

Electronic Supplementary Information

***C–F Bond Activation of perfluorinated arenes at NHC-stabilized Cobalt
Halfsandwich Complexes***

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1. Additional Figures and Tables

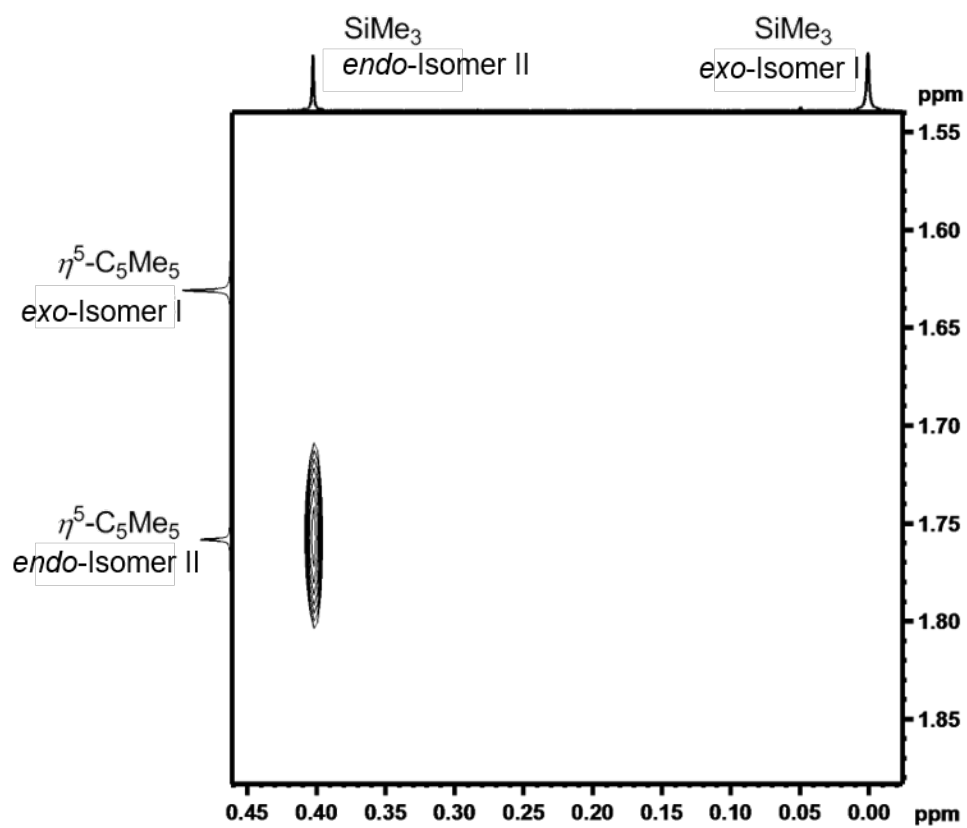


Figure S1: Section of the ^1H - ^1H -NOESY correlation spectrum of the mixture of isomers of $[\text{Cp}^*\text{Co}(i\text{Pr}_2\text{Im})(\eta^2\text{-C}_2\text{H}_3(\text{SiMe}_3))]$ **6**.

Table S1: Selected NMR spectroscopic data of the complexes **1 - 6**.

	¹ H NMR [ppm]			¹³ C{ ¹ H} NMR [ppm]
	Cp-H (s)	C ₂ H ₄	NCHCHN (s)	Cp
1	4.59	0.91 2.54	Me ₂ Im: 5.93	80.6
2	4.68	1.11 2.57	<i>i</i> Pr ₂ Im: 6.20	80.5
		C ₂ H ₃ SiCH ₃		
3	4.61	0.35	Me ₂ Im: 5.90	80.2
4	4.72	0.35	<i>i</i> Pr ₂ Im: 6.20	80.1
	Cp-CH ₃ (s)			C ₅ (CH ₃) ₅
5	1.61	-0.07	Me ₂ Im: 6.07 6.11	88.2
6	<i>exo</i> - 6 : 1.64 <i>endo</i> - 6 : 1.77	0.00 0.41	<i>i</i> Pr ₂ Im: 6.26 6.35 6.13 6.26	88.3 88.5

Table S2: Selected bond lengths (Å) and angles (°) of the complexes **2, 4, and 6 - 11**.

	d Co-C1	d Co-C ₅ R ₅	d Co-L	∠ C1-Co-C ₅ R ₅	∠ C1-Co-L
2	1.891(2)	R = H: 1.713(3)	L = C ₂ H ₄ 1.866(3)	R = H: 130.43(1)	L = C ₂ H ₄ 93.04(1)
4	1.892(2)	R = H: 1.714(1)	L = C ₂ H ₃ SiMe ₃ 1.867(1)	R = H: 129.03(6)	L = C ₂ H ₃ SiMe ₃ 92.03(5)
6	1.926(2)	R = Me: 1.814(2)	L = C ₂ H ₃ SiMe ₃ 1.882(2)	R = Me: 128.87(7)	L = C ₂ H ₃ SiMe ₃ 97.41(8)
7	1.928(2)	R = H: 1.714(2)	L = C ₆ F ₅ 1.951(1)	R = H: 132.03(6)	L = C ₆ F ₅ 96.60(7)
8	1.992(4)	R = H: 1.781(2)	L = C ₇ F ₇ 1.994(4)	R = H: 131.19(6)	L = C ₇ F ₇ 95.02(1)
9	1.922(2)	R = H: 1.721(6)	L = C ₁₂ F ₉ 1.952(2)	R = H: 132.99(4)	L = C ₁₂ F ₉ 93.80(7)
10	1.897(3)	R = Me: 1.690(2)	L = C ₆ F ₅ 1.939(4)	R = Me: 133.71(6)	L = C ₆ F ₅ 97.65(1)
11	1.937(3)	R = Me: 1.720(9)	L = C ₇ F ₇ 1.946(4)	R = Me: 135.20(1)	L = C ₇ F ₇ 95.11(1)

Table S3: Selected NMR spectroscopic data of the dinuclear complexes **13** - **16**.

	¹ H NMR [ppm]		¹³ C{ ¹ H} NMR [ppm]	¹⁹ F NMR [ppm]
	Cp- <i>H</i> (s)	NCHCHN (s)	Cp	Ar- <i>F</i>
13	4.69 (10 H)	Me ₂ Im: 6.01 (2 H) Me ₂ Im: 6.09 (2 H)	84.9	-145.2 -159.2 -194.3
14	4.82 (10 H)	<i>i</i> Pr ₂ Im: 6.32 (2 H) 6.45 (2 H)	84.8	-142.4 -158.5 -192.7
15	4.67 (5 H) 4.67 (5 H)	Me ₂ Im: 5.99 (2 H) 6.07 (1 H) 6.09 (1 H)	85.0 85.3	-55.1 (CF ₃) -119.2 -145.4 -185.2 -200.3
16	4.79 (5 H) 4.79 (5 H)	<i>i</i> Pr ₂ Im: 6.31 (1 H) 6.32 (1 H) 6.42 (1 H) 6.43 (1 H)	84.8 85.0	-55.6 (CF ₃) -118.4 -142.1 -142.9 -183.8 -198.8

Table S4: Selected bond lengths (Å) and angles (°) of the **13**, **14**, **16**, **18** and **19**.

	d Co-C1	d Co-Cp	d Co-Ar ^F	∠ C1-Co-Cp	∠ C1-Co-Ar ^F	∠ Cp-Co-Ar ^F
13	1.905(4)	1.724(4)	1.809(4)	124.70(7)	91.4.90(7)	140.34(8)
14	1.905(6)	1.738(4)	1.813(5)	124.58(9)	95.11(2)	140.30(9)
16	1.911(2)	1.734(2)	1.813(3)	123.28(9)	95.86(9)	140.86(1)
18	1.911(3)	1.731(1)	1.812(2)	125.91(4)	94.17(3)	139.92(4)
19	1.915(3)	1.725(3)	1.808(3)	123.90(7)	94.07(8)	142.01(5)

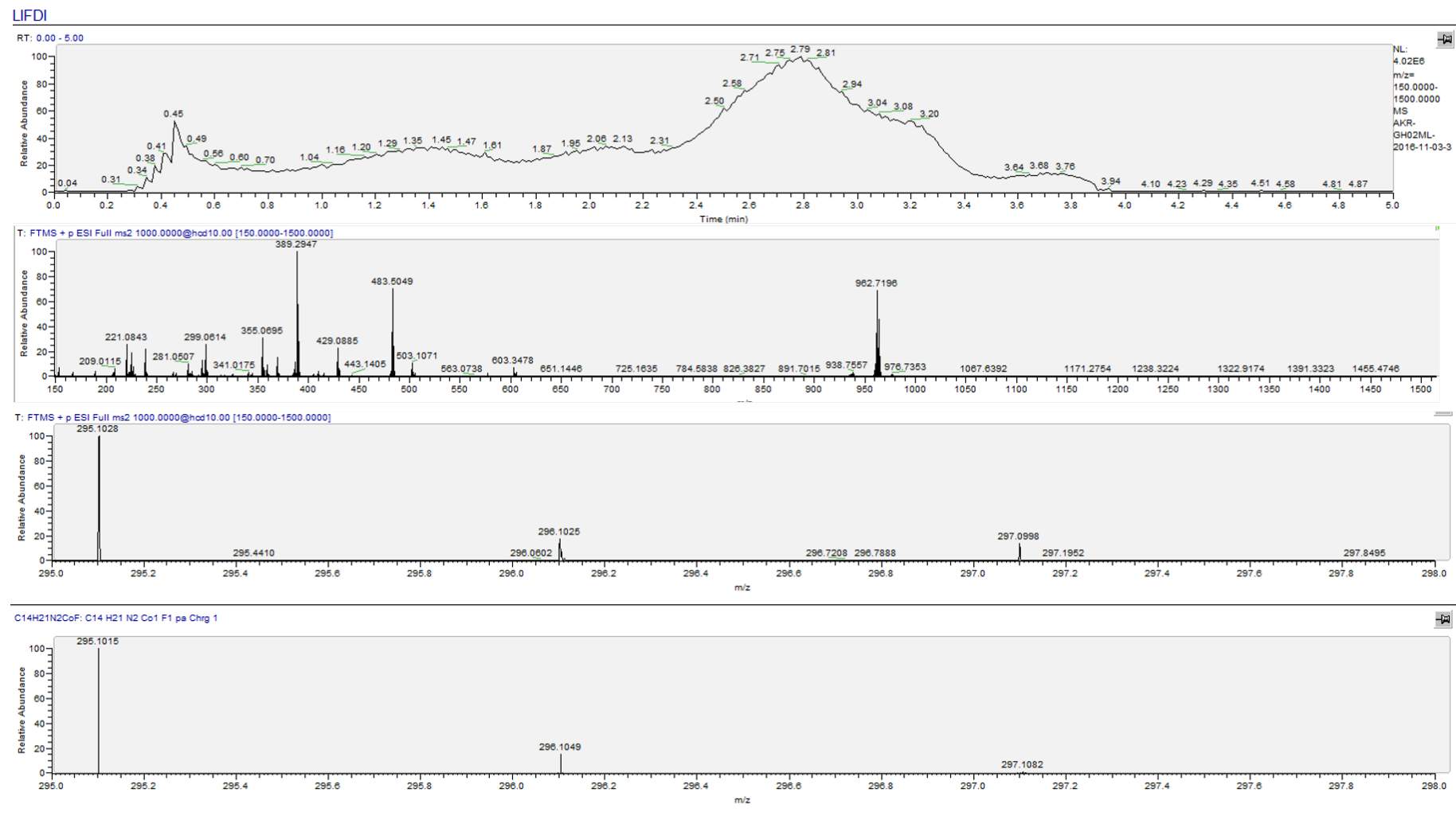


Figure S2: Mass spectrum of the reaction mixture of the conversion of $[\text{CpCo}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_2\text{H}_4)]$ **2** with hexafluorobenzene after 24 h at 100°C. The signal of the cobaltfluoride complex $[\text{CpCo}(\text{iPr}_2\text{Im})(\text{F})]$ (calcd. $[\text{M}/z]^+$: 295.1021, found: 295.1015) is zoomed in.

2. NMR-Spectra

[CpCo(Me₂Im)(η²-C₂H₄)] **1**

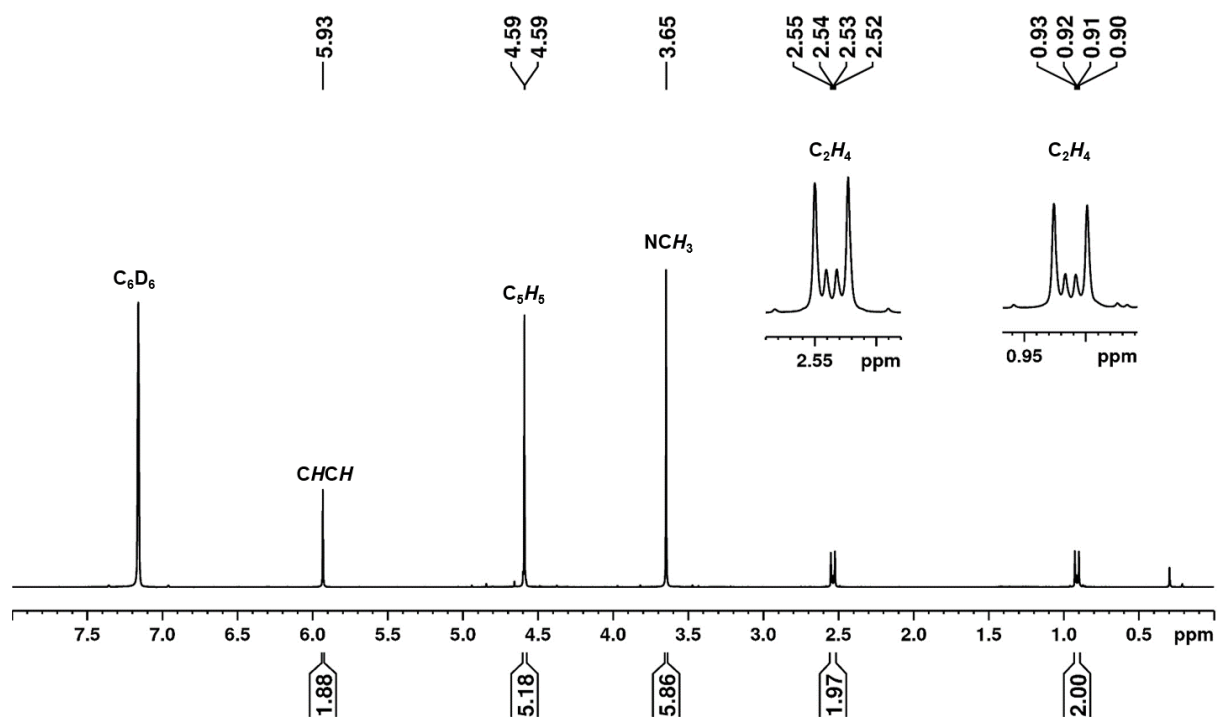


Figure S3: ¹H NMR spectrum of complex [CpCo(Me₂Im)(η²-C₂H₄)] **1** in C₆D₆.

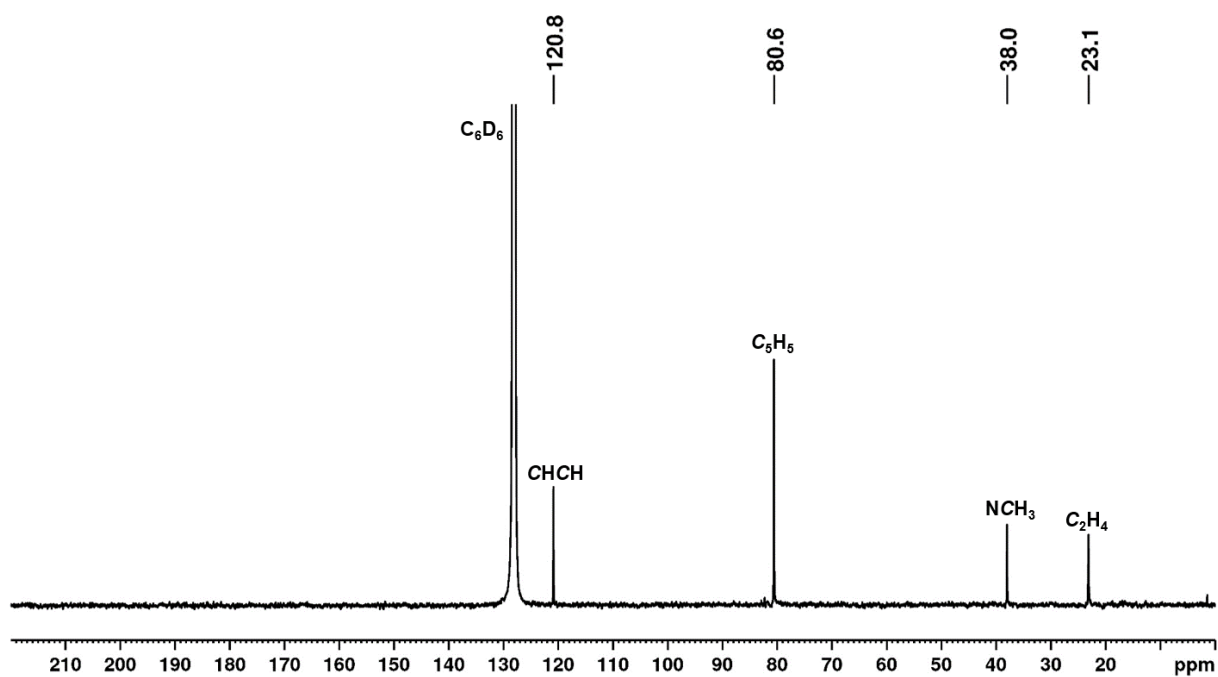


Figure S4: ¹³C{¹H} NMR spectrum of complex [CpCo(Me₂Im)(η²-C₂H₄)] **1** in C₆D₆.

