Electronic Supplementary Information for

Brønsted Acid-Promoted C – F Bond Activation in [P,S]-Ligated Neutral and Anionic Perfluoronickelacyclopentanes

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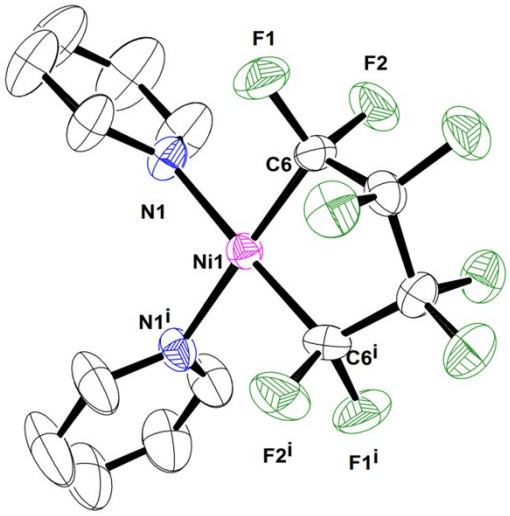

Figure S1. ORTEP representation of the molecular structure of complex **4c**. Thermal ellipsoids are set at the 40% probability level. Hydrogen atoms of pyridine rings are omitted for clarity.

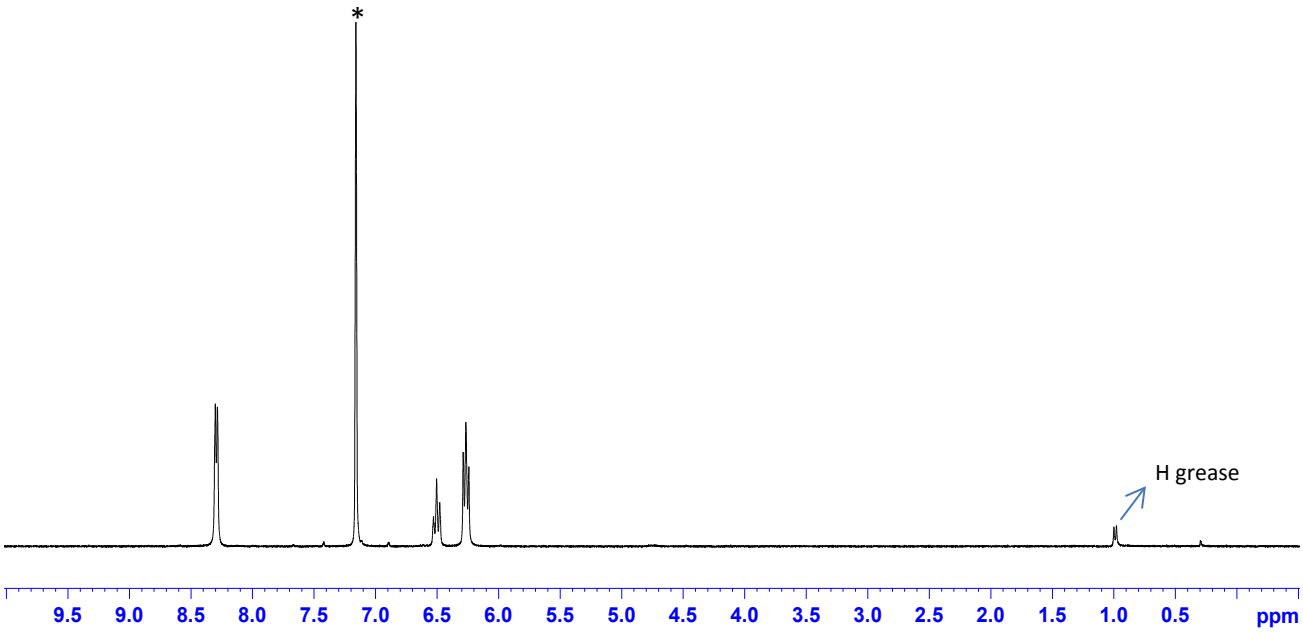

Figure S2. ^{1}H NMR (300 MHz, C_6D_6) spectrum for complex **4c**. The residual protio-solvent peak is labeled '*'.

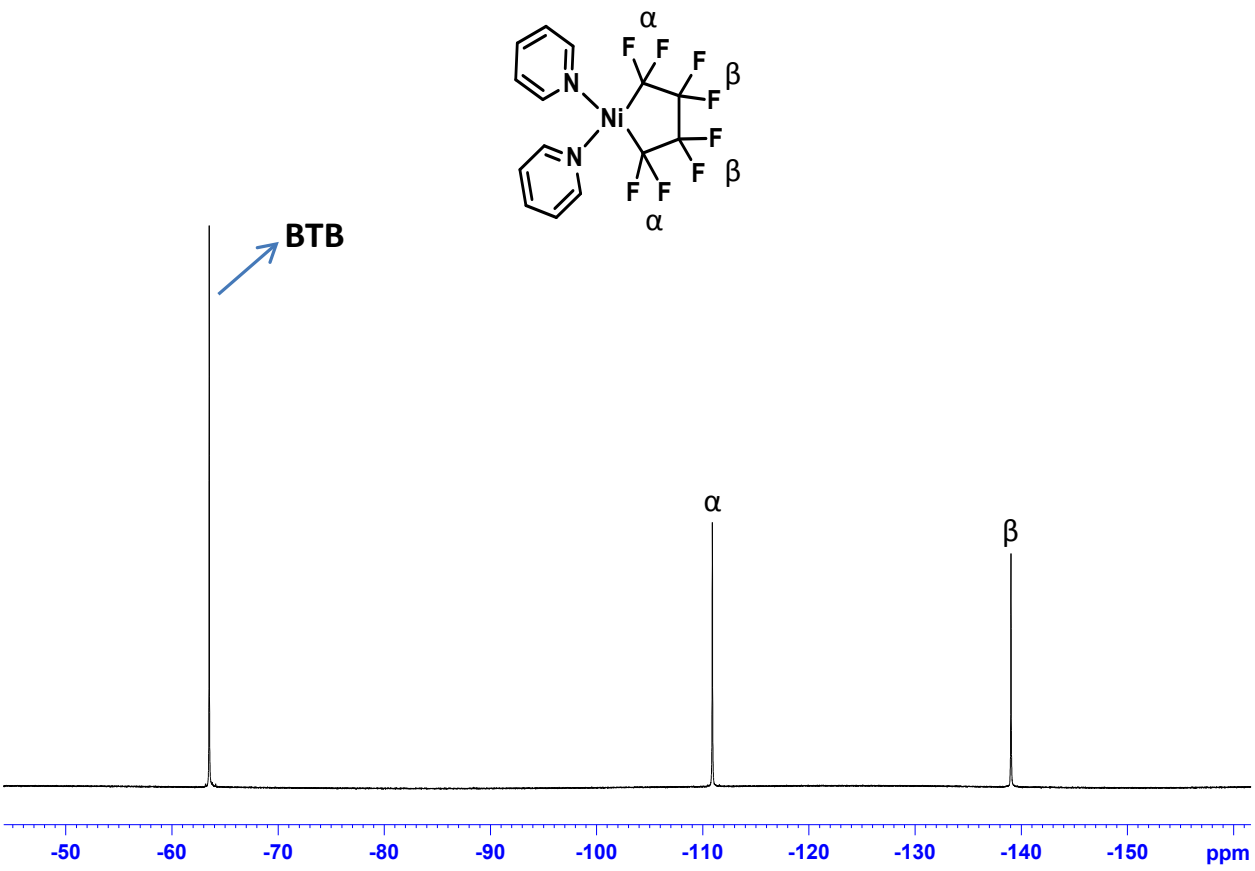

Figure S3. ^{19}F NMR (282 MHz, C_6D_6) spectrum for complex **4c**. 1,3-Bis(trifluoromethyl)benzene (BTB) used as an internal NMR standard.

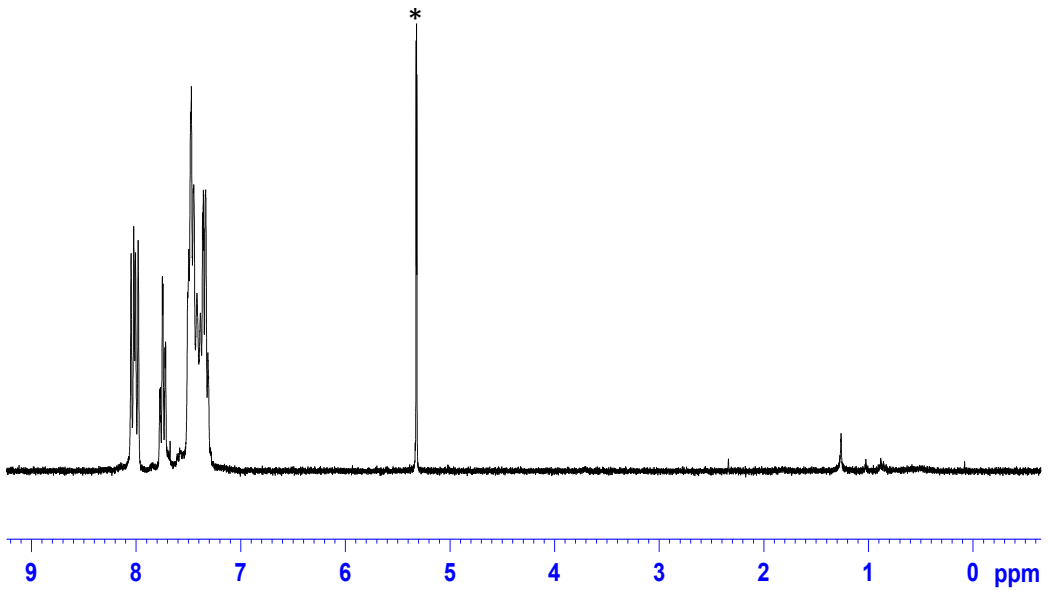

Figure S4. ^{1}H NMR (300 MHz, CD_2Cl_2) spectrum for complex **5a**. The residual protio-solvent peak is labeled '*'.

