Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information for

A T-shaped Ni[κ^2-$(CF_2)_4$-] NHC complex: Unusual Csp3-F and M-CF bond functionalization reactions†

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Contents

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-d$_6$ (C_6D_6) was dried by stirring over activated alumina (ca. 10 wt. %) overnight, followed by filtration. Acetonitrile-d$_3$ (CD_3CN) was dried by refluxing over calcium hydride under nitrogen. After distillation, CD_3CN 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 (Me_3SiOTf, Aldrich, 99%), bis(1,5-cyclooctadiene)nickel (0) ($Ni(cod)_2$, Strem, 98+%), triisopropyl phosphite ($P(O^iPr)_3$, Aldrich, 95%), tri-*ortho*-tolyl phosphite (P(O-*o*-tolyl)$_3$), 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 $Ni[P(O^iPr)_3]_2(C_4F_8)$ was made by oxidative addition of tetrafluoroethylene to $Ni[P(O^iPr)_3]_4$ using slightly modified literature procedures.[2] $Ni[P(O^iPr)_3]_4$ complex was prepared from $Ni(COD)_2$ following reported methods.[2] Metallacycle $Ni(C_4F_8)$[P(O-*o*-tolyl)$_3$]$_2$ was prepared by addition of TFE to Ni[P(O-*o*-tolyl)$_3$]$_3$ using slightly modified literature procedures.[3] $Ni[P(O\text{-}^iPr)_3]_4$ complex was prepared from $Ni(COD)_2$ following reported methods.[2] ^1H, ^{19}F, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ 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 (C_6D_6: 7.16 ppm; CD_3CN: 1.94 ppm). ^{19}F 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. $^{31}P\{^1H\}$ NMR data were referenced to external H_3PO_4 (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, ^{19}F, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ 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_2O, **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.[5] Systematic absences in the diffraction data set and unit-cell parameters were consistent with monoclinic **P**$2_1/c$ (№14) for complexes **2**, **4a** and **5c**, and orthorhombic **P**$2_12_12_1$ (№19) 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 F^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.

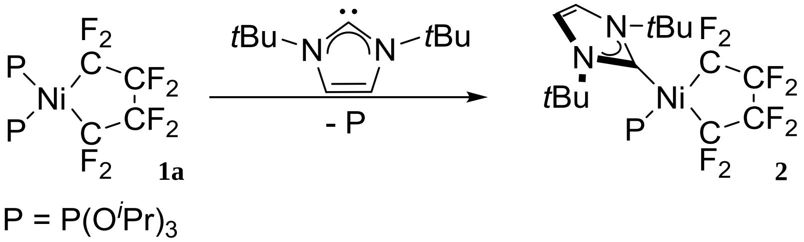
The structural model for complex **4a** contains one target molecule and one fully occupied hexane solvent molecule in the lattice. The complex molecule is located in the general position and the hexane solvent molecule is located on the inversion center of the space group.

Diffraction data for the crystal of complex **5c** were collected to 0.75Å resolution; however, due to small crystal size and weak diffraction it was discovered that both R(int) and R(sigma) exceeded 35% for the data below 1.00Å resolution. Based on R(sigma) value, data were truncated to 0.95Å 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[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.

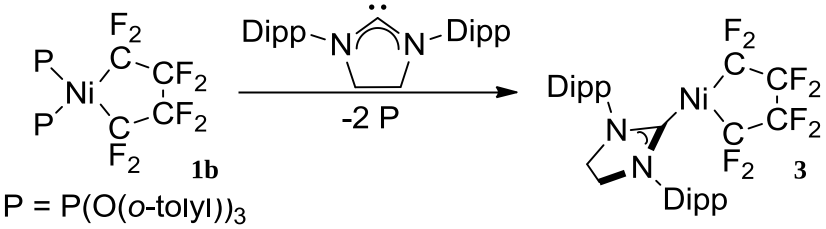
For all the compounds hydrogen atoms positions were calculated based on the geometry of related non-hydrogen atoms. All hydrogen atoms were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.[7] Metrical data for **2**, **3**, **3**•H_2O, **4a** and **5c** are presented in Table S1and S11, and the CCDC files 968465 (**2**), 968466 (**3**), 968467 (**4a**), 1028645 (**5c**) and 1412522 (**3**•H_2O) contain the supplementary crystallographic data. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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.

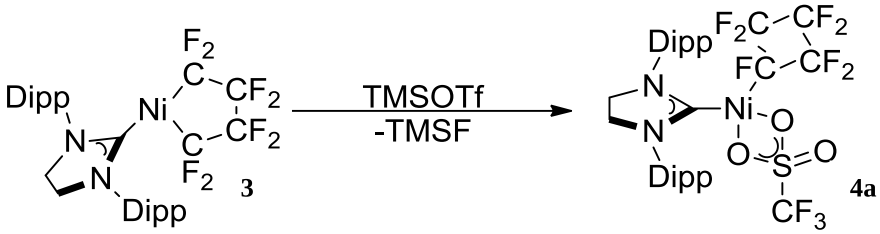
Experimental.



Synthesis of Ni[κ_2-$(CF_2)_4$-](ItBu)[P(O^{i}Pr)$_3$] (2). Yellow complex Ni[κ_2-$(CF_2)_4$-][P(O^{i}Pr)$_3$]$_2$ (**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[κ_2-$(CF_2)_4$-][P(O^{i}Pr)$_3$]$_2$). The isolated material was stored at room temperature under nitrogen. UV-vis (1.0 mM in THF): λmax(ε) = 322(341). ^{1}H NMR (300 MHz, CD_3CN) δ 1.19 (d, J ≈ 6 Hz, 18H, Me^{i}Pr) 1.94 (s, 18H, Me*t*Bu), 4.65 (sept, m, J ≈ 6 Hz, 3H, ^{i}Pr H) 7.34 (s, 2H, CHIm). ^{19}F NMR (282 MHz, CD_3CN) δ -100.50 (d 'quint', $^3J_{FP}$ = 31, $^3J_{FF} \approx {}^4J_{FF}$ = 6 Hz, 2F$_\alpha$), -102.93 (d 'quint', $^3J_{FP}$ = 33, $^3J_{FF} \approx {}^4J_{FF}$ = 4 Hz, 2F$_\alpha$), -137.03, -138.54 (mult, 2F$_\beta$). ^{31}P{^{1}H} NMR (121 MHz, CD_3CN) 115.8 ppm ('quint' 'tr', $^3J_{PF} \approx 32$, $^4J_{PF} \approx 7$ Hz). Anal. Calc. for $C_{24}H_{41}F_8N_2NiO_3P$: C, 44.54, H, 6.39, N, 4.33. Found: C, 44.54, H, 6.53, N, 4.28. See Figures S7-9 for ^{1}H, ^{19}F, ^{31}P{^{1}H} NMR spectra.

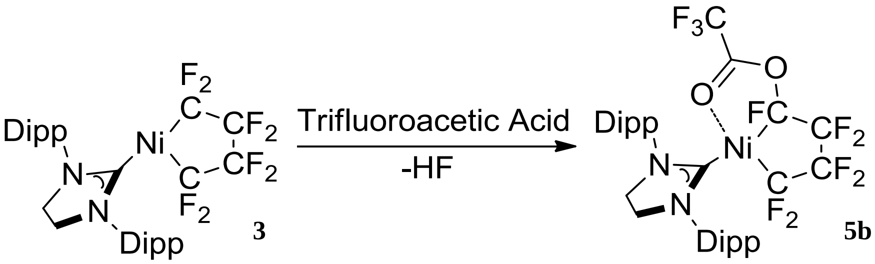


Synthesis of Ni[κ_2-$(CF_2)_4$-](SIPr) (3). Yellow complex Ni[κ_2-$(CF_2)_4$-][P((O-o-tol)]$_3$]$_2$ (**1b**) (1.00 g, 1.04 mmol) was placed in a 20 mL scintillation vial and dissolved in ~ 10 mL of benzene. Colorless [SIPr] (446 mg, 1.14 mmol) was then added to the stirred mixture and the mixture heated 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[κ_2-$(CF_2)_4$-][P(O-o-tol)$_3$]$_2$. The isolated material was stored at room temperature under nitrogen. UV-vis (1.5 mM in benzene): λmax(ε) = 486(461). ^{1}H NMR (300 MHz, C_6D_6) 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 ^{i}Pr H), 3.13 (s, 4H, 2 CH2Im), 7.00-7.30 (mult, 6H, 6 Ar-H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 24.78, 24.96, 29.40, 53.50, 125.63, 127-129, 129.57, 131.26, 147.67. ^{19}F NMR (282 MHz, C_6D_6, 25 °C) δ -101.90 (s, 4F$_\alpha$), -138.63 (s, 4F$_\beta$). ^{19}F NMR (282 MHz, CD_2Cl_2, -50 °C) δ -99.32 (s, 2F'$_\alpha$), -103.07 (br s, 4F$_\alpha$), -119.17 (s, 2F'$_\alpha$), -138.37 (s, 2F'$_\beta$), -139.64 (br s, 4F$_\beta$), -141.21 (s, 2F'$_\beta$). Anal. Calc. for $C_{31}H_{38}F_8N_2Ni$: 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**•H_2O Anal. Calc. for $C_{31}H_{40}F_8N_2NiO$: C, 55.79, H, 6.04, N, 4.20. See below: Figure 34, Table S11- 12) See Figures S10-12 for the ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra.

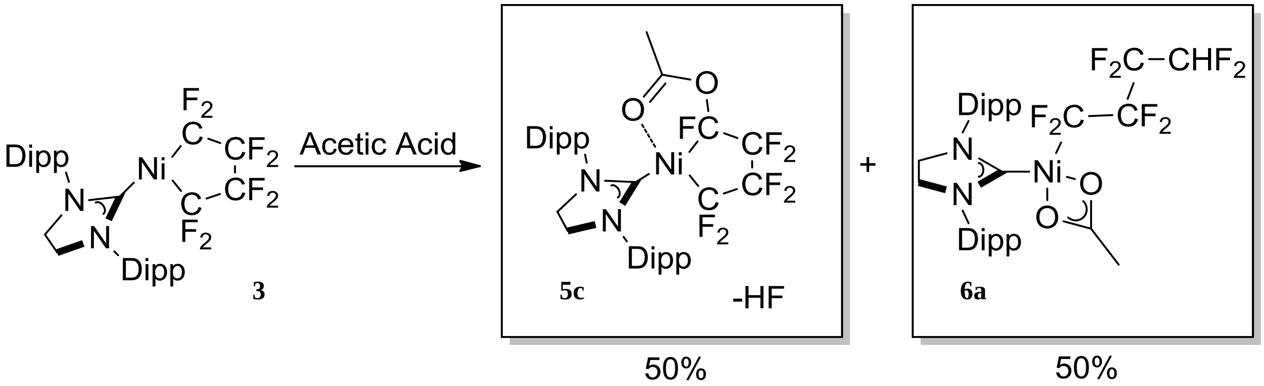


Synthesis of Ni[κ$_1$-(*cyclo*-C_4F_7)](SIPr)(OTf) (4a). Red complex Ni[κ$_2$-$(CF_2)_4$-](SIPr) (**3**) (0.100 g, 0.15 mmol) was placed in a 15 mL scintillation vial and dissolved in ~ 7 mL of benzene. Me_3SiOTf (42 μL, 0.23 mmol) was added to the stirred mixture and left to stir at room temperature 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[κ$_2$-(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). ^{1}H NMR (300 MHz, C_6D_6) 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 ^{i}Pr H + 2 CH2Im), 3.4 (br mult, 2H, CH2Im), 6.5-7.8 (mult, 6H, 6 Ar-H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 24.78, 24.96, 28.53, 28.87, 53.37, 124.3-125, 130.02, 133.96, 146.89.^{19}F NMR (282 MHz, C_6D_6) δ -77.60 (s, CF_3), -110.01 (br d, $^2J_{FF}$ ≈ 228 Hz, 2F$_\beta$), -123.75 (d, $^2J_{FF}$ = 229 Hz, 1F$_\beta$), -123.79 (d, $^2J_{FF}$ = 229 Hz, 1F$_\beta$) -129.80 (d mult, $^2J_{FF}$ = 222 Hz, F$_\gamma$), -131.59 (d, $^2J_{FF}$ = 222 Hz, F$_\gamma$), -197.74 (br s, F$_\alpha$). ^{19}F NMR (282 MHz, CD_2Cl_2, -50 °C) δ -78.93 (s, CF_3), -109.27 (d mult, ^{2}JFF ≈ 227 Hz, 1F$_\beta$), -112.22 (d mult, $^2J_{FF}$ ≈ 231 Hz, 1F$_\beta$), -124.18 (d, $^2J_{FF}$ = 227 Hz, 1F$_\beta$), -124.26 (d, $^2J_{FF}$ = 231 Hz, 1F$_\beta$) -129.80 (d mult, $^2J_{FF}$ = 222 Hz, F$_\gamma$), -131.59 (d, $^2J_{FF}$ = 222 Hz, F$_\gamma$), -197.74 (br s, F$_\alpha$). Anal. Calc. for $C_{32}H_{38}F_{10}N_2NiO_3S$: C, 49.31, H, 4.91, N, 3.59, S, 4.11. (These values reflect those expected for the water adduct Anal. Calc. for $C_{32}H_{40}F_{10}N_2NiO_4S$: 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 ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra.

^{19}F NMR spectrum of intermediate leading to 4a, Ni[κ_3-(CF$_2$)$_3$CF(OTf)-](SIPr) (5a): ^{19}F NMR (282 MHz, Tol-d$_8$, -35 °C) δ -73.27(d, $^{5}J_{\mathrm{FF}}$ = 11 Hz, CF$_3$[OTf]), -83.98 (d mult, $^{2}J_{\mathrm{FF}}$ = 225 Hz, F$_{\alpha}$), -99.73 (d mult, $^{2}J_{\mathrm{FF}}$ = 225 Hz, F$_{\alpha}$), -106.29 (br mult, F$_{\alpha}$), -127.11 (d mult, $^{2}J_{\mathrm{FF}}$ = 246 Hz, F$_{\beta}$), -129.23 (d mult, $^{2}J_{\mathrm{FF}}$ = 246, F$_{\beta}$), -137.07 (d mult, $^{2}J_{\mathrm{FF}}$ = 246 Hz, F$_{\beta}$), -144.71 (d mult, $^{2}J_{\mathrm{FF}}$ = 246, F$_{\beta}$).