[CpCo(*i*Pr₂Im)(η^2 -C₂H₄)] 2

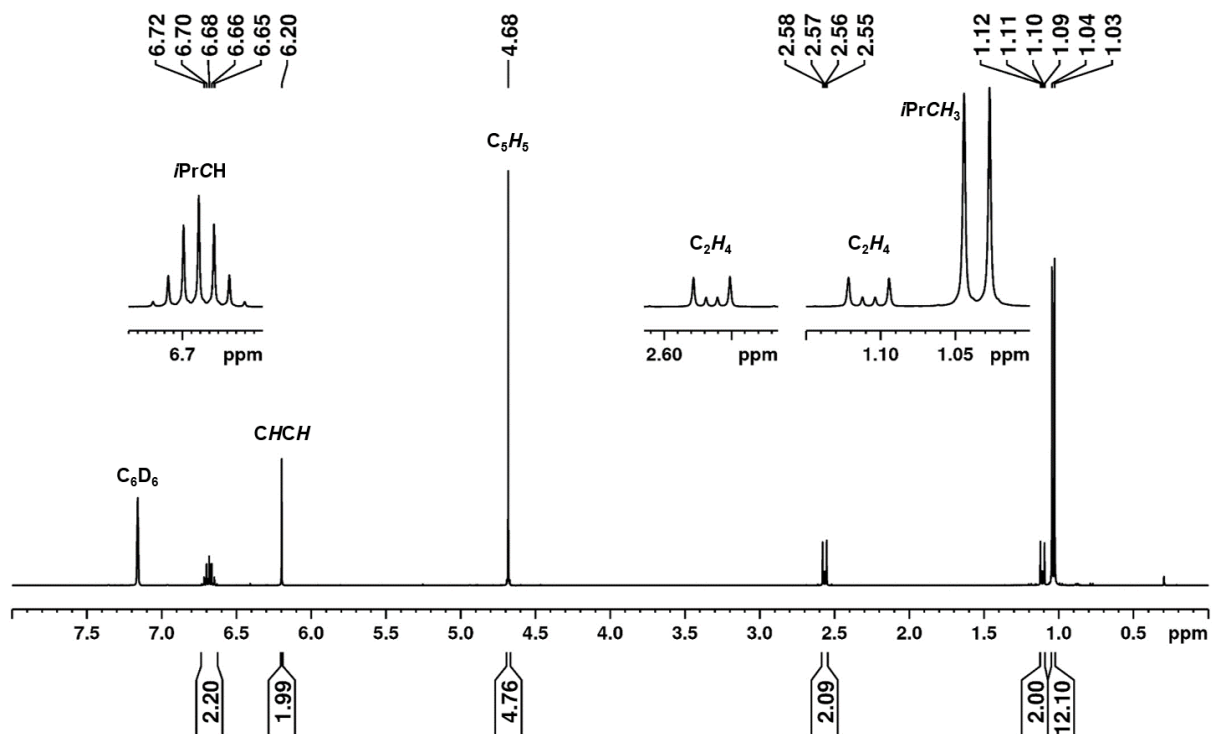


Figure S5: ¹H NMR spectrum of complex [CpCo(*i*Pr₂Im)(η^2 -C₂H₄)] 2 in C₆D₆.

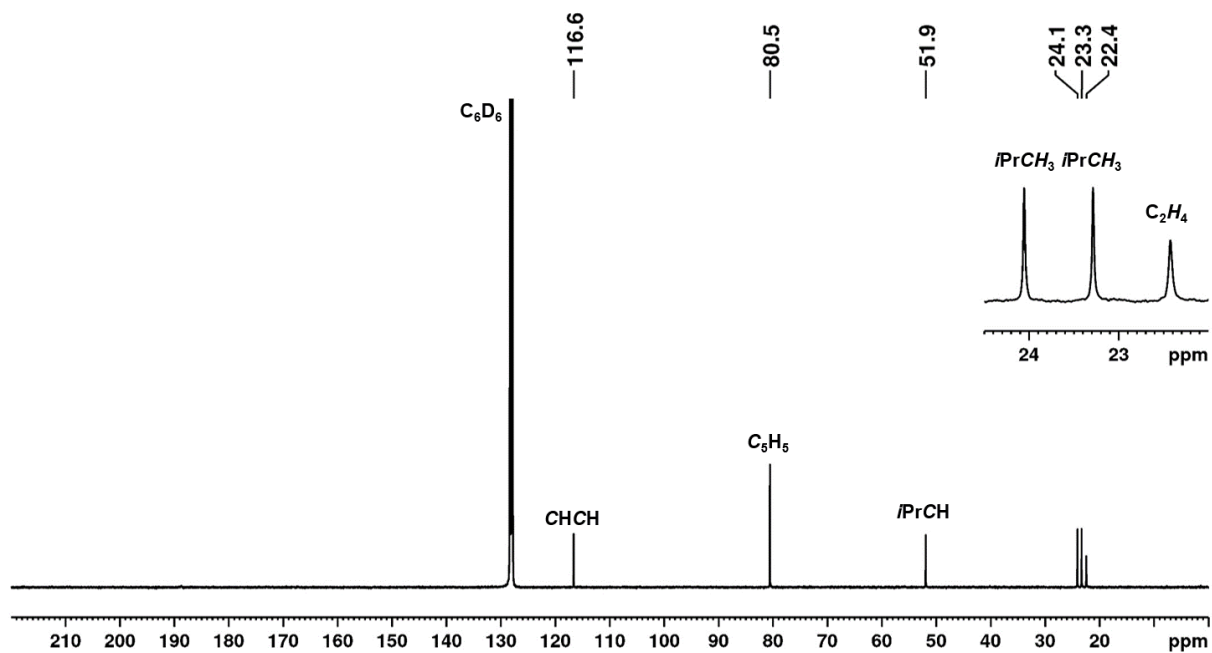


Figure S6: ¹³C{¹H} NMR spectrum of complex [CpCo(*i*Pr₂Im)(η^2 -C₂H₄)] 2 in C₆D₆.

[CpCo(Me₂Im)(η²-C₂H₃(SiMe₃)) 3

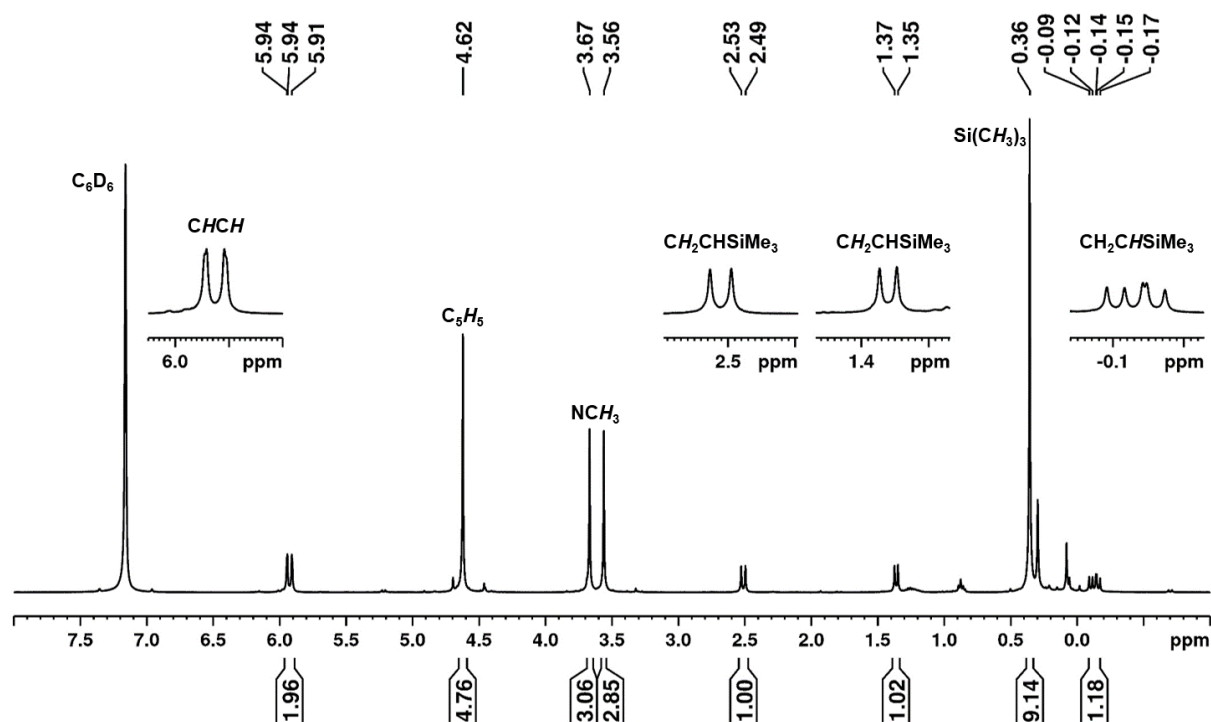


Figure S7: ¹H NMR spectrum of complex [CpCo(Me₂Im)(η²-C₂H₃(SiMe₃)) 3 in C₆D₆.

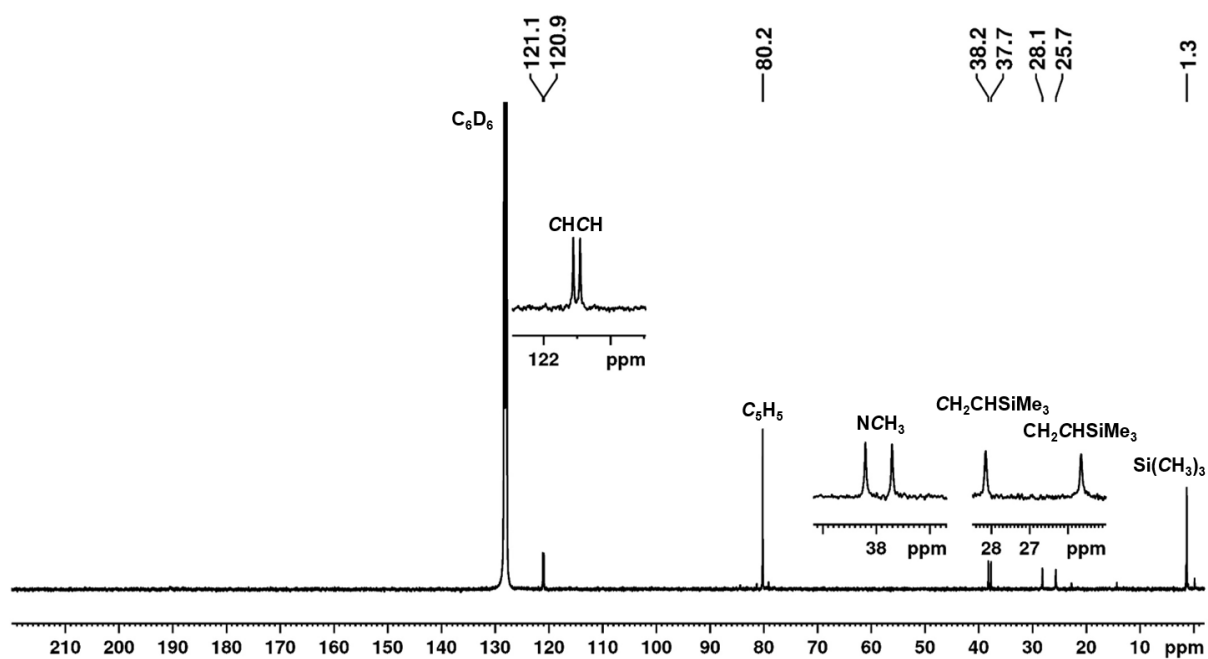


Figure S8: ¹³C{¹H} NMR spectrum of complex [CpCo(Me₂Im)(η²-C₂H₃(SiMe₃)) 3 in C₆D₆.

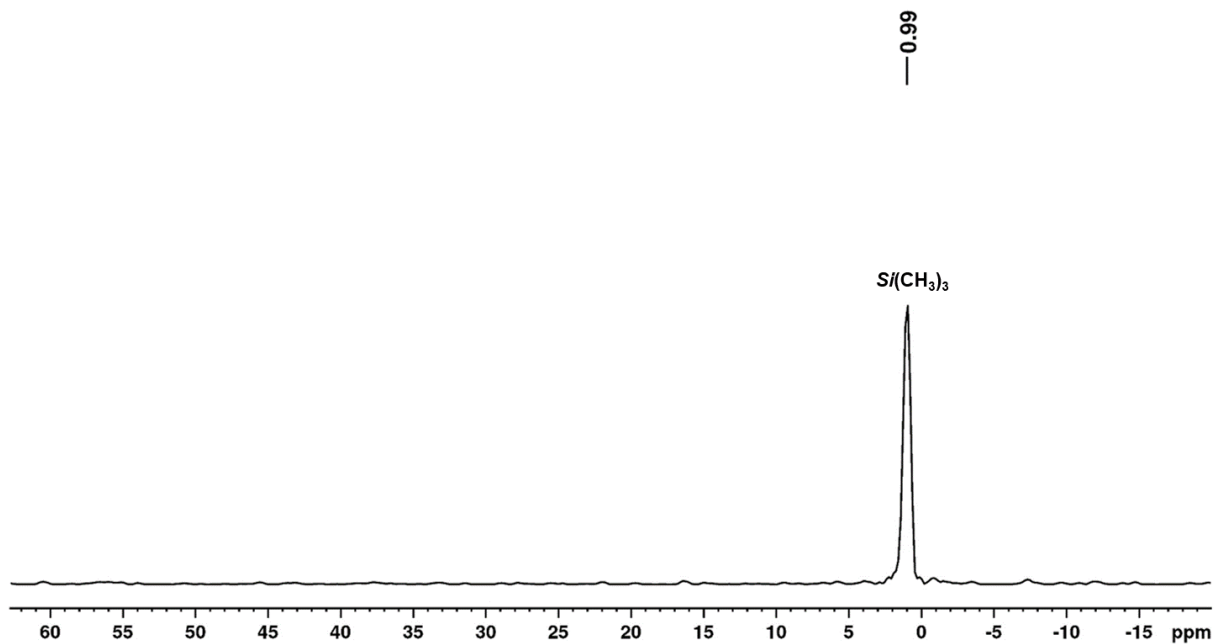


Figure S9: ^{29}Si NMR spectrum of complex $[\text{CpCo}(\text{Me}_2\text{Im})(\eta^2\text{-C}_2\text{H}_3(\text{SiMe}_3))]$ **3** in C_6D_6 .

$[\text{CpCo}(i\text{Pr}_2\text{Im})(\eta^2\text{-C}_2\text{H}_3(\text{SiMe}_3))]$ **4**

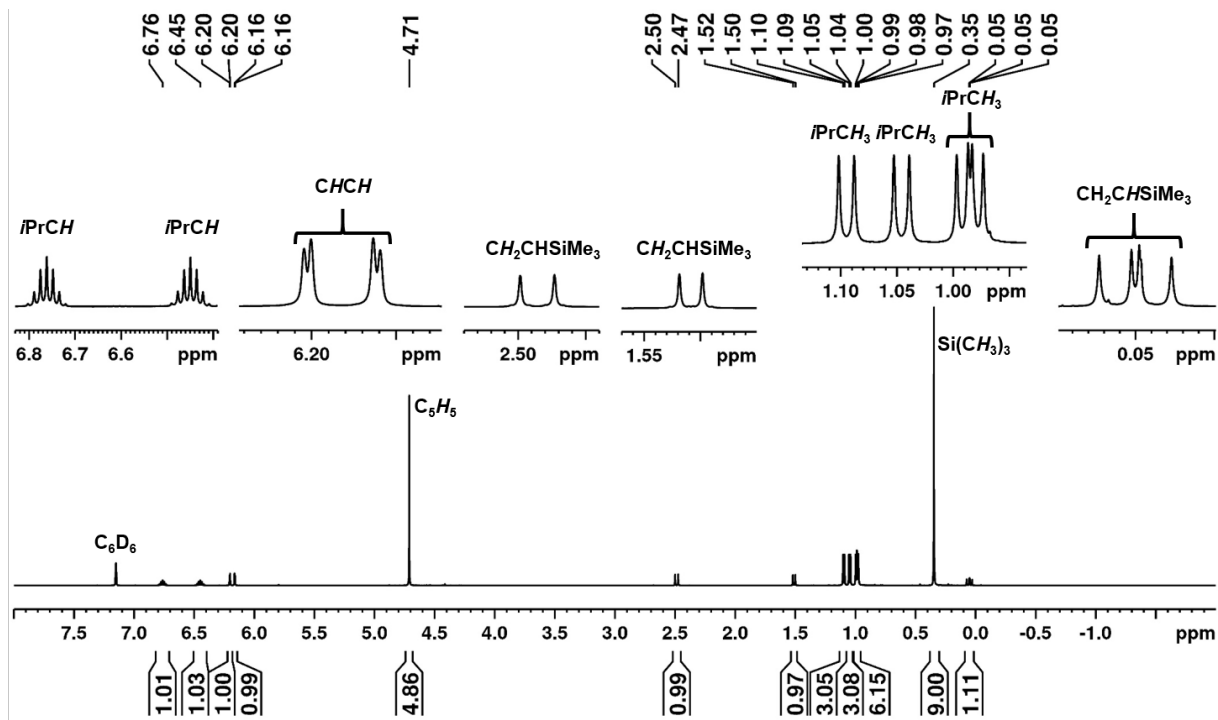


Figure S10: ^1H NMR spectrum of complex $[\text{CpCo}(i\text{Pr}_2\text{Im})(\eta^2\text{-C}_2\text{H}_3(\text{SiMe}_3))]$ **4** in C_6D_6 .

