

Supplementary Materials

Synthesis of Tris(trifluoromethyl)nickelates(II) – Coping with the C₂F₅ Problem

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Figure S2. ¹H NMR spectrum (300 MHz, MeCN-d₃) of the mixture of species (NMe₄)[Ni(CF₃)_x(C₂F₅)_y(MeCN)] (x + y = 3) with partial CF₃ to C₂F₅ replacement.

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Supplementary Tables

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Table S2. Selected bond lengths (Å) and angles (°) of *cis*-(NMe₄)[Ni(CF₃)₂(C₂F₅)(MeCN)] from sc-XRD.

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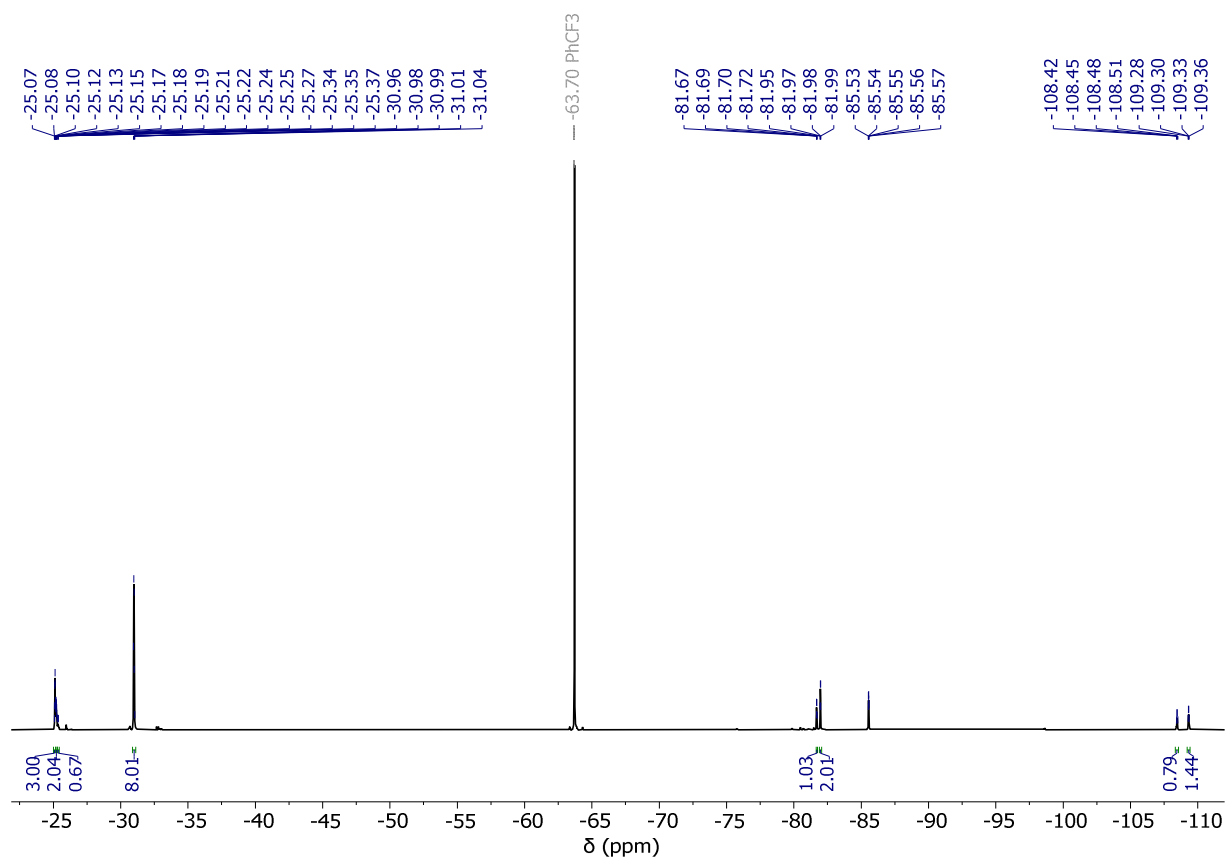


Figure S1. ¹⁹F NMR spectrum (282 MHz, MeCN-d₃) of the mixture of species (NMe₄)[Ni(CF₃)_x(C₂F₅)_y(MeCN)] ($x + y = 3$) with partial CF₃ to C₂F₅ replacement.

