ALKYLATION OF 2,4,5-TRIIODOIMIDAZOLE MOLECULES

by

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Thank you Dr Handy. Thank you committee members. Thank you Zach for helping me and being my best lab mate. Thank you mommy. Thank you best friends and sisters. Thank you MTSU chemistry staff. Couldn't have done it without every single one of you.

ABSTRACT

Alkylated 2,4,5,-triiodoimidazole molecules could be of interesting in a variety of situations, including pharmaceuticals and complex molecule synthesis. The most obvious route to such compounds is the alkylation of 2,4,5-triiodoimidazoles with alkyl halides. Interestingly, little has been reported in this area. In conjunction with our interest in highly iodinated compounds, we undertook a study of this alkylation. Reactions of various types of alkyl halides were studied. In most cases, reactions were performed at room temperature in dimethylformamide (DMF) with potassium carbonate, although some less reactive alkyl halides required heating. The future goal is to use these alkylated triiodoimidazoles in energetic and biological applications. In an attempt to synthesize energetic binders to replace current isocyanate-based binders, my target begins with 2,4,5-triiodoimidazole which is alkylated on one of the nitrogens using allyl bromide. The tethered alkene can be later used to crosslink the final polymer, replacing the isocyanate crosslinker. These energetic binders make transporting volatile materials safer. This stabilization is provided by a surrounding structure of the binder molecule, that upon crosslinking will combine to become larger units. The resulting matrix makes the explosive more thermodynamically stable by being able to absorb more shock.

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CHAPTER ONE

INTRODUCTION

1.1 Background

Binders in explosives are polymers whose purpose is to bind/surround explosive materials. They are used to make the explosive material more stable when being transported and handled. This stabilization is provided by a surrounding structure of the binder molecule, that upon crosslinking will combine to become larger units.[1] The resulting matrix makes the explosive more stable by being able to absorb more shock (Figure 1).

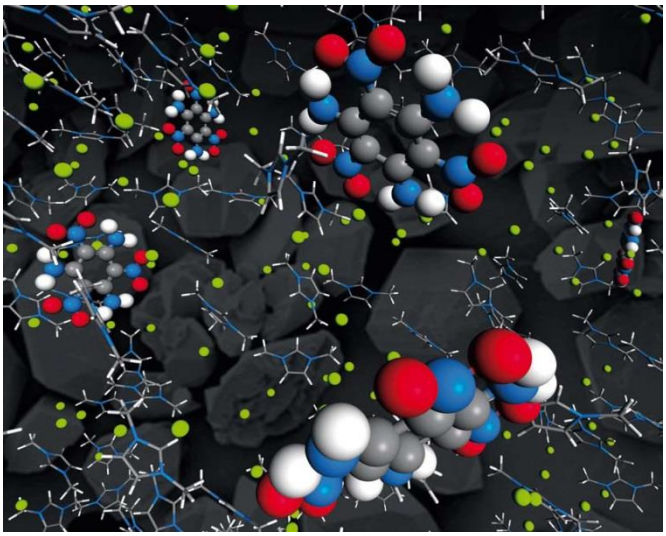


Figure 1: 3D representation of polymer binders.

Image courtesy of Lawrence Livermore National Laboratory

One of the earliest binders used in energetic materials was a mixture of nitrocellulose and nitroglycerine, where the nitrocellulose was used to thicken the nitroglycerine and reduce impact and friction sensitivity.[2] Explosives, when handled, undergo small buildups of temperature called hotspots that are caused by the explosive material being exposed to friction.[3] Hot spot temperature determines sensitivity. As hotspot temperatures grow they can lead to an irreversible increase in temperature which most likely will end in an accidental detonation of the explosive. To decrease hot spot temperatures, there would have to be an increase in surface area to which the hotspot material is exposed. Integrating binders gives a low density charged surface area to which the explosive material is exposed.[3] Binders provide a small pore size of increased surface area, which decreases the amount of exposure that the explosive materials receive before inducing detonation. When the explosive gets hotspots, the temperature output cannot increase past the small pores in the surface area of the binder and this effect decreases sensitivity. An increase in surface area means a decrease in hotspot temperature which leads to a decrease in shock sensitivity.

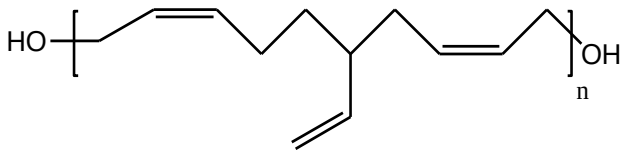


Figure 2: Hydroxyl terminated polybutadiene (HTPB)

Figure 2 represents a popular binder, hydroxyl terminated polybutadiene (HTPB), that encapsulates explosive material with HTPB acting as a binder, cross-linked with isocyanates, and containing a plasticizer.[1] The isocyanates in the binder act as the cross-linker. The cross-linker will react with a hydroxyl to form an amide and results in a partially interpenetrating network.[3] The included plasticizer improves the physical properties of an energetic material by increasing elasticity while having force applied to it.[4] The role of plasticizer is to provide durability because of the importance of the explosive material remaining inert from creation to detonation. Dibutyl phthalate (DBP) is a commonly used inert plasticizer (Figure 3).

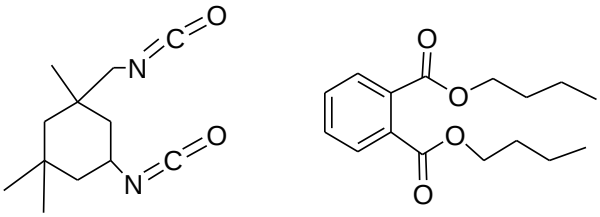


Figure 3: Isophorone diisocyanate and dibutyl phthalate (DBP)

While these binders add valuable physical properties to explosives in regard to safety, they also make the molecular weight heavier for the entire explosive device while providing no increase in energy output. This in turn means more of the sensitive material is needed to get the same amount of energy output as the device gave before the binders were integrated. For example, HTPB requires a theoretical solids loading of 92% by weight of ammonium perchlorate

for complete combustion, but 15-20% of binder is required to prepare a processable formulation.[1] If space needs to be made for the binder then this will require some space for explosive material to be taken away. Less space for the volatile compound means less explosive compound. With the addition of a binder there will need to be more explosive material added to achieve maximum combustion. This additional material which will affect cost of production and also increase danger of production because there will need to be handling of more hazardous materials.

1.2 Energetic Binder Development

Although these binders improve the safety conditions, they also decrease the output of energy for an explosive device. Since a molecular component is being added to explosives there was further research to see if this component could aid the entirety of the explosive itself, particularly by increasing the power output of the device. This would allow less explosive material to be used while obtaining the same energy output. These materials would be termed energetic binders because of their original function as a binder and secondary function as an energetic. In order to be an energetic binder, the molecule would need to contain multiple double and/or triple bonds. When double bonds and triple bonds are broken and new triple and double bonds are formed this produces a large amount of energy. To compare the values of bond energy that is created after the formation a new bond, the table below shows the value of many single, double and triple bonds [5]. Not all bond pairs are used for energetic binders. Compounds

that contain multiple nitrogen bonds have small activation energy, but breaking them apart and reforming nitrogen gas is large exothermic reaction. Triple bonded nitrogen gas is the highest value on the table. Carbon-carbon bonds, carbon-nitrogen, nitrogen-oxygen, nitrogen-hydrogen and nitrogen-nitrogen are among the most popular in energetic binder research. An ideal explosive would require a substantial but easily achievable force to detonate the device.

Table 1: Bond energies [5]

Bond	Bond Energy (kJ/mol)
N ≡ N	941
C ≡ C	812
C ≡ N	891
N = N	418
C = C	620
O – H	460
C - H	414
C - O	351
C - N	276
N - N	193
C - C	347

The values in the chart correlate to this information by displaying the highest values for double and triple bonds. The values in the chart are commonly used bonds in energetic molecule synthesis. Early energetic binder development with multiple bonded elements included researching azido-functionalized polymers such as glycidyl azide polymer (GAP) [Figure 4]. This was one of the first energetic polymers developed.[6] The table above shows some of the bonds that are present in the molecule GAP, among other bonds that are often used in energetics research. To test the effectiveness of an energetic binder molecule such as GAP, it would be compared to another similar inert binder. What these comparisons do is show that the energetic binder is just as stable as an inert binder. The molecule GAP was compared to HTPB in a device filled with cyclotrimethylenetrinitramine, a popular explosive and both yielded the same safety output values.[6] The advantages of using GAP over HTPB is that GAP provides a secondary energy yield while performing as a binder , whereas HTPB is only an inert binder molecule.

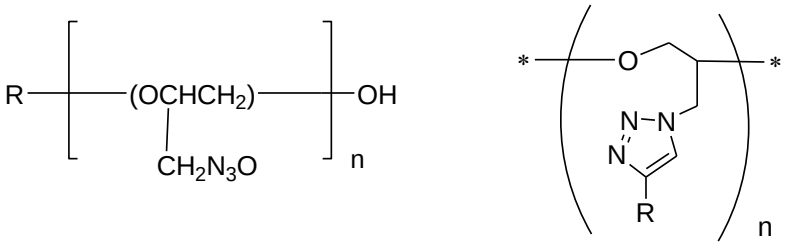


Figure 4: Glycidyl azide polymer (GAP) (left), the skeletal structure of GAP (right)

1.3 Click Chemistry

First generation energetic binders, such as GAP and related materials containing azides were certainly successful from an energetic standpoint. At the same time, azides display limited stability. In particular, when subjected to shock, these compounds decompose in a highly exothermic reaction. Such sensitive molecules to shock are not desirable, and a more stable alternative is highly desirable. In addition, azides are also toxic. When mixed with certain solvents, azide containing molecules decompose to produce a toxic gas (hydrazoic acid). On the other hand, triazoles could serve as a stable and non-toxic alternative to azides. Triazoles contain nitrogen-nitrogen multiple bonds that, when decomposed and reformed to make nitrogen gas would give off higher energy than carbon-carbon bonds. This is particularly true of compounds containing nitrogen, since the product of decomposition is nitrogen gas, an extremely stable compound, as evidenced by the bond dissociation energy value from Table 1 of 941 KJ/mol. Thus, much more energy is released compared to the combustion of simple C-C bonds. Further, the formation of nitrogen gas as the combustion product avoids the production of smoke and soot, which often result from the combustion of all-carbon materials. Decreased smoke and soot formation is a clear and obvious advantage in military applications.

The question that needed addressed was how to make these multiple nitrogen bond cyclic molecules using a simple mechanism that can be applied in every lab. This was answered with click chemistry. Click chemistry was first

introduced by Sharpless and coworkers in 2001 as a new development to drug synthesis.[7] The goal was to develop a reaction that was easy to perform with readily available materials that are unreactive with oxygen and water, that would also be stereospecific, and be easily performed under simple reaction conditions.[7] Click chemistry allows small structural units to be combined together to make larger molecules. Of the many potential "click reactions", the combination of alkynes and azides in a 1,3 dipolar cycloaddition (shown below) has become the most popular and versatile and is now generally simply referred to as a "click reaction" (Figure 5).

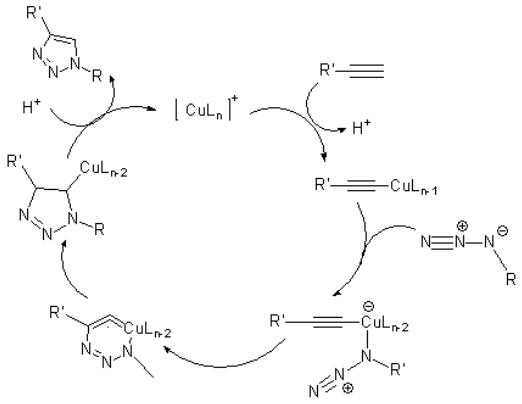


Figure 5: 1,3 dipolar azide-alkyne cycloaddition

In this "click" reaction, a 1,3-dipolar cycloaddition is performed between a 1,3-dipole and a dipolarophile to form a five-membered ring.[8] The mechanism involves 2 π-electrons of the dipolarophile and 4 electrons of the dipolar compound moving in a pericyclic fashion (Figure 6). Figure 7 gives a closer look

at the specific pericyclic mechanism with an organic azide and an alkyne to generate 1, 2, 3-triazole.

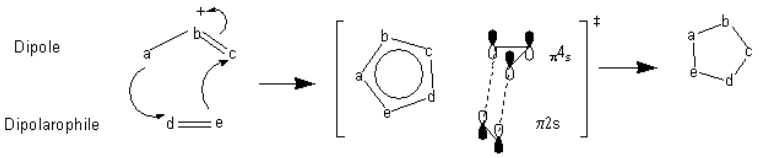


Figure 6: Electron transfer in Dipole and Dipolarophile

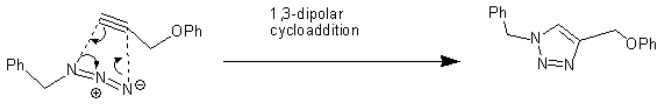


Figure 7: Azide pericyclic mechanism with an alkyne

Along with ease of synthesis and using readily available materials, click chemistry can readily be made regiospecific by means of a copper catalyst. This is termed a Copper-catalyzed Azide–Alkyne Cycloaddition (CuAAC).[9] The regiospecificity of the click mechanism yields exclusively the 1,4-regioisomer of the 1,4-disubstituted 1,2,3-triazoles as the final product.

1.4 Polymerization

Triazoles have been gaining use in the energetic materials sciences more recently by utilizing them as derivatives. 1,2,3-triazole crosslinked polymers have been explored for potential use as a binder system while utilizing polycaprolactone ether (PCE) prepolymer.[10] These potential binders for use in solid rocket propellants were prepared by mixing an azide chain-terminated diazide prepolymer, a dipolarophile curing agent, which acts as a crosslinker, and a plasticizer with an alkyne bond.[10] Results from this study concluded that the binder network prepared from the PCE prepolymer collapsed due to its low degree of crosslinking.[10] Without the crosslinking providing the backbone of the molecule structure then there is no formation of a true binder. Having a low degree of crosslinking means there is a problem in keeping proper shape for the device. Without proper shape then there is no functionality of the binder molecule.

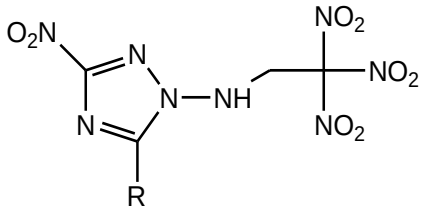


Figure 8. N-Functionalized nitrotriazoles

Beyond applications in binders, triazoles have also been explored as alternatives to traditional energetics. In particular, N-functionalized nitrotriazoles

(Figure 8) showed adequate to exceptional thermal stabilities with good density qualities as well.[11] Collected data based on impact and friction tests show that these compounds range from very sensitive to insensitive. Theoretical calculations were carried out using Gaussian 03 to demonstrate admissible to excellent detonation pressures and velocities, however there have been some cited limitations to triazole energetic research. The energetic derivatives of 5-nitro-1,2,3-2H-triazole, which include 2-(methyl or amino)-4-(nitramino, azido, or nitro)-5-nitro-1,2,3-2H-triazoles, were prepared in only moderate yields (Figure 9).[12]

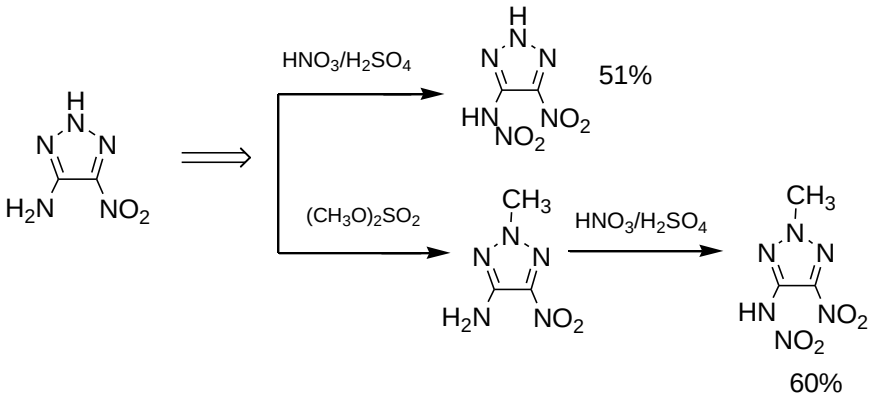


Figure 9. The energetic derivatives of 5-nitro-1,2,3-2H-triazole

Returning to the idea of energetic binders, the first step is polymerization of the molecule so that it can form a repeating chain of modular units. The use of alkenes is popular in polymerization because of the stability of the resulting carbon-carbon bond.[13] Molecules are linked using the alkene functional group. All the identical binder monomers undergo a process where an activated monomer

(containing a radical) attacks and attaches to the double bond of another monomer molecule.[13] This process links the binder molecules together again and again to form a chain. These chains of polymers are then held together by a backbone that contains carbons (Figure 10).

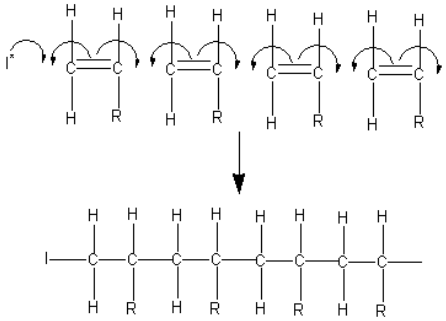


Figure 10: Polymerization of an alkene

1.5 Crosslinking Polymers

After formation of the desired polymer, the next stage in forming a binder is crosslinking. This is performed after individual modular units are polymerized and shaped into a chain. These chains are then crosslinked to form a matrix for the explosive material. Crosslinking is a mechanism whereby bonds are formed that link one polymer chain to another.[14] This is done to synthetic polymers to generate a difference in physical shape or property (see Figure 11), particularly improving rigidity and/or melting point. Figure 11 shows a polyepoxide example that demonstrates the change in physical properties that crosslinking can provide. The molecule began as a solid and was eventually transformed into a gelled solid

because of the chemical crosslinking. This type of polymer curing may be achieved by reacting an epoxy with itself, called homopolymerisation, or by the formation of a copolymer with polyfunctional curatives.[15] When the reactive groups link together to form the chain extensions they begin to build molecular weight, meaning the crosslinkers start to build a network that leads to a rapid rise in molecular weight and thus the increase in viscosity. These changes in bonds change the physical properties of the molecule, providing higher chemical and temperature resistance. Figure 12 demonstrates the before and after of a polymer chain with thiol reactive groups that are parallel to one another. An oxidation reaction creates a link between the two chains allowing them to be one larger linked structure.

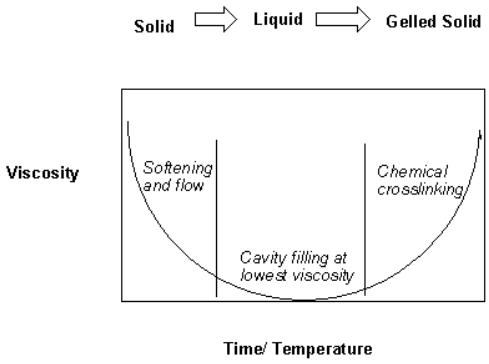


Figure 11: Demonstration of change in polyepoxide

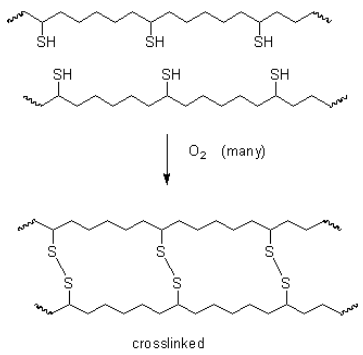


Figure 12: Crosslinking under oxidation with a polymer chain containing thiol bonds

Methods used to initiate crosslinking range from heat exposure, pressure, radiation exposure or a change in pH.[14] This mechanism employs the polymers to become tied together in a network. When binders form that polymer network and an explosive material generates a hotspot, the temperature output cannot increase past the small pores in the surface area of the binder that has become more stable through chemical crosslinking. The hotspot also cannot release in any way around the matrix because the binder network is surrounding. When all the polymer molecules are linked together they aren't easily broken apart from one another, providing stability to the compound. Figure 13 shows the polymerization and crosslinking of the previous discussed binder HTPB.

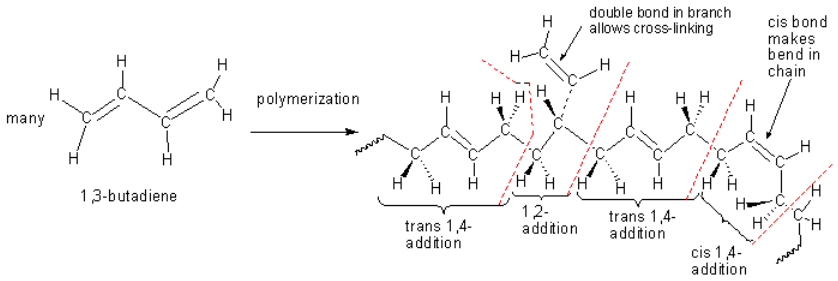


Figure 13: HTPB polymerization and crosslinking

1.6 Current Problems in Energetic Binder Research

Multiple bond containing monomers are a target product material in energetic binder synthesis. The more bonds, the more stable the molecule is. At the same time, most existing energetic binders (such as GAP in Figure 4), are simply azide-functionalized versions of traditional polymers. As a result, the crosslinking of these polymers has been reliant on the reaction of alcohols in the polymers with isocyanates. (Figure 14). The crosslinking isocyanates are volatile and toxic and are able to react with moisture in the environment or with change in temperatures. As such, they are often used in excess for crosslinking purposes. This results in unreacted isocyanate being present and creates a clear hazard to both personnel and the environment. Indeed, isocyanates have been phased out of commercial use in plastics and in environmental products. A classic example of the removal of isocyanates from both products and processes is that of Sevin, a pesticide or insecticide that has been banned from use because of use of harmful isocyanates in its production (Figure 15).[16] This has formulated a need to research and synthesize non-isocyanate containing energetic binders that are energy output

efficient and cost effective. This is why alkenes have been studied as an alternative to using these isocyanate crosslinkers. They are safer and easily attainable. Alkenes have been used successfully in crosslinking research. There was reported success in copolymerization while using alkenes for monomer mixtures of poly(OEPMOB-co-1-hydroxy-2-methoxybenzene, which resulted in a crosslinking conjugated network.[21]

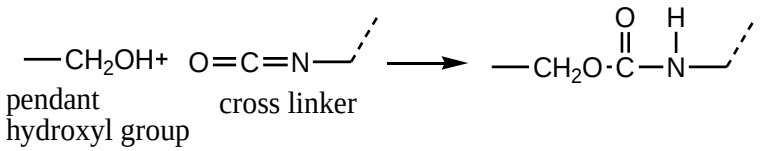


Figure 14: Isocyanate crosslinkers

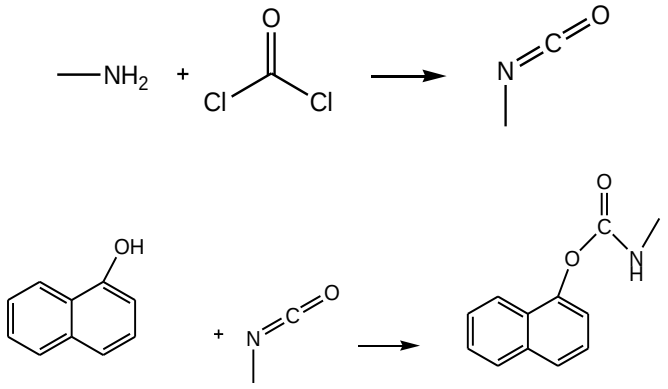


Figure 15: Use of isocyanate in the synthesis of Sevin

In addition to hazard concerns, energetic binder synthesis also often involves time-consuming methods and sometimes many materials. There are many reasons why a simpler synthesis with less steps and isolation extractions is needed. Using the synthesis of the popular energetic binder 3,3-bis(3-

azidomethyl)oxetane (BAMO) as an example (Figure 16), most energetic binders are time-consuming, labor-intensive, costly projects. BAMO requires the production of a precursor, 3,3-bis(chloromethyl)oxetane (BCMO), before the molecule BAMO can be made. Making the precursor requires refluxing, distillation, separation, and filtration. Some of these steps require heating and some require a running water condenser that adds to cost of production. Some steps can also take up to 24 hours to complete. After the creation of the precursor then the synthesis of BAMO can start which requires heat and a 24 hour reaction period with isolation techniques following.

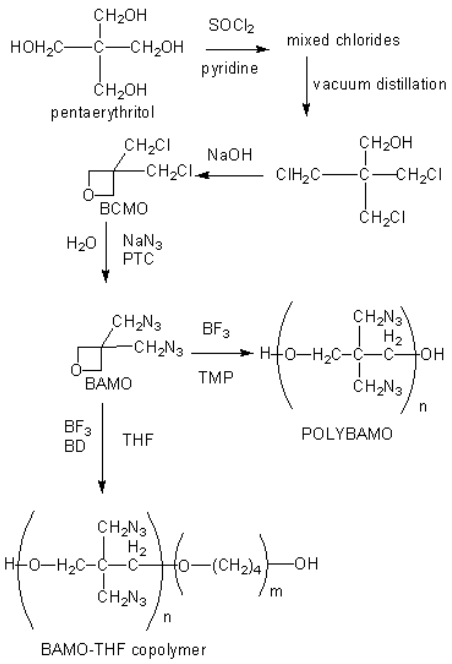


Figure 16: Synthesis of BAMO

1.7 Current Research Approach

The focus of current research falls on improving synthesis methods and avoiding the need to use isocyanate cross-linkers, while also generating a polymerizable small molecule with considerable thermodynamic energy built in.

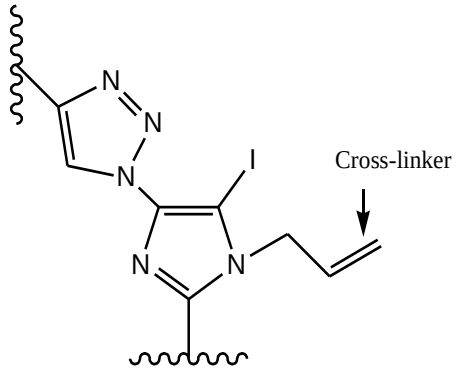


Figure 17: Proposed energetic binder structure

Figure 17 represents the focus of this research. The target molecule uses no isocyanate bonds as cross-linkers but instead is a high nitrogen content molecule that is energy rich. Triazoles were a competent replacement in that they also contain multiple double bonds and nitrogen elements. The triazoles would be formed via a 1,3 dipolar azide-alkyne cycloaddition using an azide that is formed via copper-catalyzed *in situ* azidation of the iodoimidazole. This would provide the energy rich components that are being utilized in energetics yet are non-toxic and also stable.

Steps forming the monomer precursor include an alkyl halide substitution followed by alkyne substitution with one of the substituent iodines on the

imidazole. The tethered alkene will perform as the non-toxic alternative to the isocyanate cross-linker.