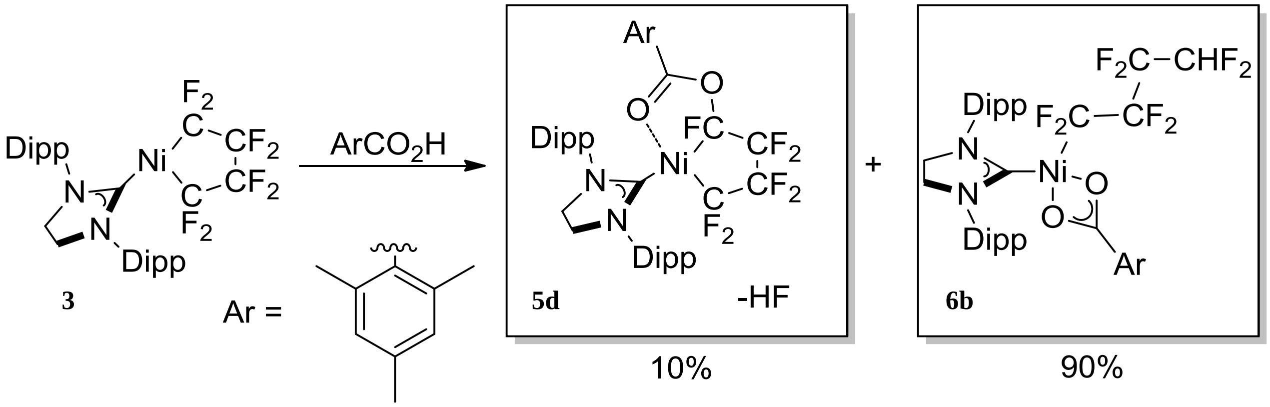


Synthesis of Ni[κ_3-(CF$_2$)$_3$CF(O$_2$CCF$_3$)-](SIPr) (5b). Red complex Ni[κ_2-(CF$_2$)$_4$-](SIPr) (**3**) (50 mg, 0.08 mmol) was placed in a 20 mL scintillation vial and dissolved in ~ 7 mL of benzene. Trifluoroacetic acid (7 μL, 0.085 mmol) was added to the stirred mixture (**reaction should not 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[κ_2-(CF$_2$)$_4$-](SIPr). The isolated material was stored at room temperature under nitrogen. UV-vis (1.5 mM in benzene): λmax(ε) = 486(461). ^{1}H NMR (300 MHz, C$_6$D$_6$) 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, ov mult, 3H, 3 ^{i}Pr H), 3.37 (br, ov mult, 5H, i-Pr H + 2 CH2Im), 6.80-7.06 (mult, 6H, 6 Ar-H). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$) δ 22.66, 22.82, 26.17, 26.28, 28.41, 53.89, 124.20, 124.39, 127-129, 129.33, 146.57. ^{19}F NMR (282 MHz, C$_6$D$_6$, 25 °C) δ -72.97 (s, CF$_3$), -90.06 (d mult, $^{3}J_{\mathrm{FF}}$ = 245 Hz, 1F$_{\alpha}$), -99.09 (d mult, $^{3}J_{\mathrm{FF}}$ = 245 Hz, 1F$_{\alpha}$), -116.17 (d d, $^{3}J_{\mathrm{FF}}$ = 22, 11 Hz, 1F$_{\alpha}$), -126.14 (d mult, $^{3}J_{\mathrm{FF}}$ = 248 Hz, 1F, 1 C$_{\beta}$F$_2$), -130.76 (d d mult, $^{3}J_{\mathrm{FF}}$ = 248, 22 Hz, 1F$_{\beta}$), -134.17 (d mult, $^{3}J_{\mathrm{FF}}$ = 248 Hz, 1F$_{\beta}$), -142.71 (d d mult, $^{3}J_{\mathrm{FF}}$ = 248, 11 Hz, 1F$_{\beta}$). Anal. Calc. for C$_{33}$H$_{38}$F$_{10}$N$_2$NiO$_2$: 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 ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra.



Synthesis of Ni[κ_3-(CF$_2$)$_3$CF(O$_2$CCH$_3$)-](SIPr) (5c). Red complex Ni[κ_2-(CF$_2$)$_4$-](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 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[κ_2-$(CF_2)_4$-](SIPr). The isolated material was stored at room temperature under nitrogen. UV-vis (1.0 mM in benzene): λmax(ε) = 632 (361); 103 (485). ^{1}H NMR (300 MHz, C_6D_6) 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 ^{i}Pr H), 3.37 (br, 4H, 2 CH2Im), 6.80-7.06 (m, 6H, 6 Ar-H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 22.66, 22.82, 26.17, 26.28, 28.41, 53.89, 124.20, 124.39, 27-129, 129.33, 146.57. ^{19}F NMR (282 MHz, C_6D_6, 25 °C) δ -91.23(d mult, $^2J_{FF}$ = 253 Hz, F_α) , -101.86 (d mult, ^{2}JFF = 253 Hz, F_α), -119.78 (d d, $^3J_{FF}$ = 17, 15 Hz, F_α), -126.35 (d mult, $^2J_{FF}$ = 247 Hz, F_β), -130.90 (d d mult, $^2J_{FF}$ = 247, $^3J_{FF}$ = 15 Hz, F_β), -135.10 (d mult, $^2J_{FF}$ = 248 Hz, F_β), -143.33 (d d, $^2J_{FF}$ = 248, $^3J_{FF}$ = 17 Hz, F_β), Anal. Calc. for $C_{34}H_{43}F_7N_2NiO_2$: 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 ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra.

Synthesis of Ni[κ_1-(C_4F_8H)](SIPr)(OAc) (6a). Red complex Ni[κ_2-$(CF_2)_4$-](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[κ_2-$(CF_2)_4$-](SIPr). UV-vis (1.0 mM in benzene): λmax(ε) = 296(343) ;427(494). ^{1}H NMR (300 MHz, C_6D_6) 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 ^{i}Pr H), 3.20 (sept, J ≈ 7 Hz, 1H, 1 ^{i}Pr H), 3.21 (s, 2H, 1 CH_2Im), 3.42 (sept, J ≈ 7 Hz, 1H, 1 ^{i}Pr H), 3.45 (sept, J ≈ 7 Hz, 1H, ^{i}Pr H), 3.48 (s, 2H, 1 CH_2Im), 5.65 (tr tr, $^2J_{FH}$ = 53 Hz, $^3J_{FH}$ = 6 Hz, 1H, CF_2H), 6.90-7.75 (mult, 6H, 6 Ar-H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 21.73, 22.73, 23.04, 26.43, 26.66, 28.33, 28.63, 53.57, 124.22, 124.64, 129.53, 135.29, 147.06, 147.56, 191.30; ^{19}F NMR (282 MHz, C_6D_6) δ -95.90 (br tr, $^3J_{FF}$ = 9 Hz, F_α), -120.47 (br tr, $^3J_{FF}$ = 7 Hz, $2F_\beta$), -130.98 (br d mult, $^3J_{FH}$ = 6 Hz, $2F_\gamma$), -137.99 (br d mult, $^2J_{FH}$ = 52 Hz, $2F_\delta$); m/z calcd for {Ni[κ_1-(C_4F_7H)](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 ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra.



Synthesis of Ni[κ$_1$-(C_4F_8H)](SIPr)(O_2Cmes)] (6b). Red complex Ni[κ$_2$-(CF_2)$_4$-](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[κ$_2$-(CF_2)$_4$-](SIPr). UV-vis (1.5 mM in benzene): λmax(ε) = 486(461). ^{1}H NMR (300 MHz, C_6D_6) δ 0.95 (d, J ≈ 7 Hz, 6H, 2Me), 1.04 (d, J ≈ 7 Hz, 6H, 2 Me), 1.07 (d, J ≈ 7 Hz, 6H, 2 Me), 1.51 (d, J ≈ 7Hz, 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, CH_2Im), 3.12 (sept, J ≈ 7 Hz, 2H, 1 ^{i}Pr H), 3. (sept, J ≈ 7 Hz, 1H, ^{i}Pr H), 3.40 (s, 2H, 1 CH_2Im), 3.54 (sept, J ≈ 7 Hz, 1H, 1 ^{i}Pr H), 5.65 (tr tr, $^2J_{FH}$ ≈ 52 Hz, $^3J_{FH}$ ≈ 6 Hz, 1H, CF_2H), 6.34 (mult, 2H, Ar H), 7-7.20 (mult, 6H, 6 Ar-H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) 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. ^{19}F NMR (282 MHz, C_6D_6) δ -95.90 (br tr, $^3J_{FF}$ = 8 Hz, 2F$_α$), -120.80 (br tr, $^3J_{FF}$ = 8 Hz, 2F$_β$), -130.99 (d mult, $^3J_{FH}$ = 6 Hz, 2F$_γ$), -138.68 (br mult, $^2J_{FH}$ ≈ 52 Hz, 2F$_δ$); m/z calcd for{[Ni[κ$_1$-(C_4F_7H)](SIPr)(OAr)]}K+ (% 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), 855.41(10), 856.3 (4), 857.3 (2); See Figures S25-27 for the ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra.

^{19}F NMR spectrum of minor product, Ni[κ$_3$-(CF_2)$_3$CF(O_2Cmes)-](SIPr) (5d): ^{19}F NMR (282 MHz, C_6D_6, 25 °C) δ -91.22 (d mult, $^2J_{FF}$ = 254 Hz, F$_α$), -101.86 (d mult, $^2J_{FF}$ = 254 Hz, F$_α$), -119.74 (d d, $^3J_{FF}$ = 17, 15 Hz, F$_α$), -126.25 (d mult, $^2J_{FF}$ = 245 Hz, F$_β$), -130.80 (d d mult, $^2J_{FF}$ = 245, $^3J_{FF}$ = 17 Hz, F$_β$), -135.05 (d mult, $^2J_{FF}$ = 248 Hz, F$_β$), -143.27 (d d, $^2J_{FF}$ = 248, $^3J_{FF}$ = 15 Hz, F$_β$).

Variable-temperature ^{19}F NMR spectra of reaction intermediates leading to 4a:

Red complex Ni[κ^2-(CF_2)$_4$-](SIPr) **(3)** (10 mg, 0.015 mmol) was dissolved in 0.5 mL of CD_2Cl_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_2Cl_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.

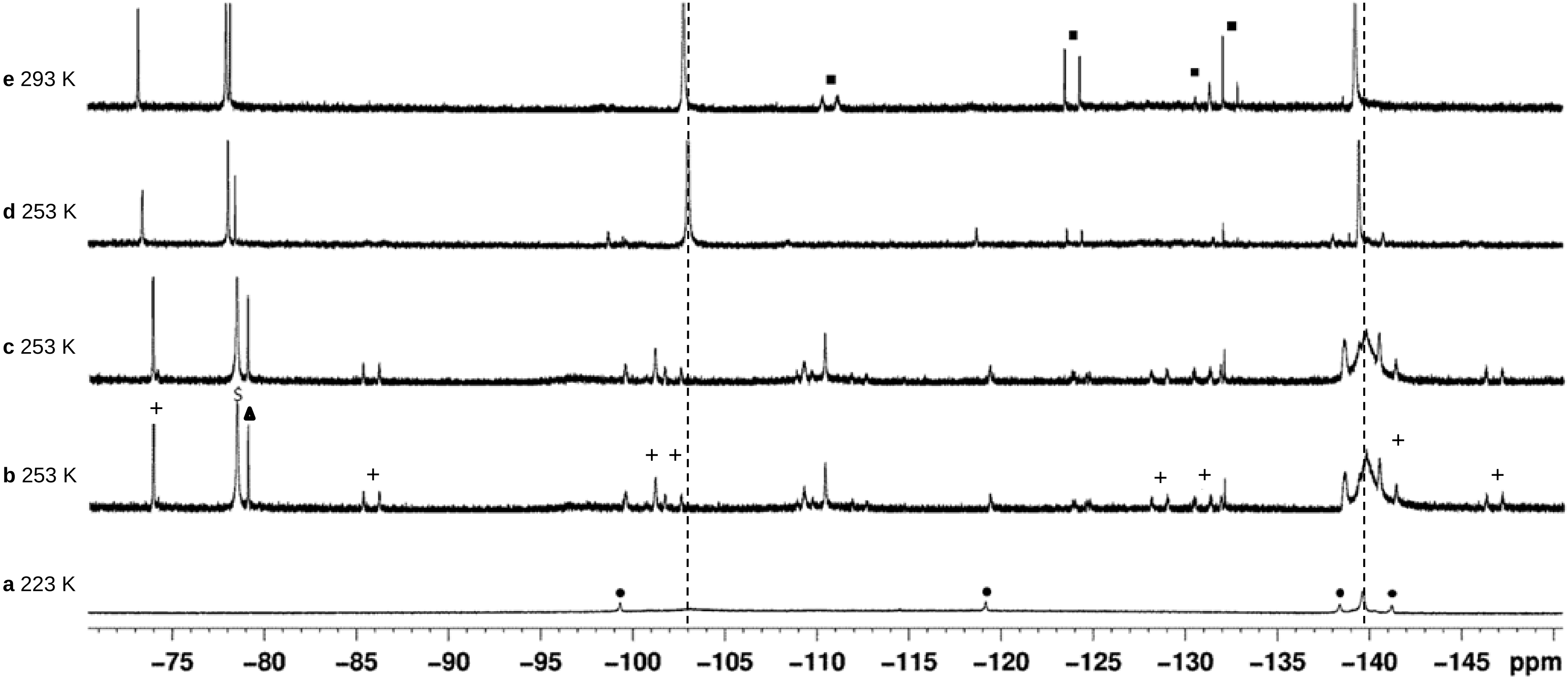


Figure S1. Low-temperature ^{19}F NMR spectra (282 MHz, CD_2Cl_2) of intermediate **5a** generation leading to product **4a**. Addition time is 0 (**a**), 30 min (**b**), 2 hours (**c**) and 3hours (**d**). Spectrum **e** was recorded after one hour additional reaction time at room temperature. The dashed line represents the trace of **3** across all reactions [223 K ^{19}F NMR spectra (282, CD_2Cl_2), provided below].“$” is TMSOTf, “▲” is impurity present in TMSOTf, “●” is impurity at low temperature, “+” is **5a** and “■” is **4a** [223 K 19F NMR spectra (282 MHz, CD_2Cl_2), provided below]. Due to experimental limitations, the impurities are most likely due to water contamination.