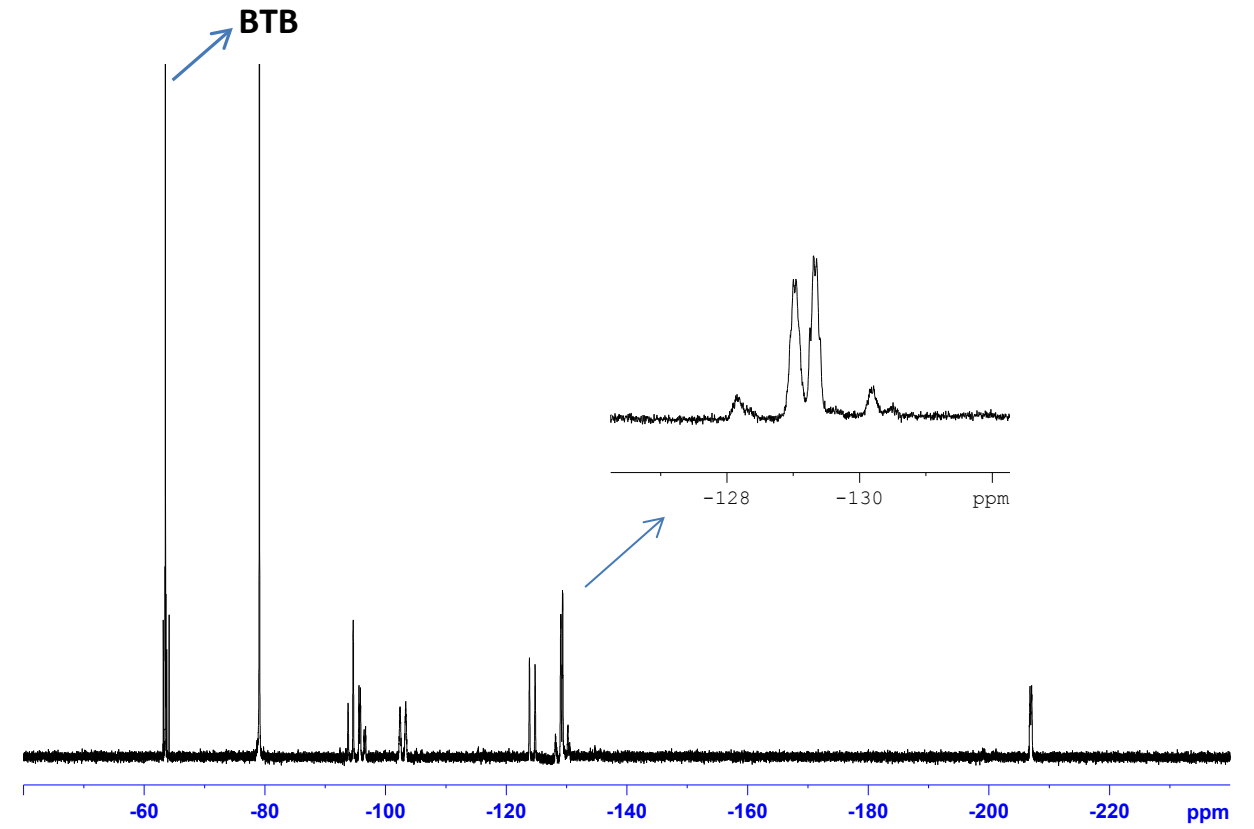

Figure S5. ^{19}F NMR (282 MHz, CD_2Cl_2) spectrum for complex **5a**. 1,3-Bis(trifluoromethyl)benzene (BTB) used as an internal NMR standard. The inset shows the expanded (horizontal scale) peaks associated with the indicated fluorines.

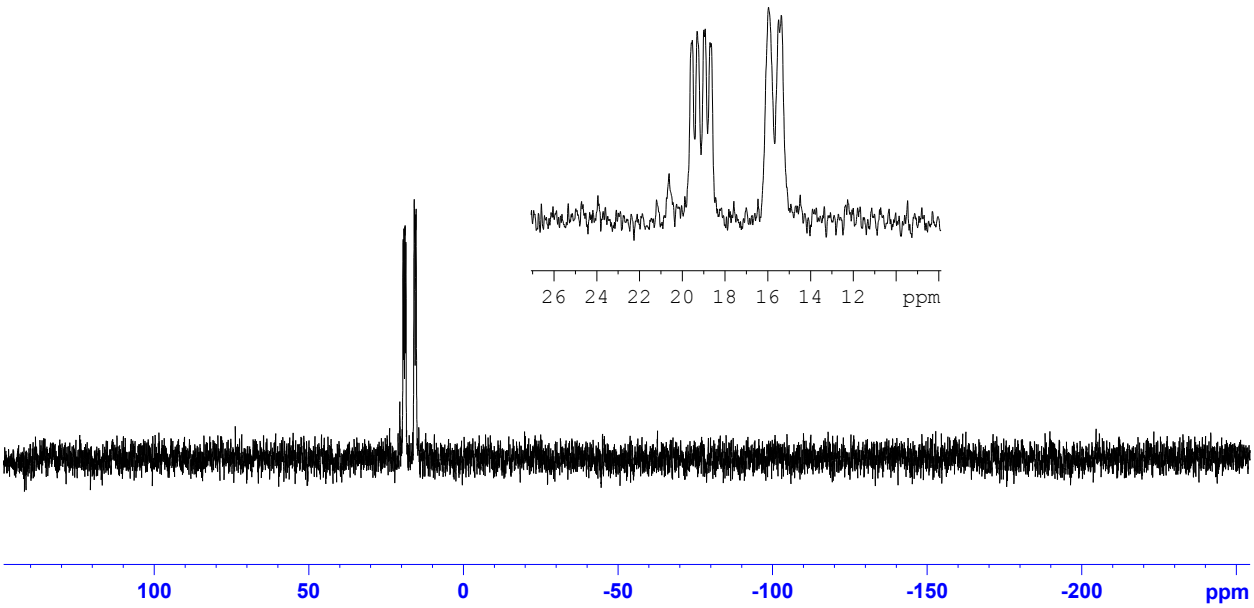

Figure S6. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2) spectrum for **5a**. The inset shows the expanded (horizontal scale) signal.

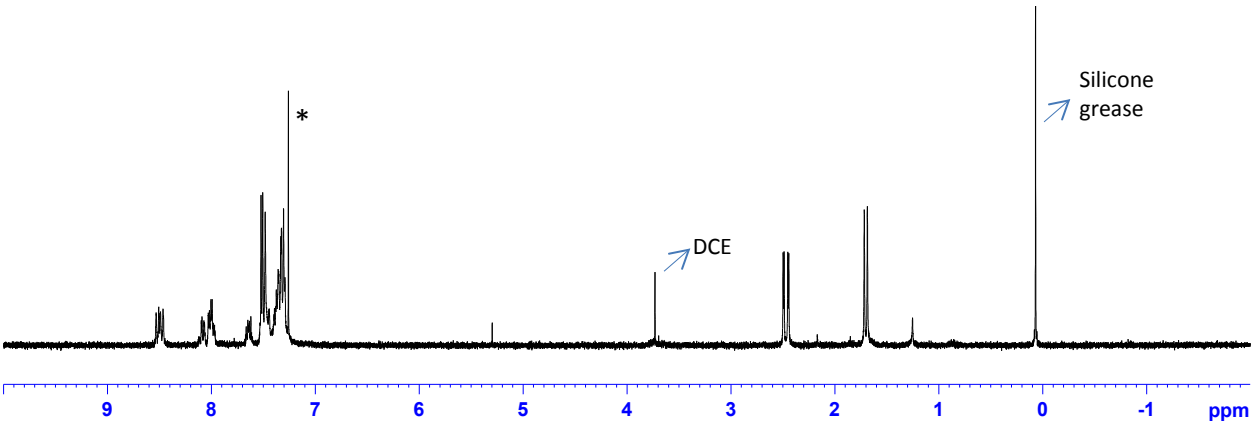

Figure S7. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for complex **5b**. The residual protio-solvent peak is labeled '*'.