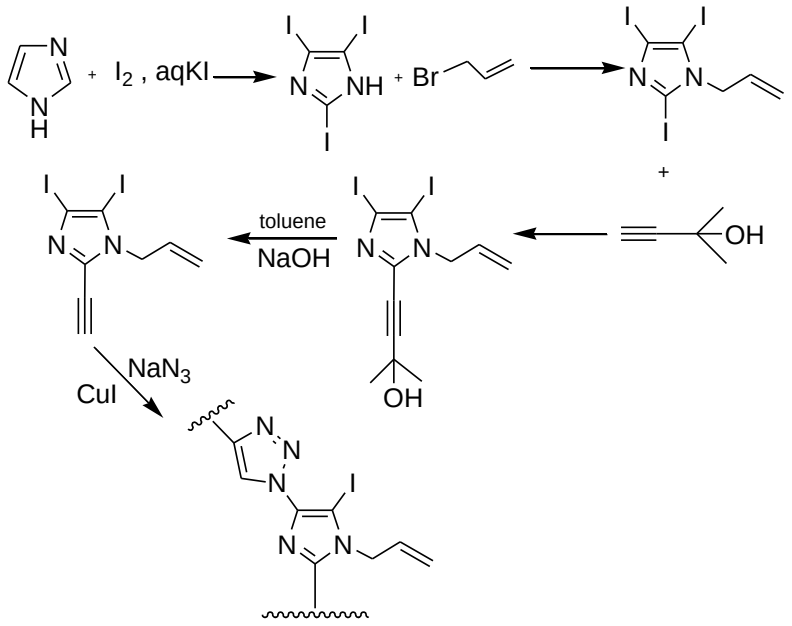


Figure 18: Proposed synthesis of target molecule

Every step is performed in a round bottom flask with or without heat including a stir bar and pre-determined amount of time that ranges between 6 and 12 hours (Figure 18). This improves the amount of time consumed by these reactions. Reactions which are completed in one flask (such as the azidation and polymerization) will provide additional benefit as there is no need for isolation and handling of the intermediate azide.

CHAPTER TWO

EXPERIMENTAL

All ^{1}H NMR spectra were collected using a JEOL 500 MHz spectrometer with the chemical shifts values reported in δ (ppm) relative to TMS. ^{13}C NMR spectra were collected using a JEOL 500 MHz spectrometer and values are reported in δ (ppm) relative to the TMS signal. Infrared spectra were taken using a Varian 800 FT-IR. Mass spectroscopy was performed using a Liquid Chromatography Mass Spectrometer with ethanol as the eluting solvent.

Compound Diallylated 2,4,5-triiodoimidazole (1)

To a vial was added 2.00g (4.12mmol) of 2,4,5-triiodoimidazole, 542.8 mg (4.50 mmol) of allyl bromide, and 10.0 mL of acetonitrile. The reaction was left on a hot plate with stirring overnight at 80°C. After cooling, the reaction was diluted with ethyl acetate (50 mL) and extracted with water (50 mL). The formed solid was filtered with Hirsch funnel under vacuum and washed with water to afford an off white solid. ^{1}H NMR (500 MHz, Dimethyl sulfoxide-D6) 6.05-5.91 (m, 1H), 5.37 (d, J = 15 Hz, 1H), 5.20 (d, J = 25 Hz, 1H), 4.85 (d, J = 10 Hz, 2H). LC-Mass Spec M+1 401.0.

1-allyl-2,4,5-triiodo-1H-imidazole

To a vial was added 500 mg (1.12 mmol) of 2,4,5-triiodoimidazole, 155 mg (0.56 mmol) of potassium carbonate, 135.7 mg (1.12 mmol) of allyl bromide, and 10.0 mL of N,N-dimethylformamide (DMF). The reaction was left on a hot plate with

stirring for 10 hours at room temperature. After cooling, the reaction was diluted with water (30 mL) and extracted with ethyl acetate (30 mL). The organic layer was separated and the solvent removed *in vacuo*. The resulting material was purified via column chromatography using 30% ethyl acetate in hexanes as eluent to afford 300 mg (55%) of the desired product as a white solid. mp = 115-117 °C, ^{1}H NMR (500 MHz, Acetone-D6) 5.89-5.86 (m, 1H), 5.24 (d, J = 10 Hz, 1H), 4.88 (d, J = 15 Hz, 1H), 4.76 (d, J = 10 Hz, 2H), ^{13}C NMR (125 MHz, Acetone-D6) 131.7, 117.3, 97.1, 91.2, 85.33, 53.87. IR (neat) 3085, 2926, 2854, 1644, 1442, 1386, 1357, 1173, 1114 cm^{-1}. LC-Mass Spec M+1 486.67.

1-ethyl-2,4,5-triiodo-1H-imidazole[22]

To a vial was added 200 mg (0.449 mmol) of 2,4,5-triiodoimidazole, 31.02 mg (0.224 mmol) of potassium carbonate, 70.00 mg (0.449 mmol) of iodoethane, and 5.0 mL of N,N-dimethylformamide (DMF). The reaction was left on a hot plate with stirring for 10 hours at room temperature. After cooling, the reaction was diluted with water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was separated and the solvent removed *in vacuo*. The resulting material was purified via column chromatography using 30% ethyl acetate in hexanes as eluent to afford 136 mg (64%) of the desired product as an yellow oil. ^{1}H NMR (500MHz, Acetone-D6) 4.17-4.13 (q, J =6.85 Hz, 2H), 1.28-1.25 (t, J =7.45 Hz, 3H). ^{13}C NMR (125 MHz, Acetone-D6) 97.0, 90.2, 61.9, 14.8, 13.6. IR (neat) 29.30, 28.57, 17.46, 1442, 1381, 1321, 1214, 1184, 1112 cm^{-1}. LC-Mass Spec M+1 474.75.

2,4,5-triiodo-1-isopropyl-1H-imidazole

To a vial was added 200 mg (0.498 mmol) of 2,4,5-triiodoimidazole, 31.02 mg (0.224 mmol) of potassium carbonate, 55.20 mg (0.449 mmol) of 2-bromopropane, and 5.0 mL of N,N-dimethylformamide (DMF). The reaction was left on a hot plate with stirring for 10 hours at 80 °C. After cooling, the reaction was diluted with water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was separated and the solvent removed *in vacuo*. The resulting material was purified via column chromatography using 30% ethyl acetate in hexanes as eluent to afford 73.2 mg (34%) of the desired product as an white solid. Mp = 123-127 °C, ^{1}H NMR (500MHz, Acetone-D6) 4.81-4.79 (m, 1H), 1.61-1.58 (m, 6H) ^{13}C NMR (125 MHz, Acetone-D6) 55.7, 20.9. IR (neat) 2923, 2865, 1454, 1369, 1190, 1053, 1011 cm^{-1}. LC-Mass Spec M+1 488.73.

2,4,5-triiodo-1-methyl-1H-imidazole[23]

To a vial was added 200 mg (0.449 mmol) of 2,4,5-triiodoimidazole, 31.02 mg (0.224 mmol) of potassium carbonate, 63.70 mg (0.449 mmol) of iodomethane, and 5.0 mL of N,N-dimethylformamide (DMF). The reaction was left on a hot plate with stirring for 10 hours at room temperature. After cooling, the reaction was diluted with water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was separated and the solvent removed *in vacuo*. The resulting material was purified via column chromatography using 30% ethyl acetate in hexanes as eluent to afford 126.4 mg (61%) of the desired product as an off yellow solid. Mp = 120-123 °C, ^{1}H NMR (500MHz, Acetone-D6) 3.76 (s,3H)

^{13}C NMR (125 MHz, Acetone-D6) 96.3, 91.5, 86.0, 39.5. IR (neat) 2924, 2853, 1435, 1375, 1344, 1192 cm^{-1}. LC-Mass Spec M+1 460.74.

1-butyl-2,4,5-triiodo-1H-imidazole

To a vial was added 200 mg (0.449 mmol) of 2,4,5-triiodoimidazole, 31.02 mg (0.224 mmol) of potassium carbonate, 82.58 mg (0.449 mmol) of 1-iodobutane, and 5.0 mL of N,N-dimethylformamide (DMF). The reaction was left on a hot plate with stirring for 10 hours at room temperature. After cooling, the reaction was diluted with water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was separated and the solvent removed *in vacuo*. The resulting material was purified via column chromatography using 30% ethyl acetate in hexanes as eluent to afford 69.3 mg (31%) of the desired product as an off pale yellow solid. Mp = 63-65 °C, ^{1}H NMR (500MHz, Acetone-D6) 4.10-4.07 (t, J = 8.05 Hz, 2H), 1.66 (m, 2H), 1.40-1.39 (m, 2H), .97-.94 (t, J = 7.45Hz, 3H) ^{13}C NMR (125 MHz, Acetone-D6) 97.1, 90.9, 84.9, 51.8, 32.2, 19.5, 13.1. IR (neat) 2959, 2929, 2856, 2573, 1455, 1368, 1314, 1269, 1188, 1122 cm^{-1}. LC-Mass Spec M+1 501.7.

2-(2,4,5-triiodo-1H-imidazole-1yl)acetonitrile

To a vial was added 200 mg (0.449 mmol) of 2,4,5-triiodoimidazole, 31.02 mg (0.224 mmol) of potassium carbonate, 33.88 mg (0.449 mmol) of chloroacetonitrile, and 5.0 mL of N,N-dimethylformamide (DMF). The reaction was left on a hot plate with stirring for 10 hours at 50 °C. After cooling, the

reaction was diluted with water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was separated and the solvent removed *in vacuo*. The resulting material was purified via column chromatography using 30% ethyl acetate in hexanes as eluent to afford 159.2 mg (73%) of the desired product as an off white solid. Mp = 160-163 °C, ^{1}H NMR (500MHz, Acetone-D6) 5.39 (s, 2H) ^{13}C NMR (125 MHz, Acetone-D6) 113.9, 98.1, 92.1, 85.9, 40.3. IR (neat) 2927, 2854, 1746, 1455, 1172 cm^{-1}. LC-Mass Spec M+1 485.6.

Ethyl-2-(2,4,5-triiodo-1H-imidazole-1yl)acetate

To a vial was added 200 mg (0.449 mmol) of 2,4,5-triiodoimidazole, 31.02 mg (0.224 mmol) of potassium carbonate, 74.9 mg (0.449 mmol) of ethyl bromoacetate, and 5.0 mL of N,N-dimethylformamide (DMF). The reaction was left on a hot plate with stirring for 10 hours at room temperature. After cooling, the reaction was diluted with water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was separated and the solvent removed *in vacuo*. The resulting material was purified via column chromatography using 30% ethyl acetate in hexanes as eluent to afford 124.5 mg (52%) of the desired product as a white solid. Mp = 131-133 °C, ^{1}H NMR (500MHz, Acetone-D6) 4.9 (s, 2H), 4.25-4.21(q, J = 6.9 Hz, 2H), 1.27-1.24 (t, J = 7.45 Hz, 3H) ^{13}C NMR (125 MHz, Acetone-D6) 166.3, 96.9, 92.4, 86.5, 61.9, 53.0, 13.6. IR (neat) 2927, 1730, 1455, 1414, 1389, 1226 cm^{-1}. LC-Mass Spec M+1 532.72.

1-butyl-2,4,5-triiodo-1H-imidazole

To a vial was added 200 mg (0.449 mmol) of 2,4,5-triiodoimidazole, 31.02 mg (0.224 mmol) of potassium carbonate, 61.5 mg (0.449 mmol) of 1-bromobutane, and 5.0 mL of N,N-dimethylformamide (DMF). The reaction was left on a hot plate with stirring for 10 hours at room temperature. After cooling, the reaction was diluted with water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was separated and the solvent removed *in vacuo*. The resulting material was purified via column chromatography using 30% ethyl acetate in hexanes as eluent to afford 56.5 mg (25%) of the desired product as an yellow oil. Spectra reported above.

1-decyl-2,4,5-triiodo-1H-imidazole

To a vial was added 200 mg (0.449 mmol) of 2,4,5-triiodoimidazole, 31.02 mg (0.224 mmol) of potassium carbonate, 79.3 mg (0.449 mmol) of 1-chlorodecane, and 5.0 mL of N,N-dimethylformamide (DMF). The reaction was left on a hot plate with stirring for 10 hours at 80 °C. After cooling, the reaction was diluted with water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was separated and the solvent removed *in vacuo*. The resulting material was purified via column chromatography using 30% ethyl acetate in hexanes as eluent to afford 77 mg (30%) of the desired product as an clear oil. ^{1}H NMR (500MHz, Acetone-D6) 4.1-4.07 (t, J = 8 Hz,2H), 1.78-1.69 (m, 8H), 1.37-1.25 (m, 4H), .86-.83 (t, J = 6.85Hz, 3H). ^{13}C NMR (125 MHz, Acetone-D6) 97.1, 90.8, 84.9, 52.1, 31.8, 29.6, 29.5, 29.3, 29.2 (signal coincident with acetone signal) 28.9, 26.2,

22.5, 13.6. IR (neat) 2925, 2852, 2681, 1737, 1455, 1367, 1187, 1121, 1096 cm^{-1}. LC-Mass Spec M+1 586.80.

2,4,5-triiodo-1-pentyl-1H-imidazole

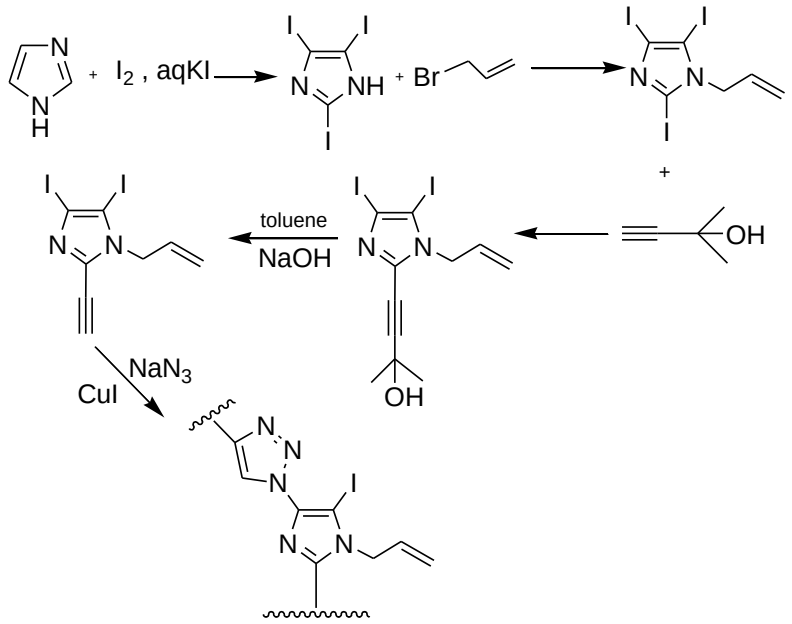
To a vial was added 200 mg (0.498 mmol) of 2,4,5-triiodoimidazole, 31.02 mg (0.224 mmol) of potassium carbonate, 89.7 mg (0.449 mmol) of 1-iodopentane, and 5.0 mL of N,N-dimethylformamide (DMF). The reaction was left on a hot plate with stirring for 10 hours at room temperature. After cooling, the reaction was diluted with water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was separated and the solvent removed *in vacuo*. The resulting material was purified via column chromatography using 30% ethyl acetate in hexanes as eluent to afford 133 mg (57%) of the desired product as an pale yellow oil. ^{1}H NMR (500MHz, Acetone-D6) 4.09-4.06 (t, J = 8 Hz, 2H), 1.79-1.66 (m, 2H), 1.37-1.35 (m, 4H), .90-.87 (t, J = 6.85 Hz, 3H) ^{13}C NMR (125 MHz, Acetone-D6) 97.0, 90.8, 84.8, 51.9, 30.8, 29.1 21.9, 13.3. IR (neat) 2920, 2865, 1733, 1454, 1183, 1054, 1013 cm^{-1}. LC-Mass Spec M+1 516.73.

CHAPTER THREE

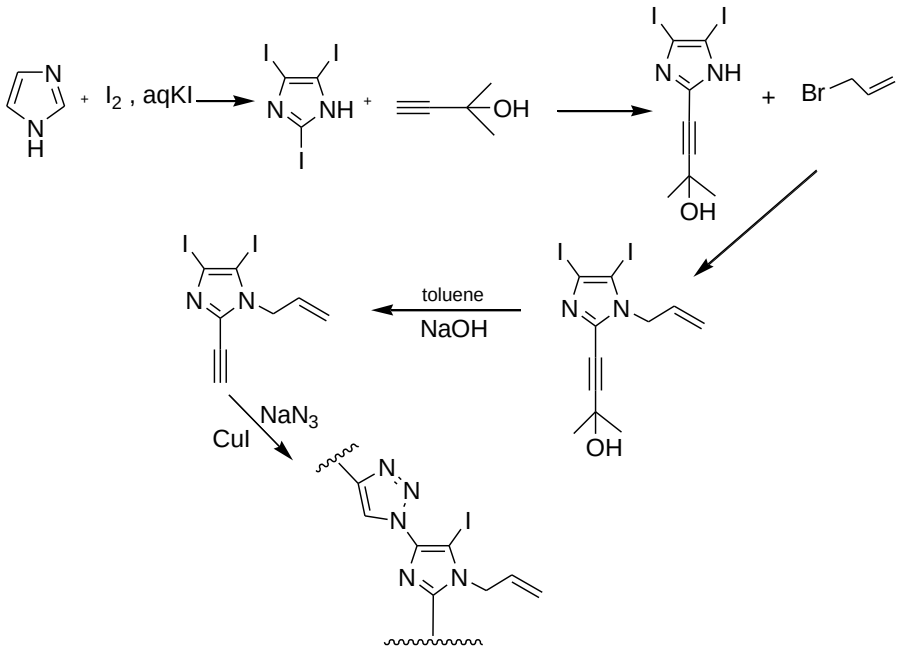
RESULTS AND DISCUSSION

When exploring options for energetic molecules, a triazolated imidazole met all the requirements of a proper substrate for energetic binder use. These nitrogen rich compounds with multiple bonds will provide the energy rich components needed for such materials. In addition, the high-nitrogen content will also decrease the amount of smoke and soot created during combustion. Further, triazoles can be easily prepared via Click chemistry in a completely atom economical method. The precursor for the synthesis of such a binder would be an alkynylated imidazole, which in turn would come from a haloimidazole. Finally, crosslinking could be accomplished using a tethered alkene, such as an allyl group off the nitrogen of the imidazole.

There are two ways to approach the synthesis of such a compound (Schemes 1 and 2). The first proposed approach was to halogenate the imidazole, then to N-alkylate the halogenated molecule and then displace iodine with alkyne. The second approach was to do the opposite: first halogenate the imidazole, then to displace iodine with alkyne and N-alkylate. Assuming that alkylation of a nitrogen off the imidazole with an alkyl halide would form a stable molecule to further work with, it was the first approach that was investigated.

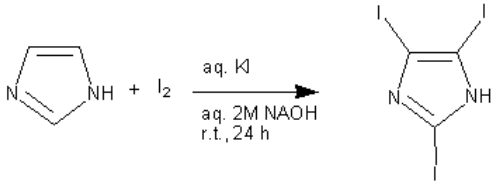


Scheme 1. Approach 1



Scheme 2. Approach 2

To begin the synthesis, 2,4,5-triiodoimidazole was selected as the starting material. As reported by Low, imidazole was dissolved in aqueous 2M sodium hydroxide and then treated with molecular iodine and aqueous potassium iodide.[17] (Scheme 3)

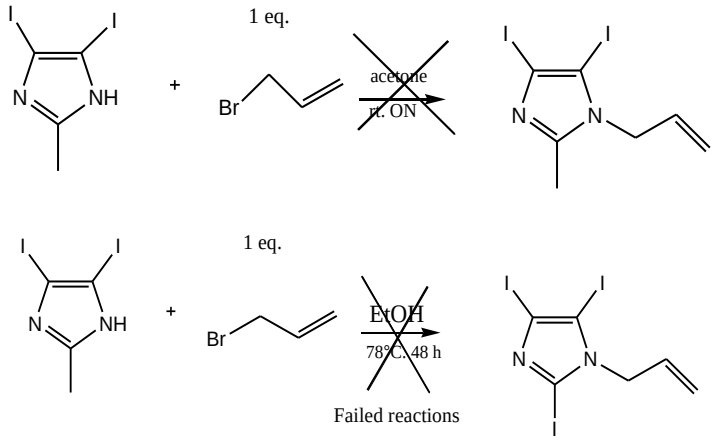


Scheme 3. Synthesis of 2,4,5,-triiodoimidazole

Unfortunately, this chemistry did not work as reported. A diiodinated product, 4,5-diiodoimidazole, was produced. Attempts were made to further convert this 4,5-diiodoimidazole to the desired 2,4,5-triiodoimidazole, but, at best, only provided a 3:1 ratio of both products with the 4,5-diiodoimidazole being the major one. After repeating this chemistry numerous times, it was finally decided to see if there was an issue with one of the reagents. Using a different source of all reagents except imidazole, the reaction was attempted again with success to afford 2,4,5,-triiodoimidazole in a high yield of 80%.

With the desired triiodoimidazole in hand, alkylation was first attempted using allyl bromide as our alkylating agent. This alkyl halide was selected both due to its high reactivity in alkylation reactions and because the alkene could be used in crosslinking the resulting polymers. Problems started from the beginning

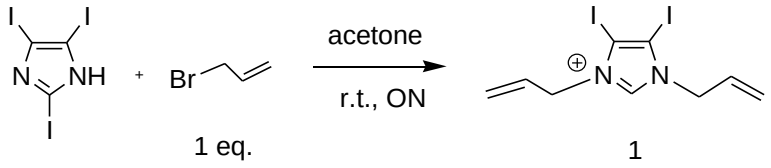
because of repeated failed attempts to create a completely soluble mixture of the reaction components. The solvent acetonitrile was first used because of its application as a general purpose solvent. Unfortunately, solubility issues for the 2,4,5,-triiodoimidazole became an problem. The solubility of 2,4,5,-triiodoimidazole was tested in many different common organic solvents such as chloroform, benzene, and tetrahydrofuran with no homogenous dissolution. Indeed, in all cases, it appeared that the triiodoimidazole was completely insoluble in the reaction solvent.



Scheme 4. Acetone and ethanol as solvents for the attempted alkylation of triiodoimidazole with allyl bromide

Eventually, limited solubility was achieved in solvents such as ethanol and acetone, and a number of reaction conditions were explored, including room temperature stirring overnight with acetone as a solvent, and 78°C for 48 hours with ethanol as a solvent (Scheme 4). In these cases, a solid precipitate product was formed during liquid-liquid extraction and was filtered out using a Hirsch funnel. This product was purified by column chromatography using 30% ethyl

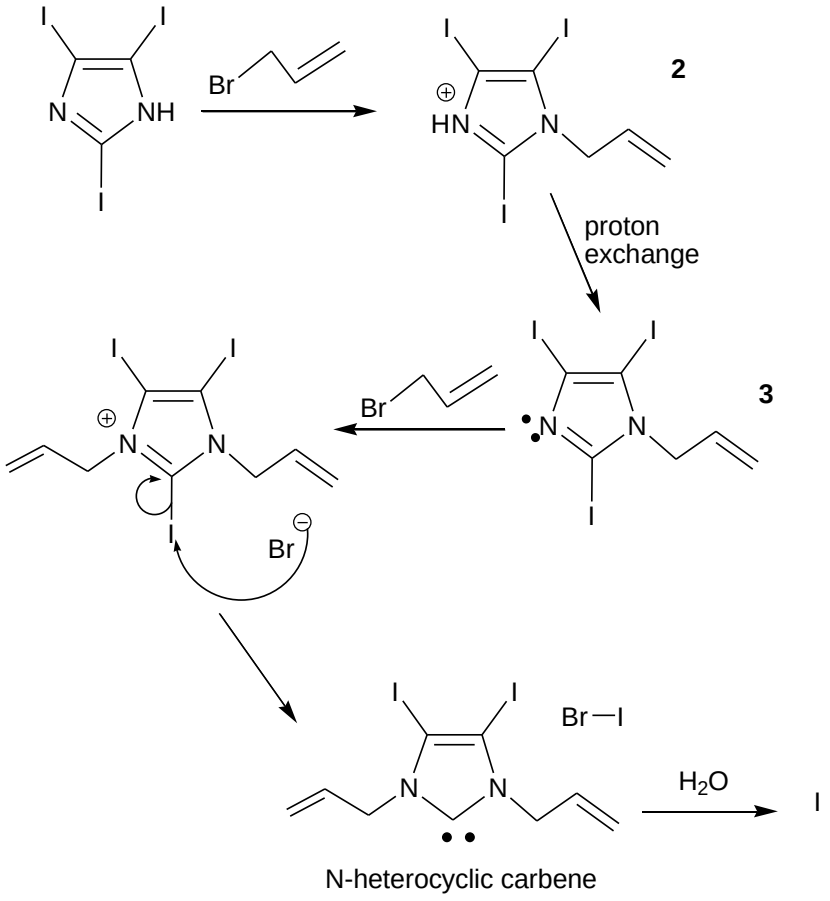
acetate in hexanes and analyzed via spectroscopy. Interestingly, the ^{1}H NMR spectrum appeared consistent with the desired product as the peaks for the allyl group off the imidazole were clearly visible.



Scheme 5. Formation of diallylated product 1

Unfortunately mass spectroscopic analysis of this solid product clearly demonstrated that not one, but two allyl groups had added (Scheme 5). The mass spectrum came back with a weight of 401 m/z for the M+1 peak. Our target monoallylated molecule should have an M+1 peak of 486 m/z. After calculations it was realized that two allyl groups had added and there was an iodine missing. The original target weight of 485.8 m/z minus 126.9 m/z for an iodine and adding 41m/z for the weight of an allyl group plus H gives 400.9 m/z for M+1 peak. Although a definitive mechanism for this unexpected result has not been established, it would seem plausible that it involves formation of the diallylated triiodoimidazole salt. This compound then undergoes formation of a carbene by loss of the iodine leaving group at C2 to form a well-known N-heterocyclic carbene.[24] Finally, this N-heterocyclic carbine would be reprotonated during the aqueous work up. What is unclear, is why it was not possible to stop the allylation at the mono-substituted stage. Given subsequent results, it may be that acid-base exchange between the protonated monoallylated compound **2** and

starting material may be faster than the initial allylation. If this new monoallylated material **3** is a better nucleophile than the starting material, this could help to explain our results.



Scheme 6. Proposed mechanism for the formation of compound 1

Repeated attempts with varying amounts of allyl bromide and with variations in temperature, ranging from room temperature to 80°C, failed completely to avoid this diallylation. Similarly, adjusting reaction times from 6 hours to 48 hours also failed to stop the reaction at one addition of the allyl group.

The low yield was also a problem, always being in the range of 20-30 % no matter the amount of starting material used.

Table 2 shows all the variations of conditions that were used including the solvent, amount of allyl bromide and triiodoimidazole, reaction time, and reaction temperature. Please note that, according to the proposed mechanism, the maximum yield (based upon triiodoimidazole) would be 50%. The product was exceedingly difficult to completely dry, so yields in excess of 50% reflect considerable remaining water.

Table 2. Table of reaction conditions for compound 1

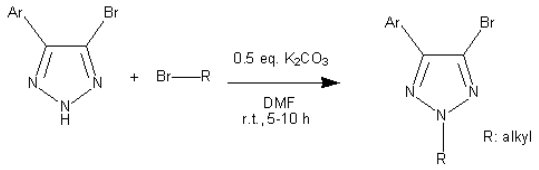
Solvents	Allyl bromide amounts	Time	Temperature	% yield
Acetonitrile	.5 eq.	24 h	80°C	24%
Acetonitrile	1 eq.	6 h	80°C	57%[a]
Acetonitrile	1 eq.	10 h	80°C	77%[a]
Acetonitrile	1 eq.	24 h	50°C	43%[a]
Acetonitrile	1 eq.	24 h	80°C	88%[a]
Ethanol	1 eq.	24 h	80°C	0%[b]
Ethanol	1 eq.	48 h	80°C	34%[b]
Methanol	1eq.	72h	50°C	0%
Acetone	1 eq.	24 h	23°C	86%[a]

a) wet with solvent b) after column chromatography

In light of this problem, the literature was searched for methods to alkylate highly halogenated, nitrogen-containing heteroaromatics. Although nothing has been reported on halogenated imidazoles, a method has been reported for 1,2,3-

triazoles. Wang and co-workers reported the reaction of 4-bromo-NH-1,2,3-triazoles with alkyl halides in the presence of K_2CO_3 in N,N-dimethylformamide to produce the corresponding 2-substituted 4-bromo-1,2,3-triazoles.[18] (Scheme 6) The conditions stated were room temperature for 10 hours. Because of the similarity between the triazoles and imidazoles and the use of alkyl halides for substitution on nitrogen these reaction conditions were explored.