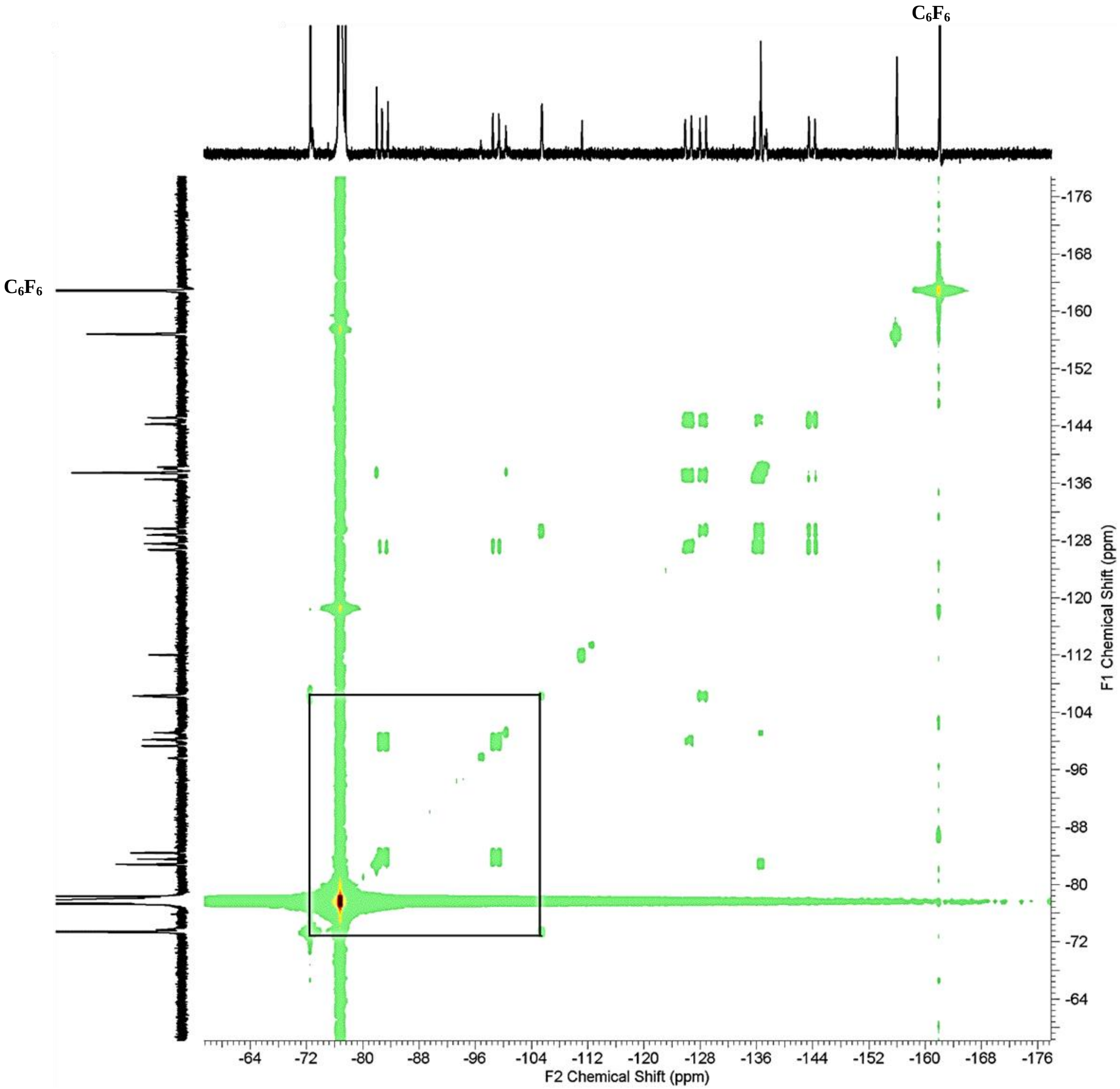
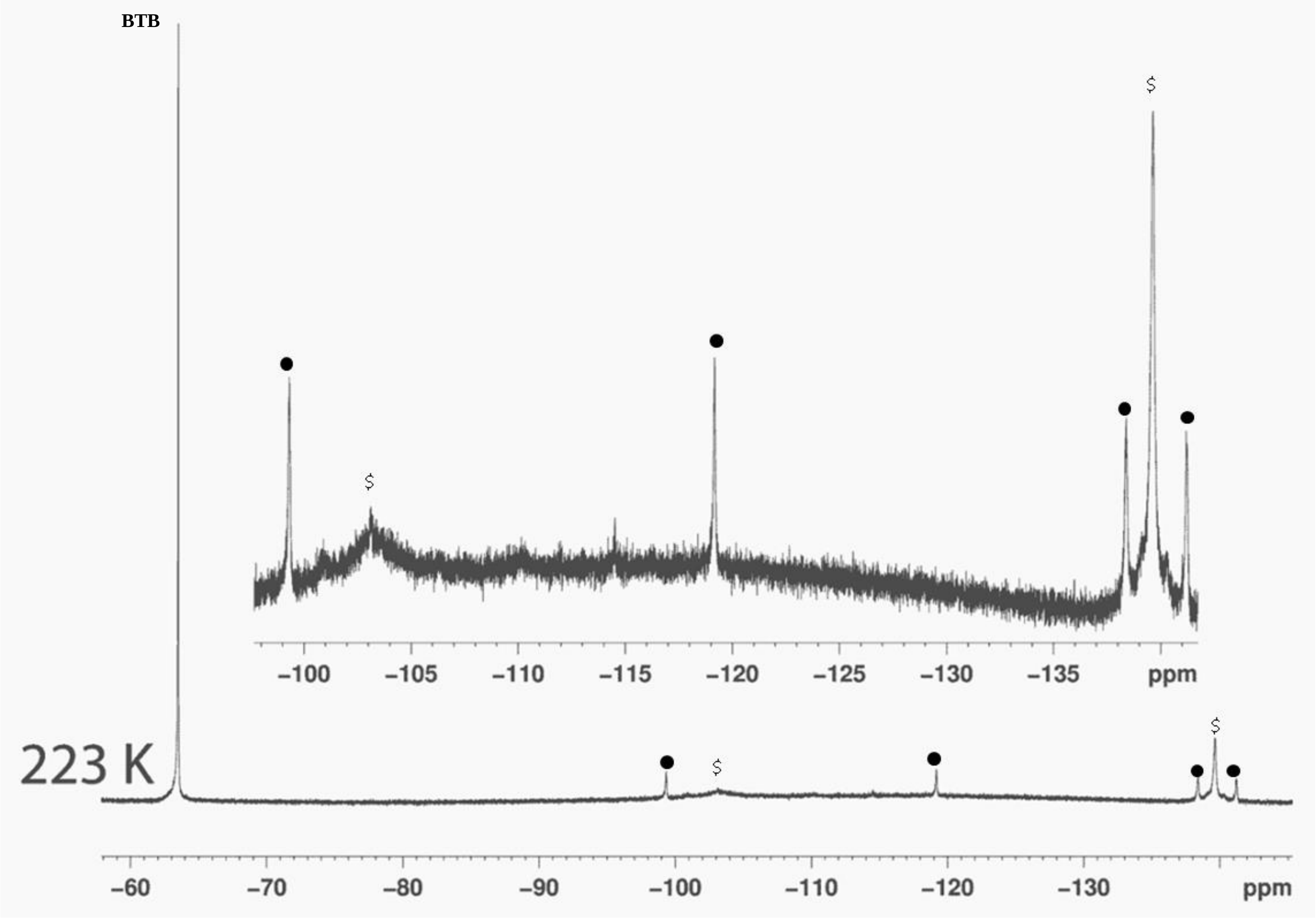


Figure S2. ^{19}F-^{19}F COSY NMR (282 MHz, Tol-d_8, 223 K) data for **5a**. Black box denotes through bond correlation of F (OTf) and F (C_α), $^5J_{FF}$ = 11 Hz Hexafluorobenzene (C_6F_6) was used as an internal NMR standard



9

Figure S3. Low-temperature ^{19}F NMR spectrum (282 MHz, CD_2Cl_2, 223 K) of **3**. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard. “$” = **3**, “●” = impurity.

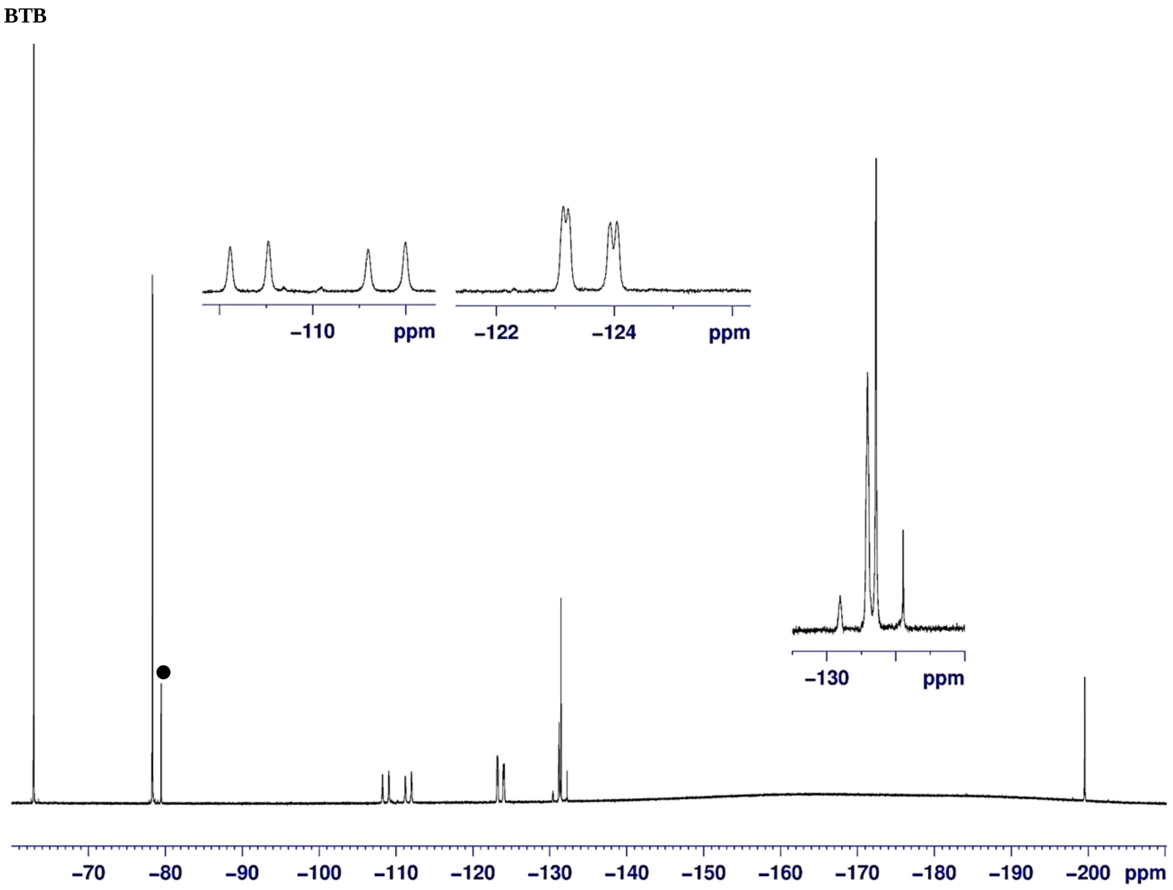


Figure S4. Low temperature ^{19}F NMR spectra (282 MHz, CD_2Cl_2) of **4**. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard. "●" = OTf impurity.

Decomposition of 4a:

Pink complex Ni[κ^1-(*cyclo*-C_4F_7)](SIPr)(OTf) **(4a)** (15 mg, 0.02 mmol) was dissolved in 0.5 mL of C_6D_6 in a J. Young NMR tube. The solvent-containing part of the tube was heated to 80 °C for 24 h. ^{19}F NMR Yield of PFCB: 21 %. We expect the discrepancy arises from the volatility of the PFCB.

Note: Upon addition of PPh_3 to the reaction mixture [after heating], PPh_3F_2 was identified as a major product, suggesting formation of a Ni-F thermolysis byproduct.

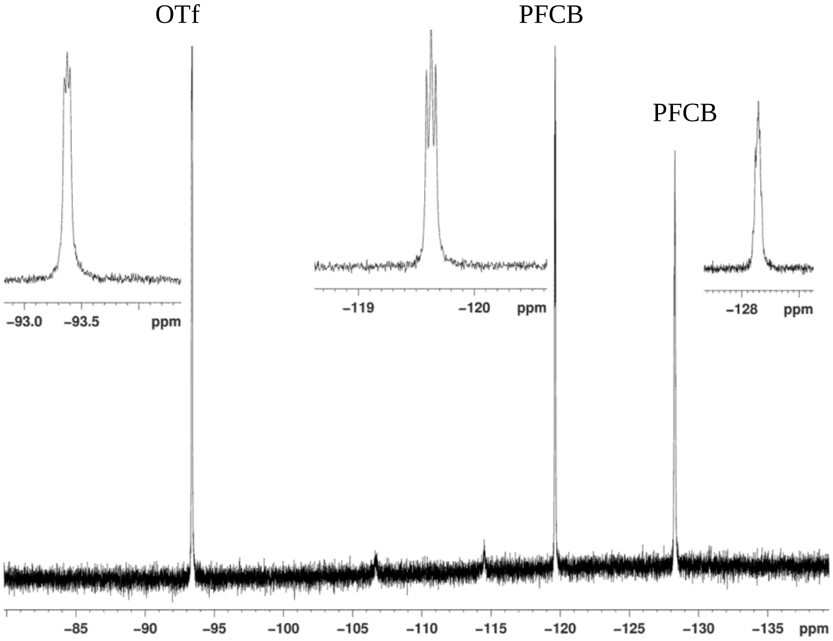


Figure S5. ^{19}F NMR spectrum (282 MHz, C_6D_6) after decomposition of **4a** to give perfluorocyclobutene (PFCB).

Product distributions of reactions with Brønsted acids:

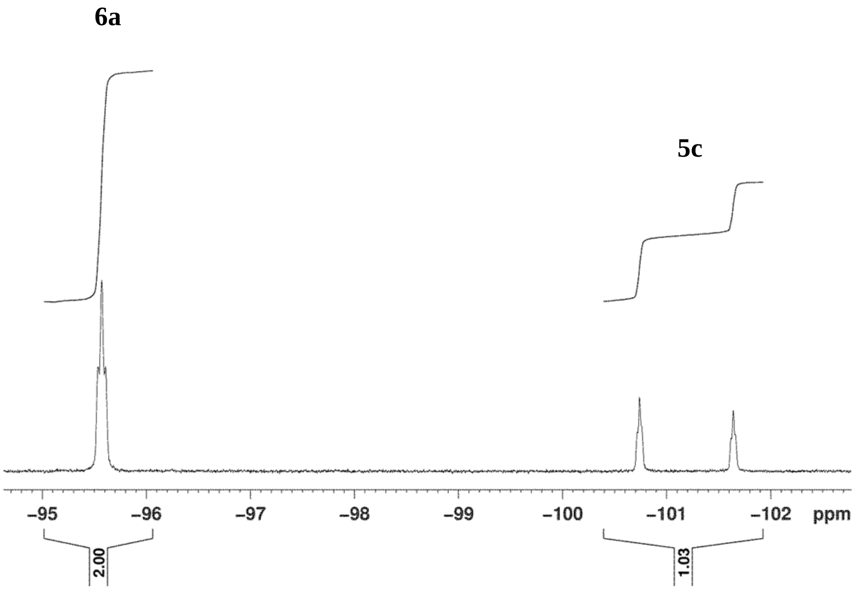


Figure S6. F$_\alpha$ region of ^{19}F NMR spectrum (282 MHz, C$_6$D$_6$) of reaction of **3** with acetic acid showing formation of **5c** and **6a** in a 1:1 ratio.

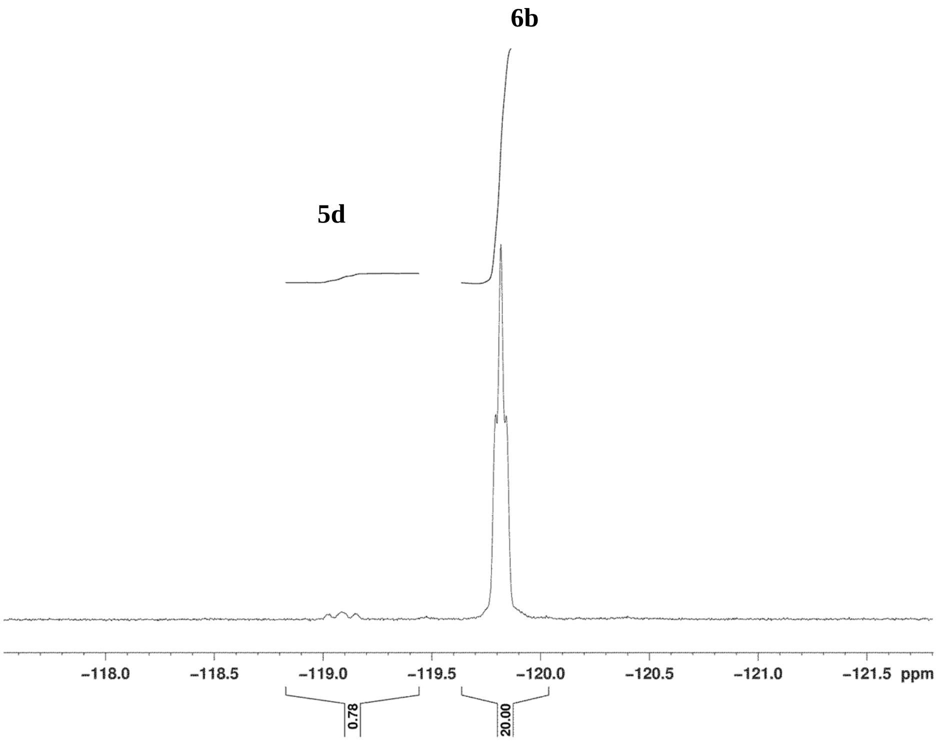


Figure S7. F$_\alpha$ region of ^{19}F NMR spectrum (282 MHz, C$_6$D$_6$) of reaction of **3** with 2,4,6–trimethylbenzoic acid to yield **5d** and **6b** in a 1:10 ratio.