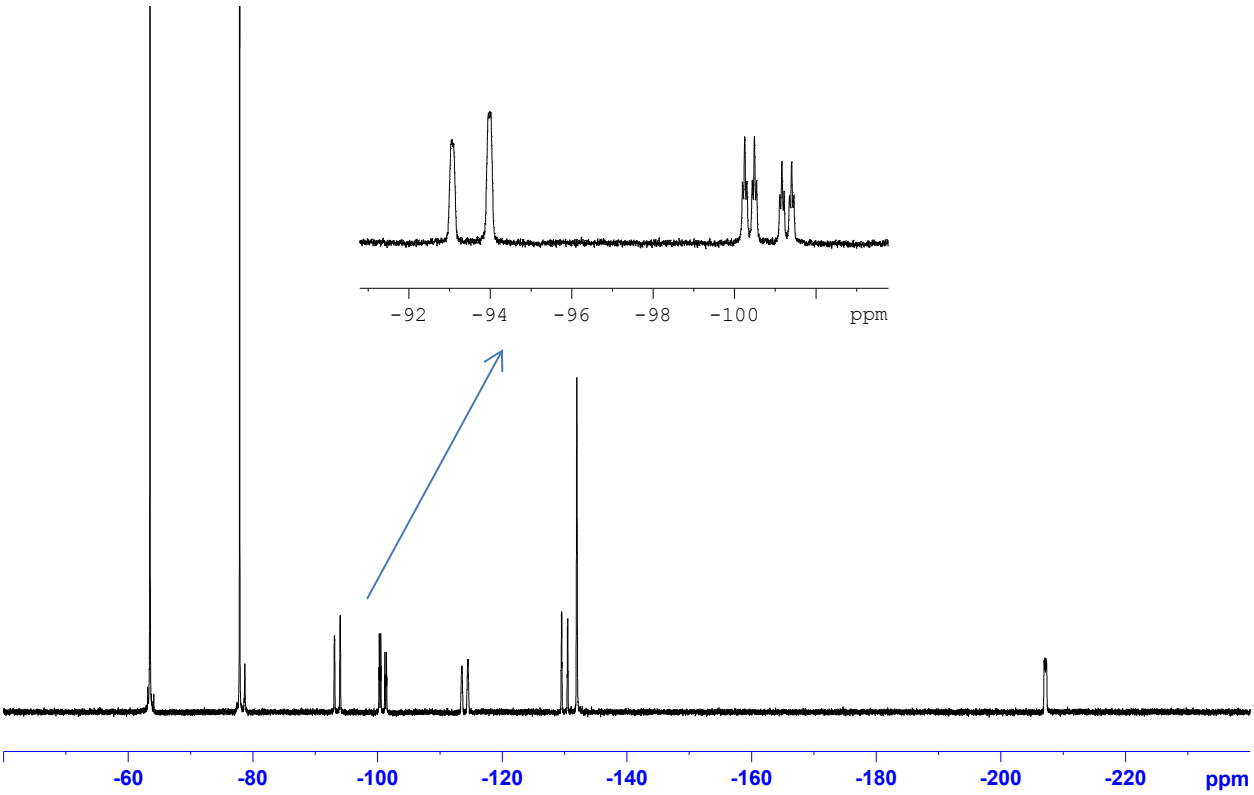

Figure S8. ^{19}F NMR (282 MHz, $CDCl_3$) spectrum for complex **5b**. The inset shows the expanded (horizontal scale) peaks associated with the indicated fluorines.

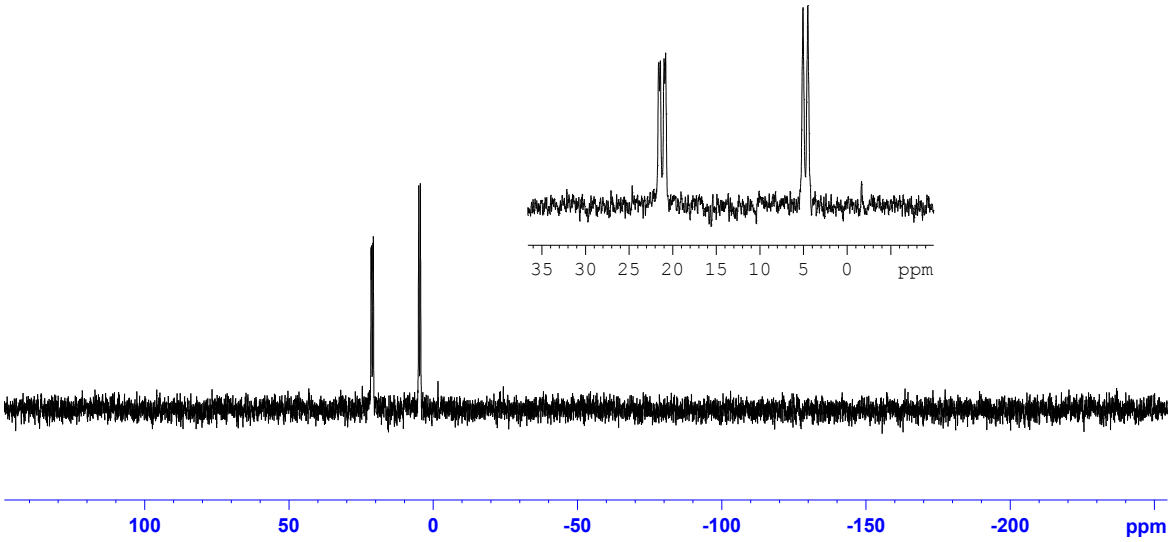

Figure S9. $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) spectrum for **5b**. The inset shows the expanded (horizontal scale) signal.

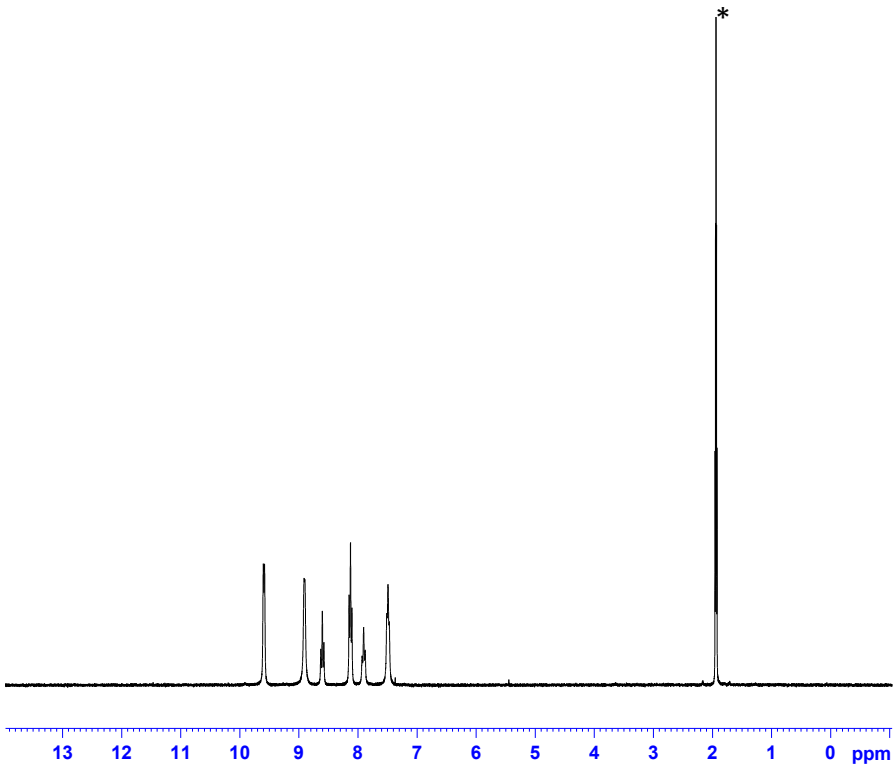

Figure S10. ^{1}H NMR (300 MHz, CD_3CN) spectrum for complex **5c·CD$_3$CN**. The residual protio-solvent peak is labeled '*'.

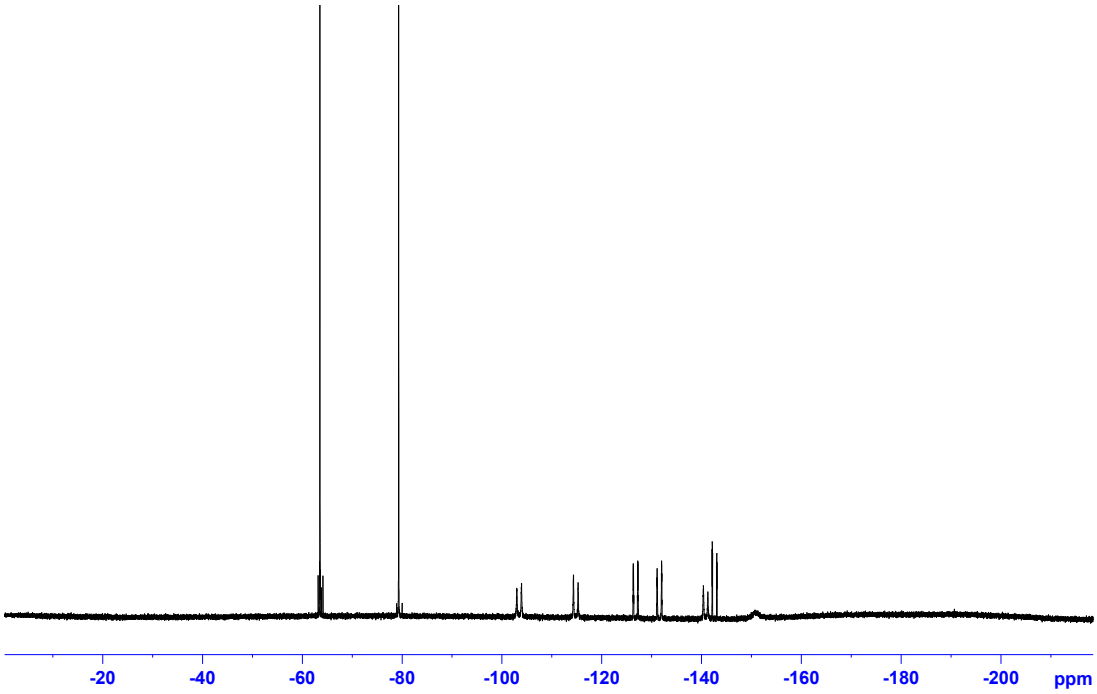

Figure S11. ^{19}F NMR (282 MHz, CD_3CN) spectrum for complex **5c·CD_3CN**.

