2015

Explore the physical and chemical properties of 1,2,3-triazole: from fluorescence sensor to ligand in metal catalysis

Yanwei Zhang

Explore the physical and chemical properties of 1,2,3-triazole: from fluorescence sensor to ligand in metal catalysis

Yanwei Zhang

**Dissertation submitted
to the Eberly College of Arts and Sciences
at West Virginia University**

in partial fulfillment of the requirements for the degree of

**Doctor of Philosophy in
Chemistry**

**Björn Söderberg, Ph.D., Chair
Jessica Hoover, Ph.D.
Jeffrey Petersen, Ph.D.
Brian Popp, Ph.D.
Yon Rojanasakul, Ph.D.**

C. Eugene Bennett Department of Chemistry

**Morgantown, West Virginia
2015**

Keywords: Functional 1,2,3-Triazoles, Transition Metal Catalysis, Fluorescence sensor, Ligand

Abstract

Explore the physical and chemical properties of 1,2,3-triazole: from fluorescence sensor to ligand in metal catalysis

Yanwei Zhang

1,2,3-Triazole gold (TA–Au) catalysts were developed by Shi's group and employed in several transformations involving propargyl ester rearrangement. Besides the excellent air, moisture and thermal stability introduced through triazole ligands, unique chemoselectivity was observed for these novel Au(I) complexes. The chemoselectivity allowed the effective activation of the alkyne without affecting the reactivity of the allene ester intermediates. These results led to the investigation of the preparation of allene ester intermediates with TA–Au catalysts under anhydrous conditions. As expected, the desired 3,3-rearrangement products were obtained in excellent yields. Besides the typical ester migrating groups, carbonates and carbamates were also found to be suitable for this transformation, which provided a highly efficient, practical method for the preparation of substituted allenes.

Previously research results confirmed TA-Au as a chemoselective catalyst in promoting alkyne activation with high efficiency and improved ligand economy. TA-Au analogues were sequentially revealed as the effective catalysts in promoting allene hydration, giving the enones with excellent yields. Furthermore, the gold-catalyzed intermolecular [2+2] cycloaddition of propargyl esters was achieved with good stereoselectivity. The 'silver-free' condition was critical for this transformation, while only a trace amount of [2+2] products were obtained in the presence of silver under otherwise identical conditions.

Additionally, naphthalene-bridged bis-triazole (NBT) compounds were prepared and characterized for investigation of their photophysical properties. Unlike our previously reported N-2-aryl triazoles (NATs), which gave strong emissions through the planar intramolecular charge transfer mechanism (PICT), this newly developed NBTs adopted a noncoplanar conformation between triazole and naphthalene, achieving fluorescence through twisted intramolecular charge transfer (TICT).

Acknowledgements

Firstly, I would wish to express my sincere gratitude to my advisor, Dr. Xiaodong Michael Shi, for his guidance, understanding, patience and most importantly, his encouragement during my graduate studies at West Virginia University. He provided me enough independence to express my own individuality and self-sufficiency. He taught me how to be not only an experimentalist and a chemist but also an independent thinker. Without his support, there is no way for me to finish my Ph.D study.

I would like to give my sincere appreciation to Dr. Björn Söderberg. Thank you for your kindness to accept me in your research group in the past several months. I would like to gratefully thank Dr Brian Popp, and Dr Jessica Hoover in my academic development. All the valuable comments and suggestions I got from them are appreciated and recognized. I would also like to thank Dr. Jeffrey L. Petersen for his help of X-ray crystallographic structure analysis and guidance during my graduate studies. Moreover, I am deeply grateful to the above mentioned and Dr. Yon Rojanasakul for being my Doctoral Research Committee.

I would like to acknowledge my colleagues who I've had the pleasure of working with, Dr. Dawei Wang, Dr. Yijin Su, Dr. Haihui Peng, Dr. Wuming Yan, Dr. Lekn Nath Gautam, Tao Liao, Dr. Qiaoyi Wang, Dr. Xiaohan Ye, Rong Cai, Sraven Kumar, Siddhita Aparaj, Seyedmorteza Hosseyni, Boliang Dong, Stephen Motika, Yumeng Xi and Ying He for all the assistance they have given me in the last five years. I would also like to thank Dr. Novruz Akhmedov for helping me solve the NMR experiment.

Finally, and most importantly, I would like to thank my parents, my husband and my friends. Their support, encouragement, patience and love were the most solid base of my life in the past five years. With everything they gave, I have gained so much energy and courage to overcome the challenge in my Ph.D study.

Financial supports from the C. Eugene Bennett Department of Chemistry at West Virginia University and the National Science Foundation are also gratefully acknowledged.

TABLE OF CONTENTS

LIST OF SCHEMES

LIST OF TABLES

Chapter One: Triazole-Au(I) Complex as chemoselective catalyst in promoting propargyl ester rearrangements.

1.1 Introduction

1.1.1 Background of gold catalysis development

In the past decade, homogeneous gold catalysis has developed rapidly for activating sp hybridized carbon transformations.[1] Gold catalysis has been applied in numerous synthetic applications to achieve previously challenging transformations with higher yield or/and better regioselectivity.[2] Compared to traditional metal catalysis, gold catalysis presents several advantages:

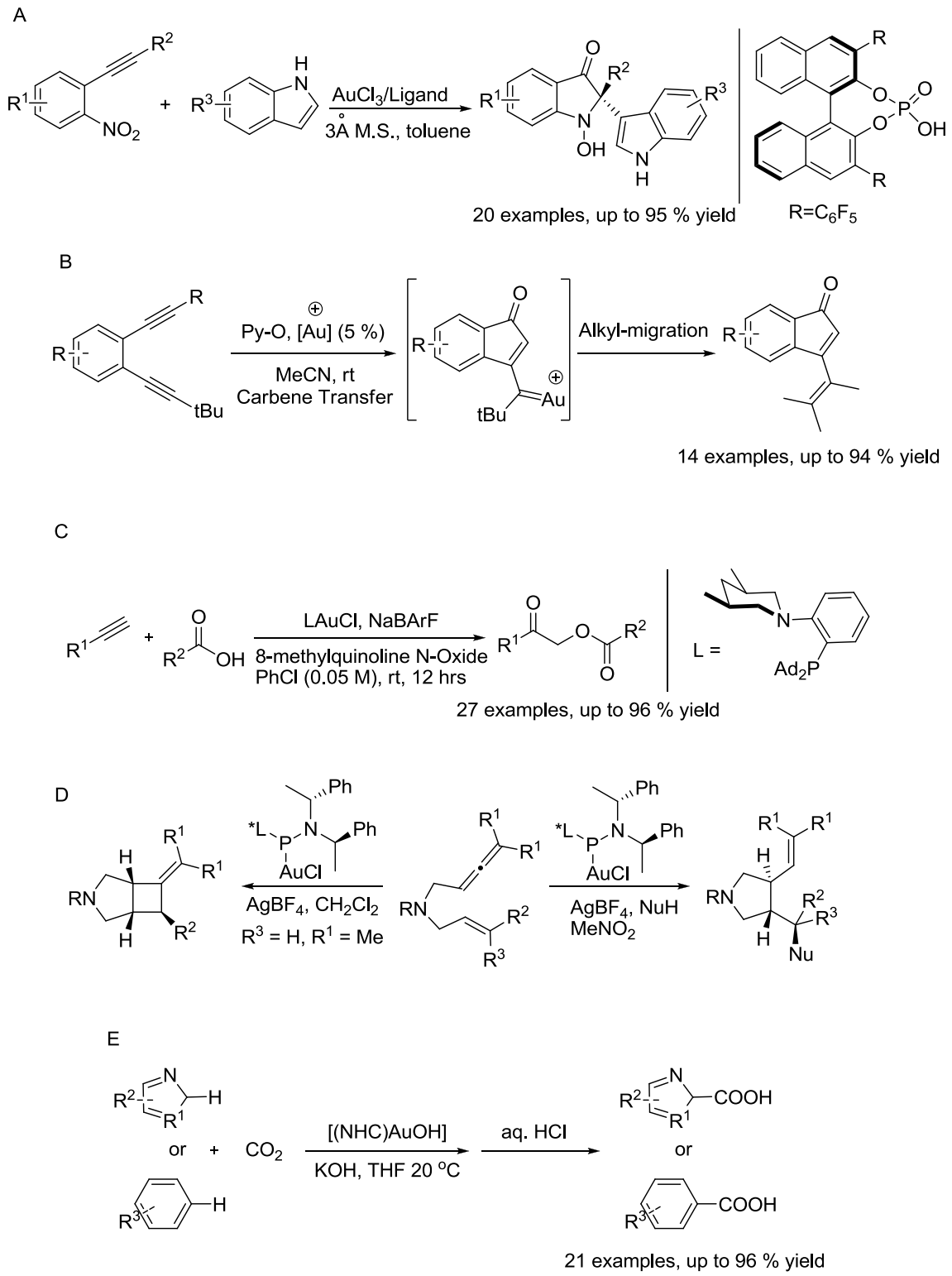
1) In most reported cases, gold catalyst can act as a strong π-acid towards alkynes/allenes and activate the starting material with high selectivity.

2) The gold catalyst presents highly reactivity while comparing with other transition metals such as Pd, Ru, Rh or Cu (< 1 mol % loading for gold vs approximately 10 mol % loading for others)

3) The mechanism of gold catalysis is flexible based on different reaction patterns (such as ligand, solvent, temp.), leading to diverse products even with the similar starting materials.

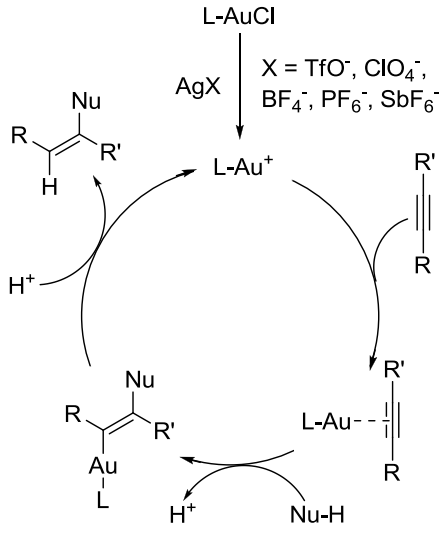
Scheme 1 shows several representative examples from the recently developed gold catalysis transformations reported with high yield and low catalyst loading.

Scheme 1. Representative Samples from Recent Gold Catalysis Chemistry



Of the two most common oxidation states, Au(I) and Au(III), more studies have been focused on Au(I) due to easier preparation and better pre-catalyst thermal stability. Most often, Au(III) is simply considered as common Lewis acid to activate heteroatoms (such as O, N) while Au(I) can serve as π-acid for alkyne/allene activation.[3,4] In the gold catalytic process, one key step to generate the active catalyst complex is to dissociate the Au-Cl bond. The most common method adopted is relying on silver salts as Cl scavenger by forming AgCl precipitate. As a result, active cationic gold species were afforded with counter anions introduced by the silver salts such as BF_4^-, PF_6^-, SbF_6^-, TfO^-, and ClO_4^-. It is accepted by the research community that Au(I) complexes present two coordination sites with 180° linear geometry (although some exceptions exist). The actual catalysts involved in alkyne/alkene activation are of the type $[L–Au]^+$, with the open coordination site on the opposite side of the ligand (L) for substrate binding.

Scheme 2. Catalytic Cycle for Au(I) Catalysis for Common Gold Activated Alkyne Reaction



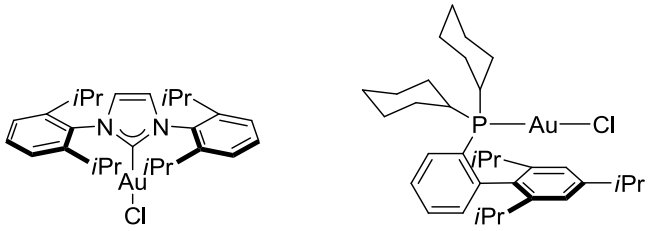
Given the use of an alkyne as a specific reactive substrate, the mechanism of Nu-H (such as alcohol, amine) addition across the C-C triple bond via an Au(I) catalytic cycle is shown in **Scheme 2**. In this process, the stable L-Au-Cl usually serve as catalyst precursor to generate the active L-Au^+ complex in situ with the removal of the bonded Cl counter anion. This newly opened coordination site will facilitate the substrate (alkyne utilizing the C-C triple bond) binding. After the coordination, the nucleophile attacks the gold activated alkyne complex and forms the corresponding alkene-gold intermediate. The final product is formed by proto deauration and meanwhile, the Au cation was released for the next catalytic cycle.

One major drawback in traditional gold catalysis is the stability of cationic gold complex, since it tends to decompose (formation of Au(0) species) under raised temperature or reductive environment. To improve the stability of gold complex, various research groups are focusing on developing novel ligands to increase the stability of Au(I) catalyst.

The NH carbene is one of the most important ligands currently employed in gold catalysis.[5] The NH carbene has a unique chemical nature for its lone electron pair and π-acceptor orbital. On one hand, the lone pair electrons make NH carbene a good σ-donor to coordinate towards most transition metals. On the other hand, the π-backbonding from a metal d-orbital to the π* orbital of NH carbene, makes the coordination between the metal and NH carbene even stronger (shorter C-M bond) than other heteroatom ligands, and thus the stability of the gold-NH carbene complex is significantly improved.

Another notable primary ligand in gold catalysis is the phosphine ligand. The bonding between gold and phosphine is typically strong, which can help stabilize the complex.[6] Additionally, unique spatial conformation of several phosphine ligands can make the complexes more stable. For example, as shown in **Scheme 3**, in the 3-D structure of XPhosAuCl, the Ar group introduced by XPhos will block one site of the linear L-Au-Cl complex due to the irreplaceable spatial geometry expendation.[7]

Scheme 3. IPrAuCl and XPhosAuCl Complexes with Improved Au Cation Stability

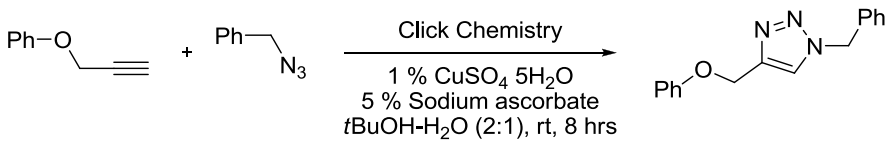


IPrAuCl XPhosAuCl

1.1.2 The role of different 1,2,3-triazole as counter ligand 'X-factor' in gold chemistry

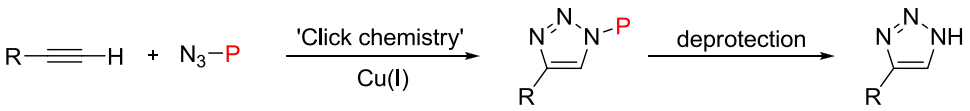
Triazole compounds have been prepared as a unique heterocyclic structure with interesting electronic effect in last century.[8] In 2001, 'Click chemistry' was first reported by Professor Sharpless, which facilitated access to various 1,4-disubstituted 1,2,3-triazoles with moderate to good yield.[9] In a 'Click chemistry', the active Cu(I) catalyst is generated in situ from Cu(II) salts (such as $CuSO_4$), while using sodium ascorbate as the reducing reagent. Additionally, by adding an excess amount of sodium ascorbate, the formation of oxidative homo-coupling products could be successfully avoided in late stage of the reaction (**Scheme 4**).[10, 11]

Scheme 4. One Typical Example of 'Click Chemistry'



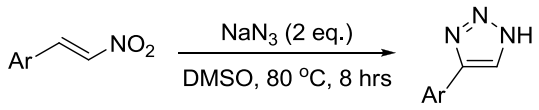
One major drawback of ‘Click chemistry’ is that unsubstituted triazole ring could not be achieved with NaN_3 or HN_3 as a coupling partner. To achieve NH-1,2,3 triazole, ‘Click chemistry’ was modified by using the N-substituted azide with removable functional groups (**Scheme 5**).[12] After reaching the 1,4-disubstituted 1,2,3-triazole, NH-1,2,3-triazole can be synthesized through a simple N-deprotection. This method significantly improved the scope of the 1,2,3-triazole synthesis, whereby post-functionalization was possible at the free NH site of 1,2,3-triazole.

Scheme 5. Synthesis of NH-1,2,3-triazoles



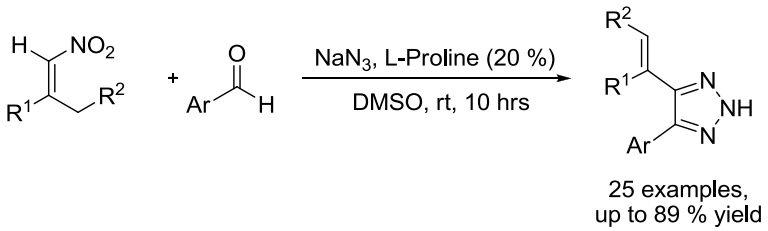
In 2005, another efficient synthesis method towards NH-1,2,3-triazoles is developed by Professor Zard based on the 1,3-dipolar addition between the nitroalkene and sodium azide. NH-1,2,3-triazoles with different aryl substituents can be achieved with good to excellent yields, only trace amounts of predictable by-products were observed (**Scheme 6**). [13, 14]

Scheme 6. Thermal Condensation of Nitroalkene and Sodium Azide



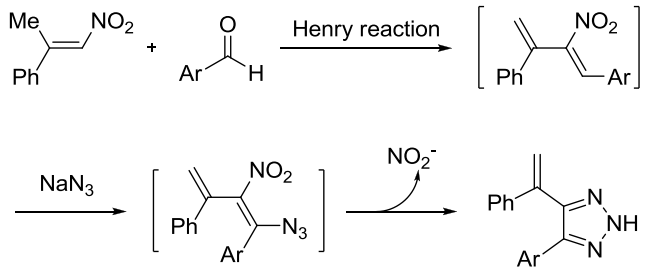
Although the synthesis of 4-mono-substituted 1,2,3-triazole has been reported in various methods, how to reach 4,5-di-substituted 1,2,3-triazoles still remained challenge. In 2008, Professor Shi and co-workers successfully developed the methodology with which to synthesize 4,5-disubstituted NH-1,2,3-triazoles based on a Lewis base-catalyzed cascade condensation (Aza-Henry reaction) using nitroalkene, aldehyde and sodium azide as reaction precursors as shown in **scheme 7**.[15] With this method, a series of 4,5-disubstituted NH-1,2,3-triazoles were produced with good to excellent yields.

Scheme 7. Lewis Base-catalyzed Cascade Condensation to NH-1,2,3-triazole



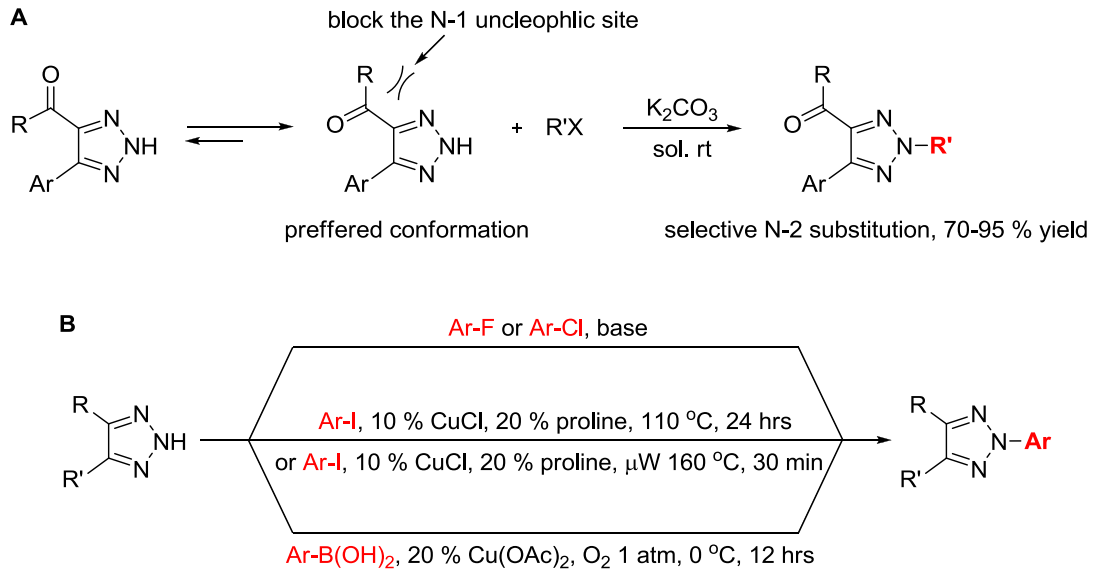
Subsequently, the mechanism of this reaction has been investigated. As described in **Scheme 8**, initially, the Henry reaction occurred between the nitroalkene and aldehyde, after which, sodium azide addition of the alkene intermediate occurred and formed a new azide intermediate. Follow by the elimination of NO_2 anion, the desired triazole was generated as the final product.

Scheme 8. Mechanism for Synthesis of 4,5-disubstituted *NH*-1,2,3-triazoles



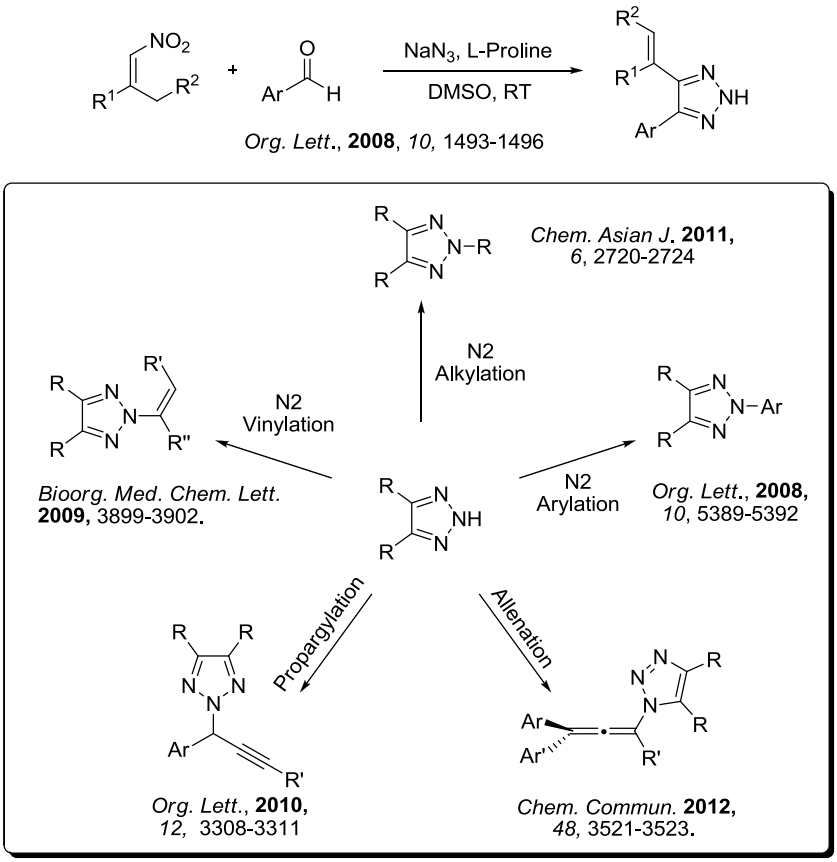
At this stage, Shi's group focused on the development of triazole post functionalization. With the appropriate electrophiles and reaction conditions, N-substituted 1,2,3-triazole derivatives could be obtained with NH-triazole as a nucleophile. However, in this type of reaction, the regioselectivity between N-1 and N-2 substitution arose as one major concern. Moreover, the N-1 substitution dominates in most reported results due to its thermodynamic stability.[16] Shi's group subsequently investigated the selective synthesis towards N-2 substituted 1,2,3-triazole derivatives. With 4,5-disubstituted 1,2,3-triazole derivatives, the increased steric hindrance from the two substituents on C-4 and C-5 positions can theoretically block the N-1 nucleophilic sites, which will further lead to the N-2 regioselectivity over N-1 (**Scheme 9A**).[17-18] Three different approaches were developed to attain the N-2 aryl substituted derivatives with base or Cu(I) catalyzed coupling between NH-1,2,3-triaozle and heteroatom substituted aromatic compounds (**Scheme 9B**).

Scheme 9. Synthesis to N-2 Alkyl/Aryl Substituted 1,2,3-triaozle



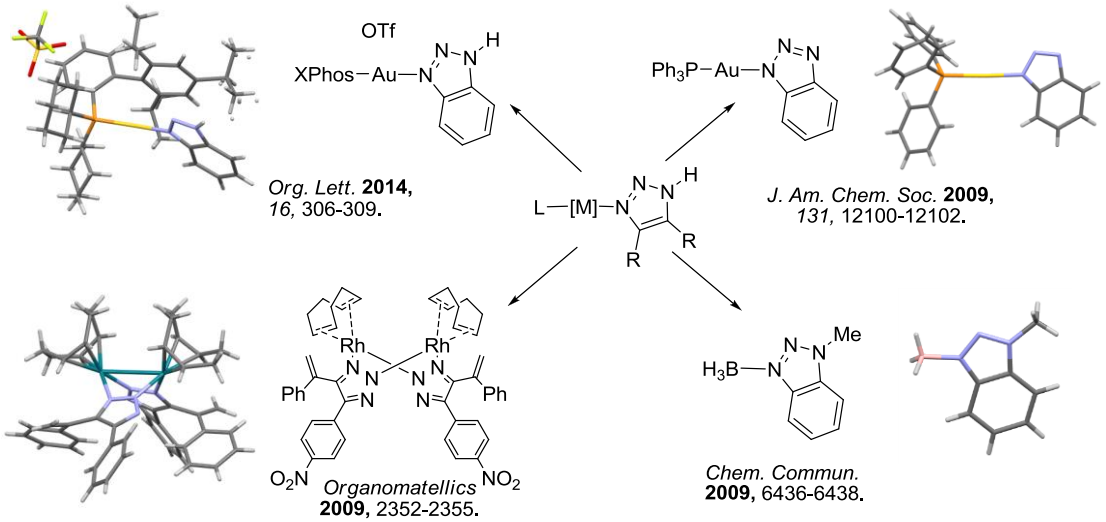
Additionally, our group has developed the post-triazole functionalization to obtain more complicated 1,2,3-triazoles derivatives through alkylation, vinylation, arylation, propargylation and allenation (**Scheme 10**).

Scheme 10. Different Post-triazole Functionalization Discovered by Prof. Shi's Group



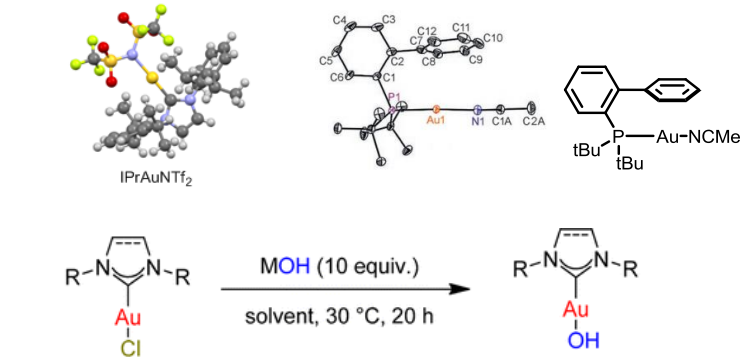
With all well-developed synthetic methodologies, Shi's group decided to investigate the binding of 1,2.3-triazole as ligand with transition metals (such as Rh, B, Au) and examine the reactivities displayed by the novel transition metal complexes (**Scheme 11**).[19-21] Despite the fact that all these complexes exhibit interesting reactivities, 1,2,3-triazole Au(I) complexes would be the major focus in this dissertation.

Scheme 11. Different 1,2,3-triazole Metal Complexes Obtained by Prof. Shi's Group



As mentioned, Au(I) complexes adopt a linear geometry with two coordination sites. One coordination site is occupied by a primary ligand, such as N-heterocyclic carbene or phosphine ligand. Recent research discovered that the second coordination position could be occupied by a weakly bound Lewis donor, such as pyridine, Tf_2N^-, OH^-, or MeCN. These Lewis donor compounds are categorized as 'X-factors' (**Scheme 12**).[22] More and more recent evidence indicated the significant of these 'X-factors'. Subsequently, Shi's group initiated an effort to evaluate the bonding ability of 1,2,3-triazole towards Au(I) as 'X-factor' and examine the reactivity displayed by the resultant triazole Au(I) complexes.

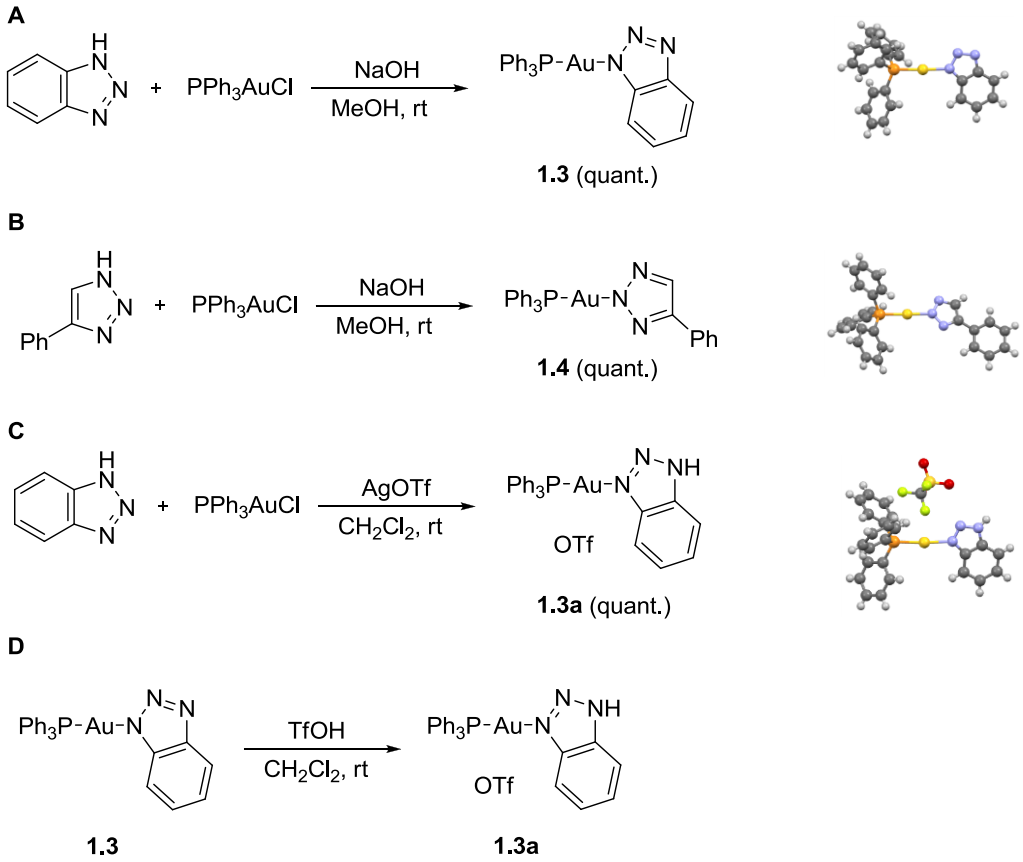
Scheme 12. X-factors in Au(I) Catalysis



NHC = IPr, SIPr, IPr^{Cl}, IPr^{Me}, IPr*, IPr*^{Tol}, IMes, SIMes, I^{t}Bu, IAd, ICy, IDD
M = K, Cs

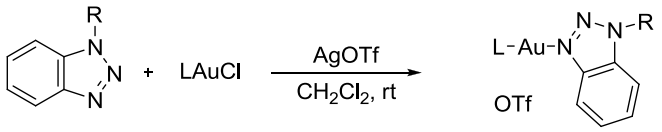
The earliest case of triazole Au(I) complexes was reported in 1998 by Nomiya et al. They obtained the triazole Au(I) complexes by using NaOH in acetone with moderate yield.[23] Our group prepared the neutral 1,2,3-triazole gold complexes with the analogous strategy. Simply treating the NH-triazoles with PPh_3AuCl in methanol under basic conditions at room temperature gave the neutral TA-Au **1.3** and **1.4** in > 90 % yield. The 'cationic' complex TA-Au **1.3a** was prepared either by the reaction between $PPh_3Au^+X^-$ (prepared from PPh_3AuCl and AgX) and benzotriazole or from the addition of HOTf to TA-Au **1.3**. Both complexes were stable and could be further purified by recrystallization to ensure no extra Ag^+ or acid remained in the catalysts (**Scheme 13**).

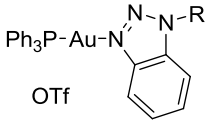
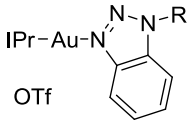
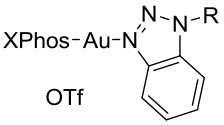
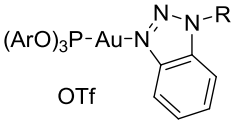
Scheme 13. Examples of Triazole Au(I) Complexes



By using the methodologies introduced in **Scheme 13**, Shi's group synthesized a library of different benzotriazole gold complexes (**Scheme 14**).

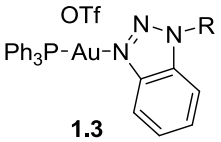
Scheme 14. A Library of Au(I) Complexes with Different Primary Ligands and Triazoles



L = PPh_3	 **1.3**	R = H **1.3a**; R = Me **1.3b**; R = Ph **1.3c**; R = *p*-F-Ph **1.3d**; R = *p*-Me-Ph **1.3e**; R = *p*-OMe-Ph **1.3f**; R = 2.4-dinitro-Ph **1.3g**; R = *p*-nitro-Ph **1.3h**
L = IPr	 **1.5**	R = H **1.5a**; R = Me **1.5b**
L = XPhos	 **1.6**	R = H **1.6a**; R = Me **1.6b**; R = *p*-nitro-Ph **1.6c**
L = $P(OAr)_3$ Ar = 2,4-ditert butylphenyl	 **1.7**	R = H **1.7a**; R = Me **1.7b**; R = Ph **1.7c**; R = 2.4-dinitro-Ph **1.7d**

To investigate the electronic structure of gold-benzotriazole complexes, ^{31}P NMR is applied to investigate the chemical shift of triazole gold complexes with different benzotriazoles as 'X-factors'. The ^{31}P NMR chemical shifts of different gold-benzotriazole complexes together with L-Au-Cl and $PPh_3Au^+OTf^-$ are listed in the following table (**Table 1**).

Table 1. ^{31}P NMR Data of Substituted TA-Au Complexes [a]



1.3

complex	PPh_3AuCl	R = *p*-OMe-Ph **1.3f**	R = *p*-Me-Ph **1.3e**	R = Me **1.3b**	R = H **1.3a**
chemical shift (ppm)	34.31	31.89	30.67	30.65	30.59
complex	R = Ph **1.3c**	R = *p*-F-Ph **1.3d**	R = *p*-nitro-Ph **1.3h**	R = 2.4-dinitro-Ph **1.3g**	$PPh_3Au^+OTf^-$
chemical shift (ppm)	30.44	30.28	30.19	29.80	28.80

[a] ^{31}P NMR spectra of different Au(I) samples.

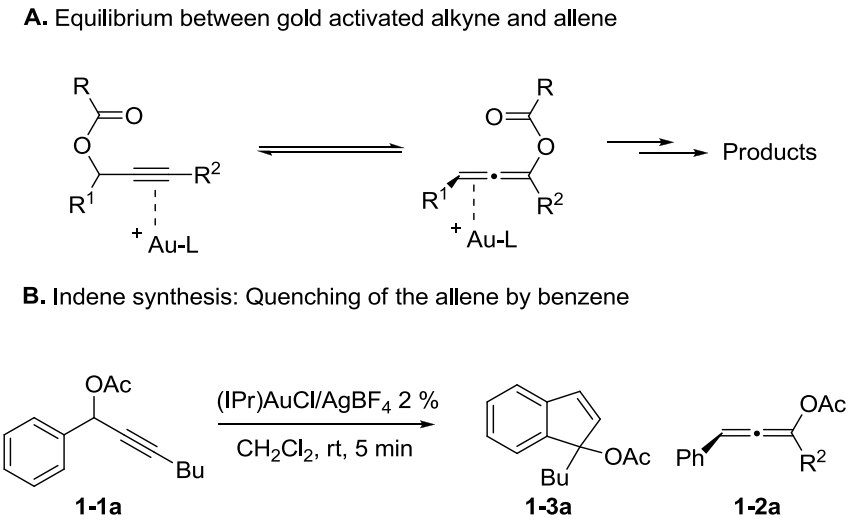
The ^{31}P NMR data in **Table 1** clearly showed that with different substituted groups, different chemical shifts of benzotriazole gold compounds were observed. The theoretically most unreactive Au(I) chloride had the chemical shift of 34.31 ppm. And the theoretically most reactive cationic Au(I) complex $PPh_3Au^+OTf^-$ exhibited the lowest ^{31}P chemical shift at 28.80 ppm. All triazole gold complexes ^{31}P NMR data lying between these two extreme cases, exhibited a trend which perfectly lined with the electron negativity of different N-1 aromatic substitutions. Complex **1.4f** was the one which contains the most electronic rich R-substituent gave the ^{31}P NMR chemical shift (δ 31.89 ppm) closest to L-Au-Cl. In contrast, complex **1.4g** with the most electronic deficient R-substituent gave the ^{31}P NMR chemical shift (δ 29.80 ppm) closest to $PPh_3Au^+OTf^-$. Based on the diverse chemical shift, the reactivity for different gold (I) benzotriazole complexes are tuned with a small range to apply in gold catalysis.

To better evaluate the reactivity of benzotriazole Au(I) complexes and compare the catalytic performance of benzotriazole Au(I) complexes with other Au(I) catalysts, we chose to study the 3,3-rearrangement of propargyl ester to allene promoted by triazole Au(I) complexes.

1.2 Propargyl ester rearrangements promoted by triazole Au(I) complex as chemoselective catalyst.

The propargyl ester rearrangement was considered as one of the most important reaction modes in Au(I) promoted transformations.[24-34] Recent experimental and computational mechanistic studies showed that the 3,3-rearrangement to form the allene ester intermediate as the key step in this transformation (**Scheme 15A**).[35-37] Both experimental and theoretical investigations confirmed the reversibility between allene and propargyl ester due to effective activation of both functional groups by the Au(I) catalysts. As a result, it was extremely challenging to obtain the allene intermediates with good yields.

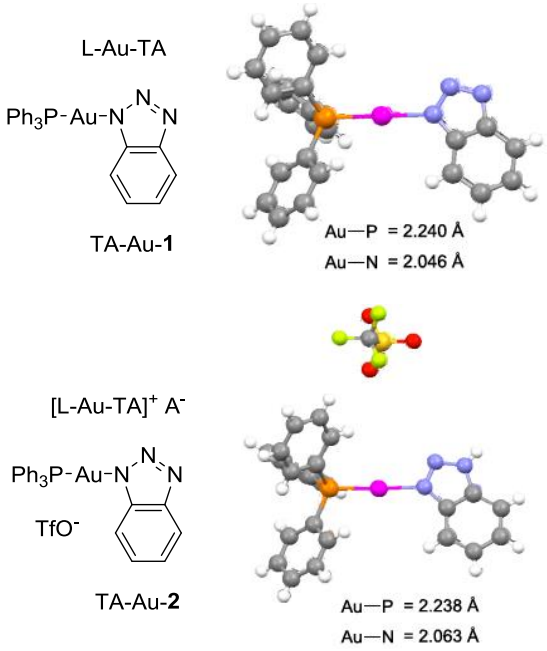
Scheme 15. The Challenge of The Synthesis of Allenes through Au(I) Activated Alkynes



Many strategies have been developed to make the Au(I)-activated allene esters react with other proper substrates, forming interesting new products in a cascade fashion. Different types of Au(I) complexes have been applied in the investigation of this reaction, such as IPrAuCl/$AgBF_4$. In 2006, Nolan et al developed the synthesis to indene compounds, which is a good example highlighting the importance of the cascade process.[38] As shown in **Scheme 15B**, with the $[IPr\text{-}Au]^+$ catalyst, only a trace amount of allene was obtained. The major product was derived from the Friedel-Crafts addition of the aromatic ring to the gold activated allene. Therefore, selective activation of the alkyne over the allene was considered as a significant challenge in gold catalysis.

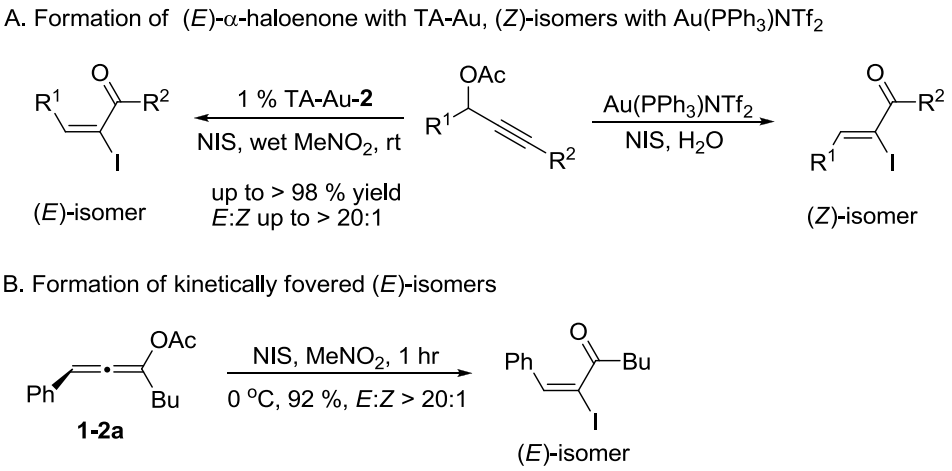
Our group reported the synthesis and characterization of the 1,2,3-triazole coordinated Au(I) complexes.[39-43] As revealed by the X-ray crystal structures (**Scheme 16**), both neutral and anionic triazoles can coordinate with the Au(I) cation, forming stable TA-Au complexes.[44]

Scheme 16. X-ray Crystal Structures of Two Different Types of 1,2,3-triazole–Au Complexes



The crystal structures revealed nearly identical Au-P bond distance of 2.24 Å for both the anionic and neutral triazole coordinated Au(I) complexes. The longer Au-N bond in TA-Au-**2** implies that the neutral triazole dissociates more easily to release the coordination site for substrate activation. This new class of compounds offers improved thermal stability and substrate stability in the Au(I) promoted hydroamination and Hashimi phenol synthesis,[45] which makes them interesting novel catalysts in the field of gold catalysis. One particular new development of the TA-Au catalysis that attracted our attention was the synthesis of α-iodoenone from propargyl esters (**Scheme 17**).[46]

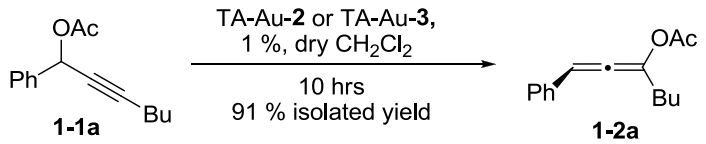
Scheme 17. Synthesis of α-Iodoenone Compounds from Propargyl Esters



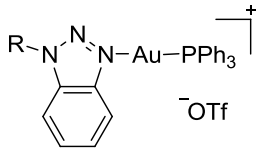
As indicated in **Scheme 17A**, the typical [L-Au]$^+$ catalyst promoted the sequential rearrangement and iodination, giving the thermally, dynamically stable(*Z*)-isomer.[47-49] The cationic TA-Au catalyst, on the other hand, produced the kinetically favored (*E*)-isomer. Notably, treating the allene ester with NIS gave the (*E*)-isomer (**Scheme 17B**). The typical [L-Au]$^+$ catalyst influenced the allene reactivity, probably through gold catalyzed allene activation. The fact that TA-Au gave the dominant (*E*)-isomers strongly suggests that these complexes may be applied as a chemoselective catalyst in alkyne activation over allene.

The reaction of propargyl ester **1-1a** with TA-Au catalysts were then investigated as shown in **Scheme 18**.

Scheme 18. Chemoselective Activation of Alkyne over Allene by the TA-Au Catalysts



t	indene **1-3a**	**1-2a**	*t*	indene 1-**3a**	**1-2a**
10 min	0	15 %	20 hrs	0	> 98 %
4 hrs	0	83 %	48 hrs	0	> 98 %
8 hrs	0	95 %			

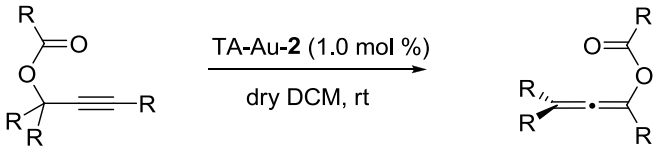


R=H, TA-Au-**2**;

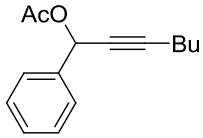
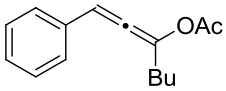
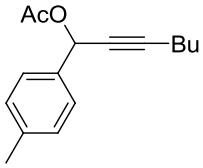
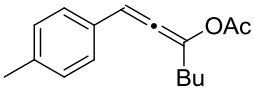
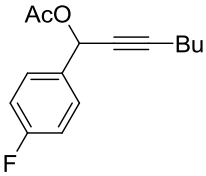
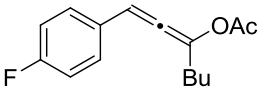
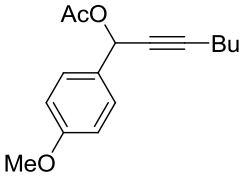
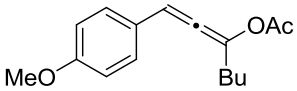
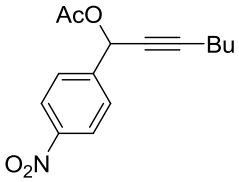
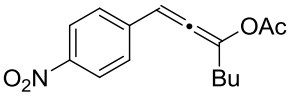
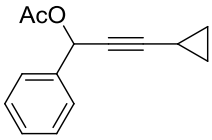
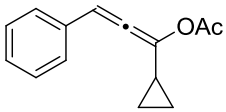
R=Me, TA-Au-**3**

This transformation proceeded smoothly with substrates having both an aromatic group on the propargyl side and an aliphatic group on the alkyne side (entries 1-6) as shown in **Table 2**. The desired allene products were formed in excellent yields, with 1 % catalyst loading. The electronic density on the aromatic ring did not have a strong impact on the transformation: Both electron donating and electron-withdrawing groups were suitable for the reaction. Again, no indene by-products were observed in any of the tested cases, even with the electron-enriched *p*-OMe substituted alkyne **1-1d**. These results highlighted the excellent chemoselective nature of the TA-Au catalyst.

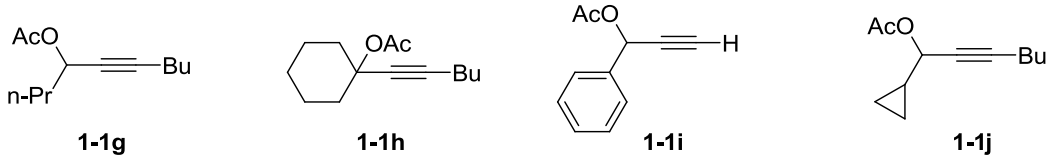
Table 2. The Reaction Substrate Scope [a]



1-1 **1-2**

Entry	Substrate		Product		Yield
1		**1-1a**		**1-2a**	91 %
2		**1-1b**		**1-2b**	90 %
3		**1-1c**		**1-2c**	87 %
4		**1-1d**		**1-2d**	89 %
5		**1-1e**		**1-2e**	89 %
6		**1-1f**		**1-2f**	85 %

Substrates that did not form the desired allenes[b]



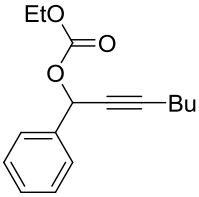
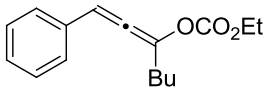
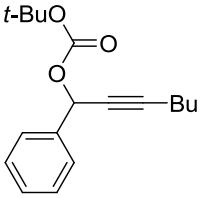
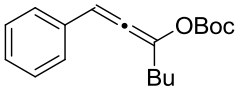
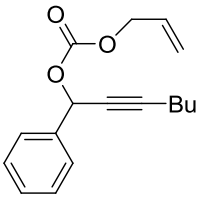
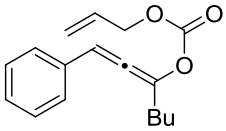
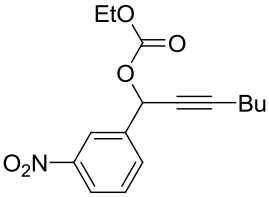
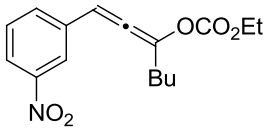
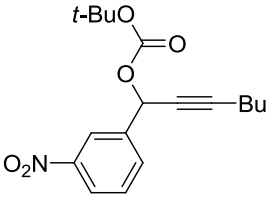
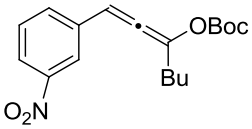
1-1g **1-1h** **1-1i** **1-1j**

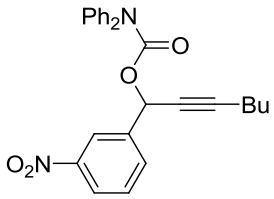
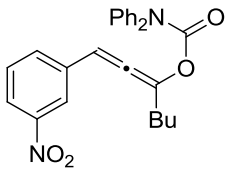
[a]General reaction condition: **1-1** (0.25 mmol) and TA-Au-**2** (1.0 mol %) in dry DCM (2.5 mL), the reaction were monitored by TLC (2-10 hrs), rt. [b]TA-Au-**1**, TA-Au-**2** and TA-Au-**3** did not catalyze the reaction under the standard conditions.

The terminal alkyne **1-1i** did not give any product when treated in the presence of the TA-Au catalyst, even after an extended reaction time (24 hrs). This was probably caused by the preferred 1,2-rearrangement with the formation of the vinyl-Au intermediate. The aliphatic propargyl ester (**1-1g**, **1-1h**) also did not give any desired allene products although enones from hydrations were produced after a long reaction time (24-48h). The crude NMR of the reaction mixtures did not show an evidence of any allene products. This may be caused by the high reactivity of the corresponding aliphatic allenes under the reaction conditions (activated by TA-Au) and the overall better stability of the propargyl ester compared to the aliphatic substituted allenes (equilibrium favored the starting material). The reaction of cyclopropyl substituted propargyl ester **1-1j** with the TA-Au catalyst gave a complex reaction mixture, which suggests possible ring opening and sequential cyclization as reported previously.[50] Overall, this study suggests that the propargyl ester rearrangement to form allene is highly substrate dependent. This could either be due to the similar reactivity of the alkyne and the allene (giving an equilibrium state favoring the alkyne over the allene) or it could be due to a preferred alternative migration path (2,3-migration versus 3,3-migration). In any case, the TA-Au catalyst clearly displayed interesting chemoselectivity.

To study the feasibility of this migration, we then investigated migrating groups other than esters. The results are summarized in **Table 3**.

Table 3. Different Migrating Groups [a]

Entry	Substrate		Product		Yield
1		**4a**		**5a**	92 %
2		**4b**		**5b**	91 %
3		**4c**		**5c**	88 %
4		**4d**		**5d**	92 %
5		**4e**		**5e**	89 %

6		**4f**		**5f**	85 %

[a]General reaction condition: **1-4** (0.25 mmol) and TA-Au-**2** (1.0 mol %) in dry DCM (2.5 mL), the reactions were monitored by TLC (2-10 hrs), rt.

As indicated in **Table 3**, carbonates (entries 1-5) and carbamate (entry 6) were also suitable for this transformation. Compared to the allene-acetates, the allene-carbonates and allene-carbamate were more stable in water. Notably, although the alkene was considered as a readily reactive functional group in gold catalysis, the substrate **1-4c** was suitable for this transformation, giving the desired allene-ene **1-5c** in excellent yield.

1.3 Conclusion

In this research, we reported the application of triazole-coordinated Au(I) complexes as the effective catalysts for the promotion of the propargyl ester, carbonate and carbamate 3,3-rearrangement for the synthesis of the corresponding substituted allene derivatives. The chemoselective nature of the TA-Au catalysts was clearly demonstrated, which makes them an interesting class of new catalysts for promoting organic transformations. The application of the allene-carbonates and allene-carbamates as building blocks for development of new synthetic methodologies is currently underway in our group.

1.4 Contribution

Dr. Dawei Wang was the researchers who had first investigated the reaction. Together Dr. Wang and Yanwei Zhang were responsible for the substrate scope evaluation and manuscript completion for successful submission to *Beilstein J. Org. Chem.*. Detailed X-ray crystallographic data analysis of compound TA-Au-**1** and TA-Au-**2** was done by Prof. Jeffrey L. Petersen, C. Eugene Bennett Department of Chemistry, West Virginia University.

Chapter Two: Further transformations from allene intermediate formed by triazole-Au(I) Complex promoted propargyl ester rearrangements.

2.1 Triazole gold promoted, effective synthesis of enones from propargylic esters and alcohols

2.1.1 Introduction

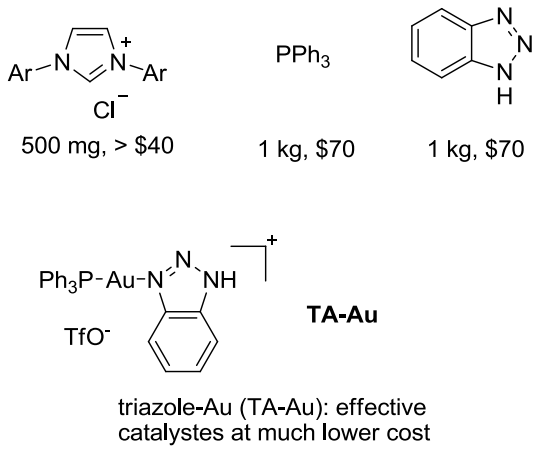
Among previous reported Au(I) catalysts, none of them exhibits a 'real' chemoseletivity towards alkyne over allene. All the allene intermediates generated from the corresponding 3,3-rearrangement were further activated by the Au(I) catalysts and transformed to other products. As mentioned above, TA-Au complex could selectively activate alkyne over allene, the isolated allene analogues have been achieved from the Au(I) activated transformation effectively for the first time. These allene analogues alone could serve as very interesting reaction precursors.

Shi's group successfully synthesized and characterized a library of 1,2,3-triazole gold complexes (TA-Au) as effective catalysts. These complexes exhibit significantly improved thermal and substrate stability. These results opened up a new strategy in tuning gold reactivity through secondary ligand as 'X-factor'. Herein, we report the application of the 1,2,3-triazole-coordinated[52] PPh_3-Au catalysts in promoting the propargylic ester rearrangement and sequential hydration to form the enone with high efficiency (0.2 % catalyst loading, up to 97 % isolated yields), unique reactivity (combining the chemoselectivity and acidity) and improved ligand-economy (utilization

of the much cheaper triazole and PPh_3 ligands as compared with NHC ligands). In addition, with the significantly improved thermal stability, TA-Au was further applied as the effective catalyst in promoting the propargylic alcohol Meyer-Schuster rearrangement to give the enones (0.5 % catalyst loading, up to 98 % yields), which highlighted the advantage of this complex compared with other conventional L-Au^+ catalysts.

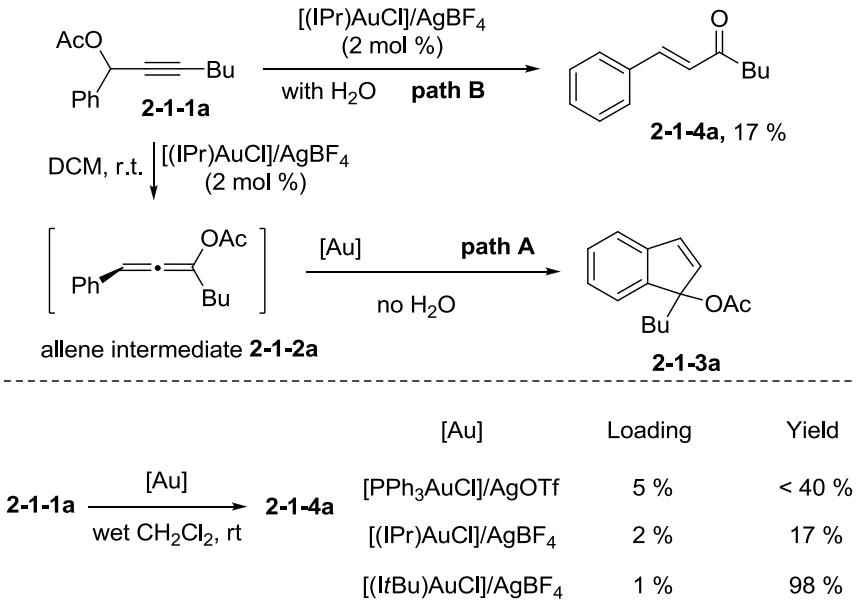
As indicated in **scheme 19**, one advantage of the TA-Au catalyst is the significantly low cost of the ligands. Compared with the NHC ligands, the combination of the PPh_3 primary ligand and triazole as X factor, the cost can be only 1,000th that of a single NHC primary ligand. Our original intention was to test whether TA-Au could promote transformations that previously required the expensive NHC primary ligands (to improve the ligand economy of the overall reaction). This initiated our investigation on the enone synthesis from the propargylic esters with our TA-Au catalyst.

Scheme 19. NHC: Good Ligand in Gold Catalysis but at High Cost



The gold-catalyzed Propargylic ester 3,3-rearrangement is a well-studied transformation.[53] One application of this process was the synthesis of enones from sequential hydration of the allene-acetate **2-1-2a** intermediates.[54] Although this transformation provided one attractive strategy in preparing enones under mild conditions, it suffered from a limited substrate scope due to the side reactions caused by the gold-promoted allene activation. One side reaction was the intramolecular Friedel-Crafts cyclization of **2-1-2a**, giving the indene **2-1-3a**.[55] As a result, a simple Au(I) catalyst, such as PPh_3Au^+, gave poor overall yields of the desired enones (5 % $Ph_3PAuCl/AgOTf$, < 40 % yields) (**Scheme 20**).

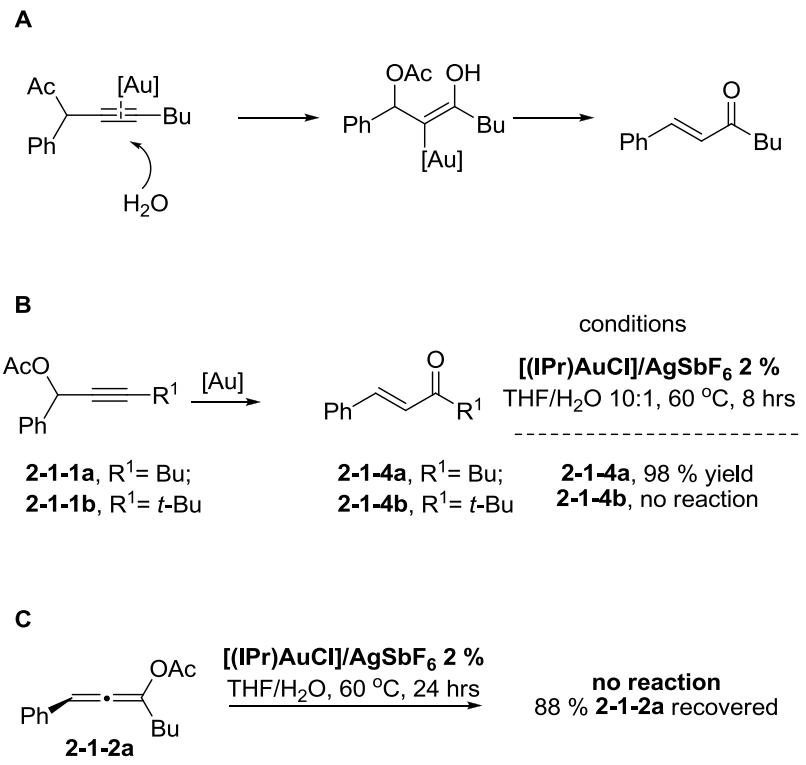
Scheme 20. L-Au^+: Effective Catalysts Activating both Alkyne and Allene



To overcome this problem, Nolan and co-workers investigated different N-heterocyclic carbene ligands.[56] The more steric hindered $[(ItBu)Au]^+$ complex was revealed as the optimal catalyst for the formation of enones with high efficiency (1 % loading, up to 98 % yields). The authors have performed comprehensive mechanistic

investigations.[54] Through both experimental and computational studies, the S_N2' water addition to the gold-activated alkyne was suggested as the mechanism by avoiding the formation of allene (**Scheme 21A**). This mechanism is further supported by two other experimental observations: (i) no enone formation was observed with the *t*-Bu-substituted alkyne **2-1-1b** (**Scheme 21B**), and (ii) treating allene ester **2-1-2a** with the NHC-Au catalyst did not give enone **2-1-4a** (**Scheme 21C**).

Scheme 21. Proposed S_N2' Addition Mechanism by Nolan

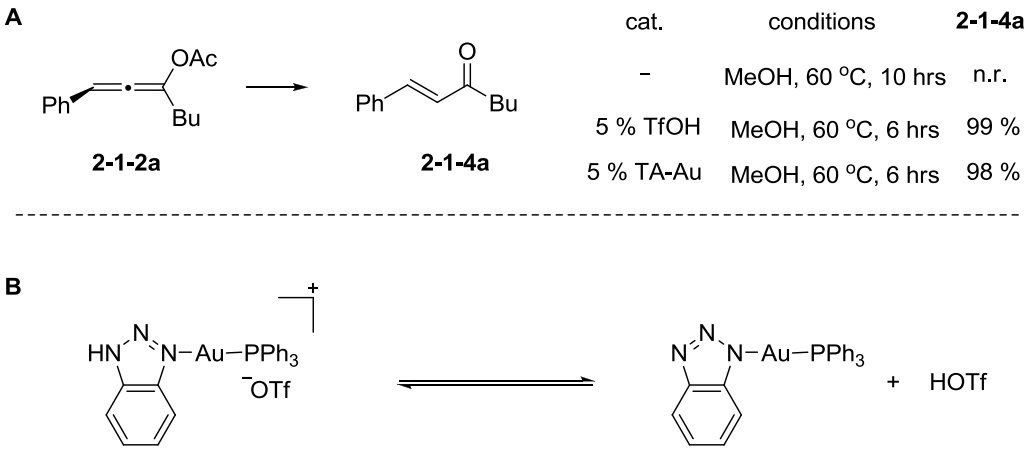


2.1.2 Triazole gold promoted, effective synthesis of enones from prypargylic esters and alcohols: a catalyst offering chemoselectivity, acidity and ligand economy

Recently, we reported the synthesis of *E*-α-iodo-enone from a propargylic ester 3,3-rearrangment followed by the iodination of the allene ester. Interestingly, while all other $[L\text{-}Au]^+$ catalysts (such as $[NHC\text{-}Au]^+$ and $[PPh_3\text{-}Au]^+$) gave only the thermodynamically stable *Z*-isomers, the application of TA-Au led to the selective formation of the kinetically favored *E*-isomers. These results suggested that TA-Au was a chemoselective catalyst, which could effectively promote alkyne activation without interrupting the inherent reactivity of the allene intermediates.[46]

Moreover, as shown in **Scheme 22A**, although the allene ester **2-1-2a** is rather stable even at elevated temperatures, treatment of this compound with a catalytic amount of acid could effectively convert the allene to the desired enones with excellent yields. Interestingly, unlike the previously reported NHC-Au complexes (**Scheme 21C**), TA-Au could effectively catalyze the hydration of **2-1-2a** at either room temperature or elevated temperature, giving the desired enone in excellent yields. This was likely caused by the equilibrium shown in **Scheme 22B**, where a catalytic amount of HOTf was released to serve as the Bronsted acid in promoting the hydration.

Scheme 22. TA-Au Serves as Bronsted Acid in Hydration Transformation



We then postulated that TA-Au might be the effective catalyst in promoting the propargylic ester rearrangement and hydration to give enones. Unlike the previously reported [(I*t*Bu)Au]$^+$ catalyst, TA-Au promoted this reaction through a chemoselective rearrangement followed by an effective hydration with the same pre-catalysts, which therefore provides an alternative to prepare enones compared with the S_N2' mechanism by the more expensive [(I*t*Bu)Au]$^+$ catalysts.

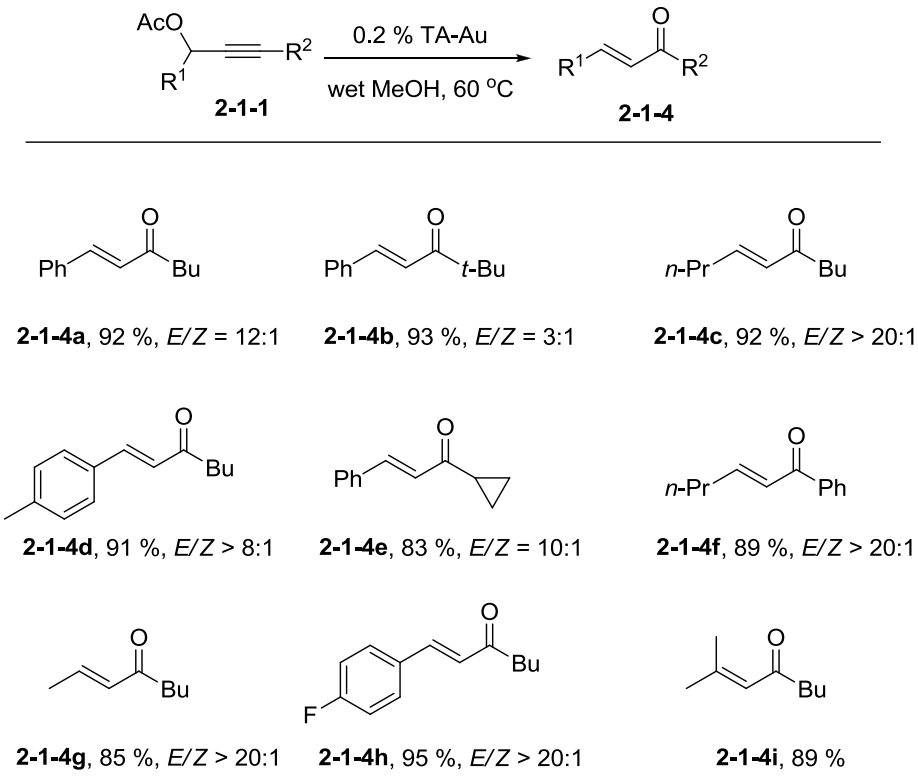
As expected, with the TA-Au catalyst, enone **2-1-4** was obtained in excellent yields. No indene by-product was observed, which highlighted the chemoselective nature of the TA-Au catalyst.

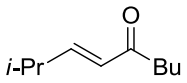
TfOH was not a suitable catalyst for this reaction since the 3,3-rearrangement did not occur with only TfOH. Screening of solvents revealed MeOH as the optimal choice. The reaction worked smoothly at room temperature and gave the enone product in excellent yields over 24 h. Increasing the temperature decreased the reaction time to 3-

6 h. As a result, the enones **2-1-4** were obtained with near quantitative yields (> 99 % NMR yields) at very low catalyst loading (0.2 %).

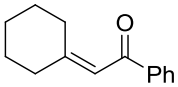
As shown in **Table 4**, the reaction tolerated large group substrates, giving the desired enone in excellent yields and good double-bond selectivity (dominant trans-isomers). The *t*-Bu-substituted alkyne **2-1-2b**, which was not suitable with the NHC-Au catalyst due to the S_N2' mechanism, proceeded smoothly under these alternative conditions although with slightly decreased *Z/E* selectivity (**2-1-4b**). The high efficiency makes TA-Au a very attractive and practical catalyst for this transformation: at least 5 times lower catalyst loading than NHC-Au^+ with much less expensive ligands.

Table 4. TA-Au Catalyzed Propargyl Ester Hydrolysis [a, b]

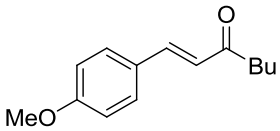




2-1-4j, 93 %, *E/Z* > 20:1



2-1-4k, 87 %

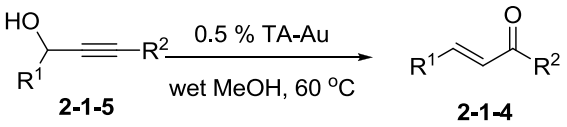


2-1-4l, 97 %, *E/Z* > 20:1

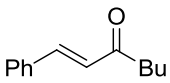
[a]General reaction condition: **2-1-1** (1.0 eq.) and TA-Au (0.2 mol %) in wet MeOH (0.25 M), the reaction were monitored by TLC (3-6 h), 60 ^{o}C. [b]Isolated yields; *E/Z* ratios were determined by ^{1}H NMR.

Heating the [(IPr)AuCl]/$AgBF_4$ in wet MeOH at 60 ^{o}C produced a black solution/participate within 30 min, indicating the rapid decomposition of the catalyst. In contrast TA-Au, on the other hand, showed much improved stability, with no decomposition after more than 6 h under the same conditions. Considering the good thermal stability of TA-Au, we wondered whether this catalyst could also be used to promote the challenging Meyer-Schuster arrangement of propargylic alcohols **2-1-5** at higher temperature.[57] Impressively, the desired enone products were formed with excellent yields. The reaction also tolerated a large group of substrates (**Table 5**).

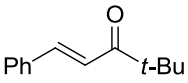
Table 5. TA-Au Catalyzed Meyer-Schuster Rearrangement [a, b]



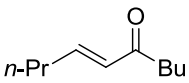
2-1-5 **2-1-4**



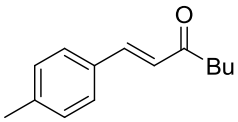
2-1-4a, 89 %, *E/Z* = 9:1



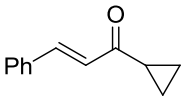
2-1-4b, 90 %, *E/Z* = 3:1



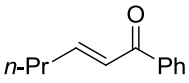
2-1-4c, 91 %, *E/Z* > 20:1



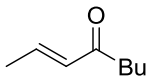
2-1-4d, 97 %, *E/Z*= 6:1



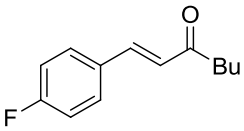
2-1-4e, 89 %, *E/Z* = 11:1



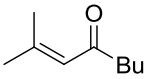
2-1-4f, 85 %, *E/Z* > 20:1



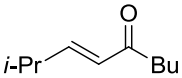
2-1-4g, 94%, *E/Z* >20:1



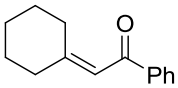
2-1-4h, 91%, *E/Z* >20:1



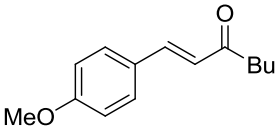
2-1-4i, 98%



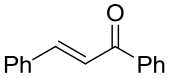
2-1-4j, 96 %, *E/Z* > 20:1



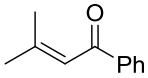
2-1-4k, 84 %



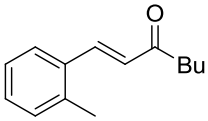
2-1-4l, 95 %, *E/Z* > 20:1



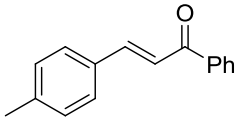
2-1-4m, 93 %, *E/Z* > 20:1



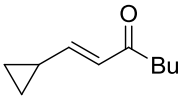
2-1-4n, 92 %



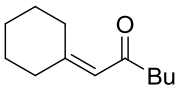
2-1-4o, 94 %, *E/Z* = 13:1



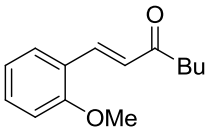
2-1-4p, 97 %, *E/Z* = 16:1



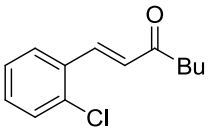
2-1-4q, 92 %, *E/Z* > 20:1



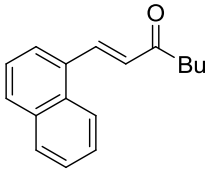
2-1-4r, 87 %



2-1-4s, 93 %, *E/Z* > 20:1



2-1-4t, 98 %, *E/Z* > 20:1



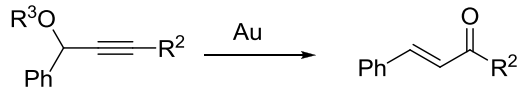
2-1-4u, 88 %, *E/Z* > 20:1

---

[a]General reaction condition: **2-1-5** (1.0 eq.) and TA-Au (0.5 mol %) in wet MeOH (0.2 M), the reaction were monitored by TLC (4-12 h), 60 ^{o}C. [b]Isolated yields; *E/Z* ratios were determined by ^{1}H NMR.

Surprisingly, the bulky tert-butyl-substituted alkyne **2-1-5b** was also suitable for this reaction, which suggested the effective water addition to the sterically hindered alkyne at higher temperature. The terminal alkyne propargylic alcohol gave enal in modest yields, which were probably caused by the longer reaction time required for the less favored anti-Markovnikov addition. [58-59]

Scheme 23. Comparison with the Best Results Obtained in the Literature



2-1-1 or 2-1-5 **2-1-4**

2-1-1a: R^3 =Ac, R^2 = *n*-Bu	[(IPr)AuCl]/$AgSbF_6$ (2.0 %): 98 % yield (IPr)AuOH (2.0 %): 91 % yield **TA-Au (0.2 %): 92 % yield**
2-1-1b: R^3 =Ac, R^2 = *t*-Bu	[(IPr)AuCl]/$AgSbF_6$ (2.0 %): no reaction **TA-Au (0.2 %): 93 % yield**
2-1-5a: R^3 =Ac, R^2 = *n*-Bu	(IPr)AuOH (2.0 %): 97 % yield **TA-Au (0.5 %): 89 % yield**
2-1-5b: R^3 =Ac, R^2 = *t*-Bu	(IPr)AuOH (2.0 %): 75 % yield **TA-Au (0.5 %): 90 % yield**

Continuous addition of catalysts could improve the overall yields. Nevertheless, the feasibility of this challenging substrate highlighted the strength of the TA-Au catalyst over the $[NHC\text{-}Au]^+$ catalyst (**Scheme 23**) by tolerating the much harsher conditions.[60]

2.1.3 Conclusion

In conclusion, we have reported herein the application of triazole-coordinated Au(I) complex (TA-Au) as an effective catalyst in promoting propargylic ester rearrangement and hydration for the synthesis of substituted enones. The key for the success of the TA-Au catalyst was the combination of its unique chemoselectivity and acidity. Extension of this transformation to the Meyer-Schuster rearrangement by taking advantage of the thermal stability of the TA-Au further improved the atom economy. Compared with the more expensive NHC-Au catalysts, TA-Au promoted the reaction

through a different mechanism and achieved better performance with lower overall costs.

2.1.4 Contribution

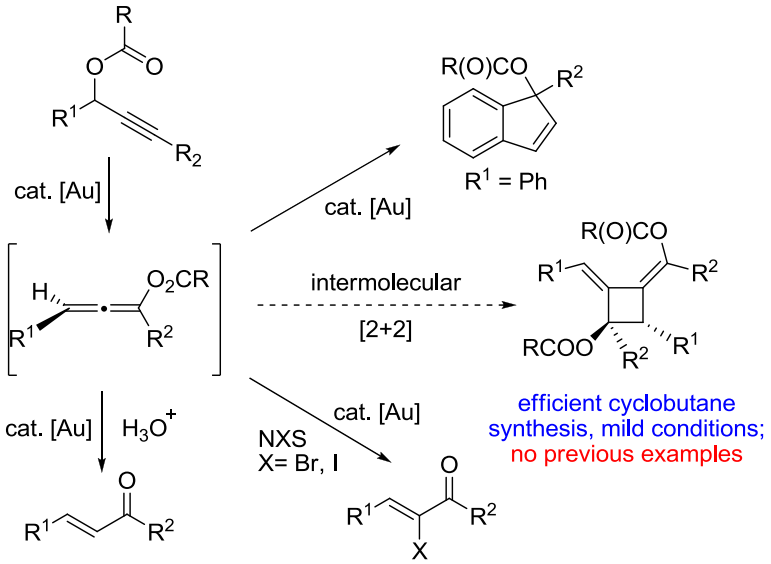
Dr. Dawei Wang was the researcher who had first investigated the reaction condition and mechanism investigation. Together, Dr. Wang and Yanwei Zhang were responsible for substrate scope, NMR spectrum, and manuscript completion for successful submission to *Advanced Synthesis and Catalysis*.

2.2 Ambient Intermolecular [2+2] cycloaddition of allene intermediate

2.2.1 Introduction

As mentioned, Au(I) catalyzed alkyne transformations typically undergo 3,3-rearrangement. The allene intermediates can be further activated by the same gold species and converted into various products, such as indenes, enones, and vinyl halides.

Scheme 24. Gold-catalyzed Propargyl Ester Activation



The formation of indene, enones and *E*-α-haloenones has been introduced in chapter 1 and 2.1. One more important application of allene substrate is the intermolecular [2+2] cyclization forming the multiple substituted cyclobutane. In this transformation, TA-Au complexes chemoselectivity was applied in the well-developed process of forming an allene intermediate. The allene intermediate then facilitated the

[2+2] cyclization process, achieved the cyclobutane under the absolutely 'Silver-free' condition.

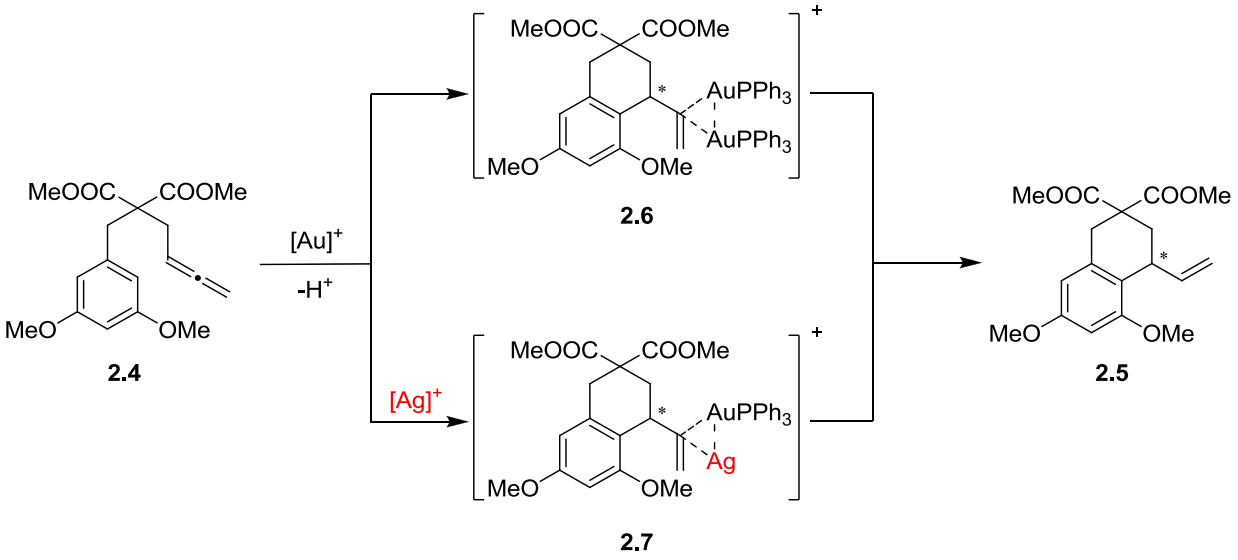
2.2.2 'Silver effect' in homogeneous gold (I) catalysis

Along with the development of gold catalysis, it is possible to get some traditionally challenging transformation to occur by tuning the reactivity of gold complexes with different primary ligands. However, it still remains one critical issue in gold catalysis, which is referred as ‘Silver effect’ in the transformations. As indicated above, silver salts are generally adopted to dissociate the Au-Cl bond in L-Au-Cl complex by forming AgCl precipitate. Because these cationic gold complexes slowly decompose over time, they are always freshly prepared right before the reaction setup or generated in situ.

Typically, the resulting AgCl precipitate can be removed by simply passing the reaction solution mixture through cotton plug or filter paper.[61] However, recent research indicates that: a) practically, more than necessary silver salt is applied in the reaction mixture, therefore, not all Ag^+ is converted to AgCl precipitate. The additional amount of Ag^+ left in the catalyst system affects the transformation; b) in presence of Au^+ and Ag^+, an unexpected Au-Ag di-metal co-catalysis system is observed in the resting state and leads to diverse reaction patterns.

The first evidence for Au-Ag di-metal co-catalysis was published in 2009. For first time, researchers realized that silver presented a more significant effect in the catalyst system behavior other than just forming AgCl precipitate (**Scheme 25**).[62]

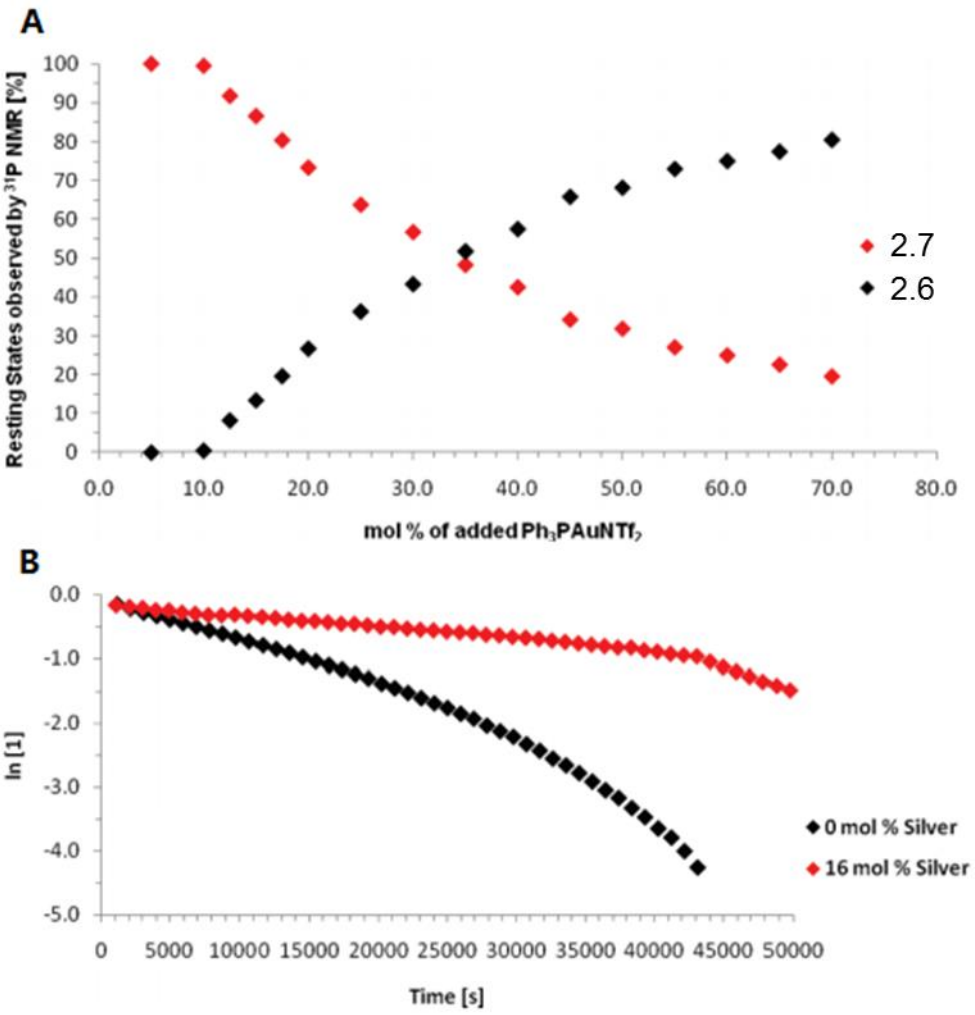
Scheme 25. Different Resting States in the Au(I) Catalysis when Silver is Presented



As shown in **Scheme 25**, there were two resting states of Au(I) activated Friedel-Crafts reaction in this transformation. One (**2.6**) was established with two Au^+ atoms, and the other one (**2.7**) was formed with one Au^+ and one Ag^+. The ratio of these two resting states was differing based on the amount of silver salt introduced in the reaction mixture. Although these two very similar resting states gave the identical product in this specific case, the reaction rates were significantly different. Furthermore, by adding an excess amount of $AgNTf_2$, the reaction was quenched (**Scheme 26B**).[63]

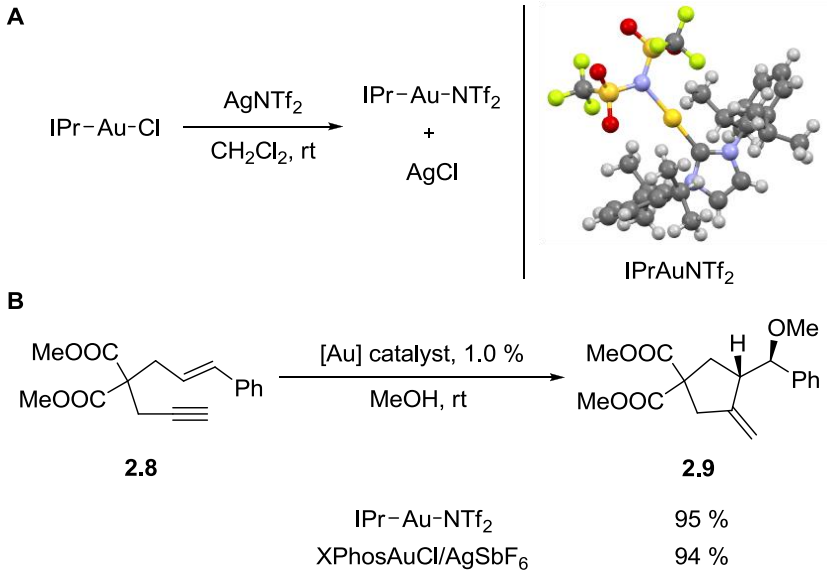
This case demonstrated that in gold catalysis, Ag^+ might serve as an important candidate which participated in the catalysis pattern. Subsequently, more and more effort has been devoted to investigating the mechanism of 'silver effect' in gold catalysis. Additionally, to better understand 'silver effect', 'silver free' gold catalyst system is desired as standard in gold catalysis.

Scheme 26. The Reaction Rate is Slowed Down by Adding $AgNTf_2$



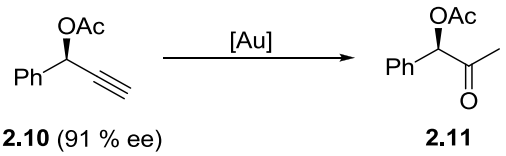
In 2007, the original 'silver free' Au(I) catalyst was developed by Prof. Gagosz et al. The bis(trifluoromethanesulfonyl)imidate moiety (Tf_2N^-) was applied as the counter ion for Au(I) complexes (**Scheme 27A**). It was shown that $AuNTf_2$ is stable enough to perform a recrystallization purification and obtain the 'silver free' gold complexes as a crystal solid.[64] As mentioned above, the coordination between gold cation and Tf_2N^- is weak and enabled the significant ligand exchange between the Tf_2N^- and reacting substrates without influencing the reactivity of gold catalysts (**Scheme 27B**).[65]

Scheme 27. Synthesis and Application of [IPrAuNTf$_2$]



The triazole gold complexes are also able to achieve the 'silver free' crystal by recrystallization due to their moisture and air stability. As a consequence, triazole gold complexes provide us a good ‘silver free’ model to investigate the 'silver effect' in gold catalysis. To comprehensively understand the function of Ag^+ in gold catalysis, an alkyne hydration reaction was investigated with both Au-Ag co-catalysts and ‘silver free’ Au(I) catalysts (such as TA-Au). The consequences of different gold catalysts are summarized in **Table 6**.

Table 6. Silver Effect in Alkyne Hydration [a]



Entry	Catalyst	Conditions	Yield (%)[b]	ee (%)
1	1 % TA-Au	5 hrs	87	90

2	**10 % AgX** [c]	**12 hrs**	**0**	**-**
3	**2 % $[PPh_3Au]^+X^-$** [c]	**12 hrs**	**0**	**-**
4	2 % $PPh_3AuCl/AgOTf$	12 hrs	90	0
5	2 % $PPh_3AuCl/AgSbF_6$	8 hrs	97	0
6	2 % $PPh_3AuCl/AgOTf$	5 hrs (N_2)	92	90
7	2 % $[PPh_3Au]^+SbF_6^-$ + $AgSbF_6$	12 hrs	91	-

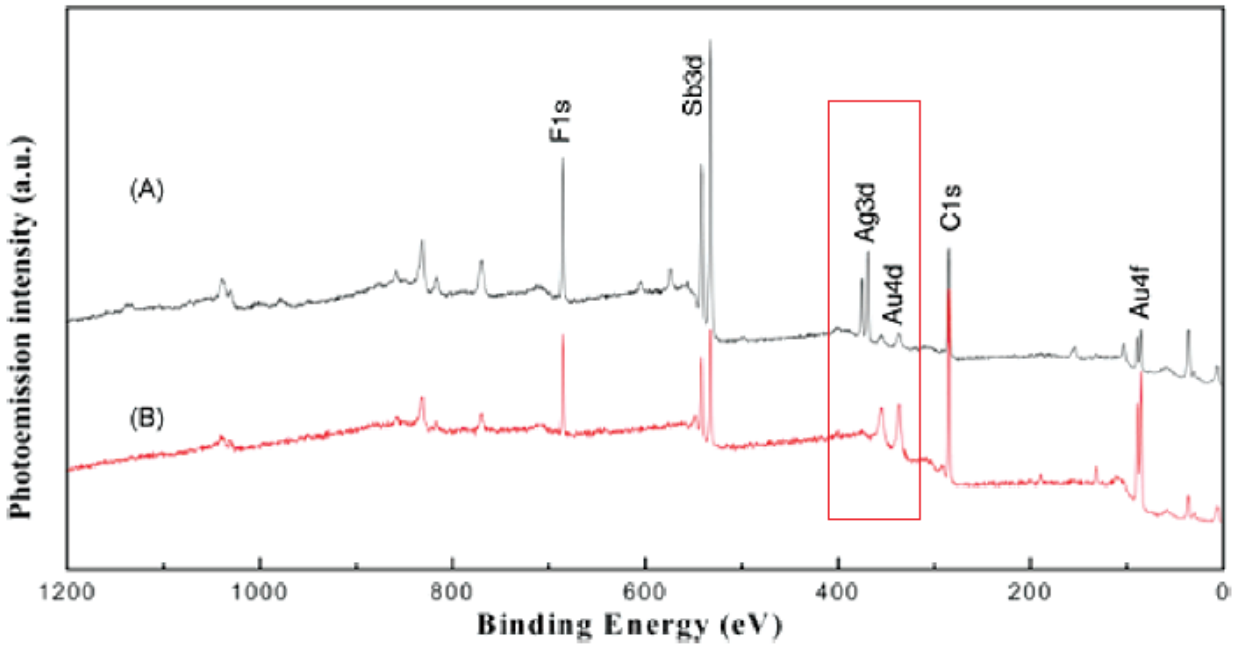
[a]General reaction conditions: **2.10** (1.0 equiv) and catalyst in 2.5 mL of dioxane/water (H_2O, 3.0 equiv) at rt. Reactions were monitored by TLC. [b]NMR yields. [c]X^- = TfO^-, SbF_6^-, BF_4^-.

The results indicated that Ag^+ by itself did not perform any reactivity towards this transformation (entry 2). Additionally, entry 3 (gravity celite filtration) showed that when using the 'silver free' Au^+ catalyst, there was no desired product observed no matter what primary ligand was applied. However, when using a mixture of L-Au-Cl and AgX (entry 4 and 5, cotton plug or filter paper filtration) as pre-catalyst, the reaction proceeded with high yield under the identical conditions. In addition, a high ee value was observed as reported under N_2 protection (entry 6). To confirm the effect of Ag^+ in this transformation, entry 7 was designed with a mixture of 'silver free' $[(PPh_3)Au]^+$ OTf^- and back-addition $AgSbF_6$ ($AgSbF_6$ was added to the reaction mixture after the celite filtration). The consistent result was observed as entry 5, which verified this reaction was actually catalyzed by Au-Ag co-catalysts.

The only difference between entry 3 and entries 4, 5 here was the filtration precedure. Entry 3 was using a cotton plug or filter paper to remove the AgCl, while in entry 4 and 5, celite pipette was used to reach the same target. The gravity filtration through the celite pipette was a quite efficient and reliable process to remove all

remaining Ag^+, which was further confirmed by X-ray photoelectron spectroscopy (XPS) (**Scheme 28**).

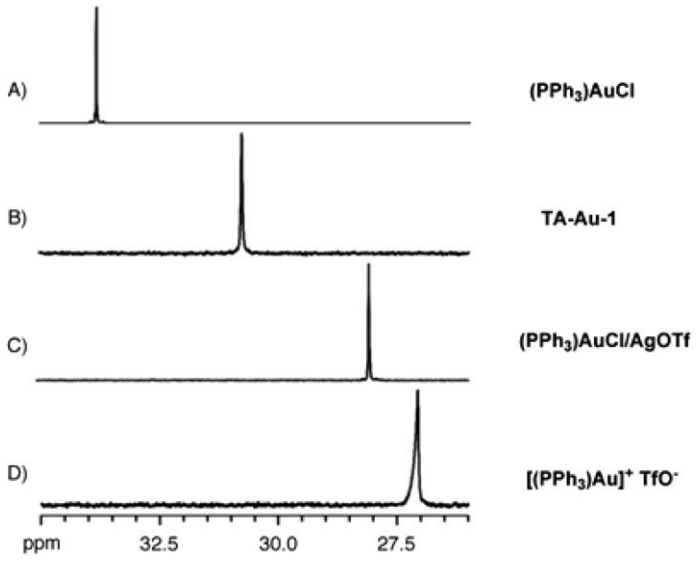
Scheme 28. XPS Spectra of $(PPh_3)AuCl/AgSbF_6$ Mixtures



In **Scheme 28**, both spectra showed the signal of Au^+ at the binding energy as Au $4f_{7/2}$, 85.5 eV; Au $4f_{5/2}$, 89.2 eV, while the signal of Ag^+ (Ag $3d_{5/2}$, 368.7 eV; Ag $3d_{3/2}$, 374.7 eV) was only observed in spectrum A which regular cotton plug or filter paper was applied in the filtration step. No corresponding Ag^+ signal was observed which indicated no presence of silver in spectrum B with celite pipette filtration. This result is sufficient to prove that gravity celite filtration procedure is reliable to produce 'silver free' gold catalyst even with excess amount Ag^+ ((PPh3)AuCl:AgSbF6 = 1:1.5).

Meanwhile, ^{31}P NMR spectroscopy is applied to inspect the existence of Ag^+ in Au(I) complexes (**Scheme 29)**.

Scheme 29. ^{31}P NMR Spectra of Different Au(I) Species



The data in **Scheme 29** released the relationship between chemical shift of ^{31}P and the reactivity of Au(I) complexes (more downfield chemical shift, lower reactivity). The unreactive $(PPh_3)AuCl$ presented the most downfield chemical shift due to the strong coordination between Au and Cl. The freshly prepared 'silver free' $[(PPh_3)Au]^+TfO^-$ through gravity celite filtration presented the most upfield chemical shift (which is considered as the most reactive catalyst). The $(PPh_3)AuCl/AgOTf$ mixture without any filtration presented a chemical shift between these two mentioned cases. These results indicated that silver here can, to some extent, influence the reactivity of Au(I) complexes.

2.2.3 Ambient intermolecular [2+2] cycloaddition: an example of carbophilicity and oxophilicity competition in Au/Ag catalysis

Recently, special gold catalysts have been reported to achieve high yields of allene intermediates, including the triazole gold reported by our group. While this chemistry

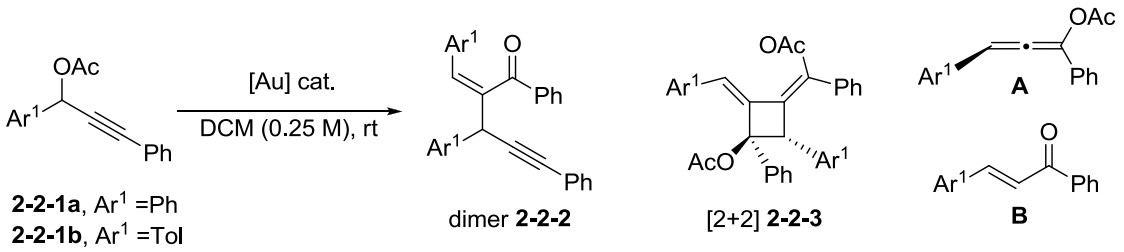
seems well understood, one 'concealed' problem was that most of these transformations generally lack tolerance for the diaryl substituted internal alkynes (R^1, R^2= aryl groups). For example, simply treating diphenyl propargyl ester **2-2-1a** (R^1 = R^2 = Ph, R = CH_3) with various LAuCl/AgX (L = PPh_3, IPr, XPhos; X = TfO^-, Tf_2N^-, SbF_6^-, BF_4^-) catalysts gave complex reaction mixtures with little indene or allene obtained. In order to determine the product for diaryl propargyl ester in presence of gold catalysts, we conducted detailed investigations with the diaryl propargyl ester starting material.

We herewith report the different products formed from this diaryl propargyl ester rearrangement and the intermolecular allene [2+2] cycloaddition at ambient temperature. In addition, the ‘silver-free’ condition is critical in this transformation. In the presence of silver, even a catalytic amount, dimer **2-2-2** was observed over the [2+2] products due to the silver-activated substitution. Considering the extensive efforts from various research groups toward understanding the role of silver in gold catalysis, this work provides another example of silver influence as an oxophilic Lewis acid, which deviates from the gold reaction pathway.[66]

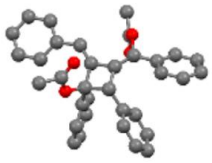
The cationic gold complexes are effective carbophilic π-acids, which can effectively activate both an alkyne and allene.[67] According to the literature, three types of chemoselective gold catalyst (activate alkyne over allene) have been reported as gold-oxo complexes, gold-pyridine/Et_3N complexes, and 1,2,3-triazole gold complexes (TA-Au).[68-70] Surprisingly, among all the reported gold-catalyzed propargyl ester rearrangements, diaryl propargyl esters are not viable substrates. In fact, during our investigations of the triazole gold (TA-Au) catalyzed allene synthesis, complex reaction mixtures were observed. In order for us to understand how this particular type of

substrate reacts, we monitored the reactions of compound **2-2-1a** with various gold catalysts (**Scheme 30**).

Scheme 30. Analyzing the Propargyl Rearrangement of **2-2-1a**



catalyst	time	**2-2-2a**	**2-2-3a**
PPh_3AuCl/AgX 5 %	5 min	50 %	0 %
$[PPh_3Au(TA\text{-}H)]OTf$ 2 % TA-H = NH-benzotriazole	12 hrs	30 %	10 % + other isomers



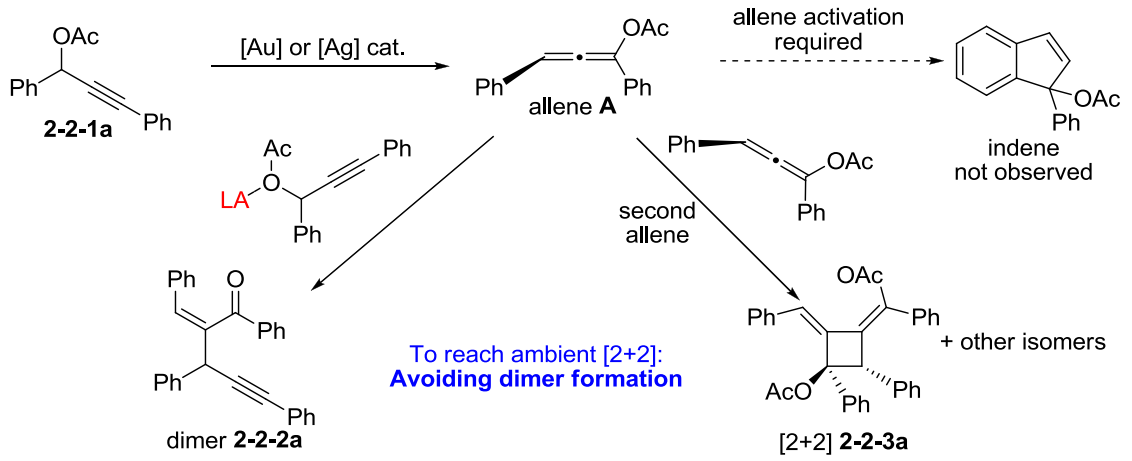
X-ray of **2-2-3a**

First, the treatment of **2-2-1a** with LAuCl/AgX (5 % loading, L = PPh_3, IPr, XPhos, X = OTf, NTf_2 or SbF_6) gave complex reaction mixtures. Through careful examination, dimer **2-2-2a** was identified as the major product (50 % yield using anhydrous solvent; see detailed structure analysis in the Supporting Information). With the triazole gold (TA-Au) catalysts, the reaction was much cleaner (less polymerization and decomposition). However, several other products were observed in addition to the dimer **2-2-2a** (30 %). Fortunately, the structure of one major product was determined by X-ray crystallography as the [2+2] cycloaddition product **2-2-3a**. Other minor products were identified as the stereoisomers generated from the [2+2] cycloaddition.

This result was exciting because it was the first example of an intermolecular allene [2+2] reaction through a propargyl ester rearrangement. Notably, indene was not

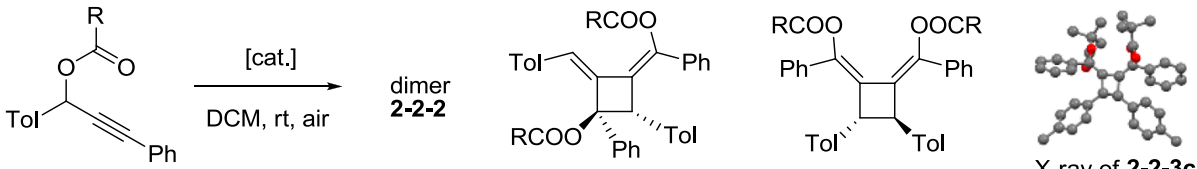
observed in this case. The successful confirmation of the dimer and the [2+2] cycloaddition products greatly enhanced our understanding of this reaction. A proposed reaction mechanism is shown in **Scheme 31**.

Scheme 31. Propargyl Ester Activation



Cyclobutanes are very attractive as building blocks in organic synthesis, and this reaction is conducted under mild conditions (rt) with simple starting materials. Thus the discovery shown above revealed an interesting new approach to access substituted cyclobutanes under mild conditions. As shown in **Scheme 31**, the allene should be formed prior to either dimerization or cyclization. This was confirmed by monitoring the reaction with NMR: allene A was the only product formed during the first 2 h of reaction when treating **2-2-1a** with TA-Au catalysts. Efforts to isolate allene **A** were unsuccessful due to the poor stability. In order to improve the chemoselectivity ([2+2] over dimer) and stereoselectivity (different cyclobutane isomers), we prepared various propargyl ester derivatives and examined them under the conditions of gold catalysis. The results are summarized in **Table 7**.

Table 7. Optimization of Au(I)-catalyzed Allene [2+2] [a]



2-2-1 **2-2-3** **2-2-3'**

X-ray of **2-2-3c'**
R= *t*-Bu

entry	cat. (%)	R	temp (°C)	time (h)	conv (%)[b]	yield (%)[b]			
						2-2-2	2-2-3	2-2-3'	other isomer
1	$PPh_3AuCl/AgOTf$ (5 %)	CH_3	rt	1	100	67	trace	trace	-
2[c]	$[PPh_3Au(TA\text{-}H)]OTf$ (1 %)	CH_3	rt	12	100	43	10	8	35
3[d]	$[PPh_3Au(TA\text{-}Me)]OTf$ (1 %)	CH_3	rt	12	100	12	16	13	50
4	$[PPh_3Au(TA\text{-}Me)]OTf$ (1 %)	Ph	rt	12	100	53	trace	trace	trace
5	$[PPh_3Au(TA\text{-}H)]OTf$ (1 %)	*t*-Bu	rt	16	100	<5	68	12	<5
6	$[PPh_3AuO]OTf$ (1 %)	*t*-Bu	rt	20	100	trace	69	14	<5
7	$[PPh_3Au(TA^{-}H)]OTf$ (1 %) + 2 % AgOTf	*t*-Bu	rt	1	100	63	trace	trace	trace
8	$AgSbF_6$ (5 %)	*t*-Bu	rt	16	100	45	trace	trace	trace
9	HOTf (5 %)	*t*-Bu	rt	16	60	0	0	0	0
10[e]	$PtCl_2$ (5 %)	*t*-Bu	80	16	100	0	56	14	<5

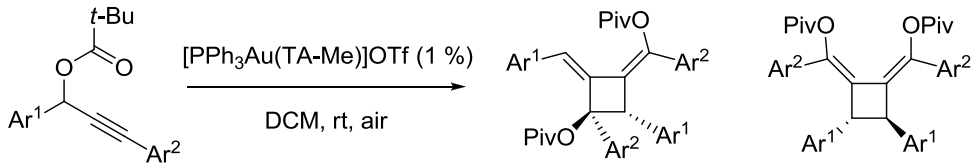
[a]Reaction conditions: **2-2-1** (0.2 mmol) and catalyst in DCM (0.8 mL), rt, time. [b]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard. [c]TA-H = benzotriazole. [d]TA-Me = N-methyl benzotriazole. [e]15 % yield of (*E*)-1-phenyl-3-(*p*-tolyl)prop-2-en-1-one.

The $PPh_3AuCl/AgOTf$ catalysts gave only dimer **2-2-2** with no cycloaddition product **2-2-3** observed (entry 1). The silver-free TA-Au catalyst produced the desired [2+2] products as mixtures of isomers. With the NH-triazole (TA-H) as the ligand, 43 % dimer was obtained (entry 2). The amount of dimer was decreased when N-methyl triazole (TA-Me) was used (entry 3), probably due to the elimination of an acidic proton on NH-triazole (activating the OAc leaving group). Switching acetate to benzoylate resulted in the exclusive formation of a dimer due to the better propargyl leaving group ($PhCOO^-$ vs CH_3COO^-). Finally, application of pivalate achieved excellent chemoselectivity, giving

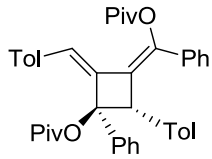
the [2+2] products in good yields (>85 % combining all isomers, entry 5). Moreover, the bulky pivalate group also gave significantly improved stereoselectivity with only two major cycloaddition products obtained (**2-2-3** and **2-2-3′**) in a 5:1 ratio. The structure of the minor isomer, **2-2-3′**, was also confirmed by the X-ray crystallography. The silver-free gold oxo catalyst $[(PPh_3Au)_3O]OTf$ could also promote this reaction effectively (entry 6), though with a slightly lower reaction rate compared with the use of TA-Au.

The silver salt was crucial in this transformation. As shown in entry 7, the addition of 2 % AgOTf led to the formation of only dimer **2-2-2** without obtaining any cycloaddition product **2-2-3** obtained. Using a silver catalyst alone (entry 8) gave the same dimer product with a slower reaction rate, likely due to the decreased reactivity of the silver catalyst toward alkyne activation (compared with gold catalyst). Triflate acid did not promote the rearrangement at all, giving only the propargyl ester decomposition over time (entry 9). Finally, the silver-free $PtCl_2$ catalyst gave a similar cycloaddition reaction, albeit at elevated temperature (entry 10). In view of these results, it is clear that the propargyl rearrangement is the initiation step. The reactivity of the three well-known π-acids follows the general trend Au(I) > AgX > $PtCl_2$ in this transformation. Besides alkyne activation, the silver cation (more oxophilic) can also activate the acetate as a leaving group, giving dimer **2-2-2** as the only product. The silver-free TA-Au catalyst indicated excellent reactivity toward alkyne activation over the undesired oxygen activation, which led to the successful cycloaddition of allene for the first time. The scope of reaction substrate is shown in **Table 8**.

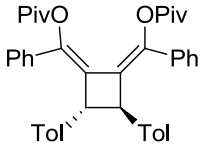
Table 8. Reaction Scope of [2+2] Cycloaddition [a, b]



2-2-3 **2-2-3'**



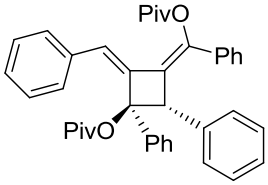
2-2-3c, 68 %



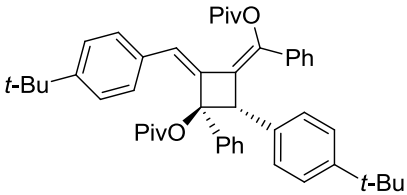
2-2-3c', 12 %

total [2+2], 80 %
3:3' = 5.6:1

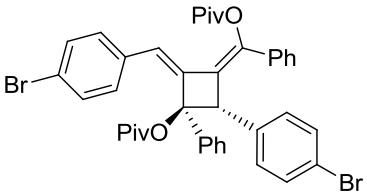
Ar[1]



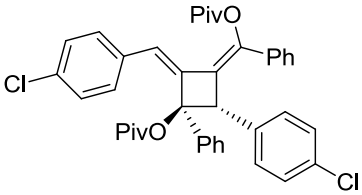
2-2-3d, 75 %;
2-2-3d', 13 %



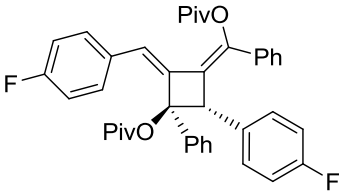
2-2-3e, 65 %;
2-2-3e', 19 %



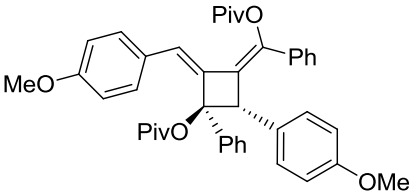
2-2-3f, 74 %;
2-2-3f', 16 %



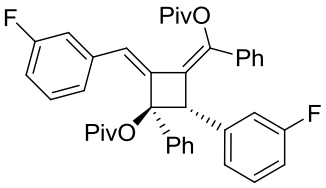
2-2-3g, 80 %;
2-2-3g', 17 %



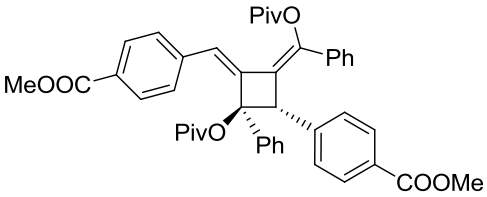
2-2-3h, 76 %;
2-2-3h', 19 %



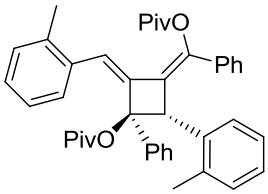
2-2-3i, 68 %;
2-2-3i', 12 %



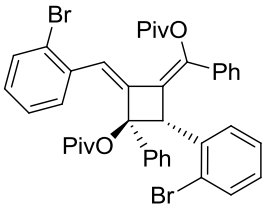
2-2-3j, 76 %;
2-2-3j', 17 %



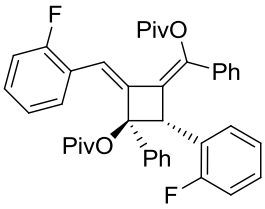
2-2-3k, 71 %;
2-2-3k', 12 %



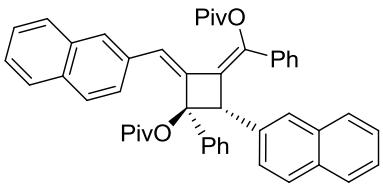
2-2-3l, 73 %;
2-2-3l', 18 %



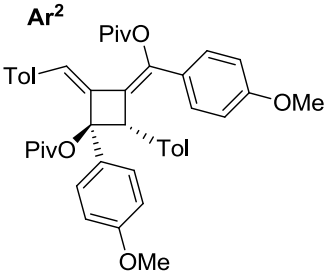
2-2-3m, 63 %;
2-2-3m', 18 %



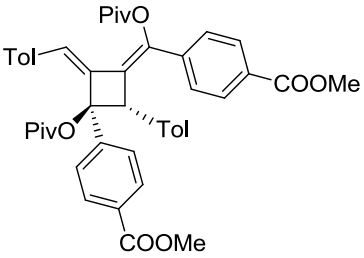
2-2-3n, 74 %;
2-2-3n', 18 %



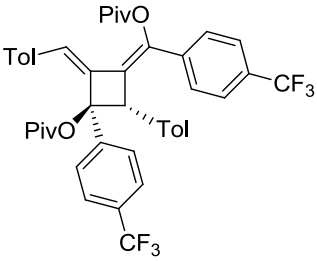
2-2-3o, 43 %;
2-2-3o', 24 %



2-2-3p, 68 %;
2-2-3p', 10 %[c]



2-2-3p, NR



2-2-3r, NR

---

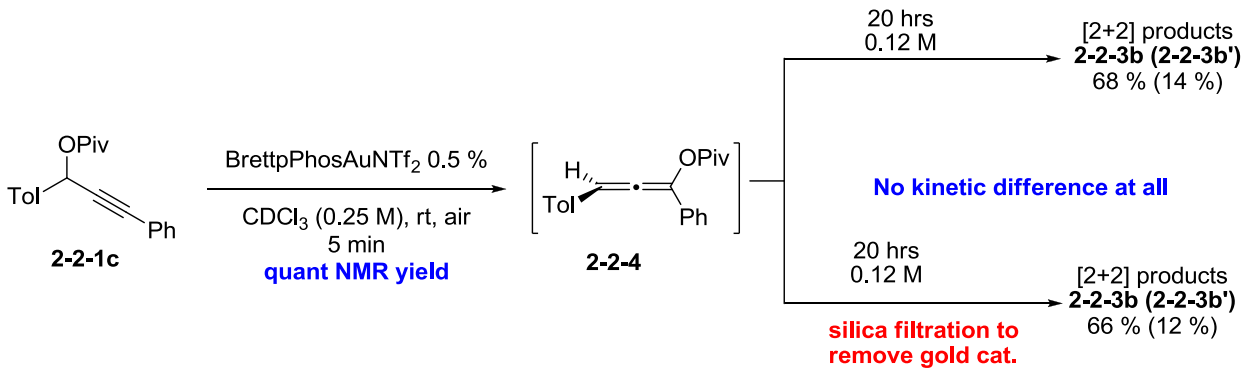
[a]Reaction conditions: **2-2-1** (0.2 mmol) and [PPh_3Au(TA-Me)]OTf in DCM (0.8 mL). [b]Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. [c]1 mol % of [$(PPh_3Au)_3O$]OTf was used instead of [PPh_3Au(TA-Me)]OTf.

The reaction tolerates a good substrate scope on the propargyl aryl position (Ar1). Electron-withdrawing groups (**2-2-3h**, **2-2-3k**) were suitable for this reaction, giving the desired cycloaddition products with good yields. The electron-donating group modified substrate (**2-2-3i**) gave the dimer as one of the major products with TA-Au catalysts, probably due to the improved ability to form a propargyl carbon cation. This problem was resolved by using [$(PPh_3Au)_3O$]OTf as the catalyst with a longer reaction time. Steric hindrance was not an issue in this transformation based on the fact that ortho-substituted substrates (**2-2-3l−2-2-3n**) worked fine under the optimal conditions with the formation of the desired [2+2] cycloaddition products in excellent yields and similar isomer ratios. Poor selectivity was observed with naphthalene-substituted derivative **2-**

2-3o (1.8:1). This result implied the plausibility of π−π stacking during the [2+2] cycloaddition process.

A greater electronic effect was observed at the alkyne terminal Ar2 position. The electron-donating p-methoxyphenyl substituted alkyne gave the desired cyclobutane **2-2-3p** in excellent yield when $[(PPh_3Au)_3O]OTf$ was used as the catalyst. However, an electron-withdrawing group reduced the reaction rate for propargyl ester rearrangement due to either the poor reactivity of alkyne toward π-acid activation (lower electron density) or the unfavored 3,3-migration (over the electronically preferred 1,2-rearrangement). Increasing the reaction temperature to 80 °C (with dichloroethane as the solvent) gave the allenes at low yields (< 20 %), along with a significant amount of unidentified side products. These results suggest that the ambient [2+2] cycloaddition is substrate-dependent, which raises the concern whether gold catalysts were involved in the cycloaddition process. To verify the potential role of gold catalysts in the cycloaddition step, we monitored the reaction as shown in **Scheme 32**.

Scheme 32. Investigation on the Role of Au in [2+2] Step



Treating propargyl ester **2-2-1c** with silver-free BrettPhosAuNTf$_2$ (0.5 %) gave rapid rearrangement (5 min) to allene **2-2-4** in quantitative NMR yield. Because allene **2-2-4** will decompose upon condensation, it is difficult to isolate **2-2-4** in pure form. Thus the reaction mixture was divided into two parts. One part continued to react under the identical conditions (in the presence of the gold catalyst). The other part was filtered through a silica plug so as to completely remove the gold catalyst. The resulting solvent was condensed to ensure a concentration that was identical to that in the case with the gold catalyst. As reviewed by NMR, for both cases, similar reaction rates were observed, which confirmed that the allene [2+2] cycloaddition was a thermal reaction and gold activation was not required.[71]

2.2.4 Conclusion

In conclusion, with the silver-free gold catalyst, the selective [2+2] cycloaddition was achieved with high efficiency under mild conditions (ambient temperature, open flask). Although the minor isomers were obtained, the fact that only two isolatable cyclobutane isomers were obtained highlighted the good selectivity and high efficiency of this transformation. The silver-free condition was identified as the crucial factor for the success of this transformation. The strong influence of silver salts (even in catalytic amounts) raised a viable concern for future investigations on gold catalysis, especially when an oxophilic catalyst may be involved.

2.2.5 Contribution

Dr. Yijin Su and Yanwei Zhang were the researchers who had first investigated the reaction kinetic profile. Together Dr Jijin Su, and Yanwei Zhang were responsible for the [2+2] complexes synthesis, NMR spectrum investigation and manuscript completion for successful submission to *Organic Letters*. The detailed X-ray crystallographic data analysis of compound **2-2-3a** and **2-2-3c'** was done by Prof. Jeffrey L. Petersen, C. Eugene Bennett Department of Chemistry, West Virginia University.

Chapter Three: Synthesis and characterization of bis-N-2-aryl triazole as efficient fluorescence probe

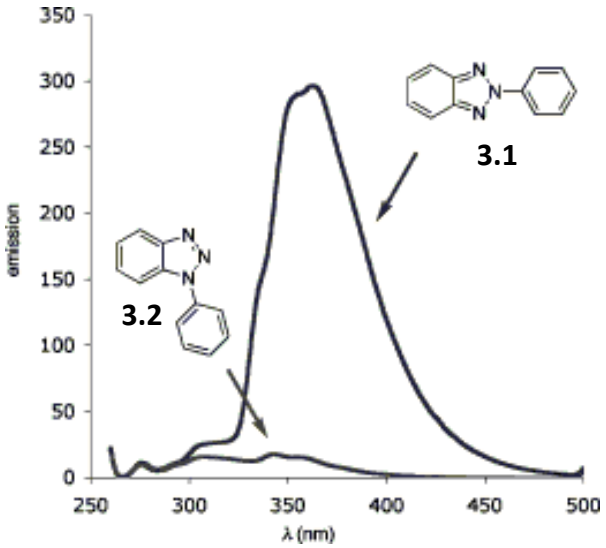
3.1 Introduction

Small organic molecules providing strong fluorescence emission are of great importance to the scientific community.[72] These molecular fluorophores have been applied into a wide range of research areas, including chemistry, biology and material science.[73] In 2009, Professor Clement Sanchez and co-workers discovered a novel photoactive crystalline highly porous titanium (IV) dicarboxylate. In the year of 2010, Professor Martin Albrecht and co-workers reported that N-heterocyclic carbene complexes worked not only as catalysts but also components in medicinal, luminescent, and functional material areas. [74-76]

Two notable aspects influence the efficiency of fluorescence: 1) quantum yield, and 2) the wavelengths of excitation and emission.

In 2011, Shi's group reported N-2-aryl-1,2,3-triazoles (NAT) as novel fluorophores with strong emission in the high-energy UV/blue region.[77] The first interest was initiated by the attractive phenomenon that in the N-1 phenyl triazole **3.1**, basically no emission was observed while the N-2 isomer exhibited a relatively strong fluorescence emission (λ = 362 nm) under the identical excitation wavelength (λ = 254 nm) (**Scheme 33**).

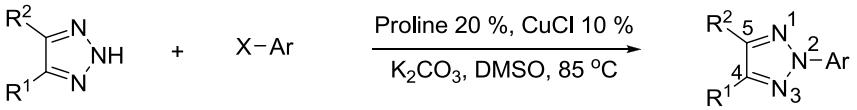
Scheme 33. Photoluminescent Spectra of N-2-aryl-1,2,3-triazoles



Sample preparation: 1.0×10^{-5} mol L^{-1} in MeOH, excitation at λ = 254 nm with 5 nm slit, quantum yield of **3.1** Φ = 0.154, quantum yield of **3.2** Φ = 0.009.

Based on this result, it is suggested that, the fluorescence is presumably resulted from the coplanar conformation between the phenyl ring and the benzotriazole in the N-2-aryl-triazoles (NATs). Therefore, we decided to implement the NATs complexes as effective fluorophores in further fluorescence study based on their fluorescence properties. As a result, a series of new N-2-aryl-triazoles (NATs) were synthesized and characterized (**Scheme 34)**.

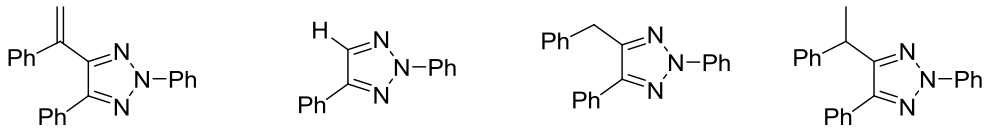
Scheme 34. Synthesis of N-2-aryl-triazoles (NATs)



Three different effects are discussed in this NATs fluorescence investigation. The first investigation is the substituent effect on the C-4 and C-5 positions. Different

substituted groups were introduced to the C-4 and C-5 positions in the NATs. As discussed previously, the fluorescence emission is possibly resulted from the coplanar structure of the NATs. It was plausible that C-4 and C-5 substitution may influence the fluorescence emission through the conjugation of the entire NAT molecule. Moreover, all of these substrates presented strong emission in the UV/blue-light range with λ_{max} at approximately 350 nm.