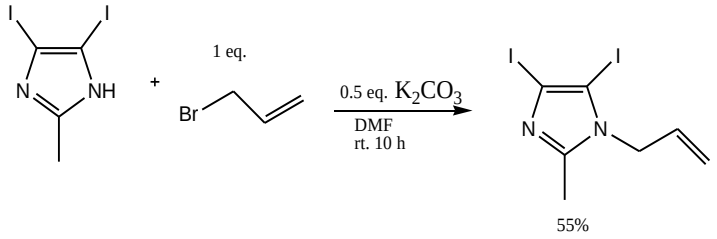
Scheme 7 shows the successful substitution reaction of allyl bromide and 2,4,5-triiodoimiazole to create 1-allyl-2,4,5-triiodo-1H-imidazole. 2,4,5-triidoimidazole was dissolved in DMF with 1 equivalent of allyl bromide added to the reaction flask. One half millimolar (0.5) equivalent of potassium carbonate was used and the reaction was stirred at room temperature for 10 hours.



Scheme 7. Reaction of 4-bromo-NH-1,2,3-triazoles with alkyl halides to produce 2-substituted 4-bromo-1,2,3-triazoles.

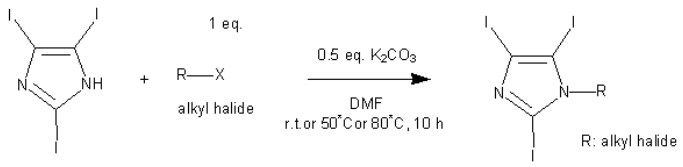
After 10 hours, the reaction was completely homogeneous and was worked up with ethyl acetate and water. The organic layer was concentrated to give a crude product. This product was purified using column chromatography with 30% ethyl acetate in hexane as eluent to give a 55% yield of 1-allyl-2,4,5-triiodo-1H-imidazole. The product was soluble in chloroform and other common

organic solvents which was a drastic change from the diallylated molecule which had limited solubility in most common organic solvents. The successful creation of the desired molecule was confirmed with mass spectroscopy showing the correct weight of a monoallylated 2,4,5-triiodoimidazole.



Scheme 8. Reaction of allyl bromide and 2,4,5-triiodoimiazole to create 1-allyl-2,4,5-triiodo-1H-imidazole

Armed with this success, the scope of this alkylation was explored. Table 3 shows the results of reaction with various types of alkyl halides. The method of using DMF as a solvent in the presence of potassium carbonate with these alkyl halides and 2,4,5-triiodoimidazole was proven to be successful. Scheme 8 is the generic reaction conditions that were used for 10 reactions with 2,4,5,-triiodoimidazole being the starting material for all reactions. Variations came in the types of functional groups included in the alkyl group and in the halogen present.

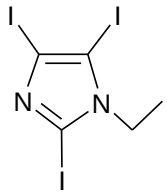


Scheme 9. Generic scheme used for alkyl halide substitutions

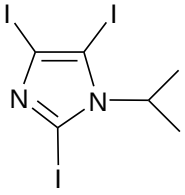
Table 3. Reported actual and percent yields for selected alkyl halides

	Alkyl halide	Actual yield	Percent yield	Temperature
1	Allyl Bromide	300 mg	55%	23°C
2	Iodoethane	136 mg	64%	23°C
3	Iodomethane	126.4 mg	61%	23°C
4	1-Iodobutane	69.3 mg	31%	23°C
5	Ethyl Bromoacetate	124.5 mg	52 %	23°C
6	1-Bromobutane	56.5 mg	25%	23°C
7	1-Iodopentane	133 mg	57%	23°C
8	2-Bromopropane	0 mg	0 %	23°C
9	2-Bromopropane	20 mg	10 %	50° C
10	2-Bromopropane	73.2 mg	34 %	80° C
11	Chloroacetonitrile	0 mg	0 %	23°C
12	Chloroacetonitrile	159.2 mg	73%	50° C
13	1-Chlorodecane	0 mg	0 %	23°C
14	1-Chlorodecane	15 mg	6 %	50° C
15	1-Chlorodecane	77 mg	30 %	80° C

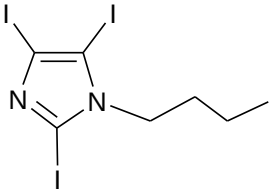
As reported in the table all the percent yields fell into acceptable ranges. The highest yield was entry 13 obtained by the chloroacetonitrile addition which was heated to 50°C for 10 hours. This higher temperature was clearly important, as the same reaction at room temperature yielded nothing but starting material as confirmed by LC-MS (Table 3, entry 12). The failed attempt could be attributed to the chlorine being a poorer leaving group. Heating the reaction provided sufficient energy for the substitution reaction to occur.



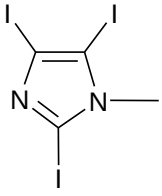
1-ethyl-2,4,5-triiodo-1*H*-imidazole



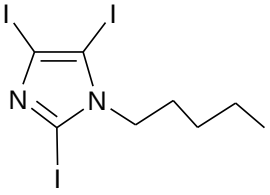
2,4,5-triiodo-1-isopropyl-1*H*-imidazole



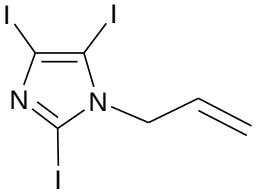
1-butyl-2,4,5-triiodo-1*H*-imidazole



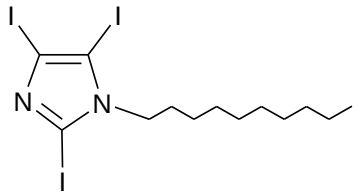
2,4,5-triiodo-1-methyl-1*H*-imidazole



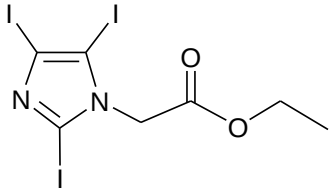
2,4,5-triiodo-1-pentyl-1*H*-imidazole



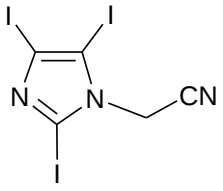
1-allyl-2,4,5-triiodo-1*H*-imidazole



1-decyl-2,4,5-triiodo-1*H*-imidazole



ethyl 2-(2,4,5-triiodo-1*H*-imidazol-1-yl)acetate



2-(2,4,5-triiodo-1*H*-imidazol-1-yl)acetonitrile

Figure 19: structures and names of alkylated compounds

There was also difficulty in the substitution reactions of 2-bromopropane and 1-chlorodecane, entries 9-11 and 14-16 respectively. All alkyl halides were run the first time without heat to test the success and yield of the reaction. If no reaction occurred after 10 hours with no heat then a second reaction with heat was attempted. The second reaction was performed at 50°C and if similar issues of starting material and low yields were encountered the temperature was further raised to 80°C.

2-Bromopropane experienced difficulty in alkylation of the nitrogen on the imidazole because of the steric hindrance of the isopropyl group. The bromide on the 2-bromopropane is attached to a secondary position which will provide a slower rate of reaction in an S_N2 reaction. After 3 attempts at different temperatures, the yields were increased from 0% to 10% and to 34% respectively, see entries 9-11. Although still low, this last option does cleanly afford the desired compound after a simple isolation. Presumably a longer reaction time and/or higher reaction temperature could further improve this result.

The 1-chlorodecane reaction was also run at three different temperatures (room temperature, 50°C and 80°C). The yield improved with each increase in temperature but the highest yield was entry 16 which was 30% at 80°C. This is still a relatively low yield, with the mass balance presumed to be unreacted starting material. Chlorine as a leaving group was the issue with this substitution. The boiling point of the alkyl halide limits the temperature from being raised

further, although longer reaction times might also improve the yield for this substrate.

With no certain explanation of why, the lowest reported yield was from the addition of the alkyl halide 1-bromobutane, entry 7. The formation of 1-butyl-2,4,5-triiodo-1H-imidazole with 1-bromobutane gave a yield of 25% at room temperature and 10 hours of reaction time. Low yield was also first reported in entry 3 for the first attempt with iodomethane which gave a yield of 23%. Repeating this reaction after further experience in performing and purifying these alkylation reactions resulted in a dramatic improvement, with the product being isolated in 61% yield, see entry 4.

Purification of these products was easy, involving liquid-liquid extraction using ethyl acetate and water. To ensure purity and remove any unreacted starting material (the only significant by-product in most cases), the crude material obtained from extraction was further purified via column chromatography using 30% ethyl acetate in hexanes. This provided good rates of elution from the column and also good separation of any compounds.

All purified compounds were analyzed with ^{1}H NMR and ^{13}C NMR spectroscopy. This gave confirmation of successful formation of target molecules. When confirmed, samples of the alkylated molecules were submitted for mass spectrometric analysis to confirm correct molecular weight. Ethanol was the solvent used for the LC-MS. Melting points were collected for all solid samples.

Infrared spectroscopy was also taken of every alkylated molecule using a Varian 800 FT-IR.

CHAPTER FOUR

CONCLUSIONS

In conclusion, successful conditions were developed that enable the selective monoalkylation of 2,4,5-triiodoimidazoles with various types of alkyl halides, including several functionalized systems. The success of these substitutions was found through many trials of failed reactions. Not being able to fully dissolve the reactants in various solvents and also substituting both nitrogen's on the imidazole provided barriers to reach our target structure. Research had to be done to find reaction conditions that would yield a monoalkylated product and fully dissolved starting materials. Literature was found where a successful alkyl halide substitution was performed on halogenated 1,2,3-triazoles where only one nitrogen was substituted. Because of similarity between imidazole and triazole rings these discovered conditions were applied. The conditions proved to be successfully applied to the 2,4,5-triiodoimidazole starting material and chosen alkyl halide.

Since so much difficulty was encountered with this starting material there was thought to see how these conditions would work with various types of alkyl halides. There was variation in the types of leaving groups and the types of functional groups that were to be used as substitutes. This functionality is valuable as it could enable further manipulation and diversification. These various types of functional groups such as alkane chains and carbonyls and nitriles could provide building blocks for biological research in pharmaceuticals. The initial

focus of this research was in energetics but these alkylated 2,4,5-triiodoimidazole molecules could be used for many different purposes.

Future research opportunities with molecules includes using the 1-allyl-2,4,5-triiodo-1H-imidazole as a building block for an energetic materials molecule. Polymerization would be achieved by an initial Sonogashira coupling to introduce an alkyne, followed by a one-pot azidation/click reaction to afford the alternating imidazole/triazole backbone. The alkene then provides a site for crosslinking thus enabling its potential application as an energetic binder.

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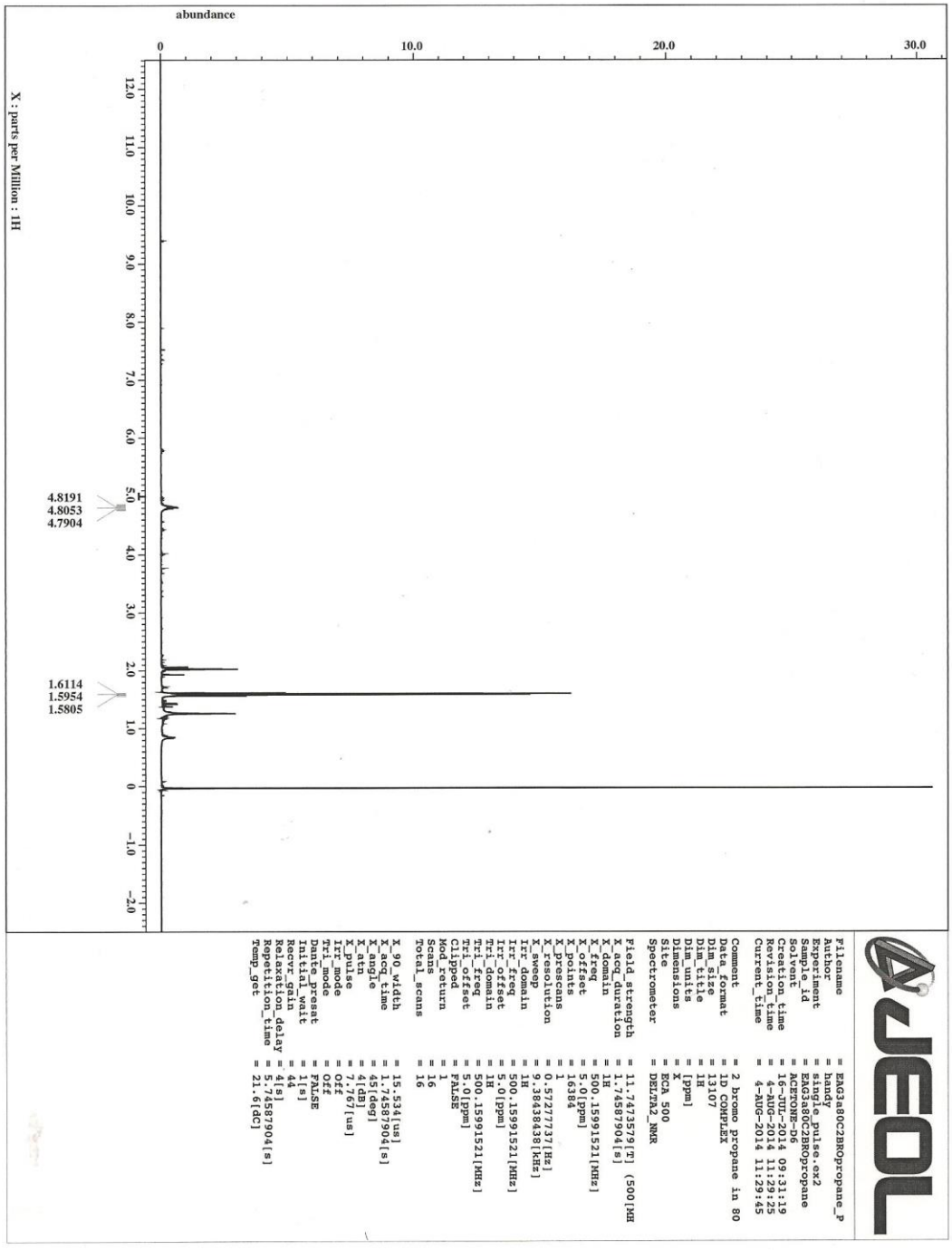
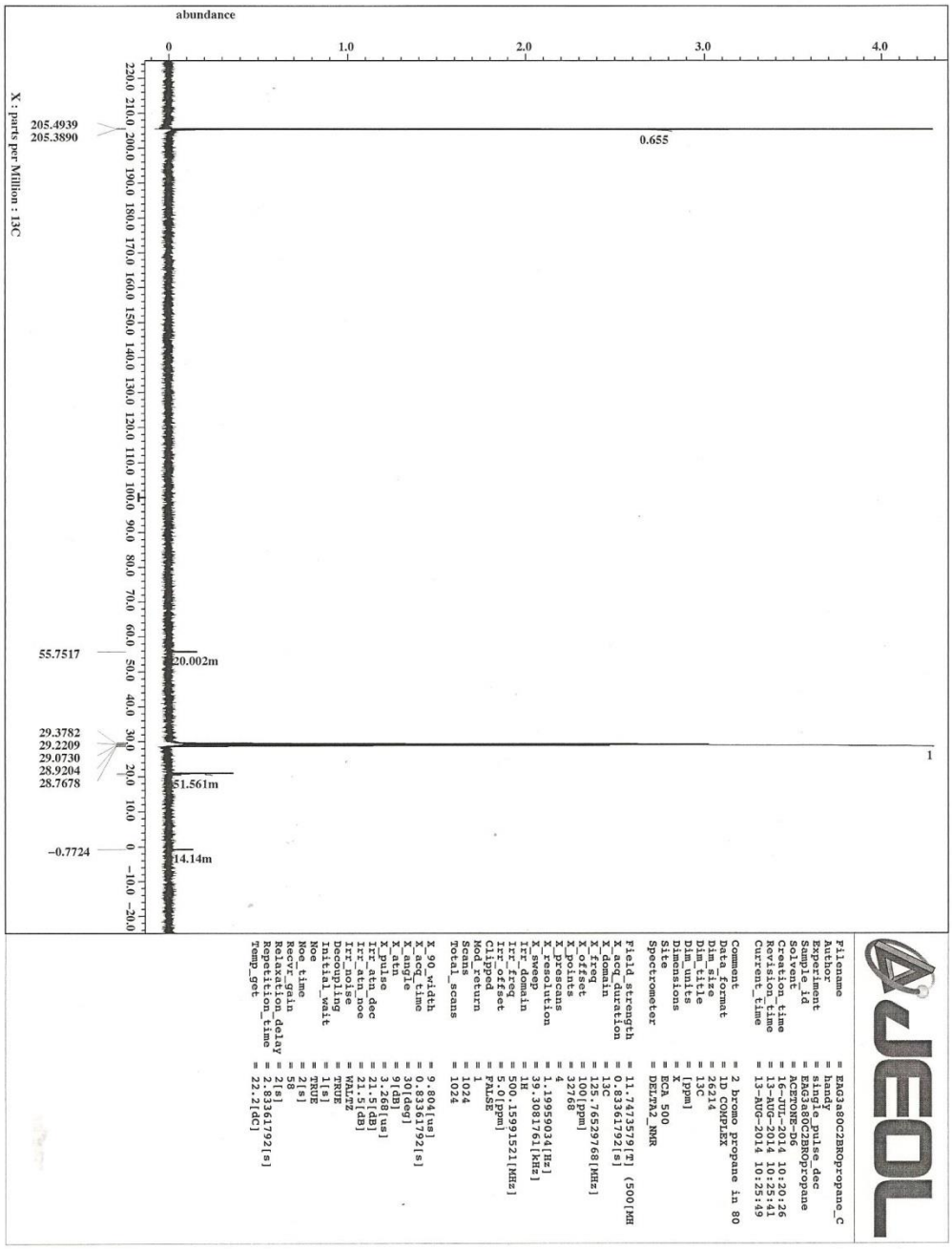
APPENDICES

APPENDIX A

SPECTRA



^{1}H NMR (500 MHz, acetone-d6) spectrum of 2,4,5-triiodo-1-isopropyl-1H-imidazole



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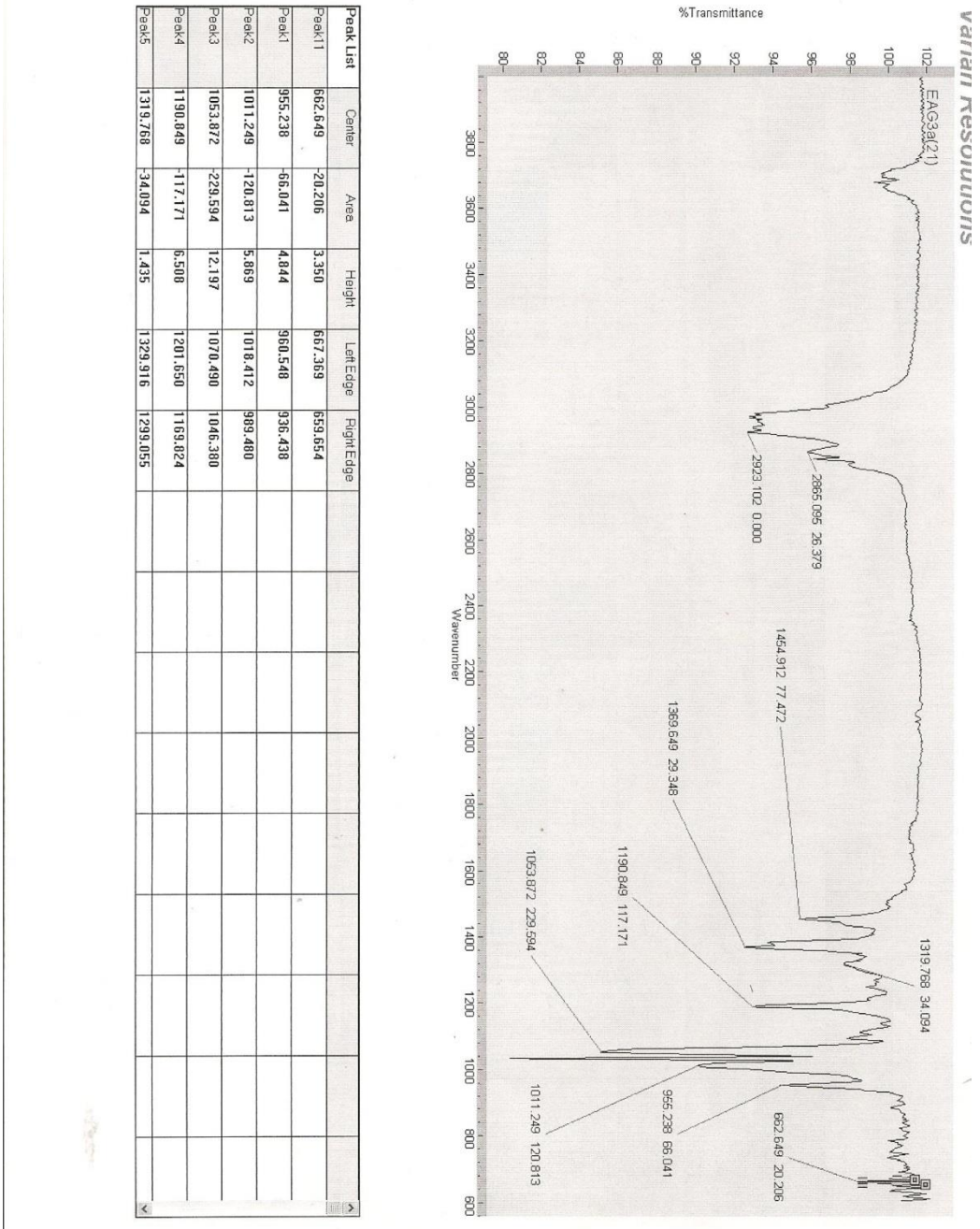
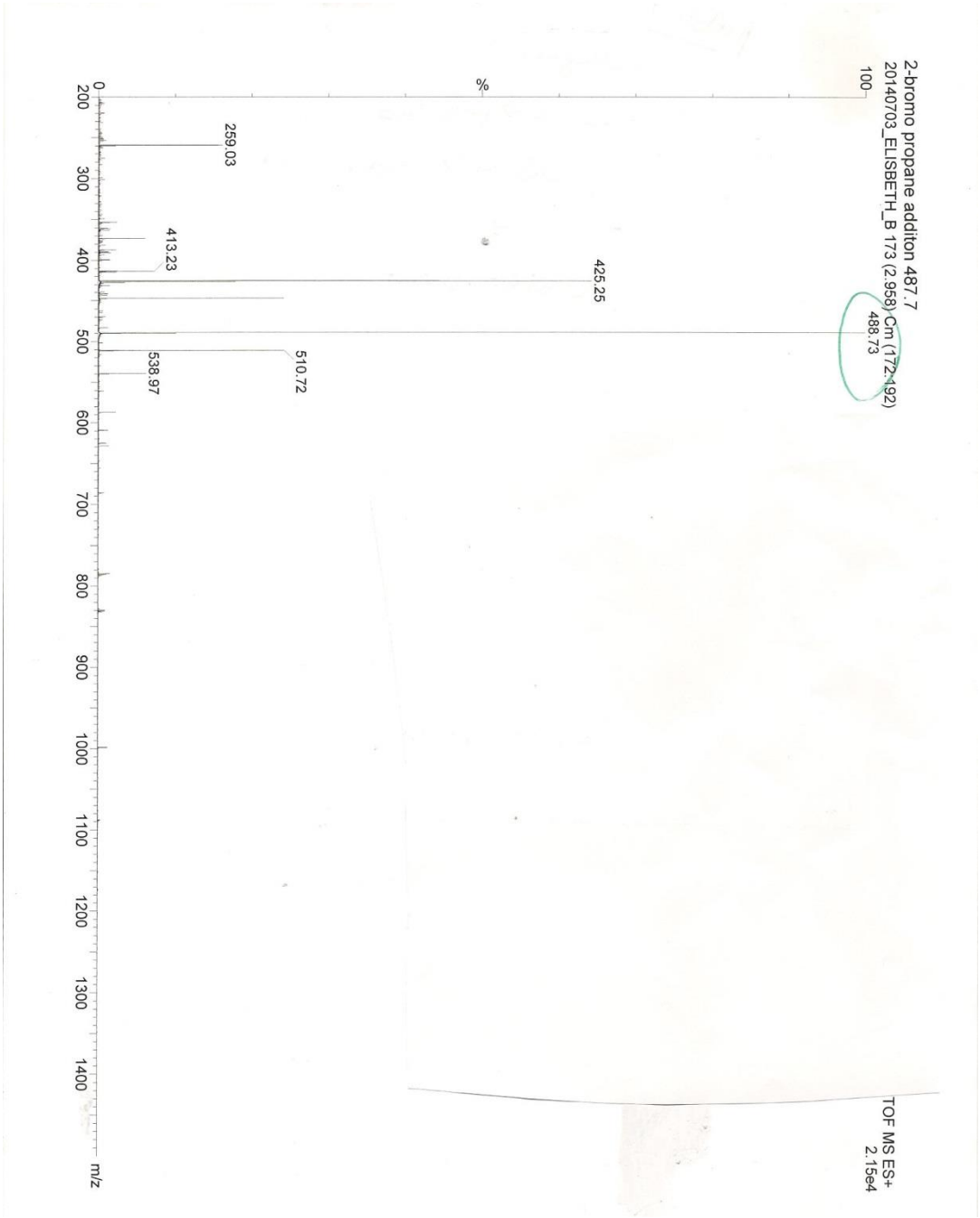
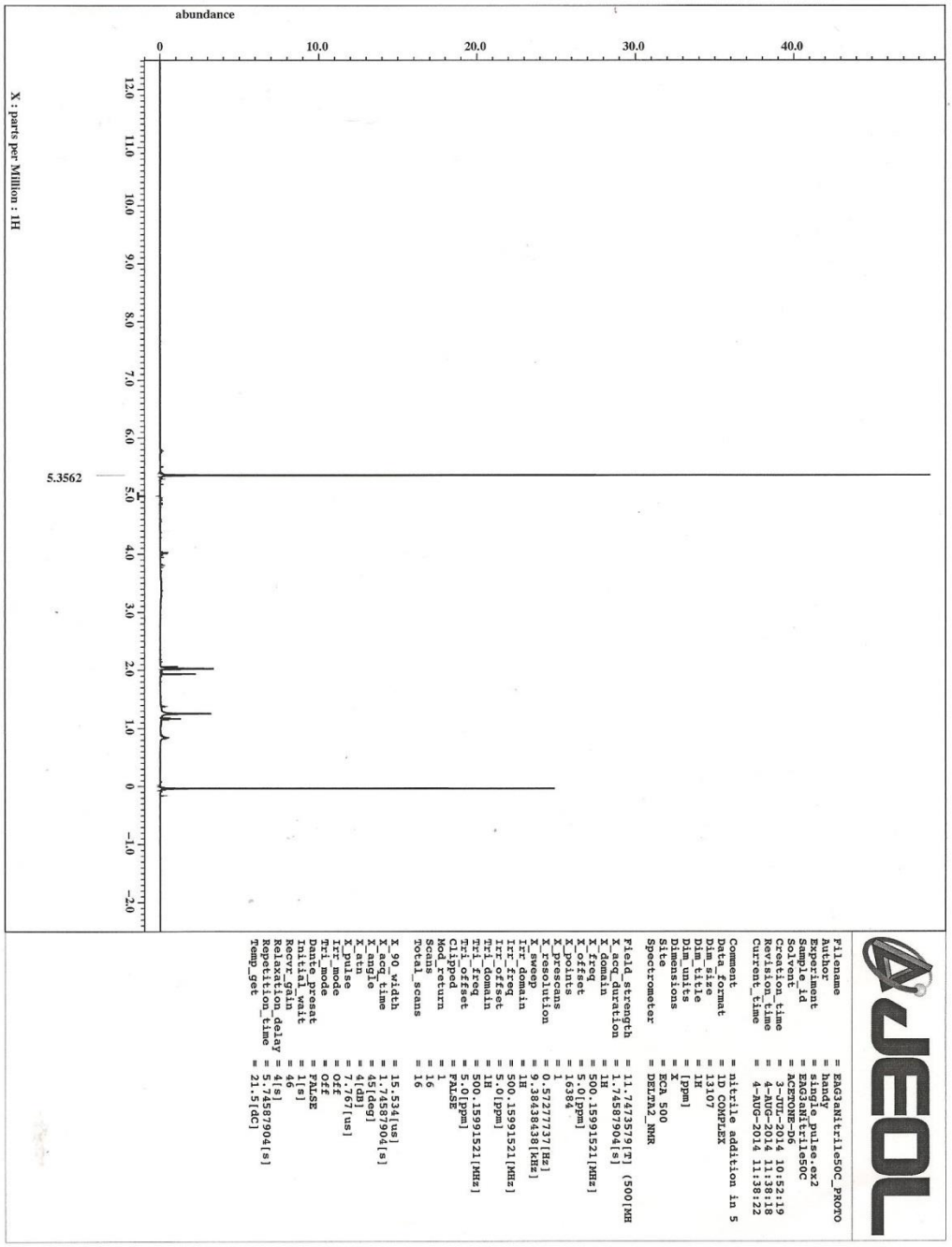


