Carbon-Carbon Bond Formation via Nucleophilic Attack of Iron-Diene Complexes Using Potassium Organotrifluoroborates



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I hereby recognize and pledge to fulfill my responsibilities as defined in the Honor Code, and to maintain the integrity of myself and the college community as a whole.

Pledge_____

Acknowledgments

I would like to thank my parents, who made all of this possible. Without their unwavering support I never could have made it this far. I would also like to thank Dr. Persichini for overseeing this research and helping as much as possible. I thank Allegheny College and the Department of Chemistry for the funding to carry out this research.

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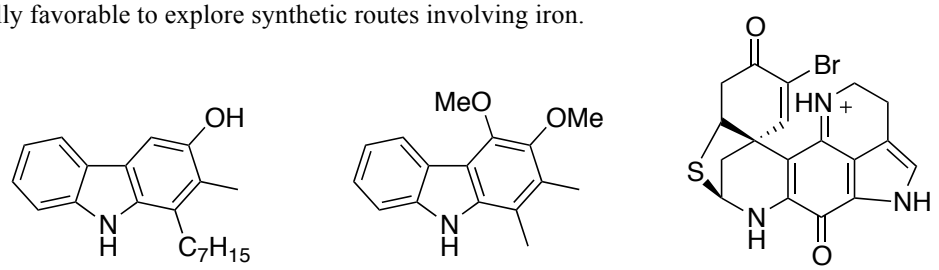
Abstract

The formation of new carbon-carbon bonds by combining organometallic compounds with tetravalent borates is not presented in current literature. It is of interest to explore this methodology as a new way to form carbon-carbon bonds. By using cationic iron complexes and potassium organotrifluoroborates, it has been possible to nucleophilically add alkyl groups, which satisfy certain electronic and steric requirements to the complex. Upon optimization of reaction conditions, it was observed that yields vary drastically, from 0% to near quantitative, based on the electronic properties of the tetravalent borate used.

Introduction

One of the most important transformations in the field of organic chemistry is the formation of new carbon-carbon bonds. So important is this transformation, that it has been the subject of multiple Nobel Prizes. When synthesizing natural products, the formation of new carbon-carbon bonds and the stereochemistry of those new bonds must be taken into consideration. Three natural products well represented in the literature are presented in **Figure 1**. Carazostatin is a free radical scavenger, carbazomycin A is a potent antibacterial, inhibiting the growth of gram positive organisms, and discorhabdin A, originally isolated from a marine sponge is used as an antitumor agent. These and many other natural products having a similar carbon skeleton have recently been the focus of improved methodologies for total synthesis. One such area of organic chemistry pursuing these methodologies is the field of organometallic chemistry. By introducing transition metals to organic substrates, it becomes possible to manipulate substrates in ways typically not permitted. The use of precious transition metals such as gold and palladium can be very expensive as they only occur naturally in minute quantities. A way to combat this is to use cheap, abundant transition metals such as iron. Iron constitutes 5.63% of the earth's crust by mass.[1] Because of this relative abundance iron precursors are very cheap, as well as environmentally friendly. It is both economically and environmentally favorable to explore synthetic routes involving iron.



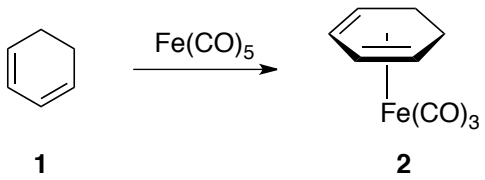
carazostatin **carbazomycin A** **Discorhabdin A**

Figure 1. Natural products with biological activity interesting to synthetic chemists

Another important class of compounds in organic synthesis are organoboranes. Boranes have the capacity to serve as excellent reducing agents, a general example being sodium borohydride. The also have the capability of serving as alkylating agents under certain conditions, as described by Persichini.[2] The utility of the borane alkylating agents is that they can be much easier to work with than classical alkylating agents such as alkyllithiums or Grignards. The focus of this research is to combine two known methodologies in a novel way to form new, stereospecific carbon-carbon bonds.

Diene-irontricarbonyl Complexes

In 1958, the first cyclic conjugated diene was complexed with iron by Pauson and co-workers. By using iron(0) pentacarbonyl and 1,3-cyclohexadiene under thermal conditions, the group was able to form tricarbonyl(η^4-1,3-cyclohexadiene)iron **2**.[3]

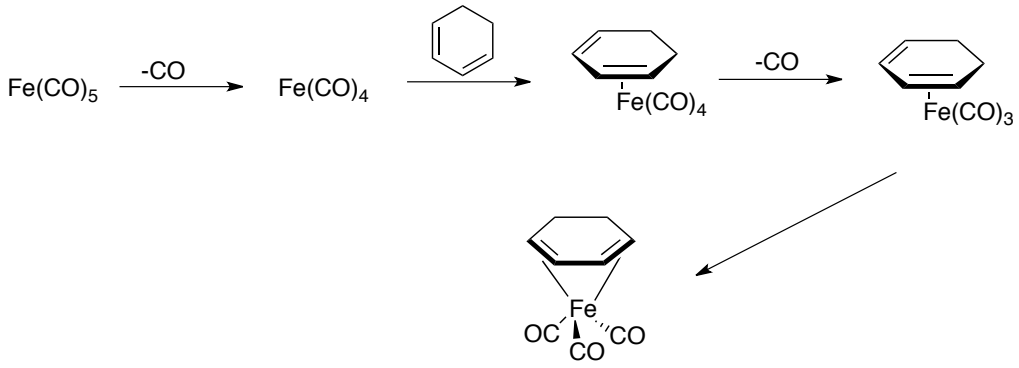


Scheme 1. Complexation of 1,3-cyclohexadiene with iron(0) pentacarbonyl

It was reported that complex **2** does not decompose when introduced to concentrated sulfuric acid. This is a peculiar observation, as it would be expected that the diene would be protonated under acidic conditions. This would then be followed by nucleophilic attack from water, forming a diol, however no diol was detected. This suggests that the complexed diene is far less nucleophilic than the free diene. Another interesting observation is that the iron-diene complex cannot be catalytically hydrogenated. It is well known that alkenes undergo catalytic hydrogenation in the presence of hydrogen and a catalyst such as palladium or nickel. In order for this to occur however, the diene must first associate with the metal catalyst. It is apparent that this does not happen in the case of the iron-diene complex, further supporting the theory that the complexed diene is electron-deficient. A third observation is that the complex cannot be induced to undergo a Diels-Alder reaction. This, again is further evidence that the complexed diene is electron-deficient, as Diels-Alder reactions require the diene to be relatively electron-rich. These results suggest that the reactivity of the complexed diene varies drastically from the free diene. Not only is the complex more stable, but also there appears to be less electron density in the conjugated π system of the complexed diene.

Synthesis of tricarbonyl(η^4-1,3-cyclohexadiene)iron

Since the first synthetic pathway to tricarbonyl(η^4-1,3-cyclohexadiene)iron was discovered in 1958, efforts have been made to improve the yield and utility of the complexation. It is possible to complex the diene directly using $Fe(CO)_5$ as reported by Pauson, however the initial yields for the thermal complexation of 1,3-cyclohexadiene were very low. New methods were later developed which drastically increased yield. The reaction proceeds by thermal loss of a CO ligand from the iron center, making it a reactive 16-electron species. Two electrons are donated from the diene forming a favorable 18 electron complex. Thermal loss of a second CO ligand reestablishes a 16-electron configuration. Subsequent complexation with the second alkene quenches the electron deficiency, forming product **2**.

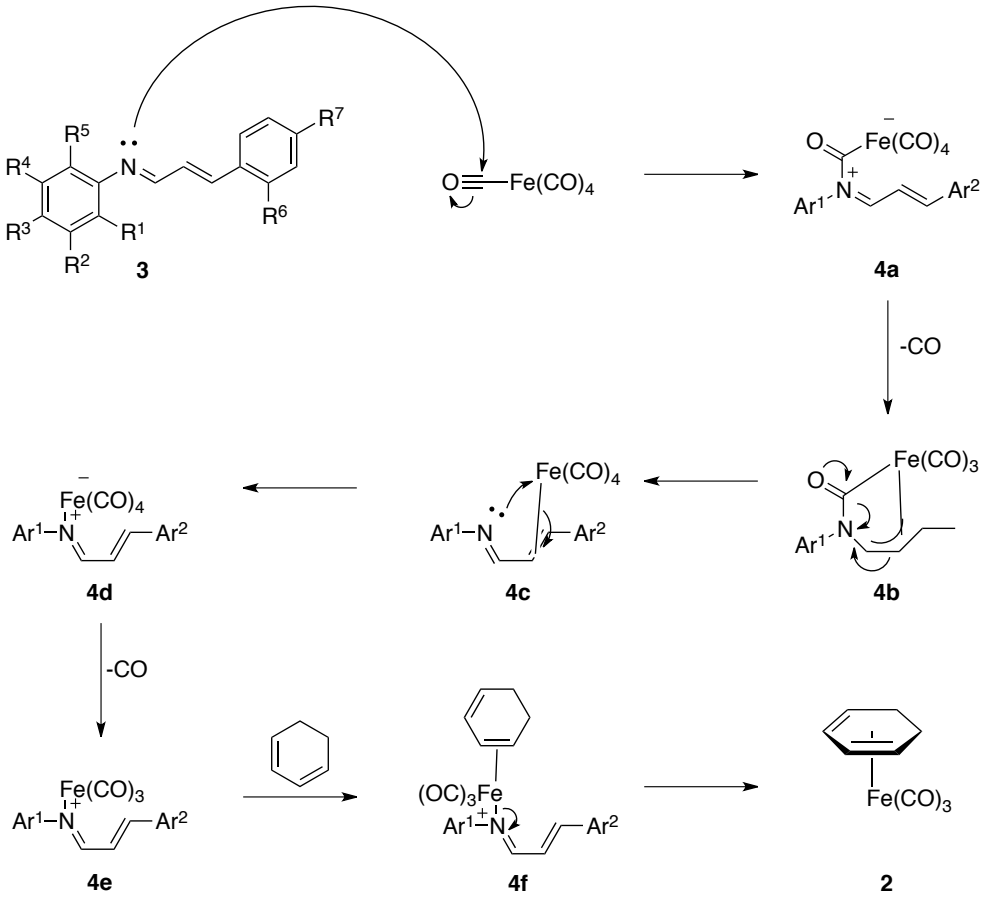


2

Scheme 2. Complexation of 1,3-cyclohexadiene

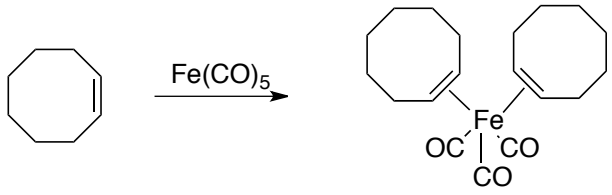
Other iron carbonyl species have also been used such as diirononacarbonyl, and triirondodecacarbonyl.[4,5] The same general mechanism applies with these dimers and trimers of $Fe(CO)_5$, however increased reactivity is observed using these reagents due to the lower activation barrier that must be overcome to dissociate a carbonyl ligand. This is due to the fact that each iron center shares three CO ligands; therefore the ligands are not bound as tightly. Thus less thermal energy is required to dissociate these CO ligands. A strategy of catalytic complexation has also been explored. This strategy uses substituted 1-aza-1,3-butadienes as transfer catalysts.[6,7] The benefit of using these transfer catalysts is mainly the achievement of more favorable reaction conditions, namely a drastic decrease in the required temperature. The lone pair on nitrogen nucleophilically attacks a carbonyl ligand, forming intermediate **4a**. In order to quench the formal negative charge on the iron center, a carbonyl ligand is lost. A haptotropic shift occurs, and the electron density on the carbonyl oxygen collapses, forming intermediate **4b**. At this point, the lone pair on nitrogen nucleophilically attacks the iron center directly, liberating it from the double bond of the diene. This again

places a formal negative charge on the iron center. To rid itself of this charge, another ligand loss is necessary. This forms intermediate **4e**. At this point, the 16-electron iron species **4f** complexes with 1,3-cyclohexadiene, regenerating catalyst **3**. The catalyst can be recovered easily via recrystallization or column chromatography.



Scheme 3. Complexation of 1-aza-1,3-butadiene transfer catalysts

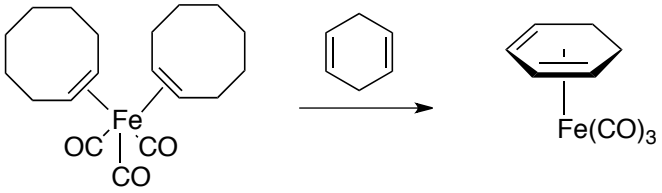
Another method of synthesis of **2** involves the use of Grevel's reagent **5**.[8] This reagent can be generated by the reaction of cyclooctane with ironpentacarbonyl under photolytic conditions. Grevel's reagent is another transfer reagent, however it must be used stoichiometrically.



5

Scheme 4. Synthesis of Grevel's reagent

The benefits of using Grevel's reagent is that complexation of 1,3-cyclohexadiene can be done at temperatures below 0°C in less than an hour. A drawback is that Grevel's reagent is not stable in solution above -30°C. 1,4-cyclohexadiene isomerizes in the presence of Grevel's reagent to 1,3-cyclohexadiene, followed by complexation to afford **2**.

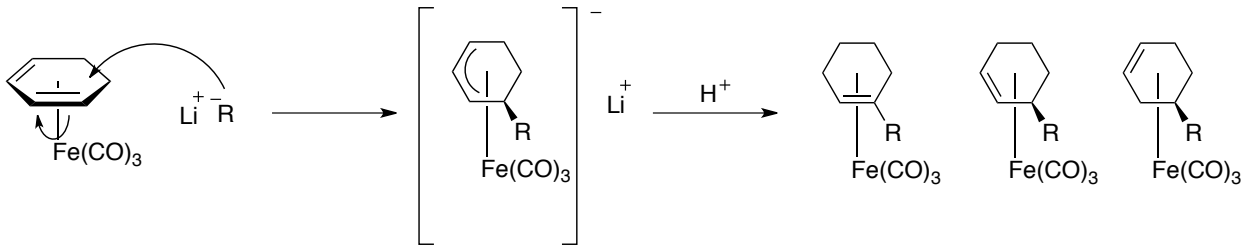


5 **2**

Scheme 5. Isomerization and subsequent complexation of 1,4-cyclohexadiene

Reactions of tricarbonyl(η^4-1,3-cyclohexadiene)iron

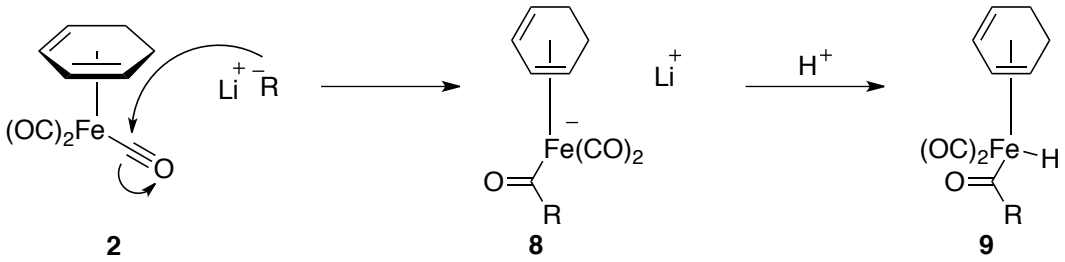
Due to the decrease in electron density of the conjugated π system of the complexed diene, it is possible to add strong nucleophiles such as unstabilized organolithiums to this complex.[9] Organolithiums attack diene **2** at the terminus of the conjugated π system pushing the electron density onto the adjacent carbon. This forms the negatively charged, delocalized intermediate **6**. This intermediate can be protonated at one of three possible positions, producing **7a**, **7b**, and **7c.**



2 **6** **7a** **7b** **7c**

Scheme 6. Nucleophilic addition to complexed dienes

Although it is difficult to control regioselectivity, the nucleophile adds *trans* to the iron center nearly every time. This observation is a result of the steric bulk of the irontricarbonyl group directing the nucleophile to the β face of the diene. Due to the highly nucleophilic nature of the organolithium, multiple side reactions can occur. Nucleophilic attack can take place at the carbon center of a carbonyl ligand as well (**Scheme 7**), forming intermediate **8,** where the negative charge is localized on the iron center. This causes iron to accept a proton during workup, forming metal ester **9**.

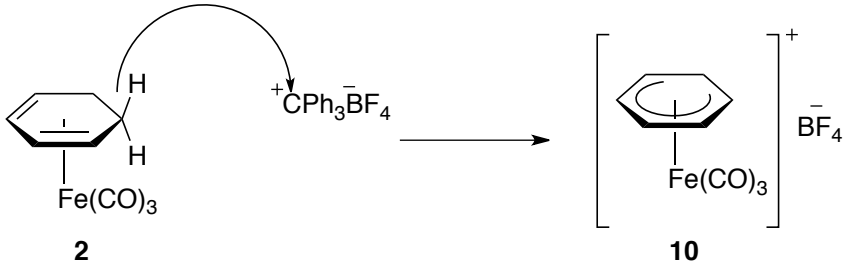


Scheme 7. Nucleophilic attack at carbonyl ligand

Due to the harsh conditions and multiple side products, there is limited utility for direct nucleophilic attack of tricarbonyl(η^4-1,3-cyclohexadiene)iron.

Iron-cyclohexadiene cationic complexes

In 1960, Fischer discovered that the abstraction of hydride by the use of triphenylcarbenium tetrafluoroborate yields tricarbonyl(η^5-1,3-cyclohexadienilium)iron **3.**[10] The compound was found to be very stable; it could be recrystallized from water with high purity, and it could be stored indefinitely. This indicates that the complexed cation is more stable than the free conjugated cation, which is difficult to form and short-lived.



Scheme 8. Hydride abstraction using triphenylcarbenium tetrafluoroborate

The relative stability of the η^5 cationic ligand is attributed to π backbonding stemming from the carbonyl ligands of the iron. Carbonyl ligands are not only excellent σ donors, but also good π acceptors. Due to the relatively low energy of the $L_nM(CO)$ π* antibonding orbital, electron density is able to flow from the occupied *d* orbitals of the iron center to this π* antibonding orbital. From there, electron density can flow into the π* antibonding orbital (LUMO) of the carbonyl ligand.

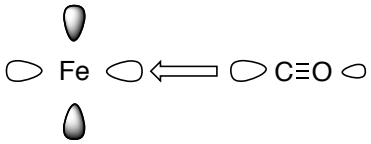


Figure 2. σ donation of HOMO electron density of carbonyl ligand to *d* orbital of metal center

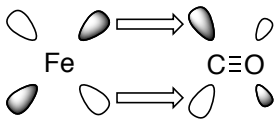


Figure 3. π backbonding between electro-rich *d* orbitals of metal center and π* antibonding orbital (LUMO) of carbonyl ligand

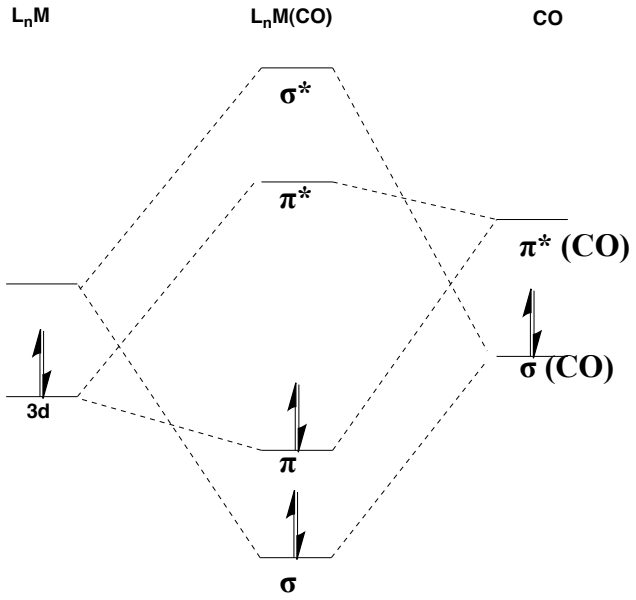
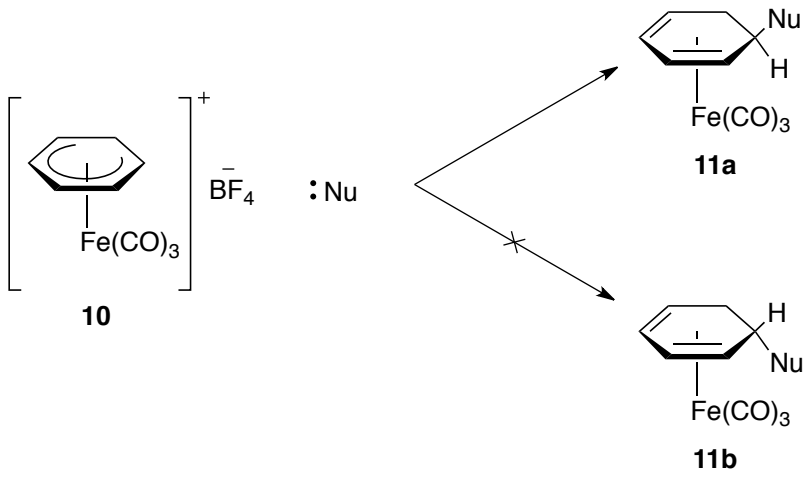


Figure 4. Molecular orbital diagram of $L_nM(CO)$

When hydride is abstracted from the diene, the system is able to stabilize itself by withdrawing more electron density from these π* antibonding orbitals. Because of the cationic character of the organic ligand, nucleophiles readily add the terminal position of the conjugated system; *trans* to the irontricarbonyl moiety forming adduct **11a**.



