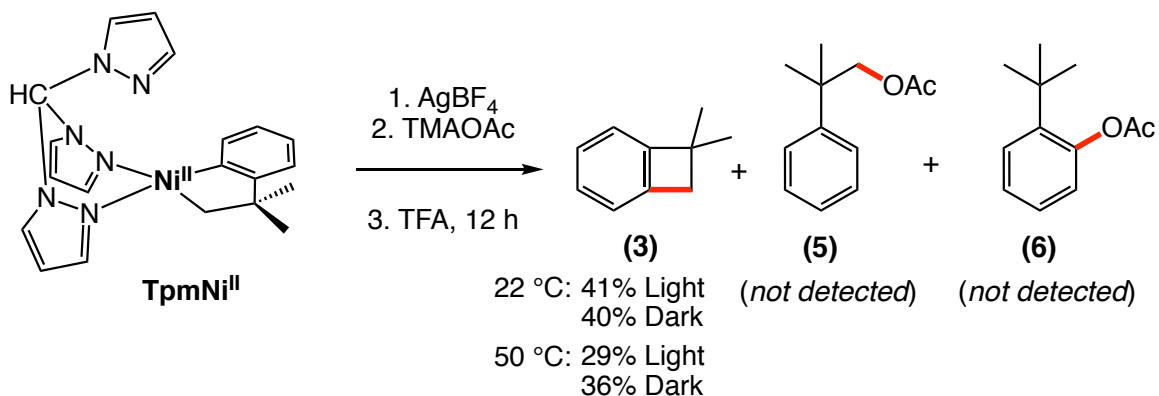


Figure S17. ^1H NMR spectrum of the crude reaction mixture of $2\text{-Ni}^{\text{IV}+}$ at $70\text{ }^\circ\text{C}$ for 3 h in the dark. Standard = 1,3,5-trimethoxybenzene

VI. Reactivity Studies of 1-Ni^{III+} and 2-Ni^{IV+} with NMe₄OAc

Reactivity of 1-Ni^{III+} in the Presence of Acetate



Experimental Procedure: All reagents, vials, solvent, and filters were cooled to $-35\text{ }^{\circ}\text{C}$ in the glovebox freezer. Eight 4-mL vials were charged with tetramethylammonium acetate (3.1 mg, 0.023 mmol, 2.0 equiv). A solution of **TpmNi^{II}** (38.7 mg, 0.092 mmol, 1.0 equiv) and trimethoxybenzene (15.5 mg, 0.092 mmol, 1.0 equiv) in CD₃CN (2 mL) was added to a vial containing AgBF₄ (17.9 mg, 0.092 mmol, 1.0 equiv). The vial was shaken, and the solution immediately turned dark red and Ag⁰ formation was observed. The vial was placed in a $-35\text{ }^{\circ}\text{C}$ freezer for 10 min. The resulting solution was filtered through a pad of Celite and washed with CD₃CN to give a total volume of 4.0 mL of CD₃CN. A 0.5 mL aliquot of this solution was added to each vial containing tetramethylammonium acetate. The resulting orange solutions were then transferred to screw cap NMR tubes, which were sealed with Teflon-lined caps and removed from the glovebox. Four NMR tubes were kept at 22 °C for 12 h (2 tubes in the light and 2 tubes in the dark). Four NMR tubes were kept at 50 °C for 6 h (2 tubes in the light and 2 tubes in the dark). Each crude reaction was then analyzed by ¹H NMR spectroscopy to determine the yield of 1,1-dimethylbenzocyclobutane **3**. Trifluoroacetic acid (200 μL of a ~10% solution of TFA in CD₃CN) was added and the mixture was allowed to stand for 12 h at 22 °C to protonate any Ni–C bonds. The resulting solutions were analyzed by ¹H NMR spectroscopy and GCMS, which showed no trace of products **5** or **6**.

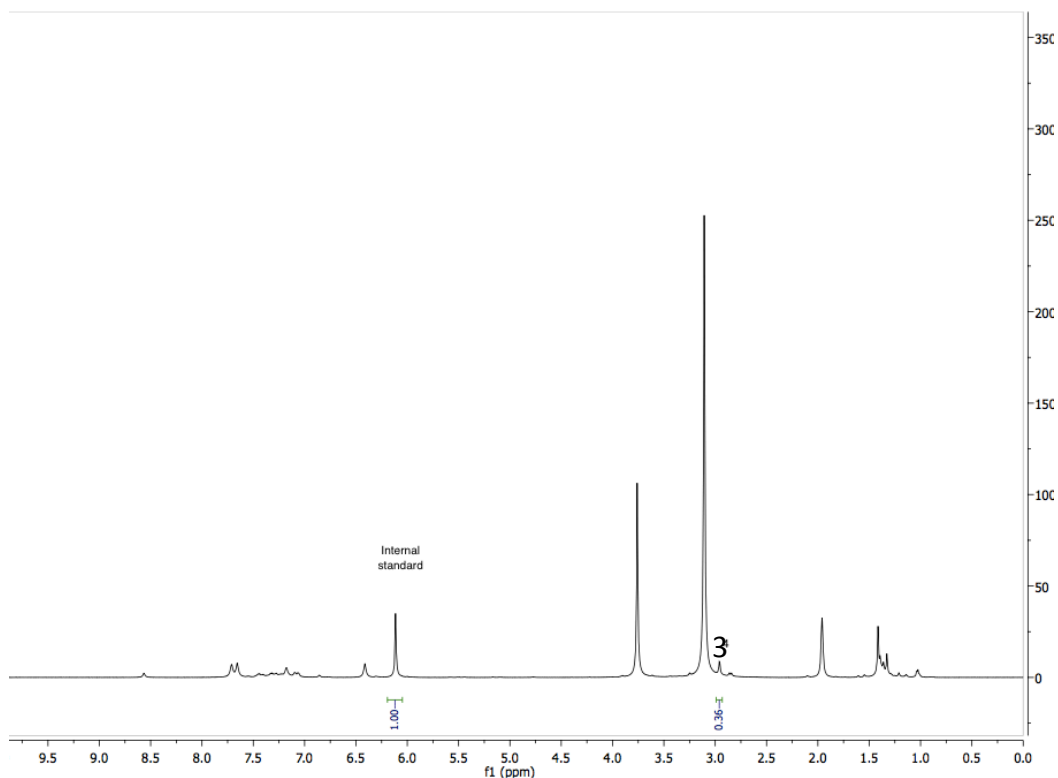


Figure S18. ^1H NMR spectrum of the crude reaction mixture after treating $1\text{-Ni}^{\text{III}+}$ with 2 equiv of NMe_4OAc for 12 h at 22 °C in the light. Standard 1,3,5-trimethoxybenzene

