Supporting Information for

A T-shaped Ni[κ²-(CF₂)]₄- NHC complex: Unusual Csp3-F and M-CF bond functionalization reactions†

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**General Procedures.** Experiments were conducted under nitrogen, using Schlenk techniques or an MBraun glove box. All solvents were deoxygenated by purging with nitrogen. Toluene, hexanes, diethyl ether (DEE) and tetrahydrofuran (THF) were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contour®) solvent purification system. Benzene-d₈ (C₆D₈) was dried by stirring over activated alumina (ca. 10 wt. %) overnight, followed by filtration. Acetonitrile-d₃ (CD₃CN) was dried by refluxing over calcium hydride under nitrogen. After distillation, CD₃CN was further dried by stirring over activated alumina (ca. 5 wt. %) overnight, followed by filtration. All solvents were stored over activated (heated at ca. 250°C for >10 h under vacuum) 4 Å molecular sieves. Glassware was oven-dried at 120°C for >2 h. The following chemicals were obtained commercially, as indicated: trimethylsilyl trifluoromethanesulfonate (Me₃SiOTf, Aldrich, 99%), bis(1,5-cyclooctadiene)nickel (0) (Ni(cod)$_2$, Strem, 98+%), triisopropyl phosphite (P(OR)$_3$, Aldrich, 95%), tri-ortho-tolyl phosphite (P(OT$_3$)$_3$, Alfa Aesar, 97%), 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene (SIPr, Sigma-Aldrich) and 1,3-di-tert-butylimidazol-2-ylidene (ItBu, Sigma-Aldrich). Tetrafluoroethylene (TFE) was purchased from ABCR (99%) or made by pyrolysis of polytetrafluoroethylene (Scientific Polymer Products, powdered) under vacuum, using a slightly modified literature procedure [10-20 mTorr, 650°C, 30 g scale, product stabilized with R(+-)limonene (Aldrich, 97%), giving TFE of ca. 97% purity].¹ Compound Ni[P(OR)$_3$)$_2$(C,F$_8$) was made by oxidative addition of tetrafluoroethylene to Ni[P(OR)$_3$)$_3$ using slightly modified literature procedures.² Ni[P(OR)$_3$]$_4$ complex was prepared from Ni(COD)$_2$ following reported methods.² Metallacycle Ni(C,F$_3$)[P(O-tolyl)]$_2$ was prepared by addition of TFE to Ni[P(O-tolyl)]$_3$ using slightly modified literature procedures.³ Ni[P(O-Pr)$_3$]$_4$ complex was prepared from Ni(COD)$_2$ following reported methods.² ¹H, ¹⁹F, ³¹P{¹H}, and ¹³C{¹H} NMR spectra were recorded on a 300 MHz Bruker Avance instrument at room-temperature (21-23°C) unless stated otherwise. ¹H NMR spectra were referenced to residual proton peaks associated with the deuterated solvents (C₆D₈: 7.16 ppm; CD₃CN: 1.94 ppm). ¹⁹F NMR spectra were referenced to internal 1,3-bis(trifluoromethyl)benzene (BTB) [unless stated otherwise] (Aldrich, 99%, deoxygenated by purging with nitrogen, stored over activated 4 Å molecular sieves), set to −63.5 ppm. ³¹P{¹H} NMR data were referenced to external H$_3$PO₄ (85% aqueous solution), set to 0.0 ppm. Electrospray ionization mass spectral data were collected using an Applied Biosystem API2000 triple quadrupole mass spectrometer. UV-vis spectra were recorded on a Cary 100 instrument, using sealable quartz cuvettes (1.0 cm pathlength). Elemental analyses were performed by Laboratoire d'analyse élémentaire, Université de Montréal. (Montreal, Quebec, Canada). Note that the NMR spectra (¹H, ¹⁹F, ³¹F{¹H}, and ³¹P{¹H}) for the title compounds are displayed at the end of the Supporting Information (Figures S7-27).

**X-ray Crystallography.** Data collection results for complexes 2, 3, 3•H$_2$O, 4a and 5c represent the best data sets obtained in several trials for each sample (Table S1 and Table S11). The crystals were mounted on thin glass fibers using paraffin oil. Prior to data collection crystals were cooled to 200 K. Data were collected on a Bruker AXS KAPPA single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) APEX II CCD detector. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.⁴ Diffraction data for all the samples were collected with a sequence of 0.5° ω scans at 0, 120, and 240° in ϕ. Initial unit cell parameters were determined from 60 data frames with 0.3° ω scan each, collected at the different
sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied. Systematic absences in the diffraction data set and unit-cell parameters were consistent with monoclinic \textbf{P}2\textsubscript{1}/\textit{c} (\textnumero14) for complexes 2, 4a and 5c, and orthorhombic \textbf{P}2\textsubscript{2}/2\textsubscript{1}/2\textsubscript{1} (\textnumero19) for 3. Solutions in the centrosymmetric space groups for complexes 2, 4a and 5c yielded chemically reasonable and computationally stable results of refinement. Data for the complex 3 suggested a non-centrosymmetric space group for the model refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on \textbf{F}\textsuperscript{2}.

Refinement of the structural model for 2 revealed one target molecule located in general position. Similarly, the structure of 3 displayed only one molecule of interest located in the general position. In this case, however, final refinement numbers suggested the presence of racemic twinning in the crystal. In order to take twinning into consideration the default TWIN instruction was employed. After additional refinement cycles the BASF parameter was refined to 0.14413.

The structural model for complex 4a contains one target molecule and one fully occupied hexane solvent molecule in the lattice. The complex molecule is located in the general position and the hexane solvent molecule is located on the inversion center of the space group.

Diffraction data for the crystal of complex 5c were collected to 0.75\textdegree resolution; however, due to small crystal size and weak diffraction it was discovered that both \textbf{R}(\text{int}) and \textbf{R}(\text{sigma}) exceeded 35\% for the data below 1.00\textdegree resolution. Based on \textbf{R}(\text{sigma}) value, data were truncated to 0.95\textdegree resolution for refinement. The asymmetric unit for this crystallographic model of 5c consists of one target complex molecule located in the general position. Refinement results for the compound 5c suggested the presence of two non-merohedrally twinned domains. Careful examination of the original data frames and reciprocal space diffraction pictures confirmed the initial twinning assumption. In order to find independent orientation matrices 3258 reflections were collected from 4 sets of 40 frames each in different sections of the Ewald sphere. Collected reflection data were processed with CELL_NOW software\textsuperscript{6} and produced two independent orientation matrices. 2636 reflections out of the original array were assigned exclusively to the first domain and 1521 (330 exclusively) reflections were assigned to the second domain. The data set was re-integrated with two independent orientation matrices, treated for twinning absorption corrections and consecutive model refinement was performed using HKLF5 reflection data file. Twinning domain ratio coefficient (BASF) was refined to 0.1115.

For all the compounds hydrogen atoms positions were calculated based on the geometry of related non-hydrogen atoms. All hydrogen atoms were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.\textsuperscript{7} Metrical data for 2, 3, 3\textcdot H\textsubscript{2}O, 4a and 5c are presented in Table S1 and S11, and the CCDC files 968465 (2), 968466 (3),
Computational Methods. Density Functional Theory (DFT) calculations were performed for each structure using the Gaussian 09 package. Geometry optimization at the B3LYP/TZVP level of theory (with and without the empirical dispersion correction GD3 of Grimme) was performed using the molecular structure of 3 from the X-ray diffraction experiment as a starting point. Harmonic frequency calculations were used to characterize the stationary points obtained during the geometry optimization. Tight SCF convergence was used in each calculation. Mulliken population analysis (MPA) - compositions of molecular orbitals, and 2- and 3-center Mayer bond orders were calculated using the AOMix package (www.sg-chem.net). Optimized structure coordinates are presented in Tables S7-10.

Experimental.

Synthesis of Ni[κ₂-(CF₂)₄]-[ItBu][P(OiPr)₃] (2). Yellow complex Ni[κ₂-(CF₂)₄-][P(OiPr)₃]₂ (1a) (0.100 g, 0.15 mmol) was placed in a 15 mL scintillation vial and dissolved in ~7 mL of toluene. Colorless [ItBu] (29 mg, 0.16 mmol) was then added to the mixture and left to sit at 25 °C for ~24 hours. Large yellow block crystals suitable for X-ray analysis formed. They were filtered off (30 mL medium pore fritted funnel), washed with pre-cooled hexanes (4 °C, 3 x 3 mL), and dried in vacuo to yield 85 mg of 2 (0.13 mmol, 89 % based on Ni[κ₂-(CF₂)₄-][P(OiPr)₃]₂). The isolated material was stored at room temperature under nitrogen. UV-vis (1.0 mM in THF): λmax(ε) = 322(341). ¹H NMR (300 MHz, CD₃CN) δ 1.19 (d, J ≈ 6 Hz, 18H, MeᵢPr) 1.94 (s, 18H, MeᵢBu), 4.65 (sept, m, J ≈ 6 Hz, 3H, iPrH) 7.34 (s, 2H, CHIm). ¹⁹F NMR (282 MHz, CD₃CN) δ -100.50 (d 'quint', 3JFP ≈ 32, 3JFF ≈ 4 Hz, 2Fα), -102.93 (d 'quint', 3JFP ≈ 33, 3JFF ≈ 4JFF = 6 Hz, 2Fα), -102.93 (d 'quint', 3JFP ≈ 33, 3JFF ≈ 4JFF = 6 Hz, 2Fα), -107.34 (d 'quint', 3JFP ≈ 33, 3JFF ≈ 4JFF = 6 Hz, 2Fα). Anal. Calc. for C₂₄H₄₁F₈N₂NiO₃P: C, 44.54, H, 6.39, N, 4.33. Found: C, 44.54, H, 6.53, N, 4.38. See Figures S7-9 for ¹H, ¹⁹F, ³¹P{¹H} NMR spectra.

Synthesis of Ni[κ₂-(CF₂)₄]-[SIPr] (3). Yellow complex Ni[κ₂-(CF₂)₄-][P(O-o-tol)]₃]₂ (1b) (1.00 g, 1.04 mmol) was placed in a 20 mL scintillation vial and dissolved in ~ 10 mL of benzene. Colorless [SIPr] (446 mg, 1.14 mmol) was...
then added to the stirred mixture and the mixture heated at 35 °C for ~24 hours. The resulting deep red solution was concentrated in vacuo to a thick paste with some red precipitate. Hexanes (15 mL) were then added to precipitate the product which was subsequently filtered (30 mL medium pore fritted funnel), washed with pre-cooled hexanes (4 °C, 3 x 5 mL), and dried in vacuo, affording 3 as a light red powder. Yield: 506 mg (0.78 mmol, 75 % based on Ni[k2-(CF2)4-][P(O-o-tol)]2. The isolated material was stored at room temperature under nitrogen. UV-vis (1.5 mM in benzene): λmax(ε) = 486(461). 1H NMR (300 MHz, C6D6) δ 1.09 (d, J = 6 Hz, 12H, 4 Me), 1.68 (d, J = 6 Hz, 12H, 4 Me), 3.04 (sept, J ≈ 6 Hz, 4H, 4 Pr H), 3.13 (s, 4H, 2 CH2Im), 7.00-7.30 (mult, 6H, 6 Ar-H). 13C{1H} NMR (75 MHz, C6D6) δ 24.78, 24.96, 29.40, 53.50, 125.63, 127-129, 129.57, 131.26, 147.67. 19F NMR (282 MHz, C6D6, 25 °C) δ -101.90 (s, 4Fα), -138.63 (s, 4Fβ). 19F NMR (282 MHz, CD2Cl2, -50 °C) δ -99.32 (s, 2F′α), -103.07 (br s, 4Fα), -119.17 (s, 2F′α), -138.37 (s, 2F′β), -139.64 (br s, 4Fβ), -141.21 (s, 2F′β). Anal. Calc. for C31H38F4N2NiO: C, 57.34, H, 5.90, N, 4.31. Found: C, 56.22, H, 6.18, N, 4.17. (These values reflect those expected for the water adduct 3•H2O Anal. Calc. for C31H38F4N2NiO: C, 57.79, H, 6.04, N, 4.20. See below: Figure 34, Table S11-12) See Figures S10-12 for the 1H, 13C{1H} and 19F NMR spectra.

