Supporting Information for:

Carbon–Carbon Bond-Forming Reductive Elimination from Isolated Nickel(III) Complexes

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I. General Procedures and Materials and Methods

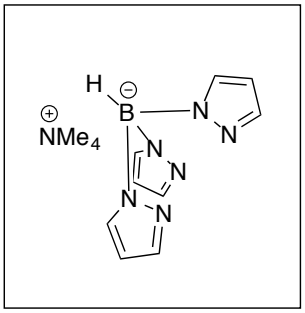
General Procedures

All manipulations were performed inside an N_2 filled glovebox unless otherwise noted. NMR spectra were obtained on a Varian VNMR 700 (699.76 MHz for ^{1}H; 175.95 MHz for ^{13}C) or a Varian VNMR 500 (500.09 MHz for ^{1}H; 470.56 MHz for ^{19}F; 125.75 MHz for ^{13}C; 225 or 128 MHz for ^{11}B) spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ^{19}F NMR chemical shifts are reported in ppm relative to CCl_3F. ^{11}B NMR spectra are referenced to $BF_3{\bullet}Et_2O$. Abbreviations used in the NMR data are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bq, broad quartet; br, broad signal; quint, quintet. Yields of reactions that generate fluorinated products were determined by ^{19}F NMR analysis using a relaxation delay of 12 s. Quantitative ^{11}B NMR were recorded according to the literature[1] at a 90º pulse angle with a 125 s relaxation delay (longest T_1 = 23 s) and a 10 s acquisition period and were checked against a calibration curve. Magnetic susceptibilities were determined by the Evans method in CH_3CN at 23 ºC on a 700 MHz spectrometer.[2] Mass spectral data were obtained on a Micromass Magnetic Sector Mass Spectrometer in electrospray ionization mode. Elemental analyses were conducted by Midwest Microlabs. Cyclic voltammetry was performed using a CHI600C potentiostat from CH Instruments. EPR spectra were collected at –176 ºC using a Bruker EMX ESR Spectrometer with a nitrogen-cooled cryostat. X-ray crystallographic data were collected on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer. Flash chromatography was performed using a Biotage Isolera One system with cartridges containing high performance silica gel.

Materials and Methods

The following compounds were prepared via literature procedures: $(PPh_3)_2Ni(CF_3)(OTFA)$,[3] (dtbpy)$Ni(CF_3)(Ph)$,[4] $NMe_4Ni(Tp)(CF_3)_2$,[4] $K[(Tp)Ni^{II}(CH_2CMe_2\text{-}o\text{-}C_6H_4)]$,[5] $(MeCN)_2Ni(CF_3)_2$,[6] $(PEt_3)_4Ni^0$,[7] $(PhCN)_2Ni(C_6F_5)_2$,[8] $AcFcBF_4$,[9] $Cp^*_2FeBF_4$,[9] and $BrMg(C_6F_5)$[10]. $Ni(COD)_2$, biphenylene, $NOBF_4$, $AgBF_4$, and Ph_2Zn were purchased from Strem Chemicals. 4,4'-di-*tert*-butylbipyridine (dtbpy), Cp_2FePF_6, PPh_3, and C_6F_5Br, were purchased from Aldrich. 4,4'-difluorobiphenyl was purchased from Oakwood Chemicals. KTp was purchased from Alfa Aesar. $ZnMe_2$ and Mg turnings were purchased from Acros. Dichloromethane (Fisher), pentane (Fisher), diethyl ether (EMD), toluene (Fisher), and tetrahydrofuran (Fisher) were deaerated via a N_2 sparge and were purified by a solvent purification system. Acetonitrile (Acros) and benzonitrile (Acros), diisopropyl ether (Acros) were sparged and used without further purification. CD_2Cl_2, C_6D_6, CD_3CN, and acetone-d_6 were obtained from Cambridge Isotopes Laboratories and were stored over activated 4 Å molecular sieves (EMD Millipore). Basic alumina (Aldrich) was dried for 48 h under vacuum at 210 °C. 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. Unless otherwise noted, all manipulations were performed under an inert atmosphere in a N_2 glovebox.

II. Synthesis of NMe_4Tp



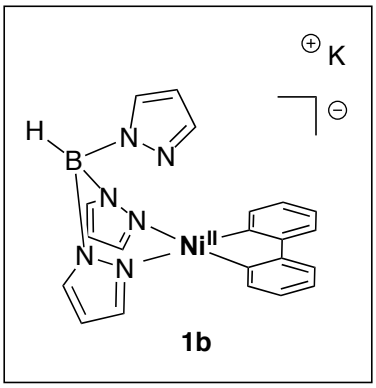
Under ambient atmosphere, a 100 mL round bottom flask was charged with KTp (2.01 g, 7.97 mmol, 1.0 equiv), tetramethylammonium chloride (0.874 g, 7.96 mmol, 1.0 equiv), and methanol (30 mL). The resulting suspension was stirred for 1 h at room temperature, and then the volatiles were removed under vacuum. The solid was taken up in acetonitrile (25 mL) and filtered through a fine glass frit. The filtrate was concentrated to dryness. The resulting white solid was collected and dried under vacuum at 70 ºC for 4 h to afford NMe_4Tp (1.92 g, 84% yield).

^{1}H NMR (500 MHz, CD_3CN, 23 ºC): δ 7.45 (d, J_{HH} = 1.5 Hz, 3H), 7.40 (d, J_{HH} = 2.1 Hz, 3H), 6.16-6.03 (br, 3H), 4.86 (bq, B-***H***, 1H), 2.99 (s, 12H).

^{13}C NMR (126 MHz, CD_3CN, 23 ºC): δ 138.70, 132.96, 102.92, 55.05.

^{11}B NMR (128 MHz, CD_3CN, 23 ºC): δ –1.09 (d, J_{BH} = 111 Hz, ***B***-H).

III. Synthesis of $[(Tp)Ni^{II}(R)(R^1)]^-$ Complexes



1b

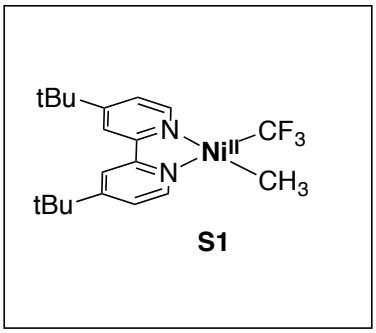
Synthesis of $K[(Tp)Ni^{II}(C_6H_4\text{-}o\text{-}C_6H_4)]$ (1b): A 20 mL vial equipped with a magnetic stir bar was charged with $Ni(PEt_3)_4$ (200 mg, 0.55 mmol, 1.0 equiv), and the yellow solid was dissolved in THF (5 mL) to afford a deep purple solution. To this was added a solution of KTp (134 mg, 0.55 mmol, 1.0 equiv) in THF (2 mL) followed by a solution of biphenylene (85 mg, 0.55 mmol, 1.0 equiv) in THF (2 mL). The resulting dark orange solution was allowed to stir for 2 h to produce a light orange solution. The solvent was removed under reduced pressure, and the resulting light orange solid was washed with pentane (3 x 10 mL) to afford complex **1b** as a bright yellow powder (229 mg, 91% yield). We were unable to obtain analytically pure samples of this complex (see elemental analysis below), but carried it forward to the Ni(III) complex **2b** and purified at that stage.

^{1}H NMR (700 MHz, CD_3CN, 23 ºC): δ 8.05 (br, 3H), 7.62 (br, 3H), 7.06 (d, J_{HH} = 7.2 Hz, 2H), 6.78 (t, J_{HH}= 7.2 Hz, 2H), 6.70 (d, J_{HH} = 7.2 Hz, 2H), 6.54 (t, J_{HH} = 7.2 Hz, 2H), 6.17 (br, 3H), 4.92 (bq, B-***H***, 1H).

^{13}C NMR (176 MHz, CD_2Cl_2, 23 ºC): δ 166.32, 158.82, 141.93, 137.79, 135.12, 122.87, 122.45, 117.01, 103.72.

^{11}B NMR (225 MHz, CD_3CN, 23 ºC): δ –2.22 (d, J_{BH} = 108 Hz, ***B***-H).

Elemental analysis calcd for $C_{21}H_{18}BN_6KNi$, C: 54.48, H: 3.92, N: 18.15; found, C: 55.67, H: 5.29, N: 15.21



S1

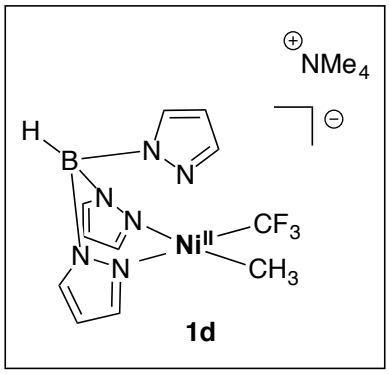
Synthesis of [(dtbpy)Ni^{II}(CF$_3$)(Me)] (S1): A 150 mL round bottom flask was charged with (dtbpy)Ni^{II}(CF$_3$)(OTFA)[3] (600 mg, 1.18 mmol, 1.0 equiv), and the yellow solid dissolved in THF (60 mL). The resulting yellow-orange solution was cooled to –35 ºC, and then $ZnMe_2$ (0.55 mL of a 1.2 M solution in toluene, 0.55 equiv) was added. The reaction mixture was allowed to warm to room temperature over approximately 5 min, during which time the solution changed color from dark orange to dark red. The solution was then filtered through a 3 cm pad of basic alumina, and the pad was washed with THF (5 mL). The washes were combined, and the volatiles were removed under reduced pressure. The resulting dark red residue was triturated with pentane (10 mL), and the solids were collected by filtration. The solids were washed with additional pentane (40 mL) and then dried under reduced pressure to yield the title compound as a red solid (189 mg, 39% yield).

^{1}H NMR (700 MHz, CD_2Cl_2, 23 ºC): δ 8.82 (d, J_{HH} = 6.0 Hz, 1H), 8.45 (d, J_{HH} = 6.0 Hz, 1H), 7.93-7.83 (multiple peaks, 2H), 7.51-7.43 (multiple peaks, 2H), 1.42 (s, 18H), –0.01 (s, 3H).

^{13}C NMR (176 MHz, CD_2Cl_2, 23 ºC): δ 163.06, 162.56, 155.68, 153.73, 151.03, 148.07, 142.05 (Ni-***C***F$_3$ shift extracted from ^{19}F–^{13}C HMBC spectrum) 123.59, 122.99, 117.38, 117.20, 29.91, –6.26.

^{19}F NMR (377 MHz, CD_2Cl_2, 23 ºC): δ –24.65 (s, 3F).

Elemental Analysis calcd for $C_{20}H_{27}F_3N_2Ni$, C: 58.43, H: 6.62, N: 6.81; found, C: 58.33, H: 6.28, N: 6.72.



1d

Synthesis of NMe_4[(Tp)Ni^{II}(CF_3)(Me)] (1d) A 20 mL vial was charged with (dtbpy)Ni^{II}(CF_3)(Me) (180 mg, 0.44 mmol, 1.0 equiv), and the red solid was dissolved in a minimal amount of acetonitrile (10 mL). A solution of NMe_4Tp (132 mg, 0.46 mmol, 1.05 equiv) in acetonitrile (3 mL) was added, and the resulting dark orange solution immediately changed color to yellow-brown. Over the course of approximately 5 min, 4,4'-di-*tert*-butylbipyridine (dtbpy) precipitated from solution in the form of a white crystalline solid. The solution was concentrated to approximately 3 mL, which led to further precipitation of dtbpy. The precipitate was collected on a fritted filter and washed with acetonitrile (5 mL). The filtrate was collected and concentrated under reduced pressure. The resulting brown residue was washed with diethyl ether (3 x 10 mL) and pentane (3 x 10 mL) and the remaining solids were collected to afford complex **1d** as a light tan powder (41 mg, 22% yield).

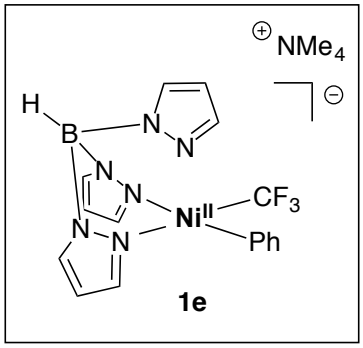
^{1}H NMR (700 MHz, CD_3CN, 23 ºC): δ 7.88 (br, 3H), 7.58 (br, 3H), 6.17 (br, 3H), 4.73 (bq, B-***H***, 1H), 3.07 (s, 12H), –0.54 (s, 3H).

^{13}C NMR (176 MHz, CD_3CN, 23 ºC): δ 140.72, 140.50 (Ni-***C***F_3 shift extracted from ^{19}F–^{13}C HMBC spectrum), 134.79, 103.83, 55.88, –9.01.

^{11}B NMR (225 MHz, CD_3CN, 23 ºC): δ –2.55 (d, J_{BH} = 113 Hz, ***B***-H).

^{19}F NMR (471 MHz, CD_3CN, 23 ºC): δ –23.22 (s, 3F).

Elemental Analysis calcd for $C_{15}H_{25}BF_3N_7Ni$, C: 41.91, H: 5.86, N: 22.81; found, C: 41.46, H: 6.05, N: 22.59.



1e

Synthesis of NMe_4[(Tp)Ni^{II}(CF_3)(Ph)] (1e): This procedure is based on the previous synthesis of the NBu_4 analogue.[4] A 20 mL vial was charged with (dtbpy)Ni^{II}(CF_3)(Ph) (90 mg, 0.19 mmol, 1.1 equiv), and the orange solid was dissolved in a minimal amount of acetonitrile (2 mL). A solution of NMe_4Tp (49.8 mg, 0.17 mmol, 1.0 equiv) in acetonitrile (1 mL) was added, and the resulting dark orange solution immediately changed color to yellow-brown. Over the course of approximately 10 min, 4,4'-di-tert-butylbipyridine (dtbpy) precipitated from solution in the form of a white crystalline solid. The solution was concentrated to approximately 1 mL, which led to further precipitation of dtbpy. The solution was then stored at –35 ºC for 20 min. The precipitate was collected on a paper filter and was washed with 1 mL of cold (–35 ºC) acetonitrile. The filtrate was collected and concentrated under reduced pressure to about 1.5 mL. This solution was then filtered through a pipette filter to remove additional precipitate. The filter was washed with cold acetonitrile (1 mL). The combined filtrates were reduced to a brown viscous residue. The resulting residue was suspended in 5 mL of 1:1 pentane/Et_2O. The residue was scraped with a spatula until it became a solid. The solid was collected over a frit and washed with (3 x 2 mL) and pentane (3 x 5 mL), and the remaining solid was collected to afford complex **1e** as a light tan powder (60 mg, 71% yield).

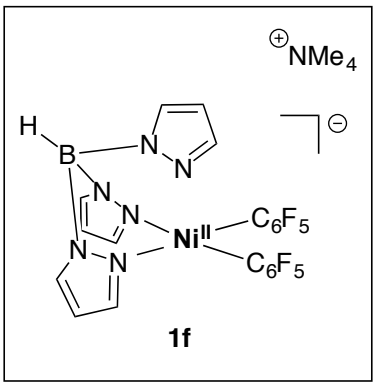
^{1}H NMR (700 MHz, CD_3CN, 23 ºC): δ 7.90 (br, 3H), 7.44 (d, J_{HH} = 7.5 Hz, 2H), 7.29 (br, 3H) 6.77 (t, J_{HH} = 7.5 Hz, 1H), 6.67 (t, J_{HH} = 7.3 Hz, 1H), 6.15 (br, 3H), 4.66 (bq, B-***H***, 1H) 3.08 (s, 12H).

^{13}C NMR (176 MHz, CD_3CN, 23 ºC): δ 164.51, 141.54, 139.82 (q, J_{CF} = 369.9 Hz), 136.45, 134.75, 120.59, 103.97, 55.05.

^{11}B NMR (225 MHz, CD_3CN, 23º C): δ –2.26 (d, J_{BH} = 110 Hz, ***B***-H).

^{19}F NMR (371 MHz, CD_3CN, 23 ºC): δ -21.32 (s, 3F).

Elemental Analysis calcd for $C_{20}H_{27}BF_3N_7N$, C: 48.83, H: 5.53, N: 19.93; found, C: 49.02, H: 5.79, N: 19.90



1f

Synthesis of $NMe_4[(Tp)Ni^{II}(C_6F_5)_2]$ (1f): A 20 mL vial was charged with $(PhCN)_2Ni(C_6F_5)_2$ [8] (102 mg, 0.169 mmol), NMe_4Tp (48.7 mg, 0.168 mmol), and MeCN (5 mL). The reaction was then stirred for 10 min. The volatiles were removed, and the resultant oil was taken up in 1:1 mixture of pentane: ether (7 mL). The oil was scraped with a spatula until a yellow solid formed. The solvent was removed with a pipette. Care was taken not to disturb the powder at the bottom. The powder was then dried under vacuum and scraped with a spatula to form a fine powder. This powder was then triturated with pentane (2 x 5 mL) to afford **1f** as a fine yellow powder (109 mg, 84% yield).

^{1}H NMR (700 MHz, CD_3CN, 23 ºC): δ 7.78 (br, 3H), 7.13 (br, 3H), 6.15 (br, 3H), 5.05-4.39 (br, B-***H***, 1H), 3.08 (s, 12H).

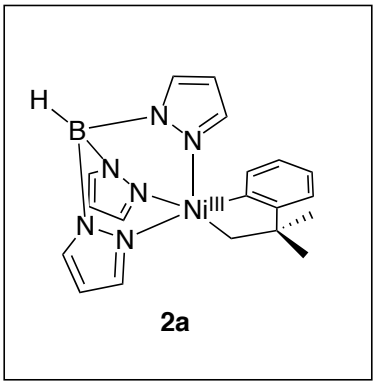
^{19}F NMR (471 MHz, CD_3CN, 23 ºC): δ –117.02 (d, J_{FF} = 25.6 Hz, 2F), –165.08 (t, J_{FF} = 19.2 Hz, 1F), –166.88 (t, J_{FF} = 19.2 Hz, 2F).

^{11}B NMR (128 MHz, CD_3CN, 23 ºC): δ –2.46 (d, J_{BH} = 112 Hz, ***B***-H).

Due to extensive C-F coupling and the highly fluxional nature of this molecule, the ^{13}C NMR spectrum is poorly resolved. Therefore, peak assignments were not made. The ^{13}C NMR spectrum is provided in the spectral data section.

Elemental Analysis calcd for $C_{25}H_{22}BN_7F_{10}Ni$, C: 44.16; H: 3.26; N: 14.42; found, C: 43.99; H: 3.43; N: 14.38.

IV. Synthesis of [(Tp)Ni^{III}(R)(R^1)] Complexes



2a

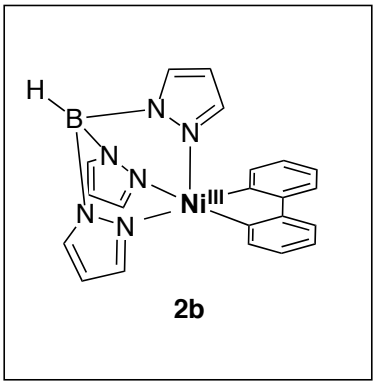
Synthesis of [(Tp)Ni^{III}(CH_2CMe_2-*o*-C_6H_4)] (2a) In a glovebox, a 20 mL vial was charged with K[(Tp)Ni^{II}(CH_2CMe_2-*o*-C_6H_4)][5] (180 mg, 0.41 mmol, 1.0 equiv). The yellow solid was dissolved in acetonitrile (10 mL), and a solution of $AgBF_4$ (78 mg, 0.41 mmol, 1.0 equiv) in acetonitrile (5 mL) was added at -35 ºC. The orange solution immediately turned dark red, with concomitant precipitation of a Ag^0. The crude reaction mixture was then filtered through a celite plug. The plug was washed with acetonitrile (5 mL), and the filtrates were combined and concentrated to approximately 3 mL. Orange crystals precipitated from the solution over the course of 10 min. These crystals were collected, washed with acetonitrile (5 mL), and dried under vacuum to afford **2a** as an orange solid (98 mg, 60% yield). Samples for elemental analysis were obtained by cooling a saturated solution of **2a** in acetonitrile to –35 ºC to obtain orange-red crystals of **2a**.

^{11}B NMR (225 MHz, CD_3CN, 23 ºC): δ –3.07 (br, ***B***-H).

Elemental Analysis calcd for $C_{19}H_{22}BN_6Ni$, C: 56.50, H: 5.49, N: 20.81; found, C: 56.63, H: 5.52, N: 20.83.

μ_{eff}(CH_3CN, 23 ºC) = 1.88

HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{19}H_{22}BN_6Ni$, 403.1352; found, 403.1352.



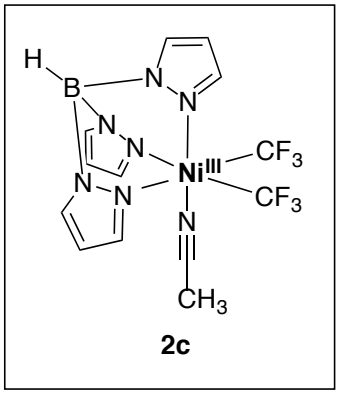
2b

Synthesis of [(Tp)Ni^{III}(C_6H_4-*o*-C_6H_4)] (2b): In the glovebox, a 20 mL vial equipped with a magnetic stir bar was charged with K[Ni^{II}(Tp)(C_6H_4-*o*-C_6H_4)$_2$] (**1**) (100 mg, 0.22 mmol, 1.0 equiv) and acetonitrile (4 mL). This solution was cooled to –35 ºC, and a solution of $AgBF_4$ (42 mg, 0.22 mmol, 1.0 equiv) in acetonitrile (1 mL) was added. The yellow solution immediately turned brown, with concomitant precipitation of Ag^0. This dark brown suspension was filtered through a plug of celite at –35 ºC. The dark orange/brown filtrate was reduced to a solid under vacuum. The resulting brown solid was extracted with diethyl ether (10 mL) at –35 ºC. The extract was filtered through a plug of celite at –35 ºC, and the filtrate was collected and concentrated under vacuum. The resulting brown solid was washed with a minimal amount of pentane (2 mL) at –35 ºC and dried under vacuum overnight to yield complex **2b** as a light brown solid (28 mg, 31% yield).

^{11}B NMR (225 MHz, CD_3CN, 23 ºC): δ –2.69 (d, J_{BH} = 90 Hz, ***B***-H).

Elemental Analysis calcd for $C_{21}H_{18}BN_6Ni$, C: 59.50, H: 4.28, N: 19.82; found, C: 59.04, H: 4.43, N: 19.36.

μ_{eff}(CH_3CN, 23 ºC) = 1.84



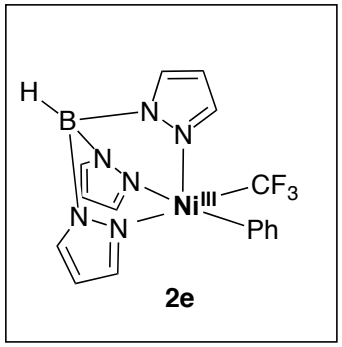
2c

Synthesis of [(Tp)Ni^{III}(CF$_3$)$_2$(MeCN)] (2c) In the glovebox, a 20 mL vial was charged with (MeCN)$_2$Ni^{II}(CF$_3$)$_2$[6] (150 mg, 0.54 mmol, 1.0 equiv). The solid was dissolved in acetonitrile (8 mL). A solution of NMe$_4$Tp (163 mg, 0.57 mmol, 1.05 equiv) in acetonitrile (3 mL) was added, and the yellow-brown solution immediately turned orange-brown. A solution of $AgBF_4$ (105 mg, 0.54 mmol, 1.0 equiv) in acetonitrile (2 mL) was then added to the reaction mixture at –35 ºC. The orange-brown reaction mixture immediately changed color to purple, with concomitant formation of a Ag mirror. The crude reaction mixture was removed from the glovebox and filtered through a celite plug. The celite plug was washed with acetonitrile (10 mL), and the combined filtrates were concentrated to dryness under reduced pressure. The crude purple-brown solid was purified further by flash chromatography on silica gel (mobile phase: hexanes/ethyl acetate with a gradient from 90:10 to 80:20). Compound **2c** was obtained as a purple solid (132 mg, 54% yield).

^{11}B NMR (225 MHz, CD_3CN, 23 ºC): δ –14.03 (br).

Elemental Analysis calcd for $C_{13}H_{13}BF_6N_7Ni$, C: 34.64, H: 2.91, N: 21.75; found, C: 34.80, H: 2.98, N: 21.77.

μ_{eff}(CH_3CN, 23 ºC) = 1.75



2e

Synthesis of [(Tp)Ni^{III}(CF$_3$)(Ph)] (2e): In the glovebox, a 20 mL vial was charged with a magnetic stirbar, $NMe_4[Ni^{II}(Tp)(CF_3)(Ph)]$ (40 mg, 0.081 mmol, 1.0 equiv), and acetonitrile (1.5 mL). A separate 4 mL vial was charged with $AgBF_4$ (15.6 mg, 0.081 mmol, 1.0 equiv) and acetonitrile (0.5 mL). The two solutions were then cooled to –35 ºC over 20 min. To a rapidly stirring solution of **1e**, the $AgBF_4$ solution was added dropwise over 30 s. Upon the addition of $AgBF_4$ a black precipitate immediately formed. The combined solutions were then allowed to stand at –35 ºC for 2 min before they were filtered through a 2 cm cold (–35 ºC) silica pad. The orange filtrate was concentrated to near dryness as a waxy solid. This solid was taken up in a minimum (approximately 7 mL) of cold diethyl ether (–35 ºC), at which point it turned green. The ethereal solution of **2e** was filtered through an additional wet-packed (Et_2O) silica pad pre-cooled to -35 ºC. The volatiles were quickly removed under vacuum, and the solid was taken up in a minimum amount of cold diisopropyl ether (–35 ºC, approximately 2 mL). To the diisopropyl ether solution was added cold pentane (-35 ºC, ~3 mL). This solution was stored in a –35 ºC freezer for 4 d to afford green X-ray quality crystals of **2e**. The solvent was decanted, the crystals were washed with 1 mL of cold pentane (-35 ºC), and the crystals were dried under vacuum for 20 min at room temperature to give **2e** as an emerald green crystalline solid (29 mg, 87% yield).

Note: Complex **2e** decomposes to an unknown gray/green solid slowly over approximately 48 h at room temperature in the solid state. It should be kept below –15 ºC for prolonged storage. Samples of **2e** could be stored without major decomposition for over 3 months at –35 ºC.

^{11}B NMR (128 MHz, in CD_3CN): δ –5.30 (d, J_{BH}= 47 Hz, ***B***-H).

Elemental Analysis calcd for $C_{16}H_{15}BN_6F_3$, C: 45.99, H: 3.62, N: 20.11; found, C: 45.50, H: 3.43, N: 19.95.

μ_{eff} (CH_3CN, 23 ºC) = 1.81

V. Cyclic Voltammetry Methods

Experimental Procedure: Cyclic voltammetry on complexes **1a-f** 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 $AgBF_4$ (0.01 M) and NBu_4PF_6 (0.1 M) in acetonitrile, and a Pt wire counter electrode. A 2 mL solution of each complex (0.01 M) and NBu_4PF_6 (0.1 M) in acetonitrile was added to the electrochemical cell. Cyclic voltammetry scans were taken at 100 mV/s. After obtaining the CV for each complex, ferrocene was added as an internal reference.

CVs at variable scan rates (50 to 250 or 500 mV/s) and full potential window CVs can be found on p. S70.

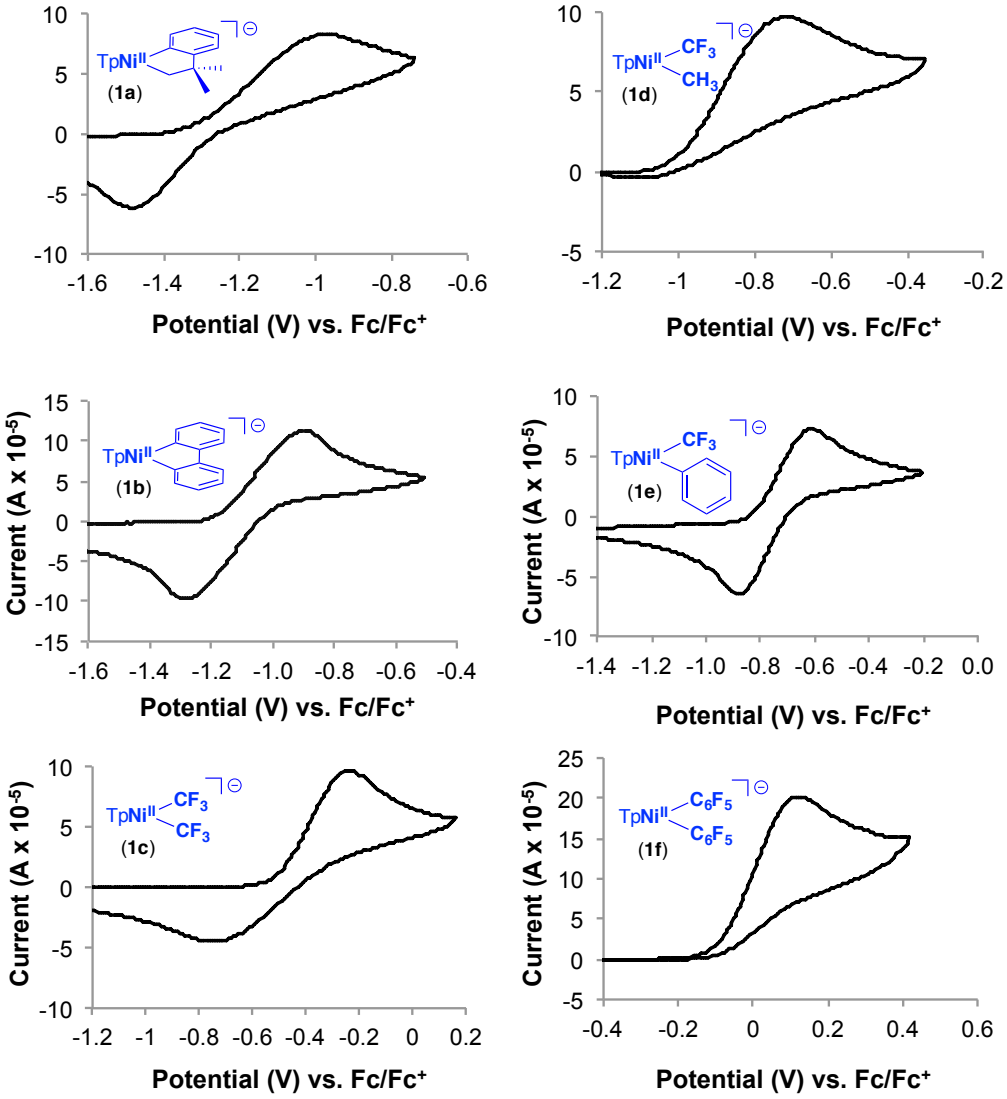


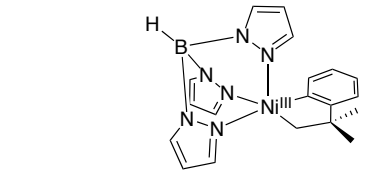
Figure S1. Cyclic voltammograms of complexes **1a-f**.

VI. EPR Studies

General procedure for the attempted detection of complexes 2d and 2f:
A 4 mL scintillation vial was charged with the appropriate $NMe_4[Ni^{II}(Tp)(R)(R^1)]$ complex (0.005 mmol) and acetonitrile (1 mL). A separate 4 mL vial was charged with $FcBF_4$ (0.02 mmol) and acetonitrile (1 mL). Both solutions were then cooled to –78 ºC in a glovebox cold well. After 10 min, 200 µL of the $FcBF_4$ solution (0.004 mmol, 0.8 equiv) was added in one portion via syringe to the solution of $NMe_4[Ni^{II}(Tp)(R)(R^1)]$. The vial was quickly shaken, resulting in the immediate disappearance of the blue $FcBF_4$ salt, indicating rapid consumption of the oxidant. Four drops of this solution were transferred to 300 µL of a precooled (–78 ºC) solution of 3:1 PrCN:MeCN. The sample was then flash-frozen (at –196 ºC) in a septum-capped EPR tube until analysis. EPR signals consistent with the formation of **2d** and **2f** were not observed.

Procedure for EPR detection of compounds 2a, 2b, 2c, and 2e.
A 4 mL vial was charged with the appropriate $[Ni^{III}(Tp)(R)(R^1)]$ complex (0.005 mmol) and acetonitrile (1 mL). 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 until analysis.

These complexes could also be generated *in situ* by a procedure directly analogous to the method described for compounds **2d** and **2f**. The *in situ* EPR spectra were in good agreement with the authentic samples.



2a

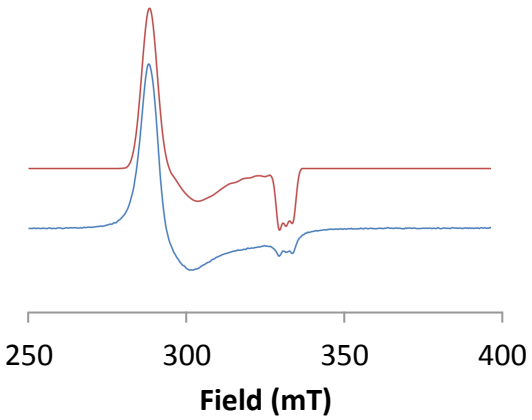


Figure S2. EPR spectrum of **2a** (bottom/blue) and the simulated spectrum (top/red). Fit using the following parameters: $g_x = 2.29$, $g_y = 2.25$, $g_z = 2.01$, $A_N = 21$ G.

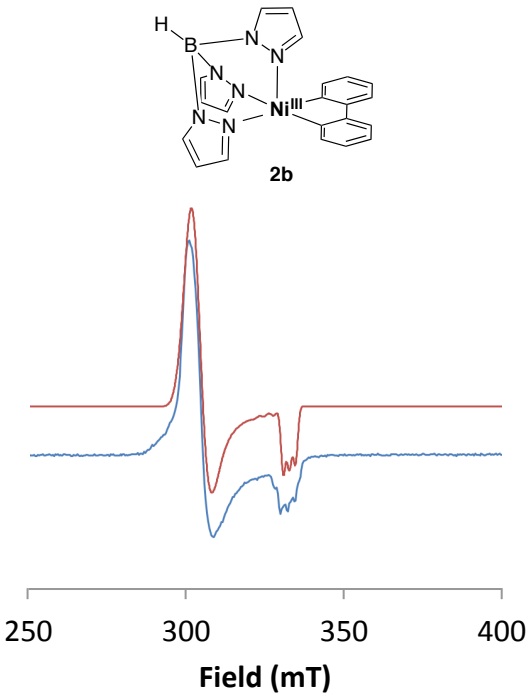


Figure S3. EPR spectrum of **2b** (bottom/blue) and the simulated spectrum (top/red). Fit using the following parameters: $g_x = 2.20$, $g_y = 2.19$, $g_z = 2.01$, $A_N = 19G$.

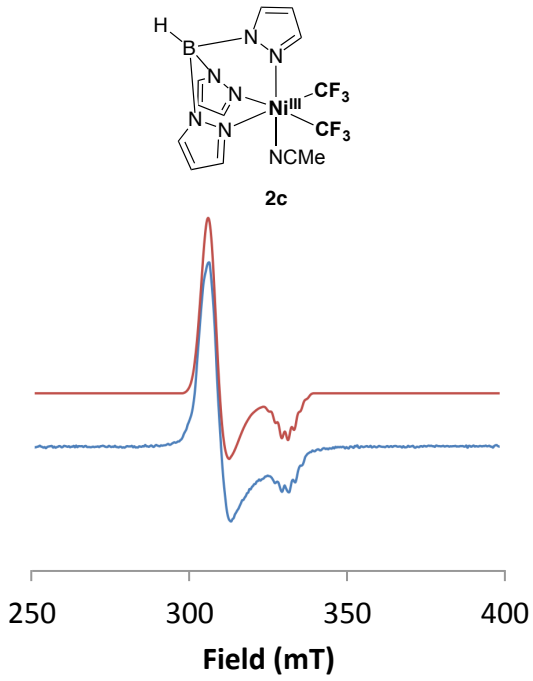


Figure S4. EPR spectrum of **2c** (bottom/blue) and the simulated spectrum (top/red). Fit using the following parameters: $g_x = 2.18$, $g_y = 2.15$, $g_z = 2.00$, $A_N(N) = 21G$, $A_{N'}(N') = 18G$.

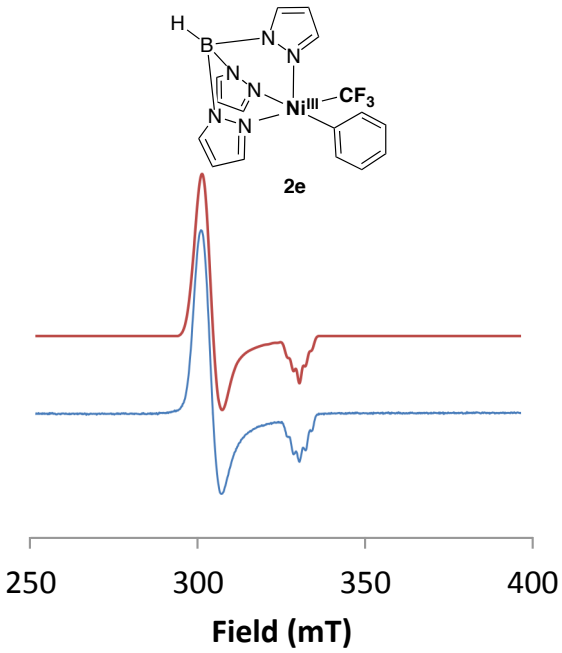
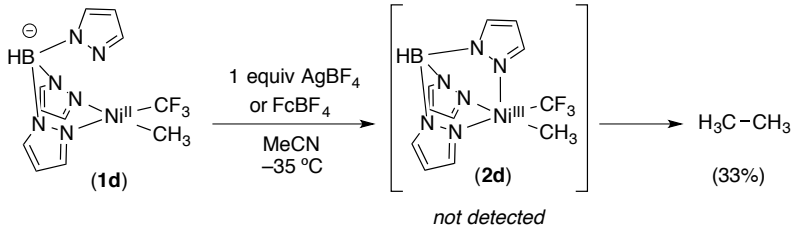


Figure S5. EPR spectrum of **2b** (bottom/blue) and the simulated spectrum (top/red). Fit using the following parameters: $g_x = 2.22$, $g_y = 2.19$, $g_z = 2.01$, $A_N(2N) = 18G$.

VII. C-C Coupling Experiments

Procedure for the oxidation of 1d: A 4 mL vial was charged with **1d** (5.0 mg, 0.012 mmol, 1.0 equiv), 1,3,5-trimethoxybenzene (2.0 mg, 0.012 mmol, 1.0 equiv) as an internal ^{1}H NMR standard, and CD_3CN (0.5 mL). This light yellow solution was transferred to a screw cap NMR tube and cooled to –35 ºC. A cooled solution of ferrocenium tetrafluoroborate ($FcBF_4$, 3.1 mg, 0.012 mmol, 1.0 equiv) in CD_3CN was added at –35 ºC, filling the NMR tube completely. The tube was quickly capped, shaken vigorously, and was analyzed by ^{1}H NMR spectroscopy after 30 min at room temperature to determine the yield of ethane (33 %). A final spectrum was taken 2 h later at which point no additional ethane was observed.



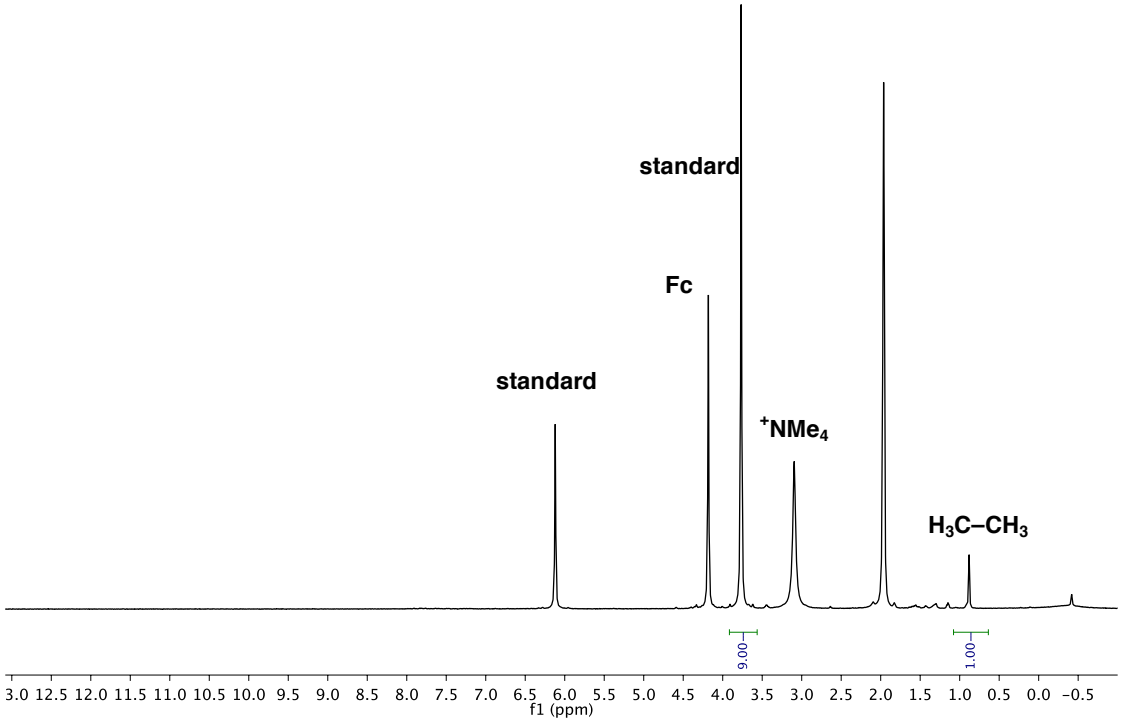
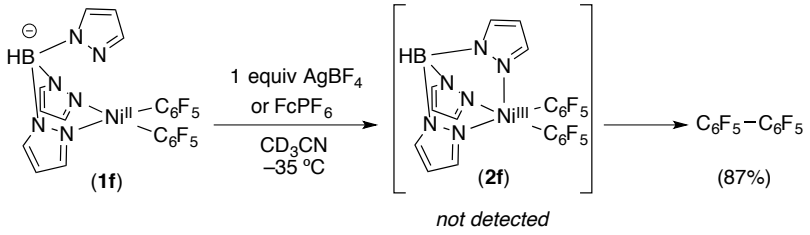


Figure S6. ^{1}H NMR spectrum of the crude reaction mixture after oxidation of **1d** with $FcBF_4$. Standard = 1,3,5-trimethoxybenzene

Procedure for the oxidation of 1f: A 4 mL vial was charged with **1f** (8.1 mg, 0.012 mmol, 1.0 equiv), 4,4'-difluorobiphenyl (4.7 mg, 0.025 mmol, 2.0 equiv), and CD_3CN (0.5 mL). This yellow solution was cooled to –35 ºC. A separate 4 mL vial was charged with ferrocenium hexafluorophosphate ($FcPF_6$, 4.1 mg, 0.012 mmol, 1.0 equiv). The solution of **1f** and internal standard was then transferred to the vial containing the $FcPF_6$ in one portion. The combined solution turned green then rapidly (~1s) turned yellow. After 10 minutes the solution was transferred to a Teflon-capped NMR tube and was then analyzed by ^{19}F NMR spectroscopy to determine the yield of decafluorobiphenyl (87%).