Scheme 9. Stereochemical outcome of nucleophilic addition to cationic complex

The increase in reactivity and predictability of products make the cationic complexes very useful to organic synthesis. They no longer require powerful alkylating agents such as organolithiums, but instead can be done with a variety of mild nucleophiles.[11,12] Most of the commonly used nucleophiles are moisture-sensitive compounds which must be manipulated under an inert atmosphere. This can pose potential problems in a scale-up operation, so it becomes necessary to explore the option of using alternative, more stable nucleophiles. One such class of nucleophiles are organoborates.

Organoborates

Organoboranes have the general formula BR_3, where R can be a variety of functionalities including hydride, alkoxy groups, amino groups, and alkyl groups. Because boranes are sp^2 hybridized, they contain a vacant *p* orbital in which donated lone pairs from Lewis bases can be housed (**Scheme 10**). When the boron center accepts these electrons, it is converted from the neutral, trigonal planar borane to the negatively charged, tetrahedral borate. These reactive borates, whether they are generated *in situ* or added directly to the reaction pot are responsible for nearly every organic transformation involving boron.



Scheme 10. Nucleophilic attack on neutral boron center, forming anionic tetrahedral borate complex

Borates can serve as both reducing agents as well as alkylating agents.[13,14,15] One of the most important reactions involving the use of organoboranes is Suzuki coupling.[16] This reaction results in the formation of new carbon-carbon bonds between aryl halides or triflates with organoboranes via a palladium catalyzed cross-coupling (**Figure 5**).

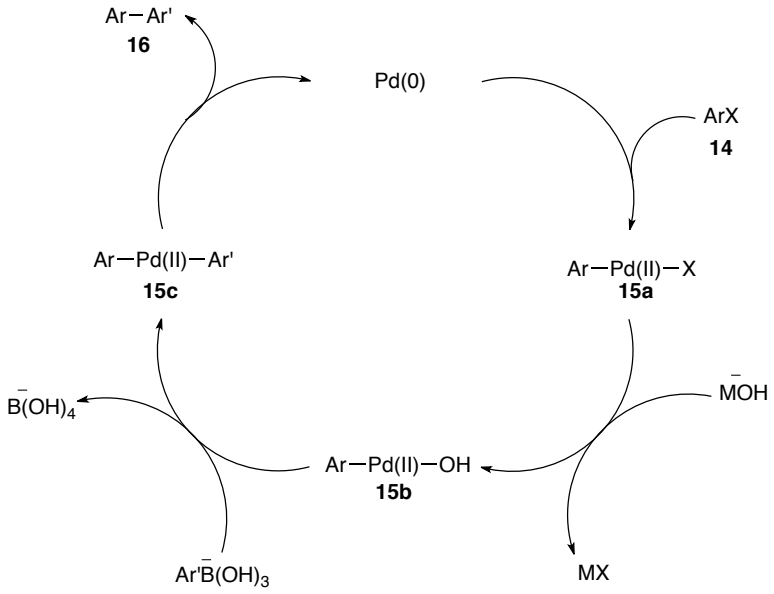


Figure 5. Catalytic cycle of palladium-catalyzed Suzuki cross-coupling

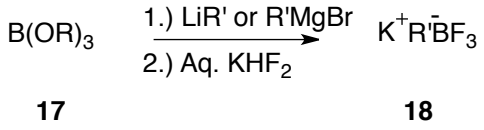
The mechanism is initiated by the oxidative addition of **14** to the palladium(0) catalyst to form the palladium(II) complex **15a**. A hydroxy anion is employed in a substitution reaction forming **15b** and liberating a metal halide. Due to hydroxide being present in the reaction pot, the boronic acid can exist as the borate complex. These complexes undergo transmetallation with palladium, exchanging their aryl or alkyl group for the hydroxy group on the palladium center and forming complex **15c**.The palladium center undergoes reductive elimination, forming product **16** and regenerating the palladium(0) catalyst. The 2010 Nobel Prize in chemistry was awarded to Akira Suzuki, Richard Heck, and Ei-ichi Negishi for the development of this reaction. The Suzuki coupling reaction allows the formation of new carbon-carbon bonds in very high yield, however because of the high electrophilicity of boranes, they often degrade when exposed to the atmosphere. It was for this reason that another route to the coupling reaction was explored. Potassium organotrifluoroborates have been shown to undergo Suzuki cross coupling under extremely mild conditions with exceptional yield.[18]

Potassium organotrifluoroborates

Potassium organotrifluoroborates ($KRBF_3$) are air-stable salts of boronic acids. Because the boron center is already in its sp^3 hybridized form, no further degradation can occur do to Lewis acid-base interaction between the boron center and atmospheric moisture. Due to the high electrophilicity of fluorine, it is very difficult to remove fluoride from the boron center thus the weakest bond is the B-R bond. This relatively weak bond makes potassium organotrifluoroborates not only excellent reagents for Suzuki cross coupling, but also good nucleophiles. Unlike organolithiums, organostannanes, and other classic alkylating agents, potassium organotrifluoroborates are solids at room temperature, resistant to multiple forms of chemical degradation, and can be store indefinitely.

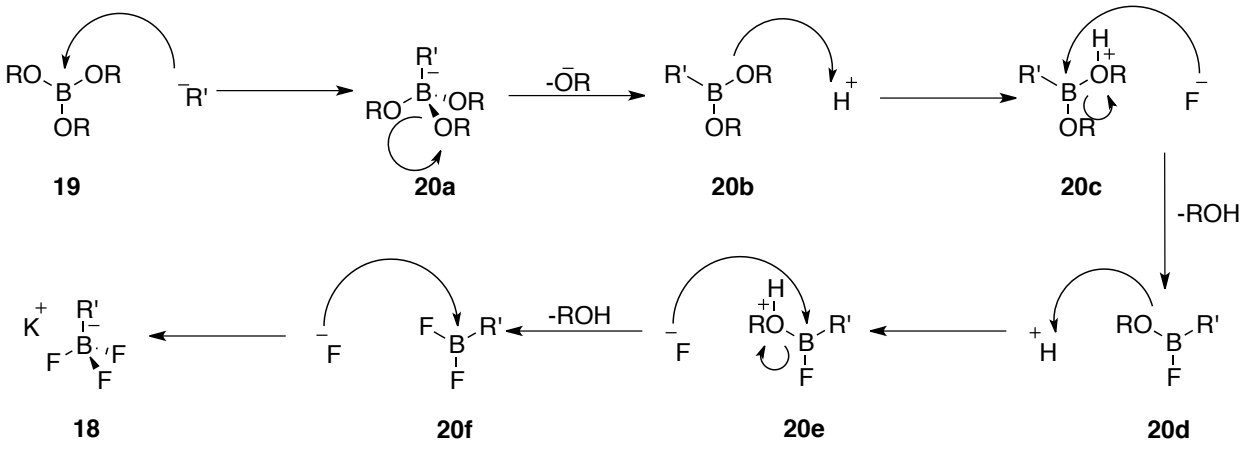
Synthesis of potassium organotrifluoroborates

These compounds can be synthesized using a variety of methods, the most general being the reaction of trimethoxy or triisopropylborate with a suitable nucleophile such as an organolithium or Grignard, followed by cleavage of the OR groups using aqueous KHF_2 (**Scheme 11**).[19,20,21]



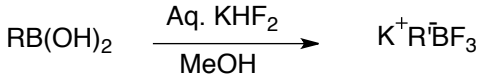
Scheme 11. Common preparation of potassium organotrifluoroborates

The mechanism proceeds first by nucleophilic attack on substrate **19**. This then forces one of the OR groups to leave forming adduct **20b**. Upon introduction of aqueous KHF_2, an OR group is protonated and displaced with a fluoride anion. This step is repeated for the remaining OR group. Once organodifluoroborane **20f** is present, immediate addition of another fluoride forms potassium organotrifluoroborates **18**.



Scheme 12. Mechanism of potassium organotrifluoroborate formation

Another more convenient method of synthesis is the reaction of aqueous KHF_2 with a boronic acid in methanol to form the potassium organotrifluoroborate (**Scheme 13**).[22] This method is extremely convenient, as nearly any boronic acid can be converted and purified quickly and in excellent yield.

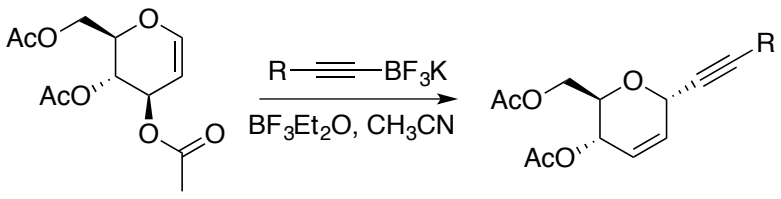


21 **18**

Scheme 13. Formation of potassium organotrifluoroborates from boronic acids

Organotrifluoroborates as nucleophiles

Organotrifluoroborates have been used as nucleophiles in a variety of reactions. Stefani et al. report the nucleophilic addition of alkynyltrifluoroborates to *D*-glucal. BF_3•Et_2O was employed as a Lewis acid to coordinate to the acetoxy carbonyl oxygen, making the substrate more electrophilic.[23] This suggests that organotrifluoroborates are not very powerful nucleophiles.

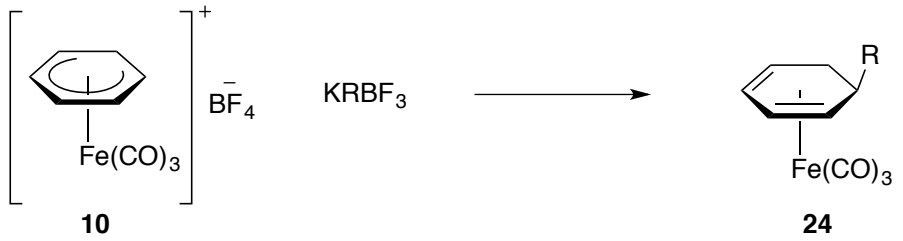


22 **23**

Mayr and coworkers reported the use of organotrifluoroborates as nucleophiles on substrates with multiple electron-withdrawing groups.[24] This again suggests that certain electronic parameters must be met in order for trifluoroborates to be used as appropriate nucleophiles.

Proposed carbon-carbon bond formation using $KRBF_3$

By combining the use of cationic iron-diene complexes and nucleophilic potassium organotrifluoroborates, it should be possible to form a new stereospecific carbon-carbon bond (**Scheme 14**).



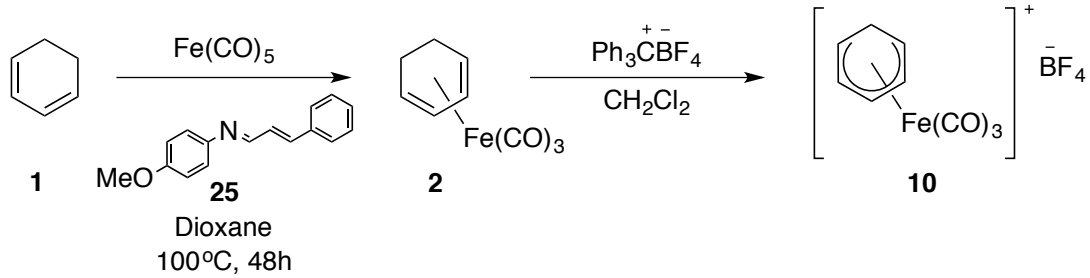
10 **24**

Scheme 14. Proposed carbon-carbon bond formation between complexed cation and potassium organotrifluoroborate

Previous work in the Persichini group shows that it is possible to nucleophilically add potassium phenyltrifluoroborate to **10** giving adduct **24**.[23] The full scope of nucleophilic addition to iron-diene complexes via potassium organotrifluoroborates has yet to be investigated. It is therefore the goal of this research to synthesize a variety of different potassium organotrifluoroborates each with unique chemical properties, and examine their reactivity towards the complexed cation substrate. By examining the effects of different functionalities on the R group, it is hoped that some light will be shed on the nucleophilic character of potassium organotrifluoroborates. This particular methodology of stereospecific carbon-carbon bond formation has never appeared in published literature, and is therefore interesting as a carbon-carbon bond forming method.

Results and Discussion

Tricarbonyl(η^4-1,3-cyclohexadiene)iron **2** was synthesized in very high yield (91%) and purity using the transfer catalyst **25**. This was converted to the cation **10** quantitatively via hydride abstraction with triphenylcarbenium tetrafluoroborate (**Scheme 15)**.[10]

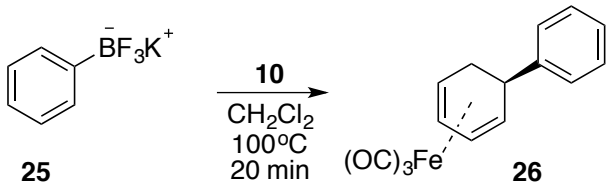


1 **25** **2** **10**

Scheme 15. Synthesis of cationic complex

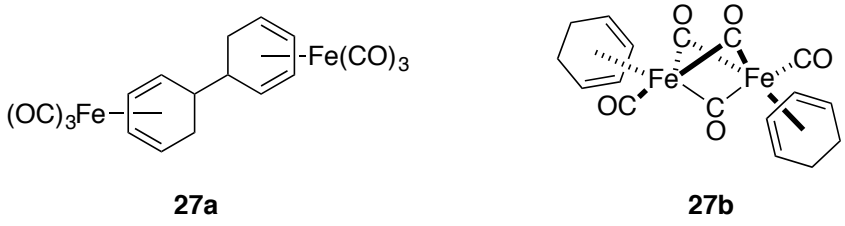
In order to fully understand the scope of the reaction between organotrifluoroborates and iron-diene complex, multiple organotrifluoroborates were synthesized. It was predicted that typical electronic influences such as the presence of electron-withdrawing and electron-releasing groups play a vital role in reactivity. It was also theorized that the relative stability of the alkyl anions associated with the organotrifluoroborates play an important role. To probe these theories, alkyl, alkenyl, and aryltrifluoroborates were synthesized and used as nucleophiles. Both electron-withdrawing and electron-releasing groups were present on the aryltrifluoroborates.

The first nucleophile was potassium phenyltrifluoroborate **25**. Because the phenyl group is stabilized and overall electron neutral, this provided a good basis to probe the effects of other functionalities present. Product **26** was synthesized successfully using complex **10** and potassium phenyltrifluoroborate under microwave conditions (**Scheme 16**).



Scheme 16. Addition of phenyl group to complexed cation

Upon workup, several products were present. Spectroscopic analysis (NMR and GC-MS) suggests that these side reactions are due to electron-transfer reduction of the cation converting it to the neutral complexed diene. It is believed that this neutral complexed diene then undergoes dimerization under thermal conditions, liberating carbon monoxide (**Scheme 17**).

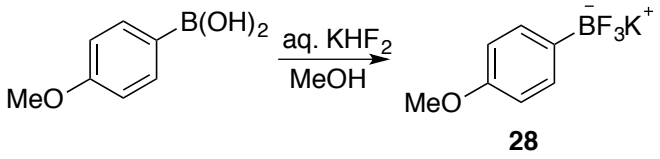


Scheme 17. Dimers formed under thermal conditions

The electron-transfer reduction may be attributed to impurities in solvent or atmospheric oxygen. This unwanted side-reaction was unable to be eliminated despite the excessive care taken to purify the solvent and carry out the reaction under an inert atmosphere. Both nitrogen and argon were used as an atmosphere, the results of each being

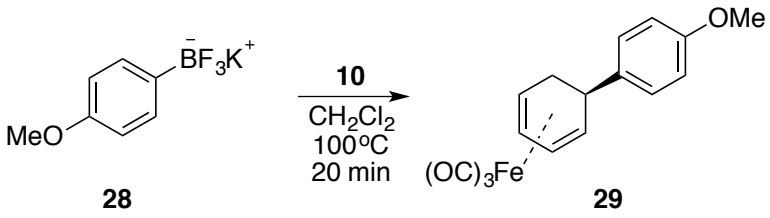
the same. Extensive literature research revealed very little information about the potential dimerization and trimerization.[26, 27] There appeared to be a competition between the formation of desired product, and the formation of dimers and neutral complex. Adding multiple equivalents of the BF_3 salt reduced the yield of the neutral complex and dimers, and increased the yield of the desired product. Another interesting factor that influenced the formation of the neutral complex was the solubility of the starting materials. In solvents where the cationic complex was soluble (MeCN, MeOH), only neutral complex and the dimers were formed; no addition product was detected. This indicates that the progress of the reaction is heavily dependent on solubility. It was for this reason that CH_2Cl_2 was chosen as a solvent Using CH_2Cl_2 made the insoluble salts easier to separate from the product, as only the desired product, neutral complex, and dimers were soluble in the solvent. By using two equivalents of phenyl BF_3, a 21% yield was obtained.

To probe the electronic effects of functional groups present on the aryl ring, potassium (4 methoxyphenyl)trifluoroborate was synthesized using 4-methoxyphenylboronic acid (**Scheme 18)**.



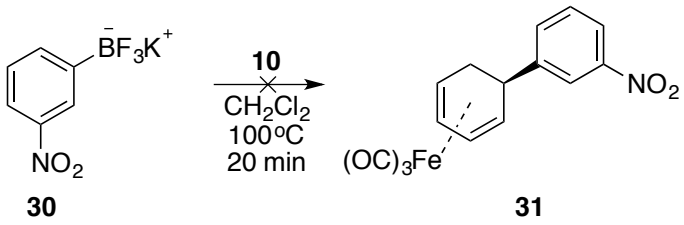
Scheme 18. Preparation of organotrifluoroborates from appropriate boronic acids.

The result of the reaction of this salt with the cation proceeded as expected, forming **29** with 40% conversion (**Scheme 19**). The product was confirmed via NMR and GC-MS. It was noted that under the intense thermal conditions of gas chromatography, all complexed products decomplexed, and the diene aromatized. This had to be taken into consideration when analyzing MS spectra.



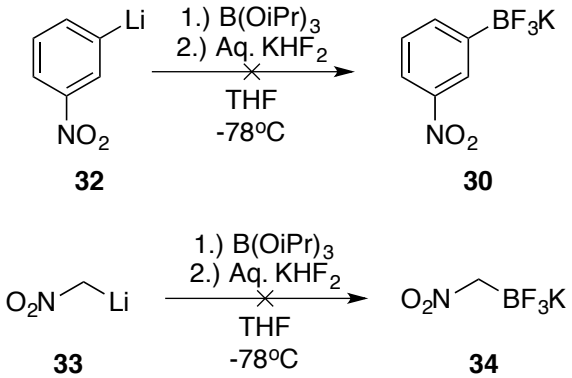
Scheme 18. Use of aryl trifluoroborates with electron-releasing groups.

Neutral complex, as well as the dimer products were also present as mentioned in the synthesis of **23**. The increase in yield compared to phenyl BF_3 supports the theory that electron-releasing functionalities increase the reactivity of the BF_3 salt. Potassium (3-nitrophenyl)trifluoroborate **30** was synthesized in the same manner as the methoxyphenyl BF_3. The reaction conditions were kept the same in order to examine the effects of electron-withdrawing functionalities present.



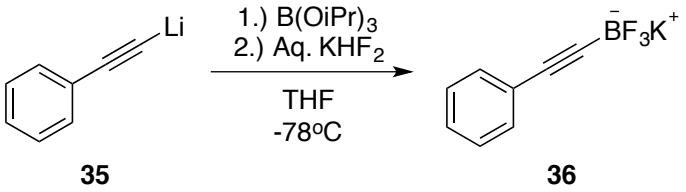
Scheme 19. Use of aryl trifluoroborate with electron-withdrawing group.

Upon workup, product **31** was not detected via GC-MS or crude NMR (**Scheme 20**). This is an interesting result, as it was expected that the reaction would proceed, however a low yield would be observed. It appears that in order for an aryl BF_3 to react, the aryl group must be electron-neutral or electron-rich. A similar situation was observed when attempting to synthesize potassium organotrifluoroborates with electron-withdrawing groups. It was found that anions stabilized by an α-nitro group would not add to the boron center (**Scheme 20**). It is believed that the nitro group withdraws too much electron density from the anion, substantially decreasing its nucleophilicity.



Scheme 20. Attempted synthesis of triflyoroborates from nitro-stabilized anions

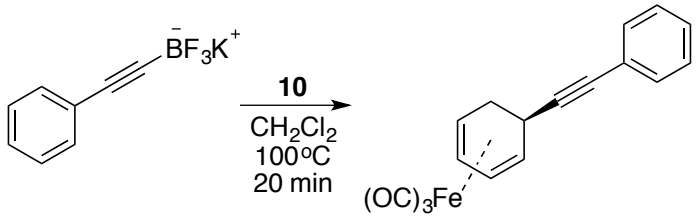
literature search revealed that in order to synthesize such compounds, expensive palladium catalysts must be employed to facilitate the addition.[28] The final aryltrifluoroborates that was used was potassium (phenylethynyl)trifluoroborate **35**. This was synthesized via nucleophilic attack of triisopropylborate, followed by a workup in aqueous KHF_2 (**Scheme 21**).



35 **36**

Scheme 21. Synthesis of trifluoroborates from appropriate alkyllithiums

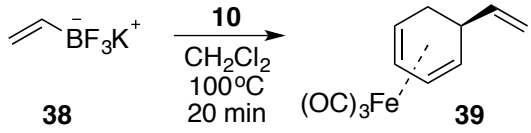
Under the same conditions as the previous reaction, only the desired product **37** was formed with near-quantitative conversion. This result indicates that sterics also play a vital role in reactivity (**Scheme 22**).