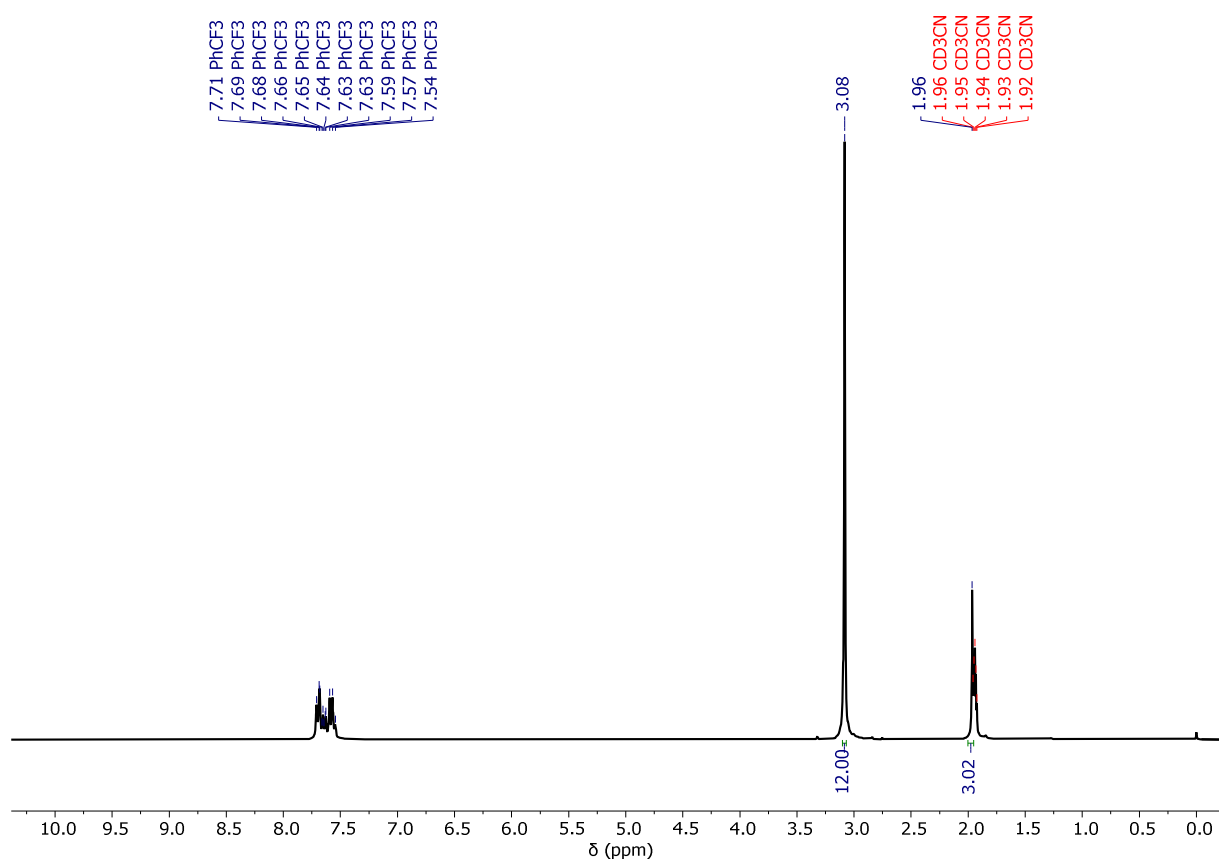


Figure S2. ^1H NMR spectrum (300 MHz, MeCN-d_3) of the mixture of species $(\text{NMe}_4)[\text{Ni}(\text{CF}_3)_x(\text{C}_2\text{F}_5)_y(\text{MeCN})]$ ($x + y = 3$) with partial CF_3 to C_2F_5 replacement.