**Synthesis of Ni[k1-(cyclo-CaF4)](SIPr)(OTf) (4a).** Red complex Ni[k2-(CF2)4-](SIPr) (3) (0.100 g, 0.15 mmol) was placed in a 15 mL scintillation vial and dissolved in ~ 7 mL of benzene. Me3SiOTf (42 µL, 0.23 mmol) was added to the stirred mixture and left to stir at room temperature for ~24 hours. (N.B. Product 4 is unstable under these reaction conditions for prolonged periods of time, reaction times longer than 24 hours will lead to the formation of perfluorocyclobutene in the reaction medium). The deep pink solution was concentrated in vacuo and the resulting pink powder 4a was washed with pre-cooled hexanes (4 °C, 3 x 5 mL) and dried in vacuo. Yield: 0.108 g, 0.14 mmol, 90 % based on Ni[k2-(CF2)4-](SIPr). The isolated material was stored at room temperature under nitrogen. UV-vis (1.0 mM in benzene): λmax(ε) = 503(218), 332(312). 1H NMR (300 MHz, C6D6) δ 1.04 (d, J = 7 Hz, 12H, 4 Me), 1.60 (br d, J ≈ 5 Hz, 6H, 2 Me), 1.71 (br, 6H, 2 Me) 3.2 (br ov mult, 6H, 4 Pr H + 2 CH2Im ), 3.4 (br mult, 2H, CH2Im), 6.5-7.8 (mult, 6H, 6 Ar-H). 13C{1H} NMR (75 MHz, C6D6) δ 24.78, 24.96, 28.53, 28.87, 53.37, 124.3-125, 130.02, 133.96, 146.89. 19F NMR (282 MHz, C6D6) δ -77.60 (s, CF3), -110.01 (br d, 2JFF ≈ 228 Hz, 2Fβ), -123.75 (d, 2JFF = 229 Hz, 1Fβ), -123.79 (d, 2JFF = 229 Hz, 1Fβ) -129.80 (d mult, 2JFF = 222 Hz, Fγ), -131.59 (d, 2JFF = 222 Hz, Fγ), -197.74 (br s, Fα). 19F NMR (282 MHz, CD2Cl2, -50 °C) δ -78.93 (s, CF3), -109.27 (d mult, 2JFF ≈ 227 Hz, 1Fβ), -112.22 (d mult, 2JFF ≈ 231 Hz, 1Fβ), -124.18 (d, 2JFF = 227 Hz, 1Fβ), -124.26 (d, 2JFF = 231 Hz, 1Fβ) -129.80 (d mult, 2JFF = 222 Hz, Fγ), -131.59 (d, 2JFF = 222 Hz, Fγ), -197.74 (br s, Fα). Anal. Calc. for C32H84F18O12N2NiO3S: C, 49.31, H, 4.91, N, 3.59, S, 4.11. (These values reflect those expected for the water adduct Anal. Calc. for C32H84F18O12NiO3S: C, 48.20, H, 5.06, N, 3.51, S, 4.02.) Found: C, 47.53, H, 5.05, N, 2.76, S, 4.21. See Figures S13-15 for the 1H, 13C{1H} and 19F NMR spectra.
The reaction should not be attempted in toluene. 3r

\[
\begin{align*}
\text{Synthesis of Ni}[\kappa_3-(\text{CF}_2)_3\text{CF}(\text{OTf})\_3]\text{(SIPr)} (5a): & \text{ 19F NMR (282 MHz, Tolu-d}_8, \text{ -35 °C) } \delta -73.27(\text{d}, J_{\text{FF}} = 11 \text{ Hz, CF}_3(\text{OTf})) , -83.98 (\text{d mult}, J_{\text{FF}} = 225 \text{ Hz, F}_a), -99.73 (\text{d mult}, J_{\text{FF}} = 225 \text{ Hz, F}_b), -106.29 (\text{br mult}, F_a), -127.11 (\text{d mult}, J_{\text{FF}} = 246 \text{ Hz, F}_b), -129.23 (\text{d mult}, J_{\text{FF}} = 246, F_b), -137.07 (\text{d mult}, J_{\text{FF}} = 246 \text{ Hz, F}_b), -144.71 (\text{d mult}, J_{\text{FF}} = 246, F_b). \\
\end{align*}
\]

**Synthesis of Ni[\kappa_3-(\text{CF}_2)_3\text{CF}(\text{OTf})\_3]\text{(SIPr)} (5b).** Red complex Ni[\kappa_2-(\text{CF}_2)_4]\text{(SIPr)} (3) (50 mg, 0.08 mmol) was placed in a 20 mL scintillation vial and dissolved in ~ 7 mL of benzene. Trifluoroacetic acid (7 μL, 0.085 mmol) was added to the stirred mixture (reaction should not be attempted in toluene) and left to stir at 25 °C for 10 minutes. The fluorescent yellow solution was concentrated in vacuo until a thick paste with some light yellow precipitate was remaining. Cold hexanes (4 °C, 3 x 5 mL) were added and decanted off to wash. The resulting product was dried in vacuo, affording 5b as a light yellow powder. Yield: 47 mg (0.06 mmol, 82 % based on Ni[\kappa_2-(\text{CF}_2)_4]\text{(SIPr)}. The isolated material was stored at room temperature under nitrogen. UV-vis (1.5 mM in benzene): \(\lambda_{\text{max}}(\text{solv}) = 461 \text{ nm}\). \(\text{H NMR (300 MHz, C}_6\text{D}_6\) \(\delta 1.05 (\text{ov d}, J \approx 6 \text{ Hz, 12H, 4 Me}), 1.36 (\text{d}, J \approx 6 \text{ Hz, 6H, 2 Me}), 1.47 (\text{br}, 6H, 2 Me), 3.19 (\text{br, ov mult, 3H, 3} \text{Pr H}), 3.37 (\text{br, ov mult, 5H, i-Pr H + 2 CH}_2\text{Im}), 6.80-7.06 \text{ (mult, 6H, 6 Ar-H). \[\text{C}^{\text{13}}\text{H}] \text{ NMR (75 MHz, C}_6\text{D}_6\) \(\delta 22.66, 22.82, 26.17, 26.28, 28.41, 53.89, 124.20, 124.39, 127-129, 129.33, 146.57, \text{19F NMR (282 MHz, C}_6\text{D}_6, 25 °C) \delta -72.97 \text{ (s, CF}_3\text{), -90.06 (d mult, J}_{\text{FF}} = 245 \text{ Hz, 1F}_a), -99.09 (d mult, J}_{\text{FF}} = 245 \text{ Hz, F}_a), -116.17 (d d, J}_{\text{FF}} = 22, 11 \text{ Hz, 1F}_a), -126.14 (d mult, J}_{\text{FF}} = 248 \text{ Hz, 1F}, 1 \text{C}_3\text{F}_2), -130.76 (d d mult, J}_{\text{FF}} = 248, 22 \text{ Hz, 1F}_b), -134.17 (d mult, J}_{\text{FF}} = 248 \text{ Hz, 1F}_b), -142.71 (d d mult, J}_{\text{FF}} = 248, 11 \text{ Hz, 1F}_b). \text{Anal. Calc. for C}_3\text{H}_9\text{F}_{10}\text{Ni}_2\text{O}_2: C, 53.32, H, 5.15, N, 3.77. Found: C, 53.15, H, 6.01, N, 3.87. See Figures S16-18 for the \text{1H, 13C}^{\text{13}}\text{H} \text{ and 19F NMR spectra.}
\]

\[\begin{align*}
\text{Synthesis of Ni[\kappa_3-(\text{CF}_2)_3\text{CF}(\text{O}_2\text{CCH}_3)_3}\text{(SIPr) (5c).} & \text{ 3r}
\end{align*}\]
added to the stirred mixture and left to stir at 25 °C for 24 hours. The deep yellow solution was concentrated in vacuo (~1 mL). 5 mL of hexanes was added and the product was crystallized (~20 °C). The supernatant was decanted and the yellow crystals of 5c were washed with hexanes (2 x 5 mL) and dried in vacuo. Yield: 20 mg, 0.063 mmol, 38 % based on Ni[κ₂-(CF₂)₃]-)(SIPr). The isolated material was stored at room temperature under nitrogen. UV-vis (1.0 mM in benzene): λmax(ε) = 632 (361); 103 (485). ¹H NMR (300 MHz, CD₆D₆) δ 1.05 (ov d, J ≈ 6 Hz, 12H, 4 Me), 1.36 (d, J ≈ 6 Hz, 6H, 2 Me), 1.47 (br, 6H, 2 Me), 3.19 (br, 4H, 4 Pr H), 3.37 (br, 4H, 2 CHIm), 6.80-7.06 (m, 6H, 6 Ar-H). ¹³C [¹H] NMR (75 MHz, CD₆D₆) δ 22.66, 22.82, 26.17, 26.28, 28.41, 53.89, 124.20, 124.39, 27-129, 129.33, 146.57. ¹⁹F NMR (282 MHz, CD₆D₆, 25 °C) δ -91.23(d multif, ²JFF = 253 Hz, F, δ -101.86 (d multif, ²JFF = 253 Hz, F, δ -119.78 (d d, ²JFF = 17, 15 Hz, F, δ -126.35 (d multif, ²JFF = 247 Hz, F), δ -130.90 (d d multif, ²JFF = 247, ³JFF = 15 Hz, F, δ -135.10 (d multif, ³JFF = 248 Hz, F), δ -143.33 (d d, ³JFF = 248, ³JFF = 17 Hz, F, δ Anal. Calc. for C₉H₈F₇NiO₂: C, 57.49, H, 6.16, N, 3.98. Found: C, 57.05, H, 6.21, N, 4.11. See Figures S19-21 for the ¹H, ¹³C [¹H] and ¹⁹F NMR spectra.