Peak List	Center	Area	Height	Left Edge	Right Edge
Peak11	662.649	20.206	3.350	667.369	659.654
Peak1	955.238	66.041	4.844	960.548	936.438
Peak2	1011.249	120.813	5.869	1018.412	989.480
Peak3	1053.872	229.594	12.197	1070.490	1046.380
Peak4	1190.849	117.171	6.508	1201.650	1169.824
Peak5	1319.768	34.094	1.435	1329.916	1299.055

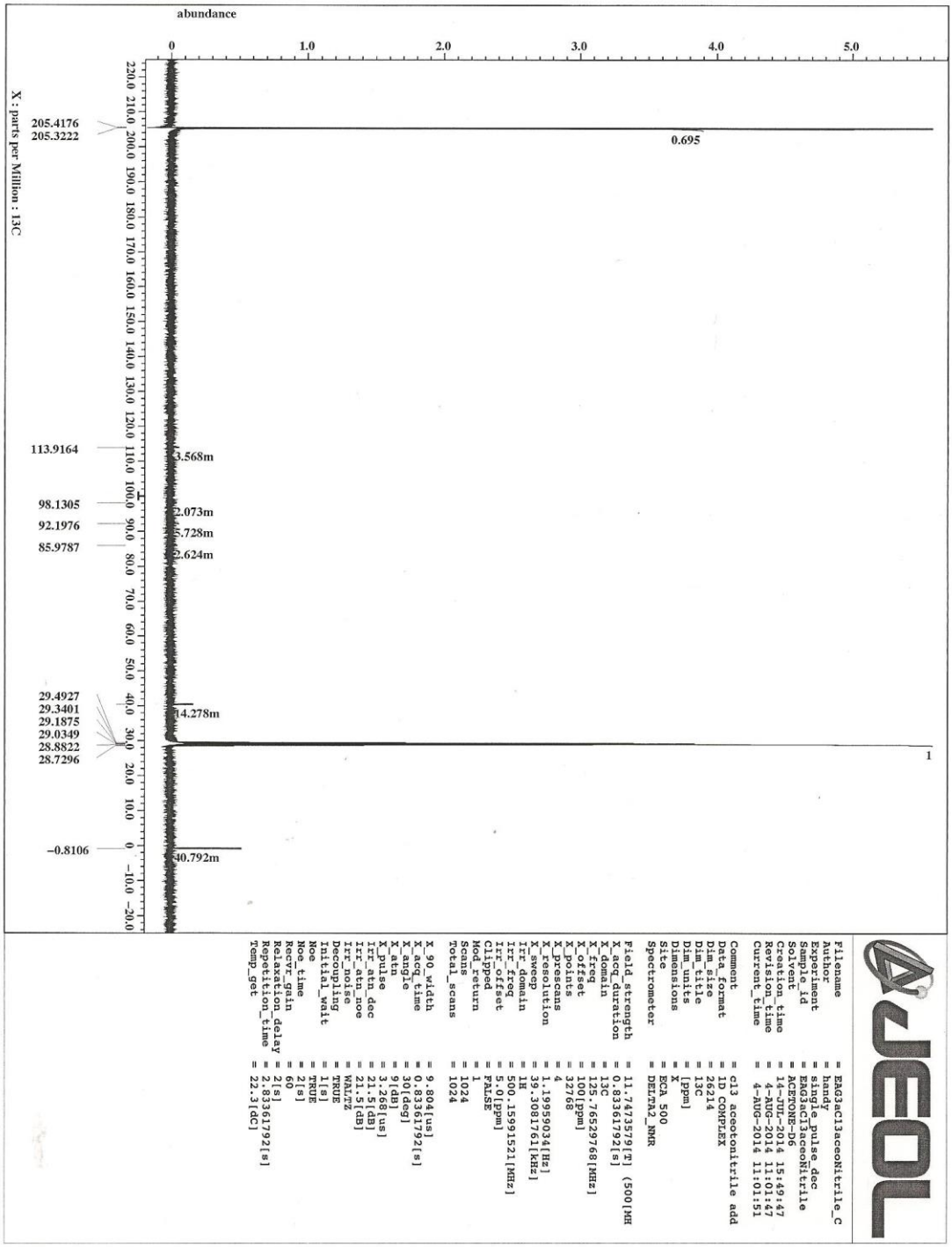
IR spectrum of 2,4,5-triiodo-1-isopropyl-1H-imidazole



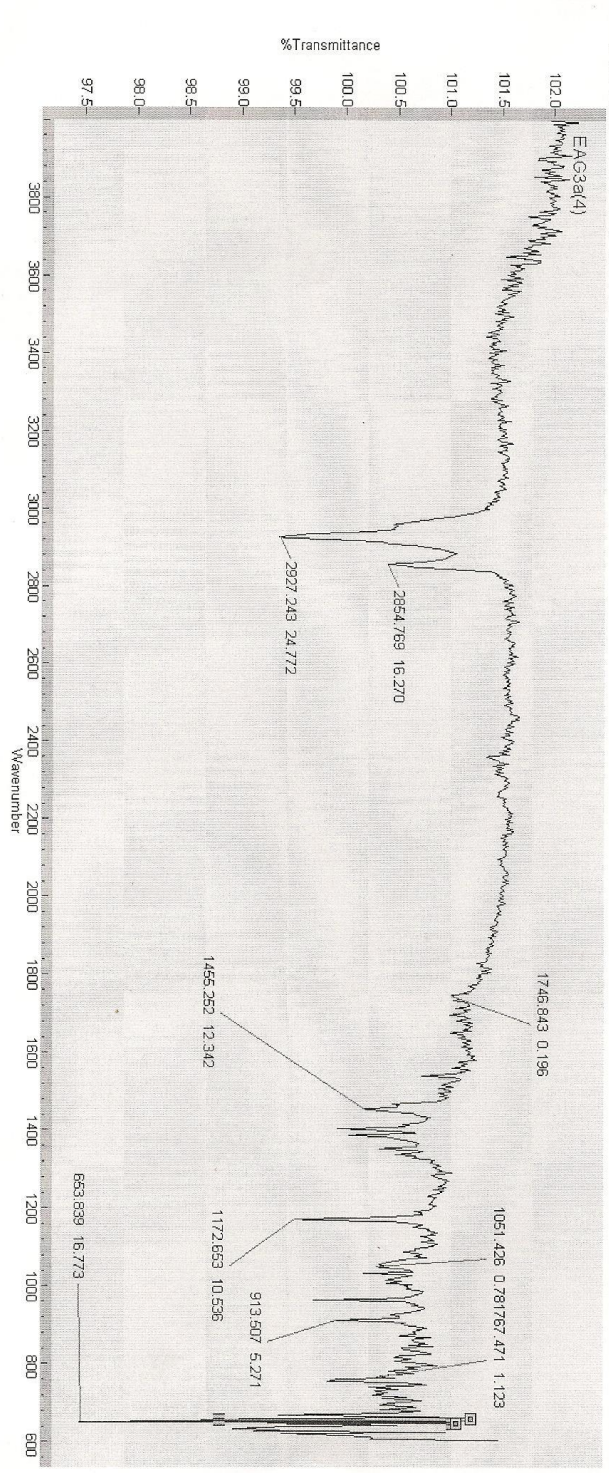
LC-MS spectrum of 2,4,5-triiodo-1-isopropyl-1H-imidazole



[1] H NMR (500 MHz, acetone-d6) spectrum of 2-(2,4,5-triiodo-1H-imidazole-1yl)acetonitrile



^{13} C NMR (500 MHz, acetone-d6) spectrum of 2-(2,4,5-triiodo-1H-imidazole-1yl)acetonitrile



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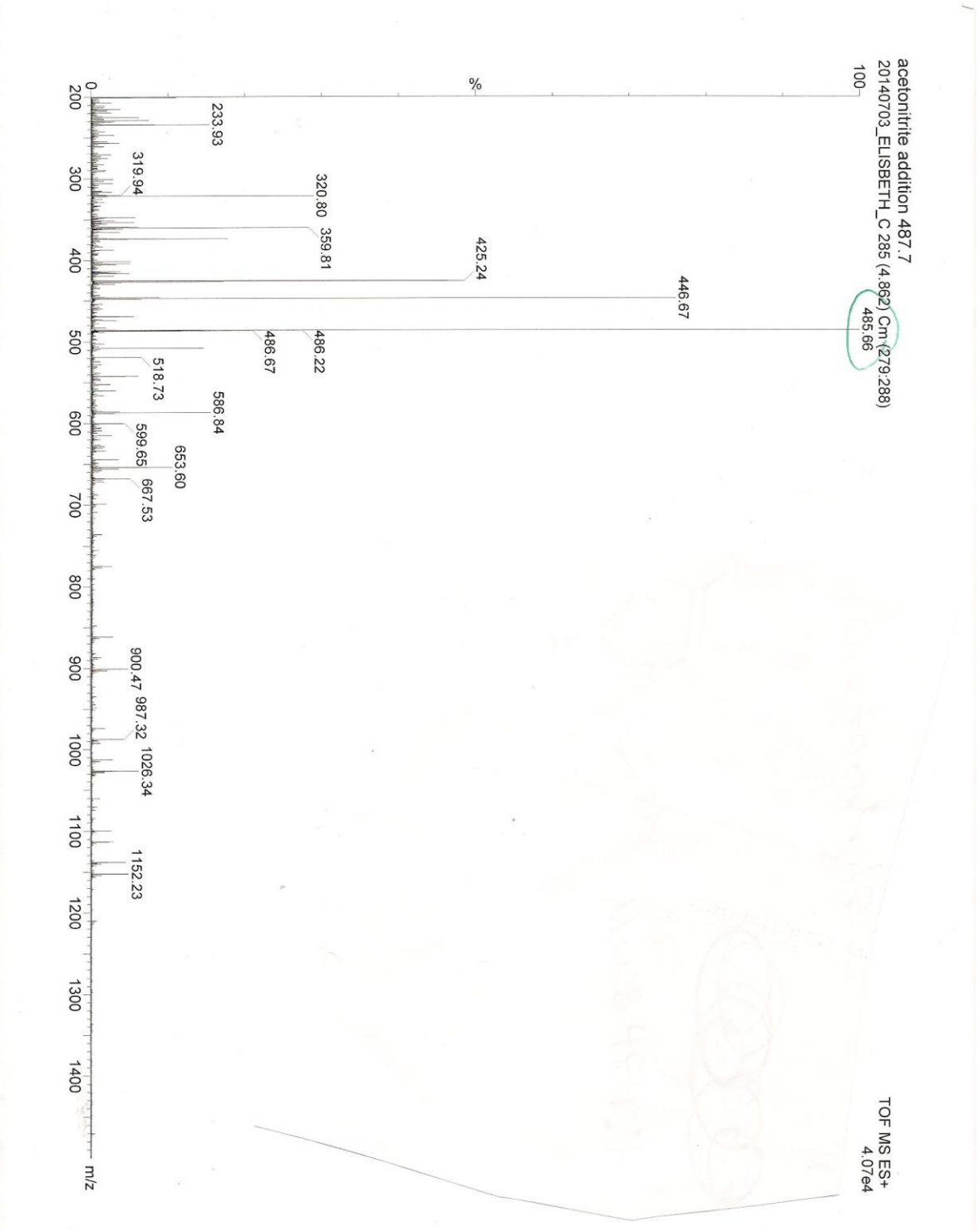
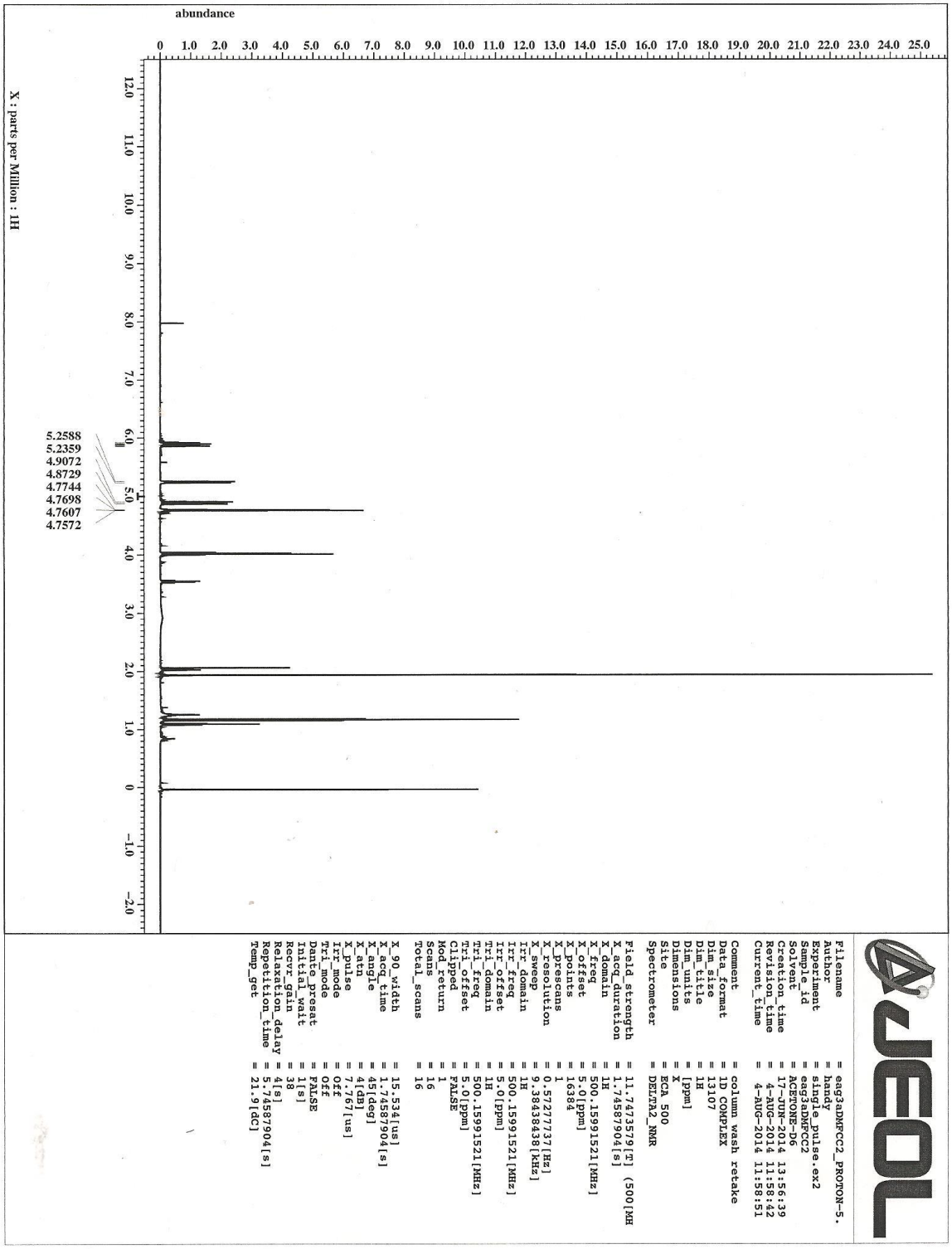
Peak2	913.507	-5.271	0.721	919.079	904.613
Peak3	1051.426	-0.781	0.146	1055.060	1047.345
Peak4	1172.653	-10.536	1.222	1178.504	1165.967
Peak5	1455.252	-12.342	0.704	1470.719	1444.680

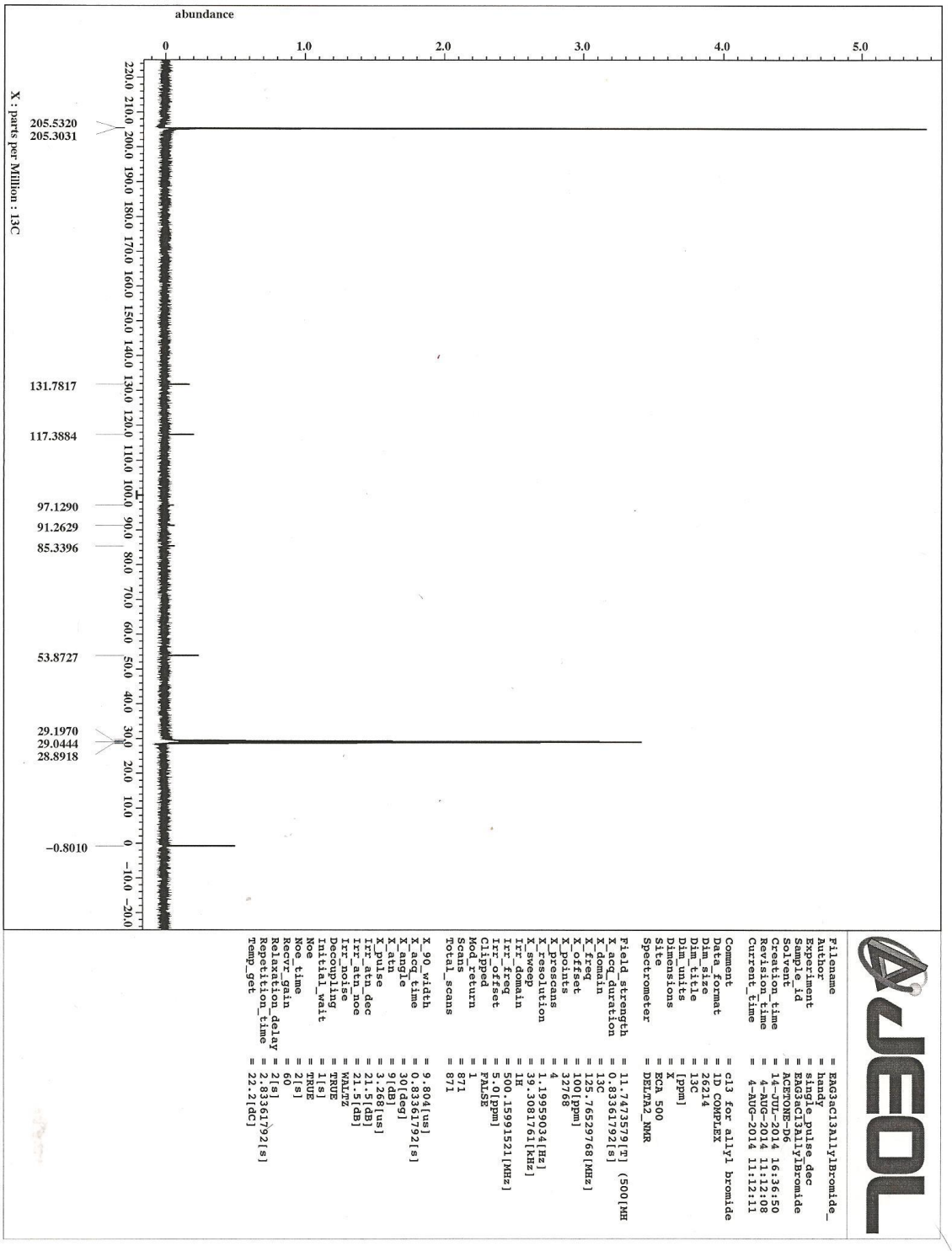
IR spectrum of 2-(2,4,5-triiodo-1H-imidazole-1yl)acetonitrile



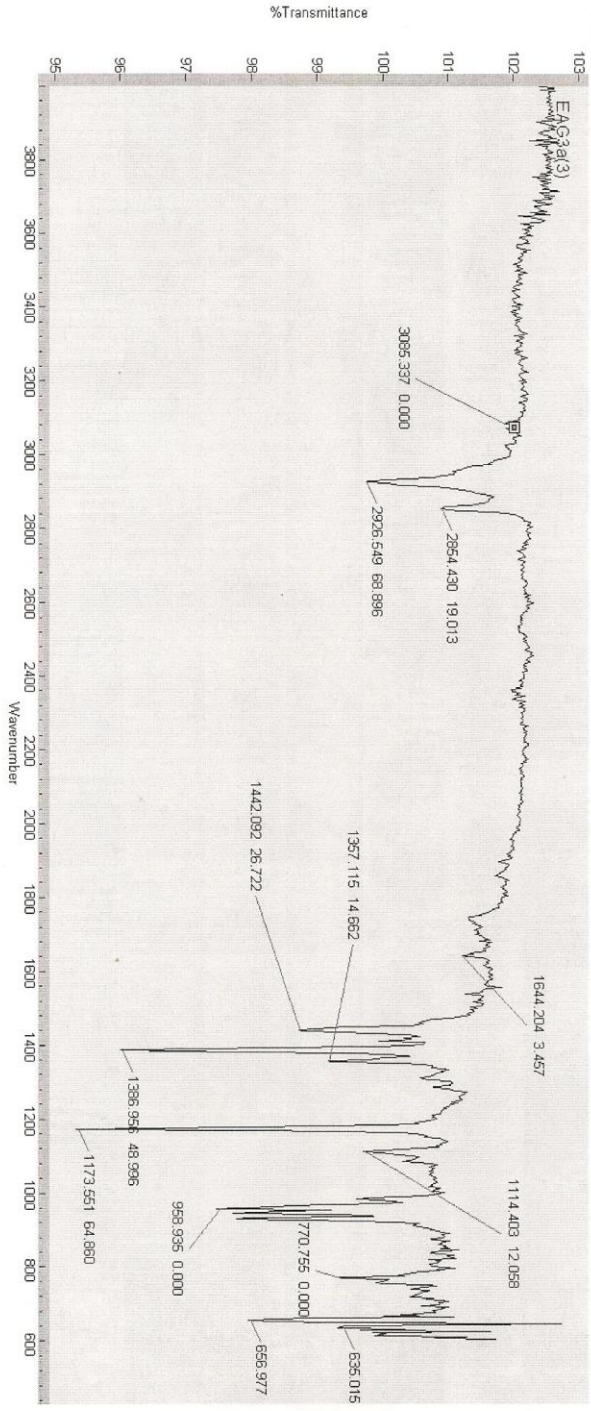
LC-MS spectrum of 2-(2,4,5-triiodo-1H-imidazole-1yl)acetonitrile



[1] H NMR (500 MHz, acetone-d6) spectrum of 1-allyl-2,4,5-triiodo-1H-imidazole



[13] C NMR (500 MHz, acetone-d6) spectrum of 1-allyl-2,4,5-triiodo-1H-imidazole



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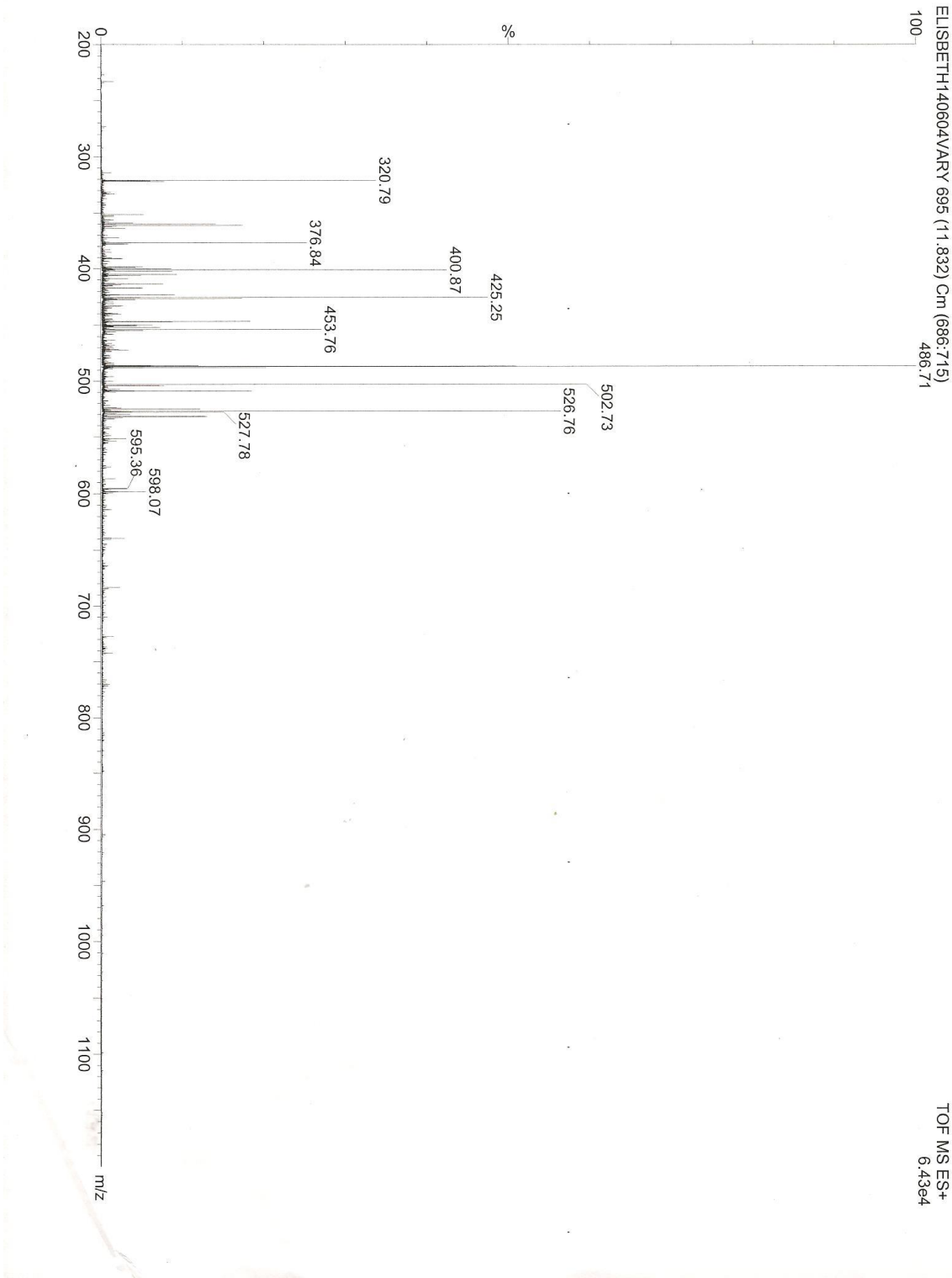
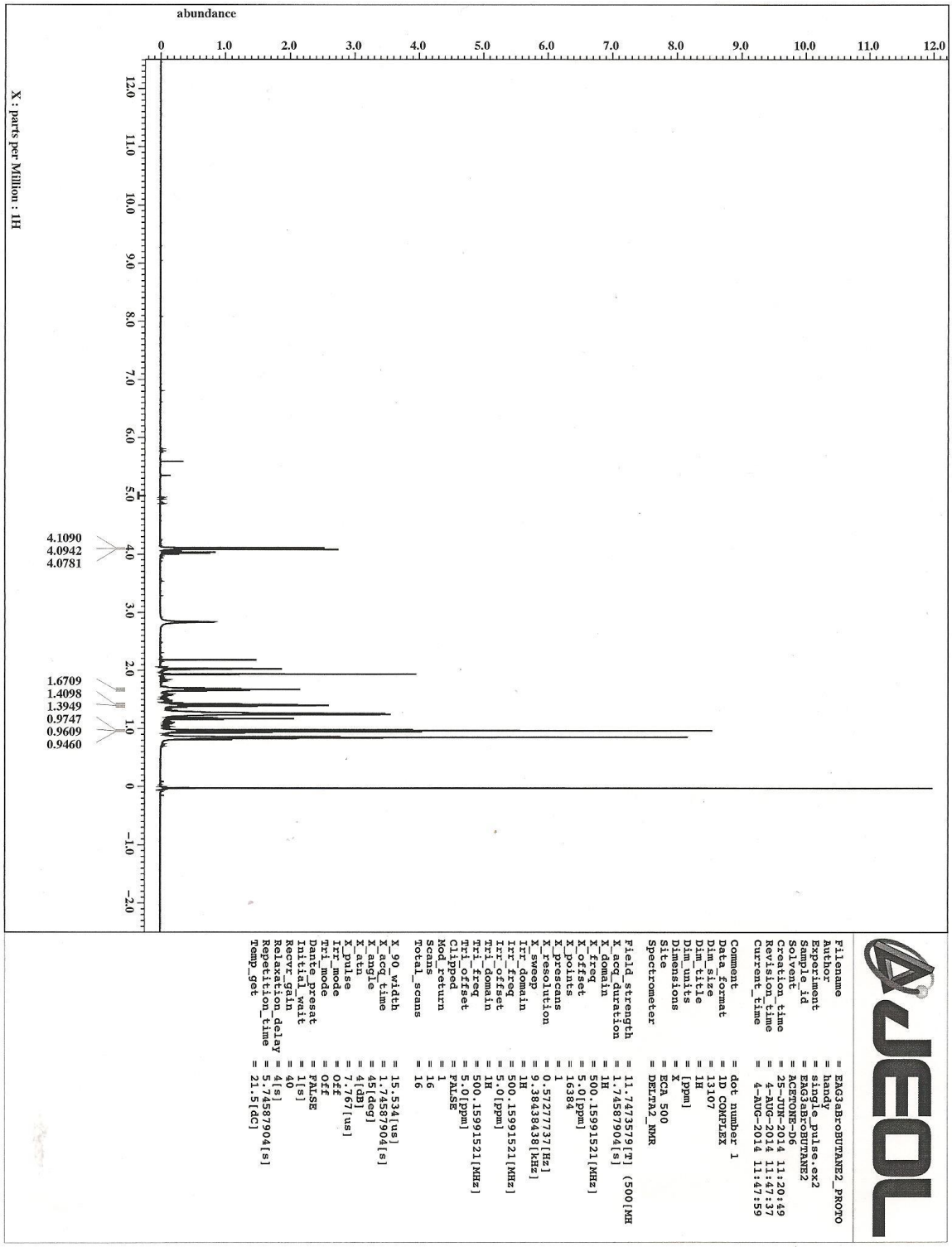
Peak2	770.755	0.000	0.618	765.738	765.738
Peak3	958.935	0.000	1.555	954.762	954.762
Peak4	1114.403	-12.058	1.044	1124.497	1103.280
Peak5	1173.551	-64.860	5.681	1187.183	1155.358

