

N-HETEROCYCLIC CARBENE AND BIS(PYRAZOLYL)METHANE
SUPPORTED COPPER(I) AND SILVER(I) COMPLEXES OF
ORGANOTRIFLUOROBORATES

by

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ABSTRACT

N-HETEROCYCLIC CARBENE AND BIS(PYRAZOLYL)METHANE SUPPORTED COPPER(I) AND SILVER(I) COMPLEXES OF ORGANOTRIFLUOROBORATES

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The University of Texas at Arlington, 2019

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Organotrifluoroborates have gone from capturing the imagination of the scientific community to being used extensively in a host of applications ranging from being employed to study boron intermediates to being used as a means of introducing trifluoroborate moieties on molecules for custom chemical synthesis. There has been a lot of research done on the application of these molecules as reagents in carbon-carbon coupling reactions such as the Suzuki-Miyaura cross coupling reaction. Despite all of these efforts to understand the versatility of organotrifluoroborates, the possibility of using these molecules as potential ligands in transition metal complexes has not been extensively studied. The novelty of the concept of using these molecules as potential ligands encouraged us to explore the possibility of using coinage metal centers such as Cu(I) and Ag(I) and studying the structure and bonding properties of the resulting species. This thesis encapsulates the study of Ag (I) and Cu (I) complexes of trifluorovinylborates supported by two kinds of ligands. N-heterocyclic carbenes are

useful as supporting ligands because their electron donating properties can be easily modified by changes made to their architecture and also have an influence on their steric properties by the imposition of geometrical constraints on the N-substituents. The other class of ligands that we were interested in using were pyrazoles, specifically bis(pyrazolyl)methanes, since their co-ordination properties can be easily varied by changing the substituents on the pyrazole ring. The electron donating properties of bis(pyrazolyl)methanes have been shown to be affected by the electron donating ability of the functional groups and the presence of bulky groups on the pyrazole ring influences the sterics of co-ordination of the metal center with other ligands in the co-ordination sphere.

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Chapter-1

1.1 Introduction to Organotrifluoroborates

The first reported preparation of organotrifluoroborates was in 1940 by Fowler and Kross.¹ Twenty years later in 1960, Chambers prepared the potassium (trifluoromethyl)trifluoroborate salt by treating boron trifluoride gas with (trifluoromethyl)-trimethylstannane followed by potassium fluoride.²

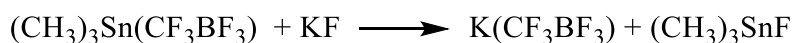


Figure 1: Synthesis of potassium trifluoroborates

Although the barium and ammonium salts were also synthesized later, they were found to be very unstable and readily decomposed. The potassium salt on the other hand was found to be thermally stable and also displayed remarkable non-hygroscopic behavior. These properties were found to be extremely attractive and were used to synthesize the first potassium vinyl and methyl trifluoroborates by the displacement of tin in tetravinyltin with boron by Stafford.³

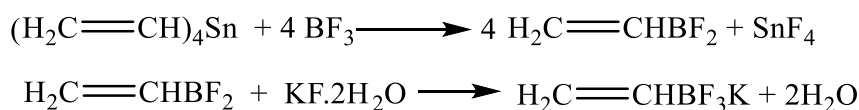


Figure 2: Synthesis of potassiumtrifluorovinylborate

The physical properties and solubility of these trifluorovinylborate salts are dictated by the counter cation.⁴ The potassium salt is often most favored due to its free flowing crystalline nature and its relatively simple method of preparation⁵ thanks to the commercial availability of one of the primary reagents employed in its synthesis, KHF_2 .

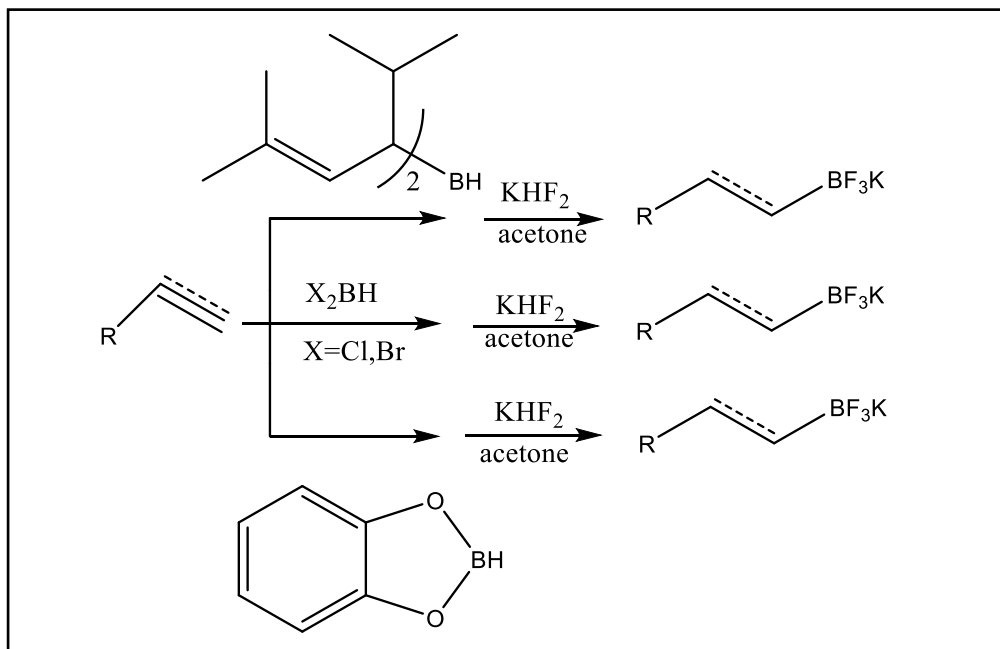


Figure 3: Hydroboration routes to Potassium(organo)trifluoroborates

In traditional multi-step organic synthesis the concept of using protecting groups to preserve certain functional moieties is well established. However the concept of using so called protecting groups in organometallic chemistry is not well understood. In this regard, organoboranes serve as a useful means to preserve the boron moiety since they are found to be resistant to attack from nucleophiles, bases and oxidants which are typically used in a majority of functional group transformation reactions.⁶ This has allowed researchers to develop a variety of different highly functionalized organotrifluoroborates which can be easily treated with nucleophiles to give a host of products that cannot otherwise be obtained using conventional means of boron introduction such as hydroboration and transmetalation.⁶

Another major application where organotrifluoroborates have received widespread attention is its use as nucleophilic carbon-carbon coupling agent in cross coupling

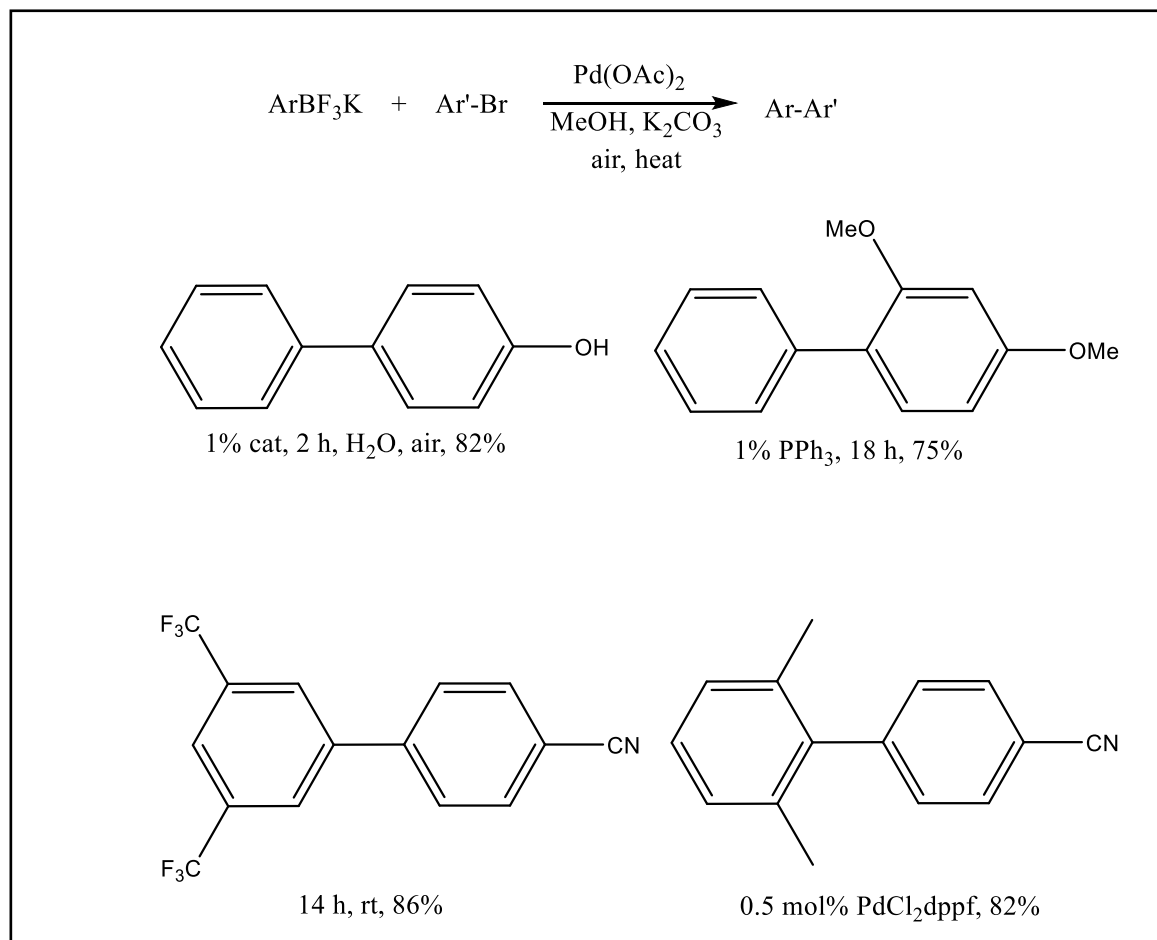


Figure 4: Aryl/aryl cross-coupling reactions

reactions such as the Suzuki-Miyaura cross coupling reaction.⁷ Traditionally when these reactions were first studied, organoboranes such as boronic acids and boronic esters were used. There were a host of problems associated with using these reagents. Boronic acids were usually synthesized as waxy solids which were not stable and not easy to handle. They were also difficult to purify and readily formed an equilibrium with trimeric cyclic anhydrides which were found to influence the stoichiometry of the reaction.⁶ It did not help that at this time, there was no reliable means to ascertain the exact amount of boronic acid present in a synthesized sample.