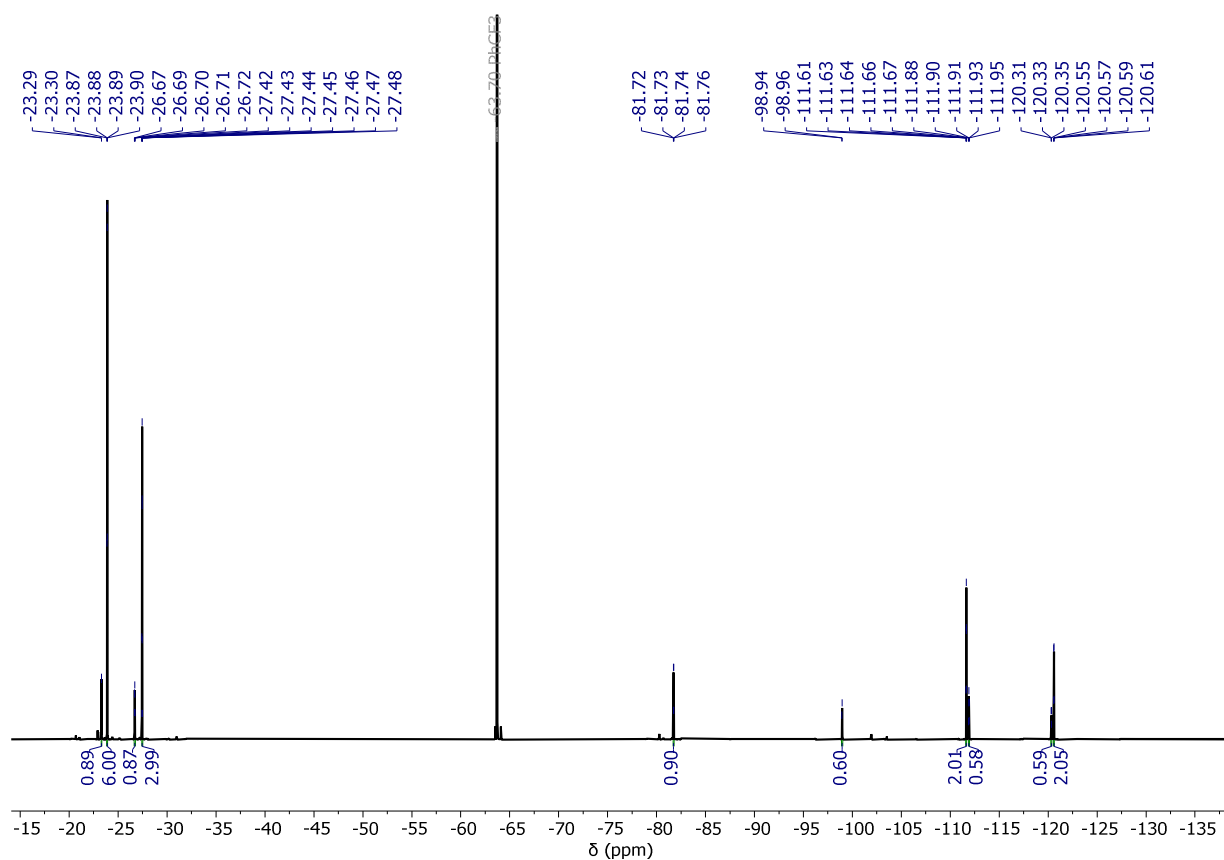


Figure S3. ^{19}F NMR spectrum (282 MHz, MeCN-d_3) of the mixture of species $(\text{NMe}_4)[\text{Ni}(\text{CF}_3)_x(\text{C}_2\text{F}_5)_y(\text{F-NHC})]$ ($x + y = 3$, $\text{F-NHC} = N,N$ -bis(2,4-difluorophenyl)imidazolyldiene) with partial CF_3 to C_2F_5 replacement.

