Doctoral Dissertation

Study on unreactive chemical bond cleavage reaction of organic azides by sulfonium ions

（スルホニウムイオンを用いた有機アジドの

不活性化学結合開裂反応に関する研究）

September 2021

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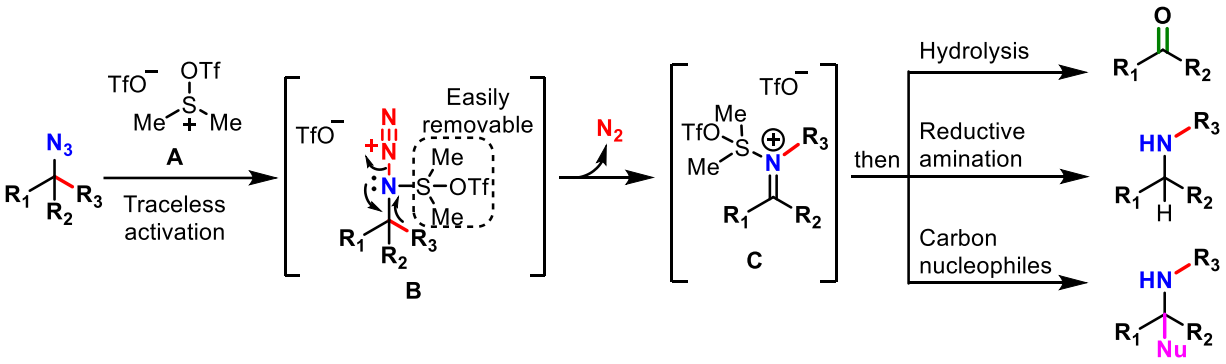
Abstract

[CHAPTER 1] General Introduction

The azido group is a functional group consisting of three cumulated nitrogen atoms and is easy to introduce to organic compounds. With the characteristics of chemical bond migration driven by the energetically favorable loss of nitrogen, organic azides have long been focused on the structural renovation of organic compounds. For example, the azide functionality accompanies the cleavage of unreactive chemical bonds such as carbon-hydrogen (C–H) and carbon-carbon (C–C) bonds, leading to the direct functionalization of unreactive bonds.

Among the reaction of azides, the Schmidt reaction, a reaction of alkyl azides with various carbon electrophiles leading to C–H and C–C bond cleavage in the molecules, represents one of the transformative reactions most widely used. However, carbon electrophiles, such as carbonyls or carbocations, are generally required as coupling partners for azido groups, which may remain in the products as unnecessary substituents. In the case of carbon electrophile-free reactions, even with reactive molecules (carbonyl-α- or benzylic azides), the functionalization of unreactive chemical bonds requires severe reaction conditions such as the use of excess strong acids or high temperature.

In my doctoral research, I aimed to develop a novel method for the "traceless" activation of organic azides (traceless Schmidt reaction) and its synthetic application. The new activation method is based on the essential complexation of an azide with highly electrophilic sulfonium species **A** (complex **B**) by way of *in situ* preparation of **A** from dimethyl sulfoxide (DMSO) and triflic anhydride (Tf_2O). **B** could induce the cleavage of the C–H or C–C bond through 1,2-migration, and the substituent R_3 would be moved onto the nitrogen atom associated with the elimination of dinitrogen to furnish iminium cation intermediate **C**, without unnecessary substituent from the sulfonium activators.



[CHAPTER 2] Functionalization of Primary and Secondary Alkyl Azides via Cleavage of a C–H Bond

Based on the above strategy, chapter 2 deals with the traceless Schmidt reaction of primary and secondary alkyl azides, including the cleavage of unreactive C–H bond (R_3 = H). As I expected, the reactions of primary and secondary alkyl azides with DMSO in the presence of Tf_2O proceeded smoothly to give iminium cations **C** accompanied by the generation of N_2. The ^1H NMR study proves the presence of iminium cations intermediate **C**, showing a broad signal of C–H aldiminium cation structure. Furthermore, the subsequent hydrolysis produced various aldehydes and ketones in moderate to excellent yields. This method allows general alkyl azides as substrates, which the precedented reports cannot convert even with harsh reaction conditions.

[CHAPTER 3] Functionalization of Tertiary Alkyl Azides via Cleavage of a C–C Bond

In chapter 3, I investigated the traceless Schmidt reaction of *tert*-alkyl azides ($R_1 = R_2 = R_3$ = carbon substituents). The reaction of *tert*-alkyl azides was expected to involve the unreactive C–C bond cleavage. Indeed, the treatment of *tert*-alkyl azides with *in situ*-generated highly electrophilic sulfonium **A** followed by the hydrolysis gave the corresponding ketones with primary amines via the formation of *N*-alkyliminium cations **C**. Reaction of a cyclic *tert*-alkyl azide resulted in the ring-expansion accompanied with C–C bond cleavage to give an *N*-containing cyclic product. Among the substrates tested, benzyl and methyl groups were found to be the most cleavable moiety to migrate onto the nitrogen atom of azide. Other alkyl groups such as butyl, decyl, benzoyl, and cyclododecyl can also be cleaved to give functionalized products. The present method provides a convenient way to renovate general *tert*-alkyl azides via unreactive C–C bond cleavage, while precedent methods are only available at benzylic or carbonyl-α-positioning *tert*-alkyl azides.

[CHAPTER 4] Application of the Traceless Schmidt Reaction: One-Pot Functionalization and C–H Azidation

In chapter 4, I describe the one-pot synthetic transformation of alkyl azides that consists of the formation of the imine via C–H or C–C cleavage and the addition of carbon nucleophiles to the imines. *In-situ* formed iminium cations **C** underwent nucleophilic additions by subsequent addition of organomagnesium reagent giving functionalized alkyl amines. Meanwhile, treatment of imines by trimethylsilyl cyanide provided α-aminonitriles of amino acid precursors. Furthermore, an inactive alkyl chain in an unfunctionalized compound was successfully modified through remote C–H azidation followed by C–C bond cleavage by this traceless Schmidt reaction to afford the functionalized product.

[CHAPTER 5] Summary

The C–H functionalization of primary and secondary alkyl azides and C–C functionalization of tertiary alkyl azides were successfully achieved by developing the traceless Schmidt reaction with sulfonium ions. The subsequent transformations were accomplished to the functionalized compounds through one-pot reactions.

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List of Schemes

List of Abbreviations

^{13}C NMR	Carbon Nuclear Magnetic Resonance
DMSO	Dimethyl Sulfoxide
E2	Bimolecular Elimination Reaction
^{1}H NMR	Proton Nuclear Magnetic Resonance
HRMS	High Resolution Mass Spectrometry
IR	Infrared Spectroscopy
LRMS	Low Resolution Mass Spectrometry
R_f	Retention factor
S_N2	Bimolecular Nucleophilic Substitution

CHAPTER 1 General Introduction

1.1 Functionalization of Unreactive C–H and C–C Bonds

Organic compounds are arranged by a consecutive series of C–H and C–C bonds. These frameworks are sometimes interrupted and decorated by heteroatoms (notably oxygen, nitrogen, sulfur, and halogen atoms) called functional groups (FG).[1] The motifs underlie remarkable arrays of small and complex molecules, including bioactive natural products and pharmaceutical ingredients.[2] From the viewpoint of organic synthesis, functional groups could be scaffolds for the transformation of the molecular structures by their chemical reactivity (Figure 1.1A). On the other hand, general C–H and C–C bonds are robust enough to keep the structures of molecules under various reaction conditions. However, from the viewpoint of structural modification, the robustness opposes derivatization.[3]

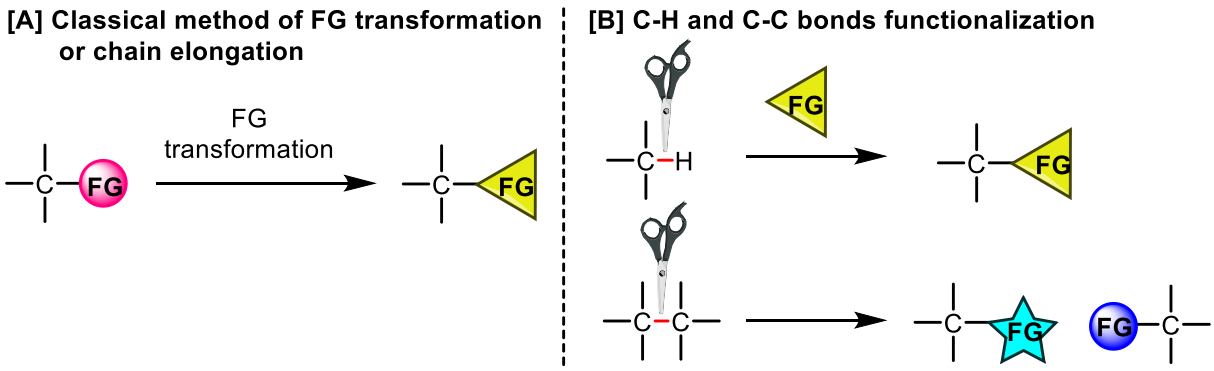
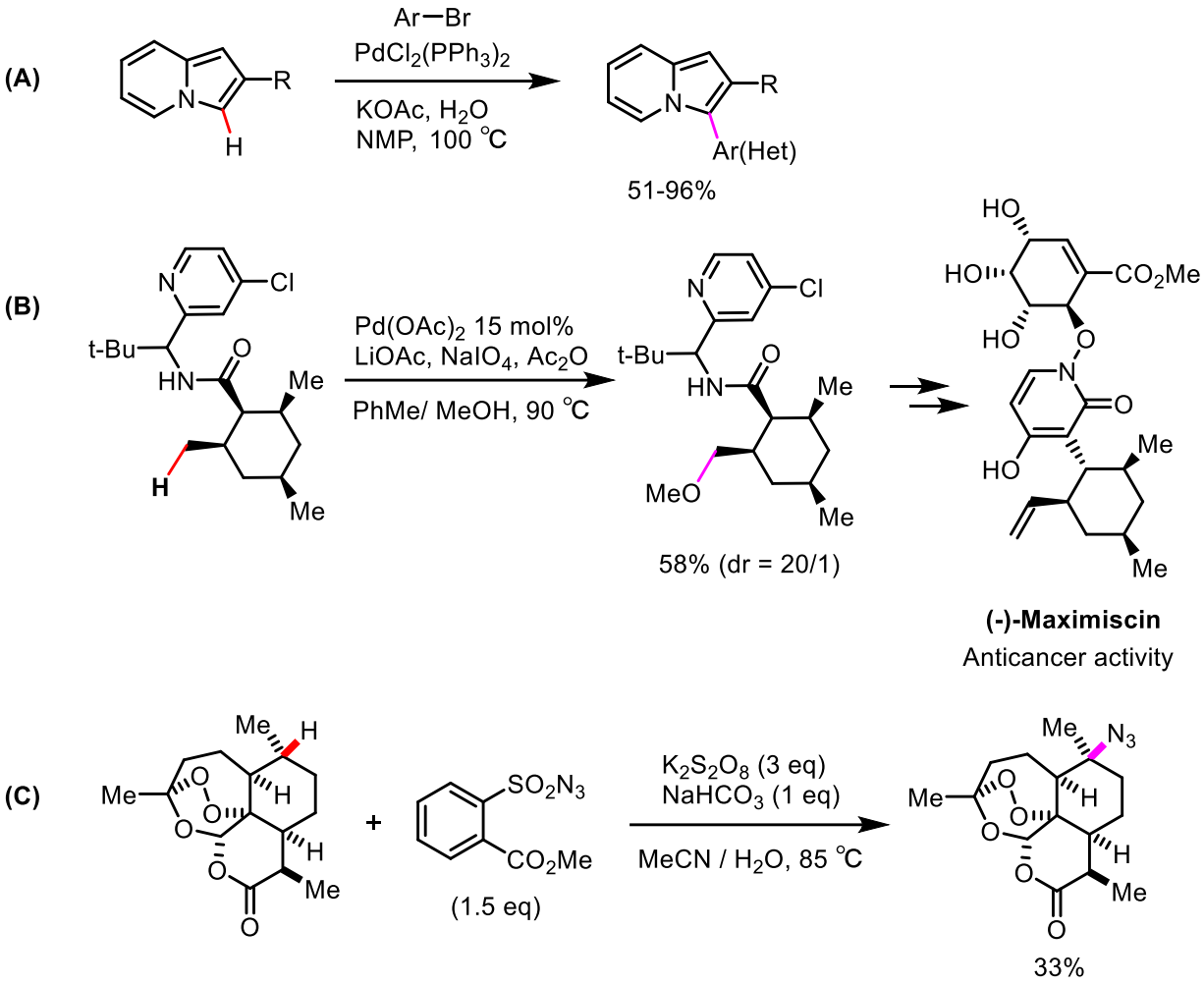


Figure 1.1 (A) Classical method and (B) Unreactive C–H and C–C bonds functionalization for the introduction of functional groups

In this regard, renovating the structure of organic compounds through activation of unreactive chemical bonding such as C–H and C–C bonds enables the dramatic development of functional chemical probes and potent pharmaceuticals. Functionalization of these unreactive bonds allow the use readily accessible substrates to develop complex structures containing diverse scaffolds. (Figure 1.1B).

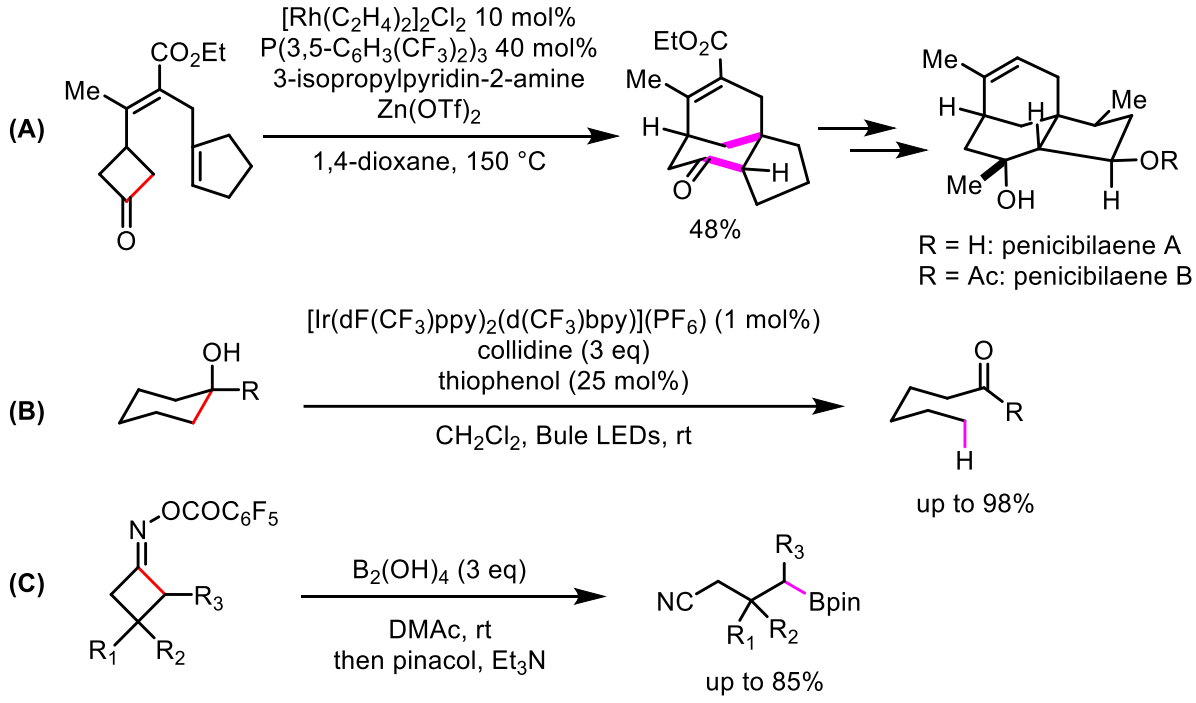
C–H Bond Functionalization. Functionalization of unreactive C–H bond (C–H functionalization) is considered as potential strategy on atom- and step-economy without pre-activation steps of substrates.[4] By the progress on this chemistry over the past two decades, various methods have been developed.[5-9] For instance, Gevorgyan *et al.* investigated the efficient palladium-assisted C_{sp2}–H functionalization of indolizine through arylation and heteroarylation, providing rapid access to substituted indolizines with broad functional group tolerant (Scheme 1.1A).[5c] C_{sp3}–H functionalization has also been achieved.[6] For example, directed palladium-catalyzed methoxylation of the C–H bond is performed as a crucial step in the total synthesis of anticancer natural product (–)-maximiscin (Scheme 1.1B).[6c] Although much less developed than the directed functionalization, considerable efforts in undirected C–H bonds functionalization were reported.[10] As proof, Tang *et al.* demonstrated remote C–H azidation of complex molecules (Scheme 1.1C).[10b]



Scheme 1.1. Examples of (A) Aromatic and (B-C) Aliphatic C–H bonds functionalization

C–C Bond Functionalization. The cleavage of C–C bonds is of fundamental interest and plays a key role in the synthesis of complex molecules.[11] However, C–C bond functionalization is relatively underexplored than selective C–H bond functionalization. The main reason for this could be that C–C bonds are more robust than C–H bonds.[12] Most of the C–C bond cleavage require the help of transition metal catalysts,[12-16] and offer robust C–C bonding scission.[13] For instance, deconstructive formation of tricyclic skeleton via C–C bond activation of cyclobutanone was employed in the total synthesis of penicibilaenes (Scheme 1.2A).[13b] Furthermore, the ring-opening reaction of cyclic alcohols by iridium photoredox catalyst via C–C β-scission was successfully conducted, delivering acyclic

ketones in moderate to excellent yields (Scheme 1.2B).[17] On the contrary, examples of transition-metal-free C–C bond cleavage are limited.[18] Guo *et al.* investigated C–C bond cleavage/ borylation of cycloketone oxime esters by tetrahydroxydiboron (Scheme 1.2C).[18a] As shown above, C–H and C–C bond functionalization may deliver a shortcut to renovate the structure of organic compounds. However, most C–C bond cleavage reactions require transition metal catalysts and sometimes harsh reaction conditions.[19,20] Also, the issues on transition-metal-free conditions are still under exploration, especially on selectivity.



Scheme 1.2. Examples of C–C bond cleavage in small as well as complex molecules

1.2 C–H and C–C Bonds Cleavage in Organic Azides

Organic azides have been recognized as versatile molecules in organic chemistry with wide application in materials science, pharmaceutical, and chemical biology.[21-23] The

multipurpose of this class of compounds is caused by their unique properties and exceptional reactivity among the nitrogen atoms in the azido group (Figure 1.2A). The N1 position can acts as a nucleophile (in Schmidt-type reaction), whereas the N3 position can work as an electrophile (such as in the Staudinger reaction). Meanwhile, N1-N3 of the whole azido group can work together as dipolar in cycloaddition reaction.[23] In this context, the azido group has also been known not only as amine precursor and molecular click conjugation scaffold, but also for its potent reactivity to lead ring-expansion, -opening, or fragmentation of molecules *via* disconnection of unreactive C–H and C–C bonds (Figure 1.2B).[24,25] The most popular reactions, involving the unreactive C–H and C–C bond cleavage of organic azides, are Curtius rearrangement and Schmidt (Boyer-Schmidt) reaction.

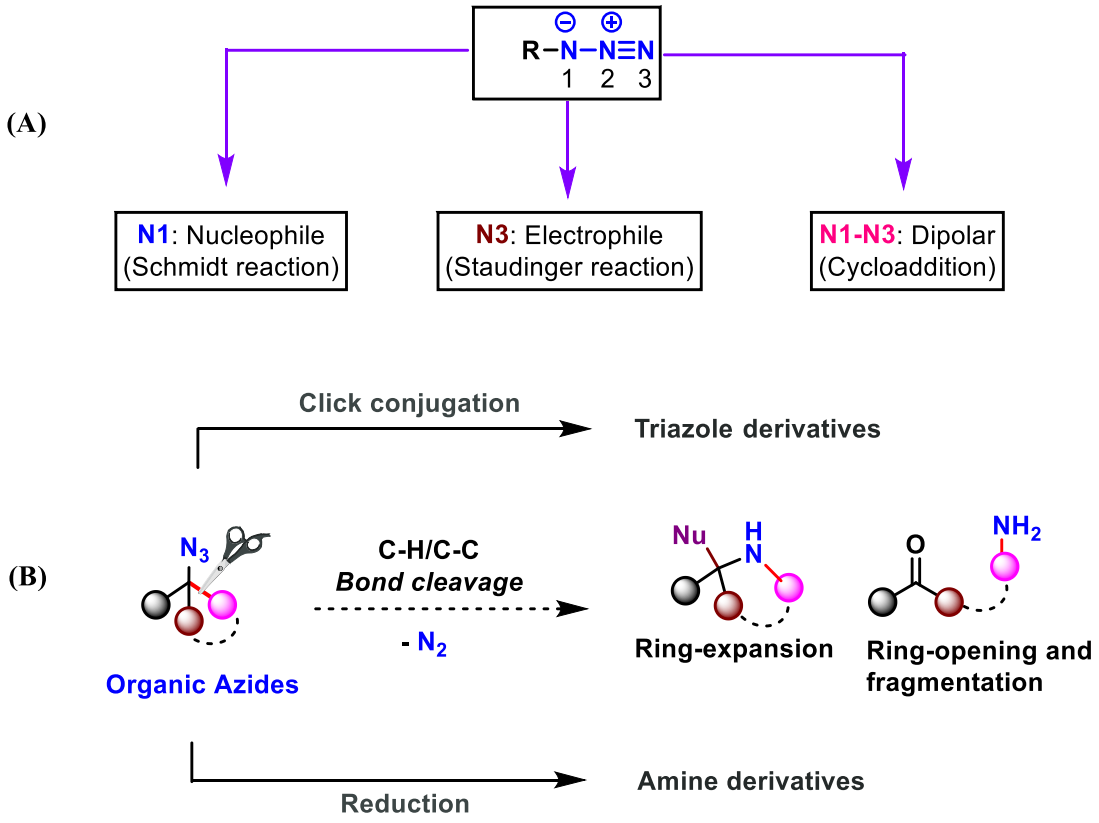
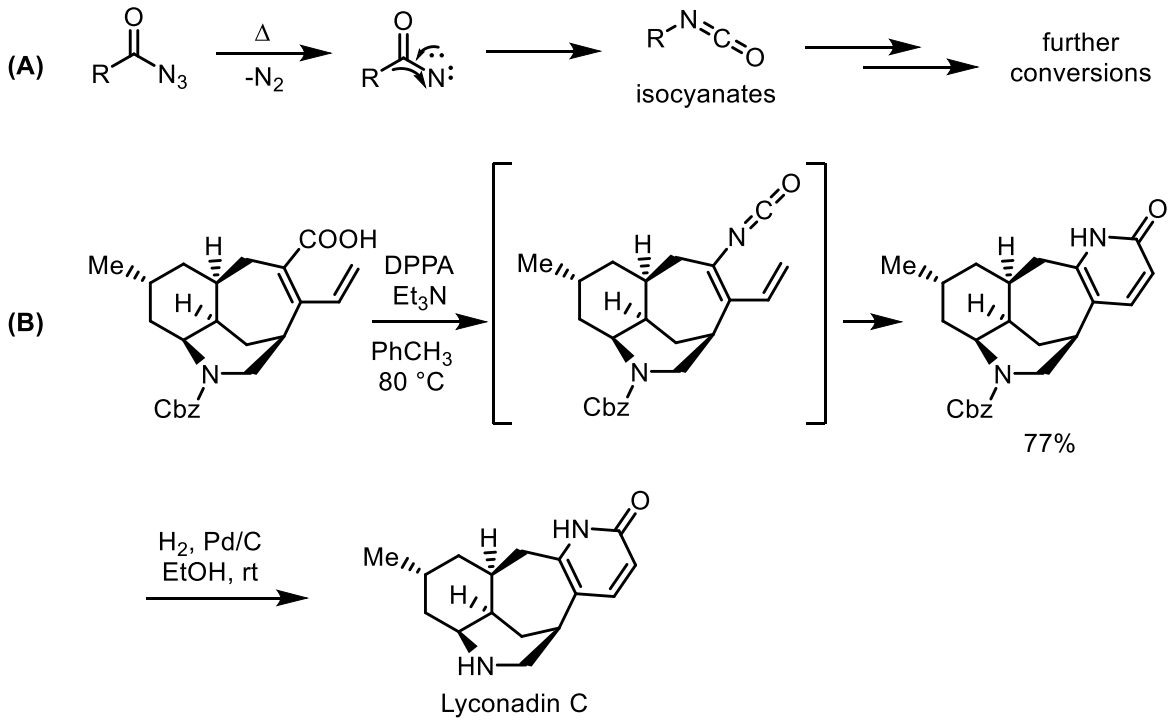


Figure 1.2. (A) The function of nitrogen atoms in azido group, (B) Reaction of organic azides including proposed C–H and C–C bond cleavage

Curtius Rearrangement. By Theodor Curtius in 1885, a thermal rearrangement of an acyl azide to isocyanate through acyl nitrene intermediates, later called Curtius rearrangement, was discovered. During the decomposition of acyl azide, molecular nitrogen is expulsed. At the same time, a substituent attached to the carbonyl group undergoes 1,2-shift with retention of configuration (Scheme 1.3A). The isocyanate generated can be readily transformed into various functional groups by the additional nucleophiles, for example, carbamates by alcohols, primary amines through decarboxylation by water, and ureas by amines.[26] Curtius rearrangement has been widely exploited to synthesize functional molecules as well as complex natural products.[27a-f] In the total synthesis of (–)-lyconadin C, pyridone annulation through tandem Curtius rearrangement/6π-electrocyclization was demonstrated (Scheme 1.3B).[27e]

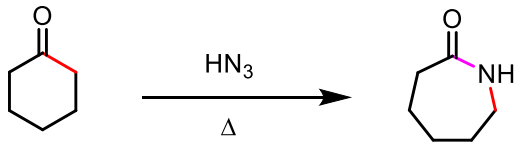


Scheme 1.3. (A) Mechanism of Curtius rearrangement and (B) Application of Curtius rearrangement in the synthesis of lyconadin C

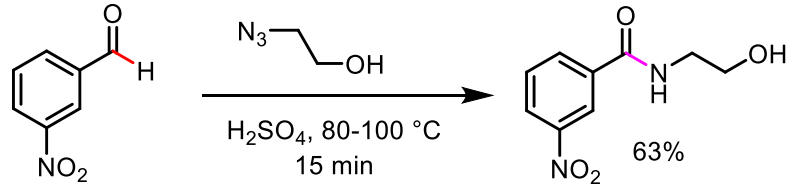
Schmidt / Boyer-Schmidt Reaction. The Schmidt reaction is classically known as the insertion of inorganic azide into a ketone. It is named after Karl Friedrich Schmidt (1887-1971), successfully transforming cyclohexanone to a ring-expanded lactam, azepan-2-one, in the presence of hydrazoic acid (Scheme 1.4A).[28] This type of reaction is useful and important to prepare nitrogen-containing heterocycles.[29] Due to the harmful properties of hydrazoic acid (classical Schmidt reaction), several attempts have been shown to replace it with alkyl azides under strong acid conditions.[30] From 1955 through 1959, Boyer and co-authors have expanded the scope of Schmidt reactions, involving the reaction of alkyl azides with various carbonyl substrates.[31,32] For instance, the reaction of 2-azidoethanol with *m*-nitrobenzaldehyde gave aliphatic amide via C–H cleavage (Scheme 1.4B).[31a] Alkyl group migration was not observed in any of those trials. Successful intramolecular Boyer-Schmidt reaction of alkyl azides with ketones and aldehydes was first established by J. Aubé. By employing Lewis acids such as trifluoroacetic acid or $TiCl_4$ as catalysts, a bicyclic lactam was generated (Scheme 1.4C).[33] After that, the intramolecular Schmidt reaction was then expanded to carbocations from alcohols or olefins (Scheme 1.4D), oxonium ions, and carboxylic acids.[34-39]

Due to the accessibility to provide nitrogen-containing cyclic compounds, numerous researchers have exploited the Schmidt reaction for synthesizing natural products, especially from the alkaloid family.[40-44] Synthesis of (+)-Aspidospermidine, Gephyrotoxin intermediate, and Indolizidine 251F were performed successfully, featuring an intramolecular Schmidt reaction as the key step (Scheme 1.5A and 1.5B).[40-42] Non-acidic environment in Schmidt reaction of azido-alcohol was accomplished in the synthesis of Indolizidine (–)-167B, through S_N2-type reaction (Scheme 1.5C).[42b]

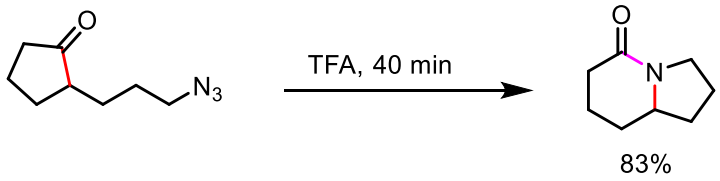
(A) First Schmidt reaction in 1924

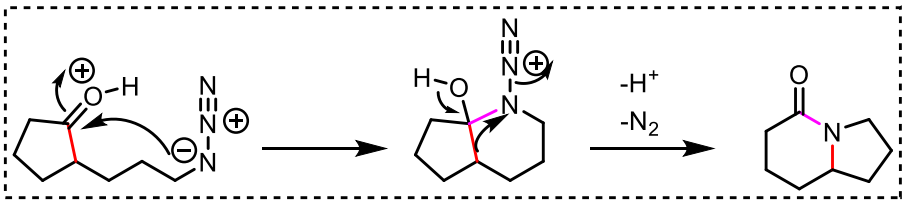


(B) Extended Schmidt reaction by Boyer in 1955

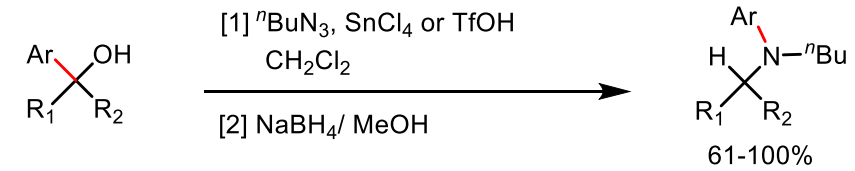


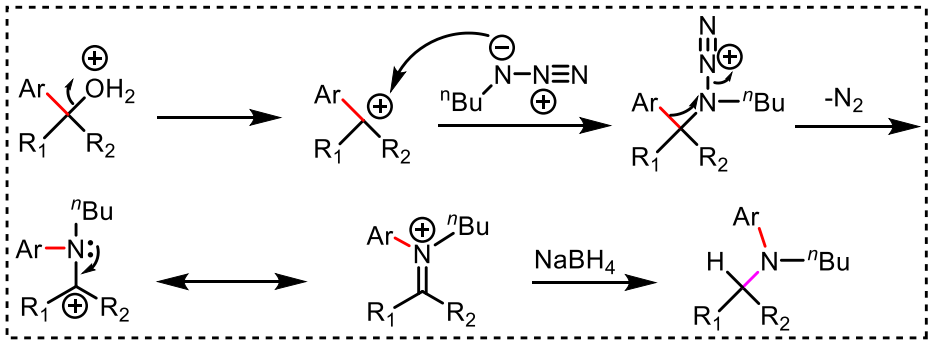
(C) Boyer-Schmidt reaction catalyzed by Lewis acid (J. Aube, 1991)



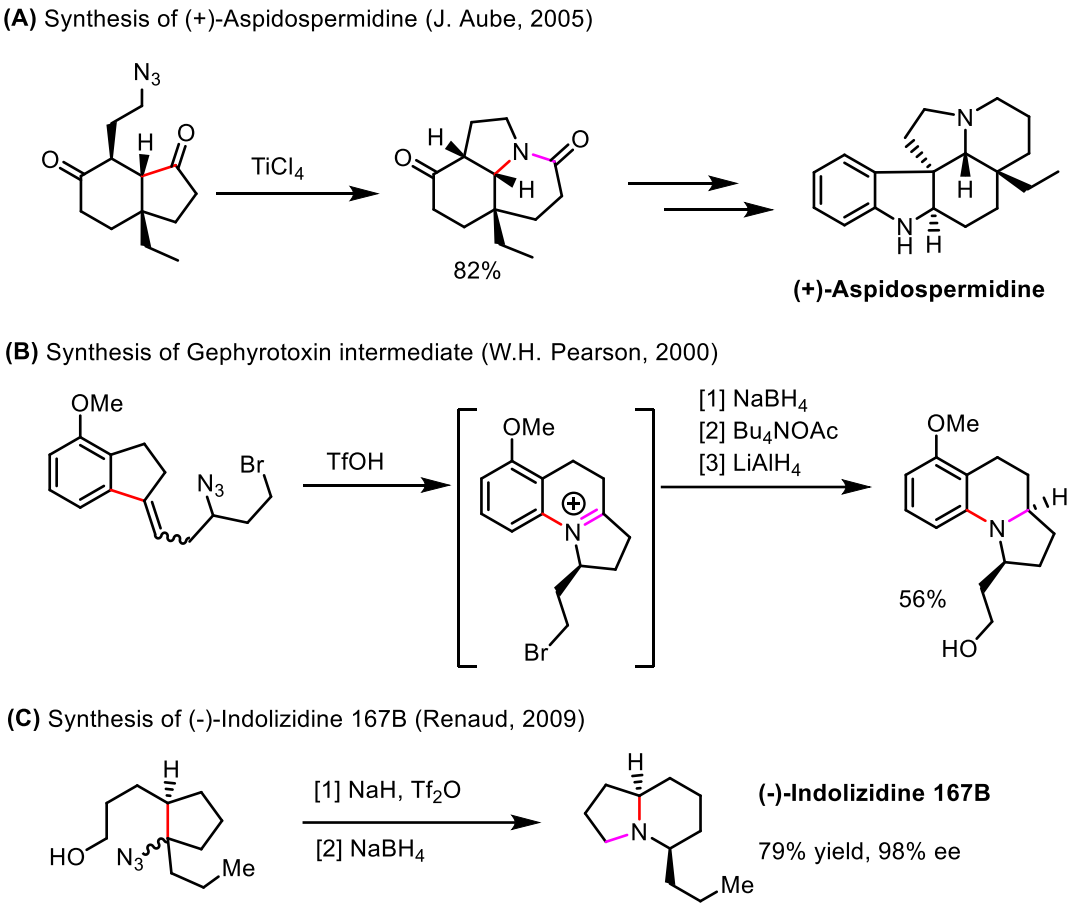


(D) Boyer-Schmidt Schmidt reaction of alkyl azides with carbocation (W.H. Pearson, 1995)





Scheme 1.4. Early development of Schmidt reaction

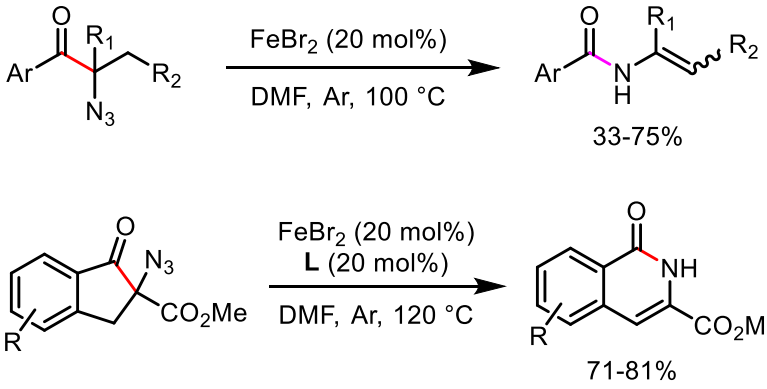


Scheme 1.5. Schmidt reaction in the synthesis of alkaloids

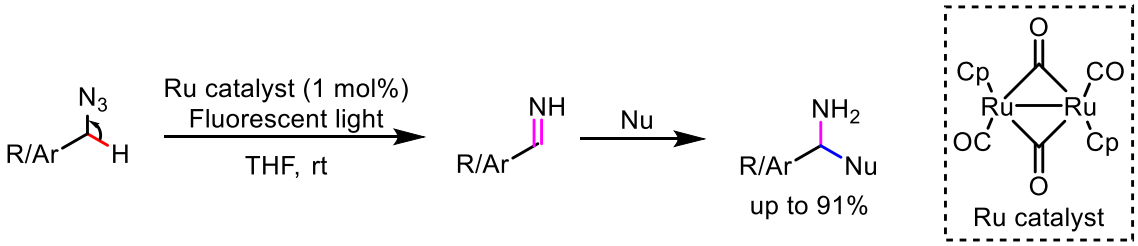
Recent C–H / C–C Bond Cleavage Reactions of Organic Azides. As investigated in numerous works above, the Schmidt reactions have been generally performed under strong acidic conditions to activate the carbon electrophile partners for C–H or C–C bond cleavage because of the weak nucleophilicity of organic azides. In contrast, in the following examples, C–H or C–C cleavage can be performed without the role of nitrogen nucleophile (N1) of organic azides. With metal reagents or catalysts, the chemical bond cleavage can work without electrophilic partners of covalent bonding. For instance, 1,2-benzoyl migration in α-azidoketones were observed with the help of iron(II) bromide at high temperature, affording enamide derivatives in moderate to good yields. Furthermore, isoquinolones were obtained by applying this method for cyclic substrates (Scheme 1.6A).[45] Park *et al.*

developed photocatalytic system based on ruthenium complex for C–H cleavage in primary and secondary alkyl azides, generating *N*–H imines which can be further treated by nucleophilic addition (Scheme 1.6B).[46] Later, Park *et al.* examined the C–C bond cleavage in β-hydroxy azides, enabling the formation of *N*–H imines and carbonyl compounds (Scheme 1.6C).[47] Kirsch *et al.* have developed geminal diazide chemistry of very reactive structure (Scheme 1.6D). Thermolysis of carbonyl-α geminal diazides in *o*-xylene allows aryl migration onto the nitrogen atom of azide, then removal of molecular nitrogen, followed by cyclization to successfully give tetrazole derivatives.[48]

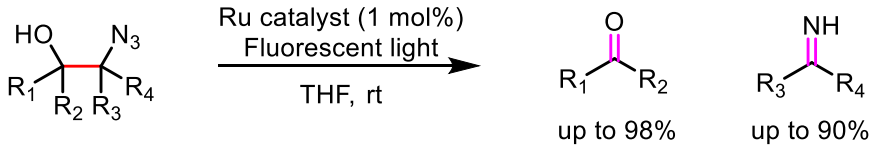
(A) Iron-catalyzed acyl migration in α-azidoketones[45]



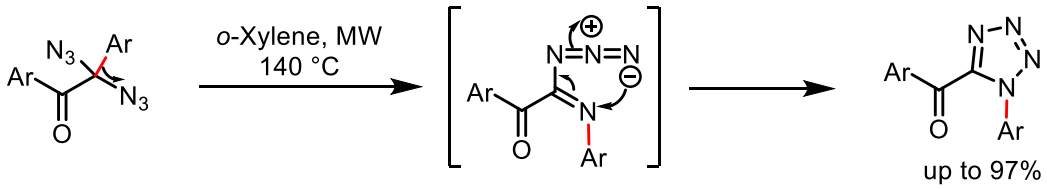
(B) Activation of primary and secondary azides to N-H imines by Ru photocatalyst[46]



(C) C-C bond cleavage of β-hydroxy azides assisted by Ru photocatalyst[47]



(D) Thermolysis of α-carbonyl geminal diazides to fashion tetrazoles[48]



Scheme 1.6. Precedented examples of organic azides activation

1.3 Research Background and Purpose

As shown above, organic azides are versatile scaffolds for connecting the component (click reaction) and structural renovation through chemical bond cleavage (Schmidt reaction and the related conversion reactions). However, several issues to be solved remain. Due to the low nucleophilicity of organic azides, Schmidt reactions generally require carbon electrophile partners for the activation of unreactive bonds in azido compounds, such as carbocations, carbonyl compounds, and carbon center connected with strong leaving groups. Thus, unnecessary substituents remain in the products (Figure 1.3A). Although chemical bond functionalization of organic azides without carbon electrophiles has been investigated, activation of those azido groups mainly occurs at the reactive sites such as benzylic or carbonyl α-positions, as shown in precedented examples (Scheme 1.6A, B, D).[45,49-51] Alternatively, activation of azido moiety requires existing functional groups such as hydroxyl groups neighboring to the azido moiety (Scheme 1.6C).[47] However, the activation of general alkyl azides usually need harsh reaction conditions such as the use of excess strong acids or high temperature over 100 °C.[52] Although C–H bond cleavage of primary and secondary alkyl azides has also been reported (Scheme 1.6B), the examples are quite limited.[46,53,54] Moreover, the C–C bond activation of *tert*-alkyl substrates is still challenging.[47]

To solve the issues above (Figure 1.3A), I proposed to use reactive sulfonium ion species for activation of general alkyl azides (Figure 1.3B). As demonstrated in Pummerer rearrangement, the reactive sulfonium species are potent electrophiles and can be easily prepared from ubiquitous sulfoxides.[55,56] These species would be the vital activators of low-nucleophilic alkyl azides, promoting the migration of the substituent (H– or R–) onto the nitrogen atom in the azido group by the expulsion of molecular nitrogen. The benefits of using sulfonium ions are as follows: (1) The formed N–S bond could be easily removed at

the stage of imine formation or aqueous treatment. (2) The undesired migration of the *S*-substituents could be suppressed by the cationic sulfonium species. (3) Using non-steric sulfonium ions, it would be possible to access bulky *tert*-alkyl azides for C–C bond cleavage. In short, Schmidt reaction of organic azides by sulfonium ions should afford initial iminium cation intermediates connected with an easily removable sulfonium group (called traceless activation). It is also advantageous that the *in-situ* generated iminium cations can be further delivered to various transformations for the structural reconstruction in one pot. In this thesis, sulfonium ion-induced traceless Schmidt reaction of primary, secondary, and tertiary alkyl azides is presented.

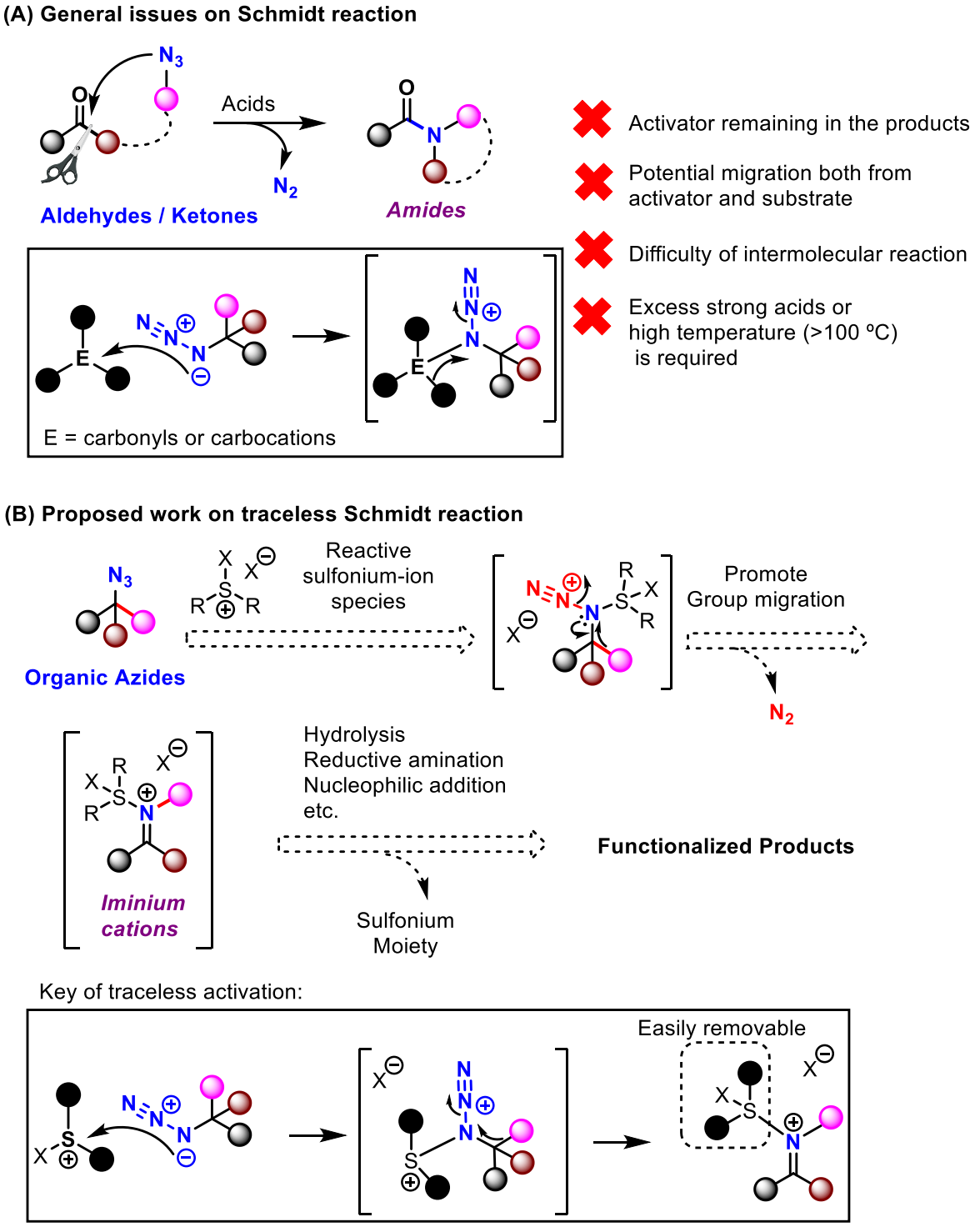


Figure 1.3. General issues on Schmidt reaction and proposed work allowing unreactive bond cleavage

1.4 References

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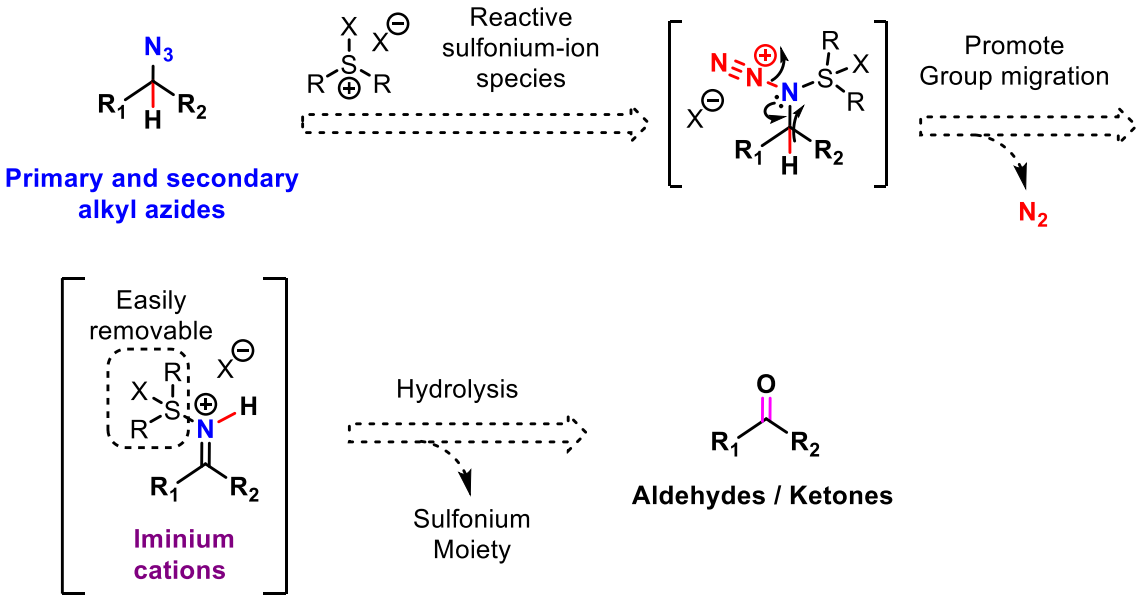
CHAPTER 2 Functionalization of Primary and Secondary Alkyl Azides via Cleavage of a C–H Bond

2. 1 Introduction

As mentioned in Chapter 1, C–H activation of primary and secondary alkyl azides without the help of carbon electrophiles has already been reported. However, those are quite limited.[1,2] In addition, harsh reaction conditions such as elevated temperature and excess use of strong acids are required, albeit in reactive molecules like benzylic and carbonyl-α azides.[3-5] To develop unreactive bond cleavage which covers general alkyl azides having low nucleophilicity, herein, sulfonium ions are utilized. These highly electrophilic species are prepared *in-situ* by the reaction of sulfoxides and activators.[6,7] Reaction of alkyl azides with generated sulfonium ions could promote α-hydrogen migration from primary or secondary alkyl azide to the nitrogen atom of azido group, giving iminium cations as versatile intermediates (Scheme 2.1). The reaction would furnish initial iminium cations connected with an easily removable sulfonium moiety from the activators. Thus, after hydrolysis, aldehydes or ketones could be delivered from primary or secondary alkyl azides.

In this chapter, the optimization of conditions for the traceless Schmidt reaction of alkyl azides is described first. Several parameters such as temperature, solvents, and sulfoxides as well as activating reagents are screened. Second, understanding of reaction progress is also discussed, according to the ^{1}H NMR spectra of the reaction mixture. Finally, the scope of C–H bond cleavage in primary and secondary alkyl azides including diazide is examined.



Scheme 2.1. Working hypothesis on traceless Schmidt reaction of primary and secondary alkyl azides

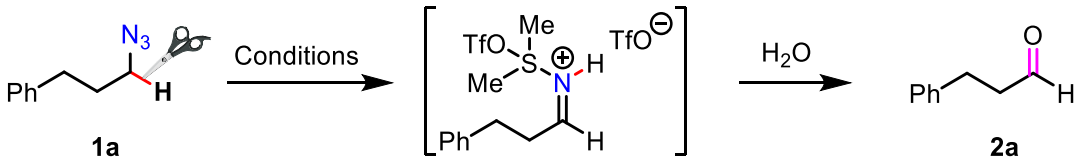
2. 2 Optimization of Reaction Conditions

The investigations began with 3-phenylpropyl azide (**1a**) as a non-benzylic alkyl azide substrate (Table 1). The reaction conditions were explored to afford 3-phenylpropanal (**2a**) by aqueous workup for hydrolysis. The sole use of triflic anhydride did not work (entry 1). On the other hand, the reaction with *in-situ* generated sulfonium ion from dimethyl sulfoxide and triflic anhydride at room temperature in dichloromethane successfully provided **2a** in 14% yield (entry 2). At the initial attempts, I expected the reaction would be smoothly proceeded at low temperature, as demonstrated in Swern oxidation employing activated sulfoxide species.[8-11] However, the reactions at 0 or -78 °C ended with unsatisfactory results (entries 3 and 4). It may be due to the low nucleophilicity of alkyl azides that could not attack the generated sulfonium ions at the low temperature. In addition, polar solvents such as acetonitrile and nitromethane gave **2a** in low yields (entries 5 and 6). Gratifyingly, the yield of **2a** was improved in toluene as a less polar solvent at room temperature (entry 7). Other sulfoxides such as diphenyl and dibenzyl sulfoxide were not

suitable for the desired transformation (entries 8 and 9). Increasing the amount of triflic anhydride can furnish **2a** in a notable 64% yield (entry 10). Then, different activators of sulfoxides were carried out. Nonafluorobutanesulfonic anhydride required longer reaction time to serve the desired product, albeit in a lower yield (4 h in entry 10 for 64% of **2a**, and 19 h in entry 11 for 55% of **2a**). This finding suggested that both non-steric sulfoxide and activator may play an important role in the reactions. The transformations did not occur when utilizing nonafluorobutanesulfonyl fluoride or *p*-toluenesulfonic anhydride. These indicate that the sulfonium ions generated should be strongly electrophilic, and the nucleophilic halide producing unreactive sulfonium halide should be removed (entries 12 and 13).

After extensive investigation, the use of *tert*-butylbenzene as a solvent afforded **2a** in 70% yield and allowed large-scale reaction (entry 14). The use of DMSO-d6 did not affect the results (entry 15). Reducing the reagents also provided similar yields with prolonged reaction time (2.5 h for entry 14; 5 h for entry 16). In order to check whether this C–H bond cleavage conversion is under catalytic process or not, 0.5 equivalent of reagents were used. Resultantly, this condition dramatically decreased **2a** to 24% yield (entry 17). It signified the reactions underwent via a non-catalytic process. Probably, sulfonium group is still attached to the iminium cation intermediate before hydrolysis. Other similar benzene-type solvents also provided **2a**, even in lower yields (entries 18-20).

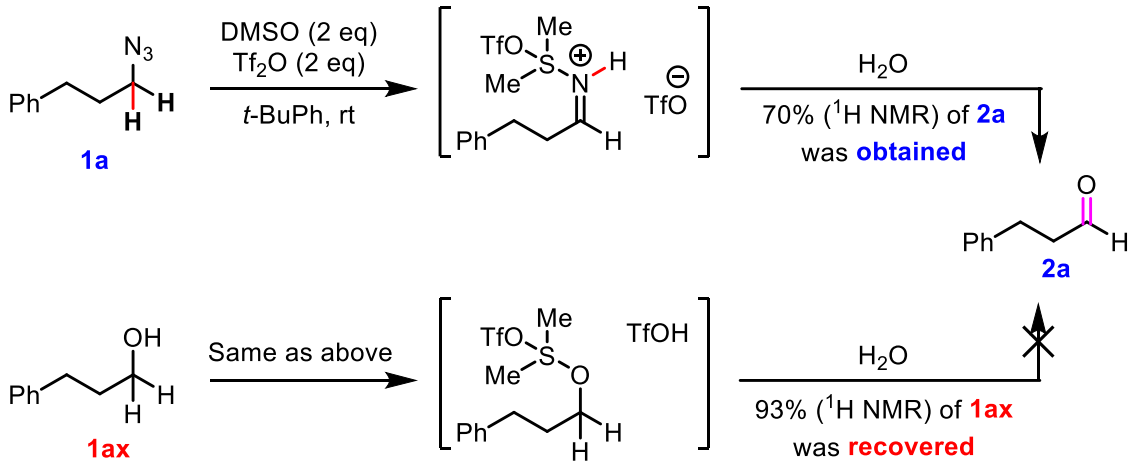
Table 2.1 Optimization of the reaction conditions



Entry[a]	Sulfoxide / Activator	Solvent	Temp. (°C)	Yield (%)[b]	Recovery (%)[b]
1	- / Tf_2O (2 eq)	CH_2Cl_2	rt	0	99
2	DMSO (2 eq) / Tf_2O (2 eq)	CH_2Cl_2	rt	14	0
3	DMSO (2 eq) / Tf_2O (2 eq)	CH_2Cl_2	0	28	47
4	DMSO (2 eq) / Tf_2O (2 eq)	CH_2Cl_2	-78	0	92
5	DMSO (2 eq) / Tf_2O (2 eq)	CH_3CN	rt	10	50
6	DMSO (2 eq) / Tf_2O (2 eq)	CH_3NO_2	rt	5	0
7	DMSO (2 eq) / Tf_2O (2 eq)	CH_3Ph	rt	50	13
8	Bn_2S=O (2 eq) / Tf_2O (2 eq)	CH_3Ph	rt	14	0
9	Ph_2S=O (2 eq) / Tf_2O (2 eq)	CH_3Ph	rt	9	91
10	DMSO (2 eq) / Tf_2O (4 eq)	CH_3Ph	rt	64	5
11	DMSO (2 eq) / (n-$C_4F_9SO_2)_2O$ (4 eq)	CH_3Ph	0 to rt	55	8
12	DMSO (2 eq) / n-$C_4F_9SO_2F$ (4 eq)	CH_3Ph	rt	0	97
13	DMSO (2 eq) / Ts_2O (4 eq)	CH_3Ph	rt	0	0
14	**DMSO (2 eq) / Tf_2O (2 eq)**	***t*-BuPh**	**rt**	**70 (60)[c]**	**0**
				[65 (61)][d]	**0**
15	DMSO-d6 (2 eq) / Tf_2O (2 eq)	*t*-BuPh	rt	63	0
16	DMSO (1.2 eq) / Tf_2O (1.2 eq)	*t*-BuPh	rt	64	0
17	DMSO (0.5 eq) / Tf_2O (0.5 eq)	*t*-BuPh	rt	24	57
18	DMSO (2 eq) / Tf_2O (2 eq)	*i*-PrPh	rt	50	5
19	DMSO (2 eq) / Tf_2O (2 eq)	CF_3Ph	rt	56	0
20	DMSO (2 eq) / Tf_2O (2 eq)	Cl-Ph	rt	36	5

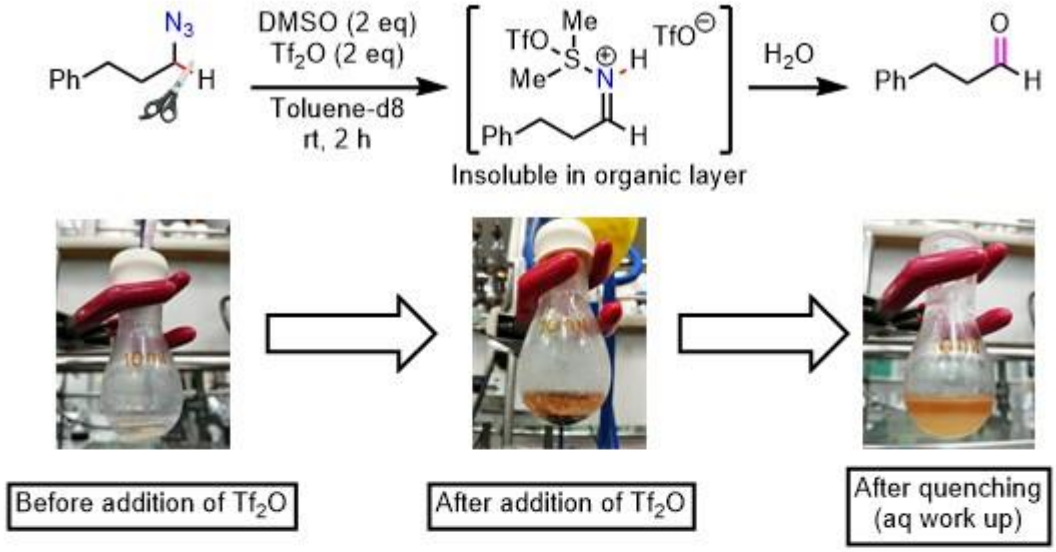
[a]0.2 mmol scale reactions. [b]Yield and recovery based on ^{1}H NMR with $(CHCl_2)_2$ internal standard. [c]Isolated yield. [d]2.0 mmol scale reaction.

To evaluate potential DMSO oxidation of the alcohol as demonstrated in Swern oxidation,[8-11] 3-phenyl-1-propanol (**1ax**) was submitted to give same aldehyde **2a** from the azide **1a** (Scheme 2.2). The alcohol starting material **1ax** was totally consumed in 15 min after addition of triflic anhydride (checked by TLC). However, pleasingly, **2a** was not obtained (alcohol **1ax** was recovered in 93% in ^{1}H NMR yield). Although hydroxyl group can react quickly with sulfonium ion or triflic anhydride,[12,13] aqueous treatment without the corresponding base such as triethylamine recovered the starting alcohol. On the other hand, alkyl azide **1a** was successfully converted to give **2a** in 70% ^{1}H NMR yield. These results suggest the C–H activation method is capable of assisting chemoselective oxidation of azido group rather than hydroxyl group to corresponding carbonyl compound.



Scheme 2.2. Selective C–H activation of azido group instead of hydroxyl group

(A) Physical changes during the traceless Schmidt reaction



(B) ^{1}H NMR spectra of the reaction mixture

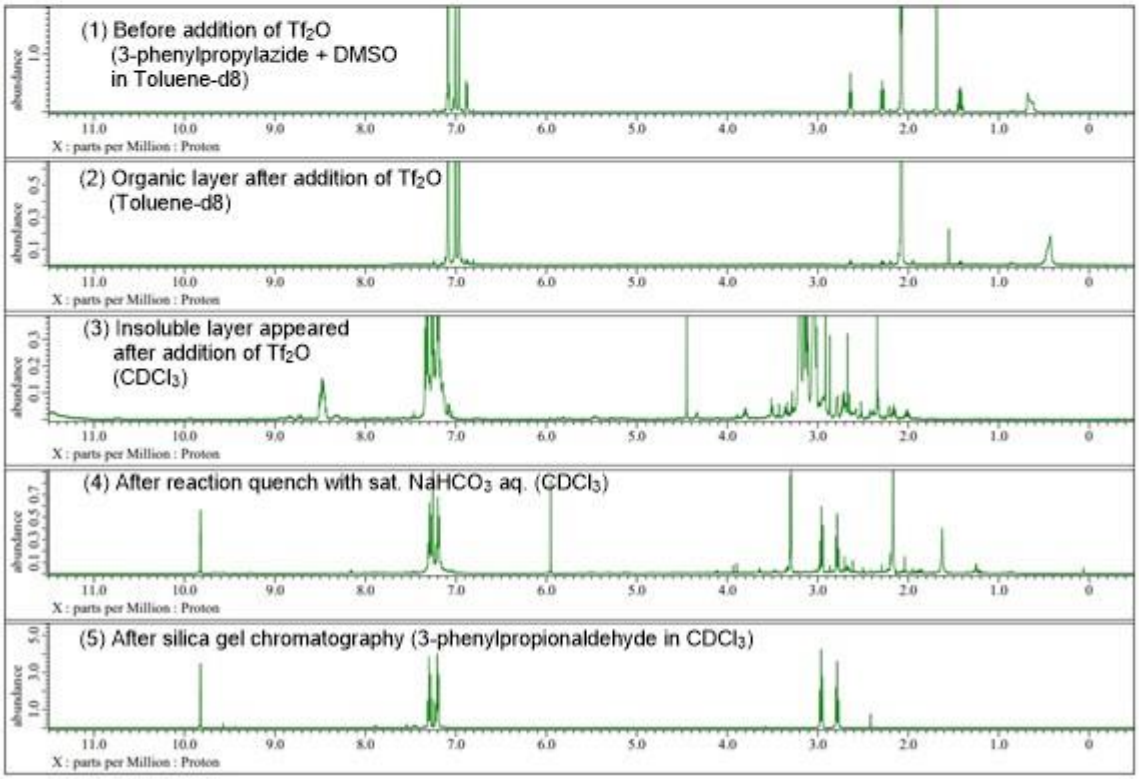


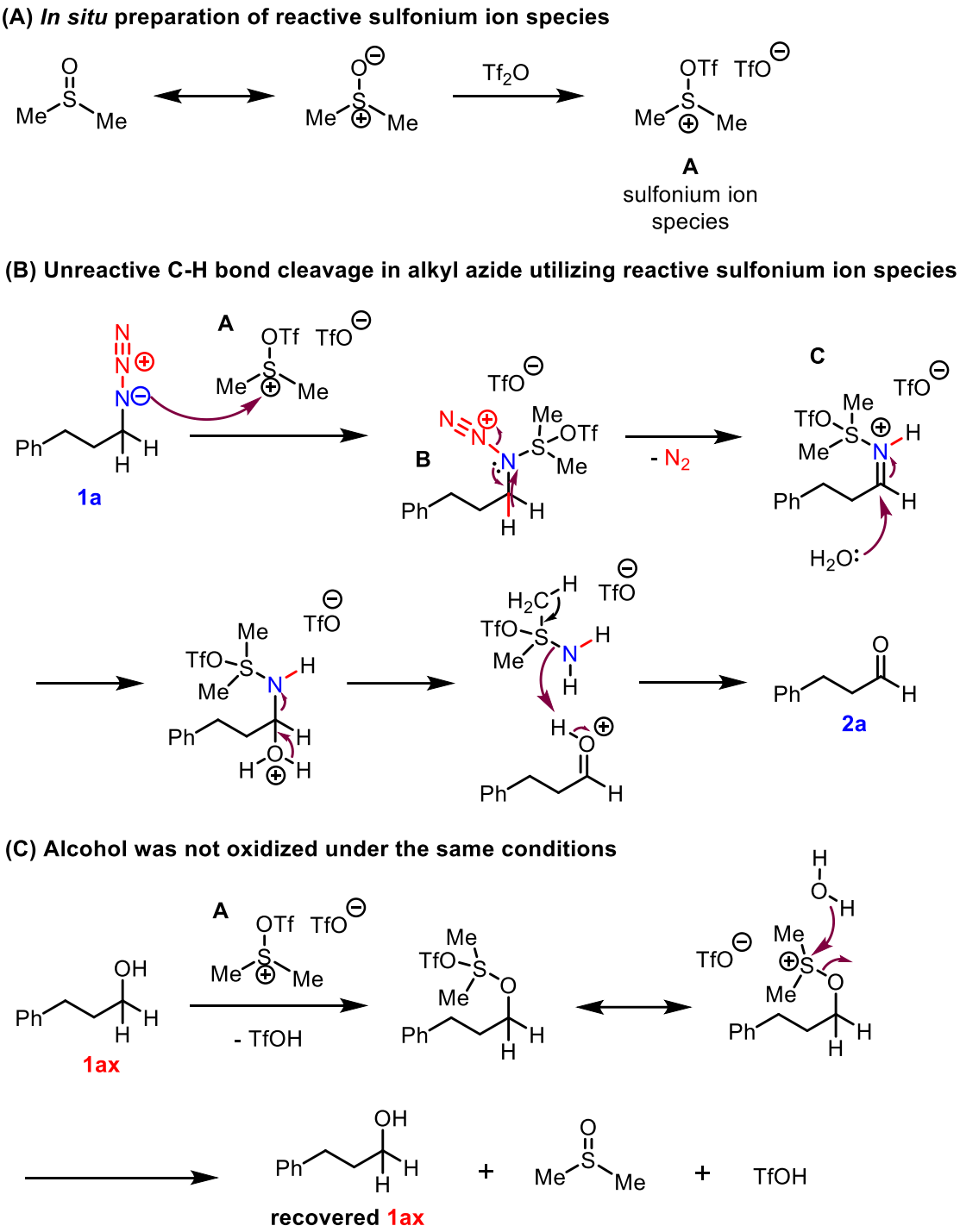
Figure 2.1. Physical changes during the reaction and ^{1}H NMR spectra of the mixture

To understand the reaction progress, ^{1}H NMR study was examined in toluene-d8 (Figure 2.1). The initial clear solution contains **1a**, dimethyl sulfoxide, and toluene-d8 (Figure 2.1B-

1). After the addition of triflic anhydride, white solid was subsequently observed at the bottom of the flask (Figure 2.1A). This phenomenon indicated that the reactive sulfonium ion species, dimethyl(trifluoromethanesulfonyl)sulfonium salt, is successfully generated.[14] The suspension turned to light-yellow oil and then to brown oil insoluble in the organic layer, accompanied with the evolution of bubble probably from expulsed nitrogen. After that, ^{1}H NMR spectroscopy was taken from both organic and insoluble layers. Appealingly, no substrate-derived materials other than trace **1a** were found in the organic layer (Figure 2.1B-2). Conversely, organic components were observed from the insoluble brown oil layer (Figure 2.1B-3, taken in $CDCl_3$). At this point, aldehyde **2a** has not been generated. However, a broad peak at 8.47 ppm to be assigned as C–H of aldiminium cation structure was found (Figure 2.1B-3).[15-17] After an aqueous quench, **2a** was generated (Figure 2.1B-4 and -5). These observations strongly suggest the presence of iminium cation intermediate during the reaction before hydrolysis.

2. 3 Plausible Mechanism

According to the above investigation and corresponding results, the plausible mechanism of unreactive bond cleavage in alkyl azides by traceless Schmidt reaction is proposed. DMSO attack the triflic anhydride to give reactive sulfonium ion species **A** (Scheme 2.3A).[14] Reaction of **1a** with *in situ* prepared sulfonium ion **A** gave azido-sulfonium complex **B** (Scheme 2.3B). The presence of sulfonium group could induce the group migration (–H) to the nitrogen atom of azide. At the same time, molecular nitrogen is eliminated and form the iminium cation intermediate **C**, which was detected during ^{1}H NMR study. Subsequent hydrolysis of this intermediate provides **2a**. On the other hand, alcohol **1ax** was not converted to **2a** under the same reaction conditions. Probably, hydrolysis occurred at the sulfonium ion recovered the starting material (Scheme 2.3C).



Scheme 2.3. Plausible mechanism for selective bond cleavage by traceless Schmidt reaction

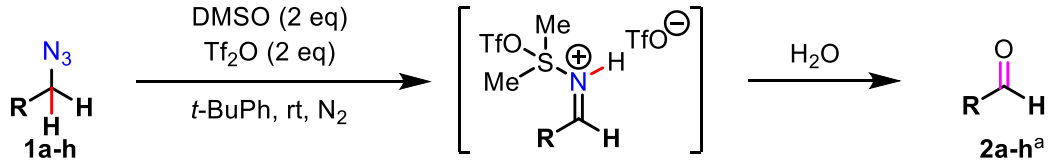
2. 4 Scope of Primary and Secondary Alkyl Azides Through C–H Bond Cleavage

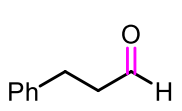
As investigated above, the optimized conditions were found as follows: DMSO (2 equiv.), Tf_2O (2 equiv.), in *tert*-butylbenzene at room temperature, as shown in Table 1

entry 14. Having established the optimized conditions, the substrate scope of this C–H activation protocol for primary and secondary alkyl azides was then assessed.

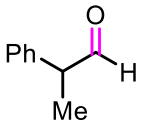
For primary alkyl azides, linear and branched substrates were converted successfully to give aldehydes **2a** and **2b** (Table 2.2). The presence of unsaturated carbon-carbon bond significantly reduced the product yield of **2c**. As observed in the previous reports, carbon-carbon double bond can react with sulfonium ions through addition reaction to form ionic compound as a highly polar material.[18-20] Unfortunately, in this work, I could not isolate the addition reaction product. Substrate bearing bulky alkyl group such as adamantane was also transformed to aldehyde **2d** in good yield. From these results, the substitution degree of the adjacent position from the azido group did not affect the reactivity to afford corresponding aldehydes **2a**, **2b**, and **2d**. A monoterpene compound tetrahydrogeraniol derived alkyl azido substrate **1e** was converted to aldehyde **2e** in 87% yield. Product **2f** was not observed from the corresponding starting material **1f** containing the alkoxy group. It is attributable to the reaction of triflic anhydride with alkoxy group forming alkyl triflate, which may lead to the degradation of starting material.[21,22] On the other hand, the ester and hydroxyl groups were tolerable to afford **2g** and **2h**. In the case of substrate **1h**, 2.5 equivalent of reagents was used to consume the reagents in the presence of hydroxyl group. In general, aldehydes were obtained in good yields unless their instability over column chromatography gives a considerable loss of isolation yields.

Table 2.2 Scope of primary alkyl azides activation to aldehydes

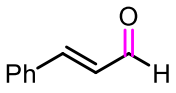




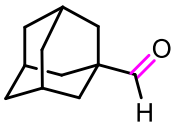
2a
70% (60%)



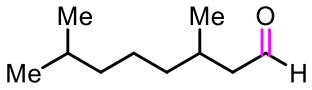
2b
44% (26%)



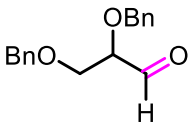
2c
19% (17%)



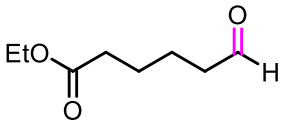
2d
82% (62%)



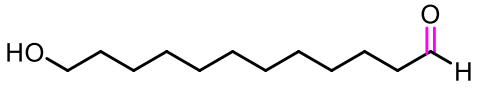
2e
87% (52%)



2f
0%



2g
50% (44%)



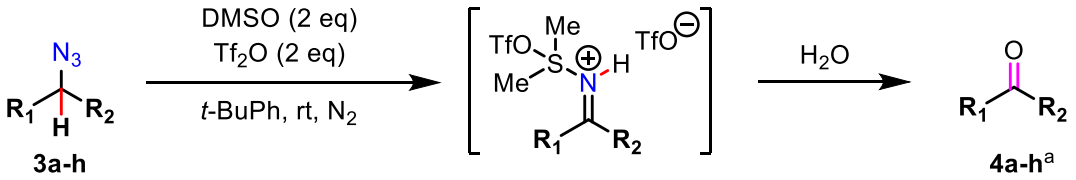
2h
48% (39%)b

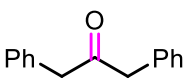
0.2 mmol scale reactions. [a]Yield based on ^{1}H NMR with $(CHCl_2)_2$ internal standard (isolated yields in brackets). [b]2.5 equiv of reagents were used.

Subsequently, the secondary alkyl azides delivering ketones were screened (Table 2.3). Unlike the unstable aldehydes, acyclic ketones **4a**-**4d** were obtained in moderate to excellent yields from corresponding secondary alkyl azides **3a**-**3d**. Secondary alkyl azide **3e** bearing hydroxyl group was successfully transformed to unstable hydroxy ketone **4e**, and isolated in moderate yield as **4ee** after acetylation. Furthermore, cyclic substrates **3f**-**3h** were transformed to corresponding **4f**-**4h** in moderate yields. Lower yields of cyclic products **4f**-**4h** compared to acyclic **4a**-**4d** indicated the cyclic ketimine intermediates are more rigid, bulky, and unstable than the acyclic forms, preventing hydrolysis to the desired ketones. Finally, both primary and secondary alkyl azido groups in diazide **3i** was smoothly

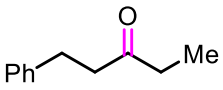
functionalized to give the corresponding ketoaldehyde compound **4i** in 75% ^{1}H NMR yield (68% isolated yield; Scheme 2.4). Thus, this traceless Schmidt reaction is capable for cleavage of the unreactive C–H bond in both primary and secondary alkyl azides. Moreover, not only monoazido substrates but also diazide can be activated by this developed method.

Table 2.3 Scope of secondary alkyl azides activation to ketones

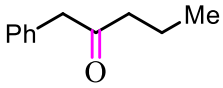




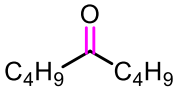
4a
92% (90%)



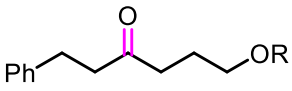
4b
83% (81%)



4c
82% (80%)

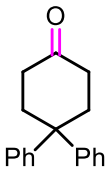


4d
63% (37%)



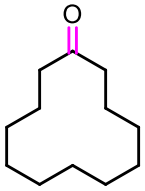
4e[b] R = H
4ee R = OAc

Ac_2O, pyridine, 0 °C
33% for 2 steps



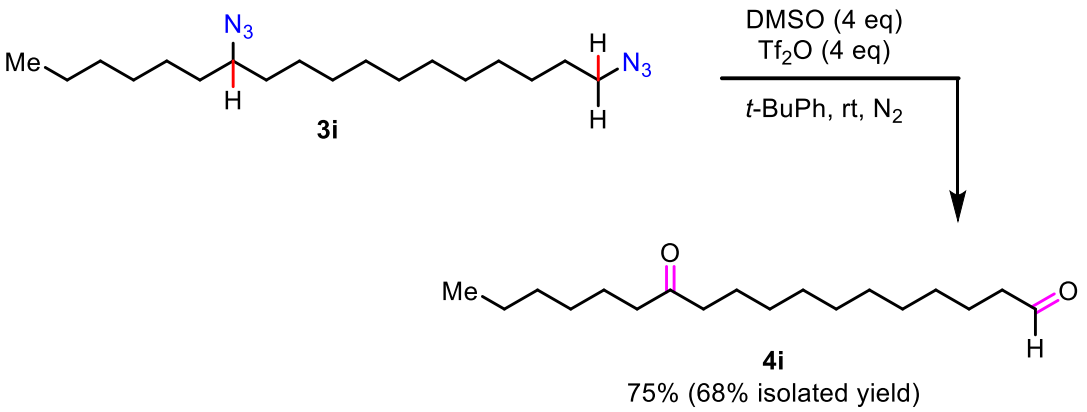
4f
42% (40%)

4g
39% (38%)



4h
36% (34%)

0.2 mmol scale reactions. [a]Yield based on ^{1}H NMR with $(CHCl_2)_2$ internal standard (isolated yields in brackets). [b]2.5 equiv of reagents were used.



Scheme 2.4. Traceless Schmidt reaction of diazide compound **3i**

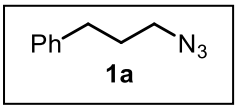
2. 5 Summary

C–H activation of primary and secondary alkyl azides was successfully carried out by using sulfonium ion generated from commercial sulfoxide and triflic anhydride via the traceless Schmidt reaction. The reaction of sulfonium ion with primary or secondary alkyl azide can promote migration of α-hydrogen atom onto the nitrogen atom of azide to give *N*–H iminium cation intermediates. These intermediates are subsequently hydrolyzed by an aqueous quench to afford aldehydes/ ketones in moderate to excellent yields. Ester and hydroxyl functionalities were tolerated under the reaction conditions, whereas alkoxy and olefin moieties were not compatible due to their reactions with sulfonium ions. Furthermore, diazide compound containing primary and secondary alkyl azido groups were smoothly transformed to the desired ketoaldehyde product in good yield.

2. 6 Experimental Data

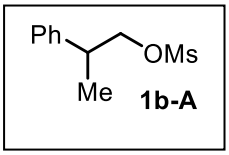
2.6.1 Preparation of Organic Azide Substrates

3-Phenylpropyl azide (1a)



Prepared in accordance with previous report. [23]

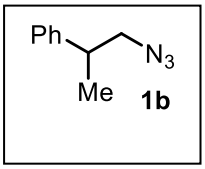
2-Phenylpropyl methanesulfonate (1b-A)



In a flask containing dichloromethane (0.5 M, 8 mL) at room temperature, commercially available 2-phenyl-1-propanol (0.56 mL, 4.0 mmol) and triethylamine (0.62 mL, 4.48 mmol) were added and stirred. To this mixture, methanesulfonyl chloride (347 μL, 4.48 mmol) was added dropwise over 5 min at 0 °C. Then, the mixture was warmed up to room temperature and additionally stirred for 2 h. After reaction completion, it was first treated by adding 1 M HCl aq., and dichloromethane was removed under reduced pressure. The mixture was then extracted with ethyl acetate, washed with water and brine, and the combined organic layer was dried over sodium sulfate and concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (neutral silica gel, hexane / ethyl acetate = 10/1) to afford **1b-A** (848 mg, 99%) as a colorless oil.

Colorless oil; R_f value 0.29 (hexane / ethyl acetate = 4 / 1); IR (NaCl, neat) ν_{max} 3029, 2973, 2939, 1495, 1454, 1353, 1174, 959, 841, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, 2H, *J* = 7.5 Hz, *J* = 7.5 Hz), 7.28–7.24 (m, 3H), 4.31 (dd, 1H, *J* = 9.5 Hz, *J* = 6.5 Hz), 4.25 (dd, 1H, *J* = 9.5 Hz, *J* = 7.5 Hz), 3.19 (qt, 1H, *J* = 6.5, 6.5 Hz), 2.80 (s, 3H), 1.37 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 128.7, 127.4, 127.2, 74.6, 39.4, 37.2, 17.4; HRMS (CI) calcd for $C_{10}H_{15}O_3S$ $[M+H]^+$ 215.0742, found 215.0741.

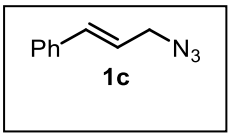
(1-Azidopropan-2-yl)benzene (1b)



To a stirred solution of 2-phenylpropyl methanesulfonate **1b-A** (428.6 mg, 2.0 mmol) in DMF (1 mL, 2 M), sodium azide (195.0 mg, 3.0 mmol) was added at room temperature. Then, the stirred mixture was heated at 80 ºC for 19 h. After completion, the mixture was cooled to room temperature, then was extracted with ethyl acetate. The extract was washed with water and brine and the organic layer was dried over sodium sulfate. After removal of organic solvent *in vacuo*, the obtained crude material was purified by silica gel chromatography (hexane elution to hexane / ethyl acetate = 20 / 1) to afford **1b** as a colorless oil. The analytical data were in good agreement with the literature.[24]

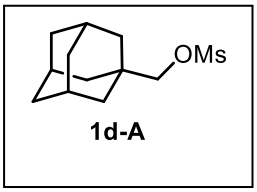
Colorless oil; R_f value 0.68 (hexane / ethyl acetate = 4 / 1); IR (NaCl, neat) ν_{max} 3033, 2966, 2099, 1495, 1452, 1267 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, 2H, *J* = 7.0, 7.0 Hz), 7.25 (m, 3H), 3.48 (dd, 1H, *J* = 12.0, 7.5 Hz), 3.38 (dd, 1H, *J* = 12.0, 7.5 Hz), 3.01 (ddq, 1H, *J* = 7.5, 7.5, 7.5 Hz), 1.34 (d, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 128.6, 127.1, 126.9, 58.2, 39.9, 18.9; HRMS (CI) calcd for $C_9H_{12}N_3$ $[M+H]^+$ 162.1031, found 162.1027.

Cinnamyl azide (1c)



Prepared in accordance with our previous report.[25]

(Adamantan-1-yl)methyl methanesulfonate (1d-A)

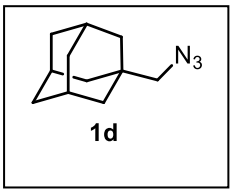


To a stirred solution of commercially available 1-adamantanemethanol (1.66 g, 10.0 mmol) and triethylamine (1.56 mL, 11.2 mmol) in dichloromethane (0.5M, 20 mL) was added methanesulfonyl chloride (0.87 mL, 11.2 mmol) dropwise over 5 min at 0 ºC. The mixture was then warmed up to room temperature and was stirred for 5 h. After completion, the reaction was quenched with 1 M HCl aq., and the dichloromethane was removed under reduced pressure. The remaining mixture was

then extracted with ethyl acetate, followed by wash with water and brine. The combined organic layer was dried over sodium sulfate and concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (neutral silica gel, hexane / ethyl acetate = 20 / 1) to afford **1d-A** (2.43 g, 99%) as a white solid. The analytical data were in good agreement with the literature.[26]

White solid; R_f value 0.33 (hexane / ethyl acetate = 4 / 1); m.p. 76–78 °C; IR (KBr, pellet) ν_{max} 2909, 2849, 1450, 1384, 1171, 956, 941, 854 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.78 (s, 2H), 3.00 (s, 3H), 2.01 (s, 3H), 1.74 (d, 3H, *J* = 12.0 Hz), 1.65 (d, 3H, *J* = 12.0 Hz), 1.57 (d, 6H, *J* = 2.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 79.4, 38.7, 37.0, 36.7, 33.4, 27.8; HRMS (CI) calcd for $C_{12}H_{19}O_3S$ $[M-H]^+$ 243.1055, found 243.1057.

1-(Azidomethyl)adamantane (1d)

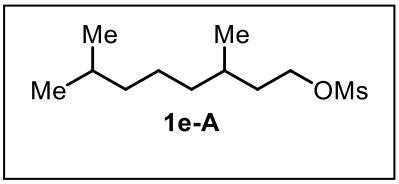


1d

To a stirred solution of (adamantan-1-yl)methyl methanesulfonate **1c-A** (489 mg, 2.0 mmol) in DMSO (10 mL, 0.2 M) was added sodium azide (520 mg, 8.0 mmol) was added, and the mixture was heated at 130 ºC for 21 h. After completion, the mixture was cooled down to room temperature and quenched with water. Then, the organic components were extracted with ethyl acetate. The organic layer was washed with water and brine, and then was dried over sodium sulfate. After removal of organic solvent *in vacuo*, the obtained crude material was purified by silica gel chromatography (hexane elution) to afford **1d** (307 mg, 80%) as a colorless oil.

Colorless oil; R_f value 0.75 (hexane / ethyl acetate = 8 / 1); IR (NaCl, neat) ν_{max} 2904, 2846, 2099, 1448, 1313, 1267 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.95 (s, 2H), 1.99 (s, 3H), 1.72 (d, 3H, *J* = 12.5 Hz), 1.63 (d, 3H, *J* = 12.5 Hz), 1.52 (d, 6H, *J* = 2.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 64.3, 40.0, 36.8, 34.7, 28.1; HRMS (CI) calcd for $C_{11}H_{18}N_3$ $[M+H]^+$ 192.1501, found 192.1507.

3,7-Dimethyloctyl methanesulfonate (1e-A)

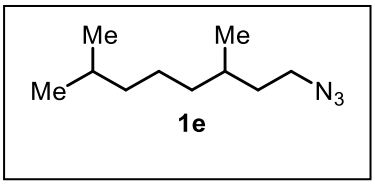


1e-A

To a stirred solution of commercially available 3,7-dimethyl-1-octanol (554 mg, 3.5 mmol) and triethylamine (0.54 mL, 3.92 mmol) in dichloromethane (0.5 M, 7 mL) at room temperature was added methanesulfonyl chloride (304 μL, 3.92 mmol) dropwise over 5 min at 0 ºC. Then, the mixture was warmed up to room temperature and was stirred for 3.5 h. After completion, the reaction was quenched with 1 M HCl aq., and dichloromethane was removed under reduced pressure. The residual mixture was then extracted with ethyl acetate, followed by washing with water and brine. The combined organic layer was dried over sodium sulfate. After removal of organic solvent *in vacuo*, the obtained crude material was purified by neutral silica gel chromatography (hexane / ethyl acetate = 20 / 1) to afford **1e-A** (799 mg, 97%) as a colorless oil.

Colorless oil; R_f value 0.44 (hexane / ethyl acetate = 4 / 1); IR (NaCl, neat) ν_{max} 2955, 2928, 2870, 1468, 1355, 1176, 975, 943 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.26 (m, 2H), 3.00 (s, 3H), 1.79 (m, 1H), 1.61–1.48 (m, 3H), 1.32–1.10 (m, 6H), 0.92 (d, 3H, J = 6.5 Hz), 0.86 (d, 6H, J = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 68.6, 39.1, 37.3, 36.9, 35.9, 29.3, 27.9, 24.5, 22.6, 22.5, 19.2; HRMS (CI) calcd for $C_{11}H_{23}O_3S$ $[M-H]^+$ 235.1368.

1-Azido-3,7-dimethyloctane (1e)



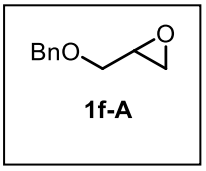
1e

To a stirred solution of 3,7-dimethyloctyl methanesulfonate **1e-A** (473 mg, 2.0 mmol) in DMSO (4 mL, 0.5 M) was added sodium azide (520 mg, 8.0 mmol), and the mixture was stirred at room temperature for 22 h. After completion, the reaction was quenched with water, then was extracted with hexane. The organic layer was washed with water and brine followed by drying over sodium sulfate. Removal of organic solvent *in vacuo* followed by silica gel

chromatography (hexane elution) to afford **1e** (329 mg, 90%) as a colorless oil. The analytical data were in good agreement with the literature.[27]

Colorless oil; R_f value 0.80 (hexane / ethyl acetate = 10 / 1); IR (NaCl, neat) ν_{max} 2955, 2927, 2871, 2095, 1465, 1383, 1366, 1263 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.28 (m, 2H), 1.66–1.08 (m, 10H), 0.90 (d, 3H, *J* = 6.5 Hz), 0.87 (d, 6H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 49.5, 39.2, 37.0, 35.7, 30.3, 27.9, 24.6, 22.7, 22.6, 19.3; HRMS (CI) calcd for $C_{10}H_{22}N_3$ $[M+H]^+$ 184.1814, found 184.1814.

2-((benzyloxy)methyl)oxirane (1f-A)

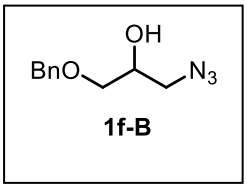


1f-A

To a stirred solution of glycidol (663 μL, 10 mmol) in DMF (20 mL, 0.50 M), sodium hydride (480 mg, 12 mmol, 60% in oil) was added at 0 °C. After 15 min, benzyl bromide (1.31 mL, 11 mmol) was added at the same temperature, which allow immediate color change to yellow oil with foam. The mixture was then warmed up to room temperature with gently stirring for 4 h. Then, the mixture was extracted with diethyl ether, and was washed with water and brine. The collected organic layer was dried over sodium sulfate, and was concentrated *in vacuo* to obtain crude material which was purified by silica gel chromatography (hexane / ethyl acetate 10 / 1 to 5 / 1) to afford 2-((benzyloxy)methyl)oxirane **1f-A** (971 mg, 59%) as a light yellow oil.

Light yellow oil; R_f value 0.59 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 3028, 2919, 2861, 1494, 1452, 1386, 1340, 1251, 1092, 898 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.28 (m, 5H), 4.62 (d, 1H, *J* = 11.5 Hz), 4.56 (d, 1H, *J* = 11.5 Hz), 3.78 (dd, 1H, *J* = 11.5, 3.0 Hz), 3.44 (dd, 1H, *J* = 11.5, 5.5 Hz), 3.20 (m, 1H), 2.81 (dd, 1H, *J* = 5.0, 4.0 Hz), 2.63 (dd, 1H, *J* = 5.0, 3.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 128.4, 127.8, 73.3, 70.8, 50.9, 44.3; LRMS (EI, M = $C_{10}H_{12}O_2$) *m/z* 164 (M^+, 5%), 107 (51), 105 (29%), 91 (100), 86 (43%), 84 (67%), 79 (24%); HRMS (EI) calcd for $C_{10}H_{12}O_2$ (M^+) 164.0837, found 164.0836.

1-Azido-3-(benzyloxy)propan-2-ol (1f-B)

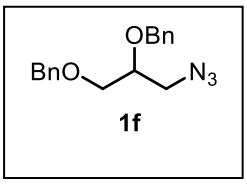


1f-B

To a stirred solution of 2-((benzyloxy)methyl)oxirane **1f-A** (839 mg, 5.11 mmol) in DMSO (2 mL, 2.5 M) at room temperature was added sodium azide (498 mg, 7.67 mmol) and ammonium chloride (342 mg, 6.39 mmol), and the mixture was stirred for 24 h. then the mixture was extracted with diethyl ether, and was washed with water and brine. The collected organic layer was dried over sodium sulfate, and was concentrated *in vacuo*. The obtained crude material was purified by silica gel chromatography (hexane/ ethyl acetate = 10 / 1 to 5 / 1) to afford 1-azido-3-(benzyloxy)propan-2-ol **1f-B** (817 mg, 77%) as a light yellow oil.

Light yellow oil; R_f value 0.42 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 3420, 3030, 2920, 2866, 2102, 1454, 1287, 1092, 741, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.30 (m, 5H), 4.56 (s, 2H), 3.97 (m, 1H), 3.54 (dd, 1H. *J* = 9.5, 4.5 Hz), 3.50 (dd, 1H, *J* = 9.5, 6.0 Hz), 3.40 (dd, 1H, *J* = 12.5, 4.5 Hz), 3.37 (dd, 1H, *J* = 12.5, 6.5 Hz), 2.50 (d, 1H, *J* = 4.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 128.5, 128.0, 127.8, 73.5, 71.2, 69.7, 53.4; HRMS (CI) calcd for $C_{10}H_{14}N_3O_2$ $[M+H]^+$ 208.1086, found 208.1082.

(((3-azidopropane-1,2-diyl)bis(oxy))bis(methylene))dibenzene (1f)



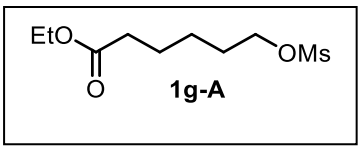
1f

To a stirred solution of 1-azido-3-(benzyloxy)propan-2-ol **1f-B** (464 mg, 2.23 mmol) in DMF (4.46 mL, 0.50 M), sodium hydride (105.6 mg, 2.64 mmol, 60% in oil) was added at 0 °C. After 15 min, benzyl bromide (292 μL, 2.45 mmol) was added at the same temperature, which allowed immediate color change to yellow oil with foam. The mixture was then warmed up to room temperature with gently stirring for 1 h. The reaction mixture was extracted with diethyl ether, and was washed with water and brine. The collected organic layer was dried over sodium sulfate, and was concentrated *in vacuo*. The obtained crude material was purified by silica gel chromatography (hexane / ethyl acetate

= 20 / 1) to afford (((3-azidopropane-1,2-diyl)bis(oxy))bis(methylene))dibenzene **1f** (588.7 mg, 89%) as a colorless oil.

Colorless oil; R_f value 0.80 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 3063, 3031, 2865, 2099, 1496, 1545, 1281, 1099, 737, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.30 (m, 10H), 4.69 (d, 1H, *J* = 12.5 Hz), 4.66 (d, 1H, *J* = 12.5 Hz), 4.54 (s, 2H), 3.76 (tt, 1H, *J* = 5.0 Hz), 3.60 (dd, 1H, *J* = 20.0, 5.0 Hz), 3.56 (dd, 1H, *J* = 20.0 Hz), 3.42 (d, 2H, *J* = 5.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.80, 137.76, 128.4, 128.2, 127.81, 127.76, 127.7, 77.2, 73.4, 72.3, 69.4, 52.0; HRMS (ESI) calcd for $C_{17}H_{19}N_3O_2Na$ $[M+Na]^+$ 320.13750, found 320.13669.

Ethyl 6-((methylsulfonyl)oxy)hexanoate (1g-A)

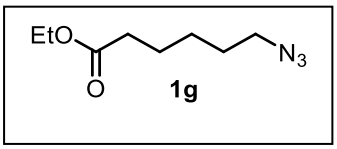


1g-A

To a stirred solution of commercially available ethyl 6-hydroxyhexanoate (561 mg, 3.50 mmol) and triethylamine (0.54 mL, 3.92 mmol) in dichloromethane (0.5 M, 7 mL) was added methanesulfonyl chloride (304 μL, 3.92 mmol) dropwise over 5 min at 0 ºC, and the mixture was stirred at room temperature. After 18 h, the reaction was quenched with 1 M HCl aq., the organic layer was washed with sodium bicarbonate aqueous solution, water, and brine. The combined organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1 to 5 / 1) to afford **1g-A** (813.4 mg, 98%) as a colorless oil.

Colorless oil; R_f value 0.40 (hexane / ethyl acetate = 1 / 1); IR (NaCl, neat) ν_{max} 2943, 2873, 1731, 1464, 1352, 1174, 1096, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.22 (t, 2H, *J* = 6.0 Hz), 4.12 (q, 2H, *J* = 7.5 Hz), 3.00 (s, 3H), 2.31 (t, 2H, *J* = 7.5 Hz), 1.77 (tt, 2H, *J* = 9.5, 6.0 Hz), 1.66 (tt, 2H, *J* = 7.5, 7.0 Hz), 1.44 (m, 2H, *J* = 8.5, 6.0 Hz), 1.25 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 69.7, 60.3, 37.3, 33.9, 28.8, 24.9, 24.2, 14.2; HRMS (CI) calcd for $C_9H_{19}O_5S$ $[M+H]^+$ 239.0953, found 239.0959.

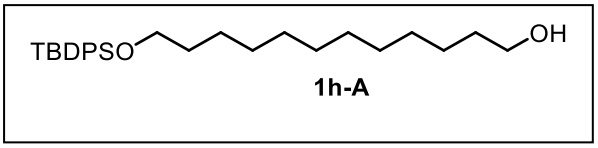
Ethyl 6-azidohexanoate (1g)



To a stirred solution of ethyl 6-((methylsulfonyl)oxy)hexanoate **1g-A** (642 mg, 2.71 mmol) in DMSO (5.4 mL, 0.5 M) at 80 °C, was added sodium azide (352 mg, 5.42 mmol), and the mixture was stirred for 3 h. After cooling down to room temperature, the reaction was quenched with water, and was extracted with ethyl acetate to wash with water and brine. The collected organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1) to afford **1g** (450 mg, 90%) as a colorless oil.

Colorless oil; R_f value 0.60 (hexane / ethyl acetate = 3 / 1); IR (NaCl, neat) ν_{max} 2943, 2870, 2099, 1735, 1464, 1375, 1255, 1185, 1100, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.12 (q, 2H, *J* = 7.5 Hz), 3.27 (t, 2H, *J* = 6.5 Hz), 2.30 (t, 2H, *J* = 7.5 Hz), 1.68–1.58 (m, 4H), 1.43–1.37 (m, 2H), 1.25 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 60.3, 51.2, 34.1, 28.5, 26.2, 24.4, 14.2; HRMS (CI) calcd for $C_8H_{16}N_3O_2$ $[M+H]^+$ 186.1243, found 186.1242.

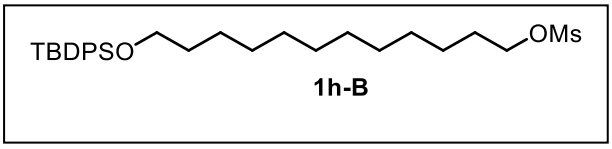
12-((*tert*-Butyldiphenylsilyl)oxy)dodecan-1-ol (1h-A)



The reaction was performed according to previous reported work.[28] To a stirred solution of commercially available 1,12-dodecandiol (1.01 g, 5.0 mmol) and imidazole (1.02 g, 15 mmol) in dichloromethane / dimethylformamide mixture with ratio of 2 : 1 (0.35 M, 14.2 mL) was added *tert*-butyl(chloro)diphenylsilane (1.49 mL, 5.75 mmol) at room temperature. After 19 h, water was added to the mixture, then it was extracted with dichloromethane. The organic layer was dried over sodium sulfate, and was concentrated *in vacuo*. The crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 40 / 1 to 2 / 1) to afford **1h-A** (826 mg, 38%) as a viscous colorless oil. The analytical data were in good agreement with the literature.[28]

Viscous colorless oil; R_f value 0.50 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 3330, 3071, 2927, 2854, 1468, 1425, 1112 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, 4H, *J* = 8.0, 2.0 Hz), 7.44–7.37 (m, 6H), 3.67–3.63 (m, 4H), 1.60–1.54 (m, 4H), 1.35–1.26 (m, 17H), 1.06 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 134.1, 129.4, 127.5, 64.0, 63.1, 32.8, 32.6, 29.59, 29.56, 29.4, 29.3, 26.8, 25.73, 25.71, 19.2; HRMS (CI) calcd for $C_{28}H_{45}O_2Si$ $[M+H]^+$ 441.3189, found 441.3186.

12-((*tert*-Butyldiphenylsilyl)oxy)dodecyl methanesulfonate (1h-B)

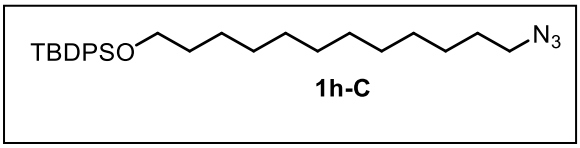


1h-B

To a stirred solution of 12-((*tert*-butyldiphenylsilyl)oxy)dodecan-1-ol **1h-A** (729 mg, 1.65 mmol) and triethylamine (255 μL, 1.85 mmol) in dichloromethane (0.5 M, 3.3 mL) was added methanesulfonyl chloride (143 μL, 1.85 mmol) dropwise over 5 min at 0 ºC, and the mixture was stirred at room temperature. After 1.5 h, the reaction was quenched with water, then the organic layer was washed with sodium bicarbonate aqueous solution, water and brine. The combined organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1 to 5 / 1) to afford **1h-B** (813 mg, 95%) as a viscous colorless oil.

Viscous colorless oil; R_f value 0.52 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 3071, 2927, 2854, 1471, 1429, 1360, 1177, 1112 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, 4H, *J* = 7.5, 1.5 Hz), 7.44–7.36 (m, 6H), 4.22 (t, 2H, *J* = 7.0 Hz), 3.65 (t, 2H, *J* = 7.0 Hz), 3.00 (s, 3H), 1.75 (tt, 2H, *J* = 7.0, 7.0 Hz), 1.55 (tt, 2H, *J* = 7.0, 7.0 Hz), 1.42–1.25 (m, 16H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 134.1, 129.5, 127.5, 70.2, 64.0, 37.3, 32.6, 29.6, 29.52, 29.49, 29.4, 29.3, 29.1, 29.0, 26.8, 25.7, 25.4, 19.2; HRMS (CI) calcd for $C_{29}H_{47}O_4SSi$ $[M+H]^+$ 519.2964, found 519.2958.

((12-azidododecyl)oxy)(tert-butyl)diphenylsilane (1h-C)

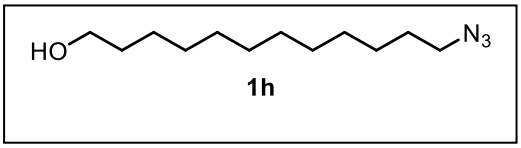


1h-C

To a stirred solution of 12-((*tert*-butyldiphenylsilyl)oxy) dodecyl methane -sulfonate **1h-B** (761 mg, 1.47 mmol) in DMSO (2.9 mL, 0.5 M) at room temperature, was added sodium azide (191 mg, 2.94 mmol), and the mixture was stirred for 45 h. The reaction was quenched with water, and the mixture was extracted with dichloromethane to wash with water and brine. The collected organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1) to afford **1h-C** (580 mg, 85%) as a viscous colorless oil.

Viscous colorless oil; R_f value 0.60 (hexane / ethyl acetate = 6 / 1); IR (NaCl, neat) ν_{max} 3071, 2927, 2854, 2095, 1468, 1429, 1112 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, 4H, *J* = 8.0, 2.0 Hz), 7.44–7.36 (m, 6H), 3.65 (t, 2H, *J* = 6.5 Hz), 3.26 (t, 2H, *J* = 7.0 Hz), 1.63–1.53 (m, 4H), 1.38–1.25 (m, 16H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 134.1, 129.4, 127.5, 64.0, 51.5, 32.6, 29.6, 29.53, 29.51, 29.47, 29.3, 29.1, 28.8, 26.8, 26.7, 25.7, 19.2; HRMS (CI) calcd for $C_{28}H_{44}N_3OSi$ $[M+H]^+$ 466.3254, found 466.3263.

12-Azidododecan-1-ol (1h)



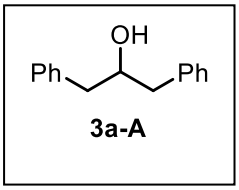
1h

To a stirred solution of ((12-azidododecyl)oxy)(*tert*-butyl)diphenylsilane **1h-C** (343 mg, 0.74 mmol) in tetrahydrofuran (7.4 mL, 0.1 M) at 0 ºC, was added tetrabutylammonium fluoride 1 M in tetrahydrofuran (3.69 mL, 3.69 mmol). After completion of the addition, the mixture was warmed up to room temperature, and was stirred for 4 h. The reaction was quenched with 1 N HCl aq., and the mixture was extracted with dichloromethane. The organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography

(hexane / ethyl acetate = 30 / 1 to 5 / 1) to afford **1h** (141 mg, 84%) as a colorless oil. The analytical data were in good agreement with the literature.[29]

Colorless oil; R_f value 0.30 (hexane / ethyl acetate = 3 / 1); IR (NaCl, neat) ν_{max} 3342, 2927, 2854, 2095, 1464, 1263, 1054 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.64 (m, 2H), 3.25 (t, 2H, *J* = 7.0 Hz), 1.62–1.53 (m, 4H), 1.36–1.20 (m, 17H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 63.1, 51.5, 32.8, 29.6, 29.51, 29.49, 29.45, 29.4, 29.1, 28.8, 26.7, 25.7; HRMS (CI) calcd for $C_{12}H_{26}N_3O$ $[M+H]^+$ 228.2076, found 228.2074.

1,3-Diphenylpropan-2-ol (3a-A)

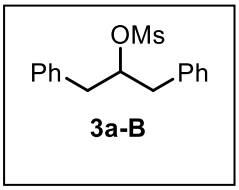


3a-A

The reduction reaction was performed according to the previous report.[30] To a stirred solution of commercially available 1,3-diphenylpropan-2-one (526 mg, 2.5 mmol) in methanol (12.5 mL, 0.2 M) was added sodium borohydride (114 mg, 3.0 mmol) at 0 °C. The reaction was carried out under vigorous stirring for 15 min. Then, the reaction was quenched with saturated sodium bicarbonate aqueous solution that allowed generation of white suspension. After methanol removal *in vacuo*, the residue was extracted with dichloromethane to wash with water and brine. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1) to afford **3a-A** (511 mg, 96%) as a viscous yellow oil.

Viscous yellow oil; R_f value 0.45 (hexane / ethyl acetate = 4 / 1); IR (NaCl, neat) ν_{max} 3434, 3029, 2943, 1644, 1495, 1456, 1081, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 4H), 7.24 (m, 6H), 4.07 (m, 1H), 2.87 (dd, 2H, *J* = 13.5, 4.5 Hz), 2.77 (dd, 2H, *J* = 13.5, 8.0 Hz), 1.62 (d, 1H, *J* = 3.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.4, 129.4, 128.5, 126.5, 73.6, 43.4; LRMS (EI, M = $C_{15}H_{16}O$) *m/z* 212 (M^+, 9%), 121 (41), 103 (30), 92 (100), 91 (70), 77 (10); HRMS (EI) calcd for $C_{15}H_{16}O$ (M^+) 212.1201, found 212.1196.

1,3-Diphenylpropan-2-yl methanesulfonate (3a-B)

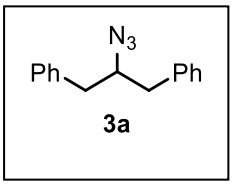


3a-B

To a stirred solution of 1,3-diphenylpropan-2-ol **3a-A** (463 mg, 2.18 mmol) and triethylamine (334 μL, 2.44 mmol) in dichloromethane (0.5 M, 4.4 mL) was added methanesulfonyl chloride (189 μL, 2.44 mmol) dropwise over 5 min at 0 ºC, and the mixture was stirred at room temperature for 2 h. After completion, the reaction was quenched with 1 M HCl aq., and dichloromethane was removed under reduced pressure. The residual material was then extracted with ethyl acetate to wash with water and brine. The combined organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 50 / 1 to 10 / 1) to afford **3a-B** (535.7 mg, 85%) as a white solid.

White solid; R_f value 0.50 (hexane / ethyl acetate = 4 / 1); m.p. 70–72 °C; IR (KBr, disc) ν_{max} 3031, 2932, 1496, 1449, 1342, 1174, 970, 900 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.30 (m, 4H), 7.28–7.22 (m, 6H), 4.91 (quint, 1H, *J* = 7.0 Hz), 3.01 (d, 4H, *J* = 7.0 Hz), 2.17 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.5, 129.7, 128.7, 127.1, 86.0, 41.1, 37.1; LRMS (EI, M = $C_{16}H_{18}O_3S$) *m*/*z* 290 (M^+, 0.1%), 194 (20), 91 (100), 89 (6), 78 (9), 65 (23); HRMS (EI) calcd for $C_{16}H_{18}O_3S$ (M^+) 290.0977, found 290.0973.