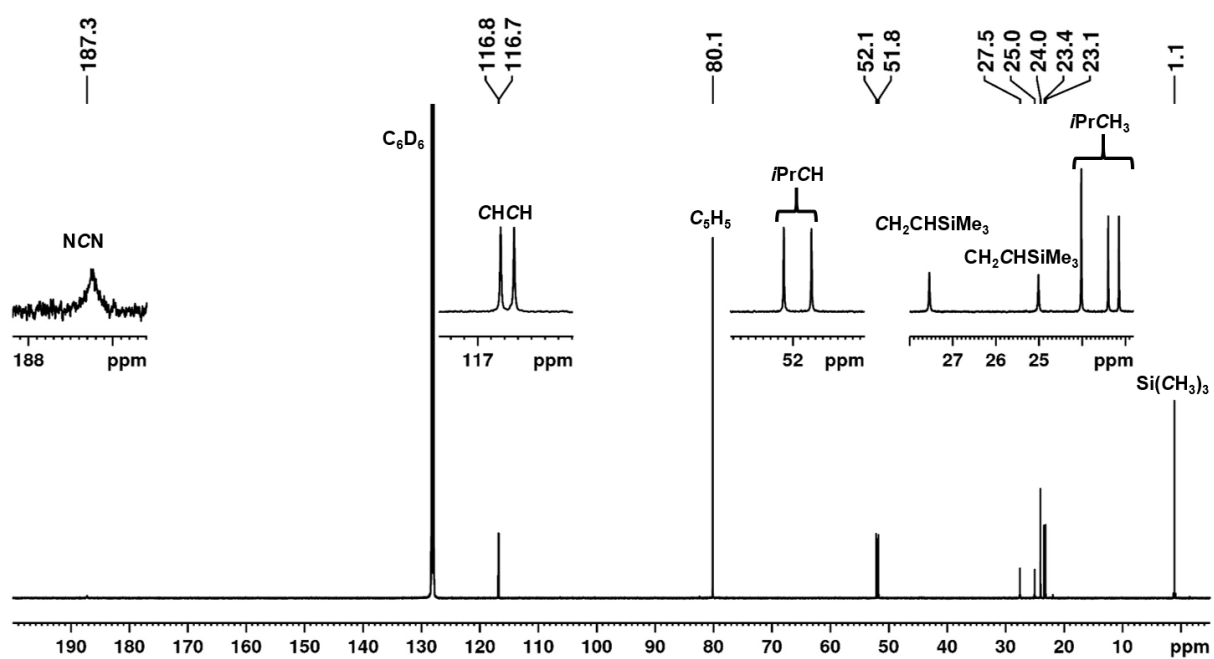


Figure S11: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex $[\text{CpCo}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_2\text{H}_3(\text{SiMe}_3))]$ **4** in C_6D_6 .

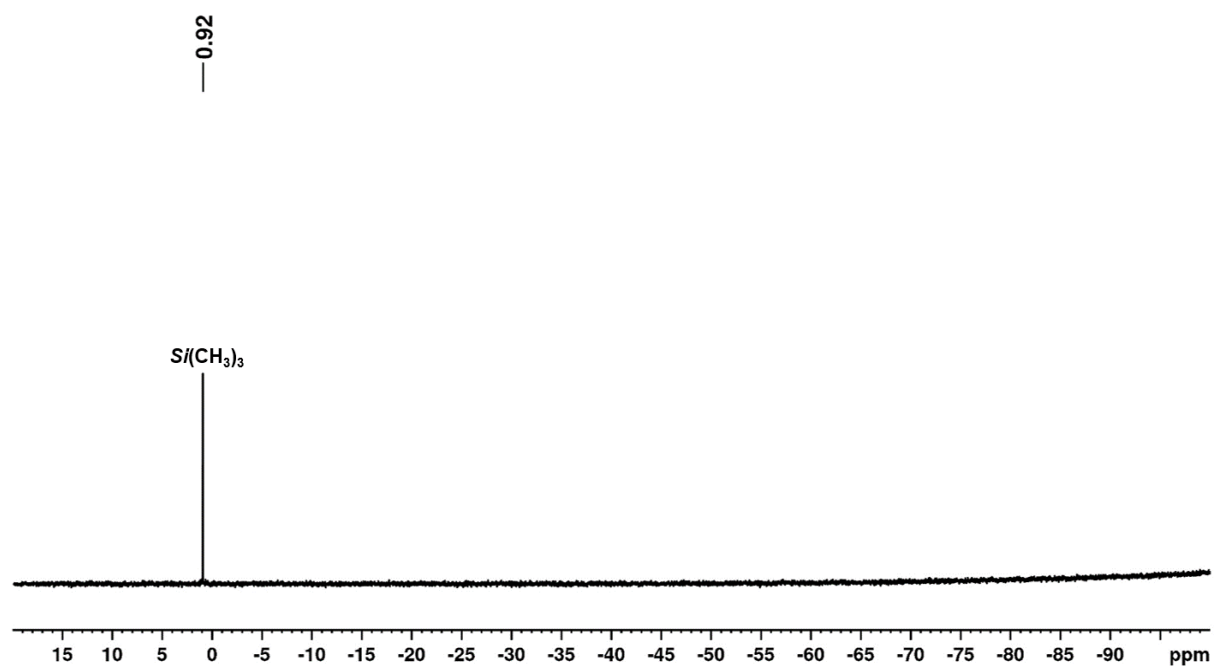


Figure S12: ^{29}Si NMR spectrum of complex $[\text{CpCo}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_2\text{H}_3(\text{SiMe}_3))]$ **4** in C_6D_6 .

[Cp*Co(Me₂Im){η²-C₂H₃(SiMe₃)}] 5

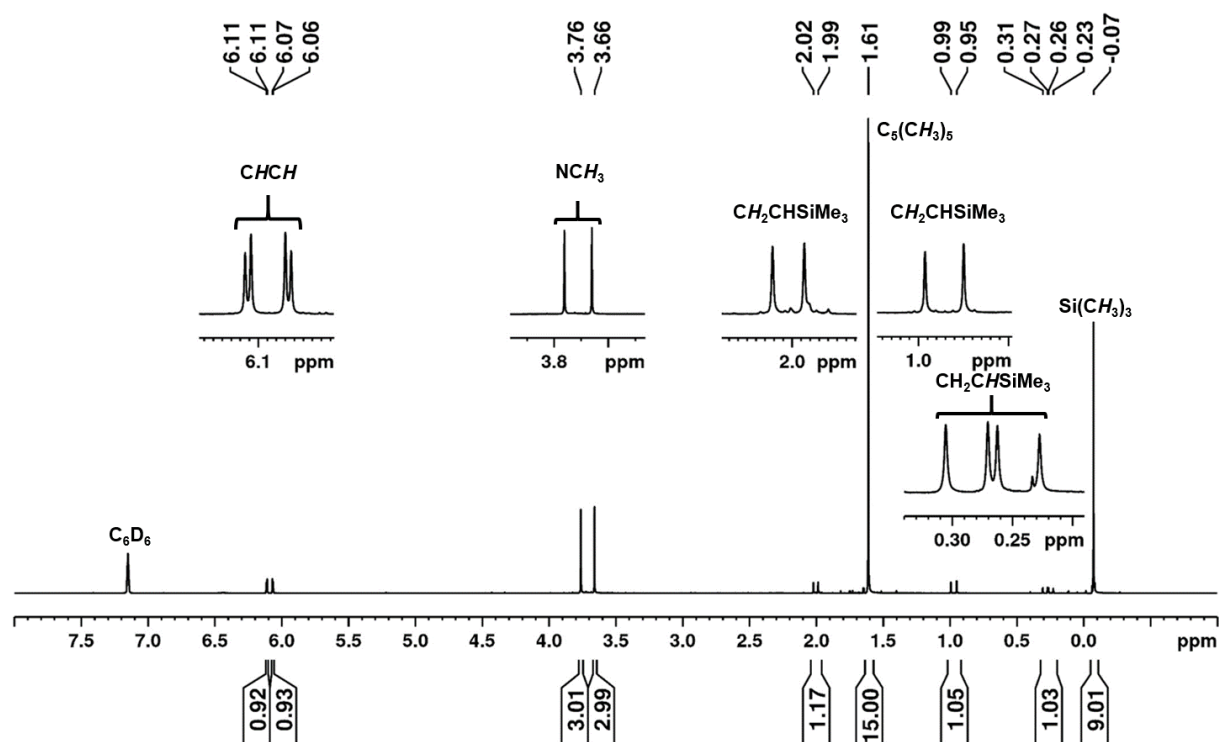


Figure S13: ¹H NMR spectrum of complex [Cp*Co(Me₂Im)(η²-C₂H₃(SiMe₃))] **5** in C₆D₆.

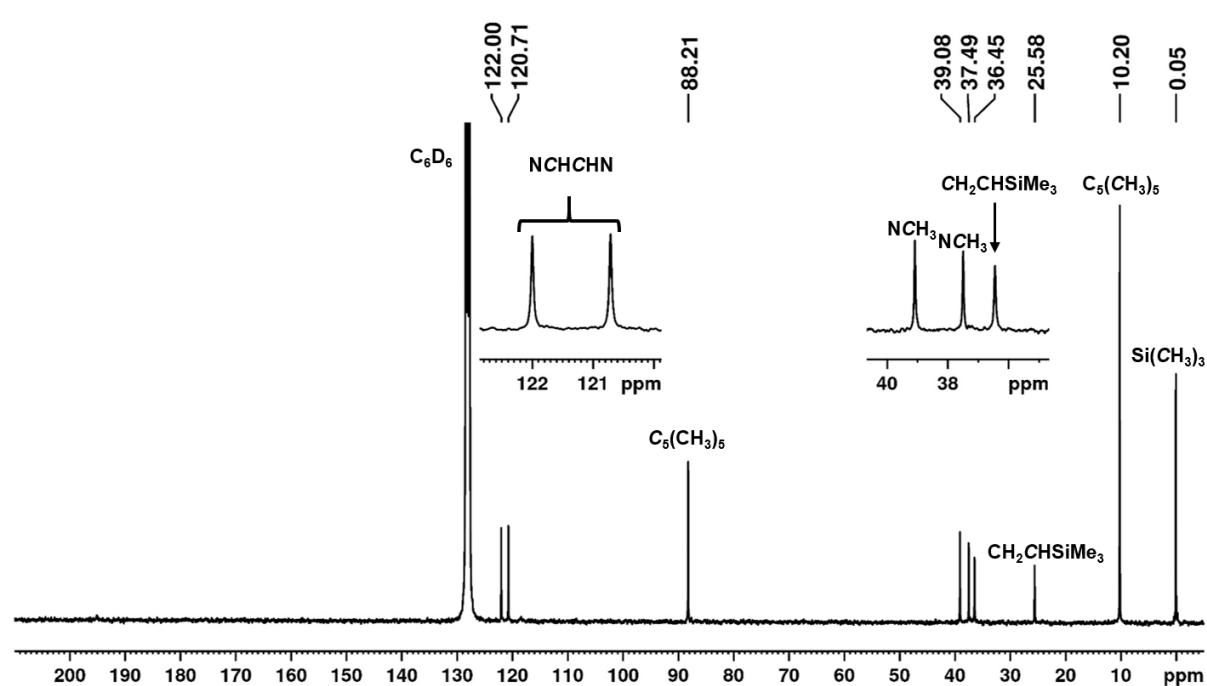


Figure S14: ¹³C{¹H} NMR spectrum of complex [Cp*Co(Me₂Im)(η²-C₂H₃(SiMe₃))] **5** in C₆D₆.

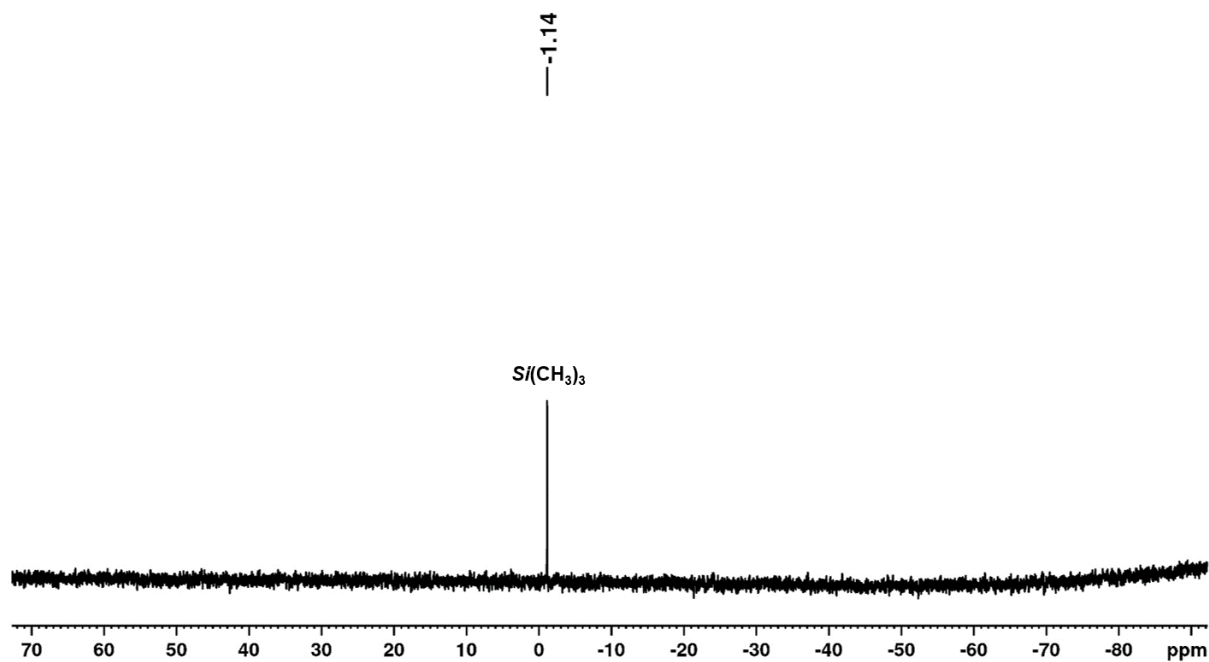


Figure S15: ²⁹Si NMR spectrum of complex [Cp*Co(Me₂Im)(η²-C₂H₃(SiMe₃))] **5** in C₆D₆.

[Cp*Co(*i*Pr₂Im)(η²-C₂H₃(SiMe₃))] **6**

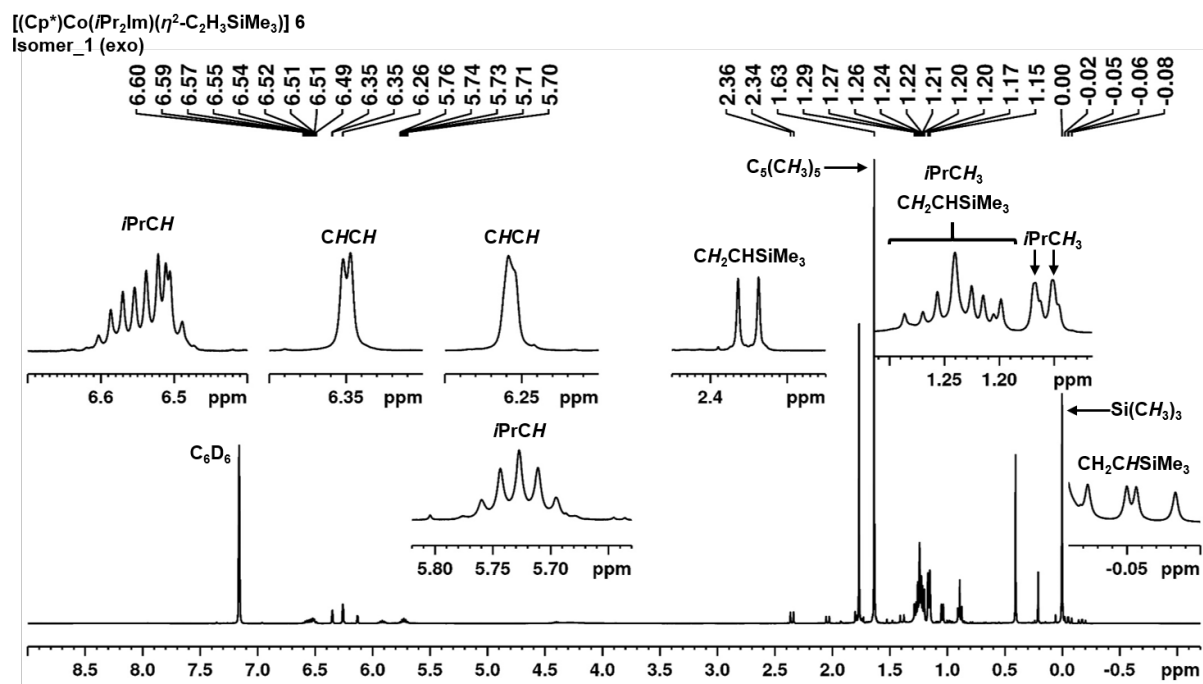


Figure S16: ¹H NMR spectrum of isomer mixture of complex [Cp*Co(*i*Pr₂Im)(η²-C₂H₃(SiMe₃))] **6** in C₆D₆ (isomer I is marked).

