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# Synthesis and Applications of Cyclobutenes

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# SYNTHESIS AND APPLICATIONS OF CYCLOBUTENES

by

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# SYNTHESIS AND APPLICATIONS OF CYCLOBUTENES

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Our group is interested in cyclobutene analogs of fatty acids as reactive coatings, potential antibiotics, and as a new class of bioconjugate linkers. A convenient synthesis of this class of molecules was previously reported from our lab. However, ammonia, a key reagent in the earlier route, was recently reclassified as a highly corrosive gas requiring highly specialized equipment for storage and handling. The goal of this research was to find a convenient synthesis for the formation of cyclobutene that did not involve the use of ammonia.

The other part of this thesis describes the preparation of a short chain cyclobutene fatty acid as a substrate for conjugation to an amino acid as part of a collaboration targeting the synthesis of proteins, which could be selectively modified using the cyclobutene/tetrazine "click" reaction.

ACKNOWLEDGMENTS

I would like to thank my advisor Dr. Dussault for all his help and guidance. I would not have made it this far without him. I would also like to thank my lab group for all the fun and advice for my chemistry. I would like to thank my friends from my church and for all their moral and emotional support, without them I don't think I would have been able to keep going all these years. I would like to thank my family for all their support and help through this chapter in my life. Finally, I would like to give credit to God for bringing me on this path and for giving me the ability to make it this far.

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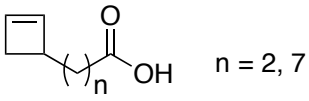
## Introduction

As described below, our group is interested in cyclobutene analogs of fatty acids as reactive coatings, potential antibiotics, and as a new class of bioconjugate linkers. The goal of my research project was to explore methods for the convenient synthesis of the cyclobutene fatty acid derivatives with varying chain lengths as shown in figure 1. Cyclobutenes are more much more reactive than a typical alkene and also was proven to be much more difficult to synthesize.

**Figure 1: Cyclobutene Fatty Acid Derivative**

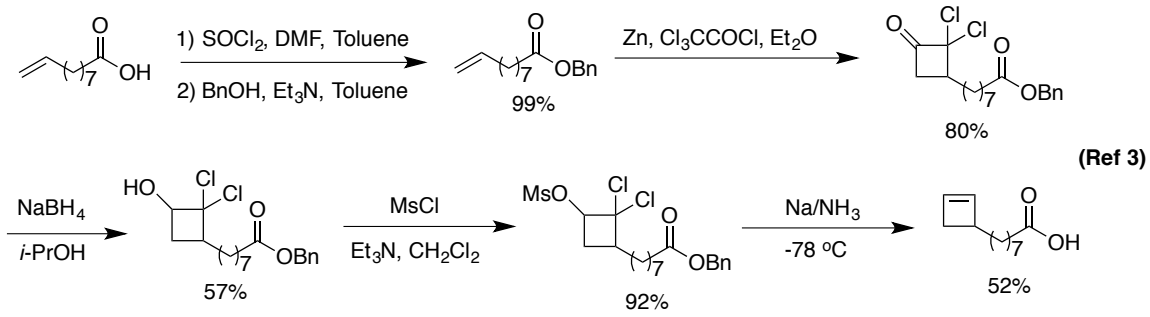



Cyclobutene has several useful applications that are currently being explored. Cyclobutene has been shown to be useful in bioorthogonal chemistry as a strained alkene capable of reacting selectively with tetrazine via an inverse-electron-demand Diels-Alder reaction[1]. Previous work done by Dr. Wantanee Sittiwong also showed that a variety of cyclobutene derivatives demonstrated inhibition of growth of *Mycobacterium tuberculosis*, the causative agent of human tuberculosis.[2] Finally the cyclobutene can potentially act as a polymerizable coating on surfaces or nanoparticles. [3-4]

Previous synthetic efforts towards amphiphilic cyclobutenes, performed by Dr. Wantanee Sittiwong, are summarized in Scheme 1.[3] The use of a reductive

fragmentation of dichlorocyclobutanol derivatives is based upon approaches previously reported by Greene[5] and Baldwin.[6]

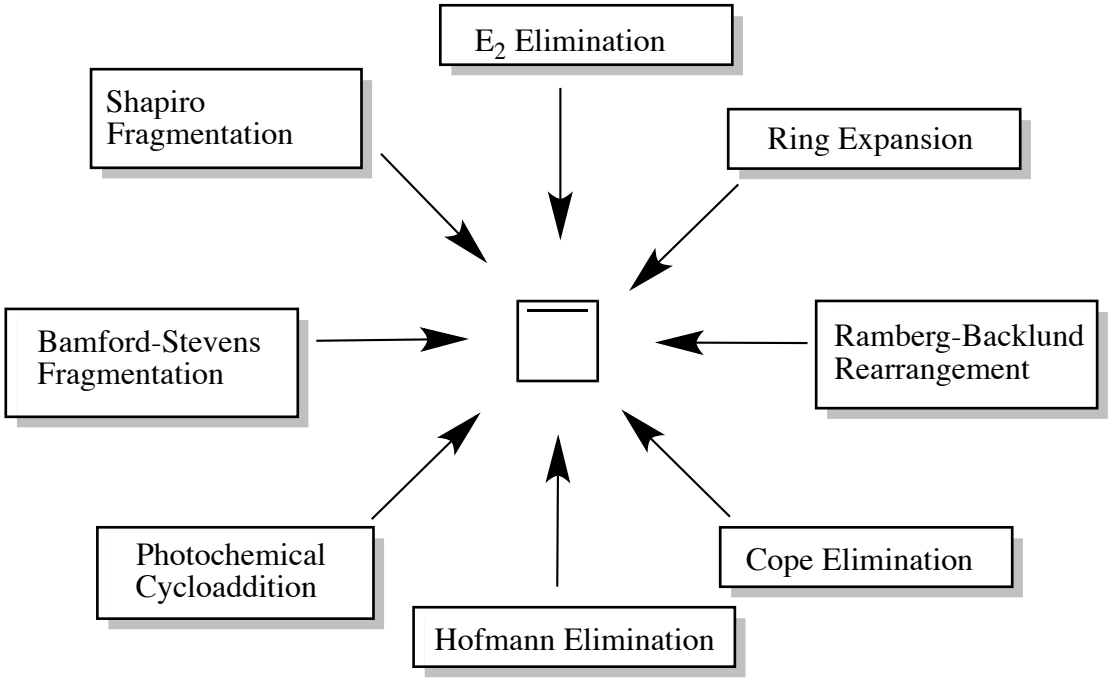
**Scheme 1: Previous Work Done by Dr. Wantanee Sittiwong[3]**




The problem with this otherwise efficient synthetic approach is the use of ammonia, a highly corrosive gas. The University of Nebraska-Lincoln Office of Environmental Health and Safety (EHS) recently reclassified ammonia as a class 2 corrosive gas that must be stored and dispensed from a specialized gas cabinet if used in amounts greater than that contained in a small lecture bottle.[7] Our department does not have such a cabinet, and we were concerned that our planned studies would require purchase, use, and disposal of large numbers of lecture bottles of ammonia that would have to be used, which could get very costly very quickly. As a result, we chose to investigate a new approach that was not dependent upon ammonia. Several synthetic approaches were proposed and are expanded on in part 1 and part 2 of this thesis.

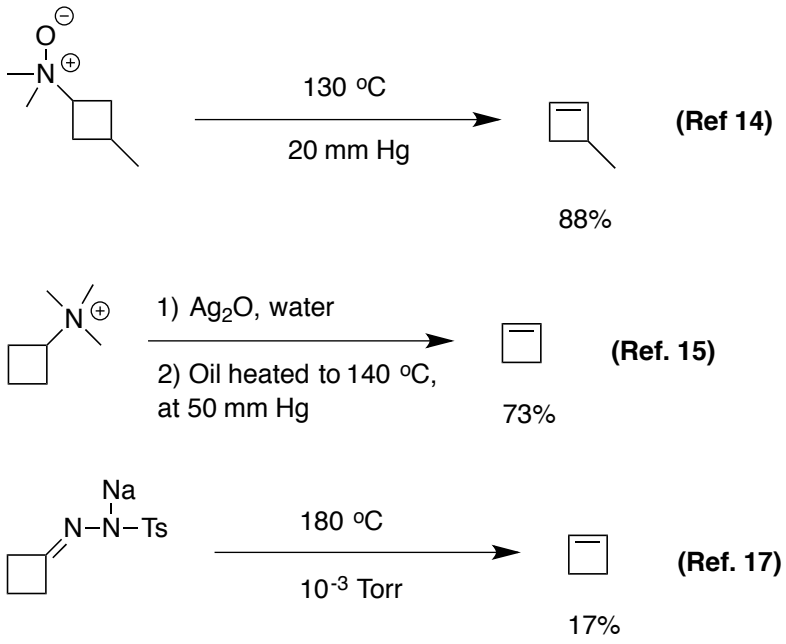
Many methods for the synthesis of cyclobutene have been reported; some of the major approaches are summarized in Figure 2.

**Figure 2: Summary of Previous Approaches to Cyclobutenes[8]**




Some of the first reported methods for synthesis of cyclobutenes involved the Cope and Hoffman eliminations as well as the Bamford Stevens. The Cope elimination often involves thermolysis of an N-Oxide under vacuum (for example 130 $^{o}$C at 20 mm Hg)[14] conditions that enable rapid removal of the cyclobutene product via distillation. In the Hofmann elimination, thermolysis of a quaternary ammonium hydroxide, typically generated by methylation of an amine followed by ion exchange with silver oxide, results in generation of cyclobutene under conditions that often achieve simultaneous distillation of the product from the reaction flask. The Bamford-Stevens reaction involves fragmentation of a ketone-derived hydrazone in the presence of strong base and high temperatures.

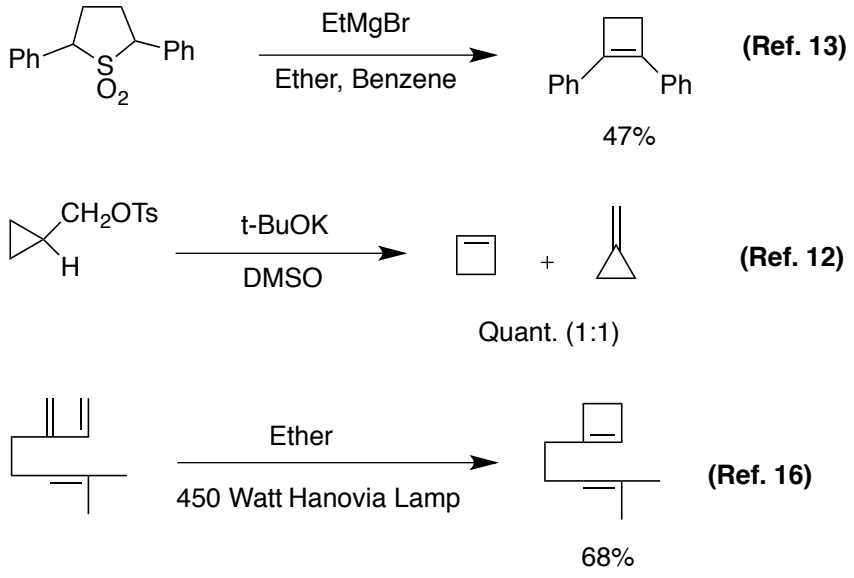
**Scheme 2: Cope Elimination, Hofmann Elimination, and Bamford Stevens Fragmentation**




Cyclobutenes can undergo ring-opening thermolysis at higher temperatures.[20] The reactions shown in Scheme 2 expose the cyclobutene products only briefly to higher temperatures. However, the class of substrates I was pursuing have a much greater molecular weight and might prove difficult to remove by distillation. As a result, we became interested in several reactions that did not involve exposure to high-temperature: the Ramburg-Backlund rearrangement, a cyclopropyl carbonyl ring expansion, and a photocycloaddition (Scheme 3). The Ramburg Backlund rearrangement utilizes an α-halo sulfone, which when treated with base, will eliminate HX to form a thiirane dioxide. In the presence of base, the thiirane dioxide decomposes to give the alkene and sulfur dioxide. The ring expansion involves reaction of cyclopropyl methyl tosylate with potassium tert-butoxide which gave the cyclobutene and methylenecyclopropane in a 1:1 ratio. It

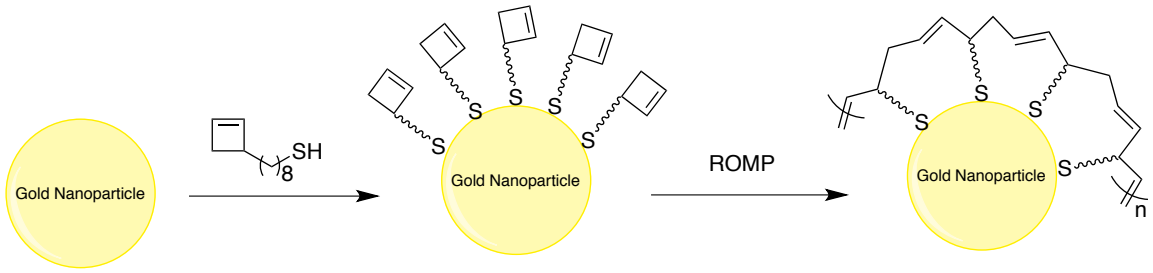
was theorized that the cyclobutene came from an equilibrium between the cyclopropyl methyl tosylate and the cyclopropylmethyl cation. The final reaction discussed in this section, photocycloaddition, involves prolonged irradiation of a terminal diene with a UV source.

**Scheme 3: Ramburg Backlund Rearrangement, Ring Expansion, Photolysis**




My goal was to find a convenient synthetic route to cyclobutene amphiphiles that did not involve ammonia, and to investigate the functionalized cyclobutenes as substrates for ring-opening metathesis polymerization (ROMP) to crosslink the monovalent amphiphile into a polymeric coating (Figure 3).

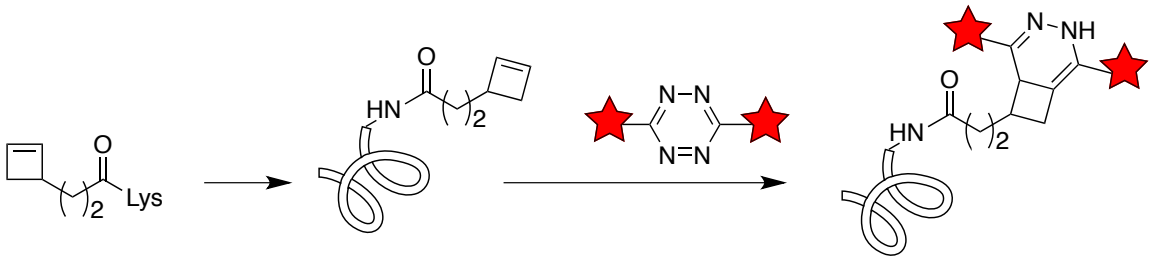
**Figure 3: Proposed Cyclobutene ROMP Around a Gold Nanoparticle**




Amphiphiles capable of multivalent attachment to a surface have been demonstrated to exhibit greater stability[21]. By doing ROMP with cyclobutene, a polymeric amphiphile with many anchoring chains could be made on the surface of a nanoparticle making an even more degradation resistant coating. At the same time allowing for incorporation of various other functional molecules by taking advantage of the ROMP, such as adding small amounts of alkenes or dienes with desired tags.[10] Work on this concept in the literature has been conducted using norbornene as the amphiphile in a ROMP as well as several examples of cross-metathesis using other compounds, but cyclobutene has not been explored.[4]

We were also interested in preparing a low-molecular weight cyclobutene carboxylic acid that could be incorporated into unnatural amino acids and thereafter proteins.[22] The presence of the cyclobutenes in the modified proteins would provide a "clickable" group possessing reactivity orthogonal to the better-known azide/alkyne systems.

**Figure 4: Cyclobutene Used as a Bioconjugate Linker**



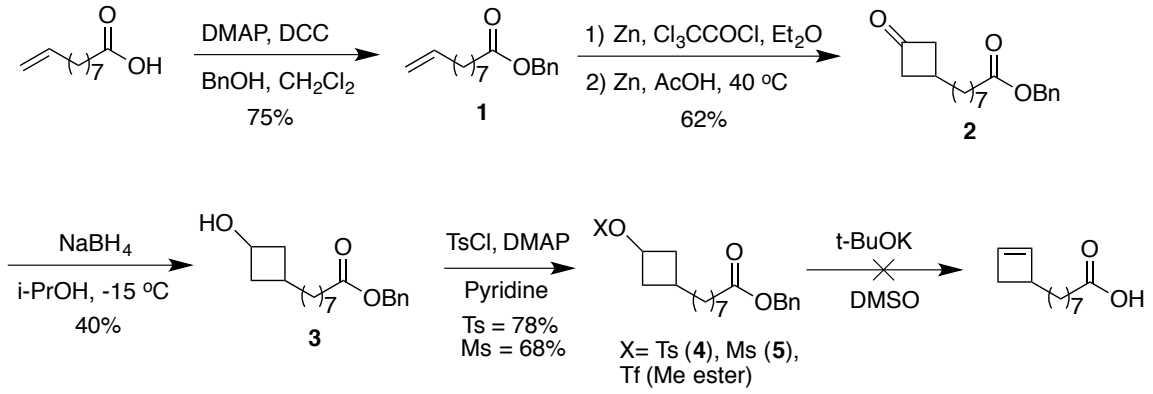

Once a cyclobutene fatty acid was formed, it could be reacted with lysine, incorporated into a protein, and potentially tagged using a tetrazine derivative.

## Part 1: Ester Synthesis

### Introduction

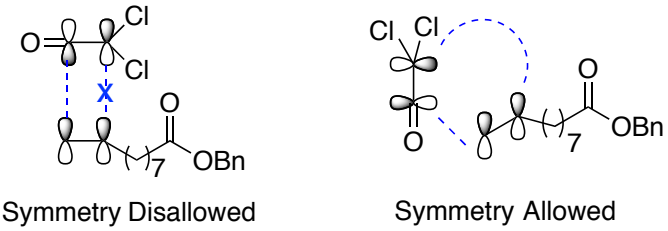
My first attempt is illustrated in Scheme 4. The initial portion of this synthesis is based upon research reported by Dr. Wantanee Sittiwong.[3]

**Scheme 4: Ester Synthesis**




Going from **1** to **2** this reaction undergoes a [2+2] cycloaddition. This can occur one of two modes: antarafacial or suprafacial

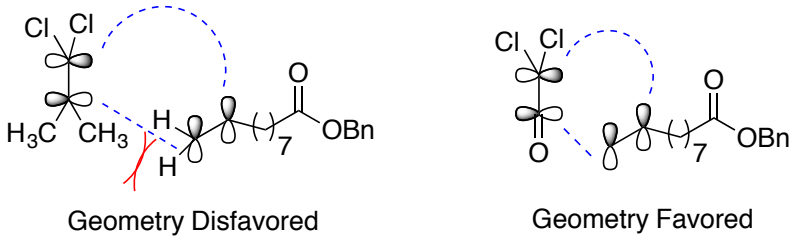
**Figure 5: Orbitals of a [2+2] Cycloaddition**




Symmetry Disallowed  Symmetry Allowed

For cycloadditon to occur there must be constructive overlap between the HOMO (highest occupied molecular orbital) of the alkene and the LUMO (lowest unoccupied molecular orbital) of the ketene. For a [2+2] cycloaddition, the alkene HOMO and ketene LUMO are out of phase, excluding the face-to-face approach required for suprafacial addition. However, an antarafacial approach of the ketene LUMO with the alkene HOMO does allow constructive overlap. In the Antarafacial, one of the orbitals points in the opposite direction of the other, so when the HOMO and LUMO come together, they will not overlap. In our [2+2] cycloaddition, a dichloroketene is formed during the reaction, which is what drives the reaction to the product. The dichloroketene does not have the correct orbital symmetry between its HOMO and LUMO for a suprafacial addition, so it undergoes an antarafacial addition as shown in Figure 4. Dichloroketene is used instead of a simple alkene because of its geometric restrictions as shown in Figure 6. Because of the sp hybridization on the ketene carbon, it does not possess as much steric bulk thus making the reaction more favorable.

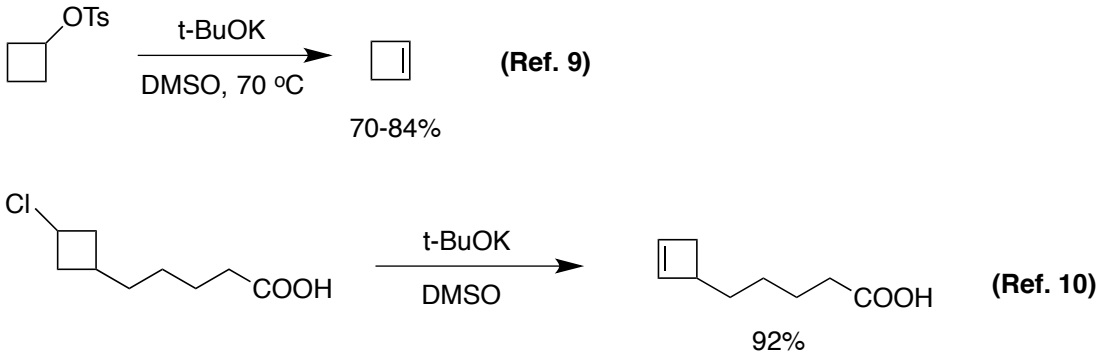
**Figure 6: Dichloroketene vs. Simple alkene**




Once the ring was formed, dechlorination was performed using zinc and acetic acid.[23]

We next investigated $E_2$-type eliminations. In the literature it was demonstrated that cyclobutene could be formed through elimination of a simple sulfonate or halide derivative (Scheme 5).[9] So after reducing the ketone, the alcohol could be converted to a tosylate, which according to the literature could be eliminated to form the desired cyclobutene. Related $E_2$ reactions in the literature reported elimination of a chloride[10] and a bromide.[11]

**Scheme 5: Examples of $E_2$ eliminations**



## Results

Because the dichlorocyclobutanone products of the ketene/alkene cycloaddition were often observed to be unstable to purification, they were often directly reduced to the cyclobutanol. This step was initially problematic. The obstacle encountered was the persistent presence of the monochlorocyclobutanone. It was finally discovered that the undesired formation of monocyclobutanone could be avoided by heating the crude cycloaddition reaction solution overnight at 40 $^{o}$C in the presence of 5-10 equivilents of additional zinc.

Another obstacle that was run into was the reduction with sodium borohydride. The reaction produced an impurity that was almost inseparable by column chromatography in various solvent systems. Instead the product was isolated with some of the impurity with the intention of using HPLC to attempt separation, but by accident it was discovered that the impurity could be removed by recrystallization in hexanes. Higher yields than the ones reported could be obtained if the crude mixture was simply recrystallized in hexanes. The tosylate reaction gave unusually low yields, which was why mesylate was also tried in its place. It was later found that the low yields were due to an unidentified impurity that was inseparable using column chromatography, but was almost identical to the desired product. It was accidently found that the impurity could be removed by recrystallization in hexanes. The identity of the impurity was never determined since we could not isolate it, but it appeared that something was happening to the benzyl ester as seen by NMR. Conversion to the methanesulfonate (mesylate) could be accomplished in good yields; lower yields were obtained for conversion to the toluenesulfonate

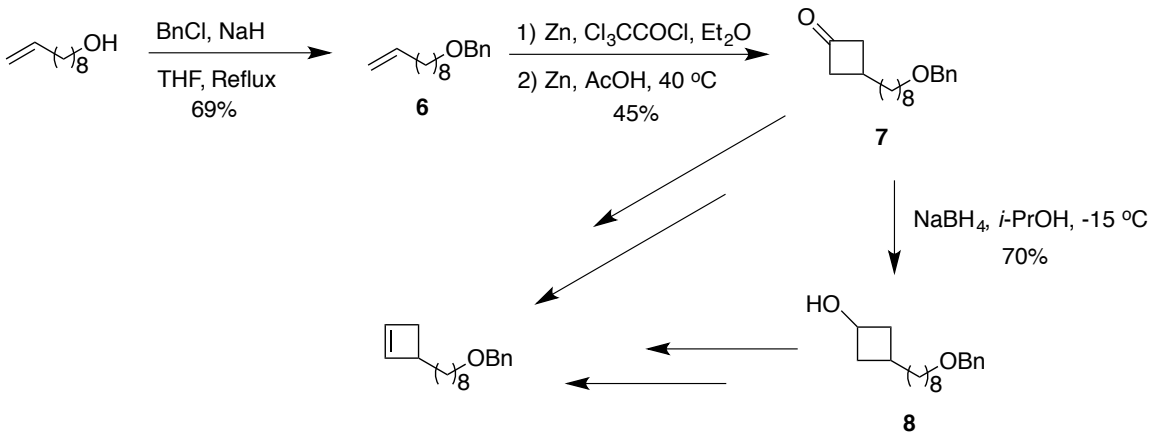
(tosylate). When treated with potassium tert-butoxide, the tosylate did not eliminate to the cyclobutene as shown in the literature[9] even when heated to high temperatures. When the mesylate was treated with the potassium tert-butoxide, it simply deprotected instead of eliminating. Finally a triflate was attempted on a methyl ester derivative, but resulted in ring opening of the cyclobutane ring as indicated by a terminal alkene in the NMR.

## Part 2: Ether Synthesis

### Introduction

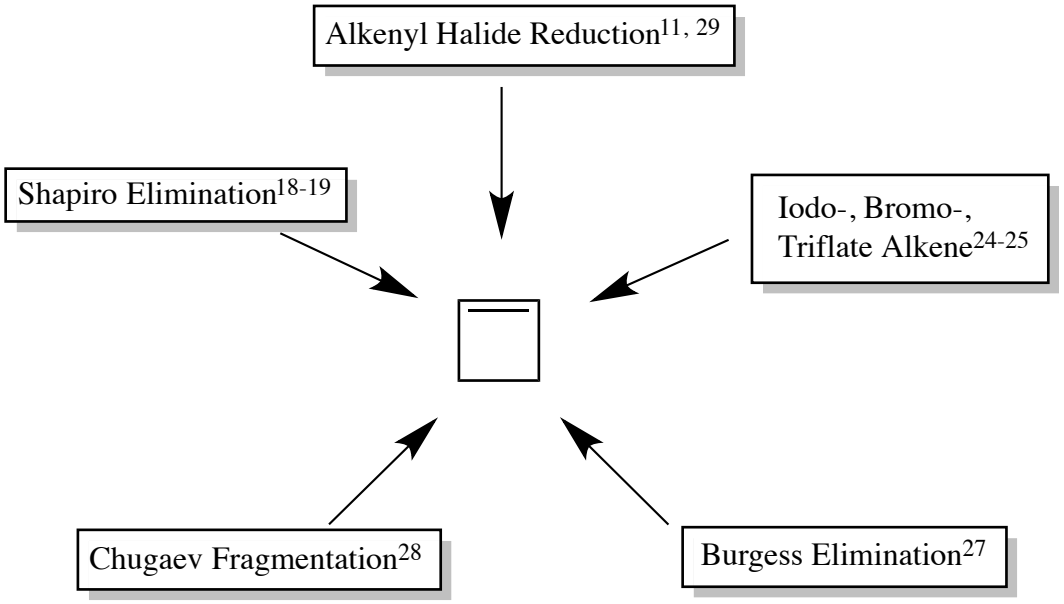
Some of the difficulties experienced during attempted synthesis of the cyclobutene-functionalized fatty acid ester were related to undesired side reactions of the carboxylate ester. As a result, we modified the synthetic approach so that the elimination reactions would be conducted on an ether rather than an ester (Scheme 4).

**Scheme 6: Ether Synthesis**



The cyclobutanone and cyclobutanol substrates were prepared as shown in Figure 6. At the ketone and alcohol, several promising reactions were looked into that took different approaches to the desired cyclobutene as shown in Scheme 6.

**Figure 7: Cyclobutene Synthesis Using Alcohol and Ketone**



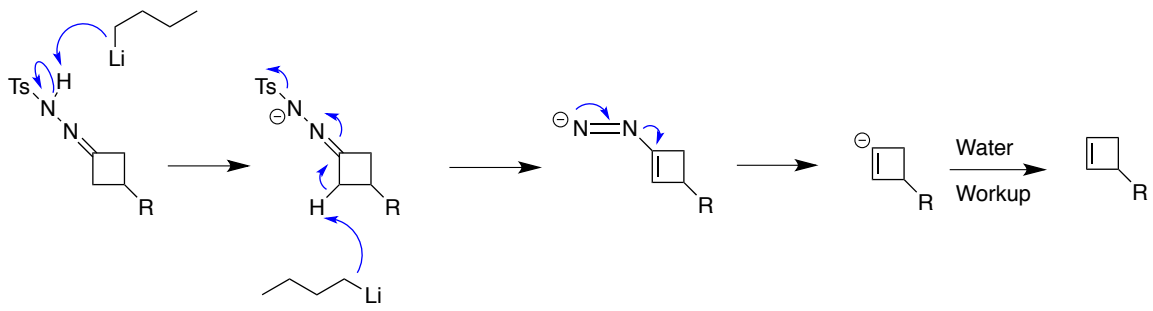

The first of these new approaches investigated conversions of the cyclobutanone to a cyclobutene via Shapiro fragmentation of sulfonyl hydrazones[18-19], or reduction of an iodo-[24], bromo-[25], or triflatealkene[26].