(2-Azidopropane-1,3-diyl)dibenzene (3a)



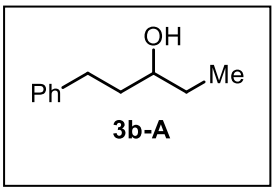
3a

To a stirred solution of 1,3-diphenylpropan-2-yl methanesulfonate **3a-B** (448 mg, 1.54 mmol) in DMSO (3.1 mL, 0.5 M) was added sodium azide (401 mg, 6.16 mmol) at room temperature, and the mixture was stirred at room temperature for 25 h. After completion, the reaction was quenched with water, and the mixture was extracted with ethyl acetate to wash with water and brine. The collected organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1) to afford **3a**

(300.7 mg, 82%) as a colorless oil. The analytical data were in good agreement with the literature.[31]

Colorless oil; R_f value 0.60 (hexane / ethyl acetate = 20 / 1); IR (NaCl, neat) ν_{max} 3029, 2922, 2852, 2108, 1599, 1495, 1446, 1340, 1261, 1081, 1024 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, 4H, *J* = 7.5, 7.5 Hz), 7.26 (m, 2H), 7.22 (d, 4H, *J* = 7.5 Hz), 3.78 (m, 1H), 2.88 (dd, 2H, *J* = 13.5, 5.0 Hz), 2.82 (*J* = 13.5, 8.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 129.3, 128.6, 126.8, 65.4, 40.7; LRMS (EI, M = $C_{15}H_{15}N_3$) *m/z* 237 (M^+, 1%), 210 (5%), 119 (4%), 118 (7%), 92 (19), 91 (100), 65 (21); HRMS (EI) calcd for $C_{15}H_{15}N_3$ (M^+) 237.1266, found 237.1260.

1-Phenylpentan-3-ol (3b-A)



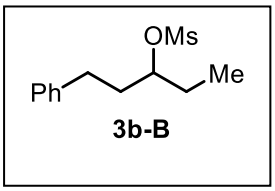
3b-A

The reaction was performed according to previous report.[32] To a stirred solution of commercially available 3-phenylpropionaldehyde (805 mg, 6.0 mmol) in tetrahydrofuran (12.2 mL) was added dropwise ethylmagnesium bromide (1 M solution in tetrahydrofuran, 7.8 mmol, 7.8 mL) at -78 °C then was stirred for 2 h. The reaction was quenched with saturated ammonium chloride aqueous solution. Then, reaction mixture was extracted with diethyl ether to wash with sodium bicarbonate, water, and brine. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 4 / 1) to afford **3b-A** (470 mg, 48%) as a light-yellow oil. The analytical data were in good agreement with the literature.[32]

Light-yellow oil; R_f value 0.43 (hexane / ethyl acetate = 4 / 1); IR (NaCl, neat) ν_{max} 3365, 3025, 2962, 2935, 2877, 1604, 1495, 1456, 1119, 1031, 933 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31–7.26 (m, 2H), 7.22–7.18 (m, 3H), 3.57 (m, 1H, *J* = 4.0 Hz), 2.84–2.78 (m, 1H), 2.71–2.65 (m, 1H), 1.83–1.71 (m, 2H), 1.58–1.45 (m, 2H) 1.39 (d, 1H, *J* = 4.5 Hz), 0.95 (t, 3H, *J* = 7.5

Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 128.4, 128.3, 125.7, 72.6, 38.5, 32.0, 30.2, 9.8; LRMS (EI, M = $C_{11}H_{16}O$) *m/z* 164 (M^+, 8%), 146 (51), 117 (75), 104 (30), 91 (100), 77 (29), 59 (11); HRMS (EI) calcd for $C_{11}H_{16}O$ (M^+) 164.1201, found 164.1199.

1-Phenylpentan-3-yl methanesulfonate (3b-B)

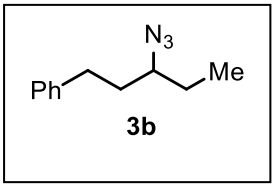


3b-B

To a stirred solution of 1-phenylpentan-3-ol **3b-A** (566 mg, 3.45 mmol) and triethylamine (0.54 mL, 3.86 mmol) in dichloromethane (0.5 M, 6.9 mL) was added methanesulfonyl chloride (0.30 mL, 3.86 mmol) dropwise over 5 min at 0 ºC, and the mixture was stirred at room temperature. After 5 h, the reaction was quenched with 1 M HCl aq., the organic layer was washed with sodium bicarbonate aqueous solution, water, and brine. The combined organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 40 / 1 to 15 / 1) to afford **3b-B** (622.9 mg, 75%) as a light-yellow oil. The analytical data were in good agreement with the literature.[33]

Light-yellow oil; R_f value 0.40 (hexane / ethyl acetate = 4 / 1); IR (KBr, disc) ν_{max} 3029, 2974, 2939, 1495, 1456, 1348, 1173, 969, 911 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.28 (m, 2H), 7.22–7.19 (m, 3H), 4.73 (tt, 1H, *J* = 6.0, 6.0 Hz), 3.00 (s, 3H), 2.80–2.67 (m, 2H), 2.08–1.97 (m, 2H), 1.83–1.77 (m, 2H), 1.00 (t, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 128.5, 128.3, 126.1, 84.4, 38.7, 35.6, 31.3, 27.4, 9.2; LRMS (EI, M = $C_{12}H_{18}O_3S$) *m/z* 242 (M^+, 0.2%), 146 (48), 117 (100), 104 (45), 91 (68); HRMS (EI) calcd for $C_{12}H_{18}O_3S$ (M^+) 242.0977, found 242.0981.

(3-Azidopentyl)benzene (3b)



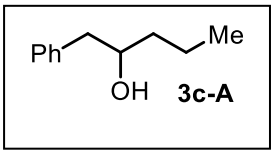
3b

To a stirred solution of 1-phenylpentan-3-yl methanesulfonate **3b-B** (557 mg, 2.30 mmol) in DMSO (4.6 mL, 0.5 M) at 60ºC, was added sodium azide (299 mg, 4.60 mmol), and the mixture was stirred for 5 h.

After cooling down to room temperature, the reaction was quenched with water, and was extracted with ethyl acetate to wash with water and brine. The collected organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (hexane as eluent) to afford **3b** (385.5 mg, 89%) as a colorless oil.

Colorless oil; R_f value 0.65 (hexane / ethyl acetate = 8 / 1); IR (NaCl, neat) ν_{max} 3027, 2968, 2936, 2877, 2095, 1646, 1496, 1455, 1340 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.30 (m, 2H), 7.24–7.21 (m, 3H), 3.22 (tt, 1H, *J* = 7.5, 7.5 Hz), 2.85–2.79 (ddd, 1H, *J* = 14.0, 8.5, 6.0 Hz), 2.69 (dt, 1H, *J* = 14.0, 7.5 Hz), 1.88–1.78 (m, 2H), 1.67–1.58 (m, 2H), 1.01 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 128.5, 128.4, 126.0, 63.6, 35.7, 32.4, 27.5, 10.4; HRMS (CI) calcd for $C_{11}H_{16}N_3$ $[M+H]^+$ 190.1344, found 190.1336.

1-phenylpentan-2-ol (3c-A)

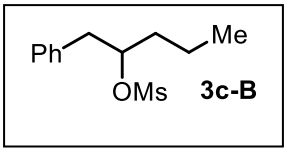


To a stirred solution of commercially available butyraldehyde (1.08 mL, 12.0 mmol) in diethyl ether (12 mL, 1 M) at -78 °C was added dropwise benzylmagnesium bromide (2 M solution in tetrahydrofuran, 13.2 mmol, 6.6 mL). After 4 h, the reaction was quenched with 1 M HCl aq. Then, the mixture was extracted with diethyl ether to wash with water, sodium bicarbonate and brine. The organic layer was dried over sodium sulfate. The crude material of 1-phenylpental-2-ol by removal of organic solvent *in vacuo* was subjected to silica gel column chromatography (hexane / ethyl acetate = 60 / 1 to 40 / 1) to afford **3c-A** (630 mg, 32%) as a colorless oil. The analytical data were in good agreement with the literature.[34]

Colorless oil; R_f value 0.50 (hexane / ethyl acetate = 3 / 1); IR (NaCl, neat) ν_{max} 3369, 3028, 2958, 2931, 2870, 1602, 1496, 1452, 1123, 1081, 1015 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.31 (m, 2H), 7.25–7.21 (m, 3H), 3.86–3.81 (m, 1H), 2.83 (dd, 1H, *J* = 13.5, 4.0 Hz), 2.65

(dd, 1H, *J* = 13.5, 8.0 Hz), 1.56–1.48 (m, 4H), 1.43–1.38 (m, 1H), 0.94 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.6, 129.4, 128.5, 126.4, 72.4, 44.0, 38.9, 19.0, 14.1; LRMS (EI, M = $C_{11}H_{16}O$) *m/z* 164 (M^+, 2%), 93 (12), 92 (100), 91 (49), 86 (21), 85 (33), 65 (10); HRMS (EI) calcd for $C_{11}H_{16}O$ (M^+) 164.1201, found 164.1205.

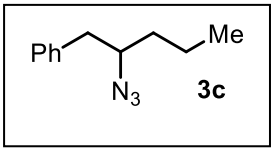
1-Phenylpentan-2-yl methanesulfonate (3c-B)



To a stirred solution of 1-phenylpentan-2-ol **3c-A** (408 mg, 2.48 mmol) and triethylamine (380 μL, 2.78 mmol) in dichloromethane (0.5 M, 5 mL) was added dropwise methanesulfonyl chloride (216 μL, 2.78 mmol) over 5 min at 0 ºC, and the mixture was stirred at room temperature. After 4.5 h, the reaction was quenched with 1 M HCl aq., then the mixture was extracted with dichloromethane to wash with 1 M HCl aq., sodium bicarbonate and brine. The combined organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 50 / 1 to 30 / 1) to afford **3c-B** (511 mg, 85%) as a colorless oil.

Colorless oil; R_f value 0.42 (hexane / ethyl acetate = 3 / 1); IR (NaCl, neat) ν_{max} 3030, 2962, 2937, 2874, 1604, 1496, 1455, 1352, 1174, 972, 910 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.31 (m, 2H), 7.27–7.24 (m, 3H), 4.86–4.81 (m, 1H), 3.02–2.93 (m, 2H), 2.45 (s, 3H), 1.78–1.65 (m, 2H), 1.59–1.41 (m, 2H), 0.95 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.9, 129.6, 128.6, 126.9, 85.1, 41.0, 37.6, 37.0, 18.3, 13.7; HRMS (CI) calcd for $C_{12}H_{19}O_3S$ $[M+H]^+$ 243.1055, found 243.1054.

(2-Azidopentyl)benzene (3c)

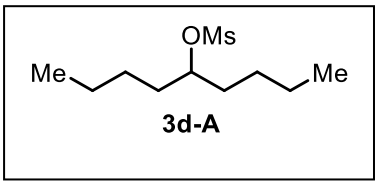


To a stirred solution of 1-phenylpentan-2-yl methanesulfonate **3c-A** (391 mg, 1.61 mmol) in DMSO (6.4 mL, 0.25 M) at room temperature, was added sodium azide (209 mg, 3.22 mmol), and the mixture was

stirred for 13 h. The reaction was quenched with water and was extracted with ethyl acetate to wash with water and brine. The collected organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 60 / 1) to afford **3c** (210 mg, 69%) as a colorless oil.

Colorless oil; R_f value 0.60 (hexane / ethyl acetate = 10 / 1); IR (NaCl, neat) ν_{max} 3029, 2959, 2934, 2873, 2099, 1496, 1455, 1255 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.28–7.22 (m, 3H), 3.51 (qd, 1H, *J* = 7.0, 6.5 Hz), 2.86–2.78 (m, 2H, *J* = 6.5 Hz), 1.58–1.49 (m, 3H), 1.46–1.39 (m, 1H), 0.94 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 129.3, 128.5, 126.7, 64.0, 41.0, 36.1, 19.4, 13.8; LRMS (EI, M = $C_{11}H_{15}N_3$) *m/z* 189 (M^+, 1%), 133 (38), 118 (11), 92 (75), 91 (100), 65 (39); HRMS (EI) calcd for $C_{11}H_{15}N_3$ (M^+) 189.1266, found 189.1267.

Nonan-5-yl methanesulfonate (3d-A)



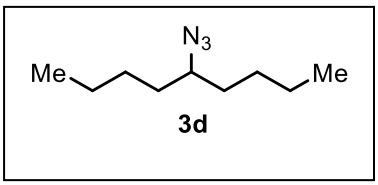
3d-A

To a stirred solution of commercially available 5-nonanol (0.61 mL, 3.5 mmol) and triethylamine (0.54 mL, 3.92 mmol) in dichloromethane (0.5M, 7 mL) was added methanesulfonyl chloride (304 μL, 3.92 mmol) dropwise over 5 min at 0 ºC. The mixture was warmed up to room temperature and was stirred for 4 h. After completion, the reaction was quenched with 1 M HCl aq., and dichloromethane was removed under reduced pressure. The residual material was then extracted with ethyl acetate and was washed with water and brine. The combined organic layer was dried over sodium sulfate and was dried *in vacuo*. The residual crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1) to afford **3d-A** (716 mg, 92%) as a light-yellow oil.

Light yellow oil; R_f value 0.44 (hexane / ethyl acetate = 4 / 1); IR (NaCl, neat) ν_{max} 2957, 2936, 2872, 1468, 1354, 1175, 910 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.70 (quint, 1H, *J* = 5.5 Hz), 3.00 (s, 3H), 1.69 (m, 4H), 1.41–1.31 (m, 8H), 0.91 (t, 6H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz,

$CDCl_3$) δ 84.4, 38.7, 34.1, 27.1, 22.5, 13.9; HRMS (CI) calcd for $C_{10}H_{23}O_3S$ $[M+H]^+$ 223.1368, found 223.1363.

5-Azidononane (3d)

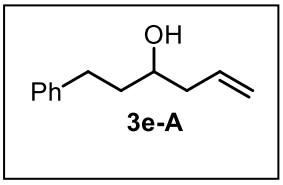


3d

To a stirred solution of nonan-5-yl methanesulfonate **3d-A** (445 mg, 2.0 mmol) in DMSO (10 mL, 0.2 M) was added sodium azide (520 mg, 8.0 mmol) at room temperature. The mixture was then heated at 80 ºC for 18 h. After completion, the reaction was quenched with water, and then was extracted with ethyl acetate. The organic layer was washed with water and brine and was dried over sodium sulfate. Removal of organic solvent *in vacuo* followed by silica gel column chromatography (hexane elution) to afford 5-Azidononane (173 mg, 51%) as a slightly volatile colorless oil.

Colorless oil; R_f value 0.72 (hexane / ethyl acetate = 8 / 1); IR (NaCl, neat) ν_{max} 2958, 2934, 2872, 2861, 2097, 1467, 1380, 1342, 1274, 1255, 1120, 961, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.22 (quint, 1H, J = 6.0), 1.53–1.29 (m, 12H), 0.91 (t, 6H, J = 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 63.1, 34.1, 28.3, 22.5, 14.0; HRMS (CI) calcd for $C_9H_{20}N_3$ $[M+H]^+$ 170.1657, found 170.1660.

1-Phenylhex-5-en-3-ol (3e-A)



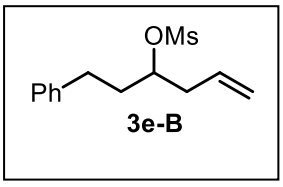
3e-A

To a stirred solution of commercially available 3-phenylpropionaldehyde (805 mg, 6.0 mmol) in tetrahydrofuran (6 mL, 1 M) was added dropwise allylmagnesium bromide (1 M solution in ether, 7.2 mL, 7.2 mmol) at 0 °C. After completion of the addition, the reaction was warmed up to room temperature and stirred for 3 h. The reaction was quenched with saturated ammonium chloride aqueous solution. Then, reaction mixture was extracted with diethyl ether to wash with sodium bicarbonate and brine. The organic layer was dried over sodium sulfate.

The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1) to afford **3e-A** (681 mg, 64%) as a colorless oil.

Colorless oil; R_f value 0.34 (hexane / ethyl acetate = 4 / 1); IR (NaCl, neat) ν_{max} 3366, 3076, 3026, 2930, 1640, 1603, 1496, 1454, 1048, 994, 916 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, 2H), 7.22 (m, 3H), 5.84 (m, 1H), 5.18–5.15 (m, 2H), 3.70 (m, 1H), 2.86–2.80 (m, 1H), 2.74–2.68 (m, 1H), 2.37–2.32 (m, 1H), 2.24–2.18 (m, 1H), 1.86–1.76 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 134.6, 128.32, 128.28, 125.7, 118.1, 69.9, 41.9, 38.3, 31.9; LRMS (EI, M = $C_{12}H_{16}O$) *m/z* 176 (M^+, 1%), 135 (27), 117 (31), 91 (100); HRMS (EI) calcd for $C_{12}H_{16}O$ (M^+) 176.2590, found 176.1201.

1-Phenylhex-5-en-3-yl methanesulfonate (3e-B)



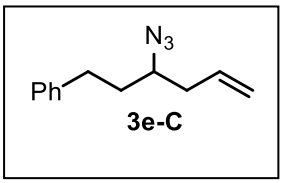
3e-B

To a stirred solution of 1-phenylhex-5-en-3-ol **3e-A** (1.03 g, 5.86 mmol) and triethylamine (2.41 mL, 17.58 mmol) in dichloromethane (0.5 M, 11.7 mL) was added methanesulfonyl chloride (0.68 mL, 8.79 mmol) dropwise over 5 min at 0 ºC, and the mixture was stirred at room temperature. After 1 h, brine and diethyl ether were added into the mixture. The organic layer was washed with 10% citric acid aqueous solution, saturated sodium bicarbonate solution, and brine. The combined organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 30 / 1) to afford **3e-B** (1.44 g, 96%) as a colorless oil.

Colorless oil; R_f value 0.47 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 3071, 3029, 2939, 2862, 1348, 1173, 910 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.29 (t, 2H), 7.21 (m, 3H), 5.85–5.76 (m, 1H), 5.20–5.16 (m, 2H), 4.80 (tt, 1H, *J* = 5.5, 5.5 Hz), 3.01 (s, 3H), 2.82–2.76 (m, 1H), 2.74–2.68 (m, 1H), 2.55–2.52 (m, 2H), 2.08–1.97 (m, 2H); ^{13}C NMR (126 MHz,

$CDCl_3$) δ 140.7, 132.2, 128.5, 128.3, 126.1, 119.2, 81.9, 39.1, 38.7, 35.7, 31.2; LRMS (EI, M = $C_{13}H_{18}O_3S$) *m/z* 254 (M^+, 0.05%), 158 (19), 117 (100), 104 (15), 91 (53); HRMS (EI) calcd for $C_{13}H_{18}O_3S$ (M^+) 254.0977, found 254.0970.

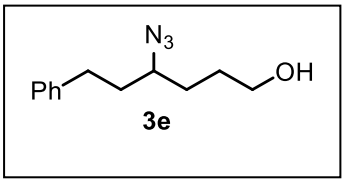
(3-Azidohex-5-en-1-yl)benzene (3e-C)



To a stirred solution of 1-phenylhex-5-en-3-yl methanesulfonate **3e-B** (1.26 g, 4.93 mmol) in DMF (9.9 mL, 0.5 M), was added sodium azide (1.61 g, 24.7 mmol), and the mixture was stirred for 6 h at 100 °C. After cooling down to room temperature, the reaction was quenched with water, and the organic components were extracted with diethyl ether to wash with water and brine. The collected organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (hexane as eluent) to afford **3e-C** (768 mg, 77%) as a colorless oil.

Colorless oil; R_f value 0.66 (hexane / ethyl acetate = 10 / 1); IR (NaCl, neat) ν_{max} 2944, 2098, 1643, 1604, 1496, 1455, 1339, 1258 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, 2H, *J* = 7.5 Hz), 7.20 (m, 3H), 5.85–5.76 (m, 1H), 5.18–5.12 (m, 2H), 3.35 (m, 1H), 2.83–2.78 (m, 1H), 2.70–2.64 (m, 1H), 2.35 (t, 2H, *J* = 6.5 Hz), 1.88–1.76 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 133.7, 128.5, 128.4, 126.1, 118.3, 61.4, 38.8, 35.6, 32.3; HRMS (CI) calcd for $C_{12}H_{15}N_3$ $[M+H]^+$ 202.1344, found 202.1346.

4-Azido-6-phenylhexan-1-ol (3e)

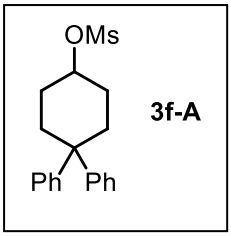


To a stirred solution of (3-azidohex-5-en-1-yl)benzene **3e-C** (400 mg, 1.99 mmol) in tetrahydrofuran (3 mL, 0.66 M) at 0 °C, was added dropwise borane–tetrahydrofuran complex (1 M in tetrahydrofuran, 3.98 mL, 3.98 mmol). After completion of addition, the mixture was warmed up to room temperature, and was stirred for 8 h. To perform oxidation reaction, 3 M NaOH

aqueous solution (1.19 mL, 3.58 mmol) and hydrogen peroxide 30% (0.40 mL, 3.90 mmol) were added sequentially, and the mixture was stirred for 4 h. The mixture was extracted with ethyl acetate to wash with water and brine. The collected organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 50 / 1 to 5 / 1) to afford **3e** (72.6 mg, 17% yield over 2 steps) as a colorless oil. The analytical data were in good agreement with the literature.[35]

Colorless oil; R_f value 0.40 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 3342, 3029, 2947, 2866, 2099, 1495, 1456, 1344, 1252, 1058 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.29 (m, 2H), 7.22–7.19 (m, 3H), 3.67 (m, 2H), 3.30 (m, 1H), 2.80 (dt, 1H, *J* = 14.0, 7.0 Hz), 2.68 (dt, 1H, *J* = 14.0, 8.0 Hz), 1.87–1.82 (m, 2H), 1.74–1.61 (m, 4H), 1.35 (t, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 128.5, 128.4, 126.1, 62.4, 62.0, 36.2, 32.3, 30.8, 29.1; HRMS (CI) calcd for $C_{12}H_{18}N_3O$ $[M+H]^+$ 220.1450, found 220.1454.

4,4-Diphenylcyclohexyl methanesulfonate (3f-A)

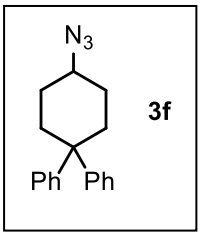


3f-A

To a stirred solution of commercially available 4,4-diphenylcyclohexanol (303 mg, 1.20 mmol) and triethylamine (185 μL, 1.34 mmol) in dichloromethane (0.25 M, 4.8 mL) was added methanesulfonyl chloride (104 μL, 1.34 mmol) dropwise over 5 min at 0 ºC, and the mixture was stirred at room temperature. After 1.5 h, the reaction was quenched with 1 N HCl aqueous solution. The organic layer was washed with saturated sodium bicarbonate solution and brine. The combined organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1 to 5 / 1) to afford **3f-A** (377 mg, 95%) as a viscous colorless oil.

Viscous colorless oil; R_f value 0.65 (hexane / ethyl acetate = 1 / 2); IR (NaCl, neat) ν_{max} 3060, 3027, 2948, 2873, 1600, 1495, 1448, 1352, 1174 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29–7.26 (m, 8H), 7.17 (br, 2H), 4.85 (br, 1H), 3.00 (m, 3H), 2.58 (br, 2H), 2.27 (br, 2H), 1.97–1.93 (br, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 146.6, 128.52, 128.47, 126.9, 126.7, 125.9, 80.1, 45.2, 38.8, 32.6, 28.8; LRMS (EI, M = $C_{19}H_{22}O_3S$) *m/z* 330 (M^+, 38%), 234 (35), 205 (100), 193 (28), 165 (19), 115 (26), 91 (32); HRMS (EI) calcd for $C_{19}H_{22}O_3S$ (M^+) 330.1290, found 330.1283.

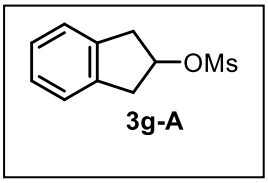
(4-Azidocyclohexane-1,1-diyl)dibenzene (3f)



To a stirred solution of 4,4-diphenylcyclohexyl methanesulfonate **3f-A** (356 mg, 1.08 mmol) in DMSO (4.3 mL, 0.25 M), was added sodium azide (140.4 mg, 2.16 mmol), and the mixture was stirred at room temperature for 12 h and then at 80 °C for 5 h. After cooling to room temperature, the reaction was quenched with water, and the organic components were extracted with ethyl acetate to wash with water and brine. The collected organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (hexane as eluent) to afford **3f** (234 mg, 78%) as a viscous colorless oil.

Viscous colorless oil; R_f value 0.70 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 3060, 2947, 2870, 2095, 1600, 1495, 1448, 1252, 1015 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36–7.29 (m, 8H), 7.25–7.19 (m, 2H), 3.64 (m, 1H), 2.66 (br-m, 2H), 2.21 (t, 2H), 1.97–1.93 (br-m, 2H), 1.74–1.67 (br-m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 146.1, 128.5, 128.3, 127.1, 126.6, 125.8, 125.7, 59.2, 45.4, 33.6, 27.7; LRMS (EI, M = $C_{18}H_{19}N_3$) *m/z* 277 (M^+, 7%), 249 (56), 220 (56), 193 (100), 178 (47), 165 (52), 115 (84), 91 (53); HRMS (EI) calcd for $C_{18}H_{19}N_3$ (M^+) 277.1579, found 277.1577.

2,3-Dihydro-1*H*-inden-2-yl methanesulfonate (3g-A)

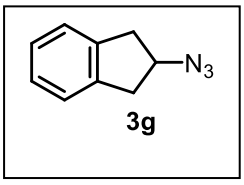


3g-A

To a stirred solution of commercially available 2,3-dihydro-1*H*-inden-2-ol (499 mg, 3.72 mmol) and triethylamine (1.02 mL, 7.44 mmol) in dichloromethane (0.5 M, 7.4 mL) was added methanesulfonyl chloride (0.58 mL, 7.44 mmol) dropwise over 5 min at 0 ºC, and the mixture was stirred at room temperature for 2 h. After completion, the reaction was quenched with 1 M HCl aq., the organic layer was washed with sodium bicarbonate aqueous solution, water, and brine. The combined organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 10 / 1 to 2 / 1) to afford **3g-A** (691 mg, 88%) as a white solid.

White solid; R_f value 0.61 (hexane / ethyl acetate = 2 / 1); m.p. 84–85 °C; IR (KBr, disc) ν_{max} 3030, 2965, 2913, 1475, 1421, 1333, 1162 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26–7.24 (m, 2H), 7.23–7.20 (m, 2H), 5.52 (m, 1H), 3.36 (dd, 2H, *J* = 17.0, 6.5 Hz), 3.25 (dd, 2H, *J* = 17.0, 3.0 Hz), 3.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 127.1, 124.6, 81.8, 40.1, 38.5; LRMS (EI, M = $C_{10}H_{12}O_3S$) *m*/*z* 212 (0.1%), 116 (100), 105 (11), 77 (5); HRMS (EI) calcd for $C_{10}H_{12}O_3S$ (M^+) 212.0507, found 212.0505.

2-azido-2,3-dihydro-1*H*-indene (3g)

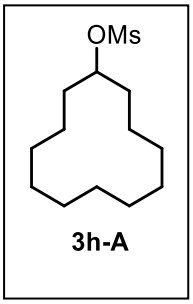


3g

To a stirred solution of 2,3-dihydro-1*H*-inden-2-yl methanesulfonate **3g-A** (425 mg, 2 mmol) in DMSO (4 mL, 0.5 M) was added sodium azide (195 mg, 3 mmol) at 80 ºC. After 5 h, the reaction was quenched with water, and the mixture was extracted with ethyl acetate to wash with water and brine. The collected organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (hexane as eluent) to afford **3g** (256 mg, 80%) as a colorless oil. The analytical data were in good agreement with the literature.[36]

Colorless oil; R_f value 0.41 (hexane); IR (NaCl, neat) ν_{max} 3071, 3025, 2945, 2907, 2844, 2099, 1483, 1426, 1317, 1271, 1208 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.28 (m, 2H), 7.27–7.24 (m, 2H), 4.41 (m, 1H), 3.29 (dd, 2H, *J* = 16.0, 6.0 Hz), 3.07 (dd, 2H, *J* = 16.0, 4.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 126.9, 124.6, 61.7, 38.9; LRMS (EI, M = $C_9H_9N_3$) *m/z* 159 (M^+, 28%), 130 (13%), 104 (100%), 89 (16%), 78 (43%); HRMS (EI) calcd for $C_9H_9N_3$ (M^+) 159.0796, found 159.0794.

Cyclododecyl methanesulfonate (3h-A)

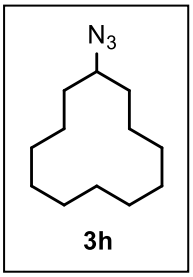


3h-A

To a stirred solution of dichloromethane (0.5M, 5.5 mL) commercially available cyclododecanol (506.9 mg, 2.75 mmol) and triethylamine (424 μL, 3.08 mmol) was added methanesulfonyl chloride (239 μL, 3.08 mmol) dropwise over 5 min at 0 ºC. The mixture was warmed up to room temperature and additionally stirred for 4 h. After completion, the reaction was quenched with 1 M HCl aq., and dichloromethane was removed under reduced pressure. The residual mixture was then extracted with ethyl acetate, and then was washed with water and brine. The combined organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 30 / 1 to 10 / 1) to afford **3h-A** (540 mg, 75%) as a white solid. The analytical data were in good agreement with the literature.[37]

White solid; R_f value 0.46 (hexane / ethyl acetate = 4 / 1); IR (NaCl, neat) ν_{max} 2933, 2853, 1472, 1342, 1171, 980, 915 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.88 (m, 1H), 2.99 (s, 3H), 1.91–1.84 (m, 2H), 1.72–1.66 (m, 2H), 1.49–1.34 (m, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 82.0, 38.7, 30.1, 24.0, 23.8, 23.2, 23.0, 20.6; HRMS (CI) calcd for $C_{13}H_{27}O_3S$ $[M+H]^+$ 263.1681, found 263.1682.

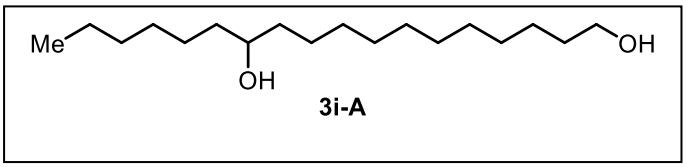
Azidocyclododecane (3h)



To a stirred solution of cyclododecyl methanesulfonate **3h-A** (399 mg, 1.52 mmol) in DMSO (3.0 mL, 0.5 M) was added sodium azide (395 mg, 6.08 mmol) at room temperature, and the mixture was heated at 80 ºC for 18 h. After completion, the reaction was quenched with water, and the mixture was extracted with ethyl acetate to wash with water and brine. The collected organic layer was dried over sodium sulfate. This crude material after removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane elution) to afford **3h** (271 mg, 85%) as a colorless oil. The analytical data were in good agreement with the literature.[38]

Colorless oil; R_f value 0.60 (hexane); IR (NaCl, neat) ν_{max} 2934, 2863, 2095, 1470, 1445, 1250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.48 (m, 1H), 1.72–1.66 (m, 2H), 1.53–1.46 (m, 4H), 1.43–1.33 (m, 16H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 59.2, 29.0, 23.9, 23.7, 23.3, 23.2, 21.3; HRMS (CI) calcd for $C_{12}H_{24}N_3$ $[M+H]^+$ 210.1970, found 210.1971.

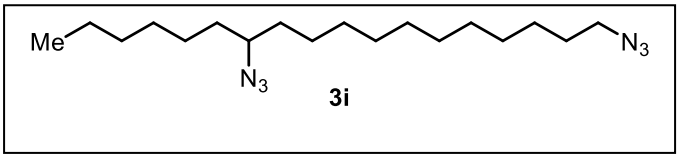
Octadecane-1,12-diol (3i-A)



To a stirred solution of 12-hydroxystearic acid (1.50 g, 5.0 mmol) in tetrahydrofuran (20 mL, 0.25 M to starting material) was added dropwise borane tetrahydrofuran complex solution (1 M, 10 mL) at room temperature. After 17 h, the reaction was quenched with 1 M HCl aqueous solution. Then, reaction mixture was extracted with ethyl acetate to wash with 1 M HCl aqueous solution. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1 to 2 / 1) to afford octadecane-1,12-diol **3i-A** (1.36 g, 95%) as a white solid.

White solid; R_f value 0.25 (hexane / ethyl acetate = 4 / 1); m.p. 66.7–68.1 °C; IR (KBr, disc) ν_{max} 3450, 2918, 2849, 1464 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.64 (t, 2H, *J* = 6.5 Hz), 3.59–3.57 (m, 1H), 1.56 (tt, 2H, *J* = 7.0, 6.5 Hz), 1.44–1.16 (br-m, 30H), 0.88 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 72.0, 63.1, 37.5, 32.8, 31.8, 29.68, 29.60, 29.57, 29.55, 29.39, 29.38, 25.7, 25.64, 25.62, 22.6, 14.1; HRMS (CI) calcd for $C_{18}H_{39}O_2$ $[M+H]^+$ 287.2950, found 287.2953.

1,12-Diazidooctadecane (3i)



3i

To a stirred solution of octadecane-1,12-diol **3i-A** (573.0 mg, 2.0 mmol) and triethylamine (1.38 mL, 10.0 mmol) in tetrahydrofuran (0.2 M, 10 mL) was added methanesulfonyl chloride (470 μL, 6.0 mmol) dropwise at room temperature. After 24 h, the reaction was quenched with 1 M HCl aqueous solution. The reaction mixture was extracted with ethyl acetate to wash with 1 M HCl aqueous solution, saturated sodium bicarbonate aqueous solution, and brine. The combined organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The crude material, octadecane-1,12-diyl dimethanesulfonate (654.6 mg, light-yellow oil) was used for the next step without further purification.

To a stirred solution of crude octadecane-1,12-diyl dimethanesulfonate (654.6 mg) in DMSO (5 mL, 0.4 M), was added sodium azide (520.1 mg, 8.0 mmol), and the mixture was stirred at 60 ºC for 19 h. After cooling down to room temperature, the reaction was quenched with water, and the organic components were extracted with ethyl acetate to wash with water and brine. The collected organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (hexane as eluent) to afford 1,12-diazidooctadecane **3i** (242.9 mg, 36% over 2 steps) as a colorless oil.

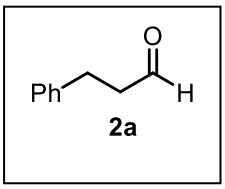
Colorless oil; R_f value 0.25 (hexane); IR (KBr, disc) ν_{max} 2927, 2854, 2095, 1464 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.27–3.20 (m, 3H), 1.59 (tt, 2H, *J* = 7.0, 6.5 Hz), 1.52–1.28 (br-m, 28H), 0.89 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 63.1, 51.5, 34.4, 31.7, 29.47, 29.43, 29.12, 29.10, 28.8, 26.7, 26.10, 26.08, 22.6, 14.1; HRMS (CI) calcd for $C_{18}H_{37}N_6$ $[M+H]^+$ 337.3080, found 337.3084.

2.6.2 Traceless Schmidt Reaction of Primary and Secondary Alkyl Azides

General Procedure

The primary or secondary alkyl azide **1** or **2** (0.20 mmol) and dimethyl sulfoxide (DMSO, 28 μL, 0.40 mmol, 2 equiv) were dissolved in *tert*-butylbenzene (1 mL, 0.2 M), and the mixture was stirred at room temperature under nitrogen atmosphere. Then, distilled trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol, 2 equiv) was added to the mixture dropwise over 1 min, which subsequently generated suspension and then a light-yellow oil layer at the bottom of the flask. The mixture was kept stirred at room temperature. Upon completion of the reaction, the mixture was cooled down to 0 °C, and the reaction was stopped by addition of saturated sodium bicarbonate aqueous solution. The mixture was then extracted with ethyl acetate and washed with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. The crude material was obtained by removing the organic solvent *in vacuo*, and then analyzed by ^1H NMR to measure NMR yields before the purification. 1,1,2,2-Tetrachloroethane (21 μL, 0.20 mmol, 1 equiv, 5.96 ppm on ^1H NMR, 2H) was used as an internal standard. After that, the crude material was purified by column chromatography using neutral silica gel to afford the corresponding aldehyde **2** or ketone **4**.

3-Phenylpropanal (2a)

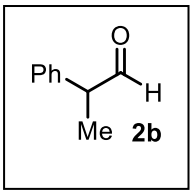


0.2 mmol scale reaction: The reaction with 3-phenylpropylazide **1a** (32.2 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 2.5 h, followed by silica gel chromatography (hexane / ethyl acetate = 70 / 1 to 20 / 1) gave **2a** (70% yield on ^{1}H NMR before purification, 16.0 mg, 60% isolated yield) as a light-yellow oil.

2.0 mmol scale reaction: The reaction with 3-phenylpropylazide **1a** (322 mg, 2.0 mmol), DMSO (284 μL, 4.0 mmol), and trifluoromethanesulfonic anhydride (656 μL, 4.0 mmol) in *tert*-butylbenzene (10 mL, 0.2 M) for 2.5 h, followed by neutral silica gel chromatography (hexane / ethyl acetate = 70 / 1 to 30 / 1), gave **2a** (65% yield on ^{1}H NMR before purification in the presence of 1,1,2,2-tetrachloroethane (210 μL, 2.0 mmol) as an internal standard, 163 mg, 61% isolated yield) as a light-yellow oil.

Light yellow oil; R_f value 0.51 (hexane / ethyl acetate = 4 / 1); IR (NaCl, neat) ν_{max} 3027, 2926, 2823, 2721, 1723, 1686, 1496, 1454 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.83 (t, 1H, *J* = 1.5 Hz), 7.30 (dd, 2H, *J* = 7.5, 7.5 Hz), 7.21 (m, 3H), 2.96 (t, 2H, *J* = 7.5 Hz), 2.79 (td, 2H, *J* = 7.5, 1.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.7, 140.3, 128.6, 128.3, 126.3, 45.3, 28.0; LRMS (EI, M = $C_9H_{10}O$) *m*/*z* 134 (M^+, 62%), 91 (100), 78 (48); HRMS (EI) calcd for $C_9H_{10}O$ (M^+) 134.0732, found 134.0730.

2-Phenylpropanal (2b)

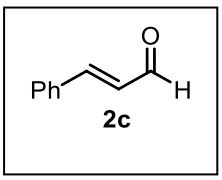


The reaction with (1-azidopropan-2-yl)benzene **1b** (32.2 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 2.5 h, followed by short-path neutral silica gel chromatography (hexane / ethyl acetate = 10 / 1) gave **2b** (44% yield on ^{1}H NMR before purification, 7.0 mg, 26% isolated yield) as a volatile light-yellow oil. This

compound was partially decomposed during chromatographic purification. Spectroscopic data were in good agreement with literature[39] and those of the commercial authentic sample.

Volatile light yellow oil; R_f value 0.44 (hexane / ethyl acetate = 6 / 1); IR (NaCl, neat) ν_{max} 3029, 2968, 2927, 2873, 2816, 2714, 1718, 1600, 1495, 1451, 1019, 912, 787, 747 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.69 (d, 1H, *J* = 1.5 Hz), 7.40–7.37 (m, 2H), 7.33–7.30 (m, 1H), 7.23–7.20 (m, 2H), 3.65 (qd, 1H, *J* = 6.5, 1.0 Hz), 1.45 (d, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.2, 137.6, 129.1, 128.3, 127.5, 53.0, 14.6; HRMS (CI) calcd for $C_9H_{11}O$ $[M+H]^+$ 135.0810, found 135.0809.

Cinnamaldehyde (2c)

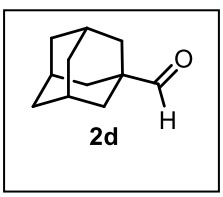


2c

The reaction with cinnamyl azide **1c** (31.8 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 2.5 h, followed by neutral silica gel column chromatography (hexane / ethyl acetate = 20 / 1), gave **2c** (19% yield on ^1H NMR before purification, 4.8 mg, 18% isolated yield) as a yellow oil.

Yellow oil; R_f value 0.36 (hexane / ethyl acetate = 6 / 1); IR (NaCl, neat) ν_{max} 3025, 2962, 2811, 1677, 1623, 1448, 1123, 971, 748, 689 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.72 (d, 1H, *J* = 7.5 Hz), 7.58 (dd, 2H), 7.49 (d, 1H, *J* = 16 Hz), 7.44 (m, 3H), 6.73 (dd, 1H, *J* = 7.5, 16 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.9, 152.9, 133.9, 131.3, 129.1, 128.55, 128.50; LRMS (EI, M = C_9H_8O) *m*/*z* 132 (M^+, 52%), 131 (71%), 104 (62%), 103 (88%), 78 (85%), 77 (100%), 51 (65%); HRMS (CI) calcd for C_9H_9O $[M+H]^+$ 133.0653, found 133.0645.

Adamantane-1-carbaldehyde (2d)



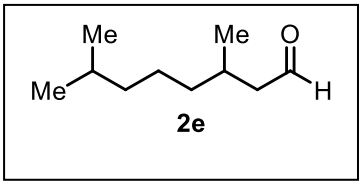
2d

The reaction with 1-(azidomethyl)adamantane **1d** (38.3 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 4 h, followed by neutral

silica gel chromatography (hexane as an eluent), gave **2d** (82% yield on ^{1}H NMR before purification, 20.3 mg, 62% isolated yield) as a white solid. The analytical data were in good agreement with the literature.[40]

White solid; R_f value 0.42 (hexane); m.p. 141–143 °C; IR (KBr, disc) ν_{max} 2912, 2854, 1712, 1452, 1283, 1098, 964 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (s, 1H), 2.07 (s, 3H), 1.79–1.68 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.1, 44.8, 36.6, 35.8, 27.3; HRMS (CI) calcd for $C_{11}H_{17}O$ $[M+H]^+$ 165.1279, found 165.1277.

3,7-Dimethyloctanal (2e)

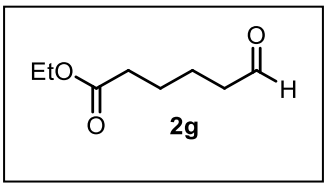


2e

The reaction with 1-Azido-3,7-dimethyloctane **1e** (36.7 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 1.5 h, followed by neutral silica gel column chromatography (hexane as an eluent), gave **2e** (87% yield on ^{1}H NMR before purification, 16.3 mg, 52% isolated yield) as a colorless oil. The product was moderately volatile. The analytical data were in good agreement with the literature.[41]

Colorless oil; R_f value 0.44 (hexane / ethyl acetate = 10 / 1); IR (NaCl, neat) ν_{max} 2955, 2928, 2871, 2713, 1727, 1465, 1383, 1366 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (t, 1H, J = 2.0 Hz), 2.39 (ddd, 1H, J = 15.0, 5.5, 2.0 Hz), 2.22 (ddd, 1H, J = 15.0, 10.0, 2.5 Hz), 2.06 (m, 1H), 1.52 (m, 1H), 1.32–1.13 (m, 6H), 0.96 (d, 3H, J = 6.5 Hz), 0.86 (d, 6H, J = 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.2, 51.1, 39.0, 37.1, 28.2, 27.9, 24.7, 22.6, 22.5, 20.0; HRMS (CI) calcd for $C_{10}H_{21}O$ $[M+H]^+$ 157.1592, found 157.1588.

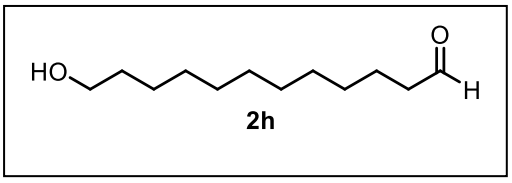
Ethyl 6-oxohexanoate (2g)



The reaction with ethyl 6-azidohexanoate **1g** (37.0 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M), followed by activated alumina column chromatography (hexane / ethyl acetate = 20 / 1 to 5 / 1), gave **2f** (50% yield on ^{1}H NMR before purification, 13.9 mg, 44% isolated yield) as a colorless oil. The analytical data were in good agreement with the literature.[42]

Colorless oil; R_f value 0.37 (hexane / ethyl acetate = 3 / 1); IR (NaCl, neat) ν_{max} 2939, 2870, 2722, 1731, 1375, 1259, 1185, 1096, 1035 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (t, 1H, *J* = 1.5 Hz), 4.13 (q, 2H, *J* = 7.5 Hz), 2.47 (m, 2H), 2.33 (m, 2H, *J* = 1.5 Hz), 1.66 (m, 4H), 1.25 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 173.3, 60.4, 43.5, 34.0, 24.3, 21.5, 14.2; HRMS (CI) calcd for $C_8H_{15}O_3$ $[M+H]^+$ 159.1020, found 159.1020.

12-Hydroxydodecanal (2h)

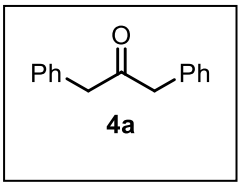


The reaction with 12-azidododecan-1-ol **1h** (45.5 mg, 0.20 mmol), DMSO (36 μL, 0.50 mmol), and trifluoromethanesulfonic anhydride (82 μL, 0.50 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 2.5 h, followed by activated alumina column chromatography (hexane / ethyl acetate = 20 / 1 to 1 / 1), gave **2g** (48% yield on ^{1}H NMR before purification, 15.6 mg, 39% isolated yield, containing small impurity inseparable). The analytical data were in good agreement with the literature.[43]

Light-yellow oil; R_f value 0.40 (hexane / ethyl acetate = 1 / 1); IR (NaCl, neat) ν_{max} 3377, 2924, 2854, 1723, 1460, 1054 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) selected peak δ 9.76 (s, 1H), 3.64 (t, 2H, *J* = 7.0 Hz), 2.42 (t, 2H, *J* = 7.0 Hz), 1.64–1.61 (m, 2H), 1.58–1.53 (m, 2H), 1.28 (br-m,

15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.1, 63.1, 43.9, 32.8, 29.53, 29.45, 29.4, 29.3, 29.1, 25.7, 22.0; HRMS (CI) calcd for $C_{12}H_{25}O_2$ $[M+H]^+$ 201.1855, found 201.1855.

1,3-Diphenylpropan-2-one (4a)

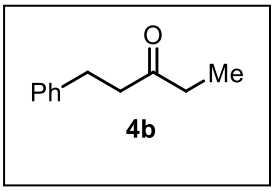


4a

The reaction with (2-Azidopropane-1,3-diyl)dibenzene **3a** (47.5 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 3 h, followed by neutral silica gel column chromatography (hexane / ethyl acetate = 40 / 1 to 20 / 1), gave **4a** (92% yield on ^{1}H NMR before purification, 37.9 mg, 90% isolated yield) as a light-yellow solid. The analytical data were in good agreement with the literature.[44]

Light-yellow solid; R_f value 0.40 (hexane / ethyl acetate = 10 / 1); m.p. 31–32 °C; IR (KBr, disc) ν_{max} 3027, 2896, 1710, 1494, 1450, 1332, 1167, 1090 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 4H), 7.28 (m, 2H), 7.16 (m, 4H), 3.73 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.7, 134.0, 129.5, 128.7, 127.0, 49.1; LRMS (EI, M = $C_{15}H_{14}O$) *m/z* 210 (M^+, 21%), 119 (17), 91 (100), 65 (24); HRMS (EI) calcd for $C_{15}H_{14}O$ (M^+) 210.1045, found 210.1039.

1-Phenylpentan-3-one (4b)



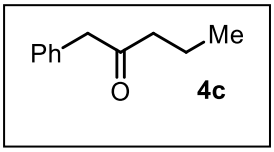
4b

The reaction with (3-Azidopentyl)benzene **3b** (37.9 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 2.5 h, followed by neutral silica gel column chromatography (hexane / ethyl acetate = 25 / 1), gave **4b** (83% yield on ^{1}H NMR before purification, 26.2 mg, 81% isolated yield) as a colorless oil. The analytical data were in good agreement with the literature.[45]

Colorless oil; R_f value 0.40 (hexane / ethyl acetate = 10 / 1); IR (KBr, disc) ν_{max} 3025, 2978, 2939, 1712, 1654, 1495, 1452, 1410, 1371, 1112 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 2H), 7.21–7.18 (m, 3H), 2.91 (t, 2H, *J* = 8.0 Hz), 2.74 (t, 2H, *J* = 8.0 Hz), 2.41 (q, 2H,

J = 7.5 Hz), 1.05 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 141.1, 128.4, 128.3, 126.0, 43.9, 36.1, 29.8, 7.7; LRMS (EI, M = $C_{11}H_{14}O$) *m/z* 162 (M^+, 62%), 133 (37%), 105 (100%), 91 (95%), 84 (13%), 77 (17%), 57 (32%); HRMS (EI) calcd for $C_{11}H_{14}O$ (M^+) 162.1045, found 162.1046.

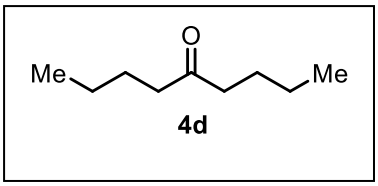
1-Phenylpentan-2-one (4c)



The reaction with (2-Azidopentyl)benzene **3c** (37.9 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 2.5 h, followed by neutral silica gel column chromatography (hexane / ethyl acetate = 20 / 1), gave **4c** (82% yield on ^{1}H NMR before purification, 25.9 mg, 80% isolated yield) as a light-yellow oil. The analytical data were in good agreement with the literature.[46]

Light-yellow oil; R_f value 0.36 (hexane / ethyl acetate = 10 / 1); IR (NaCl, neat) ν_{max} 3030, 2962, 2935, 2873, 1712, 1495, 1456, 1409, 1364, 1123, 1048 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.26 (m, 1H), 7.20 (d, 2H, 7.0 Hz), 3.68 (s, 2H), 2.43 (t, 2H, *J* = 7.0 Hz), 1.58 (m, 2H, *J* = 7.5, 7.0 Hz), 0.87 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.6. 134.3, 129.4, 128.7, 126.9, 50.2, 43.9, 17.1, 13.6; LRMS (EI, M = $C_{11}H_{14}O$) *m/z* 162 (M^+, 26%), 91 (73), 71 (100), 65 (25); HRMS (EI) calcd for $C_{11}H_{14}O$ (M^+) 162.1045, found 162.1045.

5-Nonanone (4d)

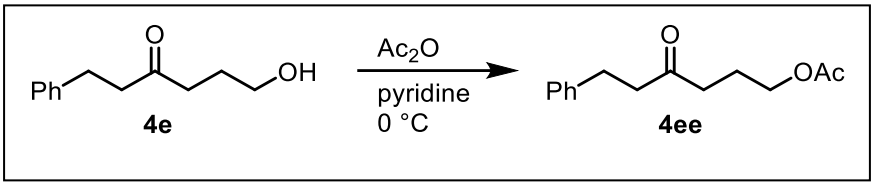


The reaction with 5-Azidononane **3d** (33.9 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 3.5 h, followed by neutral silica gel column chromatography (hexane / ethyl acetate = 30 / 1), gave **4d** (63% yield on ^{1}H NMR before purification, 10.6 mg, 37% isolated yield) as a

volatile colorless oil. The analytical data were in good agreement with those of commercially available authentic 5-nonanone.

Colorless oil; R_f value 0.32 (hexane / ethyl acetate = 15 / 1); IR (NaCl, neat) ν_{max} 2958, 2933, 2873, 1714, 1466, 1411, 1379, 1133, 1043, 772 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.39 (t, 4H, *J* = 7.5 Hz), 1.54 (tt, 4H, *J* = 7.5, 7.5 Hz), 1.30 (qt, 4H, *J* = 7.5, 7.5 Hz), 0.90 (t, 6H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.7, 42.5, 26.0, 22.4, 13.9; HRMS (CI) calcd for $C_9H_{19}O$ $[M+H]^+$ 143.1436, found 143.1432.

6-Hydroxy-1-phenylhexan-3-one (4e) and 4-oxo-6-phenylhexyl acetate (4ee)



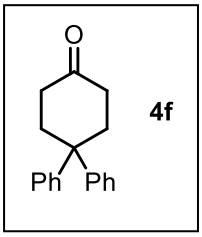
The reaction with 4-Azido-6-phenylhexan-1-ol **3e** (43.9 mg, 0.20 mmol), DMSO (36 μL, 0.50 mmol), and trifluoromethanesulfonic anhydride (82 μL, 0.50 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 5 h, followed by concentration *in vacuo*, gave **4e** (53% yield on ^1H NMR before purification). Due to the instability of the compound against silica gel purification, acetylation was performed to obtain a stable derivative.

To a stirred solution of crude 6-hydroxy-1-phenylhexan-3-one **4e** in pyridine (0.24 mL, 3.0 mmol) at 0 °C, acetic anhydride (0.20 mL, 2.0 mmol) was added dropwise. After 1 h, toluene was added into the mixture for azeotropic removal of pyridine, and then it was concentrated *in vacuo*. The obtained crude material was purified by neutral silica gel column chromatography (hexane / ethyl acetate = 80 / 1 to 20 / 1) to afford **4ee** (15.5 mg, 33% isolated yield over 2 steps) as a light-yellow oil. The analytical data were in good agreement with the literature.[47]

Light-yellow oil; R_f value 0.40 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 3029, 2958, 2893, 1739, 1715, 1495, 1452, 1363, 1243, 1039 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 2H), 7.21–7.17 (m, 3H), 4.04 (t, 2H, *J* = 7.0 Hz), 2.90 (t, 2H, *J* = 7.0 Hz), 2.75 (t, 2H,

J = 8.0 Hz), 2.47 (t, 2H, *J* = 7.5 Hz), 2.03 (s, 3H), 1.90 (tt, 2H, *J* = 7.0, 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.9, 171.1, 140.9, 128.5, 128.3, 126.1, 63.6, 44.3, 39.1, 29.7, 22.6, 20.9; LRMS (EI, M = $C_{14}H_{18}O_3$) *m/z* 234 (M^+, 8%), 174 (99), 105 (71), 91 (100), 87 (43); HRMS (EI) calcd for $C_{14}H_{18}O_3$ (M^+) 234.1256, found 234.1261.

4,4-Diphenylcyclohexan-1-one (4f)

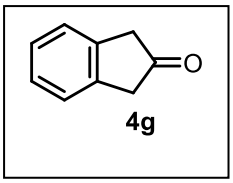


4f

The reaction with (4-azidocyclohexane-1,1-diyl)dibenzene **3f** (55.5 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 6.5 h, followed by neutral silica gel column chromatography (hexane / ethyl acetate = 30 / 1 to 10 / 1), gave **4f** (42% yield on ^{1}H NMR before purification, 20.0 mg, 40% isolated yield) as a white solid. The analytical data were in good agreement with the literature.[48]

White solid; R_f value 0.50 (hexane / ethyl acetate = 2 / 1); m.p. 131.7–132.9 °C; IR (KBr, disc) ν_{max} 3060, 2943, 2885, 1704, 1600, 1495, 1444, 1181 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.31 (m, 8H), 7.23–7.19 (m, 2H), 2.67 (t, 4H, *J* = 7.0 Hz), 2.45 (t, 4H, *J* = 7.0 Hz), ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 145.8, 128.7, 126.8, 126.3, 45.5, 38.6, 36.4; LRMS (EI, M = $C_{18}H_{18}O$) *m/z* 250 (M^+, 50%), 193 (100), 180 (50), 165 (26), 115 (29), 91 (14); HRMS (EI) calcd for $C_{18}H_{18}O$ (M^+) 250.1358, found 250.1359.

1,3-Dihydro-2*H*-inden-2-one (4g)

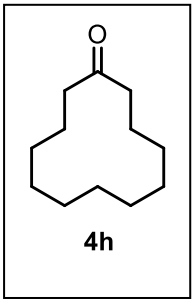


4g

The reaction with 2-azido-2,3-dihydro-1*H*-indene **3g** (31.8 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 3.5 h, followed by neutral silica gel column chromatography (hexane / ethyl acetate = 30 / 1), gave **4g** (39% yield on ^{1}H NMR before purification, 10.1 mg, 38% isolated yield) as a light-brown solid. The analytical data were in good agreement with the literature.[49]

Light-brown solid; R_f value 0.40 (hexane / ethyl acetate = 8 / 1); m.p. 53.5–54.5 °C; IR (KBr, disc) ν_{max} 3031, 2925, 1723, 1604, 1465, 1389, 1296, 1202, 1164, 1051 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.27 (m, 4H), 3.58 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.2, 137.8, 127.4, 125.0, 44.1; LRMS (EI, M = C_9H_8O) *m/z* 132 (M^+, 5%), 104 (19%), 86 (64%), 84 (100%), 58 (14%); HRMS (EI) calcd for C_9H_8O (M^+) 132.0575, found 132.05775.

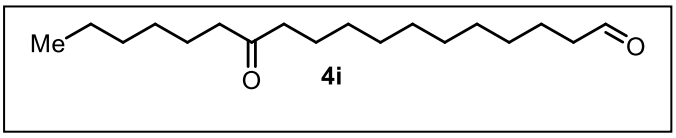
Cyclododecanone (4h)



The reaction with azidocyclododecane **3h** (41.9 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 5 h, followed by neutral silica gel column chromatography (hexane / ethyl acetate = 40 / 1), gave **4h** (36% yield on ^1H NMR before purification, 12.5 mg, 34% isolated yield) as a white solid. The analytical data were in good agreement with the literature.[50]

White solid; R_f value 0.56 (hexane / ethyl acetate = 7 / 1); IR (KBr, disc) ν_{max} 2930, 2863, 1706, 1471, 1437, 1362, 1247, 1205, 1131, 1019 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.46 (m, 4H), 1.71 (m, 4H), 1.31–1.27 (m, 14H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.0, 40.4, 24.7, 24.6, 24.2, 22.5, 22.3; HRMS (CI) calcd for $C_{12}H_{23}O$ $[M+H]^+$ 183.1749, found 183.1750.

12-Oxooctadecanal (4i)



The reaction with 1,12-Diazidooctadecane **3i** (67.3 mg, 0.20 mmol), DMSO (56 μL, 0.80 mmol) and trifluoromethanesulfonic anhydride (132 μL, 0.80 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) for 5 h, followed by neutral silica gel column chromatography (hexane / ethyl acetate = 100 / 1 to 10 / 1) gave **4i** (75% yield on ^1H NMR before purification, 38.4 mg, 68% isolated yield) as a white solid.

White solid; R_f value 0.30 (hexane / ethyl acetate = 10 / 1); m.p. 45.3–46.5 °C; IR (KBr, disc) ν_{max} 2916, 2850, 1710, 1464, 1416, 1209 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.76 (t, 1H, *J* = 1.5 Hz), 2.43–2.36 (m, 6H), 1.65–1.54 (m, 6H), 1.29–1.26 (br-m, 18H), 0.87 (t, 3H, *J* = 6.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.7, 203.0, 43.9, 42.83, 42.79, 31.6, 29.36, 29.33, 29.30, 29.23, 29.1, 28.9, 23.8, 22.5, 22.1, 14.0; LRMS (EI, M = $C_{18}H_{34}O_2$) *m/z* 282 (M^+, 8%),128 (76), 113 (100), 95 (51), 85 (46), 71 (60), 58 (72), 55 (49); HRMS (CI) calcd for $C_{18}H_{35}O_2$ $[M+H]^+$ 283.2637, found 283.2634.

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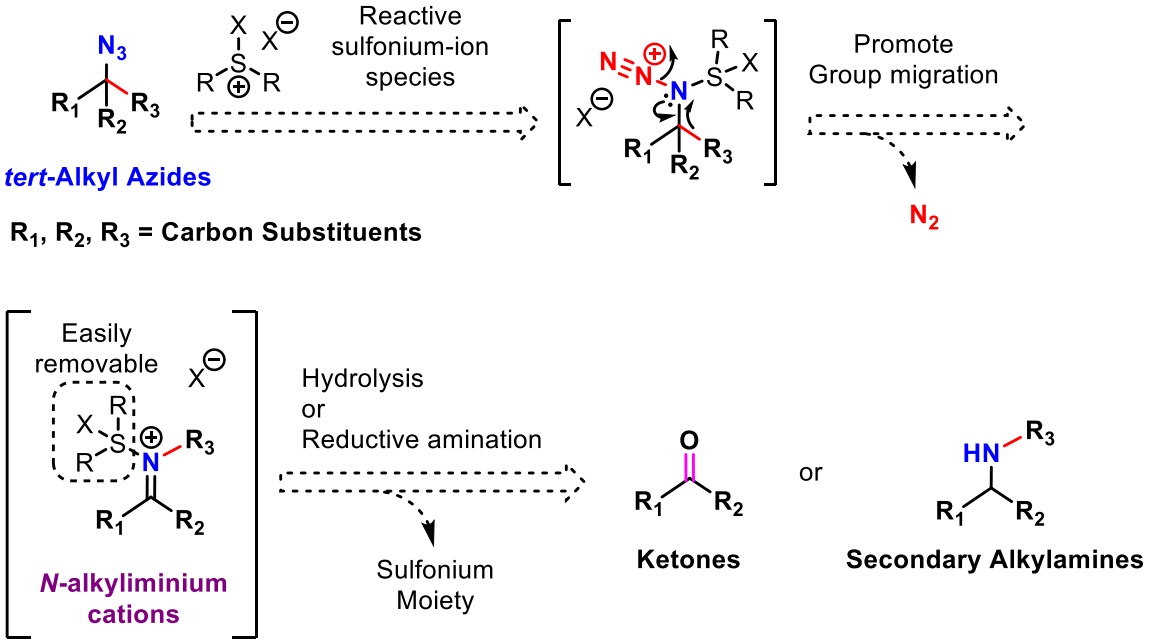
CHAPTER 3 Functionalization of Tertiary Alkyl Azides via Cleavage of a C–C Bond

3. 1 Introduction

To date, C–C bond cleavage in organic azides has been focused mainly on reactive molecules like acyl azide substrates, as demonstrated in Curtius rearrangement.[1,2] On the other hand, Schmidt-type reaction enables C–C bond cleavage in unreactive alkyl azides but requires carbon electrophile partners for the activation process.[3] This condition would make unnecessary and unremovable substitution onto the products by the carbon electrophiles. Although precedent examples of C–C bond cleavage in organic azides without the need of carbon electrophile partners have also been developed recently, the substrates are quite limited, such as benzylic and carbonyl-α azides.[4-7] In order to promote unreactive C–C bond cleavage which covers general *tert*-alkyl azides, herein, highly electrophile sulfonium ions species are utilized for the traceless Schmidt reaction.[8-10]



Scheme 3.1. Working hypothesis on traceless Schmidt reaction of *tert*-alkyl azides

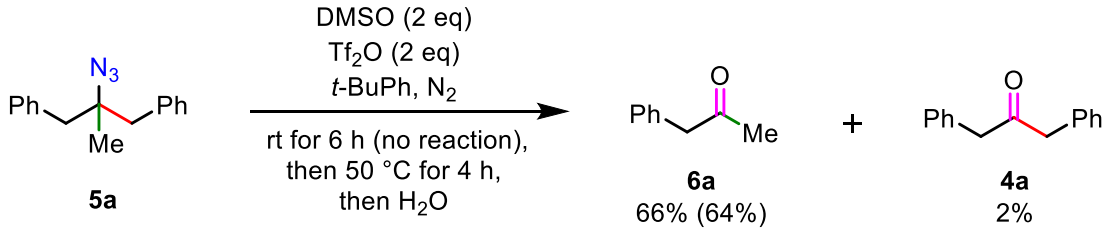
As shown in Chapter 2, functionalization of general primary and secondary alkyl azides allowed unreactive C–H bond cleavage, resulting in the migration of α-hydrogen atom onto the nitrogen atom of azide forming *N*–H iminium cation intermediates. In the context of *tert*-alkyl azides, all substituents are alkyl groups. Thus, the reaction of *tert*-alkyl azides was expected to involve unreactive C–C bond cleavage (Scheme 3.1). This reaction would give versatile intermediates, *N*-substituted alkyliminium cation intermediates. These are the key intermediates for subsequent organic transformation. The intermediates could be delivered to substituent-removed ketones by hydrolysis, or secondary alkylamine derivatives by reductive amination sequence, respectively.

3. 2 Scope of Tertiary Alkyl Azides Through C–C Bond Cleavage

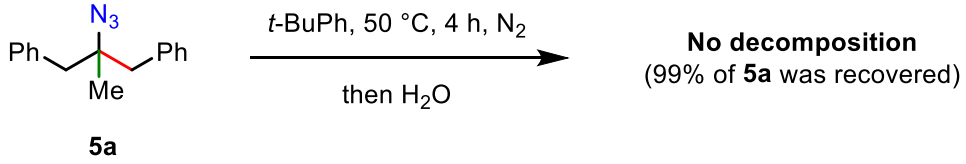
Tertiary alkyl azides are sterically hindered due to the presence of three alkyl groups attached to the molecules. For this reason, even the reactive sulfonium ion was difficult to reach the azide group of the tertiary compounds at room temperature, unlike those of primary and secondary alkyl azides. To check this presumpstion, *tert*-alkyl azide **5a** bearing one methyl and two benzyl groups was examined under the estblished optimum reaction conditions (2 equiv. of DMSO and Tf_2O, in *tert*-butylbenzene) at room temperature. Although reactive sulfonium ion was generated as indicated by the formation of white solid at the bottom of flask, there was no change on thin layer chromatography profile of the reaction mixture after 6 h. This observation suggested that the reaction of **5a** with generated sulfonium ion does not take place. Subsequent heating of the mixture to 50 °C allowed the generation of insoluble brown oil accompanied by expulsion of bubble, as observed in the primary and secondary alkyl azide cases. Gratifyingly, after stirring the mixture for 4 h at this temperature and then aqueous workup for hydrolysis, ketones **6a** and **4a** were obtained in 66% ^{1}H NMR yield (64% isolated yield) and 2% ^{1}H NMR yield, respectively (Scheme

3.2A). Although the desired reaction was achieved, alkyl azides may undergo the same 1,2-migration, decomposition, or several undesired chemical transformations under the high-temperature heating conditions, as reported in the precedented reports.[11,12] With this consideration, thermal stability of *tert*-alkyl azide **5a** at 50 °C was evaluated without reagents. Fortunately, no decomposition was observed after heating the azide to give back **5a** in 99% recovery (Scheme 3.2B). Thus, the heating condition at 50 °C with the reagents generating sulfonium ions was applied instead of room temperature condition.

(A) First trial on the Schmidt reaction of *tert*-alkyl azide **5a**



(B) Control experiment of *tert*-alkyl azide **5a** under heating condition without reagents

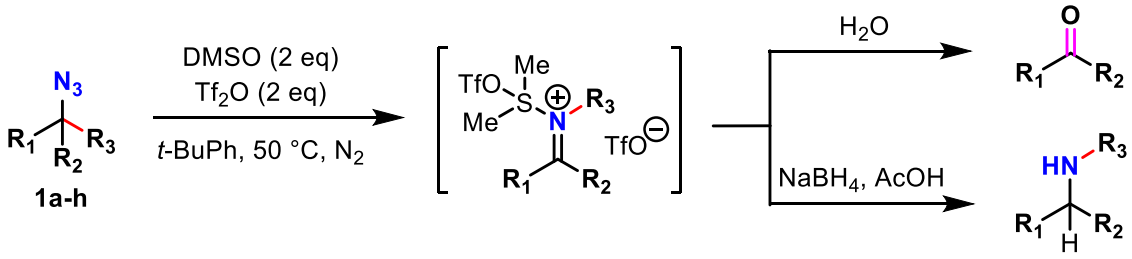


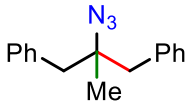
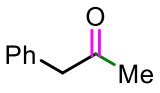
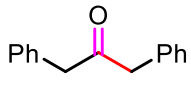
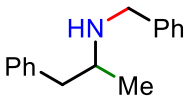
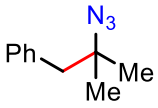
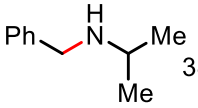
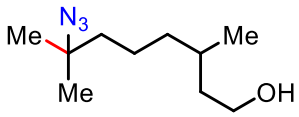
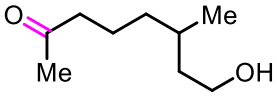
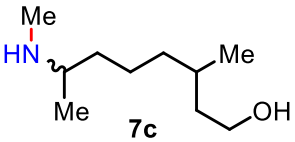
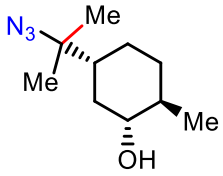
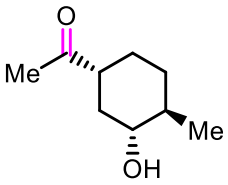
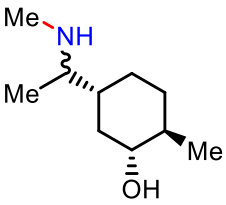
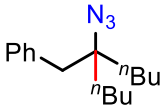
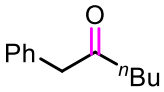
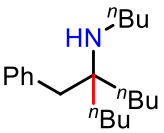
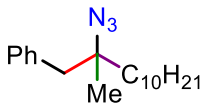
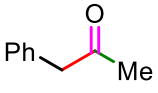
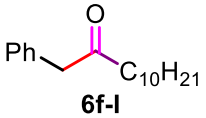
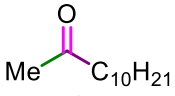
Scheme 3.2. C–C bond cleavage of azide **5a** and control experiment

With the reaction conditions for *tert*-alkyl azides evaluated, substrate scope of traceless Schmidt reaction in *tert*-alkyl azides was then examined (Table 3.1). Again, conducting the reaction of sulfonium ion with azide **5a** at 50 °C from the beginning (without stirring for 6 h at room temperature, as in Scheme 3.2A), successfully afforded ketones **6a** and **4a** in slightly higher yields (70%, with 67% isolated yield of **6a**; and 5%, with 3% isolated yield

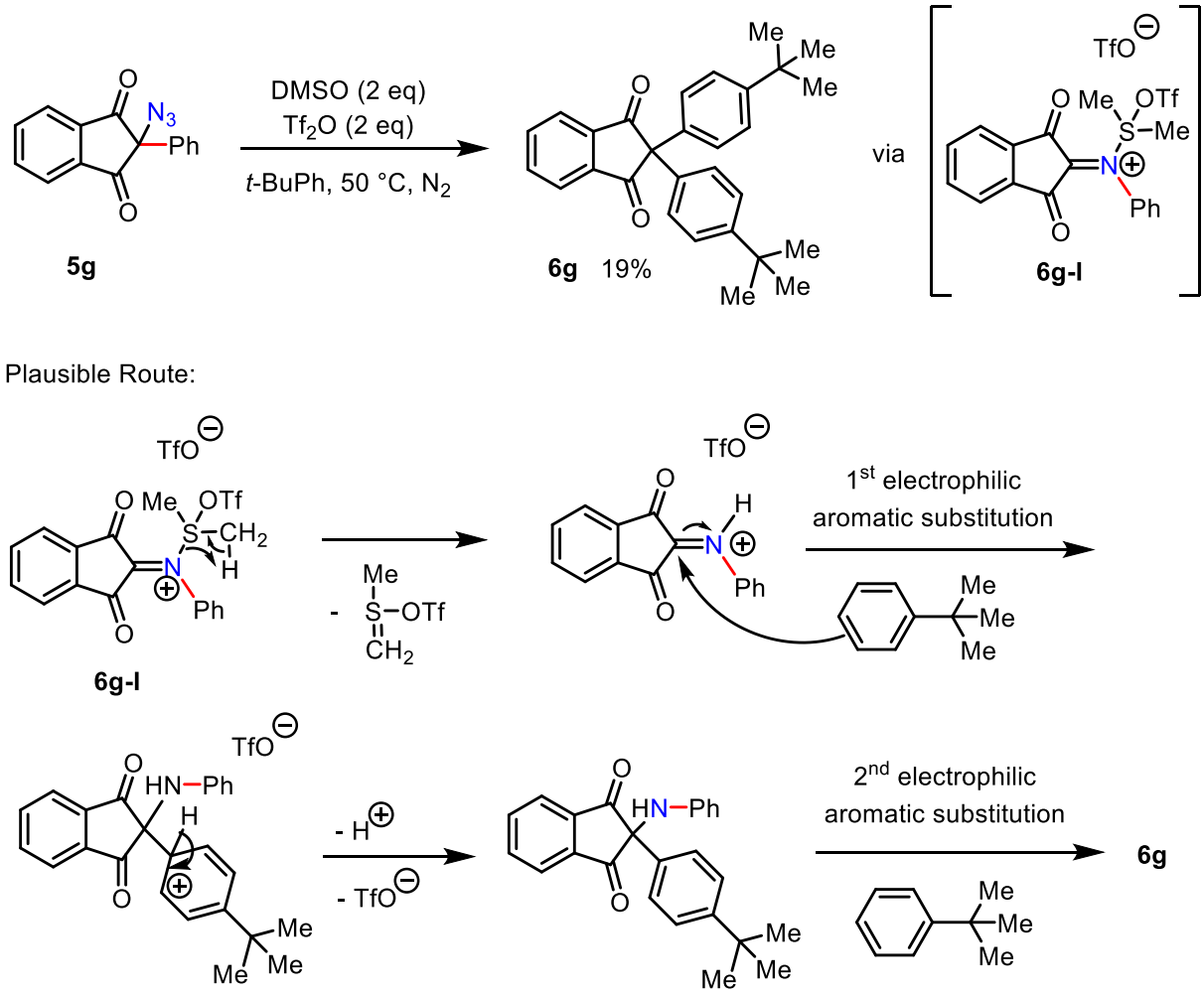
of **4a**, respectively). Pleasingly, reductive amination sequence of **5a** afforded secondary alkyl amine **7a** in 90% yield based on ^{1}H NMR (88% isolated yield), as a benzyl-migrated product. Reductive amination of imine generated from substrate **5b** having one benzyl and two methyl groups also furnished benzyl isopropylamine **7b** in 38% (34%) through benzyl migration. The low yield obtained may due to the formation of azaallyl or related species, $[C{=}N{-}CH]^{-}$ from iminium cation intermediate, which lead to decomposition.[13] However, methyl-migrated product was not obtained in this reaction. Aqueous quench for hydrolysis of **5b** was not performed due to the low boiling point or high polarity of expected products (acetone and benzylamine). In the tertiary substrate with two methyl and one long-chain alkyl groups (**5c**), and substrate with two methyl and one cyclic alkyl groups (**5d**), methyl group-removed ketones **6c** and **6d** were obtained in moderate yields through hydrolysis. Unfortunately, compound **7c** or **7d** was not afforded under the reductive amination sequence, probably due to the S_N2-type removal of the small methyl groups in the activated iminium intermediates. Interestingly, even in the presence of the benzyl group, the butyl group in **5e** was migrated to obtain compound **6e** or **7e** after hydrolysis or reductive amination. To check the order of group migration, substrate **5f** bearing three different alkyl groups was examined. Resultantly, decyl-removed ketone **6a** was the major product, followed by methyl-migrated **6f-I**, and benzyl-migrated **6f-II** as the minor product.

Table 3.1 Scope of *tert*-alkyl azides through C–C bond cleavage



Substrates	Products[a]	
	Hydrolysis	Reductive Amination
5a 	**6a** 70% (67%)  **4a** 5% (3%) 	**7a** 90% (88%) 
5b 		**7b** 38% (34%) 
5c[b] 	**6c** 46% (45%) 	 **7c** 0%
5d[b] 	**6d** 56% (55%) 	 **7d** 0%
5e 	**6e** 38% (37%) 	 **7e** 35% (32%)
5f 	**6a** (30%)  **6f-I** 19%  **6f-II** 7% 	

0.2 mmol scale reactions. [a]Yield based on ^{1}H NMR with $(CHCl_2)_2$ internal standard (isolated yields in brackets). [b]2.5 equiv of reagents were used.



Scheme 3.3. C–C bond cleavage of **5g** then electrophilic aromatic substitution reaction

Compound **5g**, as an example of carbonyl-α-azide was also examined. This substrate has been previously reported to furnish ring-expanded product by photoirradiation or heating at 180 °C.[14] In contrast, applying this traceless Schmidt reaction to the reactive azide **5g** resulted in the generation of the complex mixture containing many spots based on thin-layer chromatography. Fortunately, one product can be identified as **6g** (Scheme 3.3). This product was obtained through phenyl cleavage giving the *N*-phenyliminium cation intermediate (**6g-I**). The activated iminium cation in acidic condition would be a good electrophile for Friedel-Crafts-type reaction with solvent molecule (*tert*-butylbenzene) to

furnish compound **6g**. This type of the products is previously reported in the Friedel-Crafts reaction with ninhydrin.[15] Herein, I demonstrate the similar compound from the electrophilic aromatic substitution that occurred at the carbon of the iminium cation intermediate, which was generated from C–C bond cleavage of the molecule.

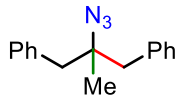
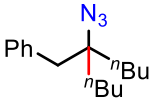
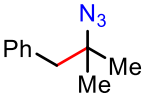
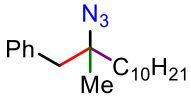
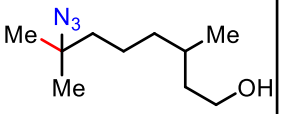
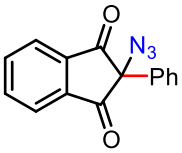
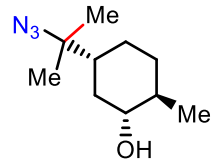
3. 3 Factors that Influence the Groups Migration

In the case of *tert*-alkyl azides bearing benzyl and methyl groups (**5a,b**), cleaving of benzyl group is easier than methyl group (Table 3.2). According to basic organic chemistry, delocalized benzylic carbanion is more stable than that of methyl group. Thus, I thought that the order of group migration would only depend on the stability of carbanion formed. Moreover, migration phenomena in substrates **5c** and **5d** gave further evidence for the above factor. Methyl groups cleavage in **5c** and **5d** and then migration to the electron-poor nitrogen of azide was observed due to the higher stability of methyl anion compred to the long-chain alkyl group or a cyclic alkyl group. The stable carbanion would make the group readily cleavable to form a new carbon-nitrogen bond of iminium cation intermediates.

Interestingly, methyl and decyl groups in compounds **5e** and **5f** were found to be the most active group to migrate to the nitrogen atom of azides, even in the presence of the more stable benzyl group in viewpoint of carbanion formed. In addition, the phenyl group in **5g** was successfully migrated rather than the electron-deficient benzoyl group. In contrast, the benzoyl group was migrated easily to the nitrogen atom of azide, as presented in compound **5h** (see next part 3.4 in this chapter, about ring expansion of cyclic *tert*-alkyl azides). These different phenomena showed complexity of bond cleavage by Schmidt reaction, and the stability of carbanion is not the only one factor that influence the group migration in general. The low selectivity of group migration was also observed in the previous reports during Baeyer-Villiger oxidation and Lewis acid-dependent Schmidt

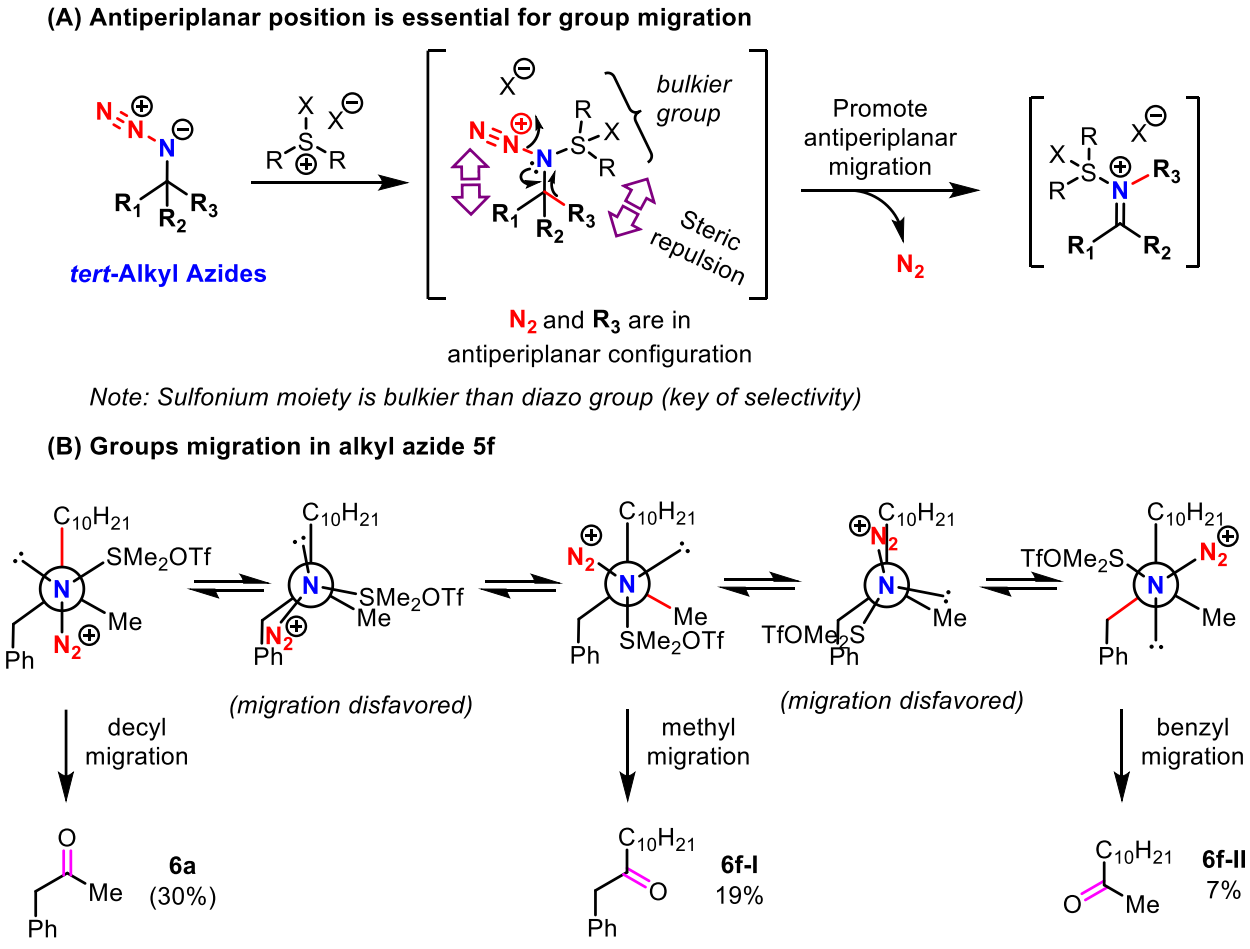
reaction of alkyl azides.[16,17] Probably, both group characteristics and the antiperiplanar orientation between migrating and molecular nitrogen leaving groups are important for the group migration.

Table 3.2 Migrating groups in each substrate

Substrates	Migrating Group	Substrates	Migrating Group
5a 	Benzyl > Methyl	**5e** 	n-Butyl
5b 	Benzyl	**5f** 	Decyl > Methyl > Benzyl
5c 	Methyl	**5g** 	Phenyl
5d 	Methyl		

As mentioned above, the antiperiplanar orientation in azido-sulfonium complex is supposed to be an important factor in the traceless Schmidt reaction. Antiperiplanar position is a conformation describing the dihedral angle of 150-180° between two groups separated by three chemical bonds. This conformation is essential for well-known organic reactions, such as bimolecular elimination reaction (E_2) and pinacol rearrangement. Assuming the antiperiplanar migration in the azido-sulfonium complex (Scheme 3.4A; red alkyl bond indicates the bond antiperiplanar to the dinitrogen leaving group), alkyl group migration is possible, avoiding the steric repulsion between larger groups both at nitrogen and carbon centers. After the reaction of alkyl azides with *in situ*-prepared sulfonium ion,

azido-sulfonium complex was generated. R_3 group can migrate to the nitrogen atom of azide because its conformation is on antiperiplanar with dinitrogen leaving group, forming iminium cation intermediates which can be further delivered to functionalized products (Scheme 3.4A). For example, alkyl azide **5f** generating product **6a** when decyl group and dinitrogen are in antiperiplanar conformation (Scheme 3.4B). Probably, **6a** can be obtained in the highest yield due to minimum steric repulsion between sulfonium moiety (bulkier group at the nitrogen of azide) and aromatic group (bulkier group at the carbon center).



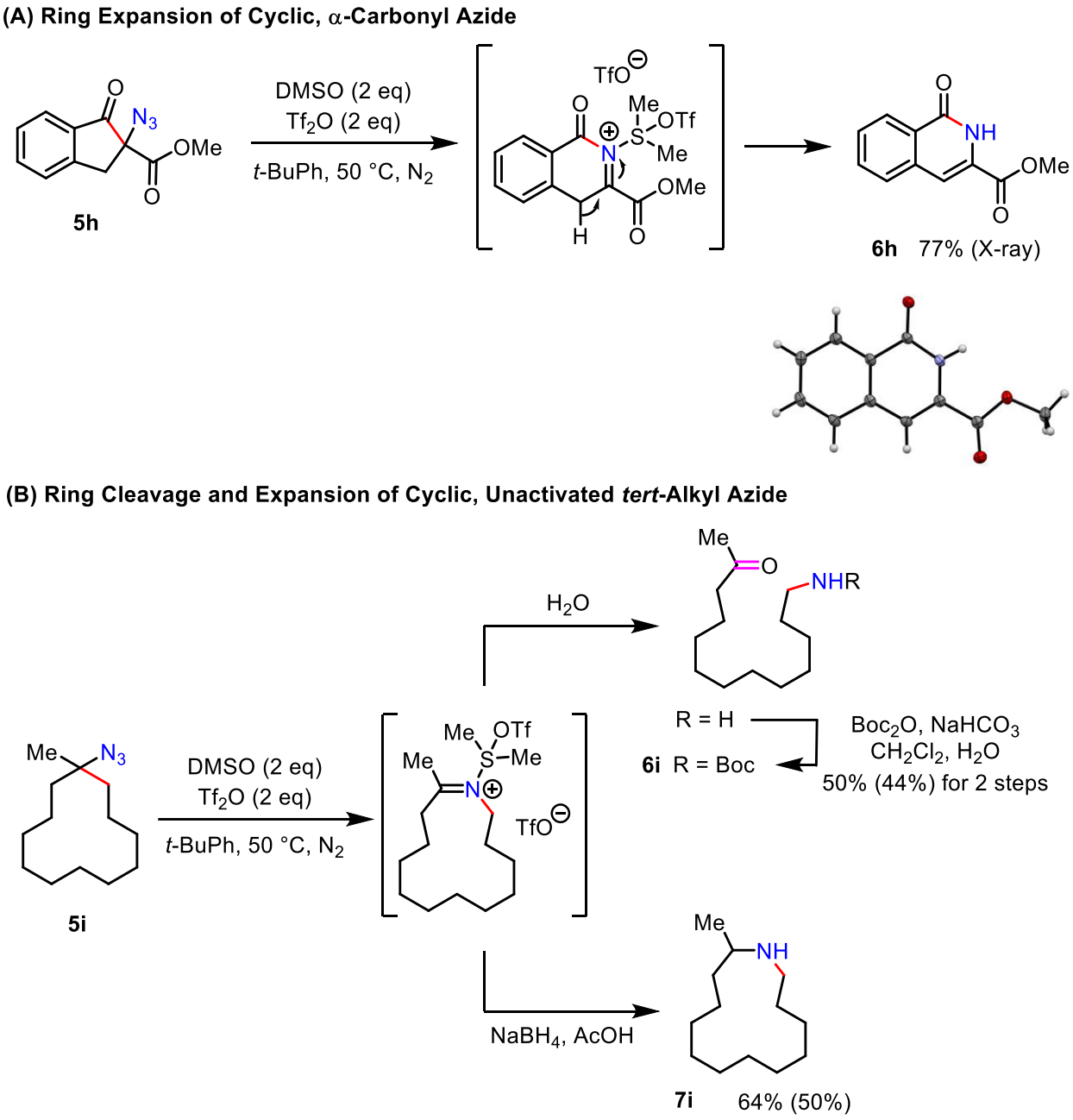
Scheme 3.4. Group migration through antiperiplanar conformation in traceless Schmidt reaction

3. 4 Ring Cleavage and Expansion of Tertiary Alkyl Azides Leading to Heterocycles

Nitrogen-containing heterocycles have been recognized as one of the most important structural motifs of pharmaceuticals.[18-20] Specifically, isoquinolines and aza-crown macrocycles are denoted to possess variable biological activities, such as antitumor, antimicrobial, anticancer, and antioxidant.[21-24] No doubt, chemists continue to devise novel methods for their syntheses.[25]

As established in the earlier part, the traceless Schmidt reaction can cleave the unreactive C–C bonds through subsequent 1,2-migration. Concerning this process, I expected that *N*-alkyl cyclic ketiminium cation intermediate could be generated by way of the ring expansion of cyclic *tert*-alkyl azide substrates. In such cases, ring-expanded nitrogen-containing cyclic products should be obtained.

In a previous report, iron(II) bromide catalyst at elevated temperature was reported to assist ring expansion of tertiary α-azidyl ketones to afford isoquinoline derivatives through 1,2-benzoyl migration from α-carbon to the nitrogen atom of azide.[4] To check the accessibility of traceless Schmidt reaction for ring expansion of cyclic tertiary α-azidyl ketones, compound **5h** was examined. The reaction was smoothly proceeded to give isoquinolinone **6h,** which was further confirmed by X-ray analysis (Scheme 3.5A). A 1,2-benzoyl migration to the nitrogen atom of azide gave cyclic ketiminium cation intermediate and then underwent aromatization to furnish **6h** in good yield. This result highlighted a promising alternative for isoquinoline synthesis, avoiding harsh reaction conditions such as high temperature over 100 °C.



Scheme 3.5. Ring cleavage and expansion of *tert*-alkyl azides

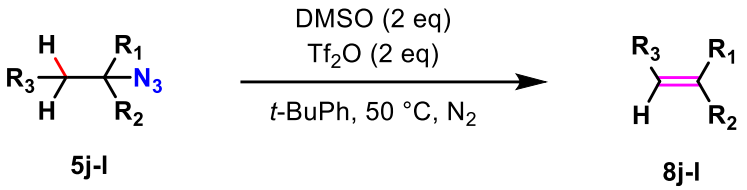
Producing nitrogen-containing heterocycles from the starting point of *tert*-alkyl azides via Schmidt reaction is undoubtedly attractive, especially in the route of alkaloid compounds.[26] However, the synthesis of such compounds in the absence of coupling partners for the azido group in the molecules, remains problematic.[27-30] Herein, **5i** was used

as a model compound of cyclic, unreactive *tert*-alkyl azide (Scheme 3.5B). To check ring cleavage of this substrate, traceless Schmidt reaction of **5i** followed by aqueous workup for hydrolysis successfully gave acyclic compound **6i**. This observation suggested the occurrence of ring cleavage and then 1,2-migration forming ring-expanded cyclic *N*-alkylketiminium cation intermediate. Again, compound **5i** was treated with the same reaction conditions, followed by a reductive amination sequence successfully afforded aza-crown macrocycle **7i**. Hence, this traceless Schmidt reaction provides a new way for accessing nitrogen macrocycles, utilizing unreactive cyclic *tert*-alkyl azides as substrates.

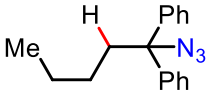
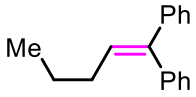
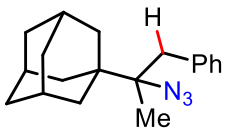
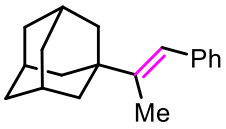
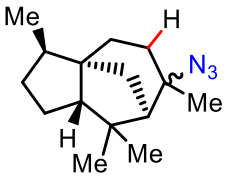
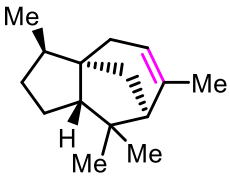
3. 5 Tertiary Alkyl Azides Leading to Elimination Reaction

Although the traceless Schmidt reaction can be applied to the various substrates promoting C–C bond cleavage, some *tert*-alkyl azides were unsuccessful to give desired transformation products (Table 3.3). For example, compound **5j** bearing two phenyl groups gave an elimination product, olefin **8j**. Moreover, substrate **5k** connected with neopentyl group also faced elimination to furnish compound **8k**. Meanwhile, alkyl azide **5l** derived from cedrol natural product also resulted in the elimination of β-hydrogen to afford α-cedrene **8l**.

Table 3.3 *tert*-Alkyl azides Leading to Elimination Reaction

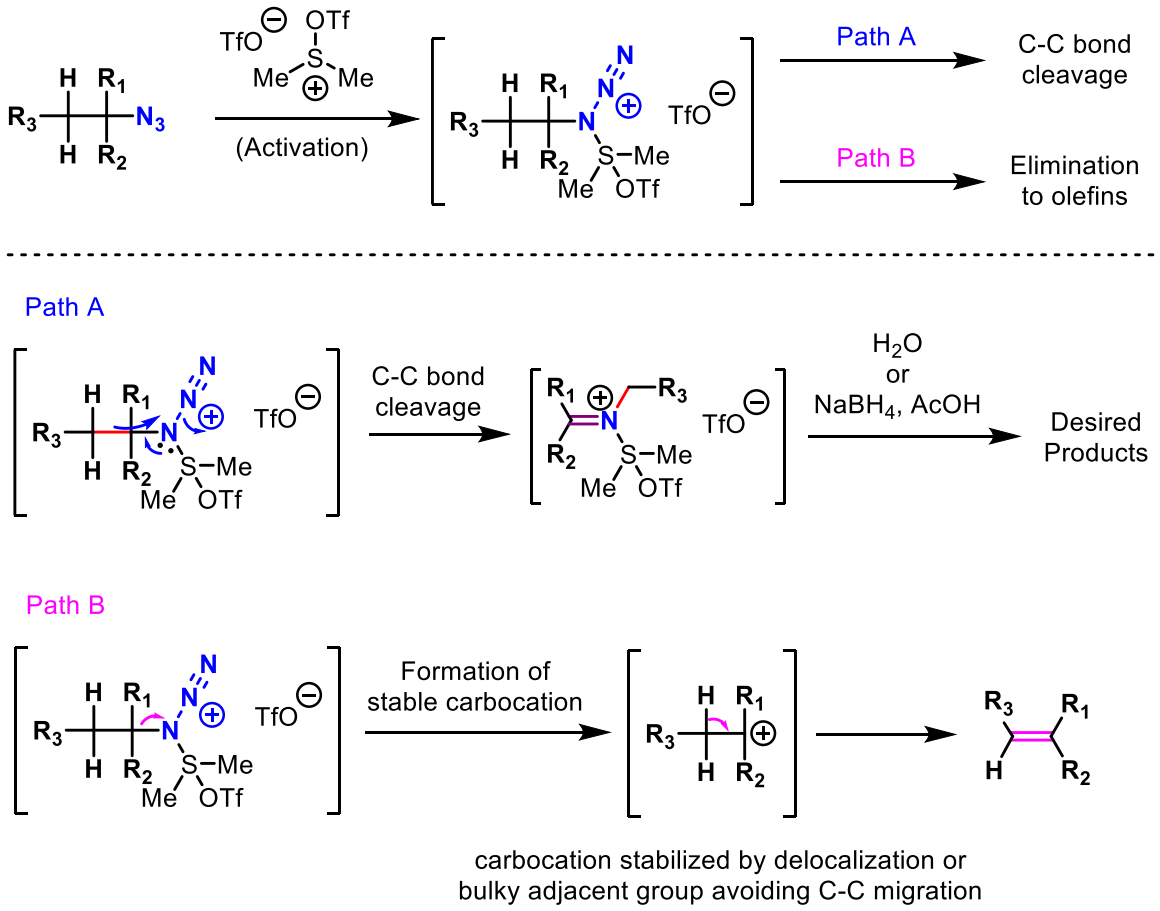


5j-l **8j-l**

Substrates		Elimination Products[a]		
5j[b]		**8j**		87% (72%)
5k		**8k**		68% (44%)
5l		**8l**		85% (46%)

0.2 mmol scale reactions. [a]Yield based on ^{1}H NMR with $(CHCl_2)_2$ internal standard (isolated yields in brackets). [b]Reaction was performed at room temperature

The stable benzylic carbocation, such as from compound **5j**, was generated upon removal of azido-sulfonium complexes (Scheme 3.6 Path B). After that, the elimination of β-hydrogen took place to give olefins. Moreover, tertiary alkyl azido groups close to the bulky or rigid carbon centers are sterically hindered to approach the sulfonium ion electrophile, for examples, neopentylic positioning **5k** and bycyclic **5l**. These structures would avoid the migration-favorable conformations and lead to elimination of the azido group or probably azido-sulfonium complexed group to yield olefins. In contrast, in the absence of these structural features, unreactive C–C bond cleavage in *tert*-alkyl azides can be successfully achieved (Scheme 3.6 Path A).



Scheme 3.6. Desired transformation (Path A) and plausible mechanism of elimination (Path B)

3. 6 Summary

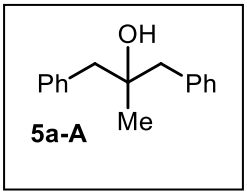
The sulfonium ion-mediated traceless Schmidt reaction was successfully achieved to functionalize the tertiary alkyl azides through unreactive C–C bond cleavage. The reaction of sulfonium ion with *tert*-alkyl azides can promote β-carbon cleavage and then 1,2-migration of respected alkyl group onto the nitrogen atom of azide, giving *N*-alkylketiminium cation intermediates. These intermediates are subsequently treated by aqueous workup for hydrolysis and reductive amination sequence to afford corresponding ketones and secondary alkyl amines,

respectively. Nitrogen-containing heterocyclic compounds were successfully obtained employing cyclic *tert*-alkyl azides as substrates via ring cleavage and expansion.

3. 7 Experimental Data

3.7.1 Preparation of Organic Azide Substrates

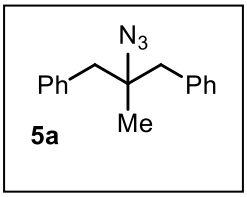
2-Methyl-1,3-diphenylpropan-2-ol (5a-A)



To a stirred solution of methylmagnesium bromide (0.89 M in diethyl ether, 21.9 mL, 19.5 mmol) was added commercially available 1,3-diphenylpropan-2-one solution (1.05 g, 5.0 mmol) dissolved in diethyl ether (10 mL) dropwise at -78 °C under nitrogen atmosphere. After 1 h, the mixture was warmed up to room temperature and was stirred for additional 18 h. After that, it was cooled to 0 °C and was quenched with 1 M HCl aqueous solution. Then, reaction mixture was extracted with diethyl ether to wash with 1 M HCl aqueous solution and brine. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 40 / 1 to 20 / 1) to afford **5a-A** (798 mg, 71%) as a viscous colorless oil. The spectroscopic data were identical to those in the literature.[31]

Viscous colorless oil; R_f value 0.60 (hexane / ethyl acetate = 4 / 1); IR (NaCl, neat) ν_{max} 3446, 3029, 2970, 2920, 2854, 1600, 1495, 1452, 1375, 1220, 1092 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.30 (m, 4H), 7.27–7.23 (m, 6H), 2.86 (d, 2H, *J* = 14.0 Hz), 2.79 (d, 2H, *J* = 13.5 Hz), 1.42 (s, br, 1H), 1.07 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 130.7, 128.1, 126.5, 72.4, 48.3, 26.3; LRMS (EI, M = $C_{16}H_{18}O$) *m/z* 226 (M^+, 1%),135 (100), 134 (23), 117 (16), 92 (33), 91 (41); HRMS (EI) calcd for $C_{16}H_{18}O$ (M^+) 226.1358, found 226.1356.

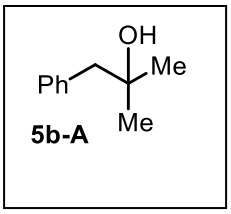
(2-Azido-2-methylpropane-1,3-diyl)dibenzene (5a)



The azidation reaction of the *tert*-alcohols was performed by the Moran's method.[32] To a stirred solution of 2-methyl-1,3-diphenylpropan-2-ol **5a-A** (113 mg, 0.5 mmol) in nitromethane (250 μL, 2 M) at room temperature was added dropwise azidotrimethylsilane (199 μL, 1.5 mmol and finally was added $B(C_6F_5)_3$ (12.8 mg, 0.025 mmol, 5 mol%). The mixture was stirred for 3 h. After removal of volatile components, the crude material was purified by silica gel column chromatography (hexane as eluent) to afford **5a** (68.3 mg, 54%) as a viscous colorless oil.

Viscous colorless oil; R_f value 0.60 (hexane / ethyl acetate = 8 / 1); IR (NaCl, neat) ν_{max} 3063, 3029, 2974, 2920, 2099, 1495, 1452, 1263, 1220, 1089 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 6H), 7.26–7.23 (m, 4H), 2.89 (d, 2H, *J* = 13.5 Hz), 2.78 (d, 2H, *J* = 13.5 Hz), 1.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 130.7, 128.1, 126.8, 64.3, 46.6, 22.0; LRMS (EI, M = $C_{16}H_{17}N_3$) *m/z* 251 (M^+, 0.04%),132 (10), 92 (9), 91 (100); HRMS (EI) calcd for $C_{16}H_{17}N_3$ (M^+) 251.1422, found 251.1427.

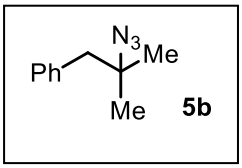
2-Methyl-1-phenylpropan-2-ol (5b-A)



To a stirred solution of benzylmagnesium chloride (2 M in tetrahydrofuran, 2.75 mL, 5.5 mmol) in 5.5 mL diethyl ether at 0 °C was added dropwise acetone (367 μL, 5.0 mmol) dissolved in diethyl ether (2mL). After 3 h, the mixture was stopped with 1 M HCl aqueous solution. Then, it was extracted with diethyl ether to wash with 1 M HCl aqueous solution and brine. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 30 / 1 to 10 / 1) to afford **5b-A** (660 mg, 88%) as a colorless oil. The analytical data were in good agreement with the literature.[33]

Colorless oil; R_f value 0.46 (hexane / ethyl acetate = 3 / 1); IR (NaCl, neat) ν_{max} 3392, 3029, 2970, 2931, 1495, 1452, 1375, 1150, 903 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.20 (m, 5H), 2.76 (s, 2H), 1.43 (s, 1H, OH), 1.23 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 130.4, 128.2, 126.5, 70.7, 49.7, 29.1; LRMS (EI, M = $C_{10}H_{14}O$) *m/z* 150 (M^+, 2%), 135 (13), 92 (100), 91 (36), 84 (12), 59 (43); HRMS (EI) calcd for $C_{10}H_{14}O$ (M^+) 150.1045, found 150.1041.

(2-Azido-2-methylpropyl)benzene (5b)

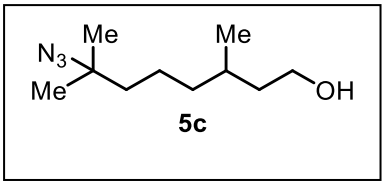


5b

The azidation reaction of the *tert*-alcohols was performed by the Moran's method.[32] To a stirred solution of 2-methyl-1-phenylpropan-2-ol (75.1 mg, 0.5 mmol) in nitromethane (250 μL, 2 M) at room temperature was added dropwise azidotrimethylsilane (199 μL, 1.5 mmol), and then, iron(III) chloride hexahydrate (6.8 mg, 0.025 mmol, 5 mol%) was added. The mixture was stirred for 1 h. After removal of volatile components, the crude material was purified by silica gel column chromatography (hexane elution) to afford **5b** (59.9 mg, 68%) as a colorless oil. The analytical data were in good agreement with the literature.[32]

Colorless oil; R_f value 0.80 (hexane / ethyl acetate = 3 / 1); IR (NaCl, neat) ν_{max} 3033, 2978, 2931, 2094, 1491, 1456, 1375, 1259, 1127 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.25 (m, 3H), 7.22–7.20 (m, 2H), 2.77 (s, 2H), 1.27 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7, 130.5, 128.1, 126.7, 61.8, 47.4, 25.9; HRMS (CI) calcd for $C_{10}H_{14}N_3$ $[M+H]^+$ 176.1188, found 176.1186.

7-Azido-3,7-dimethyloctan-1-ol (5c)



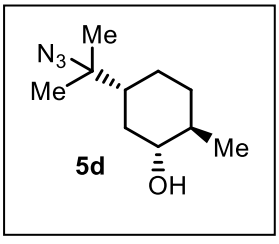
5c

The azidation reaction of the alkenes was performed by Boger's procedure.[34] Iron(III) oxalate hexahydrate (483.8 mg, 1.0 mmol) was dissolved in 20 mL water and stirred for 2 h. After

all material dissolved, the solution was cooled down to 0 °C and was simply degassed by nitrogen bubbling. Then, sodium azide (97.5 mg, 1.5 mmol) was added to the solution, allowing subsequent color change from yellowish green to red brown oil. The mixture was diluted by adding 10 mL ethanol, then the flask filled with nitrogen gas. After that, a solution of commercially available citronellol (78.1 mg, 0.50 mmol, in 10 mL ethanol) was added dropwise. Then, half portion of sodium borohydride (60.5 mg, 1.60 mmol) was added, followed by another portion (60.5 mg, 1.60 mmol) 5 min after the first addition. The resulting mixture was then stirred for 1 h. Finally, it was quenched by addition of 28% NH_4OH (8 mL). The mixture was extracted with dichloromethane/ methanol = 9 / 1. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1 to 5 / 1) to afford **5c** (59.2 mg, 59%) as a colorless oil. The analytical data were in good agreement with the literature.[34]

Colorless oil; R_f value 0.40 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 3397, 2938, 2096, 1642, 1460, 1367, 1258, 1054 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.68 (m, 2H), 1.63–1.56 (m, 2H), 1.48–1.27 (m, 7H), 1.25 (s, 6H), 1.19–1.12 (m, 1H), 0.91 (d, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 61.7, 61.1, 41.6, 39.8, 37.3, 29.4, 26.02, 25.96, 21.6, 19.5; HRMS (CI) calcd for $C_{10}H_{22}N_3O$ $[M+H]^+$ 200.1763, found 200.1763.

