

Supporting Information for:

A Five-Coordinate Nickel(II) Fluoroalkyl Complex as a Precursor to a Spectroscopically Detectable Ni(III) Species

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Experimental Procedures

General Considerations. All manipulations were performed using standard Schlenk and high vacuum techniques or in a nitrogen filled glovebox. Solvents were distilled from Na/benzophenone or CaH₂. DMF was distilled over BaO under reduced pressure. All reagents were used as received from commercial vendors, unless otherwise noted. Elemental analyses were performed by Columbia Analytical Services. ¹H NMR spectra were recorded at ambient temperature (unless otherwise noted) on a Varian Oxford 300 MHz spectrometer and referenced to residual proton solvent signals. ¹³C NMR spectra were recorded on the Varian Oxford spectrometers operating 75 MHz or 126 MHz and referenced to solvent signals unless otherwise noted. ¹⁹F spectra were recorded on the Varian Oxford spectrometer operating at 282 MHz unless otherwise noted and were referenced to α,α,α -trifluorotoluene as an internal standard ($\delta = -63.7$). Magnetic susceptibilities were calculated according to the Evan's NMR Method.¹ EI-the mass spectrum of **8** was measured with a Finnigan MAT95-DF (EI pos using 20 eV). Simulations were performed using ISOPRO 3.0. Elemental analyses of **8** were carried out using a Hekatech CHNS EuroEA 3000 Analyzer.

Abbreviations: tpy = 2,2':6',2''-terpyridine
 tpy' = 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine

Preparation of [(CH₃CN)₂Ni(CF₃)₂] (1): TMSCF₃ (380 mg, 2.5 mmol) and AgF (260 mg, 2.0 mmol) were added into 20 mL of dry CH₃CN. The mixture was stirred at room temperature for 2 hours. Then NiBr₂·DME (310 mg, 1.0 mmol) was added. The reaction mixture was kept stirring for 2 days, and filtered. The filtrate was evaporated on a vacuum line to give a yellow solid (253 mg, 90%). ¹H NMR (DMSO-d₆, 300 MHz): δ 2.02 (s). ¹⁹F NMR (DMSO-d₆, 282 MHz): δ -26.1. ¹³C NMR (DMSO-d₆, 125 MHz): δ 125.1 (q, $J = 368$ Hz, CF₃), 117.8, 0.78. Anal. Calcd (found) for C₆H₆F₆N₂Ni: C, 25.85 (25.65); H, 2.17 (2.25).

In a similar way, [(CH₃CN)₂Ni(C₂F₅)₂] (**2**) can be prepared: AgF (383 mg, 2 equiv.) and TMSC₂F₅ (731 mg, 2.5 equiv.) were added into 15 mL CH₃CN. The mixture was stirred at room temperature for 2 h then NiBr₂·DME (445 mg, 1.5 mmol) was added. The reaction mixture was kept stirring for two days. Then the solution was filtered through the Celite. The filtrate was evaporated on vacuum line. The yellow solid was obtained (500 mg, 89%). ¹H NMR (DMSO-d₆, 500 MHz): δ 2.04 (s). ¹⁹F NMR (acetonitrile-d₃, 470 MHz): δ -81.5 (CF₃), -102.5 (CF₂). Anal. Calcd (found) for C₈H₆F₁₀N₂Ni: C, 25.36 (25.30); H, 1.60 (1.62).

Preparation of [(TMEDA)Ni(CF₃)₂] (3): Me₃SiCF₃ (200 mg, 1.3 mmol) and AgF (130 mg, 1.0 mmol) were added into 10 mL of dry CH₃CN. The mixture was stirred at room temperature for 2 hours. Then NiBr₂·DME (158 mg, 0.5 mmol) was added. One hour later, *N,N,N,N*-tetramethylethane-1,2-diamine (70 mg, 0.6 mmol) was added. The reaction mixture was kept stirring for 2 days, and filtered. The filtrate was evaporated on a vacuum line. The residue was extracted by dichloromethane (10mL). The dichloromethane solution was left standing at room temperature for 0.5 h, then filtered and dried on a vacuum line to give a yellow solid (142 mg, 91%). ¹H NMR (CD₂Cl₂, 300 MHz): δ 2.49 (s, 12H), 2.30 (s, 4H). ¹⁹F NMR (CD₂Cl₂, 282 MHz): δ -27.9 (s, 6F). ¹³C NMR (CD₂Cl₂, 125 MHz): δ 127.6 (q, *J* = 368 Hz, CF₃), 61.4, 49.2. Anal. Calcd (found) for C₈H₁₆F₆N₂Ni: C, 30.71 (31.01); H, 5.15 (5.00).

Preparation of [(TEEDA)Ni(CF₃)₂] (4): Me₃SiCF₃ (200 mg, 1.3 mmol) and AgF (126 mg, 1.0 mmol) were added into 10 mL of dry CH₃CN. The mixture was stirred at room temperature for 2 hours. Then NiBr₂·DME (158mg, 0.5 mmol) was added. After two days, the reaction mixture was filtered. *N,N,N,N*-tetraethylethane-1,2-diamine (172mg, 1.0 mmol) was added into the filtrate. The mixture was stirred at room temperature for another 4 hours, then evaporated on a vacuum line. The residue was washed with pentane (3 x 5 mL) and extracted with dichloromethane (8 mL). The dichloromethane solution was left standing at room temperature for 0.5 h, filtered and dried on a vacuum line to give a yellow solid (151 mg, 82%). ¹H NMR (CD₂Cl₂, 500 MHz): δ 3.02 (m, 4H), 2.61 (m, 4H), 2.42 (s, 4H), 1.57 (t, *J* = 6.7Hz, 12H). ¹⁹F NMR (CD₂Cl₂, 282 MHz): δ -28.8 (s, 6F). ¹³C NMR (CD₂Cl₂, 125 MHz): δ 125.6 (q, *J* = 369 Hz, CF₃), 51.5, 49.8, 10.8. Anal. Calcd (found) for C₁₂H₂₄F₆N₂Ni: C, 39.06 (38.70); H, 6.56 (6.38).

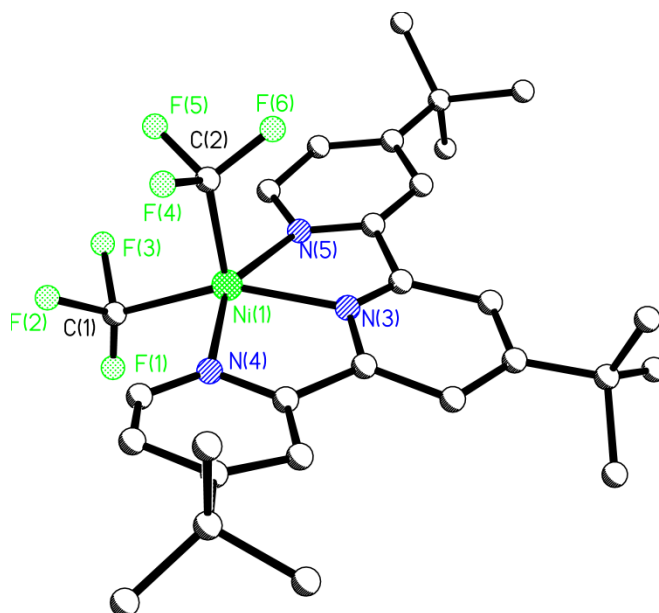
New procedure for the preparation of [(4,4'-dtbpy)Ni(CF₃)₂] (5): [(CH₃CN)₂Ni(CF₃)₂] (28 mg, 0.10 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (30 mg, 0.11mmol) were dissolved in 5 mL of dry THF. The mixture was stirred at room temperature for 0.5 h and filtered. Then 15 mL of dry pentane was added slowly into the filtrate. The mixture was stored in a freezer (-35 °C) in a glovebox overnight. Finally, yellow crystals of [(4,4'-dtbpy)Ni(CF₃)₂](THF) were formed, which was further washed by pentane (46 mg, 0.086 mmol, 86%). Analytical data matched literature values (Yamaguchi, Y.; Ichioka, H.; Klein, A.; Brennessel, W. W.; Vivic, D. A. *Organometallics* **2012**, *31*, 1477).

Preparation of [(6,6'-dmbpy)Ni(CF₃)₂(CH₃CN)] (6): [(CH₃CN)₂Ni(CF₃)₂] (20 mg, 0.072 mmol) and 6,6'-dimethyl-2,2'-bipyridine (15 mg, 0.082 mmol) were dissolved in 4 mL of dry THF. The mixture was stirred at

room temperature for 20 minutes and filtered. Then 15 mL of dry pentane was added slowly into the filtrate. The mixture was stored in a freezer (-35°C) in a glovebox. Finally, orange crystals were formed (24 mg, 0.057 mmol, 79%). Anal. Calcd (found) for $C_{16}H_{15}F_6N_3Ni$: C, 45.54 (45.60); H, 3.58 (3.62). 1H NMR (CD_3CN , 500 MHz): δ 8.21 (d, J = 7.9 Hz, 2H), 7.90 (t, J = 7.8 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 3.66 (s, 6H). The acetonitrile ligand was not observed due to rapid exchange with deuterated solvent. ^{19}F NMR (CD_3CN , 470 MHz): δ -26.5 (s, 6F).

Preparation of [(tpy)Ni(CF₃)₂] (7): [(CH₃CN)₂Ni(CF₃)₂] (84 mg, 0.3 mmol) and 2:2',6':2''-terpyridine (78 mg, 98%, 0.33 mmol) were dissolved in 6 mL of dry CH₃CN. The mixture was stirred at room temperature for 0.5 hour. Then 18 mL of dry diethyl ether (Et₂O) was added slowly. The mixture was stored in a freezer (-35°C) in a glovebox. Several days later, brown solid was isolated, washed with pentane and dried to give the desired product (104 mg, 0.242 mmol, 81%). Anal. Calcd (found) for $C_{17}H_{11}F_6N_3Ni$: C, 47.49 (47.27); H, 2.58 (2.76).

Preparation of [(tpy')Ni(CF₃)₂] (8): [(CH₃CN)₂Ni(CF₃)₂] (112mg, 0.4mmol) and 4,4',4''-tri-*tert*-butyl-2:2',6':2''-terpyridine (175mg, 95%, 0.41mmol) were dissolved in 6 mL of dry THF. The mixture was stirred at room temperature for 0.5 hour, then filtered. 15 mL of dry pentane was added slowly into the filtrate. The mixture was left in a freezer (-35°C). Finally, brown solid was formed, which was further washed by pentane and dried to give the desired product (156 mg, 0.26 mmol, 65 %). Anal. Calc. (found) for $C_{29}H_{35}F_6N_3Ni$ (598.29): C, 58.22 (58.18); H, 5.90 (5.89); N, 7.02 (7.00). The 1H NMR spectrum of **8** is largely dominated by residual solvent peaks from the deuterated solvent. However, the full 1H NMR spectrum is provided at the end of this section. ^{19}F NMR signals were not observed. EI-MS: 597 [M]⁺, 528 [M-CF₃]⁺, 401 [tButpy]⁺, 386 [tButpy-CH₃]⁺. A solution magnetic susceptibility measurement was taken (Evan's Method, THF-d₈ solvent, 23 °C) and the μ_{eff} was determined to be 2.38 μ_B . Preliminary X-ray data confirms connectivity (hydrogen atoms removed for clarity):



Preparation of [(tpy')Ni(C₂F₅)₂] (9): [(CH₃CN)₂Ni(C₂F₅)₂] (94 mg, 0.25 mmol), tpy' (120 mg, 0.3 mmol) and TMS-C₂F₅ (61 mg, 0.32 mmol) were dissolved in 4 mL of dry THF. The solution turns purple. The solution was stirred at room temperature for 2 h and then filtered through a glass frit. The filtrate was dried on a high vacuum line, leaving a dark purple solid (Yield 92%). Recrystallized from toluene/pentane and gave dark amber brown/purple crystals. Anal. Calcd (found) for C₃₁H₃₅F₁₀N₃Ni: C, 53.32 (53.42); H, 5.05 (5.30). Complex **8** slowly (minutes) decomposes in solution phase. A solution magnetic susceptibility measurement was taken (Evan's Method, toluene-d₈ solvent, 23 °C) and the μ_{eff} was determined to be 2.59 μ_{B} . The ¹H NMR spectrum of **9** is largely dominated by residual solvent peaks from the deuterated solvent. However, the full ¹H NMR spectrum is provided at the end of this section. ¹⁹F NMR signals were not observed.