**Synthesis of Ni[κ₁-(C₅F₅H)](SIPr)(OAc) (6a).** Red complex Ni[κ₂-(CF₂)₃]-)(SIPr) (3) (50 mg, 0.08 mmol) was placed in a 20 mL scintillation vial and dissolved in ~7 mL of toluene. Acetic acid (5 μL, 0.085 mmol) was added to the mixture and left to stir at 25 °C for 24 hours. The deep yellow solution was concentrated in vacuo to ca. 1 mL, 5 mL of hexanes were added and the product allowed to crystallize at -20 °C. The supernatant was decanted, concentrated and filtered through a short silica column (eluent: benzene), the first yellow band was collected. The volatiles were removed in vacuo. Yield of 6c: 25 mg (0.035 mmol, 45 % based on Ni[κ₂-(CF₂)₃]-)(SIPr). UV-vis (1.0 mM in benzene): λmax(ε) = 296(343); 427(494). ¹H NMR (300 MHz, CD₆D₆) δ 1.01 (s, 3H, 1 Me), 1.05 (d, J ≈ 7 Hz, 6H, 2 Me), 1.07 (d, J ≈ 7 Hz, 6H, 2 Me), 1.55 (d, J ≈ 7 Hz, 6H, 2 Me), 1.55 (d, J ≈ 7Hz, 6H, 2 Me), 3.13 (sept, J ≈ 7 Hz, 1H, 1 Pr H), 3.20 (sept, J ≈ 7 Hz, 1H, 1 Pr H), 3.21 (s, 2H, 1 CHIm), 3.42 (sept, J ≈ 7 Hz, 1H, 1 Pr H), 3.45 (sept, J ≈ 7 Hz, 1H, 1 Pr H), 3.48 (s, 2H, 1 CHIm), 5.65 (tr tr, ³JFH = 53 Hz, ³JFH = 6 Hz, 1H, CF₂H), 6.90-7.75 (mult, 6H, 6 Ar-H). ¹³C [¹H] NMR (75 MHz, CD₆D₆) δ 21.73, 22.73, 23.04, 24.63, 26.66, 28.33, 28.63, 53.57, 124.22, 124.64, 129.53, 135.29, 147.06, 147.56, 191.30; ¹⁹F NMR (282 MHz, CD₆D₆) δ -95.90 (br tr, ³JFF = 9 Hz, F), δ -120.47 (br tr, ³JFF = 7 Hz, 2F), δ -130.98 (br d multif, ³JFH = 6 Hz, 2F), δ -137.99 (br d multif, ³JFH = 52 Hz, 2F); m/z caled for [Ni[κ₁-(C₅F₅H)](SIPr)(OAc)][K+] (% intensity), 747.2 (100), 748.2 (36), 749.2 (46), 749.2(6.8) 751.2 (20), 752.2(3), 753.2 (2); m/z found, 747.3 (100), 748.3 (36), 749.2 (50), 751.2 (19), 752.2(3), 753.2 (1); See Figures S22-24 for the ¹H, ¹³C [¹H] and ¹⁹F NMR spectra.
Synthesis of Ni[κ1-(C₄F₃H)][SIPr](O₂Cmes)] (6b). Red complex Ni[κ₂-(CF₃)₂][SIPr] (3) (50 mg, 0.08 mmol) was placed in a 20 mL scintillation vial and dissolved in ~7 mL of toluene. 2,4,6-trimethylbenzoic acid (14 mg, 0.085 mmol) was added to the stirred mixture and left to stir at 25 °C for 24 hours. The deep yellow solution was concentrated in vacuo to 1 mL. 5 mL of hexanes were added and the product allowed to crystallize at -20 °C. The supernatant was decanted and the crystals were washed with hexanes (2 x 5 mL). Yield of 6d: 48 mg (0.06 mmol, 77% based on Ni[κ₂-(CF₃)₃][SIPr]). UV-vis (1.5 mM in benzene): λmax(ε) = 486 (461). ¹H NMR (300 MHz, C₆D₆) δ 0.95 (d, J ≈ 7 Hz, 6H, 2 Me), 1.04 (d, J ≈ 7 Hz, 6H, 2 Me), 1.07 (d, J ≈ 7 Hz, 6H, 2 Me), 1.51 (d, J ≈ 7 Hz, 6H, 2 Me), 1.56 (d, J ≈ 7 Hz, 6H, 2 Me), 1.78 (s, 3H, MeAr), 1.94 (s, 6H, 2 MeAr), 3.09 (s, 2H, CH₂Im), 3.12 (sept, J ≈ 7 Hz, 2H, 1 Pr H), 3 (sept, J ≈ 7 Hz, 1H, Pr H), 3.40 (s, 2H, 1 CH₂Im), 3.54 (sept, J ≈ 7 Hz, 1H, 1 Pr H), 5.65 (tr tr, ²JFH ≈ 52 Hz, ³JFH ≈ 6 Hz, ¹H, CF₂H), 6.34 (mult, 2H, Ar H), 7.10 (mult, 6H, 6 Ar-H). ¹³C{¹H} NMR (75 MHz, C₆D₆) δ 19.52, 20.62, 23.05, 23.44, 26.15, 26.56, 28.39, 28.80, 53.85, 124.52, 124.70, 129.38, 134.94, 135.62, 138.55, 146.61, 147.46, 189.86. ¹⁹F NMR (282 MHz, C₆D₆) δ -95.90 (br tr, ³JFF = 8 Hz, 2F₁), -120.80 (br tr, ³JFF = 8 Hz, 2F₁o), -130.99 (d mult, ³JFF = 6 Hz, 2F₁), -138.68 (br mult, ³JFF = 52 Hz, 2F₁o); m/z calcd for [[Ni[κ₁-(C₄F₃H)][SIPr](O₂Cmes)]]⁺ (% intensity), 851.3 (100), 852.3 (45), 853.3 (46), 853.3 (10), 854.3 (22), 855.3 (9), 856.3 (4), 857.3 (2); m/z found, 851.4 (100), 852.3 (46), 853.4 (49), 854.3 (22), 855.4 (10), 856.3 (4), 857.3 (2); See Figures S25-27 for the ¹H, ¹³C{¹H} and ¹⁹F NMR spectra.

¹⁹F NMR spectrum of minor product, Ni[κ₁-(CF₃)₃CF(O₂Cmes)]{SIPr} (5d): ¹⁹F NMR (282 MHz, C₆D₆, 25 °C) δ -91.22 (d mult, ³JFF = 254 Hz, F₀), -101.86 (d mult, ³JFF = 254 Hz, F₀), -119.74 (d d, ³JFF = 17, 15 Hz, F₀), -126.25 (d mult, ³JFF = 245 Hz, F₀), -130.80 (d d mult, ³JFF = 245, ³JFF = 17 Hz, F₀), -135.05 (d mult, ³JFF = 248 Hz, F₀), -143.27 (d d, ³JFF = 248, ³JFF = 15 Hz, F₀).
Variable-temperature $^{19}$F NMR spectra of reaction intermediates leading to 4a:

Red complex Ni[$\kappa^3$-(CF$_2$)$_2$]-)(SIPr) (3) (10 mg, 0.015 mmol) was dissolved in 0.5 mL of CD$_2$Cl$_2$ in a screw cap NMR tube. The solution was precooled to 193 K and then placed in the NMR probe cooled to 223 K and a $^{19}$F NMR spectrum was obtained (Figure S3) after 5 minutes to allow for temperature equilibration. The low temperature $^{19}$F NMR, clearly indicates no decoalescence of signals associated with 3, this indicates the presence of low energy processes which are consistent with our calculations. However, four new signals develop at this temperature, which may indicate interference and the formation of a new product possibly involving trace water coordination. The sample was removed from the probe and recooled to 193K. A pre-prepared solution of TMSOTf (4 µL, 0.023 mmol) in 0.5 mL of CD$_2$Cl$_2$ was injected into the NMR tube. The NMR tube was then placed in the NMR probe. The probe was cooled to 223 K and the $^{19}$F NMR spectrum was obtained (Figure S1) after 5 minutes to allow for temperature equilibration. The sample was warmed to 253 K and low temperature $^{19}$F NMR spectra were acquired at 30 min, 2 hours and 3 hours corresponding to Figures S1 a-d respectively. It is noted that a distinct intermediate possessing $^{19}$F NMR signals similar to those observed for 5b, c is present in solution already after 5 minutes. However, the intermediate quickly dissipates even at low temperature after only 2 hours. After warming to room temperature, the intermediate is no longer present.
Figure S1. Low-temperature $^{19}\text{F}$ NMR spectra (282 MHz, CD$_2$Cl$_2$) of intermediate 5a generation leading to product 4a. Addition time is 0 (a), 30 min (b), 2 hours (c) and 3 hours (d). Spectrum e was recorded after one hour additional reaction time at room temperature. The dashed line represents the trace of 3 across all reactions [223 K $^{19}\text{F}$ NMR spectra (282, CD$_2$Cl$_2$), provided below].“$\text{S}$” is TMSOTf, “▲” is impurity present in TMSOTf, “●” is impurity at low temperature, “+$\text{+}$” is 5a and “▄” is 4a [223 K 19F NMR spectra (282 MHz, CD$_2$Cl$_2$), provided below]. Due to experimental limitations, the impurities are most likely due to water contamination.
Figure S2. $^{19}$F-$^{19}$F COSY NMR (282 MHz, Tol-$d_8$, 223 K) data for 5a. Black box denotes through bond correlation of F (OTf) and F (C$_\alpha$), $^3$J$_{FF}$ = 11 Hz
Hexafluorobenzene (C$_6$F$_6$) was used as an internal NMR standard
Figure S3. Low-temperature $^{19}\text{F}$ NMR spectrum (282 MHz, CD$_2$Cl$_2$, 223 K) of 3. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard. "$\$" = 3, "●" = impurity.
**Figure S4.** Low temperature $^{19}$F NMR spectra (282 MHz, CD$_2$Cl$_2$) of 4. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard. “●” = OTf impurity.
Decomposition of 4a:
Pink complex Ni[x¹-(cyclo-C₄F₇)](SIPr)(OTf) (4a) (15 mg, 0.02 mmol) was dissolved in 0.5 mL of C₆D₆ in a J. Young NMR tube. The solvent-containing part of the tube was heated to 80 °C for 24 h. ¹⁹F NMR Yield of PFCB: 21 %. We expect the discrepancy arises from the volatility of the PFCB.

Note: Upon addition of PPh₃ to the reaction mixture [after heating], PPh₃F₂ was identified as a major product, suggesting formation of a Ni-F thermolysis byproduct.

![Figure S5. ¹⁹F NMR spectrum (282 MHz, C₆D₆) after decomposition of 4a to give perfluorocyclobutene (PFCB).](image)
Product distributions of reactions with Brønsted acids:

**Figure S6.** $F_\alpha$ region of $^{19}$F NMR spectrum (282 MHz, C$_6$D$_6$) of reaction of 3 with acetic acid showing formation of 5c and 6a in a 1:1 ratio.

**Figure S7.** $F_\alpha$ region of $^{19}$F NMR spectrum (282 MHz, C$_6$D$_6$) of reaction of 3 with 2,4,6-trimethylbenzoic acid to yield 5d and 6b in a 1:10 ratio.
NMR Spectra for Title Compounds

**Figure S8.** $^1$H NMR spectrum (300 MHz, C$_6$D$_6$) of 2. The insets show the expanded (horizontal scale) signals.

**Figure S9.** $^{19}$F NMR spectrum (282 MHz, C$_6$D$_6$) of 2. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard. The insets show the expanded (horizontal scale) signals.
Figure S10. $^{31}$P$^{[1]}$H NMR spectrum (121 MHz, C$_6$D$_6$) of 2. The inset shows the expanded (horizontal scale) signal.

Figure S11. $^1$H NMR spectrum (300 MHz, C$_6$D$_6$) of 3. The residual protio-solvent peak is labeled ‘*’. The inset shows the expanded (horizontal scale) signal.
Figure S12. $^{13}$C [$^1$H] NMR spectrum (75 MHz, C$_6$D$_6$) of 3. The residual solvent peak is labeled ‘*’. The inset shows the expanded (horizontal scale) signal.

Figure S13. $^{19}$F NMR spectrum (282 MHz, C$_6$D$_6$) of 3. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard.
Figure S14. $^1$H NMR spectrum (300 MHz, C$_6$D$_6$) of 4a. The residual protio-solvent peak is labeled ‘*’. The inset shows the expanded (horizontal scale) signal.