(1*R*,2*R*,5*R*)-5-(2-Azidopropan-2-yl)-2-methylcyclohexan-1-ol (5d)

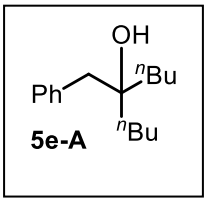


The azidation reaction of the alkenes was performed by Boger's procedure.[34] Iron(III) oxalate hexahydrate (484 mg, 1.0 mmol) was dissolved in 20 mL water and stirred for 2 h. After all material dissolved, the solution was cooled down to 0 °C and was simply degassed by nitrogen bubbling. Then, sodium azide (97.5 mg, 1.5 mmol) was added to the solution, allowing subsequent color change from yellowish green to red brown oil. The mixture was diluted by

adding 10 mL ethanol, then the flask was filled with nitrogen gas. After that, a solution of commercially available (+)-dihydrocarvone ((2*R*,5*R*)-2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one) (76.1 mg, 0.50 mmol, in 10 mL ethanol) was added dropwise. The, half portion of sodium borohydride (60.5 mg, 1.60 mmol) was added, followed by another portion (60.5 mg, 1.60 mmol) 5 min after the first addition. The resulting mixture was then stirred for 7 h. Finally, it was quenched by addition of 28% NH_4OH (8 mL). The mixture was extracted with dichloromethane/ methanol = 9 / 1. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 30 / 1 to 5 / 1) to afford **5d** (49.4 mg, 50%) as a colorless oil.

Colorless oil; R_f value 0.40 (hexane / ethyl acetate = 2 / 1); $[\alpha]_D^{24} = -13.7$ (c = 0.1, $CHCl_3$); IR (NaCl, neat) ν_{max} 3423, 2947, 2870, 2100, 1644, 1457, 1370, 1261, 1050 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.14 (ddd, 1H, *J* = 10.0, 4.5, 3.5 Hz), 2.06–2.02 (m, 1H), 1.79–1.70 (m, 2H), 1.43 (m, 1H), 1.29–1.22 (m, 2H), 1.24 (s, 6H), 1.11–0.95 (m, 3H), 1.01 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 76.3, 63.8, 46.2, 40.0, 36.5, 32.8, 26.7, 23.6, 18.2; LRMS (EI, M = $C_{10}H_{19}N_3O$) *m/z* 197 (M^+, 0.1%), 137 (15), 95 (55), 81 (10), 69 (12), 56 (100); HRMS (EI) calcd for $C_{10}H_{19}N_3O$ (M^+) 197.1528, found 197.1525.

5-Benzylnonan-5-ol (5e-A)

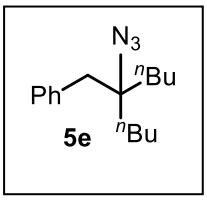


To a stirred solution of benzylmagnesium chloride (2 M in tetrahydrofuran, 6.5 mL, 13.0 mmol) was added commercially available 5-nonanone (1.42 g, 10.0 mmol) dissolved in tetrahydrofuran (20 mL) at 0 °C under nitrogen atmosphere. After stirred for 1 h at this temperature, the mixture was then warmed up to room temperature and stirred for additional 7 h. The reaction was stopped with 1 M HCl aqueous solution. Then, it was extracted with ethyl acetate to wash with 1 M HCl aqueous solution and

brine. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1 to 5 / 1) to afford **5e-A** (2.32 g, 99%) as a colorless oil.

Colorless oil; R_f value 0.60 (hexane / ethyl acetate = 5 / 1); IR (NaCl, neat) ν_{max} 3465, 3029, 2954, 2935, 2866, 1642, 1456, 1380, 1135, 1004 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.29 (m, 2H), 7.26–7.20 (m, 3H), 2.75 (s, 2H), 1.43–1.27 (m, 12H), 1.20 (s, 1H, OH), 0.92 (t, 6H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.5, 130.6, 128.2, 126.4, 74.2, 45.6, 38.4, 25.9, 23.2, 14.1; HRMS (MALDI-Spiral-TOF) calcd for $C_{16}H_{26}ONa$ $[M+Na]^+$ 257.1881, found 257.1876.

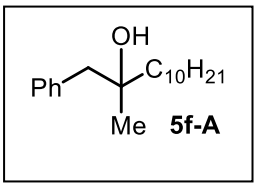
(2-Azido-2-butylhexyl)benzene (5e)



The azidation reaction of the *tert*-alcohols was performed by the Moran's method.[32] To a stirred solution of 5-benzylnonan-5-ol (234 mg, 1.0 mmol) in nitromethane (0.5 mL, 2 M) at room temperature was added dropwise azidotrimethylsilane (398 μL, 3.0 mmol), and then, tris(pentafluorophenyl)borane (25.6 mg, 0.05 mmol, 5 mol%) was added. The mixture was stirred for 3 min. After removal of volatile components, the crude material was purified by silica gel column chromatography (hexane elution) to afford **5e** (124 mg, 48%) as a colorless oil.

Colorless oil; R_f value 0.50 (hexane); IR (NaCl, neat) ν_{max} 2958, 2935, 2867, 2095, 1641, 1458, 1255 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.29 (m, 2H), 7.27–7.24 (m, 1H), 7.22–7.21 (m, 2H), 2.79 (s, 2H), 1.50–1.47 (m, 4H), 1.41–1.26 (m, 8H), 0.93 (t, 6H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.6, 130.4, 128.1, 126.6, 66.9, 43.2, 35.6, 25.9, 23.0, 14.0; HRMS (CI) calcd for $C_{16}H_{26}N_3$ $[M+H]^+$ 260.2127, found 260.2129.

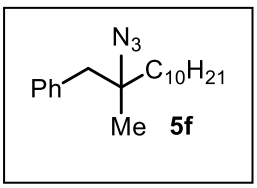
2-Methyl-1-phenyldodecan-2-ol (5f-A)



To a stirred solution of benzylmagnesium chloride (2 M in tetrahydrofuran, 4.6 mL, 9.1 mmol) at 0 °C was added dropwise commercially available dodecan-2-one solution (1.29 g, 7.0 mmol, dissolved in 14 mL tetrahydrofuran). After stirred for 1 h at this temperature, the mixture was then warmed up to room temperature and stirred for additional 11 h. The reaction was stopped with 1 M HCl aqueous solution. Then, it was extracted with diethyl ether to wash with 1 M HCl aqueous solution. The organic layer was dried over sodium sulfate. The crude material obtained by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1) to afford **5f-A** (1.89 g, 97%) as a colorless oil.

Colorless oil; R_f value 0.40 (hexane / ethyl acetate = 6 / 1); IR (NaCl, neat) ν_{max} 3431, 3029, 2927, 2858, 1460, 1375, 1139 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.30 (m, 2H), 7.26–7.21 (m, 3H), 2.79 (d, 1H, *J* = 13.0 Hz), 2.73 (d, 1H, *J* = 13.0 Hz), 1.47–1.41 (m, 4H), 1.33–1.28 (br-m, 15H), 1.14 (s, 3H), 0.89 (t, 3H, *J* = 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 130.5, 128.1, 126.4, 72.5, 47.9, 41.9, 31.9, 30.2, 29.65, 29.60, 29.3, 26.5, 24.0, 22.7, 14.1; LRMS (EI, M = $C_{19}H_{32}O$) *m/z* 276 (M^+, 0.1%), 185 (82), 135 (19), 97 (14), 92 (100), 69 (18); HRMS (EI) calcd for $C_{19}H_{32}O$ (M^+) 276.2453, found 276.2445.

(2-Azido-2-methyldodecyl)benzene (5f)

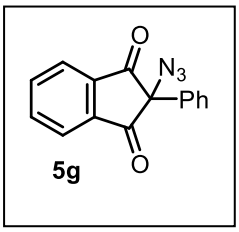


The azidation reaction of the *tert*-alcohols was performed by the Moran's method.[32] To a stirred solution of 2-methyl-1-phenyldodecan-2-ol **5f-A** (277 mg, 1.0 mmol) in nitromethane (0.5 mL, 2 M) at room temperature was added dropwise azidotrimethylsilane (398 μL, 3.0 mmol), and finally was added tris(pentafluorophenyl)borane (25.6 mg, 0.05 mmol, 5 mol%). The mixture was stirred for 18

h. After removal of volatile components, the crude material was purified by silica gel column chromatography (hexane as eluent) to afford **5f** (166 mg, 55%) as a colorless oil.

Colorless oil; R_f value 0.40 (hexane); IR (NaCl, neat) ν_{max} 3029, 2927, 2858, 2099, 1460, 1375, 1259 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.29 (m, 2H), 7.27–7.24 (m, 1H), 7.22–7.20 (m, 2H), 2.81 (d, 1H, *J* = 14.0 Hz), 2.74 (d, 1H, *J* = 14.0 Hz), 1.53–1.41 (m, 4H), 1.32–1.27 (br-m, 14H), 1.20 (s, 3H), 0.88 (t, 3H, *J* = 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7, 130.5, 128.1, 126.7, 64.4, 45.9, 39.6, 31.9, 29.9, 29.6, 29.3, 24.0, 22.9, 22.7, 14.1; LRMS (EI, M = $C_{19}H_{31}N_3$) *m/z* 259 ($[M-N_3]^+$, 2%), 182 (69), 147 (36), 91 (100), 85 (26), 71 (23), 57 (45); HRMS (EI) calcd for $C_{19}H_{31}$ $[M-N_3]^+$ 259.2426, found 259.2433.

2-Azido-2-phenyl-1*H*-indene-1,3(2*H*)-dione (5g)



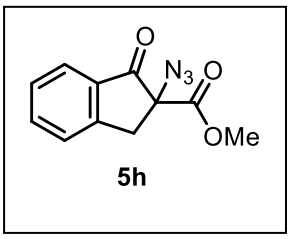
The synthesis was in accordance with the reported method.[14c]

To a stirred solution of commercially available 2-phenyl-1*H*-indene-1,3(2*H*)-dione (667 mg, 3.0 mmol) in DMSO / water (2 / 1, 30 mL, 0.1 M), sodium azide (1.09 g, 5.6 mmol) and molecular iodine (1.68 g, 6.6 mmol) was added successively at room temperature, and the mixture was stirred for overnight. The reaction was quenched with saturated solution of sodium thiosulfate, and the mixture was extracted with ethyl acetate. The collected organic layer was dried over sodium sulfate and was concentrated *in vacuo*. The obtained crude material was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1 to 2 / 1) to afford **5g** (466 mg, 59%) as a colorless oil. The analytical data were in good agreement with the literature.[14c]

Viscous light-yellow oil; R_f value 0.50 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 2107, 1712, 1591, 1242 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.08–8.06 (m, 2H), 7.95–7.93 (m, 2H) 7.53–7.51 (m, 2H) 7.42–7.39 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.8, 140.6, 136.9,

132.1, 129.8, 129.3, 127.5, 124.5, 70.7; HRMS (ESI) calcd for $C_{15}H_9N_3O_2Na$ $[M+Na]^+$ 286.0592, found 286.0591.

Methyl 2-azido-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (5h)



5h

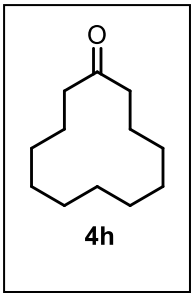
The synthesis was in accordance with the reported method.[4] To a stirred suspension of sodium hydride (60% in oil, 0.36 g, 9.0 mmol) in 5 mL dimethyl carbonate was added a solution of commercially available 1-indanone (396.5 mg, 3.0 mmol, dissolved in 5 mL dimethyl carbonate) dropwise at room temperature. The resulting mixture was then refluxed for 5 h. After cooling down to room temperature, reaction was stopped by addition of cold water. pH of the mixture was adjusted to less than 4 by 1 M HCl aqueous solution. The mixture was extracted with ethyl acetate to wash with 1 M HCl aqueous solution. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was subjected to the next step without purification.

The obtained crude material was dissolved in dimethyl sulfoxide (21 mL). After that, sodium azide aqueous solution (682.6 mg, 10.5 mmol, in 11 mL distilled water) was added dropwise to give dark brown solution. Finally, molecular iodine (1.14 g, 4.5 mmol) was added to the mixture and stirred for 3.5 h. The reaction was stopped by saturated sodium thiosulfate solution to give yellow oil solution. The mixture was extracted with ethyl acetate to wash with brine. The organic layer was dried over sodium sulfate. After discarding volatile materials *in vacuo*, the crude product was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1 to 10 / 1) to afford **5h** (606 mg, 87% over two steps) as a yellow solid. The analytical data were in good agreement with the literature.[4]

Yellow solid; R_f value 0.60 (hexane / ethyl acetate = 2 / 1); m.p. 65–66 °C [Lit. 69–70 °C][4]; IR (KBr, disc) ν_{max} 2955, 2100, 1747, 1712, 1604, 1472, 1435, 1282, 1227, 1050 cm^{-1}; ^1H NMR

(500 MHz, $CDCl_3$) δ 7.84 (d, 1H, *J* = 7.5 Hz), 7.69 (ddd, 1H, *J* = 7.5, 7.5, 1.0 Hz), 7.48–7.45 (m, 2H), 3.81 (s, 3H), 3.68 (d, 1H, *J* = 17.5 Hz), 3.05 (d, 1H, *J* = 17.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 168.9, 152.0, 136.5, 132.9, 128.4, 126.4, 125.6, 70.1, 53.5, 38.4; HRMS (CI) calcd for $C_{11}H_{10}N_3O_3$ $[M+H]^+$ 232.0722, found 232.0723.

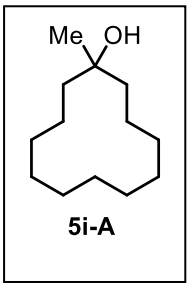
Cyclododecanone (4h) from cyclododecanol



4h

Pyridinium chlorochromate (2.26 g, 10.5 mmol) and silica gel 60 (2.26 g) was mixed and ground using a pestle and mortar, then placed in 100 mL flask together with 20 mL dichloromethane. The suspension was stirred for 10 min. A solution of commercially available cyclododecanol (1.29 g, 7.0 mmol; dissolved in 20 mL dichloromethane) was added dropwise at room temperature, then continue to stir for 5 h. Reaction mixture was filtered through Celite and rinsed with dichloromethane. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane/ ethyl acetate = 10 / 1 to 5 / 1) to afford **4h** (1.24 g, 97%) as a white solid. The spectroscopic data were identical to those prepared from azidocyclododecane **3h**.

1-Methylcyclododecan-1-ol (5i-A)



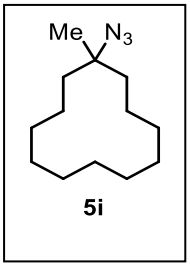
5i-A

To a stirred solution of methylmagnesium iodide (0.89 M in diethyl ether, 6.7 mL, 6.0 mmol) was added cyclododecanone **4h** (729.2 mg, 4.0 mmol) dissolved in diethyl ether (5 mL) at 0 °C under nitrogen. After addition was over, the mixture was then warmed up to room temperature and stirred for additional 4 h. The reaction was stopped with 1 M HCl aqueous solution. Then, the mixture was extracted with ethyl acetate to wash with 1 M HCl aqueous solution and brine. The organic layer was dried over sodium sulfate. The crude material obtained by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl

acetate = 20 / 1 to 10 / 1) to afford **5i-A** (666.7 mg, 84%) as a white solid. The analytical data were in good agreement with the literature.[35]

White solid; R_f value 0.40 (hexane / ethyl acetate = 4 / 1); m.p. 87.5–88.7 °C; IR (KBr, disc) ν_{max} 3300, 2943, 2900, 2862, 2846, 1471, 1444, 1367, 1224, 1166, 1092 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.58–1.53 (m, 2H), 1.44–1.26 (m, 20H), 1.24 (s, 1H), 1.17 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 73.7, 36.1, 29.0, 26.4, 26.0, 22.5, 22.0, 19.9; LRMS (EI, M = $C_{13}H_{26}O$) *m/z* 198 (M^+, 22%), 183 (34), 138 (16), 96 (16), 71 (100), 59 (29), 58 (63); HRMS (EI) calcd for $C_{13}H_{26}O$ (M^+) 198.1984, found 198.1989.

1-Azido-1-methylcyclododecane (5i)

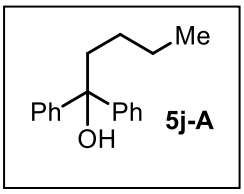


5i

The azidation reaction of the *tert*-alcohols was performed by the Moran's method.[32] To a stirred solution of 1-methylcyclododecan-1-ol **5i-A** (219 mg, 1.10 mmol) in nitromethane (0.55 mL, 2 M) at room temperature was added dropwise azidotrimethylsilane (438 μL, 3.30 mmol), and then, tris(pentafluorophenyl)borane (28.2 mg, 0.055 mmol, 5 mol%) was added. The mixture was stirred for 4 h. After removal of volatile components, the crude material was purified by silica gel column chromatography (hexane as eluent) to afford **5i** (170 mg, 69%) as a colorless oil.

Colorless oil; R_f value 0.44 (hexane); IR (NaCl, neat) ν_{max} 2935, 2854, 2095, 1471, 1444, 1379, 1252, 1162, 1077 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.63–1.57 (m, 2H), 1.48–1.34 (m, 20H), 1.24 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 64.8, 33.5, 26.2, 25.9, 25.2, 22.5, 22.0, 19.6; LRMS (EI, M = $C_{13}H_{25}N_3$) *m/z* 223 (M^+, 0.07%), 211 (31), 152 (29), 124 (21), 111 (50), 110 (31), 97 (68), 96 (34), 84 (30), 83 (71), 55 (100); HRMS (EI) calcd for $C_{13}H_{25}N_3$ (M^+) 223.2048, found 223.2053.

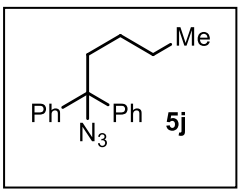
1,1-Diphenylpentan-1-ol (5j-A)



Addition reaction was performed according to literature with small modification.[36] To a stirred solution of *n*-butyllithium (1.6 M in hexane, 3 mL, 4.8 mmol) at room temperature under nitrogen, was added commercially available benzophenone (729 mg, 4.0 mmol) dissolved in 12 mL of tetrahydrofuran / diethyl ether / hexane (4 / 1 / 1) dropwise over 10 min. After 10 h, the reaction was stopped with 1 M HCl aqueous solution. Then, it was extracted with ethyl acetate to wash with 1 M HCl aqueous solution. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 50 / 1 to 16 / 1) to afford **5j-A** (424 mg, 44%) as a colorless oil.

Colorless oil; R_f value 0.40 (hexane / ethyl acetate = 10 / 1); IR (NaCl, neat) ν_{max} 3458, 3060, 2954, 2870, 1495, 1448, 1220, 771, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43–7.40 (m, 4H), 7.33–7.29 (m, 4H), 7.24–7.21 (m, 2H), 2.30–2.26 (m, 2H), 2.11 (s, 1H), 1.39–1.31 (m, 2H), 1.29–1.23 (m, 2H), 0.88 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 128.1, 126.7, 126.0, 78.2, 41.7, 25.9, 23.1, 14.1; LRMS (EI, M = $C_{17}H_{20}O$) *m/z* 240 (M^+, 0.1%), 183 (100), 105 (39), 77 (16); HRMS (EI) calcd for $C_{17}H_{20}O$ (M^+) 240.1514, found 240.1517.

(1-Azidopentane-1,1-diyl)dibenzene (5j)

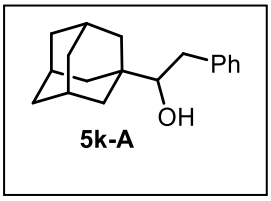


The azidation reaction of the *tert*-alcohols was performed by the Moran's method.[32] To a stirred solution of 1,1-diphenylpentan-1-ol **5j-A** (169 mg, 0.70 mmol) in nitromethane (350 μL, 2 M) at room temperature was added dropwise azidotrimethylsilane (279 μL, 2.10 mmol), and finally was added tris(pentafluorophenyl)borane (17.9 mg, 0.035 mmol, 5 mol%). The mixture was stirred for 40 min. After removal of volatile components, the crude material was purified by silica gel column

chromatography (hexane as eluent) and then further purified by gel permeation chromatography (chloroform as eluent) to afford **5j** (138 mg, 74%) as a colorless oil. The analytical data were in good agreement with the literature.[37]

Colorless oil; R_f value 0.40 (hexane); IR (NaCl, neat) ν_{max} 3063, 3029, 2954, 2873, 2099, 1495, 1444, 1255 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29–7.23 (m, 8H), 7.22–7.19 (m, 2H), 2.34–2.31 (m, 2H), 1.28 (tt, 2H, *J* = 7.5, 7.5 Hz), 1.16–1.09 (m, 2H), 0.81 (t, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 128.2, 127.3, 127.0, 72.6, 38.5, 26.2, 22.9, 14.0; LRMS (EI, M = $C_{17}H_{19}N_3$) *m/z* 265 (M^+, 0.1%), 223 (15), 193 (14), 181 (17), 180 (100), 91 (21), 77 (32); HRMS (EI) calcd for $C_{17}H_{19}N_3$ (M^+) 265.1579, found 265.1574.

1-(Adamantan-1-yl)-2-phenylethan-1-ol (5k-A)



5k-A

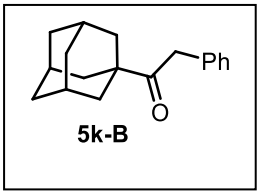
Pyridinium chlorochromate (3.88 g, 18 mmol) and silica gel 60 (3.88 g) was mixed and ground using a pestle and mortar, then placed in 100 mL flask together with 30 mL dichloromethane. The suspension was stirred for 10 min. A solution of commercially available 1-adamantanemethanol (2.49 g, 15 mmol; dissolved in 30 mL dichloromethane) was added dropwise at room temperature, then continue to stir for 6 h. Reaction mixture was filtered through Celite No. 503 and rinsed with dichloromethane. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane/ ethyl acetate = 10 / 1) to afford adamantane-1-carbaldehyde **2d** (2.36 g, 96%) as a white solid. The analytical data of this aldehyde are identical to those obtained from traceless Schmidt reaction.

To a stirred solution of benzylmagnesium chloride (2 M in tetrahydrofuran, 6.5 mL, 13 mmol) at 0 °C under nitrogen, was added dropwise adamantane-1-carbaldehyde solution **2d** (1.64 g, 10 mmol, dissolved in 20 mL tetrahydrofuran) over 10 min. After stirred for 3 h at this temperature, the mixture was then warmed up to room temperature and stirred for additional 6

h. The reaction was stopped with 1 M HCl aqueous solution. Then, it was extracted with ethyl acetate to wash with 1 M HCl aqueous solution, water, and brine. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 20 / 1 to 10 / 1) to afford **5k-A** (1.66 g, 65%) as a white solid.

White solid; R_f value 0.38 (hexane / ethyl acetate = 10 / 1); m.p. 118–119 °C; IR (KBr, disc) ν_{max} 3423, 3025, 2904, 2846, 1495, 1448, 1054, 1000 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.30 (m, 2H), 7.24–7.21 (m, 3H), 3.28–3.25 (ddd, 1H, *J* = 10.5, 5.0, 2.0 Hz), 2.91 (dd, 1H, *J* = 13.5, 2.0 Hz), 2.48 (dd, 1H, *J* = 13.5, 11.0 Hz), 2.04 (br-s, 3H), 1.77–1.62 (m, 12H), 1.37 (d, 1H, *J* = 4.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 129.4, 128.5, 126.2, 80.8, 38.1, 37.3, 36.9, 36.6, 28.4; LRMS (EI, M = $C_{18}H_{24}O$) *m/z* 256 (M^+, 1%), 165 (37), 135 (25), 93 (16), 92 (100); HRMS (EI) calcd for $C_{18}H_{24}O$ (M^+) 256.1827, found 256.1824.

1-(Adamantan-1-yl)-2-phenylethan-1-one (5k-B)



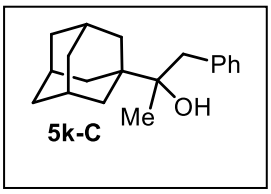
5k-B

Pyridinium chlorochromate (1.58 g, 7.31 mmol) and silica gel (1.58 g) was mixed and ground using a pestle and mortar, then placed in 50 mL flask together with 12.2 mL dichloromethane. The suspension was stirred for 10 min. A solution of 1-(adamantan-1-yl)-2-phenylethan-1-ol **5k-A** (1.56 g, 6.09 mmol; dissolved in 12.2 mL dichloromethane) was added dropwise at room temperature, then continue to stir for 5 h. Reaction mixture was filtered through Celite and rinsed with dichloromethane. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane/ ethyl acetate = 40 / 1 to 10 / 1) to afford **5k-B** (1.36 g, 88%) as a white solid. The analytical data were in good agreement with the literature.[38]

White solid; R_f value 0.60 (hexane / ethyl acetate = 5 / 1); m.p. 68–69 °C; IR (KBr, disc) ν_{max} 3025, 2904, 2850, 1696, 1452, 1344, 1162, 1015 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–

7.29 (m, 2H), 7.24–7.21 (m, 1H), 7.17–7.15 (d, 2H, *J* = 7.0 Hz), 3.77 (s, 2H), 2.06 (br-s, 3H), 1.87 (br-d, 6H, *J* = 2.5 Hz), 1.76 (d, 3H, *J* = 13.0 Hz), 1.70 (d, 3H, *J* = 13.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.5, 134.9, 129.6, 128.4, 126.5, 46.9, 42.8, 38.2, 36.5, 27.9; LRMS (EI, M = $C_{18}H_{22}O$) *m/z* 254 (M^+, 1%), 163 (14), 136 (11), 135 (100), 91 (11); HRMS (EI) calcd for $C_{18}H_{22}O$ (M^+) 254.1671, found 254.1671.

2-(Adamantan-1-yl)-1-phenylpropan-2-ol (5k-C)

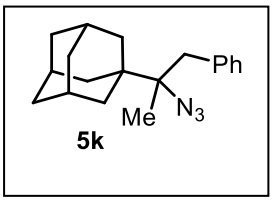


5k-C

To a stirred solution of methylmagnesium iodide (0.89 M in diethyl ether, 5.6 mL, 5.0 mmol) at 0 °C under nitrogen, was added dropwise solution of 1-(adamantan-1-yl)-2-phenylethan-1-one **5k-B** (254 mg, 1.0 mmol, dissolved in 4 mL diethyl ether). After 6 h, the reaction was stopped with 1 M HCl aqueous solution. Then, it was extracted with ethyl acetate to wash with 1 M HCl aqueous solution and brine. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 35 / 1 to 20 / 1) to afford **5k-C** (193 mg, 71%) as a white solid. The analytical data were in good agreement with the literature.[39]

White solid; R_f value 0.56 (hexane / ethyl acetate = 5 / 1); m.p. 95–96 °C; IR (KBr, disc) ν_{max} 3489, 3029, 2904, 2846, 1491, 1452, 1352, 1123, 1096 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.29 (m, 2H), 7.25–7.20 (m, 3H), 2.93 (d, 1H, *J* = 12.5 Hz), 2.57 (d, 1H, *J* = 13.5 Hz), 2.06 (br-s, 3H), 1.77 (br-d, 6H, *J* = 1.5 Hz), 1.76 (d, 3H, *J* = 12.5 Hz), 1.68 (d, 3H, *J* = 11.5 Hz), 1.07 (s, 1H), 0.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.6, 131.1, 128.0, 126.1, 75.6, 41.0, 39.2, 37.2, 36.3, 28.7, 20.7; HRMS (CI) calcd for $C_{19}H_{25}O$ $[M-H]^+$ 269.1905, found 269.1902.

1-(2-Azido-1-phenylpropan-2-yl)adamantane (5k)

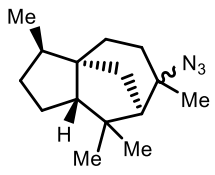


5k

The azidation reaction of the *tert*-alcohols was performed by the Moran's method.[32] To a stirred solution of 2-(adamantan-1-yl)-1-phenylpropan-2-ol **5k-C** (246 mg, 0.91 mmol) in nitromethane (455 μL, 2 M) at room temperature was added dropwise azidotrimethylsilane (362 μL, 2.73 mmol), and finally was added tris(pentafluorophenyl)borane (23.3 mg, 0.0455 mmol, 5 mol%). The mixture was stirred for 3 h. After removal of volatile components, the crude material was purified by silica gel column chromatography (hexane as eluent) and then further purified by gel permeation chromatography (chloroform as eluent) to afford **5k** (179 mg, 67%) as a white solid.

White solid; R_f value 0.40 (hexane); m.p. 97–98 °C; IR (KBr, disc) ν_{max} 2978, 2908, 2854, 2103, 1452, 1286, 1259 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.29 (m, 2H), 7.27–7.22 (m, 3H), 2.93 (d, 1H, *J* = 13.5 Hz), 2.57 (d, 1H, *J* = 13.5 Hz), 2.06 (br-s, 3H), 1.78–1.65 (m, 12H), 1.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 131.0, 128.0, 126.5, 69.5, 40.5, 40.1, 37.0, 36.6, 28.6, 15.8; HRMS (CI) calcd for $C_{19}H_{25}N$ $[M-N_2]^+$ 267.1987, found 267.1983.

Cedryl azide (5l)



5l
(1 : 1 diastereomeric mixture)

The azidation reaction of the *tert*-alcohols was performed by the Moran's method.[32] To a stirred solution of commercially available cedrol (445 mg, 2.0 mmol) in nitromethane (1 mL, 2 M) at room temperature was added dropwise azidotrimethylsilane (0.8 mL, 6.0 mmol), and finally was added tris(pentafluorophenyl)borane (51.2 mg, 0.10 mmol, 5 mol%). The mixture was stirred for 6 h. After removal of volatile components, the crude material was purified by silica gel column chromatography (hexane as eluent) and then further purified by gel permeation chromatography (chloroform as eluent) to afford an inseparable 1:1 diastereomeric mixture of

5l (192 mg, 39%) as a colorless oil. The following analytical data were collected as a 1:1 mixture.

Colorless oil; R_f value 0.60 (hexane); $[\alpha]_D^{21} = +21.4$ (c = 1.0, $CHCl_3$); IR (KBr, disc) ν_{max} 2958, 2099, 1460, 1379, 1259 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.91–1.48 (m, 18H), 1.46–1.24 (m, 16H), 1.16 (s, 4H), 1.03 (s, 3H), 1.00 (s, 3H), 0.85 (d, 3H, *J* = 1.0 Hz), 0.84 (d, 3H, *J* = 2.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 67.0, 64.9, 58.4, 57.4, 57.0, 56.3, 54.0, 53.3, 43.5, 42.8, 41.7, 41.5, 40.94, 40.89, 36.9, 31.9, 31.8, 30.8, 30.6, 29.1, 28.6, 28.1, 26.6, 26.24, 26.17, 25.38, 25.29, 15.5, 15.4; LRMS (EI, M = $C_{15}H_{25}N_3$) *m/z* 247 (M^+, 0.25%), 205 (100), 204 (57), 149 (34), 135 (34), 121 (57), 119 (35), 109 (33), 107 (44), 95 (44), 93 (44); HRMS (EI) calcd for $C_{15}H_{25}N_3$ (M^+) 247.2048, found 247.2042.

3.7.2 General Procedure for Tertiary Alkyl Azides

The tertiary alkyl azide **5** (0.20 mmol) and dimethyl sulfoxide (DMSO, 28 μL, 0.40 mmol, 2 equiv) were dissolved in *tert*-butylbenzene (1 mL, 0.2 M), and the mixture was stirred at room temperature under nitrogen atmosphere. Then, distilled trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol, 2 equiv) was added to the mixture dropwise over 1 min, which subsequently generated suspension and then a light-yellow / brown oil layer at the bottom of the flask. The stirred mixture was warmed up to 50 °C. Upon completion of the reaction, the mixture was cooled down to 0 °C.

General Procedure for hydrolysis after the traceless Schmidt reaction

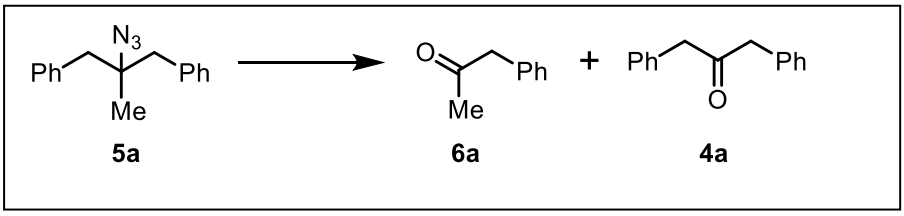
The reaction was stopped by addition of saturated sodium bicarbonate aqueous solution. The mixture was then extracted with ethyl acetate and washed with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. The crude material was obtained by removing the organic solvent *in vacuo*, and then analyzed

by ^{1}H NMR to measure NMR yields before the purification. 1,1,2,2-Tetrachloroethane (21 μL, 0.20 mmol, 1 equiv, 5.96 ppm on ^{1}H NMR, 2H) was used as an internal standard. After that, the crude material was purified by column chromatography using neutral silica gel to afford the corresponding ketones **6**, **4a**, or lactam **6h**.

General Procedure for one-pot reductive amination after the traceless Schmidt reaction

To the cooled reaction mixture, sodium borohydride (75.7 mg, 2.0 mmol) and glacial acetic acid (0.6 mL, 10.0 mmol, dropwise addition) were added successively. The method of reaction quench and the extraction is noted in each reaction section. The obtained crude material analyzed by ^{1}H NMR to measure NMR yields before the purification. 1,1,2,2-Tetrachloroethane (21 μL, 0.20 mmol, 1 equiv, 5.96 ppm on ^{1}H NMR, 2H) was used as an internal standard. The crude material was purified by column chromatography neutral silica gel pre-treated with 1% triethylamine in an eluent of alumina to afford the corresponding amine **7**.

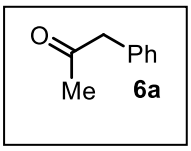
Traceless Schmidt reaction of 5a followed by hydrolysis



The reaction was performed with (2-Azido-2-methylpropane-1,3-diyl)dibenzene **5a** (50.3 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 4 h. The reaction was quenched with saturated sodium bicarbonate aqueous solution at 0 °C. The mixture was extracted with ethyl acetate to wash with saturated sodium bicarbonate aqueous solution, water and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel chromatography (hexane / ethyl acetate = 80 / 1 to 30 / 1) and recycling gel permeation chromatography for further purification

(chloroform as a mobile phase) gave **6aa** (70% yield on ^{1}H NMR before purification, 17.9 mg, 67% isolated yield) as a light-yellow oil and **4a** (5% yield on ^{1}H NMR before purification, 1.3 mg, 3% isolated yield).

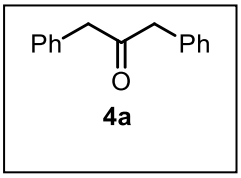
1-Phenylpropan-2-one (6a)



The analytical data were in good agreement with the literature.[40]

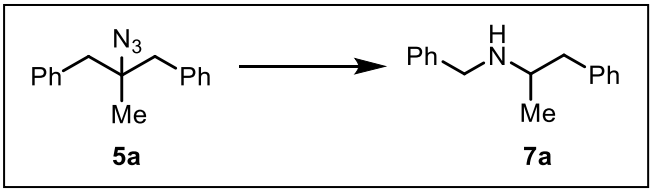
Light-yellow oil; R_f value 0.30 (hexane / ethyl acetate = 6 / 1); IR (NaCl, neat) ν_{max} 3033, 2924, 2854, 1713, 1499, 1452, 1357, 1224, 1154 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.33 (m, 2H), 7.29–7.27 (m, 1H), 7.22–7.20 (m, 2H), 3.70 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.5, 134.2, 129.4, 128.8, 127.1, 51.0, 29.3; LRMS (EI, M = $C_9H_{10}O$) *m/z* 134 (M^+, 35%), 92 (28), 91 (100), 86 (26), 84 (40), 65 (17); HRMS (EI) calcd for $C_9H_{10}O$ (M^+) 134.0732, found 134.0731.

1,3-Diphenylpropan-2-one (4a)



The spectra are shown in the section of secondary alkyl azides.

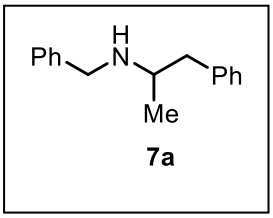
Traceless Schmidt reaction of 5a followed by reductive amination



The reaction was performed with **5a** (50.3 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 4 h. Then, to the stirred mixture cooled at 0 °C, sodium borohydride (75.7 mg, 2.0 mmol) and glacial acetic acid (0.6 mL, 10.0 mmol) were added successively. After 2 h, the reaction was quenched with

saturated sodium bicarbonate aqueous solution. The mixture was extracted with ethyl acetate to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel chromatography (hexane / ethyl acetate = 30 / 1 to 5 / 1 with 1% triethylamine) gave **7a** (90% yield on ^{1}H NMR before purification, 39.7 mg, 88% isolated yield) as a light-yellow oil.

***N*-Benzyl-1-phenylpropan-2-amine (7a)**

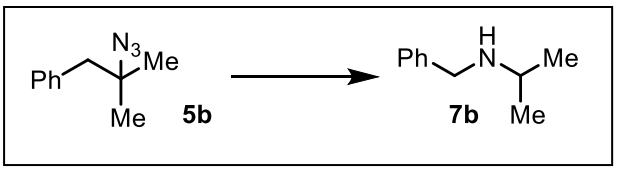


7a

The analytical data were in good agreement with the literature.[41]

Light-yellow oil; R_f value 0.20 (hexane / ethyl acetate = 1 / 2); IR (NaCl, neat) ν_{max} 3319, 3063, 3025, 2966, 2927, 2850, 1604, 1495, 1452, 1371, 1344, 1220, 1143 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.26 (m, 4H), 7.24–7.20 (m, 4H), 7.17–7.16 (m, 2H), 3.86 (d, 1H, *J* = 13.5 Hz), 3.74 (d, 1H, *J* = 13.5 Hz), 2.95 (qt, 1H, *J* = 6.0, 6.0 Hz), 2.78 (dd, 1H, *J* = 13.5, 7.0 Hz), 2.65 (dd, 1H, *J* = 13.5, 6.0 Hz), 1.10 (d, 3H, *J* = 6.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.3, 129.3, 128.4, 128.0, 126.8, 126.2, 53.7, 51.2, 43.5, 20.1; HRMS (CI) calcd for $C_{16}H_{20}N$ $[M+H]^+$ 226.1596, found 226.1599.

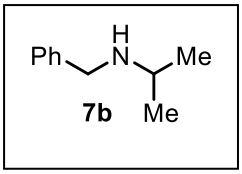
Traceless Schmidt reaction of 5b followed by reductive amination



The reaction was performed with (2-Azido-2-methylpropyl)benzene **5b** (35.1 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M), at 50 °C for 1 h. After cooling the mixture down to 0 °C, sodium borohydride (75.7 mg, 2.0 mmol) and glacial acetic acid (0.6 mL, 10.0 mmol) were added successively. The mixture was warmed up to room temperature and was stirred for an additional 2 h. Then, the reaction was quenched with water at 0 °C. The mixture was extracted with dichloromethane to wash with sodium

bicarbonate, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel chromatography (hexane / ethyl acetate = 20 / 1 to 1 / 20 with 1% triethylamine) gave **7b** (38% yield on ^{1}H NMR before purification, 10.1 mg, 34%) as a light-yellow oil.

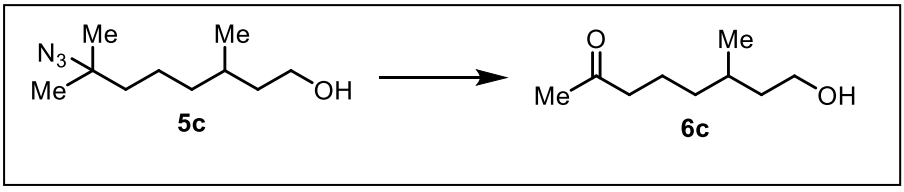
_N_-Benzylpropan-2-amine (7b)



The analytical data were in good agreement with the literature.[42]

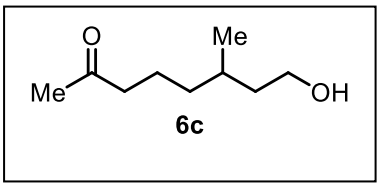
Light-yellow oil; R_f value 0.20 (ethyl acetate); IR (NaCl, neat) ν_{max} 3029, 2961, 2866, 1460, 1279, 1245, 1163, 1030, 787, 759 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.32 (m, 4H), 7.25–7.23 (m, 1H), 3.78 (s, 2H), 2.86 (heptet, 1H, *J* = 5.5 Hz), 1.10 (d, 6H, *J* = 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 128.4, 128.1, 126.8, 51.6, 48.1, 22.9; HRMS (CI) calcd for $C_{10}H_{16}N$ $[M+H]^+$ 150.1283, found 150.1279.

Traceless Schmidt reaction of 5c followed by hydrolysis



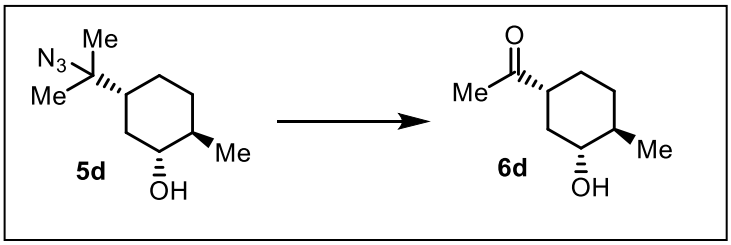
The reaction was performed with 7-Azido-3,7-dimethyloctan-1-ol **5c** (39.9 mg, 0.20 mmol), DMSO (36 μL, 0.50 mmol), and trifluoromethanesulfonic anhydride (82 μL, 0.50 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 1.5 h. The reaction was quenched with saturated sodium bicarbonate aqueous solution at 0 °C. The mixture was extracted with dichloromethane / methanol = 9 / 1 to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel chromatography (dichloromethane / methanol = 60 / 1 to 10 / 1) gave **6c** (46% yield on ^{1}H NMR before purification, 14.1 mg, 45% isolated yield) as a light-yellow oil.

8-Hydroxy-6-methyloctan-2-one (6c)



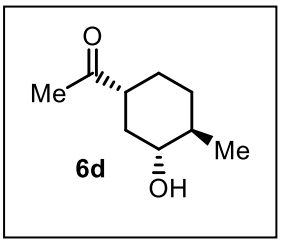
Light-yellow oil; R_f value 0.60 (dichloromethane / methanol = 6 / 1); IR (NaCl, neat) ν_{max} 3404, 2931, 2870, 1708, 1460, 1414, 1360, 1220, 1166, 1058, 771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.67 (m, 2H), 2.42 (t, 1H, *J* = 7.0 Hz), 2.41 (t, 1H, *J* = 7.0 Hz), 2.13 (s, 3H), 1.64–1.50 (m, 5H), 1.42–1.25 (m, 2H), 1.18–1.08 (m, 1H), 0.90 (d, 3H, *J* = 6.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.3, 61.0, 43.9, 39.7, 36.4, 29.9, 29.3, 21.1, 19.4; HRMS (CI) calcd for $C_9H_{19}O_2$ $[M+H]^+$ 159.1385, found 159.1385.

Traceless Schmidt reaction of 5d followed by hydrolysis



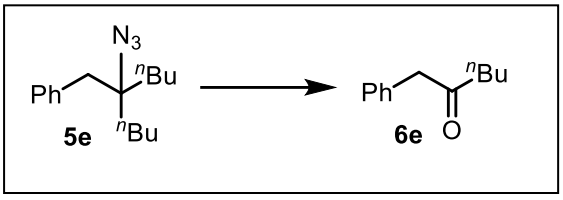
The reaction was performed with (-)-(1*R*,2*R*,5*R*)-5-(2-azidopropan-2-yl)-2-methylcyclohexan-1-ol **5d** (39.5 mg, 0.20 mmol), DMSO (36 μL, 0.50 mmol), and trifluoromethanesulfonic anhydride (82 μL, 0.50 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 2.5 h. After cooling down to 0 °C, the reaction was quenched with water, and the mixture was extracted with dichloromethane / methanol = 9 / 1 to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel chromatography (dichloromethane / methanol = 100 / 1 to 50 / 1) gave **6d** (56% yield on ^1H NMR before purification, 17.2 mg, 55% isolated yield) as a light-yellow solid.

1-((1*R*,3*R*,4*R*)-3-Hydroxy-4-methylcyclohexyl)ethan-1-one (6d)



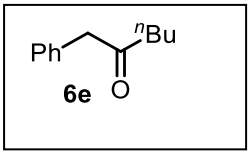
Light-yellow solid; R_f value 0.70 (dichloromethane / methanol = 4 / 1); m.p. 41.5–42.4 °C, $[\alpha]_D^{24} = -22.8$ (c = 0.1, $CHCl_3$); IR (NaCl, neat) ν_{max} 3433, 2931, 1697, 1644, 1456, 1356, 1220, 1050 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.20 (ddd, 1H, *J* = 11.0, 9.5, 4.5 Hz), 2.43 (tt, 1H, *J* = 12.0, 3.0 Hz), 2.17–2.12 (m, 1H), 2.15 (s, 3H), 1.88–1.79 (m, 2H), 1.37–1.25 (m, 3H), 1.11–1.05 (m, 1H), 1.03 (d, 3H, *J* = 6.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 75.6, 50.4, 39.7, 36.8, 32.5, 27.9, 27.7, 18.1; LRMS (EI, M = $C_9H_{16}O_2$) *m/z* 156 (M^+, 12%), 138 (25), 113 (36), 95 (100), 86 (21), 84 (33), 81 (58), 71 (22), 55 (26); HRMS (EI) calcd for $C_9H_{16}O_2$ (M^+) 156.1150, found 156.11557.

Traceless Schmidt reaction of 5e followed by hydrolysis



The reaction was performed with (2-Azido-2-butylhexyl)benzene **5e** (51.9 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 4 h. The reaction was quenched at 0 °C with water, and the mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel chromatography (hexane / ethyl acetate = 100 / 1) gave **6e** (38% yield on ^1H NMR before purification, 13.2 mg, 37% isolated yield) as a light-yellow oil.

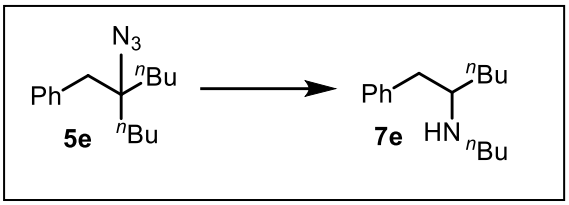
1-Phenylhexan-2-one (6e)



The analytical data were in good agreement with the literature.[43]

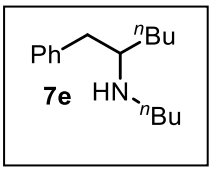
Light-yellow oil; R_f value 0.45 (hexane / ethyl acetate = 10 / 1); IR (NaCl, neat) ν_{max} 3030, 2958, 2931, 2873, 1712, 1495, 1456 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.31 (m, 2H), 7.28–7.25 (m, 1H), 7.21–7.20 (m, 2H), 3.68 (s, 2H), 2.44 (t, 2H, *J* = 7.5 Hz), 1.56–1.50 (tt, 2H, *J* = 7.5, 7.5 Hz), 1.26 (qt, 2H, *J* = 7.5 Hz), 0.86 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.7, 134.4, 129.4, 128.7, 126.9, 50.1, 41.7, 25.8, 22.2, 13.8; LRMS (EI, M = $C_{12}H_{16}O$) *m/z* 176 (M^+, 7%), 91 (42), 85 (100), 65 (51), 57 (94); HRMS (EI) calcd for $C_{12}H_{16}O$ (M^+) 176.1201, found 176.1202.

Traceless Schmidt reaction of 5e followed by reductive amination



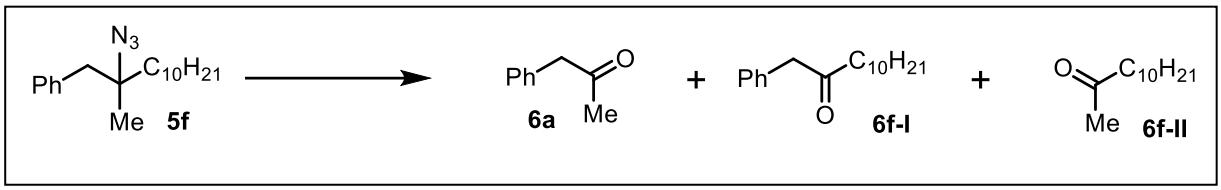
The reaction was performed with (2-Azido-2-butylhexyl)benzene (51.9 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 4 h. To perform reduction reaction, the reaction mixture was cooled down to 0 °C and then was treated with sodium borohydride (75.7 mg, 2.0 mmol), followed by dropwise addition of glacial acetic acid (0.6 mL, 10.0 mmol). After 2.5 h, the reaction was quenched with saturated sodium bicarbonate aqueous solution, and the mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed neutral silica gel chromatography silica gel column chromatography (hexane / ethyl acetate = 10 / 1 to 1 / 1 with 1% triethylamine) gave **7e** (35% yield on ^1H NMR before purification, 14.9 mg, 32% isolated yield) as a light-yellow oil.

***N*-Butyl-1-phenylhexan-2-amine (7e)**



Light-yellow oil; R_f value 0.30 (ethyl acetate); IR (NaCl, neat) ν_{max} 3338, 3029, 2958, 2928, 2862, 1495, 1455, 1375, 1131 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31–7.28 (m, 2H), 7.22–7.17 (m, 3H), 2.74–2.69 (m, 2H), 2.66–2.58 (m, 2H), 2.53–2.48 (m, 1H), 1.46–1.21 (m, 11H), 0.89 (t, 3H), 0.86 (t, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 129.2, 128.3, 126.0, 59.3, 46.9, 40.7, 33.5, 32.4, 28.0, 23.0, 20.4, 14.1, 14.0; HRMS (CI) calcd for $C_{16}H_{28}N$ $[M+H]^+$ 234.2222, found 234.2221.

Traceless Schmidt reaction of 5f followed by hydrolysis

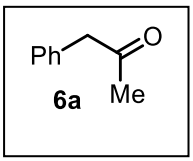


The reaction was performed with (2-Azido-2-methyldodecyl)benzene **5f** (60.3 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 2.5 h. The reaction was quenched at 0 °C with water, and the mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate and was concentrated *in vacuo* to obtain crude material. The mixture was purified by neutral silica gel column chromatography (hexane / ethyl acetate = 100 / 1 to 10 / 1) to afford **6a** (8.1 mg, 30% isolated yield) as a light-yellow oil and an inseparable mixture of **6fa** and **6fb** as a yellow oil (12.4 mg, **6fa** : **6fb** = 1 : 2.7 on ^1H NMR, 7% for **6fa** and 19% for **6fb**, respectively).

To obtain the analytical data, the inseparable mixture from two reaction trials were combined and then further purified by gel permeation chromatography (chloroform as an eluent) to give

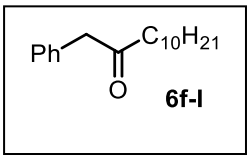
pure **6fb** as a light-yellow oil. Unfortunately, **6fa** was not found after this process. Thus, the yields of **6fa** and **6fb** were measure on ^{1}H NMR as a mixture.

1-Phenylpropan-2-one (6a)



The spectra are shown in the reaction of **5a**.

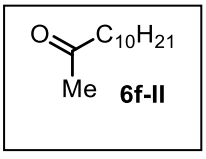
1-Phenyldodecan-2-one (6f-I)



The analytical data were in good agreement with the literature.[44]

Light-yellow oil; R_f value 0.52 (hexane / ethyl acetate = 6 / 1); IR (KBr, disc) ν_{max} 2924, 2854, 1715, 1495, 1456 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.33 (m, 2H), 7.28–7.24 (m, 1H), 7.21–7.19 (m, 2H), 3.67 (s, 2H), 2.43 (t, 2H, *J* = 7.5 Hz), 1.56–1.53 (m, 2H), 1.30–1.23 (m, 14H), 0.88 (t, 3H, *J* = 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.6, 134.4, 129.4, 128.7, 126.9, 50.1, 42.0, 31.9, 29.5, 29.4, 29.34, 29.27, 29.1, 23.7, 22.7, 14.1; LRMS (EI, M = $C_{18}H_{28}O$) *m/z* 260 (M^+, 2%), 169 (100), 105 (21), 91 (38), 85 (24); HRMS (EI) calcd for $C_{18}H_{28}O$ (M^+) 260.2140, found 260.2133.

Dodecan-2-one (6f-II)

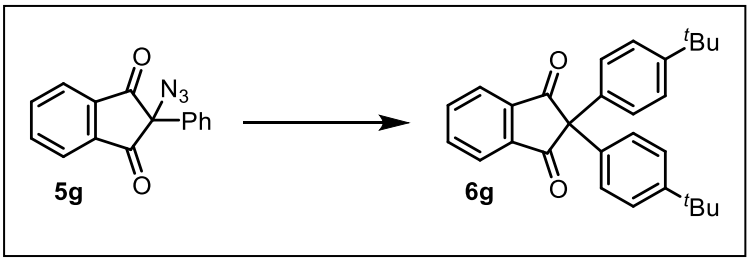


Analytical data are shown as a mixture with 1-phenyldodecan-2-one **6f-I**. The presence was identified by HRMS, and ^{1}H and ^{13}C NMR spectra were in good agreement with the commercially available authentic 2-dodecanone.

Yellow oil; R_f value 0.50 (hexane / ethyl acetate = 6 / 1); IR (NaCl, neat) ν_{max} 2927, 2854, 1719, 1468, 1410, 1360, 1162, 771 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, as a mixture with 1-phenyldodecan-2-one **6f-I**) δ 7.34–7.31 (m, 5.58H), 7.27–7.24 (m, 3.45H), 7.21–7.19 (m,

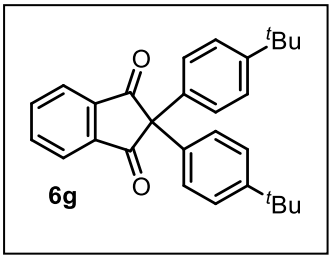
4.99H), 3.67 (s, 5.45H for Ph-C$\underline{H_2}$-COR of **6f-I**), 2.45–2.40 (m, 7.75H), 2.13 (s, 3H for Me of **6f-II**), 1.33–1.23 (m, 65.5H), 0.89–0.86 (m, 14.18H); ^{13}C NMR (126 MHz, $CDCl_3$, as a mixture with 1-phenyldodecan-2-one **6f-I**) δ 209.4 (**6f-II**), 208.7 (**6f-I**), 134.4 (**6f-I**), 129.4 (**6f-I**), 128.7 (**6f-I**), 126.9 (**6f-I**), 50.1 (**6f-I**), 43.8 (**6f-II**), 42.0 (**6f-I**), 31.9 (**6f-II**), 29.8 (**6f-II**), 29.55 (**6f-II**), 29.52 (**6f-I**), 29.46 (**6f-II**), 29.42 (**6f-I**), 29.39 (**6f-II**), 29.34 (**6f-I**), 29.29 (**6f-I** and **6f-II**), 29.18 (**6f-II**), 29.1 (**6f-I**), 23.9 (**6f-II**), 23.7 (**6f-I**), 22.7 (**6f-II**), 14.1 (**6f-II**); HRMS (EI) calcd for $C_{12}H_{24}O$ (M^+) 184.1827, found 184.1827.

Traceless Schmidt reaction of 5g followed by hydrolysis



The reaction was performed with 2-Azido-2-phenyl-1*H*-indene-1,3(2*H*)-dione **5g** (51.9 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 4 h. The reaction was quenched at 0 °C with water, and the mixture was extracted with ethyl acetate to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel chromatography (hexane / ethyl acetate = 40 / 1 to 1 / 1) to afford **6g** (15.2 mg, 19% isolated yield) as a yellow solid.

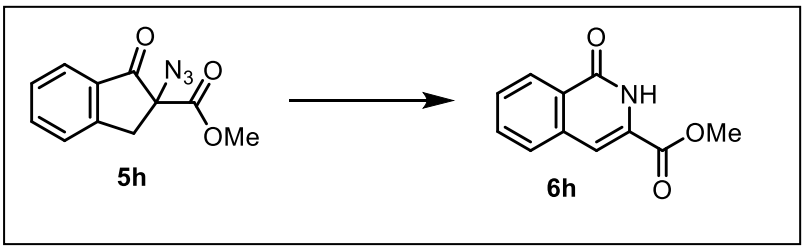
2,2-Bis(4-(*tert*-butyl)phenyl)-1*H*-indene-1,3(2*H*)-dione (6g)



Yellow solid; R_f value 0.64 (hexane / ethyl acetate = 2 / 1); m.p. 207–209 °C; IR (KBr, disc) ν_{max} 2958, 2870, 1708, 1507, 1255, 818 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08–8.07 (m, 2H), 7.89–7.87 (m, 2H) 7.32–7.30 (m, 4H) 7.21–7.19 (m, 4H), 1.27 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.2, 150.5, 141.7, 136.1, 135.0, 128.3, 125.6, 124.1, 67.0, 34.4,

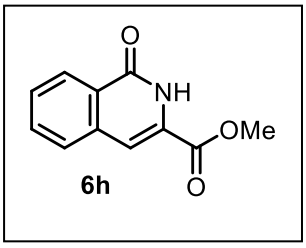
31.2; LRMS (EI, M = $C_{29}H_{30}O_2$) *m/z* 410 (M^+, 36%), 395 (33), 86 (58), 85 (66), 84 (92), 83 (100); HRMS (EI) calcd for $C_{29}H_{30}O_2$ (M^+) 410.2246, found 410.2249.

Traceless Schmidt reaction of 5h followed by hydrolysis



The reaction was performed with Methyl 2-azido-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate **5h** (46.2 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 17 h. Then, the reaction was quenched at 0 °C with water. The mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel chromatography (hexane / ethyl acetate = 30 / 1 to 1 / 1 with 1% triethylamine) gave **6h** (79% yield on ^{1}H NMR before purification, 31.2 mg, 77% isolated yield) as a white solid.

Methyl 1-oxo-1,2-dihydroisoquinoline-3-carboxylate (6h, CCDC No. 2083663)

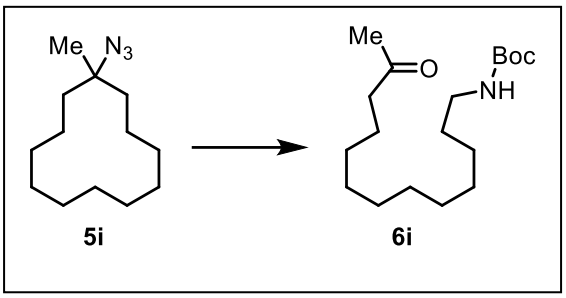


The analytical data were in good agreement with the literature.[4]

White solid; R_f value 0.50 (hexane / ethyl acetate = 1 / 2); m.p. 160.1–161.1 °C; IR (KBr, disc) ν_{max} 3169, 3060, 3012, 2953, 1730, 1663, 1604, 1468, 1435, 1305 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (s-br, 1H), 8.46 (d, 1H, *J* = 8.0 Hz), 7.74 (ddd, 1H, *J* = 8.0, 8.0, 1.0 Hz), 7.69 (d, 1H, *J* = 7.0 Hz), 7.64 (ddd, 1H, *J* = 8.0, 7.0, 1.0 Hz), 7.39 (s, 1H), 4.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 161.7, 135.9, 133.1, 129.4, 128.3, 128.2, 127.9, 127.6, 111.3, 53.2; LRMS (EI, M =

$C_{11}H_9NO_3$) *m/z* 203 (M^+, 100%), 145 (40), 144 (39), 143 (83), 115 (38), 89 (77); HRMS (EI) calcd for $C_{11}H_9NO_3$ (M^+) 203.0582, found 203.0576.

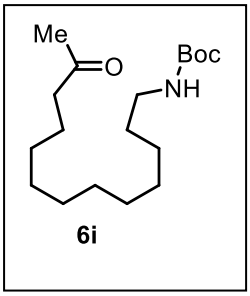
Traceless Schmidt reaction of 5i followed by hydrolysis and Boc protection



The reaction was performed with 1-azido-1-methylcyclododecane **5i** (44.7 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 ˚C for 1 h. Then, the reaction was quenched at 0 °C with saturated sodium bicarbonate aqueous solution. The mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. The concentration *in vacuo* gave crude material.

For the Boc protection, the obtained crude material was dissolved in dichloromethane (1 mL). To the stirred mixture, saturated sodium bicarbonate aqueous solution (0.2 mL) and di-*tert*-butyl dicarbonate (175 mg, 0.80 mmol) were then added successively at room temperature. The resulting mixture was stirred for 22 h at the same temperature. Then, the mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water and brine. The collected organic layer was dried over sodium sulfate. The concentration of the organic component *in vacuo* followed by neutral silica gel column chromatography (dichloromethane / methanol = 80 / 1 to 60 / 1) gave **6i** (50% yield on ^{1}H NMR before purification, 27.6 mg, 44% isolated yield) as a light-yellow solid.

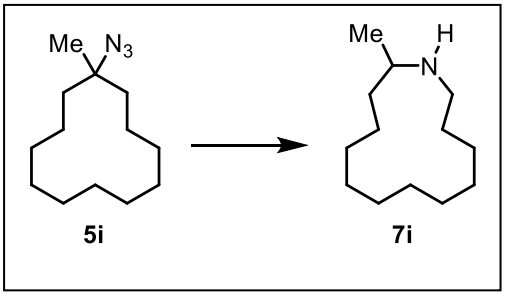
***tert*-Butyl (12-oxotridecyl)carbamate (6i)**



6i

Light yellow solid; R_f value 0.60 (dichloromethane / methanol = 15 / 1); m.p. 42–43 °C; IR (KBr, disc) ν_{max} 3362, 2926, 2854, 1712, 1521, 1456, 1390, 1364, 1250, 1173 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.50 (s, 1H), 3.10 (q, 2H, *J* = 7.0, 7.0 Hz), 2.42 (t, 2H, *J* = 7.5 Hz), 2.14 (s, 3H), 1.57–1.54 (m, 2H), 1.44 (s, 9H), 1.26–1.25 (br-m, 16H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.6, 155.9, 79.0, 43.8, 40.6, 30.0, 29.9, 29.50, 29.47, 29.39, 29.37, 29.26, 29.1, 28.4, 26.8, 23.8; HRMS (CI) calcd for $C_{18}H_{36}NO_3$ $[M+H]^+$ 314.2695, found 314.2689.

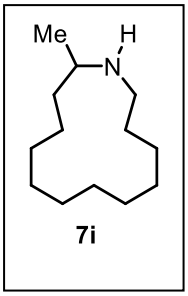
Traceless Schmidt reaction of 5i followed by reductive amination



5i **7i**

The reaction was performed with 1-Azido-1-methylcyclododecane (44.7 mg, 0.20 mmol) **5i**, DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 1 h. To perform reduction reaction, the reaction mixture was cooled down to 0 °C and then was treated with sodium borohydride (75.7 mg, 2.0 mmol), followed by dropwise addition of glacial acetic acid (0.6 mL, 10.0 mmol). The mixture was warmed up to room temperature and was stirred for additional 5 h. Then, the reaction was quenched with water at 0 °C. The mixture was extracted with dichloromethane to wash with 4 M sodium hydroxide, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel chromatography (hexane / ethyl acetate = 50 / 1 to ethyl acetate with 1% triethylamine) gave **7i** (64% yield on ^1H NMR before purification, 19.6 mg, 50% isolated yield) as a light-yellow oil.

2-Methylazacyclotridecane (7i)

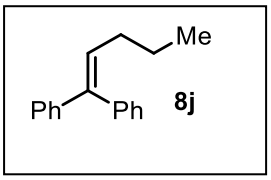


The analytical data were in good agreement with the literature.[45]

Light-yellow oil; R_f value 0.50 (dichloromethane / methanol = 6 / 1); IR (NaCl, neat) ν_{max} 3303, 2924, 2858, 1460, 1367, 1259, 1100, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.78 (ddd, 1H, *J* = 12.0, 5.5, 4.5 Hz), 2.66–2.63 (m, 1H), 2.52 (ddd, 1H, *J* = 12.0, 8.5, 4.0 Hz), 1.60–1.25 (m, 21H), 1.02 (d, 3H, *J* = 6.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 51.9, 45.4, 35.6, 28.1, 26.44, 26.36, 26.31, 25.6, 25.1, 24.9, 24.2, 23.4, 21.4; HRMS (CI) calcd for $C_{13}H_{28}N$ $[M+H]^+$ 198.2222, found 198.2221.

Unsuccessful Schmidt reactions (elimination) of the tertiary alkyl azides

Pent-1-ene-1,1-diyldibenzene (8j)

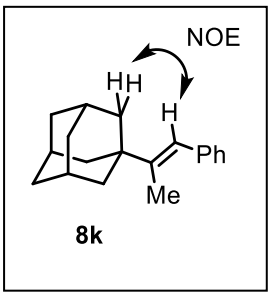


The reaction with (1-azidopentane-1,1-diyl)dibenzene **5j** (53.1 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at room temperature for 1.5 h, followed by concentration under vacuum line at 50 °C to remove *tert*-butylbenzene, purification by neutral silica gel column chromatography (hexane as eluent), and further purification by recycling GPC (chloroform as eluent), gave **8j** (87% yield from ^1H NMR before purification, 32.0 mg, 72% isolated yield) as a colorless oil. The analytical data were in good agreement with the literature.[46]

Colorless oil; R_f value 0.60 (hexane); IR (NaCl, neat) ν_{max} 3060, 3025, 2958, 2927, 2866, 1596, 1495, 1444, 1371, 1073, 895 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.18 (m, 10H), 6.09 (t, 1H, *J* = 7.5 Hz), 2.10 (dt, 2H, *J* = 7.5, 7.5 Hz), 1.47 (tq, 2H, *J* = 7.5, 7.5 Hz), 0.91 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 141.5, 140.3, 130.1, 130.0, 128.1, 128.0, 127.2,

126.8, 126.7, 31.8, 23.2, 13.9; LRMS (EI, M = $C_{17}H_{18}$) *m/z* 222 (M^+, 55%), 193 (100), 178 (27), 165 (20), 115 (64), 91 (24); HRMS (EI) calcd for $C_{17}H_{18}$ (M^+) 222.1409, found 222.1404.

1-((*E*)-1-Phenylprop-1-en-2-yl)adamantane (8k)

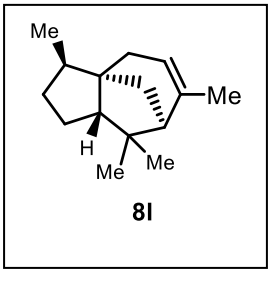


8k

The reaction with 1-(2-Azido-1-phenylpropan-2-yl)adamantane **5k** (59.1 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 30 min, followed by concentrated under vacuum line at 50 °C to remove *tert*-butylbenzene, purification by neutral silica gel column chromatography (hexane / ethyl acetate = 100 / 1), and further purification by recycling GPC (chloroform as eluent), gave **8k** (68% yield from ^{1}H NMR before purification, 22.1 mg, 44% isolated yield) as a white solid.

White solid; R_f value 0.80 (hexane / ethyl acetate = 5 / 1); m.p. 56–58 °C; IR (KBr, disc) ν_{max} 2904, 2846, 1631, 1495, 1444 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.29 (m, 2H), 7.22 (d, 2H, *J* = 7.5 Hz), 7.19–7.16 (m, 1H), 6.28 (s, 1H), 2.06 (br-s, 3H), 1.80–1.69 (m, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 139.6, 129.1, 127.8, 125.6, 121.9, 40.9, 38.2, 37.0, 28.8, 13.4; LRMS (EI, M = $C_{19}H_{24}$) *m/z* 252 (M^+, 100%), 156 (19), 141 (16), 135 (25), 117 (13), 91 (23); HRMS (CI) calcd for $C_{19}H_{24}$ (M^+) 252.1878, found 252.1884.

(-)-α-Cedrene (8l)



8l

The reaction with diastereomeric mixture of cedryl azide **5l** (49.5 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at room temperature for 1 h, followed by concentration under vacuum line at 50 °C to remove *tert*-butylbenzene and purification by neutral silica gel column

chromatography (hexane as eluent), gave **8l** (85% yield from ^{1}H NMR before purification, 18.6 mg, 46% isolated yield) as a colorless oil. The analytical data were in good agreement with the literature.[47]

Colorless oil; R_f value 0.80 (hexane); $[\alpha]_D^{21} =$ -89.7 (c = 1.0, $CHCl_3$); IR (KBr, disc) ν_{max} 2947, 2900, 2870, 2827, 1460, 1379 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.22 (s-br, 1H), 2.19–2.15 (dt, 1H, *J* = 16.5 Hz, *J* = 4.5 Hz), 1.89–1.54 (m, 10H), 1.42–1.33 (m, 3H), 1.02 (s, 3H), 0.95 (s, 3H), 0.84 (d, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 119.2, 58.9, 54.8, 53.8, 48.1, 41.4, 40.6, 38.8, 36.1, 27.6, 25.6, 24.78, 24.75, 15.4; LRMS (EI, M = $C_{15}H_{24}$) *m/z* 204 (M^+, 4%), 161 (16), 119 (100), 105 (27), 93 (33); HRMS (EI) calcd for $C_{15}H_{24}$ (M^+) 204.1878, found 204.1878.

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CHAPTER 4 Application of the Traceless Schmidt Reaction: One-Pot Functionalization and C–H Azidation

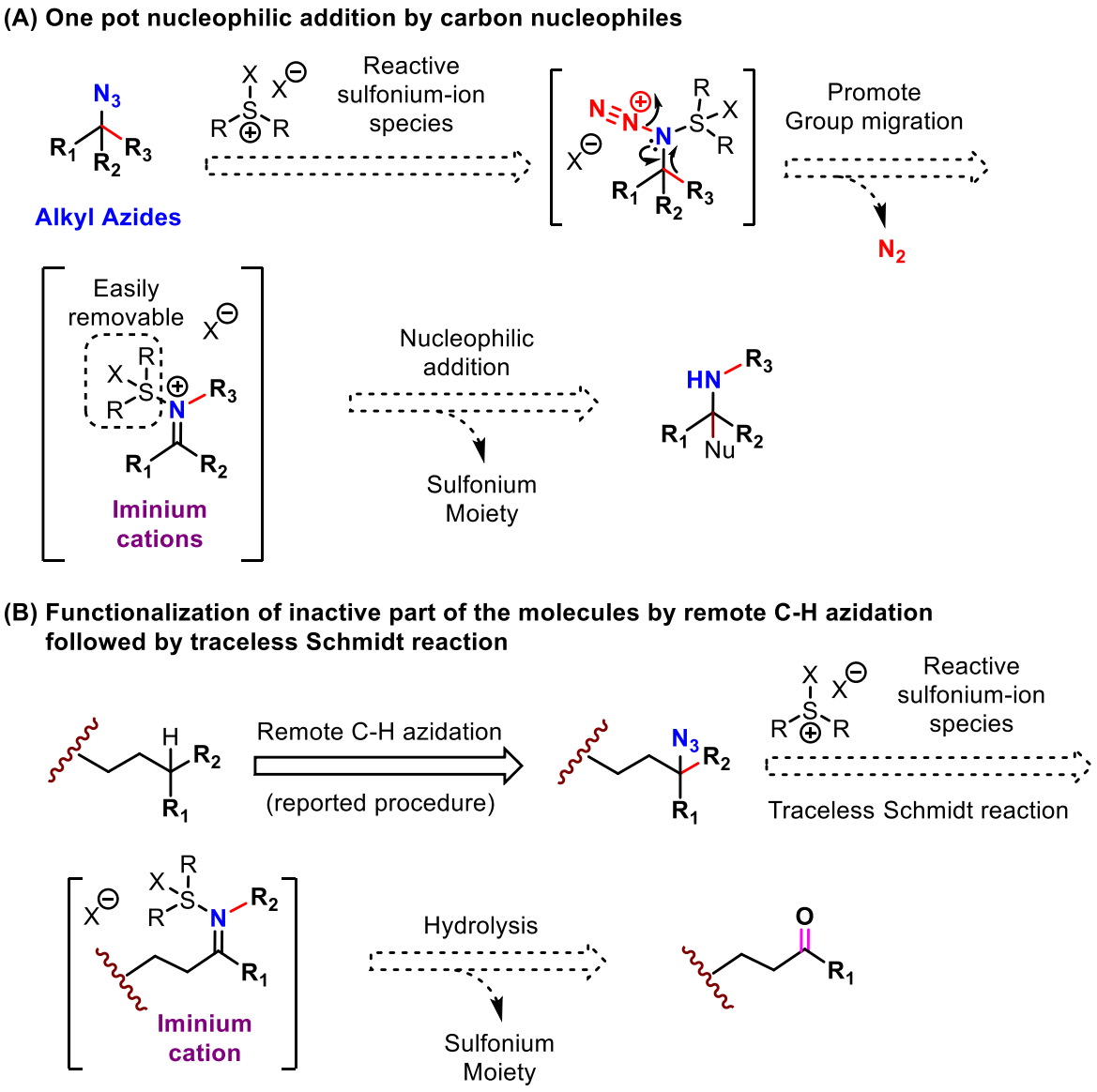
4. 1 Introduction

Imines ($R_1R_2C=N–R_3$) have long been recognized as useful intermediates in the area of synthetic organic chemistry.[1] Classically, they can be prepared from condensation reactions between carbonyl compounds and ammonia or primary amines.[2] Imines themselves can be found as a class of compounds possessing efficient biological activities. In addition, the C=N bonds of the imines are also the key to access many valuable nitrogen-containing organic molecules.[3-9] For example, they have been reported to undergo nucleophilic addition, Diels-Alder reaction leading to fused ring heterocycles, and cascade reactions constructing *N*-heterocyclic motifs such as alkaloids.[10-12] With the versatile characters as intermediates, searching novel strategies on the preparation of imines as well as their derivatization are still urgently required.

As shown in Chapters 2 and 3, functionalization of alkyl azides via cleavage of a C–H or a C–C bond using sulfonium ion successfully provided aldiminium cations (from primary substrates), *N*-H ketiminium cations (from secondary substrates), or *N*-substituted ketiminium cations (from tertiary substrates). The generated iminium cation intermediates have been successfully treated by two different ways (hydrolysis or reductive amination) to give functionalized products. From these results, I envisioned that the *in-situ* generated iminium cations could accept further functionalization in one pot toward the structural rebuilding of organic compounds.

In this chapter, I describe the one-pot functionalization of alkyl azides by way of nucleophilic addition reactions to the generated iminium cation intermediates (Scheme

4.1A). For further application, a combination of the traceless Schmidt reaction with C–H azidation[13] is also described, which allows the functionalization of the inactive alkyl chains (Scheme 4.1B).



Scheme 4.1. Working hypothesis on one-pot functionalization of alkyl azides, and modification of unfunctionalized hydrocarbon chain by traceless Schmidt reaction following C–H azidation

4. 2 One-Pot Functionalization of Alkyl Azides by Carbon Nucleophiles

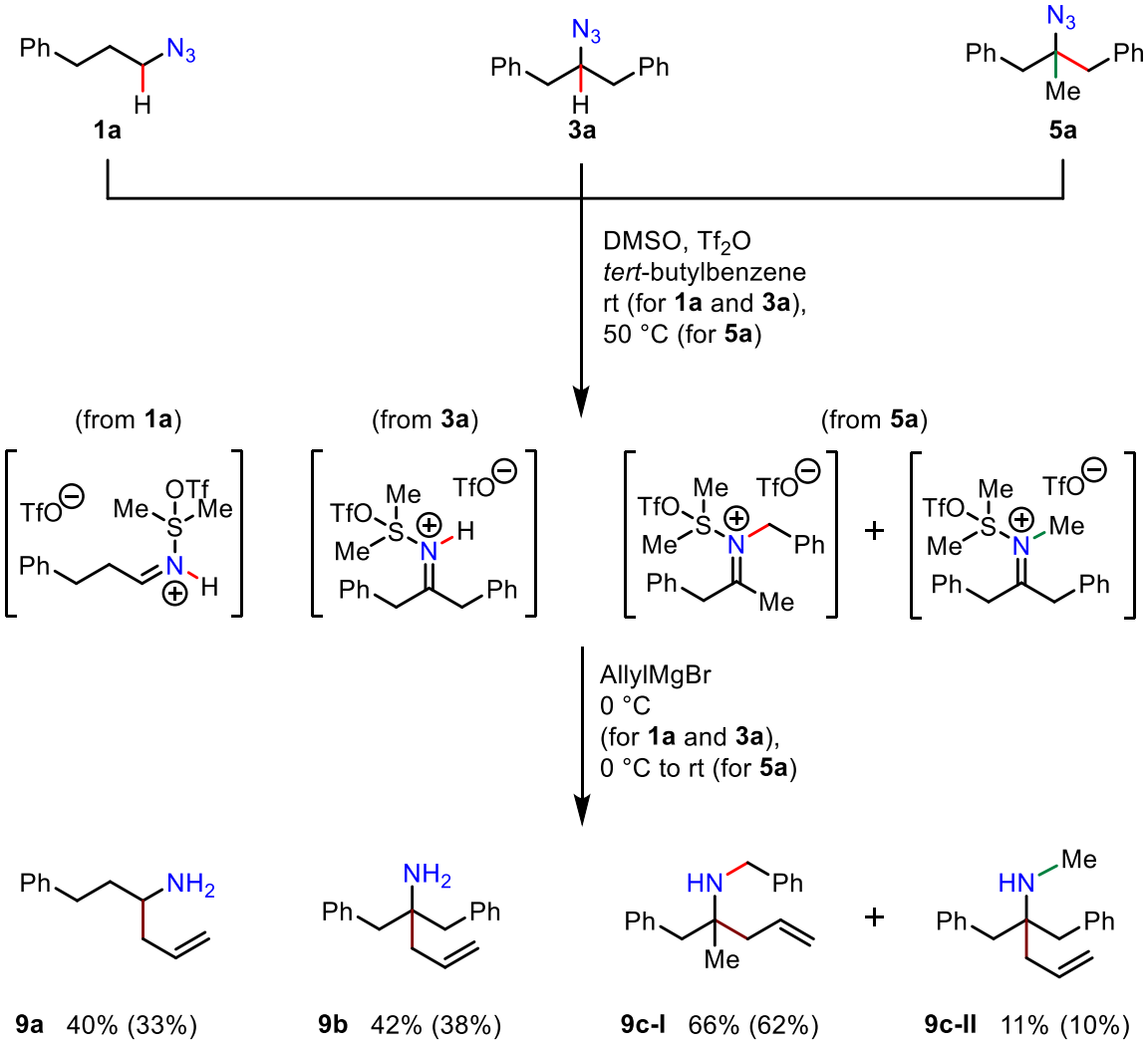
Because nitrogen atom is less electronegative than oxygen atom, C=N (iminyl) is less reactive than C=O (carbonyl) towards nucleophilic attacks.[14-16] Thus, only strong nucleophiles such as organometallic reagents can react with imines. Although strong nucleophiles employed, imine substrates that can smoothly react with those reagents are generally limited to benzylic-positioning aldimines, or ketimines with activating groups at the nitrogen atom of imine.[17,18] However, activating (or protecting) groups in imines such as sulfonimines, *N*-diphenylphosphinylimines, and *N*-(diethoxyphosphoryl)aldimines are difficult to remove and sometimes require additional steps to remove these moieties.[19,20] In this work, I present the traceless Schmidt reaction facilitating the formation of iminium cation intermediates attached with an easily removable sulfonium group. This condition has two advantageous points: (1) The generated iminium cations are already activated *in situ* by the presence of sulfonium ion attached, or activated by acidic environment due to the existence of released triflic acid; (2) Additional deprotection step is not necessary to give the desired products without any trace from activating reagents.

Addition of Organomagnesium Reagent to the Imines. Alkyl-substituted amine derivatives, especially homoallylic amines, are important building blocks for the synthesis of biologically active compounds and complex natural products.[19] These compounds were typically prepared by 1,2-addition of allylic nucleophiles to the imines.[17] Although allylation of imines has been developed, the substrate scopes are quite limited to reactive aldimines or activated ketimines, as mentioned earlier. Thus, herein, allylation of iminium cations generated from general alkyl azides (unreactive alkyl azides) were investigated (Scheme 4.2A). Primary alkyl azide **1a** was subjected to the traceless Schmidt reaction with *in situ* prepared sulfonium ion to give aldiminium cation intermediate. To the iminium cation solution, subsequent addition of allylmagnesium bromide reagent afforded secondary

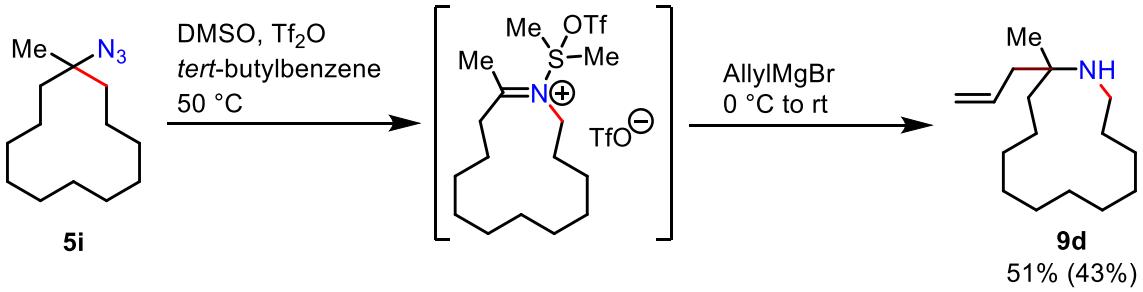
alkylamine **9a** in 40% ^{1}H NMR yield (33% isolated yield) over two steps in one pot. Gratifyingly, under the same reaction conditions, secondary alkyl azide **3a** gave *N*-unsubstituted *tert*-alkylamine **9b** in 42% (38% isolated yield). With **3a**, the construction of nitrogen-attached tetrasubstituted carbon centers has been achieved via one-pot functionalization. This successful addition is attributed to electron-deficient sulfonium moiety on the nitrogen atom of ketiminium cation intermediate, activating the C=N bond during nucleophile attack. In contrast, the precedent reports were difficult to access general ketimines because the imine moiety was not activated.

Considering the importance of nitrogen-comprising tetrasubstituted carbon centers in natural products and pharmaceuticals,[21,22] the nucleophilic addition reaction was extended to the *N*-substituted ketiminium cation intermediates generated from *tert*-alkyl azide **5a**. After traceless Schmidt reaction, these intermediates underwent smooth allylation to afford benzyl-migrated **9c-I** (66%, 62% isolated yield) as a major product and methyl-migrated **9c-II** (11%, 10% isolated yield) as a minor component. Not only acyclic substrates but also cyclic alkyl azide **5i** can be functionalized in one pot to furnish ring-expanded allylated *tert*-alkylamine **9d** (Scheme 4.2B). These results emphasized the successful one-pot functionalization of alkyl azides by means of nucleophilic addition of organomagnesium reagent, which was useful for the generation of versatile alkylamine derivatives, particularly amines integrated with tetrasubstituted carbon centers.

(A) One pot functionalization of acyclic alkyl azides by organomagnesium reagent



(B) One pot functionalization of cyclic alkyl azide by organomagnesium reagent



Scheme 4.2. One-pot functionalization of alkyl azides by organomagnesium reagent

Addition of Trimethylsilyl Cyanide to The Imines (Strecker Reaction) Leading to α-Aminonitriles. Strecker reaction is classically defined as the addition reaction of highly toxic hydrogen cyanide to the imines, generated from carbonyl compounds and ammonia, leading to α-aminonitriles (Figure 4.1A). For synthetic chemists, they have been known as useful synthones for the preparation of α-amino acids, hydantoin, imidazoles and other *N*-containing heterocyclic derivatives (Figure 4.1B).[23-28] α-Aminonitriles have emerged as an important class in chemical biology due to their existence in developed drugs molecules, such as vildagliptin and anagliptin (Figure 4.1C).[29] To date, α-aminonitriles are generally synthesized using various safer cyanide sources in the presence of Lewis acid or Lewis base catalysts.[30] However, similar to the addition of organomagnesium reagent to the imines, the scope of imines in Strecker reaction is generally limited to aldimines. On the other hand, ketimines are difficult to undergo the Strecker reaction due to their low electrophilic character and steric hindrance. The Strecker reaction with ketimines can serve aminonitriles with tetrasubstituted carbon centers, which are efficient precursors of α-substituted-α-amino acids found in bioactive natural products. In this work, the addition of cyanide ions to the iminium cations prepared from unreactive alkyl azides is investigated.

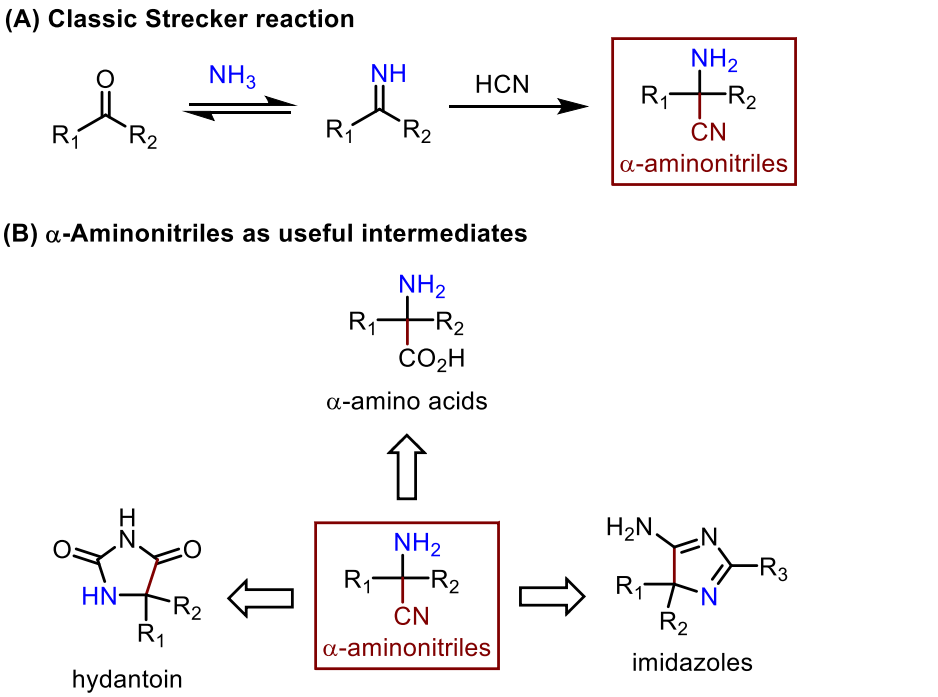
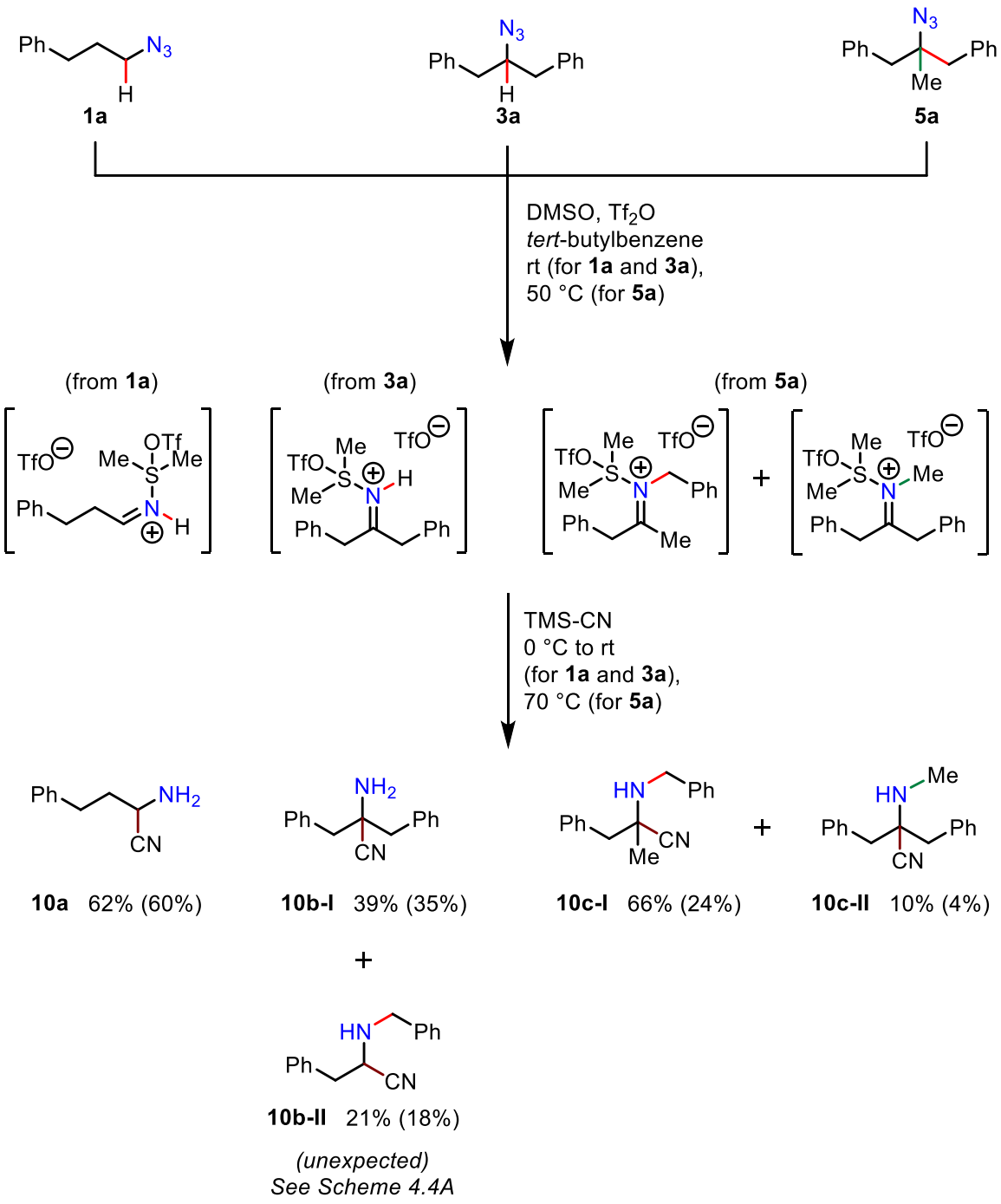


Figure 4.1. Strecker reaction and the importance of α-aminonitriles

In this one-pot Strecker reaction, I speculated that Lewis acid or Lewis base additives are not required because the generated iminium cations are already activated in the reaction mixture after the traceless Schmidt reaction (Scheme 4.3). Pleasingly, treating the aldiminium cation generated from alkyl azide **1a** only with trimethylsilyl cyanide (TMS-CN), successfully furnished α-aminonitrile **10a** in 62% ^{1}H NMR yield (60% isolated yield) over two steps in one pot. Not only aldiminium, but also *N*-H ketiminium cation from secondary alkyl azide **3a** was tolerable under the reaction conditions to provide tetrasubstituted α-aminonitrile **10b-I** in 39% (35% isolated yield). In Chapter 2, Schmidt reaction of **3a** followed by hydrolysis successfully gave ketone **4a** in 90% isolated yield as

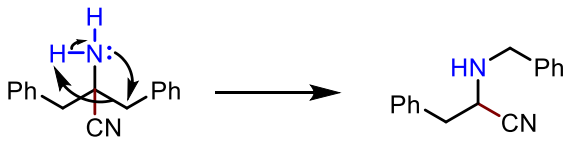
a sole product. Interestingly, one-pot functionalization followed by Strecker reaction of **3a** also gave benzyl-migrated product **10b-II** in non-negligible 21% yield (18% isolated yield). This unexpected product was formed probably by intra- or intermolecular rearrangement of compound **10b-I** (Scheme 4.4A). Finally, *tert*-alkyl azide **5a** generating *N*-alkylketiminium cations was then treated with TMS-CN under heating conditions. Then, tetrasubstituted α-aminonitriles **10c-I** in 66% (24% isolated yield) as a major product via benzyl migration and **10c-II** in 10% (4% isolated yield) as a minor product via methyl migration are afforded. The low isolation yields of tetrasubstituted α-aminonitriles are probably due to partial decomposition of the products via retro-Strecker reaction during silica gel or alumina column chromatography (Scheme 4.4B).[31,32] The decomposition process involves the formation of tertiary carbocations stabilized by *N*-alkylamino electron-donating group forming imines. Silica gel or alumina assisted the hydrolysis of the imines to give ketones **6a** of a retro-Strecker product from **10c-I**, and **4a** from **10c-II**. The observation is proved by ^{1}H NMR of the decomposed material (Figure 4.2). Fortunately, pure products were isolated through short-path column chromatography, minimizing the decomposition. Although some products were isolated in low yields due to their instability, this one-pot method presents a convenient way for accessing alkyl aminonitriles, which are denoted as useful intermediates for delivering highly functional materials such as amino acids.



Scheme 4.3. One-pot functionalization of alkyl azides by Strecker reaction

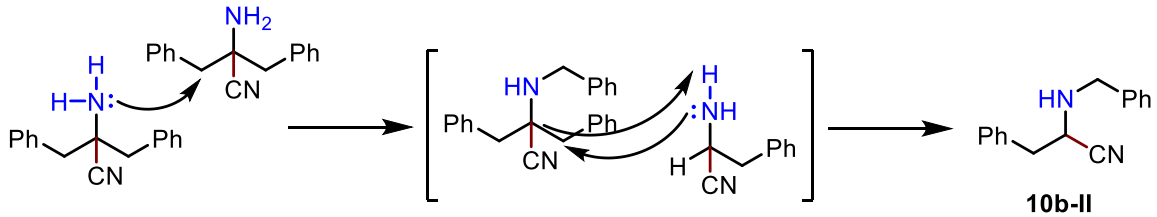
(A) Plausible mechanism for rearrangement of 10b-I to form 10b-II

Intramolecular rearrangement



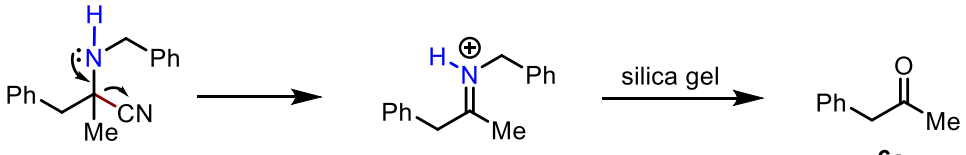
10b-I **10b-II**

Intermolecular rearrangement



10b-I **10b-II**

(B) Plausible mechanism for retro-Strecker reaction of 10c occured during chromatography



10c-I **6a**

Scheme 4.4. A plausible mechanism of the observed byproducts during Strecker reaction

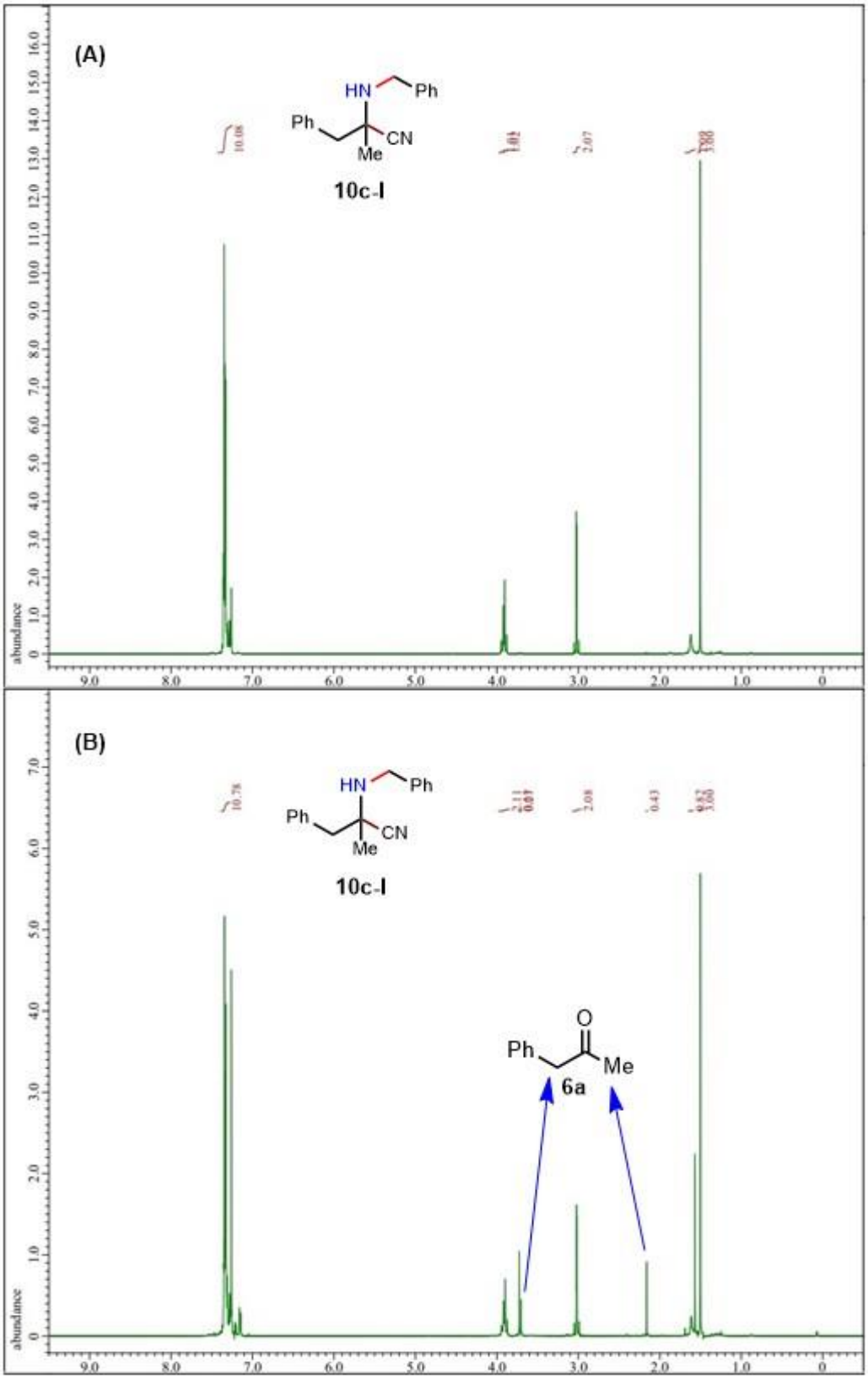
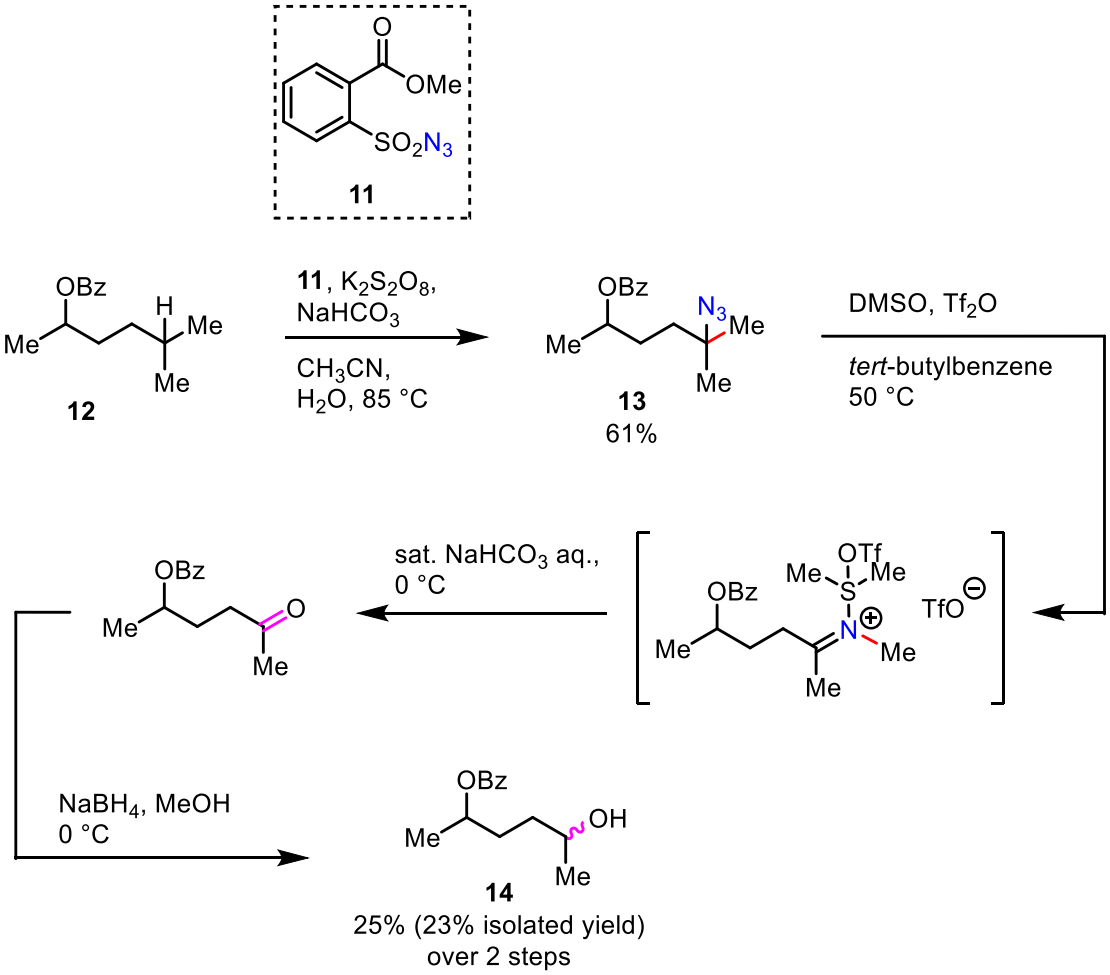


Figure 4.2. ^{1}H NMR spectra of (A) Pure aminonitrile **10c-I**, (B) Mixture after chromatography

4. 3 Functionalization of Inactive Part of the Molecule by Remote C–H Azidation and Traceless Schmidt Reaction

Direct introduction of functional groups to the hydrocarbon chain in certain molecules that lacks of directing group is a challenging task.[33] In this framework, C–H azidation is considered the important method for the direct installation of C–N bond from the saturated C–H bond.[34,35] Such C–H bond functionalization would establish a significant impact in many areas of synthetic chemistry.[33] In line with this, I demonstrate the modification of the unfunctionalized hydrocarbon chain in a molecule with the traceless Schmidt reaction following the C–H azidation method (Scheme 4.5). For instance, remote C–H azidation of compound **12** by Tang and co-workers successfully afforded azide product **13**.[36] In short, applying the traceless Schmidt reaction to this *tert*-alkyl azide substrate under the established conditions followed by aqueous workup for hydrolysis furnished methyl ketone product via methyl migration. Because the ketone was inseparable from the impurities, the target compound was isolated as a corresponding alcohol derivative **14** after reduction. Therefore, the traceless Schmidt reaction combined with the C–H azidation successfully modified the structure of the hydrocarbon through C–H and C–C bond functionalization.



Scheme 4.5. Structural modification of unfunctionalized carbon chain by traceless Schmidt reaction following C–H azidation

4. 4 Summary

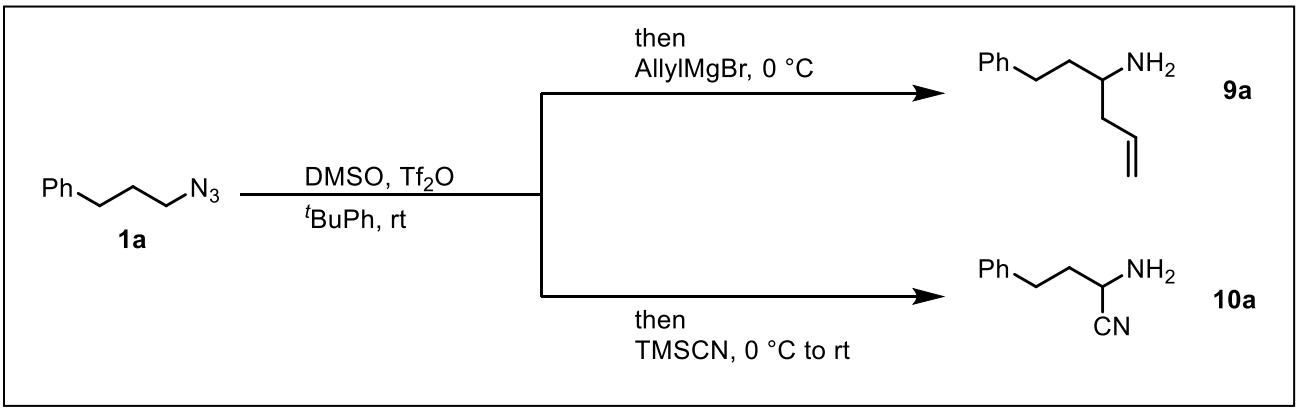
Iminium cation intermediates generated from alkyl azides by the traceless Schmidt reaction were successfully delivered to functionalized alkylamine derivatives through the addition of organomagnesium reagent and to α-aminonitriles via the addition of trimethylsilyl cyanide for Strecker reaction, respectively in one pot. Transformation of iminium cations to the products proceeded smoothly in one pot and can be achieved without the need of additional activators such as Lewis acids or bases in the second step. For the structural modification of the

unfunctionalized hydrocarbon, combination with C–H azidation and C–C bond cleavage by the traceless Schmidt reaction successfully afforded the functionalized product.

4. 5 Experimental Data

4.5.1 One Pot Nucleophilic Addition Reaction After Traceless Schmidt Reaction

One-pot conversion of 1a



The reactions were performed with 3-Phenylpropylazide **1a** (32.2 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at room temperature for 2.5 h, as following the general procedure. After consumption of **1a**, the following process was done in one pot.

Grignard reaction

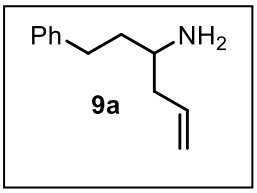
The reaction mixture was cooled to 0 °C and allylmagnesium bromide (1.0 M in diethyl ether, 0.6 mL, 0.60 mmol) was added dropwise. After 6 h stirred at this temperature, the reaction was quenched with water. The mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel column

chromatography (dichloromethane / methanol = 50 / 1 to 30 / 1 with 1% triethylamine) gave **9a** (40% yield on ^{1}H NMR before purification, 11.5 mg, 33% isolated yield) as a light-yellow oil.

Strecker reaction

The reaction mixture was cooled to 0 °C and trimethylsilyl cyanide (74 μL, 0.60 mmol) was added dropwise to the stirred mixture. Then, the mixture was warmed up to room temperature and stirred for overnight. The reaction was quenched with saturated sodium bicarbonate aqueous solution. The mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel column chromatography (hexane / ethyl acetate = 10 / 1 to 1 / 2 with 1% triethylamine) gave **10a** (62% yield on ^{1}H NMR before purification, 19.2 mg, 60% isolated yield) as a light-yellow oil.