Preparation of [(tpy')₂Ni][Ni(μ-F)(CF₃)₂]₂ (10): (CH₃CN)₂Ni(CF₃)₂ (56 mg, 0.2 mmol) and tpy' (82 mg, 1 equiv) were dissolved in THF (2 mL) and transferred to a sealed tube. The mixture was stirred at 50 °C for 2.5 h and then filtered through a glass frit. Then, 20 mL pentane was added to the filtrate which precipitated a brown powder (62 mg, 71%). X-ray quality crystals were grown from THF/pentane at room temperature. Anal. Calcd (found) for C₅₈H₇₀F₁₄N₆Ni₃: C, 53.86 (53.99); H, 5.46 (5.50). ¹⁹F NMR (CD₃CN, 470 MHz): δ -27.2 (s). The bridging fluorides could not be observed.

Preparation of [(tpy')Ni(CF₃)] [PF₆] (14): (CH₃CN)₂Ni(CF₃)₂ (28 mg, 0.1 mmol) and 4,4',4''-tri-*tert*-butyl-2:2',6':2''-terpyridine (46 mg, 0.11mmol) were dissolved in 4 mL of dry THF. The solution was stirred at room temperature for 0.5 hour. Then ferrocenium hexafluorophosphate ([Cp₂Fe][PF₆], 34 mg, 0.1 mmol) was added. The mixture was kept stirring for 23 hours, and filtered. Then, 16 mL of pentane was added slowly into the filtrate. The mixture was left in a freezer (-35°C) to grow crystals. Finally, yellow crystals were formed, which was further washed with pentane and dried to give the desired product (63 mg, 0.093 mmol, 93%). ¹H NMR (300MHz, CD₂Cl₂): 8.37 (d, *J* = 6.2 Hz, 2H), 8.01 (s, 2H), 8.00 (d, *J* = 2.1 Hz, 2H), 7.59 (dd, *J* = 6.2 Hz, *J* = 2.1 Hz, 2H), 1.54 (s, 9H), 1.45 (s, 18H). ¹⁹F NMR (282MHz, CD₂Cl₂): -34.5 (s, 3F), -72.6 (d, *J* = 713 Hz, 6F). ¹³C NMR (125MHz, CD₂Cl₂): 170.1, 168.1, 156.2, 154.5 (q, *J* = 4.6 Hz), 153.1, 125.6, 120.6, 119.6, 37.2, 36.3, 30.4, 30.1. Anal. Calcd (found) for [(tpy')Ni(CF₃)] [PF₆]·THF (C₂₈H₃₅F₉N₃NiP) : C, 51.50 (51.66); H, 5.81 (5.51). X-ray structure consistent with co-crystallized THF.

Magnetic moment determination:

Sample calculation of the diamagnetic susceptibility of [(tpy')Ni(C₂F₅)₂] (9) in toluene-d₈:

15 x C (aromatic ring)=	15(-6.24e-6)	=	-93.6 e-6 emu
35 x H	=	35(-2.93e-6)	= -102.55 e-6 emu
3 x N (aromatic ring) =	3(-4.6e-6)	=	-13.8 e-6 emu
16 x C (nonaromatic) =	16(-6.0e-6)	=	-96.0 e-6 emu
10 x F	=	10(-6.3e-6)	= -63 e-6 emu
1 x Ni	=	1(-12.8e-6)	= -12.8 e-6 emu
			-381.75 e-6 emu

Solution magnetic susceptibilities were then calculated using the Evans NMR method with a superconducting NMR spectrometer according to eq 1:

Diamagnetic correction for THF solvent: -0.735 e-6 cm³g⁻¹.

Diamagnetic correction for toluene solvent: -0.7176 e-6 cm³g⁻¹.

Sample calculation of μ_{eff} for [(tpy')Ni(C₂F₅)₂] (9) in toluene-d₈:

$$\chi_g = 3\Delta\nu/4\pi\nu c + \chi_o \quad (1)$$

where:

χ_g = gram susceptibility

c = concentration in g/mL

$\Delta\nu$ = observed shift difference in Hz

ν = spectrometer frequency in Hz

χ_o = mass susceptibility of solvent

$$\chi_g = [3(130 \text{ Hz})/4\pi(500 \text{ e}^6 \text{ Hz})(0.0147 \text{ g/mL})] - 0.7176 \text{ e-6 cm}^3\text{g}^{-1}$$

$$\chi_g = 3.507 \text{ e-6 cm}^3\text{g}^{-1}$$

$$\chi_m = (\chi_g)(\text{formula weight}) = (3.507 \text{ e-6 cm}^3\text{g}^{-1})(698.3071 \text{ g/mol}) = 2.449 \text{ e-3 emu}$$

$$\chi_{\text{corrected}} = (\chi_m) - \text{diamagnetic correction} = 2.449 \text{ e-3} + 381.75 \text{ e-6} = 2.831 \text{ e-3 emu}$$

$$\mu_{\text{eff}} = 2.828[(\chi_{\text{corrected}})(T)]^{1/2}$$

$$\mu_{\text{eff}} = 2.828[(2.831 \text{ e-3})(295.58 \text{ K})]^{1/2} = 2.588 \mu_B$$

Electronic structure calculations: Quantum calculations were performed with the Gaussian09W software.² Unconstrained geometry optimizations were performed using the spin unrestricted B3LYP exchange-correlation functional.^{3,4} The m6-31G* basis set was used for nickel,⁵ and the 6-31g* was used for all other atoms. All calculations have been checked for the absence of imaginary frequencies, and the wavefunctions were tested for appropriateness of the spin multiplicities using the *Stable* keyword in Gaussian. Optimizations for **6** involved fixing the Ni-N_{MeCN} bond length to that found in the crystal structure and optimizing the positions of all other atoms.

Table S1. Optimized Cartesian Coordinates for triplet [(terpyridine)Ni(CF₃)₂] **7**.

Row	atom	X	Y	Z
1	Ni	3.4705133	3.4060904	-1.9565180
2	F	1.1709412	2.1667599	-0.8813583
3	F	0.7991948	3.0739049	-2.8255338
4	F	3.6227654	3.0267495	-4.8044874
5	F	4.9654688	4.5625469	-4.0299175
6	F	2.8493971	4.9969929	-4.3213703
7	F	1.8595045	1.1759962	-2.6971722
8	N	3.9494574	3.1608441	0.0052643
9	N	2.5398788	5.0944997	-1.0157388
10	N	4.7868529	1.7012192	-1.9770477
11	C	4.6836377	2.0946687	0.3766433
12	C	1.9475067	6.0608434	1.0999846
13	C	3.5755964	3.7522016	2.2855396
14	C	1.2080820	7.0465238	0.4508880
15	C	2.6018195	5.0889490	0.3362594
16	C	5.1927624	1.2847845	-0.7555445
17	C	4.3402359	2.6578370	2.6864823

18	C	3.7019986	4.0203472	-3.8419522
19	C	1.8237003	6.0399593	-1.6371691
20	C	4.9023493	1.8144631	1.7284997
21	C	5.1647246	1.0167428	-3.0636653
22	C	1.1411472	7.0368288	-0.9418897
23	C	6.0147200	0.1636066	-0.6024401
24	C	5.9770057	-0.1136847	-2.9885553
25	C	6.4112557	-0.5432241	-1.7352378
26	C	1.7602060	2.4105918	-2.1112041
27	C	3.3935619	3.9801230	0.9179073
28	H	2.0083113	6.0493416	2.1826098
29	H	3.1306066	4.4069883	3.0258017
30	H	0.6911676	7.8085829	1.0268332
31	H	4.4933421	2.4590704	3.7428559
32	H	1.8168143	5.9788654	-2.7187484
33	H	5.4899226	0.9564188	2.0339808
34	H	4.7962704	1.4028642	-4.0069140
35	H	0.5720611	7.7831004	-1.4862149
36	H	6.3410916	-0.1551575	0.3813565
37	H	6.2576438	-0.6391941	-3.8952890
38	H	7.0486148	-1.4172243	-1.6375251

Table S2. Optimized Cartesian Coordinates for doublet [(terpyridine)Ni(CF₃)₂]⁺.

Row	atom	X	Y	Z
1	Ni	3.3957751	3.3399113	-1.9038114
2	F	0.8967977	2.8212616	-1.0318246
3	F	1.1214458	2.0123589	-3.0341298
4	F	3.2737281	2.7237520	-4.6204201
5	F	4.2165277	4.5727729	-3.9275802
6	F	2.0389778	4.4212196	-4.0835144
7	F	2.1042785	1.0356582	-1.3668280
8	N	3.7859809	3.0516990	-0.0126006
9	N	2.6827958	5.1440728	-1.0707970
10	N	4.8815610	1.8475844	-2.0313323
11	C	4.5400534	1.9952115	0.3353843
12	C	1.9615509	6.0682640	1.0280260
13	C	3.4171322	3.6445407	2.2551304
14	C	1.4262053	7.1745897	0.3668356
15	C	2.5931111	5.0727538	0.2853652
16	C	5.1416368	1.2877550	-0.8180124
17	C	4.1503561	2.5228205	2.6436514
18	C	3.1448777	3.7359350	-3.7458450
19	C	2.1735288	6.2129153	-1.6987161
20	C	4.7370867	1.6951190	1.6856567
21	C	5.4385339	1.3103804	-3.1258336
22	C	1.5437582	7.2547278	-1.0171919

23	C	5.9515625	0.1607417	-0.6937456
24	C	6.2732677	0.1937542	-3.0728942
25	C	6.5247404	-0.3957433	-1.8380358
26	C	1.7699983	2.2408968	-1.8883843
27	C	3.2565651	3.8951043	0.8899364
28	H	1.8849893	5.9876843	2.1062388
29	H	2.9960631	4.3075842	3.0012861
30	H	0.9301475	7.9592746	0.9292696
31	H	4.2854634	2.3061313	3.6985905
32	H	2.2679572	6.2283947	-2.7763194
33	H	5.3392365	0.8478128	1.9907978
34	H	5.2016156	1.7859853	-4.0682422
35	H	1.1531390	8.1004662	-1.5722009
36	H	6.1367540	-0.2812617	0.2784597
37	H	6.7043103	-0.1979819	-3.9875821
38	H	7.1586315	-1.2733157	-1.7593763

Table S3. Optimized Cartesian Coordinates for triplet [(6,6'-dmbpy)Ni(CF₃)₂(MeCN)] (**6**).

Row	Symbol	X	Y	Z
1	Ni	-0.0020425	1.7436133	6.2520961
2	F	2.7355589	2.5981076	5.7144063
3	F	2.2722552	2.6479635	7.8332583
4	F	1.4768541	4.1937826	6.5138898
5	F	-0.9968509	3.3230831	4.1813745
6	F	0.9638790	2.6128836	3.5452886

7	F	-0.7661629	1.3054679	3.3779631
8	N	-1.8240274	1.1120458	6.0397404
9	N	-0.3137973	1.6300364	8.3787126
10	N	0.8993806	-0.0971883	6.7187191
11	C	1.6957493	2.8238285	6.5827365
12	C	-0.1389338	2.2271545	4.2430546
13	C	-2.7466343	0.9770824	5.3479365
14	C	-3.7820586	0.8771586	4.3302534
15	C	-1.2987642	3.8479694	8.4034501
16	C	-0.8383829	2.6125375	9.1288164
17	C	-0.9296356	2.4800019	10.5183989
18	C	-0.4527354	1.3187060	11.1207224
19	C	0.1064412	0.3188986	10.3314340
20	C	0.1609654	0.5063974	8.9442635
21	C	0.7814566	-0.4759409	8.0158256
22	C	1.2665479	-1.7095798	8.4615808
23	C	1.9101583	-2.5497000	7.5598009
24	C	2.0717995	-2.1281386	6.2458188
25	C	1.5596274	-0.8871296	5.8450911
26	C	1.7520561	-0.3916253	4.4414872
27	H	0.5035889	-0.5758954	10.7947735
28	H	-0.5055347	1.1960952	12.1988002
29	H	-1.3617419	3.2806213	11.1099347
30	H	-2.0781948	3.5992123	7.6737216
31	H	-0.4618294	4.2906498	7.8522351

32	H	-1.6991394	4.5919584	9.0975633
33	H	1.1481746	-2.0114818	9.4947436
34	H	2.2922384	-3.5135064	7.8840023
35	H	2.5922215	-2.7451496	5.5209648
36	H	2.1886637	0.6101197	4.4561218
37	H	0.7984611	-0.3117196	3.9120394
38	H	2.4090605	-1.0658401	3.8847018
39	H	-3.3294099	1.1821083	3.3794332
40	H	-4.6221989	1.5372890	4.5656700
41	H	-4.1474311	-0.1509644	4.2480695

Table S4. Optimized Cartesian Coordinates for doublet [(terpyridine)Ni(CF₃)₂]⁻.