36 **37**

Scheme 22. Use of aryl-stabilized linear trifluoroborate

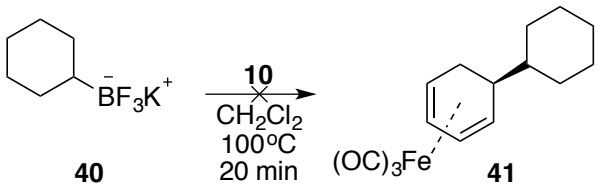
Because the alkynyl anion stabilized by the phenyl ring is linear, the steric requirements are minimum. It is believed that the rate at which this particular reaction occurs does not allow enough time for the formation of the neutral complex and corresponding dimers. It was decided to extend this methodology to a stabilized anion that was not stabilized by a phenyl ring. The salt chosen was potassium vinyltrifluoroborate **38**. Under the same conditions, product **39** was obtained in 15% yield (**Scheme 23**). GC-MS showed strong evidence that **39** was formed, however NMR data was inconclusive. The ^{1}H NMR shifts were not consistent with the literature values, however ^{13}C NMR revealed that two carbons were indeed added.[28]



38 **39**

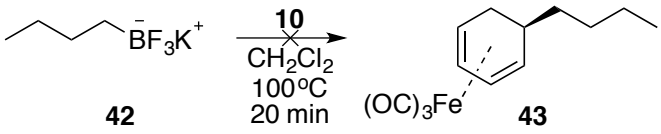
Scheme 23. Reaction between vinyltrifluoroborate and **10**

It was theorized that a phenyl ring must be present in order to stabilize the anion and achieve high yields. To test this, potassium cyclohexyltrifluoroborate **40** was synthesized using the respective boronic acid and aqueous KHF_2. When reacted with **10**, no product was detected via GC-MS or crude NMR (**Scheme 24**).



Scheme 24. Reaction between cyclohexyltrifluoroborate and **10**

This validates the theory that the anion must be stable in order to react. To further prove this hypothesis, potassium butyltrifluoroborate was also used. Because primary alkyl anions are more stable than secondary, this painted a better picture of the true nature of the reactivity of alkyltrifluoroborates. Again, no product was detected when reacted with **10** (**Scheme 25**).



Scheme 25. Reaction between butyltrifluoroborate and **10**

A summation of these findings are presented in **Table 1**. It appears as though the initial theory that anion stability plays a vital role in the reactivity of potassium organotrifluoroborates as nucleophiles was correct. Based on the relative reactivity of phenylethynyl BF_3, it appears that sterics also play a crucial role in this reaction.

With these data, it can be said that we were able to successfully add a variety of nucleophiles to the cationic iron complex. The benefit of these particular nucleophiles is their relative stability in air and moisture. Unlike typical alkylating agents such as organolithiums or Grignard reagents, these BF_3 salts can remain in air indefinitely without decomposing. They are also safe, easy to work with, and environmentally inert. Using this methodology, carbon-carbon bond formation can be achieved safely, quickly, and stereoselectively.

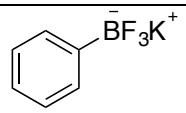
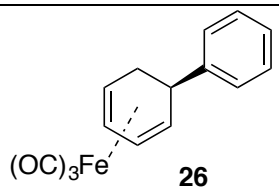
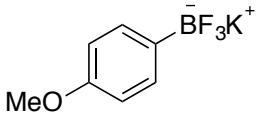
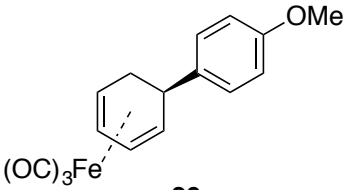
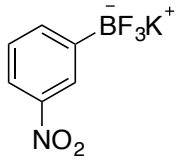
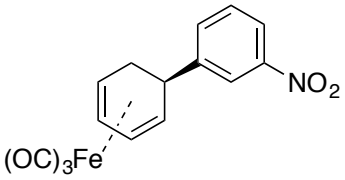
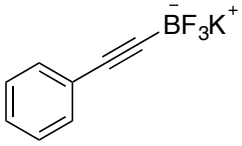
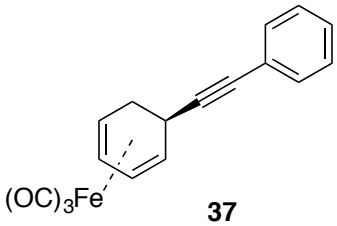
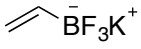
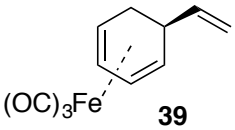
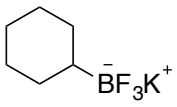
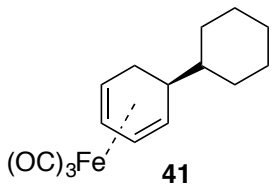
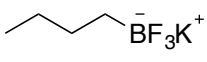
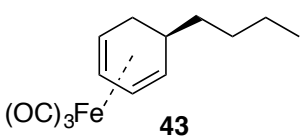
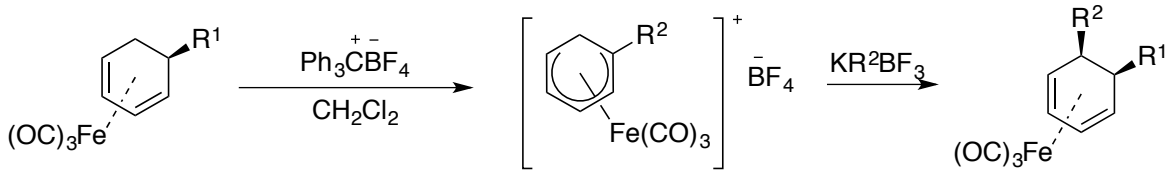
Potassium organotrifluoroborate	Product	Yield (%)
 **25**	 **26**	21
 **28**	 **29**	40
 **30**	 **31**	0
 **36**	 **37**	100[a]
 **38**	 **39**	15[b]
 **40**	 **41**	0
 **42**	 **43**	0

Table 1. Yield of product for various potassium organotrifluoroborates. [a]Yield determined after required purification. Hexanes may account for extra mass. [b]Yield assuming product was formed, however NMR data was inconclusive.

Future Work

Further optimization of reaction conditions is necessary to achieve higher yields. Subsequent reactions would be interesting to study as seen in **Scheme 26**.



Scheme 26. Proposed future reaction with iron-diene complex

It would also be interesting to study the effects of particular ligands on the iron center. By altering the electronic effects of the ligands, different selectivity may be achieved; perhaps causing different BF_3 salts to react with the substrate. It would be interesting to examine the possibility of using this methodology as a synthetic route to natural products. Overall, the reaction works when certain electronic criterion is met, and perhaps by optimization any alkyl group will be able to transfer.

Experimental

General Considerations

All reactions, unless stated otherwise, were carried out under a nitrogen atmosphere and in dried solvents and oven-dried glassware.

Tricarbonyl(η^4-1,3-cyclohexadiene)iron (2). To a three-neck 50mL roundbottom fitted with a reflux condenser, stopper, and nitrogen line was added 2.1827g (6 mmol, 2 eq) diiron nonacarbonyl and 21mL dry benzene. To this was then added 0.28mL (3 mmol, 1 eq) 1,3-cyclohexadiene. The reaction mixture was refluxed for 2h, at which point 0.5457g (1.5 mmol, 0.5 eq) diiron nonacarbonyl was added. The reaction mixture was refluxed for an additional hour then allowed to cool. The mixture was run through a silica plug and concentrated in vacuo to yield a dark brown oil. There appeared to be iron contaminants in the product, as the yield was greater than 100%.

1-(4-Methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (25). 3.0772g (25 mmol, 1 eq) *p*-anisidine was dissolved in 50mL dry benzene under a nitrogen atmosphere. To this was then added 3.15mL (25 mmol, 1 eq) *trans*-cinnamaldehyde and approximately 2g $MgSO_4$ as a desiccant. The reaction mixture was stirred for 24h at room temperature. The mixture was then concentrated in vacuo to afford orange solid which was dissolved in the minimal amount of EtAcO. Pentane was then added until crystals began to form. At this point the mixture was rapidly cooled to -20°C which caused precipitation of a solid. The mixture was then filtered and the residue dried.

Tricarbonyl(η^4-1,3-cyclohexadiene)iron (2). To a dry 100mL roundbottom was added 0.1635g (0.69 mmol) **24**. This was dissolved in 15mL 1,4-dioxane. To this was added 0.68mL (5 mmol, 1 eq) iron pentacarbonyl and 0.48mL (5 mmol, 1 eq) 1,3-cyclohexadiene. The reaction mixture was refluxed under nitrogen for 45h at which point the mixture was concentrated in vacuo and purified via flash chromatography (hexanes). The product was isolated as an orange oil (0.9981g, 91%).

Tricarbonyl(η^5-1,3-cyclohexadienilium)iron (10). To a 50mL roundbottom was added 0.1800g (5.45 mmol) triphenylcarbenium tetrafluoroborate in 5mL methylene chloride. To this was then added 0.9981g **2**. The reaction was stirred at room temperature for two hours. Ethyl ether was then added, causing the precipitation of a bright yellow solid. This was filtered and washed with ether to afford tricarbonyl(η^5-1,3-cyclohexadienilium)iron in 93% yield.

Potassium (4-methoxyphenyl)trifluoroborate (28). To a 50mL roundbottom flask was added 1.5913g (10mmol) 4-methoxyphenylboronic acid. This was dissolved in 12mL MeOH and cooled to 0°C. To this was then added 8mL

of a saturated KHF_2 solution. A white precipitate began to form. The reaction was allowed to stir for 30 min. The reaction mixture was then filtered and rinsed with ether yielding **28** as a flaky white solid in 90% yield.

Potassium (phenylethynyl)trifluoroborate (36). To a dry 100mL roundbottom cooled to -78°C was added 0.4mL (3.68 mmol) phenylacetylene in 5mL THF. To this was then added 2mL(3.2 mmol) 1.6M n-BuLi dropwise over 10min. The yellow solution was allowed to stir for 30min. It was then transferred via cannula to a second 100mL roundbottom cooled to -78°C containing 0.7mL (3 mmol) $B(OiPr)_3$ in 5mL THF. The reaction mixture was allowed to stir for 1h then warmed to room temperature over an hour. The solvent was evaporated off and warm acetone was added. The insoluble material was filtered off and ethyl ether was added to the filtrate until an off-white solid precipitated. This was filtered and dried. 14% yield.

Tricarbonyl(5-phenyl- η^4-1,3-cyclohexadienyl)iron (26). To a 2-5mL Biotage microwave vial was added 0.1538g (0.5 mmol, 1 eq.) **10** and 0.1849g (1 mmol, 2 eq.) **25** in 3mL CH_2Cl_2. The reaction was run in a Biotage microwave reactor at 100°C for 20min with 15 second prestir and normal absorption. Hexanes were then added, and the reaction mixture was run through a short pad of silica (hexanes). The product was purified via flash chromatography (hexanes) to yield 0.0615g (21%) as a brown oil.

Tricarbonyl(5-phenylethynyl- η^4-1,3-cyclohexadienyl)iron (37). To a 2-5mL Biotage microwave vial was added 0.1197g (0.38 mmol, 1 eq.) **10** and 0.1614g (0.77 mmol, 2 eq.) **36** in 2.3mL CH_2Cl_2. The reaction was run in a Biotage microwave reactor at 100°C for 16min with 15 second prestir and normal absorption. Hexanes were then added, and the reaction mixture was run through a short pad of silica (5:1 hexanes/EtAcO) to yield 0.1265g (100%) as a dark brown oil.

Tricarbonyl(5-(4-methoxyphenyl)- η^4-1,3-cyclohexadienyl)iron (29). To a 2-5mL Biotage microwave vial was added 0.1524g (0.5 mmol, 1 eq.) **10** and 0.2149g (1 mmol, 2 eq.) **28** in 3mL CH_2Cl_2. The reaction was run in a Biotage microwave reactor at 100°C for 20min with 15 second prestir and normal absorption. Hexanes were then added, and the reaction mixture was run through a short pad of silica using hexanes, followed by EtAcO. The EtAcO fraction was concentrated in vacuo to yield 0.1618g (50%) as a yellow oil.

Tricarbonyl(5-vinyl- η^4-1,3-cyclohexadienyl)iron (39). To a 2-5mL Biotage microwave vial was added 0.1336g (0.5 mmol, 1 eq.) **10** and 0.2149g (1 mmol, 2 eq.) **38** in 3mL CH_2Cl_2. The reaction was run in a Biotage microwave reactor at 100°C for 20min with 15 second prestir and normal absorption. Hexanes were then added, and the reaction

mixture was run through a short pad of silica using hexanes. The mixture was concentrated down purified via flash chromatography (hexanes) giving **39** in 15% yield as a yellow-orange oil.