Elimination of cyclobutanones to cyclobutenes:

The first reaction we looked into was the Shapiro alkene synthesis. This reaction employs fragmentation of sulfonyl hydrazones in the presence of alkyl lithium bases; the mechanism is illustrated in figure 8. Upon exposure to a strong base such as alkyl lithiums, the tosyl hydrazone will decompose to form alkenes as

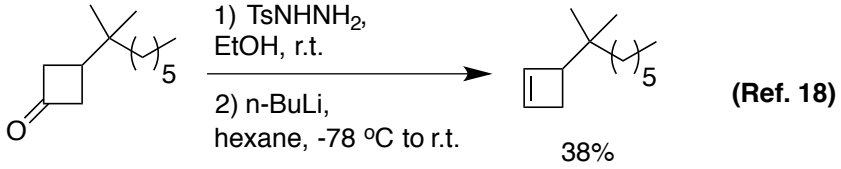
shown in figure 8. As described below, the Shapiro reaction has been previously used to establish cyclobutenes.

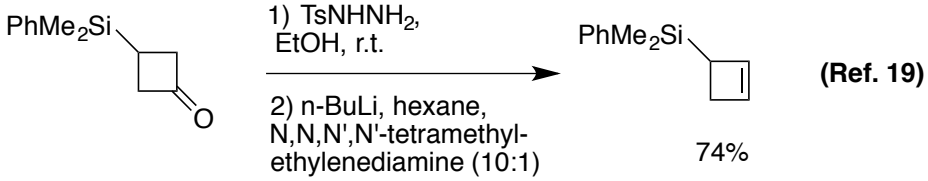
**Figure 8: Shapiro Mechanism**




Several literature examples describing the use of the Shapiro reaction to cyclobutene synthesis are summarized in the literature as shown in Scheme 7.

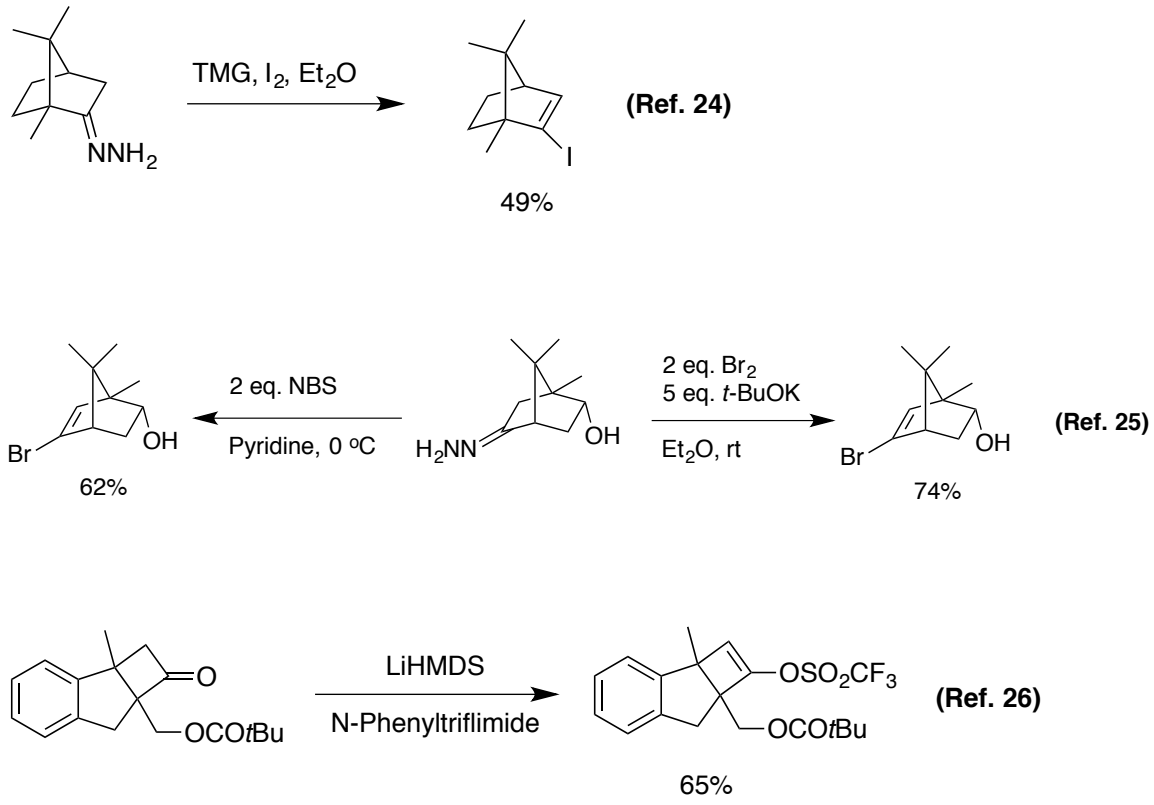
**Scheme 7: Examples of Cyclobutene Being Formed From Shapiro Reaction**




Fragmentation of simple hydrazones to form iodoalkenes or bromoalkenes as well as forming enol triflate alkenes from an enolate is also known, as illustrated in Scheme 8.

**Scheme 8: Iodoalkenes, Bromoalkenes, Enol Triflate Alkenes**

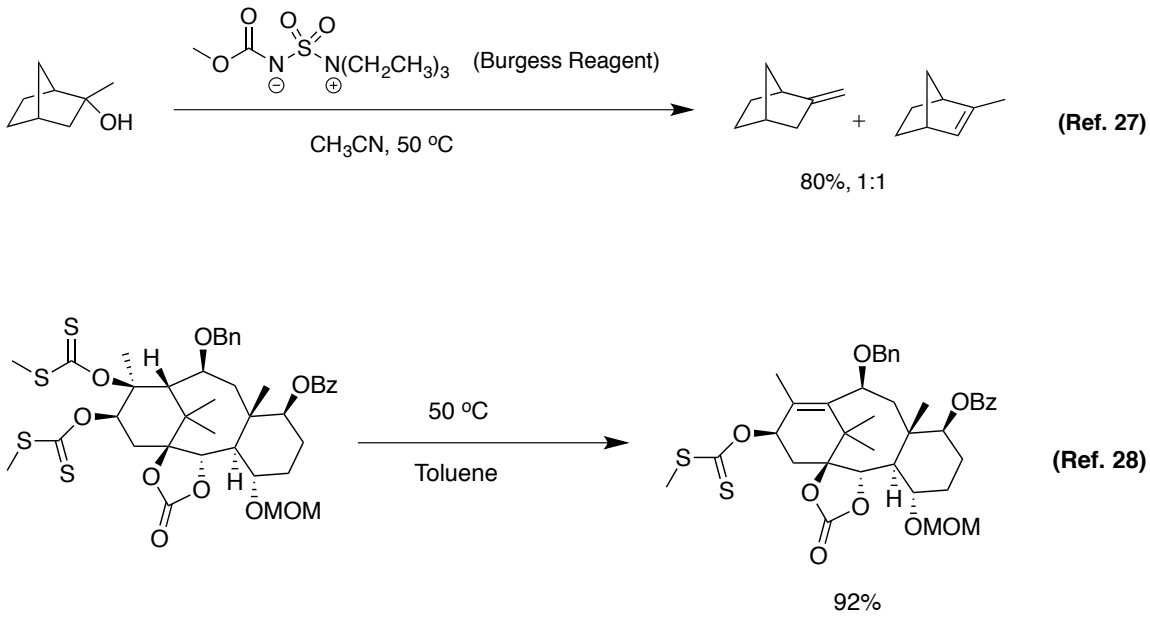



Their substrates were done on bicyclics, which we reasoned would be a good model for cyclobutene since they were also strained skeletons. It was our hope that the iodo-, bromocyclobutene, or the enol triflate could be converted to the alkene by metal halogen exchange.

Elimination of cyclobutanols to cyclobutenes:

We also explored several approaches to a substituted cyclobutene based upon the cyclobutanol: Chugaev fragmentation,[28] elimination with the Burgess reagent,[27] and $E_2$ reactions with different leaving groups such as bromine[11], and iodine[29]. Two interesting dehydrating agents that stood out were the Burgess[27] and the Chugaev[28]; literature examples involving these reagents are shown in Scheme 9.

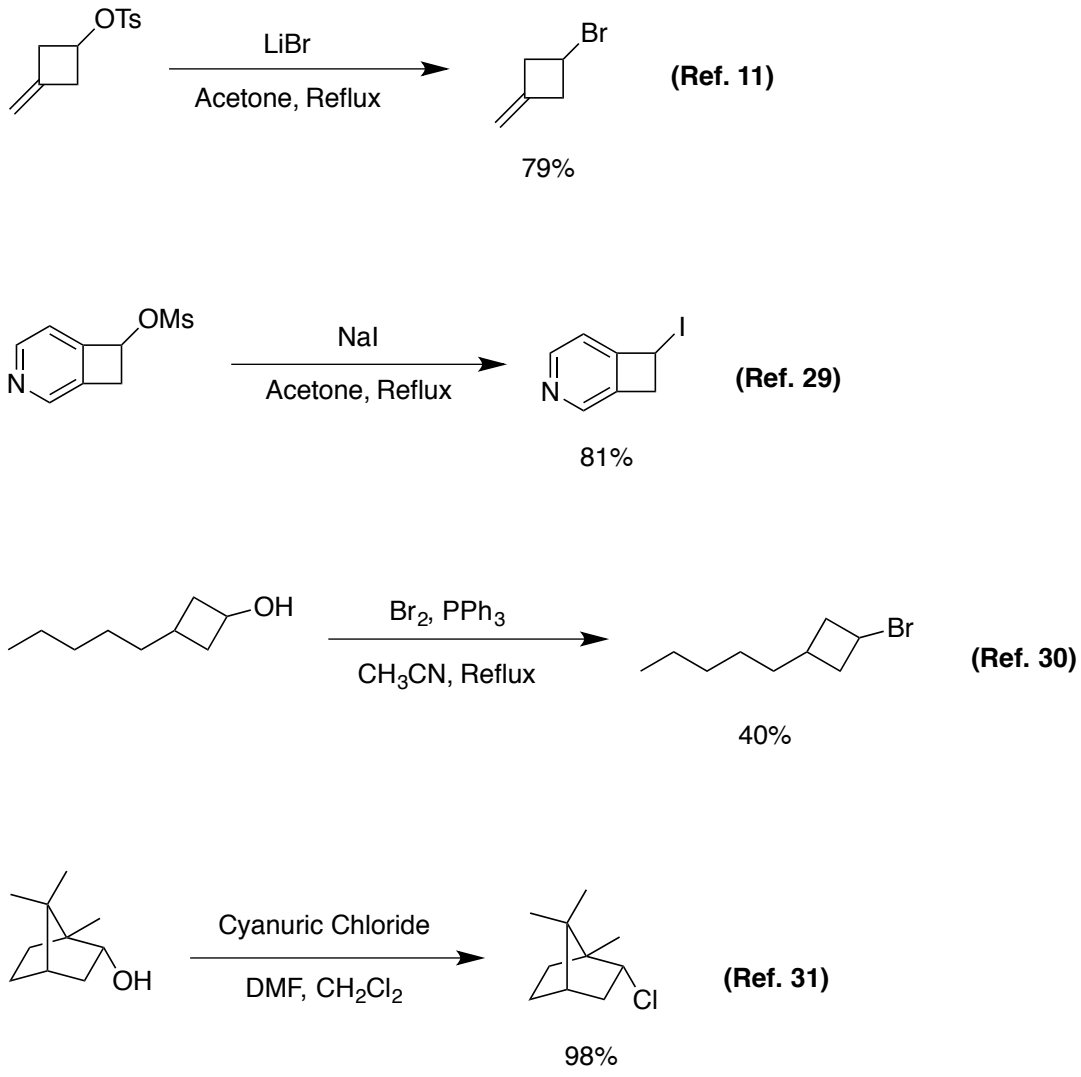
**Scheme 9: Burgess Elimination and Chugaev Fragmentation**




Most of the examples in the literature are run at over one hundred degrees Celsius which we thought was going to be a concern for our cyclobutene[20]. However the low temperature examples shown in Scheme 9 showed promise for our cyclobutene derivatives.

Finally we revisited the $E_2$ elimination with a focus on chloro-[31], bromo-[11,30], or iodocyclobutane[29] substrates. A number of literature reports suggested that direct preparation of these substrates could be accomplished (Scheme 10); however, as will be discussed, this set of transformations proved problematic.

**Scheme 10: $S_N2$ Substitutions on Cyclobutane Rings**



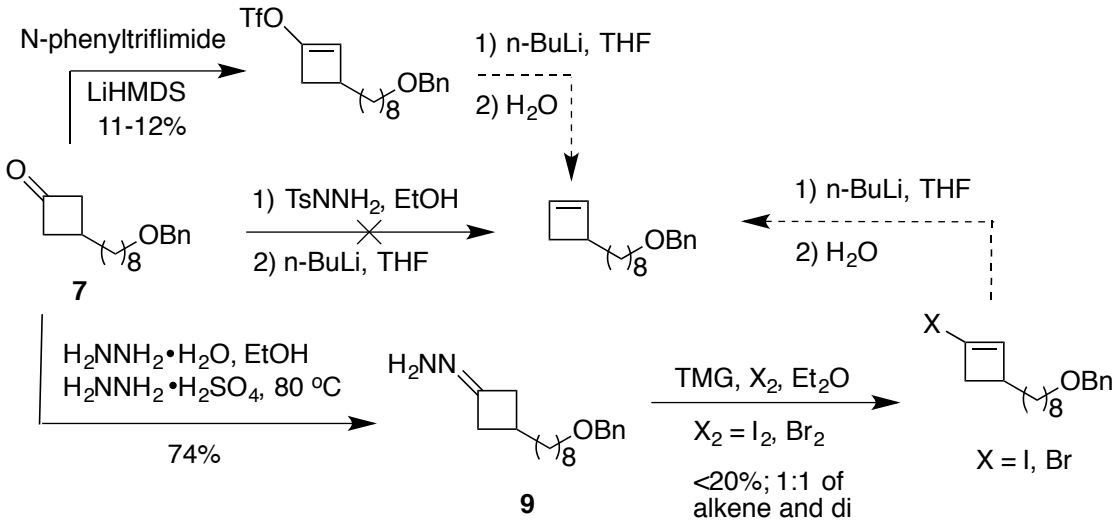

If we could access a halogen-substituted cyclobutane, it was hoped that we could achieve $E_2$ elimination using tert-butoxide in DMSO (Scheme 5). .

## Results

As stated above, the goal here was to reach either the cyclobutanone **7** or the cyclobutanol **8**. From either of these substrates, it was predicted based on the

literature that we could get to the cyclobutene. The first possibilities we focused on were based on the ketone as shown in Scheme 11.

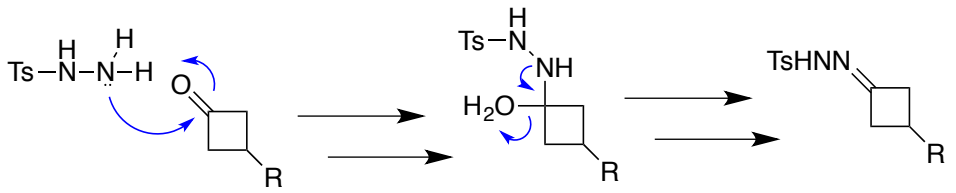
**Scheme 11: Different Approaches Based on Ketone**




The first approach from the ketone involved Shapiro fragmentation of an intermediate tosyl (toluenesulfonyl) hydrazone. This looked like a fairly simple reaction with high yields to the alkene. Since there were several examples of cyclobutenes being synthesized by this route[18-19], it seemed like a very promising route. Early attempts to prepare the precursor hydrazone looked slightly promising by TLC as one product seemed to stand out over several other byproducts. However, the $R_f$ of the major spot changed during purification by chromatography and I suspected that it was decomposing on the column. I therefore repeated the hydrazone formation in an NMR tube ($CD_3OD$), monitoring the progress of the reaction by NMR every ten minutes. The starting material was being consumed, but the patterns did not match what was expected for the desired product. Upon

comparing to the literature reports for tosyl hydrazones, it was confirmed that the desired product was not forming. We thought that the failure of this apparently simple reaction was related to the difficulty in losing water from the tetrahedral intermediate (Figure 9) and/or the possibility of some type of ring expansion involving cleavage of the N-N linkage.

**Figure 9: Mechanism for Formation of Sulfonyl Hydrazone**




The initial attack of the tosyl hydrazine onto the carbonyl should be fairly fast since it is helping to relieve the angle strain of the cyclobutanone. However, by the same rationale, the elimination of water to form the tosyl hydrazine requires reintroduction of the same strain. To overcome this possible barrier, we tried using an acid catalyst, heat, titanium chloride as a Lewis acid, and molecular sieves. All of these different methods yielded similar results, multiple by products with no trace of the desired product. After testing the reagents on several model compounds with successful results, it was determined that the reaction was not going to work on our cyclobutanone derivative.

The next reaction sequence we explored involved the attempted formation of an iodo- or bromoalkene (Scheme 11). Assuming we could generate these intermediates, it was our assumption that these could be reduced via formation and protonation of an intermediate organolithium. Synthesis of the haloalkene required

initial formation of an unsubstituted hydrazone from the cyclobutanone. Several attempts to form a hydrazone were tried, with the final attempt using hydrazine hydrate as the solvent with a small excess of hydrazine sulfate as the catalyst. Initial analysis by Thin Layer Chromatography suggested that product formation was successful but that a small amount of starting material remained. The use of a small amount of ethanol to act as an azeotrope to remove water was successfully used to drive the reaction to completion. Conversion to the alkenyl iodide was investigated in the presence of two different bases previously applied for this transformation used in the literature; triethyl amine and tetramethyl guanidine. Both gave similar results, providing between 10-20% of the iodoalkene and about the same amount of the 1,1- diiodocyclobutane (NMR). We thought perhaps the iodoalkene itself was not particularly stable, so instead we decided to try forming a bromocyclubutene using bromine and one of several different bases; tetramethyl guanidine, tert-butoxide, and pyridine. Once again, similar results were obtained, low yields of the bromoalkene accompanied by the 1,1-dibromide as a contaminant.

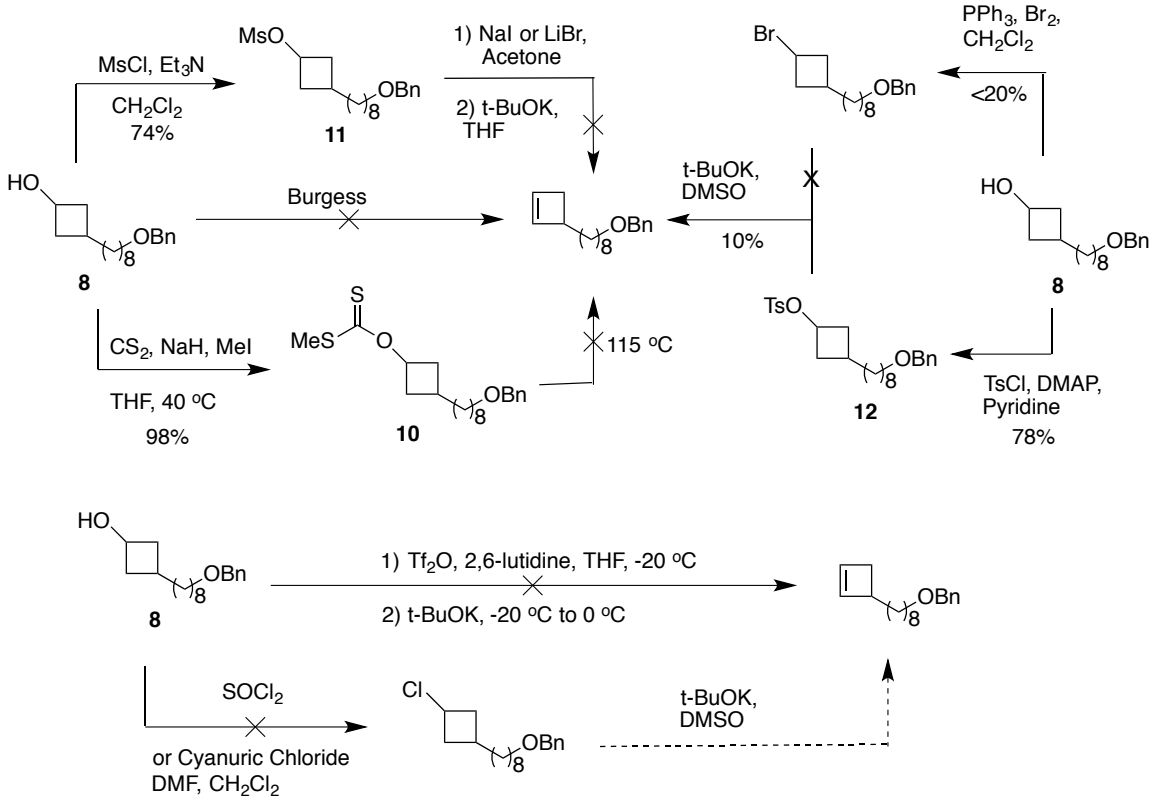
We also investigated the use of hydrazone **9** as a precursor for the tosyl hydrazone we had been unable to reach directly (Scheme 11). However, reaction of the hydrazone with tosyl chloride failed to give the desired product.

Finally the enol triflate was prepared from the cyclobutanone by room temperature deprotonation with lithium bis(trimethylsilyl)amide followed by addition of *N*-phenyl triflimide. The mass of the product after chromatography corresponded to about a 23% yield but the NMR spectra revealed about a 1:1 ratio

of a substituted arene byproduct. The reaction was also done at -78 °C, but only starting material was recovered.

After getting poor results with the ketone approaches, we decided to try some different approaches using the alcohol as shown in scheme 12.

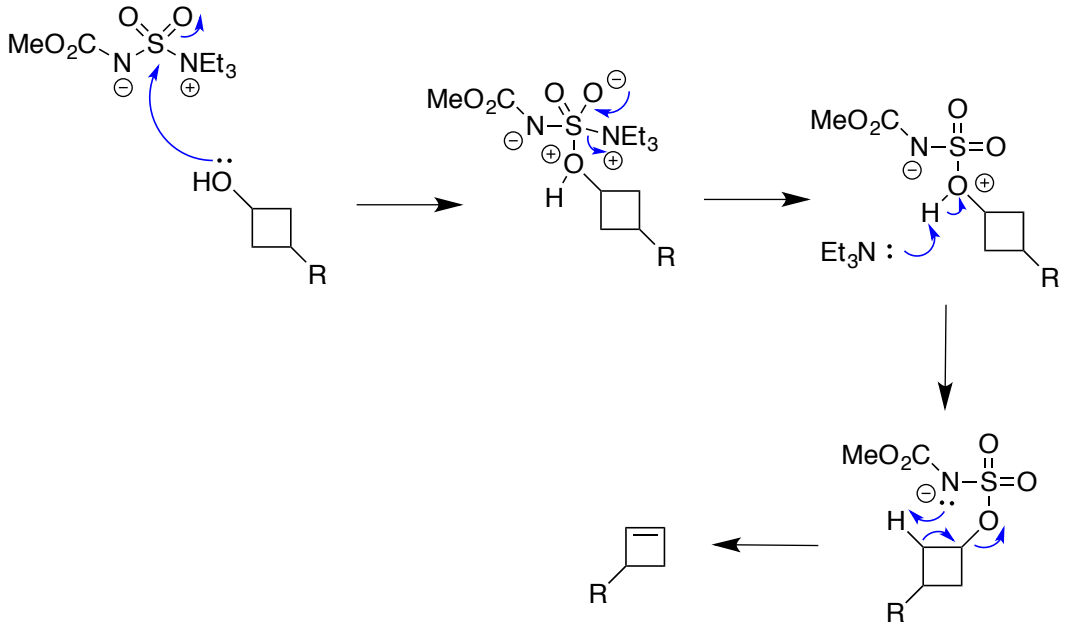
**Scheme 12: Different Approaches Based on Alcohol**




The first two approaches we investigated were the Chugaev rearrangement of the corresponding xanthate and the Burgess elimination. We were initially concerned that most examples of these reactions involved use of high temperatures. However, as described earlier, we also found examples of the use of both reactions at moderate temperature within strained scaffolds. The Burgess forms an

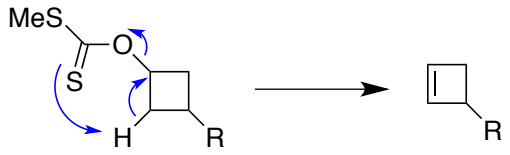
intermediate, which decomposes at higher temperatures to give the alkene as shown in figure 10.

**Figure 10: Burgess Mechanism**[32]




The Chugaev involves intramolecular elimination upon thermolysis of a xanthate derivate derived from an alcohol (figure 11)

**Figure 11: Chugaev Mechanism**[33]

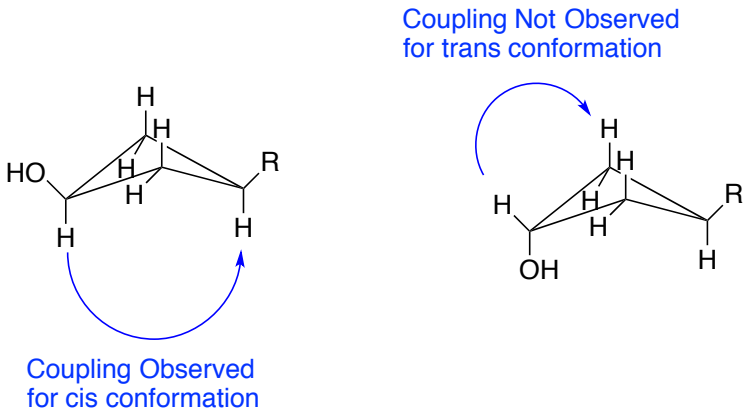



Based upon TLC monitoring, the elimination using the Burgess reagent appeared slow, but promising in terms of formation of a high $R_f$ product assumed to be cyclobutene. However, upon NMR analysis, it was revealed that no alkene was

present. Conversion of the alcohol to the xanthate ester (**13**) required for the Chugaev reaction was easily achieved. However, no reaction was observed upon heating to 100 $^{o}$C; heating to 115 $^{o}$C resulted in the formation of unidentified products which were not the desired cyclobutene.

Finally we went back to looking into a route to a cyclobutene based upon preparation of a chloro-, bromo-, or iodocyclobutane followed by $E_2$ elimination. Based on the structure of cyclobutane, it was suspected that the angles were not ideal for a substitution reaction as shown in figure 12. It was also shown by NOESY NMR that the1,3-disubstituted ring featured a cis relationship of the hydroxyl group and the alkyl chain (Figure 12). This could potentially explain why the tosyl would not eliminate as an $E_2$ requires that the leaving group and the proton be anti or pseudoaxial. In order to achieve axial, the ring would have to flip thus causing a costly 1,3 diaxial interaction. This would be even more costly once a tosyl group was put on making the elimination very difficult.

**Figure 12: Structure of Cyclobutane Ring Based on NOESY**



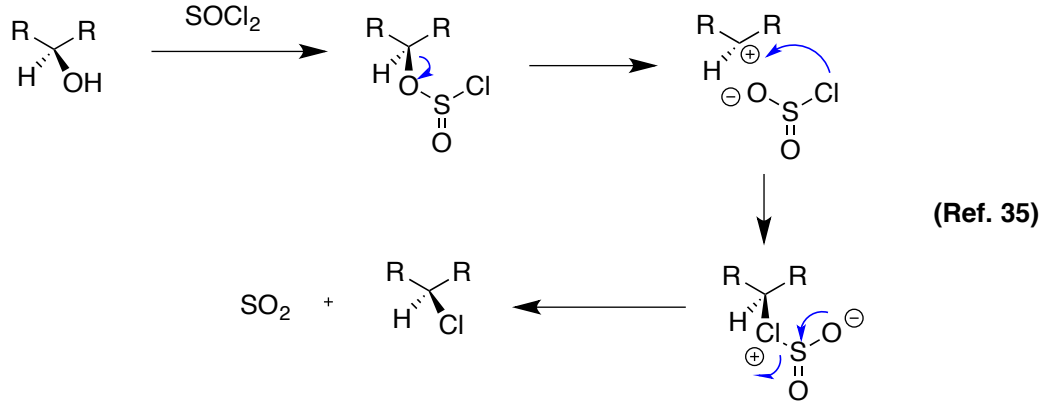
We attempted to prepare the iodo- or bromocyclobutene via a displacement reaction involving mesylate **14**. Reaction with NaI took place over a period of days and gave a low yield of what appeared to be the iodide product. As decomposition products were observed almost immediately, it was suspected that the product was decomposing under reaction conditions. So LiBr was attempted instead due to the stability issues involved with the iodine. The LiBr reaction took place over a week, but once again failed to give the desired substitution reaction.

Since the iodine seemed to be replacing the mesylate, we decided to attempt Appel substitution ($PPh_3/CBr_4$) on cyclobutanol **8**.[30] Very low yields of product were obtained using $CBr_4$; a faster reaction was observed in the presence of iodine, but the desired iodocylobutane was not isolated.

We had also tried doing a triflate at -20 $^oC$, then eliminate it by adding potassium tert-butoxide and warming it to 0 $^oC$. However, this reaction did not give any alkenes.

Next we tried to put a chlorine onto the ring by using thionyl chloride. When done without any base present, this reaction goes by an $S_Ni$ mechanism in which the nucleophile attacks the same side as the leaving group leaves thus retaining the stereochemistry. Since the $S_N2$ reactions did not seem to work due to the unfavorable angles (internal angles of $88^o$)[34], this sounded promising.

**Figure 13: $S_Ni$ Mechanism**




In the $S_Ni$ the key step is the formation of an intimate ion pair at which point the chlorine attacks as the sulfonyl leaves. As promising as this reaction looked, it did not work when applied to my compound. It seemed to give one product, but by NMR the cyclobutane seemed to have decomposed in the reaction.