Note: The $FcPF_6$ (~ –71ppm) salt was used to avoid BF_4 (~ –151 ppm) peak overlap in the ^{19}F NMR



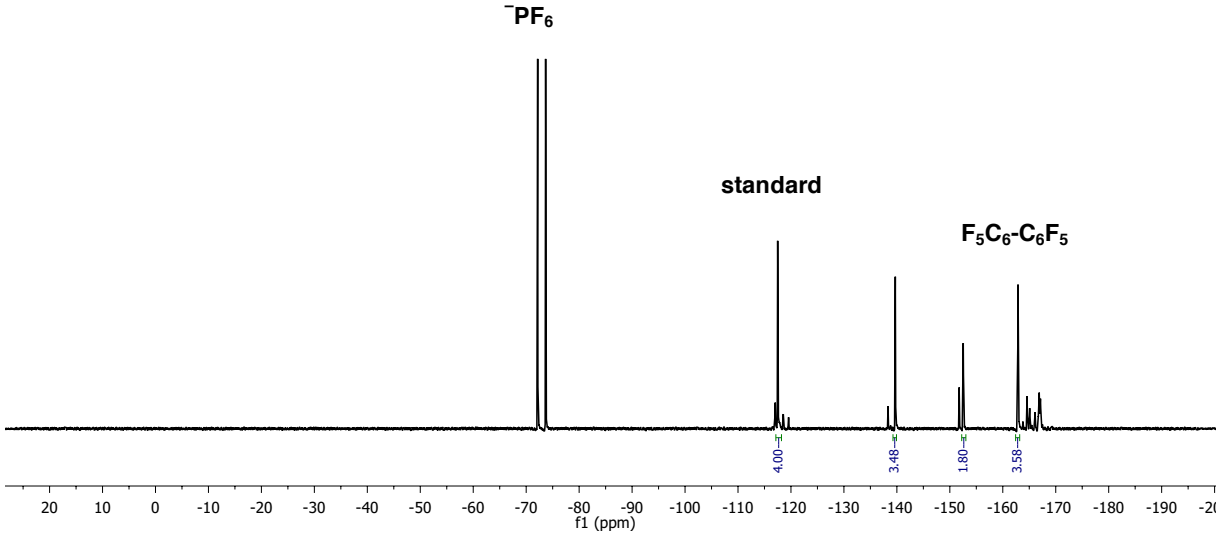
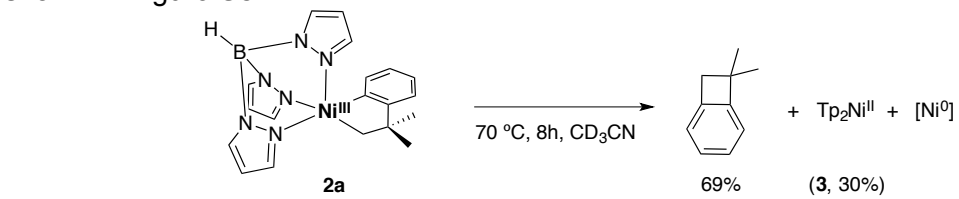


Figure S7. ^{19}F NMR spectrum of the crude reaction mixture after oxidation of **1f** with $FcPF_6$. Standard = 4,4'-difluorobiphenyl.

Procedure for the thermolysis of 2a: A 4 mL vial was charged with **2a** (5 mg, 0.012 mmol, 1.0 equiv), 1,3,5-trimethoxybenzene (2.1 mg, 0.0124 mmol, 1.0 equiv) as an internal ^{1}H NMR standard, and CD_3CN (0.5 mL). The resulting orange solution was transferred to a teflon-lined screw cap NMR tube and removed from the glovebox. The NMR tube was heated in an oil bath at 70 ºC for 8 h. The solution was then analyzed by ^{1}H NMR spectroscopy to determine the yield of 3,3-dimethylbenzocylobutane (69% yield). The NMR tube was then brought back into the glove box. Next, NBu_4BF_4 (0.038 M in MeCN, 1.0 equiv) was added to the NMR tube as an ^{11}B NMR standard. The tube was capped, and the sample was analyzed by quantitative ^{11}B NMR spectroscopy to determine the yield of $Ni^{II}Tp_2$ (30% based on Ni). Representative NMR spectra are shown in Figure S8.



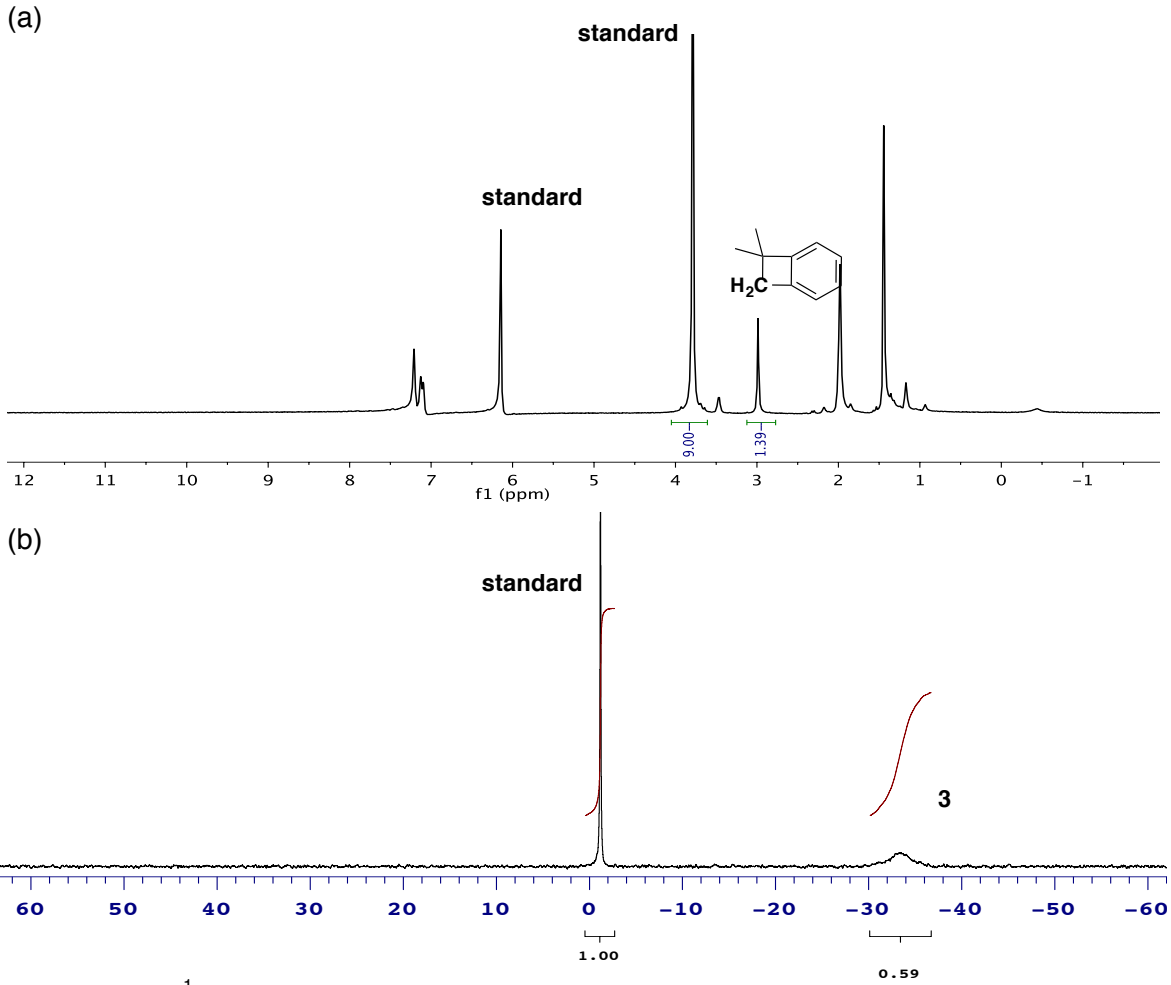
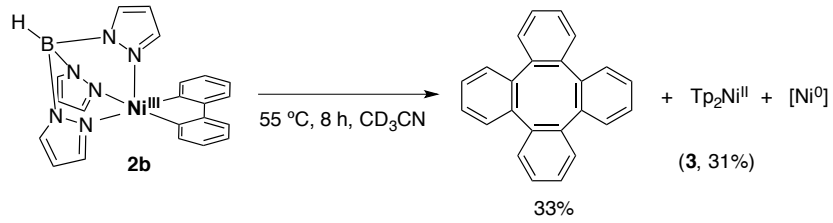
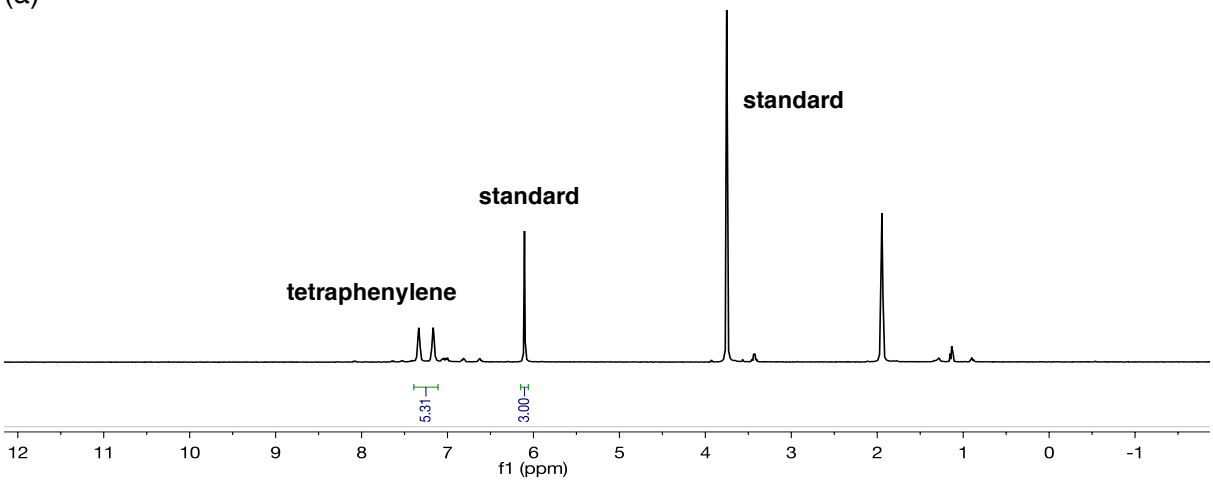


Figure S8. (a) ^{1}H NMR spectrum of the crude reaction mixture after heating **2a** at 70 ºC for 8 h. Standard = 1,3,5-trimethoxybenzene; (b) ^{11}B NMR spectrum of the reaction mixture after heating for 70 ºC for 8 h. Standard = NBu_4BF_4.

Procedure for the thermolysis of 2b: A 4 mL vial was charged with **2b** (5 mg, 0.0118 mmol, 1.0 equiv), 1,3,5-trimethoxybenzene (1.98 mg, 0.0118 mmol, 1.0 equiv), and CD_3CN (0.8 mL). The resulting orange solution was transferred to a teflon-lined screw cap NMR tube and removed from the glovebox. The NMR tube was heated in an oil bath at 55 ºC for 8 h. The solution was then analyzed by ^1H NMR spectroscopy to determine the yield of tetraphenylene (33% yield). The NMR tube was then brought back into the glovebox. NBu_4BF_4 (0.31 mL, 0.038 M in MeCN, 1.0 equiv) was added to the NMR tube as an ^{11}B NMR standard. The tube was capped, and the sample was analyzed by quantitative ^{11}B NMR spectroscopy to determine the yield of $Ni^{II}Tp_2$ (31% based on Ni). Representative NMR spectra are shown in Figure S9.



(a)



(b)

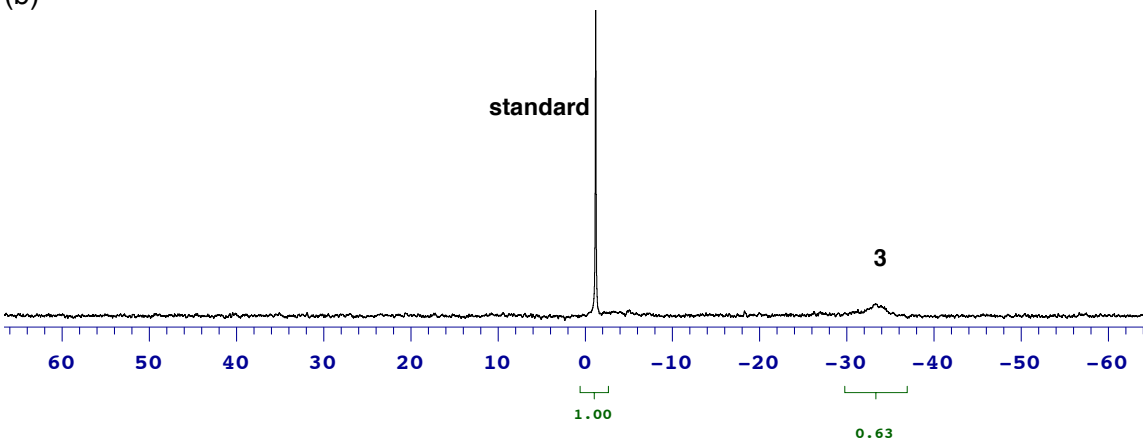
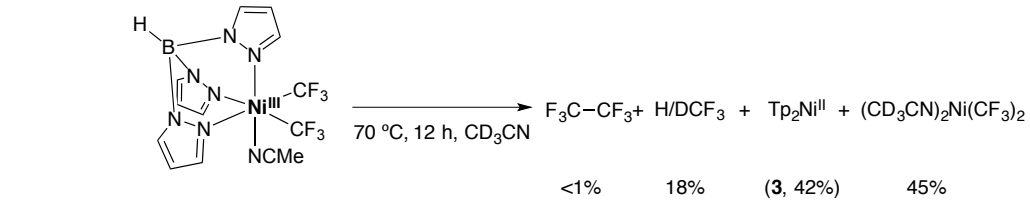
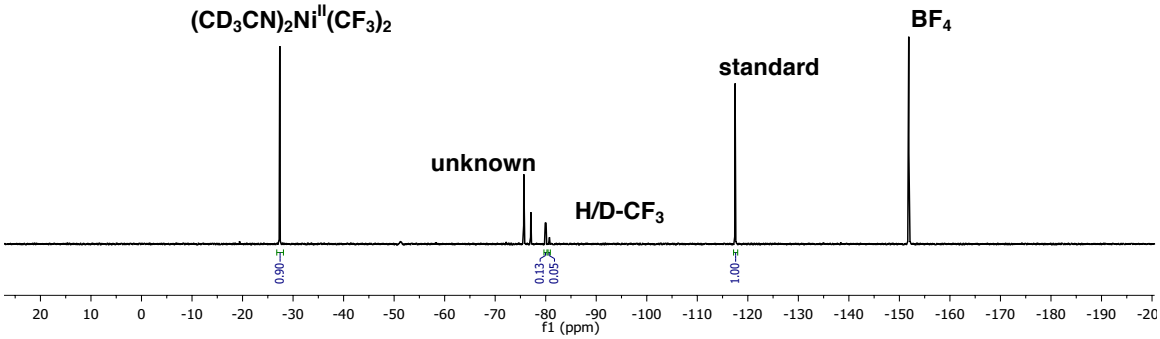


Figure S9. (a) ^1H NMR spectrum of the crude reaction mixture after heating **2b** at 55 ºC for 8 h. Standard = 1,3,5-trimethoxybenzene; (b) ^{11}B NMR spectrum of the reaction mixture after heating for 55 ºC for 8 h. Standard = NBu_4BF_4.

Procedure for the thermolysis of 2c: A 4 mL vial was charged with **2c** (3.4 mg, 0.0075 mmol), and CD_3CN (0.5 mL). The resulting purple solution was transferred to a teflon-lined screw cap NMR tube and removed from the glovebox. The NMR tube was heated in an oil bath at 70 ºC for 12 h. The NMR tube was then brought back in the glove box, and 0.2 mL of a stock solution containing NBu_4BF_4 (0.038 M in MeCN, 1.0 equiv) and 4,4'-difluorobiphenyl (0.056 M, 1.5 equiv) were added to the NMR tube. The NMR tube was capped, and the sample was analyzed by quantitative ^{19}F and ^{11}B NMR spectroscopy to determine the yield of H/D-CF_3, $(CD_3CN)_2Ni(CF_3)_2$ and $Ni^{II}Tp_2$. Representative NMR spectra are shown in Figure S10.



(a)



(b)

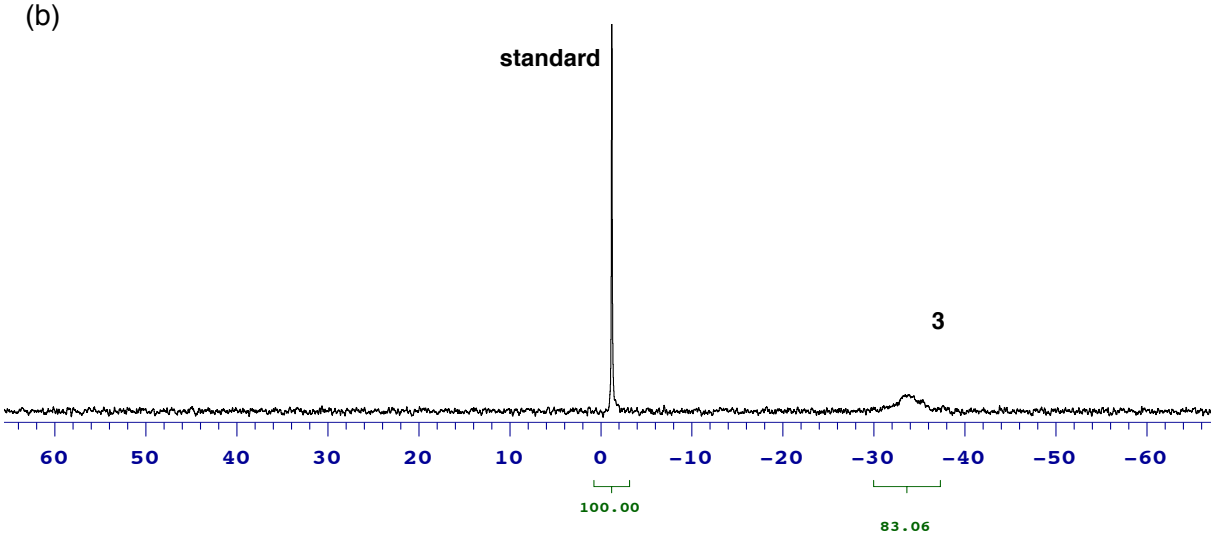
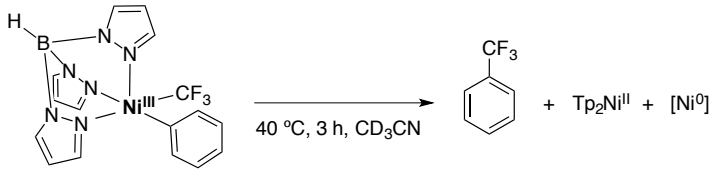


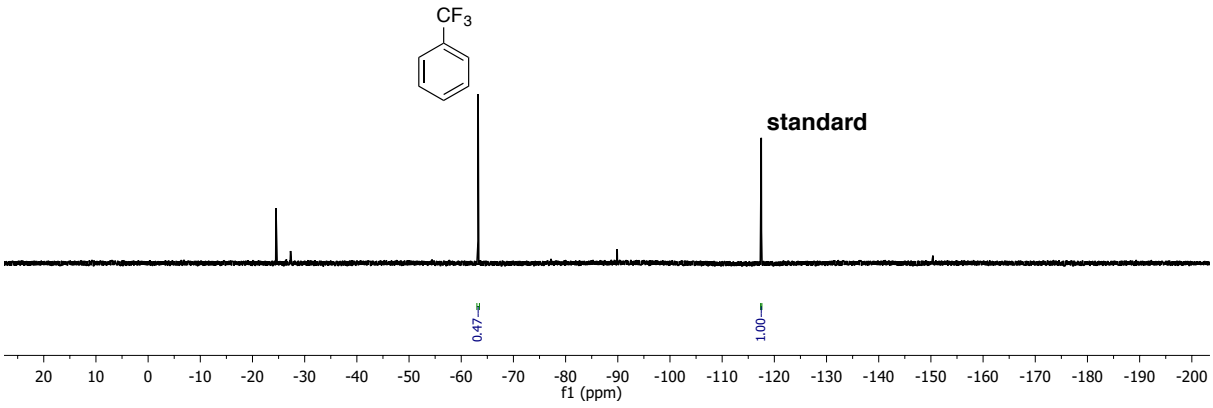
Figure S10. (a) ^{19}F NMR spectrum of the crude reaction mixture after heating **2c** at 70 ºC for 12 h. Standard =4,4'-difluorobiphenyl; (b) ^{11}B NMR of the reaction mixture after heating for 70 ºC for 12 h. Standard = NBu_4BF_4.

Procedure for the thermolysis of 2e: A 4 mL vial was charged with **2e** (3.1 mg, 0.0075 mmol) and 4,4'-difluorobiphenyl (0.5 mL in 0.023M CD_3CN, 1.5 equiv). The resulting orange solution was transferred to a teflon-lined screw cap NMR tube and removed from the glovebox. The NMR tube was heated in an oil bath at 40 ºC for 3 h or 80 ºC for 5 min. The solution was then analyzed by ^{19}F NMR spectroscopy to determine the yield of benzotrifluoride. The NMR tube was then brought back in the glove box, and NBu_4BF_4 (0.2 mL, 0.038 M in MeCN, 1.0 equiv) was added to the NMR tube as an ^{11}B NMR standard. The tube was capped, and the sample was analyzed by quantitative ^{11}B NMR spectroscopy to determine the yield of $Ni^{II}Tp_2$. Representative NMR spectra are shown in Figure S11 and S12.



2e 47% (**3**, 30%)

(a)



(b)

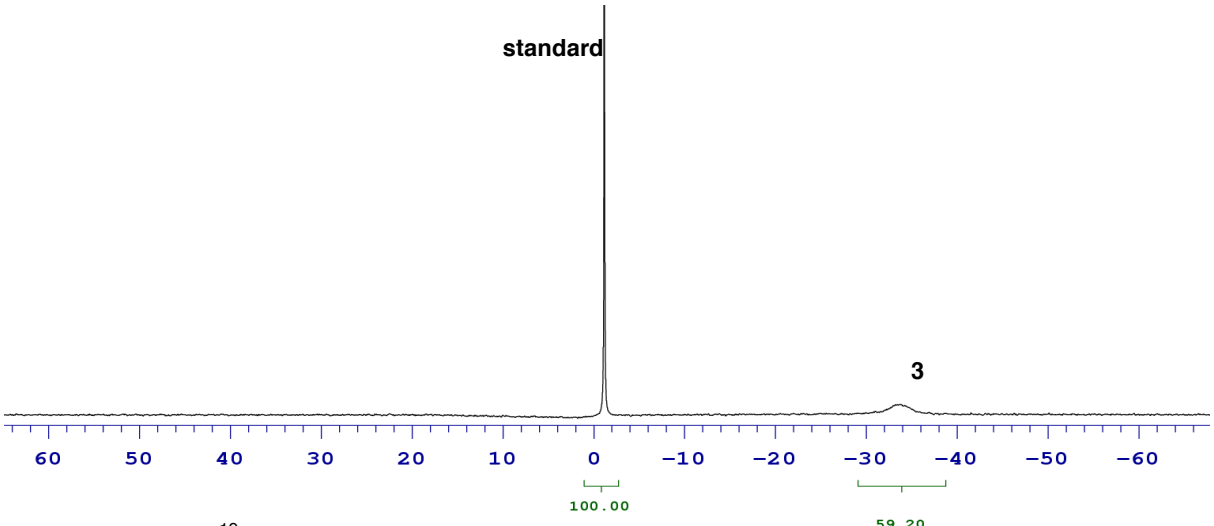


Figure S11. (a) ^{19}F NMR spectrum of the crude reaction mixture after heating **2e** at 40 ºC for 3 h. Standard = 4,4-difluorobiphenyl; (b) ^{11}B NMR spectrum of the reaction mixture after heating for 40 ºC for 3 h. Standard = NBu_4BF_4

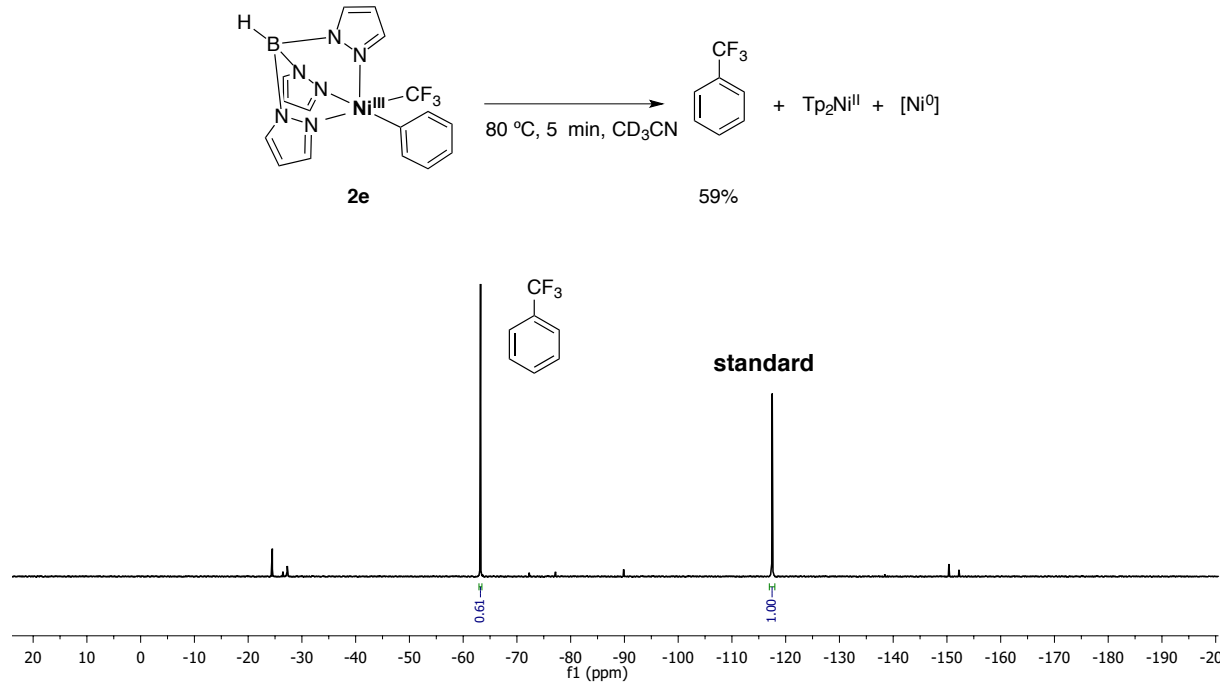
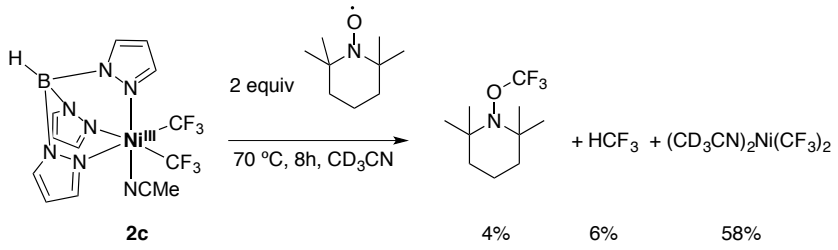


Figure S12. (a) A representative ^{19}F NMR spectrum of the crude reaction mixture after heating **2e** at 80 ºC for 5 min. Standard = 4,4-difluorobiphenyl.

VIII. Mechanistic Investigations

Radical Trap Experiments

Procedure for the thermolysis of 2c in the presence of TEMPO: A 4 mL vial was charged with **2c** (3.4 mg, 0.0075 mmol, 1.0 equiv), TEMPO (2.4 mg, 0.015 mmol, 2.0 equiv), and CD_3CN (0.5 mL). The resulting purple solution was transferred to a teflon-lined screw cap NMR tube and removed from the glovebox. The NMR tube was heated in an oil bath at 70 ºC for 8 h. The NMR tube was then brought back in the glove box, and 0.2 mL of a stock solution containing the standard 4,4'-difluorobiphenyl (0.056 M in MeCN, 1.5 equiv) was added to the NMR tube. The solution was removed from the glove box, and the sample was analyzed by ^{19}F NMR spectroscopy. TEMPO-CF_3 was detected in low yield (4%). Additional heating caused the disappearance of TEMPO-CF_3 suggesting that it is unstable under these conditions. A representative ^{19}F NMR spectrum is shown in Figure S13.



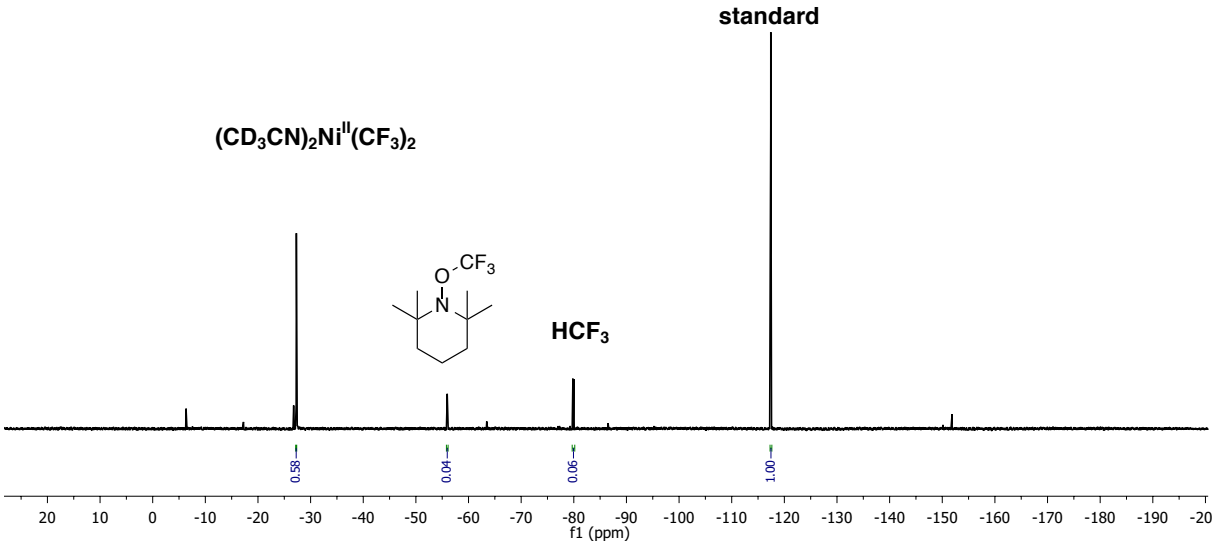


Figure S13. ^{19}F NMR spectrum of **2c** and TEMPO after heating at 70 ºC for 8 h. Standard = 4,4'-difluorobiphenyl.

Procedure for the thermolysis of 2e in the presence of TEMPO: A 4 mL vial was charged with **2e** (3.1 mg, 0.0075 mmol, 1.0 equiv), TEMPO (2.4 mg, 0.015 mmol, 2.0 equiv), and CD_3CN (0.5 mL). The resulting orange solution was transferred to a teflon-lined screw cap NMR tube and removed from the glovebox. The NMR tube was heated in an oil bath at 40 ºC for 3 h. The NMR tube was then brought back in the glove box, and the standard 4,4'-difluorobiphenyl (0.2 mL in 0.056 M MeCN, 1.5 equiv) was added to the NMR tube. The tube was capped, and the sample was analyzed by ^{19}F NMR spectroscopy to determine the yield of Ph-CF_3 (57%). Neither TEMPO-CF_3 nor CF_3H/D were detected by ^{19}F NMR spectroscopy. A representative ^{19}F NMR spectrum is shown in Figure S14.

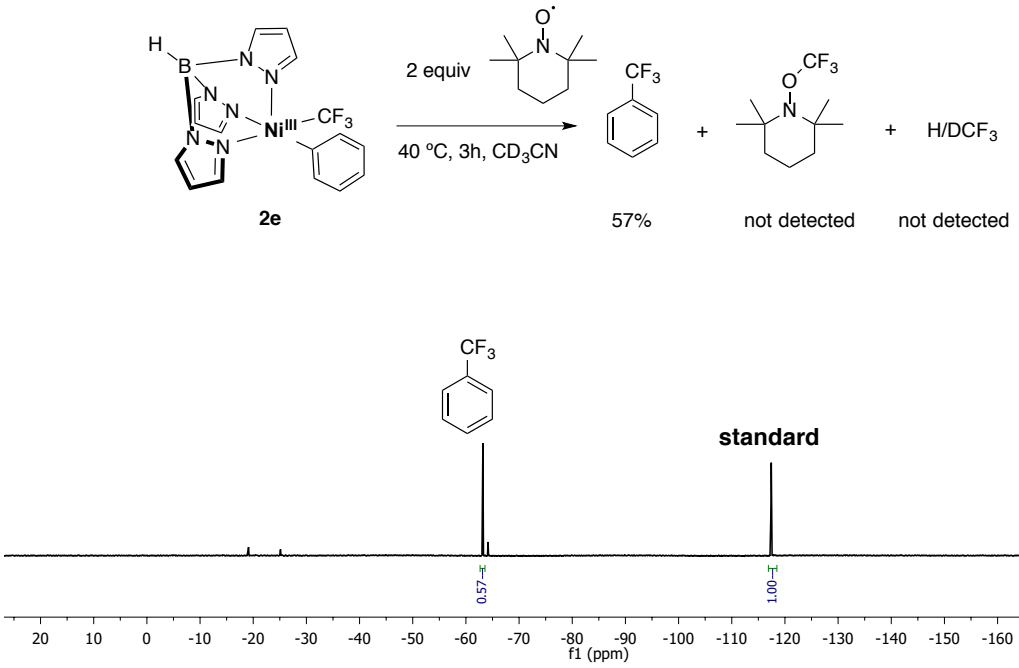


Figure S14. ^{19}F NMR spectrum of **2e** and TEMPO after heating at 40 ºC for 3 h. Standard = 4,4'-difluorobiphenyl.

Procedure for attempted solvent trapping of CF_3 radicals: A 4 mL vial was charged with **2e** (3.1 mg, 0.0075 mmol, 1 equiv) and the standard 4,4'-difluorobiphenyl (0.5 mL, 0.022 M in C_6D_6, 1.5 equiv). The resulting yellow-green solution was transferred to a teflon-lined screw cap NMR tube and removed from the glovebox. The NMR tube was heated in an oil bath at 40 ºC for 5 h. The solution was then analyzed by ^1H and ^{19}F NMR spectroscopy to determine the yield of benzotrifluoride. The ^1H NMR spectrum confirms the presence of $C_6H_5CF_3$ in 63% yield (54% by ^{19}F NMR spectroscopy). Representative NMR spectra are shown in Figure S15.

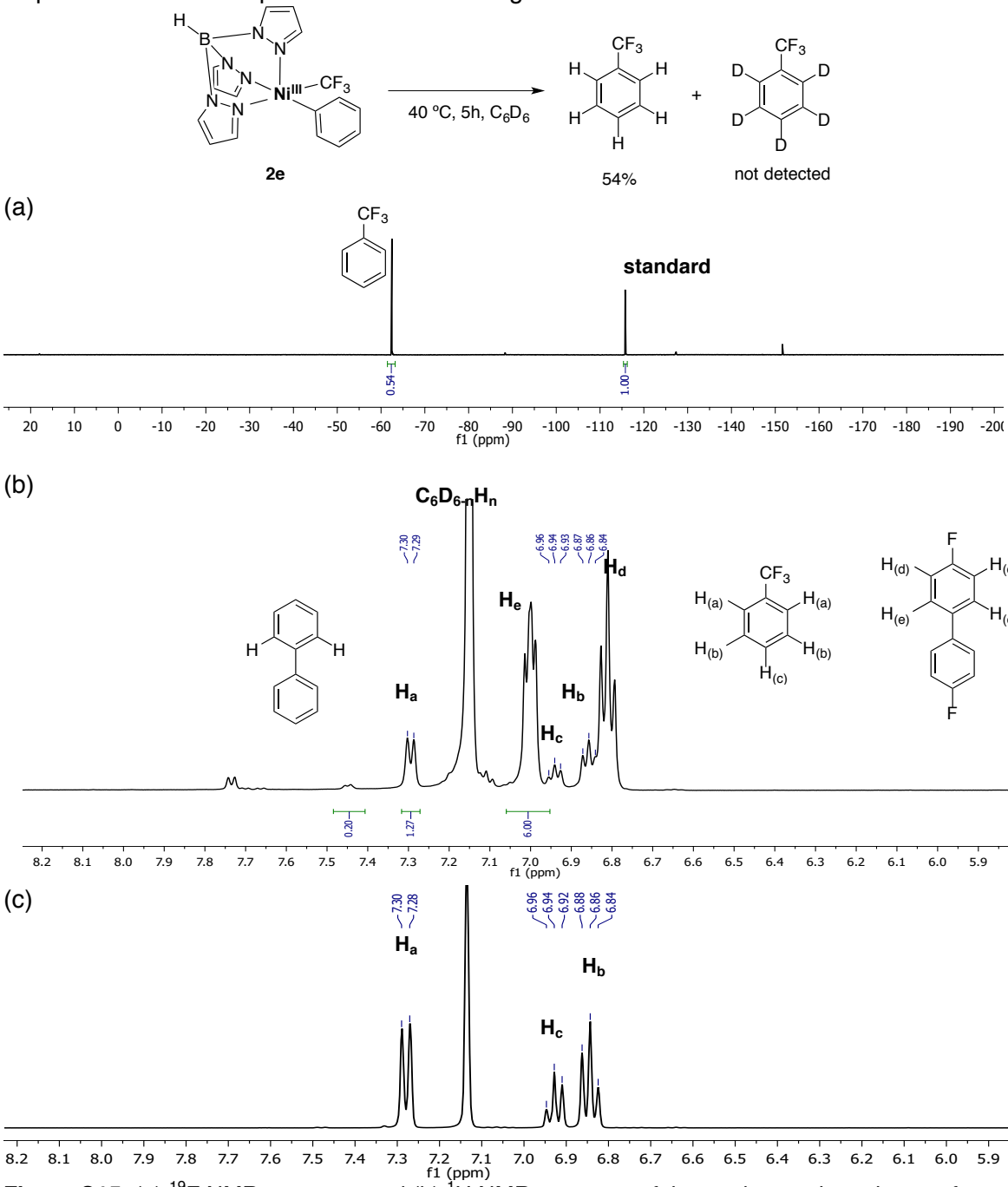


Figure S15. (a) ^{19}F NMR spectrum and (b) ^1H NMR spectrum of the crude reaction mixture after heating **2e** at 40 ºC for 5 h; (c) ^1H NMR spectrum of authentic $C_6H_5CF_3$ in C_6D_6 for comparison.

Oxidatively Induced Coupling Studies

Procedure for low temperature oxidatively induced coupling from 2e with $NOBF_4$: A 4 mL vial was charged with **2e** (3.1 mg, 0.0075 mmol, 1.0 equiv) and the standard 4,4'-difluorobiphenyl (0.5 mL in 0.023 M CD_3CN, 1.5 equiv). The resulting orange solution was transferred to septum-capped NMR tube and removed from the glovebox. The NMR tube was cooled to 0 ºC in an ice bath over 5 minutes. Next, $NOBF_4$ was added via syringe as a stock solution (150 μL, 0.05 M in room temperature CD_3CN, 1.0 equiv). The solution was vigorously shaken for about 3 s before it was inserted into a precooled (–30 ºC) NMR probe. A new ^{19}F NMR resonance consistent with a new diamagnetic [Ni-CF_3] complex (~31% yield) was detected at –30.85 ppm, along with benzotrifluoride (33%) (Figure S14a). After a spectrum was collected at –30 ºC, the NMR probe was warmed to room temperature over 1 min. A second spectrum was collected approximately 2 min later to determine the yield of benzotrifluoride (50%, Figure S14b). A final spectrum was taken 30 min later, at which point no additional benzotrifluoride was observed.

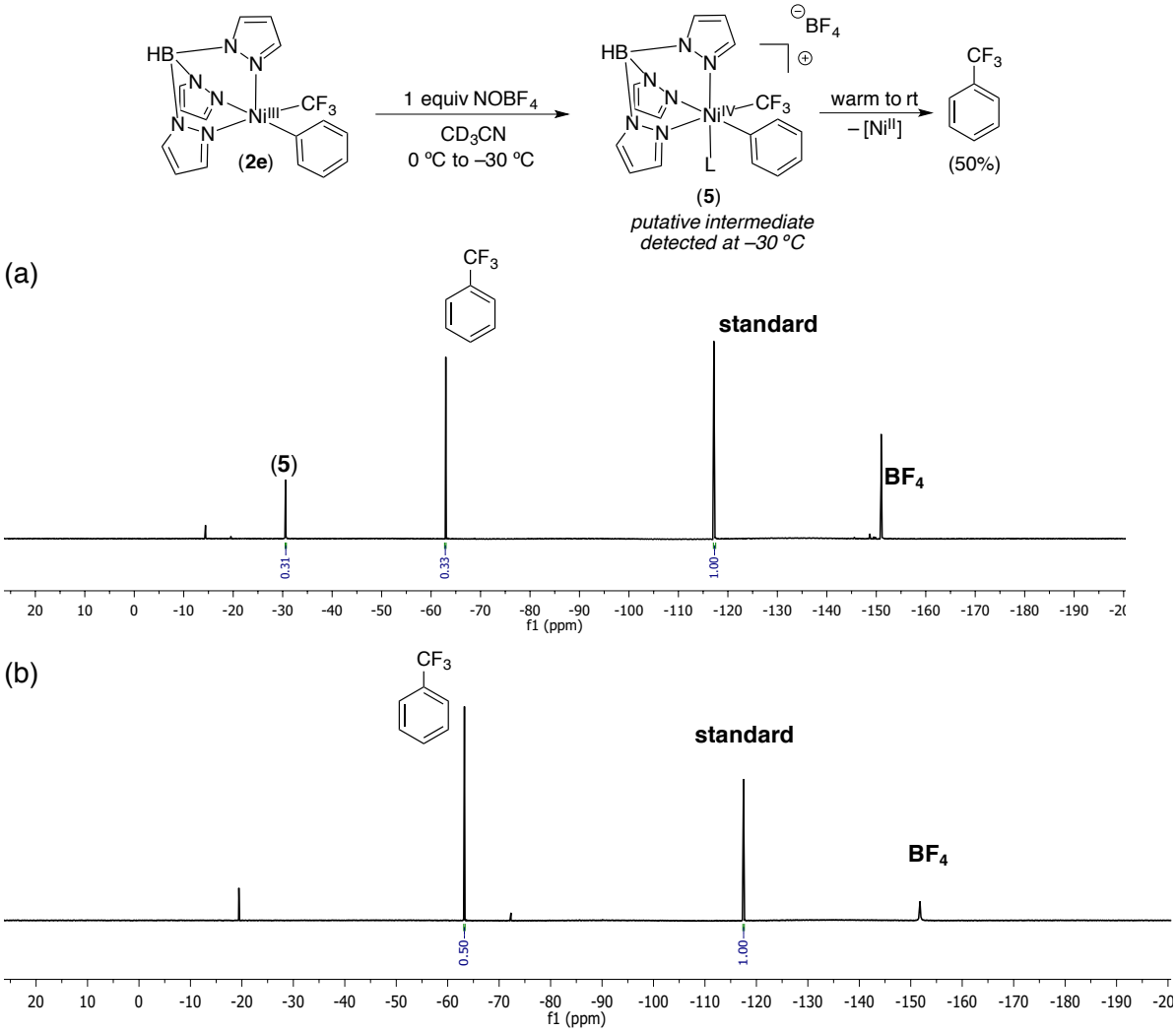


Figure S16. ^{19}F NMR spectrum of **2e** when reacted with 1 equiv of $NOBF_4$ at (a) –30 ºC after 1 min and (b) after warming to room temperature for 2 min

Procedure for oxidatively induced C-C coupling 2e with acetyl ferrocenium tetrafluoroborate: A 4 mL vial was charged with **2e** (3.1 mg, 0.0075 mmol, 1.0 equiv), the standard 4,4'-difluorobiphenyl (0.5 mL in 0.023 M CD_3CN, 1.5 equiv), and acetyl ferrocenium tetrafluoroborate (2.4 mg, 0.0075 mmol, 1 equiv) $AcFcBF_4$. Over 30 min at room temperature the blue green solution slowly turned yellow. The solution was then analyzed by ^{19}F NMR spectroscopy to determine the yield of benzotrifluoride (98%).