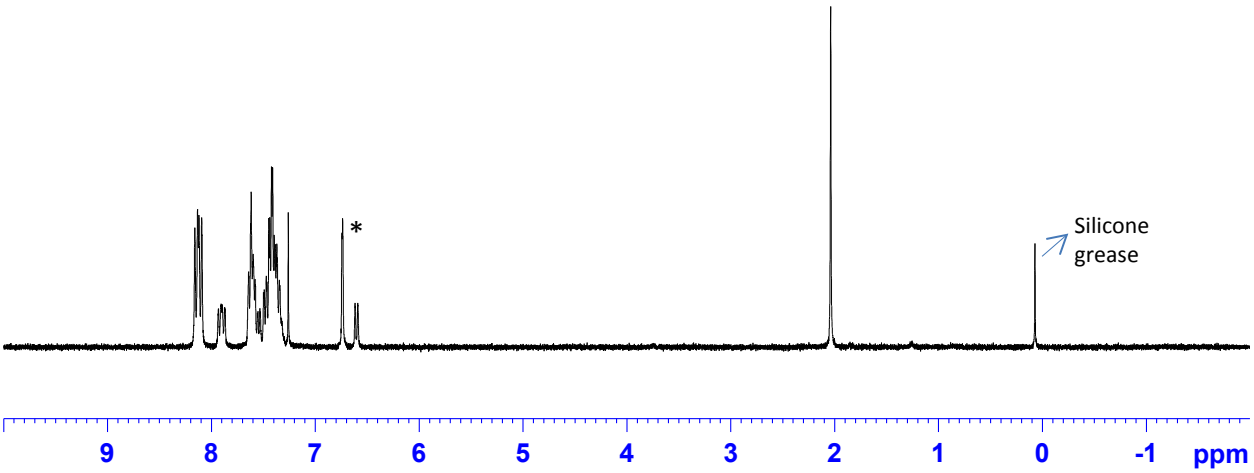

Figure S12. ^1H NMR (300 MHz, $CDCl_3$) spectrum for complex **6a**. The residual protio-solvent peak is labeled '*'.

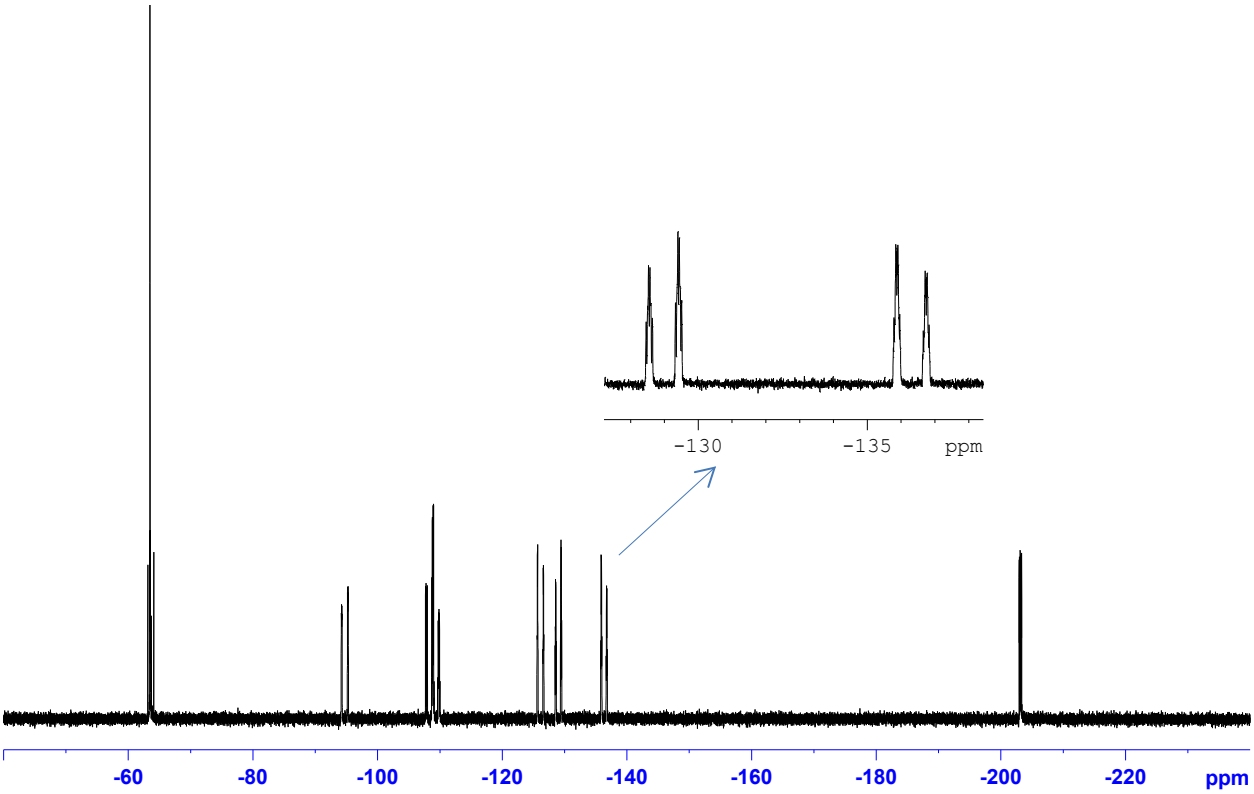

Figure S13. ^{19}F NMR (282 MHz, $CDCl_3$) spectrum for complex **6a**. The inset shows the expanded (horizontal scale) peaks associated with the indicated fluorines.

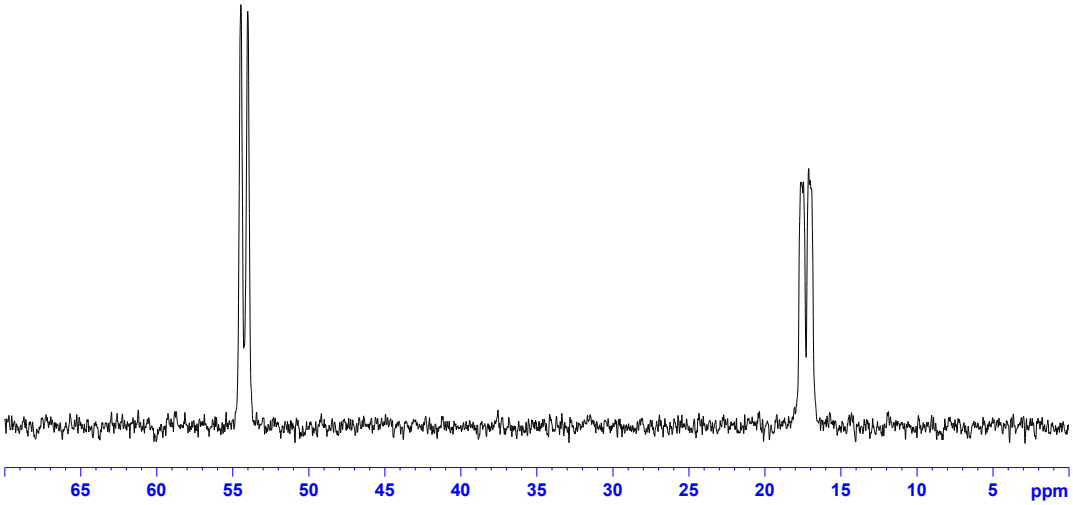

Figure S14. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) spectrum for **6a**.

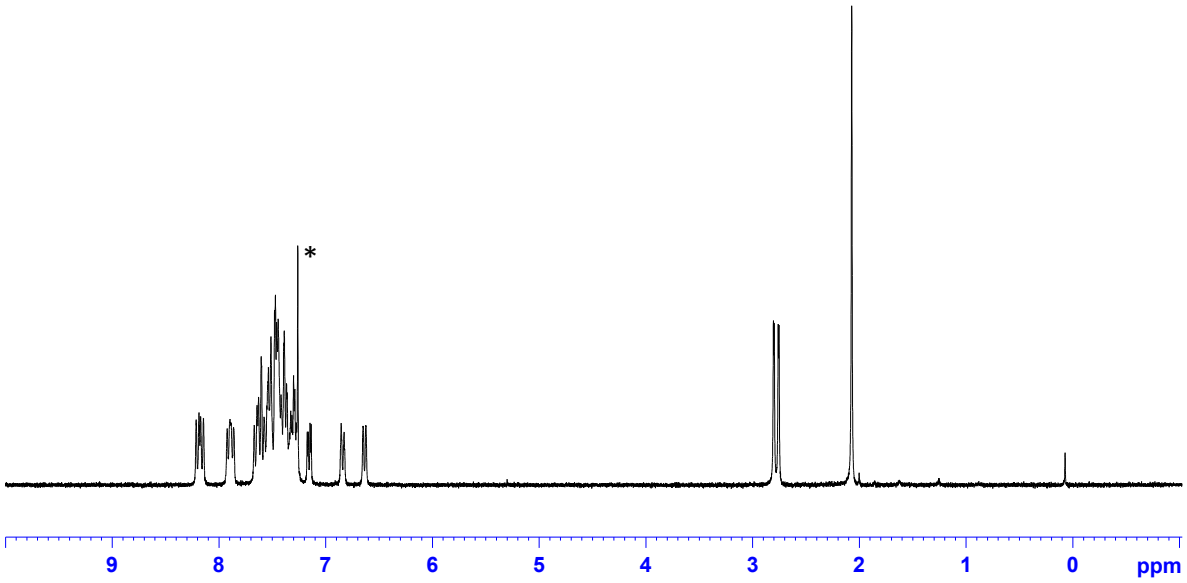

Figure S15. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for complex **6b**. The residual protio-solvent peak is labeled '*'.