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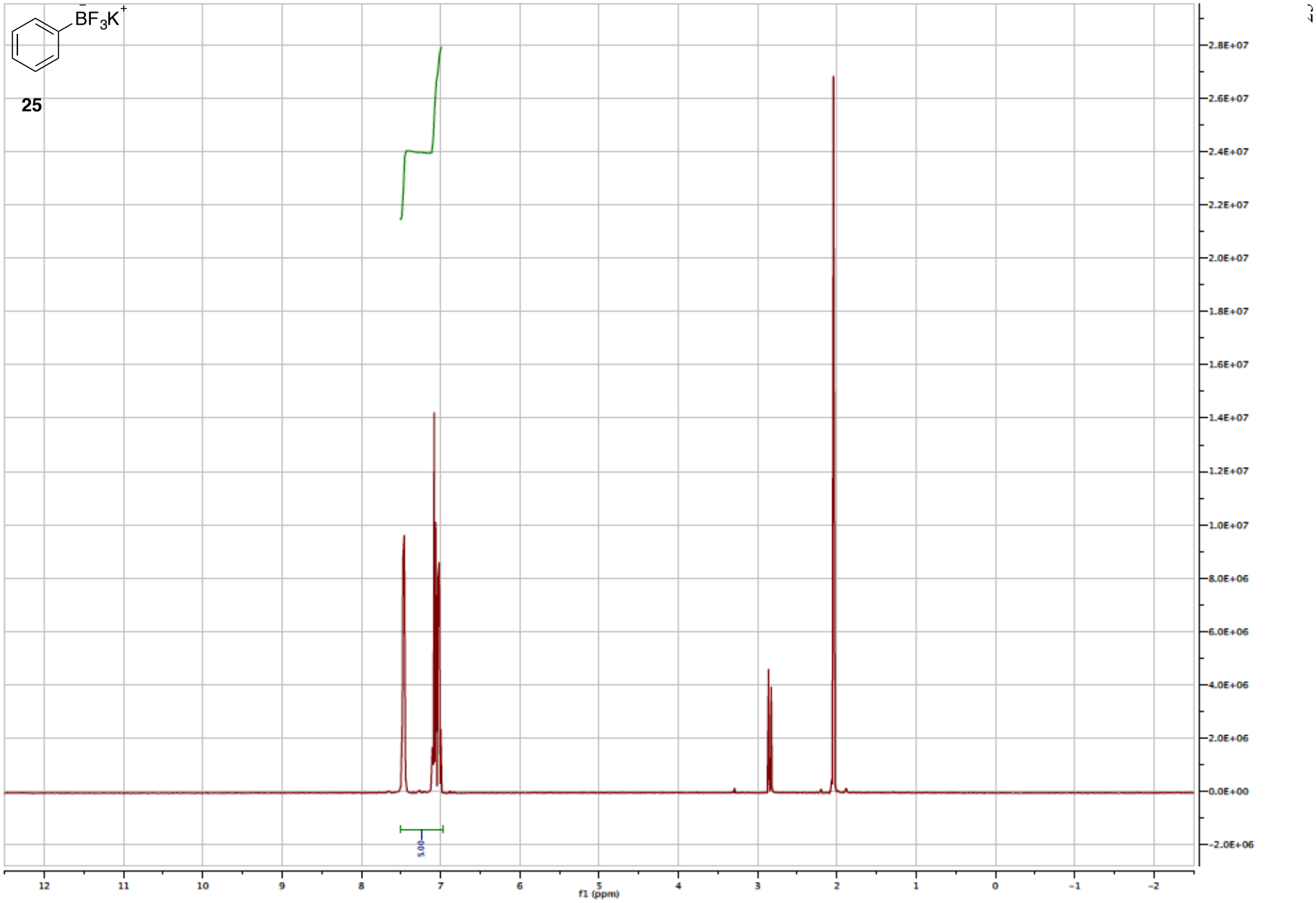
BF3K
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2.4E+07
2.2E+07
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1.8E+07
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1.4E+07
1.2E+07
1.0E+07
8.0E+06
6.0E+06
4.0E+06
2.0E+06
0.0E+00
-2.0E+06
5.00
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11
10
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8
7
6
5
4
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2
1
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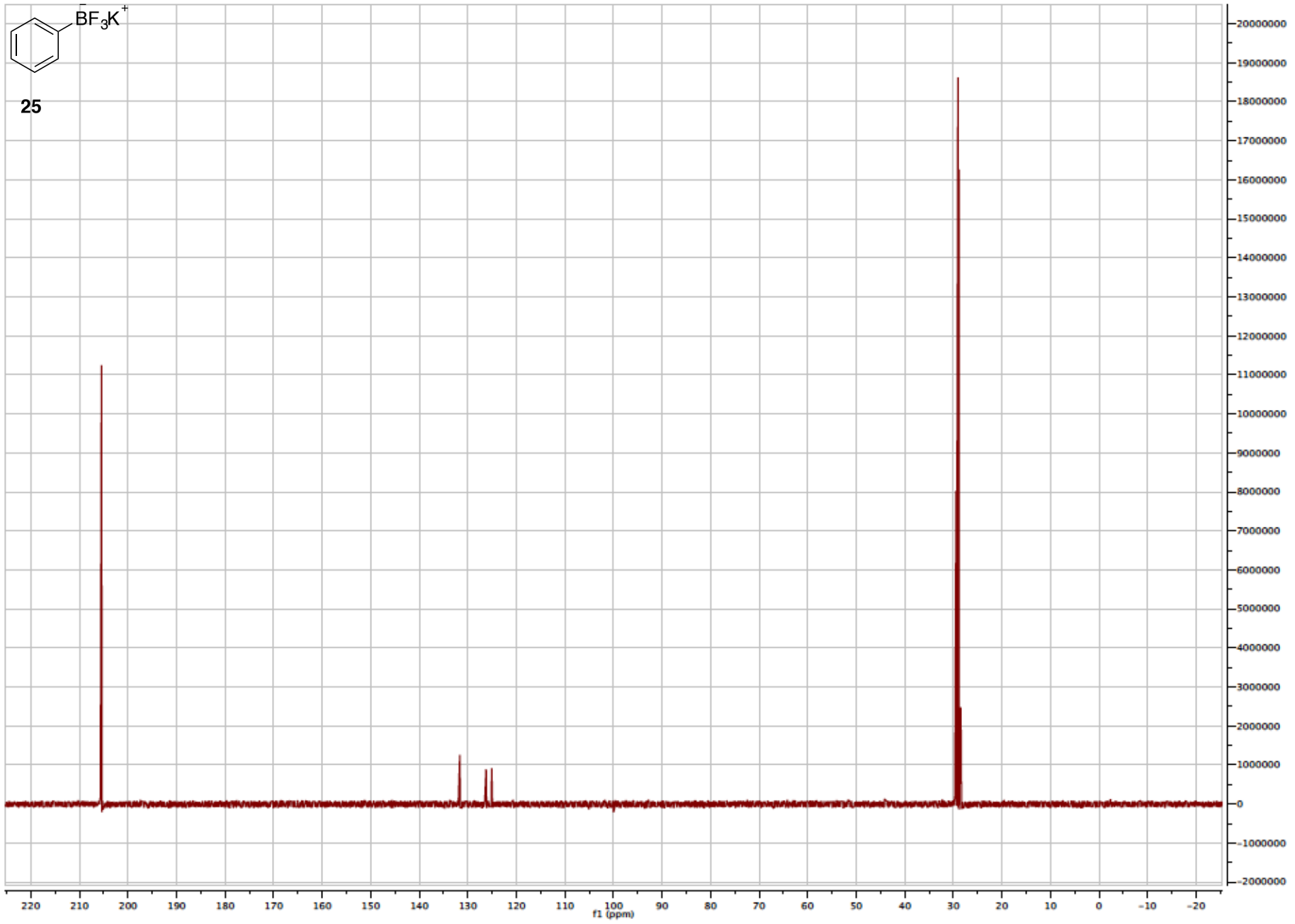
-2
f1 (ppm)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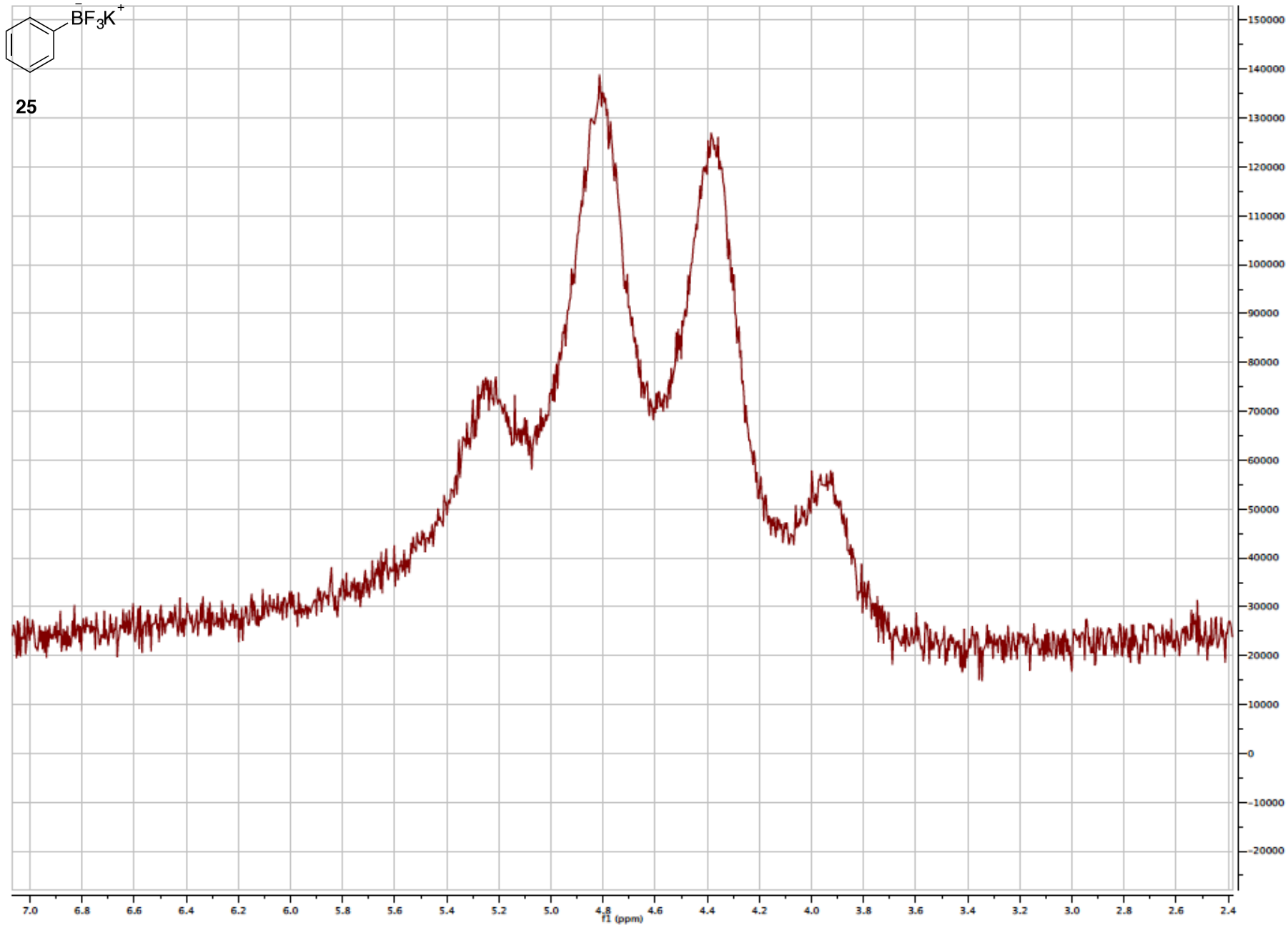
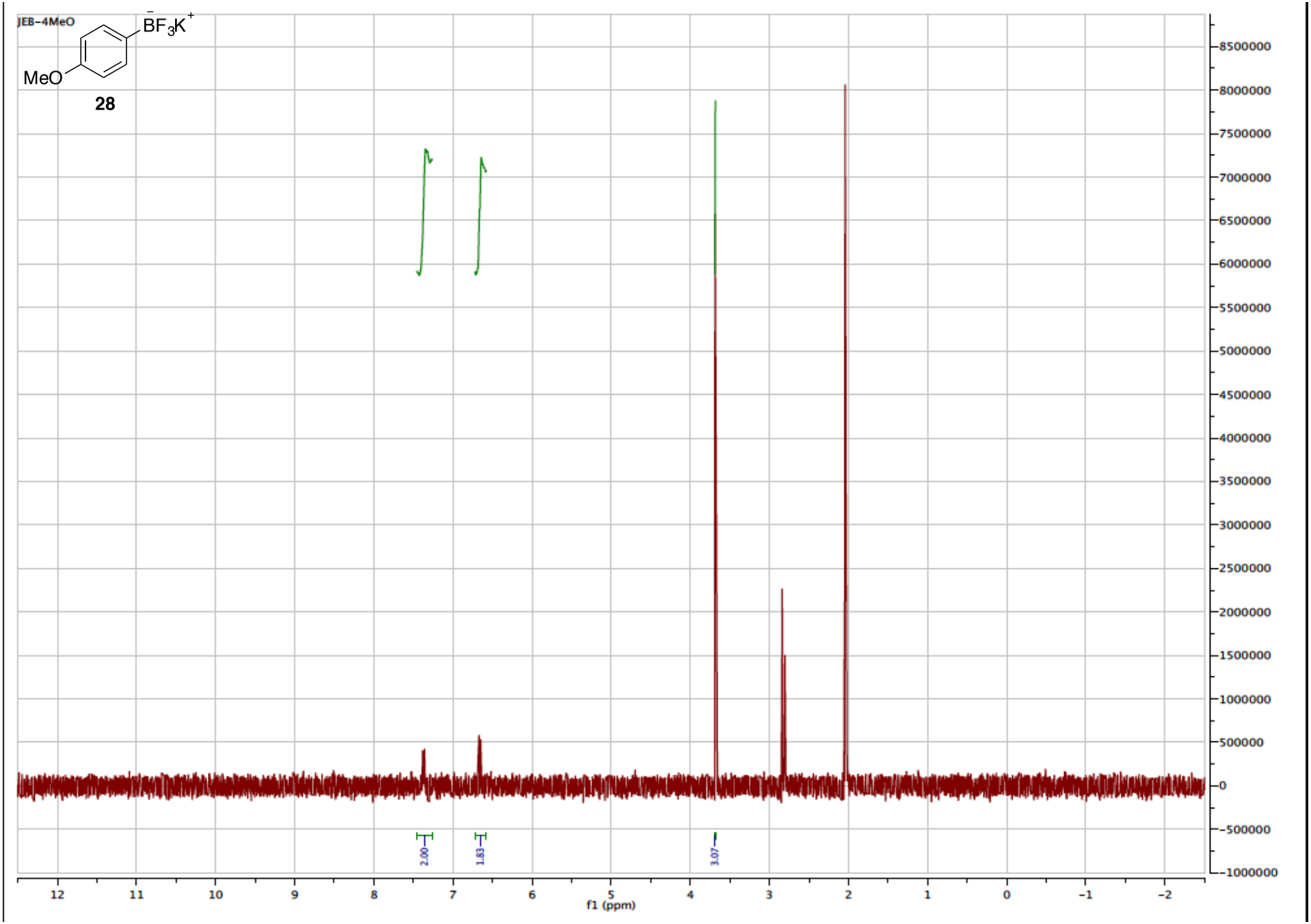
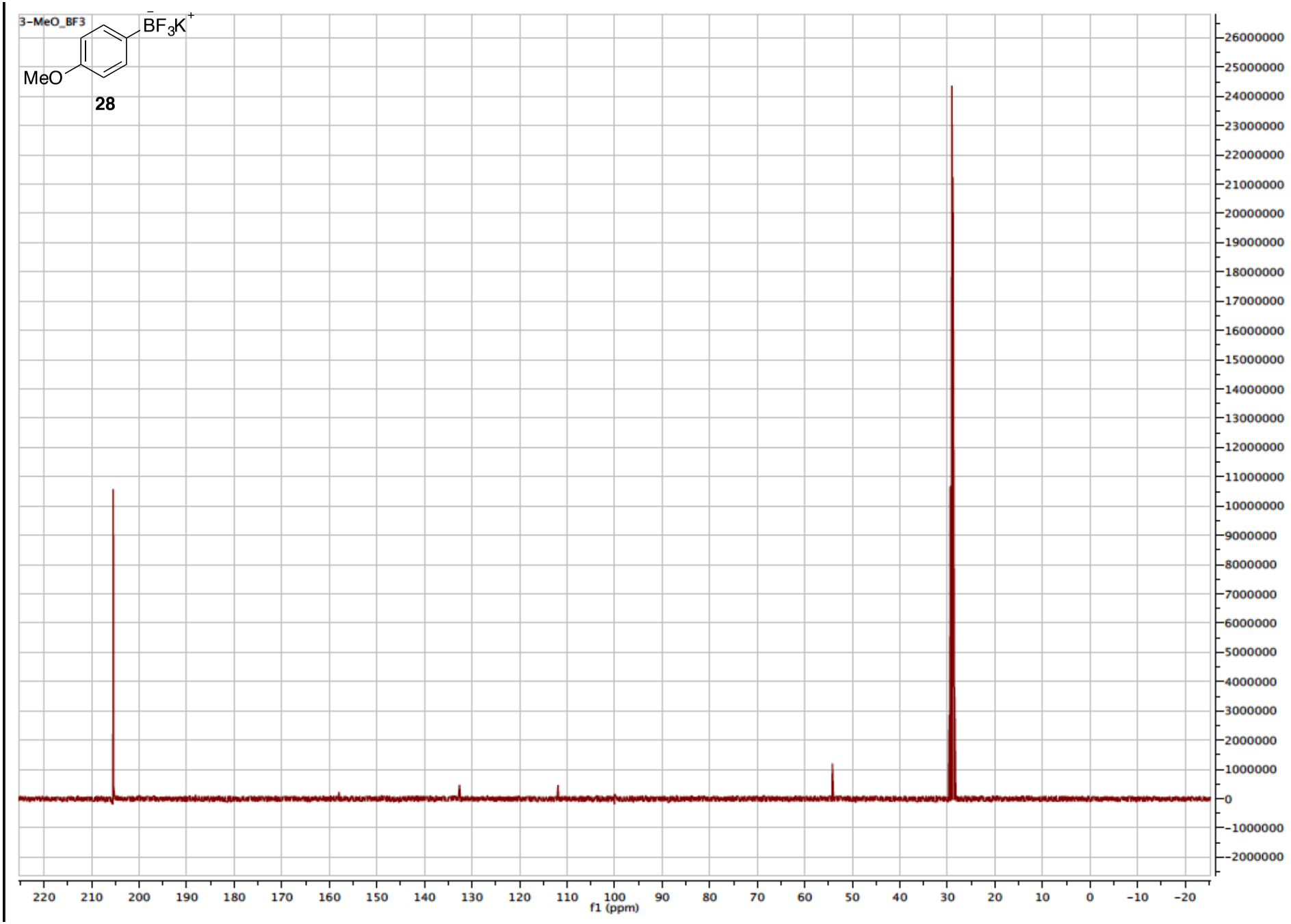
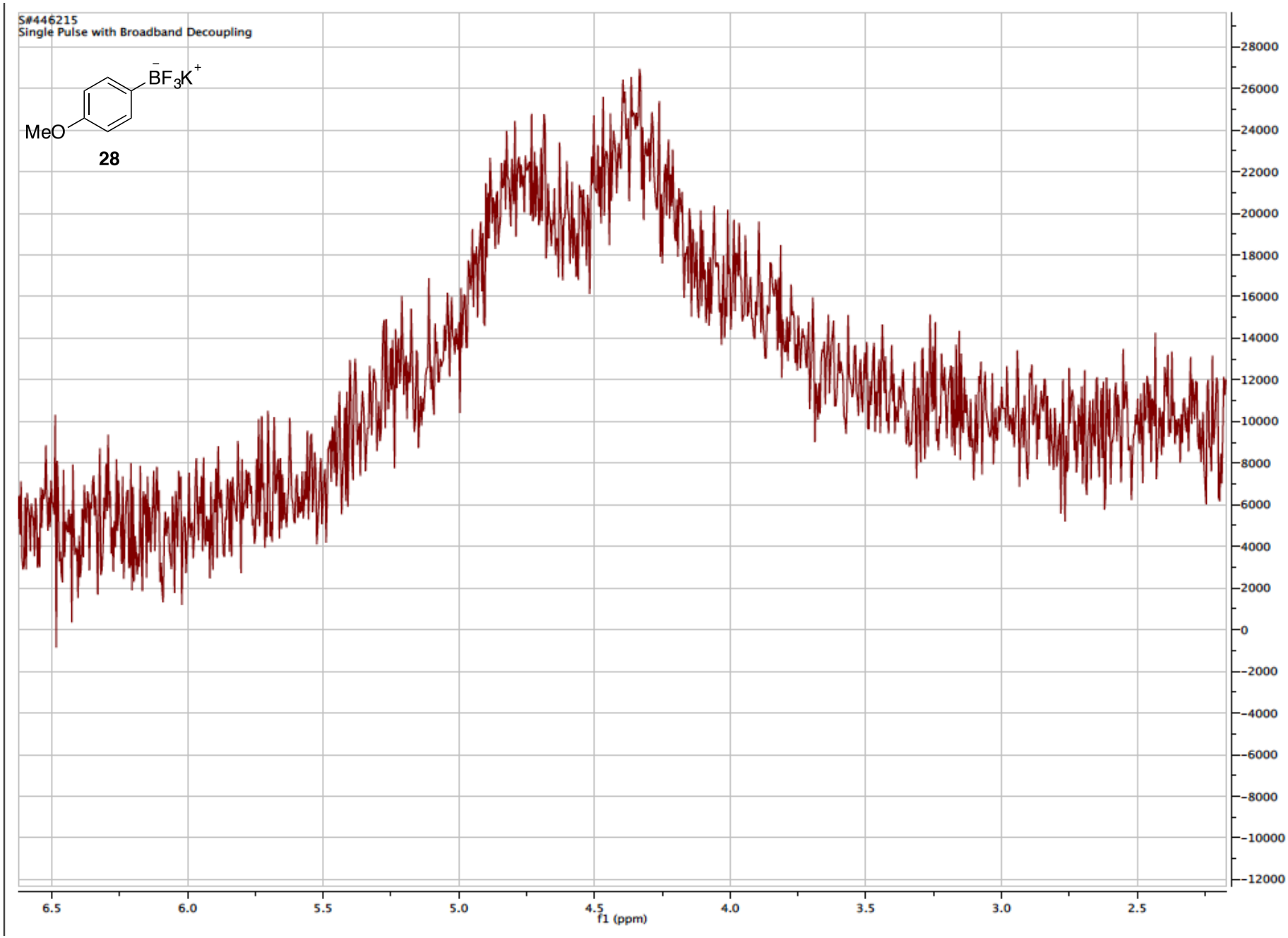
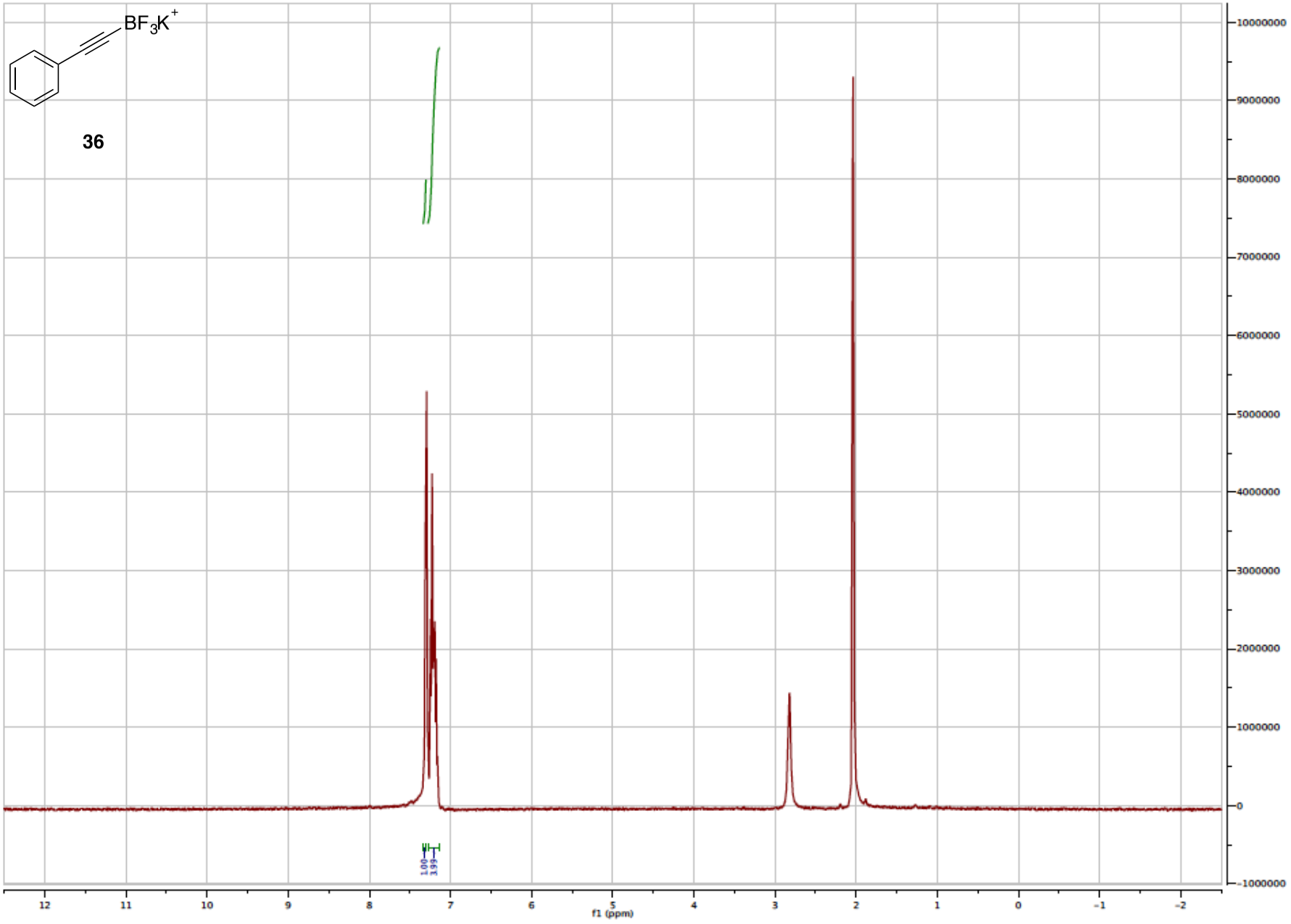
0
-1000000
-2000000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

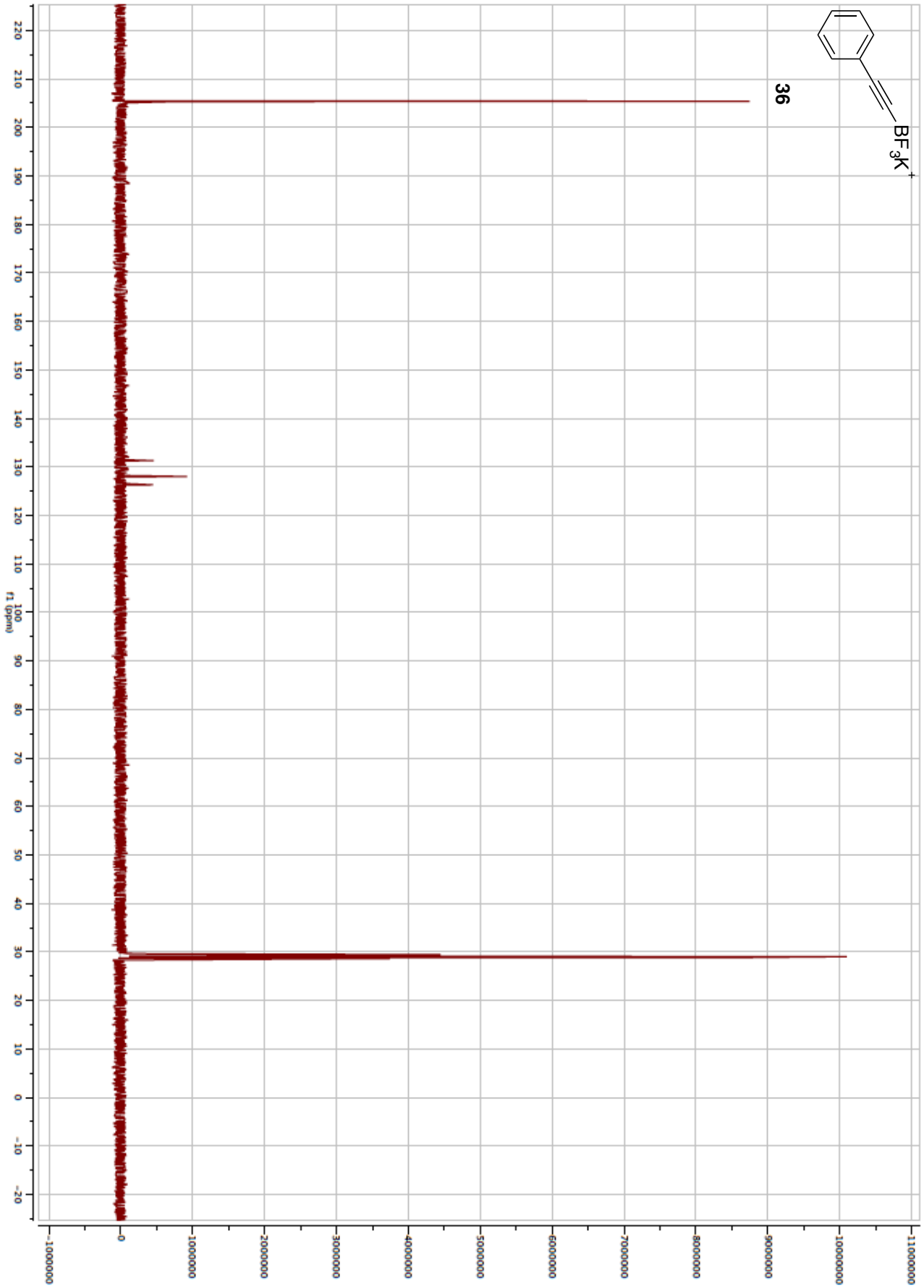

BF3K
25
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
f1 (ppm)

