

Supporting Information

CpCo(III) precatalysts for [2+2+2] cycloaddition reactions

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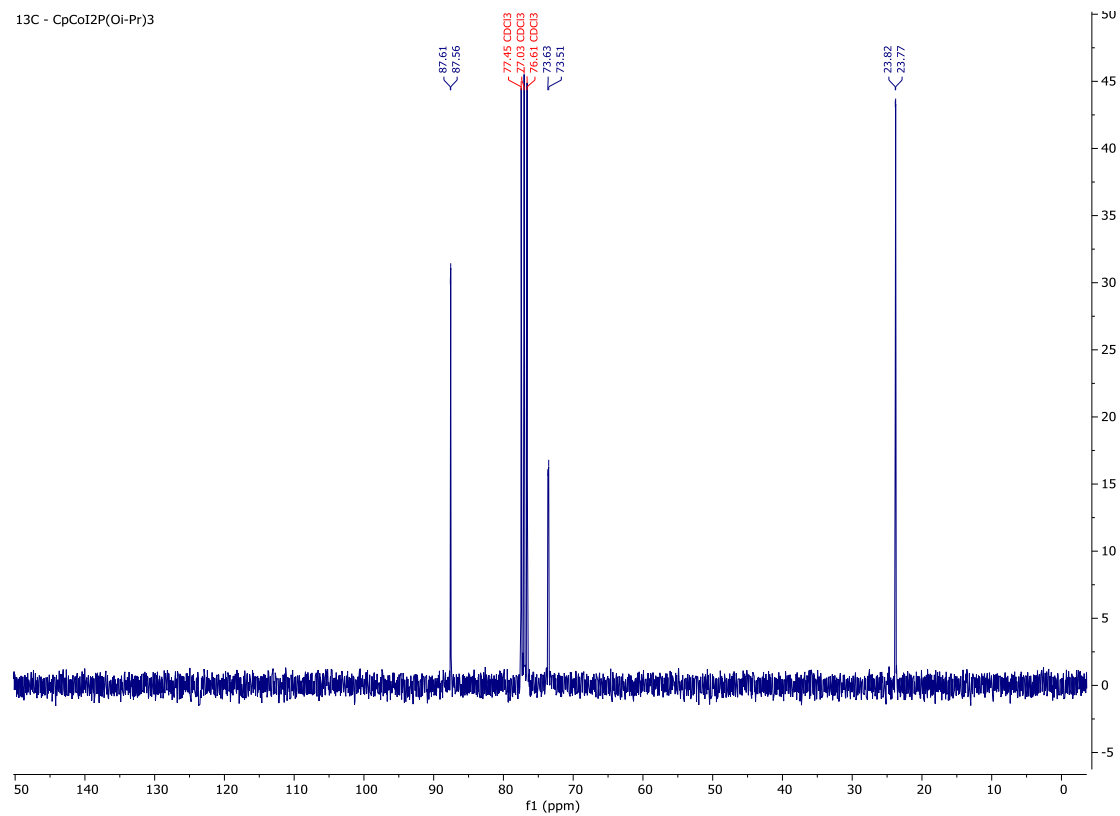
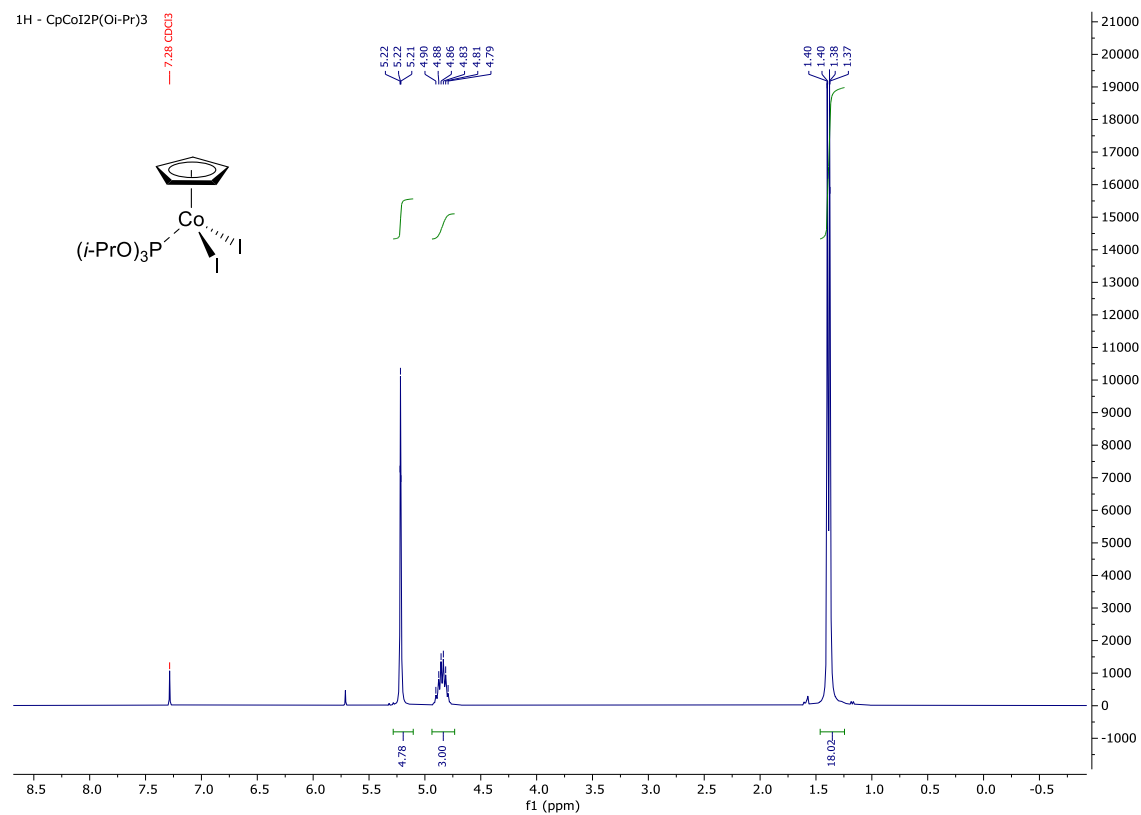
1. General methods and materials

All experiments were carried out under inert gas atmosphere (argon) in flame dried Schlenk tubes or glass reaction vials. The anhydrous solvents (tetrahydrofuran, toluene, dichloromethane and *n*-hexane) were dried in a solvent purification system MD-5 from Inert (former Innovative Technology). All NMR spectra were recorded on a Bruker AV 300, AV 400, AV 500 or Fourier 300 NMR spectrometer. Elemental analysis was performed at a Perkin Elmer AAS-Analyst 300 (Co), Leco Microanalysator-TruSpec CHNS (C, H), Radiometer Analytical SAS (Titrator) Titrab 870-TIM 870 (Br) and a Perkin Elmer UV/VIS-spectrometer Lambda 2 (P).

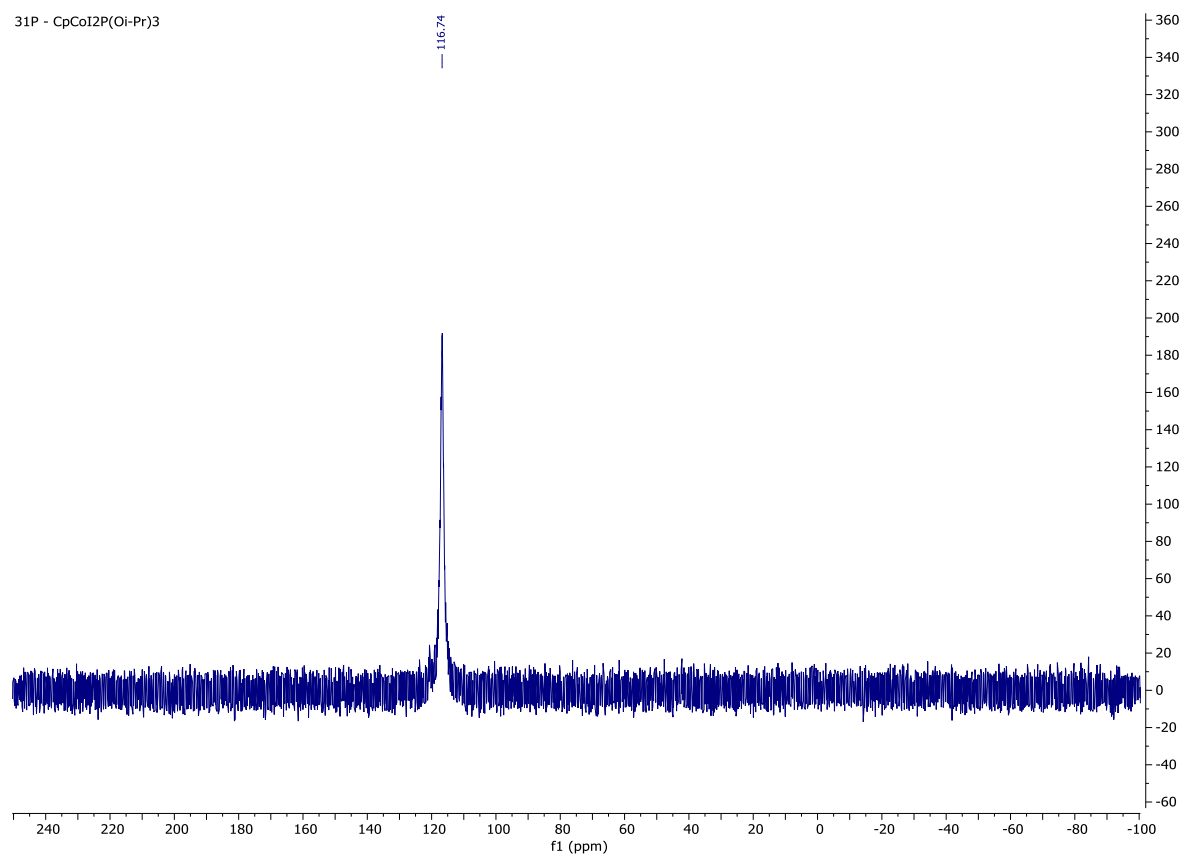
The phosphites $\text{P}(\text{O}i\text{Pr})_3$, $\text{P}[\text{OCH}_2(\text{CF}_3)_2]_3$ and tris[2,4-bis(*tert*-butyl)phenyl]phosphite are commercially available and have been dried by addition of spherical molecular sieve A4. They were only distilled in vacuum, if the purity was <98%. Tricyclohexylphosphite has been synthesized according to a recently reported literature reference.¹ $\text{CpCo}(\text{CO})_2$, $\text{Co}_2(\text{CO})_8$ and NaCp have been purchased and used as received. The Grignard reagent MeMgBr was commercially purchased.

2. Analytical data of complexes

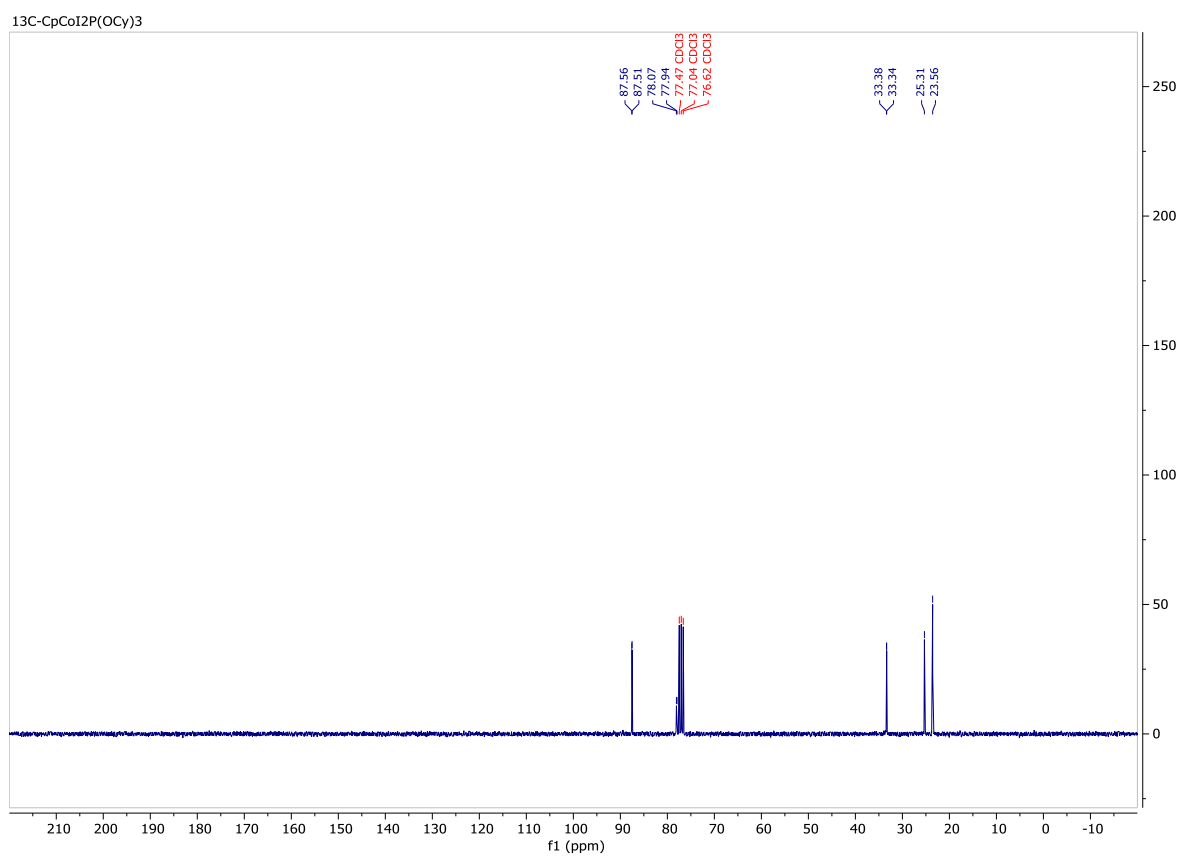
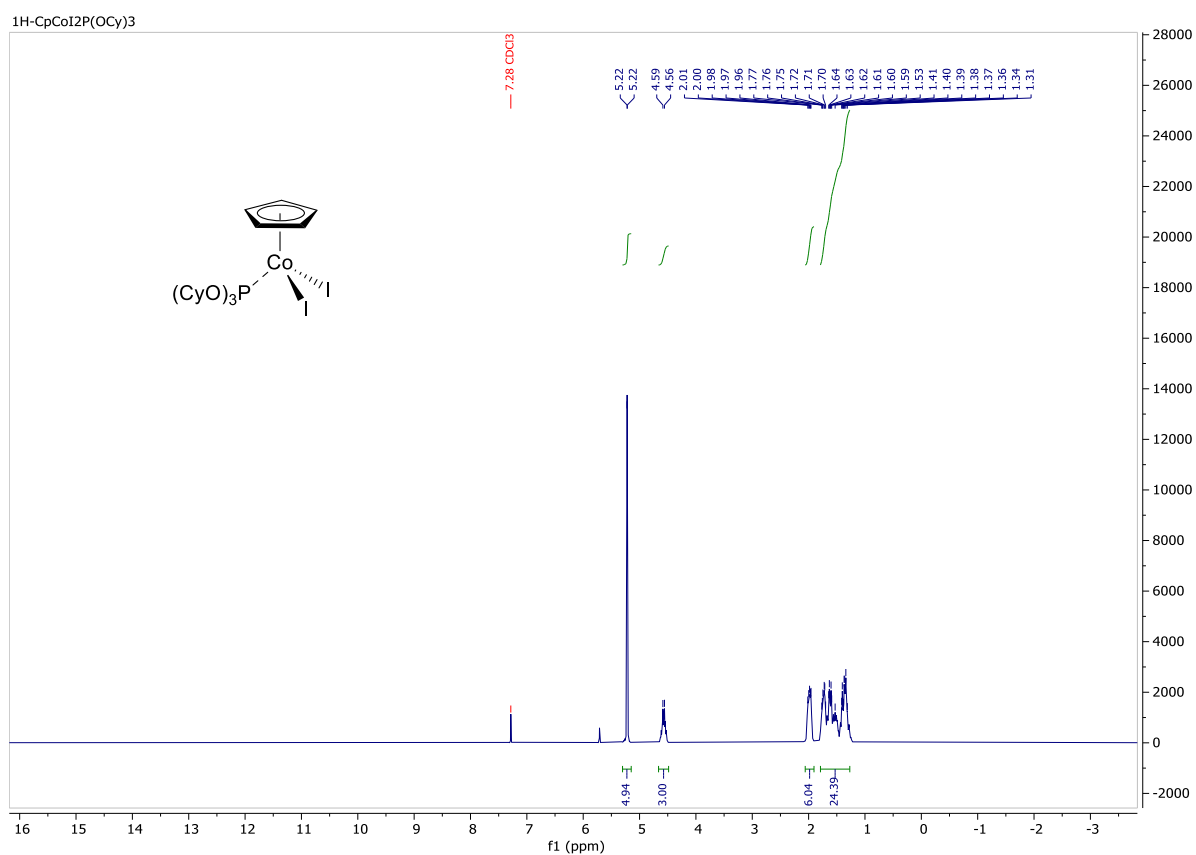
Complex 2:



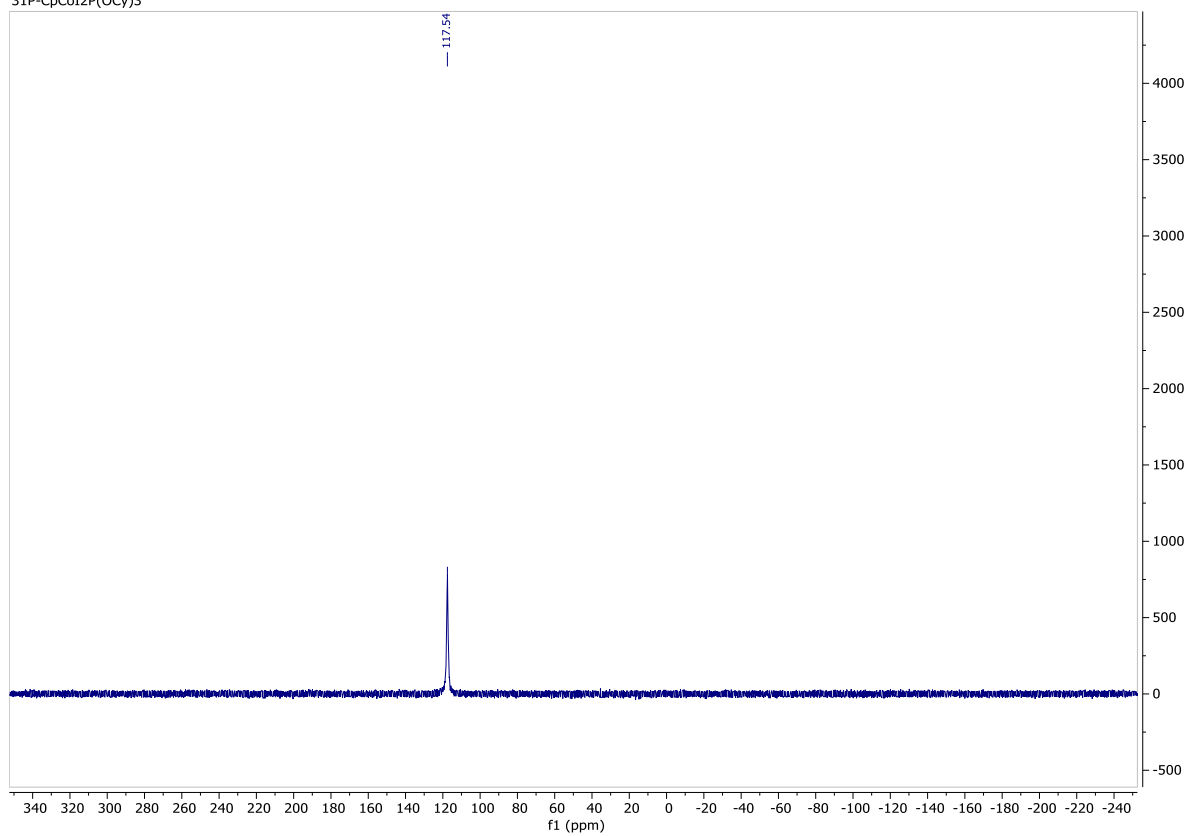
³¹P - CpCoI2P(Oi-Pr)₃



Complex 3:

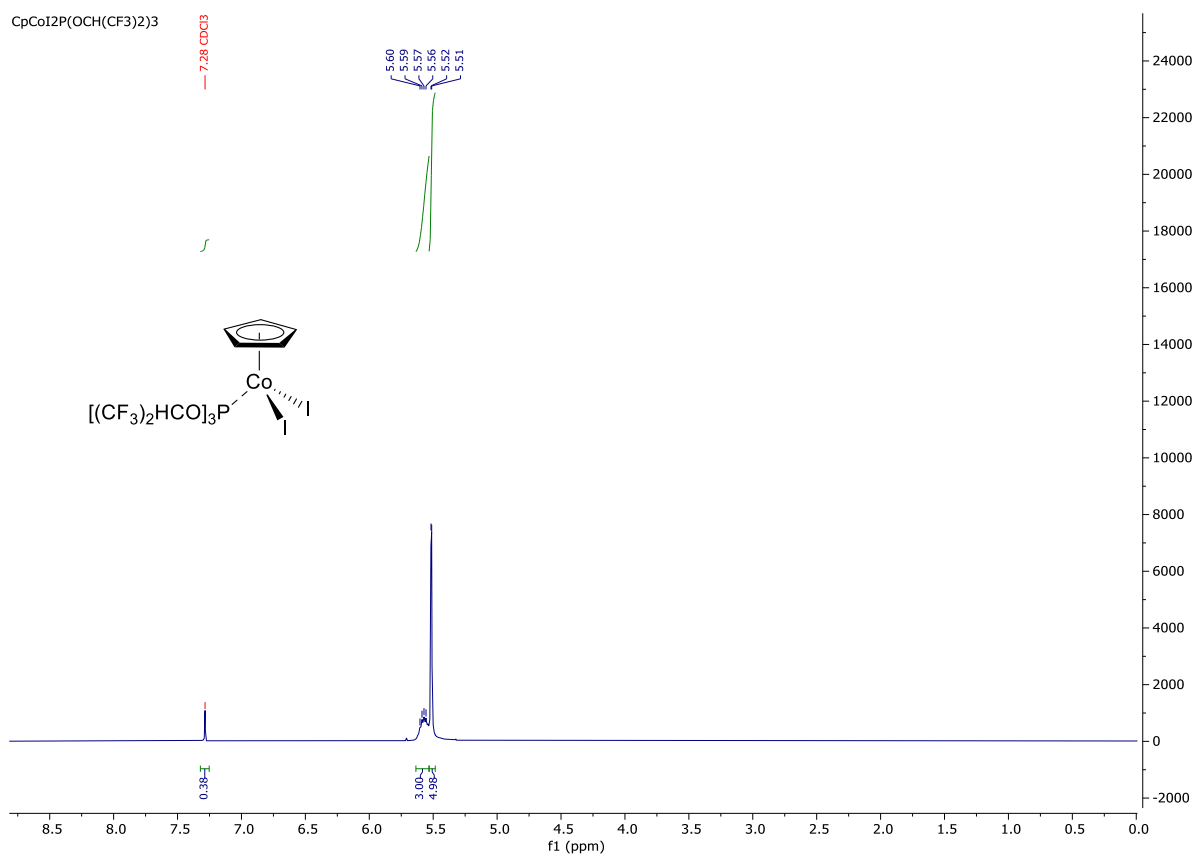


^{31}P -CpCoI₂P(OCy)₃

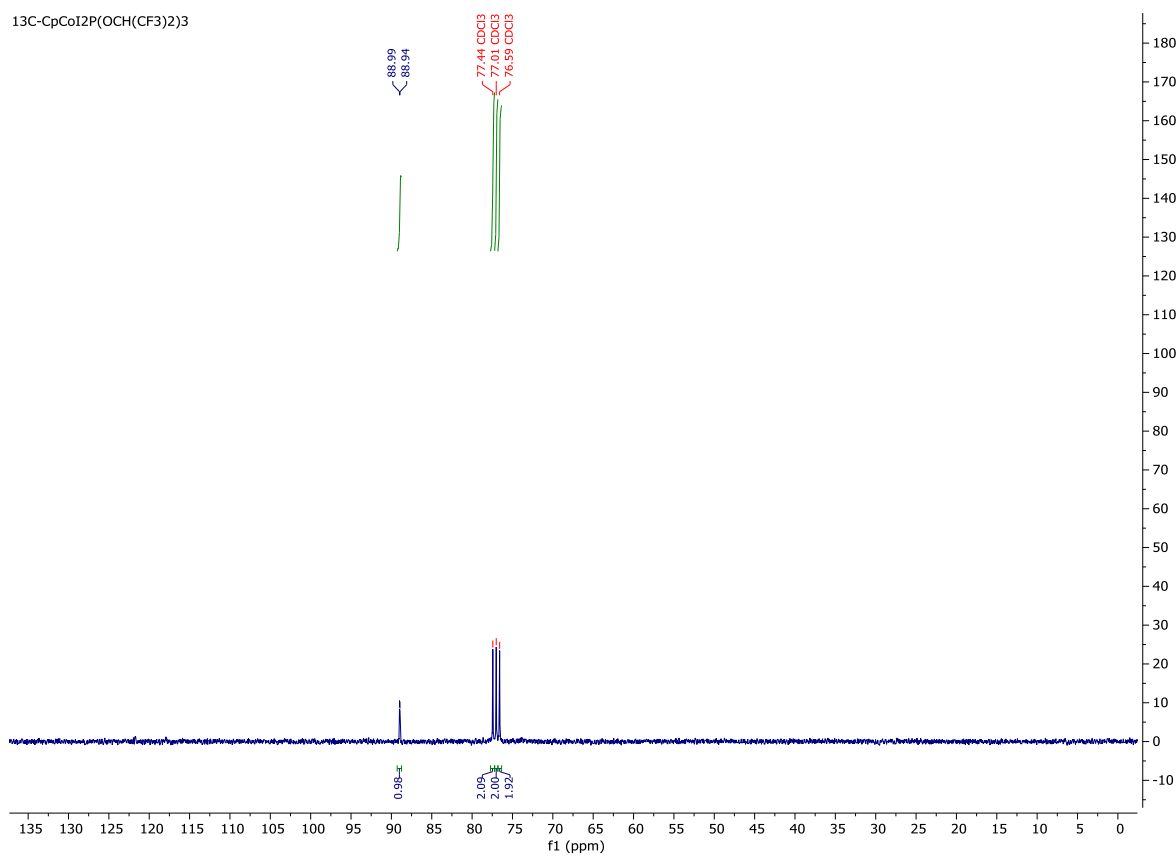


Complex 4:

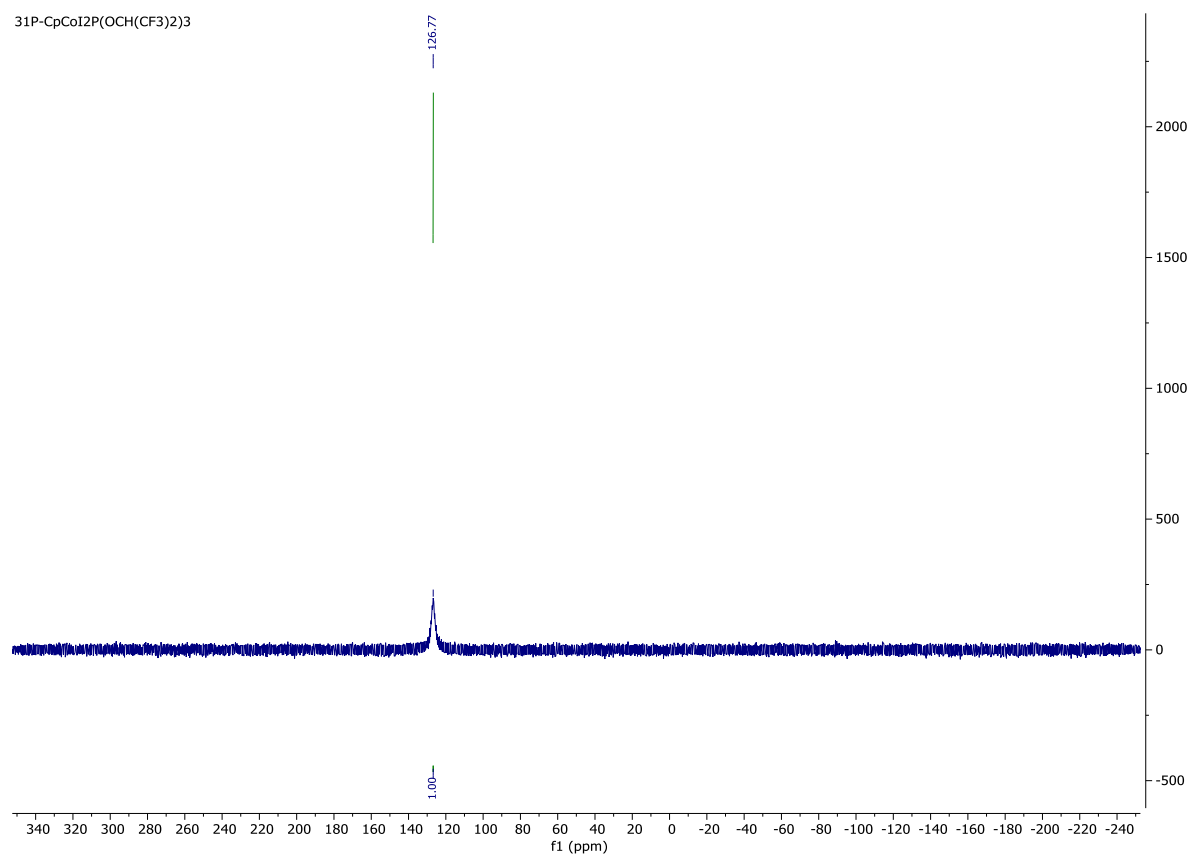
CpCoI₂P(OCH(CF₃)₂)₃



¹³C-CpCoI₂P(OCH(CF₃)₂)₃

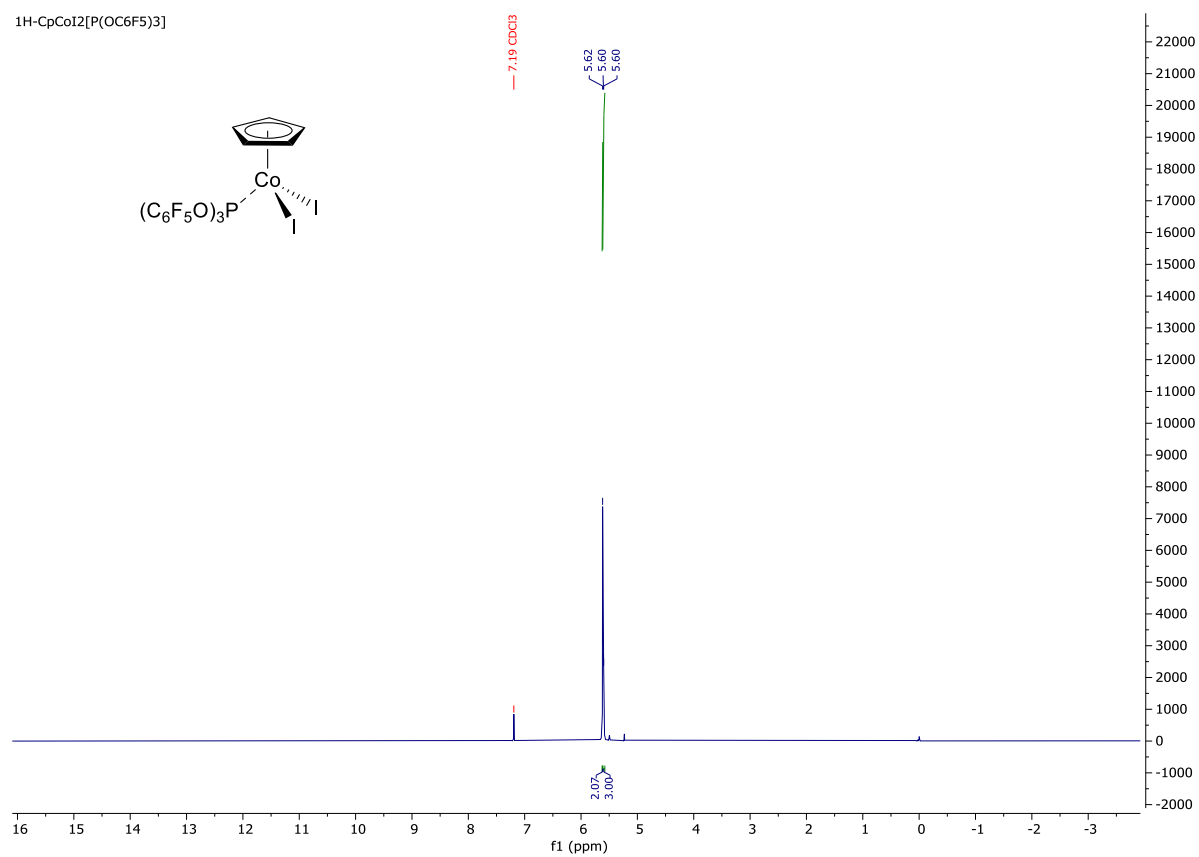
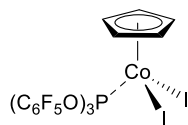