Boronic esters also suffered from forming pinacols which generated a large number of by-products which lowered the yield of the reaction significantly.

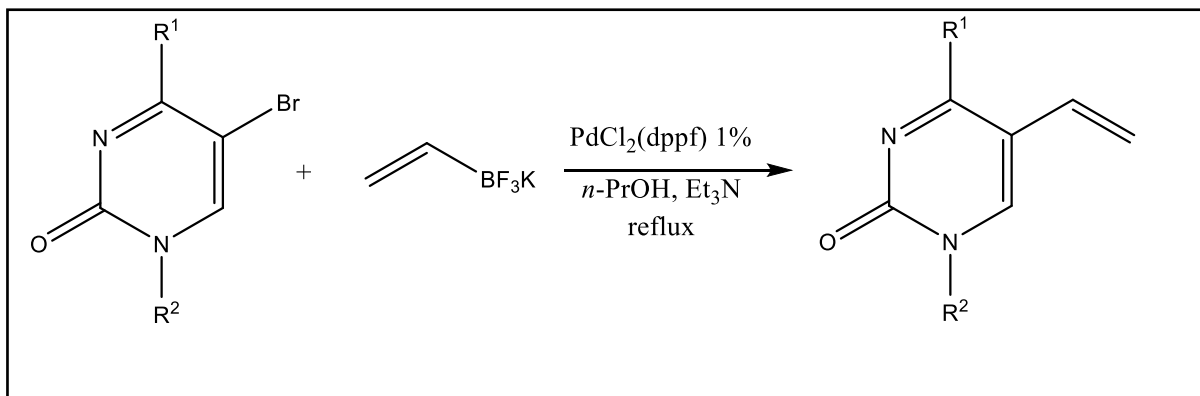


Figure 5: Cross-coupling of trifluorovinylborates with bromopyrimidines

Organotrifluoroborates solved these problems since they were indefinitely air stable and allowed reactions to be associated with a high atom economy thus minimizing the formation of wasteful by-products. In addition to this, it was also found that potassium salts of aryltrifluoroborates were also easily able to carry out coupling reactions in substrates that are sterically strained, which would ordinarily not be possible with the use of organoboronic acids and esters.⁸

1.2 Organotrifluoroborates as ligands in transition metal complexes

In spite of all the research efforts that have been directed at studying the various applications of organotrifluoroborates, the prospect of using them to serve as ligands that are part of the co-ordination sphere of transition metal complexes has not been explored until recently. In 2018, Wang and coworkers⁹ synthesized the first complex containing organotrifluoroborates, specifically, trifluorovinylborate attached to a silver (I) metal center supported by an *N*-heterocyclic carbene (NHC) carbene ligand, namely, 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene, which can be abbreviated as SIPr respectively.

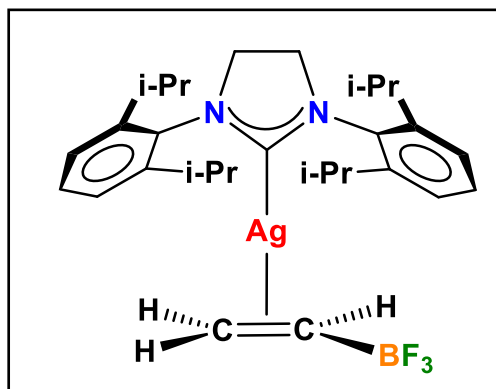


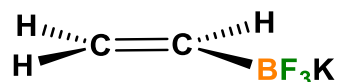
Figure 6: SIPrAgvinylBF₃

This is the first instance of trifluorovinylborates being studied as potential ligands due to their nucleophilic character. Having studied the synthesis of this complex, using a cheaper metal in place of silver(I) such as copper(I) was found to be an attractive prospect since there would be a good comparison of the structure and bonding properties between both these complexes.

2. Results and Discussion

Copper(I) nitrate supported by an NHC ligand was selected for this work because of the fact that the bond between copper and the nitrate group is relatively weak and so it can be easily broken and made to react with potassium trifluorovinylborate to form the complex of interest, copper(I) trifluorovinylborate. We had initially tried to use the copper(I) chloride analog of this complex to ascertain if it would be reactive enough but we found that no reaction was observed. The SIPrCuNO₃ used as a precursor in this work could be easily synthesized by reacting SIPrCuCl with an equivalent amount of AgNO₃ in dichloromethane. While SIPrCuNO₃ showed good solubility in dichloromethane, it was found that potassium trifluorovinylborate had poor solubility. To circumvent this problem, acetonitrile was used as a cosolvent. The reaction was carried out at room temperature to afford the product in good yield.

(>70%). The product was found to be soluble in halogenated solvents such as dichloromethane and chloroform but was found to be insoluble in solvents such as hexane and ether.



NMR Parameter (CDCl ₃)		SIPrCu(MeCN)C ₂ H ₃ BF ₃ (1)	Free KC ₂ H ₃ BF ₃ (2)
¹ H	H ₂ C=CH	4.35 (br.d)	5.22-5.13 (m)
		4.66 (dd)	
		5.12-5.06 (m)	5.84-5.69 (m)
¹⁹ F	BF ₃	-142.5 (s)	-139.5 (s)
¹³ C	C=C	111.76	120

Table 1. NMR spectroscopic data (in ppm) of SIPrCu(MeCN)C₂H₃BF₃

¹H NMR data revealed that there was an upfield shift of the vinylic protons at $\delta = 5.10$, 4.68 and 4.36 ppm respectively in comparison to the free potassiumtrifluorovinylborate molecule, whose peaks were observed at 5.07 and 5.69 ppm. (Table 1)

The ¹³C NMR of the methylene carbon of the copper(I) co-ordinated trifluorovinylborate was found to show a considerable upfield shift from 120 ppm to 111.76 ppm, which is due to the increased π -back-bond donation of electron rich copper(I) metal center bonded to the trifluorovinylborate ligand. Crystals suitable for X-ray crystallography were obtained from a mixture of dichloromethane and hexane.

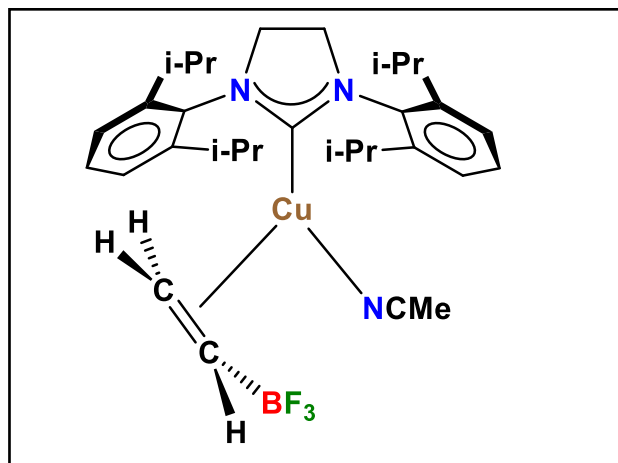


Figure 7: SIPrCu(MeCN)vinylBF₃ (**2**)

The crystal structure obtained revealed that the complex was monomeric copper(I) trifluorovinylborate bonded to each other in a η_2 fashion which is consistent with late transition metals of lower oxidation states forming complexes with π acid ligands. The carbon-carbon double bond length of the vinylic moiety is found to be 1.368 Å which is significantly longer than the double bond length of free potassium trifluorovinylborate molecule (1.286 Å). There is no data on the structural features of free trifluorovinylborate anion. However there has been a report⁹ of a silver(I) dimer of an N-heterocyclic carbene with free trifluorovinylborate as a counter anion whose double bond length was found to be 1.286 Å. The authors of the aforementioned study⁹ also performed theoretical calculations pertaining to the double bond length of the vinylic moiety of trifluorovinylborate and reported a value of 1.341 Å. The lower than expected carbon-carbon double length is found to be attributed to libration effects. The increase in the carbon-carbon double bond length of metal co-ordinated trifluorovinylborate is also observed in case of SIPrAg(vinyl)BF₃ (1.370 Å) and other similar transition metal ethylene complexes such as 1,3,5-triazapentadienyl supported copper(I)ethylene (1.377 Å). The Cu-C

(NHC) bond distance was found to be 1.975 Å. While the Cu-C (vinyltrifluoroborate anion) distance was found to be 2.106 Å and 2.094 Å. However, it was also found that there was an acetonitrile adduct that was part of the co-ordination sphere. This was a rather unprecedented observation and we were curious to see if the use of a more sterically crowded supporting ligand would prevent acetonitrile from binding to the copper metal center. Our research group had done extensive work pertaining to the study and application of pyrazole based ligands in organometallic chemistry.¹¹ It is known that these type of ligands can be easily modified with bulky substituents which would influence the stereochemistry of the ligand,¹² making it a more crowded environment in which copper(I) could exclusively co-ordinate with trifluorovinylborate without acetonitrile being part of the co-ordination sphere.