Finally we returned to elimination of the toluenesulfonate (tosylate). Our previous failures with this elimination were complicated by the instability of a carboxylate ester and we were interested in attempting this reaction on a molecule possessing a more base-stabile ether. Forming the tosylate initially gave low yields until the addition of 4-dimethylaminopyridine, which gave high yields. The tosylcylobutane was subjected to tert-butoxide in DMSO dried sequentially over activated molecular sieves. This reaction gave a 10% yield of the desired cyclobutene.

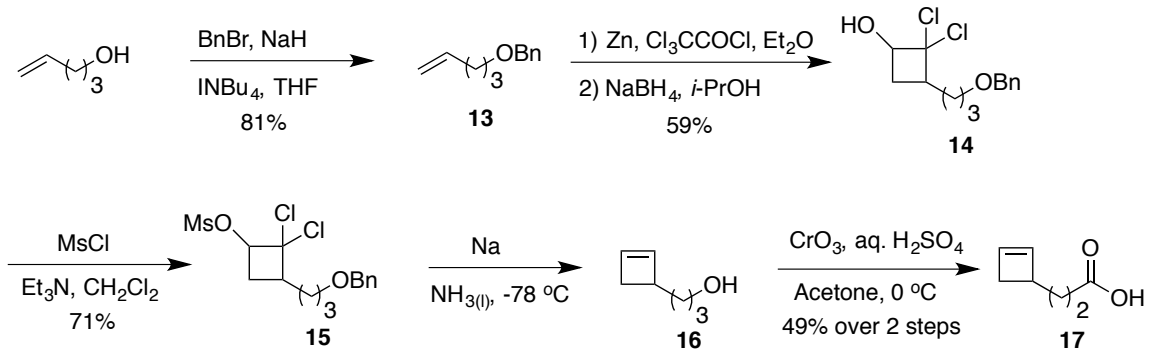
## Part 3: Short Chain Cyclobutene for Unnatural Amino Acids

### Introduction

The final goal of this research was to make an unnatural amino acid that could be incorporated into a protein (Figure 4). This work would be based on the ability to use codon reassignment or quadruplet codon decoding to allow unnatural amino acids to be biosynthetically incorporated into the genetic code.[36] Once the cyclobutene functional group was incorporated into a protein, various proteins can be screened to see if a tetrazine could tag the protein via a click reaction.

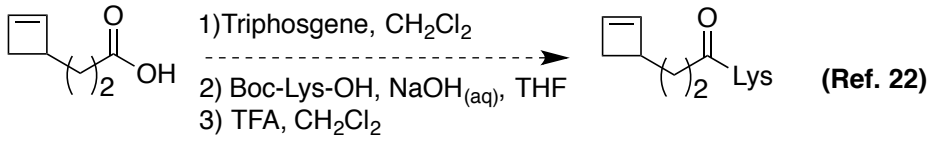
Our initial attempt to prepare a cyclobutene-substituted short chain acid (**17**, Scheme 13) pursued an approach similar to that pioneered by Dr. Sittiwong in longer-chain substrates (Scheme 1)[3] The route (not shown) was successful until the final step, a dissolving metal reduction to install the cyclobutene and deblock the benzyl ester. This reaction gave a mixture of products, none of which was the desired cyclobutenyl propanoic acid. We suspected that the reduction and cleavage of the dichlorocyclobutanyl mesylate occurred more rapidly than the reductive deblocking of the benzyl ester, and that the intermediate cyclobutenyl anion was rapidly attacking the nearby carbonyl to form a strained ketone. As a result, we pursued a modified route using a benzyl-protected alcohol as a precursor for the required carboxylic acid (Scheme 13).

**Scheme 13: Synthetic Approach of Short Chain Cyclobutene**




Once the short chain cyclobutene is synthesized, it will be given to Dr. Guo to incorporate it into a protein (Scheme 14).

**Scheme 14: Incorporation into an unnatural Amino Acid**




**(Ref. 22)**

## Results

Our synthesis of the short chain cyclobutene acid (Scheme 13) was initially complicated by a new bottle of trichloroacetyl chloride and new zinc. It was found that the new reagents did not run at room temperature like the previous older counterparts in forming **16**. It was determined that the 2+2 cycloaddition required refluxing in order for the reaction to take place. Different sources of trichloroacetyl chloride and were investigated. We also investigated activation of zinc[37], but had the same results. So a new approach was developed in order to safely do the reaction in order to avoid exotherms, which had frequently been a problem for us in running

this reaction with the new reagents. Another concern was the volatility of the cyclobutenyl propanoic acid and the alcohol precursor. In order to overcome this, a small amount was purified by column chromatography for the purpose of spectra and the rest of the crude was carried on to the next step. Once the carboxylic acid was formed, volatility was not as much of a concern, so the compound was purified by using acidified silica. This compound was then given to Dr Guo at the University of Nebraska-Lincoln for incorporation into a protein.

## Conclusion

In conclusion multiple routes to make cyclobutene amphiphiles while avoiding use of ammonia were attempted, however a useful alternate route was not found. Looking back on this work, I would have liked to try several more approaches had I had the time. One of these was based on figure 12. It was believed that because the substituents were cis, it could not get into the correct configuration for elimination. It would have been nice to explore other reducing agents to see if we could find one that would put the substituents in the trans, which was believed could have eliminated. We looked into this briefly by trying L-selectride, and $BH_3$. The L-selectride still gave all cis, but the $BH_3$ gave the cis and trans in a 3:1 ratio. It would have been interesting to at least take this mixture to the tosylate and try an $E_2$ or see if we could get it to do an $S_N2$.

Another reaction I would like to go back and look at was the Appel with $CBr_4$. When I did this reaction, I got around 20% yields. What bothered me at the time was the fact that the TLC showed consumption of starting material and only one spot

indicating to me a nearly quantitative yield. However, after columning, the yield was far less than I had expected based on the TLC. So I think that the product was decomposing on the silica.

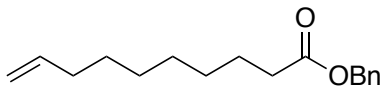
The final reaction I wanted to go back and look at again was eliminating the tosylcyclobutane ether derivative with tert-butoxide in DMSO. It was suspected that the DMSO available had absorbed enough water to cause problems in the reaction. NMR had been taken early in this work and showed no water present, but later it was suspected that water was present despite that evidence since the elimination was failing to give the desired cyclobutene. So the DMSO was dried sequentially over activated molecular sieves, then the reaction tried again providing a 10% yield of the desired cyclobutene. It was suspected that the yield could be improved if extra steps were taken to purify the DMSO. Once again due to lack of time, I was not able to go back and explore this reaction further.

## Experimental Section

All solvents and reagents were used as purchased, except for the THF, $CH_2Cl_2$, and diethyl ether, which were distilled from sodium/benzophenone, calcium hydride, and sodium/benzophenone respectively. In some cases activated zinc was used, but not in the reported methodology. Reaction flasks were equipped with magnetic stir bars, flame dried and flushed with nitrogen prior to use. All reactions were done under nitrogen and were followed by thin layer chromatography (TLC) done on .25 mm hard-layer silica plates. Plates were developed with a UV lamp or by staining in

a solutions of (ammonium molybdate tetrahydrate, ceric sulfate, 10% sulfuric acid), (potassium permanganate, water), and (vanillin, 200 proof ethanol, concentrated sulfuric acid). Plates were developed by heating. $^{1}H$ NMR and $^{13}C$ NMR were obtained from a broker advance 400 MHz NMR. $^{1}H$ NMR spin systems are reported as ppm (multiplicity, integration, J coupling when possible). Infrared spectra were done with neat films (diamond, ATR mode) with selected absorbances reported in wavenumbers ($cm^{-1}$).

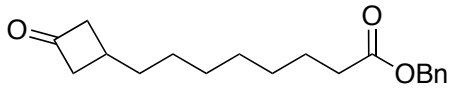
Abbriviations: tetrahydrofuran (THF), hexanes (Hex), ethyl acetate (EtOAc), diethyl ether (ether).




**1**

**Benzyl dec-9-enoate (1)** (Procedure BDE-6-32) To a room temperature solution of 9-decenoic acid (0.8682 g; 5.10 mmol) in methylene chloride (18 mL) was added DMAP (0.1578 g; 1.29 mmol), DCC (1.2974 g; 6.29 mmol), and benzyl alcohol (1.0840 g; 10.02 mmol). The suspension was stirred at room temperature over night. The reaction was filtered through sand and concentrated under reduced pressure. The residue was purified by silica flash column chromatography (1% EtOAc/hexane) to give benzyl dec-9-enoate (**1**, 1.0014 g, 75% yield) as a yellow liquid. $R_f$ in 10% EtOAc/Hex: (0.69). $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 1.311-1.390 (8H),

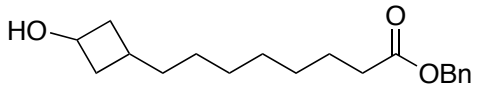
1.653 (p, 2H, J= 7.0 Hz), 2.040 (q, 2H, J= 7.0 Hz), 2.361 (t, 2H, J= 7.0 Hz), 4.937 (ddt, 1H, J= 10.2, 1.7, 1.0 Hz), 4.998 (ddt, 1H, J= 10.2, 1.7, 1.0 Hz), 5.017 (s, 2H), 5.811 (ddt, 1H, J= 17.2, 10.2, 6.7 Hz), 7.362 (5H). $^{13}$C NMR (400 MHz): δ 25.08, 28.97, 29.05, 29.20, 29.23, 33.90, 34.43, 66.16, 114.37, 128.27, 128.66, 136.34, 139.17, 173.67. Spectra matched those previously reported for this molecule.[3]




**2**

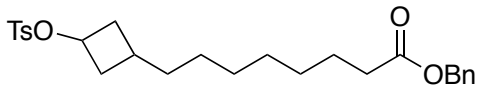
**Benzyl 8-(3-oxocyclobutyl)octanoate (2)** (Procedure BDE-6-37) To a room temperature solution of **2** (1.0014 g; 3.85 mmol), and Zn (1.2877g; 19.69 mmol) in dry ether (28 mL) was added a solution of trichloroacetyl chloride (2.1238 g; 11.68 mmol) dissolved in dry ether (11 mL) over 20 minutes. The suspension was stirred at room temperature for one hour, then acetic acid (12 mL) was added dropwise. More zinc (1.2821 g; 19.60 mmol) was added and the reaction stirred at 50 $^{o}$C over night. More zinc was added the next day (1.3356 g; 20.42 mmol) and once again it was stirred at 50 $^{o}$C over night. The reaction was then diluted with water (100 mL), extracted with EtOAc (3x100 mL), and washed with saturated sodium bicarbonate (200 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was purified by silica flash column chromatography (5% EtOAc/hexane) to give benzyl 8-(3-oxocyclobutyl)octanoate (**2**, .7224 g, 62% yield) as a clear oil. $R_f$ in 25% EtOAc/Hex: (0.63). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.316 (m, 8H), 1.566 (m, 2H), 1.654 (m, 2H), 2.322 (m, 1H), 2.364 (t,

2H, J= 7.6 Hz), 2.650 (m, 2H), 3.126 (m, 2H), 5.123 (s, 2H), 7.359 (5H). $^{13}$C NMR (400 MHz): δ 23.94, 25.00, 28.29, 29.14, 29.28, 29.31, 34.38, 36.42, 52.63, 66.17, 128.28, 128.65, 136.25, 173.69, 208.71. Spectra matched those previously reported for this molecule.[3]



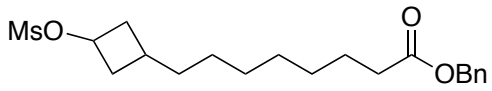

**3**

**Cis-Benzyl 8-(3-hydroxycyclobutyl)octanoate (3)** (Procedure BDE-7-75) To a solution of **2** (0.9001 g; 2.98 mmol) in isopropanol (43 mL) was added sodium borohydride (0.1780 g; 4.71 mmol) at -15 $^{o}$C. The suspension was stirred for 2.5 hours, then warmed to -10 $^{o}$C for 2 hours. The reaction was quenched with saturated sodium bicarbonate (50 mL), extracted with Hex (2x50 mL), then extracted with EtOAc(3x50 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was purified by silica flash column chromatography (15% EtOAc/hexane), then recrystallized in Hex (10 mL) to give Cis-benzyl 8-(3-hydroxycyclobutyl)octanoate (**3**, .3656 g, 40% yield) as a white powder (M.P. 32.5-33.0 $^{o}$C). $R_f$ in 25% EtOAc/Hex: (0.31). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.242-1.470 (12H), 1.585-1.642 (3H), 2.354 (t, 2H, J= 7.3 Hz), 2.445 (m, 2H), 4.089 (dt, 1H, J= 14.2, 6.9 Hz), 5.118 (s, 2H), 7.359 (5H). $^{13}$C NMR (400 MHz): δ 25.05, 25.55, 27.47, 29.19, 29.33, 29.43, 34.44, 37.19, 37.95, 40.00, 64.15, 66.18, 128.28, 128.66, 136.26, 173.80. Spectra matched those previously reported for this molecule.[3]



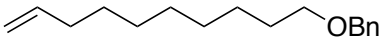

**4**

**Cis-Benzyl 8-(3-(tosyloxy)cyclobutyl)octanoate (4)** (Procedure BDE-7-85) To a room temperature solution of **3** (0.2034 g; .67 mmol) in dry pyridine (2 mL) was added DMAP (0.0159 g; .13 mmol), and tosyl chloride (0.1525 g; .80 mmol). The suspension was stirred at room temperature for 2 days. The reaction was quenched with water (5 mL), diluted with 1M HCl (10 mL), and then extracted with dichloromethane (4x30 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was purified by silica flash column chromatography (10% EtOAc/hexane) to give Cis-benzyl 8-(3-(tosyloxy)cyclobutyl)octanoate (**4**, 0.2377 g, 78% yield) as a clear oil. $R_f$ in 25% EtOAc/Hex: (0.64). $^1$H NMR (400 MHz, $CDCl_3$): δ 1.186-1.376 (12H), 1.617 (m, 2H), 1.719 (m, 2H), 2.328 (m 1H), 2.346 (t, 2H, J= 7.4 Hz) 2.455 (s, 3H), 4.641 (dt, 1H, J= 14.9, 7.6 Hz), 5.119 (s, 2H), 7.328-7.359 (7H), 7.787 (d, 2H, J= 8.4 Hz). $^{13}$C NMR (400 MHz): δ 21.76, 25.00, 26.83, 27.17, 29.13, 29.25, 29.29, 34.39, 36.78, 37.09, 66.18, 71.52, 127.92, 128.28, 128.66, 129.86, 134.29, 136.24, 144.67, 173.74. HRMS (ESI): calcd for $C_{26}H_{34}O_5S$ $(M+Na)^+$ 481.2025; found: 481.2032. IR: 2925, 2852, 1732, 1455, 1361, 1174, 1096, 1009, 913, 851, 814, 737, 696, 667.



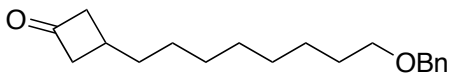

**5**

**Cis-Benzyl 8-(3-((methylsulfonyl)oxy)cyclobutyl)octanoate (5)** (Procedure BDE-7-84) To a room temperature solution of **3** (01989 g; .65 mmol) in methylene chloride (3 mL) was added mesyl chloride (0.1042 g; 1.0082 mmol). Triethyl amine (.1410 g; 1.39 mmol) was added dropwise at -78 $^{o}$C. The suspension was stirred for 10 minutes, then quenched slowly with water (5 mL) and warmed to room temperature. It was diluted with 1M HCl (5 mL) and extracted with dichloromethane (4x5 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was purified by silica flash column chromatography (15% EtOAc/hexane) to give Cis-benzyl 8-(3-((methylsulfonyl)oxy)cyclobutyl)octanoate (**5**, 0.1700 g, 68% yield) as a white solid (M.P. 25.0-26.0 $^{o}$C). $R_f$ in 25% EtOAc/Hex: (0.40). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.225-1.278 (8H), 1.430 (m, 2H), 1.639 (m, 2H), 1.818-1.882 (3H), 2.354 (t, 2H, J= 7.6 Hz), 2.562 (m, 2H), 2.966 (s, 3H), 4.826 (dt, 1H, J= 14.8, 7.4 Hz), 5.118 (s, 2H), 7.344-7.357 (5H). $^{13}$C NMR (400 MHz): δ 25.01, 26.78, 27.20, 29.14, 29.28, 29.32, 34.40, 36.87, 37.29, 38.41, 66.19, 71.23, 128.28, 128.66, 136.25, 173.75. HRMS (ESI): calcd for $C_{20}H_{30}O_5SNa$ $(M+Na)^+$ 405.1712; found: 405.1730. IR: 2916, 2848, 1737, 1343, 1330, 1172, 1112, 1015, 970, 912, 854, 786, 746, 727, 690.




**6**

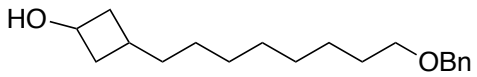
**Benzyloxy decene (6)** (Procedure BDE-6-46) To a room temperature solution of 9-decen-1-ol (0.1613 g; 1.03 mmol) in THF (1 mL) was added NaH (0.0514 g; 1.29 mmol; 60% in oil). The suspension was heated to reflux and stirred for 30 minutes, then benzyl chloride (0.1500 g; 1.19 mmol) was slowly added drop wise. After stirring over night, the reaction was quenched with water (5 mL), extracted with Hex (2x25 mL), then EtOAc (3x25 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was purified by silica column chromatography (1% EtOAc/hexane) to give ((dec-9-en-1-yloxy)methyl)benzene (**6**, 0.1758 g, 69%) as a yellow liquid. $R_f$ in 25% EtOAc/Hex: (0.87). $^1$H NMR (400 MHz, $CDCl_3$): δ 1.311-1.392 (10H), 1.633 (p, 2H, J= 7.0 Hz), 2.057 (q, 2H, J= 6.9 Hz), 3.483 (t, 2H, J= 6.0 Hz), 4.522 (s, 2H), 4.949 (d, 1H, J= 9.8 Hz), 5.012 (d, 1H, 16.8 Hz), 5.831 (ddt, 1H, J= 16.2, 10.4, 6.4 Hz), 7.291-7.365 (5H). $^{13}$C NMR (400 MHz): δ 26.34, 29.07, 29.23, 29.58, 29.93, 33.96, 70.65, 73.00, 114.28, 127.59, 127.74, 128.47, 138.88, 139.32. HRMS (EI): calcd for $C_{17}H_{26}O$ (M+) 246.1984; found: 246.1978. IR: 3076, 2924, 2852, 2360, 1640, 1495, 1453, 1361, 1307, 1203, 1099, 1027, 992, 907, 732, 695.




**7**

**3-(8-(benzyloxy)octyl)cyclobutan-1-one (7)** (Procedure BDE-6-71) To a room temperature solution of **6** (3.8940 g; 15.8 mmol) in dry ether (110 mL) was added

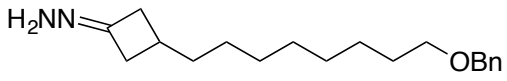
zinc (5.3167 g; 81.28 mmol). Trichloroacetyl chloride (8.74 g; 48.1 mmol) dissolved in ether (50 mL) was added slowly to the reaction over 20 minutes. After stirring for 1 h, acetic acid was added dropwise (50 mL) followed by more zinc (10.5101 g; 160.68 mmol). The reaction was heated to 40 $^{o}$C over night. It was diluted with water (100 mL) and then extracted with EtOAc (3x100mL). The combined organic extracts were washed with $NaHCO_3$ (200 mL), dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified by silica column chromatography (3% EtOAc/hexane) to give (**7**, 2.0486 g, 45%) as a slightly yellow liquid. $R_f$ in 25% EtOAc/Hex: (0.70) $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.318-1.371 (10H), 1.568-1.644 (4H), 2.351 (septet, 1H, J= 7.5 Hz), 2.659 (m, 2H), 3.132 (m, 2H), 3.477 (t, 2H, J= 6.6 Hz), 4.513 (s, 2H), 7.270-7.305 (5H). $^{13}$C NMR (400 MHz): δ 23.97, 26.30, 28.37, 29.48, 29.53, 29.63, 29.88, 36.47, 52.64, 70.60, 72.98, 127.58, 127.71, 138.83, 208.79. HRMS (EI): calcd for $C_{19}H_{28}O_2$ (M+) 288.2089; found: 288.2089. IR: 2922, 2851, 1780, 1495, 1453, 1385, 1361, 1204, 1096, 1027, 696, 611.




**8**

**Cis-3-(8-(benzyloxy)cyclobutan-1-ol (8)** (Procedure BDE-7-27) To a solution of **7** (1.1472 g; 3.98 mmol) in isopropanol (70 mL) was added $NaBH_4$ (.2269 g; 6.43 mmol) at -15 $^{o}$C. The suspension was stirred for 2.5 hours, and then quenched slowly with saturated sodium bicarbonate (100 mL). The mixture was extracted sequentially with Hex (3x100 mL) and then EtOAc (2x100 mL). The combined

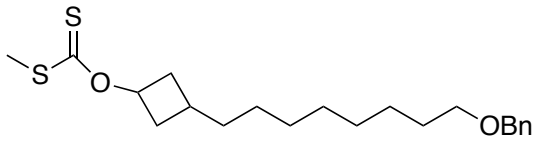
organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was purified by silica flash column chromatography (1% EtOAc/hexane) to give Cis-3-(8-(benzyloxy)cyclobutan-1-ol (**8**, 0.8064 g, 70%) as a yellow oil. $R_f$ in 25% EtOAc/Hex: (0.27) $^1$H NMR (400 MHz, $CDCl_3$): δ 1.270-1.461 (14H), 1.598-1.653 (4H), 2.016 (m, 1H), 2.450 (m, 2H), 3.470 (t, 2H, J= 6.6 Hz), 4.090 (sextet, 1H, J= 7.0 Hz), 4.510 (s, 2H), 7.343-7.353 (5H). $^{13}$C NMR (400 MHz): δ 25.59, 26.30, 27.55, 29.56, 29.60, 29.69, 29.88, 37.24, 39.99, 64.10, 70.64, 72.97, 127.73, 128.45, 138.83. HRMS (ESI): calcd for $C_{19}H_{30}O_2Na$ $(M+Na)^+$ 313.2144; found: 313.2136. IR: 3413, 3319, 2921, 2850, 1454, 1361, 1327, 1232, 1099, 1074, 1059, 1027, 732, 696, 606.




**9**

**(3-(8-(benzyloxy)octyl)cyclobutylidene)hydrazone (9)** (Procedure BDE-7-30) To a room temperature solution of hydrazine sulfate (0.0780 g; 0.60 mmol) in hydrazine hydrate (1.19 mL) was added **7** (0.1450 g; 0.50 mmol) and 200 proof ethanol (0.5 mL). The suspension was heated to 80 $^o$C and stirred overnight. The reaction was extracted with ether (3x5 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure to give benzyl (3-(8-(benzyloxy)octyl)cyclobutylidene)hydrazone (**9**, 0.1119 g, 74% yield) as a clear oil. $R_f$ in EtOAc (0.17) $^1$H NMR (400 MHz, $CDCl_3$): δ 1.284-1.359 (10H), 1.490 (m, 2H), 1.608 (m, 2H), 2.305 (m, 2H), 2.465 (m, 1H), 2.860 (m, 2H), 3.468 (t, 2H, J=

7.6 Hz), 4.505 (s, 2H), 7.337-7.347 (5H). $^{13}$C NMR (400 MHz): δ 26.30, 27.67, 28.04, 29.53, 29.65, 29.88, 35.76, 36.56, 39.57, 70.61, 72.97, 127.57, 127.72, 128.45, 138.83, 151.79. Compound decomposed in a few hours, so mass spec was not taken. IR: 2922.18, 2850.32, 2358.43, 1681, 1495.52, 1453.63, 1405.42, 1361.50, 1098.76, 1027.63, 803.76, 733.36, 696.23, 669.12.

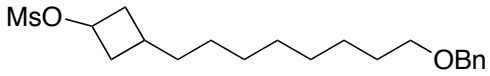



**10**

**Cis-O-(3-(8-(benzyloxy)octyl)cyclobutyl) S-methyl carbonodithioate (10)**

(Procedure BDE-7-32) To a solution of NaH (0.0885 g; 2.21 mmol; 60% in oil) in dry THF (17 mL) was added **8** (0.2769 g; 0.95 mmol) at 0 $^{o}$C. The suspension was warmed to room temperature and stirred for 30 minutes. Carbon disulfide (0.28 g; 3.73 mmol) was added at 0 $^{o}$C. The reaction was stirred at room temperature for 1.5 hours and then methyl iodide (1.14 g; 8.03 mmol) was added. The reaction was stirred over night. The reaction was slowly quenched with water (15 mL). The resulting mixture was extracted with Hex (2x25 mL) and then EtOAc (2x25 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was purified by silica flash column chromatography (1% EtOAc/hexane) to give Cis-O-(3-(8-(benzyloxy)octyl)cyclobutyl) S-methyl carbonodithioate (**10**, 0.3546 g, 98% yield) as a yellow liquid.

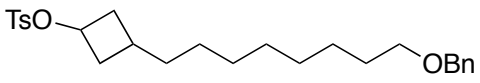
$R_f$ in 25% EtOAc/Hex: (0.71) $^1$H NMR (400 MHz, $CDCl_3$): δ1.266-1.447 (m, 10H, additional hydrocarbon. Potentially grease[38]), 1.607 (m, 2H), 1.790 (m, 2H), 1.865 (m, 1H), 2.548 (s, 3H), 2.619 (m, 2H), 3.467 (t, 2H, J= 6.8 Hz), 4.507 (s, 2H), 5.402 (p, 1H, J= 7.5 Hz), 7.339 (5H). $^{13}$C NMR (400 MHz): δ 19.15, 26.31, 27.34, 29.55, 29.67, 29.89, 34.70, 36.48, 37.12, 70.63, 72.98, 74.69, 127.58, 127.73, 128.46, 138.85, 214.49. HRMS (ESI): calcd for $C_{21}H_{32}O_2S_2Na$ $(M+Na)^+$ 403.1742; Found: 403.1746. IR: 2922.53, 2851.12, 1453.67, 1239.54, 1213.05, 1074.92, 907.38, 730.58, 696.15.




**11**

**Cis-3-(8-(benzyloxy)octylcyclobutyl methanesulfonate (11)** (Procedure BDE-7-46) To a room temperature solution of **8** (0.6181 g; 2.13 mmol) in dry dichloromethane (11 mL) was added methanesulfonyl chloride (0.3552 g; 3.10 mmol). Triethylamine (0.3630 g; 3.59 mmol) was added dropwise at -78 $^o$C. After stirring for 10 minutes, the reaction was quenched by slowly adding water (5 mL) and then allowing the mixture to warm to room temperature. The mixture was diluted with 1M HCl (15 mL) and then extracted with dichloromethane (3x15 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was purified by silica column chromatography (15% EtOAc/hexane) to give Cis-3-(8-(benzyloxy)octylcyclobutyl methanesulfonate (**11**, 0.5769 g, 74%) as a white solid (M.P. 24.0-25.0 $^o$C). $R_f$ in 25% EtOAc/Hex: (0.39) $^1$H NMR (400 MHz, $CDCl_3$): δ 1.275-1.466 (12H), 1.609 (p, 2H, J= 7.2 Hz), 2.563 (m, 2H),

2.970 (s, 3H), 3.470 (t, 2H, J= 6.3 Hz), 4.510 (s, 2H), 4.832 (m, 1H,), 7.342-7.353 (5H). $^{13}$C NMR (400 MHz): δ 26.29, 26.80, 27.27, 29.48, 29.52, 29.62, 29.88, 36.91, 37.30, 38.41, 70.62, 71.26, 72.98, 127.59, 127.73, 128.46, 138.83. HRMS (EI): calcd for $C_{20}H_{32}O_4S$ (M+) 368.2022; found 368.2010. IR: 2921, 2849, 1452, 1333, 1126, 1117, 1105, 1024, 1008, 968, 918, 856, 737, 696.

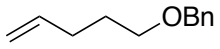



**12**

**Cis-3-(8-(benzyloxy)octyl)cyclobutyl 4-methylbenzenesulfonate (12)**

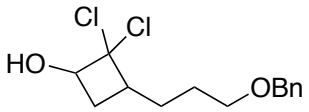
(Procedure BDE-7-70) To a room temperature solution of **8** (0.2899 g; 1.00 mmol) in dry pyridine (1 mL) was added DMAP (0.0406 g; .33 mmol), and tosyl chloride (0.2591 g; 1.36 mmol). The suspension was stirred at room temperature for 7 hours. The reaction was quenched with 1M HCl (5 mL), and then extracted with dichloromethane (4x10 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was purified by silica flash column chromatography (10% EtOAc/hexane) to give the toluenesulfonate (**12**, 0.3455 g, 78% yield) as a white solid (M.P. 27.5-28.0 $^{o}$C). $R_f$ in 25% EtOAc/Hex: (0.67) $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.135-1.345 (12H), 1.603 (p, 2H, J= 7.6 Hz), 1.721 (m, 2H), 2.341 (m, 2H), 2.454 (s, 3H), 3.461 (t, 2H, J= 6.7 Hz), 4.505 (s, 2H), 4.641 (dddd, 1H, J= 7.5, 7.5, 3.6, 2.8 Hz), 7.339-7.348 (7H), 7.785 (d, 2H, J= 8.5 Hz). $^{13}$C NMR (400 MHz): δ 21.76, 26.28, 26.85, 27.24, 29.45, 29.51, 29.60, 29.87, 36.82, 37.10, 70.61, 71.56, 72.98, 127.58, 127.72, 127.92, 128.45, 129.86, 134.31, 138.83,

144.66. HRMS (EI): calcd for $C_{26}H_{36}O_4S$ (M+) 444.2335; found 444.2331. IR: 2920, 2847, 1454, 1359, 1188, 1174, 1096, 918, 899, 846, 812, 730, 694, 669.