[[Cp*Co(*i*Pr₂Im)(η²-C₂H₃SiMe₃)] 6
Isomer_2 (endo)

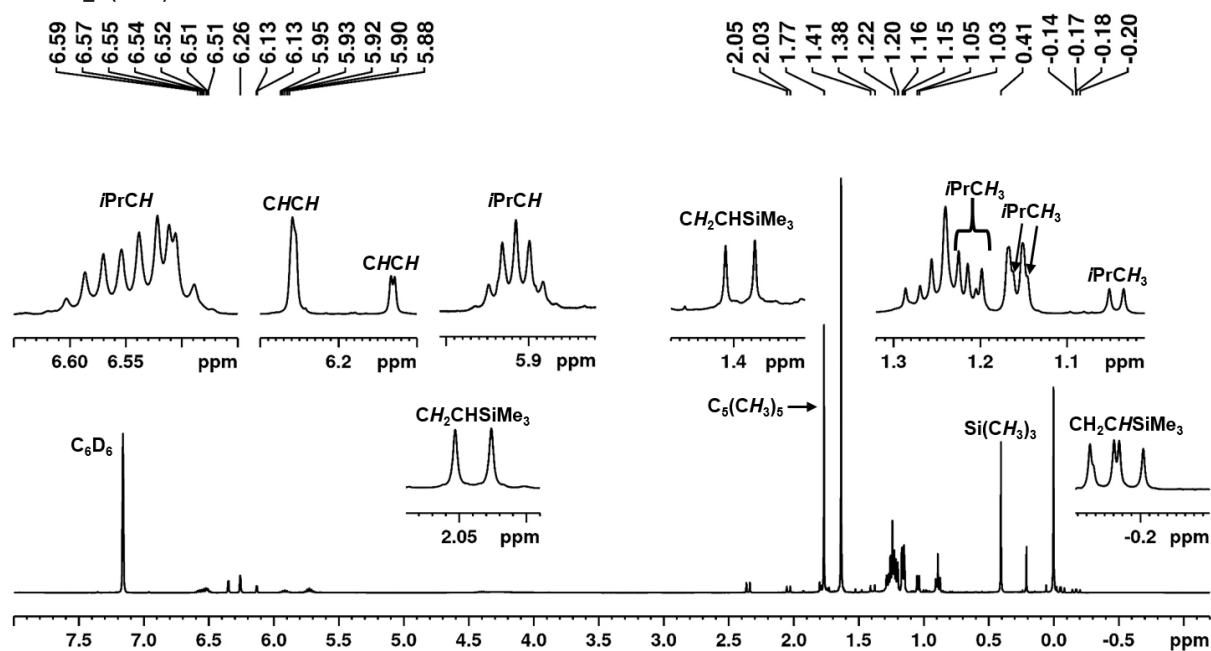


Figure S17: ¹H NMR spectrum of isomer mixture of complex [Cp*Co(*i*Pr₂Im)(η²-C₂H₃(SiMe₃))] **6** in C₆D₆ (isomer II is marked).

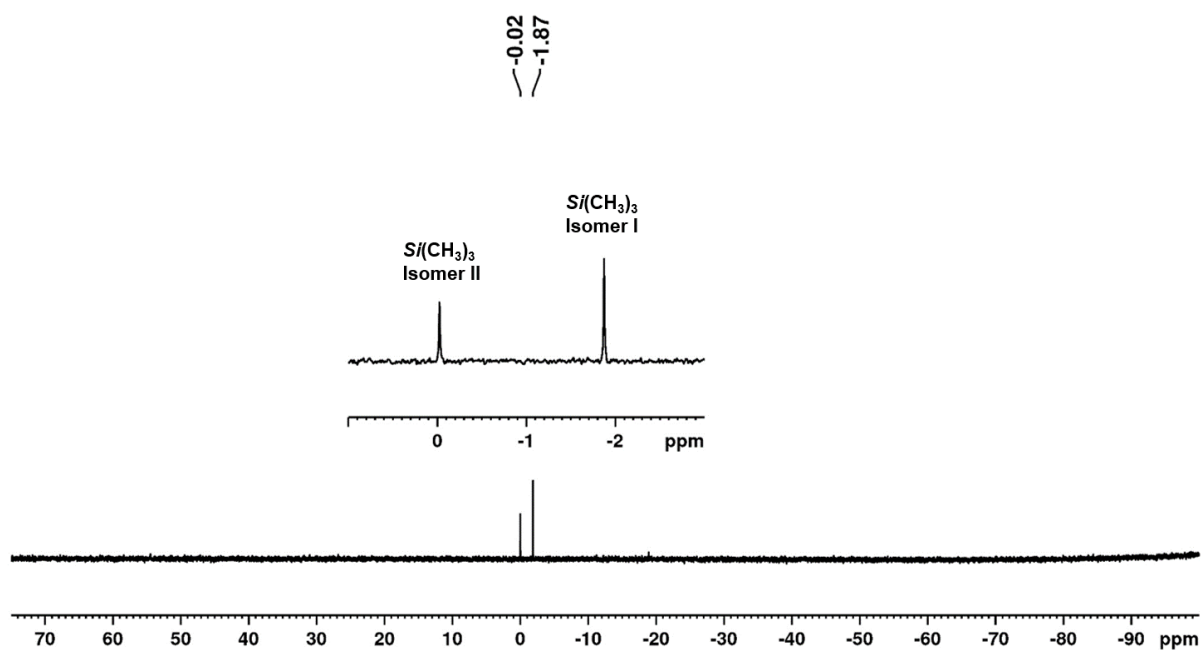


Figure S18: ²⁹Si NMR (99.4 MHz) spectrum of isomer mixture of complex [Cp*Co(*i*Pr₂Im)(η²-C₂H₃(SiMe₃))] **6** in C₆D₆.

[{CpCo(Me₂Im)}₂(η²,η²-C₆F₆)] 13

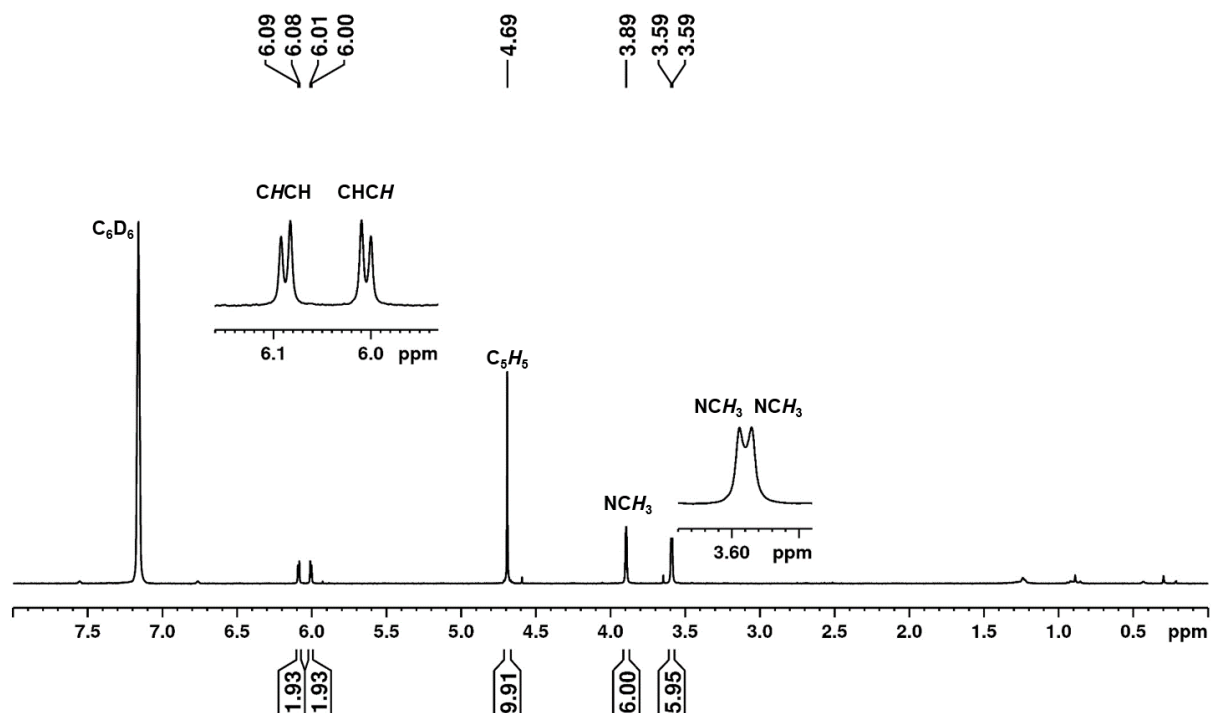


Figure S19: ¹H NMR spectrum of complex [{CpCo(Me₂Im)}₂(η²,η²-C₆F₆)] **13** in C₆D₆.

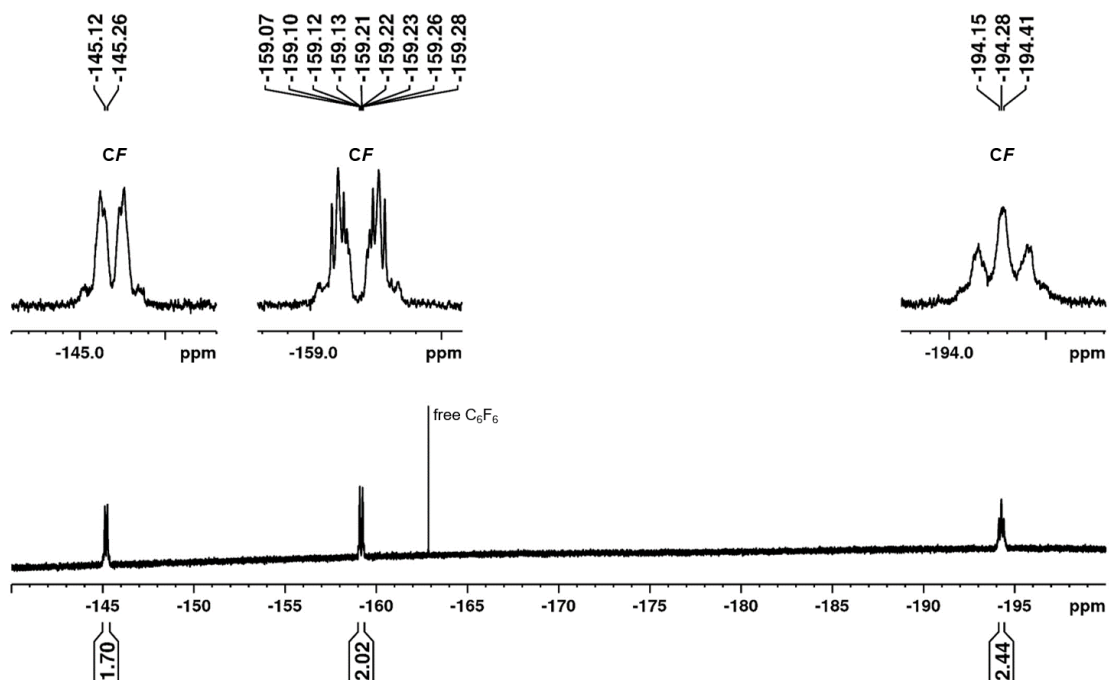


Figure S20: ¹⁹F-NMR spectrum of complex [{CpCo(Me₂Im)}₂(η²,η²-C₆F₆)] **13** in C₆D₆.

[{CpCo(*i*Pr₂Im)}₂(η²,η²-C₆F₆)] **14**

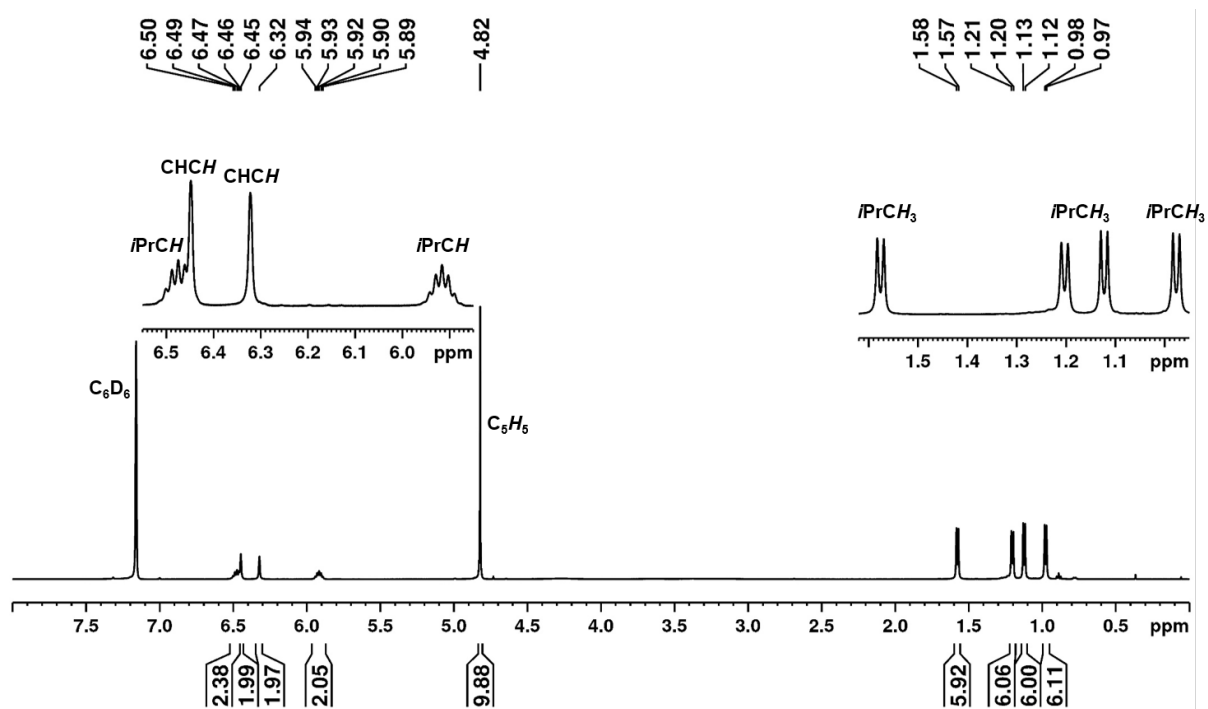


Figure S21: ¹H-NMR spectrum of complex [{CpCo(*i*Pr₂Im)}₂(η²,η²-C₆F₆)] **14** in C₆D₆.

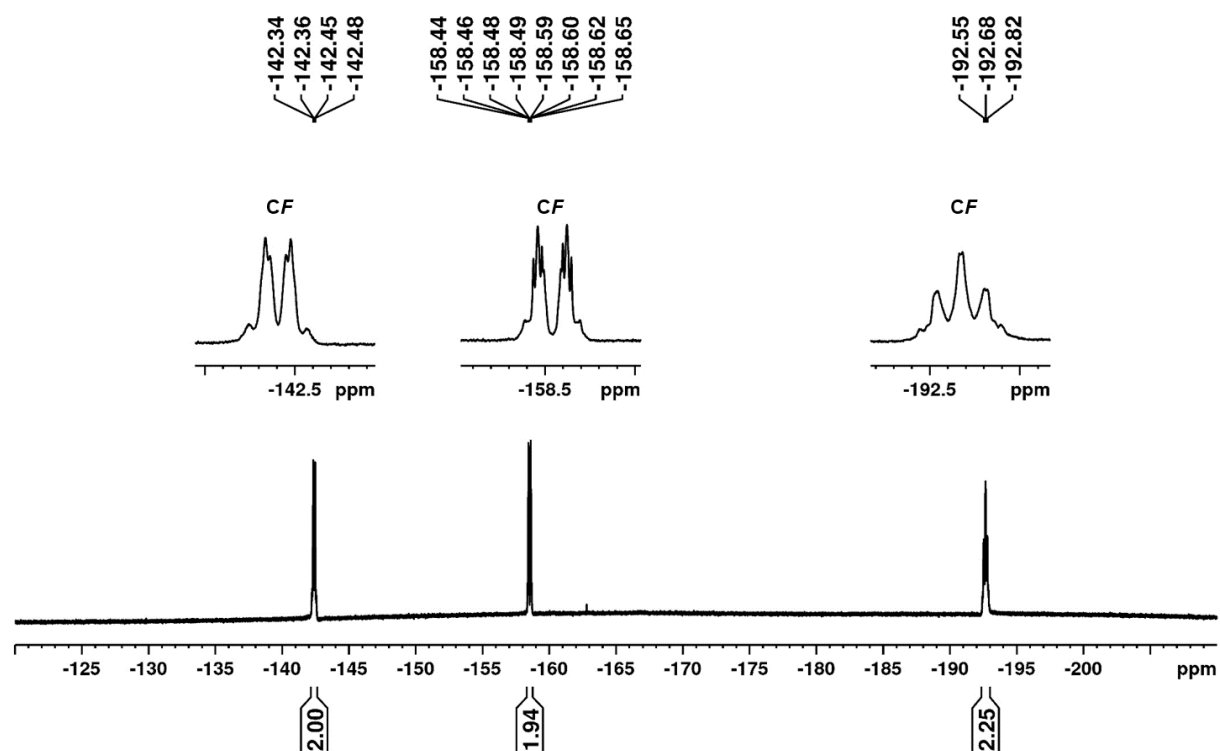


Figure S22: ¹⁹F-NMR spectrum of complex [{CpCo(*i*Pr₂Im)}₂(η²,η²-C₆F₆)] **14** in C₆D₆.