Row	Symbol	X	Y	Z
1	Ni	3.3283446	3.2781623	-1.8445719
2	F	0.7754118	2.6696415	-0.8449805
3	F	0.9568797	1.9561542	-2.8857226
4	F	3.1343457	2.5984683	-4.5566759
5	F	4.1155529	4.4893795	-4.1084186
6	F	1.9450220	4.3385255	-4.0369582
7	F	1.9577693	0.8938705	-1.2820886
8	N	3.7265032	3.0093090	-0.0031563
9	N	2.8455863	5.1336731	-1.0926667
10	N	4.9412212	2.0088821	-2.0042959
11	C	4.5187793	1.9665247	0.3378629
12	C	1.9421158	6.0581507	0.9710785

13	C	3.3912139	3.6250917	2.2932072
14	C	1.4765713	7.1655633	0.2910238
15	C	2.6397492	5.0423715	0.2779876
16	C	5.1322936	1.3411967	-0.8005365
17	C	4.1210647	2.4966088	2.6655934
18	C	3.0828384	3.6564779	-3.6839521
19	C	2.3662326	6.2152150	-1.7317446
20	C	4.7131904	1.6603214	1.7208061
21	C	5.5271078	1.5055755	-3.1047949
22	C	1.7000610	7.2560232	-1.1001607
23	C	5.9182334	0.1666279	-0.7458818
24	C	6.3309921	0.3741880	-3.1061893
25	C	6.5218350	-0.3162974	-1.8892473
26	C	1.6927830	2.1670072	-1.7472908
27	C	3.2264521	3.8857662	0.8977996
28	H	1.7675975	5.9487218	2.0375138
29	H	2.9819183	4.2999118	3.0366357
30	H	0.9397497	7.9507590	0.8188439
31	H	4.2579407	2.2800862	3.7243830
32	H	2.5422026	6.2341100	-2.8009593
33	H	5.3238754	0.8165604	2.0220590
34	H	5.3376385	2.0547626	-4.0197579
35	H	1.3663751	8.1145609	-1.6751547
36	H	6.0293438	-0.3535268	0.2011368
37	H	6.7970785	0.0410722	-4.0285732

38 H 7.1282811 -1.2186563 -1.8527451

Table S5. Calculated energies of nickel complexes at different spin states. The lowest energy state is in boldface.

<i>Complex</i>	<i>Total Energy (Hartrees)</i>	
(tpy)Ni(CF₃)₂	singlet: -2925.87160474	triplet: -2925.87188471
(6,6'-dmbpy)Ni(CF₃)₂(MeCN)	singlet: -2890.17735698	triplet: -2890.15191484
[(tpy)Ni(CF₃)₂]⁺	doublet: -2925.67871718	quartet: -2925.57684330

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Electrochemistry and EPR data:

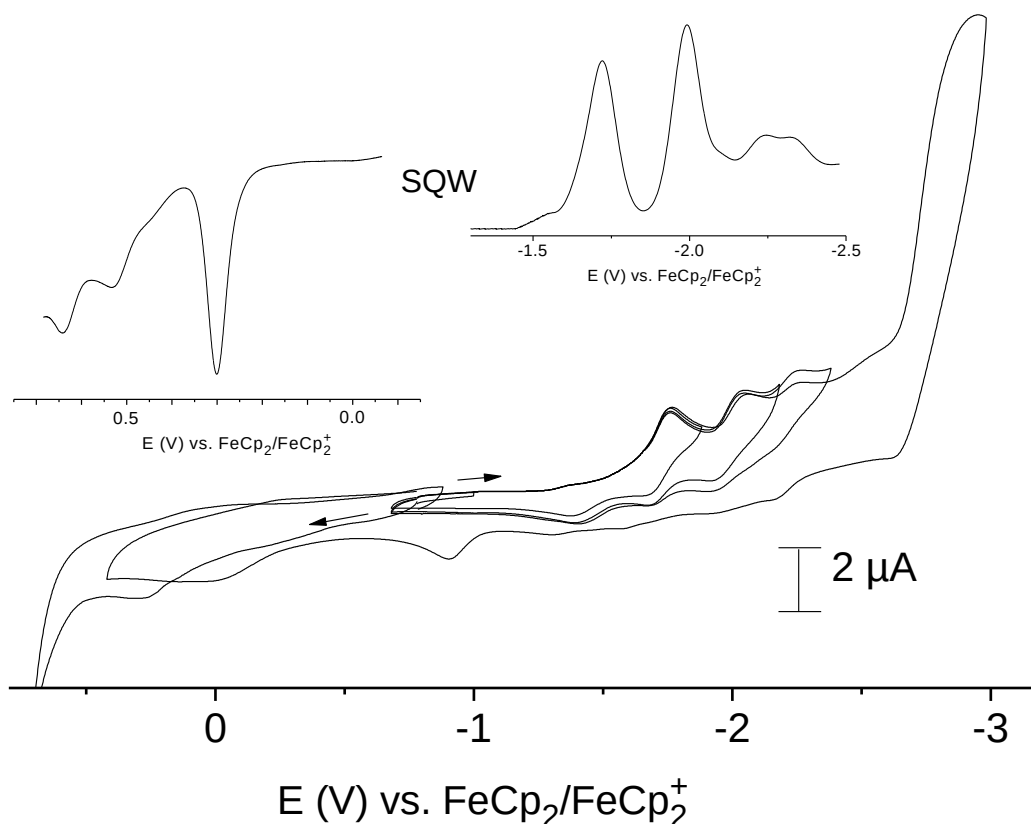


Figure S1, Cyclic voltammograms and square wave voltammograms (SQW; inserts on top) of **8** in THF/ $n\text{Bu}_4\text{NPF}_6$ at 298 K.

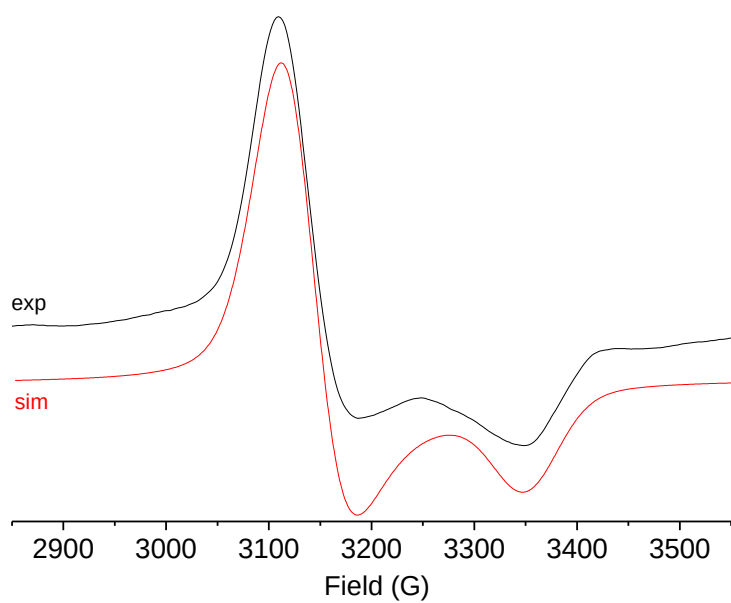
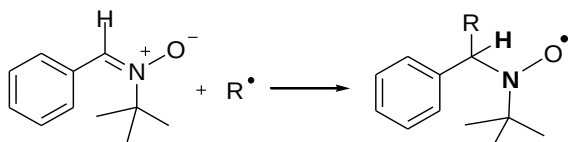


Figure S2 EPR spectrum of the partially oxidized complex **8 (powder, 298 K) with simulation in red (parameters: $g_{\perp} = 2.154$ and $g_{\parallel} = 2.010$, line widths: 50, 50 and 55 G).**

Spin trap experiment:



Scheme S1. Reaction of the spin trap PBN with a radical. Nuclei in bold represent possible coupling partners with the unpaired electron. Note that nuclei of the R group might possibly also couple.

The spectrum of the CF₃-PBN spin trap in the paper (Fig. 4) was recorded only in one of several experiments. In all other experiments we observed the major signal for the CF₃-PBN spin trap alongside an additional minor three-line signal. Since other possibilities have been ruled out by blank experiments, the second signal might be attributed to a nickel- containing by-product and is thus worth mentioning.

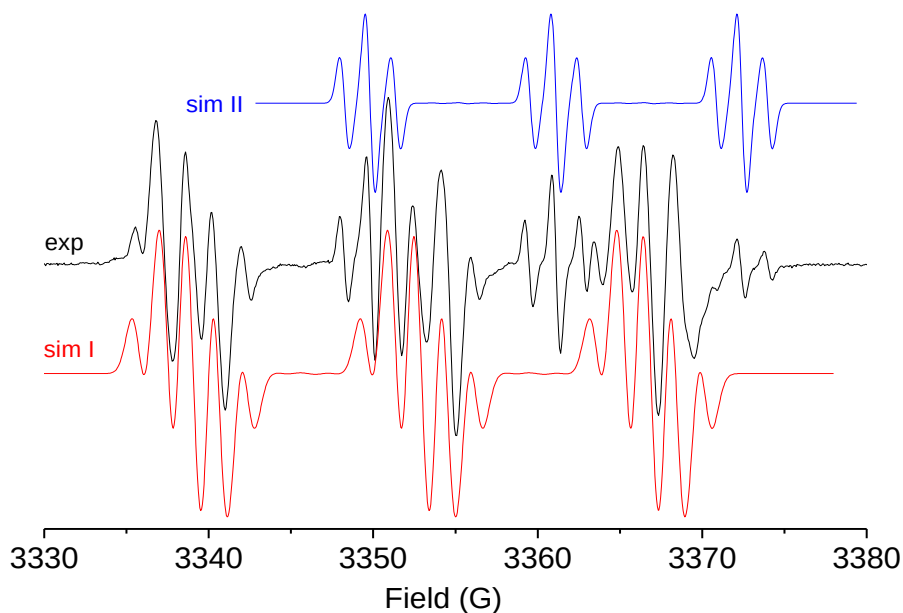


Figure S3. X-band EPR spectrum obtained during anodic electrolysis of **8** in THF/*n*Bu₄NPF₆ at 298 K in the presence of PBN. The black line represents the experimental spectrum (exp) the red line (bottom, sim I) represents the expected CF₃-PBN spin trap, simulated with the parameters $a_N = 14.1$ G, $a_H = 1.17$ G and $a_F(\text{CF}_3) = 1.77$ G. The spectrum in blue (sim II) is simulated using $a_N = 11.3$ G, $a_H = 1.51$ G and $a_X = 1.6$ G (1 X = nucleus with $I = \frac{1}{2}$).

In the above spectrum we can unequivocally assign one set of signals to the trapped •CF₃ radical (CF₃-PBN) (compare Fig. 4 in the paper). The other species remains unclear although a reasonable simulation could be achieved. Following the corresponding simulation parameters, the species is also a PBN radical ($a_N + a_H\beta$

couplings). The a_X coupling is rather small, thus the possibility that $F = X$ can be discarded. The F-PBN is reported with an a_F of 34 G (Gille 1994), the here found $X = 1.6$ G might either represent a CFR_2 group with a F atom in γ position or an unknown nickel derivative.