Figure S15. $^{19}$F NMR spectrum (282 MHz, C$_6$D$_6$) of 4a. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard.
**Figure S16.** $^{13}$C\{\textsuperscript{1}H\} NMR spectrum (75 MHz, C\textsubscript{6}D\textsubscript{6}) of 4a. The inset shows the expanded (horizontal scale) signal.

**Figure S17.** $^1$H NMR spectrum (300 MHz, C\textsubscript{6}D\textsubscript{6}) of 5b.
Figure S18. $^{19}$F NMR spectrum (282 MHz, C$_6$D$_6$) of 5b. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard.

Figure S19. $^{13}$C [$^1$H] NMR spectrum (75 MHz, C$_6$D$_6$) of 5b. The inset shows the expanded (horizontal scale) signal.
Figure S20. $^1$H NMR spectrum (300 MHz, C$_6$D$_6$) of 5c.

Figure S21. $^{19}$F NMR spectrum (282 MHz, C$_6$D$_6$) of 5c. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard.
Figure S22. $^{13}$C-$^1$H NMR spectrum (75 MHz, C$_6$D$_6$) of 5c. The inset shows the expanded (horizontal scale) signal.

Figure S23. $^1$H NMR spectrum (300 MHz, C$_6$D$_6$) of 6a. The residual protio-solvent peak is labeled ‘*’. The inset shows the expanded (horizontal scale) signal.
Figure S24. $^{19}$F NMR spectrum (282 MHz, C$_6$D$_6$) of 6a. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard.

Figure S25. $^{13}$C/$^1$H NMR spectrum (75 MHz, C$_6$D$_6$) of 6a. The inset shows the expanded (horizontal scale) signal.
**Figure S26.** $^1$H NMR spectrum (300 MHz, C$_6$D$_6$) of 6b. The residual protio-solvent peak is labeled ‘*’. The inset shows the expanded (horizontal scale) signal.

**Figure S27.** $^{19}$F NMR spectrum (282 MHz, C$_6$D$_6$) of 6b. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard.
Figure S28. $^{13}$C$^{1}$H NMR spectrum (75 MHz, C₆D₆) of 6b. The inset shows the expanded (horizontal scale) signal.

Figure S29. ORTEP representation of the molecular structure of 2 with thermal ellipsoid probability set to 30 % and hydrogen atoms omitted for clarity.
The HOMO of 3 ($\varepsilon = -6.01$ eV; Figure 2, left) is localized on the Ni (87%), primarily from a $d_{z^2}$ orbital contribution (71%). Lower-lying orbitals display interactions between metal $d_{xz}$, $d_{yz}$ orbitals and the $\pi$-system of the aryl group.[22] The LUMO ($\varepsilon = -1.96$ eV; Figure 3, right) is an anti-bonding combination of the metal $d_{x^2-y^2}$ orbital (total Ni character of 45%) with the $\pi$-donor orbitals of the NHC and C$_4$F$_8$ ligands.

Figure S30. The HOMO (left) and LUMO (right) of 3. Isosurface values of 0.04 au are used.

Figure S31: HOMO-1 of 3. Isosurface values of 0.04 au are used.
Figure S32: HOMO-4 of 3. Isosurface values of 0.04 au are used.

Figure S33: HOMO-9 of 3. Isosurface values of 0.04 au are used.
| Complex | 2 | 3 | 4a | 5c |
|---------|---|---|----|----|
| ID code | tb060 | tb065 | tb070 | tb132_5 |
| Formula | C$_{24}$H$_{41}$F$_{8}$NiO$_{3}$P | C$_{31}$H$_{38}$F$_{8}$Ni | C$_{35}$H$_{45}$F$_{10}$NiO$_{3}$S | C$_{33}$H$_{41}$F$_{7}$NiO$_{2}$ |
| Mw | 647.27 | 649.34 | 822.50 | 689.39 |
| Color | yellow | Light red | pink | yellow |
| Temp (K) | 200(2) | 200(2) | 200(2) | 200(2) |
| Crystal system | Monoclinic | Orthorhombic | Monoclinic | Monoclinic |
| Space group | P2(1)/c | P2(1)2(1)2(1) | P2(1)/c | P2(1)/c |
| a/Å | 15.5474(12) | 10.8851(4) | 10.2361(5) | 9.7181(4) |
| b/Å | 9.9548(8) | 15.5440(6) | 16.5042(8) | 18.2160(7) |
| c/Å | 19.6379(15) | 18.9208(7) | 22.6115(11) | 19.2228(7) |
| α/° | 90.00 | 90 | 90 | 90 |
| β/° | 92.862(4) | 90 | 90.960(2) | 92.180(2) |
| γ/° | 90.00 | 90 | 90 | 90 |
| V/Å$^3$ | 3035.6(4) | 3201.4(2) | 3819.4(3) | 3400.5(2) |
| Z | 4 | 4 | 4 | 4 |
| Dc/g cm$^{-1}$ | 1.416 | 1.347 | 1.430 | 1.347 |
| μ/mm$^{-1}$ | 0.768 | 0.675 | 0.648 | 0.640 |
| F(000) | 1352 | 1352 | 1708 | 1440 |
| Crystal size/mm | 0.17x0.12x0.10 | 0.21x0.11x0.07 | 0.19x0.11x0.07 | 0.14x0.11x0.09 |
| 2θ range/° | 2.08-28.47 | 2.15-28.32 | 1.53-28.36 | 1.54-23.43 |
| Index range | -20<h<20 | -14<ś<ś14 | -13<ś<ś13 | -10<ś<ś10 |
| Index range | -21<ś<ś21 | -20<k<20 | -21<ś<ś21 | 0<ś<ś20 |
| Index range | -20<ś<ś26 | -25<ś<ś25 | -30<ś<ś28 | 0<ś<ś21 |
| Indep. reflns collected/unique | 29150/7565 | 45918/7927 | 65889/9440 | 11781/6216 |
| Max. and min. transmission | 0.9271 and 0.8805 | 0.9543 and 0.8713 | 0.9561 and 0.8868 | 0.7449 and 0.5352 |
| (Rint) | 0.0226 | 0.0281 | 0.0396 | ? |
| R1, wR2 (I>2θ(I)) | 0.0326, 0.0838 | 0.0266, 0.0643 | 0.0580, 0.1410 | 0.0687, 0.1292 |
| R1, wR2( all data) | 0.0399, 0.0880 | 0.0318, 0.0663 | 0.0727, 0.1513 | 0.1053, 0.1475 |
| Goodness of fit, F$^2$ | 1.011 | 1.035 | 1.046 | 1.062 |
| Data/restraints/para | 7565/0/352 | 79270/380 | 94400/469 | 92160/407 |
| Largest diff. peak, | 0.944, -0.261 | 0.327, -0.224 | 0.944, -0.717 | 0.871, -0.423 |
### Table S2. Comparison of $^{19}$F NMR δ (ppm) of Cα-substituted fluoronickelacycles (5a, 5b, 5c, 5d).

| Complex 5a | Complex 5b | Complex 5c | Complex 5d |
|------------|------------|------------|------------|
| -73.27     | -72.97     | ---        | ---        |
| -83.98     | -90.06     | -91.23     | -91.22     |
| -99.73     | -99.09     | -101.86    | -101.86    |
| -106.29    | -116.17    | -119.78    | -119.74    |
| -127.11    | -126.14    | -126.35    | -126.25    |
| -129.23    | -130.76    | -130.90    | -130.80    |
| -137.07    | -134.17    | -135.10    | -135.05    |
| -144.71    | -142.71    | -143.33    | -143.27    |

### Table S3. Bond lengths [Å] and angles [°] for complex 2.

| Bond                  | Length [Å] | Angle [°] |
|-----------------------|------------|-----------|
| Ni(1)-C(5)            | 1.9454(14) |           |
| Ni(1)-C(4)            | 1.9447(15) |           |
| Ni(1)-C(1)            | 1.9555(16) |           |
| Ni(1)-P(1)            | 2.2150(5)  |           |
| P(1)-O(2)             | 1.5818(14) |           |
| P(1)-O(3)             | 1.5926(13) |           |
| P(1)-O(1)             | 1.5943(13) |           |
| O(1)-C(16)            | 1.437(3)   |           |
| O(2)-C(19)            | 1.459(2)   |           |
| O(3)-C(22)            | 1.439(2)   |           |
| N(1)-C(5)             | 1.3647(19) |           |
| N(1)-C(6)             | 1.383(2)   |           |
| N(1)-C(8)             | 1.500(2)   |           |
| N(2)-C(5)             | 1.3654(19) |           |
| N(2)-C(7)             | 1.388(2)   |           |
| N(2)-C(12)            | 1.496(2)   |           |
| C(1)-F(1)             | 1.3798(19) |           |
| C(1)-F(2)             | 1.392(2)   |           |
| C(1)-C(2)             | 1.530(2)   |           |
| C(2)-F(3)             | 1.356(2)   |           |
| C(2)-F(4)             | 1.358(2)   |           |
| C(2)-C(3)             | 1.509(2)   |           |
| C(3)-F(5)             | 1.3509(19) |           |
| C(3)-F(6)             | 1.367(2)   |           |
| C(3)-C(4)             | 1.525(2)   |           |
| C(4)-F(8)             | 1.3871(18) |           |
| C(4)-F(7)             | 1.3904(19) |           |
| C(6)-C(7)             | 1.329(3)   |           |
| C(8)-C(11)            | 1.506(2)   |           |
| C(8)-C(9)             | 1.526(3)   |           |
| C(12)-C(15)           | 1.514(2)   |           |
| C(12)-C(13)           | 1.531(2)   |           |
| C(12)-C(14)           | 1.535(2)   |           |
| C(16)-C(17)           | 1.511(3)   |           |
| C(16)-C(18)           | 1.504(3)   |           |
| C(19)-C(20)           | 1.507(3)   |           |
| C(19)-C(21)           | 1.504(4)   |           |
| C(22)-C(23)           | 1.511(3)   |           |
| C(22)-C(24)           | 1.511(3)   |           |
| C(5)-Ni(1)-C(4)       | 171.33(6)  |           |
| C(5)-Ni(1)-C(1)       | 88.21(6)   |           |
| C(4)-Ni(1)-C(1)       | 85.19(7)   |           |
| C(5)-Ni(1)-P(1)       | 94.69(4)   |           |
| C(4)-Ni(1)-P(1)       | 91.89(5)   |           |
| C(1)-Ni(1)-P(1)       | 177.09(5)  |           |
| O(2)-P(1)-O(3)        | 106.95(8)  |           |
| O(2)-P(1)-O(1)        | 101.38(8)  |           |
| Bond Lengths [Å] | Angle [°] |
|------------------|-----------|
| O(3)-P(1)-O(1)  | 98.41(7)  |
| O(2)-P(1)-Ni(1) | 107.63(5) |
| O(3)-P(1)-Ni(1) | 122.62(5) |
| O(1)-P(1)-Ni(1) | 117.52(6) |
| C(16)-O(1)-P(1) | 127.70(14) |
| C(19)-O(2)-P(1) | 127.05(13) |
| C(22)-O(3)-P(1) | 129.83(11) |
| C(5)-N(1)-C(6)  | 110.74(13) |
| C(5)-N(1)-C(8)  | 130.13(12) |
| C(6)-N(1)-C(8)  | 119.12(13) |
| C(5)-N(2)-C(7)  | 110.57(13) |
| C(5)-N(2)-C(12) | 129.98(12) |
| C(7)-N(2)-C(12) | 119.45(13) |
| F(1)-C(1)-F(2)  | 103.24(13) |
| F(1)-C(1)-C(2)  | 105.80(14) |
| F(2)-C(1)-C(2)  | 104.81(13) |
| F(1)-C(1)-Ni(1) | 118.00(11) |
| F(2)-C(1)-Ni(1) | 111.83(11) |
| C(2)-C(1)-Ni(1) | 112.00(11) |
| F(3)-C(2)-F(4)  | 106.18(14) |
| F(3)-C(2)-C(3)  | 107.96(15) |
| F(4)-C(2)-C(3)  | 111.81(15) |
| F(3)-C(2)-C(1)  | 109.24(15) |
| F(4)-C(2)-C(1)  | 114.68(14) |
| C(3)-C(2)-C(1)  | 106.80(13) |
| F(5)-C(3)-F(6)  | 105.63(14) |
| F(5)-C(3)-C(2)  | 112.03(15) |
| F(6)-C(3)-C(2)  | 107.77(15) |
| F(5)-C(3)-C(4)  | 115.02(15) |
| F(6)-C(3)-C(4)  | 108.42(14) |
| C(2)-C(3)-C(4)  | 107.69(13) |
| F(8)-C(4)-F(7)  | 103.15(12) |
| F(8)-C(4)-C(3)  | 106.04(13) |
| F(7)-C(4)-C(3)  | 104.25(13) |
| F(8)-C(4)-Ni(1) | 119.13(11) |
| F(7)-C(4)-Ni(1) | 110.84(10) |
| C(3)-C(4)-Ni(1) | 112.09(10) |
| N(1)-C(5)-N(2)  | 104.10(12) |
| N(1)-C(5)-Ni(1) | 126.14(11) |
| N(2)-C(5)-Ni(1) | 129.23(11) |
| C(7)-C(6)-N(1)  | 107.34(14) |
| C(6)-C(7)-N(2)  | 107.25(14) |
| N(1)-C(8)-C(11) | 112.67(13) |
| N(1)-C(8)-C(9)  | 108.14(15) |
| C(11)-C(8)-C(9) | 108.68(17) |
| N(1)-C(8)-C(10) | 107.49(15) |
| C(11)-C(8)-C(10)| 109.72(17) |
| C(9)-C(8)-C(10)| 110.11(17) |
| N(2)-C(12)-C(15) | 112.22(13) |
| N(2)-C(12)-C(13) | 108.62(14) |
| C(15)-C(12)-C(13) | 110.57(15) |
| N(2)-C(12)-C(14) | 107.68(13) |
| C(15)-C(12)-C(14)| 108.47(15) |
| C(13)-C(12)-C(14)| 110.25(15) |
| O(1)-C(16)-C(17)| 107.99(19) |
| O(1)-C(16)-C(18)| 110.9(2) |
| C(17)-C(16)-C(18)| 113.14(19) |
| O(2)-C(19)-C(20)| 105.71(19) |
| O(2)-C(19)-C(21)| 108.6(2) |
| C(20)-C(19)-C(21)| 112.7(2) |
| O(3)-C(22)-C(23)| 106.23(18) |
| O(3)-C(22)-C(24)| 109.22(18) |
| C(23)-C(22)-C(24)| 112.0(2) |