NMR Spectra for Title Compounds

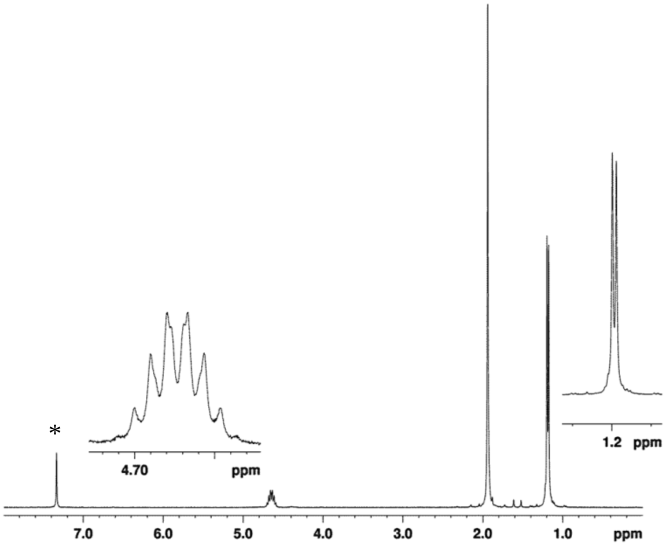


Figure S8. ^{1}H NMR spectrum (300 MHz, C_6D_6) of **2**. The insets show the expanded (horizontal scale) signals.

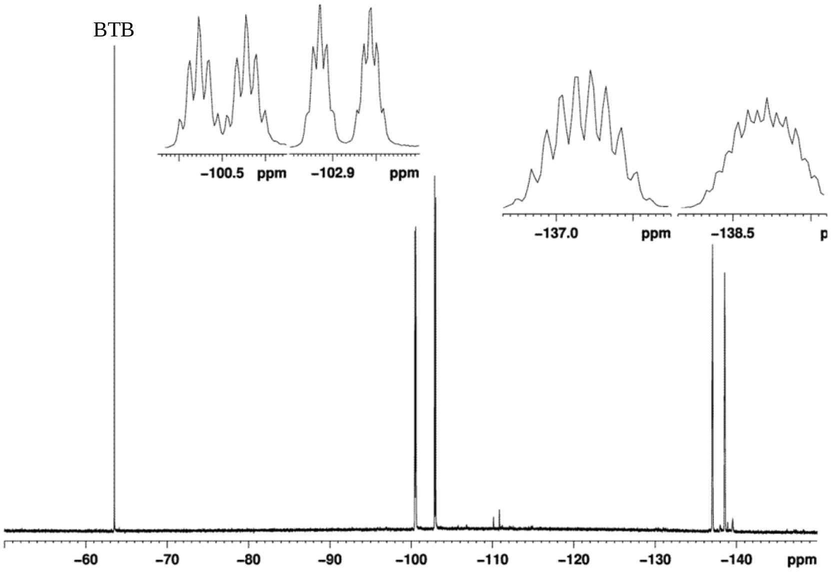


Figure S9. ^{19}F NMR spectrum (282 MHz, C_6D_6) of **2**. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard. The insets show the expanded (horizontal scale) signals.

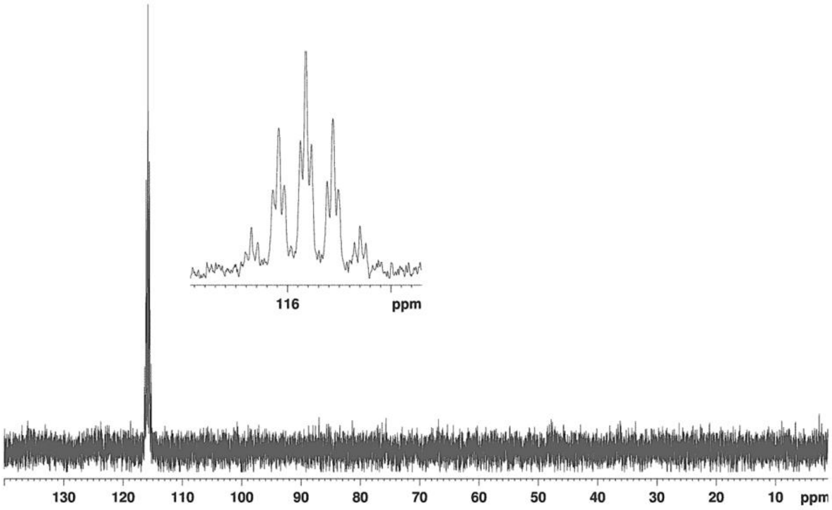


Figure S10. $^{31}P\{^1H\}$ NMR spectrum (121 MHz, C_6D_6) of **2**. The inset shows the expanded (horizontal scale) signal.

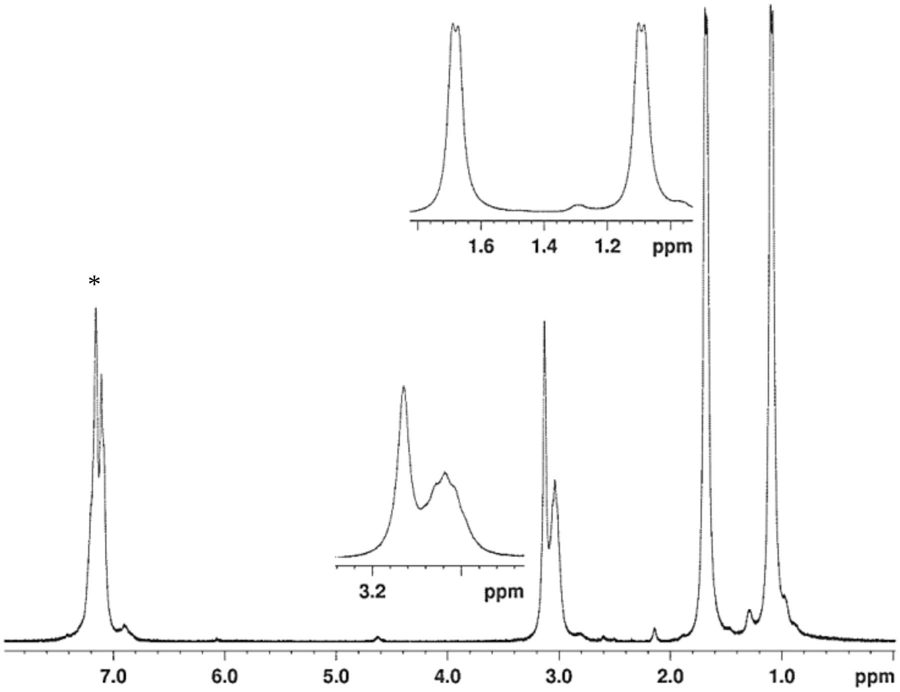


Figure S11. ^1H NMR spectrum (300 MHz, C_6D_6) of **3**. The residual protio-solvent peak is labeled '*'. The inset shows the expanded (horizontal scale) signal.

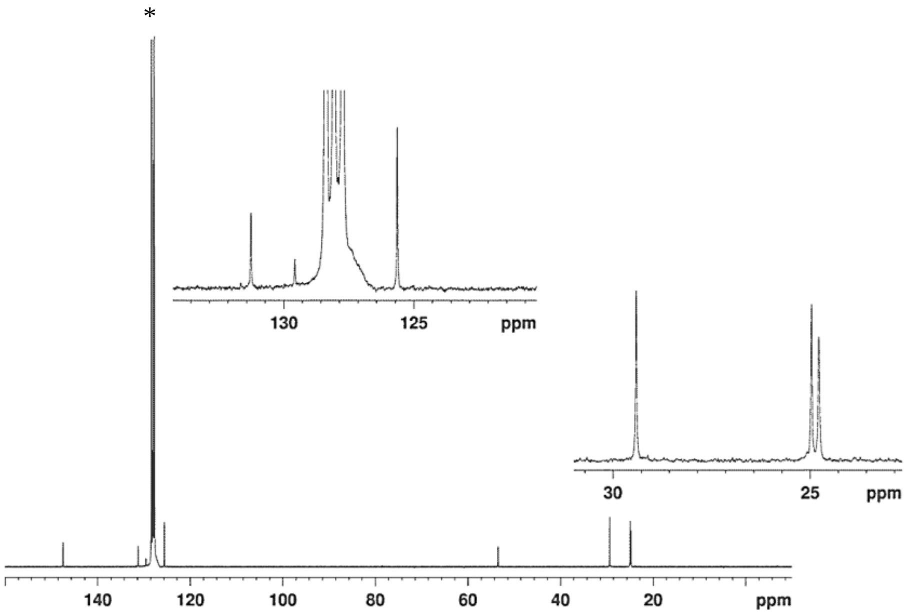


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, C_6D_6) of **3.** The residual solvent peak is labeled '*'. The inset shows the expanded (horizontal scale) signal.

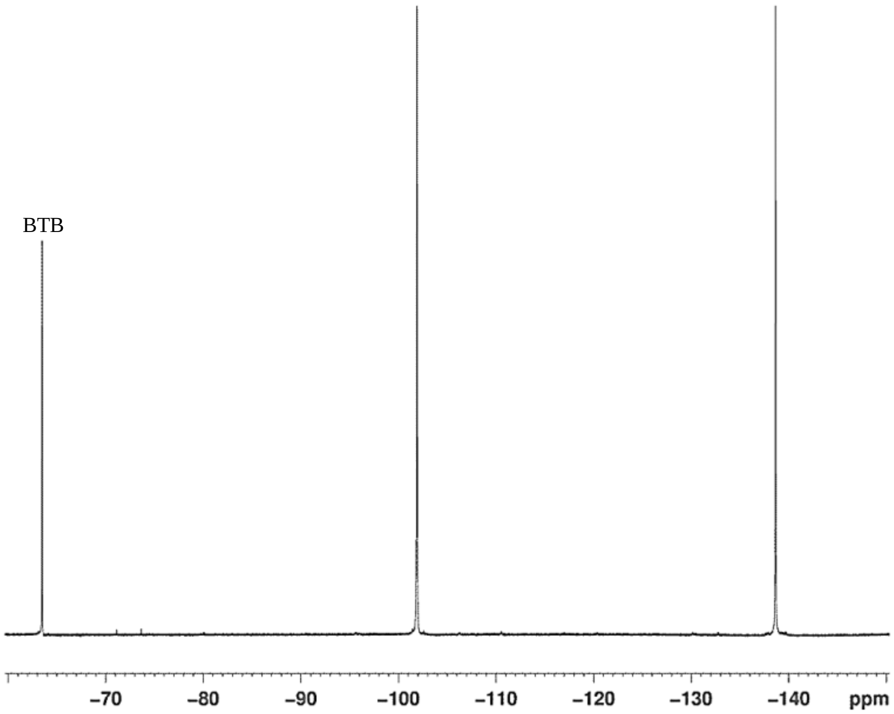


Figure S13. ^{19}F NMR spectrum (282 MHz, C_6D_6) of **3**. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard.

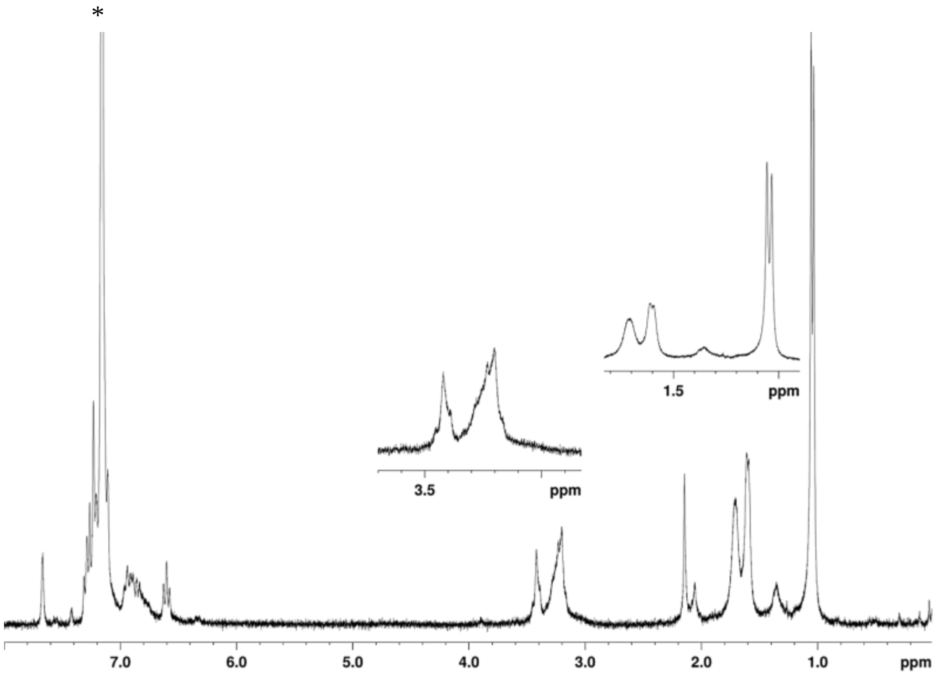


Figure S14. ^{1}H NMR spectrum (300 MHz, C_6D_6) of **4a**. The residual protio-solvent peak is labeled '*'. The inset shows the expanded (horizontal scale) signal.