IR spectrum of 1-allyl-2,4,5-triiodo-1H-imidazole



LC-MS spectrum of 1-allyl-2,4,5-triiodo-1H-imidazole



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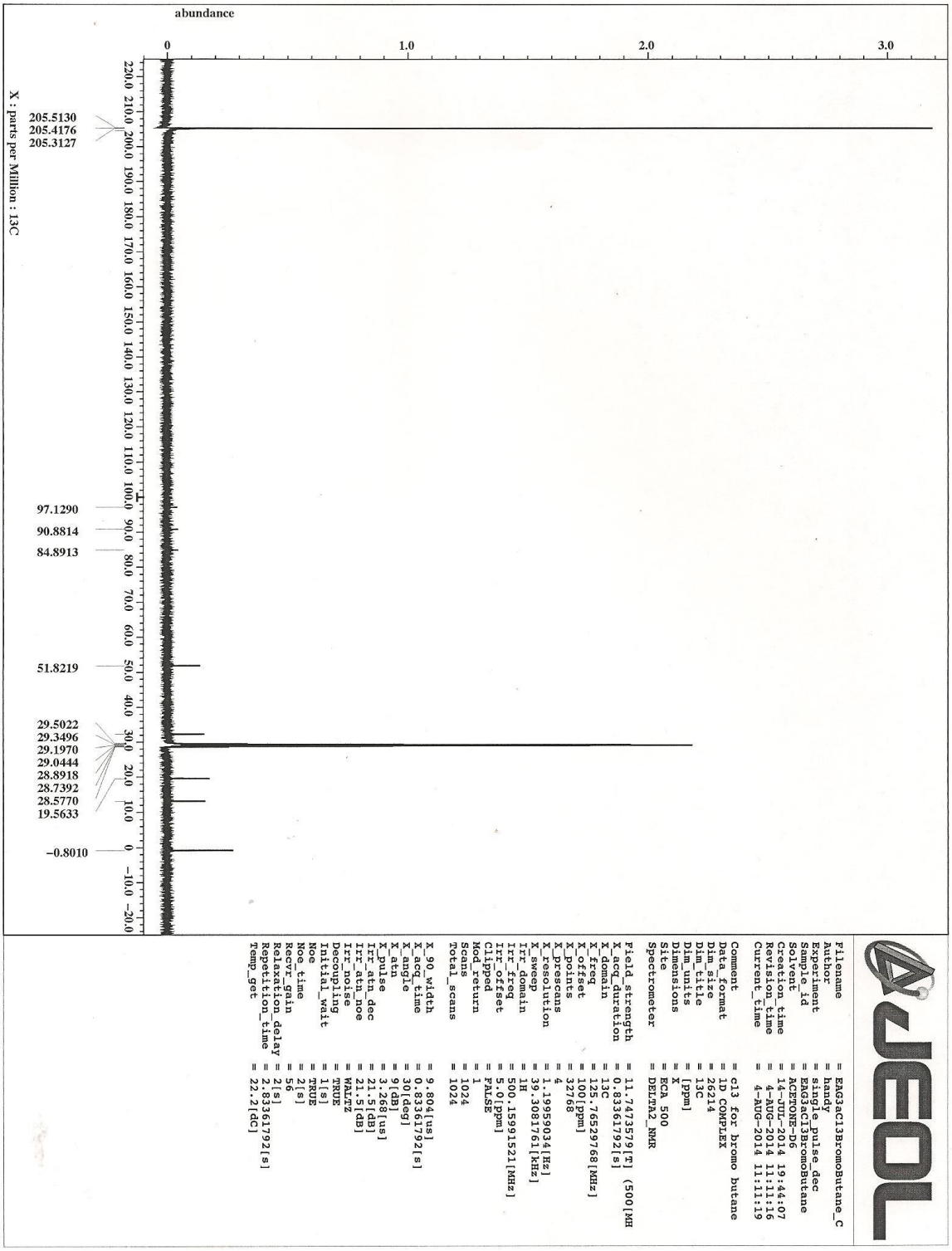
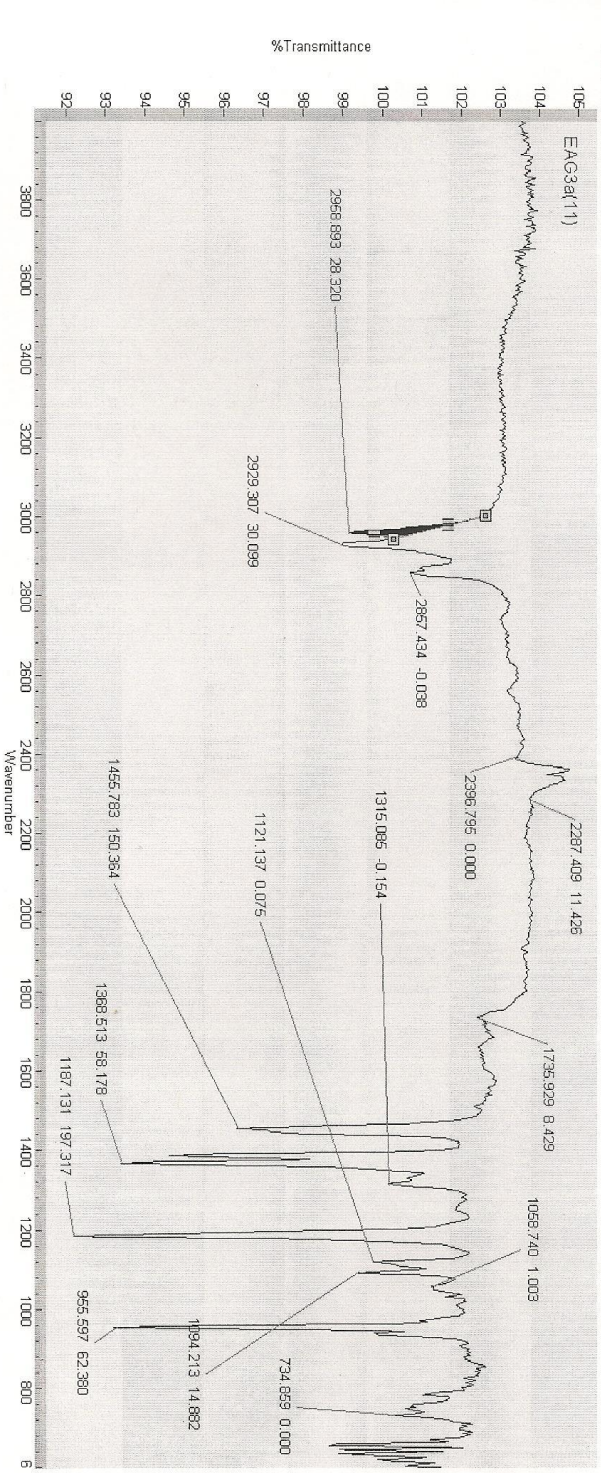


[13] C NMR (500 MHz, acetone-d6) spectrum of 1-butyl-2,4,5-triiodo-1H-imidazole



Peak List	Center	Area	Height	Left Edge	Right Edge
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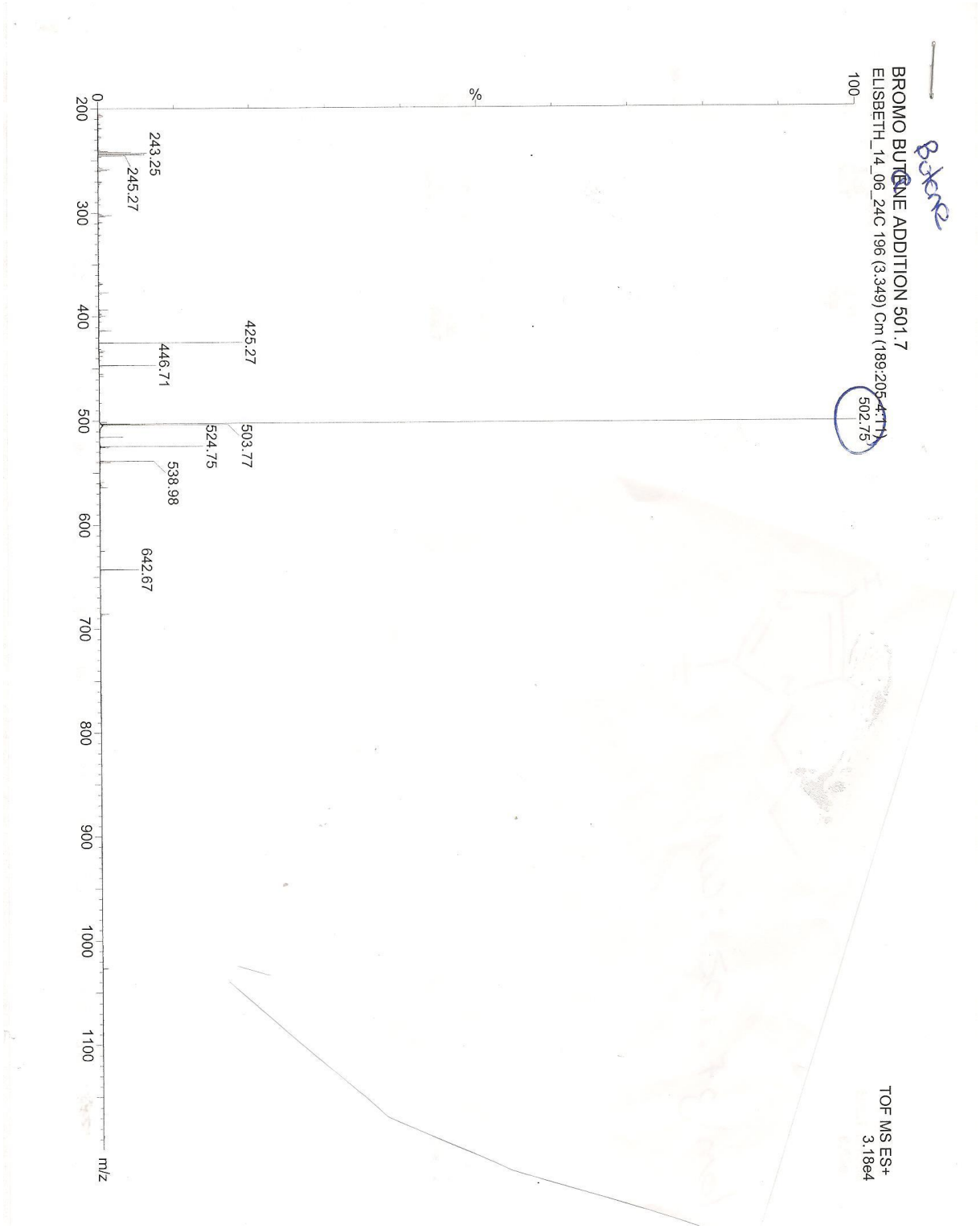
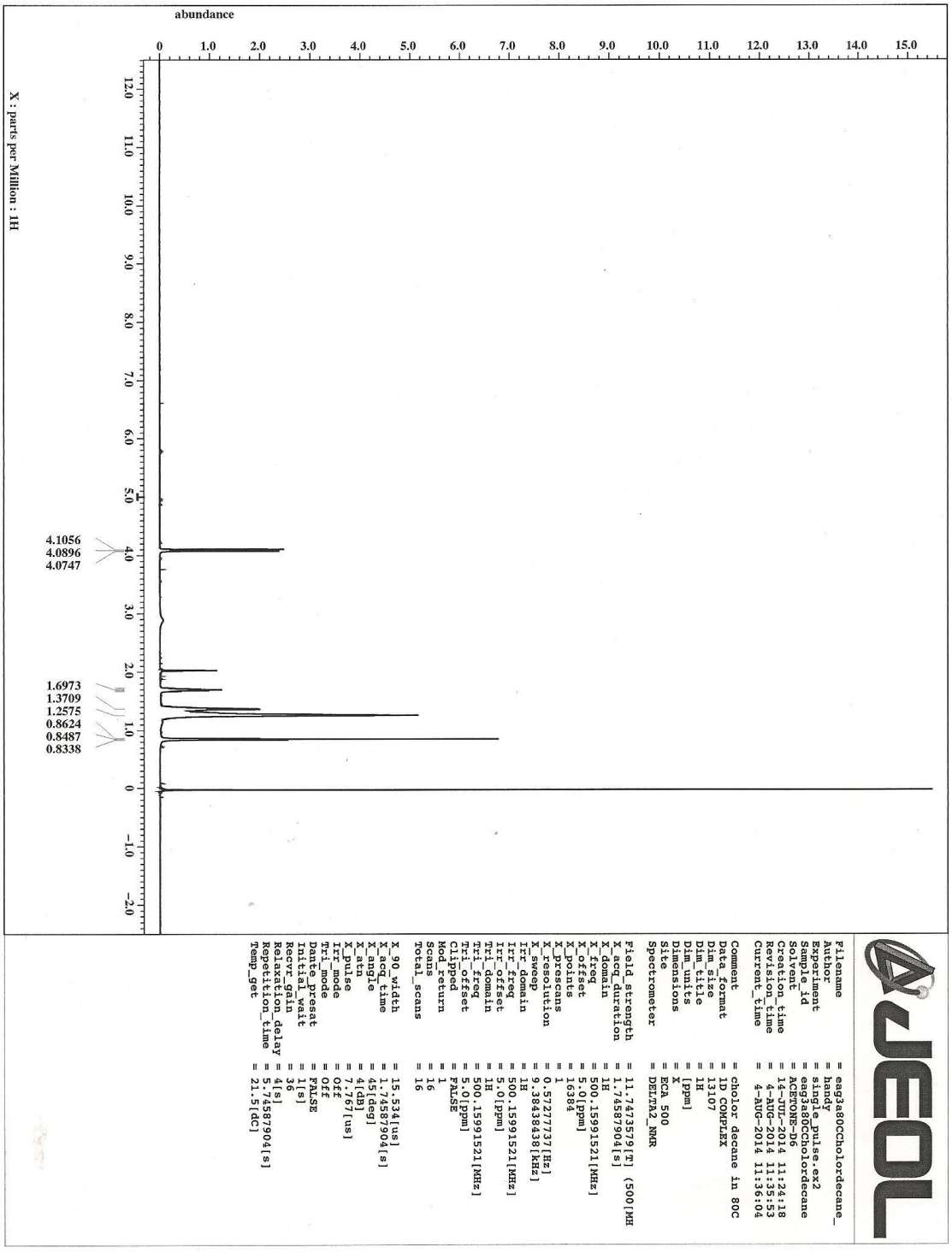
Peak1	955.597	-62.380	7.809	962.477	948.975
Peak2	1058.740	-1.003	0.165	1064.704	1055.060
Peak3	1094.213	-14.882	1.961	1099.423	1085.921
Peak4	1121.137	-0.075	0.108	1116.782	1109.067
Peak5	1187.131	-197.317	10.120	1210.329	1165.967

IR spectrum of 1-butyl-2,4,5-triiodo-1H-imidazole



LC-MS spectrum of 1-butyl-2,4,5-triiodo-1H-imidazole



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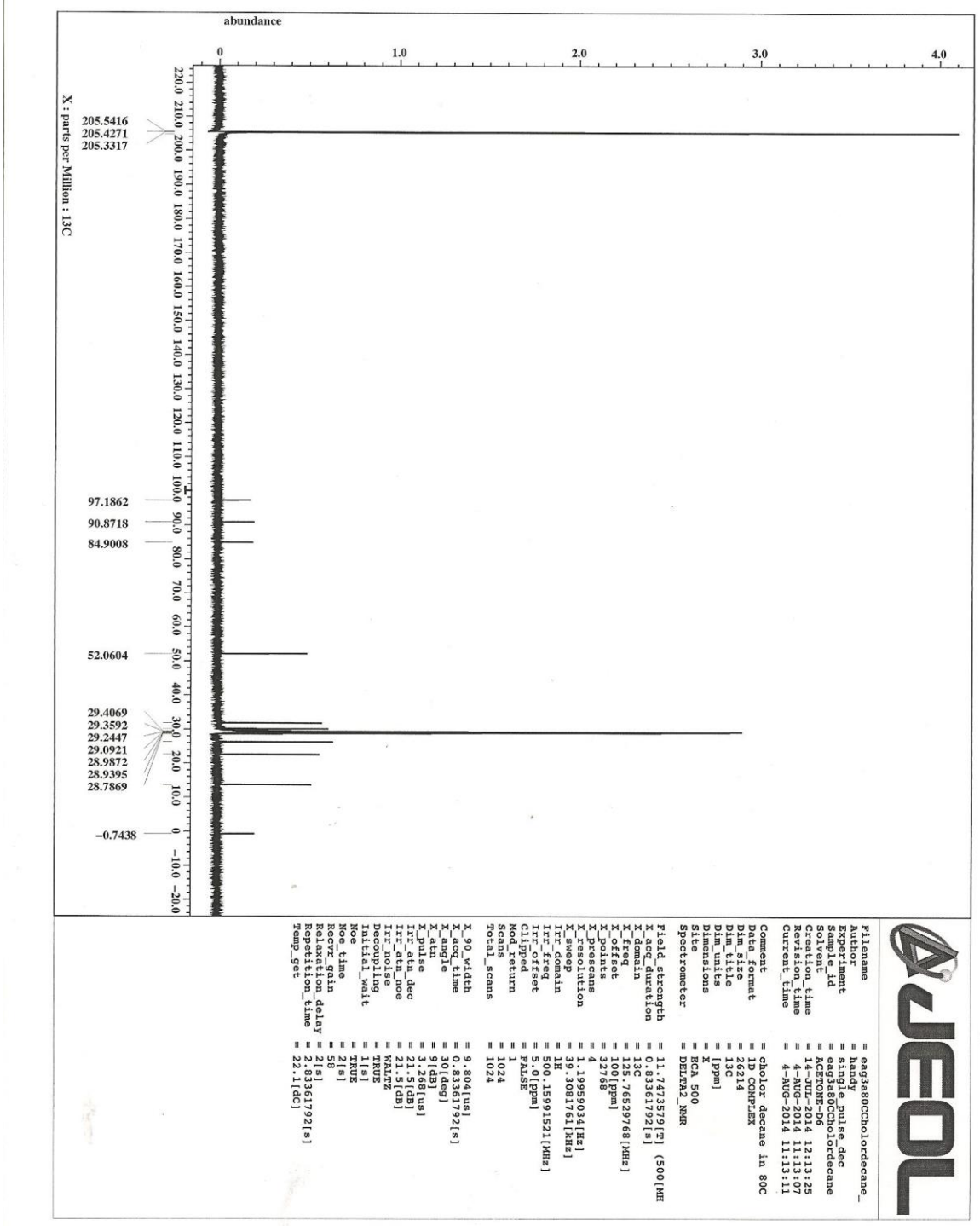

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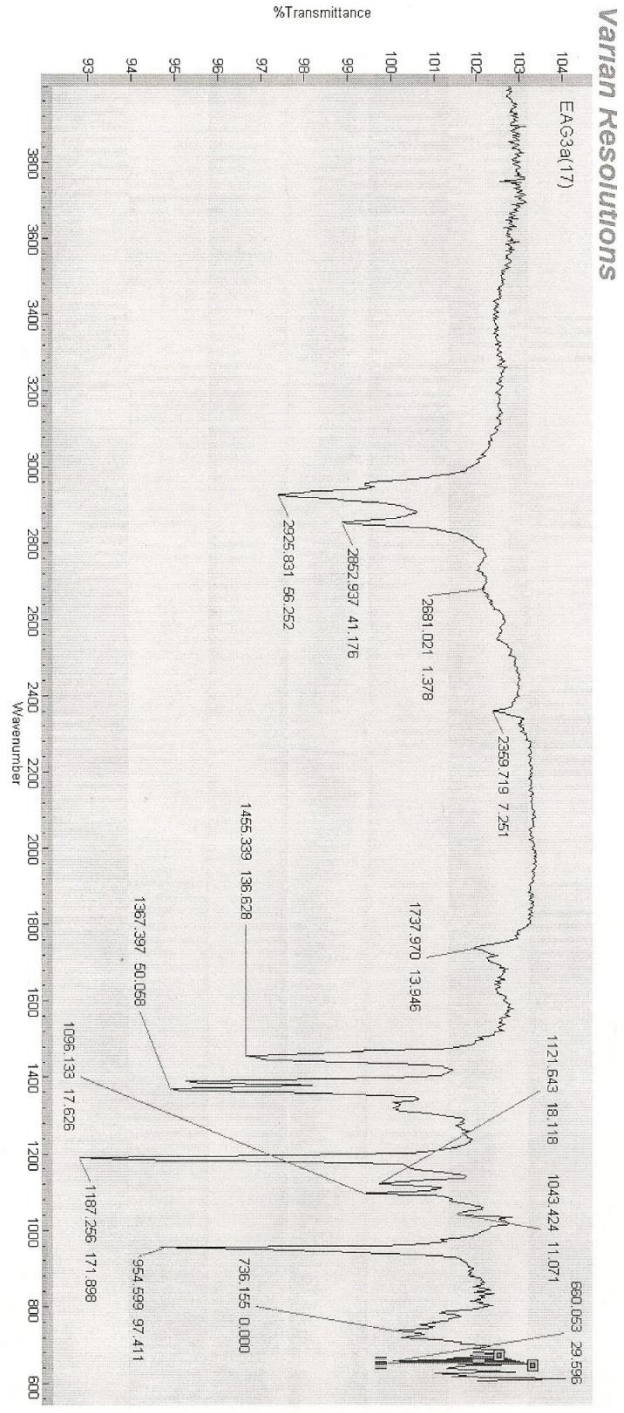