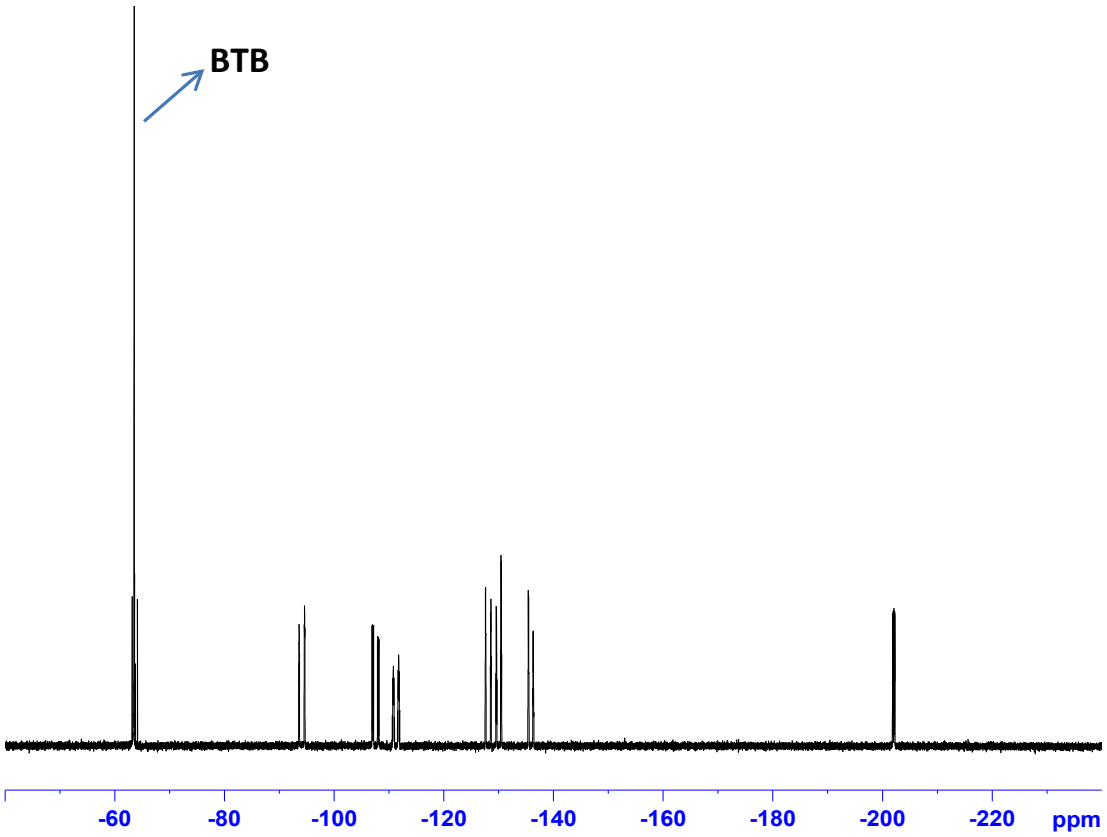

Figure S16. ^{19}F NMR (282 MHz, $CDCl_3$) spectrum for complex **6b**.

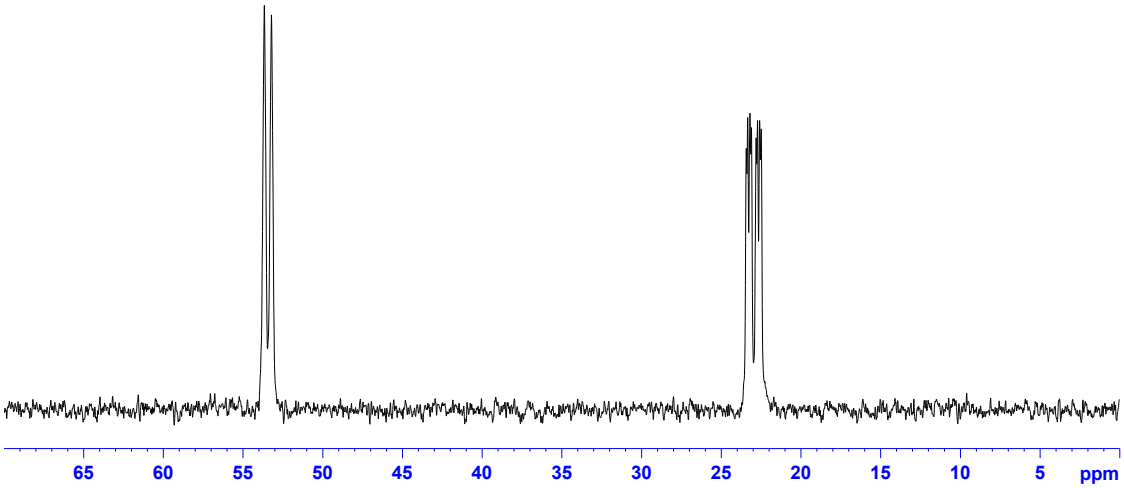

Figure S17. $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) spectrum for **6b**.

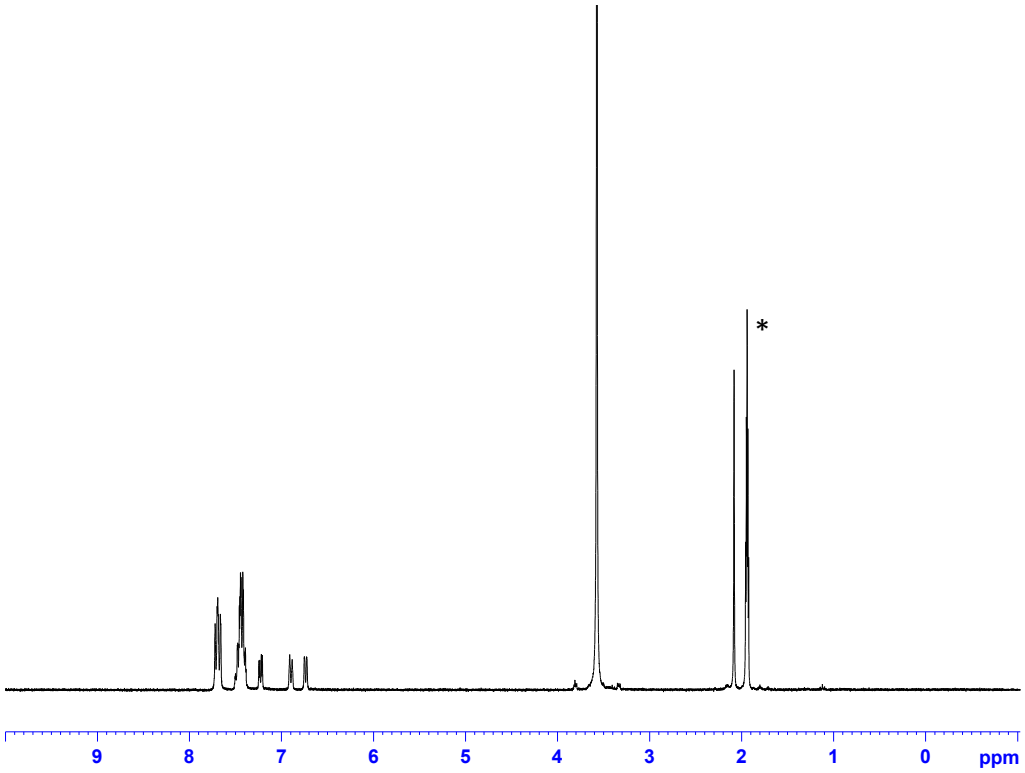

Figure S18. ^{1}H NMR (300 MHz, CD_3CN) spectrum for complex **7**. The residual protio-solvent peak is labeled '*'.

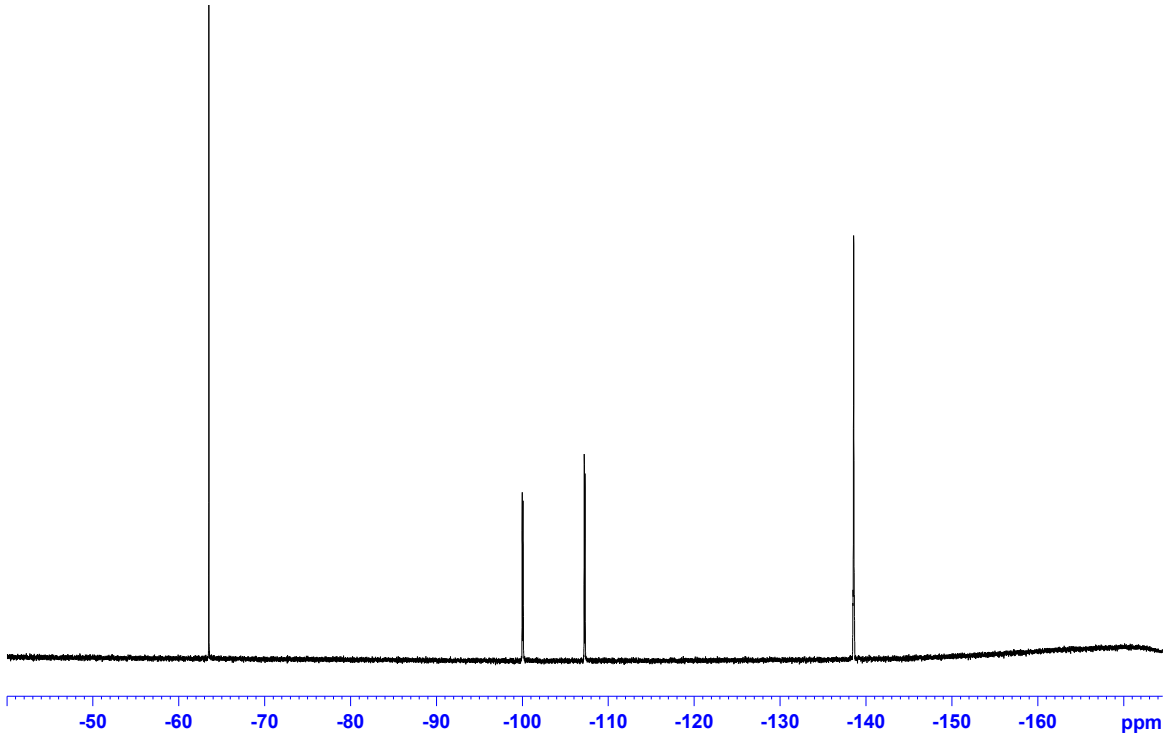

Figure S19. ^{19}F NMR (282 MHz, CD_3CN) spectrum for complex **7**.