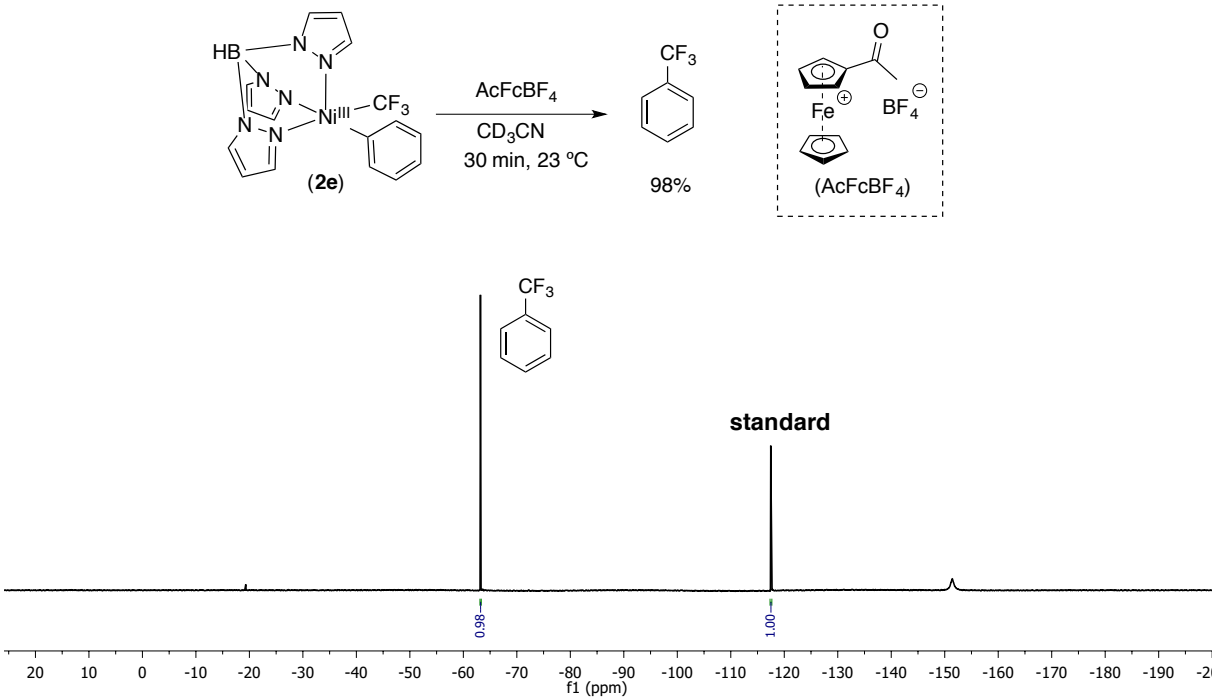
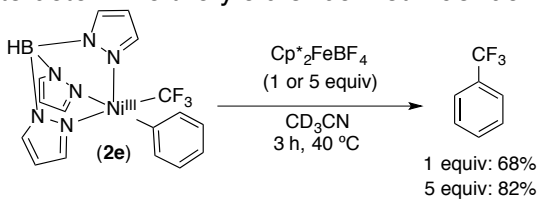


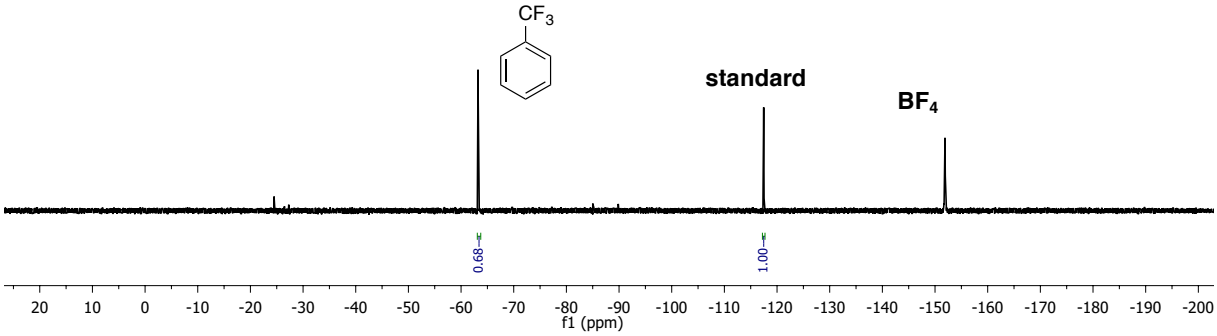
Figure S17. ^{19}F NMR spectrum of the crude reaction mixture 30 minutes after treating **2e** with 1 equiv of acetyl ferrocenium tetrafluoroborate.

The Effect of Additives on C-C Coupling from 2e

Procedure for the thermolysis of 2e with added weak oxidant: A 4 mL vial was charged with **2e** (3.1 mg, 0.0075 mmol, 1.0 equiv), the standard 4,4'-difluorobiphenyl (0.5 mL in 0.023M CD_3CN, 1.5 equiv), and the corresponding amount of decamethylferrocenium tetrafluoroborate $Cp^*_2FeBF_4$. The resulting green solution was transferred to a teflon-lined screw cap NMR tube and removed from the glovebox. The NMR tube was heated in an oil bath at 40 ºC for 3 h. The solution was then analyzed by ^{19}F NMR spectroscopy to determine the yield of benzotrifluoride.



(a) 1 equiv of $Cp_2^*FeBF_4$



(b) 5 equiv of $Cp_2^*FeBF_4$

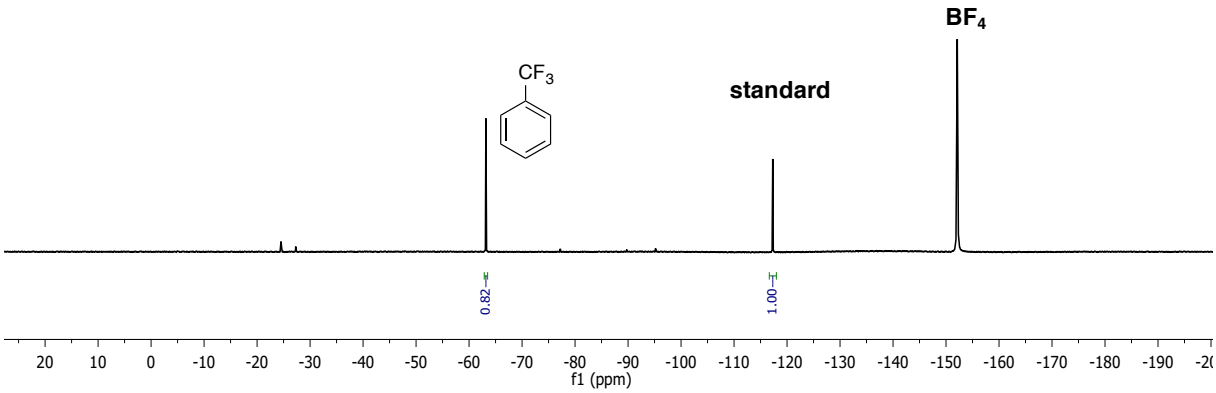
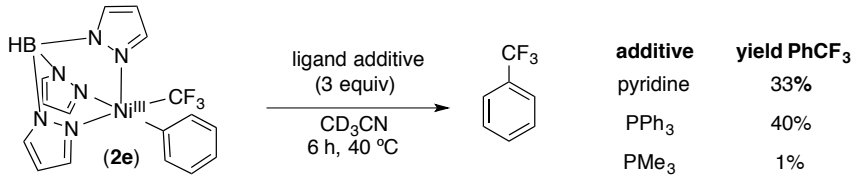


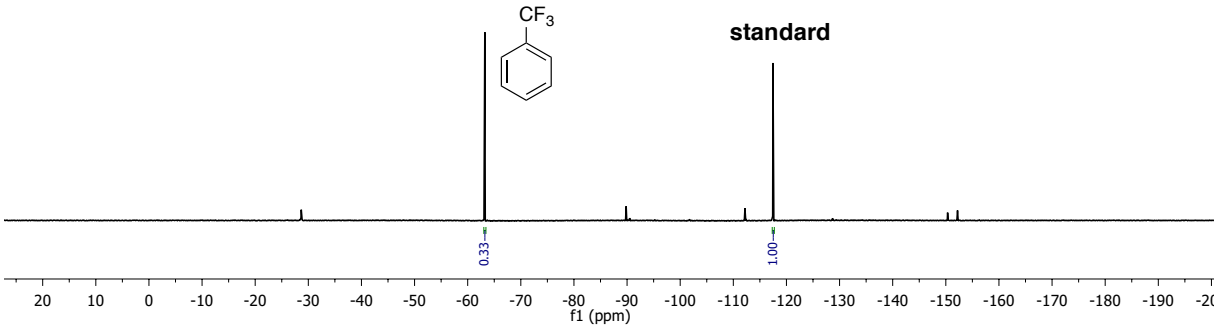
Figure S18. ^{19}F NMR spectrum of the crude reaction mixture after heating **2e** at 40 ºC for 5 h in the presence of (a) 1 equiv of $Cp_2^*FeBF_4$ or (b) 5 equiv of $Cp_2^*FeBF_4$.

General procedure for the thermolysis of 2e in the presence of exogenous ligand: A 4 mL vial was charged with **2e** (3.1 mg, 0.0075 mmol, 1.0 equiv), the standard 4,4'-difluorobiphenyl (0.5 mL in 0.023M CD_3CN, 1.5 equiv), and 3 equiv of the corresponding ligand (pyridine and PMe_3 were added from a stock solution with the internal standard, PPh_3 was added as a solid). The resulting orange (with the addition of PPh_3 and pyridine) or brown (with the addition of PMe_3) solution was transferred to a teflon-lined screw cap NMR tube and removed from the glovebox. The NMR tube was heated in an oil bath at 40 ºC for 6 h. The solution was then analyzed by ^{19}F NMR spectroscopy to determine the yield of benzotrifluoride. Representative NMR spectra are shown in Figure S19.

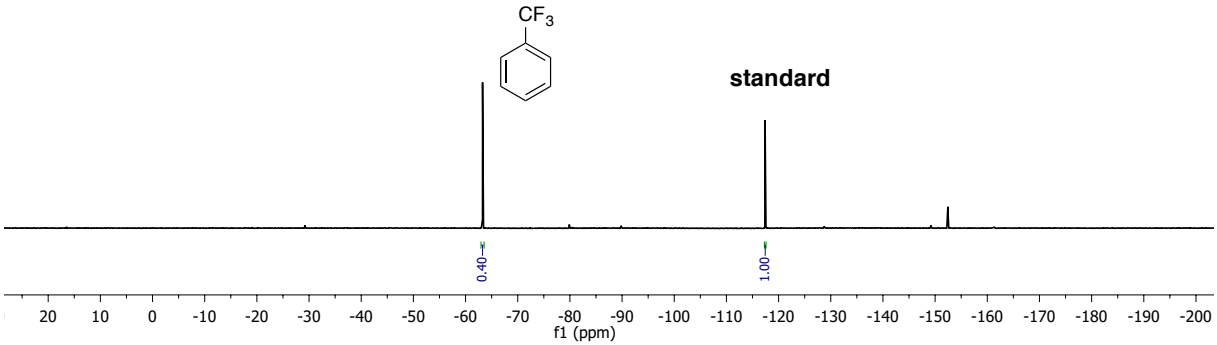


additive	yield $PhCF_3$
pyridine	33%
PPh_3	40%
PMe_3	1%

(a) 3 equiv of pyridine



(b) 3 equiv of PPh_3



(c) 3 equiv of PMe_3

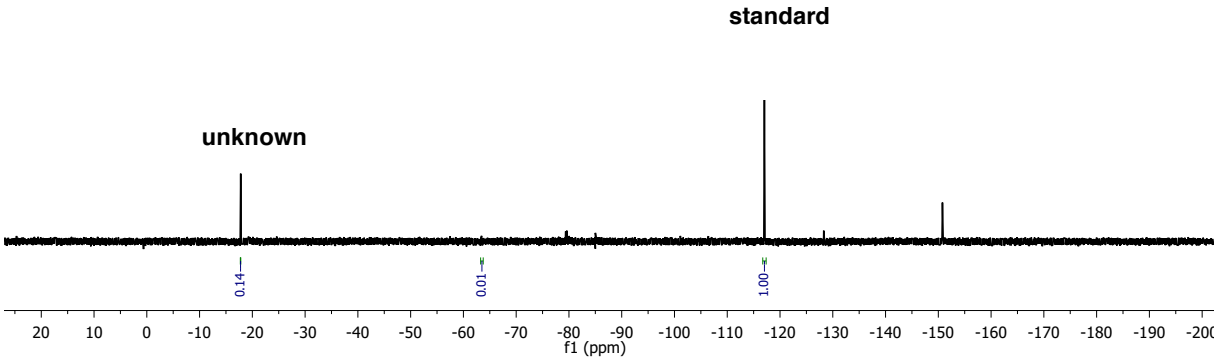
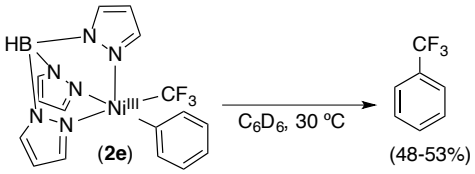


Figure S19. ^{19}F NMR spectrum of the crude reaction mixture after heating **2e** at 40 ºC for 6 h in the presence of 3 equiv of (a) pyridine, (b) PPh_3, or (c) PMe_3.

IX. Rate Studies

Determining the order in 2e for Ar-CF_3 Coupling



Experimental procedure: Complex **2e** and 4,4'-difluorobiphenyl (1.5 equiv) were added directly to a Teflon-capped NMR tube from a freshly prepared stock solution in C_6D_6. This solution was then diluted to the appropriate concentration by the addition C_6D_6 via syringe ([**2e**] = 0.01M to 0.03 M). The resulting solution was capped and brought outside of the glovebox to be flash frozen at –78 °C until analysis. The NMR tubes were thawed at room temperature and then placed in the NMR probe pre-warmed to 30 °C. The formation of Ph-CF_3 was monitored by ^{19}F NMR spectroscopy at this temperature. Concentration versus time data were obtained through integration of the C***F***$_3$ signals of Ph-CF_3. Initial rates were obtained from the average of two trials by taking the slopes of linear-fit lines for the first 6% of the reaction progress (Figure S18). When a plot of these rates was fit to $A=m[Ni]^X$ the order in nickel was found to be 0.80 (Figure S19). *Note: Given the thermal instability of **2e** even in the solid state, the stock solution of **2e** and internal standard was prepared within 2 h of use and was stored as a solid at –35 °C.*

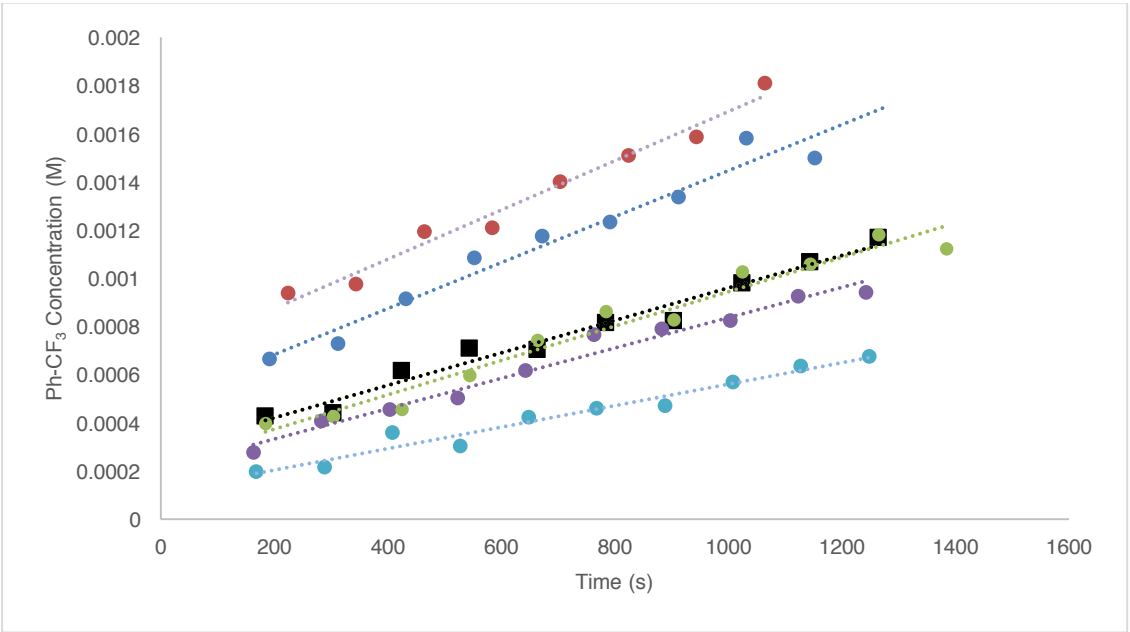
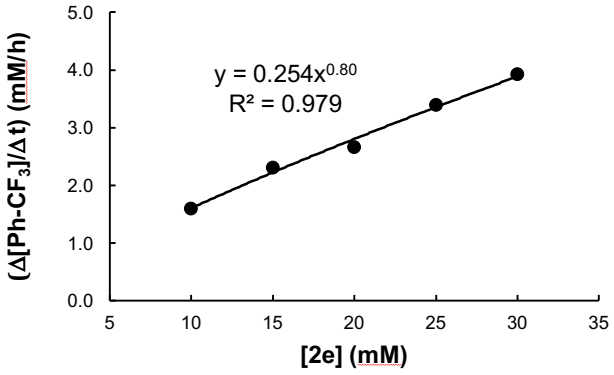


Figure S20. Representative initial rates plots of concentration vs. time for reductive elimination from **2e** to form Ph-CF_3. ● = 0.03M [Ni], y= $6.42e^{-4}$+ $1.08e^{-6}$x, R^2=0.979. ● = 0.025M [Ni], y= $5.35xe^{-4}$+ $9.65e^{-7}$x, R^2=0.960. ● = 0.02M [Ni], y= $2.88e^{-4}$+ $6.82e^{-7}$x, R^2=0.978. ● = 0.015M [Ni], y= $2.07e^{-4}$+ $6.30e^{-7}$e, R^2=0.975. ● = 0.01M [Ni], y= $1.16e^{-4}$+ $4.45e^{-7}$x, R^2=0.962. ■ = 0.02 M [Ni] + 15 equiv MeCN, y= $2.88e^{-4}$ + $6.73e^{-7}$x, R^2= 0.966

(a)



(b)

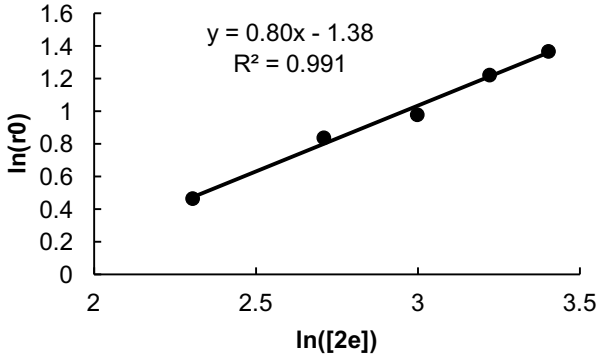


Figure S21. (a) Plot of initial rates of Ph-CF_3 formation versus [Ni] for Ph-CF_3 coupling from **2e** fit to $y=a[X]^n$. (b) A log-log plot of initial rate of Ph-CF_3 formation as a function of nickel concentration

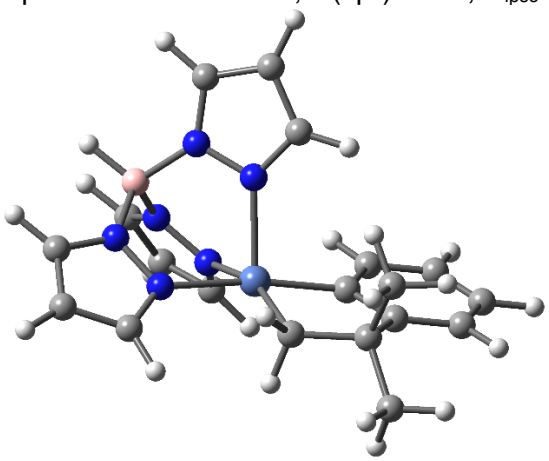
X. Computational Details

Gaussian 09[11] was used at the ucam-B3LYP[12] level of density functional theory (DFT) for geometry optimization in the gas phase. The Stuttgart/Dresden ECP (SDD) was used to describe Ni,[13] and the 6-31G(d) basis set was used for other atoms.

Calculated spin density values >0.02 are limited to nickel and atoms bonded to nickel, and are given below with structural data.

Complex 2a:

Spin densities: Ni 1.18, C(sp^3) -0.18, C_{ipso} -0.12, N_{axial} 0.08.



Ni	5.833961	14.526450	5.833474
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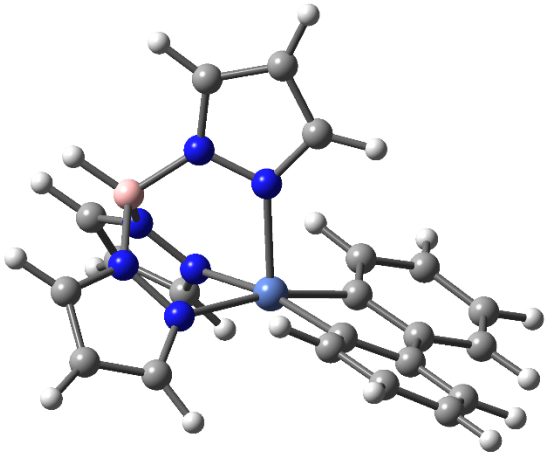
N	5.298089	11.831646	4.814155
N	7.542171	13.368925	6.014852
N	7.389609	12.033155	6.131019
N	5.001887	13.381765	7.356499
N	5.177778	12.044516	7.304519
C	4.602752	13.187062	3.290225
H	4.399436	14.140582	2.824921
C	4.341362	11.897045	2.820557
H	3.884367	11.611561	1.885820
C	4.801504	11.068318	3.827016
H	4.811732	9.991767	3.911992
C	8.848809	13.603675	5.913225
H	9.208845	14.618244	5.818582
C	9.564720	12.403447	5.969147
H	10.633777	12.265823	5.920251
C	8.591053	11.431690	6.106182
H	8.666265	10.357388	6.188051
C	4.357774	13.646508	8.487816
H	4.125342	14.668700	8.748331
C	4.097645	12.462462	9.188472
H	3.589824	12.349009	10.133731

C	4.641713	11.469885	8.396531
H	4.688307	10.399171	8.530364
C	6.371453	16.048048	6.886100
C	7.431414	15.986109	7.793633
H	7.983570	15.063575	7.931772
C	7.782154	17.103453	8.548705
H	8.609504	17.041349	9.250391
C	7.074660	18.292751	8.409333
H	7.352209	19.164974	8.994228
C	6.001453	18.357872	7.528499
H	5.435866	19.281732	7.433934
C	5.643421	17.240767	6.775954
C	4.445764	17.164452	5.862242
C	4.639366	15.861624	5.075091
H	5.181641	16.051103	4.136455
H	3.698236	15.357598	4.838943
C	3.156650	17.083224	6.696939
H	3.159518	16.196577	7.337272
H	2.277718	17.025031	6.044384
H	3.046077	17.964300	7.337486
C	4.344896	18.362435	4.906183
H	4.166596	19.297183	5.449069
H	3.514138	18.225180	4.204775
H	5.265999	18.481121	4.326361
B	5.970796	11.425929	6.142944
H	6.020798	10.230616	6.243634

Complex 2b:

Spin densities: Ni 1.16, C_{ipso} -0.14 and -0.15, N_{axial} 0.07.



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N	7.392128	12.041378	6.156373
N	4.993155	13.471338	7.235172
N	5.133897	12.129816	7.243195
C	4.904345	13.144048	3.122422
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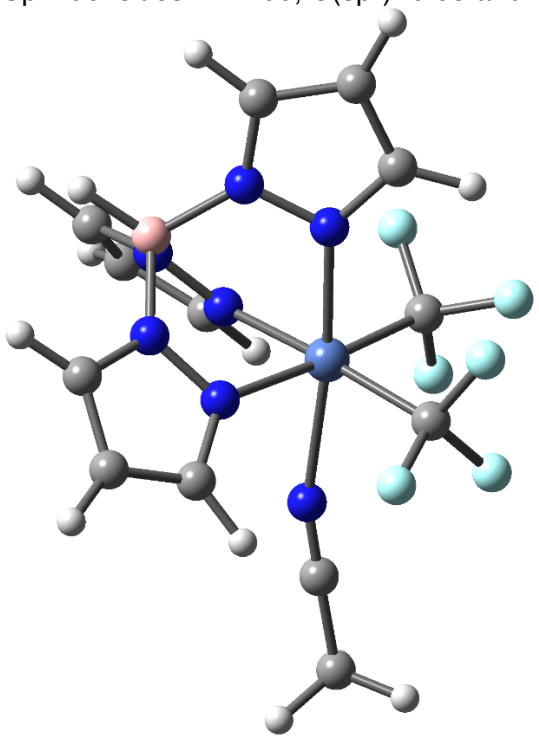
C	4.703116	11.842391	2.654375
H	4.377200	11.534300	1.673101
C	5.013446	11.038070	3.735414
H	5.009044	9.963734	3.845831
C	8.883609	13.571767	5.859595
H	9.262324	14.572235	5.709952
C	9.575683	12.365569	6.000623
H	10.642559	12.207056	5.974402
C	8.583052	11.420813	6.184939
H	8.638061	10.352426	6.333027
C	4.240684	13.796858	8.279354
H	3.999990	14.833760	8.465426
C	3.878643	12.645462	8.989678
H	3.273992	12.579352	9.880861
C	4.470465	11.609831	8.292024
H	4.467941	10.543722	8.464878
C	6.646546	16.054990	6.677602
C	7.679303	15.994827	7.604174
H	8.093346	15.040845	7.910246
C	8.194229	17.170268	8.159329
H	9.006414	17.113400	8.878522
C	7.672446	18.404571	7.794972
H	8.080189	19.316282	8.221480
C	6.606885	18.472710	6.901662

H	6.172764	19.436299	6.649531
C	6.084038	17.303928	6.357432
B	5.962823	11.453974	6.142681
H	5.989965	10.263165	6.288800
C	4.569097	15.835109	5.244040
C	4.882233	17.176738	5.528370
C	3.361933	15.538168	4.624764
C	4.030669	18.200208	5.124642
C	2.501973	16.568225	4.231694
H	3.070712	14.509758	4.443693
C	2.844121	17.893903	4.464098
H	4.277103	19.235823	5.342213
H	1.562702	16.326118	3.742536
H	2.177992	18.692042	4.150052

Complex 2c:
Spin densities: Ni 1.00, C(sp^3) -0.05 and -0.06, N_{axial} 0.09, N_{MeCN} -0.05.



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N	7.444860	13.534507	6.179131
N	7.325267	12.195921	6.316912
N	4.801777	13.432494	7.271923
N	5.004721	12.099586	7.232965
C	4.856190	13.222444	3.179780
H	4.664225	14.176167	2.711091
C	4.688894	11.925649	2.687049
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C	5.057250	11.107651	3.740270
H	5.092057	10.031775	3.826515
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C	9.485586	12.650496	6.442881
H	10.555106	12.556148	6.549426
C	8.538639	11.644449	6.477776
H	8.638495	10.576832	6.605792
C	3.927457	13.667488	8.244368
H	3.612596	14.679170	8.448441
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H	4.300826	10.423880	8.302729
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H	6.049395	10.324371	6.294753
C	4.073089	15.507832	5.393446
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F	5.529828	16.150138	8.081005
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C	8.020526	17.458809	2.646530
H	9.041637	17.170713	2.386746
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H	7.438924	17.580417	1.729850
C	7.409500	16.440757	3.489964
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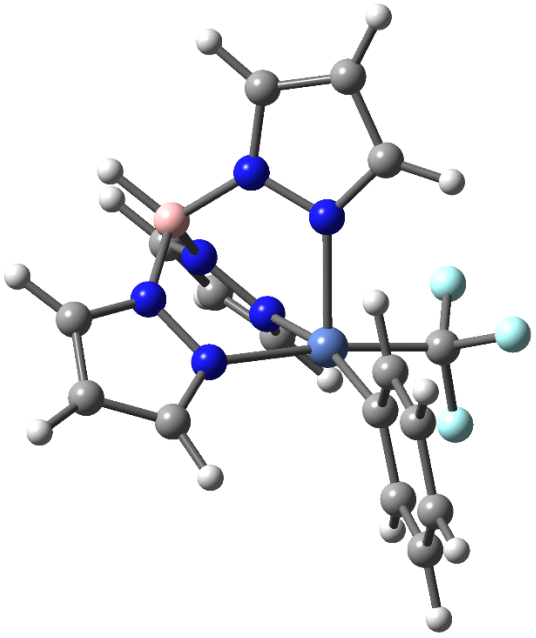
H	8.041503	18.410547	3.182854
H	7.438924	17.580417	1.729850
C	7.409500	16.440757	3.489964
N	6.917478	15.650265	4.164683

Complex 2e

Spin densities: Ni 1.14, C(sp^3) -0.08, C_{ipso} -0.13, N_{axial} 0.07.



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N	7.427809	13.512697	6.231896
N	7.344563	12.170148	6.349820
N	4.757226	13.377662	7.248711
N	5.001486	12.050382	7.220112
C	4.831989	13.187123	3.201686
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H	4.371526	11.598870	1.707449
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C	6.438402	16.043956	6.783549

C	7.026485	17.069661	6.047476
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H	8.160868	18.895082	6.115609
H	7.244186	17.103230	9.905427
H	8.305792	18.923042	8.593415
F	3.195953	14.891594	5.042309
F	3.778220	16.491689	6.341408
F	4.576270	16.394854	4.316486

XI. References

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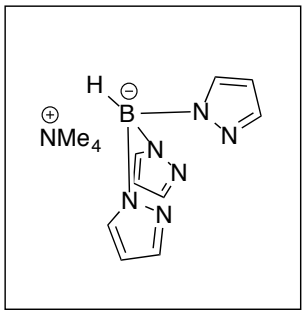
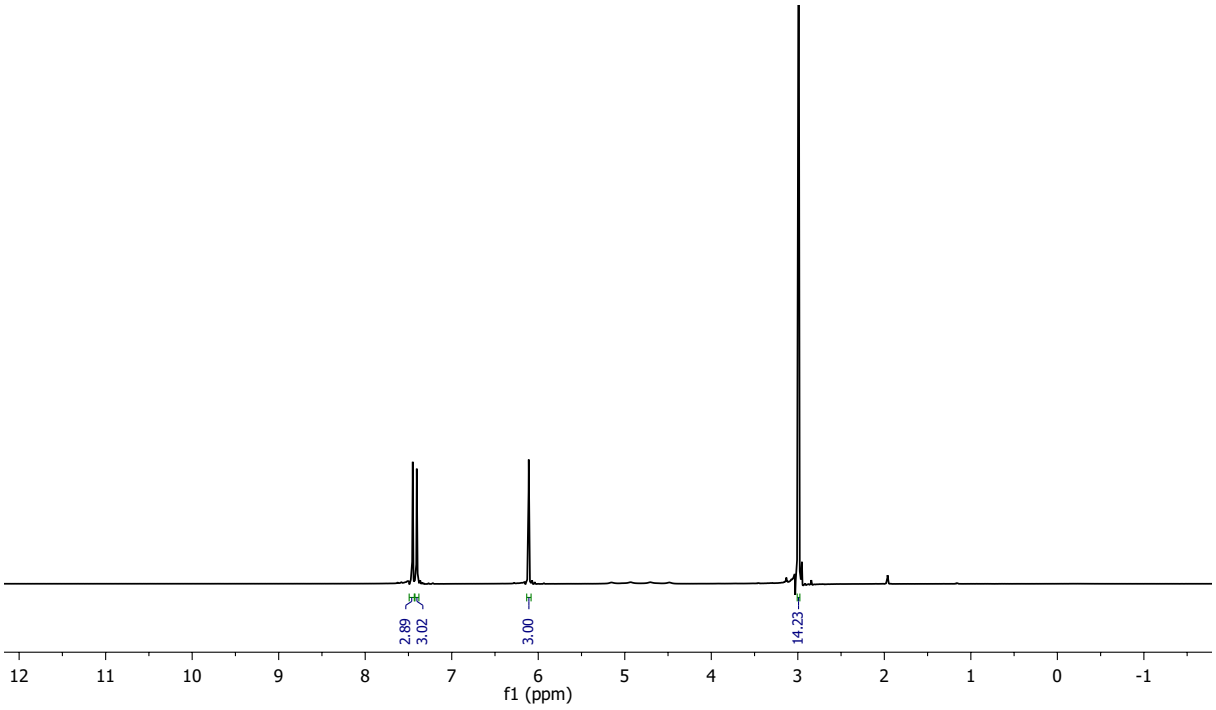
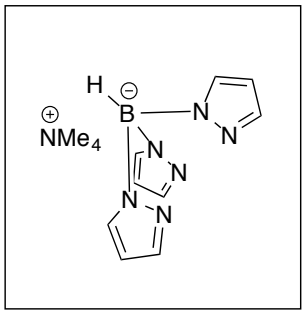
XII. Spectral Data

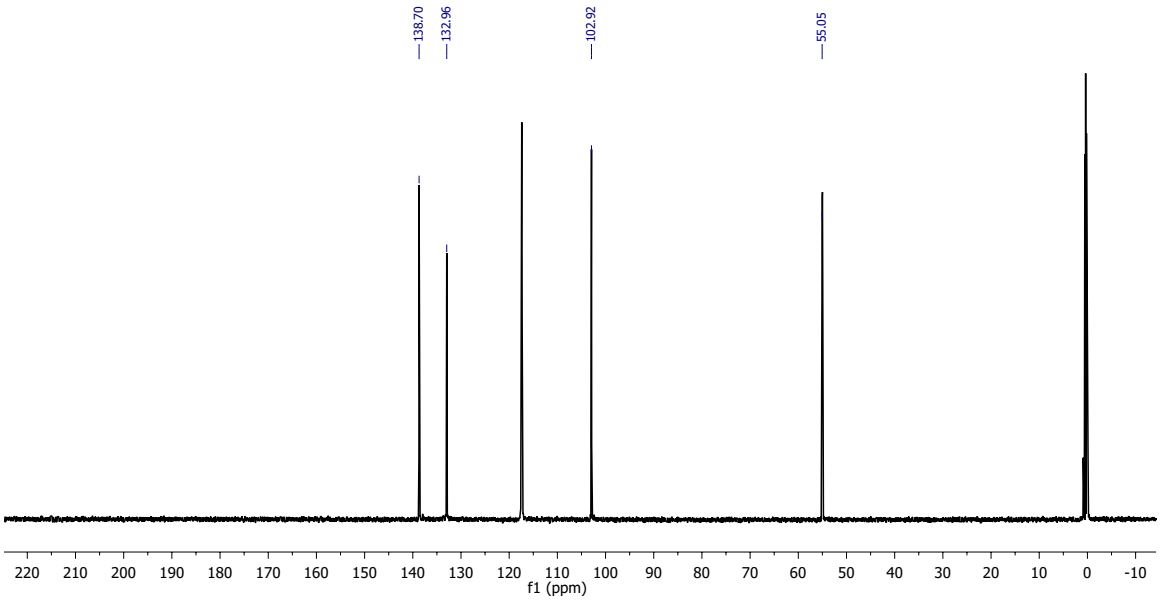
^{1}H NMR of NMe_4Tp at 23 °C (CD_3CN)



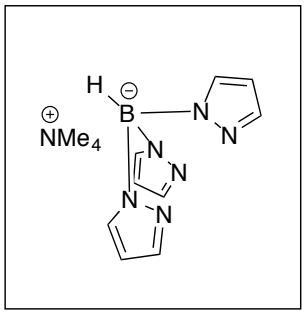


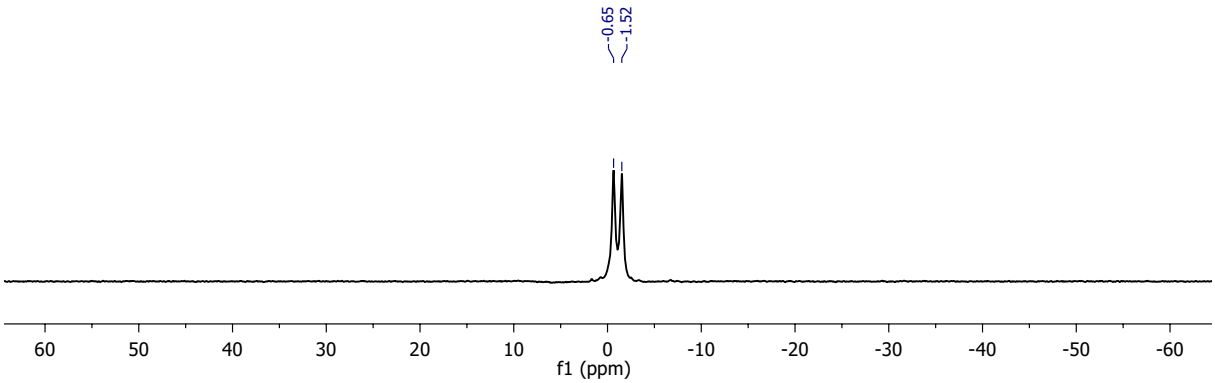
^{13}C NMR of NMe_4Tp at 23 ºC (CD_3CN)



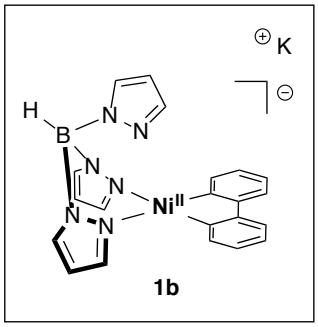


^{11}B NMR of NMe_4Tp at 23 ºC (CD_3CN)





^{1}H NMR of 1b at 23 ºC (CD_3CN)



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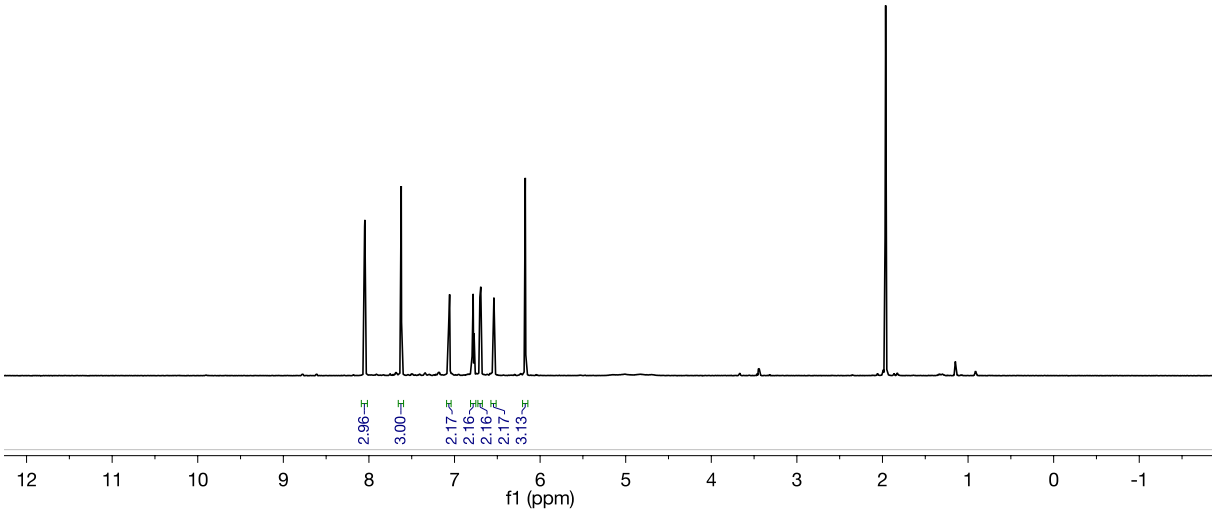
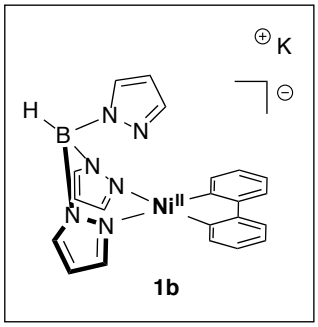


^{13}C NMR of 1b at 23 ºC (CD_3CN)



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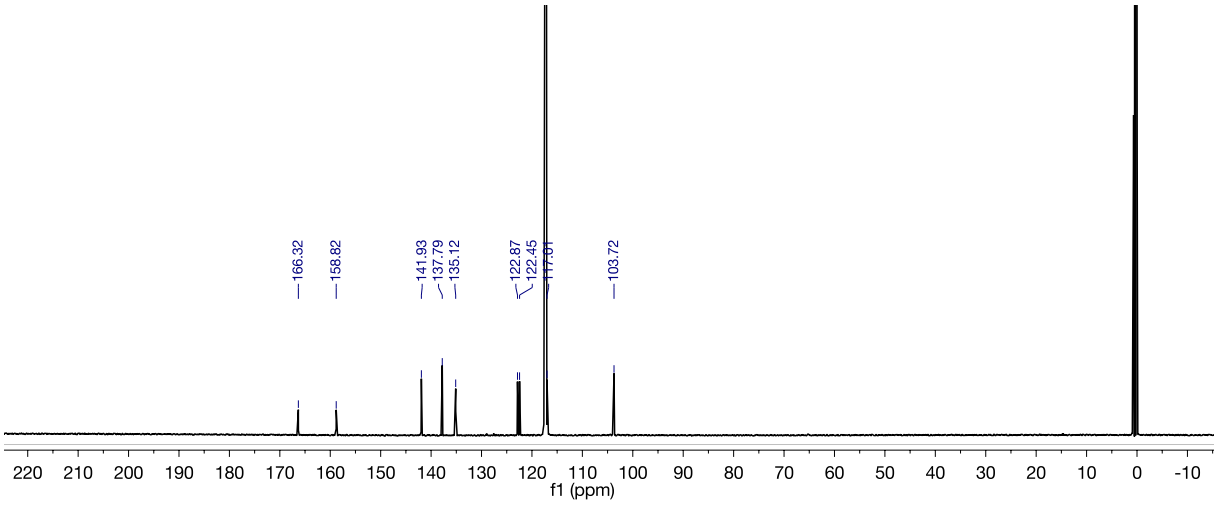
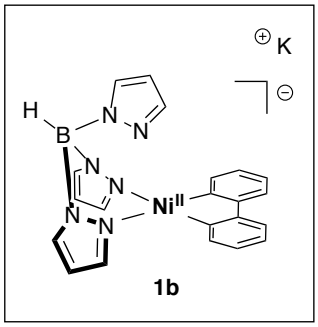


^{11}B NMR of 1b at 23 ºC (CD_3CN)



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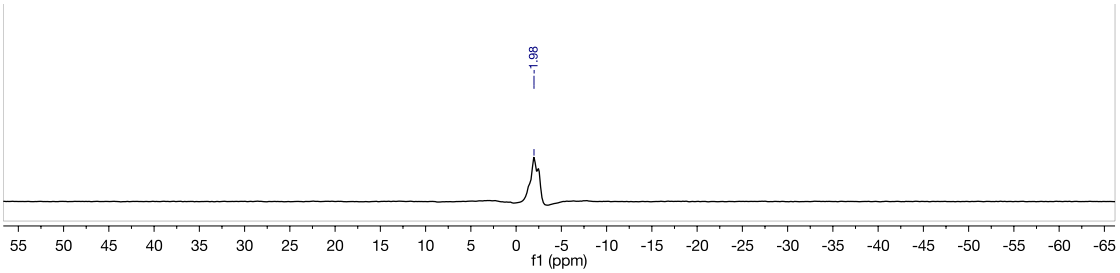
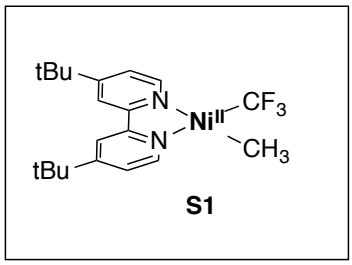
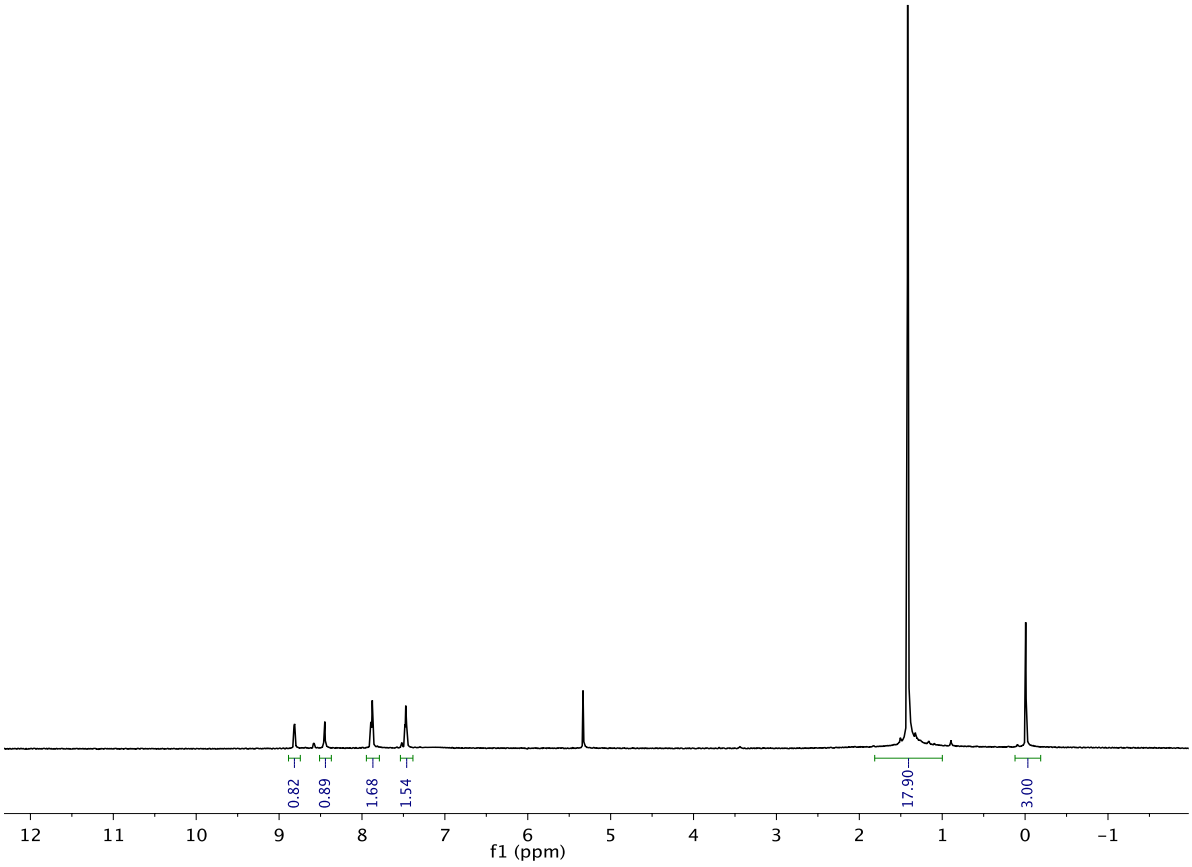