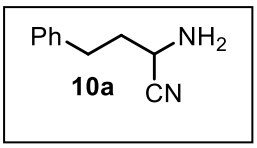
1-Phenylhex-5-en-3-amine (9a)



The analytical data were in good agreement with the literature.[37]

Light yellow oil; R_f value 0.30 (dichloromethane / methanol = 8 / 1); IR (NaCl, neat) ν_{max} 3063, 3029, 2923, 2854, 1638, 1491, 1451, 1286, 1248 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 2H), 7.21–7.17 (m, 3H), 5.78 (m, 1H), 5.13–5.09 (m, 2H), 2.85 (m, 1H), 2.76 (ddd, 1H, *J* = 14.0, 9.5, 6.0 Hz), 2.65 (ddd, 1H, *J* = 14.0, 9.5, 6.5 Hz), 2.29 (m, 1H), 2.06 (td, 1H, *J* = 13.5, 7.5 Hz), 1.83 (s, 2H), 1.81–1.74 (m, 1H), 1.68–1.60 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 135.6, 128.4, 128.3, 125.8, 117.5, 50.1, 42.6, 39.3, 32.6; HRMS (CI) calcd for $C_{12}H_{18}N$ $[M+H]^+$ 176.1439, found 176.1440.

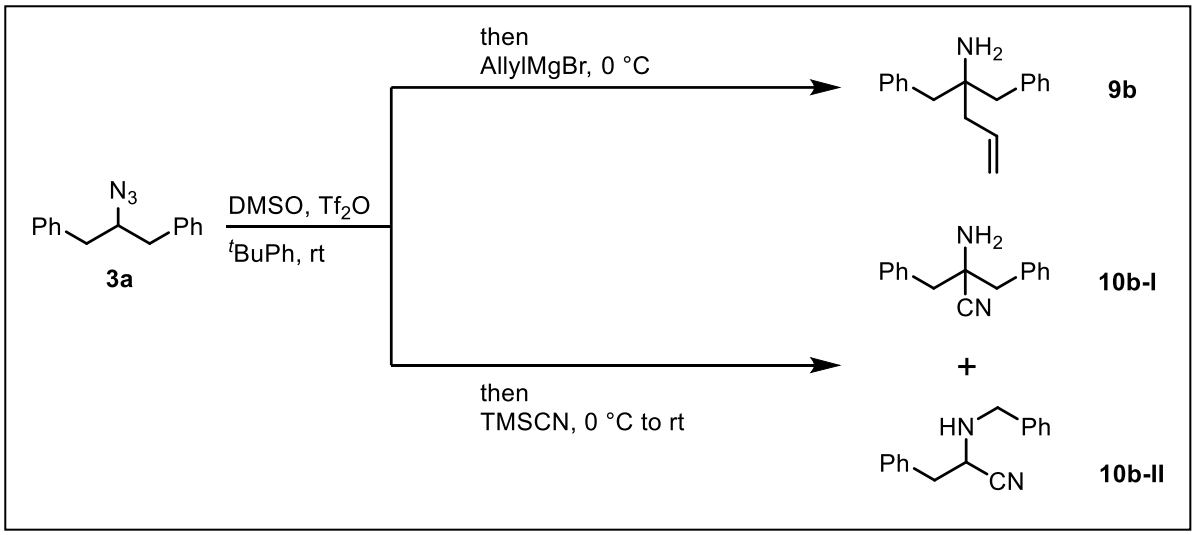
2-Amino-4-phenylbutanenitrile (10a)



The analytical data were in good agreement with the literature.[38]

Light yellow oil; R_f value 0.62 (ethyl acetate); IR (NaCl, neat) ν_{max} 3381, 3315, 3063, 3029, 2924, 2862, 2226, 1604, 1495, 1452 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.30 (m, 2H), 7.25–7.21 (m, 3H), 3.62 (t, 1H, *J* = 7.0 Hz), 2.89 (dt, 1H, *J* = 14.5, 7.5 Hz), 2.81 (dt, 1H, *J* = 15.0, 8.0 Hz), 2.06 (td, 2H, *J* = 7.5, 7.5 Hz), 1.63 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7, 128.7, 128.4, 126.5, 122.0, 42.6, 36.8, 31.6; LRMS (EI, M = $C_{10}H_{12}N_2$) *m/z* 160 (M^+, 10%), 143 (100), 116 (34), 105 (69), 91 (87); HRMS (EI) calcd for $C_{10}H_{12}N_2$ (M^+) 160.1000, found 160.1008.

One-pot conversion of 3a



The reaction was performed with (2-Azidopropane-1,3-diyl)dibenzene **3a** (47.5 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at room temperature for 3 h, as following the general procedure. After consumption of **3a**, the following process was done in one pot.

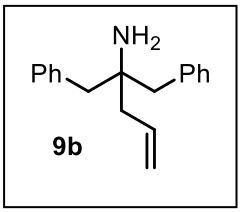
Grignard reaction

The reaction mixture was cooled to 0 °C and allylmagnesium bromide (1.0 M in diethyl ether, 0.6 mL, 0.60 mmol) was added dropwise to the stirred mixture. After 6 h stirred at this temperature, the reaction was quenched with water. The mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel column chromatography (hexane / ethyl acetate = 20 / 1 to 5 / 1 with 1% triethylamine) gave **9b** (42% yield on 1H NMR before purification, 19.1 mg, 38% isolated yield) as a viscous light-yellow oil.

Strecker reaction

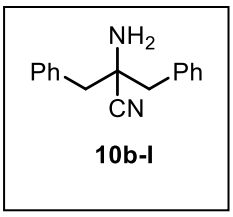
The reaction mixture was cooled to 0 °C and trimethylsilyl cyanide (74 μL, 0.60 mmol) was added dropwise to the stirred mixture. The mixture was then warmed up to room temperature and stirred for overnight. The reaction was quenched with saturated sodium bicarbonate aqueous solution. The mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel column chromatography (hexane / ethyl acetate = 50 / 1 to 3 / 1 with 1% triethylamine) gave 2-amino-2-benzyl-3-phenylpropanenitrile **10b-I** (39% yield on ^{1}H NMR before purification, 16.6 mg, 35% isolated yield) as a light-yellow solid and 2-(benzylamino)-3-phenylpropanenitrile **10b-I** (21% yield on ^{1}H NMR before purification, 8.5 mg, 18%) as a viscous colorless oil.

2-Benzyl-1-phenylpent-4-en-2-amine (9b)



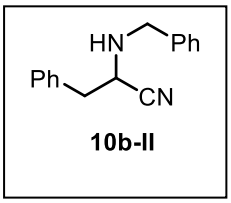
Viscous light-yellow oil; R_f value 0.40 (ethyl acetate); IR (NaCl, neat) ν_{max} 3365, 3063, 3029, 2920, 2850, 1638, 1600, 1491, 1448 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.29 (m, 4H), 7.26–7.21 (m, 6H), 6.01 (ddt, 1H, *J* = 17.0, 10.0, 7.5 Hz), 5.20 (m, 1H), 5.11 (m, 1H), 2.78 (d, 2H, *J* = 13.5 Hz), 2.69 (d, 2H, *J* = 13.0 Hz), 2.08 (d, 2H), 1.33 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 134.5, 130.8, 128.1, 126.3, 118.7, 54.5, 46.4, 43.7; HRMS (CI) calcd for $C_{18}H_{22}N$ $[M+H]^+$ 252.1752, found 252.1758.

2-Amino-2-benzyl-3-phenylpropanenitrile (10b-I)



Light yellow solid; R_f value 0.20 (hexane / ethyl acetate = 3 / 1); m.p. 105.5–106.9 °C; IR (KBr, disc) ν_{max} 3381, 3319, 3063, 3029, 2954, 2924, 2854, 2219, 1600, 1495, 1452 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40–7.33 (m, 10H), 3.12 (d, 2H, *J* = 13.5 Hz), 2.91 (d, 2H, *J* = 13.5 Hz), 1.66 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.2, 130.5, 128.7, 127.8, 122.7, 54.8, 46.6; LRMS (EI, M = $C_{16}H_{16}N_2$) *m/z* 236 (M^+, 4%), 209 (17), 191 (12), 145 (100), 118 (34), 92 (24), 91 (74); HRMS (EI) calcd for $C_{16}H_{16}N_2$ (M^+) 236.1313, found 236.1309.

2-(Benzylamino)-3-phenylpropanenitrile (10b-II)

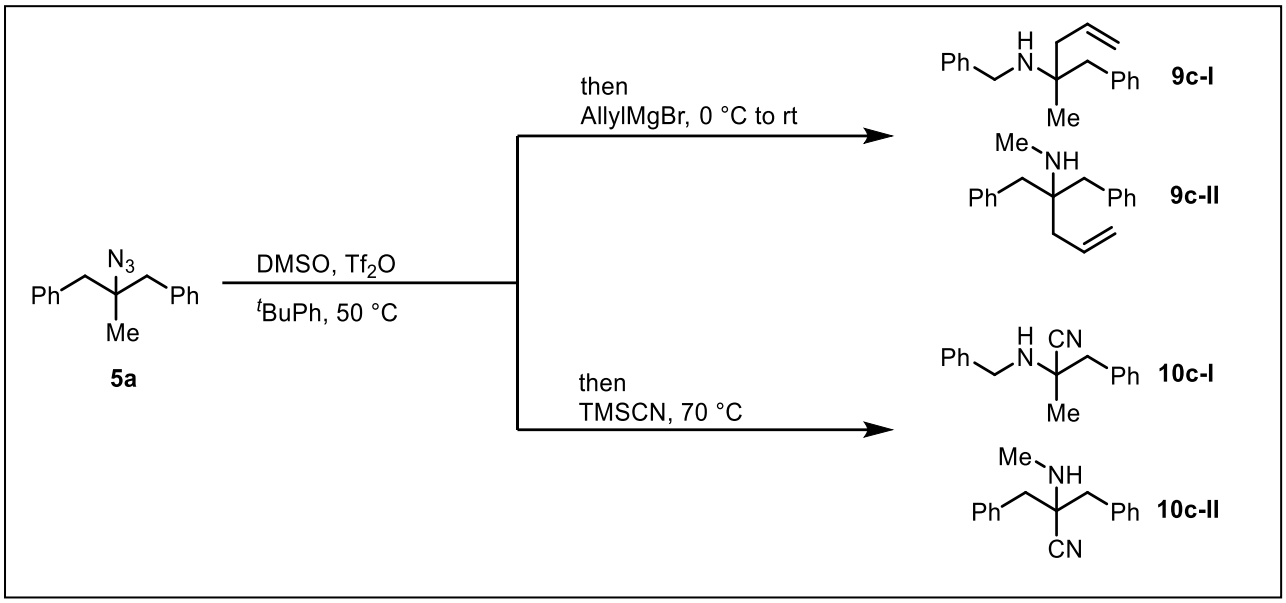


The analytical data were in good agreement with the literature.[39]

Viscous colorless oil; R_f value 0.40 (hexane / ethyl acetate = 3 / 1); IR (NaCl, neat) ν_{max} 3319, 3063, 3029, 2924, 2850, 2224, 1604, 1495, 1452, 1263, 1119, 1027 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.27 (m, 10H), 4.06 (d, 1H, *J* = 13.0 Hz), 3.82 (d, 1H, *J* = 13.0 Hz), 3.74 (t, 1H, *J* = 6.5 Hz), 3.10 (dd, 1H, *J* = 13.0, 5.5 Hz), 3.03 (dd, 1H, *J* = 13.0, 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.1, 135.0, 129.5, 128.8, 128.6, 128.3,

127.6, 119.6, 51.5, 50.7, 39.3; LRMS (EI, M = $C_{16}H_{16}N_2$) *m/z* 236 (M^+, 6%), 209 (13), 145 (25), 91 (100); HRMS (EI) calcd for $C_{16}H_{16}N_2$ (M^+) 236.1313, found 236.1314.

One-pot conversion of 5a



The reaction was performed with (2-Azido-2-methylpropane-1,3-diyl)dibenzene **5a** (50.3 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 4 h, as following the general procedure. After consumption of **3a**, the following process was done in one pot.

Grignard reaction

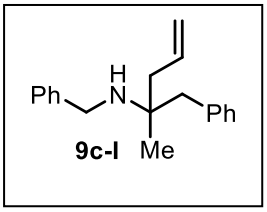
The mixture was cooled to 0 °C and allylmagnesium bromide (1.0 M in diethyl ether, 0.8 mL, 0.80 mmol) was added dropwise to the stirred mixture. After that, the mixture was warmed up to room temperature and was stirred for overnight. The reaction was quenched with water. The mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel column chromatography (hexane / ethyl acetate = 30 / 1 to 2 / 1 with 1% triethylamine) gave *N*-benzyl-2-methyl-1-phenylpent-4-en-2-amine **9ca** (66% yield on ^{1}H NMR before purification, 32.9 mg, 62% isolated yield) as a light-

yellow oil and 2-benzyl-*N*-methyl-1-phenylpent-4-en-2-amine **9cb** (11% yield on ^{1}H NMR before purification, 5.3 mg, 10% isolated yield) as a light-yellow oil.

Strecker reaction

The mixture was cooled down to 0 °C and trimethylsilyl cyanide (99 μL, 0.80 mmol) was added dropwise. After that, the mixture was heated at 70 °C for 4 h. Then, the mixture was cooled down to 0 °C again and the reaction was quenched with saturated sodium bicarbonate aqueous solution. Then, the mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. The concentration of the organic component *in vacuo* followed by short-path neutral silica gel column chromatography (hexane / ethyl acetate = 15 / 1 to 5 / 1) gave 2-(benzylamino)-2-methyl-3-phenylpropanenitrile **10c-I** (66% on ^{1}H NMR before purification, 12.0 mg, 24% isolated yield) as a light-yellow oil and 2-benzyl-2-(methylamino)-3-phenylpropanenitrile **10c-II** (10% yield on ^{1}H NMR before purification, 1.8 mg, 4% isolated yield) as a light-yellow oil.

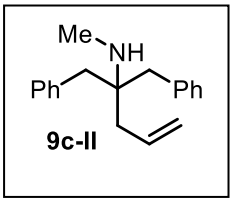
***N*-Benzyl-2-methyl-1-phenylpent-4-en-2-amine (9c-I)**



9c-I

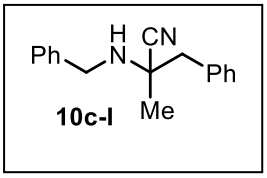
Light yellow oil; R_f value 0.72 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 3063, 3027, 2962, 2924, 2850, 1494, 1452, 1374 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.21 (m, 10H), 5.97 (tdd, 1H, *J* = 16.5, 10.0, 7.5 Hz), 5.16–5.13 (m, 2H), 3.86 (d, 1H, *J* = 12.0 Hz), 3.81 (d, 1H, *J* = 12.0 Hz), 2.83 (d, 1H, *J* = 13.0 Hz), 2.76 (d, 1H, *J* = 13.0 Hz), 2.32 (dd, 1H, *J* = 14.0, 7.0 Hz), 2.21 (dd, 1H, *J* = 14.0, 7.0 Hz), 1.07 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 138.2, 134.7, 130.6, 128.4, 128.1, 128.0, 126.8, 126.1, 117.9, 55.7, 46.3, 45.1, 43.1, 24.7; HRMS (CI) calcd for $C_{19}H_{24}N$ $[M+H]^+$ 266.1909, found 266.1902.

2-Benzyl-*N*-methyl-1-phenylpent-4-en-2-amine (9c-II)



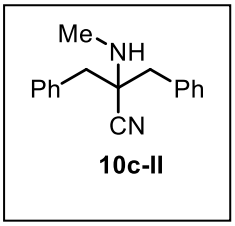
Light yellow oil; R_f value 0.20 (hexane / ethyl acetate = 2 / 1); IR (NaCl, neat) ν_{max} 3063, 3025, 2927, 2854, 1600, 1491, 1452, 913, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 4H), 7.24–7.21 (m, 6H) 5.97 (tdd, 1H, *J* = 17.0, 10.5, 7.0 Hz), 5.14 (dd, 1H, *J* = 10.0, 2.0 Hz), 5.05 (dd, 1H, *J* = 17.0, 2.0 Hz), 2.78 (d, 2H, *J* = 14.0 Hz), 2.72 (d, 2H, *J* = 14.0 Hz), 2.51 (s, 3H), 2.07 (d, 2H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.1, 134.7, 130.7, 128.0, 126.1, 118.1, 58.6, 41.1, 40.1, 28.8; HRMS (CI) calcd for $C_{19}H_{24}N$ $[M+H]^+$ 266.1909, found 266.1906.

2-(Benzylamino)-2-methyl-3-phenylpropanenitrile (10c-I)



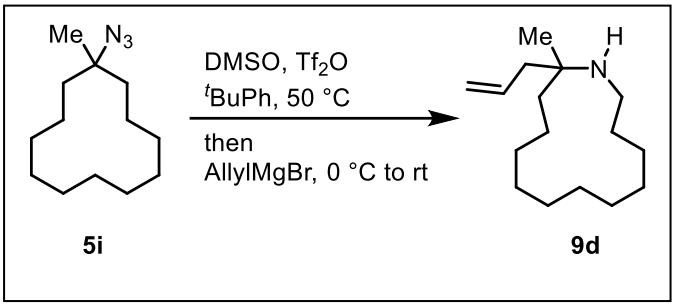
Light yellow oil; R_f value 0.40 (hexane / ethyl acetate = 3 / 1); IR (NaCl, neat) ν_{max} 3315, 3030, 2926, 2850, 2231, 1715, 1600, 1495, 1452, 1374, 1220, 1157 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.27 (m, 10H), 3.93 (d, 1H, *J* = 12.0 Hz), 3.89 (d, 1H, *J* = 12.0 Hz), 3.04 (d, 1H, *J* = 13.0 Hz), 3.01 (d, 1H, *J* = 14.0 Hz), 1.62 (s, 1H), 1.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 134.2, 130.5, 128.64, 128.56, 128.1, 127.7, 127.4, 121.7, 56.3, 49.1, 46.3, 25.2; HRMS (CI) calcd for $C_{17}H_{19}N_2$ $[M+H]^+$ 251.1548, found 251.1545.

2-Benzyl-2-(methylamino)-3-phenylpropanenitrile (10c-II)



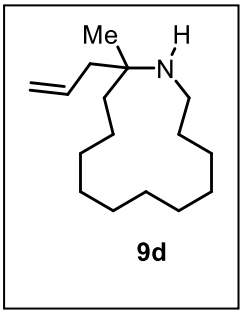
Light yellow oil; R_f value 0.20 (hexane / ethyl acetate = 3 / 1); IR (NaCl, neat) ν_{max} 3334, 3033, 2959, 2258, 1715, 1495, 1450, 1259, 1127, 1085, 1027 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.30 (m, 10H), 2.97 (d, 1H, *J* = 13.5 Hz), 2.91 (d, 1H, *J* = 13.5 Hz), 2.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.1, 130.6, 128.6, 127.6, 120.3, 61.1, 43.3, 31.1; HRMS (CI) calcd for $C_{17}H_{19}N_2$ $[M+H]^+$ 251.1548, found 251.1549.

One-pot allylation of 5g



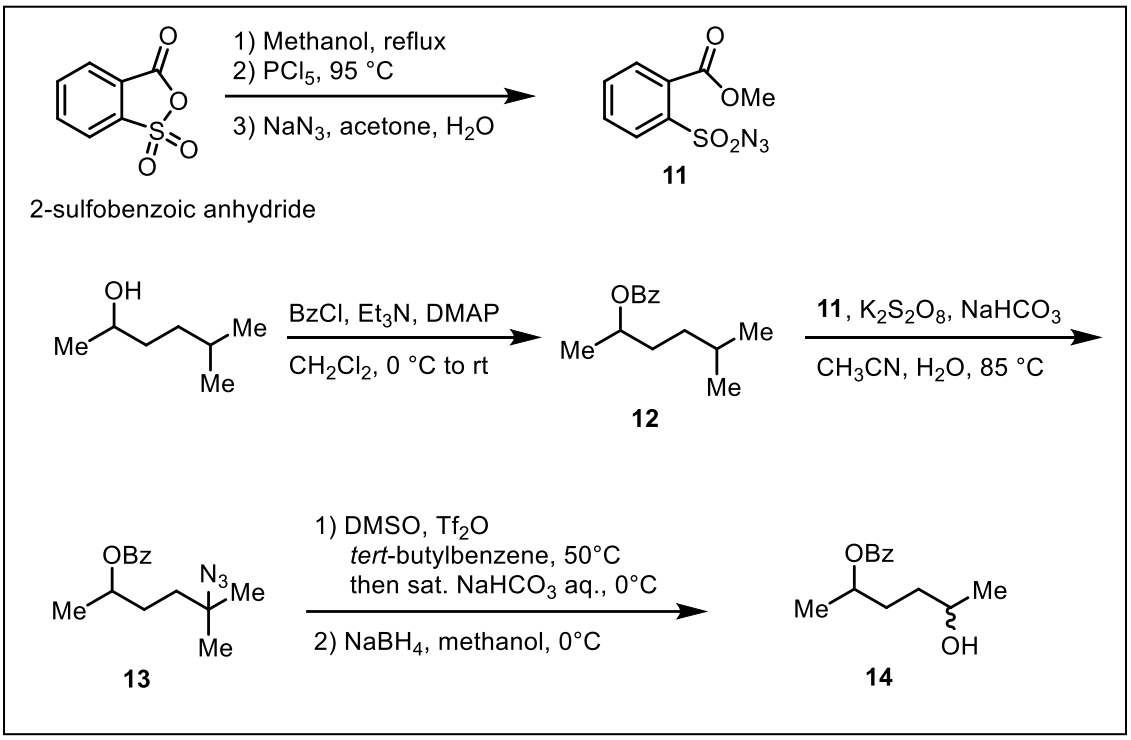
The reaction was performed with 1-azido-1-methylcyclododecane **5i** (44.7 mg, 0.20 mmol), DMSO (28 μL, 0.40 mmol), and trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) in *tert*-butylbenzene (1 mL, 0.2 M) at 50 °C for 1 h. Upon completion, the mixture was cooled to 0 °C and allylmagnesium bromide (1.0 M in diethyl ether, 0.8 mL, 0.80 mmol) was added dropwise. After that, the mixture was warmed up to room temperature and was stirred for overnight. The reaction was quenched with water. The mixture was extracted with dichloromethane to wash with saturated sodium bicarbonate aqueous solution, water, and brine. The collected organic layer was dried over sodium sulfate. Concentration *in vacuo* followed by neutral silica gel column chromatography (dichloromethane / methanol = 80 / 1 to 60 / 1 with 1% triethylamine) gave **9d** (51% yield on ^{1}H NMR before purification, 20.6 mg, 43% isolated yield) as a light-yellow oil.

2-Allyl-2-methylazacyclotridecane (9d)

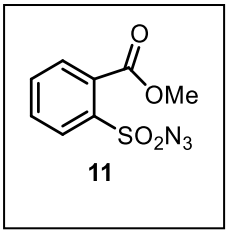


Light yellow oil; R_f value 0.40 (dichloromethane / methanol = 6 / 1); IR (NaCl, neat) ν_{max} 3075, 2927, 2853, 1462, 912 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (m, 1H), 5.07 (s, 1H), 5.04 (m, 1H), 2.52 (m, 2H), 2.19–2.13 (m, 1H), 2.09–2.06 (m, 1H), 1.49 (br-s, 2H), 1.45–1.27 (m, 19H), 1.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.9, 117.4, 54.7, 44.9, 39.3, 36.5, 29.4, 28.3, 26.9, 26.4, 25.8, 25.7, 25.6, 25.1, 24.3, 20.3; HRMS (CI) calcd for $C_{16}H_{32}N$ $[M+H]^+$ 238.2535, found 238.2527.

4.5.2 Molecular Transformation by Way of C-H Azidation Followed by Traceless Schmidt Reaction



Methyl 2-(azidosulfonyl)benzoate (11)

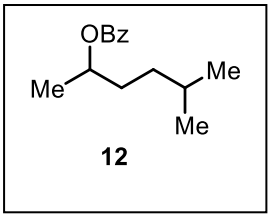


The compound was prepared according to previous method.[40] 2-Sulfobenzoic anhydride (1.84 g, 10 mmol) was dissolved in methanol (5 mL), and the solution was refluxed for 1 h. After cooling down to room temperature, volatile component was removed under vacuo to afford 2-(methoxycarbonyl)benzenesulfonic acid (2.10 g) as a viscous light-yellow oil which was used for the next step without further purification. Phosphorus pentachloride (5.21 g, 25 mmol) was added slowly to the 2-(Methoxycarbonyl)benzenesulfonic acid (2.1 g) above, and then it was warmed up to 95 °C for 3 h. After cooling down to room temperature, the material was dissolved in diethyl ether and washed quickly with ice water (exothermic reaction!). Organic layer was

dried over sodium sulfate and was concentrated to afford 2.85 g of methyl 2-(chlorosulfonyl)benzoate as a viscous light-yellow oil, which was used for the next step without further purification. To ethyl 2-(chlorosulfonyl)benzoate (2.85 g) solution in acetone (24 mL) at 0 °C, was added dropwise sodium azide (975.2 mg, 15 mmol) solution in water (8 mL) over 15 min. The mixture was warmed up to room temperature and stirred for additional 12 h. The mixture was then extracted with ethyl acetate to wash with water, saturated sodium carbonate aqueous solution, water, and finally brine. Organic layer was dried over sodium sulfate. After removing organic component, methyl 2-(azidosulfonyl)benzoate was obtained (1.84 g, 76% over 3 steps) as a light-yellow solid. Spectroscopic data were in accordance with literature.[40]

Light-yellow solid; R_f value 0.60 (hexane / ethyl acetate = 1 / 1); m.p. 56.3–57.8 °C; IR (KBr, disc) ν_{max} 2956, 2145, 1735, 1436, 1371, 1294, 1173, 1120, 1058 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.12–8.10 (m, 1H), 7.78–7.68 (m, 3H), 3.99 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 137.2, 134.4, 132.3, 131.5, 130.2, 130.1, 53.6; HRMS (DART) calcd for $C_8H_8N_3O_4S$ $[M+H]^+$ 242.0230, found 242.0231.

5-Methylhexan-2-yl benzoate (12)



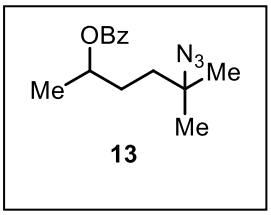
12

Benzoylation reaction was performed according to previous reported work.[41] To a stirred solution of 5-methyl-2-hexanol (581.0 mg, 5 mmol), triethylamine (1 mL, 7.5 mmol) and 4-dimethylaminopyridine (122.2 mg, 1 mmol) in dichloromethane (0.2M, 25 mL) at 0 ºC was added dropwise benzoyl chloride (0.7 mL, 6 mmol) over 5 min. The mixture was warmed up to room temperature and additionally stirred for 7 h. After completion, the reaction was quenched with water. The mixture was then extracted with dichloromethane to wash with water. The combined organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 50 / 1 to

25 / 1) to afford 5-methylhexan-2-yl benzoate (932.7 mg, 85%) as a colorless oil. Spectroscopic data were in accordance with literature.[41]

Colorless oil; R_f value 0.60 (hexane / ethyl acetate = 8 / 1); IR (NaCl, neat) ν_{max} 2955, 2870, 1716, 1453, 1276, 1173, 1110, 1069, 1024 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.05–8.04 (m, 2H), 7.57–7.53 (m, 1H), 7.46–7.43 (m, 2H), 5.13 (qt, 1H, *J* = 6.0, 6.0 Hz), 1.77–1.70 (m, 1H), 1.65–1.52 (m, 2H), 1.34 (d, 3H, *J* = 6.0 Hz), 1.31–1.20 (m, 2H), 0.89 (d, 6H, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 132.7, 130.9, 129.5, 128.3, 72.0, 34.5, 33.9, 27.9, 22.6, 22.5, 20.1; HRMS (DART) calcd for $C_{14}H_{21}O_2$ $[M+H]^+$ 221.1536, found 221.1537.

5-Azido-5-methylhexan-2-yl benzoate (13)

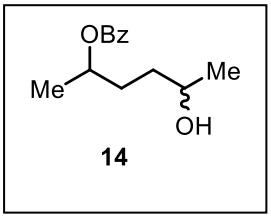


Remote C–H azidation was performed according to Tang *et al* procedure.[36] Into round-bottom flask, methyl 2-(azidosulfonyl)benzoate (361.8 mg, 1.5 mmol), sodium bicarbonate (84.0 mg, 1.0 mmol), and potassium peroxodisulfate (811.0 mg, 3 mmol) were added sequentially. The flask was filled by nitrogen. Acetonitrile / water solvent (3 / 2, 0.08 M, 12.5 mL) was added via syringe, and finally 5-methylhexan-2-yl benzoate (220.3 mg, 1 mmol) was added dropwise via syringe. The mixture was warmed up to 85 ºC and stirred for 4 h. The mixture was extracted with ethyl acetate to wash with water. The organic layer was dried over sodium sulfate. The crude material by removal of organic solvent *in vacuo* was purified by silica gel column chromatography (hexane / ethyl acetate = 50 / 1) to afford 5-azido-5-methylhexan-2-yl benzoate (160.2 mg, 61%) as a colorless oil. Spectroscopic data were in accordance with literature.[36]

Colorless oil; R_f value 0.50 (hexane / ethyl acetate = 8 / 1); IR (NaCl, neat) ν_{max} 2976, 2099, 1715, 1453, 1373, 1275, 1175, 1112, 1065 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.05–8.03 (m, 2H), 7.58–7.55 (m, 1H), 7.46–7.39 (m, 2H), 5.14 (qt, 1H, *J* = 6.0, 6.5 Hz), 1.85–1.77 (m, 1H), 1.76–1.69 (m, 1H), 1.66–1.60 (m, 1H), 1.57–1.51 (m, 1H), 1.37 (d, 3H, *J* = 6.5 Hz), 1.28 (s,

6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 132.8, 130.6, 129.5, 128.3, 71.4, 61.2, 37.1, 30.8, 26.1, 25.9, 20.1; HRMS (DART) calcd for $C_{14}H_{20}N_3O_2$ $[M+H]^+$ 262.1550, found 262.1546.

5-Hydroxyhexan-2-yl benzoate (14)



14

5-Azido-5-methylhexan-2-yl benzoate (52.3 mg, 0.20 mmol) and DMSO (28 μL, 0.40 mmol) were dissolved in *tert*-butylbenzene (1 mL, 0.2 M), and the mixture was stirred at room temperature under nitrogen. To the mixture, trifluoromethanesulfonic anhydride (66 μL, 0.40 mmol) was added dropwise over 1 min, allowing subsequent generation of white suspension and then light-yellow oil. After addition was over, the mixture was warmed up to 50 ˚C and stirred for additional 1 h. The reaction was quenched at 0 ℃ with saturated sodium bicarbonate aqueous solution, and the mixture was extracted with ethyl acetate to wash with saturated sodium bicarbonate aqueous solution, water and brine. The collected organic layer was dried over sodium sulfate, and was concentrated *in vacuo* to obtain crude material of methyl ketone product (via methyl group C–C bond migration). Because of its instability, reduction was performed. This crude material was re-dissolved in methanol (1 mL). After that, sodium borohydride (37.8 mg, 1.0 mmol) was added at 0 ℃. The resulting mixture was stirred for 1 h before being quenched with water. The mixture was extracted with ethyl acetate to wash with water. The organic layer was dried over sodium sulfate, and was concentrated *in vacuo* to obtain crude material. Analysis of crude material by ^{1}H NMR using 1,1,2,2-tetrachloroethane (21 μL, 0.20 mmol) as an internal standard proved that 5-hydroxyhexan-2-yl benzoate was formed in 25% yield. The crude material was purified by neutral silica gel column chromatography (hexane / ethyl acetate = 10 / 1 to 4 / 1) to afford 10.2 mg (23% over 2 steps) of the title compound as a light-yellow oil. (1:1 diastereomeric mixture).

Light-yellow oil; R_f value 0.20 (hexane / ethyl acetate = 4 / 1); IR (NaCl, neat) ν_{max} 3450, 2970, 2927, 1712, 1452, 1278, 1115, 1067, 1023 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05–8.03 (m,

2H), 7.57–7.54 (m, 1H), 7.46–7.42 (m, 2H), 5.23–5.15 (m, 1H), 3.88–3.81 (m, 1H), 1.90–1.66 (m, 2H), 1.62–1.49 (m, 3H), 1.36 (d, 3H, J = 6.5 Hz), 1.21 (d, 3H, J = 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.26, 166.22 (diastereomer), 132.8, 130.7, 129.5, 128.3, 71.6, 71.4 (diastereomer), 67.9, 67.8 (diastereomer), 35.0, 34.8 (diastereomer), 32.4, 32.2 (diastereomer), 23.6, 20.1; HRMS (DART) calcd for $C_{13}H_{19}O_3$ $[M+H]^+$ 223.1329, found 223.1326.

4.6 References

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CHAPTER 5 Summary

5.1 Summary of Chapters

Schmidt reaction refers to a chemical reaction wherein organic azides are incorporated to the electrophiles, such as carbonyl compounds, olefins, or alcohols to give rise to amines, nitrile, amides, or imines, involving unreactive C–H or C–C bond cleavage of organic azides. However, even with reactive molecules (carbonyl-α- or benzylic azides), the activation of azido groups requires severe reaction conditions such as the use of excess strong acids or elevated temperature. Because the Schmidt reaction generally requires carbon electrophile partners for unreactive bond cleavage activation in azide compounds, the final products may contain remaining unnecessary substituents from activators. With the limitations above, I report herein the "traceless" activation reaction of organic azides (traceless Schmidt reaction).

Inspired by the action of activated sulfoxide in interrupted Pummerer rearrangement, herein highly electrophile sulfonium ion would be the key species for activating the unreactive general alkyl azides. Upon reaction with this sulfonium ion, functionalization of alkyl azides could be possible via cleavage of a C–H (in primary and secondary substrates) or a C–C (in tertiary substrates) bond followed by 1,2-migration onto the nitrogen atom of azide, generating initial iminium cation intermediates connected with the sulfonium group. The key point of this traceless reaction is that the sulfonium group will not be a part of the final products because of the easily cleavable N-S bond in the intermediates.

Chapter 2 is dedicated to study the optimization of reaction conditions for the unreactive chemical bond cleavage by traceless Schmidt reaction. After investigation of sulfoxides, activators, solvents, temperature and equivalent of the reagents, highly

electrophilic sulfonium ion *in-situ* prepared from dimethyl sulfoxide (2 equiv.) and triflic anhydride (2 equiv.) is utilized. The established reaction conditions in *tert*-butylbenzene at room temperature promoted the cleavage and migration of α-hydrogen atom to the nitrogen atom of azides to give iminium cations, which were subjected to hydrolysis to obtain the corresponding aldehydes and ketones. The presence of iminium cation intermediate is proved by the ^{1}H NMR study, showing a broad peak of C–H aldiminium cation structure (a primary alkyl azide as model substrate). Various primary and secondary alkyl azides as well as diazide compound were successfully converted into the corresponding aldehydes and ketones in medium to excellent yields after hydrolysis of the corresponding iminium cations, respectively. This method allows general alkyl azides as substrates, which the precedented reports cannot convert even with harsh reaction conditions.

In Chapter 3, functionalization of *tert*-alkyl azides through unreactive C–C bond cleavage is presented, enabling the formation of the new carbon-nitrogen bonds. The treatment of *tert*-alkyl azides with *in-situ* prepared sulfonium ions allowed the desired substituent migration under moderate heating conditions without carbon electrophiles. *N*-alkyliminium cations of the 1,2-migration products were delivered to the corresponding substituent-removed ketones after hydrolysis and to the corresponding amines after reduction. This method also offers the ring-expanded aza-cyclic product through functionalization of unreactive C–C bond in cyclic *tert*-alkyl azide as well as ring-opening reaction. Selectivity on group migration is influenced by nature group characteristics as well as the orientation of migrating group and molecular nitrogen leaving group. The present method gives an alternative way to renovate general *tert*-alkyl azides via unreactive C–C bond cleavage in mild conditions, while previous examples are only available at reactive substrates such as azides attaching carbonyl group at α-position.

Taking into consideration of imines and related species as versatile synthones, one-pot nucleophilic addition is then examined in Chapter 4. Carbon nucleophiles such as organomagnesium reagent and trimethylsilyl cyanide (TMS-CN) for Strecker reaction were successfully incorporated to the generated iminium cation intermediates to access functional alkylamines and α-aminonitriles, respectively. The iminium cations generated by the established traceless Schmidt reaction were submitted to the reactions above in one pot. These one-pot reactions achieved further conversion of the iminium cation intermediates to useful building blocks such as alkylamine and α-aminonitrile derivatives containing tetrasubstituted carbon centers. As a further application of this reaction, inactive unfunctionalized hydrocarbon chain was modified through C–H azidation followed by C–C functionalization by the traceless Schmidt reaction to afford functionalized compound.

5.2 Concluding Remarks

Unreactive chemical bond cleavage reaction of organic azides have been successfully achieved through traceless Schmidt reaction utilizing sulfonium ion electrophile. C–H bond cleavage of primary or secondary alkyl azides, and C–C bond cleavage of tertiary alkyl azides proceeded smoothly to fashion iminium cation intermediates. These intermediates can be treated by three different conditions: (1) Aqueous workup for hydrolysis affording aldehydes (in primary alkyl azide cases) or ketones (in secondary and tertiary alkyl azide cases), (2) Reductive amination of the iminium cations of tertiary alkyl azides, giving secondary alkyl amine derivatives, (3) One-pot functionalization of iminium cations by carbon nucleophiles furnishing alkylamines and α-aminonitriles with interesting skeletal features. All of the products can be obtained without any trace of unnecessary moiety from sulfonium activator. Furthermore, combination of C–H azidation and C–C bond cleavage of

this traceless Schmidt reaction successfully modified the inactive hydrocarbon chain in the unfunctionalized compound.

In future, I hope this work on unreactive chemical bond cleavage of alkyl azides through traceless Schmidt reaction will be beneficial in the area synthetic chemistry especially the chemistry of heterocyclic compounds. I envision that a variety of nitrogen-containing heterocycles could be approached by this method through the further one-pot transformation of iminium cation intermediates. Moreover, remote aliphatic C–H azidation combined with these C–H or C–C bonds functionalization will provide great opportunities for the late-stage structural modification of natural products and drugs molecules, contributing rapidly in medicinal chemistry settings.

Acknowledgements

In the name of Allah, the Most Gracious, the Most Merciful. Praise be to the Lord of all worlds. Prayers and peace be upon the Prophet Muhammad ﷺ, his family, and all of his companions.

My sincere gratitude goes to Prof. Tsuyoshi Kawai as a Head of Photonic and Reactive Molecular Science Laboratory, and Prof. Kiyomi Kakiuchi as a former Head of Synthetic Organic Chemistry Laboratory. Both are excellent supervisors, giving me guidance and continuous support for this study.

I would like to express my deep appreciation and gratitude to my direct supervisor, Assoc. Prof. Hiroki Tanimoto (University of Toyama) for his continuous support, guidance, excellent discussion, and technical assistance during my study. I also wish to express my profound gratitude to Assoc. Prof. Tsumoru Morimoto for his continuous support especially during the difficult time of this study.

I would like to thank Prof. Hironari Kamikubo and Assoc. Prof. Takashi Matsuo as doctoral advisory committee members for their valuable discussion and suggestion. I also thank all the faculty staffs at Photonic and Reactive Molecular Science Laboratory, and lab's secretaries including our former secretary Ms. Hisayo Fujiki, for finest help and support especially during the difficult time of this study.

I thank Ms. Yoshiko Nishikawa for HRMS measurements and Mr. Shohei Katao for X-ray analysis. My thanks also goes to all past and present student members of our lab for their help, friendship, an enjoyable moment.

I would like to convey my utmost gratitude to my beloved parents, parents in law, my wife with my daughter, my brothers, and my sisters for their everlasting love and pray.

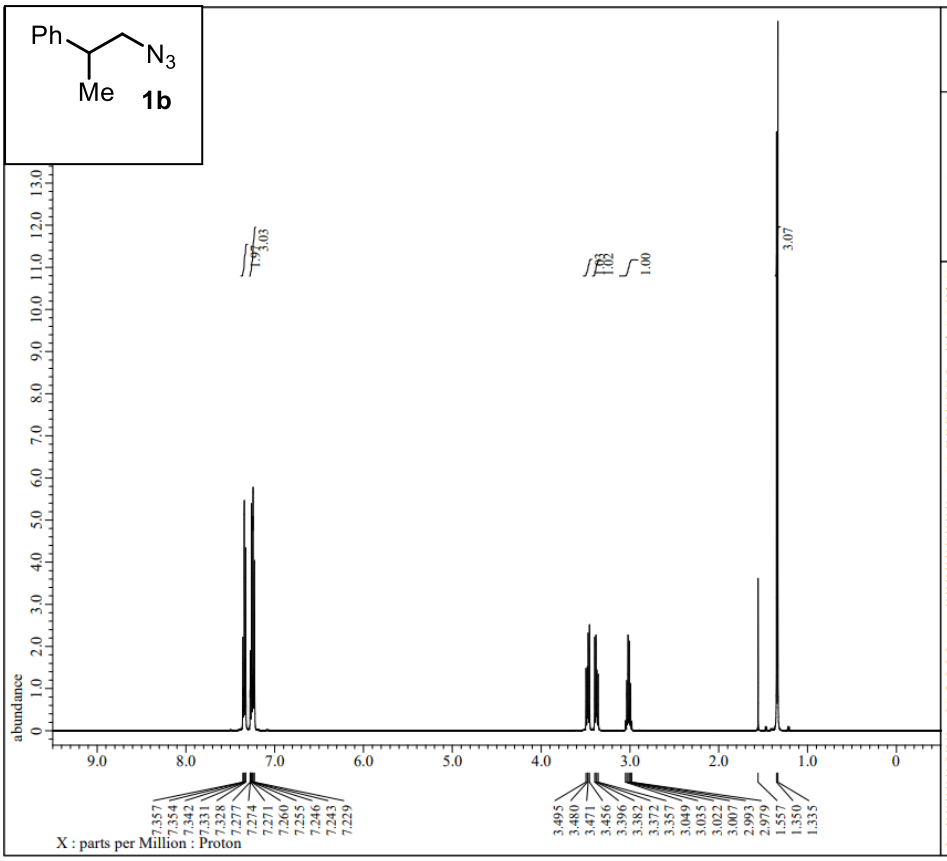
I am deeply appreciate Nara Institute of Science and Technology (NAIST) for providing financial support through NAIST International Scholarship for study and living in Japan.

I would also like to thank Universitas Indonesia for giving me permission to continue my study in Japan.

Supporting Information

[1] ^{1}H and ^{13}C NMR Spectra of Azide Substrates and the Products

[2] X-ray Structure of Compound 6h

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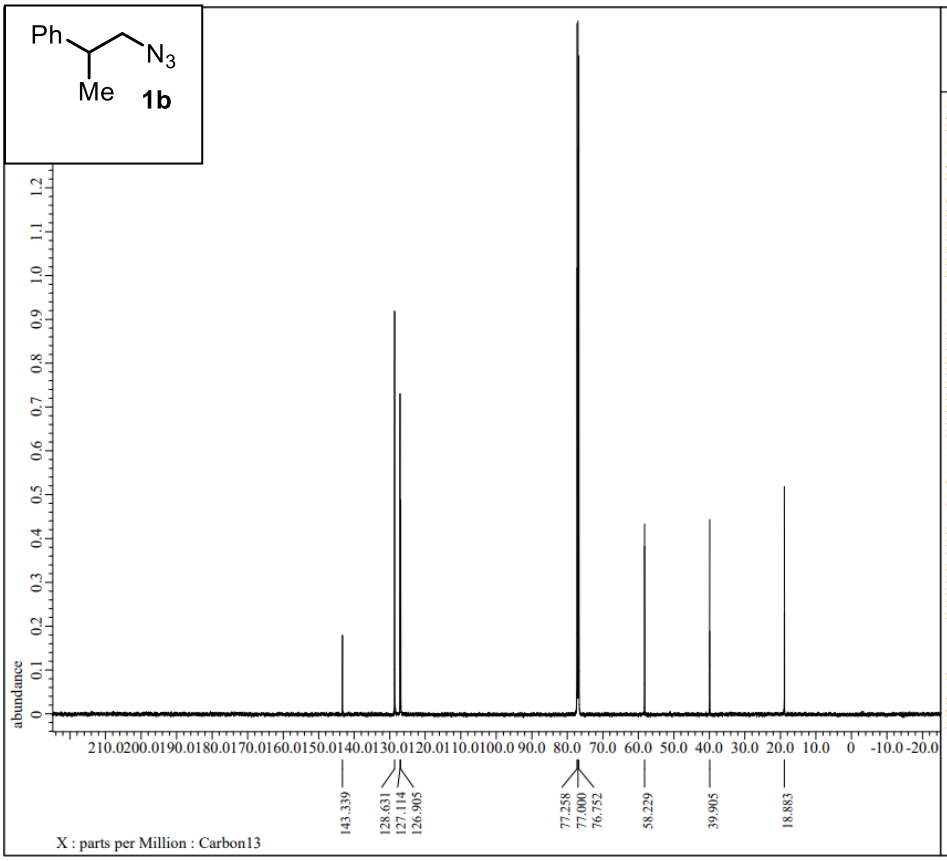


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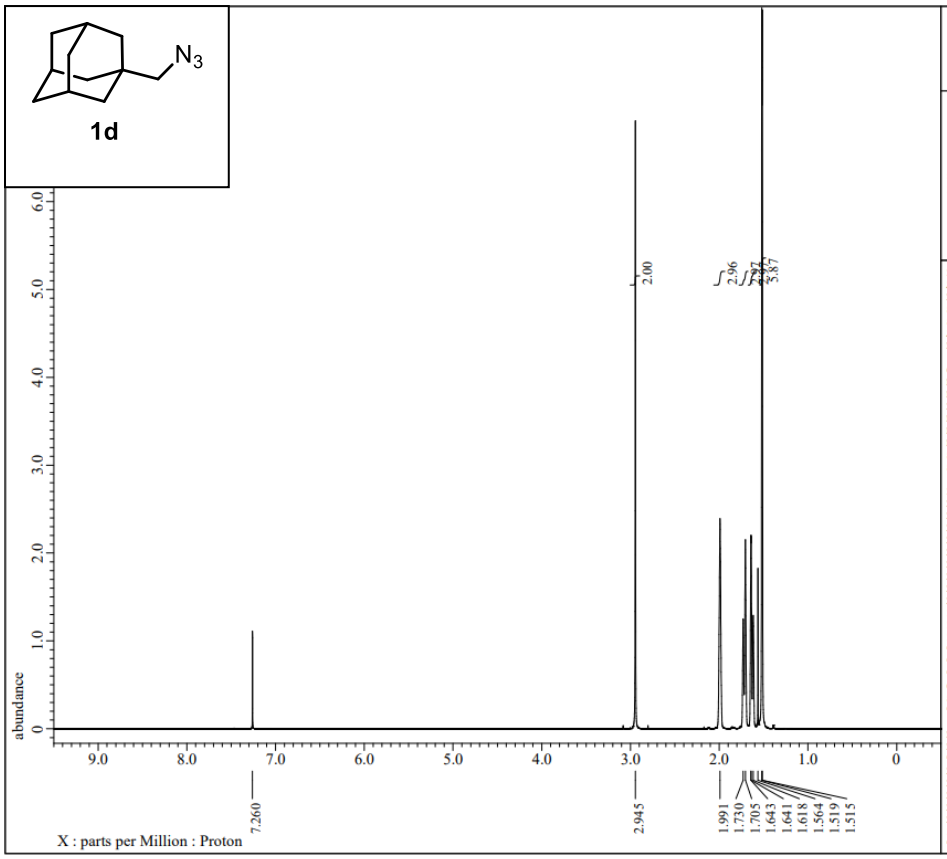


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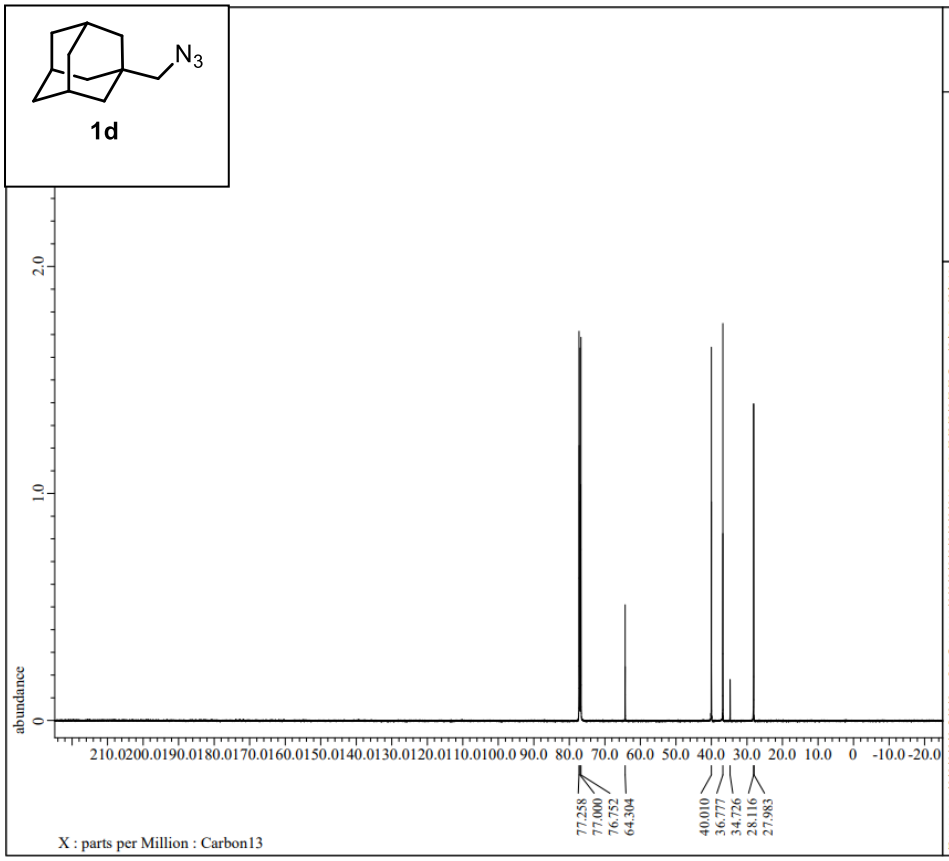


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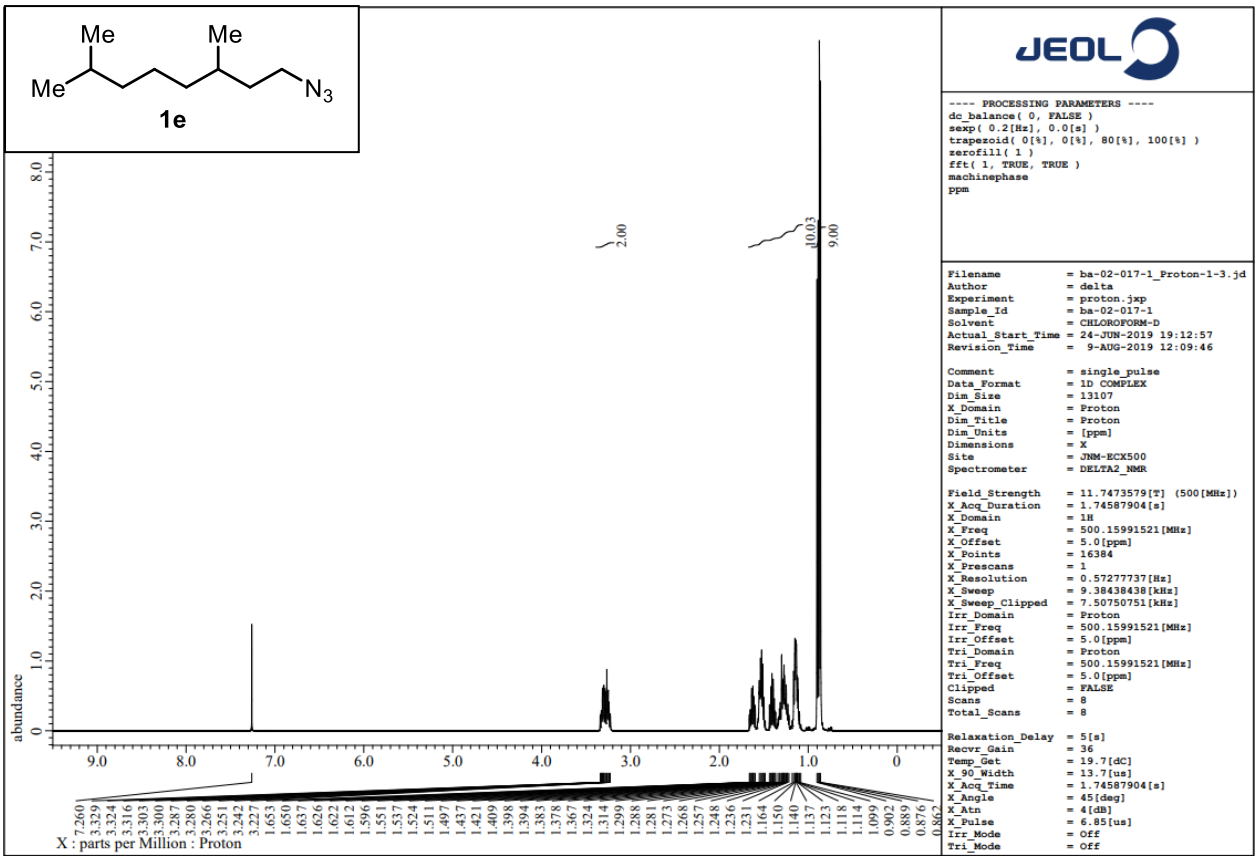


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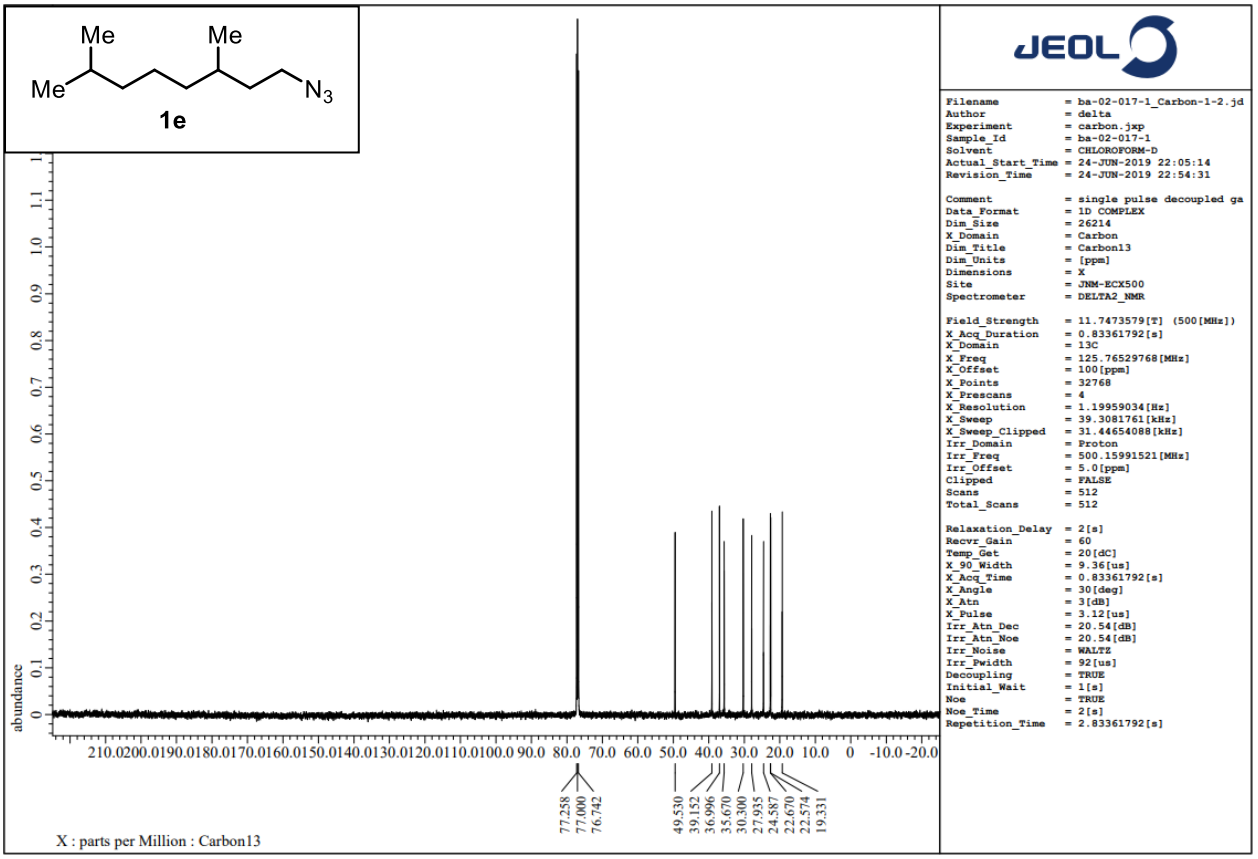


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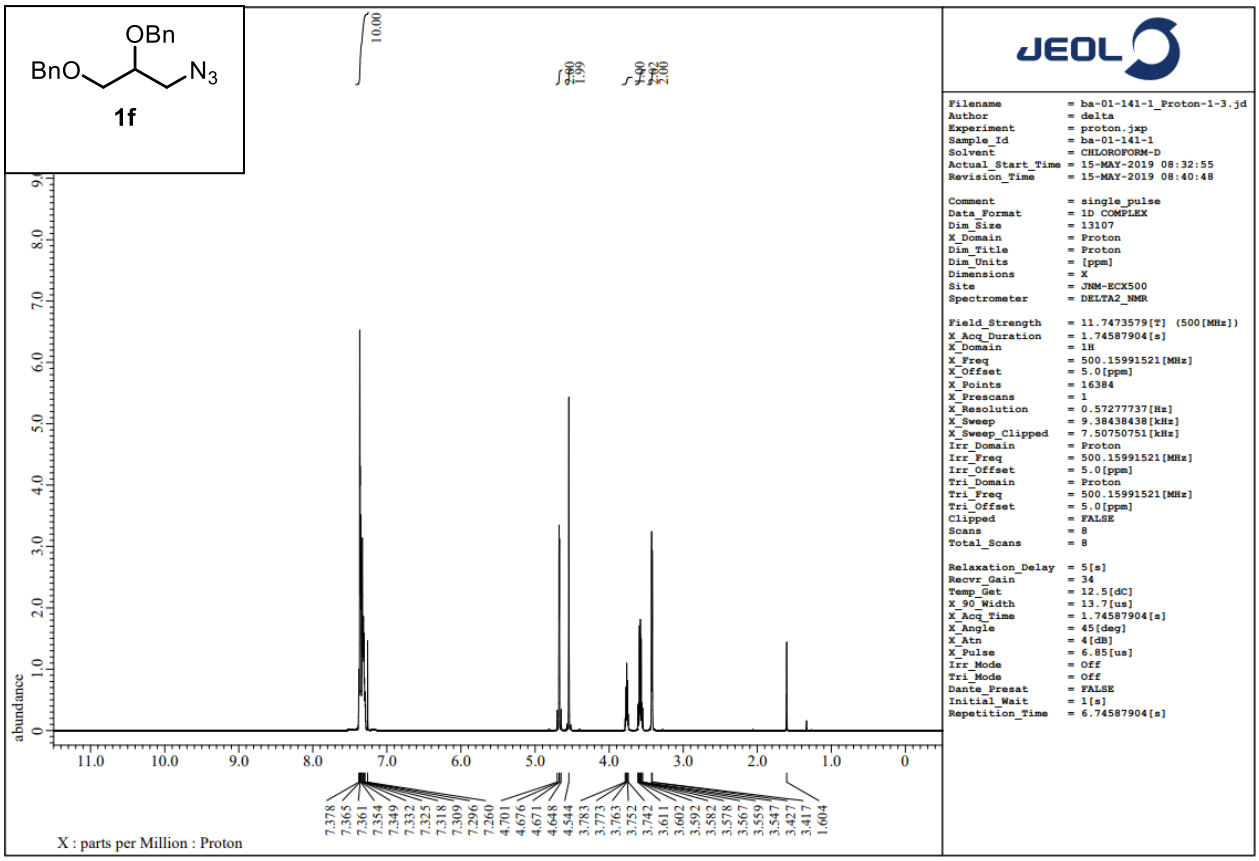
Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T]  (500[MHz])
X_Acq_Duration      = 0.83361792[s]
X_Domain            = 13C
X_Freq              = 125.76529768[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.19959034[Hz]
X_Sweep             = 39.3081761[kHz]
X_Sweep_Clipped     = 31.44654088[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 512
Total_Scans         = 512

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 20[dC]
X_90_Width          = 9.36[us]
X_Acq_Time          = 0.83361792[s]
X_Angle             = 30[deg]
X_Atn               = 3[dB]
X_Pulse             = 3.12[us]
Irr_Atn_Dec         = 20.54[dB]
Irr_Atn_Noe         = 20.54[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 92[us]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 2.83361792[s]
```

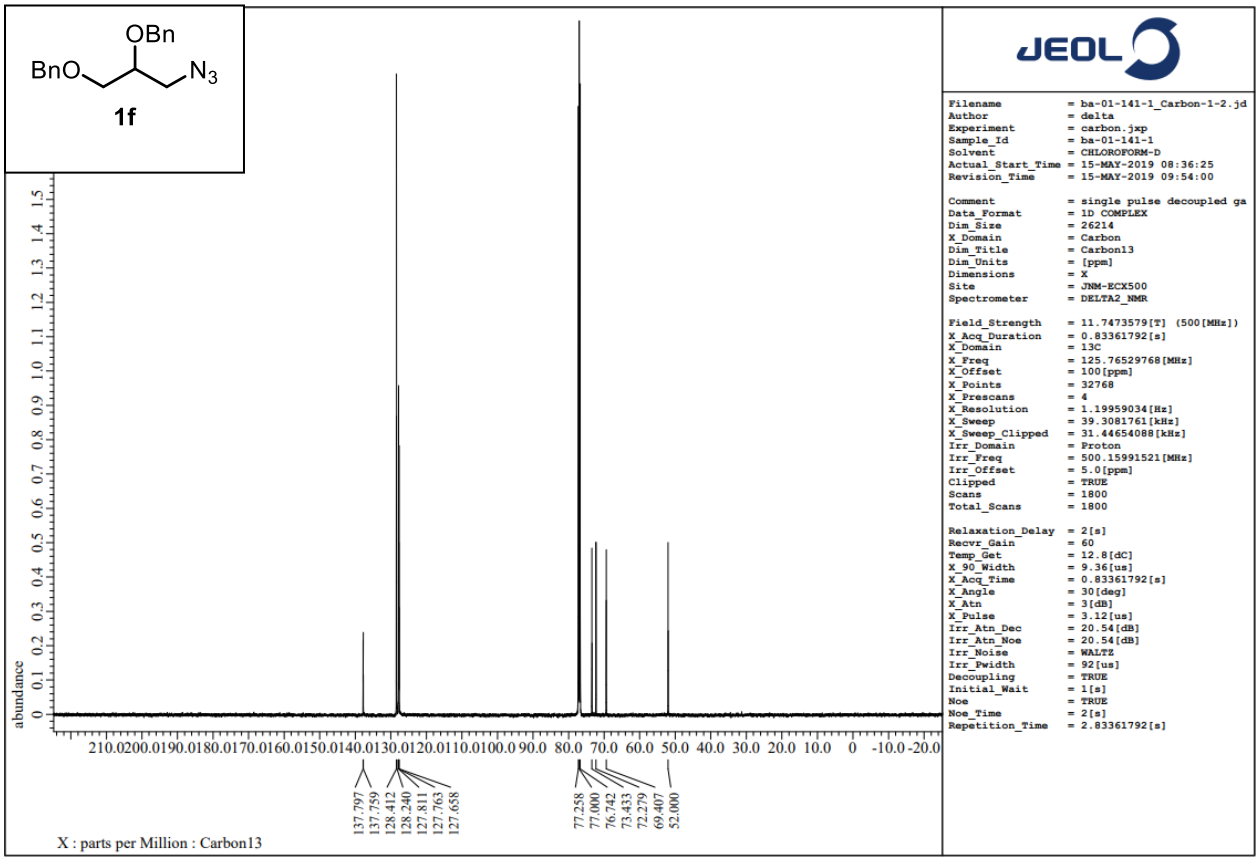



```
Filename          = ba-01-141-1_Proton-1-3.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-01-141-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 15-MAY-2019 08:32:55
Revision_Time     = 15-MAY-2019 08:40:48

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 34
Temp_Get          = 12.5[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

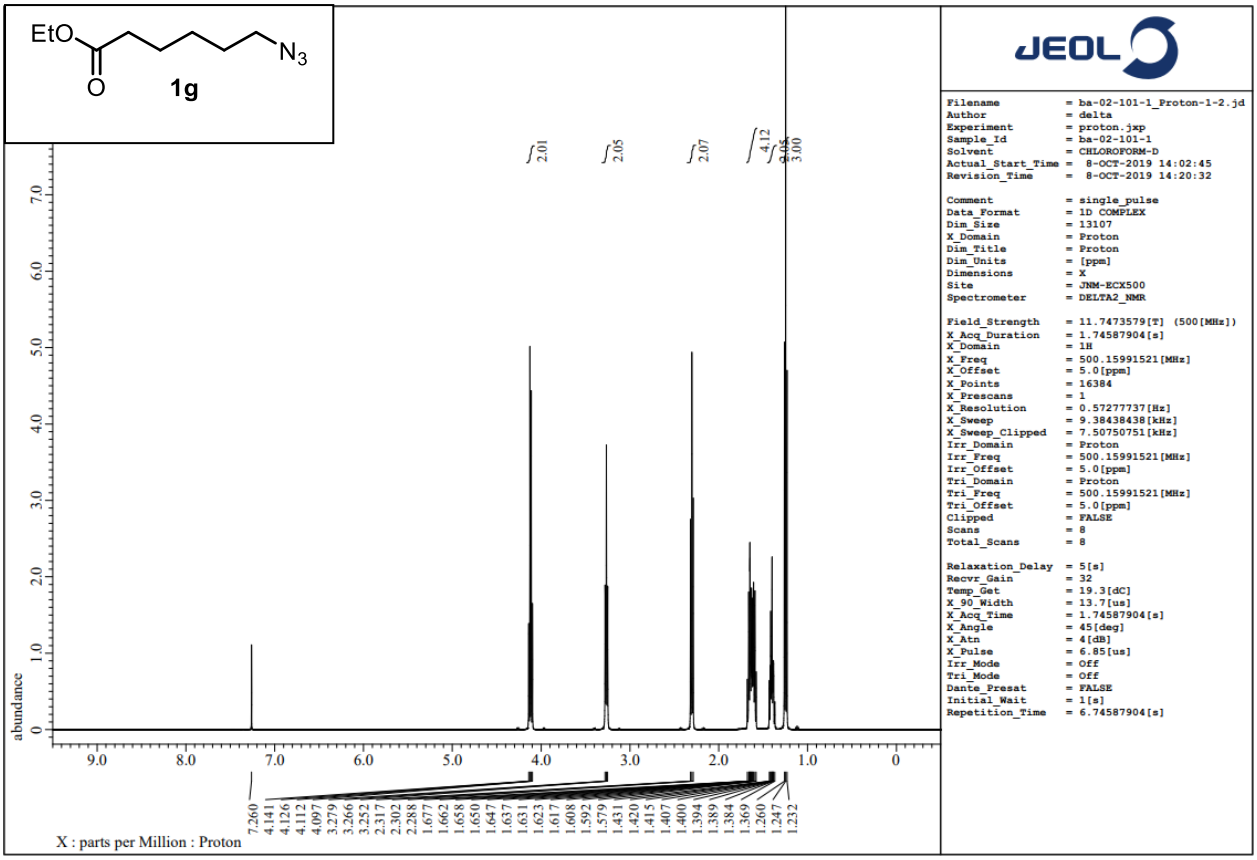


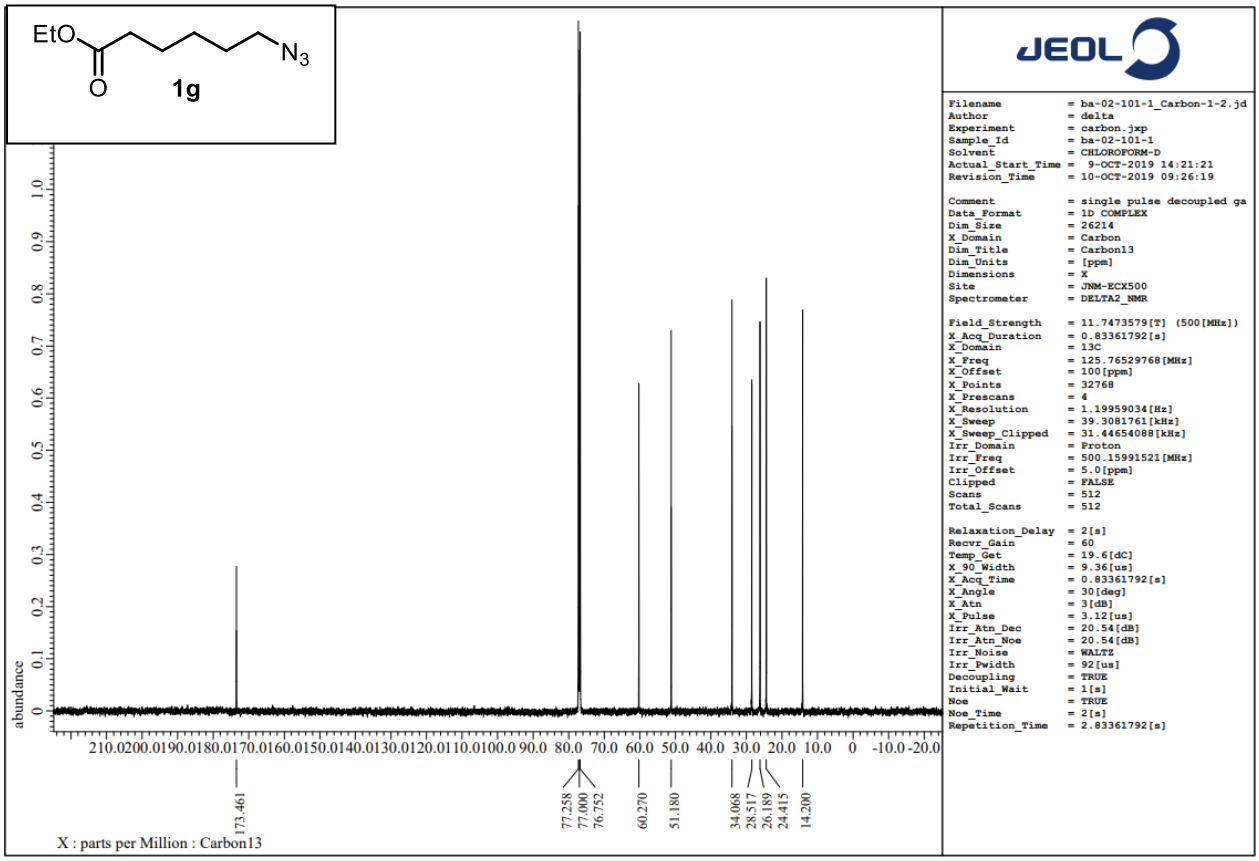

```
Filename          = ba-01-141-1_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-01-141-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 15-MAY-2019 08:36:25
Revision_Time     = 15-MAY-2019 09:54:00

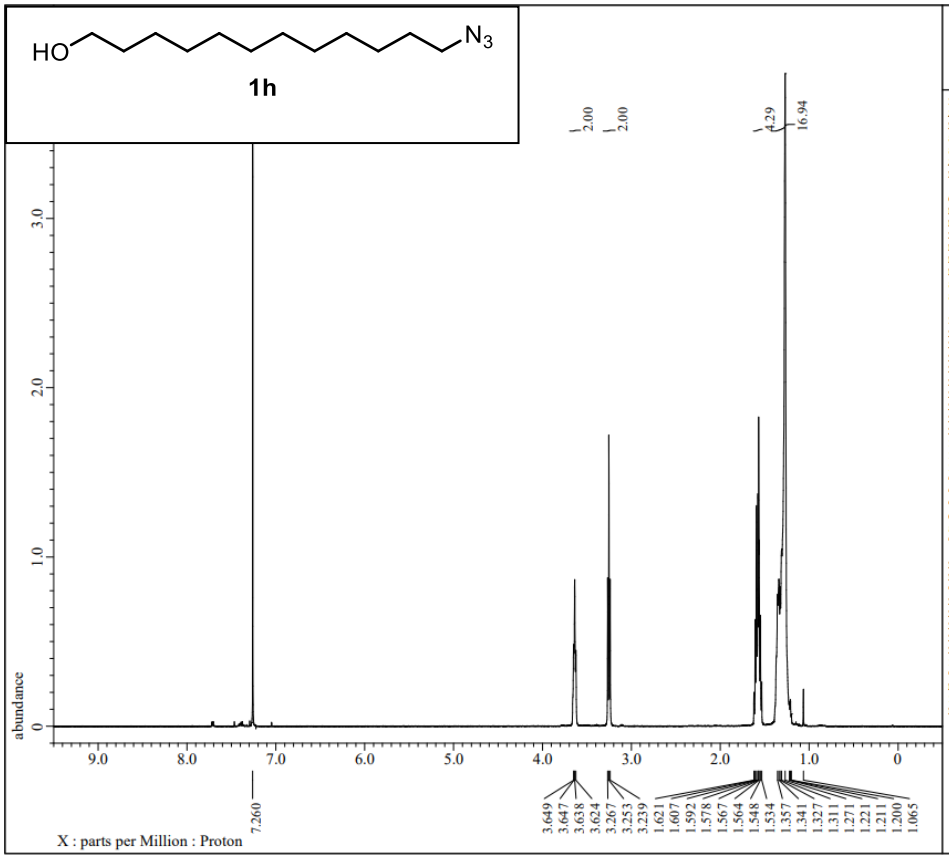
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = TRUE
Scans             = 1800
Total_Scans       = 1800

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 12.8[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


EtO
O
N3
1g
2.01
2.05
2.07
4.12
2.08
3.00
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
4.141
4.126
4.112
4.097
3.279
3.266
3.252
2.317
2.302
2.288
1.677
1.662
1.658
1.650
1.647
1.637
1.631
1.623
1.617
1.608
1.592
1.579
1.431
1.420
1.415
1.407
1.400
1.394
1.389
1.384
1.369
1.260
1.247
1.232
X : parts per Million : Proton
JEOL
Filename = ba-02-101-1_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-02-101-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 8-OCT-2019 14:02:45
Revision_Time = 8-OCT-2019 14:20:32
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 32
Temp_Get = 19.3[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


EtO
O
N3
1g
abundance
210.0200.0190.0180.0170.0160.0150.0140.0130.0120.0110.0100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
173.461
77.258
77.000
76.752
60.270
51.180
34.068
28.517
26.189
24.415
14.200
X : parts per Million : Carbon13
JEOL
Filename = ba-02-101-1_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-02-101-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 9-OCT-2019 14:21:21
Revision_Time = 10-OCT-2019 09:26:19
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 512
Total_Scans = 512
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 19.6[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

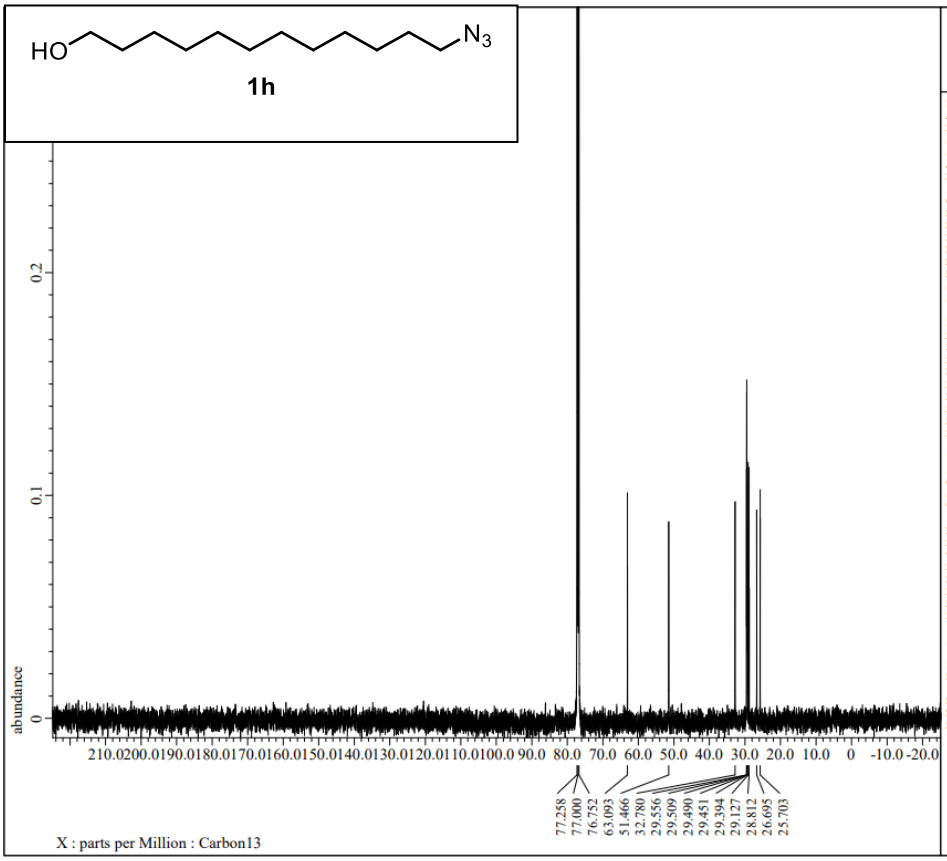



```
Filename          = ba-02-123-3_Proton-1-2.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-02-123-3
Solvent           = CHLOROFORM-D
Actual_Start_Time =  7-NOV-2019 14:07:29
Revision_Time     =  7-NOV-2019 14:05:38

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 42
Temp_Get          = 16.7[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

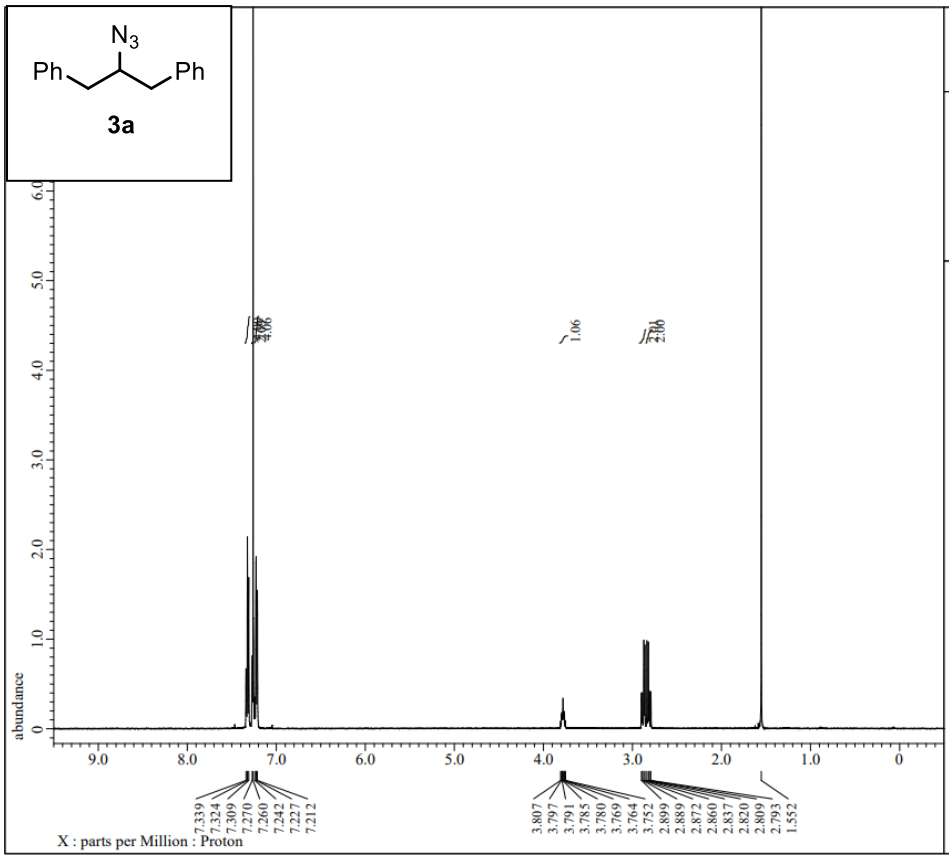



```
Filename          = ba-02-123-3_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-02-123-3
Solvent           = CHLOROFORM-D
Actual_Start_Time =  7-NOV-2019 21:31:19
Revision_Time     =  7-NOV-2019 22:10:20

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

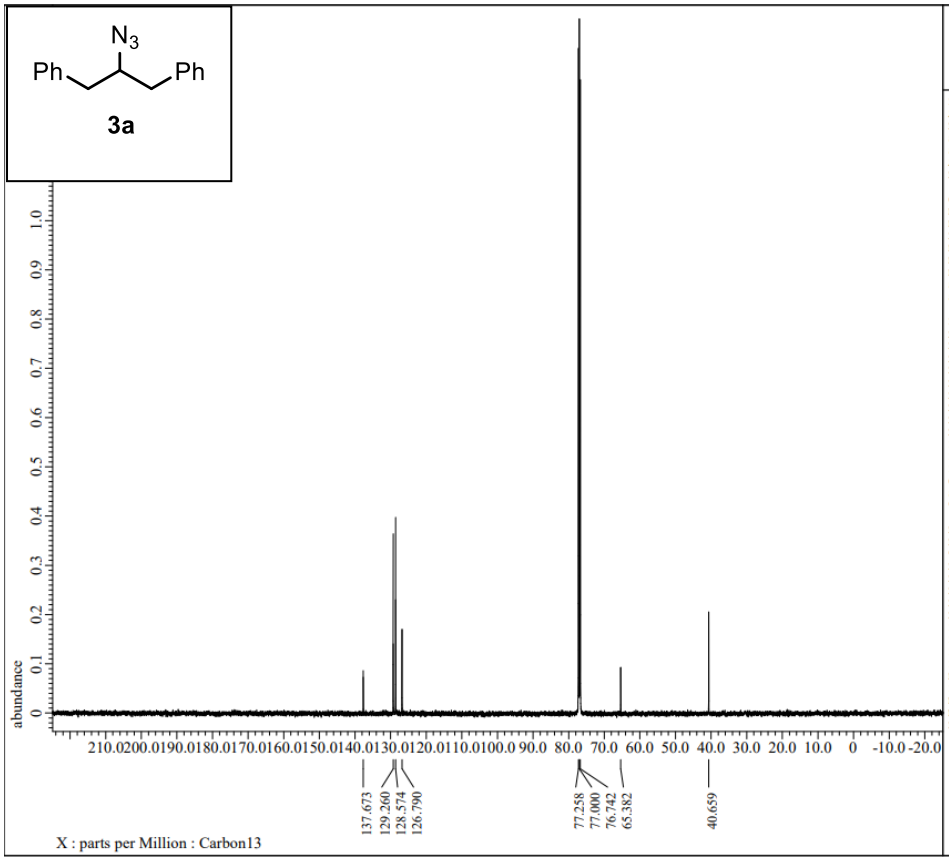
Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 17[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```



JEOL

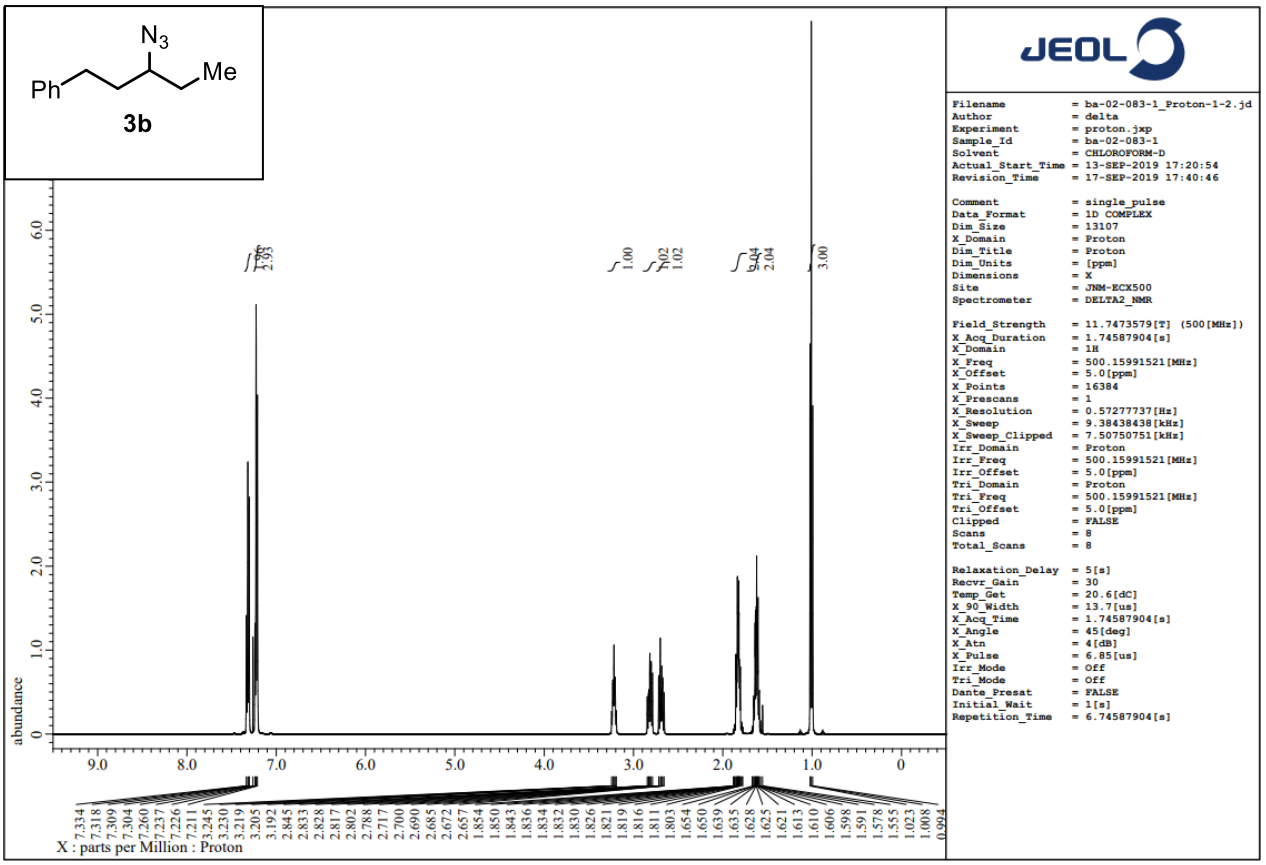
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

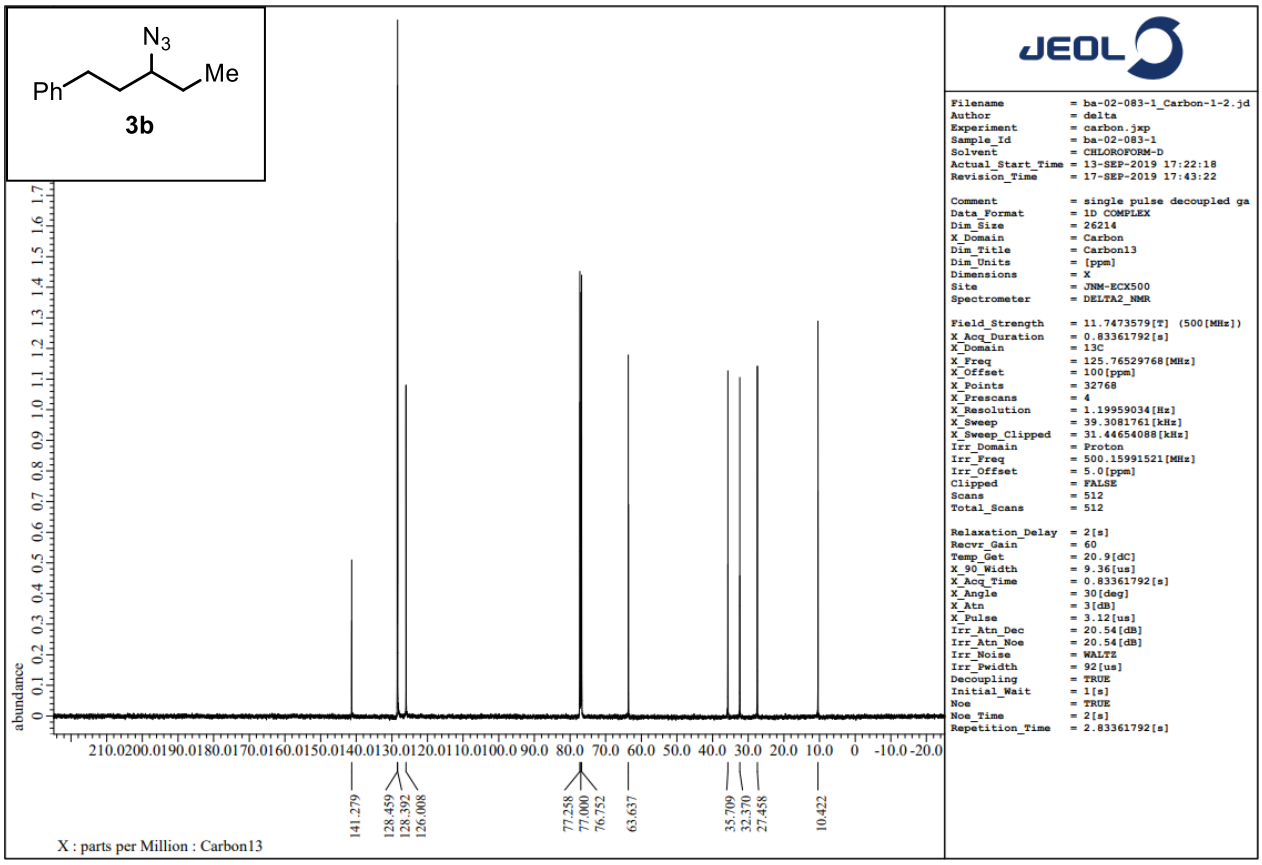
Filename	= ba-02-035-1-B_Proton-1-4.
Author	= delta
Experiment	= proton.jxp
Sample_Id	= ba-02-035-1-B
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 20-JUL-2019 01:00:27
Revision_Time	= 10-AUG-2019 13:06:21
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 13107
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECX500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.7473579[T] (500[MHz])
X_Acq_Duration	= 1.74587904[s]
X_Domain	= 1H
X_Freq	= 500.15991521[MHz]
X_Offset	= 5.0[ppm]
X_Points	= 16384
X_Prescans	= 1
X_Resolution	= 0.57277737[Hz]
X_Sweep	= 9.38438438[kHz]
X_Sweep_Clipped	= 7.50750751[kHz]
Irr_Domain	= Proton
Irr_Freq	= 500.15991521[MHz]
Irr_Offset	= 5.0[ppm]
Tri_Domain	= Proton
Tri_Freq	= 500.15991521[MHz]
Tri_Offset	= 5.0[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 48
Temp_Get	= 20.6[dC]
X_90_Width	= 13.7[us]
X_Acq_Time	= 1.74587904[s]
X_Angle	= 45[deg]
X_Atn	= 4[dB]
X_Pulse	= 6.85[us]
Irr_Mode	= Off
Tri_Mode	= Off

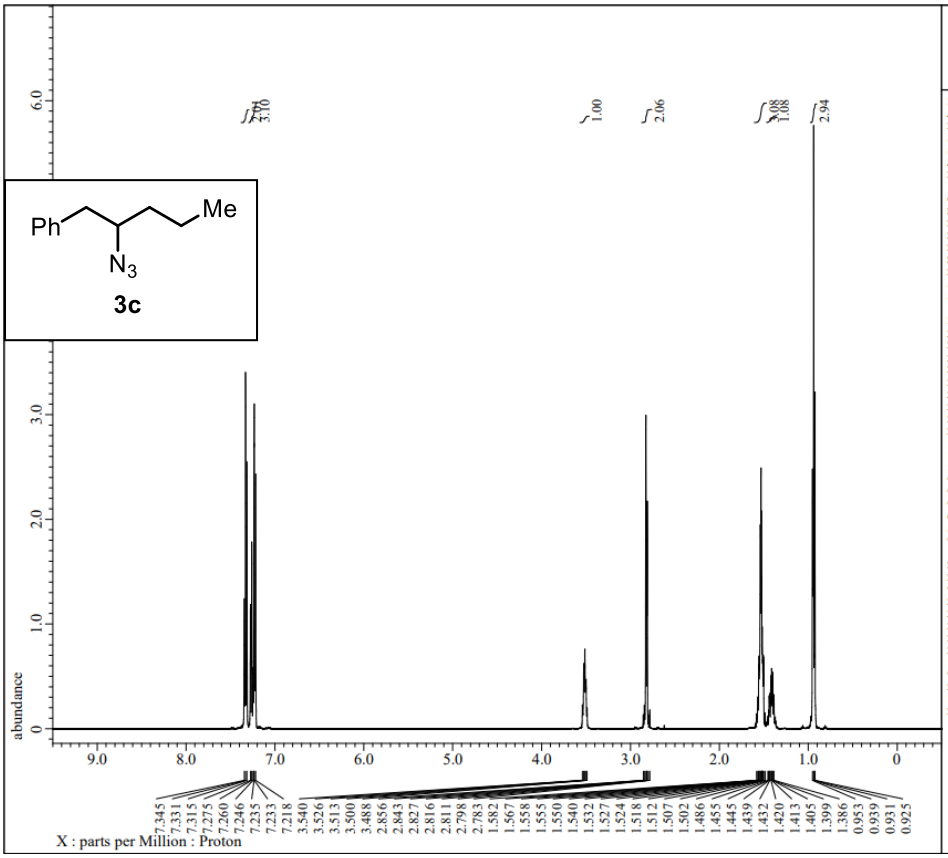


JEOL

Filename	= ba-02-035-1-B_Carbon-1-2.
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= ba-02-035-1-B
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 22-JUL-2019 11:05:31
Revision_Time	= 22-JUL-2019 15:43:59
Comment	= single pulse decoupled ga
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Carbon
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECX500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.7473579[T] (500[MHz])
X_Acq_Duration	= 0.83361792[s]
X_Domain	= 13C
X_Freq	= 125.76529768[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 1.19959034[Hz]
X_Sweep	= 39.3081761[kHz]
X_Sweep_Clipped	= 31.44654088[kHz]
Irr_Domain	= Proton
Irr_Freq	= 500.15991521[MHz]
Irr_Offset	= 5.0[ppm]
Clipped	= FALSE
Scans	= 1024
Total_Scans	= 1024
Relaxation_Delay	= 2[s]
Recvr_Gain	= 60
Temp_Get	= 21.8[dC]
X_90_Width	= 9.36[us]
X_Acq_Time	= 0.83361792[s]
X_Angle	= 30[deg]
X_Atn	= 3[dB]
X_Pulse	= 3.12[us]
Irr_Atn_Dec	= 20.54[dB]
Irr_Atn_Noe	= 20.54[dB]
Irr_Noise	= WALTZ
Irr_Pwidth	= 92[us]
Decoupling	= TRUE
Initial_Wait	= 1[s]
Noe	= TRUE
Noe_Time	= 2[s]
Repetition_Time	= 2.83361792[s]


N3
Ph
Me
3b
abundance
X : parts per Million : Proton
Filename = ba-02-083-1_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-02-083-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 13-SEP-2019 17:20:54
Revision_Time = 17-SEP-2019 17:40:46
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 30
Temp_Get = 20.6[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


N3
Ph
Me
3b
abundance
X : parts per Million : Carbon13
141.279
128.459
128.392
126.008
77.258
77.000
76.752
63.637
35.709
32.370
27.458
10.422
Filename = ba-02-083-1_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-02-083-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 13-SEP-2019 17:22:18
Revision_Time = 17-SEP-2019 17:43:22
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 512
Total_Scans = 512
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 20.9[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

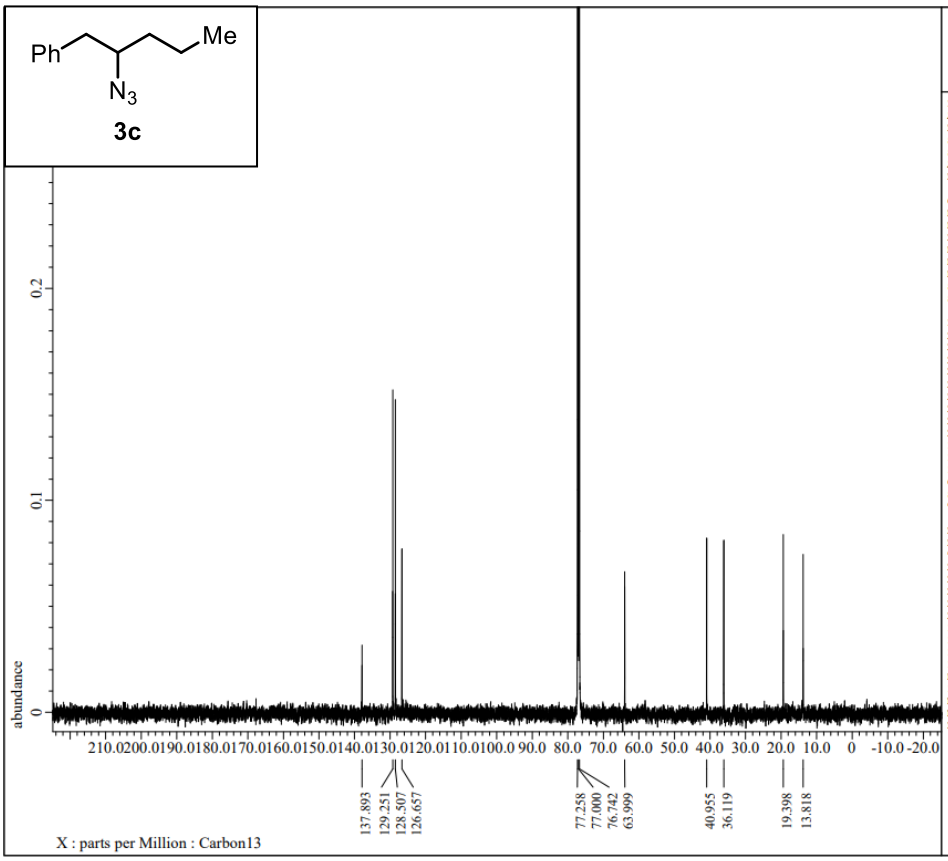



```
Filename          = ba-03-014-1_Proton-1-2.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-03-014-1
Solvent           = CHLOROFORM-D
Actual_Start_Time =  8-JAN-2020 13:32:00
Revision_Time     =  8-JAN-2020 13:25:41

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 32
Temp_Get          = 15.8[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

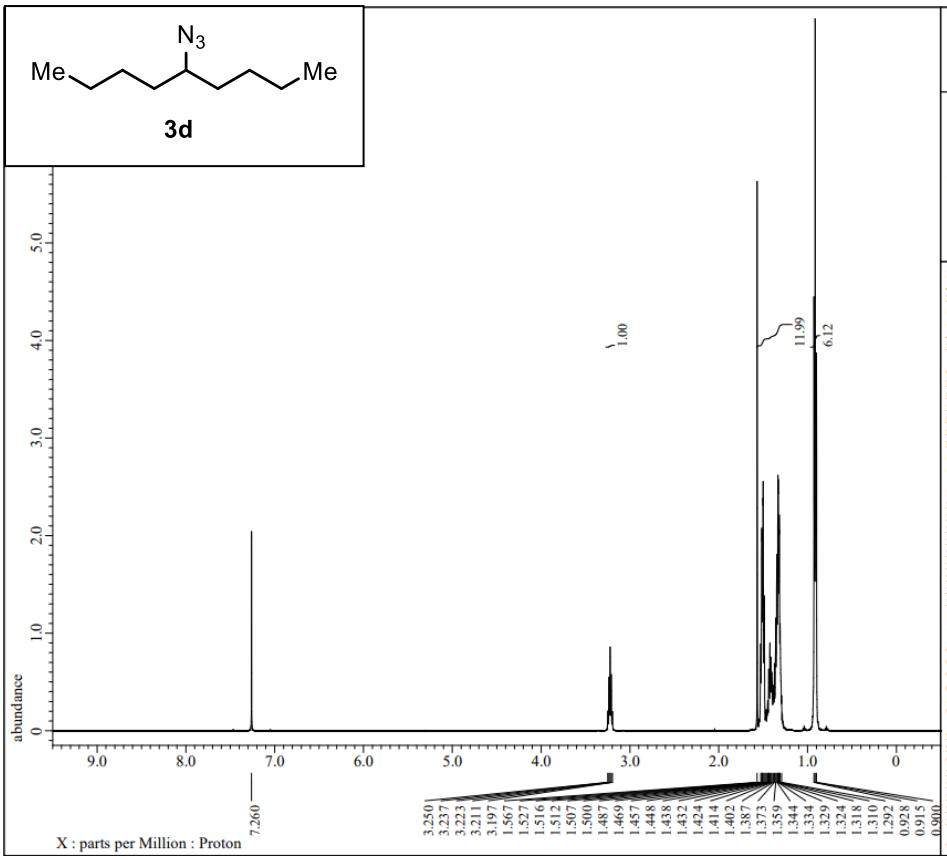



```
Filename          = ba-03-010-B-3_Carbon-1-2.
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-03-010-B-3
Solvent           = CHLOROFORM-D
Actual_Start_Time = 25-DEC-2019 22:57:46
Revision_Time     = 26-DEC-2019 00:32:39

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

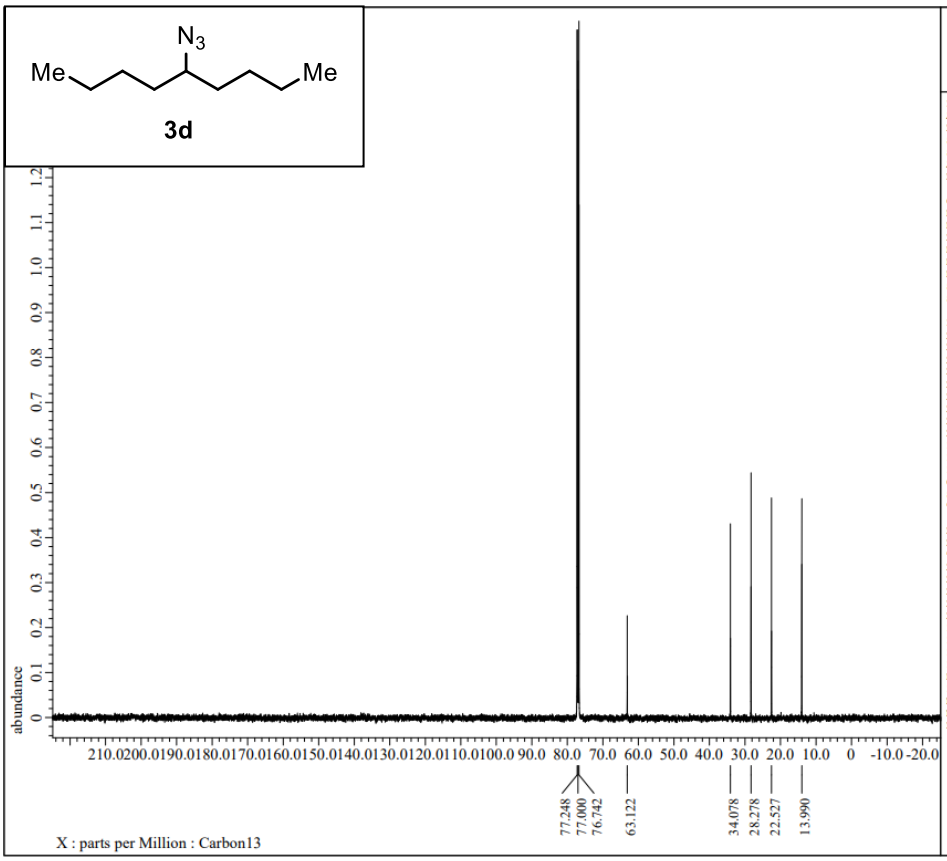
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 15.6[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

Filename	= ba-02-013-1_Proton-1-3.jd
Author	= delta
Experiment	= proton.jxp
Sample_Id	= ba-02-013-1
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 17-JUN-2019 17:51:22
Revision_Time	= 9-AUG-2019 13:27:55
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 13107
X_Domain	= Proton
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECX500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.7473579[T] (500[MHz])
X_Acq_Duration	= 1.74587904[s]
X_Domain	= 1H
X_Freq	= 500.15991521[MHz]
X_Offset	= 5.0[ppm]
X_Points	= 16384
X_Prescans	= 1
X_Resolution	= 0.57277737[Hz]
X_Sweep	= 9.38438438[kHz]
X_Sweep_Clipped	= 7.50750751[kHz]
Irr_Domain	= Proton
Irr_Freq	= 500.15991521[MHz]
Irr_Offset	= 5.0[ppm]
Tri_Domain	= Proton
Tri_Freq	= 500.15991521[MHz]
Tri_Offset	= 5.0[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 40
Temp_Get	= 18.5[dC]
X_90_Width	= 13.7[us]
X_Acq_Time	= 1.74587904[s]
X_Angle	= 45[deg]
X_Atn	= 4[dB]
X_Pulse	= 6.85[us]
Irr_Mode	= Off
Tri_Mode	= Off

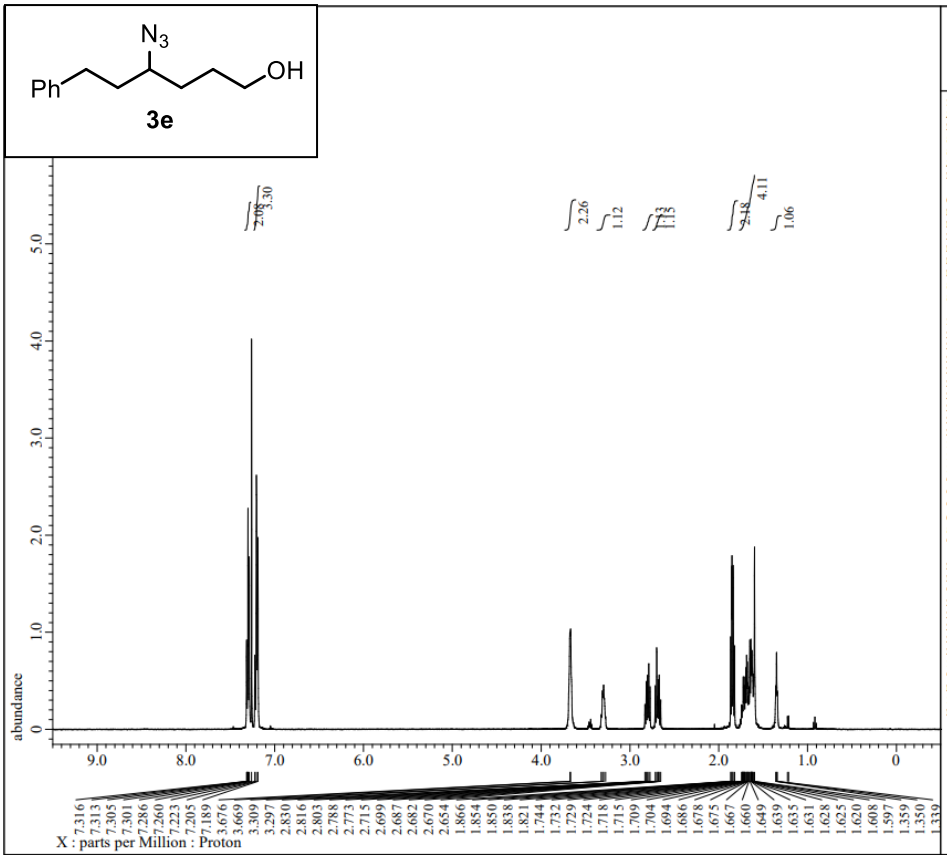