**13**

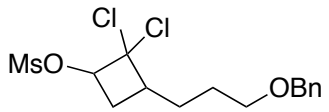
**((pent-4-en-1-yloxy)methyl)benzene (13)** (Procedure BDE-7-66) To a room temperature solution of NaH (1.1307 g; 28.28 mmol; 60% in oil) in THF (180 mL) was added tetrabutylammonium iodide (1.3921 g; 3.77 mmol) and 4-penten-1-ol (1.5152 g; 17.59 mmol). The suspension was stirred at room temperature for 30 minutes, and then benzyl bromide (0.1500 g; 1.19 mmol) was added. After stirring over night, the reaction was quenched with water (200 mL), extracted with Hex (2x100 mL) and then EtOAc (3x100 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was purified by silica column chromatography (1% Ether/pentane) to give ((pent-4-en-1-yloxy)methyl)benzene (**13**, 2.5207 g, 81%) as a clear liquid. $R_f$ in 25% EtOAc/Hex: (0.77). $^1$H NMR (400 MHz, $CDCl_3$): δ 1.740 (p, 2H, J= 7.0), 2.171 (dd, 2H, J= 13.6, 6.3 Hz), 3.507 (t, 2H, J= 6.4 Hz), 4.523 (s, 2H), 4.980 (dd, 1H, 10.2, 1.1 Hz), 5.043 (dd, 1H, 1.5, 17.1 Hz) 5.841 (ddt, 1H, J= 17.0, 11.1, 6.6 Hz), 7.294-7.367 (5H). $^{13}$C NMR (400 MHz): δ 29.10, 30.48, 69.86, 73.03, 114.85, 127.62, 127.75, 128.48, 138.44, 138.77. HRMS (EI): calcd for $C_{12}H_{16}O$ (M+) 176.1201; found: 176.1198. IR: 2850, 1449, 1201, 1092, 1068, 1027, 993, 910, 735, 694, 680, 661, 635, 608.




**14**

**Cis-3-(3-(benzyloxy)propyl)-2,2-dichlorocyclobutan-1-ol (14)** (Procedure BDE-7-77) To a room temperature solution of **13** (3.1295 g; 17.76 mmol) in dry ether (130 mL) was added zinc (5.8342 g; 89.19 mmol). The suspension was heated to 30 $^{o}$C and trichloroacetyl chloride (9.72 g; 53.5 mmol) dissolved in dry ether (50 mL) was added dropwise through a reflux condenser. The reaction was stirred for 1 hour at which point it began to reflux. It was quickly cooled in an ice bath, and stirred for 10 minutes. The reaction was poured over ice (50 mL), then extracted with EtOAc (3x200 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was diluted in isopropanol (260 mL) and sodium borohydride (1.2112 g; 32.02 mmol) was added at 0 $^{o}$C. The reaction was stirred at room temperature for 30 minutes, then quenched with saturated sodium bicarbonate (250 mL). Extracted with Hex (6x100 mL), dried over sodium sulfate, and then evaporated the solvent. The residue was purified by silica flash column chromatography (15% EtOAc/hexane) to give Cis-3-(3-(benzyloxy)propyl)-2,2-dichlorocyclobutan-1-ol (**14**, 3.0203 g, 59% yield) as a thick yellow oil. $R_f$ in 25% EtOAc/Hex: (0.38). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.475 (m, 1H), 1.642 (m, 2H), 1.686 (m, 2H), 1.778 (m, 2H), 2.462 (m, 2H), 2.510 (d, 1H, J= 10.8), 3.512 (dd, 2H, J= 9.9, 5.6 Hz), 4.304 (m, 1H), 4.520 (s, 2H), 7.347 (5H). $^{13}$C NMR (400 MHz): δ 26.80, 27.00, 34.83, 45.62, 69.88, 73.04, 75.56, 92.96, 127.70, 127.76,

128.51, 138.57. HRMS (EI): calcd for $C_{14}H_{18}Cl_2O_2$ (M+) 288.0684; found: 288.0697. IR: 3383, 2943, 2856, 1495, 1452, 1362, 1192, 1163, 1094, 1074, 1027, 959, 766, 735, 696.

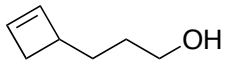



**15**

**Cis-3-(3-(benzyloxy)propyl)-2,2-dichlorocyclobutyl methanesulfonate (15)**

(Procedure BDE-7-78) To a room temperature solution of **14** (5.2748 g; 18.24 mmol) in dry dichloromethane (100 mL) was added mesyl chloride (2.96 g; 25.8 mmol). Triethylamine (3.15 g; 31.1 mmol) was added at -78 $^{o}$C. The suspension was warmed to room temperature and stirred for 1 hour. The reaction was quenched with water (30 mL), diluted with 1M HCl (100 mL), and then extracted with dichloromethane (4x100 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was purified by silica flash column chromatography (12% EtOAc/hexane) to give Cis-3-(3-(benzyloxy)propyl)-2,2-dichlorocyclobutyl methanesulfonate (**15**, 4.7337 g, 71% yield) as a thick yellow oil. $R_f$ in 25% EtOAc/Hex: (0.25). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.789 (m, 5H), 2.322 (m, 2H), 3.199 (s, 3H), 3.507 (ddd, 2H, J= 5.9, 3.0, 2.6 Hz), 4.518 (s, 2H), 5.119 (t, 1H, J= 8.7), 7.347-7.362 (5H). $^{13}$C NMR (400 MHz): δ 26.75, 26.94, 31.73, 39.55, 45.90, 69.67, 73.09, 78.52, 88.41, 127.77, 128.54, 138.49. HRMS (ESI): calcd for $C_{15}H_{20}Cl_2O_4S$ (M+) 366.0460; found: 366.0455. IR: 2940, 2860, 1453,

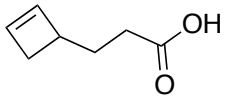
1361, 1361, 1178, 1147, 1097, 1061, 1027, 971, 952, 77, 851, 809, 775, 736, 697, 657.




**16**

**3-(cyclobut-2-en-1-yl)propan-1-ol (16)** (Procedure BDE-7-85, spectra BDE-7-80) To a room temperature solution of sodium (3.53 g; 153 mmol) in liquid ammonia (172 mL) at -78 $^{o}$C was added **15** (3.1667 g; 8.62 mmol) dissolved in dry THF (2 mL). The suspension was stirred at -78 $^{o}$C for 1 hour, after which more sodium (2.06 g; 89.6 g) was added. The reaction was stirred for 30 minutes, then very slowly quenched with saturated ammonium chloride (100 mL). The liquid ammonia was allowed to evaporate over 5 hours while warming to room temperature. The reaction was diluted with 1M HCl (100 mL), and then extracted with ether (4x50 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. A small portion was purified by silica flash column chromatography (20% Ether/pentane) to give **3**-(cyclobut-2-en-1-yl)propan-1-ol (**16**) as a clear liquid. The rest of the crude material was taken directly to the next step due to concerns about volatility. $R_f$ in 25% EtOAc/Hex: (0.31). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.572 (m, 4H), 2.073 (d, 1H, J= 13.4), 2.671 (dd, 1H, J= 13.7, 4.2 Hz), 2.823 (ddd, 1H, J= 6.1, 4.2 Hz), 3.659 (t, 2H, J=6.3), 6.058 (d, 1H, 2.6 Hz), 6.111 (d, 1H, J= 2.4 Hz) $^{13}$C NMR (400 MHz): δ 30.76, 31.27, 36.88, 43.89, 63.19, 135.53, 140.78. HRMS (EI): calcd for $C_7H_{12}O$ (M+) 112.0888; found: 118.0773 (Exact mass of

congruent molecule not found)[39]. IR: 3314, 3037, 2914, 2846, 1451, 1325, 1288, 1052, 1008, 918, 902, 694.




**17**

**3-(cyclobut-2-en-1-yl)propanoic acid (17)** (Procedure BDE-7-83) To a solution of crude **16** in acetone (105 mL) was added Jone's Reagent (2 M, 21 mL) at 0 $^{o}$C. The suspension was stirred 10 minutes and then extracted with pentane (8x75 mL). The combined pentane extracts were extracted with 1M NaOH (4x50 mL), then cooled in an ice bath and acidified with 6 M HCl to a pH of 1. The acidified aqueous layer was extracted with ether (5x150 mL). The combined organic layers were dried over sodium sulfate then evaporated under reduced pressure. The residue was purified by acidified silica (200 mL of silica rinsed with .1M sulfuric acid, and baked in the oven over night) column chromatography (50% Ether/pentane) to give 3-(cyclobut-2-en-1-yl)propanoic acid (**17**, .5343 g, 49% over two steps) as a light yellow liquid. $R_f$ in 25% EtOAc/Hex: (0.22). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.834 (q, 2H, J= 7.2 Hz), 2.096 (d, 1H, J= 13.9), 2.386 (t, 2H, J= 7.2 Hz), 2.681 (dd, 1H, 13.9, 4.5 Hz), 2.862 (ddd, 1H, J= 7.2, 4.6, 4.6 Hz), 6.084 (m, 2H), 11.514 (s, 1H). $^{13}$C NMR (400 MHz): δ 29.39, 32.48, 36.39, 43.16, 135.95, 139.94, 180.57. HRMS (EI): calcd for $C_7H_{10}O_2$ (M+) 126.0681; found: 126.0683. IR: 2915, 1702, 1410, 1274, 1216, 935, 700, 680.

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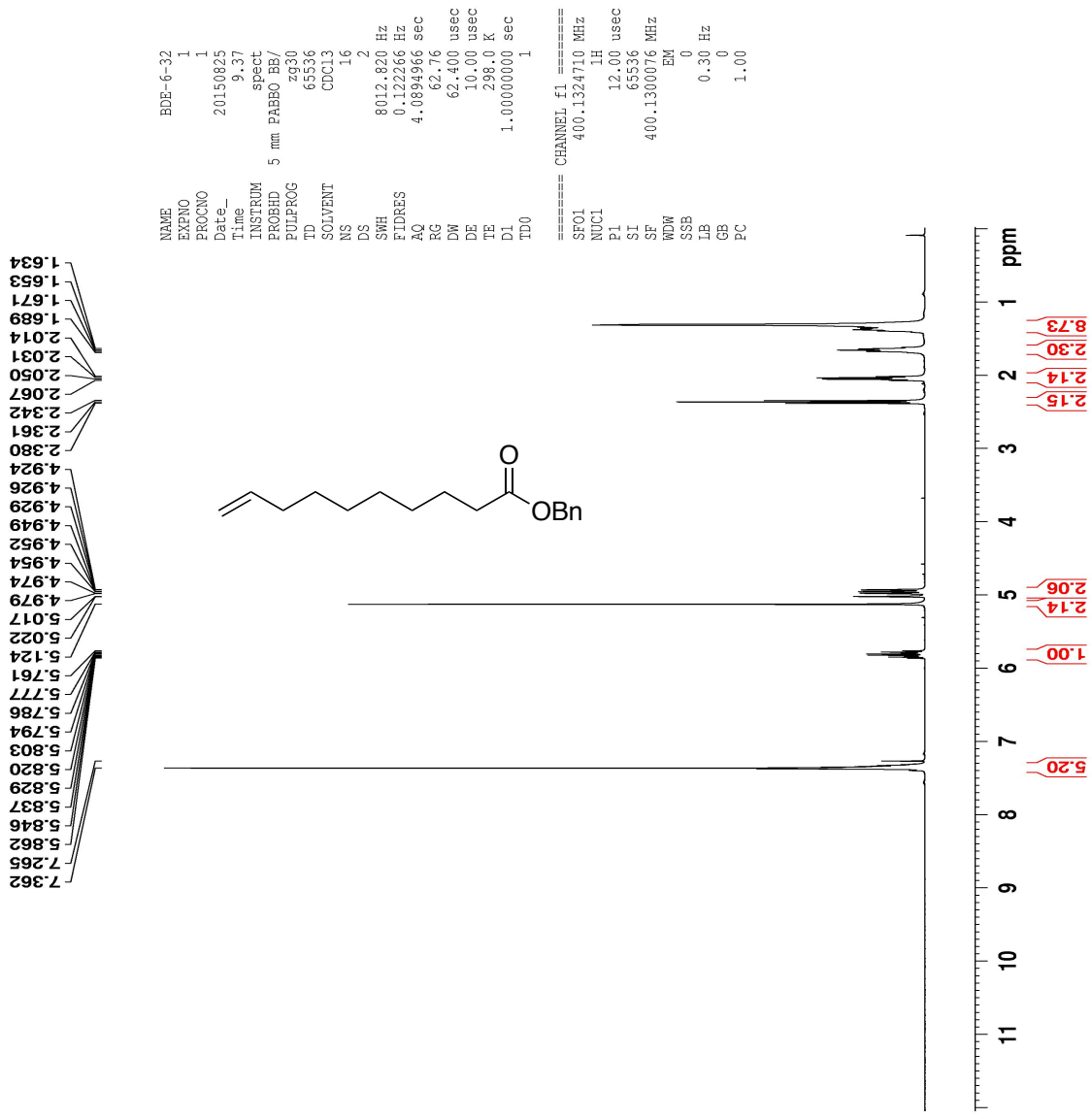
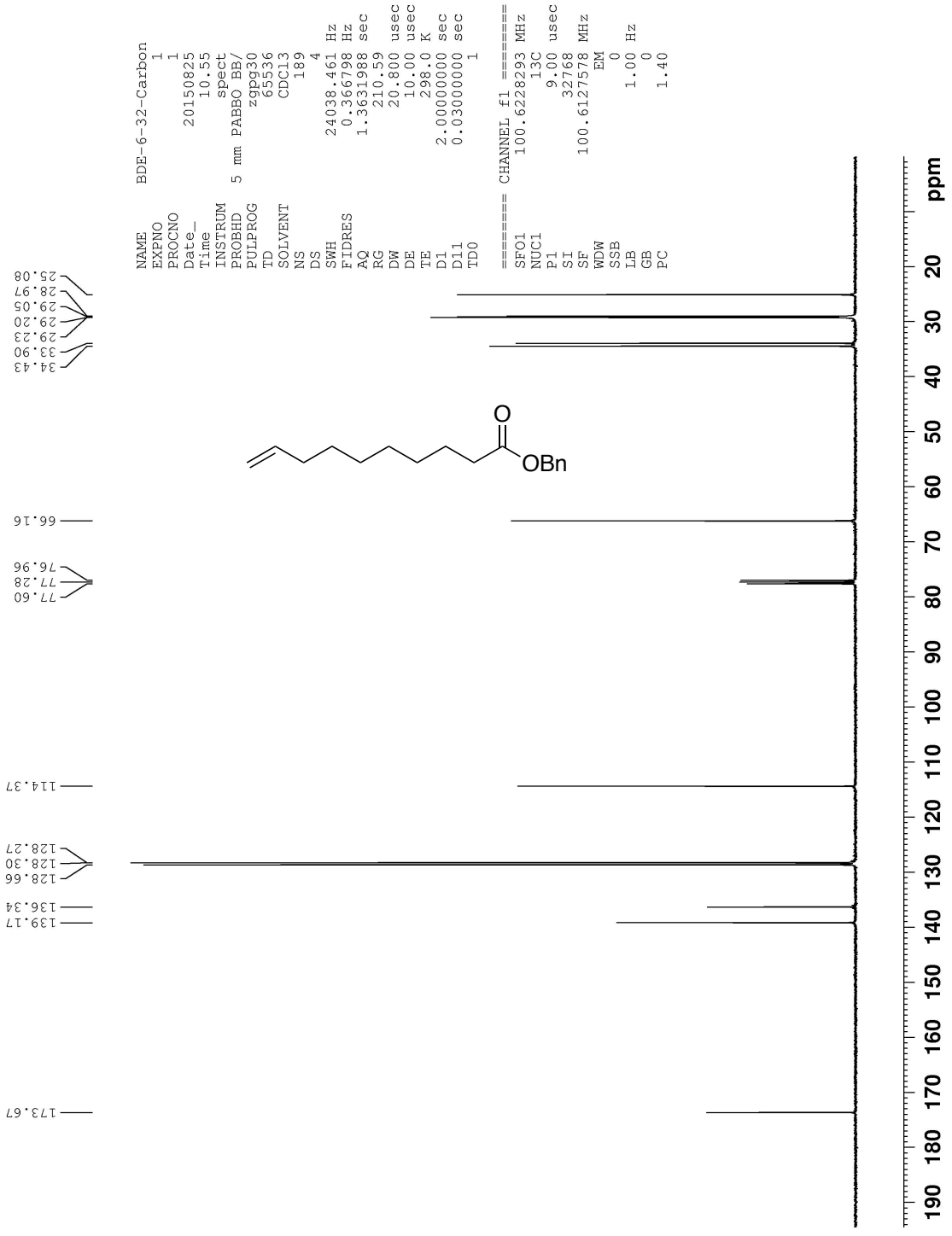
# $^{1}H$ and $^{13}C$ NMR Spectra