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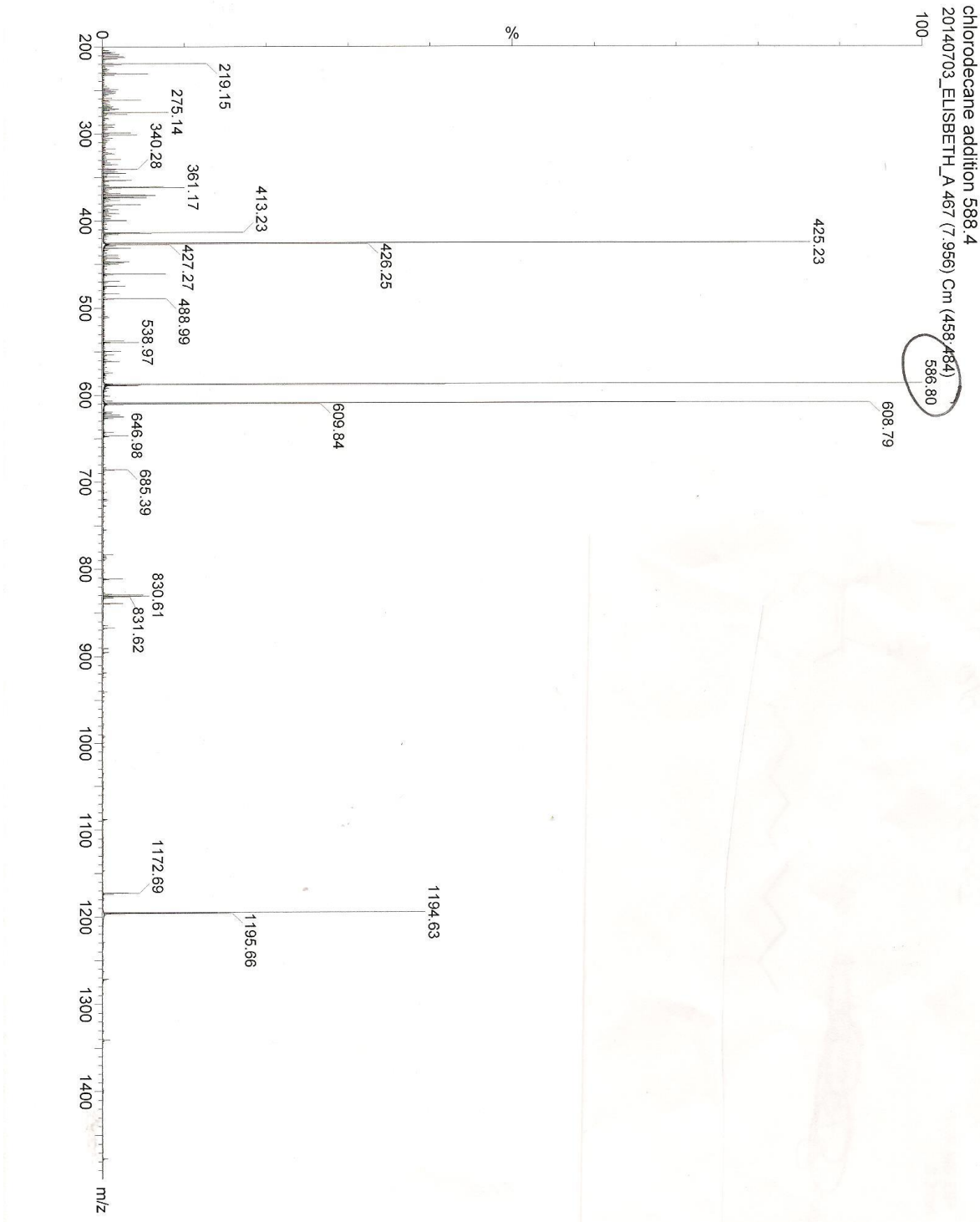
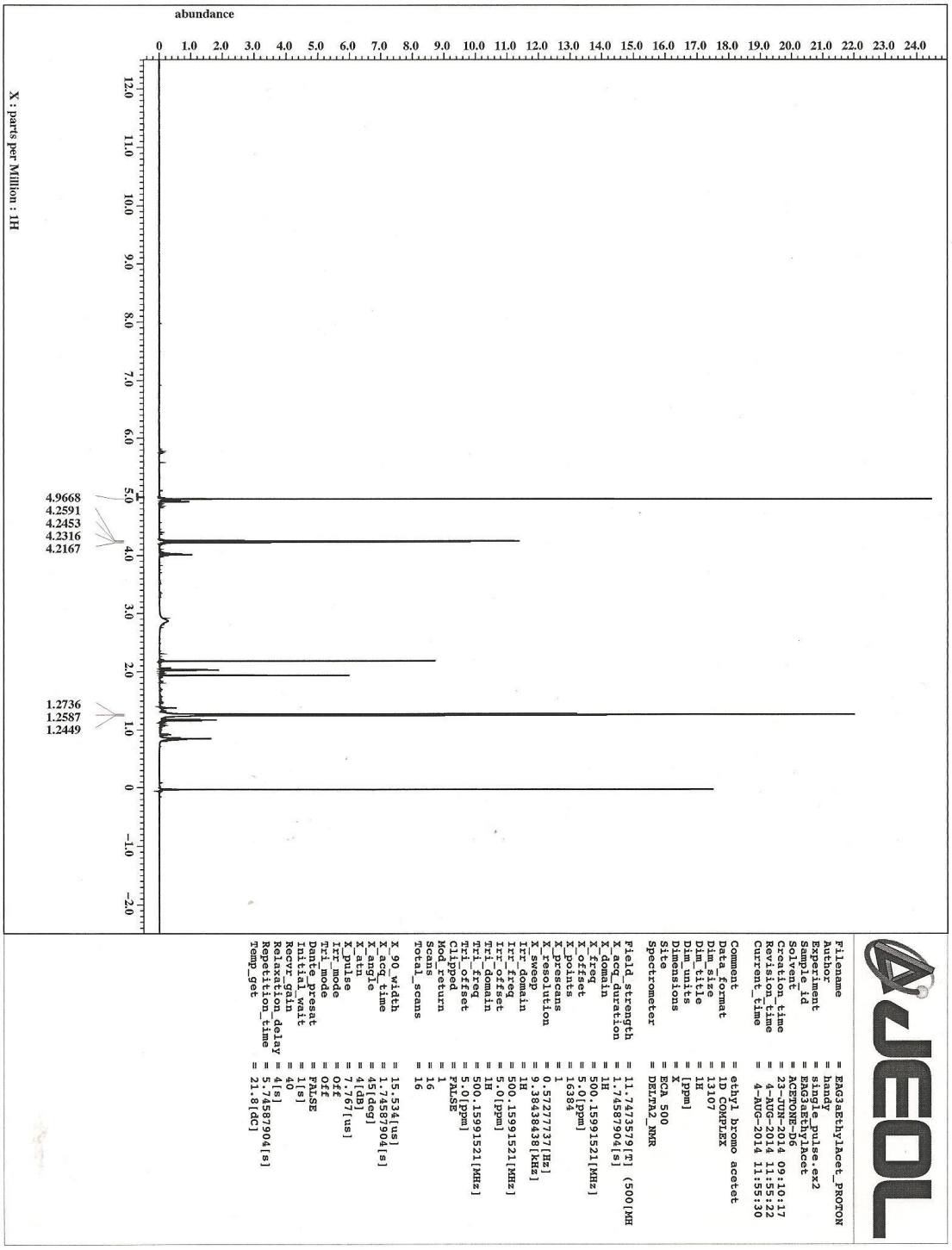
Peak2	954.599	97.411	6.773	960.548	924.865
Peak3	1043.424	11.071	1.029	1053.131	1038.665
Peak4	1096.133	17.626	1.941	1104.245	1089.778
Peak5	1121.643	18.118	1.662	1132.212	1116.782

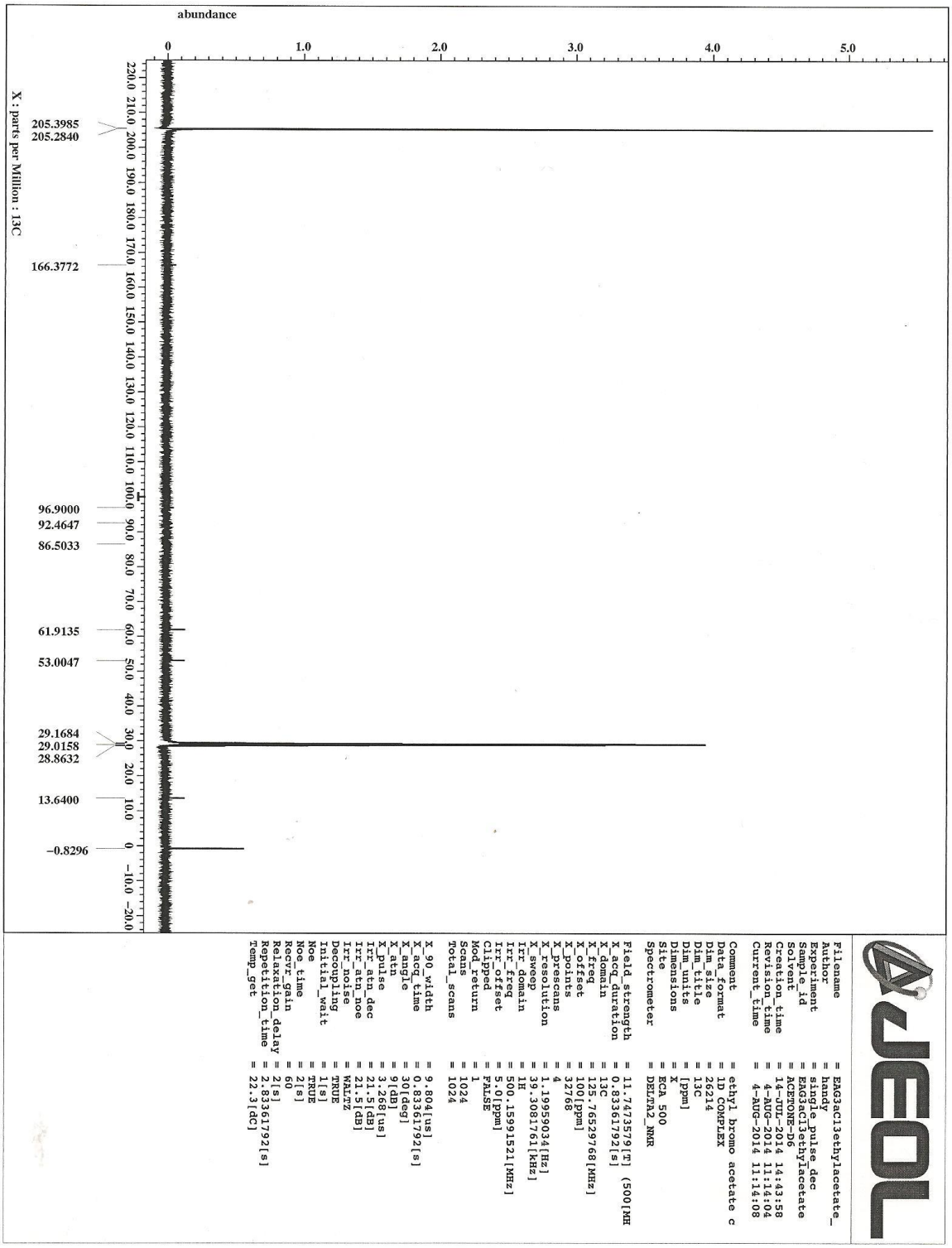
IR spectrum of 1-decyl-2,4,5-triiodo-1H-imidazole



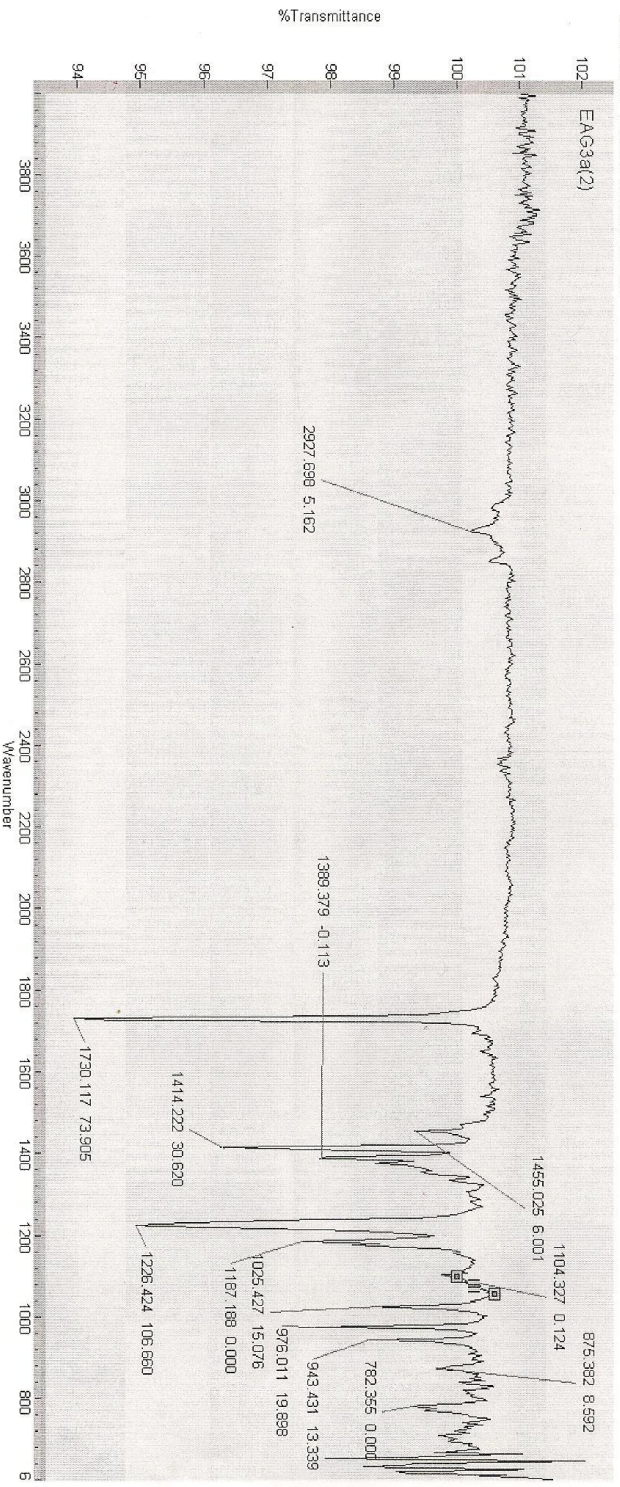
LC-MS spectrum of 1-decyl-2,4,5-triiodo-1H-imidazole



[1] H NMR (500 MHz, acetone-d6) spectrum of ethyl-2-(2,4,5-triiodo-1H-imidazole-1yl)acetate

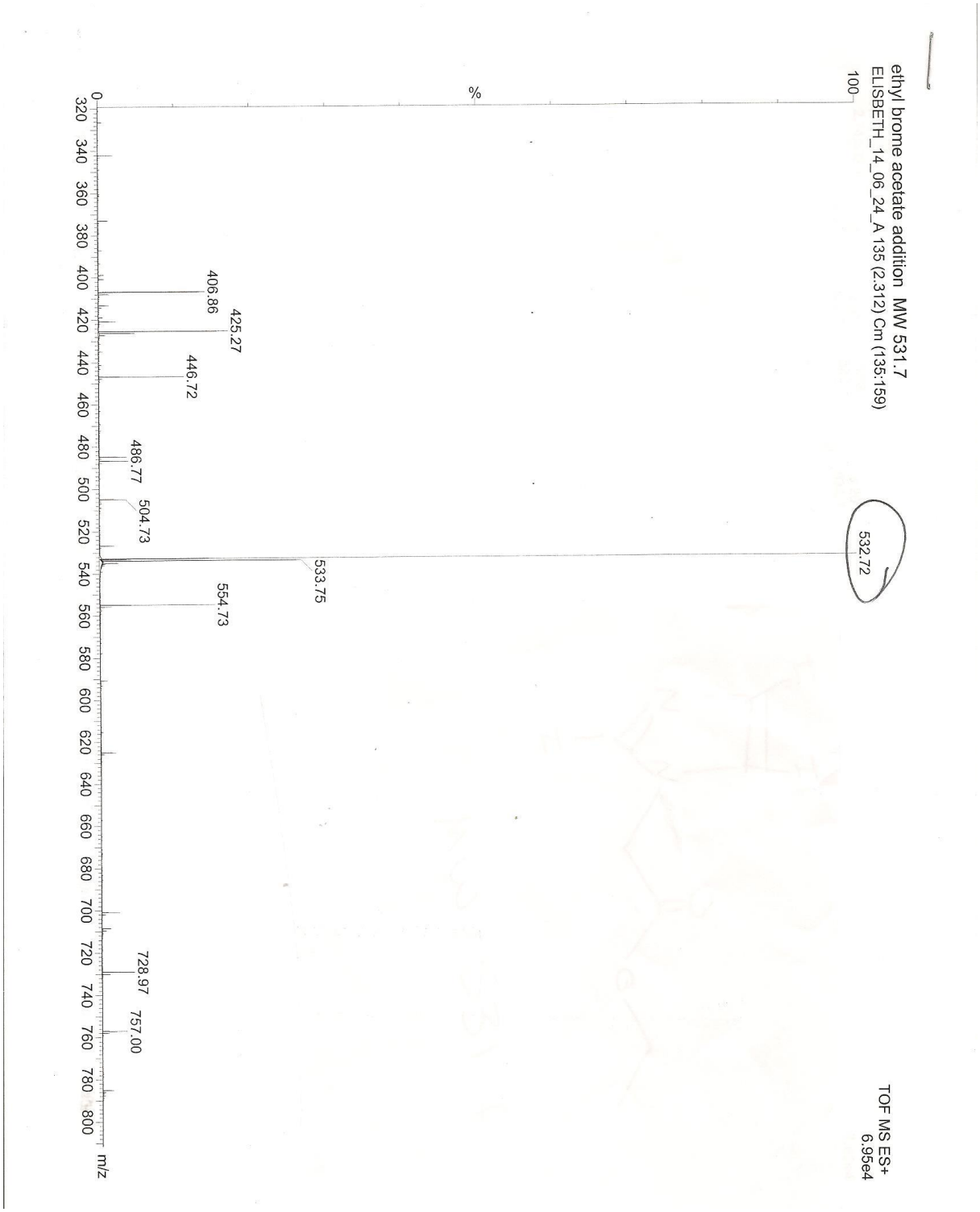


[13] C NMR (500 MHz, acetone-d6) spectrum of ethyl-2-(2,4,5-triiodo-1H-imidazole-1yl)acetate

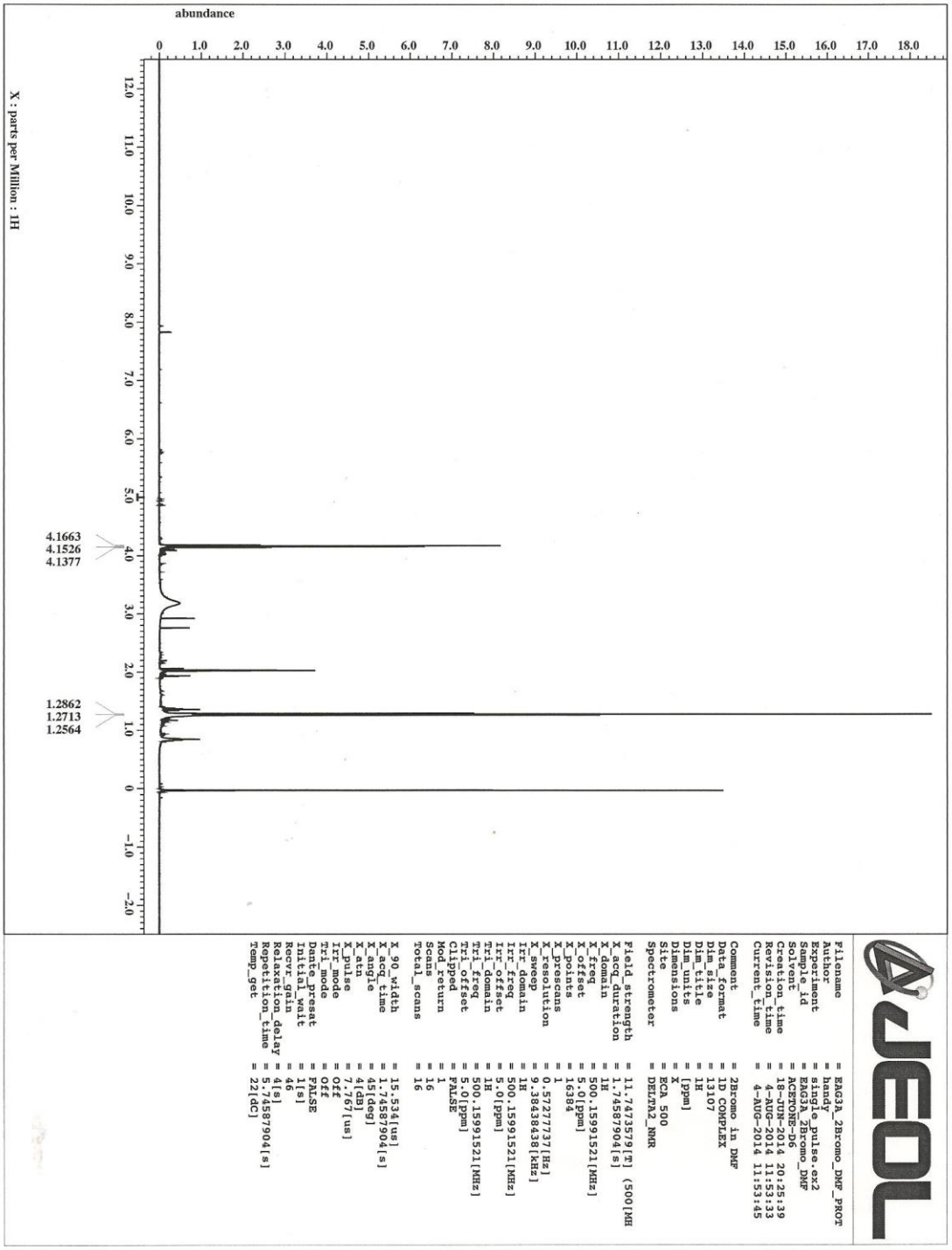


Peak List	Center	Area	Height	Left Edge	Right Edge
Peak14	782.355	0.000	0.405	777.311	777.311
Peak1	875.382	-8.592	0.744	884.360	865.072
Peak2	943.431	-13.339	1.716	951.868	936.438
Peak3	976.011	-19.898	2.637	988.516	967.299
Peak4	1025.427	-15.076	1.556	1029.021	1013.590
Peak5	1104.327	-0.124	0.192	1099.423	1078.206

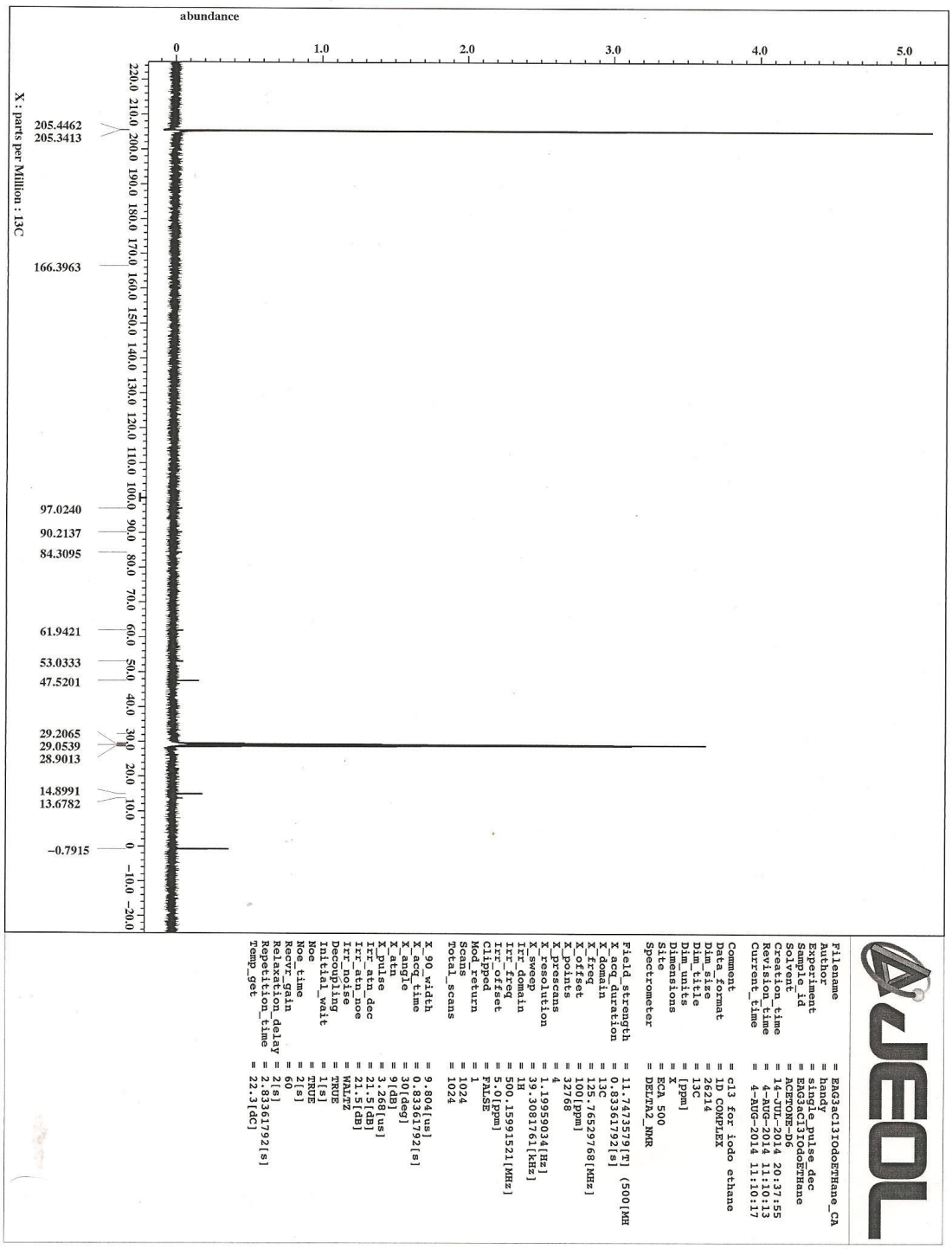
IR spectrum of ethyl-2-(2,4,5-triiodo-1H-imidazole-1yl)acetate



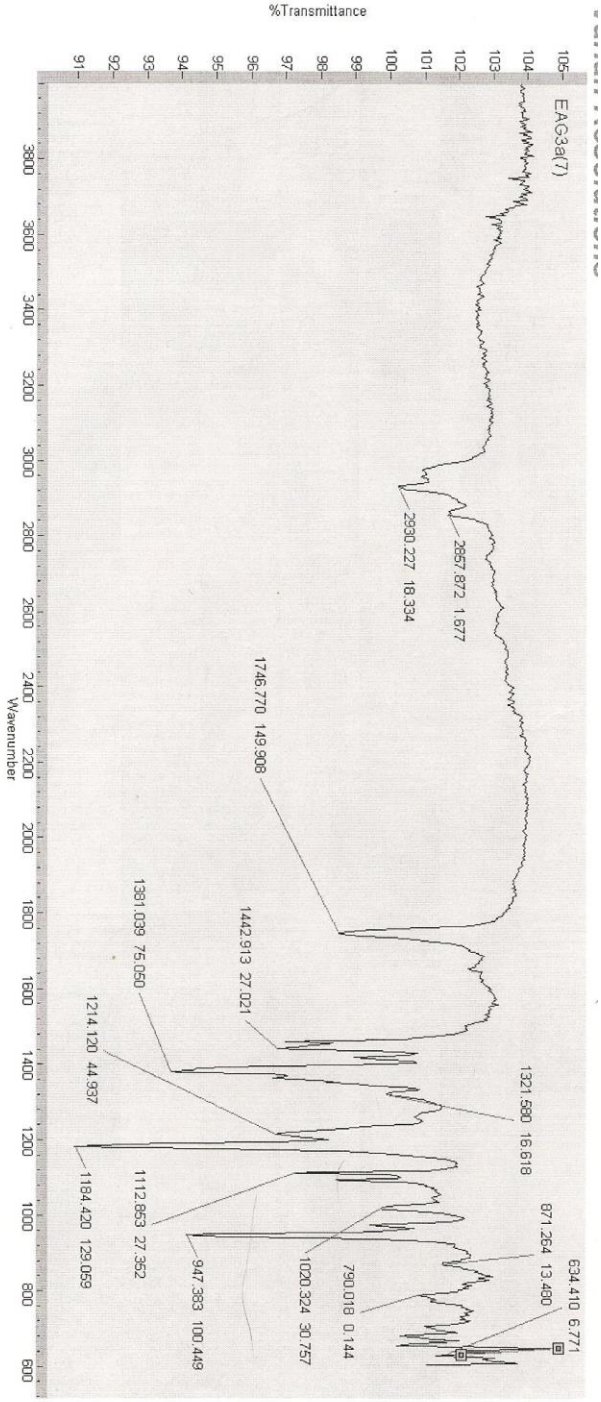
LC-MS spectrum of ethyl-2-(2,4,5-triiodo-1H-imidazole-1yl)acetate