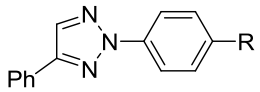
Scheme 35. Fluorescence Emission Behavior of Compounds with Different C-5 Substituents



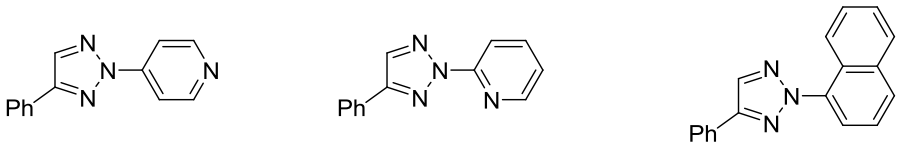
3.3 **3.4** **3.5** **3.6**

The second investigation was focused on the N-2 position substitution. Because the fluorescence was generated from the coplanar structure, we hypothesized that the variation of substituted group on N-2 position could have a significant influence on fluorescence emission.

Scheme 36. Substituted Group Effect on the N-2 Position



3.7: R = CN; **3.8**: R = F; **3.9**: R = Cl;
3.10: R = OMe; **3.11**: R = NO_2; **3.12**: R = COPh

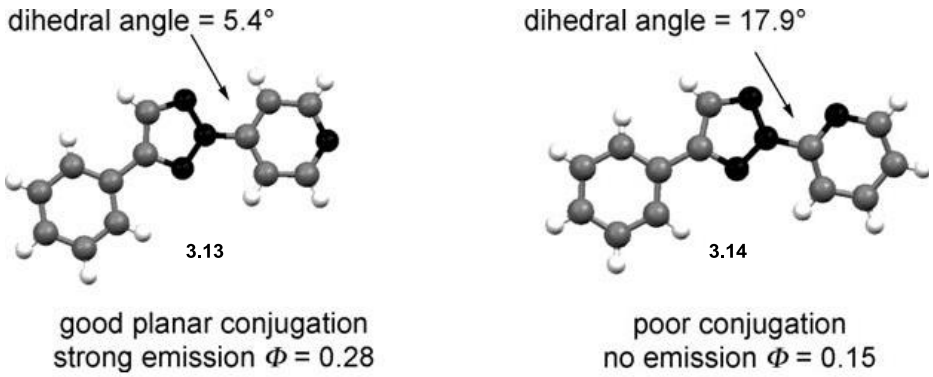


3.13 **3.14** **3.15**

Subsequent to synthesis of the above NATs (**Scheme 36**), the subsequent fluorescence study indicated that most compounds had good fluorescence emission and the overall quantum yield for these NATs is approximately 30 %. This result consequently confirmed the application potential of NATs as fluorophores in further research.

Meanwhile, the crystal structures of **3.13** and **3.14** revealed the importance of coplanar structure in the generation of fluorescence. As shown in **Scheme 37**, due to the electron repulsion between the lone pair elections of the nitrogen atoms on both triazole and pyridine rings, the dihedral angle between the triazole ring and N-2 substituted group in **3.14** (17.9^{o}) was much larger than in **3.13** (5.4^{o}). As a result, the coplanar conjugation of **3.14** was relatively weaker than **3.13**. Therefore, **3.14** presented almost no emission but **3.13** presented a relatively strong emission. This result was sufficient to support the hypothesis that the coplanar structure was the key point in the process of generating intense fluorescence emission in the NATs types of compounds.

Scheme 37. X-ray Crystal Structures of **3.13** and **3.14**

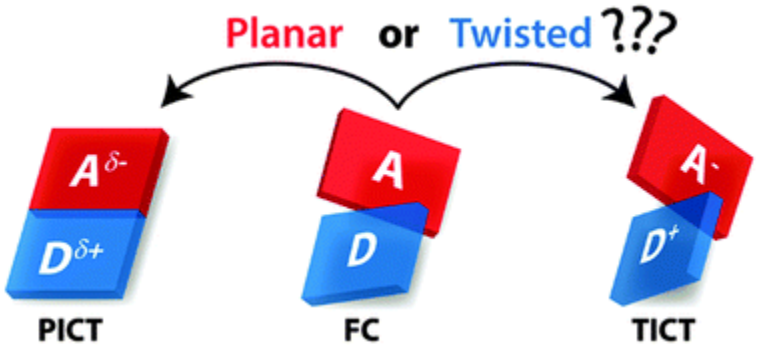


The last investigation here concerns the substituted groups on N-2 substituted aromatic ring. Based on various electronic effects introduced by substituted groups (-Cl, -CN, -OMe), the fluorescence intensity and the emission wavelength can be tuned to a considerable degree.

From all these above results, the NATs compounds have been demonstrated as a type of potential fluorophore in multiple research areas. Furthermore, we concluded that the strong fluorescence emission of NATs compounds is resulted from the coplanar conjugation between the triazole ring and N-2 substituted aromatic ring.

Given a molecule in the excited state, there are basically two intramolecular charge transfer types: PICT (planar intramolecular charge transfer) and TICT (twisted intramolecular charge transfer). When the D-A (donor-acceptor) type chromophore forms the flat pattern, PICT state will be the major source for generation of fluorescence emission, whereas the twisted pattern will lead to the TICT state. Several typical model molecules have been introduced into the study of the PICT and TICT states.[78]

Scheme 38. PICT and TICT in Fluorescence Emission



As introduced, the generation of fluorescence emission for the NATs developed by Shi's group is generated by the PICT. However in other reported molecules, the TICT is

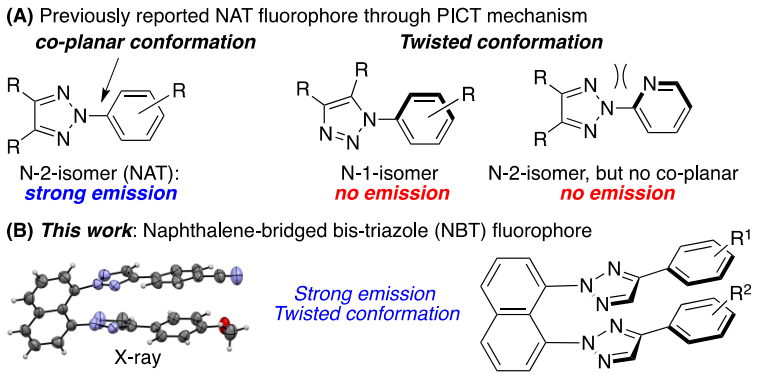
the dominate mechanism for fluorescence emission. When the electron donor (D) /acceptor (A) subgroups form a mutually perpendicular configuration, the TICT excited state will dominate.

3.2 Synthesis and characterization of naphthalene-bridged bis-N-2-aryl triazoles (NBTs) as efficient fluorescence probe through twisted intramolecular charge transfer mechanism

To investigate the difference of PICT and TICT, as well as discover a new fluorophore based on TICT mechanism, naphthalene-bridged bis-N-2-aryl triazoles (NBTs) compounds were prepared and applied in the fluorescence study.

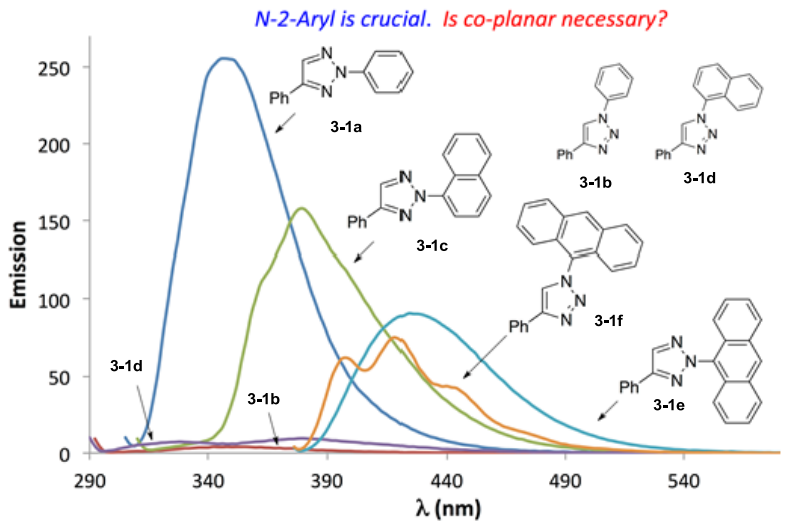
As mentioned, the PICT mechanism (observed in N-2 isomers, **Scheme 39A**) contributed the effective fluorescence emission in NATs compounds. Herein, we reported the design and synthesis of NBT compounds, which gave excellent fluorescence emission, even with a twisted conformation between triazole and N-2 aryl groups (**Scheme 39B**), suggesting the twisted intramolecular charge transfer (TICT) as the plausible mechanism for the observed strong fluorescence emission.[79]

Scheme 39. N-2-aryl Triazole Fluorophores



Previously, we reported that N-2-aryl triazole **3.1** gave very strong fluorescence emission while its N-1 isomer **3.2** gave no emission at all. Two key factors appeared to control the fluorescence emission in these NAT dyes: N-2 substitution and coplanar conformation between the two rings. However, the second assumption was greatly questioned by our recent studies of N-naphthalene triazoles. As shown in **Scheme 40**, we prepared phenyl triazole **3-1a** (N-2 isomer) and **3-1b** (N-1 isomer); N-naphthalene triazole **3-1c** (N-2 isomer) and **3-1d** (N-1 isomer). Similar to benzyl triazoles, the N-1 isomer **3-1b** and **3-1d** gave no fluorescence emission and N-2 isomer **3-1a** and **3-1c** gave strong emission. However, a closer look of **3-1c** suggests that coplanar conformation between naphthalene and triazole ring is highly unlikely due to the steric repulsion. In fact, in our previous research, we found the crystal structure of a similar analog to **3-1c** indicated a 49.5^{o} dihedral angle between the naphthalene ring and triazole ring.[80] These results initiated our interest in further exploring this new class of fluorescent dyes with the question whether the coplanar conformation is necessary.[81]

Scheme 40. Fluorescence Emission of NAT with Different Aryl Groups

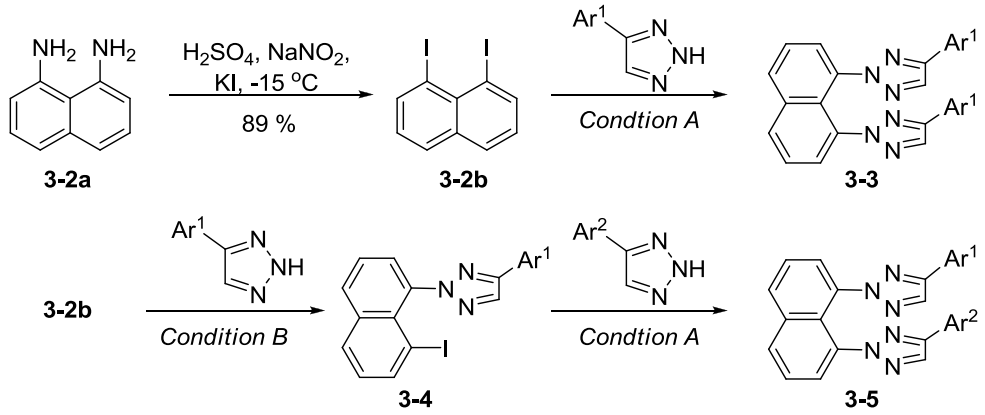


Besides the coplanar intramolecular charge transfer (PICT), another feasible photochemical process associated with this type of extended aromatic ring—i.e., the twisted intramolecular charge transfer (TICT)--was first introduced by Grabowski et al.[82] One important feature of TICT type of emission is the feasibility of the donor unit in initiating the charge transfer. Numerous nitrogen containing heterocycles have been studied as donors in TICT emitting molecules.[83] However, to the best of our knowledge 1,2,3-triazoles have not been used as a potential donor in the TICT fluorophores and their photochemical properties remain unknown.

To explore triazole derivatives as potential TICT emitting dyes, we prepared anthracene substituted triazole **3-1e** (N-2) and **3-1f** (N-1). Clearly, the anthracene should provide a large steric repulsion that can prevent the formation of coplanar conformation even in the N-2 isomer **3-1e**. Thus the fluorescence emission should be mainly from the twisted state. Interestingly, both N-1 and N-2 isomers gave good

emission. However, three different emission bands were observed in the N-1 isomer **3-1f**, which was similar to the typical emission of aromatic substituted anthracene.[84] This result suggested that triazole-anthracene compounds were not good model molecules to evaluate the triazole's influence on TICT emission due to the notable background emission from anthracene. To better evaluate the triazole influence in the twisted systems, we designed the naphthalene-bridged bis-triazole (NBT).

Scheme 41. Synthesis of Naphthalene-bridged Bis-triazoles (NBTs)

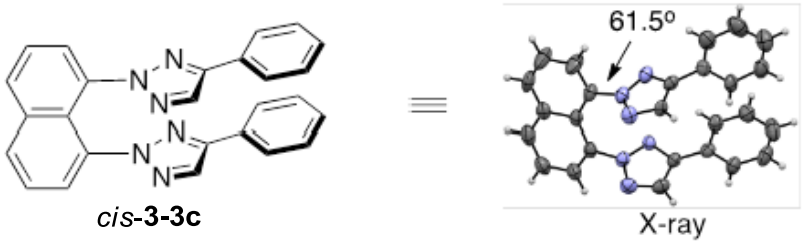


Condition A: 20 % CuI, 40 % Proline, 4.0 eq. K_2CO_3, DMSO, 120 °C;
Condition B: 20 % CuI, 40 % Proline, 4.0 eq. K_2CO_3, DMSO, 80 °C

As shown in **Scheme 41**, the bis-triazole can be readily prepared from the copper catalyzed coupling between naphthalene di-iodide **3-2b** and NH-triazole. Two different conditions were developed to reach NBT, either in a one-pot fashion (*Condition A*) or stepwise process (*Condition B*). With the use of these methods, both symmetrical NBT **3-3** and asymmetrical NBT **3-5** could be easily prepared. Notably, both N-1 and N-2 isomers were observed in all cases. The regioselectivity (ratio between N-2 and N-1 isomers) depends on the substituted groups (Ar), similar to what has been observed previously in triazoles functionalization.[85] The N-1 and N-2 isomers could be easily

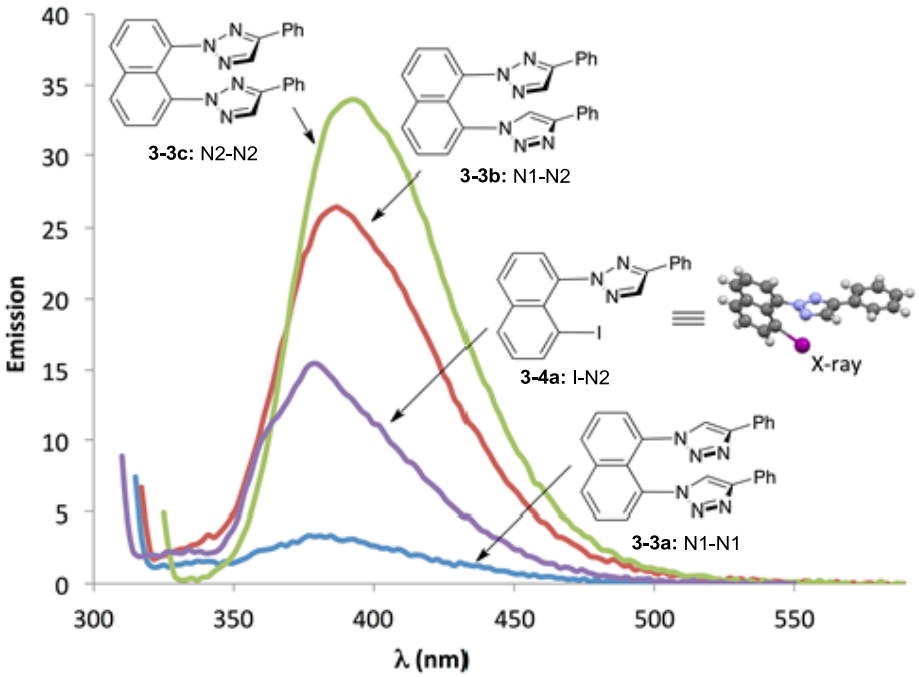
separated using column chromatography due to the significant polarity difference. Perhaps, the most important question for the synthesis of NBT was how to identify the relative position of the two triazole rings with restricted rotation. Considering the rotation of C-N bonds, theoretically two conformers (*cis* and *trans*) could be formed. Interestingly, during our synthesis, only one conformer was observed in nearly all cases, which was later confirmed to be the *cis*-conformer via X-ray crystallography (**Scheme 42**).

Scheme 42. X-ray Crystallography Confirmed the Formation of *Cis*-conformer



As shown in the X-ray crystal structure, the twisted conformation was confirmed between triazole and naphthalene rings with a dihedral angle of 61.5°. The crystal structure of mono-triazole substituted **3-4a** (Ar^1 = Ph, with I on naphthalene ring) was also obtained. Similarly, the dihedral angle observed for 3-4a between these two rings is 62.9°. With all clearly characterized NBTs, their fluorescent properties were measured and shown in **Scheme 43**.

Scheme 43. Fluorescence Emission of NBT **3-3** and **3-4a**



As shown by the solid-state crystal structures, both bis-triazole NBT **3-3** and mono-triazole **3-4** adopted a twisted conformation. However, while N-2 isomers generally gave good fluorescence emission, the N-1 isomers gave almost no emission in all cases. The emission intensity of NBT **3-3** followed a clear trend of N2-N2 > N2-N1 > N1-N1 (almost no emission). Due to the rotation strain, it is impossible for NBT **3-3** to adopt a planar conformation even in solution. Thus the observed good fluorescence emission of the N-2 isomers likely represents the photochemical process associated TICT states. The optical properties (emission, excitation and quantum yields) of compounds **3-3** and **3-4** were determined and summarized in **Table 9**.

Table 9. Comparison of Optical Properties of Different NBTs [a]

	R^1/R^2	excitation	emission	Φ	Stokes shift
NAT					
3-1a	-	298	347	0.34	49
3-4a	N2-TA-I	300	378	0.20	78
NBT					
3-3a	R^1=R^2=H (N1-N1)	-	-	<0.01	-
3-3b	R^1=R^2=H (N1-N2)	307	384	0.13	77
3-3c	R^1=R^2=H (N2-N2)	315	393	0.24	78
3-5a	R^1=R^2=Cl	305	393	0.26	88
3-5b	R^1=R^2=OMe	315	403	0.29	88
3-5c	R^1=R^2=COOMe	300	396	0.41	96
3-5d	R^1=R^2=CN	302	403	0.47	101
3-5e	R^1=OMe, R^2=CN	300	408	0.39	108

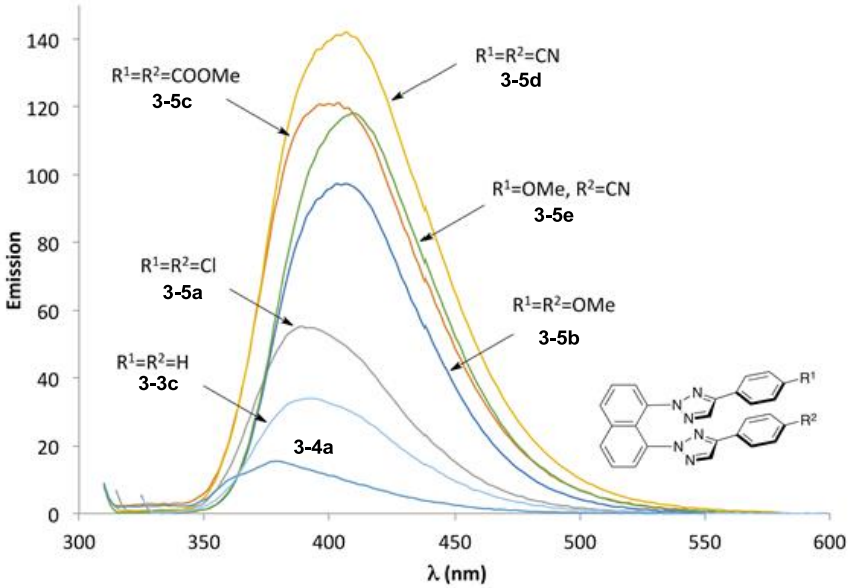
[a]Sample information: 1.0 x 10^{-6} mol/L in dichloromethane; Quantum yields (Φ) were determined based on 1.0 x 10^{-6} mol/L 9,10-diphenylanthracene in cyclohexane (Φ = 0.9); Calculated photo emission integration from the original spectra. All fluorescence data are measured under identical conditions.

While these N-2 isomers of NBTs were identified as a new class of fluorophores, one interesting feature offered by the naphthalene-bridge was the potential for π-π stacking between the two triazoles.[86] As revealed by the structural analysis of **3-3c**, the two triazoles in NBT are nearly parallel, with the distance just slightly longer than the sum of the van der Waals radii. Thus, it is reasonable to expect that the substituted groups on the triazole phenyl ring may provide various electronic effects that will influence the

overall optical properties[87] In order to explore the substituted group influence, a series of symmetrical and asymmetrical NBT 3-5 were prepared with various substituents on the triazole phenyl rings. Their photochemical properties were evaluated (**Table 9**), and the fluorescence spectra of some representative NBTs are shown in **Scheme 44**.

Among all the tested NBTs, the N-2 substitution is crucial for effective emission. Compared with previous planar NAT **3-1a**, the new twisted NBT fluorophores gave more red shift emissions approximately 400 nm (blue light). Interestingly, although the two triazole rings are nearly parallel, changing the substituent groups on phenyl rings did not influence the overall emission of the NBT. For example, with either EDG (**3-5b**) or EWG (**3-5c** and **3-5d**) substituted NBT; there were few changes on the emission and excitation wavelengths. Furthermore, substrate **3-5e** with EDG and EWG incorporated on different rings also gave similar emission, which strongly suggested that minimal π-π interactions occurred between the two rings. Notably, the substitute groups did help to improve the quantum yields (up to 47 %) through the introduction of extended conjugations.[88] Overall, in comparison with NAT, this new NBT system gave significantly higher fluorescence efficiency, which implied great potential for future applications.

Scheme 44. Fluorescence Emission of NBT **3-5** and **3-4a**



3.3 Conclusion

In conclusion, we herewith report a new type of triazole based fluorescence-active compounds: naphthalene-bridged bis-triazole (NBT). Practical syntheses have been developed and regio-isomers of compounds were characterized by X-ray crystallography. The fluorescence studies reveal that in this twisted system, the N-2 substitution is crucial for effective fluorescence emission. Comparing with previously reported NAT system, this new NBT gave higher fluorescence efficiency and larger Stokes shifts, which warrants the potential as new molecule probes for chemical and biological applications.

3.4 Contribution

Yanwei Zhang was the researcher who had first investigated the reaction condition and fluorescence property. Together, Yanwei Zhang and Xiaohan Ye were responsible for substrate scope, NMR spectrum, fluorescence data and manuscript completion for successful submission to *Journal of Organic Chemistry*. The detailed X-ray crystallographic data analysis of compound **3-3c** was done by Prof. Jeffrey L. Petersen, C. Eugene Bennett Department of Chemistry, West Virginia University.

References

[1] (a) A. S. K. Hashmi; F. D. Toste, *Modern Gold Catalyzed Synthesis,* Wiley-VCH, Weinheim, 2012; (b) A. S. K. Hashmi; M. Rudolph, *Chem. Soc. Rev*. **2012**, *41*, 2448; (c) D. J. Gorin, B. D. Sherry; F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351; (d) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266; (e) E. Jimenez-Nunez; A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326; (f) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180; (g) A. Furstner and P. W. Davies, *Angew. Chem., Int. Ed.* **2007**, *46*, 3410; (h) L. Zhang, J. Sunand S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271; (i) A. S. K. Hashmi; G. J. Hutchings*, Angew. Chem. Int. Ed.* **2006**, *45*, 7896.

[2] (a) Nösel, P.; dos Santos Comprido, L. N.; Lauterbach, T.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *J. Am. Chem. Soc.* **2013**, *135*, 15662; (b) Ji, K.; Zhao, Y.; Zhang, L. *Angew. Chem. Int. Ed.* **2013**, *52*, 6508; (c) González, A. Z.; Benitez, D.; Tkatchouk, E.; Goddard, W. A.; Toste, F. D. *J. Am. Chem. Soc.* **2011**, *133*, 5500; (d) Boogaerts, I. I. F.; Nolan, S. P. *J. Am. Chem. Soc.* **2010**, *132*, 8858.

[3] (a) A. S. K. Hashmi, J. P. Weyrauch, M. Rudolph; E. Kurpejovic, *Angew. Chem. Int. Ed.* **2004**, *43*, 6545; (b) A. S. K. Hashmi, M. Rudolph, J. P. Weyrauch, M. Wolfle, W. Frey; J. W. Bats, *Angew. Chem. Int. Ed.* **2005**, *44*, 2798; (c) N. Debono, M. Iglesias; F. Sanchez, *Adv. Synth. Catal.* **2007**, *349*, 2470; (d) A. S. K. Hashmi, M. Rudolph, H. U. Siehl, M. Tanaka, J. W. Bats; W. Frey, *Chem. Eur. J.* **2008**, *14*, 3703; (e) N. D. Shapiro, Y. Shi, F. D. Toste, *J. Am. Chem. Soc*. **2009**, *131*, 11654; (f) Y. Zhang, B. Feng; C. Zhu, *Org. Biomol. Chem.* **2012**, *10*, 9137; (g) J. A. O'Neill, G. M. Rosair, A. L. Lee, *Catal. Sci. Technol.* **2012**, *2*, 1818.

[4] (a) A. S. K. Hashmi; F. D. Toste, *Modern Gold Catalyzed Synthesis,* Wiley-VCH, Weinheim, 2012; (b) A. S. K. Hashmi; M. Rudolph, *Chem. Soc. Rev.* **2012**, *41*, 2448; (c) D. J. Gorin, B. D. Sherry; F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351; (d) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266; (e) E. Jimenez-Nunez; A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326; (f) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180; (g) A. Furstner; P. W. Davies, *Angew. Chem. Int. Ed.* **2007**, *46*, 3410; (h) L. Zhang, J. Sun; S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271; (i) A. S. K. Hashmi; G. J. Hutchings, *Angew. Chem. Int. Ed.* **2006**, *45*, 7896.

[5] (a) Gaillard, S.; Cazin, C. S. J.; Nolan, S. P. *Acc. Chem. Res.* **2011**, *45*, 778; (b) Nolan, S. P. *Acc. Chem. Res.* **2010**, *44*, 91; (c) Marion, N.; Nolan, S. P. *Chem. Soc. Rev.* **2008**, *37*, 1776; (d) Marion, N.; Carlqvist, P.; Gealageas, R.; de Frémont, P.; Maseras, F.; Nolan, S. P. *Chem. Eur. J.* **2007**, *13*, 6437.

[6] Schwerdtfeger P.; Hermann H. L.; Schmidbaur H. *Inorg. Chem.*, **2003**, *42*, 1334.

[7] (a) Mauger, C. C.; Mignani, G. A. *Aldrichimica Acta.* **2006**, *39*, 17; (b) Schlummer, B.; Scholz, U. *Adv. Synth. Catal.* **2004**, *346*, 1599.

[8] (a) Chabre, Y. M.; Roy, R. *Curr. Top. Med. Chem.* **2008**, *8*, 1237;. (b) Colombo, M.; Peretto, I. *Drug Discovery Today* **2008**, *13*, 677; (c) Hanselmann, R.; Job, G. E.; Johnson, G.; Lou, R. L.; Martynow, J. G.; Reeve, M. M. *Org. Process Res. Dev*. **2010**, *14*, 152; (d) Moumne, R.; Larue, V.; Seijo, B.; Lecourt, T.; Micouin, L.; Tisne, C. *Org. Biomol. Chem*. **2010**, *8*, 1154–1159; (e) Li, H. M.; Cheng, F. O.; Duft, A. M.; Adronov, A. *J. Am. Chem. Soc*. **2005**, *127*, 14518; (f) Rozkiewicz, D. I.; Janczewski, D.; Verboom, W.; Ravoo, B. J.; Reinhoudt, D. N. *Angew. Chem., Int. Ed*. **2006**, *45*, 5292; (g) Wyszogrodzka, M.; Haag, R. *Chem. Eur. J.* **2008**, *14*, 9202; (h) Gadzikwa,

T.; Farha, O. K.; Malliakas, C. D.; Kanatzidis, M. G.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2009**, *131*, 13613; (i) Golas, P. L.; Matyjaszewski, K. *Chem. Soc. Rev.* **2010**, *39*, 1338; (j) Hahn, M. E.; Muir, T. W. *Trends Biochem. Sci.* **2005**, *30*, 26; (k) Heal, W. P.; Wickramasinghe, S. R.; Leatherbarrow, R. J.; Tate, E. W. *Org. Biomol. Chem.* **2008**, *6*, 2308; (l) Ahsanullah, J.; Schmieder, P.; Kuhne, R.; Rademann, J. *Angew. Chem., Int. Ed*. **2009**, *48*, 5042; (m) Schneider, G. *Nat. Rev. Drug Discovery* **2010**, *9*, 273.

[9] (a) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596; (b) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004; (c) Moses, J. E.; Moorhouse, A. D. *Chem. Soc. Rev.* **2007**, *36*, 1249. (d) Wu, P.; Fokin, V. V. *Aldrichim. Acta.* **2007**, *40*, 7.

[10] (a) Wang, D.; Zhang, Y.; Harris, A.; Gautam, L. N. S.; Shi, X. *Adv. Syn. Catal.* **2011**, *353*, 2584;. (b) Wang, D.; Zhang, Y.; Cai, R.; Shi, X.; *Beilstein J. Org. Chem.* **2011**, *7*, 1014;. (c) Wang, D.; Gautam, L. N. S.; Bollinger, C.; Harris, A.; Li, M.; Shi, X. *Org. Lett.* **2011**, *13*, 2618; (d) Duan, H.; Sengupta, S.; Petersen, J. L.; Akhmedov, N.; Shi, X. *J. Am. Chem. Soc.* **2009**, *131*, 12100; (e) Duan, H.; Yan, W.; Sengupta, S.; Shi, X. *Bioorg. Med. Chem. Lett.* **2009**, 3899.

[11] (a) Aucagne, V.; Hanni, K. D.; Leigh, D. A.; Lusby, P. J.; Walker,¨D. B. *J. Am. Chem. Soc.* **2006**, *128*, 2186; (b) Suijkerbuijk, B. M. J. M.; Aerts, B. N. H.; Dijkstra, H. P.; Lutz, M.; Spek, A. L.; van Koten, G.; Gebbink, R. J. M. K. *Dalton. Trans.* **2007**, 1273; (c) Maeda, C.; Yamaguchi, S.; Ikeda, C.; Shinokubo, H.; Osuka, A.*Org. Lett.* **2008**, *10*, 549; (d) Mullen, K. M.; Gunter, M. J. *J. Org. Chem.* **2008**, *73*, 3336; (e) Detz, R. J.; Heras, S. A.; de Gelder, R.; van Leeuwen, P. W. N. M.; Hiemstra, H.; Reek, J. N.

H.; van Maarseveen, J. H. *Org. Lett.* **2006**, *8*, 3227; (f) Monkowius, U.; Ritter, S.; König, B.; Zabel, M.; Yersin, H. *Eur. J. Inorg. Chem.* **2007**, 4597; (g) Fukuzawa, S.; Oki, H.; Hosaka, M.; Sugasawa, J.; Kikuchi, S. *Org. Lett.* **2007**, *9*, 5557; (h) Richardson, C.; Fitchett, C. M.; Keene, F. R.; Steel, P. J. *Dalton Trans.* **2008**, 2534; (i) Schweinfurth, D.; Hardcastle, K. I.; Bunz, U. H. F. *Chem. Commun.* **2008**, *2203*; (j) Maisonial, A.; Serafin, P.; Traïkia, M.; Debiton, E.; Thery, V.; Aitken, D. J.;´ Lemoine, P.; Bernard, V.; Gautier, *A. Eur. J. Inorg. Chem.* **2008**, 298.

[12] Loren, Jon C.; Krasinski, Antoni; Fokin, Valery V.; Sharpless, K. Barry *Synlett,* **18**, *2005*, 2847.

[13] Zefirov, N.S.; Chapovskaya, N.K.; Kolesnikov, V. V. *Chem. Commoun.* **1971**, 1001.

[14] Béatrice Quiclet-Sire; Samir Z. Zard. *Synthesis*. **2005**, *19*, 3319.

[15] Sengupta, S.; Duan, H.; Lu, W.; Petersen, J. L.; Shi, X. *Org. Lett.* **2008**, *10*, 1493.

[16] Wang, K.; Chen, M.; Wang, Q.; Shi, X.; Lee, J. K. *J. Org. Chem.* **2013**, *78*, 7249.

[17] Yan, W.; Liao, T.; Tuguldur, O.; Zhong, C.; Petersen, J. L.; Shi, X. *Chem. Asian. J.* **2011**, *6*, 2720.

[18] (a) Chen, Y.; Liu, Y.; Petersen, J. L.; Shi, X. *Chem. Commun.* **2008**, 3254; (b) Liu, Y.; Yan, W.; Chen, Y.; Petersen, J. L.; Shi, X. *Org. Lett.* **2008**, *10*, 5389.

[19] Duan, H.; Sengupta, S.; Petersen, J. L.; Shi, X. *Organometallics* **2009**, *28*, 2352.

[20] Liao, W.; Chen, Y.; Liu, Y.; Duan, H.; Petersen, J. L.; Shi, X. *Chem. Commun.* **2009**, 6436.

[21] (a) Duan, H.; Sengupta, S.; Petersen, J. L.; Akhmedov, N. G.; Shi, X. *J. Am. Chem. Soc.* **2009**, *131*, 12100; (b) Xi, Y.; Wang, D.; Ye, X.; Akhmedov, N. G.; Petersen, J. L.; Shi, X. *Org. Lett.* **2013**, *16*, 306.

[22] (a) Herrero-Gómez, E.; Nieto-Oberhuber, C.; López, S.; Benet-Buchholz, J.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2006,** *45,* 5455. (b) Patrick, S. R.; Gómez-Suárez, A.; Slawin, A. M. Z.; Nolan, S. P. *Organometallics* **2013**, 33, 421.

[23] Nomiya, K.; Noguchi, R.; Ohsawa, K.; Tsuda, K. *J. Chem. Soc., Dalton Trans.* **1998,** 4101.

[24] Zhang, L. *J. Am. Chem. Soc.* **2005,** *127,* 16804–16805.

[25] Zhang, L.; Wang, S. *J. Am. Chem. Soc.* **2006,** *128,* 1442–1443.

[26] Buzas, A.; Istrate, F.; Gagosz, F. *Org. Lett.* **2006,** *8,* 1957–1959.

[27] Wang, S.; Zhang, L. *Org. Lett.* **2006,** *8,* 4585–4587.

[28] Wang, S.; Zhang, L. *J. Am. Chem. Soc.* **2006,** *128,* 8414–8415.

[29] Buzas, A.; Gagosz, F. *J. Am. Chem. Soc.* **2006,** *128,* 12614–12615.

[30] Wang, S.; Zhang, L. *J. Am. Chem. Soc.* **2006,** *128,* 14274–14275.

[31] Marion, N.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007,** *46,* 2750–2752.

[32] Marco-Contelles, J.; Soriano, E. *Chem.–Eur. J.* **2007,** *13,* 1350–1357.

[33] Barluenga, J.; Riesgo, L.; Vicente, R.; Lopéz, L. A.; Tomás, M. *J. Am. Chem. Soc.* **2007,** *129,* 7772–7773.

[34] Shi, F.-Q.; Li, X.; Xia, Y.; Zhang, L.; Yu, Z.-X. *J. Am. Chem. Soc.* **2007,** *129,* 15503–15512.

[35] Saucy, R.; Marbet, R.; Lindlar, H.; Isler, O. *Helv. Chim. Acta* **1959,** *42,* 1945–1955.

[36] Cherbuliez, E.; Moll, H.; Baehler, B. R.; Rabinowitz, J. *Helv. Chim. Acta* **1967,** *50,* 1154–1158.

[37] Wang, D.; Gautam, L. N. S.; Bollinger, C.; Harris, A.; Li, M.; Shi, X. *Org. Lett.* **2011,** *13,* 2618–2621.

[38] Marion, N.; Díez-González, S.; de Fremont, P.; Noble, A. R.;Nolan, S. P. *Angew. Chem., Int. Ed.* **2006,** *45,* 3647–3650.

[39] Sengupta, S.; Duan, H.; Lu, W.; Petersen, J. L.; Shi, X. *Org. Lett.* **2008,** *10,* 1493–1496.

[40] Chen, Y.; Liu, Y.; Petersen, J. L.; Shi, X. *Chem. Commun.* **2008,** 3254–3256.

[41] Liu, Y.; Yan, W.; Chen, Y.; Petersen, J. L.; Shi, X. *Org. Lett.* **2008,** *10,* 5389–5392.

[42] Duan, H.; Yan, W.; Sengupta, S.; Shi, X. *Bioorg. Med. Chem. Lett.* **2009,** *19,* 3899–3902.

[43] Yan, W.; Wang, Q.; Chen, Y.; Petersen, J. L.; Shi, X. *Org. Lett.* **2010,** *12,* 3308–3311.

[44] Duan, H.; Sengupta, S.; Petersen, J. L.; Akhmedov, N. G.; Shi, X. *J. Am. Chem. Soc.* **2009,** *131,* 12100–12102.

[45] Chen, Y.; Yan, W.; Akhmedov, N. G.; Shi, X. *Org. Lett.* **2010,** *12,* 344–347.

[46] Wang, D.; Ye, X.; Shi, X. *Org. Lett.* **2010,** *12,* 2088–2091.

[47] Yu, M.; Zhang, G.; Zhang, L. *Org. Lett.* **2007,** *9,* 2147–2150.

[48] Ye, L.; Zhang, L. *Org. Lett.* **2009,** *11,* 3646–3649.

[49] Yu, M.; Zhang, G.; Zhang, L. *Tetrahedron* **2009,** *65,* 1846–1855.

[50] Mauleón, P.; Krinsky, J. L.; Toste, F. D. *J. Am. Chem. Soc.* **2009,** *131,*4513–4520.

[51] (a) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009,** *109,* 3612–3676; (b) Fremont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009,** *253,* 862–892; (c) Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008,** *41,* 1440–1449; (d) Marion, N.; Nolan, S. P. *Chem. Soc. Rev.* **2008,** *37,* 1776–1782; (e) Diez-Gonzalez, S.; Nolan, S. P. *Acc. Chem. Res.* **2008,** *41,* 349–358.

[52] For Au-catalyzed Meyer–Schuster rearrangements, see: (a) Georgy, M.; Boucard, V.; Campagne, J.-M. *J. Am. Chem. Soc.* **2005,** *127,* 14180–14181. (b) Engel, D.; Dudley, G. B. *Org. Lett.* **2006,** *8,* 4027–4029. (c) Yu, M.; Li, G.; Wang, S.; Zhang, L.; *Adv. Synth. Catal.* **2007,** *349,* 871– 875. (d) Ramon, R. S.; Marion, N.; Nolan, S. P. *Tetrahedron* **2009,** *65,* 1767–1773. (e) Ye, L.; Zhang, L. *Org. Lett.* **2009**, *11,* 3646–3649. (f) Gaillard, S.; Bosson, J.; Ramon, R. S.; Nun, P.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Eur. J.* **2010,** *16,* 13729–13740. (g) Zanoni, G.; D'Alfonso, A.; Porta, A.; Feliciani, L.; Nolan, S. P.; Vidari, G. *Tetrahedron* **2010,** *66,* 7472–7478. (h) Merlini, V.; Gaillard, S.; Porta, A.; Zanoni, G.; Vidari, G.; Nolan, S. P. *Tetrahedron Lett.* **2011,** *52,* 1124–1127. (i) Pennell, M. N.; Unthank, M. G.; Turner, P.; Sheppard, T. D. *J. Org. Chem.* **2011,** *76,* 1479–1482.

[53] For selected examples of 1,3-shifts, see: (a) Zhang, L. *J. Am. Chem. Soc.* **2005,** *127,* 16804–16805. (b) Zhang, L; Wang, S. *J. Am. Chem. Soc.* **2006,** *128,* 1442–1443. (c) Buzas, A.; Istrate, F.; Gagosz, F. *Org. Lett.* **2006,** *8,* 1957–1959. (d) Wang, S.; Zhang, L. *Org. Lett.* **2006,** *8,* 4585–4587. (e) Wang, S.; Zhang, L. *J. Am. Chem. Soc.* **2006,** *128,* 8414–8415. (f) Buzas, A.; Gagosz, F. *J. Am. Chem. Soc.* **2006,** *128,* 12614–12615. (g) Wang, S.; Zhang, L. *J. Am. Chem. Soc.* **2006,** *128,* 14274–14275. (h) Marion, N.; Nolan, S. P. *Angew. Chem.* **2007,** *119,* 2806–2809; *Angew. Chem. Int. Ed.* **2007,** *46,* 2750–2752. (i) Marco-Contelles, J.; Soriano, E. *Chem. Eur. J*. **2007**, *13,* 1350–1357. (j) Barluenga, J.; Riesgo, L.; Vicente, R.; Lopez, L.; Tomas, M. *J. Am. Chem. Soc.* **2007,** *129,* 7772–7773. (k) Shi, F.-Q.; Li, X.; Xia, Y; . Zhang, L.; Yu, Z.-X. *J. Am. Chem. Soc.* **2007,** *129,* 15503–15512.

[54] Marion, N.; Carlqvist, P.; Gealageas, R.; Fremont, P.; Maseras, F.; Nolan, S. P. *Chem. Eur. J.* **2007,** *13,* 6437–6451.

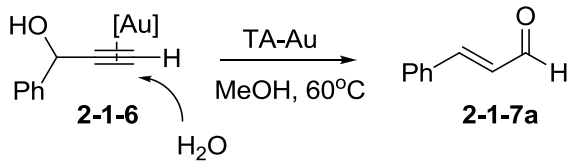
[55] Marion, N.; Diez-Gonzalez, S.; Fremont, P.; Noble, A. R.; Nolan, S. P. *Angew. Chem.* **2006,** *118,* 3729; *Angew. Chem. Int. Ed.* **2006,** *45,* 3647- 3650.

[56] Ramon, R. S.; Gaillard, S.; Slawin, A. M. Z.; Porta, A.; D'Alfonso, A.; Zanoni, G.; Nolan, S. P. *Organometallics* **2010,** *29,* 3665–3668.

[57] Significant TA-Au catalyst decomposition was observed while treating with 4a over time (after 30 h) even at room temperature.

[58] It is known that the gold cations decompose faster in the presence of terminal alkynes. The 31P NMR investigation of Au(I) decomposition in terminal alkyne has been reported.

[59] Reaction of a terminal propargylic alcohol gave poor yields due to the undesired anti-Markovnikov addition.



TA-Au 2%	12h	29%
TA-Au 0.5% x 5 times	4h x 5 times	62%

[60] The allene ester from the TA-Au propargylic ester 2-1-1 catalyzed 3,3-rearrangment has been recently isolated, which confirmed the suggested rearrangement-hydration mechanism. See: Wang, D.; Gautam, L. N. S.; Bollinger, C.; Harris, A.; Li, M.; Shi, X. *Org. Lett.* **2011,** *13,* 2618–2621.

[61] For recent reviews, see: (a) A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2010**, *49*, 5232; (b) L. Liu, G. B. Hammond, *Chem. Soc. Rev.* **2012**, *41*, 3129; (c) R. E. M. Brooner, R. A. Widenhoefer, *Angew. Chem. Int. Ed.* **2013**, *52*, 11714.

[62] (a) Weber, D.; Gagné, M. R. *Org. Lett.* **2009**, *11*, 4962; (b) Weber, D.; Tarselli, M. A.; Gagné, M. R. *Angew. Chem. Int. Ed.* **2009**, *48*, 5733.

[63] Wang, D.; Cai, R.; Sharma, S.; Jirak, J.; Thummanapelli, S. K.; Akhmedov, N. G.; Zhang, H.; Liu, X.; Petersen, J. L.; Shi, X. *J. Am. Chem. Soc.* **2012**, *134*, 9012.

[64] de Frémont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 2411.

[65] Nieto-Oberhuber, C.; Muñoz, M. P.; López, S.; Jiménez-Núñez, E.; Nevado, C.; Herrero-Gómez, E.; Raducan, M.; Echavarren, A. M. *Chem. Eur. J.* **2006**, *12*, 1677.

[66] (a)Weber, D.; Gagne, M. R. *Org. Lett.* **2009**, *11*, 4962. (b) Weber, S. G.; Rominger, F.; Straub, B. F. *Eur. J. Inorg. Chem***. 2012**, 2863. (c) Zhu, Y.; Day, C. S.; Zhang, L.; Hauser, K. J.; Jones, A. C. *Chem. Eur. J.* **2013,** *19,* 12264. (d) Homs, A.; Escofet, I.; Echavarren, A. M. *Org. Lett.* **2013**, *15,* 5782 and references cited therein.

[67] (a) Rudolph, M.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2012,** *41*, 2448. (b) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev*. **2008**, *108,* 3351. (c) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Rev.* **2008,** *108,* 3326. (d) Arcadi, A. *Chem. Rev.* **2008**, *108,* 3266. (e) Widenhoefer, R. A. *Chem. Eur. J.* **2008,** *14,* 5382.

[68] Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc*. **2004,** *126,* 15978.

[69] Nun, P.; Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun*. **2010**, *46*, 9113.

[70] (a) Wang, D.; Ye, X.; Shi, X. *Org. Lett.* **2010**, *12*, 2088. (b) Wang, D.; Gautam, L. N.; Bollinger, C.; Harris, A.; Li, M.; Shi, X. *Org. Lett*. **2011**, *13*, 2618. (c) Wang, Q.; Aparaj, S.; Akhmedov, N. G.; Petersen, J. L.; Shi, X. *Org. Lett*. **2012**, *14,* 1334. (d) Xi, Y.; Wang, Q.; Su, Y.; Li, M.; Shi, X. *Chem. Commun*. **2014,** *50*, 2158. (e) Xi, Y.; Dong, B.; Shi, X. *Beilstein J. Org. Chem*. **2013,** *9*, 2537. (f) Xi, Y.; Wang, D.; Ye, X.; Akhmedov,

N. G.; Petersen, J. L.; Shi, X. *Org. Lett*. **2014,** *16*, 306. (g) Xi, Y.; Dong, B.; McClain, E. J.; Wang, Q.; Gregg, T. L. Akhmedov, N. G.; Petersen, J. L.; Shi, X. *Angew. Chem., Int. Ed*. **2014**, *53*, 4657-4461. (h) Wang, Q.; Motika, S. E.; Akhmedov, N. G.; Petersen, J. L.; Shi, X. *Angew. Chem., Int. Ed.* **2014,** *53,* 5418-5422.

[71] Thermal [2 + 2] cycloaddition of allene: (a) Skraba, S. L.; Johnson, R. P. *J. Org. Chem.* **2012,** *77,* 11096. (b) Tejedor, D.; Méndez-Abt, G.; González-Platas, J.; Ramírez, M. A.; García-Tellado, F. *Chem. Commun*. **2009,** 2368. (c) Christl, M.; Groetsch, S.; Günther, K. *Angew. Chem., Int. Ed*. **2000,** *39,* 3261. (d) Alcaide, B.; Almendros,P.; Aragoncillo, C. *Chem. Soc. Rev.* **2010**, *39*, 783.

[72] For selected examples, see: a) Saha S.; Stoddart J. F. *Chem. Soc. Rev.* **2007**, *36*, 77. b) Sakai N.; Sisson A. L.; Burgi T.; Matile S. *J. Am. Chem. Soc.* **2007**, *129*, 15758. c) Díaz D. D.; Cid J. J.; Vazquez P.; Torres T. *Chem. Eur. J.* **2008**, *14*, 9261. d) Armstrong N. R.; Veneman P. A.; Ratcliff E.; Placencia D.; Brumbach M. *Acc. Chem. Res.* **2009**, *42*, 1748. e) Singhal K.; Kalkan A. K. *J. Am. Chem. Soc.* **2010**, *132*, 429.

[73] For selected examples, see: a) Zhang J.; Campbell R. E.; Ting A. Y.; Tsien R. Y. *Nat. Rev. Mol. Cell Biol.* **2002**, *3*, 906. b) Calzaferri G.; Pauchard M.; Maas H.; Huber S.; Khatyr A.; Schaafsma T. *J. Mater. Chem.* **2002**, *12*, 1. c) Giepmans B. N. G.; Adams S. R.; Ellisman M. H.; Tsien R. Y. *Science* **2006**, *312*, 217; Cheon J.; Lee J. H.; *Acc. Chem. Res.* **2008**, *41*, 1630. d) Domaille D. W.; Que E. L.; Chang C. J. *Nat. Chem. Biol.* **2008**, *4*, 168.

[74] For selected recent examples, see: (a) Medintz, I. L.; Uyeda, H. T.; Goldman, E. R.; Mattoussi, H. *Nat. Mater*. **2005,** *4*, 435 – 446; (b) Johnsson, N.; Johnsson, K. *ACS*

Chem. Biol. **2007**, *2*, 31 – 38; (c) Low, P. S. W.; Henne, A.; Doorneweerd, D. D. *Acc. Chem. Res.* **2008**, *41*, 120 – 129; (d) Takaoka, Y.; Sakamoto, T.; Tsukiji, S.; Narazaki, M.; Matsuda, T.; Tochio, H.; Shirakawa, M.; Hamachi, I. *Nat. Chem*. **2009,** *1,* 557 – 561; (e) Jayagopal, A.; Halfpenny, K. C.; Perez, J. W.; Wright, D. W. *J. Am. Chem. Soc.* **2010,** *132,* 9789 – 9796; (f) Yang, Y.; Seidlits, S. K.; Adams, M. M.; Lynch, V. M.; Schmidt, C. E.; Anslyn, E. V.; Shear, J. B. *J. Am. Chem. Soc.* **2010**, *132,* 13114– 13116.

[75] For selected recent examp les, see: (a) Sohn, Y. S.; Goodey, A.; Anslyn, E. V.; McDevitt, J. T.; Shear, J. B.; Neikirk, D. P. *Biosens. Bioelectron.* **2005,** *21,* 303 –312; (b) Khong, S. H.; Sivaramakrishnan, S.; Png, R. Q.; Wong, L. Y.; Chia, P. J.; Chua, L. L.; Ho, P. K. H. *Adv. Funct. Mater.* **2007,** *17,* 2490 –2499; (c) Tian, E. T.; Wang, J. X.; Zheng, Y. M.; Song, Y. L.; Jiang, L.; Zhu, D. B. *J. Mater. Chem.* **2008,** *18,* 1116 – 1122; (d) Ensafi, A. A.; Far, A. K.; Meghdadi, S. *J. Hazard. Mater.* **2009**, *35* , 1069– 1075; (e) Zhao, Y. S.; Zhan, P.; Kim, J.; Sun, C.; Huang, J. X. *ACS Nano* **2010**, *4,* 1630– 1636; (f) Sparano, B. A.; Koide, K. *J. Am. Chem. Soc.* **2007,** *129,* 4785 – 4794.

[76] (a) Yan, D. C.; Mohsseni-Ala, J.; Auner, N.; Bolte, M.; Bats, J. W*. Chem . Eur. J*. **2007,** *13,* 7204 – 7214; (b) Zhang, X. Y.; Matsuo, Y.; Naka- mura, E. *Org. Lett.* **2008,** *10,* 4145 – 4147; (c) Dan-Hardi, M.; Serre, C.; Frot, T.; Rozes, L.; Maurin, G.; Sanchez, C.; Ferey, G. *J. Am. Chem. Soc.* **2009,** *131,* 10857–10859; (d) Wahab, M. A.; Hussain, H.; He, C. *Lang-muir* **2009,** *25,* 4743 – 4750; (e) Mercs, L.; Albrecht, M.; *Chem. Soc. Rev.* **2010,** *39,* 1903 –1912.

[77] Yan W.; Wang Q.; Lin Q.; Li M.; Petersen J. L.; Shi X. *Chem. Eur. J.* **2011**, *17*, 5011.

[78] Zhong, C. *Phys. Chem. Chem. Phys.***, 2015, *17*,** 9248-9257

[79] a) Rettig W. *Angew. Chem. Int. Ed.* **1986**, *25*, 971. b) Rettig W. *Appl. Phys. B* **1988**, *45*, 145.

[80] Liu Y.; Yan W.; Chen Y.; Petersen J. L.; Shi X. *Org. Lett.* **2008**, *10*, 5389.

[81] (a) Tonzola C. J.; Kulkarni A. P.; Gifford A. P.; Kaminsky W.; Jenekhe S. A. *Adv. Funct. Mater.* **2007**, *17*, 863.(b) Tong Q. X.; Lai S. L.; Chan M. Y.; Zhou Y. C.; Kwong H. L.; Lee C. S.; Lee S. T. *Chem. Mater*. **2008**, *20*, 6310. (c) Park Y.; Lee J. H.; Jung D. H.; Liu S. H.; Lin Y. H.; Chen L. Y.; Wu C. C.; Park J. *J. Mater. Chem.* **2010**, *20*, 5930. (d) Gómez R.; Veldman D.; Langeveld B. M. W.; Segura J. L.; Janssen R. A. J. *J. Mater. Chem.* **2007**, *17*, 427.

[82] (a) Grabowski Z. R.; Rotkiewicz K.; Rubaszewska W.; Kirkorkaminska E. *Acta. Phys. Pol. A.* **1978**, *54*, 767. (b) Grabowski Z. R.; Rotkiewicz K.; Siemiarczuk A. *J. Lumin.* **1979**, *18-9*, 420. (c) Grabowski Z. R.; Rotkiewicz K.; Siemiarczuk A.; Cowley D. J.; Baumann W. *Nouv. J. Chim.* **1979**, *3*, 443. (d) Grabowski Z. R.; Dobkowski J. *Pure Appl. Chem.* **1983**, *55*, 245.

[83] Selected examples see: (a) Dash N.; Chipem F. A. S.; Swaminathan R.; Krishnamoorthy G.; *Chem. Phys. Lett.* **2008**, *460*, 119. (b) Mishra A.; Sahu S.; Dash N.; Behera S. K.; Krishnamoorthy G. *J. Phys. Chem. B* **2013**, *117*, 9469. (c) Xia J.; Zhou M.; Sun S.; Wang G.; Song P.; Ge M. *Dyes Pigm.* **2014**, *103*, 71.

[84] (a) Ishikawa J.; Sakamoto H.; Nakao S.; Wada H. *J. Org. Chem.* **1999**, *64*, 1913. (b) Thapaliya E. R.; Captain B.; Raymo F. M. *J. Org. Chem.* **2014**, *79*, 3973.

[85] (a) Sengupta S.; Duan H.; Lu W.; Petersen J. L.; Shi X. *Org. Lett.* **2008**, *10*, 1493. (b) Chen Y.; Liu Y.; Petersen J. L.; Shi X. *Chem. Commun*. **2008**, 3254. (c) Duan H.; Yan W.; Sengupta S.; Shi X. *Bioorg. Med. Chem. Lett.*, **2009**, *19*, 3899. (d) Yan W.; Wang Q.; Chen Y.; Petersen J. L.; Shi X. *Org. Lett.* **2010**, *12*, 3308.

[86] (a) Fun H. K.; Quah C. K.; Vijesh A. M.; Malladi S.; Isloor A. M. *Acta Cryst.* **2009**, *66*, 29. (b) Karimov Z.; Abdugafurov I.; Talipov S.; Tashkhodjaev B. *Acta Cryst.* **2010**, *66*, O1674. (c) Shan G. G.; Li H. B.; Zhu D. X.; Su Z. M.; Liao Y. *J. Mater. Chem.* **2012**, *22*, 12736.

[87] (a) Goodpaster J. V.; Harrison J. F.; McGuffin V. L. *J. Phys. Chem. A*. **2002**, *106*, 10645. (b) Focsaneanu K.S.; Scaiano J. C. *Photochem. Photobiol. Sci.* **2005**, *4*, 817.

[88] Brouwer A. M. *Pure Appl. Chem.* **2011**, *83*, 2213.

Appendix

Publications during Ph.D. work at West Virginia University:

1). Zhang, Y.; Ye, X.; Petersen, J. L.; Li, M.; Shi, X. *J. Org. Chem.* **2015**, *80*. 3664-3669.

2). Ye, X.; Zhang, Y.; He, Y.; Shi, X. *Tetrahedron Letters* **2015** submitted.

3). Su, Y.; Zhang, Y.; Akhmedov, N. G.; Petersen, J. L.; Shi, X. *Org. Lett.* ***2*014**, *16*, 2478-2481.

4). Senty, T. R.; Yalamanchi, M.; Zhang, Y.; Cushing, S. K.; Seehra, M. S.; Shi, X.; Bristow, A. D. *J. Appl. Phys.* ***2*014**,*115,* 163107.

5). Wang, D.; Zhang, Y.; Cai, R.; Shi, X. *Beilstein J. Org. Chem.* **2011**, *7*, 1014–1020. [special issue on gold catalysis]

6). Wang, D.; Zhang, Y.; Harris, A.; Gautam, L. N. S.; Shi, X. *Adv. Syn. Cat.* **2011**, *353*, 2584-2588.

Supporting Information

Chapter One: Triazole-Au(I) complex as chemoselective catalyst in promoting propargyl ester rearrangements.

I. General methods and materials

All of the reactions dealing with air and/or moisture-sensitive react were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from a commercial provider and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR. Flash column chromatography was performed on 230–430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer.

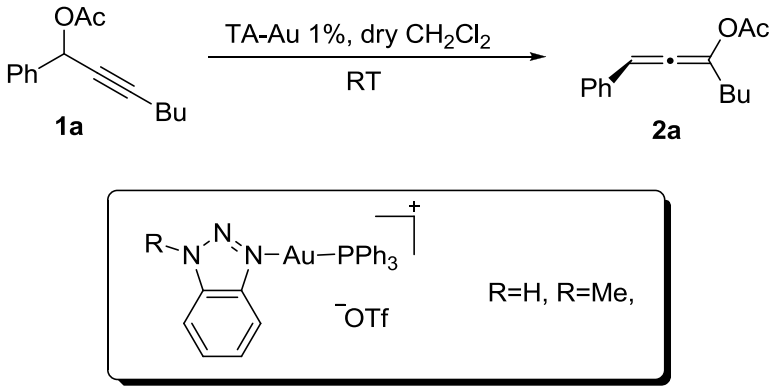
Substrates **1-1, 1-5** were synthesized according to the literatures as below:

1. Hashmi, A. S. K.; Rudolph, M. *Chem. Soc. Rev.* **2008,** *37,* 1766–1775.

2. Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008,** *108,*

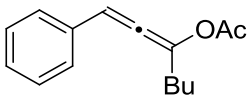
3. Arcadi, A. *Chem. Rev.* **2008,** *108,* 3266–3325.

Representative procedure for the preparation of allene 1-2a

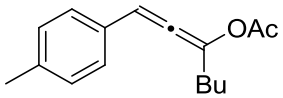


To a solution of **1-1a** (58 mg, 0.25 mmol) in dry CH2Cl2 (2.5 mL, 0.1 M), was added Au(I) catalyst (1.9 mg, 0.0025 mol, 1.0 mol %) at RT. The reaction mixture was stirred at RT and monitored by TLC. After the reaction was completed (2–10 h), the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane = 1 : 20, v/v) to give **1-2a** (91% yield) as colorless oil.

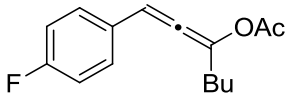
II. Compounds characterization



1-Phenylhepta-1,2-dien-3-yl acetate (1-2a): 91% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43-7.44 (m, 2H), 7.32-7.35 (m, 2H), 7.25-7.27 (m, 1H), 6.59 (t, *J* = 3.0 Hz, 1H), 2.33-2.37 (m, 2H), 2.15 (s, 3H), 1.46-1.51 (m, 2H), 1.38-1.43 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.7, 168.6, 133.9, 129.2, 128.6, 127.9, 127.0, 104.5, 31.5, 28.3, 22.1, 21.0, 13.8.

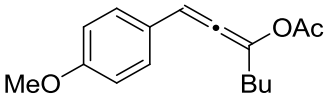


1-*p*-Tolylhepta-1,2-dien-3-yl acetate (**1-2b**): 90% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.56 (t, *J* = 3.0 Hz, 1H), 2.31-2.35 (m, 2H), 2.33 (s, 3H), 2.13 (s, 3H), 1.45-1.48 (m, 2H), 1.34-1.40 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.1, 168.6, 137.9, 131.0, 129.3, 127.7, 126.7, 104.4, 31.5, 28.3, 22.1, 21.2, 21.0, 13.8.

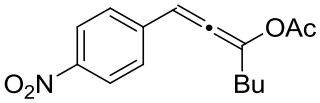


1-(4-Fluorophenyl)hepta-1,2-dien-3-yl acetate (**1-2c**): 87% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39-7.41 (m, 2H), 7.00-7.03 (m, 2H), 6.55 (t, *J* = 3.0 Hz, 1H), 2.31-2.35 (m, 2H), 2.15 (s, 3H), 1.44-1.49 (m, 2H), 1.36-1.41 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.4, 168.6, 161.8 (d, *J* = 246.5 Hz), 130.0 (d, *J* = 3.2 Hz),

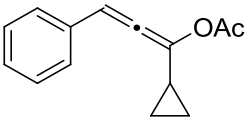
129.4 (d, *J* = 8.3 Hz), 126.9, 115.5 (d, *J* = 21.9 Hz), 103.4 (d, *J* = 2.7 Hz), 31.5, 28.3, 22.1, 21.0, 13.8.



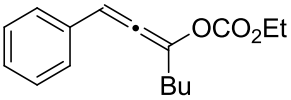
1-(4-Methoxyphenyl)hepta-1,2-dien-3-yl acetate (**1-2d**): 89% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.54 (t, *J* = 3.0 Hz, 1H), 3.81 (s, 3H), 2.28-2.34 (m, 2H), 2.14 (s, 3H), 1.44-1.47 (m, 2H), 1.35-1.39 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 195.3, 168.8, 159.6, 129.0, 126.6, 126.4, 114.2, 104.0, 55.3, 31.6, 28.4, 22.1, 21.1, 13.8.



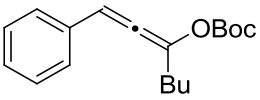
1-(4-Nitrophenyl)hepta-1,2-dien-3-yl acetate (**1-2e**): 89% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18-8.20 (m, 2H), 7.56-7.58 (m, 2H), 6.63 (t, *J* = 3.0 Hz, 1H), 2.34-2.37 (m, 2H), 2.17 (s, 3H), 1.45-1.55 (m, 2H), 1.37-1.41 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.2, 168.2, 147.2, 140.9, 128.3, 127.5, 124.0, 102.6, 31.4, 28.2, 22.1, 22.0, 13.8. HRMS Calculated for [C15H17NO4+Na]+: 298.1050, Found: 298.1050.



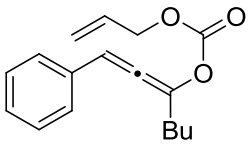
1-Cyclopropyl-3-phenylpropa-1,2-dienyl acetate (**1-2f**): 85% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39-7.40 (m, 2H), 7.31-7.33 (m, 2H), 7.23-7.24 (m, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 2.16 (s, 3H), 1.55-1.59 (m, 1H), 0.77-0.80 (m, 2H), 0.59-0.65(m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.4, 168.6, 133.7, 128.7, 128.1, 127.8, 105.1, 93.0, 20.9, 11.9, 6.4, 5.9. HRMS Calculated for [C14H14O2+H]+: 215.1066, Found: 215.1059.



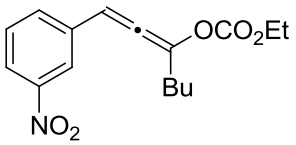
Ethyl 1-phenylhepta-1,2-dien-3-yl carbonate (1-5a): 92% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42-7.43 (m, 2H), 7.32-7.35 (m, 2H), 7.24-7.27 (m, 1H), 6.65 (t, *J* = 3.0 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.37-2.41 (m, 2H), 1.47-1.51 (m, 2H), 1.37-1.41 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.4, 153.1, 133.7, 128.7, 128.3, 128.1, 127.9, 105.7, 64.5, 31.3, 28.2, 22.1, 14.2, 13.8. HRMS Calculated for [C16H20O3+Na]+: 283.1305, Found: 283.1305.



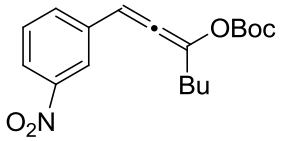
***t*-Butyl 1-phenylhepta-1,2-dien-3-yl carbonate** (**1-5b**): 91% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41-7.42 (m, 2H), 7.31-7.34 (m, 2H), 7.23-7.26 (m, 1H), 6.63 (t, *J* = 3.0 Hz, 1H), 2.35-2.39 (m, 2H), 1.50 (s, 9H), 1.46-1.48 (m, 2H), 1.37-1.41 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.7, 151.2, 134.0, 128.6, 128.1, 128.0, 127.8, 105.2, 82.9, 31.4, 28.3, 27.9, 22.1, 13.8. HRMS Calculated for [C18H24O3+Na]+: 311.1618, Found: 311.1604.



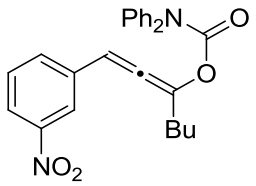
Allyl 1-phenylhepta-1,2-dien-3-yl carbonate (1-5c): 88% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.24-7.27 (m, 1H), 6.65 (s, 1H), 5.91-5.97 (m, 1H), 5.35 (d, *J* = 17.4 Hz, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 4.65 (d, *J* = 6.0 Hz, 2H), 2.30-2.34 (m, 2H), 1.47-1.53 (m, 2H), 1.36-1.43 (m, 2H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.3, 152.9, 133.7, 131.3, 128.7, 128.4, 128.1, 127.9, 119.2, 105.8, 68.9, 31.3, 28.2, 22.1, 13.8. HRMS Calculated for [C17H20O3+Na]+: 295.1305, Found: 295.1306.



Ethyl 1-(3-nitrophenyl)hepta-1,2-dien-3-yl carbonate (**1-5d**): 92% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25-8.26 (m, 1H), 8.09-8.12 (m, 1H), 7.77-7.78 (m, 1H), 7.51 (t, *J* = 8.1 Hz, 1H), 6.70 (t, *J* = 3.0 Hz, 1H), 4.24 (q, *J* = 7.4 Hz, 1H), 2.39-2.43 (m, 2H), 1.48-1.56 (m, 2H), 1.39-1.44 (m, 2H), 1.33 (t, *J* = 8.1 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.3, 152.7, 148.7, 135.9, 133.4, 129.5, 129.2, 122.7, 122.5, 103.6, 64.8, 31.3, 28.1, 22.1, 14.2, 13.7. HRMS Calculated for [C16H19NO5+Na]+: 328.1155, Found: 328.1142.

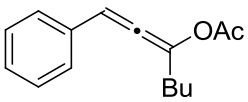


***t*-Butyl 1-(3-nitrophenyl)hepta-1,2-dien-3-yl carbonate** (**1-5e**): 89% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.23-8.24 (m, 1H), 8.09-8.11 (m, 1H), 7.77 (dt, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.50 (t, *J* = 8.1 Hz, 1H), 6.68 (t, *J* = 3.0 Hz, 1H), 2.37-2.41 (m, 2H), 1.51 (s, 9H), 1.47- 1.50 (m, 2H), 1.38-1.42 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.6, 150.8, 148.7, 136.2, 133.4, 129.5, 128.9, 122.5, 122.4, 103.2, 83.4, 31.4, 28.2, 27.7, 22.1, 13.8. HRMS Calculated for [C18H23NO5+Na]+: 356.1468, Found: 356.1454.

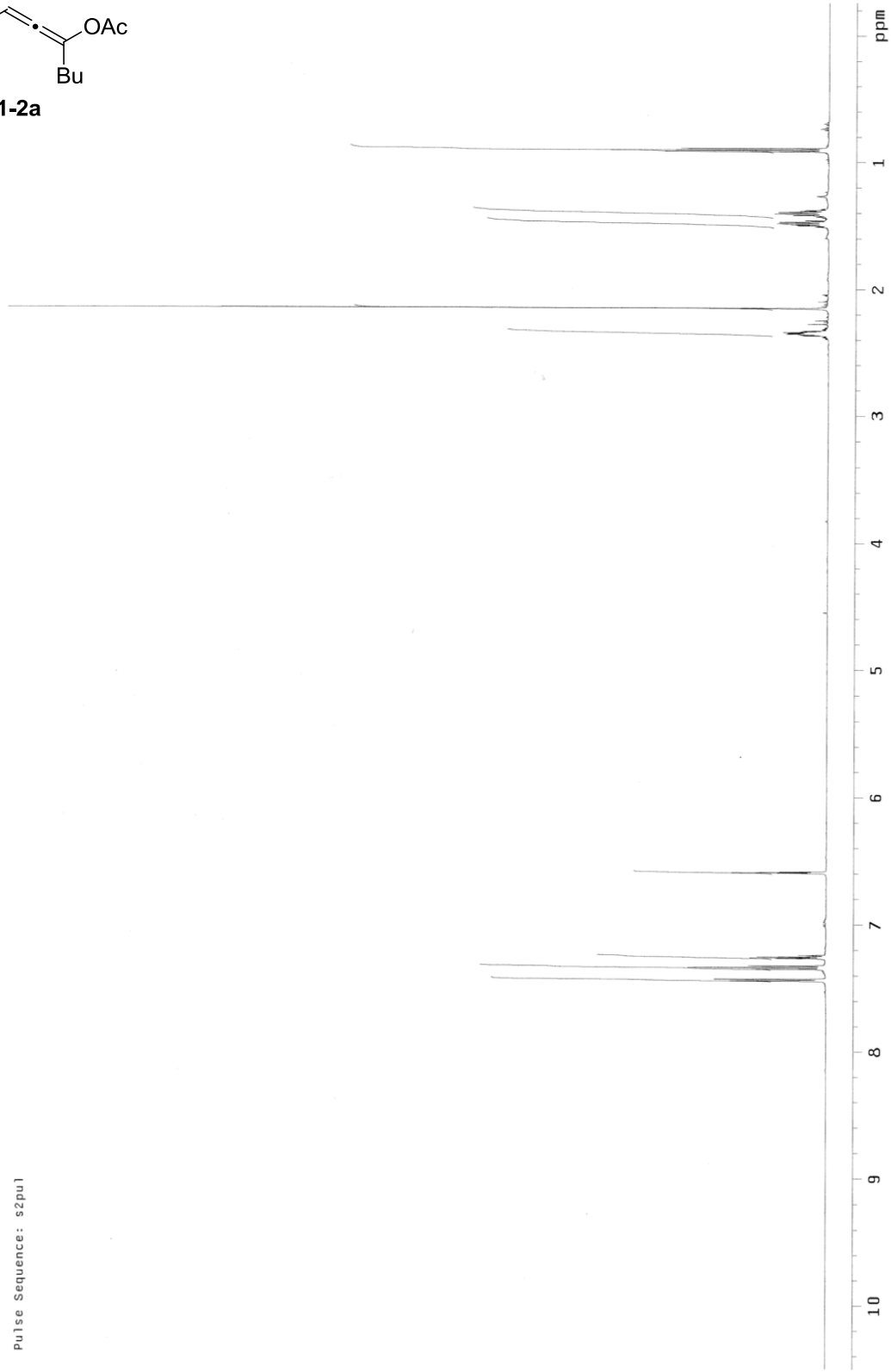


1-(3-Nitrophenyl)hepta-1,2-dien-3-yl diphenylcarbamate (**1-5f**): 85% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22 (t, *J* = 2.1 Hz, 1H), 8.07 (dq, *J* = 8.4 Hz, 1.0 Hz, 1H), 7.77 (dt, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 4H), 7.21-7.28 (m, 6H), 6.65 (t, *J* = 3.0 Hz, 1H), 2.30-2.34 (m, 2H), 1.31-1.41 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.7, 152.0, 148.6, 142.2, 136.4, 133.5, 129.5, 128.9, 128.3, 126.8, 126.4, 122.4, 122.3, 102.8, 31.6, 28.1, 21.9, 13.7. HRMS Calculated for [C26H24N2O4+Na]+: 451.1628, Found: 451.1610

III. NMR spectra



1-2a



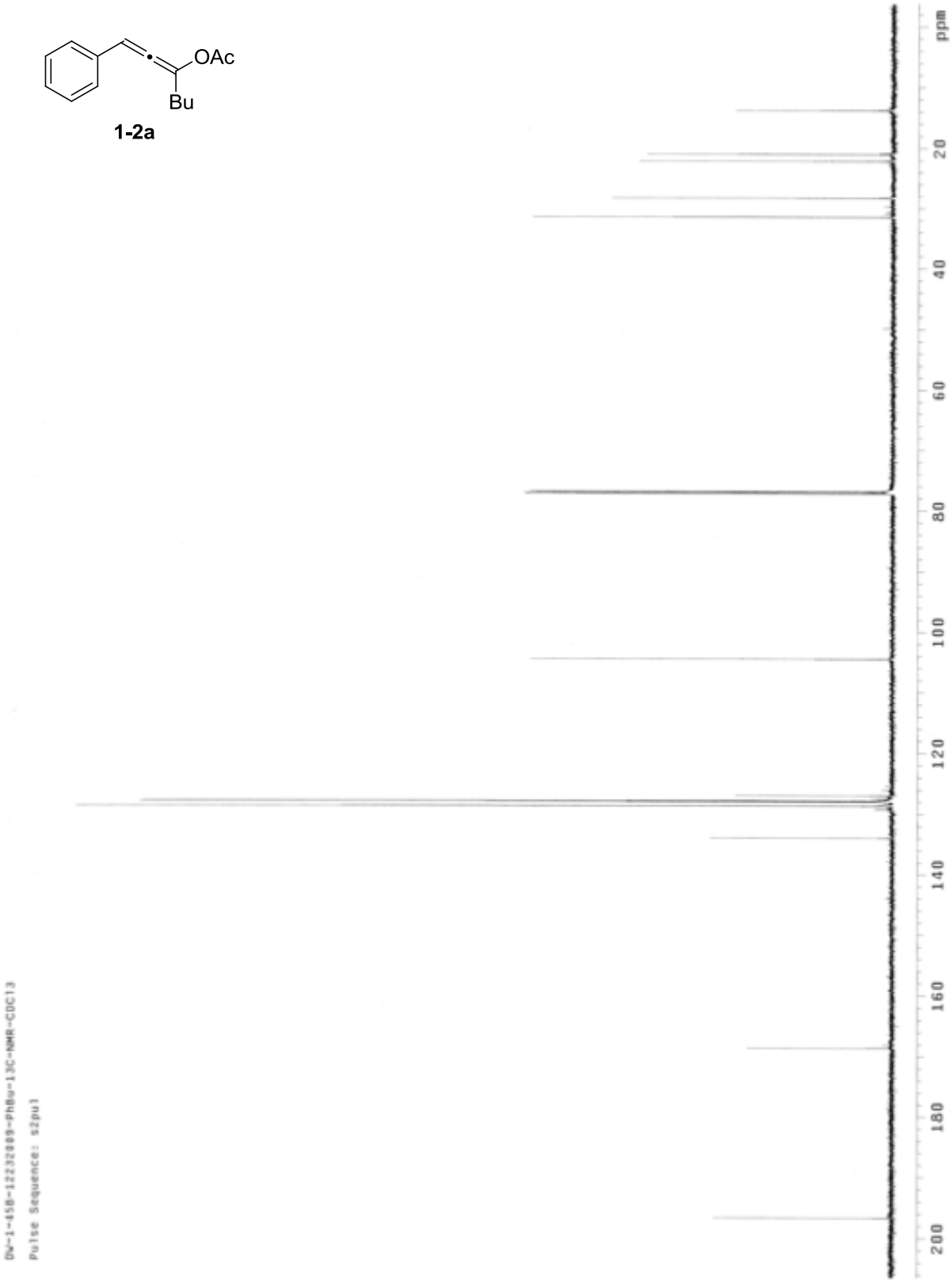
DW-1-45B-12232009-PhBu

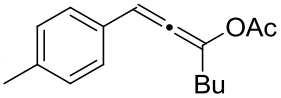
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul

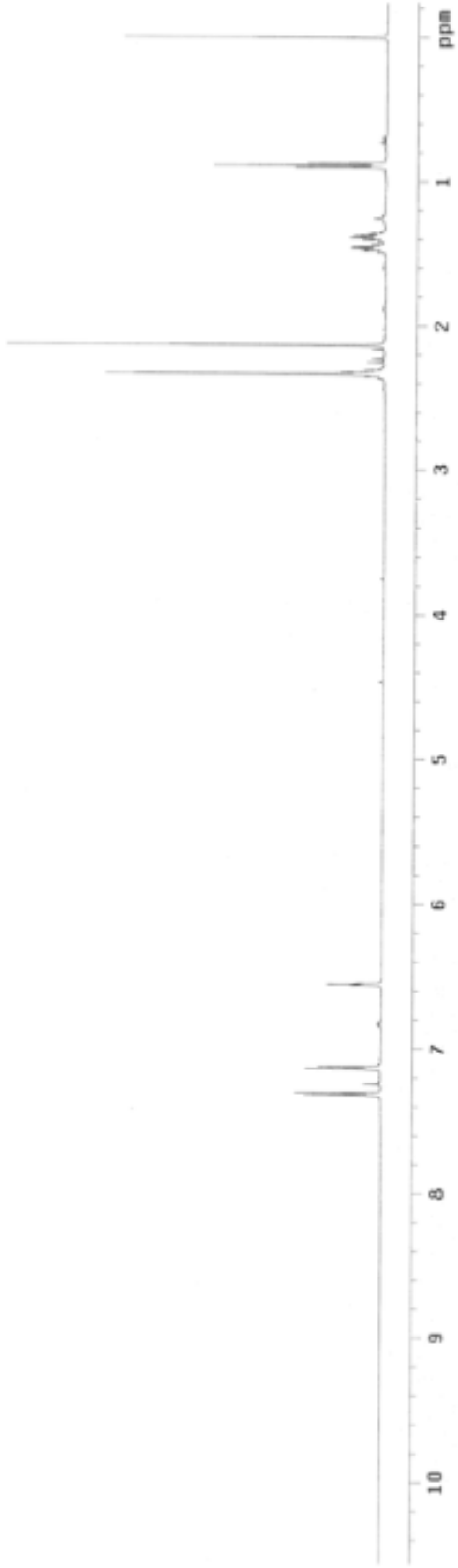
OAc
Bu

1-2a

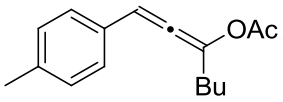

DW-1-45B-12232009-PhBu-13C-NMR-CDCl3
Pulse Sequence: s2pul
ppm
20
40
60
80
100
120
140
160
180
200



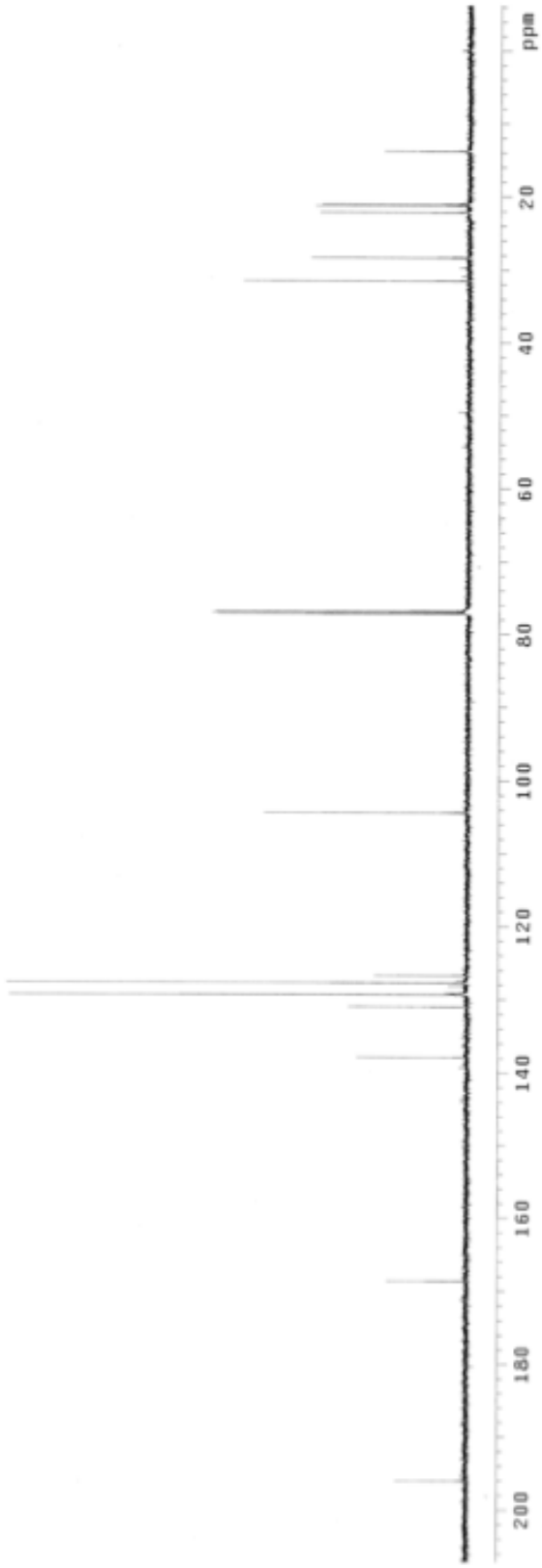
1-2b



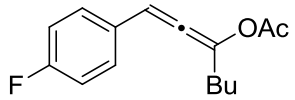
DW-1-98-1H-CDCl3
Archive directory: /export/home/vnmrl/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul



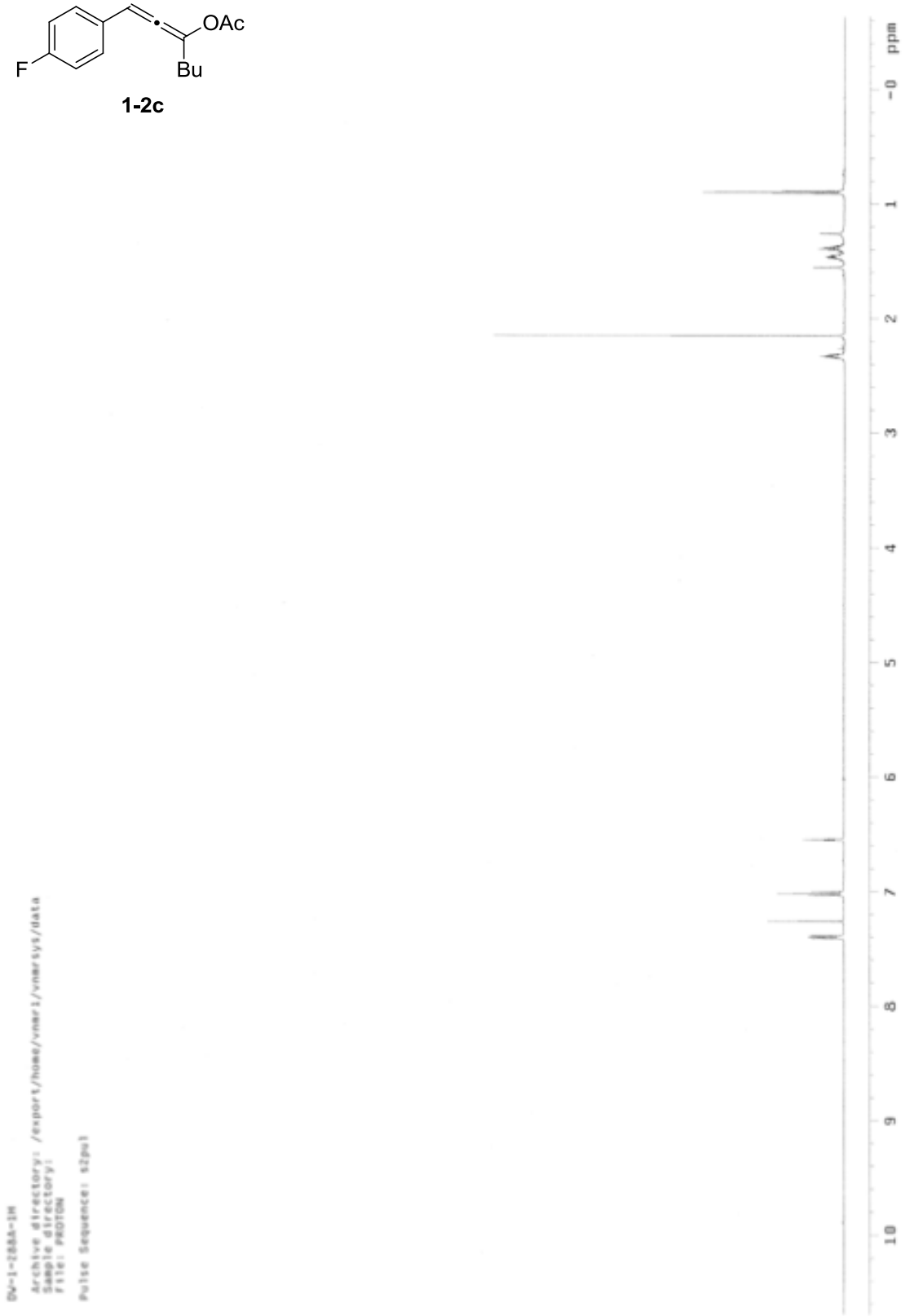
1-2b

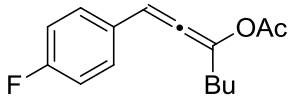


DW-1-98-13C-CDCl3
Pulse Sequence: s2pul

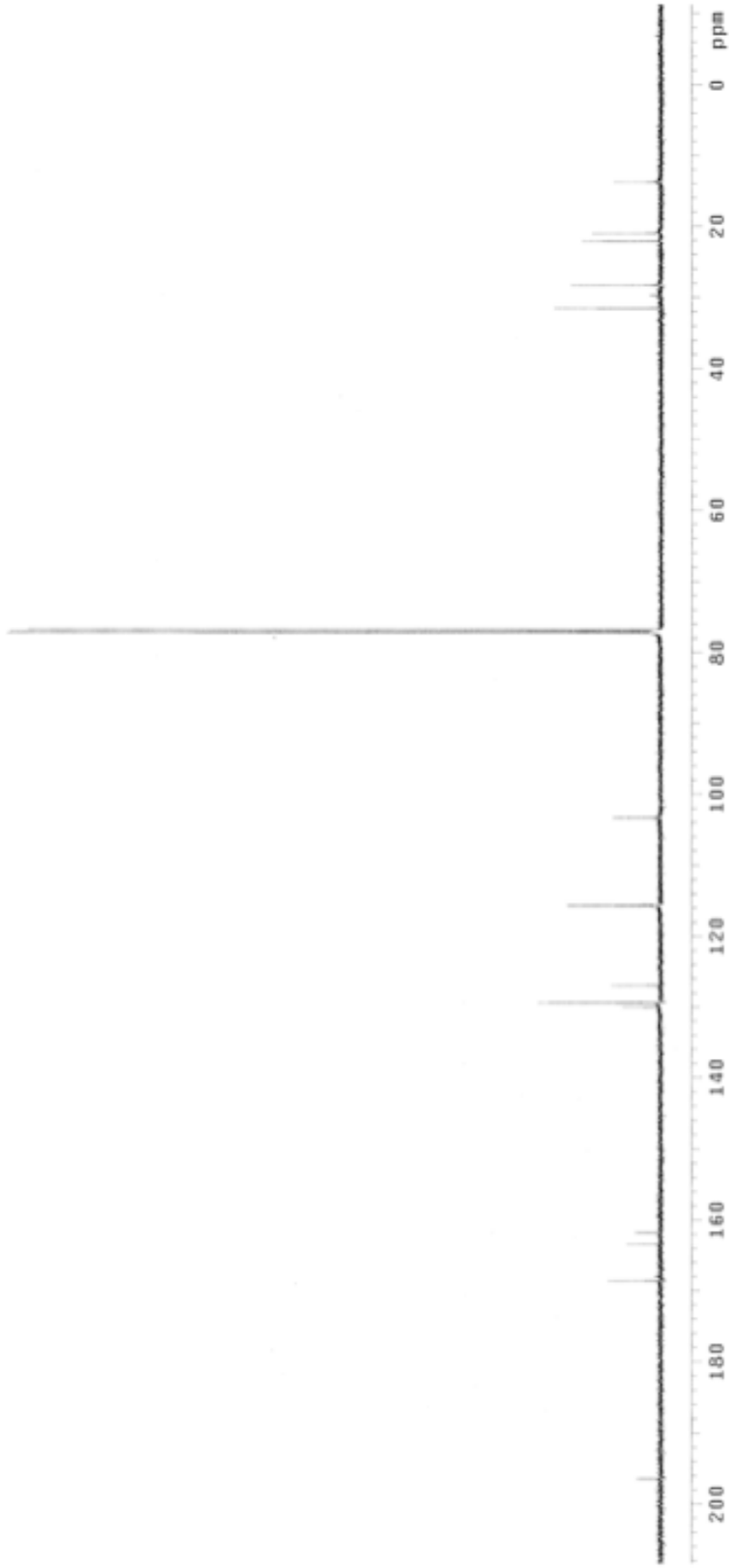

OAc
F
Bu

1-2c

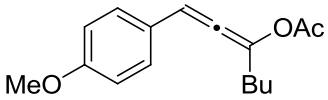

DV-1-288A-1H
Archive directory: /export/home/vnari/vnarsys/data
Sample directory1
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
-0 ppm



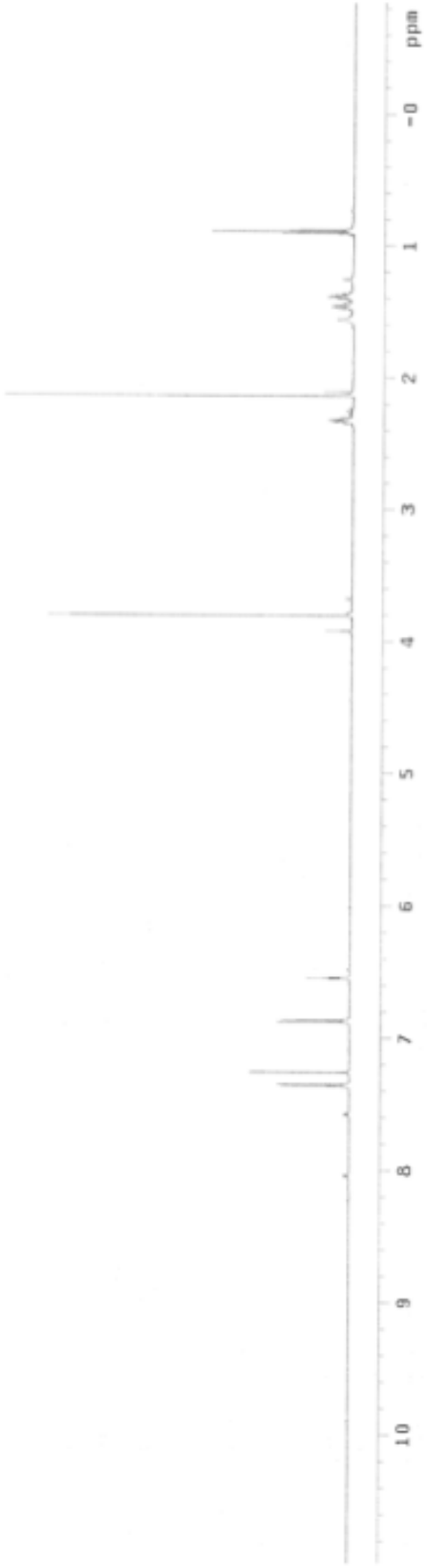
1-2c



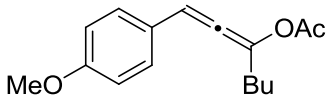
DW-1-288-A-13C
Pulse Sequence: s2pul



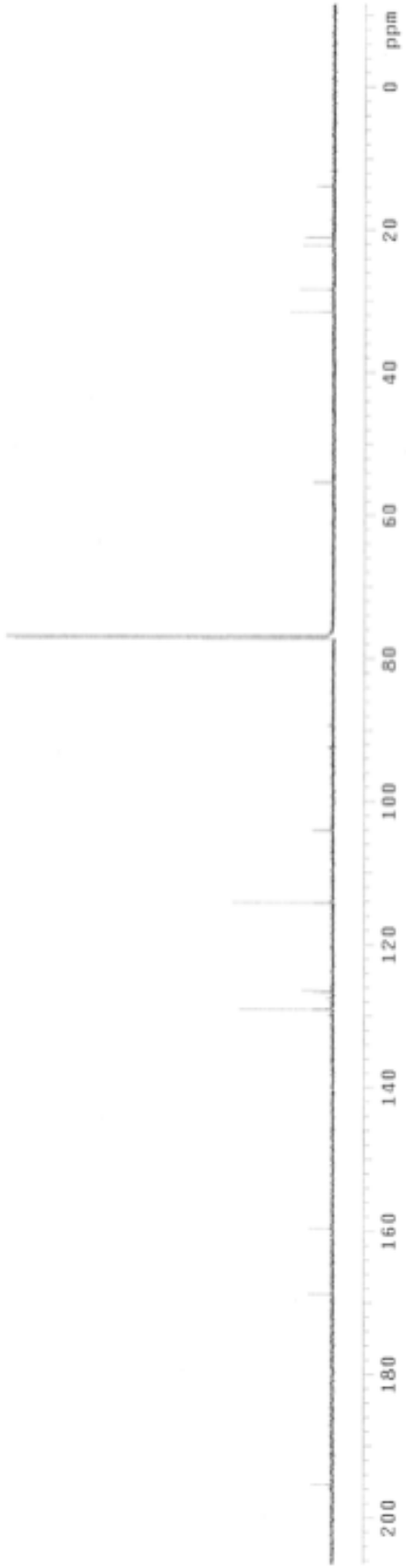
1-2d



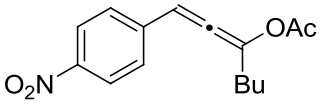
DV-1-2830-1H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul



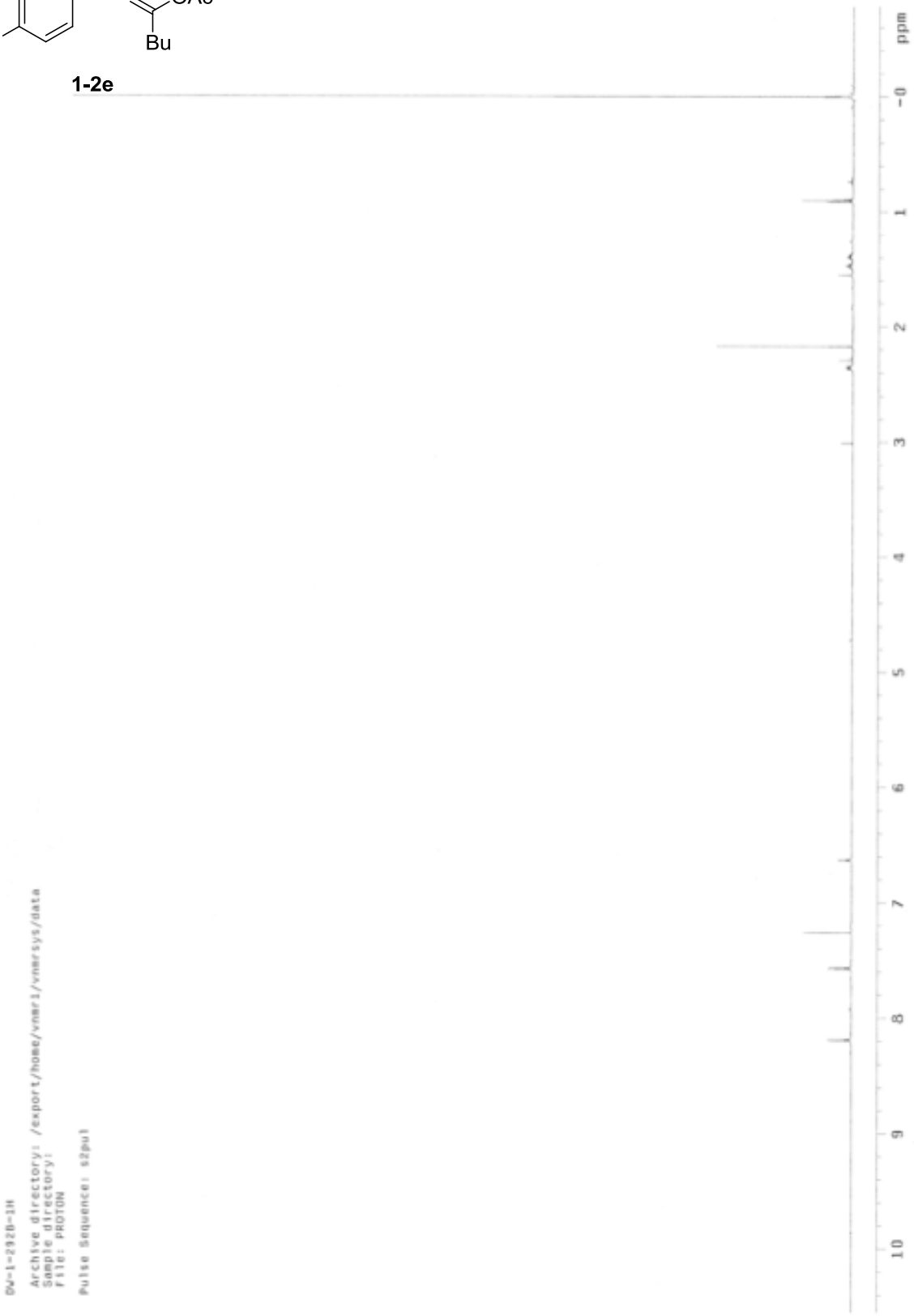
1-2d

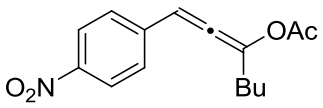


DW-1-283D-13C
Pulse Sequence: s2pul

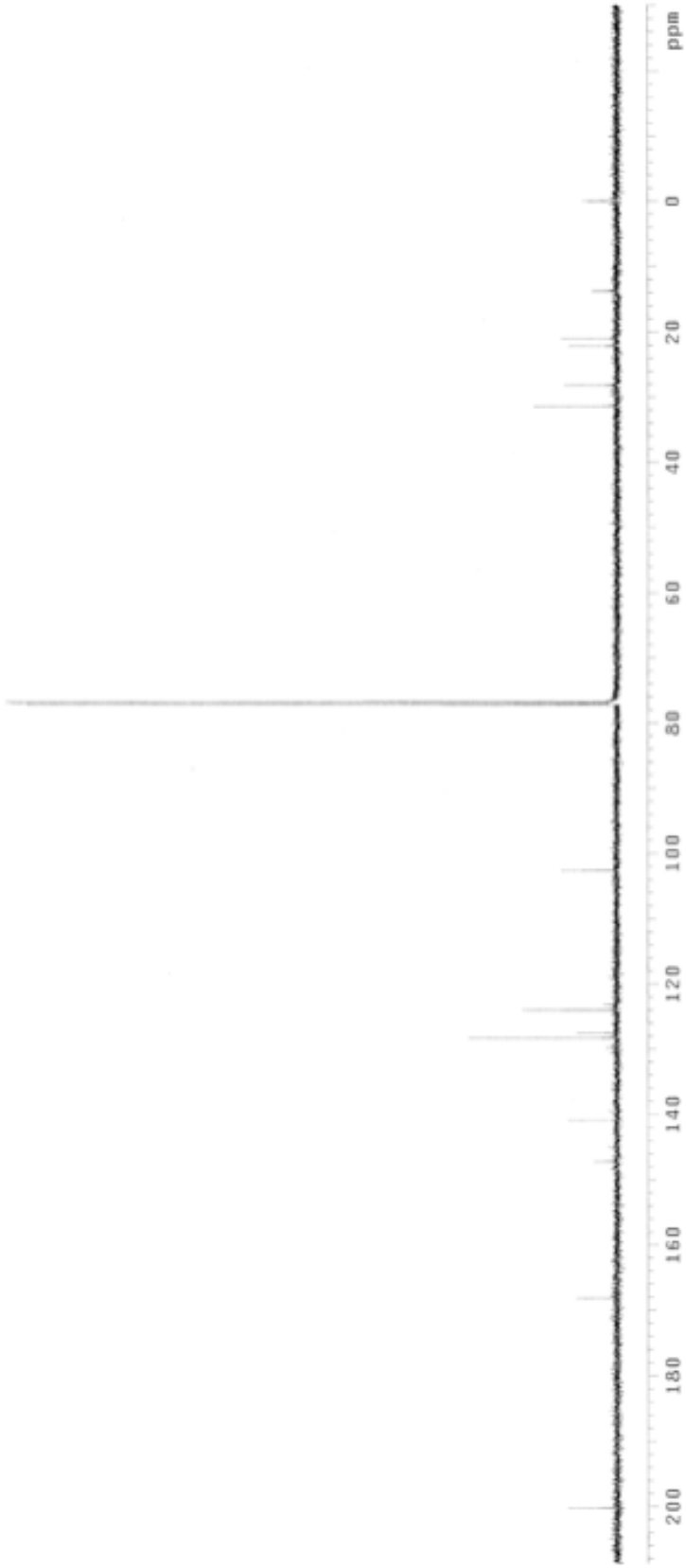

OAc
O_2N
Bu

1-2e

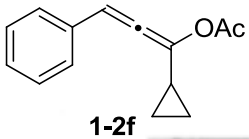

DW-1-292B-1H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
ppm
10
9
8
7
6
5
4
3
2
1
-0



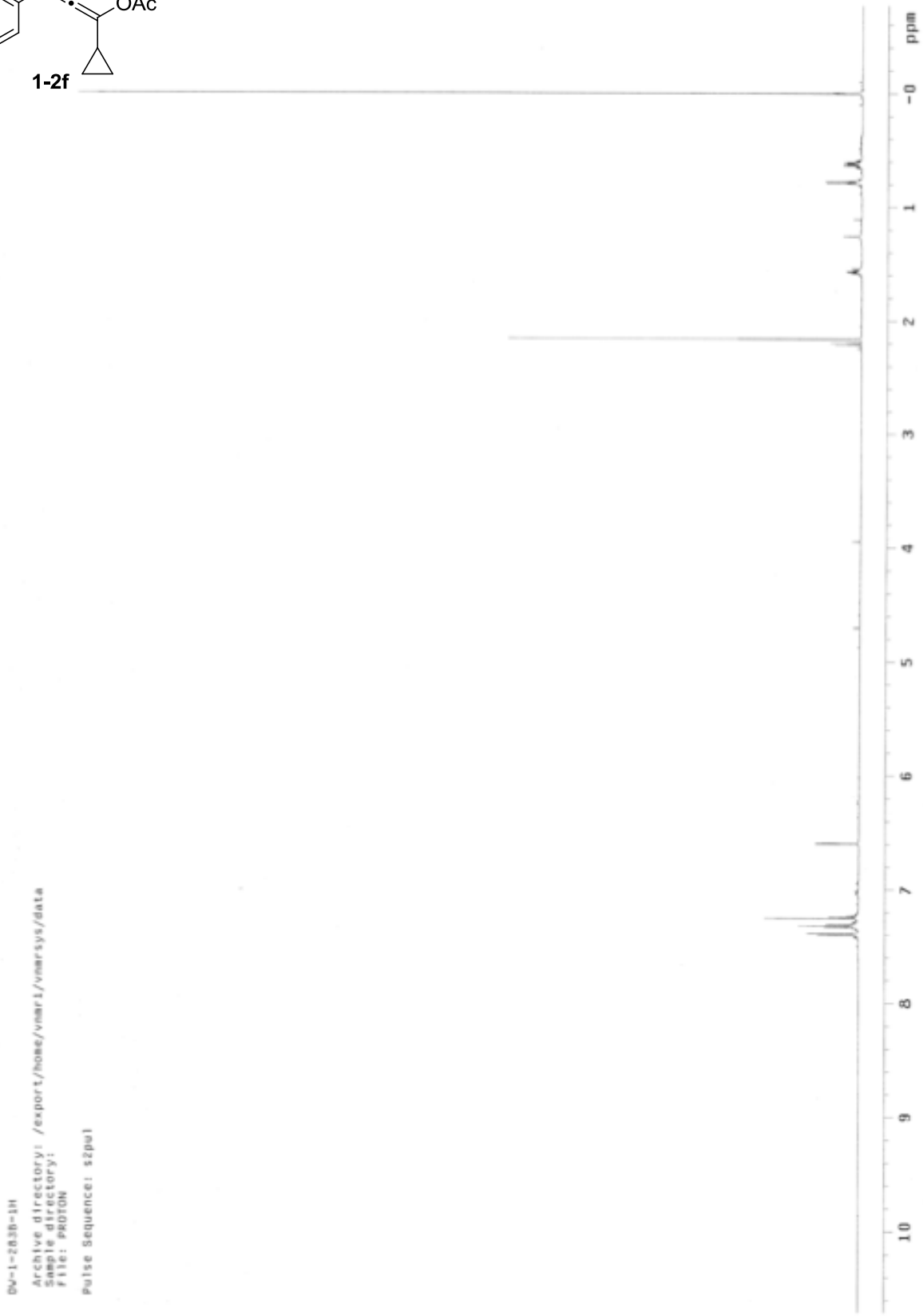
1-2e

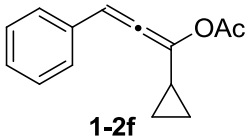


DV-1-292B-13C
Pulse Sequence: s2pul


OAc

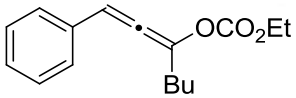
1-2f


DV-1-283b-1H
Archive directory: /export/home/vnmrs1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
ppm
10
9
8
7
6
5
4
3
2
1
-0

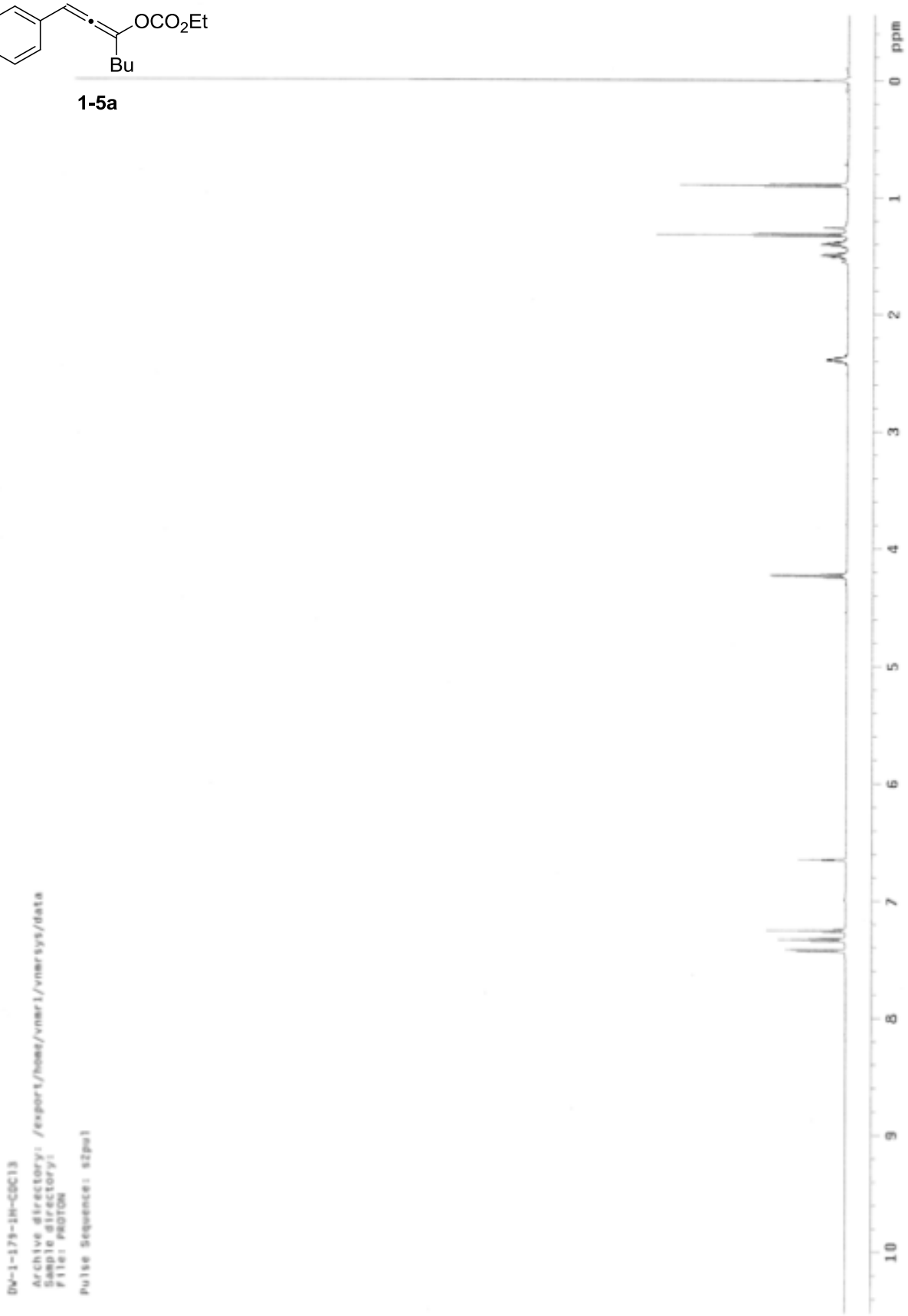


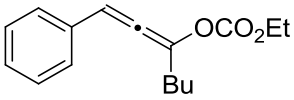
1-2f

DW-1-283B-13C
Pulse Sequence: s2pul

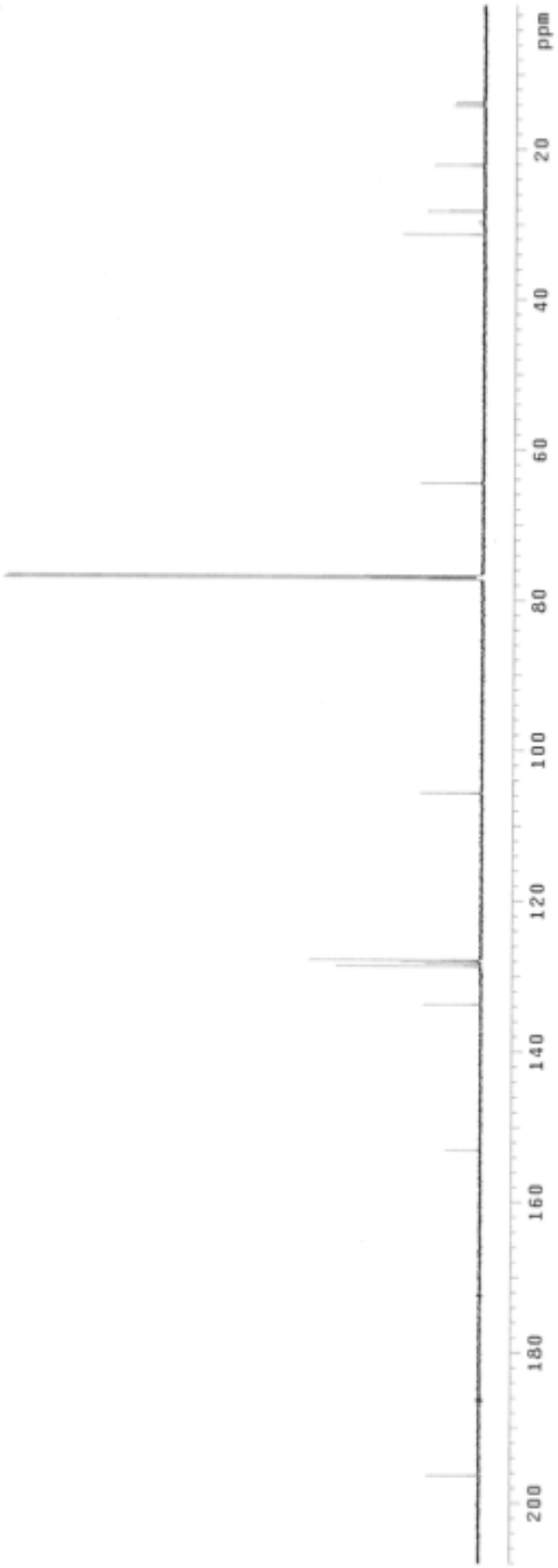

OCO2Et
Bu

1-5a

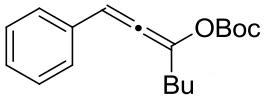

DW-1-179-1H-CDCl3
Archive directory: /export/home/vnmrl/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
ppm
0
1
2
3
4
5
6
7
8
9
10



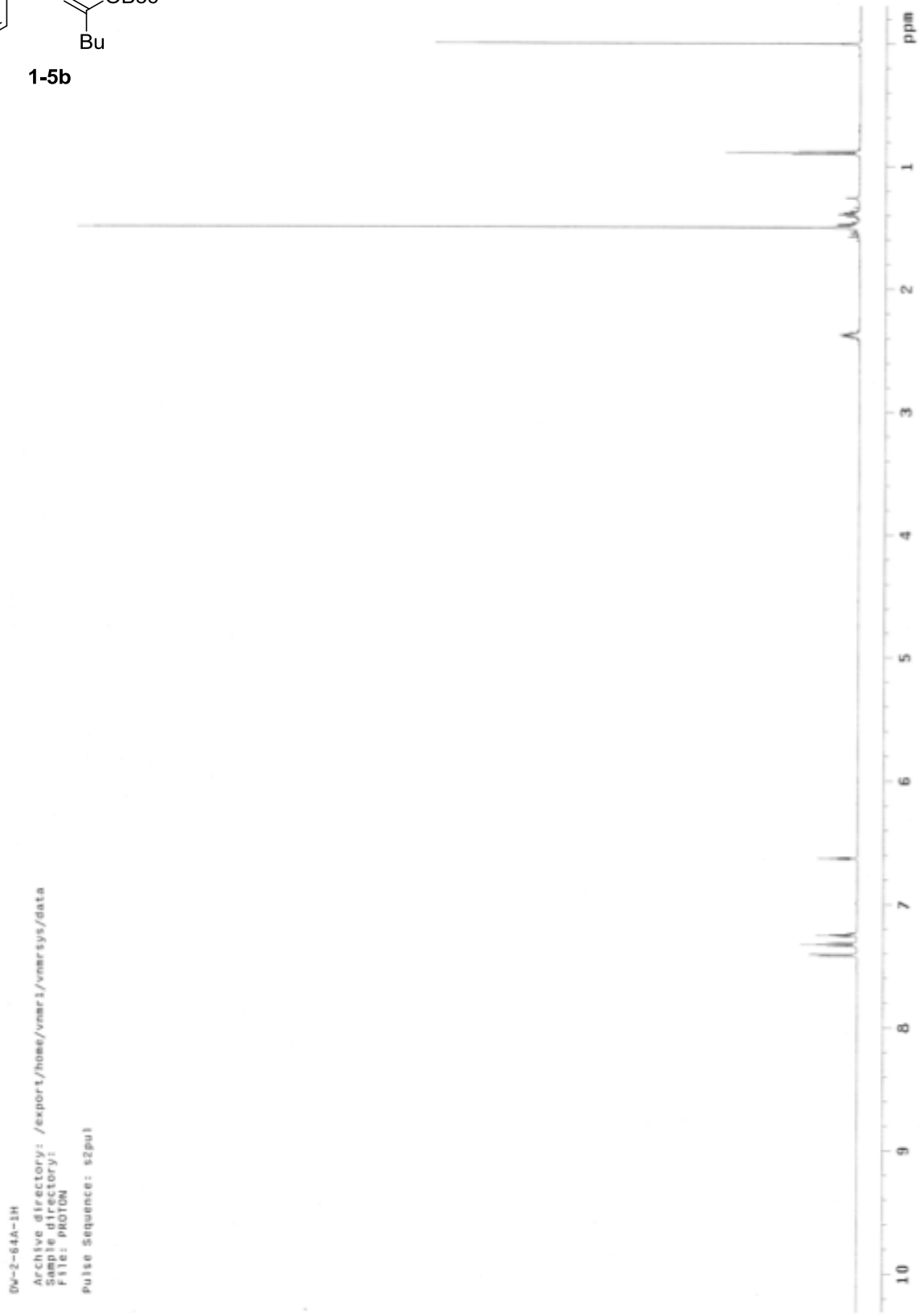
1-5a

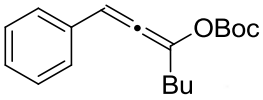


DW-1-179-13C
Pulse Sequence: s2pul

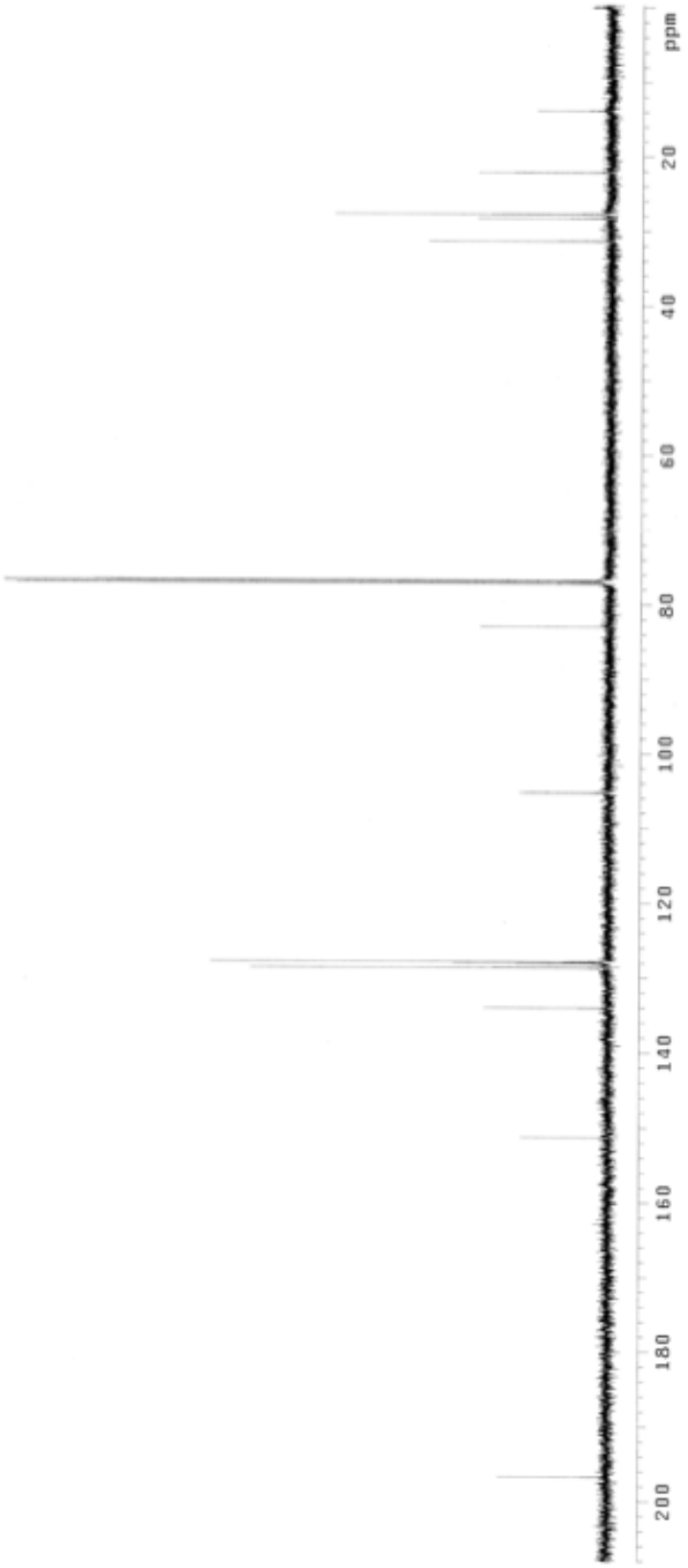

OBoc
Bu

1-5b

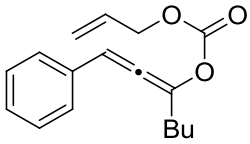

DW-2-64A-1H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
ppm
10
9
8
7
6
5
4
3
2
1