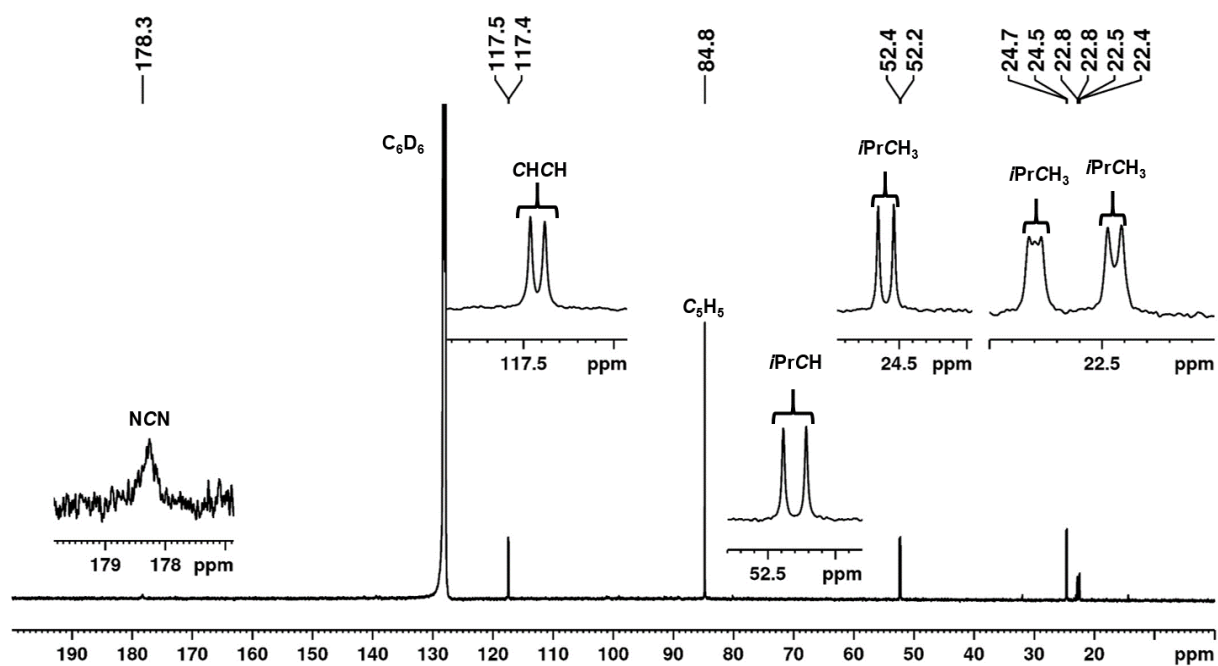


Figure S23: ^{13}C -NMR spectrum of complex $[\{\text{CpCo}(\text{iPr}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_6\text{F}_6)]$ **14** in C_6D_6 .

$[\{\text{CpCo}(\text{Me}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_7\text{F}_8)]$ **15**

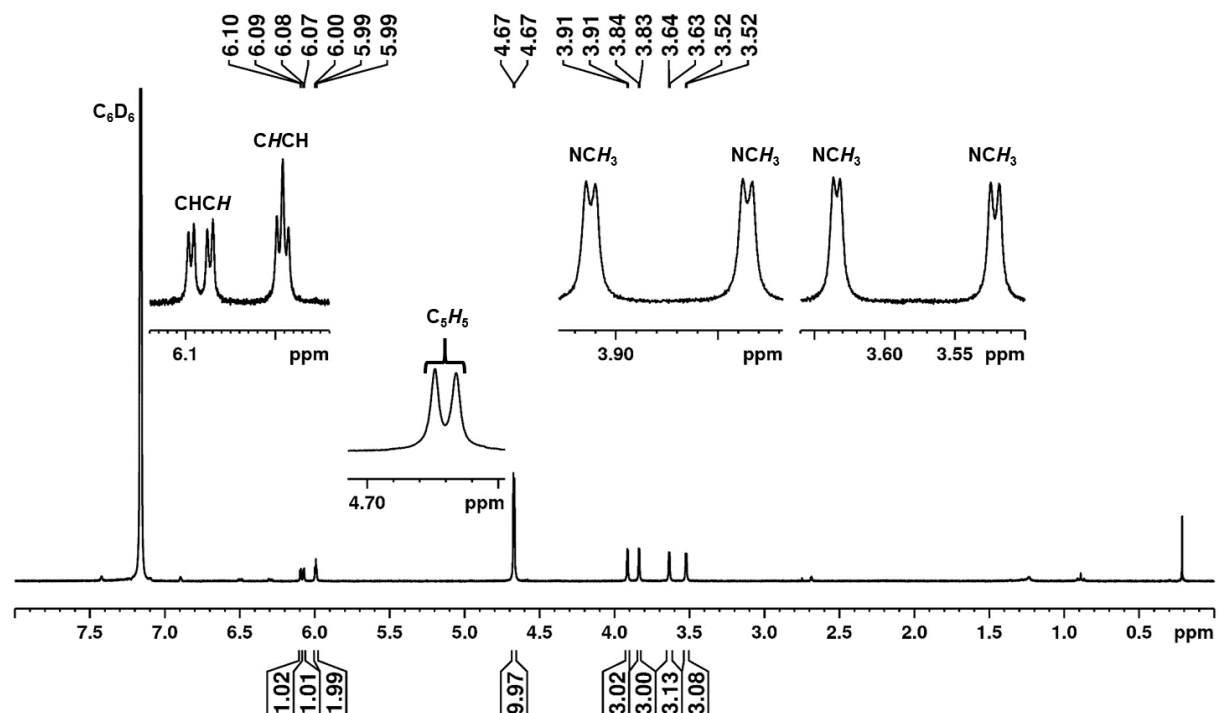


Figure S24: ^1H -NMR spectrum of complex $[\{\text{CpCo}(\text{Me}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_7\text{F}_8)]$ **15** in C_6D_6 .

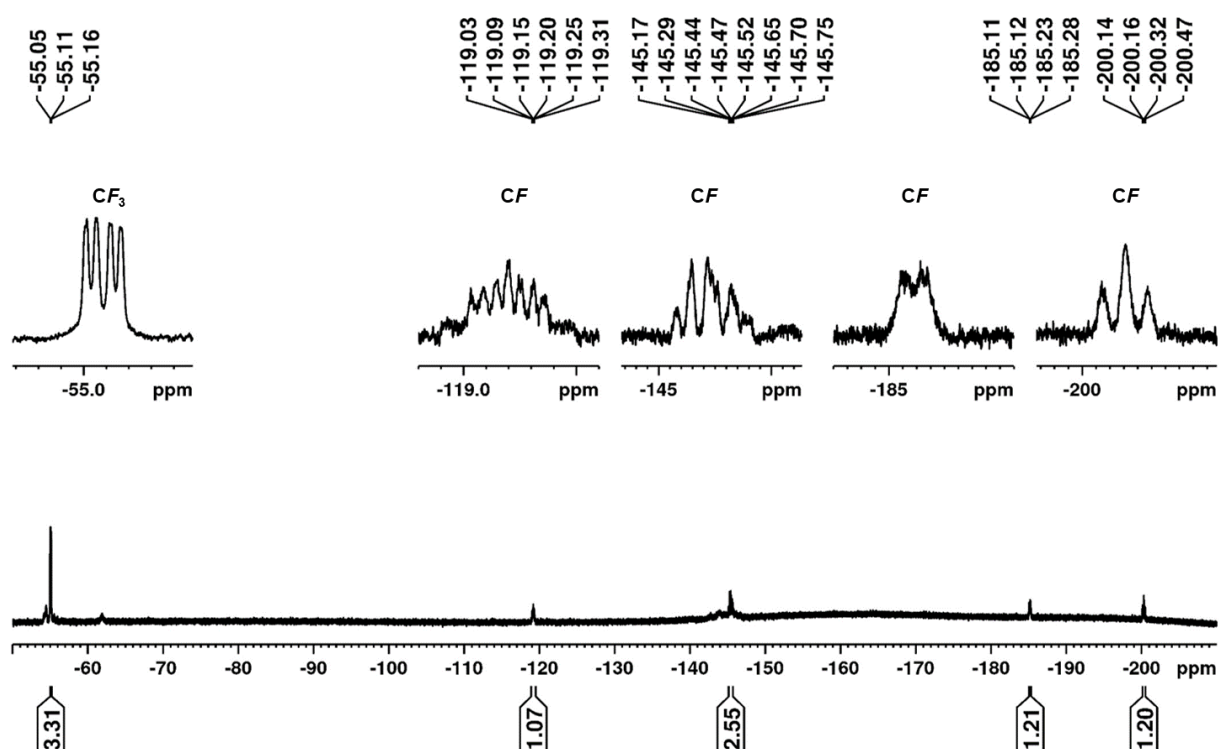


Figure S25: ^{19}F -NMR spectrum of complex $[\{\text{CpCo}(\text{Me}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_7\text{F}_8)]$ **15** in C_6D_6 .

$[\{\text{CpCo}(\text{iPr}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_7\text{F}_8)]$ **16**

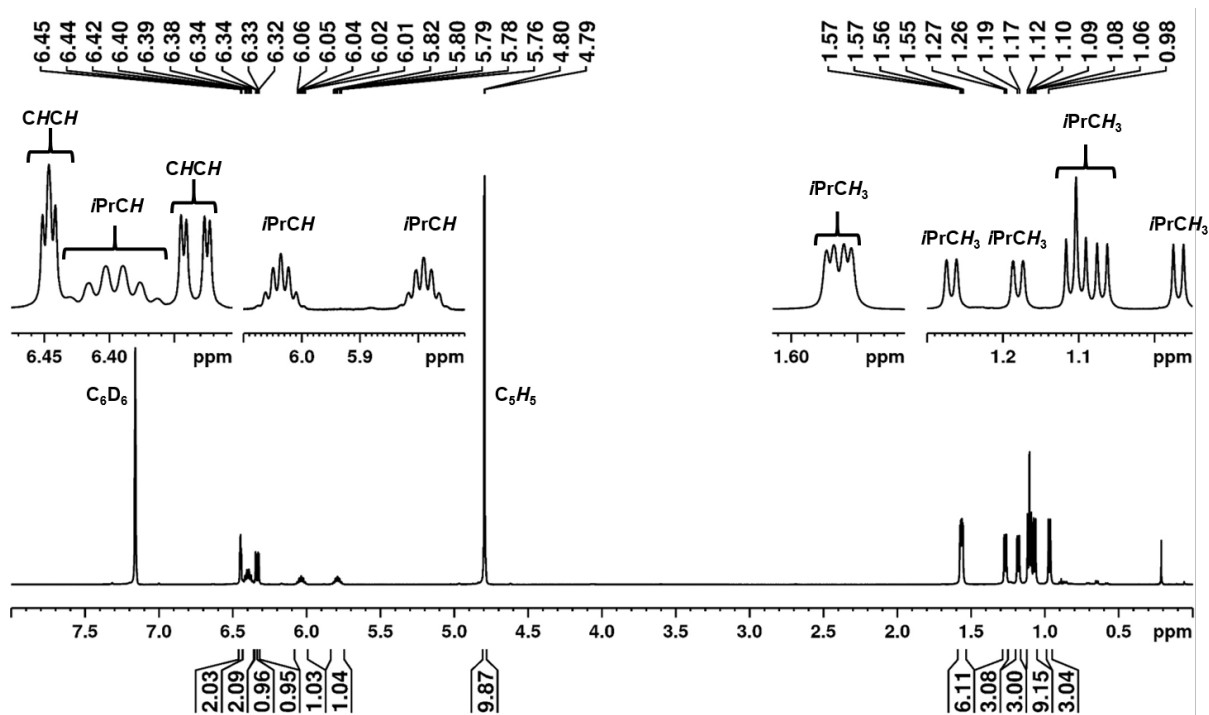


Figure S26: ^1H -NMR spectrum of complex $[\{\text{CpCo}(\text{iPr}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_7\text{F}_8)]$ **16** in C_6D_6 .

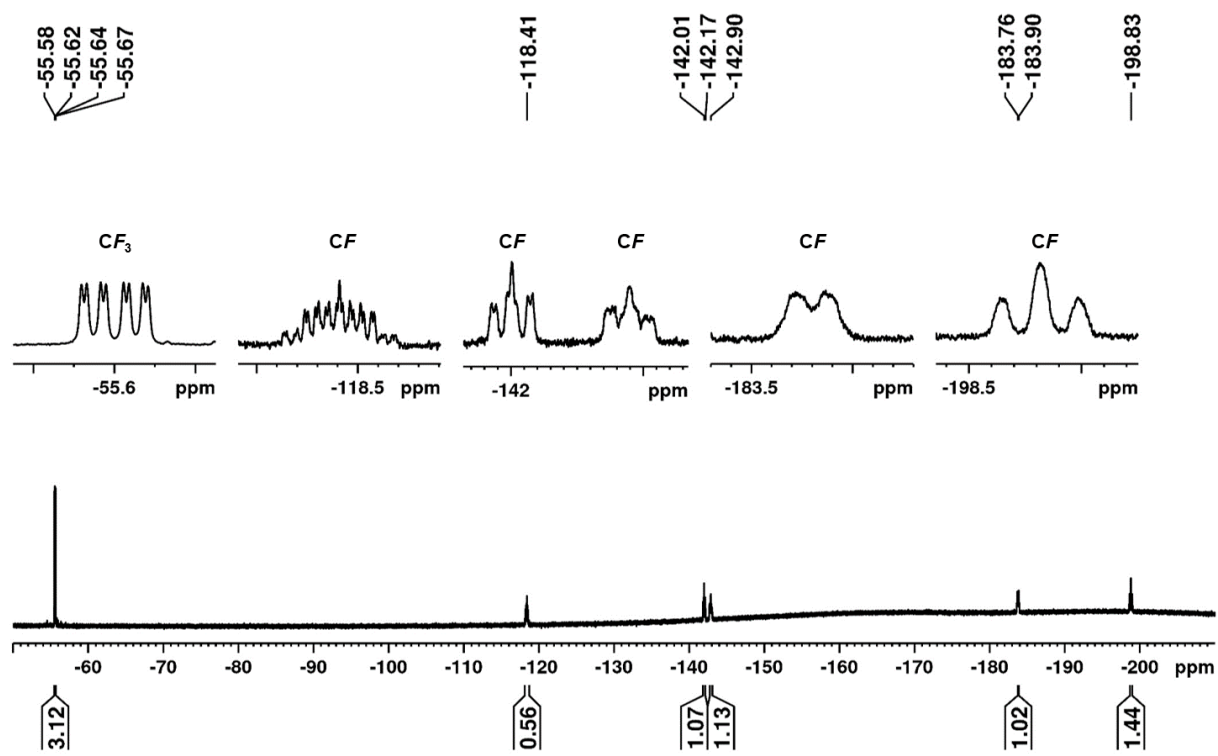


Figure S27: ^{19}F -NMR spectrum of complex $[(CpCo(iPr_2Im))_2(\eta^2, \eta^2-C_7F_8)]$ **16** in C_6D_6 .

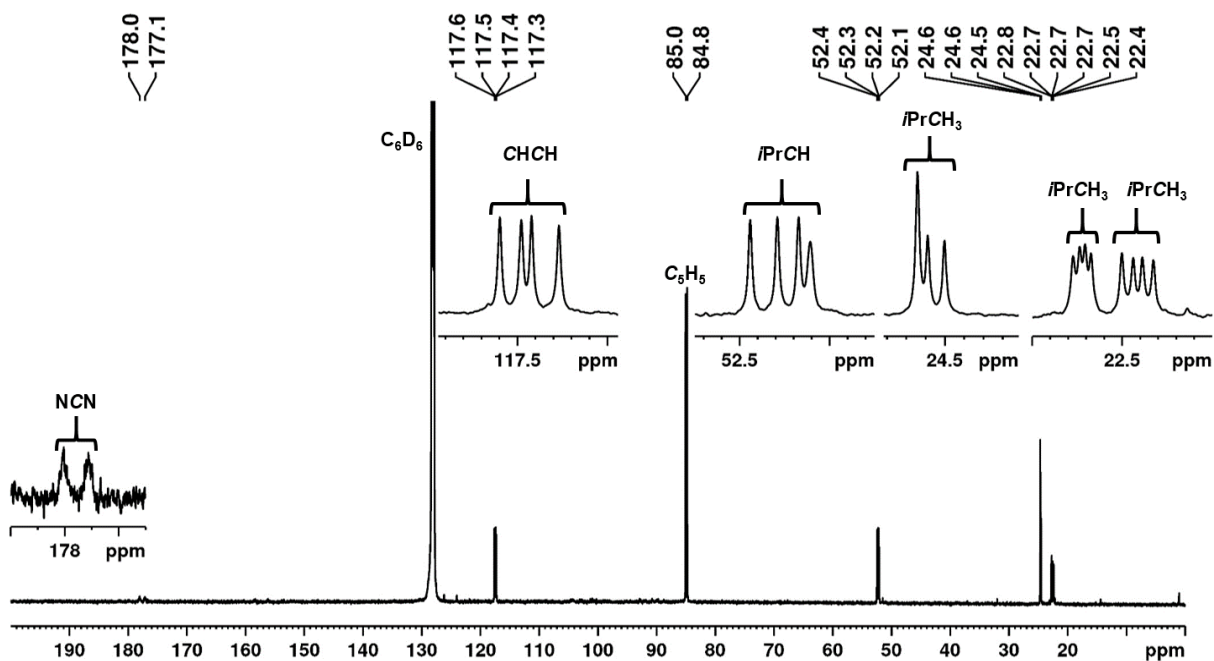


Figure S28: ^{13}C -NMR spectrum of complex $[(CpCo(iPr_2Im))_2(\eta^2, \eta^2-C_7F_8)]$ **16** in C_6D_6 .