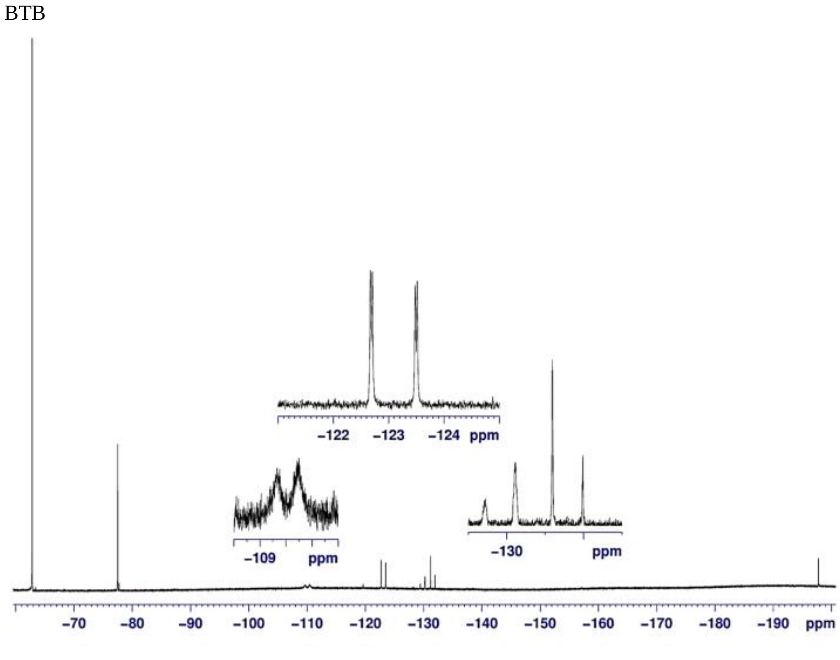


Figure S15. ^{19}F NMR spectrum (282 MHz, C_6D_6) of **4a**. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard.

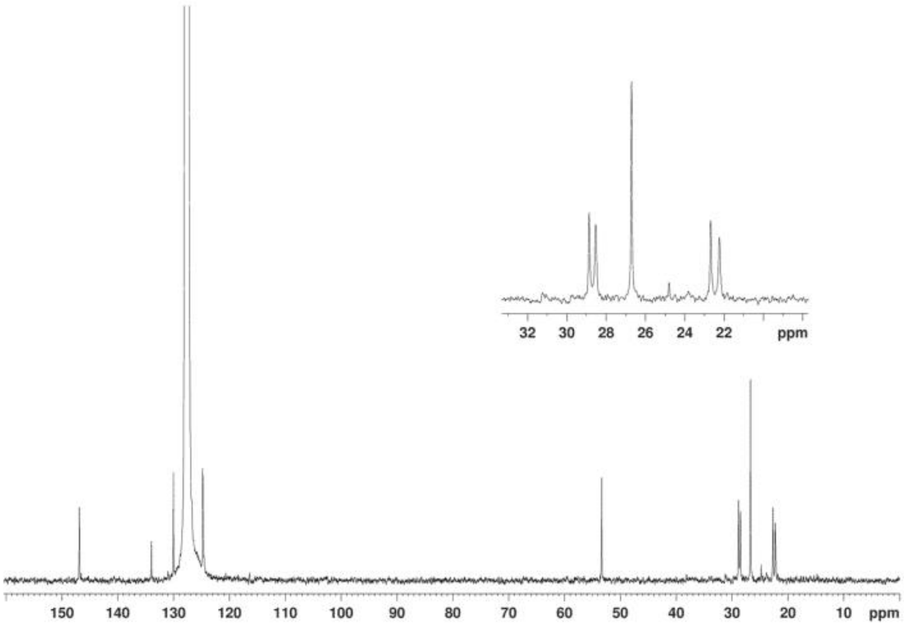


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, C_6D_6) of **4a**. The inset shows the expanded (horizontal scale) signal.

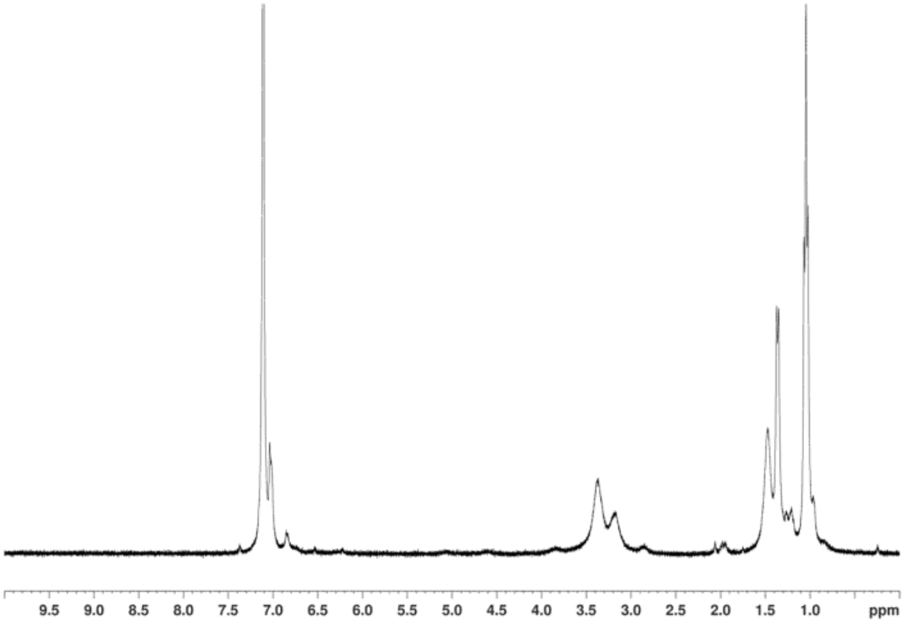


Figure S17. ^{1}H NMR spectrum (300 MHz, C_6D_6) of **5b**.

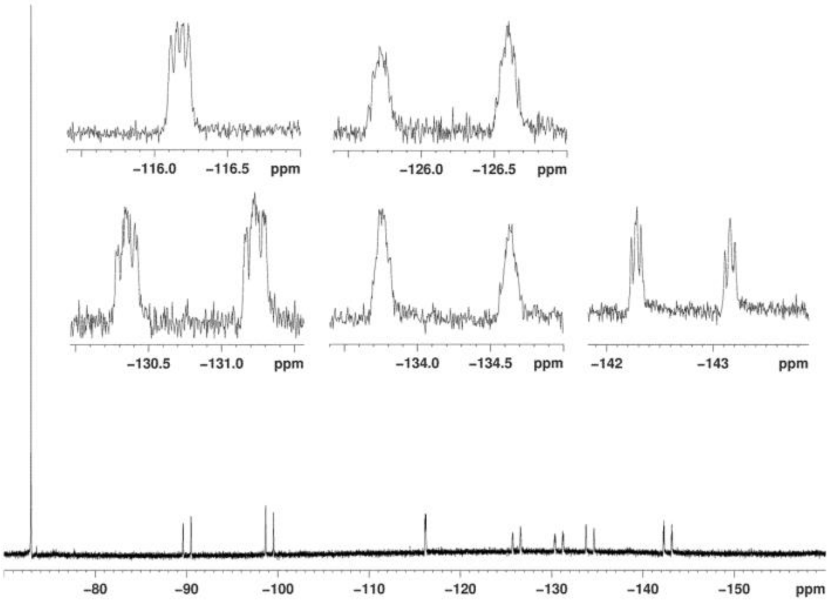


Figure S18. ^{19}F NMR spectrum (282 MHz, C_6D_6) of **5b**. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard.

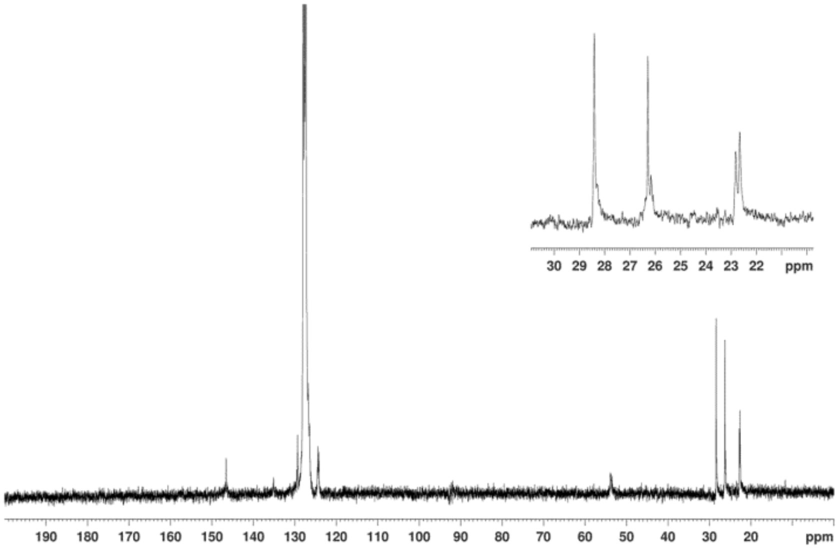


Figure S19. ^{13}C{^{1}H} NMR spectrum (75 MHz, C_6D_6) of **5b**. The inset shows the expanded (horizontal scale) signal.

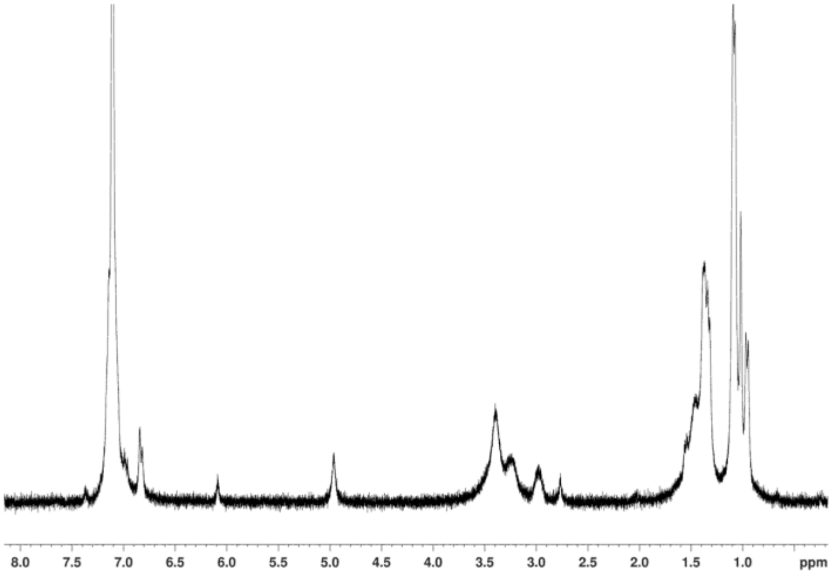


Figure S20. ^{1}H NMR spectrum (300 MHz, C_6D_6) of **5c.**

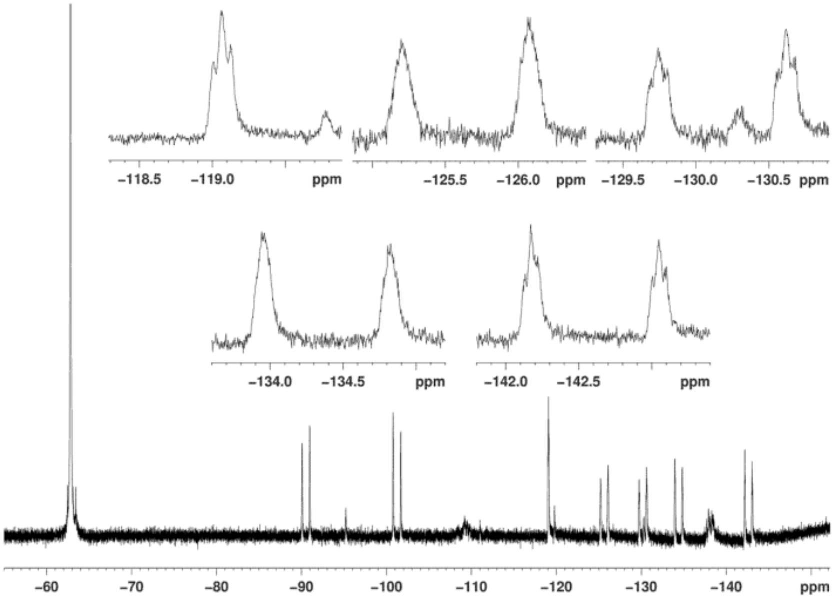


Figure S21. ^{19}F NMR spectrum (282 MHz, C_6D_6) of **5c**. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard.

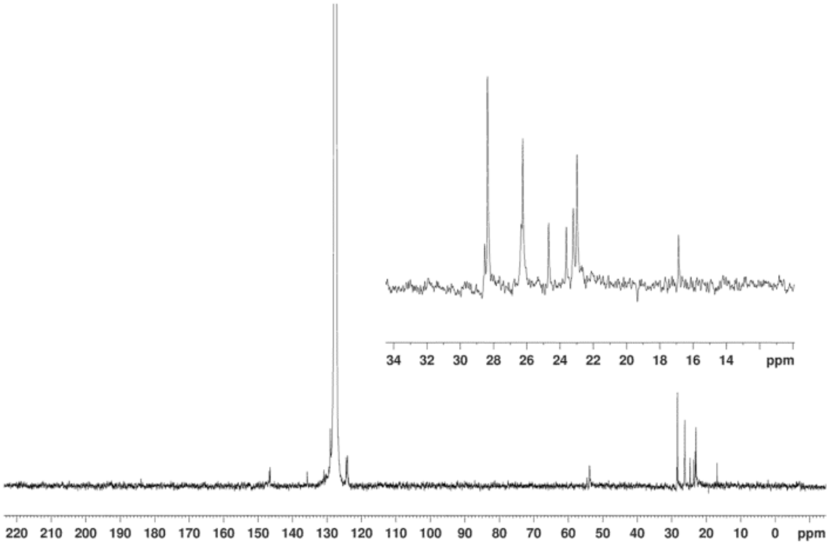


Figure S22. $^{13}C\{^1H\}$ NMR spectrum (75 MHz, C_6D_6) of **5c**. The inset shows the expanded (horizontal scale) signal.

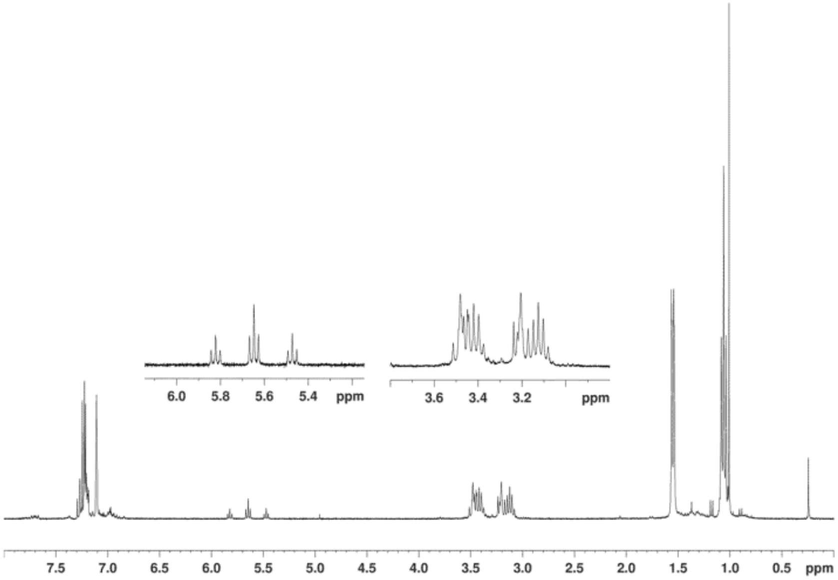


Figure S23. ^1H NMR spectrum (300 MHz, C_6D_6) of **6a**. The residual protio-solvent peak is labeled ‘*’. The inset shows the expanded (horizontal scale) signal.