^{31}P -CpCoI₂P(OCH(CF₃)₂)₃

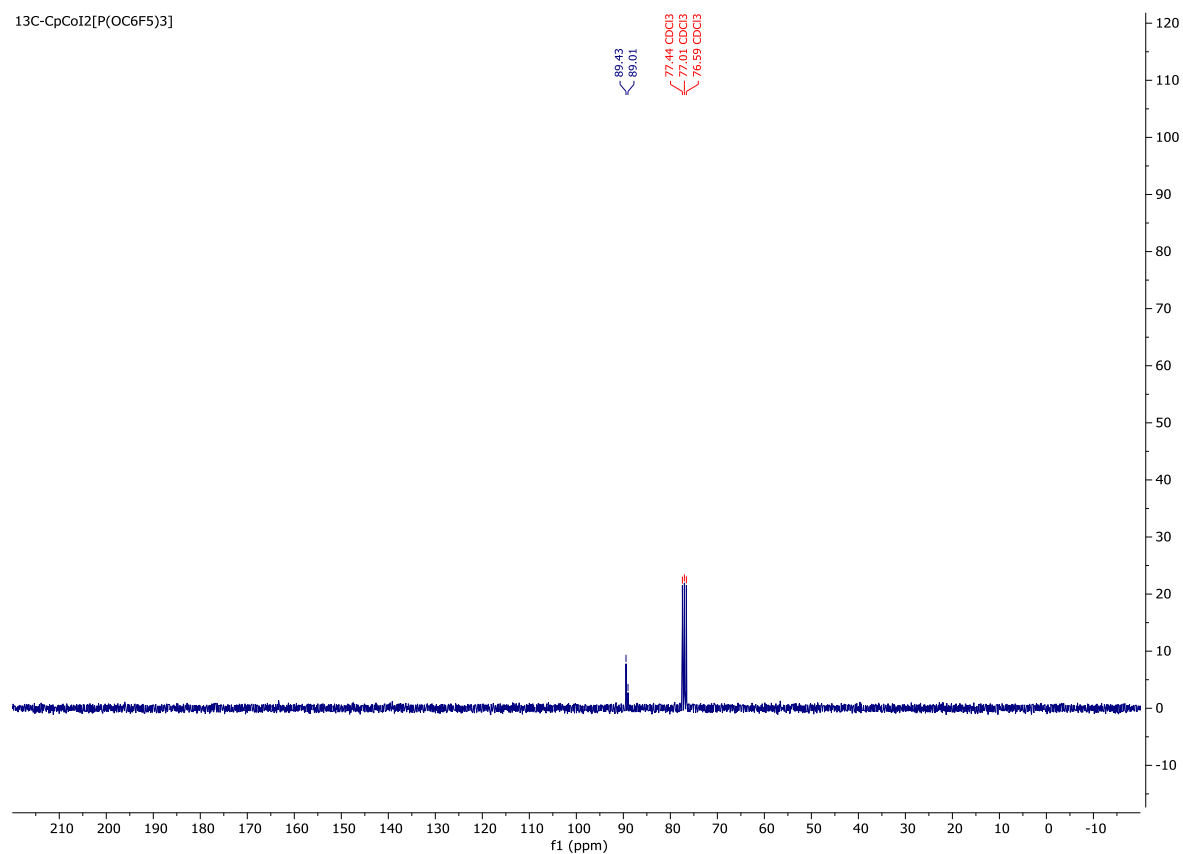


Complex 6:

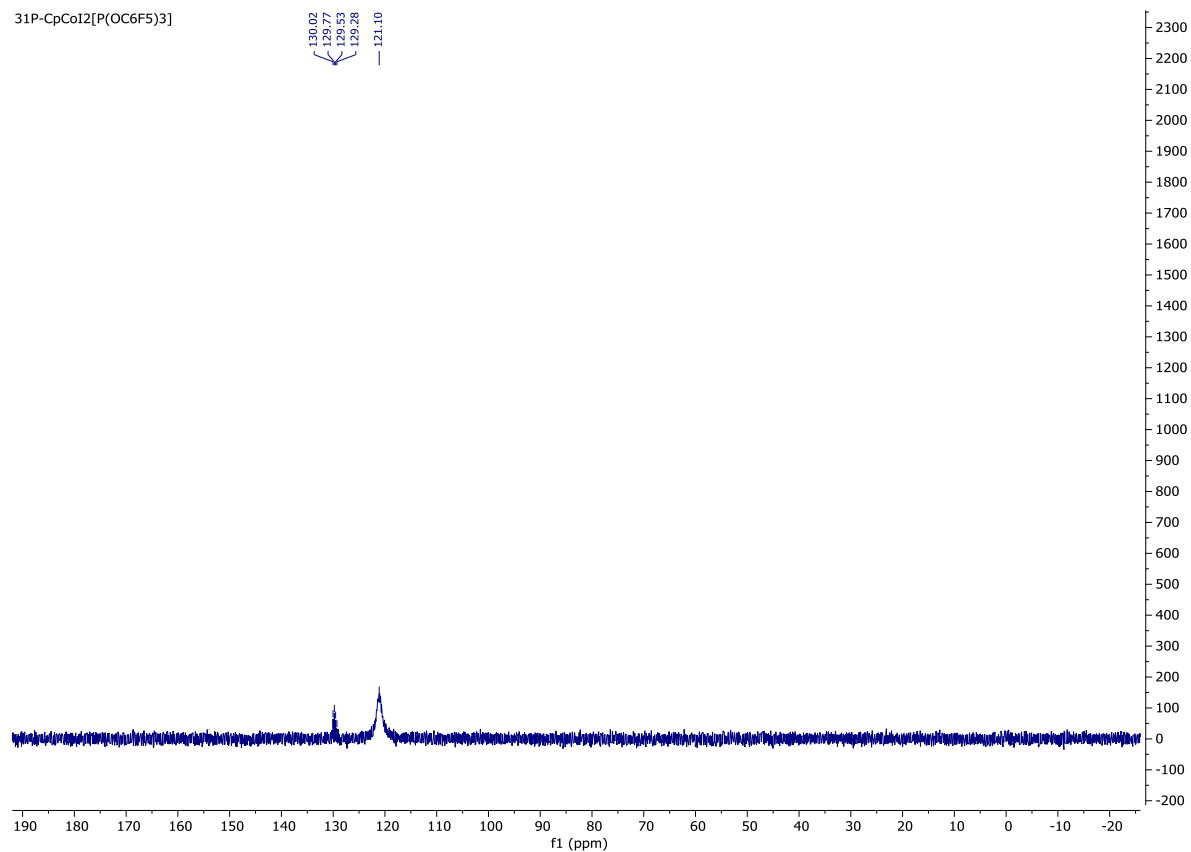
^1H -CpCoI $2[\text{P}(\text{OC}_6\text{F}_5)_3]$



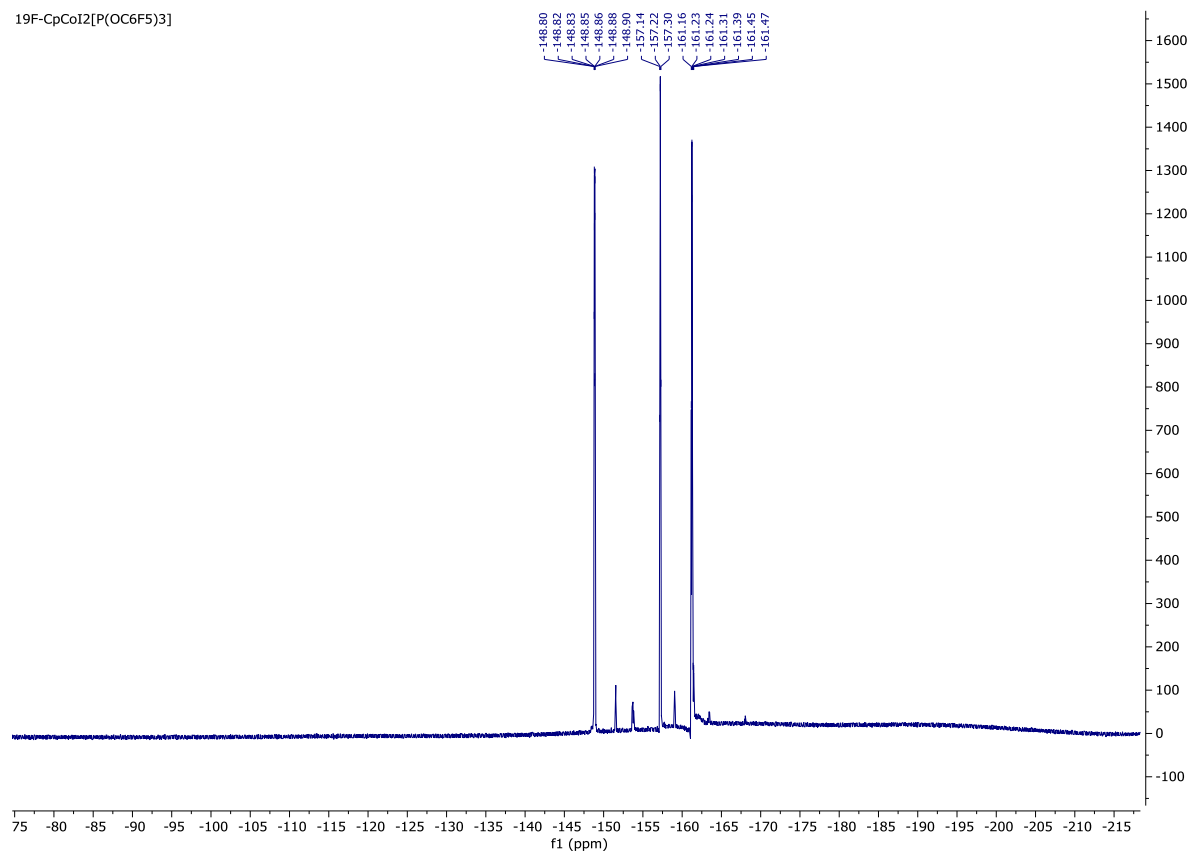
^{13}C -CpCoI $2[\text{P}(\text{OC}_6\text{F}_5)_3]$



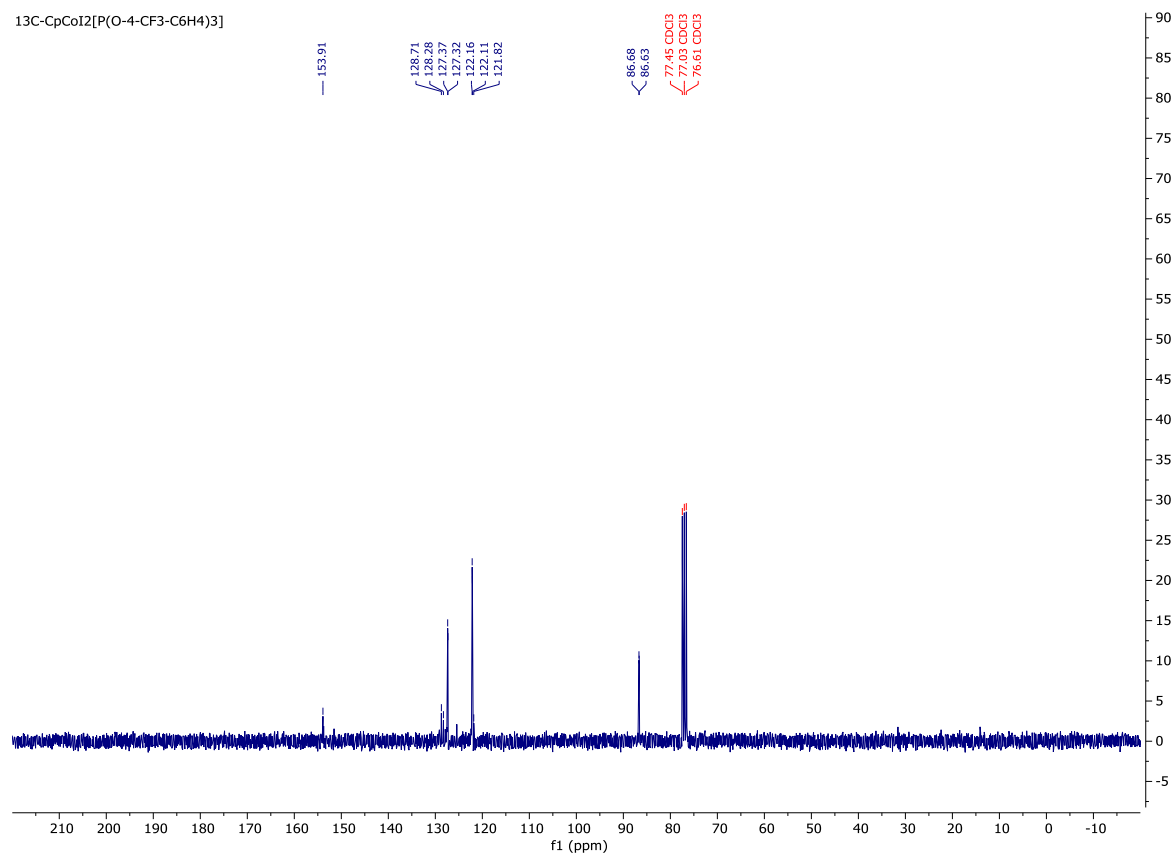
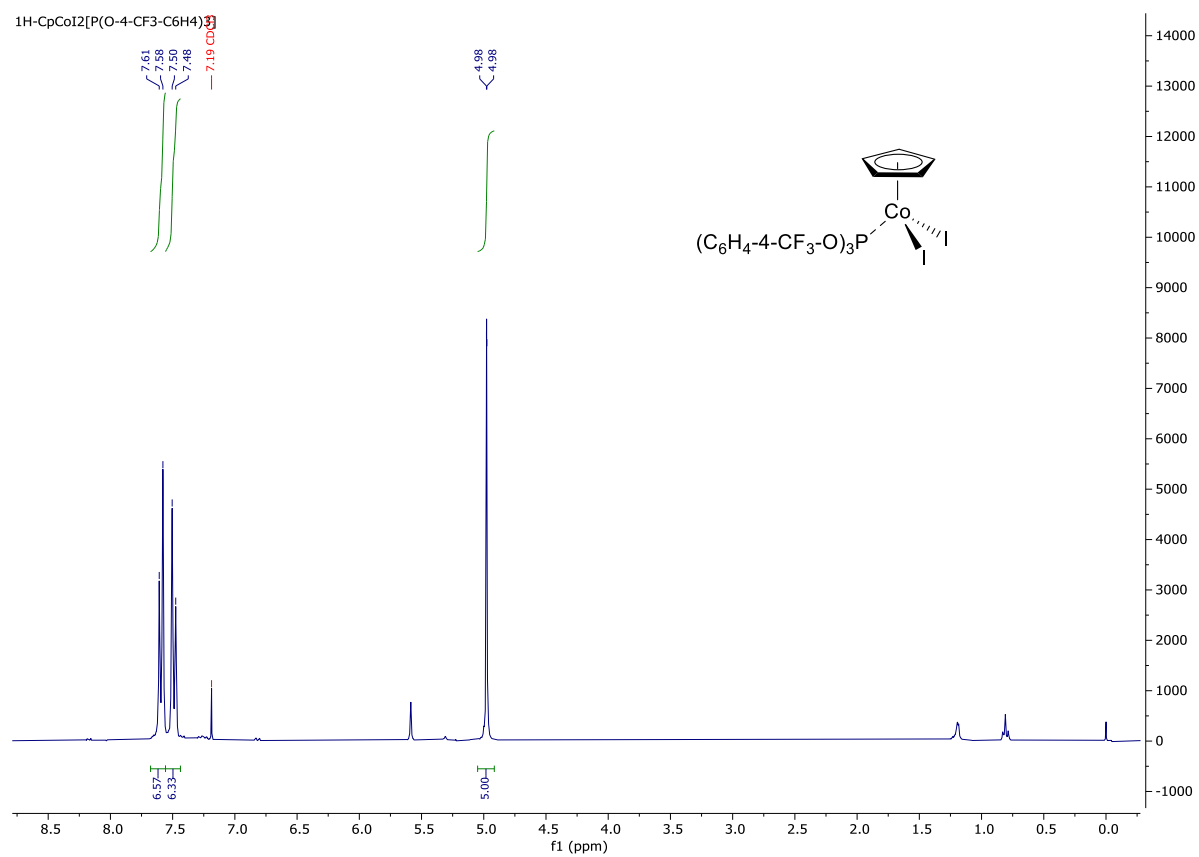
^{31}P -CpCoI₂[P(OC₆F₅)₃]