Gille, L.; Stoesser, R. *J. Fluor. Chem.* **1994**, 69, 191–194.

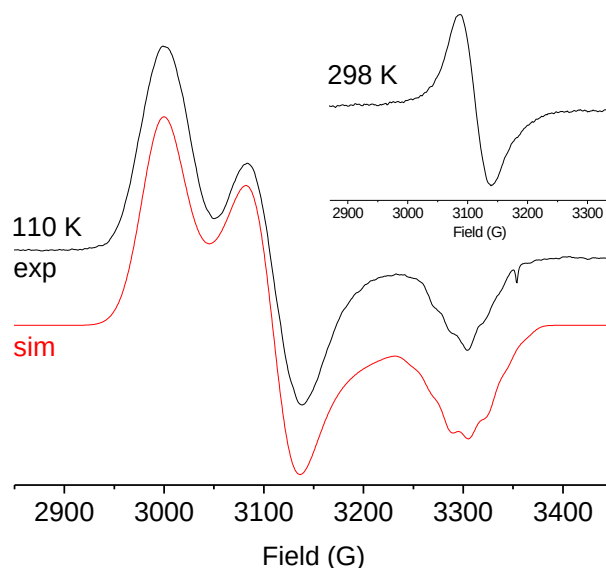


Figure S4. EPR spectra of complex **8** in THF/ nBu_4NPF_6 under reductive electrolysis at 298 K and 110 K, with simulation in red (parameters: $g_1 = 2.242$, $g_2 = 2.162$, $g_3 = 2.035$, $a_3(N) = 18.5$ G; Lorentzian line width = 42, 40, 17 G)

Table S6: EPR data of known nickel complexes

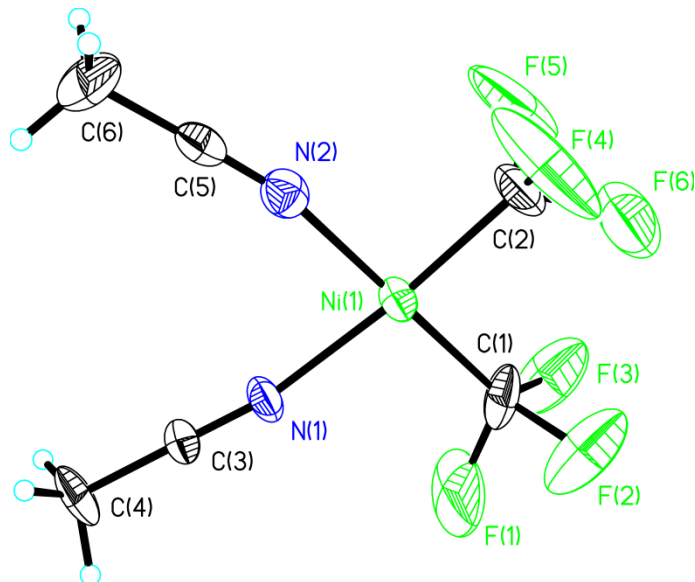
Complex	g_{iso} or av.	g_3	g_2	g_1	Δg	ref.
$[(tBu_3terpy)Ni(CF_3)_2]^{++}$	2.107	2.154	2.154	2.013	0.141	this work
$[(BOXAM)Ni(CH_3)]^{++}$	2.085	2.119	2.081	2.0252	0.094	1
$[(BOXAM)Ni(CF_3)]^{++}$	2.077	2.115	2.087	2.028	0.087	1
$[(BOXAM)NiCl]^{++}$	2.075	2.105	2.086	2.034	0.071	1
$[Ni(TMPP-O)_2]^{++}$	2.20	2.28	2.28	2.04	0.24	2
$[Ni(L^1)]^-$	2.173	2.255	2.255	2.008	0.247	3
$[Ni(L^2)]^-$	2.221	2.366	2.303	1.994	0.372	4
$[Ni(emi)]^-$	2.223	2.44	2.27	1.96	0.48	5
$[(NCN)NiCl_2]$	2.196	2.369	2.195	2.024	0.345	6
$[(PPh_3)_2Ni(Fmes)Br]^{++}$	2.435	2.825	2.453	1.947	0.878	7
$[Ni(C_6Cl_5)_4]^-$	2.533	2.84	2.84	1.92	0.92	8

^a g_{av} = averaged g value = $(g_1 + g_2 + g_3)/3$; $\Delta g = g$ anisotropy = $g_1 - g_3$. TMPP-O is the monodemethylated form of tris(2,4,6-trimethoxyphenyl)phosphine (TMPP); H_4L^1 = N -[2-(oxalylamino)phenyl]oxalamic acid; NCN = $C_6H_3(CH_2NMe_2)_{2-o,o'}$; H_4L^2 = 6,6-diethyl-3,9,9,12,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane-2,5,7,10,13-pentaone; H_4emi = N,N -ethylenebis(2-mercaptoisobutyramide); Fmes = 2,4,6-trifluoromethyl-phenyl.

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Details of X-ray Crystallography



Data Collection for Complex 1

A yellow prism crystal of $\text{C}_6\text{H}_6\text{F}_6\text{N}_2\text{Ni}$ having approximate dimensions of 0.25 x 0.20 x 0.08 mm was mounted on a glass fiber. All measurements were made on a Rigaku Mercury70 CCD diffractometer using graphite monochromated Mo-K α radiation.

The crystal-to-detector distance was 51.66 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

$$\begin{aligned} a &= 8.200(16) \text{ \AA} \\ b &= 17.10(3) \text{ \AA} \quad \beta = 90.0000^\circ \\ c &= 21.72(4) \text{ \AA} \\ V &= 3046(10) \text{ \AA}^3 \end{aligned}$$

For $Z = 12$ and F.W. = 278.82, the calculated density is 1.824 g/cm³. The reflection conditions of:

$$\begin{aligned} h0l: h+l &= 2n \\ 0k0: k &= 2n \end{aligned}$$

uniquely determine the space group to be:

$$P2_1/n \text{ (\#14)}$$

The data were collected at a temperature of $-100 \pm 1^\circ\text{C}$ to a maximum 2θ value of 54.4° . A total of 540 oscillation images were collected. A sweep of data was done using ω scans from -120.0 to 60.0° in 1.0° step, at $\chi=54.0^\circ$ and $\phi = 0.0^\circ$. The exposure rate was 25.0 [sec./ $^\circ$]. The detector swing angle was -30.07° . A second sweep was performed using ω scans from -120.0 to 60.0° in 1.0° step, at $\chi=54.0^\circ$ and $\phi = 120.0^\circ$. The exposure rate was 25.0 [sec./ $^\circ$]. The detector swing angle was -30.07° . Another sweep was performed using ω scans from -120.0 to 60.0° in 1.0° step, at $\chi=54.0^\circ$ and $\phi = 240.0^\circ$. The exposure rate was 25.0 [sec./ $^\circ$]. The detector swing angle was -30.07° . The crystal-to-detector distance was 51.66 mm. Readout was performed in the 0.137 mm pixel mode.

Data Reduction

Of the 24817 reflections that were collected, 6675 were unique ($R_{\text{int}} = 0.1463$); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku).

The linear absorption coefficient, μ , for Mo-K α radiation is 19.668 cm^{-1} . An empirical absorption correction was applied which resulted in transmission factors ranging from 0.631 to 0.854 . The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods² and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement³ on F^2 was based on 6675 observed reflections and 412 variable parameters and converged (largest parameter shift was 0.09 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.1253$$

$$wR2 = [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2} = 0.4213$$

The standard deviation of an observation of unit weight⁴ was 1.05 . Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.78 and $-1.00\text{ e}^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁵. Anomalous dispersion effects were included in F_{calc} ⁶; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁷. The values for the mass attenuation coefficients are those of Creagh and Hubbell⁸. All calculations were performed using the CrystalStructure⁹ crystallographic software package except for refinement, which

was performed using SHELXL-97¹⁰.

References

(1) CrystalClear: Rigaku Corporation, 1999. CrystalClear Software User's Guide, Molecular Structure Corporation, (c) 2000. J.W. Pflugrath (1999) Acta Cryst. D55, 1718-1725.

(2) SHELX97: Sheldrick, G.M. (1997).

(3) Least Squares function minimized: (SHELXL97)

$$\sum w(F_o^2 - F_c^2)^2 \quad \text{where } w = \text{Least Squares weights.}$$

(4) Standard deviation of an observation of unit weight:

$$[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations
 N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J. ; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku and Rigaku Americas (2000-2010). 9009 New Trails Dr. The Woodlands TX 77381 USA.

(10) SHELX97: Sheldrick, G.M. (1997).

EXPERIMENTAL DETAILS for 1

Table S7. Crystal Data

Empirical Formula	C ₆ H ₆ F ₆ N ₂ Ni
Formula Weight	278.82
Crystal Color, Habit	yellow, prism
Crystal Dimensions	0.25 X 0.20 X 0.08 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 8.200(16) Å b = 17.10(3) Å c = 21.72(4) Å β = 90.0000 ° V = 3046(10) Å ³
Space Group	P2 ₁ /n (#14)
Z value	12
D _{calc}	1.824 g/cm ³
F ₀₀₀	1656.00
μ(MoKα)	19.668 cm ⁻¹

Table S8. Intensity Measurements for 1

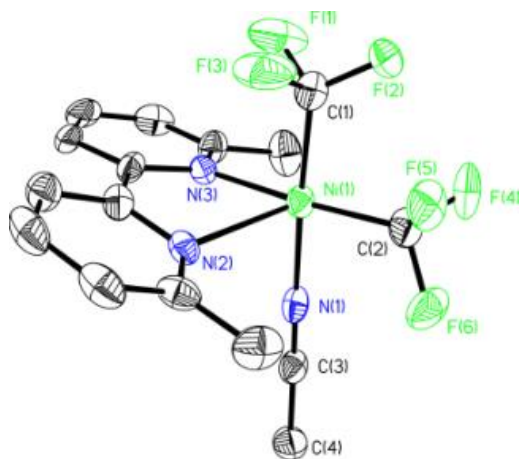
Diffractometer	Rigaku Mercury70 CCD
Radiation	MoK α (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	-100.0°C
Detector Aperture	70 x 70 mm
Data Images	540 exposures
ω oscillation Range (χ =54.0, ϕ =0.0)	-120.0 - 60.0°
Exposure Rate	25.0 sec./°
Detector Swing Angle	-30.07°
ω oscillation Range (χ =54.0, ϕ =120.0)	-120.0 - 60.0°
Exposure Rate	25.0 sec./°
Detector Swing Angle	-30.07°
ω oscillation Range (χ =54.0, ϕ =240.0)	-120.0 - 60.0°
Exposure Rate	25.0 sec./°
Detector Swing Angle	-30.07°
Detector Position	51.66 mm
Pixel Size	0.137 mm
$2\theta_{\max}$	54.4°
No. of Reflections Measured	Total: 24817 Unique: 6675 (R_{int} = 0.1463)

Corrections

Lorentz-polarization
Absorption
(trans. factors: 0.631 - 0.854)

Table S9. Structure Solution and Refinement for 1

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.2000 \cdot P)^2 + 0.0000 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	54.4 $^\circ$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	6675
No. Variables	412
Reflection/Parameter Ratio	16.20
Residuals: R1 ($I > 2.00\sigma(I)$)	0.1253
Residuals: R (All reflections)	0.2542
Residuals: wR2 (All reflections)	0.4213
Goodness of Fit Indicator	1.048
Max Shift/Error in Final Cycle	0.092
Maximum peak in Final Diff. Map	1.78 e $^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	-1.00 e $^-/\text{\AA}^3$



Data Collection for Complex 6

A colorless prism crystal of $C_{18}H_{15}F_6N_2Ni$ having approximate dimensions of 0.01 x 0.05 x 0.05 mm was mounted on a glass fiber. All measurements were made on a Rigaku Mercury275R CCD (SCX mini) diffractometer Mo- $K\alpha$ radiation. Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

$$\begin{aligned} a &= 8.015(8) \text{ \AA} \\ b &= 13.092(13) \text{ \AA} \quad \beta = 99.448(15)^\circ \\ c &= 19.236(19) \text{ \AA} \\ V &= 1991(3) \text{ \AA}^3 \end{aligned}$$

For $Z = 4$ and F.W. = 432.02, the calculated density is 1.441 g/cm³. The reflection conditions of:

$$\begin{aligned} h0l: l &= 2n \\ 0k0: k &= 2n \end{aligned}$$

uniquely determine the space group to be:

$$P2_1/c \text{ (\#14)}$$

The data were collected at a temperature of $0 \pm 1^\circ\text{C}$ to a maximum 2θ value of 54.9° . A total of 0 oscillation images were collected. The crystal-to-detector distance was 0.00 mm. Readout was performed in the 0.000 mm pixel mode.