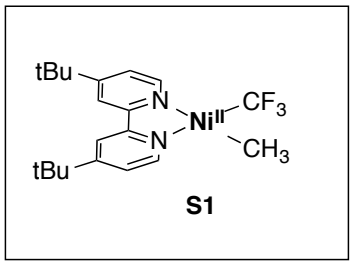
^{1}H NMR of S1 at 23 °C (CD_2Cl_2)



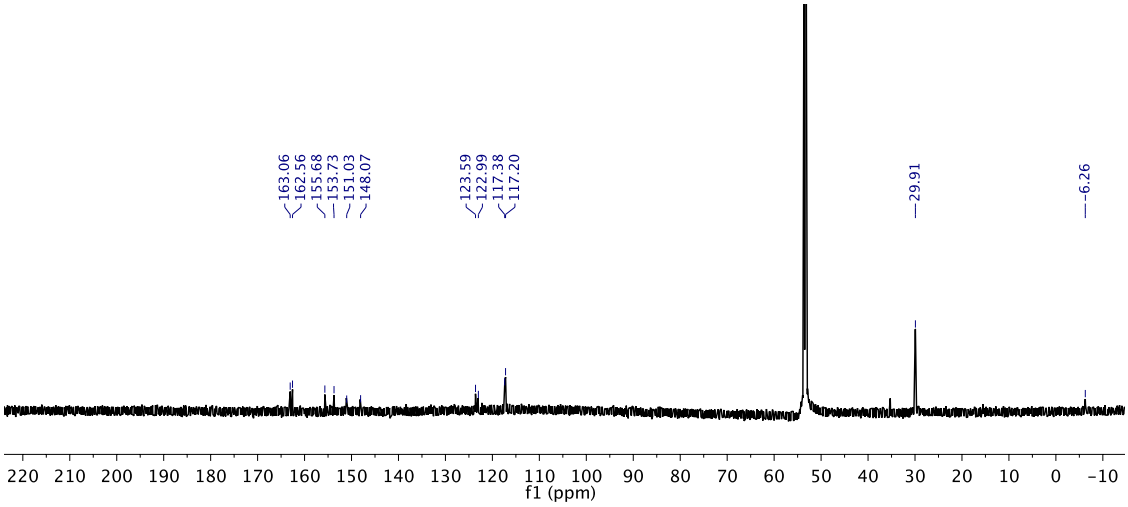
S1



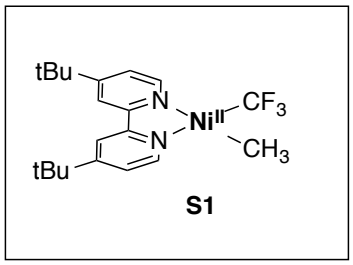
^{13}C NMR of S1 at 23 ºC (CD_2Cl_2)



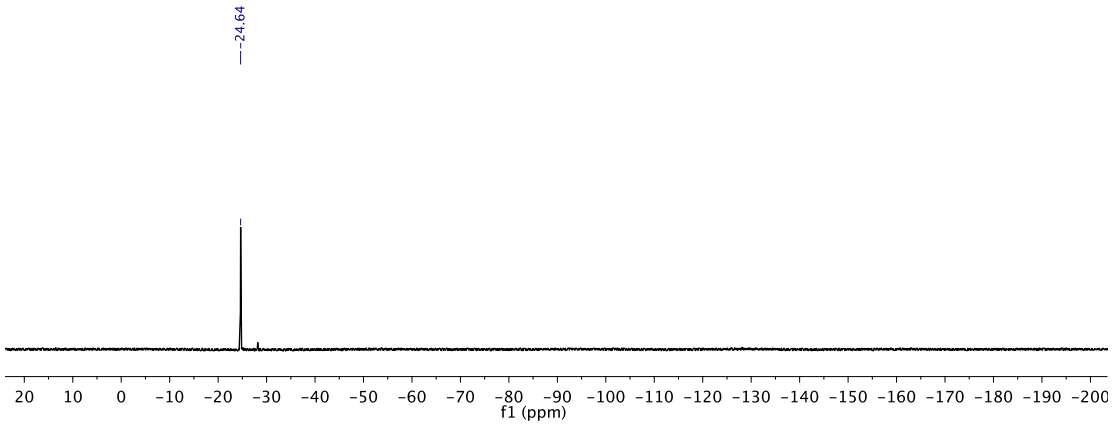
S1



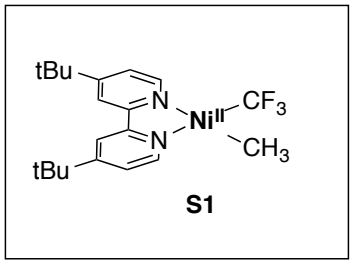
^{19}F NMR of S1 at 23 °C (CD_2Cl_2)



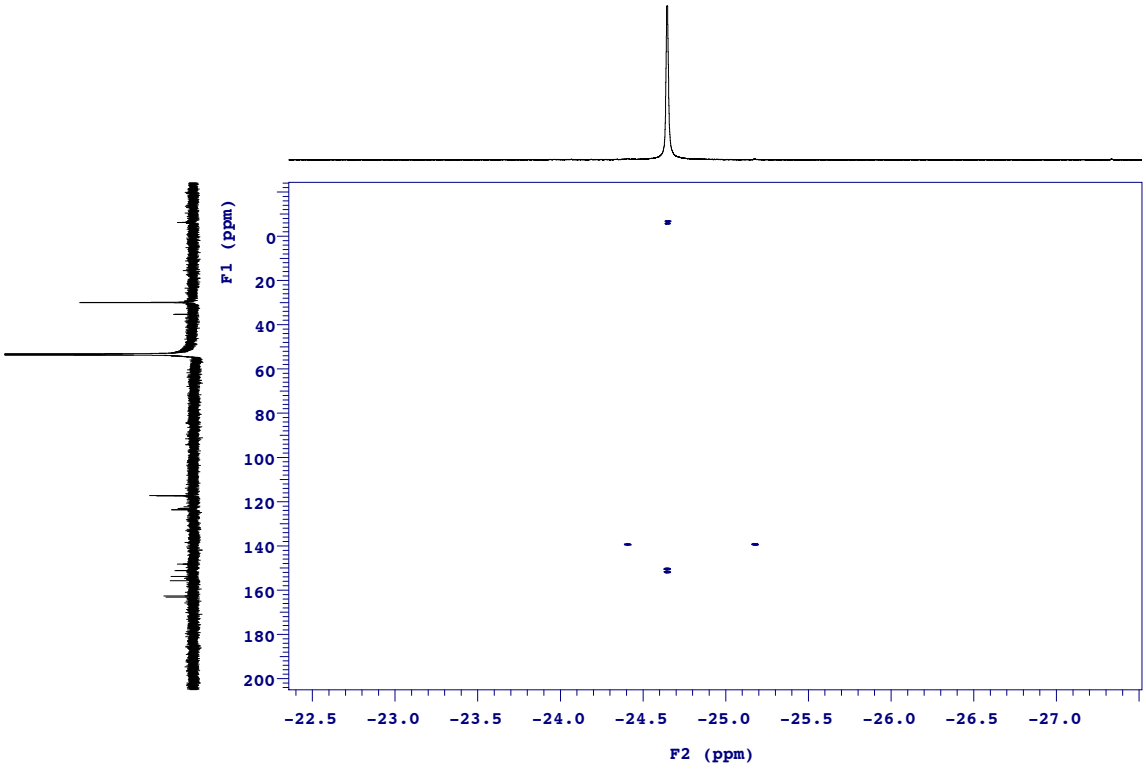
S1



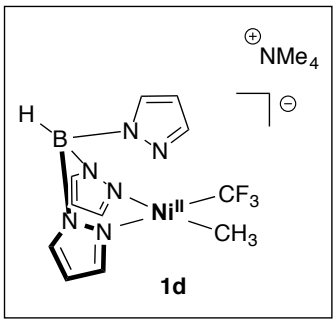
$^{13}C/^{19}F$ HMBC of S1 at 23 °C (CD_2Cl_2)



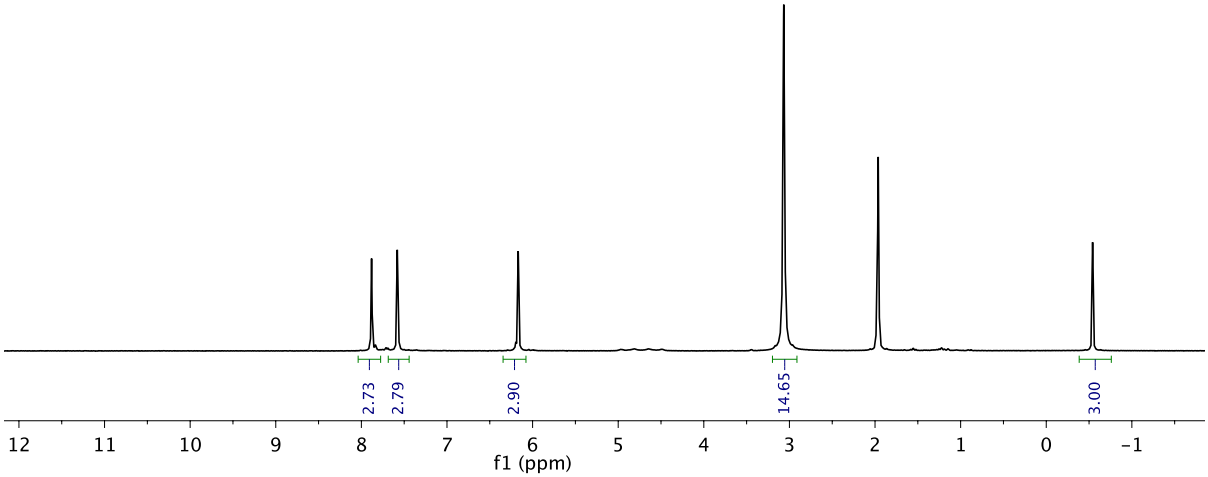
S1



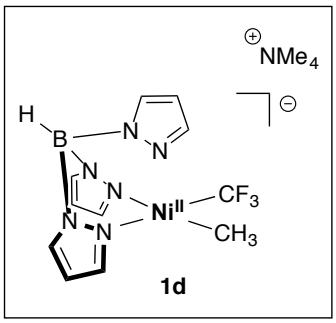
^{1}H NMR of 1d at 23 ºC (CD_3CN)



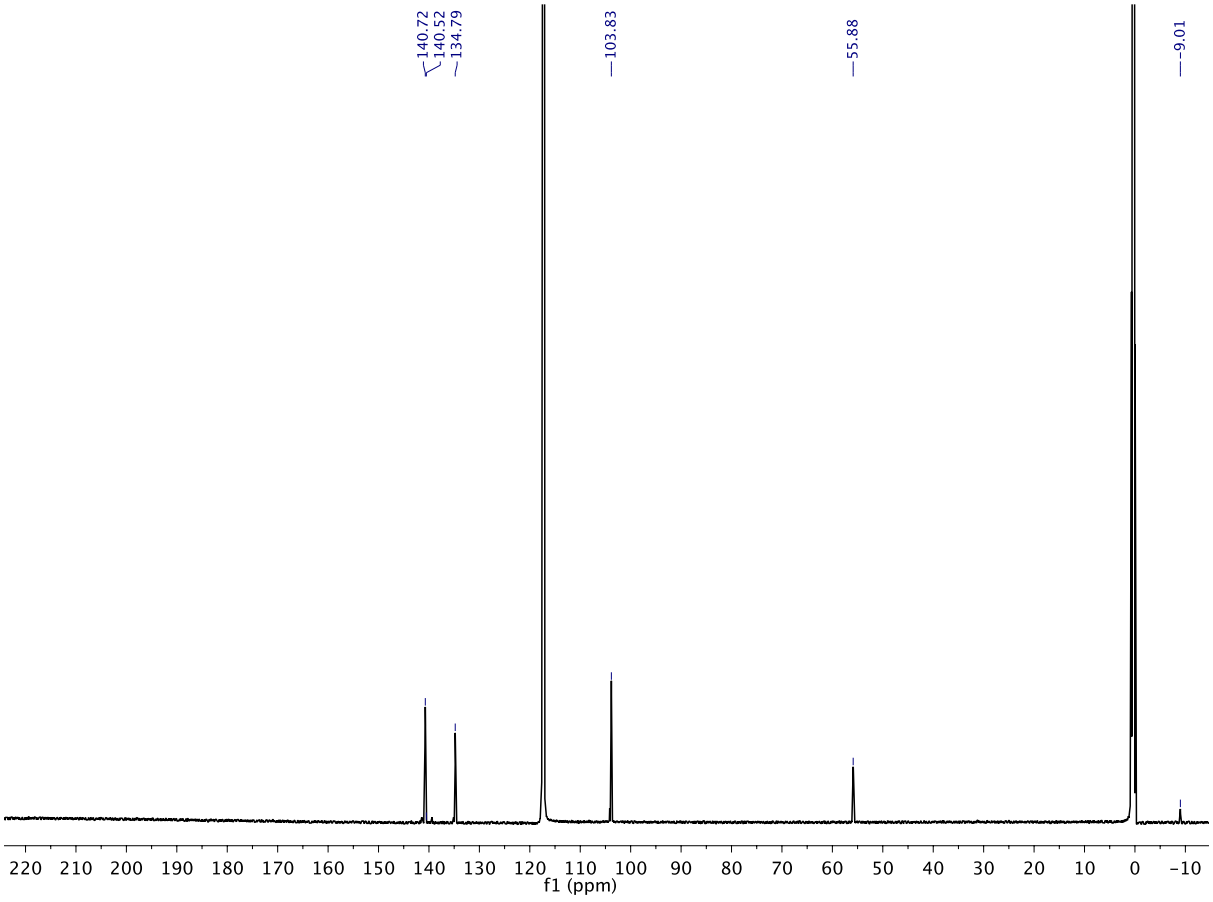
1d



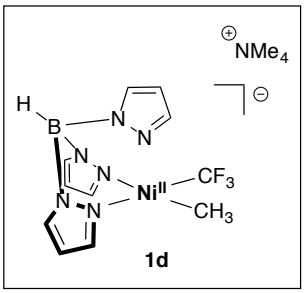
^{13}C NMR of 1d at 23 ºC (CD_3CN)



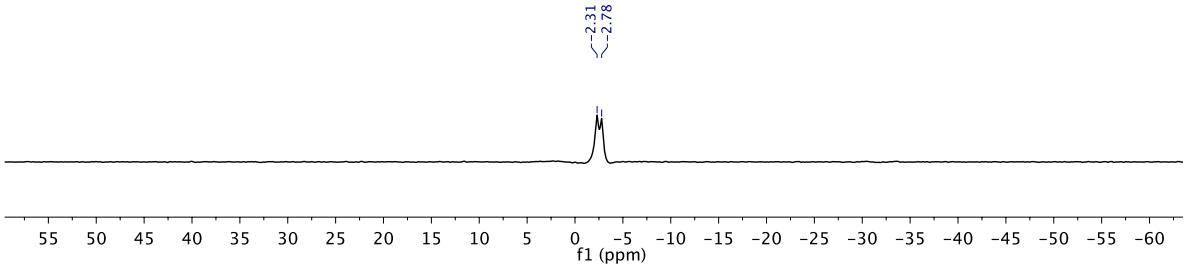
1d



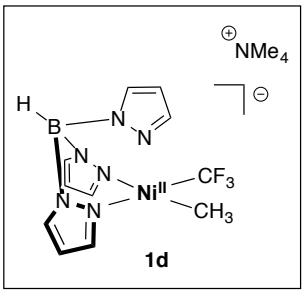
^{11}B NMR of 1d at 23 ºC (CD_3CN)



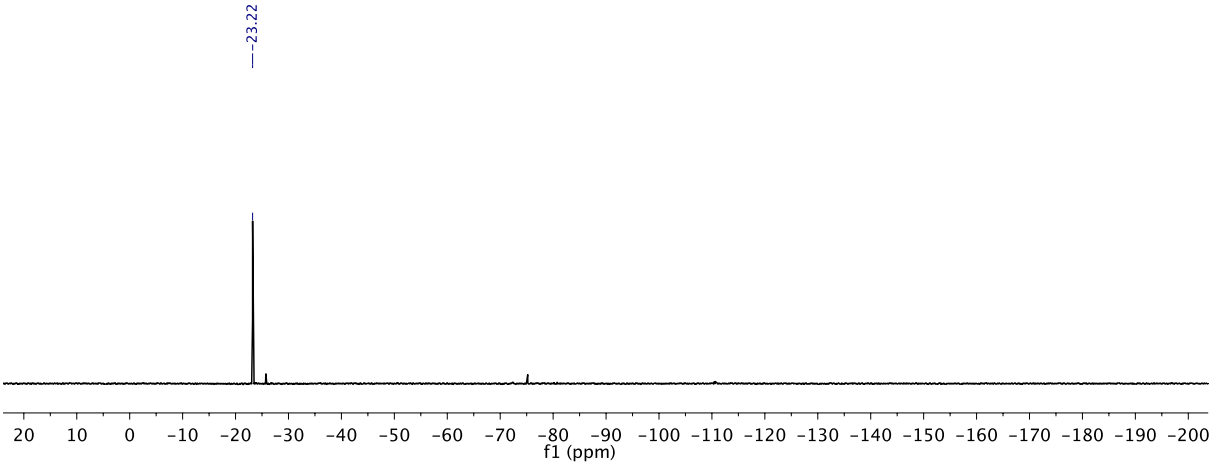
1d



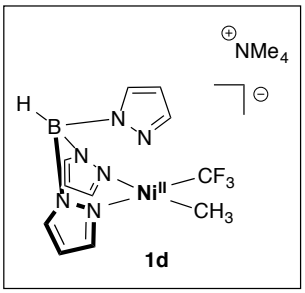
^{19}F NMR of 1d at 23 °C (CD_3CN)



1d



$^{13}C/^{19}F$ HMBC at 23 ºC (CD_3CN)



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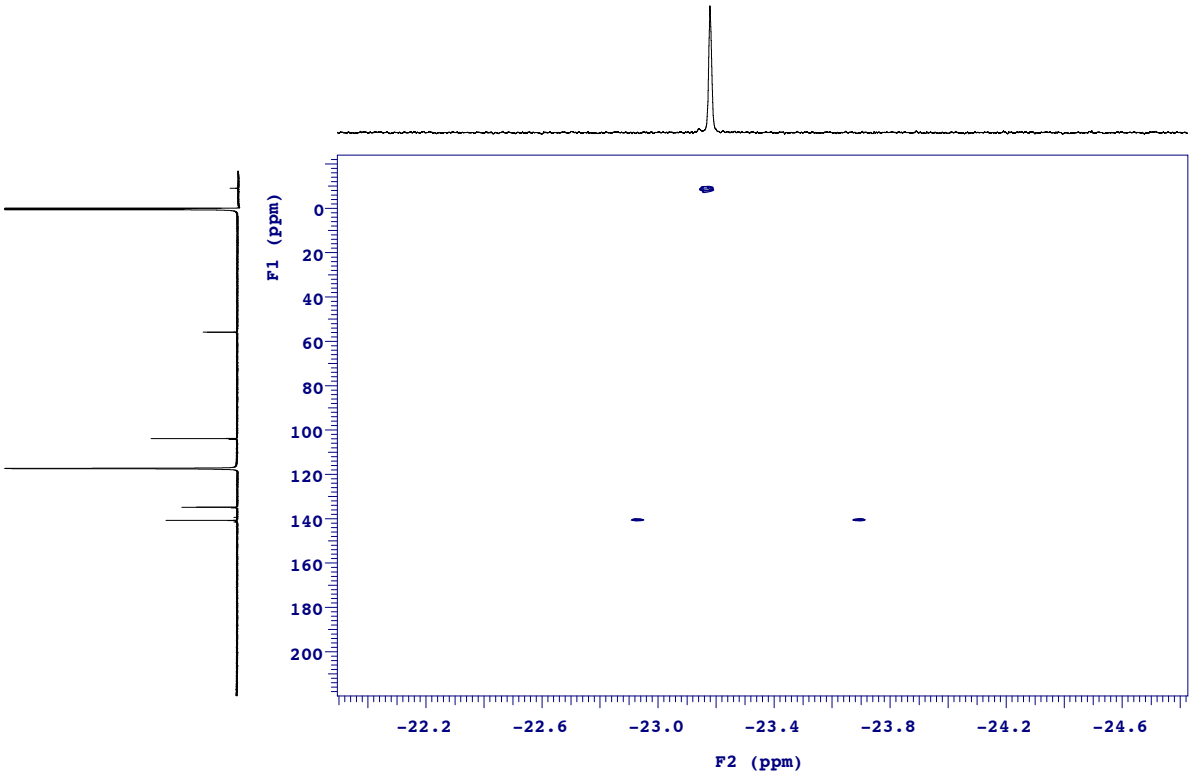
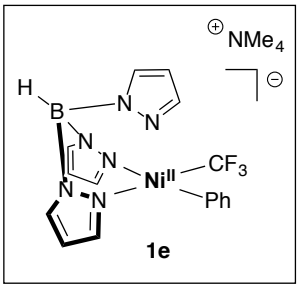
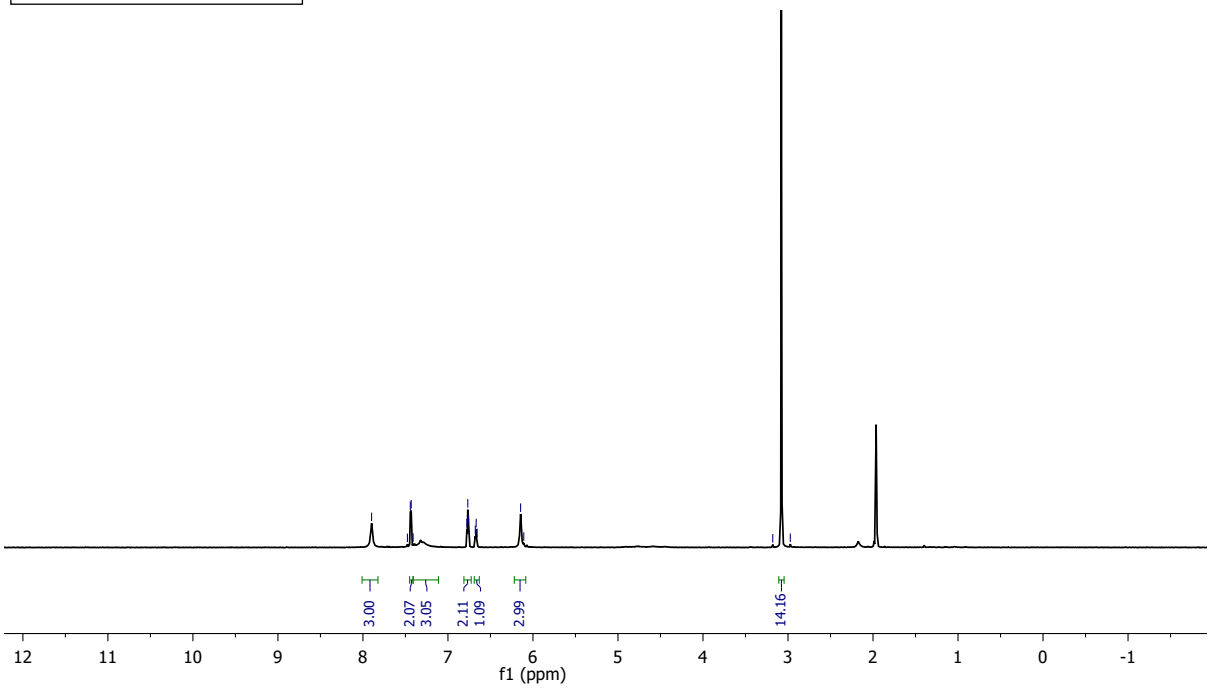
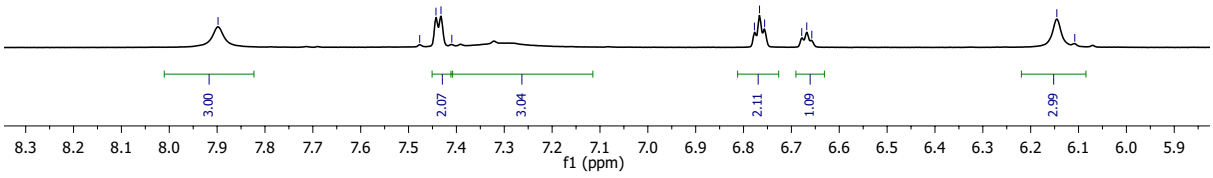


^{1}H NMR of 1e at 23 ºC (CD_3CN)

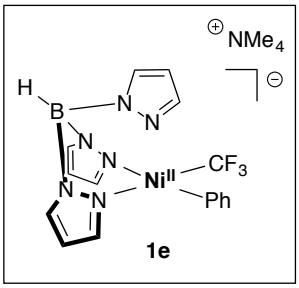


1e

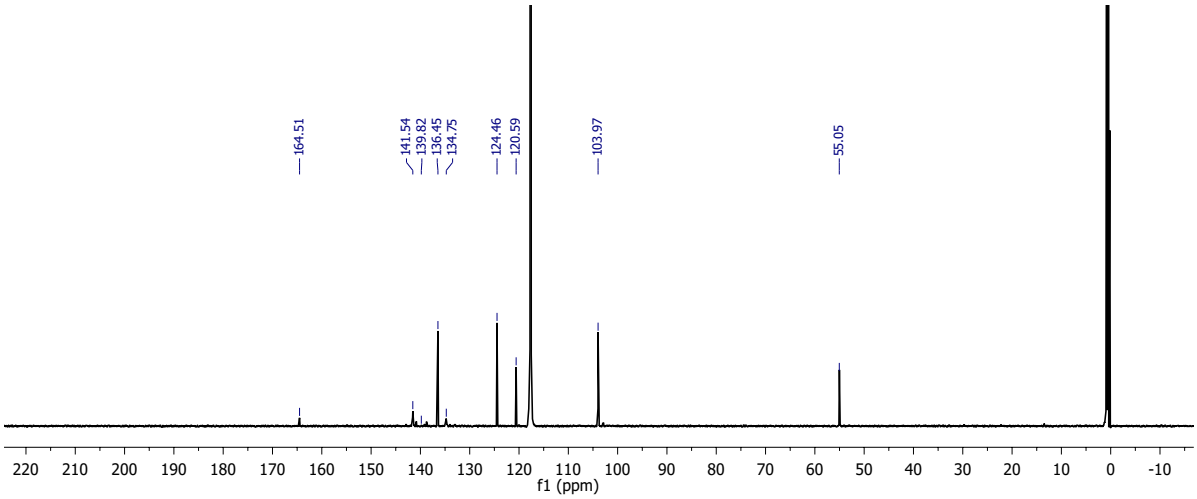




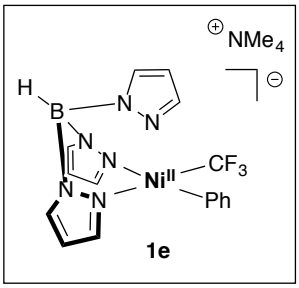
^{13}C NMR of 1e at 23 °C (CD_3CN)



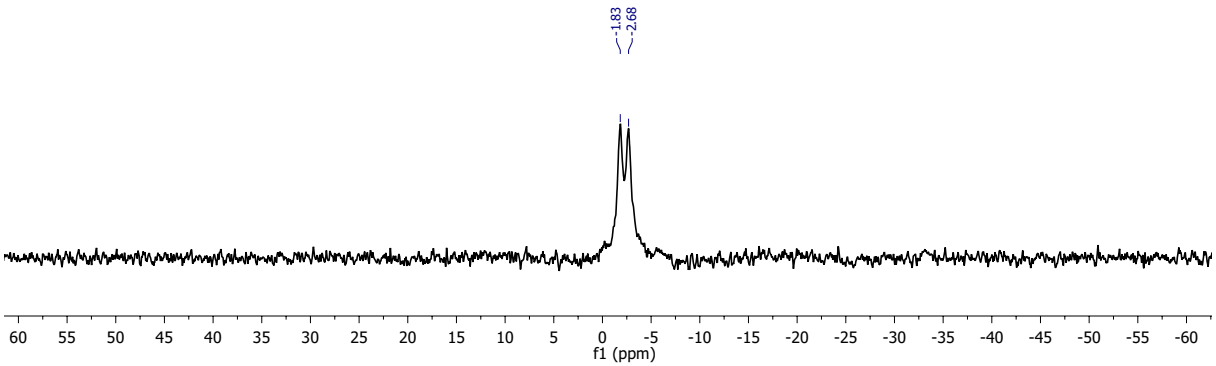
1e



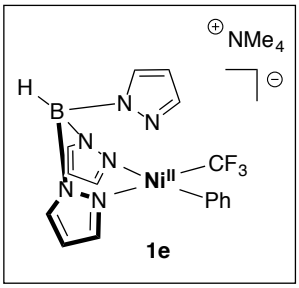
^{11}B NMR of 1e at 23 °C (CD_3CN)



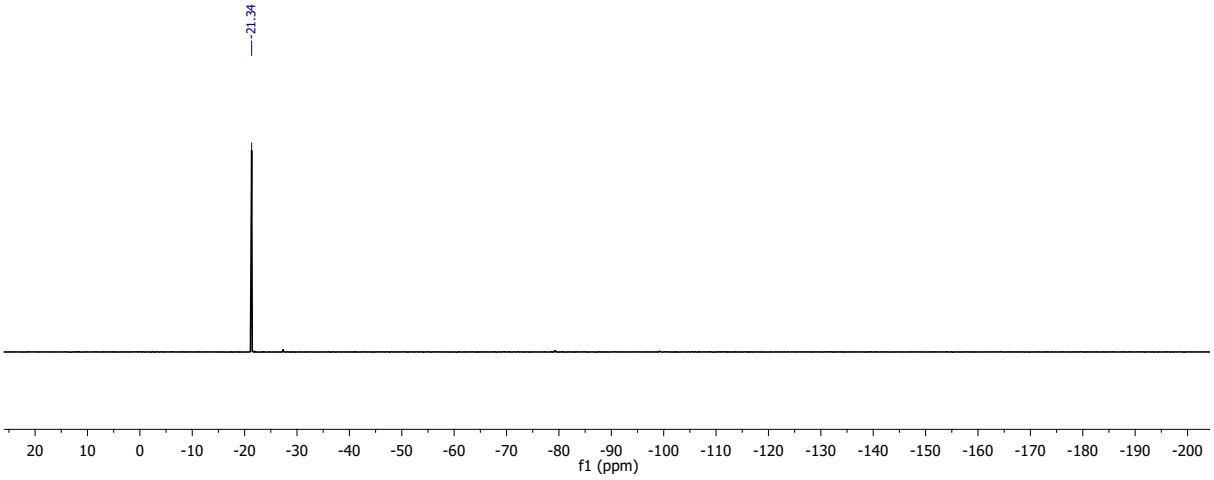
1e



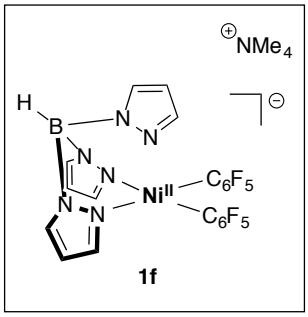
^{19}F NMR of 1e at 23 °C (CD_3CN)



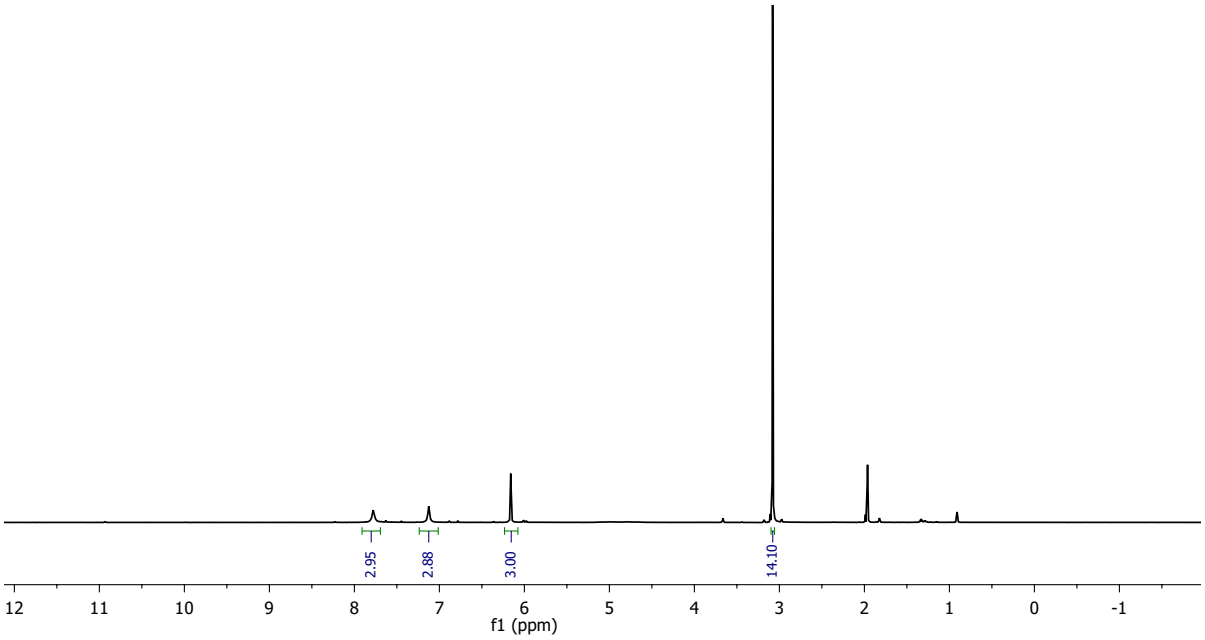
1e



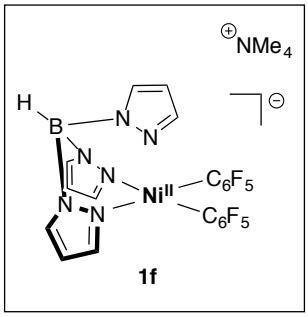
^{1}H NMR of 1f at 23 °C (CD_3CN)



1f



^{13}C NMR of 1f at 23 ºC (CD_3CN)



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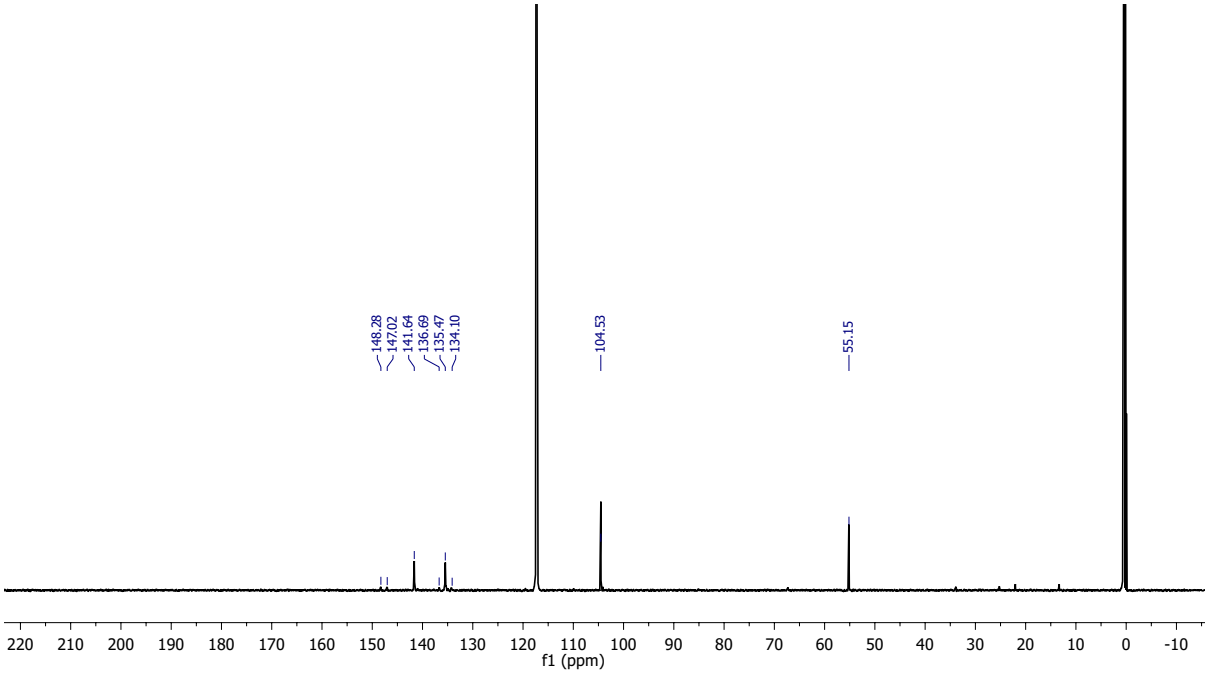
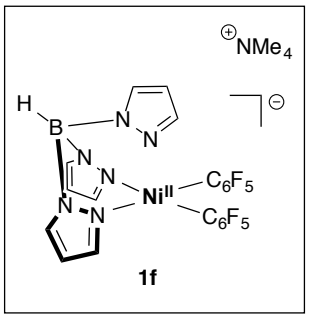


^{11}B NMR of 1f at 23 ºC (CD_3CN)



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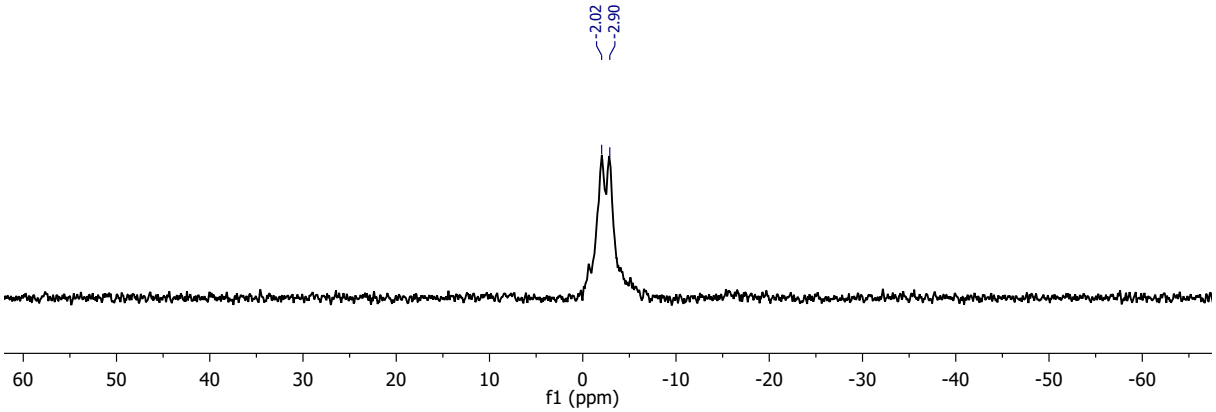
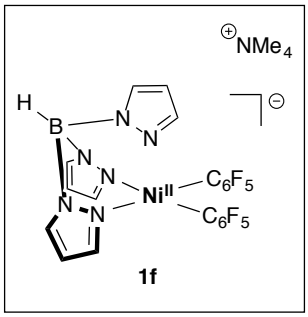


^{19}F NMR of 1f at 23 ºC (CD_3CN)



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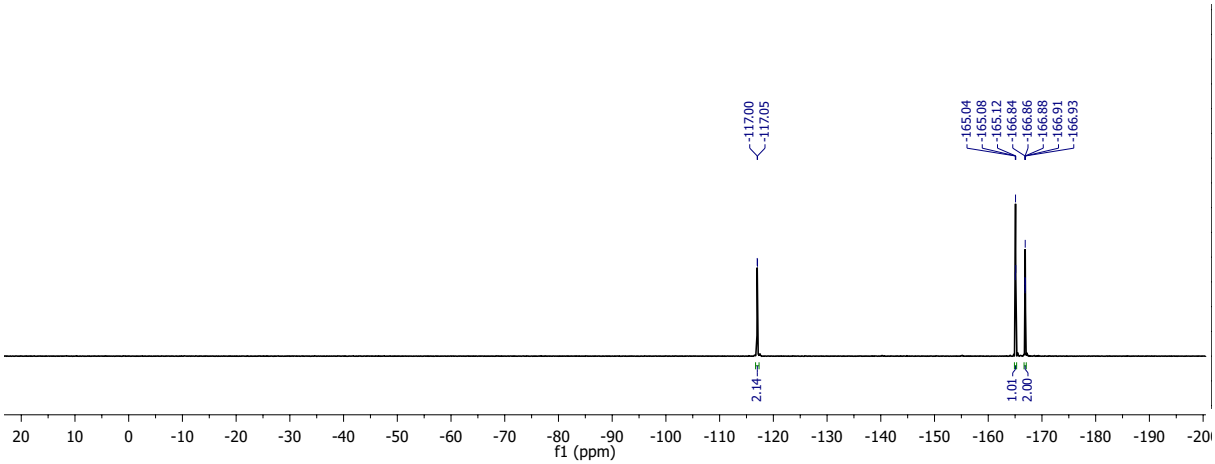
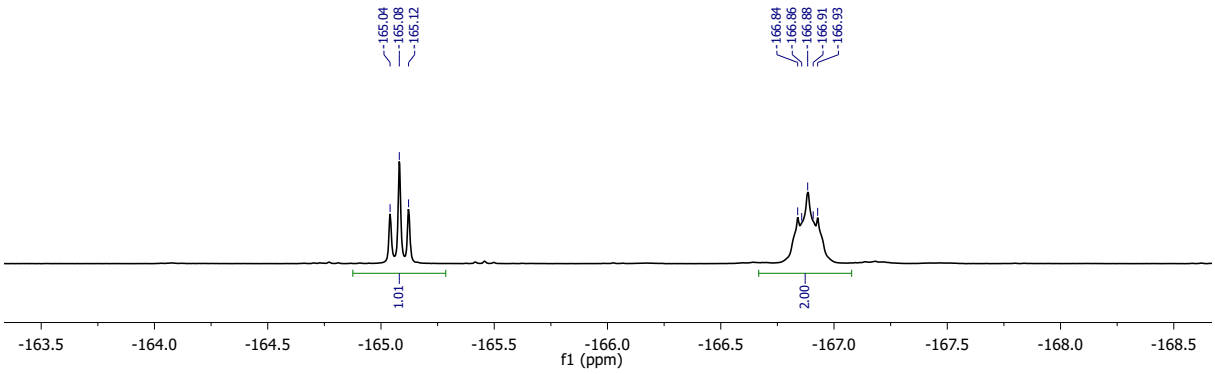
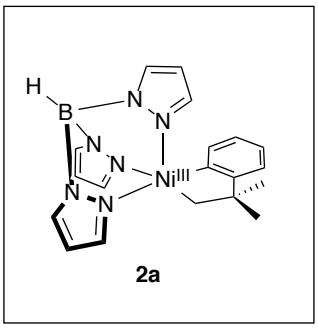
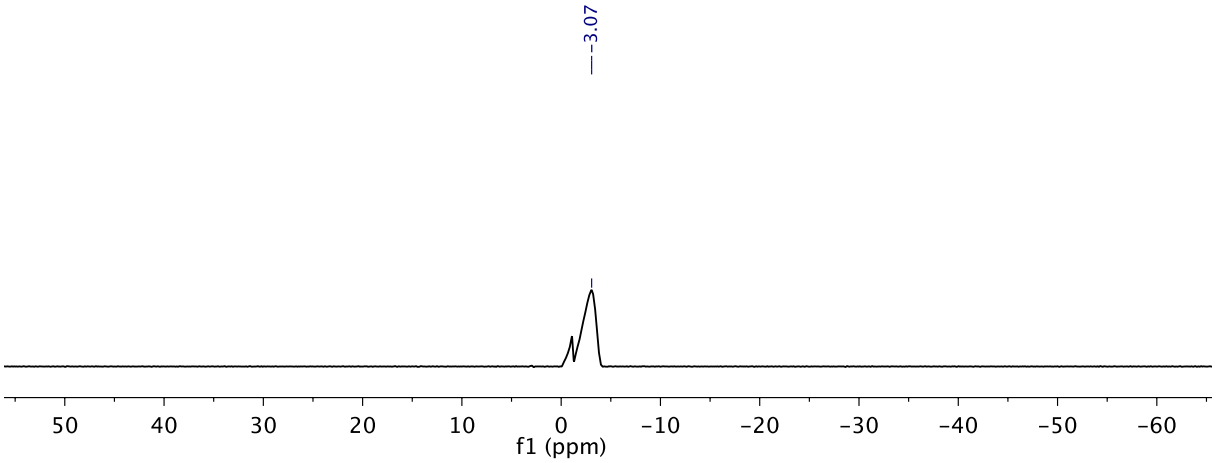