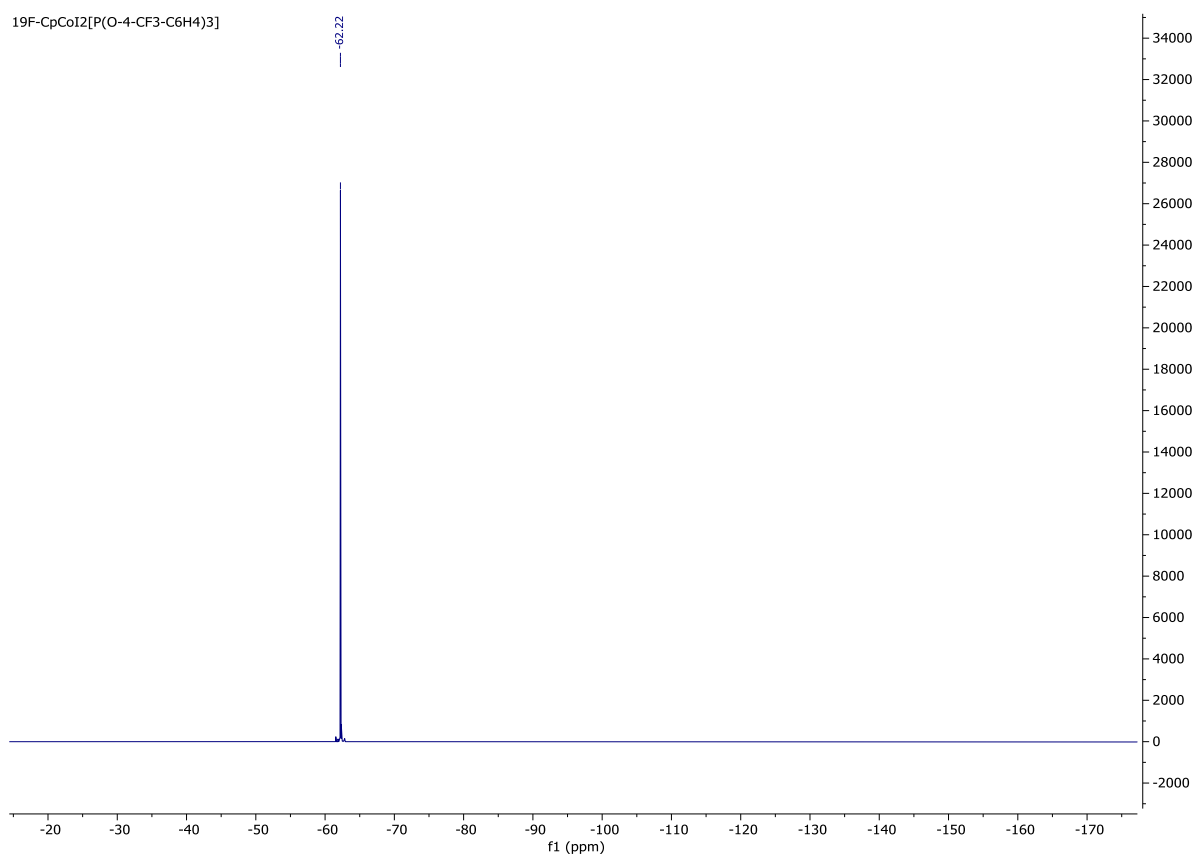
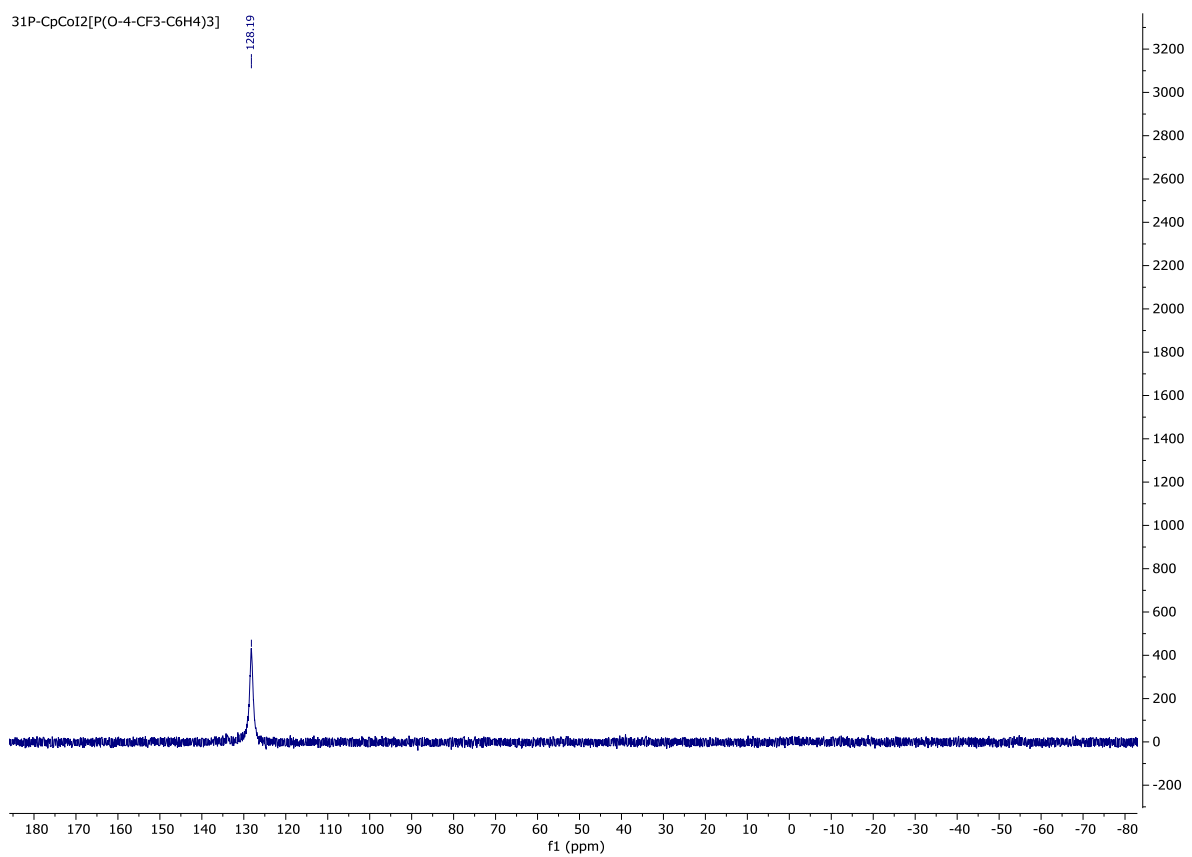


^{19}F -CpCoI₂[P(OC₆F₅)₃]

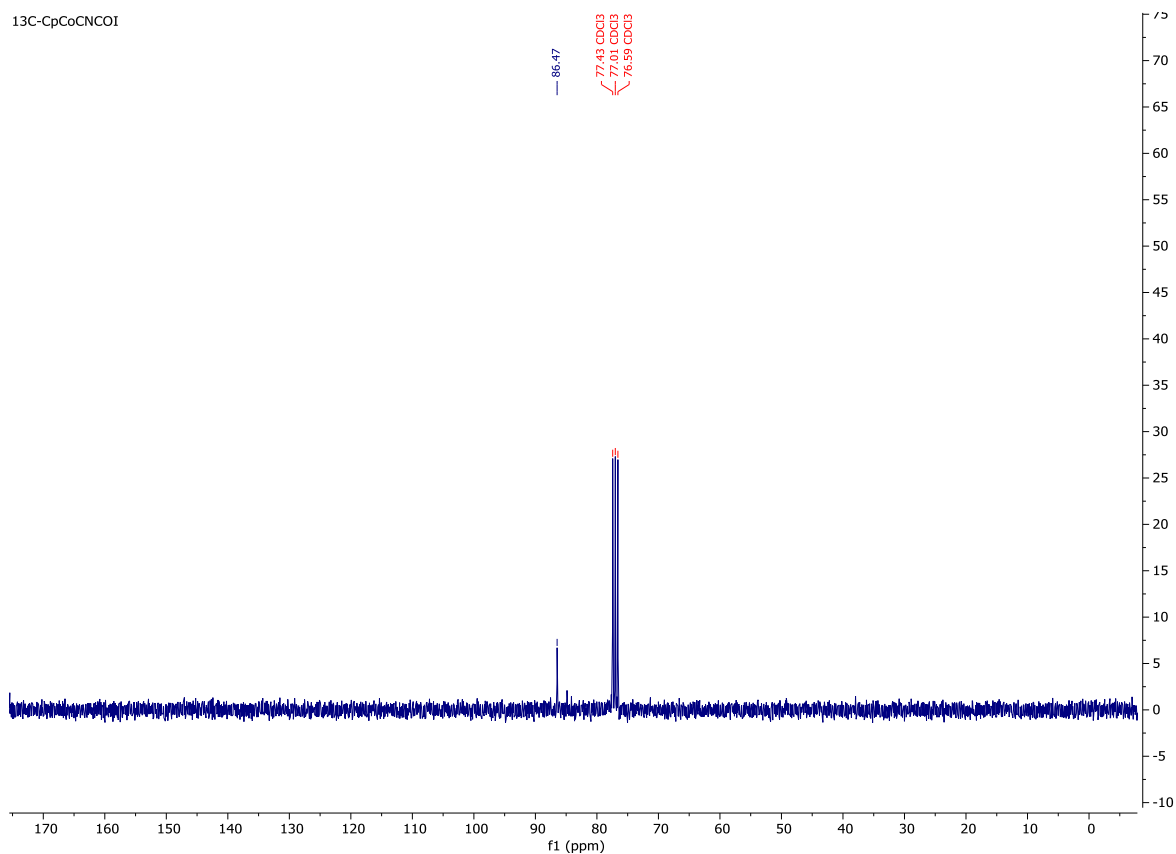
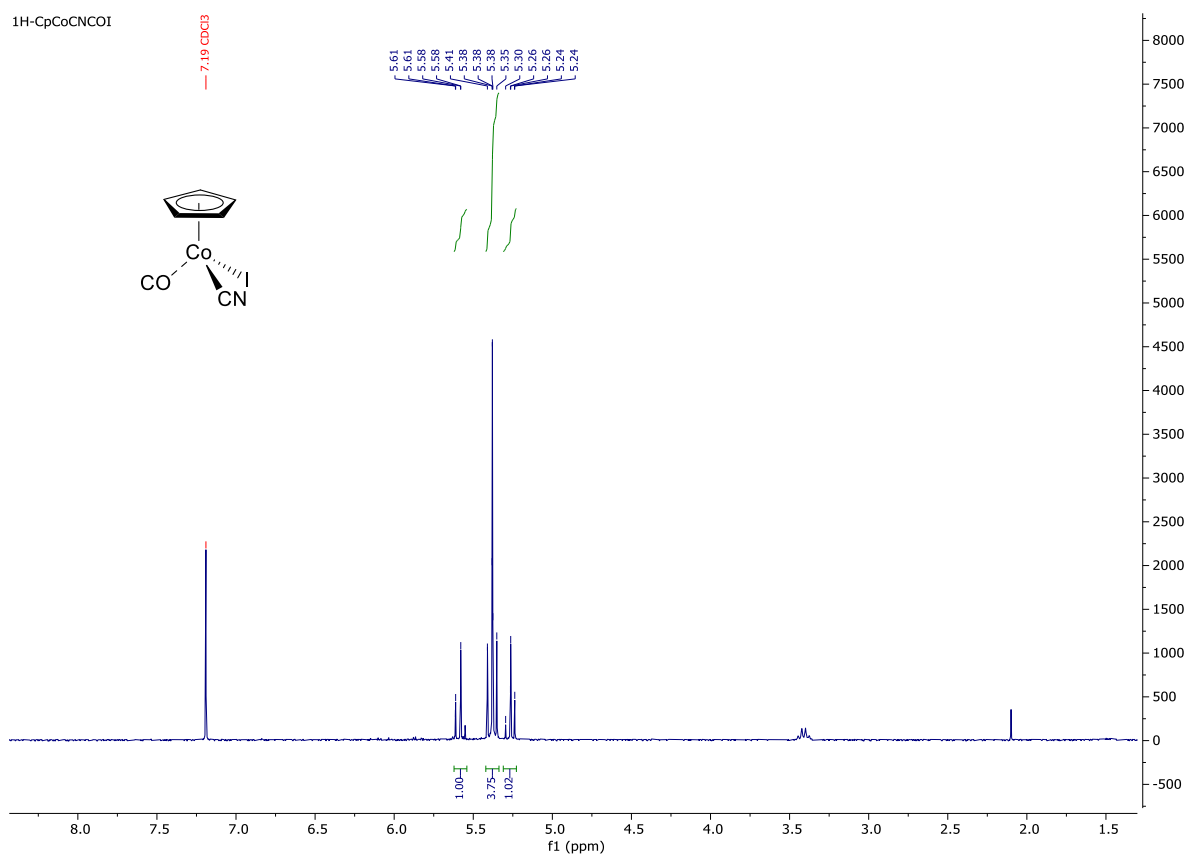


Complex 7:



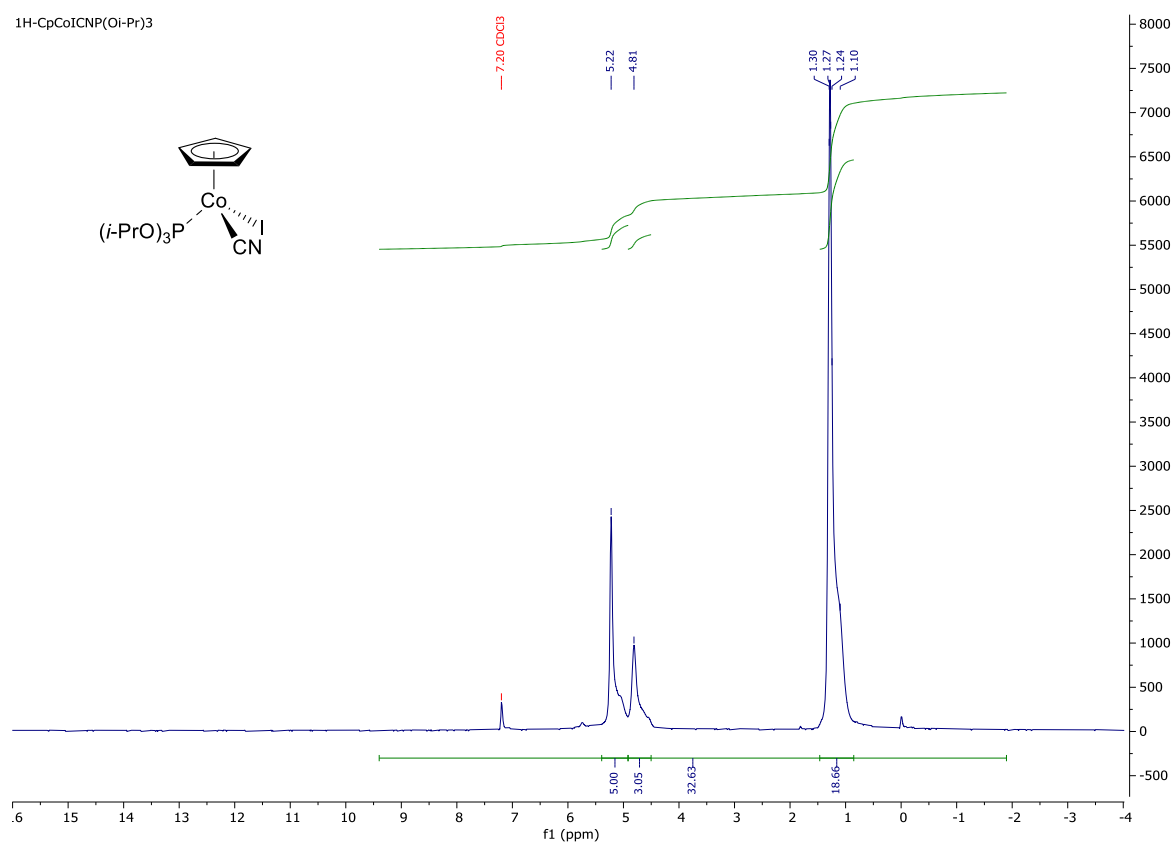


Complex 8:

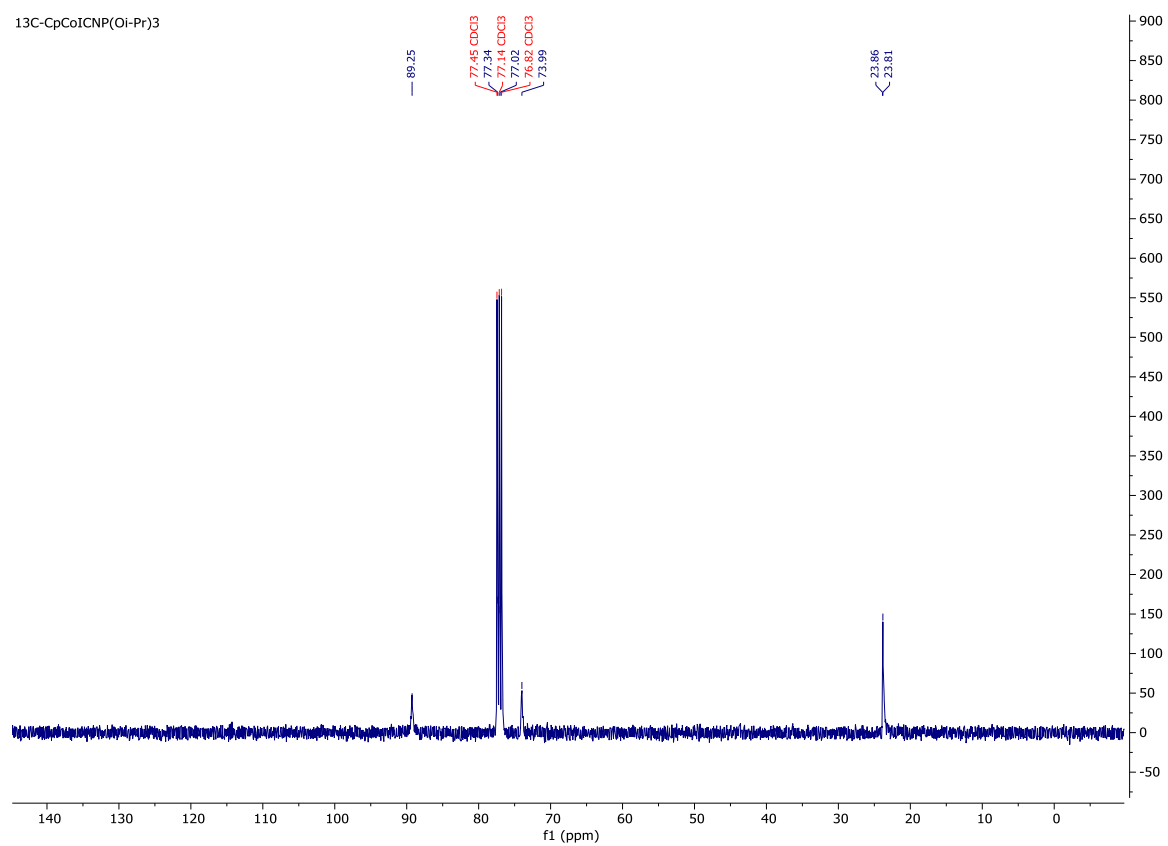


Complex 9:

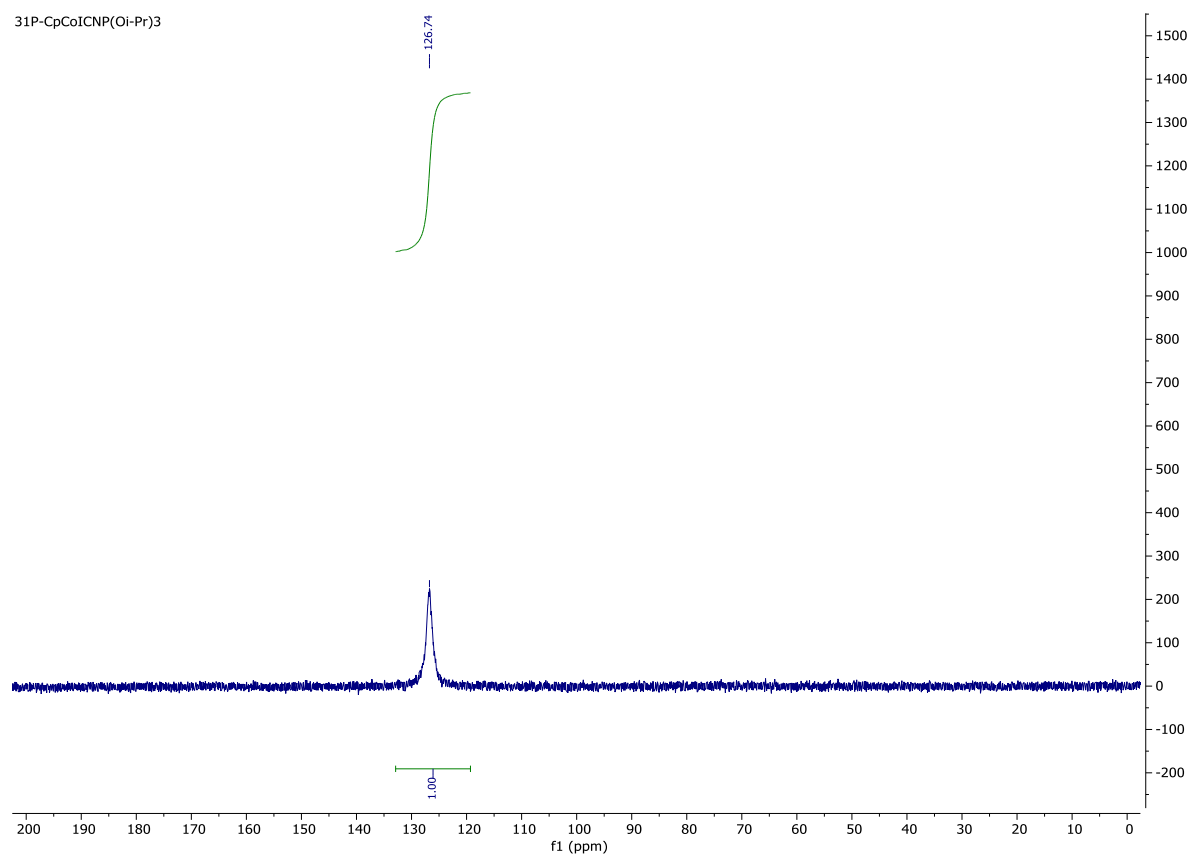
^1H -CpCoICNP(Oi-Pr) $_3$



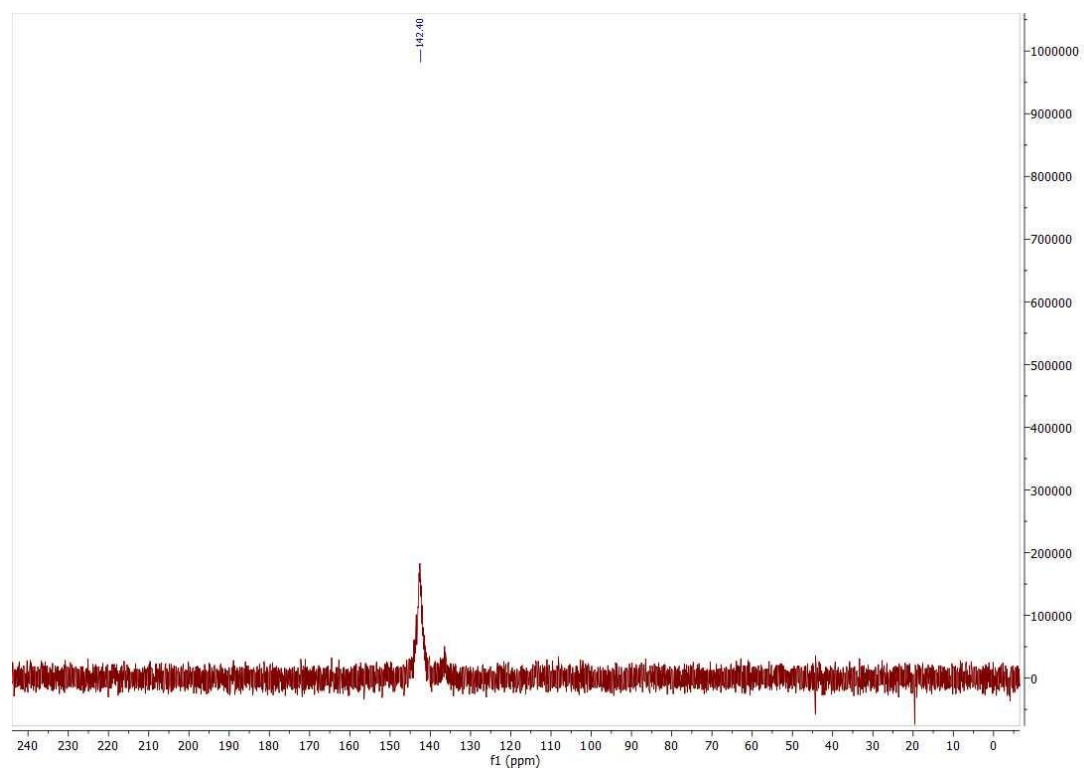
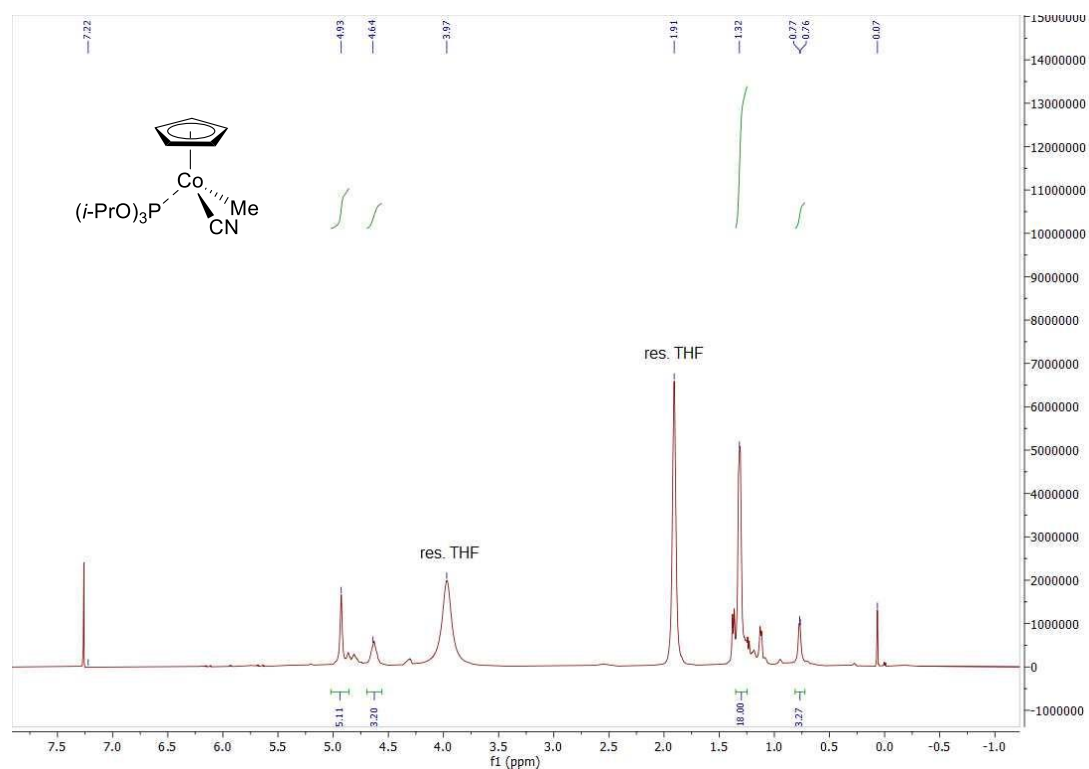
^{13}C -CpCoICNP(Oi-Pr) $_3$



^{31}P -CpCoICNP(Oi-Pr)₃

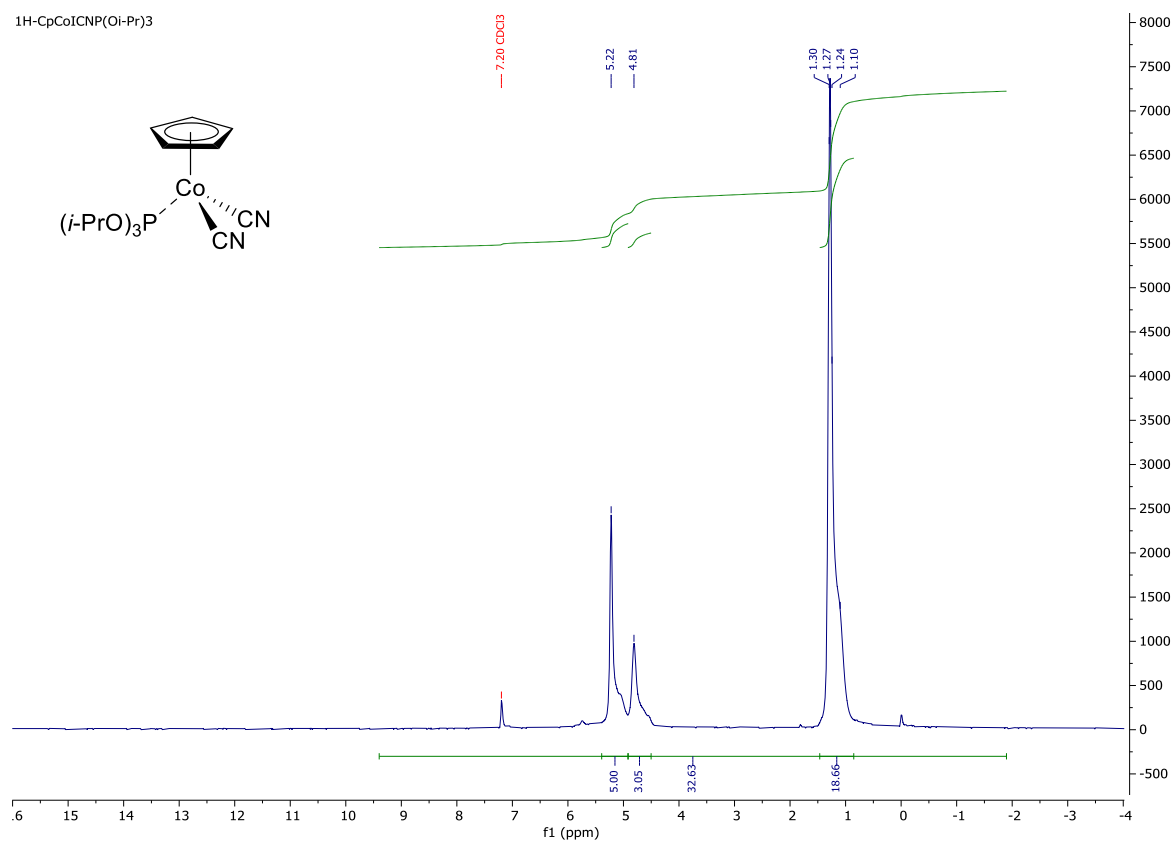
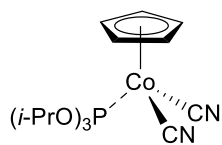


Complex 9-Me (methylation reaction of 9): Reaction control

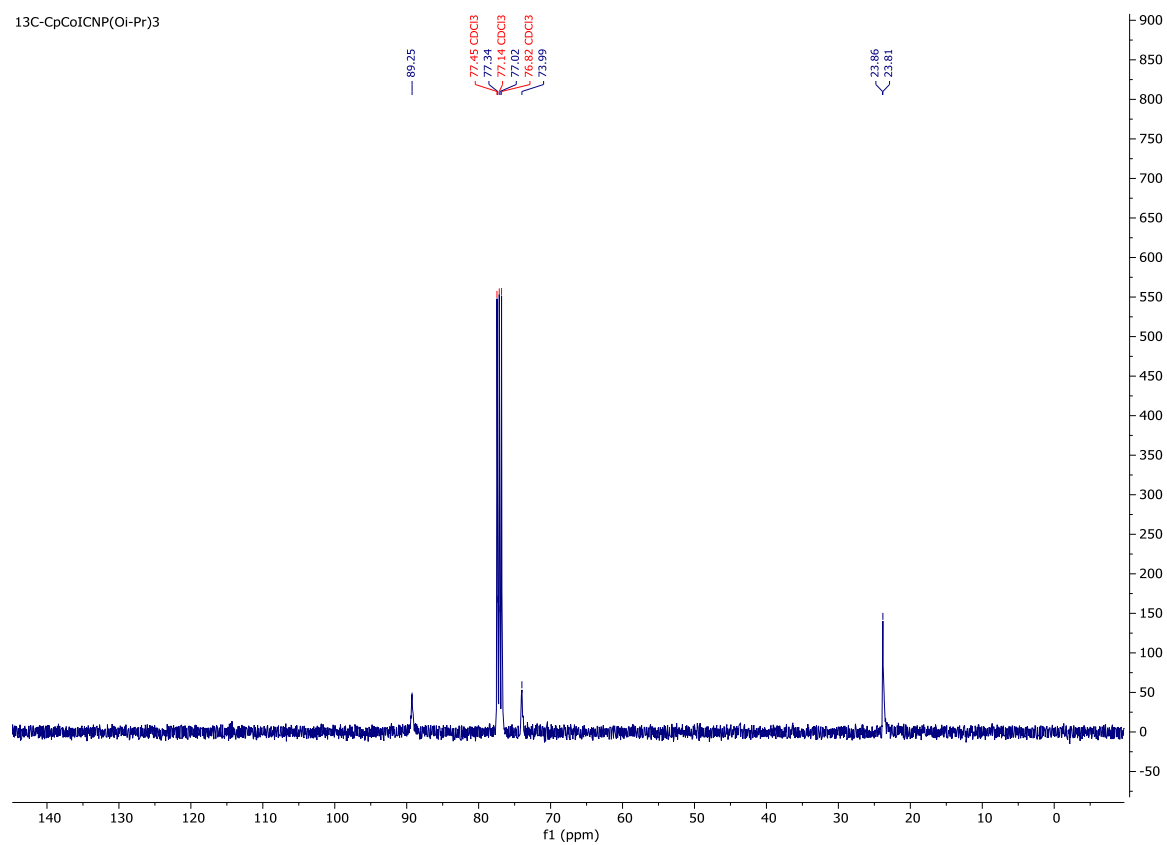


Complex 10:

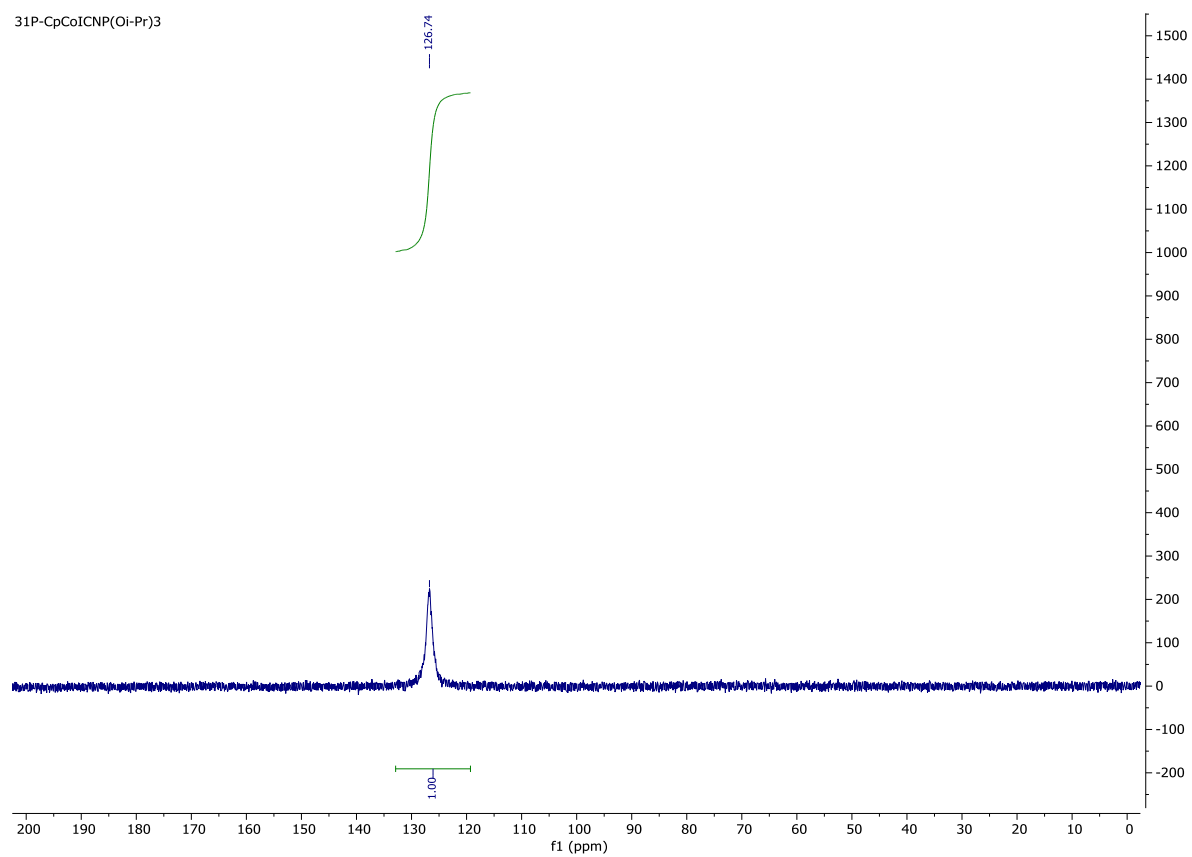
^1H -CpCoICNP(Oi-Pr) $_3$



^{13}C -CpCoICNP(Oi-Pr) $_3$

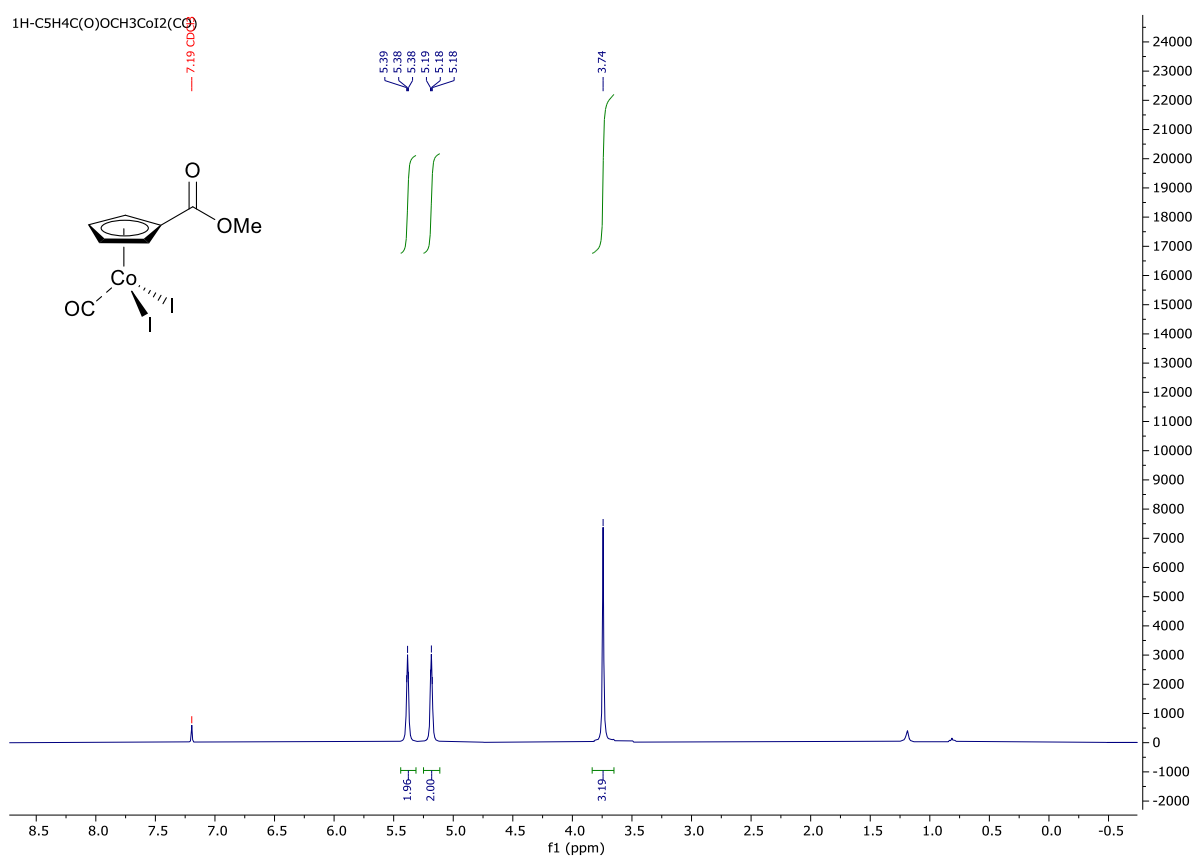


^{31}P -CpCoICNP(Oi-Pr)₃

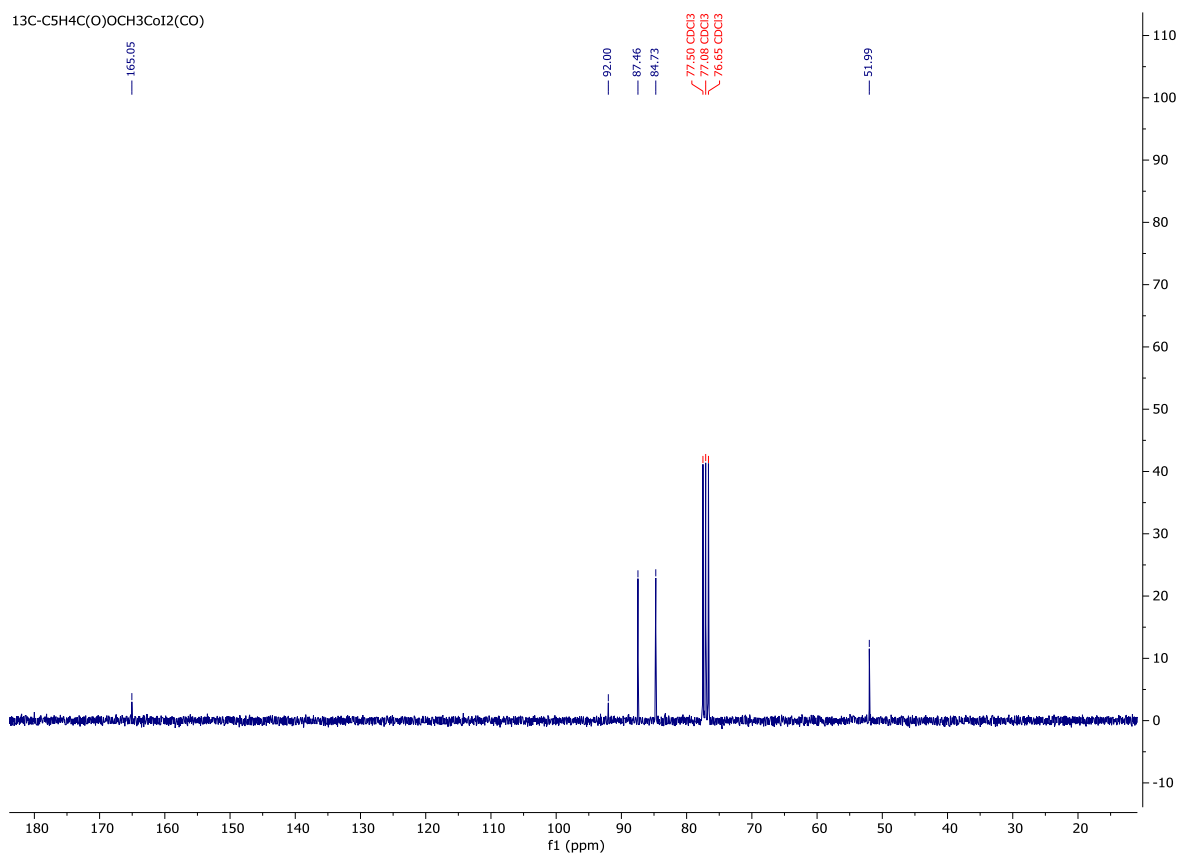


Complex 14:

$^1\text{H-C}_5\text{H}_4\text{C}(\text{O})\text{OCH}_3\text{CoI}_2(\text{CO})$

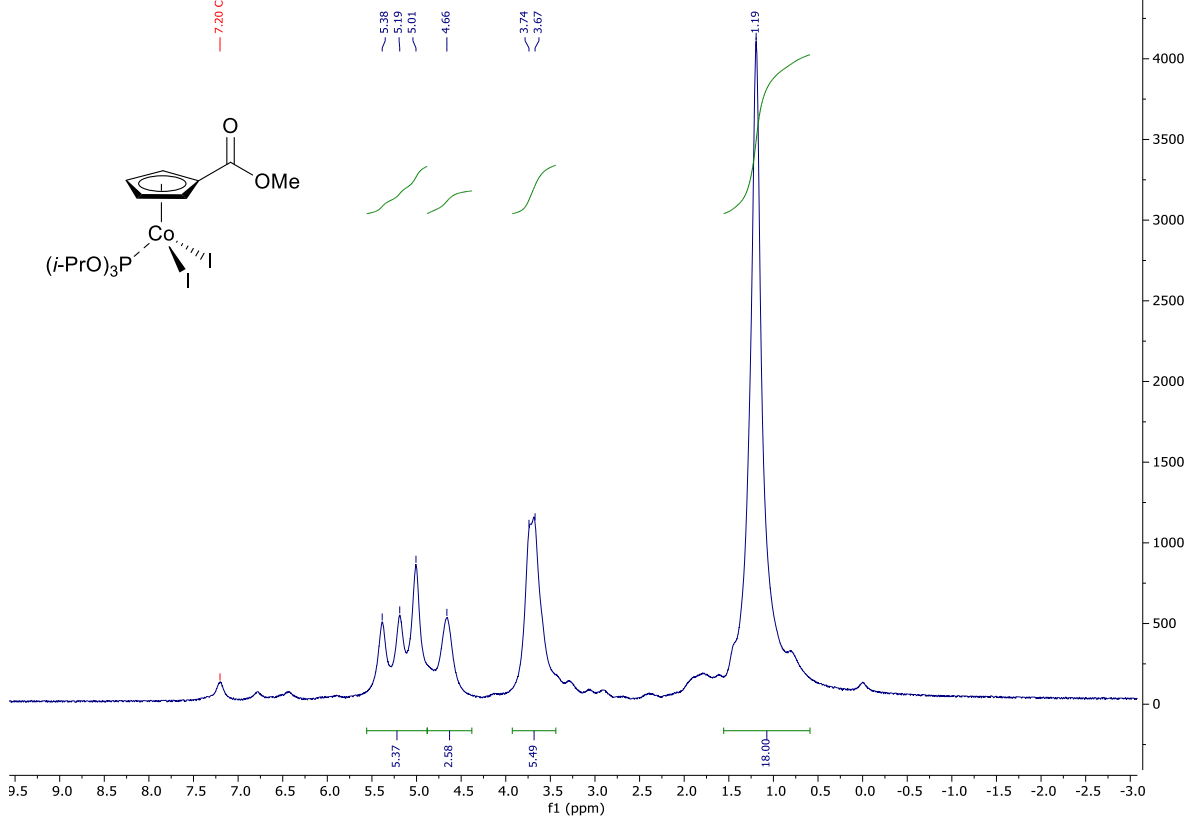


$^{13}\text{C-C}_5\text{H}_4\text{C}(\text{O})\text{OCH}_3\text{CoI}_2(\text{CO})$

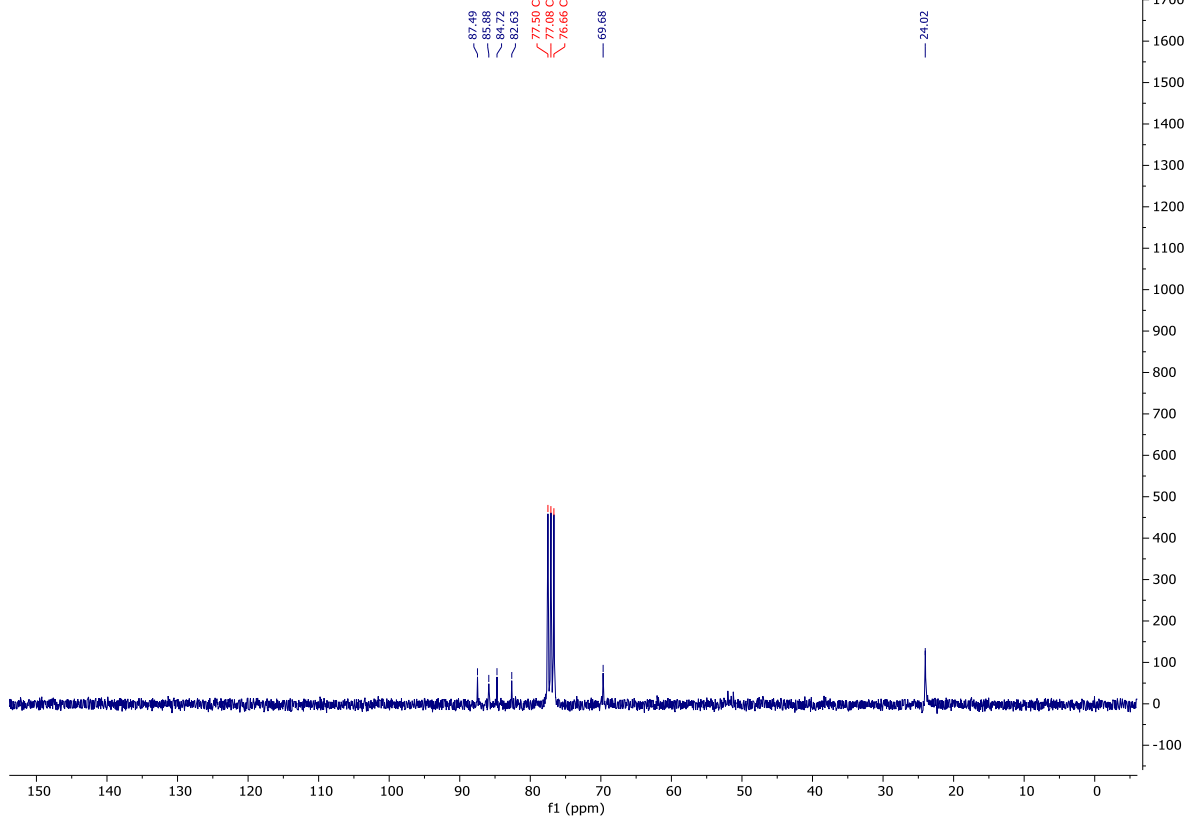


Complex 15:

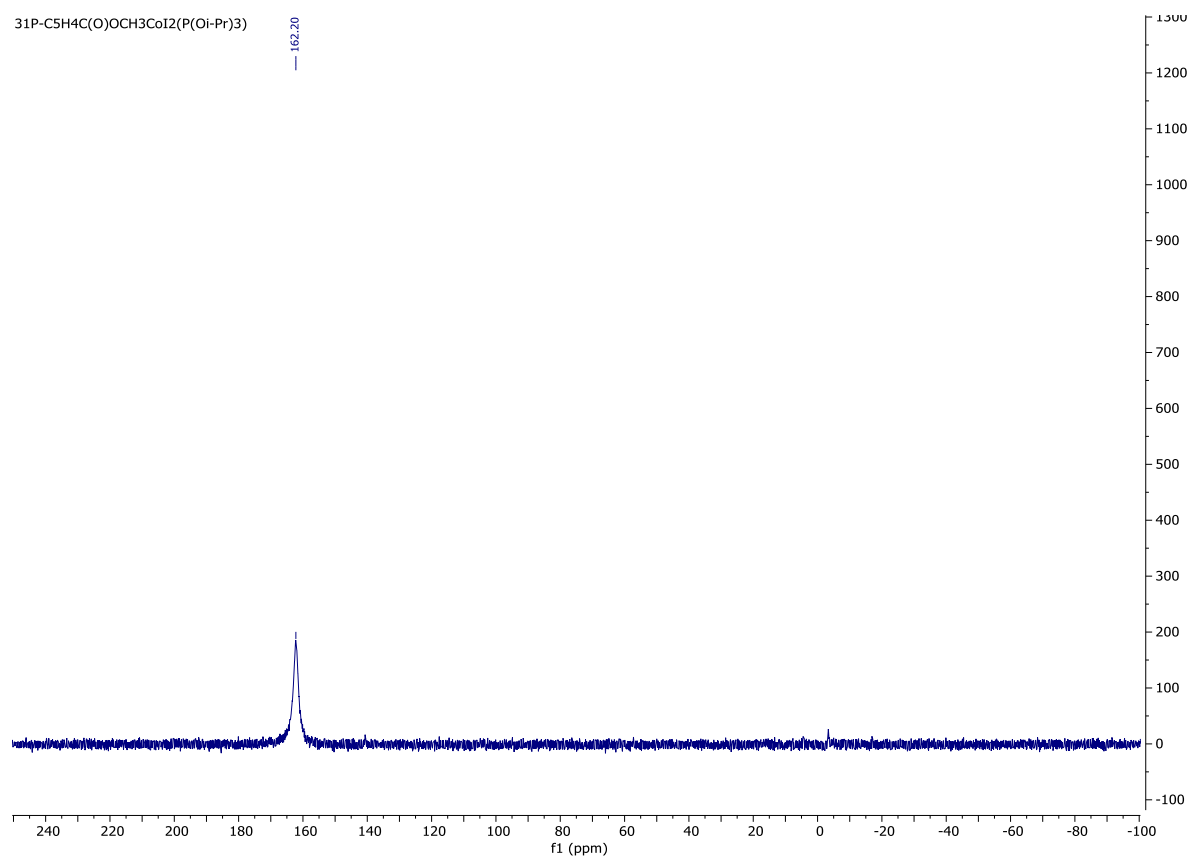
$^1\text{H-C}_5\text{H}_4\text{C}(\text{O})\text{OCH}_3\text{CoI}_2(\text{P}(\text{O}i\text{-Pr})_3)$



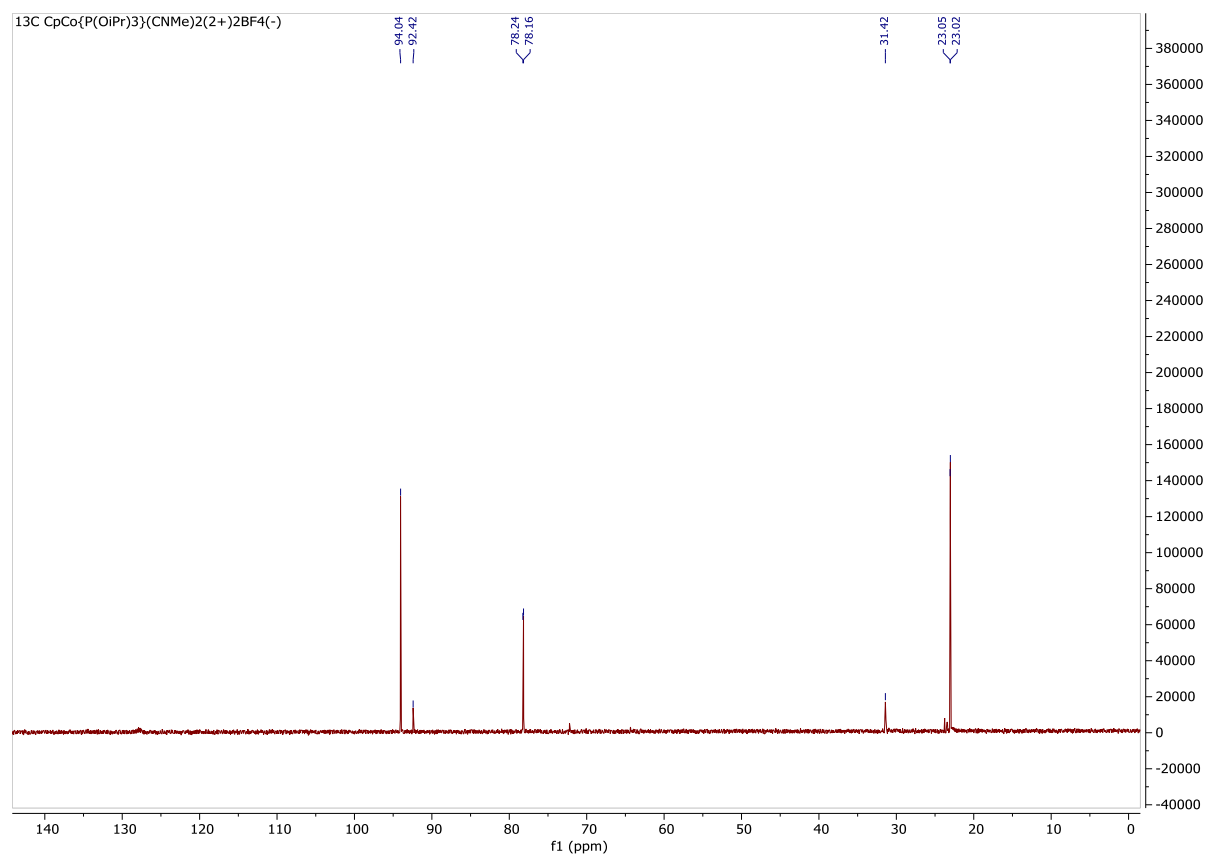
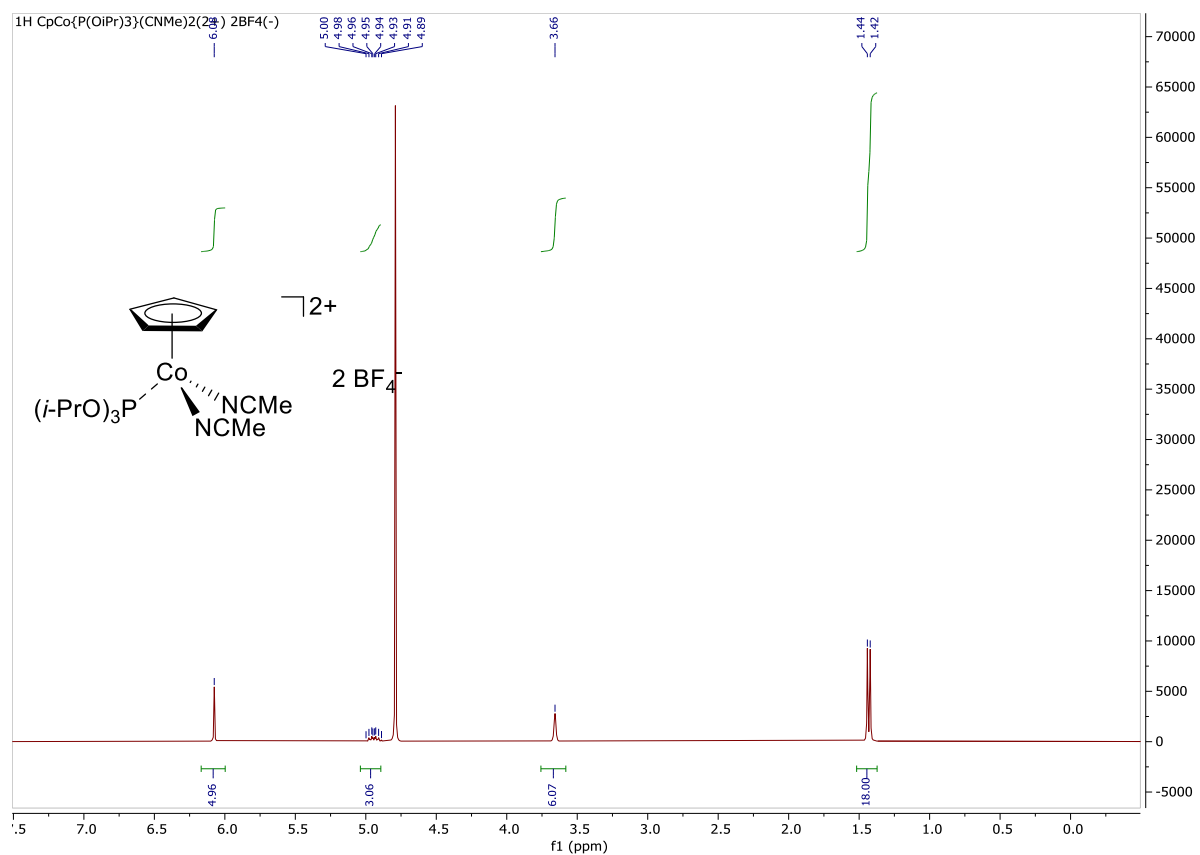
$^{13}\text{C-C}_5\text{H}_4\text{C}(\text{O})\text{OCH}_3\text{CoI}_2(\text{P}(\text{O}i\text{-Pr})_3)$

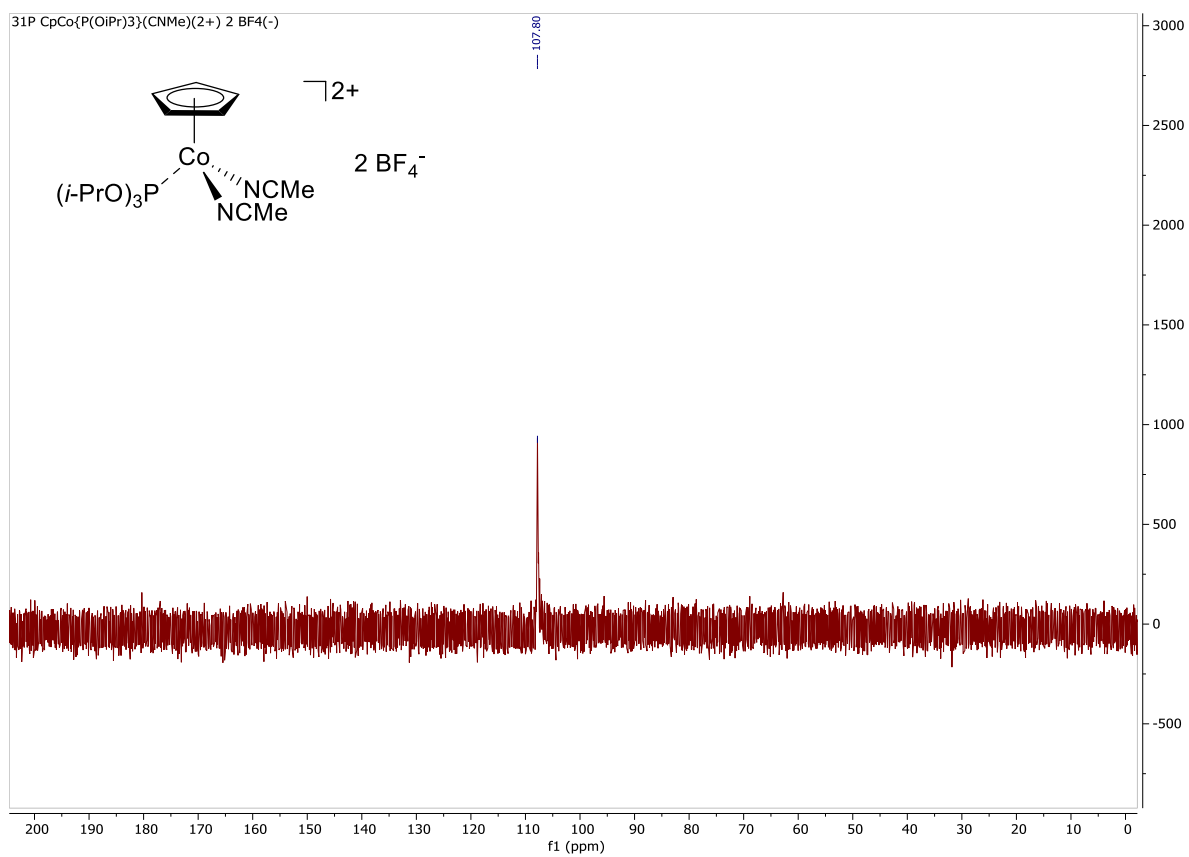


^{31}P -C₅H₄C(O)OCH₃CoI₂(P(Oi-Pr)₃)

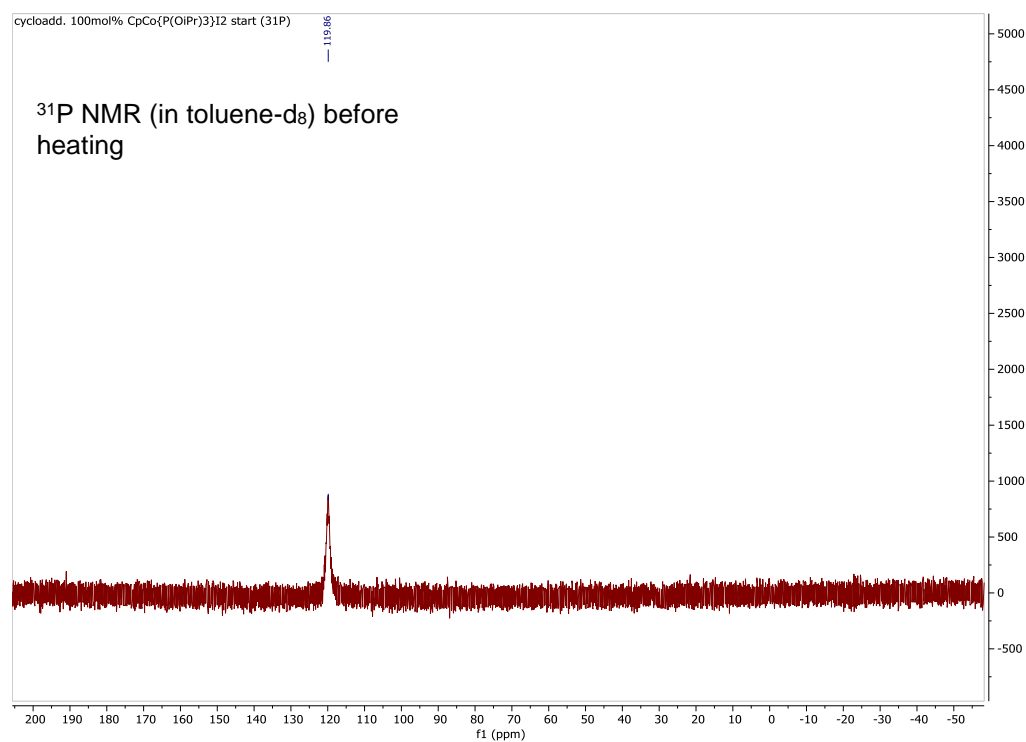
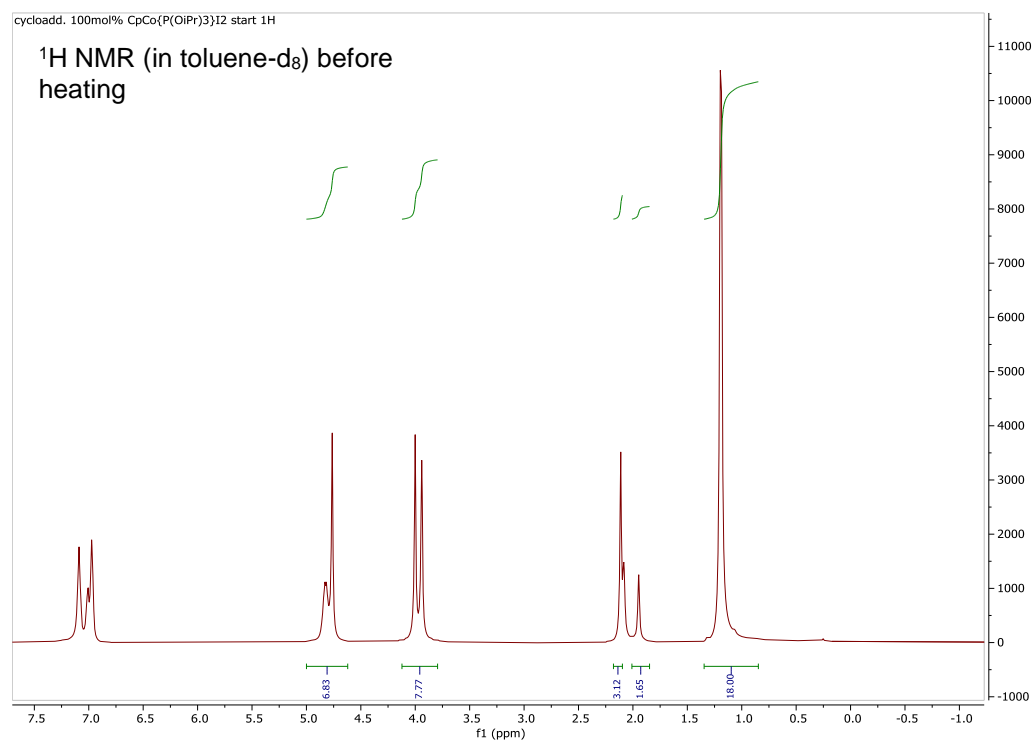