[[CpCo(Me₂Im)]₂(η²,η²-C₁₀F₈)] 17

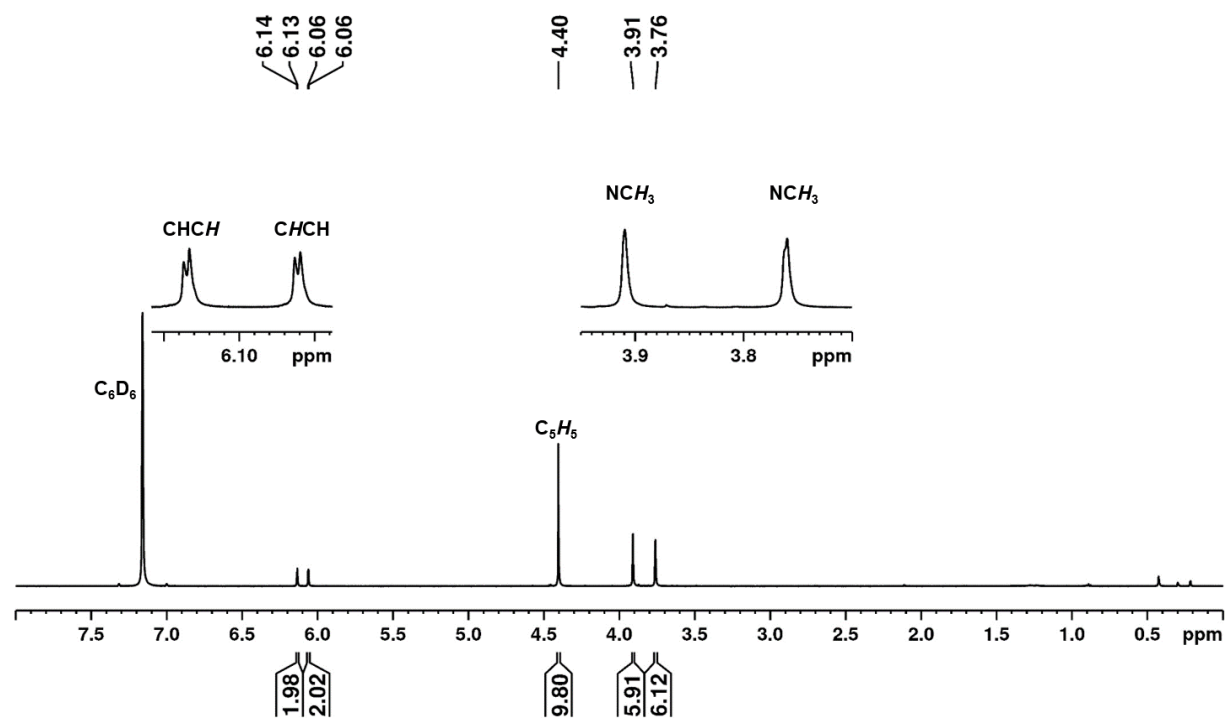


Figure S29: ¹H-NMR spectrum of complex [[CpCo(Me₂Im)]₂(η²,η²-C₁₀F₈)] **17** in C₆D₆.

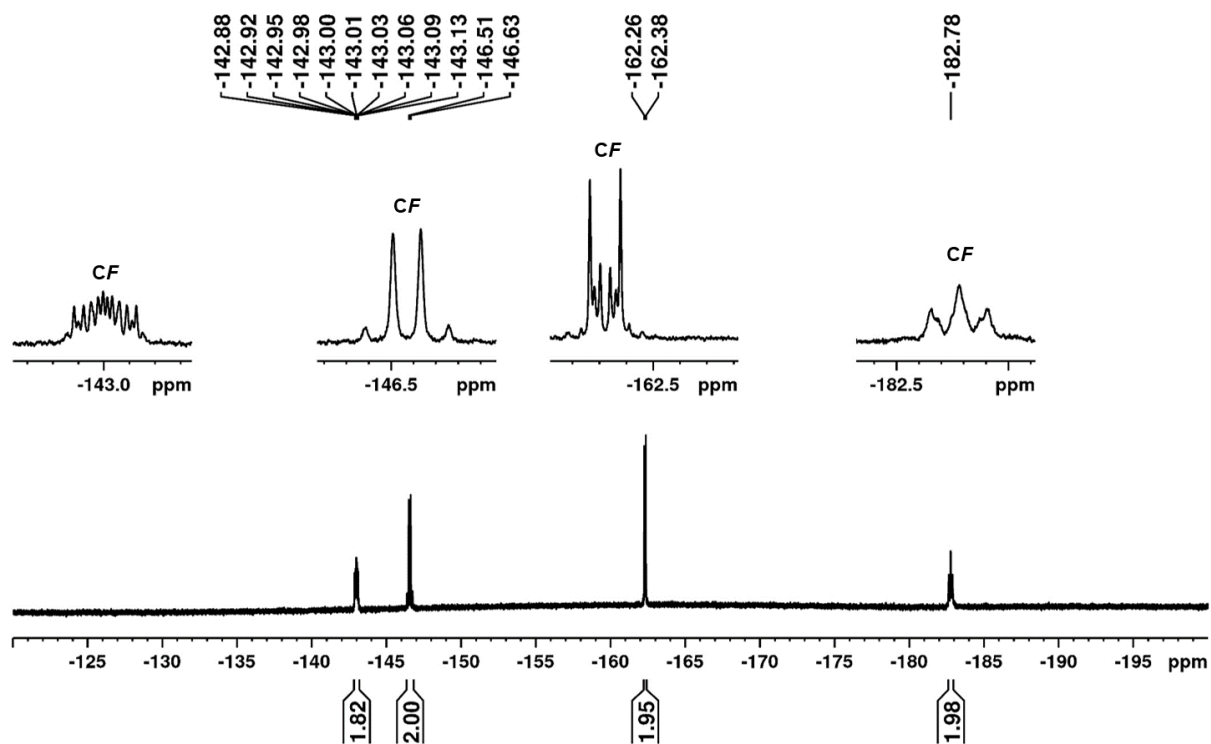


Figure S30: ¹⁹F-NMR spectrum of complex [[CpCo(Me₂Im)]₂(η²,η²-C₁₀F₈)] **17** in C₆D₆.

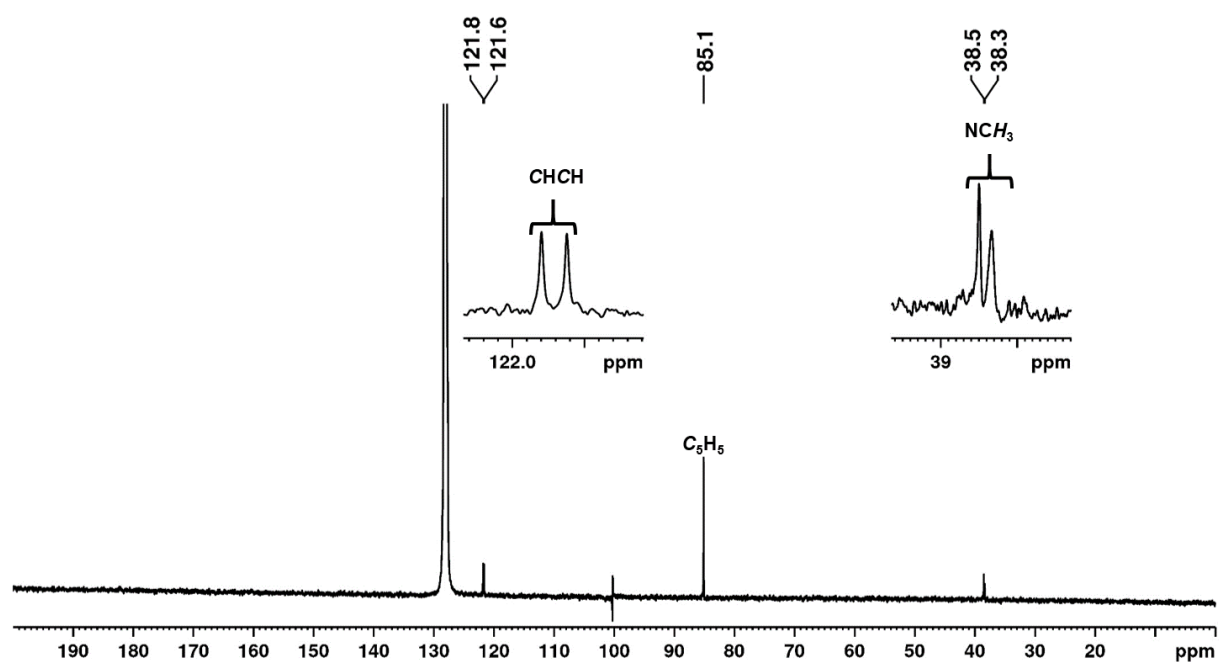


Figure S31: ^{13}C -NMR spectrum of complex $[\{\text{CpCo}(\text{Me}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_{10}\text{F}_8)]$ **17** in C_6D_6 .

$[\{\text{CpCo}(i\text{Pr}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_{10}\text{F}_8)]$ **18**

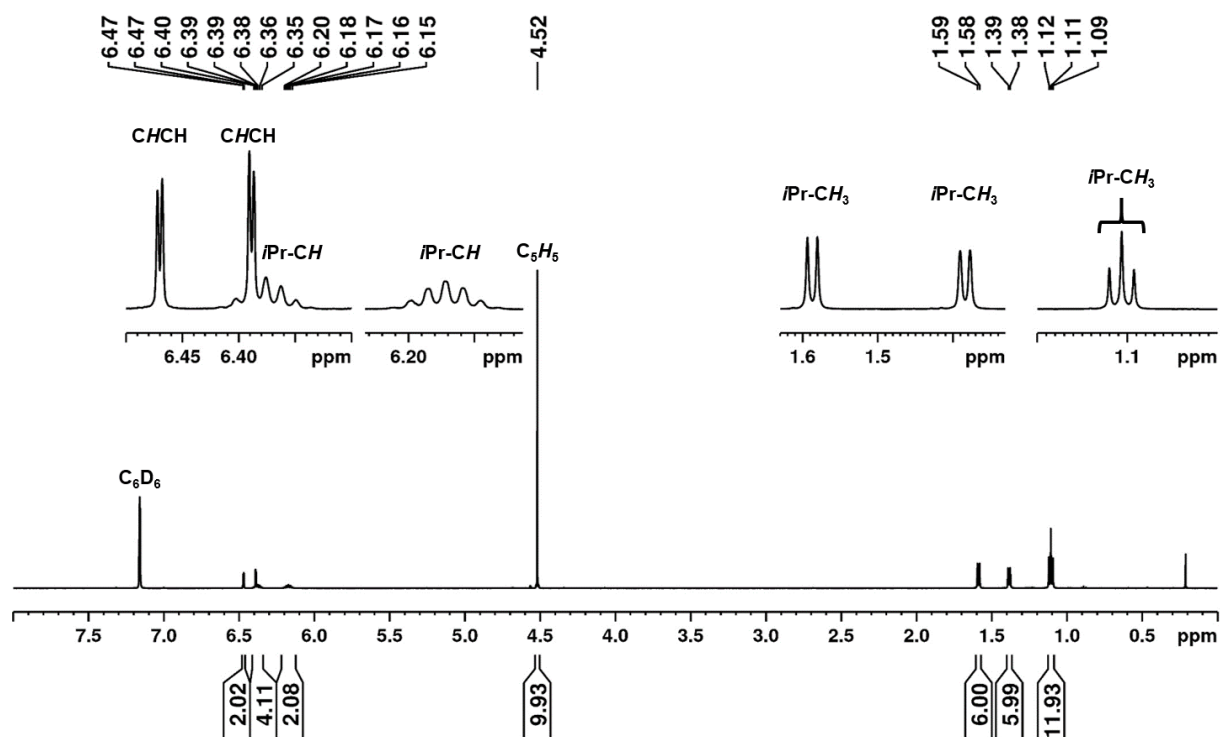


Figure S32: ^1H -NMR spectrum of complex $[\{\text{CpCo}(i\text{Pr}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_{10}\text{F}_8)]$ **18** in C_6D_6 .

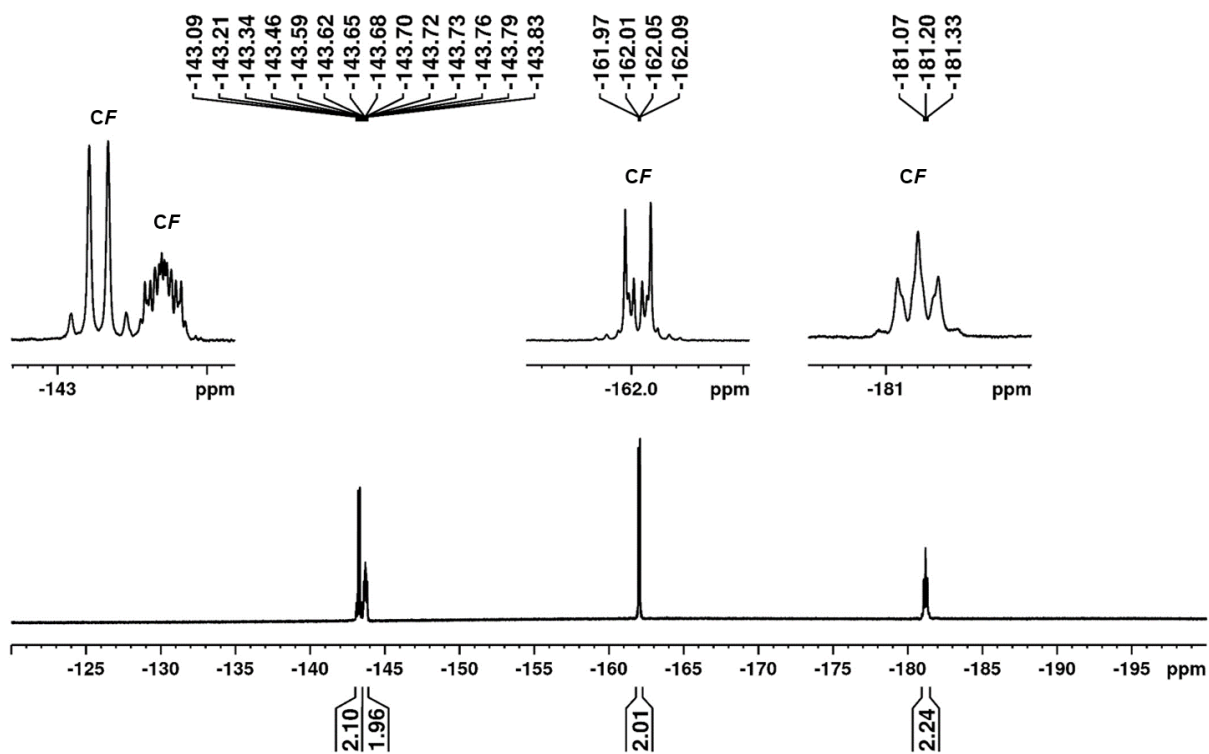


Figure S33: ^{19}F -NMR spectrum of complex $[\{\text{CpCo}(\text{iPr}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_{10}\text{F}_8)]$ **18** in C_6D_6 .

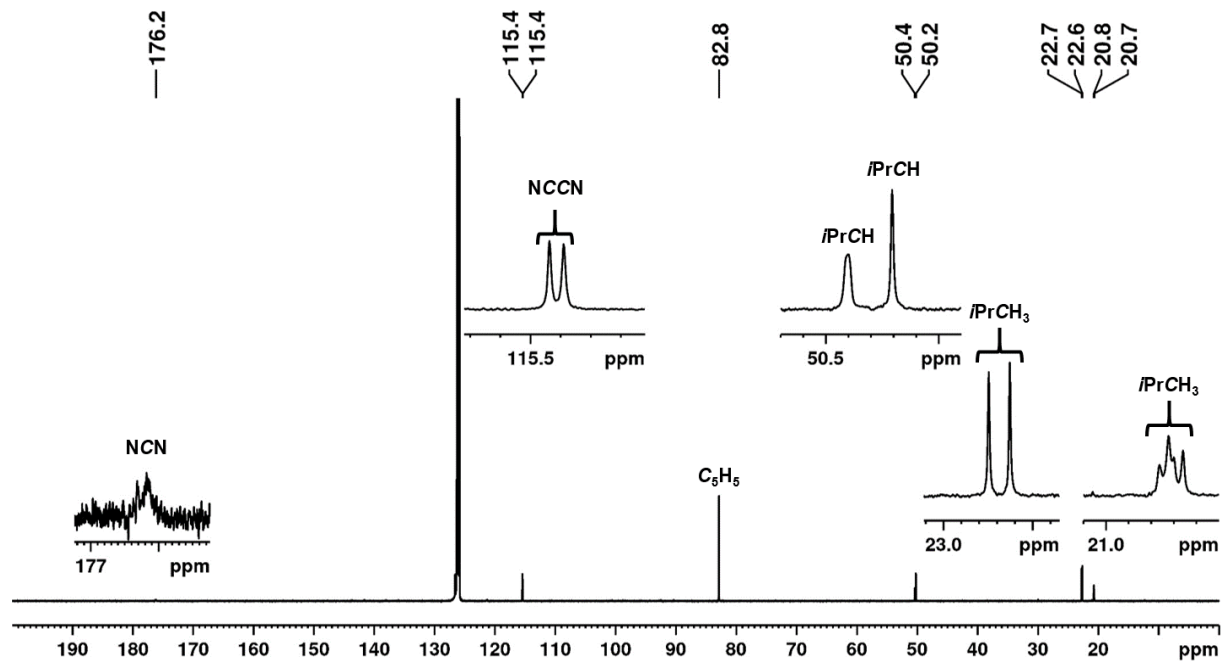


Figure S34: ^{13}C -NMR spectrum of complex $[\{\text{CpCo}(\text{iPr}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_{10}\text{F}_8)]$ **18** in C_6D_6 .