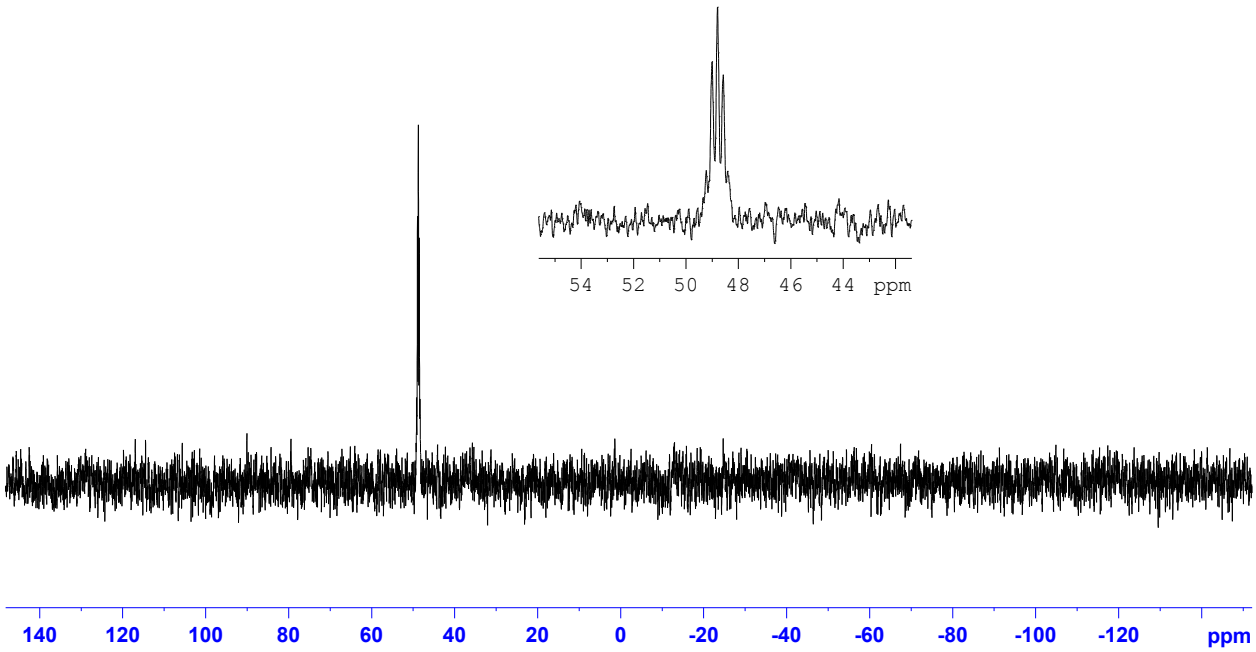

Figure S20. $^{31}P\{^1H\}$ NMR (121 MHz, CD_3CN) spectrum for **7**. The inset shows the expanded (horizontal scale) signal.

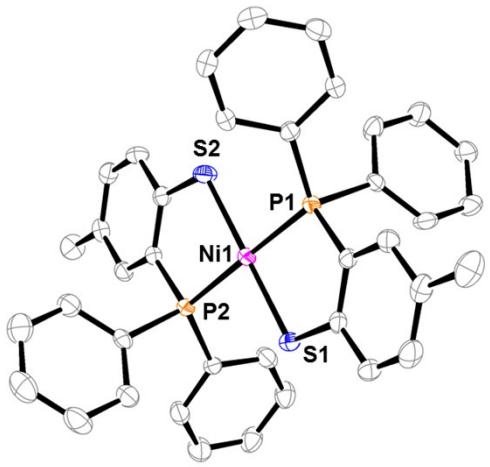

Figure S21. ORTEP representation of the molecular structure of complex **8b**. Thermal ellipsoids are set at the 40% probability level. Hydrogen atoms are omitted for clarity.

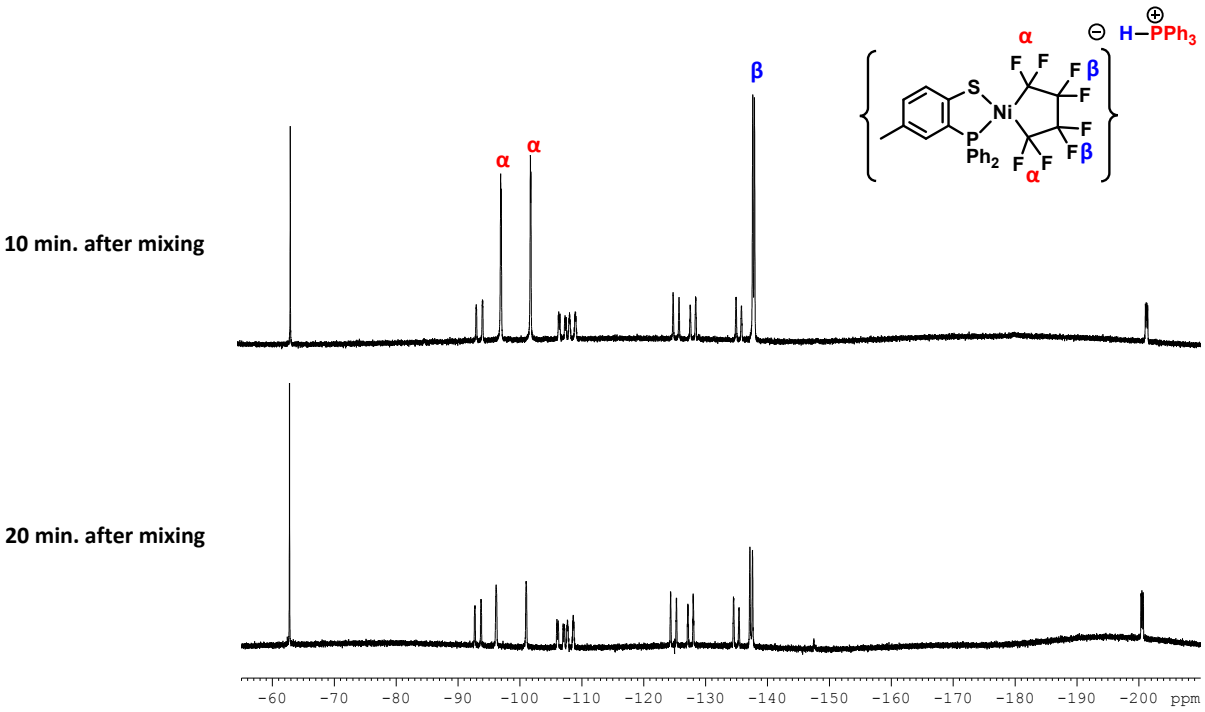

Figure S22. ^{19}F NMR (282 MHz, C_6D_6) spectra at room temperature displaying a mixture of ***Int 4*** and **6a**.

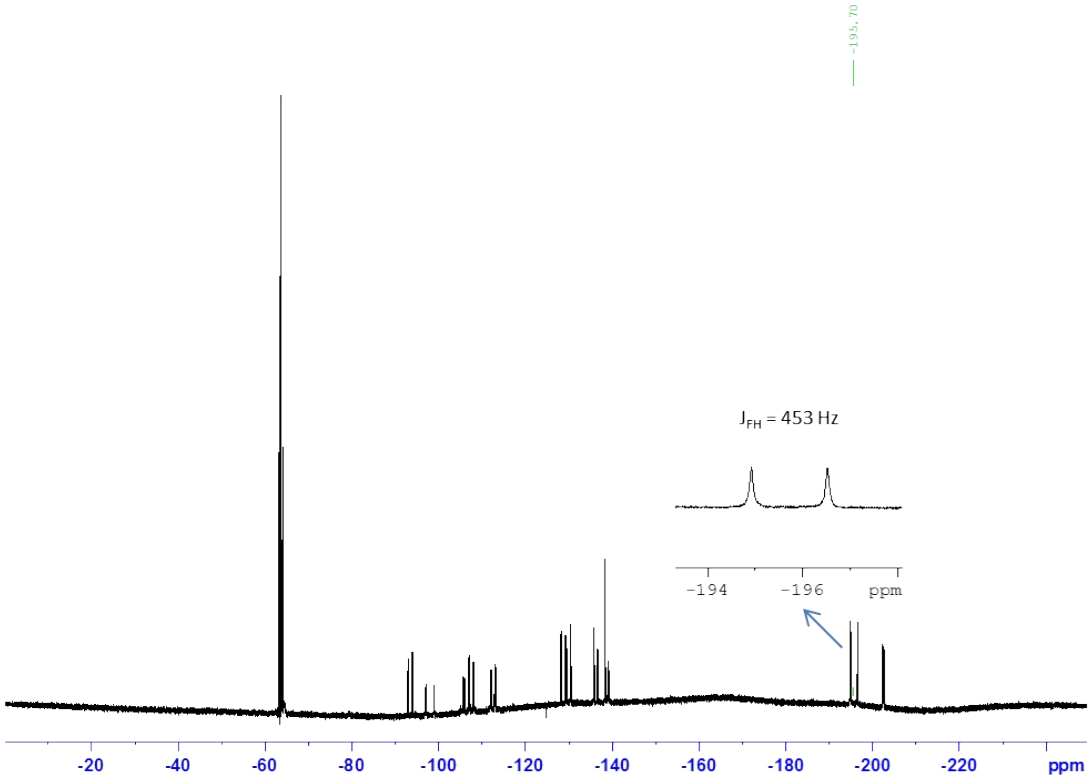

Figure S23. ^{19}F NMR (282 MHz, THF/C_6D_6 lock) spectrum of the reaction between **[P,SH]** and **4b** at room temperature. The inset shows the expanded (horizontal scale) signal for HF.