[1] H NMR (500 MHz, acetone-d6) spectrum of 1-ethyl-2,4,5-triiodo-1H-imidazole

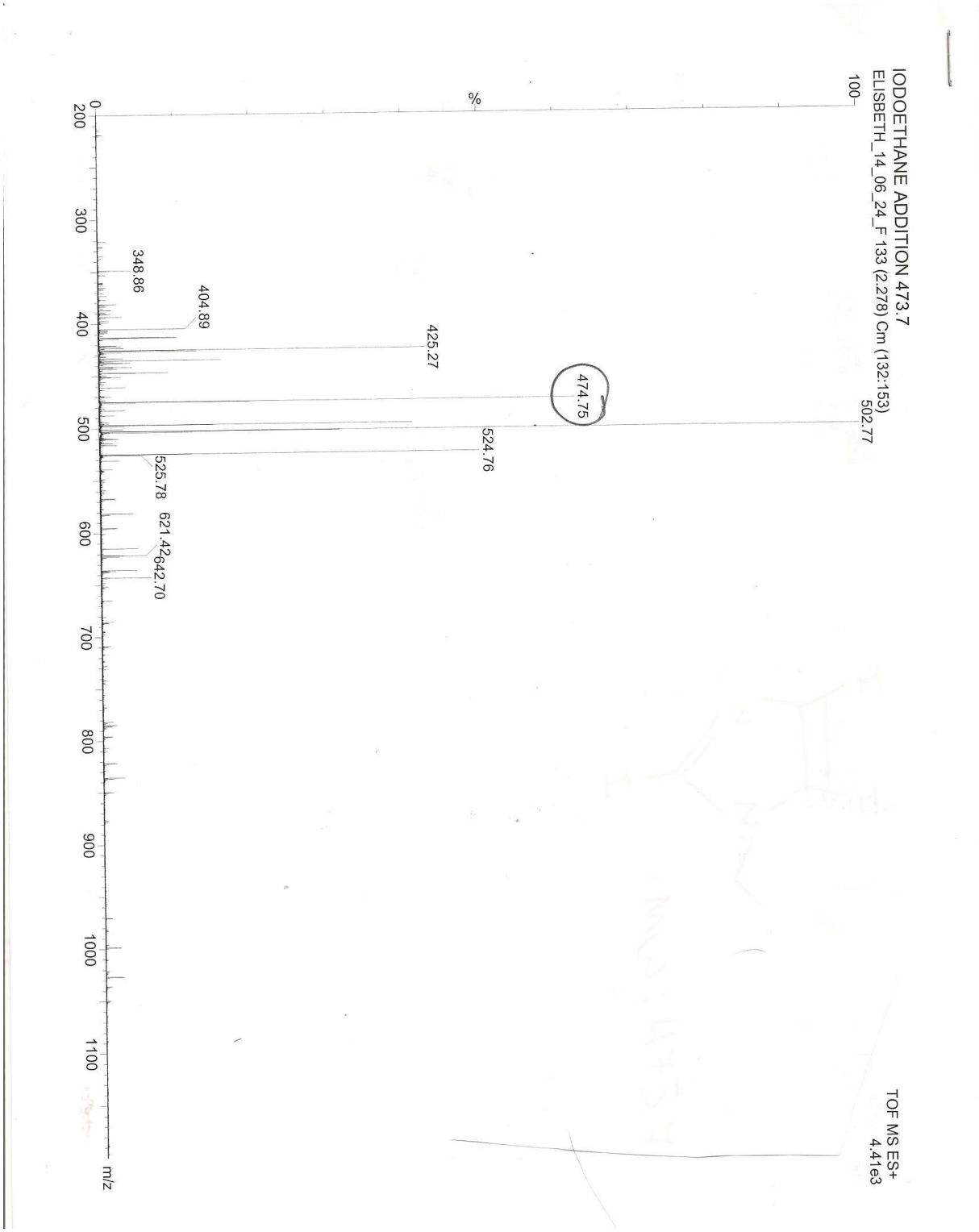


^{13} C NMR (500 MHz, acetone-d6) spectrum of 1-ethyl-2,4,5-triiodo-1H-imidazole

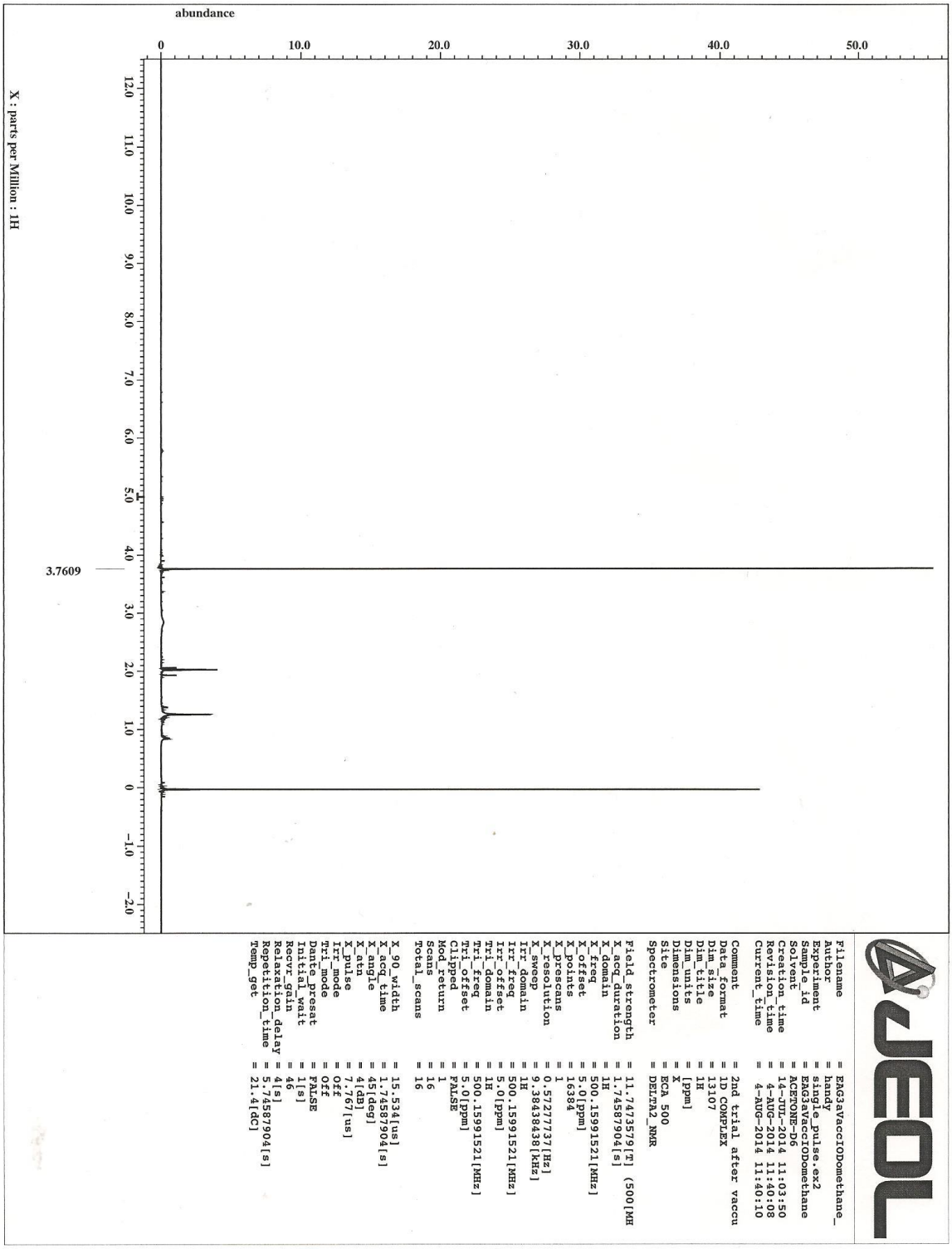


Peak List	Center	Area	Height	LeftEdge	RightEdge
Peak15	634.410	6.771	0.731	641.330	632.650
Peak1	790.018	0.144	0.167	785.026	782.133
Peak2	871.264	13.460	0.940	880.502	863.143
Peak3	947.383	100.449	7.057	956.690	922.936
Peak4	1020.324	30.757	1.982	1029.021	1006.840
Peak5	1112.853	27.352	3.674	1119.675	1106.173

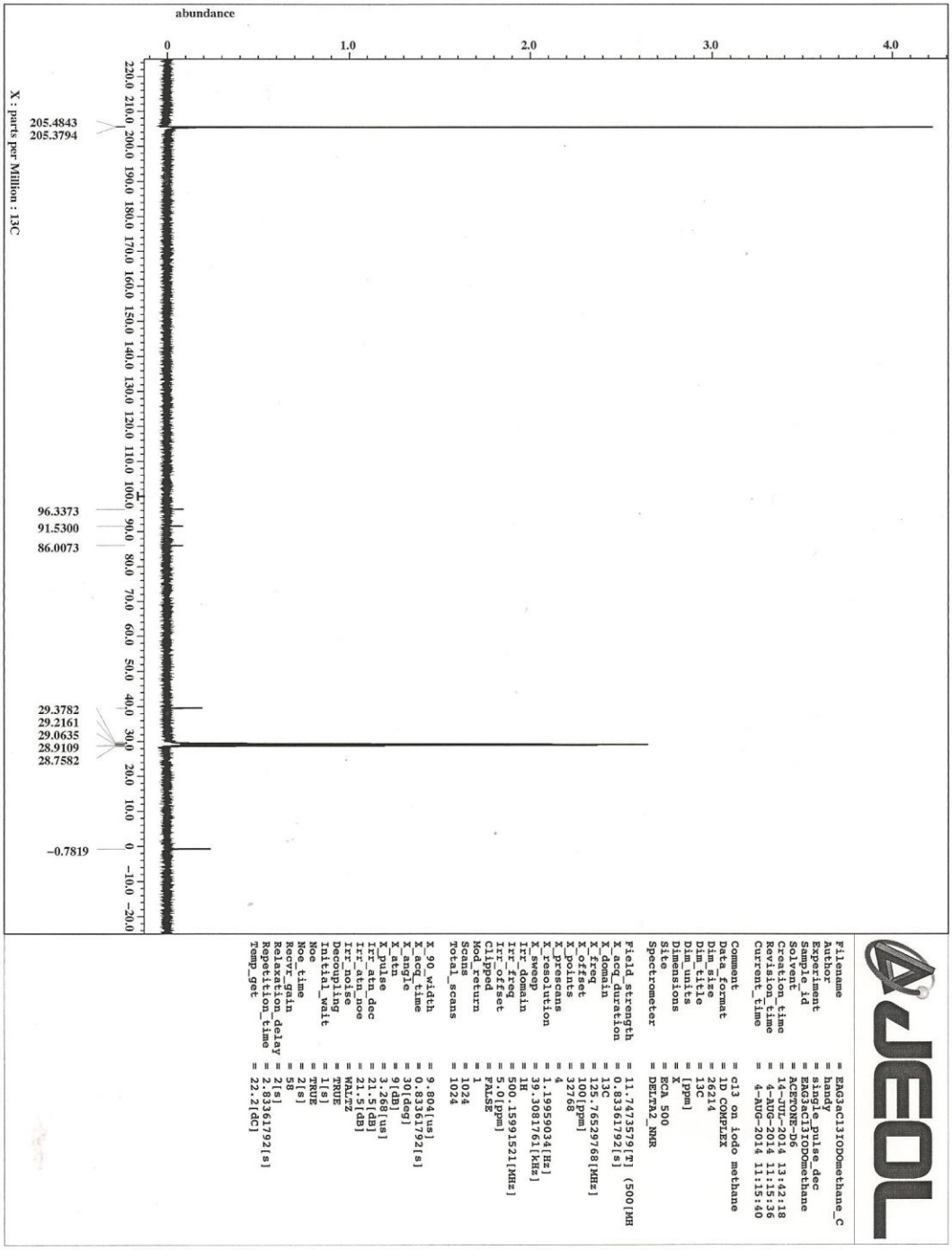
IR spectrum of 1-ethyl-2,4,5-triiodo-1H-imidazole



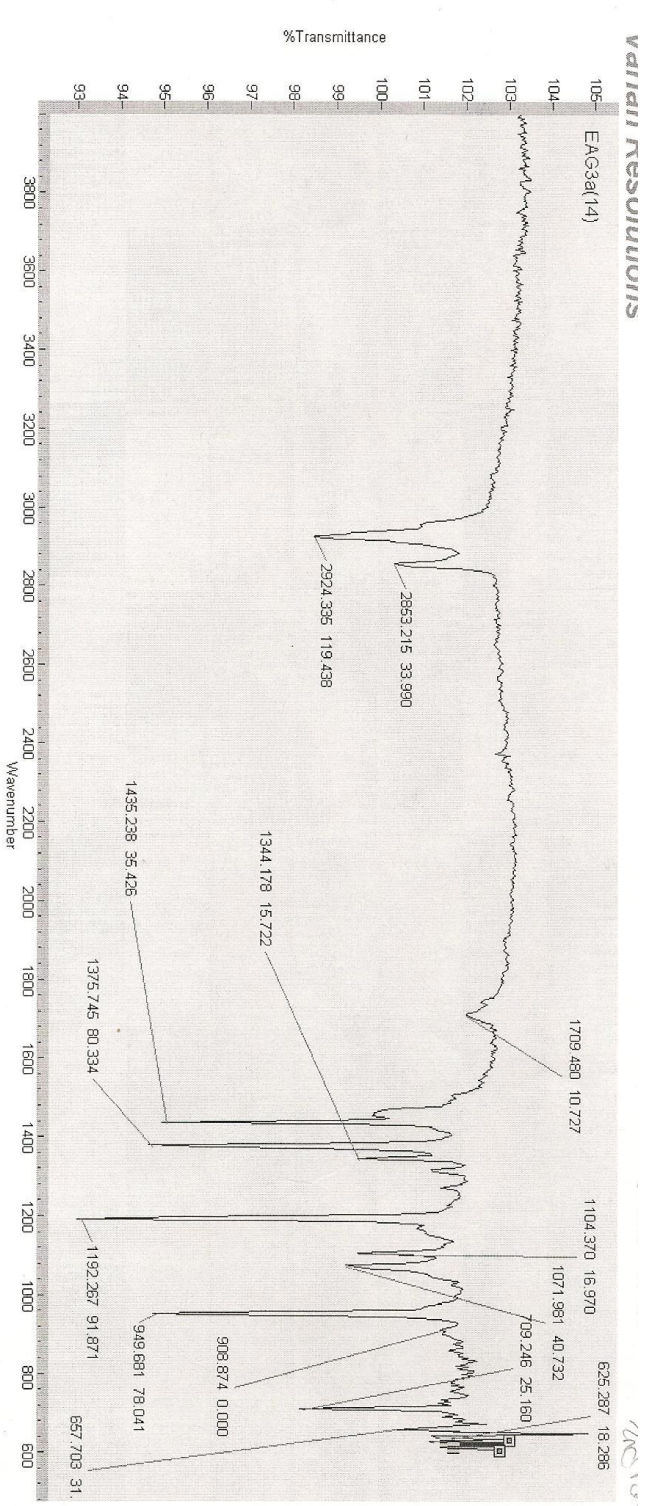
LC-MS spectrum of 1-ethyl-2,4,5-triiodo-1H-imidazole



[1] H NMR (500 MHz, acetone-d6) spectrum of 2,4,5-triiodo-1-methyl-1H-imidazole

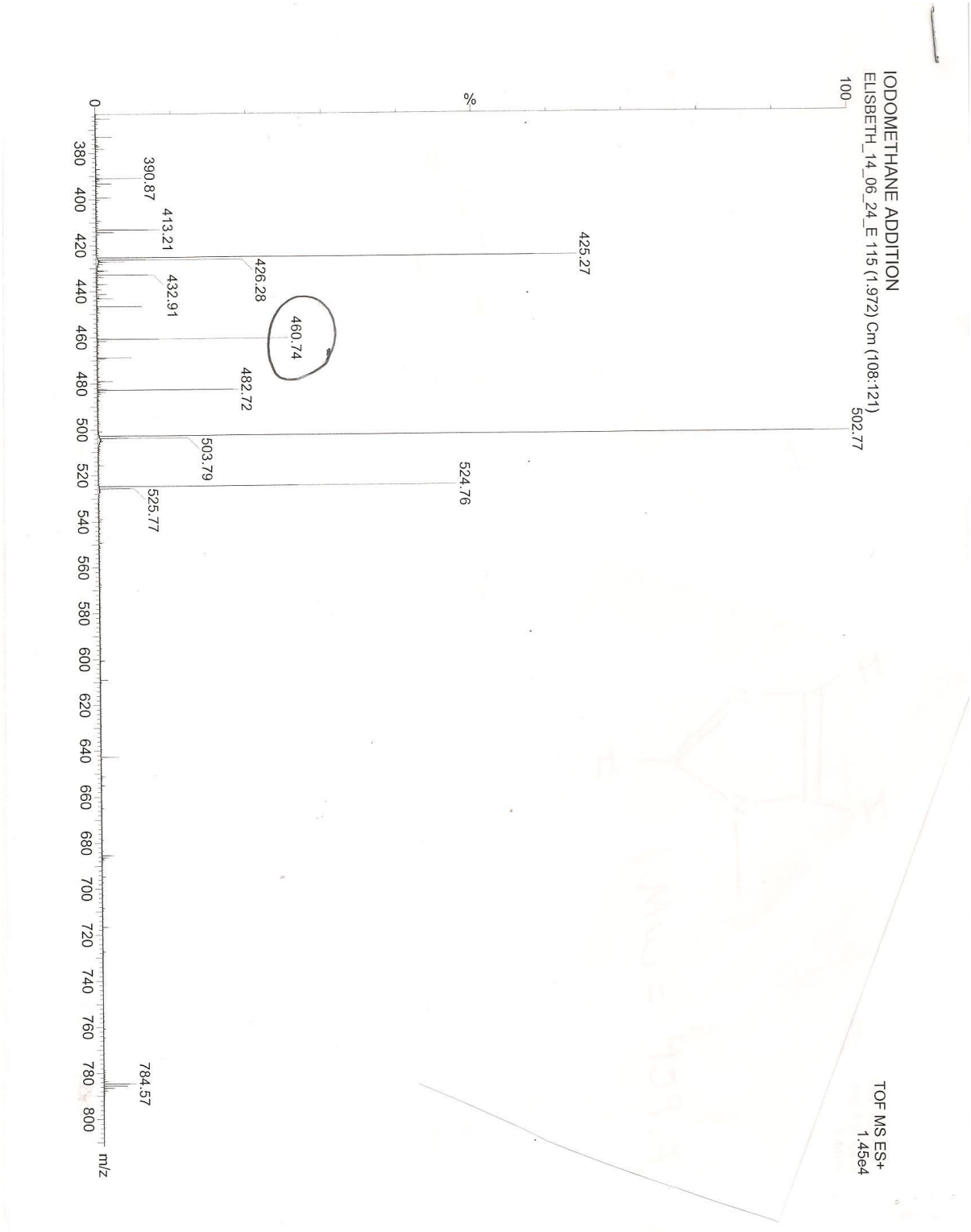


^{13} C NMR (500 MHz, acetone-d6) spectrum of 2,4,5-triiodo-1-methyl-1H-imidazole

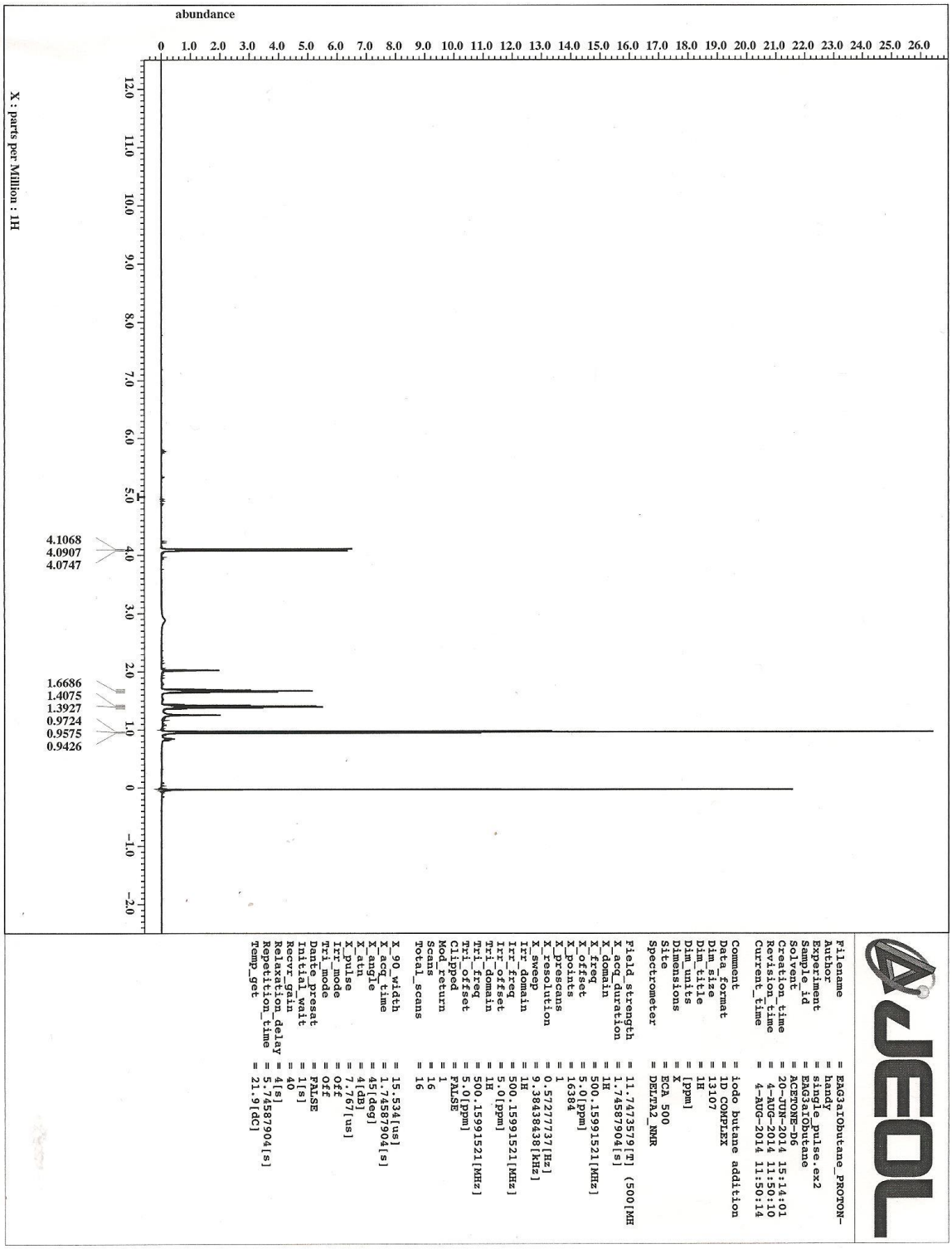


Peak List	Center	Area	Height	Left Edge	Right Edge
Peak15	625.287	-18.286	1.825	627.828	614.326
Peak1	657.703	-31.123	3.380	664.476	651.938
Peak2	709.246	-25.160	3.625	713.660	702.087
Peak3	908.874	0.000	0.071	904.613	904.613
Peak4	949.681	-78.041	6.948	962.477	938.367
Peak5	1071.981	-40.732	2.281	1081.099	1050.238

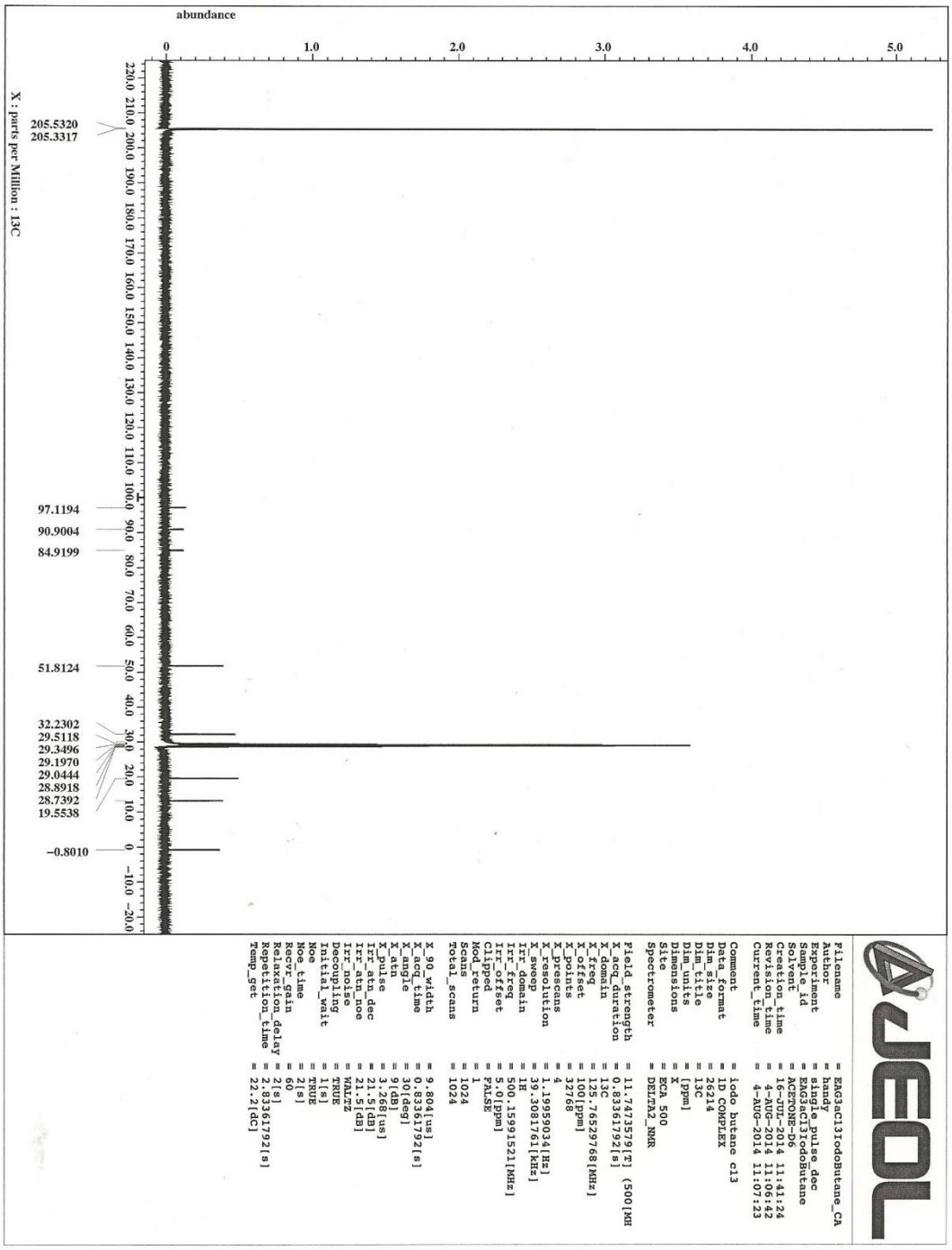
IR spectrum of 2,4,5-triiodo-1-methyl-1H-imidazole



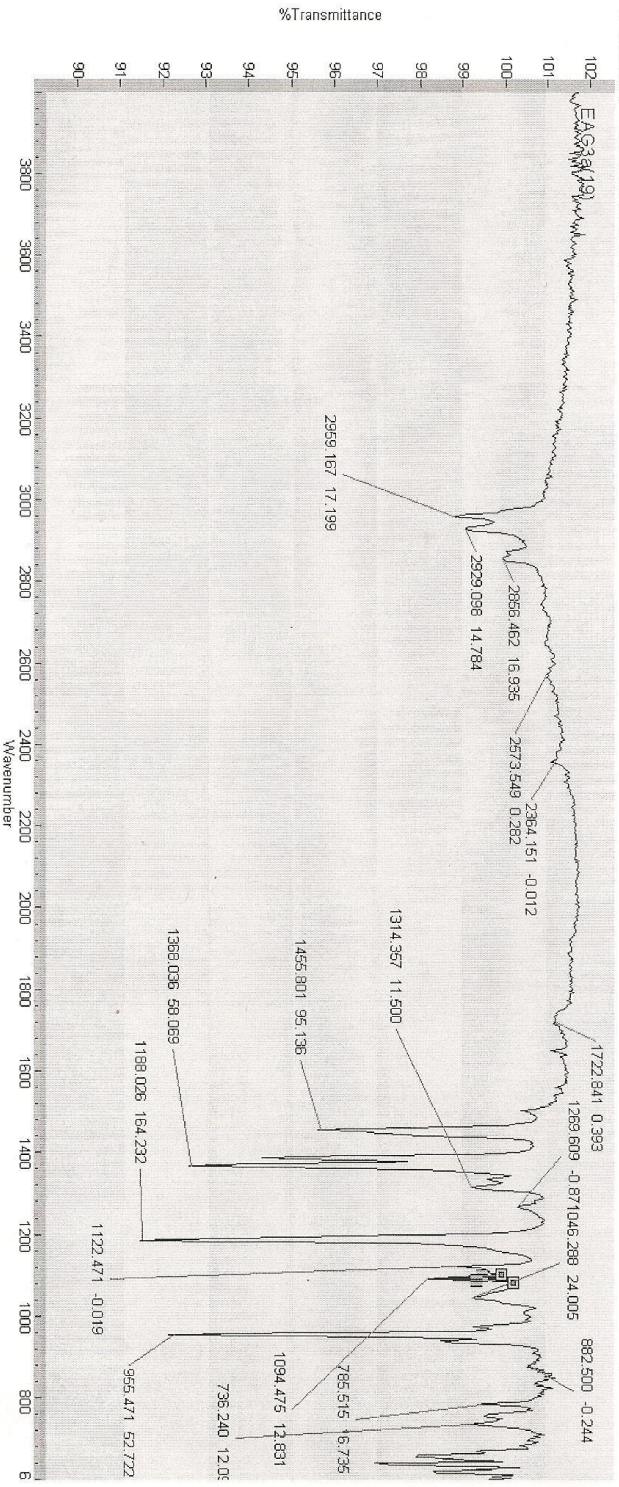
LC-MS spectrum of 2,4,5-triiodo-1-methyl-1H-imidazole