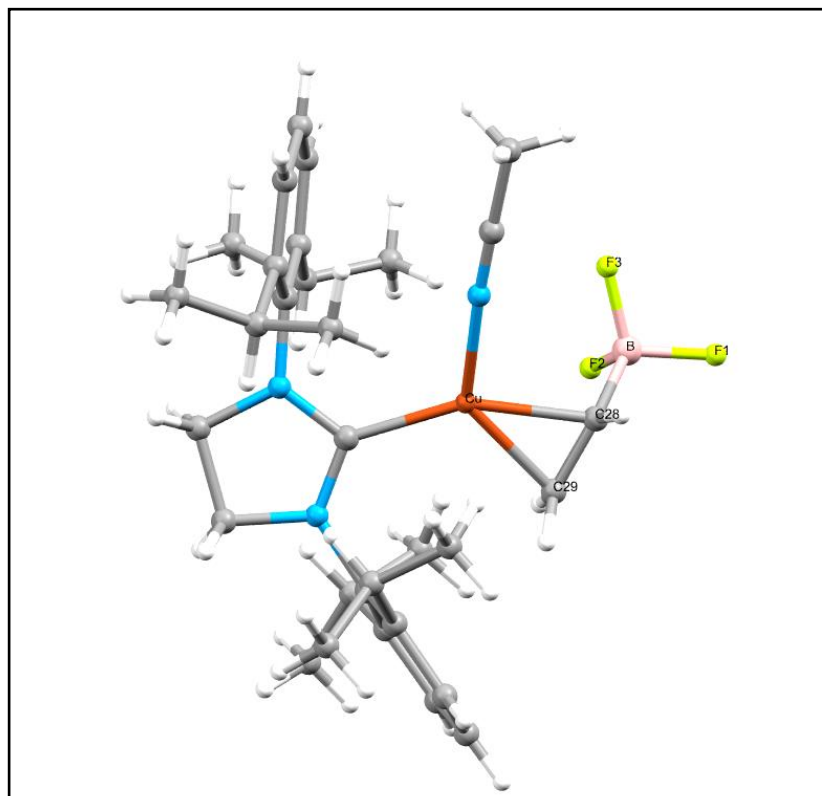


Figure 8: Molecular structure of SIPr(MeCN)vinylBF₃

Therefore we synthesized a novel tris(acetonitrile)trifluorovinylborate copper(I) complex from tetrakis(acetonitrile) copper(I)tetrafluoroborate and potassium trifluorovinylborate. This complex was unstable and difficult to isolate since it readily underwent decomposition upon isolation. However we were able to obtain ^1H NMR data which showed peaks pertaining to the vinylic moiety appearing upfield at $\delta = 5.27, 4.83, 4.64$ as opposed to the free potassium trifluorovinylborate molecule (Table 2). We attempted to take a ^{19}F NMR but we found no peaks, probably due to the decomposition. Due to its unstable nature, we realized that the insertion of an electron rich neutral supporting ligand would possibly help stabilize this molecule.

NMR Parameters ($\text{C}_6\text{D}_6\text{O}$)		$(\text{MeCN})_3\text{AgC}_2\text{H}_3\text{BF}_3$ (4)	$(\text{MeCN})_3\text{CuC}_2\text{H}_3\text{BF}_3$ (3)	Free $\text{C}_2\text{H}_3\text{BF}_3$ (1)
^1H	$\text{H}_2\text{C}=\text{CH}$	5.11 (s)	4.64 (d)	5.22-5.13 (m)
		5.24 (d)	4.83 (d)	
		5.85 (t)	5.27 (t)	5.84-5.69 (m)
^{19}F	BF_3	-141.5 (s)	-	-139.5 (s)

Table 2. NMR Spectroscopic (in ppm) of Ag(I) and Cu(I) of $\text{C}_2\text{H}_3\text{BF}_3$

The characteristics of bis(pyrazolyl)methane suitably modified with electron donating substituents like alkyl groups seemed like a perfect candidate to stabilize the analogous copper(I) complex. Therefore we prepared the tris(acetonitrile)copper(I)trifluoro-vinylborate complex under an inert atmosphere of nitrogen followed by the in-situ

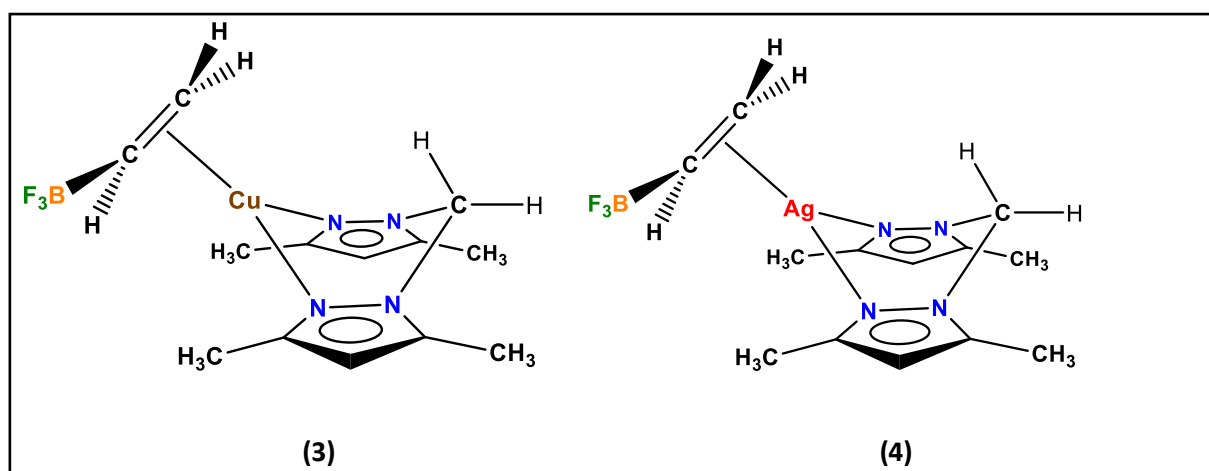


Figure 9: Trifluorovinylborate complexes of silver(I) and copper(I) supported by bis(3,5-dimethyl-1H-pyrazol-1-yl)methane

addition of the supporting ligand which was bis(3,5-dimethyl)pyrazolylmethane to give the target copper(I)trifluorovinylborate complex supported by bis(3,5dimethyl)pyrazolyl methane. The ¹H NMR revealed that there was a upfield shift observed with regard to the vinylic protons $\delta = 5.10, 4.68$ and 4.36 ppm (Table 1) in comparison with the free potassium trifluoro- vinylborate molecule, whose vinylic peaks appear at $\delta = 5.07$ and 5.69 ppm (Table 1). This gave us an indication of the formation of the desired copper trifluorovinylborate complex because of the increased electron density contributed to the copper metal center by the supporting ligand which shields the vinylic protons and hence results in an upfield shift. ¹⁹F NMR revealed that there was a small downfield shift from $\delta = -139.5$ for the free potassium trifluorovinylborate to $\delta = -139.9$ for the Cu(I) co-ordinated trifluorovinylborate complex. Since we successfully synthesized the tris(acetonitrile) copper(I)trifluorovinylborate complex,

NMR Parameters (CDCl ₃)		Bpm(CH ₃) ₂ AgC ₂ H ₃ BF ₃ (4)	Bpm(CH ₃) ₂ CuC ₂ H ₃ BF ₃ (3)	Free C ₂ H ₃ BF ₃ (1)
¹ H	H ₂ C=CH	5.33 (d)	4.64 (d)	5.22-5.13 (m)
		5.66 (d)	4.87 (d)	
		6.26-6.20 (m)	5.39-5.33 (m)	5.84-5.69 (m)
¹⁹ F	BF ₃	-142.0 (s)	-139.9 (s)	-139.5 (s)

Table 3. NMR spectroscopic data (in ppm) CH₂[(3,5-(CH₃)₂Pz)₂] Cu(I) and Ag(I) complexes of C₂H₃BF₃

we wanted to explore the possibility of synthesizing the silver(I) analogue of this molecule since to the best of our knowledge these complexes have not been reported in the literature. Tris(acetonitrile)silver(I)trifluoroborate was synthesized from silver(I)triflate and potassium vinyltrifluoroborate under nitrogen atmosphere. The isolated colorless solid was found to be soluble in polar solvents but insoluble in non-polar solvents. We were also able to isolate colorless crystals of this molecule by using a binary solvent system consisting of acetonitrile and dichloromethane. ¹H NMR analysis revealed a downfield shift of the vinylic protons which were observed at $\delta = 5.85, 5.24$ and 5.11 with reference to the free potassium trifluorovinylborate molecule (Table 2). ¹⁹F NMR revealed that there was a downfield shift to -141.2 from -139.5 for the free potassium trifluorovinylborate molecule. We subsequently added CH₂(3,5-(CH₃)₂Pz)₂ in-situ under the influence of nitrogen to isolate an air stable silver(I)trifluorovinylborate complex supported by CH₂(3,5-(CH₃)₂Pz)₂ slight downfield shift was observed for the vinylic proton situated adjacent to the trifluoroborate moiety of the silver(I)trifluorovinylborate complex with respect to

the free potassium trifluorovinylborate molecule (Table 3). This could be attributed to greater than usual π backbonding in combination with shielding of the vinylic protons due to the increased electron density on the metal center facilitated by the electron rich bispyrazolyl methane supporting ligand. As evidenced from the NMR spectral data, $[\text{CH}_2(3,5\text{-(CH}_3)_2\text{Pz)}_2]\text{Cu}(\text{vinylBF}_3)$ and $[\text{CH}_2(3,5\text{-(CH}_3)_2\text{Pz)}_2]\text{Ag}(\text{vinylBF}_3)$ follow the same trend that is observed with the corresponding $\text{SIPrCu}(\text{MeCN})\text{vinylBF}_3$ and SIPrAgvinylBF_3 complexes respectively.

3. Conclusion

In summary, we have prepared an N-heterocyclic carbene supported complex of copper(I)trifluorovinylborate and have corroborated our observations with experimental data that suggests that acetonitrile is also bound to the copper(I) metal center and is part of its co-ordination sphere. In an effort to understand whether steric factors play a role in this binding, we used bispyrazolyl methane with electron donating methyl substituents to create an electron rich, sterically bulky supporting ligand. We synthesized silver(I) and copper(I) trifluorovinylborate complexes using this supporting ligand and have found that there are similarities between the copper(I)trifluorovinylborate complexes supported by the two bulky electron rich ligands and these similarities extend to their silver analogs. These studies have helped us ascertain that trifluoro(organo)boranes can serve as ligands that coordinate with transition metals to form complexes in addition to the profound applications in synthetic chemistry.