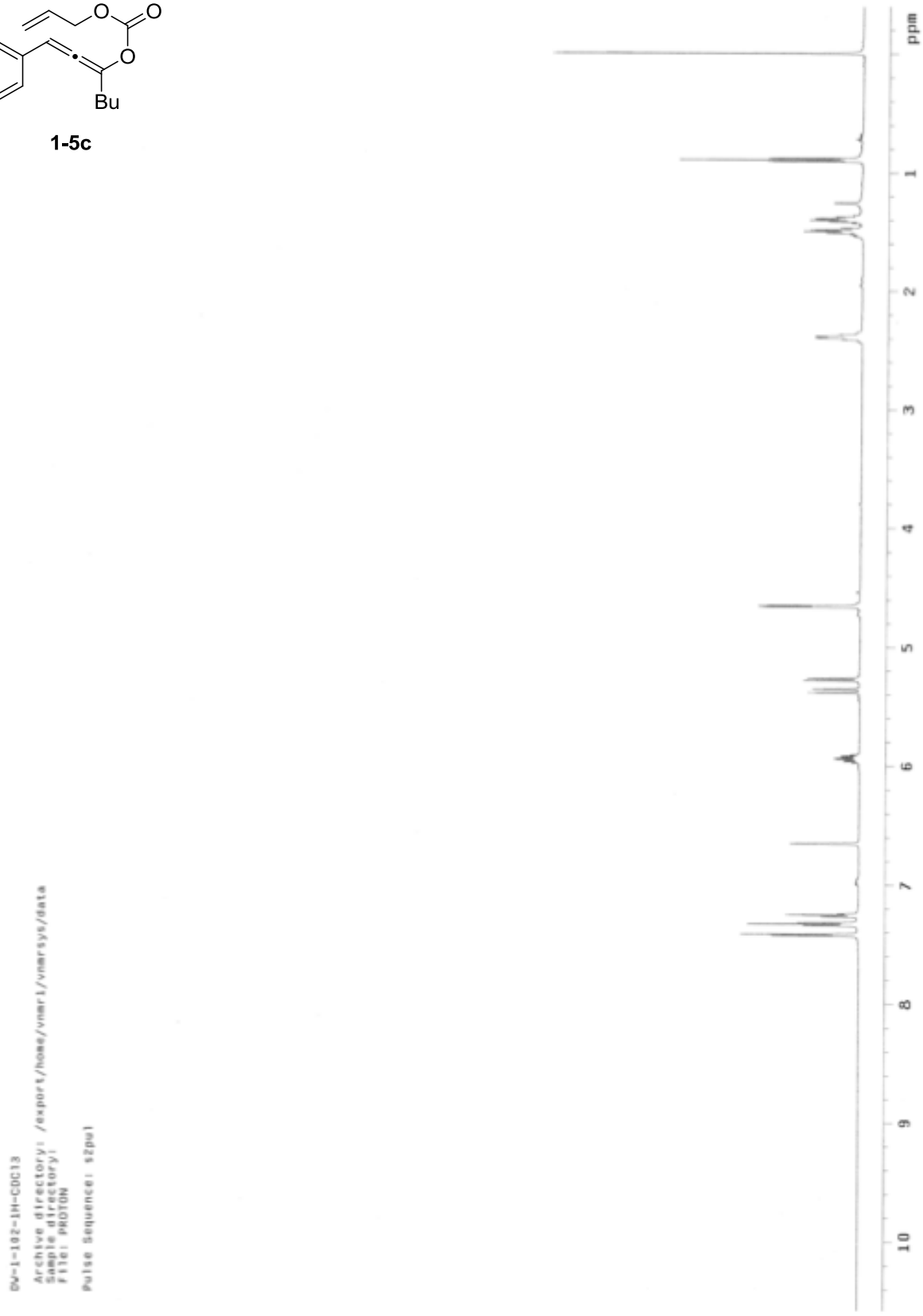
1-5b

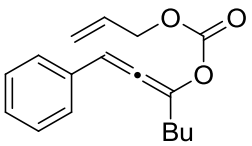


DW-2-64A1-13C
Pulse Sequence: s2pul

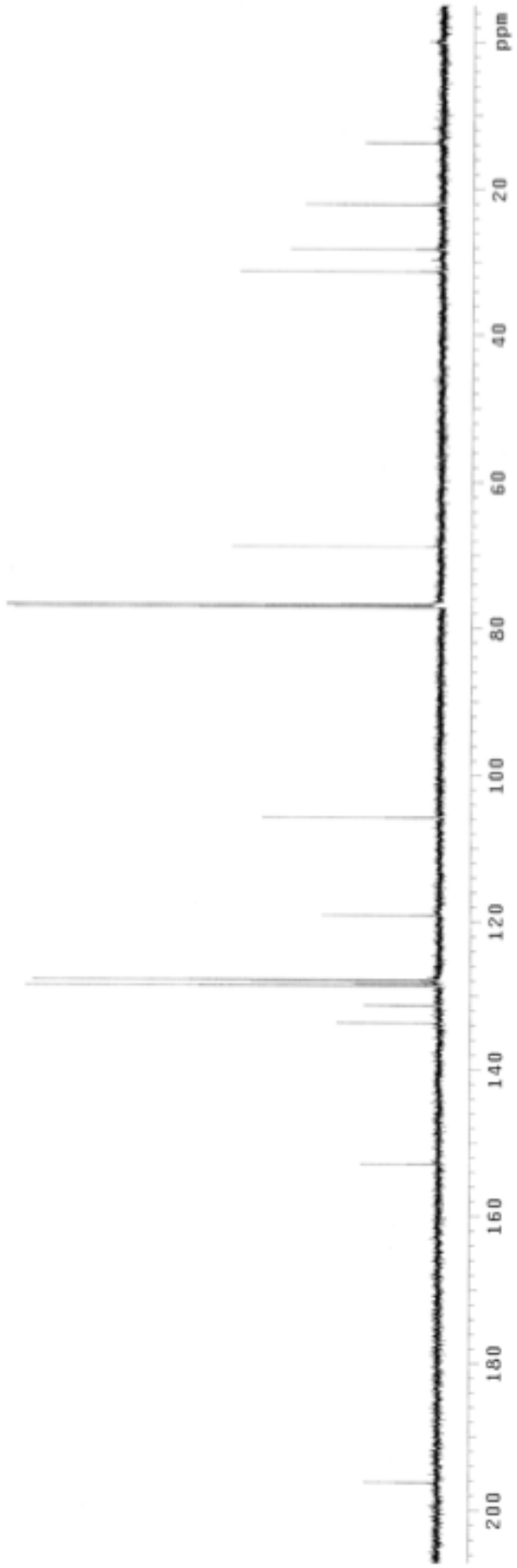


1-5c

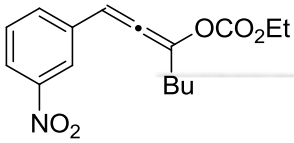

DW-1-102-1H-CDCl3
Archive directory: /export/home/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
ppm
10
9
8
7
6
5
4
3
2
1



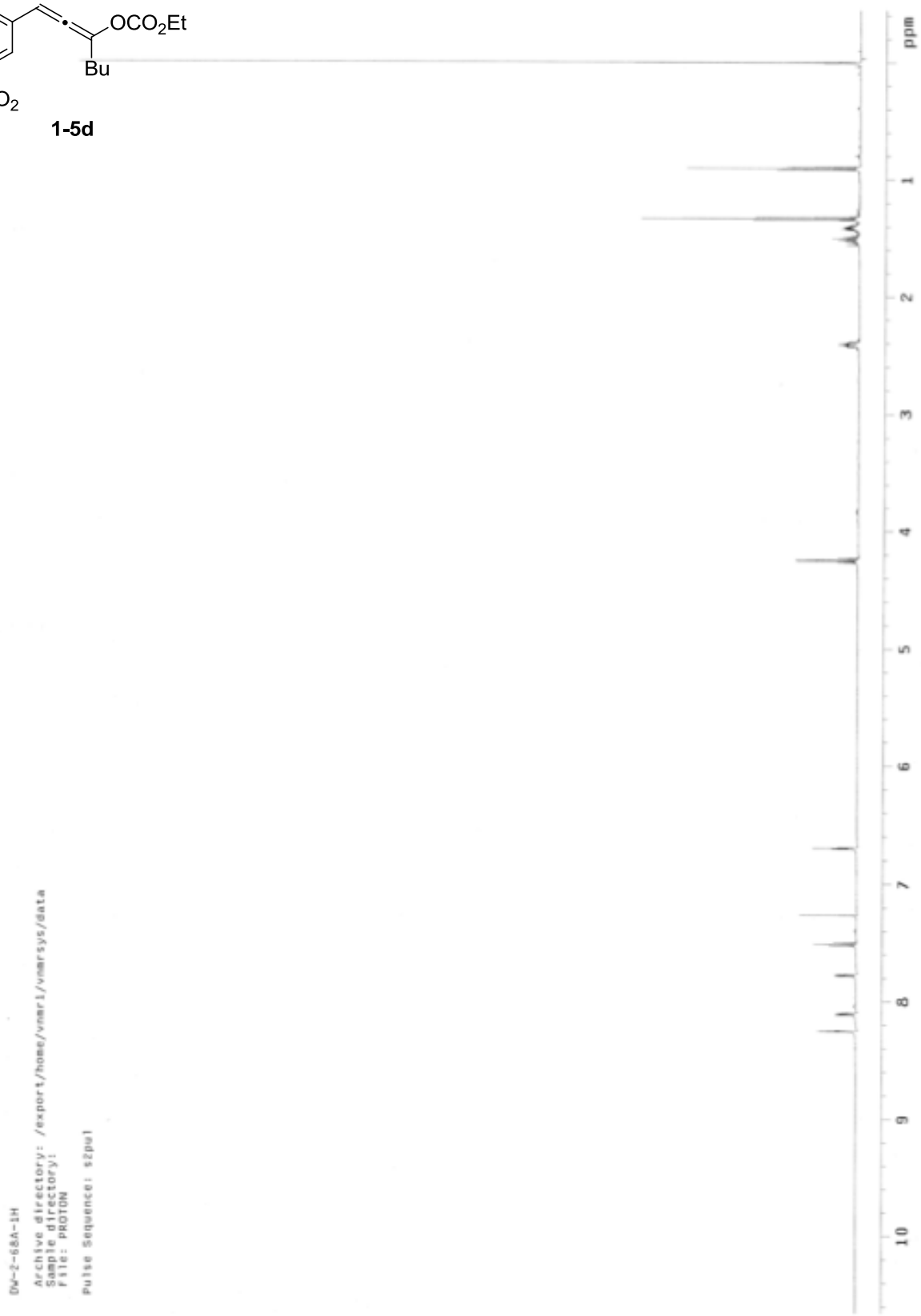
1-5c

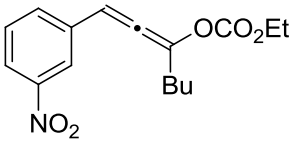


DW-1-102-13C
Pulse Sequence: s2pul


OCO2Et
Bu
NO2

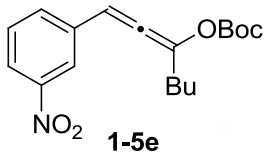
1-5d


DW-2-68A-1H
Archive directory: /export/home/vnmrl/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
ppm
10
9
8
7
6
5
4
3
2
1

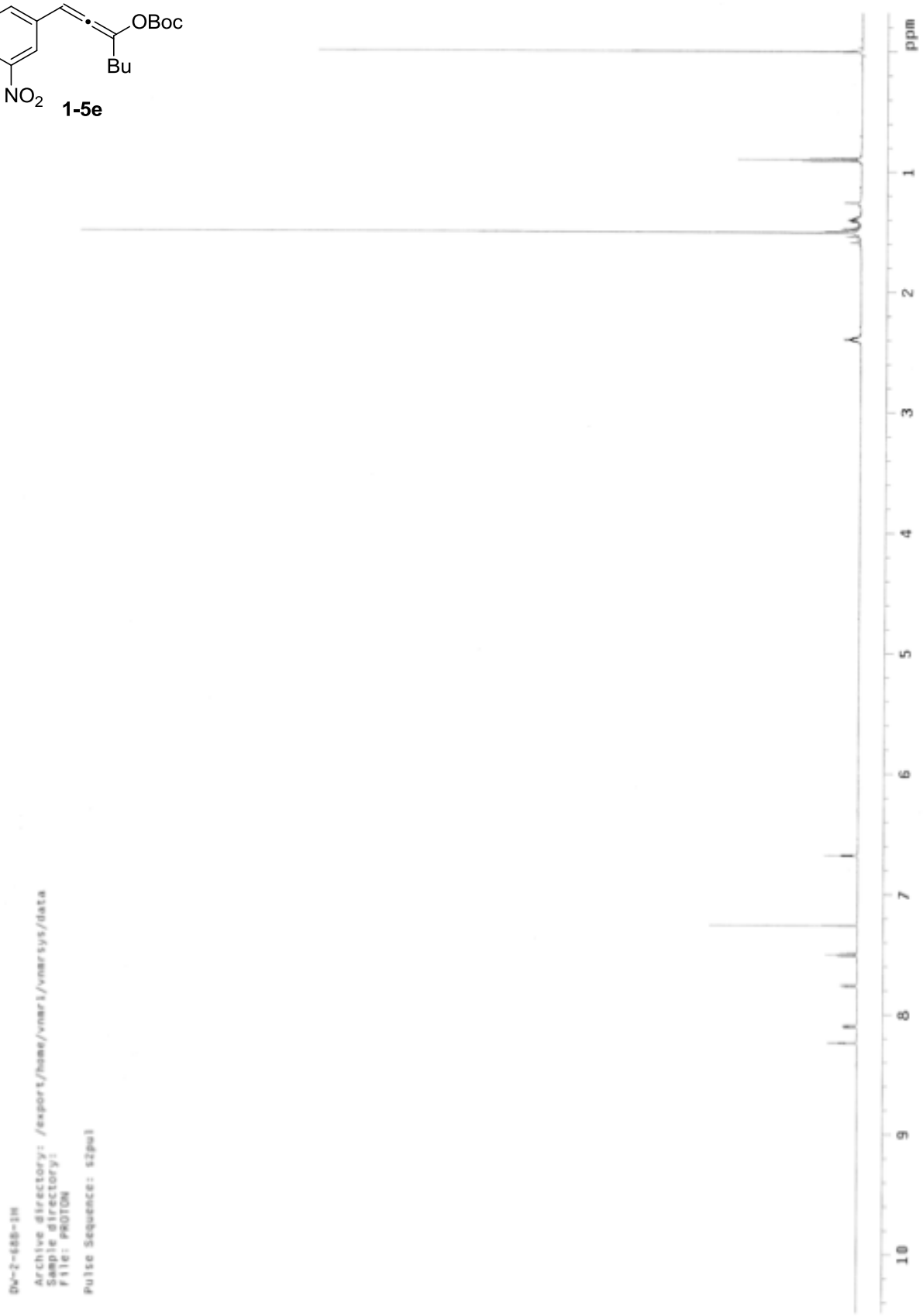


1-5d

DW-2-68A-13C
Pulse Sequence: s2pul


OBoc
Bu
NO2

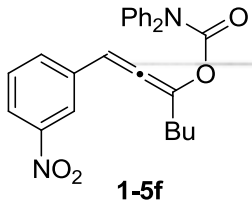
1-5e


DW-2-68B-1H
Archive directory: /export/home/vnmrl/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
ppm
10
9
8
7
6
5
4
3
2
1

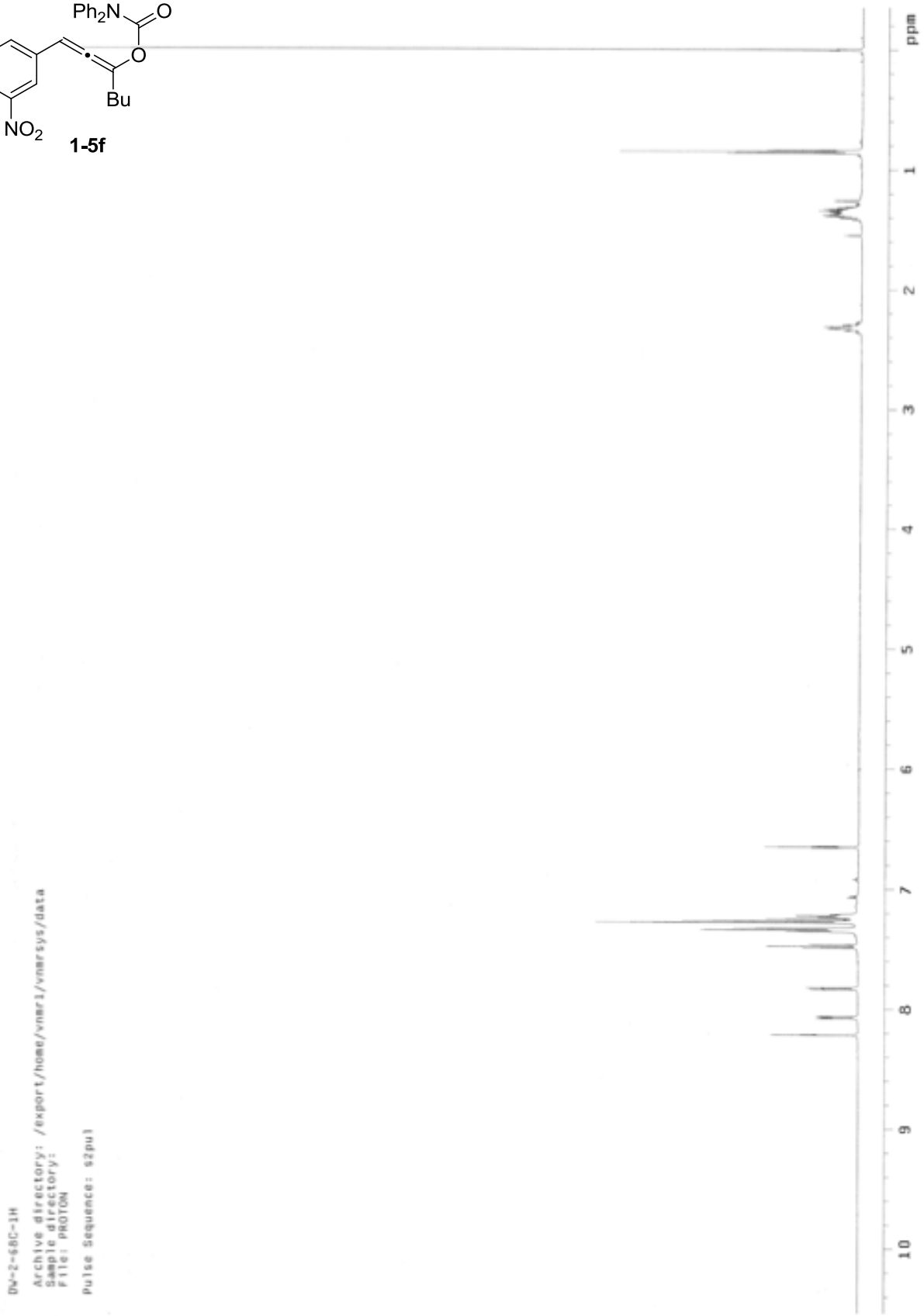
OBoc
Bu
NO2

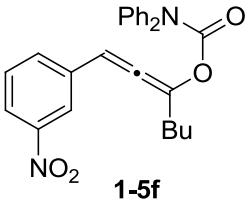
1-5e


0 ppm
20
40
60
80
100
120
140
160
180
200
DW-2-68B-13C
Pulse Sequence: s2pul

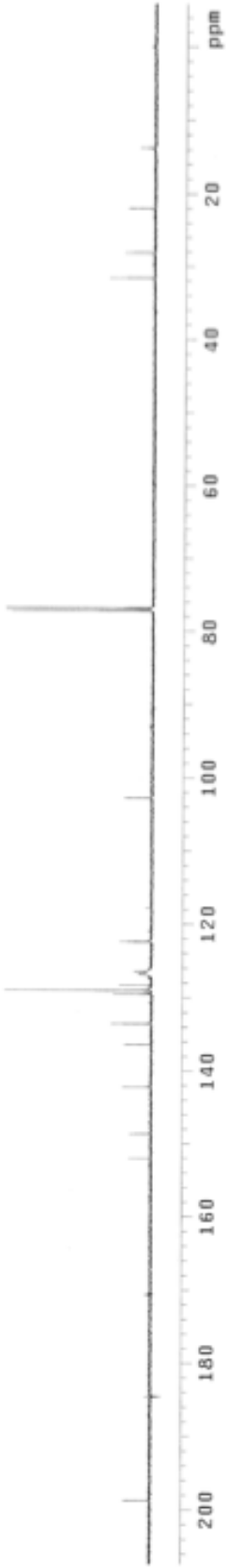

Ph2N
O
O
Bu
NO2

1-5f


DW-2-68C-1H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
ppm
10
9
8
7
6
5
4
3
2
1



1-5f



DW-2-68C-13C
Pulse Sequence: s2pul

Chapter Two: Further transformations from allene intermediate formed by Triazole-Au(I) complex as promoting propargyl ester rearrangements.

2.1 Triazole gold promoted, effective synthesis of enonoes from prypargylic esters and alcohols

I. General methods and materials

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer.

Substrates **2-1-1** and **2-1-5** were synthesized according to the literature as below:

1. M. Yu, G. Zhang, L. Zhang, *Org. Lett*. **2007**, *9*, 2147-2150.

2. N. Marion, P. Carlqvist, R. Gealageas, P. Fremont, F. Maseras, S. P. Nolan, *Chem.*

Eur. J. **2007**, *13*, 6437-6451.

Representative procedure for the preparation of *α,ß*-unsatured ketone 2-1-4a

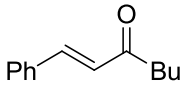
To a solution of **2-1-1a** (288 mg, 1.25 mmol) in wet MeOH (5 mL, 0.25 M, MeOH:H_2O = 100:1), was added Au(I) catalyst (1.8 mg, 0.0025 mol, 0.2 mol%) at 60 ^{o}C. The reaction mixture was stirred at 60 ^{o}C and monitored by TLC. After the reaction was completed (4 h), the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane = 1 : 20, V/V) to give **2-1-4a** (92% yield) as colorless oil.

Representative procedure for the preparation of *α,ß*-unsatured ketone 2-1-4a from 2-1-5a

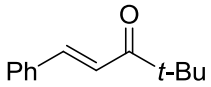
To a solution of **2-1-5a** (94 mg, 0.5 mmol) in wet MeOH (2.5 mL, MeOH:H_2O = 100:1), was added Au(I) catalyst (1.8 mg, 0.0025 mol, 0.5 mol%) at 60 ^{o}C. The reaction mixture

was stirred at 60 ^{o}C and monitored by TLC. After the reaction was completed (3 h), the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane = 1 : 20, V/V) to give **2-1-4a** (89% yield) as colorless oil.

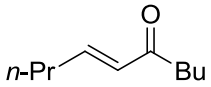
II. Compounds characterization



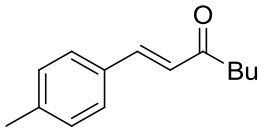
(*E*)-1-phenylhept-1-en-3-one (***E*-2-1-4a**): (Known compound, See: N. Marion, P. Carlqvist,. Gealageas, P. Fremont, F. Maseras, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 6437-6451) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53-7.56 (m, 3H), 7.38-7.40 (m, 3H), 6.73 (t, *J* = 16.2 Hz, 1H), 2.66 (t, *J* = 7.5 Hz, 2H), 1.66 (quintet, *J* = 7.5 Hz, 2H), 1.37 (sextet, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.8, 142.5, 134.8, 130.6, 129.1, 128.4, 126.5, 40.9, 26.7, 22.7, 14.1.



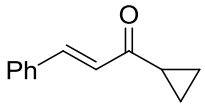
(*E*)-4,4-dimethyl-1-phenylpent-1-en-3-one (***E*-2-1-4b**): (Known compound, See: R. S. Ramon, S. Gaillard, A. M. Z. Slawin, A. Porta, A. D'Alfonso, G. Zanoni, S. P. Nolan, *Organometallics* **2010**, *29*, 3665-3668) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69 (d, *J* = 16.2 Hz, 1H, *E*), 7.56-7.58 (m, 2H, *E*), 7.53-7.54 (m, 2H, *Z*), 7.37-7.40 (m, 3H, *E*), 7.29-7.33 (m, 3H, *Z*), 7.13 (d, *J* = 15.6 Hz, 1H, *E*), 6.78 (d, *J* = 13.0 Hz, 1H, *Z*), 6.45 (d, *J* = 13.0 Hz, 1H, *Z*), 1.23 (s, 9H, *E*), 1.20 (s, 9H, *Z*). ^{13}C NMR (150 MHz, $CDCl_3$): δ 204.2, 142.9, 140.1, 134.9, 130.2, 129.5, 128.8, 128.3, 128.1, 124.3, 120.8, 43.2, 26.3, 26.2 (Z+E).



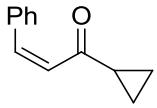
(*E*)-dec-6-en-5-one (***E*-2-1-4c**): (Known compound, See: M. N. Pennell, M. G. Unthank, P. Turner, T. D. Sheppard, *J. Org. Chem.* **2011**, *76*, 1479-1482) ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.82 (dt, *J* = 16.2, 6.6 Hz, 1H), 6.10 (dt, *J* = 15.6, 3.6 Hz, 1H), 2.53 (t, *J* = 7.8 Hz, 2H), 2.20 (qd, *J* = 7.2, 1.2 Hz, 2H), 1.60 (quintet, *J* = 7.7 Hz, 2H), 1.50 (sextet, *J* = 7.4 Hz, 2H), 1.34 (sextet, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.9, 146.9, 130.5, 39.8, 34.4, 26.4, 22.4, 21.3, 13.8, 13.6.



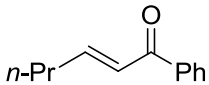
(*E*)-1-*p*-tolylhept-1-en-3-one (***E*-2-1-4d**): (Known compound, See: N. Marion, P. Carlqvist, R. Gealageas, P. Fremont, F. Maseras, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 6437-6451) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, *J* = 16.2, Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 15.6 Hz, 1H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 1.66 (quintet, *J* = 7.7 Hz, 2H), 1.37 (sextet, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ. 200.6, 142.3, 140.8, 131.8, 129.6, 128.2, 125.3, 40.5, 26.5, 22.4, 21.4, 13.8.



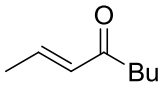
(*E*)-1-cyclopropyl-3-phenylprop-2-en-1-one (***E*-2-1-4e**): (Known compound, See: G. V. Kryshtal, G. M. Zhdankina, S. G. Zlotin, *Eur. J. Org. Chem.* **2005**, *13*, 2822-2827) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (d, *J* = 16.2 Hz, 1H), δ 7.55-7.57 (m, 2H), 7.38-7.40 (m, 3H), 6.86 (d, *J* = 16.2 Hz, 1H), 2.22-2.27 (m, 1H), 1.15-1.17 (m, 2H), 0.95-0.99 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.9, 141.9, 134.6, 130.2, 128.8, 128.2, 126.4, 19.6, 11.3.



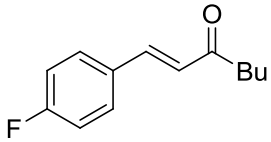
(*Z*)-1-cyclopropyl-3-phenylprop-2-en-1-one (***Z*-2-1-4e**): (Known compound, See: Kryshtal, G. M. Zhdankina, S. G. Zlotin, *Eur. J. Org. Chem.* **2005**, *13*, 2822-2827) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49-7.51 (m, 2H), 7.32-7.35 (m, 3H), 6.93 (d, *J* = 12.6 Hz, 1H), 6.24 (d, *J* = 12.6 Hz, 1H), 1.88-1.92 (m, 1H), 1.10-1.13 (m, 2H), 0.81-0.83 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 203.7, 139.3, 135.4, 129.6, 129.5, 128.9, 128.1, 22.1, 12.5.



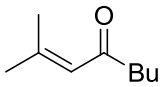
(*E*)-1-phenylhex-2-en-1-one (***E*-2-1-4f**): (Known compound, See: N. Marion, P. Carlqvist, R. Gealageas, P. Fremont, F. Maseras, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 6437-6451) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91-7.93 (m, 2H), 7.52-7.54 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.05 (dt, *J* = 15.6, 7.8 Hz, 1H), 6.86 (dt, *J* = 15.0, 1.5 Hz, 1H), 2.28 (m, 2H), 1.54 (sextet, *J* = 7.3 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 190.8, 149.6, 137.9, 132.4, 128.4, 128.3, 125.9, 34.7, 21.3, 13.6.



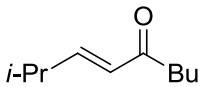
(*E*)-oct-2-en-4-one (***E*-2-1-4g**): (Known compound, See: A. R. Katritzky, D. C. Oniciu, I. Ghiviriga, F. Soti, *J. Org. Chem.* **1998**, *63*, 2110-2115) ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.85 (dq, *J* = 16.2, 6.8 Hz, 1H), 6.11 (dq, *J* = 15.6, 1.6 Hz, 1H), 2.52 (t, *J* = 7.5 Hz, 2H), 1.90 (dd, *J* = 6.6, 1.8 Hz, 3H), 1.59 (quintet, *J* = 7.5 Hz, 2H), 1.33 (sextet, *J* = 7.6 Hz, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.7, 142.2, 131.9, 39.8, 26.4, 22.4, 18.2, 13.8.



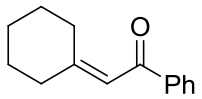
(*E*)-1-(4-fluorophenyl)hept-1-en-3-one (***E*-2-1-4h**): (Known compound, See: N. Marion, P. Carlqvist, R. Gealageas, P. Fremont, F. Maseras, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 6437-6451) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50-7.54 (m, 3H), 7.08 (t, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 16.2 Hz, 1H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.66 (quintet, *J* = 7.4 Hz, 2H), 1.38 (sextet, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.3, 163.0 (d, *J* = 249.8 Hz), 140.8, 130.8 (d, *J* = 1.8 Hz), 130.0 (d, *J* = 8.3 Hz), 125.9, 116.0 (d, *J* = 21.8 Hz), 40.7, 26.4, 22.3, 13.8.



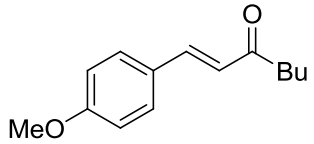
2-methyloct-2-en-4-one (**2-1-4i**): (Known compound, See: M. Yu, G. Li, S. Wang, L. Zhang, *Adv. Synth. Catal.* **2007**, *349*, 871-875) ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.06-6.08 (m, 1H), 2.40 (t, *J* = 7.5 Hz, 2H), 2.14 (d, *J* = 1.2 Hz, 3H), 1.88 (d, *J* = 1.2 Hz, 3H), 1.57 (quintet, *J* = 7.5 Hz, 2H), 1.32 (sextet, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 201.2, 154.5, 123.8, 43.9, 27.5, 26.4, 22.4, 20.6, 13.8.



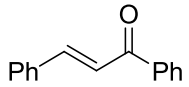
(*E*)-2-methylnon-3-en-5-one (***E*-2-1-4j**): (Known compound, See: M. Yu, G. Li, S. Wang, L. Zhang, *Adv. Synth. Catal.* **2007**, *349*, 871-875) ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.78 (dd, *J* = 16.2, 6.6 Hz, 1H), 6.03 (dd, *J* = 16.2, 1.8 Hz, 1H), 2.53 (t, *J* = 7.5 Hz, 2H), 2.41-2.48 (m, 1H), 1.59 (quintet, *J* = 7.4 Hz, 2H), 1.32 (sextet, *J* = 7.4 Hz, 2H),1.07 (d, *J* = 6.6 Hz, 6H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 201.2, 153.1, 127.5, 39.8, 31.0, 26.4, 22.4, 21.3, 13.8.



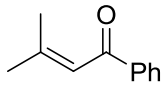
2-cyclohexylidene-1-phenylethanone (**2-1-4k**): (Known compound, See: B. Lu, C. Li, L. Zhang, *J. Am. Chem. Soc.* **2005**, *127*, 14180-14181) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93-7.95 (m, 2H), 7.51-7.54 (m, 1H), 7.43-7.46 (m, 2H), 6.60-6.61 (m, 1H), 2.76-2.78 (m, 2H), 2.31 (td, *J* = 6.3, 0.6 Hz, 2H), 1.71-1.75 (m, 2H), 1.62-1.66 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.3, 162.7, 139.3, 132.3, 128.4, 128.3, 118.7, 38.4, 30.6, 28.9, 28.0, 26.3.



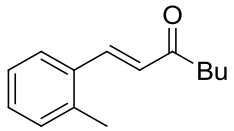
(*E*)-1-(4-methoxyphenyl)hept-1-en-3-one (***E*-2-1-4l**): (Known compound, See: N. Marion, P. Carlqvist, R. Gealageas, P. Fremont, F. Maseras, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 6437-6451) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, *J* = 15.6 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 16.2 Hz, 1H), 3.83 (s, 3H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.66 (quintet, *J* = 7.5 Hz, 2H), 1.38 (sextet, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.6, 161.5, 142.0, 129.9, 127.2, 124.1, 114.3, 55.3, 40.5, 26.6, 22.4, 13.9.



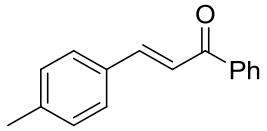
(*E*)-chalcone (***E*-2-1-4m**): (Known compound, See: N. Marion, P. Carlqvist, R. Gealageas, P. Fremont, F. Maseras, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 6437-6451) ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00-8.02 (m, 2H), 7.80 (d, *J* = 15.6 Hz, 1H), 7.62-7.63 (m, 2H), 7.55-7.58 (m, 1H), 7.52 (d, *J* = 15.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.38-7.41 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 190.4, 144.7, 138.2, 134.8, 132.7, 130.5, 128.9, 128.6, 128.4, 128.4, 122.1.



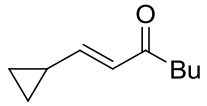
3-methyl-1-phenylbut-2-en-1-one (**2-1-4n**): (Known compound, See: P. N. Chatterjee, S. Roy, *J. Org. Chem.* **2010**, *75*, 4413-4423) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92-7.94 (m, 2H), 7.50-7.53 (m, 1H), 7.42-7.45 (m, 2H), 6.74-6.75 (m, 1H), 2.21 (d, *J* = 1.2 Hz, 3H), 2.01 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.8, 156.6, 139.2, 132.2, 128.4, 128.1, 121.1, 27.9, 21.1.



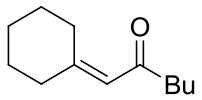
(*E*)-1-*o*-tolylhept-1-en-3-one (***E*-2-1-4o**): (Known compound, See: N. Marion, P. Carlqvist, R. Gealageas, P. Fremont, F. Maseras, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 6437-6451) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (d, *J* = 16.2 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 2H), 6.66 (d, *J* = 16.2 Hz, 1H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.67 (quintet, *J* = 7.5 Hz, 2H), 1.39 (sextet, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.4, 139.6, 137.8, 133.5, 130.7, 129.9, 127.1, 126.3, 126.2, 40.9, 26.4, 22.4, 19.6, 13.8.



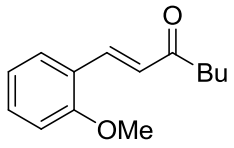
(*E*)-1-phenyl-3-*p*-tolylprop-2-en-1-one (***E*-2-1-4p**): (Known compound, See: Y. Zhang, Y.-L. Shao, H.-S. Xu, W. Wang, *J. Org. Chem.* **2011**, *76*, 1472-1474) ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00-8.01 (m, 2H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.53-7.57 (m, 3H), 7.47-7.50 (m, 3H), 7.22 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 190.6, 144.9, 141.0, 138.4, 132.6, 132.2, 129.7, 128.5, 128.4, 121.1, 21.5.



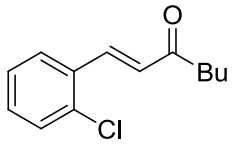
(*E*)-1-cyclopropylhept-1-en-3-one (***E*-2-1-4q**): (Known compound, See: M. N. Pennell, M. G. Unthank, P. Turner, T. D. Sheppard, *J. Org. Chem.* **2011**, *76*, 1479-1482) ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.31 (dd, *J* = 15.6 Hz, 9.6 Hz, 1H), 6.21 (d, *J* = 15.6 Hz, 1H), 2.48 (t, *J* = 7.5 Hz, 2H), 1.53-1.61 (m, 3H), 1.34 (sextet, *J* = 7.4 Hz, 2H), 0.95-0.99 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.64-0.66 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.8, 152.0, 127.2, 40.0, 26.5, 22.4, 14.5, 13.8, 8.8.



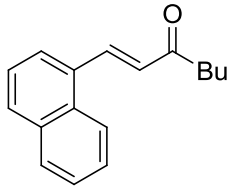
1-cyclohexylidenehexan-2-one (**2-1-4r**): (Known compound, See: M. Yu, G. Li, S. Wang, L. Zhang, Adv. Synth. Catal. 2007, 349, 871-875) ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.97 (s,1H), 2.79 (t, *J* = 5.4 Hz, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 2.16 (t, *J* = 6.3 Hz, 2H), 1.54-1.69 (m, 8H), 1.32 (sextet, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.1, 161.4, 121.0, 44.2, 38.1, 29.9, 28.8, 27.9, 26.4, 26.3, 22.4, 13.9.



(*E*)-1-(2-methoxyphenyl)hept-1-en-3-one (***E*-2-1-4s**): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 (d, *J* = 16.8 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 8.1 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 16.2 Hz, 1H), 3.89 (s, 3H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.66 (quintet, *J* = 7.5 Hz, 2H), 1.38 (sextet, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 201.2, 158.3, 137.5, 131.5, 128.3, 126.9, 123.5, 120.7, 111.1, 55.4, 40.1, 26.6, 22.4, 13.9.

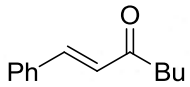


(*E*)-1-(2-chloro-5-nitrophenyl)hept-1-en-3-one (***E*-2-1-4t**): ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, *J* = 1.8 Hz, 1H), 7.67 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 16.2 Hz, 1H), 6.80 (d, *J* = 15.6 Hz, 1H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.67 (quintet, *J* = 7.5 Hz, 2H), 1.38 (sextet, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.5, 148.3, 137.8, 134.8, 132.4, 132.0, 128.8, 128.2, 124.5, 41.3, 26.1, 22.3, 13.8; HRMS Calculated for $[C_{13}H_{14}ClNO_3+Na]^+$: 290.05599, Found: 290.05585.

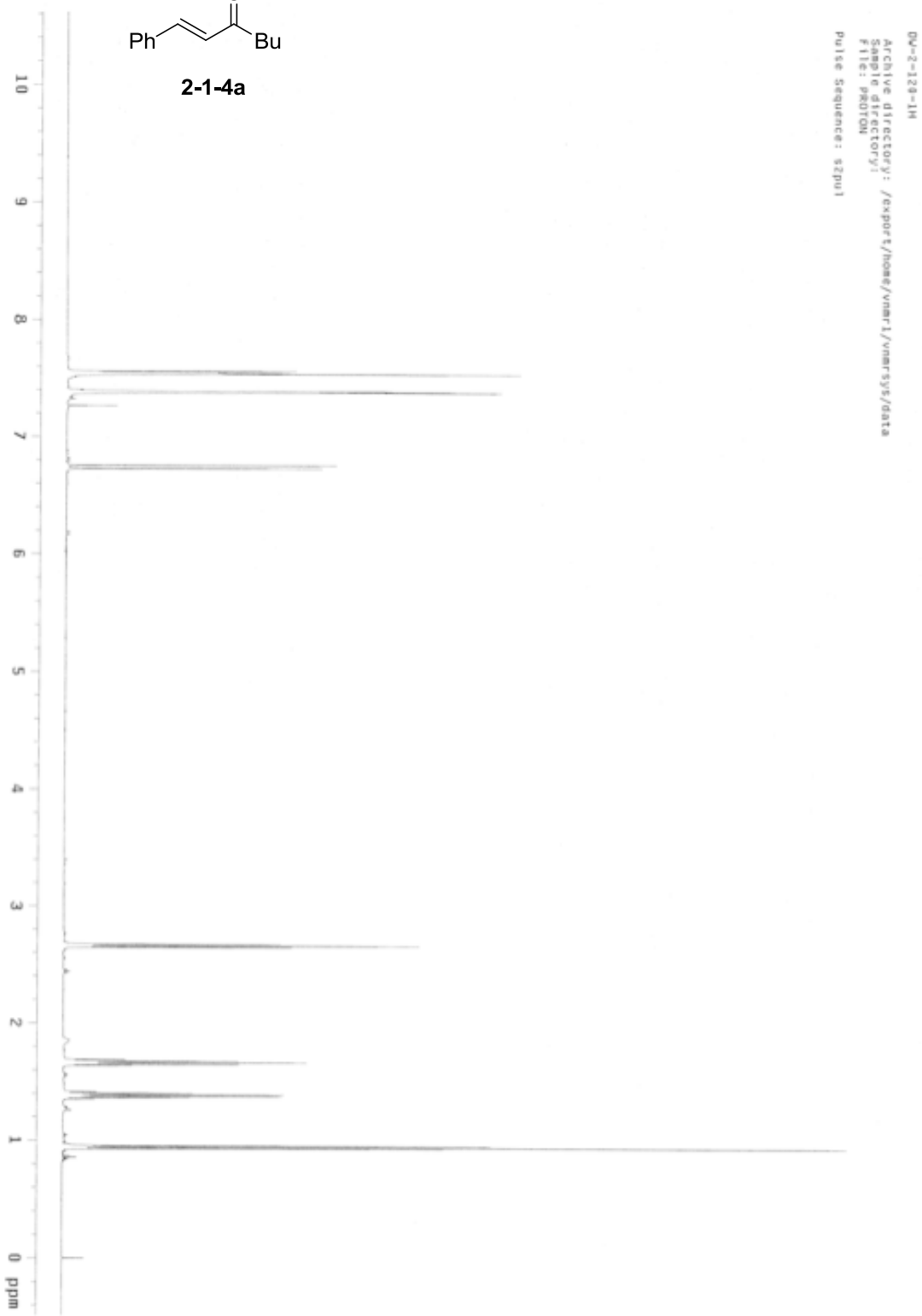


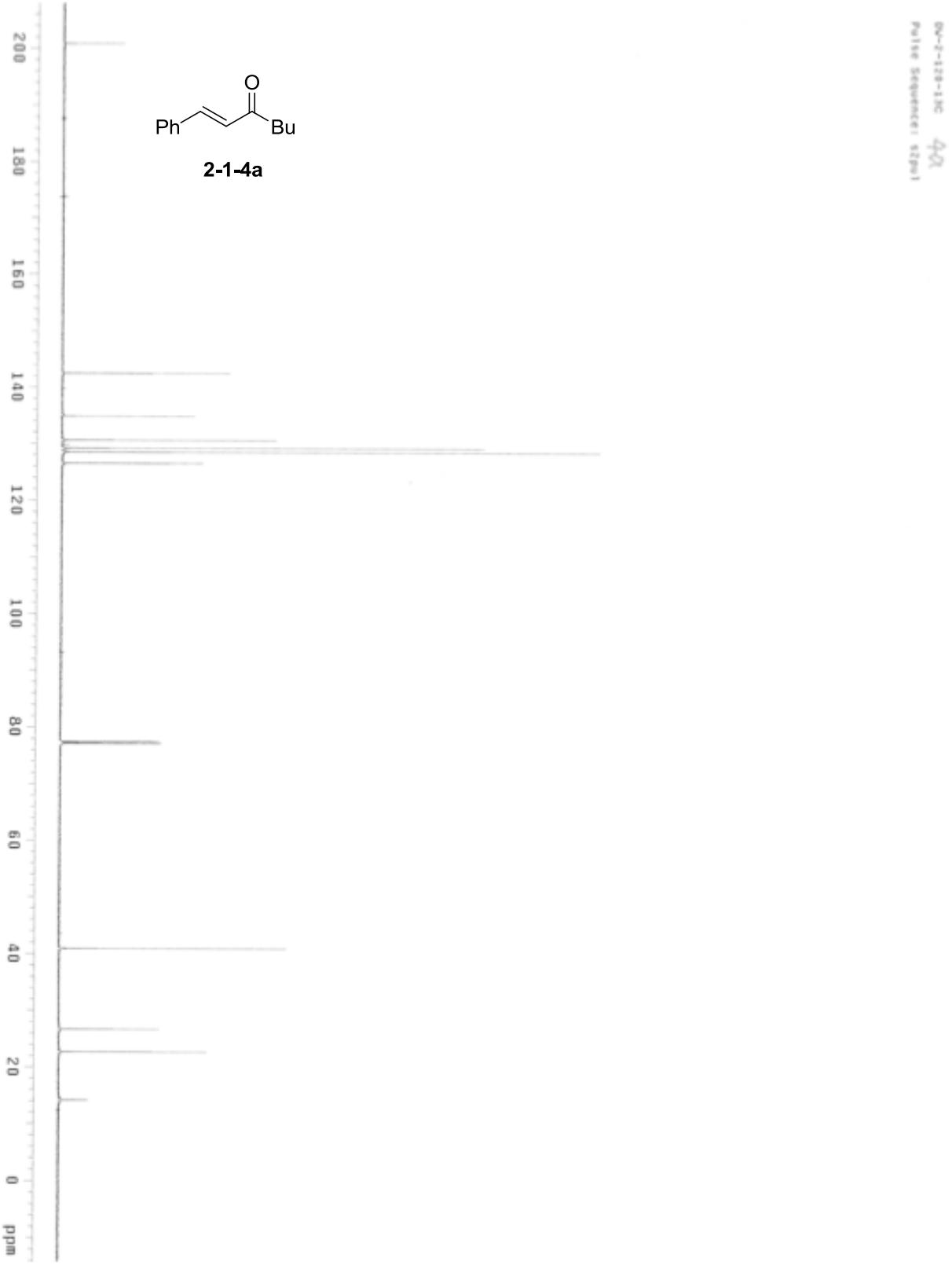
(*E*)-1-(naphthalen-4-yl)hept-1-en-3-one (***E*-2-1-4u**): (Known compound, See: R. S. Ramón, N. Marion, S. P. Nolan, *Tetrahedron*, **2009**, *65*, 1767-1773) ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.40 (d, *J* = 16.2 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.88 (t, *J* = 9.0 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 16.2 Hz, 1H), 2.73 (t, *J* = 7.5 Hz, 2H), 1.72 (quintet, *J* = 7.5 Hz, 2H), 1.42 (sextet, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.4, 139.1, 133.7, 132.0, 131.6, 130.6, 128.8, 128.7, 126.8, 126.2, 125.4, 125.0, 123.3, 41.1, 26.5, 22.5, 13.9.

III. NMR spectra


O
Ph
Bu

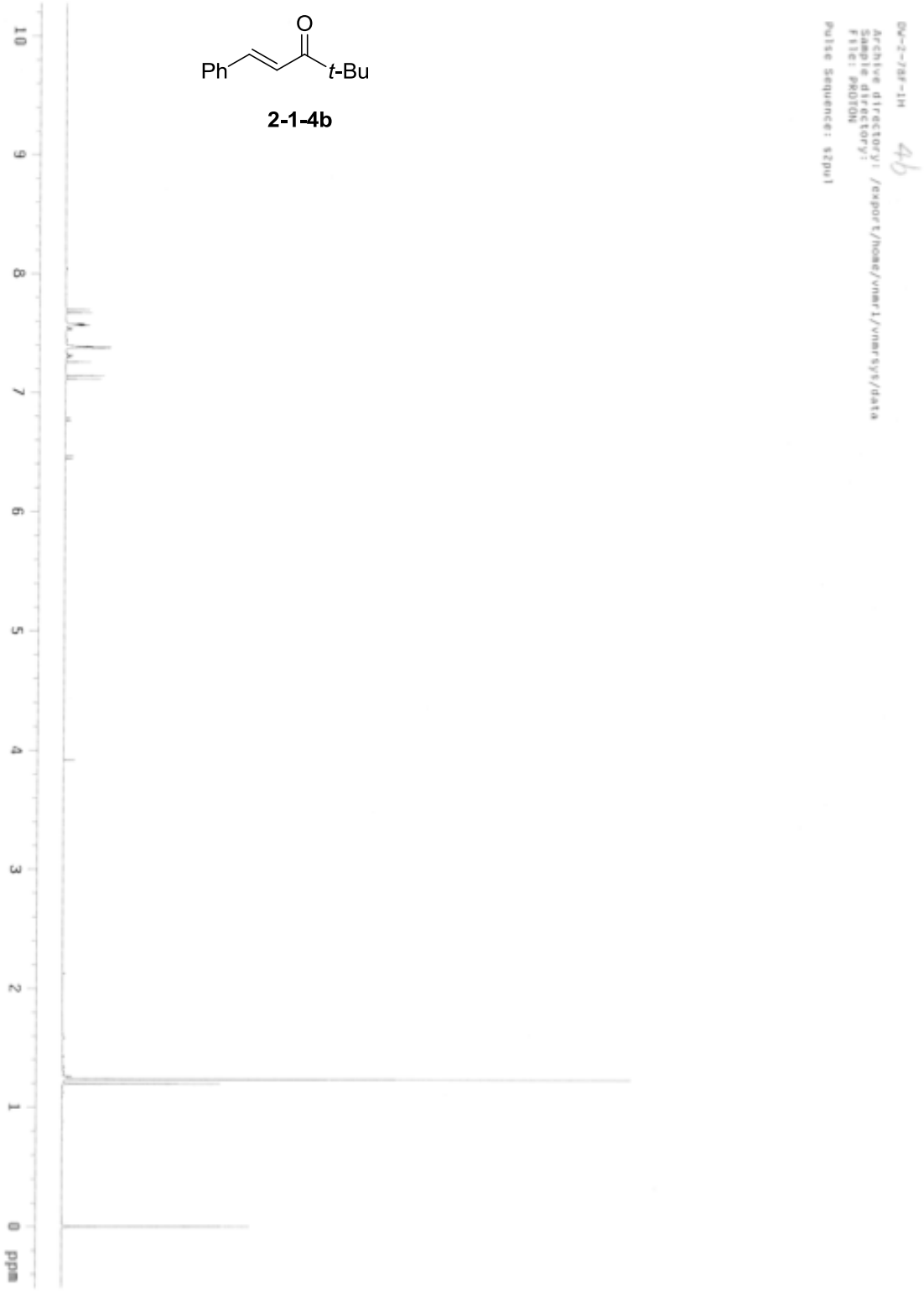
2-1-4a


DW-2-129-1H
Archive directory: /exports/home/vnmrl/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0 ppm


DV-2-120-13C
Pulse Sequence: s2pul
Ph
O
Bu
2-1-4a
200
180
160
140
120
100
80
60
40
20
0
ppm

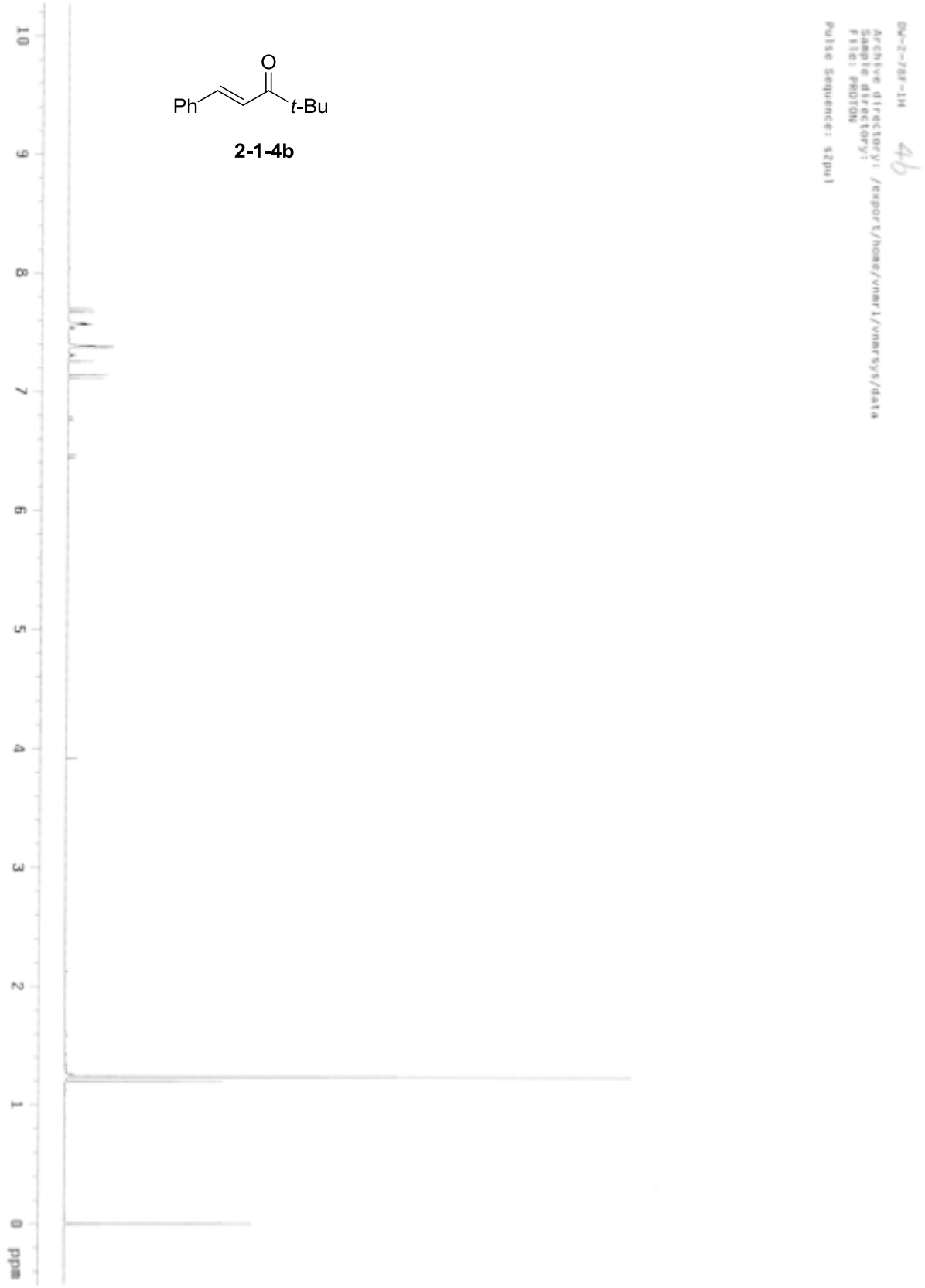
O
Ph
t-Bu

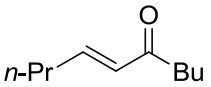
2-1-4b


DW-2-78F-1H
4b
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0
ppm

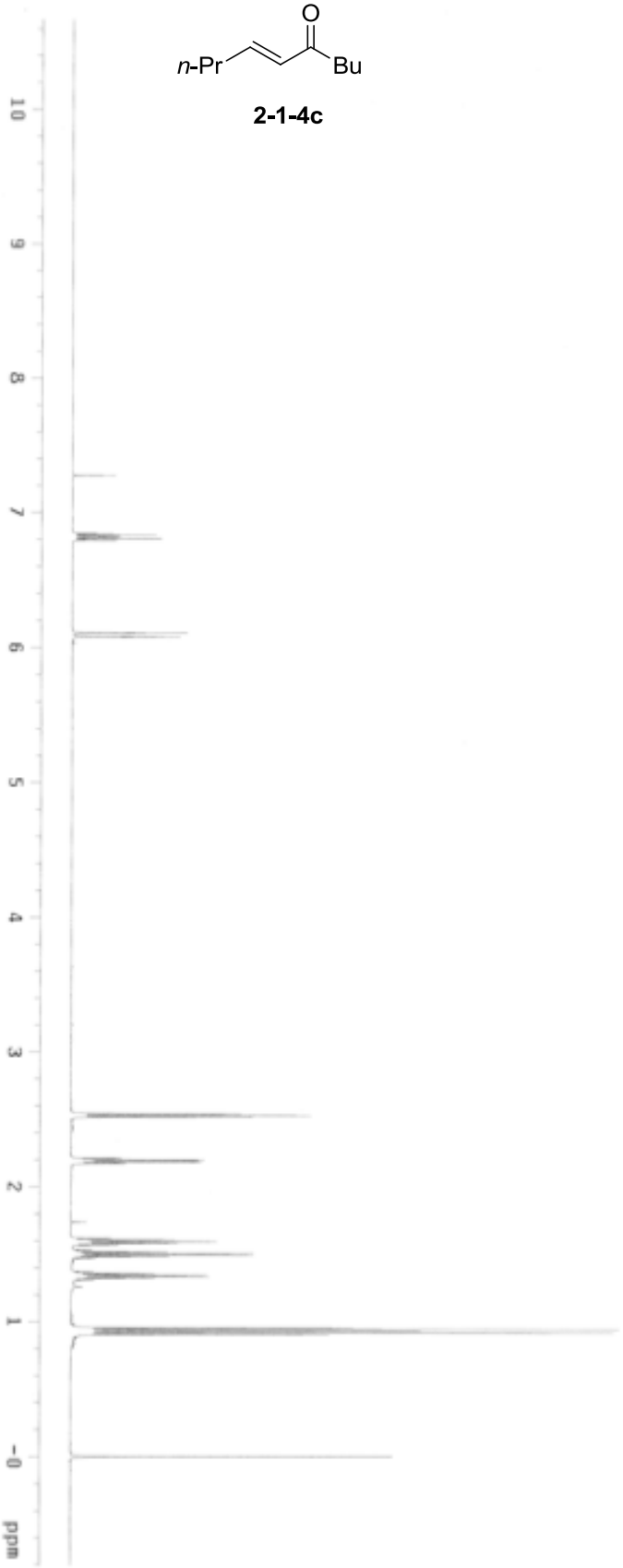
O
Ph
t-Bu

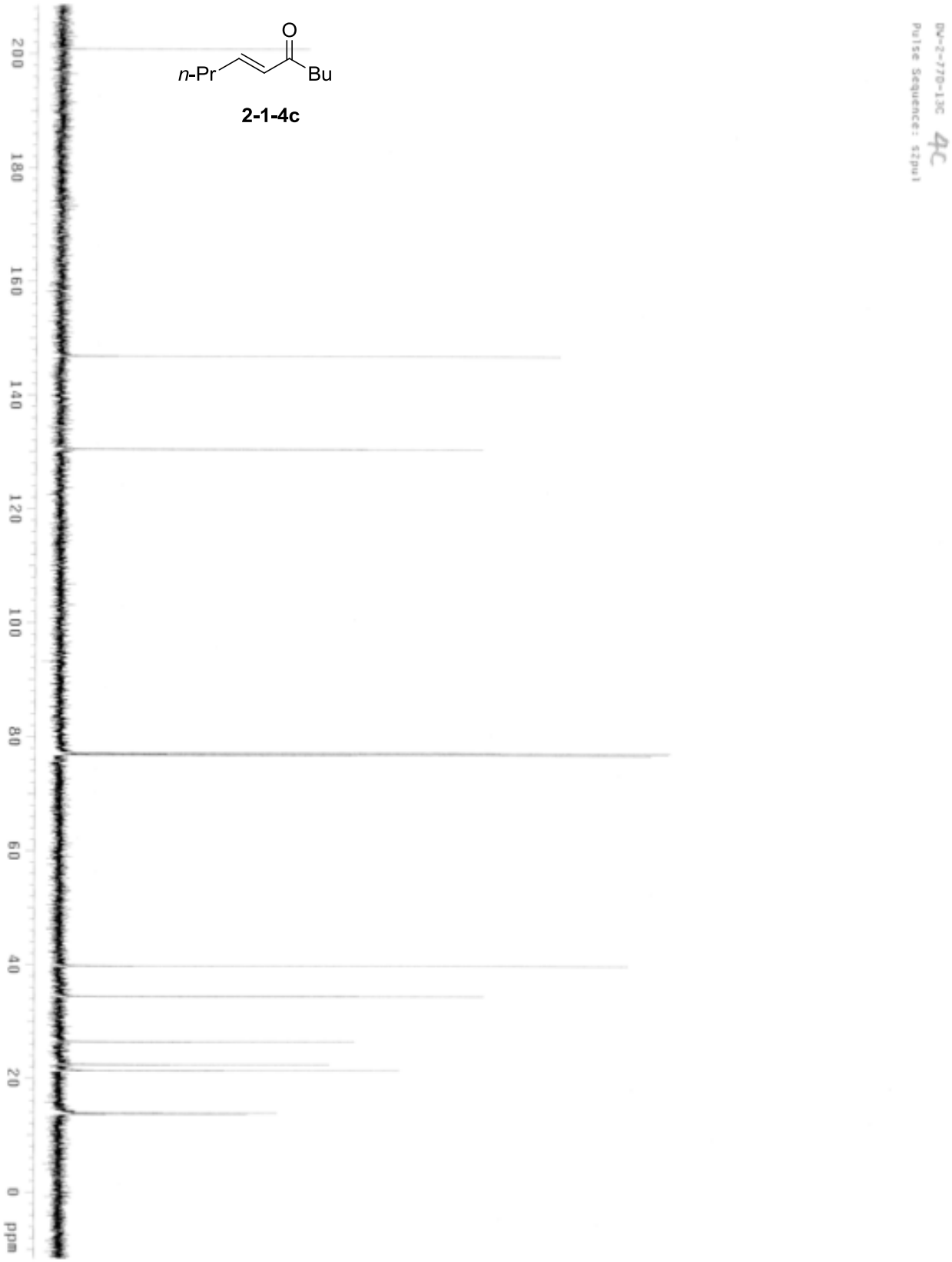
2-1-4b


DW-2-78F-1H
4b
Archive directory: /export/home/vnmrj/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0
ppm


O
n-Pr
Bu

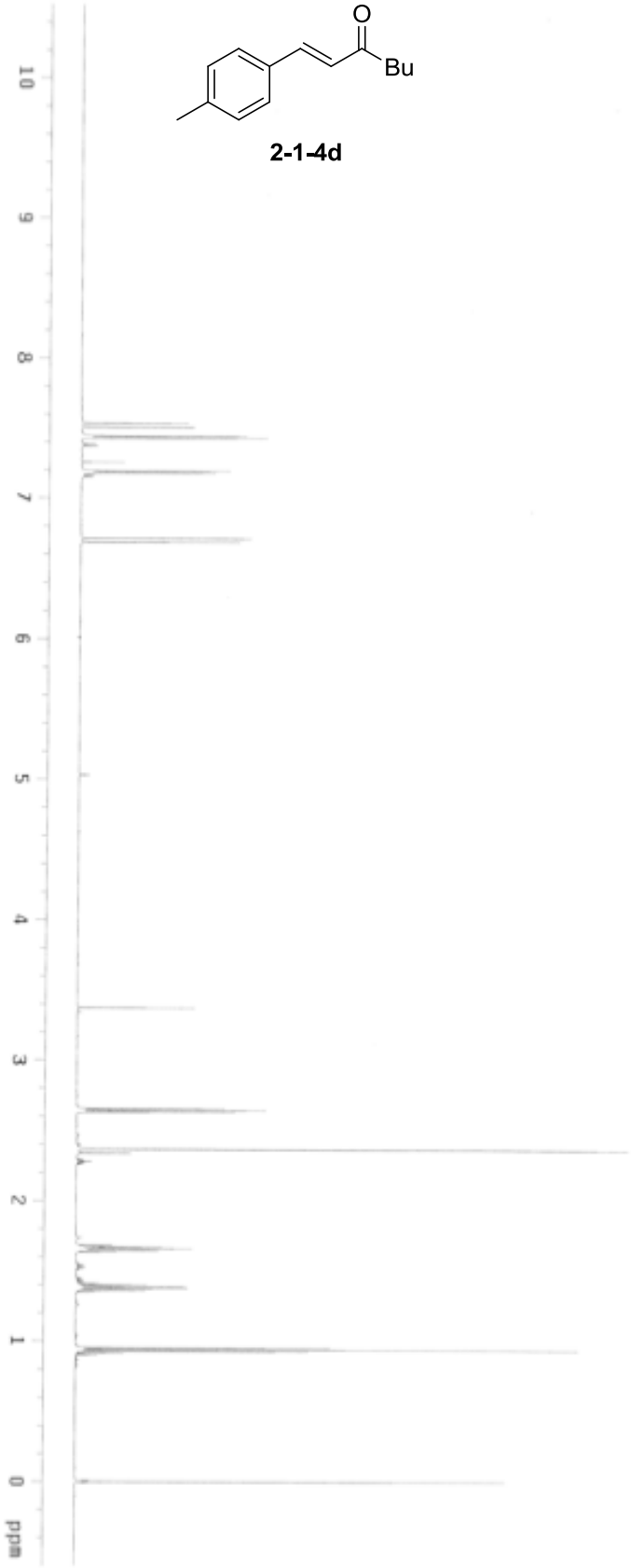
2-1-4c


BW-2-77D-1H 4C
Archive directory: /export/home/vnmrj/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
-0
ppm


DV-2-170-13C
4C
Pulse Sequence: s2pul
O
n-Pr
Bu
2-1-4c
200
180
160
140
120
100
80
60
40
20
0
ppm

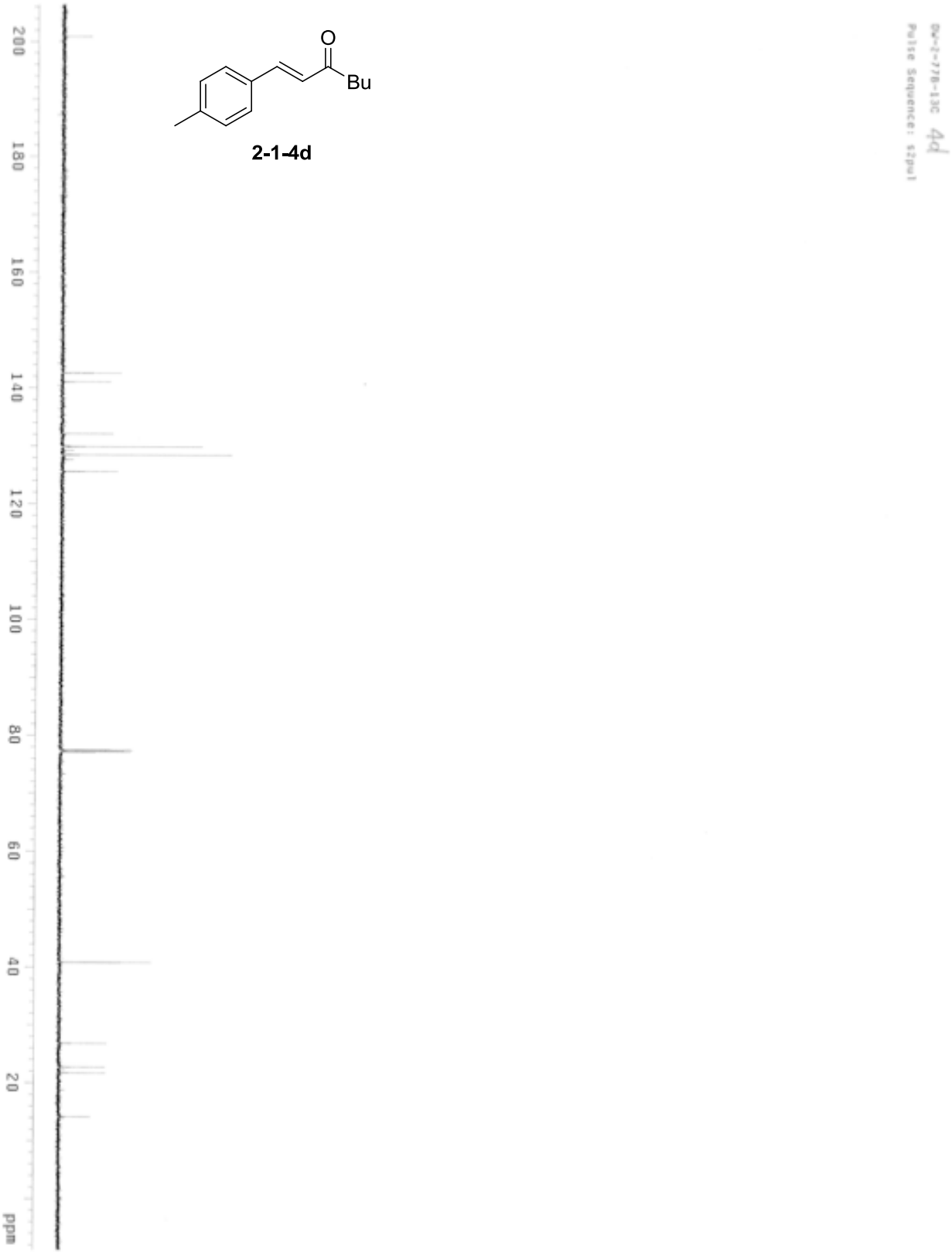
O
Bu

2-1-4d


DW-2-77B-1H 4d
Archive directory: /export/home/vnmrj/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0
ppm

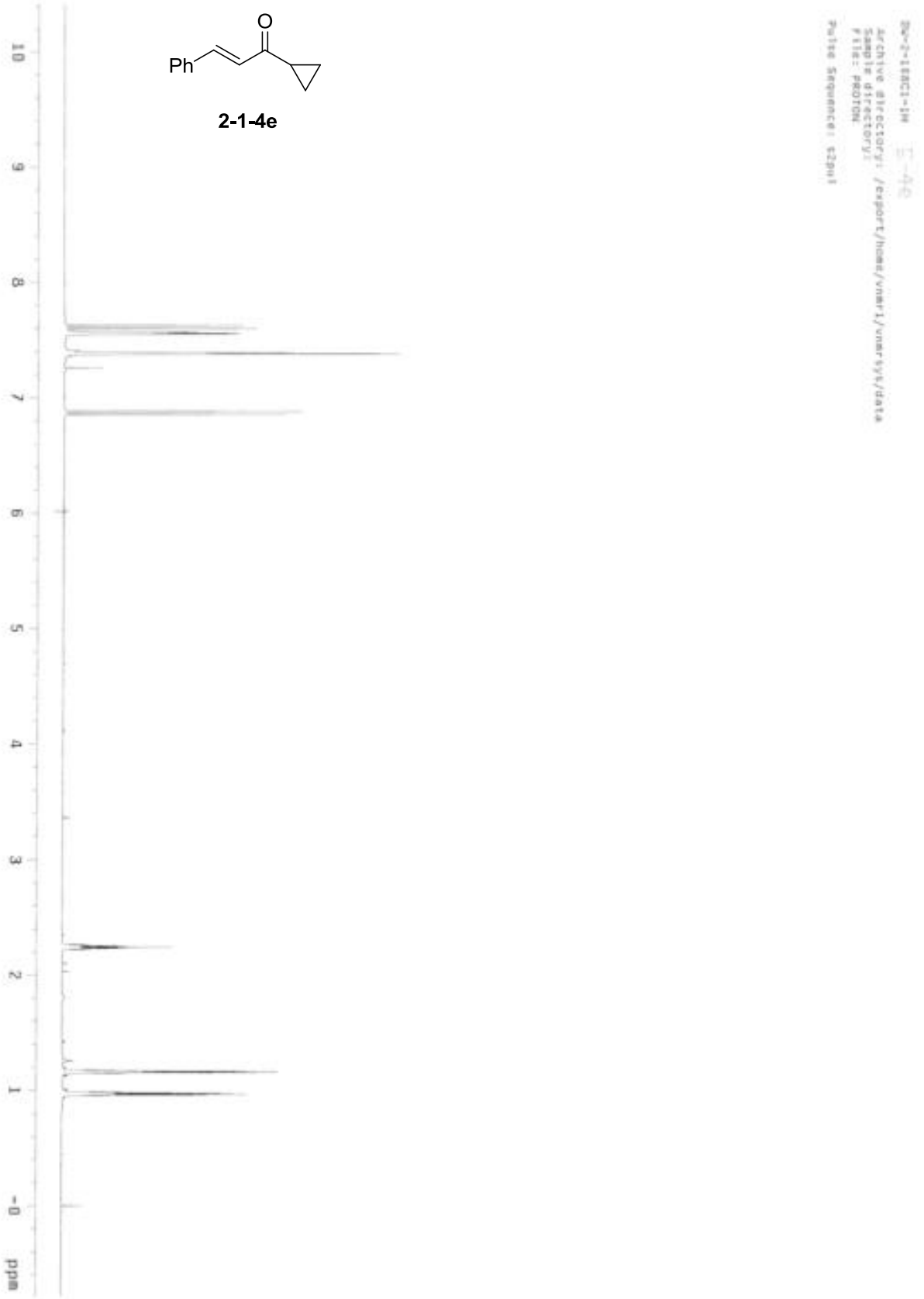
O
Bu

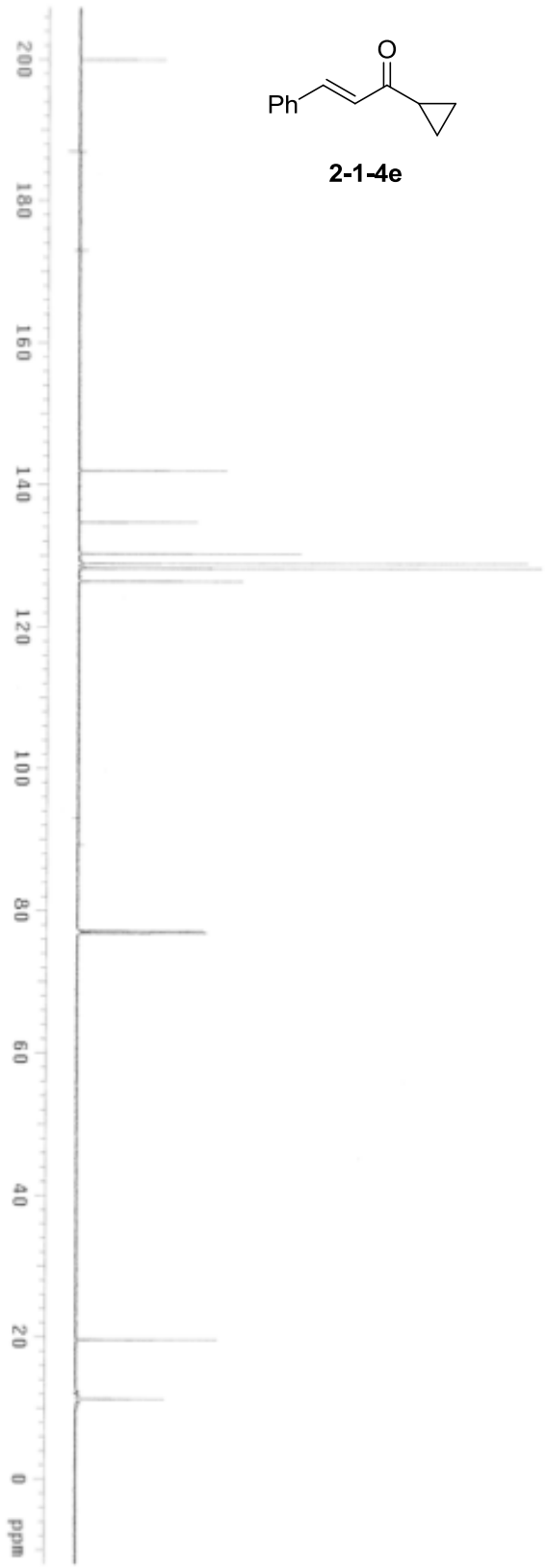
2-1-4d


BW-2-77B-13C 4d
Pulse Sequence: s2pul
ppm
20
40
60
80
100
120
140
160
180
200

O
Ph

2-1-4e

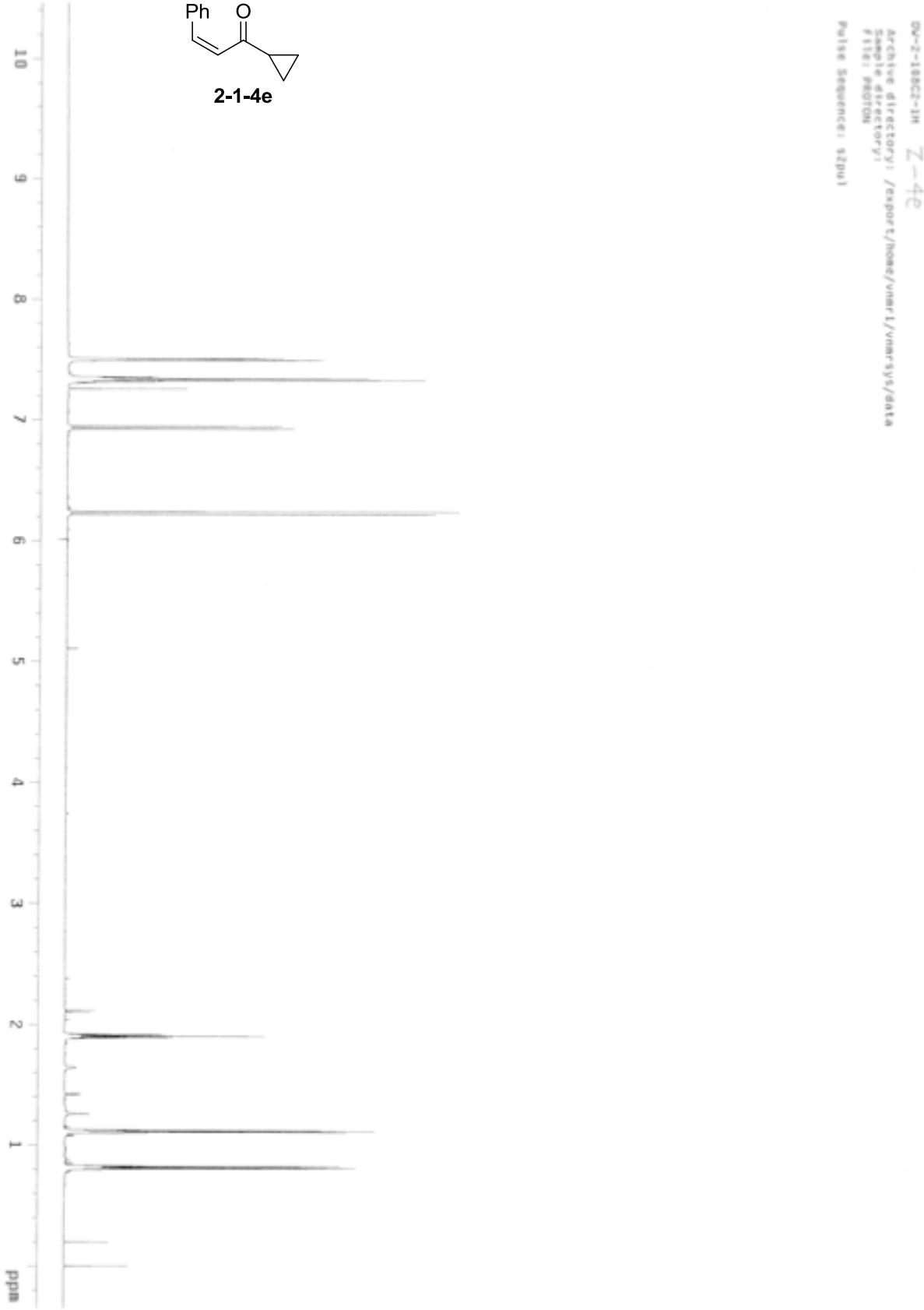

2e-2-1ESCI-1H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
-0
ppm

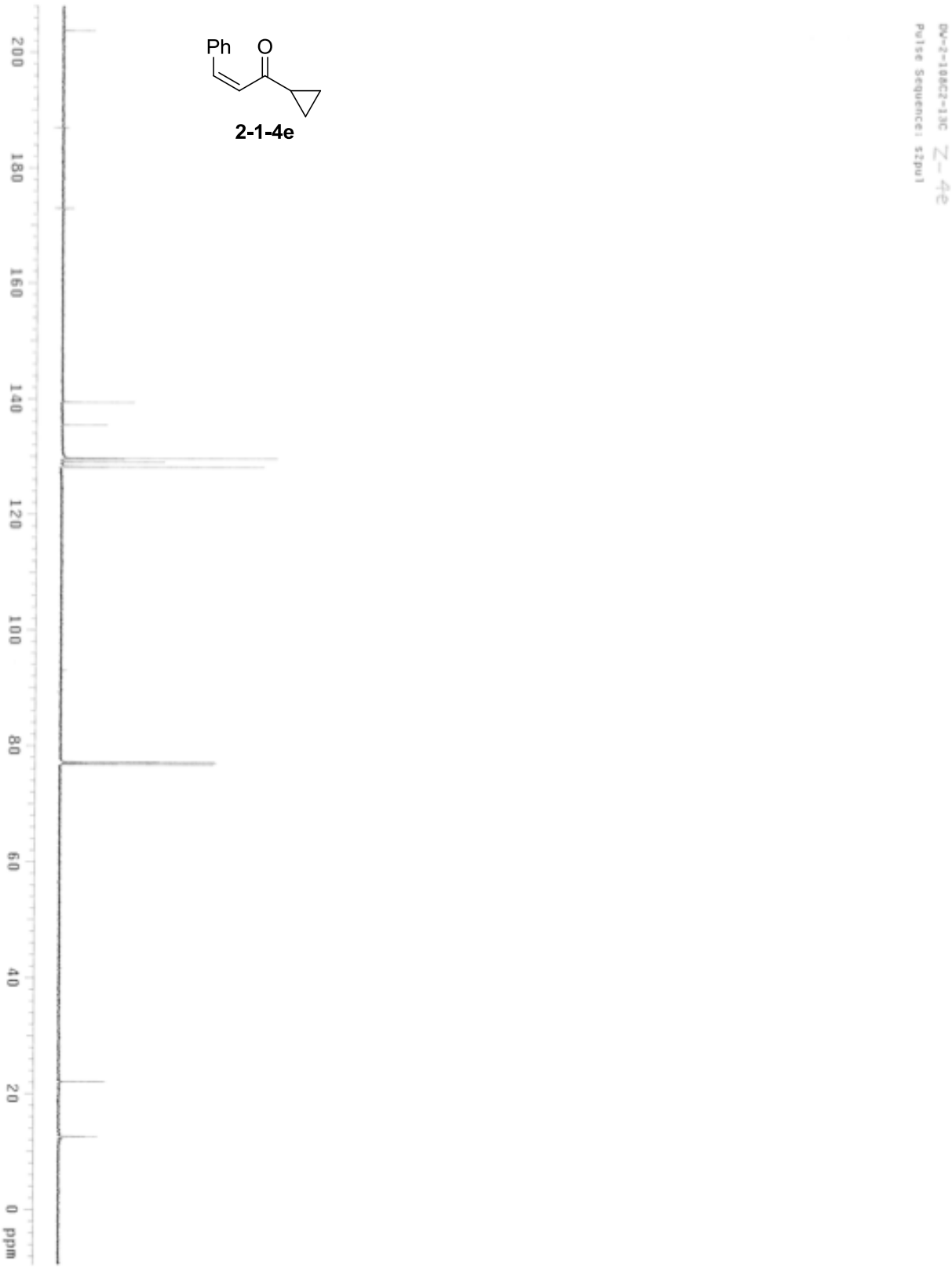


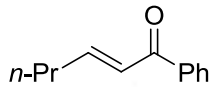
2-1-4e

Ph
O

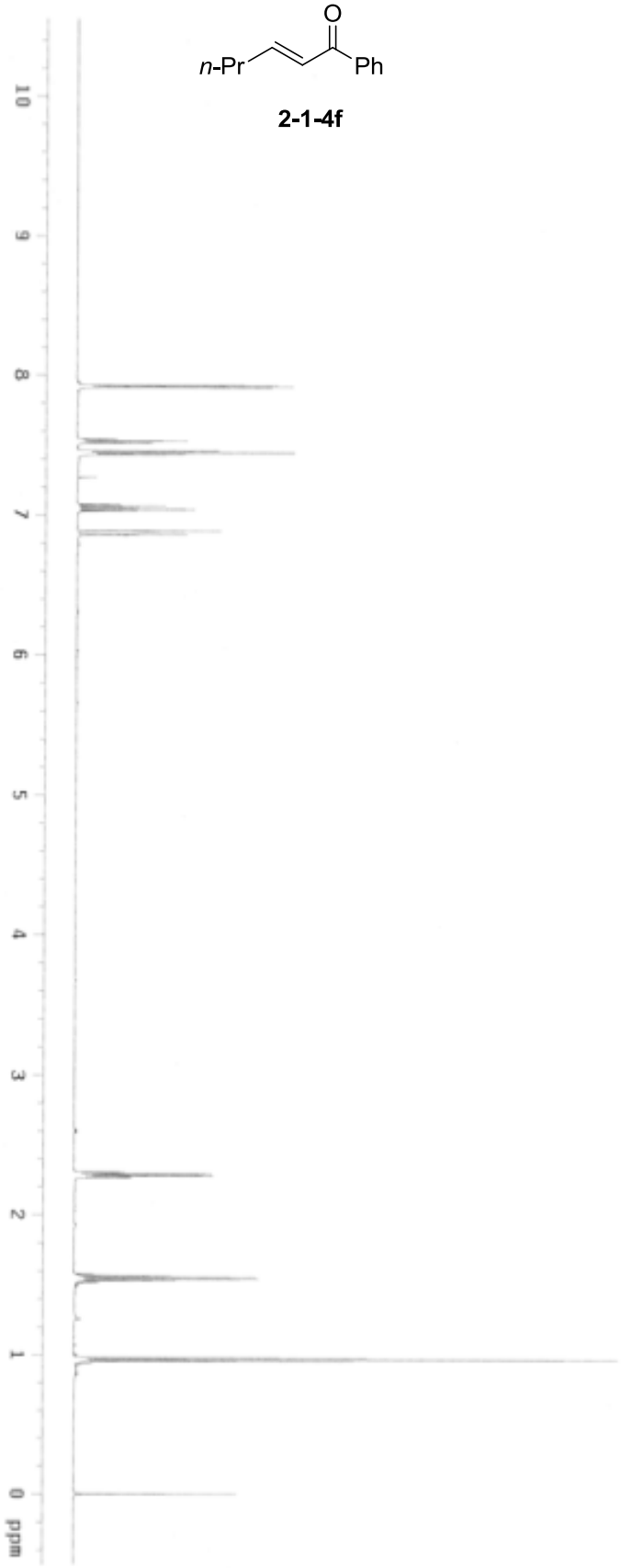
2-1-4e

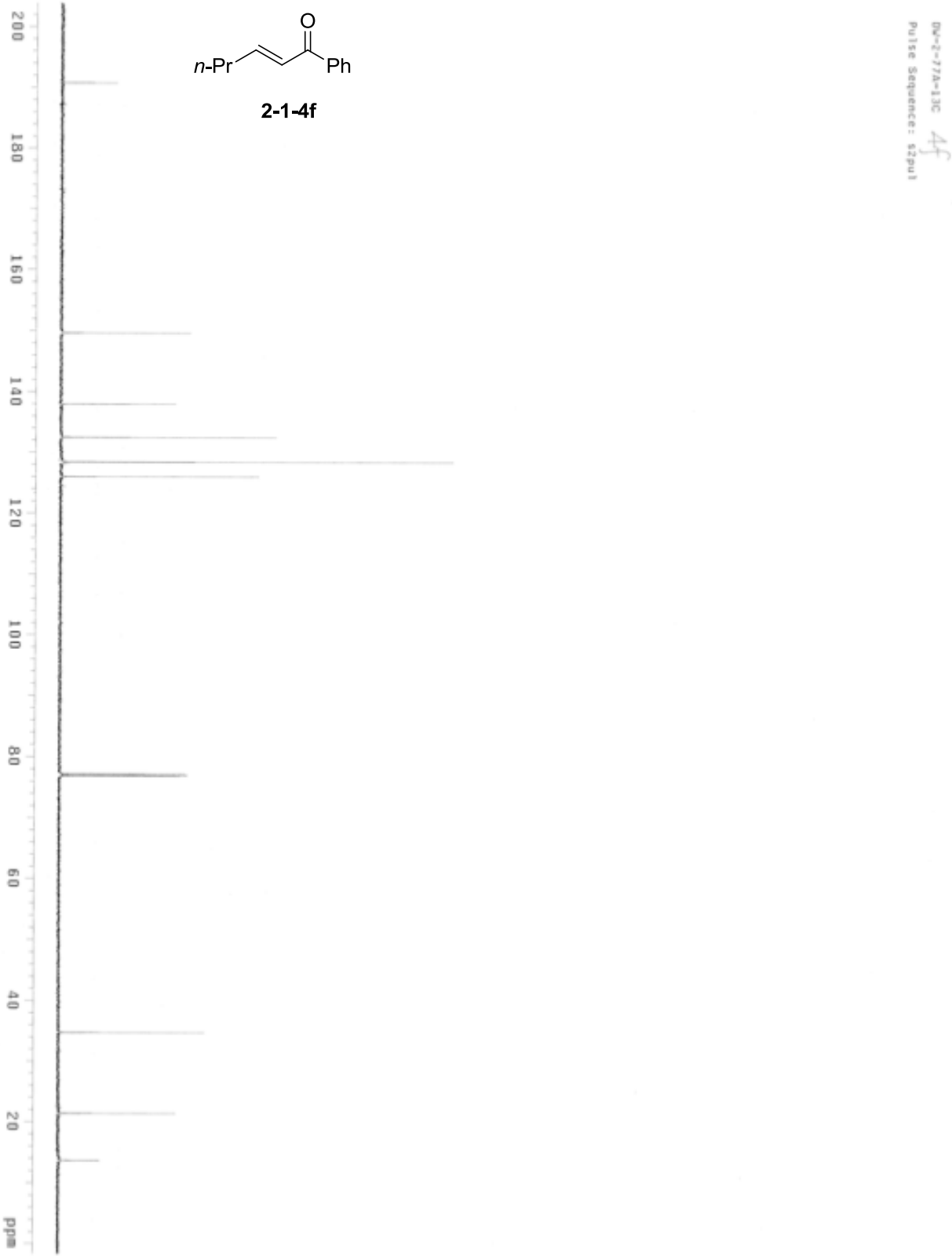

DW-2-185C2-1H Z-4e
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
ppm

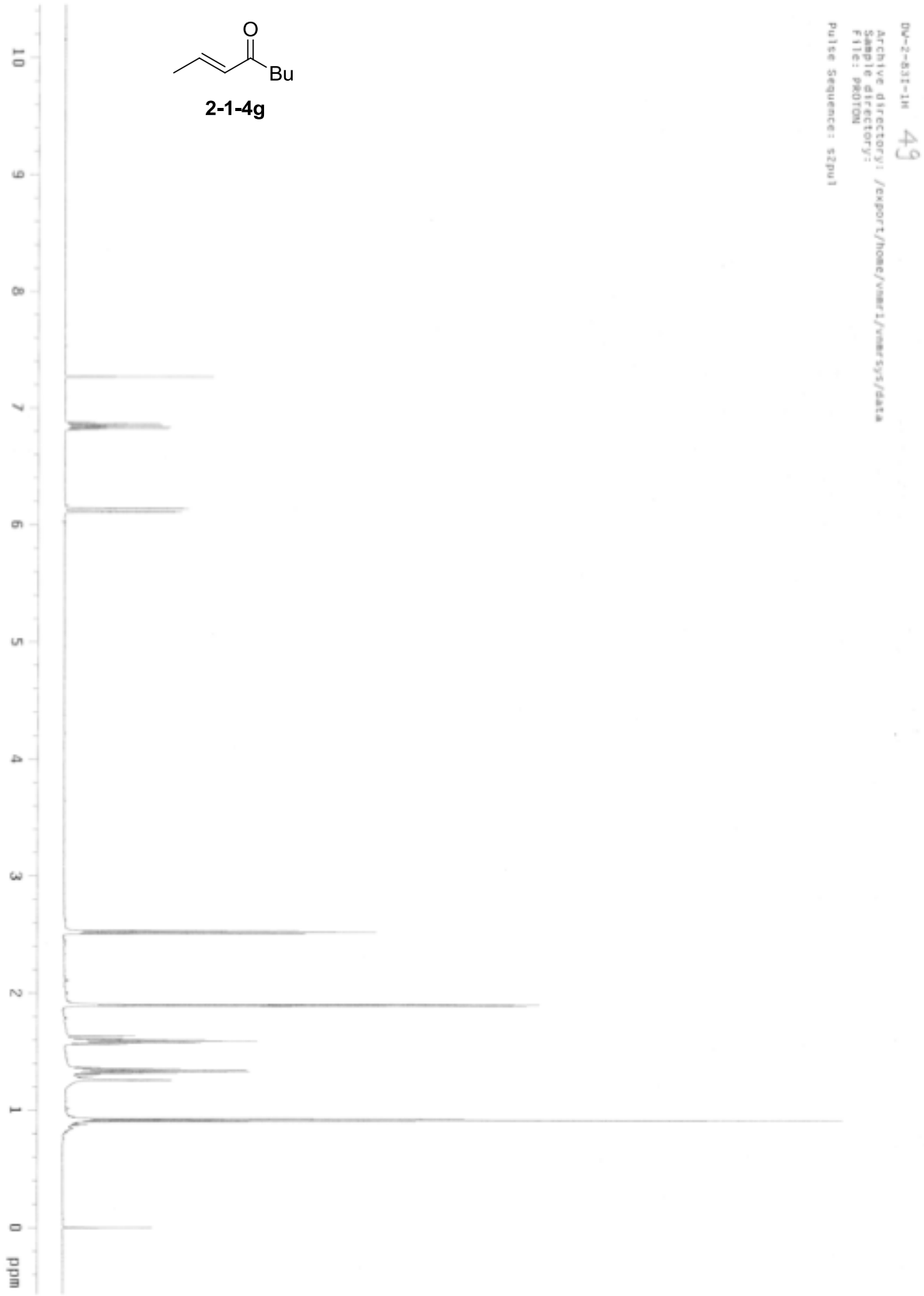

DW-2-108C2-13C Z-4e
Pulse Sequence: s2pul
Ph
O
2-1-4e
200
180
160
140
120
100
80
60
40
20
0 ppm


O
n-Pr
Ph

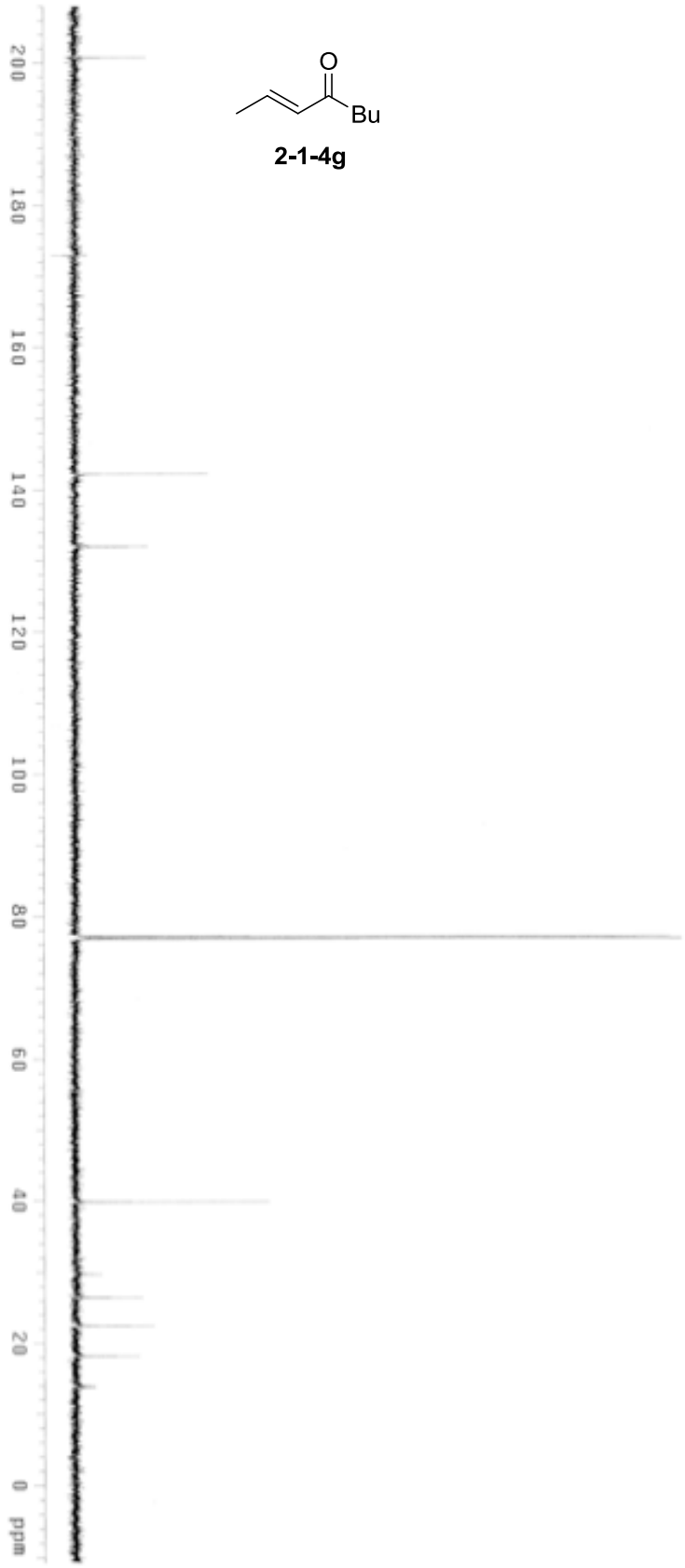
2-1-4f

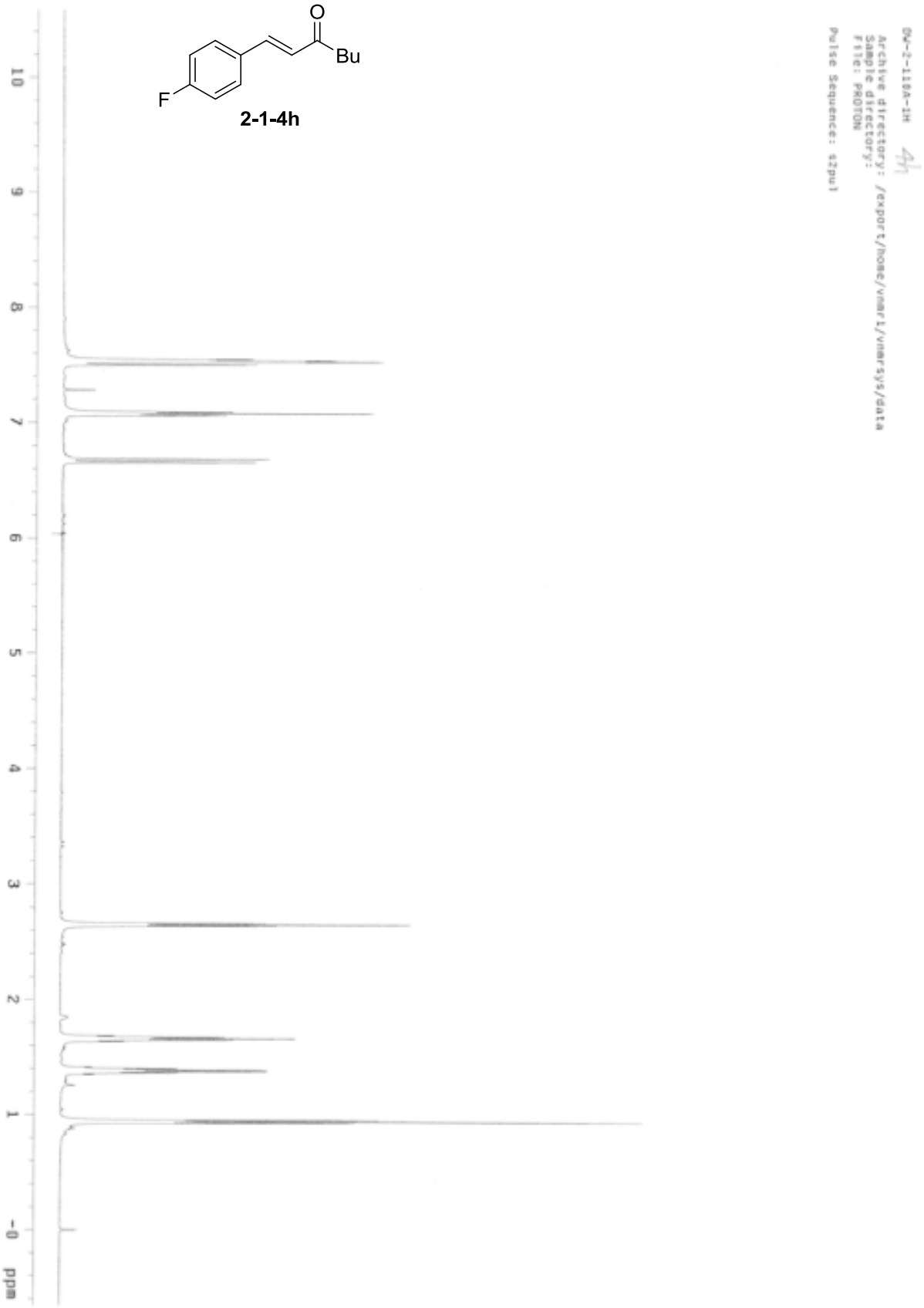

DW-2-77A-1H
Archive directory: /export/home/vnmrj/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0 ppm

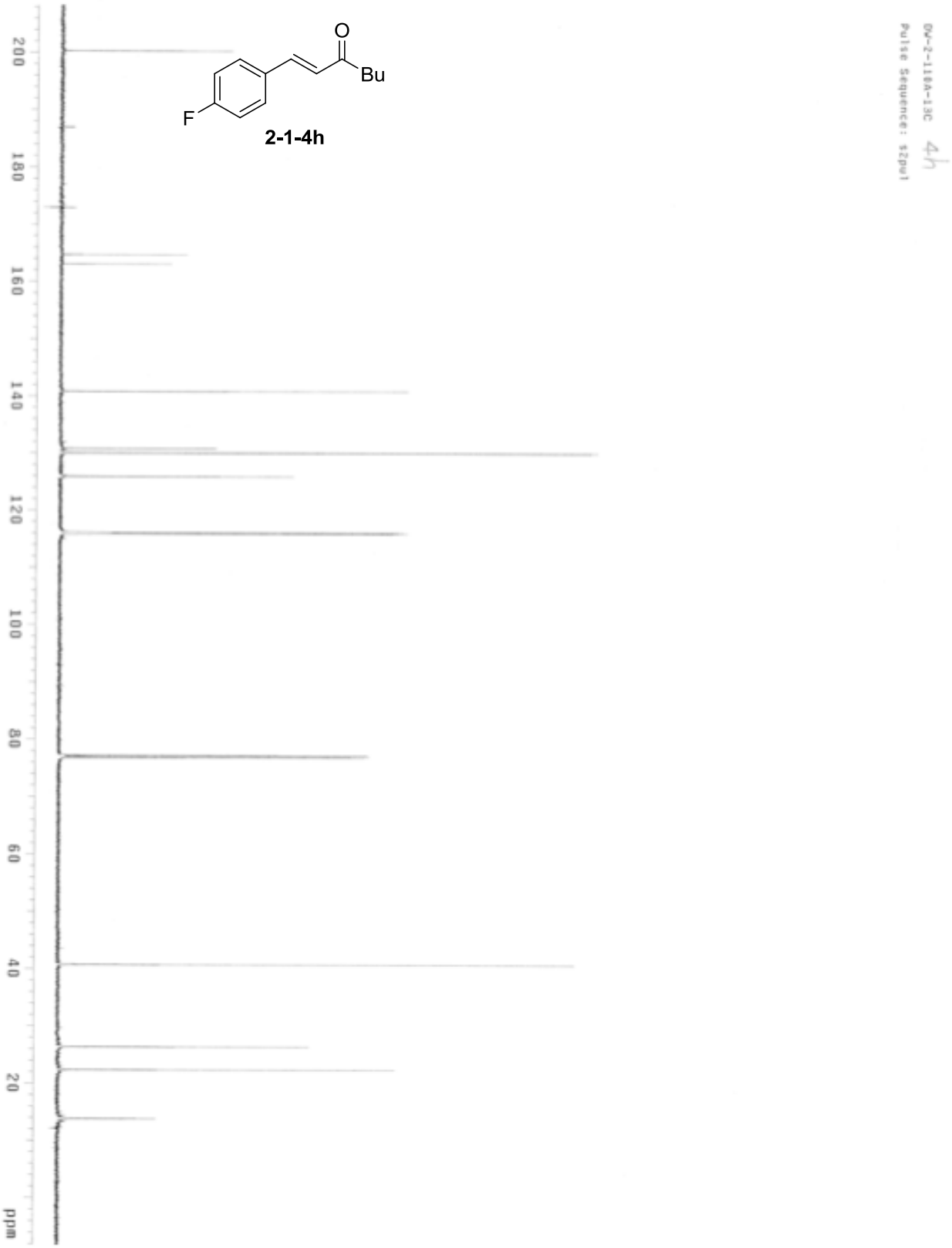

DW-2-77A-13C
Pulse Sequence: s2pul
4f
O
n-Pr
Ph
2-1-4f
200
180
160
140
120
100
80
60
40
20
ppm


DV-2-83I-1H
49
Archive directory: /export/home/vnmrj/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
O
Bu
2-1-4g
10
9
8
7
6
5
4
3
2
1
0
ppm

2-1-4g

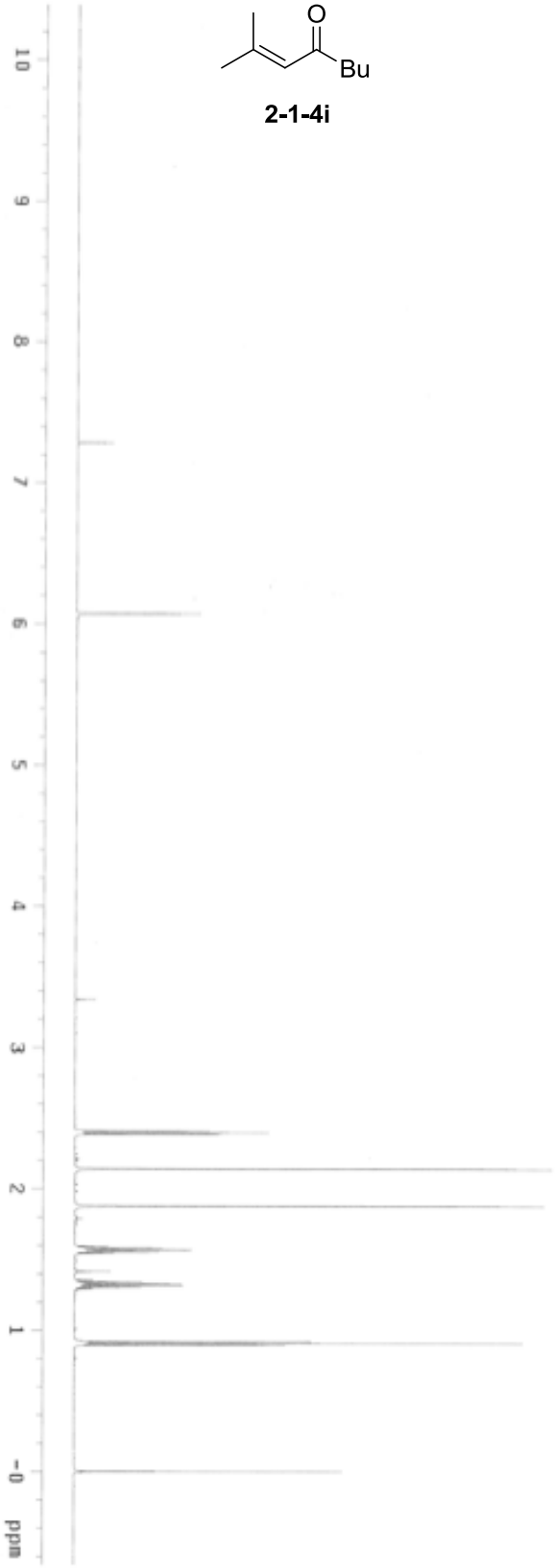


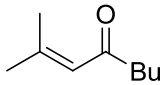

DW-2-118A-1H
Archive directory: /export/home/vnmrt/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
O
Bu
F
2-1-4h
10
9
8
7
6
5
4
3
2
1
-0
ppm


DW-2-118A-13C 4h
Pulse Sequence: s2pul
O
Bu
F
2-1-4h
200
180
160
140
120
100
80
60
40
20
ppm

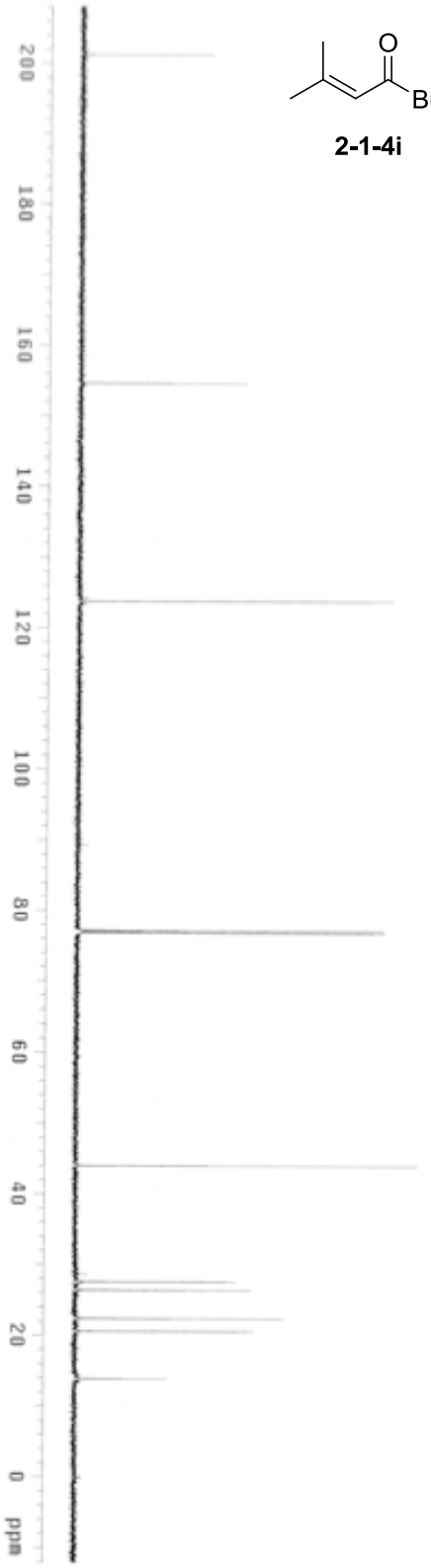
O
Bu

2-1-4i


DW-2-77E-1H
Archive directory: /export/home/vmarj/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0
ppm

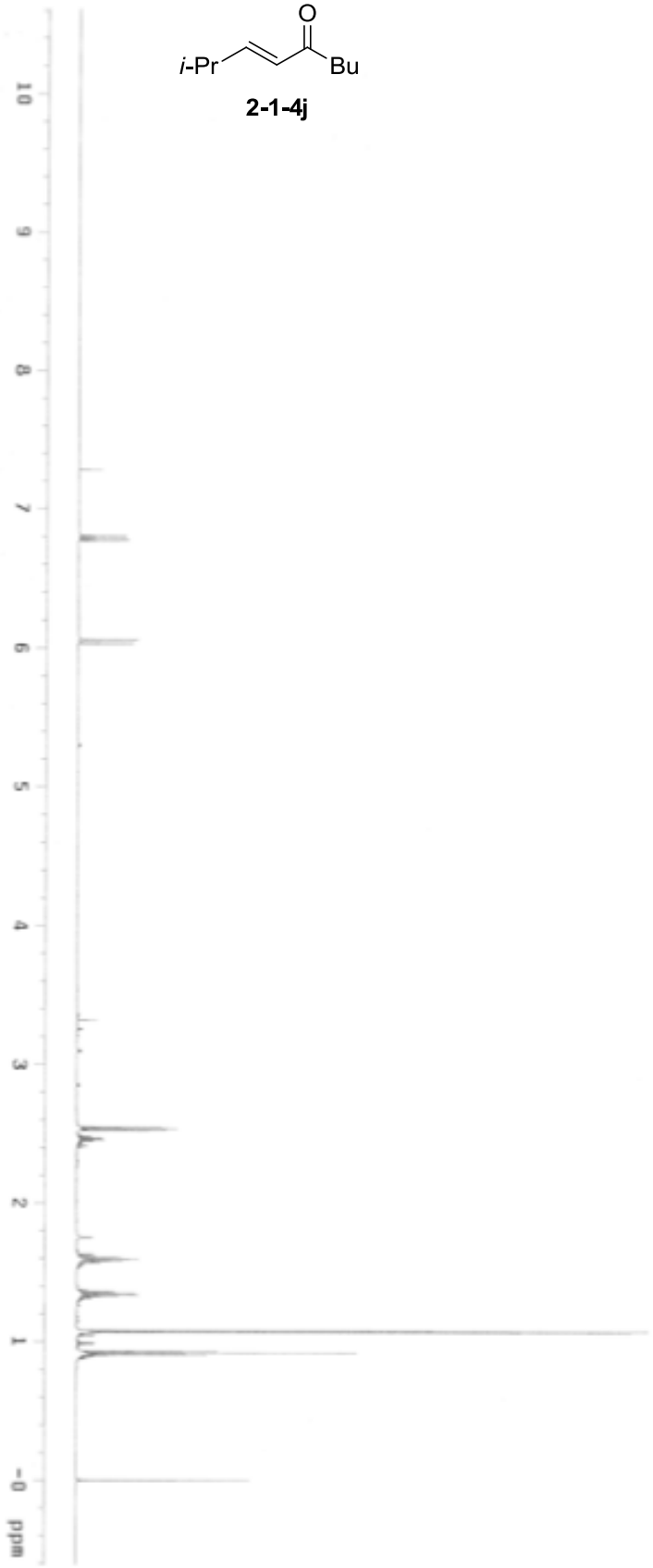


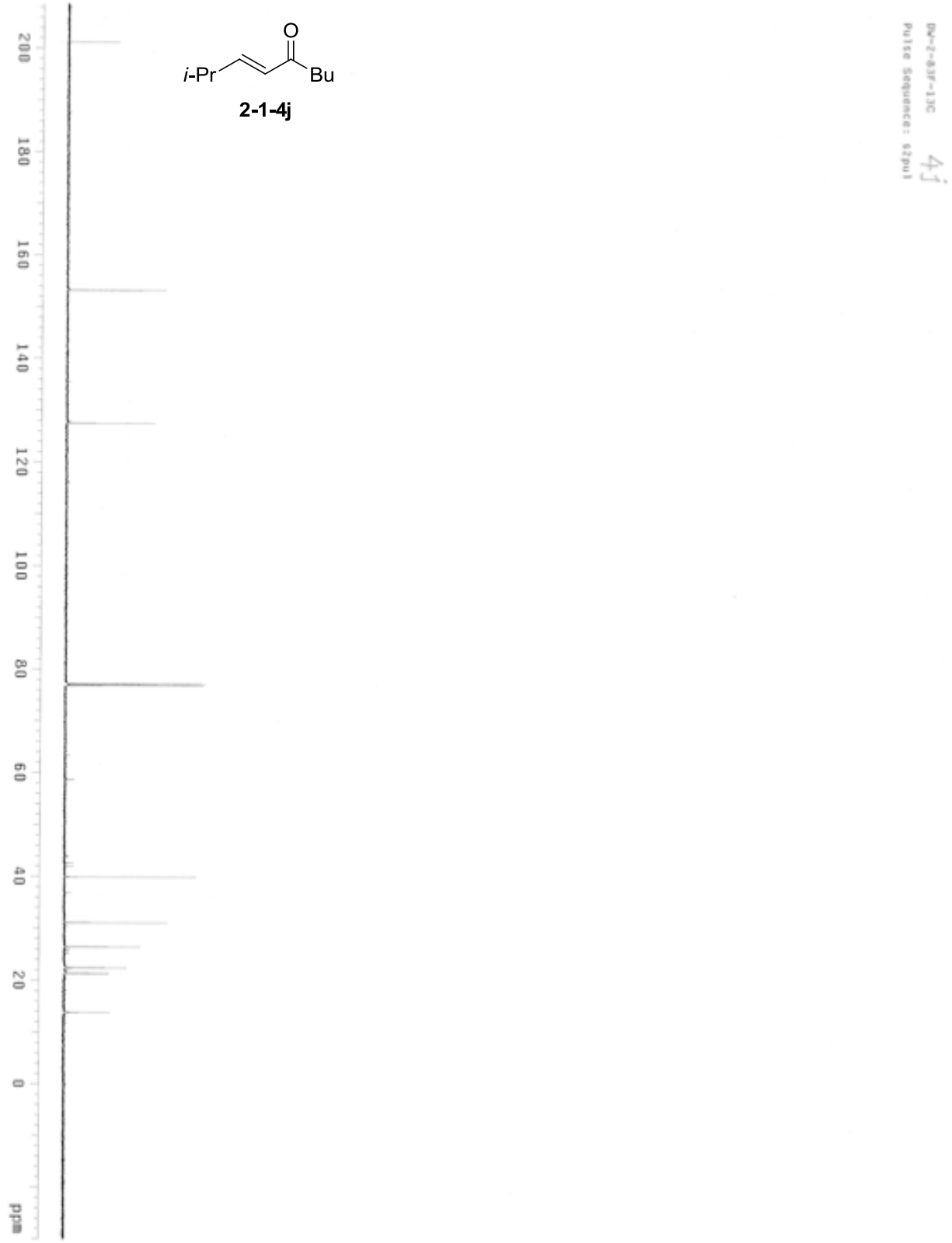
2-1-4i

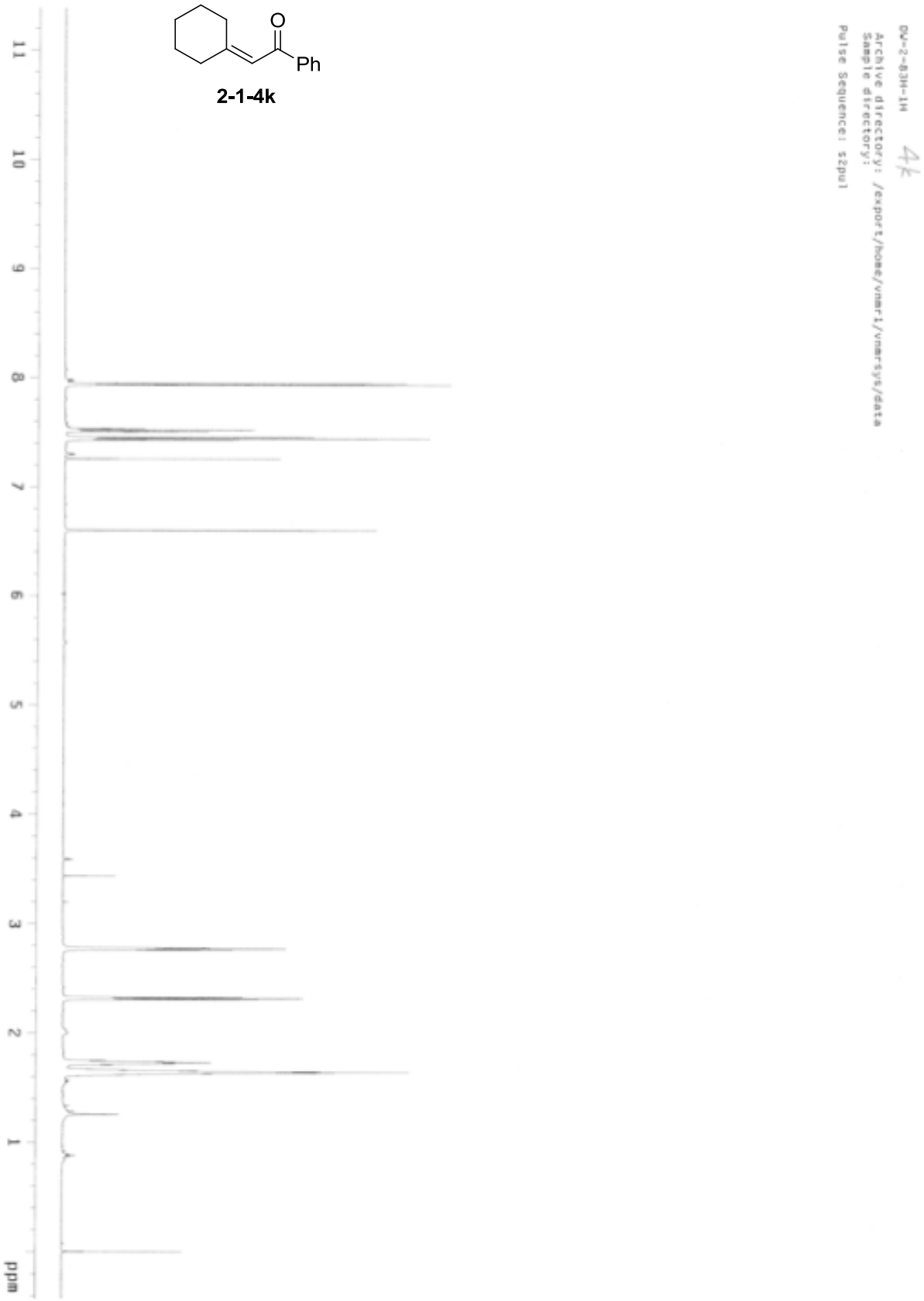


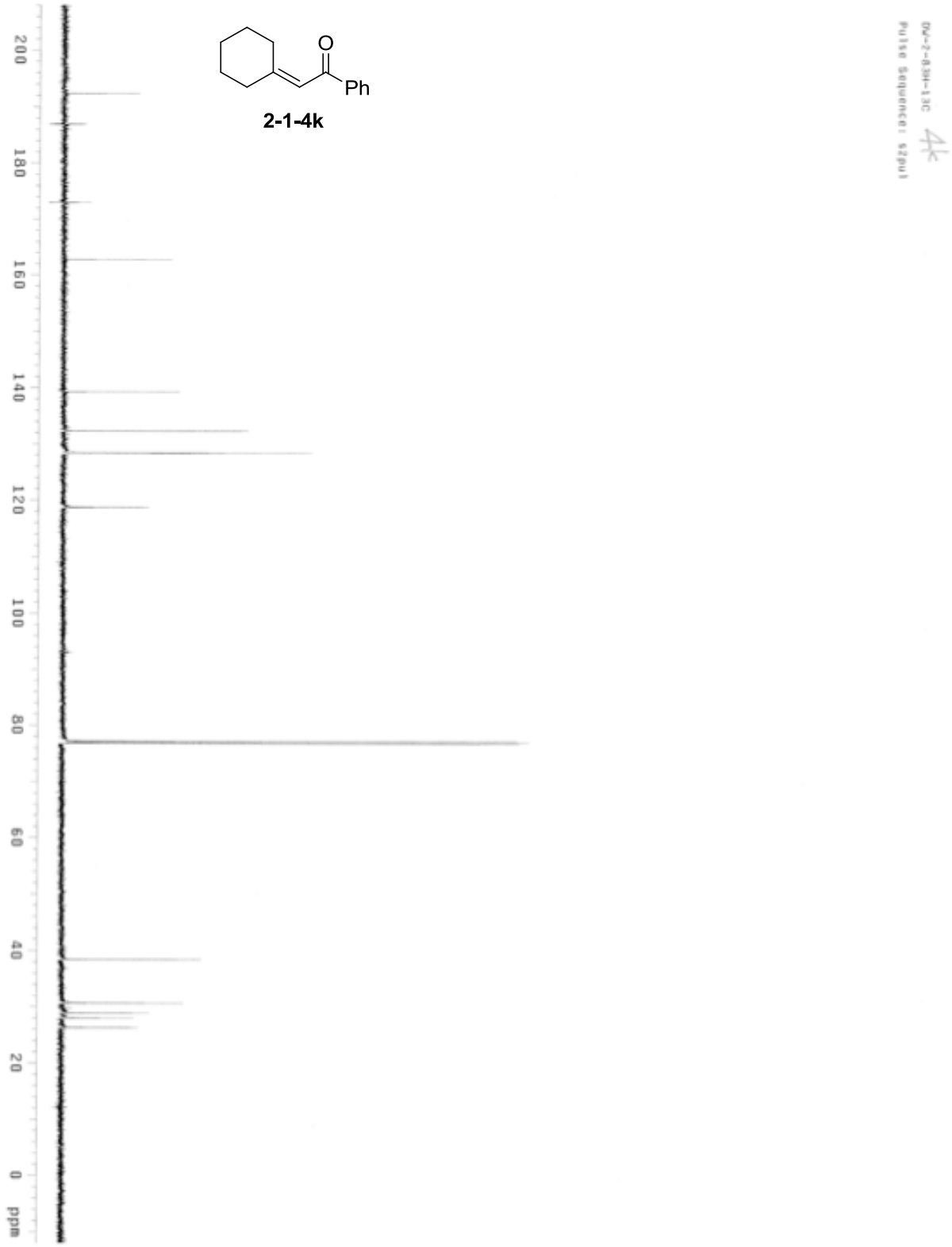
O
i-Pr
Bu

2-1-4j


DW-2-83F-1H
41
Archive directory: /export/home/vnmrt/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
-0
ppm