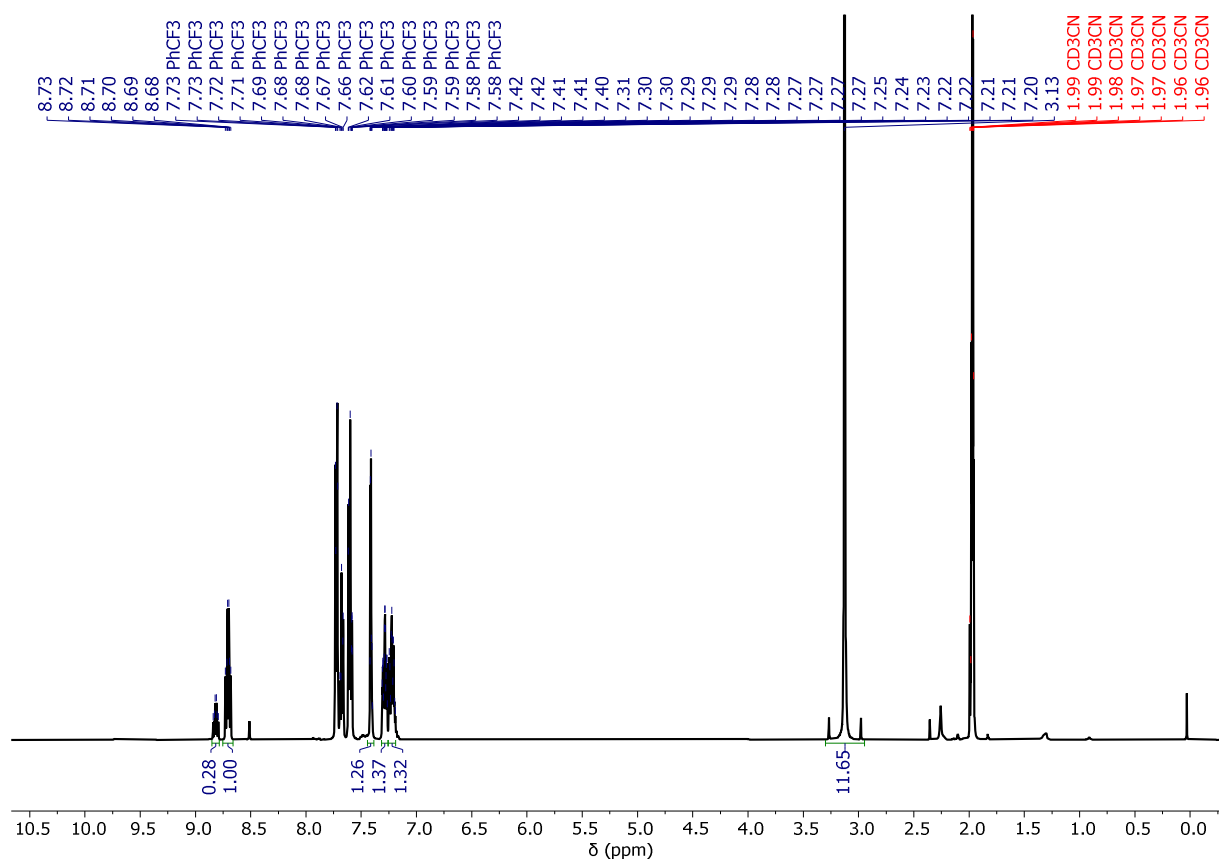


Figure S4. ^1H NMR spectrum (300 MHz, MeCN-d_3) of the mixture of species $(\text{NMe}_4)[\text{Ni}(\text{CF}_3)_x(\text{C}_2\text{F}_5)_y(\text{F-NHC})]$ ($x + y = 3$, $\text{F-NHC} = N,N\text{-bis}(2,4\text{-difluorophenyl})\text{imidazolyliene}$) with partial CF_3 to C_2F_5 replacement.