[CpCo(*i*Pr₂Im)(η^2 -C₁₀F₈)] **19**

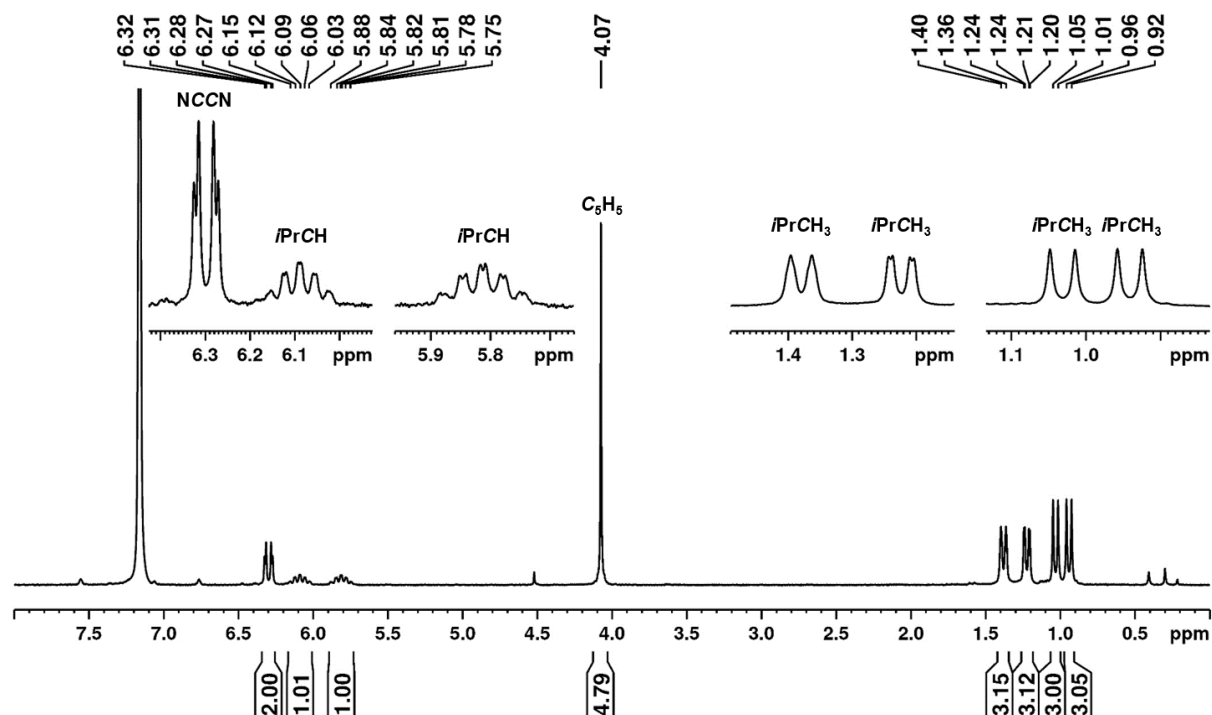


Figure S35: ¹H-NMR spectrum of complex [CpCo(*i*Pr₂Im)(η^2 -C₁₀F₈)] **19** in C₆D₆.

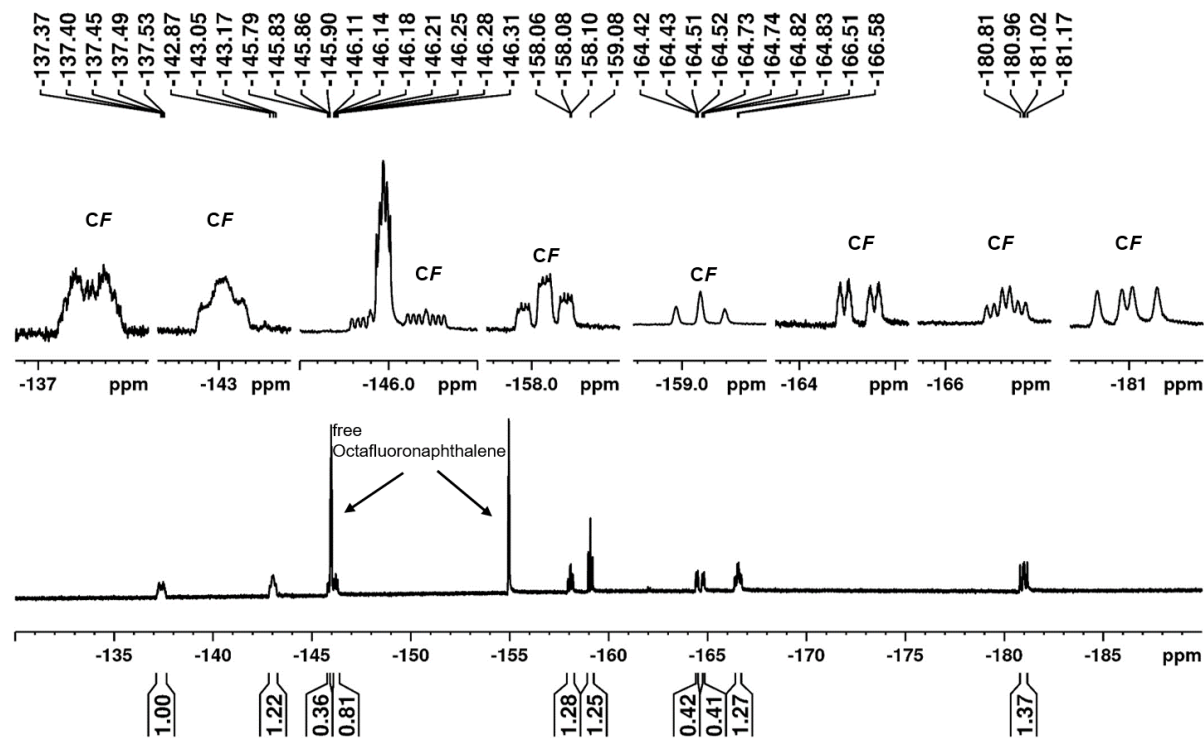


Figure S36: ¹⁹F-NMR spectrum of complex [CpCo(*i*Pr₂Im)(η^2 -C₁₀F₈)] **19** in C₆D₆.

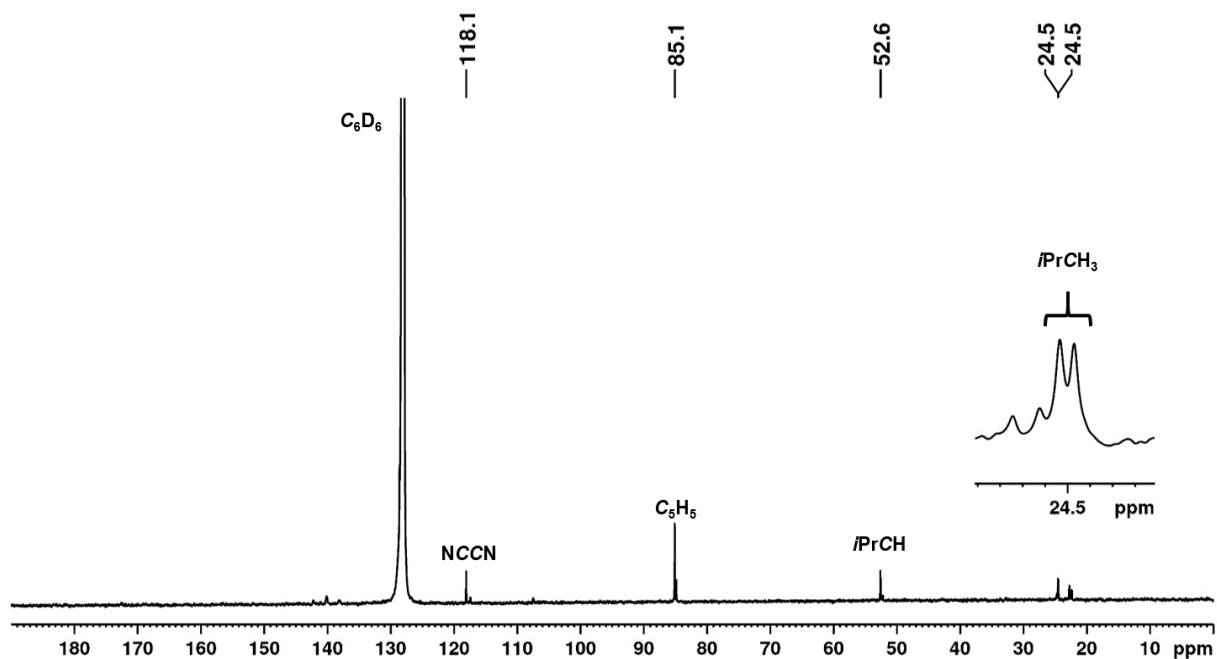


Figure S37: ^{13}C -NMR spectrum of complex $[\text{CpCo}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_{10}\text{F}_8)]$ **19** in C_6D_6 .

$[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_{10}\text{F}_8)]$ **20**

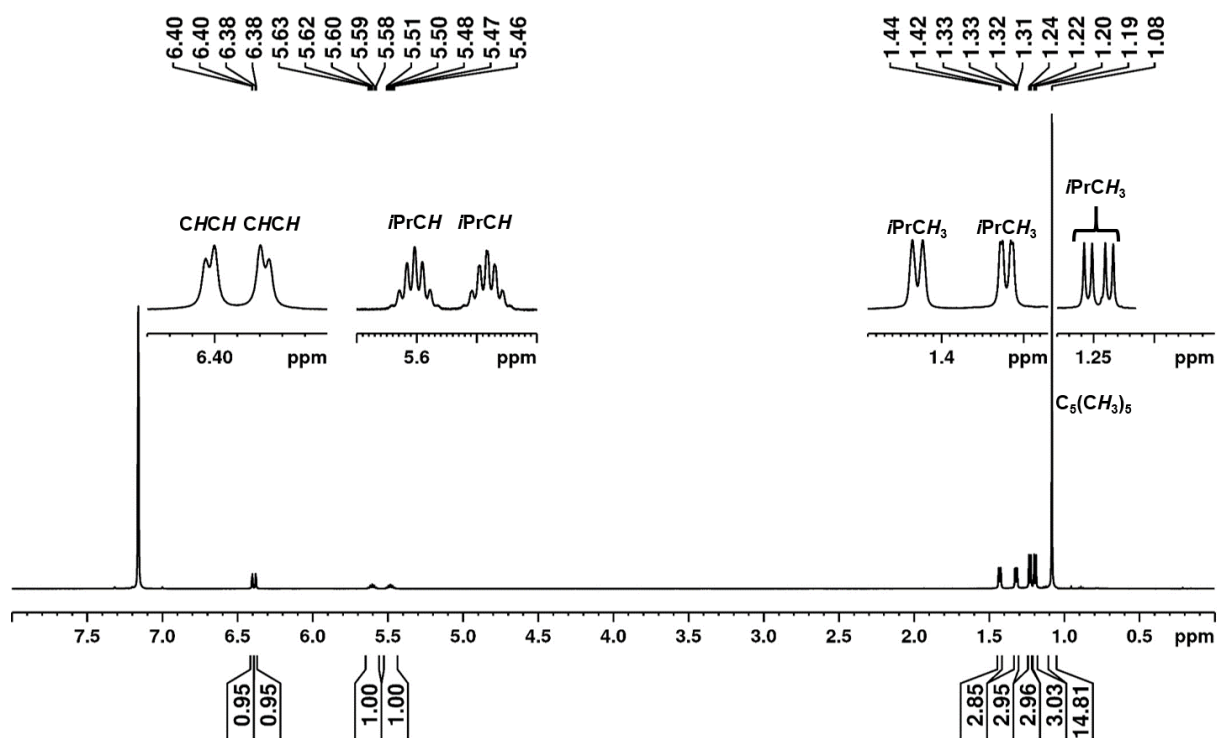


Figure S38: ^1H -NMR spectrum of complex $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_{10}\text{F}_8)]$ **20** in C_6D_6 .

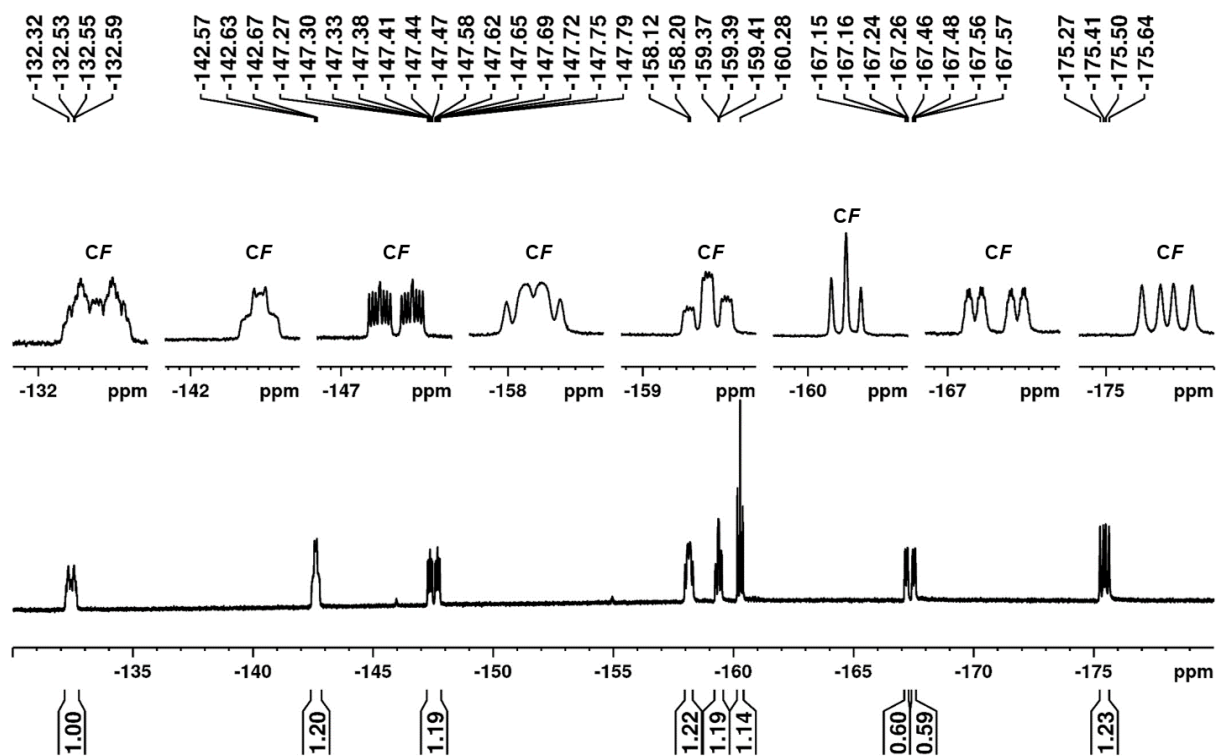


Figure S39: ^{19}F -NMR spectrum of complex $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_{10}\text{F}_8)]$ **20** in C_6D_6 .

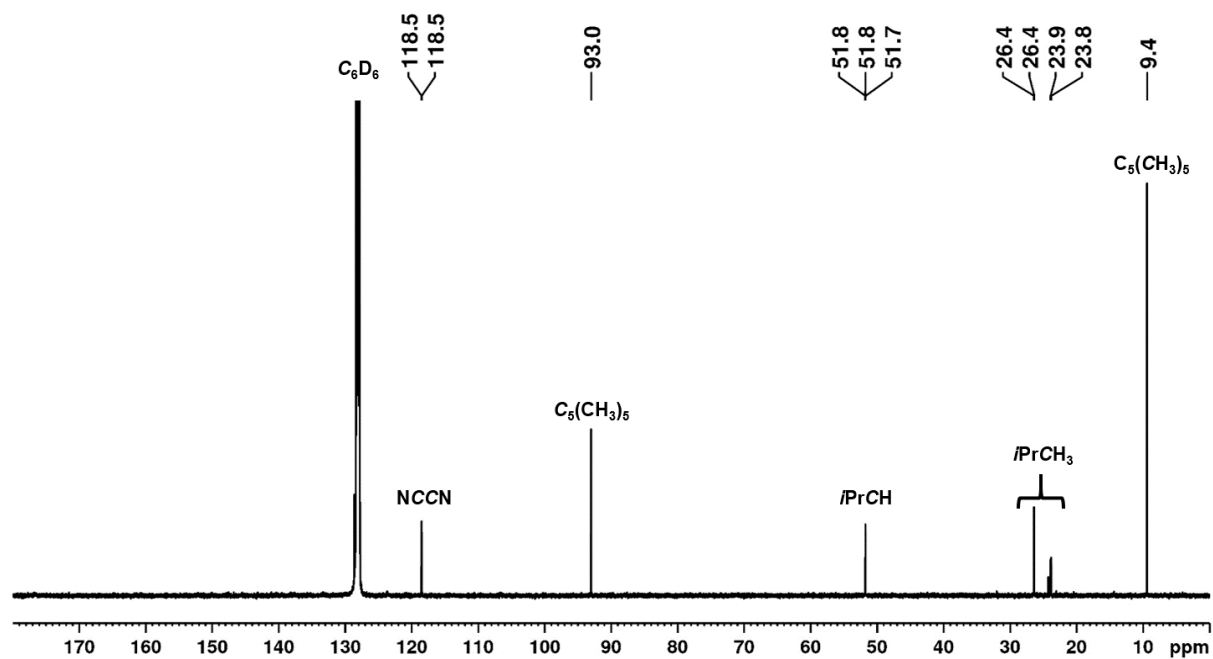


Figure S40: ^{13}C -NMR spectrum of complex $[\text{Cp}^*\text{Co}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_{10}\text{F}_8)]$ **20** in C_6D_6 .