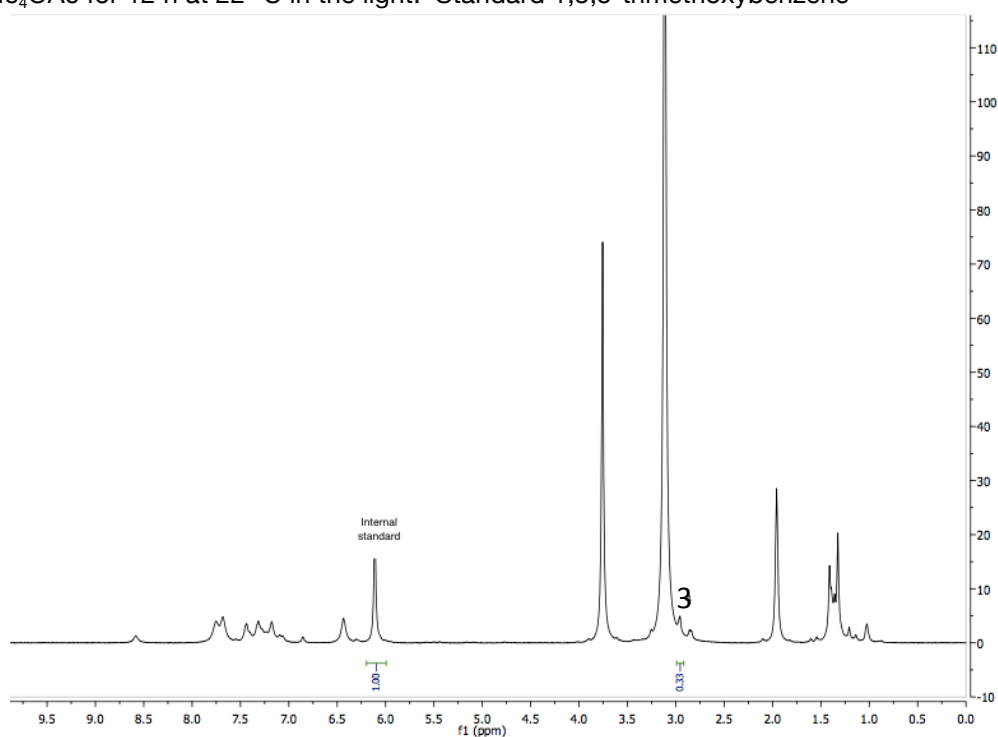


Figure S19. ^1H NMR spectrum of the crude reaction mixture after treating $1\text{-Ni}^{\text{III}+}$ with 2 equiv of NMe_4OAc for 12 h at 22 °C in the dark. Standard 1,3,5-trimethoxybenzene

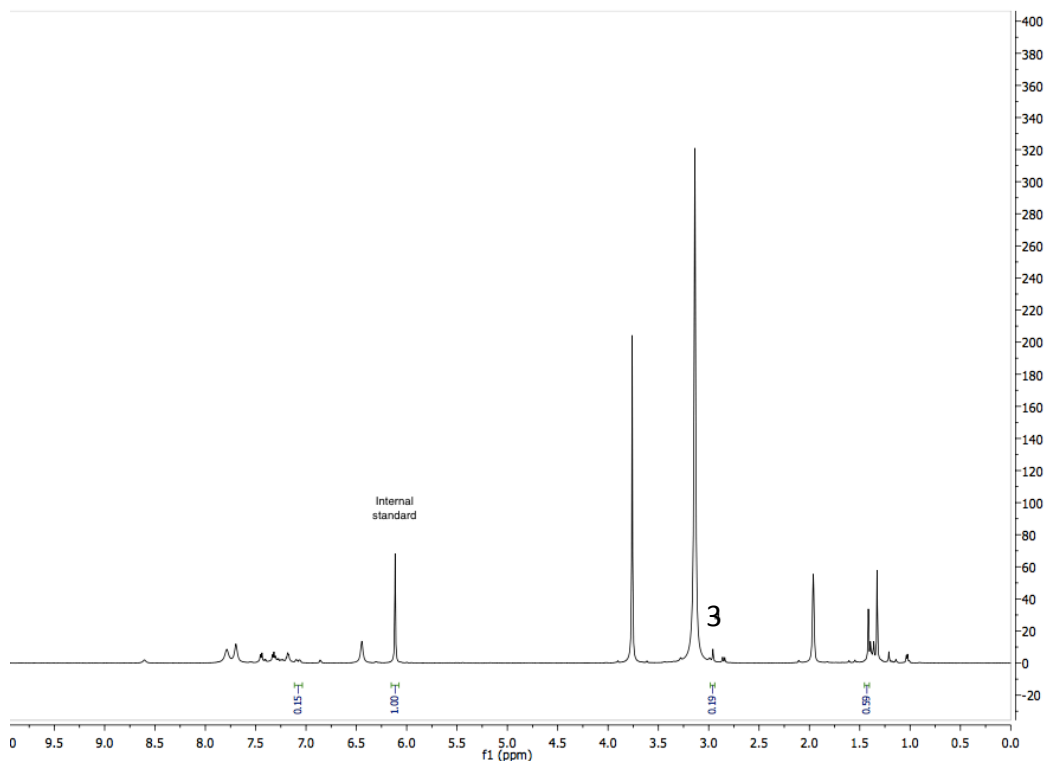


Figure S20. ^1H NMR spectrum of the crude reaction mixture after treating $\mathbf{1-Ni}^{\text{III}}$ with 2 equiv of NMe_4OAc for 6 h at 50 °C in the light followed by treatment with trifluoroacetic acid. Standard 1,3,5-trimethoxybenzene

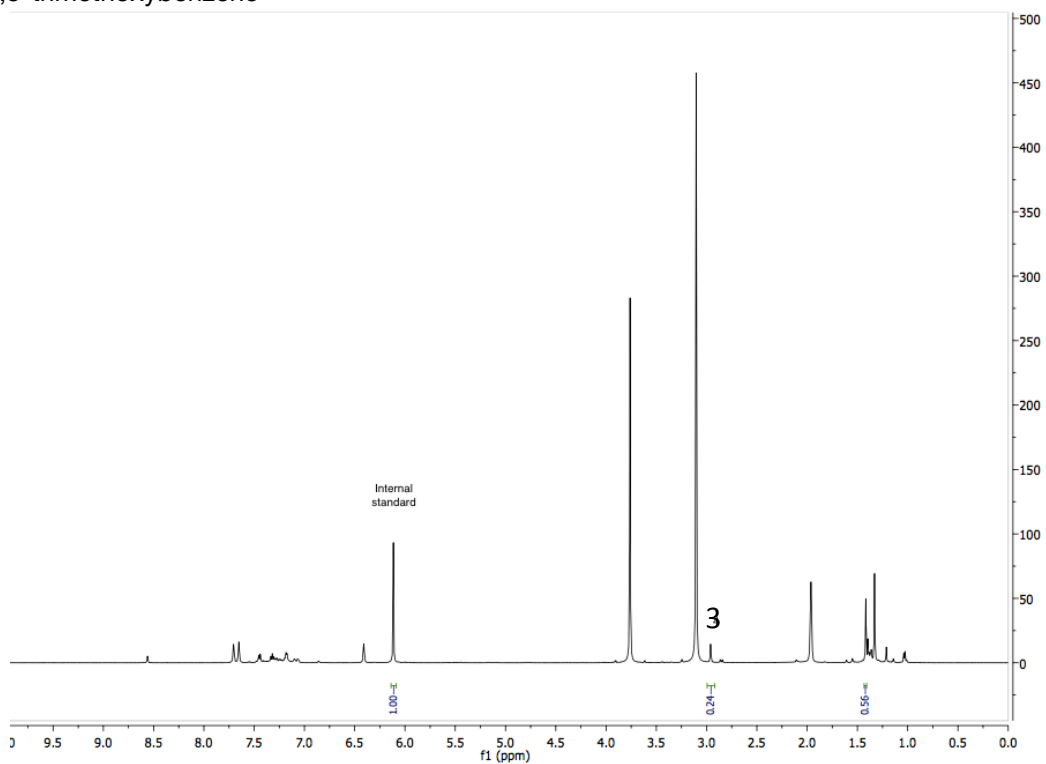
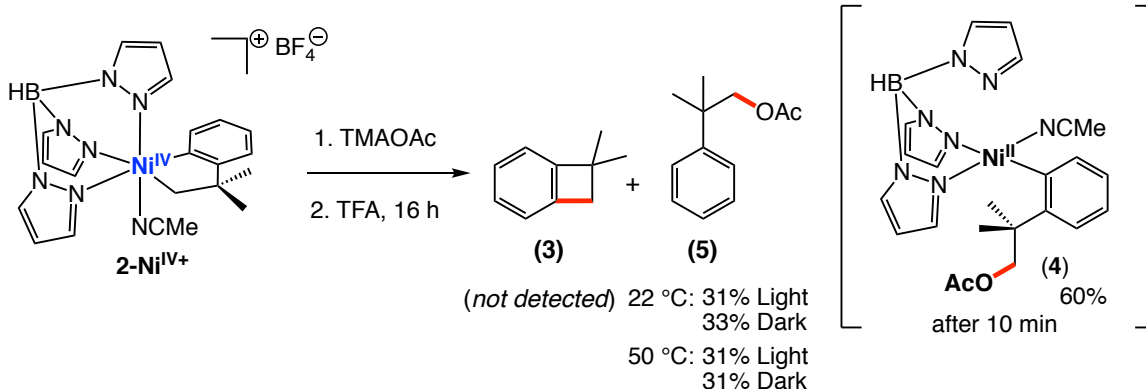


Figure S21. ^1H NMR spectrum of the crude reaction mixture after treating $\mathbf{1-Ni}^{\text{III}}$ with 2 equiv of NMe_4OAc for 6 h at 50 °C in the dark followed by treatment with trifluoroacetic acid. Standard 1,3,5-trimethoxybenzene

Reactivity of 2-Ni^{IV+} in the Presence of Acetate



Experimental Procedure: A stock solution of **2-Ni^{IV+}** and internal standard was prepared. A 20 mL vial was charged with **2-Ni^{IV+}** (53 mg, 0.092 mmol, 1.0 equiv), 1,3,5-trimethoxybenzene (15.5 mg, 0.092 mmol, 1.0 equiv) as an internal ¹H NMR standard, and 4.0 mL MeCN. Eight 4-mL vials were charged with tetramethylammonium acetate (3.1 mg, 0.023 mmol, 2.0 equiv). To each of the vials containing TMAOAc, 0.5 mL of the stock solution was added.