```
Filename          = ba-02-013-1_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-02-013-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 17-JUN-2019 18:20:09
Revision_Time     = 18-JUN-2019 18:46:27

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 512
Total_Scans       = 512

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 18.8[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```

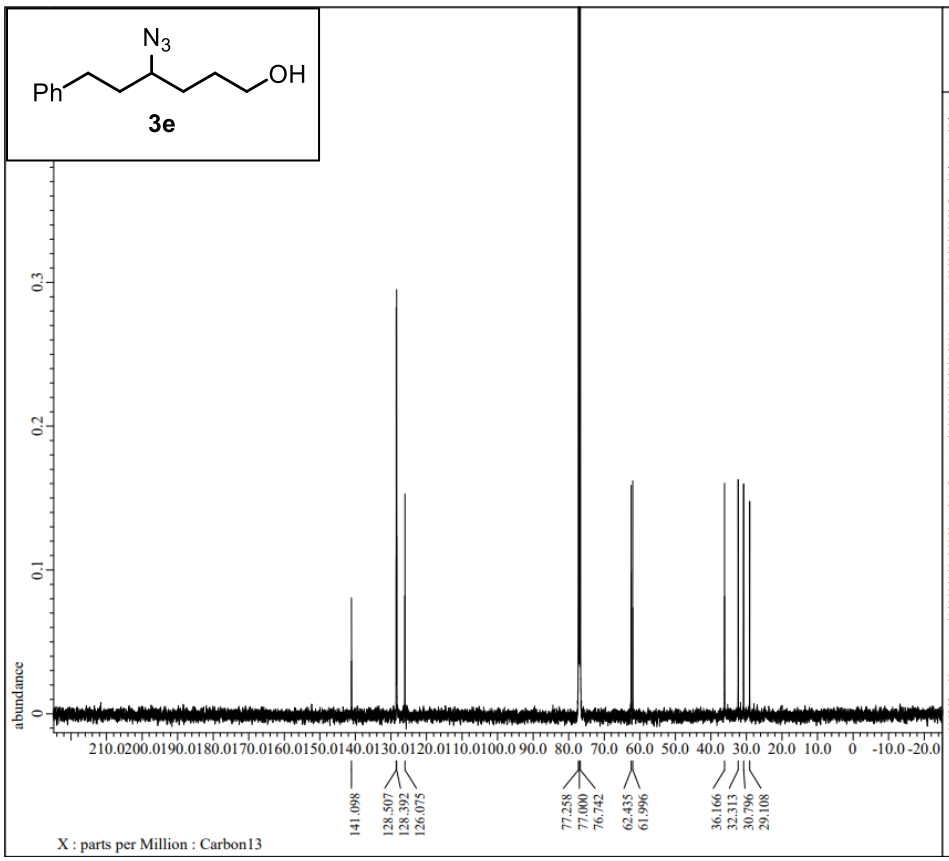



```
Filename          = ba-02-131-1_Proton-1-3.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-02-131-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 18-NOV-2019 10:59:49
Revision_Time     = 27-DEC-2019 15:44:12

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 42
Temp_Get          = 15.9[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

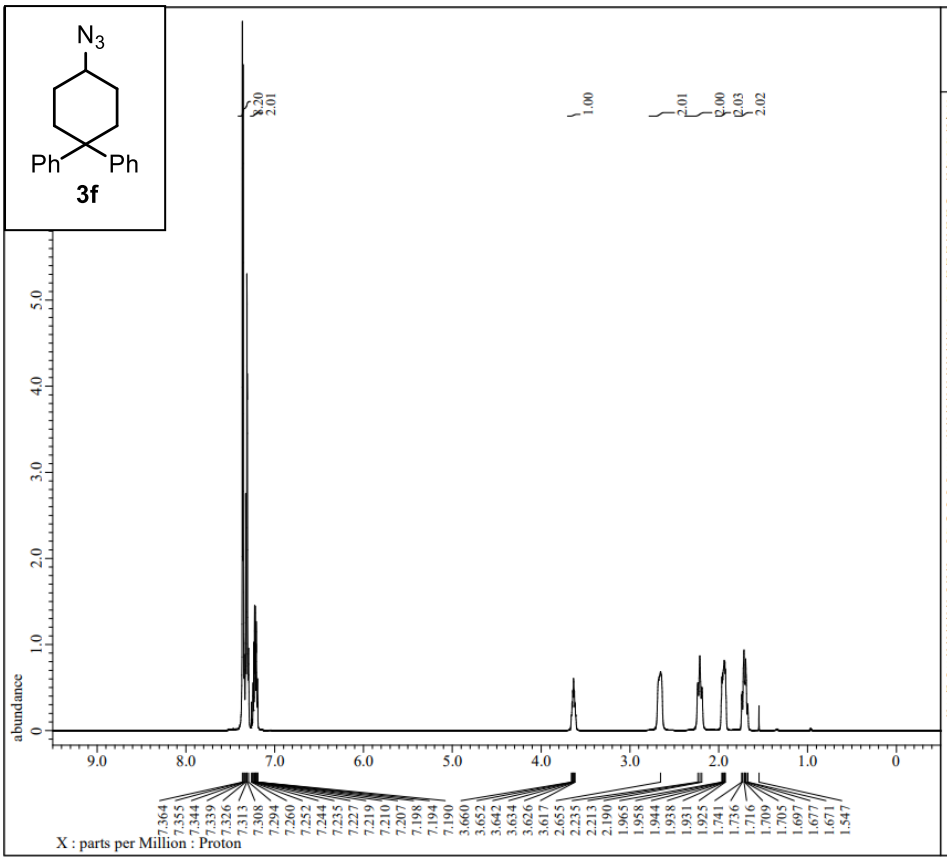



```
Filename          = ba-02-131-1_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-02-131-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 18-NOV-2019 19:22:25
Revision_Time     = 19-NOV-2019 00:17:35

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 17.3[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```

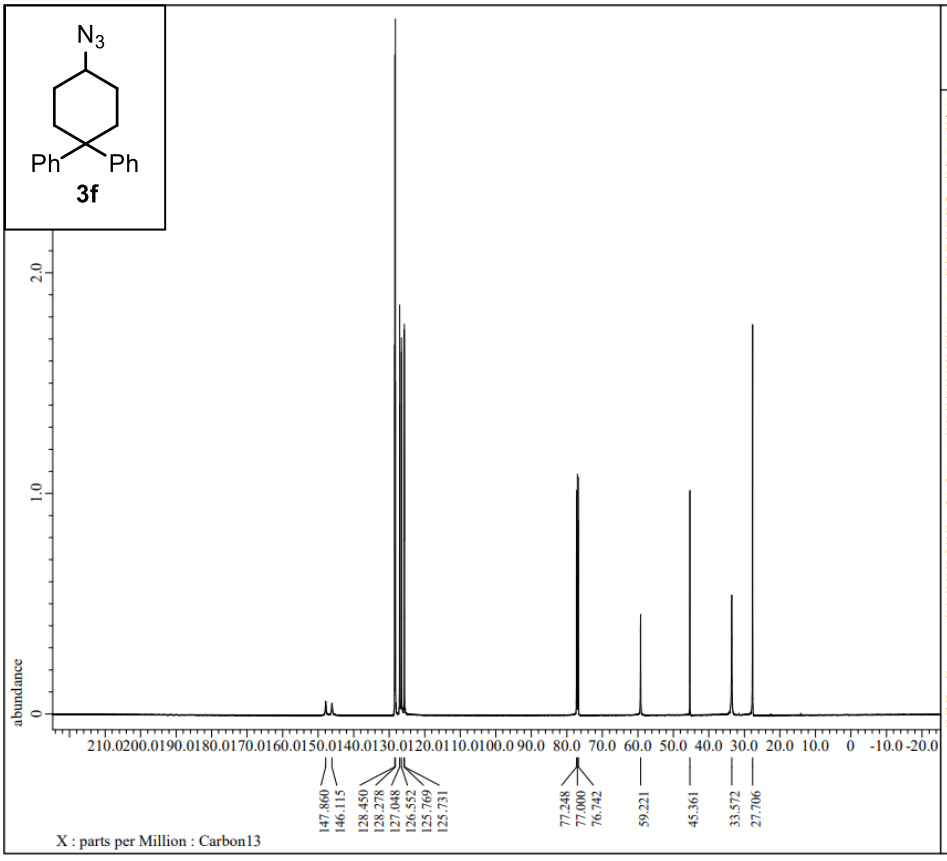



```
Filename          = ba-03-007-2_Proton-1-2.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-03-007-2
Solvent           = CHLOROFORM-D
Actual_Start_Time = 24-DEC-2019 22:34:37
Revision_Time     = 25-DEC-2019 10:54:23

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 22
Temp_Get          = 14.9[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

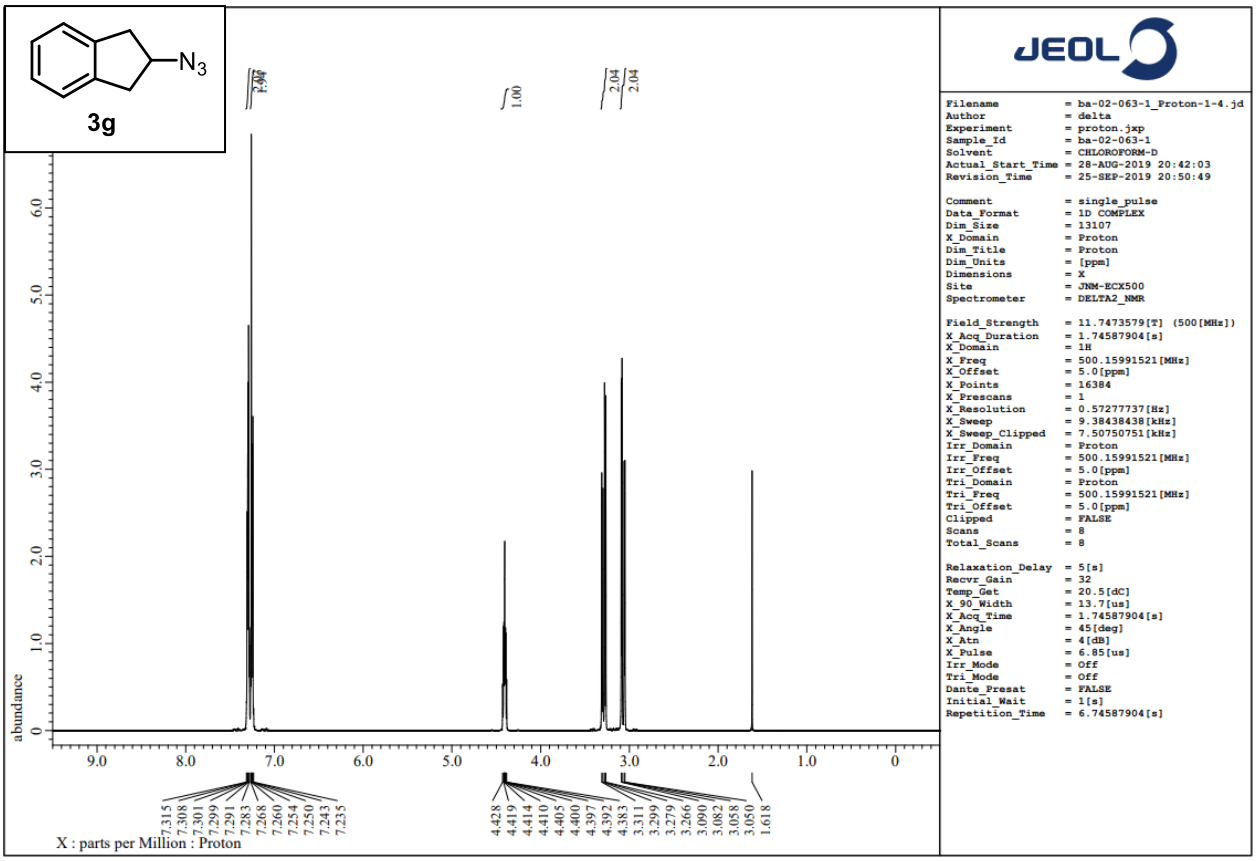


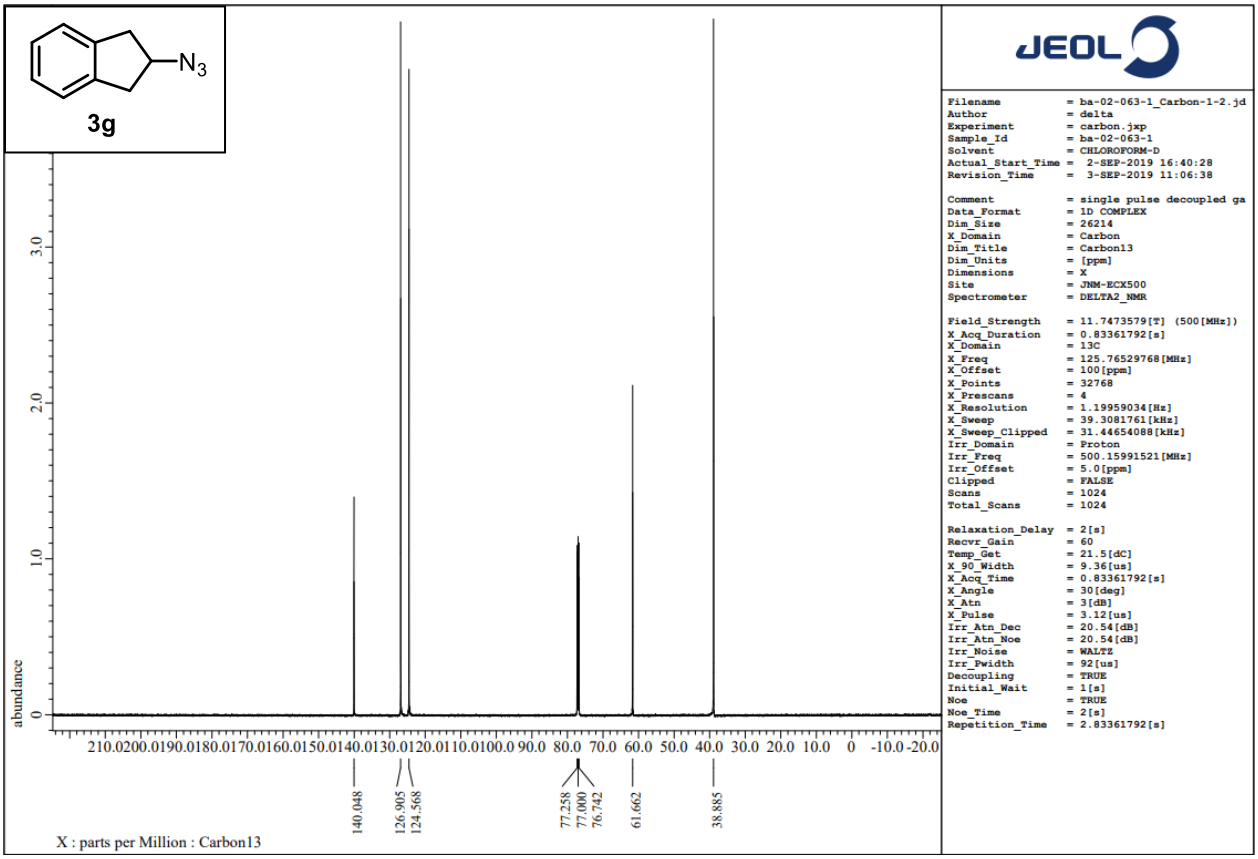

```
Filename          = ba-03-007-2_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-03-007-2
Solvent           = CHLOROFORM-D
Actual_Start_Time = 24-DEC-2019 22:36:01
Revision_Time     = 25-DEC-2019 09:17:43

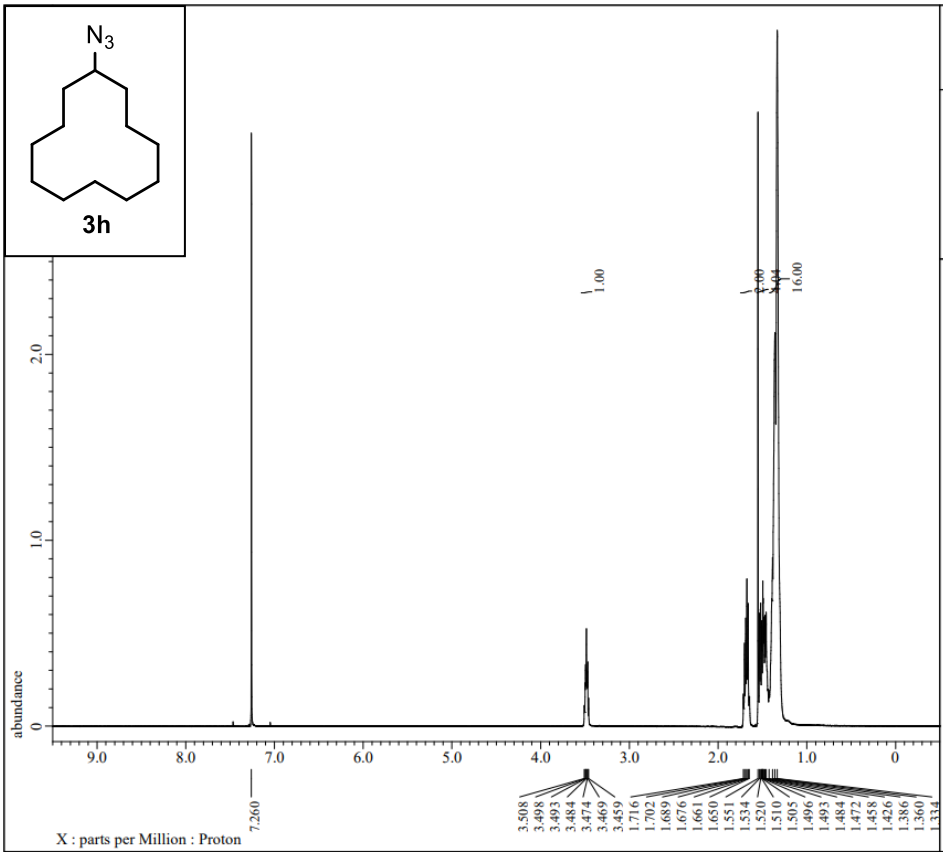
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 12000
Total_Scans       = 12000

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 15.6[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


N3
3g
1.00
2.04
2.04
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.315
7.308
7.301
7.299
7.291
7.283
7.268
7.260
7.254
7.250
7.243
7.235
4.428
4.419
4.414
4.410
4.405
4.400
4.397
4.392
4.383
3.311
3.299
3.279
3.266
3.090
3.082
3.058
3.050
1.618
X : parts per Million : Proton
JEOL
Filename = ba-02-063-1_Proton-1-4.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-02-063-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 28-AUG-2019 20:42:03
Revision_Time = 25-SEP-2019 20:50:49
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 32
Temp_Get = 20.5[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


N3
3g
abundance
210.0200.0190.0180.0170.0160.0150.0140.0130.0120.0110.0100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
140.048
126.905
124.568
77.258
77.000
76.742
61.662
38.885
X : parts per Million : Carbon13
JEOL
Filename = ba-02-063-1_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-02-063-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 2-SEP-2019 16:40:28
Revision_Time = 3-SEP-2019 11:06:38
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.5[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]



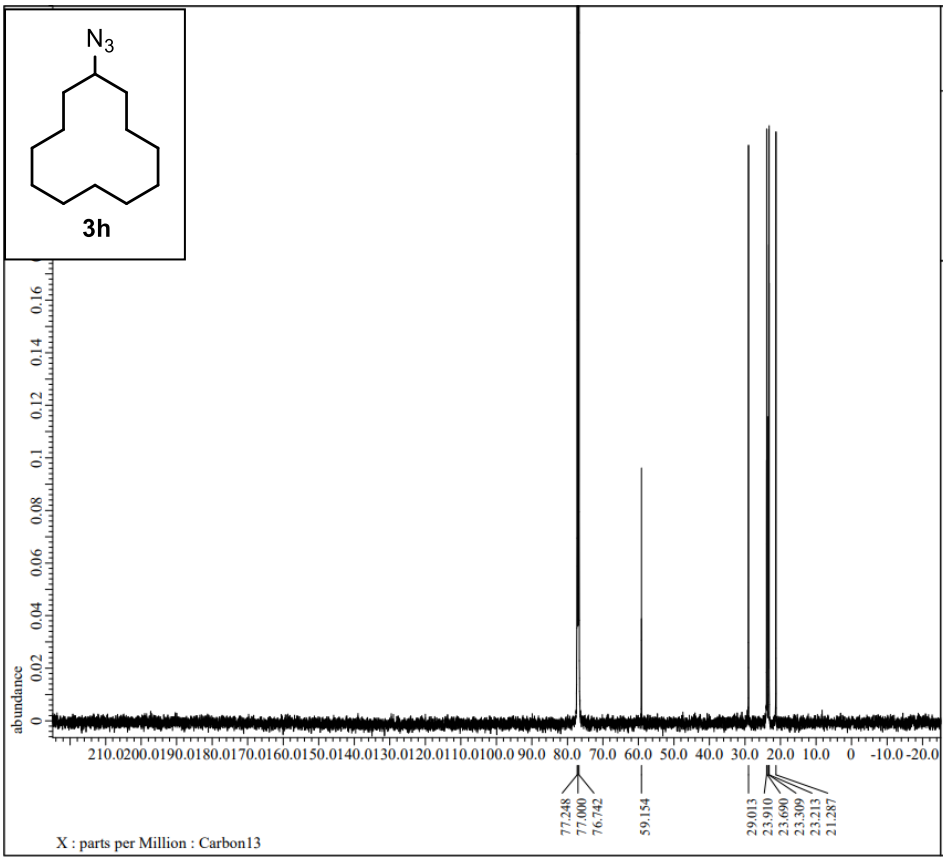

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = ba-02-023-2_Proton-1-3-2.
Author              = delta
Experiment          = proton.jxp
Sample_Id           = ba-02-023-2
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  3-JUL-2019 00:17:12
Revision_Time       = 10-AUG-2019 12:12:58

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 1.74587904[s]
X_Domain            = 1H
X_Freq              = 500.15991521[MHz]
X_Offset            = 5.0[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.57277737[Hz]
X_Sweep             = 9.38438438[kHz]
X_Sweep_Clipped     = 7.50750751[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Tri_Domain          = Proton
Tri_Freq            = 500.15991521[MHz]
Tri_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 42
Temp_Get            = 19.9[dC]
X_90_Width          = 13.7[us]
X_Acq_Time          = 1.74587904[s]
X_Angle             = 45[deg]
X_Atn               = 4[dB]
X_Pulse             = 6.85[us]
Irr_Mode            = Off
Tri_Mode            = Off
```



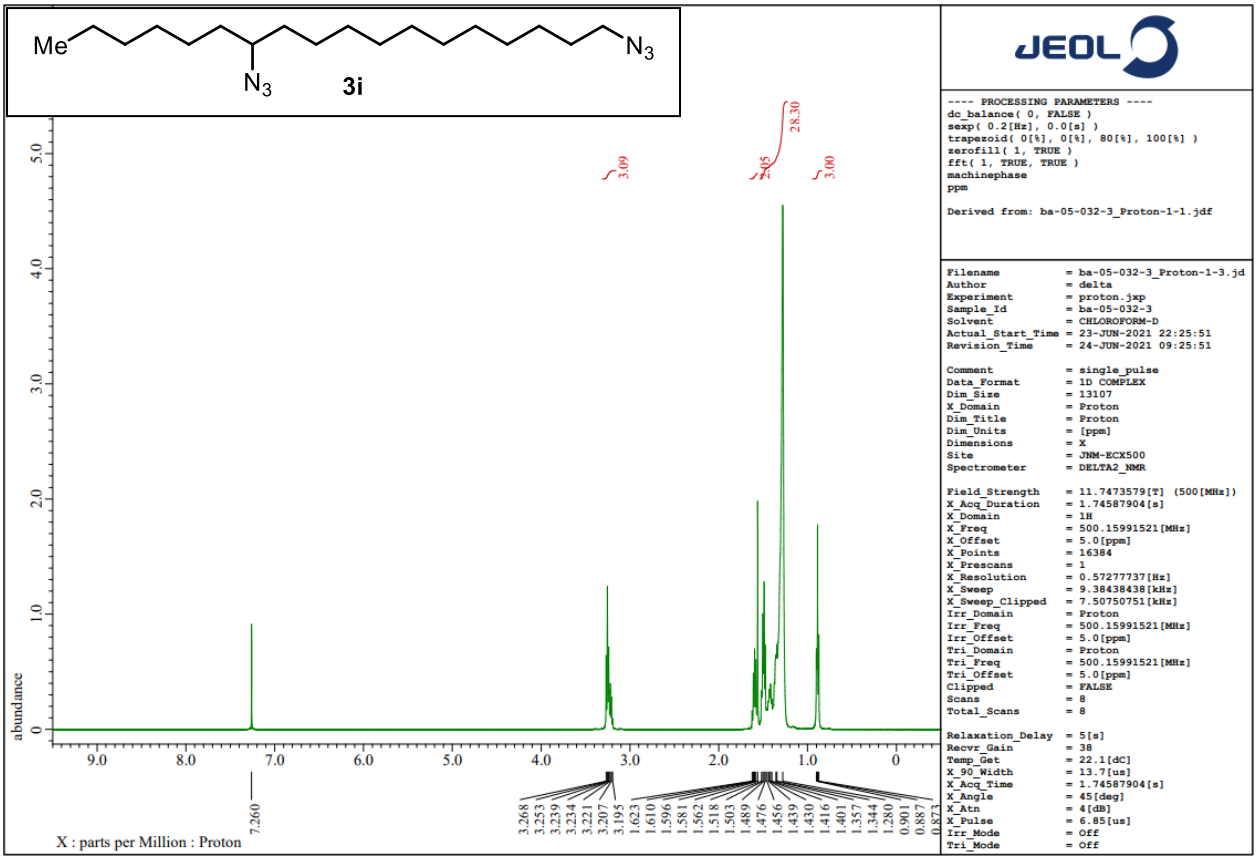

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

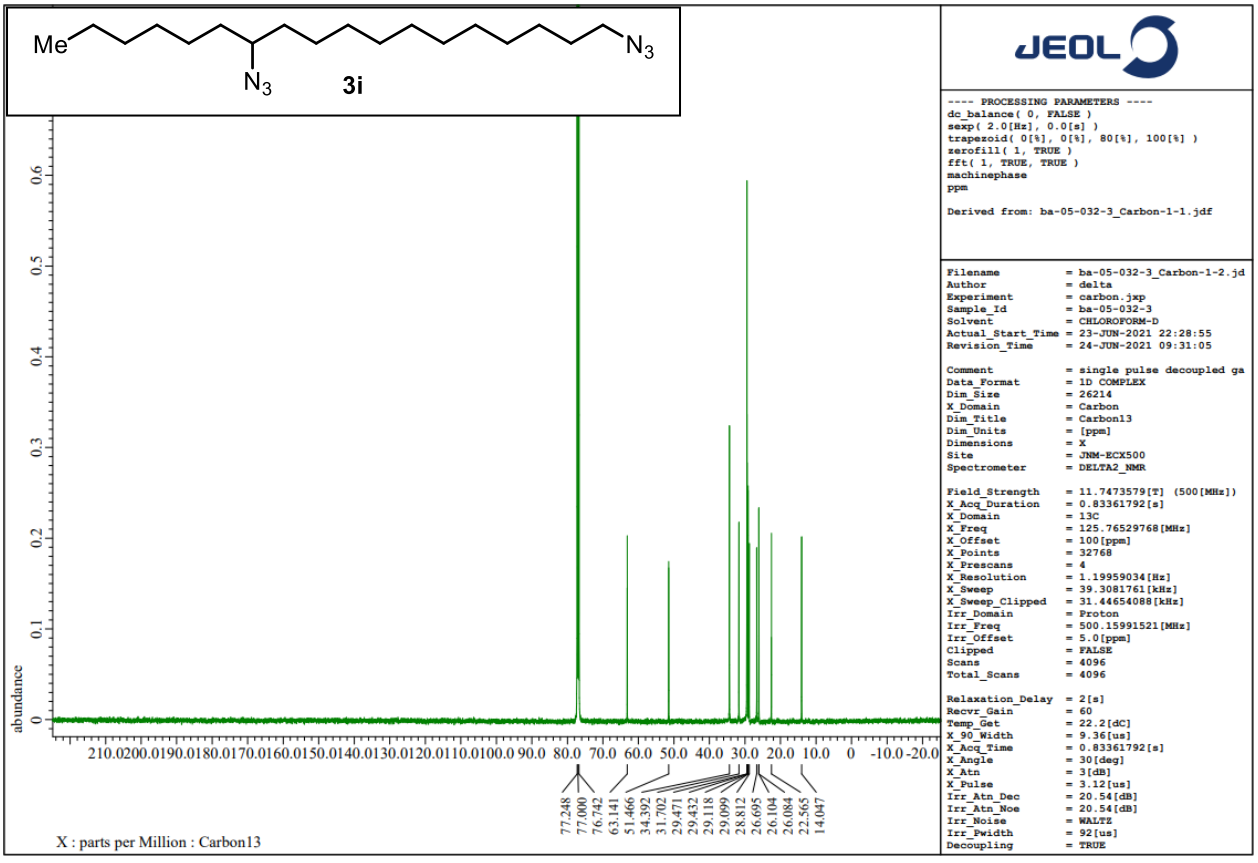
```
Filename            = ba-02-023-2_Carbon-1-2.jd
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = ba-02-023-2
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  3-JUL-2019 00:25:02
Revision_Time       =  3-JUL-2019 10:09:24

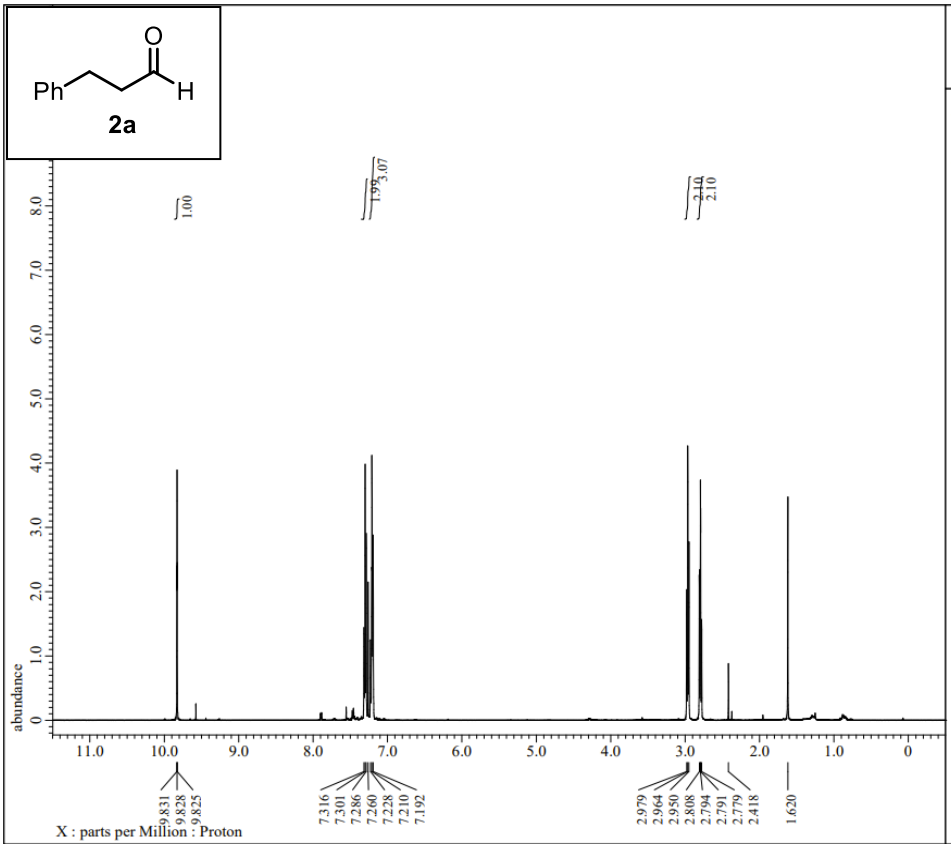
Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 0.83361792[s]
X_Domain            = 13C
X_Freq              = 125.76529768[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.19959034[Hz]
X_Sweep             = 39.3081761[kHz]
X_Sweep_Clipped     = 31.44654088[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 4096
Total_Scans         = 4096

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 20.3[dC]
X_90_Width          = 9.36[us]
X_Acq_Time          = 0.83361792[s]
X_Angle             = 30[deg]
X_Atn               = 3[dB]
X_Pulse             = 3.12[us]
Irr_Atn_Dec         = 20.54[dB]
Irr_Atn_Noe         = 20.54[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 92[us]
Decoupling          = TRUE
```


Me
N3
N3
3i
3.09
2.85
28.30
3.00
abundance
X : parts per Million : Proton
7.260
3.268
3.253
3.239
3.234
3.221
3.207
3.195
1.623
1.610
1.596
1.581
1.562
1.518
1.503
1.489
1.476
1.456
1.439
1.430
1.416
1.401
1.357
1.344
1.280
0.901
0.887
0.873
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm
Derived from: ba-05-032-3_Proton-1-1.jdf
Filename = ba-05-032-3_Proton-1-3.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-05-032-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 23-JUN-2021 22:25:51
Revision_Time = 24-JUN-2021 09:25:51
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 38
Temp_Get = 22.1[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off


Me
N3
N3
3i
abundance
X : parts per Million : Carbon13
77.248
77.000
76.742
63.141
51.466
34.392
31.702
29.471
29.432
29.118
29.099
28.812
26.695
26.104
26.084
22.565
14.047
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm
Derived from: ba-05-032-3_Carbon-1-1.jdf
Filename = ba-05-032-3_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-05-032-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 23-JUN-2021 22:28:55
Revision_Time = 24-JUN-2021 09:31:05
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 4096
Total_Scans = 4096
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 22.2[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE

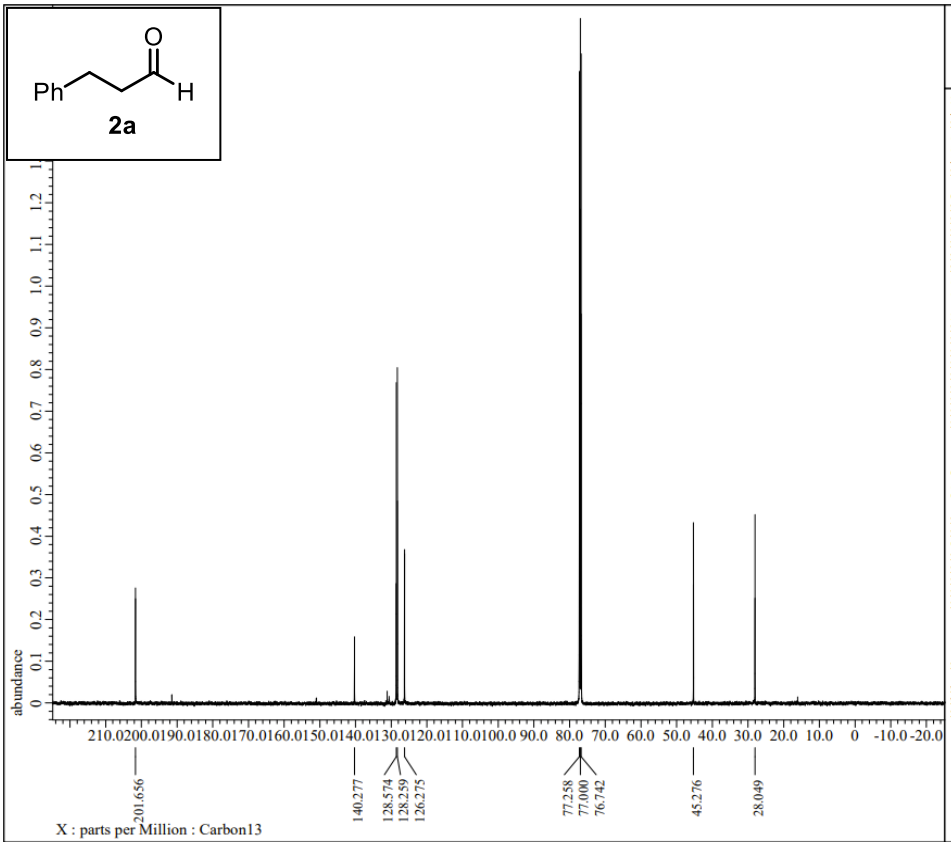



```
Filename          = [2] H-NMR PROCESSED (ba-0
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-01-117-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 19-MAR-2019 19:42:49
Revision_Time     =  5-APR-2019 20:05:20

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 38
Temp_Get          = 15[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

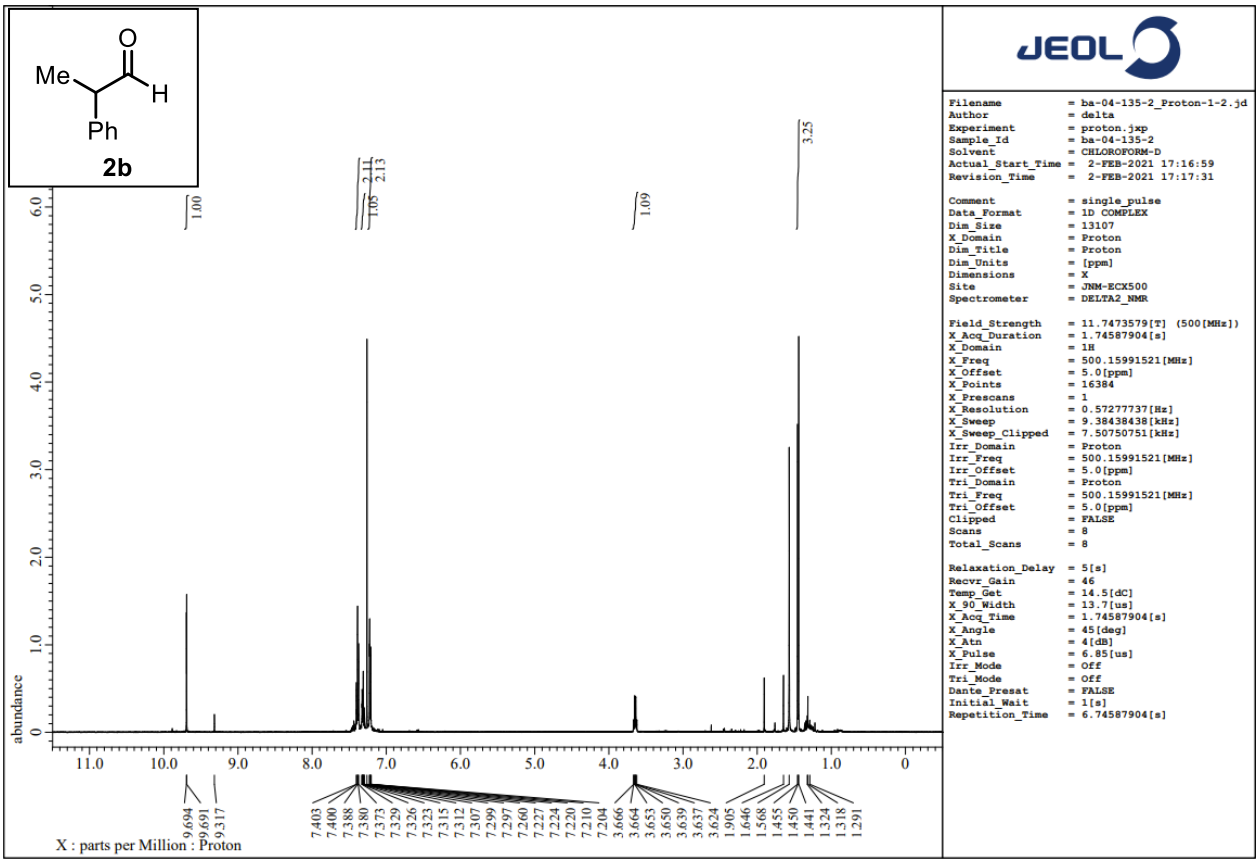


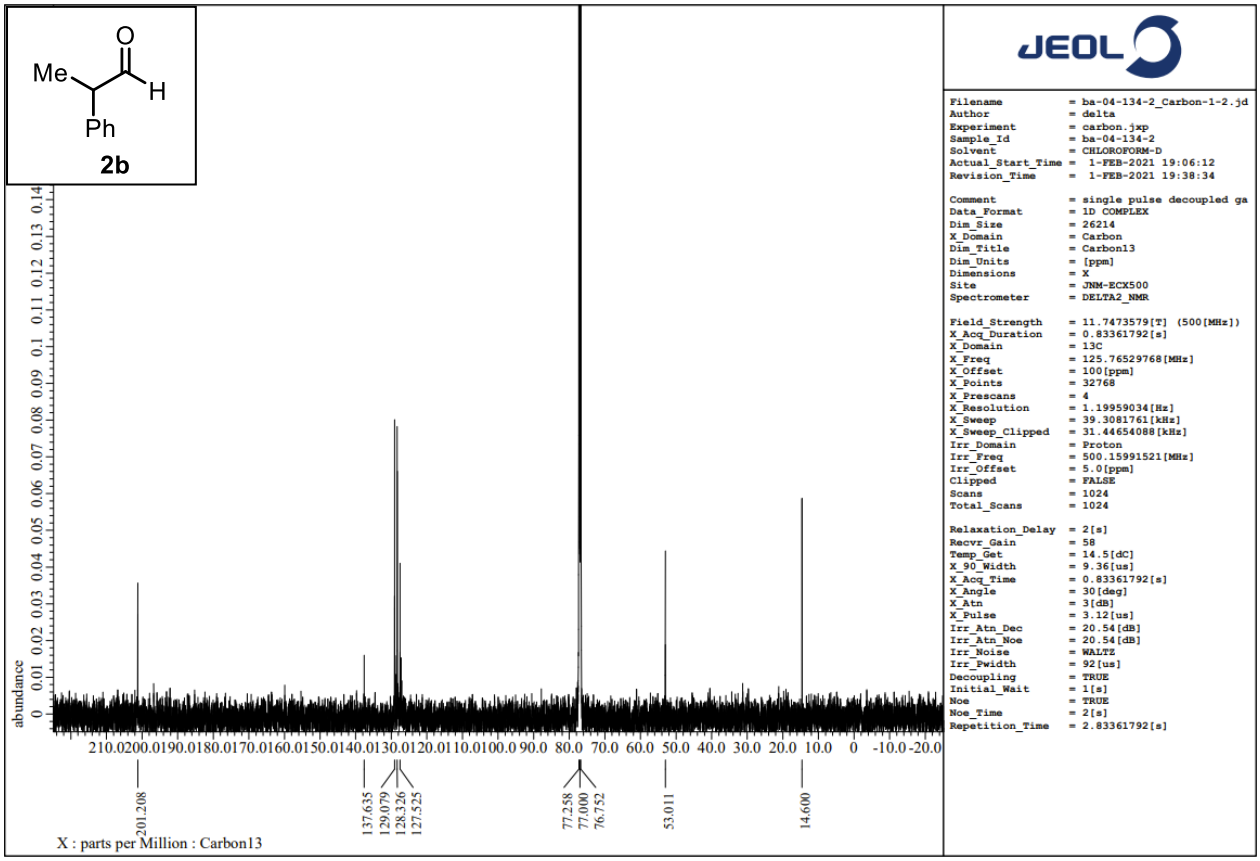

```
Filename          = ba-01-117-1_Carbon-1-1.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-01-117-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 19-MAR-2019 19:58:40
Revision_Time     = 19-MAR-2019 22:04:57

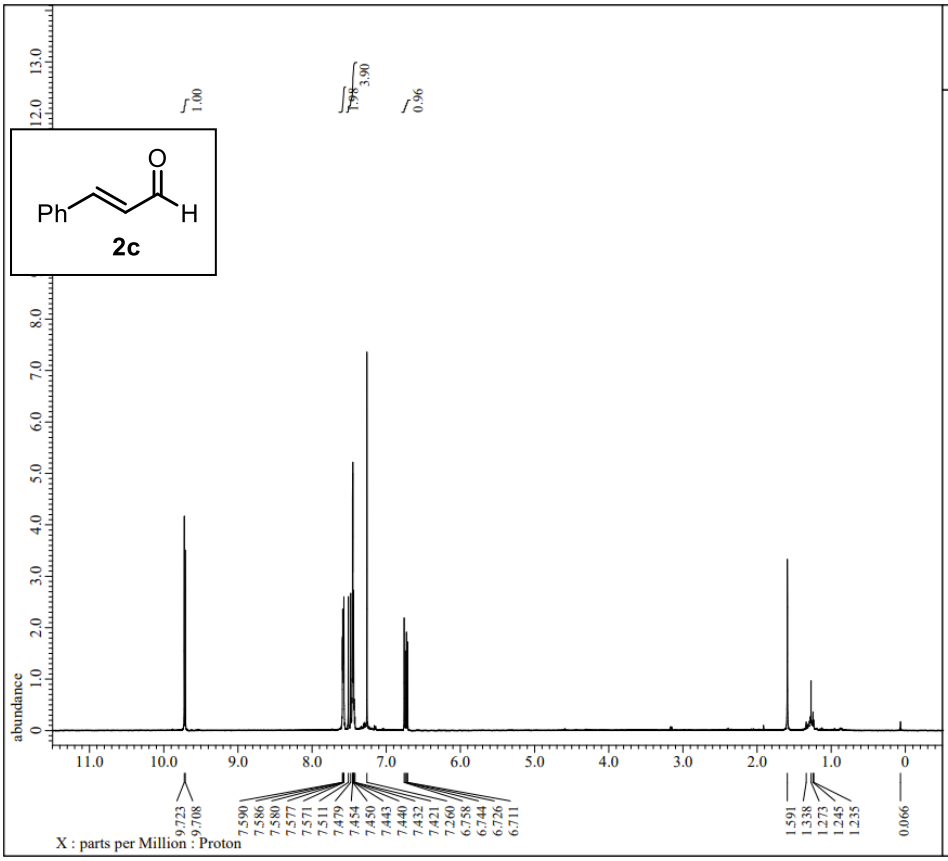
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1800
Total_Scans       = 1800

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 15.3[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


Me
O
H
Ph
2b
1.00
2.11
2.13
1.05
1.09
3.25
abundance
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
9.694 9.691 9.317
7.403 7.400 7.388 7.380 7.373 7.329 7.326 7.323 7.315 7.312 7.307 7.299 7.297 7.260 7.227 7.224 7.220 7.210 7.204 3.666 3.664 3.653 3.650 3.639 3.637 3.624 1.905 1.646 1.568 1.455 1.450 1.441 1.324 1.318 1.291
X : parts per Million : Proton
JEOL
Filename = ba-04-135-2_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-04-135-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 2-FEB-2021 17:16:59
Revision_Time = 2-FEB-2021 17:17:31
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 46
Temp_Get = 14.5[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


Me
O
H
Ph
2b
abundance
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
201.208
137.635 129.079 128.326 127.525
77.258 77.000 76.752
53.011
14.600
X : parts per Million : Carbon13
JEOL
Filename = ba-04-134-2_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-04-134-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 1-FEB-2021 19:06:12
Revision_Time = 1-FEB-2021 19:38:34
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 58
Temp_Get = 14.5[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

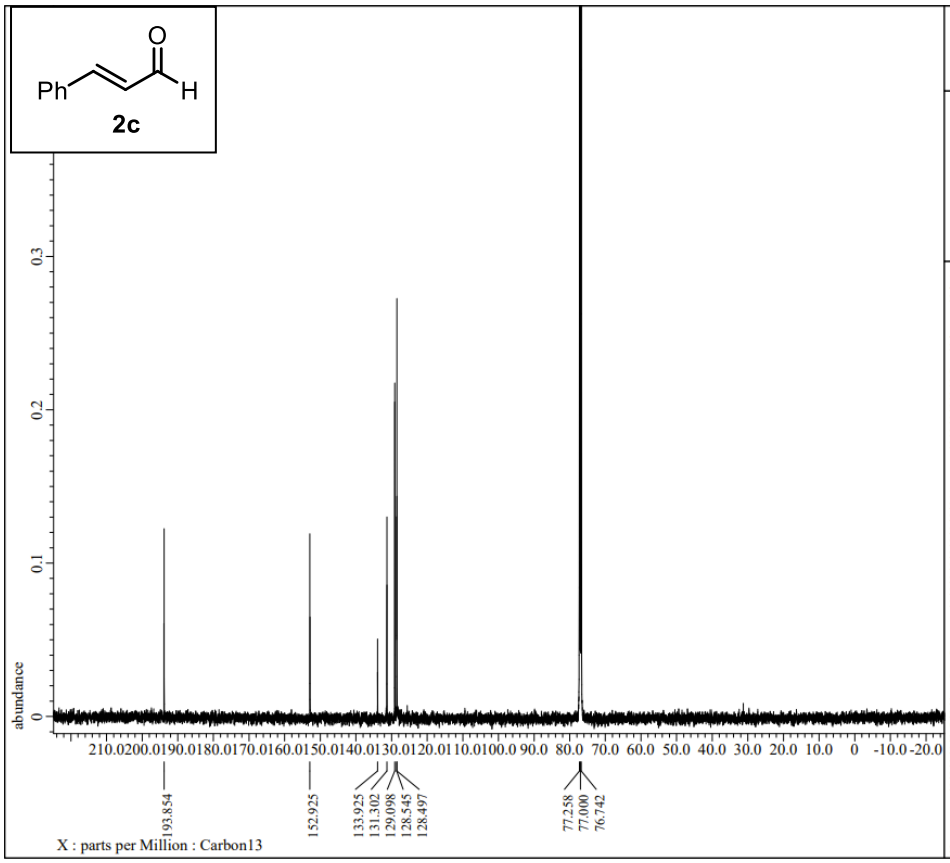



```
Filename          = ba-01-134-2-B_Proton-1-6.
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-01-134-2-B
Solvent           = CHLOROFORM-D
Actual_Start_Time = 24-APR-2019 23:35:26
Revision_Time     = 26-APR-2019 15:17:09

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 46
Temp_Get          = 12.9[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```



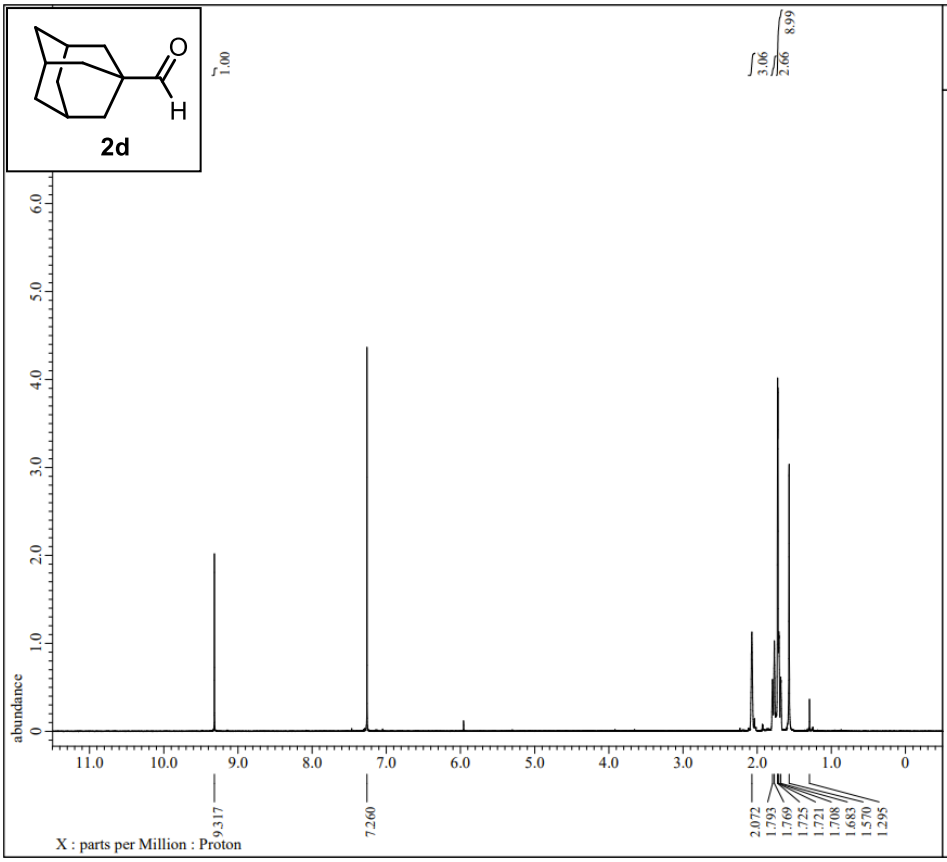

```
---- PROCESSING PARAMETERS ----
do_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename          = ba-01-134-2-B_Carbon-1-2.
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-01-134-2-B
Solvent           = CHLOROFORM-D
Actual_Start_Time = 25-APR-2019 00:11:42
Revision_Time     = 25-APR-2019 09:20:46

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1800
Total_Scans       = 1800

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 13.3[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
```

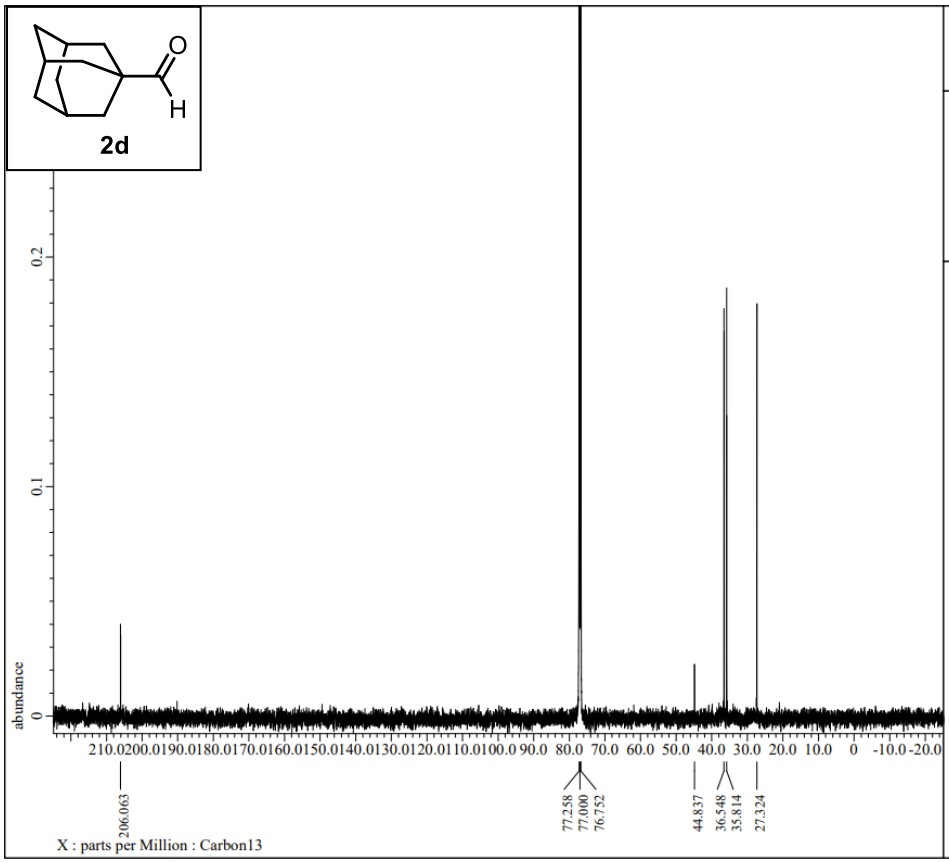



```
Filename          = ba-02-009-3_Proton-1-4.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-02-009-3
Solvent           = CHLOROFORM-D
Actual_Start_Time =  7-JUN-2019 19:31:23
Revision_Time     =  7-JUN-2019 21:22:30

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 44
Temp_Get          = 19.1[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```



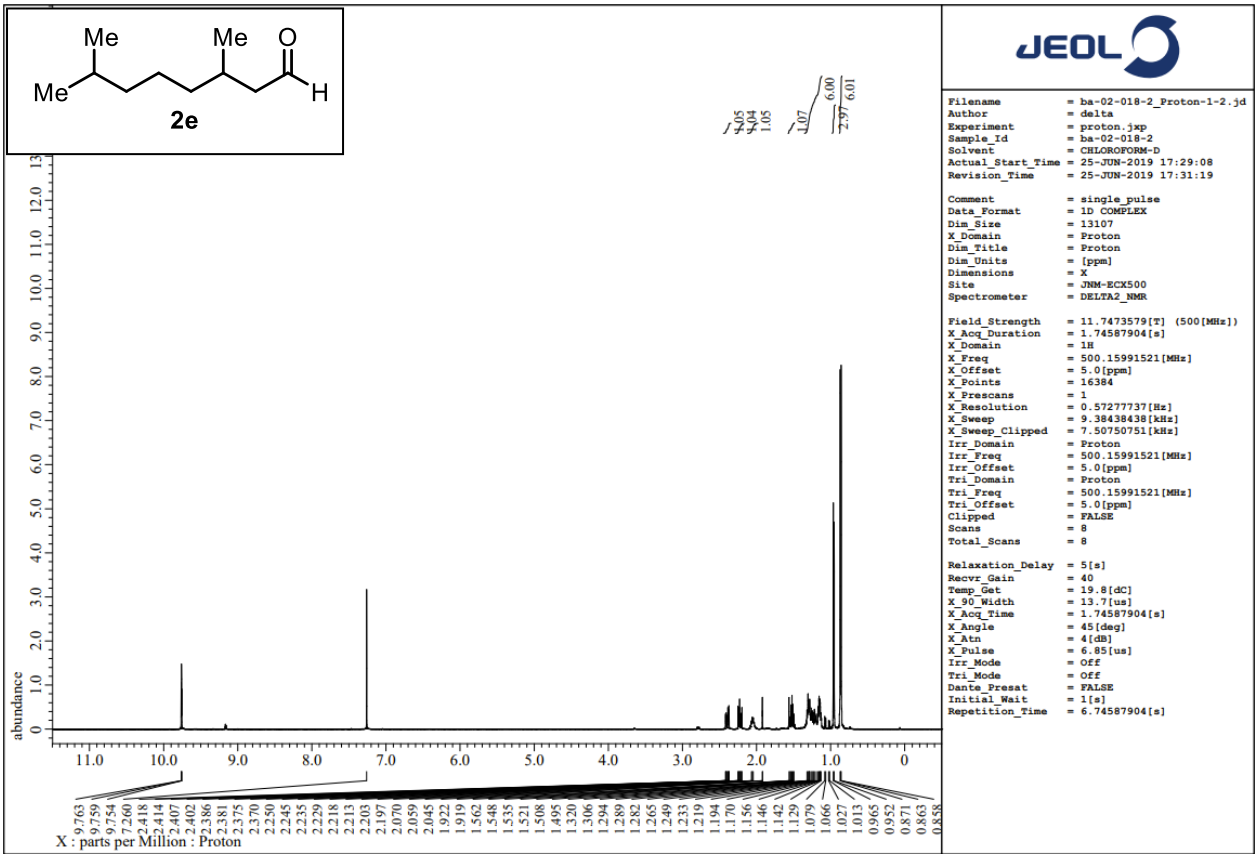

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

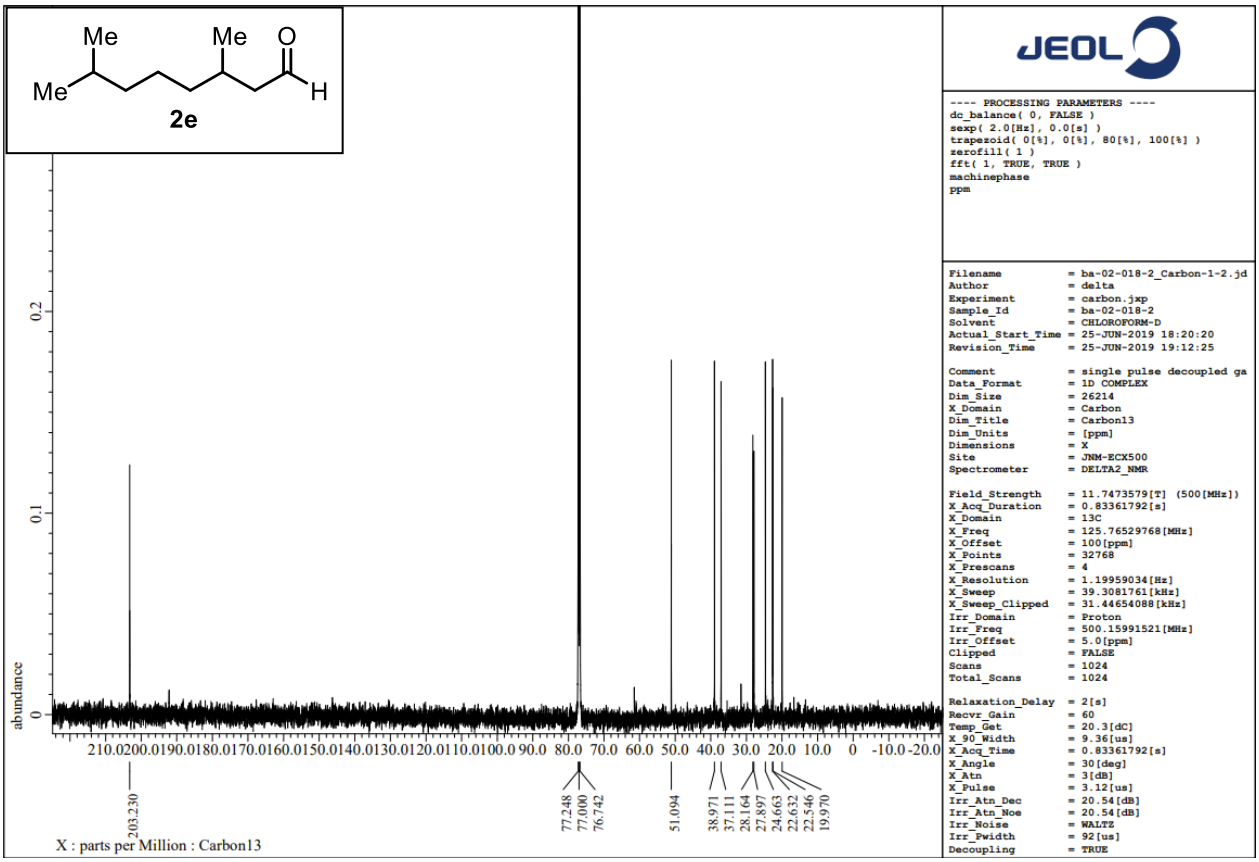
```
Filename          = ba-02-009-3_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-02-009-3
Solvent           = CHLOROFORM-D
Actual_Start_Time =  7-JUN-2019 19:58:20
Revision_Time     =  7-JUN-2019 21:21:25

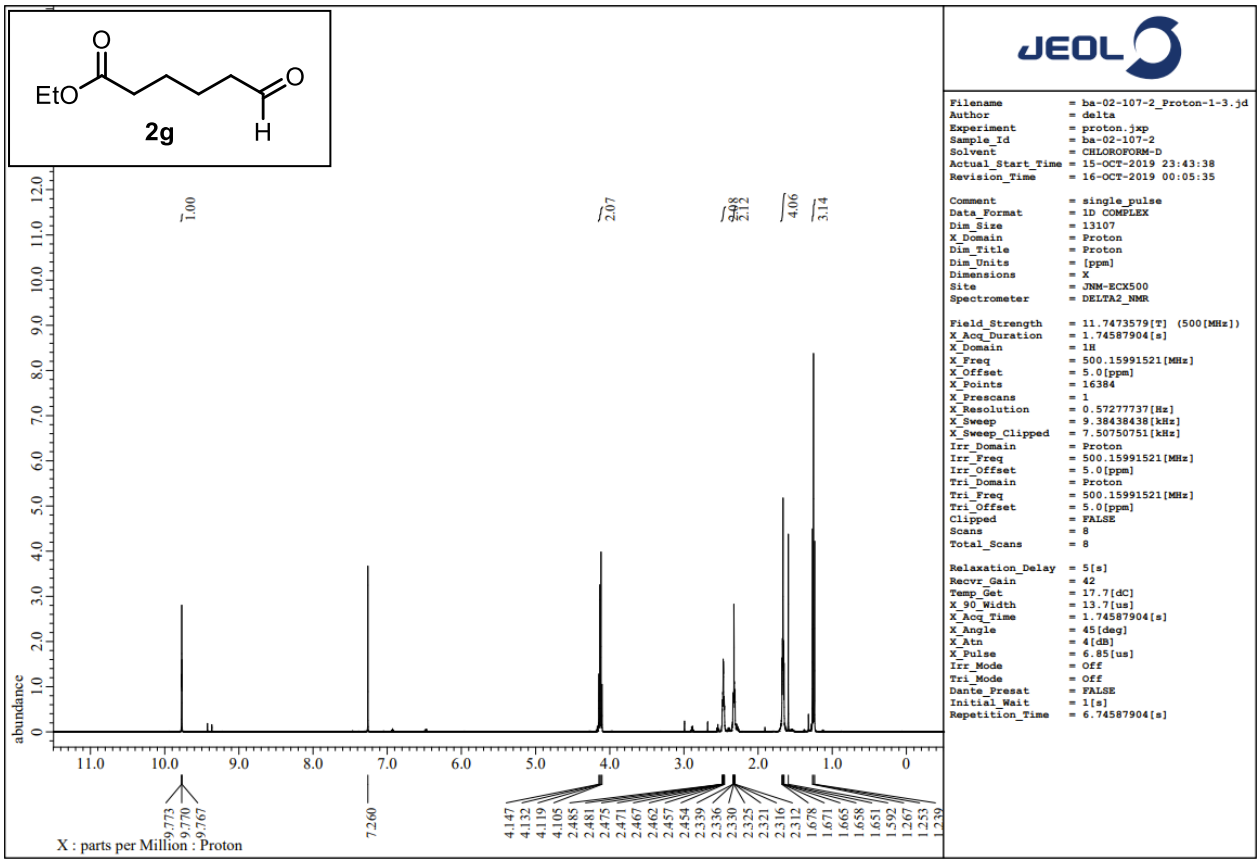
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1800
Total_Scans       = 1800

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 19.5[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
```


Me
Me
O
Me
H
2e
abundance
X : parts per Million : Proton
Filename = ba-02-018-2_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-02-018-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 25-JUN-2019 17:29:08
Revision_Time = 25-JUN-2019 17:31:19
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 40
Temp_Get = 19.8[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


Me
Me
O
Me
H
2e
abundance
X : parts per Million : Carbon13
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = ba-02-018-2_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-02-018-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 25-JUN-2019 18:20:20
Revision_Time = 25-JUN-2019 19:12:25
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 20.3[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE



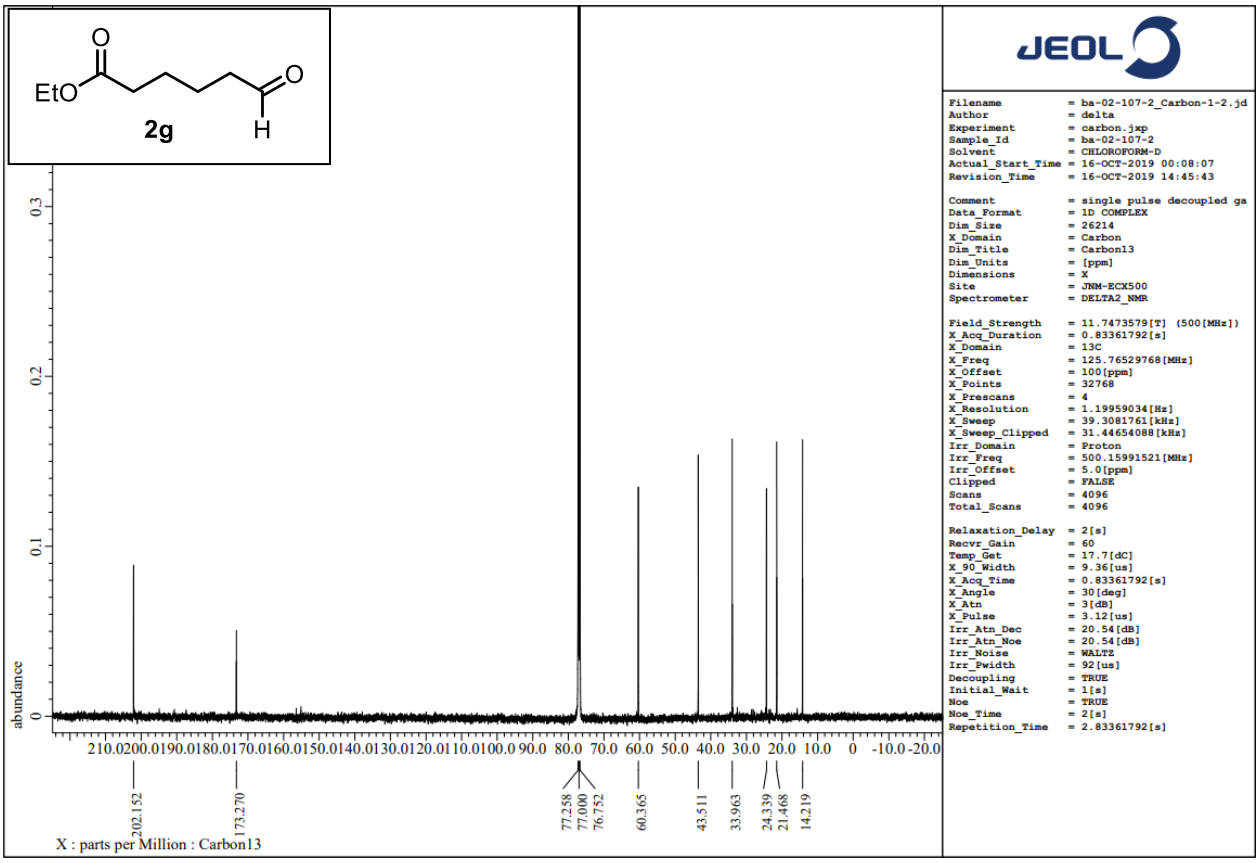
JEOL

```
Filename          = ba-02-107-2_Proton-1-3.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-02-107-2
Solvent           = CHLOROFORM-D
Actual_Start_Time = 15-OCT-2019 23:43:38
Revision_Time     = 16-OCT-2019 00:05:35

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 42
Temp_Get          = 17.7[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```



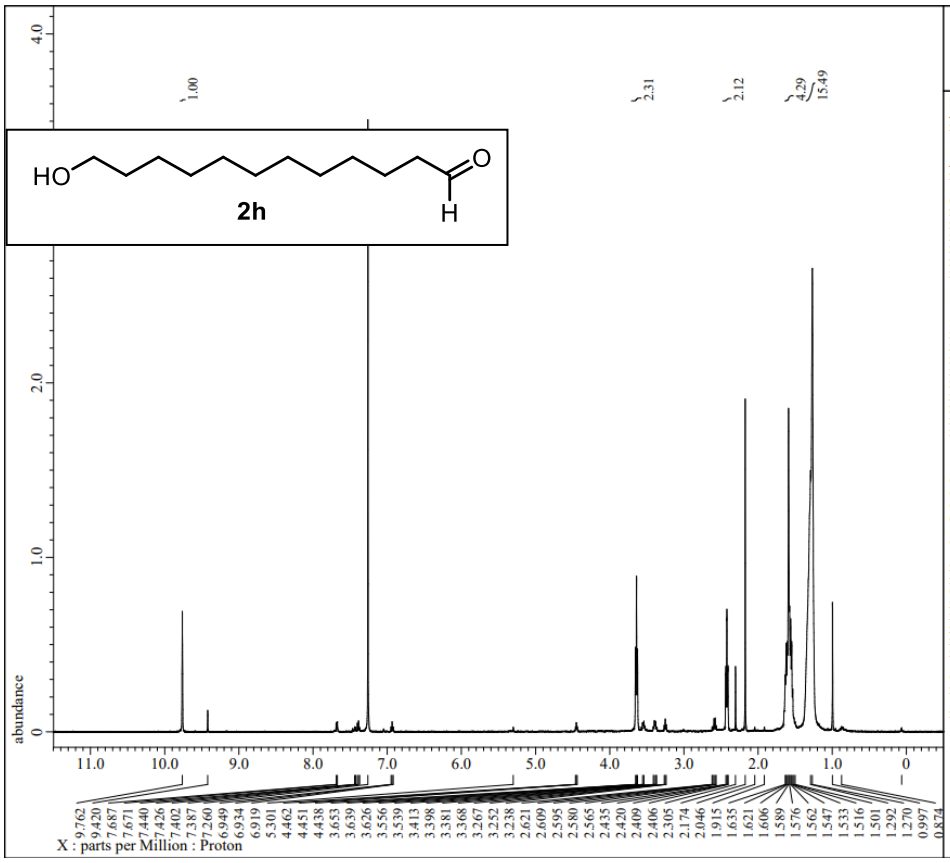
JEOL

```
Filename          = ba-02-107-2_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-02-107-2
Solvent           = CHLOROFORM-D
Actual_Start_Time = 16-OCT-2019 00:08:07
Revision_Time     = 16-OCT-2019 14:45:43

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 4096
Total_Scans       = 4096

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 17.7[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```

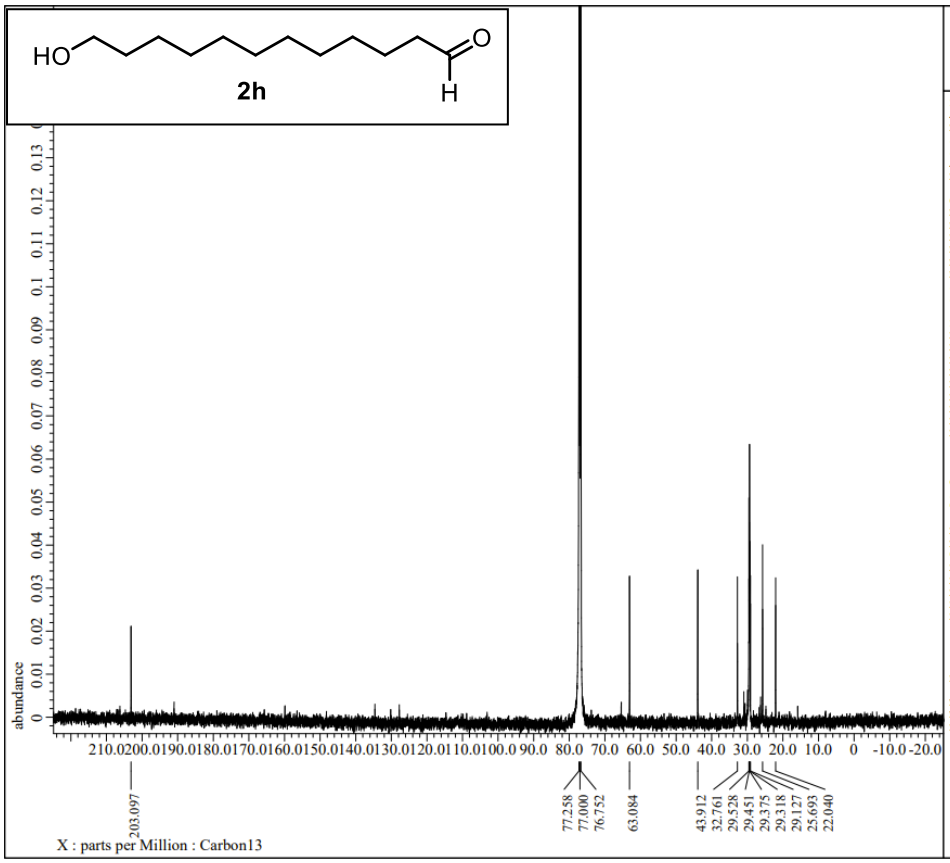



```
Filename              = ba-02-124-3_Proton-1-4.jd
Author                = delta
Experiment            = proton.jxp
Sample_Id             = ba-02-124-3
Solvent               = CHLOROFORM-D
Actual_Start_Time     = 15-NOV-2019 23:30:21
Revision_Time         = 28-JAN-2021 10:38:32

Comment               = single_pulse
Data_Format           = 1D COMPLEX
Dim_Size              = 13107
X_Domain              = Proton
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Site                  = JNM-ECX500
Spectrometer          = DELTA2_NMR

Field_Strength        = 11.7473579[T] (500[MHz])
X_Acq_Duration        = 1.74587904[s]
X_Domain              = 1H
X_Freq                = 500.15991521[MHz]
X_Offset              = 5.0[ppm]
X_Points              = 16384
X_Prescans            = 1
X_Resolution          = 0.57277737[Hz]
X_Sweep               = 9.38438438[kHz]
X_Sweep_Clipped       = 7.50750751[kHz]
Irr_Domain            = Proton
Irr_Freq              = 500.15991521[MHz]
Irr_Offset            = 5.0[ppm]
Tri_Domain            = Proton
Tri_Freq              = 500.15991521[MHz]
Tri_Offset            = 5.0[ppm]
Clipped               = FALSE
Scans                 = 8
Total_Scans           = 8

Relaxation_Delay      = 5[s]
Recvr_Gain            = 46
Temp_Get              = 15.3[dC]
X_90_Width            = 13.7[us]
X_Acq_Time            = 1.74587904[s]
X_Angle               = 45[deg]
X_Atn                 = 4[dB]
X_Pulse               = 6.85[us]
Irr_Mode              = Off
Tri_Mode              = Off
Dante_Presat          = FALSE
Initial_Wait          = 1[s]
Repetition_Time       = 6.74587904[s]
```

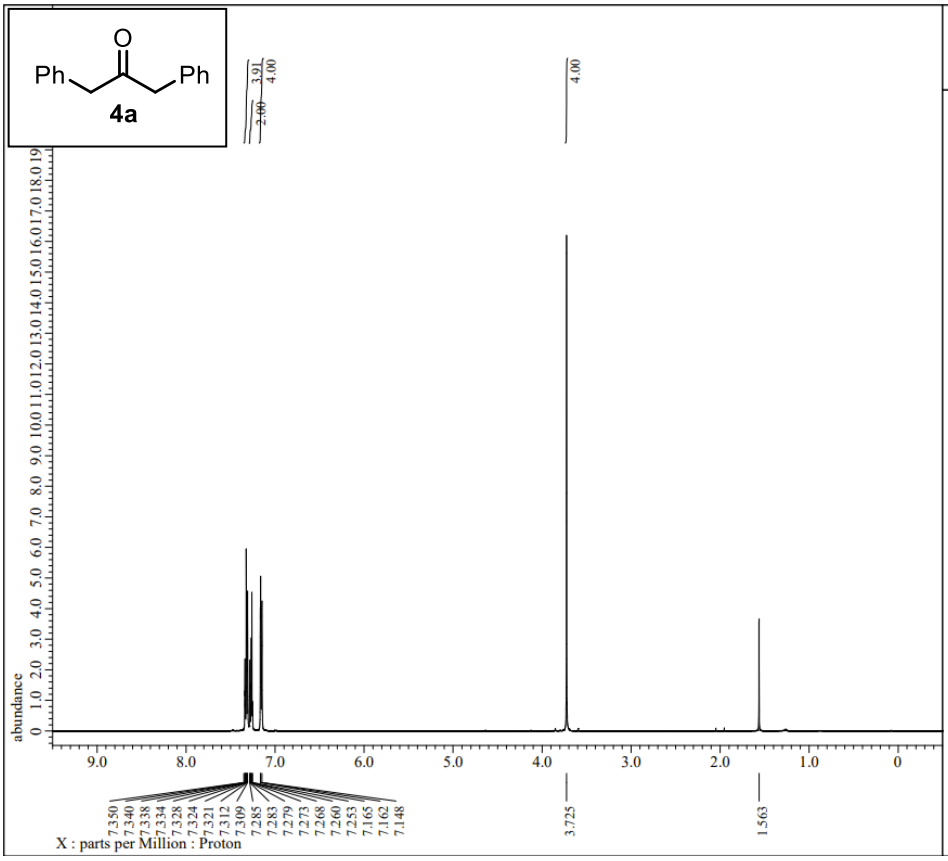



```
Filename              = ba-02-124-3_Carbon-1-2.jd
Author                = delta
Experiment            = carbon.jxp
Sample_Id             = ba-02-124-3
Solvent               = CHLOROFORM-D
Actual_Start_Time     = 18-NOV-2019 22:57:09
Revision_Time         = 19-NOV-2019 14:06:45

Comment               = single pulse decoupled ga
Data_Format           = 1D COMPLEX
Dim_Size              = 26214
X_Domain              = Carbon
Dim_Title             = Carbon13
Dim_Units             = [ppm]
Dimensions            = X
Site                  = JNM-ECX500
Spectrometer          = DELTA2_NMR

Field_Strength        = 11.7473579[T] (500[MHz])
X_Acq_Duration        = 0.83361792[s]
X_Domain              = 13C
X_Freq                = 125.76529768[MHz]
X_Offset              = 100[ppm]
X_Points              = 32768
X_Prescans            = 4
X_Resolution          = 1.19959034[Hz]
X_Sweep               = 39.3081761[kHz]
X_Sweep_Clipped       = 31.44654088[kHz]
Irr_Domain            = Proton
Irr_Freq              = 500.15991521[MHz]
Irr_Offset            = 5.0[ppm]
Clipped               = FALSE
Scans                 = 12000
Total_Scans           = 12000

Relaxation_Delay      = 2[s]
Recvr_Gain            = 60
Temp_Get              = 16.8[dC]
X_90_Width            = 9.36[us]
X_Acq_Time            = 0.83361792[s]
X_Angle               = 30[deg]
X_Atn                 = 3[dB]
X_Pulse               = 3.12[us]
Irr_Atn_Dec           = 20.54[dB]
Irr_Atn_Noe           = 20.54[dB]
Irr_Noise             = WALTZ
Irr_Pwidth            = 92[us]
Decoupling            = TRUE
Initial_Wait          = 1[s]
Noe                   = TRUE
Noe_Time              = 2[s]
Repetition_Time       = 2.83361792[s]
```

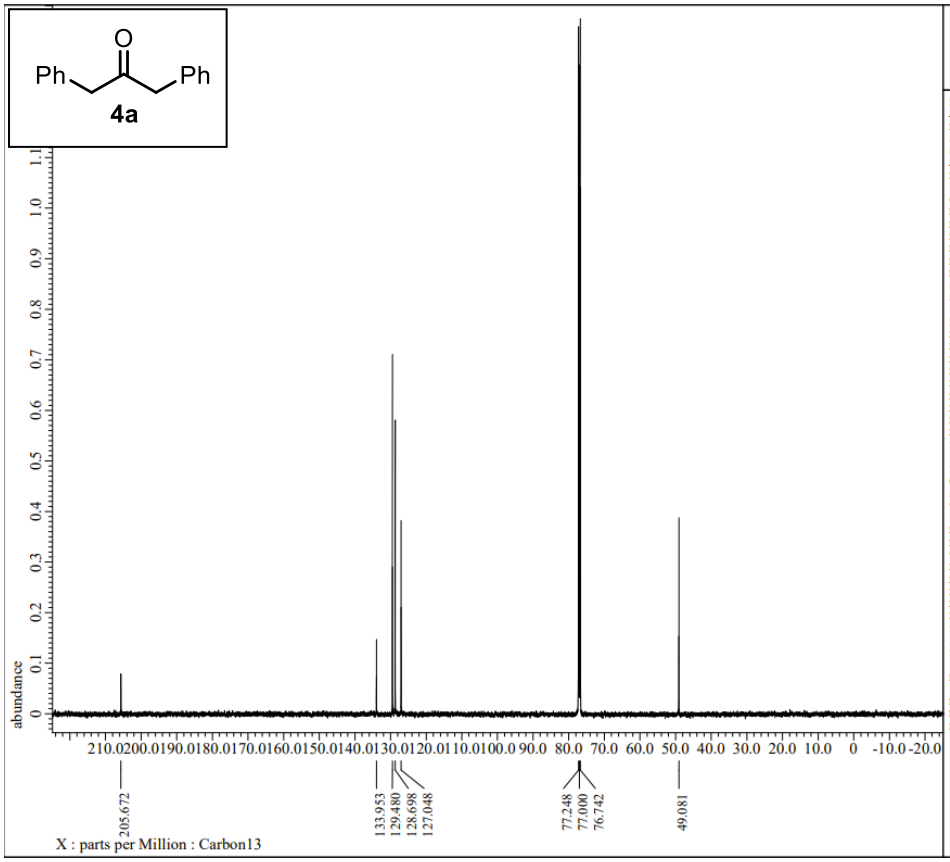



```
Filename          = ba-02-036-2_Proton-1-6.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-02-036-2
Solvent           = CHLOROFORM-D
Actual_Start_Time = 22-JUL-2019 19:20:45
Revision_Time     = 27-DEC-2019 15:37:18

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 42
Temp_Get          = 21.9[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

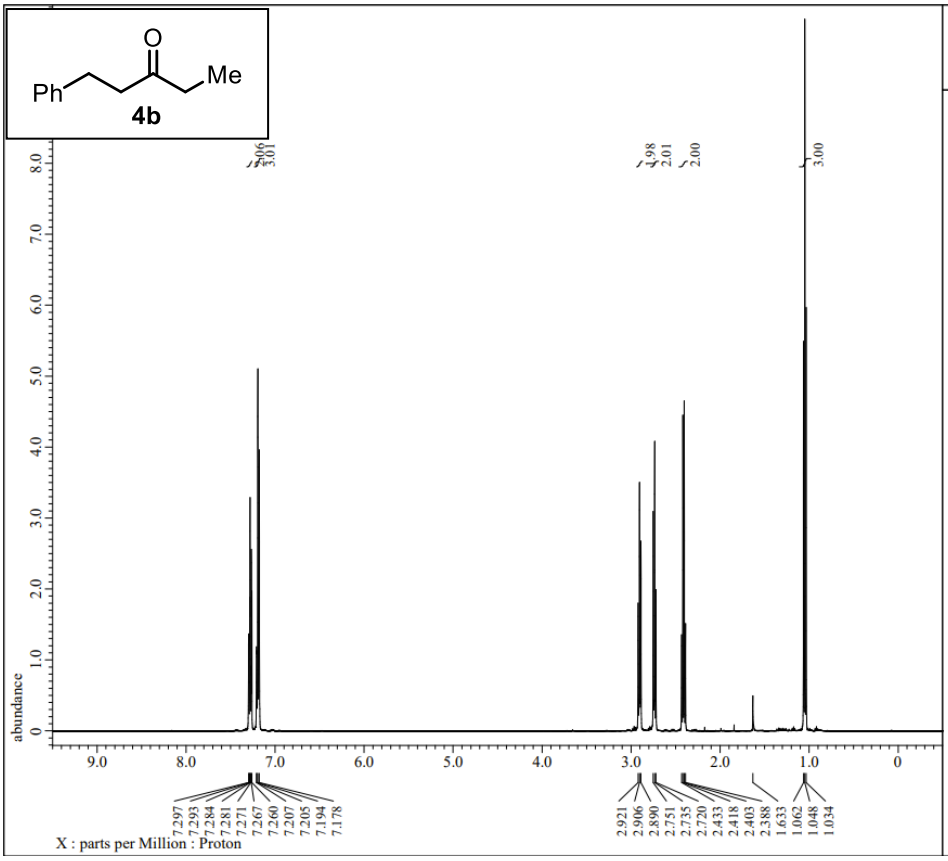



```
Filename          = ba-02-036-2_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-02-036-2
Solvent           = CHLOROFORM-D
Actual_Start_Time = 22-JUL-2019 19:24:49
Revision_Time     = 23-JUL-2019 09:47:31

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 22[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```

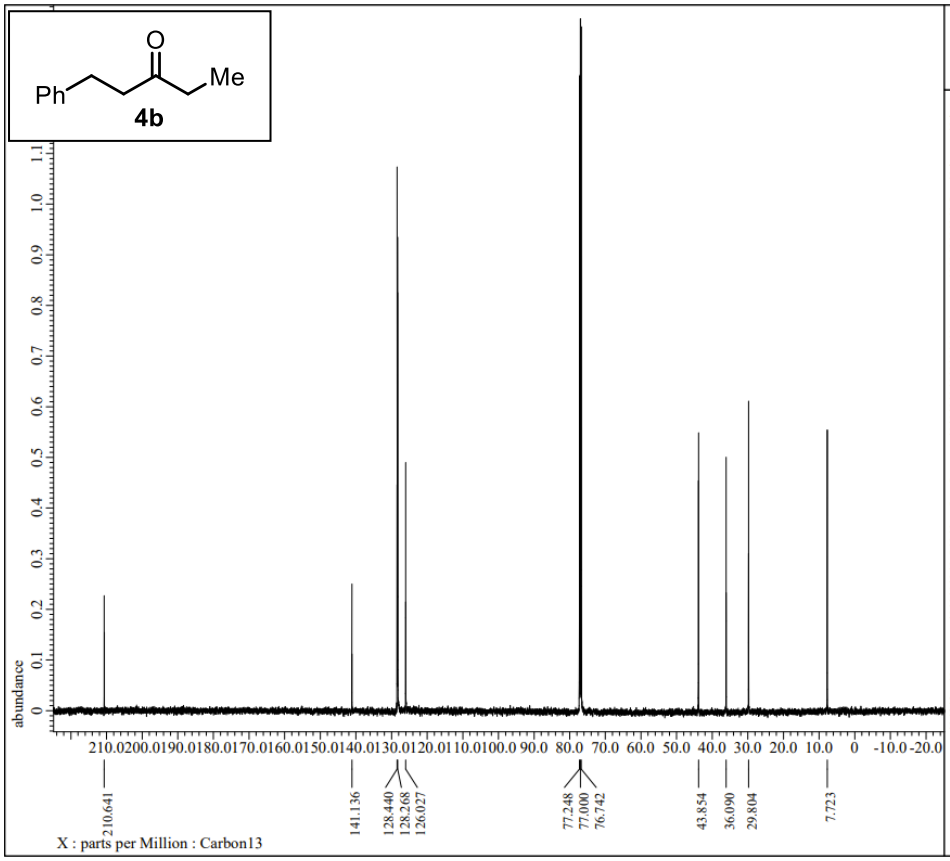



```
Filename          = ba-02-084-2_Proton-1-2.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-02-084-2
Solvent           = CHLOROFORM-D
Actual_Start_Time = 13-SEP-2019 20:47:39
Revision_Time     = 17-SEP-2019 17:50:00

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 34
Temp_Get          = 20.5[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

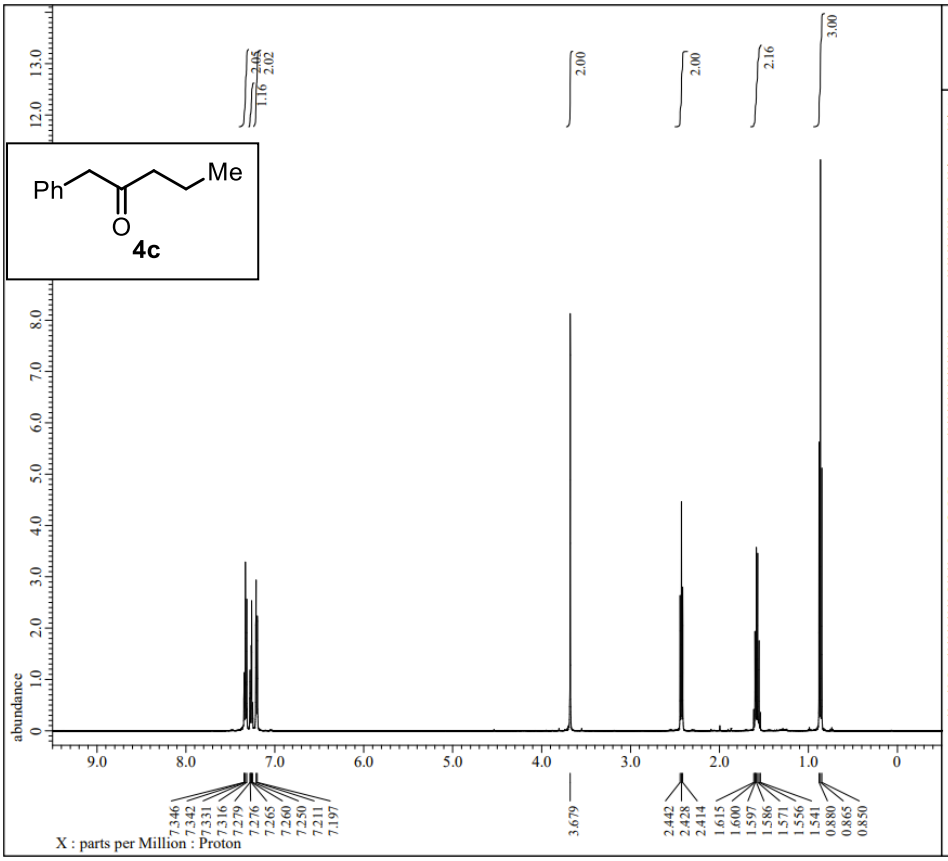



```
Filename          = ba-02-084-2_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-02-084-2
Solvent           = CHLOROFORM-D
Actual_Start_Time = 13-SEP-2019 20:49:52
Revision_Time     = 17-SEP-2019 17:52:05

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 512
Total_Scans       = 512

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 20.7[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```

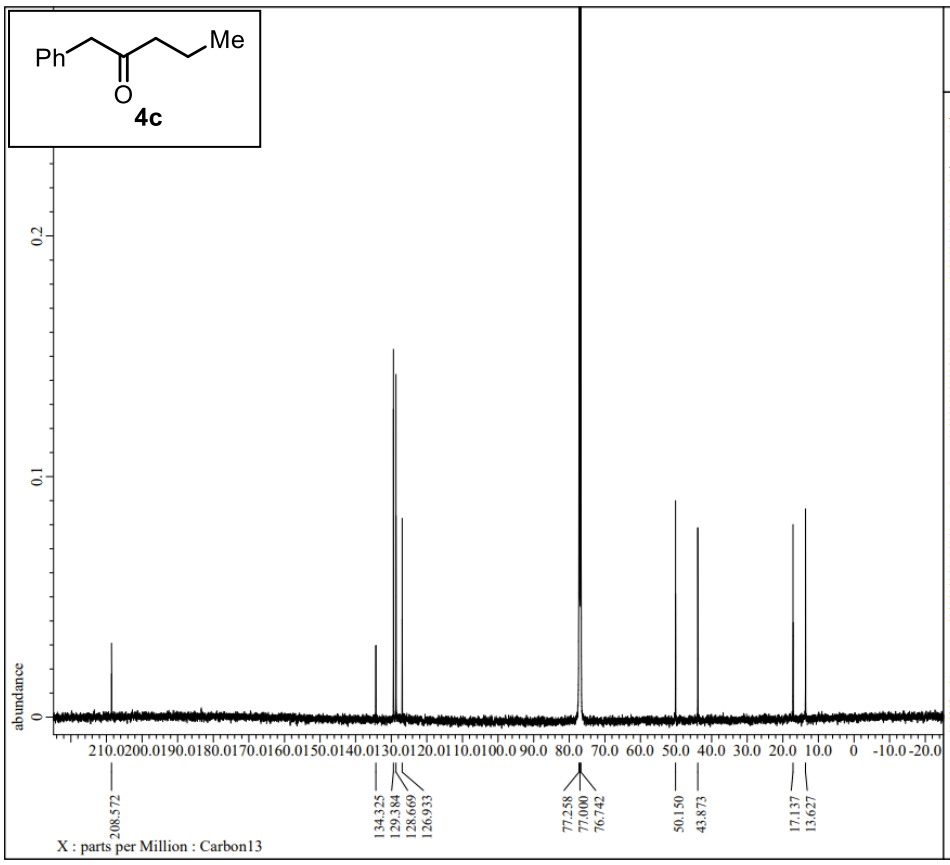



```
Filename          = ba-03-015-2_Proton-1-2.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-03-015-2
Solvent           = CHLOROFORM-D
Actual_Start_Time =  8-JAN-2020 22:41:32
Revision_Time     =  9-JAN-2020 09:08:24

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T]  (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 38
Temp_Get          = 14.9[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

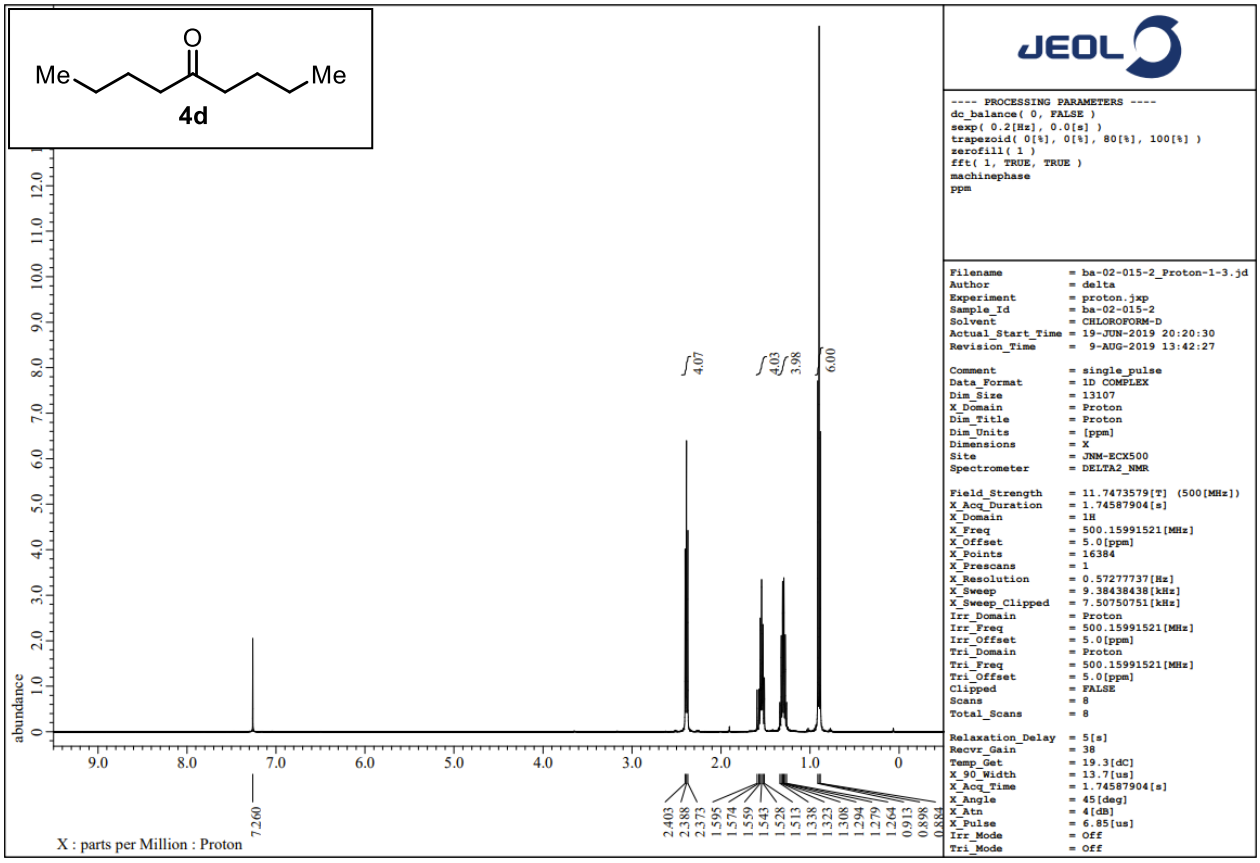


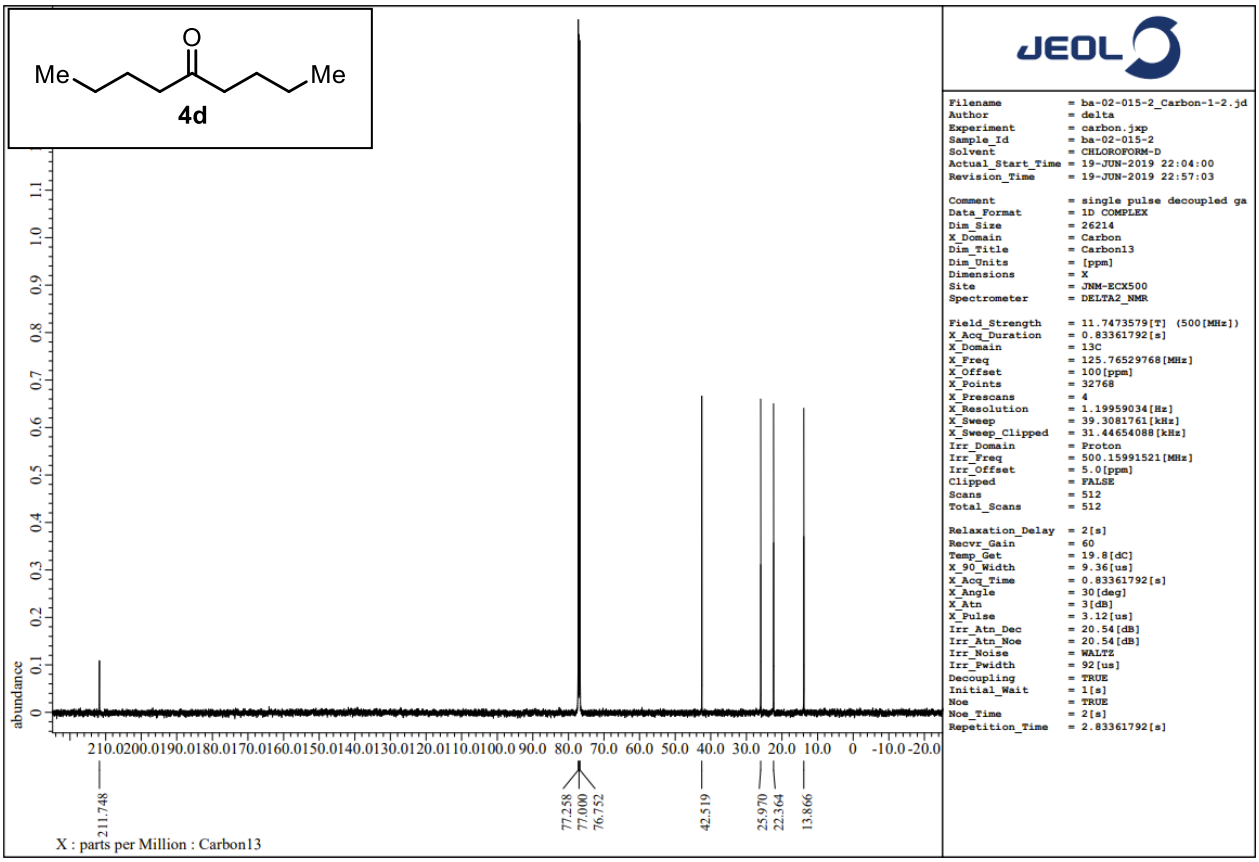

```
Filename          = ba-03-011-2_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-03-011-2
Solvent           = CHLOROFORM-D
Actual_Start_Time = 26-DEC-2019 01:46:27
Revision_Time     = 26-DEC-2019 11:28:10

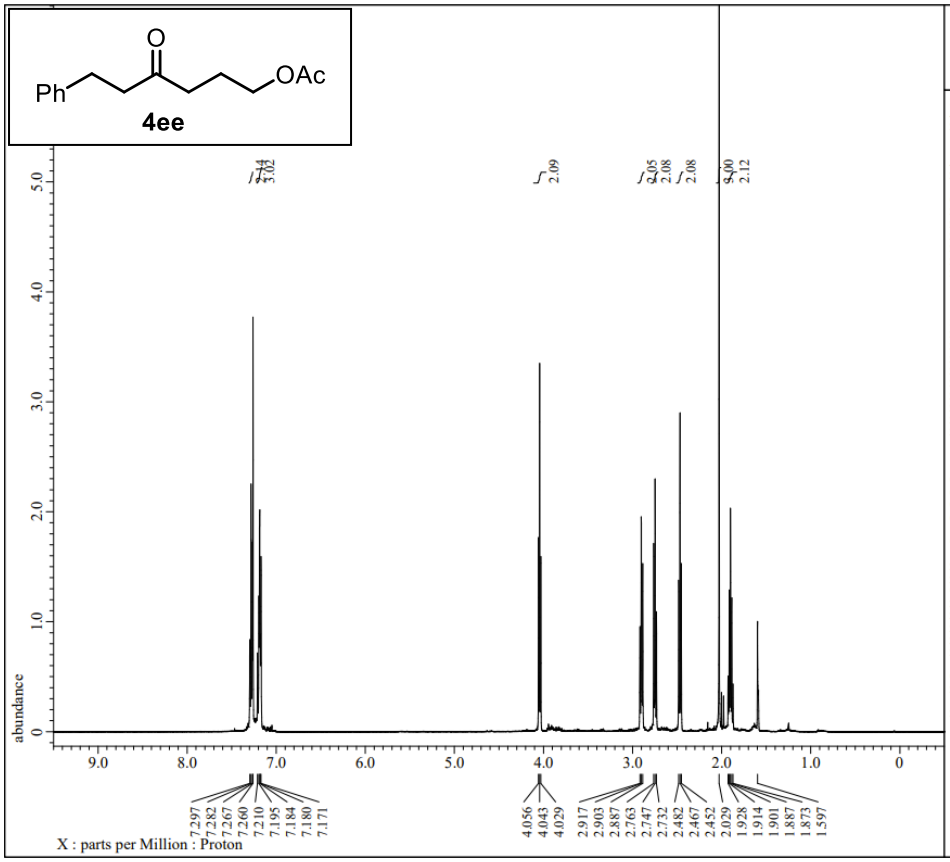
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T]  (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 5000
Total_Scans       = 5000

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 15.3[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


Me
Me
4d
JEOL
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = ba-02-015-2_Proton-1-3.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-02-015-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 19-JUN-2019 20:20:30
Revision_Time = 9-AUG-2019 13:42:27
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 38
Temp_Get = 19.3[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
4.07
4.03
3.98
6.00
abundance
X : parts per Million : Proton
7.260
2.403
2.388
2.373
1.595
1.574
1.559
1.543
1.528
1.513
1.338
1.323
1.308
1.294
1.279
1.264
0.913
0.898
0.884


Me
Me
4d
JEOL
Filename = ba-02-015-2_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-02-015-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 19-JUN-2019 22:04:00
Revision_Time = 19-JUN-2019 22:57:03
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 512
Total_Scans = 512
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 19.8[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]
abundance
X : parts per Million : Carbon13
211.748
77.258
77.000
76.752
42.519
25.970
22.364
13.866

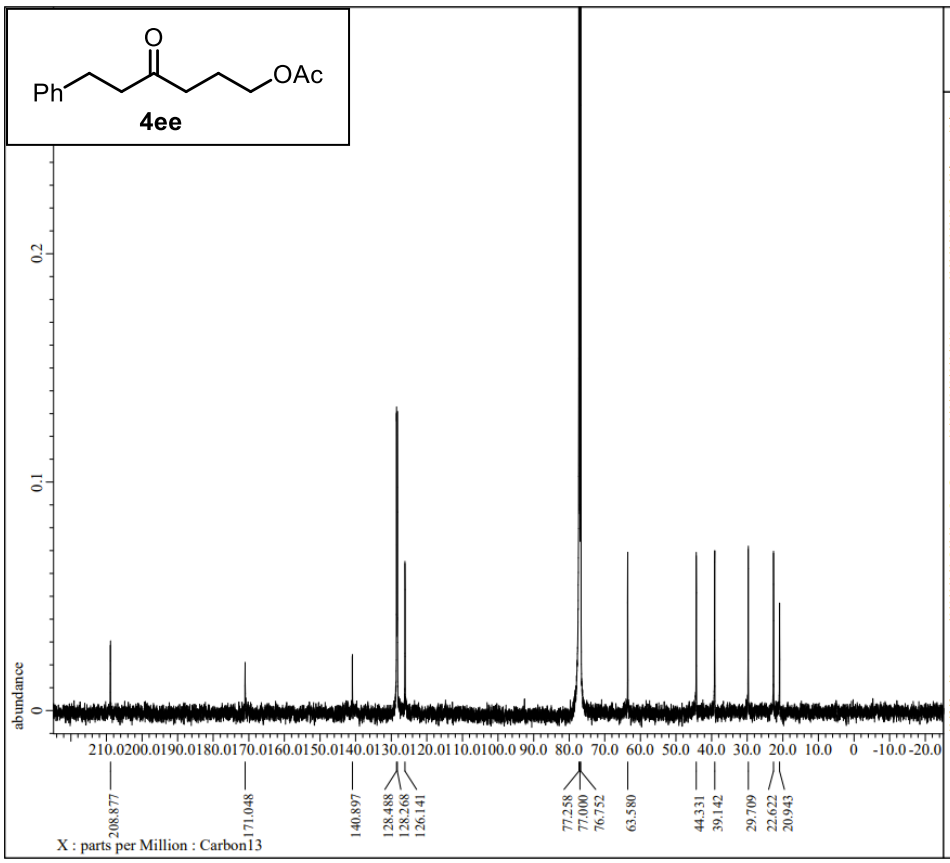