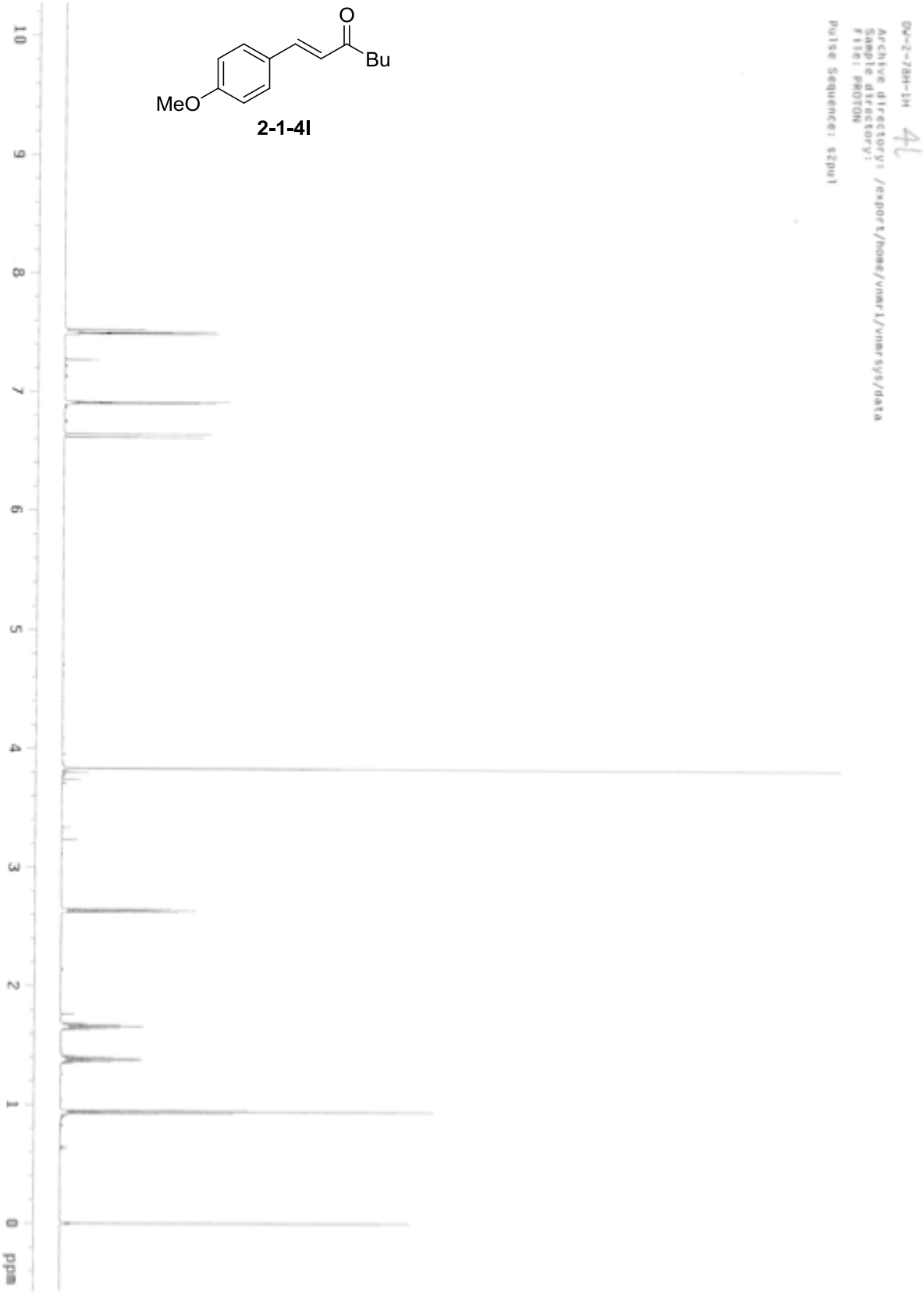

DW-2-83F-13C
4j
Pulse Sequence: s2pul
O
i-Pr
Bu
2-1-4j
200
180
160
140
120
100
80
60
40
20
0
ppm

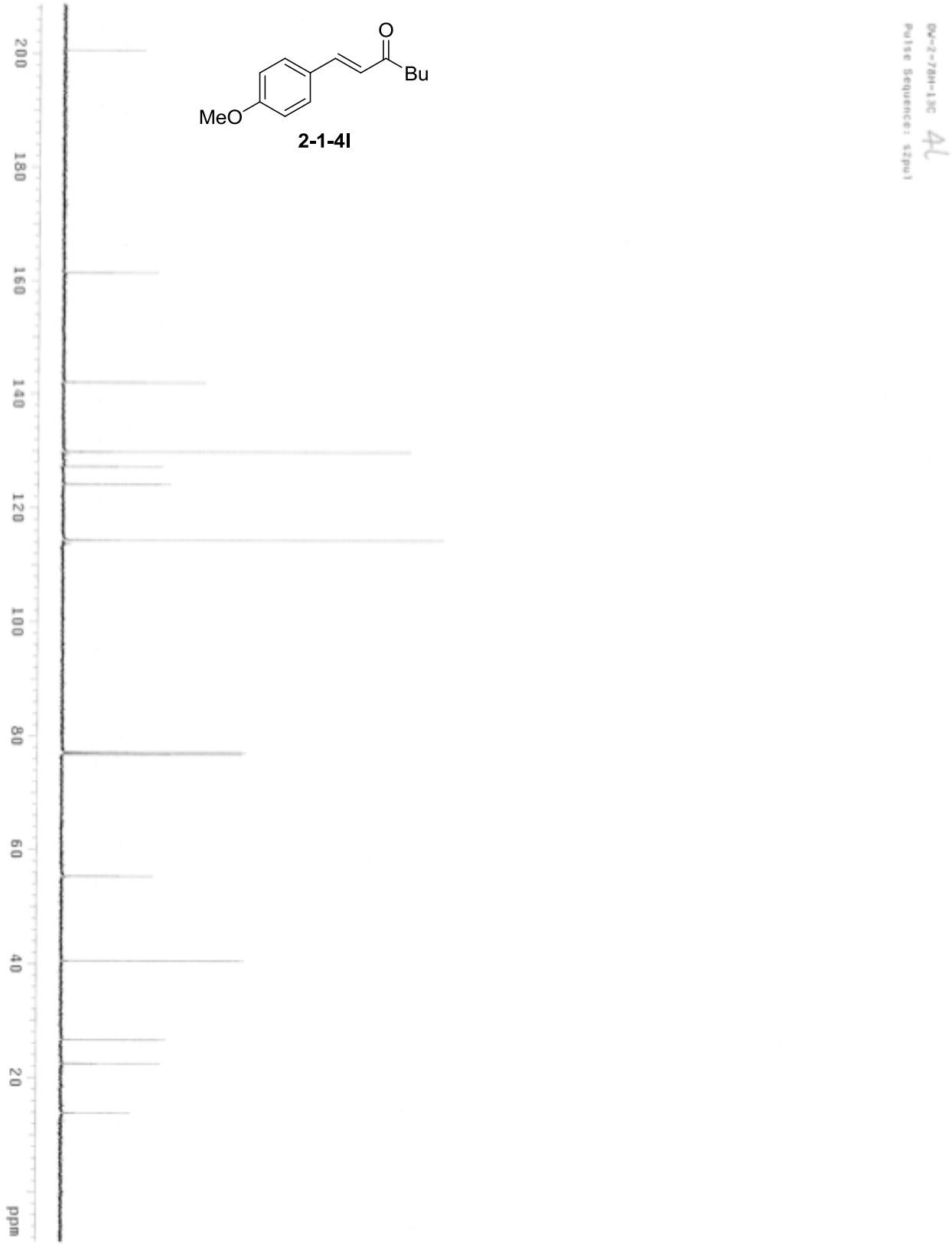

DW-2-83H-1H
4k
Archive directory: /export/home/vnmrt/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
O
Ph
2-1-4k
11
10
9
8
7
6
5
4
3
2
1
ppm

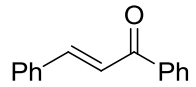

02-2-834-13C
4k
Pulse Sequence: s2pul
O
Ph
2-1-4k
200
180
160
140
120
100
80
60
40
20
0
ppm

O
Bu
MeO

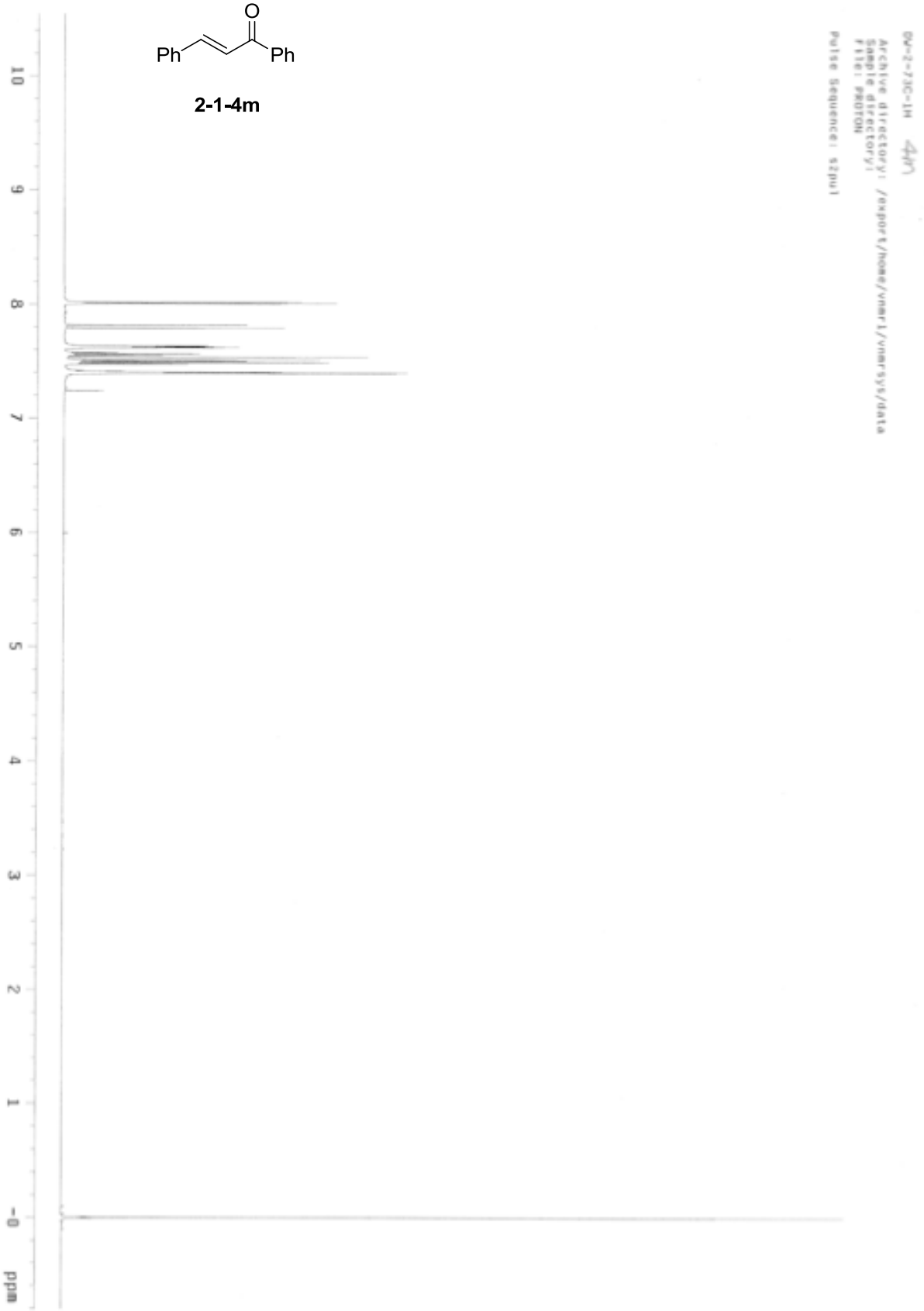
2-1-4l

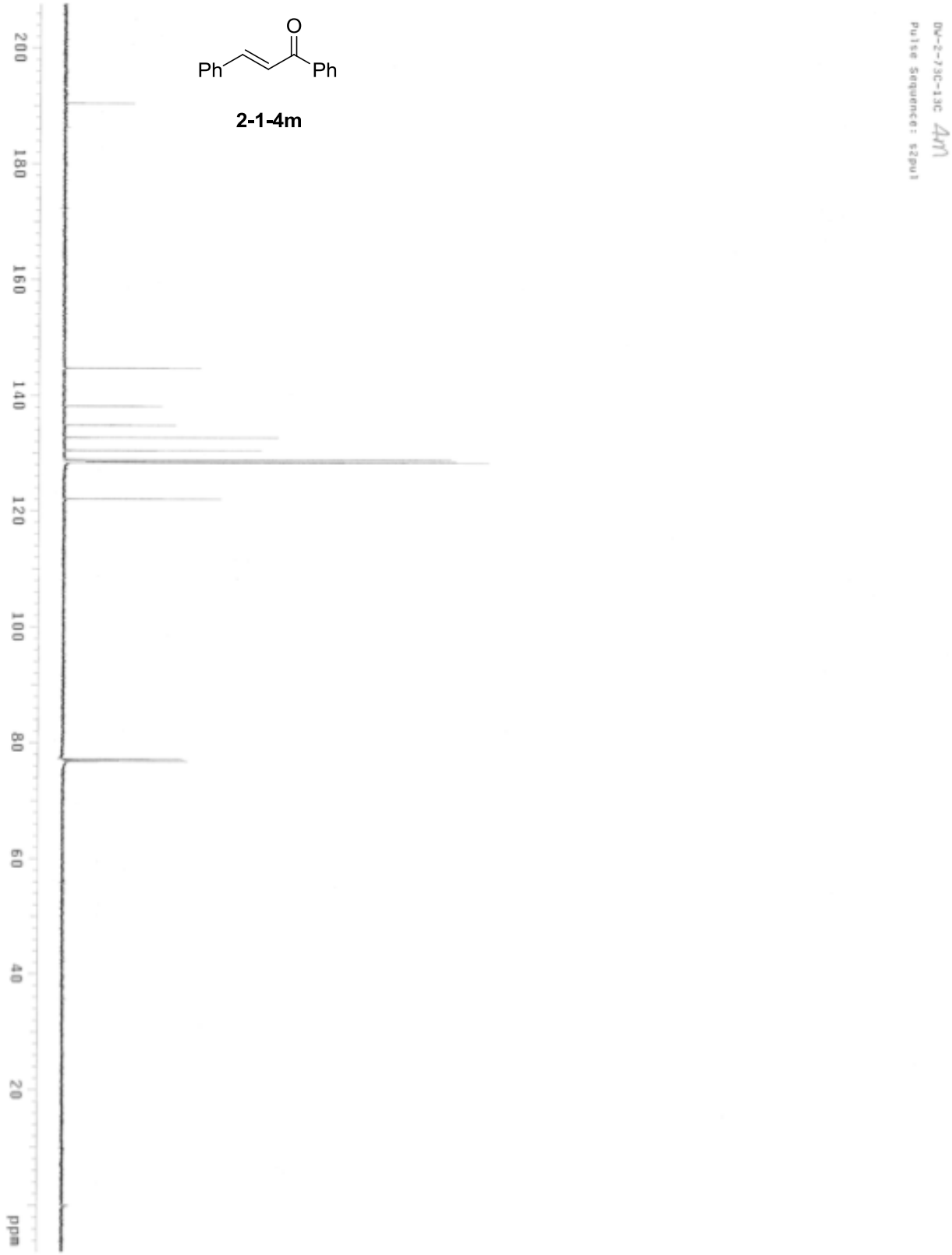

DW-2-78H-1H
4l
Archive directory: /export/home/vnmrj/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0
ppm


GW-2-78H-13C
Pulse Sequence: s2pul
O
Bu
MeO
2-1-4l
200
180
160
140
120
100
80
60
40
20
ppm



2-1-4m


BV-2-73C-1H
Archive directory: /export/home/vnmrl/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
-0
ppm

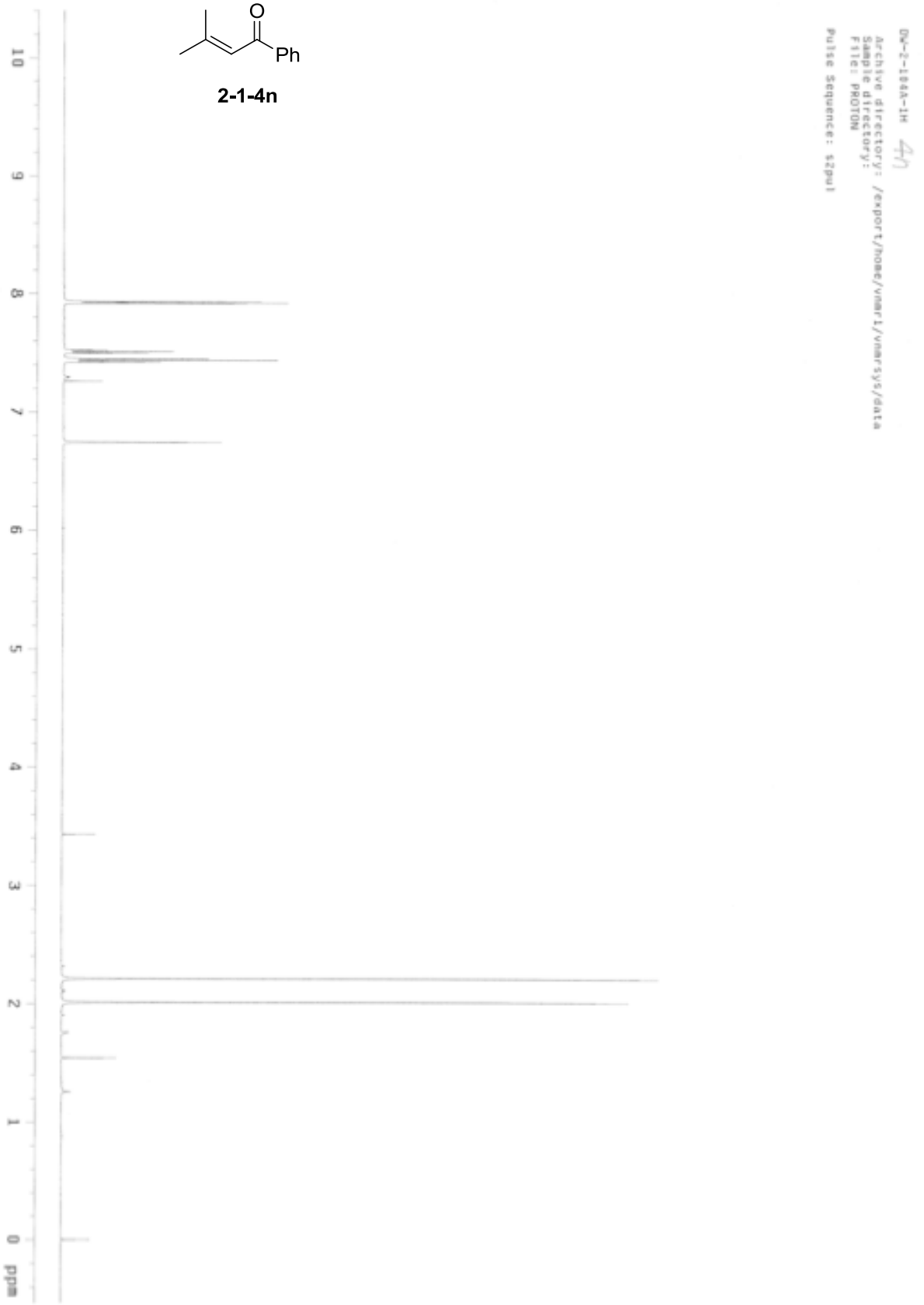

Pulse Sequence: s2pul
200
180
160
140
120
100
80
60
40
20
ppm

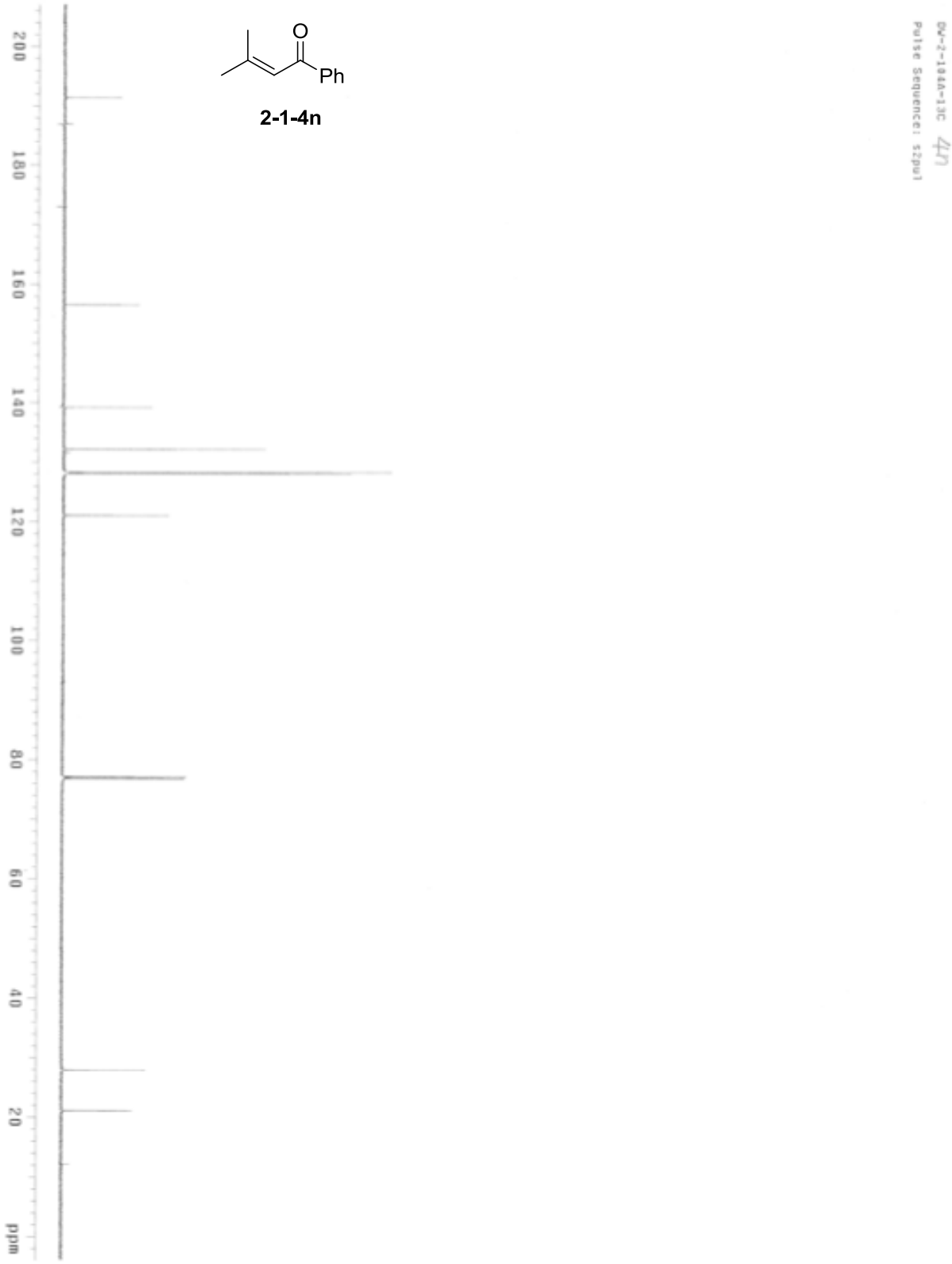
O
Ph
Ph

2-1-4m

O
Ph

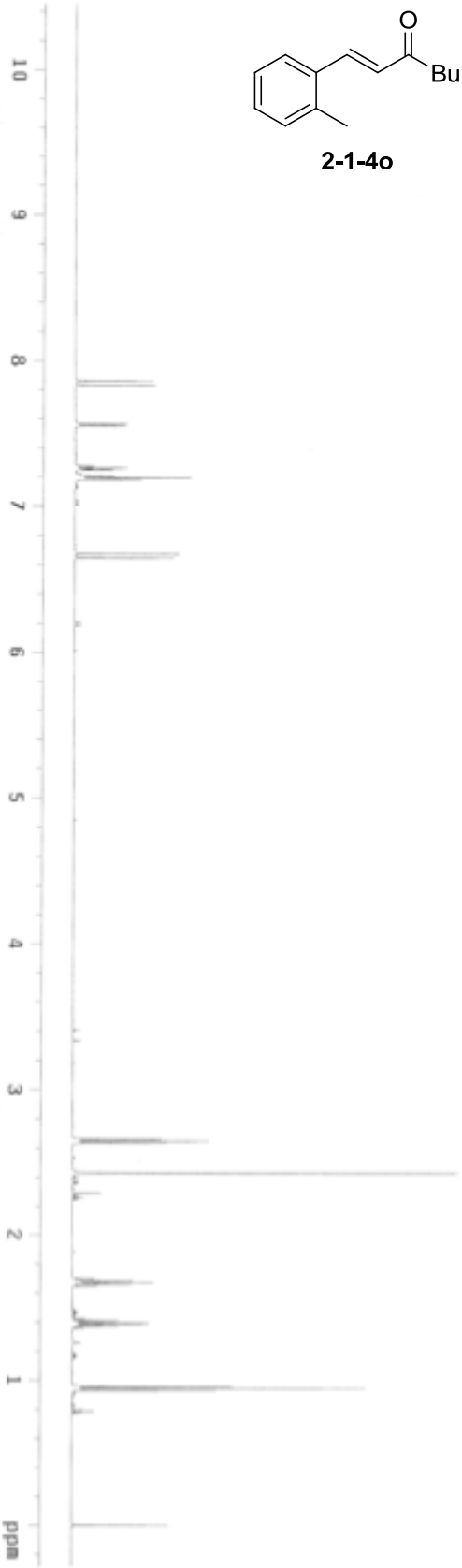
2-1-4n

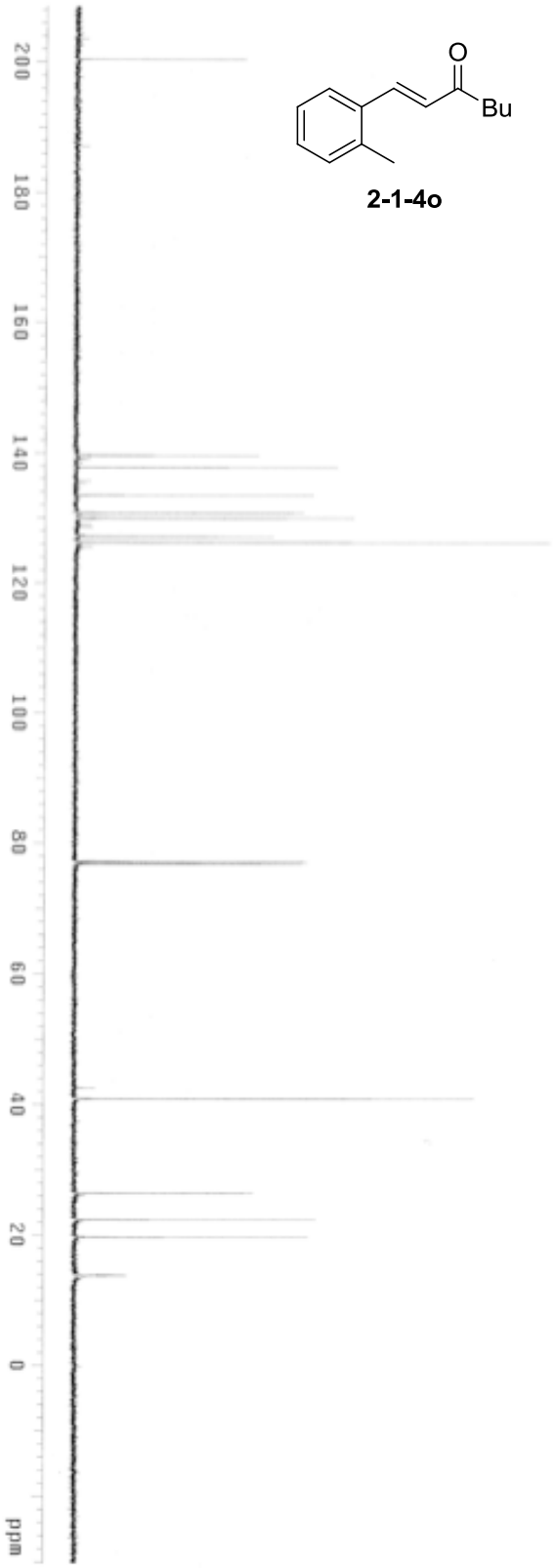

DW-2-184A-1H
Archive directory: /export/home/vmarti/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0
ppm


DW-2-104A-13C 4n
Pulse Sequence: s2pul
O
Ph
2-1-4n
200
180
160
140
120
100
80
60
40
20
ppm

O
Bu

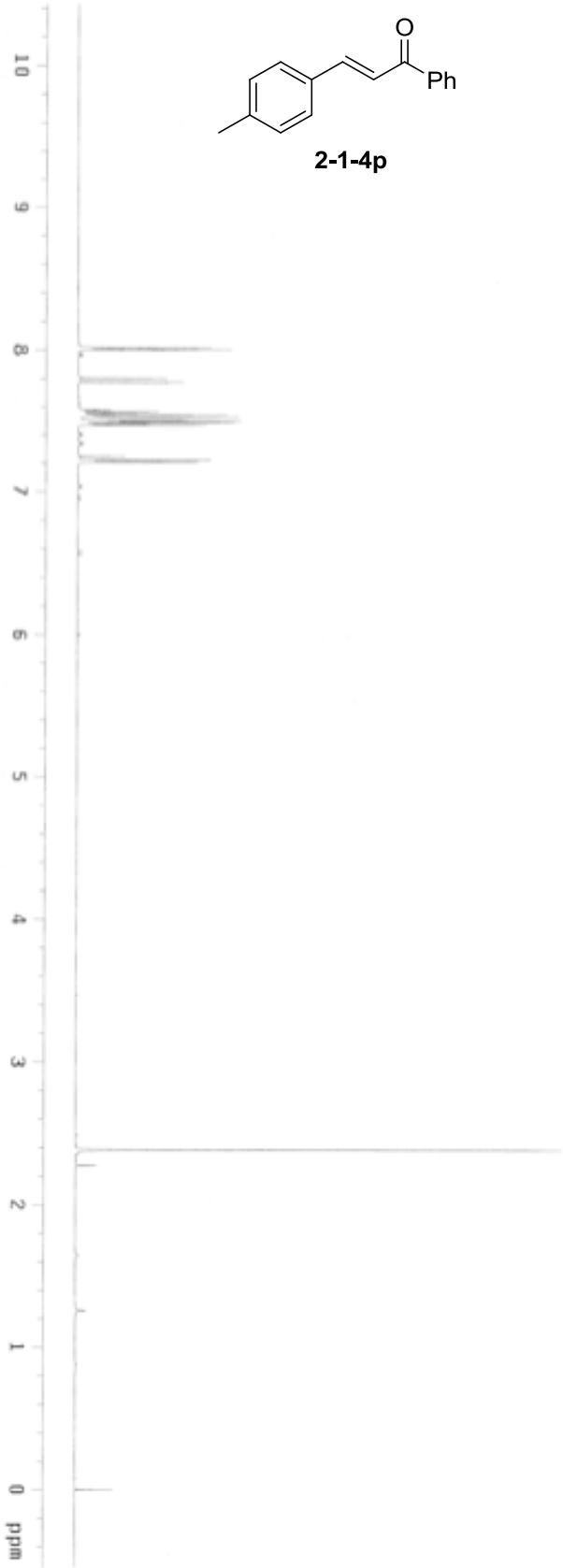
2-1-4o

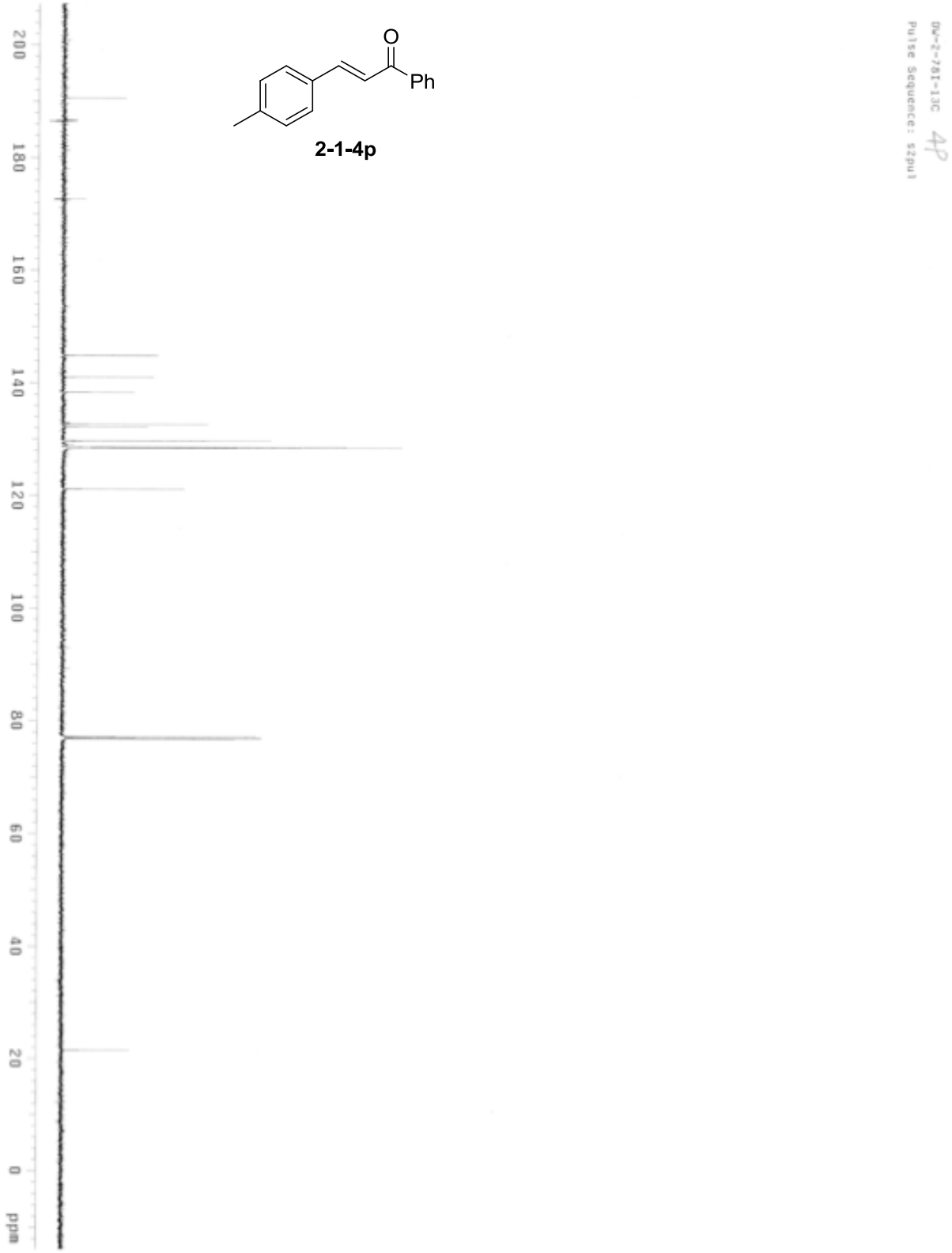

DW-2-020-1H 40
Archive directory: /export/home/vnerl/vnmrsys/data
Sample directory:
File: PROTON
Pulse sequence: s2pul
10
9
8
7
6
5
4
3
2
1
ppm

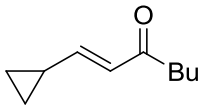

O
Bu
2-1-4o
DW-2-82D-13C 40
Pulse Sequence: s2pul
200
180
160
140
120
100
80
60
40
20
0
ppm

O
Ph

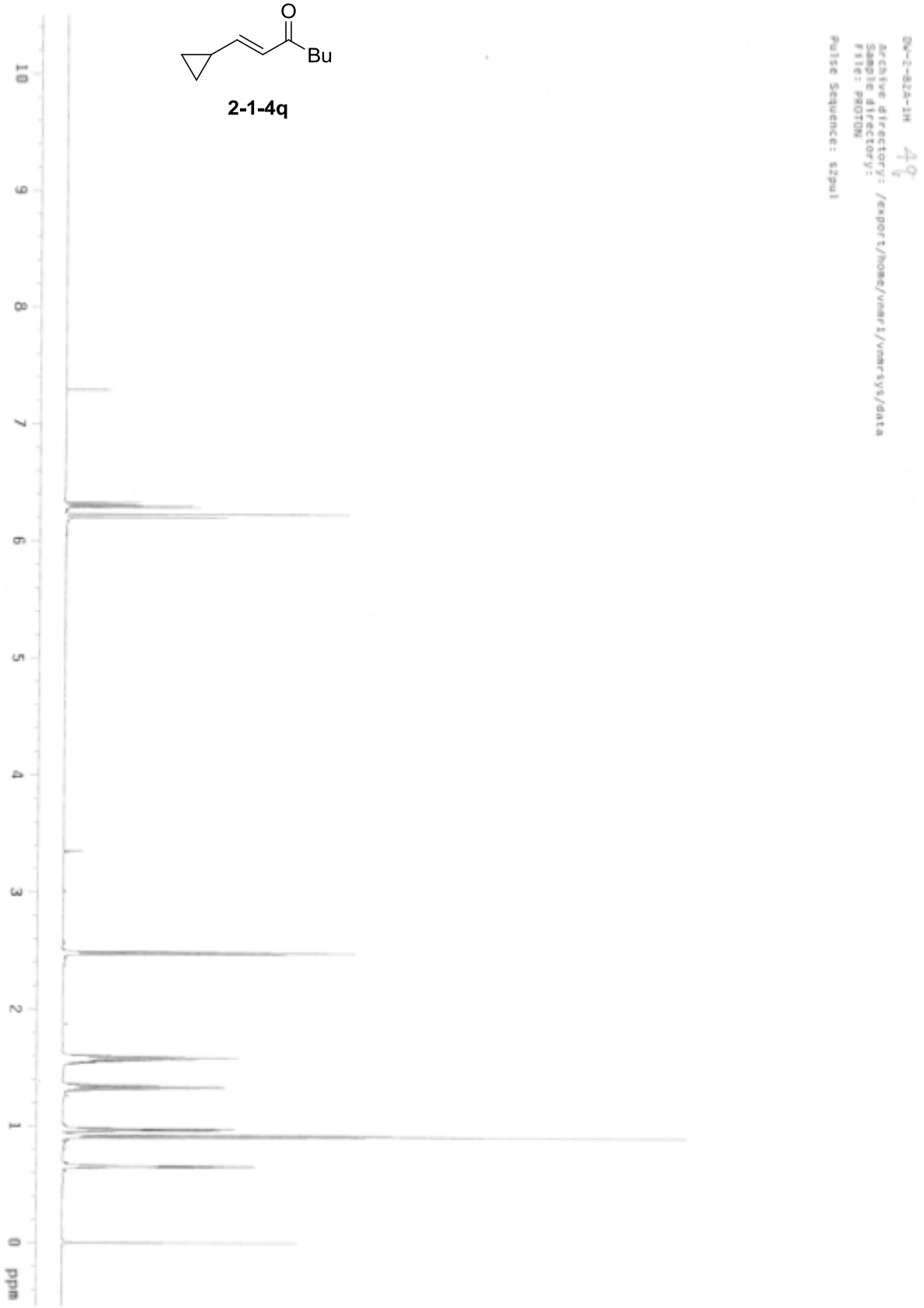
2-1-4p

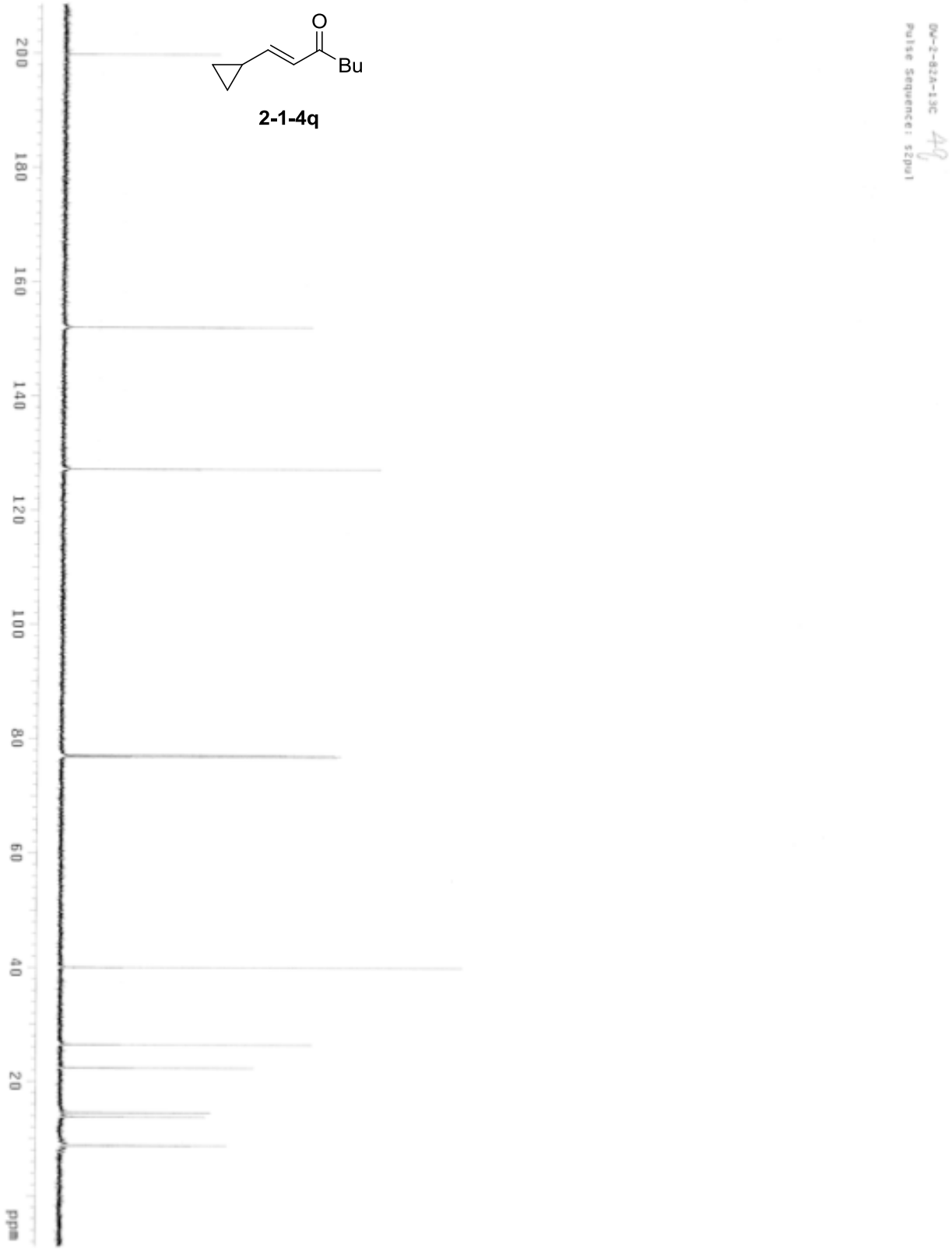

DW-2-181-1H
Archive directory: /export/home/vmarti/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0
ppm


DW-2-78I-13C
Pulse Sequence: s2pul
O
Ph
2-1-4p
200
180
160
140
120
100
80
60
40
20
0
ppm


O
Bu

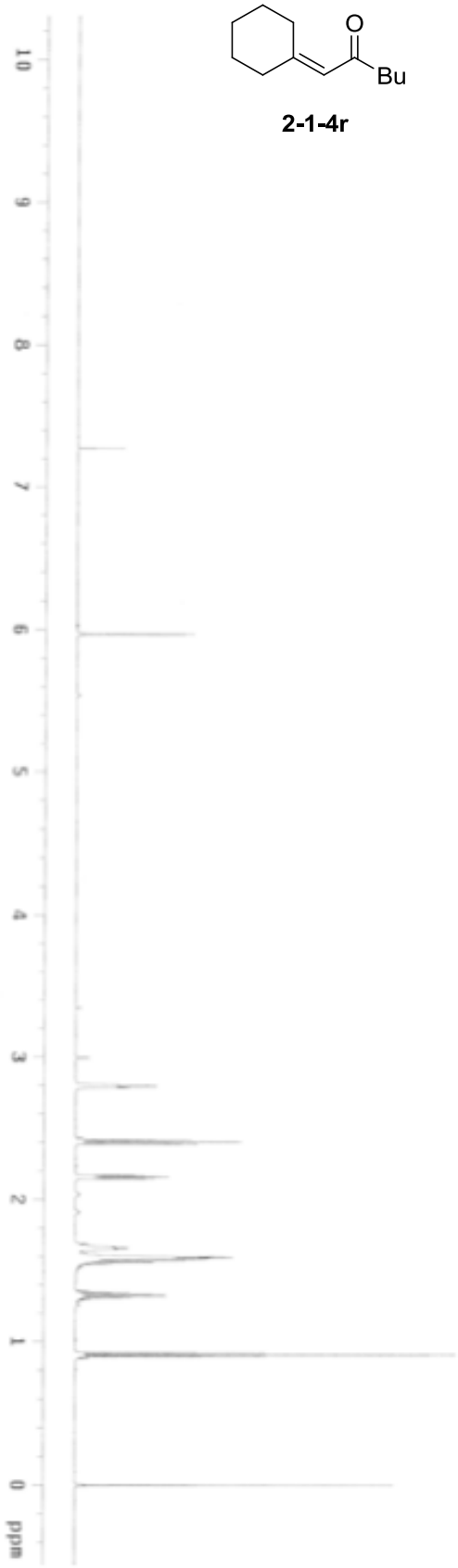
2-1-4q

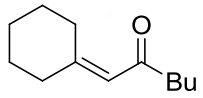

DW-2-82A-1H
Archive directory: /export/home/vnmrj/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0
ppm


DW-2-82A-13C
Pulse Sequence: s2pul
Bu
O
2-1-4q
200
180
160
140
120
100
80
60
40
20
ppm

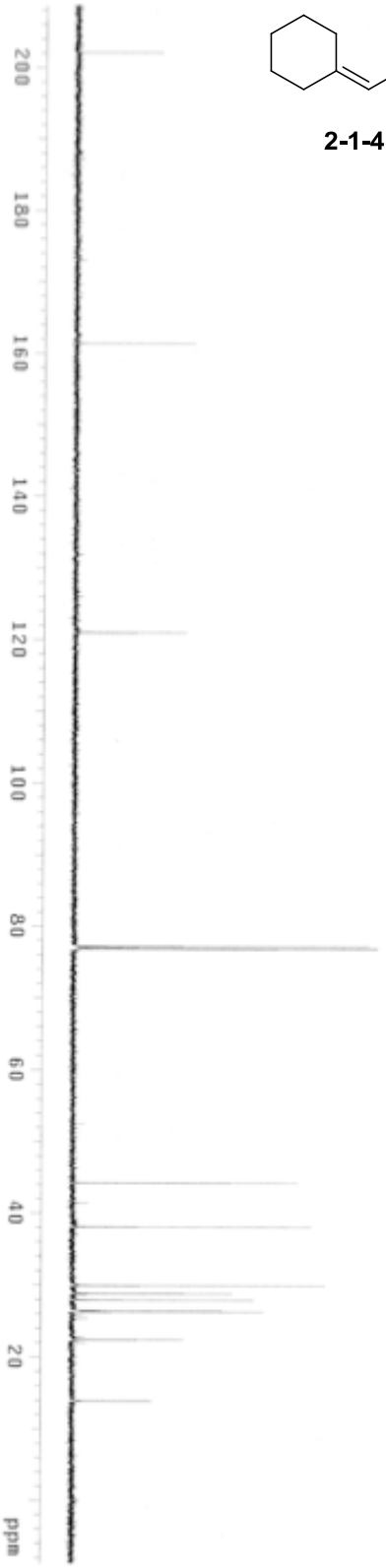
O
Bu

2-1-4r


DW-2-AZB-1H
4r
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0
ppm

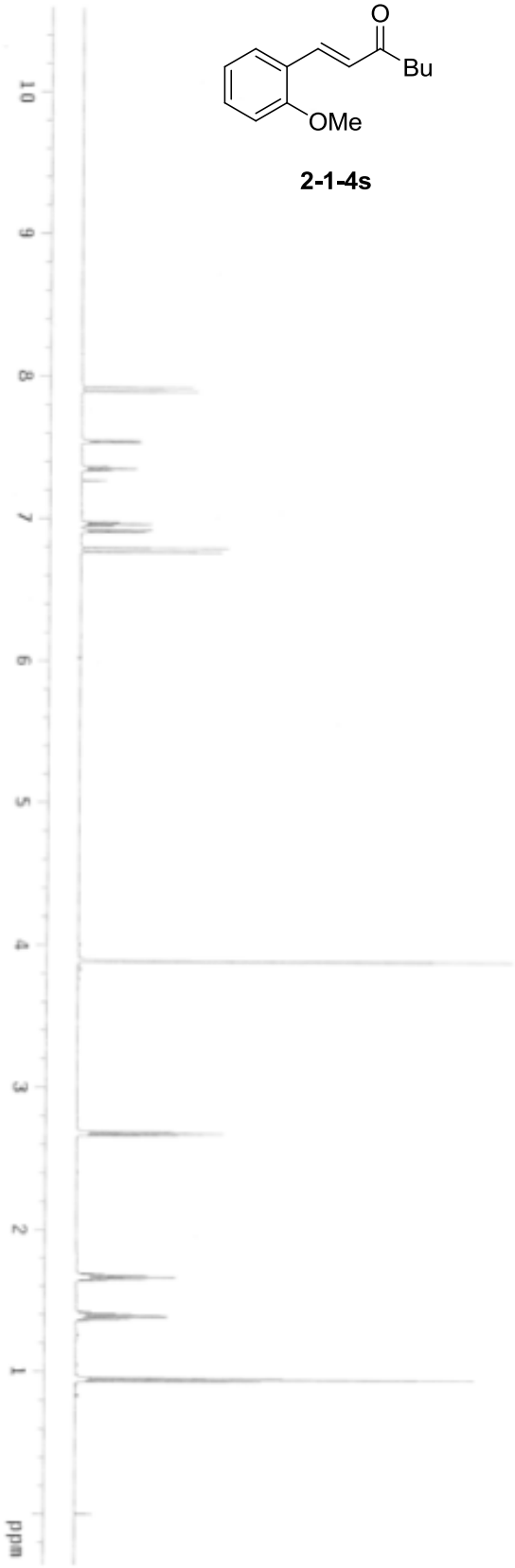

O
Bu

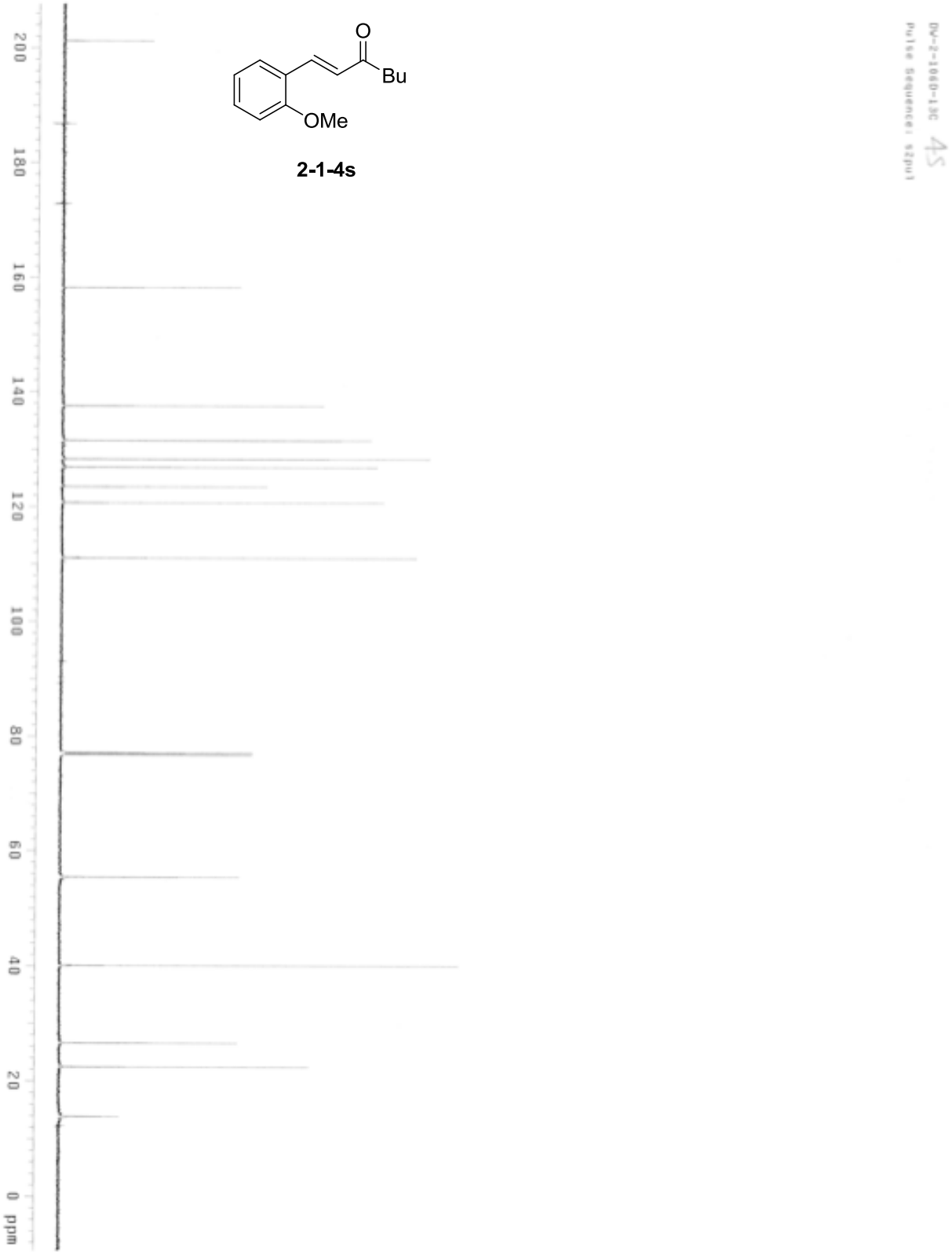
2-1-4r


DW-2-028-13C
Pulse Sequence: s2pul
200
180
160
140
120
100
80
60
40
20
ppm

O
Bu
OMe

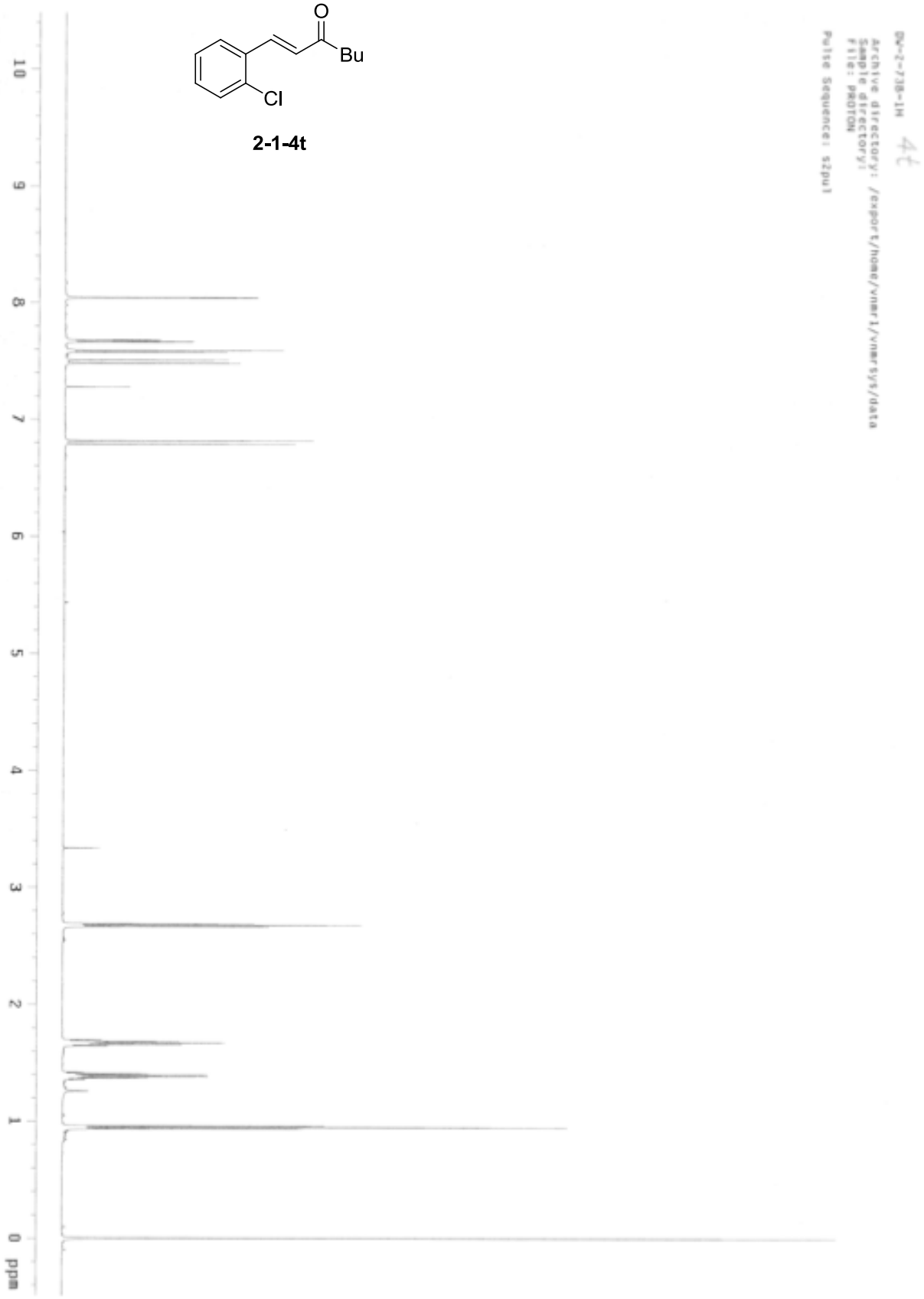
2-1-4s

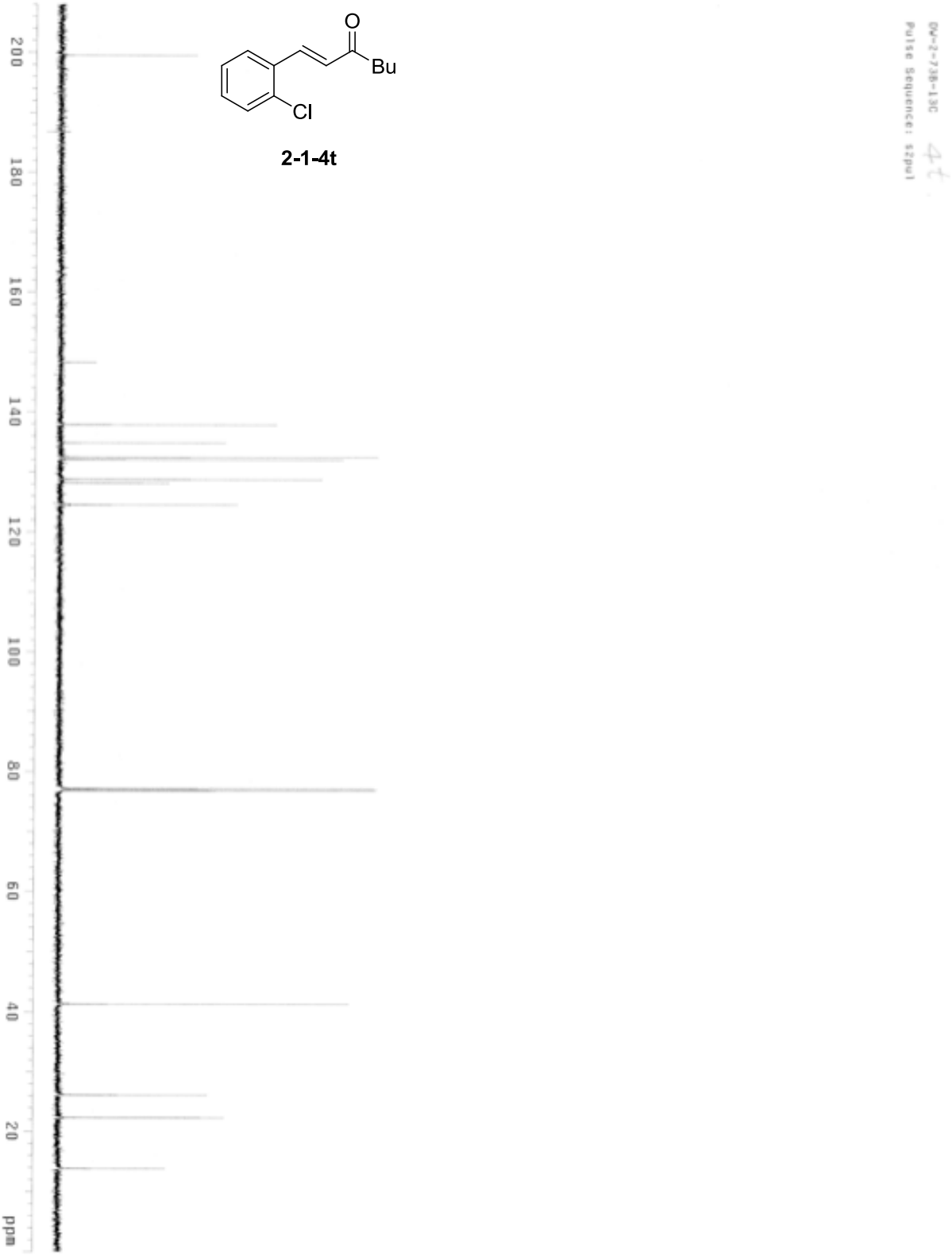

DW-2-1060-1H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
ppm

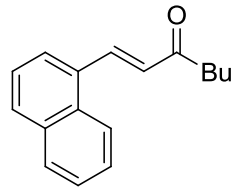

DW-2-1060-13C
Pulse Sequence: s2pul
45
O
Bu
OMe
2-1-4s
200
180
160
140
120
100
80
60
40
20
0 ppm

O
Bu
Cl

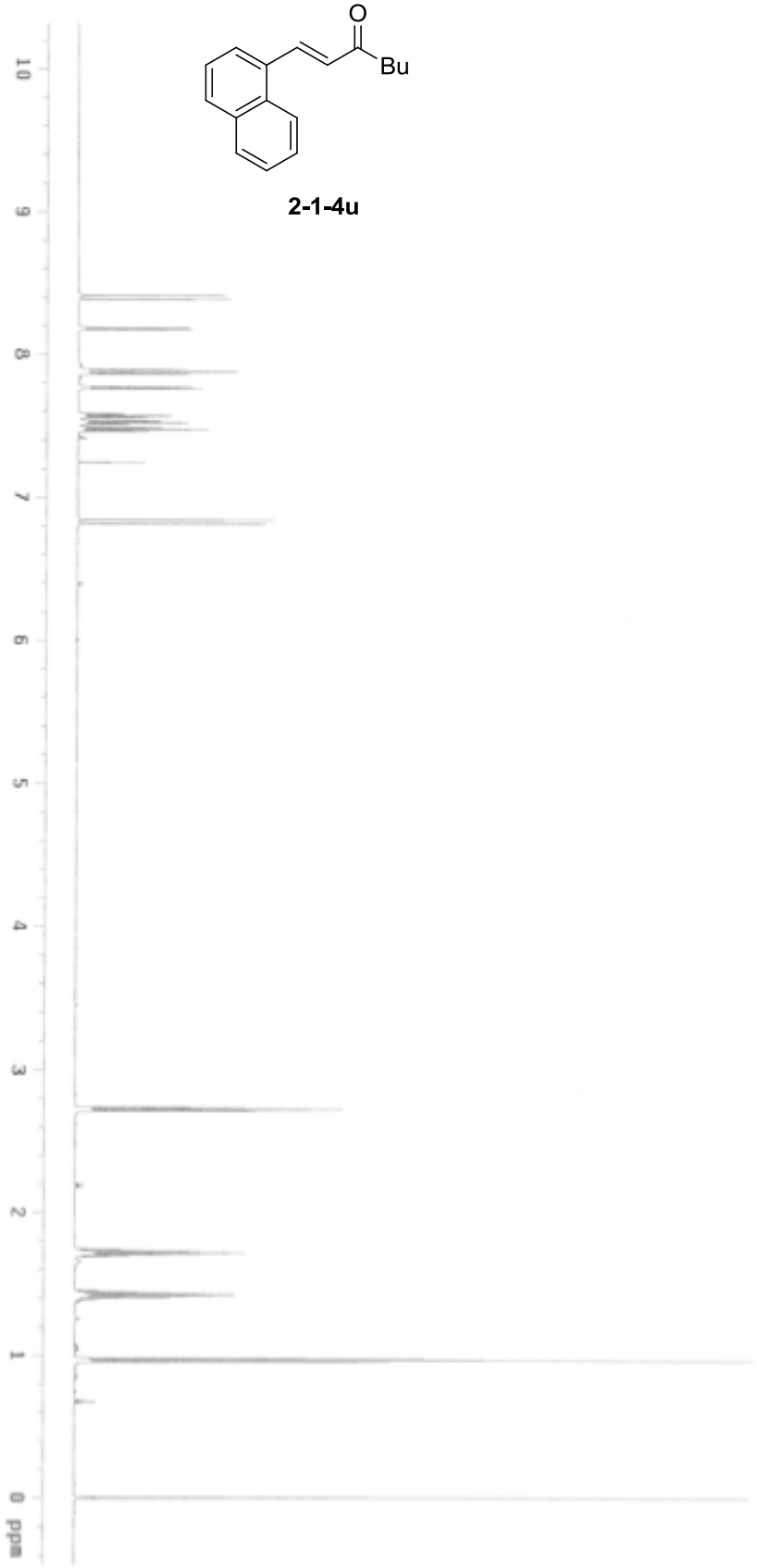
2-1-4t

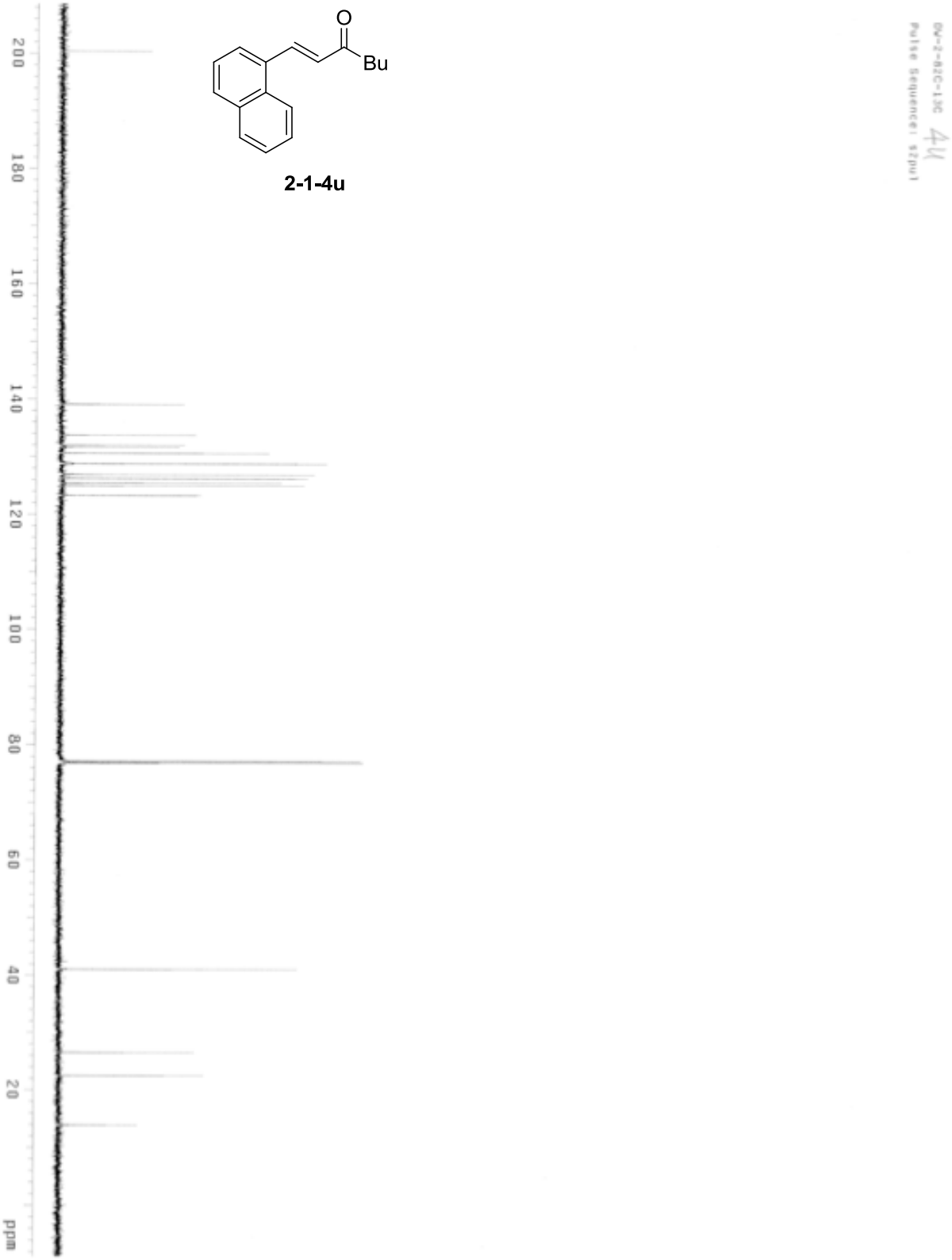

BW-2-138-1H 4t
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0 ppm


DW-2-38-13C
Pulse Sequence: s2pul
4t
O
Bu
Cl
2-1-4t
200
180
160
140
120
100
80
60
40
20
ppm


O
Bu

2-1-4u


DW-2-82C-1H
Archive directory: /export/home/vnmrj/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
10
9
8
7
6
5
4
3
2
1
0 ppm

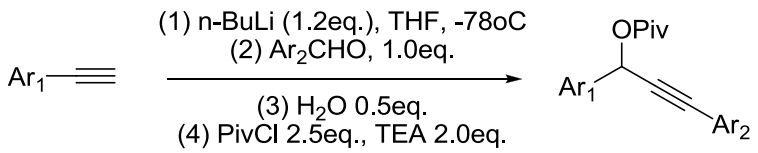

O
Bu
2-1-4u
GW-2-82C-13C 4U
Pulse Sequence: s2pul
200
180
160
140
120
100
80
60
40
20
ppm

2.2 Ambient intermolecular [2+2] cycloaddition of allene intermediate

I. General methods and materials

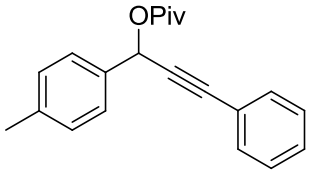
All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware. Unless otherwise noted, all commercial reagents were obtained from the commercial provider and used without further purification. Anhydrous solvents were used after general distillation strategies (Na for THF and CaH_2 for DCM). All gold complexes were synthesized from $HAuCl_4$, which was purchased from Strem. XPhos was purchased from Acros and used as received (stored at 4 ^{o}C and handled in glovebox). ^{1}H NMR, and ^{13}C NMR spectra were recorded on Varian 600 MHz and Agilent 400 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^{1}H and $CDCl_3$ (δ 77.0 ppm) for ^{13}C. Flash column chromatography was performed on 230-430 mesh silica gel. HRMS were recorded on LTQ-FTUHRA spectrometer.

General procedure of propargyl ester

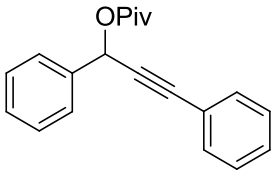


Reaction conditions: To a solution of alkyne (12 mmol) in anhydrous THF (50 mL) at –78 °C under N_2 was added *n*-BuLi (2.5 M solution in hexanes, 5.0 mL, 12.5 mmol). The reaction was stirred at this temperature for 20 min then aldehyde (10 mmol) was added to the mixture and was allowed to warm to room temperature gradually and stirred for an additional hour (TLC monitored untill the aldehyde was consumed completely). 10 Mins after addition of 0.5 eq. of H_2O, PivCl (25 mmol) and TEA (20 eq.) were added at room temperature and stirred for 6 h. The mixture was extracted with EtOAc (3 x 20 mL), and the combined organic phases were washed with water and brine, dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated, and the residue was purified through silica gel flash column chromatography (hexanes/ethyl acetate = 20/1) to yield the desired pivalate ester (70 % - 90 %).

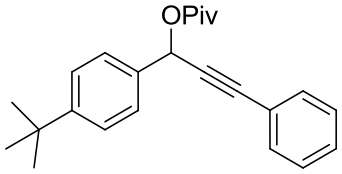
II. Compounds characterization



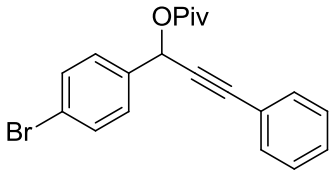
3-phenyl-1-(p-tolyl)prop-2-yn-1-yl pivalate (2-2-1c). Pale yellow solid; $_{1}$H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.47-7.44 (m, 4H), 7.32-7.27 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.64 (s, 1H), 2.36 (s, 3H), 1.23 (s, 9H); $_{13}$C-NMR ($CDCl_3$, 100MHz, ppm) δ = 177.22, 138.51, 134.59, 131.86, 129.25, 128.60, 128.21, 127.39, 122.35, 86.53, 86.0, 65.71, 38.76, 26.99, 21.19; HRMS calcd for $C_{21}H_{22}O_2Na$ $[M+Na]_+$: 329.1512, found 329.1512.



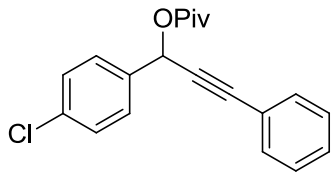
1,3-diphenylprop-2-yn-1-yl pivalate (2-2-1d). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.58-7.56 (m, 2H), 7.48-7.45 (m, 2H), 7.42-7.34 (m, 3H), 7.33-7.24 (m, 3H), 6.68 (s, 1H), 1.24 (s, 9H); $_{13}$C-NMR ($CDCl_3$, 100MHz, ppm) δ = 177.20, 137.49, 131.88, 128.68, 128.65, 128.58, 128.24, 127.38, 122.27, 86.72, 85.81, 65.80, 38.79, 26.99; HRMS calcd for $C_{20}H_{20}O_2Na$ $[M+Na]_+$: 315.1356, found 315.1356.



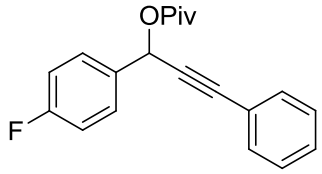
1-(4-(tert-butyl)phenyl)-3-phenylprop-2-yn-1-yl pivalate (2-2-1e). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.51-7.45 (m, 4H), 7.42-7.39 (m, 2H), 7.33-7.28 (m, 3H), 6.65 (s, 1H), 1.33 (s, 9H), 1.24 (s, 9H); $_{13}$C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.29, 151.65, 134.44, 131.89, 128.61, 128.22, 127.11, 125.53, 122.40, 86.50, 86.06, 65.63, 38.82, 31.30, 27.03; HRMS calcd for $C_{24}H_{28}O_2Na$ $[M+Na]_+$: 371.1982, found 371.1982.



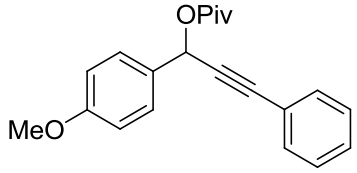
1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl pivalate (2-2-1f). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.54-7.51 (m, 2H), 7.47-7.43 (m, 4H), 7.34-7.31 (m, 3H), 6.62 (s, 1H), 1.23 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.11, 136.62, 131.89, 131.78, 129.14, 128.86, 128.30, 122.82, 122.01, 87.09, 85.22, 65.19, 38.79, 26.97; HRMS calcd for $C_{20}H_{19}BrO_2Na$ $[M+Na]_+$: 393.0461, found 393.0461.



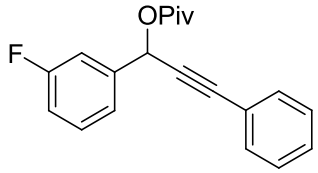
1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl pivalate (2-2-1g). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.53-7.49 (m, 2H), 7.47-7.44 (m, 2H), 7.38-7.35 (m, 2H),7.33-7.30 (m, 3H), 6.63 (s, 1H), 1.23 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.13, 147.0, 136.10, 134.63, 131.90, 128.85, 128.83, 128.30, 122.04, 87.07, 85.30, 65.15, 38.80, 26.97; HRMS calcd for $C_{20}H_{19}ClO_2Na$ $[M+Na]_+$: 349.0966, found 349.0967.



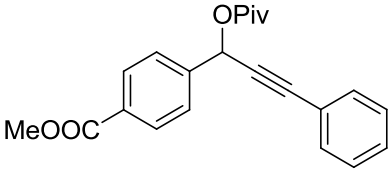
1-(4-fluorophenyl)-3-phenylprop-2-yn-1-yl pivalate (2-2-1h). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.58-7.53 (m, 2H), 7.48-7.45 (m, 2H), 7.34-7.30 (m, 3H), 7.10-7.05 (m, 2H), 6.65 (s, 1H), 1.23 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.15, 162.85 (d, *J* = 236.7 Hz), 133.44 (d, *J* = 3.8 Hz), 131.87, 129.37 (d, *J* = 8.4 Hz), 128.80, 128.28, 122.10, 115.53 (d, *J* = 21.3 Hz), 86.94, 85.54, 65.17, 38.77, 26.96; HRMS calcd for $C_{20}H_{19}FO_2Na$ $[M+Na]_+$: 333.1261, found 333.1262.



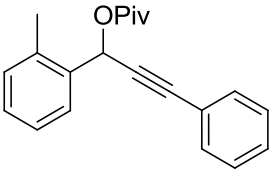
1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl pivalate (2-2-1i). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.52-7.49 (m, 2H), 7.48-7.45 (m, 2H), 7.33-7.30 (m, 3H), 6.93-6.90 (m, 2H), 6.63 (s, 1H), 3.82 (s, 3H), 1.22 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.29, 159.87, 131.86, 129.72, 128.97, 128.62, 128.23, 122.35, 113.91, 86.52, 86.05, 65.57, 55.28, 38.77, 26.99; HRMS calcd for $C_{21}H_{22}O_3Na$ $[M+Na]_+$: 345.1461, found 345.1461.



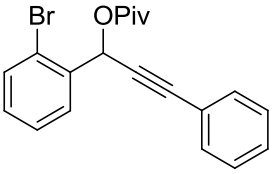
1-(3-fluorophenyl)-3-phenylprop-2-yn-1-yl pivalate (2-2-1j). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.48-7.45 (m, 2H), 7.39-7.28 (m, 6H), 7.07-7.03 (m, 1H), 6.66 (s, 1H), 1.25 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.07, 162.80 (d, *J* = 245.9 Hz), 139.92 (d, *J* = 6.8 Hz), 131.90, 130.15 (d, *J* = 8.3 Hz), 128.86, 128.29, 122.98 (d, *J* = 3.0 Hz), 122.00, 115.63 (d, *J* = 21.2 Hz), 114.37 (d, *J* = 22.8 Hz), 87.05, 85.15, 65.06 (d, *J* = 2.2 Hz), 38.81, 26.98; HRMS calcd for $C_{20}H_{19}FO_2Na$ $[M+Na]_+$: 333.1261, found 333.1262.



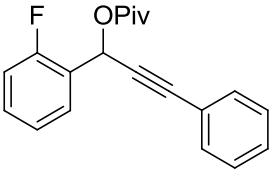
methyl 4-(3-phenyl-1-(pivaloyloxy)prop-2-yn-1-yl)benzoate (2-2-1k). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 8.09-8.06 (m, 2H), 7.66-7.62 (m, 2H), 7.48-7.45 (m, 2H), 7.35-7.29 (m, 3H), 6.71 (s, 1H), 3.92 (s, 3H), 1.25 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.05, 166.61, 142.28, 131.89, 130.39, 129.94, 128.88, 128.28, 127.25, 121.96, 87.29, 85.08, 65.26, 52.17, 38.81, 26.96; HRMS calcd for $C_{20}H_{20}O_2Na$ $[M+Na]_+$: 373.1410, found 373.1411.



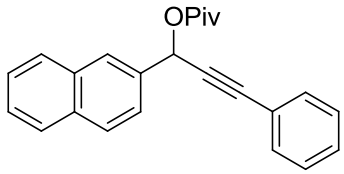
1-(2-methylphenyl)-3-phenylprop-2-yn-1-yl pivalate (2-2-1l). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.66-7.63 (m, 1H), 7.45-7.42 (m, 2H), 7.31-7.28 (m, 3H), 7.27-7.24 (m, 2H), 7.22-7.19 (m, 1H), 6.75 (s, 1H), 2.48 (s, 3H) 1.24 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.08, 136.27, 135.46, 131.83, 130.77, 128.68, 128.59, 128.21, 127.83, 126.14, 122.37, 86.52, 85.64, 64.20, 38.87, 27.04, 19.07; HRMS calcd for $C_{21}H_{22}O_2Na$ $[M+Na]_+$: 329.1512, found 329.1513.



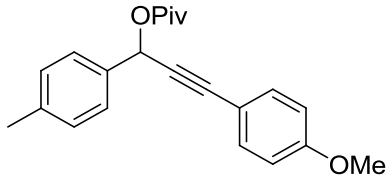
1-(2-bromophenyl)-3-phenylprop-2-yn-1-yl pivalate (2-2-1m). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.84-7.81 (m, 1H), 7.60-7.57 (m, 1H), 7.48-7.45 (m, 2H), 7.40-7.35 (m, 1H), 7.33-7.28 (m, 3H), 7.25-7.19 (m, 1H), 6.88 (s, 1H), 1.25 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 176.73, 136.56, 133.09, 131.90, 130.23, 129.47, 128.75, 128.22, 127.65, 123.28, 122.13, 87.09, 84.83, 65.55, 38.84, 27.05; HRMS calcd for $C_{20}H_{19}BrO_2Na$ $[M+Na]_+$: 393.0461, found 393.0462.



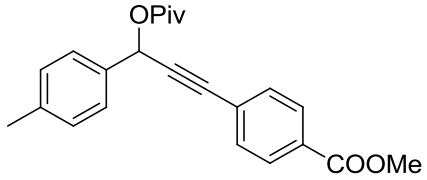
1-(2-fluorophenyl)-3-phenylprop-2-yn-1-yl pivalate (2-2-1n). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.60-7.71 (m, 1H), 7.49-7.46 (m, 2H), 7.37-7.28 (m, 4H), 7.22-7.18 (m, 1H), 7.11-6.90 (m, 1H), 6.90 (s, 1H), 1.24 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 176.85, 160.21 (d, *J* = 249 Hz), 131.92, 130.60 (d, *J* = 8.4 Hz), 129.27 (d, *J* = 3.8 Hz), 128.77, 128.24, 124.78, 124.22 (d, *J* = 3.8 Hz), 122.12, 115.66 (d, *J* = 20.5 Hz), 86.86, 84.67, 60.32 (d, *J* = 5.3 Hz), 38.78, 26.97; HRMS calcd for $C_{20}H_{19}FO_2Na$ $[M+Na]_+$: 333.1261, found 333.1262.



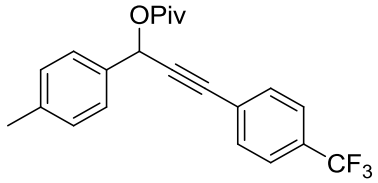
1-(naphthalen-2-yl)-3-phenylprop-2-yn-1-yl pivalate (2-2-1o). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 8.04 (s, 1H), 8.04-7.81 (m, 3H), 7.68-7.65 (m, 1H), 7.51-7.45 (m, 4H), 7.32-7.27 (m, 3H), 6.85 (s, 1H), 1.25 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.17, 134.80, 133.33, 133.03, 131.87, 128.70, 128.55, 128.25, 128.24, 127.65, 126.76, 126.50, 126.32, 124.93, 122.23, 87.03, 85.81, 66.01, 38.81, 26.99; HRMS calcd for $C_{24}H_{22}O_2Na$ $[M+Na]^+$: 365.1512, found 365.1512.



3-(4-methoxyphenyl)-1-(p-tolyl)prop-2-yn-1-yl pivalate (2-2-1p). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.46-7.44 (m, 2H), 7.42-7.37 (m, 2H), 7.20-7.18 (m, 2H), 6.85-6.80 (m, 2H), 6.62 (s, 1H), 3.80 (s, 3H), 2.36 (s, 3H), 1.22 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.28, 159.86, 138.43, 134.83, 133.38, 129.22, 127.38, 114.45, 113.84, 86.53, 84.66, 65.86, 55.26, 38.77, 27.00, 21.20; HRMS calcd for $C_{22}H_{24}O_3Na$ $[M+Na]^+$: 359.1618, found 359.1618.



methyl 4-(3-(pivaloyloxy)-3-(p-tolyl)prop-1-yn-1-yl)benzoate (2-2-1q). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.98 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.63 (s, 1H), 3.91 (s, 3H), 2.37 (s, 3H), 1.23 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.17, 166.41, 138.72, 134.20, 131.77, 129.91, 129.38, 129.34, 127.36, 126.99, 88.98, 85.65, 65.58, 52.21, 38.78, 26.98, 21.20; HRMS calcd for $C_{23}H_{24}O_4Na$ $[M+Na]^+$: 387.1567, found 387.1567.

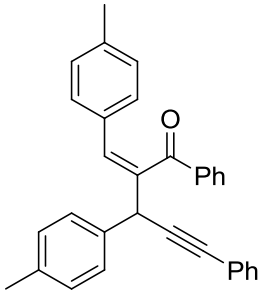


1-(p-tolyl)-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl pivalate (2-2-1r). Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.56 (s, 4H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.63 (s, 1H), 2.37 (s, 3H), 1.24 (s, 9H); contaminant: ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.68 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 1.29 (s, 9H); HRMS calcd for $C_{22}H_{21}F_3O_2Na$ $[M+Na]^+$: 397.1386, found 397.1388.

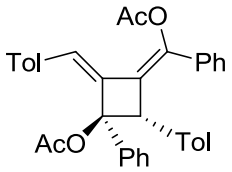
III General procedure of [2+2] cycloaddition

Reaction conditions: To a solution of **2-2-1c** (61.2 mg, 0.20 mmol) in dry CH_2Cl_2 (0.8 mL, 0.25 M), was added [PPh_3Au(TA-Me)]OTf (1.5 mg, 0.002 mol, 1.0 mol%) at RT. The reaction mixture was stirred at room temperature. After the reaction was completed (20 h), 0.1 mmol of 1,3,5-trimethoxybenzene (16.8mg) was added into the reaction mixture, and the solvent was removed under reduced pressure and the crude $_1$H NMR give the crude yield: 66 % of **2-2-3c**, and 13 % of **2-2-3c'**. Purification of **2-2-3c** and **2-2-3c'**: After silica column (Ethyl Acetate / Hexane = 1 / 10), crude product containing **2-2-3c** and **2-2-3c'** in the test tube was further purification by slow evaporation. Pure **2-2-3c** was obtained in the bottom of test tube and was washed with hexane. The pure **2-2-3c'** was obtained by prepared TLC of the residue in the test tube.

IV. Compounds characterization



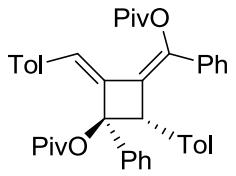
(Z)-2-(4-methylbenzylidene)-1,5-diphenyl-3-(p-tolyl)pent-4-yn-1-one (2-2-2b). Yellow liquid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.73 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.33-7.24 (m, 6H), 7.23-7.15 (m, 2H), 7.11-7.07 (m, 3H), 6.99 (d, *J*= 8.0 Hz, 2H), 6.84(d, *J* = 8.0 Hz, 2H), 5.19 (s, 1H), 2.28 (s, 3H), 2.12 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 199.55, 139.50, 137.66, 136.93, 136.50, 135.45, 132.80, 132.45, 131.55, 131.39, 129.47, 129.28, 128.83, 128.73, 128.30, 128.12, 128.05, 127. 98, 123.20, 88.46, 86.53, 43.24, 21.06, 21.04;



(2Z,3Z)-2-(4-methylbenzylidene)-1-phenyl-3-(phenyl(pivaloyloxy)methylene)-4-(p-tolyl) cyclobutyl pivalate (2-2-3b). Colorless Solid; ^{1}H-NMR ($CDCl_3$, 600MHz, ppm) δ = 7.20-7.18 (m, 2H), 7.17 (d, *J* = 9.6 Hz, 2H), 7.14-7.12 (m, 2H), 7.10 (s, 1H), 7.03-6.99 (m, 6H), 6.96 (d, *J* = 9.6 Hz, 2H), 6.68 (d, *J* = 7.2 Hz, 2H), 6.57 (d, *J* = 7.2 Hz, 2H), 5.71 (s, 1H), 2.48 (s, 3H), 2.25 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H); ^{13}C-NMR ($CDCl_3$, 125 MHz, ppm) δ = 169.57, 169.06, 141.52, 138.07, 137.85, 136.20, 135.53, 133.40, 132.17, 131.83, 129.32, 129.21, 129.03, 127.85, 127.70, 127.58, 127.50, 127.41, 127.07, 126.76, 126.39, 90.65, 57.37, 21.68, 21.22, 20.91;

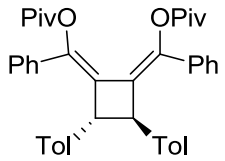
2-2-3b and **2-2-3b'**: **2-2-1b** (61.2 mg, 0.20 mmol) was used, and the NMR show that: 66 % yield of **2-2-3b [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.66 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 8.0 Hz, 2H), 5.67

(s, 1H), 2.22 (s, 3H), 2.15 (s, 3H), 1.52 (s, 9H), 1.17 (s, 9H)], and 13 % yield of **2-2-3b' [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 4.34 (s, 1H), 2.15 (s, 3H), 1.42 (s, 9H)].



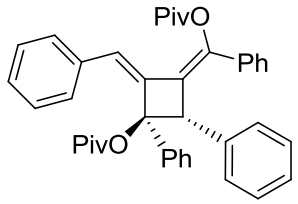
(2Z,3Z)-2-(4-methylbenzylidene)-1-phenyl-3-(phenyl(pivaloyloxy)methylene)-4-(p-tolyl)cyc

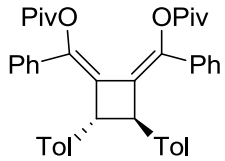
lobutyl pivalate (2-2-3c). Colorless Solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.24-7.21 (m, 2H), 7.15-7.10 (m, 5H), 7.04-6.97 (m, 6H), 6.93 (d, *J*= 8.4 Hz, 2H), 6.65 (d, *J* = 7.6 Hz, 2H), 6.53 (d, *J* = 7.6 Hz, 2H), 5.66 (s, 1H), 2.23 (s, 3H), 2.01 (s, 3H), 1.52 (s, 9H), 1.17 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 176.99, 176.27, 141.57, 138.23, 137.65, 136.68, 135.34, 133.99, 132.23, 131.94, 129.37, 129.19, 128.97, 127.74, 127.73, 127.61, 127.58, 127.49, 127.33, 126.71, 126.68, 126.46, 90.12, 57.26, 39.53, 27.66, 27.27, 21.20, 21.19, 20.92; HRMS calcd for $C_{42}H_{44}O_4Na$ $[M+Na]^+$: 635.3132, found 635.3134.



(1Z,1'Z)-(3,4-di-p-tolylcyclobutane-1,2-diylidene)bis(phenylmethanylylidene)bis

(2,2-dimethylpropanoate) (2-2-3c'). Colorless solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.16 (d, *J* = 5.2 Hz, 4H), 7.01 (s, 10H), 6.85 (d, *J* = 5.2Hz, 4H), 4.33 (s, 2H), 2.16 (s, 6H), 1.42 (s, 18H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.56, 140.17, 135.88, 135.63, 133.05, 132.15, 128.65, 128.26, 127.87, 127.54, 126.70, 59.47, 39.42, 27.39, 21.03; HRMS calcd for $C_{42}H_{44}O_4Na$ $[M+Na]^+$: 635.3132, found 635.3134.

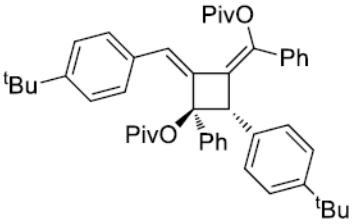




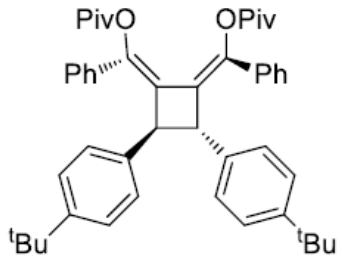
2-2-3d and **2-2-3d'**: **2-2-1d** (58.5 mg, 0.20 mmol) was used, and the NMR show that: 79 % yield of **2-2-3d [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.79-6.74 (m, 5H), 5.73 (s, 1H), 1.53 (s, 9H), 1.15 (s,

9H)], and 13 % yield of **2-2-3d' [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 4.42 (s, 1H), 1.43 (s, 9H)]. HRMS calcd for $C_{40}H_{40}O_4H$ $[M+H]^+$: 585.2999, found 585.3002.

2-2-3e and **2-2-3e'**: **2-2-1e** (34.8 mg, 0.10 mmol) was used, and the NMR show that: 65 % yield of **2-2-3e [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.71 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 5.67 (s, 1H), 1.51 (s, 9H), 1.21 (s, 9H), 1.10 (s, 9H), 1.04 (s, 9H)], and 19 % yield of **2-2-3e' [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 4.40 (s, 1H), 1.42 (s, 9H), 1.16 (s, 9H)].

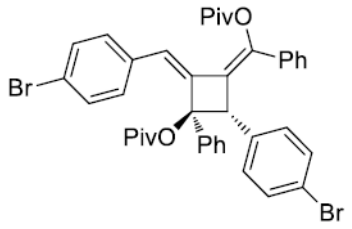


2-(4-(tert-butyl)benzylidene)-4-(4-(tert-butyl)phenyl)-1-phenyl-3-(phenyl(pivaloyloxy)methylene)cyclobutyl pivalate (2-2-3e). Colorless solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.23-7.14 (m, 8H), 7.12-7.09 (m, 2H), 7.04-6.95 (m, 8H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 5.66 (s, 1H), 1.51 (s, 9H), 1.21 (s, 9H), 1.10 (s, 9H), 1.04 (s, 9H); ^{13}C-NMR ($CDCl_3$, 150 MHz, ppm) δ = 177.0, 176.3, 150.7, 141.6, 137.0, 133.9, 132.3, 131.9, 129.1, 128.9, 127.7, 127.6, 127.5, 127.4, 127.2, 126.7, 126.4, 125.2, 123.8, 110.0, 90.2, 57.2, 39.5, 34.5, 34.0, 31.3, 31.1, 31.1, 29.7, 27.6, 27.4, 27.2; HRMS calcd for $C_{48}H_{56}O_4H$ $[M+H]^+$: 697.4251, found 697.4252.



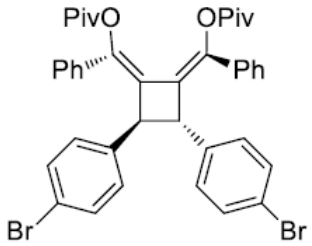
(1Z,1'Z)-(3,4-bis(4-(tert-butyl)phenyl)cyclobutane-1,2-diylidene)bis(phenylmethanylylidene) bis(2,2-dimethylpropanoate) (2-2-3e'). Colorless solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.21 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.96 (s, 5H), 4.40 (s, 1H), 1.42 (s, 9H), 1.16 (s, 9h); ^{13}C-NMR ($CDCl_3$, 150 MHz, ppm) δ = 177.6, 149.2, 135.3, 133.0, 132.9, 128.3, 127.7, 127.4, 126.7, 125.2, 124.7, 58.7, 39.4, 34.2, 31.9, 31.3, 31.1, 29.7, 27.6, 27.4; HRMS calcd for $C_{48}H_{56}O_4H$ $[M+H]^+$: 697.4251, found 697.4254.

2-2-3f and **2-2-3f'**: **2-2-1f** (74.0 mg, 0.20 mmol) was used, and the NMR show that: 74 % yield of **2-2-3f [**$_1$H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.86 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 5.66 (s, 1H), 1.51 (s, 9H), 1.17 (s, 9H)], and 16 % yield of **2-2-3f' [**$_1$H-NMR ($CDCl_3$, 400MHz, ppm) δ = 4.32 (s, 1H), 1.42 (s, 9H)].



2-(4-bromobenzylidene)-4-(4-bromophenyl)-1-phenyl-3-(phenyl(pivaloyloxy)methylene)cycl

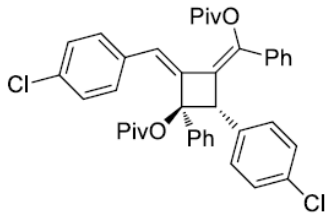
obutyl pivalate (2-2-3f). Colorless solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.24 (s, 1H), 7.21-7.17 (m, 2H), 7.11-7.01 (m, 11H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 8.0Hz), 5.65 (s, 1H), 1.51 (s, 9H), 1.17 (s, 9H); ^{13}C-NMR ($CDCl_3$, 150 MHz, ppm) δ =177.1, 176.2, 143.4, 142.6, 139.8, 135.9, 134.1, 133.7, 133.6, 132.9, 132.2, 131.4, 131.0, 130.7, 130.2, 129.8, 128.7, 128.5, 128.4, 128.0, 127.9, 127.8, 127.3, 126.5, 125.6, 125.5, 121.9, 120.2, 89.7, 56.9, 39.6, 39.5, 27.6, 27.2; HRMS calcd for $C_{40}H_{38}Br_2O_4H$ $[M+H]_+$: 741.1210, found 741.1211.



(1Z,1'Z)-(3,4-bis(4-bromophenyl)cyclobutane-1,2-diylidene)bis(phenylmethanylylidene)

bis(2,2-dimethylpropanoate) (2-2-3f'). Colorless solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm): δ = 7.18-7.11 (m, 4H), 7.07-6.96 (m, 5H), 4.31 (s, 1H), 1.42 (9H); ^{13}C-NMR ($CDCl_3$, 150 MHz, ppm) δ = 177.7, 140.5, 137.1, 132.7, 131.2, 130.9, 130.1, 128.5, 127.8, 126.8, 120.6, 59.1, 39.5, 27.4; HRMS calcd for $C_{40}H_{38}Br_2O_4H$ $[M+H]_+$: 741.1210, found 741.1213.

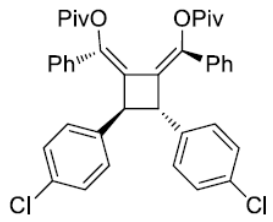
2-2-3g and **2-2-3g'**: **2-2-1g** (32.6 mg, 0.10 mmol) was used, and the NMR show that: 80 % yield of **2-2-3g [**$_1$H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.72 (s, 4H), 5.67 (s, 1H), 1.51 (s, 9H), 1.17 (s, 9H)], and 17 % yield of **2-2-3g' [**$_1$H-NMR ($CDCl_3$, 400MHz, ppm) δ = 4.33 (s, 1H), 1.42 (s, 9H)].



2-(4-chlorobenzylidene)-4-(4-chlorophenyl)-1-phenyl-3-(phenyl(pivaloyloxy)methylene)cycl

obutyl pivalate (2-2-3g). Colorless solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.21-7.15 (m, 4H), 7.12-7.06 (m, 8H), 7.03-7.01 (m, 3H), 6.71 (s, 4H), 5.66 (s, 1H), 1.51 (s, 9H), 1.17 (s, 9H); ^{13}C-NMR ($CDCl_3$, 150 MHz, ppm) δ = 177.1, 176.2, 143.3, 142.5, 139.7, 136.0, 133.6, 133.5, 133.3, 132.9,

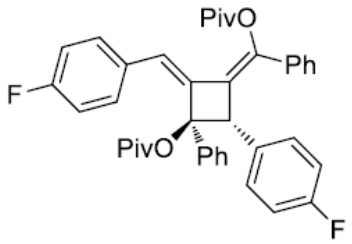
131.9, 130.6, 130.4, 129.7, 129.6, 129.3, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.3, 127.2, 126.8, 126.5, 125.5, 122.5, 89.8, 56.9, 39.6, 39.5, 27.6, 27.3; HRMS calcd for $C_{40}H_{38}Cl_2O_4H$ $[M+H]^+$: 653.2220, found 653.2222.



2-(4-chlorobenzylidene)-4-(4-chlorophenyl)-1-phenyl-3-(phenyl(pivaloyloxy)methylene)cycl

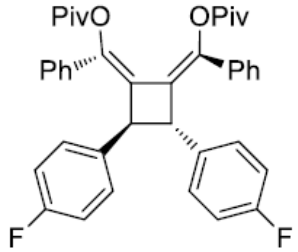
obutyl pivalate (2-2-3g'). Colorless solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.20 (d, *J* = 8.4 Hz, 2H), 7.05-6.95 (m, 7H), 4.33 (s, 1H), 1.42 (s, 9H); HRMS calcd for $C_{40}H_{38}Cl_2O_4H$ $[M+H]^+$: 653.2220, found 653.2223.

2-2-3h and **2-2-3h'**: **2-2-1h** (62.0 mg, 0.20 mmol) was used, and the NMR show that: 76 % yield of **2-2-3h [**$_1$H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.43 (t, *J* = 8.8 Hz, 2H), 5.68 (s, 1H), 1.52 (s, 9H), 1.16 (s, 9H)], and 19 % yield of **2-2-3h' [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 4.35 (s, 1H), 1.42 (s, 9H)].



2-(4-fluorobenzylidene)-4-(4-fluorophenyl)-1-phenyl-3-(phenyl(pivaloyloxy)methylene)cycl

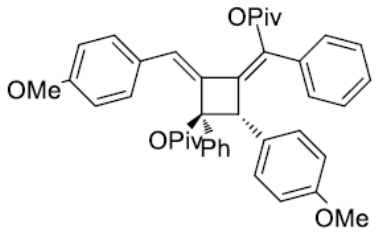
obutyl pivalate (2-2-3h). Colorless solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.24-7.19 (m, 4H), 7.12-7.05 (m, 6H), 7.02-7.00 (m, 3H), 6.85-6.80 (m, 2H), 6.77-6.73 (m, 2H), 6.41 (t, *J* = 8.8 Hz, 2H), 5.68 (s, 1H), 1.52 (s, 9H), 1.16 (s, 9H); ^{13}C-NMR ($CDCl_3$, 150 MHz, ppm) δ = 177.1, 176.3, 163.0, 162.0, 161.4, 160.4, 142.1, 138.5, 136.3, 133.7, 131.1, 131.1, 131.0, 130.9, 130.8, 130.8, 128.2, 128.0, 127.8, 127.6, 127.4, 126.5, 126.2, 125.6, 115.4, 115.3, 114.0, 113.9, 110.0, 90.0, 56.7, 39.5, 30.0, 27.6, 27.2; HRMS calcd for $C_{40}H_{38}F_2O_4H$ $[M+Na]^+$: 621.2811, found 621.2814.



3,4-bis(4-fluorophenyl)cyclobutane-1,2-diylidene)bis(phenylmethanylylidene)

bis(2,2-dimethylpropanoate (2-2-3h'). Colorless solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.24-7.20 (m, 2H), 7.05-6.95 (m, 5H), 6.72-6.69 (m, 2H), 4.34 (s, 1H), 1.42 (s, 9H); ^{13}C-NMR ($CDCl_3$, 150 MHz, ppm) δ = 177.8, 162.4, 160.8, 140.3, 133.8, 132.7, 131.7, 130.0, 129.9, 128.3, 127.6, 126.8, 114.9, 114.7, 59.0, 39.5, 27.4; HRMS calcd for $C_{40}H_{38}F_2O_4H$ $[M+H]^+$: 643.2632, found 643.2630.

2-2-3i and **2-2-3i'**: **2-2-1i** (64.4 mg, 0.20 mmol), $[(PPh_3Au)_3O]OTf_2$ 1 mol % was used instead of [PPh_3Au(TA-Me)OTf] 1 mol %, and the NMR show that: 68 % yield of **2-2-3i [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.71 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 9.6Hz, 2H), 6.29 (d, *J* = 8.4 Hz, 2H), 5.64 (s, 1H), 3.72 (s, 3H), 3.54 (s, 3H), 1.52 (s, 9H), 1.17 (s, 9H)], and 12 % yield of **2-2-3i' [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.58 (d, *J* = 8.8 Hz, 2H), 4.31 (s, 1H), 3.64 (s, 3H), 1.42 (s, 9H)].



(2Z,3Z)-2-(4-methoxybenzylidene)-4-(4-methoxyphenyl)-1-phenyl-3-(phenyl(pivaloyloxy)m

ethylene)cyclobutyl pivalate (2-2-3i).

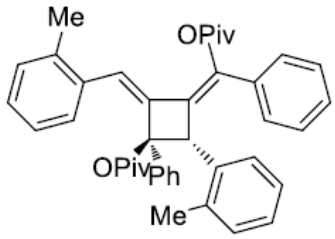
Colorless Solid; ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.24-7.18 (m, 4H), 7.12-7.09 (m, 3H), 7.07-6.97 (m, 6H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 9.6Hz, 2H), 6.29 (d, *J* = 8.4 Hz, 2H), 5.64 (s, 1H), 3.72 (s, 3H), 3.54 (s, 3H), 1.52 (s, 9H), 1.17 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.09, 176.36, 159.23, 157.73, 141.21, 136.72, 136.70, 133.94, 130.90, 130.42, 127.91, 127.73, 127.71, 127.62, 127.51, 127.45, 127.42, 127.08, 126.44, 126.40, 113.76, 112.49, 90.34, 56.93, 55.22, 55.19, 54.92, 54.90, 39.51, 27.67, 27.30; HRMS calcd for $C_{42}H_{44}O_6Na$ $[M+Na]^+$: 667.3030, found 667.3031.

2-2-3j and **2-2-3j'**: **2-2-1j** (62.0 mg, 0.20 mmol), and the NMR show that: 76 % yield of **2-2-3j [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.58 (d, *J* = 7.6 Hz, 1H), 6.50-6.43 (m, 2H), 5.69 (s, 1H), 1.52 (s, 9H), 1.18 (s, 9H)], and 17 % yield of **2-2-3j' [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 4.39 (s, 1H), 1.43 (s, 9H)].HRMS calcd for $C_{40}H_{38}F_2O_4Na$ $[M+Na]^+$: 643.2630, found 643.2633.

2-2-3k and **2-2-3k'**: **2-2-1k** (70.0 mg, 0.20 mmol), and the NMR show that: 71 % yield of **2-2-3k [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.86 (d, *J* = 7.6 Hz, 2H), 5.78 (s, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 1.54 (s, 9H), 1.17 (s, 9H)], and 11 % yield of **2-2-3k' [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 4.48 (s, 1H), 3.82 (s, 3H), 1.44 (s, 9H)]. HRMS calcd for $C_{44}H_{44}O_8H$ $[M+H]^+$: 701.3109, found 701.3111.

2-2-3l and **2-2-3l'**: **2-2-1l** (61.2 mg, 0.20 mmol), and the NMR show that: 73 % yield of **2-2-3k [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.64 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 6.31 (d, *J* = 7.6 Hz,

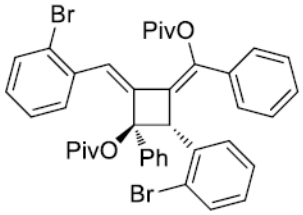
1H), 6.14 (s, 1H), 2.39 (s, 3H), 2.31 (s, 3H),1.49 (s, 9H), 0.92 (s, 9H)], and 18 % yield of **2-2-3k' [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 4.72 (s, 1H), 1.90 (s, 3H), 1.45 (s, 9H)].



(2Z,3Z)-2-(2-methylbenzylidene)-1-phenyl-3-(phenyl(pivaloyloxy)methylene)-4-(o-tolyl)cycl

obutyl pivalate (2-2-3l). Colorless solid; note: 12 % of **3k'** is contained in the **3k**, so the ^{13}C NMR can not be characterized. ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.33-7.31 (m, 2H), 7.12-6.98 (m, 12H), 6.82-6.74 (m, 2H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 6.31 (d, *J* = 7.6 Hz, 1H), 6.14 (s, 1H), 2.39 (s, 3H), 2.31 (s, 3H), 1.49 (s, 9H), 0.92 (s, 9H); HRMS calcd for $C_{42}H_{44}O_4Na$ $[M+Na]_+$: 635.3132, found 635.3133.

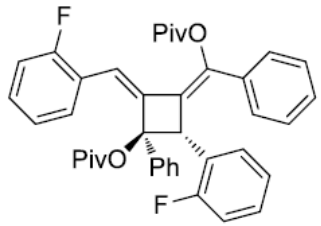
2-2-3m and **2-2-3m'**: **2-2-1m** (74.0 mg, 0.20 mmol), and the NMR show that: 63 % yield of **2-2-3m [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.62-6.56 (m, 2H), 6.44 (s, 1H), 6.41-6.36 (m, 1H), 1.52 (s, 9H), 1.00 (s, 9H)], and 18 % yield of **2-2-3m' [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.80 (dt, J_1 = 2.0 Hz, J_2 = 8.0Hz, 1H), 5.13 (s, 1H), 1.45 (s, 9H)].



(2Z,3Z)-2-(2-bromobenzylidene)-4-(2-bromophenyl)-1-phenyl-3-(phenyl(pivaloyloxy)methy

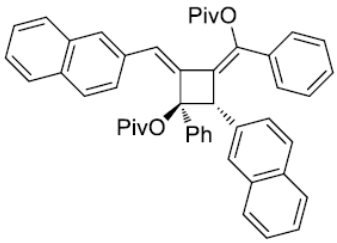
lene)cyclobutyl pivalate (2-2-3m). ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.52 (d, *J* = 1.2 Hz, 1H), 7.50 (s, 1H), 7.50-7.37 (m, 2H), 7.23-7.19 (m, 2H), 7.18-7.08 (m, 4H), 7.05-7.00 (m, 4H), 6.96-6.86 (m, 2H), 6.62-6.56 (m, 2H), 6.44 (s, 1H), 6.41-6.36 (m, 1H), 1.52 (s, 9H), 1.00 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 176.71, 176.37, 142.20, 141.12, 137.96, 134.64, 134.38, 133.71, 132.82, 131.64, 131.17, 130.03, 128.80, 128.27, 127.95, 127.66, 127.62, 127.57, 126.94, 126.80, 126.66, 125.88, 125.43, 124.90, 124.68, 124.57, 89.50, 55.52, 39.40, 39.31, 27.59, 27.27; HRMS calcd for $C_{40}H_{38}Br_2O_4Na$ $[M+Na]_+$: 763.1029, found 763.1028.

2-2-3n and **2-2-3n'**: **2-2-1n** (62.0 mg, 0.20 mmol), and the NMR show that: 74 % yield of **2-2-3n [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 6.52 (t, *J* = 8.0 Hz, 1H), 6.25 (t, *J* = 8.0 Hz, 1H), 6.14 (s, 1H), 1.53 (s,9H), 1.20 (s, 9H)], and 18 % yield of **2-2-3n' [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 4.97 (s, 1H), 1.43(s, 9H)].



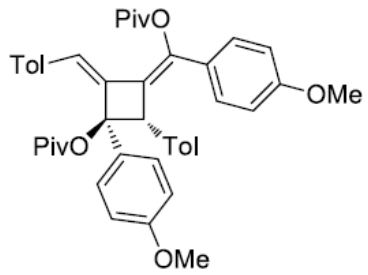
(2Z,3Z)-2-(2-fluorobenzylidene)-4-(2-fluorophenyl)-1-phenyl-3-(phenyl(pivaloyloxy)methylene)cyclobutyl pivalate (2-2-3n). ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.25-7.23 (m, 2H), 7.15-7.00 (m, 11H), 6.94 (d, *J* = 10.8 Hz, 1H), 6.83-6.78 (m, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.69-6.57 (m, 1H), 6.51-6.43 (m, 2H), 5.68 (s, 1H),1.52 (s, 9H), 1.17 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.08, 176.08, 163.79, 161.35, 160.72, 142.92, 140.49, 137.55, 137.47, 136.93, 135.92, 133.72, 129.69, 129.61, 128.50, 128.42, 128.38, 127.94, 127.89, 127.74, 127.71, 127.26, 126.76, 126.56, 125.56, 125.53, 125.32, 125.22, 125.20, 125.09, 125.06, 116.17, 115.95, 115.63, 115.41, 114.66, 114.45, 113.15, 112.94, 89.63, 57.01, 56.99, 39.59, 27.59, 27.20; HRMS calcd for $C_{40}H_{38}F_2O_4Na$ $[M+Na]_+$: 643.2630, found 643.2631.

2-2-3o and **2-2-3o'**: **2-2-1o** (68.4 mg, 0.20 mmol), and the NMR show that: 43 % yield of **2-2-3o [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 65.92 (s, 1H), 1.58 (s, 9H), 1.15 (s, 9H)], and 24 % yield of **2-2-3o' [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 5.13 (s, 1H), 1.11 (s, 9H)].



(3Z,4Z)-2-(naphthalen-2-yl)-4-(naphthalen-2-ylmethylene)-1-phenyl-3-(phenyl(pivaloyloxy)methylene)cyclobutyl pivalate (2-2-3o). ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.70 (s, 1H), 7.68-7.65 (m, 1H), 7.56-7.48 (m, 5H), 7.43-7.31 (m, 5H), 7.27-7.25 (m, 1H), 7.21-7.17 (m, 2H), 7.15-7.12 (m, 1H), 6.98-6.85 (m, 7H), 5.92 (s, 1H), 1.58 (s, 9H), 1.15 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.13, 176.32, 142.43, 139.83, 136.54, 133.90, 133.21, 133.04, 132.70, 132.66, 132.61, 131.98, 129.00, 128.65, 128.21, 128.03, 127.72, 127.64, 127.61, 127.57, 127.42, 127.26, 127.14, 126.88, 126.86, 126.51, 126.48, 126.39, 126.20, 126.09, 125.05, 124.99, 90.09, 57.68, 39.61, 29.69, 27.72, 27.27; HRMS calcd for $C_{48}H_{44}O_4Na$ $[M+Na]_+$: 685.3312, found 685.3314.

2-2-3p and **2-2-3p'**: **2-2-1p** (67.2 mg, 0.20 mmol), and the NMR show that: 66 % yield of **2-2-3p [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 5.58 (s, 1H), 3.65 (s, 3H), 3.63 (s, 3H), 2.23 (s, 3H), 2.04 (s, 3H), 1.51 (s, 9H), 1.15 (s, 9H)], and 10 % yield of **2-2-3p' [**^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 4.29 (s, 1H), 3.65 (s, 3H), 2.18 (s, 3H), 1.41 (s, 9H)].



(4-methoxyphenyl)(3-(4-methoxyphenyl)-2-(4-methylbenzylidene)-3-(pivaloyloxy)-4-(p-toly

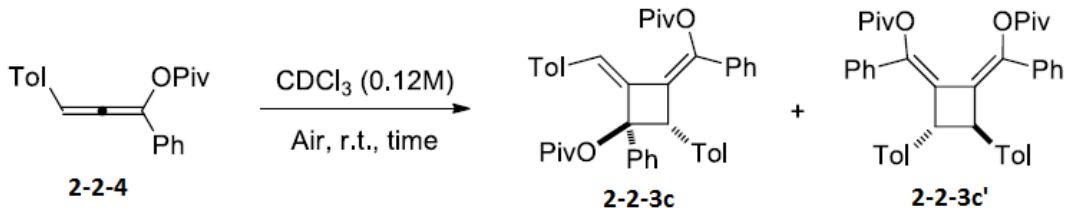
l)cyclobutylidene)methyl pivalate (2-2-3p). ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.16-7.12 (m, 4H), 7.06 (s, 1H), 7.04 (d, *J* = 5.6 Hz, 2H), 6.93 (d, *J* = 5.6 Hz), 6.57 (d, *J* = 6.4Hz, 2H), 6.52 (d, *J* = 6.4Hz, 2H), 5.57 (s, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.24 (s, 3H), 2.05 (s, 3H), 1.51 (s, 9H), 1.15 (s, 9H);^{13}C-NMR ($CDCl_3$, 100 MHz, ppm) δ = 177.0, 176.4, 159.3, 159.1, 158.7, 141.5, 138.7, 137.4, 135.3, 132.4, 132.3, 130.8, 129.7, 129.3, 129.2, 129.1, 129.0, 128.9, 128.8, 128.2, 128.0, 127.9, 127.8, 127.1, 126.6, 125.8, 124.9, 113.8, 113.1, 113.0, 110.0, 90.0, 57.1, 55.1, 39.5, 39.4, 27.7, 27.4;HRMS calcd for $C_{44}H_{48}O_6Na$ $[M+H]^+$: 673.3524, found 673.3527.

2-2-3q and **2-2-3q'**: **2-2-1q** (72.8 mg, 0.20 mmol), and the NMR show that no reaction occur.

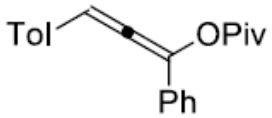
2-2-3r and **2-2-3r'**: **2-2-1r** (90 mg, 0.20 mmol), and the NMR show that no reaction occur.

V Possible role of gold in allene [2+2] step

Reaction conditions: To a solution of **2-2-1c** (61.2 mg, 0.20 mmol) in dry, base-washed $CDCl_3$ (0.8 mL, 0.25 M), was added $XphosAuNTf_2$ (2.0 mg, 0.002 mol, 1.0 mol%) at RT. The reaction mixture was monitored by ^{1}H NMR. After **2-2-1c** was transformed into allene **2-2-4** completely (around 5 mins), around half of reaction mixture went through the short silica gel column to remove the $XphosAuNTf_2$ immediately, and another 3 portions of dry, based washed $CDCl_3$ to washed the column, and the major part of solvent was removed in vacuo (make the concentration around 0.12M). ^{1}H NMR show that the 2+2 cycloaddition of allene **2-2-4** was consumed completely in 20 hours with or without $XphosAuNTf_2$ (the same concentration, 0.12M).