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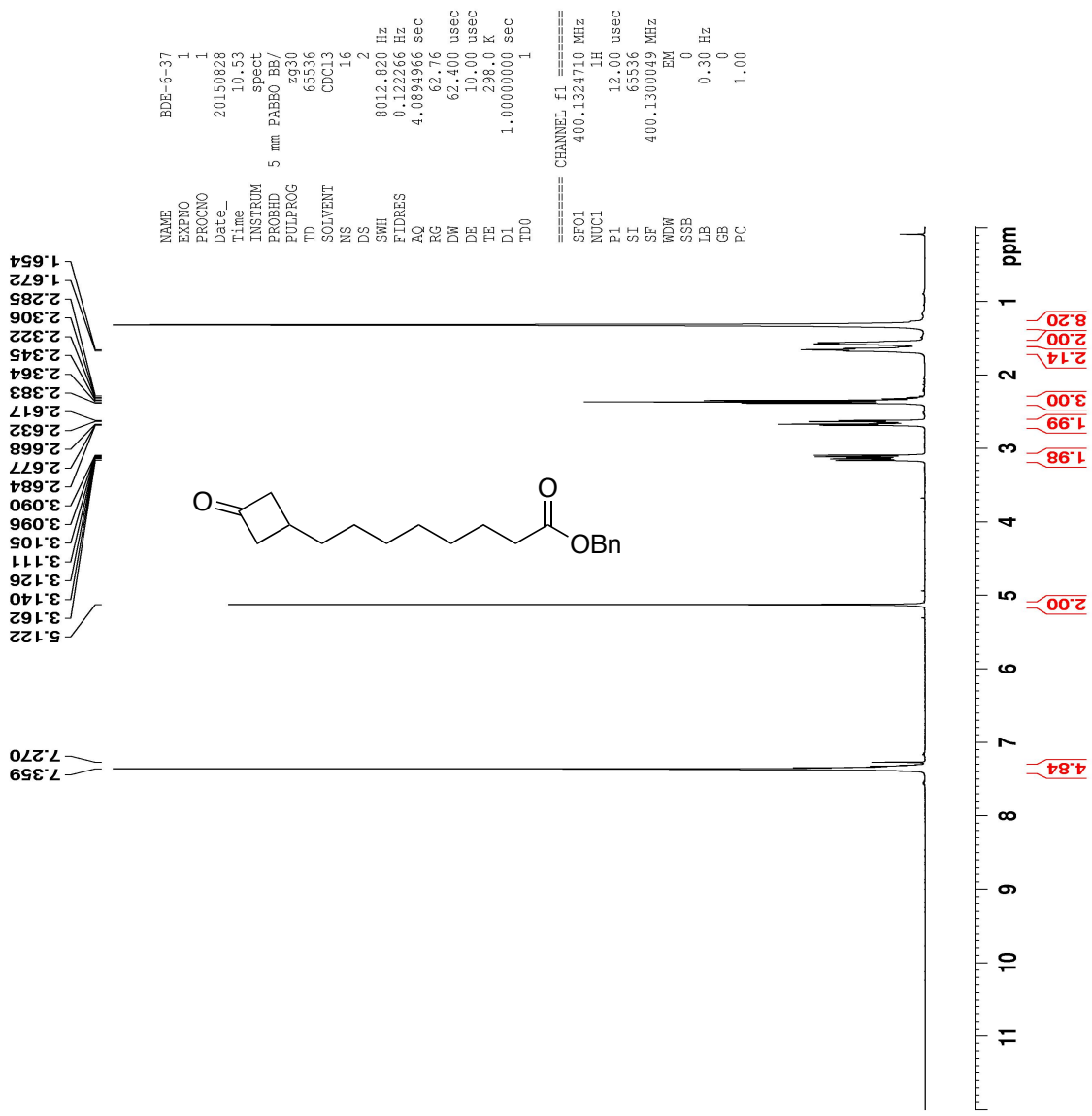
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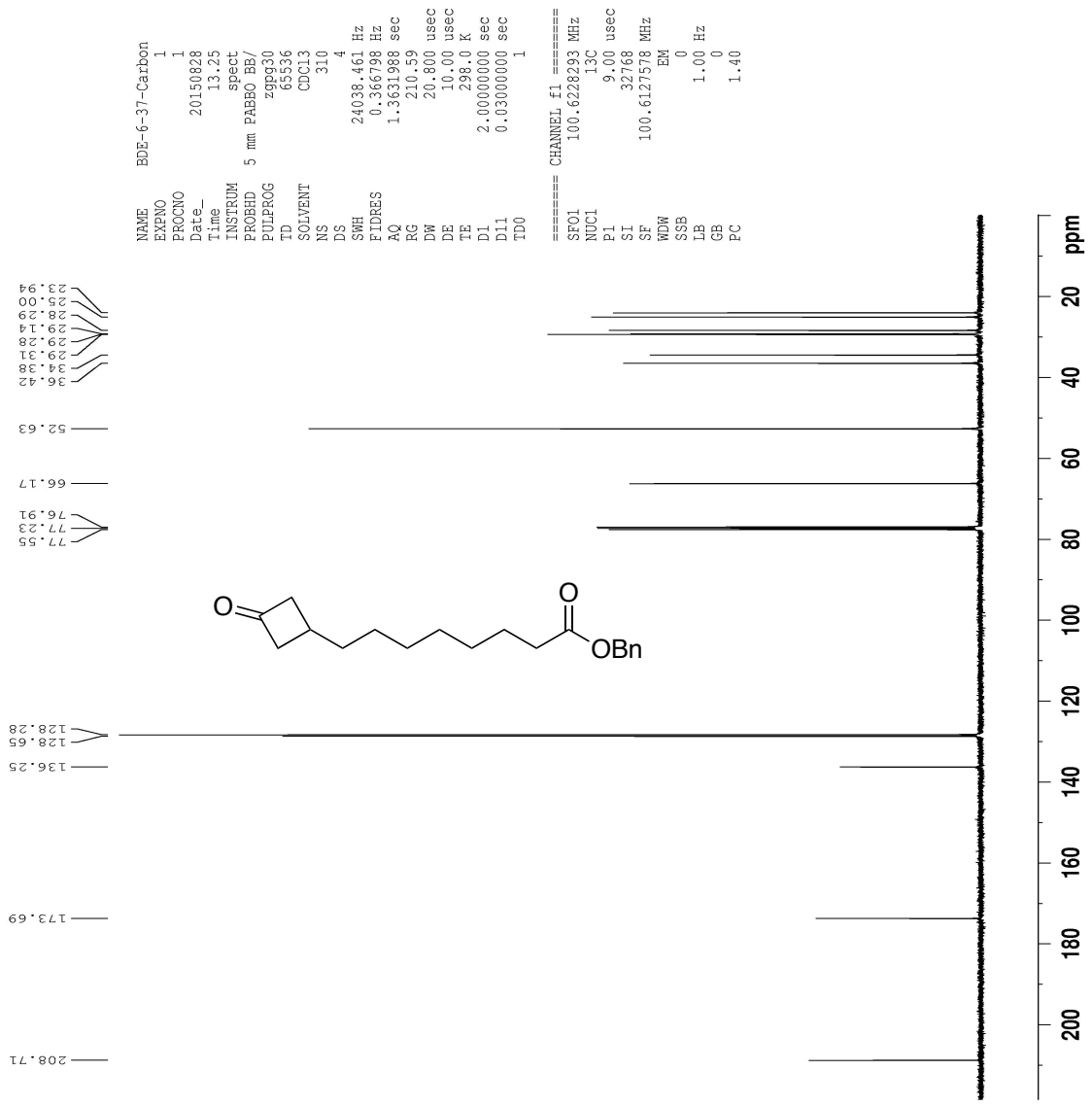
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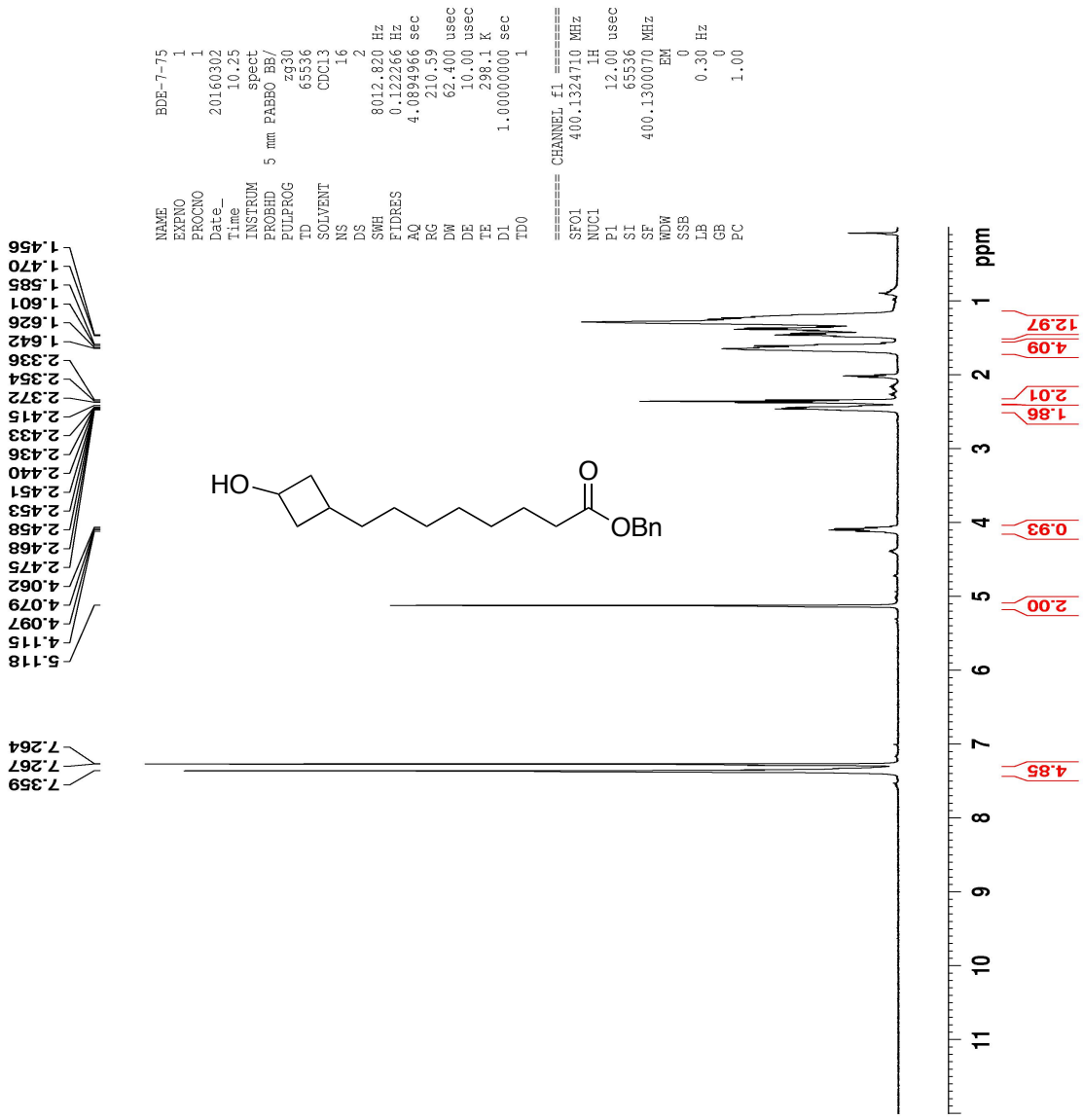
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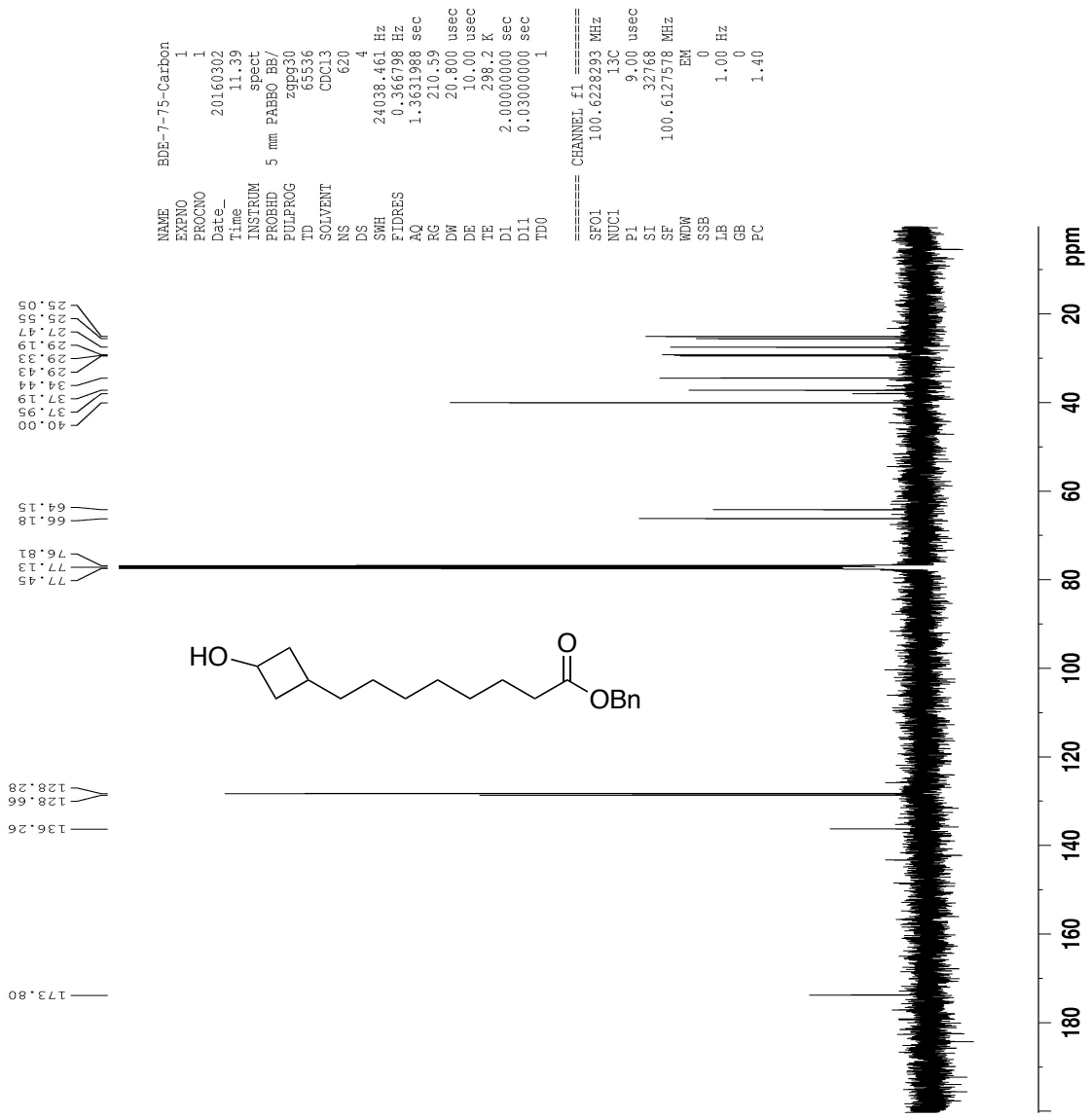
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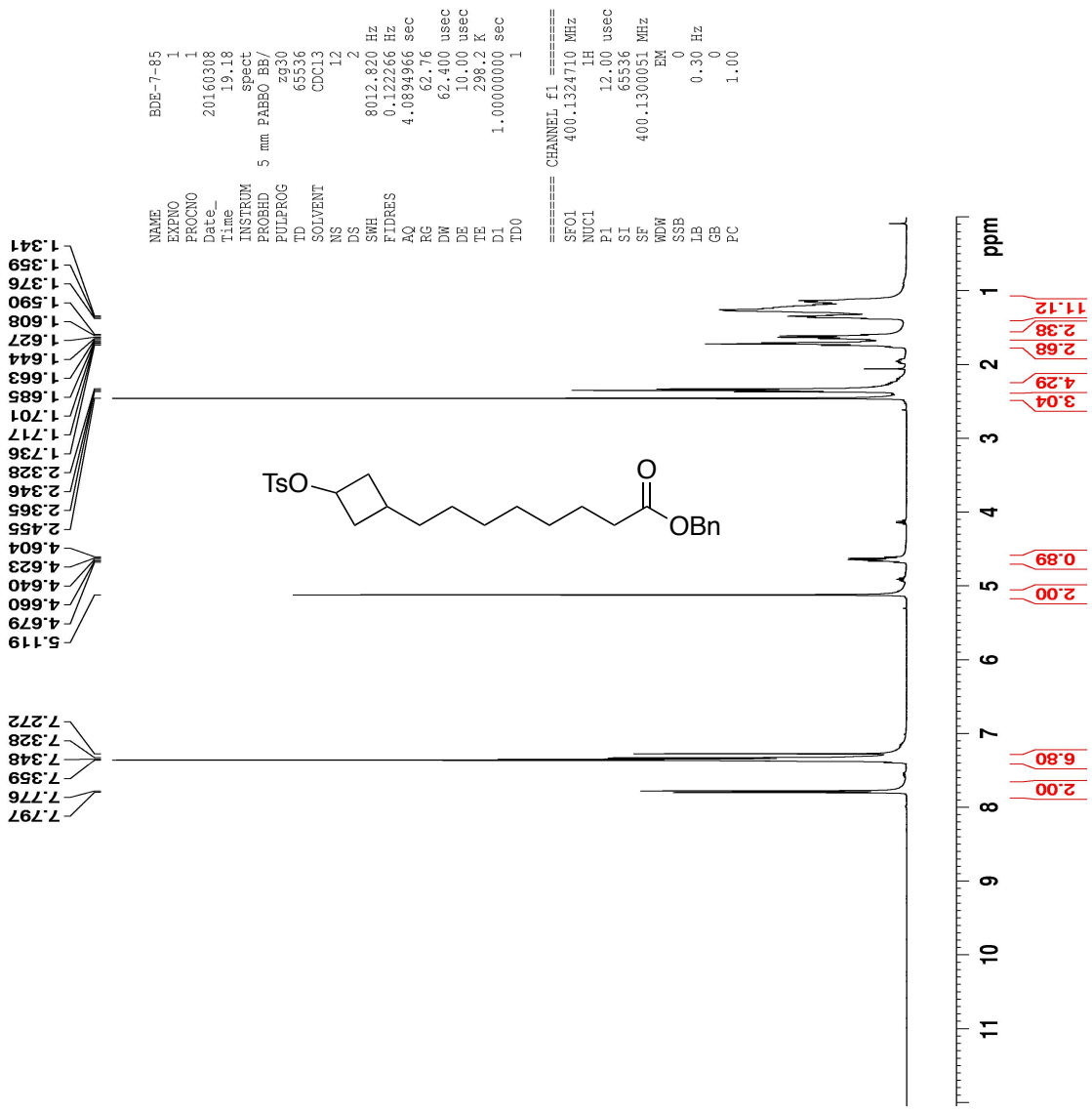
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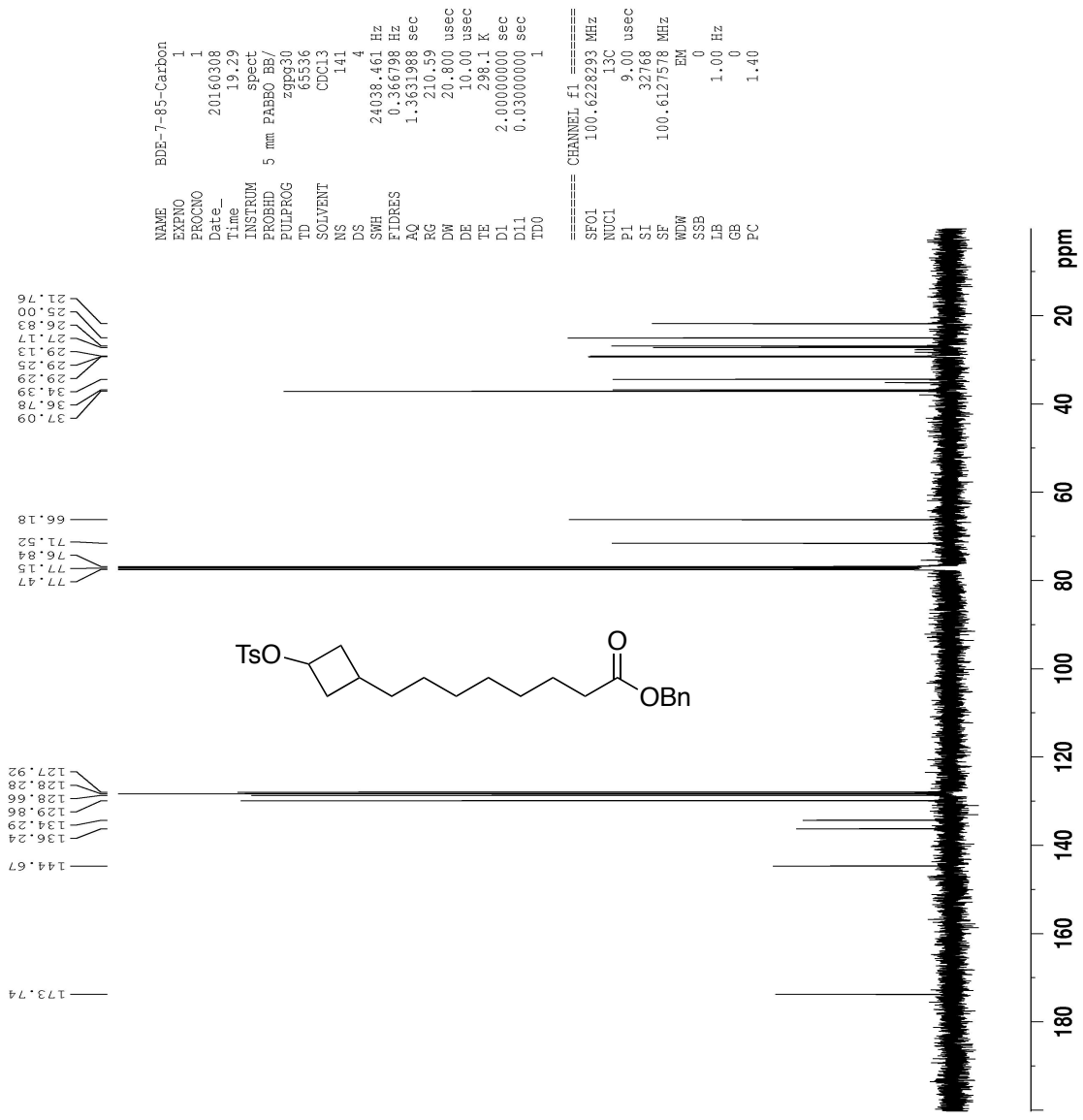
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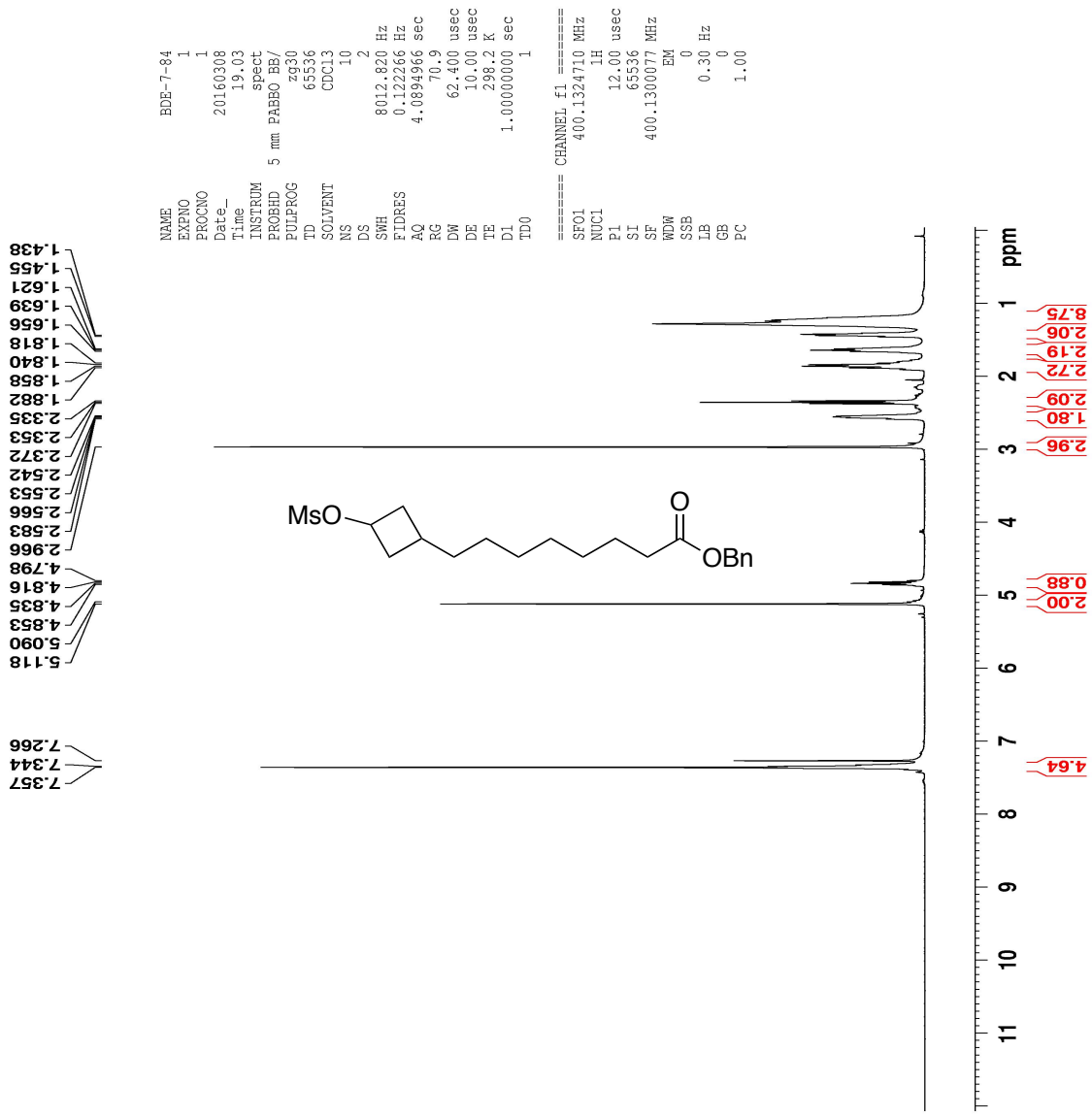
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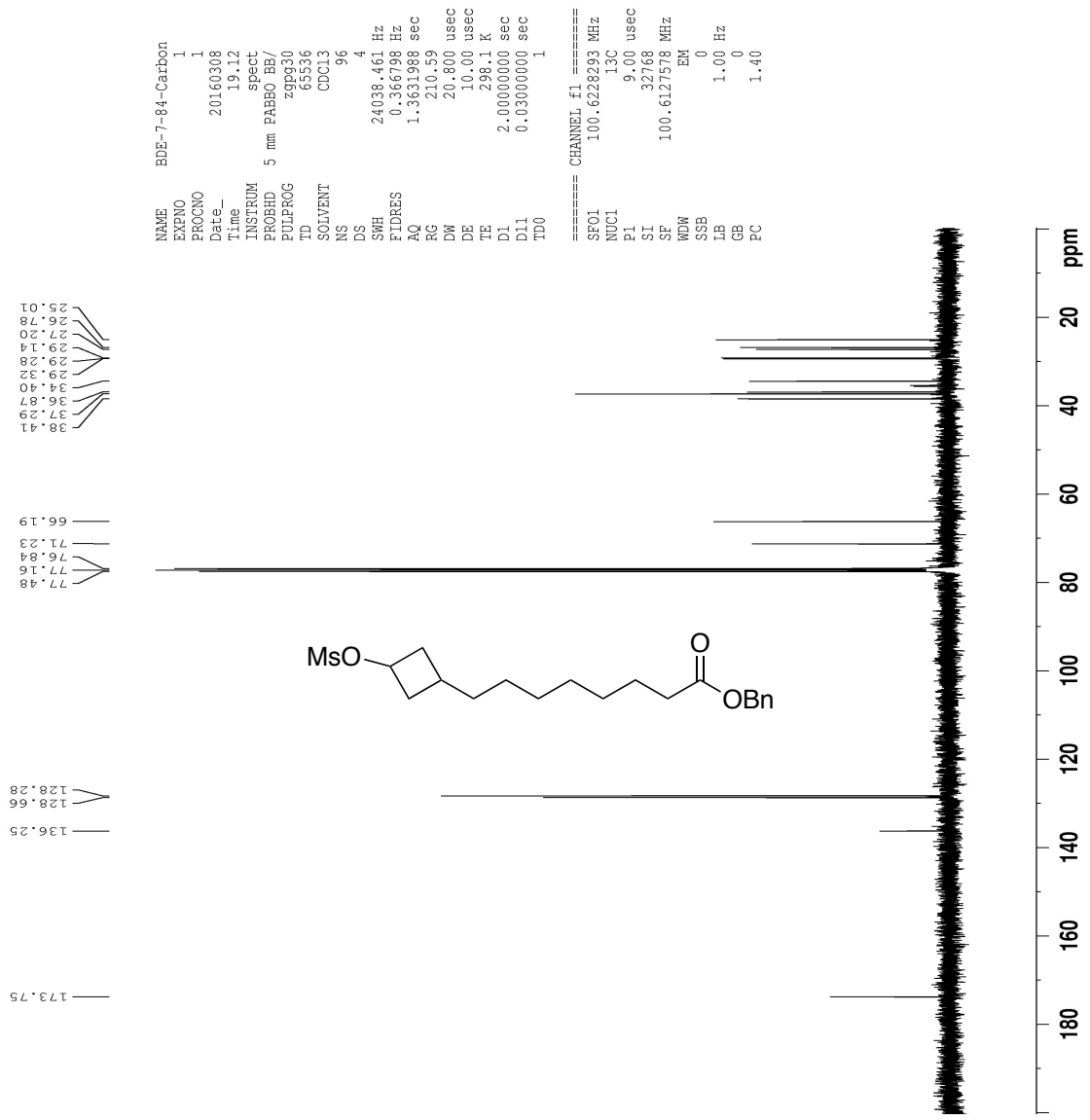
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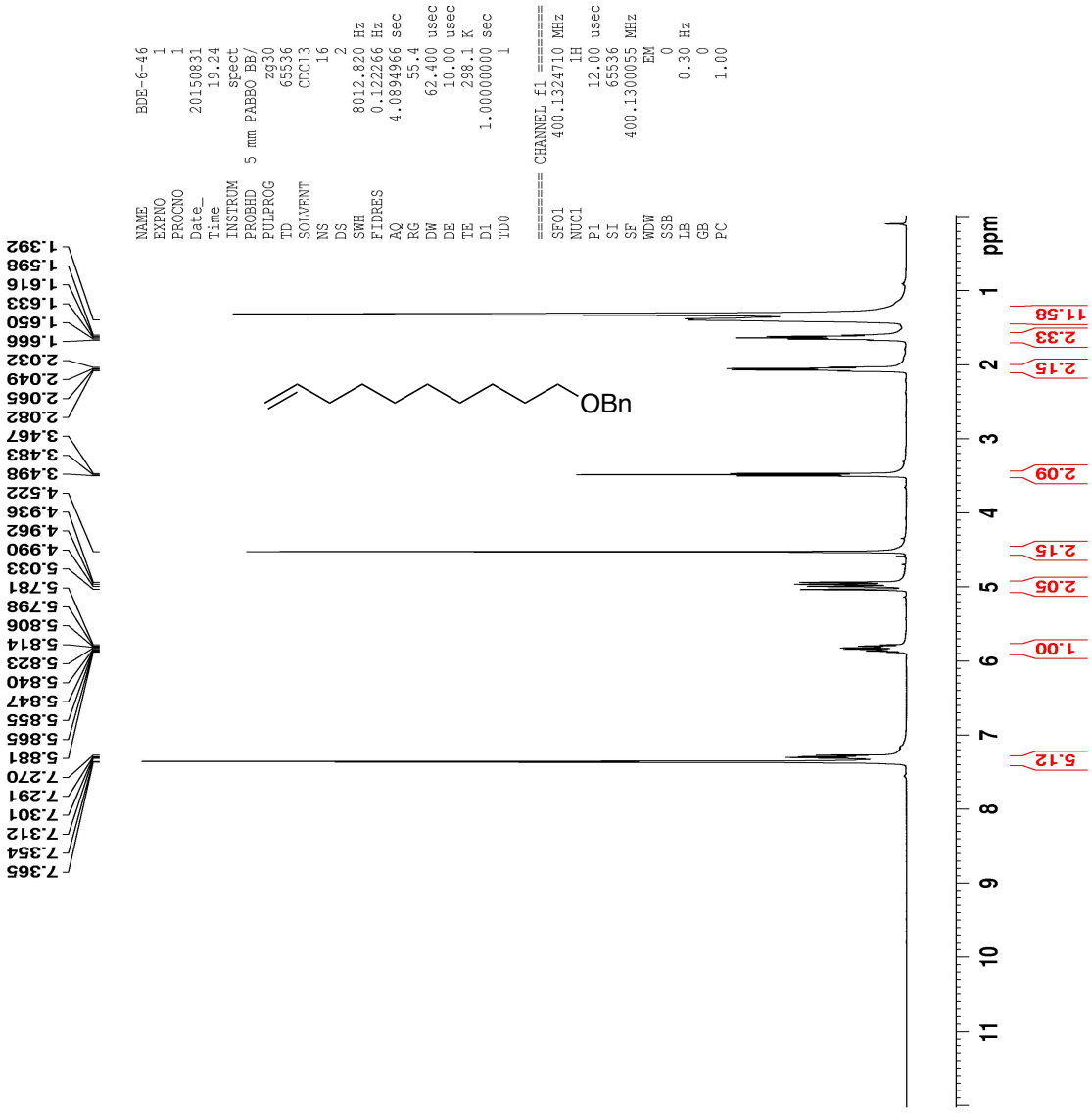
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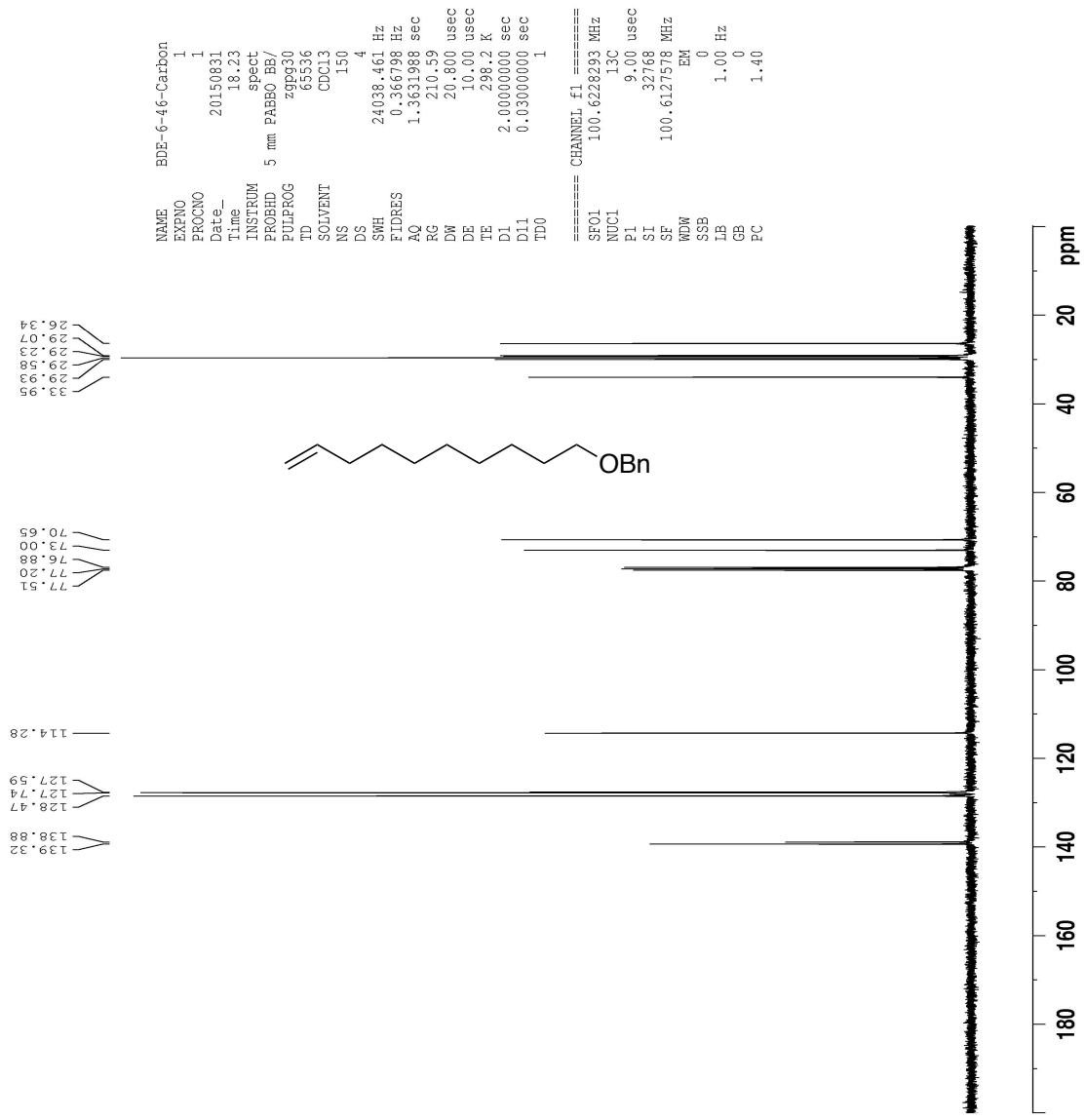
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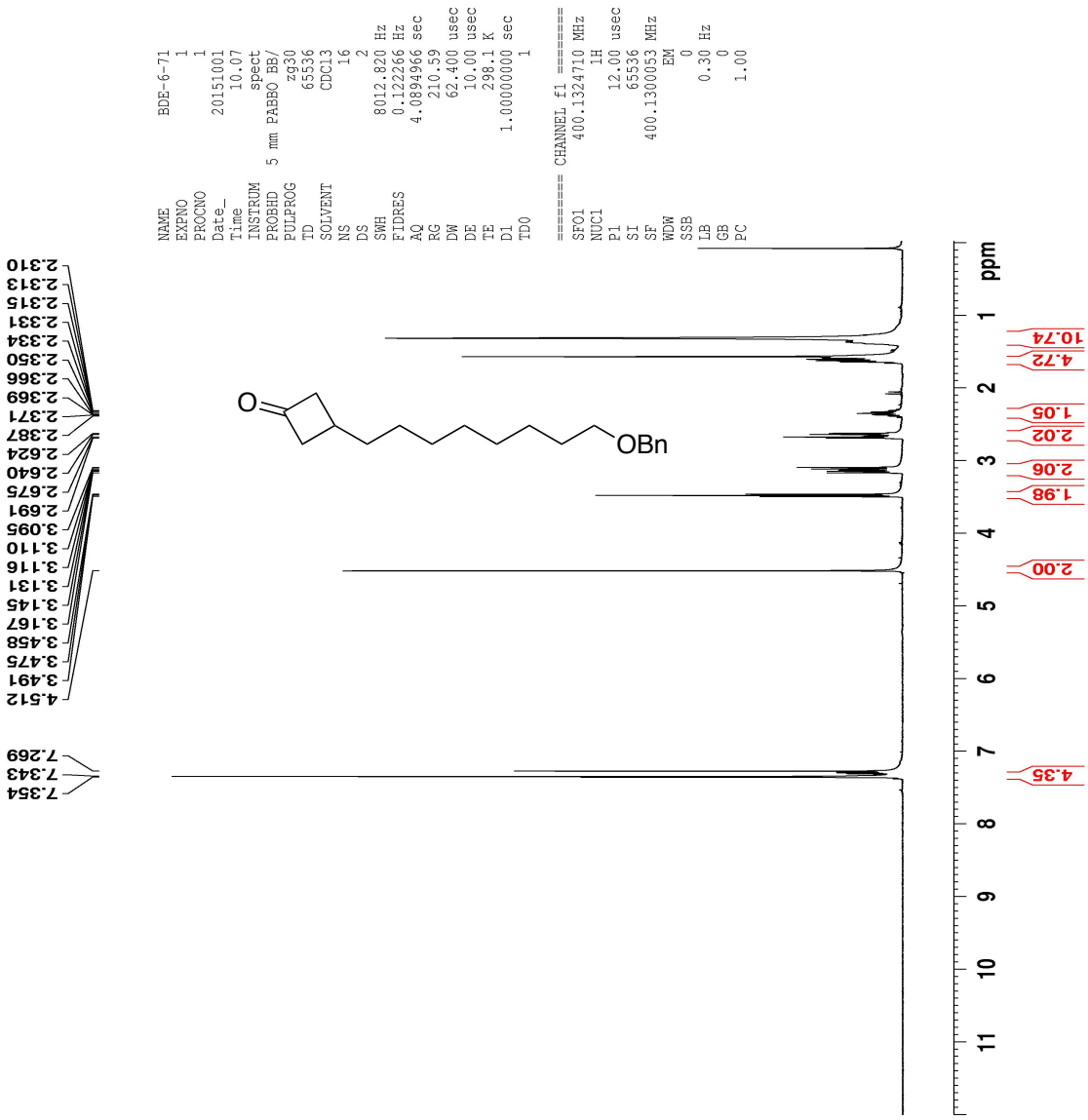
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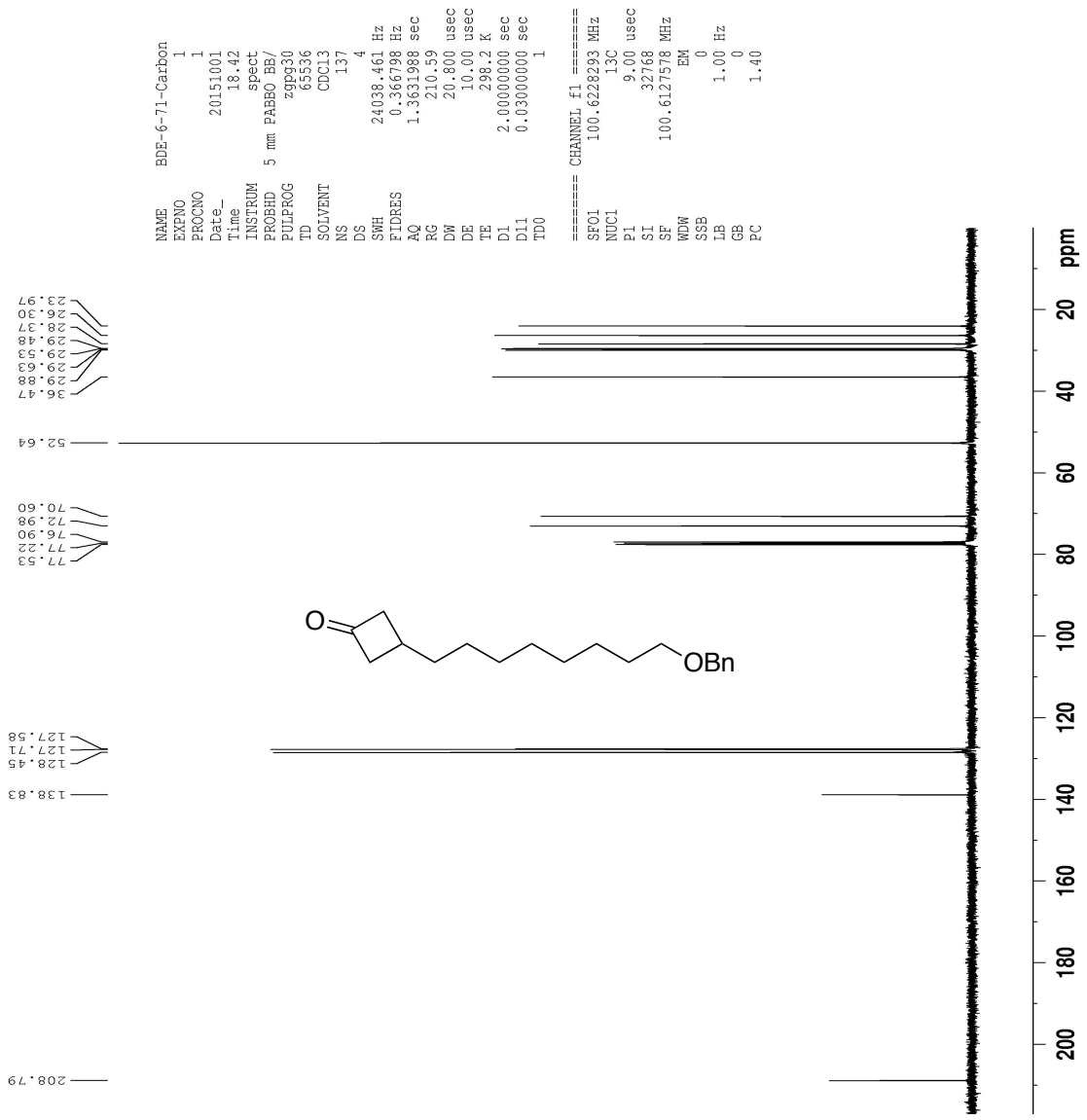
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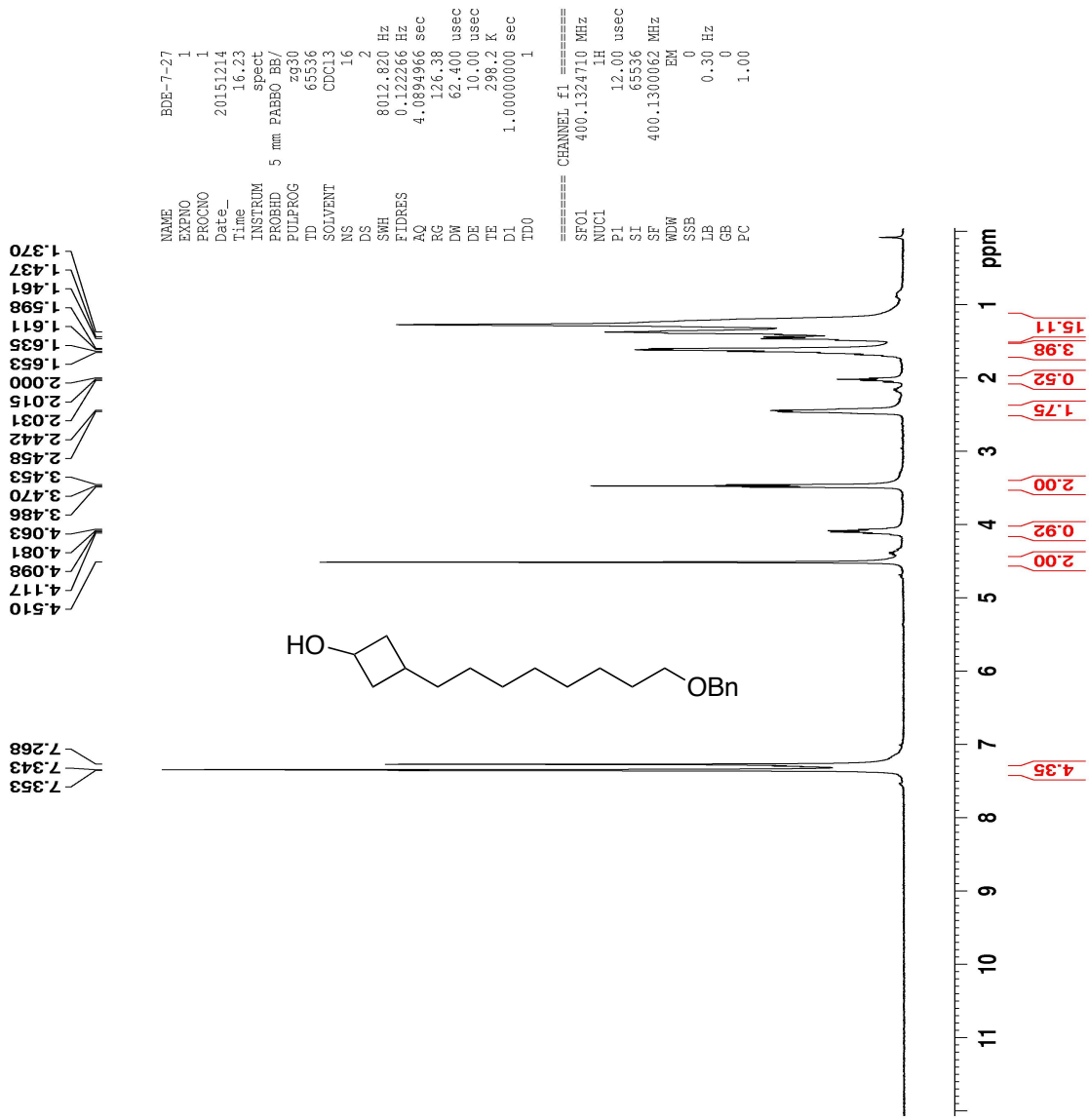
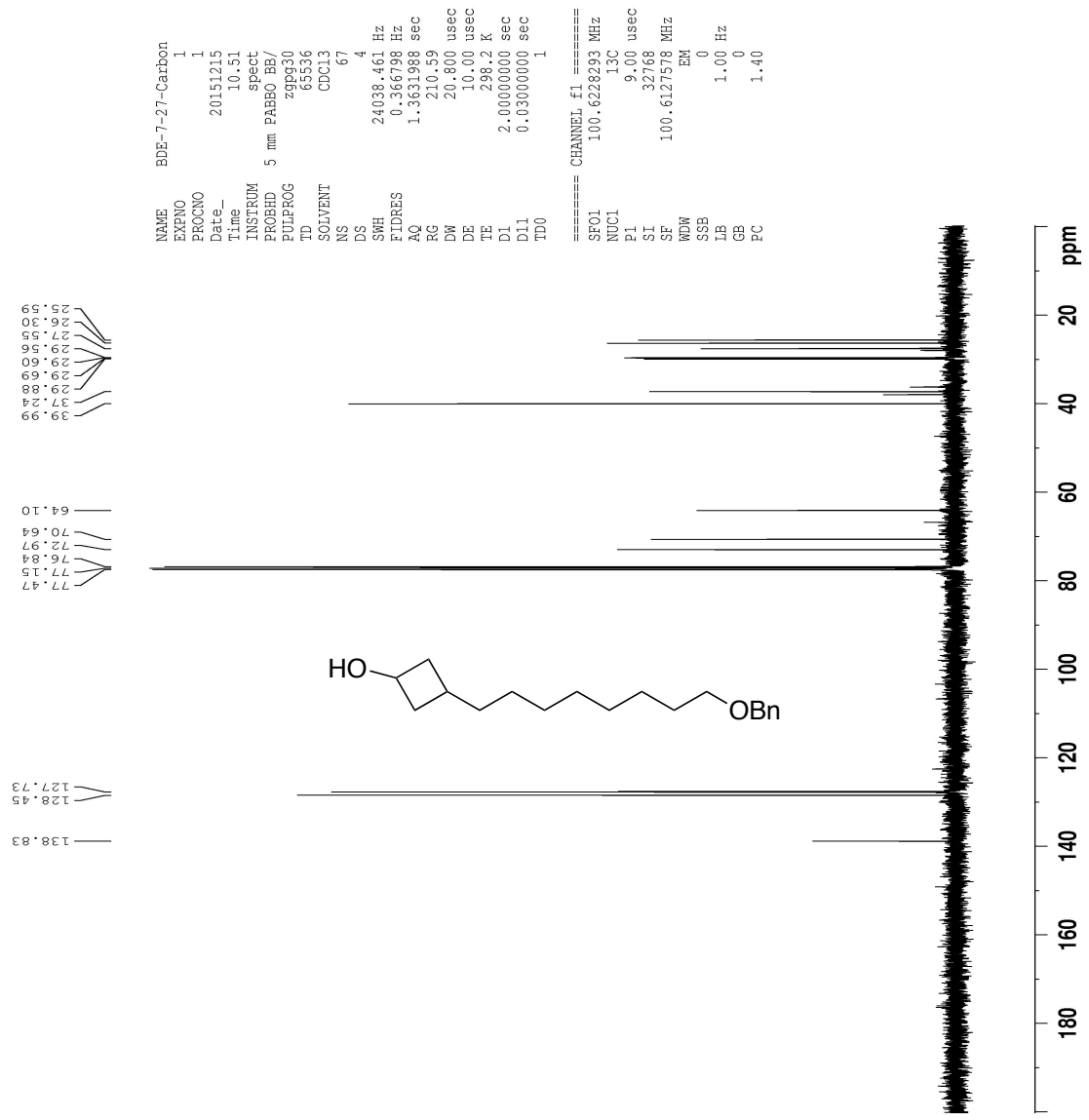
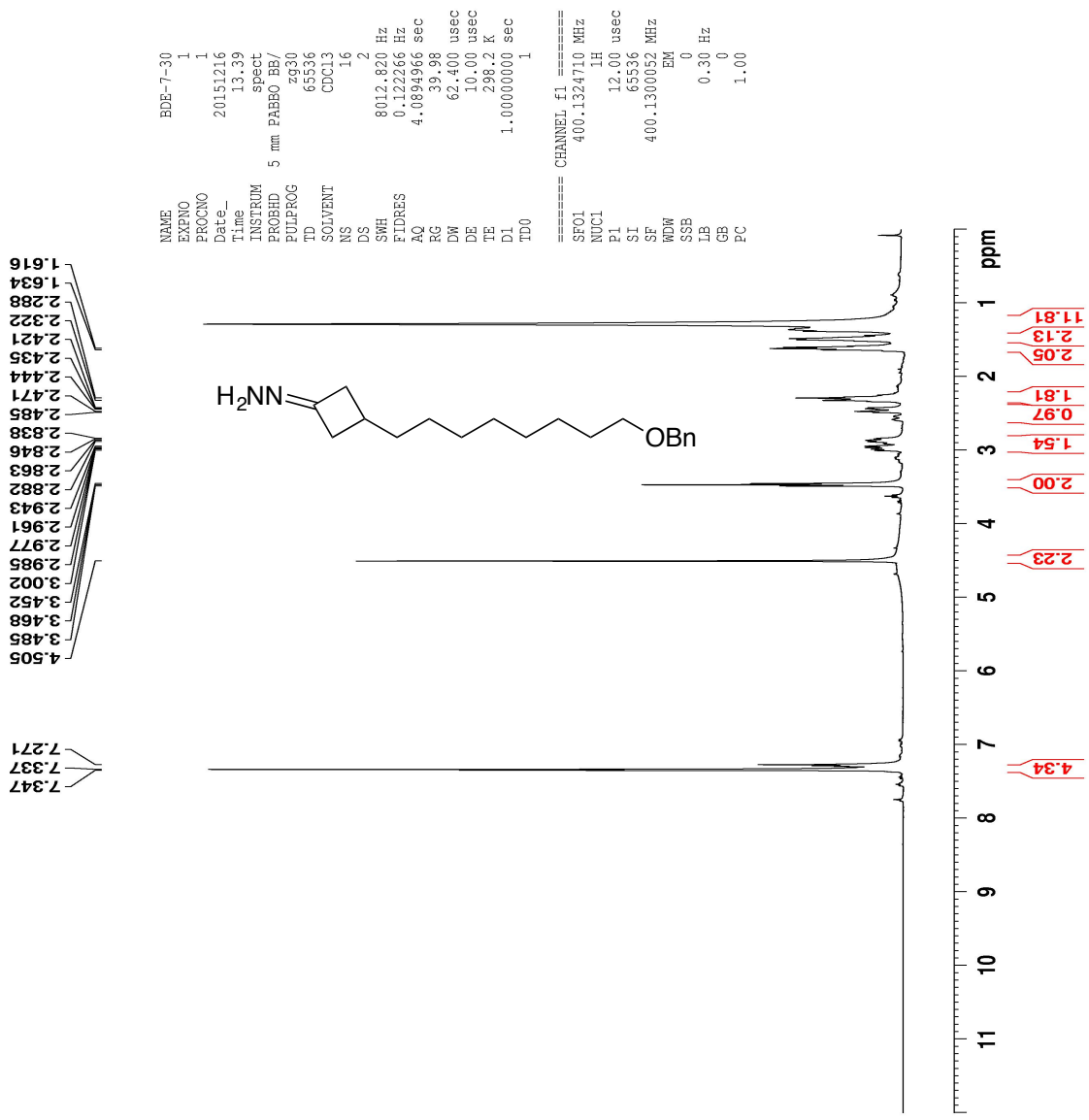
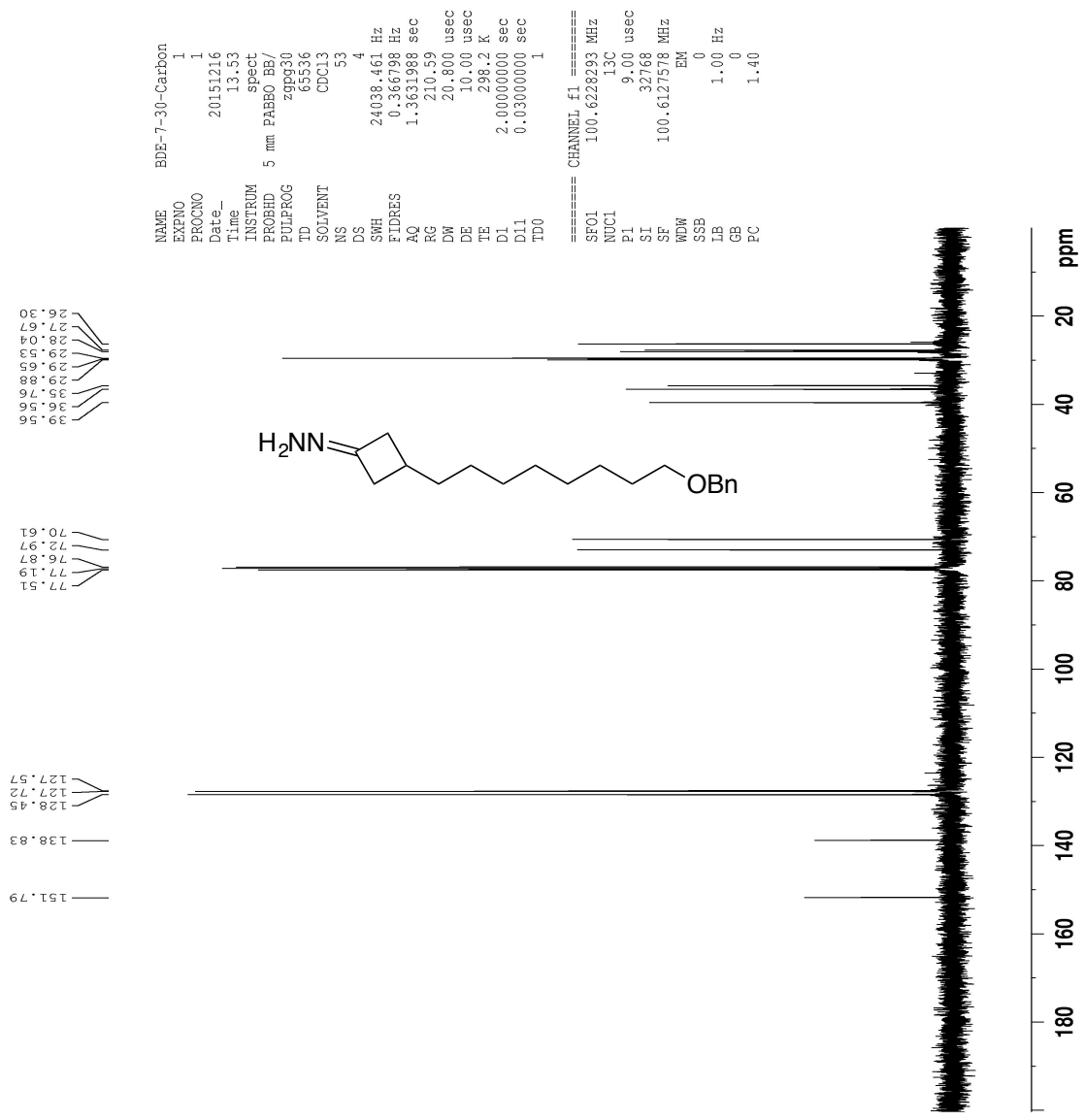
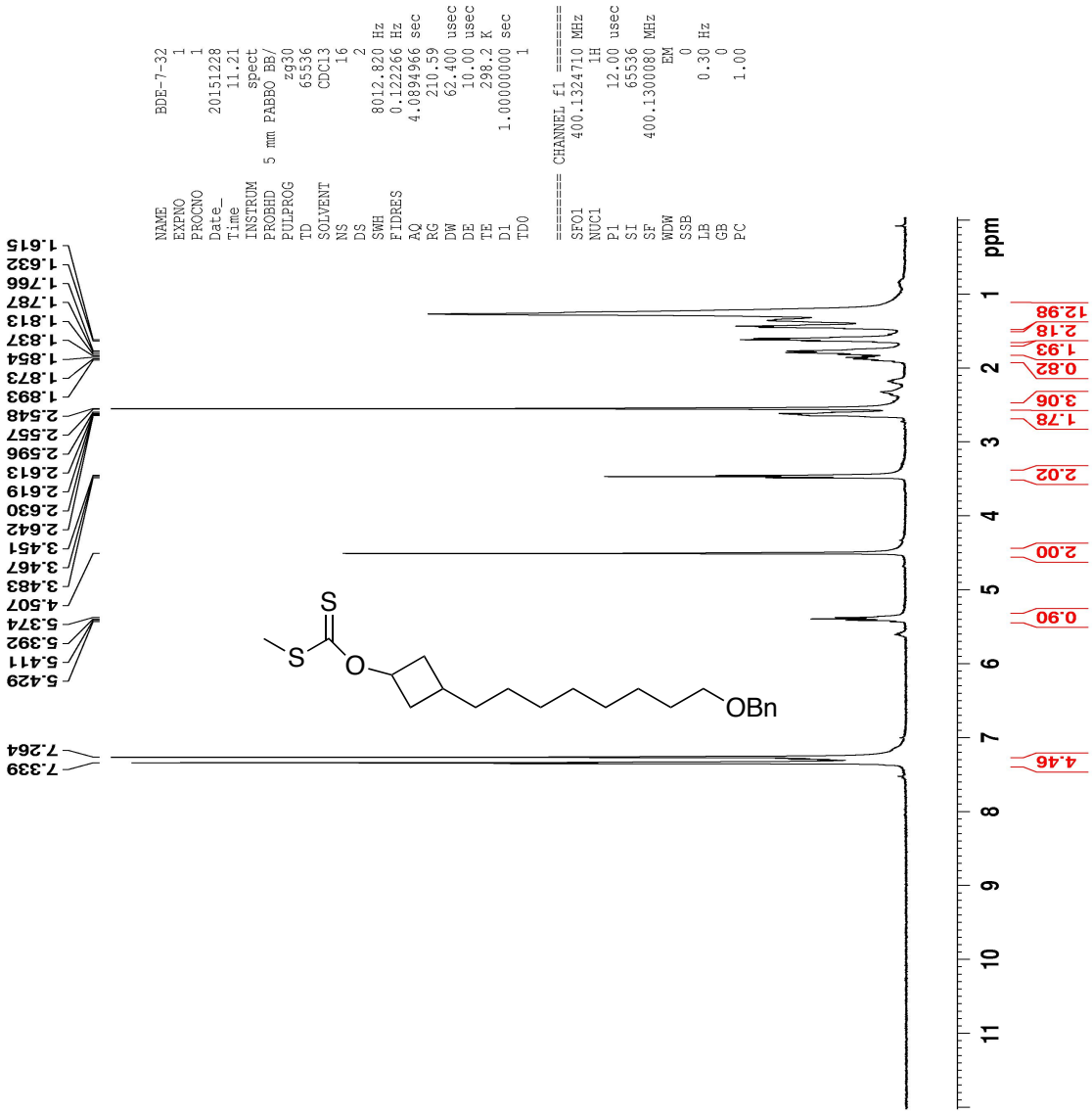
LB 1.00 Hz
GB 0
PC 1.40
23.97
26.30
28.37
29.48
29.53
29.63
29.88
36.47
52.64
70.60
72.98
76.90
77.22
77.53
127.58
127.71
128.45
138.83
208.79
O
OBn
ppm
20
40
60
80
100
120
140
160
180
200