```
Filename          = ba-02-142-2_Proton-1-2.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-02-142-2
Solvent           = CHLOROFORM-D
Actual_Start_Time =  6-DEC-2019 15:01:24
Revision_Time     =  6-DEC-2019 15:07:55

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 42
Temp_Get          = 14.8[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

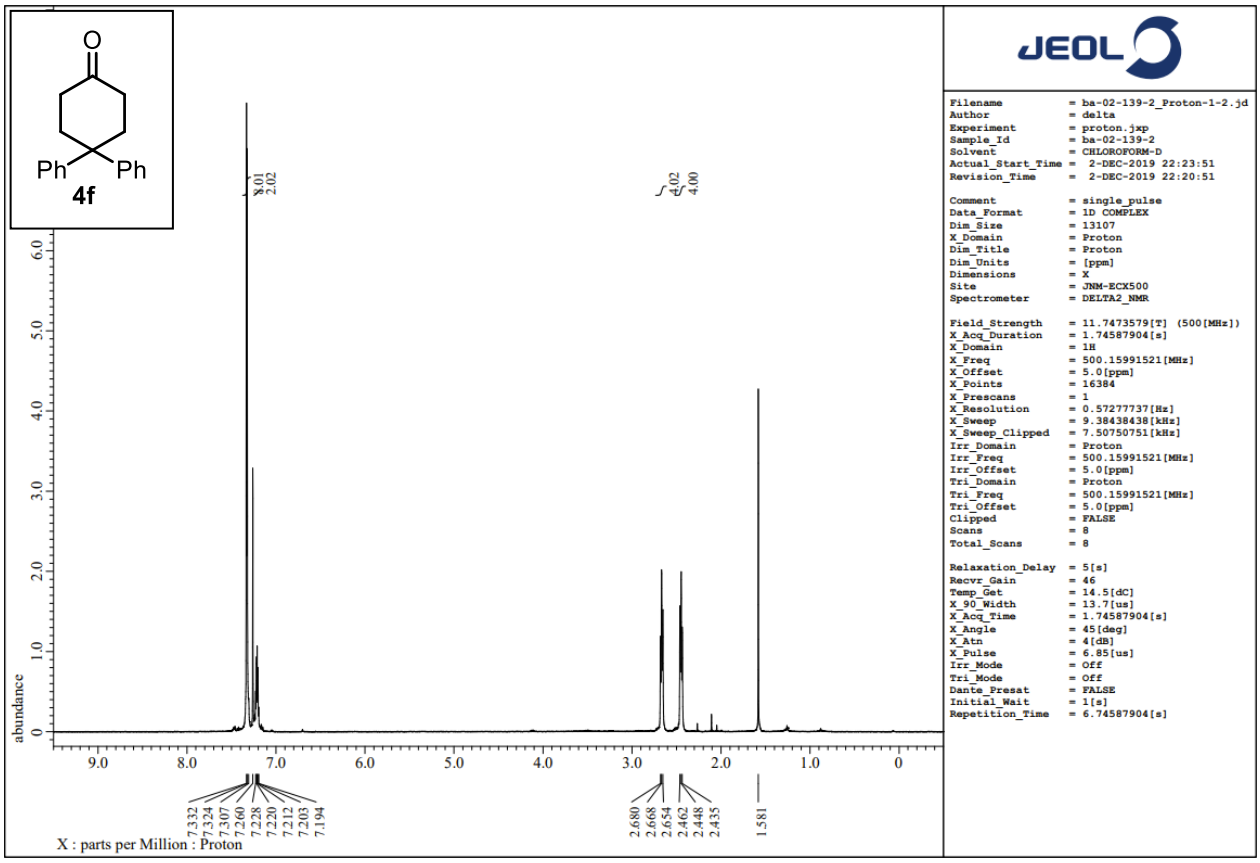


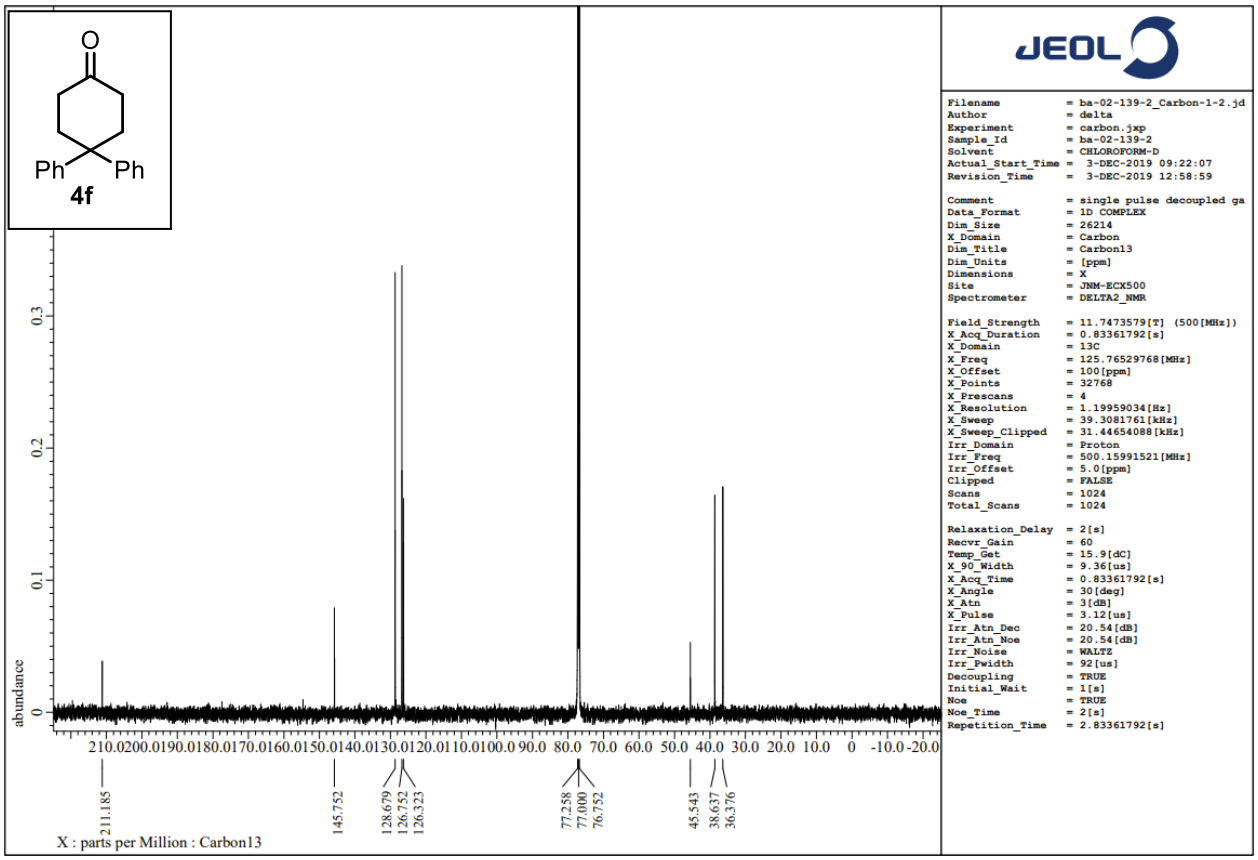

```
Filename          = ba-02-141-1_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-02-141-1
Solvent           = CHLOROFORM-D
Actual_Start_Time =  5-DEC-2019 11:31:37
Revision_Time     =  5-DEC-2019 13:32:19

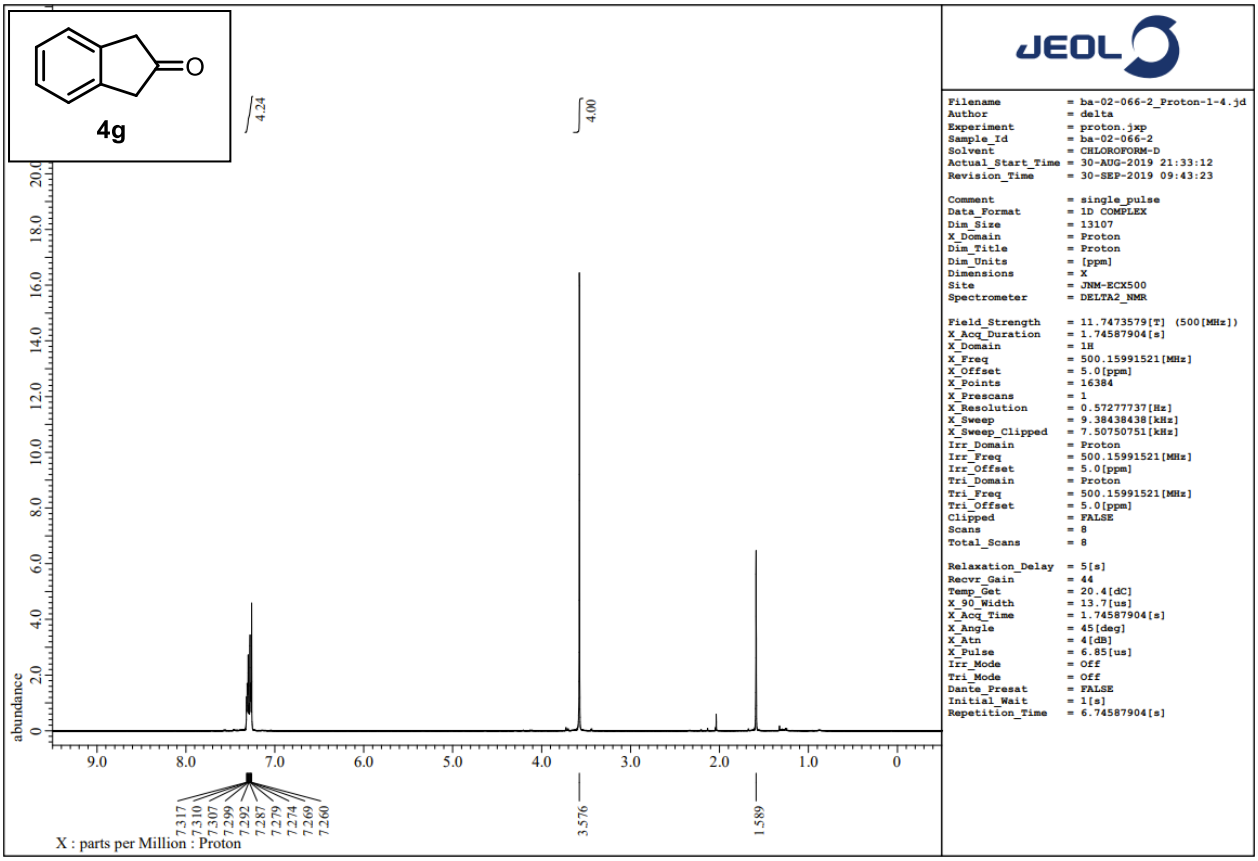
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

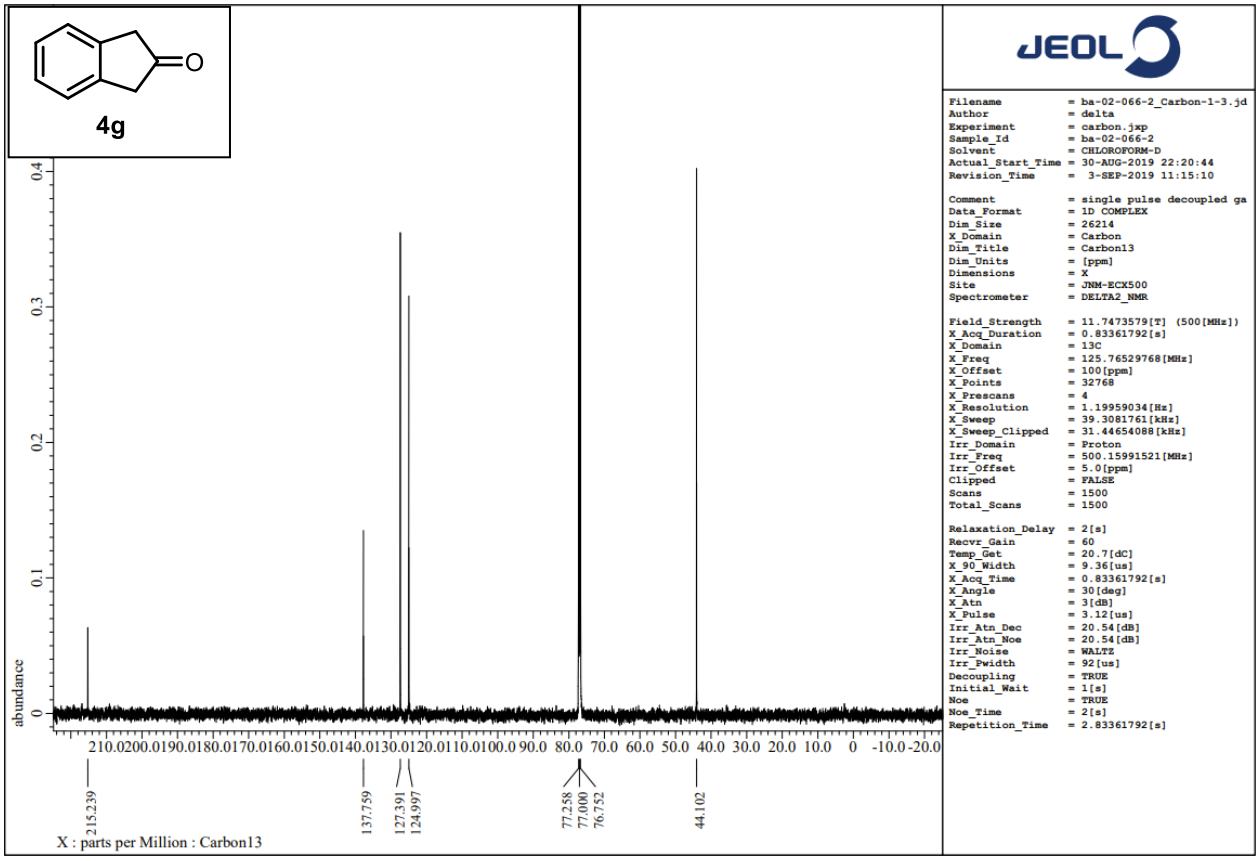
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 2048
Total_Scans       = 2048

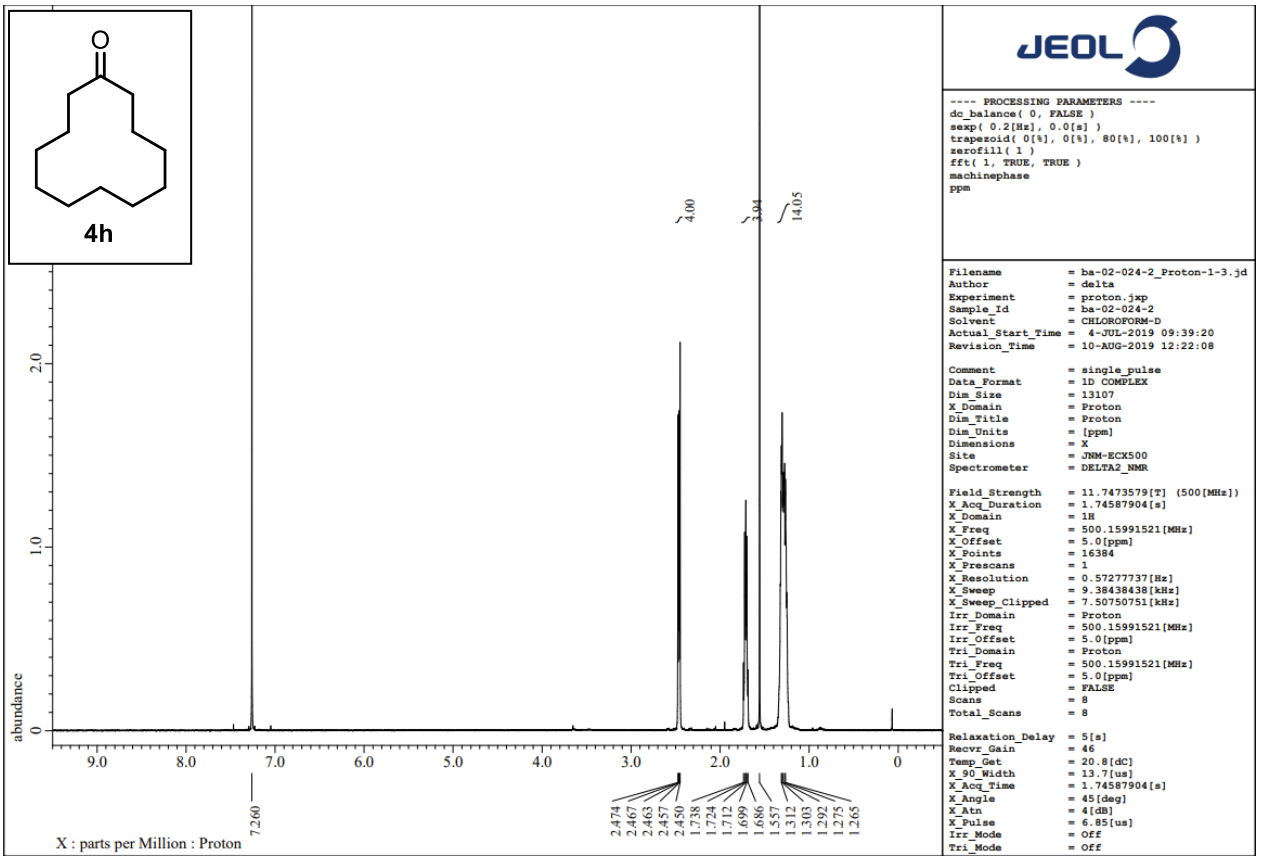
Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 16.3[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


O
Ph
Ph
4f
8.01
2.02
4.02
4.00
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.332
7.324
7.307
7.260
7.228
7.220
7.212
7.203
7.194
2.680
2.668
2.654
2.462
2.448
2.435
1.581
X : parts per Million : Proton
JEOL
Filename = ba-02-139-2_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-02-139-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 2-DEC-2019 22:23:51
Revision_Time = 2-DEC-2019 22:20:51
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 46
Temp_Get = 14.5[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


O
Ph
Ph
4f
abundance
0.3
0.2
0.1
0
210.0200.0190.0180.0170.0160.0150.0140.0130.0120.0110.0100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
211.185
145.752
128.679
126.752
126.323
77.258
77.000
76.752
45.543
38.637
36.376
X : parts per Million : Carbon13
JEOL
Filename = ba-02-139-2_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-02-139-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 3-DEC-2019 09:22:07
Revision_Time = 3-DEC-2019 12:58:59
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 15.9[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]


4g
4.24
4.00
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.317
7.310
7.307
7.299
7.292
7.287
7.279
7.274
7.269
7.260
3.576
1.589
X : parts per Million : Proton
JEOL
Filename = ba-02-066-2_Proton-1-4.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-02-066-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 30-AUG-2019 21:33:12
Revision_Time = 30-SEP-2019 09:43:23
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 44
Temp_Get = 20.4[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


4g
abundance
0.4
0.3
0.2
0.1
0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
215.239
137.759
127.391
124.997
77.258
77.000
76.752
44.102
X : parts per Million : Carbon13
JEOL
Filename = ba-02-066-2_Carbon-1-3.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-02-066-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 30-AUG-2019 22:20:44
Revision_Time = 3-SEP-2019 11:15:10
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 1500
Total_Scans = 1500
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 20.7[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]



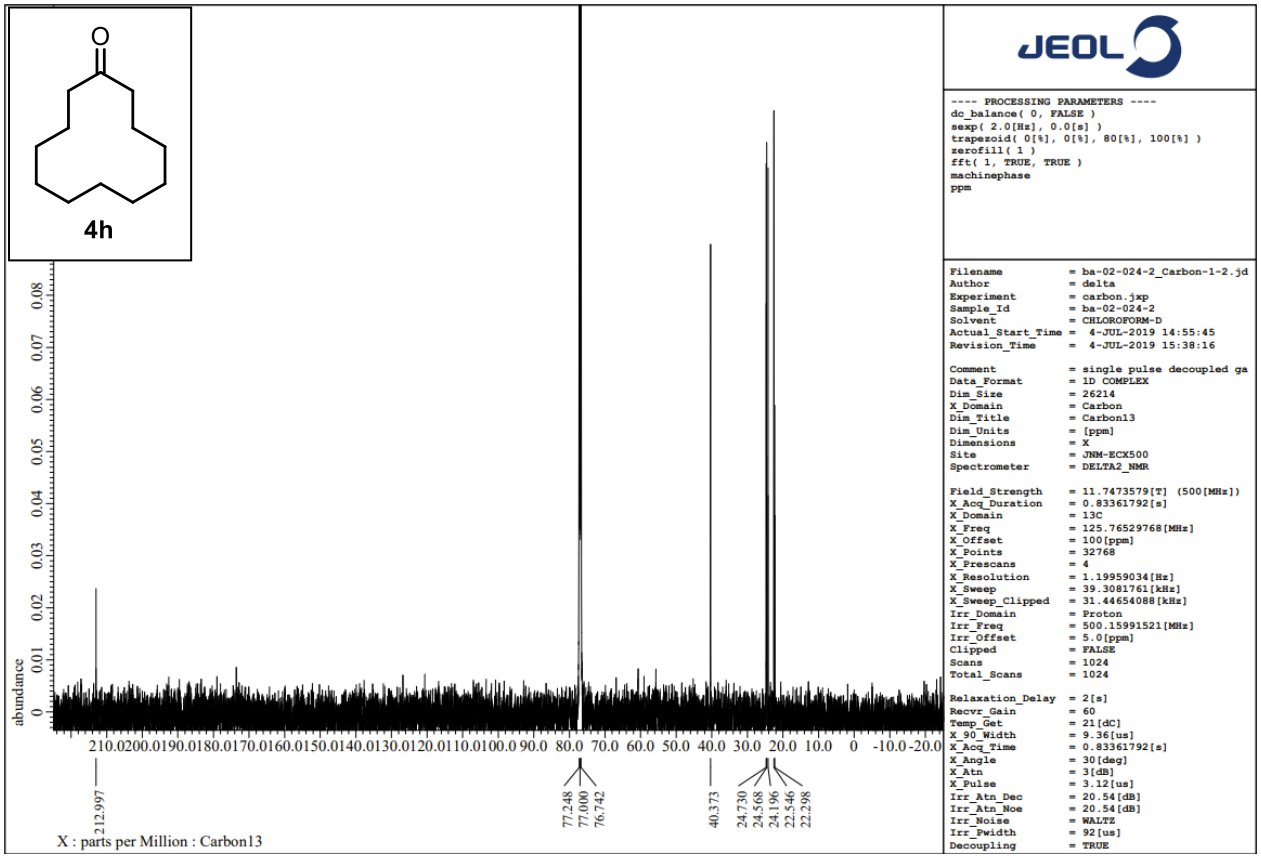

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Filename            = ba-02-024-2_Proton-1-3.jd
Author              = delta
Experiment          = proton.jxp
Sample_Id           = ba-02-024-2
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  4-JUL-2019 09:39:20
Revision_Time       = 10-AUG-2019 12:22:08

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T]  (500[MHz])
X_Acq_Duration      = 1.74587904[s]
X_Domain            = 1H
X_Freq              = 500.15991521[MHz]
X_Offset            = 5.0[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.57277737[Hz]
X_Sweep             = 9.38438438[kHz]
X_Sweep_Clipped     = 7.50750751[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Tri_Domain          = Proton
Tri_Freq            = 500.15991521[MHz]
Tri_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 46
Temp_Get            = 20.8[dC]
X_90_Width          = 13.7[us]
X_Acq_Time          = 1.74587904[s]
X_Angle             = 45[deg]
X_Atn               = 4[dB]
X_Pulse             = 6.85[us]
Irr_Mode            = Off
Tri_Mode            = Off
```



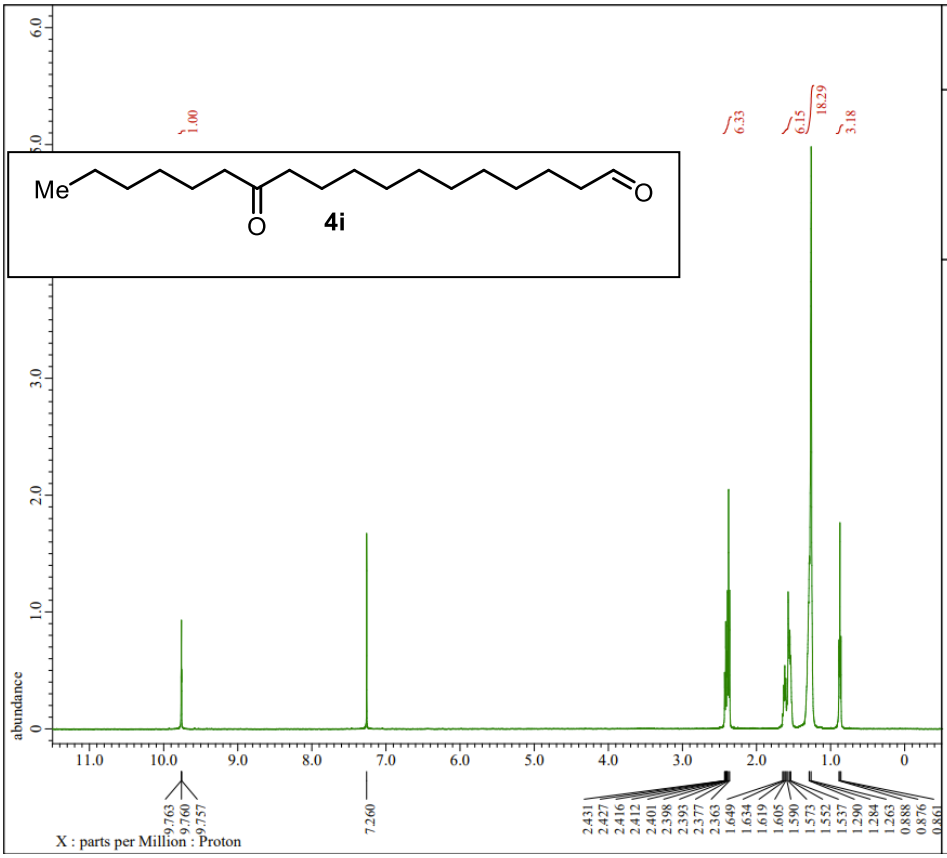

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Filename            = ba-02-024-2_Carbon-1-2.jd
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = ba-02-024-2
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  4-JUL-2019 14:55:45
Revision_Time       =  4-JUL-2019 15:38:16

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T]  (500[MHz])
X_Acq_Duration      = 0.83361792[s]
X_Domain            = 13C
X_Freq              = 125.76529768[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.19959034[Hz]
X_Sweep             = 39.3081761[kHz]
X_Sweep_Clipped     = 31.44654088[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 1024
Total_Scans         = 1024

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 21[dC]
X_90_Width          = 9.36[us]
X_Acq_Time          = 0.83361792[s]
X_Angle             = 30[deg]
X_Atn               = 3[dB]
X_Pulse             = 3.12[us]
Irr_Atn_Dec         = 20.54[dB]
Irr_Atn_Noe         = 20.54[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 92[us]
Decoupling          = TRUE
```




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

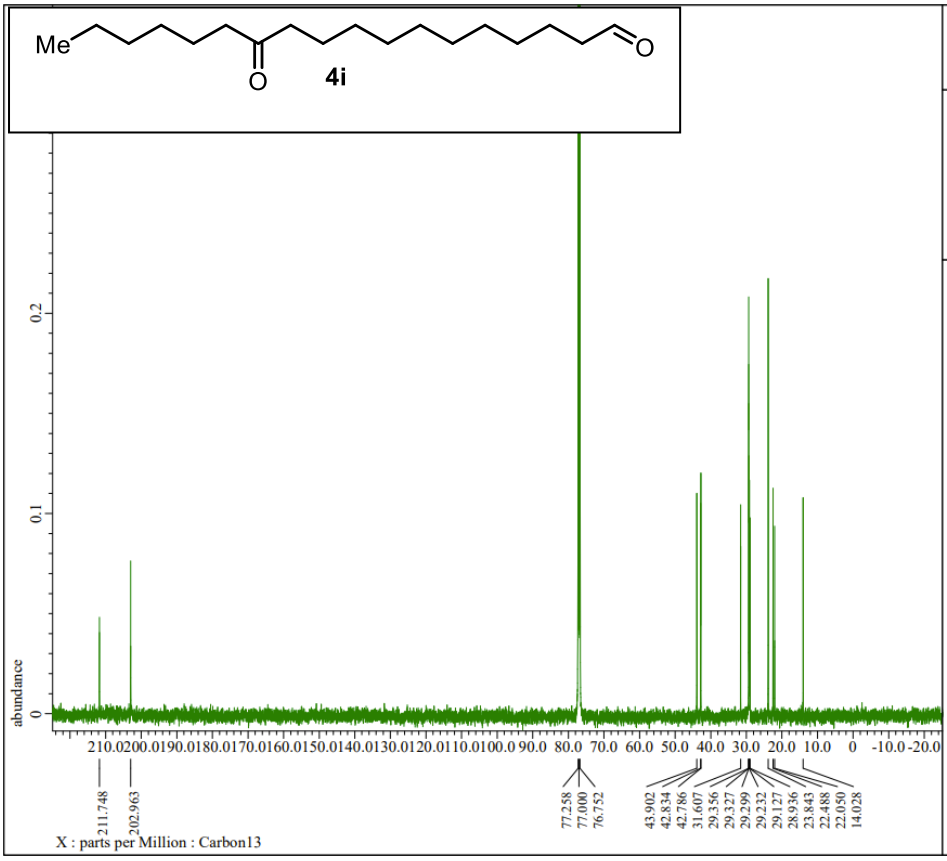
Derived from: ba-05-034-3_Proton-1-1.jdf

Filename            = ba-05-034-3_Proton-1-2.jd
Author              = delta
Experiment          = proton.jxp
Sample_Id           = ba-05-034-3
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 23-JUN-2021 13:44:21
Revision_Time       = 23-JUN-2021 13:47:42

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 1.74587904[s]
X_Domain            = 1H
X_Freq              = 500.15991521[MHz]
X_Offset            = 5.0[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.57277737[Hz]
X_Sweep             = 9.38438438[kHz]
X_Sweep_Clipped     = 7.50750751[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Tri_Domain          = Proton
Tri_Freq            = 500.15991521[MHz]
Tri_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 42
Temp_Get            = 22.2[dC]
X_90_Width          = 13.7[us]
X_Acq_Time          = 1.74587904[s]
X_Angle             = 45[deg]
X_Atn               = 4[dB]
X_Pulse             = 6.85[us]
Irr_Mode            = Off
Tri_Mode            = Off
```




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

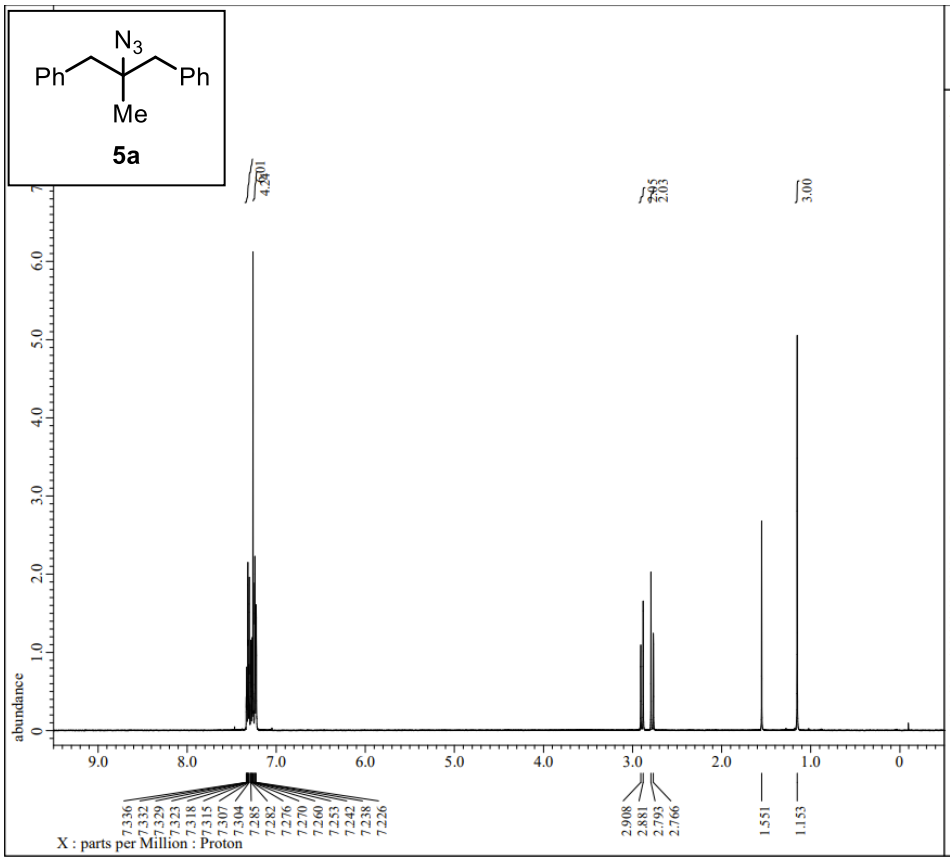
Derived from: ba-05-034-3_Carbon-1-1.jdf

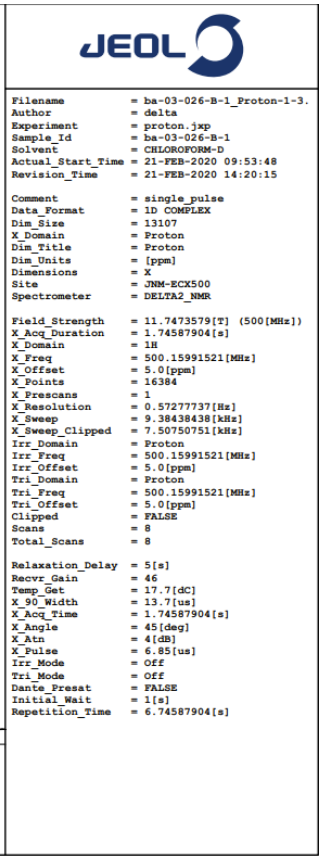
Filename            = ba-05-034-3_Carbon-1-2.jd
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = ba-05-034-3
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 23-JUN-2021 16:34:36
Revision_Time       = 23-JUN-2021 21:03:15

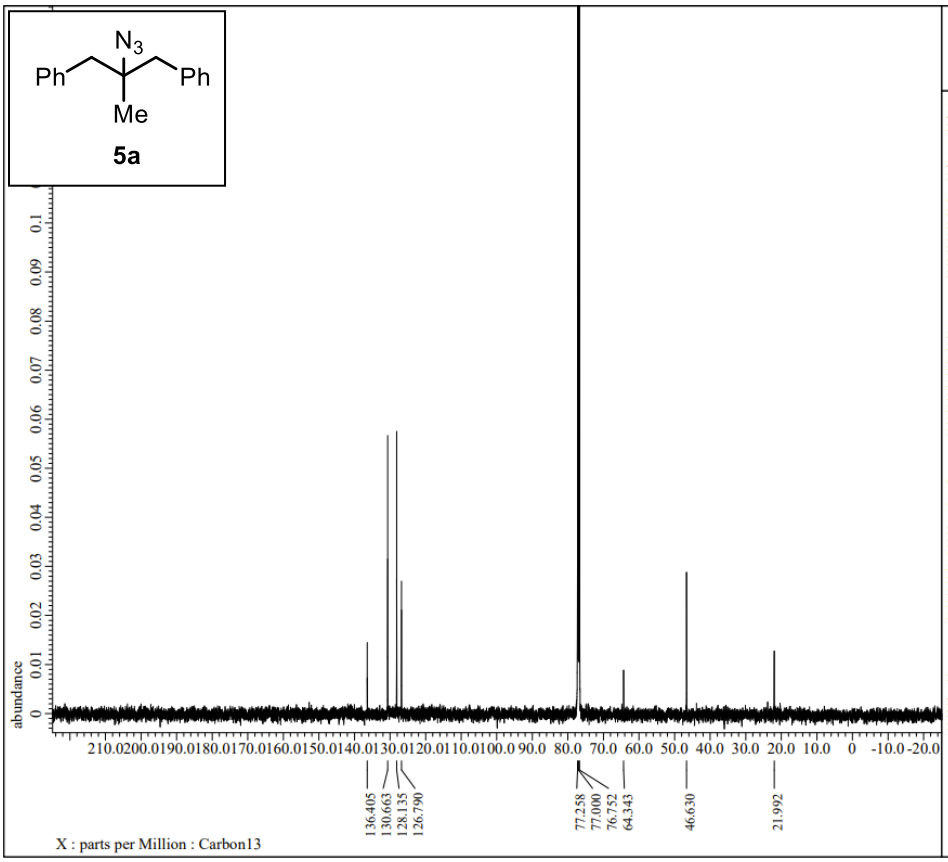
Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

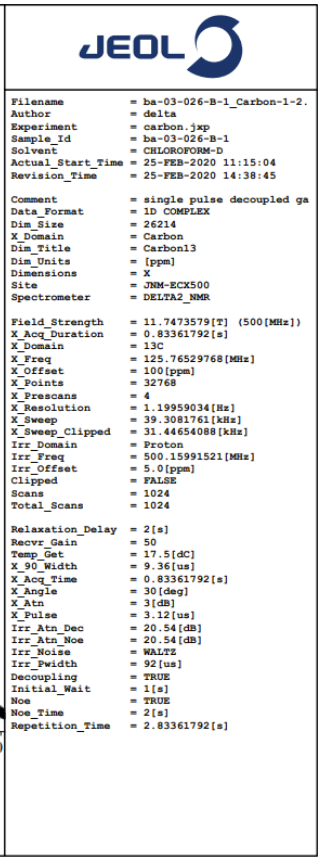
Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 0.83361792[s]
X_Domain            = 13C
X_Freq              = 125.76529768[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.19959034[Hz]
X_Sweep             = 39.3081761[kHz]
X_Sweep_Clipped     = 31.44654088[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 2048
Total_Scans         = 2048

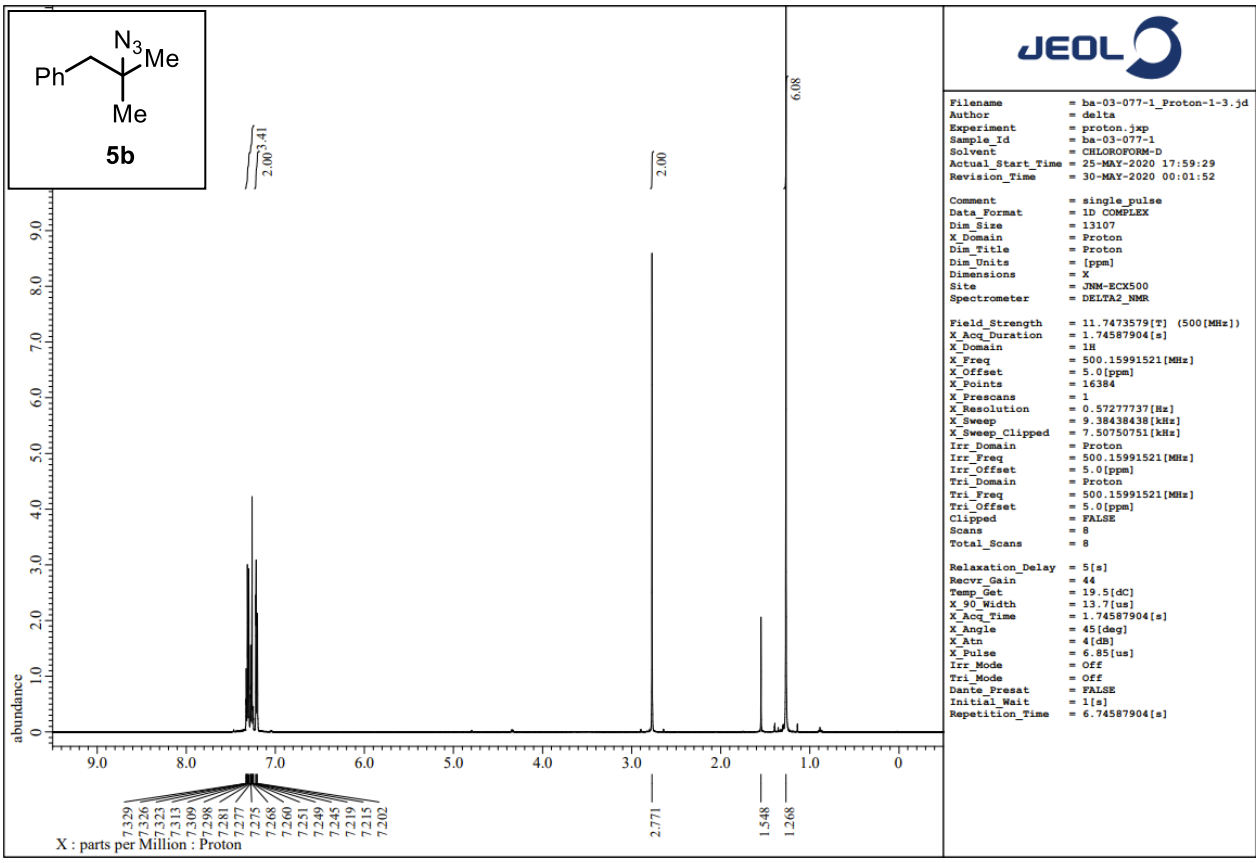
Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 22.6[dC]
X_90_Width          = 9.36[us]
X_Acq_Time          = 0.83361792[s]
X_Angle             = 30[deg]
X_Atn               = 3[dB]
X_Pulse             = 3.12[us]
Irr_Atn_Dec         = 20.54[dB]
Irr_Atn_Noe         = 20.54[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 92[us]
Decoupling          = TRUE
```

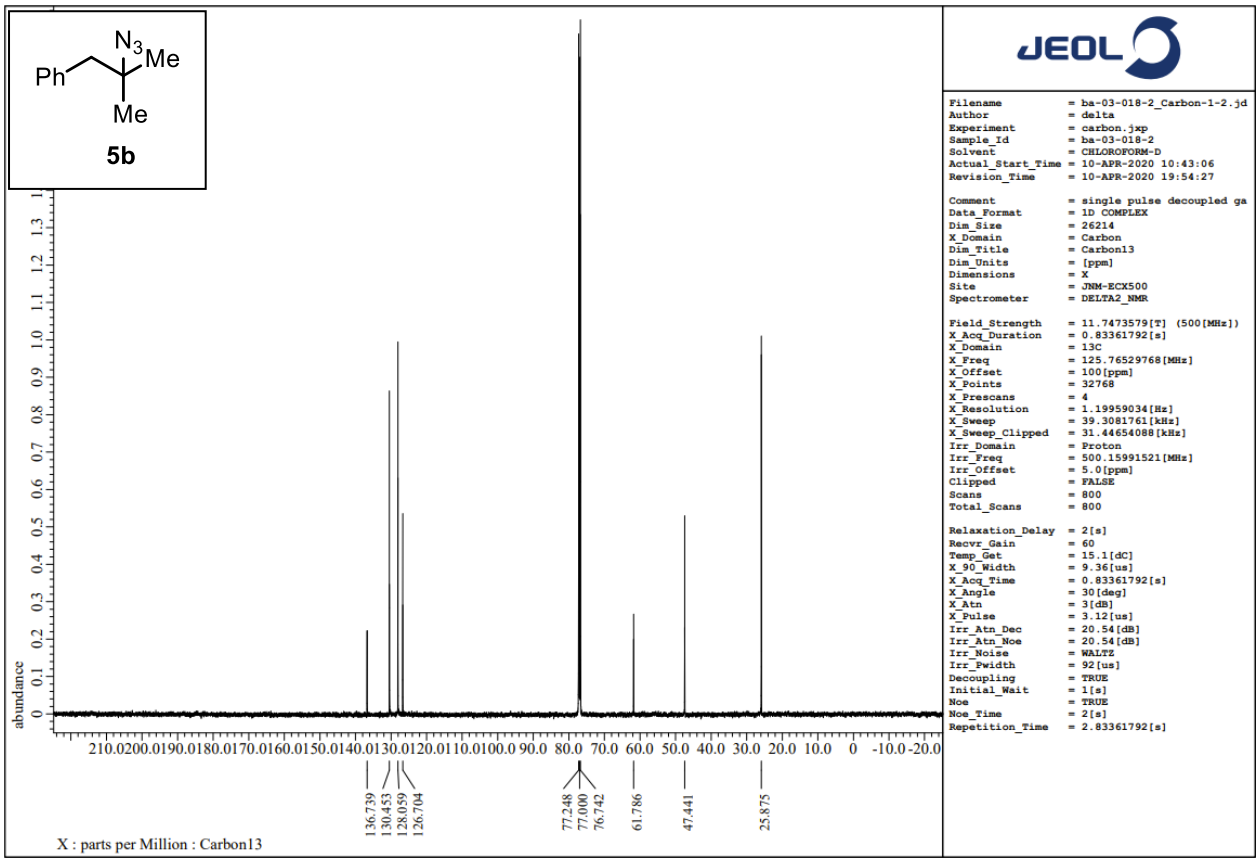

N3
Ph
Ph
Me
5a
4.501
2.045
2.033
3.000
abundance
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.336 7.332 7.329 7.323 7.318 7.315 7.307 7.304 7.285 7.282 7.276 7.270 7.260 7.253 7.242 7.238 7.226
2.908 2.881 2.793 2.766
1.551
1.153
X : parts per Million : Proton

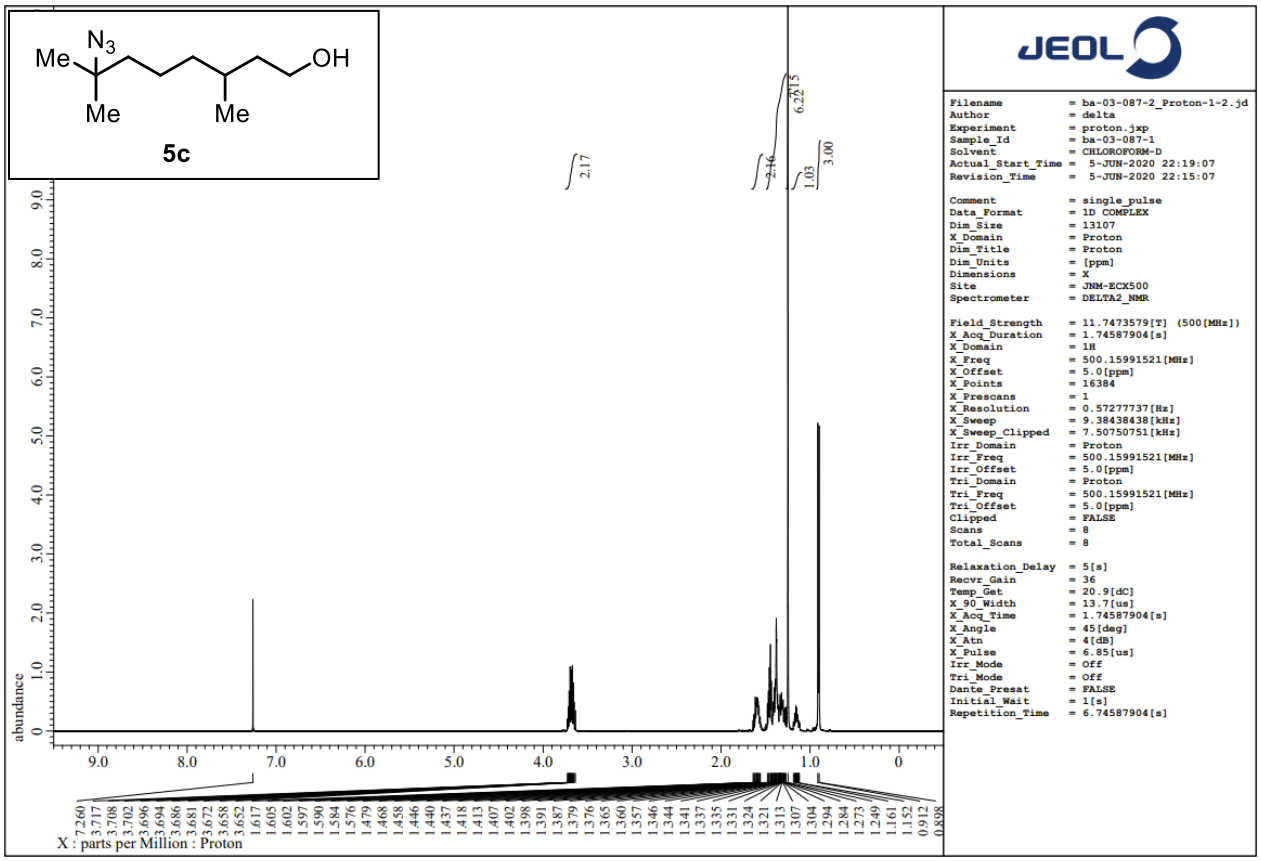

JEOL
Filename = ba-03-026-B-1_Proton-1-3.
Author = delta
Experiment = proton.jxp
Sample_Id = ba-03-026-B-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 21-FEB-2020 09:53:48
Revision_Time = 21-FEB-2020 14:20:15
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 46
Temp_Get = 17.7[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]

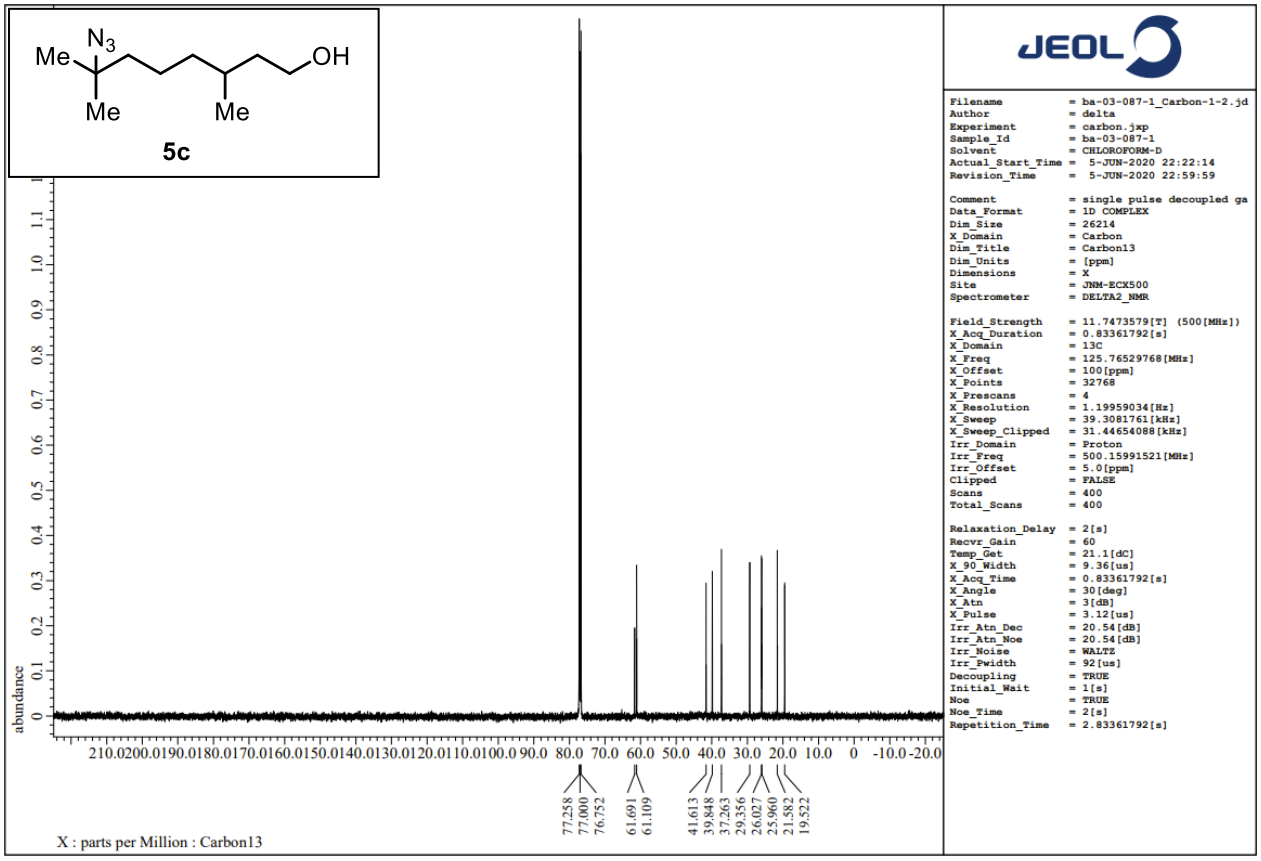

N3
Ph
Ph
Me
5a
abundance
210.0200.0190.0180.0170.0160.0150.0140.0130.0120.0110.0100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
136.405
130.663
128.135
126.790
77.258
77.000
76.752
64.343
46.630
21.992
X : parts per Million : Carbon13

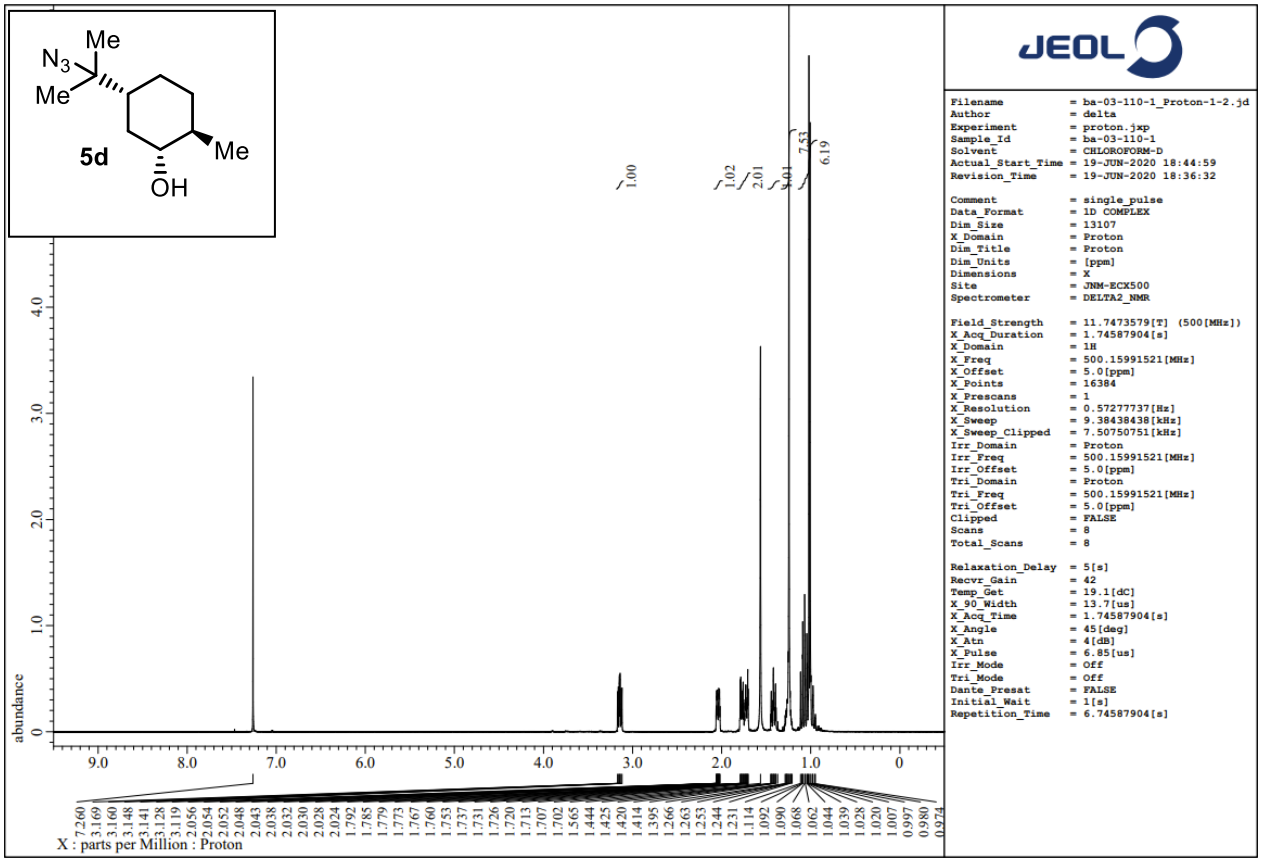

JEOL
Filename = ba-03-026-B-1_Carbon-1-2.
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-03-026-B-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 25-FEB-2020 11:15:04
Revision_Time = 25-FEB-2020 14:38:45
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 50
Temp_Get = 17.5[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

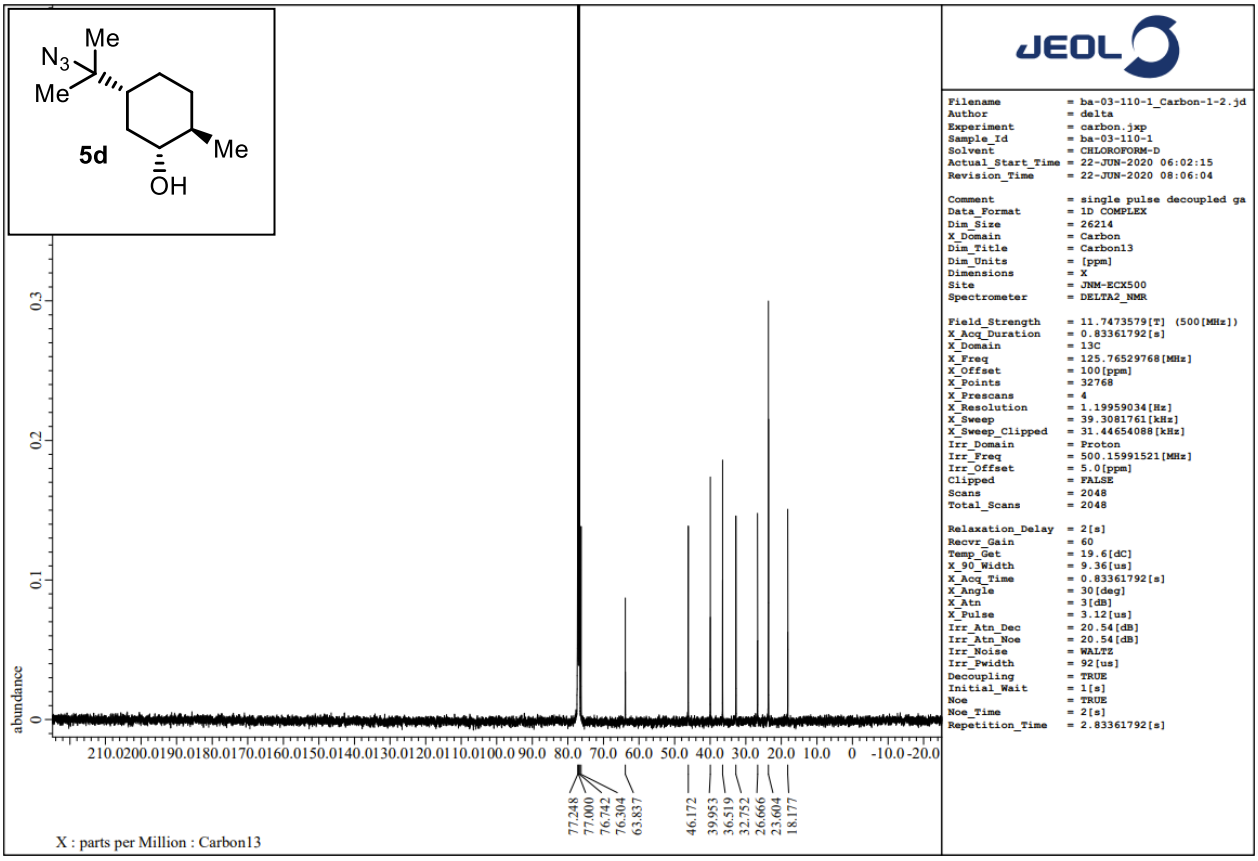

N3
Me
Ph
Me
5b
3.41
2.00
2.00
6.08
abundance
X : parts per Million : Proton
7.329
7.326
7.323
7.313
7.309
7.298
7.281
7.277
7.275
7.268
7.260
7.251
7.249
7.245
7.219
7.215
7.202
2.771
1.548
1.268
Filename = ba-03-077-1_Proton-1-3.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-03-077-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 25-MAY-2020 17:59:29
Revision_Time = 30-MAY-2020 00:01:52
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 44
Temp_Get = 19.5[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]

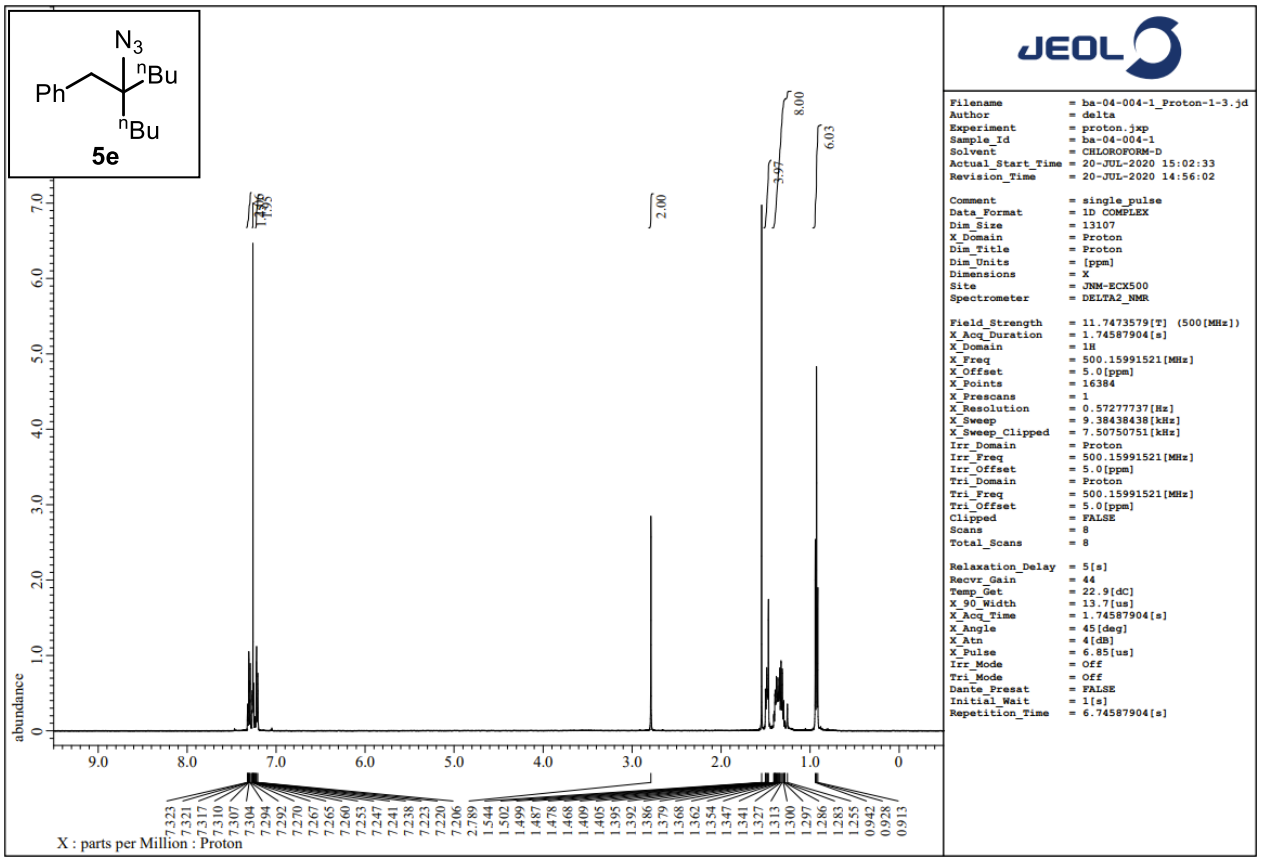

N3
Me
Ph
Me
5b
abundance
X : parts per Million : Carbon13
136.739
130.453
128.059
126.704
77.248
77.000
76.742
61.786
47.441
25.875
Filename = ba-03-018-2_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-03-018-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 10-APR-2020 10:43:06
Revision_Time = 10-APR-2020 19:54:27
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 800
Total_Scans = 800
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 15.1[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

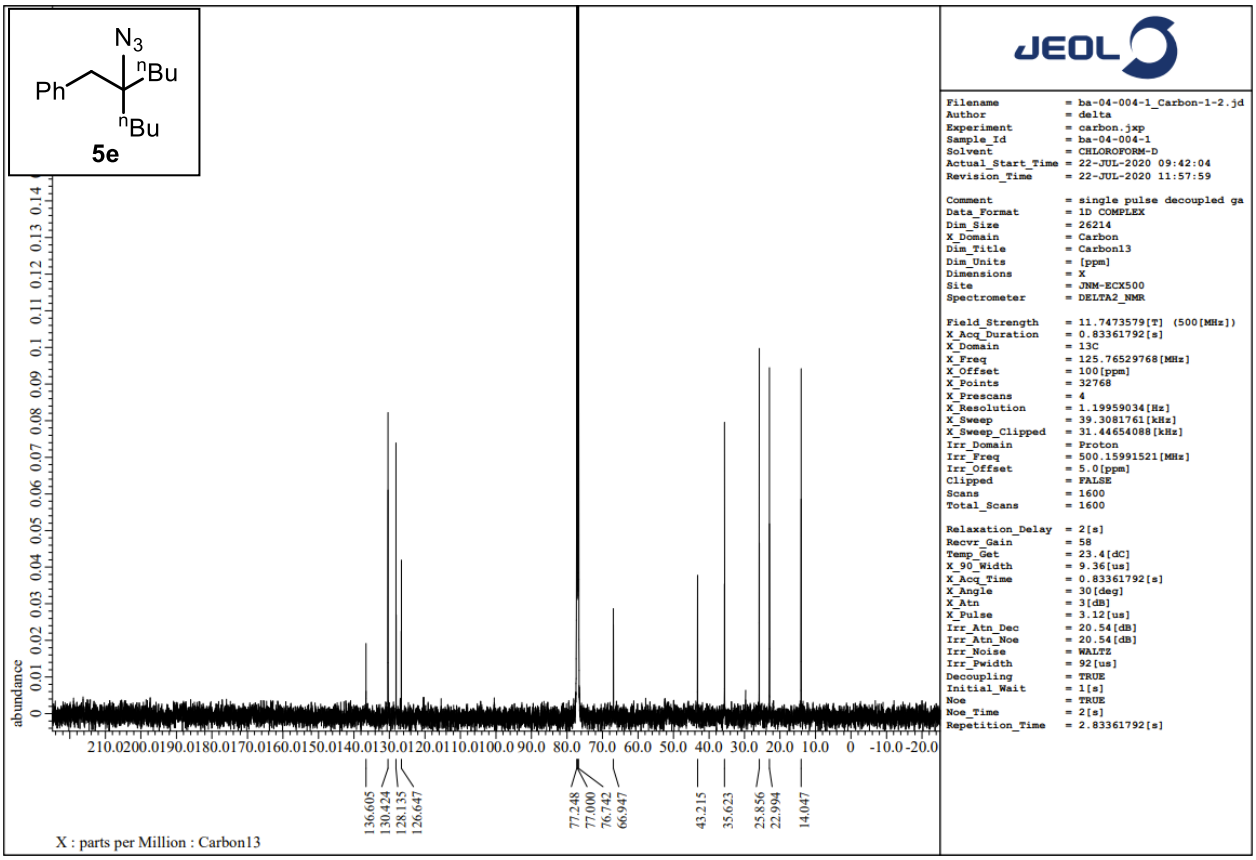

Me
N3
OH
Me
Me
5c
2.17
6.22
2.16
1.03
3.00
abundance
X : parts per Million : Proton
Filename = ba-03-087-2_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-03-087-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 5-JUN-2020 22:19:07
Revision_Time = 5-JUN-2020 22:15:07
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 36
Temp_Get = 20.9[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]

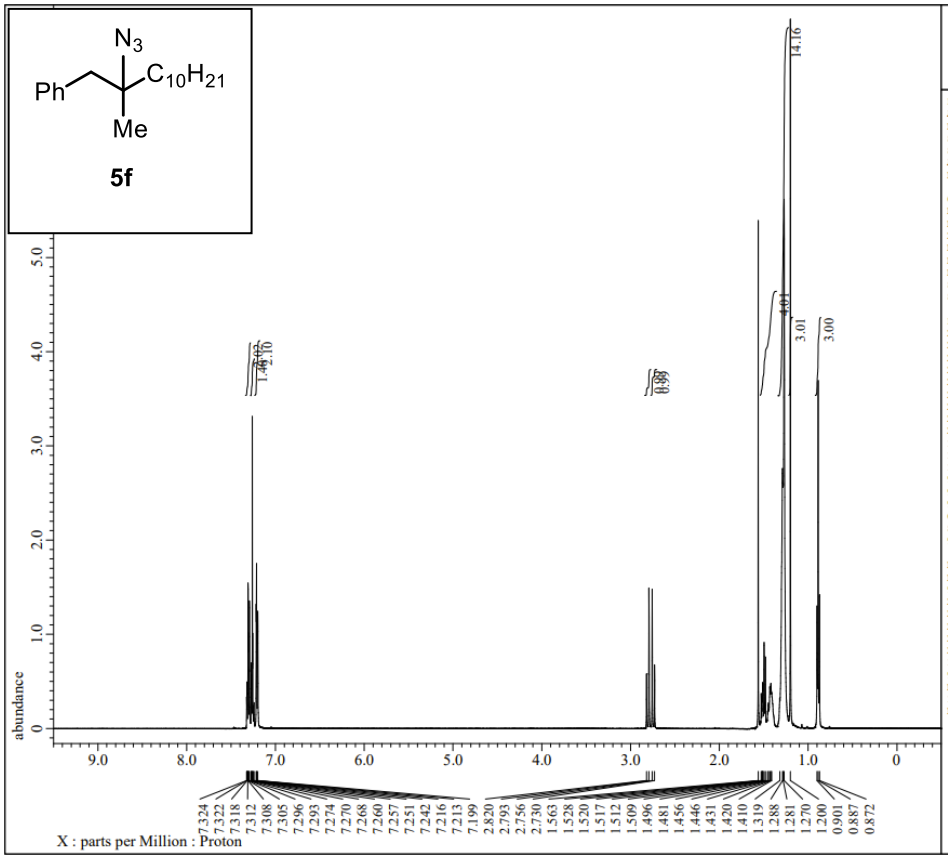

Me
N3
OH
Me
Me
5c
abundance
X : parts per Million : Carbon13
77.258
77.000
76.752
61.691
61.109
41.613
39.848
37.263
29.356
26.027
25.960
21.582
19.522
Filename = ba-03-087-1_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-03-087-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 5-JUN-2020 22:22:14
Revision_Time = 5-JUN-2020 22:59:59
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 400
Total_Scans = 400
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.1[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]


Me
N3
Me
5d
Me
OH
1.00
1.02
2.01
3.01
7.53
6.19
abundance
X : parts per Million : Proton
JEOL
Filename = ba-03-110-1_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-03-110-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 19-JUN-2020 18:44:59
Revision_Time = 19-JUN-2020 18:36:32
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 42
Temp_Get = 19.1[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


Me
N3
Me
5d
Me
OH
abundance
X : parts per Million : Carbon13
JEOL
Filename = ba-03-110-1_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-03-110-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 22-JUN-2020 06:02:15
Revision_Time = 22-JUN-2020 08:06:04
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 2048
Total_Scans = 2048
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 19.6[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]


N3
nBu
Ph
nBu
5e
8.00
6.03
3.97
2.00
abundance
X : parts per Million : Proton
Filename = ba-04-004-1_Proton-1-3.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-04-004-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 20-JUL-2020 15:02:33
Revision_Time = 20-JUL-2020 14:56:02
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 44
Temp_Get = 22.9[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


N3
nBu
Ph
nBu
5e
abundance
X : parts per Million : Carbon13
Filename = ba-04-004-1_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-04-004-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 22-JUL-2020 09:42:04
Revision_Time = 22-JUL-2020 11:57:59
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 1600
Total_Scans = 1600
Relaxation_Delay = 2[s]
Recvr_Gain = 58
Temp_Get = 23.4[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

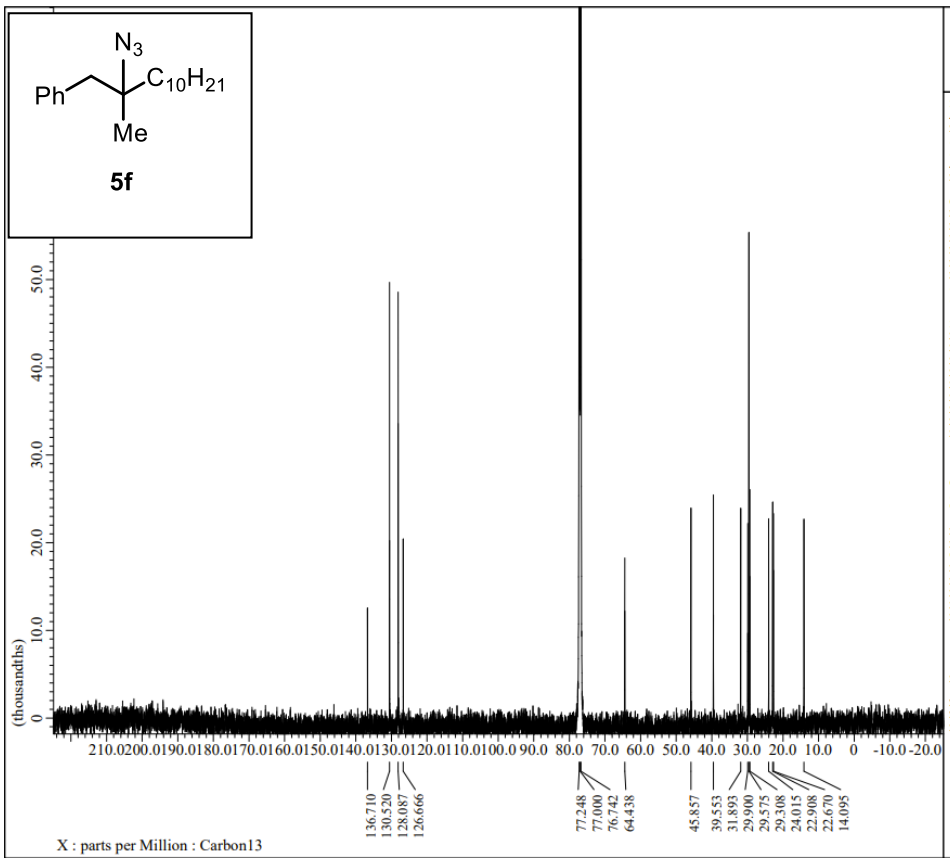



```
Filename          = ba-04-039-A-1_Proton-1-3.
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-039-A-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 10-SEP-2020 21:19:28
Revision_Time     = 10-SEP-2020 21:10:50

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 38
Temp_Get          = 21.6[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

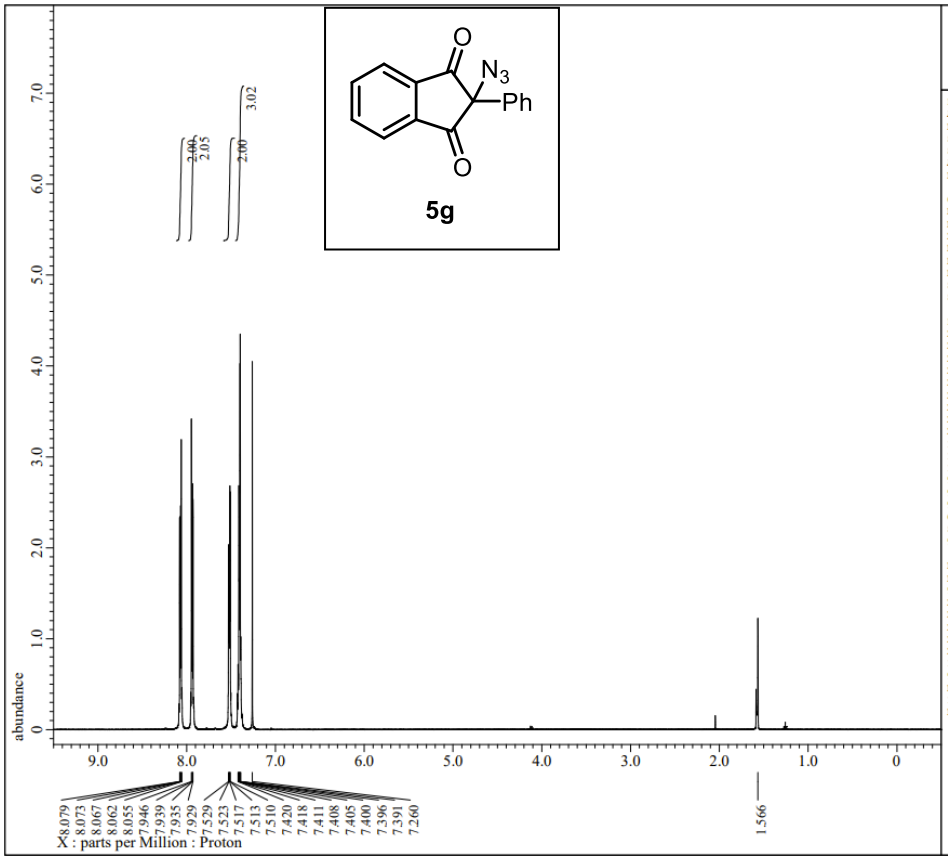



```
Filename          = ba-04-016-3_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-016-3
Solvent           = CHLOROFORM-D
Actual_Start_Time = 20-AUG-2020 22:21:39
Revision_Time     = 21-AUG-2020 09:24:37

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 9000
Total_Scans       = 9000

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 25.8[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```

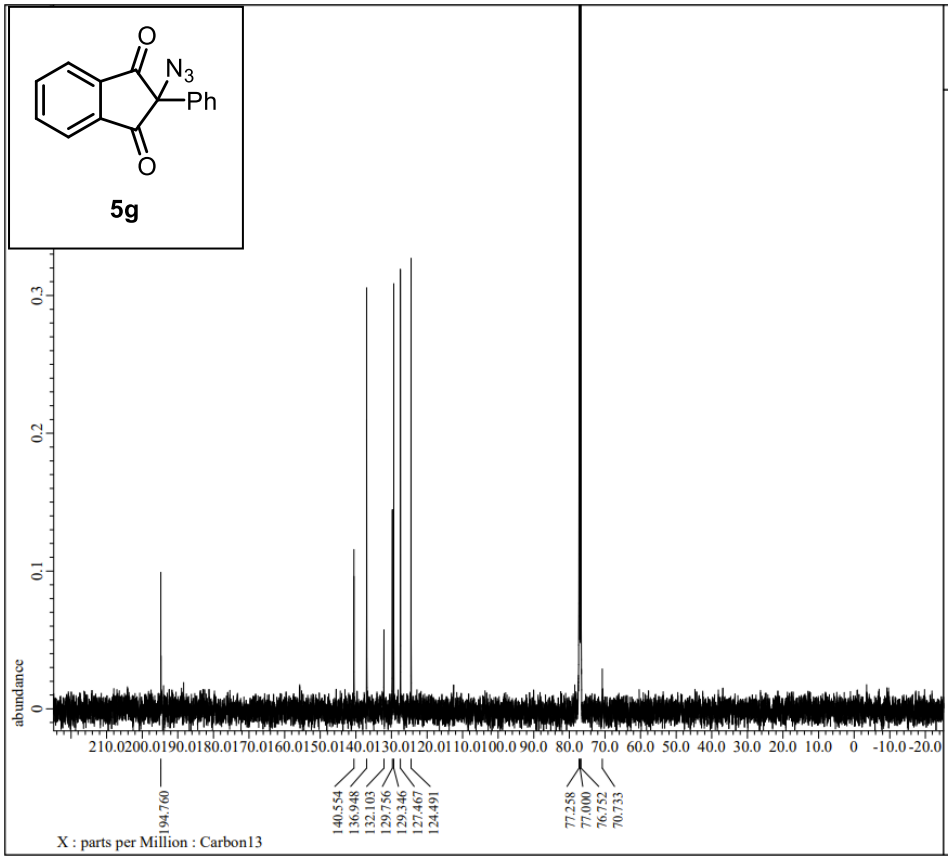



```
Filename          = ba-04-100-2_Proton-1-2.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-100-2
Solvent           = CHLOROFORM-D
Actual_Start_Time =  4-DEC-2020 14:54:04
Revision_Time     =  4-DEC-2020 14:55:58

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 44
Temp_Get          = 17.9[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

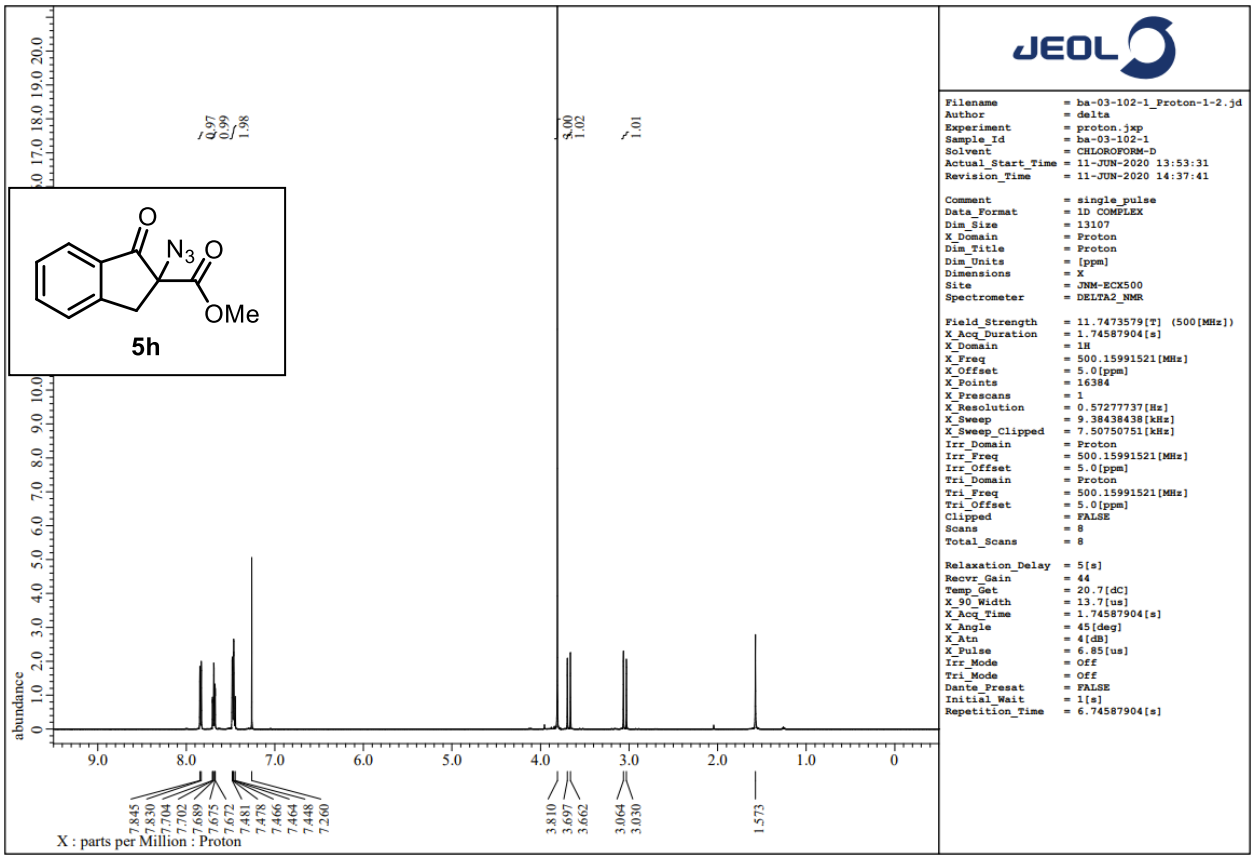


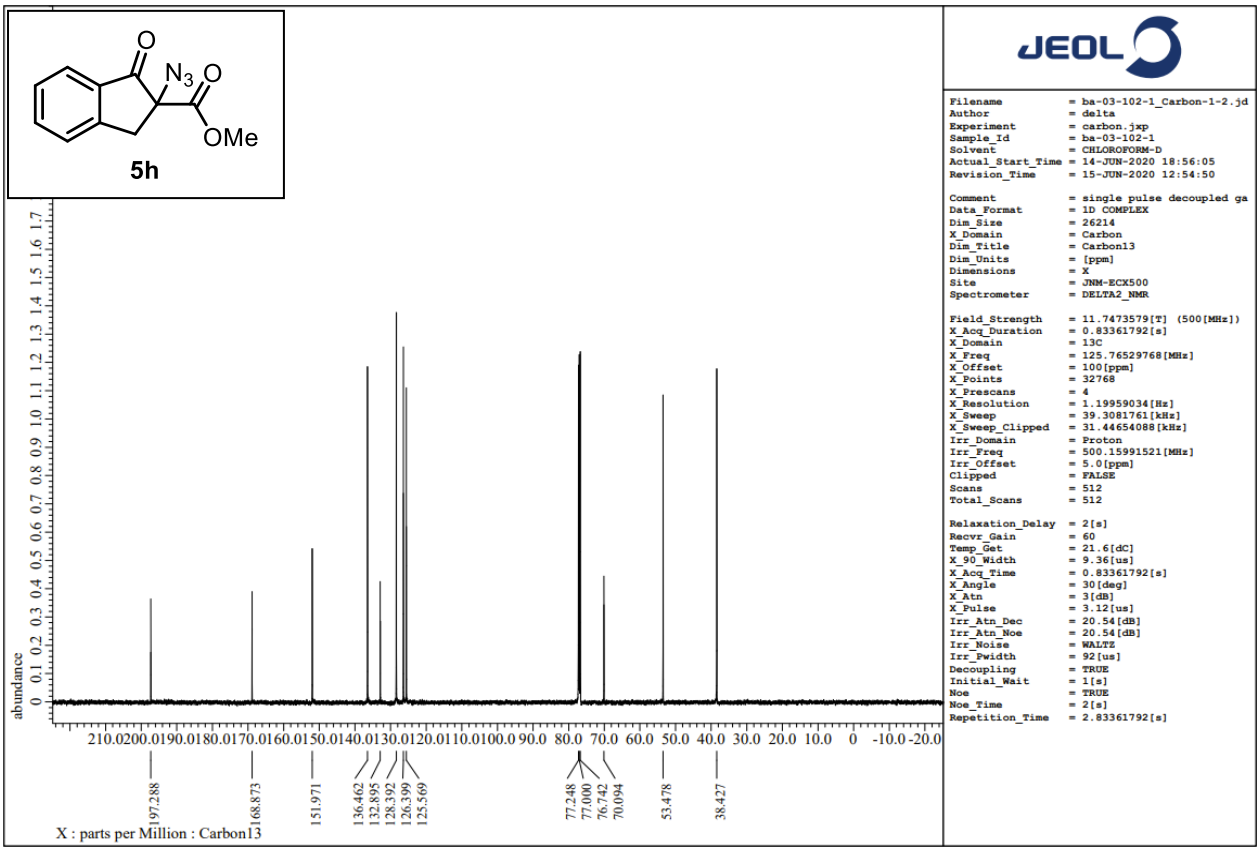

```
Filename          = ba-04-100-2_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-100-2
Solvent           = CHLOROFORM-D
Actual_Start_Time =  4-DEC-2020 14:56:59
Revision_Time     =  4-DEC-2020 14:57:31

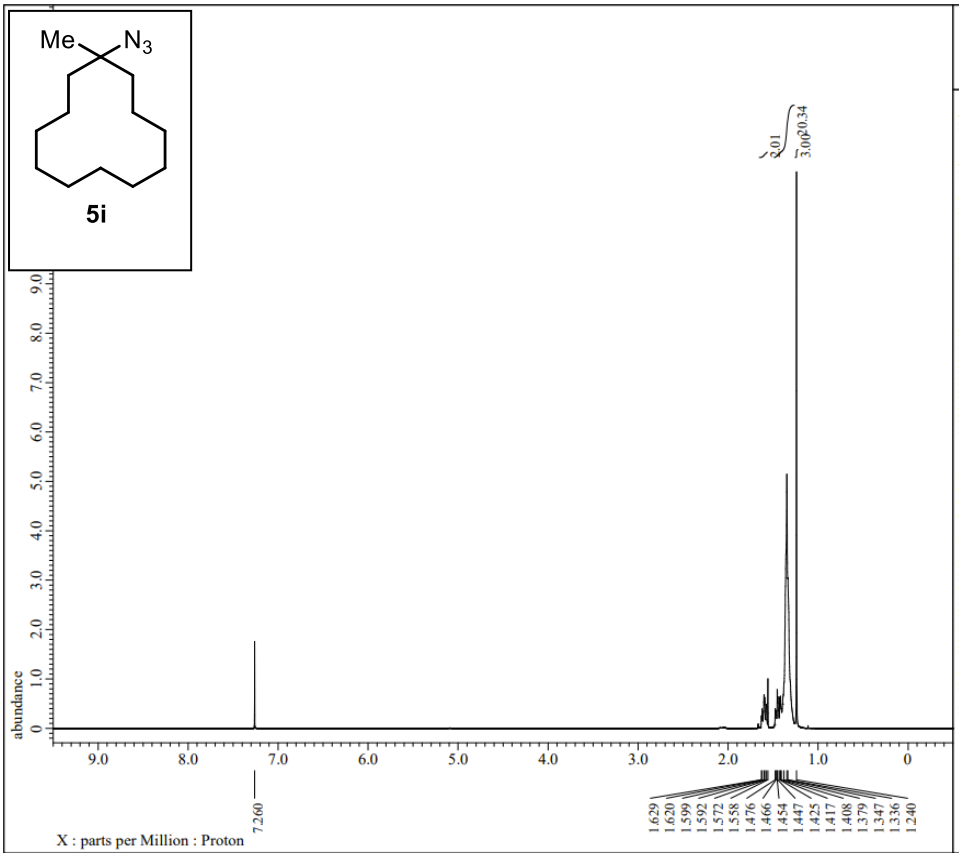
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 256
Total_Scans       = 256

Relaxation_Delay  = 2[s]
Recvr_Gain        = 58
Temp_Get          = 18.2[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


5h
abundance
X : parts per Million : Proton
7.845
7.830
7.704
7.702
7.689
7.675
7.672
7.481
7.478
7.466
7.464
7.448
7.260
3.810
3.697
3.662
3.064
3.030
1.573
Filename = ba-03-102-1_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-03-102-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 11-JUN-2020 13:53:31
Revision_Time = 11-JUN-2020 14:37:41
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 44
Temp_Get = 20.7[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


5h
abundance
X : parts per Million : Carbon13
197.288
168.873
151.971
136.462
132.895
128.392
126.399
125.569
77.248
77.000
76.742
70.094
53.478
38.427
Filename = ba-03-102-1_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-03-102-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 14-JUN-2020 18:56:05
Revision_Time = 15-JUN-2020 12:54:50
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 512
Total_Scans = 512
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.6[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]



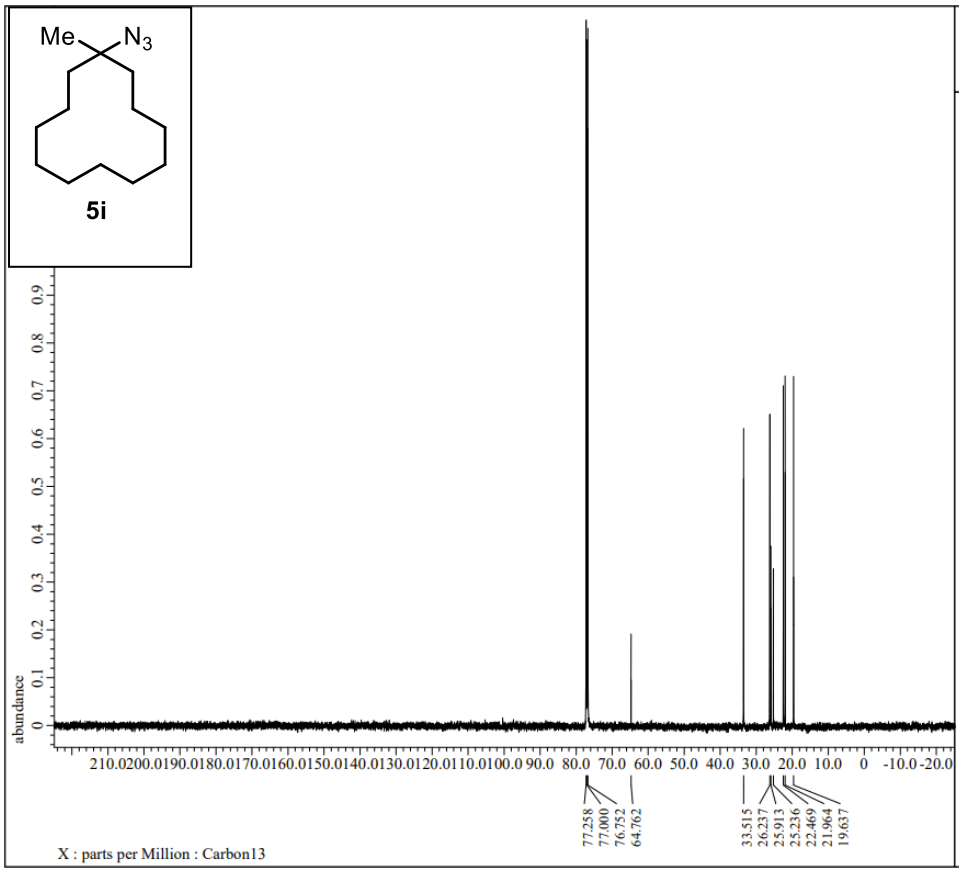
JEOL

```
Filename              = ba-04-057-1_Proton-1-3.jd
Author                = delta
Experiment            = proton.jxp
Sample_Id             = ba-04-057-1
Solvent               = CHLOROFORM-D
Actual_Start_Time     =  7-OCT-2020 15:13:46
Revision_Time         =  7-OCT-2020 15:14:18

Comment               = single_pulse
Data_Format           = 1D COMPLEX
Dim_Size              = 13107
X_Domain              = Proton
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Site                  = JNM-ECX500
Spectrometer          = DELTA2_NMR

Field_Strength        = 11.7473579[T] (500[MHz])
X_Acq_Duration        = 1.74587904[s]
X_Domain              = 1H
X_Freq                = 500.15991521[MHz]
X_Offset              = 5.0[ppm]
X_Points              = 16384
X_Prescans            = 1
X_Resolution          = 0.57277737[Hz]
X_Sweep               = 9.38438438[kHz]
X_Sweep_Clipped       = 7.50750751[kHz]
Irr_Domain            = Proton
Irr_Freq              = 500.15991521[MHz]
Irr_Offset            = 5.0[ppm]
Tri_Domain            = Proton
Tri_Freq              = 500.15991521[MHz]
Tri_Offset            = 5.0[ppm]
Clipped               = FALSE
Scans                 = 8
Total_Scans           = 8

Relaxation_Delay      = 5[s]
Recvr_Gain            = 34
Temp_Get              = 18.7[dC]
X_90_Width            = 13.7[us]
X_Acq_Time            = 1.74587904[s]
X_Angle               = 45[deg]
X_Atn                 = 4[dB]
X_Pulse               = 6.85[us]
Irr_Mode              = Off
Tri_Mode              = Off
Dante_Presat          = FALSE
Initial_Wait          = 1[s]
Repetition_Time       = 6.74587904[s]
```



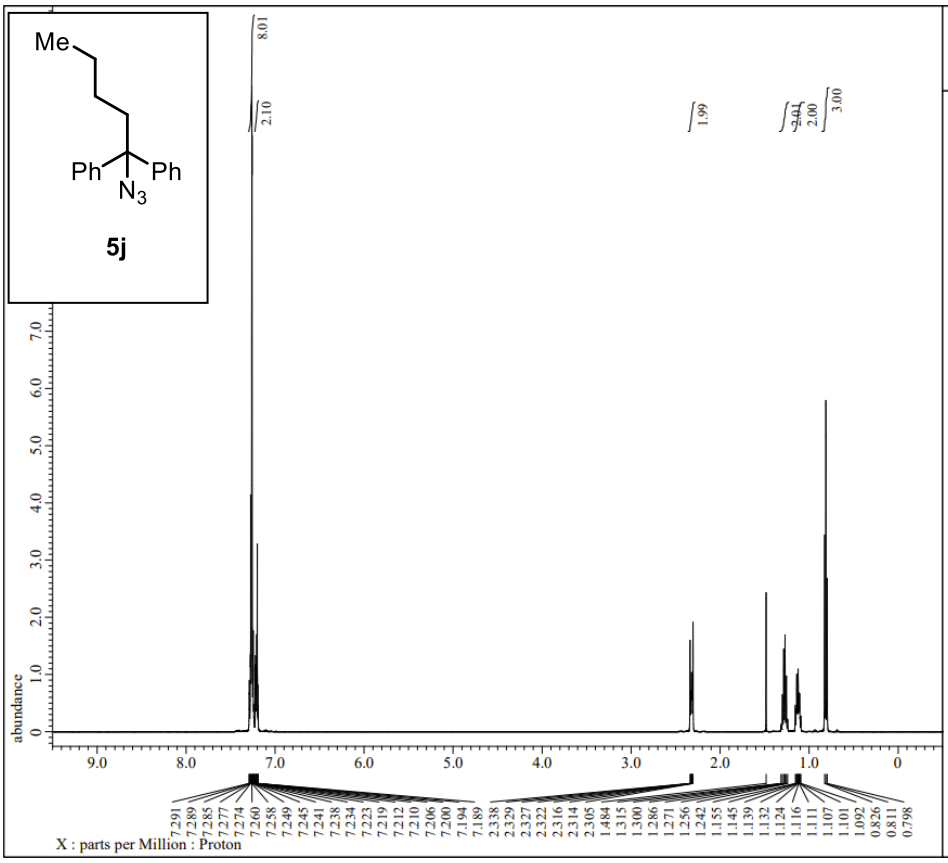
JEOL

```
Filename              = ba-04-057-1_Carbon-1-2.jd
Author                = delta
Experiment            = carbon.jxp
Sample_Id             = ba-04-057-1
Solvent               = CHLOROFORM-D
Actual_Start_Time     = 12-OCT-2020 14:56:26
Revision_Time         = 13-OCT-2020 17:17:17

Comment               = single pulse decoupled ga
Data_Format           = 1D COMPLEX
Dim_Size              = 26214
X_Domain              = Carbon
Dim_Title             = Carbon13
Dim_Units             = [ppm]
Dimensions            = X
Site                  = JNM-ECX500
Spectrometer          = DELTA2_NMR

Field_Strength        = 11.7473579[T] (500[MHz])
X_Acq_Duration        = 0.83361792[s]
X_Domain              = 13C
X_Freq                = 125.76529768[MHz]
X_Offset              = 100[ppm]
X_Points              = 32768
X_Prescans            = 4
X_Resolution          = 1.19959034[Hz]
X_Sweep               = 39.3081761[kHz]
X_Sweep_Clipped       = 31.44654088[kHz]
Irr_Domain            = Proton
Irr_Freq              = 500.15991521[MHz]
Irr_Offset            = 5.0[ppm]
Clipped               = FALSE
Scans                 = 400
Total_Scans           = 400

Relaxation_Delay      = 2[s]
Recvr_Gain            = 60
Temp_Get              = 20.3[dC]
X_90_Width            = 9.36[us]
X_Acq_Time            = 0.83361792[s]
X_Angle               = 30[deg]
X_Atn                 = 3[dB]
X_Pulse               = 3.12[us]
Irr_Atn_Dec           = 20.54[dB]
Irr_Atn_Noe           = 20.54[dB]
Irr_Noise             = WALTZ
Irr_Pwidth            = 92[us]
Decoupling            = TRUE
Initial_Wait          = 1[s]
Noe                   = TRUE
Noe_Time              = 2[s]
Repetition_Time       = 2.83361792[s]
```

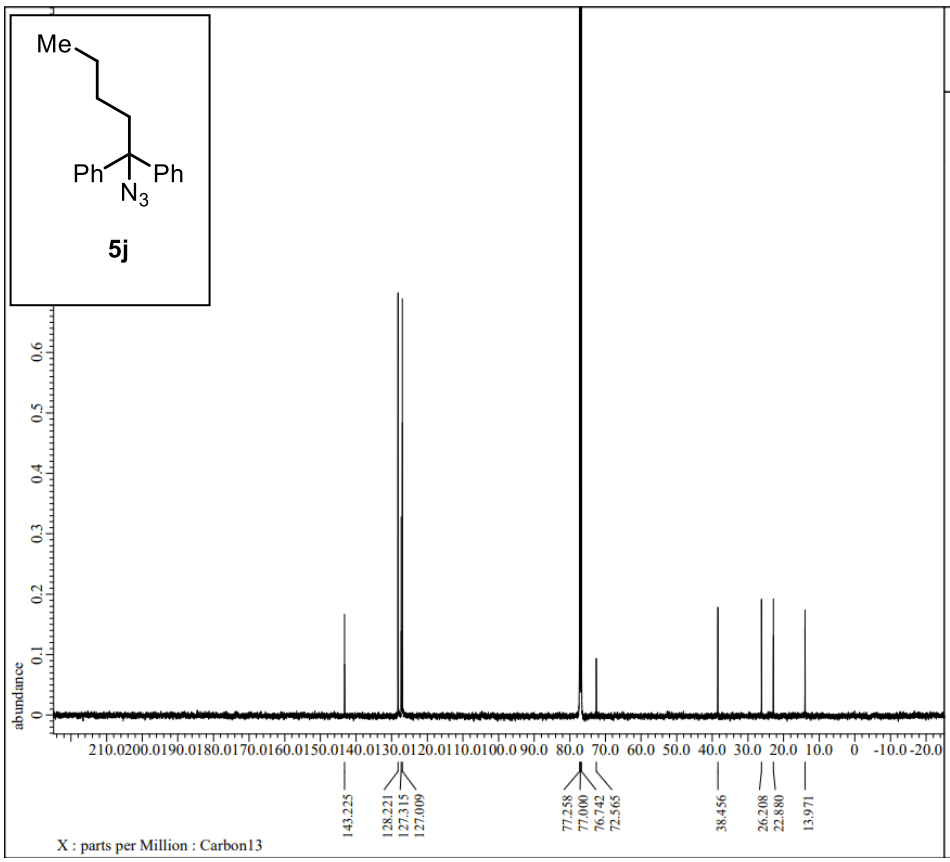



```
Filename          = ba-04-050-FA-1_Proton-1-2
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-050-FA-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 25-SEP-2020 14:38:56
Revision_Time     = 25-SEP-2020 14:37:16

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 38
Temp_Get          = 20.6[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