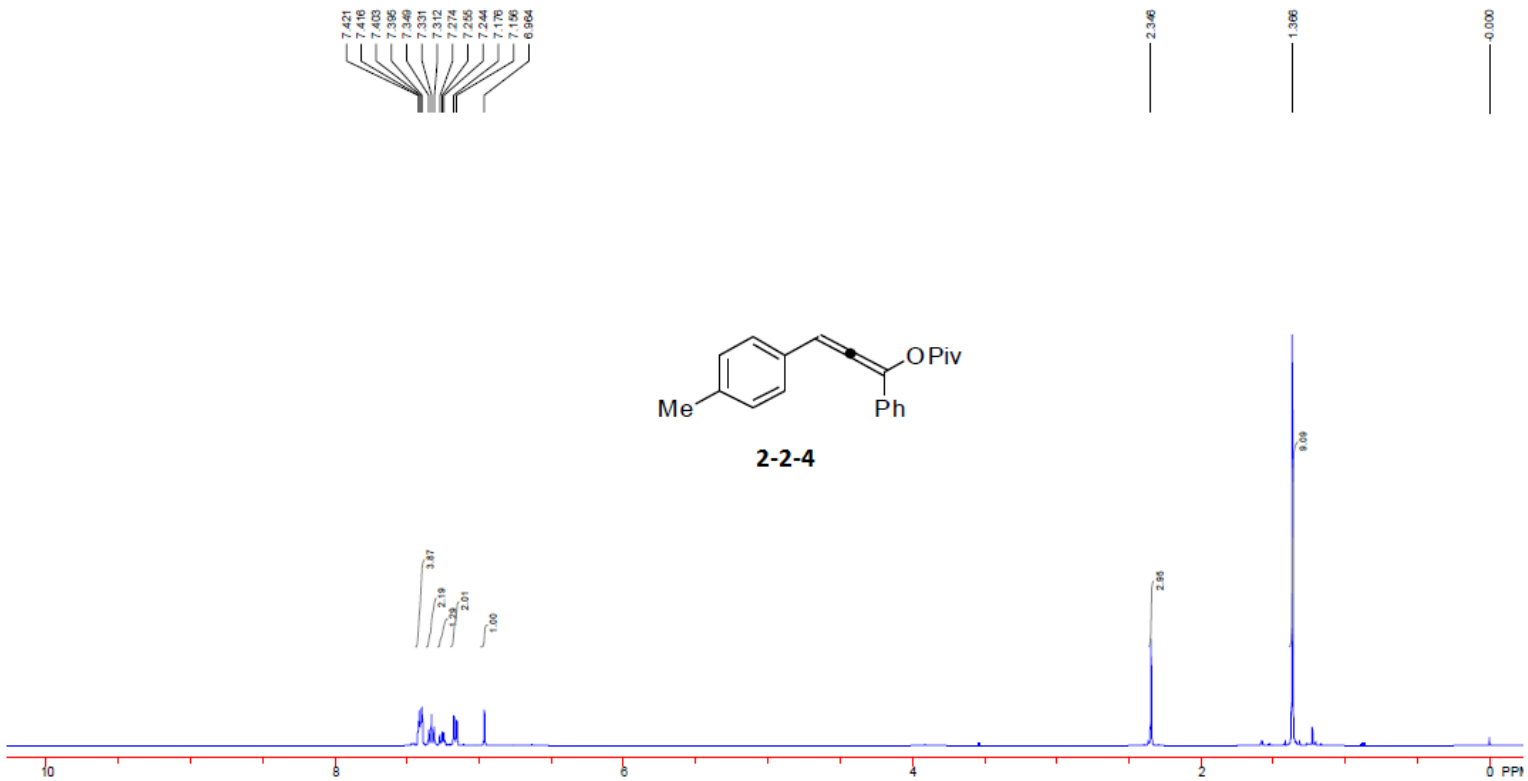


	time	yield	time	yield **3c**(**3c'**)	time	yield **3c**(**3c'**)
with gold	1.0 h	35 % (8.5 %)	5 h	50 % (12 %)	20 h	68 % (14 %)
without gold	1.0 h	34 % (8 %)	5 h	48 % (12 %)	20 h	66 % (12 %)



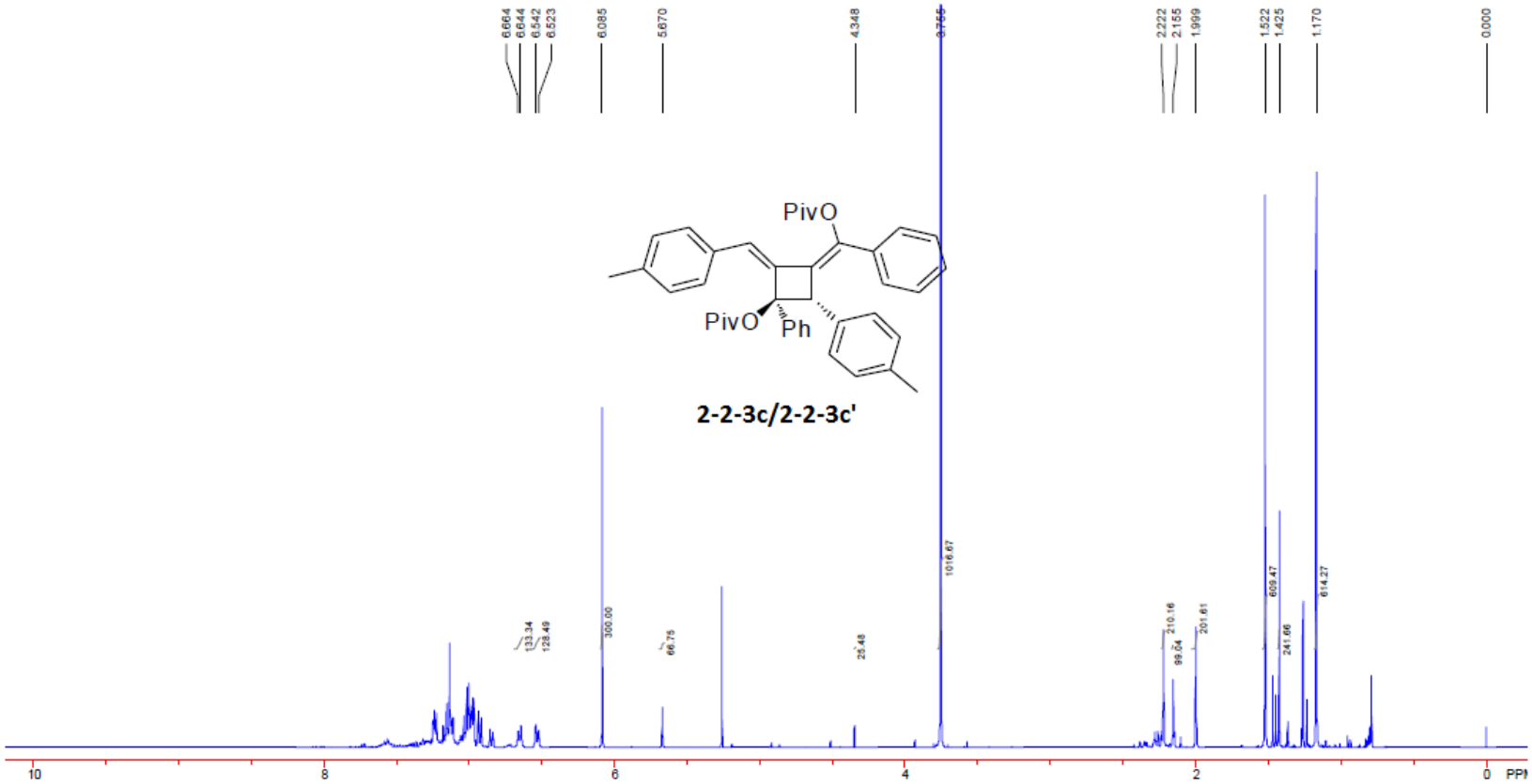
1-phenyl-3-(p-tolyl)propa-1,2-dien-1-yl pivalate (2-2-4). ^{1}H-NMR ($CDCl_3$, 400MHz, ppm) δ = 7.43-7.39 (m, 4H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28-7.24 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.96 (s, 1H), 2.35 (s, 3H), 1.37 (s, 9H).

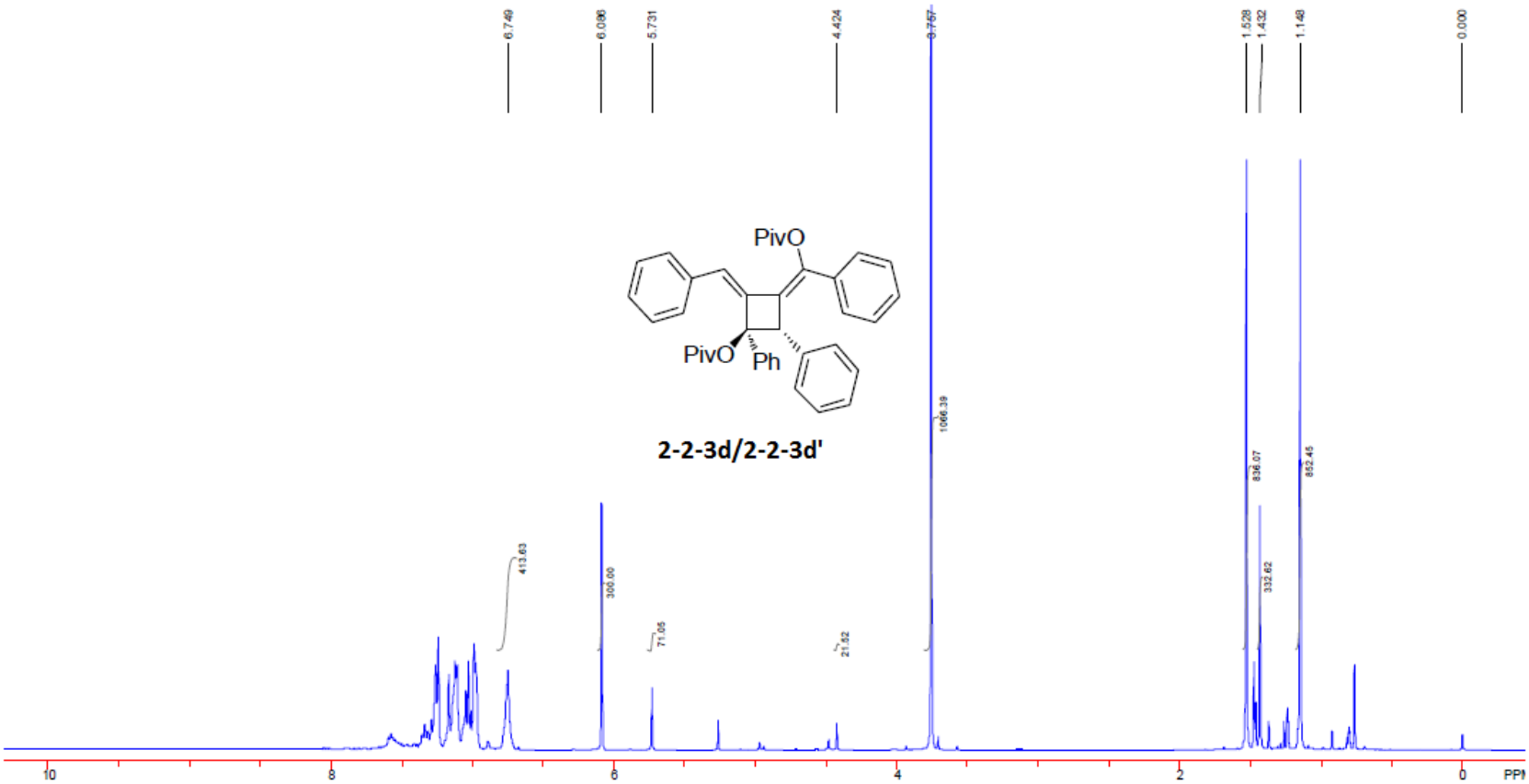
VI. NMR spectra

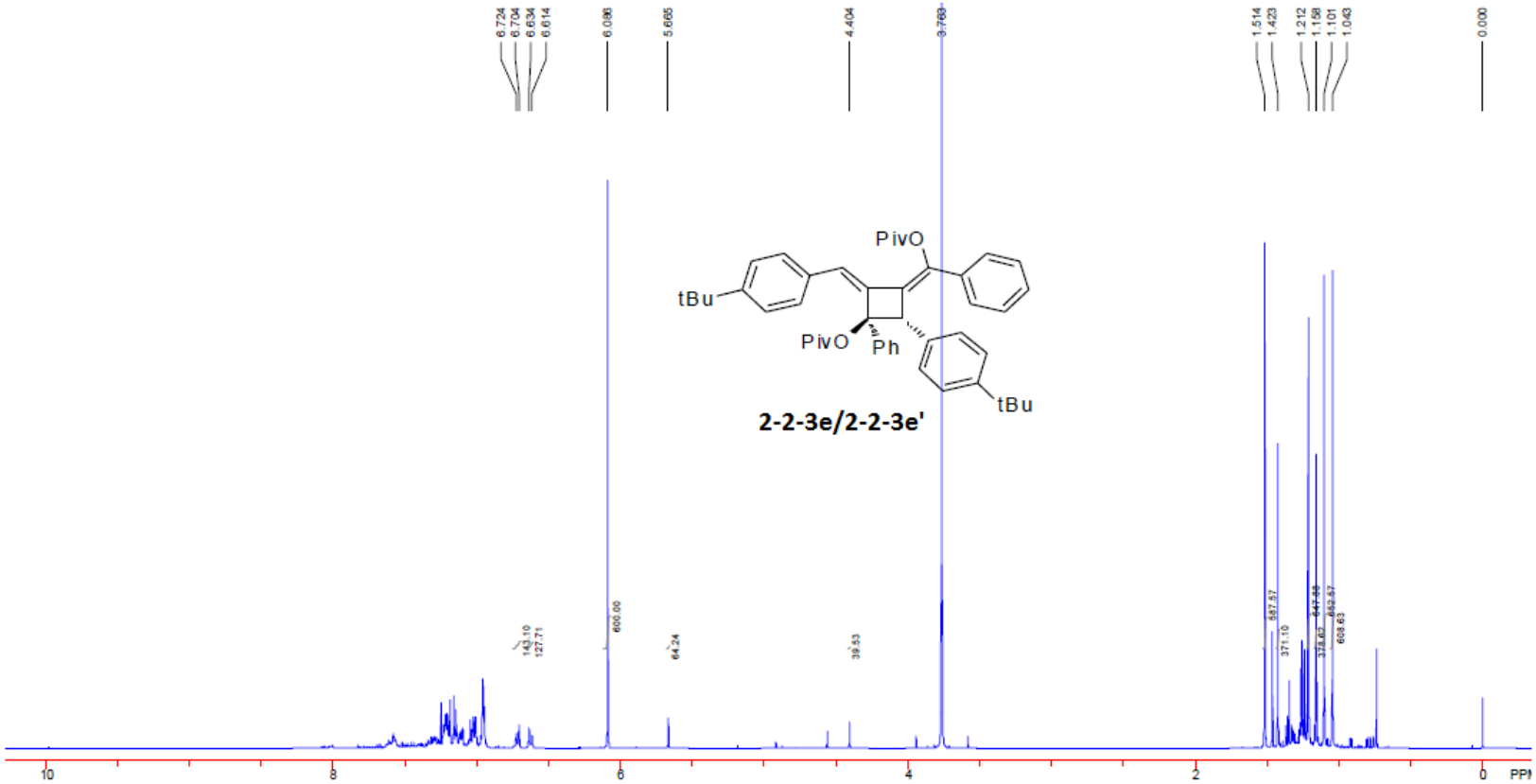

7.421
7.416
7.403
7.396
7.349
7.331
7.312
7.274
7.255
7.244
7.176
7.156
6.964
2.346
1.366
0.000
OPiv
Me
Ph
2-2-4
3.87
2.19
2.01
1.00
2.95
9.09
10
8
6
4
2
0 PPM

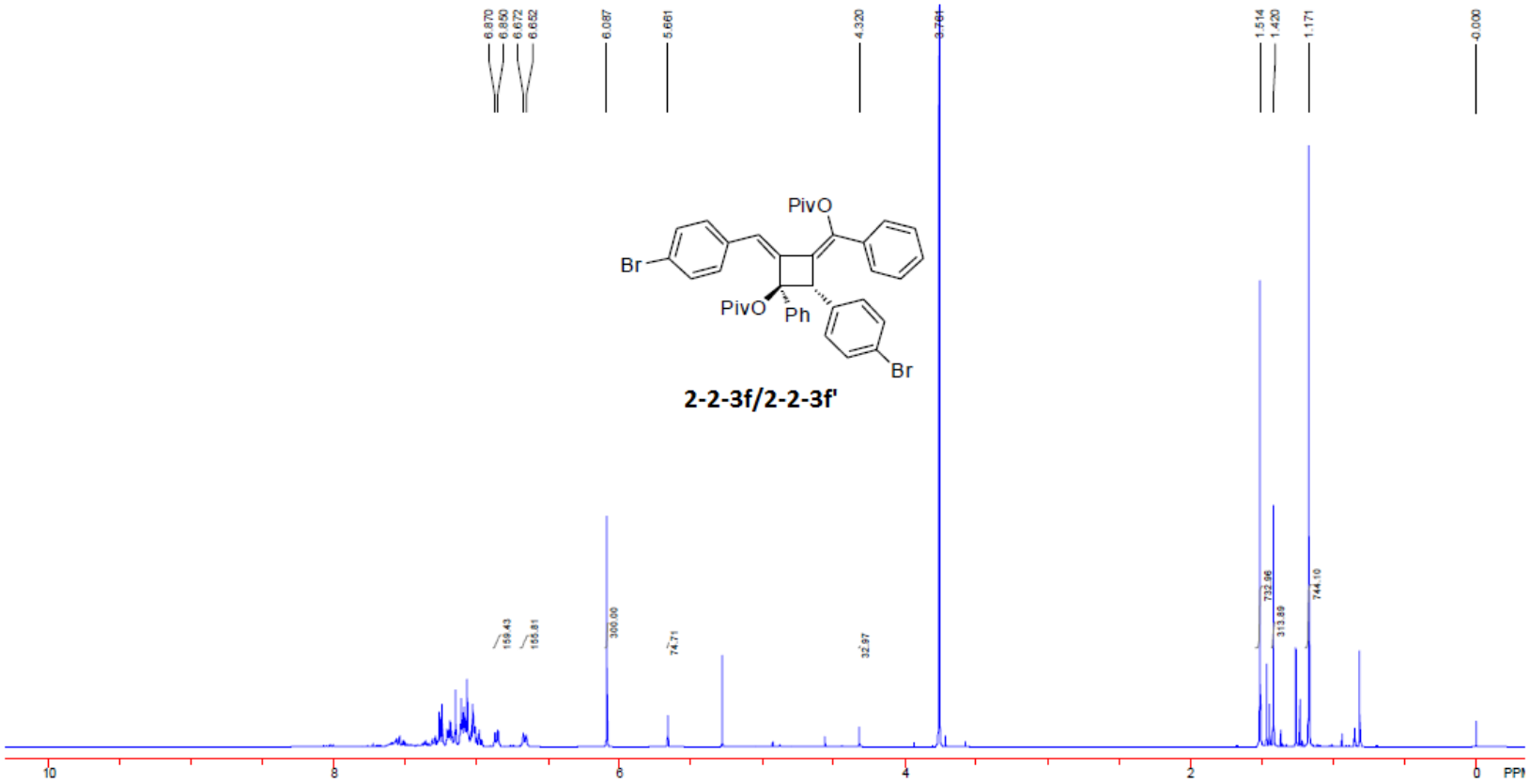
Crude NMR Spectrum

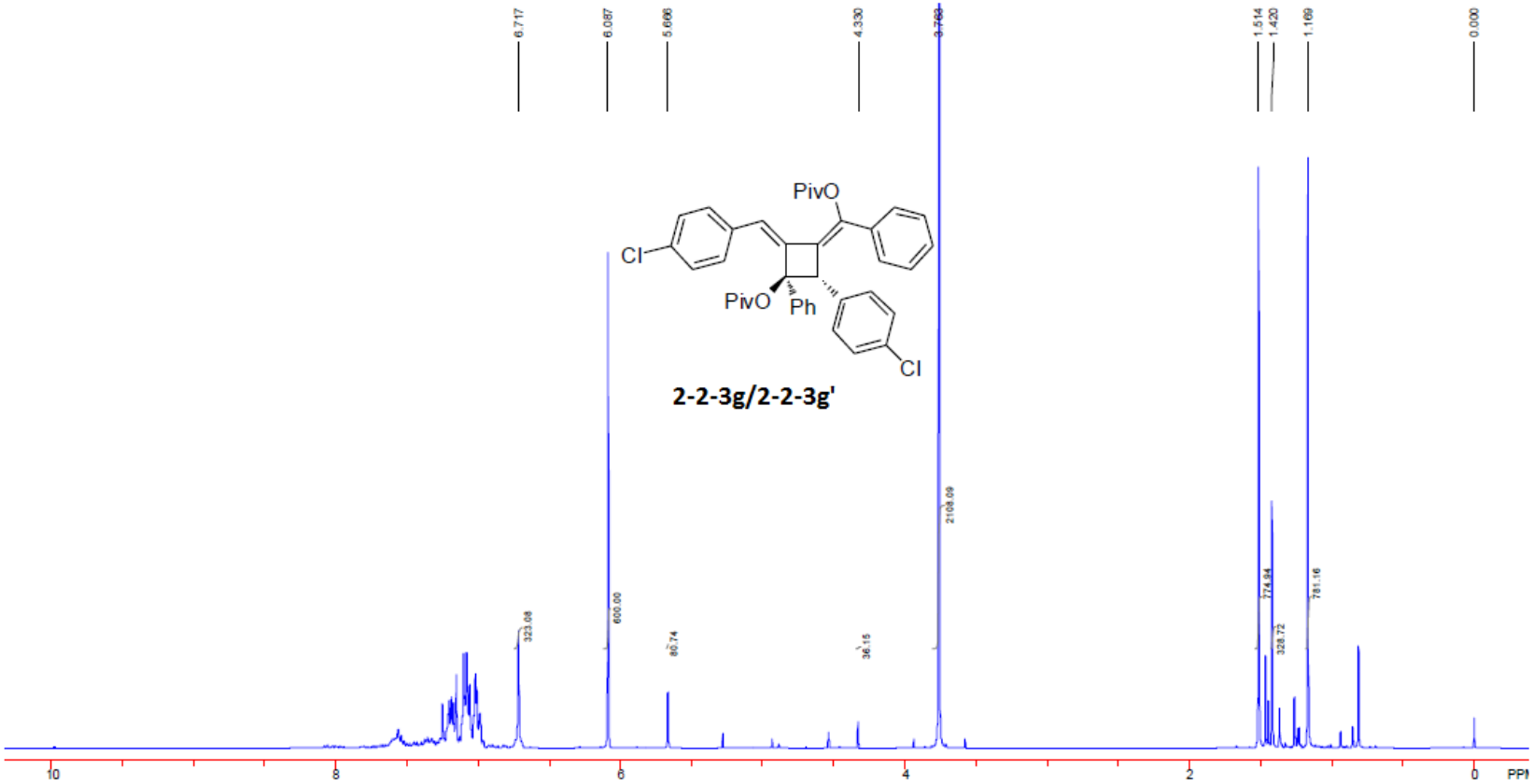
[1,3,5-trimethoxybenzene (0.1 mmol) was used as internal standard]

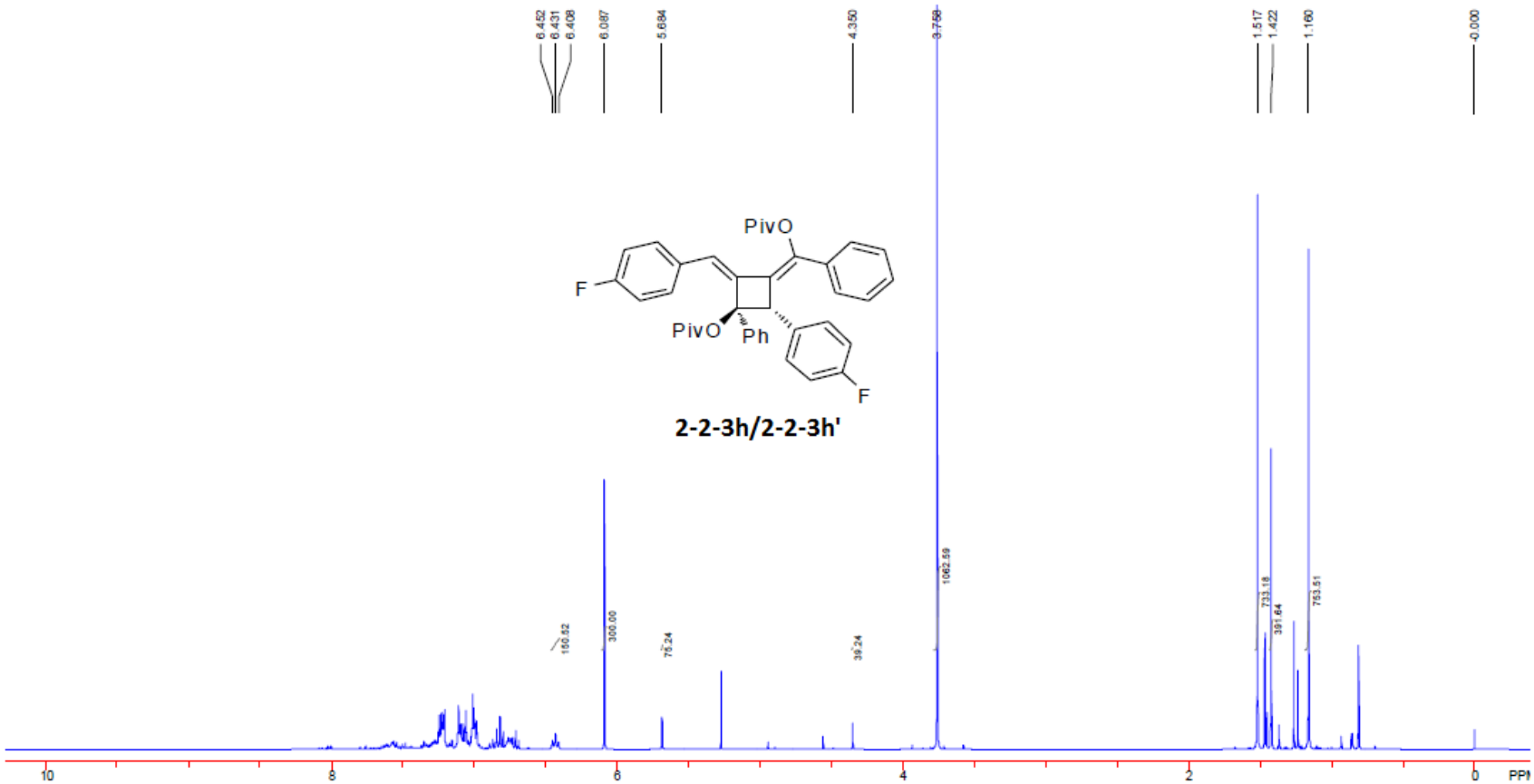

PivO
PivO
Ph
2-2-3c/2-2-3c'
6.664
6.644
6.542
6.523
6.085
5.670
4.348
3.765
2.222
2.155
1.999
1.522
1.425
1.170
0.000
133.34
128.49
300.00
66.75
25.48
1016.67
210.16
99.64
201.61
609.47
241.66
614.27
10
8
6
4
2
0
PPM

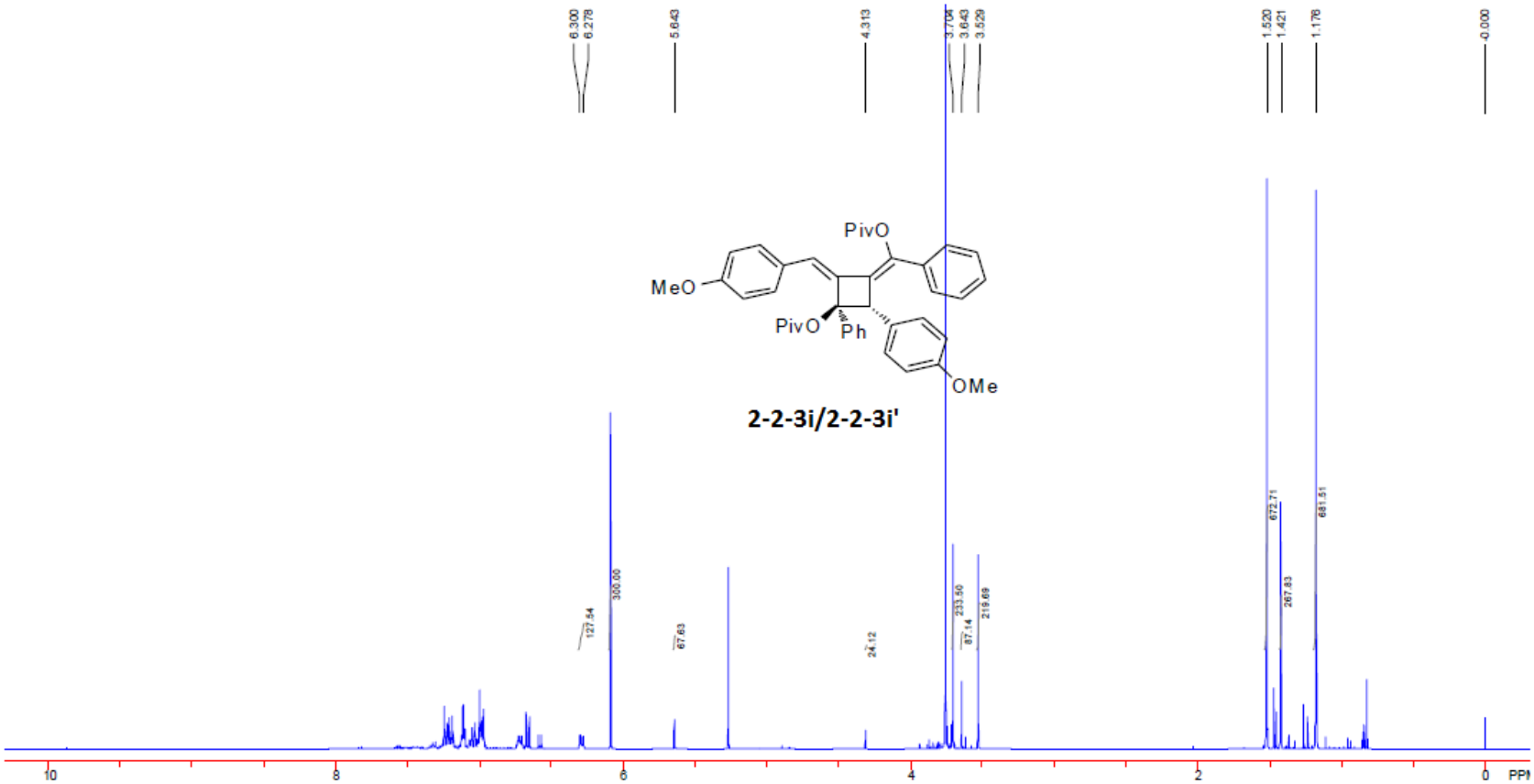

6.749
6.086
5.731
4.424
3.767
1.528
1.432
1.148
0.000
PivO
PivO
Ph
2-2-3d/2-2-3d'
413.63
300.00
77.65
21.52
1066.39
836.07
332.62
852.45
10
8
6
4
2
0
PPM

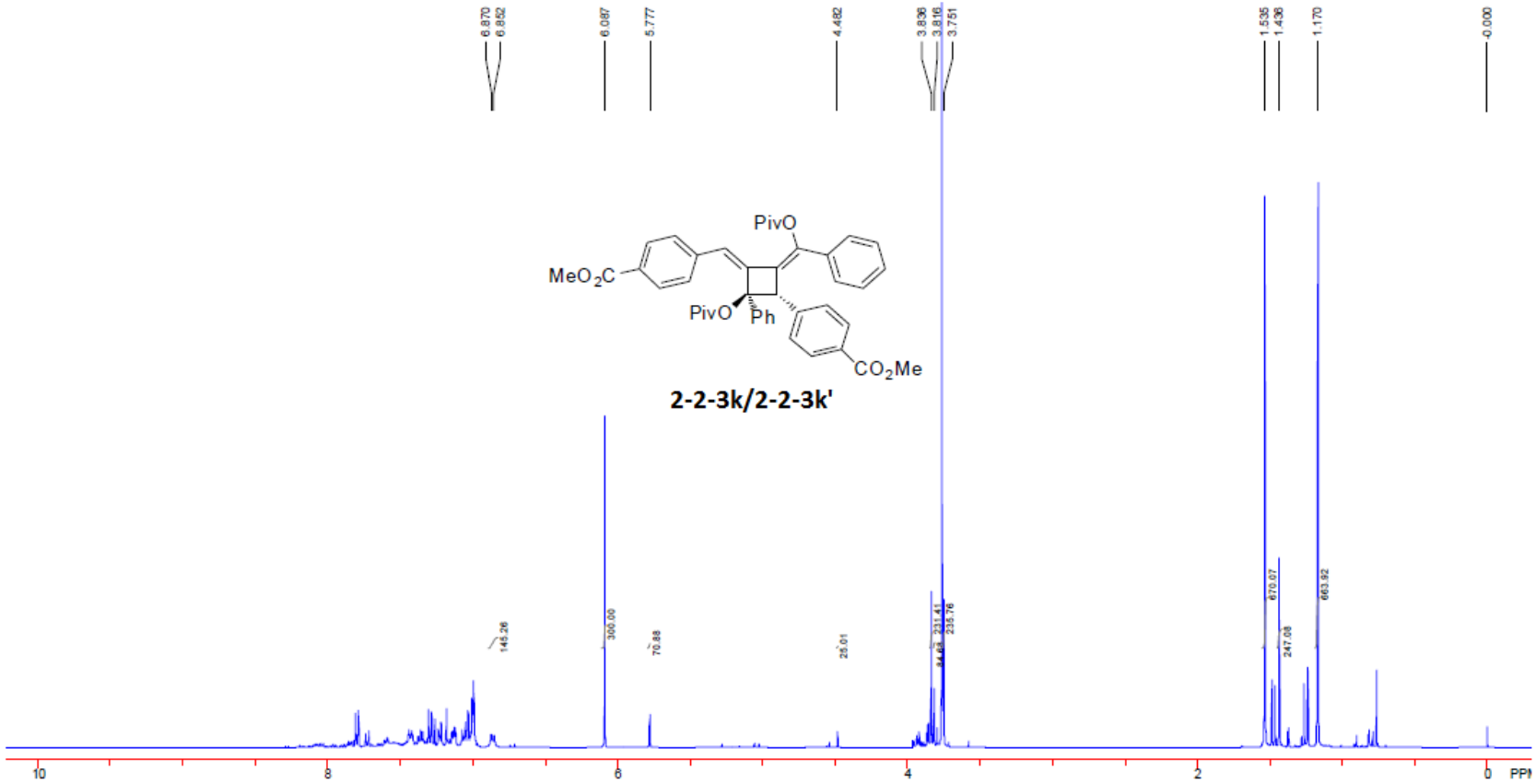

6.724
6.704
6.634
6.614
6.086
5.665
4.404
3.763
1.514
1.423
1.212
1.158
1.101
1.043
0.000
PivO
tBu
PivO
Ph
tBu
2-2-3e/2-2-3e'
143.10
127.71
600.00
64.24
39.53
587.57
371.10
641.08
375.62
853.67
608.63
10
8
6
4
2
0
PPM

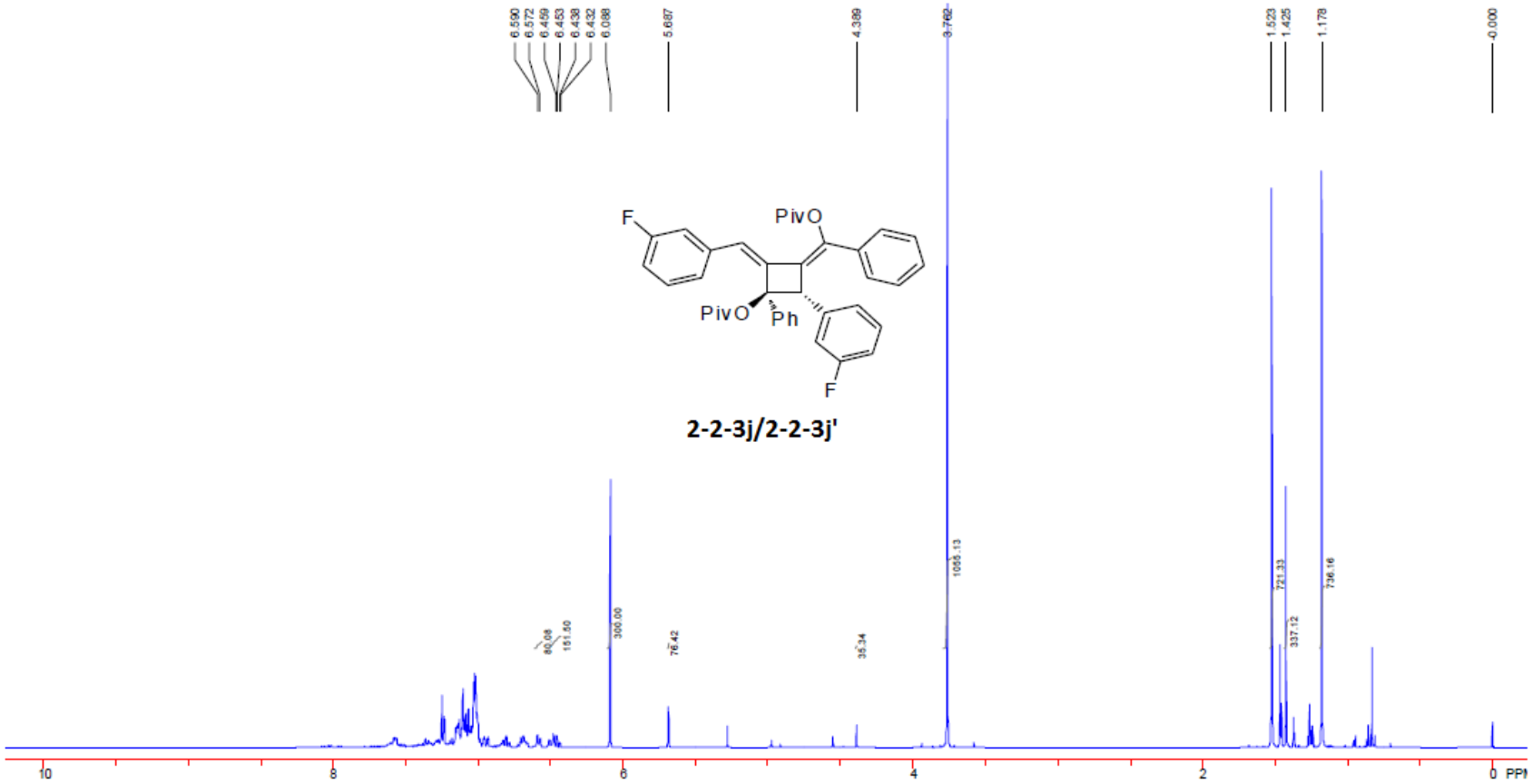

6.870
6.850
6.672
6.652
6.087
5.661
4.320
3.784
1.514
1.420
1.171
-0.000
PivO
Br
PivO
Ph
Br
2-2-3f/2-2-3f'
159.43
155.81
300.00
74.71
32.97
732.96
313.89
744.10
10
8
6
4
2
0
PPM

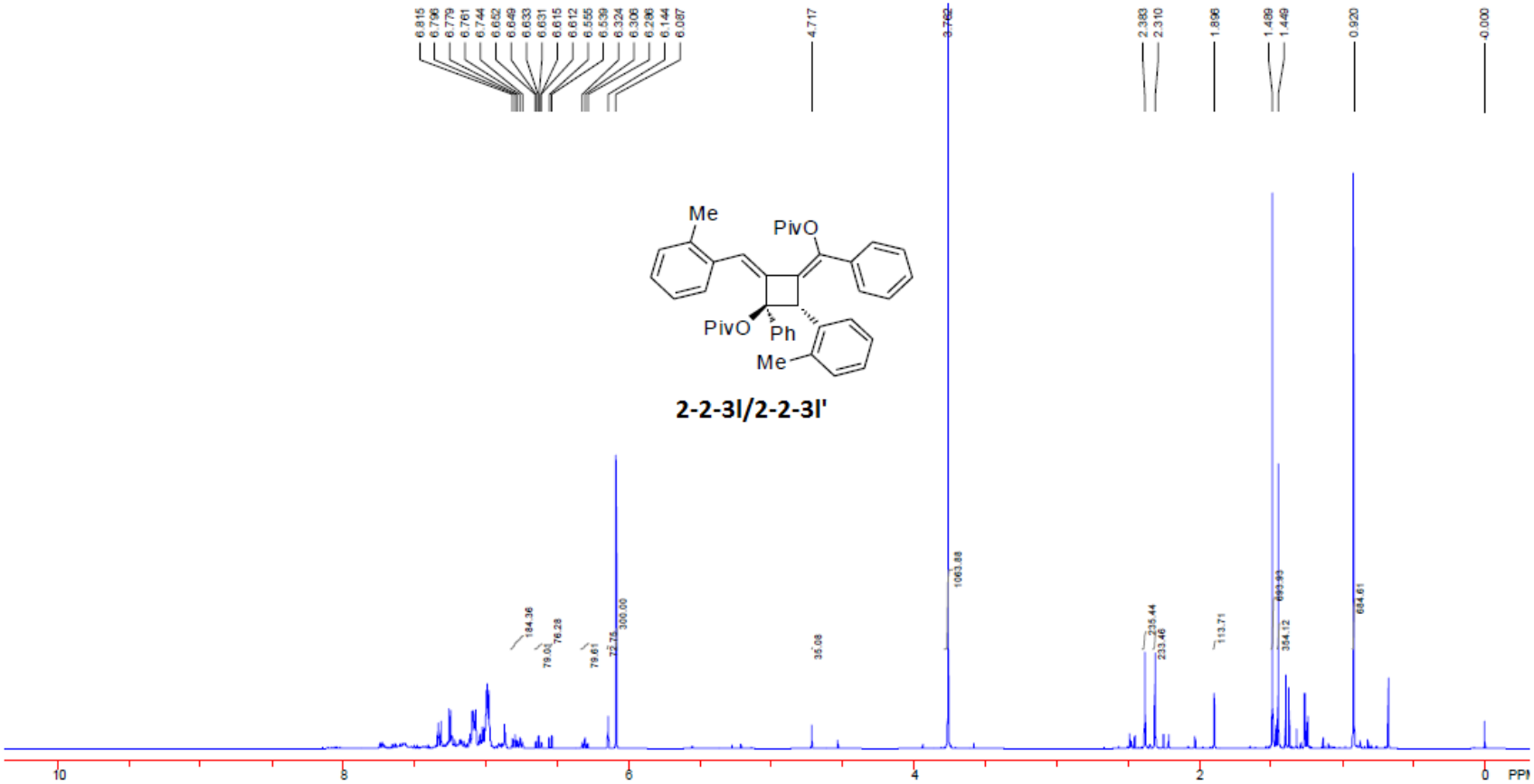

6.717
6.087
5.666
4.330
3.768
1.514
1.420
1.169
0.000
PivO
Cl
PivO
Ph
Cl
2-2-3g/2-2-3g'
323.08
600.00
86.74
36.15
2108.09
774.84
328.72
781.16
10
8
6
4
2
0
PPM

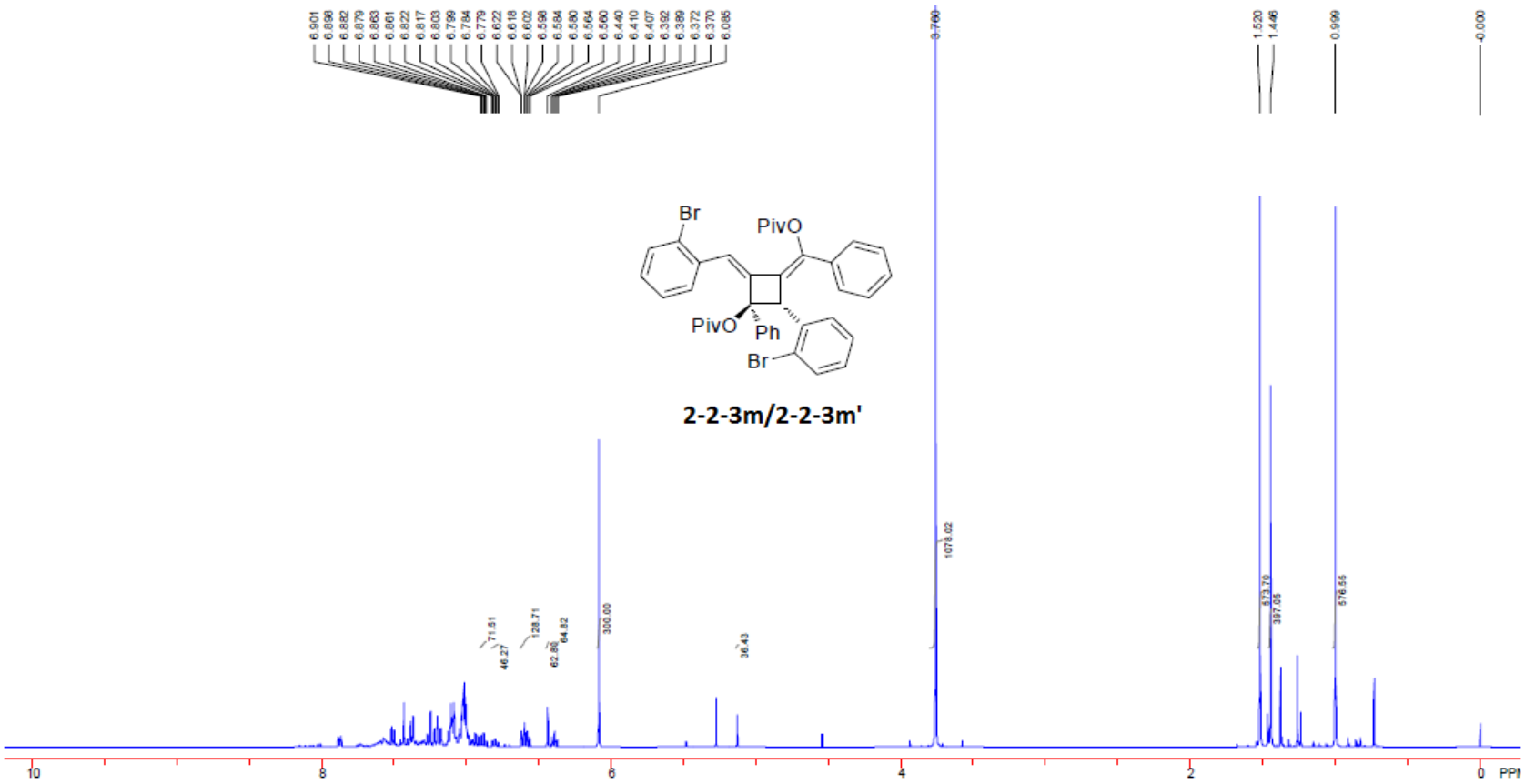

6.452
6.431
6.408
6.087
5.684
4.350
3.768
1.517
1.422
1.160
-0.000
PivO
F
PivO
Ph
F
2-2-3h/2-2-3h'
100.52
300.00
76.24
39.24
1062.59
733.18
391.64
753.51
10
8
6
4
2
0
PPM

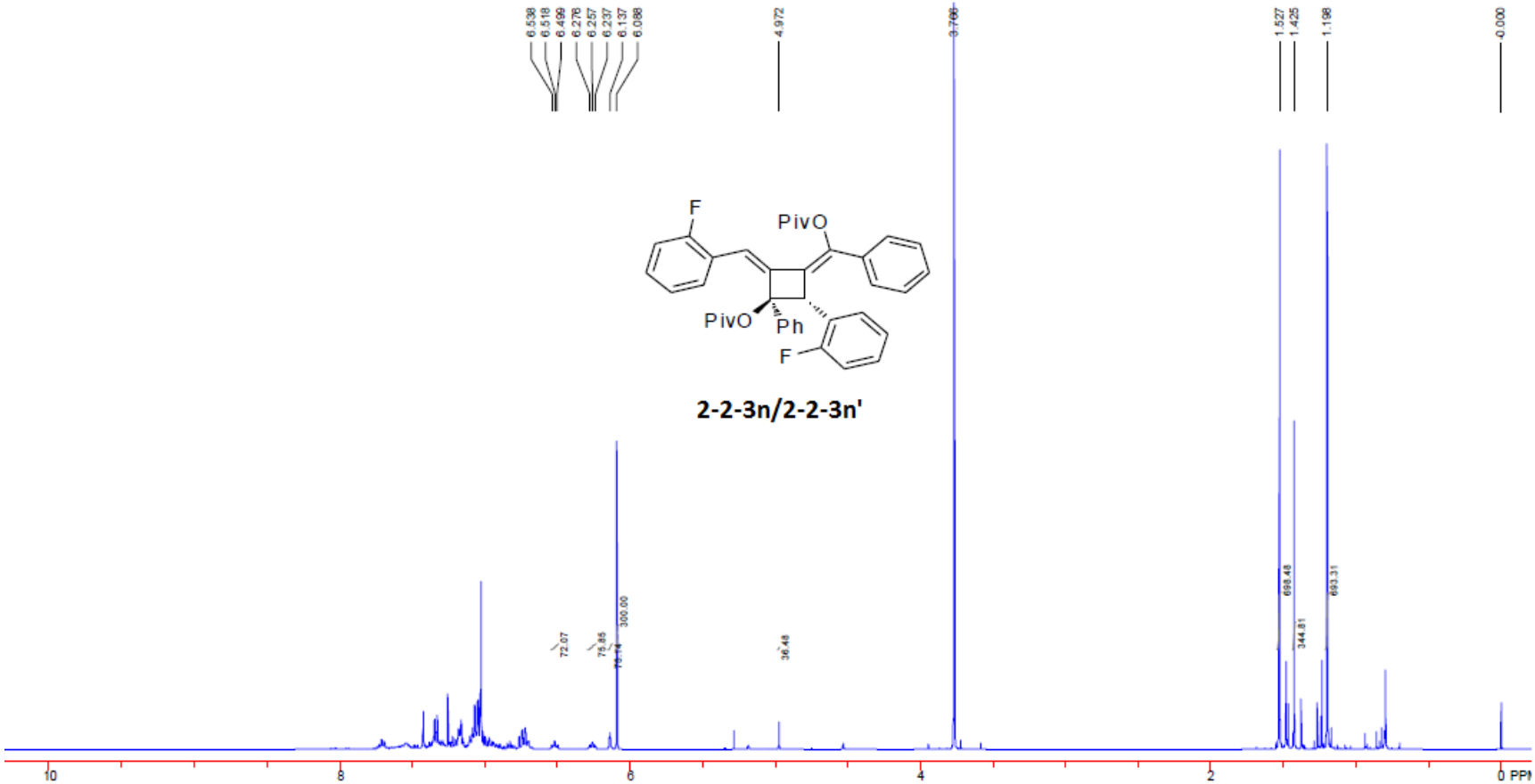

6.300
6.278
5.643
4.313
3.704
3.643
3.529
1.520
1.421
1.176
0.000
PivO
MeO
PivO
Ph
OMe
2-2-3i/2-2-3i'
127.54
300.00
67.63
24.12
233.50
87.14
219.69
672.71
267.83
681.51
10
8
6
4
2
0
PPM

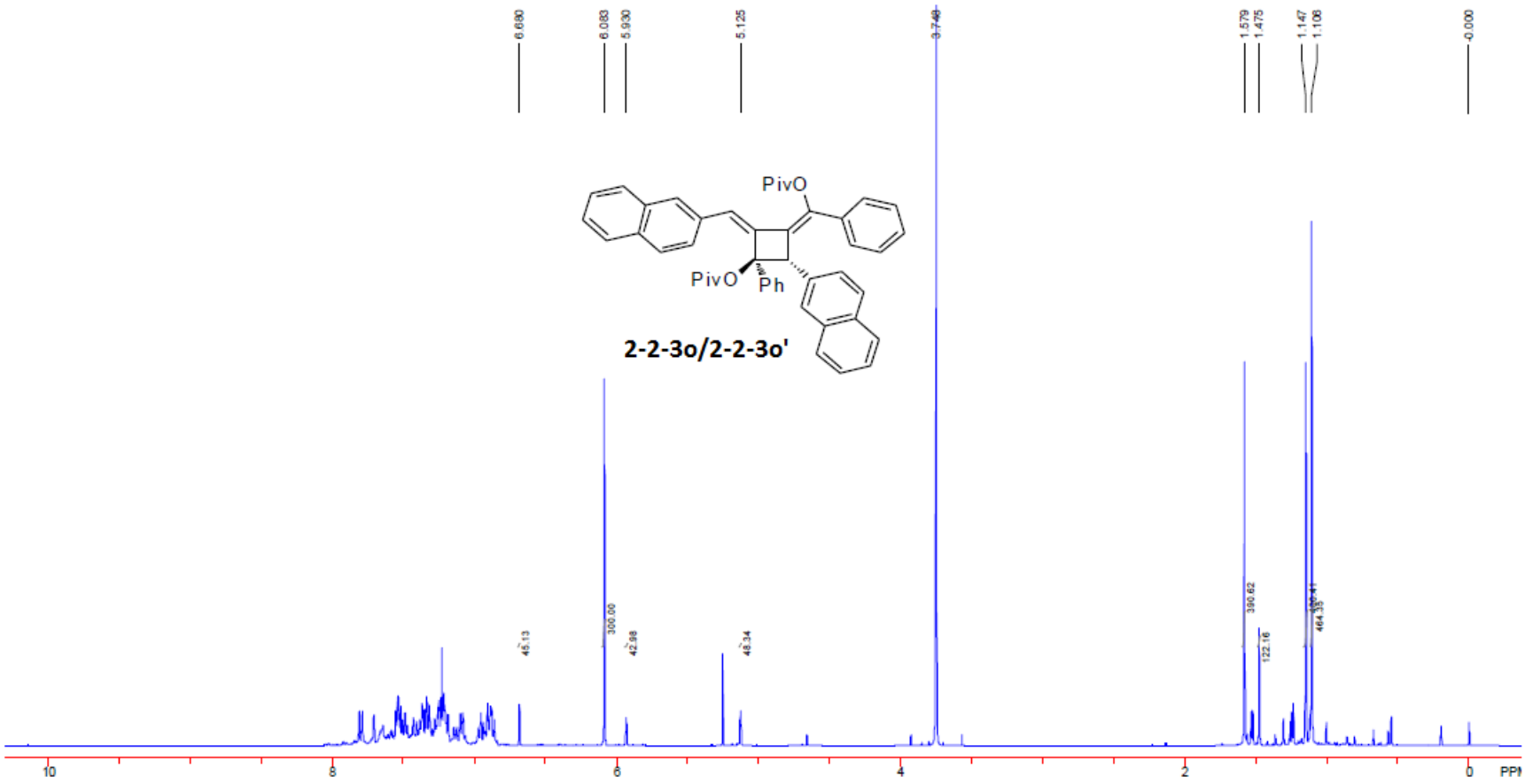

6.870
6.852
6.087
5.777
4.482
3.836
3.816
3.751
1.535
1.436
1.170
0.000
PivO
MeO2C
PivO
Ph
CO2Me
2-2-3k/2-2-3k'
143.26
300.00
70.88
25.01
231.41
235.76
670.07
247.08
663.92
10
8
6
4
2
0
PPM

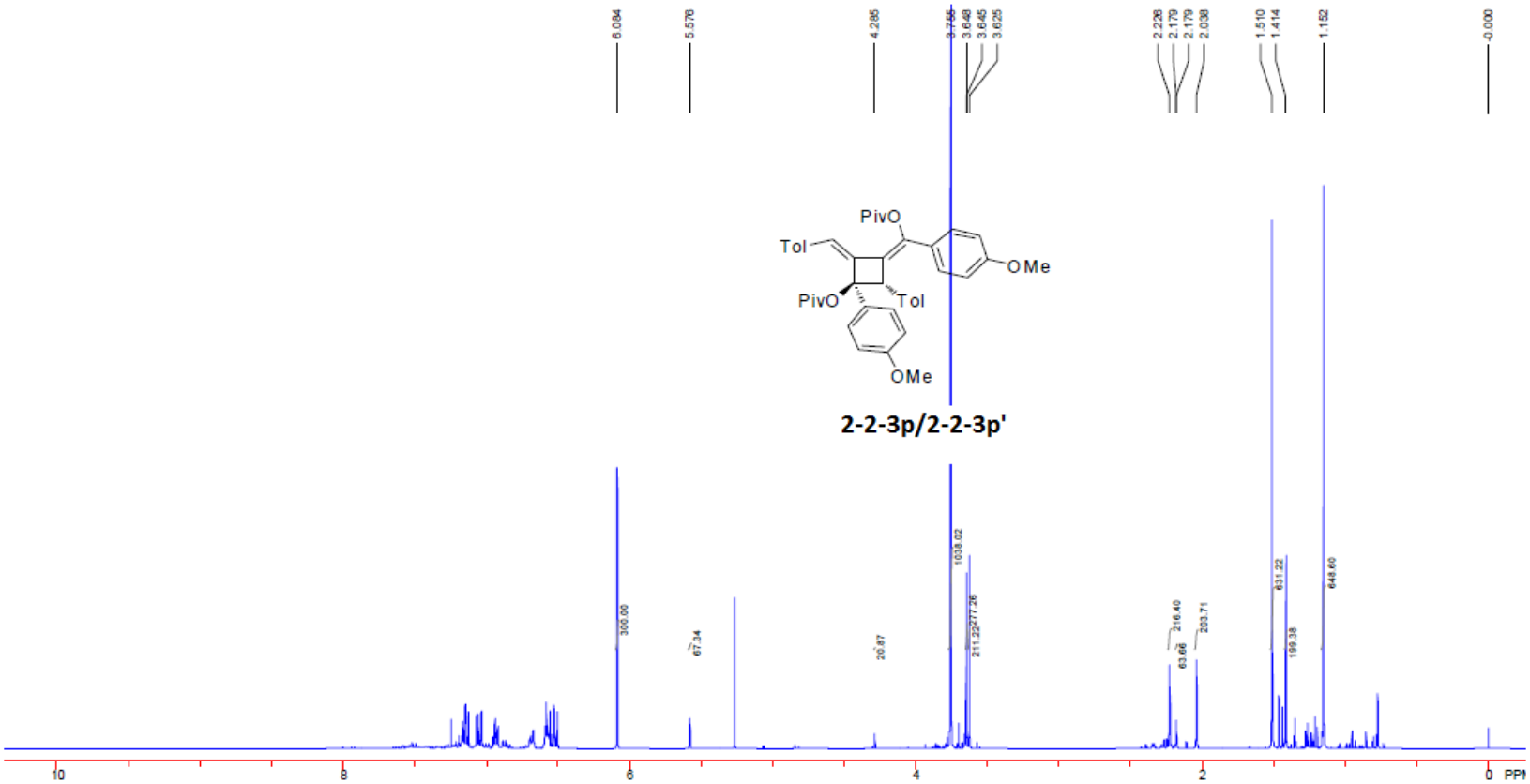

6.590
6.572
6.459
6.453
6.438
6.432
6.088
5.687
4.389
3.762
1.523
1.425
1.178
0.000
F
PivO
PivO
Ph
F
2-2-3j/2-2-3j'
80.08
161.50
300.00
76.42
35.34
1055.13
721.33
337.12
736.16
10
8
6
4
2
0 PPM

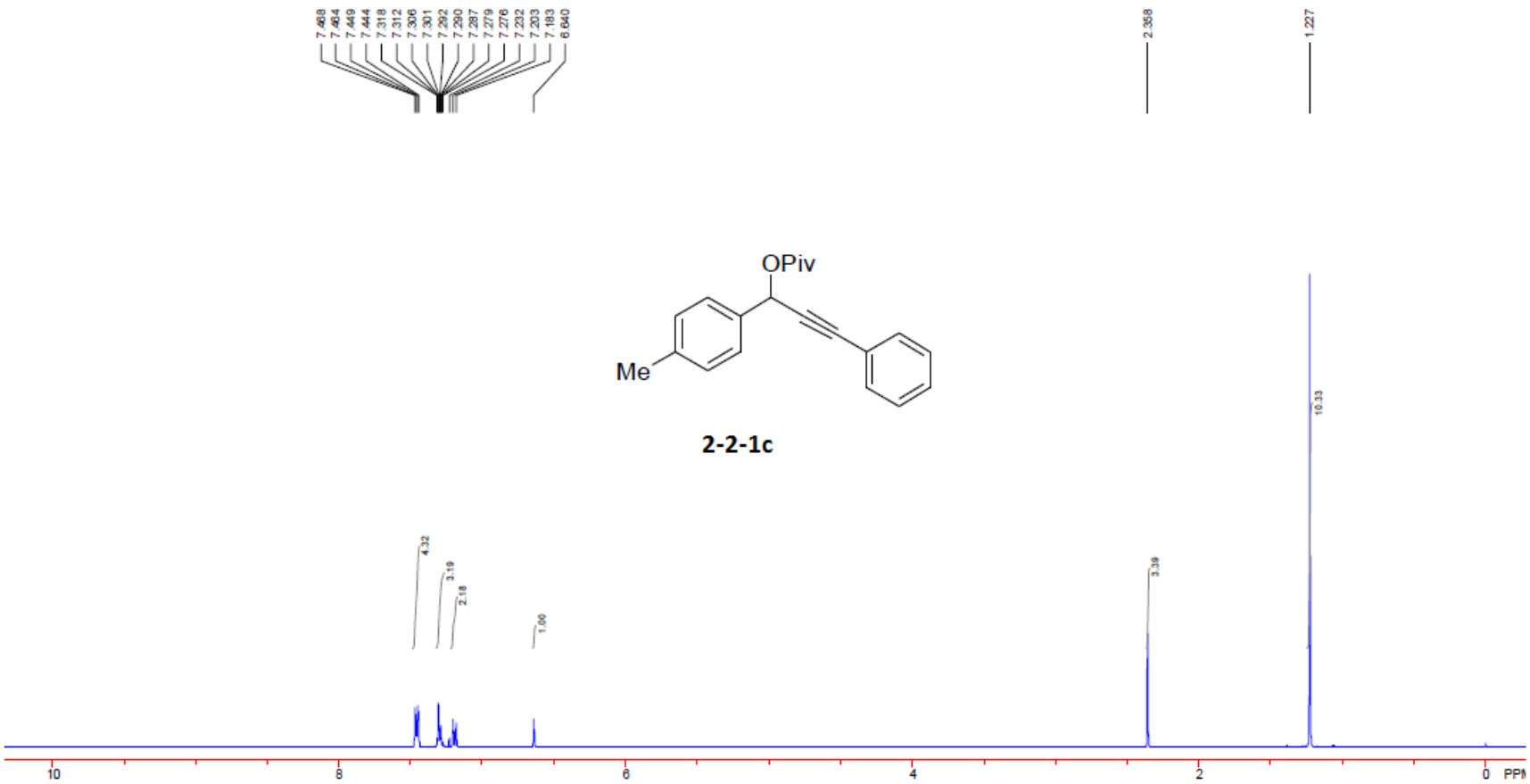

Me
PivO
PivO
Ph
Me
2-2-3l/2-2-3l'
10
8
6
4
2
0
PPM

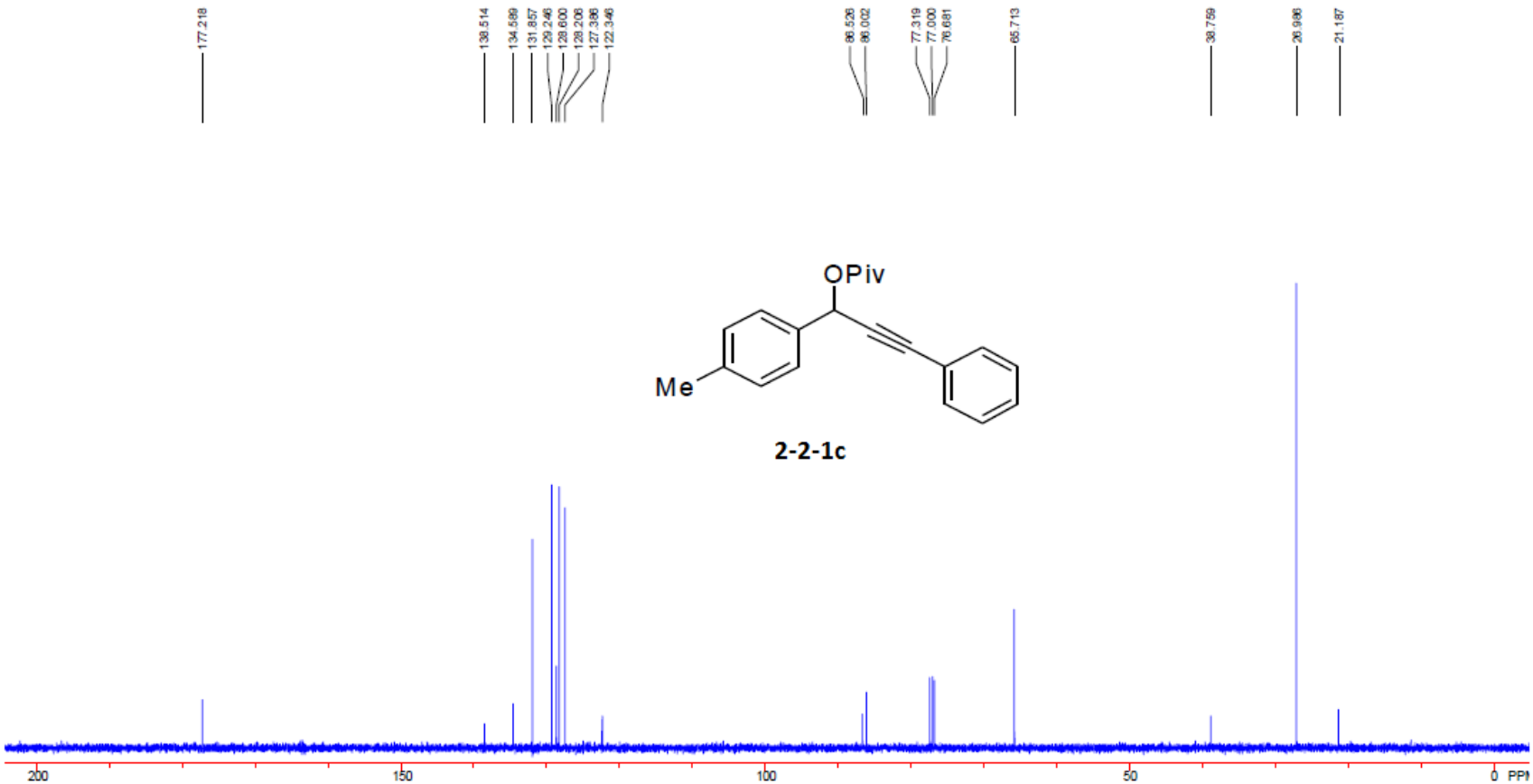

Br
PivO
PivO
Ph
Br
2-2-3m/2-2-3m'
6.901
6.898
6.882
6.879
6.863
6.861
6.822
6.817
6.803
6.799
6.784
6.779
6.622
6.618
6.602
6.598
6.584
6.580
6.564
6.560
6.440
6.410
6.407
6.392
6.389
6.372
6.370
6.085
3.760
1.520
1.446
0.999
0.000
71.51
46.27
128.71
62.86
64.82
300.00
36.43
1078.02
571.70
397.05
576.55
10
8
6
4
2
0
PPM

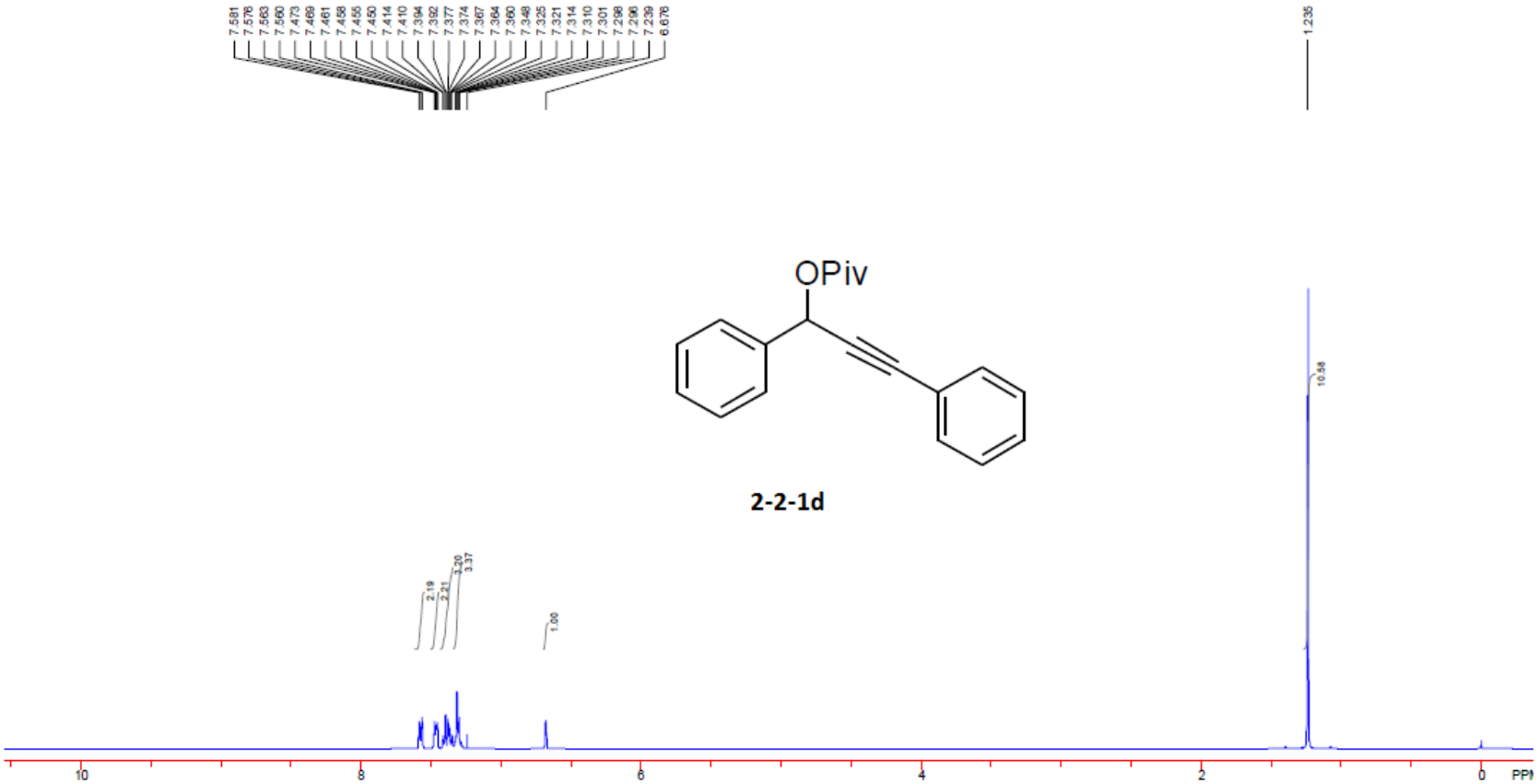

6.538
6.518
6.499
6.276
6.257
6.237
6.137
6.088
4.972
3.766
1.527
1.425
1.198
0.000
F
PivO
PivO
Ph
F
2-2-3n/2-2-3n'
72.07
75.85
76.14
300.00
36.48
698.48
344.81
693.31
10
8
6
4
2
0 PPM

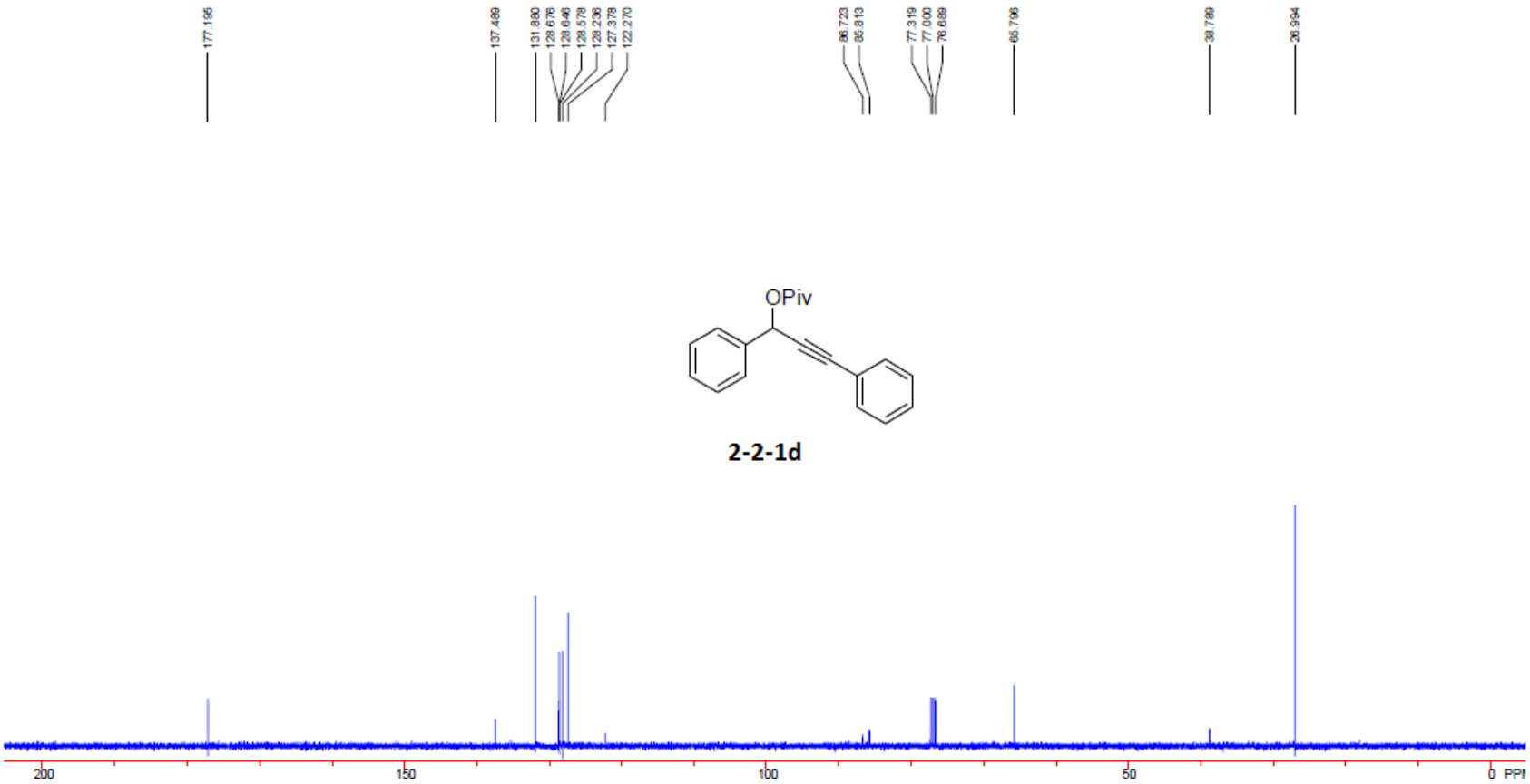

6.680
6.083
5.930
5.125
3.749
1.579
1.475
1.147
1.106
0.000
PivO
PivO
Ph
2-2-3o/2-2-3o'
45.13
300.00
42.98
48.34
390.62
122.16
464.35
10
8
6
4
2
0
PPM


6.084
5.576
4.285
3.765
3.648
3.645
3.625
2.226
2.179
2.179
2.038
1.510
1.414
1.152
-0.000
PivO
Tol
OMe
PivO
Tol
OMe
2-2-3p/2-2-3p'
300.00
67.34
20.87
1038.02
211.22
277.26
216.40
63.68
203.71
631.22
199.38
648.60
10
8
6
4
2
0
PPM

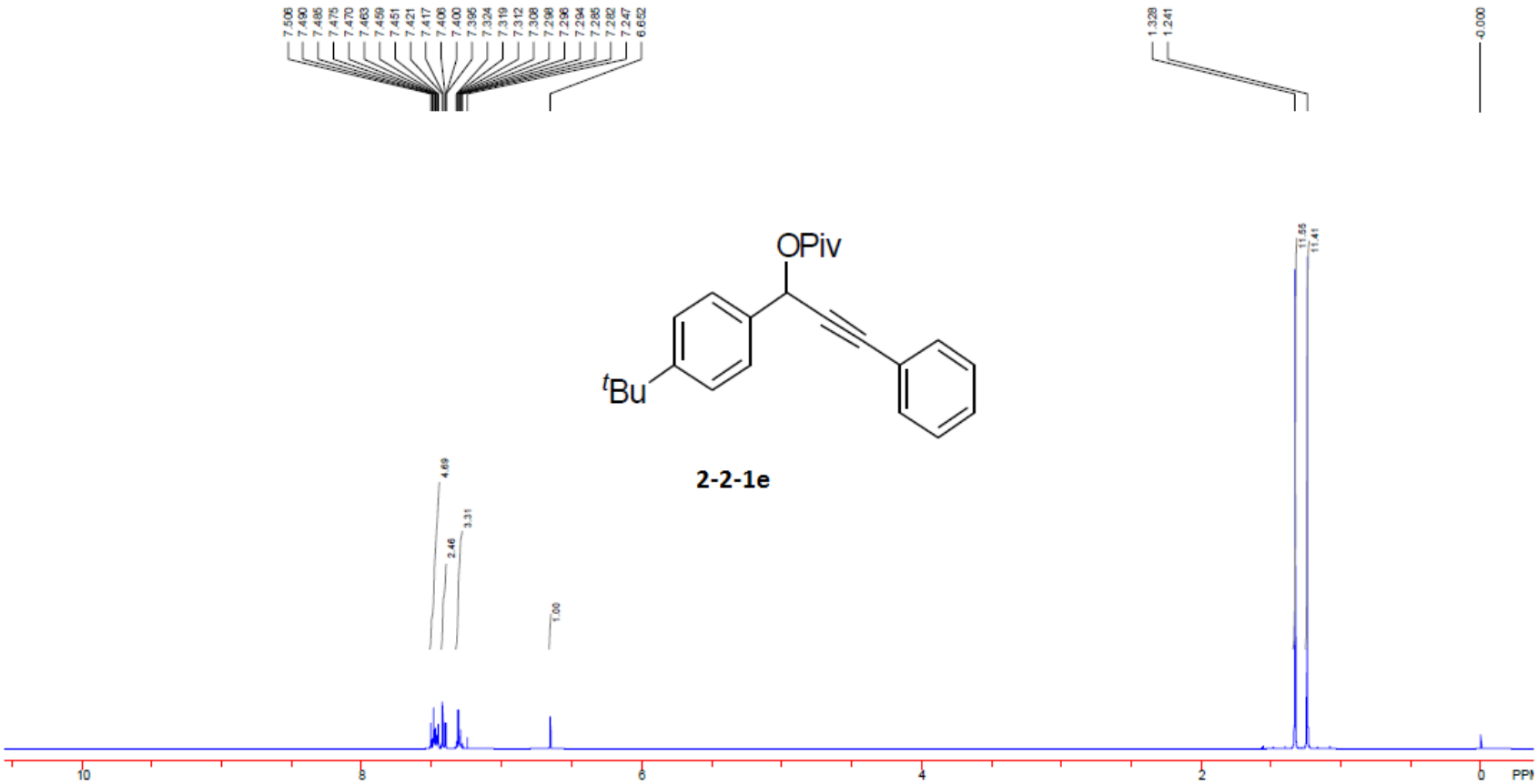

7.468
7.464
7.449
7.444
7.318
7.312
7.306
7.301
7.292
7.290
7.287
7.279
7.278
7.232
7.203
7.183
6.840
2.358
1.227
OPiv
Me
2-2-1c
10.33
4.32
3.19
2.18
1.00
3.39
10
8
6
4
2
0
PPM

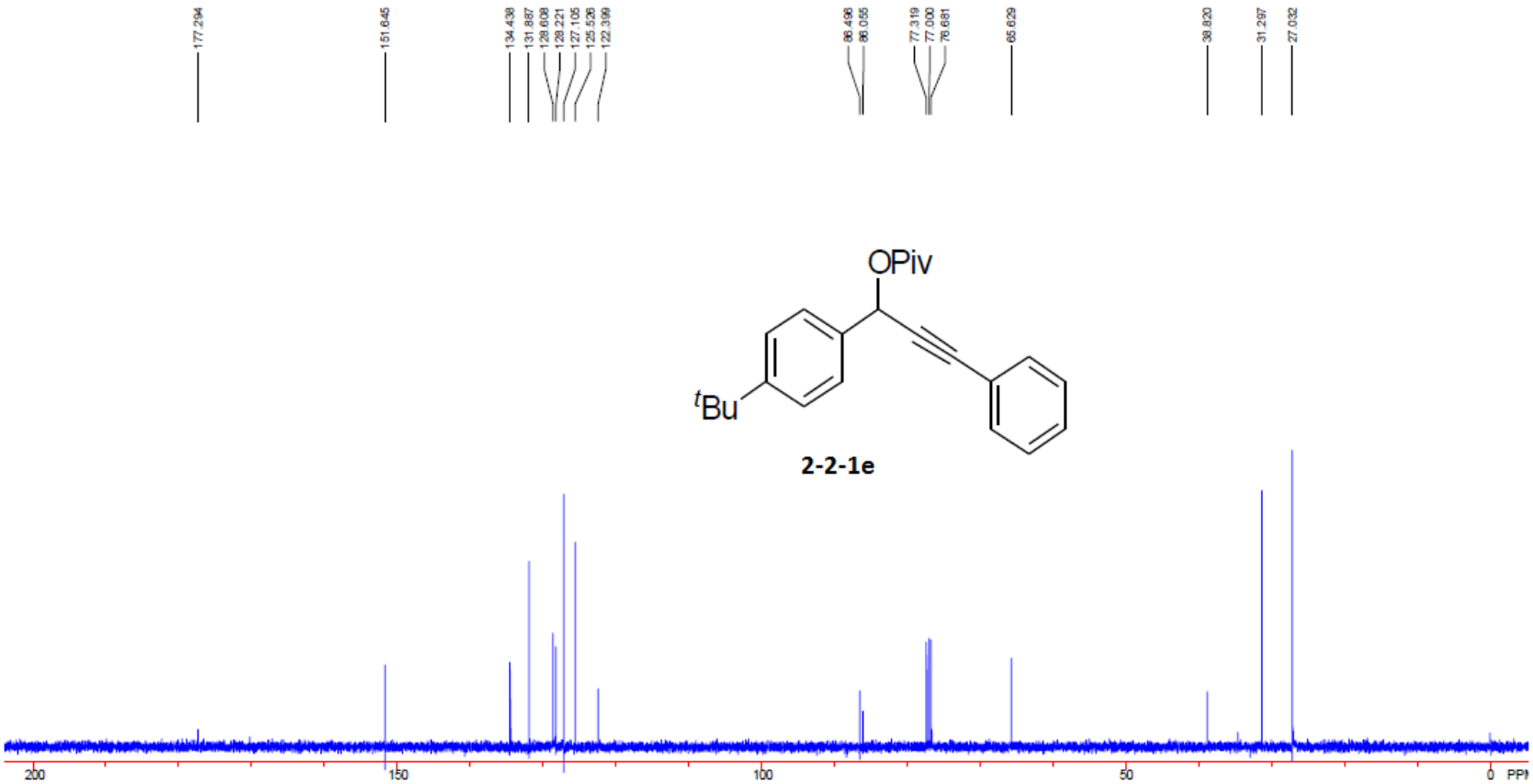

177.218
138.514
134.589
131.857
129.246
128.600
128.206
127.388
122.346
86.526
86.022
77.319
77.000
76.681
65.713
38.759
26.986
21.187
OPiv
Me
2-2-1c
200
150
100
50
0 PPM

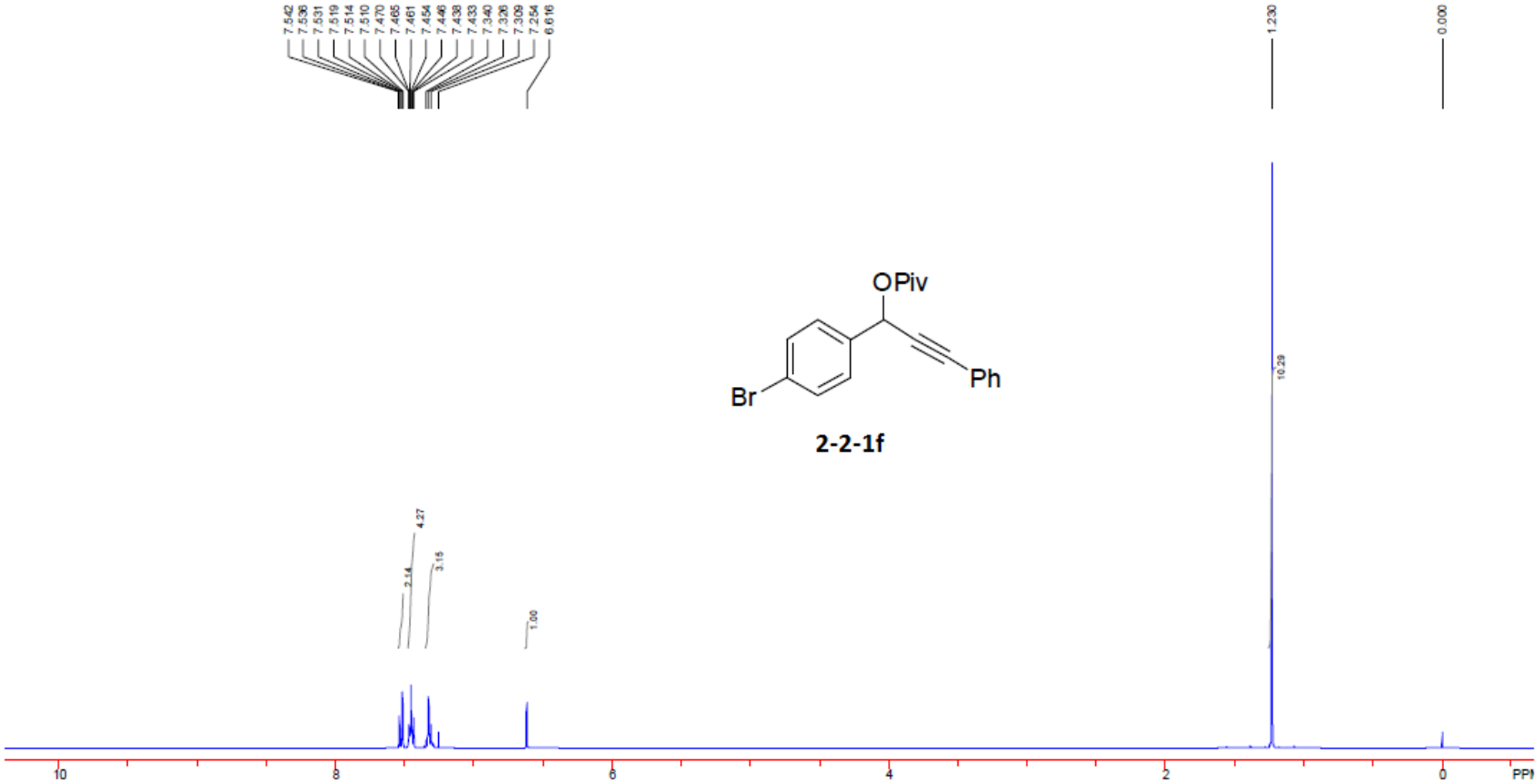

7.581
7.576
7.563
7.560
7.473
7.469
7.461
7.458
7.455
7.450
7.414
7.410
7.394
7.392
7.377
7.374
7.367
7.364
7.360
7.348
7.325
7.321
7.314
7.310
7.301
7.298
7.296
7.239
6.676
1.235
OPiv
2-2-1d
10.58
2.19
2.21
3.20
3.37
1.00
10
8
6
4
2
0
PPM

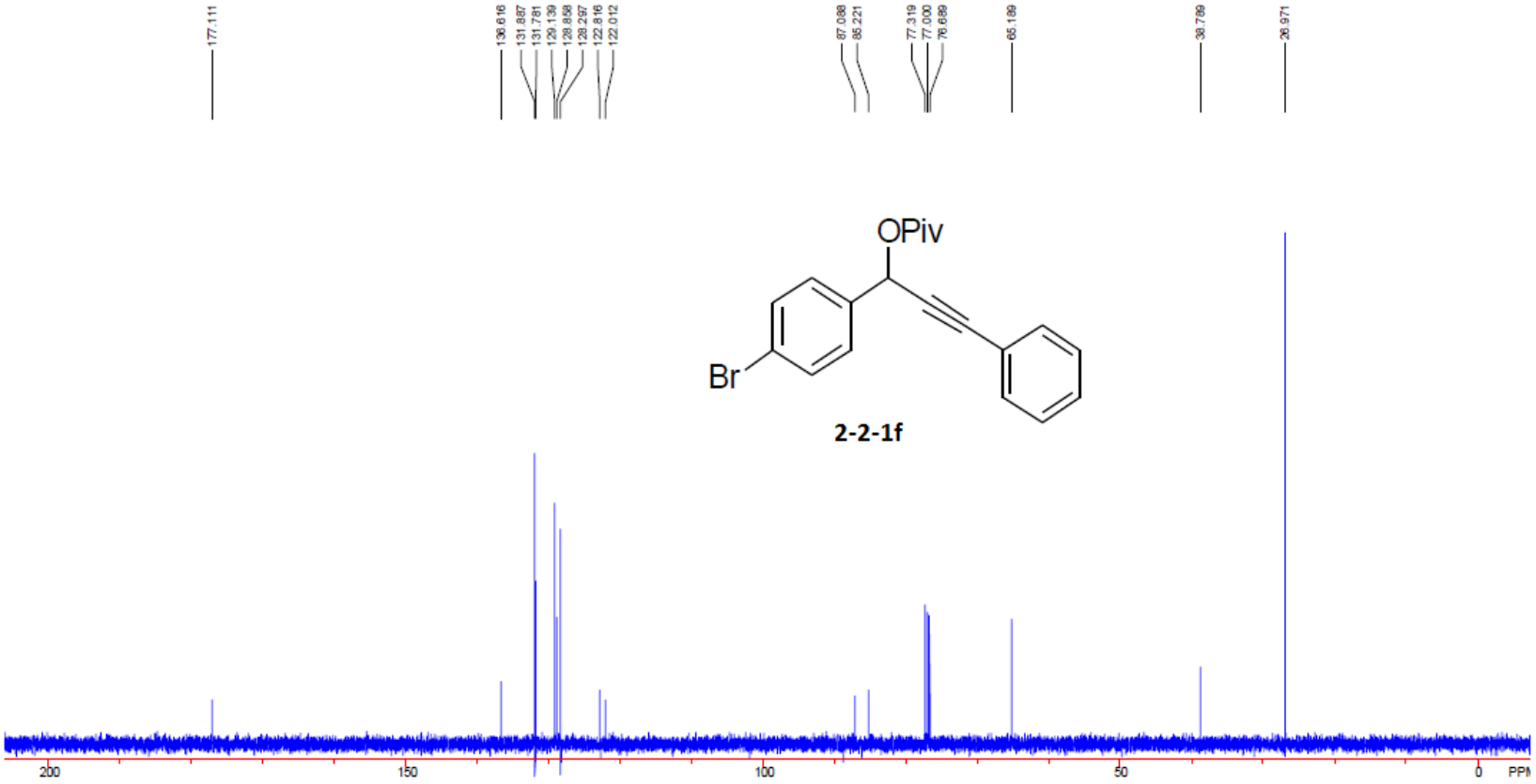

177.195
137.489
131.880
128.676
128.646
128.578
128.236
127.378
122.270
86.723
85.813
77.319
77.000
76.689
65.796
38.789
26.994
OPiv
200
150
100
50
0 PPM

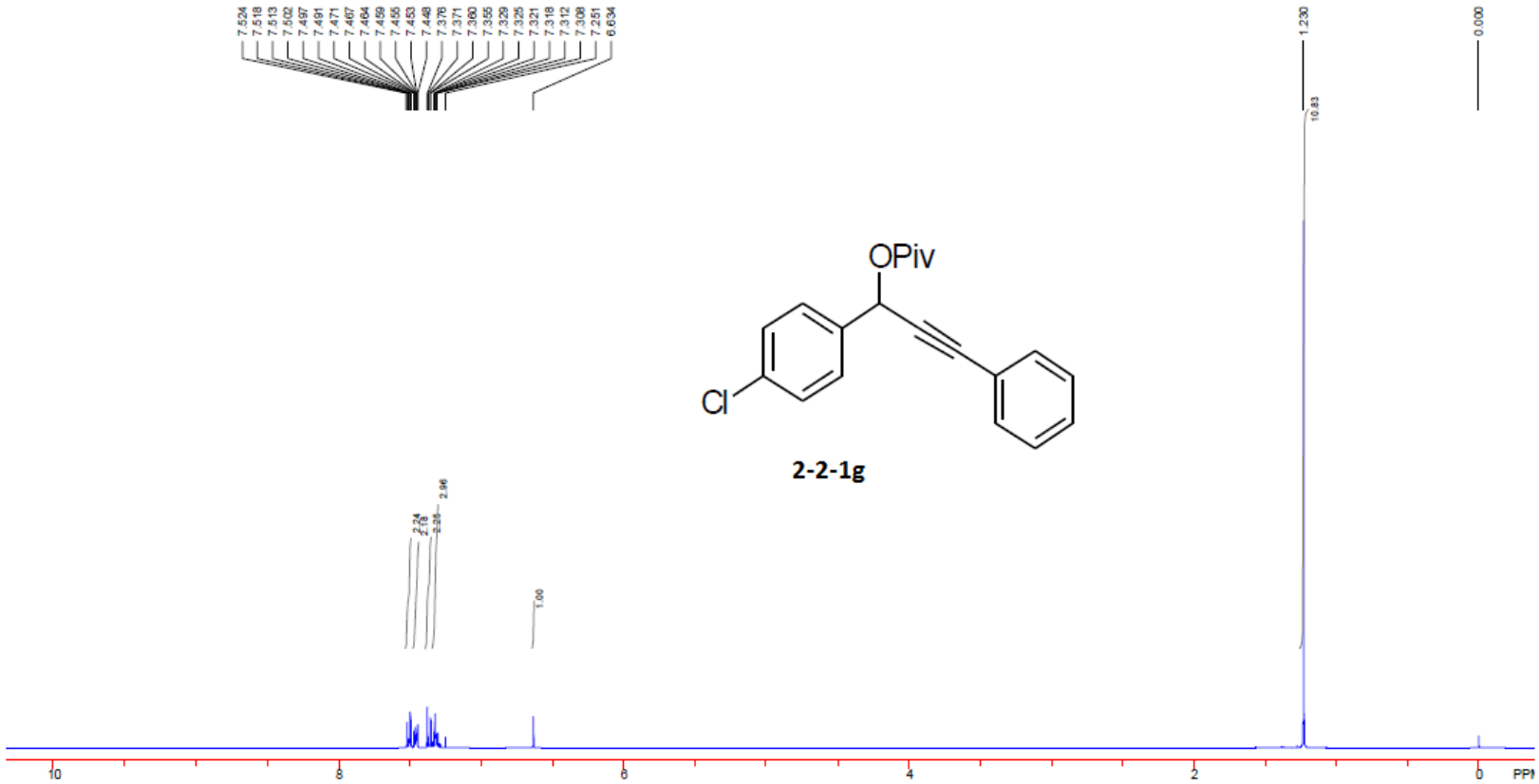
2-2-1d

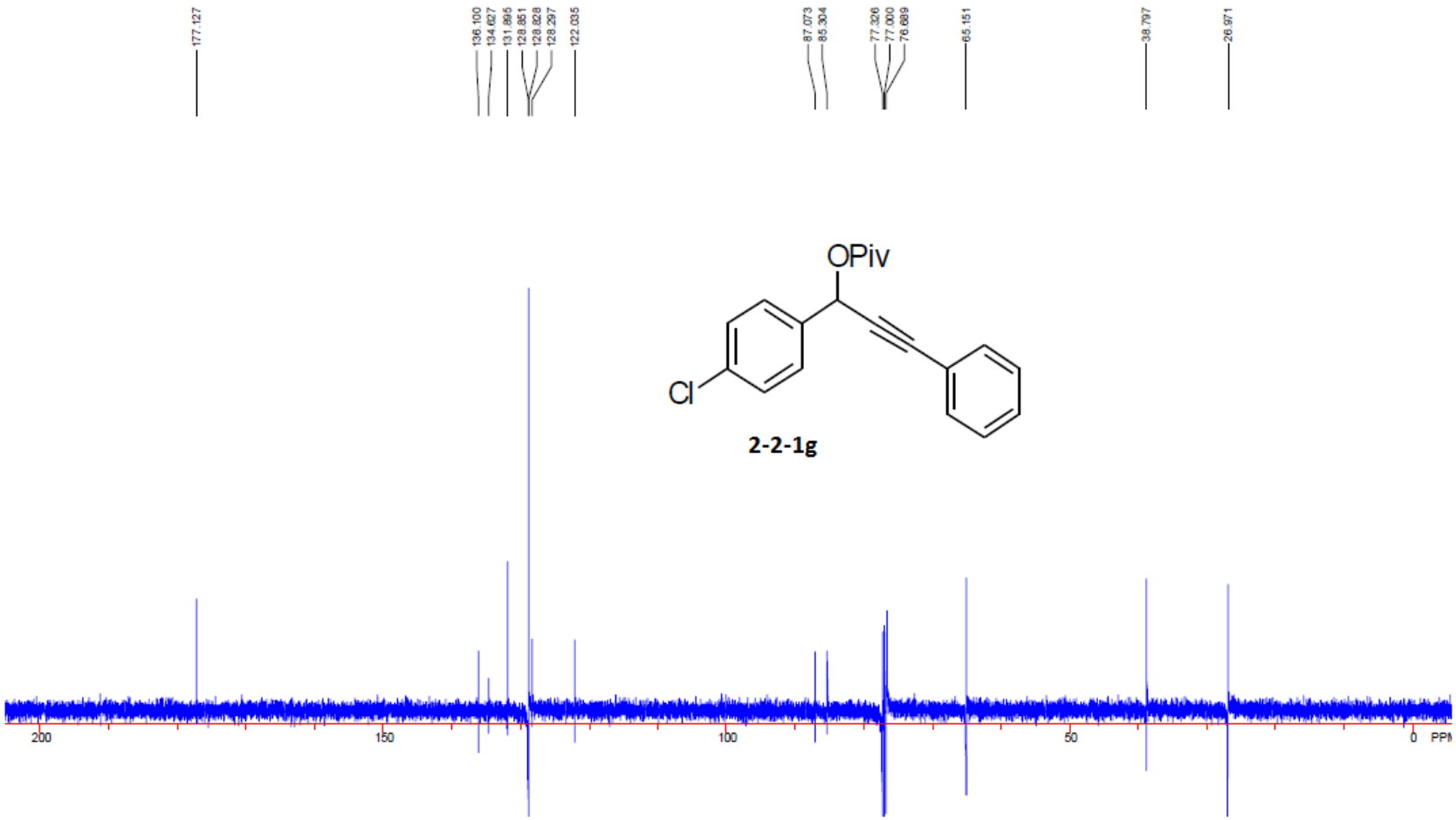

OPiv
tBu
2-2-1e
PPM

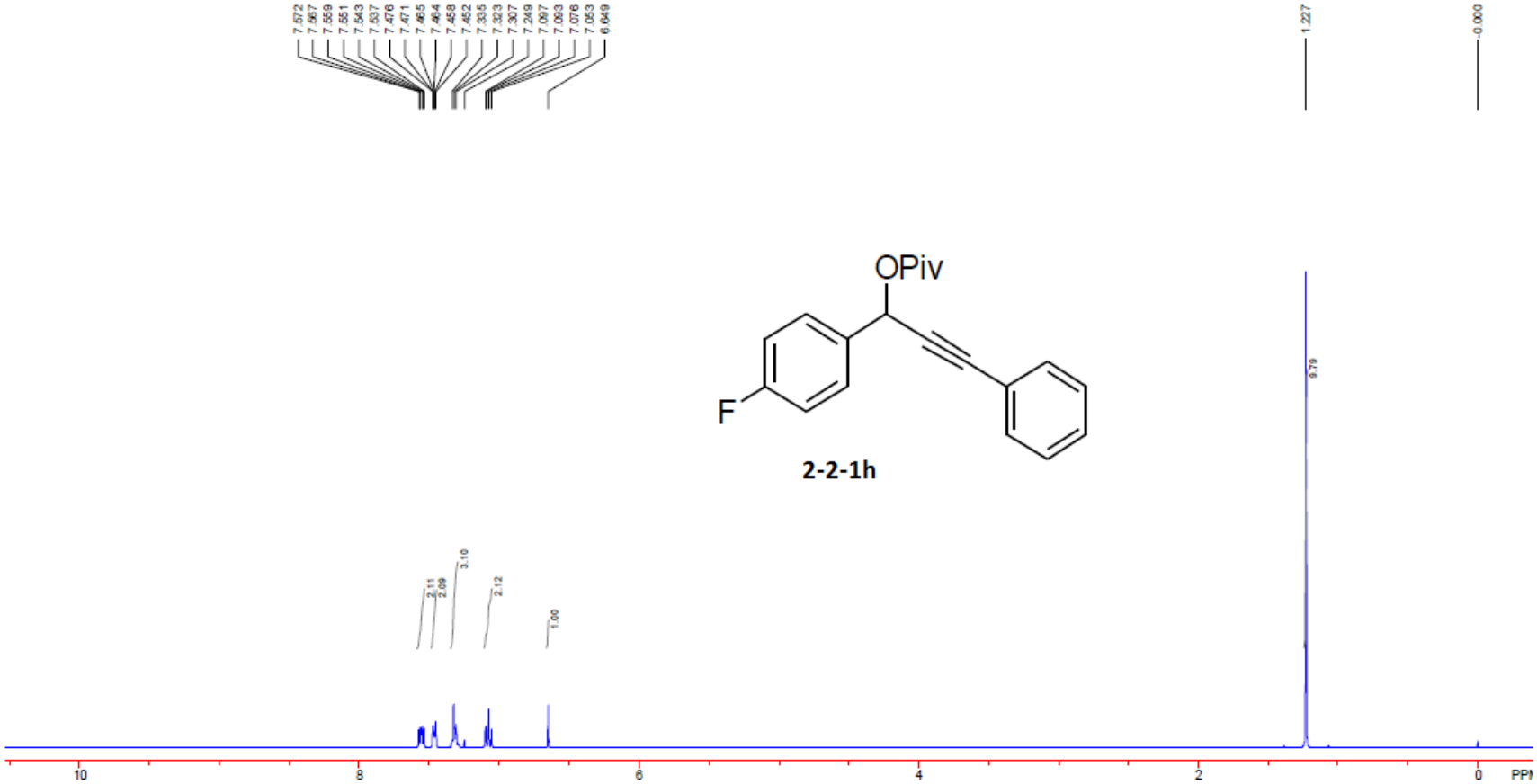

177.294
151.645
134.438
131.887
128.608
128.221
127.105
125.526
122.399
86.496
86.055
77.319
77.000
76.681
65.629
38.820
31.297
27.032
OPiv
tBu
2-2-1e
200
150
100
50
0
PPM

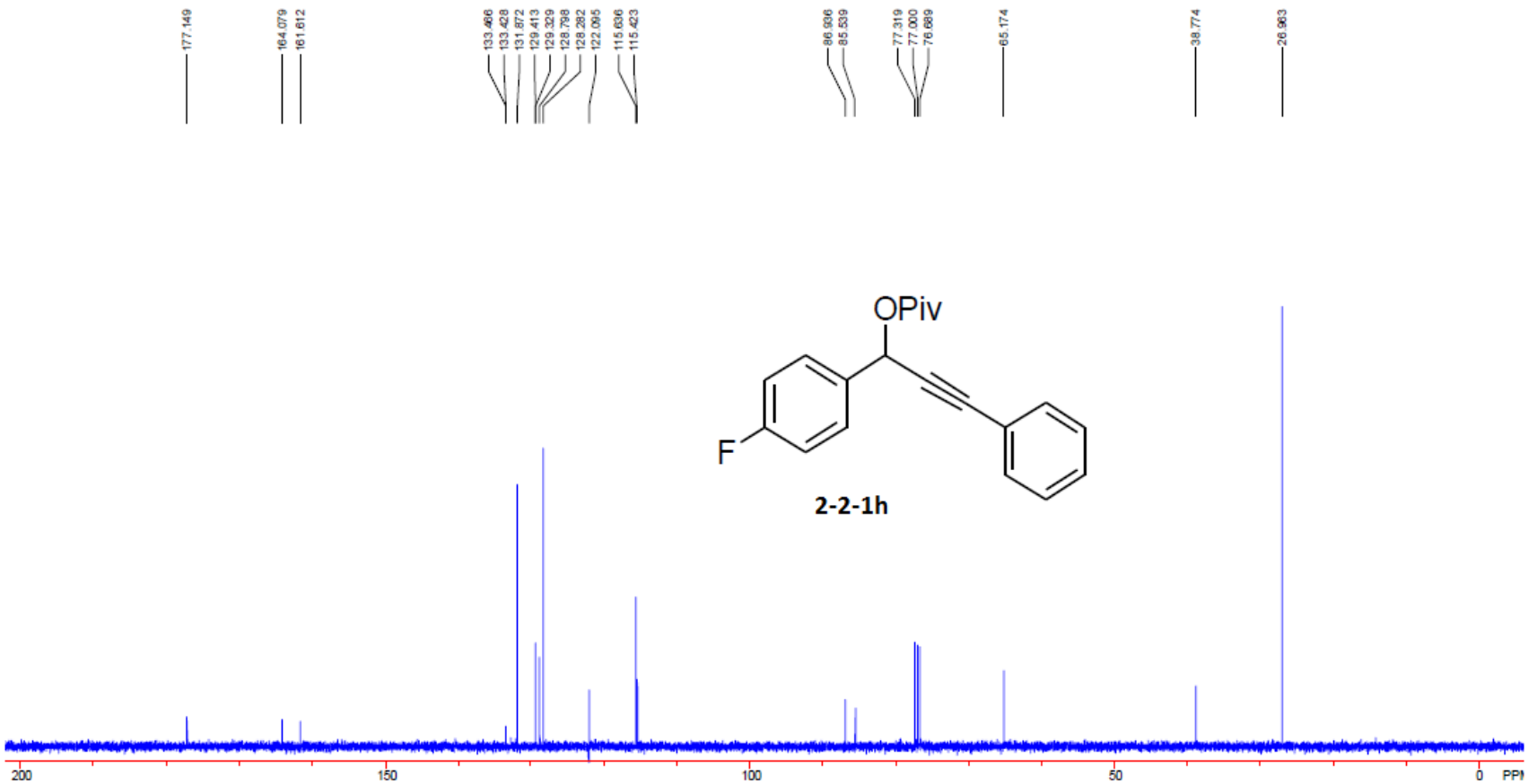

7.542
7.536
7.531
7.519
7.514
7.510
7.470
7.465
7.461
7.454
7.446
7.438
7.433
7.340
7.326
7.309
7.254
6.616
1.230
0.000
OPiv
Br
Ph
2-2-1f
4.27
2.14
3.15
1.00
10.29
10
8
6
4
2
0
PPM

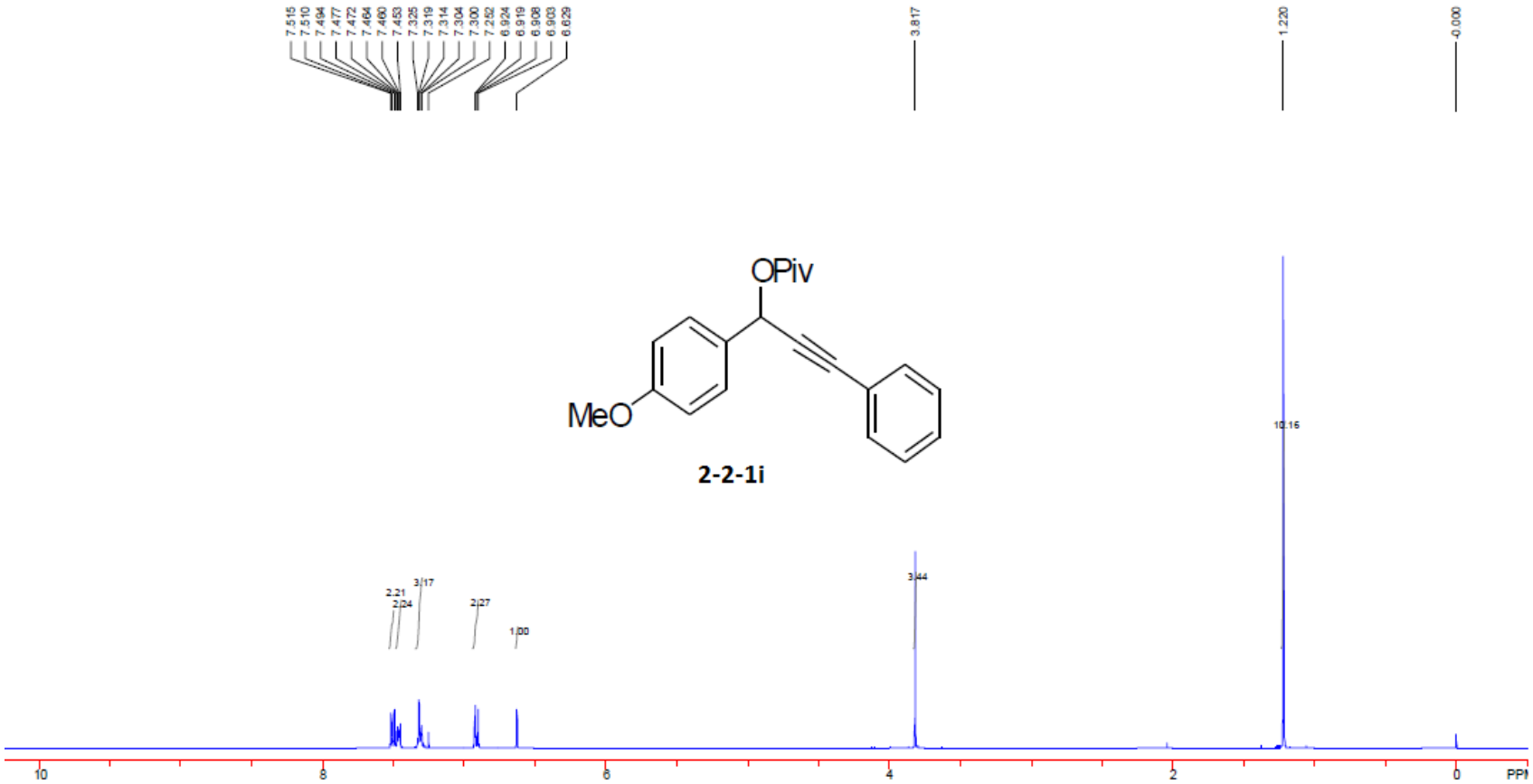

177.111
136.616
131.887
131.781
129.139
128.858
128.297
122.816
122.012
87.088
85.221
77.319
77.000
76.680
65.189
39.789
26.971
OPiv
Br
2-2-1f
200
150
100
50
0
PPM

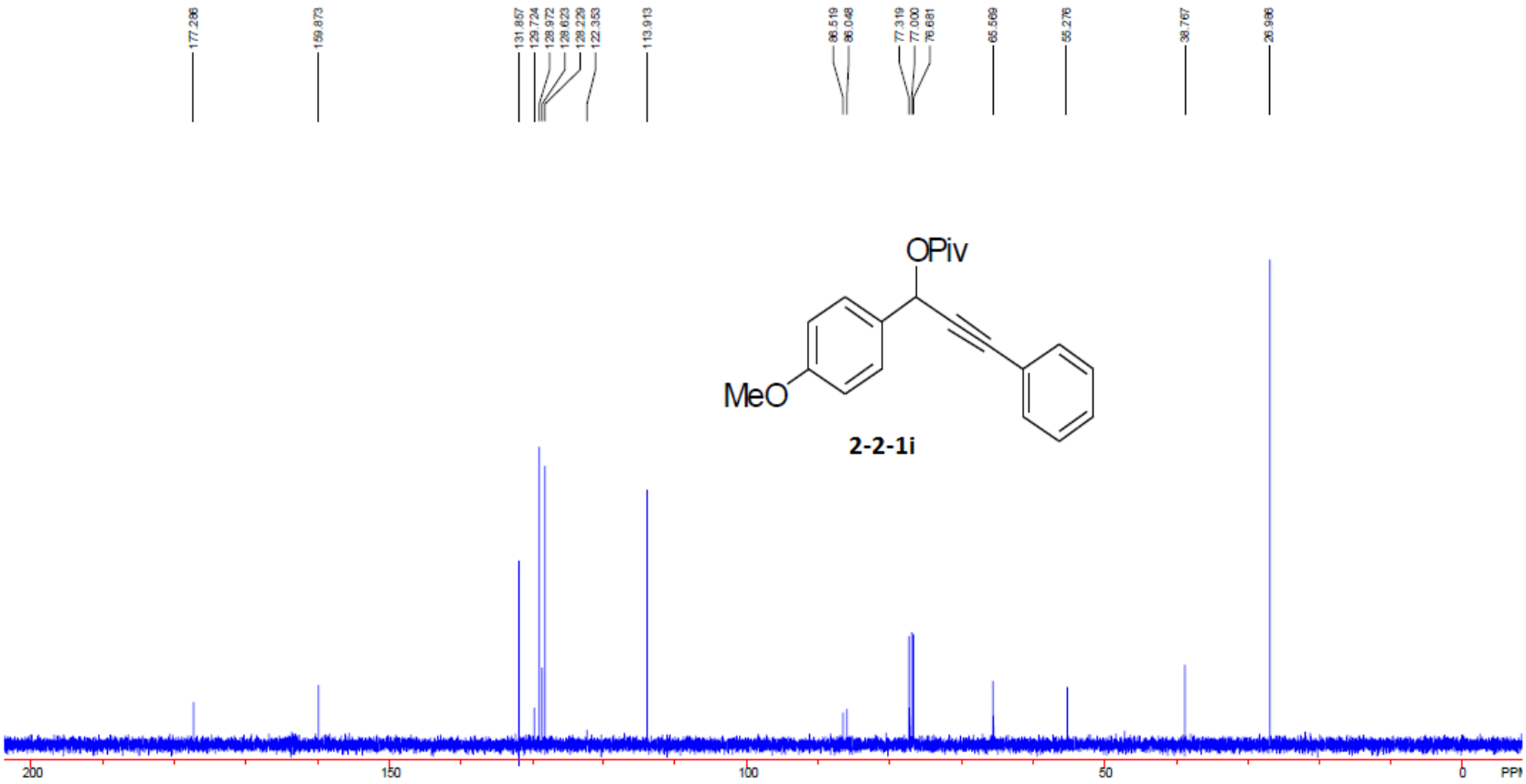

7.524
7.518
7.513
7.502
7.497
7.491
7.471
7.467
7.464
7.459
7.455
7.453
7.448
7.376
7.371
7.360
7.355
7.329
7.325
7.321
7.318
7.312
7.308
7.251
6.634
1.230
10.83
0.000
OPiv
Cl
2-2-1g
2.96
2.74
2.73
2.28
1.00
10
8
6
4
2
0
PPM

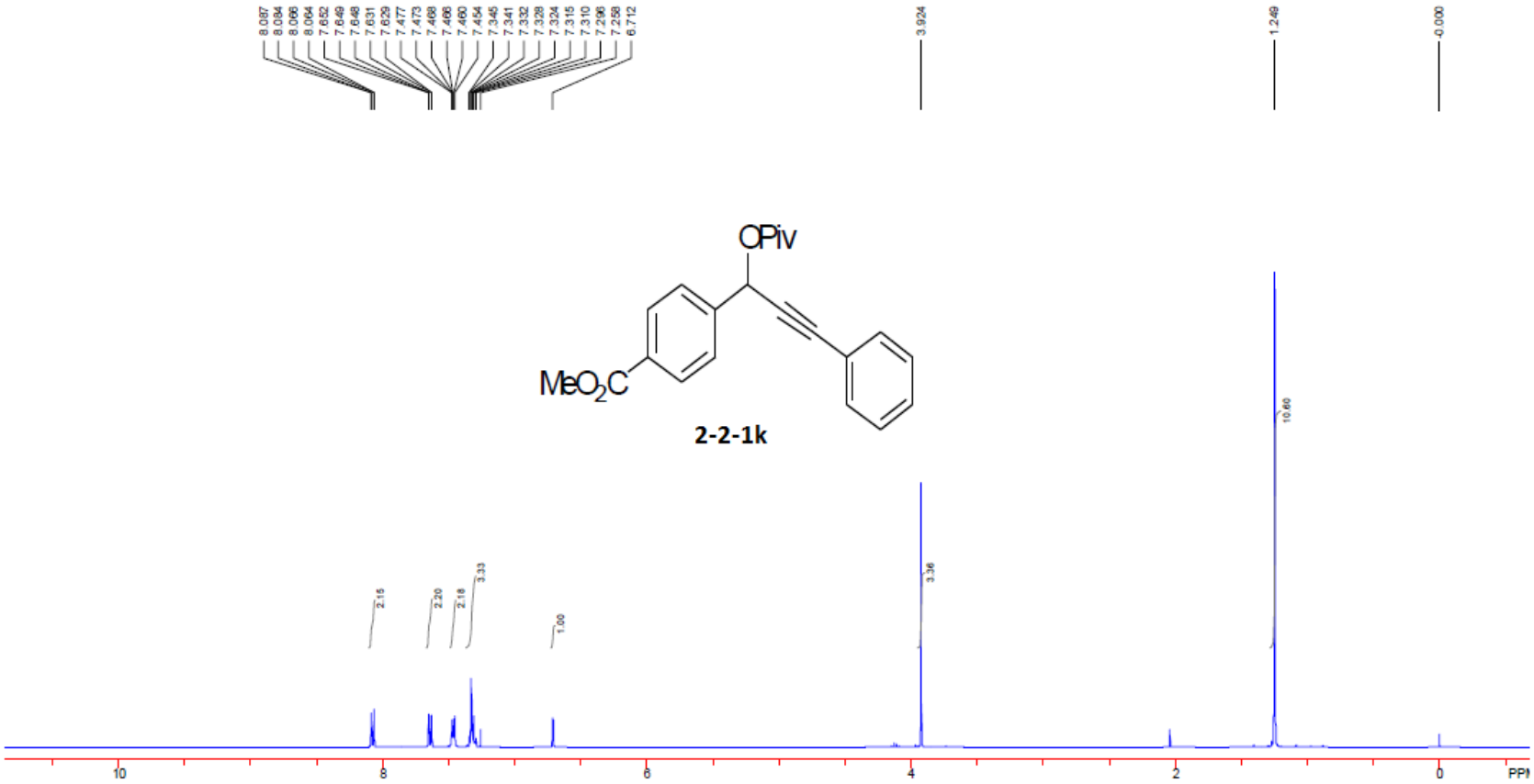

177.127
136.100
134.627
131.895
128.851
128.828
128.297
122.035
87.073
85.304
77.326
77.000
76.689
65.151
38.797
26.971
OPiv
Cl
2-2-1g
200
150
100
50
0 PPM

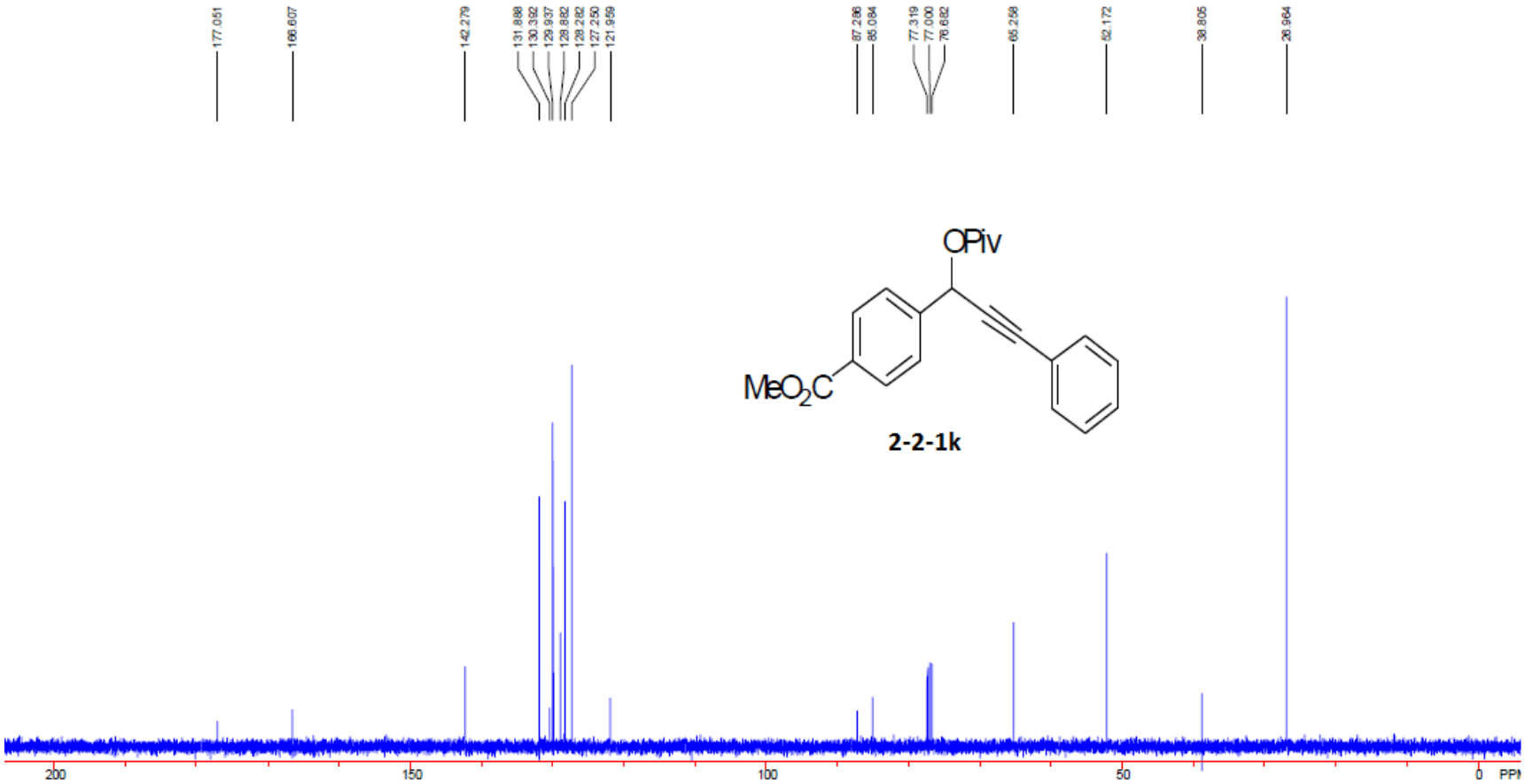

7.572
7.567
7.559
7.551
7.543
7.537
7.476
7.471
7.465
7.464
7.458
7.452
7.335
7.323
7.307
7.249
7.097
7.093
7.076
7.053
6.649
1.227
-0.000
OPiv
F
2-2-1h
9.79
2.11
2.09
3.10
2.12
1.00
10
8
6
4
2
0
PPM