4. Experimental Section

4.1 General Methods

All the experiments were performed under an atmosphere of purified nitrogen using standard Schlenk techniques or in a MBRAUN LABMaster glovebox equipped with a -10 °C refrigerator. Solvents were procured from commercial sources and purified by conventional methods prior to use. Glassware was oven dried at 150 °C overnight. The NMR spectra were recorded at room temperature on a JEOL Eclipse 500 spectrometer (^1H , 500.16 MHz; ^{13}C , 125.77 MHz and ^{19}F , 470.62 MHz). Proton and carbon chemical shifts are reported in ppm and are referenced using the residual proton and carbon signals of the deuterated solvent (^1H , CDCl_3 , $\delta = 7.26$ ppm; ^{13}C , CDCl_3 , $\delta = 77.16$ ppm). ^{19}F NMR chemical shifts were referenced relative to external CFCl_3 . Elemental analysis was performed at Intertek USA, Whitehouse, NJ. Deuterated solvents were purchased from Acros Organics and Cambridge Isotope Laboratories, respectively. The $\text{K}(\text{CH}_2=\text{CHBF}_3)$,¹³ $(\text{SIPr})\text{CuCl}$ ¹⁴ and were prepared according to literature procedure.

4.2 $(\text{SIPr})\text{CuNO}_3$: A mixture of $(\text{SIPr})\text{CuCl}$ (150 mg, 0.307 mmol) and AgNO_3 (52.21 mg, 0.307 mmol) were added to a Schlenk flask and dissolved in dichloromethane (10 mL, dry). The mixture was stirred overnight at room temperature resulting in a precipitate which was filtered through celite. The filtrate was pump dried to obtain the product as a white solid. Yield: 115.6 mg, 73%. ^1H NMR (CDCl_3 , 500.16 MHz): δ 7.40 (t, $J = 8.0\text{Hz}$, 2H, Ar-H), 4.03 (s, 4H, $\text{CH}_{\text{imidazole}}$), 3.06 (sept, 4H, $J = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.36 (d, 12H, $J = 6.7$ Hz), 1.34 (d, 12H, $J = 6.8$ Hz).

4.3 **(SIPr)Cu(MeCN)(CH₂=CHBF₃)**: A mixture of (SIPr)CuNO₃ (100 mg, 0.1937 mmol) and K(CH₂=CHBF₃) (28.54 mg, 0.213 mmol) in dichloromethane (ca. 7mL, dry) and acetonitrile (ca. 3mL, dry) was stirred overnight at room temperature. The resulting mixture was filtered and the filtrate was layered with hexanes to obtain colorless crystals of (SIPr)Cu(CH₂=CHBF₃) (91.26 mg, 75 % yield). ¹H NMR (CDCl₃, 500.16 MHz, 298 K): δ = 7.43 (t, J = 8.0 Hz, 2 H, CH_{Ar}), 7.26 (d, J = 8.0 Hz, 4 H, CH_{Ar}), 5.10 (m, 1 H, CH₂CHBF₃), 4.68 (dd, J = 21.75 Hz, J = 3.45 Hz, 1 H, CH₂CHBF₃), 4.36 (br. d, J = 8.60 Hz, 1 H, CH₂CHBF₃), 4.07 (s, 4 H, CH_{imidazole}), 3.0 (sept, J = 6.8 Hz, 4 H, CH(CH₃)₂), 2.24 (s, 3 H, NC(CH₃)), 1.33 (d, J = 6.9 Hz, 12 H, CH₃), 1.32 (d, J = 6.8 Hz, 12 H, CH₃), ¹³C{H} NMR, (CDCl₃, 125.77 Hz, 298K): δ = 201.8 (br. weak), 146.74, 134.09, 130.17, 125.72, 111.76 (s, CH₂CHBF₃), 53.84, 29.01, 25.19, 24.30, ¹⁹F NMR (CDCl₃, 470.62 MHz, 298K): δ = -142.28 (m, CH₂CHBF₃) ppm. C₃₃H₅₈BCuF₃N₃ (628.19): calcd. C 63.09, H 9.31, N 6.69; found C 63.28, H 9.48, N 6.42.

4.4 **CH₂[(3,5-(CH₃)₂Pz)₂]Cu(CH₂=CHBF₃)**: A mixture of CH₂[(3,5-(CH₃)₂Pz)₂]CuCl (150 mg, 0.4946 mmol) and K(CH₂=CHBF₃) (65.86 mg, 0.4946 mmol) was allowed to stir overnight at room temperature in 7mL of dichloromethane and 3 mL of acetonitrile. The resulting mixture was then filtered and the filtrate was vacuum dried to afford a colorless solid as the desired product (106.74 mg, 71% yield). ¹H NMR (CDCl₃, 500.16 MHz, 298K): δ = 6.04 (br.s, 4H, N(CH₂)N, CH_{pyrazole}), 5.36 (m, 1H, J = 14.7 Hz, CH₂CHBF₃), 4.87 (d, 1H, J = 18.3 Hz, CH₂CHBF₃), 4.64 (d, 1H, J = 12.3 Hz, CH₂CHBF₃), 2.39 (s, 6H, CH_{3pyrazole}), 2.28 (s, 6H, CH_{3pyrazole}). ¹⁹F NMR

(CDCl₃, 470.62 MHz, 298K): δ = -139.8 (m, CH₂CHBF₃).). C₁₄H₂₂BCuF₃N₄ (377.12): calcd. C 44.52, H 5.87, N 14.83; found C 44.73, H 5.93, N 15.17.

4.5 **CH₂[(3,5-(CH₃)₂Pz)₂]Ag(CH₂=CHBF₃):** A mixture of CH₂[3,5-(CH₃)₂Pz]₂AgNO₃ (130 mg, 0.3475 mmol) and K(CH₂=CHBF₃) (46.54 mg, 0.3475 mmol) in 7 mL of dichloromethane and 3mL of acetonitrile was allowed to stir overnight at room temperature. The resulting mixture was then filtered through celite and vacuum dried to obtain a colorless solid. (98.23 mg, 67.4% yield). ¹H NMR (CDCl₃, 500.16 MHz, 298K): δ = 6.23 (m, 1H, J= 15 Hz, CH₂CHBF₃), 6.07 (s, 2H, N(CH₂)N), 5.88 (s, 2H, CH_{pyrazole}) 5.66 (d, 1H, J=20 Hz, CH₂CHBF₃), 5.34 (br. d, 1H, J= 10 Hz, CH₂CHBF₃), 2.42 (s, 6H, CH_{3pyrazole}), 2.21 (s, 6H, CH_{3pyrazole}). ¹⁹F NMR (CDCl₃, 470.62 MHz, 298K): δ = -142.01. C₁₄H₂₂AgBF₃N₄ (422.03): calcd. C 39.84, H 5.25, N 13.28; found C 40.11, H 4.86, N 13.11.

4.6 **(MeCN)₃Ag(CH₂=CHBF₃):** A mixture of silver(I)triflate (150 mg, 0.58 mmol) and potassium trifluorovinylborate (77.7 mg, 0.58 mmol) were taken in 7 mL of acetonitrile and allowed to stir overnight at room temperature. The mixture was then filtered through celite and vacuum dried to give a white solid. (139.3 mg, 73.2%) ¹H NMR (C₃D₆O, 500.16 MHz, 298 K): δ = 5.85 (t, 1H, J = 10 Hz, CH₂=CHBF₃), 5.24 (d, 1H, J = 20 Hz, CH₂CHBF₃), 5.11 (br s, CH₂=CHBF₃). ¹⁹F NMR (CDCl₃, 470.62 MHz, 298K): δ = -142.01. C₈H₁₂AgBF₃N₃ (325.88): calcd. C 29.49, H 3.71, N 12.89; found C 29.57, H 3.88, N 12.67.

4.7 **(MeCN)₃Cu(CH₂=CHBF₃):** A mixture of copper(I)tetrakisacetonitriletetrafluoroborate (150 mg, 0.47 mmol) and potassium trifluorovinylborate (63.49 mg, 0.47 mmol) were taken in 7 mL of acetonitrile and allowed to stir overnight at room

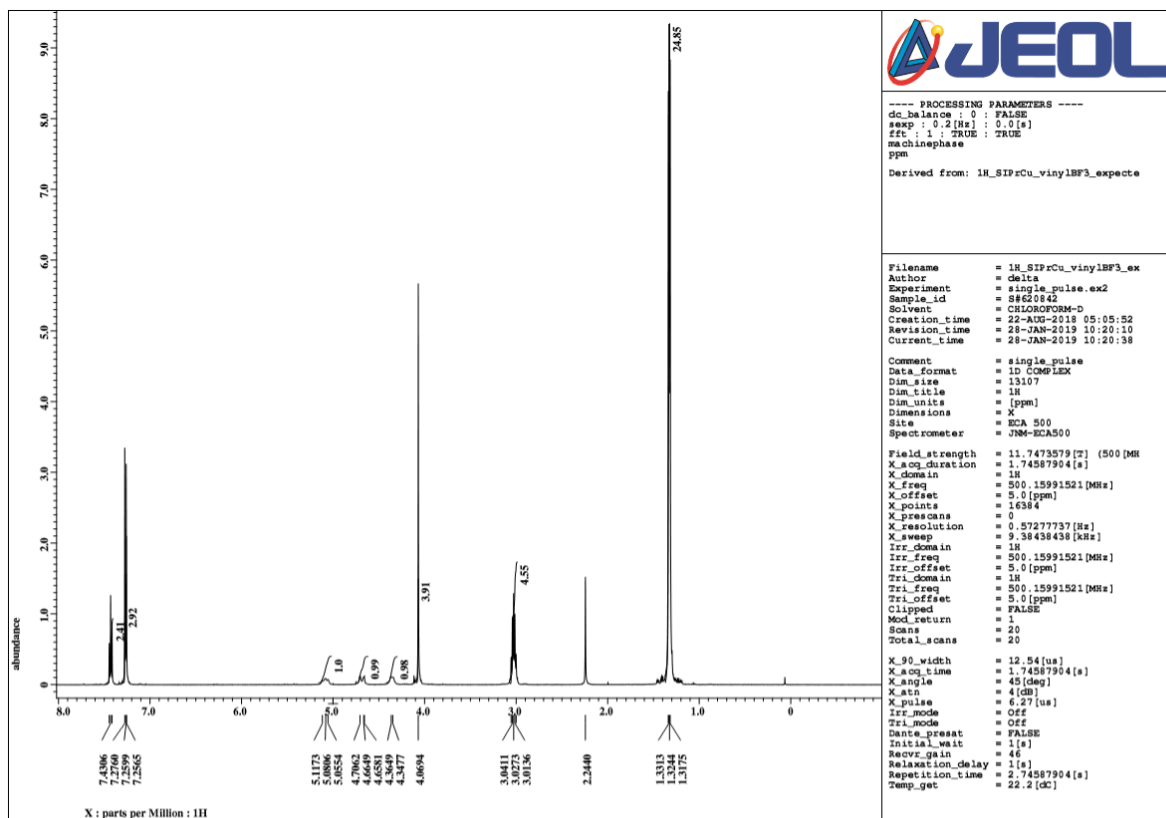
temperature. The mixture was then filtered through celite. ^1H NMR (CDCl_3 , 500.16 MHz, 298 K): δ = 5.27 (t, 1H, J = 10 Hz, CH_2CHBF_3), 4.83 (d, 1H, J = 15 Hz, CH_2CHBF_3), 4.64 (d, 1H, J = 8 Hz, CH_2CHBF_3).