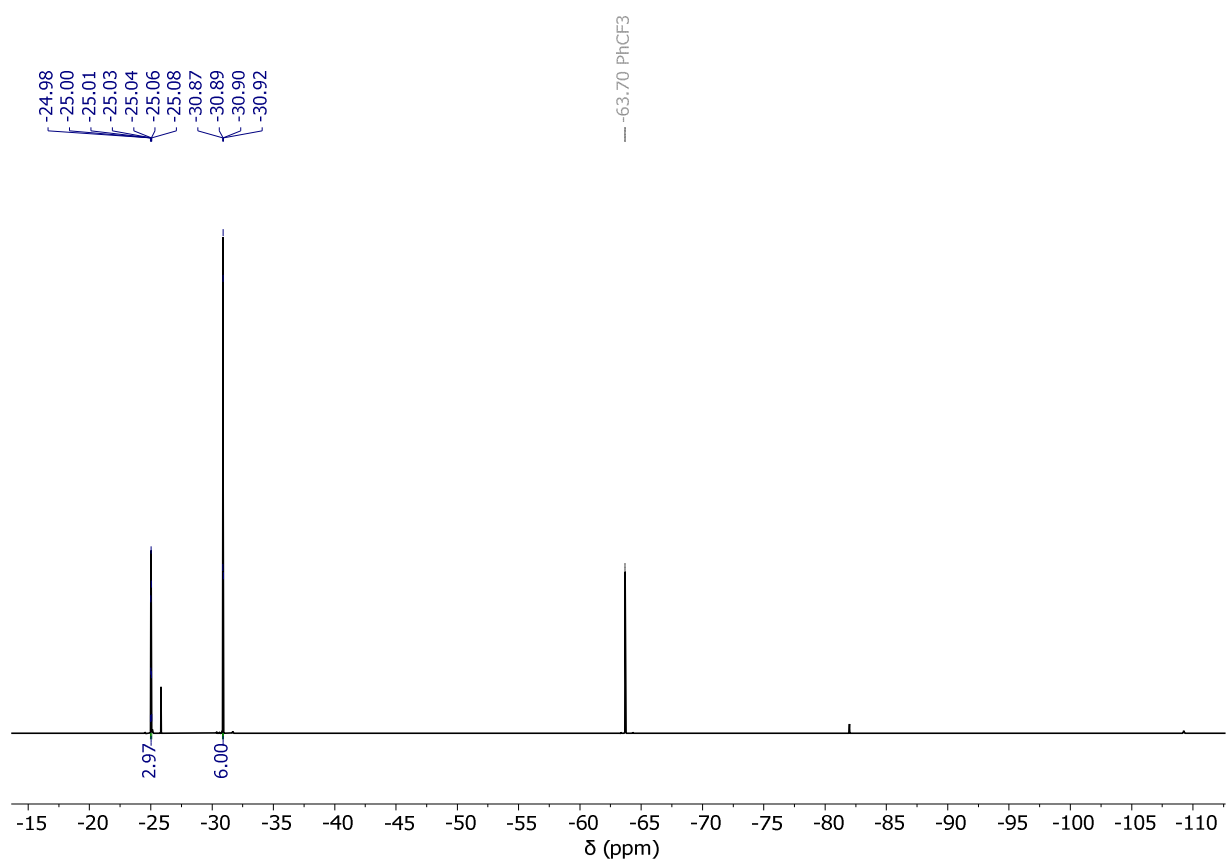


Figure S5 ^{19}F NMR spectrum (282 MHz, MeCN-d_3) of $(\text{NMe}_4)[\text{Ni}(\text{CF}_3)_3(\text{MeCN})]$ (**1**) prepared using the refined reaction procedure.