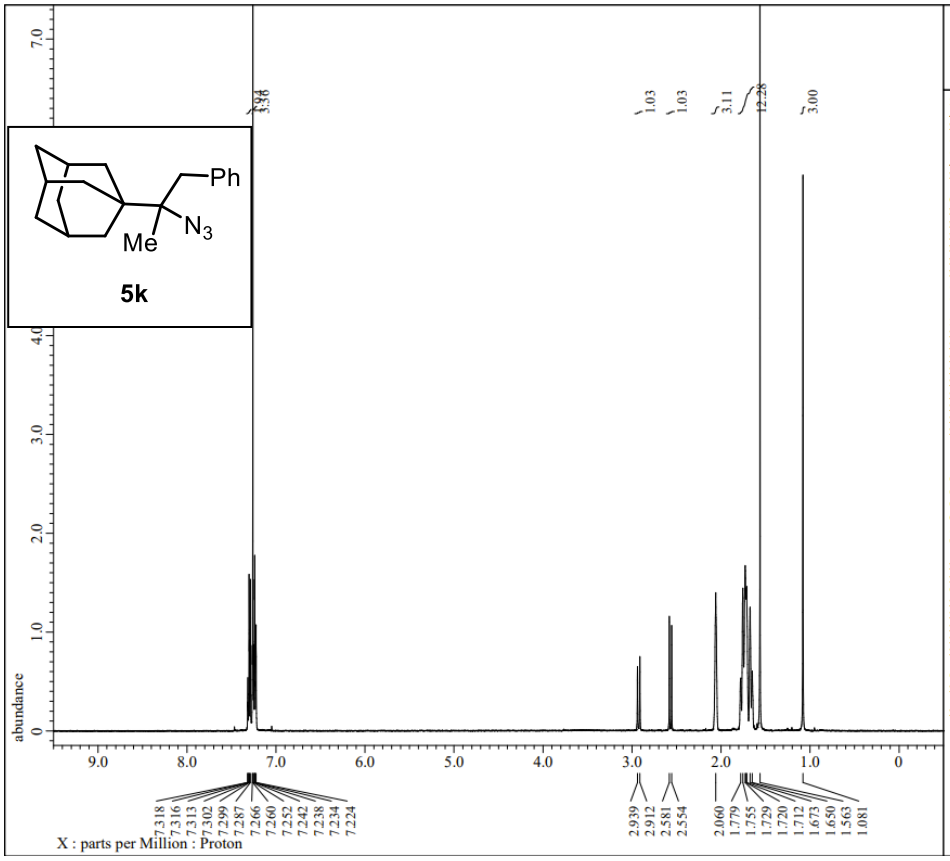



```
Filename          = ba-04-031-1_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-031-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 23-SEP-2020 21:23:37
Revision_Time     = 23-SEP-2020 22:28:37

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 21.6[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```



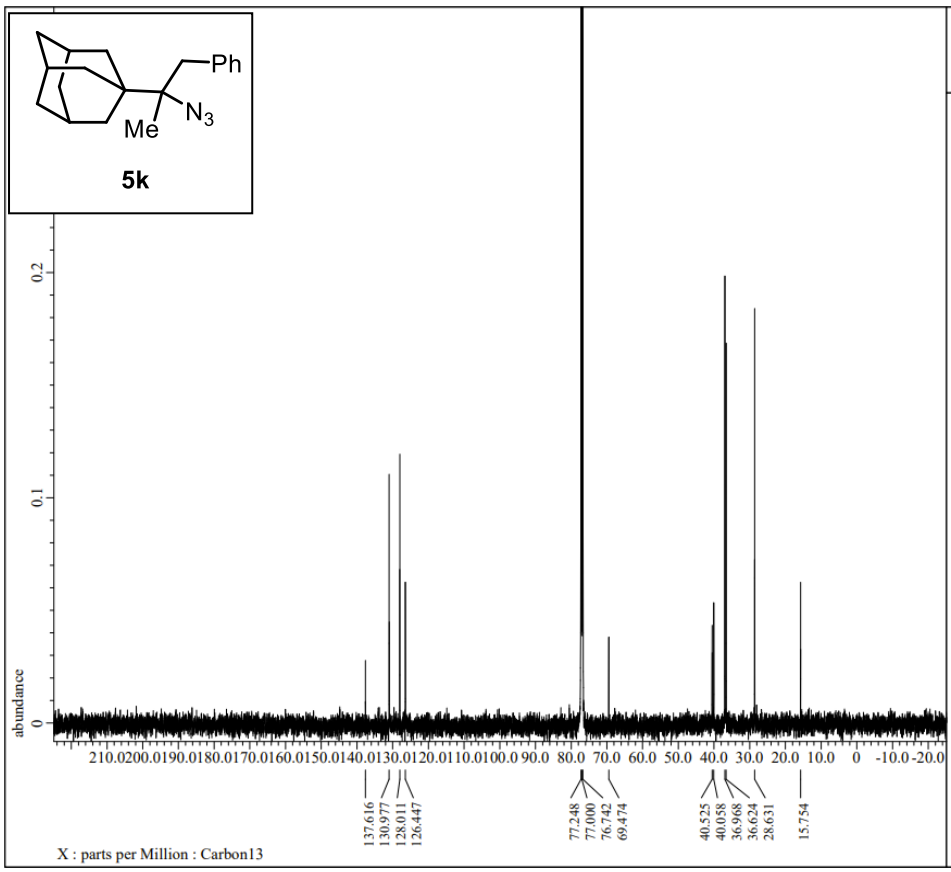
JEOL

```
Filename          = ba-04-047-F1-1_Proton-1-3
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-047-F1-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 17-SEP-2020 15:15:08
Revision_Time     = 17-SEP-2020 15:14:44

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 48
Temp_Get          = 22[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```



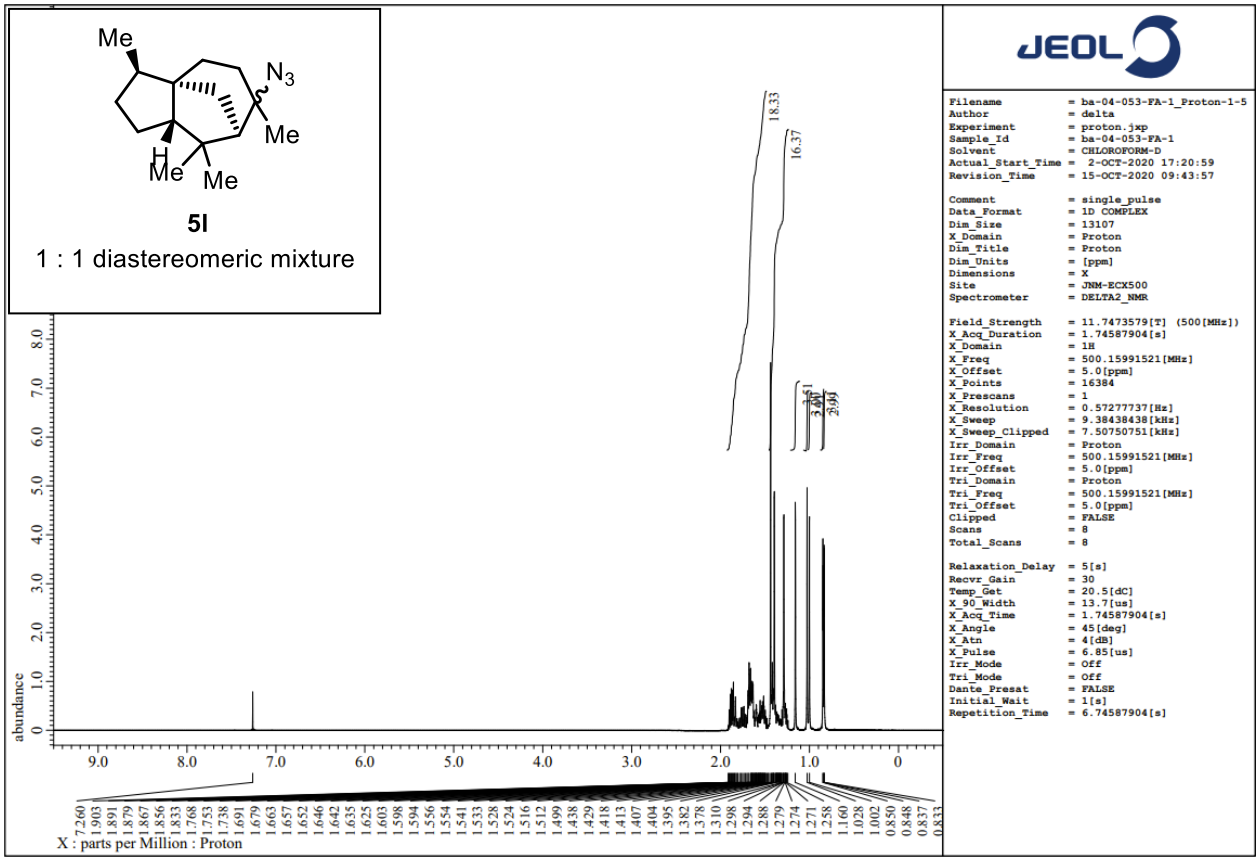
JEOL

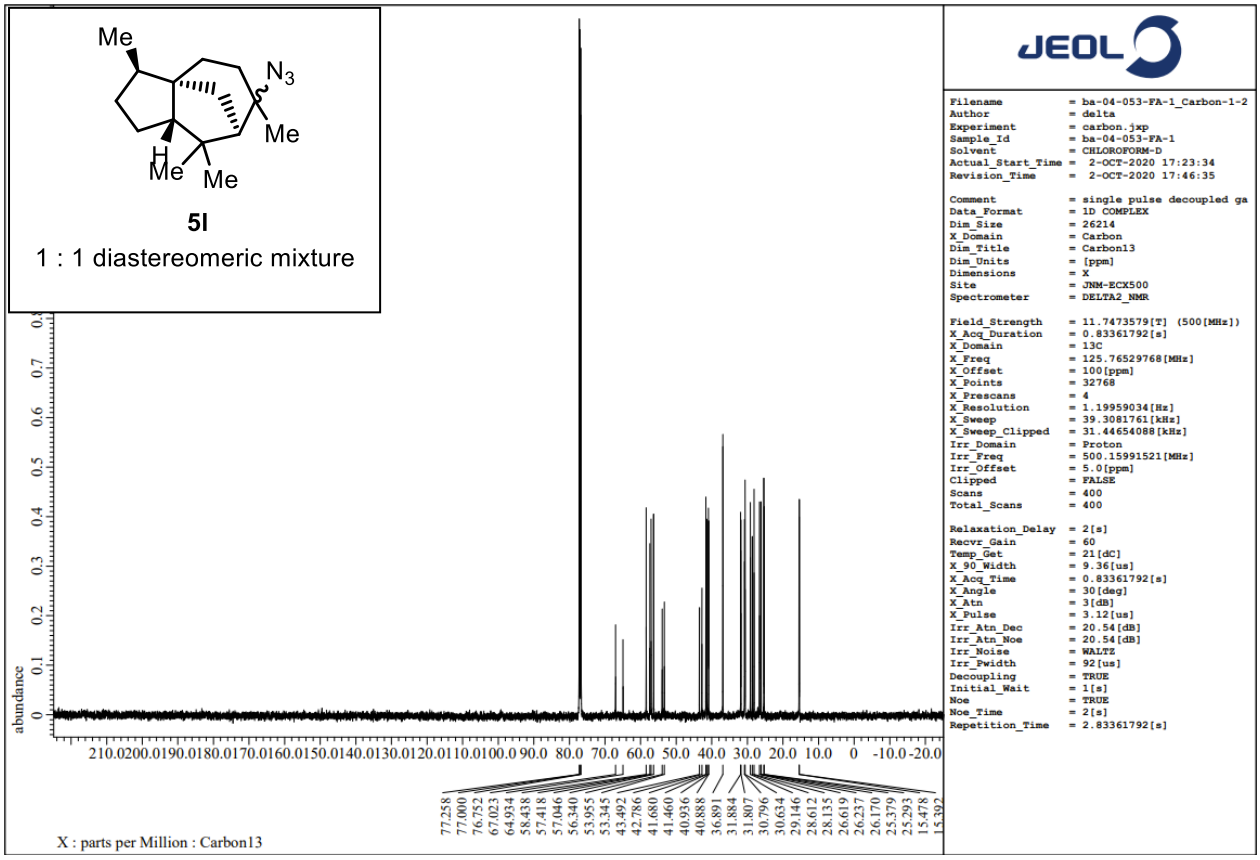
```
Filename          = ba-04-047-F1-1_Carbon-1-2
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-047-F1-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 22-SEP-2020 11:47:47
Revision_Time     = 22-SEP-2020 12:28:46

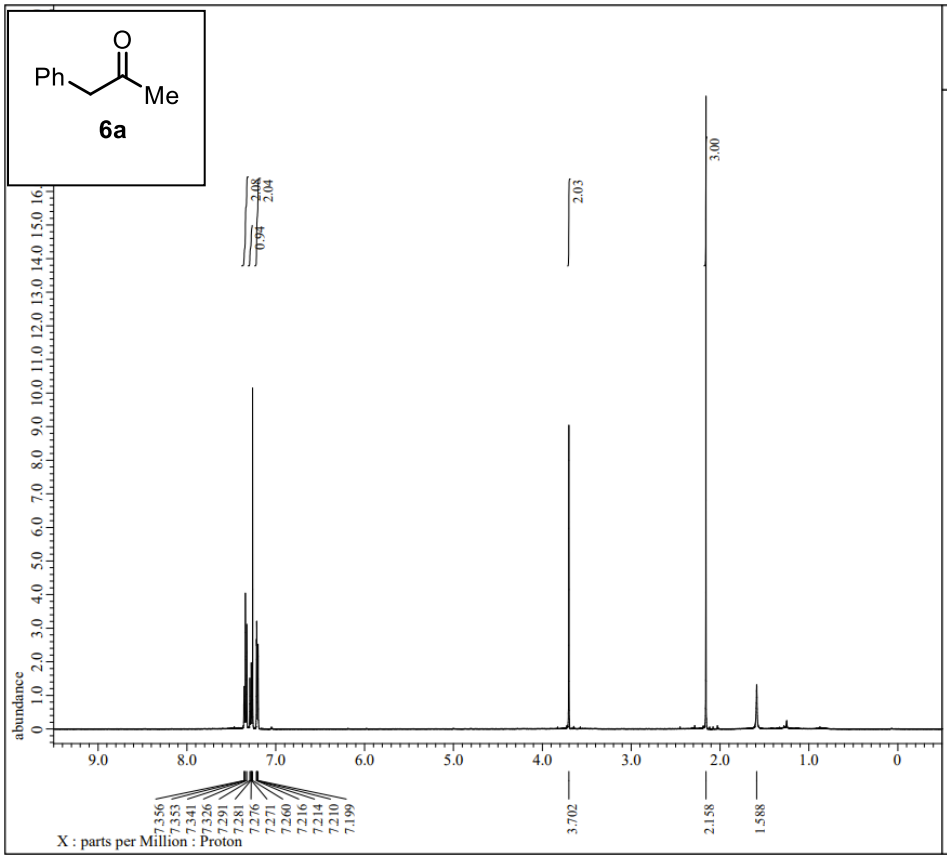
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 21.2[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


Me
N3
Me
H
Me
Me
5l
1 : 1 diastereomeric mixture
18.33
16.37
abundance
X : parts per Million : Proton
JEOL
Filename = ba-04-053-FA-1_Proton-1-5
Author = delta
Experiment = proton.jxp
Sample_Id = ba-04-053-FA-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 2-OCT-2020 17:20:59
Revision_Time = 15-OCT-2020 09:43:57
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 30
Temp_Get = 20.5[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


Me
N3
Me
H
Me
Me
5l
1 : 1 diastereomeric mixture
abundance
X : parts per Million : Carbon13
JEOL
Filename = ba-04-053-FA-1_Carbon-1-2
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-04-053-FA-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 2-OCT-2020 17:23:34
Revision_Time = 2-OCT-2020 17:46:35
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 400
Total_Scans = 400
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

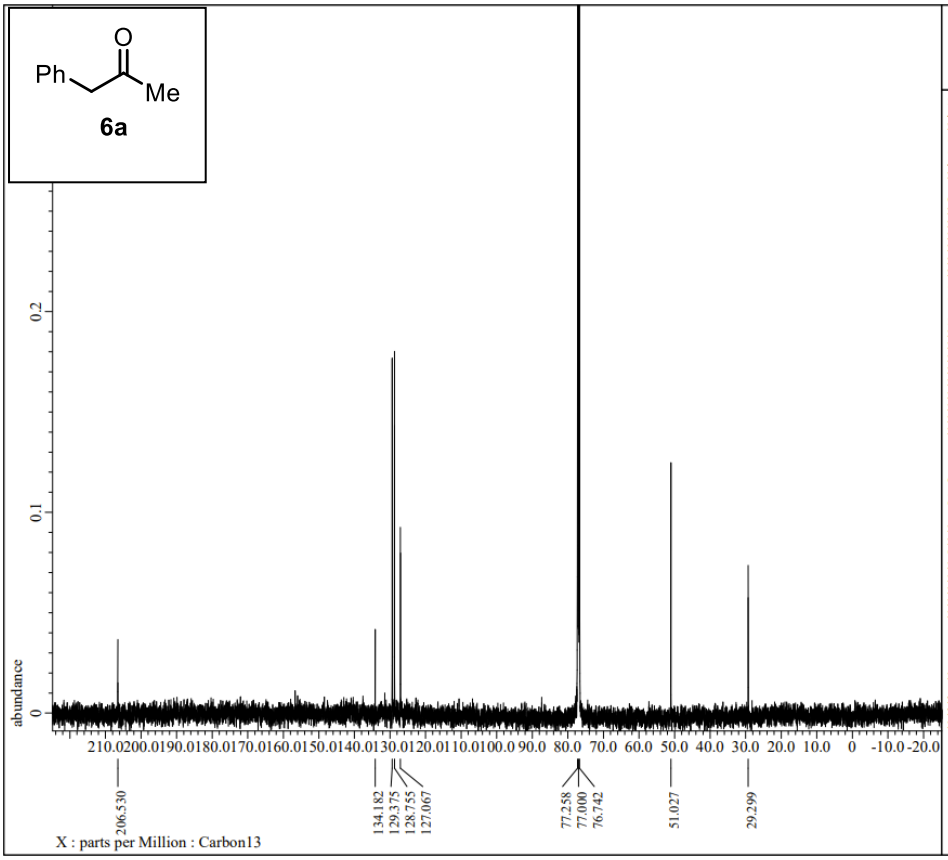



```
Filename          = ba-03-039-7-B-1_Proton-1-
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-03-039-7-B-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 11-MAR-2020 20:02:47
Revision_Time     = 11-MAR-2020 21:14:30

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 48
Temp_Get          = 15.2[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

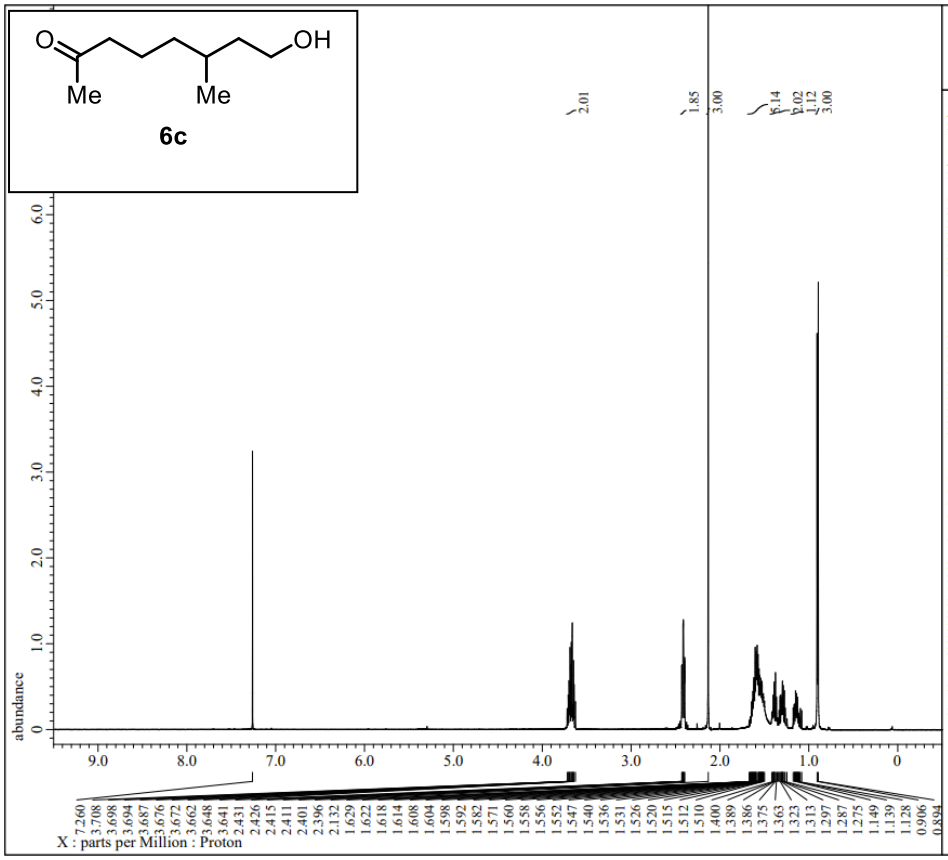



```
Filename          = ba-03-039-7-B-1_Carbon-1-
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-03-039-7-B-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 12-MAR-2020 10:28:04
Revision_Time     = 12-MAR-2020 20:52:04

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 15.8[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```

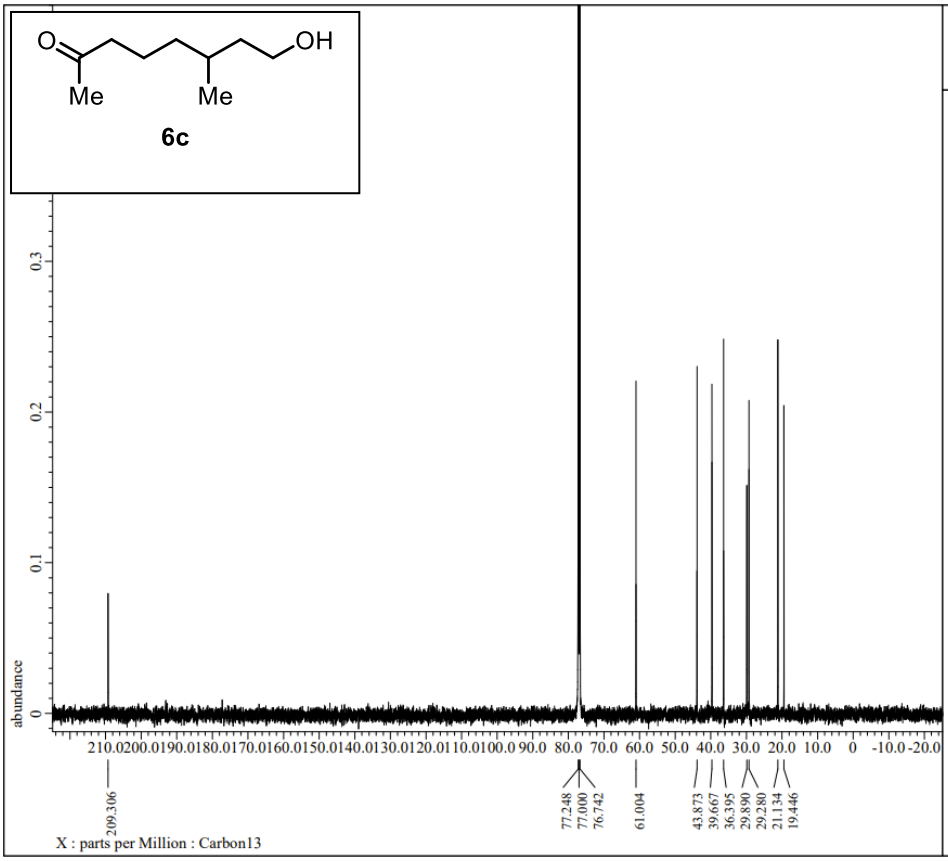



```
Filename          = ba-03-108-3_Proton-1-2.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-03-108-3
Solvent           = CHLOROFORM-D
Actual_Start_Time = 17-JUN-2020 10:53:53
Revision_Time     = 17-JUN-2020 10:44:19

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 40
Temp_Get          = 20.2[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

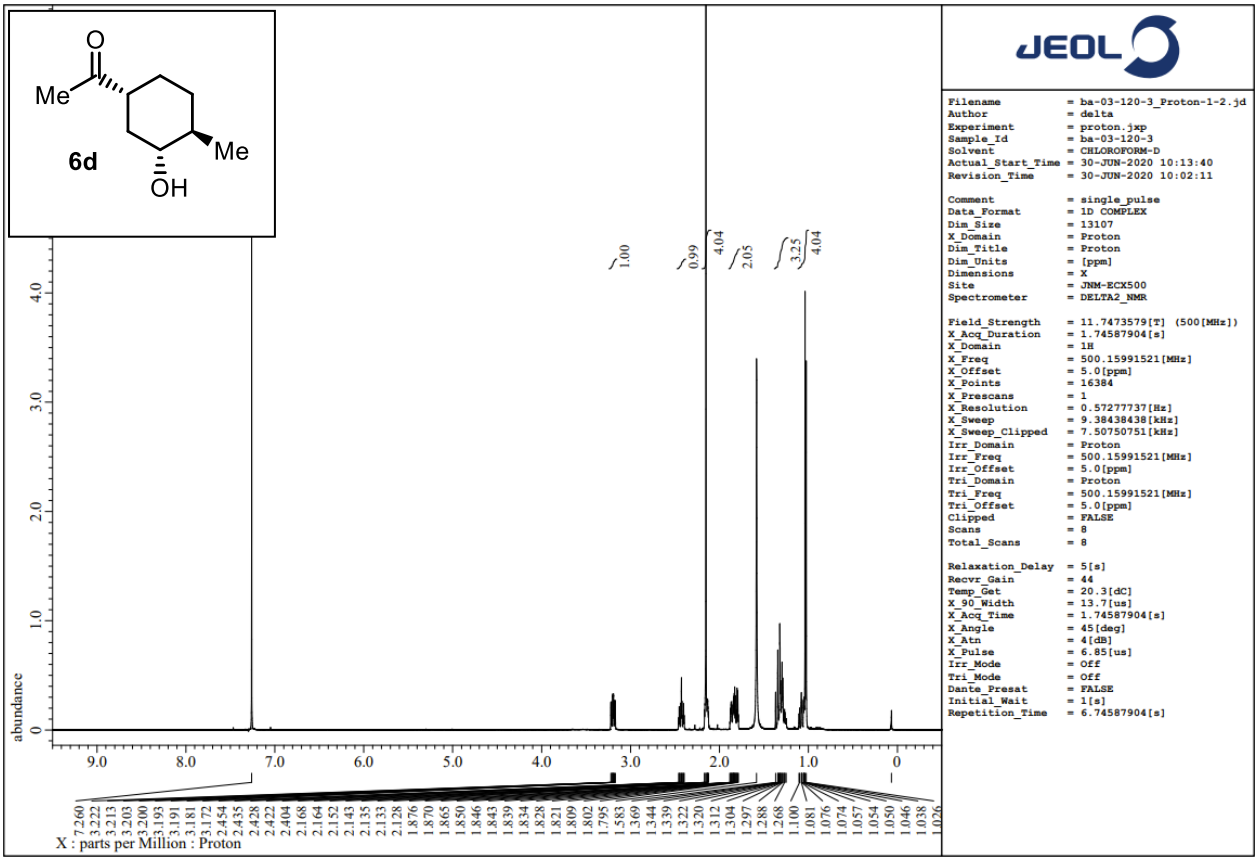


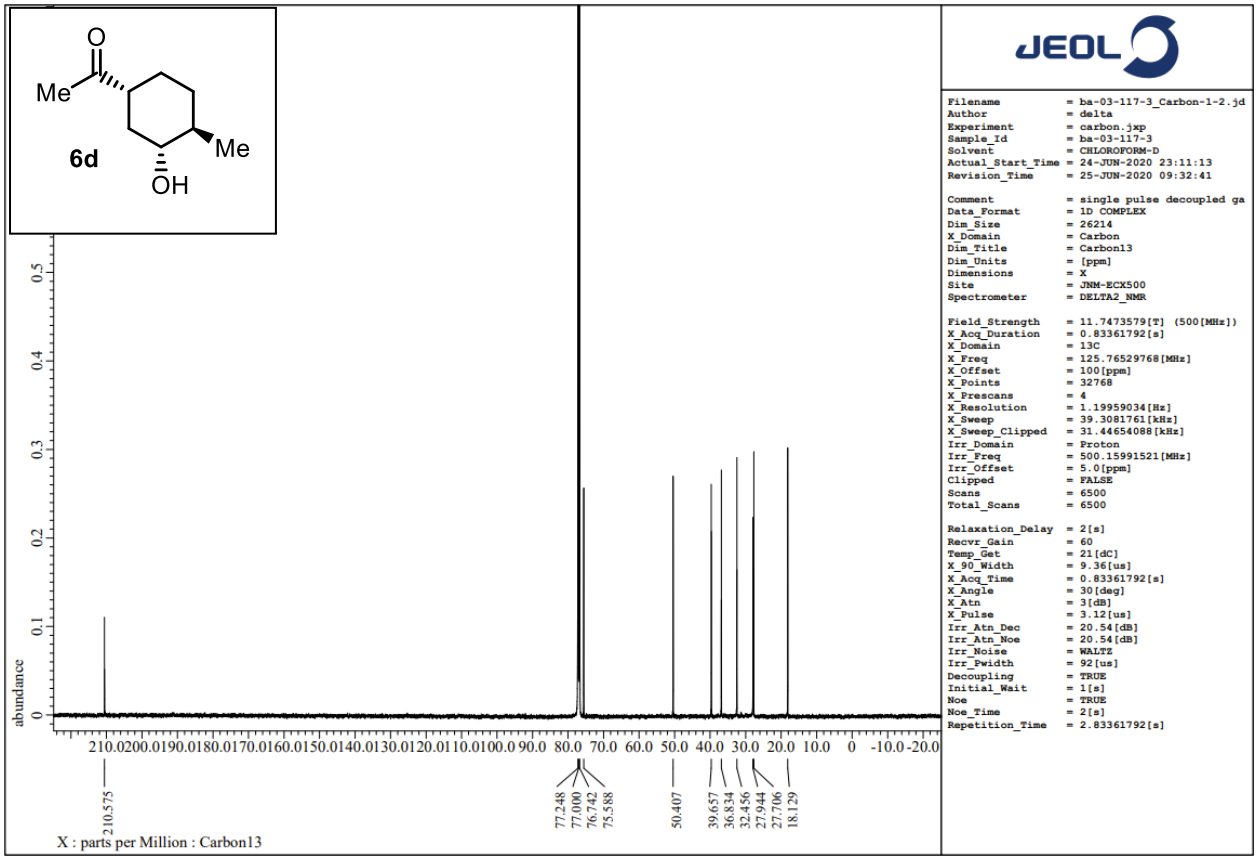

```
Filename          = ba-03-108-3_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-03-108-3
Solvent           = CHLOROFORM-D
Actual_Start_Time = 17-JUN-2020 12:22:37
Revision_Time     = 17-JUN-2020 13:27:34

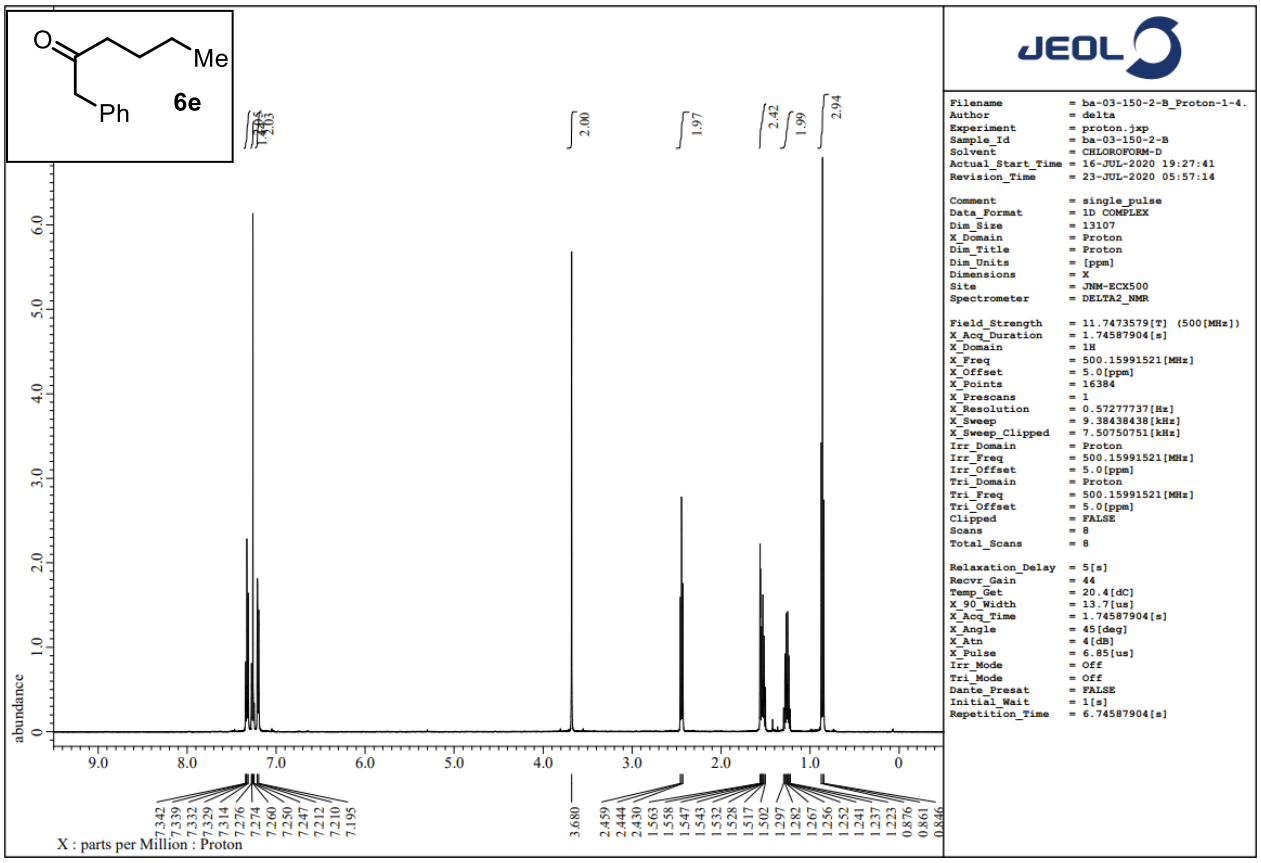
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

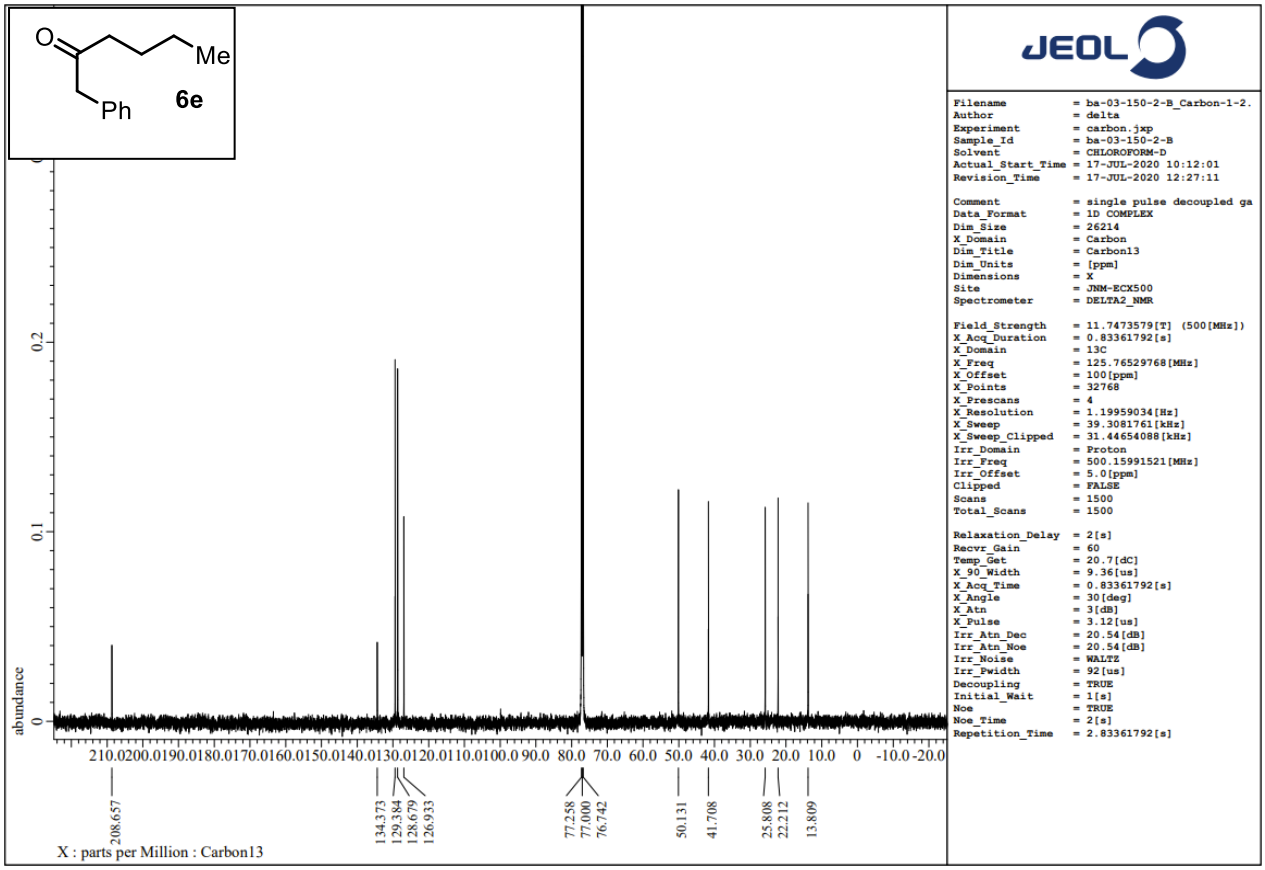
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

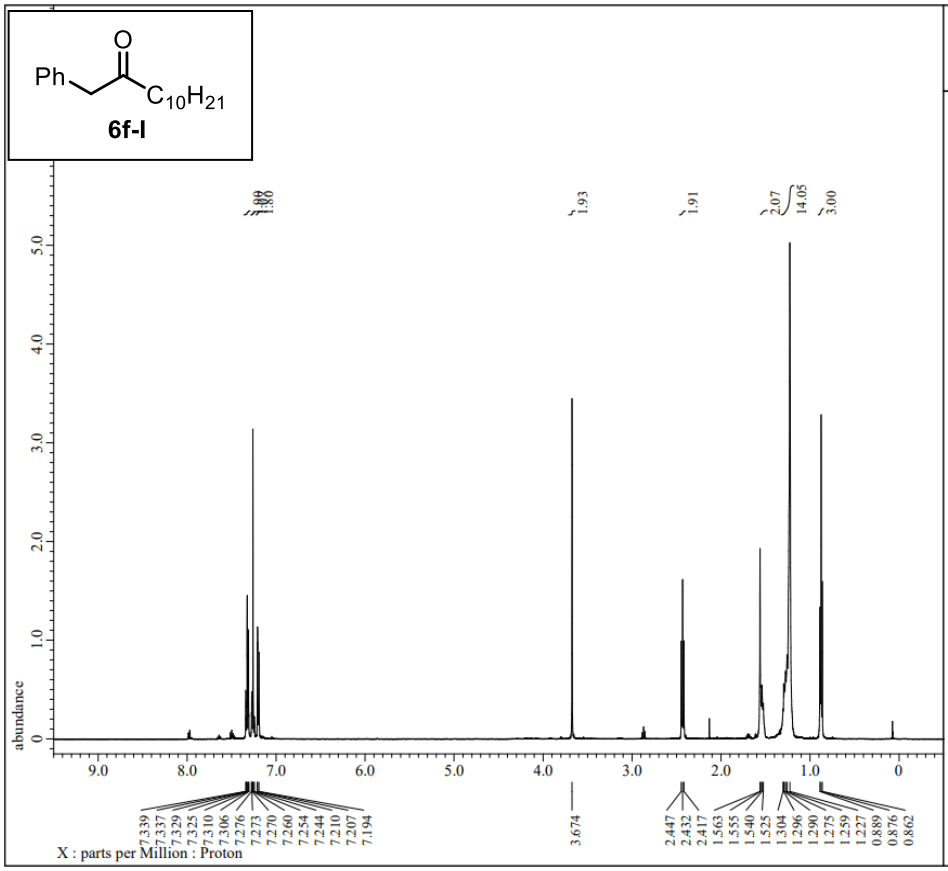
Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 20.9[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


6d
Me
Me
OH
1.00
0.99
4.04
2.05
3.25
4.04
abundance
X : parts per Million : Proton
JEOL
Filename = ba-03-120-3_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-03-120-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 30-JUN-2020 10:13:40
Revision_Time = 30-JUN-2020 10:02:11
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 44
Temp_Get = 20.3[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


6d
Me
Me
OH
210.575
77.248
77.000
76.742
75.588
50.407
39.657
36.834
32.456
27.944
27.706
18.129
abundance
X : parts per Million : Carbon13
JEOL
Filename = ba-03-117-3_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-03-117-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 24-JUN-2020 23:11:13
Revision_Time = 25-JUN-2020 09:32:41
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 6500
Total_Scans = 6500
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]


O
Me
Ph
6e
2.00
1.97
2.42
1.99
2.94
abundance
X : parts per Million : Proton
Filename = ba-03-150-2-B_Proton-1-4.
Author = delta
Experiment = proton.jxp
Sample_Id = ba-03-150-2-B
Solvent = CHLOROFORM-D
Actual_Start_Time = 16-JUL-2020 19:27:41
Revision_Time = 23-JUL-2020 05:57:14
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 44
Temp_Get = 20.4[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


O
Me
Ph
6e
abundance
X : parts per Million : Carbon13
208.657
134.373
129.384
128.679
126.933
77.258
77.000
76.742
50.131
41.708
25.808
22.212
13.809
Filename = ba-03-150-2-B_Carbon-1-2.
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-03-150-2-B
Solvent = CHLOROFORM-D
Actual_Start_Time = 17-JUL-2020 10:12:01
Revision_Time = 17-JUL-2020 12:27:11
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 1500
Total_Scans = 1500
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 20.7[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

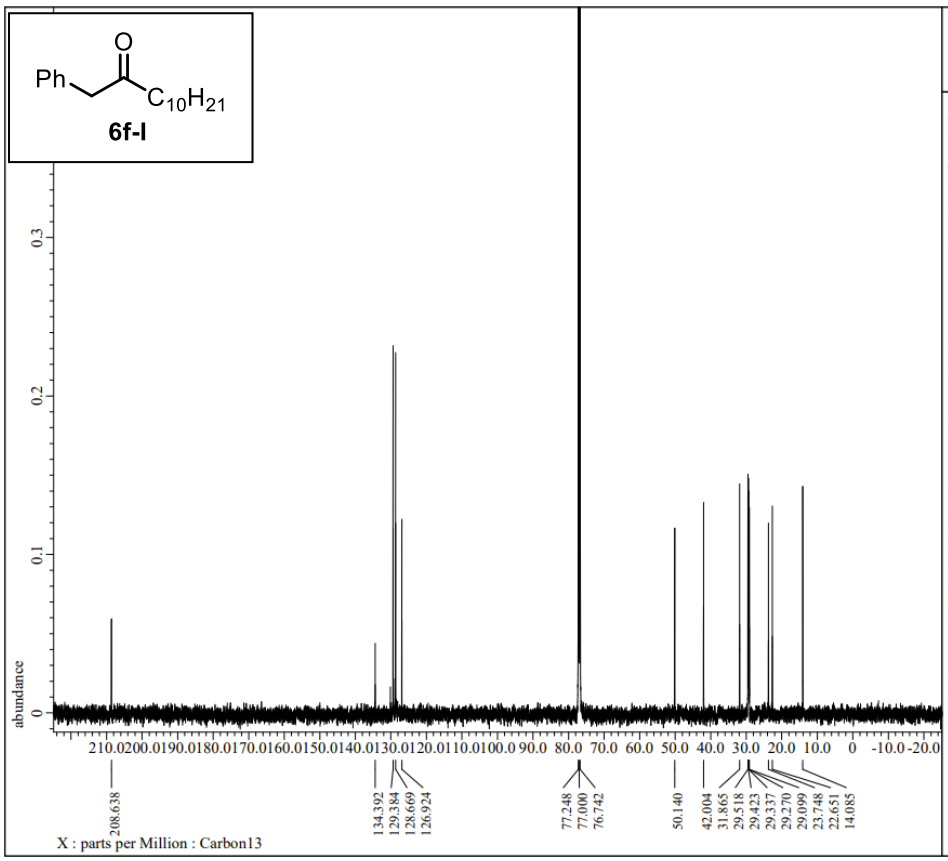



```
Filename          = ba-04-021-A2-1_Proton-1-2
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-021-A2-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 24-AUG-2020 18:05:21
Revision_Time     = 24-AUG-2020 18:22:49

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 40
Temp_Get          = 24.8[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

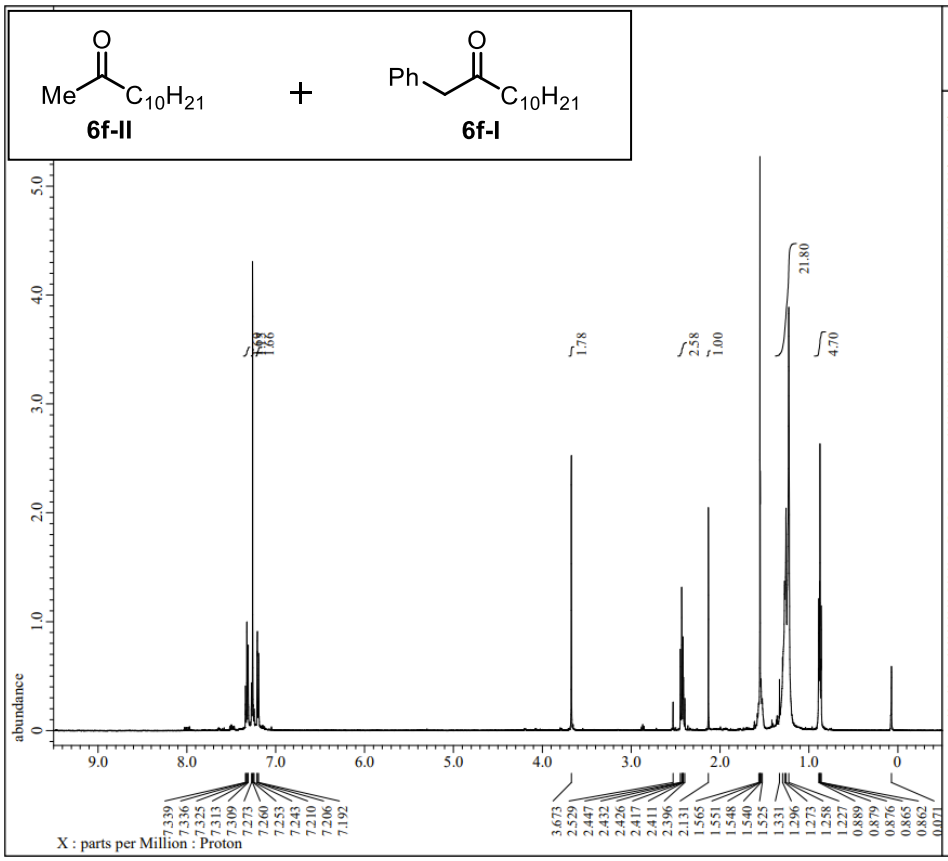



```
Filename          = ba-04-021-A2-1_Carbon-1-2
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-021-A2-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 24-AUG-2020 18:19:13
Revision_Time     = 24-AUG-2020 19:04:12

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 750
Total_Scans       = 750

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 25.2[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```



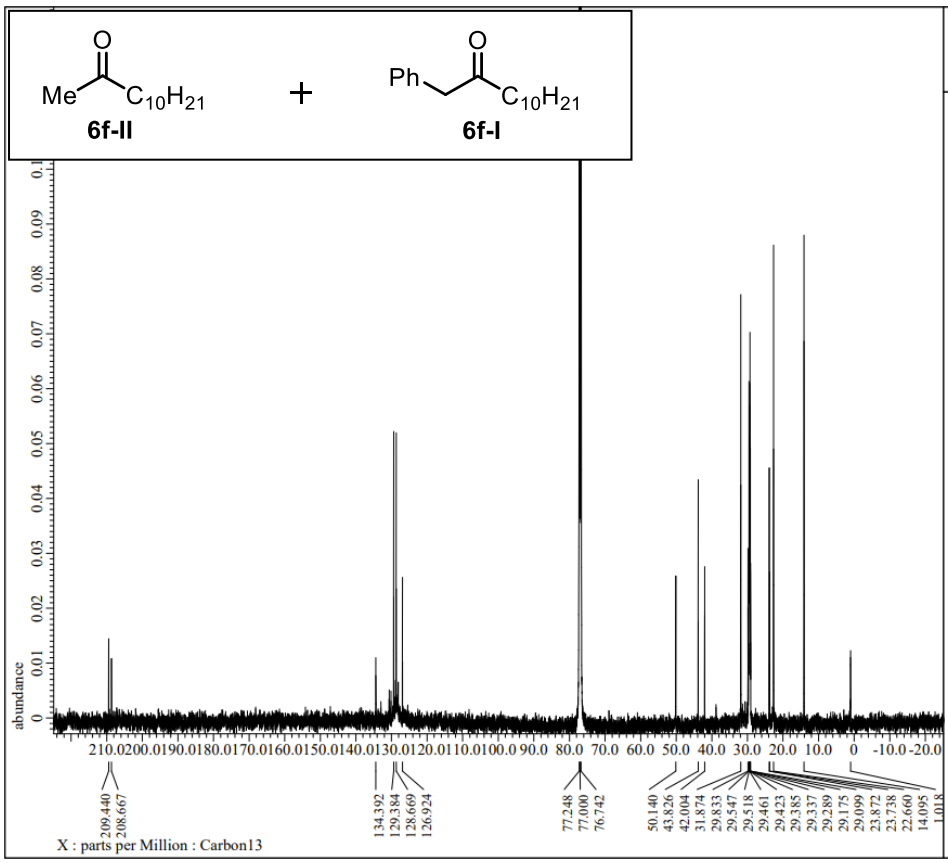
JEOL

```
Filename          = ba-04-014-2-A_Proton-1-7.
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-014-2-A
Solvent           = CHLOROFORM-D
Actual_Start_Time = 18-AUG-2020 18:41:54
Revision_Time     = 19-OCT-2020 17:33:07

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 44
Temp_Get          = 25.7[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```



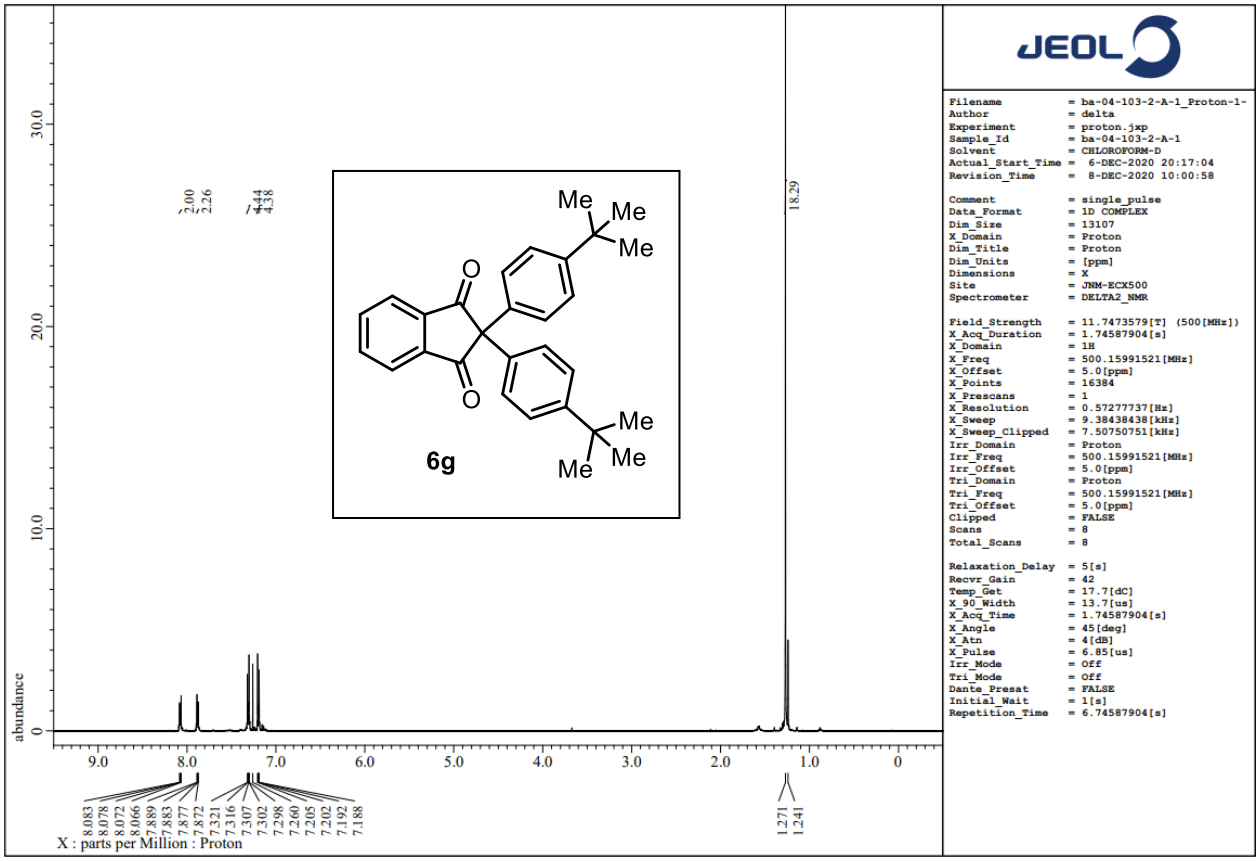
JEOL

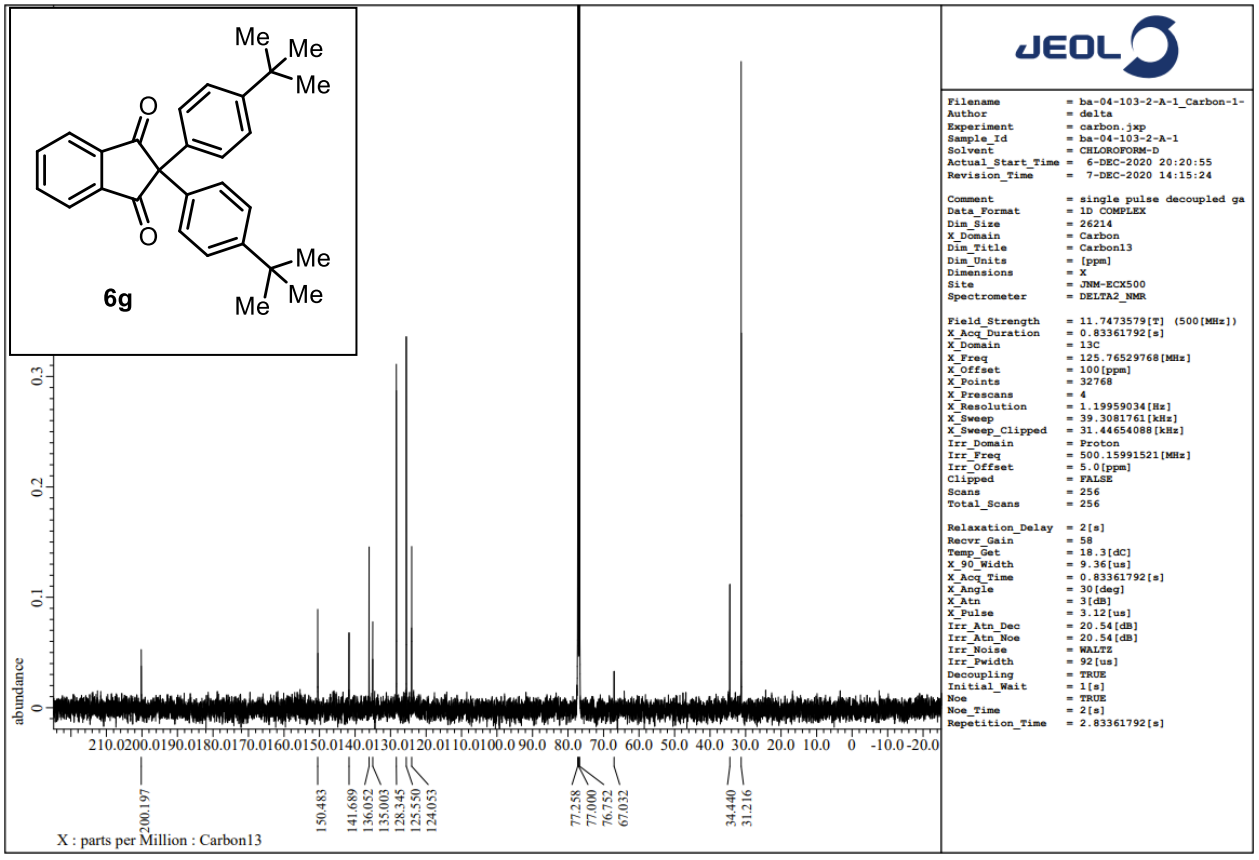
```
Filename          = ba-04-023-2-A-1_Carbon-1-
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-023-2-A-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 27-AUG-2020 22:14:55
Revision_Time     = 28-AUG-2020 09:25:55

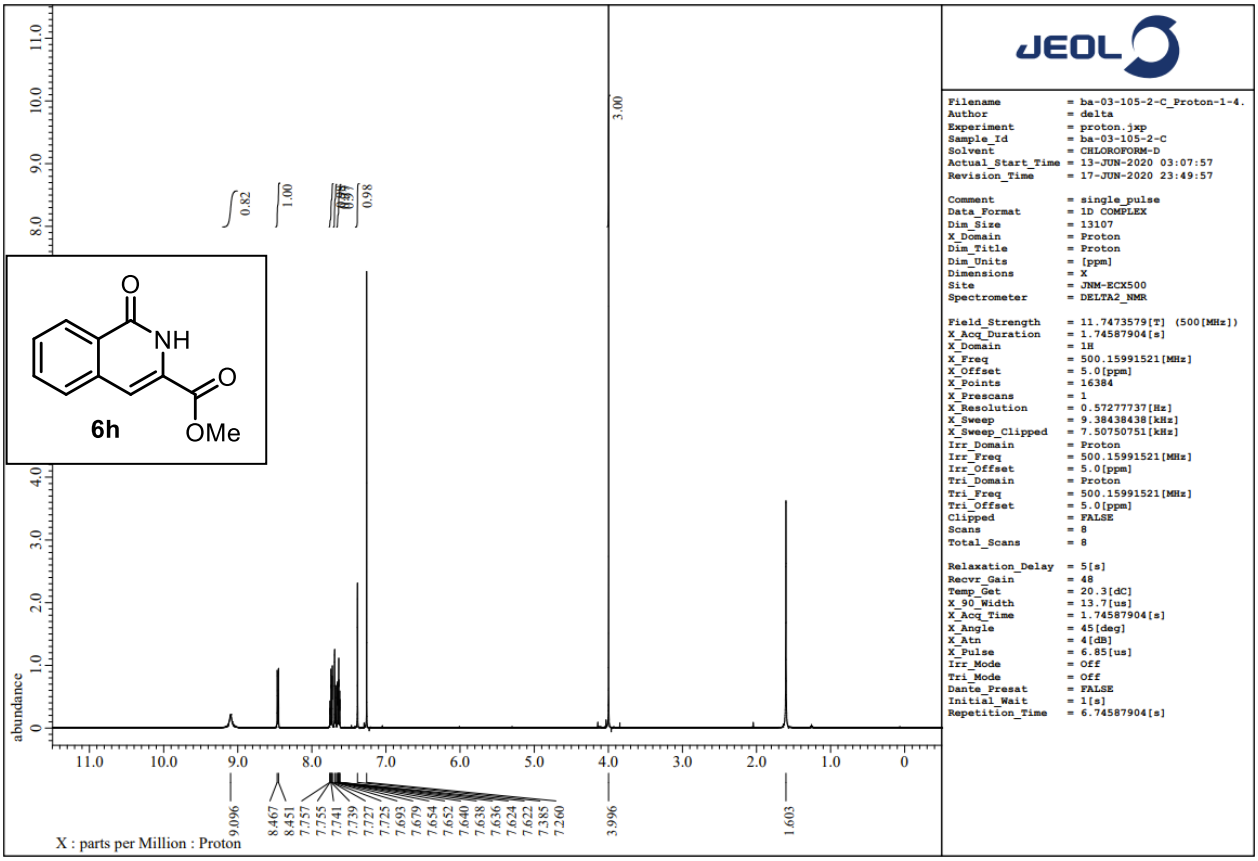
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 9000
Total_Scans       = 9000

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 24.1[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


6g
Me
Me
Me
O
O
Me
Me
Me
2.00
2.26
4.44
4.38
18.29
abundance
X : parts per Million : Proton
8.083
8.078
8.072
8.066
7.889
7.883
7.877
7.872
7.321
7.316
7.307
7.302
7.298
7.260
7.205
7.202
7.192
7.188
1.271
1.241
Filename = ba-04-103-2-A-1_Proton-1-
Author = delta
Experiment = proton.jxp
Sample_Id = ba-04-103-2-A-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 6-DEC-2020 20:17:04
Revision_Time = 8-DEC-2020 10:00:58
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 42
Temp_Get = 17.7[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


6g
Me
Me
Me
O
O
Me
Me
Me
abundance
X : parts per Million : Carbon13
200.197
150.483
141.689
136.052
135.003
128.345
125.550
124.053
77.258
77.000
76.752
67.032
34.440
31.216
Filename = ba-04-103-2-A-1_Carbon-1-
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-04-103-2-A-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 6-DEC-2020 20:20:55
Revision_Time = 7-DEC-2020 14:15:24
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 256
Total_Scans = 256
Relaxation_Delay = 2[s]
Recvr_Gain = 58
Temp_Get = 18.3[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]



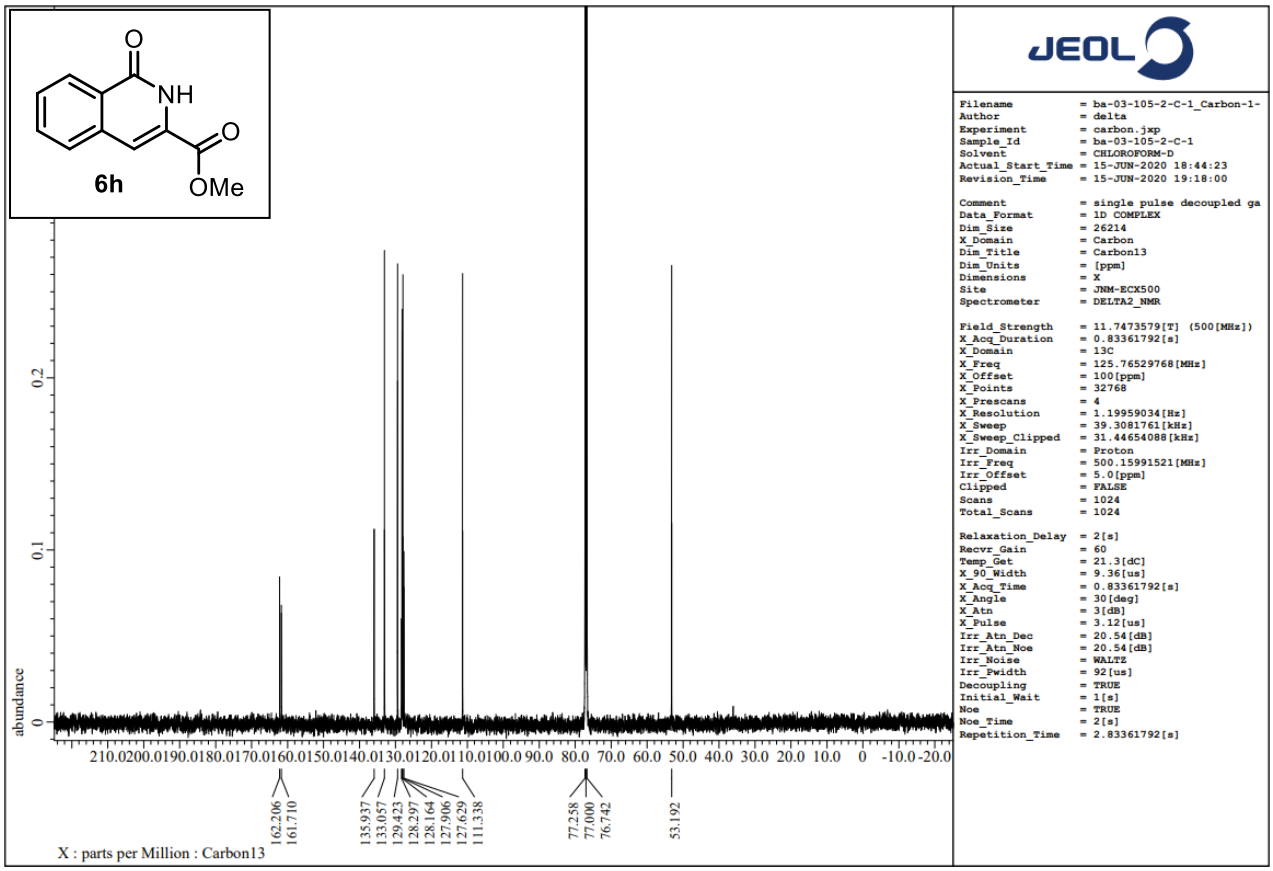
JEOL

```
Filename          = ba-03-105-2-C_Proton-1-4.
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-03-105-2-C
Solvent           = CHLOROFORM-D
Actual_Start_Time = 13-JUN-2020 03:07:57
Revision_Time     = 17-JUN-2020 23:49:57

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 48
Temp_Get          = 20.3[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```



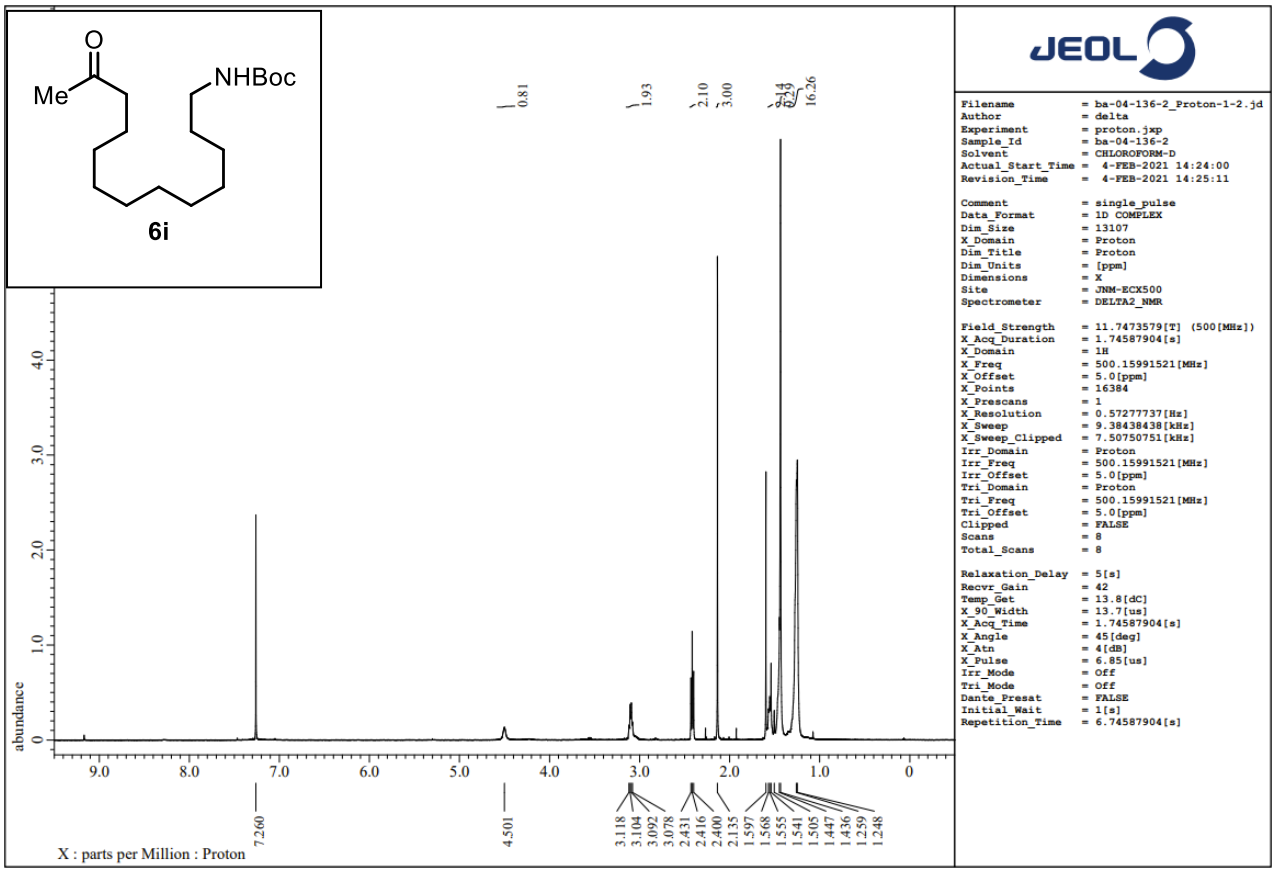
JEOL

```
Filename          = ba-03-105-2-C-1_Carbon-1-
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-03-105-2-C-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 15-JUN-2020 18:44:23
Revision_Time     = 15-JUN-2020 19:18:00

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 21.3[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```



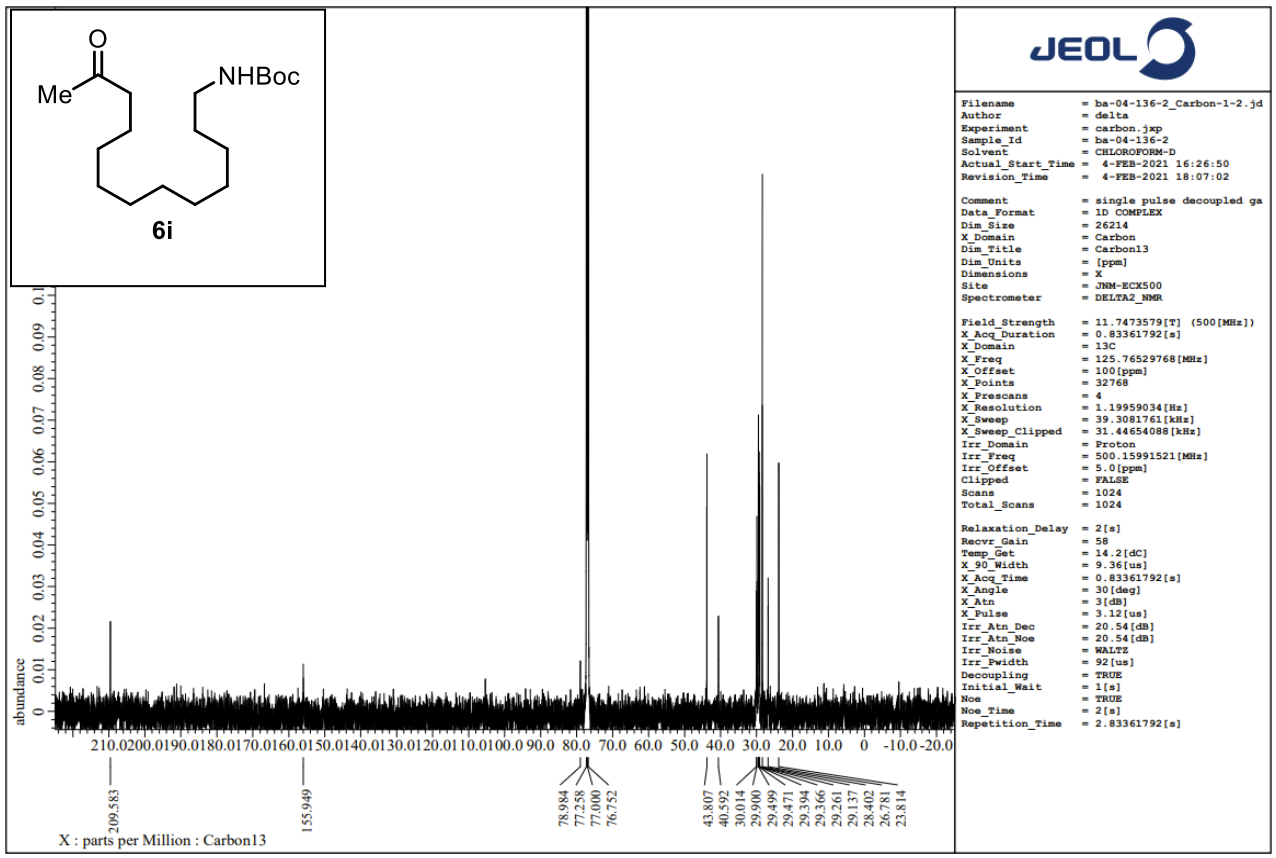
JEOL

```
Filename            = ba-04-136-2_Proton-1-2.jd
Author              = delta
Experiment          = proton.jxp
Sample_Id           = ba-04-136-2
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  4-FEB-2021 14:24:00
Revision_Time       =  4-FEB-2021 14:25:11

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 1.74587904[s]
X_Domain            = 1H
X_Freq              = 500.15991521[MHz]
X_Offset            = 5.0[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.57277737[Hz]
X_Sweep             = 9.38438438[kHz]
X_Sweep_Clipped     = 7.50750751[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Tri_Domain          = Proton
Tri_Freq            = 500.15991521[MHz]
Tri_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 42
Temp_Get            = 13.8[dC]
X_90_Width          = 13.7[us]
X_Acq_Time          = 1.74587904[s]
X_Angle             = 45[deg]
X_Atn               = 4[dB]
X_Pulse             = 6.85[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 6.74587904[s]
```



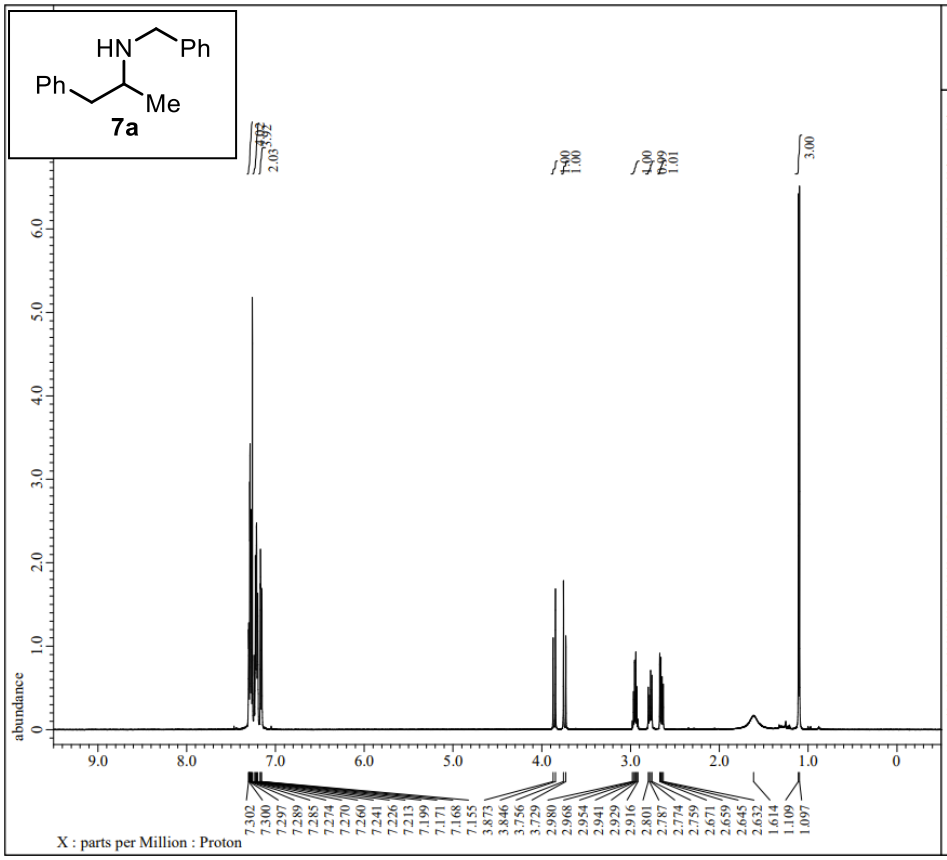
JEOL

```
Filename            = ba-04-136-2_Carbon-1-2.jd
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = ba-04-136-2
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  4-FEB-2021 16:26:50
Revision_Time       =  4-FEB-2021 18:07:02

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 0.83361792[s]
X_Domain            = 13C
X_Freq              = 125.76529768[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.19959034[Hz]
X_Sweep             = 39.3081761[kHz]
X_Sweep_Clipped     = 31.44654088[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 1024
Total_Scans         = 1024

Relaxation_Delay    = 2[s]
Recvr_Gain          = 58
Temp_Get            = 14.2[dC]
X_90_Width          = 9.36[us]
X_Acq_Time          = 0.83361792[s]
X_Angle             = 30[deg]
X_Atn               = 3[dB]
X_Pulse             = 3.12[us]
Irr_Atn_Dec         = 20.54[dB]
Irr_Atn_Noe         = 20.54[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 92[us]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 2.83361792[s]
```

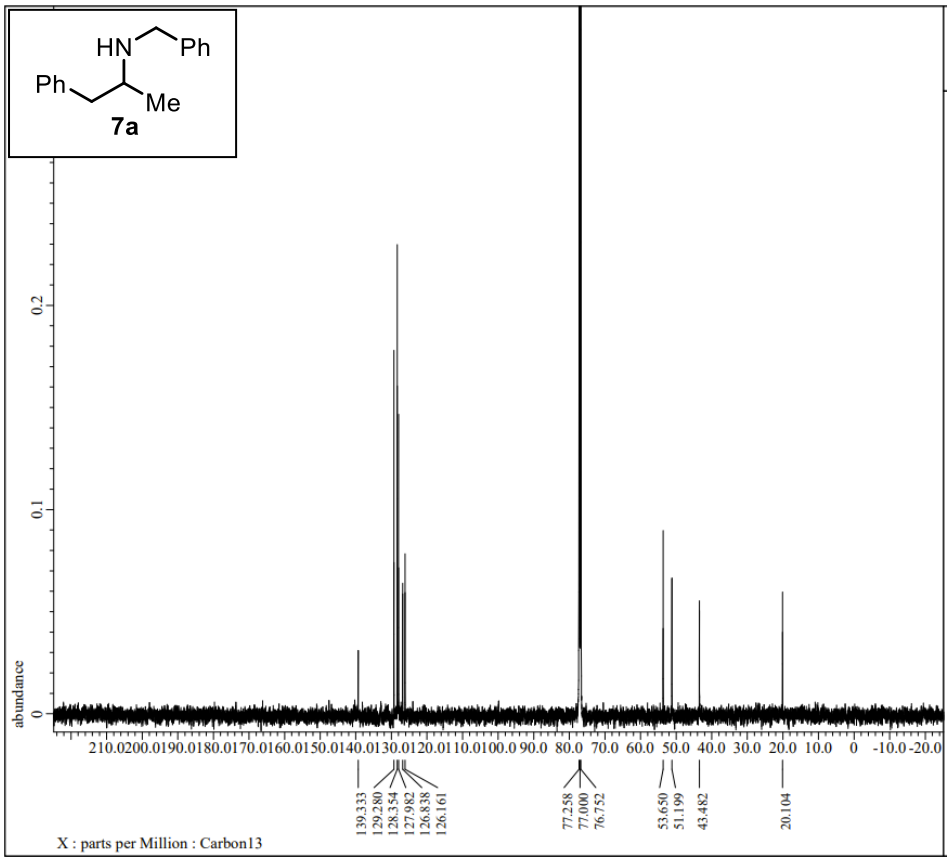



```
Filename          = ba-03-032-2_Proton-1-4.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-03-032-2
Solvent           = CHLOROFORM-D
Actual_Start_Time = 29-FEB-2020 17:44:53
Revision_Time     =  5-MAR-2020 22:00:52

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 46
Temp_Get          = 17[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

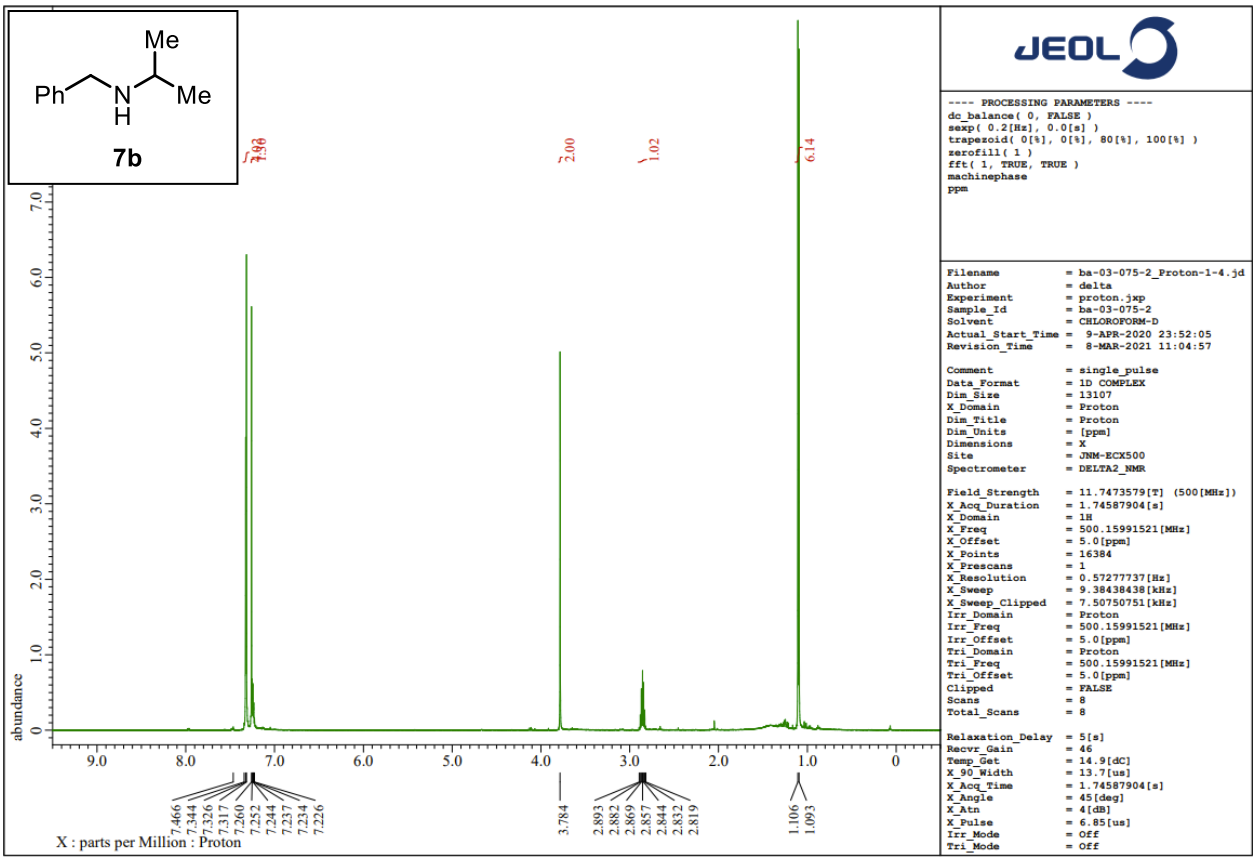


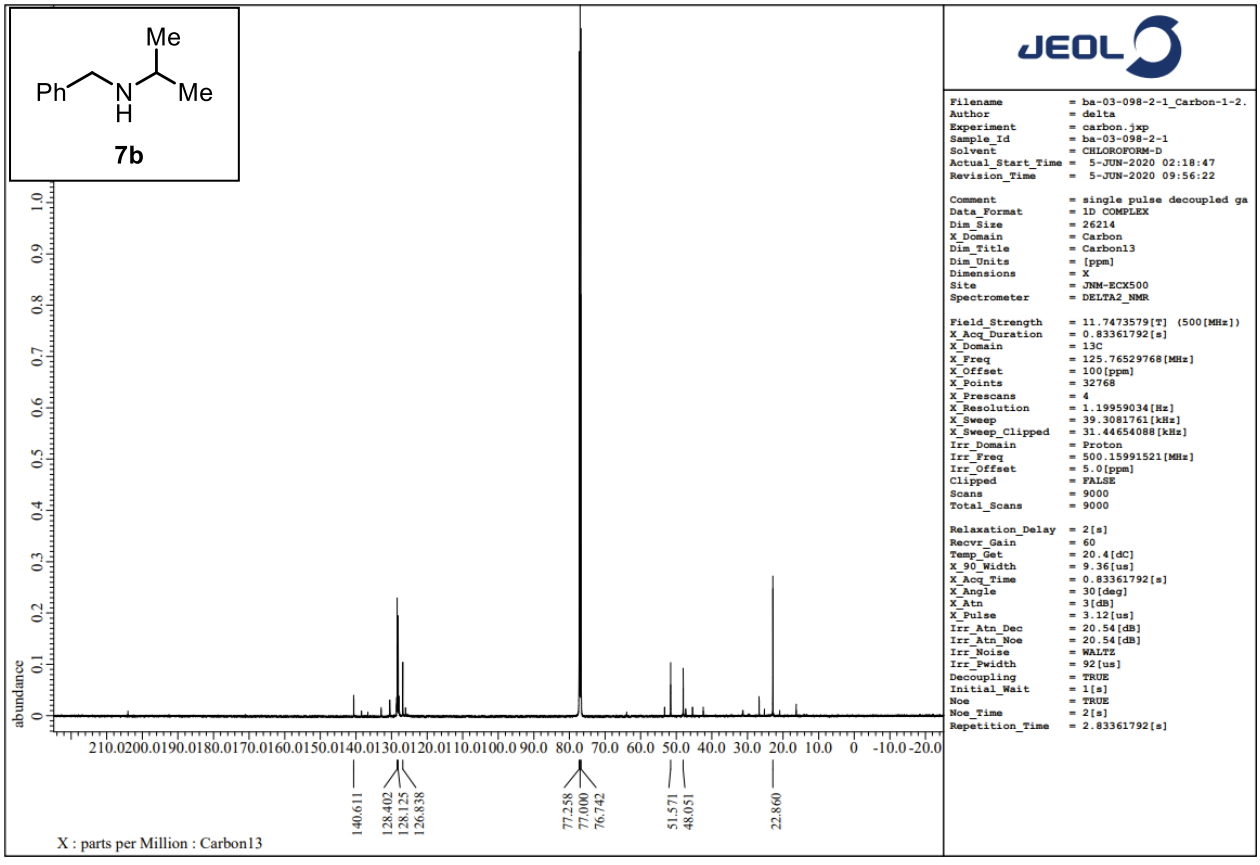

```
Filename          = ba-03-032-2_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-03-032-2
Solvent           = CHLOROFORM-D
Actual_Start_Time =  2-MAR-2020 10:38:05
Revision_Time     =  2-MAR-2020 11:44:27

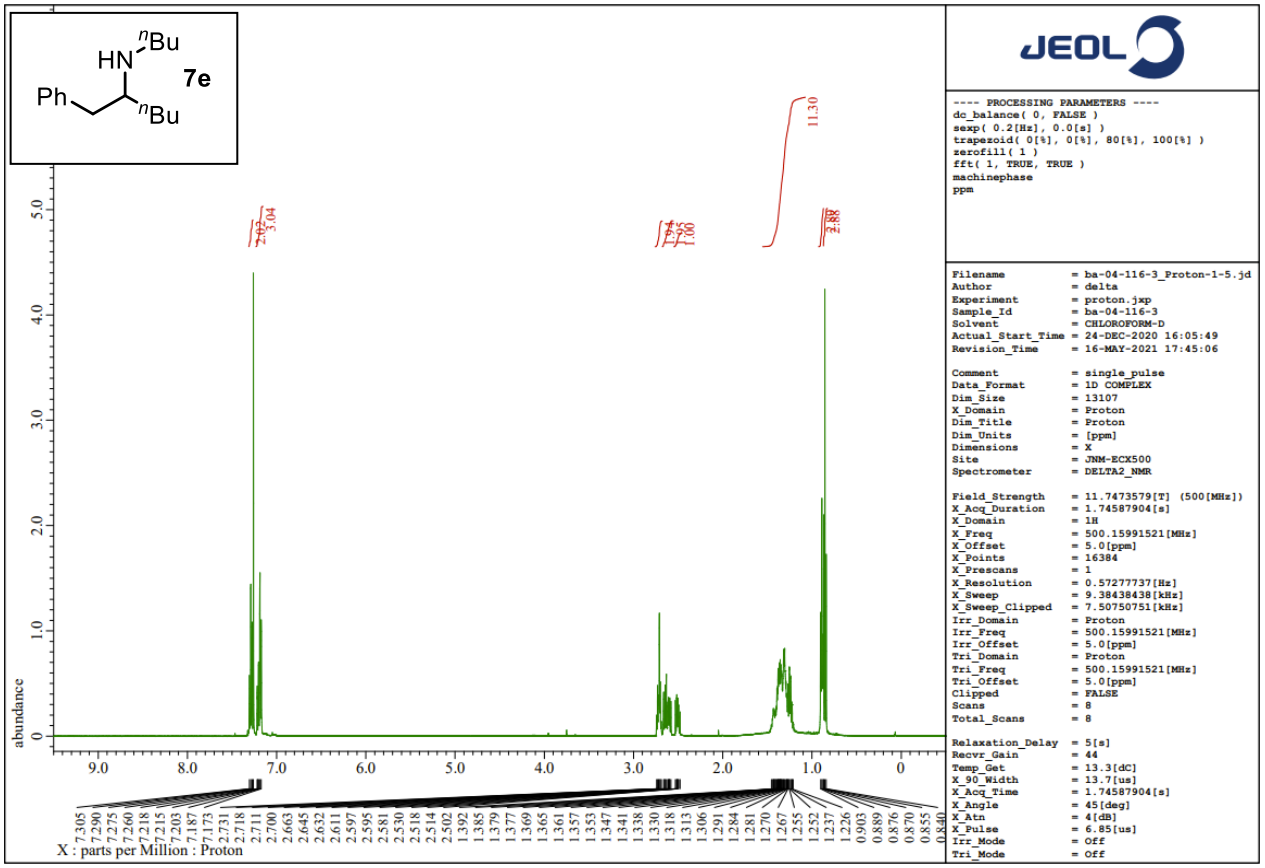
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 58
Temp_Get          = 15.9[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


Me
Ph
N
H
Me
7b
2.00
1.02
6.14
abundance
X : parts per Million : Proton
7.466
7.344
7.326
7.317
7.260
7.252
7.244
7.237
7.234
7.226
3.784
2.893
2.882
2.869
2.857
2.844
2.832
2.819
1.106
1.093
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = ba-03-075-2_Proton-1-4.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-03-075-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 9-APR-2020 23:52:05
Revision_Time = 8-MAR-2021 11:04:57
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 46
Temp_Get = 14.9[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off


Me
Ph
N
H
Me
7b
abundance
X : parts per Million : Carbon13
140.611
128.402
128.125
126.838
77.258
77.000
76.742
51.571
48.051
22.860
Filename = ba-03-098-2-1_Carbon-1-2.
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-03-098-2-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 5-JUN-2020 02:18:47
Revision_Time = 5-JUN-2020 09:56:22
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 9000
Total_Scans = 9000
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 20.4[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]



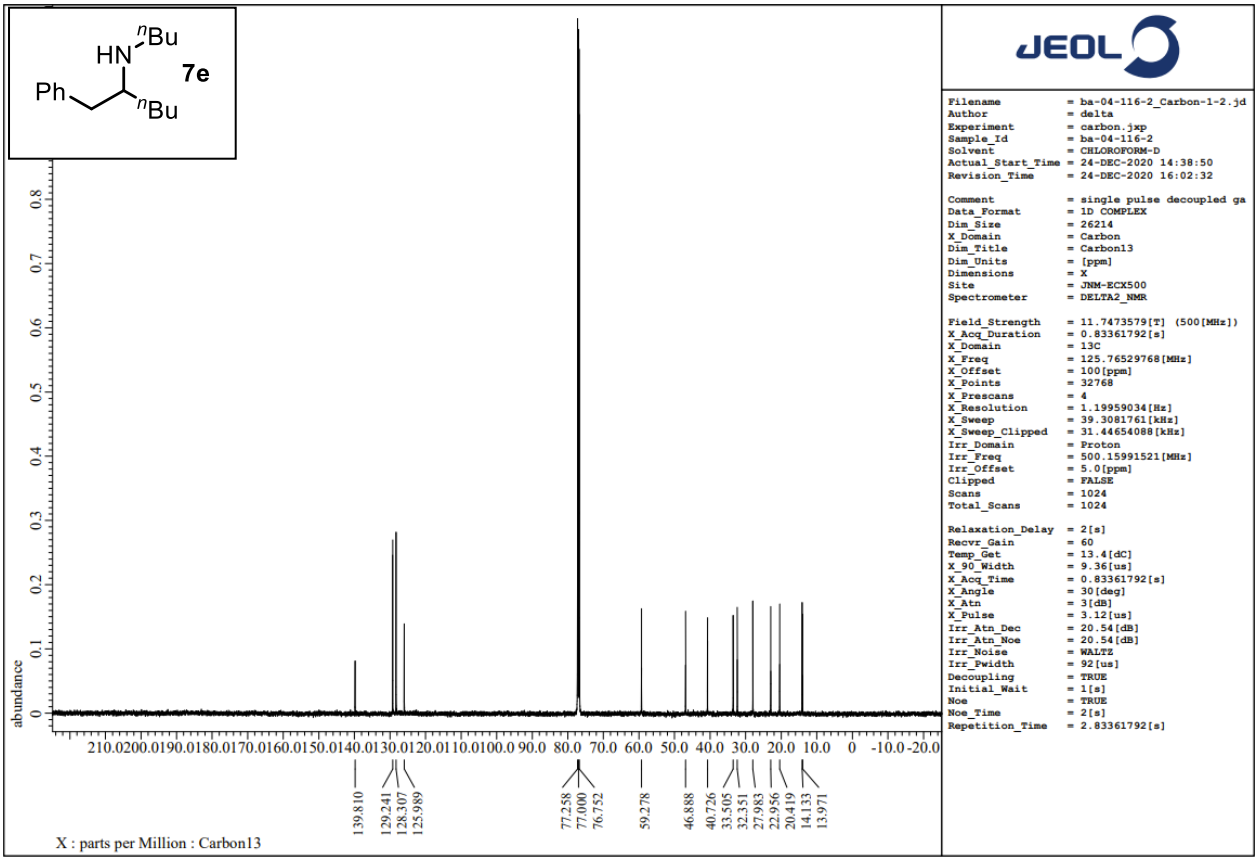

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Filename            = ba-04-116-3_Proton-1-5.jd
Author              = delta
Experiment          = proton.jxp
Sample_Id           = ba-04-116-3
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 24-DEC-2020 16:05:49
Revision_Time       = 16-MAY-2021 17:45:06

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T]  (500[MHz])
X_Acq_Duration      = 1.74587904[s]
X_Domain            = 1H
X_Freq              = 500.15991521[MHz]
X_Offset            = 5.0[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.57277737[Hz]
X_Sweep             = 9.38438438[kHz]
X_Sweep_Clipped     = 7.50750751[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Tri_Domain          = Proton
Tri_Freq            = 500.15991521[MHz]
Tri_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 44
Temp_Get            = 13.3[dC]
X_90_Width          = 13.7[us]
X_Acq_Time          = 1.74587904[s]
X_Angle             = 45[deg]
X_Atn               = 4[dB]
X_Pulse             = 6.85[us]
Irr_Mode            = Off
Tri_Mode            = Off
```

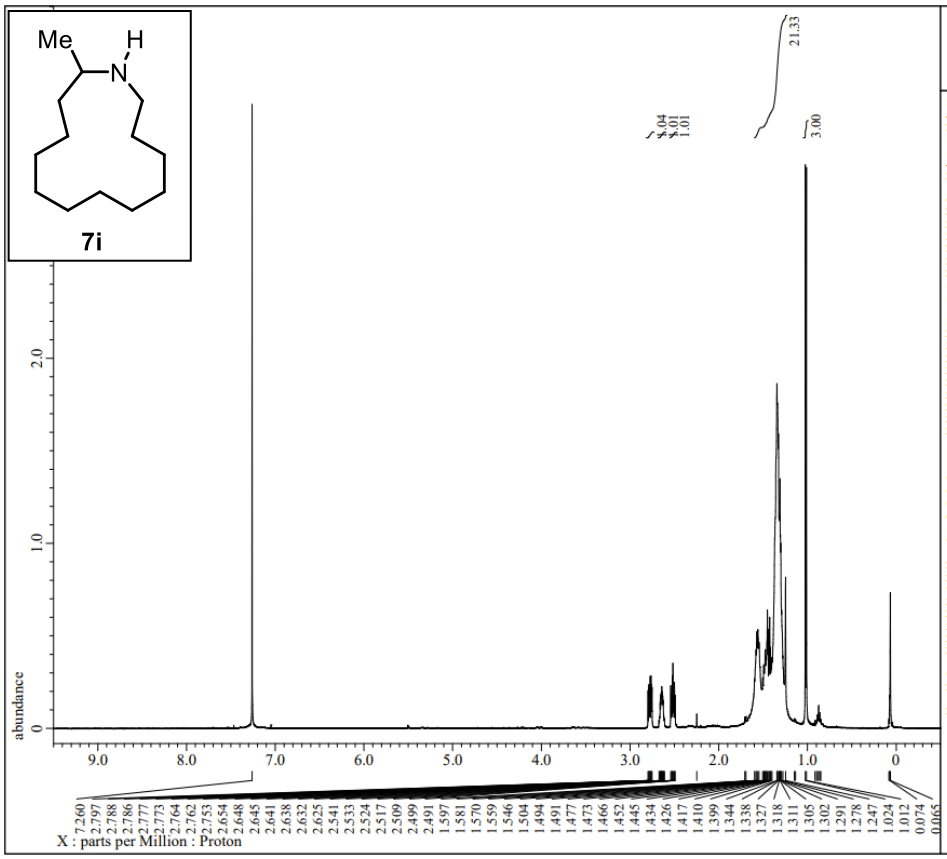



```
Filename            = ba-04-116-2_Carbon-1-2.jd
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = ba-04-116-2
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 24-DEC-2020 14:38:50
Revision_Time       = 24-DEC-2020 16:02:32

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T]  (500[MHz])
X_Acq_Duration      = 0.83361792[s]
X_Domain            = 13C
X_Freq              = 125.76529768[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.19959034[Hz]
X_Sweep             = 39.3081761[kHz]
X_Sweep_Clipped     = 31.44654088[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 1024
Total_Scans         = 1024

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 13.4[dC]
X_90_Width          = 9.36[us]
X_Acq_Time          = 0.83361792[s]
X_Angle             = 30[deg]
X_Atn               = 3[dB]
X_Pulse             = 3.12[us]
Irr_Atn_Dec         = 20.54[dB]
Irr_Atn_Noe         = 20.54[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 92[us]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 2.83361792[s]
```

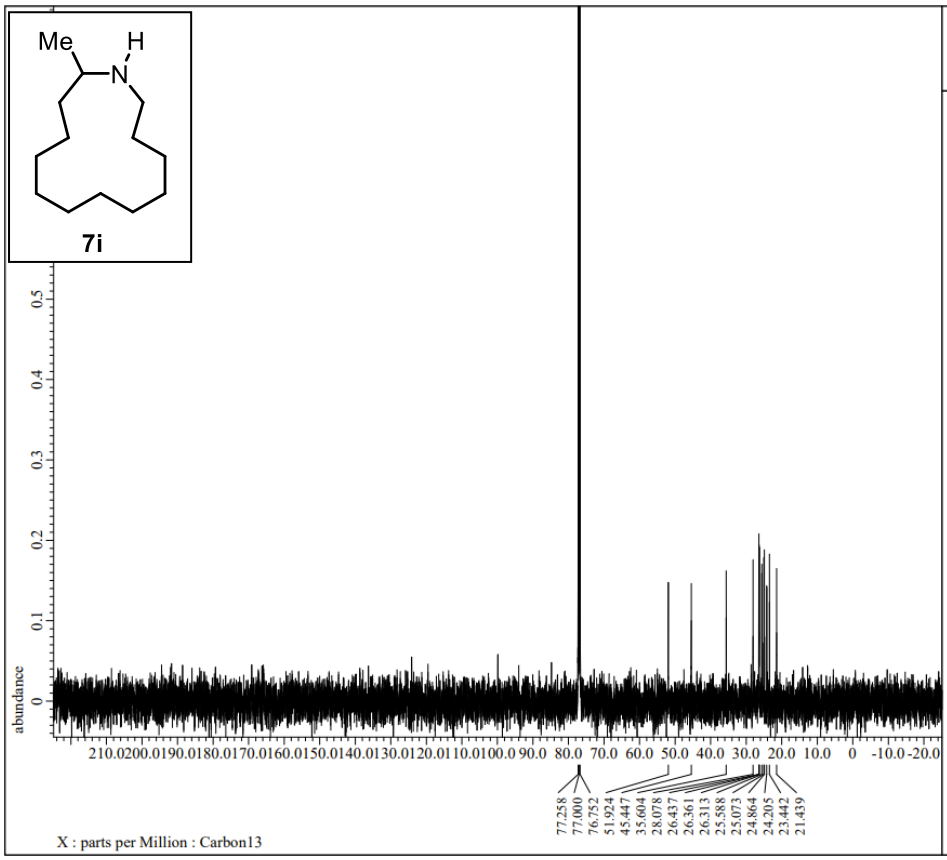



```
Filename          = ba-04-066-3_Proton-1-2.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-066-3
Solvent           = CHLOROFORM-D
Actual_Start_Time = 19-OCT-2020 16:34:59
Revision_Time     = 19-OCT-2020 16:53:04

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 42
Temp_Get          = 17.3[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

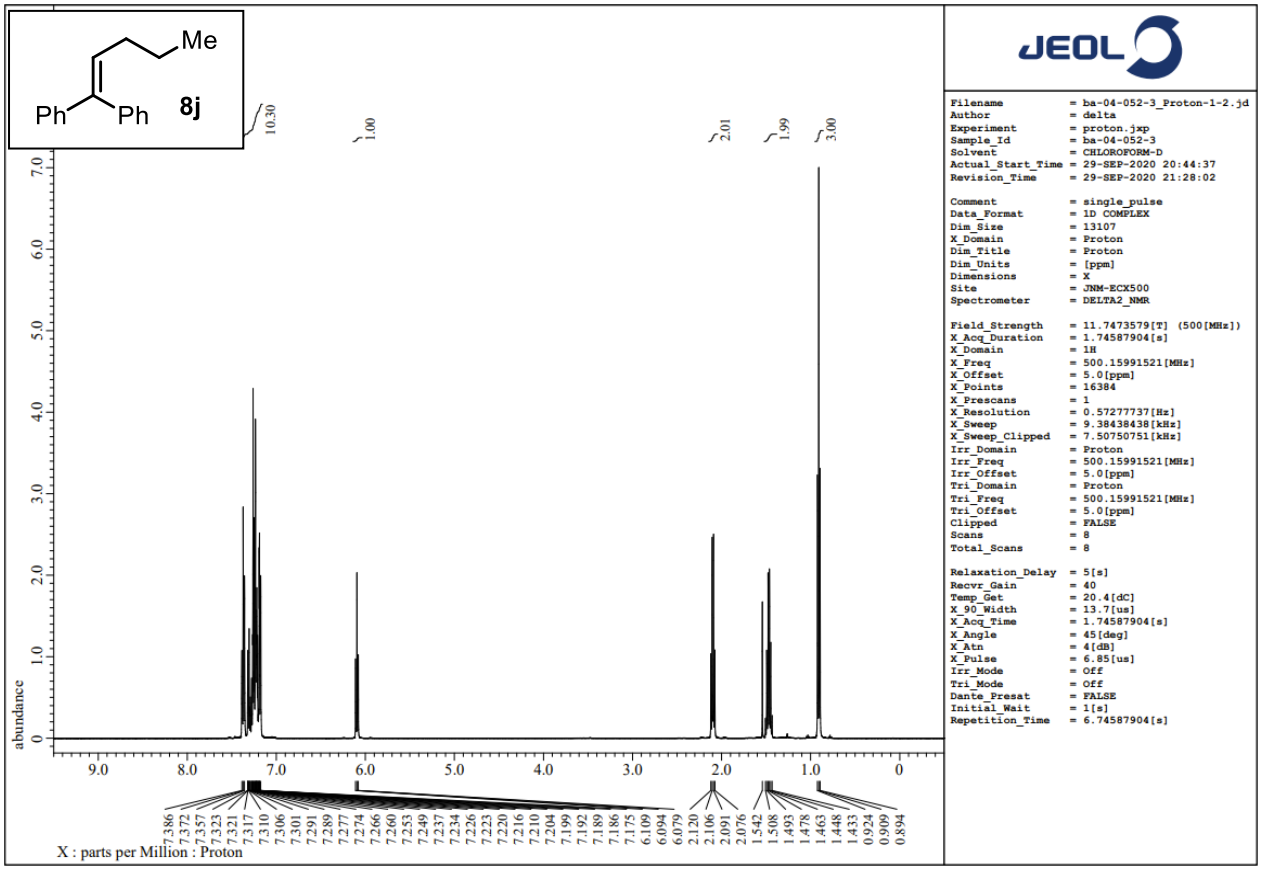


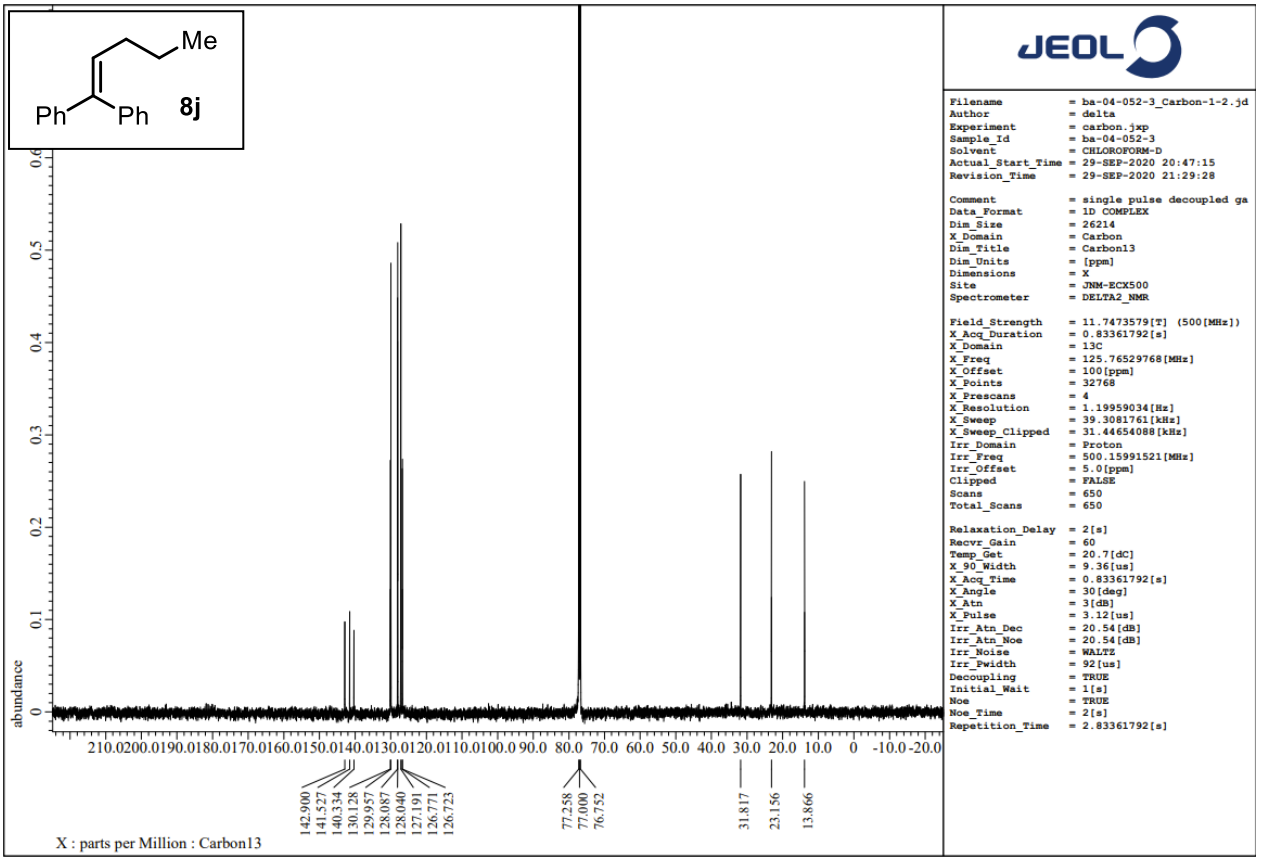