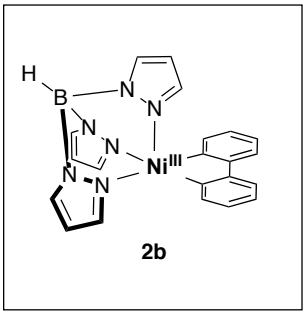
^{11}B NMR of 2a at 23 °C (CD_3CN)



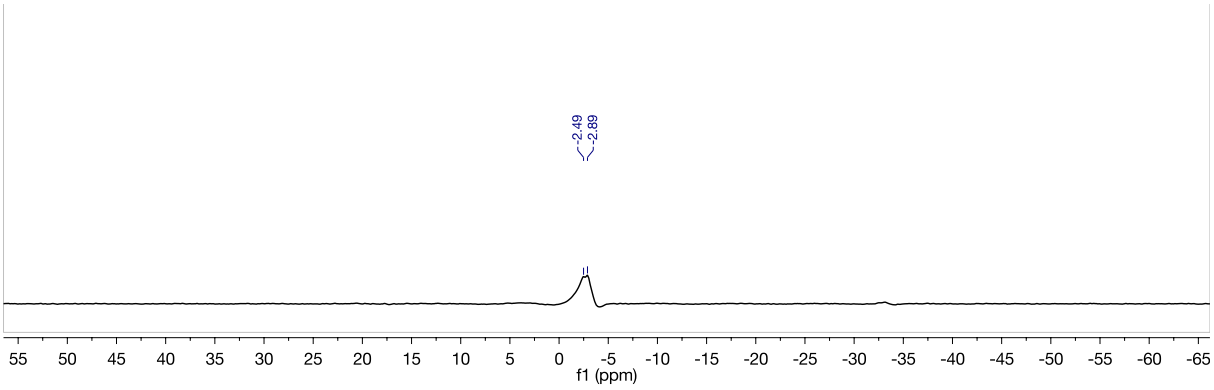
2a



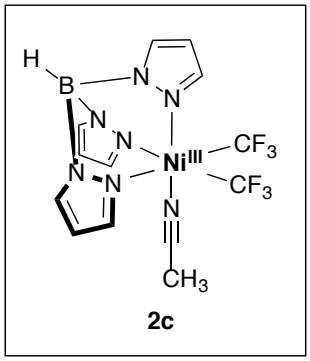
^{11}B NMR of 2b at 23 ºC (CD_3CN)



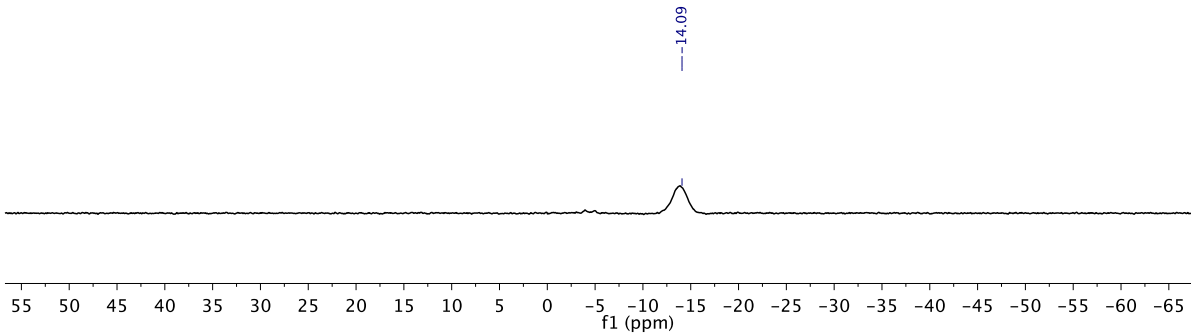
2b



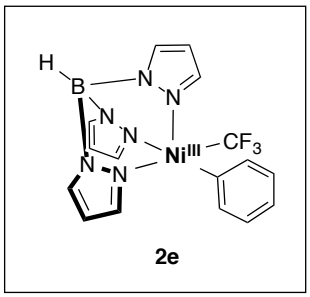
^{11}B NMR of 2c at 23 °C (CD_3CN)



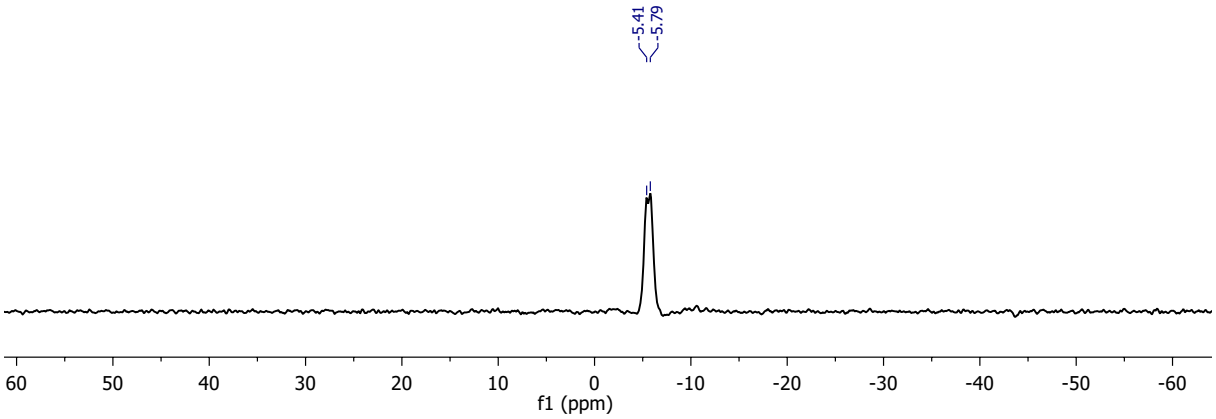
2c



^{11}B NMR of 2e at 23 °C (CD_3CN)



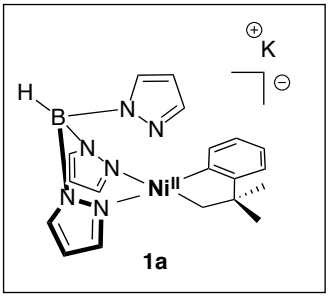
2e



XIII. Cyclic Voltammetry Experimental Data

For experimental procedures please refer to p. S13

Full CV Studies of Complex 1a



1a

Scan Rate = 50 mV/s
[$Ni^{II/III}$] (Ipc.Ipa)= 379 mV, (Ipc/Ipa)= 1.0
[$Ni^{III/IV}$] (Ipc.Ipa)= 501 mV

The peak separation of the internal standard couple [$Fe^{II/III}$] was found to be 76 mV, suggesting that the broad peak separation observed for the nickel couples is inherent to the complexes.

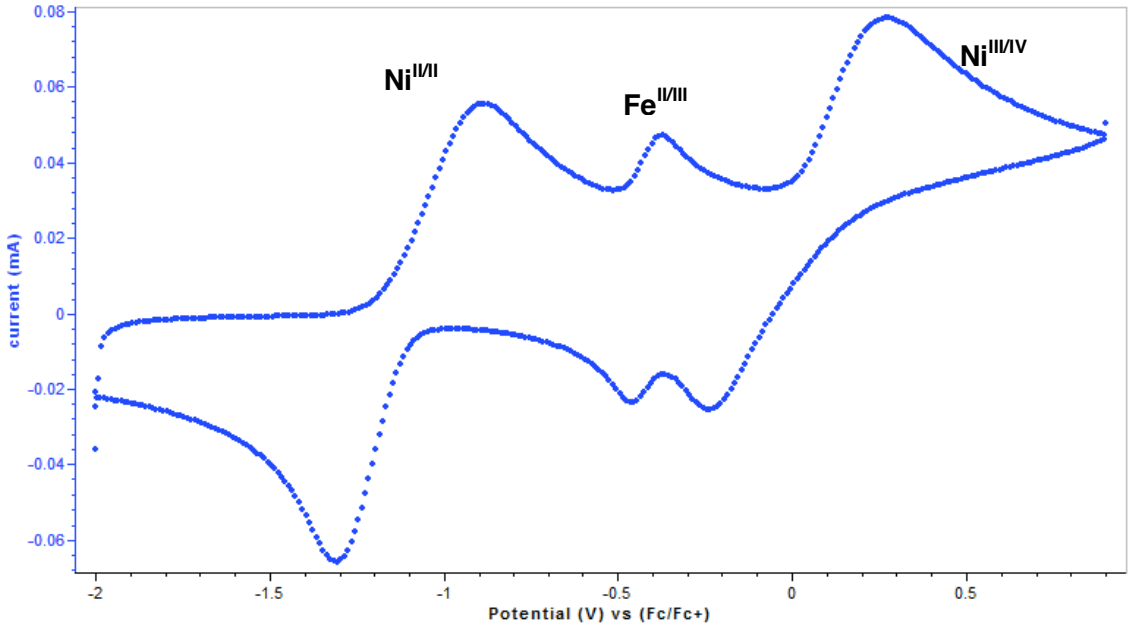


Figure S22. Cyclic voltammogram of **1a** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 50 mV/s with $(C_5Me_5)_2Fe$ added as the internal standard.

Scan Rate = **50 mV/s**
[$Ni^{II/III}$] (Ipc.Ipa)= 394 mV, (Ipc/Ipa)= 0.97
[$Ni^{III/IV}$] (Ipc.Ipa)= 520 mV

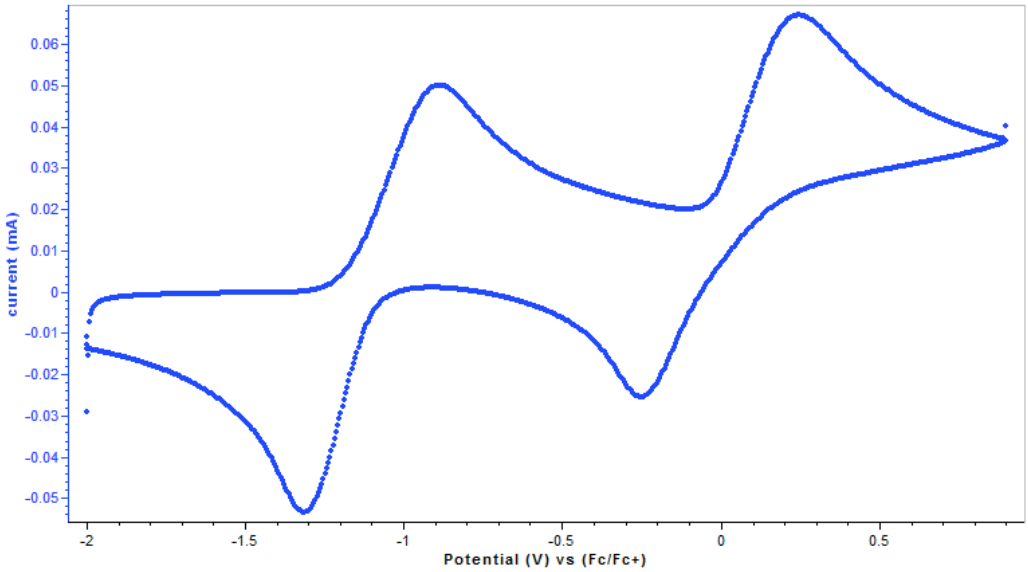


Figure S23. Cyclic voltammogram of **1a** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 50 mV/s

Scan Rate = **100 mV/s**
[$Ni^{II/III}$] (Ipc.Ipa)= 502 mV, (Ipc/Ipa)= 0.9
[$Ni^{III/IV}$] (Ipc.Ipa)= 543 mV

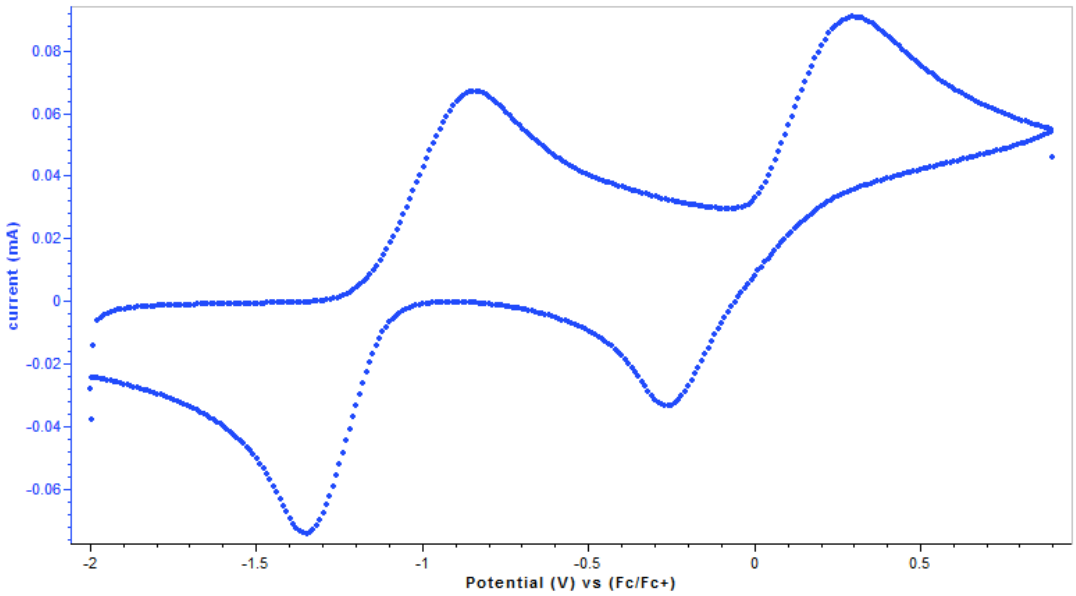


Figure S24. Cyclic voltammogram of **1a** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 100 mV/s.

Scan Rate = **250 mV/s**
[$Ni^{II/III}$] (Ipc.Ipa)= 655 mV, (Ipc/Ipa)= 0.91
[$Ni^{III/IV}$] (Ipc.Ipa)= 695 mV

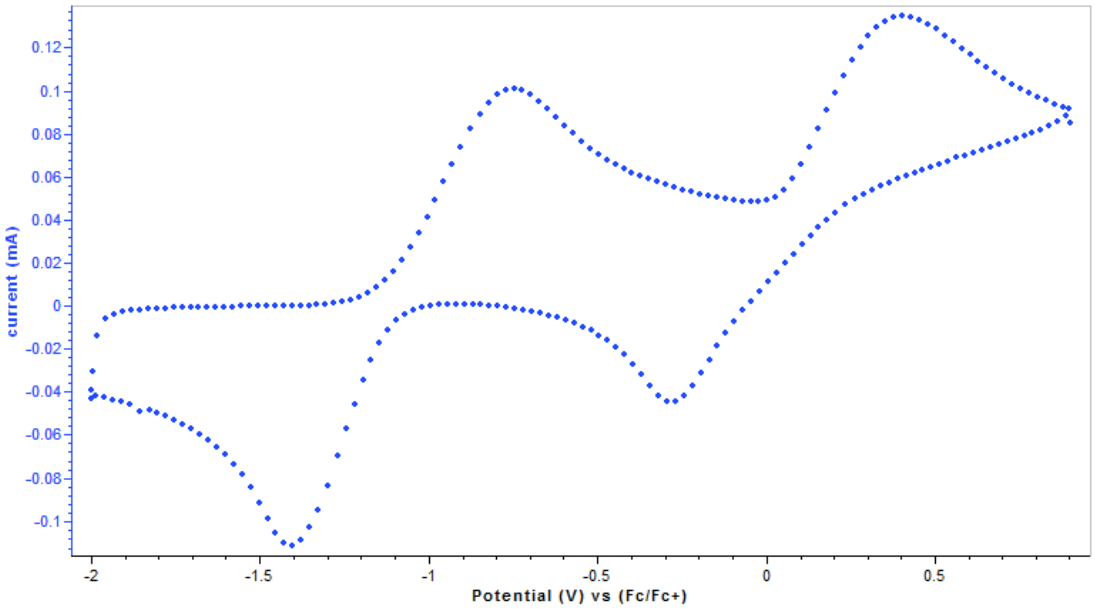
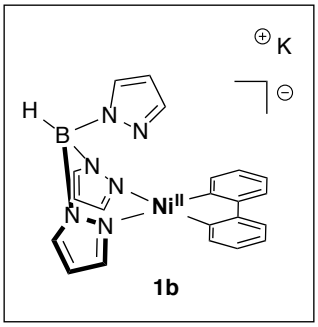


Figure S25. Cyclic voltammogram of **1a** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 250 mV/s.

Full CV Studies of Complex 1b



Scan Rate = **50 mV/s**
[$Ni^{II/III}$] (Ipc-Ipa)= 190 mV, (Ipc/Ipa)= 0.98

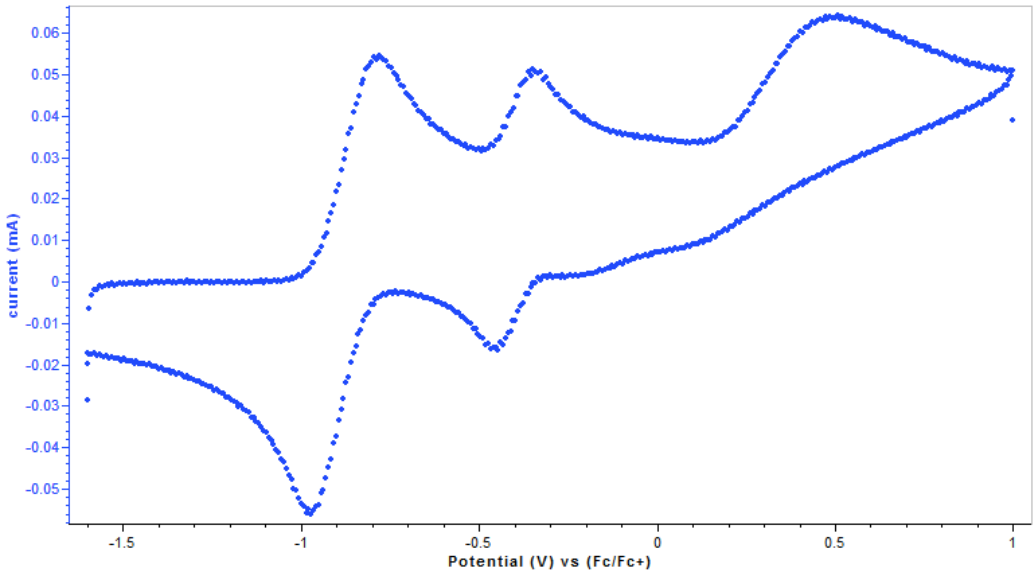


Figure S26. Cyclic voltammogram of **1b** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 50 mV/s with $(C_5Me_5)_2Fe$ added as internal standard.

Scan Rate = **100 mV/s**
[$Ni^{II/III}$] (Ipc-Ipa)= 240 mV, (Ipc/Ipa)= 0.90

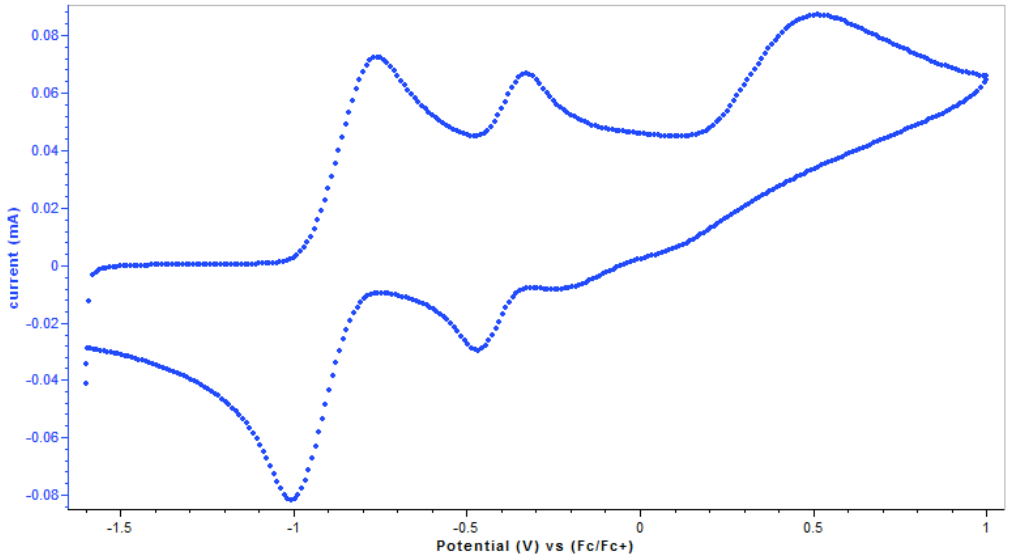


Figure S27. Cyclic voltammogram of **1b** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 100 mV/s with $(C_5Me_5)_2Fe$ added as internal standard.

Scan Rate = **250 mV/s**
[$Ni^{II/III}$] (Ipc-Ipa)= 308 mV, (Ipc/Ipa)= 0.91

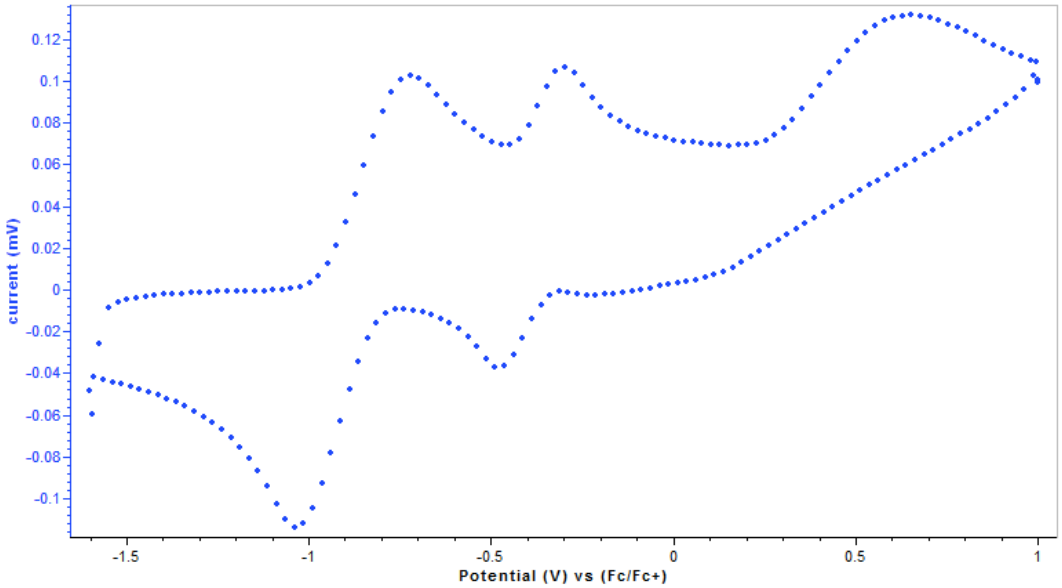
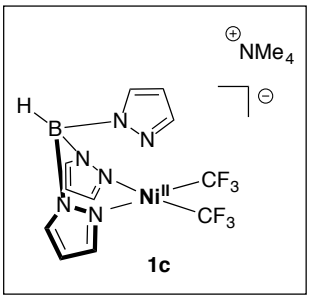


Figure S28. Cyclic voltammogram of **1b** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 250 mV/s with $(C_5Me_5)_2Fe$ added as internal standard.

Full CV Studies of Complex 1c



Scan Rate = **50 mV/s**
[$Ni^{II/III}$] (Ipc-Ipa)= 675 mV, (Ipc/Ipa)= 0.58
[$Ni^{III/IV}$] (Ipc-Ipa)= 300 mV

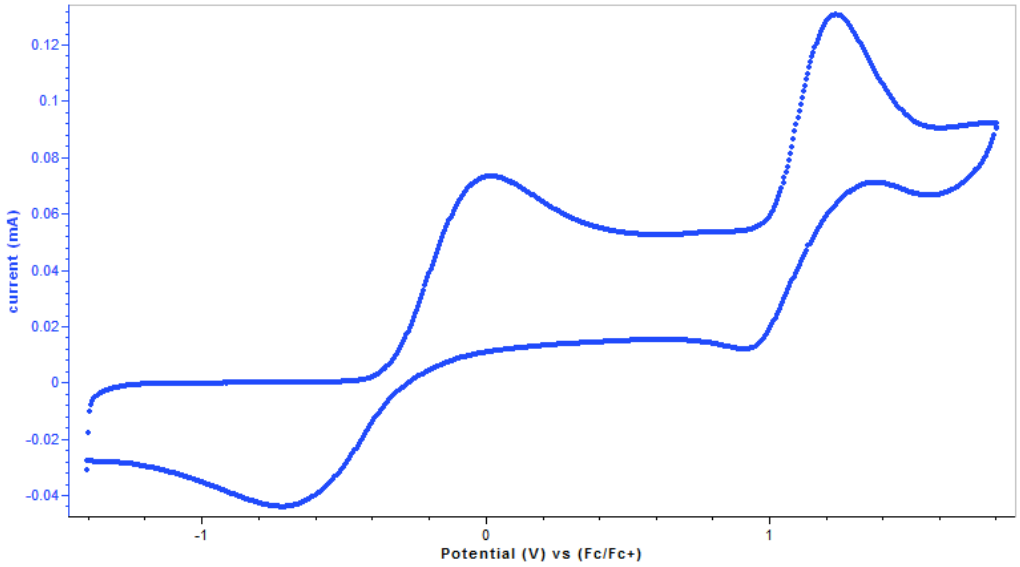


Figure S29. Cyclic voltammogram of **1c** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 50 mV/s .

Scan Rate = **100 mV/s**
[$Ni^{II/III}$] (Ipc-Ipa)= 830 mV, (Ipc/Ipa)= 0.66
[$Ni^{III/IV}$] (Ipc-Ipa)= 480 mV

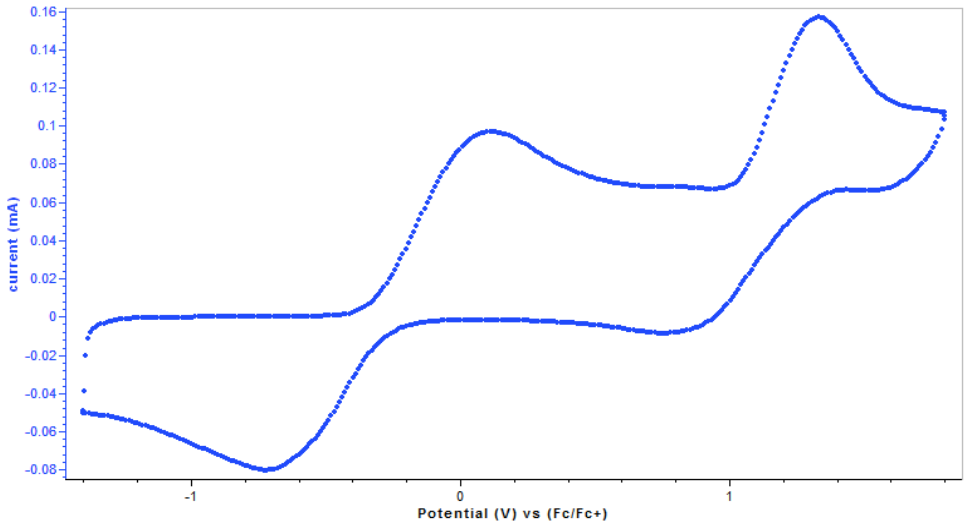


Figure S30. Cyclic voltammogram of **1c** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 100 mV/s with $(C_5Me_5)_2Fe$ added as internal standard..

Scan Rate = 250 mV/s
[$Ni^{II/III}$] (Ipc-Ipa)= 1120 mV, (Ipc/Ipa)= 0.85
[$Ni^{III/IV}$] (Ipc-Ipa)= 661 mV

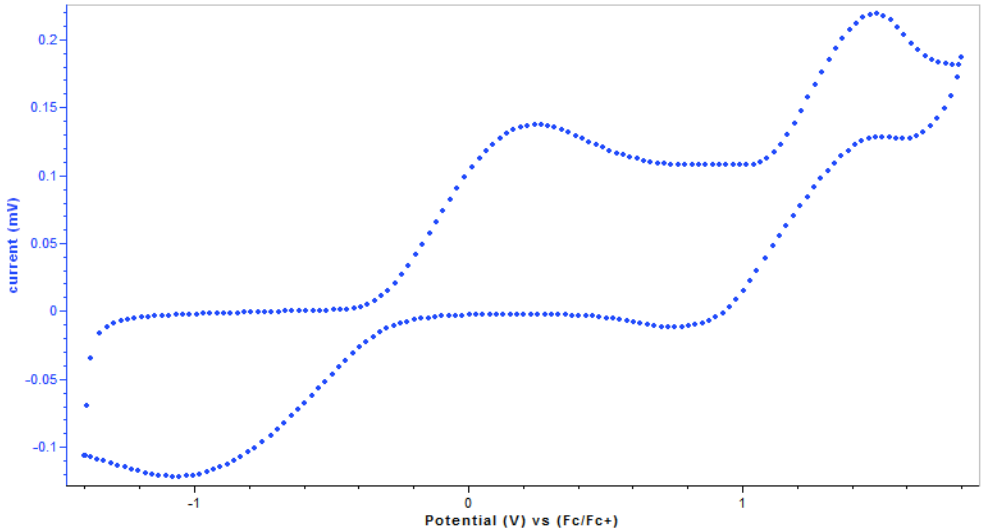
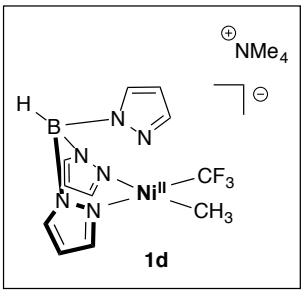


Figure S31. Cyclic voltammogram of **1c** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 250 mV/s.

Full CV Studies of Complex 1d



Scan Rate = **50 mV/s**

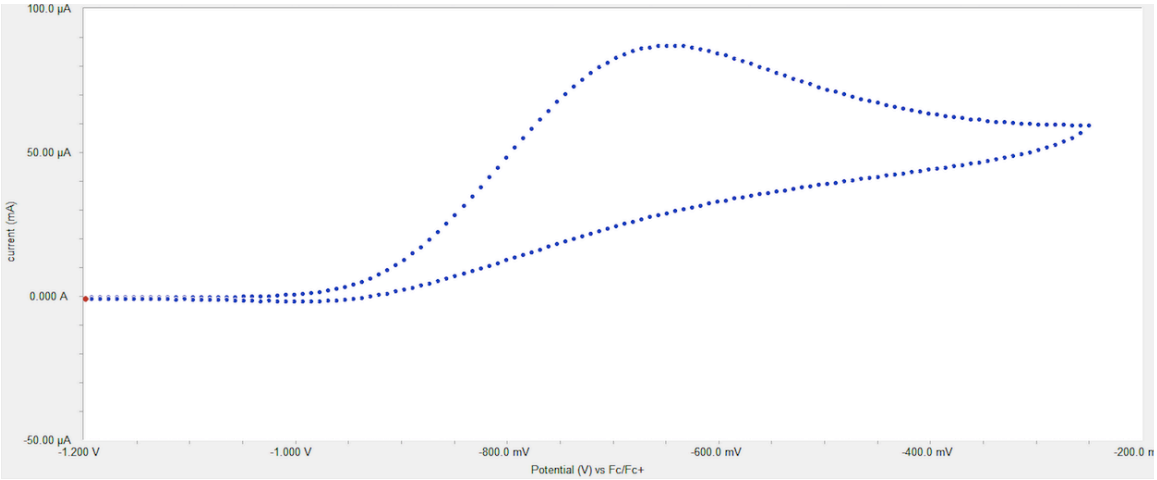


Figure S32. Cyclic voltammogram of **1d** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 50 mV/s.

Scan Rate = **100 mV/s**

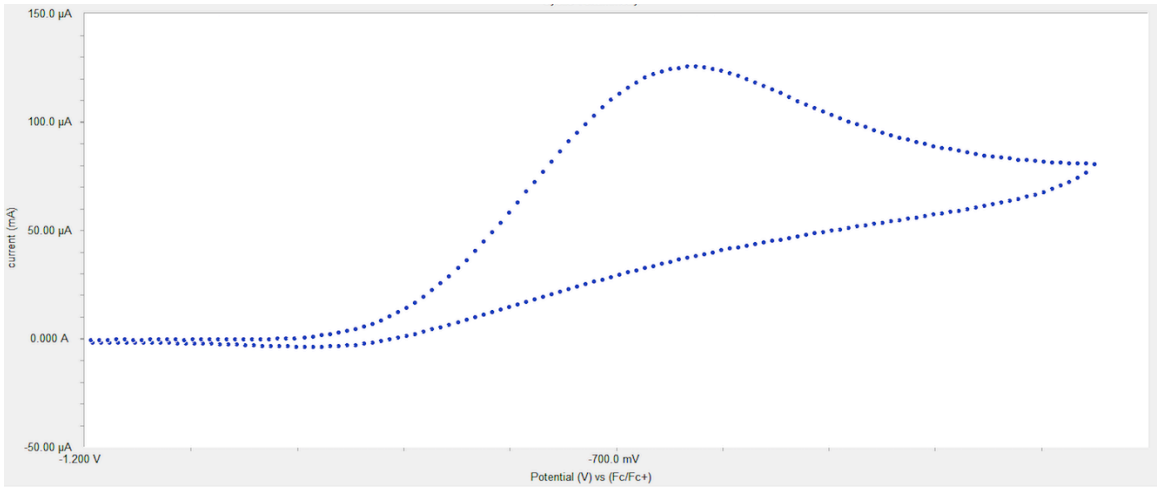


Figure S33. Cyclic voltammogram of **1d** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 100 mV/s.

Scan Rate = **500 mV/s**

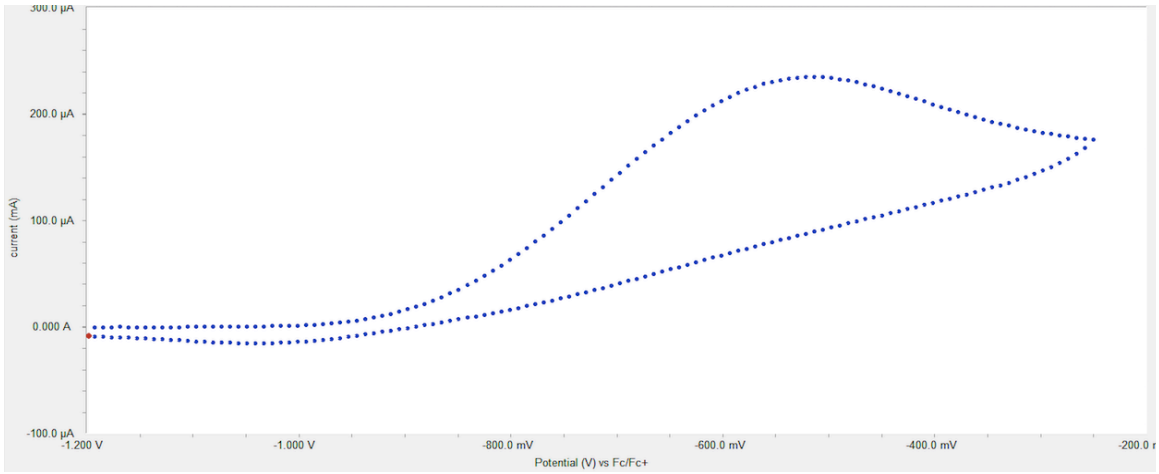
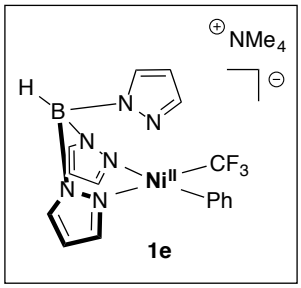


Figure S34. Cyclic voltammogram of **1d** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 500 mV/s.

Full CV Studies of Complex 1e



Scan Rate = **50 mV/s**
[$Ni^{II/III}$] (Ipc.Ipa)= 417 mV, (Ipc/Ipa)= 0.99
[$Ni^{III/IV}$] (Ipc-Ipa)= 642 mV

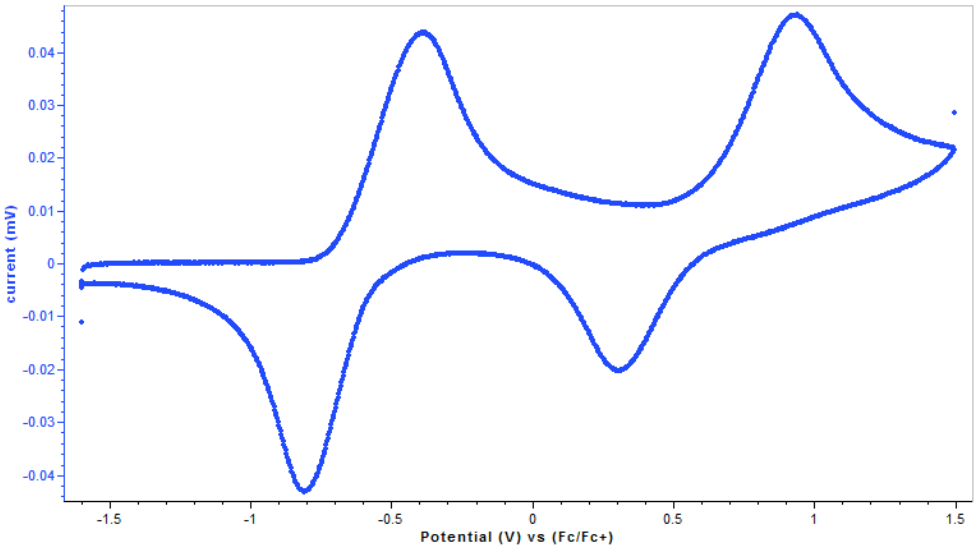


Figure S35. Cyclic voltammogram of **1e** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 50 mV/s.

Scan Rate = **100 mV/s**
[$Ni^{II/III}$] (Ipc-Ipa)= 504 mV, (Ipc/Ipa)= 1.01
[$Ni^{III/IV}$] (Ipc-Ipa)= 856 mV

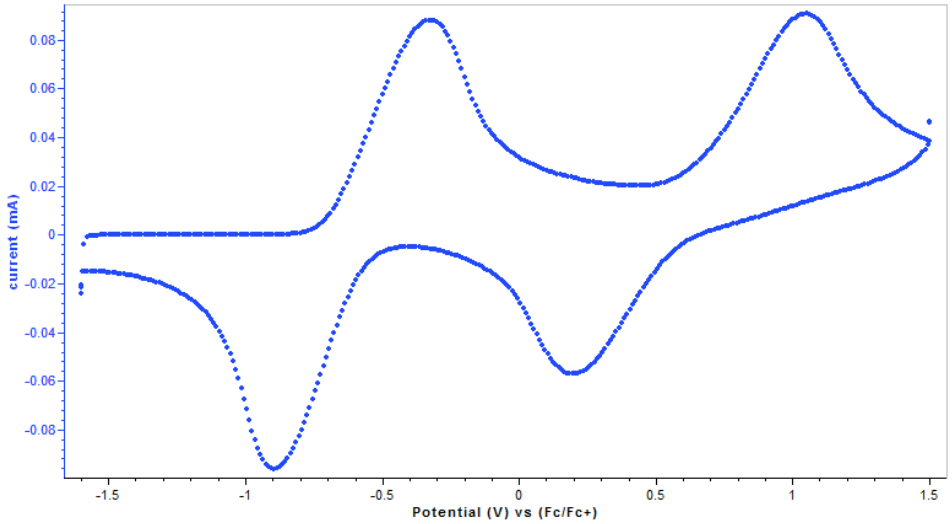


Figure S36. Cyclic voltammogram of **1e** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 100 mV/s.

Scan Rate = **250 mV/s**
[$Ni^{II/III}$] (Ipc-Ipa)= 1069 mV, (Ipc/Ipa)= 0.98
[$Ni^{III/IV}$] (Ipc-Ipa)= 977mV

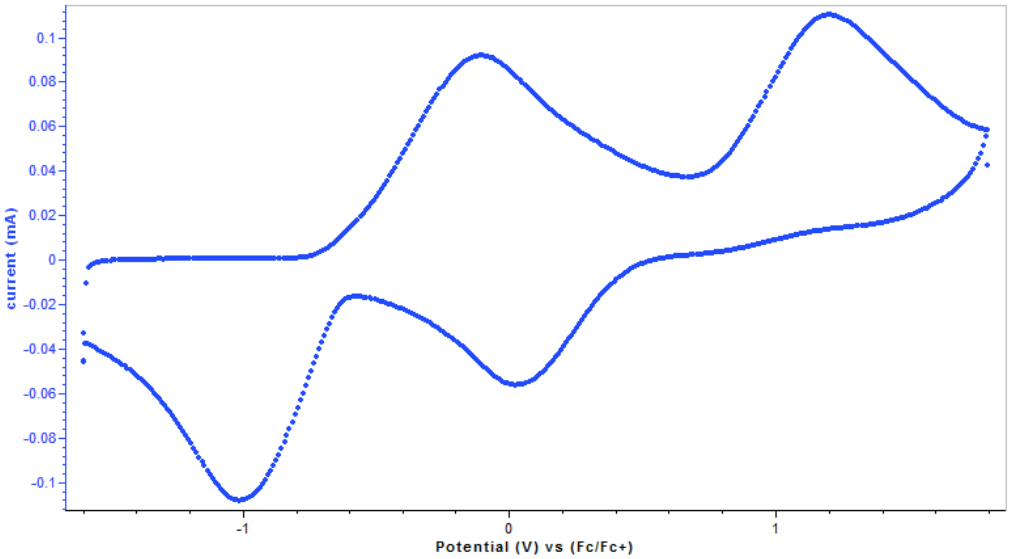
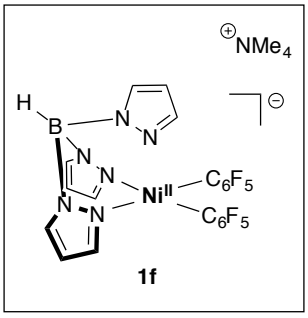


Figure S37. Cyclic voltammogram of **1e** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 250 mV/s.

Full CV Studies of Complex 1f



Scan Rate = **50 mV/s**

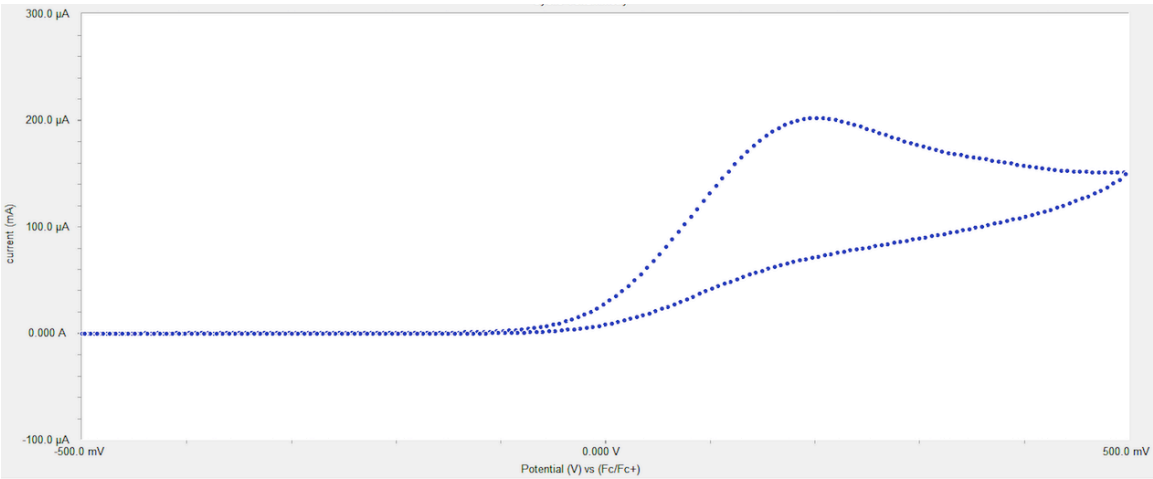


Figure S38. Cyclic voltammogram of **1f** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 50 mV/s.