**Table S4.** Bond lengths [Å] and angles [°] for complex 3.
| bond | length (Å) | bond | length (Å) |
|------|------------|------|------------|
| C(4)-C(5) | 1.402(2) | C(5)-C(4)-N(1) | 118.57(13) |
| C(5)-C(6) | 1.387(3) | C(6)-C(5)-C(10) | 117.34(17) |
| C(5)-C(10) | 1.513(3) | C(6)-C(5)-C(10) | 122.02(17) |
| C(6)-C(7) | 1.372(3) | C(4)-C(5)-C(10) | 120.63(14) |
| C(7)-C(8) | 1.362(3) | C(7)-C(6)-C(5) | 121.01(18) |
| C(8)-C(9) | 1.401(2) | C(6)-C(7)-C(8) | 120.83(17) |
| C(9)-C(13) | 1.511(2) | C(7)-C(8)-C(9) | 121.26(19) |
| C(10)-C(11) | 1.531(3) | C(4)-C(9)-C(8) | 116.88(16) |
| C(10)-C(12) | 1.531(2) | C(4)-C(9)-C(13) | 122.78(14) |
| C(13)-C(14) | 1.534(2) | C(8)-C(9)-C(13) | 120.32(16) |
| C(13)-C(15) | 1.536(2) | C(5)-C(10)-C(11) | 113.00(18) |
| C(16)-C(17) | 1.396(2) | C(5)-C(10)-C(12) | 110.36(15) |
| C(16)-C(21) | 1.408(2) | C(11)-C(10)-C(12) | 109.83(17) |
| C(17)-C(18) | 1.397(2) | C(9)-C(13)-C(14) | 110.52(14) |
| C(17)-C(22) | 1.524(2) | C(9)-C(13)-C(15) | 111.70(15) |
| C(18)-C(19) | 1.374(3) | C(14)-C(13)-C(15) | 110.26(14) |
| C(19)-C(20) | 1.382(3) | C(17)-C(16)-C(21) | 122.21(13) |
| C(20)-C(21) | 1.392(2) | C(17)-C(16)-N(2) | 118.81(13) |
| C(21)-C(25) | 1.520(2) | C(21)-C(16)-N(2) | 118.90(13) |
| C(22)-C(23) | 1.530(2) | C(16)-C(17)-C(18) | 117.81(16) |
| C(22)-C(24) | 1.532(2) | C(16)-C(17)-C(22) | 122.49(14) |
| C(25)-C(26) | 1.534(2) | C(18)-C(17)-C(22) | 119.69(15) |
| C(25)-C(27) | 1.536(2) | C(19)-C(18)-C(17) | 120.89(17) |
| C(28)-C(29) | 1.520(2) | C(18)-C(19)-C(20) | 120.57(15) |
| C(29)-C(30) | 1.521(2) | C(19)-C(20)-C(21) | 121.03(17) |
| C(30)-C(31) | 1.539(2) | C(20)-C(21)-C(16) | 117.46(16) |

| bond | length (Å) |
|------|------------|
| C(31)-Ni(1)-C(28) | 86.95(6) |
| C(31)-Ni(1)-C(1) | 96.64(6) |
| C(28)-Ni(1)-C(1) | 174.63(6) |
| C(1)-N(1)-C(4) | 124.12(11) |
| C(1)-N(1)-C(2) | 113.42(11) |
| C(1)-N(2)-C(16) | 127.41(11) |
| C(1)-N(2)-C(3) | 112.75(11) |
| C(16)-N(2)-C(3) | 119.47(11) |
| N(1)-C(1)-N(2) | 108.40(11) |
| N(1)-C(1)-Ni(1) | 118.59(10) |
| N(2)-C(1)-Ni(1) | 132.60(10) |
| N(1)-C(2)-C(3) | 102.14(12) |
| N(2)-C(3)-C(2) | 102.93(12) |
| C(9)-C(4)-C(5) | 122.67(14) |
| C(9)-C(4)-N(1) | 118.72(13) |
Table S5. Bond lengths [Å] and angles [°] for complex 4a.

| Bond          | Length [Å] | Angle [°] |
|---------------|------------|-----------|
| Ni(1)-C(1)    | 1.854(2)   |           |
| Ni(1)-C(28)   | 1.890(2)   |           |
| Ni(1)-O(1)    | 2.002(18)  |           |
| Ni(1)-O(2)    | 2.020(18)  |           |
| Ni(1)-S(1)    | 2.5148(7)  |           |
| S(1)-O(3)     | 1.419(2)   |           |
| S(1)-O(1)     | 1.467(2)   |           |
| S(1)-O(2)     | 1.471(2)   |           |
| S(1)-C(32)    | 1.829(4)   |           |
| F(1)-C(28)    | 1.384(3)   |           |
| F(2)-C(29)    | 1.343(3)   |           |
| F(3)-C(29)    | 1.338(4)   |           |
| F(4)-C(30)    | 1.346(5)   |           |
| F(5)-C(30)    | 1.325(4)   |           |
| F(6)-C(31)    | 1.336(4)   |           |
| F(7)-C(31)    | 1.331(4)   |           |
| F(8)-C(32)    | 1.313(5)   |           |
| F(9)-C(32)    | 1.320(4)   |           |
| F(10)-C(32)   | 1.315(4)   |           |
| N(1)-C(1)     | 1.340(3)   |           |
| N(1)-C(4)     | 1.438(3)   |           |
| N(1)-C(2)     | 1.489(3)   |           |
| N(2)-C(11)    | 1.344(3)   |           |
| N(2)-C(16)    | 1.440(3)   |           |
| N(2)-C(17)    | 1.405(4)   |           |
| N(2)-C(18)    | 1.420(4)   |           |
| N(2)-C(19)    | 1.370(5)   |           |
| C(1)-Ni(1)-C(28) | 93.27(10) |           |
| C(1)-Ni(1)-O(1) | 168.00(9) |           |
| C(28)-Ni(1)-O(1) | 98.34(10) |           |
| C(1)-Ni(1)-O(2) | 97.58(8)  |           |
| C(28)-Ni(1)-O(2) | 168.58(9) |           |
| O(1)-Ni(1)-O(1) | 71.04(8)  |           |
| C(1)-Ni(1)-S(1) | 133.31(7) |           |
| C(28)-Ni(1)-S(1) | 133.10(8) |           |
| O(1)-Ni(1)-S(1) | 35.66(6)  |           |
| Bond                        | Length (Å) | Bond                        | Length (Å) |
|-----------------------------|------------|-----------------------------|------------|
| O(2)-Ni(1)-S(1)            | 35.79(6)   | C(21)-C(16)-N(2)            | 119.8(2)   |
| O(3)-S(1)-O(1)             | 118.03(14) | C(17)-C(16)-N(2)            | 118.3(2)   |
| O(3)-S(1)-O(2)             | 117.65(15) | C(16)-C(17)-C(18)           | 117.6(2)   |
| O(1)-S(1)-O(2)             | 105.42(11) | C(16)-C(17)-C(22)           | 123.9(2)   |
| O(3)-S(1)-C(32)            | 105.23(17) | C(18)-C(17)-C(22)           | 118.4(2)   |
| O(1)-S(1)-C(32)            | 103.98(16) | C(19)-C(18)-C(17)           | 121.2(3)   |
| O(2)-S(1)-C(32)            | 104.94(14) | C(18)-C(19)-C(20)           | 120.2(3)   |
| O(3)-S(1)-Ni(1)            | 148.01(13) | C(19)-C(20)-C(21)           | 121.5(3)   |
| O(1)-S(1)-Ni(1)            | 52.73(7)   | C(20)-C(21)-C(16)           | 117.6(2)   |
| O(2)-S(1)-Ni(1)            | 53.45(7)   | C(20)-C(21)-C(25)           | 118.9(2)   |
| C(32)-S(1)-Ni(1)           | 106.75(12) | C(16)-C(21)-C(25)           | 123.4(2)   |
| S(1)-O(1)-Ni(1)            | 91.61(9)   | C(17)-C(22)-C(23)           | 112.4(3)   |
| S(1)-O(2)-Ni(1)            | 90.76(9)   | C(17)-C(22)-C(24)           | 110.1(3)   |
| C(1)-N(1)-C(4)             | 127.02(19) | C(23)-C(22)-C(24)           | 109.7(3)   |
| C(1)-N(1)-C(2)             | 111.06(19) | C(21)-C(25)-C(26)           | 112.4(3)   |
| C(4)-N(1)-C(2)             | 121.91(19) | C(21)-C(25)-C(27)           | 109.8(3)   |
| C(1)-N(2)-C(16)            | 126.97(19) | C(26)-C(25)-C(27)           | 110.8(3)   |
| C(1)-N(2)-C(3)             | 110.70(18) | F(1)-C(28)-C(31)            | 110.2(2)   |
| C(16)-N(2)-C(3)            | 120.27(18) | F(1)-C(28)-C(29)            | 108.8(2)   |
| N(1)-C(1)-Ni(1)            | 109.11(18) | C(31)-C(28)-C(29)           | 88.21(19)  |
| N(1)-C(1)-Ni(1)            | 123.25(16) | F(1)-C(28)-Ni(1)            | 117.22(16) |
| N(2)-C(1)-Ni(1)            | 127.47(16) | C(31)-C(28)-Ni(1)           | 114.71(19) |
| N(1)-C(2)-C(3)             | 101.69(19) | C(29)-C(28)-Ni(1)           | 114.07(17) |
| N(2)-C(3)-C(2)             | 101.73(19) | F(3)-C(29)-F(2)             | 107.4(2)   |
| C(9)-C(4)-C(5)             | 122.1(2)   | F(3)-C(29)-C(30)            | 111.6(2)   |
| C(9)-C(4)-N(1)             | 118.3(2)   | F(2)-C(29)-C(30)            | 114.7(3)   |
| C(5)-C(4)-N(1)             | 119.6(2)   | F(3)-C(29)-C(28)            | 114.1(2)   |
| C(6)-C(5)-C(4)             | 117.6(2)   | F(2)-C(29)-C(28)            | 117.6(2)   |
| C(6)-C(5)-C(10)            | 119.5(2)   | C(30)-C(29)-C(28)           | 90.9(2)    |
| C(4)-C(5)-C(10)            | 122.9(2)   | F(5)-C(30)-F(4)             | 108.5(3)   |
| C(7)-C(6)-C(5)             | 121.4(3)   | F(5)-C(30)-C(31)            | 115.1(3)   |
| C(6)-C(7)-C(8)             | 120.1(3)   | F(4)-C(30)-C(31)            | 114.2(3)   |
| C(7)-C(8)-C(9)             | 121.2(3)   | F(5)-C(30)-C(29)            | 114.3(3)   |
| C(8)-C(9)-C(4)             | 117.5(2)   | F(4)-C(30)-C(29)            | 115.3(3)   |
| C(8)-C(9)-C(13)            | 119.5(2)   | C(31)-C(30)-C(29)           | 88.5(2)    |
| C(4)-C(9)-C(13)            | 122.9(2)   | F(7)-C(31)-F(6)             | 107.6(3)   |
| C(11)-C(10)-C(5)           | 112.2(3)   | F(7)-C(31)-C(30)            | 112.1(2)   |
| C(11)-C(10)-C(12)          | 108.9(3)   | F(6)-C(31)-C(30)            | 114.3(3)   |
| C(5)-C(10)-C(12)           | 110.1(2)   | F(7)-C(31)-C(28)            | 114.8(3)   |
| C(9)-C(13)-C(14)           | 113.6(3)   | F(6)-C(31)-C(28)            | 116.3(2)   |
| C(9)-C(13)-C(15)           | 109.4(2)   | C(30)-C(31)-C(28)           | 91.1(2)    |
| C(14)-C(13)-C(15)          | 108.5(3)   | F(10)-C(32)-F(9)            | 108.5(3)   |
| C(21)-C(16)-C(17)          | 121.8(2)   | F(10)-C(32)-F(8)            | 109.4(4)   |
Table S6. Bond lengths [Å] and angles [°] for complex 5c.