The resulting orange solutions were then transferred to screw cap NMR tubes, which were sealed with Teflon-lined caps and removed from the glovebox. Four NMR tubes were kept at 22 °C for 12 h (2 tubes in the light and 2 tubes in the dark). Four NMR tubes were kept at 50 °C for 6 h (2 tubes in the light and 2 tubes in the dark). Each crude reaction was then analyzed by ¹H NMR spectroscopy to determine the yield of **3** (not detected) and **4/5**. Trifluoroacetic acid (200 μL of a ~10% solution of TFA in CD₃CN) was added and the mixture was allowed to stand for 12 h at 22 °C to protonate any Ni–C bonds. The resulting solutions were analyzed by ¹H NMR spectroscopy and GCMS, which showed no trace of products **3** or **6**.

An additional reaction was conducted according to the procedure above, but allowed to stand for just 10 min at 22 °C in the light. ¹H NMR analysis of the crude reaction mixture showed the complete conversion of **2-Ni^{IV+}** into **4**.

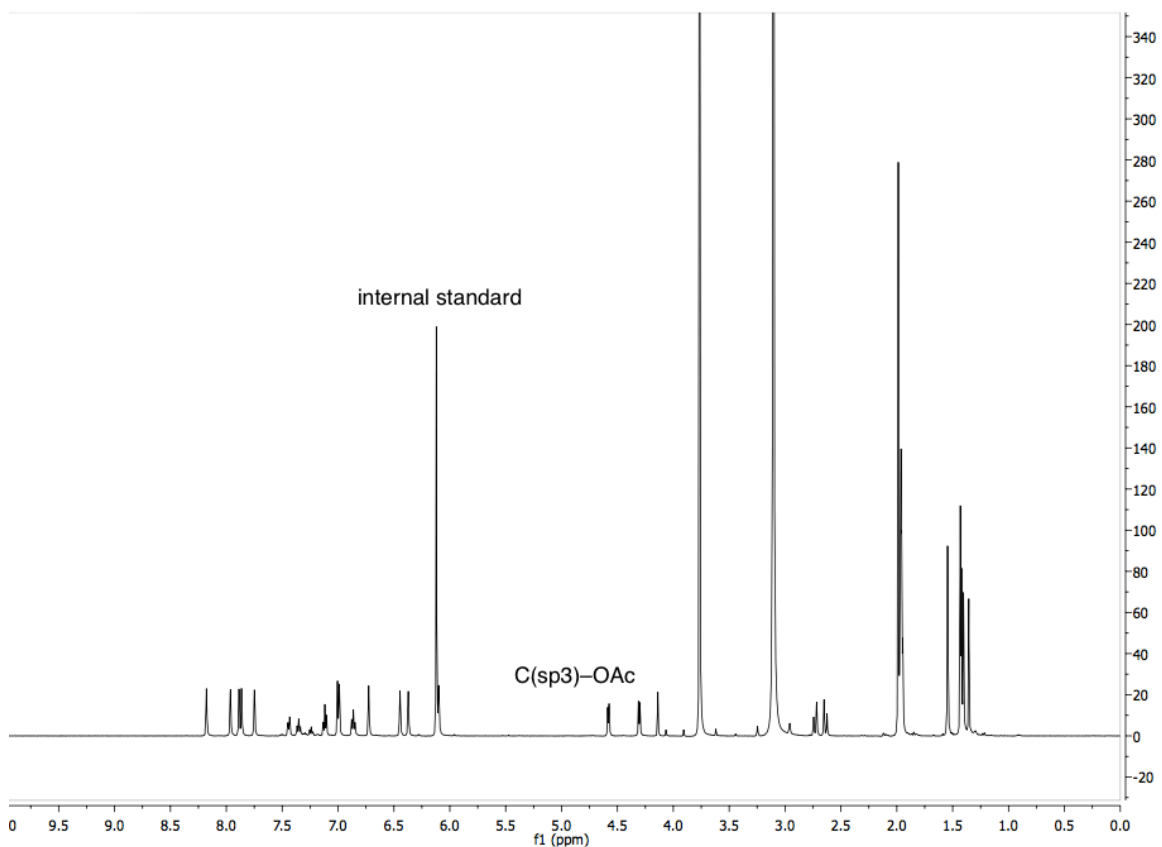


Figure S22. 10 min. ^1H NMR spectrum of the crude reaction mixture after treating $2\text{-Ni}^{\text{IV}+}$ with 2 equiv of NMe_4OAc for 10 min h at 22 °C in the light. Standard 1,3,5-trimethoxybenzene

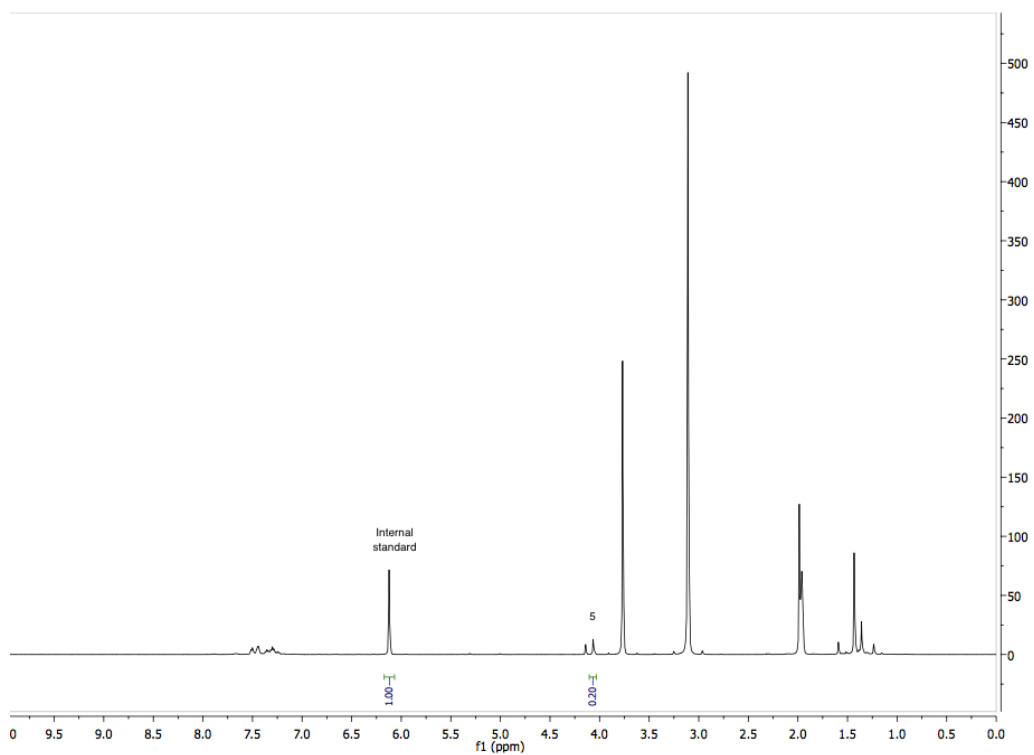


Figure S23. ^1H NMR spectrum of the crude reaction mixture after treating 2-Ni^{IV} with 2 equiv of NMe_4OAc for 12 h at 22 °C in the light followed by treatment with trifluoroacetic acid. Standard 1,3,5-trimethoxybenzene