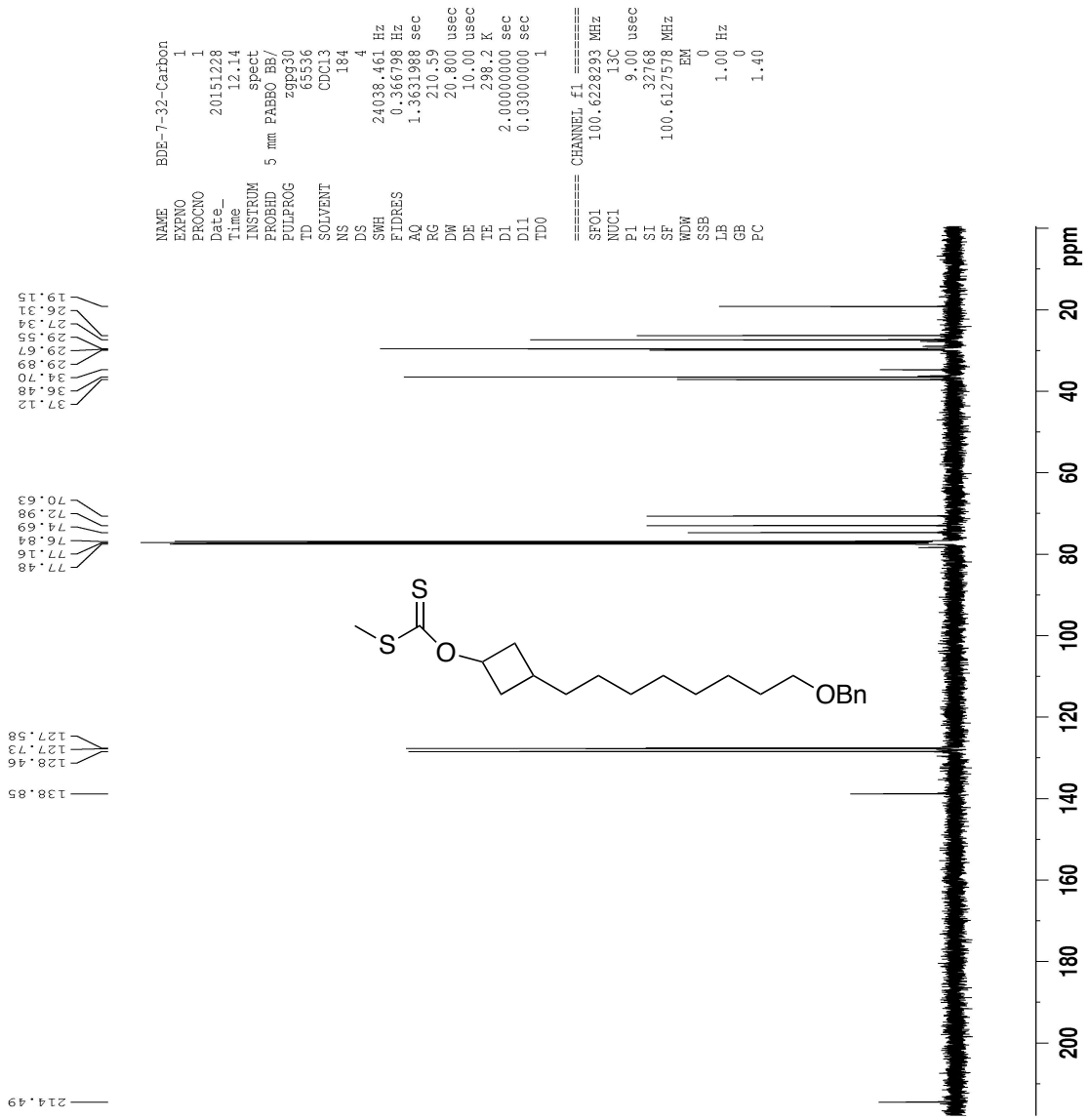

NAME BDE-7-27
EXPNO 1
PROCNO 1
Date_ 20151214
Time 16.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 126.38
DW 62.400 usec
DE 10.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.00 usec
SI 65536
SF 400.1300062 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
HO
OBn
ppm
15.11
3.98
0.52
1.75
2.00
0.92
2.00
4.35
1.370
1.437
1.461
1.598
1.611
1.635
1.653
2.000
2.015
2.031
2.442
2.458
3.453
3.470
3.486
4.063
4.081
4.098
4.117
4.510
7.268
7.343
7.353

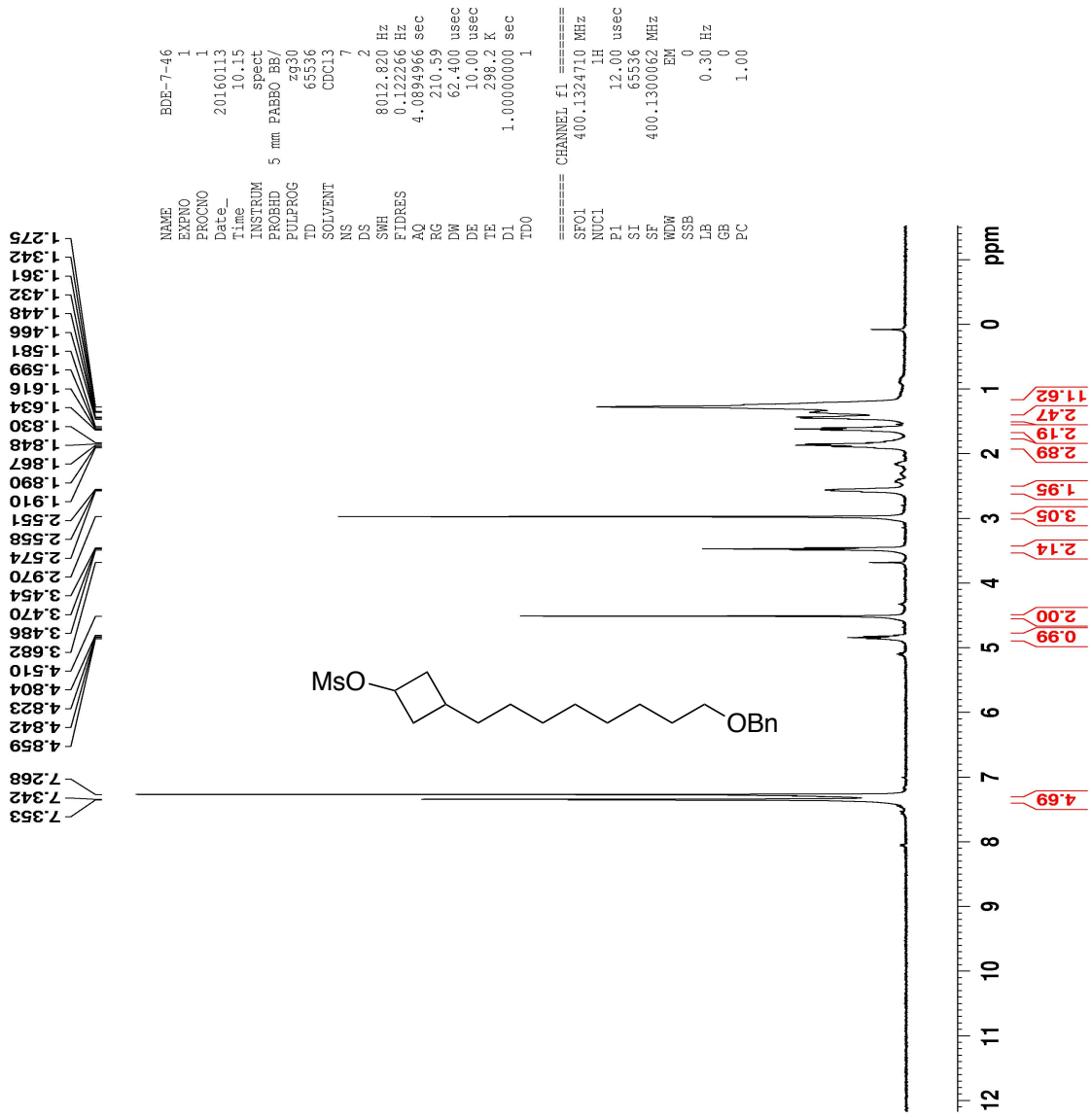

NAME BDE-7-27-Carbon
EXPNO 1
PROCNO 1
Date_ 20151215
Time 10.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 67
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 10.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.6127578 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
HO
OBn
ppm
20
40
60
80
100
120
140
160
180
25.59
26.30
27.55
29.56
29.60
29.69
29.88
37.24
39.99
64.10
70.64
72.97
76.84
77.15
77.47
127.73
128.45
138.83