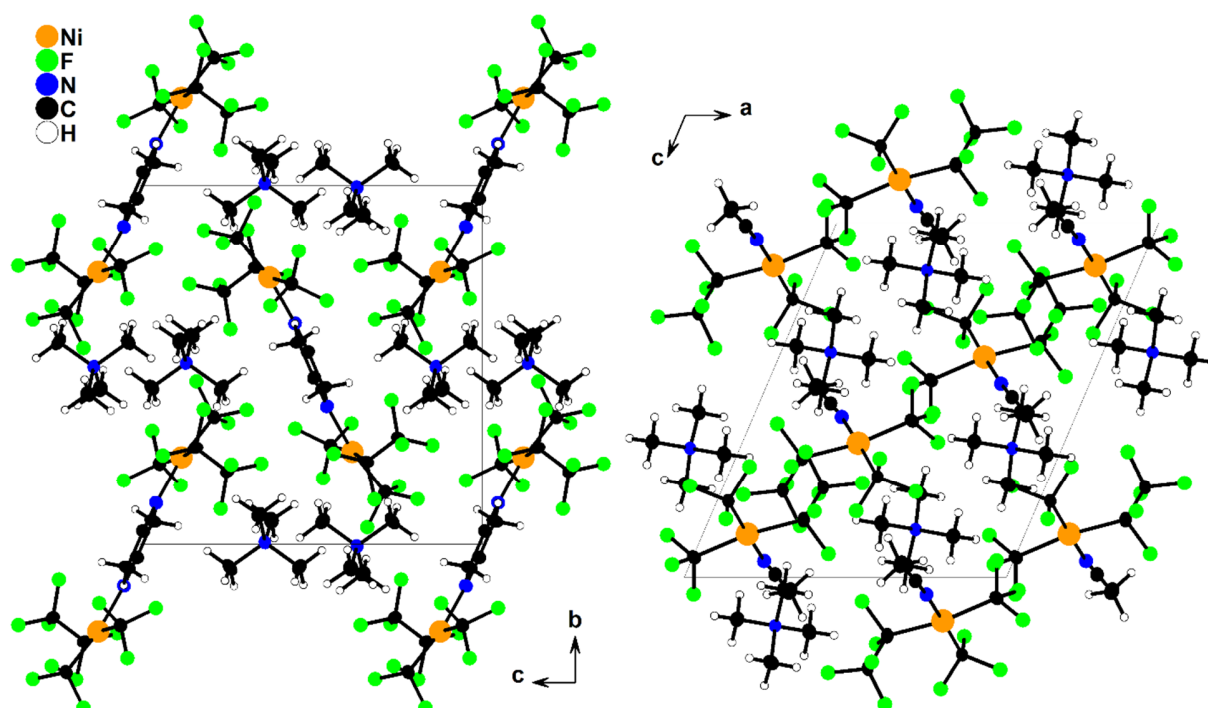


Figure S6. Crystal structure of $(\text{NMe}_4)[\text{Ni}(\text{CF}_3)_x(\text{C}_2\text{F}_5)_y(\text{MeCN})]$ ($x = 2.2$, $y = 0.8$) viewed along the crystallographic a and b axes. The split occupancy of 20% $(\text{NMe}_4)[\text{Ni}(\text{CF}_3)_3(\text{MeCN})]$ was omitted for clarity.