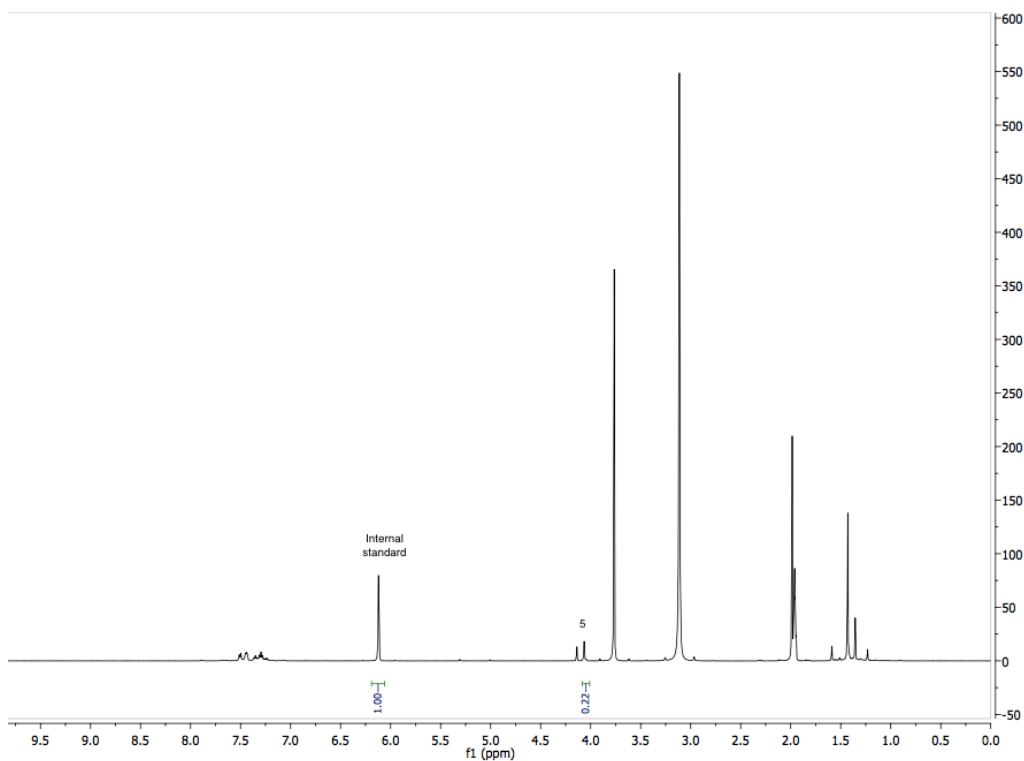


Figure S24. ^1H NMR spectrum of the crude reaction mixture after treating $2\text{-Ni}^{\text{IV}+}$ with 2 equiv of NMe_4OAc for 12 h at 22 °C in the dark followed by treatment with trifluoroacetic acid. Standard 1,3,5-trimethoxybenzene

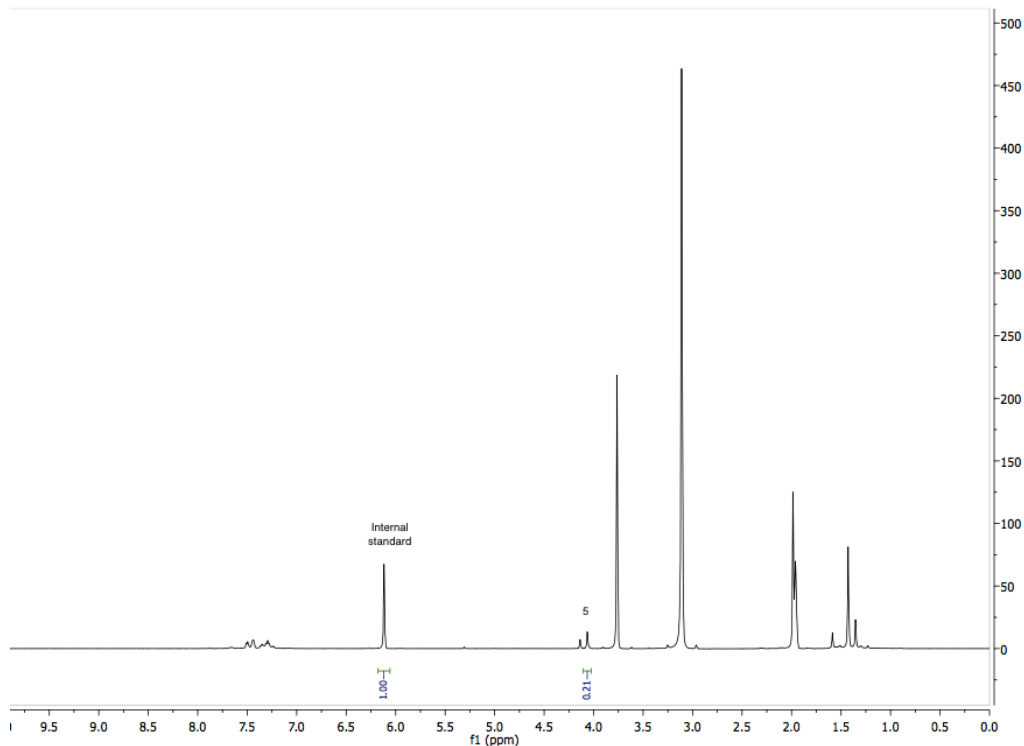


Figure S25. ^1H NMR spectrum of the crude reaction mixture after treating $2\text{-Ni}^{\text{IV}+}$ with 2 equiv of NMe_4OAc for 6 h at 50 °C in the light followed by treatment with trifluoroacetic acid. Standard 1,3,5-trimethoxybenzene

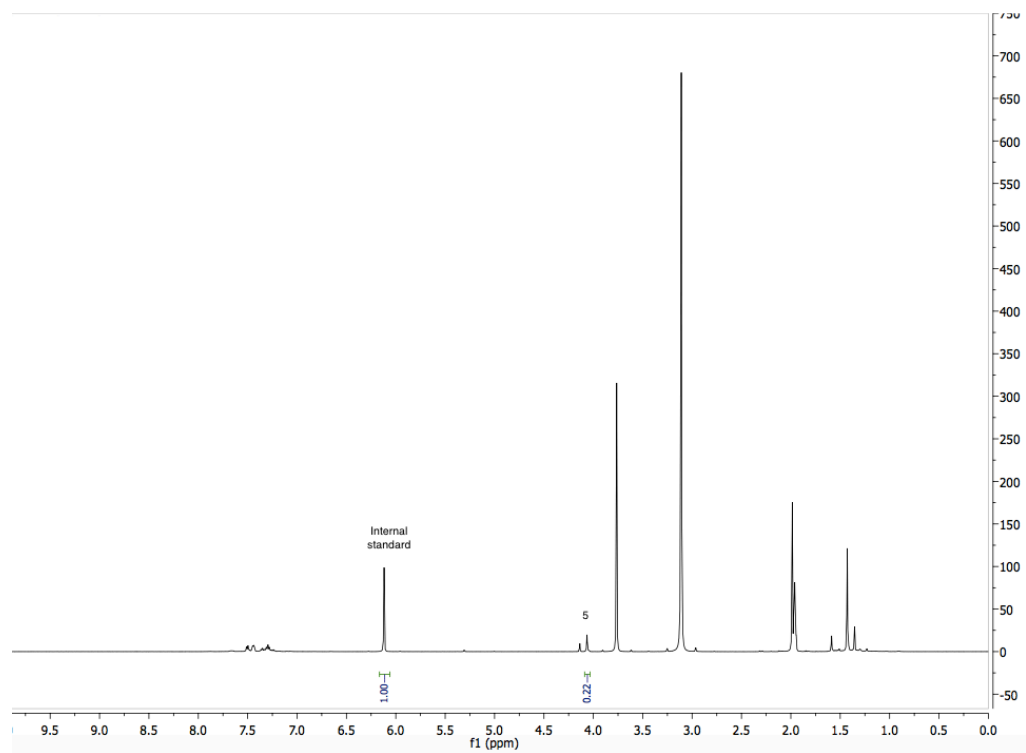


Figure S26. ^1H NMR spectrum of the crude reaction mixture after treating **2-Ni^{IV}** with 2 equiv of NMe_4OAc for 6 h at 50 °C in the dark followed by treatment with trifluoroacetic acid. Standard 1,3,5-trimethoxybenzene