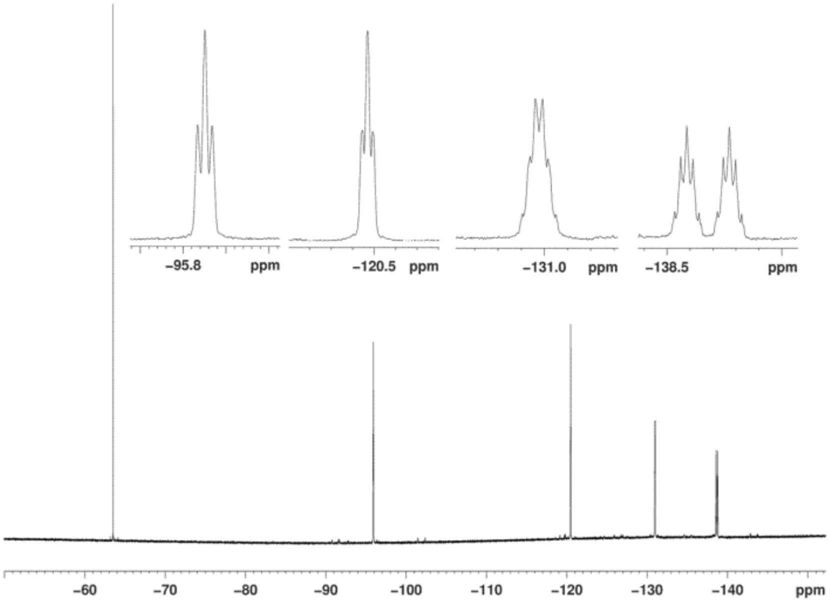


Figure S24. ^{19}F NMR spectrum (282 MHz, C_6D_6) of **6a**. 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard.

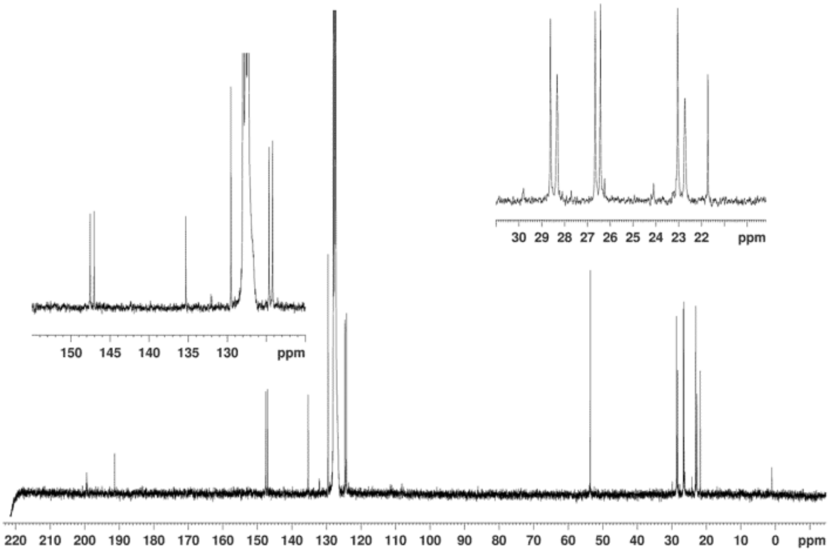


Figure S25. ^{13}C{^{1}H} NMR spectrum (75 MHz, C_6D_6) of **6a**. The inset shows the expanded (horizontal scale) signal.

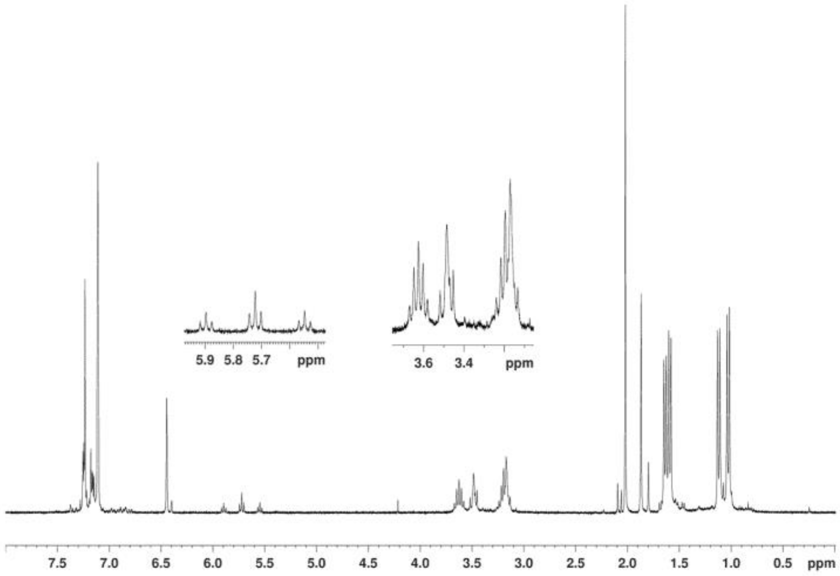


Figure S26. ^{1}H NMR spectrum (300 MHz, C_6D_6) of **6b**. The residual protio-solvent peak is labeled ‘*’. The inset shows the expanded (horizontal scale) signal.

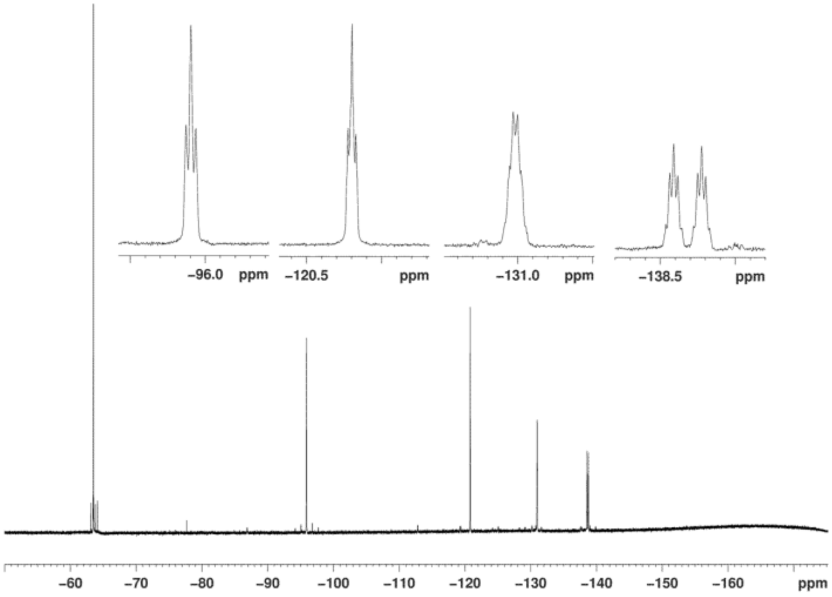


Figure S27. ^{19}F NMR spectrum (282 MHz, C_6D_6) of **6b.** 1,3-Bis(trifluoromethyl)benzene (BTB) was used as an internal NMR standard

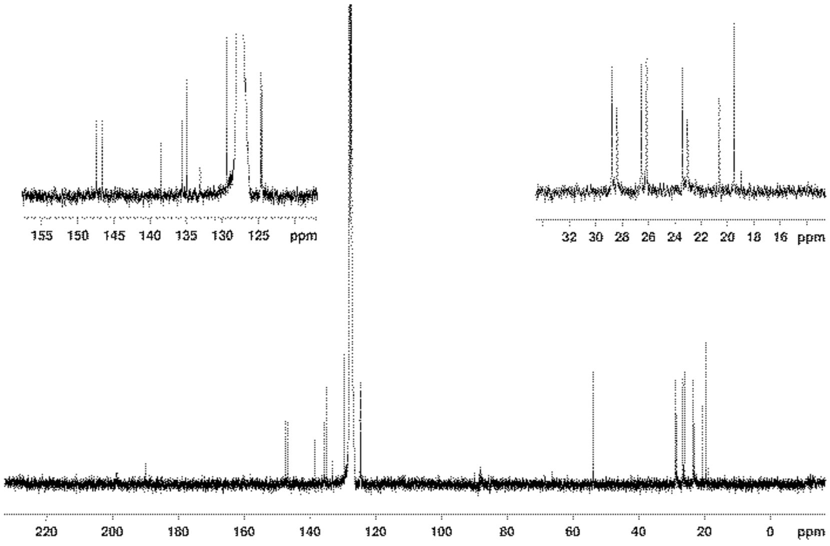


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, C_6D_6) of **6b**. The inset shows the expanded (horizontal scale) signal.

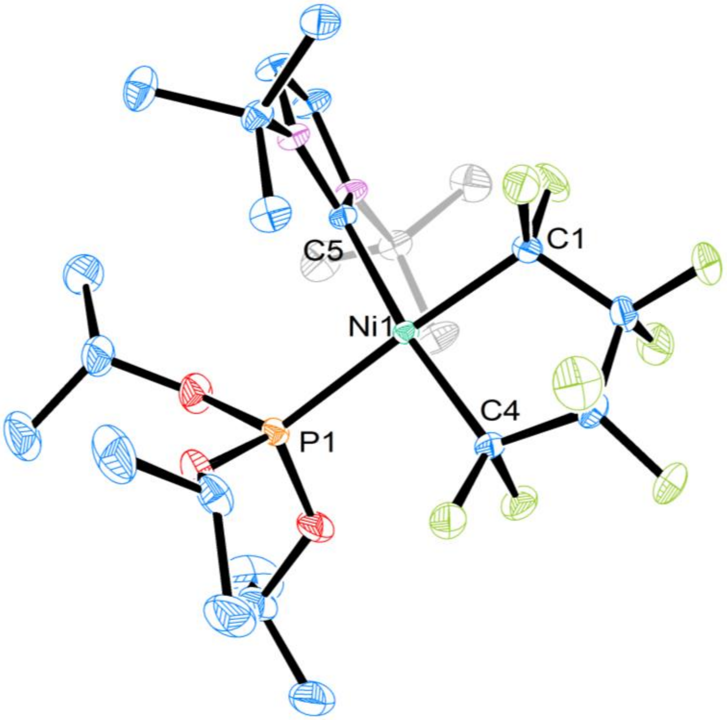


Figure S29. ORTEP representation of the molecular structure of 2 with thermal ellipsoid probability set to 30 % and hydrogen atoms omitted for clarity.

The HOMO of **3** (ε = -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 π-system of the aryl group.[22] The LUMO (ε = -1.96 eV; Figure 3, right) is an anti-bonding combination of the metal d_{x2-y2} orbital (total Ni character of 45%) with the -donor orbitals of the NHC and C_4F_8 ligands.

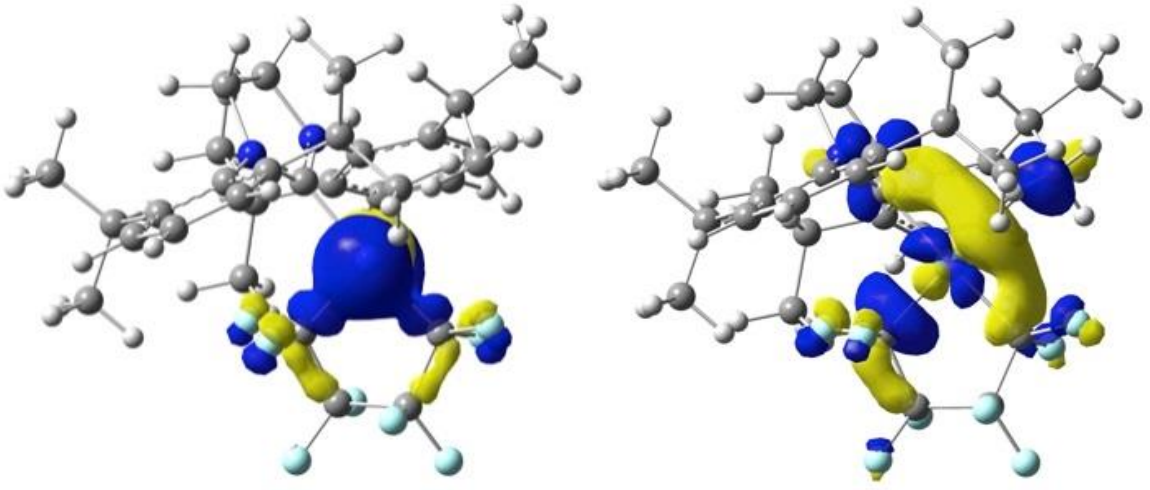


Figure S30. The HOMO (left) and LUMO (right) of **3**. Isosurface values of 0.04 au are used.

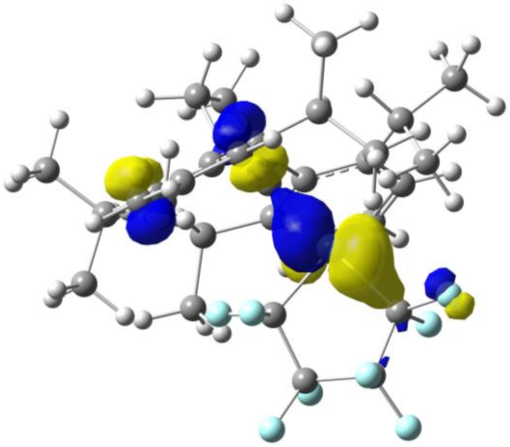


Figure S31: HOMO-1 of **3**. Isosurface values of 0.04 au are used.

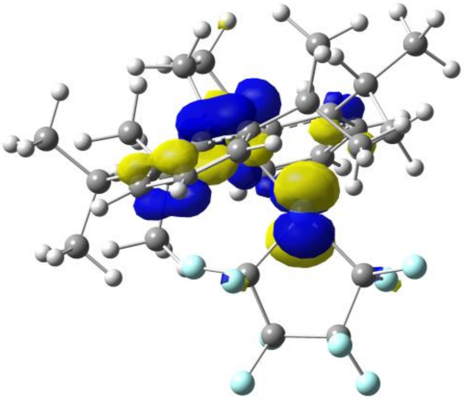


Figure S32: HOMO-4 of **3**. Isosurface values of 0.04 au are used.

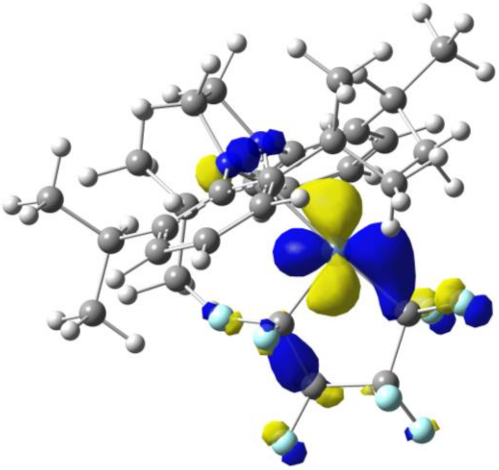


Figure S33: HOMO-9 of **3**. Isosurface values of 0.04 au are used.

Table S1. Crystal data and structure refinement

Complex	**2**	**3**	**4a**	**5c**
ID code	tb060	tb065	tb070	tb132_5
Formula	$C_{24}H_{41}F_8N_2NiO_3P$	$C_{31}H_{38}F_8N_2Ni$	$C_{35}H_{45}F_{10}N_2NiO_3S$	$C_{33}H_{41}F_7N_2NiO_2$
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/^{o}	90.00	90	90	90
β/^{o}	92.862(4)	90	90.960(2)	92.180(2)
γ/^{o}	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/^{o}	2.08-28.47	2.15-28.32	1.53-28.36	1.54-23.43
Index range	-20<h<20	-14<h<14	-13<h<13	-10<h<10
	-13<k<13	-20<k<20	-21<k<21	0<k<20
	-25<l<26	-25<l<25	-30<l<28	0<l<21
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	7927/0/380	9440/0/469	9216/0/407
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**.