Scan Rate = **100 mV/s**

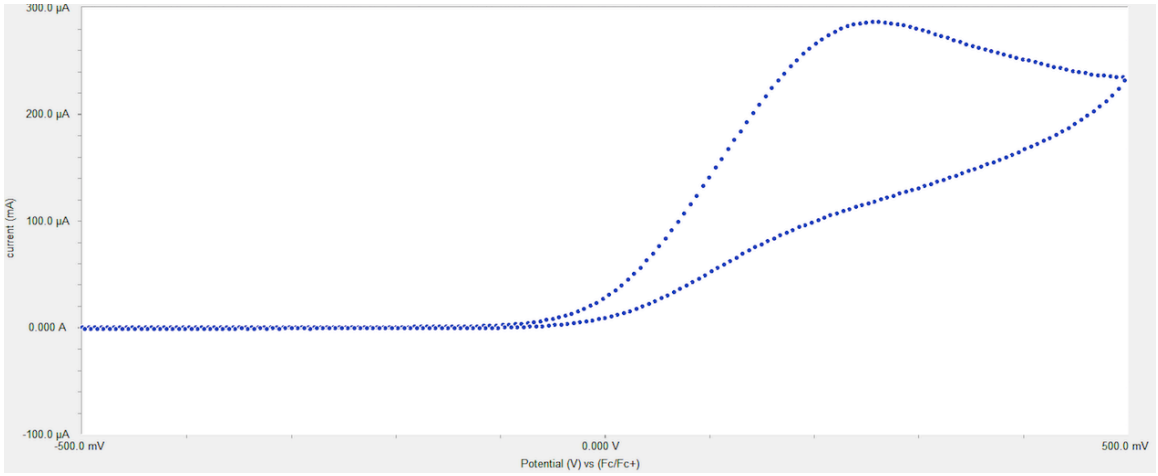


Figure S39. Cyclic voltammogram of **1f** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 100 mV/s.

Scan Rate = **500 mV/s**

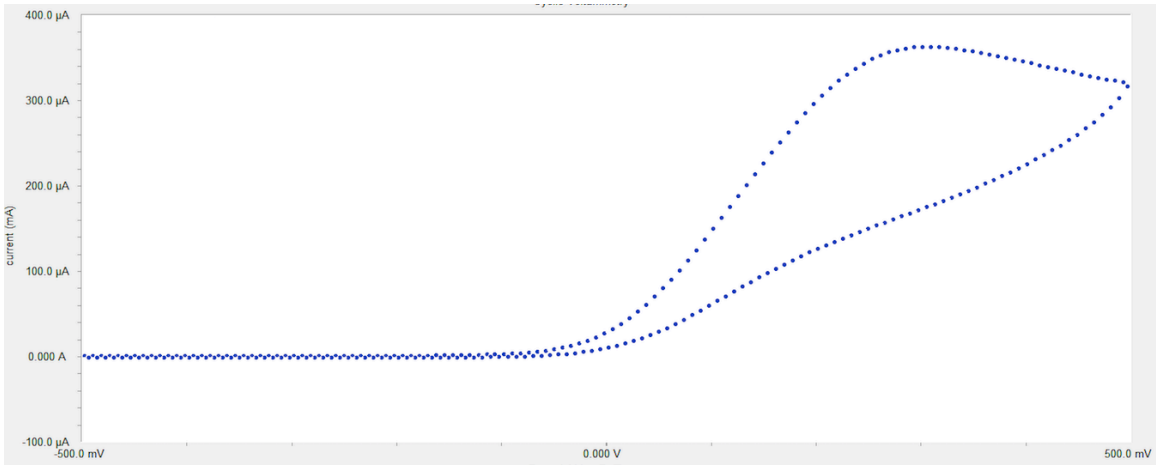
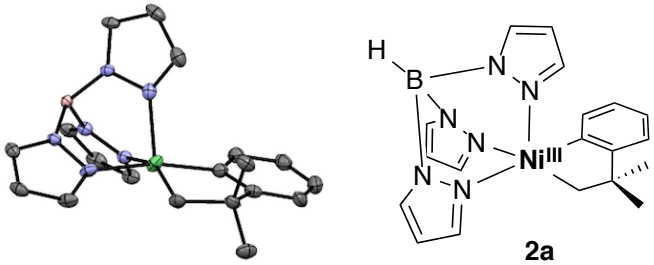


Figure S40. Cyclic voltammogram of **1f** [0.01 M] with 0.1 M NBu_4PF_6 in MeCN at a scan rate of 500 mV/s.

XIV. X-Ray Crystallography Experimental Data

Structure determination for 2a



2a

Orange plates of **2a** were grown by slow evaporation of an acetonitrile solution of the compound with a trace of added formamide at –35 ºC. A crystal of dimensions 0.24 x 0.19 x 0.02 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 (λ = 1.54187 A) 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 5 sec. for the low angle images, 30 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 32434 reflections to a maximum 2θ value of 139.12° of which 6827 were independent and 6785 were greater than 2σ(I). The final cell constants (Table S1) were based on the xyz centroids 32434 reflections above 10σ(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)/c with Z = 8 for the formula $C_{19}H_{22}BN_6Ni$. There are two crystallographically independent complexes in the asymmetric unit. The crystal was found to be a two-component pseudo-merohedral twin. The 2-methyl-2-phenylpropyl group bonded to Ni1 is partially disordered in two orientations. 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 = 0.0496 and wR2 = 0.1308 [based on I > 2sigma(I)], R1 = 0.0499 and wR2 = 0.1315 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 **2a**

Empirical Formula	$C_{19}H_{22}BN_6Ni$
Formula Weight	403.94
Temperature	85(2) K
Wavelength	1.54178 A
Crystal System	Monoclinic
Space Group	P2(1)/C
Unit Cell Dimensions	a = 7.73480(10) A alpha = 90 deg. b =20.0782(13) A beta = 90.094(2) deg c =23.8040(2) A gamma = 90 deg.
Volume	3696.78(7) A^3
Z	8
Calculated Density	1.452 mg/m^3
Absorption Coefficient	1.636 mm^{-1}
F(000)	1688
Crystal Size	0.15 x 0.14 x 0.060 mm
Theta Range for Data Collection	1.856 to 69.605 deg
Limiting Indicies	$-8\leq h\leq 9$, $-24\leq k\leq 24$, $-28\leq l\leq 20$
Reflections Collected	57506
Independent Reflections	6827 [R(int) = 0.0649]
Completeness to Theta	67.684 100.0%
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	1.00000 and 0.66772
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	6411 / 65/ 530
Goodness-of-Fit on F^2	1.083
Final R Indices [$I>2\sigma(I)$]	R1 = 0.0496, wR2 = 0.1308
R indices (all data)	R1 = 0.0499, wR2 = 0.1315
Largest Difference Peak and Hole	1.848 and -0.664 $e.A^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **2a.**

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ni(1)	2503(1)	7302(1)	5481(1)	20(1)
Ni(2)	7596(1)	7202(1)	2460(1)	16(1)
N(1)	1466(4)	6717(1)	4871(1)	19(1)
N(2)	1619(4)	6042(1)	4927(1)	15(1)
N(3)	4657(4)	6708(1)	5467(1)	17(1)
N(4)	4411(4)	6035(1)	5460(1)	16(1)
N(5)	1504(4)	6687(1)	6064(1)	21(1)
N(6)	1627(4)	6014(1)	5974(1)	16(1)
N(7)	6761(4)	6527(1)	1892(1)	19(1)
N(8)	6935(4)	5869(1)	2016(1)	18(1)
N(9)	9807(4)	6641(1)	2545(1)	18(1)
N(10)	9595(4)	5964(1)	2593(1)	18(1)
N(11)	6526(4)	6653(1)	3092(1)	17(1)
N(12)	6716(4)	5977(1)	3065(1)	17(1)
C(1)	623(5)	6829(2)	4394(2)	26(1)
C(2)	205(5)	6231(2)	4129(2)	27(1)
C(3)	866(4)	5742(2)	4482(1)	20(1)
C(4)	6360(4)	6797(2)	5494(1)	21(1)
C(5)	7235(5)	6189(2)	5500(1)	25(1)
C(6)	5932(4)	5722(2)	5478(1)	20(1)
C(7)	741(5)	6768(2)	6559(2)	23(1)
C(8)	351(5)	6147(2)	6800(1)	23(1)
C(9)	919(4)	5687(2)	6413(1)	18(1)
C(10)	3407(5)	8033(2)	5048(1)	21(1)
C(11)	4820(5)	7963(2)	4688(2)	24(1)
C(12)	5469(5)	8511(2)	4397(2)	25(1)
C(13)	4718(5)	9133(2)	4465(2)	29(1)
C(14)	3279(6)	9207(2)	4812(1)	26(1)
C(15)	2590(5)	8660(2)	5096(1)	22(1)
C(16)	994(5)	8655(2)	5456(1)	21(1)
C(17)	1057(8)	8004(3)	5813(2)	21(2)
C(18)	-652(9)	8622(3)	5098(3)	25(2)
C(19)	863(10)	9243(3)	5866(3)	28(2)

C(17A)	504(10)	7938(4)	5433(4)	26(2)
C(18A)	-344(12)	9139(4)	5215(4)	31(2)
C(19A)	1468(13)	8888(5)	6049(3)	29(2)
C(20)	6064(5)	6556(2)	1377(1)	22(1)
C(21)	5808(5)	5921(2)	1167(2)	27(1)
C(22)	6375(5)	5495(2)	1583(1)	24(1)
C(23)	11495(5)	6745(2)	2515(1)	21(1)
C(24)	12413(5)	6148(2)	2544(1)	25(1)
C(25)	11161(4)	5666(2)	2592(1)	21(1)
C(26)	5667(4)	6793(2)	3558(1)	19(1)
C(27)	5242(5)	6204(2)	3842(2)	22(1)
C(28)	5921(4)	5702(2)	3522(1)	18(1)
C(29)	8275(4)	7968(2)	2896(1)	19(1)
C(30)	9726(5)	7968(2)	3263(1)	22(1)
C(31)	10192(5)	8534(2)	3555(1)	22(1)
C(32)	9235(5)	9117(2)	3499(2)	24(1)
C(33)	7771(5)	9123(2)	3158(1)	23(1)
C(34)	7302(5)	8553(2)	2852(1)	19(1)
C(35)	5718(5)	8501(2)	2485(2)	20(1)
C(36)	5974(5)	7859(2)	2151(2)	21(1)
C(37)	4086(5)	8449(2)	2849(2)	24(1)
C(38)	5512(5)	9097(2)	2083(2)	25(1)
B(1)	2561(5)	5757(2)	5443(1)	14(1)
B(2)	7763(5)	5663(2)	2582(2)	17(1)

Table S3. Bond lengths [Å] and angles [deg] for **2a.**

Ni(1)-C(10)	1.926(4)
Ni(1)-C(17)	1.966(5)
Ni(1)-N(5)	2.011(3)
Ni(1)-C(17A)	2.008(6)
Ni(1)-N(1)	2.032(3)
Ni(1)-N(3)	2.050(3)
Ni(2)-C(29)	1.928(4)
Ni(2)-C(36)	1.963(3)
Ni(2)-N(7)	2.019(3)
Ni(2)-N(11)	2.042(3)
Ni(2)-N(9)	2.058(3)
N(1)-C(1)	1.327(5)
N(1)-N(2)	1.367(4)
N(2)-C(3)	1.348(4)
N(2)-B(1)	1.538(4)
N(3)-C(4)	1.331(5)
N(3)-N(4)	1.365(4)
N(4)-C(6)	1.335(4)
N(4)-B(1)	1.536(5)
N(5)-C(7)	1.330(4)
N(5)-N(6)	1.371(4)
N(6)-C(9)	1.351(4)
N(6)-B(1)	1.545(4)
N(7)-C(20)	1.339(5)
N(7)-N(8)	1.361(4)
N(8)-C(22)	1.345(4)
N(8)-B(2)	1.548(4)
N(9)-C(23)	1.324(5)
N(9)-N(10)	1.374(4)
N(10)-C(25)	1.351(4)
N(10)-B(2)	1.541(5)
N(11)-C(26)	1.326(4)
N(11)-N(12)	1.366(4)
N(12)-C(28)	1.366(4)
N(12)-B(2)	1.543(4)
C(1)-C(2)	1.394(6)
C(1)-H(1)	0.9500
C(2)-C(3)	1.388(5)
C(2)-H(2)	0.9500

C(3)-H(3)	0.9500
C(4)-C(5)	1.396(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.378(5)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.405(5)
C(7)-H(7)	0.9500
C(8)-C(9)	1.376(5)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(10)-C(11)	1.397(5)
C(10)-C(15)	1.413(5)
C(11)-C(12)	1.394(5)
C(11)-H(11)	0.9500
C(12)-C(13)	1.387(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.396(6)
C(13)-H(13)	0.9500
C(14)-C(15)	1.395(5)
C(14)-H(14)	0.9500
C(15)-C(16)	1.504(5)
C(16)-C(17A)	1.490(8)
C(16)-C(19A)	1.530(8)
C(16)-C(18A)	1.531(8)
C(16)-C(18)	1.533(7)
C(16)-C(19)	1.535(6)
C(16)-C(17)	1.561(6)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(17A)-H(17C)	0.9900
C(17A)-H(17D)	0.9900
C(18A)-H(18D)	0.9800
C(18A)-H(18E)	0.9800
C(18A)-H(18F)	0.9800
C(19A)-H(19D)	0.9800

C(19A)-H(19E)	0.9800
C(19A)-H(19F)	0.9800
C(20)-C(21)	1.383(5)
C(20)-H(20)	0.9500
C(21)-C(22)	1.380(5)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(23)-C(24)	1.395(5)
C(23)-H(23)	0.9500
C(24)-C(25)	1.374(5)
C(24)-H(24)	0.9500
C(25)-H(25)	0.9500
C(26)-C(27)	1.401(5)
C(26)-H(26)	0.9500
C(27)-C(28)	1.369(5)
C(27)-H(27)	0.9500
C(28)-H(28)	0.9500
C(29)-C(34)	1.399(5)
C(29)-C(30)	1.421(5)
C(30)-C(31)	1.379(5)
C(30)-H(30)	0.9500
C(31)-C(32)	1.391(5)
C(31)-H(31)	0.9500
C(32)-C(33)	1.391(6)
C(32)-H(32)	0.9500
C(33)-C(34)	1.403(5)
C(33)-H(33)	0.9500
C(34)-C(35)	1.508(5)
C(35)-C(36)	1.527(5)
C(35)-C(37)	1.535(5)
C(35)-C(38)	1.540(5)
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
B(1)-H(1B)	1.04(4)
B(2)-H(2B)	1.13(5)

C(10)-Ni(1)-C(17)	82.9(2)
C(10)-Ni(1)-N(5)	167.67(13)
C(17)-Ni(1)-N(5)	86.76(19)
C(10)-Ni(1)-C(17A)	76.4(3)
N(5)-Ni(1)-C(17A)	97.7(3)
C(10)-Ni(1)-N(1)	101.57(13)
C(17)-Ni(1)-N(1)	118.5(2)
N(5)-Ni(1)-N(1)	89.24(11)
C(17A)-Ni(1)-N(1)	91.4(3)
C(10)-Ni(1)-N(3)	97.96(14)
C(17)-Ni(1)-N(3)	152.5(2)
N(5)-Ni(1)-N(3)	88.15(12)
C(17A)-Ni(1)-N(3)	174.2(3)
N(1)-Ni(1)-N(3)	88.37(11)
C(29)-Ni(2)-C(36)	80.70(15)
C(29)-Ni(2)-N(7)	169.20(13)
C(36)-Ni(2)-N(7)	89.83(13)
C(29)-Ni(2)-N(11)	98.29(12)
C(36)-Ni(2)-N(11)	112.28(14)
N(7)-Ni(2)-N(11)	90.07(11)
C(29)-Ni(2)-N(9)	99.09(13)
C(36)-Ni(2)-N(9)	159.34(14)
N(7)-Ni(2)-N(9)	87.93(11)
N(11)-Ni(2)-N(9)	88.26(11)
C(1)-N(1)-N(2)	107.0(3)
C(1)-N(1)-Ni(1)	135.0(3)
N(2)-N(1)-Ni(1)	118.0(2)
C(3)-N(2)-N(1)	109.2(3)
C(3)-N(2)-B(1)	131.7(3)
N(1)-N(2)-B(1)	119.1(2)
C(4)-N(3)-N(4)	105.8(3)
C(4)-N(3)-Ni(1)	136.5(2)
N(4)-N(3)-Ni(1)	117.6(2)
C(6)-N(4)-N(3)	110.0(3)
C(6)-N(4)-B(1)	130.6(3)
N(3)-N(4)-B(1)	119.3(2)
C(7)-N(5)-N(6)	106.8(3)
C(7)-N(5)-Ni(1)	135.1(2)
N(6)-N(5)-Ni(1)	118.0(2)
C(9)-N(6)-N(5)	109.3(3)
C(9)-N(6)-B(1)	131.3(3)

N(5)-N(6)-B(1)	119.3(2)
C(20)-N(7)-N(8)	106.2(3)
C(20)-N(7)-Ni(2)	135.4(2)
N(8)-N(7)-Ni(2)	118.4(2)
C(22)-N(8)-N(7)	110.2(3)
C(22)-N(8)-B(2)	130.5(3)
N(7)-N(8)-B(2)	119.3(3)
C(23)-N(9)-N(10)	106.2(3)
C(23)-N(9)-Ni(2)	136.7(2)
N(10)-N(9)-Ni(2)	116.8(2)
C(25)-N(10)-N(9)	109.3(3)
C(25)-N(10)-B(2)	130.6(3)
N(9)-N(10)-B(2)	119.8(3)
C(26)-N(11)-N(12)	107.7(3)
C(26)-N(11)-Ni(2)	135.0(2)
N(12)-N(11)-Ni(2)	117.30(19)
C(28)-N(12)-N(11)	108.4(3)
C(28)-N(12)-B(2)	131.7(3)
N(11)-N(12)-B(2)	119.8(2)
N(1)-C(1)-C(2)	110.8(3)
N(1)-C(1)-H(1)	124.6
C(2)-C(1)-H(1)	124.6
C(3)-C(2)-C(1)	104.4(3)
C(3)-C(2)-H(2)	127.8
C(1)-C(2)-H(2)	127.8
N(2)-C(3)-C(2)	108.6(3)
N(2)-C(3)-H(3)	125.7
C(2)-C(3)-H(3)	125.7
N(3)-C(4)-C(5)	111.2(3)
N(3)-C(4)-H(4)	124.4
C(5)-C(4)-H(4)	124.4
C(6)-C(5)-C(4)	103.9(3)
C(6)-C(5)-H(5)	128.0
C(4)-C(5)-H(5)	128.0
N(4)-C(6)-C(5)	109.0(3)
N(4)-C(6)-H(6)	125.5
C(5)-C(6)-H(6)	125.5
N(5)-C(7)-C(8)	110.5(3)
N(5)-C(7)-H(7)	124.8
C(8)-C(7)-H(7)	124.8
C(9)-C(8)-C(7)	104.7(3)

C(9)-C(8)-H(8)	127.7
C(7)-C(8)-H(8)	127.7
N(6)-C(9)-C(8)	108.8(3)
N(6)-C(9)-H(9)	125.6
C(8)-C(9)-H(9)	125.6
C(11)-C(10)-C(15)	119.3(3)
C(11)-C(10)-Ni(1)	122.5(3)
C(15)-C(10)-Ni(1)	118.2(3)
C(12)-C(11)-C(10)	120.6(3)
C(12)-C(11)-H(11)	119.7
C(10)-C(11)-H(11)	119.7
C(13)-C(12)-C(11)	120.0(3)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(12)-C(13)-C(14)	120.0(3)
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-H(13)	120.0
C(15)-C(14)-C(13)	120.5(3)
C(15)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.7
C(14)-C(15)-C(10)	119.4(3)
C(14)-C(15)-C(16)	126.5(3)
C(10)-C(15)-C(16)	114.1(3)
C(17A)-C(16)-C(15)	101.2(4)
C(17A)-C(16)-C(19A)	112.9(6)
C(15)-C(16)-C(19A)	109.2(4)
C(17A)-C(16)-C(18A)	115.3(5)
C(15)-C(16)-C(18A)	109.7(4)
C(19A)-C(16)-C(18A)	108.2(6)
C(15)-C(16)-C(18)	111.4(3)
C(15)-C(16)-C(19)	114.4(4)
C(18)-C(16)-C(19)	109.3(4)
C(15)-C(16)-C(17)	106.9(3)
C(18)-C(16)-C(17)	106.9(4)
C(19)-C(16)-C(17)	107.5(4)
C(16)-C(17)-Ni(1)	113.5(3)
C(16)-C(17)-H(17A)	108.9
Ni(1)-C(17)-H(17A)	108.9
C(16)-C(17)-H(17B)	108.9
Ni(1)-C(17)-H(17B)	108.9
H(17A)-C(17)-H(17B)	107.7
C(16)-C(18)-H(18A)	109.5

C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(16)-C(17A)-Ni(1)	114.6(5)
C(16)-C(17A)-H(17C)	108.6
Ni(1)-C(17A)-H(17C)	108.6
C(16)-C(17A)-H(17D)	108.6
Ni(1)-C(17A)-H(17D)	108.6
H(17C)-C(17A)-H(17D)	107.6
C(16)-C(18A)-H(18D)	109.5
C(16)-C(18A)-H(18E)	109.5
H(18D)-C(18A)-H(18E)	109.5
C(16)-C(18A)-H(18F)	109.5
H(18D)-C(18A)-H(18F)	109.5
H(18E)-C(18A)-H(18F)	109.5
C(16)-C(19A)-H(19D)	109.5
C(16)-C(19A)-H(19E)	109.5
H(19D)-C(19A)-H(19E)	109.5
C(16)-C(19A)-H(19F)	109.5
H(19D)-C(19A)-H(19F)	109.5
H(19E)-C(19A)-H(19F)	109.5
N(7)-C(20)-C(21)	110.4(3)
N(7)-C(20)-H(20)	124.8
C(21)-C(20)-H(20)	124.8
C(22)-C(21)-C(20)	105.4(3)
C(22)-C(21)-H(21)	127.3
C(20)-C(21)-H(21)	127.3
N(8)-C(22)-C(21)	107.8(3)
N(8)-C(22)-H(22)	126.1
C(21)-C(22)-H(22)	126.1
N(9)-C(23)-C(24)	111.3(3)
N(9)-C(23)-H(23)	124.4
C(24)-C(23)-H(23)	124.4

C(25)-C(24)-C(23)	104.5(3)
C(25)-C(24)-H(24)	127.7
C(23)-C(24)-H(24)	127.7
N(10)-C(25)-C(24)	108.7(3)
N(10)-C(25)-H(25)	125.7
C(24)-C(25)-H(25)	125.7
N(11)-C(26)-C(27)	110.0(3)
N(11)-C(26)-H(26)	125.0
C(27)-C(26)-H(26)	125.0
C(28)-C(27)-C(26)	105.2(3)
C(28)-C(27)-H(27)	127.4
C(26)-C(27)-H(27)	127.4
N(12)-C(28)-C(27)	108.6(3)
N(12)-C(28)-H(28)	125.7
C(27)-C(28)-H(28)	125.7
C(34)-C(29)-C(30)	118.0(3)
C(34)-C(29)-Ni(2)	119.0(2)
C(30)-C(29)-Ni(2)	123.1(3)
C(31)-C(30)-C(29)	121.1(3)
C(31)-C(30)-H(30)	119.5
C(29)-C(30)-H(30)	119.5
C(30)-C(31)-C(32)	120.4(3)
C(30)-C(31)-H(31)	119.8
C(32)-C(31)-H(31)	119.8
C(31)-C(32)-C(33)	119.7(3)
C(31)-C(32)-H(32)	120.1
C(33)-C(32)-H(32)	120.1
C(32)-C(33)-C(34)	120.3(3)
C(32)-C(33)-H(33)	119.9
C(34)-C(33)-H(33)	119.9
C(29)-C(34)-C(33)	120.5(3)
C(29)-C(34)-C(35)	114.9(3)
C(33)-C(34)-C(35)	124.5(3)
C(34)-C(35)-C(36)	104.8(3)
C(34)-C(35)-C(37)	110.2(3)
C(36)-C(35)-C(37)	110.1(3)
C(34)-C(35)-C(38)	112.9(3)
C(36)-C(35)-C(38)	110.2(3)
C(37)-C(35)-C(38)	108.6(3)
C(35)-C(36)-Ni(2)	117.1(2)
C(35)-C(36)-H(36A)	108.0
Ni(2)-C(36)-H(36A)	108.0

C(35)-C(36)-H(36B)	108.0
Ni(2)-C(36)-H(36B)	108.0
H(36A)-C(36)-H(36B)	107.3
C(35)-C(37)-H(37A)	109.5
C(35)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(35)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(35)-C(38)-H(38A)	109.5
C(35)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(35)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
N(4)-B(1)-N(2)	109.0(3)
N(4)-B(1)-N(6)	107.1(2)
N(2)-B(1)-N(6)	107.9(3)
N(4)-B(1)-H(1B)	116(3)
N(2)-B(1)-H(1B)	106(3)
N(6)-B(1)-H(1B)	110(3)
N(10)-B(2)-N(12)	108.1(3)
N(10)-B(2)-N(8)	106.8(3)
N(12)-B(2)-N(8)	108.9(3)
N(10)-B(2)-H(2B)	112(3)
N(12)-B(2)-H(2B)	108(2)
N(8)-B(2)-H(2B)	113(2)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($A^2 \times 10^3$) for **2a.**

	U11	U22	U33	U23	U13	U12
Ni(1)	18(1)	16(1)	26(1)	-4(1)	10(1)	-2(1)
Ni(2)	15(1)	19(1)	15(1)	2(1)	1(1)	-1(1)
N(1)	18(2)	18(1)	21(1)	3(1)	0(1)	1(1)
N(2)	15(1)	17(1)	13(1)	-2(1)	1(1)	-1(1)
N(3)	17(1)	21(1)	14(1)	-2(1)	1(1)	-4(1)
N(4)	13(1)	19(1)	15(1)	-1(1)	1(1)	0(1)
N(5)	21(2)	20(1)	21(1)	-9(1)	6(1)	-4(1)
N(6)	17(1)	19(1)	12(1)	-1(1)	2(1)	-3(1)
N(7)	16(1)	22(1)	18(1)	3(1)	1(1)	1(1)
N(8)	21(2)	19(1)	14(1)	0(1)	1(1)	-3(1)
N(9)	18(1)	17(1)	18(1)	3(1)	-2(1)	-2(1)
N(10)	16(1)	20(1)	17(1)	4(1)	6(1)	2(1)
N(11)	17(1)	21(1)	12(1)	-2(1)	2(1)	0(1)
N(12)	17(1)	21(1)	13(1)	4(1)	2(1)	-2(1)
C(1)	24(2)	33(2)	23(2)	7(2)	-1(2)	3(2)
C(2)	22(2)	45(2)	15(2)	2(2)	-4(1)	-1(2)
C(3)	16(2)	27(2)	16(2)	-6(1)	-1(1)	-5(1)
C(4)	14(2)	30(2)	19(2)	-2(1)	3(1)	-5(1)
C(5)	15(2)	39(2)	20(2)	-4(1)	3(1)	-1(2)
C(6)	18(2)	25(2)	16(2)	-4(1)	1(1)	6(1)
C(7)	20(2)	32(2)	19(2)	-9(1)	10(1)	-8(2)
C(8)	20(2)	37(2)	13(2)	-2(1)	3(1)	-6(2)
C(9)	14(2)	25(2)	16(2)	4(1)	-1(1)	-3(1)
C(10)	22(2)	20(2)	20(2)	-3(1)	-2(1)	-1(1)
C(11)	26(2)	24(2)	21(2)	-1(1)	1(1)	-5(2)
C(12)	25(2)	31(2)	19(2)	1(1)	3(1)	-5(2)
C(13)	37(2)	26(2)	24(2)	5(2)	-1(2)	-6(2)
C(14)	40(2)	22(2)	17(2)	1(1)	-4(2)	6(2)
C(15)	25(2)	25(2)	16(1)	-4(1)	-3(2)	-1(2)
C(16)	27(2)	22(2)	14(1)	-3(1)	-2(1)	4(1)
C(17)	27(3)	21(3)	15(3)	-4(2)	3(2)	3(2)
C(18)	24(3)	32(4)	18(3)	-2(2)	-1(2)	6(3)
C(19)	30(4)	26(3)	28(3)	-10(3)	-1(3)	4(3)
C(17A)	27(4)	22(3)	29(5)	0(3)	5(4)	0(3)
C(18A)	30(4)	21(4)	41(5)	-1(3)	-1(4)	4(3)

C(19A)	32(5)	33(5)	22(4)	−5(3)	−1(3)	0(4)
C(20)	25(2)	27(2)	13(2)	3(1)	0(1)	−2(1)
C(21)	31(2)	36(2)	16(2)	1(2)	−4(2)	−3(2)
C(22)	26(2)	27(2)	17(2)	−2(1)	3(1)	−4(2)
C(23)	16(2)	27(2)	19(2)	1(1)	5(1)	−6(1)
C(24)	16(2)	34(2)	24(2)	2(1)	1(2)	5(2)
C(25)	16(2)	25(2)	21(2)	3(1)	1(1)	6(1)
C(26)	15(2)	22(2)	21(2)	1(1)	5(1)	−1(1)
C(27)	22(2)	29(2)	15(2)	2(1)	8(1)	−1(2)
C(28)	14(2)	22(2)	17(2)	6(1)	1(1)	−5(1)
C(29)	15(2)	26(2)	16(2)	5(1)	0(1)	−2(1)
C(30)	20(2)	26(2)	19(2)	8(1)	−1(1)	−2(1)
C(31)	20(2)	29(2)	17(2)	0(1)	1(1)	−4(2)
C(32)	28(2)	24(2)	19(2)	2(1)	8(2)	−7(2)
C(33)	22(2)	22(2)	25(2)	3(1)	9(2)	−2(1)
C(34)	15(2)	24(2)	17(1)	5(1)	5(1)	−4(1)
C(35)	17(2)	22(2)	21(2)	4(1)	−1(1)	1(1)
C(36)	21(2)	24(2)	19(2)	2(1)	−3(1)	3(1)
C(37)	19(2)	31(2)	24(2)	2(1)	2(2)	−1(2)
C(38)	27(2)	27(2)	22(2)	8(1)	1(2)	2(2)
B(1)	14(2)	12(1)	14(2)	0(1)	0(2)	2(1)
B(2)	16(2)	15(2)	20(2)	1(1)	1(2)	1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **2a.**

	x	y	z	U(eq)
H(1)	343	7258	4253	32
H(2)	-397	6171	3785	33
H(3)	799	5276	4421	23
H(4)	6909	7220	5508	25
H(5)	8447	6115	5516	30
H(6)	6092	5253	5476	24
H(7)	495	7186	6727	28
H(8)	-187	6063	7151	28
H(9)	829	5217	6449	22
H(11)	5342	7539	4641	29
H(12)	6427	8458	4151	30
H(13)	5183	9508	4275	35
H(14)	2765	9633	4856	31
H(17A)	-135	7832	5858	25
H(17B)	1507	8112	6192	25
H(18A)	-777	9035	4883	37
H(18B)	-1658	8564	5344	37
H(18C)	-576	8244	4839	37
H(19A)	1912	9264	6097	42
H(19B)	-145	9182	6110	42
H(19C)	737	9659	5654	42
H(17C)	-125	7855	5078	32
H(17D)	-300	7843	5746	32
H(18D)	-563	9030	4820	46
H(18E)	96	9596	5242	46
H(18F)	-1424	9102	5428	46
H(19D)	418	8918	6277	44
H(19E)	2018	9327	6029	44
H(19F)	2270	8569	6220	44
H(20)	5785	6956	1184	26
H(21)	5342	5804	811	33
H(22)	6369	5023	1567	28
H(23)	12014	7172	2480	25
H(24)	13631	6088	2532	30

H(25)	11363	5200	2621	25
H(26)	5382	7229	3683	23
H(27)	4617	6162	4183	26
H(28)	5851	5240	3603	22
H(30)	10385	7573	3308	26
H(31)	11173	8525	3795	27
H(32)	9579	9509	3692	29
H(33)	7087	9515	3133	27
H(36A)	6373	7981	1770	25
H(36B)	4833	7641	2109	25
H(37A)	4142	8043	3076	37
H(37B)	3063	8433	2606	37
H(37C)	4013	8838	3096	37
H(38A)	5259	9500	2301	38
H(38B)	4560	9010	1821	38
H(38C)	6585	9161	1872	38
H(1B)	2450(70)	5240(20)	5413(19)	39(12)
H(2B)	7790(70)	5100(20)	2650(20)	43(13)

Table S6. Torsion angles [deg] for **2a.**

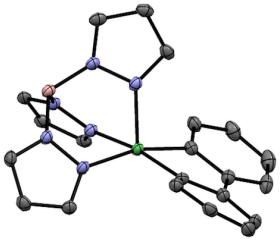
C(1)-N(1)-N(2)-C(3)	0.0(4)
Ni(1)-N(1)-N(2)-C(3)	-179.6(2)
C(1)-N(1)-N(2)-B(1)	179.6(3)
Ni(1)-N(1)-N(2)-B(1)	0.0(4)
C(4)-N(3)-N(4)-C(6)	-0.5(4)
Ni(1)-N(3)-N(4)-C(6)	-177.0(2)
C(4)-N(3)-N(4)-B(1)	178.6(3)
Ni(1)-N(3)-N(4)-B(1)	2.1(4)
C(7)-N(5)-N(6)-C(9)	0.7(4)
Ni(1)-N(5)-N(6)-C(9)	178.8(2)
C(7)-N(5)-N(6)-B(1)	-176.5(3)
Ni(1)-N(5)-N(6)-B(1)	1.7(4)
C(20)-N(7)-N(8)-C(22)	0.6(4)
Ni(2)-N(7)-N(8)-C(22)	-177.6(2)
C(20)-N(7)-N(8)-B(2)	178.2(3)
Ni(2)-N(7)-N(8)-B(2)	-0.1(4)
C(23)-N(9)-N(10)-C(25)	0.1(4)
Ni(2)-N(9)-N(10)-C(25)	174.4(2)
C(23)-N(9)-N(10)-B(2)	-174.4(3)
Ni(2)-N(9)-N(10)-B(2)	-0.2(4)
C(26)-N(11)-N(12)-C(28)	1.3(4)
Ni(2)-N(11)-N(12)-C(28)	179.9(2)
C(26)-N(11)-N(12)-B(2)	-176.5(3)
Ni(2)-N(11)-N(12)-B(2)	2.1(4)
N(2)-N(1)-C(1)-C(2)	0.2(4)
Ni(1)-N(1)-C(1)-C(2)	179.6(3)
N(1)-C(1)-C(2)-C(3)	-0.2(4)
N(1)-N(2)-C(3)-C(2)	-0.1(4)
B(1)-N(2)-C(3)-C(2)	-179.6(3)
C(1)-C(2)-C(3)-N(2)	0.2(4)
N(4)-N(3)-C(4)-C(5)	0.6(4)
Ni(1)-N(3)-C(4)-C(5)	176.1(2)
N(3)-C(4)-C(5)-C(6)	-0.4(4)
N(3)-N(4)-C(6)-C(5)	0.3(4)
B(1)-N(4)-C(6)-C(5)	-178.7(3)
C(4)-C(5)-C(6)-N(4)	0.1(4)
N(6)-N(5)-C(7)-C(8)	-0.1(4)
Ni(1)-N(5)-C(7)-C(8)	-177.8(3)

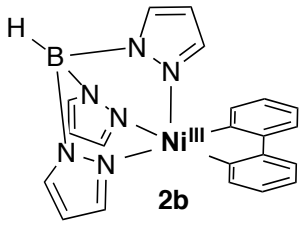
N(5)-C(7)-C(8)-C(9)	-0.4(4)
N(5)-N(6)-C(9)-C(8)	-0.9(4)
B(1)-N(6)-C(9)-C(8)	175.7(3)
C(7)-C(8)-C(9)-N(6)	0.8(4)
C(15)-C(10)-C(11)-C(12)	2.8(5)
Ni(1)-C(10)-C(11)-C(12)	-177.8(3)
C(10)-C(11)-C(12)-C(13)	0.3(6)
C(11)-C(12)-C(13)-C(14)	-1.9(6)
C(12)-C(13)-C(14)-C(15)	0.3(6)
C(13)-C(14)-C(15)-C(10)	2.7(5)
C(13)-C(14)-C(15)-C(16)	-176.3(3)
C(11)-C(10)-C(15)-C(14)	-4.3(5)
Ni(1)-C(10)-C(15)-C(14)	176.2(3)
C(11)-C(10)-C(15)-C(16)	174.9(3)
Ni(1)-C(10)-C(15)-C(16)	-4.6(4)
C(14)-C(15)-C(16)-C(17A)	156.9(5)
C(10)-C(15)-C(16)-C(17A)	-22.2(5)
C(14)-C(15)-C(16)-C(19A)	-83.8(6)
C(10)-C(15)-C(16)-C(19A)	97.1(5)
C(14)-C(15)-C(16)-C(18A)	34.6(6)
C(10)-C(15)-C(16)-C(18A)	-144.5(5)
C(14)-C(15)-C(16)-C(18)	79.7(5)
C(10)-C(15)-C(16)-C(18)	-99.3(4)
C(14)-C(15)-C(16)-C(19)	-44.9(6)
C(10)-C(15)-C(16)-C(19)	136.0(4)
C(14)-C(15)-C(16)-C(17)	-163.8(4)
C(10)-C(15)-C(16)-C(17)	17.1(4)
C(15)-C(16)-C(17)-Ni(1)	-22.8(5)
C(18)-C(16)-C(17)-Ni(1)	96.7(5)
C(19)-C(16)-C(17)-Ni(1)	-146.0(4)
C(15)-C(16)-C(17A)-Ni(1)	40.6(6)
C(19A)-C(16)-C(17A)-Ni(1)	-75.9(7)
C(18A)-C(16)-C(17A)-Ni(1)	158.9(5)
N(8)-N(7)-C(20)-C(21)	-0.7(4)
Ni(2)-N(7)-C(20)-C(21)	177.2(3)
N(7)-C(20)-C(21)-C(22)	0.5(4)
N(7)-N(8)-C(22)-C(21)	-0.4(4)
B(2)-N(8)-C(22)-C(21)	-177.6(3)
C(20)-C(21)-C(22)-N(8)	-0.1(4)
N(10)-N(9)-C(23)-C(24)	-0.1(4)
Ni(2)-N(9)-C(23)-C(24)	-172.6(3)
N(9)-C(23)-C(24)-C(25)	0.1(4)

N(9)-N(10)-C(25)-C(24)	-0.1(4)
B(2)-N(10)-C(25)-C(24)	173.6(3)
C(23)-C(24)-C(25)-N(10)	0.0(4)
N(12)-N(11)-C(26)-C(27)	-1.4(4)
Ni(2)-N(11)-C(26)-C(27)	-179.6(3)
N(11)-C(26)-C(27)-C(28)	0.9(4)
N(11)-N(12)-C(28)-C(27)	-0.7(4)
B(2)-N(12)-C(28)-C(27)	176.7(3)
C(26)-C(27)-C(28)-N(12)	-0.1(4)
C(34)-C(29)-C(30)-C(31)	-1.9(5)
Ni(2)-C(29)-C(30)-C(31)	178.1(3)
C(29)-C(30)-C(31)-C(32)	0.6(5)
C(30)-C(31)-C(32)-C(33)	1.8(5)
C(31)-C(32)-C(33)-C(34)	-2.8(5)
C(30)-C(29)-C(34)-C(33)	0.9(5)
Ni(2)-C(29)-C(34)-C(33)	-179.2(2)
C(30)-C(29)-C(34)-C(35)	-176.2(3)
Ni(2)-C(29)-C(34)-C(35)	3.8(4)
C(32)-C(33)-C(34)-C(29)	1.5(5)
C(32)-C(33)-C(34)-C(35)	178.2(3)
C(29)-C(34)-C(35)-C(36)	-14.9(4)
C(33)-C(34)-C(35)-C(36)	168.2(3)
C(29)-C(34)-C(35)-C(37)	103.5(3)
C(33)-C(34)-C(35)-C(37)	-73.4(4)
C(29)-C(34)-C(35)-C(38)	-134.9(3)
C(33)-C(34)-C(35)-C(38)	48.2(4)
C(34)-C(35)-C(36)-Ni(2)	20.7(3)
C(37)-C(35)-C(36)-Ni(2)	-97.7(3)
C(38)-C(35)-C(36)-Ni(2)	142.5(3)
C(6)-N(4)-B(1)-N(2)	-124.4(3)
N(3)-N(4)-B(1)-N(2)	56.7(3)
C(6)-N(4)-B(1)-N(6)	119.1(3)
N(3)-N(4)-B(1)-N(6)	-59.8(3)
C(3)-N(2)-B(1)-N(4)	121.3(3)
N(1)-N(2)-B(1)-N(4)	-58.2(4)
C(3)-N(2)-B(1)-N(6)	-122.7(4)
N(1)-N(2)-B(1)-N(6)	57.8(4)
C(9)-N(6)-B(1)-N(4)	-118.3(3)
N(5)-N(6)-B(1)-N(4)	58.0(4)
C(9)-N(6)-B(1)-N(2)	124.4(3)
N(5)-N(6)-B(1)-N(2)	-59.2(4)

C(25)-N(10)-B(2)-N(12)	128.6(3)
N(9)-N(10)-B(2)-N(12)	-58.2(4)
C(25)-N(10)-B(2)-N(8)	-114.4(4)
N(9)-N(10)-B(2)-N(8)	58.8(4)
C(28)-N(12)-B(2)-N(10)	-119.9(4)
N(11)-N(12)-B(2)-N(10)	57.3(4)
C(28)-N(12)-B(2)-N(8)	124.5(4)
N(11)-N(12)-B(2)-N(8)	-58.3(4)
C(22)-N(8)-B(2)-N(10)	117.8(4)
N(7)-N(8)-B(2)-N(10)	-59.2(4)
C(22)-N(8)-B(2)-N(12)	-125.7(4)
N(7)-N(8)-B(2)-N(12)	57.3(4)

Structure Determination of 2b





2b

Yellow needles of **2b** were grown from a diethylether solution of the compound at –35 ºC. A crystal of dimensions 0.20 x 0.03 x 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 (λ = 1.54187 A) 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 5 sec. for the low angle images, 40 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 54490 reflections to a maximum 2θ value of 138.99° of which 3559 were independent and 3198 were greater than 2σ(I). The final cell constants (Table S7) were based on the xyz centroids 19760 reflections above 10σ(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 Pbca with Z = 8 for the formula $C_{21}H_{18}BN_6Ni$. 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 = 0.0450 and wR2 = 0.1171 [based on I > 2sigma(I)], R1 = 0.0501 and wR2 = 0.1257 for all data. Additional details are presented in Table S7 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 S7. Crystal data and structural refinement for **2b**

Empirical Formula	$C_{21}H_{18}N_6BNi$
Formula Weight	423.93
Temperature	85(2) K
Wavelength	1.54184 A
Crystal System	Orthorhombic
Space Group	Pbca
Unit Cell Dimensions	a = 14.9798(2) A alpha = 90 deg. b =13.0128(2) A beta = 90 deg c =19.5957(2) A gamma = 90 deg.
Volume	3819.79 A^3
Z	8
Calculated Density	1.474 Mg/m^3
Absorption Coefficient	1.621 mm^{-1}
F(000)	1752
Crystal Size	0.2 x 0.03 x 0.010 mm
Theta Range for Data Collection	4.513 to 69.496 deg
Limiting Indicies	$-18\leq h\leq 16$, $-15\leq k\leq 15$, $-23\leq l\leq 23$
Reflections Collected	54490
Independent Reflections	3559 [R(int) = 0.1019]
Completeness to Theta	67.684 100.0%
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	1.00000 and 0.76349
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	3559/ 0/ 263
Goodness-of-Fit on F^2	1.073
Final R Indices [$I>2\sigma(I)$]	R1 = 0.0450, wR2 = 0.1171
R indices (all data)	R1 = 0.0501, wR2 = 0.1257
Largest Difference Peak and Hole	0.466 and -0.523 A^{-3}

Table S8. Atomic coordinates (x 10^2) and equivalent isotropic displacement parameters (A^2 x 10^2) for **2b**.