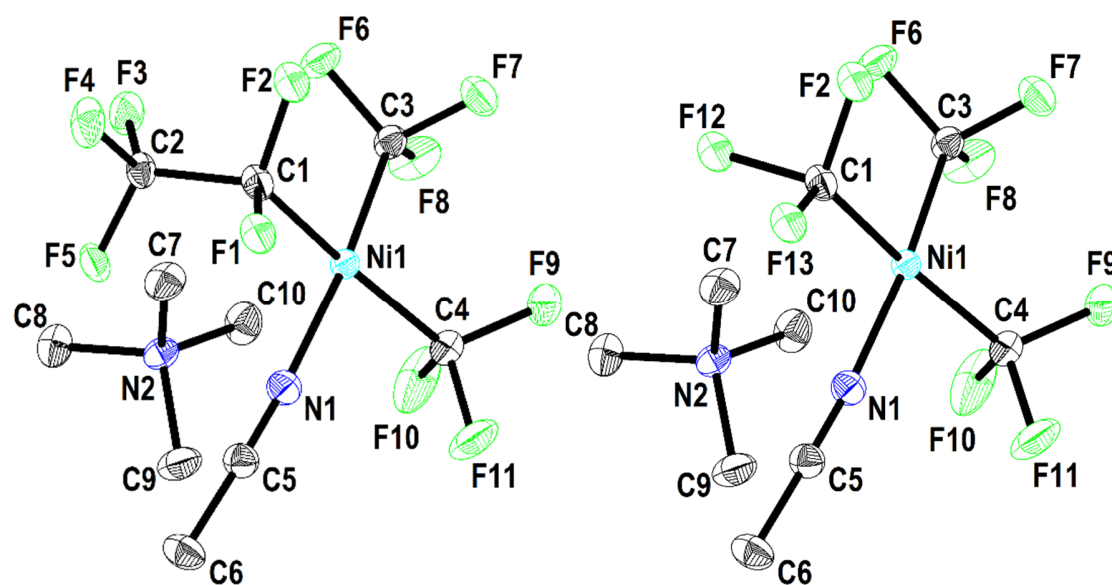


Figure S7. Molecular structures of *cis*-(NMe_4) $[\text{Ni}(\text{CF}_3)_2(\text{C}_2\text{F}_5)(\text{MeCN})]$ (left) and $(\text{NMe}_4)[\text{Ni}(\text{CF}_3)_3(\text{MeCN})]$ (right) from sc-XRD of $(\text{NMe}_4)[\text{Ni}(\text{CF}_3)_x(\text{C}_2\text{F}_5)_y(\text{MeCN})]$ ($x = 2.2$, $y = 0.8$). Thermal displacement ellipsoids shown at 40% probability, H atoms omitted for clarity. XRD data of $(\text{NMe}_4)[\text{Ni}(\text{CF}_3)_3(\text{MeCN})]$ was previously reported [1].