VIII. EPR Studies

Experimental Procedure for the EPR detection of *in situ* generated $1\text{-Ni}^{\text{III}+}$. All glassware and solvents used were pre-cooled to $-35\text{ }^{\circ}\text{C}$. A solution of TpmNi^{II} (27.5 mg, 0.068 mmol, 1.0 equiv) in acetonitrile (3 mL) was cooled to $-35\text{ }^{\circ}\text{C}$ and added to a vial containing AgBF_4 (13.2 mg, 0.068 mmol, 1.0 equiv). The resulting heterogeneous mixture was filtered after 10 seconds, providing a dark red solution of $1\text{-Ni}^{\text{III}+}$. Four drops of this solution were added to 300 μL of a 3:1 PrCN:MeCN solution. The sample was then flash-frozen in a septum-capped EPR tube in liquid nitrogen for EPR analysis (Figure S29).

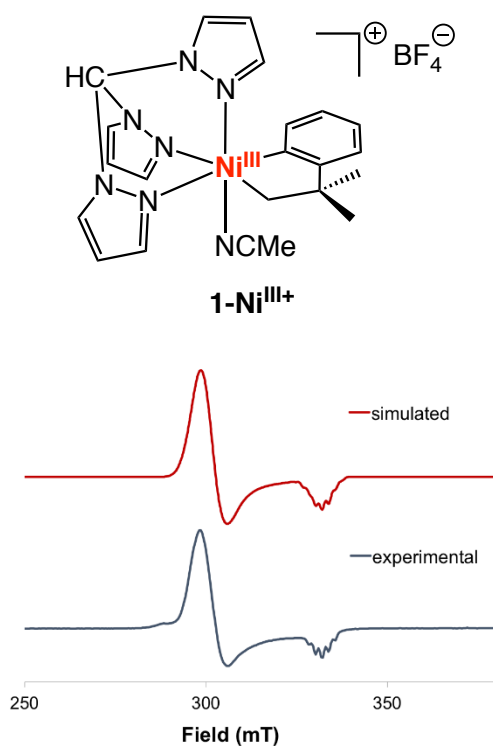


Figure S29. EPR spectrum of $1\text{-Ni}^{\text{III}+}$ (bottom/blue) and the simulated spectrum (top/red). Fit using the following parameters: $g_x = 2.23$, $g_y = 2.22$, $g_z = 2.01$, $A_N(2N) = 50\text{ G}$.

IX. CV Studies

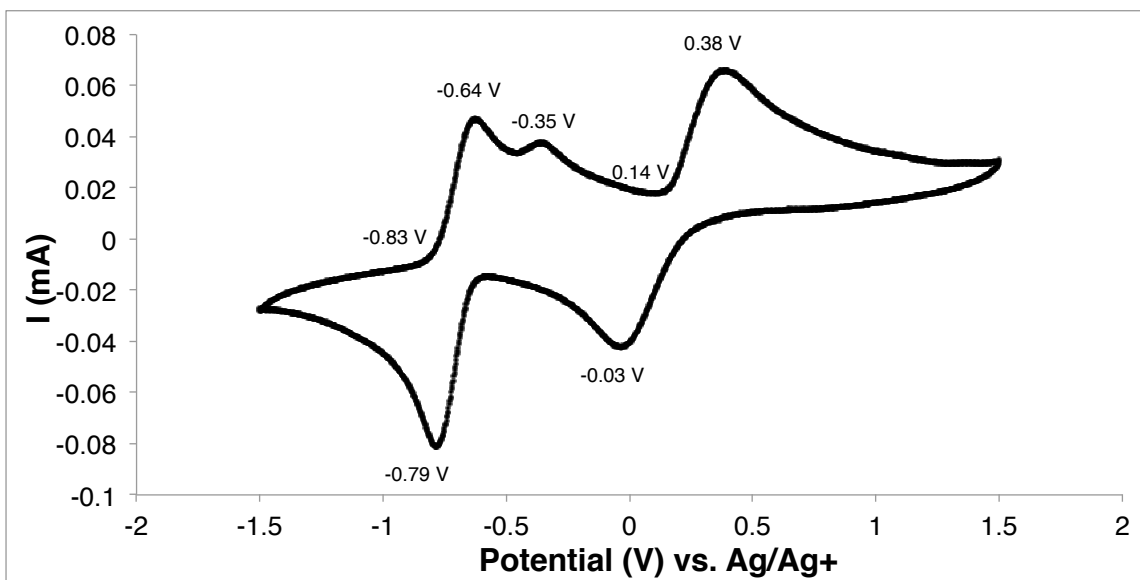


Figure S30. CV spectrum of TpmNi^{II} in MeCN/ NBu_4BF_4

Experimental Procedure: Cyclic voltammetry on complex TpmNi^{II} was performed in a 3 electrode cell consisting of a 3 mm glassy carbon disc working electrode, a Ag/Ag⁺ reference electrode with a Ag wire in a fritted chamber containing a solution of AgBF₄ (0.01 M) and NBu₄BF₄ (0.1 M) in acetonitrile, and a Pt wire counter electrode. A 2 mL solution of complex 1 (0.01 M) and NBu₄BF₄ (0.1 M) in acetonitrile was added to the electrochemical cell. Cyclic voltammetry scans were conducted at 100 mV/s starting from -2.0 to +2.0 V in the positive direction (S30). We hypothesize that the CV peak at -0.35 V is related to the lability of the Tpm ligand in MeCN (see pg. S3 for discussion of this phenomenon).