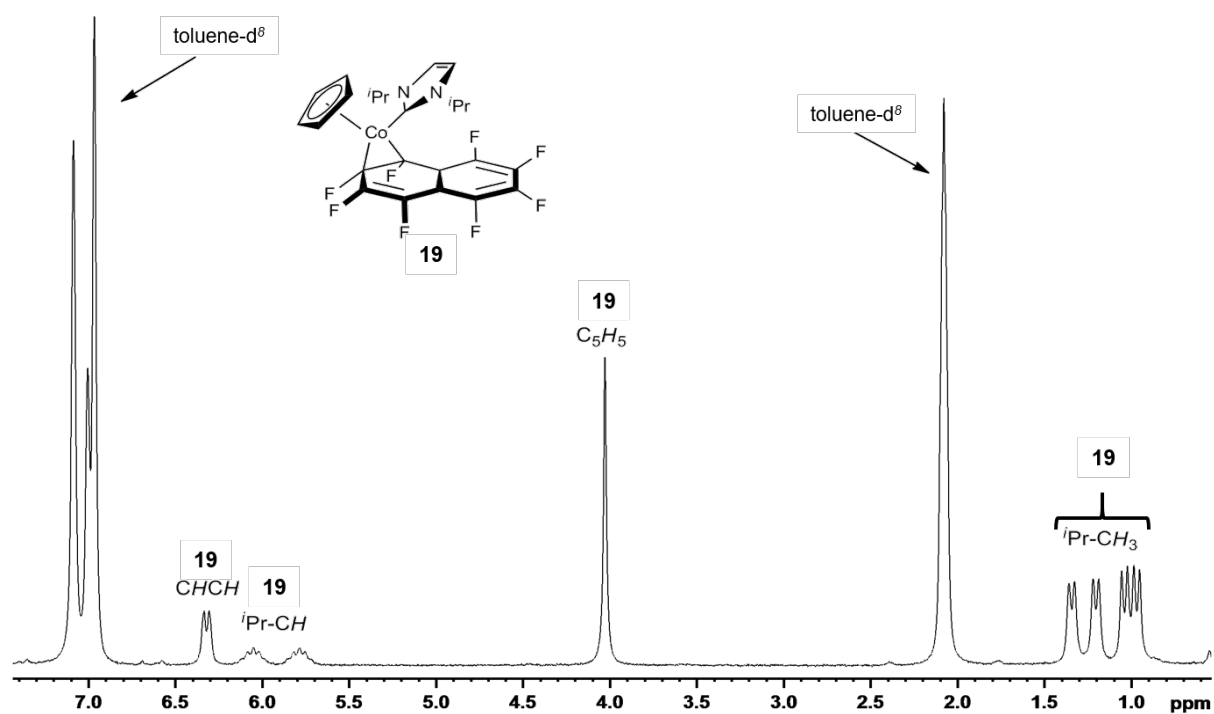


Figure S41: ^1H -NMR time resolved spectrum of the conversion of complex $[(\eta^5\text{-Cp})\text{Co}(i\text{Pr}_2\text{Im})(\eta^2\text{-C}_{10}\text{F}_8)]$ **19** to $[(\eta^5\text{-Cp})\text{Co}(i\text{Pr}_2\text{Im})]_2(\eta^2, \eta^2\text{-C}_{10}\text{F}_8)$ **18** in toluene- d^8 at 80°C and $t = 0$ min.

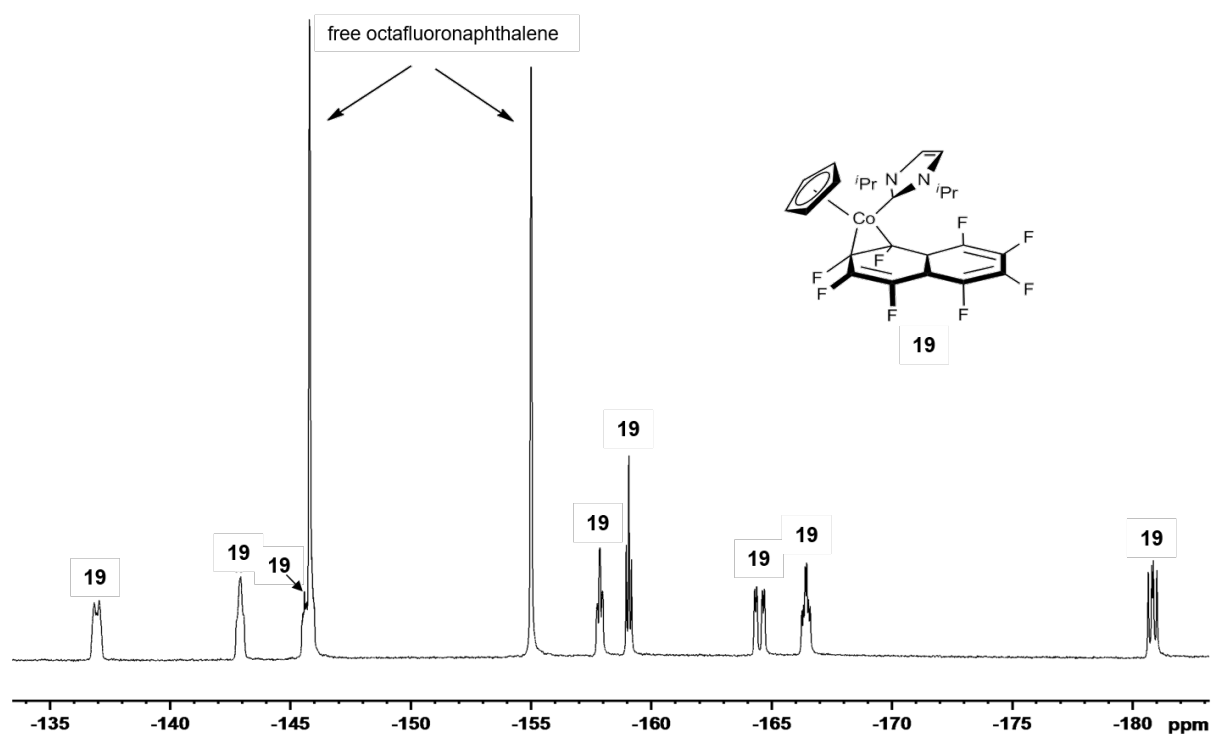


Figure S42: ^{19}F -NMR time resolved spectrum of the conversion of complex $[\text{CpCo}(i\text{Pr}_2\text{Im})(\eta^2\text{-C}_{10}\text{F}_8)]$ **19** to $[(\text{CpCo}(i\text{Pr}_2\text{Im}))_2(\eta^2, \eta^2\text{-C}_{10}\text{F}_8)]$ **18** in toluene- d^8 at 80°C and $t = 0$ min.

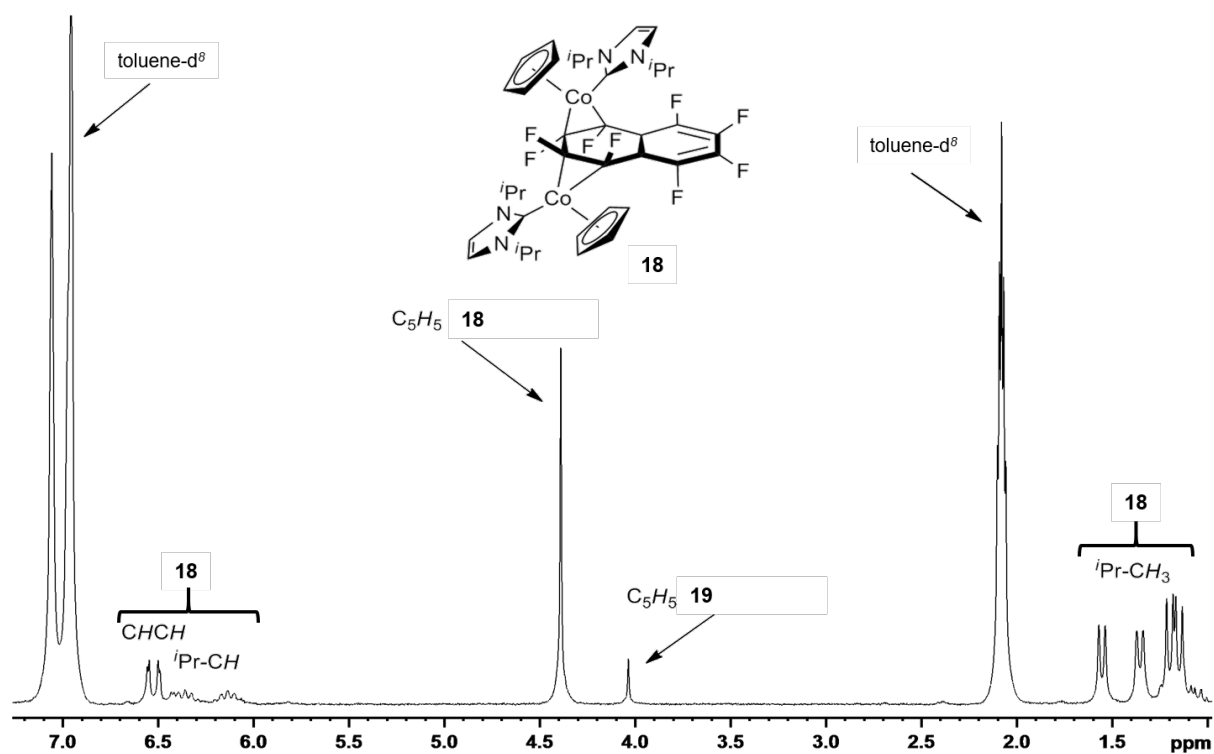


Figure S43: ^1H -NMR time resolved spectrum of the conversion of complex $[\text{CpCo}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_{10}\text{F}_8)]$ **19** to $[\{\text{CpCo}(\text{iPr}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_{10}\text{F}_8)]$ **18** in toluene- d_8 at 80°C and $t = 180$ min.

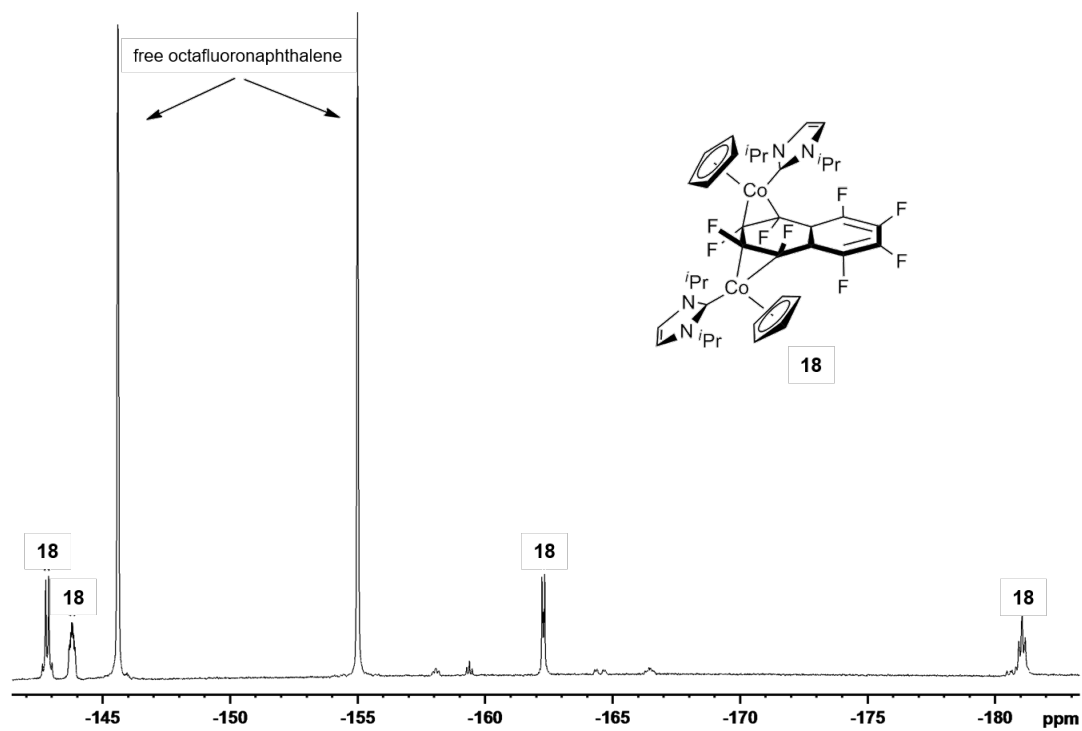


Figure S44: ^{19}F -NMR time resolved spectrum of the conversion of complex $[\text{CpCo}(\text{iPr}_2\text{Im})(\eta^2\text{-C}_{10}\text{F}_8)]$ **19** to $[\{\text{CpCo}(\text{iPr}_2\text{Im})\}_2(\eta^2, \eta^2\text{-C}_{10}\text{F}_8)]$ **18** in toluene- d_8 at 80°C and $t =$

180 min. (free uncoordinated octafluoronaphthalene couldn't be removed during the work-up procedure).

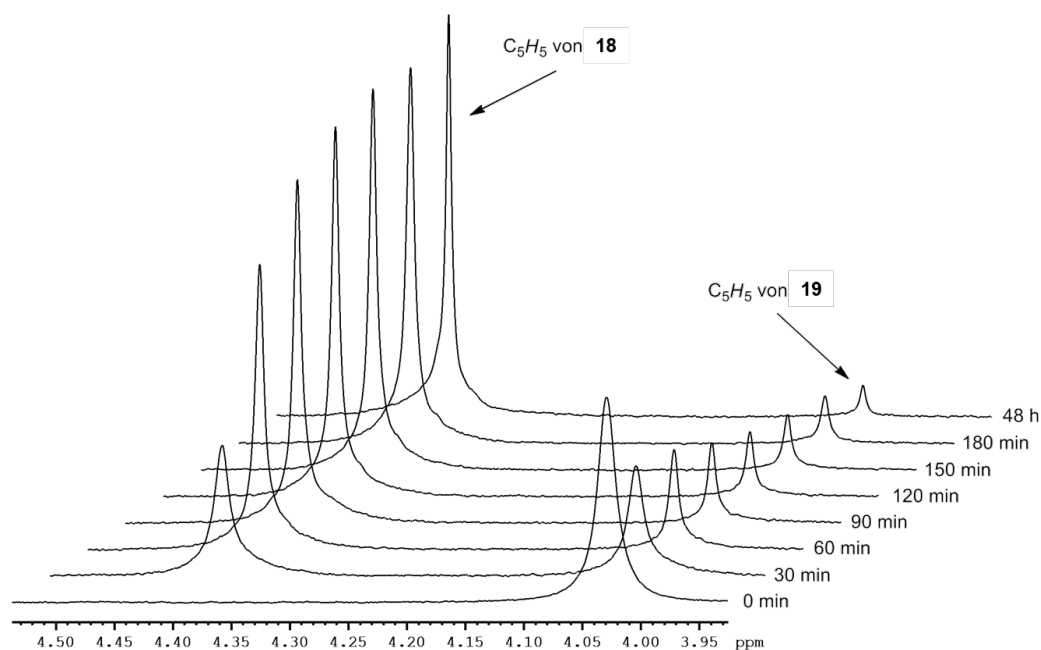


Figure S45: ¹H-NMR time resolved spectrum of the conversion of complex [CpCo(*i*Pr₂Im)(η^2 -C₁₀F₈)] **19** to [(CpCo(*i*Pr₂Im))₂(η^2, η^2 -C₁₀F₈)] **18** in toluene-d⁸ at 80 °C at different times.

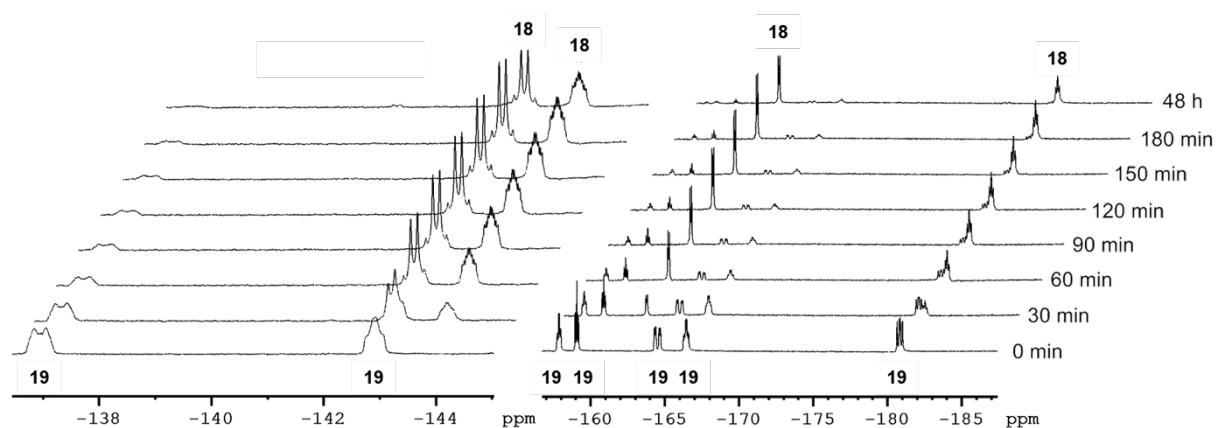


Figure S46: ¹⁹F-NMR time resolved spectrum of the conversion of complex [CpCo(*i*Pr₂Im)(η^2 -C₁₀F₈)] **19** to [(CpCo(*i*Pr₂Im))₂(η^2, η^2 -C₁₀F₈)] **18** in toluene-d⁸ at 80 °C at different times.