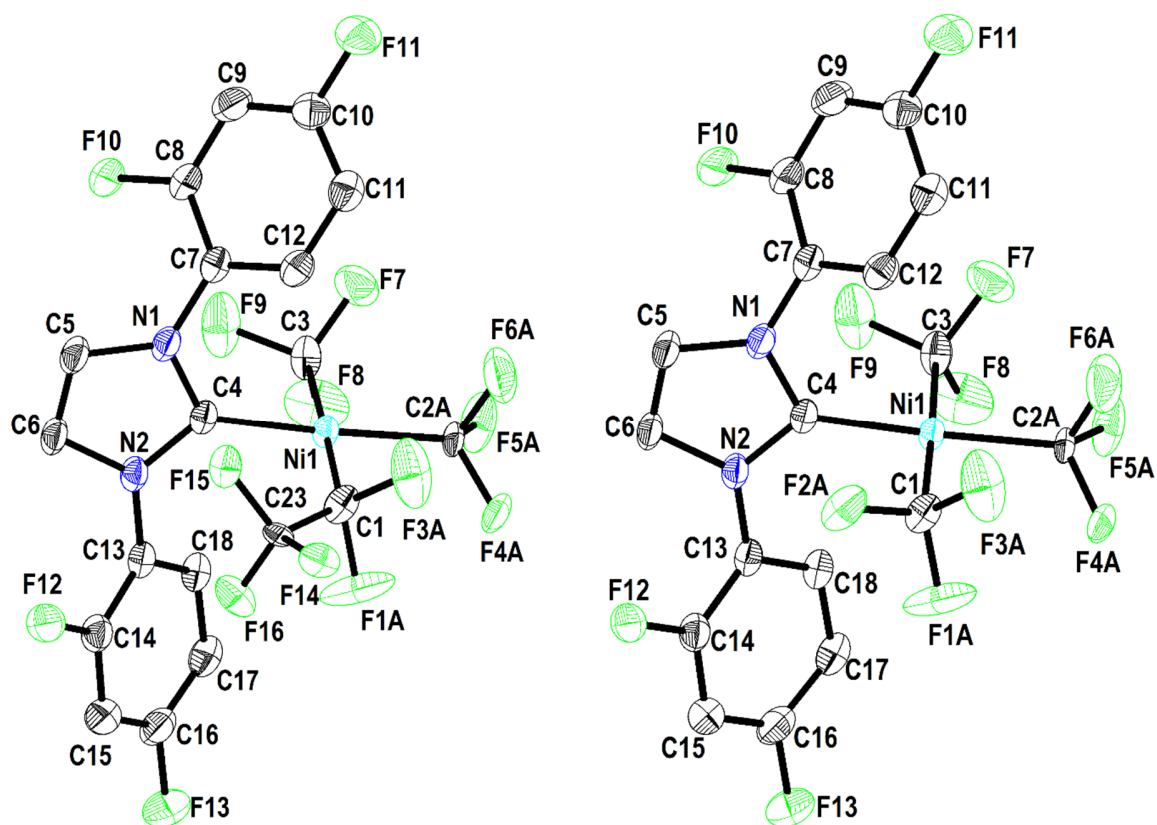


Figure S8. Molecular structures of *cis*-[Ni(CF₃)₂(C₂F₅)(F-NHC)]⁻ (F-NHC = *N,N*-bis(2,4-difluorophenyl)imidazolyliidene, left) and [Ni(CF₃)₃(F-NHC)]⁻ (right) from sc-XRD of (NMe₄)[Ni(CF₃)_x(C₂F₅)_y(MeCN)] (*x* = 2.85, *y* = 0.15). Thermal displacement ellipsoids shown at 40% probability; H atoms, rotational disorder of CF₃ ligands and counterions omitted for clarity; data previously reported [2].

Supplementary Tables

Table S1. Crystallographic and Structure Refinement Data for (NMe₄)[Ni(CF₃)_x(C₂F₅)_y(MeCN)] (x = 2.2, y = 0.8).

formula ^a / MW ^a	C ₁₀ H ₁₅ F ₁₁ N ₂ Ni / 430.92 g mol ⁻¹
temperature / wavelength	100(2) / 0.71073 Å
crystal system / space group	monoclinic, <i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å) / <i>b</i> (Å) / <i>c</i> (Å)	10.7213(4) / 12.4640(5) / 12.8859(5)
β (°)	113.166(2)
<i>V</i> (Å ³) / <i>Z</i>	1583.10 (11) / 4
<i>Q</i> _{calc} (g cm ⁻³) / <i>F</i> (000)	1.777 / 850
limiting indices	-18 < <i>h</i> < 18; -21 < <i>k</i> < 21; -22 < <i>l</i> < 21
reflections collected / unique	116248 / 8507
<i>R</i> _{int}	0.058
data / restraints / parameters	8507 / 0 / 224
Goodness-of-fit on <i>F</i> ²	1.04
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>) / all data)	0.042 / 0.052
<i>wR</i> ₂	0.116
largest diff peak and hole (e·Å ⁻³)	2.41 / -1.23
CCDC	2218331

^a Given for the major species (NMe₄)[Ni(CF₃)₂(C₂F₅)(MeCN)] (2).

Table S2. Selected bond lengths (Å) and angles (°) of *cis*-(NMe₄)[Ni(CF₃)₂(C₂F₅)(MeCN)] (2) from sc-XRD.

distances		angles	
Ni–C1	1.959(2)	C1–Ni–C3	92.71(6)
Ni–C3	1.897(2)	C3–Ni–C4	90.41(6)
Ni–C4	1.948(2)	C4–Ni–N1	89.48(6)
Ni–N1	1.895(1)	N1–Ni–C1	88.86(6)
C1–C2	1.515(3)	Ni–C1–C2	119.6(1)

References

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