X. UV Vis Studies

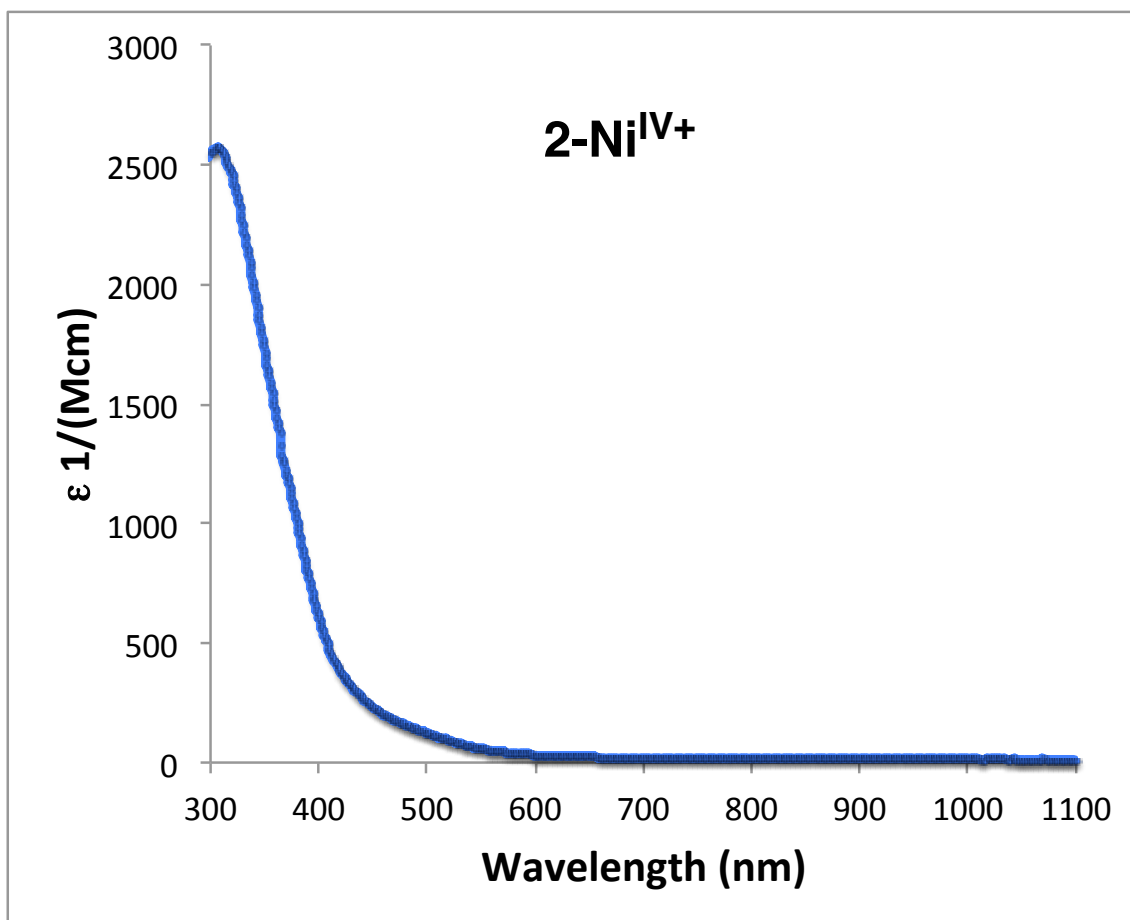


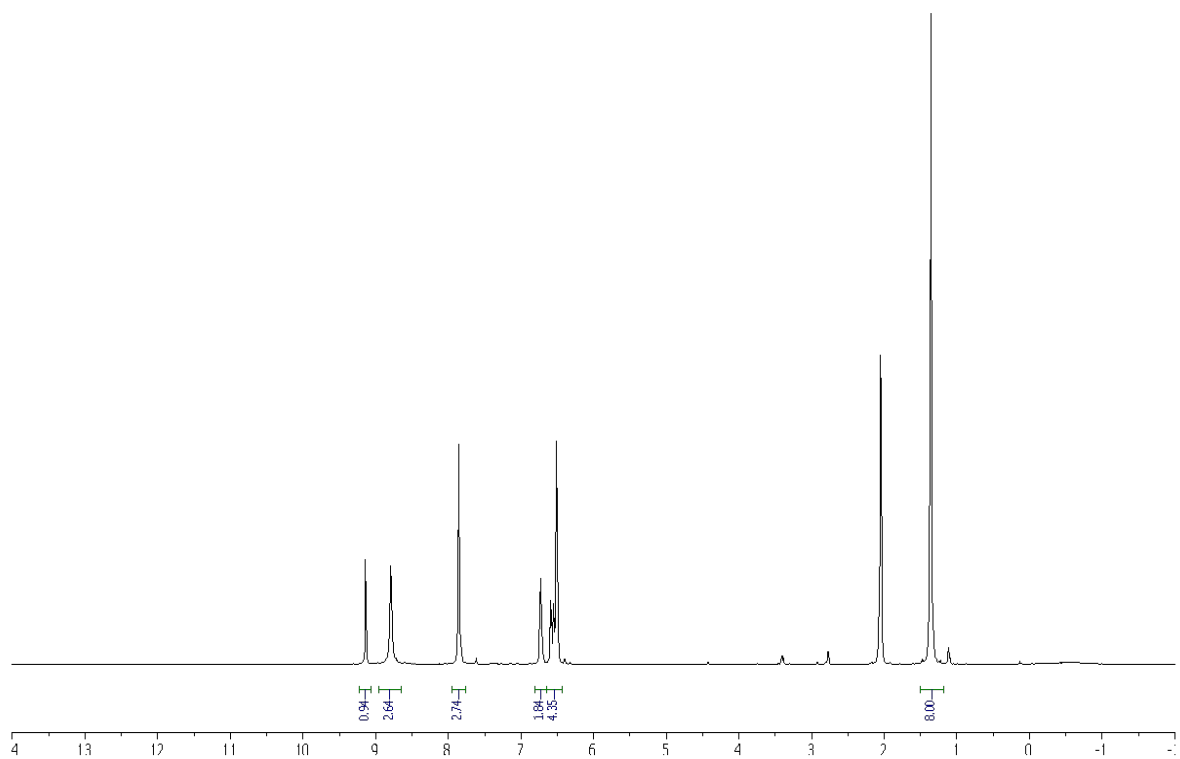
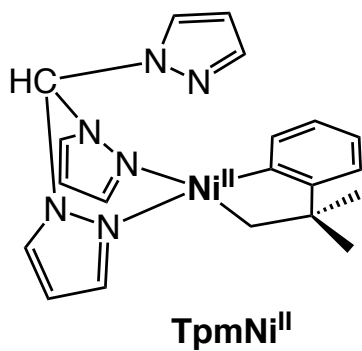
Figure S31. UV-Vis spectra of **2-Ni^{IV+}** in MeCN

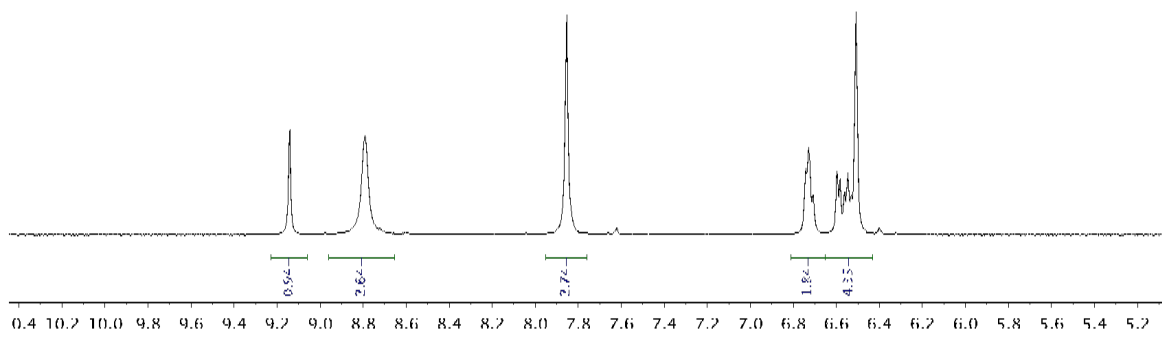
Experimental procedure: Inside a glovebox, a solution of 5 mg of **2-Ni^{IV+}** in 3 mL of MeCN was added to a quartz cuvette with a 10 mm path length. The cuvette was fitted with an air-tight Teflon stopper and analyzed via UV-vis spectroscopy. The spectrum is shown in Figure S31.

Note: Complex **1-Ni^{III+}** undergoes reaction too quickly and the appearance of the Ni^I product cannot be differentiated for the Ni^{III} starting material.