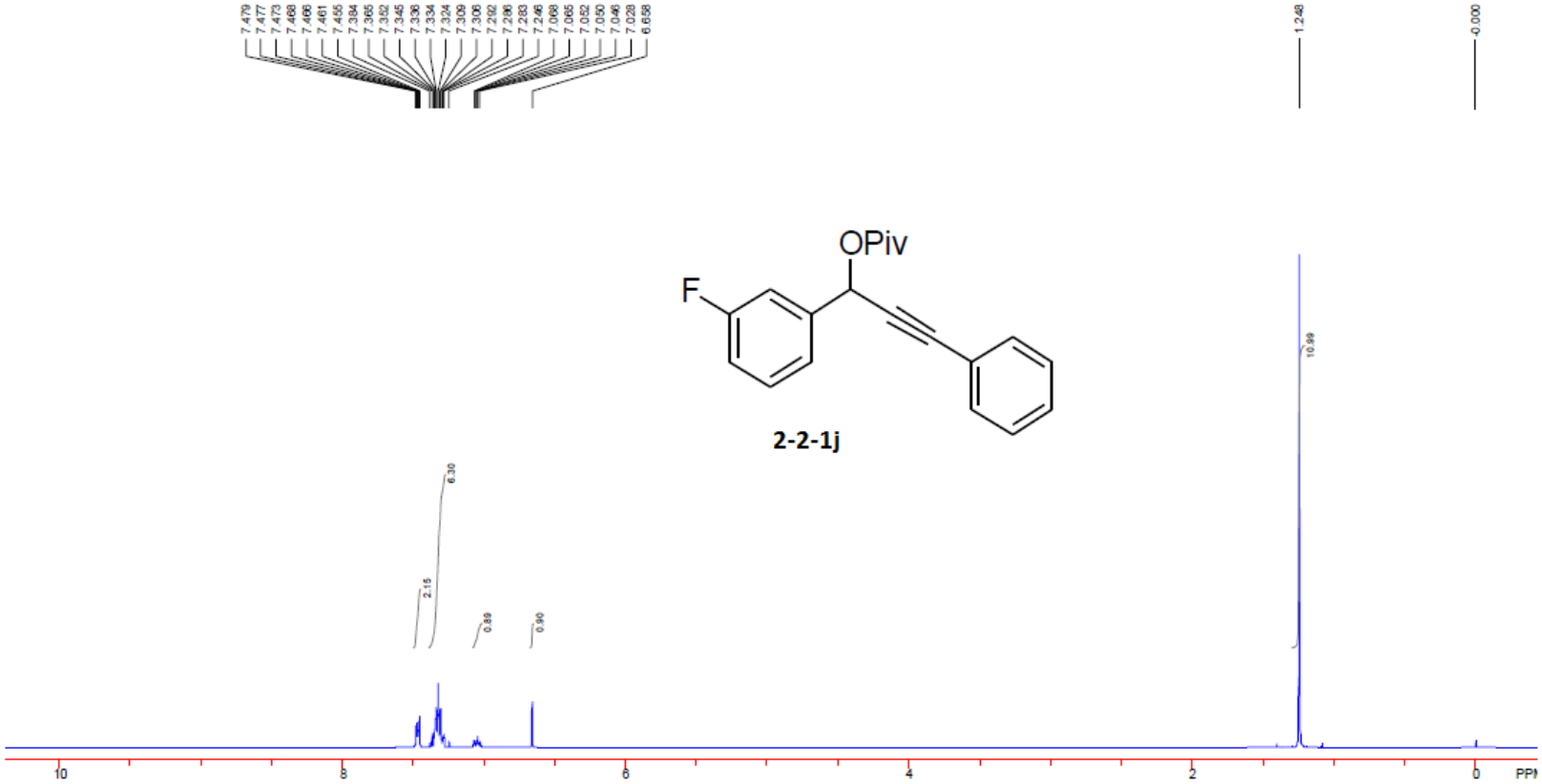

177.149
164.079
161.612
133.466
133.428
131.872
129.413
129.329
128.798
128.282
122.095
115.636
115.423
86.936
85.539
77.319
77.000
76.689
65.174
38.774
26.983
OPiv
F
2-2-1h
200
150
100
50
0
PPM

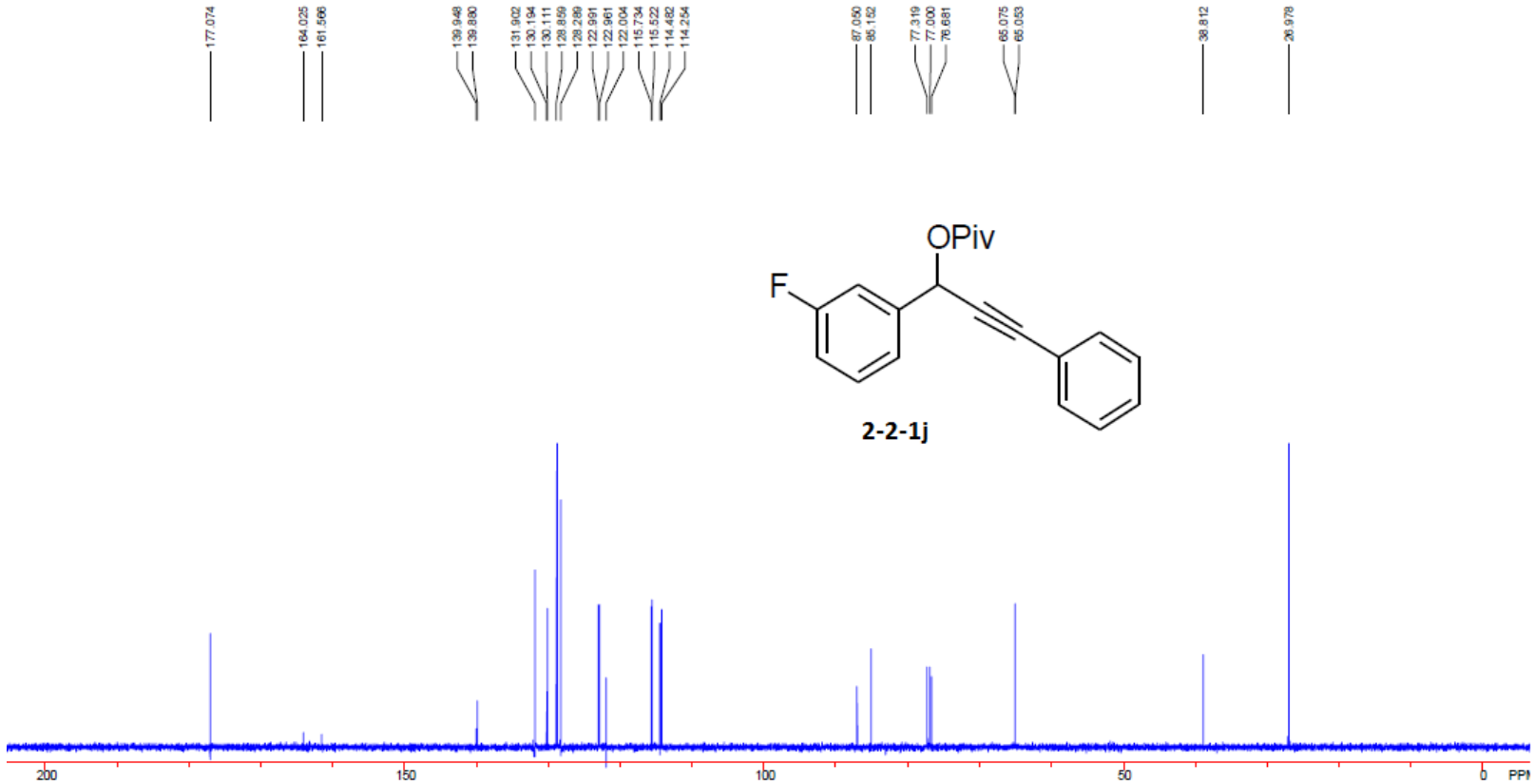

7.515
7.510
7.494
7.477
7.472
7.464
7.460
7.453
7.325
7.319
7.314
7.304
7.300
7.252
6.924
6.919
6.908
6.903
6.829
3.817
1.220
-0.000
OPiv
MeO
2-2-1i
10.15
3.44
2.21
2.24
3.17
2.27
1.00
10
8
6
4
2
0
PPM

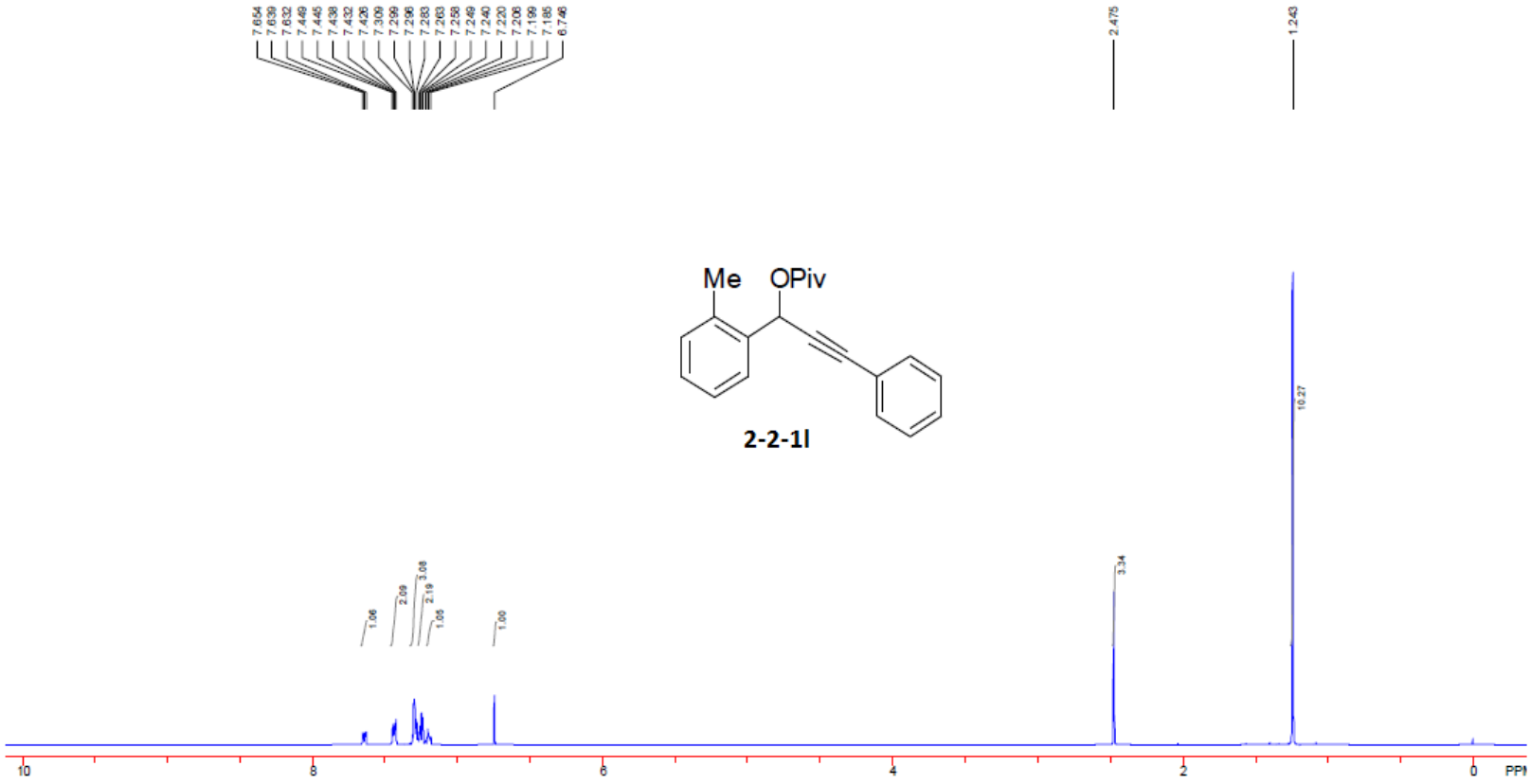

177.286
159.873
131.857
129.724
128.972
128.623
128.229
122.353
113.913
86.519
86.048
77.319
77.000
76.681
65.569
55.276
38.767
26.986
OPiv
MeO
2-2-1i
200
150
100
50
0
PPM

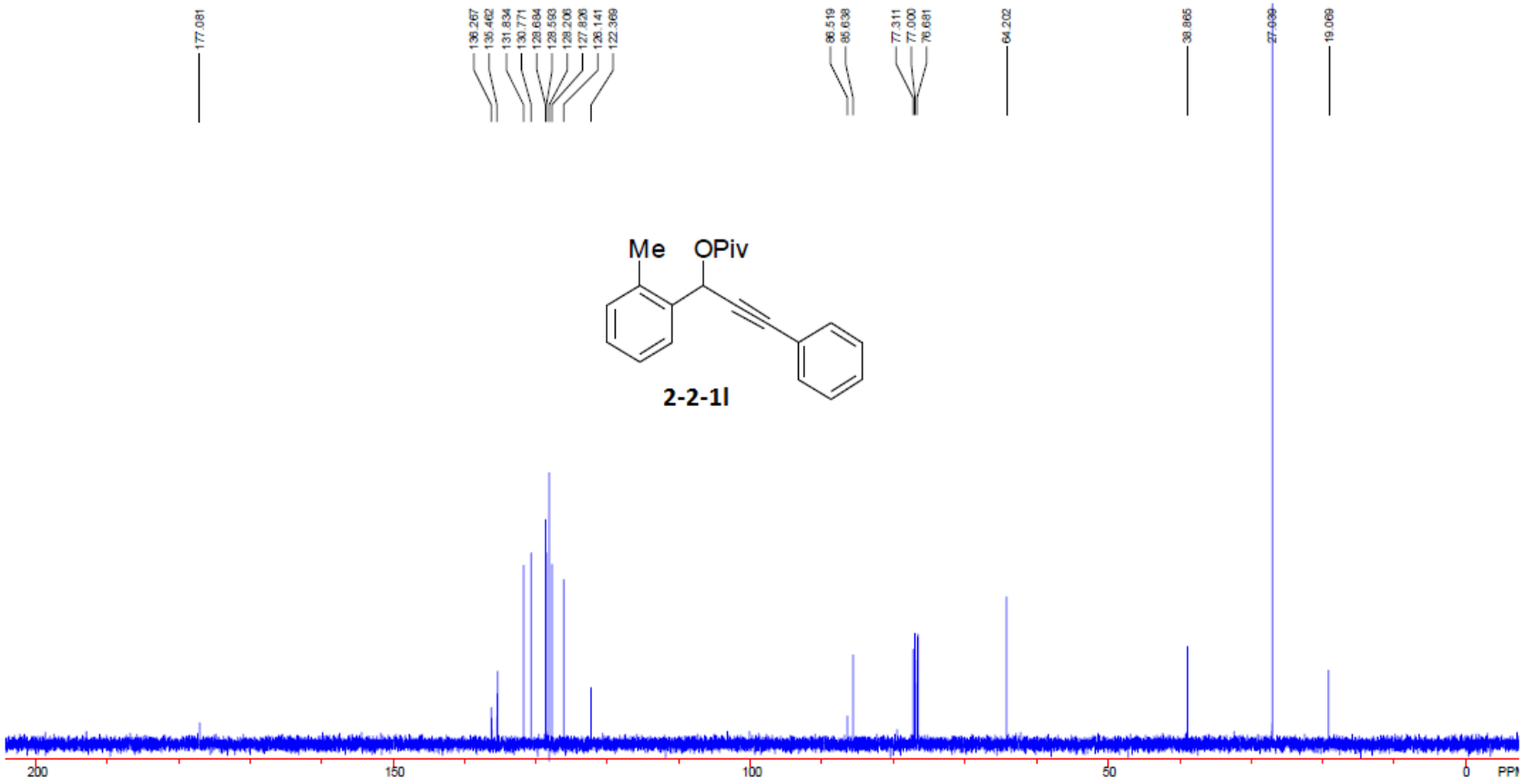

8.087
8.084
8.066
8.064
7.652
7.649
7.648
7.631
7.629
7.477
7.473
7.468
7.466
7.460
7.454
7.345
7.341
7.332
7.328
7.324
7.315
7.310
7.296
7.258
6.712
3.924
1.249
-0.000
OPiv
MeO2C
2-2-1k
2.15
2.20
2.18
3.33
1.00
3.36
10.60
10
8
6
4
2
0
PPM

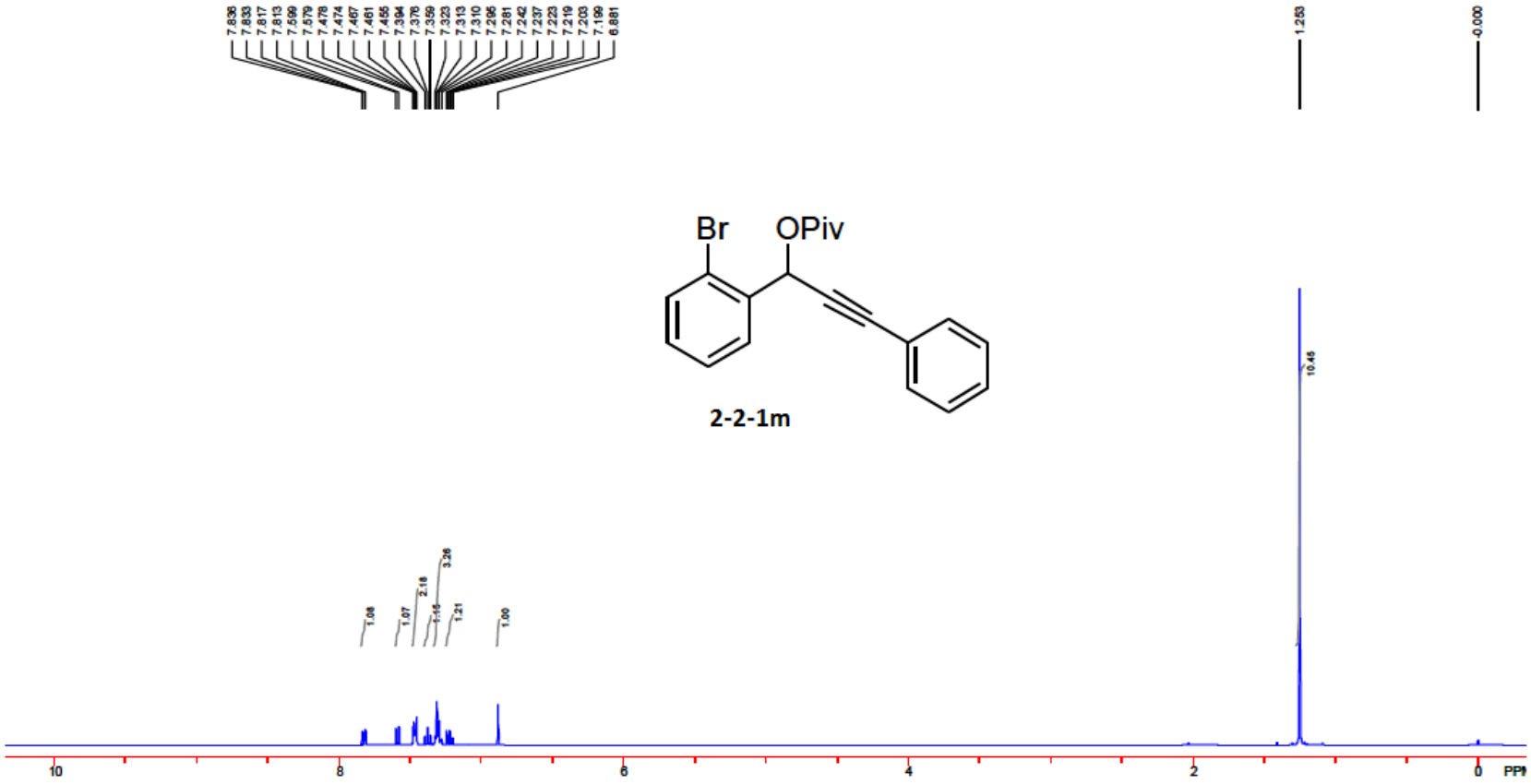

177.051
166.607
142.279
131.888
130.392
129.937
128.882
128.282
127.250
121.959
87.298
85.084
77.319
77.000
76.682
65.258
52.172
38.805
26.964
OPiv
MeO2C
2-2-1k
200
150
100
50
0
PPM

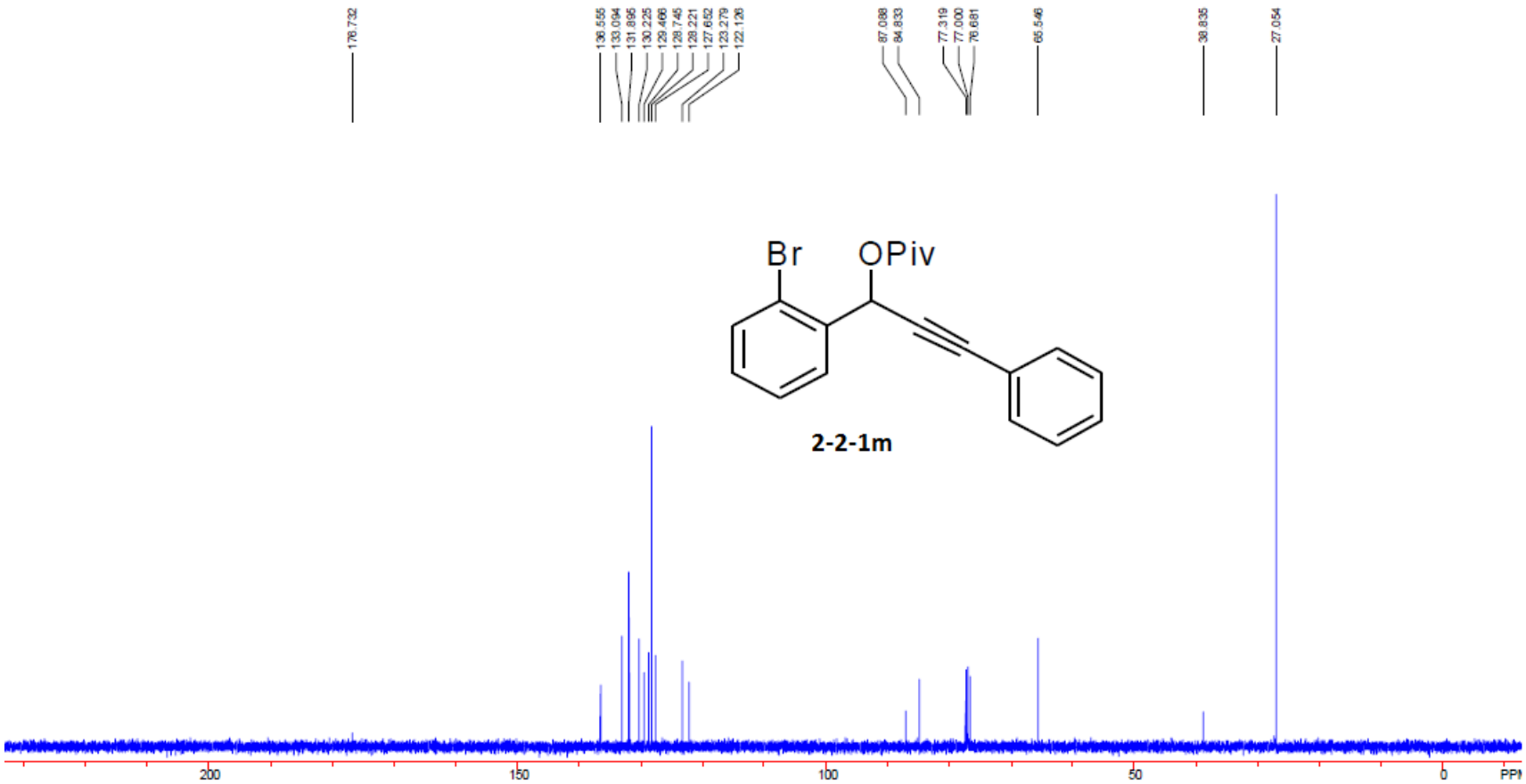

OPiv
F
2-2-1j
7.479
7.477
7.473
7.468
7.466
7.461
7.455
7.384
7.365
7.352
7.345
7.330
7.334
7.324
7.309
7.306
7.292
7.286
7.283
7.246
7.068
7.065
7.052
7.050
7.046
7.028
6.658
1.248
0.000
10.99
6.30
2.15
0.89
0.90
10
8
6
4
2
0
PPM

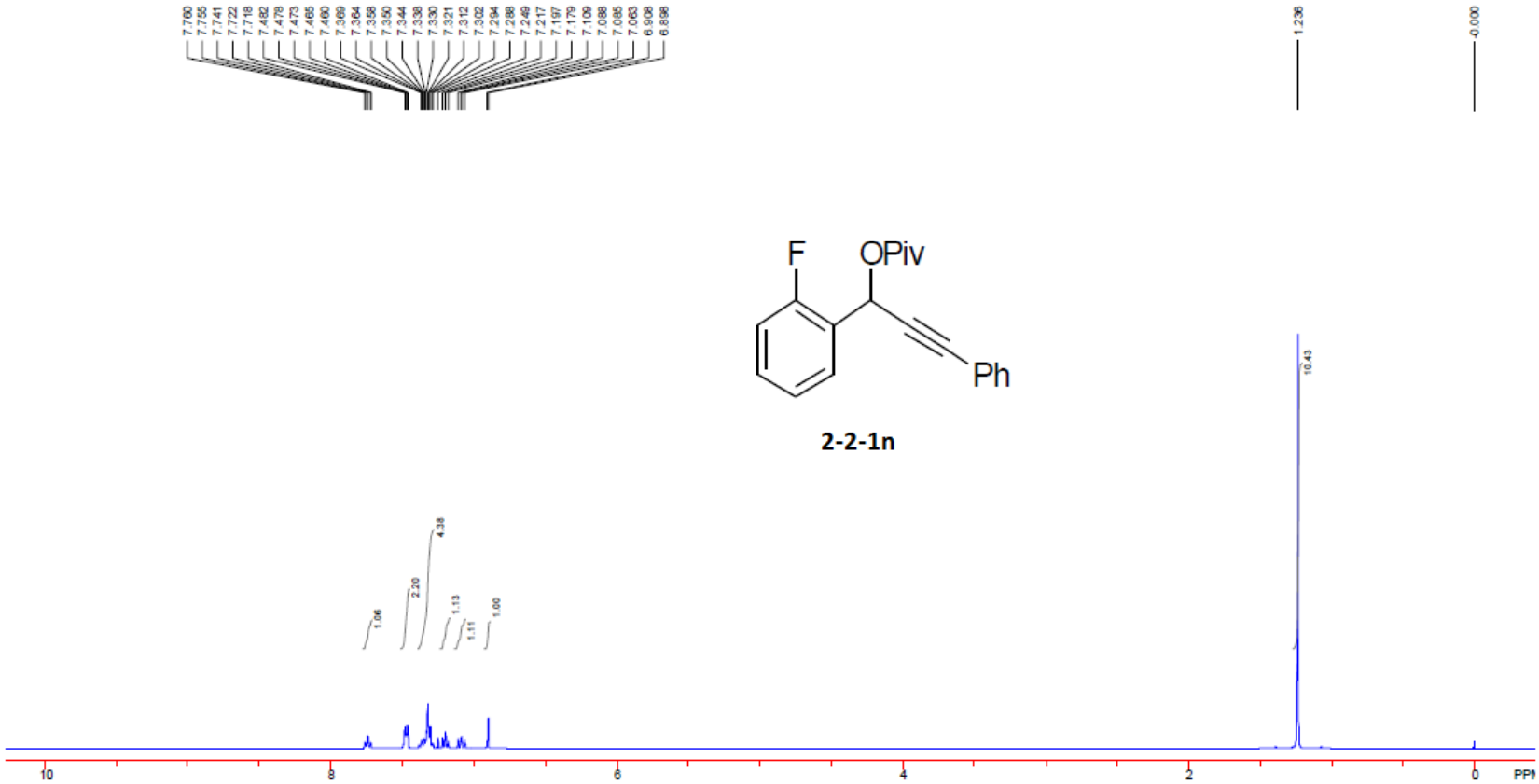

177.074
164.025
161.566
139.948
139.880
131.902
130.194
130.111
129.859
129.289
122.991
122.961
122.004
115.734
115.522
114.482
114.254
87.050
85.152
77.319
77.000
76.681
65.075
65.053
38.812
26.978
OPiv
F
2-2-1j
200
150
100
50
0
PPM

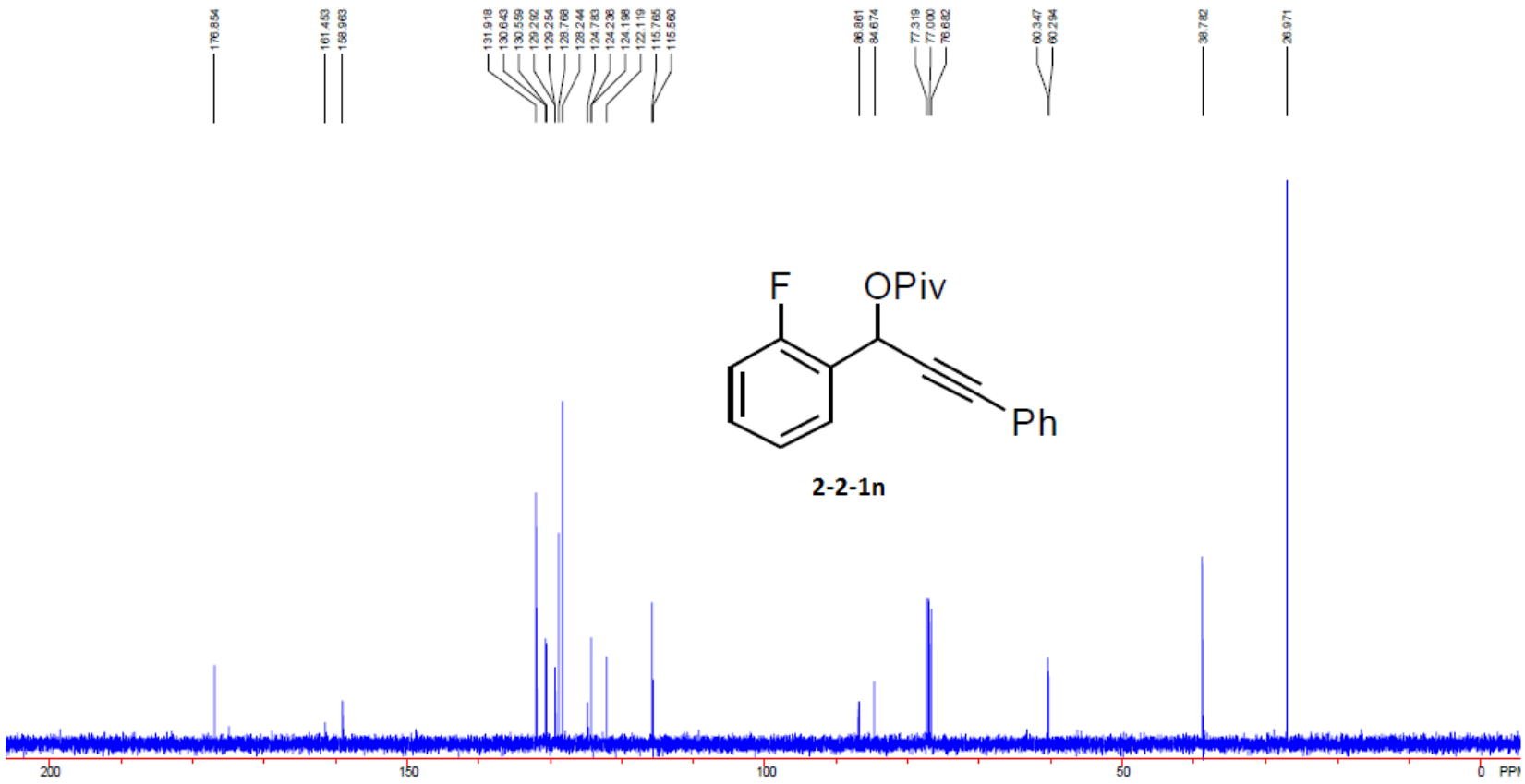

7.654
7.639
7.632
7.449
7.445
7.439
7.432
7.426
7.309
7.299
7.296
7.283
7.263
7.258
7.249
7.240
7.220
7.206
7.199
7.185
6.746
2.475
1.243
Me
OPiv
2-2-1l
1.06
2.09
3.08
2.19
1.06
1.00
3.34
10.27
10
8
6
4
2
0
PPM

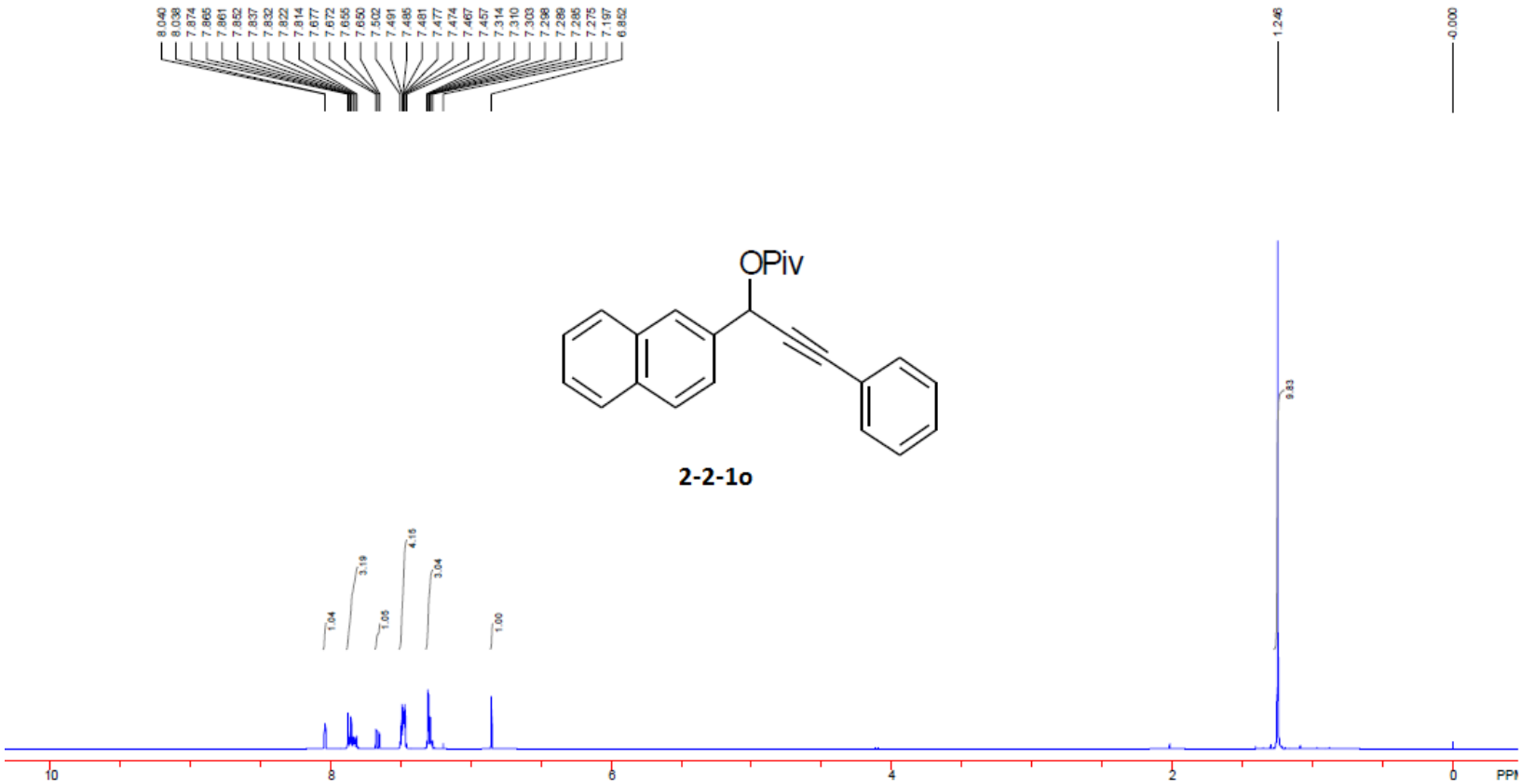

177.081
136.267
135.462
131.834
130.771
128.694
128.593
128.206
127.826
126.141
122.369
86.519
85.638
77.311
77.000
76.681
64.202
38.865
27.039
19.069
Me
OPiv
2-2-1l
200
150
100
50
0
PPM

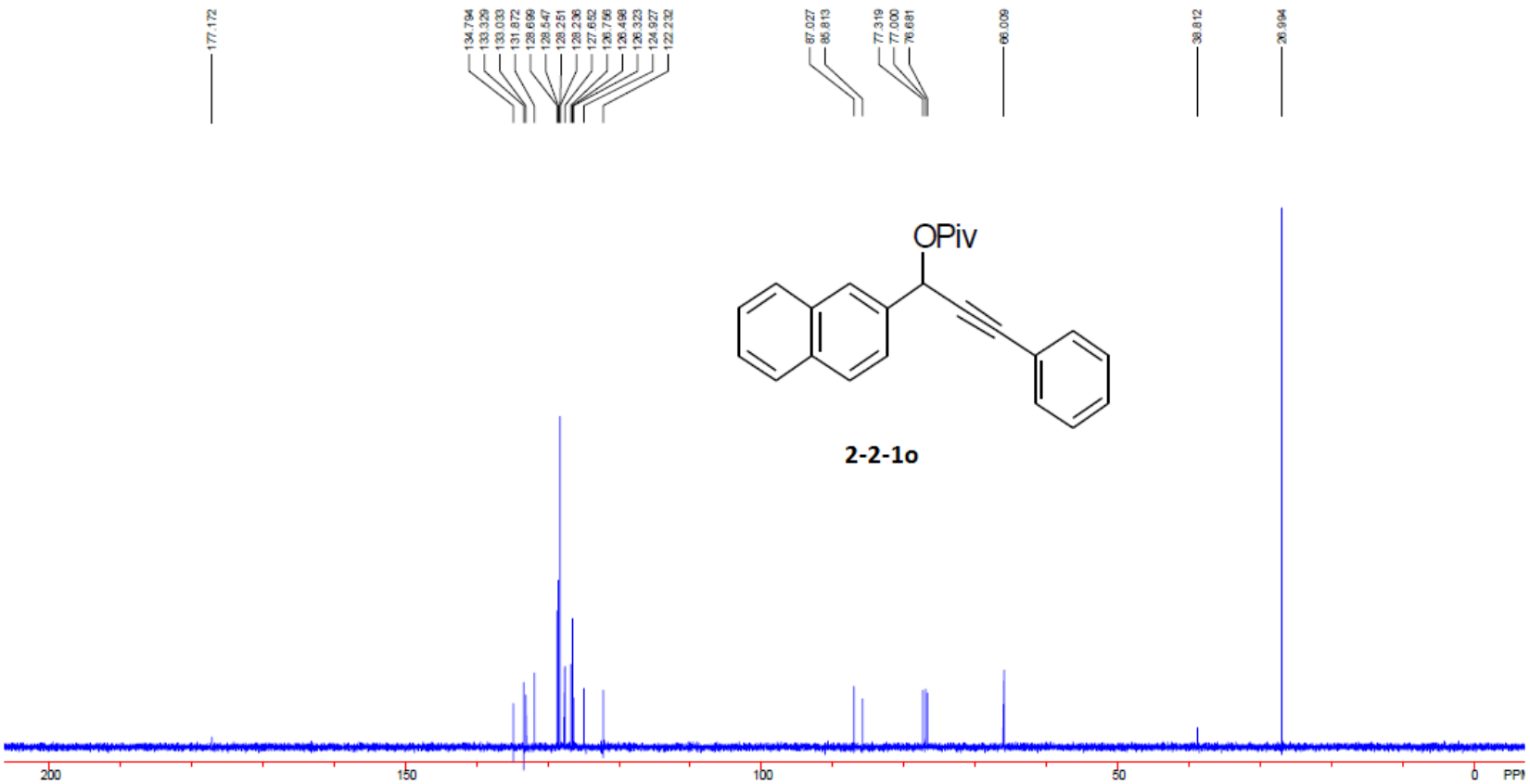

7.836
7.833
7.817
7.813
7.590
7.579
7.478
7.474
7.467
7.461
7.456
7.394
7.376
7.359
7.323
7.313
7.310
7.295
7.281
7.242
7.237
7.223
7.219
7.203
7.199
6.881
1.253
-0.000
Br
OPiv
2-2-1m
10.45
1.08
1.07
2.16
1.16
3.26
1.21
1.00
10
8
6
4
2
0
PPM

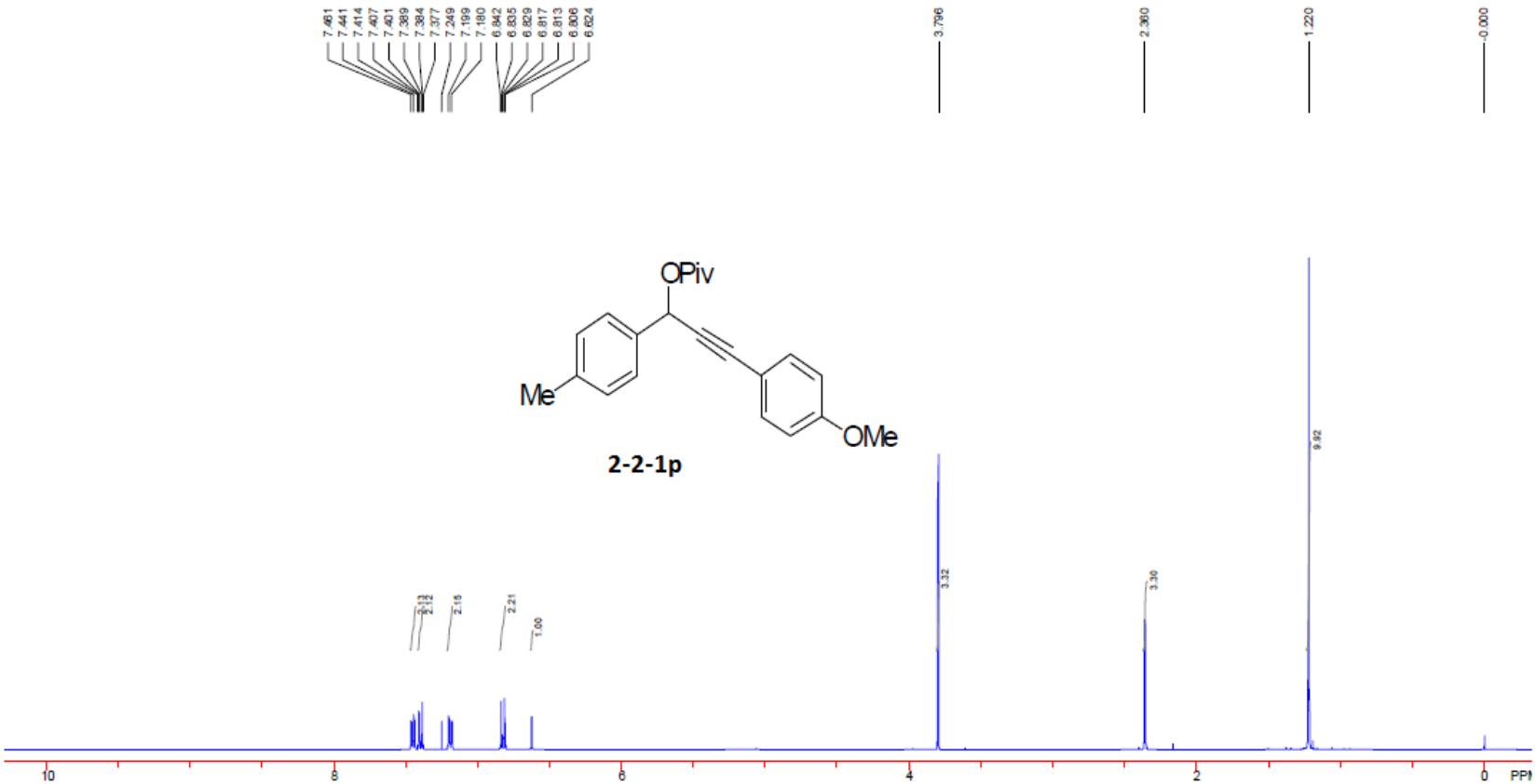

176.732
136.555
133.094
131.895
130.225
129.466
128.745
128.221
127.652
123.279
122.126
87.088
84.833
77.319
77.000
76.681
66.546
38.835
27.054
Br
OPiv
2-2-1m
200
150
100
50
0
PPM

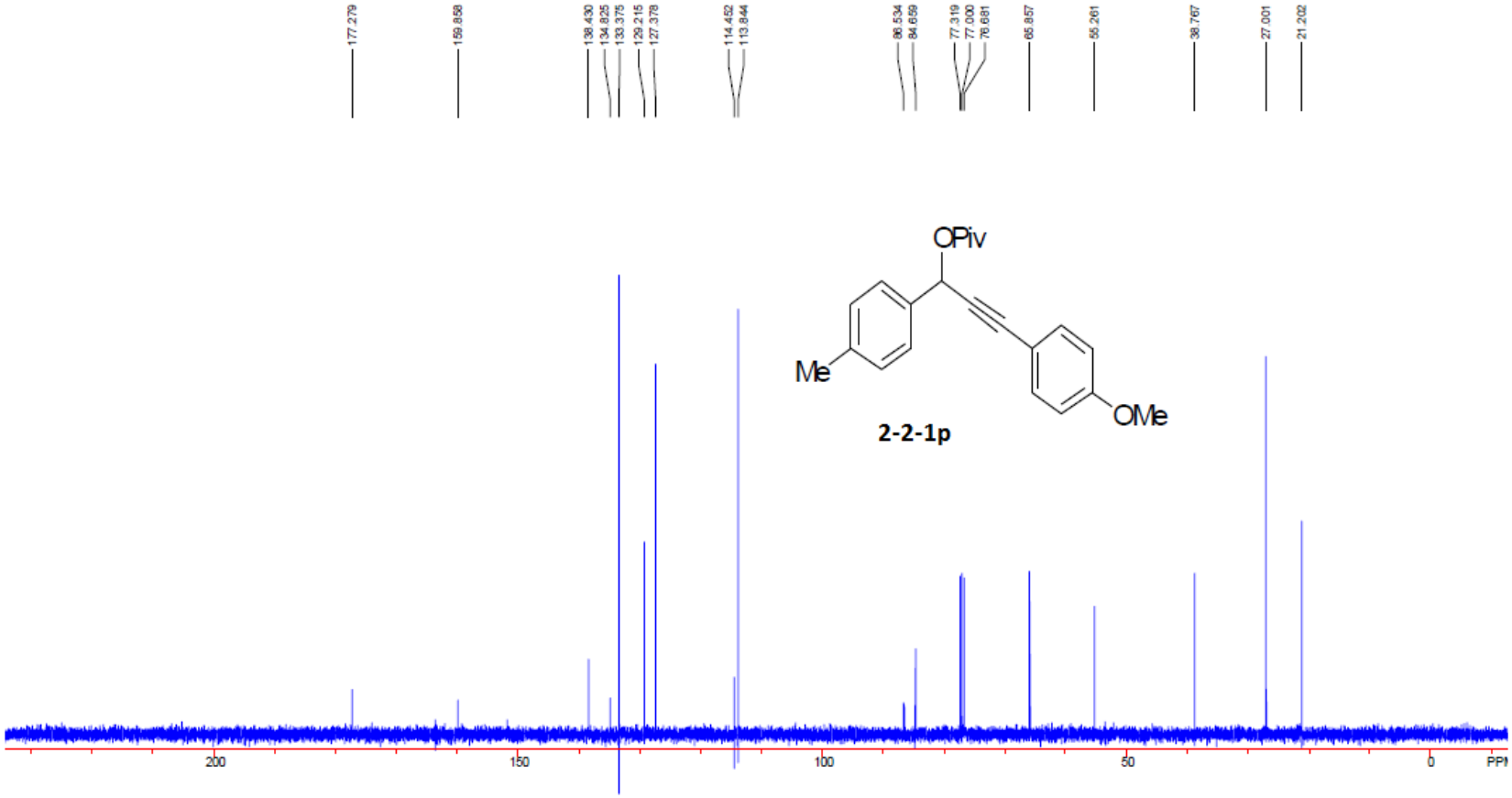

7.760
7.755
7.741
7.722
7.718
7.482
7.478
7.473
7.465
7.460
7.369
7.364
7.358
7.350
7.344
7.330
7.330
7.321
7.312
7.302
7.294
7.288
7.249
7.217
7.197
7.179
7.109
7.088
7.085
7.063
6.908
6.898
1.236
0.000
F
OPiv
Ph
2-2-1n
1.06
2.20
4.38
1.13
1.11
1.00
10.43
10
8
6
4
2
0
PPM

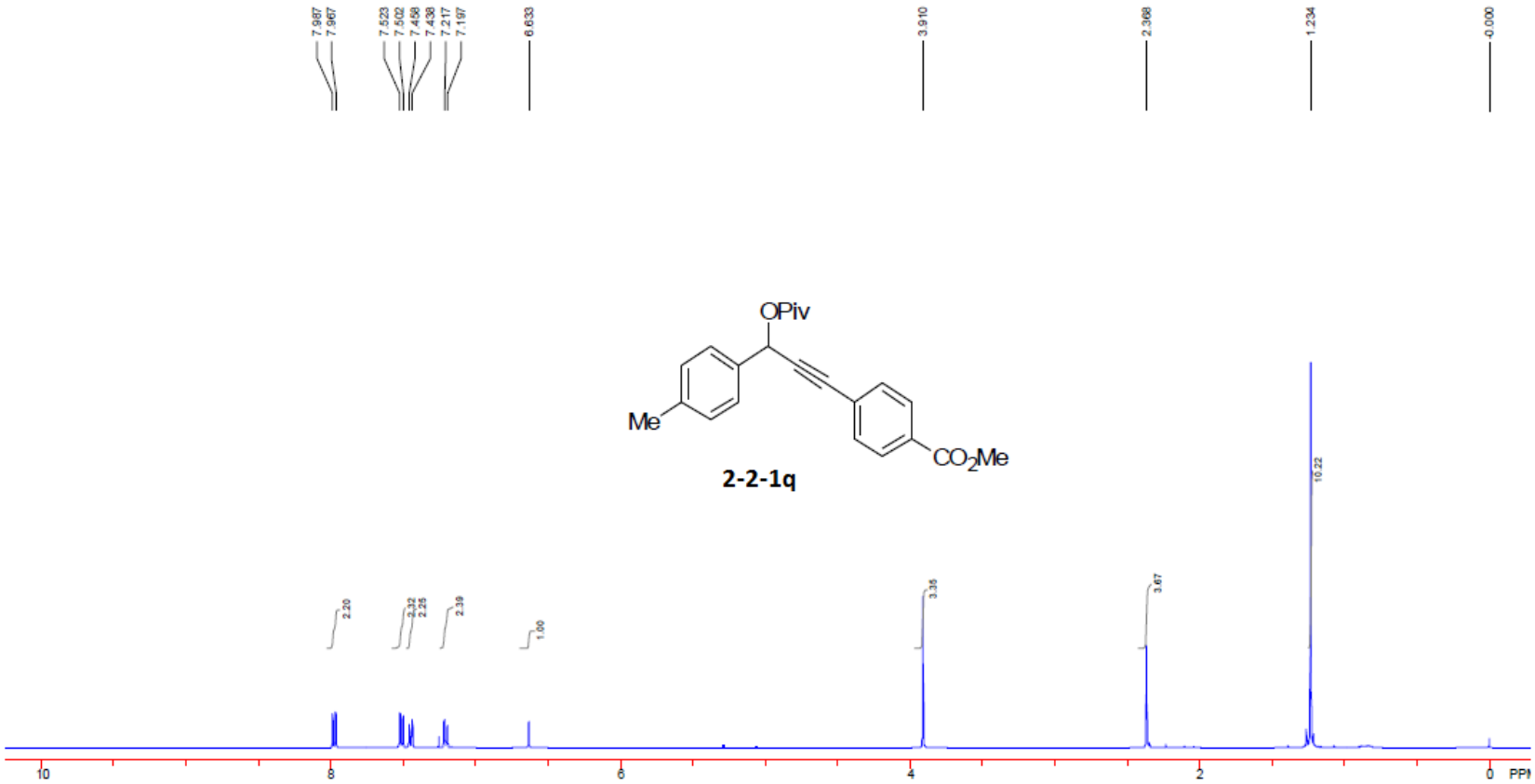

178.854
161.453
158.963
131.918
130.643
130.559
129.292
129.254
128.768
128.244
124.783
124.236
124.198
122.119
115.765
115.560
86.861
84.674
77.319
77.000
76.682
60.347
60.294
38.782
26.971
F
OPiv
Ph
2-2-1n
200
150
100
50
0
PPM

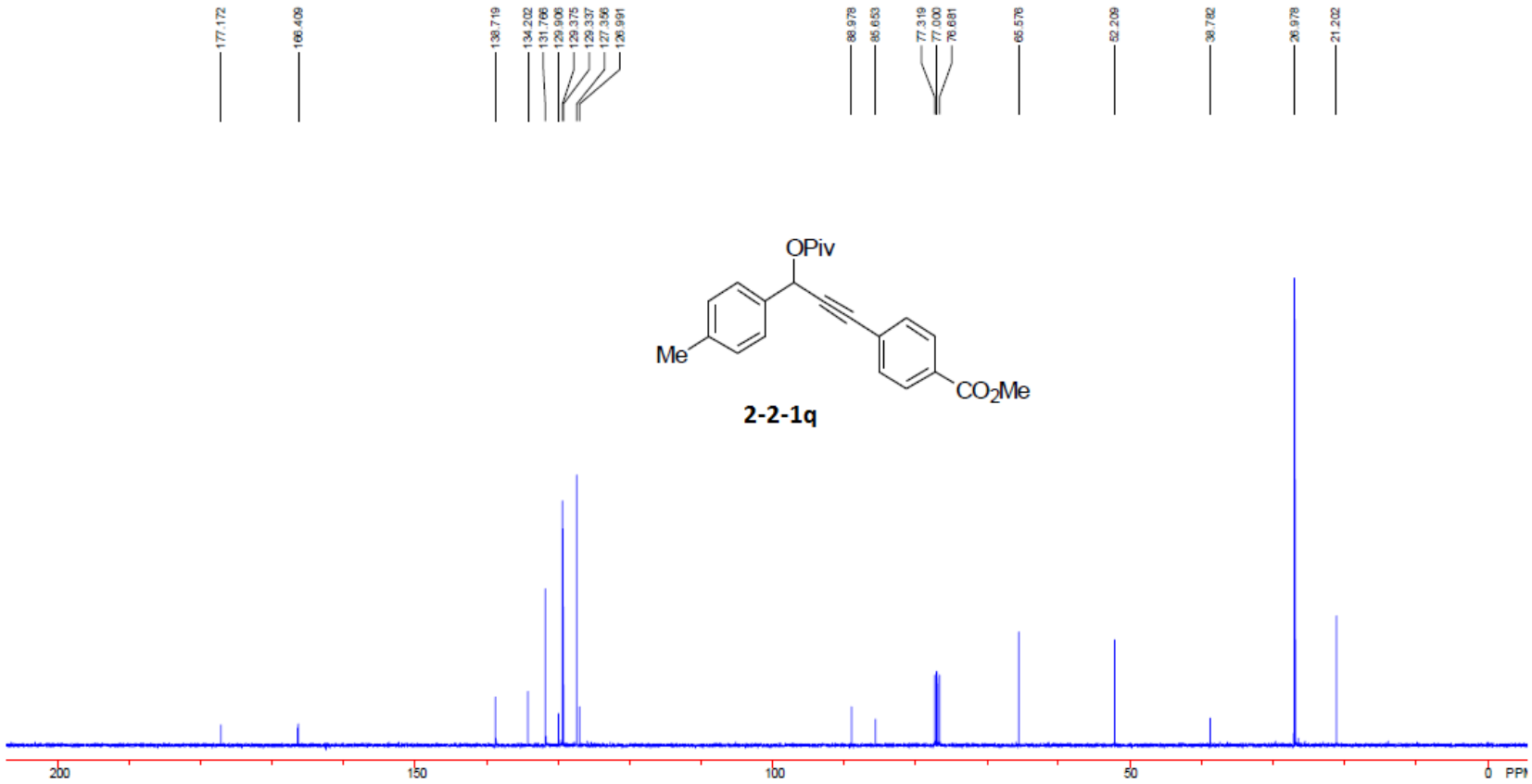

8.040
8.038
7.874
7.865
7.861
7.852
7.837
7.832
7.822
7.814
7.677
7.672
7.656
7.650
7.502
7.491
7.485
7.481
7.477
7.474
7.467
7.457
7.314
7.310
7.303
7.298
7.289
7.285
7.275
7.197
6.852
1.246
0.000
OPiv
2-2-1o
1.04
3.19
1.05
4.15
3.04
1.00
9.83
10
8
6
4
2
0
PPM

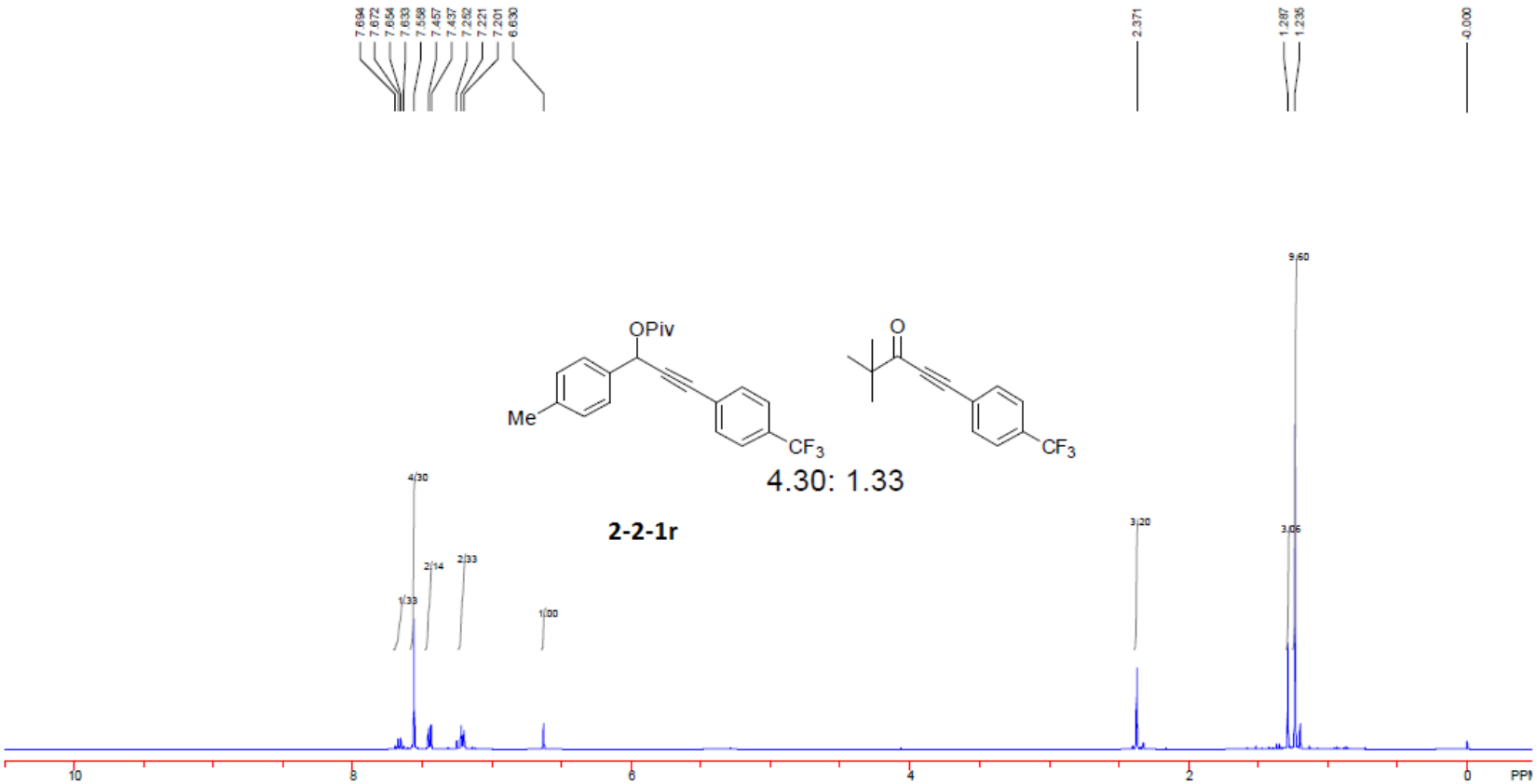

177.172
134.794
133.329
133.033
131.872
128.699
128.547
128.251
128.236
127.652
126.796
126.498
126.323
124.927
122.232
87.027
85.813
77.319
77.000
76.681
66.009
38.812
26.994
OPiv
2-2-1o
200
150
100
50
0
PPM

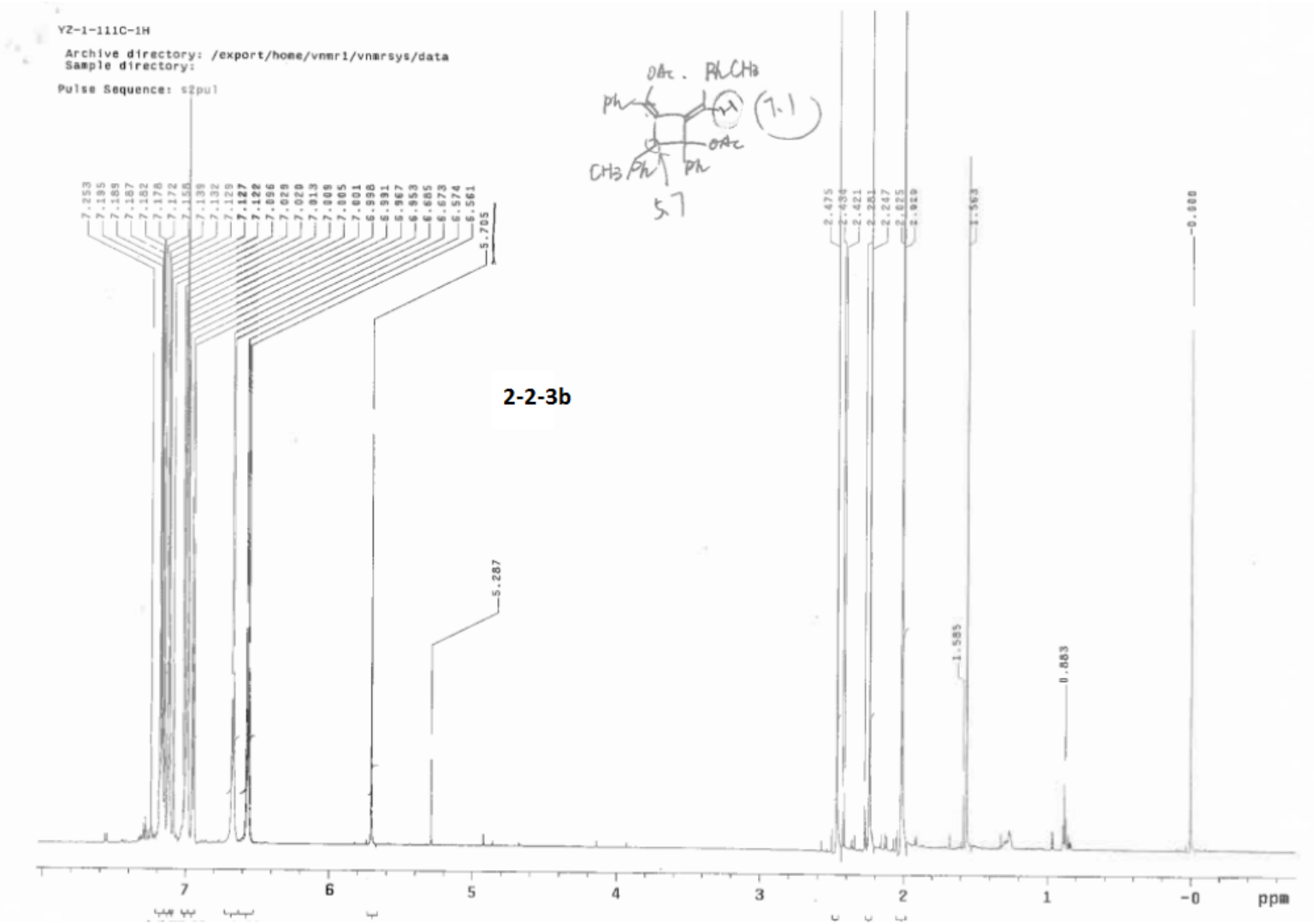

7.461
7.441
7.414
7.407
7.401
7.389
7.384
7.377
7.249
7.199
7.180
6.842
6.835
6.829
6.817
6.813
6.806
6.624
3.796
2.360
1.220
-0.000
OPiv
Me
OMe
2-2-1p
2.13
2.12
2.15
2.21
1.00
3.32
3.30
9.92
10
8
6
4
2
0
PPM


177.279
159.858
138.430
134.825
133.375
129.215
127.378
114.452
113.844
86.534
84.659
77.319
77.000
76.681
65.857
55.261
38.767
27.001
21.202
OPiv
Me
OMe
2-2-1p
200
150
100
50
0
PPM


7.987
7.967
7.523
7.502
7.458
7.438
7.217
7.197
6.633
3.910
2.368
1.234
0.000
OPiv
Me
CO2Me
2-2-1q
2.20
2.32
2.25
2.39
1.00
3.35
3.67
10.22
10
8
6
4
2
0
PPM

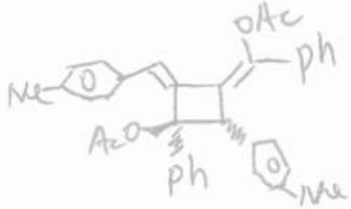

177.172
166.409
138.719
134.202
131.766
129.906
129.375
129.337
127.356
126.991
88.978
86.653
77.319
77.000
76.681
65.576
52.209
38.782
26.978
21.202
OPiv
Me
CO2Me
2-2-1q
200
150
100
50
0 PPM


7.694
7.672
7.654
7.633
7.558
7.457
7.437
7.252
7.221
7.201
6.630
2.371
1.287
1.235
0.000
OPiv
Me
CF3
O
CF3
4.30: 1.33
2-2-1r
9.60
4.30
3.20
3.06
2.14
2.33
1.33
1.00
10
8
6
4
2
0
PPM

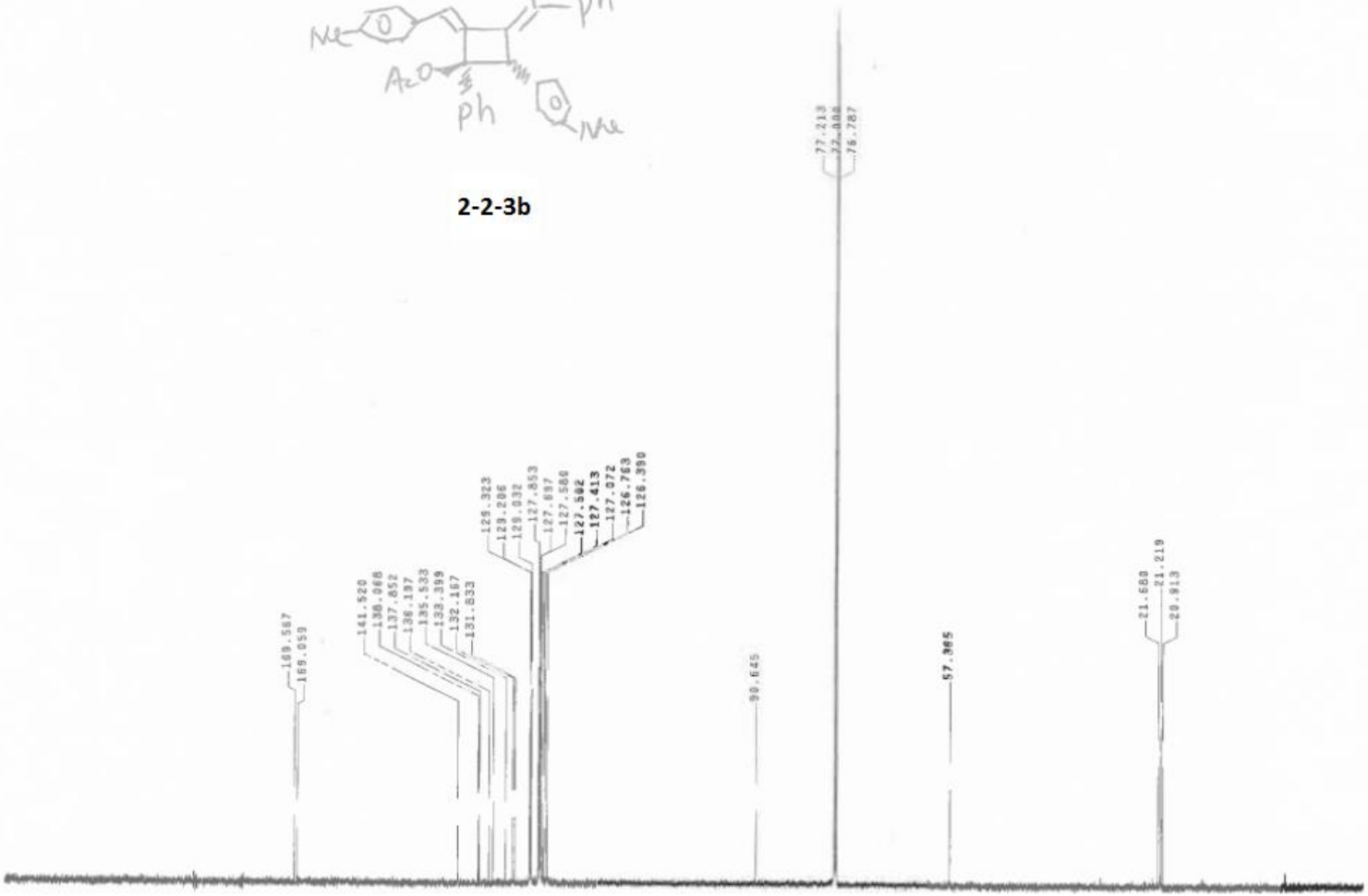

YZ-1-111C-1H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
2-2-3b
ppm

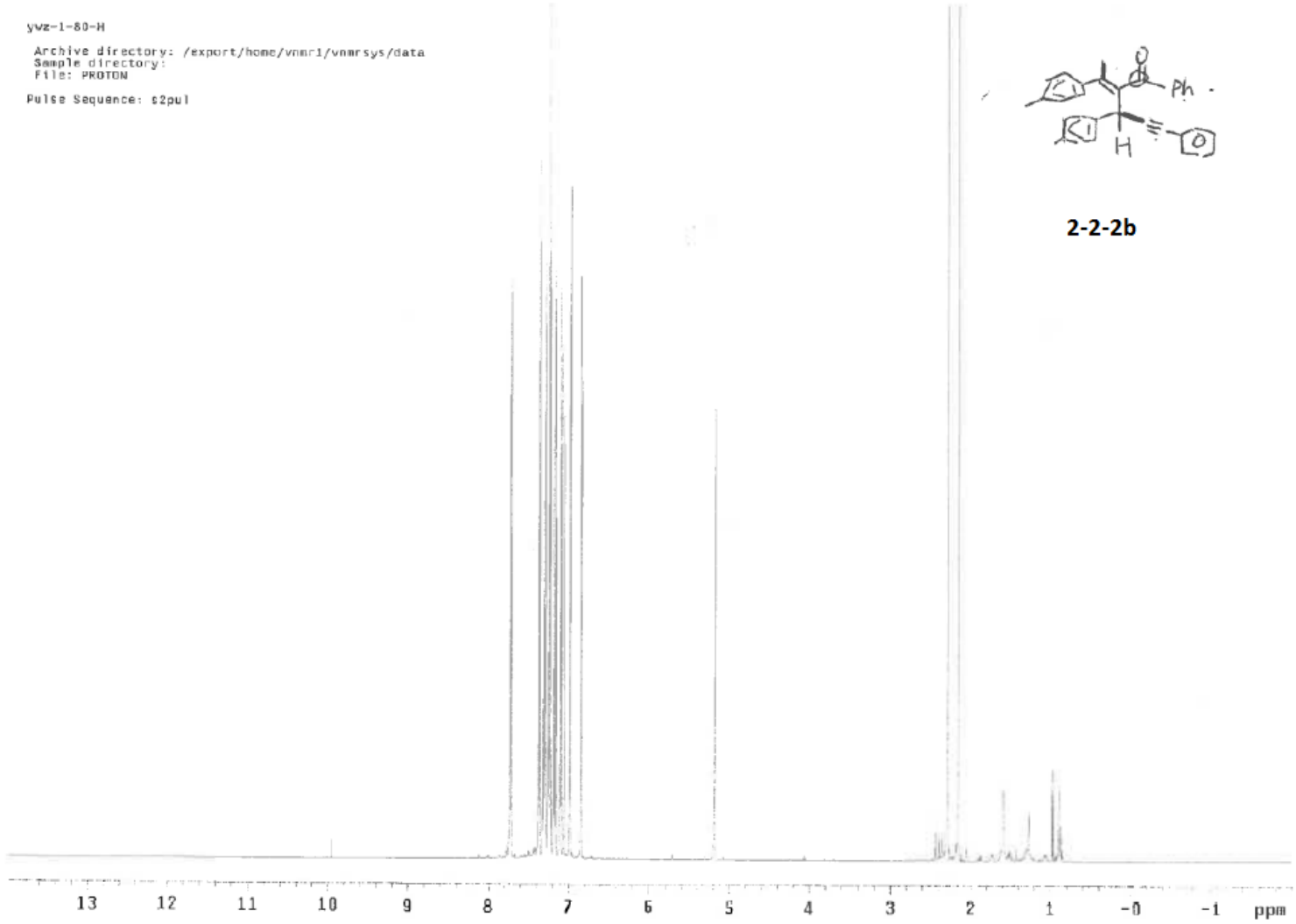
YZ-1-111C-13C

Pulse Sequence: s2pul



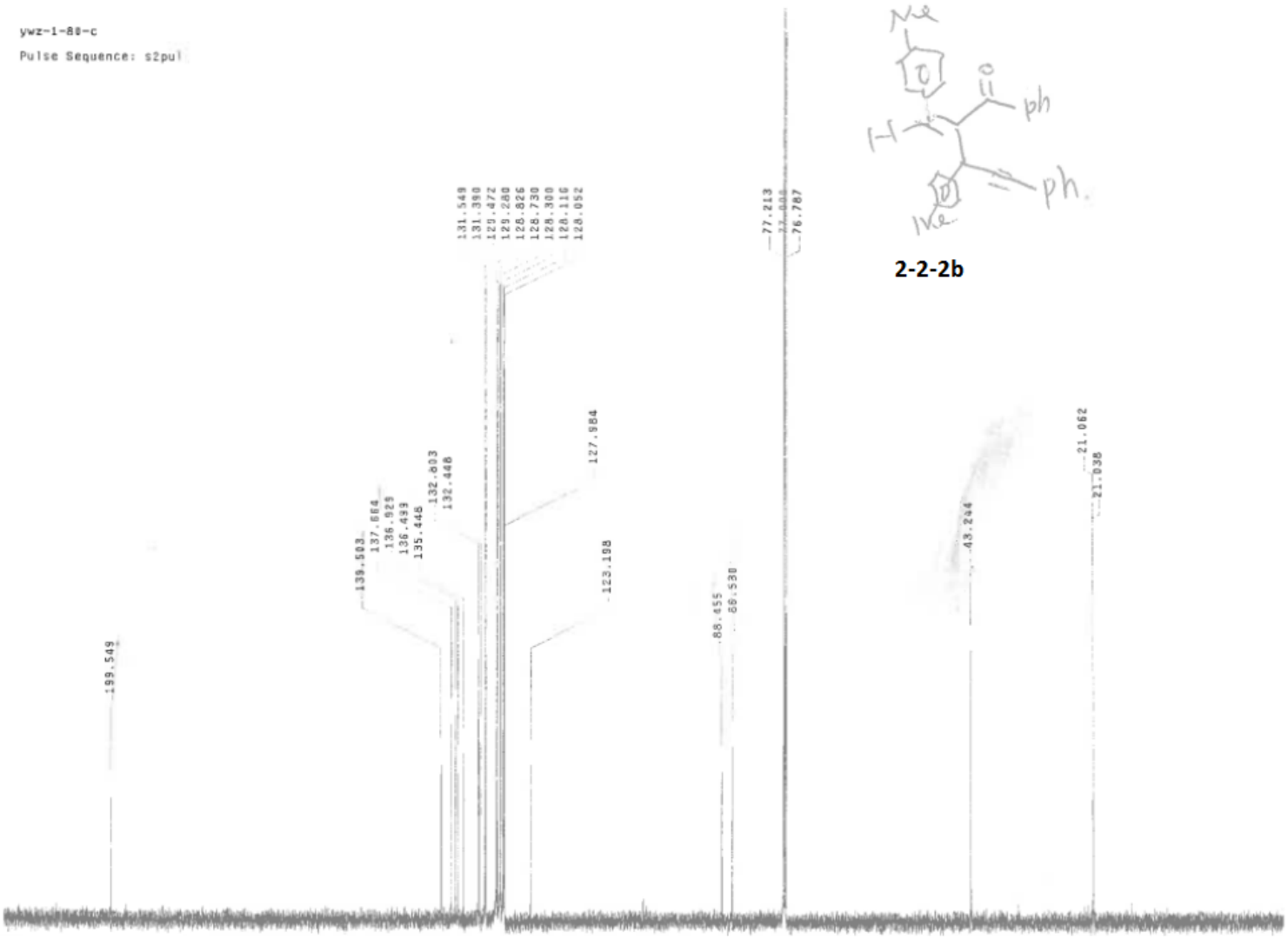
2-2-3b




yvz-1-80-H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
13
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

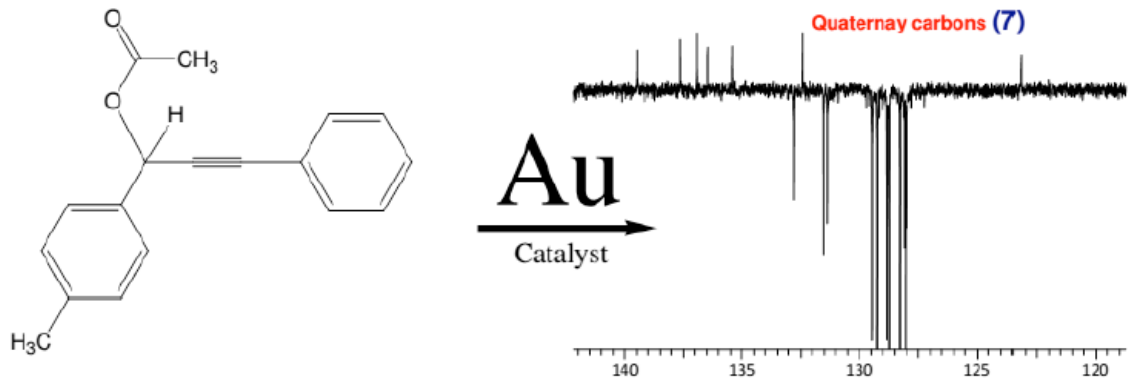
Ph
H

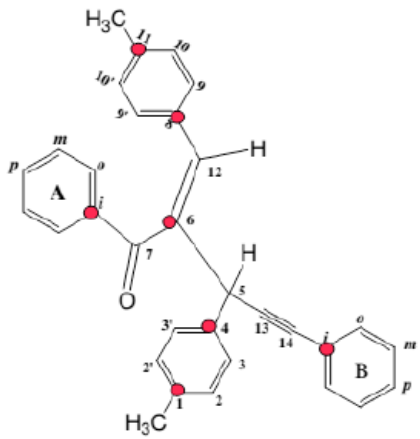
2-2-2b


ywz-1-80-c
Pulse Sequence: s2pul
199.549
139.503
137.664
136.929
136.499
135.448
132.803
132.448
131.548
131.380
129.472
129.280
128.826
128.730
128.300
128.116
128.052
127.984
123.198
88.455
80.530
77.213
77.000
76.787
43.244
21.062
21.038

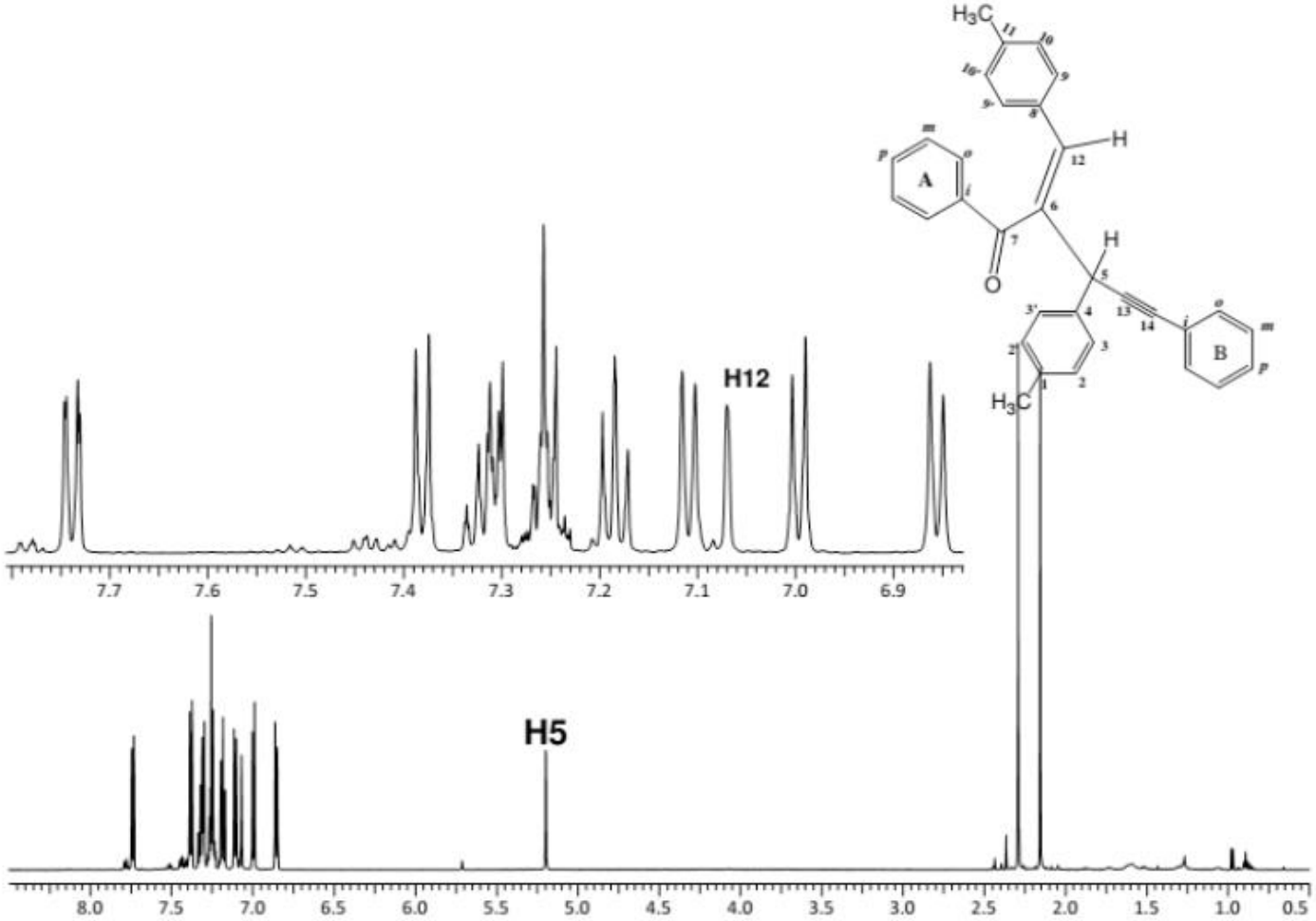
Me
O
ph
H
ph.
O
Me

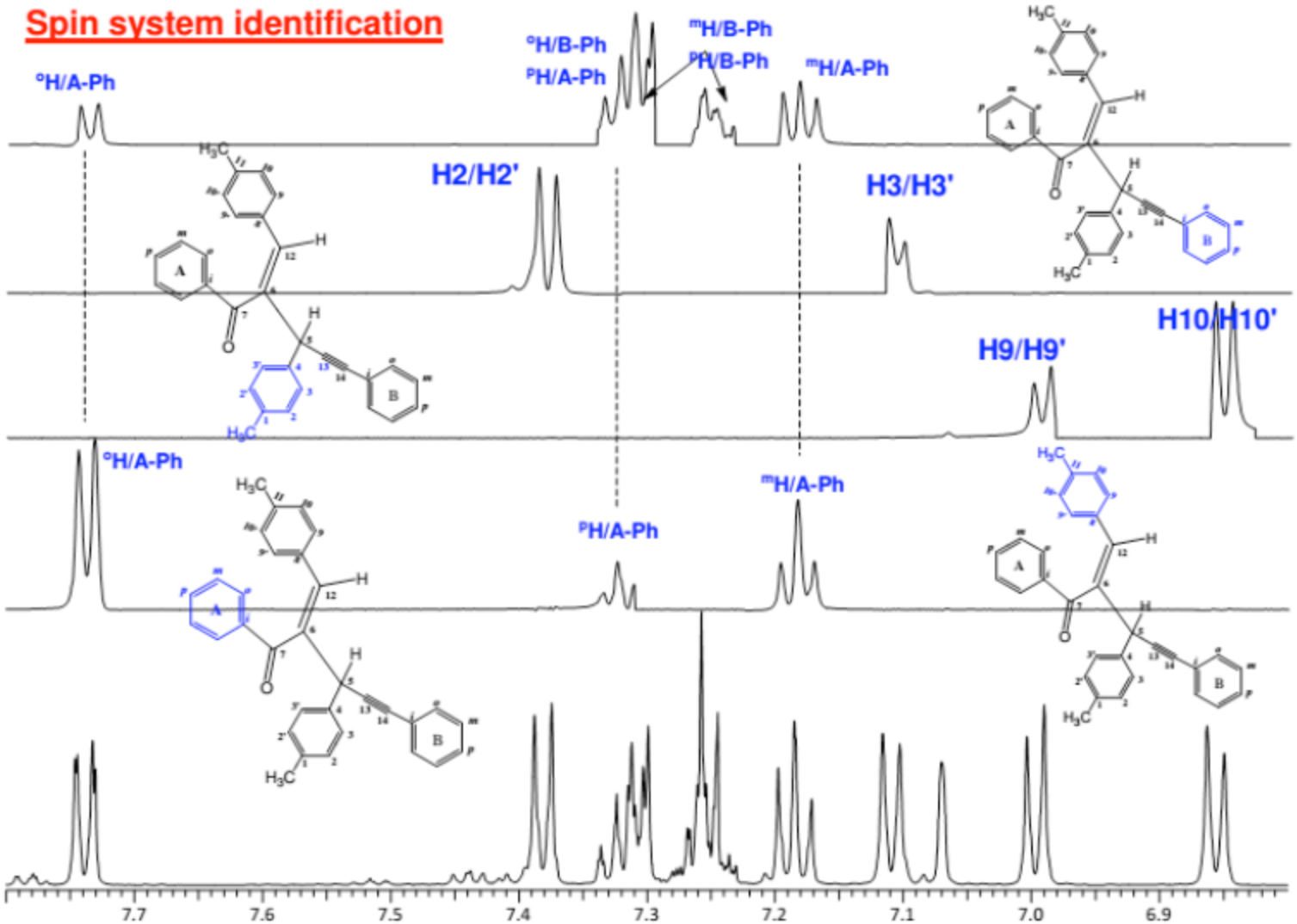
2-2-2b



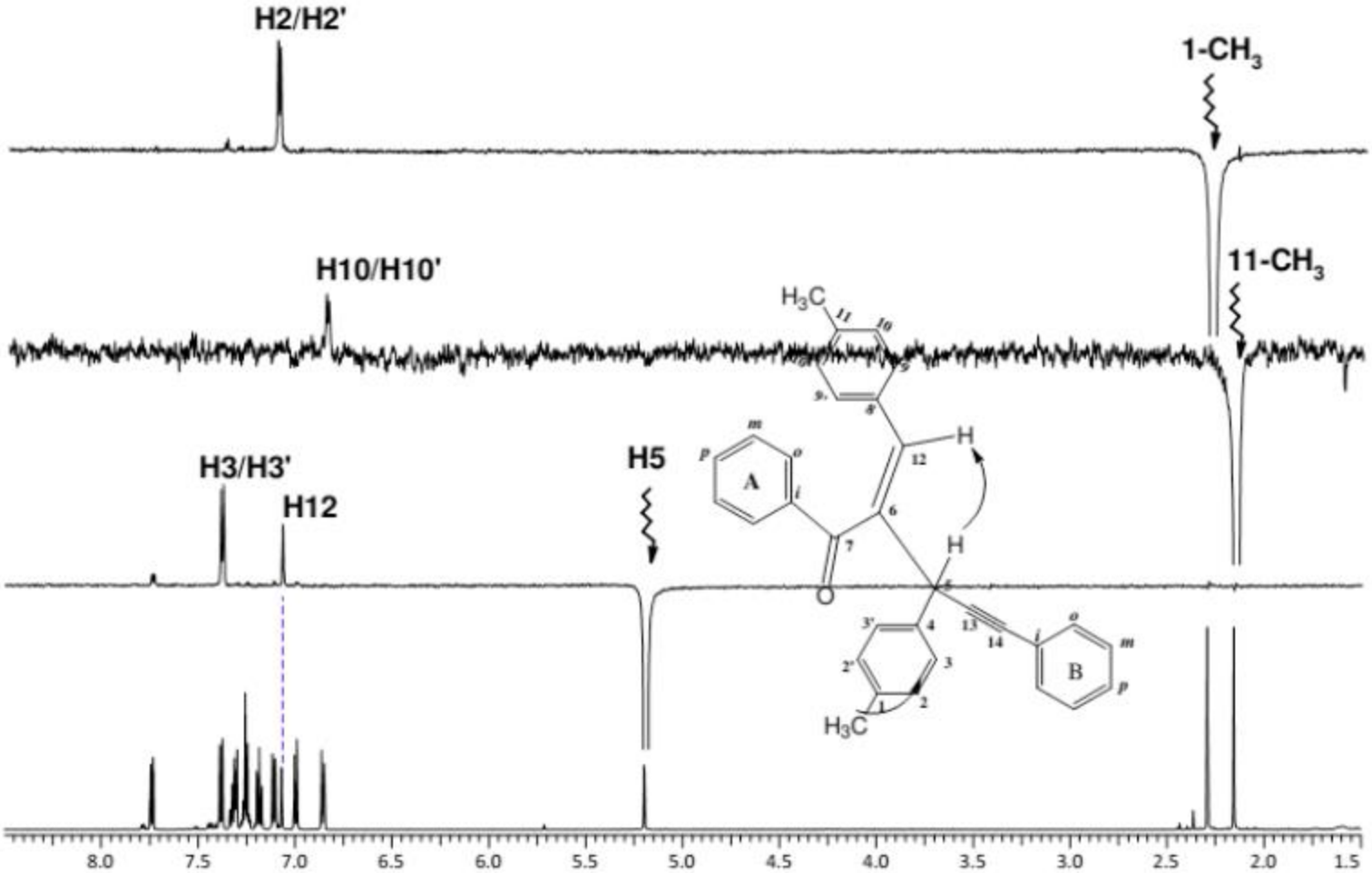


11---- CH's

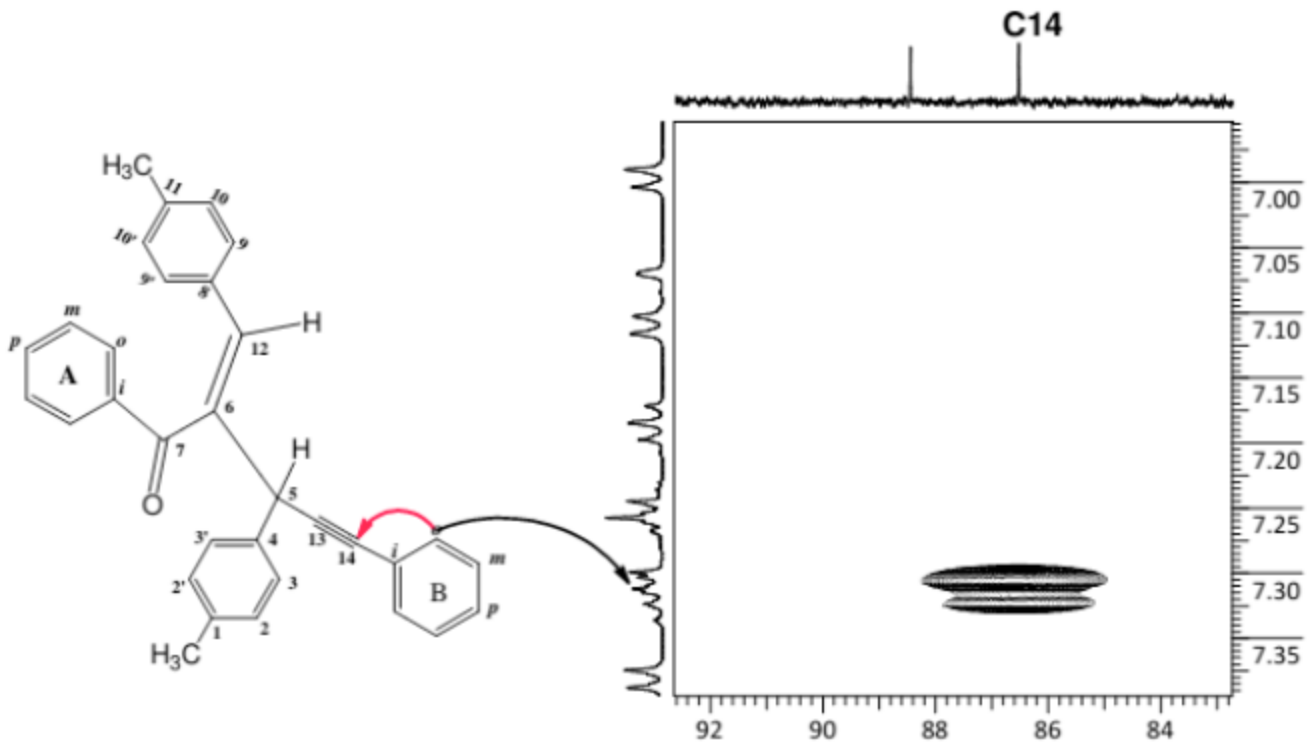

H12
H5
A
B
H3C
H3C
H
H
O
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

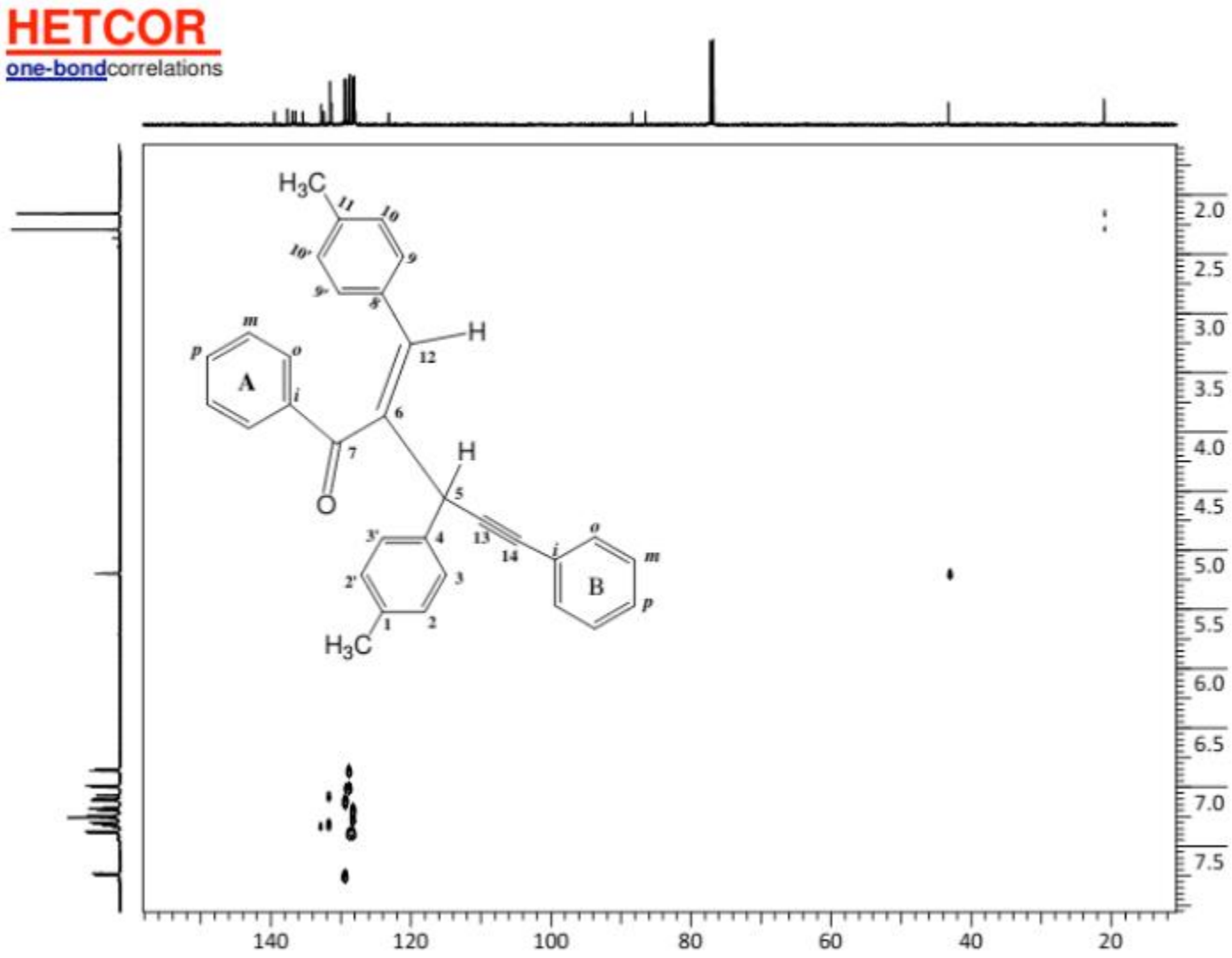

Spin system identification
°H/A-Ph
°H/B-Ph
ᵖH/A-Ph
ᵐH/B-Ph
ᵖH/B-Ph
ᵐH/A-Ph
H2/H2'
H3/H3'
H9/H9'
H10/H10'
°H/A-Ph
ᵖH/A-Ph
ᵐH/A-Ph
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9

DPFGSENOE
spectra



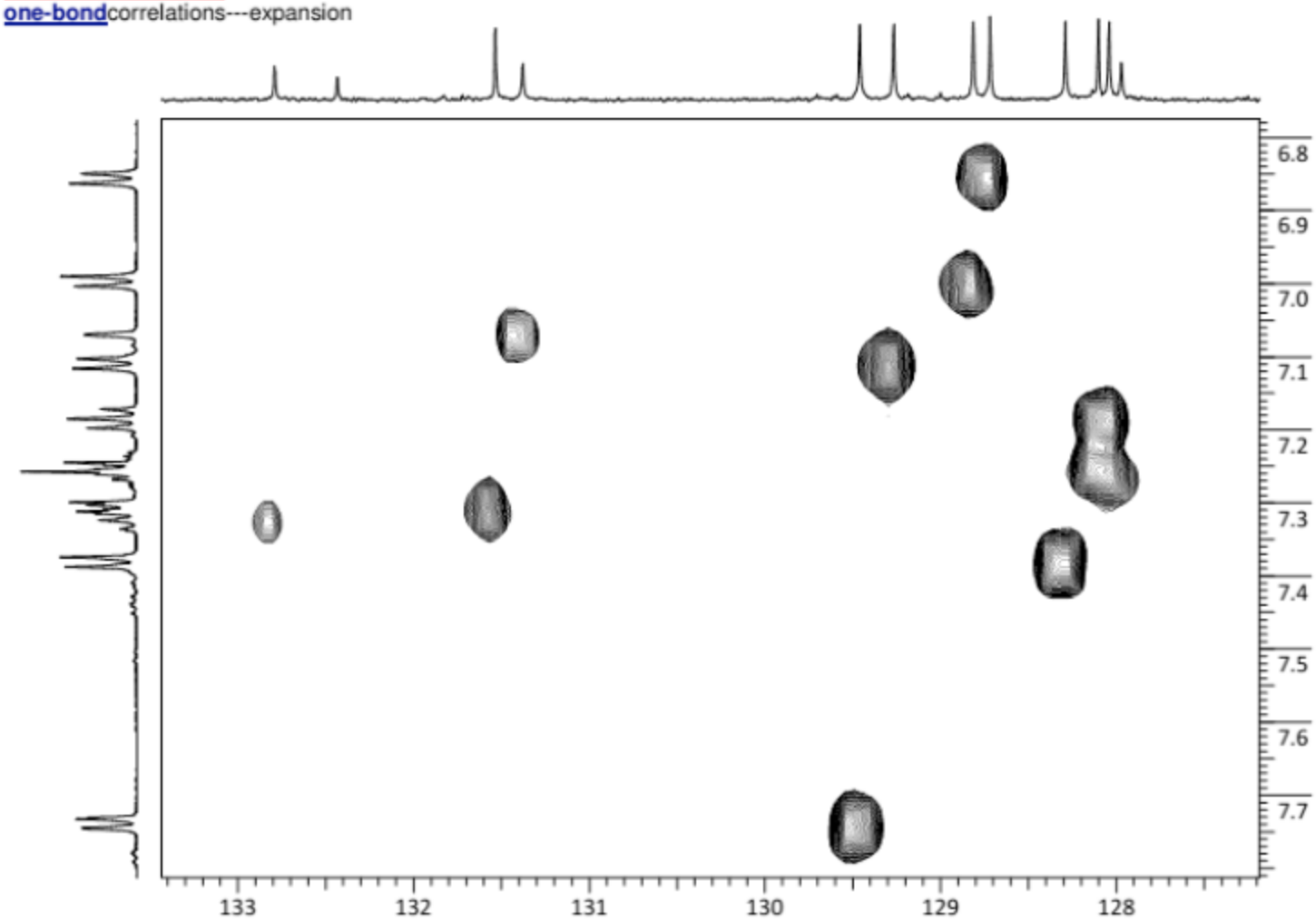
Expansion of the **HMBC** spectrum



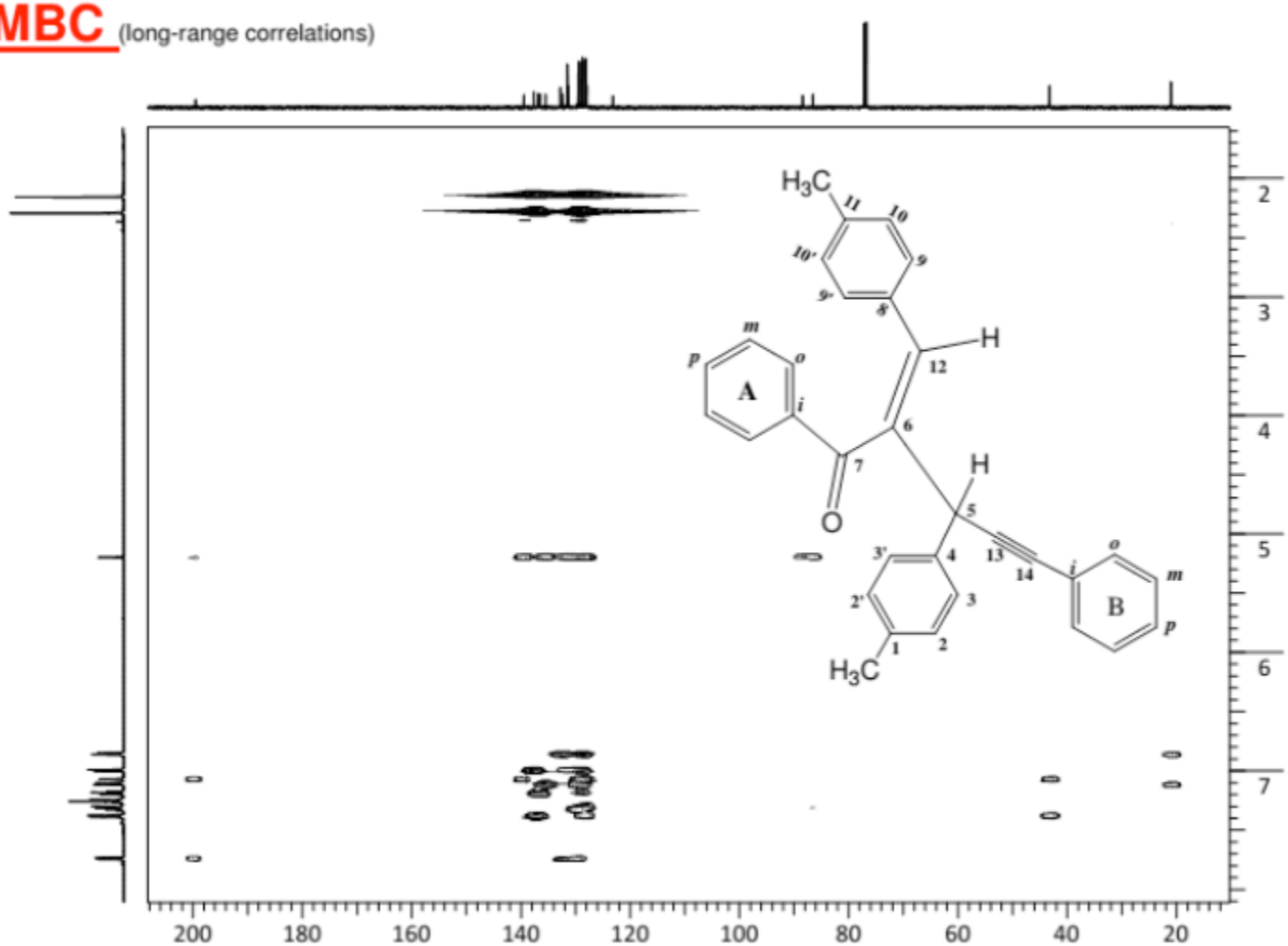

HETCOR
one-bondcorrelations
H3C
H
H
O
A
B
H3C
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
140
120
100
80
60
40
20

HETCOR

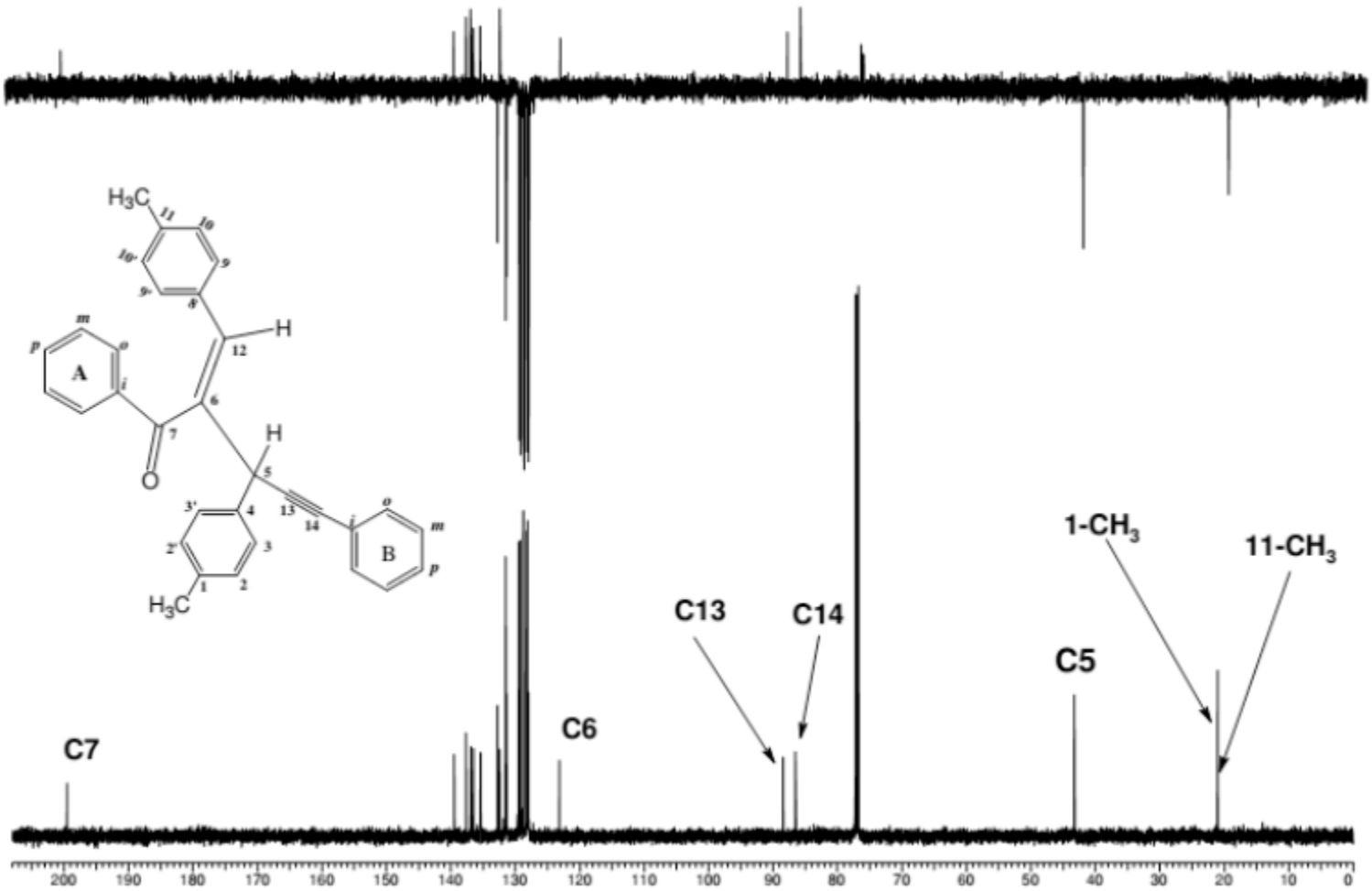
one-bondcorrelations---expansion

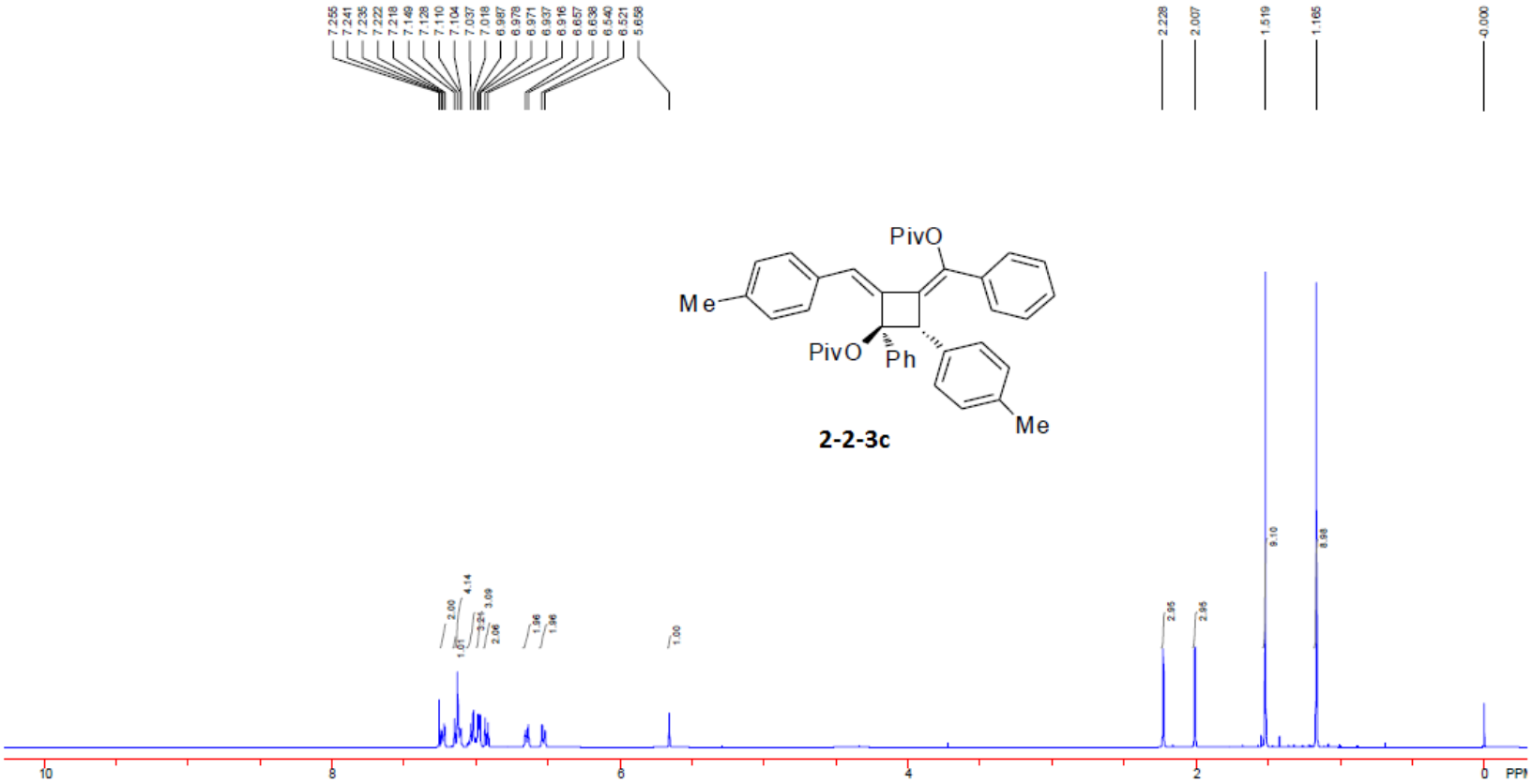


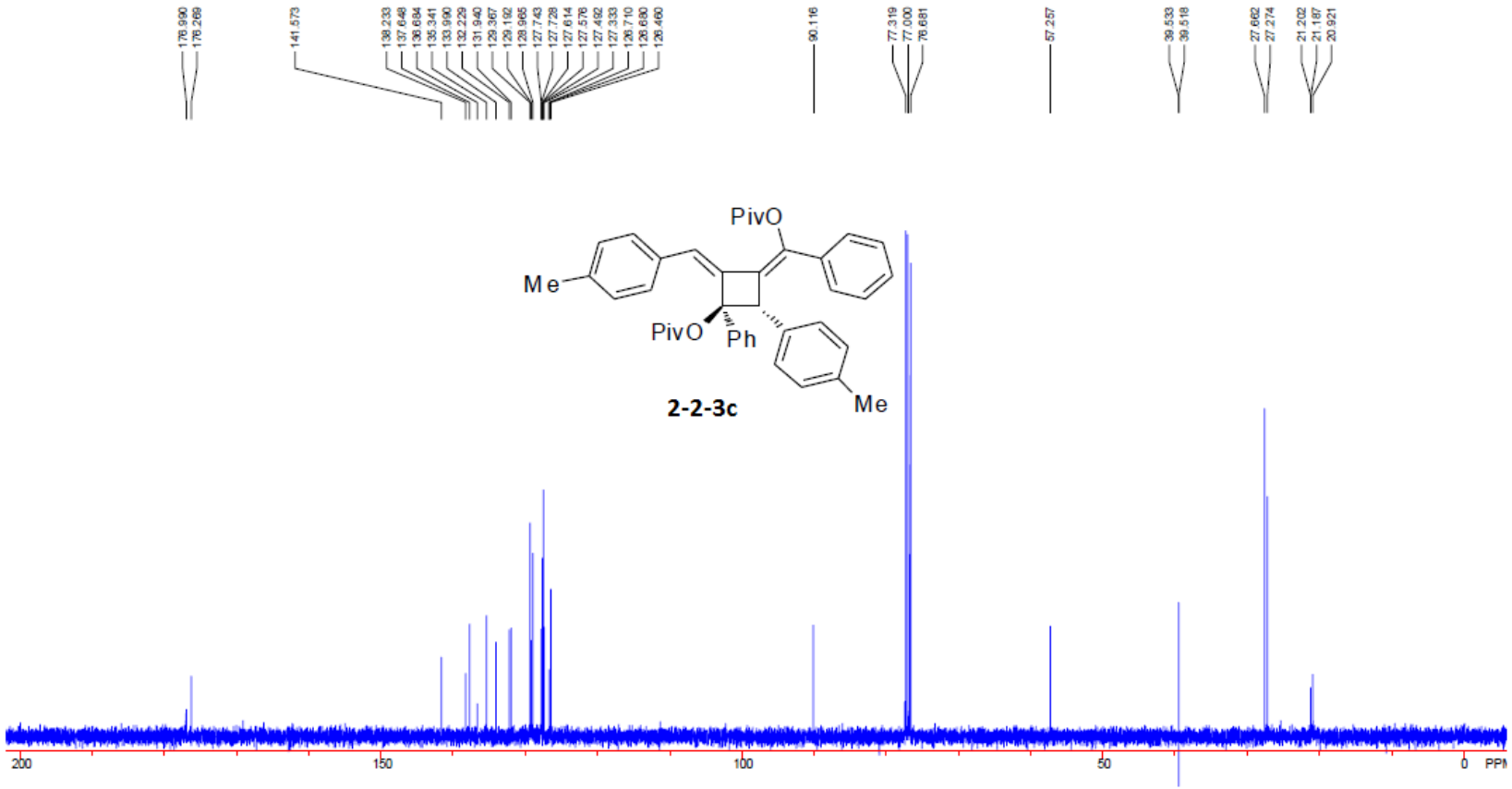
HMBC (long-range correlations)