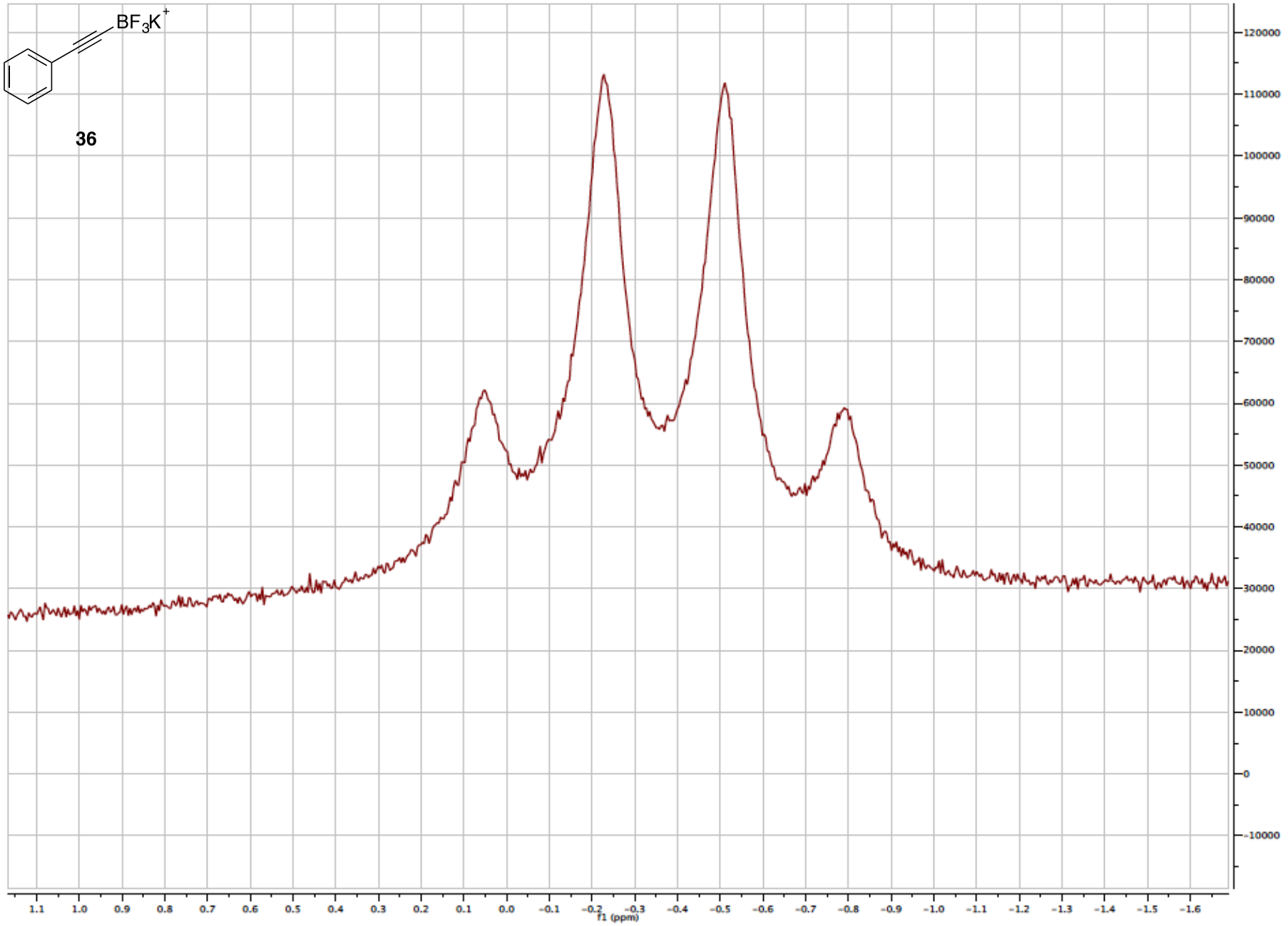

JEB-4MeO
MeO
BF_3K^+
28
2.00
1.83
3.07
f1 (ppm)

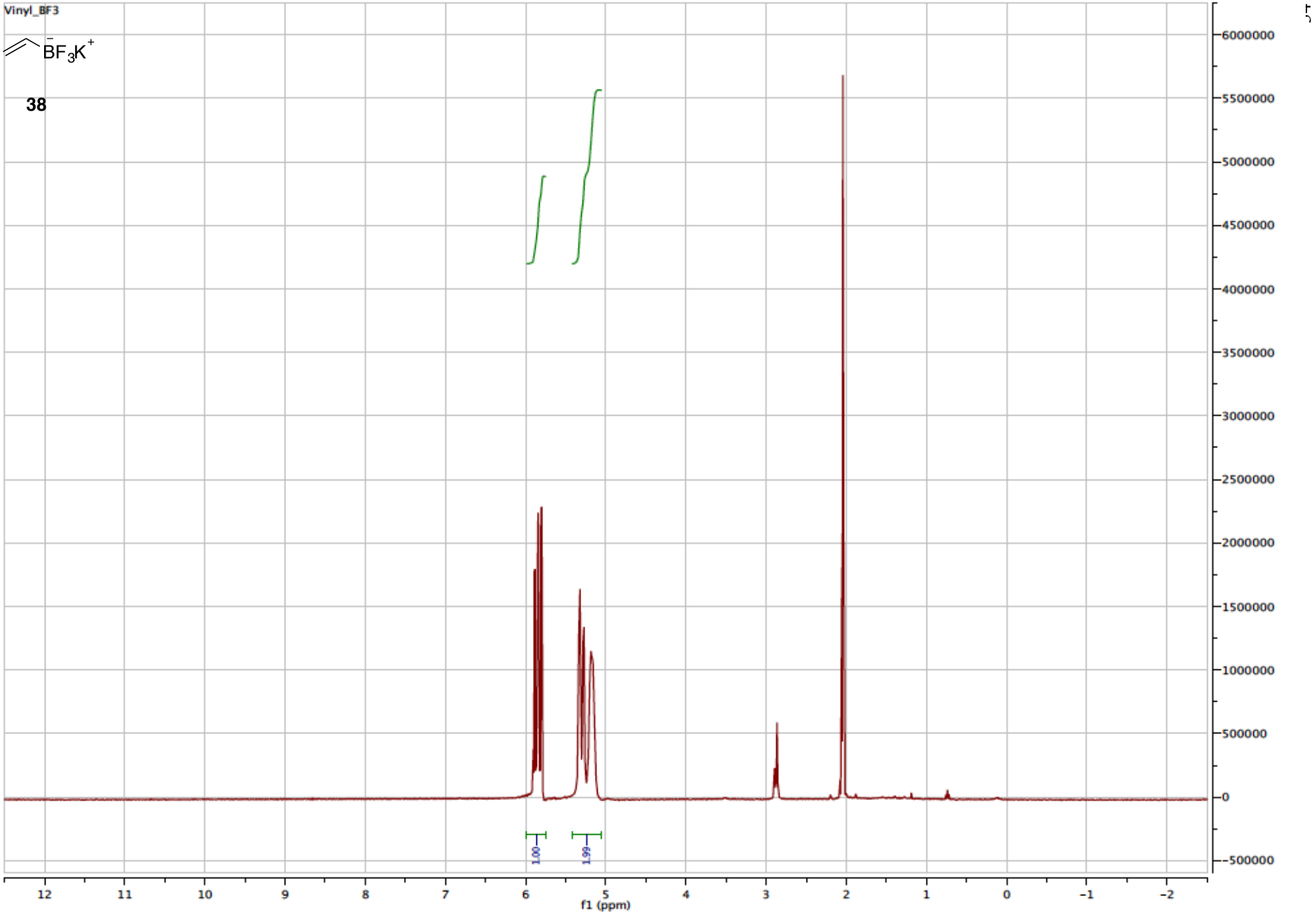

3-MeO_BF3
BF3K
MeO
28
f1 (ppm)

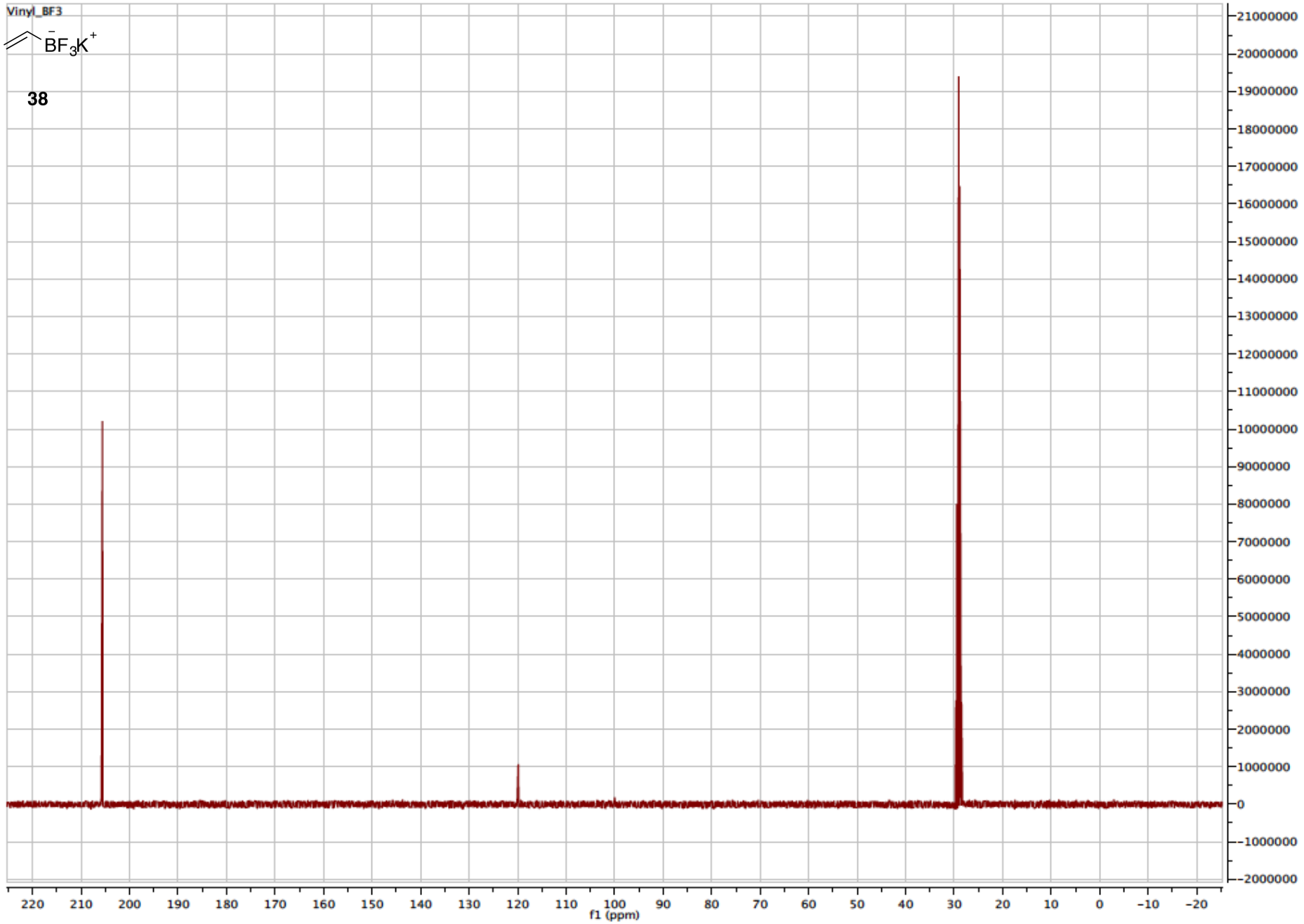

S#446215
Single Pulse with Broadband Decoupling
BF3K
MeO
28
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
-6000
-8000
-10000
-12000
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

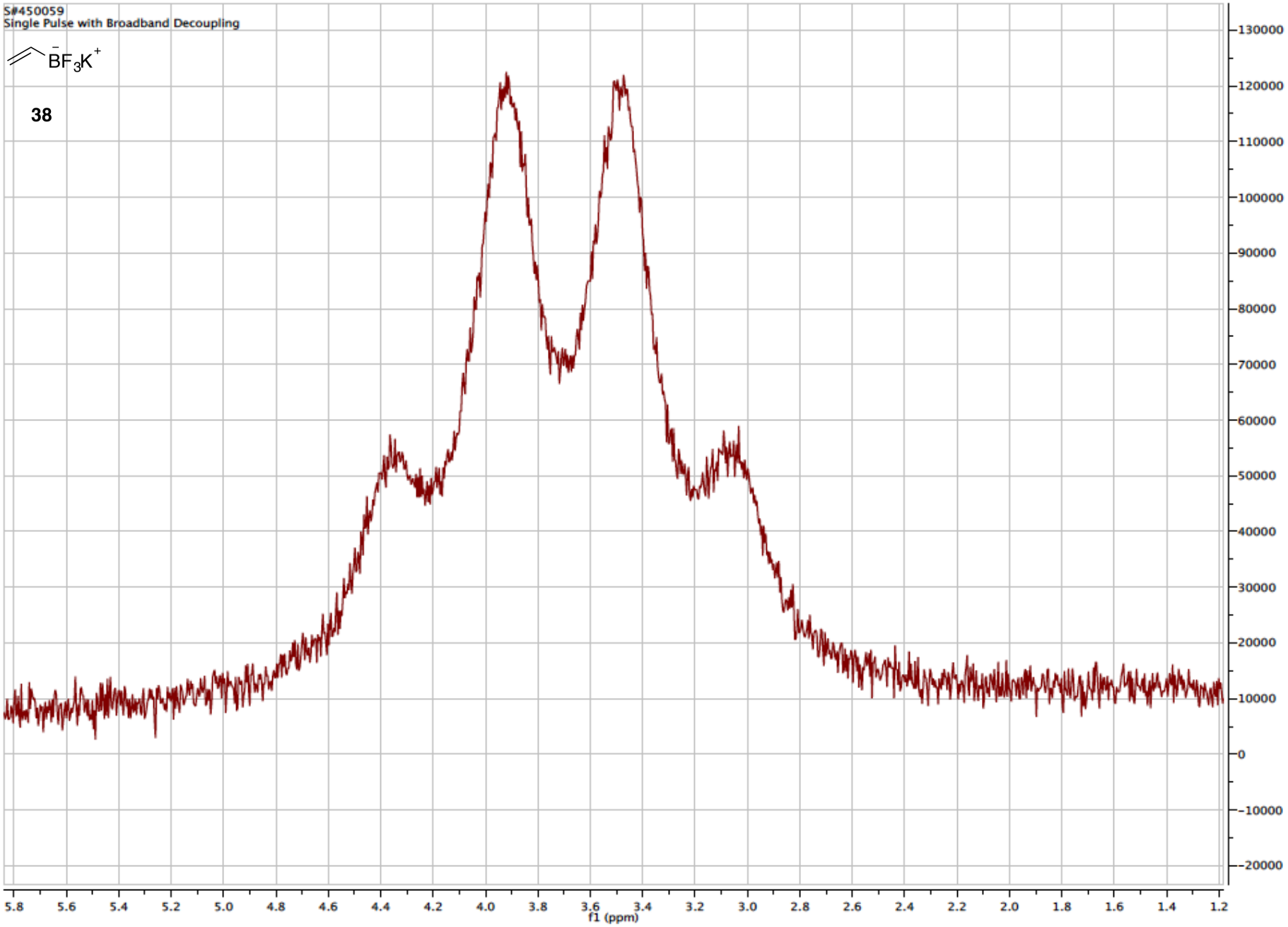

BF3K+
36
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)
1.00
3.99

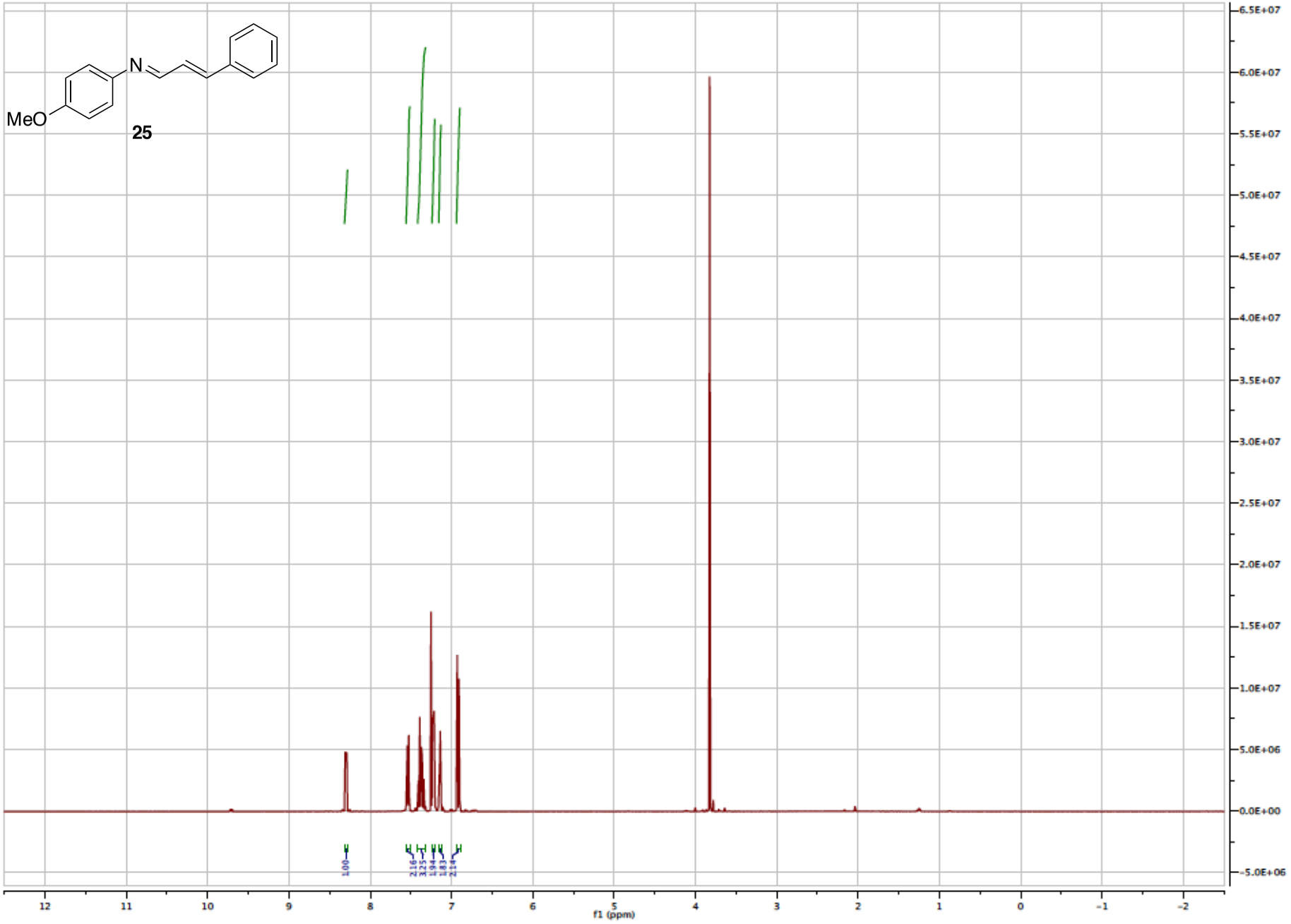

36
BF3K+
f1 (ppm)

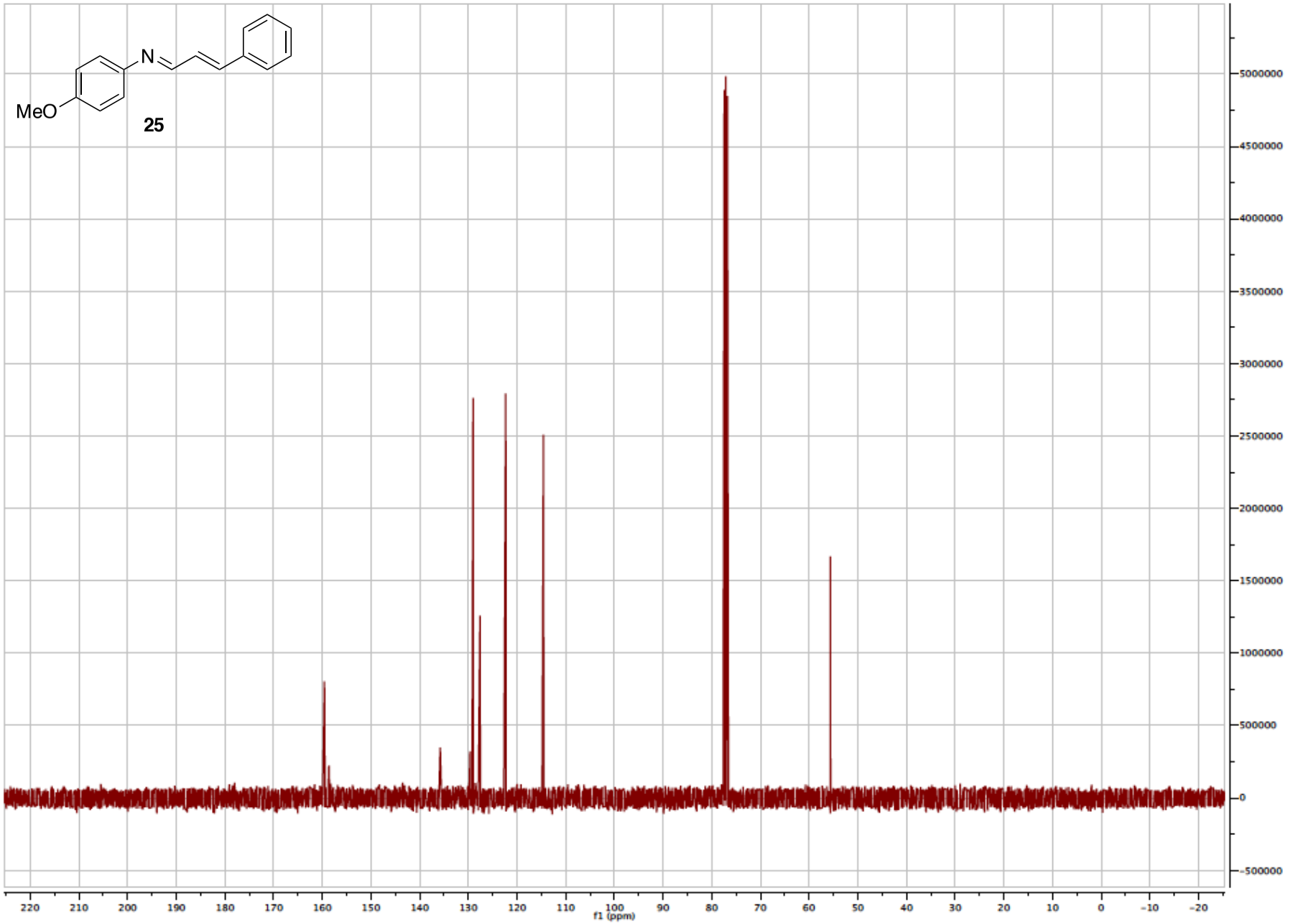

BF3K+
36
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0 -0.1 -0.2 -0.3 -0.4 -0.5 -0.6 -0.7 -0.8 -0.9 -1.0 -1.1 -1.2 -1.3 -1.4 -1.5 -1.6
f1 (ppm)