Data Reduction

Of the 6816 reflections that were collected, 3980 were unique ($R_{\text{int}} = 0.1195$); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku). The linear absorption coefficient, μ , for Mo- $K\alpha$ radiation is 10.315 cm⁻¹. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.522 to 0.814. The data were corrected for

Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods² and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement³ on F^2 was based on 3980 observed reflections and 238 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.1175$$

$$wR2 = [\sum (w (F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2} = 0.3979$$

The standard deviation of an observation of unit weight⁴ was 1.08. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.10 and -0.53 $e^-/\text{\AA}^3$, respectively. Neutral atom scattering factors were taken from Cromer and Waber⁵. Anomalous dispersion effects were included in F_{calc} ⁶; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁷. The values for the mass attenuation coefficients are those of Creagh and Hubbell⁸. All calculations were performed using the CrystalStructure⁹ crystallographic software package except for refinement, which was performed using SHELXL-97¹⁰.

References

(1) CrystalClear: Rigaku Corporation, 1999. CrystalClear Software User's Guide, Molecular Structure Corporation, (c) 2000.J.W.Pflugrath (1999) Acta Cryst. D55, 1718-1725.

(2) SHELX97: Sheldrick, G.M. (1997).

(3) Least Squares function minimized: (SHELXL97)

$$\sum w(F_o^2 - F_c^2)^2 \quad \text{where } w = \text{Least Squares weights.}$$

(4) Standard deviation of an observation of unit weight:

$$[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations
 N_v = number of variables

- (5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).
- (6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).
- (7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
- (8) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).
- (9) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku and Rigaku Americas (2000-2010). 9009 New Trails Dr. The Woodlands TX 77381 USA.
- (10) SHELX97: Sheldrick, G.M. (1997).

EXPERIMENTAL DETAILS for 6

Table S10. Crystal Data

Empirical Formula	C ₁₈ H ₁₅ F ₆ N ₂ Ni
Formula Weight	432.02
Crystal Color, Habit	orange, prism
Crystal Dimensions	0.01 X 0.05 X 0.05 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 8.015(8) Å b = 13.092(13) Å c = 19.236(19) Å β = 99.448(15) ° V = 1991(3) Å ³
Space Group	P2 ₁ /c (#14)
Z value	4
D _{calc}	1.441 g/cm ³
F ₀₀₀	876.00
μ(MoKα)	10.315 cm ⁻¹

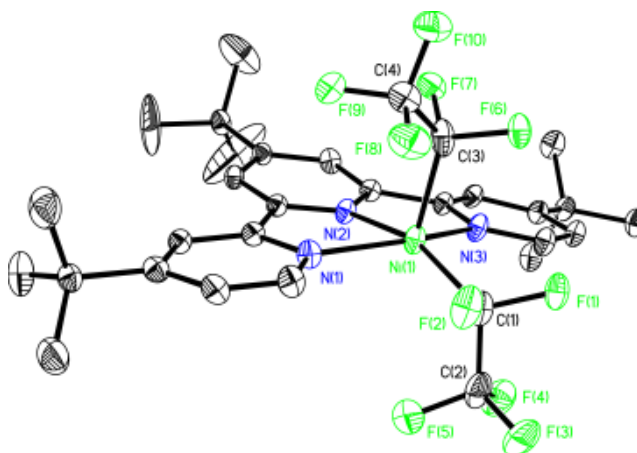
Table S11. Intensity Measurements for 6

Diffractometer	Rigaku Mercury275R CCD (SCX mini)
Radiation	MoK α (λ = 0.71075 Å)
Voltage, Current	50kV, 40mA
Temperature	-80 °C
Detector Aperture	75 mm (diameter)
Pixel Size	0.073 mm
$2\theta_{\text{max}}$	54.9°
No. of Reflections Measured	Total: 6816 Unique: 3980 (R_{int} = 0.1195)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.522 - 0.814)

Table S12. Structure Solution and Refinement for 6

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.2000 \cdot P)^2 + 0.0000 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	54.90
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	3980
No. Variables	238
Reflection/Parameter Ratio	16.72
Residuals: R1 ($I > 2.00\sigma(I)$)	0.1175
Residuals: R (All reflections)	0.2384
Residuals: wR2 (All reflections)	0.3979
Goodness of Fit Indicator	1.084
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	2.10 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.53 e ⁻ /Å ³

Data collection for 9•(toluene)₂.



A brown specimen of C₃₈H₃₅F₁₀N₃Ni, approximate dimensions 0.100 mm x 0.170 mm x 0.240 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table S13: Data collection details for 9•(toluene)₂.

Axis	dx/mm	2 θ /°	ω /°	ϕ /°	χ /°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temp/K
Omega	59.931	-28.00	-28.00	0.00	54.74	0.50	250	20.00	0.71073	50	30.0	99.95
Omega	59.931	-28.00	-28.00	90.00	54.74	0.50	250	20.00	0.71073	50	30.0	99.95
Omega	59.931	-28.00	-28.00	180.00	54.74	0.50	250	20.00	0.71073	50	30.0	99.95
Omega	59.931	-28.00	-28.00	270.00	54.74	0.50	250	20.00	0.71073	50	30.0	99.95
Omega	59.931	28.00	28.00	0.00	54.74	0.50	250	20.00	0.71073	50	30.0	99.95

A total of 1250 frames were collected. The total exposure time was 6.94 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 34054 reflections to a maximum θ angle of 25.44° (0.83 Å resolution), of which 6747 were independent (average redundancy 5.047, completeness = 99.2%, R_{int} = 5.87%, R_{sig} = 4.52%) and 4979 (73.80%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.6079(3) Å, b = 19.1642(5) Å, c = 18.4101(5) Å, β = 101.288(2)°, volume = 3670.23(17) Å³, are based upon the refinement of the XYZ-centroids of 9061 reflections above 20 $\sigma(I)$ with 5.920° < 2θ < 50.74°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.845. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8673 and 0.9415.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, C₃₈H₃₅F₁₀N₃Ni. The final anisotropic full-matrix least-squares refinement on F^2 with 518 variables converged at R_1 = 7.06%, for the observed data and wR_2 = 19.07% for all data. The goodness-of-fit was 1.069. The largest peak in the final difference electron density synthesis was 1.521 e⁻/Å³ and the largest hole was -0.611 e⁻/Å³ with an RMS deviation of 0.101 e⁻/Å³. On the basis of the final model, the calculated density was 1.416 g/cm³ and $F(000)$, 1608 e⁻.

Table S14. Sample and crystal data for 9·(toluene)₂.

Chemical formula	C ₃₈ H ₃₅ F ₁₀ N ₃ Ni	
Formula weight	782.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.170 x 0.240 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 10.6079(3) Å	α = 90°
	b = 19.1642(5) Å	β = 101.288(2)°
	c = 18.4101(5) Å	γ = 90°
Volume	3670.23(17) Å ³	
Z	4	
Density (calculated)	1.416 g/cm ³	
Absorption coefficient	0.611 mm ⁻¹	
F(000)	1608	

Table S15. Data collection and structure refinement for 9·(toluene)₂.

Theta range for data collection	2.96 to 25.44°
Index ranges	-12 ≤ h ≤ 12, -22 ≤ k ≤ 23, -22 ≤ l ≤ 22
Reflections collected	34054
Independent reflections	6747 [R(int) = 0.0587]
Coverage of independent reflections	99.2%
Absorption correction	multi-scan
Max. and min. transmission	0.9415 and 0.8673
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	6747 / 16 / 518
Goodness-of-fit on F ²	1.069
Δ/σ _{max}	0.001
Final R indices	4979 data; I > 2σ(I) R1 = 0.0706, wR2 = 0.1707

Weighting scheme

Largest diff. peak and hole

R.M.S. deviation from mean

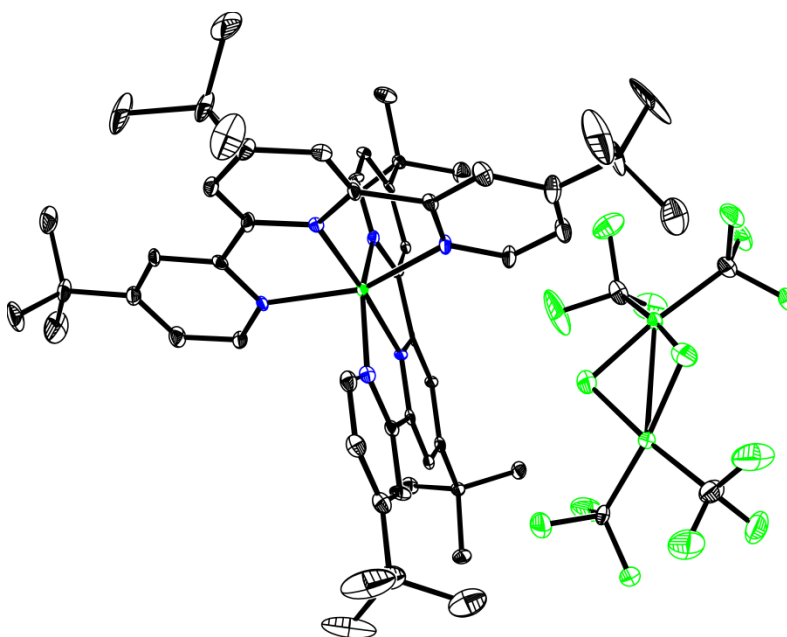
all data $R1 = 0.0994$, $wR2 = 0.1907$

$w=1/[\sigma^2(F_o^2)+(0.0804P)^2+12.7548P]$

where $P=(F_o^2+2F_c^2)/3$

1.521 and -0.611 $e\text{\AA}^{-3}$

0.101 $e\text{\AA}^{-3}$



Crystal Structure Report for Complex 10·THF·(MeCN)₂

A brown specimen of $C_{68}H_{87}F_{14}N_9Ni_3O$, approximate dimensions 0.130 mm x 0.200 mm x 0.420 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table S16: Data collection details for 10·THF·(MeCN)₂.

Axis	dx/mm	2 θ /°	ω /°	ϕ /°	χ /°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	60.007	-28.00	-28.00	0.00	54.74	0.50	250	25.00	0.71073	50	30.0	100.05
Omega	60.007	-28.00	-28.00	90.00	54.74	0.50	250	25.00	0.71073	50	30.0	100.05
Omega	60.007	-28.00	-28.00	180.00	54.74	0.50	250	25.00	0.71073	50	30.0	100.05
Omega	60.007	-28.00	-28.00	270.00	54.74	0.50	250	25.00	0.71073	50	30.0	100.05

Axis	dx/mm	2 θ /°	ω /°	ϕ /°	χ /°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	60.007	28.00	28.00	0.00	54.74	0.50	250	25.00	0.71073	50	30.0	100.05

A total of 1250 frames were collected. The total exposure time was 8.68 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 20790 reflections to a maximum θ angle of 29.24° (0.73 Å resolution), of which 13285 were independent (average redundancy 1.565, completeness = 68.0%, $R_{\text{int}} = 8.11\%$, $R_{\text{sig}} = 15.31\%$) and 6809 (51.25%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 25.819(3)$ Å, $b = 11.1285(12)$ Å, $c = 25.279(3)$ Å, $\beta = 98.476(3)^\circ$, volume = 7184.0(14) Å³, are based upon the refinement of the XYZ-centroids of 3735 reflections above $20\sigma(I)$ with $6.382^\circ < 2\theta < 52.63^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.827. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7136 and 0.8962.