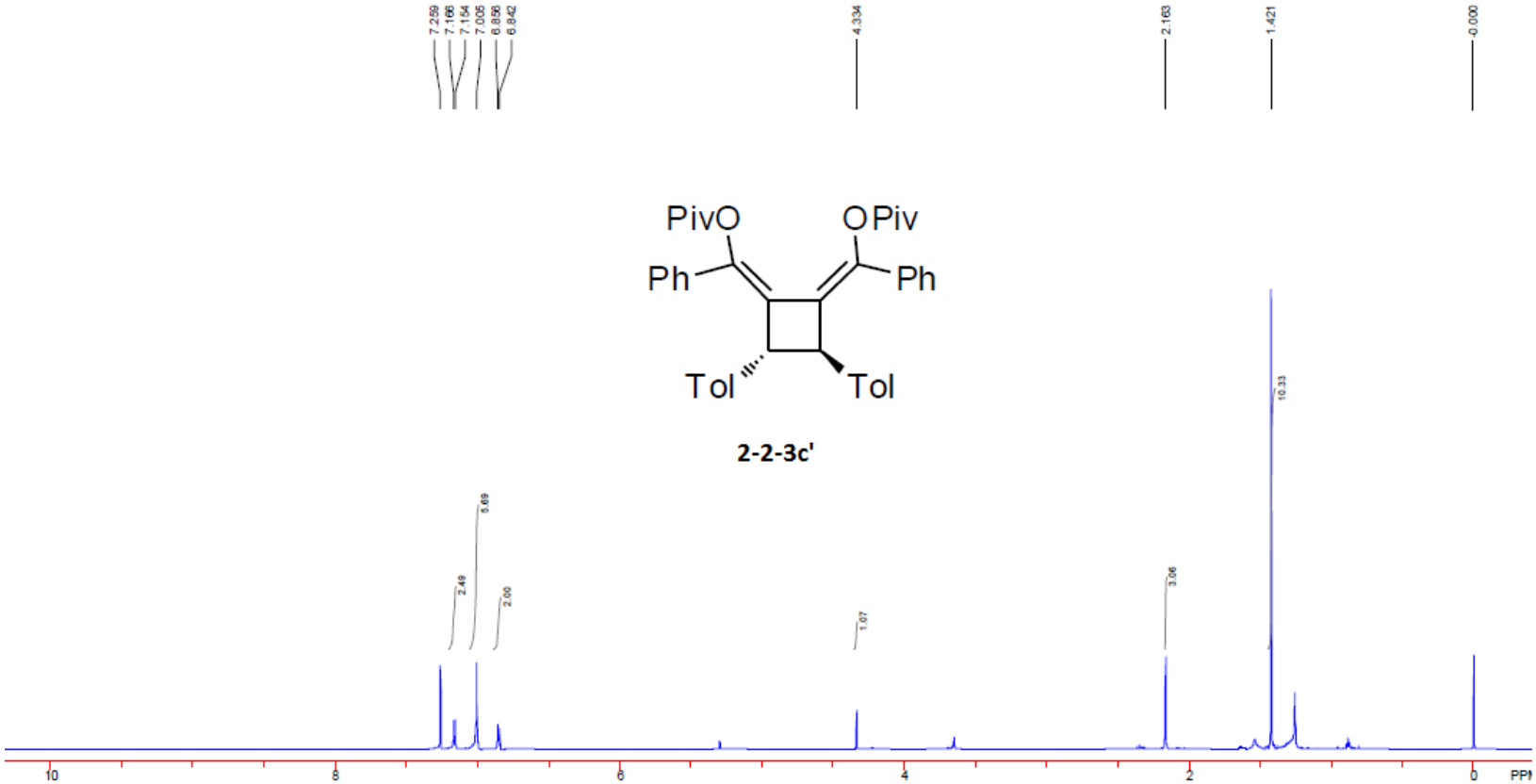


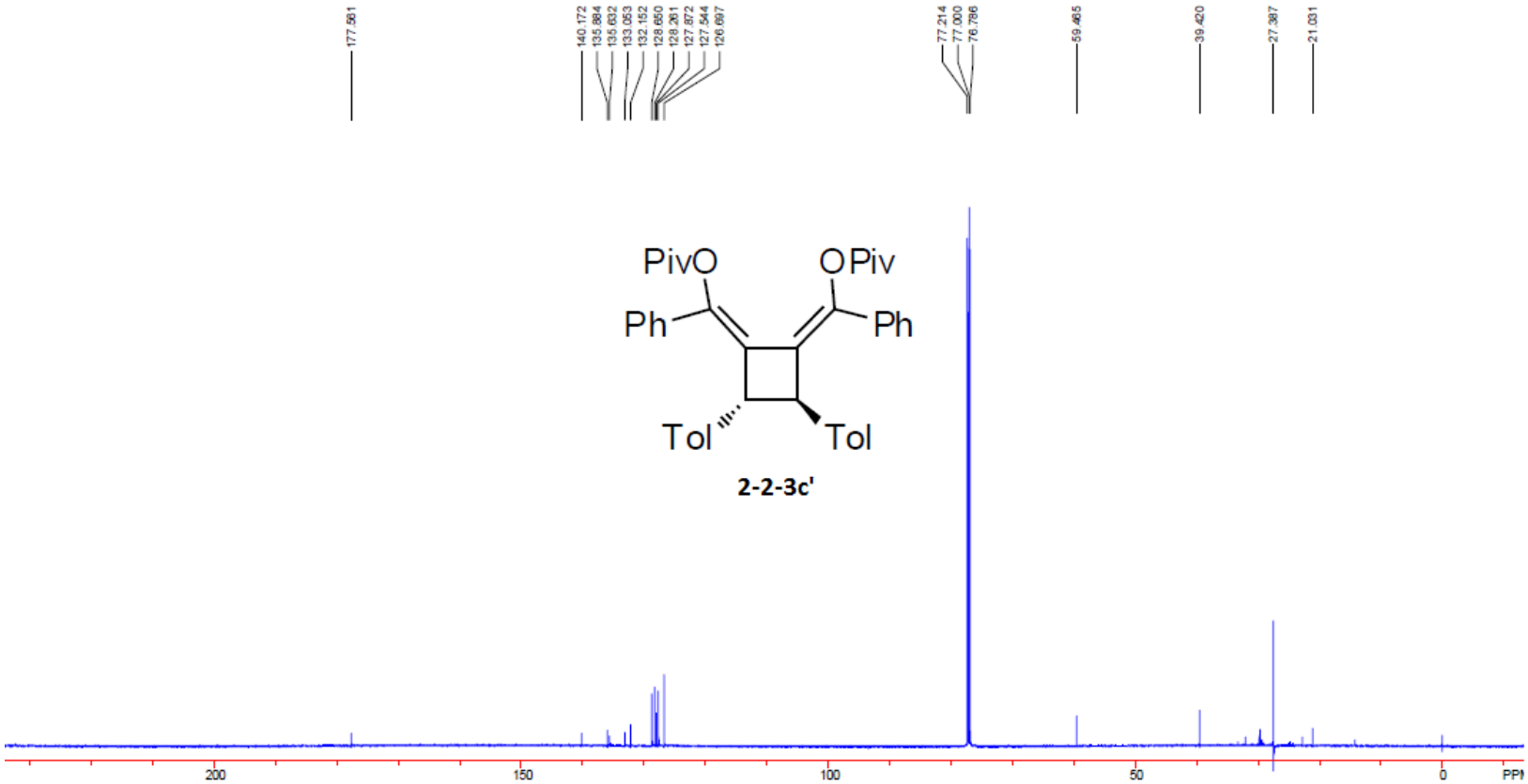
APT

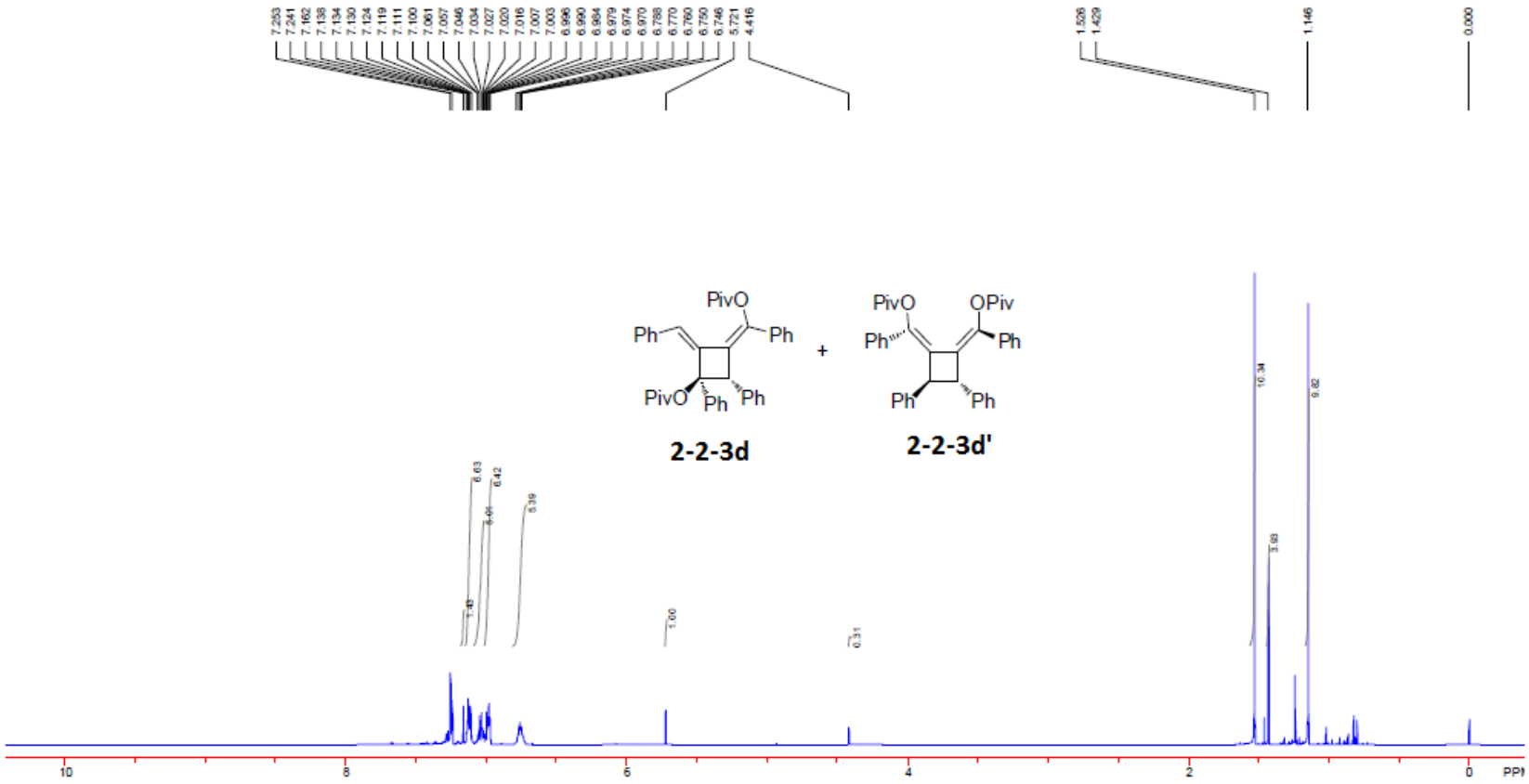

C7
C6
C13
C14
C5
1-CH3
11-CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

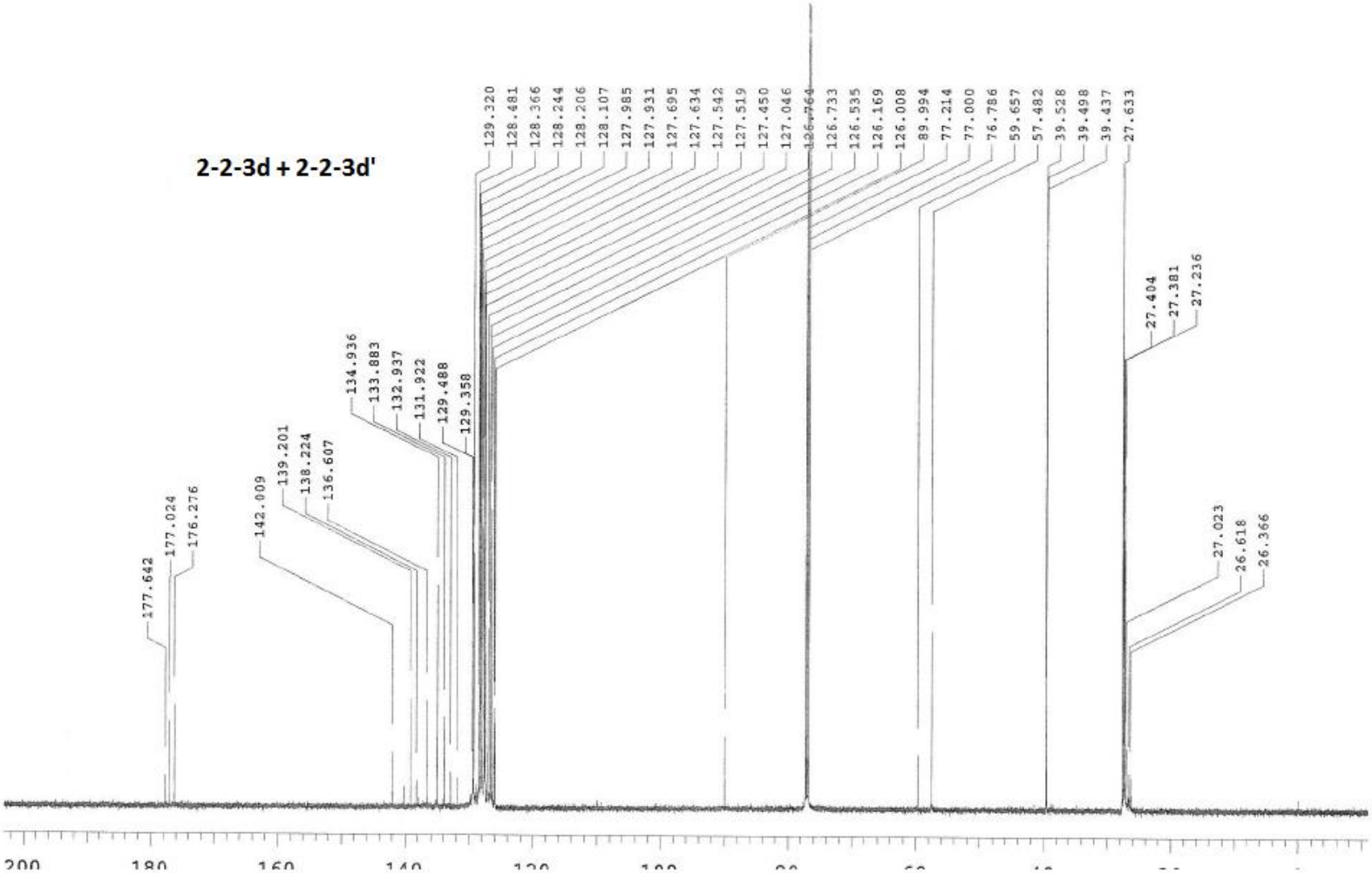

7.255
7.241
7.235
7.222
7.218
7.149
7.128
7.110
7.104
7.037
7.018
6.987
6.978
6.971
6.937
6.916
6.657
6.638
6.540
6.521
5.658
2.228
2.007
1.519
1.165
0.000
PivO
Me
PivO
Ph
Me
2-2-3c
2.00
4.14
3.09
1.07
2.94
2.06
1.96
1.96
1.00
2.95
2.95
9.10
8.98
10
8
6
4
2
0
PPM

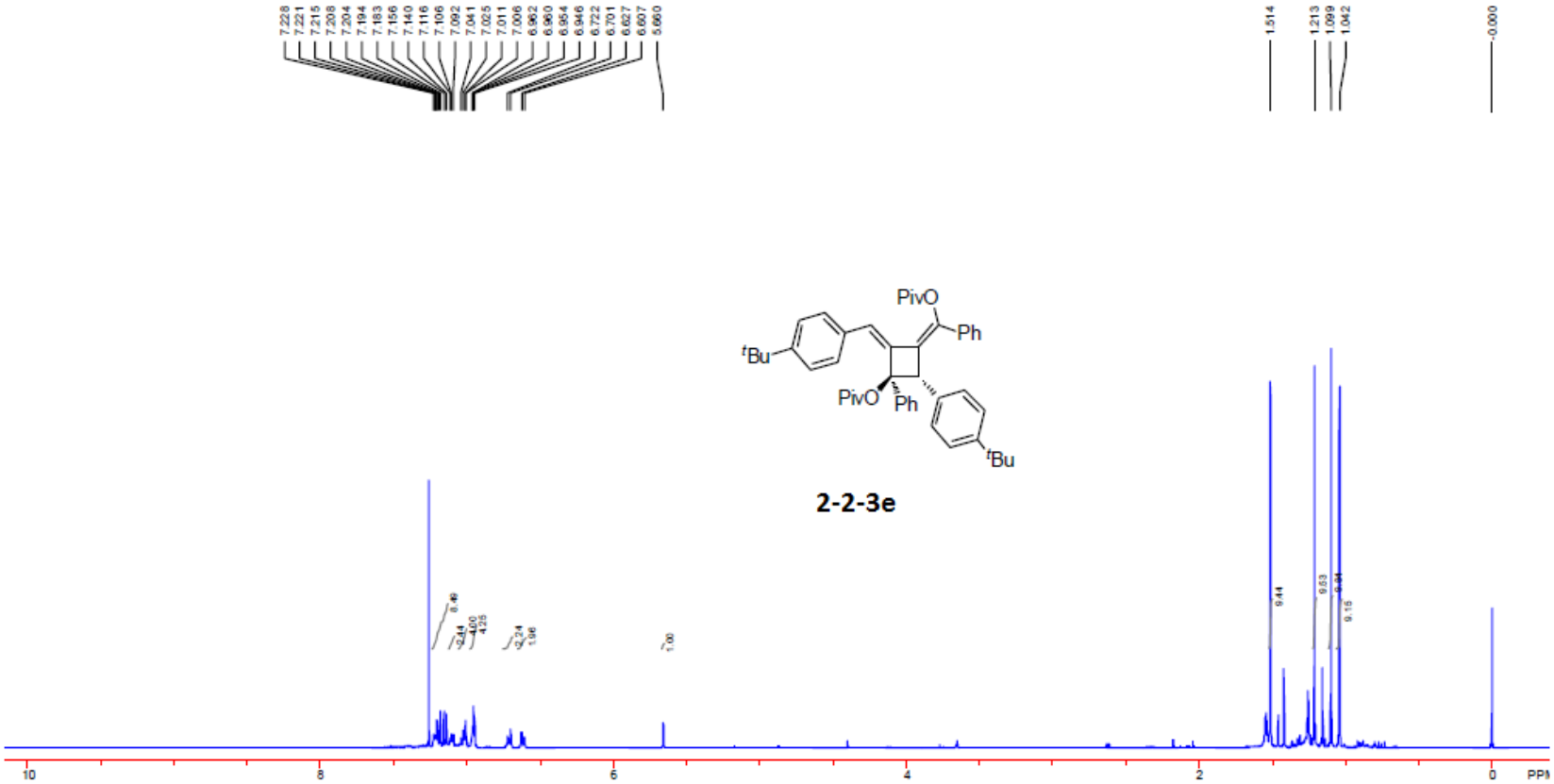

176.990
176.269
141.573
138.233
137.648
136.684
135.341
133.990
132.229
131.940
129.367
129.192
128.965
127.743
127.728
127.614
127.576
127.492
127.333
126.710
126.680
126.460
90.116
77.319
77.000
76.681
57.257
39.533
39.518
27.662
27.274
21.202
21.187
20.921
PivO
Me
PivO
Ph
Me
2-2-3c
200
150
100
50
0
PPM


7.259
7.166
7.154
7.005
6.856
6.842
4.334
2.163
1.421
0.000
PivO
OPiv
Ph
Ph
Tol
Tol
2-2-3c'
10.33
5.69
2.49
2.00
1.07
3.06
10
8
6
4
2
0
PPM

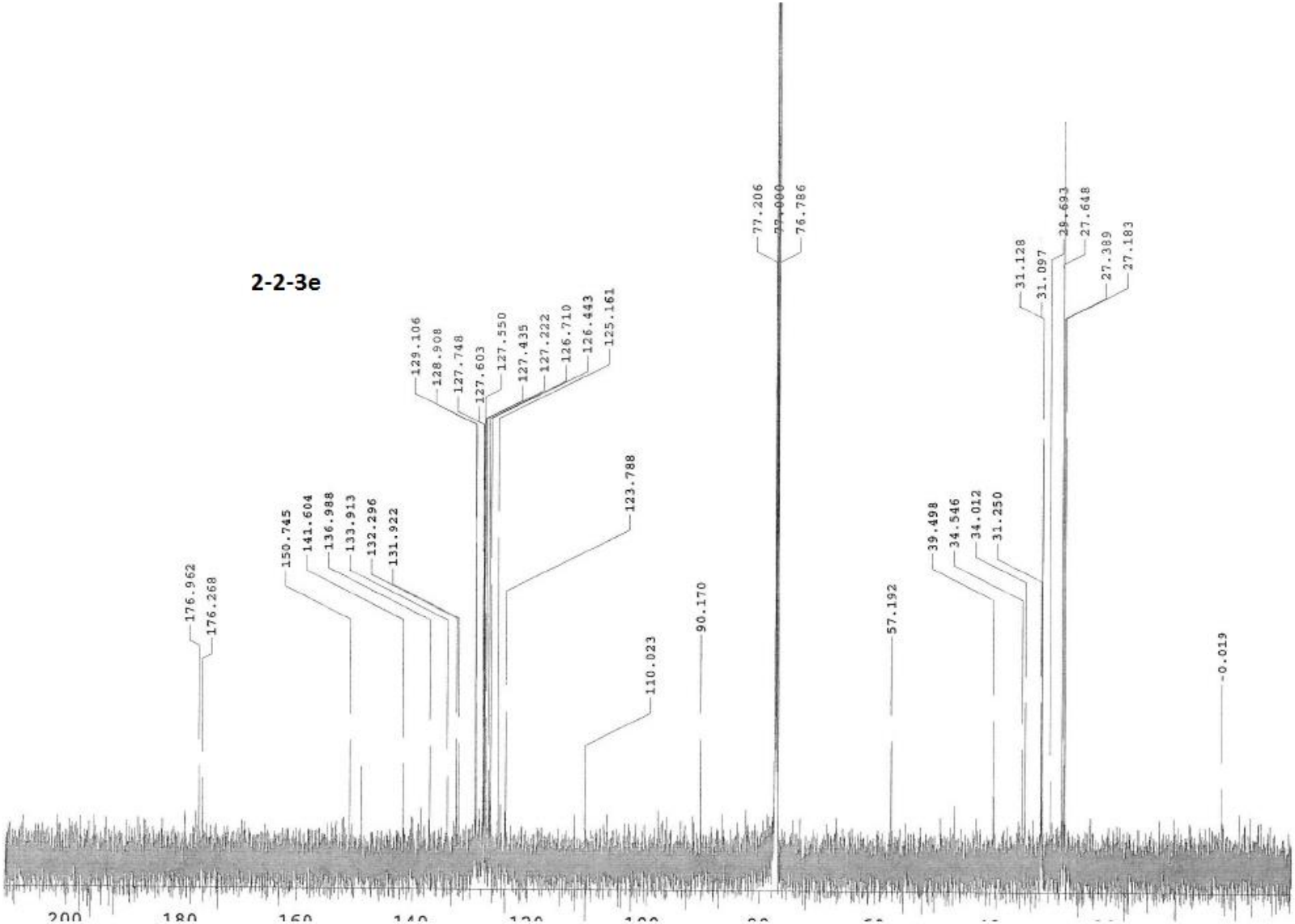

177.561
140.172
135.884
135.632
133.053
132.152
128.650
128.261
127.872
127.544
126.697
77.214
77.000
76.786
59.485
39.420
27.387
21.031
PivO
OPiv
Ph
Ph
Tol
Tol
2-2-3c'
200
150
100
50
0
PPM

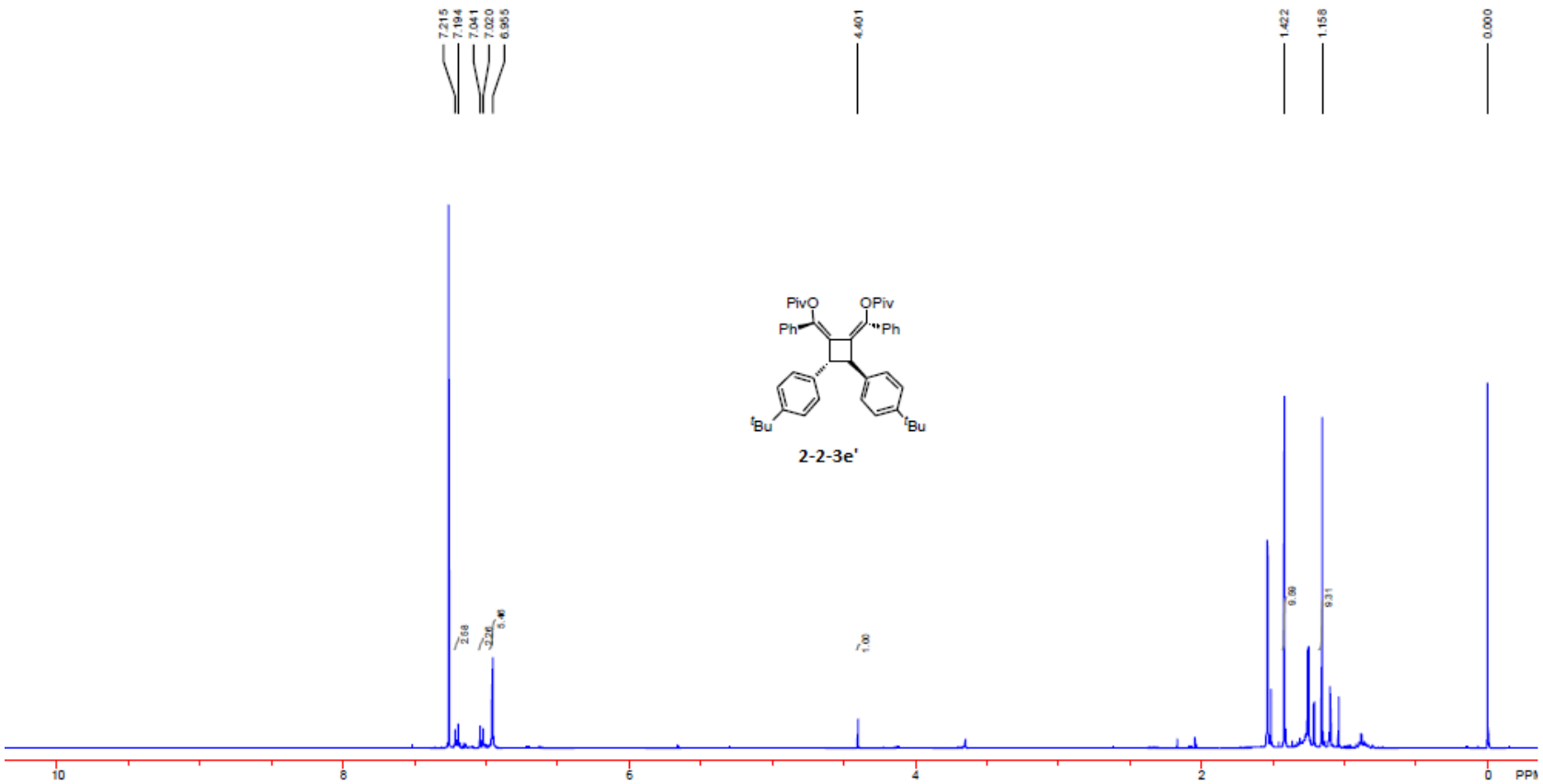

PivO
Ph
Ph
PivO
Ph
Ph
+
PivO
OPiv
Ph
Ph
Ph
Ph
2-2-3d
2-2-3d'
10
8
6
4
2
0
PPM


2-2-3d + 2-2-3d'
177.642
177.024
176.276
142.009
139.201
138.224
136.607
134.936
133.883
132.937
131.922
129.488
129.358
129.320
128.481
128.366
128.244
128.206
128.107
127.985
127.931
127.695
127.634
127.542
127.519
127.450
127.046
126.764
126.733
126.535
126.169
126.008
89.994
77.214
77.000
76.786
59.657
57.482
39.528
39.498
39.437
27.633
27.404
27.381
27.236
27.023
26.618
26.366
200
180
160
140
120
100
80
60
40
20

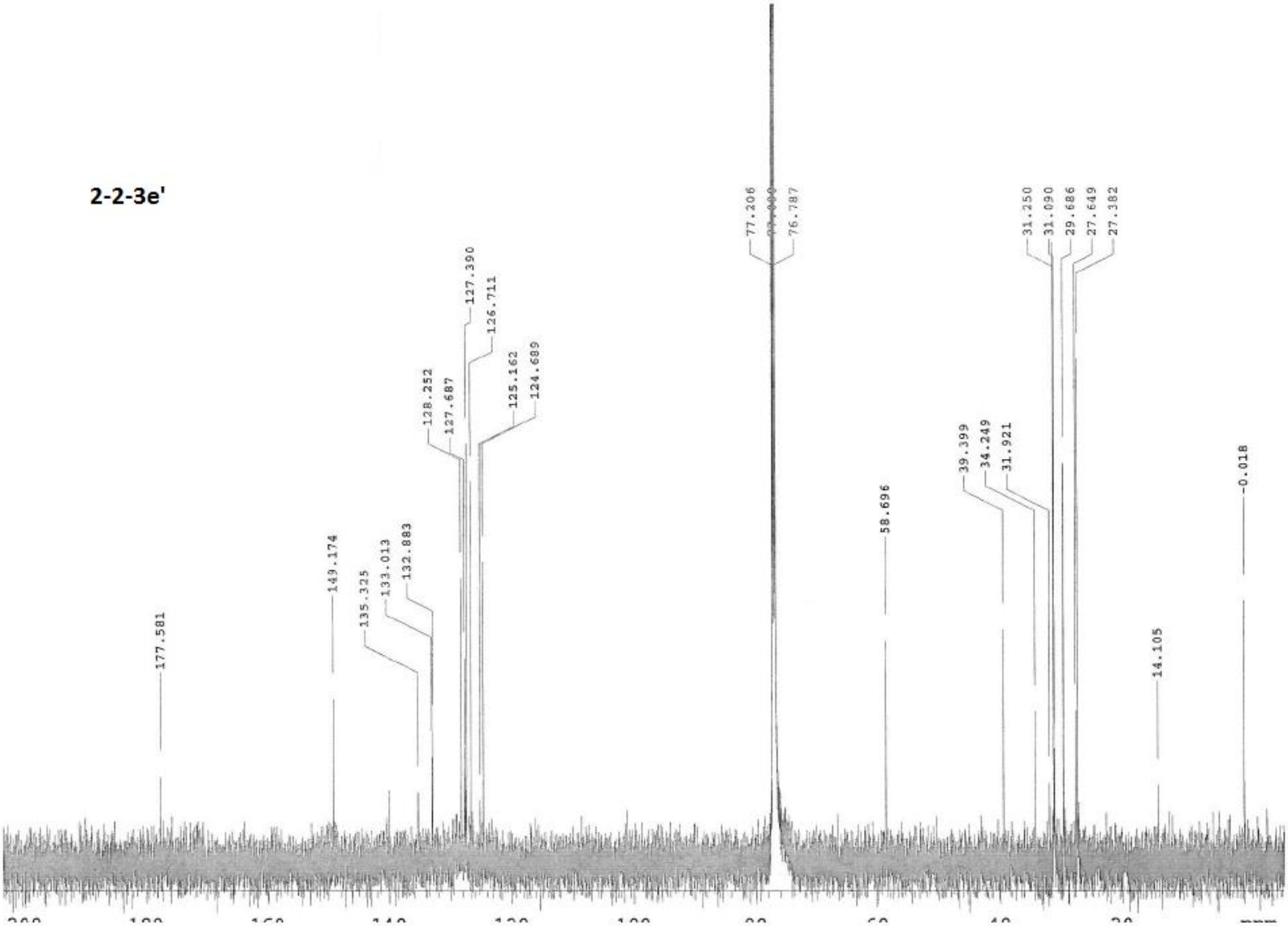

7.228
7.221
7.215
7.208
7.204
7.194
7.183
7.156
7.140
7.116
7.106
7.092
7.041
7.025
7.011
7.006
6.962
6.960
6.954
6.946
6.722
6.701
6.627
6.607
5.660
1.514
1.213
1.099
1.042
-0.000
PivO
Ph
tBu
PivO
Ph
tBu
2-2-3e
9.44
9.53
9.34
9.15
1.00
10
8
6
4
2
0
PPM

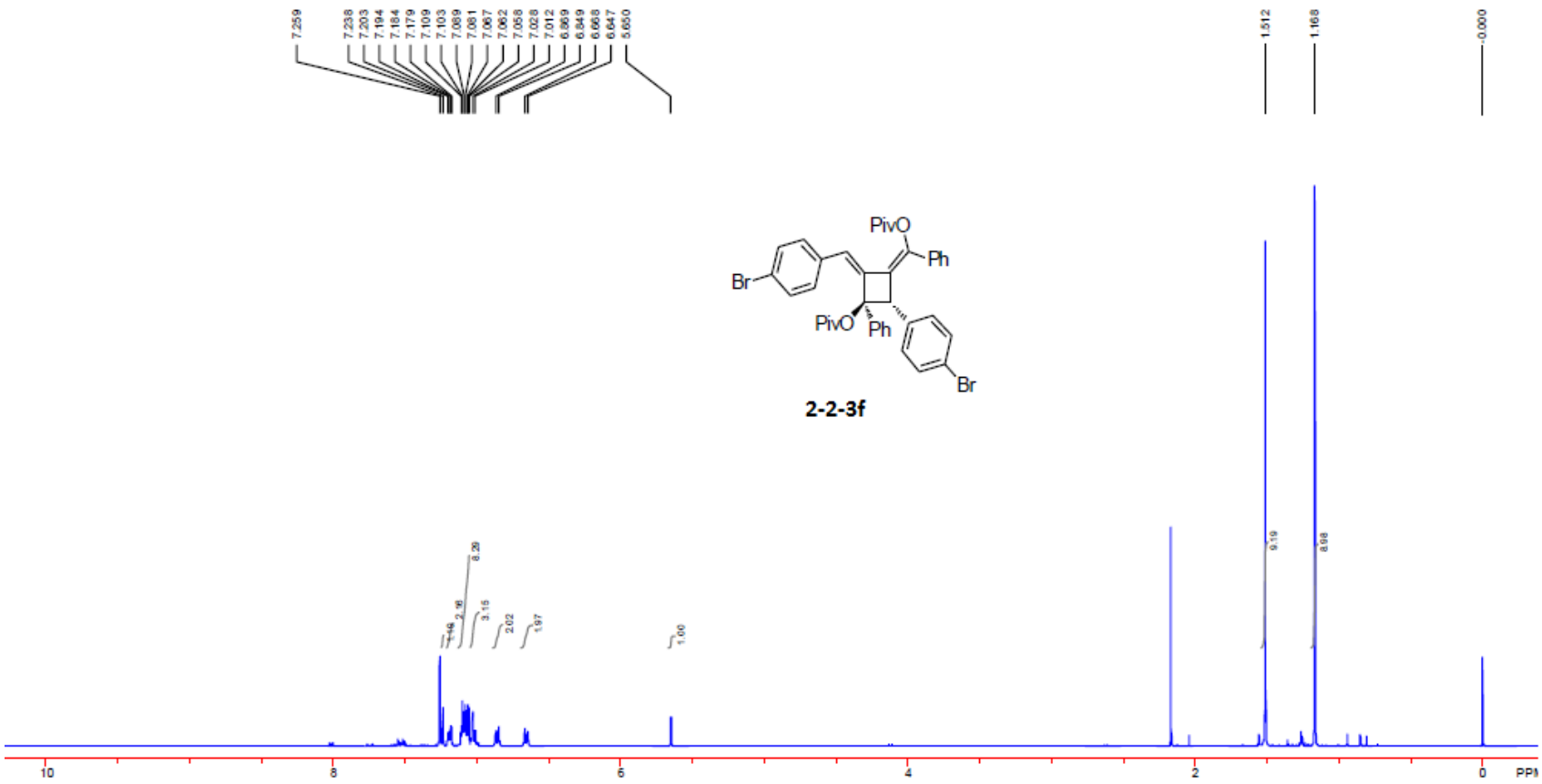
2-2-3e


176.962
176.268
150.745
141.604
136.988
133.913
132.296
131.922
129.106
128.908
127.748
127.603
127.550
127.435
127.222
126.710
126.443
125.161
123.788
110.023
90.170
77.206
77.000
76.786
57.192
39.498
34.546
34.012
31.250
31.128
31.097
28.693
27.648
27.389
27.183
-0.019
200
180
160
140
120
100
80
60
40
20
0

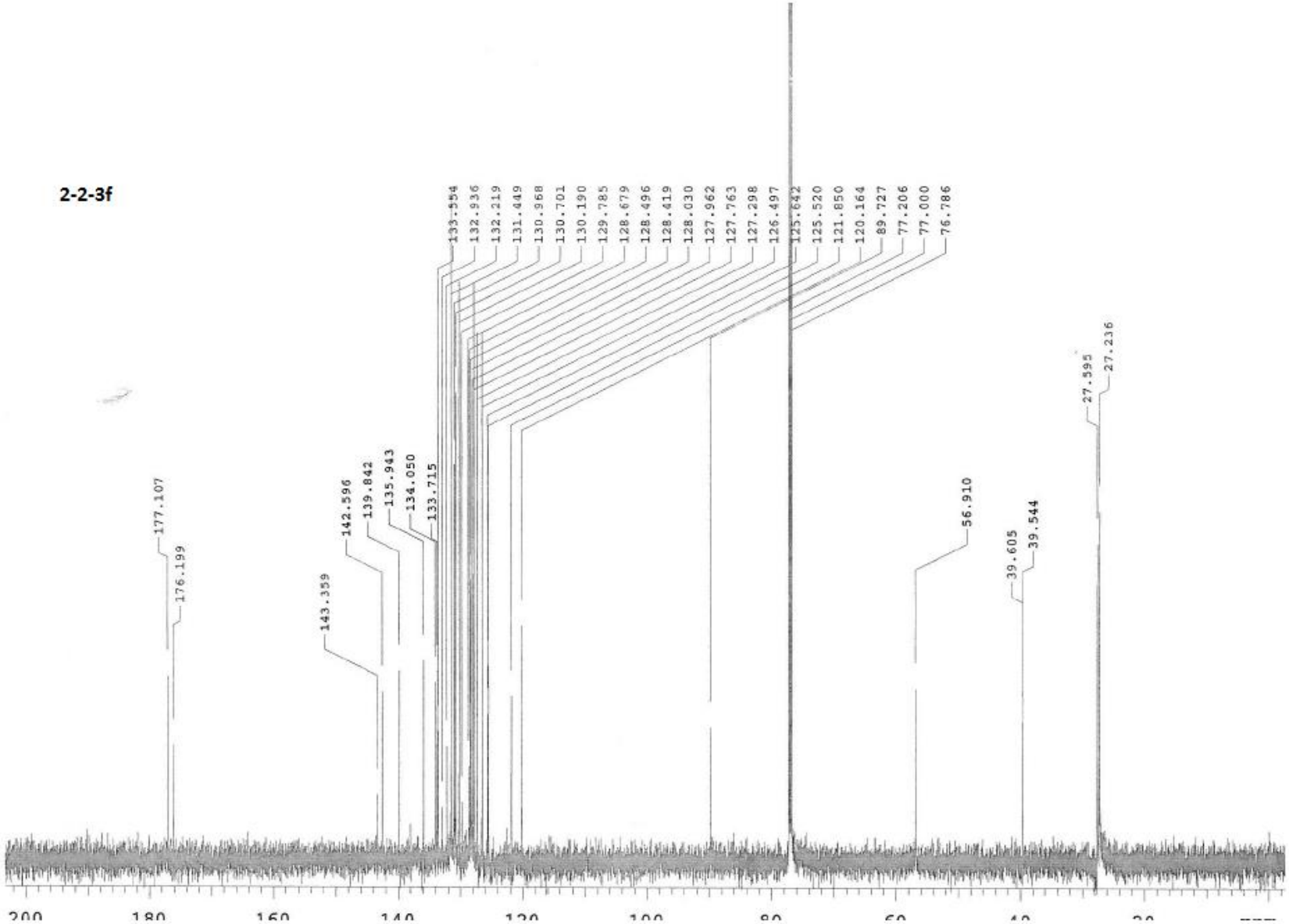

7.215
7.194
7.041
7.020
6.995
4.401
1.422
1.158
0.000
PivO
OPiv
Ph
Ph
tBu
tBu
2-2-3e'
2.68
3.26
5.48
1.00
9.99
9.31
10
8
6
4
2
0
PPM

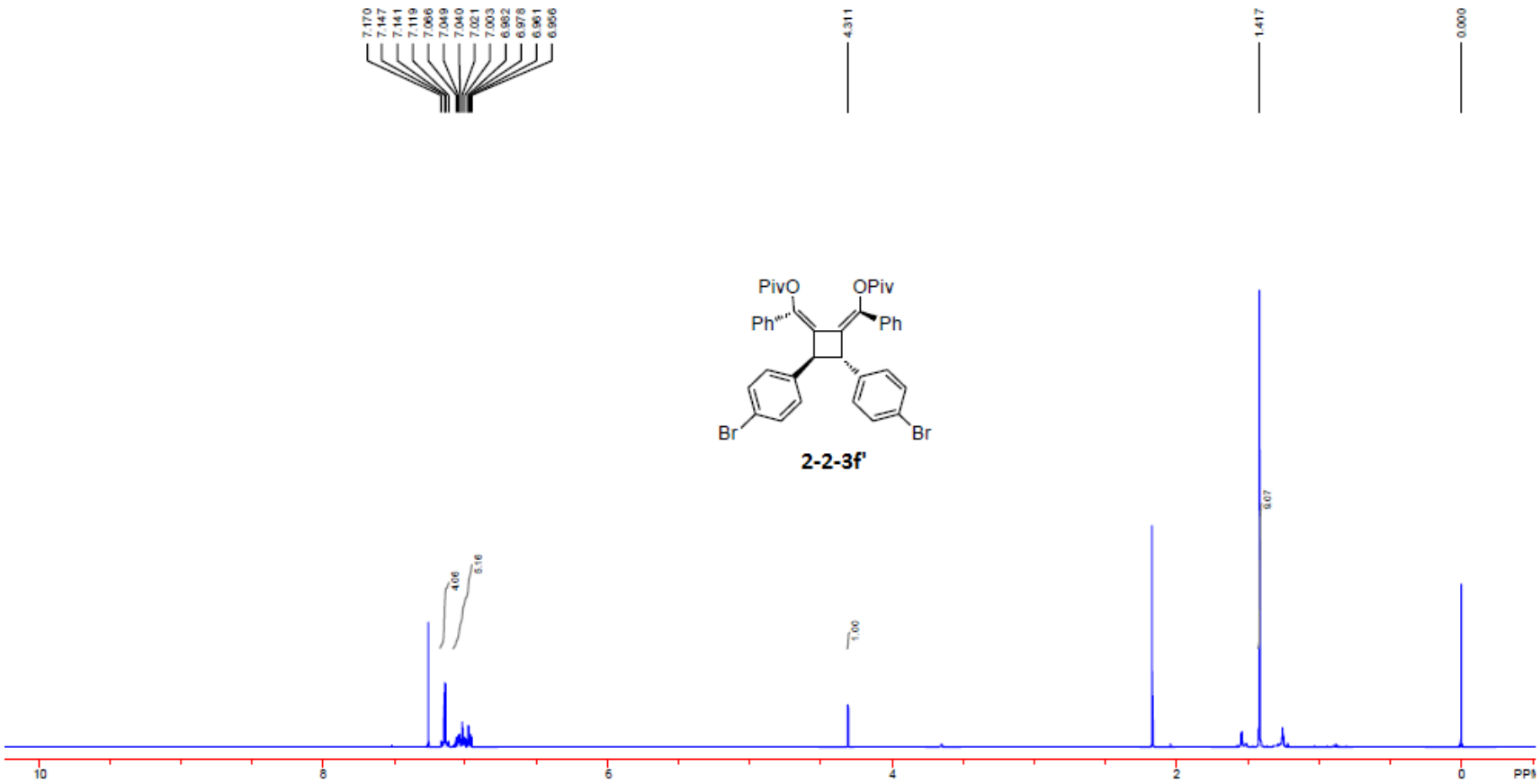
2-2-3e'


177.581
149.174
135.325
133.013
132.883
128.252
127.687
127.390
126.711
125.162
124.689
77.206
77.000
76.787
58.696
39.399
34.249
31.921
31.250
31.090
29.686
27.649
27.382
14.105
-0.018

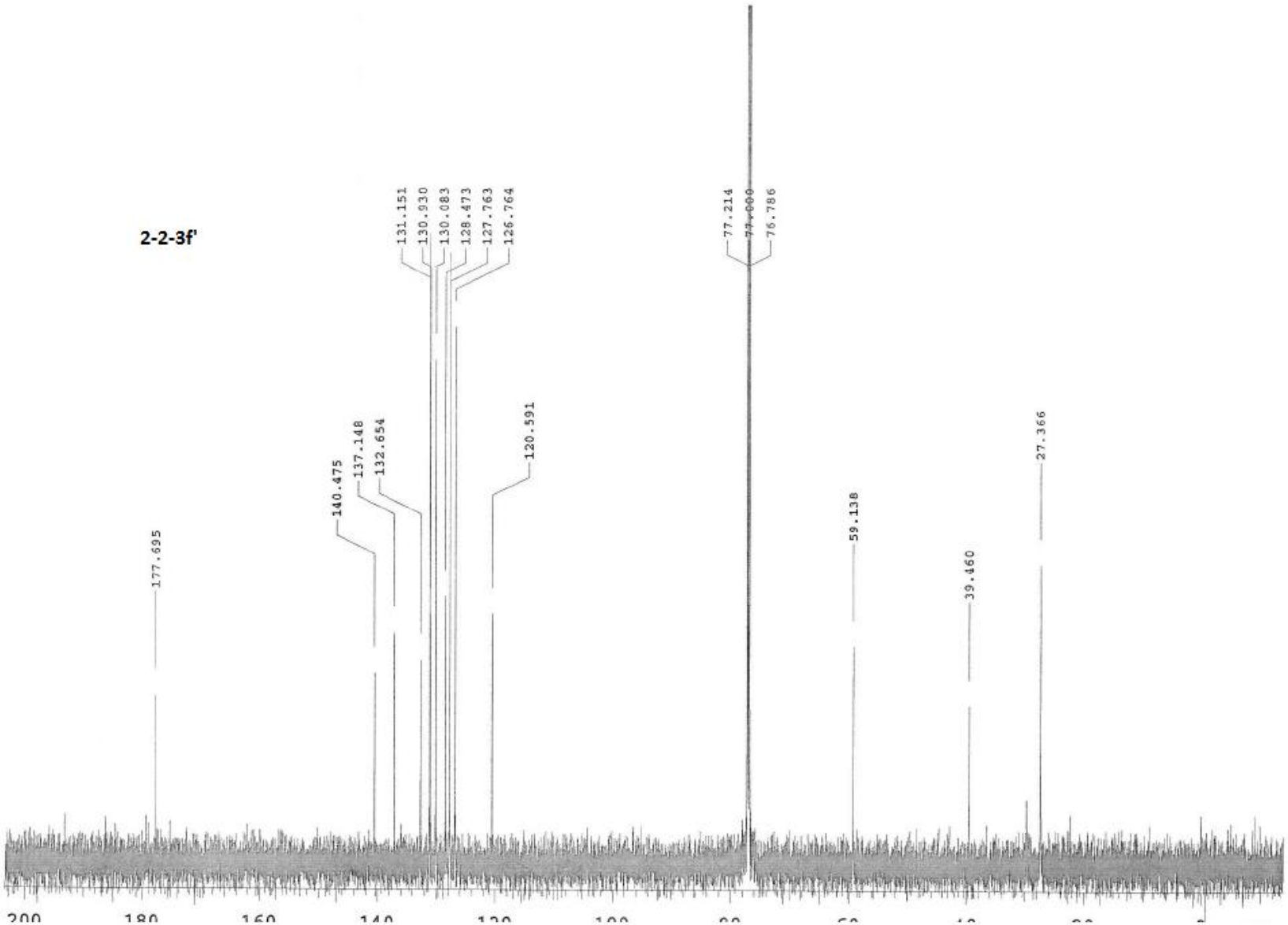

7.259
7.238
7.203
7.194
7.184
7.179
7.109
7.103
7.089
7.081
7.067
7.062
7.058
7.028
7.012
6.869
6.849
6.668
6.647
5.650
1.512
1.168
-0.000
PivO
Ph
Br
PivO
Ph
Br
2-2-3f
8.29
2.16
3.15
2.02
1.97
1.00
9.19
8.98
10
8
6
4
2
0
PPM

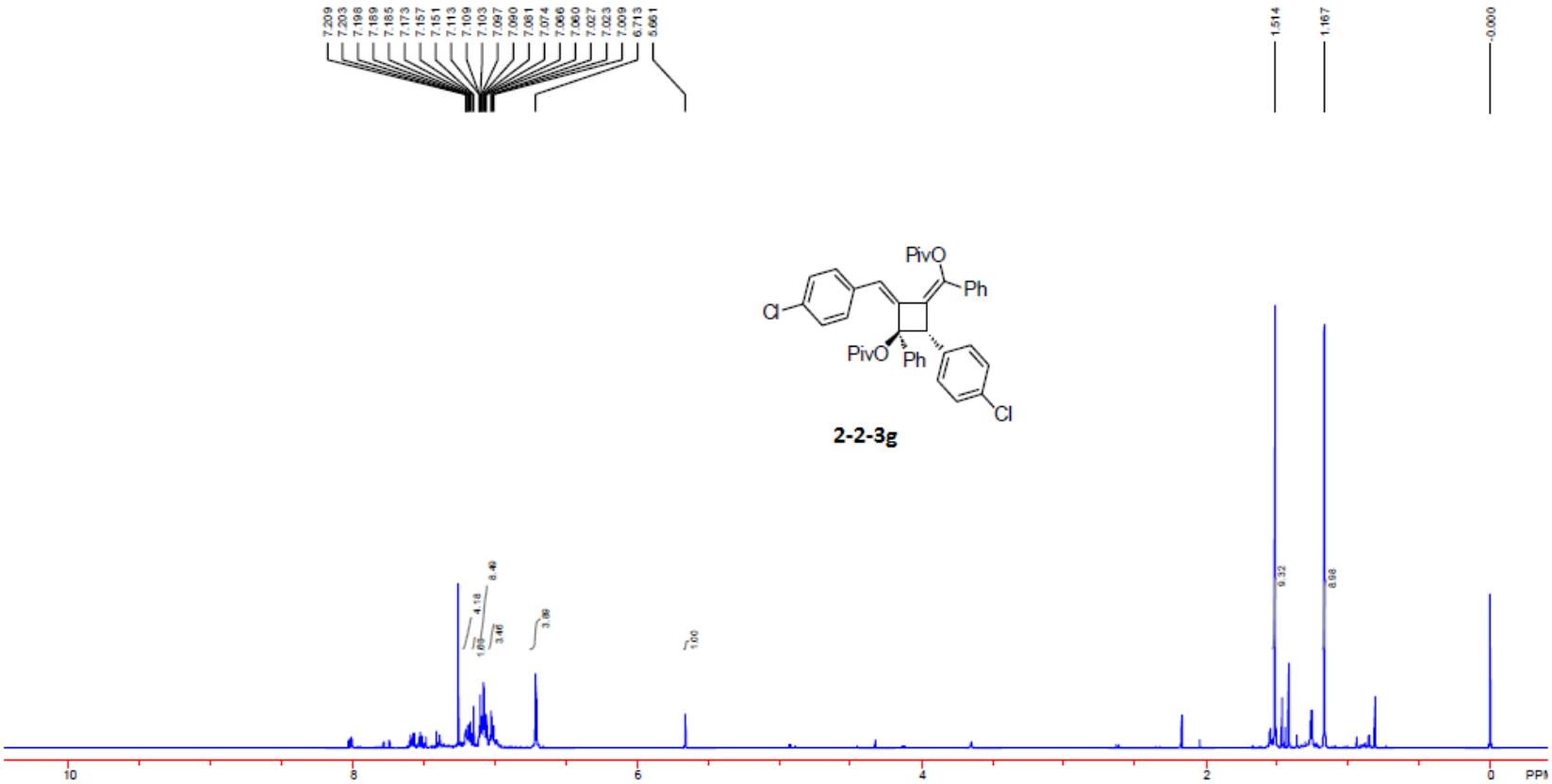
2-2-3f


177.107
176.199
143.359
142.596
139.842
135.943
134.050
133.715
133.554
132.936
132.219
131.449
130.968
130.701
130.190
129.785
128.679
128.496
128.419
128.030
127.962
127.763
127.298
126.497
125.642
125.520
121.850
120.164
89.727
77.206
77.000
76.786
56.910
39.605
39.544
27.595
27.236
200
180
160
140
120
100
80
60
40
20

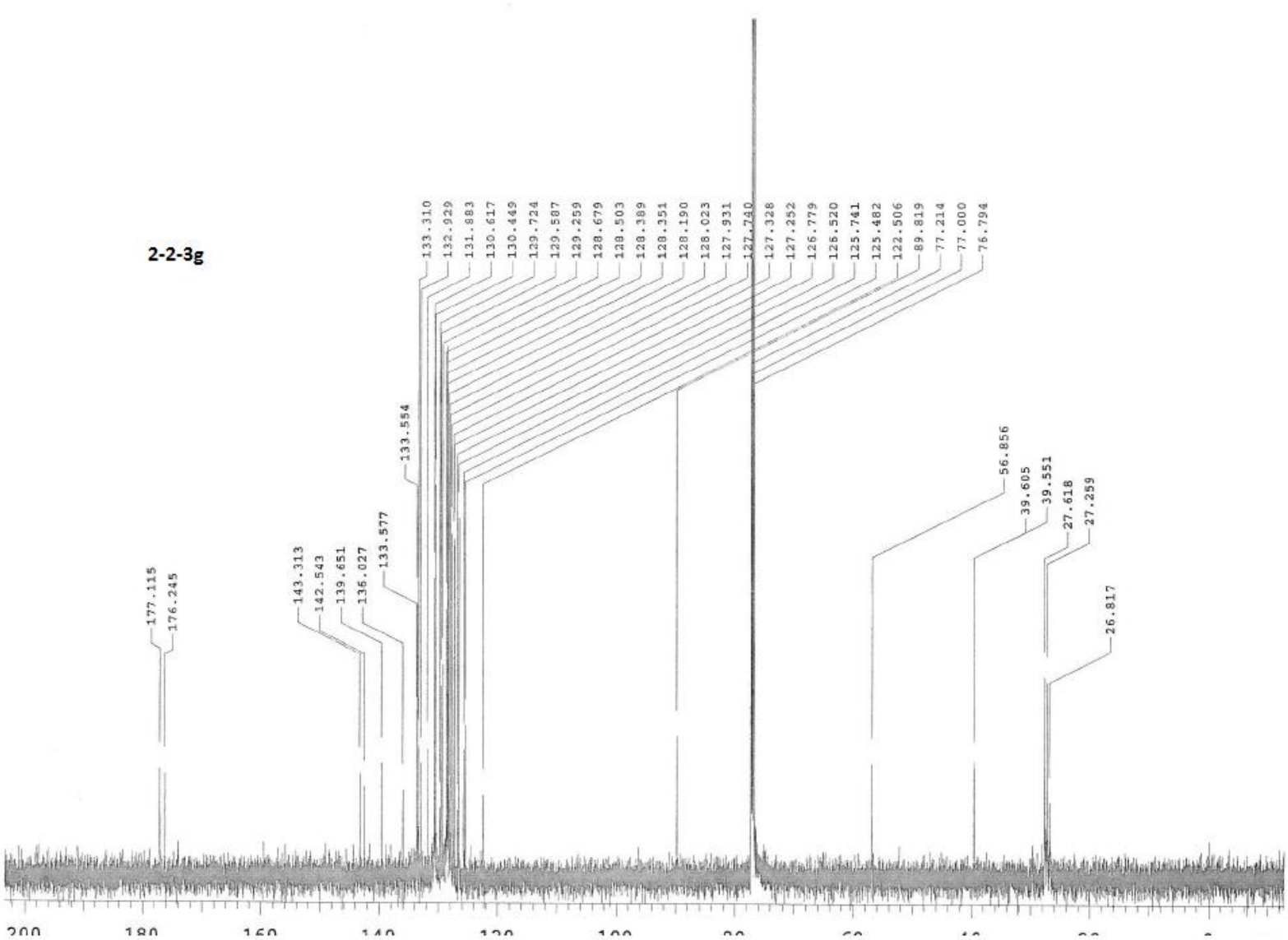

7.170
7.147
7.141
7.119
7.066
7.049
7.040
7.021
7.003
6.982
6.978
6.961
6.956
4.311
1.417
0.000
PivO
OPiv
Ph
Ph
Br
Br
2-2-3f'
4.06
5.16
1.00
9.67
10
8
6
4
2
0
PPM

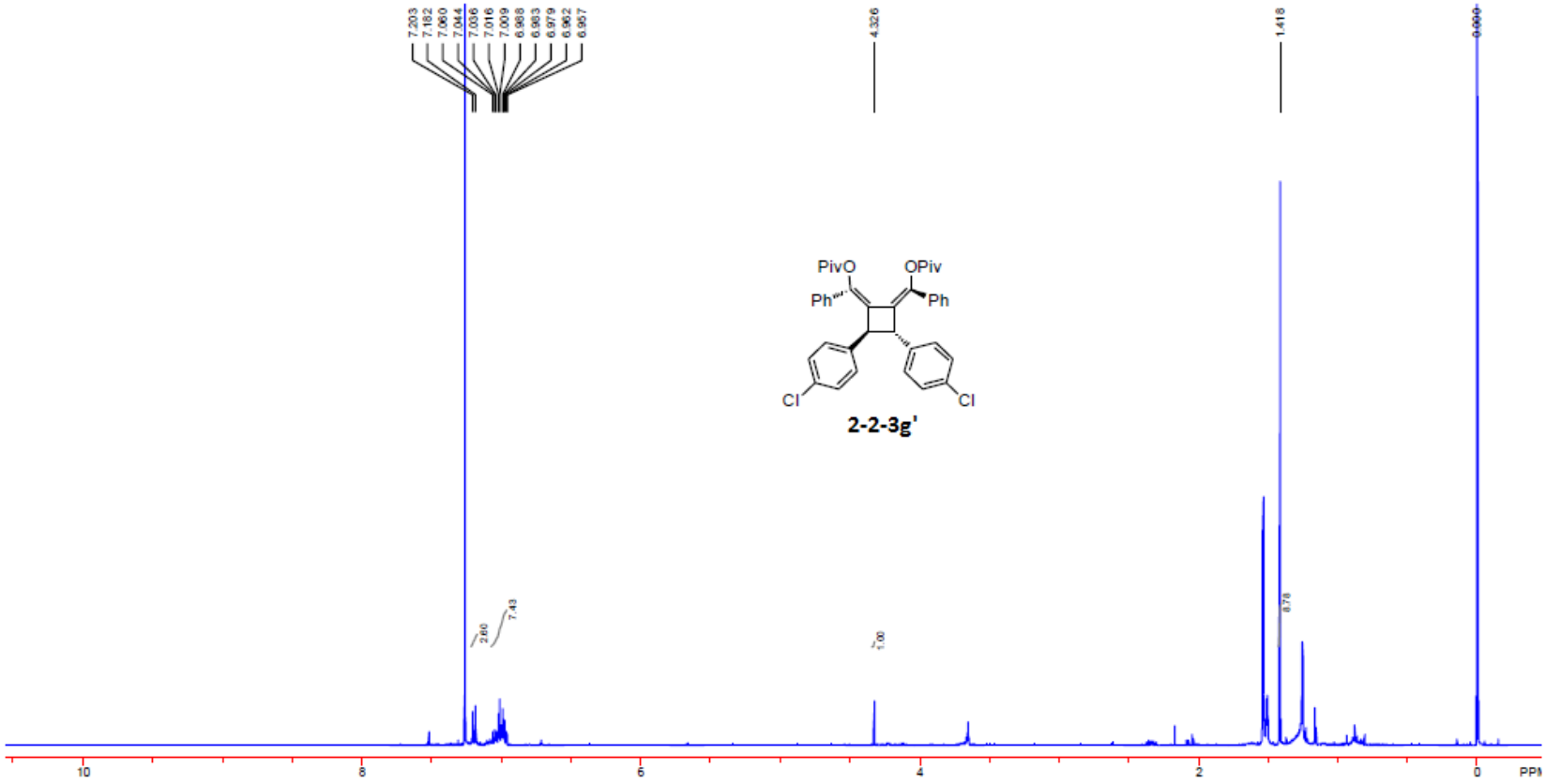
2-2-3f'

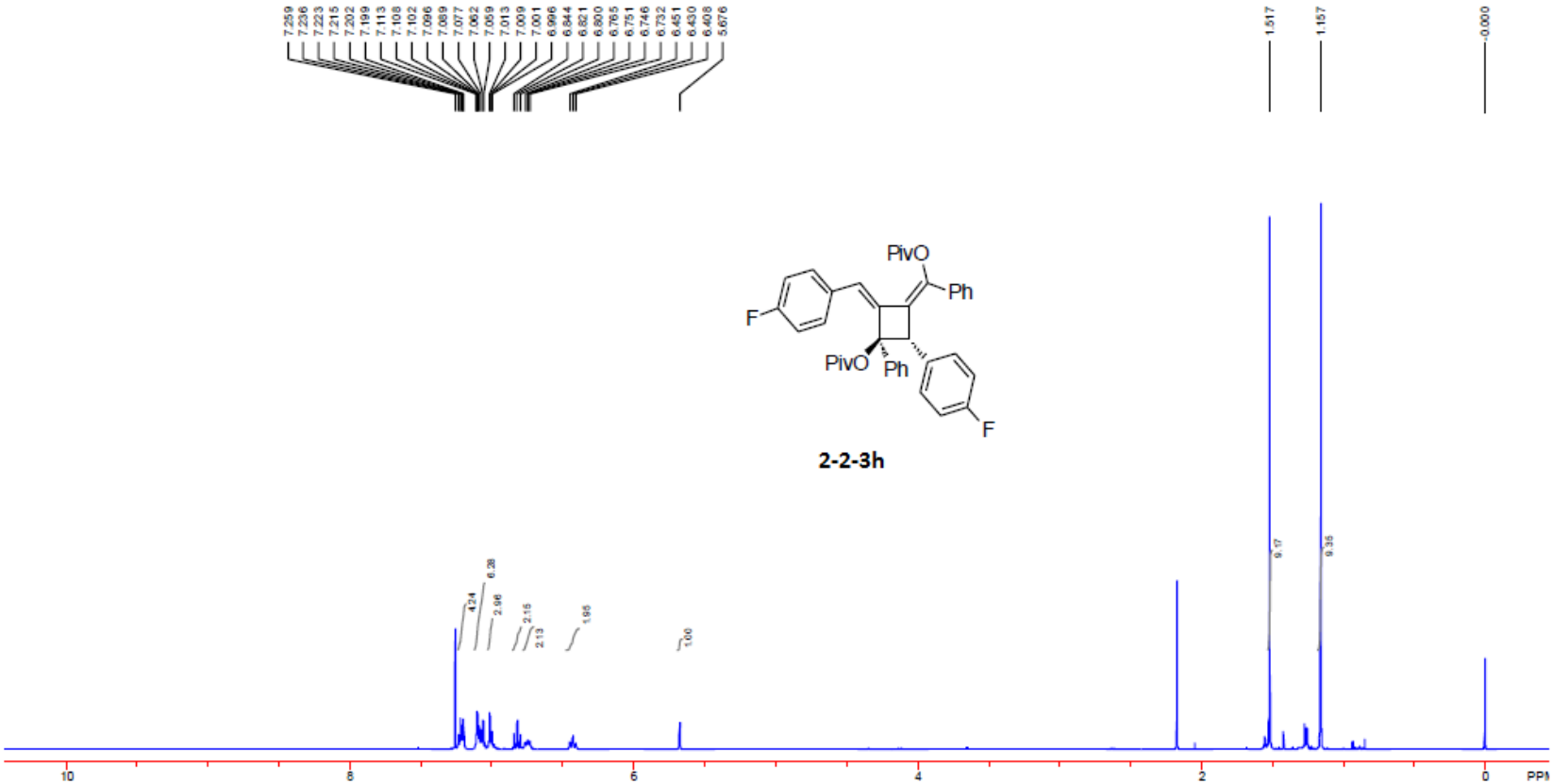

177.695
140.475
137.148
132.654
131.151
130.930
130.083
128.473
127.763
126.764
120.591
77.214
77.000
76.786
59.138
39.460
27.366
200
180
160
140
120
100
80
60
40
20
0

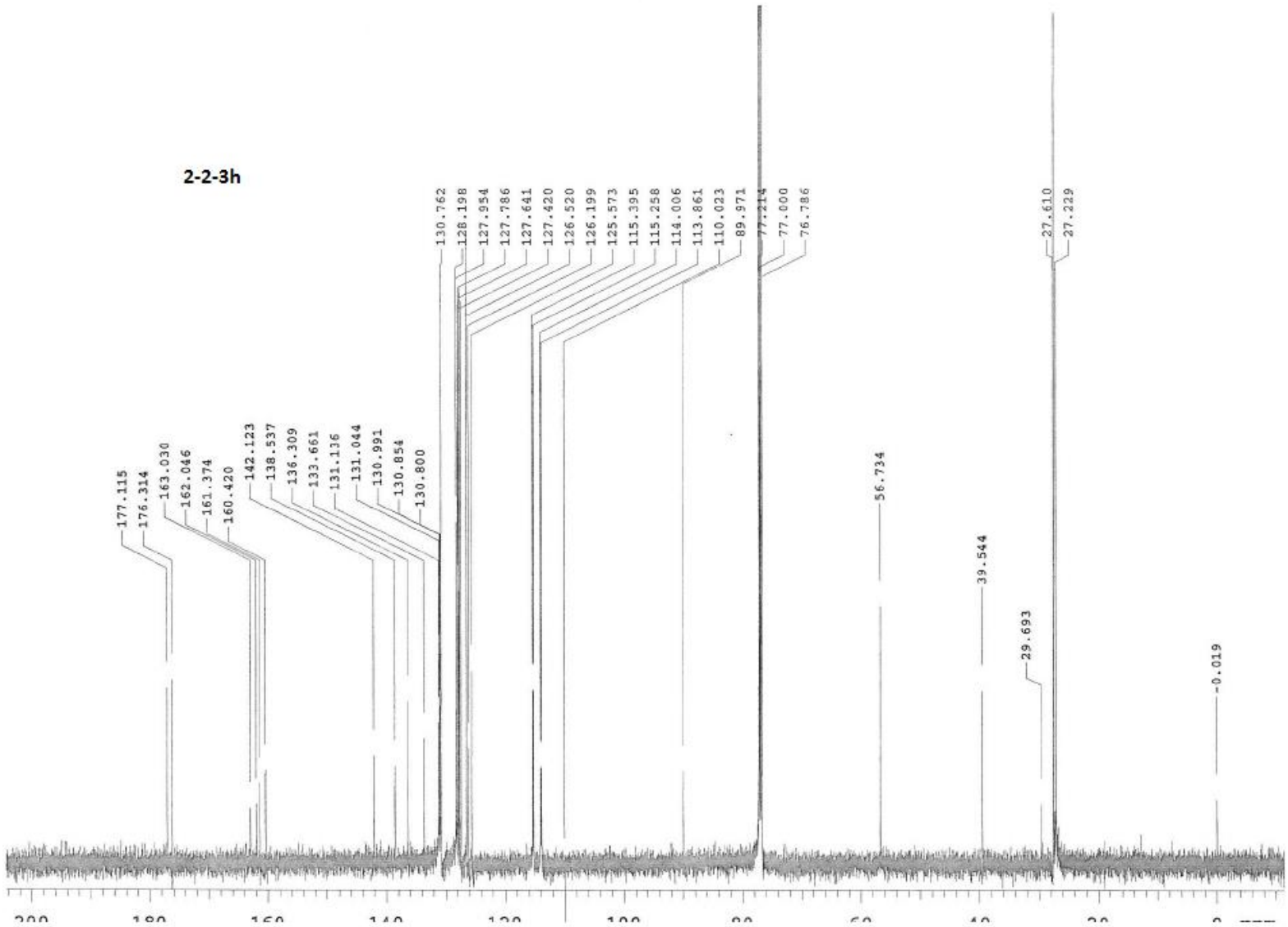

7.209
7.203
7.198
7.189
7.185
7.173
7.157
7.151
7.113
7.109
7.103
7.097
7.090
7.081
7.074
7.066
7.060
7.027
7.023
7.009
6.713
5.661
1.514
1.167
-0.000
PivO
Ph
Cl
PivO
Ph
Cl
2-2-3g
4.18
8.49
3.46
1.60
3.80
1.00
9.32
8.98
10
8
6
4
2
0
PPM

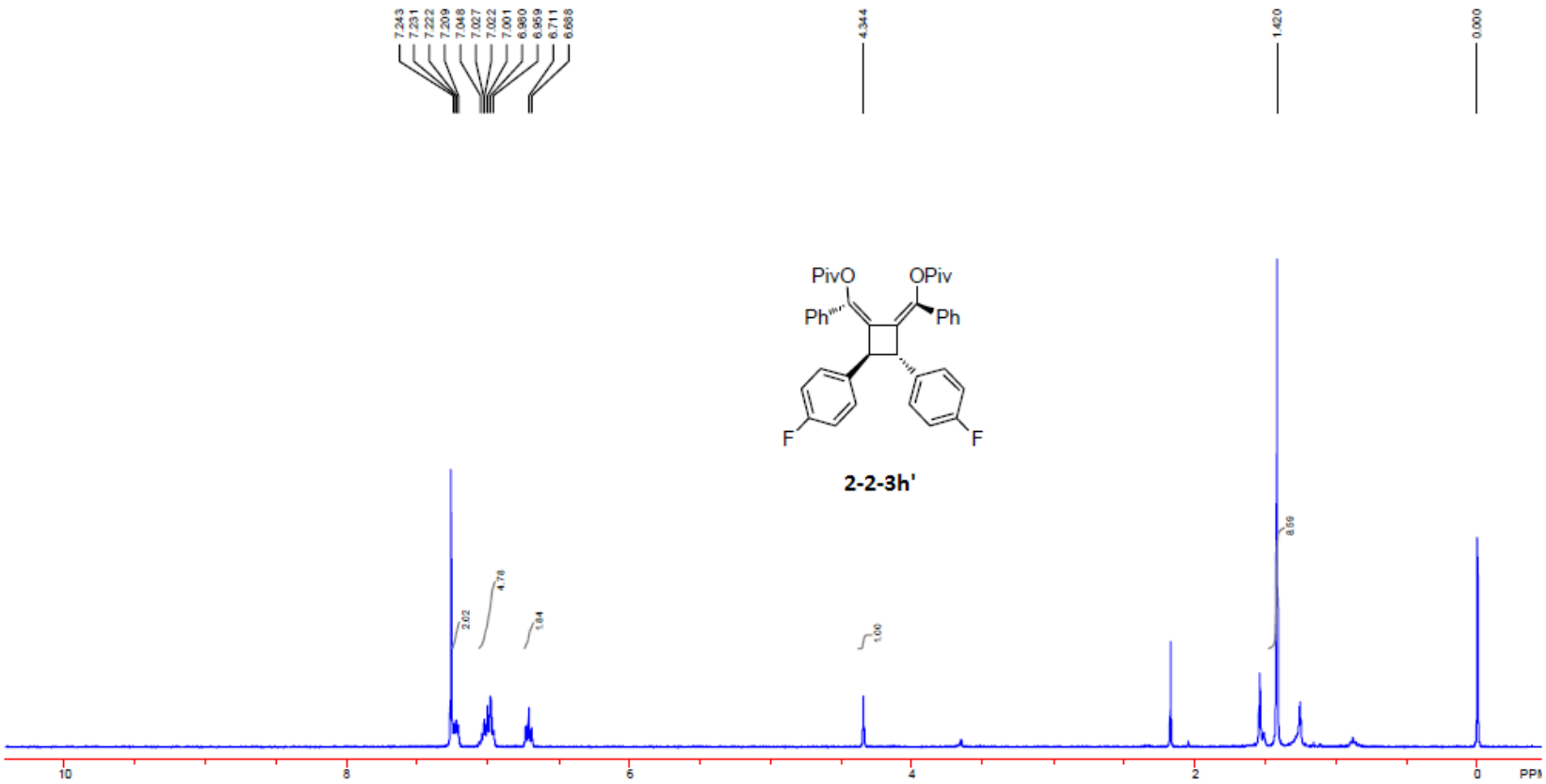
2-2-3g

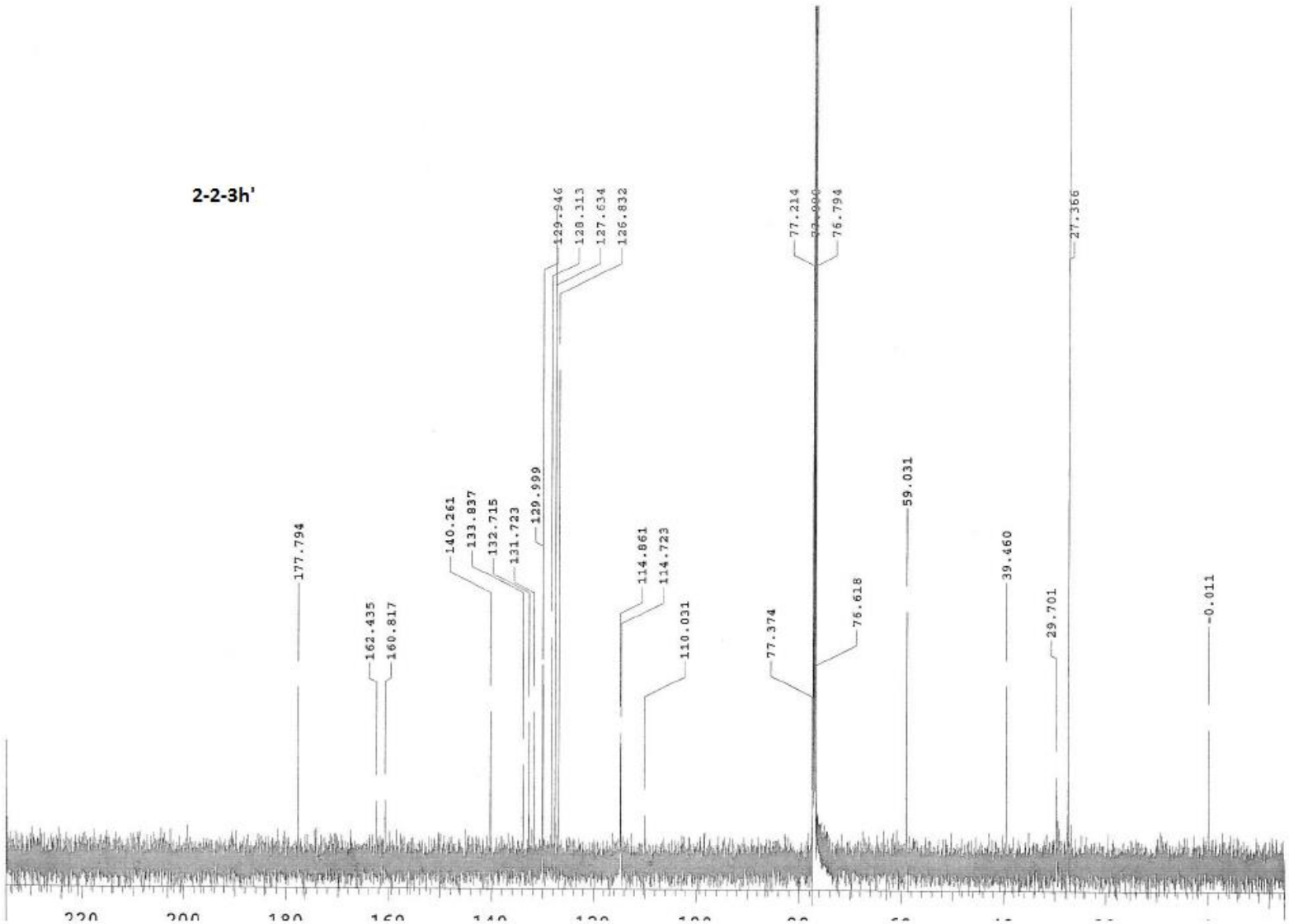

177.115
176.245
143.313
142.543
139.651
136.027
133.577
133.554
133.310
132.929
131.883
130.617
130.449
129.724
129.587
129.259
128.679
128.503
128.389
128.351
128.190
128.023
127.931
127.740
127.328
127.252
126.779
126.520
125.741
125.482
122.506
89.819
77.214
77.000
76.794
56.856
39.605
39.551
27.618
27.259
26.817
200
180
160
140
120
100
80
60
40
20
0

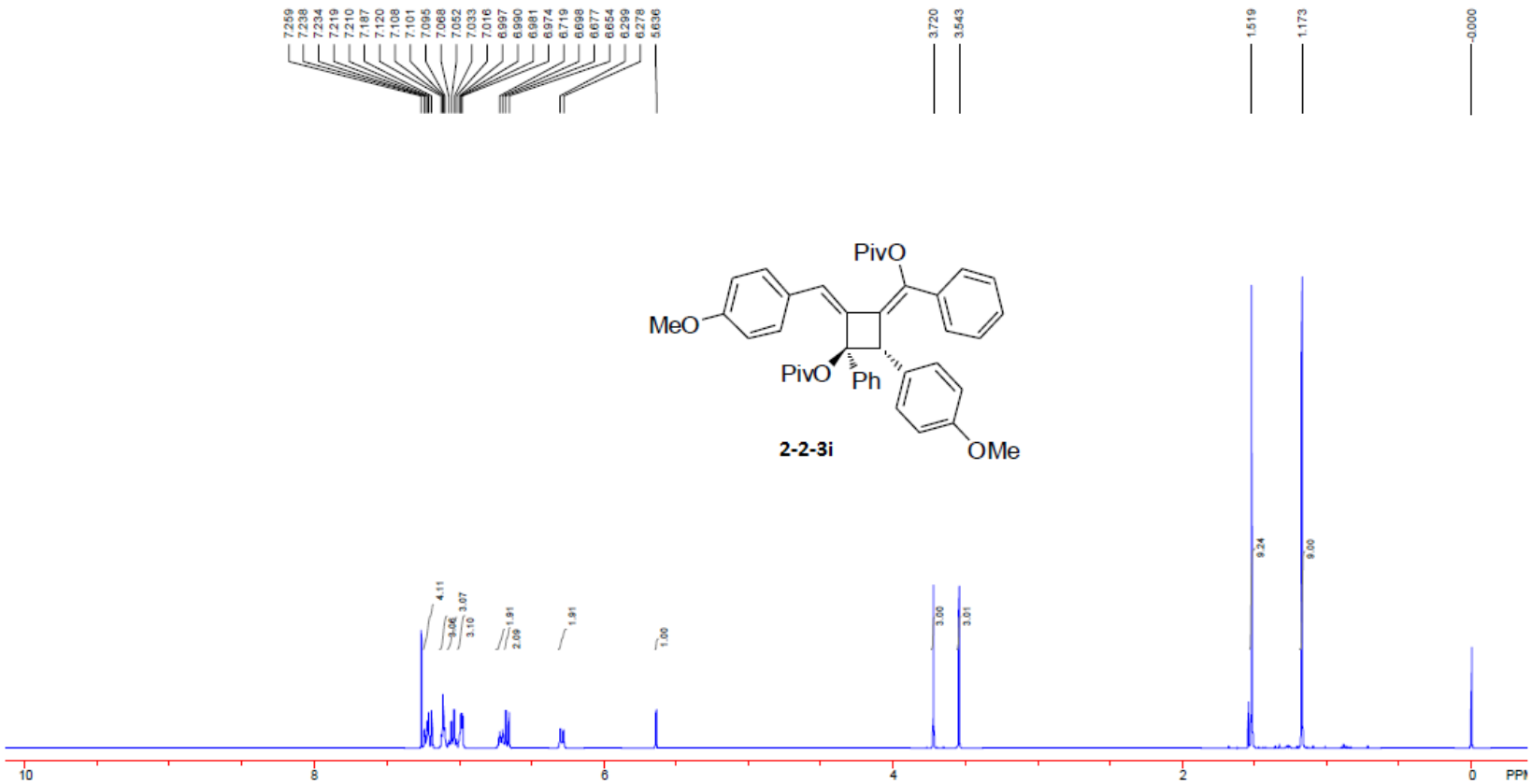

7.203
7.162
7.060
7.044
7.036
7.016
7.009
6.988
6.983
6.979
6.962
6.957
4.326
1.418
0.000
2.60
7.43
1.00
0.78
PivO
OPiv
Ph
Ph
Cl
Cl
2-2-3g'
10
8
6
4
2
0
PPM

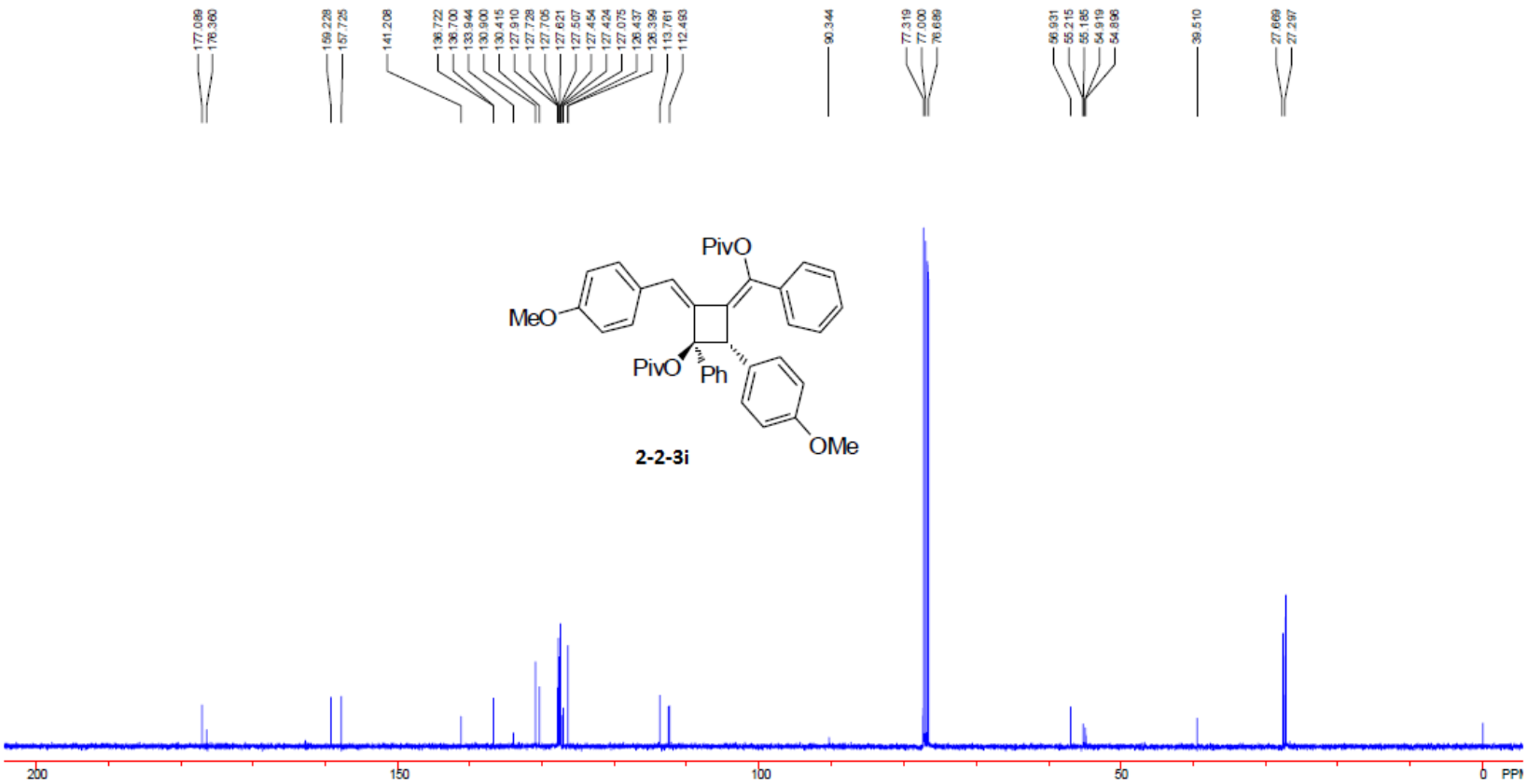

7.259
7.236
7.223
7.215
7.202
7.199
7.113
7.108
7.102
7.096
7.089
7.077
7.062
7.059
7.013
7.009
7.001
6.996
6.844
6.821
6.800
6.765
6.751
6.746
6.732
6.451
6.430
6.408
5.676
1.517
1.157
0.000
PivO
Ph
F
PivO
Ph
F
2-2-3h
4.24
6.28
2.96
2.15
2.13
1.98
1.00
9.17
9.35
10
8
6
4
2
0
PPM

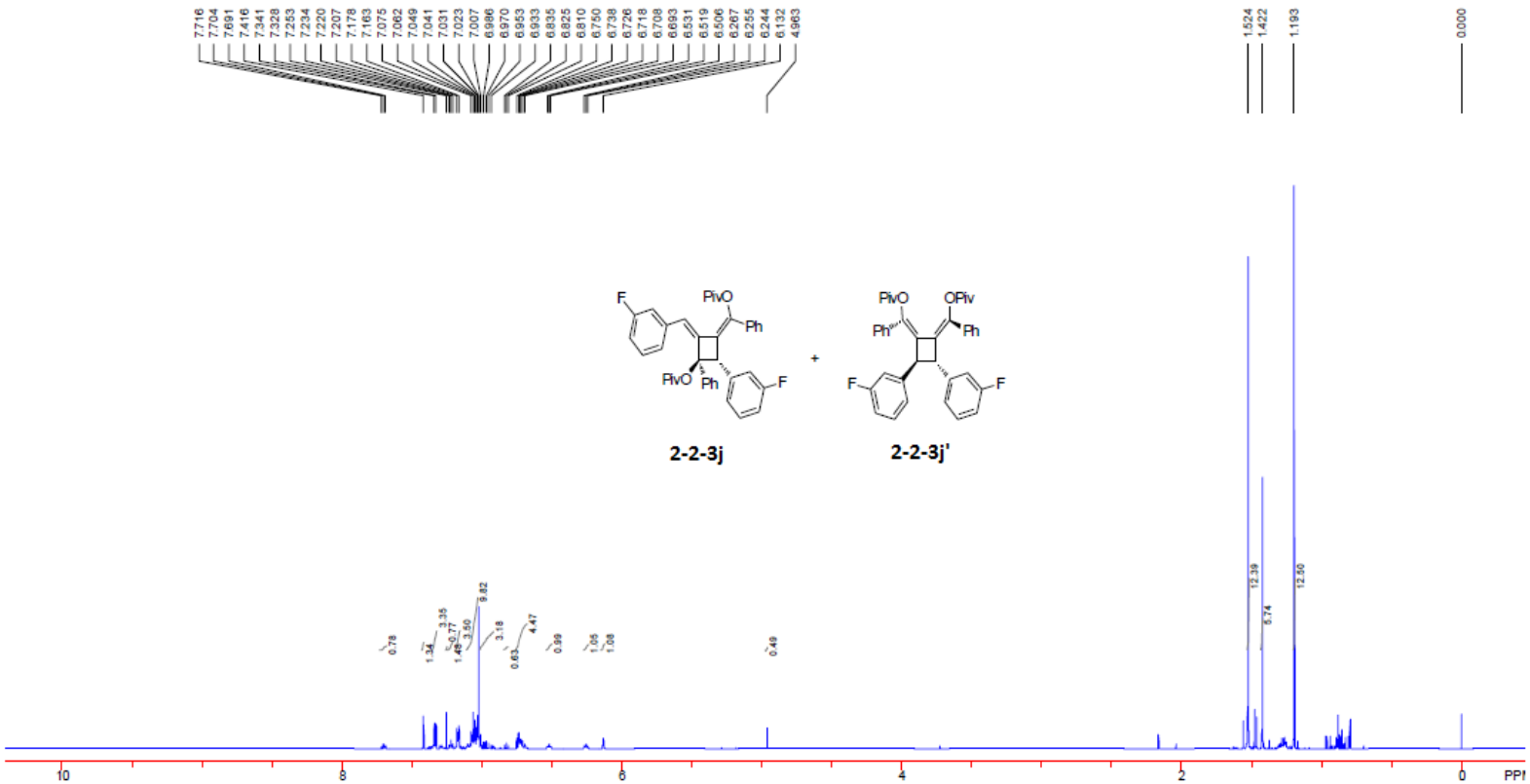

2-2-3h
177.115
176.314
163.030
162.046
161.374
160.420
142.123
138.537
136.309
133.661
131.136
131.044
130.991
130.854
130.800
130.762
128.198
127.954
127.786
127.641
127.420
126.520
126.199
125.573
115.395
115.258
114.006
113.861
110.023
89.971
77.214
77.000
76.786
56.734
39.544
29.693
27.610
27.229
-0.019

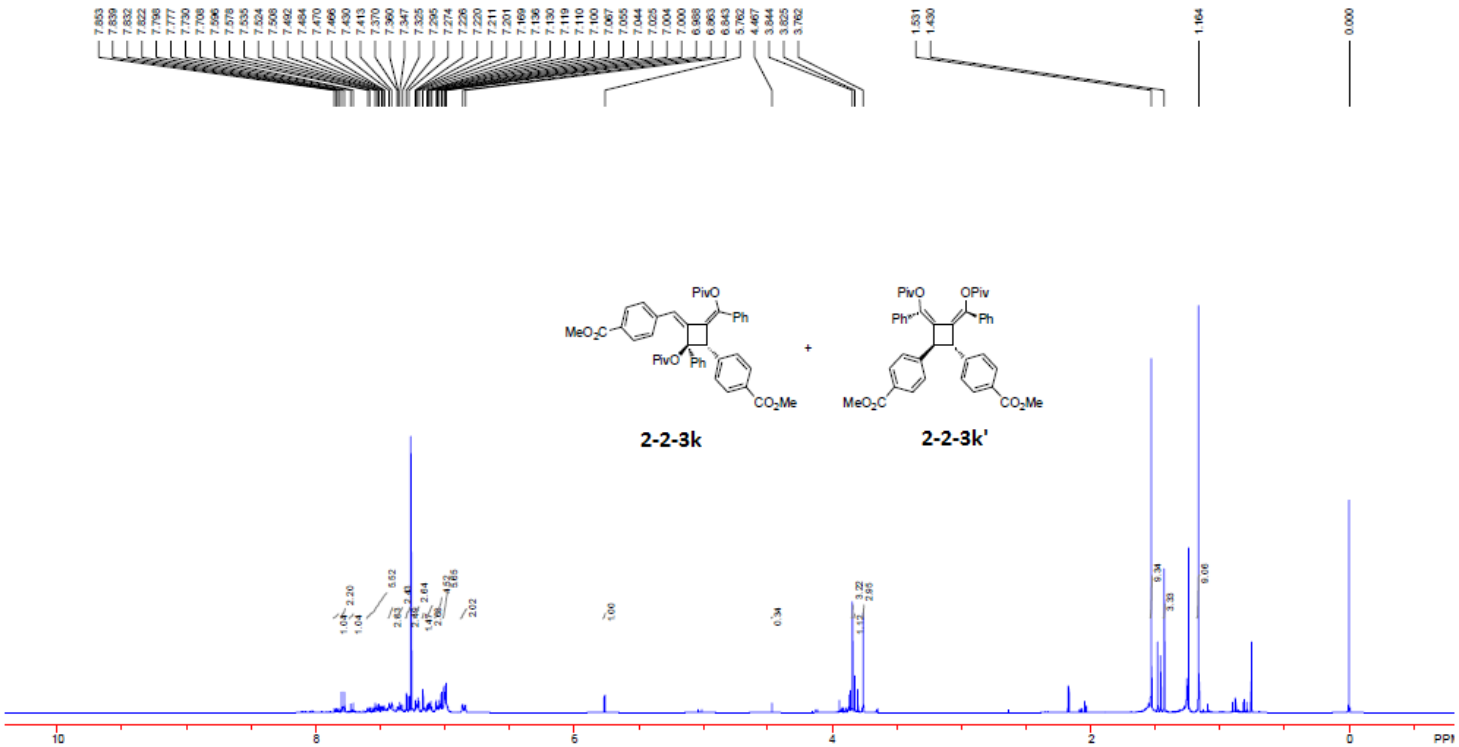

7.243
7.231
7.222
7.209
7.048
7.027
7.022
7.001
6.980
6.959
6.711
6.688
4.344
1.420
0.000
PivO
OPiv
Ph
Ph
F
F
2-2-3h'
2.02
4.78
1.04
1.00
8.69
10
8
6
4
2
0
PPM

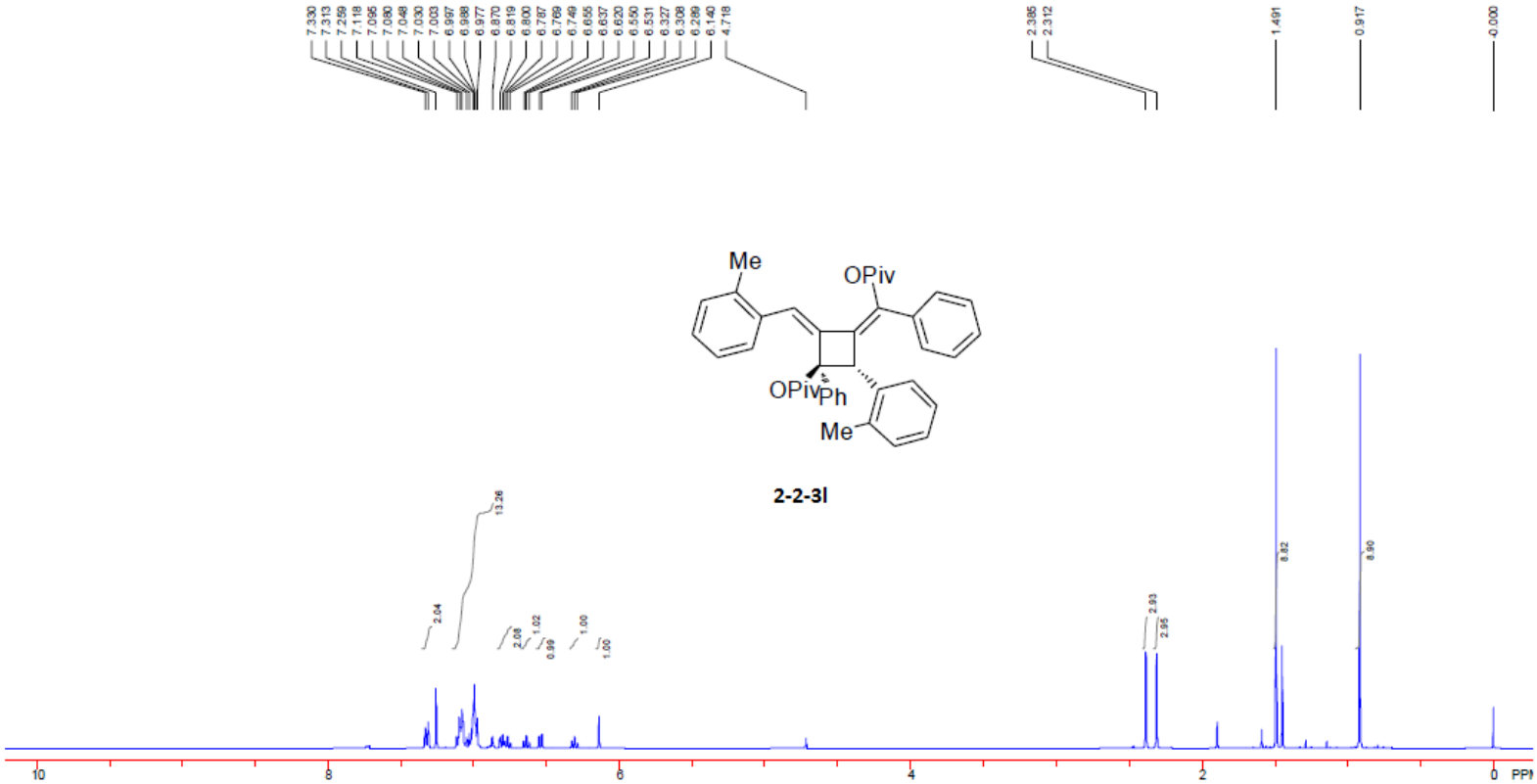

2-2-3h'
177.794
162.435
160.817
140.261
133.837
132.715
131.723
129.999
129.946
128.313
127.634
126.832
114.861
114.723
110.031
77.374
77.214
76.794
76.618
59.031
39.460
29.701
27.366
-0.011

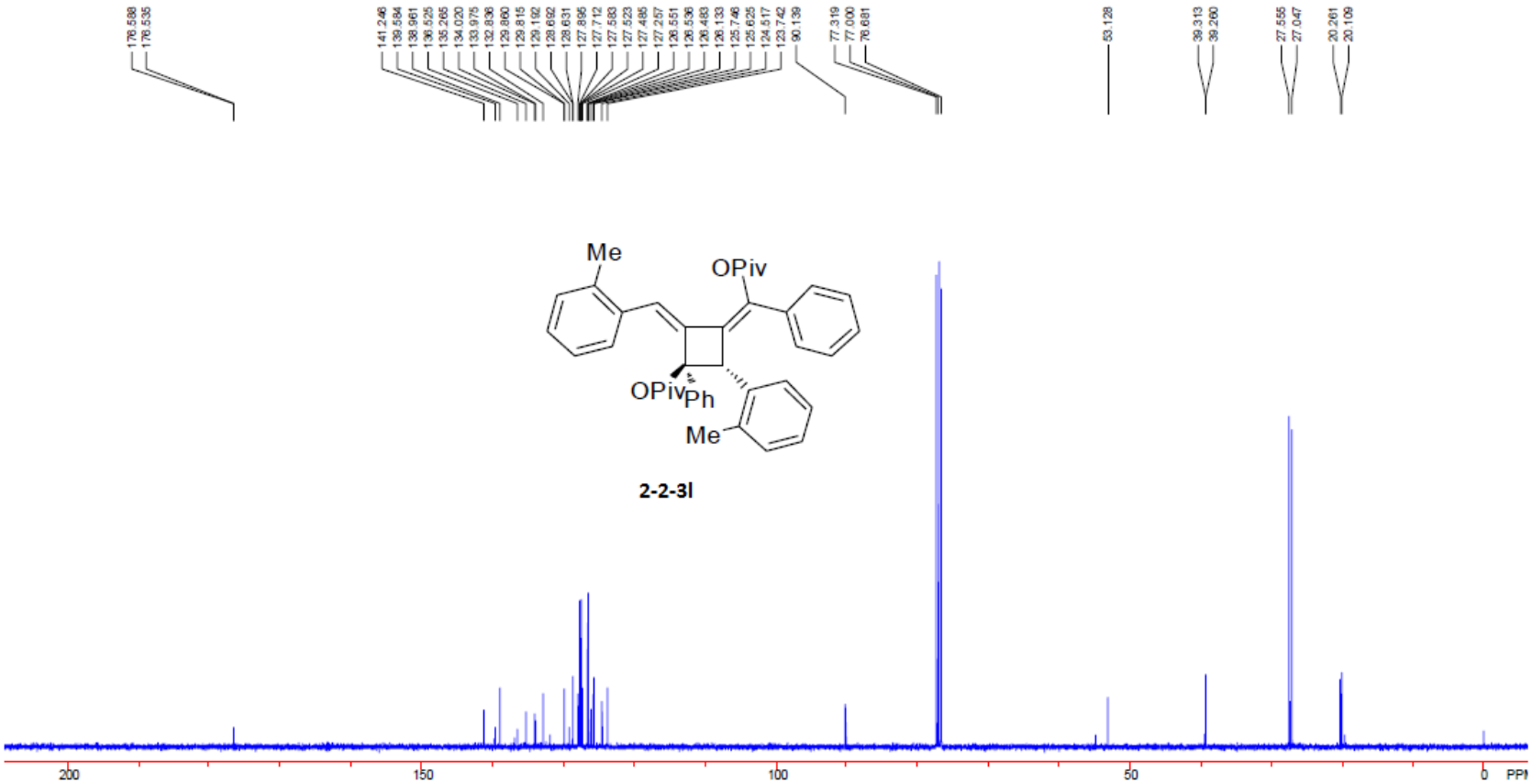

7.259
7.238
7.234
7.219
7.210
7.187
7.120
7.108
7.101
7.095
7.068
7.052
7.033
7.016
6.997
6.990
6.981
6.974
6.719
6.698
6.677
6.654
6.299
6.278
5.636
3.720
3.543
1.519
1.173
0.000
PivO
MeO
PivO
Ph
OMe
2-2-3i
4.11
3.06
3.07
3.10
1.91
2.09
1.91
1.00
3.00
3.01
9.24
9.00
10
8
6
4
2
0
PPM

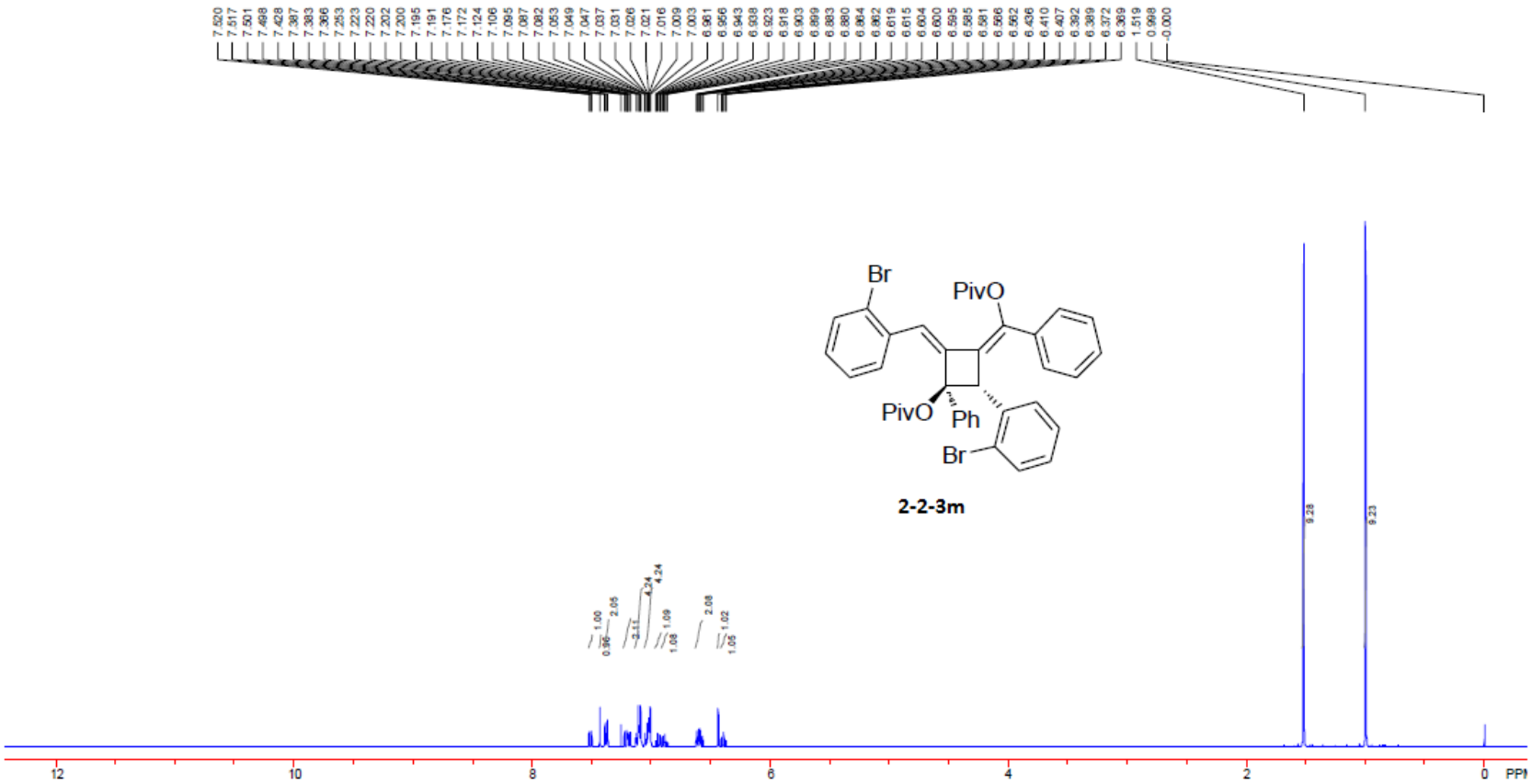

177.089
176.360
159.228
157.725
141.208
136.722
136.700
133.944
130.900
130.415
127.910
127.728
127.705
127.621
127.507
127.454
127.424
127.075
126.437
126.399
113.761
112.493
90.344
77.319
77.000
76.689
56.931
55.215
55.185
54.919
54.896
39.510
27.669
27.297
PivO
MeO
PivO
Ph
OMe
2-2-3i
200
150
100
50
0
PPM

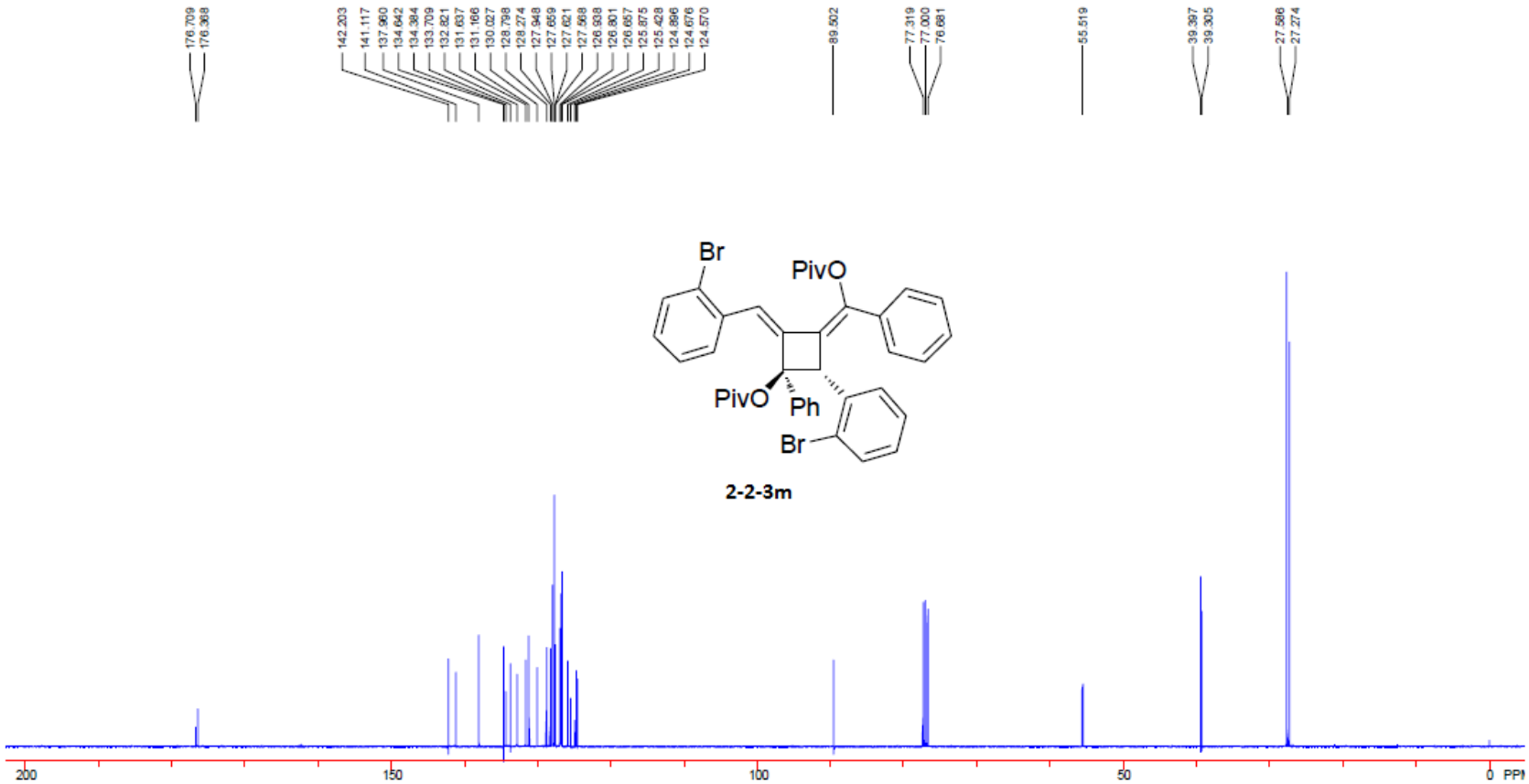

7.716
7.704
7.691
7.416
7.341
7.328
7.253
7.234
7.220
7.207
7.178
7.163
7.075
7.062
7.049
7.041
7.031
7.023
7.007
6.986
6.970
6.953
6.933
6.835
6.825
6.810
6.750
6.738
6.726
6.718
6.708
6.693
6.531
6.519
6.506
6.267
6.255
6.244
6.132
4.963
1.524
1.422
1.193
0.000
F
PivO
Ph
PivO
Ph
F
+
PivO
OPiv
Ph
Ph
F
F
2-2-3j
2-2-3j'
0.78
1.34
3.35
0.77
1.40
3.50
9.82
3.18
0.63
4.47
0.99
1.06
1.06
0.49
12.39
5.74
12.50
10
8
6
4
2
0
PPM

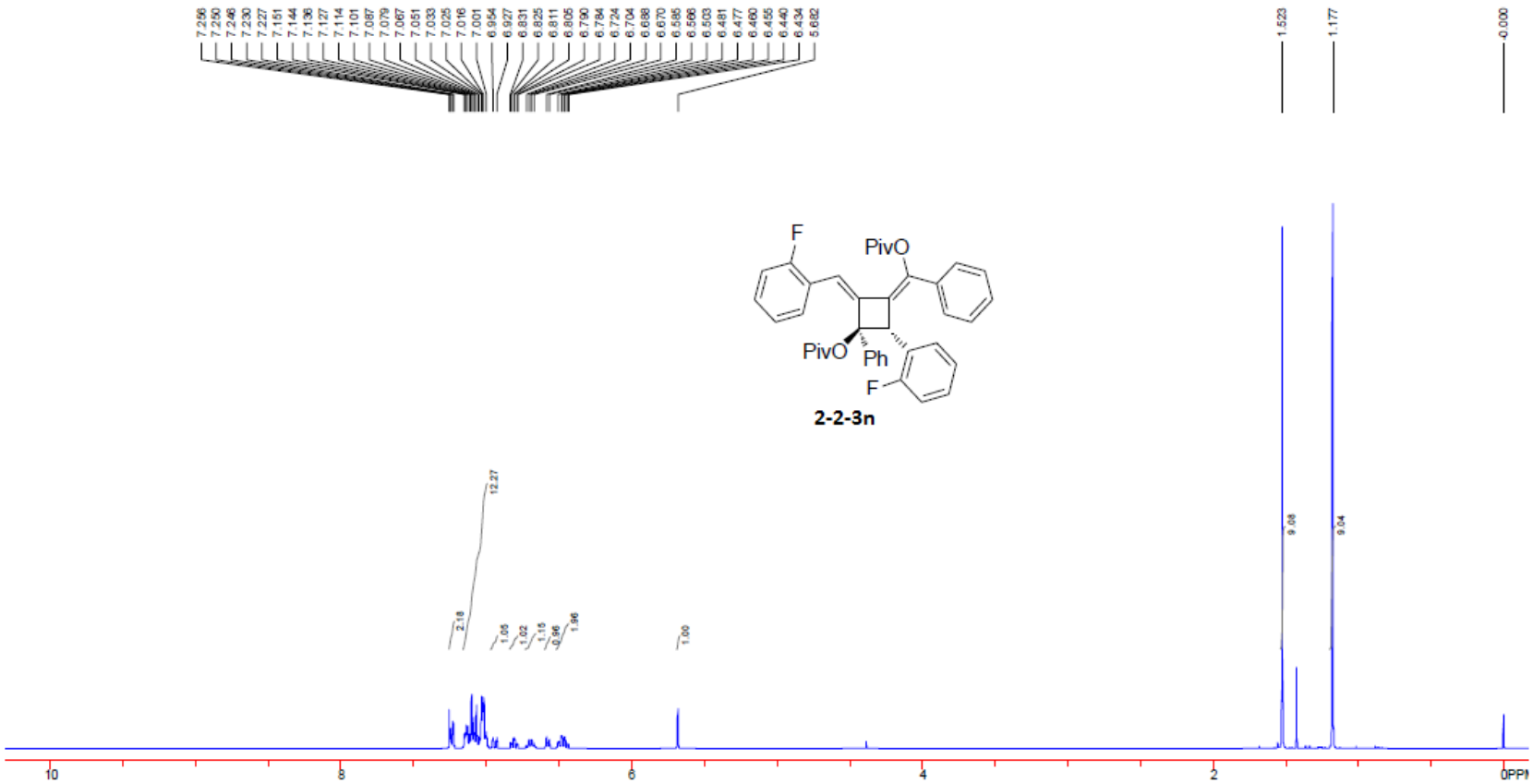

PivO
Ph
MeO2C
PivO
Ph
CO2Me
2-2-3k
PivO
OPiv
Ph
Ph
MeO2C
CO2Me
2-2-3k'
10
8
6
4
2
0
PPM

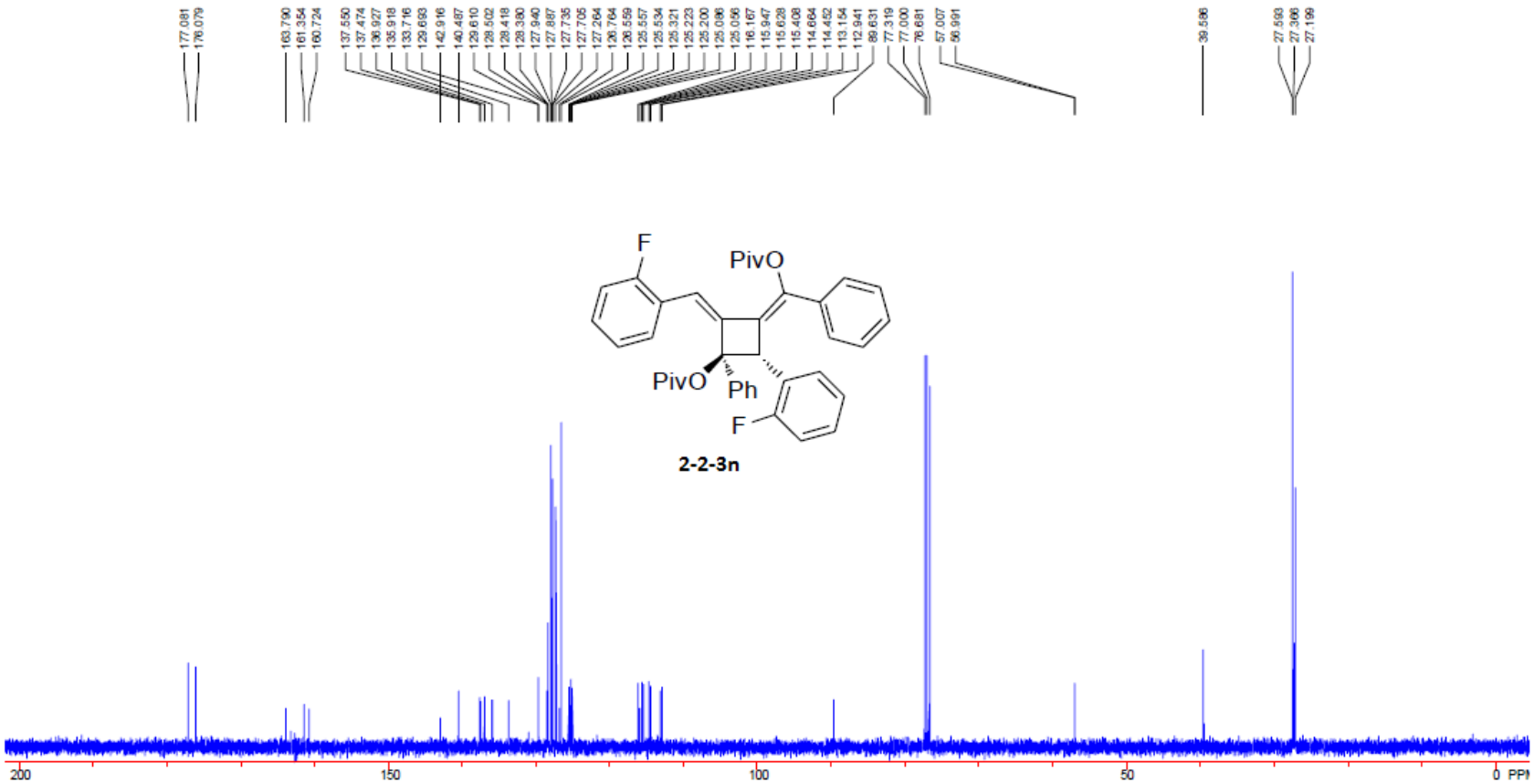

7.330
7.313
7.259
7.118
7.095
7.080
7.048
7.030
7.003
6.997
6.988
6.977
6.870
6.819
6.800
6.787
6.769
6.749
6.655
6.637
6.620
6.550
6.531
6.327
6.308
6.289
6.140
4.718
2.385
2.312
1.491
0.917
0.000
Me
OPiv
OPiv
Ph
Me
2-2-3l
13.26
2.04
2.08
1.02
0.99
1.00
1.00
2.93
2.95
8.82
8.90
10
8
6
4
2
0
PPM

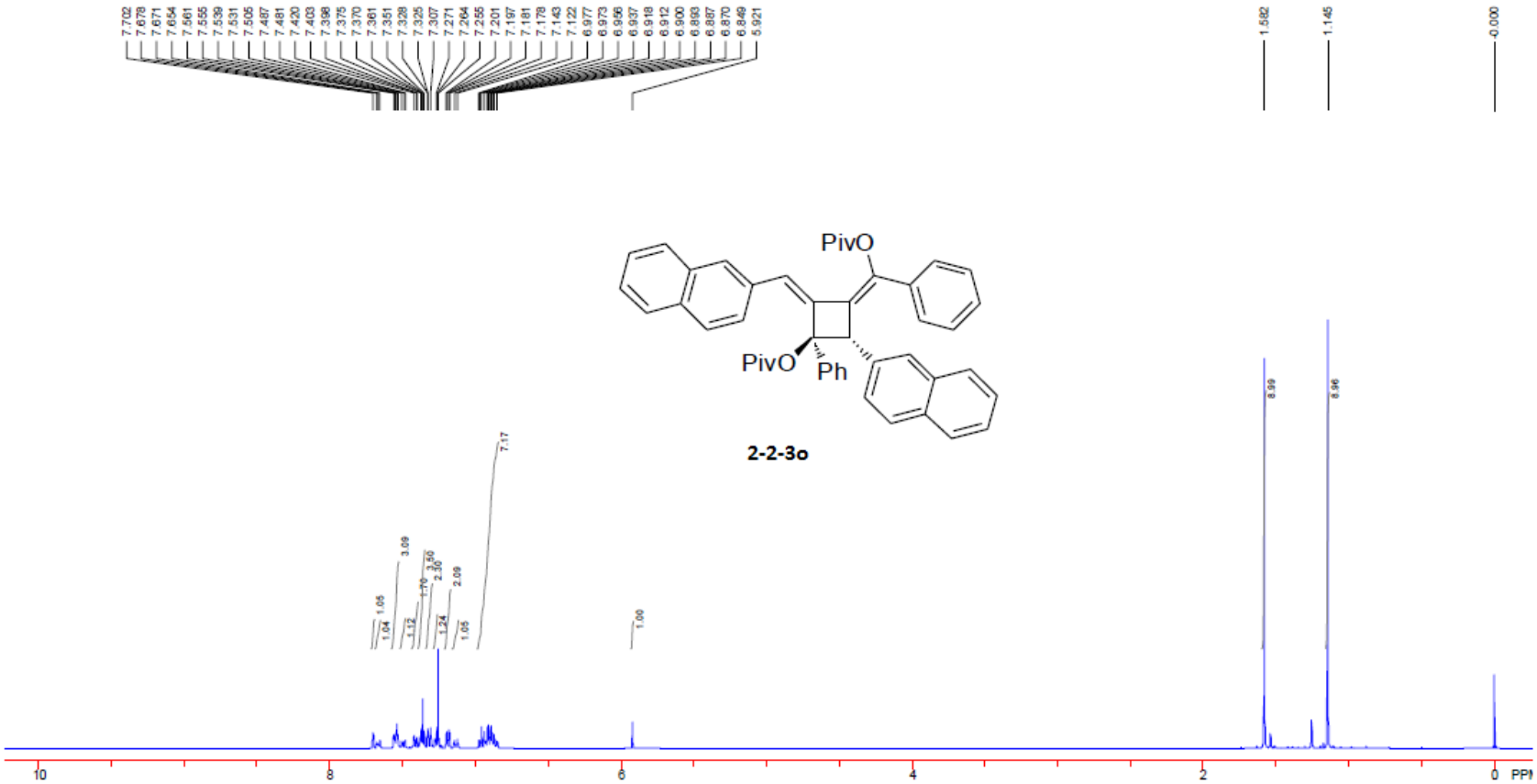

176.598
176.535
141.246
139.584
138.961
136.525
135.265
134.020
133.975
132.836
129.860
129.815
129.192
128.692
128.631
127.895
127.712
127.583
127.523
127.485
127.257
126.551
126.536
126.483
126.133
125.746
125.625
124.517
123.742
90.139
77.319
77.000
76.681
53.128
39.313
39.260
27.555
27.047
20.261
20.109
Me
OPiv
OPiv
Ph
Me
2-2-3l
200
150
100
50
0
PPM

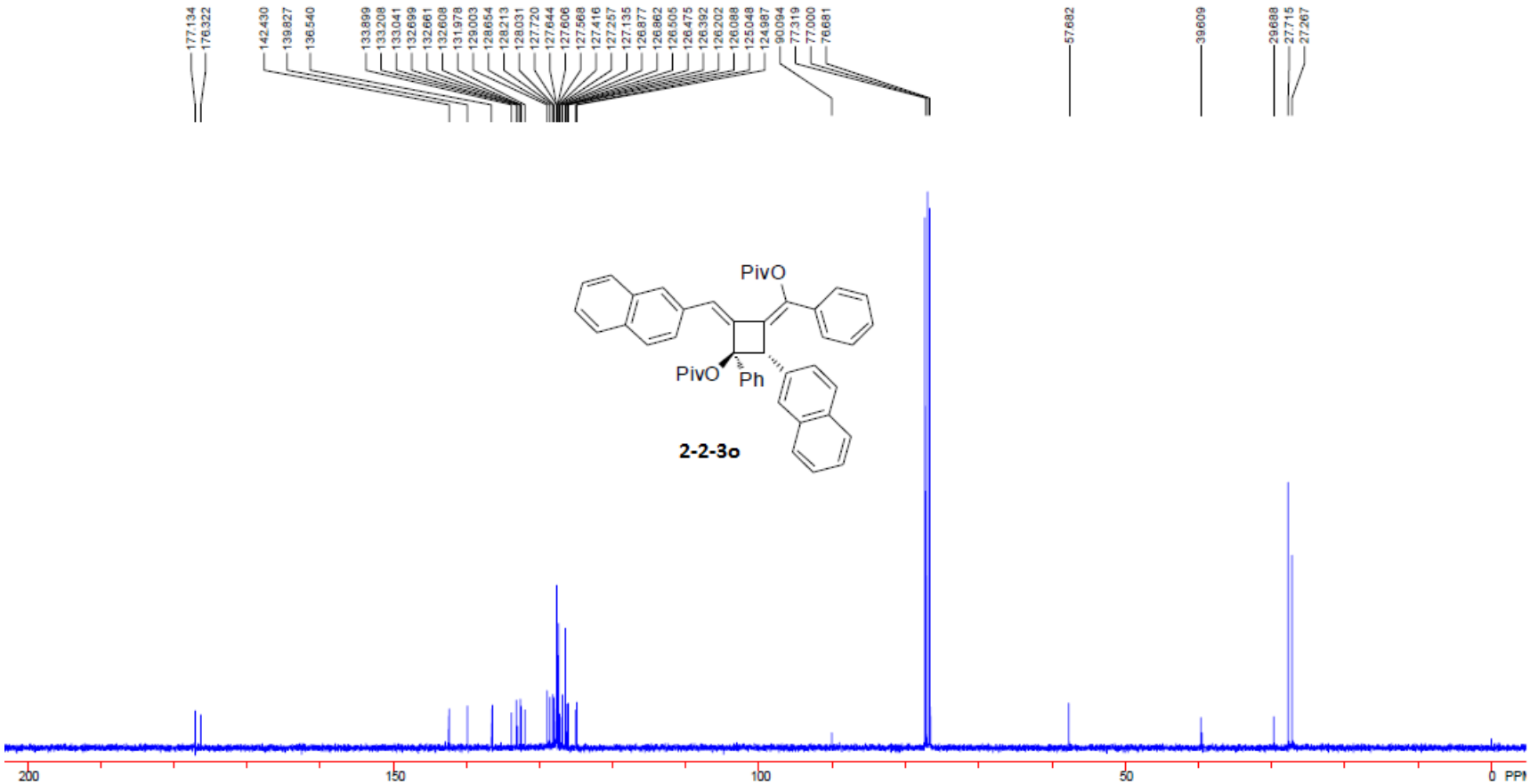

Br
PivO
PivO
Ph
Br
2-2-3m
12
10
8
6
4
2
0
PPM

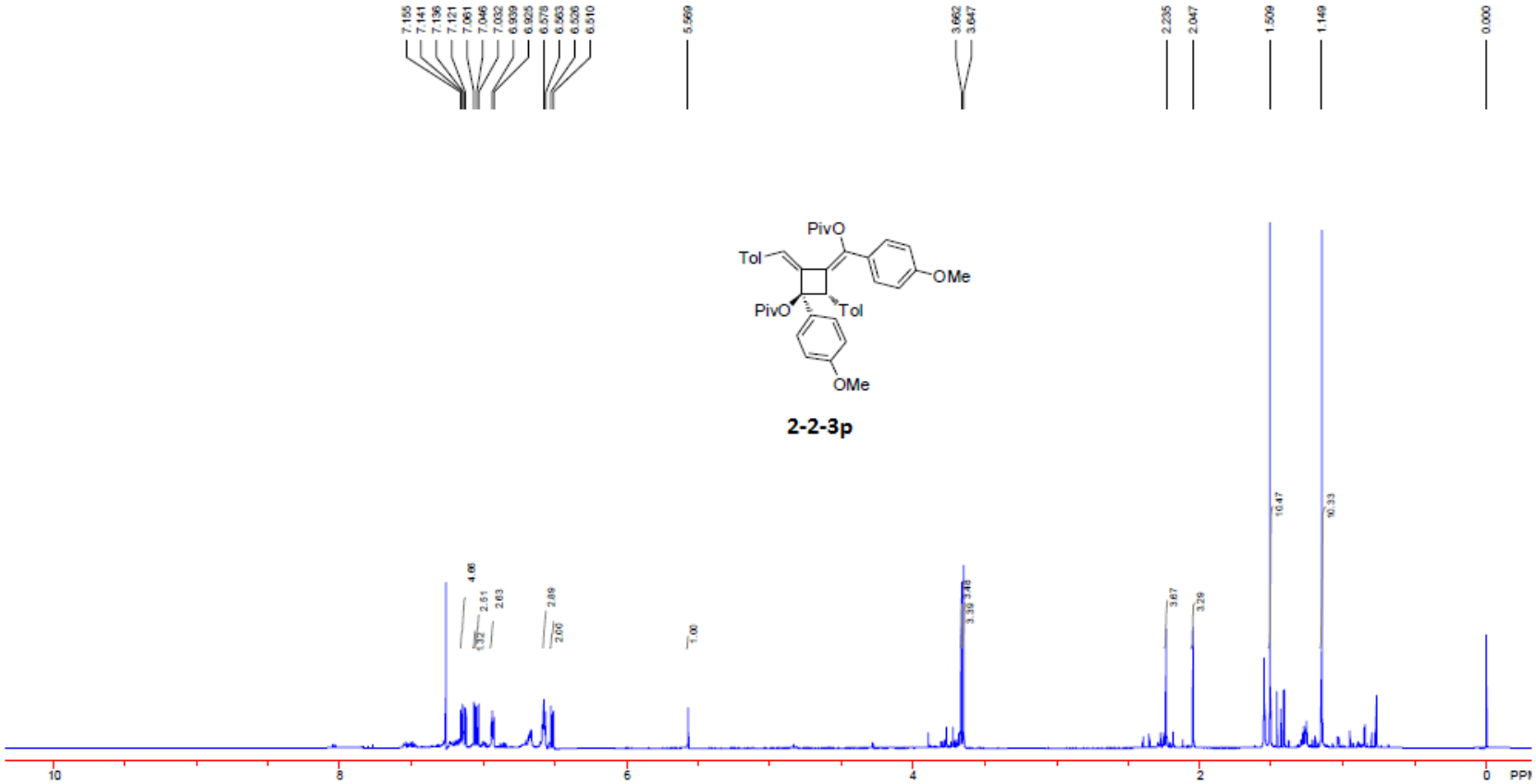

176.709
176.368
142.203
141.117
137.960
134.642
134.384
133.709
132.821
131.637
131.166
130.027
128.798
128.274
127.948
127.659
127.621
127.568
126.938
126.801
126.657
125.875
125.428
124.886
124.676
124.570
89.502
77.319
77.000
76.681
55.519
39.397
39.305
27.586
27.274
Br
PivO
PivO
Ph
Br
2-2-3m
200
150
100
50
0 PPM


F
PivO
PivO
Ph
F
2-2-3n
10
8
6
4
2
0PPM

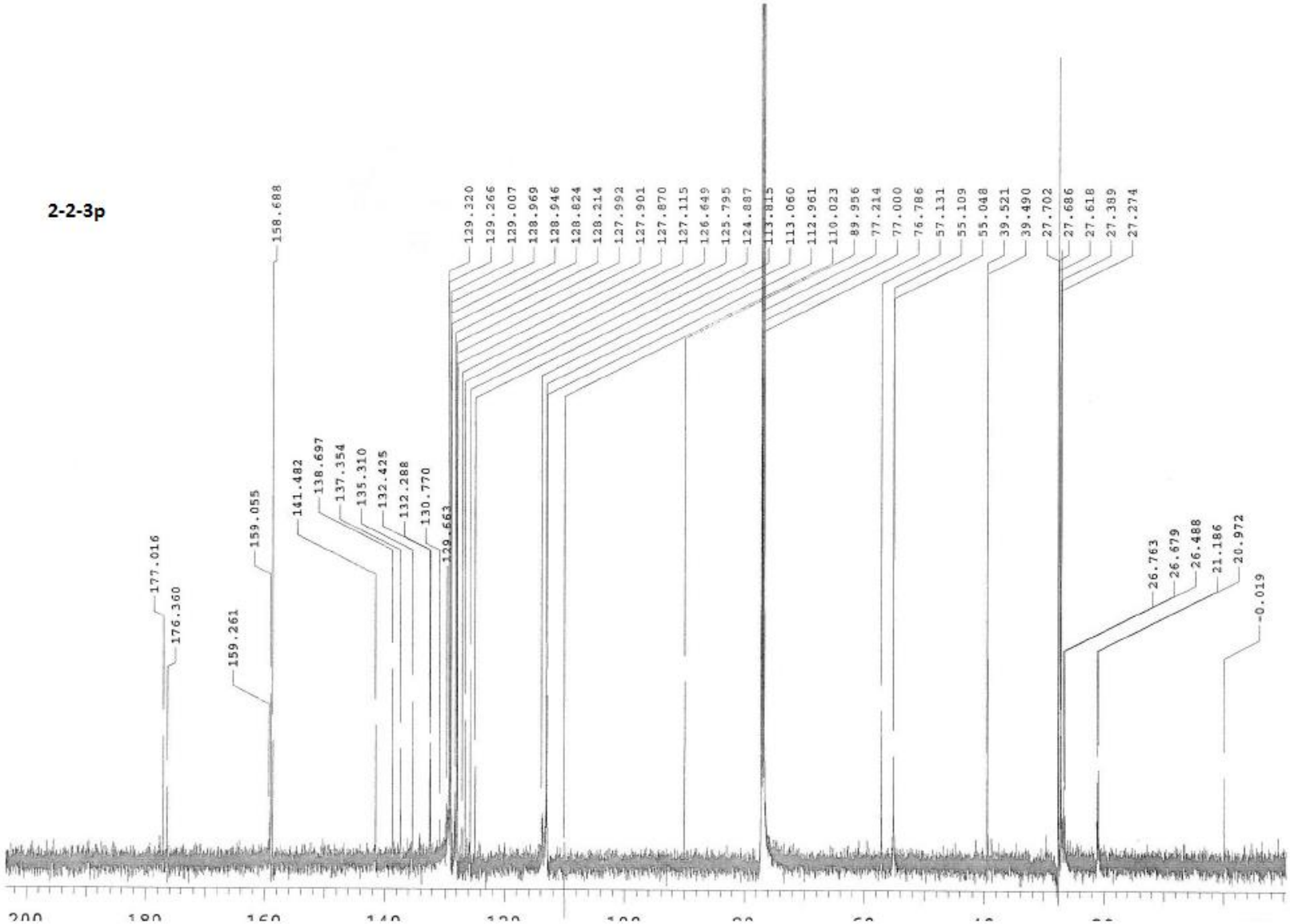

177.081
176.079
163.790
161.354
160.724
137.550
137.474
136.927
135.918
133.716
129.693
142.916
140.487
129.610
128.502
128.418
128.380
127.940
127.887
127.735
127.705
127.264
126.764
126.559
125.557
125.534
125.321
125.223
125.200
125.086
125.066
116.167
115.947
115.628
115.408
114.664
114.452
113.154
112.941
88.631
77.319
77.000
76.681
57.007
56.991
38.586
27.593
27.366
27.199
F
PivO
PivO
Ph
F
2-2-3n
200
150
100
50
0 PPM


PivO
PivO
Ph
2-2-3o
7.702
7.678
7.671
7.654
7.561
7.555
7.539
7.531
7.505
7.487
7.481
7.420
7.403
7.398
7.375
7.370
7.361
7.351
7.329
7.325
7.307
7.271
7.264
7.255
7.201
7.197
7.181
7.178
7.143
7.122
6.977
6.973
6.956
6.937
6.918
6.912
6.900
6.893
6.887
6.870
6.849
5.921
1.582
1.145
0.000
7.17
3.09
1.05
1.04
1.12
1.70
3.50
2.30
2.09
1.24
1.05
1.00
8.99
8.96
10
8
6
4
2
0
PPM


177.134
176.322
142.430
139.827
136.540
133.899
133.208
133.041
132.699
132.661
132.608
131.978
129.003
128.654
128.213
128.031
127.720
127.644
127.606
127.568
127.416
127.257
127.135
126.877
126.862
126.505
126.475
126.392
126.202
126.088
125.048
124.987
90.094
77.319
77.000
76.681
57.682
39.609
29.688
27.715
27.267
PivO
PivO
Ph
2-2-3o
200
150
100
50
0 PPM


7.155
7.141
7.136
7.121
7.061
7.046
7.032
6.939
6.925
6.578
6.563
6.526
6.510
5.569
3.662
3.647
2.235
2.047
1.509
1.149
0.000
PivO
Tol
OMe
PivO
Tol
OMe
2-2-3p
4.06
2.51
2.63
2.89
2.00
1.00
3.39
3.48
3.67
3.29
10.47
90.33
10
8
6
4
2
0
PPM

2-2-3p


177.016
176.360
159.261
159.055
158.688
141.482
138.697
137.354
135.310
132.425
132.288
130.770
129.663
129.320
129.266
129.007
128.969
128.946
128.824
128.214
127.992
127.901
127.870
127.115
126.649
125.795
124.887
113.815
113.060
112.961
110.023
89.956
77.214
77.000
76.786
57.131
55.109
55.048
39.521
39.490
27.702
27.686
27.618
27.389
27.274
26.763
26.679
26.488
21.186
20.972
-0.019
200
180
160
140
120
100
80
60
40
20

Chapter Three: Synthesis and characterization of bis-N-2-aryl triazole as efficient fluorescence probe

I. General methods and materials and compounds characterization:

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.0 ppm) or *d*6-DMSO (δ 39.5 ppm) for ^{13}C NMR.