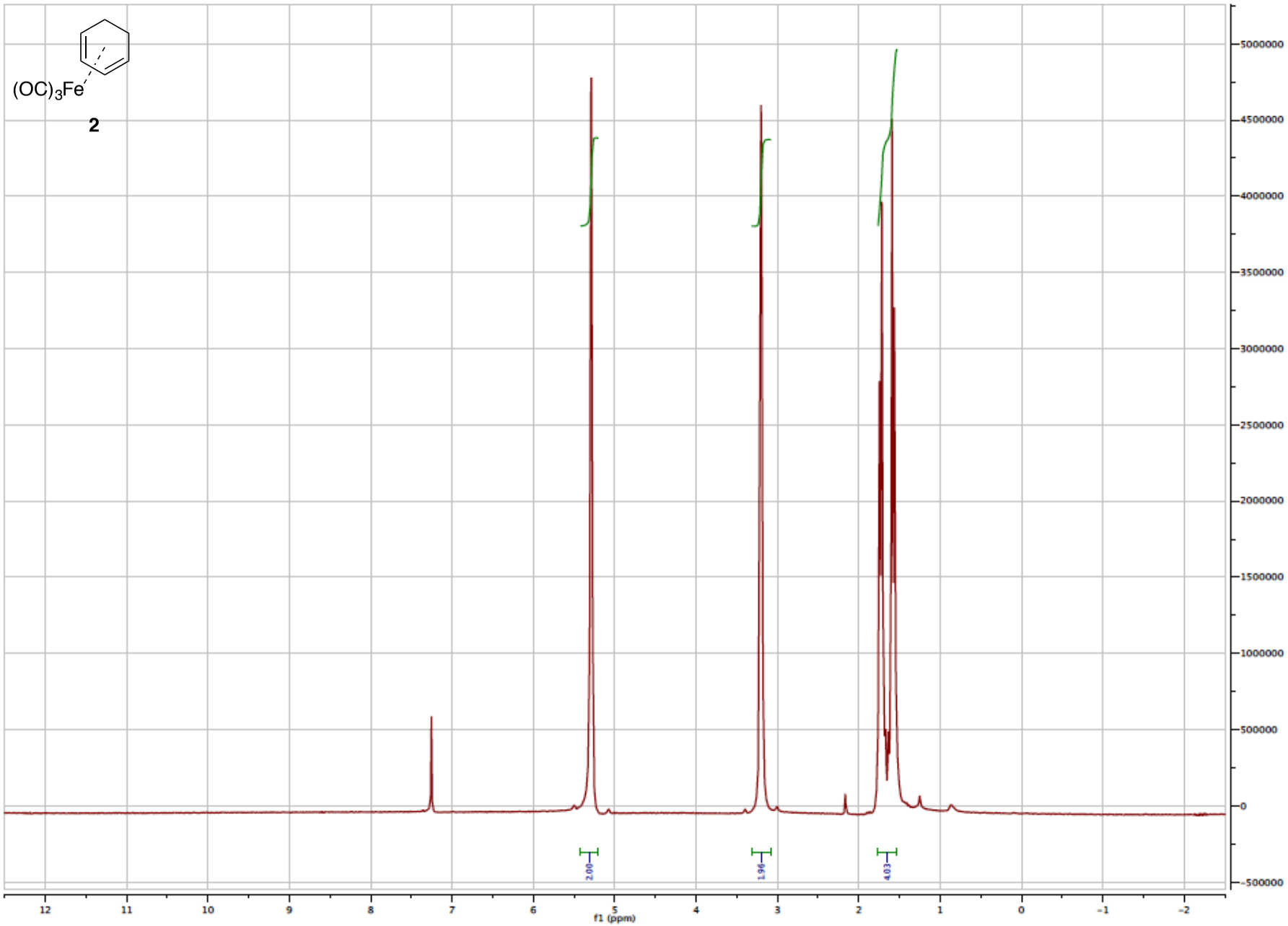

Vinyl_BF3
BF3K+
38
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
−500000
1.00
1.99
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)

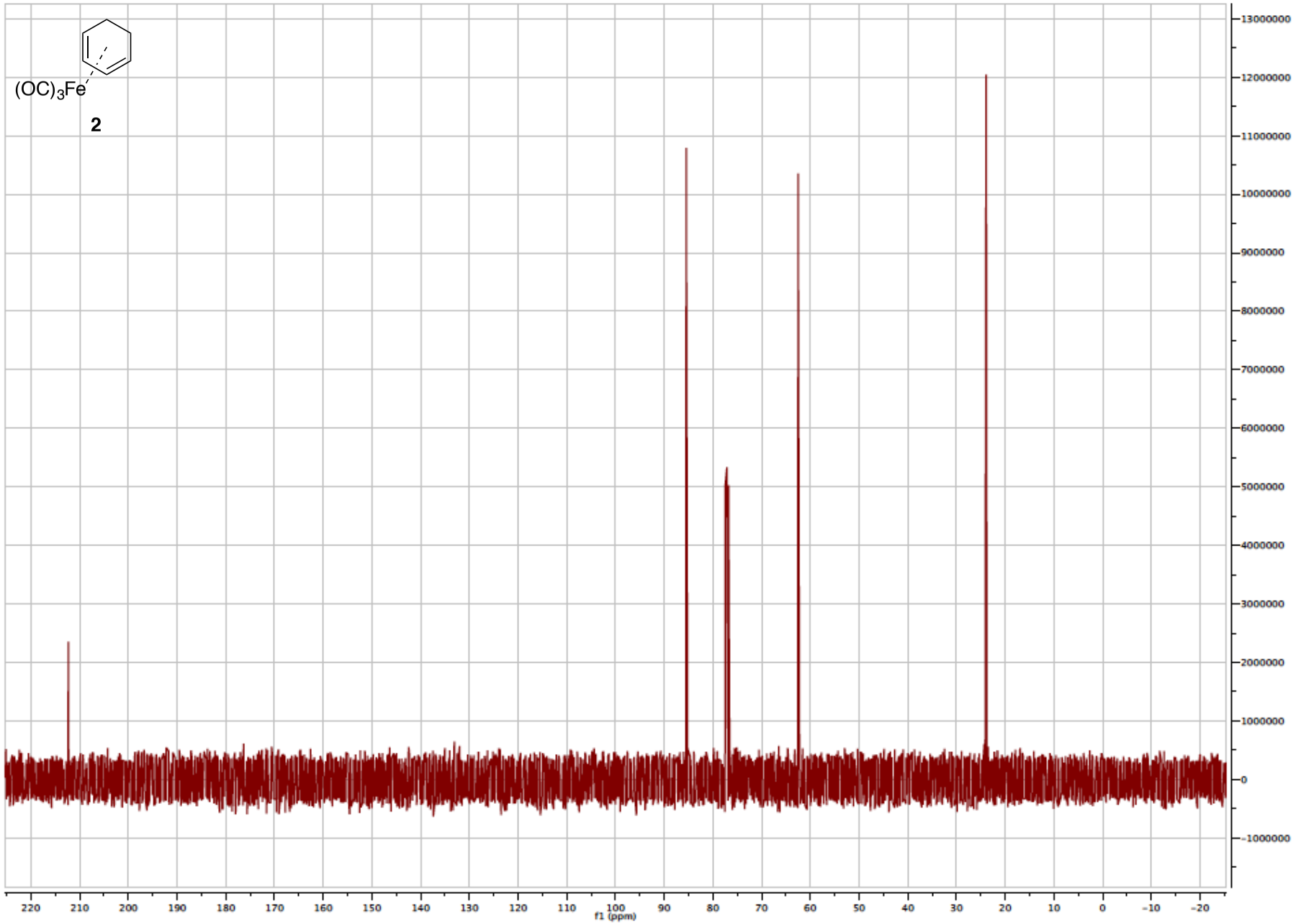

Vinyl_BF3
BF3K
38
21000000
20000000
19000000
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
-2000000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

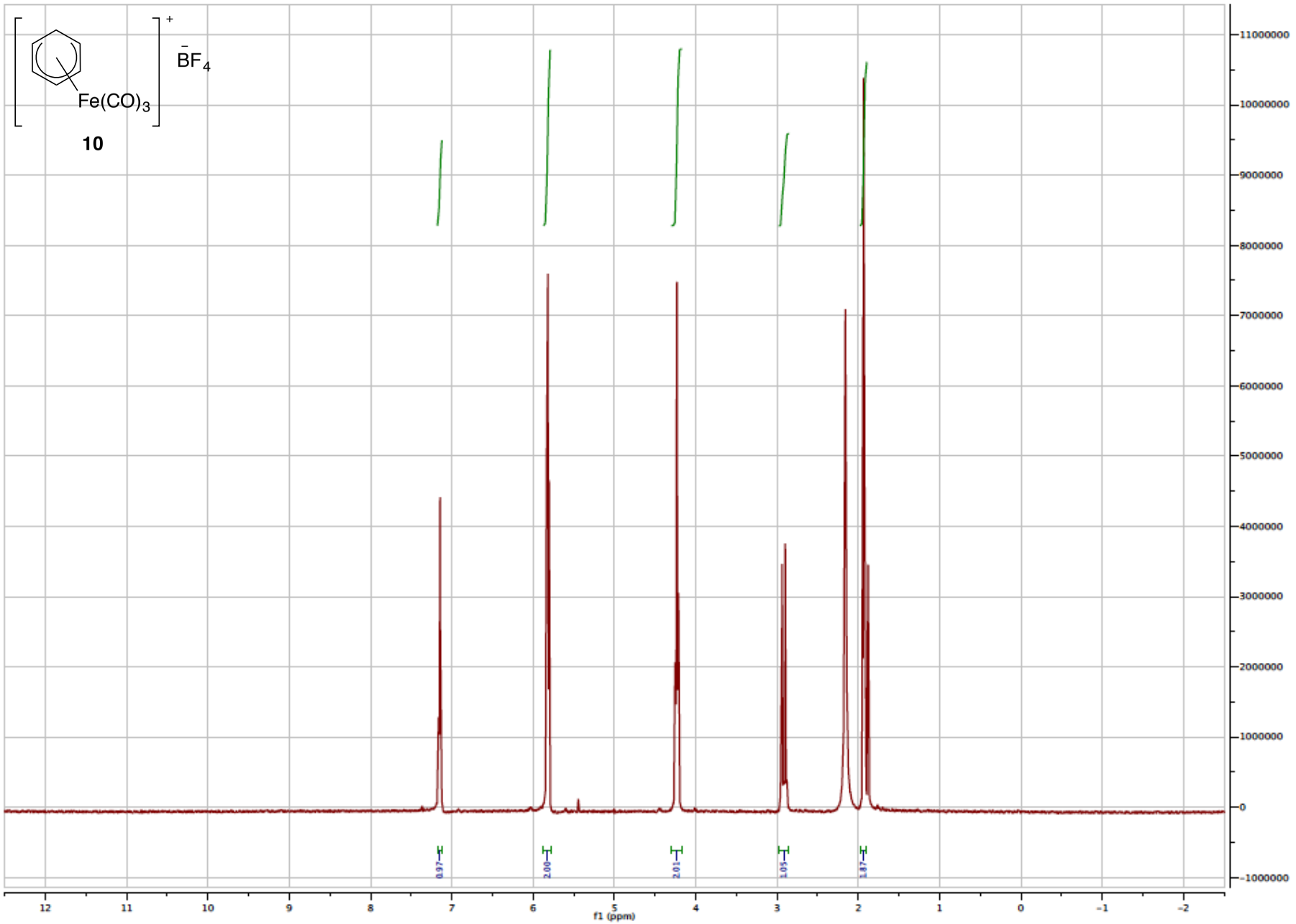

S#450059
Single Pulse with Broadband Decoupling
BF_3K^+
38
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f1 (ppm)

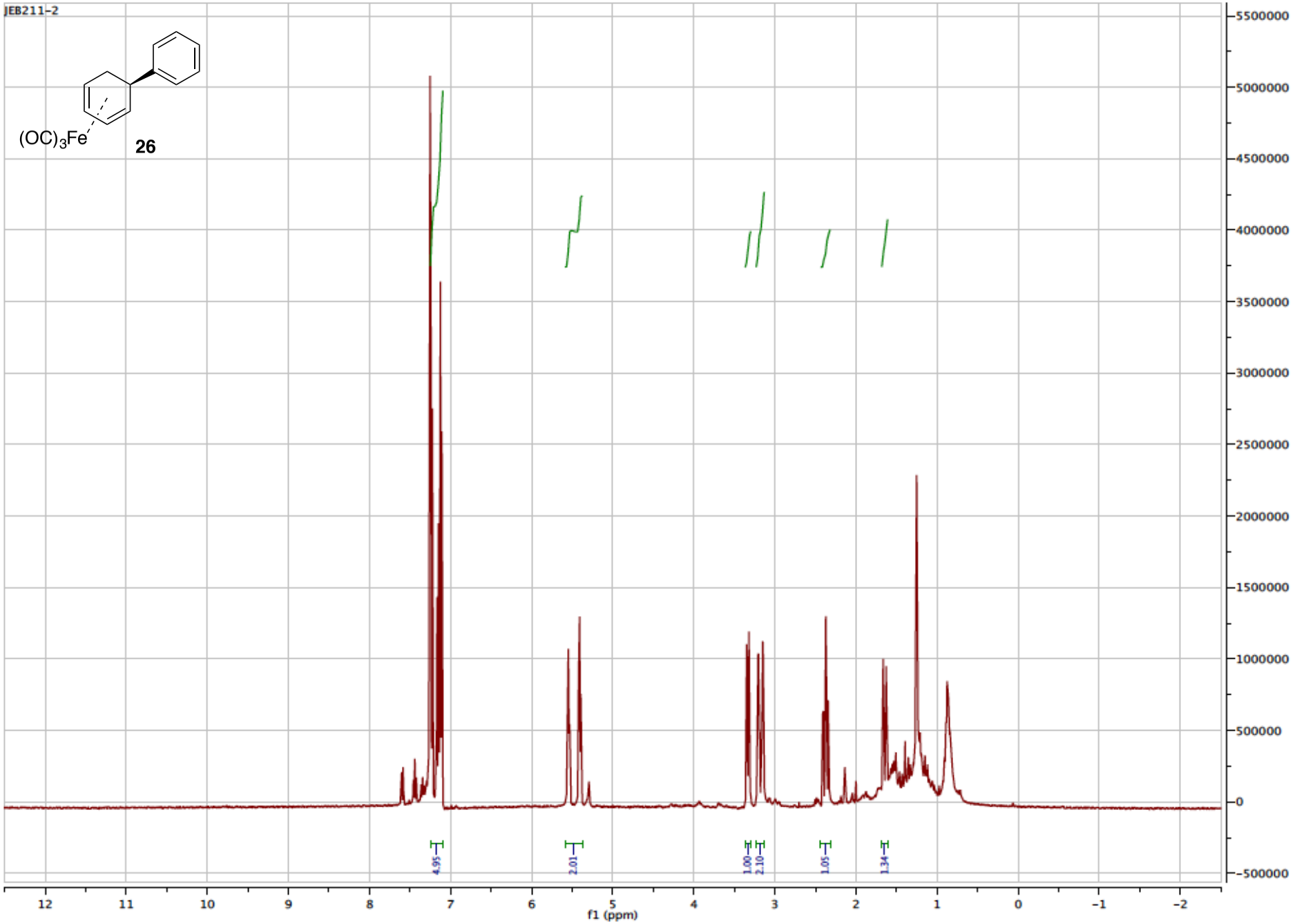

MeO
N
25
1.00
2.16
3.25
1.94
1.83
2.14
f1 (ppm)