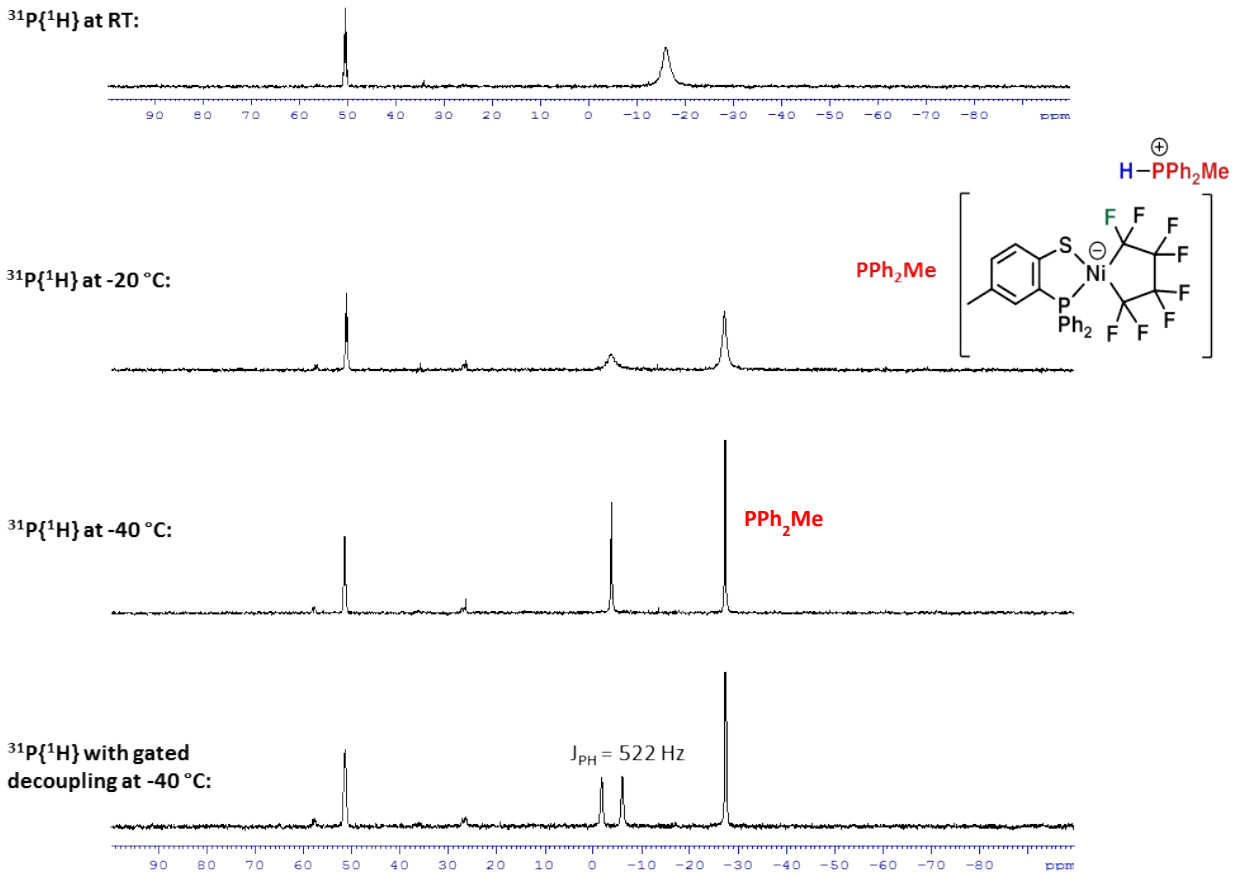

Figure S24. Variable temperature $^{31}P\{^{1}H\}$ and $^{31}P\{^{1}H\}$ with gated decoupling NMR (121 MHz, $CDCl_3$) spectra of the reaction between **[P,SH]** and **4b**.

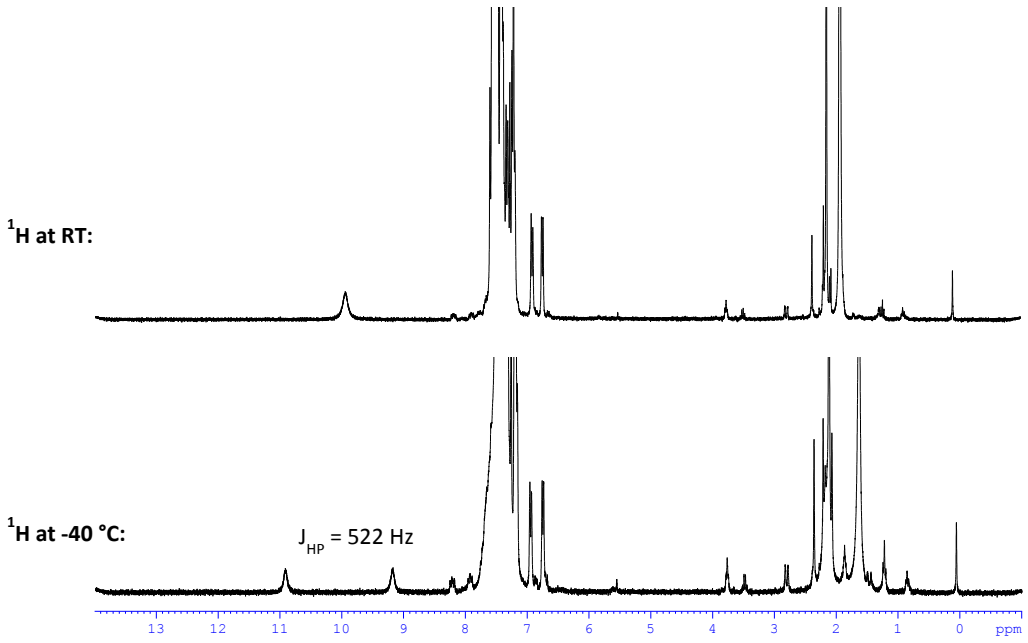

Figure S25. Variable temperature ^{1}H NMR (300 MHz, $CDCl_3$) spectra of the reaction between **[P,SH]** and **4b.**

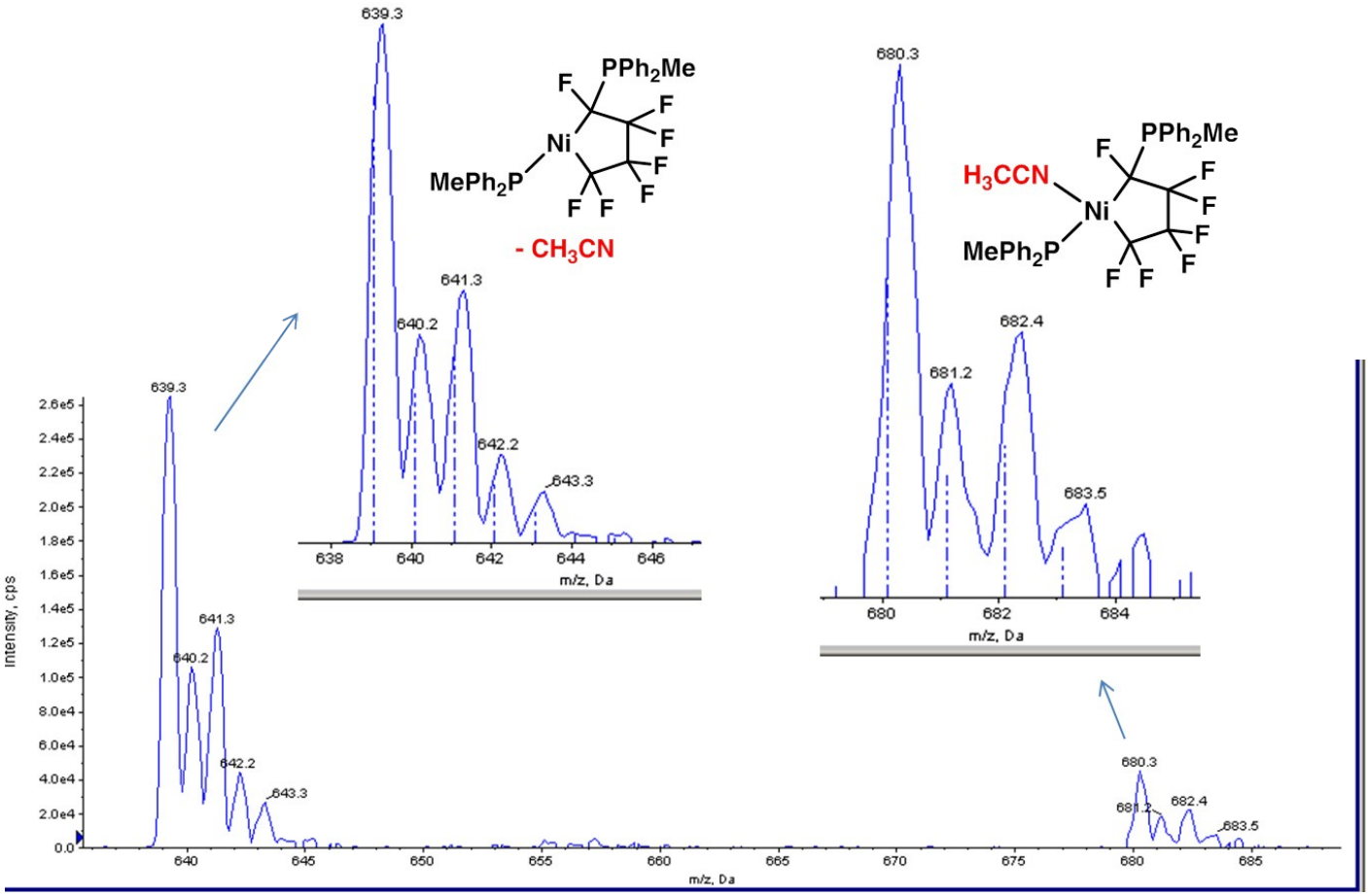

Figure S26. Selected peaks from the ESI mass spectrum (positive mode, CH_3CN) of complex **5b·CH_3CN**.