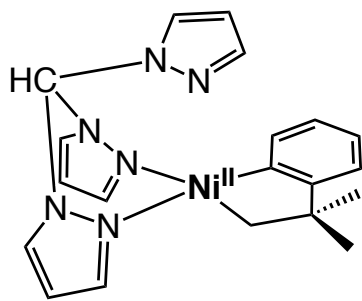
XI. Spectral Data

^1H NMR spectrum of TpmNi^{II} at 23 °C in acetone- d_6

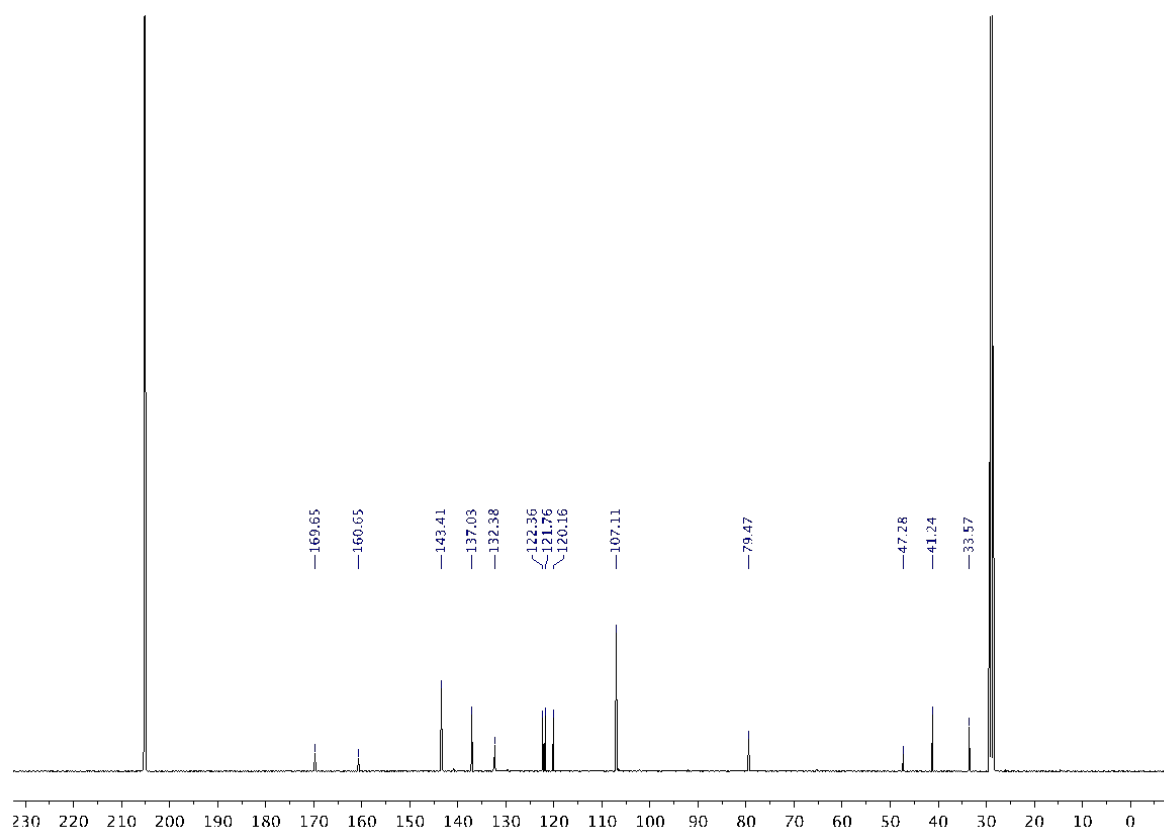




^{13}C NMR spectrum of TpmNi^{II} at 23 °C in acetone- d_6



TpmNi^{II}



XII. X-Ray Crystallography Experimental Data

CCDC 1905474 -1905476 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Structure determination for TpmNi^{II}

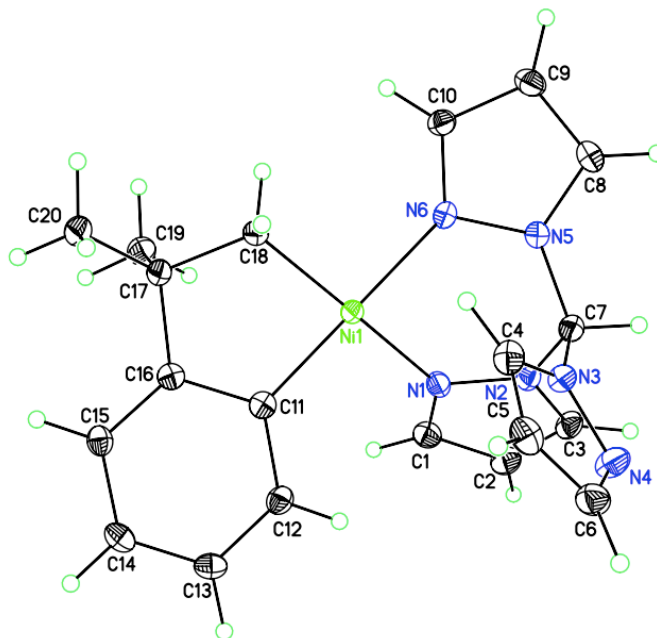


Figure S32. X-ray structure of TpmNi^{II} .

Yellow needles of TpmNi^{II} were grown from an acetonitrile solution of the compound at 22 °C. A crystal of dimensions 0.15 x 0.07 x 0.07 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187 \text{ \AA}$) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω . The exposure times were 1 sec. for the low angle images, 4 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 28006 reflections to a maximum 2θ value of 138.53° of which 3473 were independent and 3442 were greater than $2\sigma(I)$. The final cell constants (Table S1) were based on the xyz centroids 22935 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/n with $Z = 4$ for the formula $\text{C}_{20}\text{H}_{22}\text{N}_6\text{Ni}$. All non-hydrogen atoms were

refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F2 converged at $R1 = 0.0336$ and $wR2 = 0.0873$ [based on $I > 2\sigma(I)$], $R1 = 0.0338$ and $wR2 = 0.0874$ for all data. Additional details are presented in Table S1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.

CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table S1. Crystal Data and Structural Refinement for **TpmNi^{II}**.

Empirical formula	C ₂₀ H ₂₂ N ₆ Ni
Formula weight	405.14
Temperature	85(2) K
Wavelength	1.54178 Å
Crystal System	Monoclinic
Space group	P2(1)/n
Unit Cell Dimensions	a = 8.57397(6) Å, α = 90° b = 19.21509(16) Å, β = 103.3637 (7)° c = 11.64122(9) Å, γ = 90°
Volume	1865.96(3) Å ³
Z	4
Calculated density	1.442 Mg/m ³
Absorption coefficient	1.631 mm ⁻¹
F(000)	848
Crystal Size	0.150 x 0.070 x 0.067 mm
Theta range for data collection	4.532 to 69.268°
Limiting indices	-10 < h < 10, -23 < k < 21, -13 < l < 14
Reflections collected	28006
Independent collections	3473 [R(int) = 0.0517]
Completeness to theta	67.679 (99.8 %)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.88785
Refinement method	Full-matrix least-squares on F ²
Data/ restraints/ parameters	3473 / 0 / 247
Goodness-of-fit on F ²	1.083
Final R indices [I > 2σ(I)]	R1 = 0.0336, wR2 = 0.0873
R indices (all data)	R1 = 0.0338, wR2 = 0.0874
Extinction coefficient	0.0044(3)
Largest diff. peak and hole	0.344 and -0.384 e Å ⁻³

Structure determination for 1-Ni^{III+}

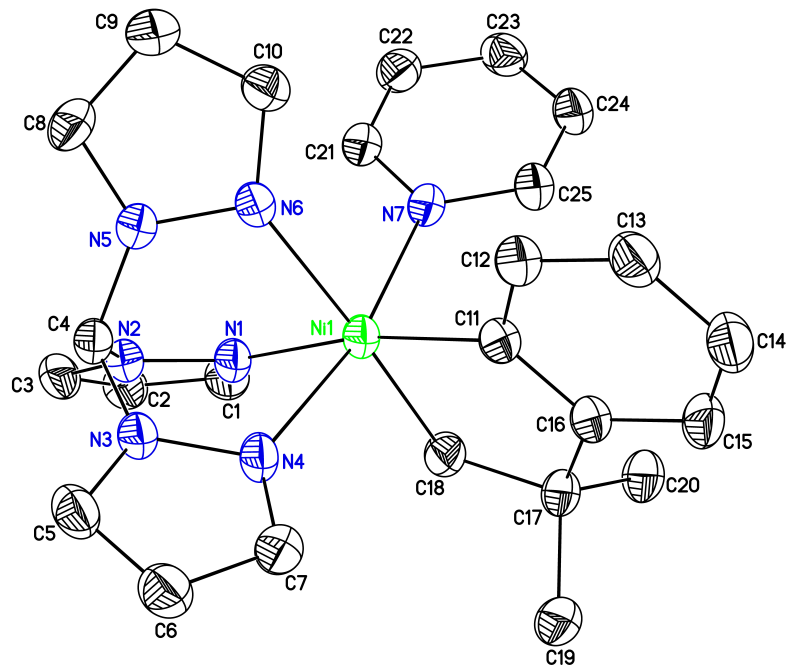


Figure S33. X-ray structure of **1-Ni^{III+}**. BF₄ counterion and THF molecule are omitted for clarity.

Structure Determination.