Complex 21:

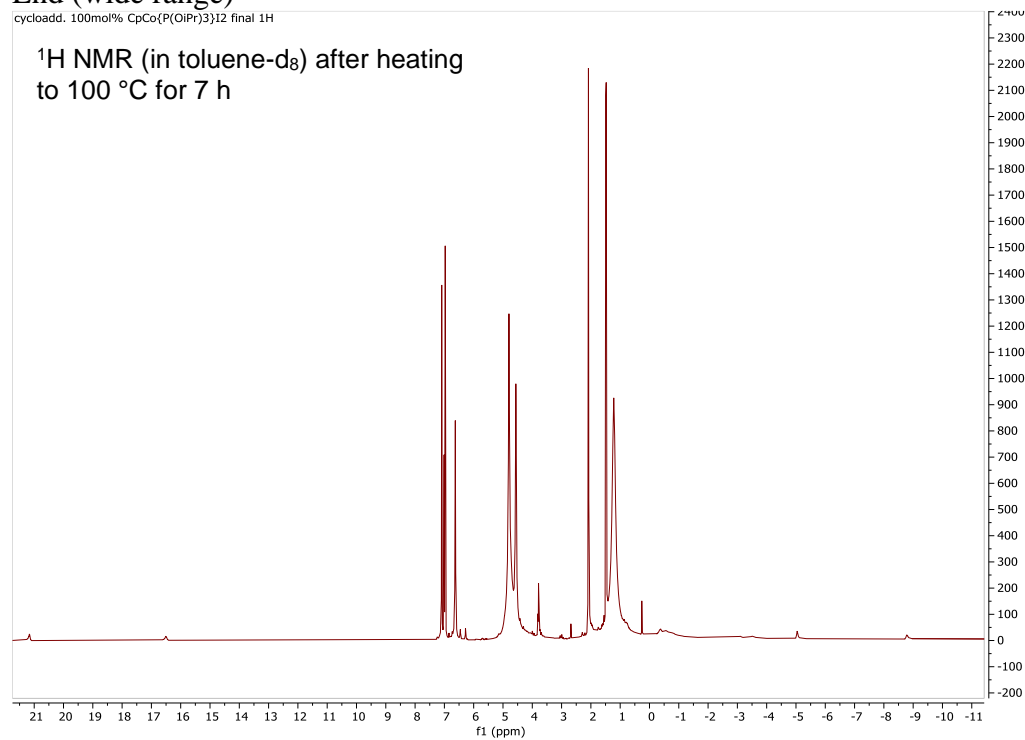




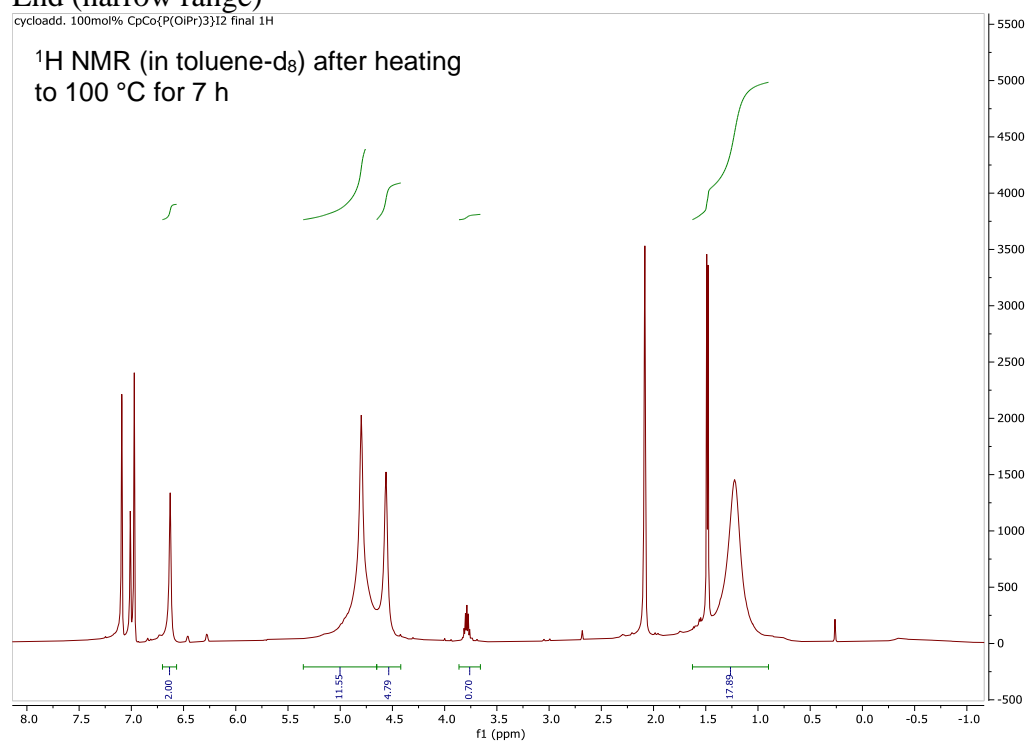
Reaction control for reaction of complex 2 and triyne 16 (Scheme 8):

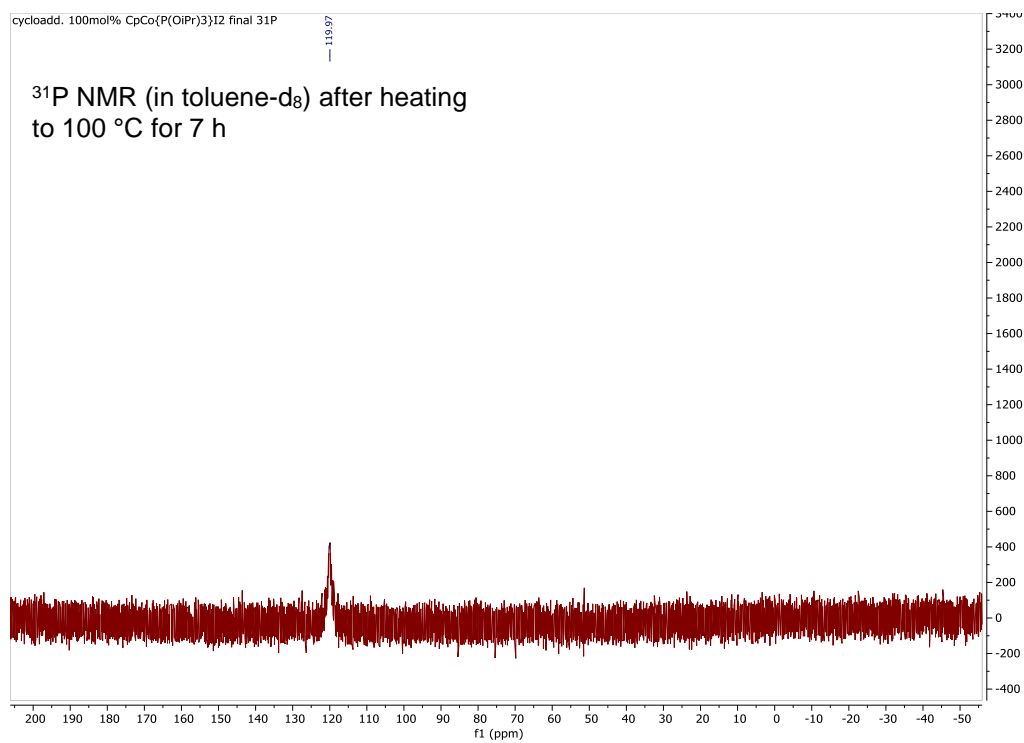


End (wide range)

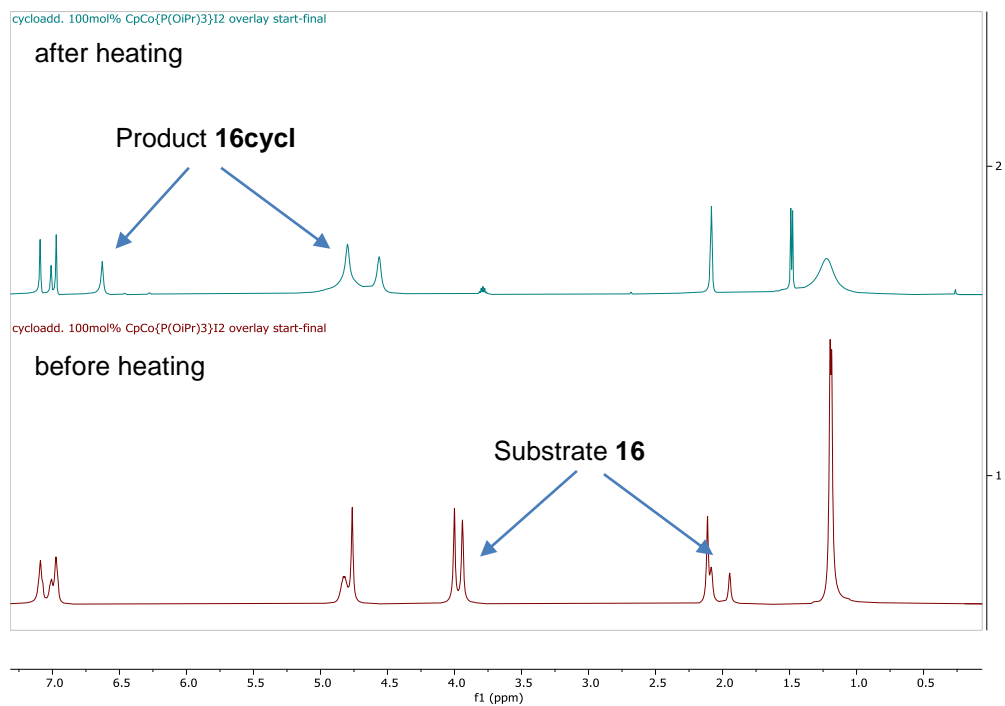


End (narrow range)

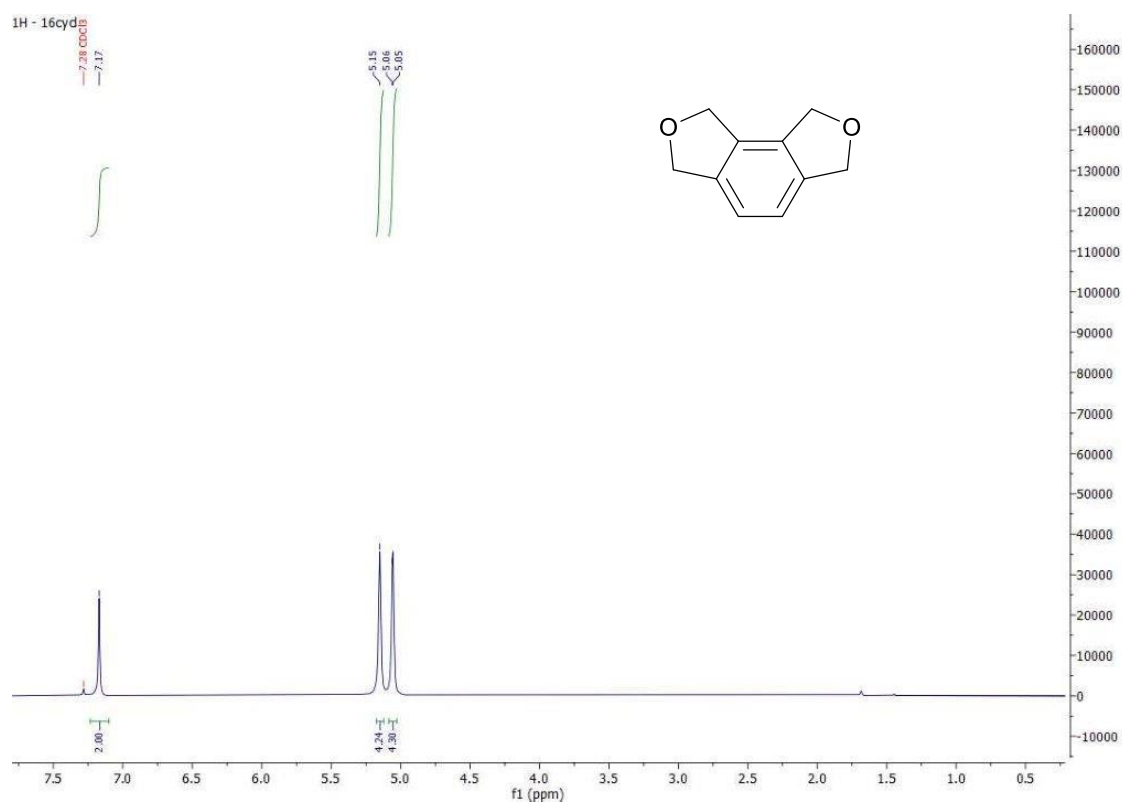




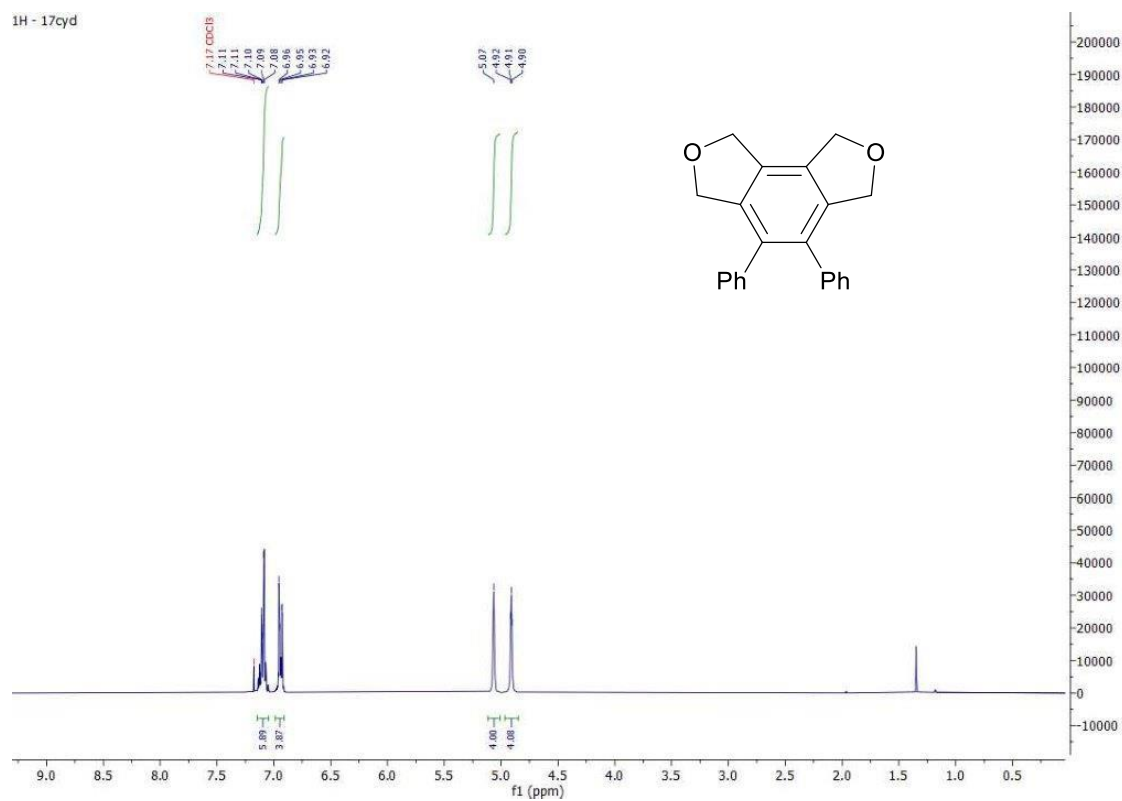
Spectra overlay



Cyclization product 16cycl (in CDCl₃):



Cyclization product 17cycl (in CDCl₃):



References

- [1] Fischer, F.; Pientka, T.; Jiao, H.; Spannenberg, A.; Hapke, M. *Catal. Sci. Tech.* **2020**, *10*, 8005-8014.