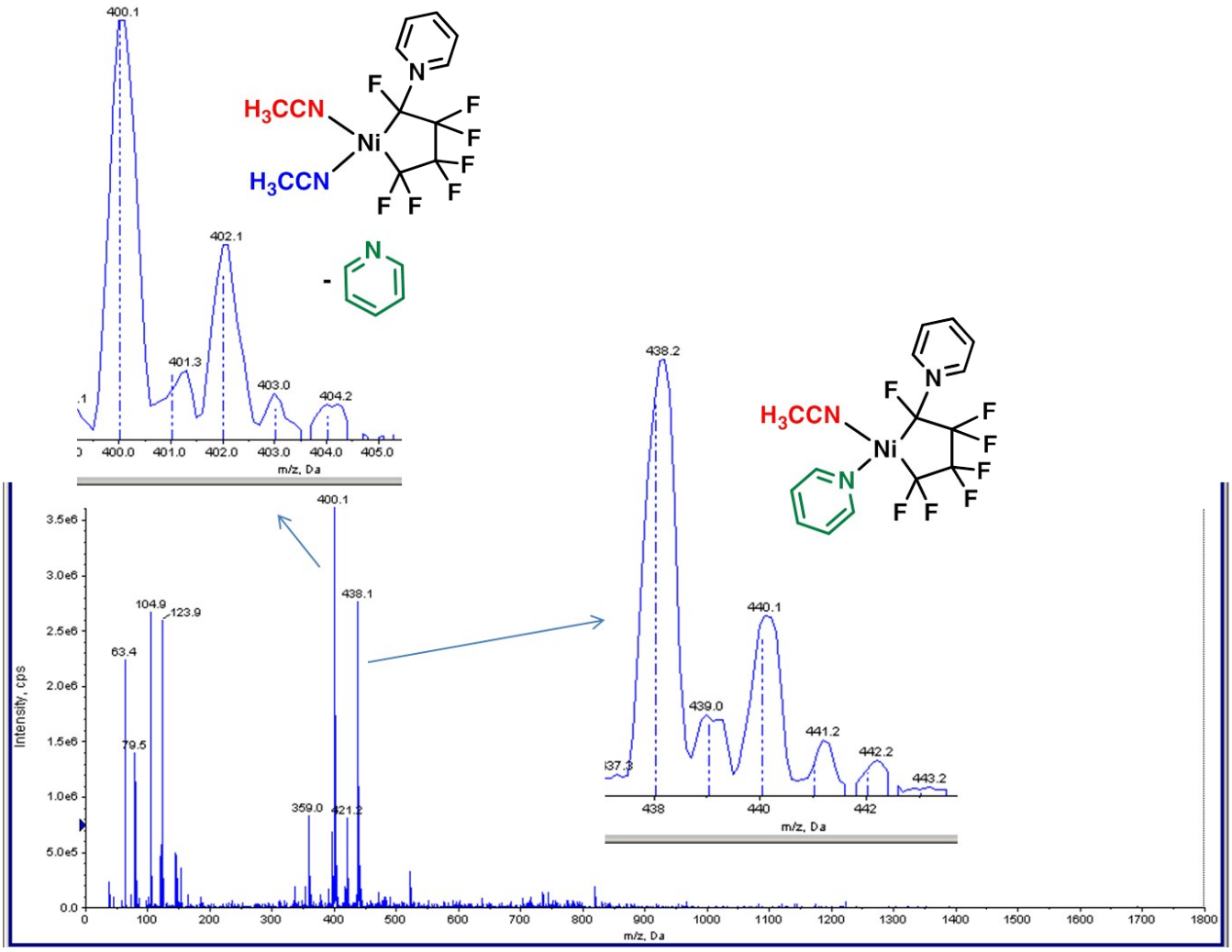

Figure S27. Selected peaks from the ESI mass spectrum (positive mode, CH_3CN) of complex **5c·CH_3CN**.

Table 1. X-ray diffraction data collection and refinement parameters for 4c, 5b, and 5c.

	4c	**5b**	**5c**
Formula	$C_{14}H_{10}F_8N_2Ni$	$C_{31}H_{26}F_{10}NiO_3P_2S$	$C_{15}H_{10}F_{10}N_2NiO_3S$
Fw	416.95	789.23	547.02
Color	Light beige	Yellow	Yellow
Temperature/K	200(2)	200(2)	200(2)
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	$P4_32_12$	$P2_1/c$	$P2_1/n$
a/Å	10.3161(13)	9.6468(4)	5.7833(3)
b/Å	10.3161(13)	11.2237(5)	30.5465(14)
c/Å	15.584(2)	29.9461(11)	10.9199(6)
α/deg	90	90	90
β/deg	90	91.210(2)	91.979(2)
γ/deg	90	90	90
V/Å^3	1658.5(5)	3241.6(2)	1927.95(17)
Z	4	4	4
D_c/Mg m^{-3}	1.670	1.617	1.885
μ/mm^{-1}	1.251	0.852	1.231
F(000)	832	1600	1088
Crystal size/mm	0.160 x 0.030 x 0.010	0.140 x 0.120 x 0.070	0.210 x 0.060 x 0.040
Reflections collected/unique	16640/2061	18525/3814	19640/4650
θ range/deg	2.368 to 28.268	1.360 to 21.965	1.333 to 28.282
Index range	-12<=h<=13, -13<=k<=13, -20<=l<=20	-10<=h<=10, -11<=k<=8, -31<=l<=31	–7<=h<=7, -36<=k<=40, -14<=l<=14
R(int)	0.0567	0.0815	0.0336
Completeness to θ	25.242°, 99.8 %	21.965°, 96.4 %	25.242°, 96.3%
Max. and min. transmission	0.7457 and 0.5419	0.7457 and 0.6534	0.7457 and 0.6296
Data/restraints/parameters	2061 / 45 / 114	3814 / 0 / 433	4650/0/289
Goodness-of-fit on F^2	0.993	1.017	1.027
R1, wR2 [I>2σ(I)]	0.0313, 0.0670	0.0463, 0.0897	0.0348, 0.0776
R1, wR2 (all data)	0.0523, 0.0747	0.0943, 0.1036	0.0493, 0.0824

Table 2. X-ray diffraction data collection and refinement parameters for 6a, 6b, 7, and 8b.

	6a	**6b**	**7·4 THF**	**8b**
Formula	$C_{41}H_{31}F_7NiP_2S$	$C_{36}H_{29}F_7NiP_2S$	$C_{47}H_{64}F_8NaNiO_9PS$	$C_{38}H_{32}NiP_2S_2$
Fw	809.37	747.30	1069.71	673.40
Color	Yellow	Yellow-orange	Orange-yellow	Green
Temperature/K	200(2)	200(2)	200(2)	200(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P–1	P2(1)/c	C 2/c	P 21/n
a/Å	9.0623(16)	9.3745(6)	22.8948(6)	12.478(2)
b/Å	12.292(2)	19.0781(11)	13.9815(4)	14.166(3)
c/Å	16.724(3)	18.2485(10)	34.7205(10)	18.643(3)
α/deg	101.318(6)	90	90	90
β/deg	92.410(6)	91.2641(19)	103.6427(12)	105.534(10)
γ/deg	100.701(7)	90	90	90
V/Å^3	3448.38(17)	3262.9(3)	10800.6(5)	3174.9(10)
Z	2	4	8	4
D_c/Mg m^{-3}	1.502	1.521	1.316	1.409
μ/mm^{-1}	0.757	0.823	0.512	0.871
F(000)	828	1528	4480	1400
Crystal size/mm	0.080 x 0.030 x 0.010	0.130 x 0.080 x 0.080	0.220 x 0.120 x 0.080	0.080 x 0.020 x 0.020
Reflections collected/unique	5457/4328	26985/7702	57572/6544	38294/5385
θ range/deg	1.905 to 23.444	1.544 to 28.323	1.720 to 21.966	1.768 to 24.829
Index range	–10<=h<=10, –13<=k<=13, 0<=l<=18	–12<=h<=7, –24<=k<=25, –24<=l<=22	–24<=h<=24, -14<=k<=14, -36<=l<=36	–14<=h<=14, -16<=k<=16, -22<=l<=21
R(int)		0.0648	0.0458	0.0761
Completeness to θ	25.2424°, 67.4%	25.242°, 95.8 %	25.242°, 67.0%	25.242°, 93.9%
Max. and min. transmission	0.744896 and 0.561624	0.7457 and 0.6022	0.7457 and 0.6454	0.7451 and 0.6219
Data/restraints/parameters	4328/798/470	7702/0/424	6544/74/614	5385/0/388
Goodness-of-fit on F^2	1.127	1.006	1.059	1.009
R1, wR2 [I>2σ(I)]	0.0802, 0.1563	0.0518, 0.1040	0.0673, 0.1772	0.0387, 0.0811
R1, wR2 (all data)	0.1638, 0.1850	0.1124, 0.1262	0.0841, 0.1893	0.0729, 0.0910