| Bond                  | Length  | Angle       |
|-----------------------|---------|-------------|
| Ni(1)-C(30)           | 1.895(7) |             |
| Ni(1)-C(32)           | 1.896(6) |             |
| Ni(1)-C(1)            | 1.928(6) |             |
| Ni(1)-O(1)            | 1.969(4) |             |
| F(1)-C(30)            | 1.418(8) |             |
| F(2)-C(32)            | 1.375(7) |             |
| F(3)-C(39)            | 1.355(8) |             |
| F(4)-C(31)            | 1.375(8) |             |
| F(5)-C(31)            | 1.343(7) |             |
| F(6)-C(39)            | 1.358(8) |             |
| F(7)-C(32)            | 1.386(7) |             |
| O(1)-C(28)            | 1.227(8) |             |
| O(2)-C(28)            | 1.320(8) |             |
| O(2)-C(30)            | 1.437(8) |             |
| N(1)-C(1)             | 1.343(7) |             |
| N(1)-C(4)             | 1.440(7) |             |
| N(1)-C(2)             | 1.474(7) |             |
| N(2)-C(1)             | 1.351(7) |             |
| N(2)-C(16)            | 1.439(7) |             |
| N(2)-C(3)             | 1.475(7) |             |
| C(2)-C(3)             | 1.521(8) |             |
| C(4)-C(9)             | 1.401(8) |             |
| C(4)-C(5)             | 1.402(9) |             |
| C(5)-C(6)             | 1.405(9) |             |
| C(5)-C(10)            | 1.507(9) |             |
| C(6)-C(7)             | 1.368(10)|             |
| C(7)-C(8)             | 1.369(10)|             |
| C(30)-Ni(1)-C(32)     | 85.8(3)  |             |
| C(30)-Ni(1)-C(1)      | 170.9(3) |             |
| C(32)-Ni(1)-C(1)      | 97.8(3)  |             |
| C(30)-Ni(1)-O(1)      | 81.5(2)  |             |
| C(32)-Ni(1)-O(1)      | 161.1(2) |             |
| C(1)-Ni(1)-O(1)       | 96.9(2)  |             |
| C(28)-O(1)-Ni(1)      | 111.3(4) |             |
| C(28)-O(2)-C(30)      | 111.6(5) |             |
| C(1)-N(1)-C(4)        | 127.4(5) |             |
| C(1)-N(1)-C(2)        | 112.3(4) |             |
| C(4)-N(1)-C(2)        | 116.3(4) |             |
| C(1)-N(2)-C(16)       | 124.8(5) |             |
| C(1)-N(2)-C(3)        | 112.9(4) |             |
| Table S7. Optimized structure (Cartesian coordinates, Å) of 3 with an isopropyl-CH₃ agostic interaction. B3LYP/TZVP without dispersion correction. |
|---------------------------------|--------|--------|--------|
| H                               | 3.720451 | -3.236486 | -2.204765 |
| H                               | 2.702810 | -0.298224 | -4.338979 |
| H                               | 2.613875 | 0.886489  | -3.031972 |
| H                               | 1.958021 | -1.418908 | -2.318226 |
| Ni                              | -0.381956 | 0.794859  | 0.529500  |
| C 3.789956                      | -2.386599 | -2.887355 |
| C 4.732575                      | -0.188091 | -0.812193 |
| C 3.136272                      | -0.001705 | -3.380984 |
| C 5.204272                      | 0.173073  | 0.439927  |
| C 3.015391                      | -1.157257 | -2.373853 |
| C 3.473593                      | -0.764873 | -0.974427 |
| C 4.423177                      | -0.048799 | 1.561865  |
| C 2.688957                      | -0.971689 | 0.178064  |
| C 3.159883                      | -0.633894 | 1.460880  |
| C 1.345736                      | -3.098112 | -0.064609 |
| C 3.065800                      | -1.971850 | 3.603219  |
| C 2.373681                      | -0.903694 | 2.737054  |
| C -0.155824                     | -3.363099 | -0.230617 |
| C -2.510594                     | -3.194565 | -3.279299 |
| C -2.537451                     | -0.677990 | -3.517885 |
| C 0.194845                      | -1.052719 | 0.104820  |
| C -2.182170                     | -1.854679 | -2.594426 |
| C 2.130146                      | 0.380203  | 3.546680  |
| C -2.863479                     | -1.748045 | -1.236859 |
| C -2.157250                     | -1.808027 | -0.021598 |
| C -4.248561                     | -1.585026 | -1.175866 |
| C -2.812007                     | -1.716507 | 1.222444  |
| C -2.038058                     | -1.758975 | 2.534128  |
| C -1.608250                     | -0.347210 | 2.961767  |
| C -4.908563                     | -1.479196 | 0.037196  |
| C -4.194515                     | -1.539550 | 1.224942  |
| C -2.803850                     | -2.443888 | 3.675974  |
| H 4.850585                      | -2.154636 | -3.008376 |
| H 3.405311                      | -2.700722 | -3.860709 |
| H 5.350594                      | -0.009642 | -1.682630 |
| H 4.180137                      | 0.263107  | -3.563524 |
| H 6.181799                      | 0.628901  | 0.540817  |
Table S8. Optimized structure (Cartesian coordinates, Å) of 3 with an isopropyl-CH$_3$ agostic interaction. B3LYP/TZVP with the dispersion correction.

| C  | -0.726022 | 3.651547 | 0.112557 |
|----|-----------|----------|----------|
| C  | -1.110190 | 2.507713 | 1.075246 |
| F  | 1.556137  | 1.968413 | -0.961254|
| F  | 0.085847  | 0.896808 | -2.185555|
| F  | 0.057112  | 3.817296 | -2.154870|
| F  | 0.470004  | 4.178748 | 0.486400 |
| F  | -1.786114 | 2.695084 | -1.770545|
| F  | -1.623891 | 4.666765 | 0.059090 |
| F  | -0.741959 | 2.868870 | 2.362460 |
| F  | -2.496075 | 2.428617 | 1.106100 |

| Ni | -0.391174 | 0.808147 | 0.452908 |
|----|-----------|----------|----------|
| C  | 3.789903  | -2.904621| -2.317653|
| C  | 4.696197  | -0.385735| -0.615341|
| C  | 3.144436  | -0.632997| -3.211219|
| C  | 5.113266  | 0.208497 | 0.566642 |
| C  | 3.008014  | -1.610101| -2.033143|
| C  | 3.443326  | -0.986950| -0.715673|
| C  | 4.280147  | 0.210513 | 1.674134 |
| C  | 2.620735  | -0.985245| 0.424107 |
| C  | 3.022073  | -0.391381| 1.631113 |
| C  | 1.262357  | -3.119865| 0.497021 |
| C  | 2.790358  | -1.144306| 4.034125 |
| C  | 2.145703  | -0.370904| 2.873074 |
| C  | -0.235944 | -3.384601| 0.291852 |
| C  | -2.317106 | -3.504546| -2.900414|
| C  | -2.259843 | -1.027211| -3.414094|
| C  | 0.150851  | -1.063846| 0.314723 |
| C  | -2.010774 | -2.103017| -2.345544|
| C  | 1.803885  | 1.069096 | 3.286176 |
| C  | -2.802131 | -1.829016| -1.076894|
| C  | -2.196200 | -1.758634| 0.186930 |
| C  | -4.179063 | -1.613165| -1.147512|
| C  | -2.921533 | -1.442490| 1.349053 |