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(8)-C(10)	1.537(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)

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)	111.22(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**

Ni(1)-C(31)	1.8746(15)
Ni(1)-C(28)	1.9341(14)
Ni(1)-C(1)	1.9408(12)
N(1)-C(1)	1.3360(17)
N(1)-C(4)	1.4363(18)
N(1)-C(2)	1.4811(17)
N(2)-C(1)	1.3362(17)
N(2)-C(16)	1.4322(18)
N(2)-C(3)	1.4810(17)
F(1)-C(28)	1.3857(19)
F(2)-C(28)	1.3876(18)
F(3)-C(29)	1.3541(17)
F(4)-C(29)	1.355(2)
F(5)-C(30)	1.349(2)
F(6)-C(30)	1.3510(18)
F(7)-C(31)	1.3629(17)
F(8)-C(31)	1.3680(17)
C(2)-C(3)	1.521(2)
C(4)-C(9)	1.393(2)

C(4)-C(5)	1.402(2)
C(5)-C(6)	1.387(3)
C(5)-C(10)	1.513(3)
C(6)-C(7)	1.372(3)
C(7)-C(8)	1.362(3)
C(8)-C(9)	1.401(2)
C(9)-C(13)	1.511(2)
C(10)-C(11)	1.531(3)
C(10)-C(12)	1.531(2)
C(13)-C(14)	1.534(2)
C(13)-C(15)	1.536(2)
C(16)-C(17)	1.396(2)
C(16)-C(21)	1.408(2)
C(17)-C(18)	1.397(2)
C(17)-C(22)	1.524(2)
C(18)-C(19)	1.374(3)
C(19)-C(20)	1.382(3)
C(20)-C(21)	1.392(2)
C(21)-C(25)	1.520(2)
C(22)-C(23)	1.530(2)
C(22)-C(24)	1.532(2)
C(25)-C(26)	1.534(2)
C(25)-C(27)	1.536(2)
C(28)-C(29)	1.520(2)
C(29)-C(30)	1.521(2)
C(30)-C(31)	1.539(2)

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(4)-N(1)-C(2)	122.33(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)
C(5)-C(4)-N(1)	118.57(13)
C(6)-C(5)-C(4)	117.34(17)
C(6)-C(5)-C(10)	122.02(17)
C(4)-C(5)-C(10)	120.63(14)
C(7)-C(6)-C(5)	121.01(18)
C(6)-C(7)-C(8)	120.83(17)
C(7)-C(8)-C(9)	121.26(19)
C(4)-C(9)-C(8)	116.88(16)
C(4)-C(9)-C(13)	122.78(14)
C(8)-C(9)-C(13)	120.32(16)
C(5)-C(10)-C(11)	113.00(18)
C(5)-C(10)-C(12)	110.36(15)
C(11)-C(10)-C(12)	109.83(17)
C(9)-C(13)-C(14)	110.52(14)
C(9)-C(13)-C(15)	111.70(15)
C(14)-C(13)-C(15)	110.26(14)
C(17)-C(16)-C(21)	122.21(13)
C(17)-C(16)-N(2)	118.81(13)
C(21)-C(16)-N(2)	118.90(13)
C(16)-C(17)-C(18)	117.81(16)
C(16)-C(17)-C(22)	122.49(14)
C(18)-C(17)-C(22)	119.69(15)
C(19)-C(18)-C(17)	120.89(17)
C(18)-C(19)-C(20)	120.57(15)
C(19)-C(20)-C(21)	121.03(17)
C(20)-C(21)-C(16)	117.46(16)
C(20)-C(21)-C(25)	119.69(15)
C(16)-C(21)-C(25)	122.85(13)
C(17)-C(22)-C(23)	112.42(14)
C(17)-C(22)-C(24)	110.15(14)
C(23)-C(22)-C(24)	109.99(14)
C(21)-C(25)-C(26)	110.53(13)
C(21)-C(25)-C(27)	112.03(14)
C(26)-C(25)-C(27)	110.41(15)
F(1)-C(28)-F(2)	103.56(13)
F(1)-C(28)-C(29)	106.05(13)
F(2)-C(28)-C(29)	107.44(12)
F(1)-C(28)-Ni(1)	110.56(10)
F(2)-C(28)-Ni(1)	116.38(11)
C(29)-C(28)-Ni(1)	112.05(10)
F(4)-C(29)-F(3)	106.32(13)
F(4)-C(29)-C(30)	108.15(14)
F(3)-C(29)-C(30)	111.25(13)

F(4)-C(29)-C(28)	109.70(13)
F(3)-C(29)-C(28)	115.48(14)
C(30)-C(29)-C(28)	105.79(11)
F(5)-C(30)-F(6)	107.37(13)
F(5)-C(30)-C(29)	108.31(14)
F(6)-C(30)-C(29)	111.98(13)
F(5)-C(30)-C(31)	108.91(13)
F(6)-C(30)-C(31)	113.32(13)
C(29)-C(30)-C(31)	106.84(12)
F(7)-C(31)-F(8)	105.13(11)
F(7)-C(31)-C(30)	106.98(12)
F(8)-C(31)-C(30)	107.48(12)
F(7)-C(31)-Ni(1)	111.18(10)
F(8)-C(31)-Ni(1)	115.03(10)
C(30)-C(31)-Ni(1)	110.60(10)

Table S5. Bond lengths [Å] and angles [°] for complex **4a.**

Ni(1)-C(1)	1.854(2)
Ni(1)-C(28)	1.890(2)
Ni(1)-O(1)	2.0020(18)
Ni(1)-O(2)	2.0204(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(1)	1.344(3)
N(2)-C(16)	1.440(3)
N(2)-C(3)	1.489(3)
C(2)-C(3)	1.507(4)
C(4)-C(9)	1.404(3)
C(4)-C(5)	1.411(3)
C(5)-C(6)	1.385(4)
C(5)-C(10)	1.522(4)
C(6)-C(7)	1.380(4)
C(7)-C(8)	1.385(4)
C(8)-C(9)	1.392(4)
C(9)-C(13)	1.522(4)
C(10)-C(11)	1.530(4)
C(10)-C(12)	1.530(4)
C(13)-C(14)	1.528(4)
C(13)-C(15)	1.538(4)
C(16)-C(21)	1.404(3)
C(16)-C(17)	1.403(4)
C(17)-C(18)	1.405(4)
C(17)-C(22)	1.520(4)
C(18)-C(19)	1.370(5)
C(19)-C(20)	1.377(4)
C(20)-C(21)	1.397(4)
C(21)-C(25)	1.518(4)
C(22)-C(23)	1.537(4)
C(22)-C(24)	1.538(5)
C(25)-C(26)	1.524(5)
C(25)-C(27)	1.538(4)
C(28)-C(31)	1.558(4)
C(28)-C(29)	1.563(3)
C(29)-C(30)	1.557(5)
C(30)-C(31)	1.555(4)
C(33)-C(34)	1.514(9)
C(34)-C(35)	1.434(9)
C(35)-C(35)#1	1.505(11)

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(2)	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)

O(2)-Ni(1)-S(1)	35.79(6)
O(3)-S(1)-O(1)	118.03(14)
O(3)-S(1)-O(2)	117.65(15)
O(1)-S(1)-O(2)	105.42(11)
O(3)-S(1)-C(32)	105.23(17)
O(1)-S(1)-C(32)	103.98(16)
O(2)-S(1)-C(32)	104.94(14)
O(3)-S(1)-Ni(1)	148.01(13)
O(1)-S(1)-Ni(1)	52.73(7)
O(2)-S(1)-Ni(1)	53.45(7)
C(32)-S(1)-Ni(1)	106.75(12)
S(1)-O(1)-Ni(1)	91.61(9)
S(1)-O(2)-Ni(1)	90.76(9)
C(1)-N(1)-C(4)	127.02(19)
C(1)-N(1)-C(2)	111.06(19)
C(4)-N(1)-C(2)	121.91(19)
C(1)-N(2)-C(16)	126.97(19)
C(1)-N(2)-C(3)	110.70(18)
C(16)-N(2)-C(3)	120.27(18)
N(1)-C(1)-N(2)	109.11(18)
N(1)-C(1)-Ni(1)	123.25(16)
N(2)-C(1)-Ni(1)	127.47(16)
N(1)-C(2)-C(3)	101.69(19)
N(2)-C(3)-C(2)	101.73(19)
C(9)-C(4)-C(5)	122.1(2)
C(9)-C(4)-N(1)	118.3(2)
C(5)-C(4)-N(1)	119.6(2)
C(6)-C(5)-C(4)	117.6(2)
C(6)-C(5)-C(10)	119.5(2)
C(4)-C(5)-C(10)	122.9(2)
C(7)-C(6)-C(5)	121.4(3)
C(6)-C(7)-C(8)	120.1(3)
C(7)-C(8)-C(9)	121.2(3)
C(8)-C(9)-C(4)	117.5(2)
C(8)-C(9)-C(13)	119.5(2)
C(4)-C(9)-C(13)	122.9(2)
C(11)-C(10)-C(5)	112.2(3)
C(11)-C(10)-C(12)	108.9(3)
C(5)-C(10)-C(12)	110.1(2)
C(9)-C(13)-C(14)	113.6(3)
C(9)-C(13)-C(15)	109.4(2)
C(14)-C(13)-C(15)	108.5(3)
C(21)-C(16)-C(17)	121.8(2)
C(21)-C(16)-N(2)	119.8(2)
C(17)-C(16)-N(2)	118.3(2)
C(16)-C(17)-C(18)	117.6(2)
C(16)-C(17)-C(22)	123.9(2)
C(18)-C(17)-C(22)	118.4(2)
C(19)-C(18)-C(17)	121.2(3)
C(18)-C(19)-C(20)	120.2(3)
C(19)-C(20)-C(21)	121.5(3)
C(20)-C(21)-C(16)	117.6(2)
C(20)-C(21)-C(25)	118.9(2)
C(16)-C(21)-C(25)	123.4(2)
C(17)-C(22)-C(23)	112.4(3)
C(17)-C(22)-C(24)	110.1(3)
C(23)-C(22)-C(24)	109.7(3)
C(21)-C(25)-C(26)	112.4(3)
C(21)-C(25)-C(27)	109.8(3)
C(26)-C(25)-C(27)	110.8(3)
F(1)-C(28)-C(31)	110.2(2)
F(1)-C(28)-C(29)	108.8(2)
C(31)-C(28)-C(29)	88.21(19)
F(1)-C(28)-Ni(1)	117.22(16)
C(31)-C(28)-Ni(1)	114.71(19)
C(29)-C(28)-Ni(1)	114.07(17)
F(3)-C(29)-F(2)	107.4(2)
F(3)-C(29)-C(30)	111.6(2)
F(2)-C(29)-C(30)	114.7(3)
F(3)-C(29)-C(28)	114.1(2)
F(2)-C(29)-C(28)	117.6(2)
C(30)-C(29)-C(28)	90.9(2)
F(5)-C(30)-F(4)	108.5(3)
F(5)-C(30)-C(31)	115.1(3)
F(4)-C(30)-C(31)	114.2(3)
F(5)-C(30)-C(29)	114.3(3)
F(4)-C(30)-C(29)	115.3(3)
C(31)-C(30)-C(29)	88.5(2)
F(7)-C(31)-F(6)	107.6(3)
F(7)-C(31)-C(30)	112.1(2)
F(6)-C(31)-C(30)	114.3(3)
F(7)-C(31)-C(28)	114.8(3)
F(6)-C(31)-C(28)	116.3(2)
C(30)-C(31)-C(28)	91.1(2)
F(10)-C(32)-F(9)	108.5(3)
F(10)-C(32)-F(8)	109.4(4)

F(9)-C(32)-F(8)	108.4(3)
F(10)-C(32)-S(1)	109.6(3)
F(9)-C(32)-S(1)	109.6(3)
F(8)-C(32)-S(1)	111.4(2)
C(35)-C(34)-C(33)	118.0(6)
C(34)-C(35)-C(35)#1	119.3(7)

Table S6. Bond lengths [Å] and angles [°] for complex **5c**.

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(8)-C(9)	1.388(9)
C(9)-C(13)	1.514(9)
C(10)-C(12)	1.526(10)
C(10)-C(11)	1.533(11)
C(13)-C(14)	1.521(9)
C(13)-C(15)	1.537(9)
C(16)-C(17)	1.393(9)
C(16)-C(21)	1.405(9)
C(17)-C(18)	1.398(9)
C(17)-C(22)	1.523(9)
C(18)-C(19)	1.373(10)
C(19)-C(20)	1.367(10)
C(20)-C(21)	1.387(9)
C(21)-C(25)	1.510(9)
C(22)-C(23)	1.521(10)
C(22)-C(24)	1.533(10)
C(25)-C(26)	1.514(9)
C(25)-C(27)	1.527(9)
C(28)-C(29)	1.475(9)
C(30)-C(31)	1.492(10)
C(31)-C(39)	1.502(9)
C(32)-C(39)	1.542(9)

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)

C(16)-N(2)-C(3)	122.3(5)
N(1)-C(1)-N(2)	107.3(5)
N(1)-C(1)-Ni(1)	134.1(4)
N(2)-C(1)-Ni(1)	118.6(4)
N(1)-C(2)-C(3)	102.1(4)
N(2)-C(3)-C(2)	101.1(4)
C(9)-C(4)-C(5)	122.6(6)
C(9)-C(4)-N(1)	118.0(5)
C(5)-C(4)-N(1)	119.0(5)
C(4)-C(5)-C(6)	116.8(6)
C(4)-C(5)-C(10)	124.5(6)
C(6)-C(5)-C(10)	118.7(6)
C(7)-C(6)-C(5)	120.9(7)
C(6)-C(7)-C(8)	121.1(6)
C(7)-C(8)-C(9)	121.1(6)
C(8)-C(9)-C(4)	117.5(6)
C(8)-C(9)-C(13)	120.2(6)
C(4)-C(9)-C(13)	122.3(5)
C(5)-C(10)-C(12)	111.6(6)
C(5)-C(10)-C(11)	111.2(6)
C(12)-C(10)-C(11)	111.5(7)
C(9)-C(13)-C(14)	111.8(5)
C(9)-C(13)-C(15)	110.5(5)
C(14)-C(13)-C(15)	110.4(6)
C(17)-C(16)-C(21)	123.1(5)
C(17)-C(16)-N(2)	118.1(5)
C(21)-C(16)-N(2)	118.8(6)
C(16)-C(17)-C(18)	117.2(6)
C(16)-C(17)-C(22)	123.8(6)
C(18)-C(17)-C(22)	118.9(6)
C(19)-C(18)-C(17)	120.3(7)
C(20)-C(19)-C(18)	121.3(6)
C(19)-C(20)-C(21)	121.4(7)
C(20)-C(21)-C(16)	116.6(6)
C(20)-C(21)-C(25)	120.5(6)
C(16)-C(21)-C(25)	122.7(5)
C(23)-C(22)-C(17)	114.0(6)
C(23)-C(22)-C(24)	110.1(6)
C(17)-C(22)-C(24)	110.3(6)
C(21)-C(25)-C(26)	114.1(6)
C(21)-C(25)-C(27)	108.9(5)
C(26)-C(25)-C(27)	110.2(6)
O(1)-C(28)-O(2)	122.2(6)
O(1)-C(28)-C(29)	123.2(7)
O(2)-C(28)-C(29)	114.6(6)
F(1)-C(30)-O(2)	104.5(5)
F(1)-C(30)-C(31)	103.4(5)
O(2)-C(30)-C(31)	112.5(6)
F(1)-C(30)-Ni(1)	113.5(5)
O(2)-C(30)-Ni(1)	110.3(5)
C(31)-C(30)-Ni(1)	112.3(5)
F(5)-C(31)-F(4)	107.0(6)
F(5)-C(31)-C(30)	116.0(6)
F(4)-C(31)-C(30)	106.0(5)
F(5)-C(31)-C(39)	113.2(6)
F(4)-C(31)-C(39)	108.9(6)
C(30)-C(31)-C(39)	105.4(6)
F(2)-C(32)-F(7)	104.0(5)
F(2)-C(32)-C(39)	108.4(5)
F(7)-C(32)-C(39)	104.7(5)
F(2)-C(32)-Ni(1)	118.3(4)
F(7)-C(32)-Ni(1)	108.1(4)
C(39)-C(32)-Ni(1)	112.1(4)
F(3)-C(39)-F(6)	105.1(5)
F(3)-C(39)-C(31)	109.5(5)
F(6)-C(39)-C(31)	110.9(6)
F(3)-C(39)-C(32)	109.1(5)
F(6)-C(39)-C(32)	113.6(5)
C(31)-C(39)-C(32)	108.5(5)

Table S7. Optimized structure (Cartesian coordinates, Å) of **3** with an isopropyl-CH$_3$ agostic interaction. B3LYP/TZVP without dispersion correction.