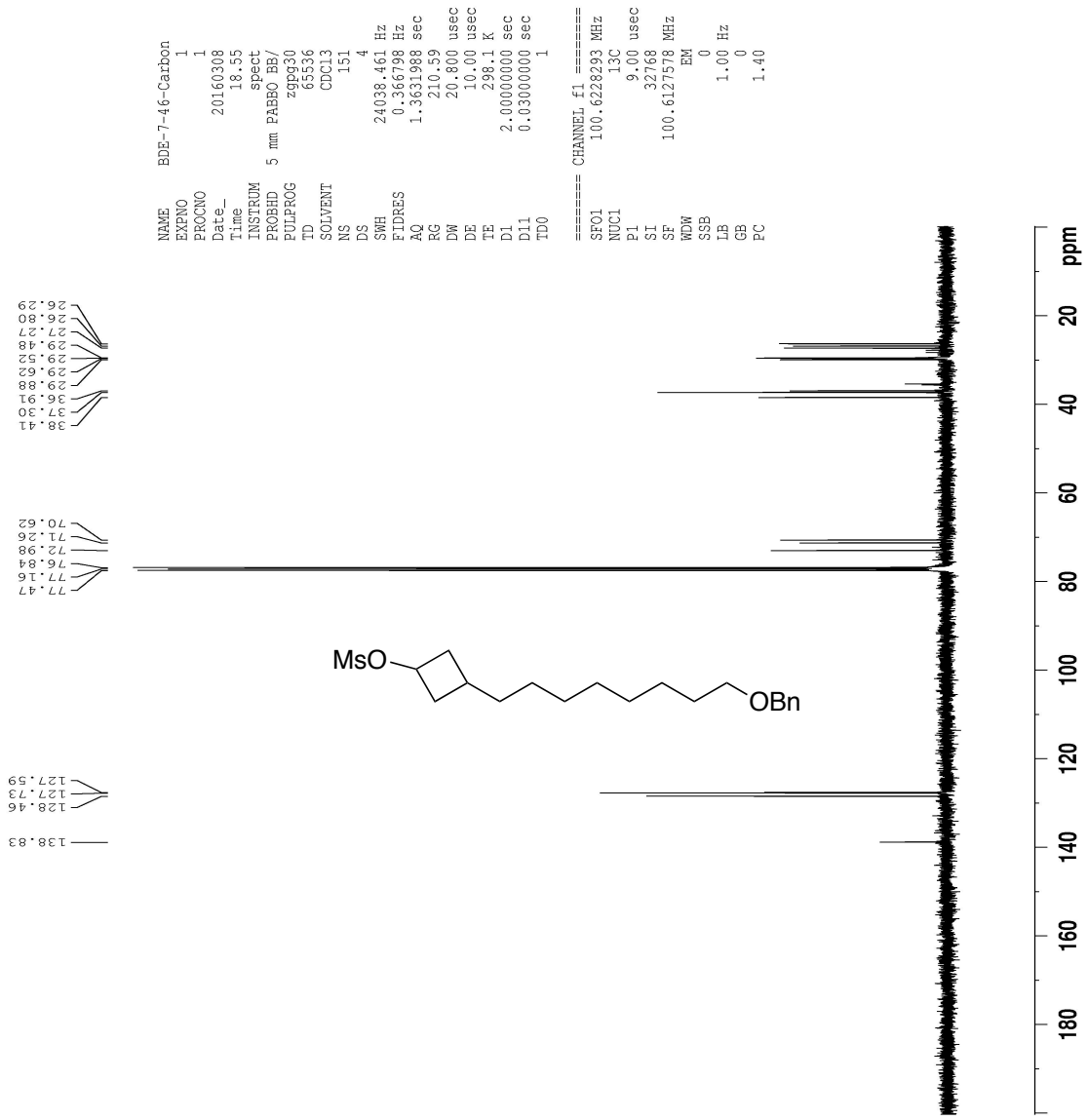

NAME BDE-7-30
EXPNO 1
PROCNO 1
Date_ 20151216
Time 13.39
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 39.98
DW 62.400 usec
DE 10.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.00 usec
SI 65536
SF 400.1300052 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
H2NN
OBn
ppm
11.81
2.13
2.05
1.81
0.97
1.54
2.00
2.23
4.34
1.616
1.634
2.288
2.322
2.421
2.435
2.444
2.471
2.485
2.838
2.846
2.863
2.882
2.943
2.961
2.977
2.985
3.002
3.452
3.468
3.485
4.505
7.271
7.337
7.347

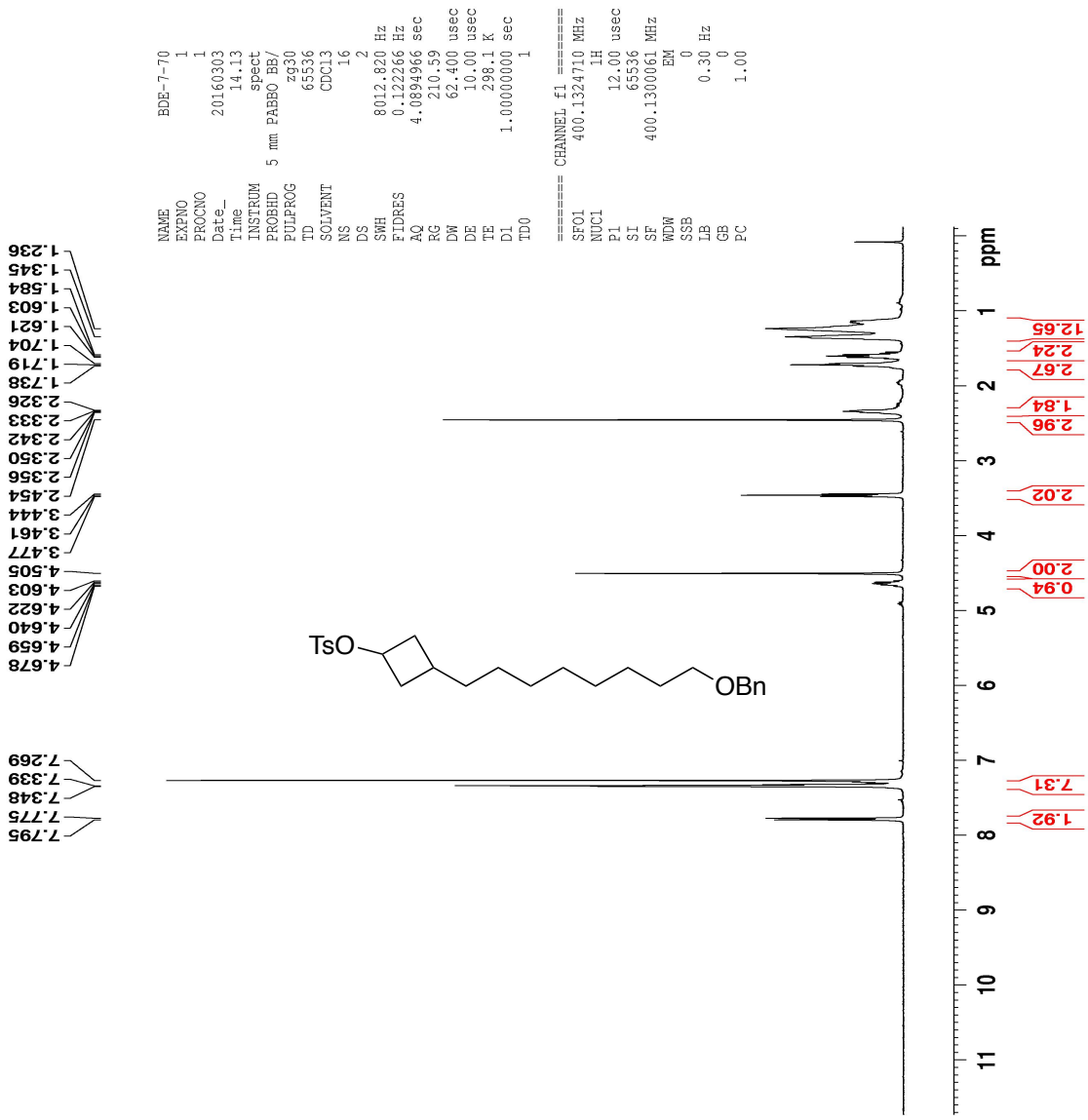

NAME BDE-7-30-Carbon
EXPNO 1
PROCNO 1
Date_ 20151216
Time 13.53
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 53
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 10.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.6127578 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
H2NN
OBn
151.79
138.83
128.45
127.72
127.57
77.51
77.19
76.87
72.97
70.61
39.56
36.56
35.76
29.88
29.65
29.53
28.04
27.67
26.30
ppm
180
160
140
120
100
80
60
40
20

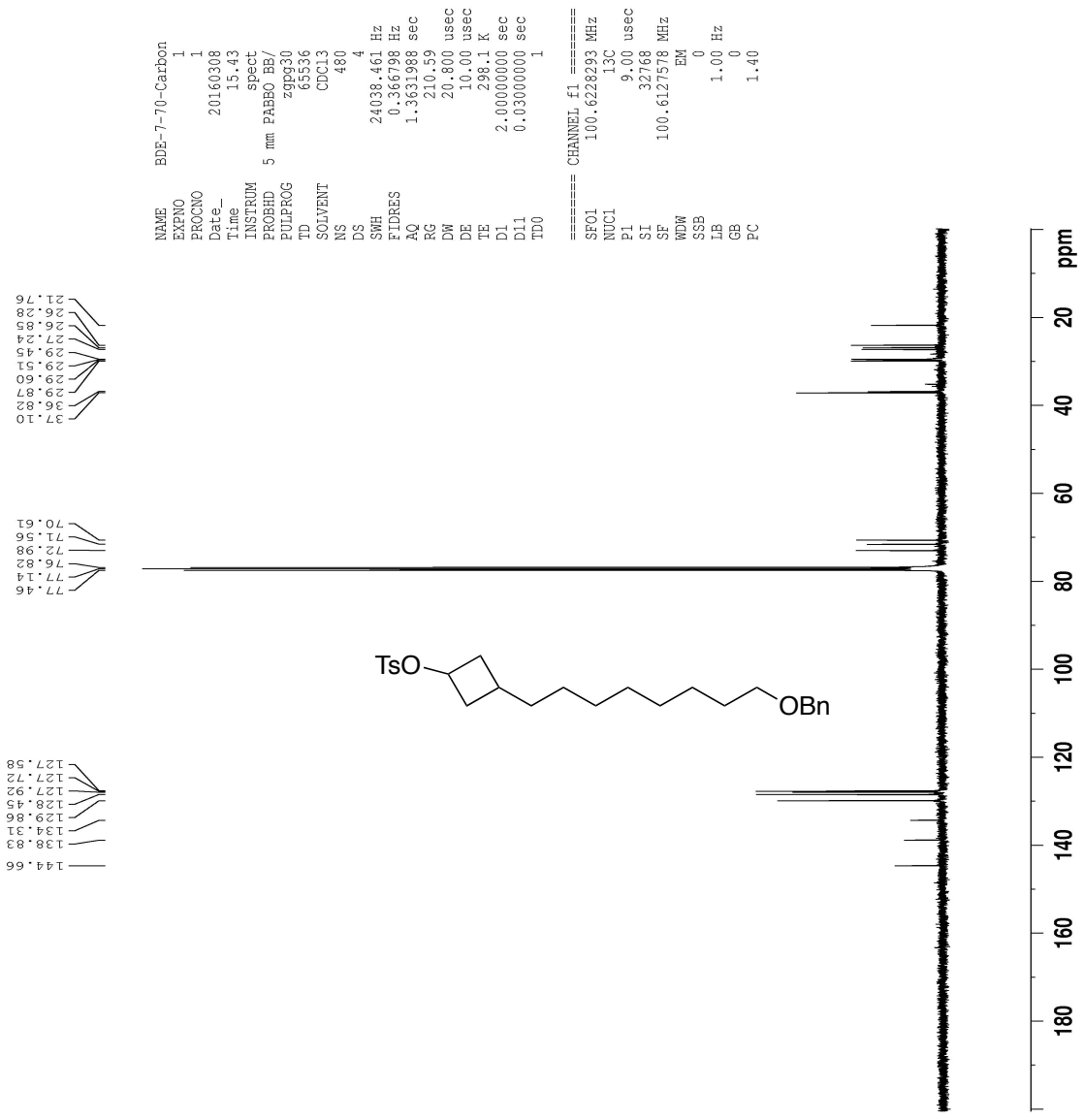

NAME BDE-7-32
EXPNO 1
PROCNO 1
Date_ 20151228
Time 11.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 210.59
DW 62.400 usec
DE 10.00 usec
TE 298.2 K
D1 1.00000000 sec
TDO 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.00 usec
SI 65536
SF 400.1300080 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.615
1.632
1.766
1.787
1.813
1.837
1.854
1.873
1.893
2.548
2.557
2.596
2.613
2.619
2.630
2.642
3.451
3.467
3.483
4.507
5.374
5.392
5.411
5.429
7.264
7.339
S
S
O
OBn
ppm
1
2
3
4
5
6
7
8
9
10
11
12.98
2.18
1.93
0.82
3.06
1.78
2.02
2.00
0.90
4.46

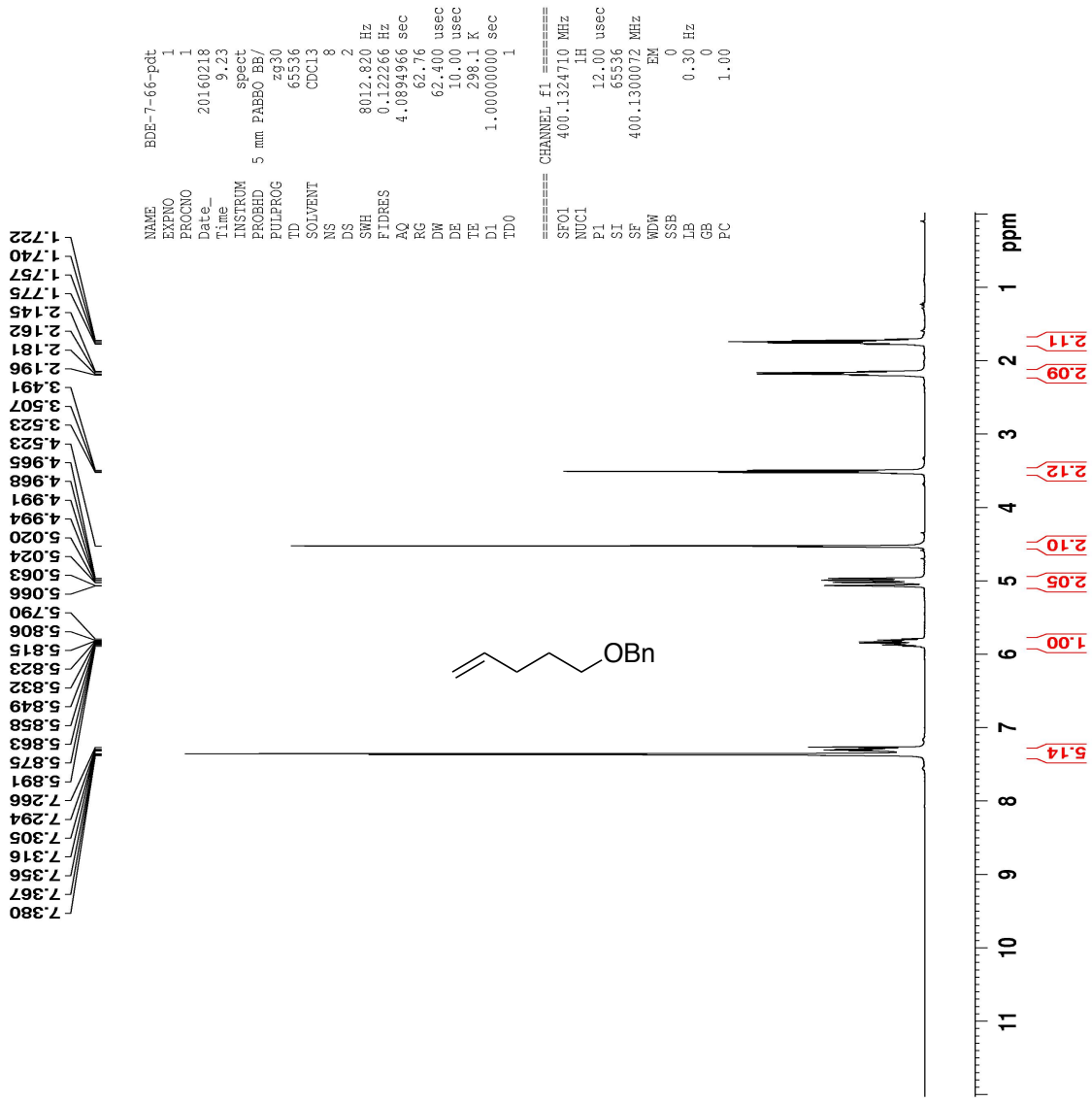

NAME BDE-7-32-Carbon
EXPNO 1
PROCNO 1
Date_ 20151228
Time 12.14
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 184
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 10.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.6127578 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
214.49
138.85
128.46
127.73
127.58
77.48
77.16
76.84
74.69
72.98
70.63
37.12
36.48
34.70
29.89
29.67
29.55
27.34
26.31
19.15
S
S
O
OBn
ppm
200
180
160
140
120
100
80
60
40
20

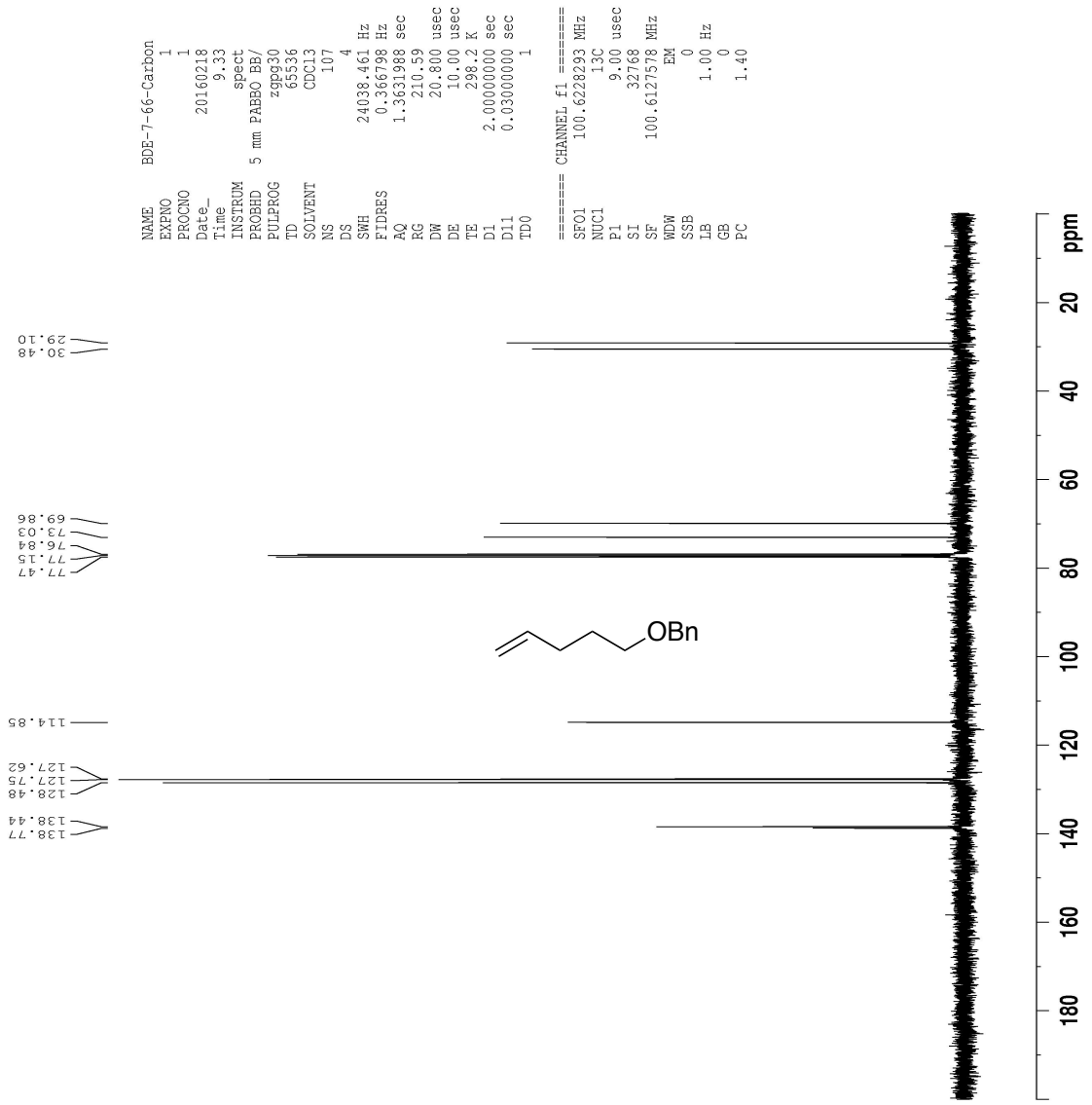

NAME BDE-7-46
EXPNO 1
PROCNO 1
Date_ 20160113
Time 10.15
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 7
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 210.59
DW 62.400 usec
DE 10.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.00 usec
SI 65536
SF 400.1300062 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
MsO
OBn
ppm
11.62
2.47
2.19
2.89
1.95
3.05
2.14
0.99
2.00
4.69
1.275
1.342
1.361
1.432
1.448
1.466
1.581
1.599
1.616
1.634
1.830
1.848
1.867
1.890
1.910
2.551
2.558
2.574
2.970
3.454
3.470
3.486
3.682
4.510
4.804
4.823
4.842
4.859
7.268
7.342
7.353

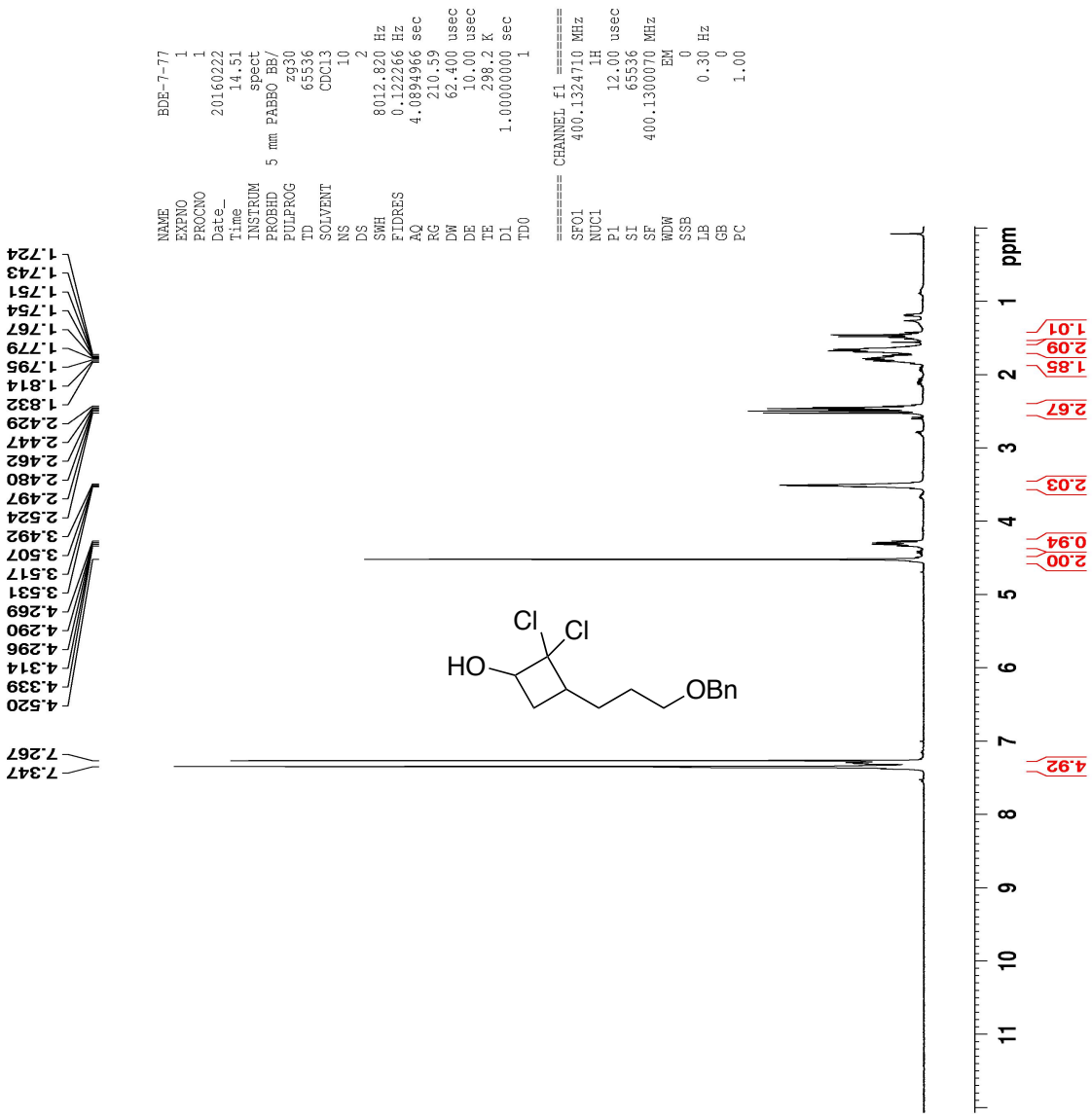

NAME BDE-7-46-Carbon
EXPNO 1
PROCNO 1
Date_ 20160308
Time 18.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 151
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 10.00 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.6127578 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
MsO
OBn
ppm

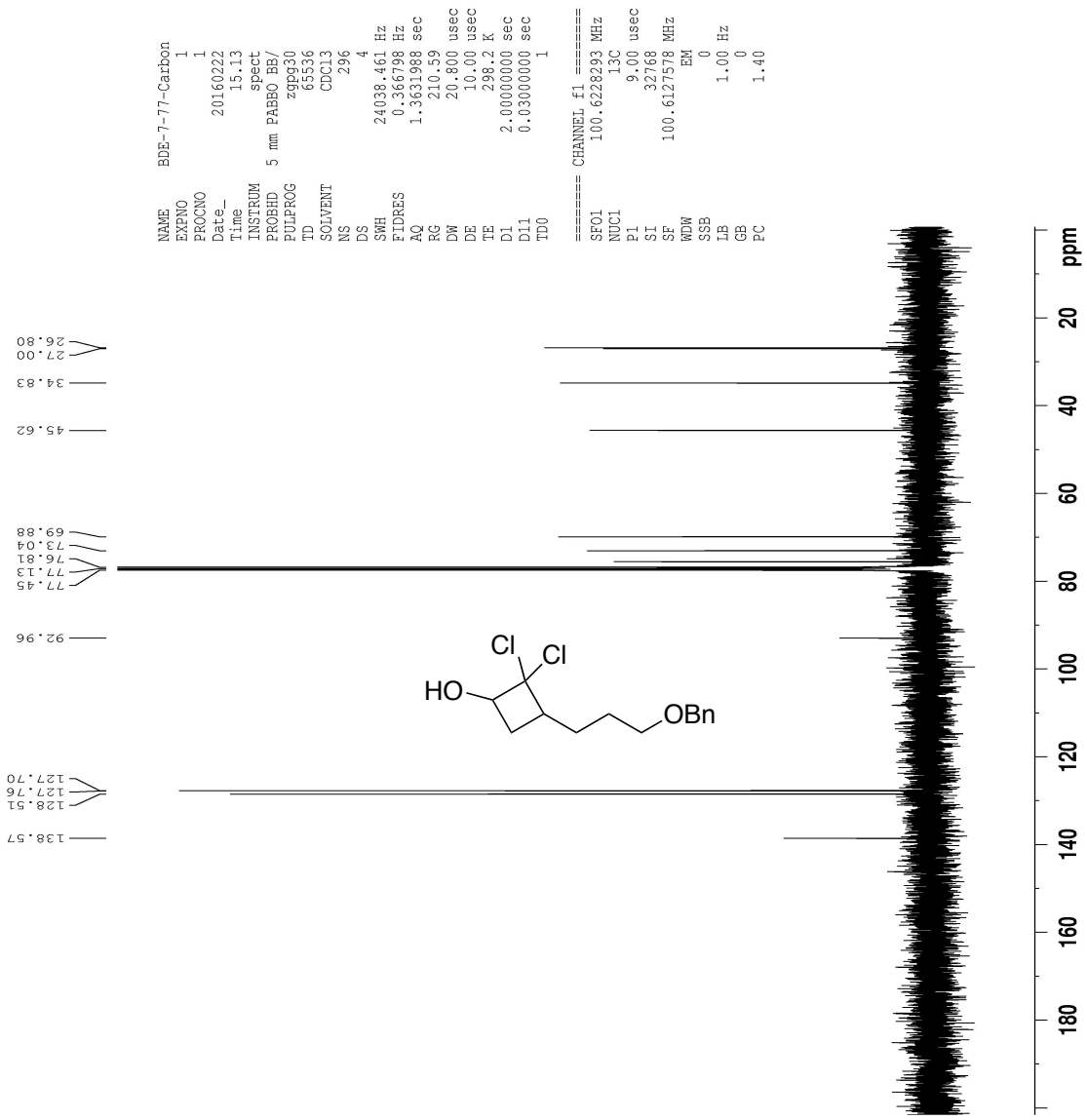

NAME BDE-7-70
EXPNO 1
PROCNO 1
Date_ 20160303
Time 14.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 210.59
DW 62.400 usec
DE 10.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.00 usec
SI 65536
SF 400.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
TsO
OBn
ppm
12.65
2.24
2.67
1.84
2.96
2.02
2.00
0.94
7.31
1.92
1.236
1.345
1.584
1.603
1.621
1.704
1.719
1.738
2.326
2.333
2.342
2.350
2.356
2.454
3.444
3.461
3.477
4.505
4.603
4.622
4.640
4.659
4.678
7.269
7.339
7.348
7.775
7.795

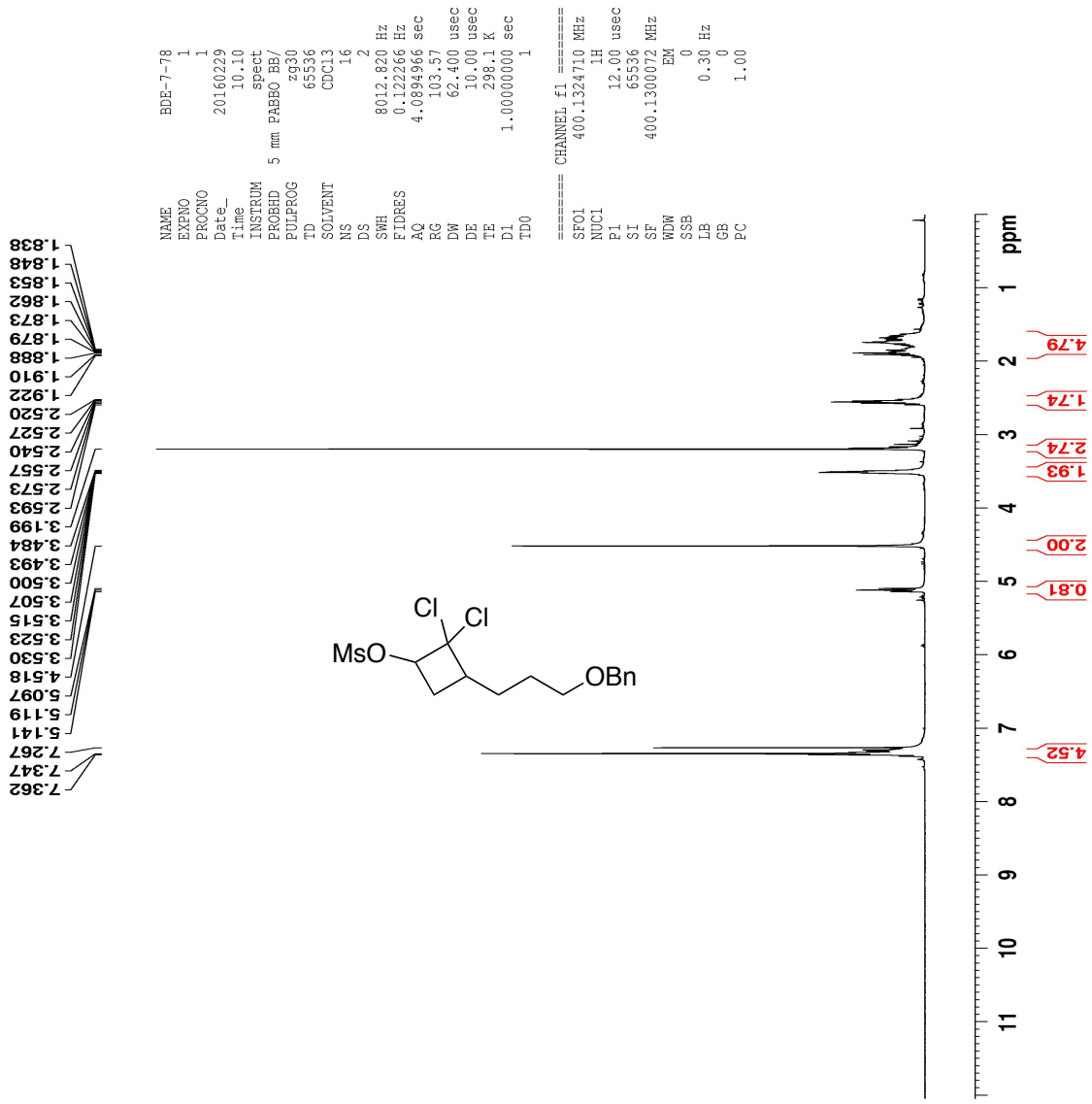

NAME BDE-7-70-Carbon
EXPNO 1
PROCNO 1
Date_ 20160308
Time 15.43
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 480
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 10.00 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.6127578 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
TsO
OBn
ppm

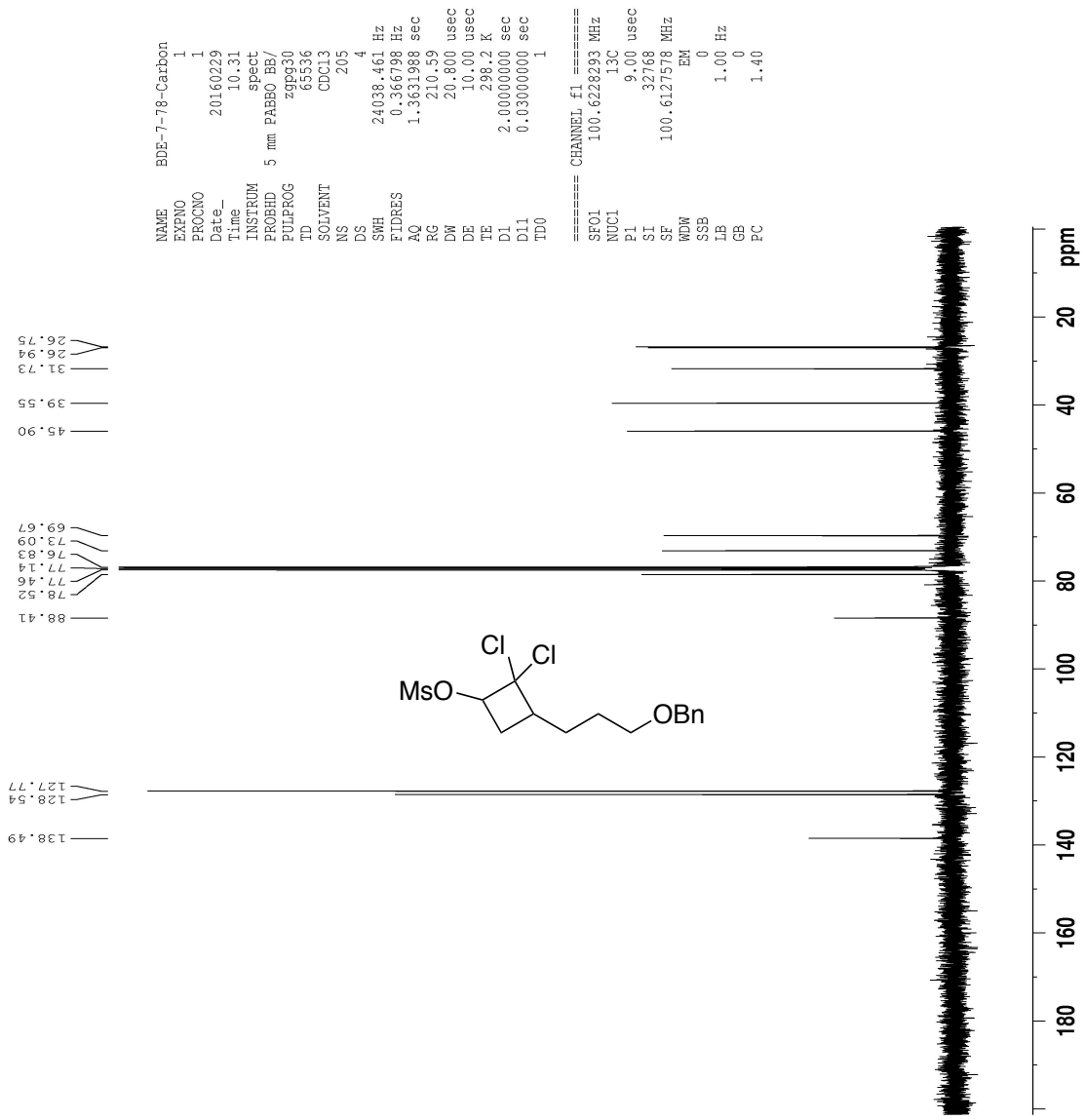

NAME BDE-7-66-pdt
EXPNO 1
PROCNO 1
Date_ 20160218
Time 9.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 62.76
DW 62.400 usec
DE 10.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.00 usec
SI 65536
SF 400.1300072 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OBn
ppm
2.11
2.09
2.12
2.10
2.05
1.00
5.14

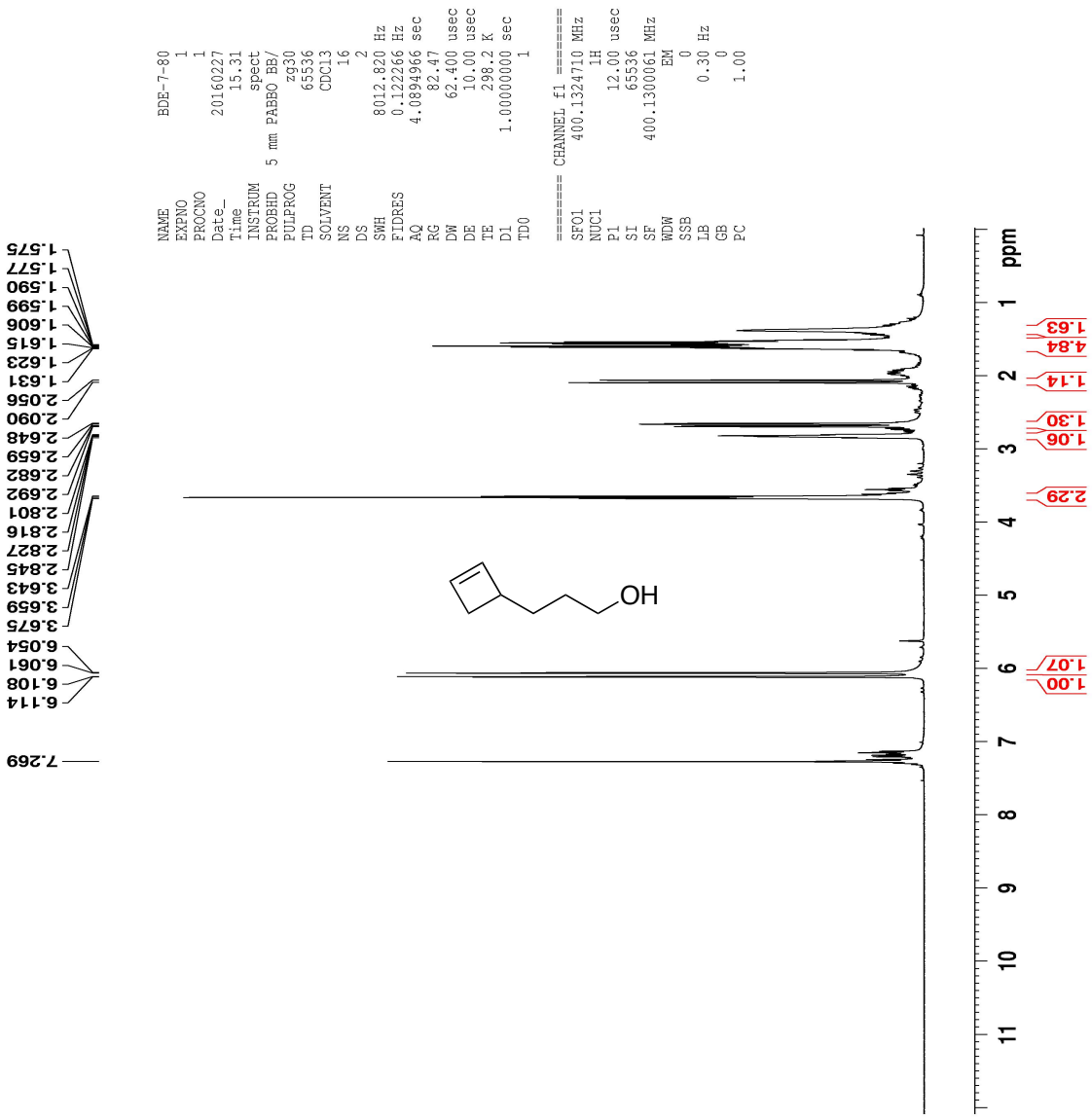

NAME BDE-7-66-Carbon
EXPNO 1
PROCNO 1
Date_ 20160218
Time 9.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 107
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 10.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.6127578 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OBn
29.10
30.48
69.86
73.03
76.84
77.15
77.47
114.85
127.62
127.75
128.48
138.44
138.77
ppm
20
40
60
80
100
120
140
160
180

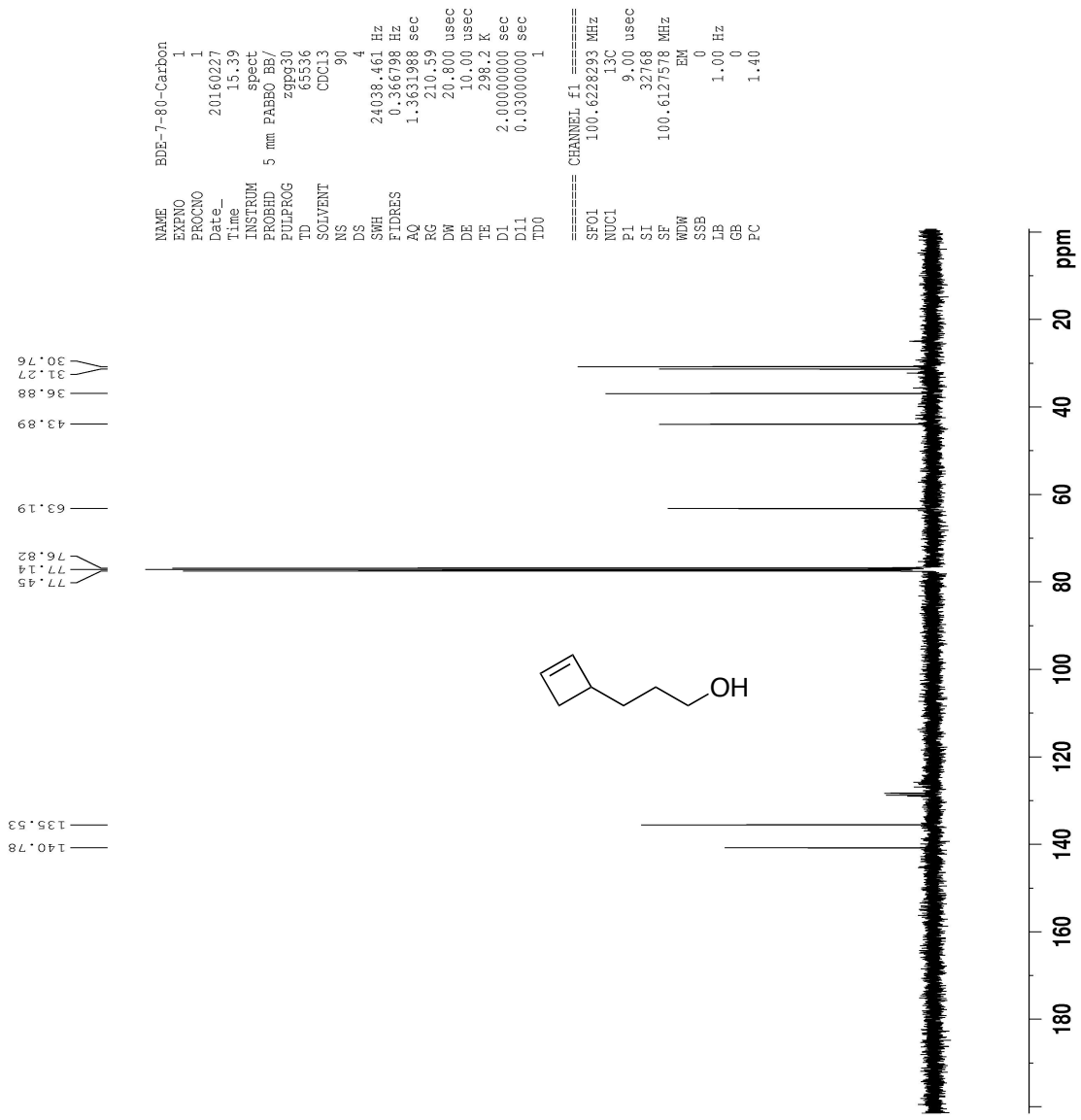

NAME BDE-7-77
EXPNO 1
PROCNO 1
Date_ 20160222
Time 14.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 10
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 210.59
DW 62.400 usec
DE 10.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.00 usec
SI 65536
SF 400.1300070 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Cl
Cl
HO
OBn
ppm
1.01
2.09
1.85
2.67
2.03
0.94
2.00
4.92
7.347
7.267
4.520
4.339
4.314
4.296
4.290
4.269
3.531
3.517
3.507
3.492
2.524
2.497
2.480
2.462
2.447
2.429
1.832
1.814
1.795
1.779
1.767
1.754
1.751
1.743
1.724

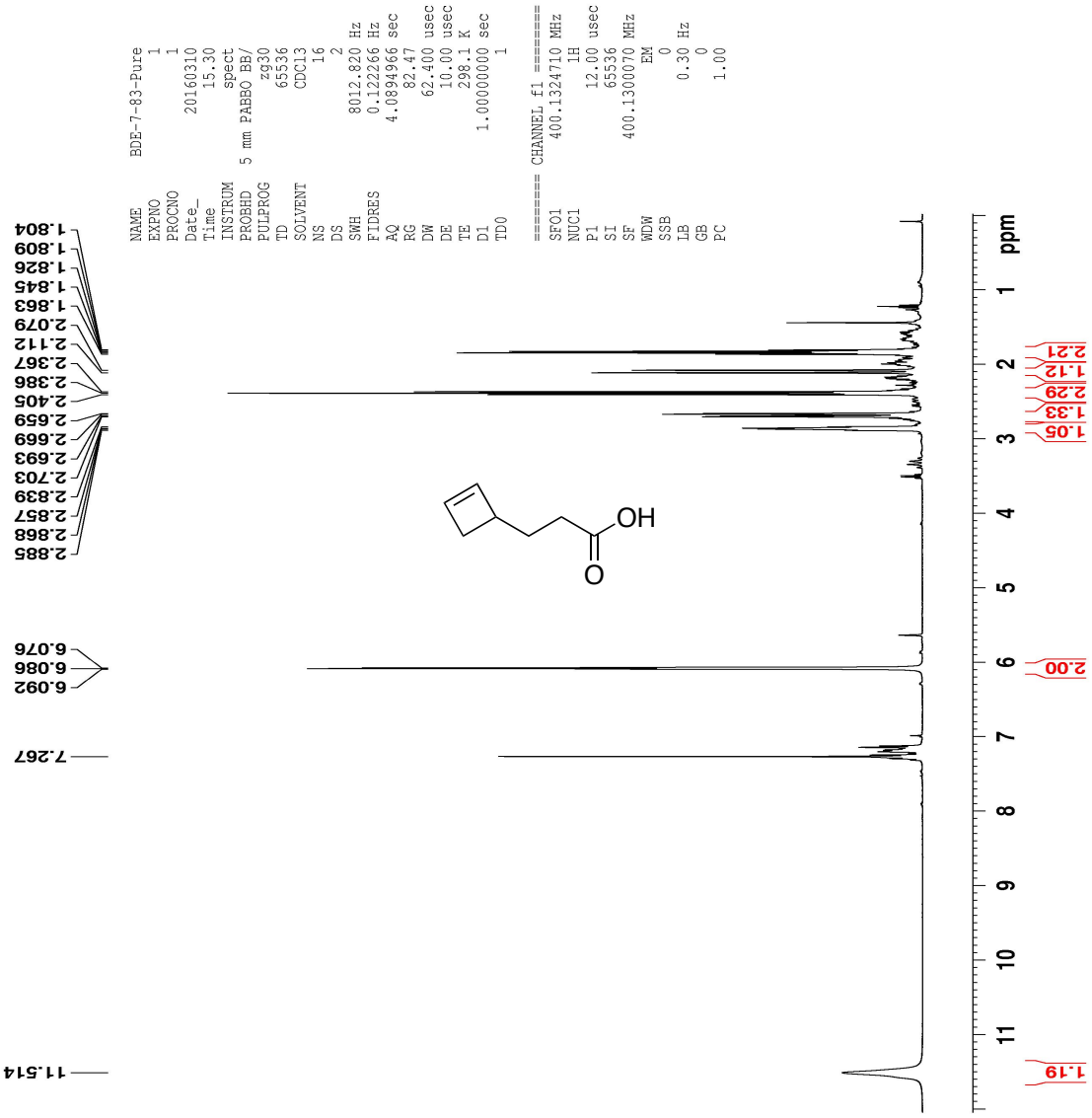

NAME BDE-7-77-Carbon
EXPNO 1
PROCNO 1
Date_ 20160222
Time 15.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 296
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 10.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.6127578 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
26.80
27.00
34.83
45.62
69.88
73.04
76.81
77.13
77.45
92.96
127.70
127.76
128.51
138.57
Cl
Cl
HO
OBn
ppm
20
40
60
80
100
120
140
160
180

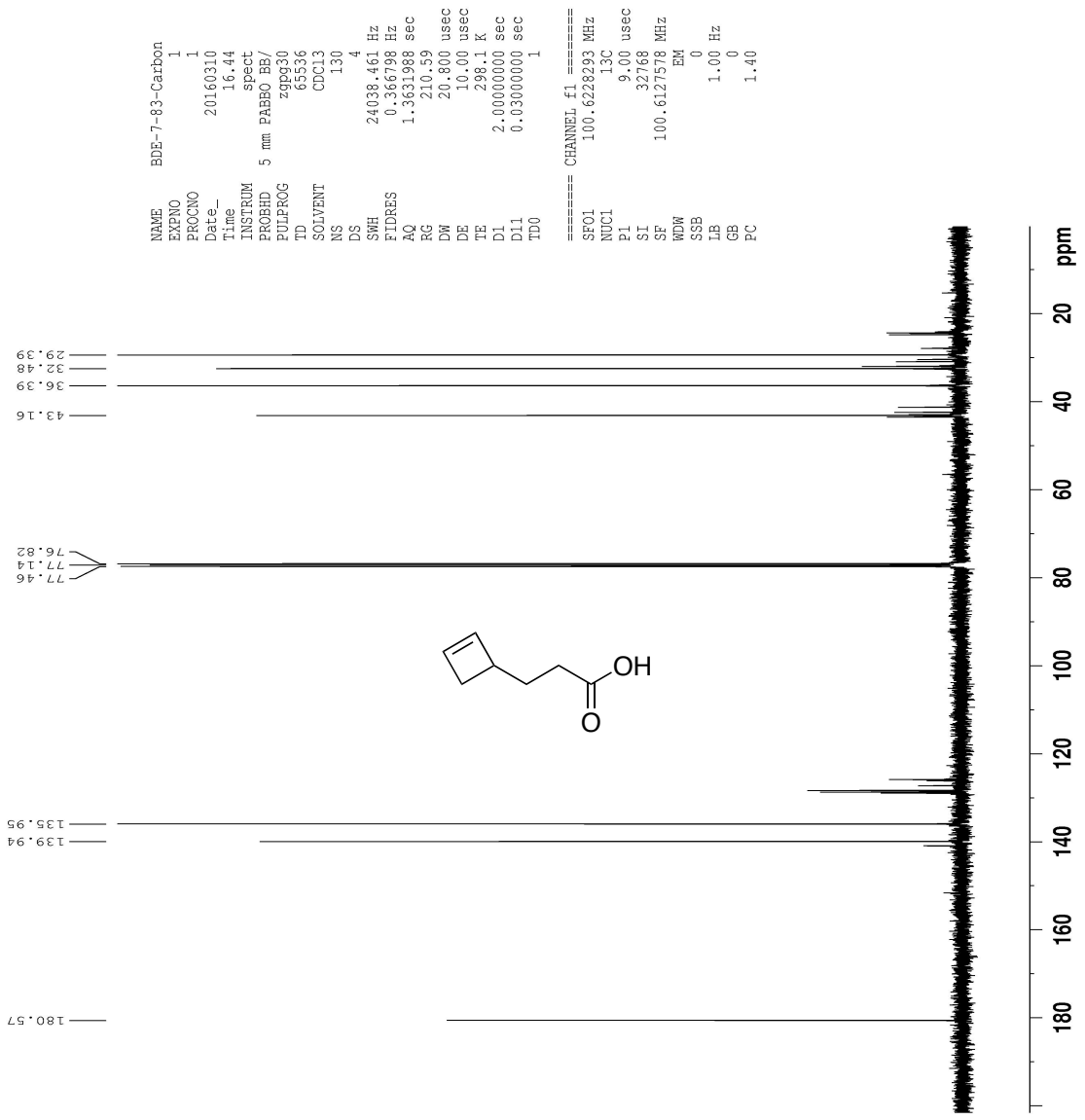

NAME BDE-7-78
EXPNO 1
PROCNO 1
Date_ 20160229
Time 10.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 103.57
DW 62.400 usec
DE 10.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.00 usec
SI 65536
SF 400.1300072 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.838
1.848
1.853
1.862
1.873
1.879
1.888
1.910
1.922
2.520
2.527
2.540
2.557
2.573
2.593
3.199
3.484
3.493
3.500
3.507
3.515
3.523
3.530
4.518
5.097
5.119
5.141
7.267
7.347
7.362
Cl
Cl
MsO
OBn
ppm
4.79
1.74
2.74
1.93
2.00
0.81
4.52


NAME BDE-7-78-Carbon
EXPNO 1
PROCNO 1
Date_ 20160229
Time 10.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 205
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 10.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.6127578 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
26.75
26.94
31.73
39.55
45.90
69.67
73.09
76.83
77.14
77.46
78.52
88.41
127.77
128.54
138.49
Cl
Cl
MsO
OBn
ppm
20
40
60
80
100
120
140
160
180


NAME BDE-7-80
EXPNO 1
PROCNO 1
Date_ 20160227
Time 15.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 82.47
DW 62.400 usec
DE 10.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.00 usec
SI 65536
SF 400.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
ppm
1.63
4.84
1.14
1.30
1.06
2.29
1.00
1.07
1.575
1.577
1.590
1.599
1.606
1.615
1.623
1.631
2.056
2.090
2.648
2.659
2.682
2.692
2.801
2.816
2.827
2.845
3.643
3.659
3.675
6.054
6.061
6.108
6.114
7.269


NAME BDE-7-80-Carbon
EXPNO 1
PROCNO 1
Date_ 20160227
Time 15.39
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 90
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 10.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.6127578 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
30.76
31.27
36.88
43.89
63.19
76.82
77.14
77.45
135.53
140.78
OH
ppm
20
40
60
80
100
120
140
160
180


NAME BDE-7-83-Pure
EXPNO 1
PROCNO 1
Date_ 20160310
Time 15.30
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 82.47
DW 62.400 usec
DE 10.00 usec
TE 298.1 K
D1 1.00000000 sec
TDO 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.00 usec
SI 65536
SF 400.1300070 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
O
ppm
1.804
1.809
1.826
1.845
1.863
2.079
2.112
2.367
2.386
2.405
2.659
2.669
2.693
2.703
2.839
2.857
2.868
2.885
6.092
6.086
6.076
7.267
11.514
2.21
1.12
2.29
1.33
1.05
2.00
1.19


NAME BDE-7-83-Carbon
EXPNO 1
PROCNO 1
Date_ 20160310
Time 16.44
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 130
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 10.00 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.6127578 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OH
O
180.57
139.94
135.95
77.46
77.14
76.82
43.16
36.39
32.48
29.39
ppm
180
160
140
120
100
80
60
40
20