| C  | -2.216599 | -1.261256| 2.685577 |
|----|-----------|----------|----------|
| C  | -1.686039 | 0.176906 | 2.812245 |
| C  | -4.915879 | -1.313062| -0.012995|
| C  | -4.290094 | -1.215473| 1.222697 |
| C  | -3.092911 | -1.605159| 3.896429 |
| H  | 4.851791  | -2.689474| -2.457197|
| H  | 3.422414  | -3.381636| -3.229295|
| H  | 5.349164  | -0.368060| -1.478459|
| H  | 4.192015  | -0.412230| -3.427054|
| H  | 6.086793  | 0.680384 | 0.621056 |
| H  | 3.710141  | -3.623233| -1.498943|
| H  | 2.709725  | -1.073501| -4.111429|
| H  | 2.630039  | 0.302745 | -3.005412|
| H  | 1.948715  | -1.857214| -1.950072|
| H  | 4.611164  | 0.687340 | 2.588021 |
| H  | 1.887580  | -3.619013| -0.239777|
| H  | 1.609405  | -3.400734| 1.494488 |
| H  | 3.011640  | -2.175588| 3.750134 |
| H  | 3.726573  | -0.679041| 4.348987 |
| H  | -1.700156 | -3.711741| -3.777850|
| H  | -1.584356 | -1.179488| -4.258498|
| H  | -0.449495 | -3.866257| -0.663251|
| H  | -0.949781 | -2.055263| -2.097533|
| H  | -2.133286 | -4.287073| -2.160588|
| H  | 2.698777  | 1.614180 | 3.591895 |
| H  | 2.121118  | -1.162692| 4.897750 |
| H  | 1.208481  | -0.874328| 2.634963 |
| H  | -0.681517 | -3.982322| 1.087404 |
| H  | -2.082453 | -0.029404| -3.017644|
| H  | -3.364314 | -3.580202| -3.202246|
| H  | 1.346461  | 1.623657 | 2.464827 |
| H  | -3.282041 | -1.072809| -3.795979|
| H  | 1.108390  | 1.075364 | 4.127991 |
| H  | -1.355685 | -1.934752| 2.704126 |
| H  | -0.765448 | 0.318719 | 2.213234 |
| H  | -4.676511 | -1.662754| -2.107508|
| H  | -1.349586 | 0.398888 | 3.826352 |
Table S9. Optimized structure (Cartesian coordinates, Å) of 3'. B3LYP/TZVP without the dispersion correction.

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | -2.426896  | 0.917255   | 2.519622   |
| H    | -2.488459  | -1.601884  | 4.805461   |
| H    | -3.546460  | -2.591903  | 3.789765   |
| H    | -5.981760  | -1.137448  | -0.091817  |
| H    | -4.878011  | -0.957176  | 2.092618   |
| H    | -3.894201  | -0.877394  | 4.038241   |
| N    | 1.351114   | -1.648937  | 0.348529   |
| N    | -0.790083  | -2.016453  | 0.306958   |
| C    | 0.350001   | 1.361073   | -1.204248  |
| C    | -0.356252  | 2.642037   | -1.705522  |
| C    | -0.582085  | 3.544211   | -0.471229  |
| C    | -1.092361  | 2.606119   | 0.642104   |
| F    | 1.691060   | 1.638045   | -1.079913  |
| F    | 0.263159   | 0.409621   | -2.204442  |
| F    | 0.332465   | 3.825202   | -2.680306  |
| F    | 0.618380   | 4.068501   | -0.239719  |
| F    | -1.570761  | 2.296314   | -2.218669  |
| F    | -1.411372  | 4.576313   | -0.766559  |
| F    | -0.822137  | 3.188036   | 1.872556   |
| F    | -2.480013  | 2.567774   | 0.559985   |
| Ni   | 0.716337   | 0.619532   | -0.128477  |
| C    | 2.380342   | -3.856324  | -2.632154  |
| C    | 4.014733   | -1.899747  | -0.799134  |
| C    | 2.332598   | -1.420464  | -3.323239  |
| C    | 4.635239   | -1.615874  | 0.406875   |
| C    | 1.993035   | -2.426788  | -2.212105  |
| C    | 2.631394   | -2.061042  | -0.878480  |
| C    | 3.885001   | -1.487694  | 1.565964   |
| C    | 1.881939   | -1.909079  | 0.308957   |
| C    | 2.499294   | -1.635936  | 1.549775   |
| C    | -0.239719  | -3.359226  | 0.460329   |
| C    | 2.050623   | -2.677984  | 3.804689   |
| C    | 1.715102   | -1.517830  | 2.850059   |
| C    | -1.701900  | -2.962338  | 0.210329   |
| C    | -3.082523  | -1.998010  | -3.485488  |
| C    | -1.971190  | 0.273643   | -3.590764  |
| C    | -0.375798  | -1.027060  | 0.096892   |
| C    | -2.361755  | -0.901306  | -2.679978  |
| C    | 1.931351   | -0.160549  | 3.538538   |
| C    | -3.199373  | -0.461860  | -1.485031  |
| C    | -2.841449  | -0.739128  | -0.152413  |
| C    | -4.396783  | 0.218135   | -1.709397  |
| C    | -3.671779  | -0.387513  | 0.928833   |
| C    | -3.336703  | -0.737720  | 2.373430   |
| C    | -3.400935  | 0.477760   | 3.312142   |
| C    | -5.218900  | 0.591279   | -0.658303  |
| C    | -4.859898  | 0.284988   | 0.645361   |
| C    | -4.252835  | -1.860869  | 2.896344   |
| H    | 3.454378   | -3.935708  | -2.813402  |
| H    | 1.865224   | -4.134374  | -3.554554  |
| H    | 4.614047   | -1.995534  | -1.695363  |
| H    | 3.398031   | -1.429748  | -3.562140  |
| H    | 5.709933   | -1.486164  | 0.443186   |
| H    | 2.121611   | -4.588494  | -1.864022  |
| H    | 1.789431   | -1.674995  | -4.236223  |
| H    | 2.069443   | -0.401368  | -3.039082  |
| H    | 0.910674   | -2.405567  | -2.079304  |
| H    | 4.384896   | -1.260939  | 2.498733   |
| H    | 0.122343   | -4.113197  | -0.239159  |
| H    | -0.068465  | -3.722476  | 1.476528   |
| H    | 1.875123   | -3.650034  | 3.338058   |
| H    | 3.097423   | -2.645540  | 4.114450   |
| H    | -2.447388  | -2.352181  | -4.301226  |
| H    | -1.311580  | -0.074478  | -4.389174  |
| H    | -2.093174  | -3.370727  | -0.723661  |
| H    | -1.433938  | -1.330542  | -2.301474  |
| H    | -3.343527  | -2.855712  | -2.861143  |
| H    | 2.966566   | -0.035354  | 3.862500   |
| H    | 1.435809   | -2.617085  | 4.705651   |
| H    | 0.653758   | -1.587805  | 2.690439   |
| H    | -2.366853  | -3.260489  | 1.018934   |
Table S10. Optimized structure (Cartesian coordinates, Å) of 3', B3LYP/TZVP with the dispersion correction.

|      |      |      |      |      |      |      |      |
|------|------|------|------|------|------|------|------|
| H    | -1.455424 | 1.054023 | -3.032996 |     | C    | 2.122962 | -2.440381 | -2.030016 |
| H    | -4.007750 | -1.619825 | -3.925726 |     | C    | 2.764253 | -2.001348 | -0.723327 |
| H    | 1.689172  | 0.669291  | 2.874312  |     | C    | 3.959247 | -1.136178 | 1.662348  |
| H    | -2.847681 | 0.722319  | -4.063225 |     | C    | 2.014991 | -1.848527 | 0.458221  |
| H    | 1.296295  | -0.085755 | 4.424053  |     | C    | 2.595481 | -1.421477 | 1.666264  |
| H    | -2.309022 | -1.103687 | 2.394946  |     | C    | -0.039204 | -3.389353 | 0.700202  |
| H    | -2.761387 | 1.284916  | 2.960386  |     | C    | 2.283461 | -2.083596 | 4.086277  |
| H    | -4.691033 | 0.456811  | -2.723682 |     | C    | 1.772772 | -1.215169 | 2.926930  |
| H    | -3.074041 | 0.191271  | 4.314709  |     | C    | -1.497644 | -3.093538 | 0.314923  |
| H    | -4.418903 | 0.863643  | 3.400604  |     | C    | -2.376732 | -1.922178 | -3.717857 |
| H    | -3.957073 | -2.156782 | 3.905897  |     | C    | -1.275287 | 0.330804  | -3.340893 |
| H    | -4.222445 | -2.748065 | 2.259953  |     | C    | -0.266403 | -1.111670 | 0.150882  |
| H    | -6.142452 | 1.122230  | -0.855138 |     | C    | -1.819957 | -0.941268 | -2.673670 |
| H    | -5.513090 | 0.576765  | 1.457902  |     | C    | 1.726787 | 0.271149  | 3.312798  |
| H    | -5.292174 | -1.527276 | 2.938679  |     | C    | -2.858149 | -0.615391 | -1.609545 |
| N    | 0.453227  | -2.073451 | 0.254768  |     | C    | -2.689536 | -0.932105 | -0.251670 |
| N    | -1.634693 | -1.479943 | 0.112348  |     | C    | -4.036982 | 0.030775  | -1.981524 |
| C    | 2.113402  | 1.923895  | -0.409702 |     | C    | -3.663568 | -0.630360 | 0.714089  |
| C    | 1.556062  | 3.351247  | -0.555902 |     | C    | -3.485538 | -0.987255 | 2.181715  |
| C    | 0.327503  | 3.405450  | 0.377597  |      | C    | -3.728693 | 0.209570  | 3.113386  |
| C    | -0.455901 | 2.082219  | 0.167922  |     | C    | -5.013348 | 0.336683  | -1.046617 |
| F    | 3.012969  | 1.924669  | 0.643199  |     | C    | -4.827614 | 0.005993  | 0.287892  |
| F    | 2.866990  | 1.616152  | -1.532163 |     | C    | -4.396876 | -2.164219 | 2.573350  |
| F    | 2.439853  | 4.338050  | -0.266911 |     | H    | 3.853721  | -3.407986 | -2.952242 |
| F    | 0.764992  | 3.456513  | 1.664829  |     | H    | 2.297863  | -3.993888 | -3.533798 |
| F    | 1.130569  | 3.540133  | -1.835271 |     | H    | 4.722827  | -1.777018 | -1.571538 |
| F    | -0.425390 | 4.509658  | 0.155660  |     | H    | 3.051637  | -0.910998 | -3.279000 |
| F    | -1.260211 | 1.882288  | 1.263039  |     | H    | 5.769449  | -1.022181 | 0.521557  |
| F    | -1.303658 | 2.258074  | -0.897087 |     | H    | 2.890136  | -4.483817 | -1.938848 |
| Ni   | 0.635538  | 0.582751  | -0.240352 |     | H    | 1.554484  | -1.580820 | -3.944946 |
| C    | 2.835043  | -3.653462 | -2.645862 |     | H    | 1.504006  | -0.422788 | -2.612838 |
| C    | 4.123693  | -1.694342 | -0.673952 |     | H    | 1.096973  | -2.741358 | -1.813962 |
| C    | 2.053758  | -1.271730 | -3.023928 |     | H    | 4.431586  | -0.782997 | 2.569871  |
| C    | 4.714874  | -1.268198 | 0.506078  |     | H    | 0.409727  | -4.187440 | 0.108811  |