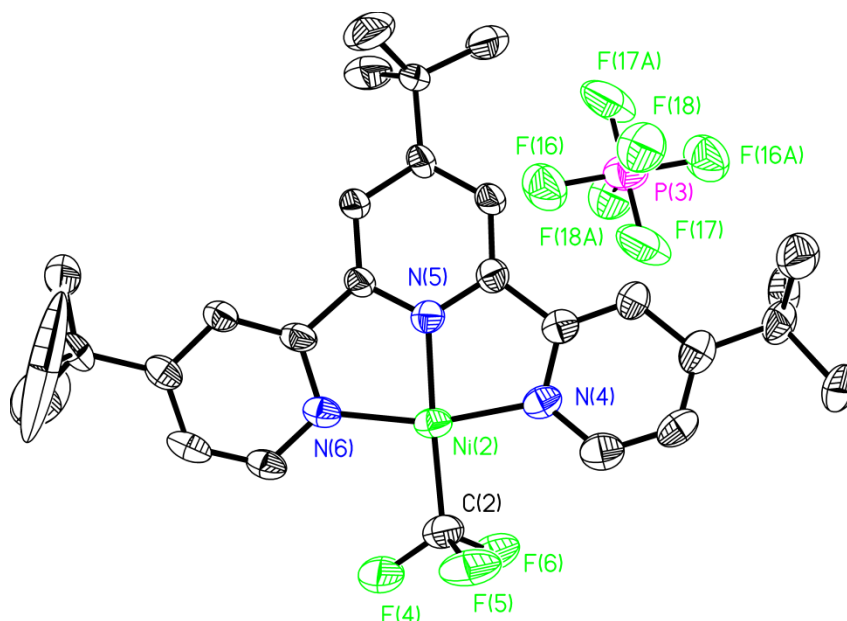
The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, C₆₈H₈₇F₁₄N₉Ni₃O. The final anisotropic full-matrix least-squares refinement on F² with 877 variables converged at R1 = 7.67%, for the observed data and wR2 = 21.35% for all data. The goodness-of-fit was 0.977. The largest peak in the final difference electron density synthesis was 1.187 e⁻/Å³ and the largest hole was -0.564 e⁻/Å³ with an RMS deviation of 0.101 e⁻/Å³. On the basis of the final model, the calculated density was 1.376 g/cm³ and F(000), 3104 e⁻.

Table S17. Sample and crystal data for 10·THF·(MeCN)₂.

Chemical formula	C ₆₈ H ₈₇ F ₁₄ N ₉ Ni ₃ O		
Formula weight	1488.60		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal size	0.130 x 0.200 x 0.420 mm		
Crystal system	monoclinic		
Space group	P 1 21/c 1		
Unit cell dimensions	a = 25.819(3) Å		
	b = 11.1285(12) Å		$\alpha = 90^\circ$
	c = 25.279(3) Å		$\beta = 98.476(3)^\circ$
	7184.0(14) Å ³		$\gamma = 90^\circ$
Volume			
Z	4		
Density (calculated)	1.376 g/cm ³		
Absorption coefficient	0.862 mm ⁻¹		
F(000)	3104		

Table S18. Data collection and structure refinement for 10·THF·(MeCN)₂

Theta range for data collection	3.01 to 29.24°
Index ranges	-12≤h≤35, -10≤k≤15, -33≤l≤17
Reflections collected	20790
Independent reflections	13285 [R(int) = 0.0811]
Coverage of independent reflections	68.0%
Absorption correction	multi-scan
Max. and min. transmission	0.8962 and 0.7136
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	13285 / 0 / 877
Goodness-of-fit on F ²	0.977
$\Delta/\sigma_{\max}$	0.004
Final R indices	6809 data; I>2σ(I) R1 = 0.0767, wR2 = 0.1765 all data R1 = 0.1635, wR2 = 0.2135
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1042P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.187 and -0.564 eÅ ⁻³
R.M.S. deviation from mean	0.101 eÅ ⁻³



Crystal Structure Report for Complex 14·THF

A specimen of $C_{30}H_{35}F_9N_3NiO_{0.50}P$, approximate dimensions 0.150 mm x 0.150 mm x 0.340 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table S19: Data collection details for Complex 14.

Axis	dx/mm	2 θ /°	ω /°	ϕ /°	χ /°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	59.942	-28.00	-28.00	0.00	54.74	0.50	250	30.00	0.71073	50	30.0	100.00
Omega	59.942	-28.00	-28.00	90.00	54.74	0.50	250	30.00	0.71073	50	30.0	100.00
Omega	59.942	-28.00	-28.00	180.00	54.74	0.50	250	30.00	0.71073	50	30.0	100.00
Omega	59.942	-28.00	-28.00	270.00	54.74	0.50	250	30.00	0.71073	50	30.0	100.00
Omega	59.942	28.00	28.00	0.00	54.74	0.50	250	30.00	0.71073	50	30.0	100.00

A total of 1250 frames were collected. The total exposure time was 10.42 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 16149 reflections to a maximum θ angle of 27.03° (0.78 Å resolution), of which 11666 were independent (average redundancy 1.384, completeness = 83.0%, R_{int} = 3.03%, R_{sig} = 7.04%) and 6901 (59.15%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 12.6900(12) Å, $\underline{b}$ = 15.1528(12) Å, $\underline{c}$ = 33.412(2)

$\text{\AA}$, $\beta = 93.893(2)^\circ$, volume = $6409.9(9) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9887 reflections above 2θ with $5.931^\circ < 2\theta < 52.79^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.869. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7883 and 0.8978.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P 1 21/c 1$, with $Z = 8$ for the formula unit, $\text{C}_{30}\text{H}_{35}\text{F}_9\text{N}_3\text{NiO}_{0.50}\text{P}$. The final anisotropic full-matrix least-squares refinement on F^2 with 798 variables converged at $R1 = 11.36\%$, for the observed data and $wR2 = 33.92\%$ for all data. The goodness-of-fit was 1.074. The largest peak in the final difference electron density synthesis was $1.493 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.998 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.117 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.464 g/cm^3 and $F(000)$, 2912 e^- .

Table S20. Sample and crystal data for Complex 14·THF.

Identification code	Complex 14·THF
Chemical formula	$\text{C}_{30}\text{H}_{35}\text{F}_9\text{N}_3\text{NiO}_{0.50}\text{P}$
Formula weight	706.29
Temperature	100(2) K

Wavelength	0.71073 Å	
Crystal size	0.150 x 0.150 x 0.340 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 12.6900(12) Å	$\alpha = 90^\circ$
	b = 15.1528(12) Å	$\beta = 93.893(2)^\circ$
	c = 33.412(2) Å	$\gamma = 90^\circ$
Volume	6409.9(9) Å ³	
Z	8	
Density (calculated)	1.464 g/cm ³	
Absorption coefficient	0.735 mm ⁻¹	
F(000)	2912	

Table S21. Data collection and structure refinement for Complex 14·THF.

Theta range for data collection	2.95 to 27.03°
Index ranges	-16<= <i>h</i> <=6, -19<= <i>k</i> <=5, -31<= <i>l</i> <=35
Reflections collected	16149
Independent reflections	11666 [R(int) = 0.0303]
Coverage of independent reflections	83.0%

Absorption correction	multi-scan
Max. and min. transmission	0.8978 and 0.7883
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	11666 / 0 / 798
Goodness-of-fit on F^2	1.074
$\Delta/\sigma_{\max}$	1.495
Final R indices	6901 data; $I > 2\sigma(I)$ R1 = 0.1136, wR2 = 0.3057 all data R1 = 0.1796, wR2 = 0.3392
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1771P)^2 + 16.7963P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	1.493 and -0.998 eÅ ⁻³
R.M.S. deviation from mean	0.117 eÅ ⁻³

Selected NMR Spectra:

Figure S5: ^1H NMR spectrum (23 °C, THF- d_8) of **8**. Solvent residual signals of deuterated solvent dominate spectrum.

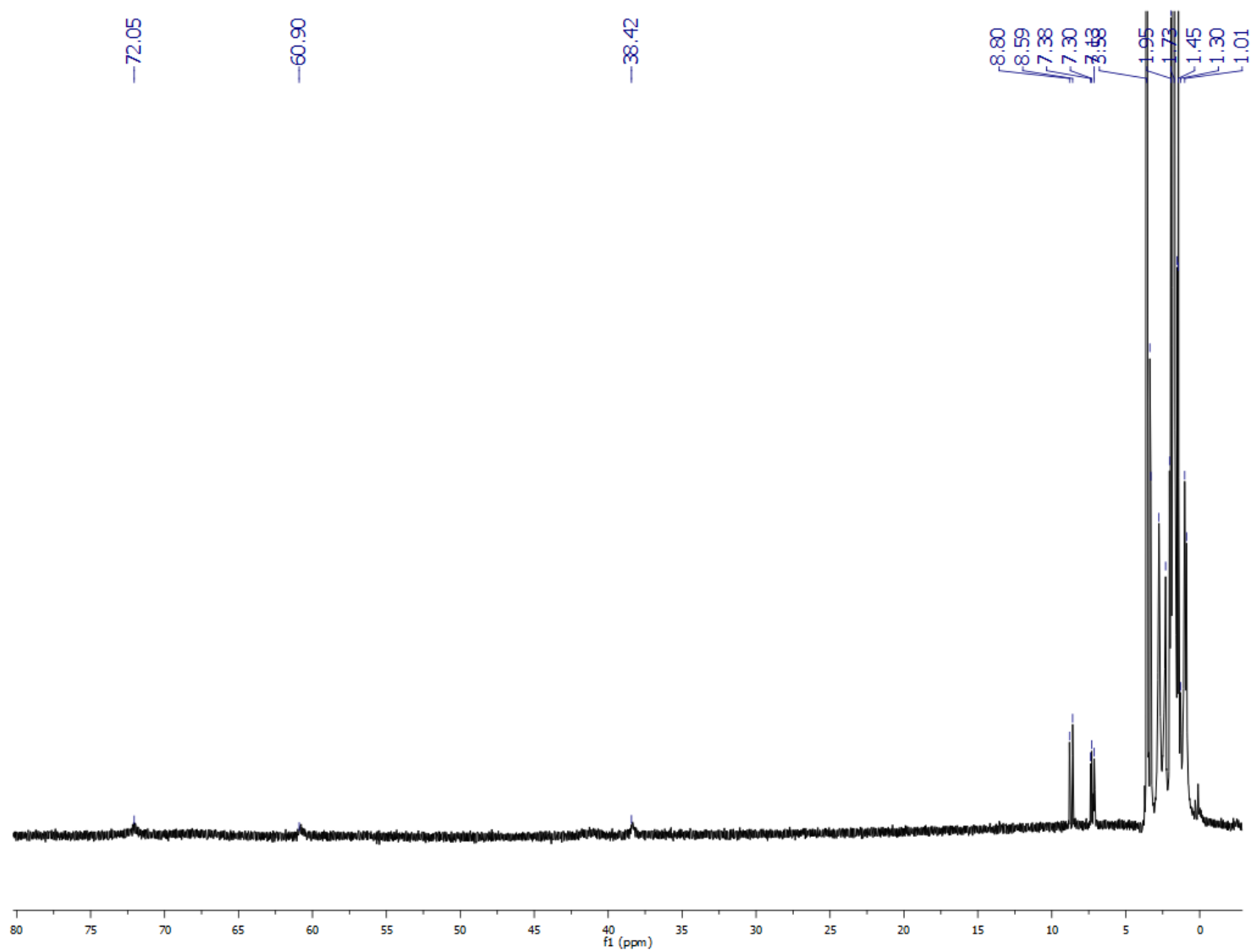


Figure S6: ^1H NMR spectrum (23 $^\circ\text{C}$, THF-d_8) of **8** (magnified view of Evans NMR experiment).