```
Filename          = ba-04-066-4_Carbon-1-1-sc
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-066-4
Solvent           = CHLOROFORM-D
Actual_Start_Time = 19-OCT-2020 19:58:47
Revision_Time     = 19-OCT-2020 19:49:23

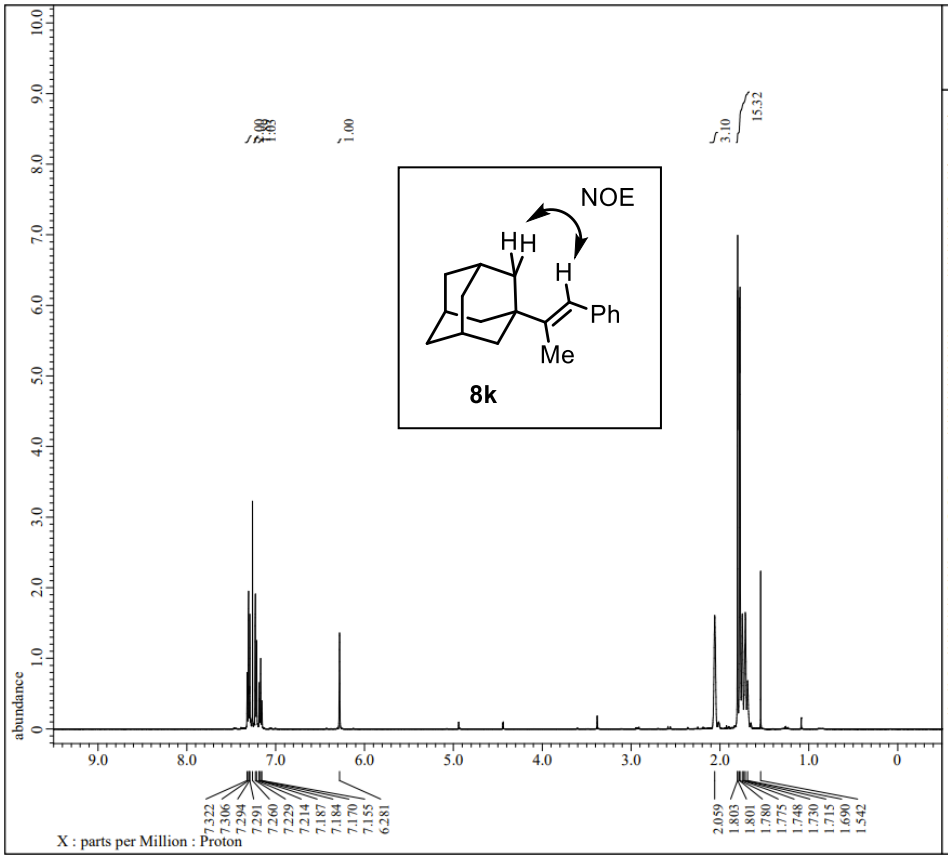
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 25
Total_Scans       = 25

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 17.8[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


Me
Ph
Ph
8j
10.30
1.00
2.01
1.99
3.00
abundance
X : parts per Million : Proton
Filename = ba-04-052-3_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-04-052-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 29-SEP-2020 20:44:37
Revision_Time = 29-SEP-2020 21:28:02
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 40
Temp_Get = 20.4[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


Me
Ph
Ph
8j
abundance
X : parts per Million : Carbon13
Filename = ba-04-052-3_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-04-052-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 29-SEP-2020 20:47:15
Revision_Time = 29-SEP-2020 21:29:28
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 650
Total_Scans = 650
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 20.7[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

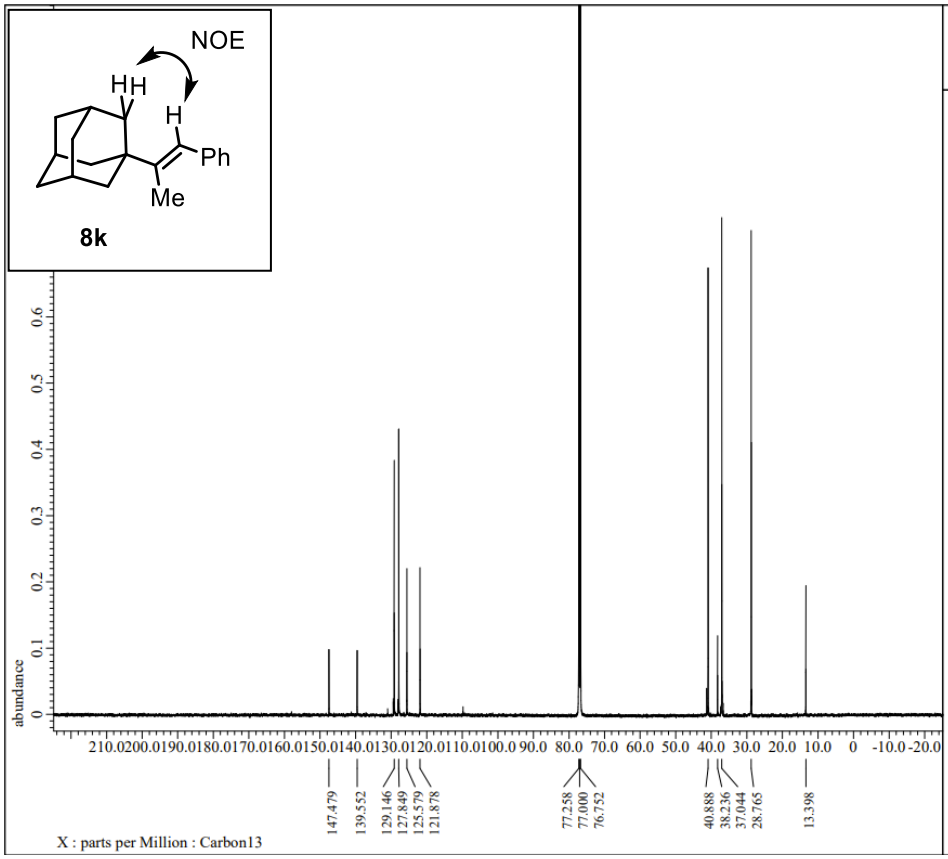



```
Filename          = ba-04-048-4-F2-1_Proton-1
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-048-4-F2-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 23-SEP-2020 17:34:04
Revision_Time     = 23-SEP-2020 17:24:32

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 38
Temp_Get          = 21.1[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

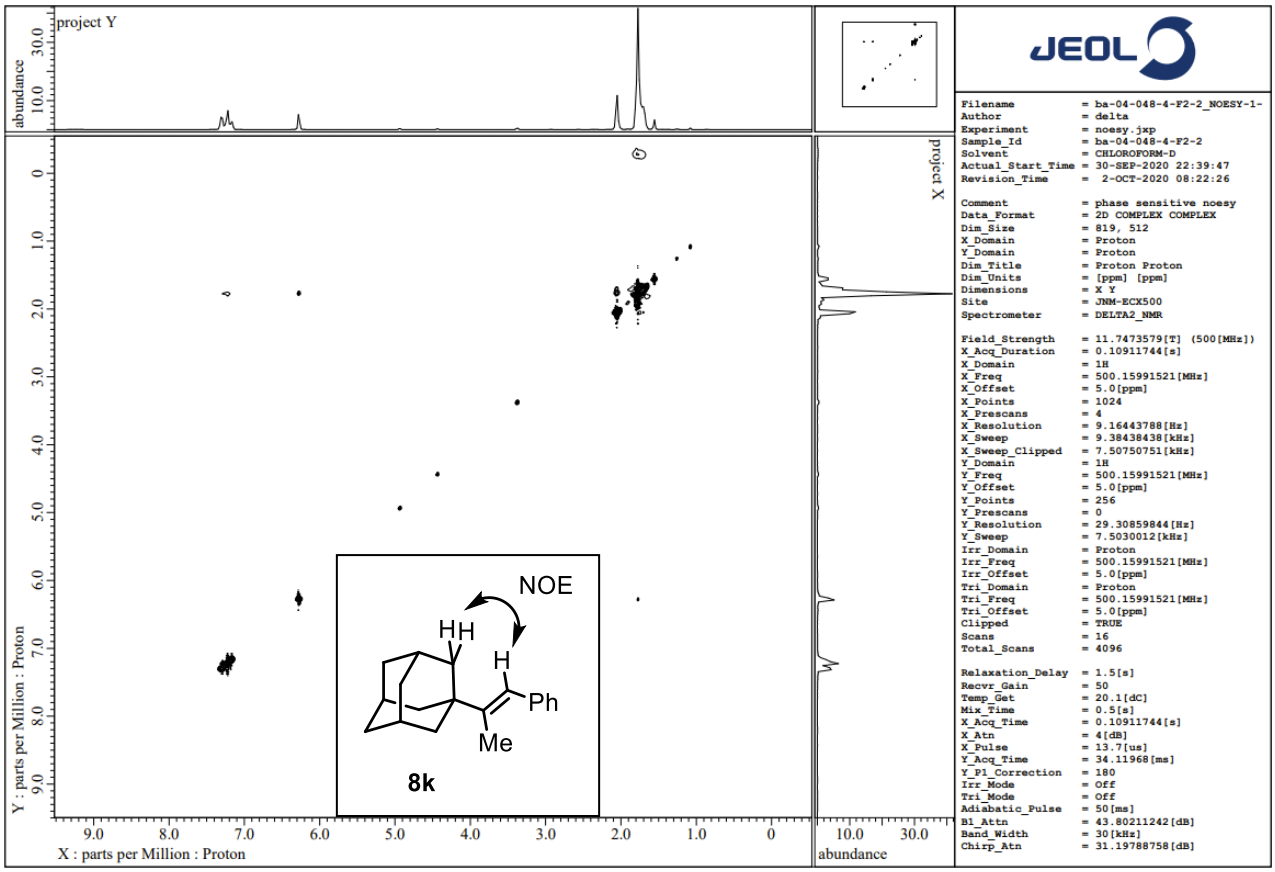


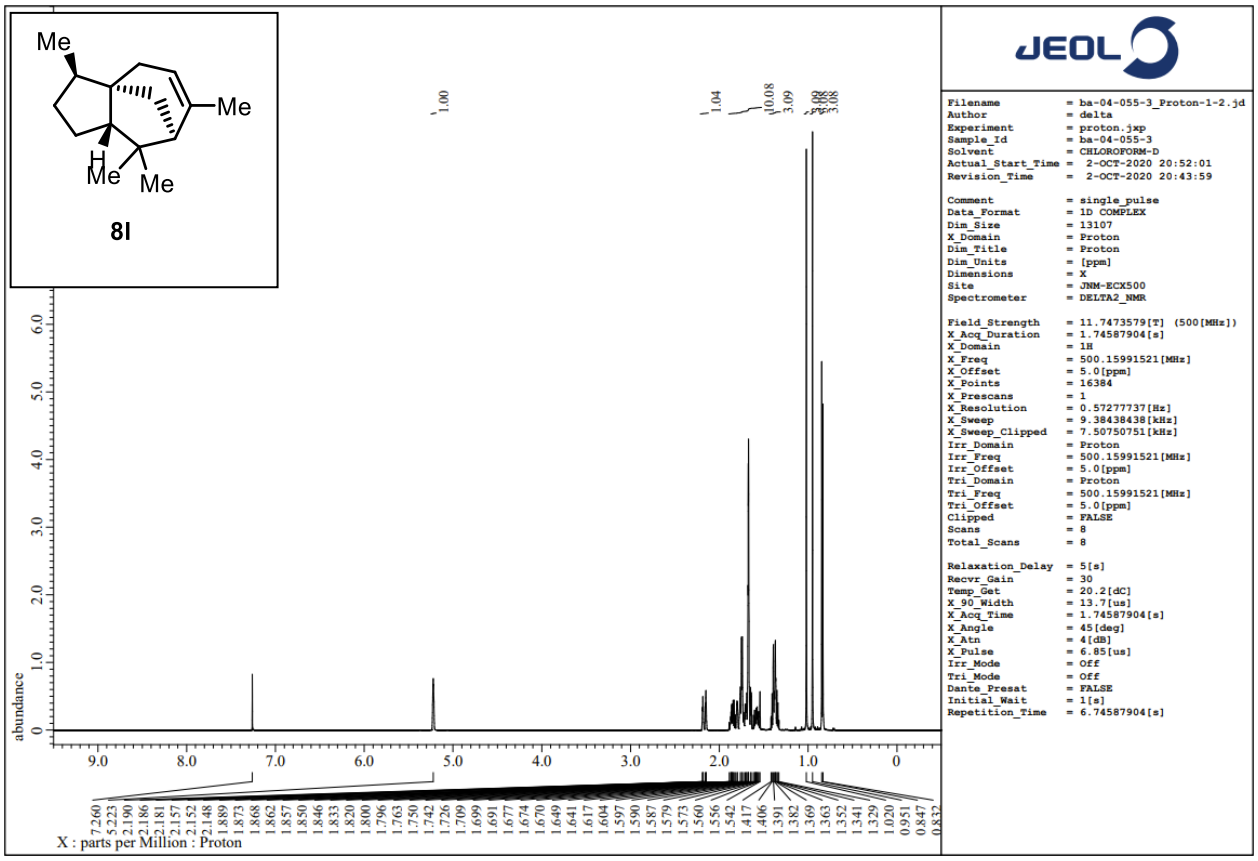

```
Filename          = ba-04-048-4-F2-1_Carbon-1
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-048-4-F2-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 23-SEP-2020 22:43:50
Revision_Time     = 24-SEP-2020 10:11:01

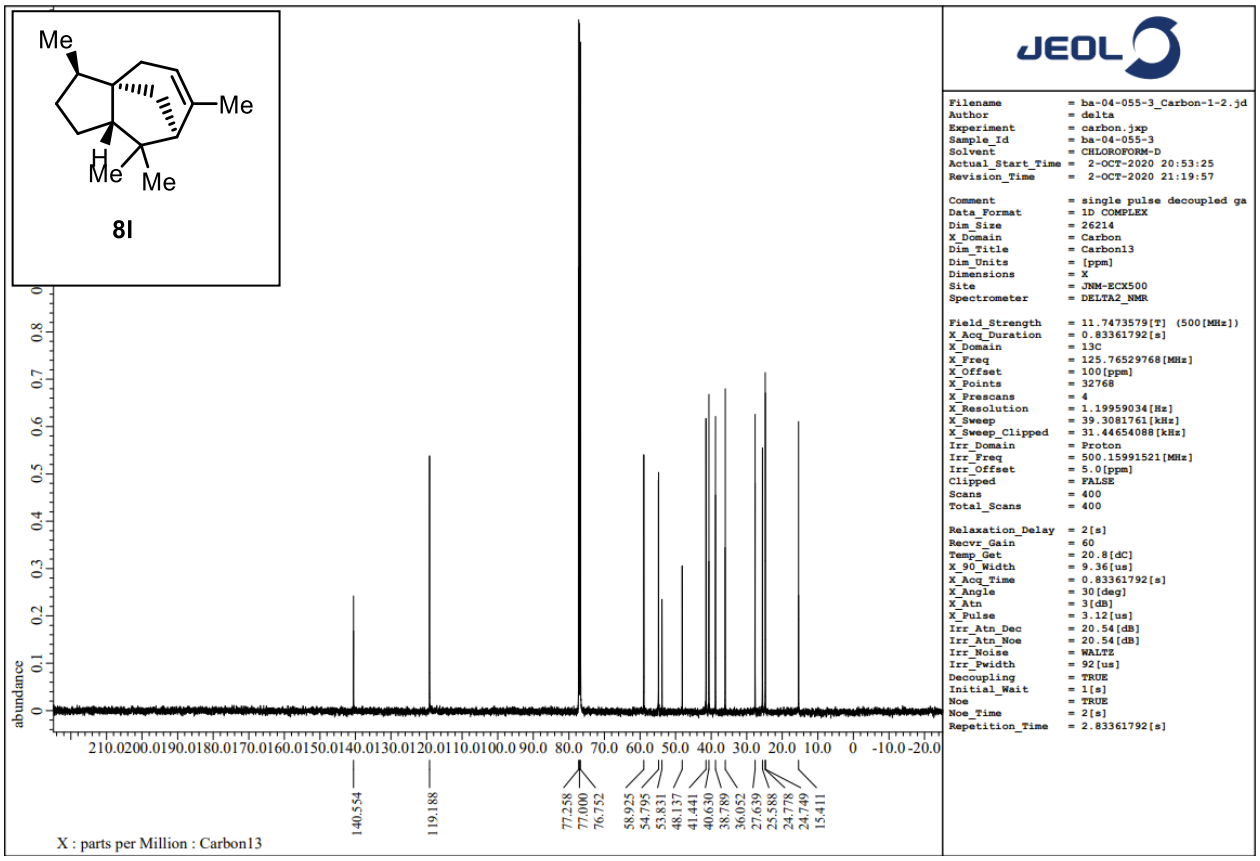
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

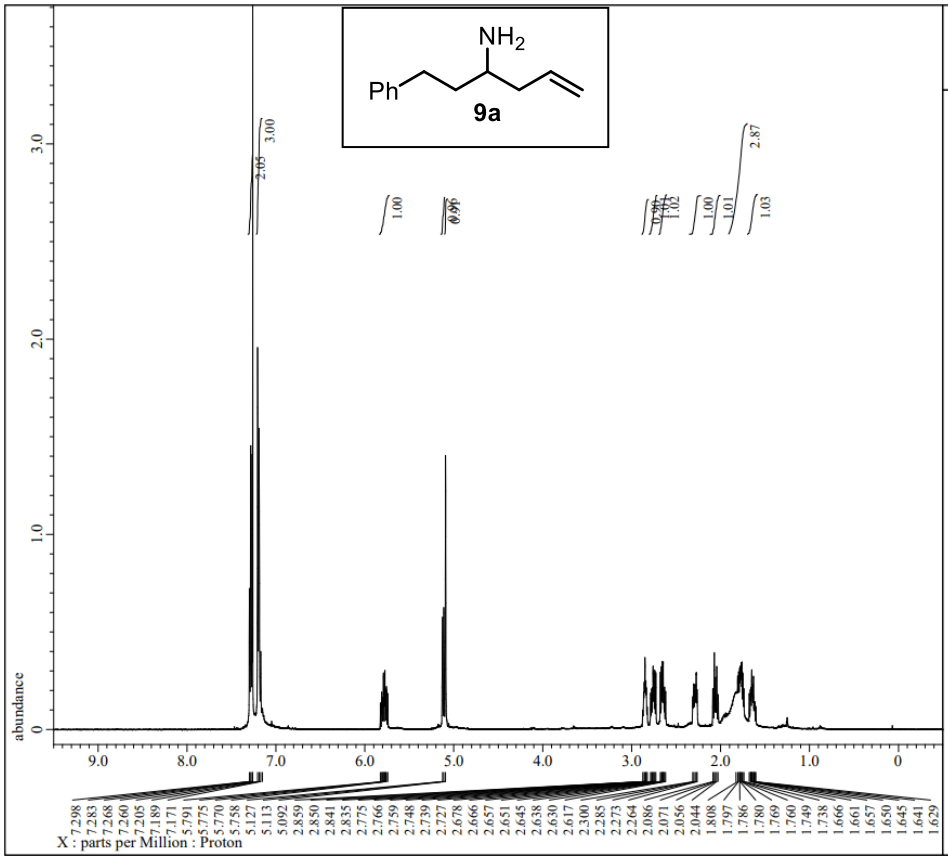
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 6000
Total_Scans       = 6000

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 21.3[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


project Y
abundance
project X
NOE
HH
H
Ph
Me
8k
Y : parts per Million : Proton
X : parts per Million : Proton
abundance
JEOL
Filename = ba-04-048-4-F2-2_NOESY-1-
Author = delta
Experiment = noesy.jxp
Sample_Id = ba-04-048-4-F2-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 30-SEP-2020 22:39:47
Revision_Time = 2-OCT-2020 08:22:26
Comment = phase sensitive noesy
Data_Format = 2D COMPLEX COMPLEX
Dim_Size = 819, 512
X_Domain = Proton
Y_Domain = Proton
Dim_Title = Proton Proton
Dim_Units = [ppm] [ppm]
Dimensions = X Y
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.10911744[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 1024
X_Prescans = 4
X_Resolution = 9.16443788[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Y_Domain = 1H
Y_Freq = 500.15991521[MHz]
Y_Offset = 5.0[ppm]
Y_Points = 256
Y_Prescans = 0
Y_Resolution = 29.30859844[Hz]
Y_Sweep = 7.5030012[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = TRUE
Scans = 16
Total_Scans = 4096
Relaxation_Delay = 1.5[s]
Recvr_Gain = 50
Temp_Get = 20.1[dC]
Mix_Time = 0.5[s]
X_Acq_Time = 0.10911744[s]
X_Atn = 4[dB]
X_Pulse = 13.7[us]
Y_Acq_Time = 34.11968[ms]
Y_Pl_Correction = 180
Irr_Mode = Off
Tri_Mode = Off
Adiabatic_Pulse = 50[ms]
Bl_Attn = 43.80211242[dB]
Band_Width = 30[kHz]
Chirp_Atn = 31.19788758[dB]


Me
Me
H
Me
Me
8l
1.00
1.04
10.08
3.09
abundance
X : parts per Million : Proton
JEOL
Filename = ba-04-055-3_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-04-055-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 2-OCT-2020 20:52:01
Revision_Time = 2-OCT-2020 20:43:59
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 30
Temp_Get = 20.2[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


Me
Me
H
Me
Me
8l
140.554
119.188
77.258
77.000
76.752
58.925
54.795
53.831
48.137
41.441
40.630
38.789
36.052
27.639
25.588
24.778
24.749
15.411
abundance
X : parts per Million : Carbon13
JEOL
Filename = ba-04-055-3_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-04-055-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 2-OCT-2020 20:53:25
Revision_Time = 2-OCT-2020 21:19:57
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 400
Total_Scans = 400
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 20.8[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

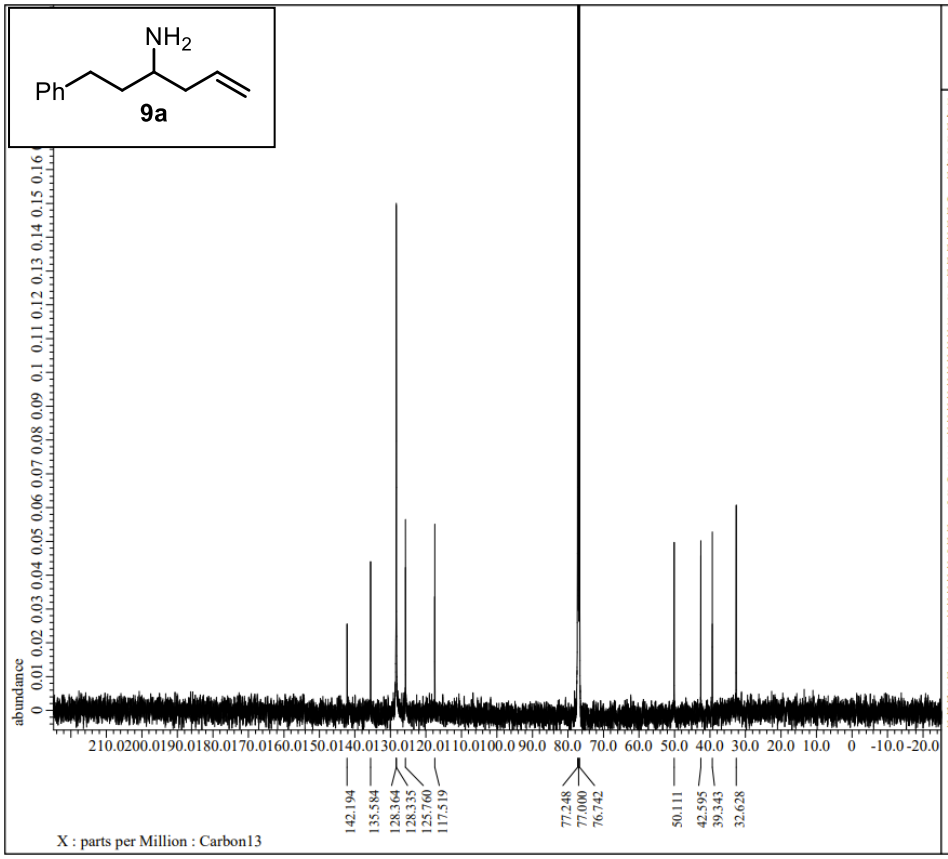



```
Filename          = ba-04-101-2_Proton-1-4.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-101-2
Solvent           = CHLOROFORM-D
Actual_Start_Time =  1-DEC-2020 21:04:48
Revision_Time     =  1-DEC-2020 21:24:14

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T]  (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 42
Temp_Get          = 17.9[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

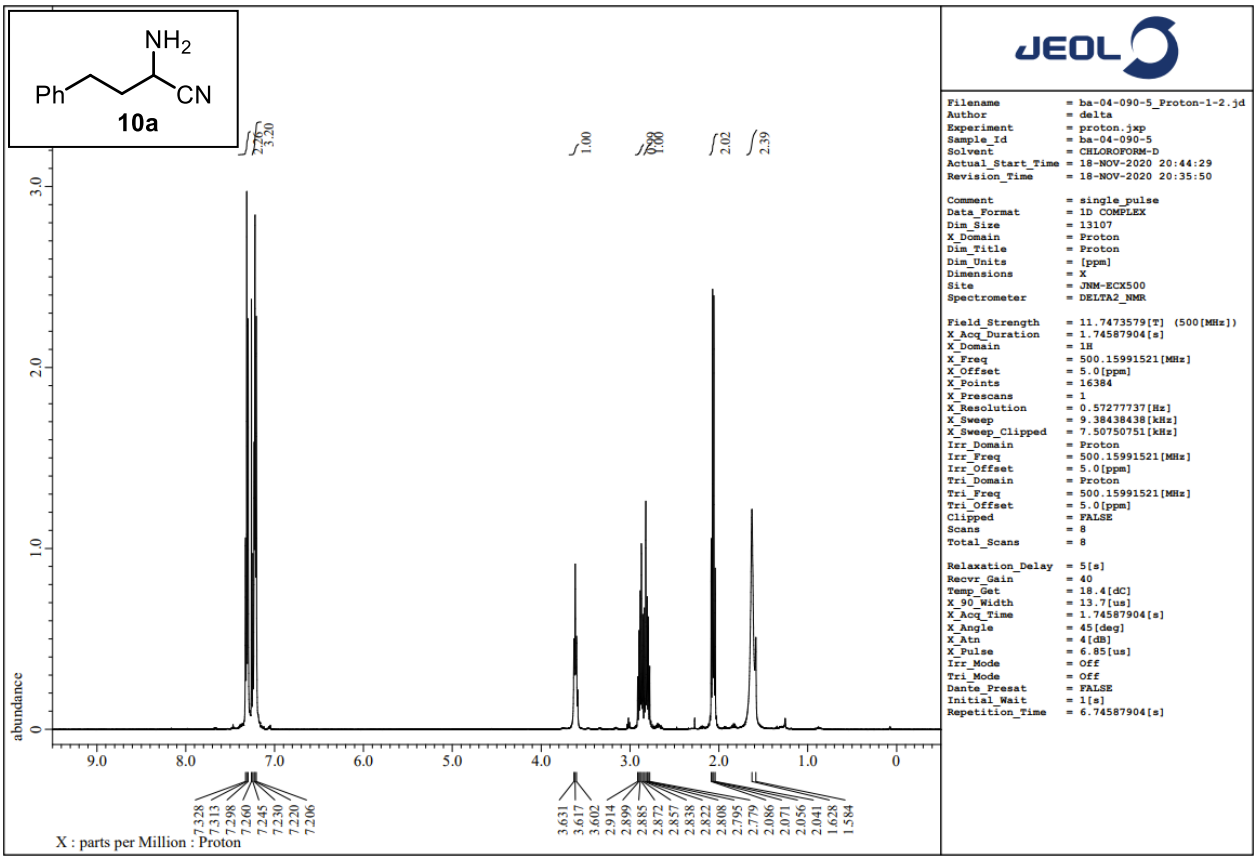


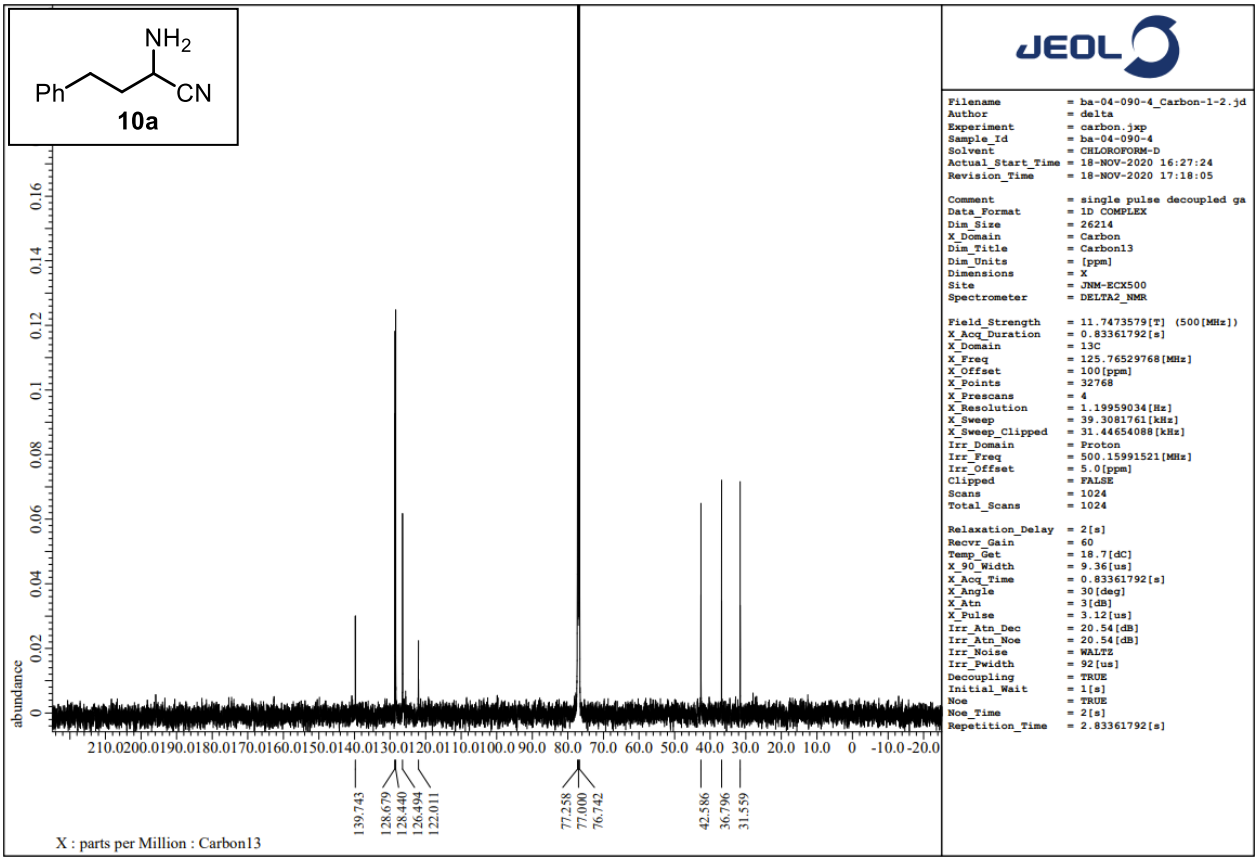

```
Filename          = ba-04-091-2B-1_Carbon-1-2
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-091-2B-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 24-NOV-2020 15:21:57
Revision_Time     = 24-NOV-2020 16:40:59

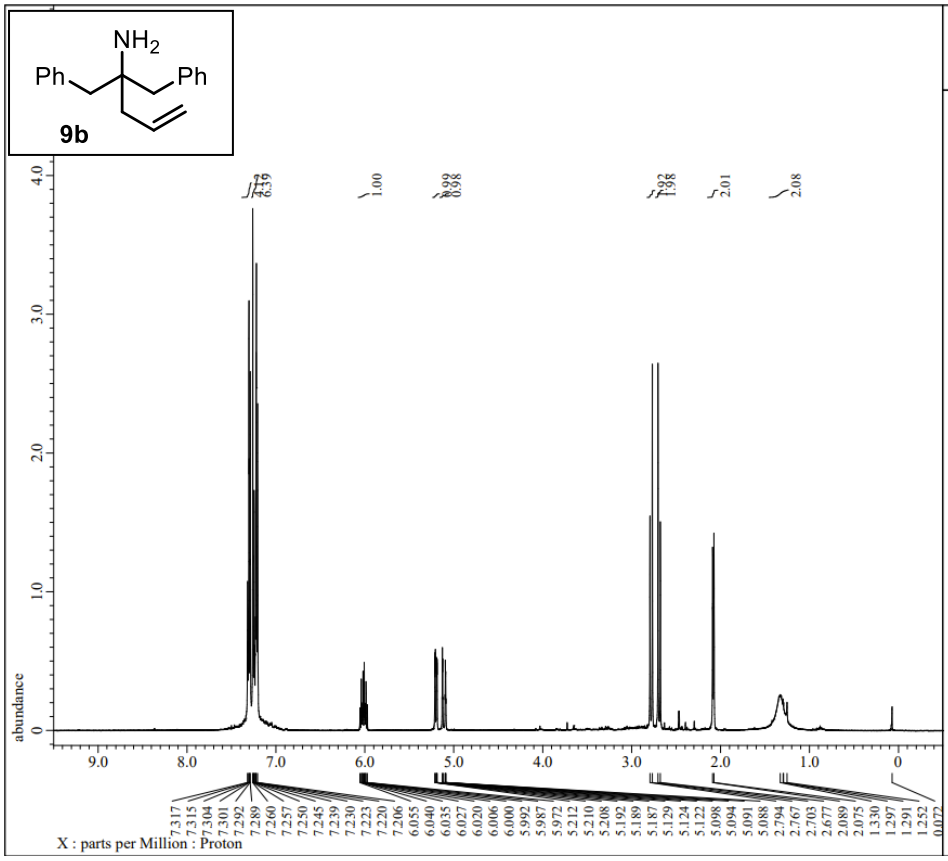
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T]  (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 17.8[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


NH2
Ph
CN
10a
abundance
X : parts per Million : Proton
Filename = ba-04-090-5_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-04-090-5
Solvent = CHLOROFORM-D
Actual_Start_Time = 18-NOV-2020 20:44:29
Revision_Time = 18-NOV-2020 20:35:50
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 40
Temp_Get = 18.4[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


NH2
Ph
CN
10a
abundance
X : parts per Million : Carbon13
Filename = ba-04-090-4_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-04-090-4
Solvent = CHLOROFORM-D
Actual_Start_Time = 18-NOV-2020 16:27:24
Revision_Time = 18-NOV-2020 17:18:05
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 18.7[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

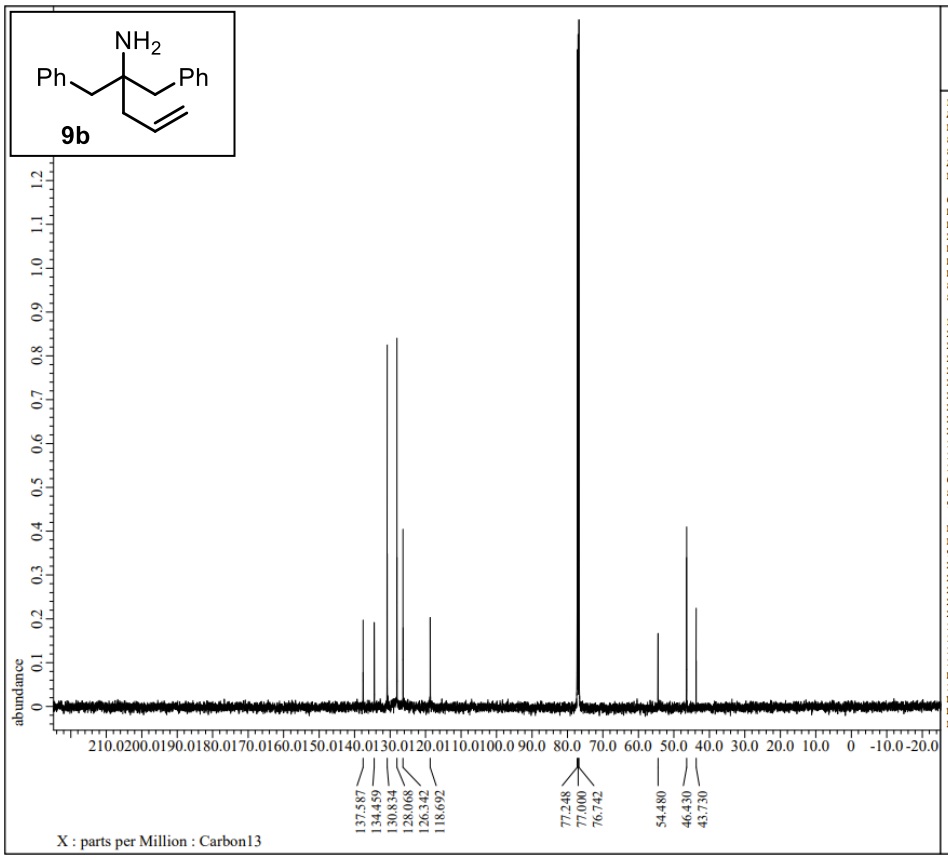



```
Filename          = ba-04-076-4_Proton-1-2.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-076-4
Solvent           = CHLOROFORM-D
Actual_Start_Time =  2-NOV-2020 21:21:37
Revision_Time     =  2-NOV-2020 21:15:35

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 40
Temp_Get          = 16.6[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

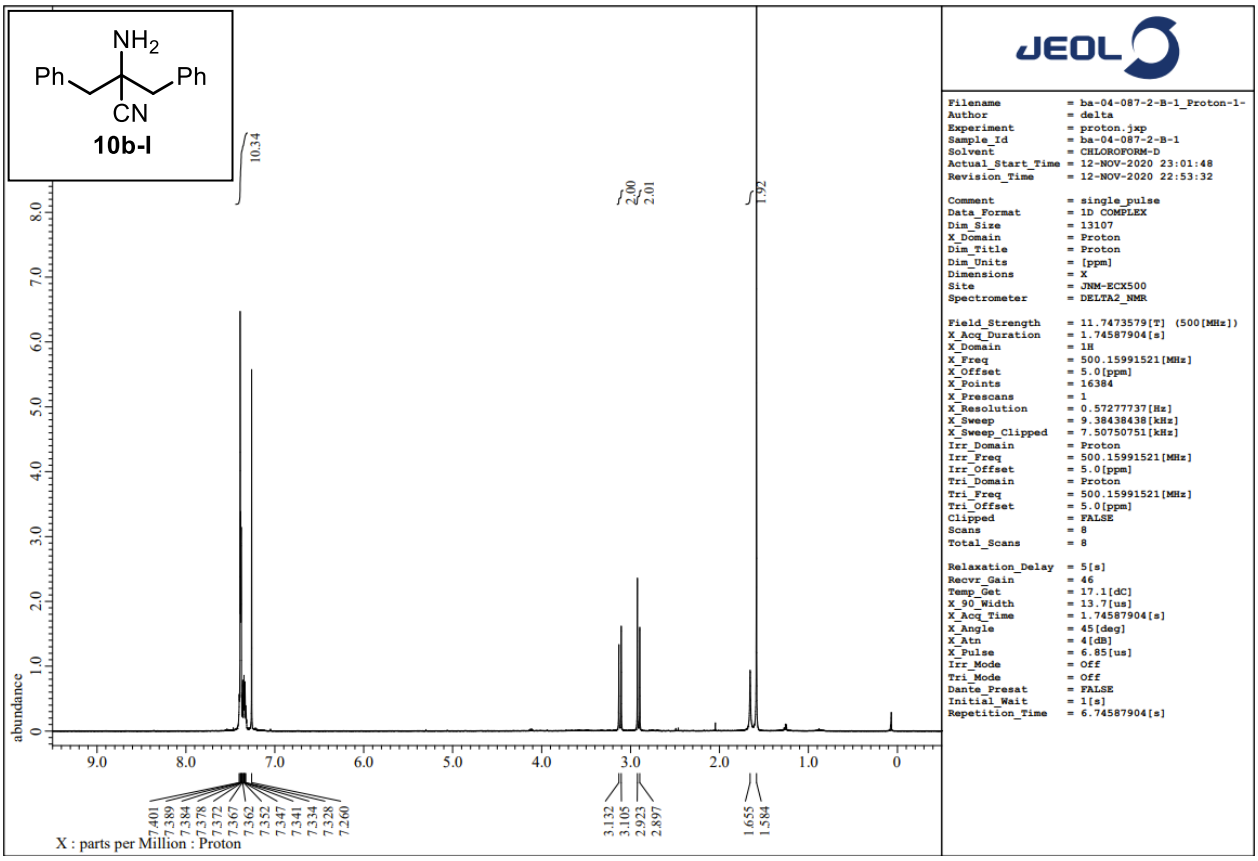


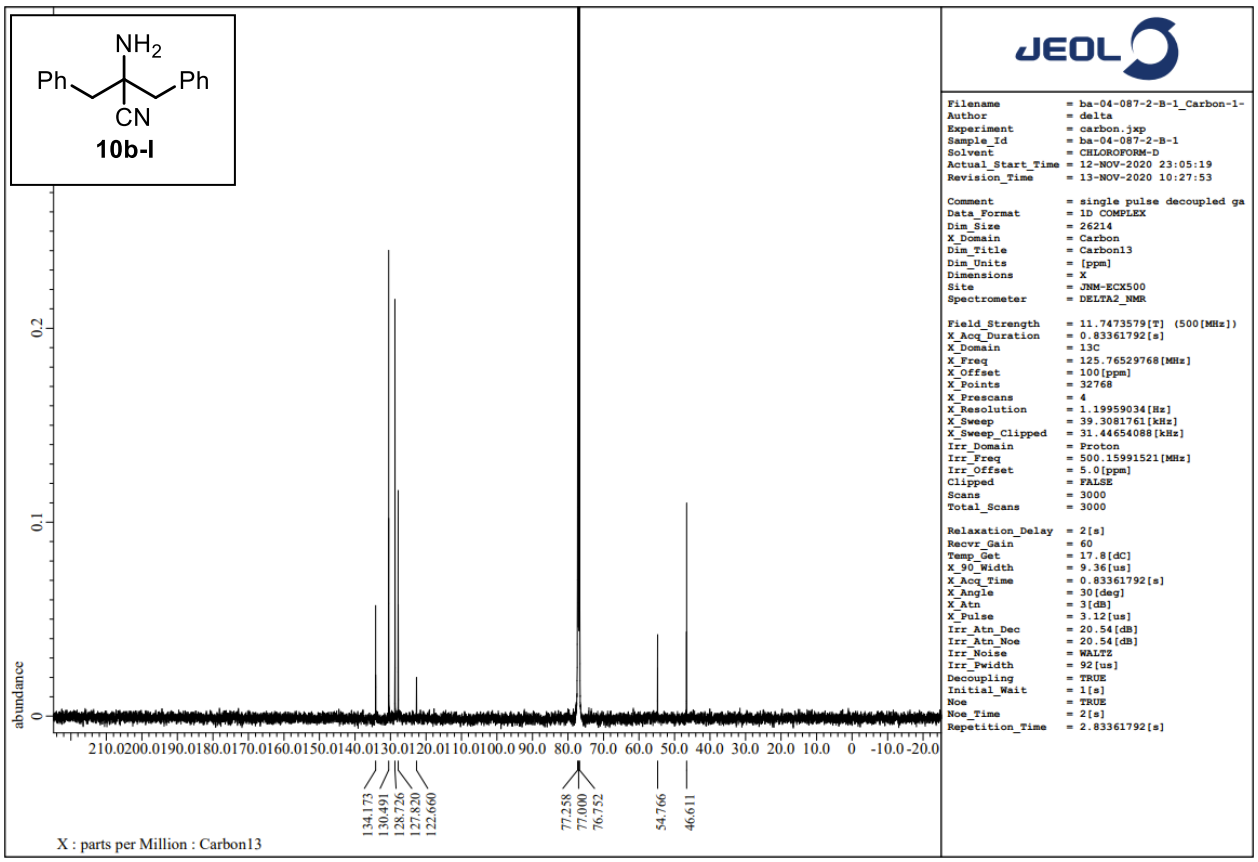

```
Filename          = ba-04-076-3_Carbon-1-2.jd
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-076-3
Solvent           = CHLOROFORM-D
Actual_Start_Time = 30-OCT-2020 20:55:15
Revision_Time     = 30-OCT-2020 21:07:23

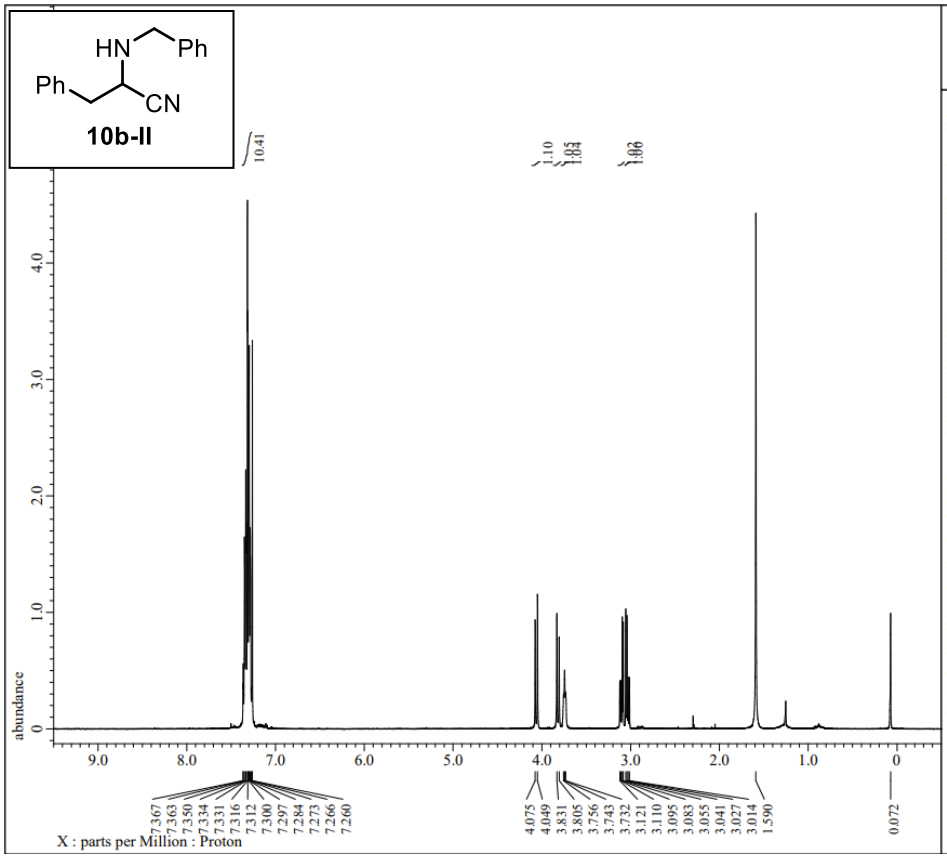
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 200
Total_Scans       = 200

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 17.4[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


NH2
Ph
Ph
CN
10b-l
10.34
2.00
2.01
1.92
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.401
7.389
7.384
7.378
7.372
7.367
7.362
7.352
7.347
7.341
7.334
7.328
7.260
3.132
3.105
2.923
2.897
1.655
1.584
X : parts per Million : Proton
JEOL
Filename = ba-04-087-2-B-1_Proton-1-
Author = delta
Experiment = proton.jxp
Sample_Id = ba-04-087-2-B-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 12-NOV-2020 23:01:48
Revision_Time = 12-NOV-2020 22:53:32
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 46
Temp_Get = 17.1[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


NH2
Ph
Ph
CN
10b-l
abundance
0.2
0.1
0
210.0200.0190.0180.0170.0160.0150.0140.0130.0120.0110.0100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
134.173
130.491
128.726
127.820
122.660
77.258
77.000
76.752
54.766
46.611
X : parts per Million : Carbon13
JEOL
Filename = ba-04-087-2-B-1_Carbon-1-
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-04-087-2-B-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 12-NOV-2020 23:05:19
Revision_Time = 13-NOV-2020 10:27:53
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 3000
Total_Scans = 3000
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 17.8[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

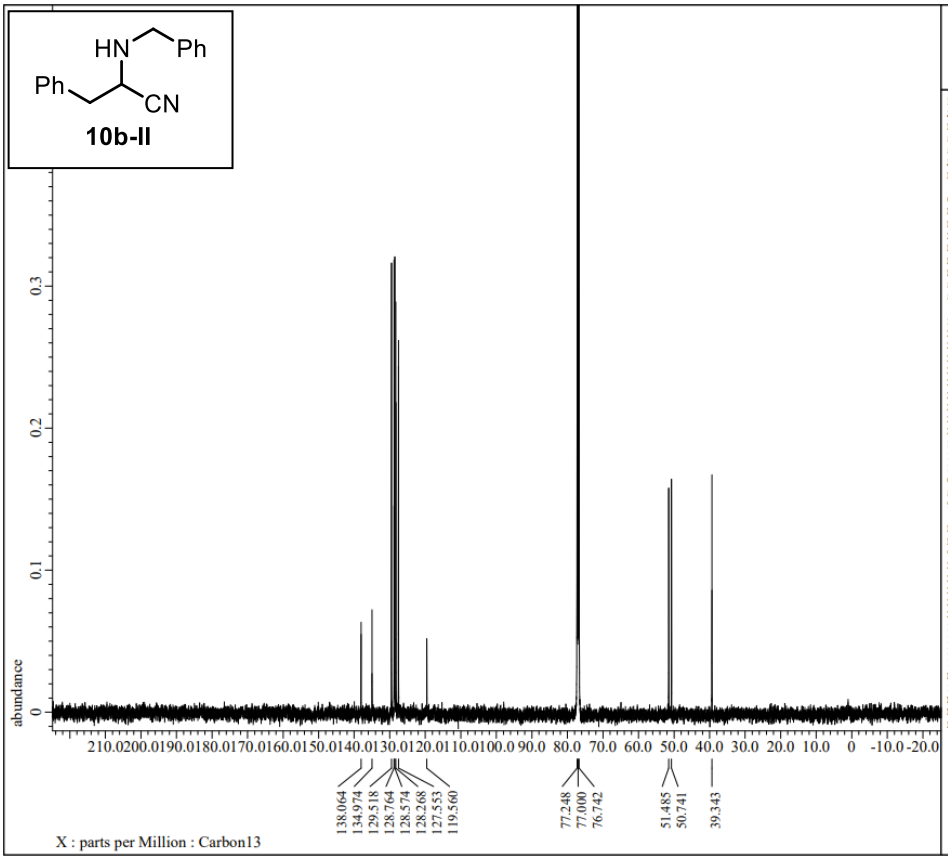



```
Filename          = ba-04-087-2-A-1_Proton-1-
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-087-2-A-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 12-NOV-2020 22:54:05
Revision_Time     = 12-NOV-2020 22:59:04

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 42
Temp_Get          = 16.9[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

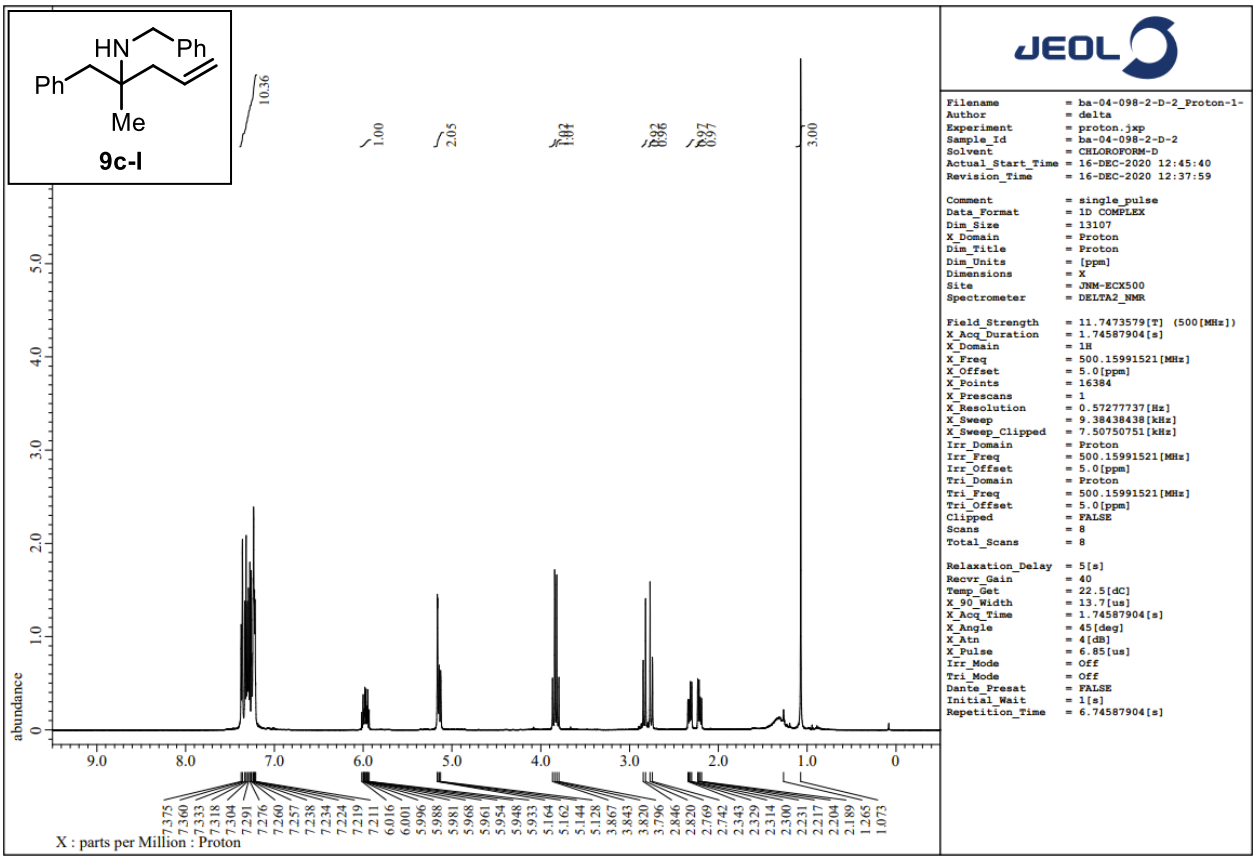


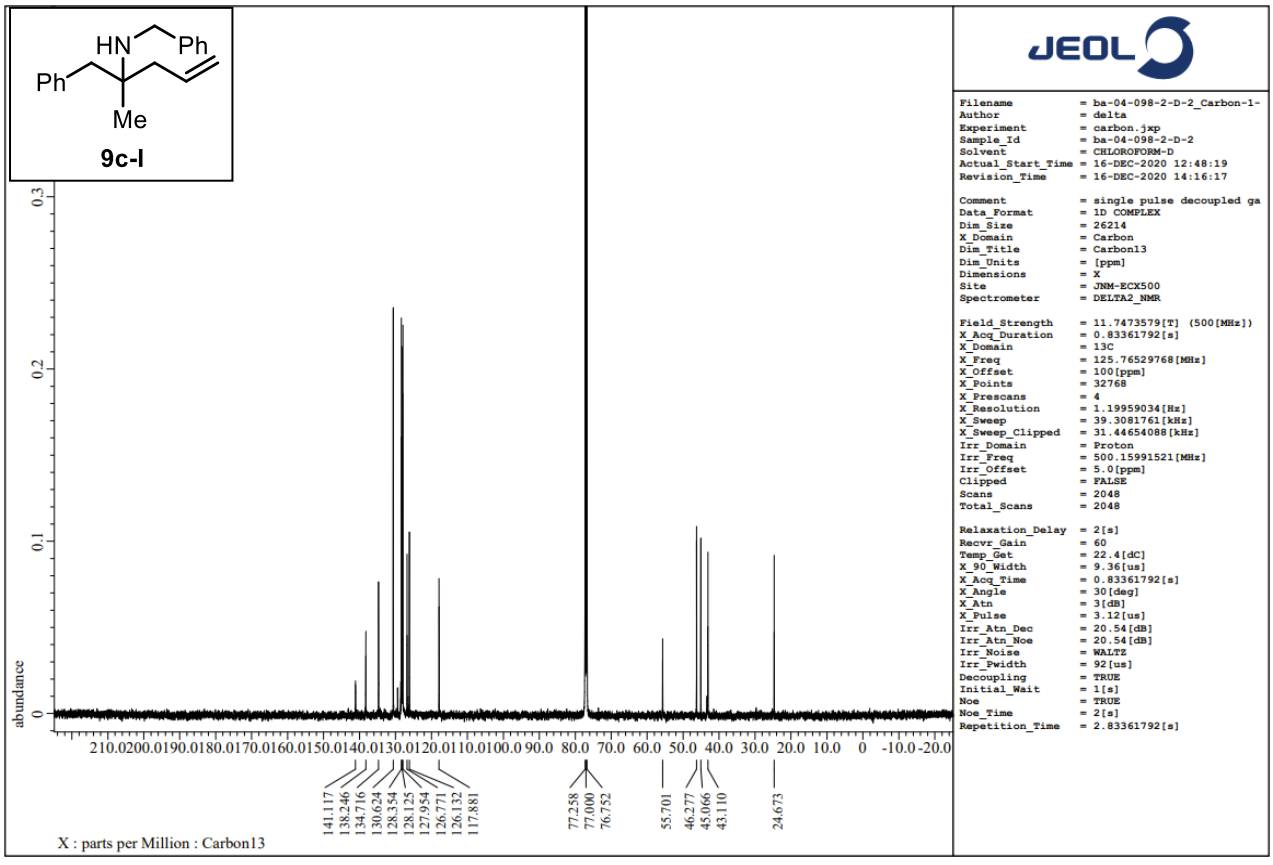

```
Filename          = ba-04-087-2-A-1 1_Carbon-
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-087-2-A-1 1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 13-NOV-2020 12:20:28
Revision_Time     = 13-NOV-2020 14:09:19

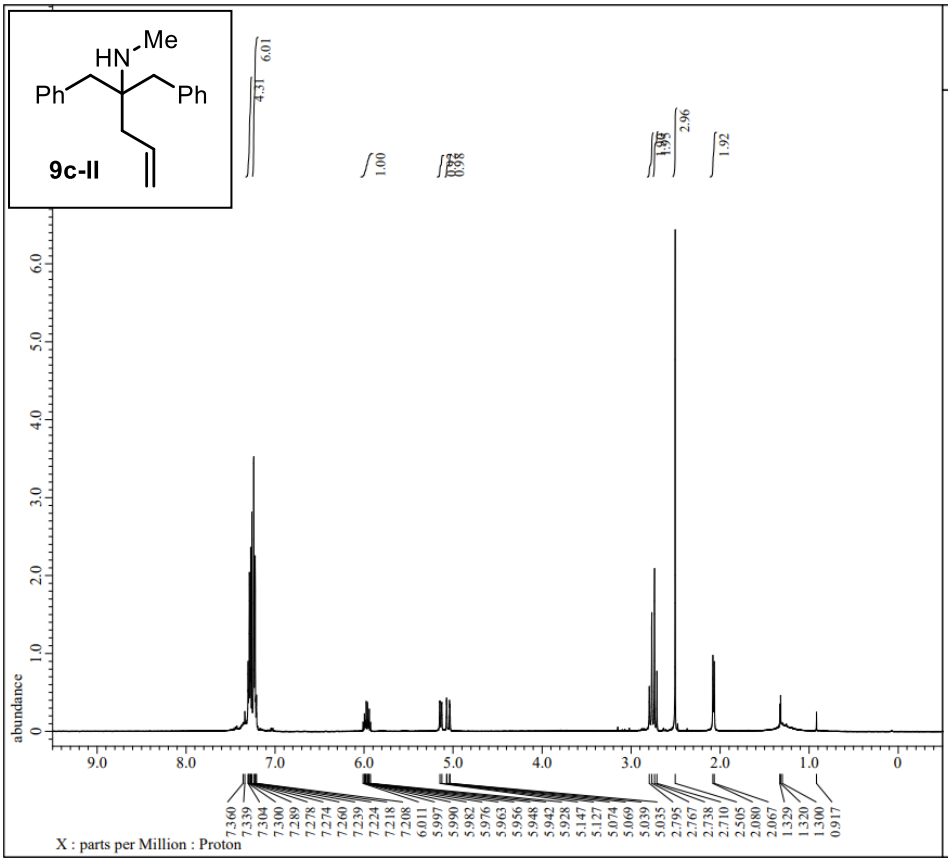
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 18.1[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```


HN
Ph
Ph
Me
9c-l
10.36
1.00
2.05
1.01
0.96
0.97
3.00
abundance
X : parts per Million : Proton
JEOL
Filename = ba-04-098-2-D-2_Proton-1-
Author = delta
Experiment = proton.jxp
Sample_Id = ba-04-098-2-D-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 16-DEC-2020 12:45:40
Revision_Time = 16-DEC-2020 12:37:59
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 40
Temp_Get = 22.5[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


HN
Ph
Ph
Me
9c-l
abundance
X : parts per Million : Carbon13
JEOL
Filename = ba-04-098-2-D-2_Carbon-1-
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-04-098-2-D-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 16-DEC-2020 12:48:19
Revision_Time = 16-DEC-2020 14:16:17
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 2048
Total_Scans = 2048
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 22.4[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]

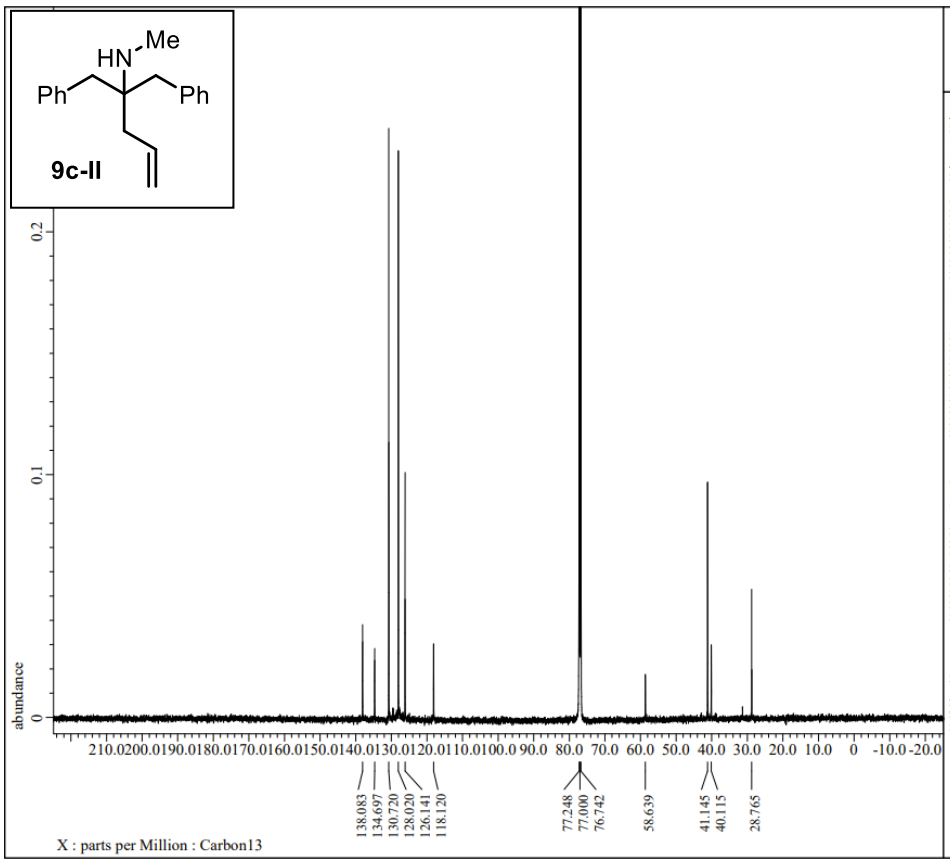



```
Filename          = ba-04-098-2-A-1_Proton-1-
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-098-2-A-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 15-DEC-2020 18:51:35
Revision_Time     = 15-DEC-2020 18:49:56

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 42
Temp_Get          = 20.8[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```

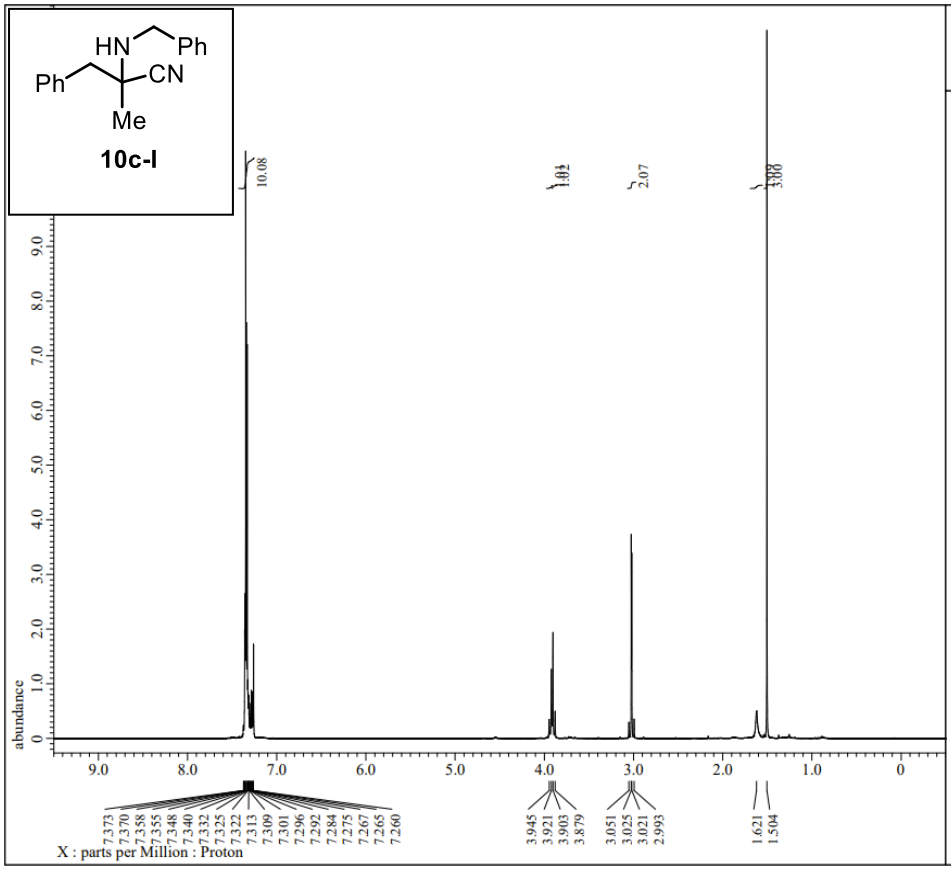



```
Filename          = ba-04-098-2-A-1_Carbon-1-
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-098-2-A-1
Solvent           = CHLOROFORM-D
Actual_Start_Time = 15-DEC-2020 22:23:42
Revision_Time     = 16-DEC-2020 09:12:56

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8192
Total_Scans       = 8192

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 22.3[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```



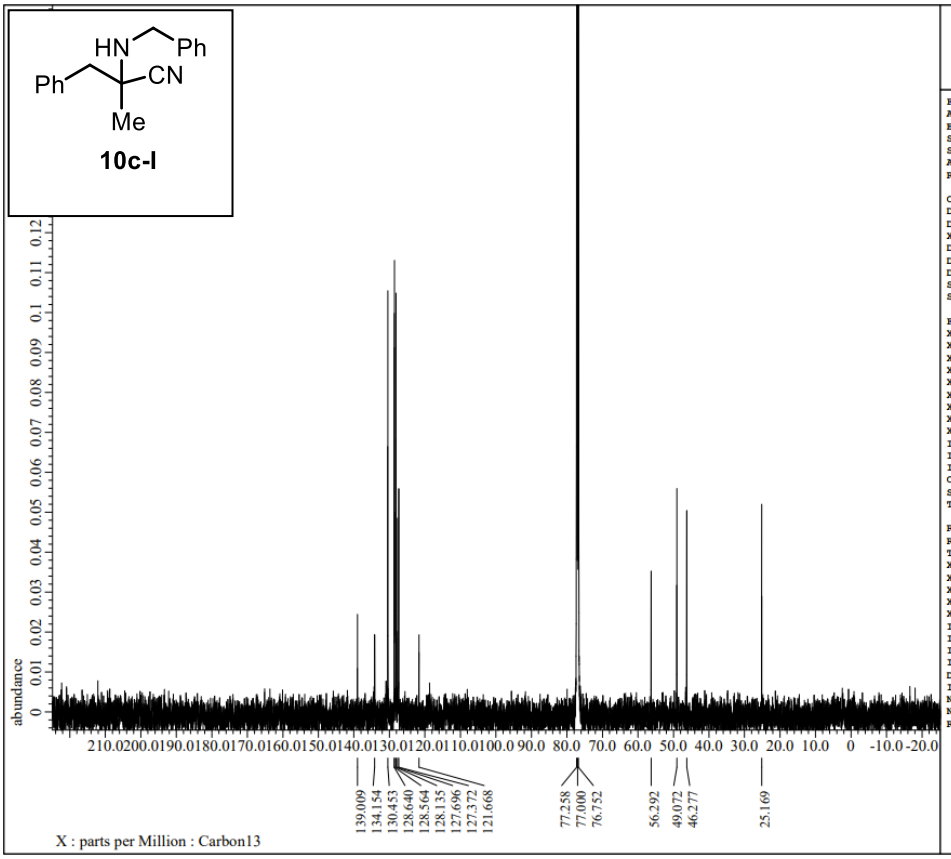
JEOL

```
Filename          = ba-04-132-2-A-1_Proton-1-
Author            = delta
Experiment        = proton.jxp
Sample_Id         = ba-04-132-2-A-1
Solvent           = CHLOROFORM-D
Actual_Start_Time =  9-FEB-2021 19:34:28
Revision_Time     =  9-FEB-2021 19:22:31

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T]  (500[MHz])
X_Acq_Duration    = 1.74587904[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.57277737[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 38
Temp_Get          = 14[dC]
X_90_Width        = 13.7[us]
X_Acq_Time        = 1.74587904[s]
X_Angle           = 45[deg]
X_Atn             = 4[dB]
X_Pulse           = 6.85[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.74587904[s]
```



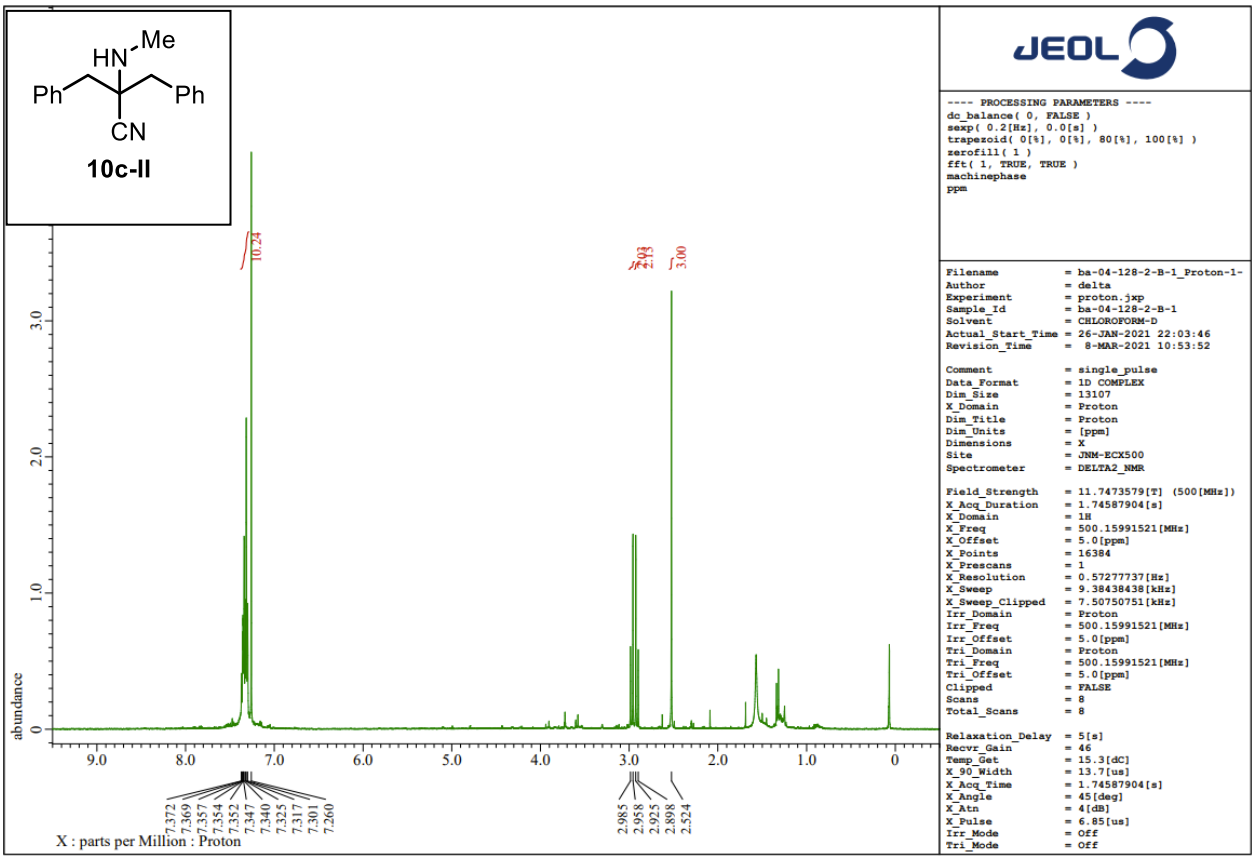
JEOL

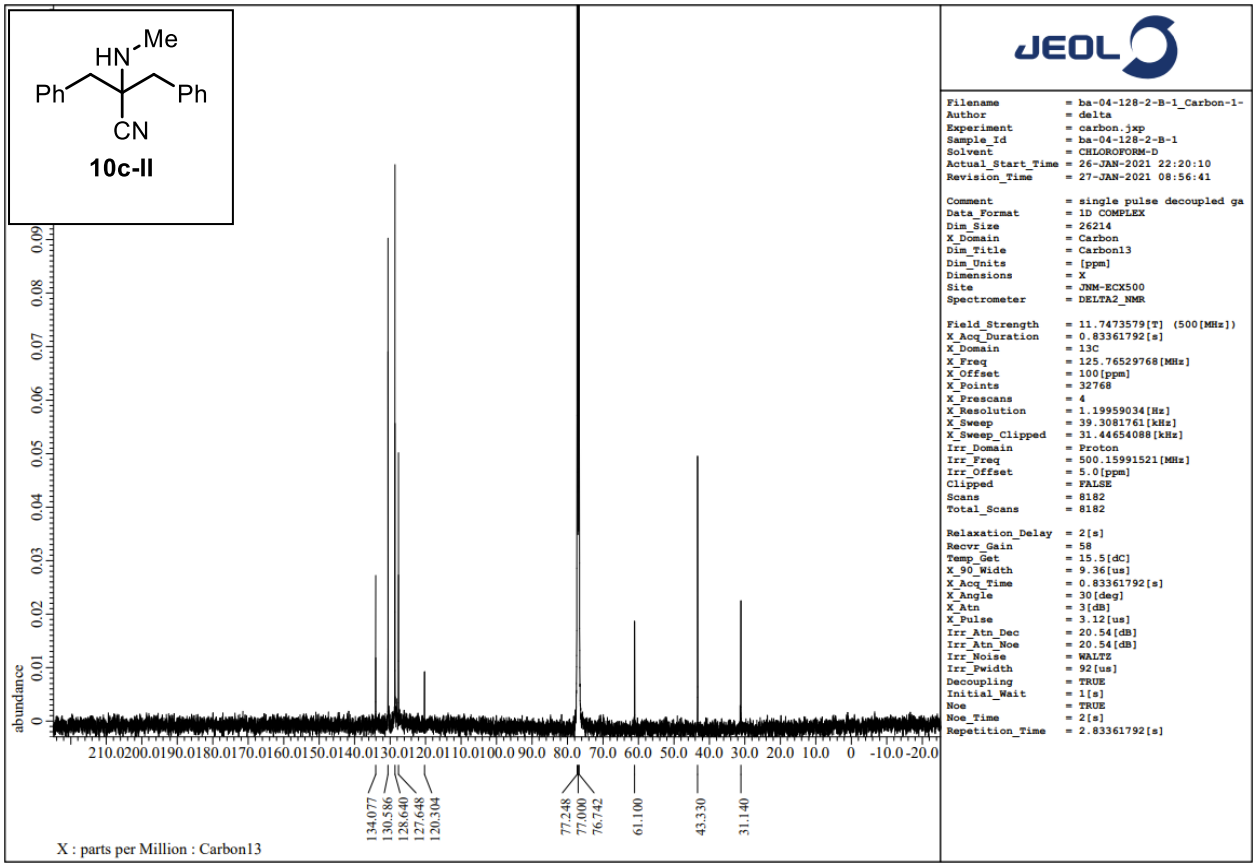
```
Filename          = ba-04-128-2-A-2_Carbon-1-
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = ba-04-128-2-A-2
Solvent           = CHLOROFORM-D
Actual_Start_Time = 27-JAN-2021 14:36:28
Revision_Time     = 27-JAN-2021 18:17:07

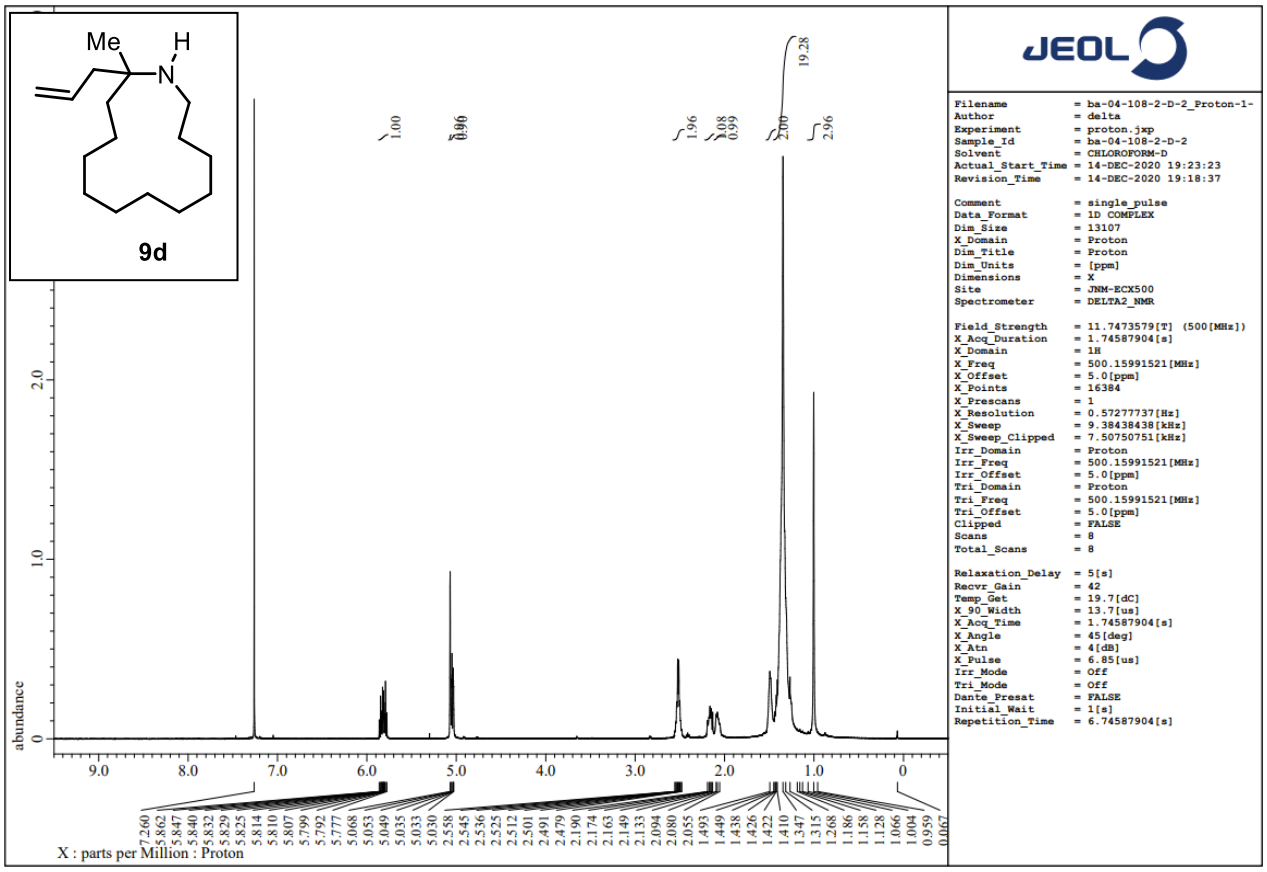
Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

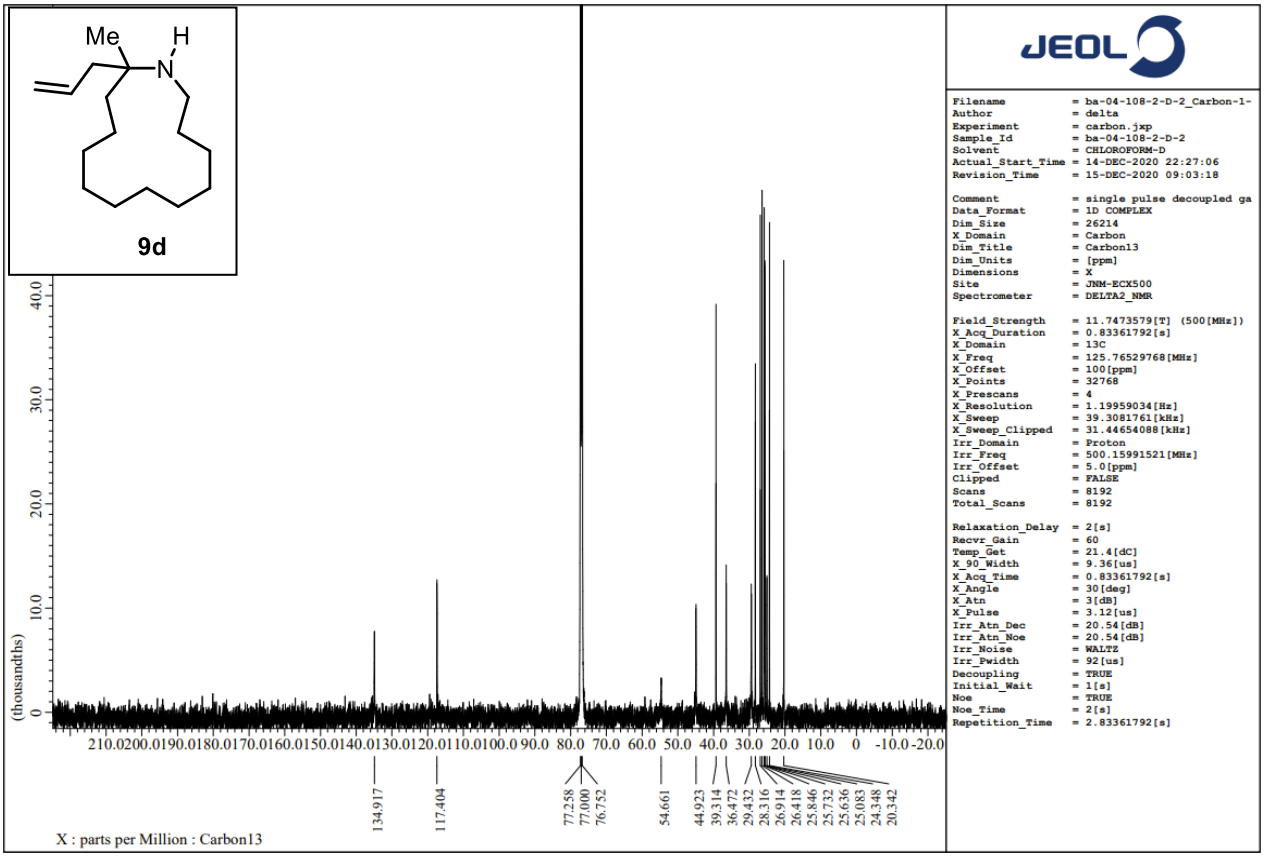
Field_Strength    = 11.7473579[T]  (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

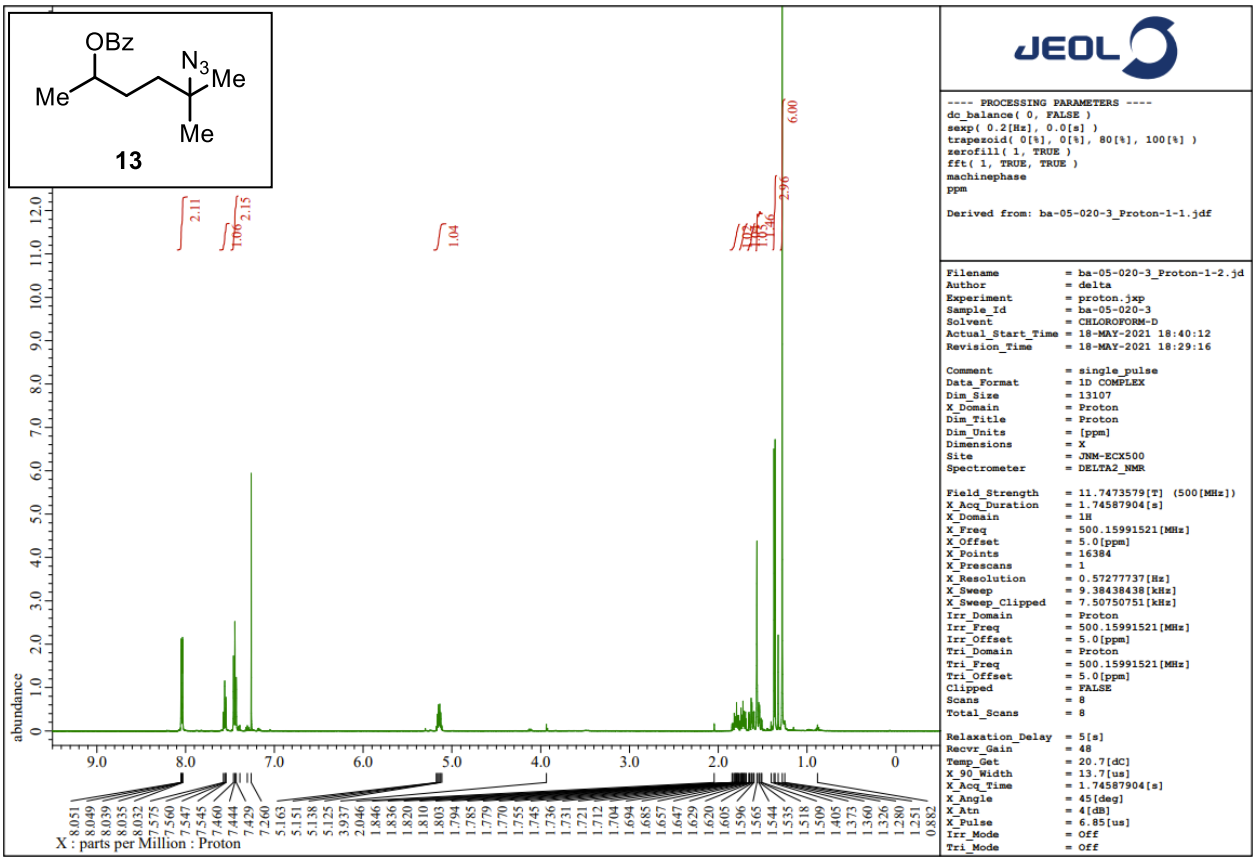
Relaxation_Delay  = 2[s]
Recvr_Gain        = 58
Temp_Get          = 15.3[dC]
X_90_Width        = 9.36[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 3[dB]
X_Pulse           = 3.12[us]
Irr_Atn_Dec       = 20.54[dB]
Irr_Atn_Noe       = 20.54[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```

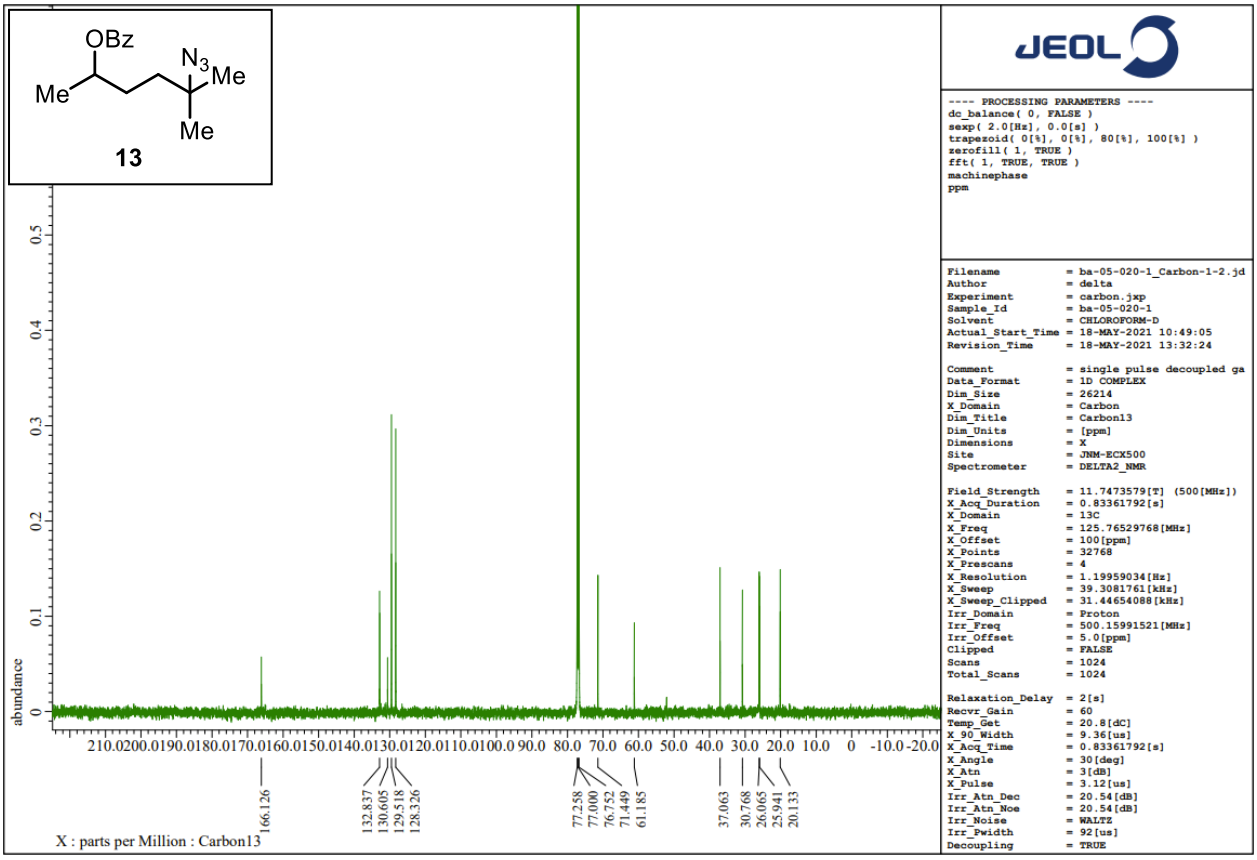

HN
Me
Ph
Ph
CN
10c-II
10.24
2.03
2.03
3.00
abundance
X : parts per Million : Proton
7.372
7.369
7.357
7.354
7.352
7.347
7.340
7.325
7.317
7.301
7.260
2.985
2.958
2.925
2.898
2.524
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = ba-04-128-2-B-1_Proton-1-
Author = delta
Experiment = proton.jxp
Sample_Id = ba-04-128-2-B-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 26-JAN-2021 22:03:46
Revision_Time = 8-MAR-2021 10:53:52
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 46
Temp_Get = 15.3[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off

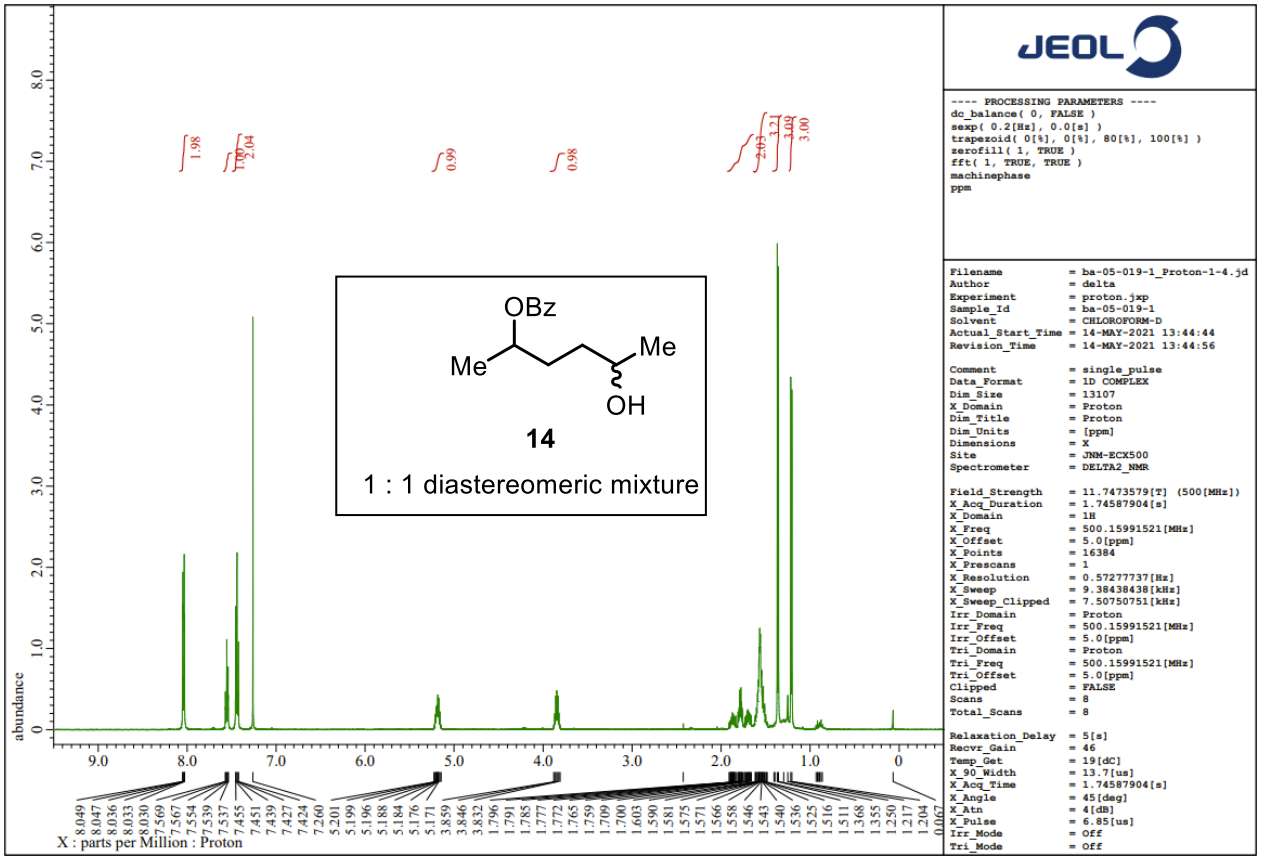

HN
Me
Ph
Ph
CN
10c-II
abundance
X : parts per Million : Carbon13
134.077
130.586
128.640
127.648
120.304
77.248
77.000
76.742
61.100
43.330
31.140
Filename = ba-04-128-2-B-1_Carbon-1-
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-04-128-2-B-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 26-JAN-2021 22:20:10
Revision_Time = 27-JAN-2021 08:56:41
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8182
Total_Scans = 8182
Relaxation_Delay = 2[s]
Recvr_Gain = 58
Temp_Get = 15.5[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]


Me
H
N
9d
abundance
X : parts per Million : Proton
Filename = ba-04-108-2-D-2_Proton-1-
Author = delta
Experiment = proton.jxp
Sample_Id = ba-04-108-2-D-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 14-DEC-2020 19:23:23
Revision_Time = 14-DEC-2020 19:18:37
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 42
Temp_Get = 19.7[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 6.74587904[s]


Me
H
N
9d
(thousandths)
X : parts per Million : Carbon13
Filename = ba-04-108-2-D-2_Carbon-1-
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-04-108-2-D-2
Solvent = CHLOROFORM-D
Actual_Start_Time = 14-DEC-2020 22:27:06
Revision_Time = 15-DEC-2020 09:03:18
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8192
Total_Scans = 8192
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.4[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]


OBz
Me
N3
Me
Me
13
abundance
X : parts per Million : Proton
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm
Derived from: ba-05-020-3_Proton-1-1.jdf
Filename = ba-05-020-3_Proton-1-2.jd
Author = delta
Experiment = proton.jxp
Sample_Id = ba-05-020-3
Solvent = CHLOROFORM-D
Actual_Start_Time = 18-MAY-2021 18:40:12
Revision_Time = 18-MAY-2021 18:29:16
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 1.74587904[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.57277737[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 48
Temp_Get = 20.7[dC]
X_90_Width = 13.7[us]
X_Acq_Time = 1.74587904[s]
X_Angle = 45[deg]
X_Atn = 4[dB]
X_Pulse = 6.85[us]
Irr_Mode = Off
Tri_Mode = Off


OBz
Me
N3
Me
Me
13
abundance
X : parts per Million : Carbon13
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm
Filename = ba-05-020-1_Carbon-1-2.jd
Author = delta
Experiment = carbon.jxp
Sample_Id = ba-05-020-1
Solvent = CHLOROFORM-D
Actual_Start_Time = 18-MAY-2021 10:49:05
Revision_Time = 18-MAY-2021 13:32:24
Comment = single pulse decoupled ga
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_Clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 20.8[dC]
X_90_Width = 9.36[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 3[dB]
X_Pulse = 3.12[us]
Irr_Atn_Dec = 20.54[dB]
Irr_Atn_Noe = 20.54[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE



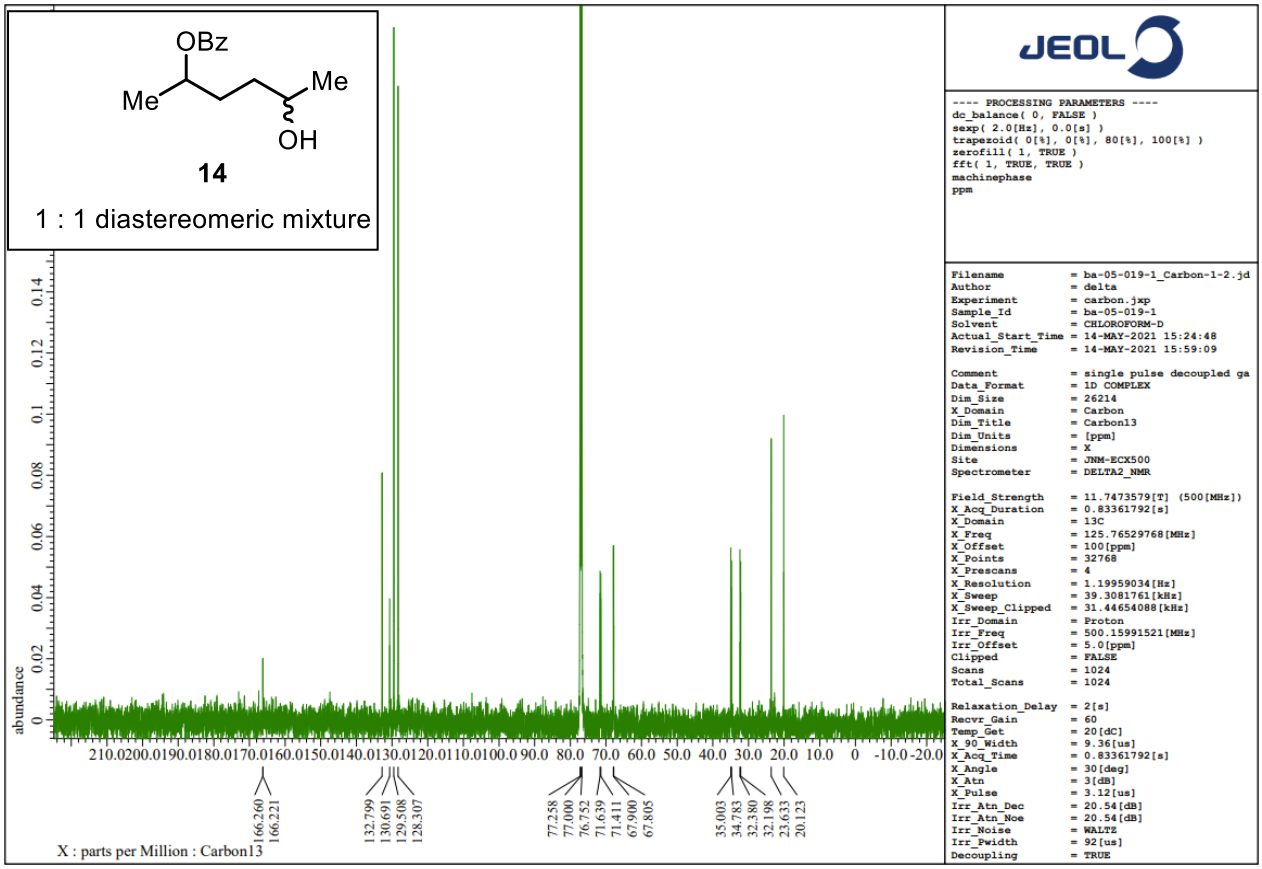

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

Filename            = ba-05-019-1_Proton-1-4.jd
Author              = delta
Experiment          = proton.jxp
Sample_Id           = ba-05-019-1
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 14-MAY-2021 13:44:44
Revision_Time       = 14-MAY-2021 13:44:56

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 1.74587904[s]
X_Domain            = 1H
X_Freq              = 500.15991521[MHz]
X_Offset            = 5.0[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.57277737[Hz]
X_Sweep             = 9.38438438[kHz]
X_Sweep_Clipped     = 7.50750751[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Tri_Domain          = Proton
Tri_Freq            = 500.15991521[MHz]
Tri_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 46
Temp_Get            = 19[dC]
X_90_Width          = 13.7[us]
X_Acq_Time          = 1.74587904[s]
X_Angle             = 45[deg]
X_Atn               = 4[dB]
X_Pulse             = 6.85[us]
Irr_Mode            = Off
Tri_Mode            = Off
```




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

Filename            = ba-05-019-1_Carbon-1-2.jd
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = ba-05-019-1
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 14-MAY-2021 15:24:48
Revision_Time       = 14-MAY-2021 15:59:09

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

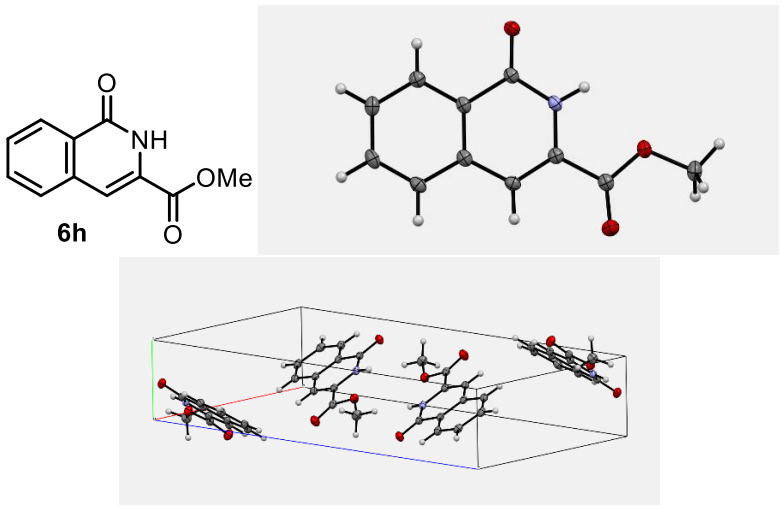
Field_Strength      = 11.7473579[T] (500[MHz])
X_Acq_Duration      = 0.83361792[s]
X_Domain            = 13C
X_Freq              = 125.76529768[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.19959034[Hz]
X_Sweep             = 39.3081761[kHz]
X_Sweep_Clipped     = 31.44654088[kHz]
Irr_Domain          = Proton
Irr_Freq            = 500.15991521[MHz]
Irr_Offset          = 5.0[ppm]
Clipped             = FALSE
Scans               = 1024
Total_Scans         = 1024

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 20[dC]
X_90_Width          = 9.36[us]
X_Acq_Time          = 0.83361792[s]
X_Angle             = 30[deg]
X_Atn               = 3[dB]
X_Pulse             = 3.12[us]
Irr_Atn_Dec         = 20.54[dB]
Irr_Atn_Noe         = 20.54[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 92[us]
Decoupling          = TRUE
```

X-ray Crystallographic Analysis Information

(ORTEP thermal ellipsoids at 50% probability)

6h (CCDC No. 2083663**)**



Empirical formula	$C_{11}H_9NO_3$
Formula weight	203.20
Temperature	-170.0 °C
Wavelength	MoKα (λ = 0.71075 Å)
Crystal system	monoclinic
Space group	$P2_1/n$ (#14)
Unit cell dimensions	a = 10.7867(4) Å
	b = 3.95279(13) Å β = 90.388(6)°
	c = 21.3580(7) Å
Volume	V = 910.63(5) Å^3
Z	4
Crystal size	0.300 × 0.080 × 0.070 mm
Density (calculated)	1.482 g/cm^3
F(000)	424.00
μ (Mo-Kα)	1.093 cm^{-1}
$2\theta_{max}$	55.0 °
No. of reflection collected	Total: 14163
	Unique: 2081 (R_{int} = 0.0349)
Transmission factor	min: 0.687, max: 0.992
Refinement method	Full-matrix least-squares on F^2
Goodness of fit indicator	1.090
Residuals [$I>2\sigma(I)$]	R_1 = 0.0431
Residuals (all reflections)	R = 0.0468 wR_2 = 0.1213
Max. and Min. in Final Diff. Map	0.66 and -0.25 e•Å^{-3}