Representative procedure for the preparation of 2-(anthracen-9-yl)-4-phenyl-2*H*-1,2,3-triazole (3-1e) (*Condition A*) To a solution of 9-bromoanthracene (514 mg, 2.0 mmol, 1.0 eq.) in dry DMSO (4 ml, 0.5 M), were added successively 4-Phenyl-1,2,3-NH-triazole (725 mg, 5.0 mmol, 2.5 eq.) and CuI (76 mg, 20%), L-Proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 eq.) under N_2 atmosphere. The mixture was stirred at 120°C and monitored by TLC. After the reaction is completed, the reaction was quenched with brine and extracted with ethyl acetate for three times. Organic phases were combined and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (Hexane - EtOAc v/v 20:1), giving desired product as yellow solid (yield: 340 mg, 53%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.66 (s, 1H), 8.37 (s, 1H), 8.32 (dd, *J* = 5.8, 3.3 Hz, 1H), 8.09 (dd, *J* = 7.1, 1.9 Hz, 2H), 8.00-7.98 (m, 2H), 7.79 (dd, *J* = 5.8, 3.3 Hz, 1H), 7.51-7.44 (m, 7H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 148.94, 134.1, 132.5, 131.3, 129.5, 129.00, 128.85, 128.70, 128.2, 127.6, 127.2, 126.2, 125.7, 122.6; HRMS Calculated for $C_{22}H_{15}N_3$ $[M+H]^+$: 322.1338, Found: 322.1342.

Representative procedure for the preparation of 1-(anthracen-9-yl)-4-phenyl-1*H*-1,2,3-triazole (3-1f) (*Condition A*) To a solution of 9-bromoanthracene (514 mg, 2.0 mmol, 1.0 eq.) in dry DMSO (4 ml, 0.5 M), were added successively 4-Phenyl-1,2,3-NH-triazole (725 mg, 5.0 mmol, 2.5 eq.) and CuI (76 mg, 20%), L-Proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 eq.) under N_2 atmosphere. The mixture was stirred at 120 ^{o}C and monitored by TLC. After the reaction is completed, the reaction was quenched with brine and extracted with ethyl acetate for three times. Organic phases were combined and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (Hexane - EtOAc v/v 15:1), giving desired product as light yellow solid (yield: 237 mg, 37%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.69 (s, 1H), 8.20 (s, 1H), 8.11 (d, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.55-7.51 (m, 5H), 7.43-7.40 (m, 2H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 147.8, 131.2, 130.3, 129.8, 129.0, 128.46,

128.35, 128.0, 127.4, 126.7, 125.97, 125.89, 124.0, 122.1; HRMS Calculated for $C_{22}H_{15}N_3$ $[M+H]^+$: 322.1338, Found: 322.1342.

Representative procedure for the preparation of 1,8-bis(4-phenyl-2*H*-1,2,3-triazol-2-yl)naphthalene (3-3c) (*Condition A*) To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 eq.) in dry DMSO (4 ml, 0.5 M), were added successively 4-Phenyl-1,2,3-NH-triazole (725 mg, 5.0 mmol, 2.5 eq.) and CuI (76 mg, 20%), L-Proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 eq.) under N_2 atmosphere. The mixture was stirred at 120 ^oC and monitored by TLC. After the reaction is completed, the reaction was quenched with brine and extracted with ethyl acetate for three times. Organic phases were combined and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (Hexane - EtOAc v/v 5:1), giving desired product as light yellow solid (yield: 472 mg, 57%). ^1H NMR (400 MHz; $CDCl_3$): δ 8.12 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.96 (dd, *J* = 7.4, 1.2 Hz, 2H), 7.71 (dd, *J* = 8.2, 7.4 Hz, 2H), 7.48-7.51 (m, 4H), 7.28-7.22 (m, 6H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 148.3, 136.1, 135.6, 131.7, 130.2, 129.4, 128.5, 128.3, 127.0, 125.9, 121.1; HRMS Calculated for $C_{26}H_{18}N_6$ $[M+H]^+$: 415.1666, Found: 415,1672.

Representative procedure for the preparation of 2-(8-iodonaphthalen-1-yl)-4-phenyl-2*H*-1,2,3-triazole (3-4a) (*Condition B*) To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 eq.) in dry DMSO (4 ml, 0.5 M), were added successively 4-Phenyl-1,2,3-NH-triazole (290 mg, 2.0 mmol, 1.0 eq.) and CuI (38 mg, 10%), L-Proline (46 mg, 20%), K_2CO_3 (552 mg, 4.0 mmol, 2.0 eq.) under N_2 atmosphere. The mixture was stirred at 80 ^oC and monitored by TLC. After the reaction is completed, the reaction was quenched with brine and extracted with ethyl acetate for three times. Organic phases were combined and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (Hexane - EtOAc v/v 10:1), giving desired product as light yellow solid (yield: 401 mg, 51%). ^1H NMR (400 MHz; $CDCl_3$): δ 8.29 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.21 (s, 1H), 8.04 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.97 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.94-7.91 (m, 2H), 7.68 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.59 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.49-7.45 (m, 2H), 7.42-7.38 (m, 1H), 7.19 (dd, *J* = 8.1, 7.4 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 149.1, 143.0, 137.2, 135.8, 132.6, 132.0, 130.1, 129.5, 129.1, 128.92, 128.75, 128.73, 127.4, 126.2, 125.2, 86.5; HRMS Calculated for $C_{18}H_{22}N_3I$ $[M+H]^+$: 398.0149, Found: 398.0155.

Representative procedure for the preparation of 1,8-bis(4-phenyl-1*H*-1,2,3-triazol-1-yl)naphthalene (3-3a) To a solution of 1,8-diazidonaphthalene (420 mg, 2.0 mmol, 1.0 eq.) in 1:1 *t*-BuOH/H_2O (5 ml, 0.4 M), were added successively phenylacetylene (1.02 g, 10.0 mmol, 5.0 eq.) and $CuSO_4$ (128 mg, 40%), and L-Ascorbic acid sodium salt (237.6 mg, 60%) under N_2 atmosphere. The mixture was stirred at 80^oC and monitored by TLC. After the reaction is completed, the reaction was quenched with brine and extracted with ethyl acetate for three times. Organic phases

were combined and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (Hexane - EtOAc v/v 5:1), giving desired product as light yellow solid (yield: 712 mg, 86%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.25 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.66 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.56 (s, 1H), 7.47-7.43 (m, 2H), 7.25-7.21 (m, 3H); ^{13}C NMR (100 MHz; *d*6-DMSO): δ 146.4, 135.7, 132.1, 131.7, 130.5, 129.4, 128.7, 128.0, 127.0, 125.8, 124.4; HRMS Calculated for $C_{26}H_{18}N_6$ $[M+H]^+$: 415.1665, Found: 415.1677.

Representative procedure for the preparation of 2,3'-(naphthalene-1,8-diyl)bis(5-phenyl-2*H*-1,2,3-triazole) (3-3b) 2-(8-azidonaphthalen-1-yl)-4-phenyl-2*H*-1,2,3-triazole is prepared from 1-azido-8-iodonaphthalene under *condition B*. Then to a solution of 2-(8-azidonaphthalen-1-yl)-4-phenyl-2*H*-1,2,3-triazole (624 mg, 2.0 mmol, 1.0 eq) in 1:1 *t*-BuOH/H_2O (5 ml, 0.4 M), were added successively phenylacetylene (510 mg, 5.0 mmol, 2.5 eq.) and $CuSO_4$ (64 mg, 20%), and L-Ascorbic acid sodium salt (118.8 mg, 30%) under N_2 atmosphere. The mixture was stirred at 120 ^{o}C and monitored by TLC. After the reaction is completed, the reaction was quenched with brine and extracted with ethyl acetate for three times. Organic phases were combined and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (Hexane - EtOAc v/v 3:1), giving desired product as light yellow solid (yield: 605 mg, 73%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.17 (dd, *J* = 7.5, 5.2 Hz, 2H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.79 (d, *J* = 7.1 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 2H), 7.63 (s, 1H), 7.52 (s, 1H), 7.45 (ddd, *J* = 12.2, 6.4, 2.7 Hz, 4H), 7.26-7.24 (t, *J* =3.0 Hz 3H), 7.18 (t, *J* = 2.8 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 149.0, 146.9, 135.8, 135.0, 132.4, 132.0, 131.1, 130.8, 129.7, 129.1, 128.52, 128.48, 128.38, 128.25, 128.08, 127.7, 126.16, 126.12, 126.04, 125.5, 122.3, 121.6, 116.0; HRMS Calculated for $C_{26}H_{18}N_6$ $[M+H]^+$: 415.1665, Found: 415.1672.

Representative procedure for the preparation of 1,8-bis(4-(4-chlorophenyl)-2*H*-1,2,3-triazol-2-yl)naphthalene (3-5a) (*Condition A*) To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 eq.) in dry DMSO (4 ml, 0.5 M), were added successively 4-(4-chlorophenyl)-1,2,3-NH-triazole (898 mg, 5.0 mmol, 2.5 eq.) and CuI (76 mg, 20%), L-Proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 eq.) under N_2 atmosphere. The mixture was stirred at 120 ^{o}C and monitored by TLC. After the reaction is completed, the reaction was quenched with brine and extracted with ethyl acetate for three times. Organic phases were combined and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (Hexane - EtOAc v/v 5:1), giving desired product as light yellow solid (yield: 580 mg, 60%). ^{1}H NMR (400 MHz; $CDCl^3$): δ 8.14 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.95 (dd, *J* = 7.4, 1.2 Hz, 2H), 7.72 (dd, *J* = 8.1, 7.6 Hz, 2H), 7.56 (s, 2H), 7.42-7.39 (m, 4H), 7.24-7.22 (m, 4H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 147.1, 136.0, 135.3, 134.3, 131.44, 131.41, 130.4, 128.7, 127.8, 127.07, 127.00, 126.0, 121.0; HRMS Calculated for $C_{26}H_{16}N_6Cl_2$ $[M+H]^+$: 483.0887, Found: 483.0897.

Representative procedure for the preparation of 1,8-bis(4-(4-methoxyphenyl)-2*H*-1,2,3-triazol-2-yl)naphthalene (3-5b) (*Condition A*) To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 eq.) in dry DMSO (4 ml, 0.5 M), were added successively 4-(4-methoxyphenyl)-1,2,3-NH-triazole (875 mg, 5.0 mmol, 2.5 eq.) and CuI (76 mg, 20%), L-Proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 eq.) under N_2 atmosphere. The mixture was stirred at 120 ^oC and monitored by TLC. After the reaction is completed, the reaction was quenched with brine and extracted with ethyl acetate for three times. Organic phases were combined and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (Hexane - EtOAc v/v 5:1), giving desired product as light yellow solid (yield: 607 mg, 64%). ^1H NMR (400 MHz; $CDCl_3$): δ 8.10 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.94 (dd, *J* = 7.4, 1.2 Hz, 2H), 7.69 (dd, *J* = 8.2, 7.4 Hz, 2H), 7.50 (s, 2H), 7.44-7.40 (m, 4H), 6.80-6.76 (m, 4H), 3.80 (s, 6H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 159.6, 148.0, 136.0, 135.6, 131.1, 130.0, 127.2, 126.9, 125.9, 122.2, 121.2, 113.8, 55.1; HRMS Calculated for $C_{28}H_{22}N_6O_2$ $[M+H]^+$: 475.1877, Found: 475.1883.

Representative procedure for the preparation of dimethyl 4,4'-(2,2'-(naphthalene-1,8-diyl)bis(2*H*-1,2,3-triazole-4,2-diyl))dibenzoate (3-5c) (*Condition A*) To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 eq.) in dry DMSO (4 ml, 0.5 M), were added successively 4-(1H-1,2,3-triazole-4-yl)-benzoic acid methyl ester (1.015 g, 5.0 mmol, 2.5 eq.) and CuI (76 mg, 20%), L-Proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 eq.) under N_2 atmosphere. The mixture was stirred at 120 ^oC and monitored by TLC. After the reaction is completed, the reaction was quenched with brine and extracted with ethyl acetate for three times. Organic phases were combined and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (Hexane - EtOAc v/v 5:1), giving desired product as light yellow solid (yield: 456 mg, 43%). ^1H NMR (400 MHz; $CDCl_3$): δ 8.15 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 7.4 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 4H), 7.73 (t, *J* = 7.8 Hz, 2H), 7.62 (s, 2H), 7.51 (d, *J* = 8.3 Hz, 4H), 3.91 (s, 6H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 166.5, 147.2, 136.0, 135.2, 133.5, 132.01, 131.96, 130.5, 129.82, 129.69, 127.2, 126.0, 125.5, 121.0, 52.1; HRMS Calculated for $C_{30}H_{22}N_6O_4$ $[M+Na]^+$: 553.1595, Found: 553.1600.

Representative procedure for the preparation of 4,4'-(2,2'-(naphthalene-1,8-diyl)bis(2*H*-1,2,3-triazole-4,2-diyl))dibenzonitrile (3-5d) (*Condition A*) To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 eq.) in dry DMSO (4 ml, 0.5 M), were added successively 4-(2H-1,2,3-triazol-4-yl)-benzonitrile (850 mg, 5.0 mmol, 2.5 eq.) and CuI (76 mg, 20%), L-Proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 eq.) under N_2 atmosphere. The mixture was stirred at 120 ^oC and monitored by TLC. After the reaction is completed, the reaction was quenched with brine and extracted with ethyl acetate for three times. Organic phases were combined and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (Hexane - EtOAc v/v 5:1), giving desired product as light yellow solid (yield: 389 mg, 42%). ^1H NMR (400 MHz; $CDCl_3$): δ 8.18 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 7.4 Hz, 2H), 7.76 (dd, *J* = 9.7, 6.0 Hz, 2H), 7.63 (s, 2H), 7.63-7.53 (m, 8H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 146.3,

136.0, 135.0, 133.5, 132.4, 131.9, 130.7, 128.4, 127.1, 126.1, 120.7, 118.3, 112.0; HRMS Calculated for $C_{28}H_{16}N_8$ $[M+Na]^+$: 487.1390, Found: 487.1396.

Representative procedure for the preparation of 3-5e (*Condition B* and *Condition A*) To a solution of 1,8-diiodonaphthalene (760 mg, 2.0 mmol, 1.0 eq.) in dry DMSO (4 ml, 0.5 M), were added successively 4-(4-methoxyphenyl)-1,2,3-NH-triazole (350 mg, 2.0 mmol, 1.0 eq.) and CuI (38 mg, 10%), L-Proline (46 mg, 20%), K_2CO_3 (552 mg, 4.0 mmol, 2.0 eq.) under N_2 atmosphere. The mixture was stirred at 80 ^oC and monitored by TLC. After the reaction is completed, the reaction was quenched with brine and extracted with ethyl acetate for three times. Organic phases were combined and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (Hexane - EtOAc v/v 10:1), giving desired intermediate 2-(8-iodonaphthalen-1-yl)-4-(4-methoxyphenyl)-2*H*-1,2,3-triazole as light yellow solid (yield: 563 mg, 66%). To a solution of 2-(8-iodonaphthalen-1-yl)-4-(4-methoxyphenyl)-2*H*-1,2,3-triazole (854 mg, 2.0 mmol, 1.0 eq.) in dry DMSO (4 ml, 0.5 M), were added successively 4-(2H-1,2,3-triazol-4-yl)-benzonitrile (850 mg, 5.0 mmol, 2.5 eq.) and CuI (76 mg, 20%), L-Proline (92 mg, 40%), and K_2CO_3 (1.1 g, 8.0 mmol, 4.0 eq.) under N_2 atmosphere. The mixture was stirred at 120 ^oC and monitored by TLC. After the reaction is completed, the reaction was quenched with brine and extracted with ethyl acetate for three times. Organic phases were combined and the solvent was removed under vacuum. The residue was purified by flash silica gel chromatography (Hexane - EtOAc v/v 5:1), giving desired product as light yellow solid (yield: 498 mg, 53%). ^1H NMR (400 MHz; $CDCl_3$): δ 8.16-8.12 (m, 2H), 7.96-7.94 (m, 2H), 7.73 (ddd, *J* = 8.3, 7.4, 1.0 Hz, 2H), 7.65 (s, 1H), 7.59-7.57 (m, 2H), 7.52-7.49 (m, 3H), 7.39-7.37 (m, 2H), 6.77-6.75 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 159.8, 148.1, 146.3, 136.0, 135.39, 135.24, 133.9, 132.3, 132.05, 132.01, 131.05, 131.01, 130.6, 130.2, 127.13, 127.05, 126.27, 126.11, 125.9, 121.8, 121.0, 118.6, 113.9, 111.5, 55.28; HRMS Calculated for $C_{28}H_{19}N_7O$ $[M+Na]^+$: 492.1543, Found: 492.1550.

UV absorption spectra The UV-Vis spectra were measured in a 10.00mm quartz cell. All samples were measured as 10^{-6} mol/L solution of bis-N-2-aryl triazole in CH_2Cl_2. The wavelength range is between 200-600 nm.

Fluorescence excitation and emission spectra Fluorescence emission and excitation spectra were measured in a 10.00 mm quartz cell. All samples were measured as a 10^{-6} mol/L solution of bis-N-2-aryl triazole in CH_2Cl_2. The emission spectra are obtained with an excitation wavelength around 300 to 310 nm, and the excitation spectra are obtained with the emission λ_{max} according to different compounds.

Quantum yield Quantum yield were calculated by using the standard 9,10-diphenylanthracene which excited at 340 nm (Φ = 0.9) in cyclohexane. Quantum yields were calculated by using the following equation, where Φ is the quantum yield, *Int* is the

area of emission peak, *A* represents absorbance at the excitation wavelength and *n* is reflective index of the solvent. The subscript reference is the respective values of the standard 9,10-diphenylanthracene. The absorption of bis-N-2-aryl triazole and 9,10-diphenylanthracene were less than 0.05 (Conc.= 10^{-6} mol/L).

$$\Phi = \Phi_{reference} \times \frac{Int \times A_{reference} \times n^2}{Int_{reference} \times A \times n_{reference}^2}$$

II. ORTEP drawing of the crystal structures

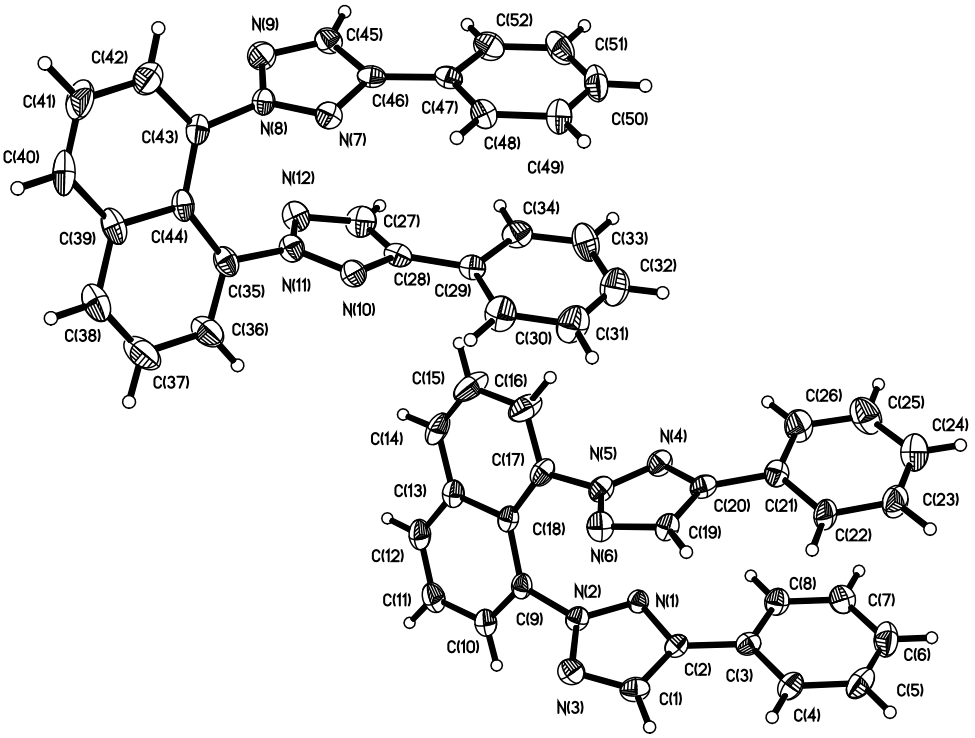


Figure 1. Perspective view of the molecular structures of the two independent molecules of **3c** ($C_{26}H_{18}N_6$) with the atom labeling scheme for the non-hydrogen atoms. The thermal ellipsoids are scaled to 30% probability. CCDC number: 1037989

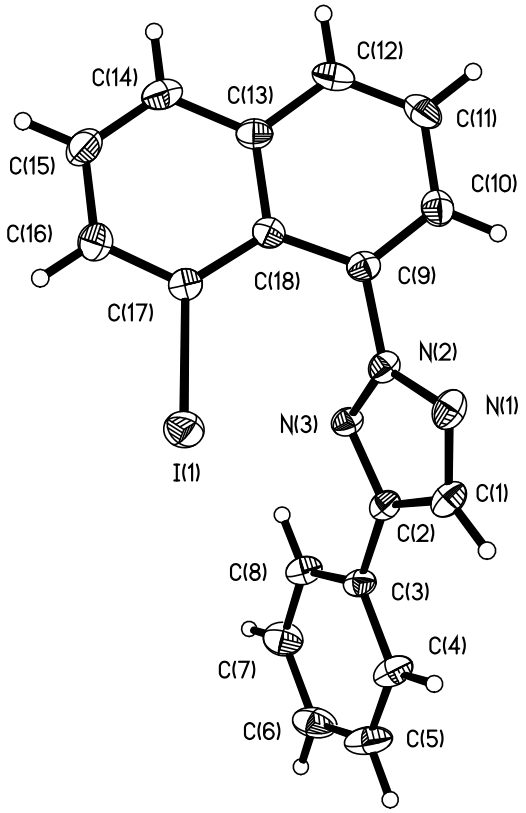


Figure 2. Perspective view of the molecular structure of **4a** ($C_{18}H_{12}N_3I$) with the atom labeling scheme for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 1037988.

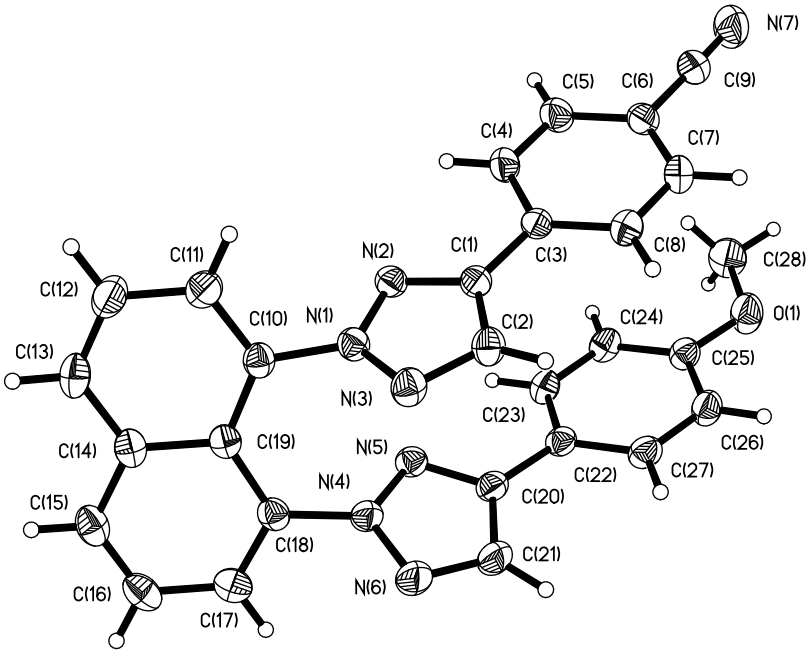


Figure 3. Perspective view of the molecular structure of **5e** ($C_{28}H_{19}N_7O$) with the atom labeling scheme for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 1038048.

III. The data of fluorophores with emission spectra

Sample preparation: To a 100 ml volumetric flask was added the NBT (0.01 mmol) in 100 ml Dichloromethane. After the NBT was absolutely dissolved, the 100μl triazole solution has been transferred to another 10 ml volumetric flask by using single-channel pipetter (20-200 μl), and was then diluted with additional 9.9 ml Dichloromethane.

Integrated emission area: All the areas were integrated from the original spectra by FL Solution 2.0 software at the wavelength range that was 300 nm to 600 nm with an excitation wavelength around 300 to 310 nm.

Quantum yield determination: All the quantum yields of samples were determined based on conc.= 10^{-6} mol/L 9,10-diphenylanthracene in cyclohexane (Φ = 0.9).

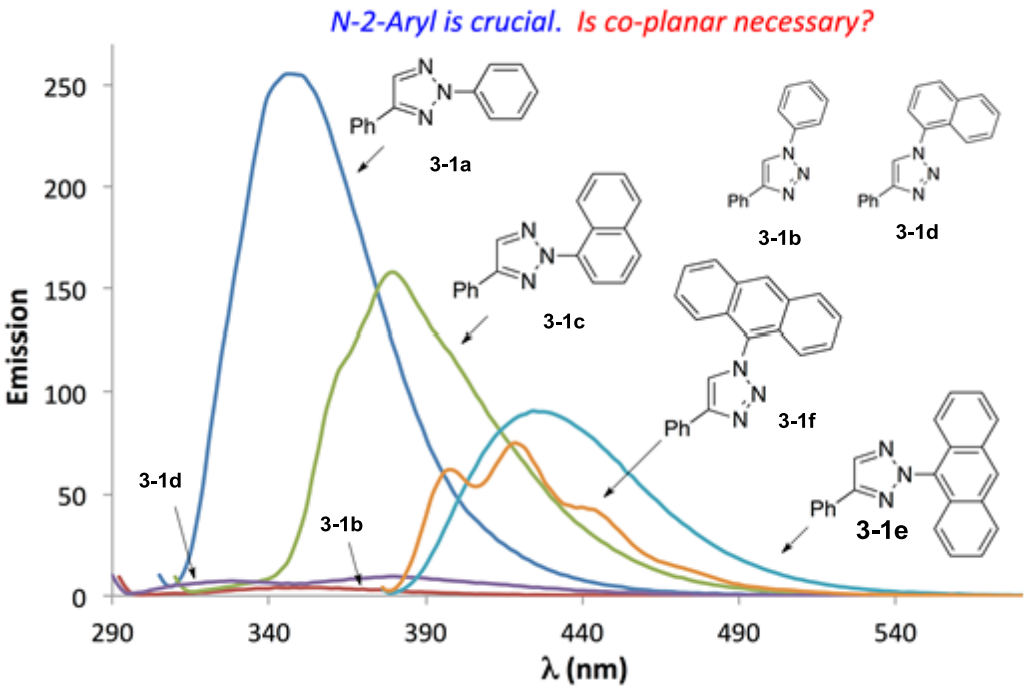


Figure 4. Fluorescence emission of NAT with different aryl groups: sample preparation: 10^{-6} mol/L in DCM.

Table 1. Comparison of optical properties of NATs.

	Absorption (nm)	Excitation (λ_{max})	Emission (λ_{max})	Stokes Shift (nm)	Φ
3-1a	295 (0.027)	298	347	49	0.34
3-1b	292 (0.009)	-	-	-	<0.1
3-1c	296 (0.021)	293	379	86	0.32
3-1d	286 (0.008)	-	-	-	<0.1
3-1e	365 (0.029)	368	420	52	0.43
3-1f	366 (0.022)	367	418[a]	51	0.27

[a] Three different emission bands were observed in **3-1f** fluorescence spectra. Peak λ=418 is the highest one. The other two peaks λ= 392 and 436.

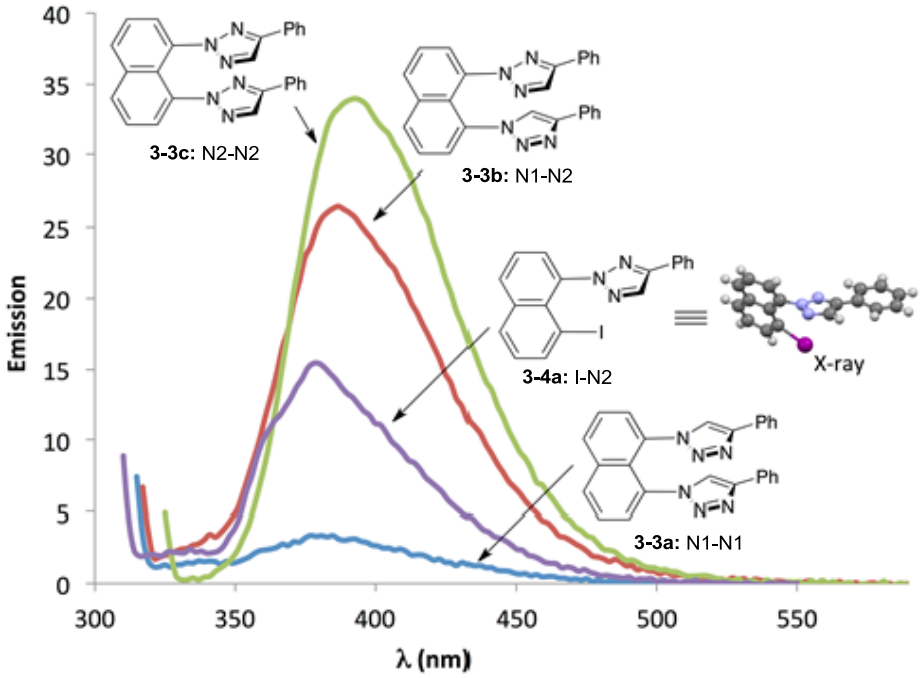


Figure 5. Fluorescence emission of NBT **3-3** and triazole iodide **3-4a** : sample preparation: 10^{-6} mol/L in DCM.

Table 2. Comparison of optical properties of NBT **3-3** and **3-4a**

	Absorption (nm)	Excitation (λ_{max})	Emission (λ_{max})	Stokes Shift (nm)	Φ
3-3a	282 (0.079)	-	-	-	<0.01
3-3b	307 (0.073)	307	384	77	0.13
3-3c	310 (0.063)	315	393	78	0.24
3-4a	297(0.064)	300	378	78	0.20

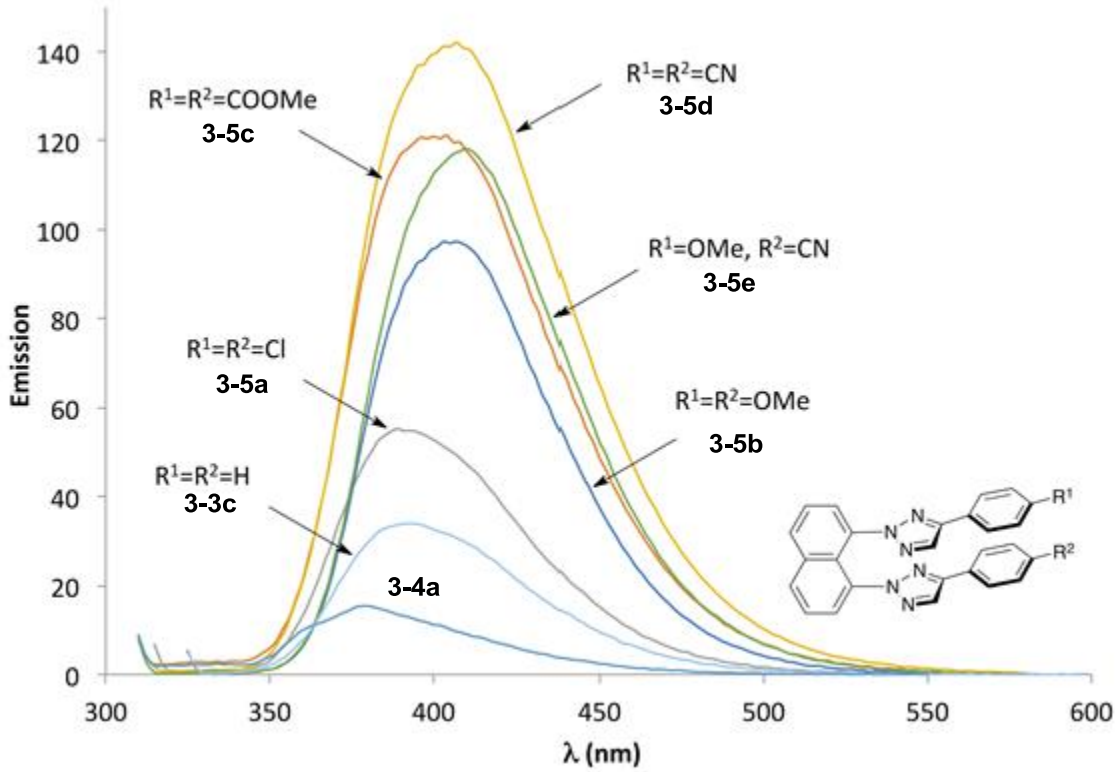


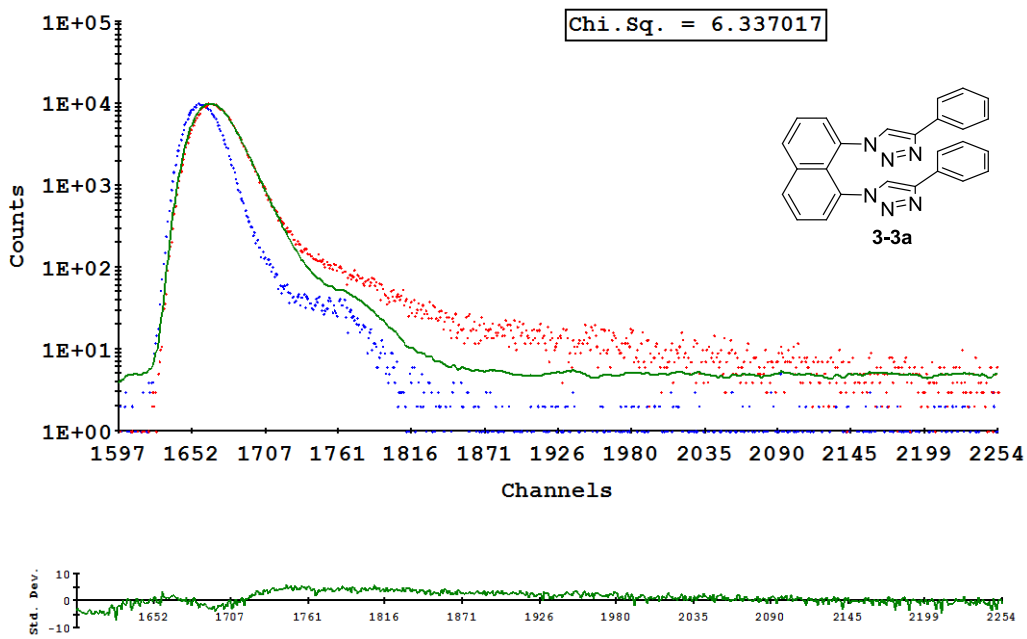
Figure 6. Fluorescence emission of NBT **3-5** and triazole iodide **3-4a**: sample preparation: 10^{-6} mol/L in DCM.

Table 3. Comparison of optical properties of NBT **3-5** and **3-4a**

	Absorption (nm)	Excitation (λ_{max})	Emission (λ_{max})	Stokes Shift (nm)	Φ
3-4a	297(0.064)	300	378	78	0.20
3-5a	306 (0.061)	305	393	88	0.26
3-5b	313 (0.061)	315	403	88	0.27
3-5c	300 (0.080)	300	396	96	0.41
3-5d	303 (0.068)	302	403	101	0.47
3-5e	300 (0.067)	300	408	108	0.39

IV. Excited state lifetime

All the sample are tested under same conditions as described above (section II). All the complexes were fitted with one exponential using DAS6.



Calculated using 1 exponential

The initial paramters are:

Shift Value = 0 ch; 0 sec
Shift Limit = 40 ch; 2.194787E-09 sec

T1 Estimate = 12.91663 ch; 7.087312E-10 sec

A Free
B1 Free

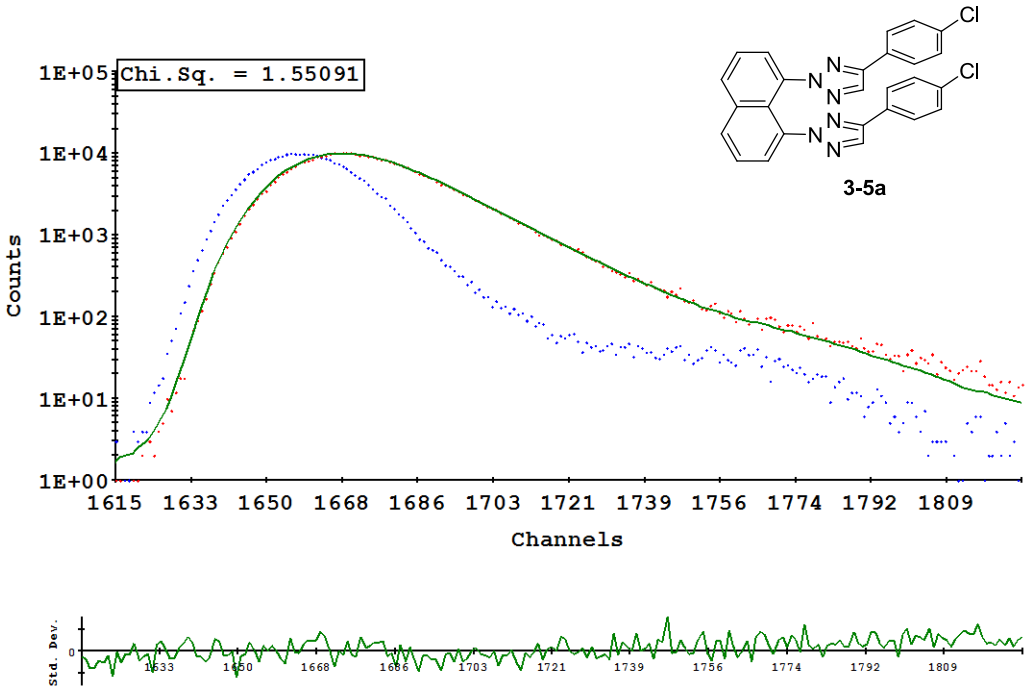
Prompt and decay LO = 1597 ch; 8.762689E-08 sec
Prompt and decay HI = 2294 ch; 1.258711E-07 sec

Background on prompt = 0 (manual)
Time calibration = 5.486969E-11 sec/ch

The fitted parameters are:

Hi reduced to: 2254 ch

SHIFT = 0.552488 ch; 3.031484E-11 sec S.Dev = 3.574068E-12 sec
T1 = 10.33031 ch; 5.668208E-10 sec S.Dev = 6.771148E-12 sec
A = 3.857545 S.Dev = 0.1000181
B1 = 0.1259739 [100.00 Rel.Ampl][1.00 Alpha] S.Dev = 2.429185E-04
Average Life Time = 5.668208E-10 sec
CHISQ = 6.337017 [654 degrees of freedom]



Calculated using 1 exponential

The initial paramters are:

Shift Value = 0 ch; 0 sec
Shift Limit = 40 ch; 2.194787E-09 sec

T1 Estimate = 15.02722 ch; 8.245389E-10 sec

A Free
B1 Free

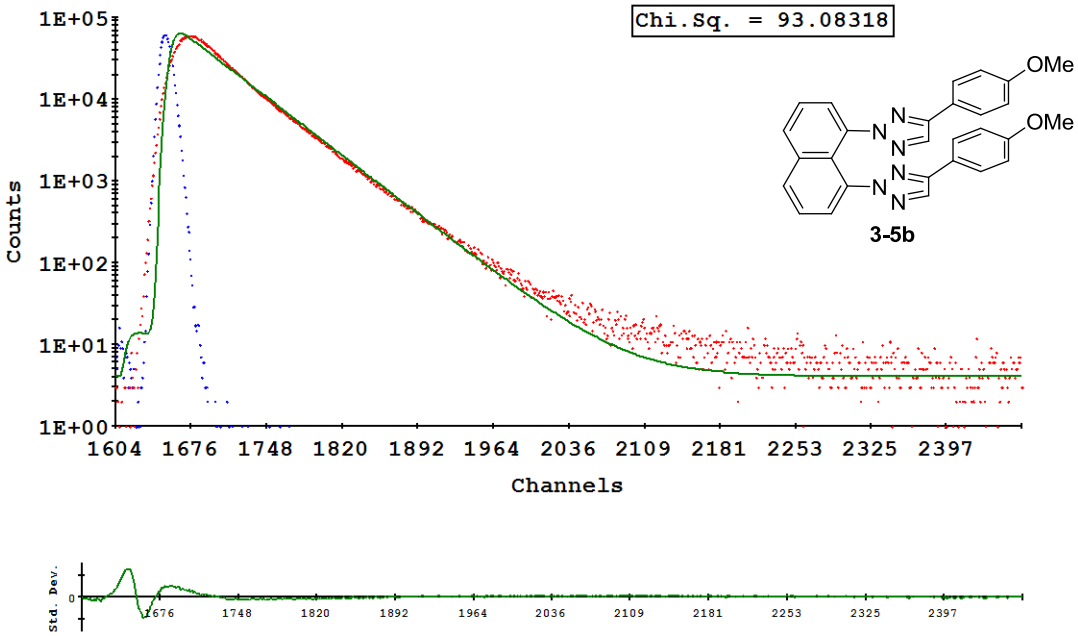
Prompt and decay LO = 1615 ch; 8.861454E-08 sec
Prompt and decay HI = 1867 ch; 1.024417E-07 sec

Background on prompt = 0 (manual)
Time calibration = 5.486969E-11 sec/ch

The fitted parameters are:

Hi reduced to: 1827 ch

SHIFT = 1.104386 ch; 6.059733E-11 sec S.Dev = 1.883257E-12 sec
T1 = 14.56462 ch; 7.99156E-10 sec S.Dev = 3.201433E-12 sec
A = 1.621187 S.Dev = 0.2953923
B1 = 9.869412E-02 [100.00 Rel.Ampl][1.00 Alpha] S.Dev = 1.800729E-04
Average Life Time = 7.99156E-10 sec
CHISQ = 1.55091 [209 degrees of freedom]



Calculated using 1 exponential

The initial paramters are:

Shift Value = 0 ch; 0 sec
Shift Limit = 40 ch; 2.194787E-09 sec

T1 Estimate = 48.82361 ch; 2.678936E-09 sec

A Free
B1 Free

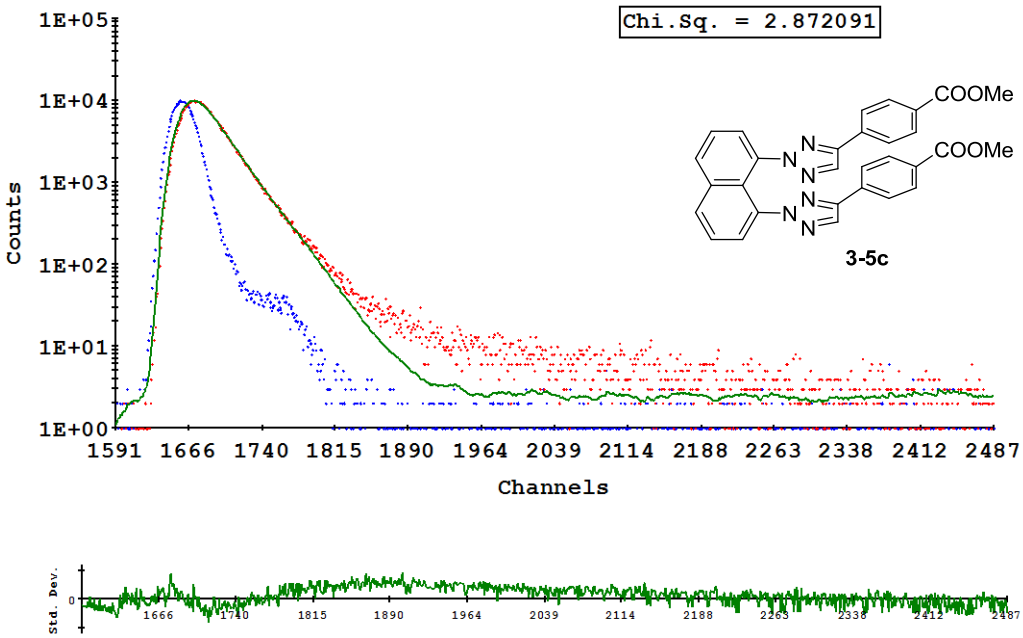
Prompt and decay LO = 1604 ch; 8.801098E-08 sec
Prompt and decay HI = 2509 ch; 1.37668E-07 sec

Background on prompt = 0 (manual)
Time calibration = 5.486969E-11 sec/ch

The fitted parameters are:

Hi reduced to: 2469 ch

SHIFT = 6.276135 ch; 3.443696E-10 sec S.Dev = 6.684059E-12 sec
T1 = 43.90302 ch; 2.408945E-09 sec S.Dev = 1.631257E-11 sec
A = 4.041021 S.Dev = 0.1016247
B1 = 0.1070184 [100.00 Rel.Ampl][1.00 Alpha] S.Dev = 7.564617E-05
Average Life Time = 2.408945E-09 sec
CHISQ = 93.08318 [862 degrees of freedom]



Calculated using 1 exponential

The initial paramters are:

Shift Value = 0 ch; 0 sec
Shift Limit = 40 ch; 2.194787E-09 sec

T1 Estimate = 26.07678 ch; 1.430825E-09 sec

A Free
B1 Free

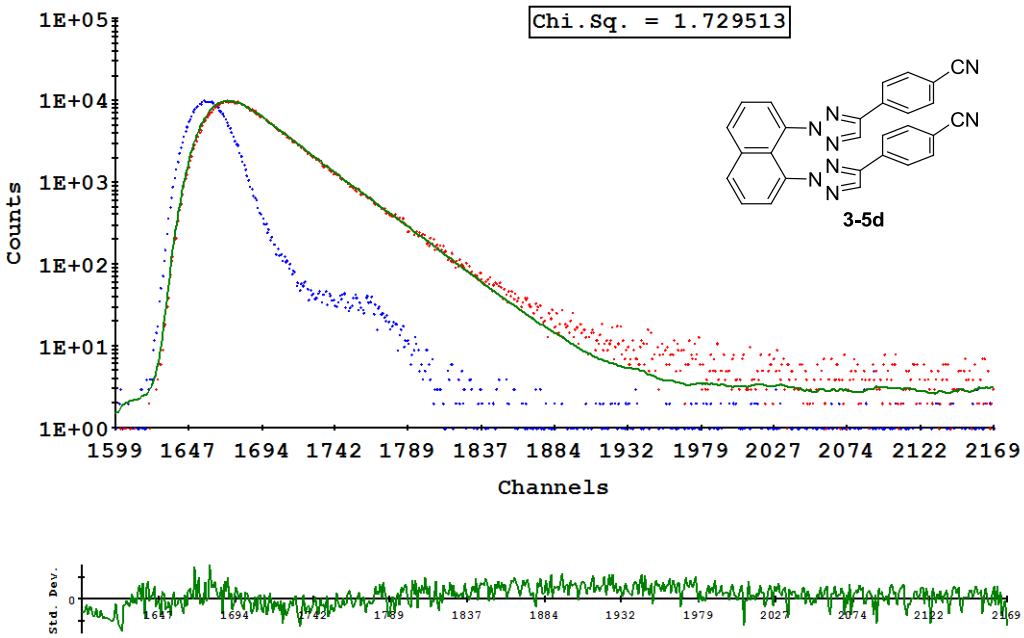
Prompt and decay LO = 1591 ch; 8.729767E-08 sec
Prompt and decay HI = 2527 ch; 1.386557E-07 sec

Background on prompt = 0 (manual)
Time calibration = 5.486969E-11 sec/ch

The fitted parameters are:

Hi reduced to: 2487 ch

SHIFT = 1.012082 ch; 5.553263E-11 sec S.Dev = 2.595552E-12 sec
T1 = 23.8283 ch; 1.307451E-09 sec S.Dev = 5.174642E-12 sec
A = 1.111919 S.Dev = 6.266093E-02
B1 = 7.393724E-02 [100.00 Rel.Ampl][1.00 Alpha] S.Dev = 1.202585E-04
Average Life Time = 1.307451E-09 sec
CHISQ = 2.872091 [893 degrees of freedom]



Calculated using 1 exponential

The initial paramters are:

Shift Value = 0 ch; 0 sec
Shift Limit = 40 ch; 2.194787E-09 sec

T1 Estimate = 29.85876 ch; 1.638341E-09 sec

A Free
B1 Free

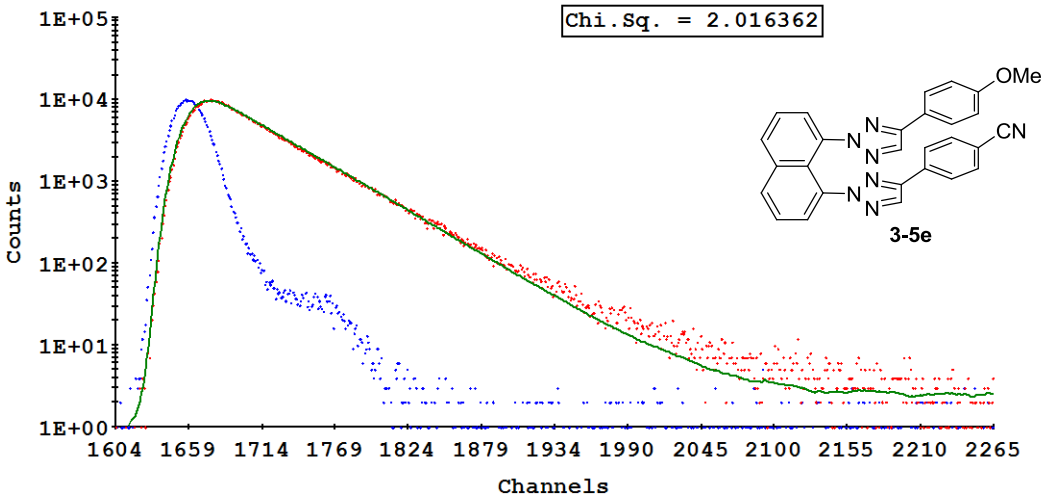
Prompt and decay LO = 1599 ch; 8.773662E-08 sec
Prompt and decay HI = 2209 ch; 1.212071E-07 sec

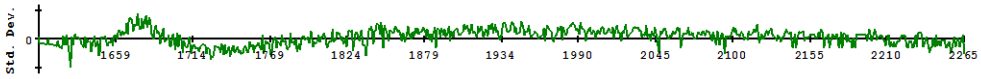
Background on prompt = 0 (manual)
Time calibration = 5.486969E-11 sec/ch

The fitted parameters are:

Hi reduced to: 2169 ch

SHIFT = 1.210837 ch; 6.643825E-11 sec S.Dev = 2.213482E-12 sec
T1 = 28.58036 ch; 1.568195E-09 sec S.Dev = 4.21055E-12 sec
A = 1.481617 S.Dev = 0.1002949
B1 = 6.720192E-02 [100.00 Rel.Ampl][1.00 Alpha] S.Dev = 1.043928E-04
Average Life Time = 1.568195E-09 sec
CHISQ = 1.729513 [567 degrees of freedom]





Calculated using 1 exponential

The initial paramters are:

Shift Value = 0	ch;	0	sec
Shift Limit = 40	ch;	2.194787E-09	sec
T1 Estimate = 45.05786 ch;		2.472311E-09	sec

A Free
B1 Free

Prompt and decay LO = 1604	ch;	8.801098E-08	sec
Prompt and decay HI = 2305	ch;	1.264746E-07	sec

Background on prompt = 0 (manual)
Time calibration = 5.486969E-11 sec/ch

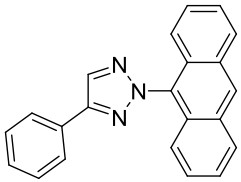
The fitted parameters are:

Hi reduced to: 2265 ch

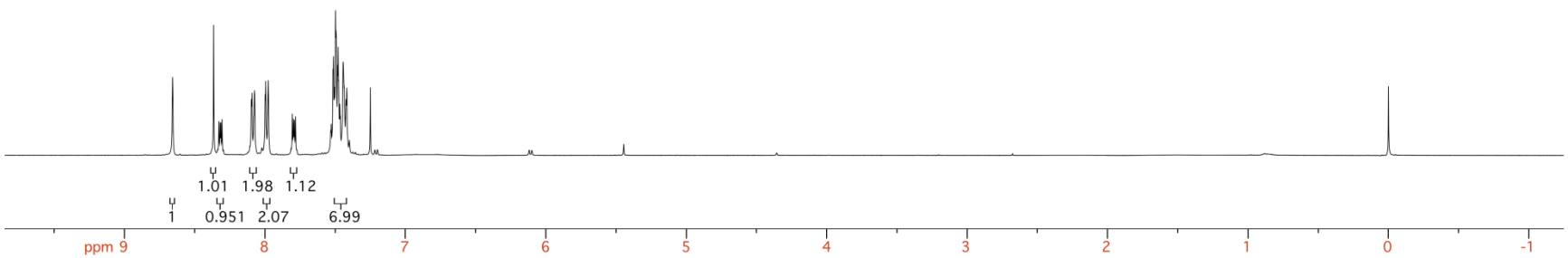
SHIFT = 0.8243643	ch;	4.523261E-11	sec	S.Dev = 2.415798E-12 sec
T1 = 44.52381	ch;	2.443007E-09	sec	S.Dev = 5.735076E-12 sec
A = 0.6034257				S.Dev = 9.464832E-02
B1 = 5.459966E-02 [100.00 Rel.Ampl][1.00 Alpha]				S.Dev = 7.483848E-05

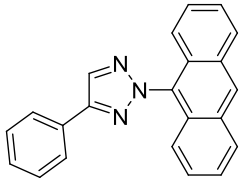
Average Life Time = 2.443007E-09 sec
CHISQ = 2.016362 [658 degrees of freedom]

V NMR spectra

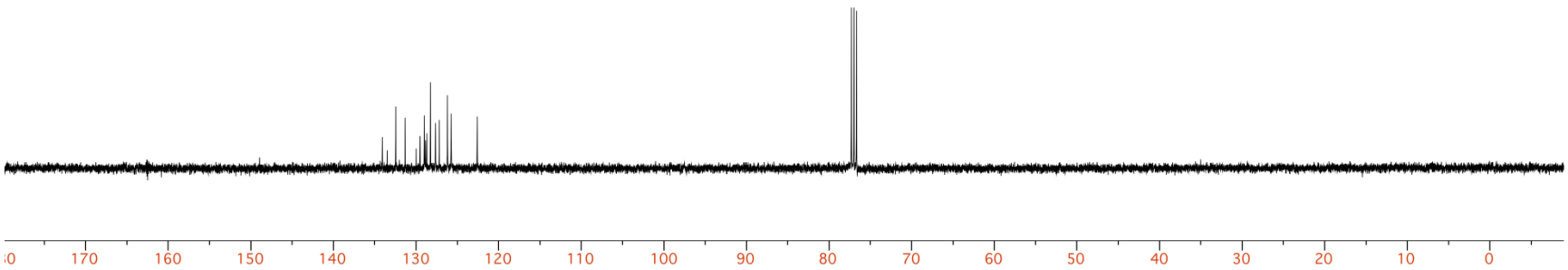


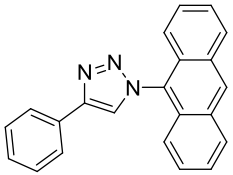
3-1e



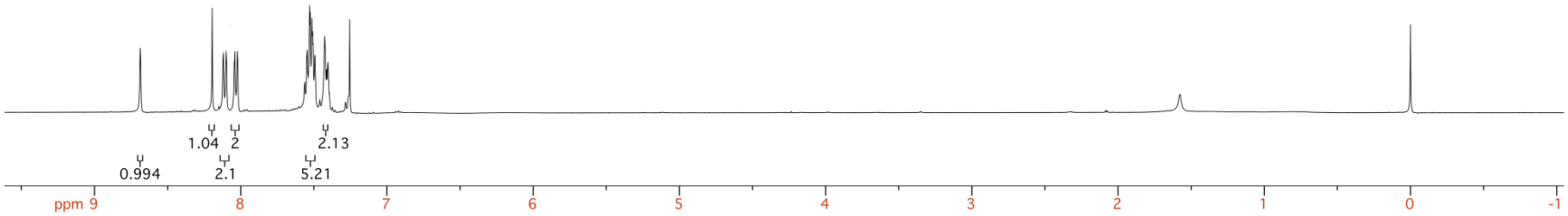


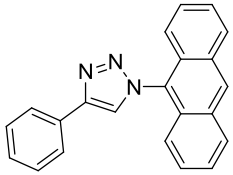
3-1e



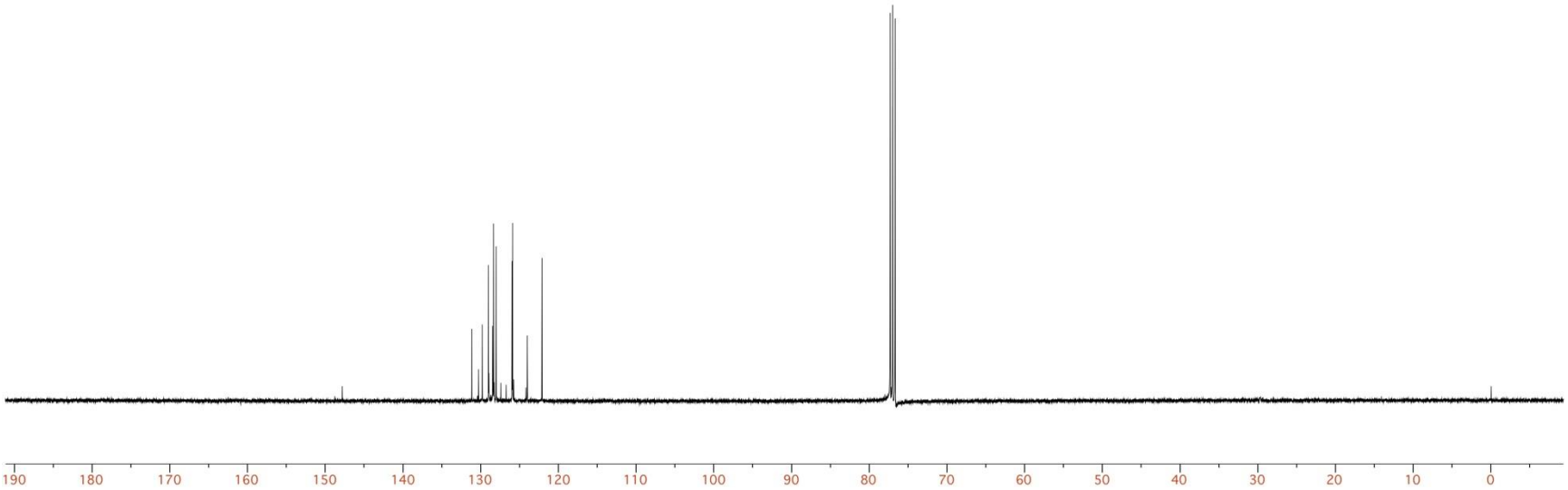


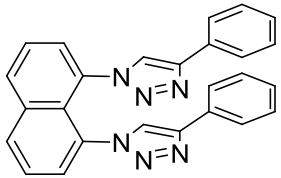
3-1f



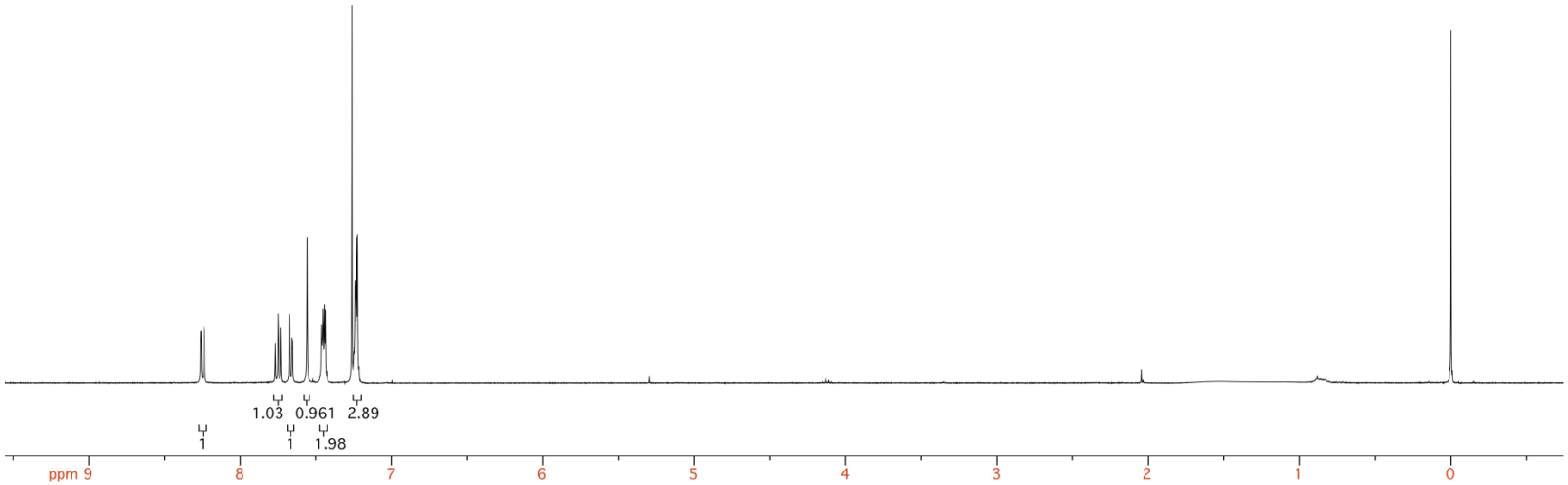


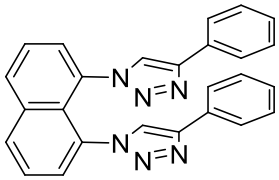
3-1f



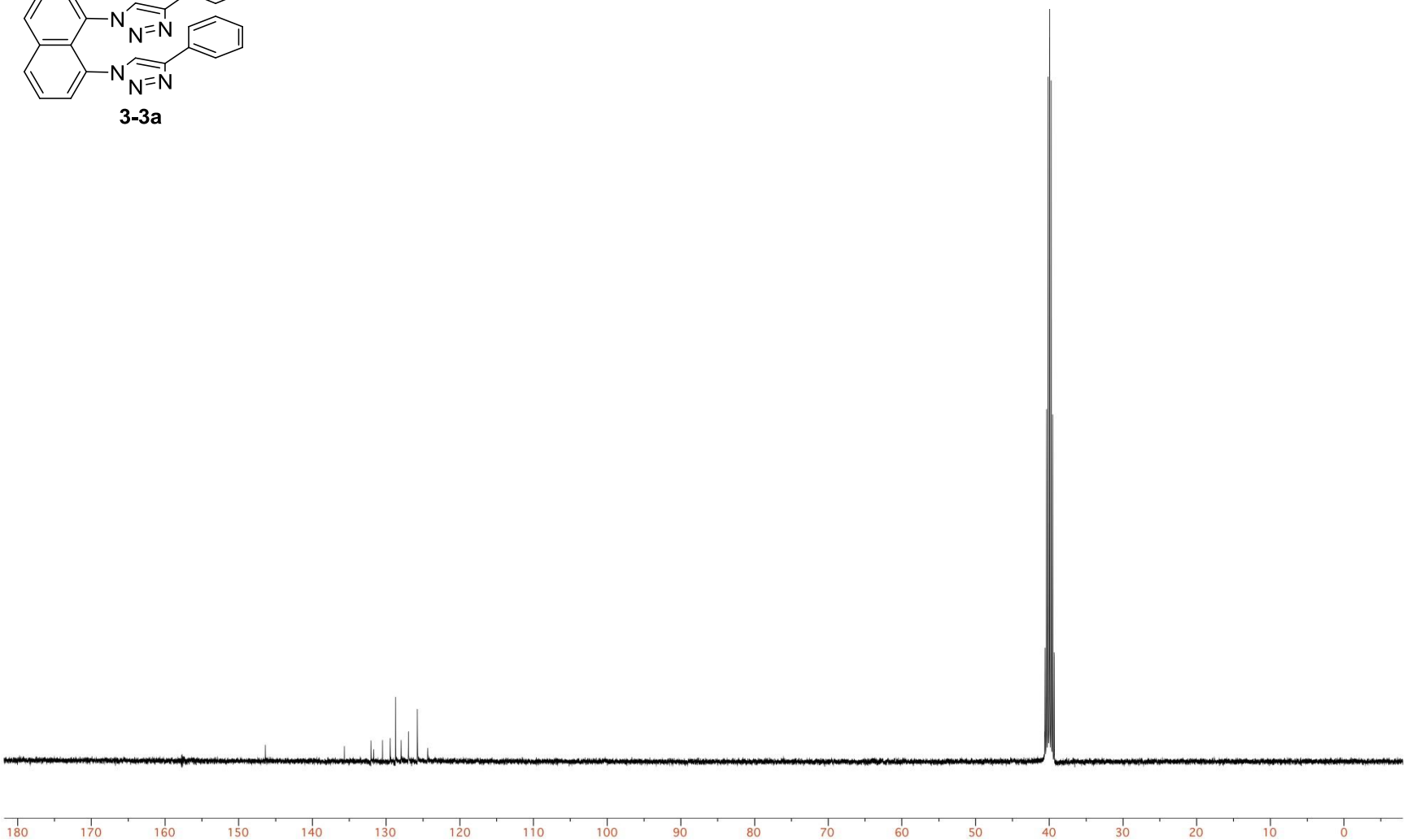


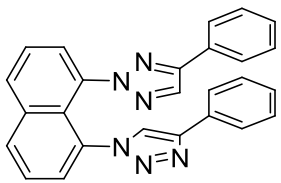
3-3a



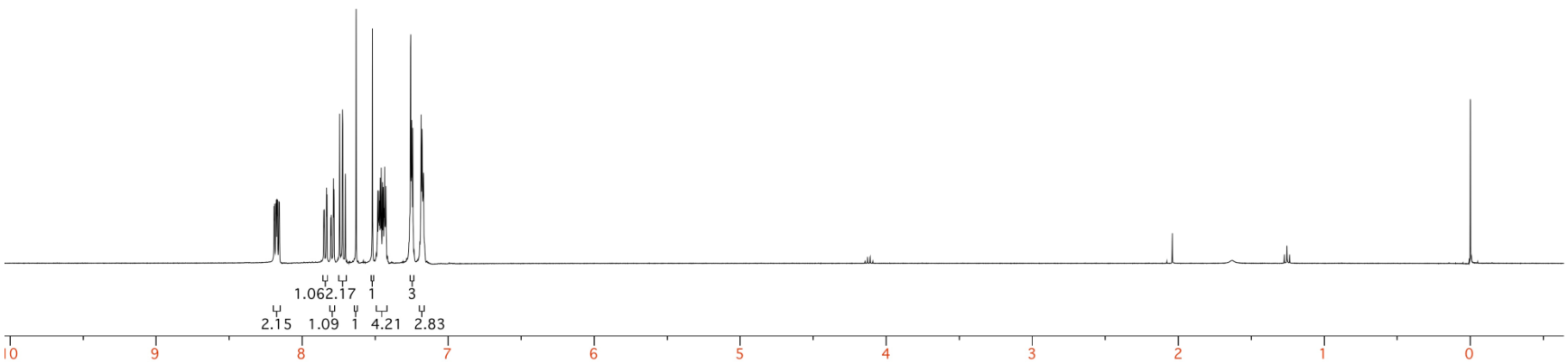


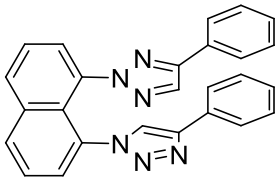
3-3a



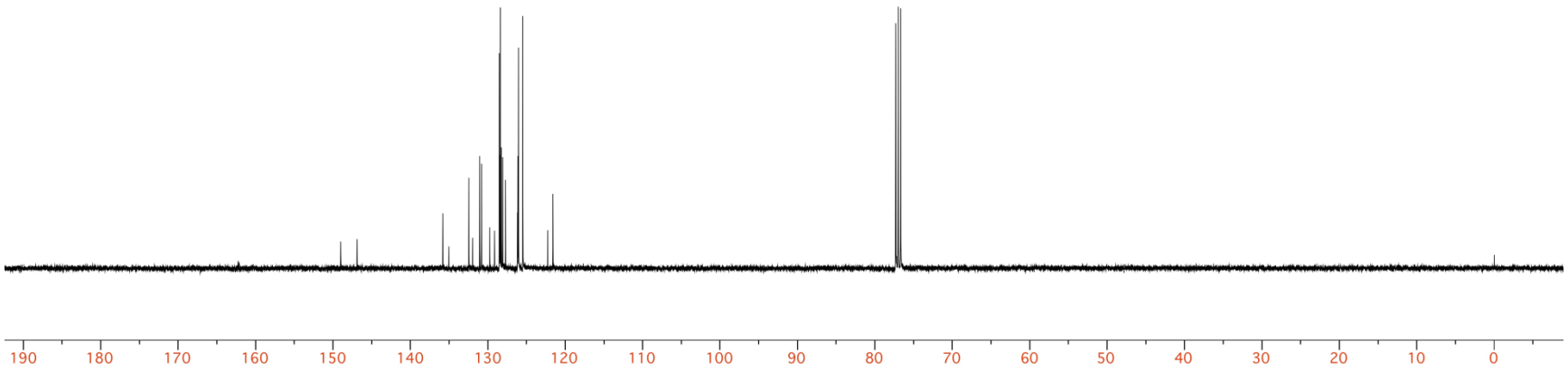


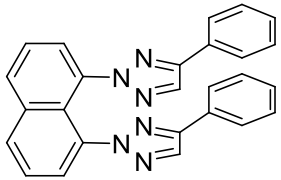
3-3b



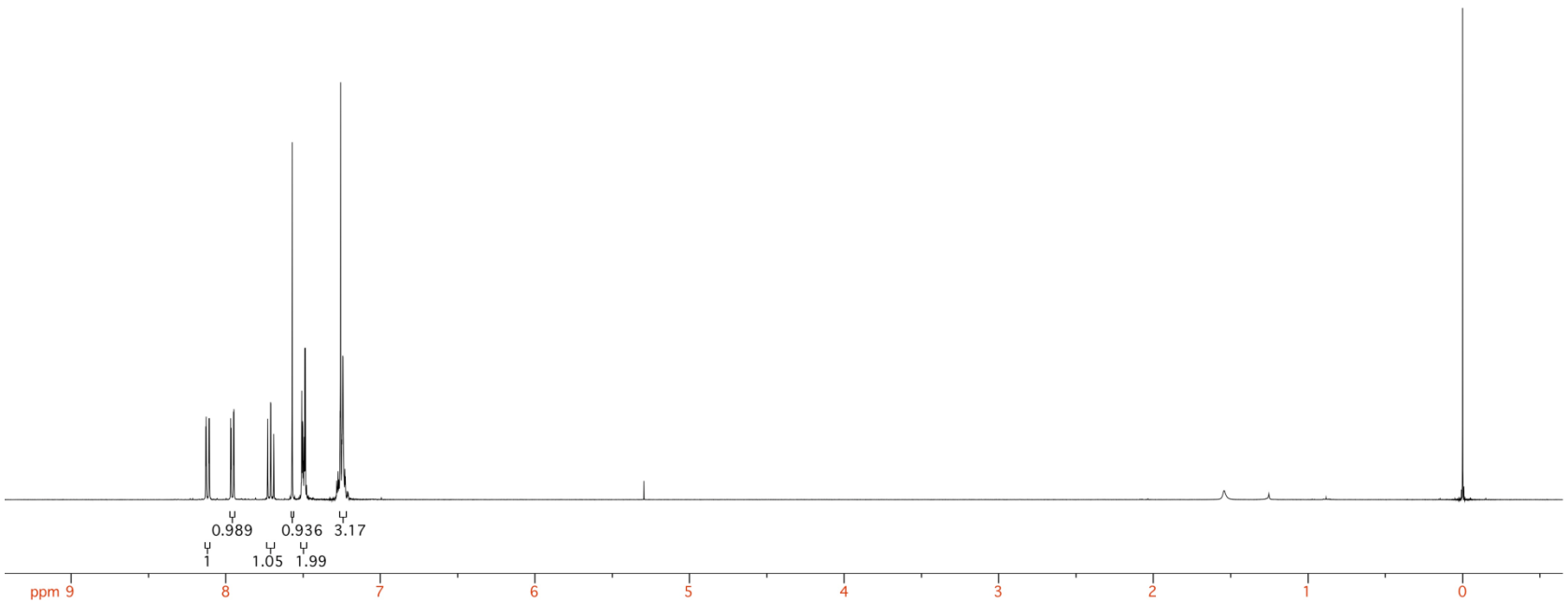


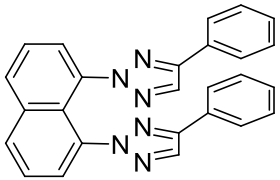
3-3b



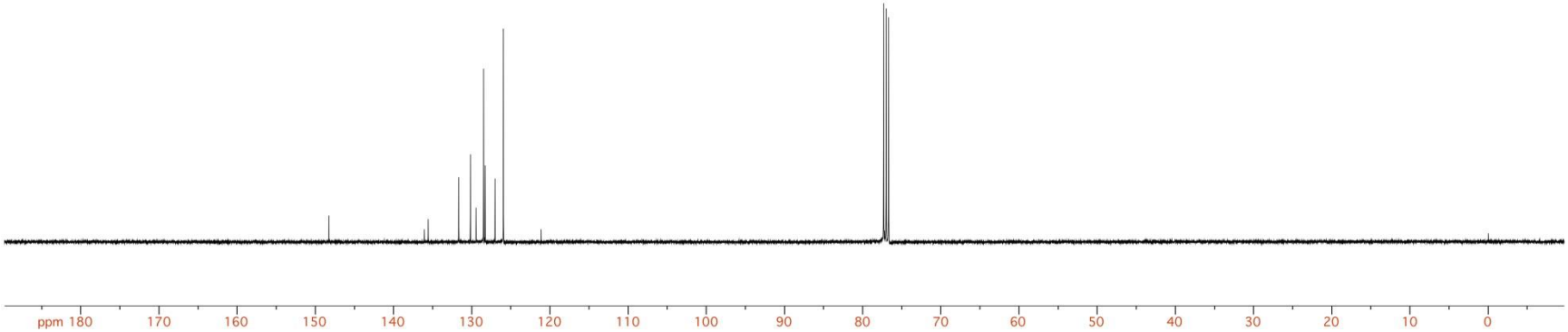


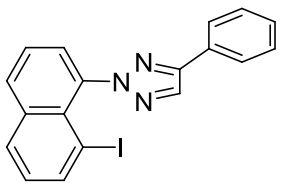
3-3c



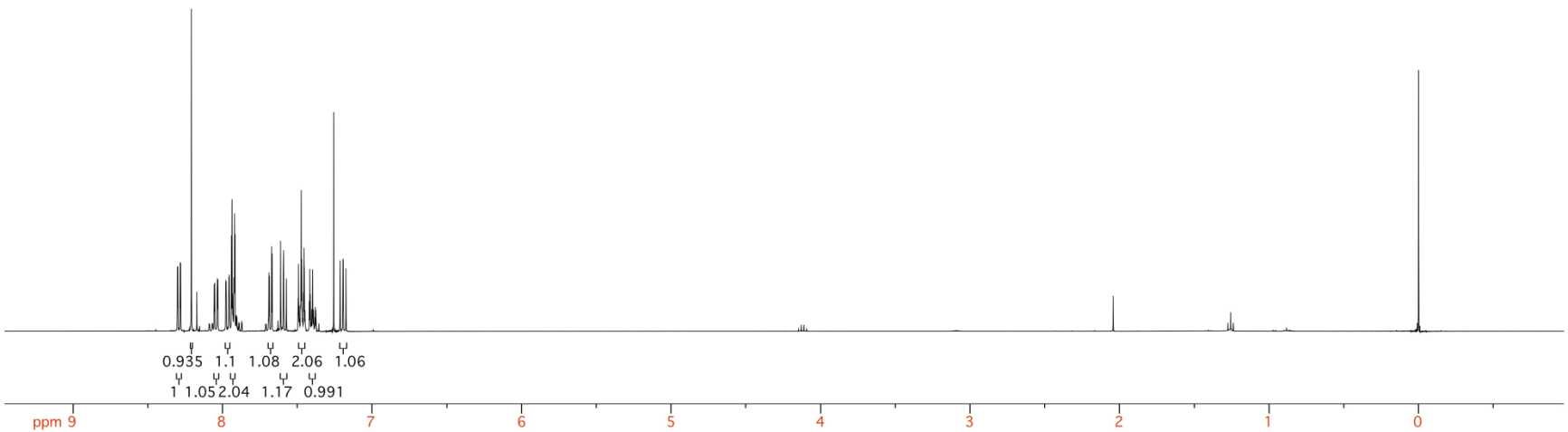


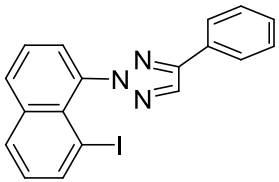
3-3c



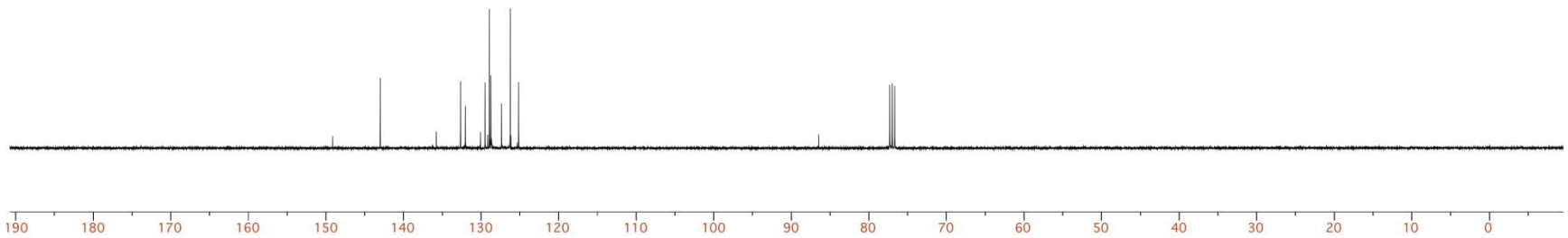


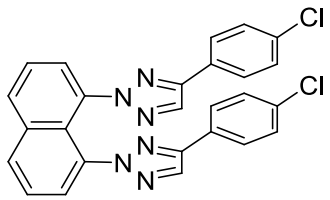
3-4a



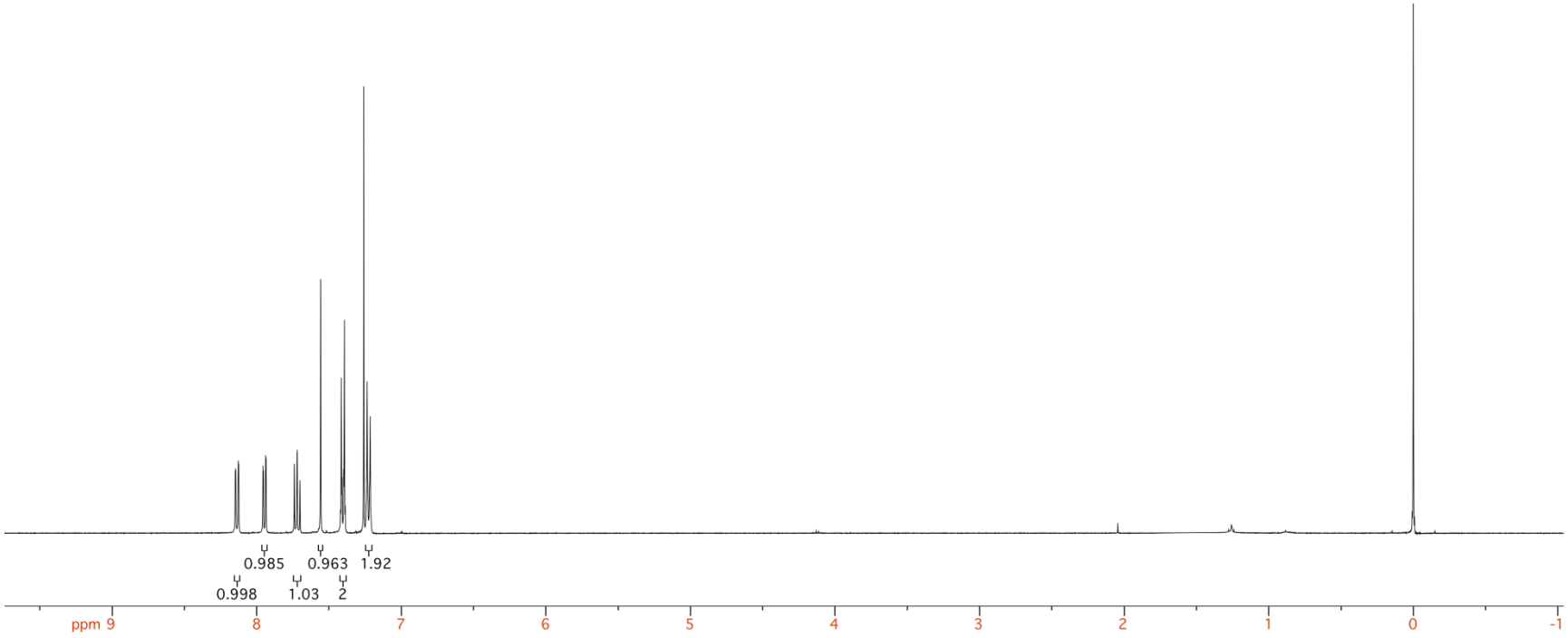


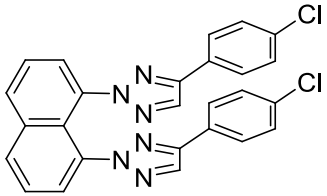
3-4a



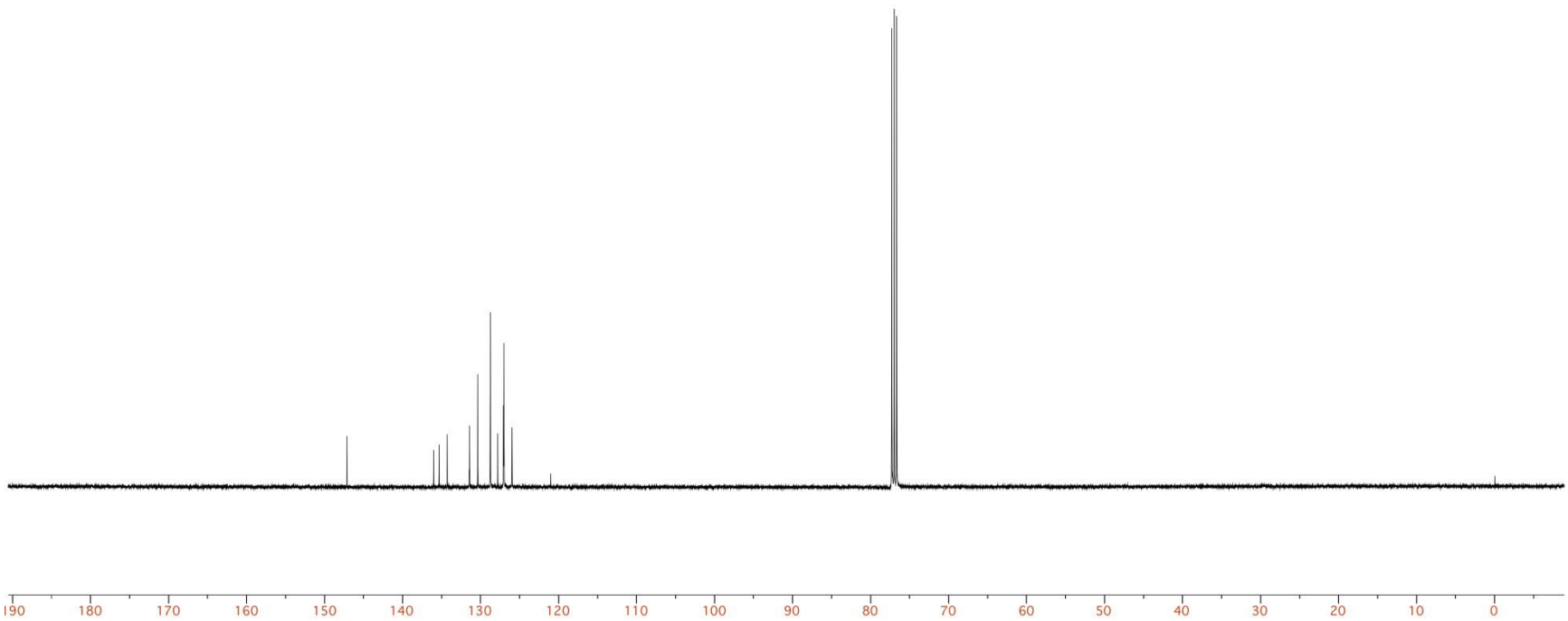


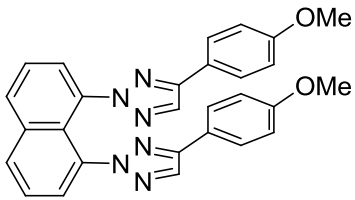
3-5a



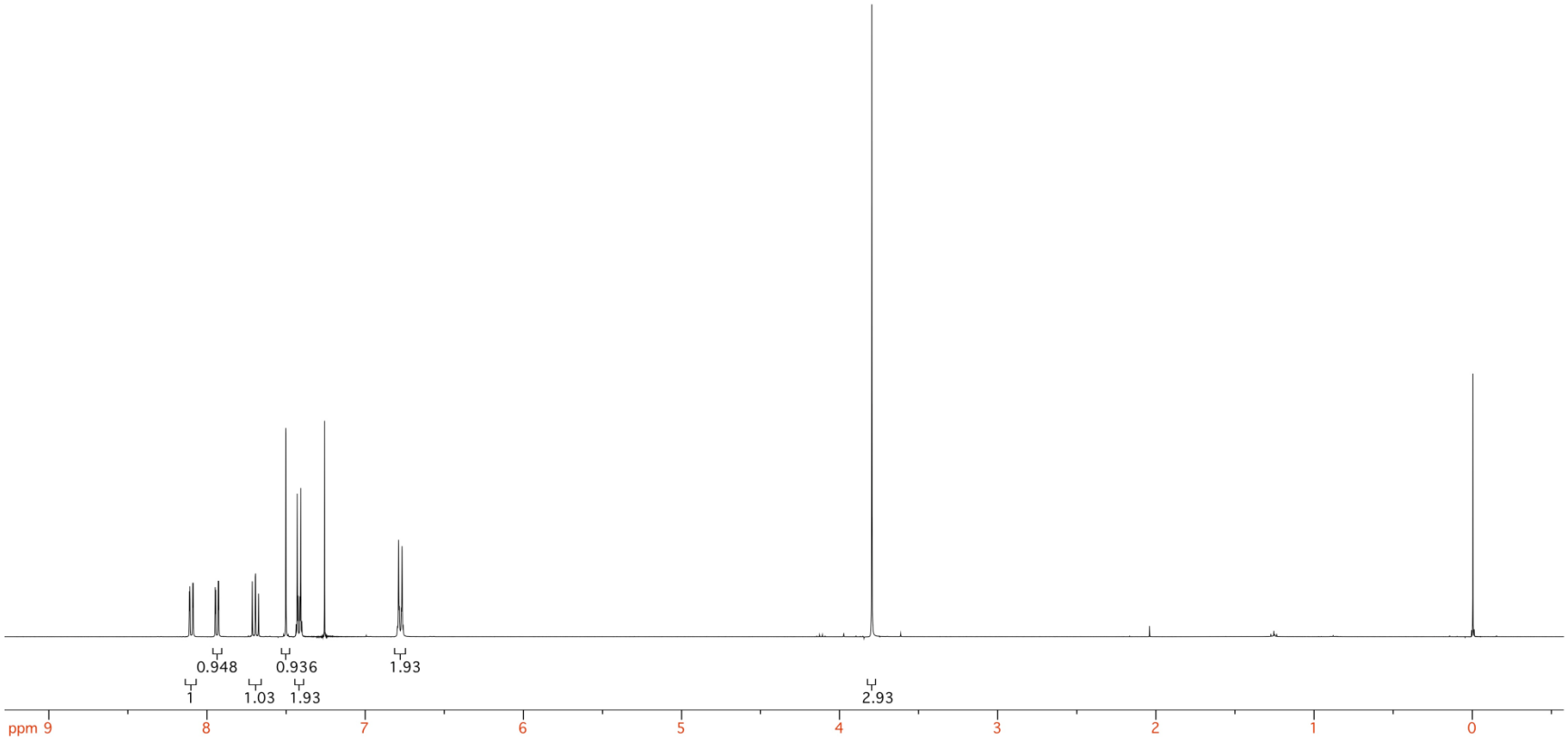

Cl
Cl
N
N
N
N
N
N

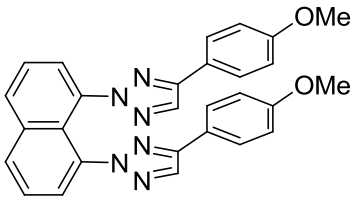
3-5a


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

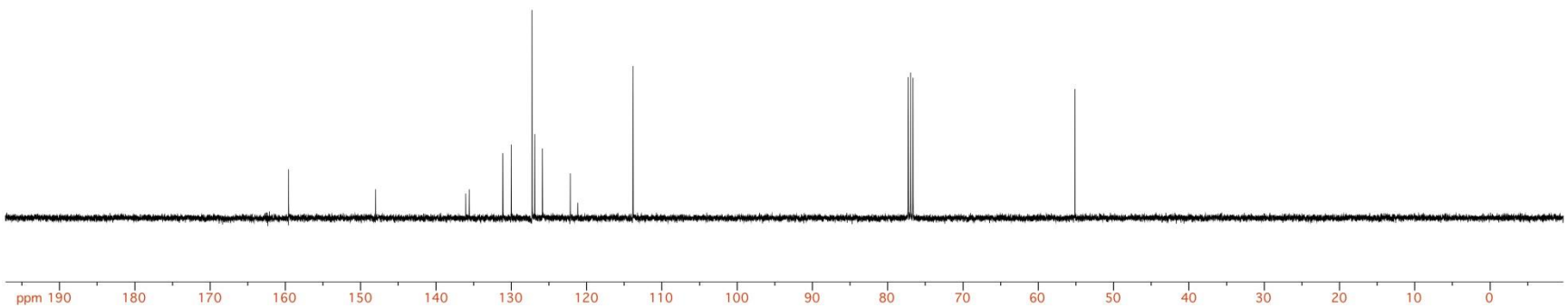


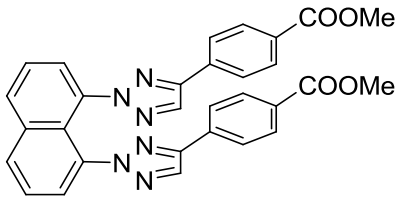
3-5b



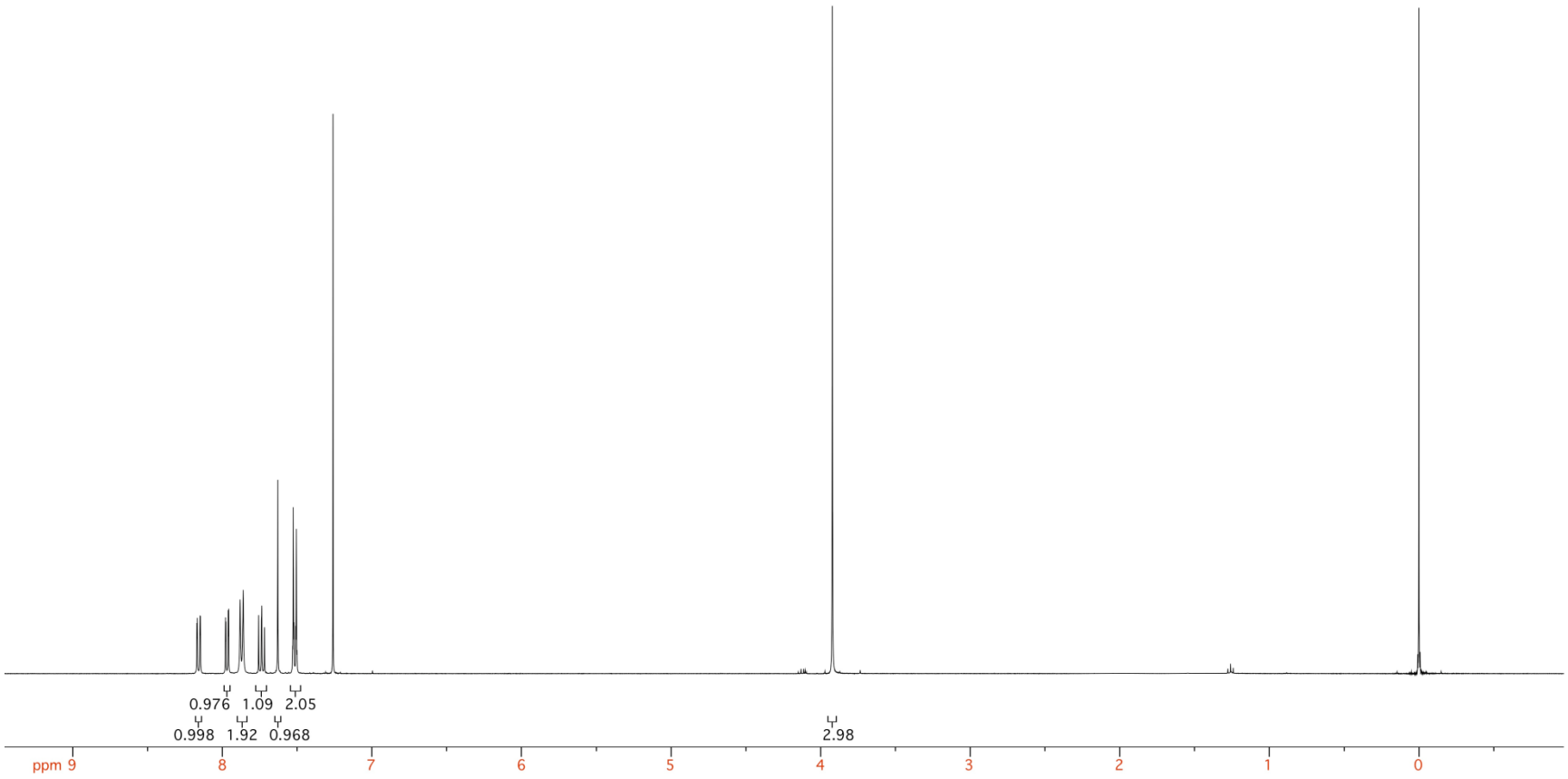

OMe
OMe
N
N
N
N
N
N

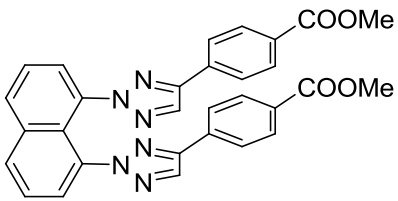
3-5b


ppm 190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

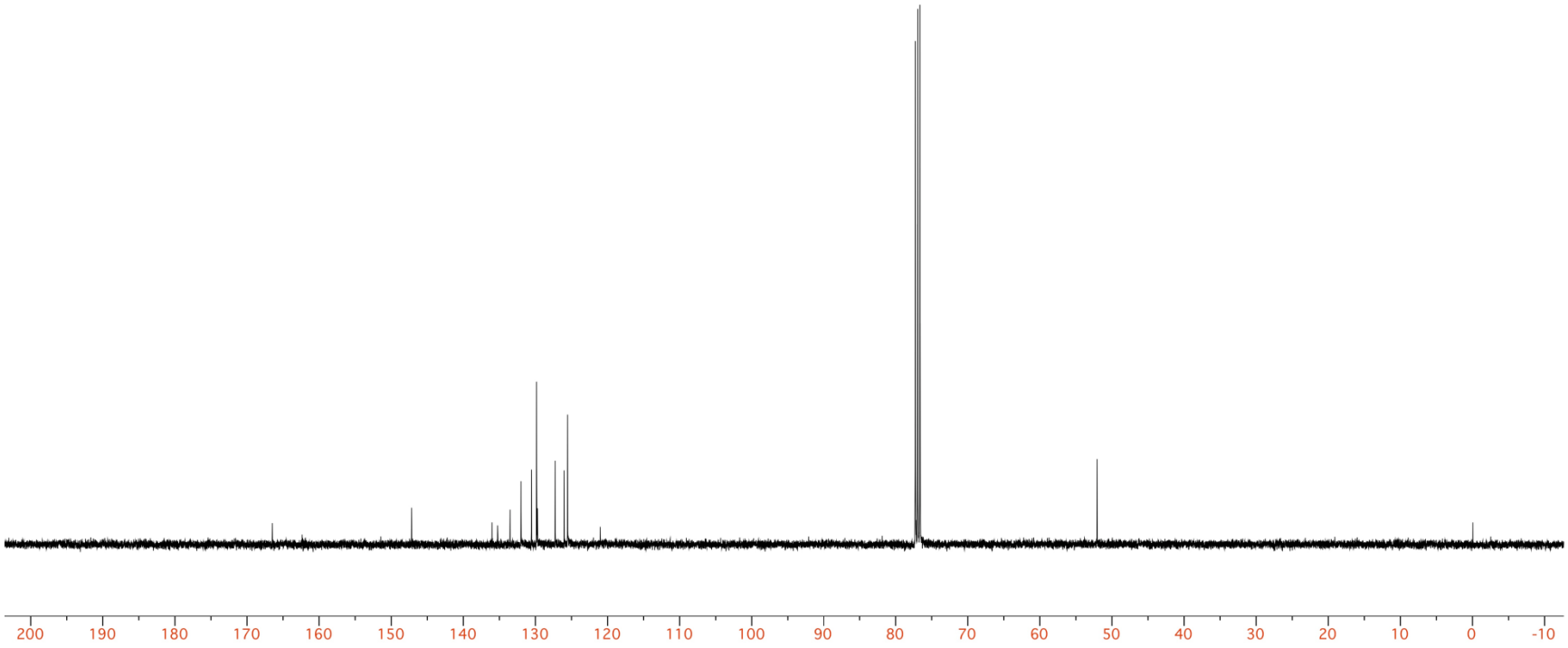

COOMe
COOMe
N
N
N
N
N
N

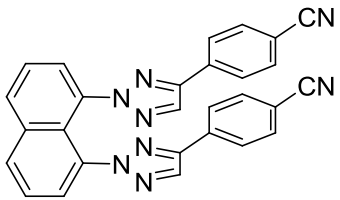
3-5c


0.976
1.09
2.05
0.998
1.92
0.968
2.98
ppm 9
8
7
6
5
4
3
2
1
0

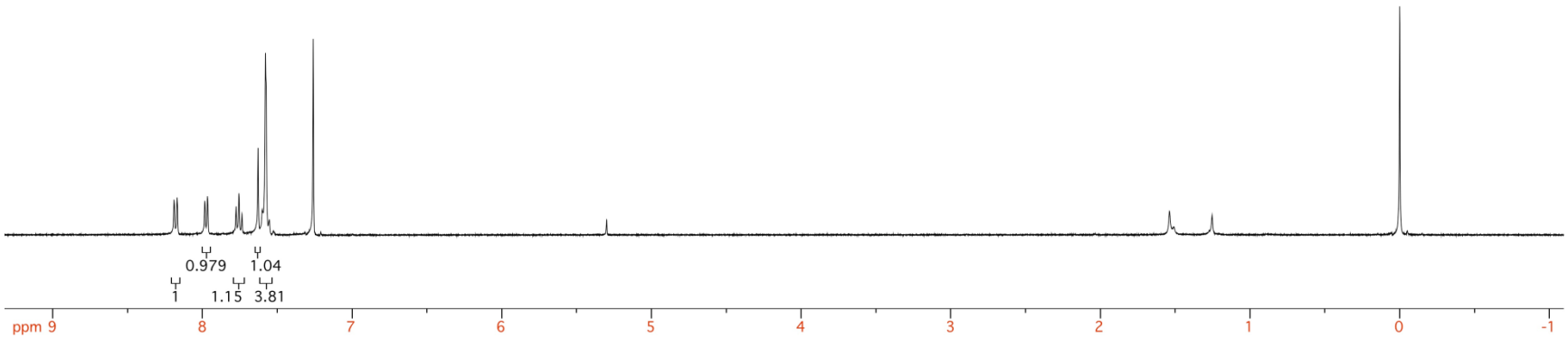

COOMe
COOMe
N
N
N
N
N
N

3-5c


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

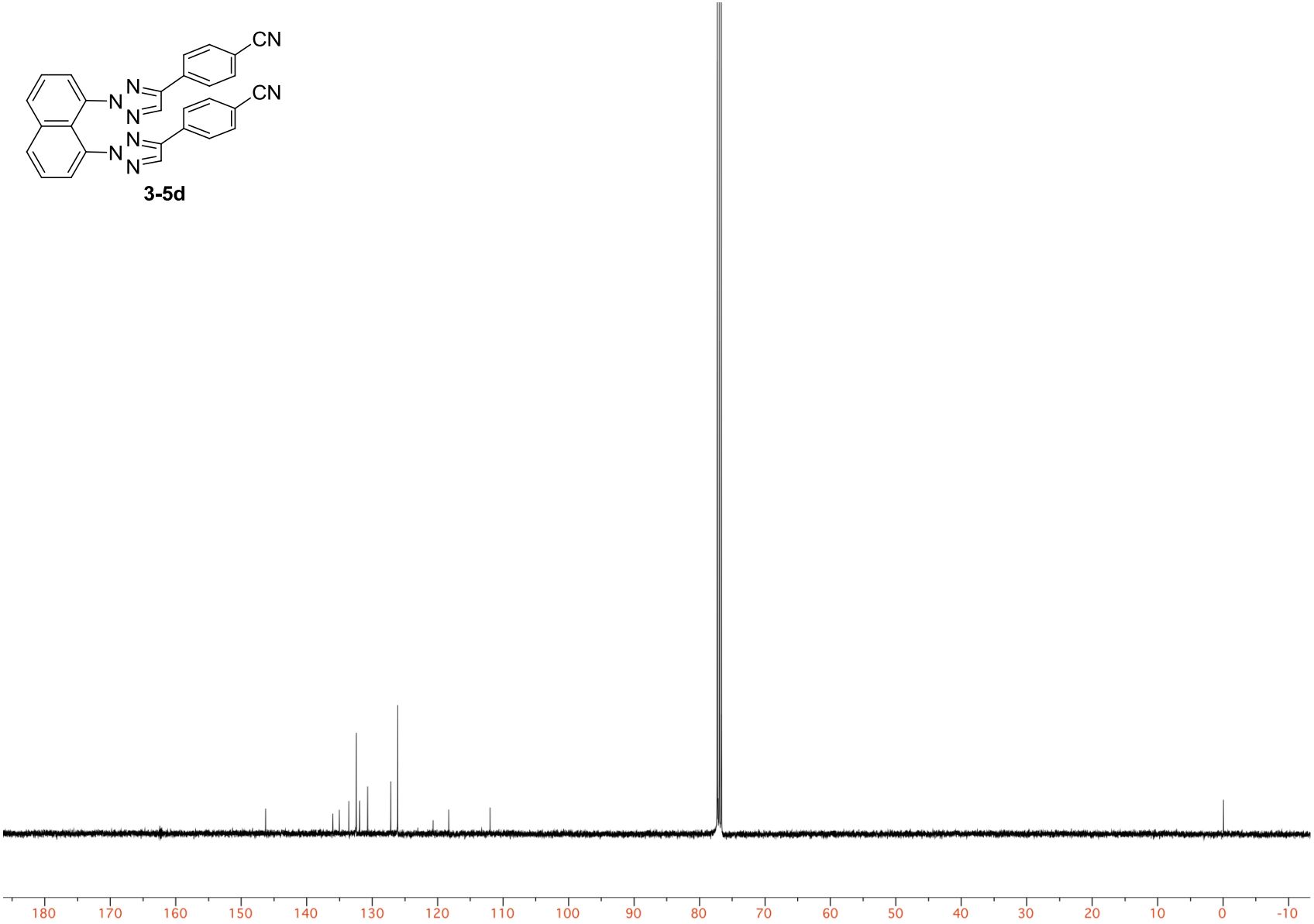


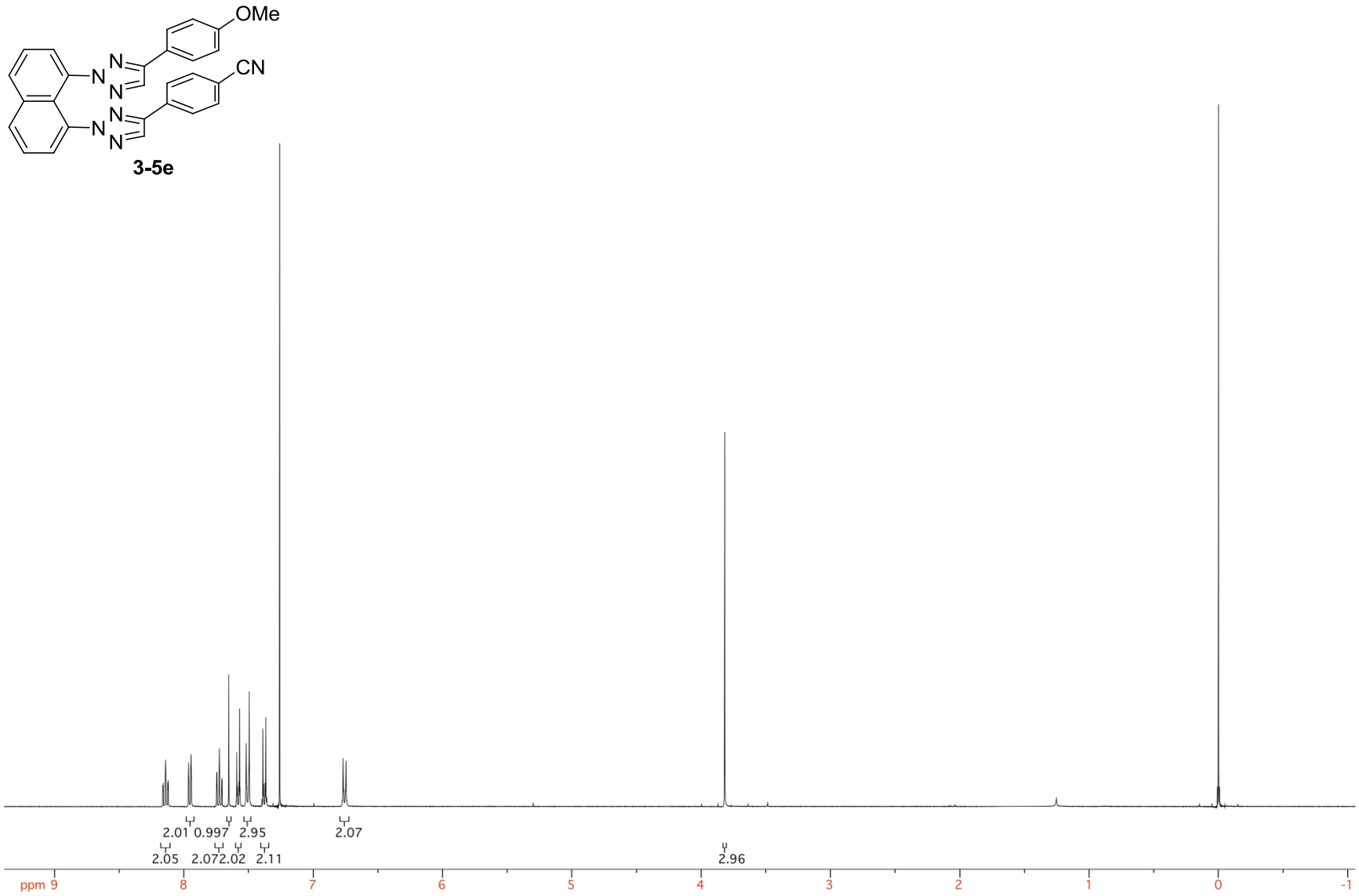
3-5d

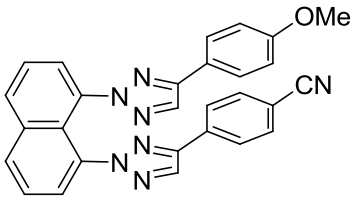


CN
CN
N
N
N
N
N
N

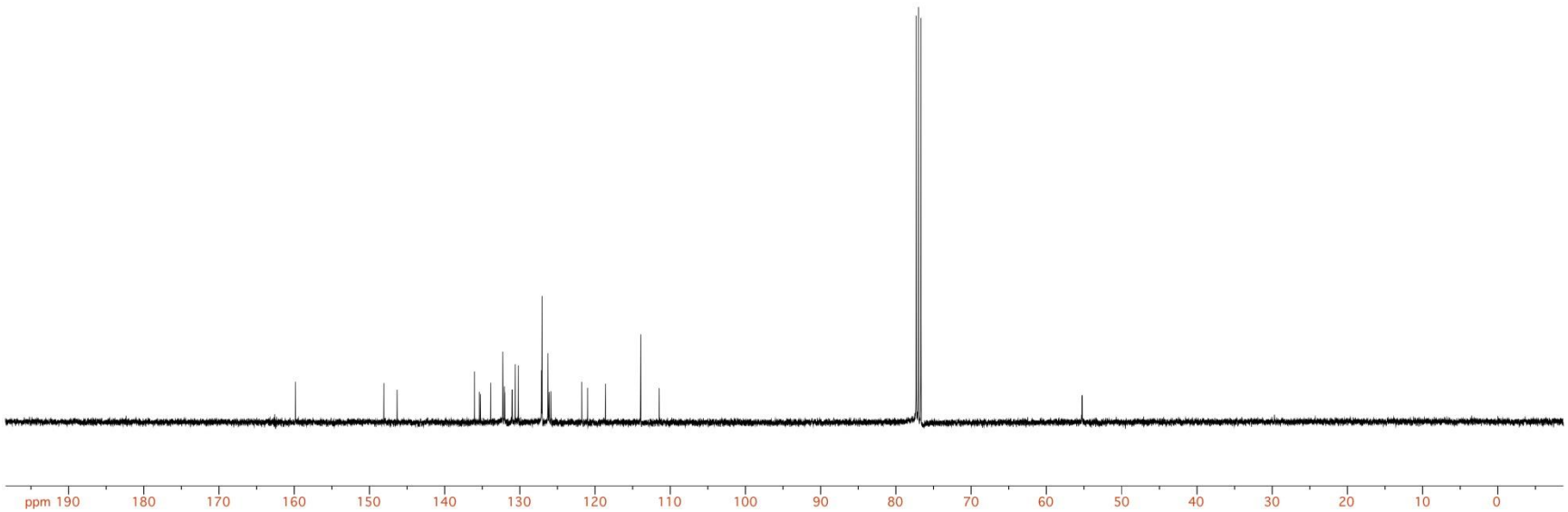
3-5d


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


OMe
CN
N
N
N
N
N
N
3-5e
2.01
0.997
2.95
2.07
2.05
2.07
2.02
2.11
2.96
ppm 9
8
7
6
5
4
3
2
1
0
-1


OMe
CN
N
N
N
N
N
N

3-5e


ppm 190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0