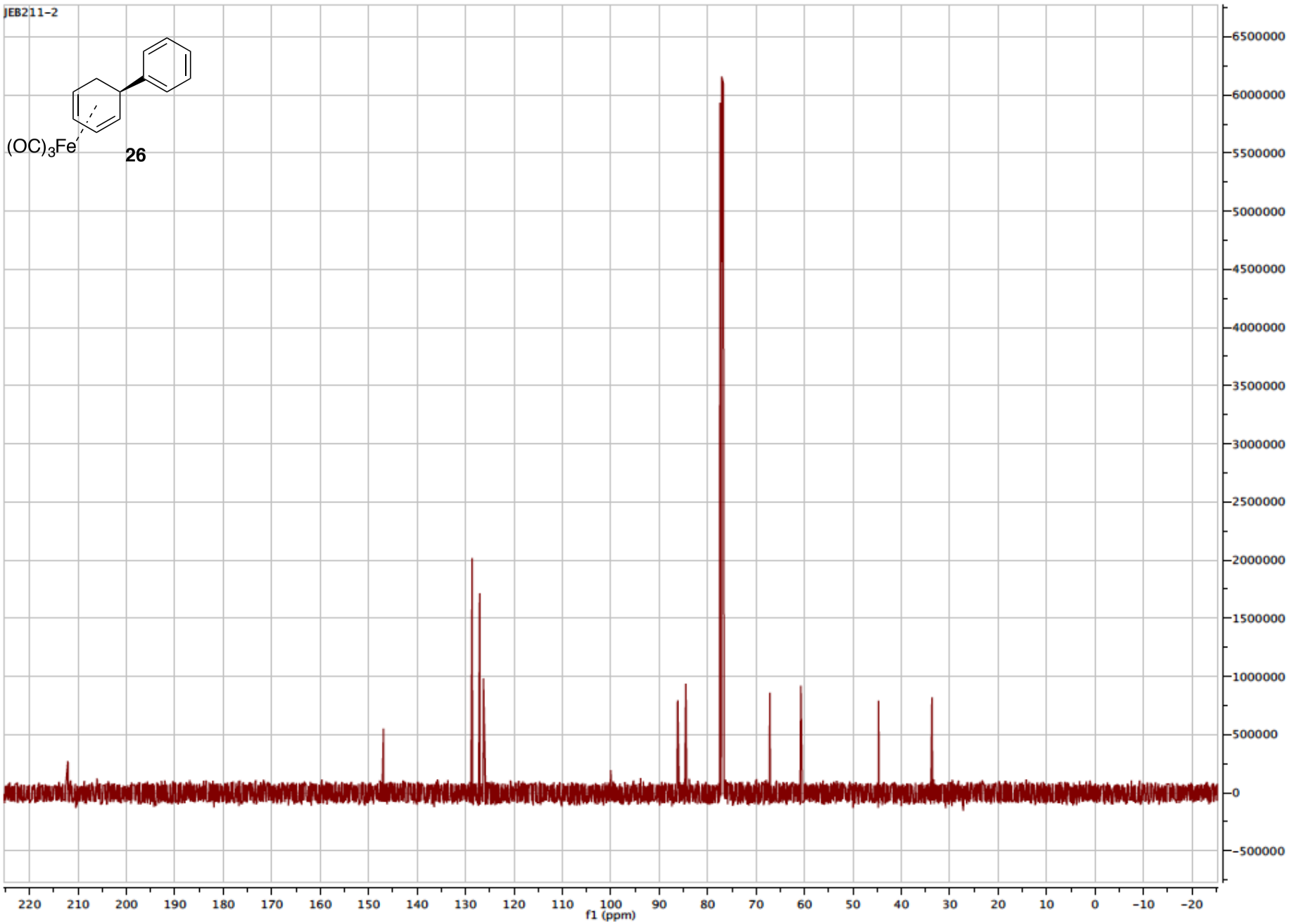

MeO
N
25
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

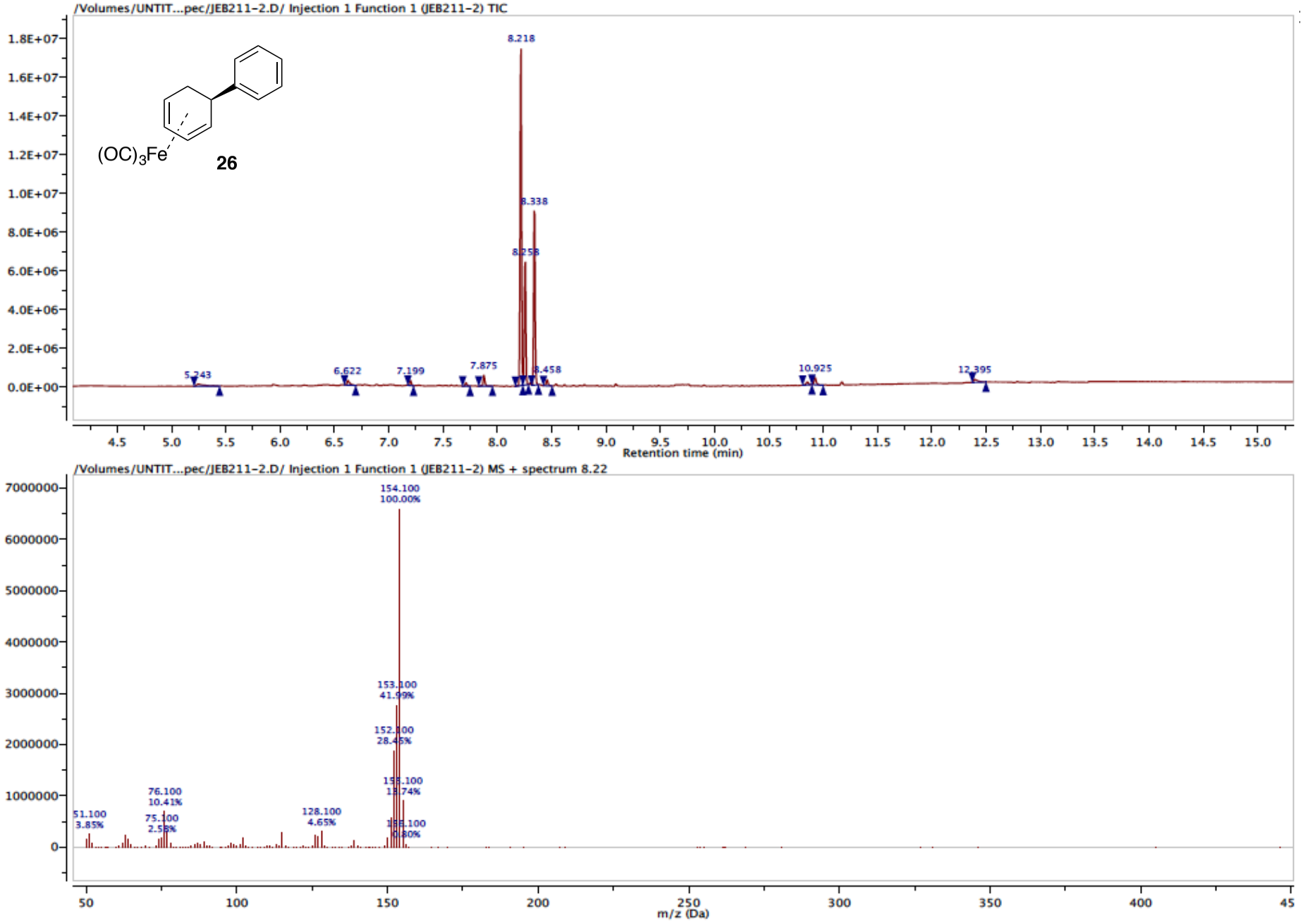

(OC)3Fe
2
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
2.00
1.96
4.03
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

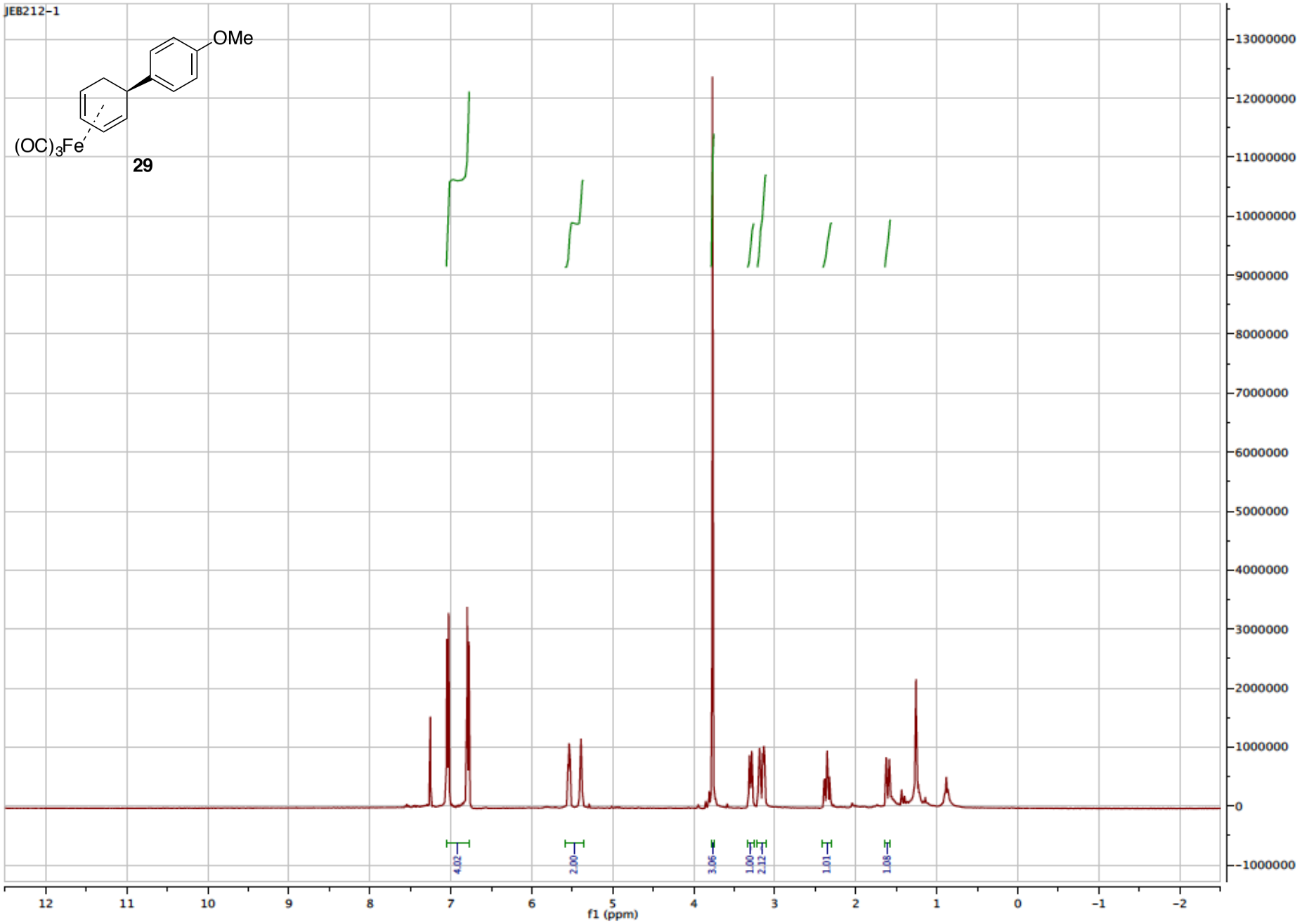

(OC)3Fe
2
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

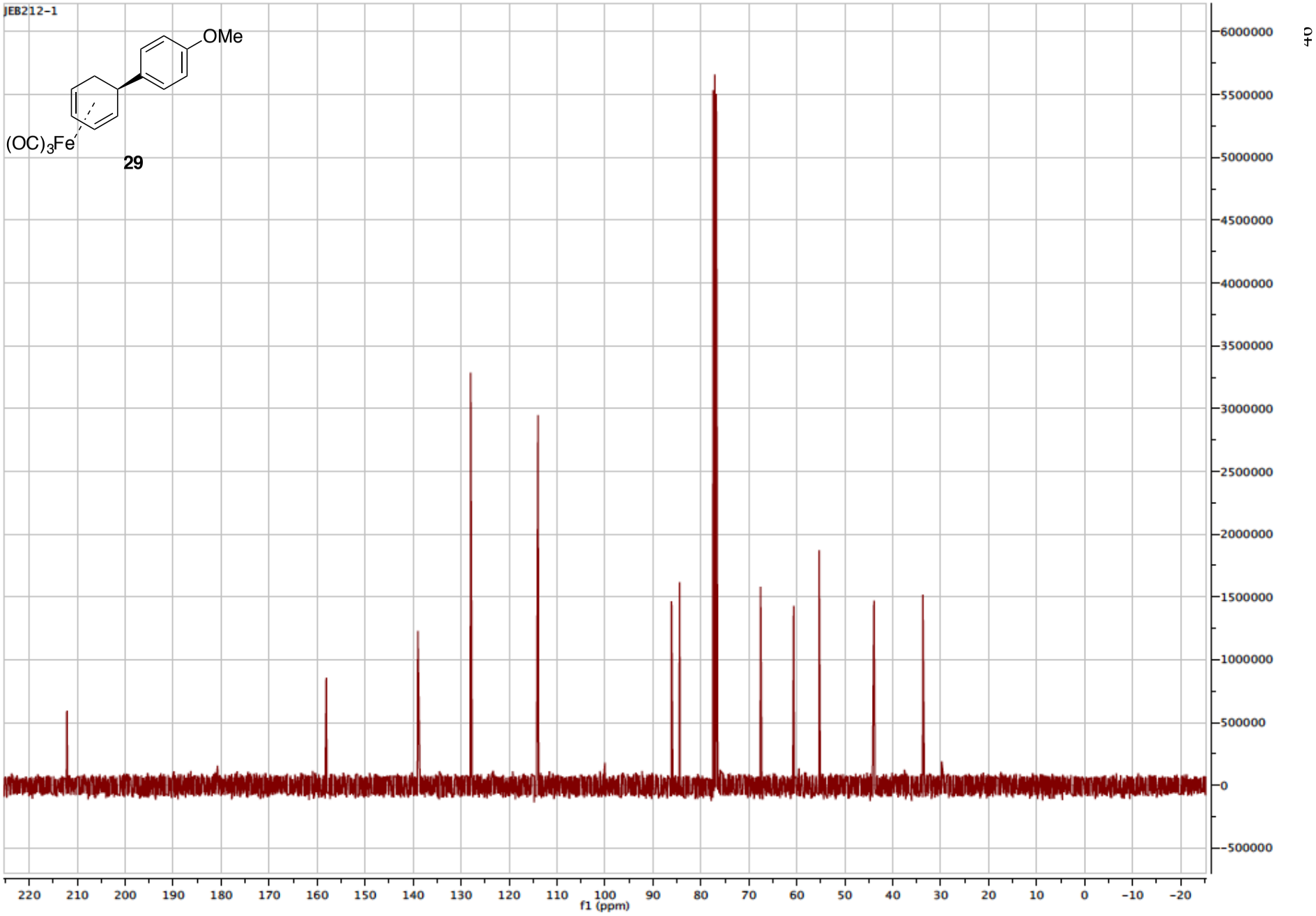

Fe(CO)3
BF4
10
f1 (ppm)

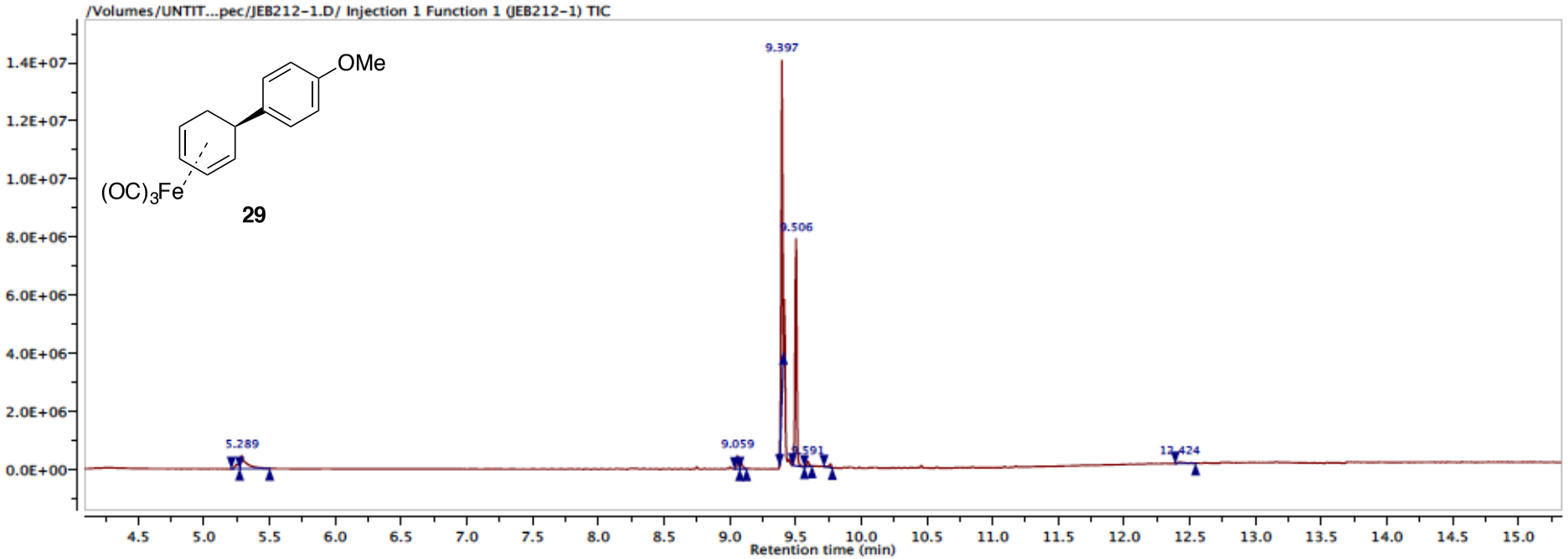

JEB211-2
(OC)3Fe
26
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
4.95
2.01
1.00
2.10
1.05
1.34
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

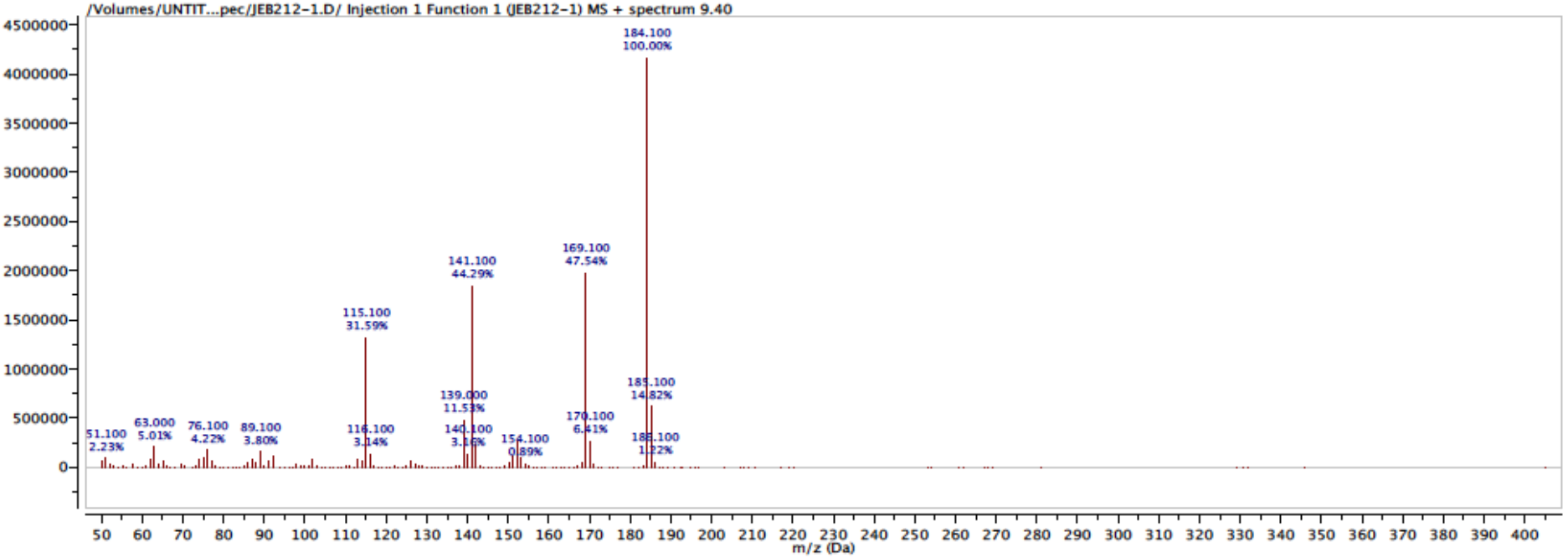

JEB211-2
(OC)3Fe
26
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

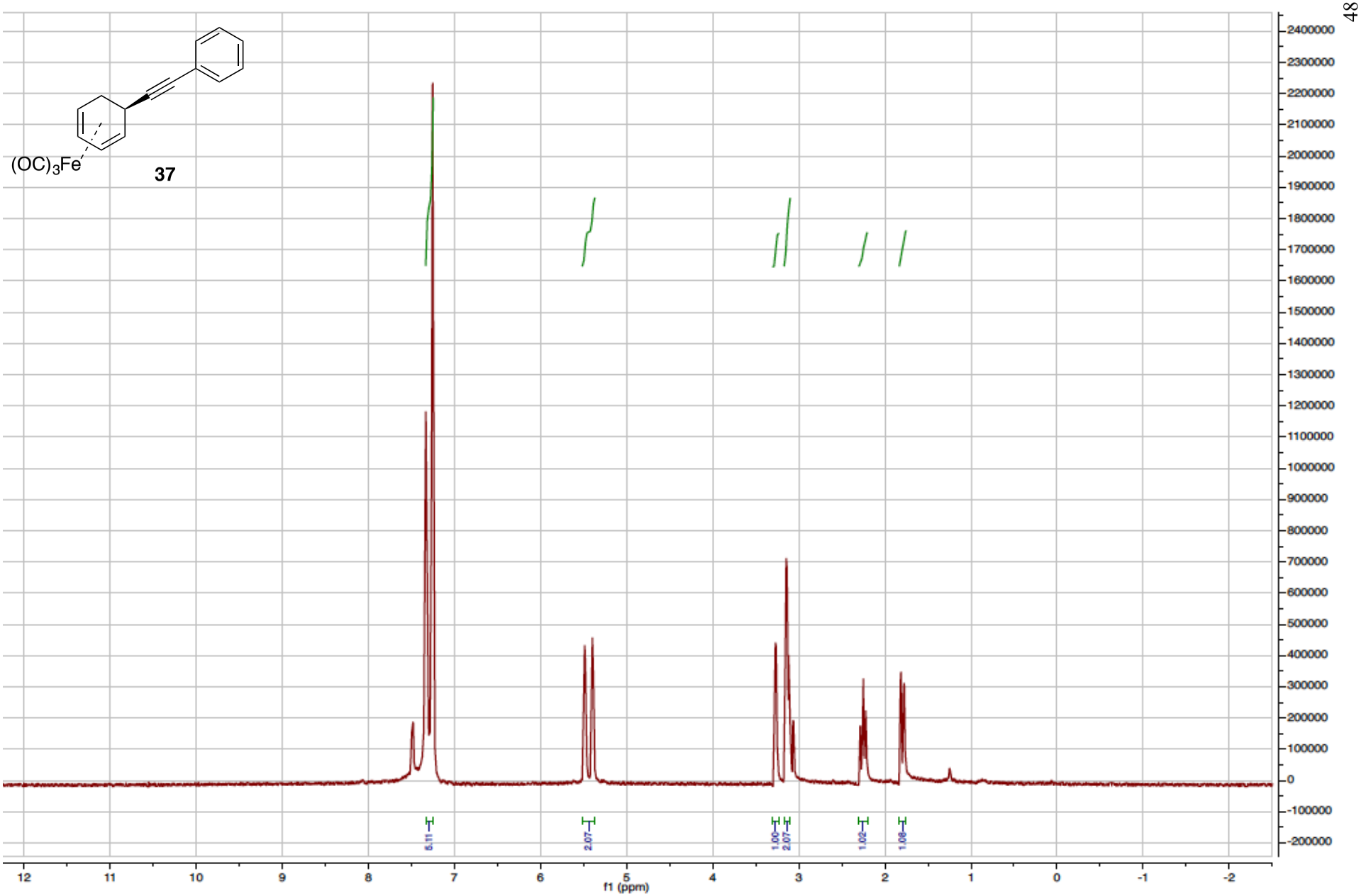

/Volumes/UNTIT...pec/JEB211-2.D/ Injection 1 Function 1 (JEB211-2) TIC
(OC)3Fe
26
8.218
8.338
8.258
5.243
6.622
7.199
7.875
8.458
10.925
12.395
Retention time (min)
/Volumes/UNTIT...pec/JEB211-2.D/ Injection 1 Function 1 (JEB211-2) MS + spectrum 8.22
154.100
100.00%
153.100
41.99%
152.100
28.45%
76.100
10.41%
75.100
2.58%
51.100
3.85%
128.100
4.65%
m/z (Da)