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ni(1)	7168(1)	3408(1)	6672(1)	15(1)
N(1)	8057(1)	4135(1)	7274(1)	17(1)
N(2)	8375(1)	3619(1)	7832(1)	17(1)
N(3)	6514(1)	3033(1)	7529(1)	18(1)
N(4)	6999(1)	2651(1)	8061(1)	17(1)
N(5)	7913(1)	2116(2)	6734(1)	17(1)
N(6)	8231(1)	1850(1)	7363(1)	17(1)
C(1)	8385(1)	5085(2)	7306(1)	19(1)
C(2)	8926(1)	5197(2)	7884(1)	21(1)
C(3)	8897(1)	4250(2)	8204(1)	19(1)
C(4)	5691(1)	3199(2)	7764(1)	20(1)
C(5)	5636(2)	2934(2)	8451(1)	21(1)
C(6)	6478(1)	2595(2)	8620(1)	20(1)
C(7)	8245(1)	1439(2)	6291(1)	20(1)
C(8)	8788(2)	732(2)	6629(1)	21(1)
C(9)	8763(1)	1022(2)	7304(1)	21(1)
C(10)	7570(2)	4041(2)	5827(1)	19(1)
C(11)	8400(2)	4488(2)	5713(1)	22(1)
C(12)	8560(2)	5031(2)	5108(1)	27(1)
C(13)	7903(2)	5114(2)	4616(1)	30(1)
C(14)	7083(2)	4644(2)	4713(1)	26(1)
C(15)	6916(2)	4100(2)	5312(1)	21(1)
C(16)	6126(2)	3482(2)	5462(1)	20(1)
C(17)	5389(2)	3311(2)	5040(1)	24(1)
C(18)	4769(2)	2558(2)	5211(1)	24(1)
C(19)	4881(2)	1982(2)	5800(1)	22(1)
C(20)	5585(1)	2193(2)	6249(1)	20(1)
C(21)	6198(1)	2955(2)	6089(1)	18(1)
B(1)	8015(2)	2532(2)	7985(1)	18(1)

Table S9. Bond lengths [Å] and angles [deg] for **2b**.

Ni(1)-C(21)	1.941(2)
Ni(1)-C(10)	1.946(2)
Ni(1)-N(3)	2.0052(18)
Ni(1)-N(1)	2.0141(18)
Ni(1)-N(5)	2.0216(19)
N(1)-C(1)	1.332(3)
N(1)-N(2)	1.369(2)
N(2)-C(3)	1.347(3)
N(2)-B(1)	1.543(3)
N(3)-C(4)	1.333(3)
N(3)-N(4)	1.365(2)
N(4)-C(6)	1.348(3)
N(4)-B(1)	1.536(3)
N(5)-C(7)	1.333(3)
N(5)-N(6)	1.366(2)
N(6)-C(9)	1.344(3)
N(6)-B(1)	1.542(3)
C(1)-C(2)	1.401(3)
C(1)-H(1)	0.9500
C(2)-C(3)	1.383(3)
C(2)-H(2)	0.9500
C(3)-H(3)	0.9500
C(4)-C(5)	1.392(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.376(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.395(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.378(3)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(10)-C(11)	1.391(3)
C(10)-C(15)	1.408(3)
C(11)-C(12)	1.401(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.383(4)
C(12)-H(12)	0.9500

C(13)-C(14)	1.386(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.394(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.461(3)
C(16)-C(17)	1.396(3)
C(16)-C(21)	1.412(3)
C(17)-C(18)	1.391(4)
C(17)-H(17)	0.9500
C(18)-C(19)	1.387(3)
C(18)-H(18)	0.9500
C(19)-C(20)	1.400(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.388(3)
C(20)-H(20)	0.9500
B(1)-H(1B)	1.0000

C(21)-Ni(1)-C(10)	81.89(9)
C(21)-Ni(1)-N(3)	93.03(8)
C(10)-Ni(1)-N(3)	165.39(8)
C(21)-Ni(1)-N(1)	169.23(8)
C(10)-Ni(1)-N(1)	95.44(8)
N(3)-Ni(1)-N(1)	87.01(7)
C(21)-Ni(1)-N(5)	101.32(8)
C(10)-Ni(1)-N(5)	103.42(8)
N(3)-Ni(1)-N(5)	90.98(7)
N(1)-Ni(1)-N(5)	89.44(7)
C(1)-N(1)-N(2)	106.81(17)
C(1)-N(1)-Ni(1)	135.01(15)
N(2)-N(1)-Ni(1)	117.86(13)
C(3)-N(2)-N(1)	109.55(17)
C(3)-N(2)-B(1)	131.07(18)
N(1)-N(2)-B(1)	118.86(16)
C(4)-N(3)-N(4)	106.77(17)
C(4)-N(3)-Ni(1)	134.54(15)
N(4)-N(3)-Ni(1)	117.87(13)
C(6)-N(4)-N(3)	109.37(17)
C(6)-N(4)-B(1)	130.38(18)
N(3)-N(4)-B(1)	119.36(17)
C(7)-N(5)-N(6)	106.85(17)
C(7)-N(5)-Ni(1)	135.76(15)

N(6)-N(5)-Ni(1)	117.23(13)
C(9)-N(6)-N(5)	109.45(17)
C(9)-N(6)-B(1)	130.78(18)
N(5)-N(6)-B(1)	119.57(17)
N(1)-C(1)-C(2)	110.38(19)
N(1)-C(1)-H(1)	124.8
C(2)-C(1)-H(1)	124.8
C(3)-C(2)-C(1)	104.78(19)
C(3)-C(2)-H(2)	127.6
C(1)-C(2)-H(2)	127.6
N(2)-C(3)-C(2)	108.49(19)
N(2)-C(3)-H(3)	125.8
C(2)-C(3)-H(3)	125.8
N(3)-C(4)-C(5)	110.34(19)
N(3)-C(4)-H(4)	124.8
C(5)-C(4)-H(4)	124.8
C(6)-C(5)-C(4)	105.01(19)
C(6)-C(5)-H(5)	127.5
C(4)-C(5)-H(5)	127.5
N(4)-C(6)-C(5)	108.50(18)
N(4)-C(6)-H(6)	125.8
C(5)-C(6)-H(6)	125.7
N(5)-C(7)-C(8)	110.14(19)
N(5)-C(7)-H(7)	124.9
C(8)-C(7)-H(7)	124.9
C(9)-C(8)-C(7)	105.04(19)
C(9)-C(8)-H(8)	127.5
C(7)-C(8)-H(8)	127.5
N(6)-C(9)-C(8)	108.52(19)
N(6)-C(9)-H(9)	125.7
C(8)-C(9)-H(9)	125.7
C(11)-C(10)-C(15)	119.00(19)
C(11)-C(10)-Ni(1)	126.15(16)
C(15)-C(10)-Ni(1)	114.69(16)
C(10)-C(11)-C(12)	120.0(2)
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-H(11)	120.0
C(13)-C(12)-C(11)	120.5(2)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
C(12)-C(13)-C(14)	120.1(2)
C(12)-C(13)-H(13)	120.0

C(14)-C(13)-H(13)	120.0
C(13)-C(14)-C(15)	119.9(2)
C(13)-C(14)-H(14)	120.1
C(15)-C(14)-H(14)	120.1
C(14)-C(15)-C(10)	120.4(2)
C(14)-C(15)-C(16)	126.4(2)
C(10)-C(15)-C(16)	112.96(19)
C(17)-C(16)-C(21)	119.9(2)
C(17)-C(16)-C(15)	127.5(2)
C(21)-C(16)-C(15)	112.35(19)
C(18)-C(17)-C(16)	119.9(2)
C(18)-C(17)-H(17)	120.1
C(16)-C(17)-H(17)	120.1
C(19)-C(18)-C(17)	120.0(2)
C(19)-C(18)-H(18)	120.0
C(17)-C(18)-H(18)	120.0
C(18)-C(19)-C(20)	120.5(2)
C(18)-C(19)-H(19)	119.7
C(20)-C(19)-H(19)	119.7
C(21)-C(20)-C(19)	119.8(2)
C(21)-C(20)-H(20)	120.1
C(19)-C(20)-H(20)	120.1
C(20)-C(21)-C(16)	119.56(19)
C(20)-C(21)-Ni(1)	125.42(15)
C(16)-C(21)-Ni(1)	115.00(16)
N(4)-B(1)-N(6)	110.10(17)
N(4)-B(1)-N(2)	105.79(17)
N(6)-B(1)-N(2)	107.53(17)
N(4)-B(1)-H(1B)	111.1
N(6)-B(1)-H(1B)	111.1
N(2)-B(1)-H(1B)	111.1

Table S10. Anisotropic displacement parameters ($A^2 \times 10^3$) for **2b**

The anisotropic displacement factor exponent takes the form:

$-2\pi i^2[h^2 a^{*2} U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ni(1)	11(1)	23(1)	13(1)	1(1)	-1(1)	0(1)
N(1)	14(1)	22(1)	16(1)	1(1)	-1(1)	1(1)
N(2)	12(1)	26(1)	15(1)	1(1)	-2(1)	1(1)
N(3)	12(1)	27(1)	14(1)	2(1)	-3(1)	1(1)
N(4)	14(1)	25(1)	13(1)	1(1)	-2(1)	0(1)
N(5)	13(1)	24(1)	15(1)	2(1)	-2(1)	-1(1)
N(6)	12(1)	24(1)	17(1)	0(1)	-3(1)	1(1)
C(1)	12(1)	23(1)	21(1)	-1(1)	3(1)	2(1)
C(2)	12(1)	26(1)	24(1)	-5(1)	0(1)	-1(1)
C(3)	10(1)	30(1)	18(1)	-4(1)	-1(1)	2(1)
C(4)	13(1)	28(1)	19(1)	0(1)	0(1)	1(1)
C(5)	16(1)	28(1)	19(1)	-2(1)	4(1)	-2(1)
C(6)	20(1)	26(1)	13(1)	1(1)	0(1)	-2(1)
C(7)	14(1)	27(1)	19(1)	-4(1)	4(1)	-3(1)
C(8)	13(1)	23(1)	28(1)	-4(1)	1(1)	1(1)
C(9)	12(1)	22(1)	27(1)	0(1)	-3(1)	0(1)
C(10)	19(1)	22(1)	15(1)	-2(1)	1(1)	2(1)
C(11)	19(1)	29(1)	18(1)	-3(1)	3(1)	-1(1)
C(12)	27(1)	32(1)	23(1)	-3(1)	8(1)	-7(1)
C(13)	41(2)	29(1)	19(1)	3(1)	4(1)	-7(1)
C(14)	34(1)	28(1)	15(1)	2(1)	-3(1)	-2(1)
C(15)	21(1)	25(1)	16(1)	-1(1)	-1(1)	1(1)
C(16)	18(1)	27(1)	15(1)	-2(1)	1(1)	2(1)
C(17)	21(1)	37(1)	14(1)	-2(1)	-4(1)	3(1)
C(18)	14(1)	39(1)	20(1)	-8(1)	-3(1)	2(1)
C(19)	13(1)	30(1)	23(1)	-7(1)	2(1)	1(1)
C(20)	16(1)	26(1)	18(1)	-3(1)	0(1)	1(1)
C(21)	14(1)	26(1)	15(1)	-2(1)	-1(1)	4(1)
B(1)	14(1)	23(1)	16(1)	1(1)	-3(1)	1(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **2b**.

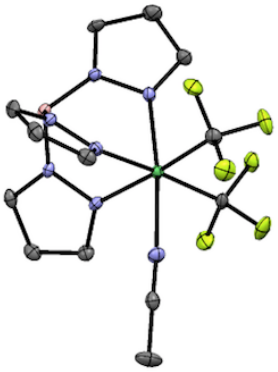
	x	y	z	U(eq)
H(1)	8267	5613	6983	22
H(2)	9243	5792	8026	25
H(3)	9194	4074	8615	23
H(4)	5210	3462	7500	24
H(5)	5129	2978	8740	25
H(6)	6660	2360	9058	23
H(7)	8128	1438	5814	24
H(8)	9106	172	6435	25
H(9)	9069	692	7668	25
H(11)	8859	4426	6046	26
H(12)	9125	5345	5035	33
H(13)	8014	5495	4211	36
H(14)	6634	4692	4371	31
H(17)	5311	3709	4638	29
H(18)	4269	2438	4923	29
H(19)	4477	1440	5900	26
H(20)	5642	1815	6662	24
H(1B)	8287	2246	8410	21

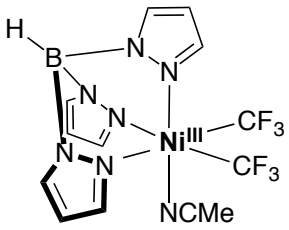
Table S12. Torsion angles [deg] for **2b**

C(1)-N(1)-N(2)-C(3)	-0.2(2)
Ni(1)-N(1)-N(2)-C(3)	-174.66(13)
C(1)-N(1)-N(2)-B(1)	172.43(18)
Ni(1)-N(1)-N(2)-B(1)	-2.0(2)
C(4)-N(3)-N(4)-C(6)	-0.6(2)
Ni(1)-N(3)-N(4)-C(6)	170.54(14)
C(4)-N(3)-N(4)-B(1)	-170.84(19)
Ni(1)-N(3)-N(4)-B(1)	0.3(2)
C(7)-N(5)-N(6)-C(9)	0.7(2)
Ni(1)-N(5)-N(6)-C(9)	-175.52(14)
C(7)-N(5)-N(6)-B(1)	176.11(18)
Ni(1)-N(5)-N(6)-B(1)	-0.1(2)
N(2)-N(1)-C(1)-C(2)	0.5(2)
Ni(1)-N(1)-C(1)-C(2)	173.54(15)
N(1)-C(1)-C(2)-C(3)	-0.6(2)
N(1)-N(2)-C(3)-C(2)	-0.2(2)
B(1)-N(2)-C(3)-C(2)	-171.6(2)
C(1)-C(2)-C(3)-N(2)	0.4(2)
N(4)-N(3)-C(4)-C(5)	0.4(2)
Ni(1)-N(3)-C(4)-C(5)	-168.62(16)
N(3)-C(4)-C(5)-C(6)	0.0(3)
N(3)-N(4)-C(6)-C(5)	0.6(2)
B(1)-N(4)-C(6)-C(5)	169.4(2)
C(4)-C(5)-C(6)-N(4)	-0.4(2)
N(6)-N(5)-C(7)-C(8)	-0.5(2)
Ni(1)-N(5)-C(7)-C(8)	174.68(16)
N(5)-C(7)-C(8)-C(9)	0.1(2)
N(5)-N(6)-C(9)-C(8)	-0.6(2)
B(1)-N(6)-C(9)-C(8)	-175.3(2)
C(7)-C(8)-C(9)-N(6)	0.3(2)
C(15)-C(10)-C(11)-C(12)	3.2(3)
Ni(1)-C(10)-C(11)-C(12)	-171.89(17)
C(10)-C(11)-C(12)-C(13)	-1.0(4)
C(11)-C(12)-C(13)-C(14)	-1.2(4)
C(12)-C(13)-C(14)-C(15)	1.0(4)
C(13)-C(14)-C(15)-C(10)	1.3(3)
C(13)-C(14)-C(15)-C(16)	-173.6(2)
C(11)-C(10)-C(15)-C(14)	-3.4(3)
Ni(1)-C(10)-C(15)-C(14)	172.26(17)

C(11)-C(10)-C(15)-C(16)	172.17(19)
Ni(1)-C(10)-C(15)-C(16)	-12.2(2)
C(14)-C(15)-C(16)-C(17)	0.2(4)
C(10)-C(15)-C(16)-C(17)	-175.0(2)
C(14)-C(15)-C(16)-C(21)	174.7(2)
C(10)-C(15)-C(16)-C(21)	-0.5(3)
C(21)-C(16)-C(17)-C(18)	-5.7(3)
C(15)-C(16)-C(17)-C(18)	168.4(2)
C(16)-C(17)-C(18)-C(19)	0.4(3)
C(17)-C(18)-C(19)-C(20)	3.9(3)
C(18)-C(19)-C(20)-C(21)	-2.7(3)
C(19)-C(20)-C(21)-C(16)	-2.6(3)
C(19)-C(20)-C(21)-Ni(1)	176.05(16)
C(17)-C(16)-C(21)-C(20)	6.8(3)
C(15)-C(16)-C(21)-C(20)	-168.18(19)
C(17)-C(16)-C(21)-Ni(1)	-171.96(16)
C(15)-C(16)-C(21)-Ni(1)	13.0(2)
C(6)-N(4)-B(1)-N(6)	135.5(2)
N(3)-N(4)-B(1)-N(6)	-56.6(2)
C(6)-N(4)-B(1)-N(2)	-108.6(2)
N(3)-N(4)-B(1)-N(2)	59.3(2)
C(9)-N(6)-B(1)-N(4)	-129.4(2)
N(5)-N(6)-B(1)-N(4)	56.4(2)
C(9)-N(6)-B(1)-N(2)	115.8(2)
N(5)-N(6)-B(1)-N(2)	-58.4(2)
C(3)-N(2)-B(1)-N(4)	112.8(2)
N(1)-N(2)-B(1)-N(4)	-58.0(2)
C(3)-N(2)-B(1)-N(6)	-129.6(2)
N(1)-N(2)-B(1)-N(6)	59.7(2)

Structure Determination of 2c





2c

Purple plates of **2c** were grown from a pentane/diethyl ether (containing a 1 drop of acetonitrile) solution of the compound at 23 ºC. A crystal of dimensions 0.14 x 0.12 x 0.12 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 (λ = 1.54187 A) 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. The integration of the data yielded a total of 24861 reflections to a maximum 2θ value of 136.46° of which 3099 were independent and 3064 were greater than 2σ(I). The final cell constants (Table S13) were based on the xyz centroids 16173 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group Pna2(1) with Z = 4 for the formula $C_{13}H_{13}BN_7F_6Ni$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0263 and wR2 = 0.0636 [based on I > 2sigma(I)], R1 = 0.0266 and wR2 = 0.0638 for all data. Additional details are presented in Table S13 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. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.

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

Table S13. Crystal Data and Structural Refinement for **2c**

Empirical Formula	$C_{13}H_{13}BF_6N_7Ni$
Formula Weight	450.82
Temperature	85(2) K
Wavelength	1.54178 A
Crystal System	Orthorhombic
Space Group	Pna2(1)
Unit Cell Dimensions	a = 17.0516(1) A alpha = 90 deg. b =7.53680(13) A beta = 90 deg c = 13.2536(2) A gamma = 90 deg.
Volume	1703.28(1) A^3
Z	4
Calculated Density	1.758 mg/m^3
Absorption Coefficient	2.390 mm^{-1}
F(000)	908
Crystal Size	0.20 x 0.14 x 0.12 mm
Theta Range for Data Collection	5.19 to 68.23 deg
Limiting Indicies	$-20\leq h\leq 20$, $-9\leq k\leq 9$, $-15\leq l\leq 15$
Reflections Collected	24861
Independent Reflections	3099 [R(int) = 0.0499]
Completeness to Theta	68.23 (100%)
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	0.7366 and 0.6464
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	3099 / 1 / 259
Goodness-of-Fit on F^2	1.183
Final R Indices [$I>2\sigma(I)$]	R1 = 0.0262, wR2 = 0.0636
R indices (all data)	R1 = 0.0266, wR2 = 0.0638
Largest Difference Peak and Hole	0.260 and -0.240 $e.A^{-3}$

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **2c.**

U_{eq} is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U_{eq}
Ni(1)	3781(1)	5526(1)	5221(1)	10(1)
F(1)	4278(1)	6250(2)	7224(1)	19(1)
F(2)	3987(1)	8558(2)	6359(1)	23(1)
F(3)	5079(1)	7227(2)	6098(1)	24(1)
F(4)	4389(1)	2136(2)	5149(1)	23(1)
F(5)	5208(1)	4122(2)	4641(1)	24(1)
F(6)	5020(1)	3678(2)	6232(1)	26(1)
N(1)	3371(1)	4185(3)	4045(2)	12(1)
N(2)	2607(1)	3666(2)	4038(2)	12(1)
N(3)	2351(1)	3582(3)	5894(2)	12(1)
N(4)	3095(1)	3990(3)	6213(2)	12(1)
N(5)	2126(1)	6344(2)	4929(1)	11(1)
N(6)	2843(1)	7140(2)	5078(1)	12(1)
N(7)	4366(1)	7262(3)	4127(2)	16(1)
C(1)	3692(1)	3647(3)	3173(2)	16(1)
C(2)	3131(2)	2746(3)	2602(2)	18(1)
C(3)	2454(2)	2793(3)	3168(2)	17(1)
C(4)	1982(1)	2621(3)	6615(2)	15(1)
C(5)	2489(2)	2398(4)	7409(2)	19(1)
C(6)	3180(2)	3271(3)	7122(2)	17(1)
C(7)	1578(1)	7599(3)	4782(2)	14(1)
C(8)	1933(1)	9249(3)	4824(2)	16(1)
C(9)	2721(1)	8888(3)	5012(2)	15(1)
C(10)	4304(1)	6923(3)	6269(2)	14(1)
C(11)	4643(1)	3816(3)	5336(2)	16(1)
C(12)	4599(1)	8324(3)	3596(2)	16(1)
C(13)	4906(2)	9673(3)	2922(2)	27(1)
B(1)	2060(2)	4311(3)	4888(2)	12(1)

Table S15. Bond lengths [Å] and angles [deg] for **2c**

Ni(1)-C(10)	1.958(3)
Ni(1)-C(11)	1.961(2)
Ni(1)-N(1)	1.985(2)
Ni(1)-N(6)	2.0179(18)
Ni(1)-N(4)	2.107(2)
Ni(1)-N(7)	2.193(2)
F(1)-C(10)	1.364(3)
F(2)-C(10)	1.351(3)
F(3)-C(10)	1.360(3)
F(4)-C(11)	1.361(3)
F(5)-C(11)	1.353(3)
F(6)-C(11)	1.354(3)
N(1)-C(1)	1.341(3)
N(1)-N(2)	1.360(3)
N(2)-C(3)	1.353(3)
N(2)-B(1)	1.542(3)
N(3)-C(4)	1.354(3)
N(3)-N(4)	1.371(3)
N(3)-B(1)	1.525(3)
N(4)-C(6)	1.329(3)
N(5)-C(7)	1.344(3)
N(5)-N(6)	1.376(2)
N(5)-B(1)	1.537(3)
N(6)-C(9)	1.337(3)
N(7)-C(12)	1.137(3)
C(1)-C(2)	1.395(4)
C(1)-H(1)	0.9500
C(2)-C(3)	1.376(4)
C(2)-H(2)	0.9500
C(3)-H(3)	0.9500
C(4)-C(5)	1.372(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.402(4)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500

C(7)-C(8)	1.385(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.394(3)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(12)-C(13)	1.451(3)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
B(1)-H(1A)	1.11(3)

C(10)-Ni(1)-C(11)	87.51(10)
C(10)-Ni(1)-N(1)	172.49(9)
C(11)-Ni(1)-N(1)	89.47(9)
C(10)-Ni(1)-N(6)	95.93(9)
C(11)-Ni(1)-N(6)	175.93(9)
N(1)-Ni(1)-N(6)	87.38(8)
C(10)-Ni(1)-N(4)	96.05(9)
C(11)-Ni(1)-N(4)	90.38(9)
N(1)-Ni(1)-N(4)	90.84(8)
N(6)-Ni(1)-N(4)	87.10(7)
C(10)-Ni(1)-N(7)	86.64(8)
C(11)-Ni(1)-N(7)	95.90(9)
N(1)-Ni(1)-N(7)	86.84(8)
N(6)-Ni(1)-N(7)	86.50(8)
N(4)-Ni(1)-N(7)	173.28(8)
C(1)-N(1)-N(2)	107.32(19)
C(1)-N(1)-Ni(1)	133.40(16)
N(2)-N(1)-Ni(1)	119.27(15)
C(3)-N(2)-N(1)	109.26(19)
C(3)-N(2)-B(1)	131.3(2)
N(1)-N(2)-B(1)	118.97(18)
C(4)-N(3)-N(4)	109.35(19)
C(4)-N(3)-B(1)	131.2(2)
N(4)-N(3)-B(1)	119.37(18)
C(6)-N(4)-N(3)	106.85(19)
C(6)-N(4)-Ni(1)	136.79(17)
N(3)-N(4)-Ni(1)	116.36(14)
C(7)-N(5)-N(6)	109.42(17)
C(7)-N(5)-B(1)	130.14(19)
N(6)-N(5)-B(1)	120.33(17)
C(9)-N(6)-N(5)	106.37(17)

C(9)-N(6)-Ni(1)	136.34(15)
N(5)-N(6)-Ni(1)	117.06(13)
C(12)-N(7)-Ni(1)	171.0(2)
N(1)-C(1)-C(2)	109.5(2)
N(1)-C(1)-H(1)	125.2
C(2)-C(1)-H(1)	125.2
C(3)-C(2)-C(1)	105.5(2)
C(3)-C(2)-H(2)	127.3
C(1)-C(2)-H(2)	127.3
N(2)-C(3)-C(2)	108.4(2)
N(2)-C(3)-H(3)	125.8
C(2)-C(3)-H(3)	125.8
N(3)-C(4)-C(5)	108.3(2)
N(3)-C(4)-H(4)	125.8
C(5)-C(4)-H(4)	125.8
C(4)-C(5)-C(6)	105.3(2)
C(4)-C(5)-H(5)	127.4
C(6)-C(5)-H(5)	127.4
N(4)-C(6)-C(5)	110.2(2)
N(4)-C(6)-H(6)	124.9
C(5)-C(6)-H(6)	124.9
N(5)-C(7)-C(8)	108.76(19)
N(5)-C(7)-H(7)	125.6
C(8)-C(7)-H(7)	125.6
C(7)-C(8)-C(9)	104.7(2)
C(7)-C(8)-H(8)	127.6
C(9)-C(8)-H(8)	127.6
N(6)-C(9)-C(8)	110.7(2)
N(6)-C(9)-H(9)	124.6
C(8)-C(9)-H(9)	124.6
F(2)-C(10)-F(3)	104.47(18)
F(2)-C(10)-F(1)	104.13(19)
F(3)-C(10)-F(1)	104.43(18)
F(2)-C(10)-Ni(1)	111.77(15)
F(3)-C(10)-Ni(1)	114.49(17)
F(1)-C(10)-Ni(1)	116.33(16)
F(5)-C(11)-F(6)	105.83(18)
F(5)-C(11)-F(4)	105.10(19)
F(6)-C(11)-F(4)	103.81(18)
F(5)-C(11)-Ni(1)	111.63(16)
F(6)-C(11)-Ni(1)	118.36(17)

F(4)-C(11)-Ni(1)	111.04(14)
N(7)-C(12)-C(13)	179.3(3)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
N(3)-B(1)-N(5)	107.74(18)
N(3)-B(1)-N(2)	109.13(19)
N(5)-B(1)-N(2)	107.16(17)
N(3)-B(1)-H(1A)	113.1(16)
N(5)-B(1)-H(1A)	109.4(15)
N(2)-B(1)-H(1A)	110.1(15)

Table S16. Anisotropic displacement parameters ($A^2 \times 10^3$) for **2c.**

The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ni(1)	9(1)	13(1)	9(1)	1(1)	0(1)	-1(1)
F(1)	18(1)	28(1)	11(1)	0(1)	-2(1)	-3(1)
F(2)	28(1)	17(1)	24(1)	-6(1)	-8(1)	-1(1)
F(3)	13(1)	39(1)	19(1)	-3(1)	2(1)	-10(1)
F(4)	24(1)	15(1)	30(1)	4(1)	-3(1)	3(1)
F(5)	15(1)	29(1)	30(1)	2(1)	9(1)	4(1)
F(6)	24(1)	33(1)	21(1)	0(1)	-11(1)	11(1)
N(1)	11(1)	14(1)	12(1)	1(1)	0(1)	0(1)
N(2)	12(1)	12(1)	12(1)	0(1)	0(1)	-2(1)
N(3)	12(1)	14(1)	10(1)	1(1)	0(1)	-4(1)
N(4)	9(1)	16(1)	12(1)	1(1)	-1(1)	0(1)
N(5)	7(1)	14(1)	12(1)	-1(1)	0(1)	0(1)
N(6)	11(1)	12(1)	13(1)	-1(1)	0(1)	-4(1)
N(7)	14(1)	20(1)	15(1)	2(1)	2(1)	-3(1)
C(1)	20(1)	17(1)	11(1)	0(1)	4(1)	3(1)
C(2)	25(1)	18(1)	11(1)	-4(1)	-4(1)	4(1)
C(3)	22(1)	17(1)	11(1)	-4(1)	-6(1)	-3(1)
C(4)	15(1)	14(1)	15(1)	2(1)	4(1)	-6(1)
C(5)	24(1)	22(1)	12(1)	2(1)	3(1)	-4(1)
C(6)	20(1)	19(1)	11(1)	2(1)	-1(1)	-2(1)
C(7)	10(1)	21(1)	12(1)	0(1)	0(1)	4(1)
C(8)	19(1)	16(1)	14(1)	0(1)	0(1)	4(1)
C(9)	16(1)	14(1)	15(1)	-2(1)	0(1)	1(1)
C(10)	10(1)	21(1)	12(1)	3(1)	-2(1)	-3(1)
C(11)	15(1)	20(1)	14(1)	1(1)	1(1)	0(1)
C(12)	13(1)	19(1)	17(1)	-1(1)	-1(1)	3(1)
C(13)	35(2)	18(1)	28(2)	8(1)	12(1)	0(1)
B(1)	10(1)	14(1)	11(1)	-1(1)	0(1)	-3(1)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **2c.**

	x	y	z	U(eq)
H(1)	4219	3849	2974	19
H(2)	3201	2212	1959	22
H(3)	1963	2296	2980	20
H(4)	1462	2178	6578	18
H(5)	2393	1784	8022	23
H(6)	3643	3338	7519	20
H(7)	1035	7388	4669	17
H(8)	1693	10378	4742	19
H(9)	3118	9765	5083	18
H(13A)	5128	10648	3319	40
H(13B)	4482	10126	2495	40
H(13C)	5317	9155	2496	40
H(1A)	1446(17)	3930(40)	4720(20)	18(7)

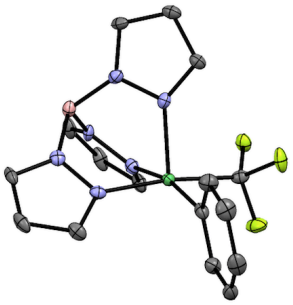
Table S18. Torsion angles [deg] for **2c.**

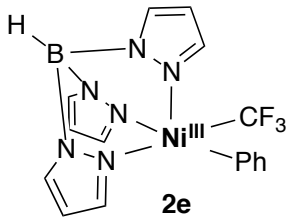
C(10)-Ni(1)-N(1)-C(1)	12.6(8)
C(11)-Ni(1)-N(1)-C(1)	-53.7(2)
N(6)-Ni(1)-N(1)-C(1)	128.9(2)
N(4)-Ni(1)-N(1)-C(1)	-144.0(2)
N(7)-Ni(1)-N(1)-C(1)	42.3(2)
C(10)-Ni(1)-N(1)-N(2)	-166.0(6)
C(11)-Ni(1)-N(1)-N(2)	127.76(17)
N(6)-Ni(1)-N(1)-N(2)	-49.66(16)
N(4)-Ni(1)-N(1)-N(2)	37.39(16)
N(7)-Ni(1)-N(1)-N(2)	-136.30(17)
C(1)-N(1)-N(2)-C(3)	0.6(3)
Ni(1)-N(1)-N(2)-C(3)	179.49(15)
C(1)-N(1)-N(2)-B(1)	-172.26(19)
Ni(1)-N(1)-N(2)-B(1)	6.6(3)
C(4)-N(3)-N(4)-C(6)	0.5(3)
B(1)-N(3)-N(4)-C(6)	176.8(2)
C(4)-N(3)-N(4)-Ni(1)	-179.03(15)
B(1)-N(3)-N(4)-Ni(1)	-2.7(2)
C(10)-Ni(1)-N(4)-C(6)	-36.0(3)
C(11)-Ni(1)-N(4)-C(6)	51.5(2)
N(1)-Ni(1)-N(4)-C(6)	141.0(2)
N(6)-Ni(1)-N(4)-C(6)	-131.7(2)
N(7)-Ni(1)-N(4)-C(6)	-149.3(6)
C(10)-Ni(1)-N(4)-N(3)	143.25(16)
C(11)-Ni(1)-N(4)-N(3)	-129.22(17)
N(1)-Ni(1)-N(4)-N(3)	-39.75(15)
N(6)-Ni(1)-N(4)-N(3)	47.59(16)
N(7)-Ni(1)-N(4)-N(3)	29.9(8)
C(7)-N(5)-N(6)-C(9)	-0.5(2)
B(1)-N(5)-N(6)-C(9)	176.10(19)
C(7)-N(5)-N(6)-Ni(1)	-175.87(14)
B(1)-N(5)-N(6)-Ni(1)	0.7(2)
C(10)-Ni(1)-N(6)-C(9)	44.8(2)
C(11)-Ni(1)-N(6)-C(9)	-167.7(13)
N(1)-Ni(1)-N(6)-C(9)	-128.4(2)
N(4)-Ni(1)-N(6)-C(9)	140.6(2)
N(7)-Ni(1)-N(6)-C(9)	-41.4(2)
C(10)-Ni(1)-N(6)-N(5)	-141.58(16)
C(11)-Ni(1)-N(6)-N(5)	5.9(14)
N(1)-Ni(1)-N(6)-N(5)	45.18(15)

N(4)-Ni(1)-N(6)-N(5)	-45.79(15)
N(7)-Ni(1)-N(6)-N(5)	132.17(15)
C(10)-Ni(1)-N(7)-C(12)	-74.9(13)
C(11)-Ni(1)-N(7)-C(12)	-162.1(13)
N(1)-Ni(1)-N(7)-C(12)	108.8(13)
N(6)-Ni(1)-N(7)-C(12)	21.2(13)
N(4)-Ni(1)-N(7)-C(12)	38.9(17)
N(2)-N(1)-C(1)-C(2)	-0.9(3)
Ni(1)-N(1)-C(1)-C(2)	-179.61(17)
N(1)-C(1)-C(2)-C(3)	0.9(3)
N(1)-N(2)-C(3)-C(2)	0.0(3)
B(1)-N(2)-C(3)-C(2)	171.6(2)
C(1)-C(2)-C(3)-N(2)	-0.5(3)
N(4)-N(3)-C(4)-C(5)	-0.2(3)
B(1)-N(3)-C(4)-C(5)	-176.0(2)
N(3)-C(4)-C(5)-C(6)	-0.2(3)
N(3)-N(4)-C(6)-C(5)	-0.6(3)
Ni(1)-N(4)-C(6)-C(5)	178.74(18)
C(4)-C(5)-C(6)-N(4)	0.5(3)
N(6)-N(5)-C(7)-C(8)	0.6(3)
B(1)-N(5)-C(7)-C(8)	-175.5(2)
N(5)-C(7)-C(8)-C(9)	-0.5(3)
N(5)-N(6)-C(9)-C(8)	0.2(3)
Ni(1)-N(6)-C(9)-C(8)	174.24(18)
C(7)-C(8)-C(9)-N(6)	0.2(3)
C(11)-Ni(1)-C(10)-F(2)	168.36(17)
N(1)-Ni(1)-C(10)-F(2)	102.0(7)
N(6)-Ni(1)-C(10)-F(2)	-13.83(17)
N(4)-Ni(1)-C(10)-F(2)	-101.53(16)
N(7)-Ni(1)-C(10)-F(2)	72.30(16)
C(11)-Ni(1)-C(10)-F(3)	49.83(17)
N(1)-Ni(1)-C(10)-F(3)	-16.5(8)
N(6)-Ni(1)-C(10)-F(3)	-132.36(16)
N(4)-Ni(1)-C(10)-F(3)	139.95(17)
N(7)-Ni(1)-C(10)-F(3)	-46.23(16)
C(11)-Ni(1)-C(10)-F(1)	-72.24(17)
N(1)-Ni(1)-C(10)-F(1)	-138.6(6)
N(6)-Ni(1)-C(10)-F(1)	105.57(17)
N(4)-Ni(1)-C(10)-F(1)	17.88(17)
N(7)-Ni(1)-C(10)-F(1)	-168.30(18)
C(10)-Ni(1)-C(11)-F(5)	-95.17(17)

N(1)-Ni(1)-C(11)-F(5)	77.95(16)
N(6)-Ni(1)-C(11)-F(5)	117.2(13)
N(4)-Ni(1)-C(11)-F(5)	168.79(16)
N(7)-Ni(1)-C(11)-F(5)	-8.81(17)
C(10)-Ni(1)-C(11)-F(6)	28.02(18)
N(1)-Ni(1)-C(11)-F(6)	-158.86(17)
N(6)-Ni(1)-C(11)-F(6)	-119.6(13)
N(4)-Ni(1)-C(11)-F(6)	-68.02(17)
N(7)-Ni(1)-C(11)-F(6)	114.38(17)
C(10)-Ni(1)-C(11)-F(4)	147.90(18)
N(1)-Ni(1)-C(11)-F(4)	-38.97(17)
N(6)-Ni(1)-C(11)-F(4)	0.3(15)
N(4)-Ni(1)-C(11)-F(4)	51.86(17)
N(7)-Ni(1)-C(11)-F(4)	-125.74(17)
Ni(1)-N(7)-C(12)-C(13)	137(22)
C(4)-N(3)-B(1)-N(5)	118.5(3)
N(4)-N(3)-B(1)-N(5)	-57.0(3)
C(4)-N(3)-B(1)-N(2)	-125.5(3)
N(4)-N(3)-B(1)-N(2)	59.0(2)
C(7)-N(5)-B(1)-N(3)	-124.3(2)
N(6)-N(5)-B(1)-N(3)	59.9(2)
C(7)-N(5)-B(1)-N(2)	118.4(2)
N(6)-N(5)-B(1)-N(2)	-57.4(3)
C(3)-N(2)-B(1)-N(3)	125.8(2)
N(1)-N(2)-B(1)-N(3)	-63.2(2)
C(3)-N(2)-B(1)-N(5)	-117.8(2)
N(1)-N(2)-B(1)-N(5)	53.2(3)

Structure Determination of 2e





2e

Green block-like crystals of **2e** were grown from a diisopropyl ether/pentane solution of the compound at –35 ºC. A crystal of dimensions 0.20 x 0.18 x 0.18 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 (λ = 1.54187 A) 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. The integration of the data yielded a total of 51388 reflections to a maximum 2θ value of 136.45° of which 6411 were independent and 6372 were greater than 2σ(I). The final cell constants (Table S19) were based on the xyz centroids 42847 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group Pca2(1) with Z = 8 for the formula $C_{16}H_{15}BN_6F_3Ni$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in both idealized and refined positions. The structure was refined as a two-component inversion twin. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0440 and wR2 = 0.1094 [based on I > 2sigma(I)], R1 = 0.0442 and wR2 = 0.1096 for all data. Additional details are presented in Table S18 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Table S19. Crystal Data and Structural Refinement for **2e**

Empirical Formula	$C_{16}H_{15}BF_3N_6Ni$
Formula Weight	417.86
Temperature	85(2) K
Wavelength	1.54178 A
Crystal System	Orthorhombic
Space Group	PCa2(1)
Unit Cell Dimensions	a = 20.4982(1) A alpha = 90 deg. b =10.1199(13) A beta = 90 deg c = 17.0418(2) A gamma = 90 deg.
Volume	3535.1(1) A^3
Z	8
Calculated Density	1.570 Mg/m^3
Absorption Coefficient	1.987 mm^{-1}
F(000)	1704
Crystal Size	0.20 x 0.18 x 0.18 mm
Theta Range for Data Collection	4.314 to 68.223 deg
Limiting Indicies	$-24\leq h\leq 24$, $-10\leq k\leq 11$, $-20\leq l\leq 20$
Reflections Collected	51388
Independent Reflections	6411 [R(int) = 0.0463]
Completeness to Theta	67.679 /99.6
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	0.7366 and 0.6464
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	6411 / 1 / 497
Goodness-of-Fit on F^2	1.063
Final R Indices [$I>2\sigma(I)$]	R1 = 0.0440, wR2 = 0.1094
R indices (all data)	R1 = 0.0442, wR2 = 0.1096
Largest Difference Peak and Hole	1.550 and -0.670 $e.A^{-3}$

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **2e.**

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Ni(1)	7115(1)	-328(1)	4632(1)	12(1)
Ni(2)	5308(1)	4730(1)	5443(1)	12(1)
F(1)	8287(1)	241(3)	3936(2)	18(1)
F(2)	7630(1)	-596(3)	3097(2)	24(1)
F(3)	7494(1)	1421(3)	3487(2)	27(1)
F(4)	4796(1)	4444(3)	6978(2)	23(1)
F(5)	4149(1)	5349(3)	6157(2)	18(1)
F(6)	4960(1)	6462(3)	6611(2)	22(1)
N(1)	6482(2)	-704(4)	5470(2)	14(1)
N(2)	6717(2)	-1195(4)	6159(2)	15(1)
N(3)	7556(2)	-2088(4)	4801(2)	14(1)
N(4)	7656(2)	-2445(4)	5564(2)	14(1)
N(5)	7808(2)	-171(4)	6118(2)	14(1)
N(6)	7701(2)	511(4)	5438(2)	15(1)
N(7)	4748(2)	5677(4)	4663(2)	15(1)
N(8)	4637(2)	5069(4)	3966(2)	13(1)
N(9)	4735(2)	2746(4)	4442(2)	12(1)
N(10)	4828(2)	3030(4)	5219(2)	12(1)
N(11)	5701(2)	3956(4)	3892(2)	14(1)
N(12)	5937(2)	4370(4)	4600(2)	14(1)
C(1)	5842(2)	-497(4)	5559(3)	18(1)
C(2)	5658(2)	-839(5)	6325(3)	21(1)
C(3)	6224(2)	-1281(4)	6682(3)	18(1)
C(4)	7844(2)	-3012(4)	4363(3)	15(1)
C(5)	8137(2)	-3960(4)	4834(3)	17(1)
C(6)	8008(2)	-3562(4)	5592(3)	16(1)
C(7)	8209(2)	518(5)	6582(3)	19(1)
C(8)	8372(2)	1668(5)	6208(3)	21(1)
C(9)	8041(2)	1638(5)	5491(3)	19(1)
C(10)	6450(2)	-687(5)	3870(3)	16(1)
C(11)	6279(2)	-1970(5)	3658(3)	21(1)

C(12)	5735(2)	−2173(5)	3185(3)	25(1)
C(13)	5365(2)	−1119(5)	2918(3)	24(1)
C(14)	5545(2)	154(5)	3129(3)	21(1)
C(15)	6086(2)	376(5)	3602(3)	17(1)
C(16)	7638(2)	185(4)	3748(3)	16(1)
C(17)	4436(2)	6837(4)	4636(3)	17(1)
C(18)	4115(2)	6981(5)	3922(3)	20(1)
C(19)	4255(2)	5836(5)	3510(3)	18(1)
C(20)	4387(2)	1613(4)	4380(3)	16(1)
C(21)	4256(2)	1139(4)	5130(3)	15(1)
C(22)	4539(2)	2069(4)	5632(2)	14(1)
C(23)	6195(2)	3901(4)	3370(3)	18(1)
C(24)	6760(2)	4264(5)	3742(3)	20(1)
C(25)	6579(2)	4545(4)	4508(3)	16(1)
C(26)	5962(2)	4205(4)	6189(3)	13(1)
C(27)	6095(2)	2886(4)	6343(3)	17(1)
C(28)	6640(2)	2551(5)	6785(3)	20(1)
C(29)	7051(2)	3526(5)	7078(3)	20(1)
C(30)	6915(2)	4837(5)	6938(3)	16(1)
C(31)	6368(2)	5180(5)	6491(3)	17(1)
C(32)	4793(2)	5227(4)	6344(3)	14(1)
B(1)	7454(2)	−1511(5)	6239(3)	16(1)
B(2)	4954(2)	3721(5)	3802(3)	14(1)