4.8 X-Ray Data Collection and Structure Determinations: A suitable crystal covered with a layer of hydrocarbon/paratone-N oil was selected and mounted on a Cryo-loop and immediately placed in the low temperature nitrogen stream. The X-Ray intensity data for $\text{SiPrCu}(\text{MeCN})\text{vinylBF}_3$ was measured at 100 K or at 106 K on a Bruker D8 Quest with a Photon 100 CMOS detector equipped with an Oxford Cryosystems 700 series cooler, a Triumph monochromator and a Mo $\text{K}\alpha$ fine focus sealed tube ($\lambda = 0.71073\text{\AA}$). Intensity data was processed using Bruker ApexII program suite. All the calculations for the structure determination were carried out using the SHELXTL package (version 6.14). Initial atomic positions were located by direct methods using XS and the structure of the molecule was refined by the least-squares method SHELXL.¹⁰ Absorption corrections were applied using SADABS. All the non-hydrogen atoms were refined anisotropically. X-ray structural figures were generated using Olex2.

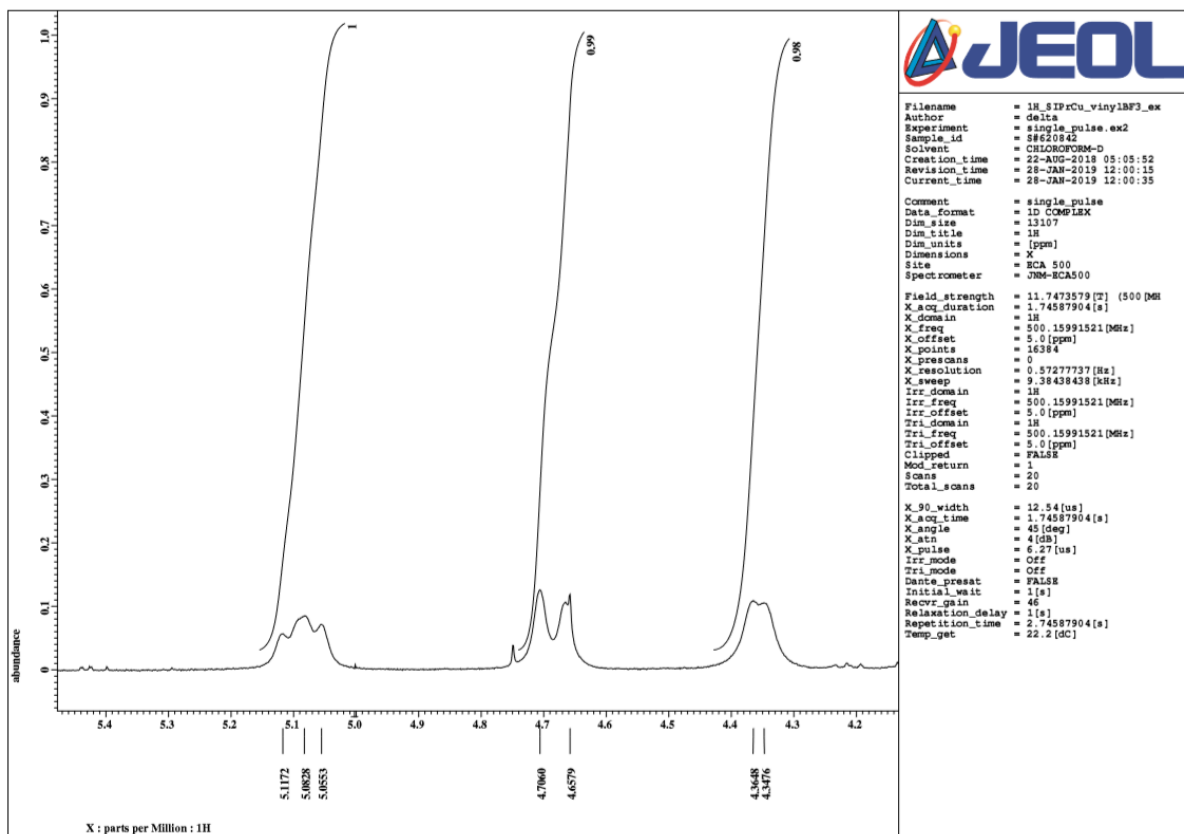
5. Supplementary Information

A) SIPrCuvinylBF₃

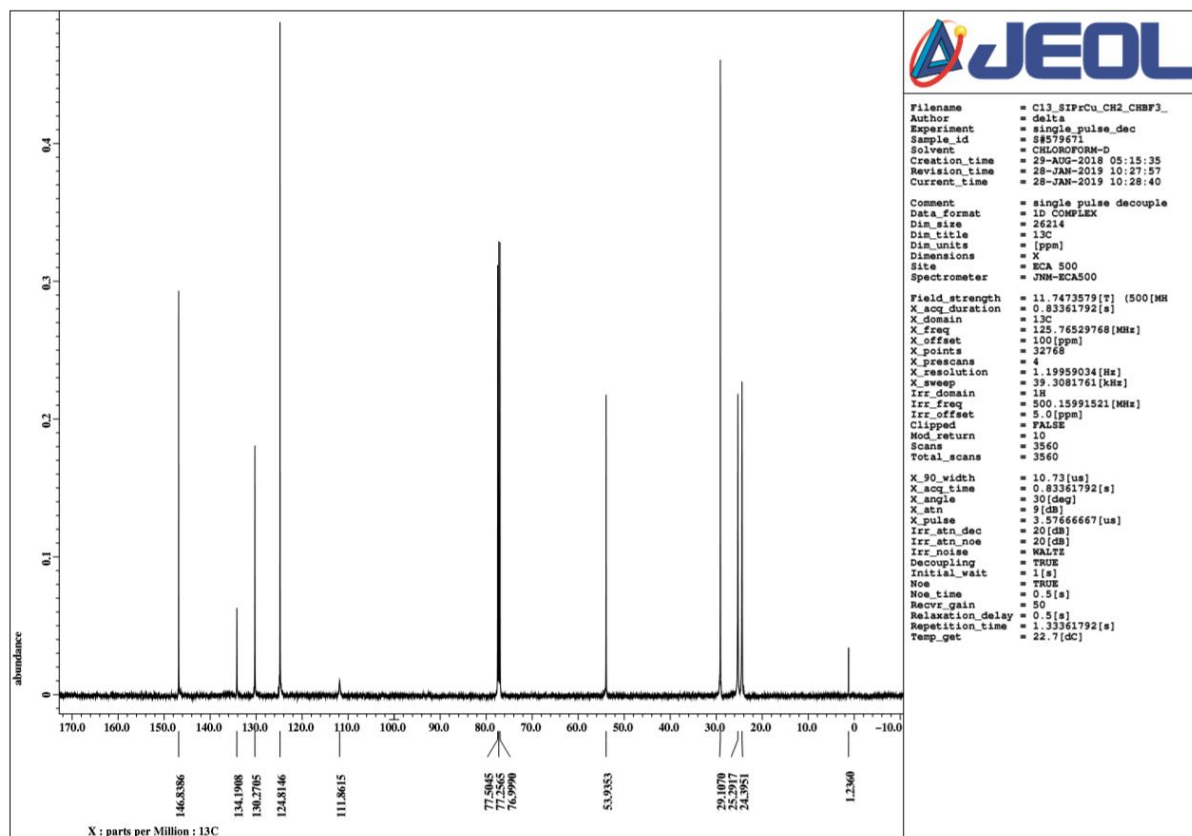
¹H NMR of SIPrCuvinylBF₃



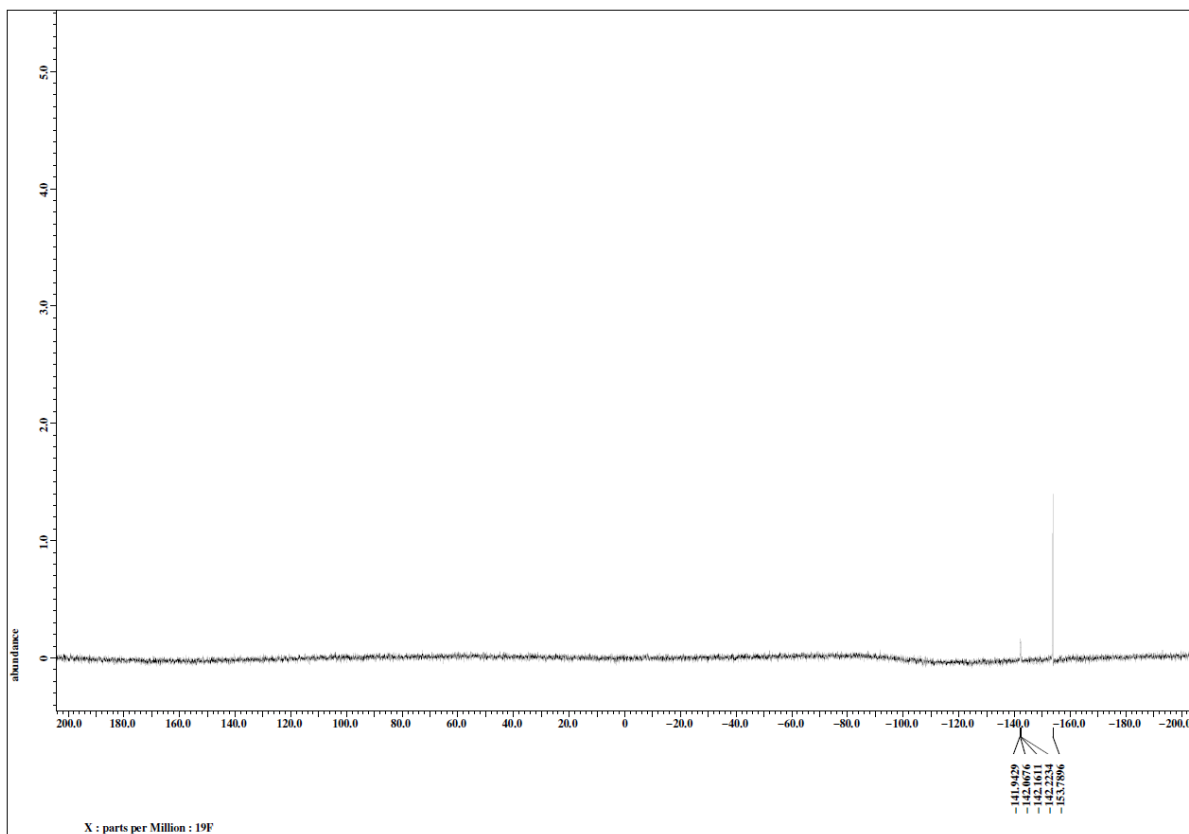
¹H NMR of SIPrCuvinylBF₃ (zoomed)