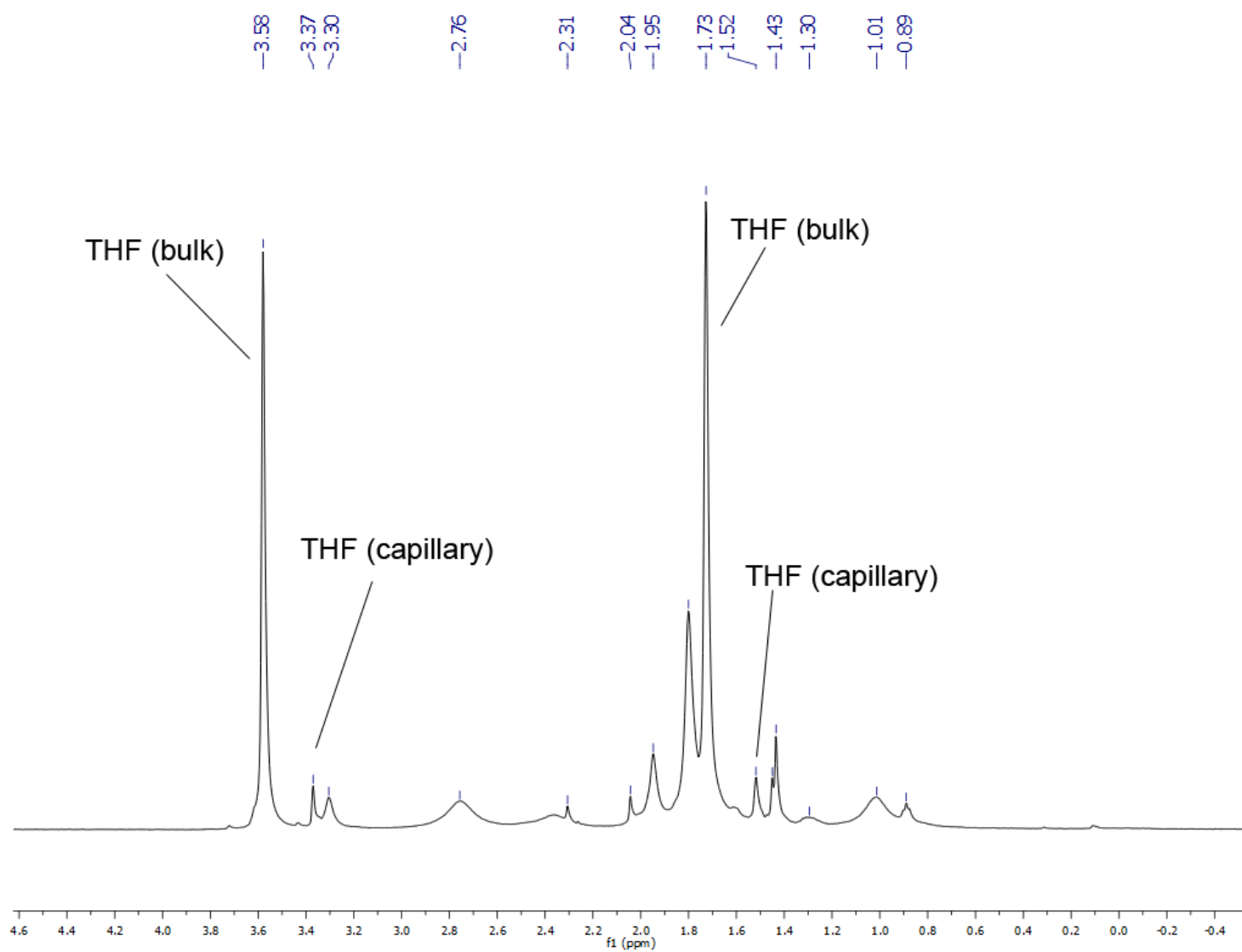


Figure S7: ^1H NMR spectrum (23 °C, toluene- d_8) of **9**.

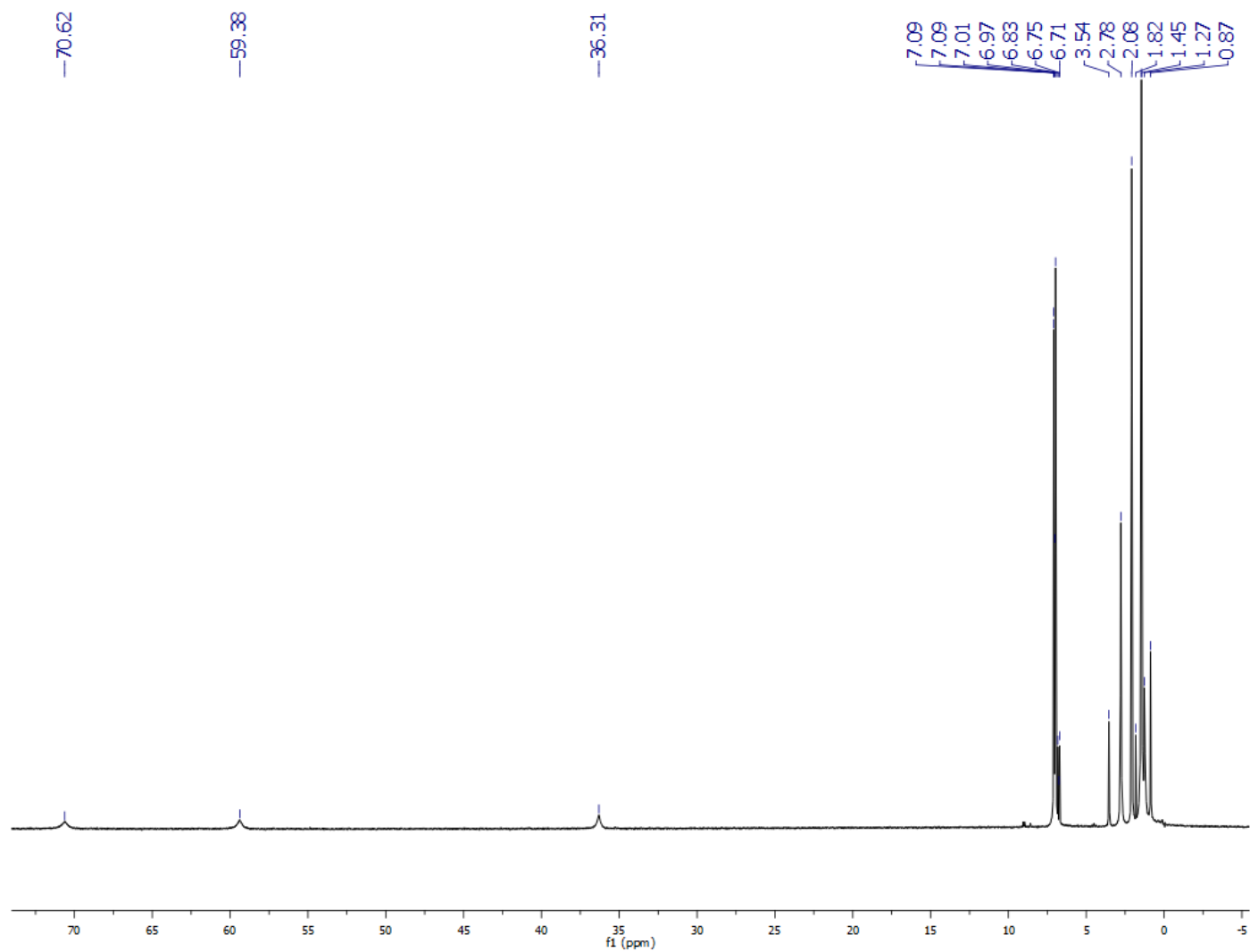


Figure S8: ^1H NMR spectrum (23 °C, toluene- d_8) of **9** (magnified view of Evans NMR experiment).

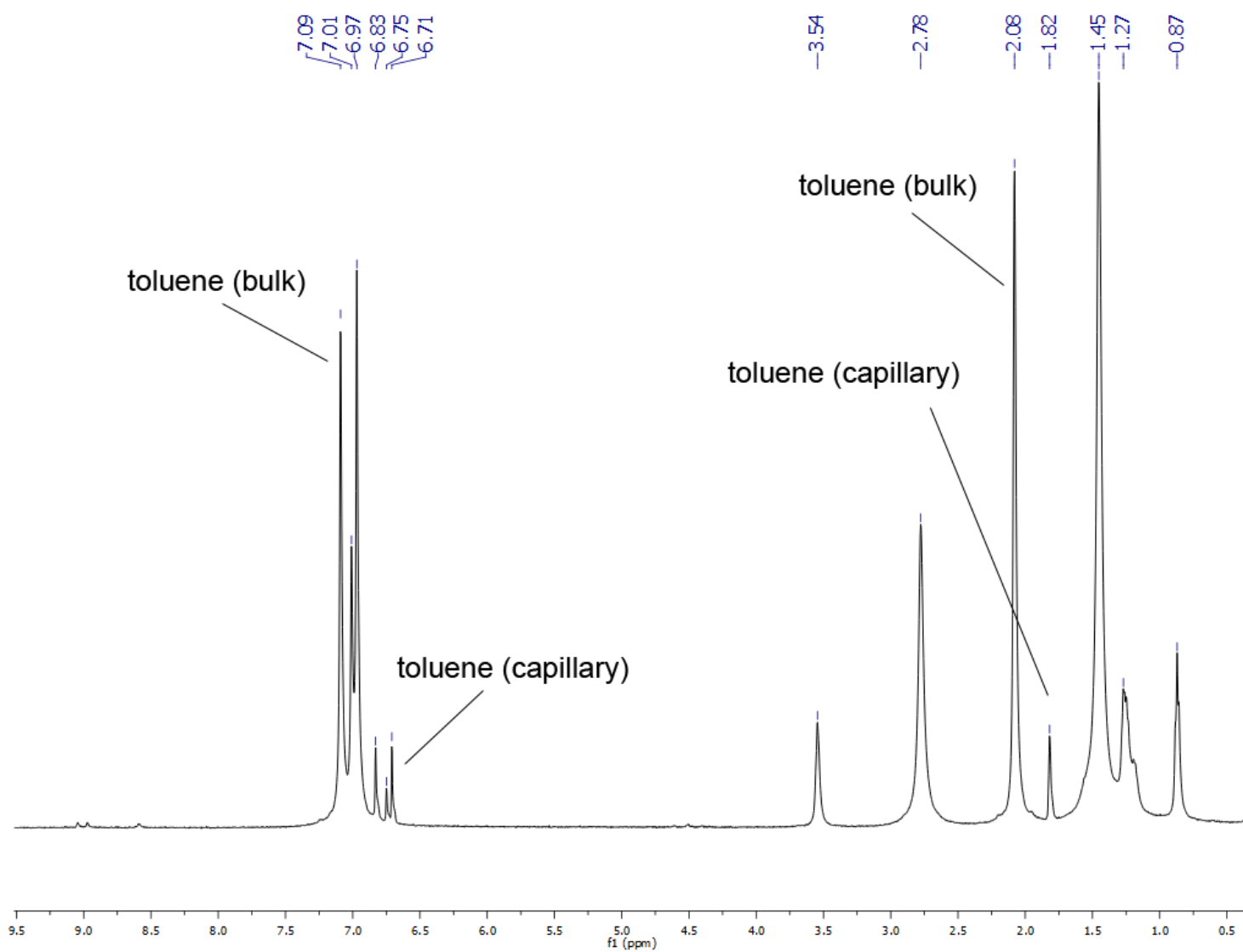


Figure S9. ^1H NMR spectrum of compound **10** in CD_3CN (expanded view).