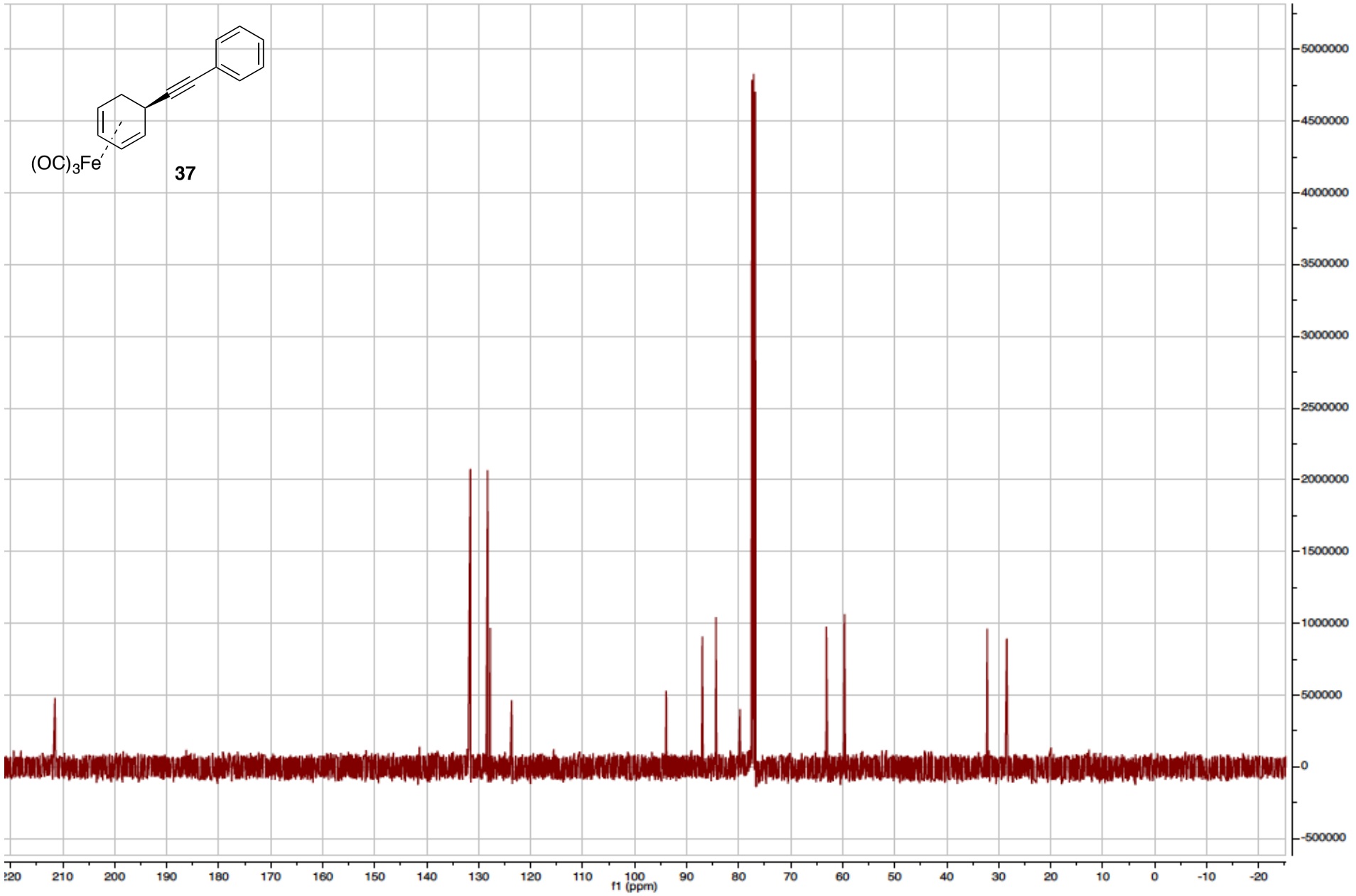

JEB212-1
OMe
(OC)3Fe
29
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
4.02
2.00
3.06
1.00
2.12
1.01
1.08
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

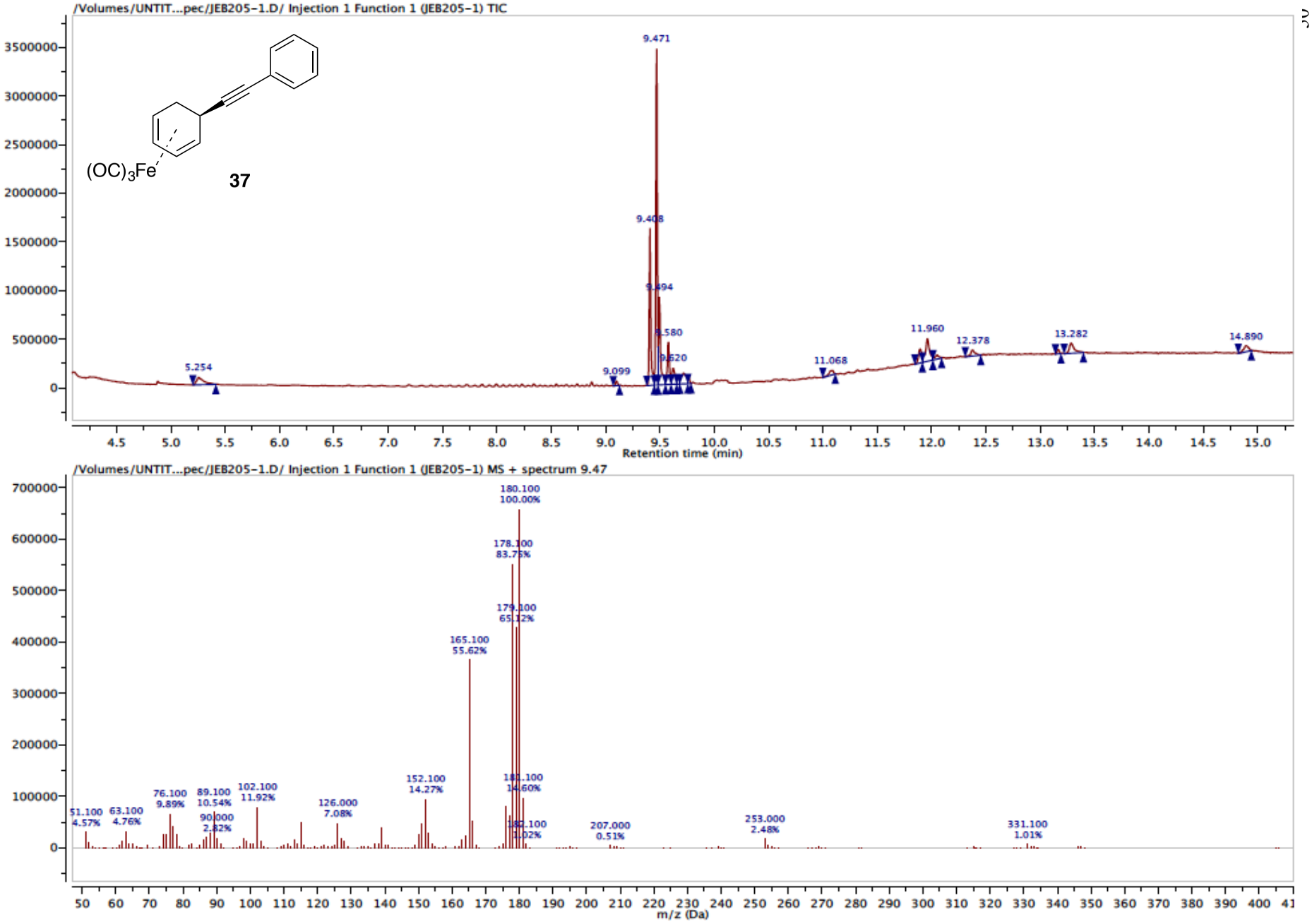

JEB212-1
OMe
(OC)3Fe
29
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

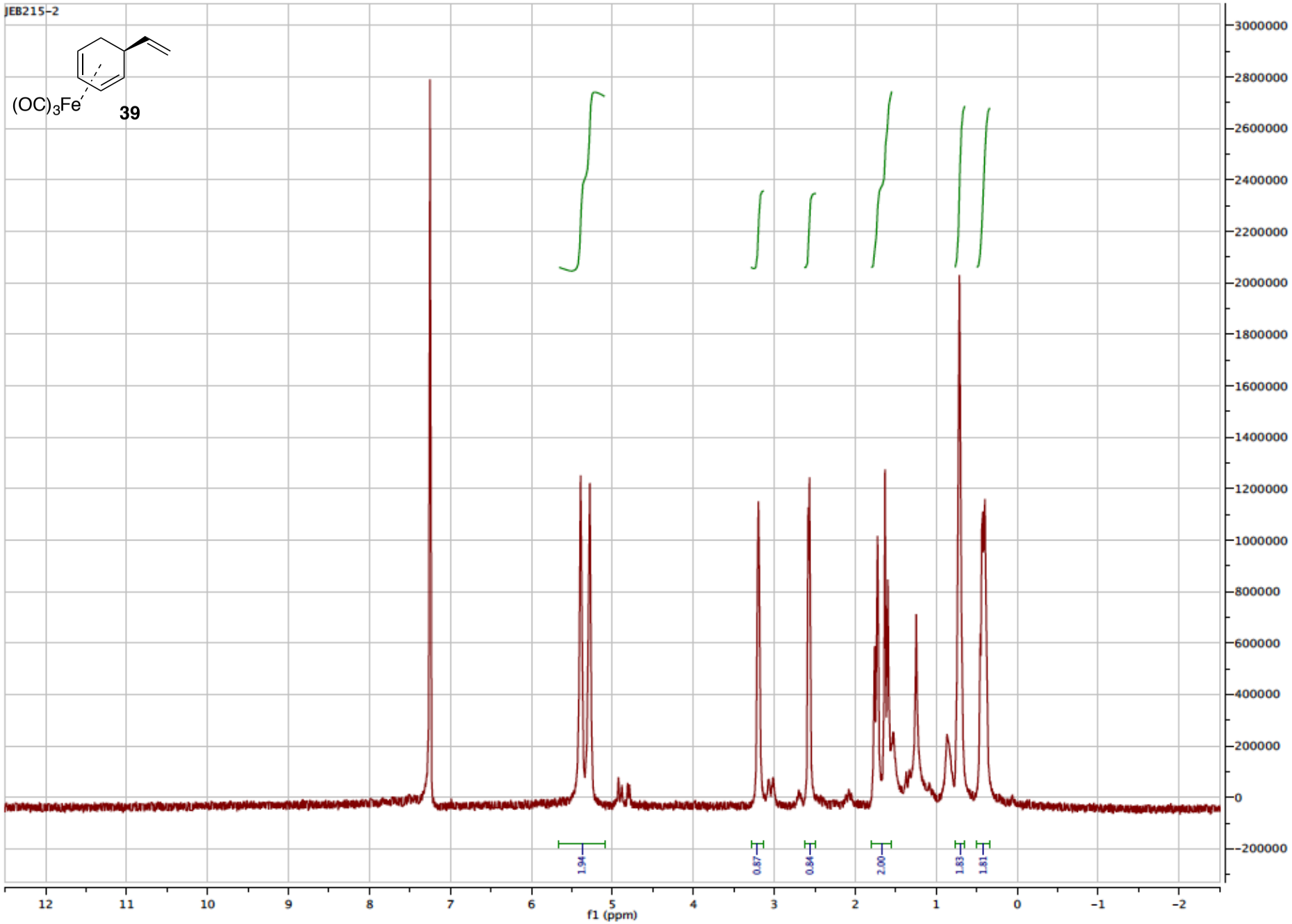

/Volumes/UNTIT...pec/JEB212-1.D/ Injection 1 Function 1 (JEB212-1) TIC
OMe
(OC)3Fe
29
9.397
9.506
5.289
9.059
9.591
12.424
Retention time (min)

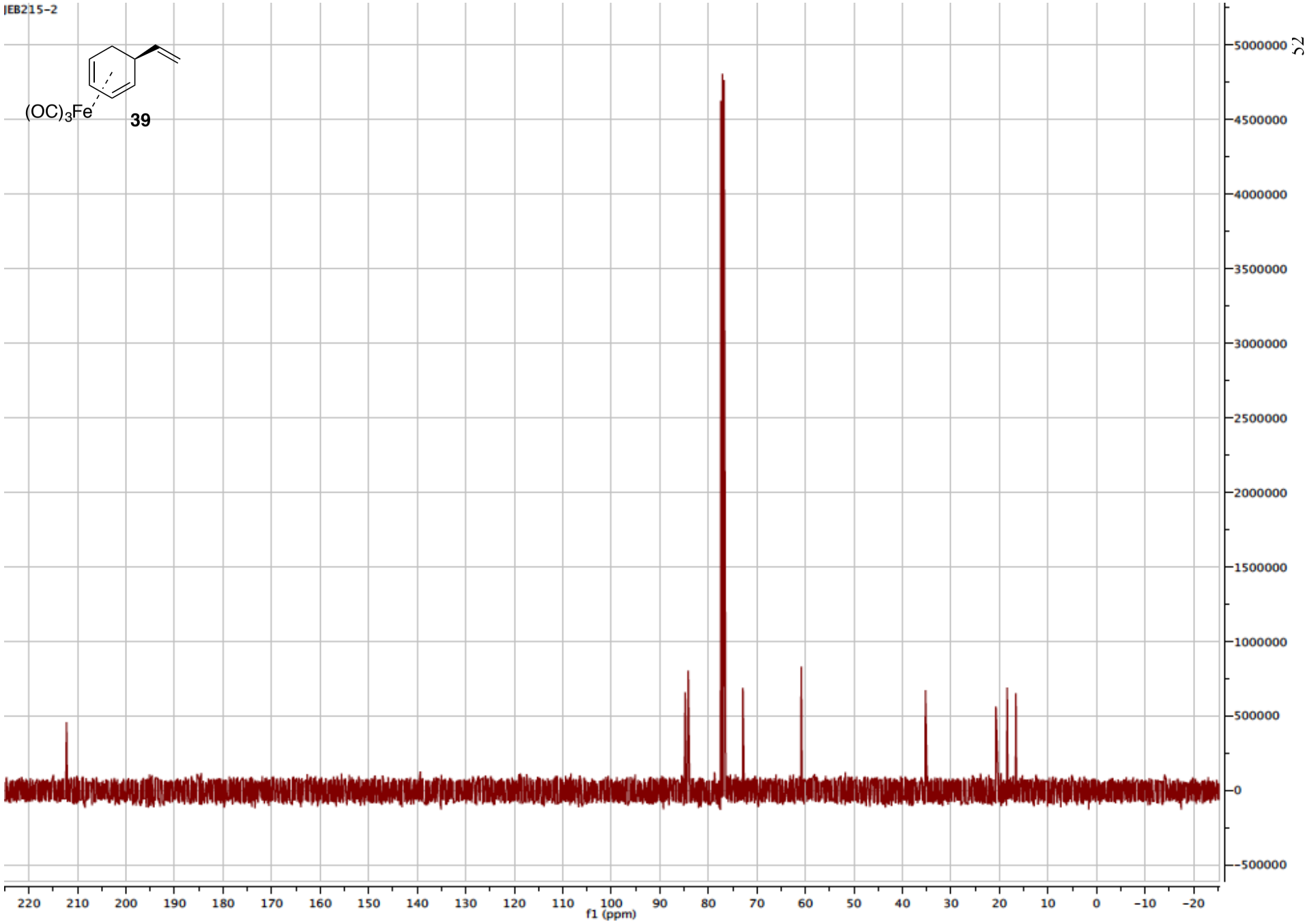

/Volumes/UNTIT...pec/JEB212-1.D/ Injection 1 Function 1 (JEB212-1) MS + spectrum 9.40
184.100
100.00%
169.100
47.54%
141.100
44.29%
115.100
31.59%
139.000
11.53%
185.100
14.82%
170.100
6.41%
63.000
5.01%
76.100
4.22%
89.100
3.80%
51.100
2.23%
116.100
3.14%
154.100
0.89%
188.100
1.22%
m/z (Da)

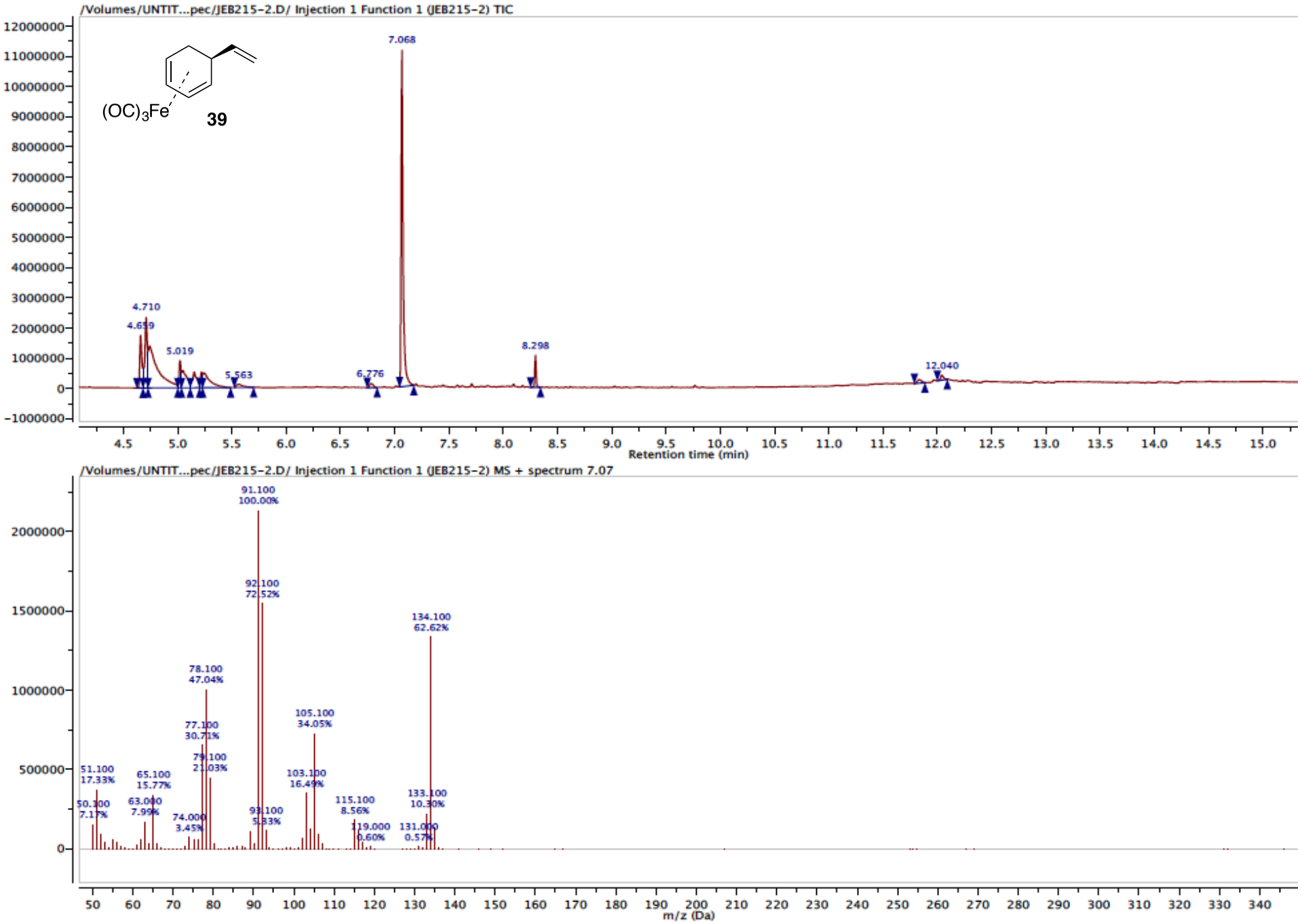

(OC)3Fe
37
5.11
2.07
1.00
2.07
1.02
1.08
f1 (ppm)


(OC)3Fe
37
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


/Volumes/UNTIT...pec/JEB205-1.D/ Injection 1 Function 1 (JEB205-1) TIC
(OC)3Fe
37
9.471
9.408
9.494
9.580
9.620
5.254
9.099
11.068
11.960
12.378
13.282
14.890
Retention time (min)
/Volumes/UNTIT...pec/JEB205-1.D/ Injection 1 Function 1 (JEB205-1) MS + spectrum 9.47
180.100 100.00%
178.100 83.75%
179.100 65.12%
165.100 55.62%
152.100 14.27%
126.000 7.08%
102.100 11.92%
89.100 10.54%
76.100 9.89%
63.100 4.76%
51.100 4.57%
90.000 2.82%
207.000 0.51%
253.000 2.48%
331.100 1.01%
m/z (Da)


JEB215-2
(OC)3Fe
39
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
1.94
0.87
0.84
2.00
1.83
1.81
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)


JEB215-2
(OC)3Fe
39
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


/Volumes/UNTIT...pec/JEB215-2.D/ Injection 1 Function 1 (JEB215-2) TIC
(OC)3Fe
39
7.068
4.710
4.659
5.019
5.563
6.776
8.298
12.040
Retention time (min)
/Volumes/UNTIT...pec/JEB215-2.D/ Injection 1 Function 1 (JEB215-2) MS + spectrum 7.07
91.100 100.00%
92.100 72.52%
134.100 62.62%
78.100 47.04%
105.100 34.05%
77.100 30.71%
79.100 21.03%
51.100 17.33%
65.100 15.77%
103.100 16.49%
115.100 8.56%
133.100 10.30%
50.100 7.17%
63.000 7.99%
74.000 3.45%
93.100 5.83%
119.000 0.60%
131.000 0.57%
m/z (Da)