¹³C NMR of SIPrCuvinyIBF3

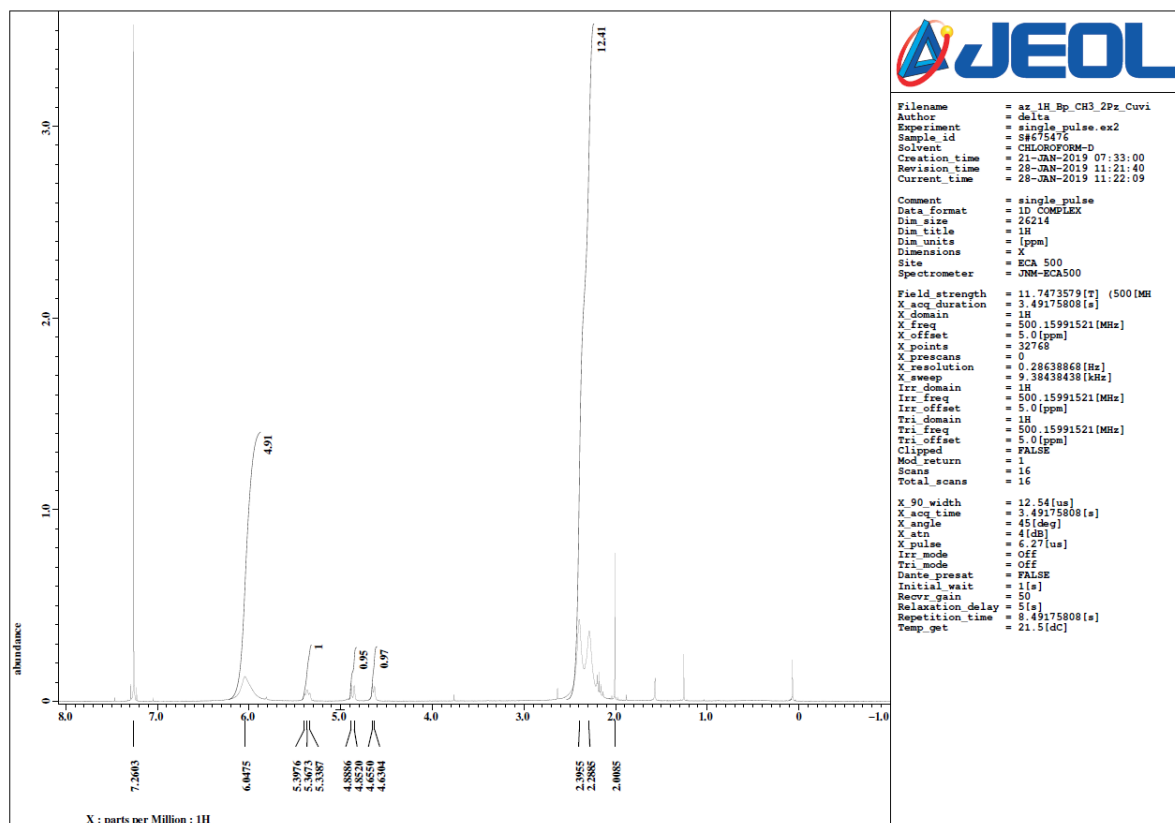


^{19}F NMR of SIPrCuvinylBF₃

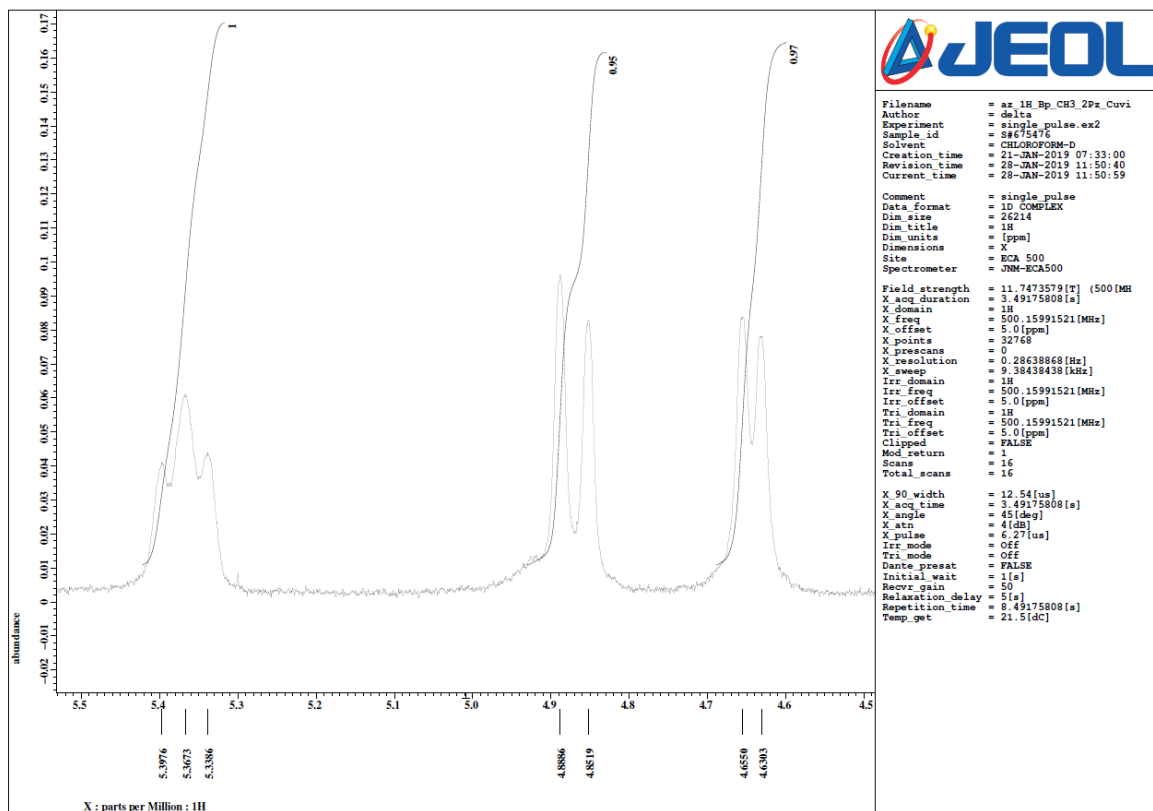


B) $\text{CH}_2[(3,5\text{-CH}_3)\text{Pz}]\text{Cu}(\text{CH}_2=\text{CHBF}_3)$

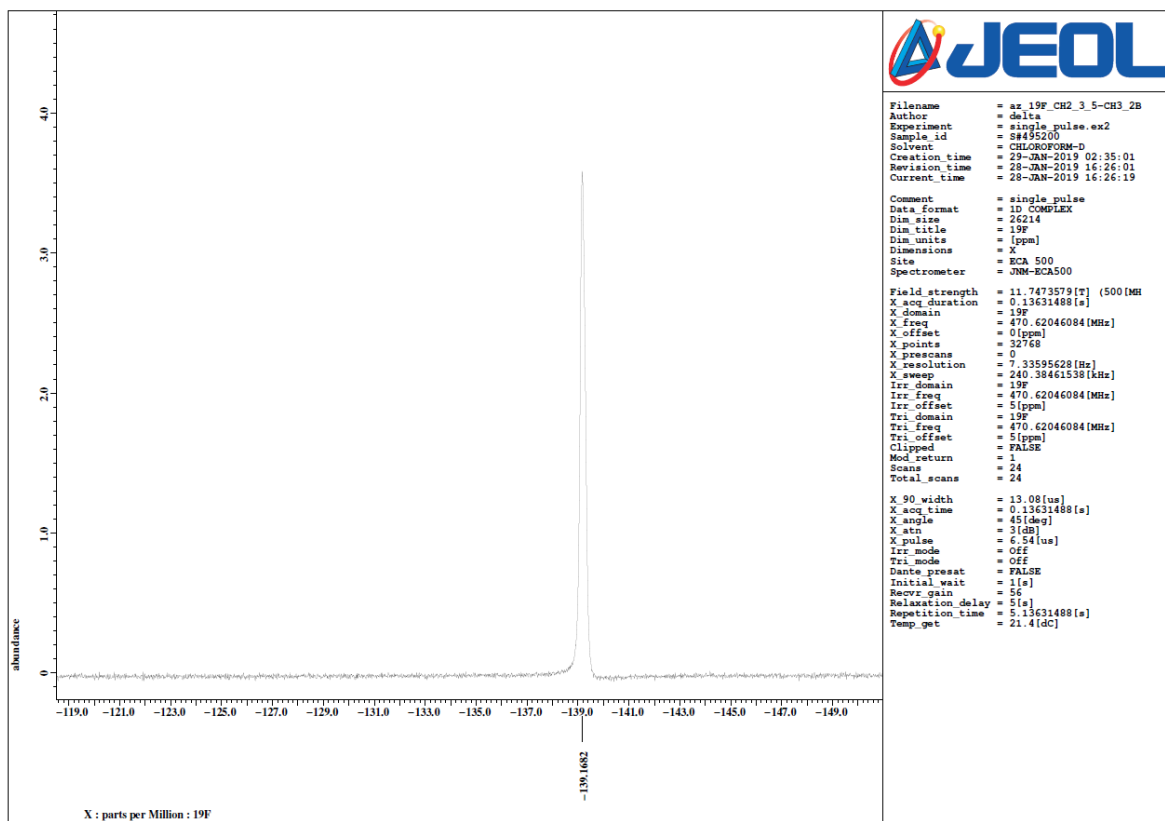
$^1\text{H NMR}$ of $\text{CH}_2[(3,5\text{-CH}_3)\text{Pz}]_2\text{Cu}(\text{CH}_2=\text{CHBF}_3)$