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	-1.175986
C	-2.812007	-1.716507	1.222244
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
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
H	4.802868	0.232007	2.536165
H	1.932433	-3.450199	-0.910811
H	1.756189	-3.543499	0.844410
H	3.225048	-2.899230	3.048613
H	4.040964	-1.626708	3.953144
H	-1.954723	-3.289885	-4.215009
H	-1.961874	-0.745617	-4.443781
H	-0.407722	-3.744126	-1.221071
H	-1.104829	-1.811474	-2.430730
H	-2.263079	-4.050610	-2.647537
H	3.067705	0.807190	3.907883
H	2.459780	-2.201744	4.483098
H	1.398447	-1.300775	2.454587
H	-0.553923	-4.055413	0.512744
H	-2.310182	0.278880	-3.050560
H	-3.574697	-3.261949	-3.517247
H	1.627716	1.143918	2.951434
H	-3.595462	-0.685860	-3.788597
H	1.510223	0.167655	4.420832
H	-1.130336	-2.343095	2.365504
H	-0.817473	0.058960	2.305163
H	-4.816945	-1.528061	-2.095367
H	-1.157284	-0.349776	3.956170
H	-2.439854	0.355611	2.954902
H	-2.144191	-2.579818	4.535374
H	-3.174831	-3.424920	3.374306
H	-5.982872	-1.342690	0.059215
H	-4.723236	-1.450525	2.164205
H	-3.655303	-1.850519	4.014284
N	1.408695	-1.619266	0.036909
N	-0.732748	-2.014721	-0.036295
C	0.218514	1.666180	-1.047528
C	-0.553105	2.988793	-1.272224

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

Table S8. Optimized structure (Cartesian coordinates, Å) of **3** with an isopropyl-CH_3 agostic interaction. B3LYP/TZVP with the dispersion correction.

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	1.073564	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

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	3.285202	-2.680306
F	0.618380	4.068501	-0.104359
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

Table S9. Optimized structure (Cartesian coordinates, Å) of **3’.** B3LYP/TZVP without the dispersion correction.

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	3.398035	-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	2.609439
H	-2.366853	-3.260489	1.018934

H	-1.455424	1.054023	-3.032996
H	-4.007750	-1.619825	-3.925726
H	1.689172	0.669291	2.874312
H	-2.847681	0.722319	-4.063225
H	1.296295	-0.085755	4.424053
H	-2.309022	-1.103687	2.394946
H	-2.761387	1.284916	2.960386
H	-4.691033	0.456811	-2.723682
H	-3.074041	0.191271	4.314709
H	-4.418903	0.863643	3.400604
H	-3.957073	-2.156782	3.905897
H	-4.222445	-2.748065	2.259953
H	-6.142452	1.122230	-0.855138
H	-5.513090	0.576765	1.457902
H	-5.292174	-1.527276	2.938679
N	0.453227	-2.073451	0.254768
N	-1.634693	-1.479943	0.112348
C	2.113402	1.923895	-0.409702
C	1.556062	3.351247	-0.555902
C	0.327503	3.405450	0.377597
C	-0.455901	2.082219	0.167922
F	3.012969	1.924669	0.643199
F	2.866990	1.616152	-1.532163
F	2.439853	4.338050	-0.266911
F	0.764992	3.456513	1.664829
F	1.130569	3.540133	-1.835271
F	-0.425390	4.509658	0.155660
F	-1.260211	1.882288	1.263039
F	-1.303658	2.258074	-0.897087

Table S10. Optimized structure (Cartesian coordinates, Å) of **3'.** B3LYP/TZVP with the dispersion correction.

Ni	0.635538	0.582751	-0.240352
C	2.835043	-3.653462	-2.645862
C	4.123693	-1.694342	-0.673952
C	2.053758	-1.271730	-3.023928
C	4.714874	-1.268198	0.506078
C	2.122962	-2.440381	-2.030016
C	2.764253	-2.001348	-0.723327
C	3.959247	-1.136178	1.662348
C	2.014991	-1.848527	0.458221
C	2.595481	-1.421477	1.666264
C	-0.039204	-3.389353	0.700202
C	2.283461	-2.083596	4.086277
C	1.772772	-1.215169	2.926930
C	-1.497644	-3.093538	0.314923
C	-2.376732	-1.922178	-3.717857
C	-1.275287	0.330804	-3.340893
C	-0.266403	-1.111670	0.150882
C	-1.819957	-0.941268	-2.673670
C	1.726787	0.271149	3.312798
C	-2.858149	-0.615391	-1.609545
C	-2.689536	-0.932105	-0.251670
C	-4.036982	0.030775	-1.981524
C	-3.663568	-0.630360	0.714089
C	-3.485538	-0.987255	2.181715
C	-3.728693	0.209570	3.113386
C	-5.013348	0.336683	-1.046617
C	-4.827614	0.005993	0.287892
C	-4.396876	-2.164219	2.573350
H	3.853721	-3.407986	-2.952242
H	2.297863	-3.993888	-3.533798
H	4.722827	-1.777018	-1.571538
H	3.051637	-0.910998	-3.279000
H	5.769449	-1.022181	0.521557
H	2.890136	-4.483817	-1.938848
H	1.554484	-1.580820	-3.944946
H	1.504006	-0.422788	-2.612838
H	1.096973	-2.741358	-1.813962
H	4.431586	-0.782997	2.569871
H	0.409727	-4.187440	0.108811
H	0.076243	-3.633402	1.759516
H	2.300816	-3.141822	3.815454
H	3.295788	-1.798905	4.380364

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

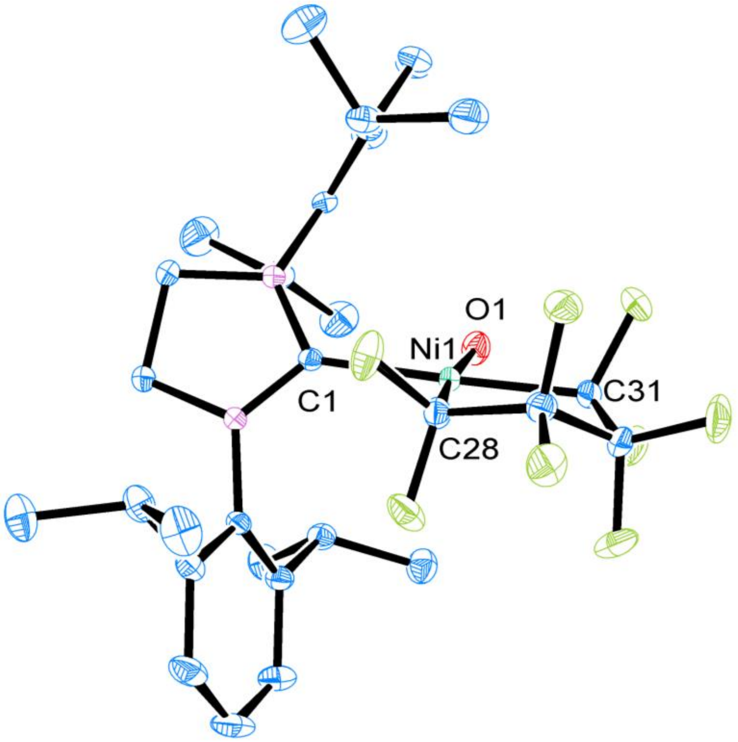


Figure S34. ORTEP representation of the molecular structure of **3**•H_2O with thermal ellipsoid probabilities set to 30 % and hydrogen atoms omitted for clarity.

Table S11. Crystal data and structure refinement for **3**•H_2O.

Complex	**3**•H_2O
ID code	tb069
Formula	$C_{37}H_{46}F_8N_2NiO$
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/Å^3	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

2θ range/°	1.99-28.36
Index range	-22<h<22 -14<k<14 -27<l<27
Indep. reflns collected/unique	50510/8894
Max. and min. transmission	0.8974 and 0.8767
(Rint)	0.0234
R1, wR2 ($I>2\theta(I)$)	0.0299, 0.0782
R1, wR2(all data)	0.0376, 0.0831
Goodness of fit, F^2	1.027
Data/restraints/params	8894/0/442
Largest diff. peak, hole/Å^3	0.360, -0.283

Table S12. Bond lengths [Å] and angles [°] for complex **3**•H_2O.

……....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(12)	1.526(2)
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)

C(29)-C(30)	1.523(2)
C(30)-C(31)	1.521(2)
C(32)-C(33)	1.358(3)
C(32)-C(37)	1.355(4)
C(33)-C(34)	1.321(4)
C(34)-C(35)	1.386(5)
C(35)-C(36)	1.392(4)
C(36)-C(37)	1.359(4)

C(28)-Ni(1)-C(31)	85.98(6)
C(28)-Ni(1)-C(1)	93.26(5)
C(31)-Ni(1)-C(1)	177.64(5)
C(28)-Ni(1)-O(1)	174.05(5)
C(31)-Ni(1)-O(1)	88.07(5)
C(1)-Ni(1)-O(1)	92.69(4)
C(1)-N(1)-C(4)	126.83(10)
C(1)-N(1)-C(2)	112.92(10)
C(4)-N(1)-C(2)	120.12(10)
C(1)-N(2)-C(16)	126.93(10)
C(1)-N(2)-C(3)	112.48(9)
C(16)-N(2)-C(3)	116.78(9)
N(2)-C(1)-N(1)	106.79(10)
N(2)-C(1)-Ni(1)	129.78(8)
N(1)-C(1)-Ni(1)	123.37(8)
N(1)-C(2)-C(3)	101.14(9)
N(2)-C(3)-C(2)	101.67(9)
C(9)-C(4)-C(5)	122.07(11)
C(9)-C(4)-N(1)	120.21(11)
C(5)-C(4)-N(1)	117.62(11)
C(6)-C(5)-C(4)	117.37(12)
C(6)-C(5)-C(10)	119.57(12)
C(4)-C(5)-C(10)	123.04(12)
C(7)-C(6)-C(5)	121.44(13)
C(8)-C(7)-C(6)	120.24(13)
C(7)-C(8)-C(9)	120.93(13)
C(4)-C(9)-C(8)	117.88(12)
C(4)-C(9)-C(13)	122.49(11)
C(8)-C(9)-C(13)	119.59(11)
C(5)-C(10)-C(12)	113.03(13)
C(5)-C(10)-C(11)	110.87(13)
C(12)-C(10)-C(11)	109.36(14)
C(9)-C(13)-C(15)	111.81(13)
C(9)-C(13)-C(14)	109.97(12)
C(15)-C(13)-C(14)	110.19(13)
C(21)-C(16)-C(17)	122.16(11)
C(21)-C(16)-N(2)	119.52(10)
C(17)-C(16)-N(2)	118.07(11)
C(18)-C(17)-C(16)	117.68(12)
C(18)-C(17)-C(22)	119.32(12)
C(16)-C(17)-C(22)	123.00(11)
C(19)-C(18)-C(17)	121.01(13)
C(18)-C(19)-C(20)	120.56(13)
C(19)-C(20)-C(21)	120.87(14)
C(20)-C(21)-C(16)	117.68(12)
C(20)-C(21)-C(25)	118.33(12)
C(16)-C(21)-C(25)	123.97(11)
C(17)-C(22)-C(23)	111.15(12)
C(17)-C(22)-C(24)	111.76(13)
C(23)-C(22)-C(24)	109.78(12)
C(21)-C(25)-C(26)	111.55(11)
C(21)-C(25)-C(27)	110.78(11)
C(26)-C(25)-C(27)	110.94(11)
F(1)-C(28)-F(2)	104.88(10)
F(1)-C(28)-C(29)	104.54(10)
F(2)-C(28)-C(29)	106.53(10)
F(1)-C(28)-Ni(1)	111.37(9)
F(2)-C(28)-Ni(1)	116.14(9)
C(29)-C(28)-Ni(1)	112.47(9)
F(4)-C(29)-F(3)	106.18(11)
F(4)-C(29)-C(30)	108.05(11)
F(3)-C(29)-C(30)	111.73(11)
F(4)-C(29)-C(28)	110.04(11)
F(3)-C(29)-C(28)	113.96(11)
C(30)-C(29)-C(28)	106.77(11)

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)

References

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[1] Hunadi, R. J.; Baum, K. *Synthesis* **1982**, *39*, 454.

[2] (a) Chambers, R. D.; Burton, D. J.; Drakesmith, F. G.; Hutchinson, J.; Kitazume, T.; Lu, L.; Percy, J. M.; Sandford, G.; Yamazaki, T. *Organofluorine Chemistry Techniques and Synthons*, Vol. 193; Springer: New York, **1997**. (b) Baker, R. T., Beatty, R. P., Sievert, A. C., Wallace, R. L., Jr. *PCT Int. Appl.* **1996**, U.S Patent 5,670,679, E. I. Du Pont de Nemours & Co., USA.

[3] (a) Chambers, R. D.; Burton, D. J.; Drakesmith, F. G.; Hutchinson, J.; Kitazume, T.; Lu, L.; Percy, J. M.; Sandford, G.; Yamazaki, T. *Organofluorine Chemistry Techniques and Synthons*, Vol. 193; Springer: New York, **1997**. (b) Baker, R. T., Beatty, R. P., Sievert, A. C., Wallace, R. L., Jr. *PCT Int. Appl.* **1996**, U.S Patent 5,670,679, E. I. Du Pont de Nemours & Co., USA.

[4] APEX Software Suite v.2012; Bruker AXS: Madison, WI, **2005**.

[5] R. Blessing, *Acta Cryst.* **1995**, *A51*, 33

[6] G. Sheldrick Cell_Now, Bruker-AXS: Madison, WI, **2004.**

[7] G. M. Sheldrick,*Acta Cryst.* **2008**, *A64*, 112.