optimized structure (Cartesian coordinates, Å) of 3', B3LYP/TZVP with the dispersion correction.
|   | X   | Y   | Z   |
|---|-----|-----|-----|
| H | -1.597811 | -2.195688 | -4.433718 |
| H | -0.515902  | 0.074805   | -4.081732  |
| H | -1.780501  | -3.546489  | -0.638748  |
| H | -0.975267  | -1.432047  | -2.190588  |
| H | -2.747515  | -2.836300  | -3.248383  |
| H | 2.721327   | 0.645131   | 3.563899   |
| H | 1.639429   | -1.963649  | 4.960236   |
| H | 0.747306   | -1.520048  | 2.714392   |
| H | -2.210880  | -3.407102  | 1.073393   |
| H | -0.827893  | 1.000311   | -2.606304  |
| H | -3.202267  | -1.479055  | -4.278490  |
| H | 1.341740   | 0.879327   | 2.495159   |
| H | -2.068347  | 0.882003   | -3.849540  |
| H | 1.078765   | 0.418814   | 4.179237   |
| H | -2.447871  | -1.294974  | 2.322624   |
| H | -3.111480  | 1.059912   | 2.830305   |
| H | -4.190101  | 0.302227   | -3.018278  |
| H | -3.488794  | -0.065342  | 4.143279   |
| H | -4.774490  | 0.523661   | 3.095566   |
| H | -4.216385  | -2.463335  | 3.608723   |
| H | -4.240152  | -3.035268  | 1.933288   |
| H | -5.919967  | 0.841521   | -1.357436  |
| H | -5.594377  | 0.255892   | 1.009912   |
| H | -5.448412  | -1.881801  | 2.484164   |
| N | 0.602752   | -2.097336  | 0.408516   |
| N | -1.501126  | -1.617006  | 0.167292   |
| C | 1.821691   | 2.045501   | -0.665664  |
| C | 1.106771   | 3.404983   | -0.566932  |
| C | 0.081834   | 3.246041   | 0.577925   |
| C | -0.610896  | 1.873823   | 0.369352   |
| F | 2.900523   | 2.063057   | 0.204625   |
| F | 2.375813   | 1.915843   | -1.930989  |
| F | 1.923377   | 4.465905   | -0.352721  |
| F | 0.753886   | 3.225057   | 1.761440   |
| F | 0.419652   | 3.633935   | -1.720403  |
| F | -0.791634  | 4.280882   | 0.619056   |
| F | -1.195774  | 1.496012   | 1.556543   |

F -1.639066  2.053177  -0.518351
Figure S34. ORTEP representation of the molecular structure of 3•H₂O with thermal ellipsoid probabilities set to 30% and hydrogen atoms omitted for clarity.

Table S11. Crystal data and structure refinement for 3•H₂O.

| Complex     | 3•H₂O       |
|-------------|-------------|
| ID code     | tb069       |
| Formula     | C₃₇H₄₆F₈N₂NiO |
| Mw          | 667.35      |
| Color       | yellow      |
| Temp (K)    | 200(2)      |
| Crystal system | Monoclinic  |
| Space group  | P2(1)/c     |
| a/Å         | 16.5255(8)  |
| b/Å         | 10.6186(5)  |
| c/Å         | 20.8839(9)  |
| α/°         | 90.00       |
| β/°         | 101.931(2)  |
| γ/°         | 90.00       |
| V/Å³        | 3585.5(3)   |
| Z           | 4           |
| Dc/g cm⁻¹   | 1.381       |
| μ/mm⁻¹      | 0.614       |
| F(000)      | 1560        |
| Crystal size/mm | 0.22x0.19x0.18 |
Table S12. Bond lengths [Å] and angles [°] for complex 3•H2O.

| Bond                  | Length  [Å] | Angle  [°] |
|-----------------------|------------|-----------|
| Ni(1)-C(28)           | 1.8868(13) |           |
| Ni(1)-C(31)           | 1.9257(14) |           |
| Ni(1)-C(1)            | 1.9580(12) |           |
| Ni(1)-O(1)            | 1.9872(10) |           |
| F(1)-C(28)            | 1.3766(15) |           |
| F(2)-C(28)            | 1.3825(16) |           |
| F(3)-C(29)            | 1.3560(15) |           |
| F(4)-C(29)            | 1.3550(15) |           |
| F(5)-C(30)            | 1.3472(16) |           |
| F(6)-C(30)            | 1.3638(16) |           |
| F(7)-C(31)            | 1.3937(15) |           |
| F(8)-C(31)            | 1.3926(15) |           |
| N(1)-C(1)             | 1.3513(15) |           |
| N(1)-C(4)             | 1.4356(15) |           |
| N(1)-C(2)             | 1.4742(16) |           |
| N(2)-C(1)             | 1.3464(15) |           |
| N(2)-C(16)            | 1.4384(14) |           |
| N(2)-C(3)             | 1.4787(15) |           |
| C(2)-C(3)             | 1.5166(17) |           |
| C(4)-C(9)             | 1.3981(17) |           |
| C(4)-C(5)             | 1.4080(18) |           |
| C(5)-C(6)             | 1.3941(19) |           |
| C(5)-C(10)            | 1.5232(19) |           |
| C(6)-C(7)             | 1.379(2)   |           |
| C(7)-C(8)             | 1.379(2)   |           |
| C(8)-C(9)             | 1.3984(18) |           |
| C(9)-C(13)            | 1.5126(18) |           |
| C(10)-C(11)           | 1.525(2)   |           |
| C(13)-C(15)           | 1.522(2)   |           |
| C(13)-C(14)           | 1.531(2)   |           |
| C(16)-C(21)           | 1.3989(17) |           |
| C(16)-C(17)           | 1.4039(16) |           |
| C(17)-C(18)           | 1.3912(19) |           |
| C(17)-C(22)           | 1.5170(18) |           |
| C(18)-C(19)           | 1.378(2)   |           |
| C(19)-C(20)           | 1.378(2)   |           |
| C(20)-C(21)           | 1.3965(18) |           |
| C(21)-C(25)           | 1.5173(17) |           |
| C(22)-C(23)           | 1.534(2)   |           |
| C(22)-C(24)           | 1.533(2)   |           |
| C(25)-C(26)           | 1.528(2)   |           |
| C(25)-C(27)           | 1.5313(19) |           |
| C(28)-C(29)           | 1.5383(18) |           |
| Bond | Distance (Å) | Bond | Distance (Å) |
|------|-------------|------|-------------|
| C(29)-C(30) | 1.523(2) | C(8)-C(9)-C(13) | 119.59(11) |
| C(30)-C(31) | 1.521(2) | C(5)-C(10)-C(12) | 113.03(13) |
| C(32)-C(33) | 1.358(3) | C(5)-C(10)-C(11) | 110.87(13) |
| C(32)-C(37) | 1.355(4) | C(12)-C(10)-C(11) | 109.36(14) |
| C(33)-C(34) | 1.321(4) | C(9)-C(13)-C(15) | 111.81(13) |
| C(34)-C(35) | 1.386(5) | C(9)-C(13)-C(14) | 109.97(12) |
| C(35)-C(36) | 1.392(4) | C(15)-C(13)-C(14) | 110.19(13) |
| C(36)-C(37) | 1.359(4) | C(21)-C(16)-C(17) | 122.16(11) |
| C(28)-Ni(1)-C(31) | 85.98(6) | C(17)-C(16)-N(2) | 119.52(10) |
| C(28)-Ni(1)-C(1) | 93.26(5) | C(17)-C(16)-N(2) | 118.07(11) |
| C(31)-Ni(1)-C(31) | 177.64(5) | C(18)-C(17)-C(22) | 119.32(12) |
| C(28)-Ni(1)-O(1) | 174.05(5) | C(16)-C(17)-C(22) | 123.00(11) |
| C(31)-Ni(1)-O(1) | 88.07(5) | C(19)-C(18)-C(17) | 121.01(13) |
| C(1)-Ni(1)-O(1) | 92.69(4) | C(18)-C(19)-C(20) | 120.56(13) |
| C(1)-N(1)-C(4) | 126.83(10) | C(19)-C(20)-C(21) | 120.87(14) |
| C(1)-N(1)-C(2) | 112.92(10) | C(20)-C(21)-C(16) | 117.68(12) |
| C(4)-N(1)-C(2) | 120.12(10) | C(20)-C(21)-C(25) | 118.33(12) |
| C(1)-N(2)-C(16) | 126.93(10) | C(16)-C(21)-C(25) | 123.97(11) |
| C(1)-N(2)-C(3) | 112.48(9) | C(17)-C(22)-C(23) | 111.15(12) |
| C(16)-N(2)-C(3) | 116.78(9) | C(17)-C(22)-C(24) | 111.76(13) |
| N(2)-C(1)-N(1) | 106.79(10) | C(23)-C(22)-C(24) | 109.78(12) |
| N(2)-C(1)-Ni(1) | 129.78(9) | C(21)-C(25)-C(26) | 111.55(11) |
| N(1)-C(1)-Ni(1) | 123.37(8) | C(21)-C(25)-C(27) | 110.78(11) |
| N(1)-C(2)-C(3) | 101.14(9) | C(26)-C(25)-C(27) | 110.94(11) |
| N(2)-C(3)-C(2) | 101.67(9) | F(1)-C(28)-F(2) | 104.88(10) |
| C(9)-C(4)-C(5) | 122.07(11) | F(1)-C(28)-C(29) | 104.54(10) |
| C(9)-C(4)-N(1) | 120.21(11) | F(2)-C(28)-C(29) | 106.53(10) |
| C(5)-C(4)-N(1) | 117.62(11) | F(1)-C(28)-Ni(1) | 111.37(9) |
| C(6)-C(5)-C(4) | 117.37(12) | F(2)-C(28)-Ni(1) | 116.14(9) |
| C(6)-C(5)-C(10) | 119.57(12) | C(29)-C(28)-Ni(1) | 112.47(9) |
| C(4)-C(5)-C(10) | 123.04(12) | F(4)-C(29)-F(3) | 106.18(11) |
| C(7)-C(6)-C(5) | 121.44(13) | F(4)-C(29)-C(30) | 108.05(11) |
| C(8)-C(7)-C(6) | 120.24(13) | F(3)-C(29)-C(30) | 111.73(11) |
| C(7)-C(8)-C(9) | 120.93(13) | F(4)-C(29)-C(28) | 110.04(11) |
| C(4)-C(9)-C(8) | 117.88(12) | F(3)-C(29)-C(28) | 113.96(11) |
| C(4)-C(9)-C(13) | 122.49(11) | C(30)-C(29)-C(28) | 106.77(11) |
| Bond                  | Angle (°)      |
|----------------------|----------------|
| F(5)-C(30)-F(6)      | 106.72(11)     |
| F(5)-C(30)-C(31)     | 109.93(12)     |
| F(6)-C(30)-C(31)     | 114.85(12)     |
| F(5)-C(30)-C(29)     | 108.71(12)     |
| F(6)-C(30)-C(29)     | 110.71(12)     |
| C(31)-C(30)-C(29)    | 105.82(10)     |
| F(8)-C(31)-F(7)      | 102.57(10)     |
| F(8)-C(31)-C(30)     | 106.35(11)     |
| F(7)-C(31)-C(30)     | 107.68(11)     |
| F(8)-C(31)-Ni(1)     | 111.21(9)      |
| F(7)-C(31)-Ni(1)     | 115.04(9)      |
| C(30)-C(31)-Ni(1)    | 113.14(9)      |
| C(33)-C(32)-C(37)    | 121.4(3)       |
| C(34)-C(33)-C(32)    | 120.5(3)       |
| C(33)-C(34)-C(35)    | 119.7(2)       |
| C(34)-C(35)-C(36)    | 120.0(3)       |
| C(37)-C(36)-C(35)    | 118.6(3)       |
| C(36)-C(37)-C(32)    | 119.7(2)       |
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