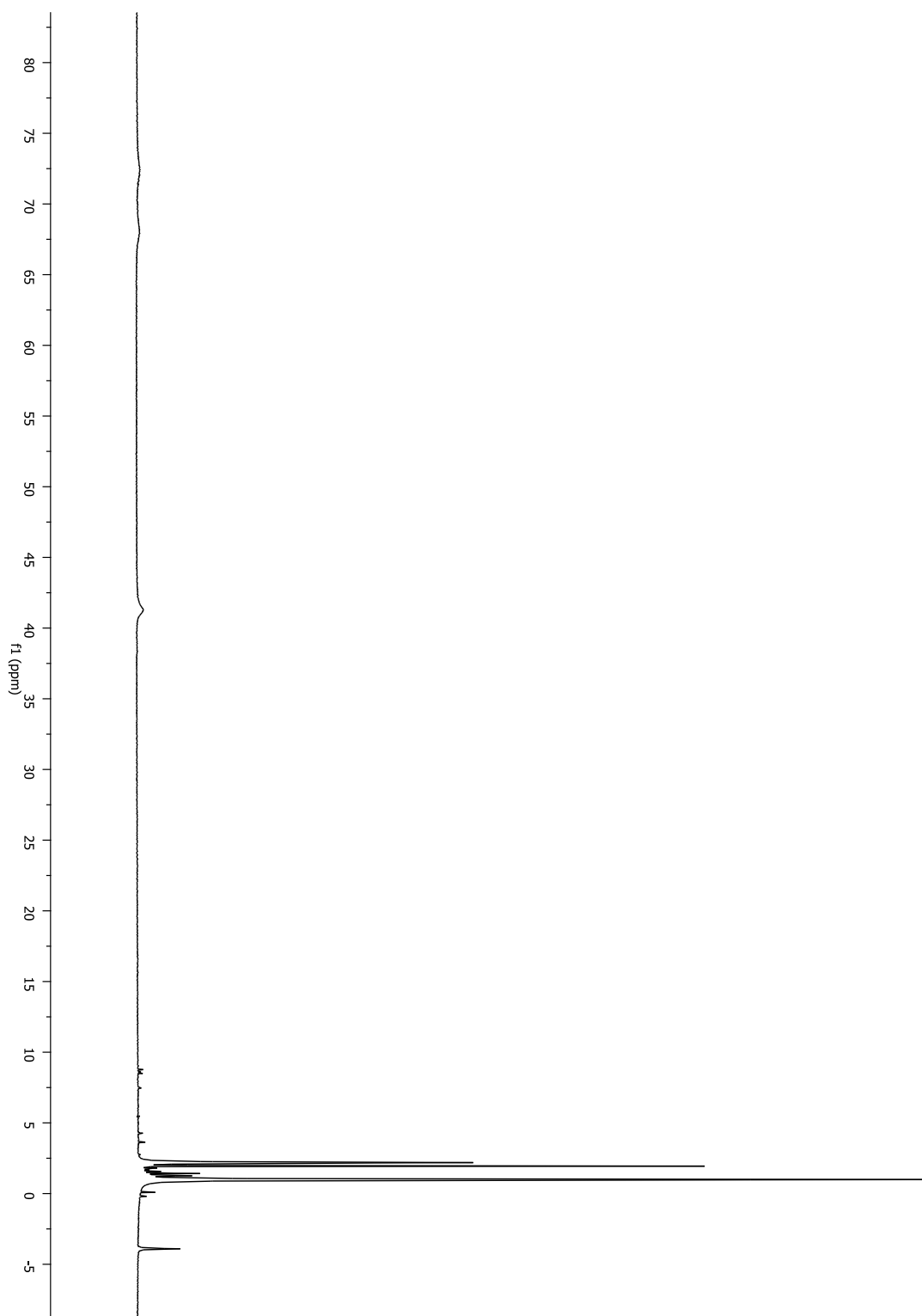


Figure S10. ^1H NMR spectrum of compound **10** in CD_3CN (magnified view).

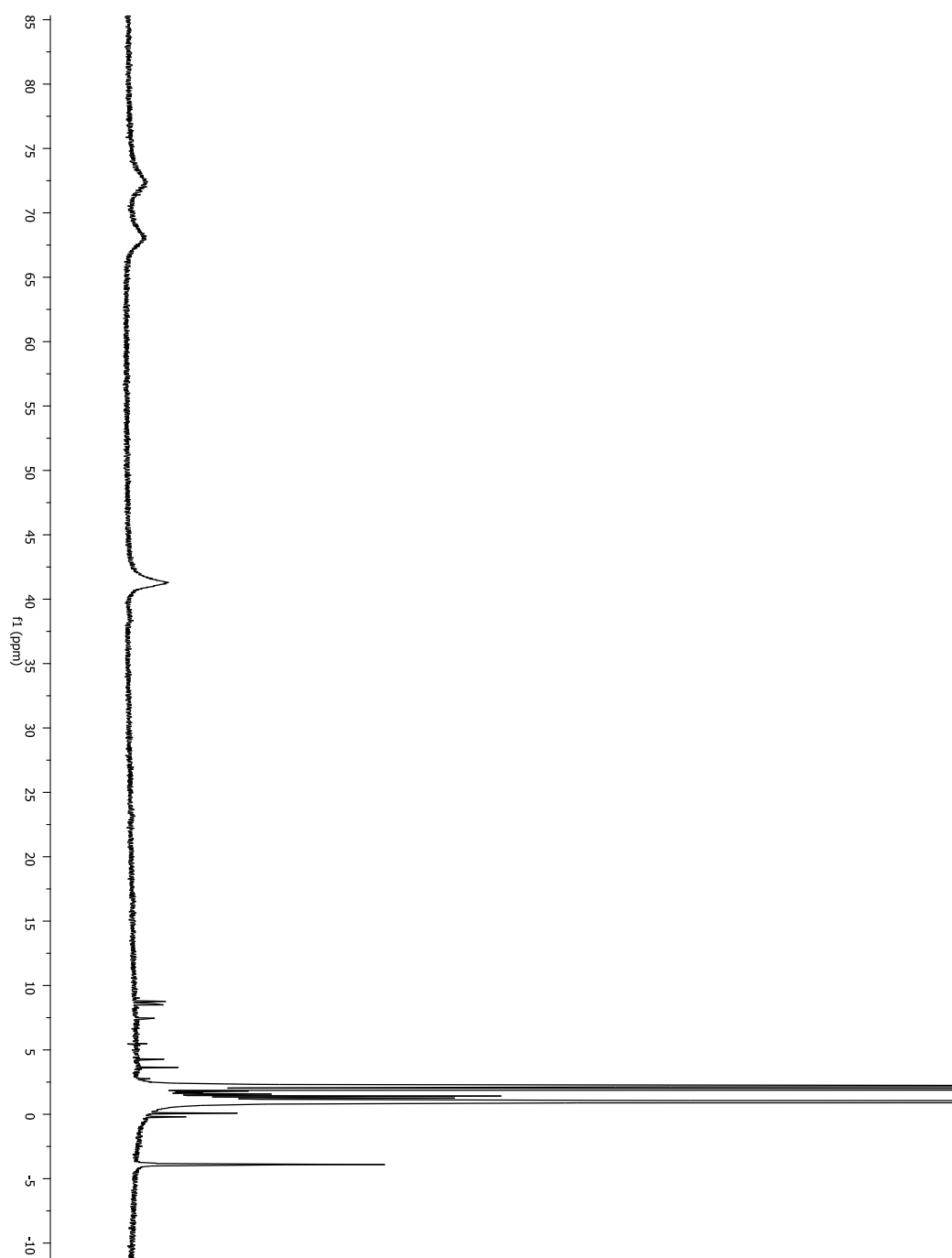


Figure S11. ^{19}F NMR spectrum of compound **10** in CD_3CN .

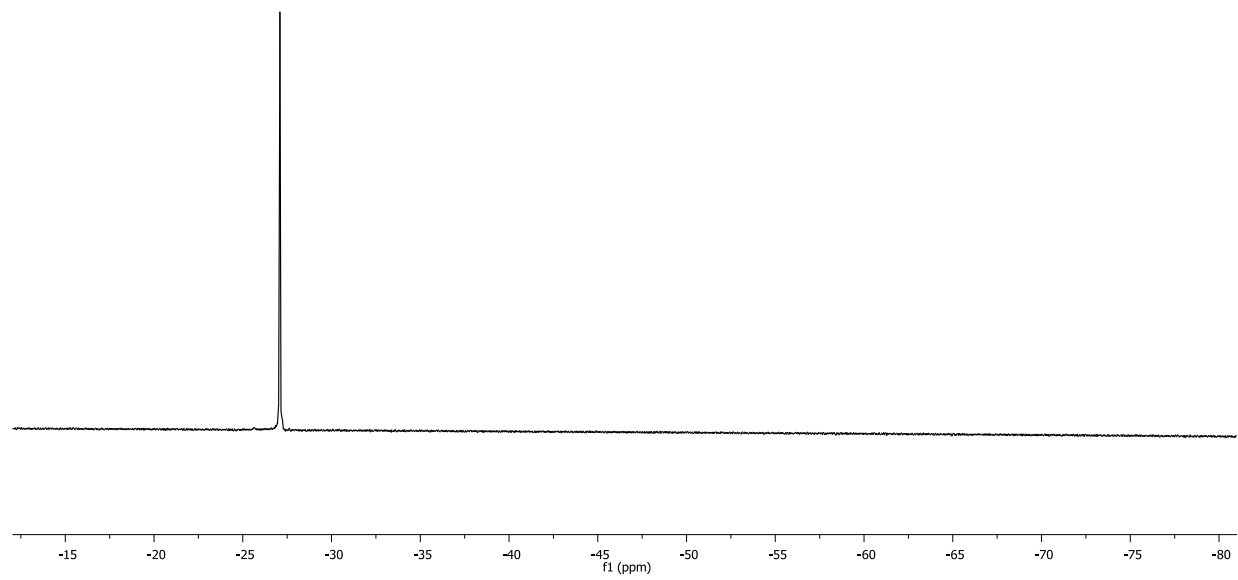


Figure S12: ^1H NMR spectrum (23 °C, CD_2Cl_2) of **14**:

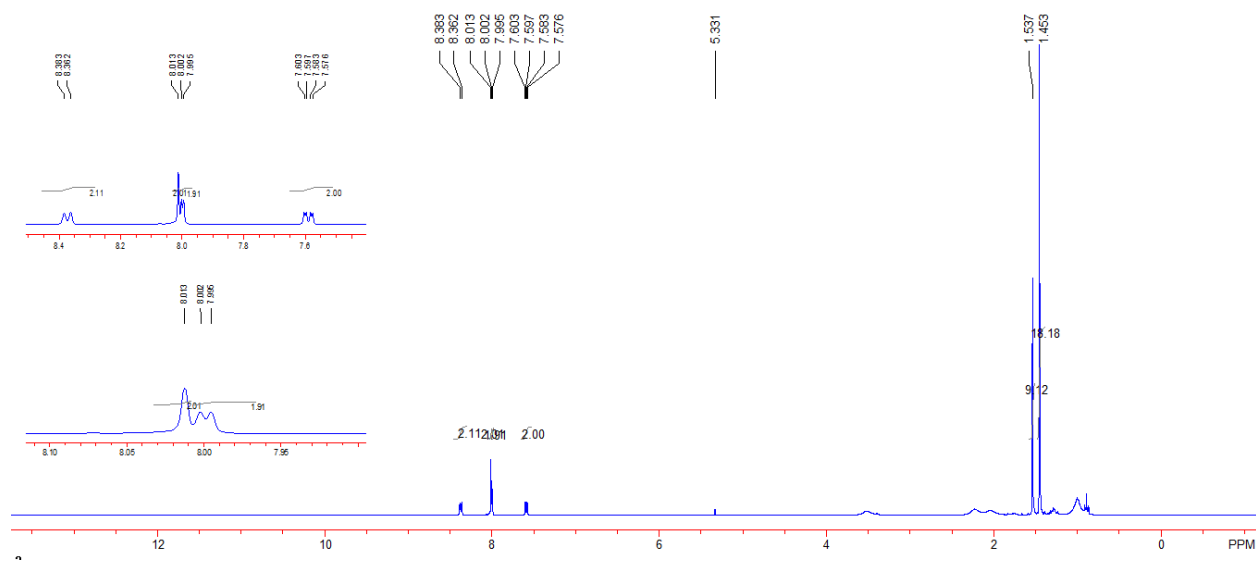


Figure S13: ^{19}F NMR spectrum (23 °C, CD_2Cl_2) of **14**:

