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Molecular Organometallic Resists of Tin and Tellurium

by

Ryan Del Re

A Thesis

Submitted to the University at Albany, State University of New York

in Partial Fulfillment of

the Requirements for the Degree of

Master of Science

College of Nanoscale Science and Engineering

2015

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Lam Research Corp. v. Inpria Corp.
IPR2025-00256 - U.S. Patent No. 11,537,048

Abstract

EUV photoresists made from organotin and organotellurium dicarboxylates were lithographically evaluated for photosensitivity and dense-line patterning. The effects of ligand structure and central metal are explored through systematic molecular modification. Through this work, two photoresists were discovered that are capable of high resolution and low line-edge roughness. Dibenzyltin dipivalate resolves 22-nm dense lines with 1.4-nm LER and dibenzyltin dibenzoate resolves 35-nm dense lines with 1.1-nm LER.

Photolithographic evaluation of thirty-one resists of the type $R_2M(O_2CR')_2$ shows ligand choice greatly affects overall resist performance. We observe that decreasing the molecular weight of carboxylate ligands improve resist sensitivity. When a carboxylate contains an olefin, the resist sensitivity improves dramatically. We also determine that decreasing the tin-carbon bond strength improves resist sensitivity.

Finally, a proposed mechanism for the photochemistry that occurs upon exposure to EUV light is presented. Detailed analysis of volatile elements by mass spectroscopy and exposed film by XPS suggests the loss of R_2 upon exposure followed by the formation of a "polymeric" stannoxane.

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Chapter I: Introduction to Extreme Ultraviolet Lithography

Overview

An integrated circuit (IC) is a vast network of transistors and other electronic components assembled on a substrate, typically silicon.[1] Since the invention of the IC by Jack Kilby in 1958,[2,3] there has been exceptional growth in many areas of research and industry. Medicinal diagnostic tool advancements, information sharing and availability progress, national defense technological improvement, and many scientific discoveries can be attributed to the use of integrated circuits.[4-8] Today, we find integrated circuits all around us. They are found in everything from the alarm clocks that wake us up to the ovens that cook our food, and, of course, in the computers we use every day. As the size of transistors decrease, integrated circuits become even more prevalent due to the minimal cost for production and consumption.

In 1965, Gordon Moore observed that the number of transistors in an integrated circuit roughly doubled every two years primarily through the reduction of transistor feature sizes (Figure 1).[9,10] More important, was his observation that the manufacturing cost of the integrated circuits of greater transistor density would remain constant. His historic paper[11] led to what we now refer to as Moore's Law, which has been the driving force for the microelectronics industry growth and can even be used to describe productivity and economic growth.[12,13] One of the primary factors for driving Moore's law forward in the microelectronics industry has been photolithography.

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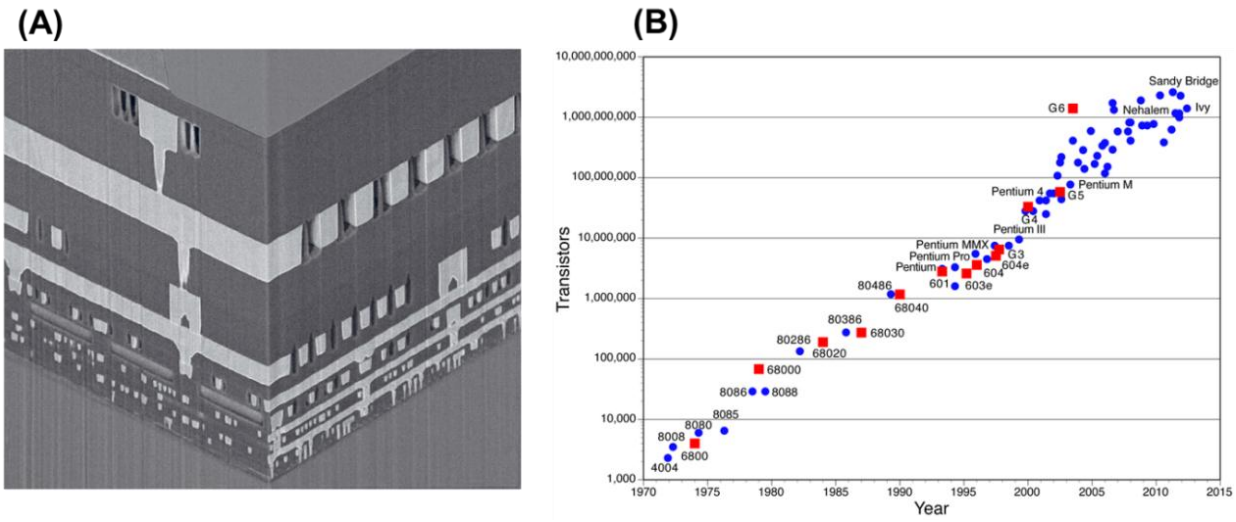

Figure 1. (A) Cross-section of a microprocessor showing multiple processed levels.[14] The lowest level is the location of the transistors and each level above contains a complex network of copper interconnects and vias. (B) Recent chart showing the number of transistors over time in Intel microprocessors.[15]

1. Introduction to Photolithography

Photolithography is the process by which light transfers a pattern from a mask to a photochemically reactive film (photoresist) applied to a substrate. Photons promote a chemical or physical change in the photoresist that can then be processed and chemically treated to selectively remove (positive tone) or keep (negative tone) only those areas that have been exposed to light. After the pattern has been created in the film, the photoresist's function is to resist the etch that occurs when transferring the pattern into the substrate, typically a single crystal silicon wafer.[16]

Photolithography typically occurs in three steps[17] (Figure 2):

(A) Application of the photoresist. A film is typically spin-coated onto a flat substrate.[18] It is essential this film be amorphous and homogeneous.

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(B) Exposure of the photoresist with light through a mask. Through a series of photochemical reactions, the mask pattern is transferred to the film. This latent image can vary greatly between resist systems, but will always be the foundation for some kind of solubility shift that will be exploited in the development step.

(C) Development of the photoresist. The photoresist is washed with a solvent that either promotes dissolution (positive tone) or inhibits dissolution (negative tone) in the exposed areas. A post exposure bake (PEB) may or may not be used before development depending on the system.

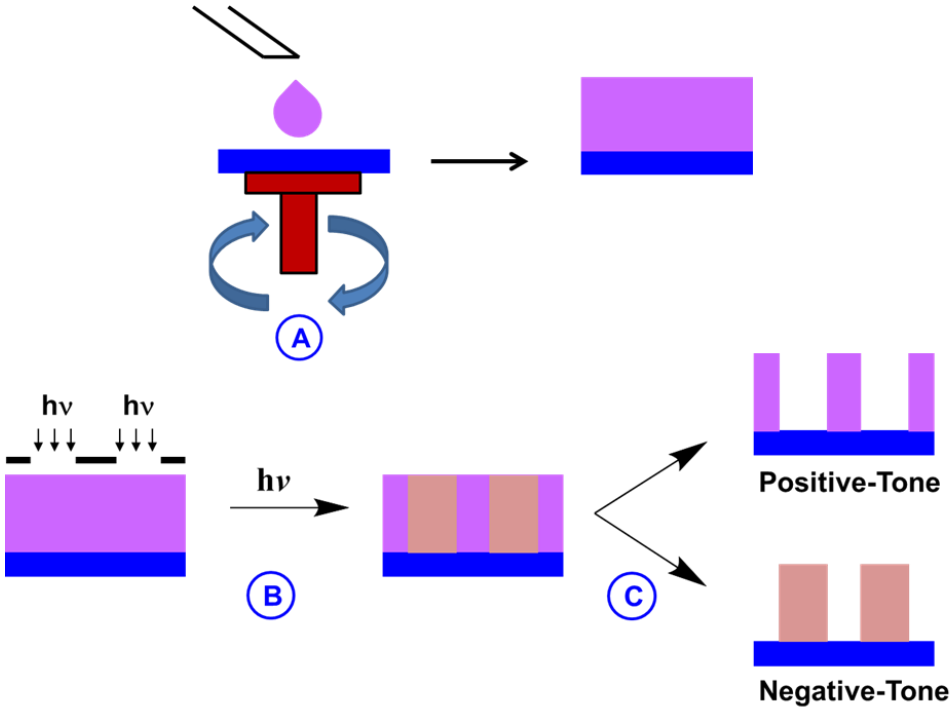

Figure 2. Three steps in photolithography. (A) Application of the photoresist on a substrate and spin-coating to create a thin film on a substrate. (B) Exposure of the photoresist through a mask to cause a selective chemical change. (C) Development of the photoresist to create patterns.

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One way to increase transistor density on a chip is to decrease the feature size of printed patterns. One powerful method of reducing the printed feature size is to decrease the wavelength of light used during exposure of the photoresist. Rayleigh's equation (Equation 1) dictates the ultimate resolution of a given photoprinting technology.[19] Through the years, the industry has progressed from λ = 436 nm (g-line) to λ = 193 nm in incremental steps (Figure 3). With each step, new photoresist platforms have been developed to best take advantage of the increasing photon energy and the photon's interactions with the film.

$$Resolution = k_1 \frac{\lambda}{NA}$$

Equation 1. Rayleigh's equation determines the minimum feature that can be printed with optical lithography. λ = wavelength of light used, NA = numerical aperture, k_1 = resolution factor.

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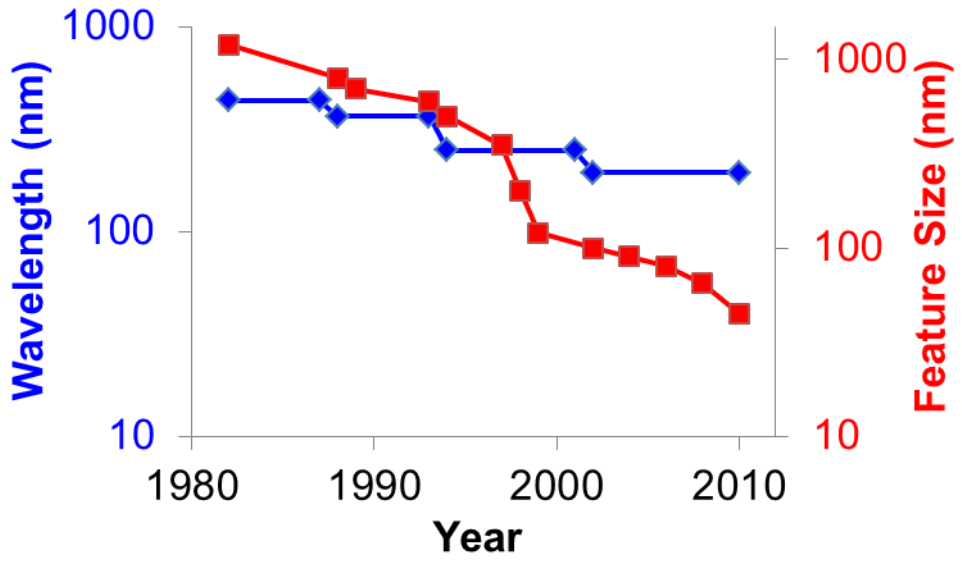

Figure 3. Reduction in the wavelength of light used to expose a photoresist has led to a reduction in the size of printed features.

State of the art photolithography uses λ = 193 nm light produced by ArF excimer lasers.[20] Increasing the numerical aperture (NA) of the optics through water immersion has further decreased the critical dimensions of the printed features.[21,22] However, we are rapidly approaching a barrier in which the cost and complexity of achieving smaller feature sizes is increasing with each new technology node.[23-25] The push to these smaller feature sizes has led to a number of new lithographic technologies being researched such as extreme ultraviolet (EUV, λ = 13.5 nm), directed self-assembly,[26,27] nanoimprint,[28] electron beam,[29,30] and proton beam.[31]

2. Introduction to Extreme Ultraviolet Lithography (EUVL)

EUVL has roots in the 1980's as soft x-ray lithography (5-40 nm). Kinoshita, *et al.*, was the first to successfully publish imaging results using these higher energy photons in 1989.[32] Eventually, experiments performed by Wood, *et al.*, led to the conclusion that using light with

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wavelengths less than 13.9 nm would be most desirable due in part to higher transparencies of the films tested (1994).[33,34] In 1998, SEMATECH started its EUVL program by focusing on the development of optics, microstepper enhancements, mask modeling, and photoresist materials testing.[35] Development of EUVL for high volume manufacturing (HVM) began in 2003 with three major exposure tool equipment suppliers: ASML, Nikon, and Canon.[36]

2.1. EUVL Challenges

Extreme ultraviolet lithography is considered by many to be the most promising next generation lithography technique,[37-43] but there are challenges[44-47] that must be resolved before it can be implemented:[48]

1. **Power Source**. In order to meet industrial demands on throughput (and ultimately cost), an EUVL tool must have >125 wafers per hour (WPH) output.[48] To achieve this target, a stable 250 watt source must be used. Currently, the highest output source is 100 watts.[49]
2. **Optics**. Traditional photolithographic optics cannot be used for EUVL due to high absorptivity of EUV photons by matter. Instead, a series of reflective mirrors consisting of multiple molybdenum/silicon stacks are used.[50-52] There are 8-12 mirrors[53] used in modern EUV exposure tools. Since each mirror is roughly 70% reflective,[54] only 1-6% of the light generated, at the source, is available to expose the photoresist.
3. **Photoresist**. EUV photoresists must have high sensitivity to compensate for the significant disparity between generated photons and photons available to the resist.[55,56] Other key metrics that determine ultimate resist performance are line edge roughness (LER, nm) and resolution (nm) (Figure 4).

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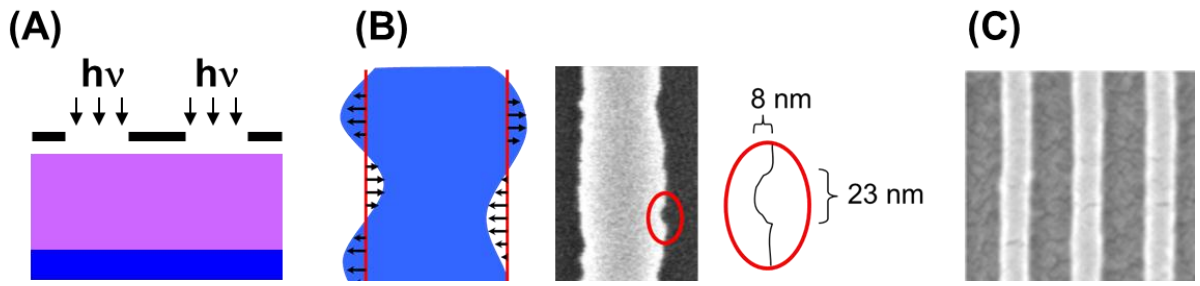

Figure 4. Three key metrics for evaluating photoresist performance are (A) sensitivity (exposure dose (mJ/cm^2) necessary to print a given feature size) (B) line-edge roughness (deviation of printed feature from straight line) and (C) resolution (feature size printed).

2.2. EUV Photoresists

Initial designs for EUV photoresists have borrowed many ideas from resists at 193-nm chemically-amplified photoresists (CAMP).[57-59] Chemical amplification improves the sensitivity of photoresists through the use of catalytic acid.[60-62] These resists use an organic polymer that is insoluble in an aqueous base. The polymer typically consists of monomers that control baseline solubility and other monomers with an acid-cleavable protecting group. Formulating the polymer with a photoacid generator (PAG) makes a polymer film soluble in aqueous base after exposure to light (positive tone). Although monomers for 193-nm are primarily based on aliphatic adamantane groups (Figure 5A), EUV polymers use more aromatics in the monomers (Figure 5B).

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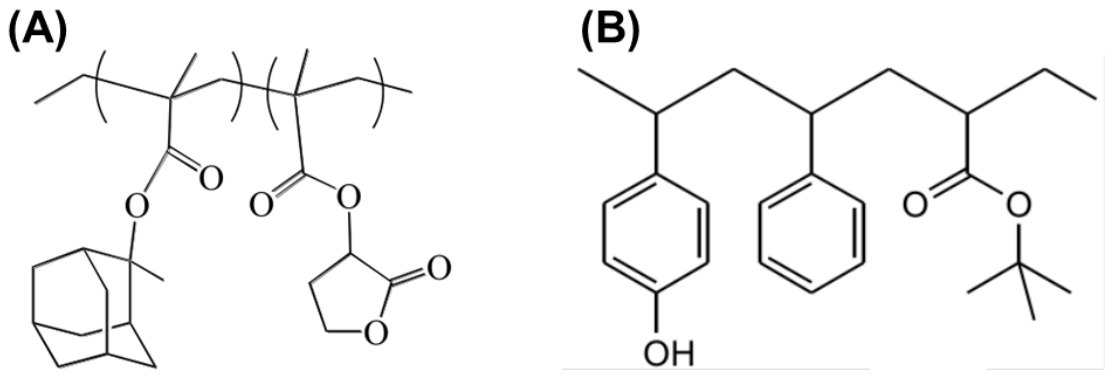

Figure 5. Transparency concerns have been a driving factor when designing (A) 193-nm resists and (B) EUV resists.

Figure 6 shows the acid catalyzed deprotection of a generic chemically amplified photoresist. PAG decomposition occurs, generating a strong acid, after exposure to light.[63] A post exposure bake (PEB) after exposure causes the catalytic acid to diffuse through the film and deprotect multiple t-butyl ester groups.[64,65] The resulting carboxylic acid causes a significant increase in solubility of the polymer when using an aqueous base developer, typically 0.26 N tetramethyl ammonium hydroxide solution.

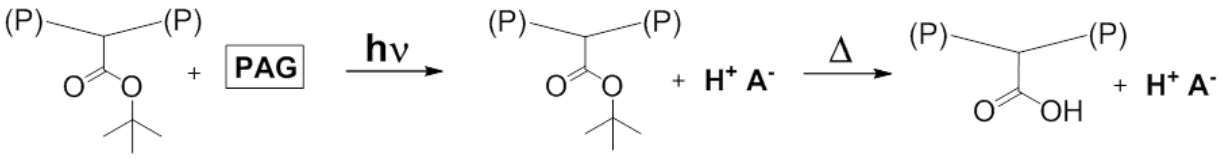

Figure 6. Exposure of a chemically-amplified photoresist results in the decomposition of a photoacid generator to a strong acid. Deprotection of the polymer occurs during a post exposure bake, leading to a significant increase in solubility in exposed areas during development.

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This approach has yielded extraordinary results from resist manufacturers such as JSR Micro (Figure 7).[66] Subtle variations in polymer and PAG composition have pushed chemically amplified resists to their limits of resolution.

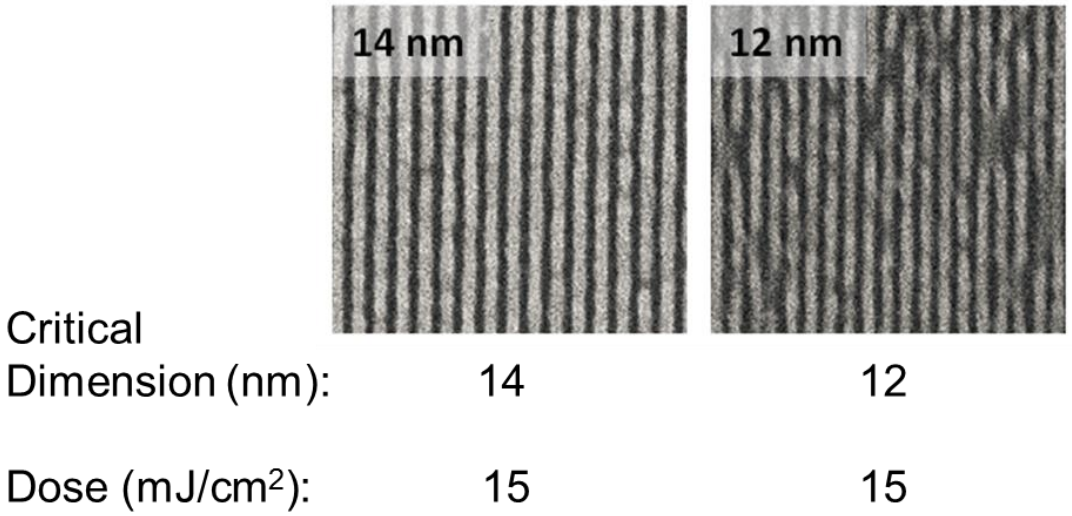

Figure 7. State of the art EUV CAMP created by JSR. This resist can pattern 14-nm half-pitch dense lines with an exposure dose of 15 mJ/cm^2.

3. Research Motivation

EUV photons (13.5 nm) are much higher in energy than are ArF photons (193 nm), so traditional photoresist design may be inadequate to continue resolving increasingly smaller patterns. As we decrease film thickness to compensate for smaller patterning without line collapse, organic films may be unable to absorb the photons efficiently,[67] which may lead to poor sensitivity and line edge roughness. Etch resistance may also be inadequate in these thinner organic films.[68]

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We have invented a new platform called Molecular Organometallic Resists for EUV (MORE) that seeks to rectify the potential obstacles that face EUV resist design. By using elements that have a high EUV optical density, we propose to create a molecular film capable of absorbing more precious EUV photons which may result in higher resolution patterns with better sensitivity and LER.

Chapter 2 focuses on tin and tellurium as metal centers for our new photoresist platform, MORE. It begins with a brief history of our early explorations with tin clusters and then discusses new molecules that have been designed and systematically modified. This approach has led to the creation of resists capable of high resolution and low LER. Work was also performed to better understand EUV exposure mechanisms of dibenzyl tin dicarboxylates. Exposure mechanism investigation has led to some future directions on how we can potentially improve tin resist systems.

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Chapter II: MORE – Molecular Resists of Tin and Tellurium

Overview

Chapter 2 focuses on the further development of a unique class of EUV photoresists we call Molecular Organometallic Resists for EUV (MORE). This chapter is primarily focused on low line-edge roughness (LER) dialkyltin dicarboxylates. For this project, we create molecules comprised of elements with high EUV optical density (OD) to enhance EUV photon absorption. Enhanced photon absorption may lead to photoresists that are capable of high resolution and sensitivity, yet maintain low line edge roughness.[1] Over the course of this work, we have analyzed many organometallic compounds made from high EUV OD elements such as: Co, Cr, Ni, Pd, Cu, Ag, Sn, Bi, Sb, and Te. These compounds were evaluated for solubility, coating quality, and lithographic performance. Mononuclear tin and tellurium were ultimately chosen for study because they:

1. Have very high EUV OD.[2]
2. Are inexpensive.
3. Have relatively easy synthetic preparations.

1. Introduction

Traditional chemically-amplified photoresists have been used in the microelectronics industry for over twenty years.[3,4] These lithographic systems have enormous capability and have achieved the photolithographic performance that allowed the industry to follow Moore's law.[5] However, the cost and complexity of achieving smaller feature sizes is increasing with each new technology node. Extreme ultraviolet lithography (EUVL, 13.5 nm) continues to rely on

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conventional chemically amplified photoresists, but these resists may be unable to meet the needs of future technology nodes. [6,7] EUV photons (92 eV) interact with matter differently than do 193-nm photons (6.4 eV), and therefore, the fundamental design of photoresists may need to change to obtain the best lithographic performance for EUVL. As we decrease film thickness to compensate for smaller patterning without line collapse,[8] organic films may be unable to absorb the photons efficiently[2] which may lead to poorer sensitivity and line edge roughness.[9] Etch resistance may also be inadequate in these thinner, organic films.[10,11] There are a number of potential problems associated with current resist technologies based on organic, chemically amplified photoresists (CAMP): Photon Absorption, Acid Diffusion, and Etch Resistance.

Photon Absorption. James Thackeray suggests that the target photon absorption in EUV resists is 50%.[12] We have calculated that a 20-nm thick film of polyhydroxystyrene absorbs just 10% of the incident photons, due in part to the low EUV OD of carbon.[2] As films get thinner, even fewer photons will be absorbed.[2,45] This low absorptivity may lead to poor resist sensitivities. Low photon absorption may also lead to increased shot noise that could detrimentally affect LER.[13]

Acid Diffusion. After exposure of the photoresist, a post exposure bake (PEB) is often performed on a CAMP. During the PEB, acid diffuses through the film catalyzing the deprotection of functional groups on a polymer. After enough deprotection events occur, the polymer will have much greater solubility in the developing solvent. The diffusion of acid into unexposed areas is called acid blur and is one reason for lost image contrast.[14] As feature sizes

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decrease, the relative diffusion distance becomes so large that it may be impossible to accurately resolve these features.

Etch Resistance. One primary purpose of the photoresist is to selectively protect the substrate from an etch process. Film thicknesses must decrease to compensate for smaller features with no pattern collapse. As films get thinner, their etch resistance may be inadequate to reach the required depth in the substrate.[10,15]

We have created a new class of EUV photoresists to overcome these three obstacles (low photon absorption, acid diffusion, etch resistance). Inspired by the work of Inpria and Cornell,[50-52] we have explored the periodic table and created EUV resists composed of organometallic complexes containing metals with high EUV optical density (Figure 1). We call this platform "Molecular Organometallic Resists for EUV" (MORE). We predict that MORE photoresists will achieve better lithographic performance than traditional organic polymer systems.

High EUV OD. Photons must be absorbed by film to perform photochemistry. MORE resists target elements that have much higher EUV OD than traditional resists. This should enable us to create thin films with better absorption of EUV photons. Better photon absorption may lead to resists with better sensitivity and LER.

High Mass Density. Inorganic films typically have much greater mass densities than do traditional films. Increased mass densities should help reduce any associated blur caused by electron diffusion and excitation in unexposed areas.

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Better Etch Rates. Cornell research has shown that metal oxide resists have significant improvements in etch resistance.[16] This benefit may apply to MORE resists.

No Acid Diffusion. MORE resists do not use photoacid generators (PAGs), so diffusion of photoacids will not create problems.

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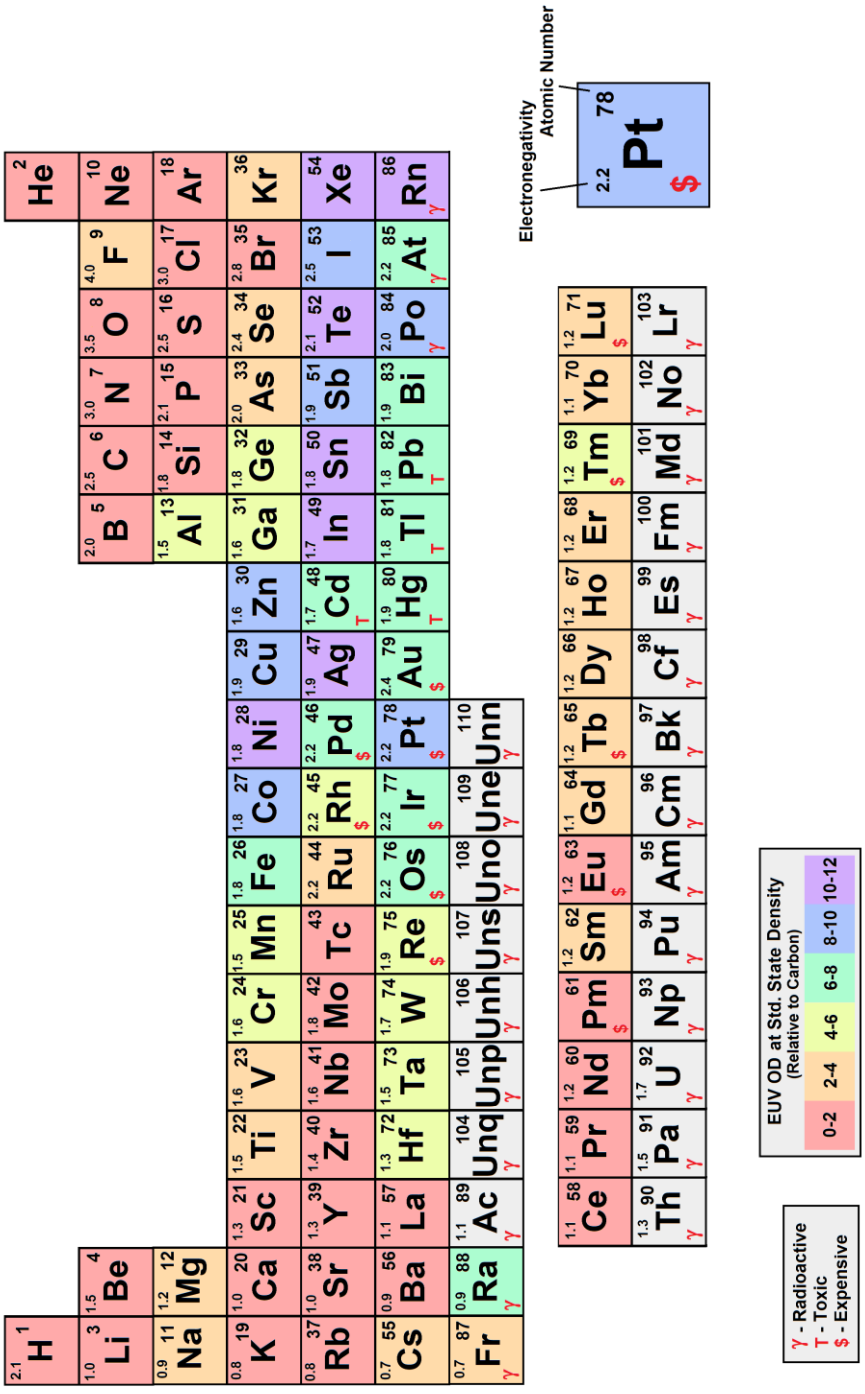

Figure 1. The EUV optical density at standard state density was calculated and normalized to carbon. All of the elements have been color coded with respect to EUV optical density for easy identification.[2] Organotin and organotellurium molecules will be discussed in this chapter.

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In this chapter, we have addressed three questions about Molecular Organometallic Resists for EUV (MORE):

1. Can mononuclear tin and tellurium compounds act as high resolution and low-LER EUV photoresists?
2. Can resist sensitivity be improved by selecting better ligands?
3. Can a photomechanism be proposed that is consistent with all experimental data?

2. MORE Photoresists of Tin and Tellurium

Organotin chemistry has a vast history and is often attributed to the beginning of organometallic chemistry.[17] Tin has the electronic configuration [Kr] $4d^{10}$ $5s^2$ $5p^2$ and the principle valence state is Sn(IV). Inorganic compounds of Sn(II) are well known. Tin has a high EUV optical density[2] and low oxidation potential (0.15 V).[17] Also, there are innumerable examples of tin compounds in the literature, so we decided to explore tin as a potential MORE candidate.

Tellurium is another potential MORE candidate due in part to a very high EUV OD and low oxidation potential. The synthetic chemistry between tin and tellurium is similar and the same synthetic procedures could be followed. Tellurium has an electron configuration [Kr] $4d^{10}$ $5s^2$ $5p^4$ with cationic oxidation states of +2, +4, and +6 available. In order to explore the effects of the central metal on resist performance, we synthesized a series of diphenyl tellurium resists that used the same carboxylates as the tin compounds above. Tellurium has an even higher EUV OD than tin,[2] so we expect resists made from tellurium to be more absorptive of EUV photons and

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potentially more sensitive. Tellurium has more available oxidation states than tin which may increase reactivity.

Tin was one of the first metals to be investigated for EUV sensitivity by our group.[18,19] Two classes of tin materials were initially investigated: Mononuclear tin (Sn-1) complexes and Sn-12 oxo-clusters. Mononuclear complexes contain one tin atom and four ligands. The Sn-12 oxo-clusters contain twelve tin atoms. Both sets of materials were found to be photoactive under EUV exposure and so extensive evaluation was carried out by our group.

We discovered that Sn-1 compounds of the type $(butyl)_2Sn(X)_2$ (X = monoanion of a carboxylic acid, e.g. dibutyltin diformate) were typically soluble and formed good quality films, but other compounds containing chelating di-acids (such as dibutyltin oxalate) were generally insoluble. This led to a hypothesis on solubility of Sn-1 complexes: Tin compounds form 6-coordinate complexes[20] which can drastically affect solubility properties. Compounds like dibutyltin oxalate are constrained to a 4-coordinate complex which results in the formation of an insoluble network through intermolecular coordination.[38] Compounds using carboxylates like formate, however, can rearrange such that each carbonyl oxygen can coordinate with the tin through intramolecular interactions and prevent crosslinking, which leads to a much more soluble product (Figure 2). Alcock, *et al*., observed the same solubility characteristics of tin carboxylates.[20] As more molecules were tested, the hypothesis seemed to accurately predict which tin compounds would be soluble.