Table S21. Bond lengths [Å] and angles [deg] for **2e.**

Ni(1)-C(10)	1.917(5)
Ni(1)-C(16)	1.920(5)
Ni(1)-N(1)	1.967(4)
Ni(1)-N(6)	2.014(4)
Ni(1)-N(3)	2.019(4)
Ni(2)-C(26)	1.922(4)
Ni(2)-C(32)	1.931(5)
Ni(2)-N(12)	1.964(4)
Ni(2)-N(7)	2.001(4)
Ni(2)-N(10)	2.018(4)
F(1)-C(16)	1.368(5)
F(2)-C(16)	1.363(5)
F(3)-C(16)	1.360(5)
F(4)-C(32)	1.340(5)
F(5)-C(32)	1.364(5)
F(6)-C(32)	1.373(5)
N(1)-C(1)	1.337(6)
N(1)-N(2)	1.362(5)
N(2)-C(3)	1.351(6)
N(2)-B(1)	1.550(6)
N(3)-C(4)	1.334(6)
N(3)-N(4)	1.365(5)
N(4)-C(6)	1.342(6)
N(4)-B(1)	1.544(6)
N(5)-C(7)	1.337(6)
N(5)-N(6)	1.366(6)
N(5)-B(1)	1.551(6)
N(6)-C(9)	1.339(6)
N(7)-C(17)	1.338(6)
N(7)-N(8)	1.356(6)
N(8)-C(19)	1.350(6)
N(8)-B(2)	1.538(6)
N(9)-C(20)	1.355(6)
N(9)-N(10)	1.369(5)
N(9)-B(2)	1.537(6)
N(10)-C(22)	1.339(6)
N(11)-C(23)	1.350(6)
N(11)-N(12)	1.367(5)

N(11)-B(2)	1.556(6)
N(12)-C(25)	1.335(6)
C(1)-C(2)	1.403(7)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.385(7)
C(2)-H(2A)	0.9500
C(3)-H(3A)	0.9500
C(4)-C(5)	1.387(6)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.379(7)
C(5)-H(5A)	0.9500
C(6)-H(6A)	0.9500
C(7)-C(8)	1.368(7)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.399(7)
C(8)-H(8A)	0.9500
C(9)-H(9A)	0.9500
C(10)-C(15)	1.386(7)
C(10)-C(11)	1.392(7)
C(11)-C(12)	1.392(7)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.386(8)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.388(8)
C(13)-H(13A)	0.9500
C(14)-C(15)	1.390(7)
C(14)-H(14A)	0.9500
C(15)-H(15A)	0.9500
C(17)-C(18)	1.391(7)
C(17)-H(17A)	0.9500
C(18)-C(19)	1.385(7)
C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9500
C(20)-C(21)	1.391(6)
C(20)-H(20A)	0.9500
C(21)-C(22)	1.397(6)
C(21)-H(21A)	0.9500
C(22)-H(22A)	0.9500
C(23)-C(24)	1.370(7)
C(23)-H(23A)	0.9500
C(24)-C(25)	1.387(7)
C(24)-H(24A)	0.9500

C(25)-H(25A)	0.9500
C(26)-C(27)	1.387(6)
C(26)-C(31)	1.390(6)
C(27)-C(28)	1.389(6)
C(27)-H(27A)	0.9500
C(28)-C(29)	1.390(7)
C(28)-H(28A)	0.9500
C(29)-C(30)	1.376(7)
C(29)-H(29A)	0.9500
C(30)-C(31)	1.400(7)
C(30)-H(30A)	0.9500
C(31)-H(31A)	0.9500
B(1)-H(1B)	1.07(6)
B(2)-H(2B)	1.10(5)

C(10)-Ni(1)-C(16)	85.31(19)
C(10)-Ni(1)-N(1)	89.23(16)
C(16)-Ni(1)-N(1)	172.07(17)
C(10)-Ni(1)-N(6)	165.19(17)
C(16)-Ni(1)-N(6)	95.00(17)
N(1)-Ni(1)-N(6)	88.81(15)
C(10)-Ni(1)-N(3)	104.34(17)
C(16)-Ni(1)-N(3)	95.76(17)
N(1)-Ni(1)-N(3)	91.15(15)
N(6)-Ni(1)-N(3)	90.38(15)
C(26)-Ni(2)-C(32)	85.78(19)
C(26)-Ni(2)-N(12)	88.59(16)
C(32)-Ni(2)-N(12)	171.50(17)
C(26)-Ni(2)-N(7)	166.39(17)
C(32)-Ni(2)-N(7)	95.14(17)
N(12)-Ni(2)-N(7)	88.84(15)
C(26)-Ni(2)-N(10)	103.25(17)
C(32)-Ni(2)-N(10)	96.10(16)
N(12)-Ni(2)-N(10)	91.38(15)
N(7)-Ni(2)-N(10)	90.17(15)
C(1)-N(1)-N(2)	107.9(4)
C(1)-N(1)-Ni(1)	134.3(3)
N(2)-N(1)-Ni(1)	117.6(3)
C(3)-N(2)-N(1)	109.1(4)
C(3)-N(2)-B(1)	131.1(4)
N(1)-N(2)-B(1)	119.7(3)

C(4)-N(3)-N(4)	106.3(3)
C(4)-N(3)-Ni(1)	137.5(3)
N(4)-N(3)-Ni(1)	115.9(3)
C(6)-N(4)-N(3)	109.7(4)
C(6)-N(4)-B(1)	129.3(4)
N(3)-N(4)-B(1)	120.4(3)
C(7)-N(5)-N(6)	109.7(4)
C(7)-N(5)-B(1)	131.7(4)
N(6)-N(5)-B(1)	118.6(4)
C(9)-N(6)-N(5)	106.8(4)
C(9)-N(6)-Ni(1)	135.6(3)
N(5)-N(6)-Ni(1)	117.5(3)
C(17)-N(7)-N(8)	106.7(4)
C(17)-N(7)-Ni(2)	135.9(3)
N(8)-N(7)-Ni(2)	117.4(3)
C(19)-N(8)-N(7)	110.0(4)
C(19)-N(8)-B(2)	130.6(4)
N(7)-N(8)-B(2)	119.4(4)
C(20)-N(9)-N(10)	109.0(3)
C(20)-N(9)-B(2)	130.0(4)
N(10)-N(9)-B(2)	120.7(3)
C(22)-N(10)-N(9)	107.1(3)
C(22)-N(10)-Ni(2)	137.4(3)
N(9)-N(10)-Ni(2)	115.5(3)
C(23)-N(11)-N(12)	109.1(3)
C(23)-N(11)-B(2)	131.9(4)
N(12)-N(11)-B(2)	118.9(3)
C(25)-N(12)-N(11)	106.7(4)
C(25)-N(12)-Ni(2)	135.0(3)
N(11)-N(12)-Ni(2)	118.0(3)
N(1)-C(1)-C(2)	109.3(4)
N(1)-C(1)-H(1A)	125.4
C(2)-C(1)-H(1A)	125.4
C(3)-C(2)-C(1)	105.3(4)
C(3)-C(2)-H(2A)	127.4
C(1)-C(2)-H(2A)	127.4
N(2)-C(3)-C(2)	108.4(4)
N(2)-C(3)-H(3A)	125.8
C(2)-C(3)-H(3A)	125.8
N(3)-C(4)-C(5)	110.7(4)
N(3)-C(4)-H(4A)	124.7
C(5)-C(4)-H(4A)	124.7

C(6)-C(5)-C(4)	104.9(4)
C(6)-C(5)-H(5A)	127.6
C(4)-C(5)-H(5A)	127.6
N(4)-C(6)-C(5)	108.4(4)
N(4)-C(6)-H(6A)	125.8
C(5)-C(6)-H(6A)	125.8
N(5)-C(7)-C(8)	108.5(4)
N(5)-C(7)-H(7A)	125.7
C(8)-C(7)-H(7A)	125.7
C(7)-C(8)-C(9)	105.7(4)
C(7)-C(8)-H(8A)	127.2
C(9)-C(8)-H(8A)	127.2
N(6)-C(9)-C(8)	109.3(4)
N(6)-C(9)-H(9A)	125.4
C(8)-C(9)-H(9A)	125.4
C(15)-C(10)-C(11)	120.3(4)
C(15)-C(10)-Ni(1)	117.2(3)
C(11)-C(10)-Ni(1)	122.1(4)
C(10)-C(11)-C(12)	119.3(5)
C(10)-C(11)-H(11A)	120.4
C(12)-C(11)-H(11A)	120.4
C(13)-C(12)-C(11)	121.0(5)
C(13)-C(12)-H(12A)	119.5
C(11)-C(12)-H(12A)	119.5
C(12)-C(13)-C(14)	118.9(4)
C(12)-C(13)-H(13A)	120.5
C(14)-C(13)-H(13A)	120.5
C(15)-C(14)-C(13)	120.9(4)
C(15)-C(14)-H(14A)	119.6
C(13)-C(14)-H(14A)	119.6
C(10)-C(15)-C(14)	119.6(4)
C(10)-C(15)-H(15A)	120.2
C(14)-C(15)-H(15A)	120.2
F(3)-C(16)-F(2)	105.3(4)
F(3)-C(16)-F(1)	104.4(3)
F(2)-C(16)-F(1)	103.1(4)
F(3)-C(16)-Ni(1)	112.6(3)
F(2)-C(16)-Ni(1)	118.3(3)
F(1)-C(16)-Ni(1)	111.8(3)
N(7)-C(17)-C(18)	110.4(4)
N(7)-C(17)-H(17A)	124.8

C(18)-C(17)-H(17A)	124.8
C(19)-C(18)-C(17)	105.0(4)
C(19)-C(18)-H(18A)	127.5
C(17)-C(18)-H(18A)	127.5
N(8)-C(19)-C(18)	107.9(4)
N(8)-C(19)-H(19A)	126.0
C(18)-C(19)-H(19A)	126.0
N(9)-C(20)-C(21)	108.8(4)
N(9)-C(20)-H(20A)	125.6
C(21)-C(20)-H(20A)	125.6
C(20)-C(21)-C(22)	104.5(4)
C(20)-C(21)-H(21A)	127.7
C(22)-C(21)-H(21A)	127.7
N(10)-C(22)-C(21)	110.6(4)
N(10)-C(22)-H(22A)	124.7
C(21)-C(22)-H(22A)	124.7
N(11)-C(23)-C(24)	108.6(4)
N(11)-C(23)-H(23A)	125.7
C(24)-C(23)-H(23A)	125.7
C(23)-C(24)-C(25)	105.3(4)
C(23)-C(24)-H(24A)	127.3
C(25)-C(24)-H(24A)	127.3
N(12)-C(25)-C(24)	110.3(4)
N(12)-C(25)-H(25A)	124.9
C(24)-C(25)-H(25A)	124.9
C(27)-C(26)-C(31)	119.7(4)
C(27)-C(26)-Ni(2)	121.9(3)
C(31)-C(26)-Ni(2)	117.8(3)
C(26)-C(27)-C(28)	119.8(4)
C(26)-C(27)-H(27A)	120.1
C(28)-C(27)-H(27A)	120.1
C(27)-C(28)-C(29)	120.5(4)
C(27)-C(28)-H(28A)	119.7
C(29)-C(28)-H(28A)	119.7
C(30)-C(29)-C(28)	120.0(4)
C(30)-C(29)-H(29A)	120.0
C(28)-C(29)-H(29A)	120.0
C(29)-C(30)-C(31)	119.7(4)
C(29)-C(30)-H(30A)	120.2
C(31)-C(30)-H(30A)	120.2
C(26)-C(31)-C(30)	120.4(4)
C(26)-C(31)-H(31A)	119.8

C(30)-C(31)-H(31A)	119.8
F(4)-C(32)-F(5)	104.2(3)
F(4)-C(32)-F(6)	105.7(3)
F(5)-C(32)-F(6)	103.6(3)
F(4)-C(32)-Ni(2)	119.0(3)
F(5)-C(32)-Ni(2)	111.5(3)
F(6)-C(32)-Ni(2)	111.4(3)
N(4)-B(1)-N(5)	108.1(3)
N(4)-B(1)-N(2)	108.7(3)
N(5)-B(1)-N(2)	105.3(4)
N(4)-B(1)-H(1B)	109(3)
N(5)-B(1)-H(1B)	121(3)
N(2)-B(1)-H(1B)	104(3)
N(8)-B(2)-N(9)	108.4(3)
N(8)-B(2)-N(11)	105.2(3)
N(9)-B(2)-N(11)	108.4(3)
N(8)-B(2)-H(2B)	113(3)
N(9)-B(2)-H(2B)	109(3)
N(11)-B(2)-H(2B)	112(3)

Table S22. Anisotropic displacement parameters ($A^2 \times 10^3$) for **2e**. The anisotropic displacement factor exponent takes the form:

$$-2\pi^2[\, h^2 a^{*2} U_{11} + ... + 2hka^* b^* U_{12} \,]$$

	U11	U22	U33	U23	U13	U12
Ni(1)	11(1)	13(1)	11(1)	-1(1)	0(1)	1(1)
Ni(2)	11(1)	14(1)	9(1)	0(1)	1(1)	3(1)
F(1)	13(1)	25(2)	17(1)	0(1)	1(1)	-2(1)
F(2)	24(2)	36(2)	12(1)	-7(1)	3(1)	-8(1)
F(3)	23(1)	20(1)	38(2)	14(1)	8(1)	5(1)
F(4)	25(1)	29(2)	16(1)	9(1)	5(1)	5(1)
F(5)	13(1)	25(2)	16(1)	-1(1)	3(1)	0(1)
F(6)	24(1)	18(1)	25(1)	-9(1)	5(1)	-4(1)
N(1)	14(2)	12(2)	17(2)	-2(2)	-1(2)	0(1)
N(2)	17(2)	11(2)	15(2)	-1(1)	1(1)	-2(1)
N(3)	15(2)	14(2)	12(2)	2(1)	0(1)	-2(1)
N(4)	13(2)	16(2)	14(2)	3(1)	0(1)	-1(1)
N(5)	16(2)	18(2)	7(2)	1(1)	0(1)	-1(1)
N(6)	13(2)	14(2)	16(2)	-1(2)	4(2)	-2(1)
N(7)	14(2)	14(2)	17(2)	-1(2)	-2(2)	2(1)
N(8)	15(2)	12(2)	12(2)	-1(1)	1(1)	0(1)
N(9)	13(2)	13(2)	9(2)	-1(1)	0(1)	-1(1)
N(10)	13(2)	12(2)	11(2)	-1(1)	0(1)	-2(1)
N(11)	14(2)	16(2)	12(2)	-1(1)	1(1)	-2(1)
N(12)	14(2)	14(2)	13(2)	-1(2)	-1(1)	2(1)
C(1)	12(2)	18(2)	24(2)	-4(2)	2(2)	-4(2)
C(2)	18(2)	17(2)	27(2)	-5(2)	12(2)	-5(2)
C(3)	23(2)	13(2)	18(2)	-2(2)	12(2)	-2(2)
C(4)	13(2)	15(2)	18(2)	-3(2)	1(2)	0(2)
C(5)	12(2)	14(2)	25(2)	-1(2)	2(2)	1(2)
C(6)	13(2)	13(2)	22(2)	5(2)	0(2)	2(2)
C(7)	13(2)	29(2)	14(2)	-4(2)	3(2)	-5(2)
C(8)	18(2)	28(2)	18(2)	-12(2)	4(2)	-10(2)
C(9)	19(2)	18(2)	19(2)	-3(2)	7(2)	-5(2)
C(10)	19(2)	15(2)	16(2)	-2(2)	6(2)	-1(2)
C(11)	18(2)	21(2)	24(2)	-1(2)	-2(2)	-1(2)
C(12)	23(2)	27(3)	25(2)	-7(2)	-5(2)	-7(2)
C(13)	14(2)	38(3)	21(2)	-5(2)	-4(2)	-4(2)

C(14)	17(2)	30(3)	15(2)	2(2)	1(2)	6(2)
C(15)	16(2)	18(2)	18(2)	-3(2)	-1(2)	0(2)
C(16)	14(2)	12(2)	21(2)	1(2)	-2(2)	-1(2)
C(17)	18(2)	15(2)	19(2)	2(2)	0(2)	7(2)
C(18)	18(2)	24(2)	19(2)	7(2)	2(2)	9(2)
C(19)	16(2)	25(2)	13(2)	5(2)	0(2)	3(2)
C(20)	11(2)	15(2)	22(2)	-3(2)	0(2)	0(2)
C(21)	13(2)	16(2)	17(2)	0(2)	3(2)	0(2)
C(22)	14(2)	14(2)	14(2)	2(2)	0(2)	2(2)
C(23)	24(2)	16(2)	14(2)	2(2)	7(2)	2(2)
C(24)	17(2)	21(2)	22(2)	-2(2)	5(2)	1(2)
C(25)	14(2)	17(2)	16(2)	0(2)	4(2)	0(2)
C(26)	12(2)	15(2)	14(2)	2(2)	1(2)	-1(2)
C(27)	15(2)	16(2)	20(2)	-1(2)	-2(2)	2(2)
C(28)	22(2)	15(2)	23(2)	-1(2)	-4(2)	7(2)
C(29)	15(2)	27(3)	19(2)	1(2)	-2(2)	4(2)
C(30)	16(2)	23(2)	11(2)	-2(2)	-1(2)	-7(2)
C(31)	23(2)	18(2)	11(2)	0(2)	4(2)	-2(2)
C(32)	17(2)	14(2)	9(2)	2(2)	0(2)	-4(2)
B(1)	15(2)	20(3)	11(2)	1(2)	1(2)	-2(2)
B(2)	12(2)	17(2)	14(2)	1(2)	0(2)	0(2)

Table S23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **2e**.

	x	y	z	U(eq)
H(1A)	5557	-169	5165	22
H(2A)	5235	-780	6551	25
H(3A)	6260	-1592	7206	22
H(4A)	7849	-3019	3806	18
H(5A)	8374	-4717	4670	20
H(6A)	8145	-4003	6056	19
H(7A)	8356	254	7087	23
H(8A)	8653	2345	6396	25
H(9A)	8054	2311	5103	22
H(11A)	6532	-2699	3834	25
H(12A)	5615	-3048	3043	30
H(13A)	4994	-1265	2595	29
H(14A)	5296	884	2948	25
H(15A)	6207	1252	3742	21
H(17A)	4434	7472	5046	21
H(18A)	3856	7706	3755	24
H(19A)	4107	5628	2996	22
H(20A)	4254	1208	3903	19
H(21A)	4027	359	5270	18
H(22A)	4527	2026	6189	17
H(23A)	6158	3653	2834	22
H(24A)	7185	4312	3522	24
H(25A)	6869	4823	4910	19
H(27A)	5815	2215	6147	20
H(28A)	6733	1647	6887	24
H(29A)	7425	3287	7374	24
H(30A)	7192	5506	7144	20
H(31A)	6273	6084	6394	21
H(1B)	7480(30)	-2030(60)	6780(40)	24(14)
H(2B)	4830(20)	3320(50)	3220(30)	14(12)

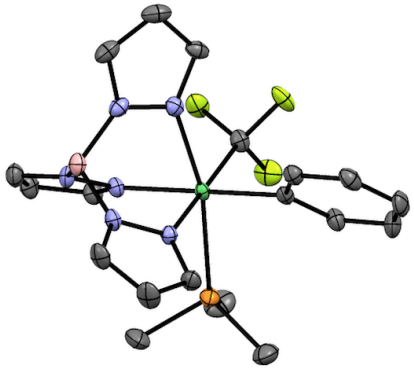
Table S24. Torsion angles [deg] for **2e.**

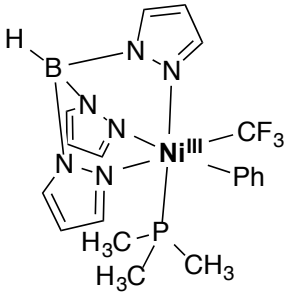
C(1)-N(1)-N(2)-C(3)	-0.7(5)
Ni(1)-N(1)-N(2)-C(3)	174.7(3)
C(1)-N(1)-N(2)-B(1)	-178.9(4)
Ni(1)-N(1)-N(2)-B(1)	-3.5(5)
C(4)-N(3)-N(4)-C(6)	0.8(4)
Ni(1)-N(3)-N(4)-C(6)	-173.9(3)
C(4)-N(3)-N(4)-B(1)	173.0(3)
Ni(1)-N(3)-N(4)-B(1)	-1.7(4)
C(7)-N(5)-N(6)-C(9)	-0.3(5)
B(1)-N(5)-N(6)-C(9)	177.8(4)
C(7)-N(5)-N(6)-Ni(1)	179.6(3)
B(1)-N(5)-N(6)-Ni(1)	-2.3(5)
C(17)-N(7)-N(8)-C(19)	-0.5(5)
Ni(2)-N(7)-N(8)-C(19)	-179.8(3)
C(17)-N(7)-N(8)-B(2)	177.8(4)
Ni(2)-N(7)-N(8)-B(2)	-1.5(5)
C(20)-N(9)-N(10)-C(22)	0.1(4)
B(2)-N(9)-N(10)-C(22)	174.6(3)
C(20)-N(9)-N(10)-Ni(2)	-177.7(3)
B(2)-N(9)-N(10)-Ni(2)	-3.2(5)
C(23)-N(11)-N(12)-C(25)	-1.0(5)
B(2)-N(11)-N(12)-C(25)	-177.5(4)
C(23)-N(11)-N(12)-Ni(2)	173.4(3)
B(2)-N(11)-N(12)-Ni(2)	-3.1(5)
N(2)-N(1)-C(1)-C(2)	1.0(5)
Ni(1)-N(1)-C(1)-C(2)	-173.3(3)
N(1)-C(1)-C(2)-C(3)	-0.9(5)
N(1)-N(2)-C(3)-C(2)	0.1(5)
B(1)-N(2)-C(3)-C(2)	178.0(4)
C(1)-C(2)-C(3)-N(2)	0.5(5)
N(4)-N(3)-C(4)-C(5)	-0.6(5)
Ni(1)-N(3)-C(4)-C(5)	172.3(3)
N(3)-C(4)-C(5)-C(6)	0.2(5)
N(3)-N(4)-C(6)-C(5)	-0.7(5)
B(1)-N(4)-C(6)-C(5)	-172.0(4)
C(4)-C(5)-C(6)-N(4)	0.3(5)
N(6)-N(5)-C(7)-C(8)	-0.2(5)
B(1)-N(5)-C(7)-C(8)	-178.0(4)

N(5)-C(7)-C(8)-C(9)	0.5(5)
N(5)-N(6)-C(9)-C(8)	0.6(5)
Ni(1)-N(6)-C(9)-C(8)	-179.2(3)
C(7)-C(8)-C(9)-N(6)	-0.7(5)
C(15)-C(10)-C(11)-C(12)	-1.0(7)
Ni(1)-C(10)-C(11)-C(12)	171.2(4)
C(10)-C(11)-C(12)-C(13)	0.6(7)
C(11)-C(12)-C(13)-C(14)	0.0(7)
C(12)-C(13)-C(14)-C(15)	-0.2(7)
C(11)-C(10)-C(15)-C(14)	0.9(7)
Ni(1)-C(10)-C(15)-C(14)	-171.8(3)
C(13)-C(14)-C(15)-C(10)	-0.3(7)
N(8)-N(7)-C(17)-C(18)	0.6(5)
Ni(2)-N(7)-C(17)-C(18)	179.7(3)
N(7)-C(17)-C(18)-C(19)	-0.5(5)
N(7)-N(8)-C(19)-C(18)	0.2(5)
B(2)-N(8)-C(19)-C(18)	-177.9(4)
C(17)-C(18)-C(19)-N(8)	0.2(5)
N(10)-N(9)-C(20)-C(21)	-0.6(5)
B(2)-N(9)-C(20)-C(21)	-174.4(4)
N(9)-C(20)-C(21)-C(22)	0.8(5)
N(9)-N(10)-C(22)-C(21)	0.4(5)
Ni(2)-N(10)-C(22)-C(21)	177.5(3)
C(20)-C(21)-C(22)-N(10)	-0.8(5)
N(12)-N(11)-C(23)-C(24)	0.9(5)
B(2)-N(11)-C(23)-C(24)	176.8(4)
N(11)-C(23)-C(24)-C(25)	-0.4(5)
N(11)-N(12)-C(25)-C(24)	0.8(5)
Ni(2)-N(12)-C(25)-C(24)	-172.3(3)
C(23)-C(24)-C(25)-N(12)	-0.3(5)
C(31)-C(26)-C(27)-C(28)	-1.2(7)
Ni(2)-C(26)-C(27)-C(28)	169.3(3)
C(26)-C(27)-C(28)-C(29)	0.4(7)
C(27)-C(28)-C(29)-C(30)	0.7(7)
C(28)-C(29)-C(30)-C(31)	-0.9(7)
C(27)-C(26)-C(31)-C(30)	1.0(7)
Ni(2)-C(26)-C(31)-C(30)	-169.9(3)
C(29)-C(30)-C(31)-C(26)	0.1(7)
C(6)-N(4)-B(1)-N(5)	113.4(5)
N(3)-N(4)-B(1)-N(5)	-57.1(5)
C(6)-N(4)-B(1)-N(2)	-132.7(4)
N(3)-N(4)-B(1)-N(2)	56.8(5)

C(7)-N(5)-B(1)-N(4)	-123.2(5)
N(6)-N(5)-B(1)-N(4)	59.2(5)
C(7)-N(5)-B(1)-N(2)	120.7(5)
N(6)-N(5)-B(1)-N(2)	-56.9(5)
C(3)-N(2)-B(1)-N(4)	128.2(5)
N(1)-N(2)-B(1)-N(4)	-54.1(5)
C(3)-N(2)-B(1)-N(5)	-116.1(5)
N(1)-N(2)-B(1)-N(5)	61.6(5)
C(19)-N(8)-B(2)-N(9)	-123.9(5)
N(7)-N(8)-B(2)-N(9)	58.2(5)
C(19)-N(8)-B(2)-N(11)	120.2(5)
N(7)-N(8)-B(2)-N(11)	-57.7(5)
C(20)-N(9)-B(2)-N(8)	117.9(5)
N(10)-N(9)-B(2)-N(8)	-55.3(5)
C(20)-N(9)-B(2)-N(11)	-128.4(4)
N(10)-N(9)-B(2)-N(11)	58.4(5)
C(23)-N(11)-B(2)-N(8)	-114.6(5)
N(12)-N(11)-B(2)-N(8)	61.0(5)
C(23)-N(11)-B(2)-N(9)	129.6(5)
N(12)-N(11)-B(2)-N(9)	-54.9(5)

Structure Determination of 2e-PMe_3





2e-PMe_3

Blue needles of **2e-PMe_3** were grown from a diisopropyl ether/pentane (net 0.04 M PMe_3) solution of **2e** at –35 ºC. A crystal of dimensions 0.15 x 0.02 x 0.02 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 (λ = 1.54187 A) 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, 8 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 17165 reflections to a maximum 2θ value of 138.53° of which 3360 were independent and 3337 were greater than 2σ(I). The final cell constants (Table S25) were based on the xyz centroids 11867 reflections above 10σ(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 Cc with Z = 4 for the formula $C_{19}H_{24}BF_3N_6PNi$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0264 and wR2 = 0.0667 [based on I > 2sigma(I)], R1 = 0.0269 and wR2 = 0.0670 for all data. Additional details are presented in Table S25 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 S25. Crystal Data and Structural Refinement for **2e-PMe$_3$**

Empirical Formula	$C_{19}H_{24}BF_3N_6NiP$
Formula Weight	493.20
Temperature	85(2) K
Wavelength	1.54184 A
Crystal System	Monoclinic
Space Group	Cc
Unit Cell Dimensions	a = 8.50891(8)A alpha = 90º b =17.83577 (13) A beta = 100.4640(9)º c = 15.13048(14) A gamma = 90º
Volume	2258.06 (1) A^3
Z	4
Calculated Density	1.453 Mg/m^3
Absorption Coefficient	2.292 mm^{-1}
F(000)	1020
Crystal Size	0.15 x 0.20 x 0.20 mm
Theta Range for Data Collection	4.959 to 69.266º
Limiting Indicies	-24≤h≤24, -10≤k≤11, -20≤l≤20
Reflections Collected	17165
Independent Reflections	3360[R(int) = 0.0610]
Completeness to Theta	67.684 /98.2
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	0.7366 and 0.6464
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	6411 / 1 / 497
Goodness-of-Fit on F^2	1.047
Final R Indices [I>2σ(I)]	R1 = 0.0264, wR2 = 0.0667
R indices (all data)	R1 = 0.0269, wR2 = 0.0670
Largest Difference Peak and Hole	0.250and -0.221A^{-3}

Table S26. Atomic coordinates (x 10^3) and equivalent isotropic displacement parameters (A^2 x 10^2) for **2e-PMe$_3$.** U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
P(1)	2318(1)	3555(1)	3793(1)	20(1)
Ni(1)	4931(1)	3751(1)	4902(1)	13(1)
F(1)	4814(2)	2201(1)	4492(1)	31(1)
F(2)	7091(2)	2715(1)	4468(1)	27(1)
F(4)	6440(2)	2436(1)	5725(1)	27(1)
N(1)	7222(3)	4143(1)	5669(2)	18(1)
N(2)	7710(3)	4837(1)	5466(2)	19(1)
N(3)	4149(3)	4792(1)	5073(2)	16(1)
N(4)	5029(3)	5396(1)	4911(2)	18(1)
N(5)	5846(3)	4107(1)	3822(2)	16(1)
N(6)	6538(3)	4798(1)	3839(2)	18(1)
C(1)	8380(4)	3871(2)	6304(2)	22(1)
C(2)	9622(3)	4386(2)	6513(2)	27(1)
C(3)	9153(3)	4992(2)	5969(2)	24(1)
C(4)	2830(3)	5053(2)	5320(2)	22(1)
C(5)	2844(4)	5836(2)	5312(2)	29(1)
C(6)	4245(4)	6029(2)	5057(2)	25(1)
C(7)	5946(4)	3809(2)	3026(2)	20(1)
C(8)	6707(4)	4297(2)	2522(2)	24(1)
C(9)	7077(4)	4916(2)	3070(2)	24(1)
C(10)	5829(4)	2741(2)	4907(2)	20(1)
C(11)	4048(3)	3405(1)	5933(2)	17(1)
C(12)	4438(4)	3810(2)	6732(2)	20(1)
C(13)	3791(4)	3623(2)	7481(2)	24(1)
C(14)	2746(4)	3024(2)	7453(2)	28(1)
C(15)	2349(4)	2618(2)	6659(2)	28(1)
C(16)	3002(4)	2799(2)	5906(2)	22(1)
C(17)	1977(4)	4355(2)	3025(2)	37(1)
C(18)	406(4)	3511(2)	4182(2)	34(1)
C(19)	2105(4)	2762(2)	3013(2)	38(1)
B(1)	6709(4)	5285(2)	4689(2)	20(1)

Table S27. Bond lengths [A] and angles [deg] for **2e-PMe$_3$**

P(1)-C(17)	1.829(3)
P(1)-C(19)	1.830(3)
P(1)-C(18)	1.830(4)
P(1)-Ni(1)	2.5540(7)
Ni(1)-C(11)	1.950(3)
Ni(1)-C(10)	1.955(3)
Ni(1)-N(3)	2.006(2)
Ni(1)-N(5)	2.035(3)
Ni(1)-N(1)	2.195(2)
F(1)-C(10)	1.368(3)
F(2)-C(10)	1.362(4)
F(4)-C(10)	1.366(3)
N(1)-C(1)	1.336(4)
N(1)-N(2)	1.358(3)
N(2)-C(3)	1.351(4)
N(2)-B(1)	1.543(4)
N(3)-C(4)	1.330(4)
N(3)-N(4)	1.360(3)
N(4)-C(6)	1.349(4)
N(4)-B(1)	1.539(4)
N(5)-C(7)	1.333(4)
N(5)-N(6)	1.365(3)
N(6)-C(9)	1.342(4)
N(6)-B(1)	1.536(4)
C(1)-C(2)	1.392(4)
C(1)-H(1)	0.9500
C(2)-C(3)	1.375(5)
C(2)-H(2)	0.9500
C(3)-H(3)	0.9500
C(4)-C(5)	1.397(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.362(5)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.392(5)
C(7)-H(7)	0.9500
C(8)-C(9)	1.383(4)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(11)-C(16)	1.396(4)
C(11)-C(12)	1.396(4)
C(12)-C(13)	1.387(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.386(5)
C(13)-H(13)	0.9500
C(14)-C(15)	1.392(5)
C(14)-H(14)	0.9500
C(15)-C(16)	1.393(5)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
B(1)-H(1B)	1.06(4)
C(17)-P(1)-C(19)	101.98(18)
C(17)-P(1)-C(18)	100.93(17)
C(19)-P(1)-C(18)	100.63(18)
C(17)-P(1)-Ni(1)	109.24(11)
C(19)-P(1)-Ni(1)	120.12(12)
C(18)-P(1)-Ni(1)	120.88(11)
C(11)-Ni(1)-C(10)	84.99(12)
C(11)-Ni(1)-N(3)	90.28(10)
C(10)-Ni(1)-N(3)	172.21(11)
C(11)-Ni(1)-N(5)	179.70(11)
C(10)-Ni(1)-N(5)	94.85(11)
N(3)-Ni(1)-N(5)	89.91(10)
C(11)-Ni(1)-N(1)	96.44(10)
C(10)-Ni(1)-N(1)	88.99(10)
N(3)-Ni(1)-N(1)	85.39(9)
N(5)-Ni(1)-N(1)	83.81(9)
C(11)-Ni(1)-P(1)	93.83(8)
C(10)-Ni(1)-P(1)	99.79(9)
N(3)-Ni(1)-P(1)	86.67(6)

N(5)-Ni(1)-P(1)	85.94(6)
N(1)-Ni(1)-P(1)	167.03(7)
C(1)-N(1)-N(2)	106.1(2)
C(1)-N(1)-Ni(1)	137.1(2)
N(2)-N(1)-Ni(1)	116.72(16)
C(3)-N(2)-N(1)	110.1(2)
C(3)-N(2)-B(1)	130.0(3)
N(1)-N(2)-B(1)	119.7(2)
C(4)-N(3)-N(4)	107.1(2)
C(4)-N(3)-Ni(1)	132.59(19)
N(4)-N(3)-Ni(1)	120.33(18)
C(6)-N(4)-N(3)	109.2(3)
C(6)-N(4)-B(1)	130.6(2)
N(3)-N(4)-B(1)	120.0(2)
C(7)-N(5)-N(6)	106.2(2)
C(7)-N(5)-Ni(1)	134.24(19)
N(6)-N(5)-Ni(1)	119.57(17)
C(9)-N(6)-N(5)	109.8(2)
C(9)-N(6)-B(1)	129.9(2)
N(5)-N(6)-B(1)	120.1(2)
N(1)-C(1)-C(2)	110.8(3)
N(1)-C(1)-H(1)	124.6
C(2)-C(1)-H(1)	124.6
C(3)-C(2)-C(1)	104.9(2)
C(3)-C(2)-H(2)	127.6
C(1)-C(2)-H(2)	127.6
N(2)-C(3)-C(2)	108.1(3)
N(2)-C(3)-H(3)	125.9
C(2)-C(3)-H(3)	125.9
N(3)-C(4)-C(5)	109.8(3)
N(3)-C(4)-H(4)	125.1
C(5)-C(4)-H(4)	125.1
C(6)-C(5)-C(4)	105.4(3)
C(6)-C(5)-H(5)	127.3
C(4)-C(5)-H(5)	127.3
N(4)-C(6)-C(5)	108.6(2)
N(4)-C(6)-H(6)	125.7
C(5)-C(6)-H(6)	125.7
N(5)-C(7)-C(8)	111.0(3)
N(5)-C(7)-H(7)	124.5
C(8)-C(7)-H(7)	124.5
C(9)-C(8)-C(7)	104.3(3)
C(9)-C(8)-H(8)	127.8
C(7)-C(8)-H(8)	127.8
N(6)-C(9)-C(8)	108.6(3)
N(6)-C(9)-H(9)	125.7
C(8)-C(9)-H(9)	125.7
F(2)-C(10)-F(4)	102.9(2)
F(2)-C(10)-F(1)	103.9(2)
F(4)-C(10)-F(1)	103.9(2)
F(2)-C(10)-Ni(1)	111.83(19)
F(4)-C(10)-Ni(1)	117.11(19)
F(1)-C(10)-Ni(1)	115.62(19)
C(16)-C(11)-C(12)	118.4(3)
C(16)-C(11)-Ni(1)	123.9(2)
C(12)-C(11)-Ni(1)	117.6(2)
C(13)-C(12)-C(11)	121.1(3)
C(13)-C(12)-H(12)	119.5
C(11)-C(12)-H(12)	119.5
C(14)-C(13)-C(12)	120.5(3)
C(14)-C(13)-H(13)	119.7
C(12)-C(13)-H(13)	119.7
C(13)-C(14)-C(15)	118.8(3)
C(13)-C(14)-H(14)	120.6
C(15)-C(14)-H(14)	120.6
C(14)-C(15)-C(16)	121.0(3)
C(14)-C(15)-H(15)	119.5
C(16)-C(15)-H(15)	119.5
C(15)-C(16)-C(11)	120.2(3)
C(15)-C(16)-H(16)	119.9
C(11)-C(16)-H(16)	119.9
P(1)-C(17)-H(17A)	109.5
P(1)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
P(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
P(1)-C(18)-H(18A)	109.5
P(1)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
P(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

P(1)-C(19)-H(19A)	109.5
P(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
P(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
N(6)-B(1)-N(4)	107.8(2)
N(6)-B(1)-N(2)	107.5(2)
N(4)-B(1)-N(2)	107.9(2)
N(6)-B(1)-H(1B)	114(2)
N(4)-B(1)-H(1B)	108(2)
N(2)-B(1)-H(1B)	112.3(19)

Table S28. Anisotropic displacement parameters ($A^2 \times 10^2$) for **2e-PMe$_3$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2} U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
P(1)	20(1)	23(1)	16(1)	1(1)	0(1)	-3(1)
Ni(1)	17(1)	11(1)	12(1)	1(1)	4(1)	1(1)
F(1)	36(1)	16(1)	38(1)	-9(1)	2(1)	0(1)
F(2)	33(1)	25(1)	26(1)	2(1)	14(1)	12(1)
F(4)	41(1)	20(1)	20(1)	5(1)	6(1)	14(1)
N(1)	20(1)	20(1)	15(1)	-1(1)	4(1)	1(1)
N(2)	17(1)	21(1)	19(1)	-4(1)	5(1)	-3(1)
N(3)	17(1)	14(1)	16(1)	0(1)	4(1)	0(1)
N(4)	24(1)	13(1)	19(1)	2(1)	5(1)	-1(1)
N(5)	20(1)	14(1)	16(1)	1(1)	4(1)	-1(1)
N(6)	22(1)	18(1)	16(1)	2(1)	7(1)	-3(1)
C(1)	21(1)	30(1)	13(1)	-1(1)	2(1)	8(1)
C(2)	18(1)	40(2)	23(2)	-11(1)	0(1)	6(1)
C(3)	18(1)	30(1)	24(2)	-11(1)	7(1)	-5(1)
C(4)	22(1)	17(1)	28(2)	3(1)	8(1)	4(1)
C(5)	38(2)	16(1)	37(2)	2(1)	16(1)	12(1)
C(6)	37(2)	11(1)	28(2)	2(1)	9(1)	5(1)
C(7)	26(2)	19(1)	16(1)	-2(1)	6(1)	0(1)
C(8)	32(2)	29(2)	15(1)	1(1)	9(1)	0(1)
C(9)	28(2)	25(1)	22(2)	6(1)	9(1)	-1(1)
C(10)	27(1)	18(1)	17(1)	-1(1)	5(1)	1(1)
C(11)	19(1)	16(1)	16(1)	2(1)	6(1)	5(1)
C(12)	23(1)	18(1)	19(1)	1(1)	5(1)	3(1)
C(13)	32(2)	26(1)	16(1)	2(1)	5(1)	8(1)
C(14)	34(2)	32(1)	20(1)	9(1)	13(1)	2(1)
C(15)	33(2)	27(1)	28(2)	7(1)	12(1)	-5(1)
C(16)	29(2)	18(1)	19(1)	3(1)	3(1)	-2(1)
C(17)	30(2)	44(2)	32(2)	16(2)	-6(1)	-1(1)
C(18)	21(2)	48(2)	33(2)	2(2)	1(1)	-5(1)
C(19)	36(2)	44(2)	31(2)	-17(1)	1(2)	-10(1)
B(1)	24(2)	16(1)	19(2)	-1(1)	7(1)	-3(1)

Table S29. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^4) for **2e-PMe$_3$.**

	x	y	z	U(eq)
H(1)	8358	3392	6577	26
H(2)	10583	4330	6939	33
H(3)	9742	5443	5949	29
H(4)	2001	4752	5477	27
H(5)	2047	6164	5455	35
H(6)	4608	6526	4991	30
H(7)	5550	3328	2829	24
H(8)	6924	4221	1934	29
H(9)	7621	5352	2927	29
H(12)	5157	4221	6763	23
H(13)	4067	3908	8017	29
H(14)	2309	2893	7967	33
H(15)	1622	2210	6630	34
H(16)	2733	2510	5372	27
H(17A)	920	4310	2644	56
H(17B)	2799	4363	2648	56
H(17C)	2030	4821	3373	56
H(18A)	-468	3485	3662	52
H(18B)	278	3960	4535	52
H(18C)	382	3065	4556	52
H(19A)	2969	2775	2664	56
H(19B)	1072	2795	2604	56
H(19C)	2159	2292	3352	56
H(1B)	7200(40)	5830(20)	4610(30)	23(9)

Table S30. Torsion angles [deg] for **2e-PMe$_3$**

C(1)-N(1)-N(2)-C(3)	0.1(3)
Ni(1)-N(1)-N(2)-C(3)	-178.11(19)
C(1)-N(1)-N(2)-B(1)	174.7(3)
Ni(1)-N(1)-N(2)-B(1)	-3.5(3)
C(4)-N(3)-N(4)-C(6)	-0.2(3)
Ni(1)-N(3)-N(4)-C(6)	178.83(19)
C(4)-N(3)-N(4)-B(1)	174.7(2)
Ni(1)-N(3)-N(4)-B(1)	-6.2(3)
C(7)-N(5)-N(6)-C(9)	-1.0(3)
Ni(1)-N(5)-N(6)-C(9)	179.21(18)
C(7)-N(5)-N(6)-B(1)	-176.7(2)
Ni(1)-N(5)-N(6)-B(1)	3.4(3)
N(2)-N(1)-C(1)-C(2)	-0.2(3)
Ni(1)-N(1)-C(1)-C(2)	177.4(2)
N(1)-C(1)-C(2)-C(3)	0.2(4)
N(1)-N(2)-C(3)-C(2)	0.1(3)
B(1)-N(2)-C(3)-C(2)	-173.8(3)
C(1)-C(2)-C(3)-N(2)	-0.2(3)
N(4)-N(3)-C(4)-C(5)	0.5(3)
Ni(1)-N(3)-C(4)-C(5)	-178.4(2)
N(3)-C(4)-C(5)-C(6)	-0.5(4)
N(3)-N(4)-C(6)-C(5)	-0.1(3)
B(1)-N(4)-C(6)-C(5)	-174.4(3)
C(4)-C(5)-C(6)-N(4)	0.4(4)
N(6)-N(5)-C(7)-C(8)	0.4(3)
Ni(1)-N(5)-C(7)-C(8)	-179.8(2)
N(5)-C(7)-C(8)-C(9)	0.3(3)
N(5)-N(6)-C(9)-C(8)	1.2(3)
B(1)-N(6)-C(9)-C(8)	176.4(3)
C(7)-C(8)-C(9)-N(6)	-0.9(3)
C(16)-C(11)-C(12)-C(13)	-0.6(4)
Ni(1)-C(11)-C(12)-C(13)	176.6(2)
C(11)-C(12)-C(13)-C(14)	0.4(4)
C(12)-C(13)-C(14)-C(15)	-0.5(5)
C(13)-C(14)-C(15)-C(16)	0.9(5)
C(14)-C(15)-C(16)-C(11)	-1.2(4)
C(12)-C(11)-C(16)-C(15)	1.0(4)
Ni(1)-C(11)-C(16)-C(15)	-176.1(2)
C(9)-N(6)-B(1)-N(4)	128.0(3)
N(5)-N(6)-B(1)-N(4)	-57.2(3)
C(9)-N(6)-B(1)-N(2)	-116.0(3)
N(5)-N(6)-B(1)-N(2)	58.8(3)
C(6)-N(4)-B(1)-N(6)	-127.0(3)
N(3)-N(4)-B(1)-N(6)	59.3(3)
C(6)-N(4)-B(1)-N(2)	117.2(3)
N(3)-N(4)-B(1)-N(2)	-56.5(3)
C(3)-N(2)-B(1)-N(6)	117.1(3)
N(1)-N(2)-B(1)-N(6)	-56.3(3)
C(3)-N(2)-B(1)-N(4)	-127.0(3)
N(1)-N(2)-B(1)-N(4)	59.7(3)