Purple needles of **1-Ni^{III+}** were grown from a tetrahydrofuran/pentane/pyridine solution of the compound at $-35\text{ }^{\circ}\text{C}$. A crystal of dimensions $0.21 \times 0.01 \times 0.01\text{ mm}$ was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187\text{ \AA}$) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω . The exposure times were 1 sec. for the low angle images, 6 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 44589 reflections to a maximum 2θ value of 139.02° of which 5618 were independent and 4765 were greater than $2\sigma(I)$. The final cell constants (Table S2) were based on the xyz centroids of 11298 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during

data collection. The structure was solved and refined with the Bruker SHELXTL (version 2016/6) software package, using the space group P2(1)/c with Z = 4 for the formula C₂₉H₃₅BN₇OF₄Ni. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F² converged at R1 = 0.0554 and wR2 = 0.1401 [based on I > 2sigma(I)], R1 = 0.0656 and wR2 = 0.1549 for all data. Additional details are presented in Table S2 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access).

CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table S2. Crystal Data and Structural Refinement for **1-Ni^{III+}**.

Empirical formula	C ₂₉ H ₂₂ N ₇ ONiBF ₄
Formula weight	643.16
Temperature	85(2) K
Wavelength	1.54184 Å
Crystal System	Monoclinic
Space group	P2(1)/c
Unit Cell Dimensions	a = 17.9856(4) Å, α = 90° b = 7.52790(10) Å, β = 97.195 (2)° c = 22.5122(4) Å, γ = 90°
Volume	3024.01(10) Å ³
Z	4
Calculated density	1.413 Mg/m ³
Absorption coefficient	1.447 mm ⁻¹
F(000)	1340
Crystal Size	0.210 x 0.010 x 0.010 mm
Theta range for data collection	2.476 to 69.514°
Limiting indices	-21 ≤ h ≤ 21, -8 ≤ k ≤ 9, -26 ≤ l ≤ 27
Reflections collected	44589
Independent collections	5618 [R(int) = 0.0920]
Completeness to theta	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.66167
Refinement method	Full-matrix least-squares on F ²
Data/ restraints/ parameters	5618 / 0 / 390
Goodness-of-fit on F ²	1.050

Final R indices [$l > 2\sigma(l)$]	R1 = 0.0554, wR2 = 0.1401
R indices (all data)	R1 = 0.0656, wR2 = 0.1549
Extinction coefficient	n/a
Largest diff. peak and hole	0.508 and -0.834 e \AA^{-3}

Structure determination for 2-Ni^{IV+}

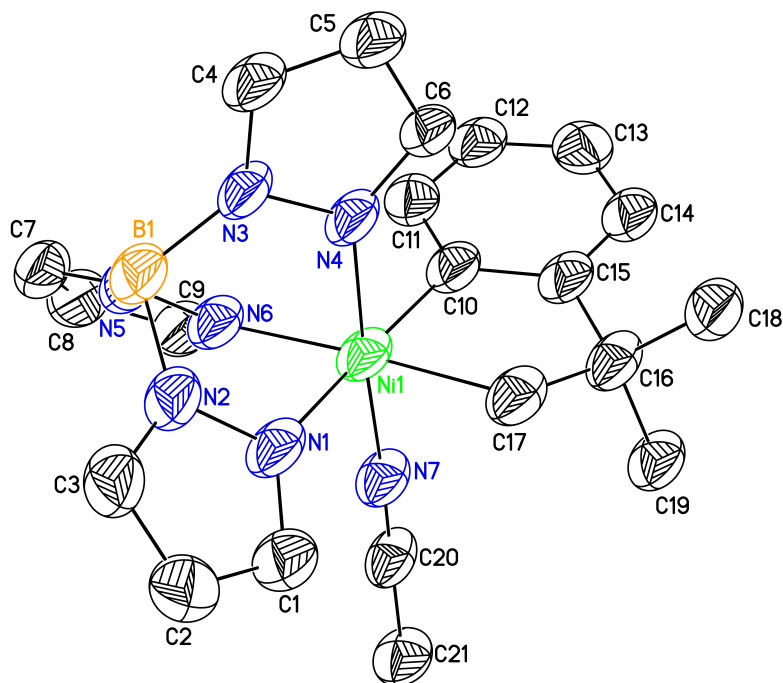


Figure S34. X-ray structure of **2-Ni^{IV+}**. BF₄ counterion and MeCN molecule are omitted for clarity.

Structure Determination.

Orange plates of **2-Ni^{IV+}** were grown from a solution of the compound containing acetonitrile/toluene/diethyl ether/pentane at $-35\text{ }^{\circ}\text{C}$. A crystal of dimensions $0.19 \times 0.14 \times 0.01$ mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187\text{ \AA}$) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω . The exposure times were 1 sec. for the low angle images, 5 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 43846 reflections to a maximum 2θ value of 138.49° of which 5445 were independent and 3881 were greater than $2\sigma(I)$. The final cell constants (Table S3) were based on the xyz

centroids of 5645 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2016/6) software package, using the space group P2(1)/c with $Z = 4$ for the formula $C_{23}H_{28}B_2NgF_4Ni + (\text{solvent})$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at $R1 = 0.0832$ and $wR2 = 0.2199$ [based on $I > 2\sigma(I)$], $R1 = 0.1088$ and $wR2 = 0.2443$ for all data. The SQUEEZE subroutine of the PLATON program suite was used to address the disordered solvent in two solvent accessible cavities present in the structure. Additional details are presented in Table S3 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", *Acta Cryst.*, C71, 3-8 (Open Access).

CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

- PLATON Reference : Spek, A.L. (2003). *J. Appl. Cryst.* 36, 7-13.
 Spek, A.L. (2009). *Acta Cryst.* D65, 148-155., v. 70414.

Table S3. Crystal Data and Structural Refinement for **2-Ni^{IV+}**.

Empirical formula	$C_{23}H_{28}N_8NiB_2F_4$
Formula weight	572.86
Temperature	85(2) K
Wavelength	1.54184 Å
Crystal System	Monoclinic
Space group	P2(1)/c
Unit Cell Dimensions	$a = 7.9832(5) \text{ \AA}$, $\alpha = 90^\circ$ $b = 14.6911(5) \text{ \AA}$, $\beta = 93.647(6)^\circ$ $c = 25.6709(17) \text{ \AA}$, $\gamma = 90^\circ$
Volume	$3004.6(3) \text{ \AA}^3$
Z	4
Calculated density	1.266 Mg/m^3
Absorption coefficient	1.372 mm^{-1}
F(000)	1184
Crystal Size	0.190 x 0.140 x 0.010 mm
Theta range for data collection	3.450 to 68.247°
Limiting indices	$-9 \leq h \leq 8$, $-17 \leq k \leq 17$, $-30 \leq l \leq 30$
Reflections collected	43846

Independent collections	5446 [R(int) = 0.1238]
Completeness to theta	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.74912
Refinement method	Full-matrix least-squares on F ²
Data/ restraints/ parameters	5445 / 0 / 347
Goodness-of-fit on F ²	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0832, wR2 = 0.2199
R indices (all data)	R1 = 0.1088, wR2 = 0.2443
Extinction coefficient	n/a
Largest diff. peak and hole	0.876 and -0.734 e Å ⁻³

XI. References

1. N. M. Camasso, M. S. Sanford, *Science* **2015**, *347*, 1218–1220.
2. J. Campora, M. del Mar Conejo, K. Mereiter, P. Palma, C. Perez, M. L. Reyes, C. J. Ruiz, *Orgmet. Chem.* **2003**, *683*, 220–239.
3. J. R. Bour, N. M. Camasso, E. A. Meucci, J. W. Kampf, A. J. Canty, M. S. Sanford, *J. Am. Chem. Soc.* **2016**, *138*, 16105–16111.
4. N. M. Camasso, A. J. Canty, A. Ariafard, M. S. Sanford, *Organometallics* **2017**, *36*, 4382–4393.
5. E. Carmona, E. Guitierrez-Puebla, J. M. Marin, A. Monge, M. Paneque, M. L. Poveda, C. Ruiz, *J. Am. Chem. Soc.* **1989**, *111*, 2883–2891.