^1H NMR of $\text{CH}_2[(3,5\text{-CH}_3)\text{Pz}]_2\text{Cu}(\text{CH}_2=\text{CHBF}_3)$ (zoomed)

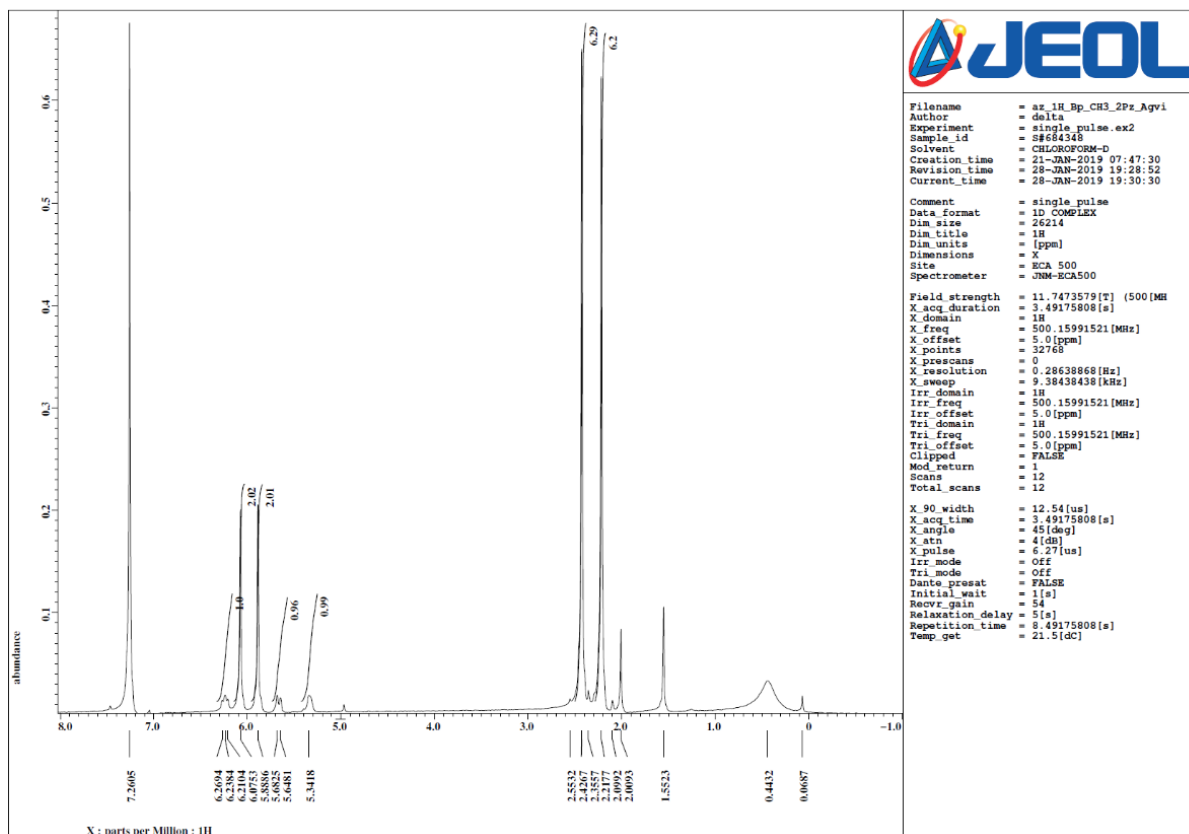


^{19}F NMR of $\text{CH}_2[(3,5\text{-CH}_3)\text{Pz}]_2\text{Cu}(\text{CH}_2=\text{CHBF}_3)$

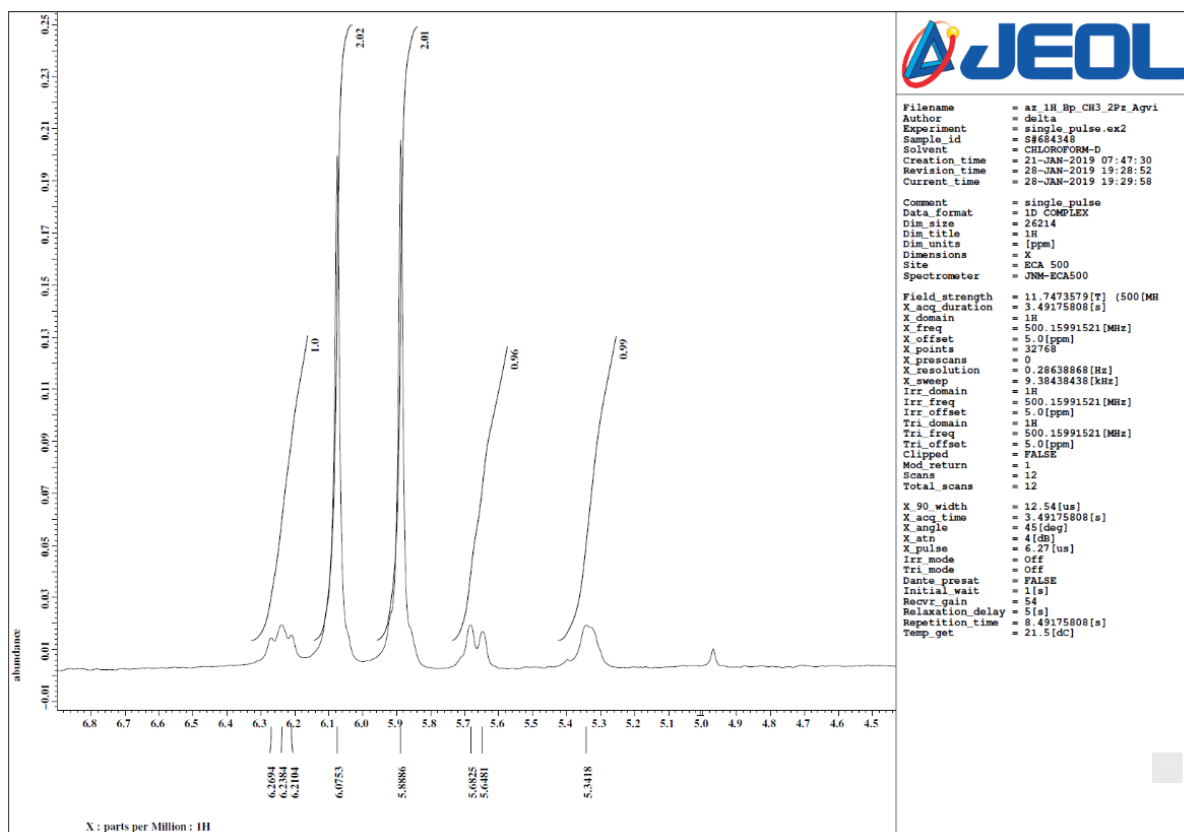


C) $\text{CH}_2[(3,5\text{-CH}_3)\text{Pz}]_2\text{Ag}(\text{CH}_2=\text{CHBF}_3)$

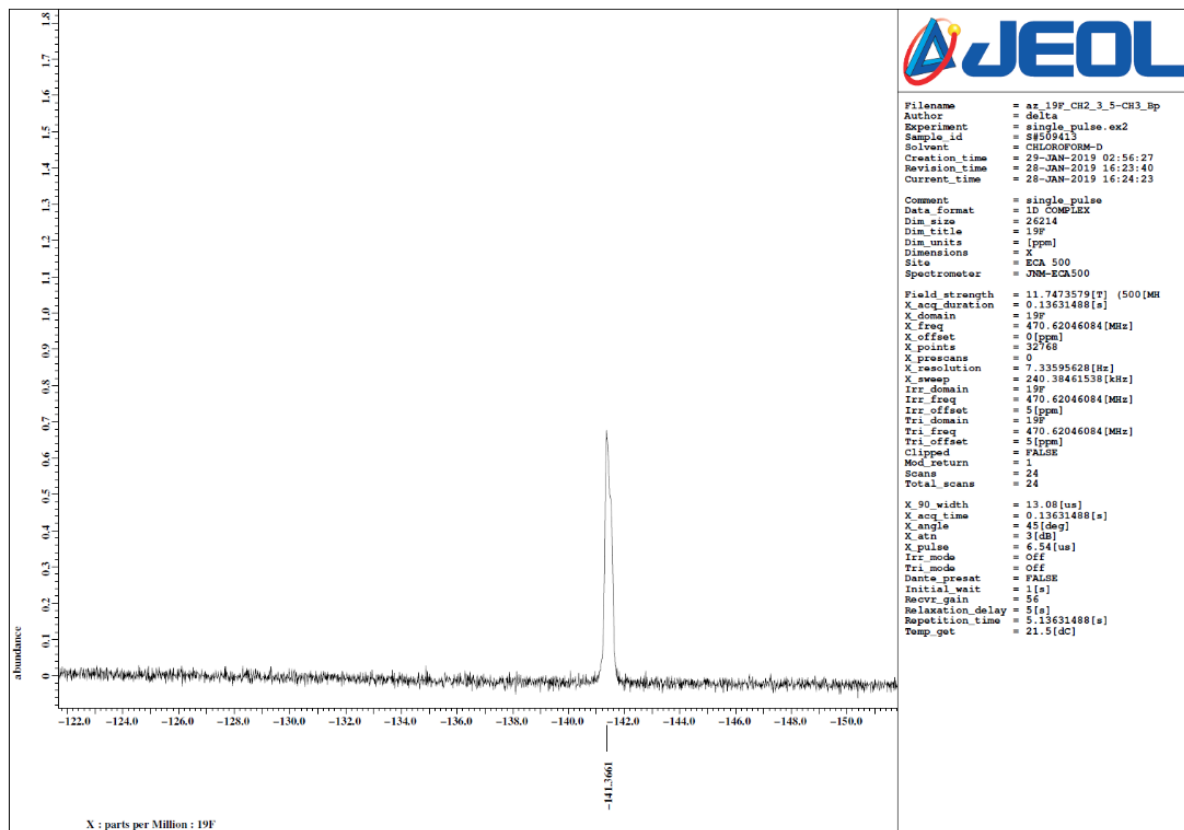
$^1\text{H NMR}$ of $\text{CH}_2[(3,5\text{-CH}_3)\text{Pz}]_2\text{Ag}(\text{CH}_2=\text{CHBF}_3)$