[1] H NMR (500 MHz, acetone-d6) spectrum of 1-butyl-2,4,5-triiodo-1H-imidazole

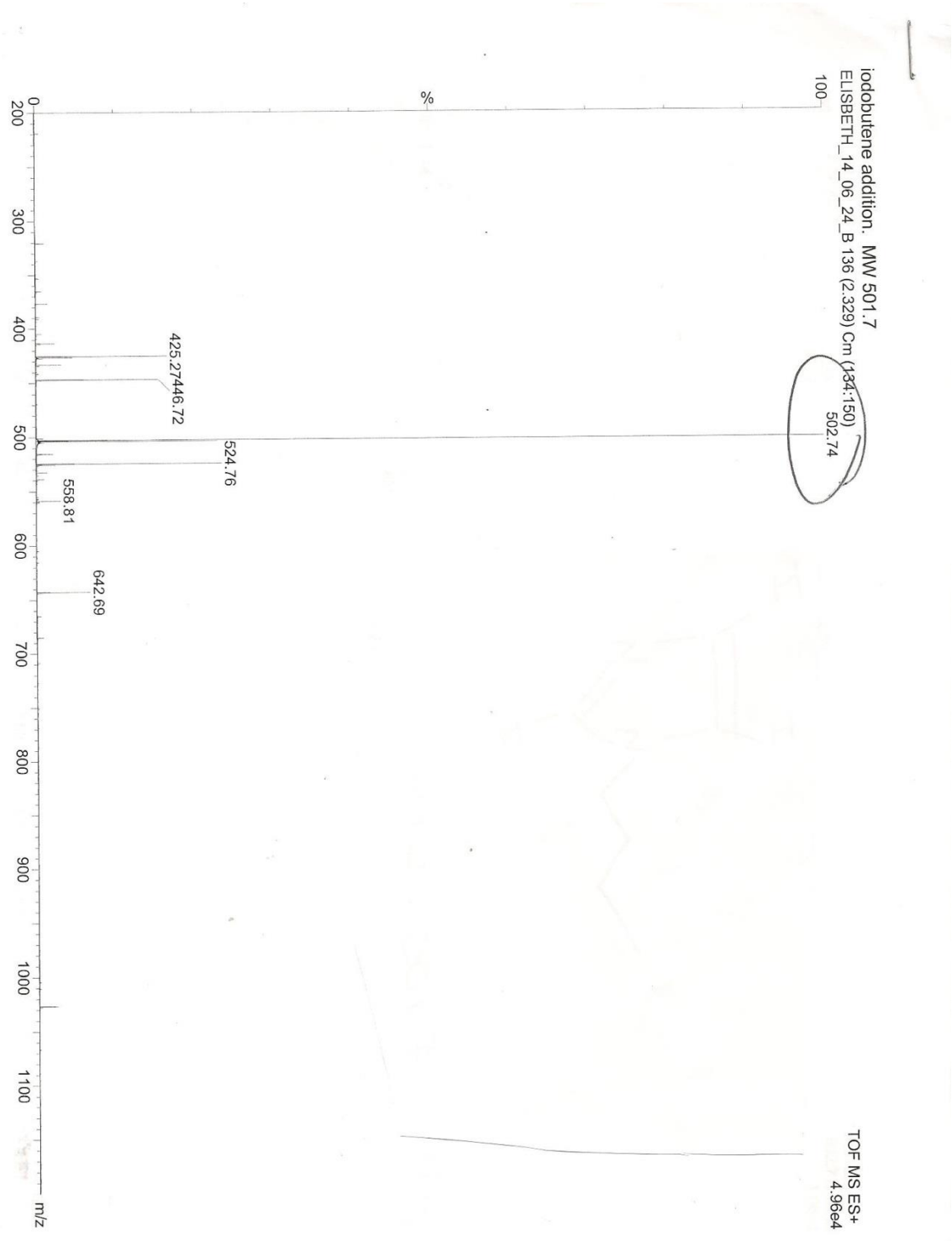


[13] C NMR (500 MHz, acetone-d6) spectrum of 1-butyl-2,4,5-triiodo-1H-imidazole

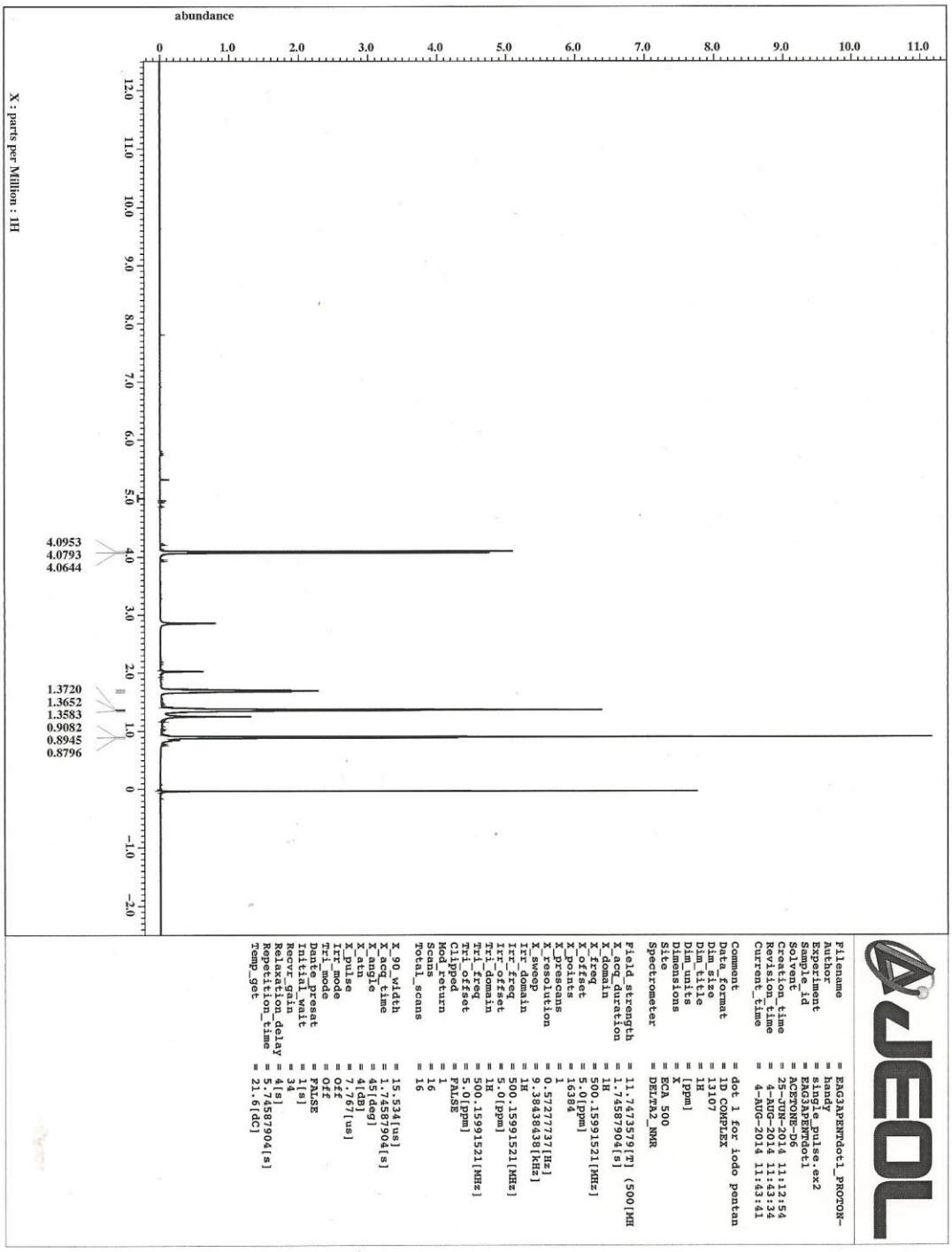


Peak List	Center	Area	Height	Left Edge	Right Edge							
Peak19	736.240	-12.095	1.180	744.521	725.233							
Peak1	785.515	-16.735	1.368	805.279	777.311							
Peak2	862.500	0.244	0.040	891.111	881.467							
Peak3	955.471	-52.722	7.535	962.477	949.940							
Peak4	1046.268	-24.005	1.265	1060.846	1034.807							
Peak5	1094.475	-12.831	1.929	1099.423	1089.778							

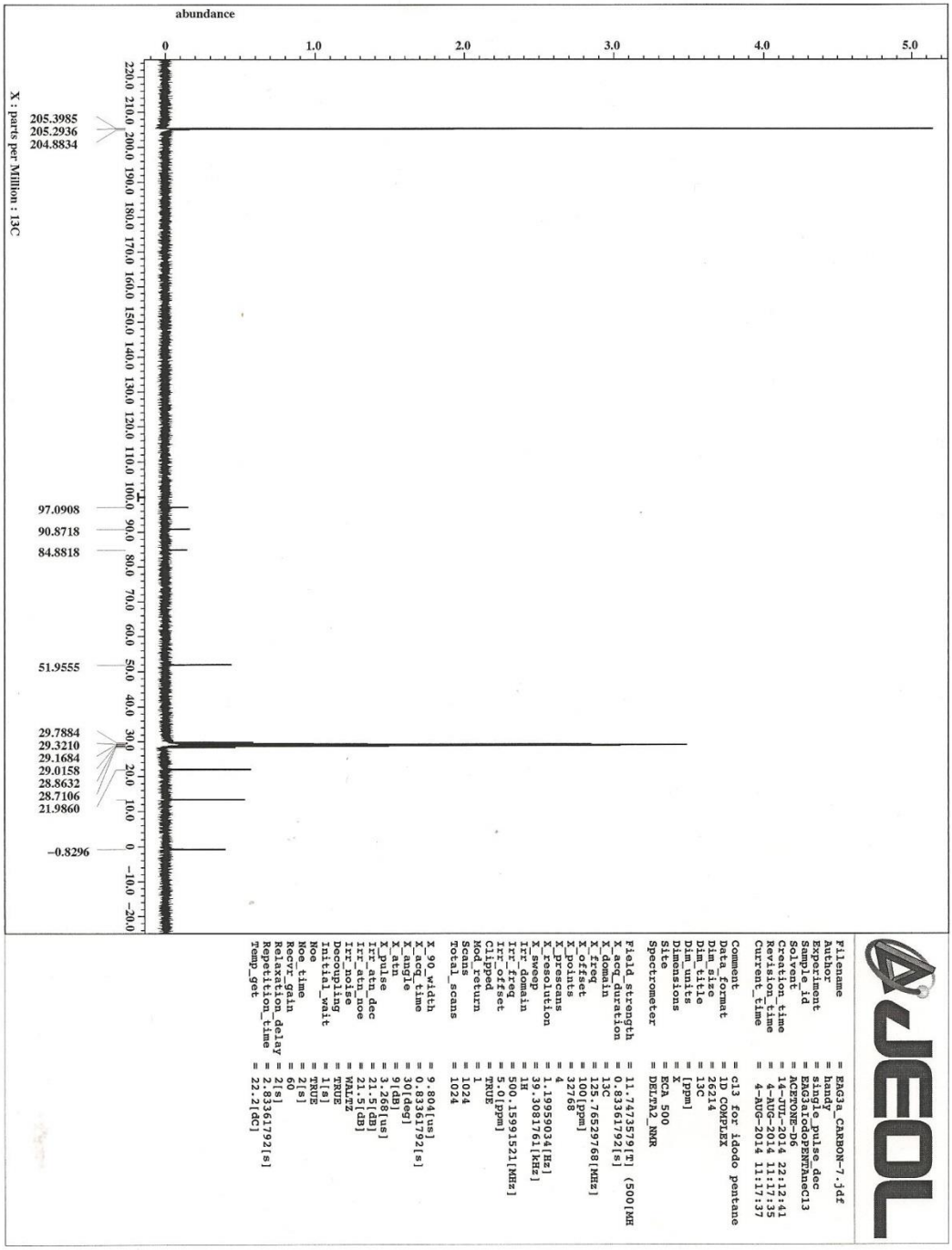
IR spectrum of 1-butyl-2,4,5-triiodo-1H-imidazole



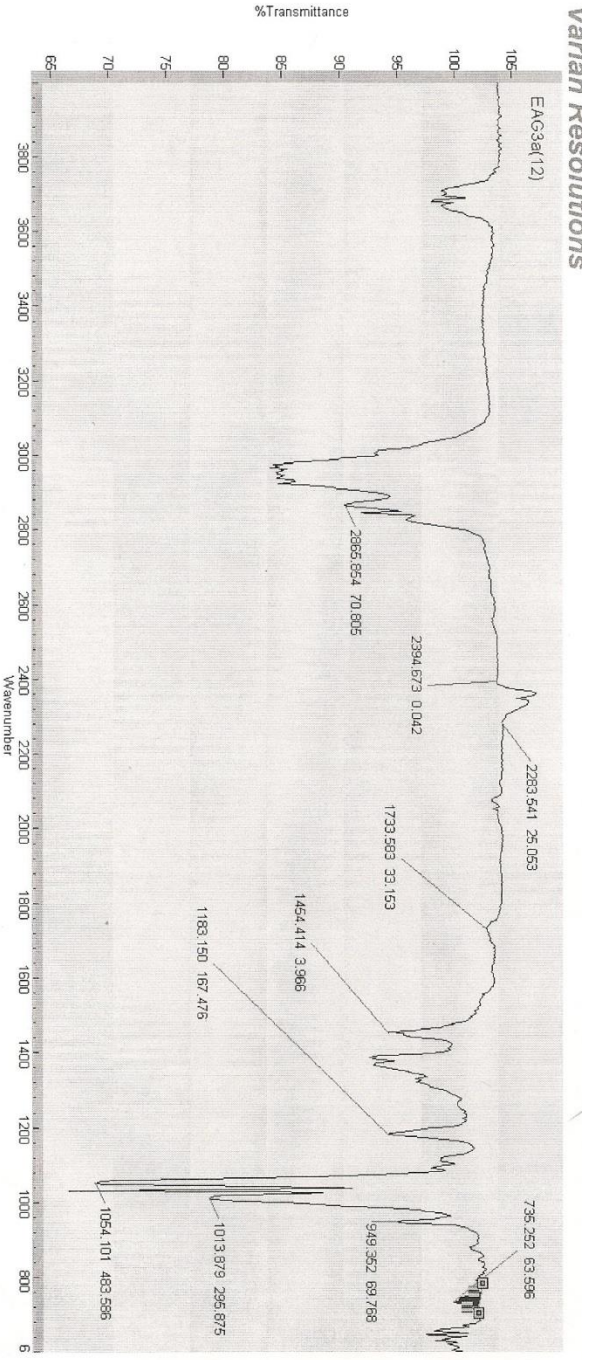
IR spectrum of 1-butyl-2,4,5-triiodo-1H-imidazole



[1] H NMR (500 MHz, acetone-d6) spectrum of 2,4,5-triiodo-1-pentyl-1H-imidazole

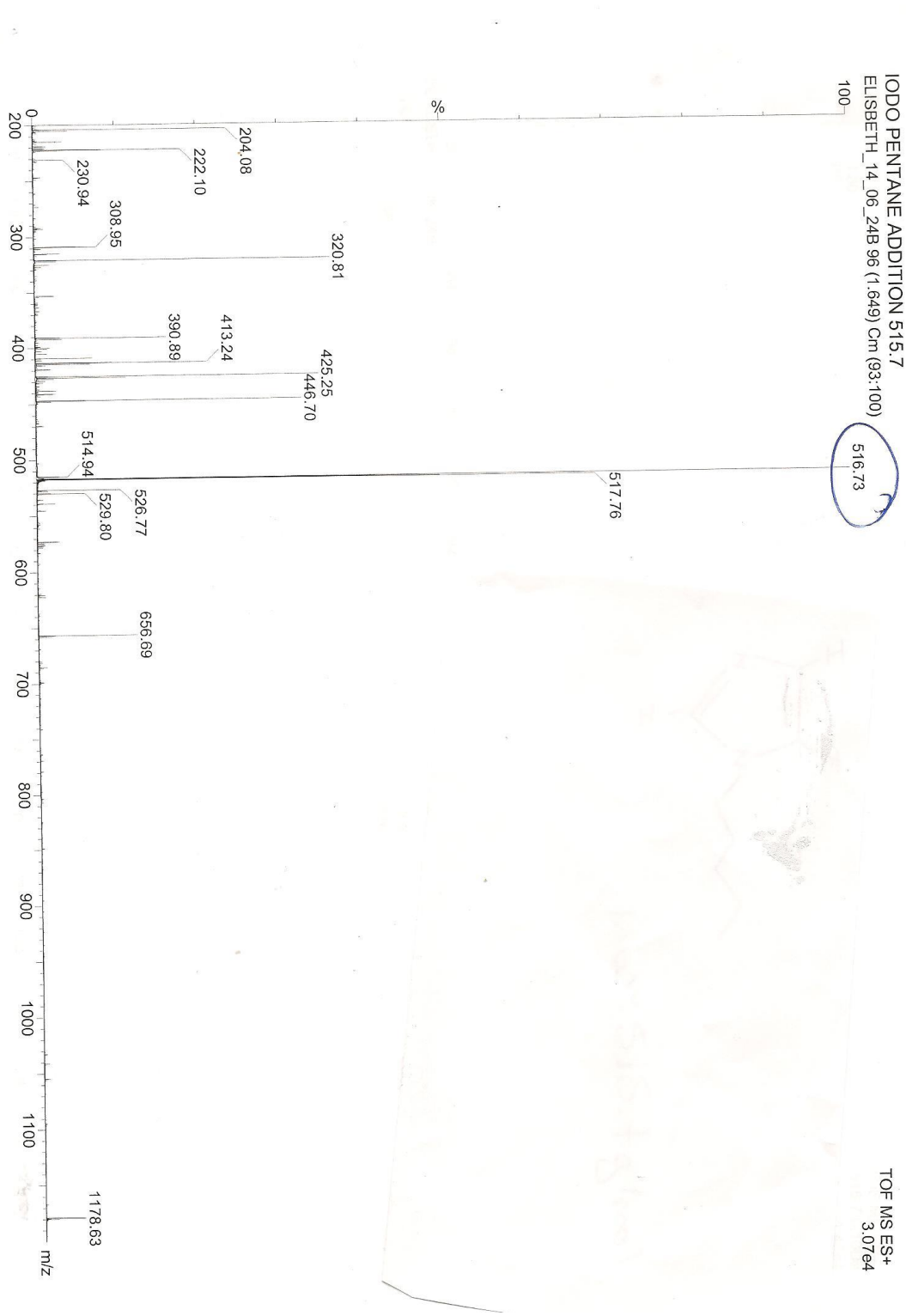


^{13} C NMR (500 MHz, acetone-d6) spectrum of 2,4,5-triiodo-1-pentyl-1H-imidazole

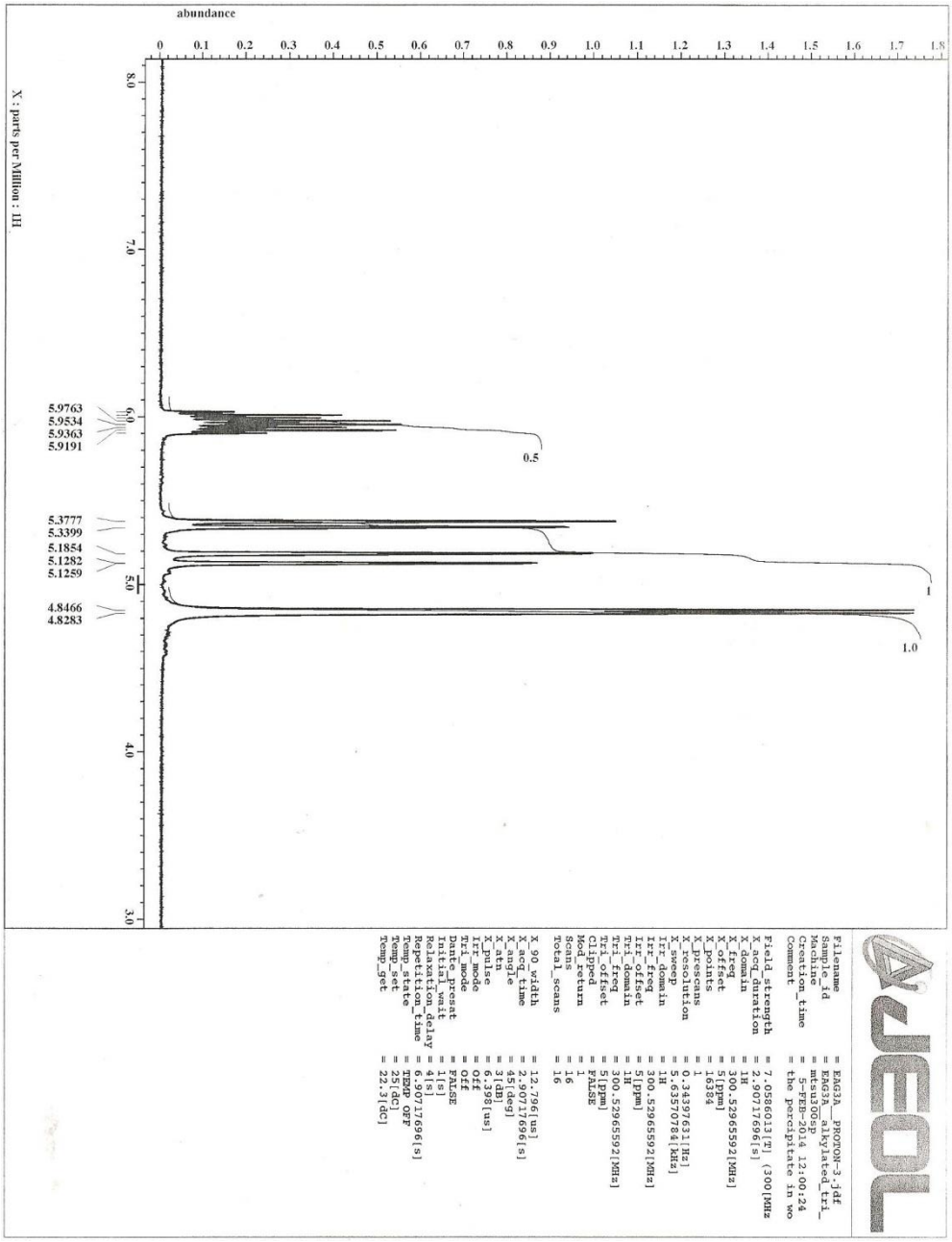


Peak List	Center	Area	Height	LeftEdge	RightEdge
Peak11	735.252	-63.596	2.360	761.881	721.375
Peak1	949.352	-69.768	5.573	956.690	931.616
Peak2	1013.879	-295.875	12.410	1020.341	988.516
Peak3	1054.101	-483.586	25.072	1070.490	1046.380
Peak4	1183.150	-167.476	7.240	1201.650	1165.002
Peak5	1454.414	-3.966	0.722	1450.466	1436.965

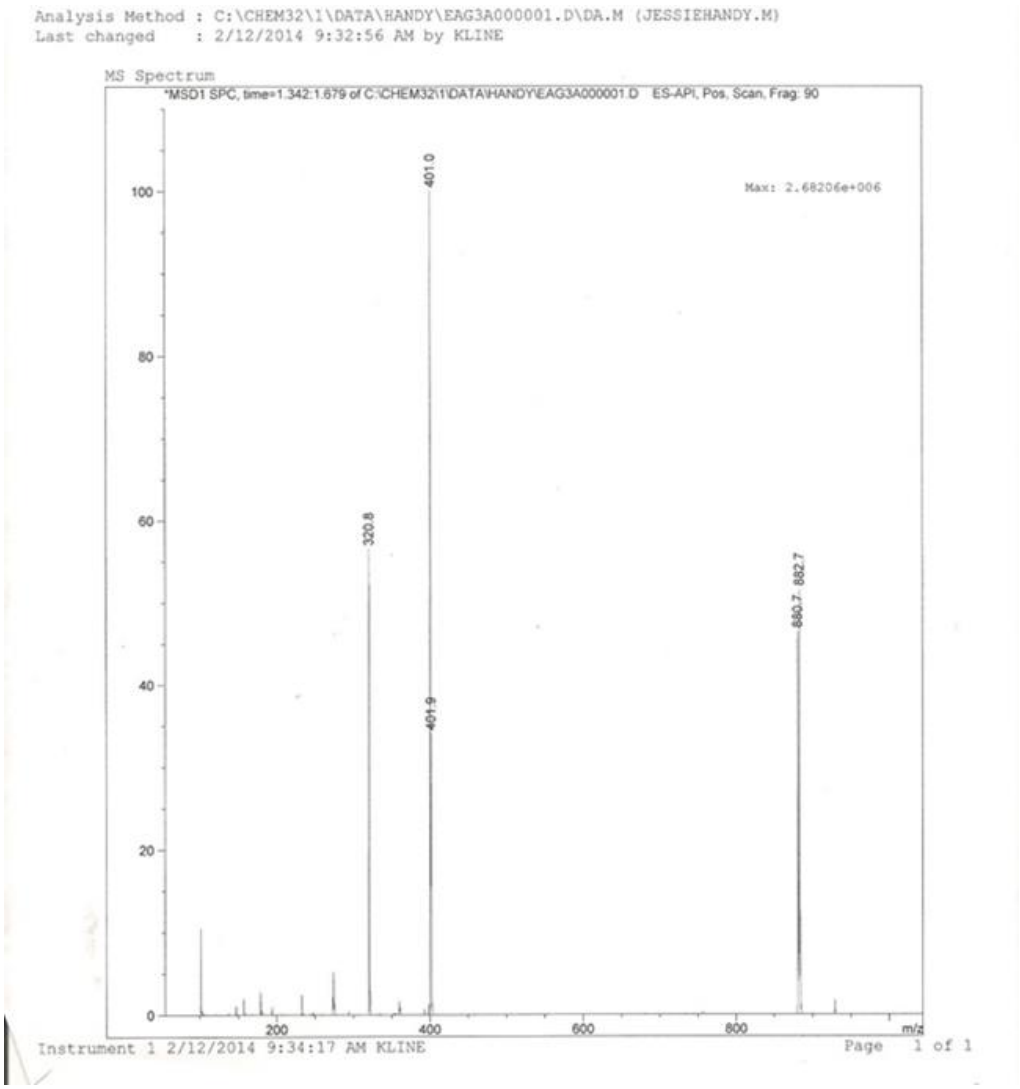
IR spectrum of 2,4,5-triiodo-1-pentyl-1H-imidazole



LC-MS spectrum of 2,4,5-triiodo-1-pentyl-1H-imidazole



^{1}H NMR (500 MHz, Dimethyl sulfoxide-D6) of compound diallylated 2,4,5-triiodoimidazole (1)



LC-MS spectrum of compound diallylated 2,4,5-triiodoimidazole (1)