^1H NMR of $\text{CH}_2[(3,5\text{-CH}_3)\text{Pz}]_2\text{Ag}(\text{CH}_2=\text{CHBF}_3)$ zoomed

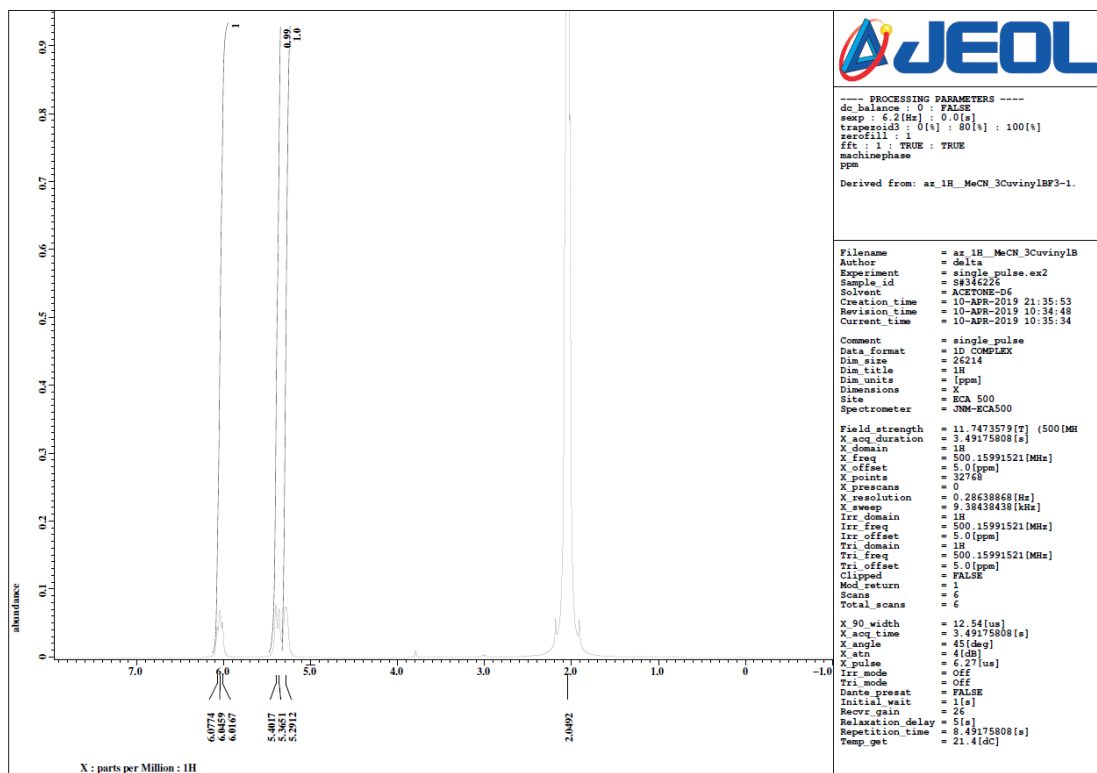


^{19}F NMR of $\text{CH}_2[(3,5\text{-CH}_3)\text{Pz}]_2\text{Ag}(\text{CH}_2=\text{CHBF}_3)$



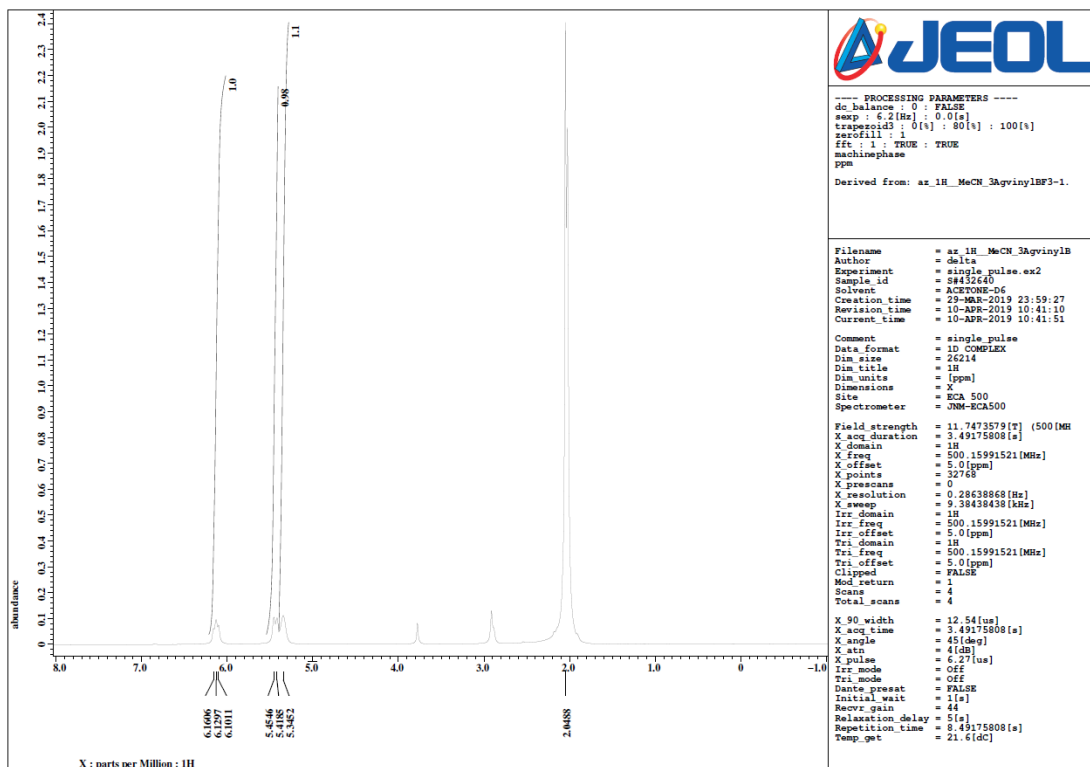
D) (MeCN)₃CuvinylBF₃

¹H NMR of (MeCN)₃CuvinylBF₃

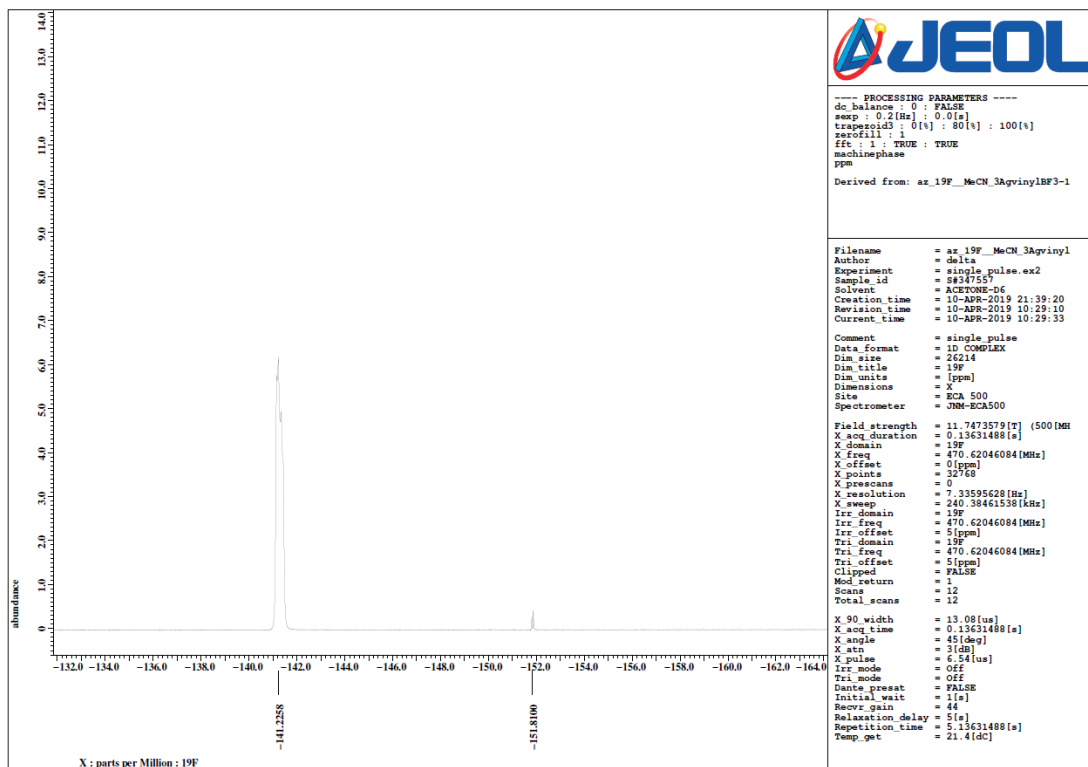


E) (MeCN)₃AgvinylBF₃

¹H NMR of (MeCN)₃AgvinylBF₃



^{19}F NMR of $(\text{MeCN})_3\text{AgvinylBF}_3$



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