Another important observation was the linear relationship between the molecular weight (g/mol) of a tin-oxo cluster and exposure dose (mJ/cm^2) to E_{max} (minimum dose required to reach maximum thickness after development)(Figure 3A). It was postulated that the anionic ligand on the cluster was not directly involved in photochemistry, rather, it acted as a volumetric

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"spacer".[18] As ligand bulk is reduced, molar volume is decreased. This possibly decreased the probability of two adjacent molecules from interacting and crosslinking. Coupled with this research was shown an inverse linear dependence on the alkyl-tin bond strength and E_{size} (dose (mJ/cm^2) to print patterns in a resist that equal the patterns on the mask) (Figure 3B).[18] These previous discoveries led me to perform more in-depth studies on mononuclear tin and tellurium dicarboxylates used as EUV photoresists.

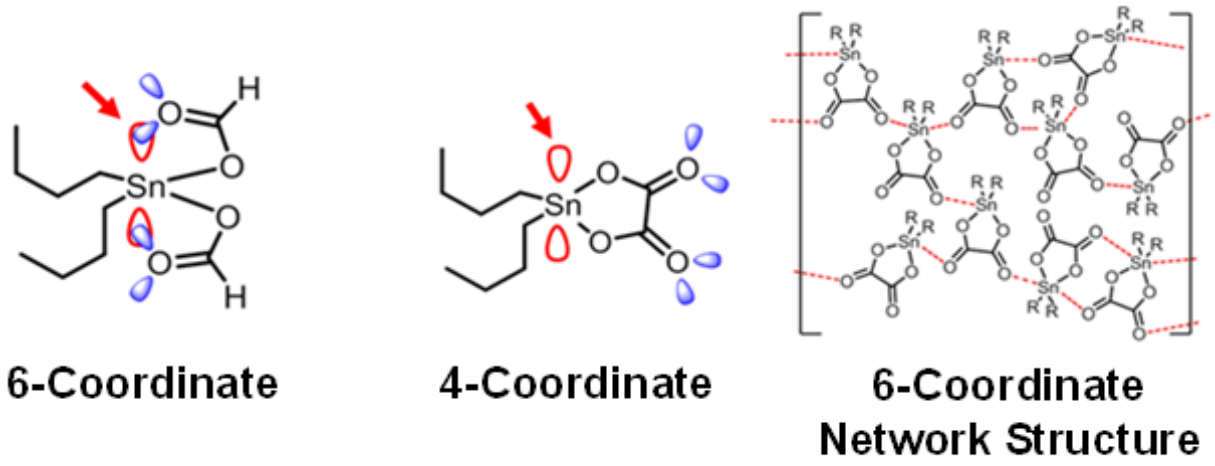

Figure 2. Proposed Solubility of Sn-1 Complexes. Compounds containing unconstrained carboxylates, like formate, have more ligand maneuverability. The carbonyl oxygens can coordinate with open coordination sites on the tin center. In a system with a constrained ligand, such as oxalate, the open coordination sites cannot be filled through intramolecular interactions and intermolecular coordination occurs. This leads to an insoluble network.

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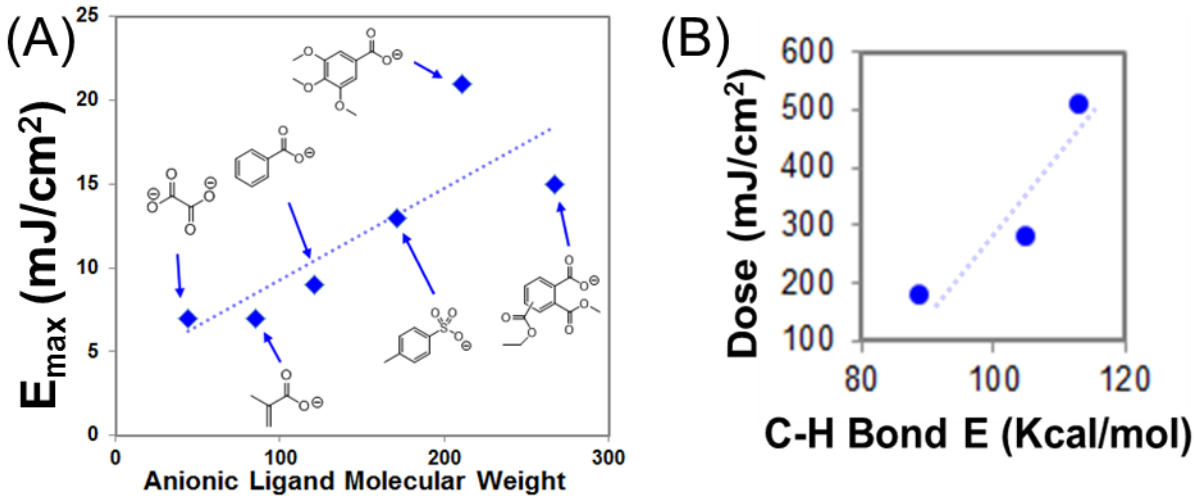

Figure 3. Sn-12 oxocluster reactivity served as basis for further experiments. (A) Linear relationship between molecular weight (g/mol) and sensitivity (mJ/cm^2) and (B) Linear relationship between bond strength and sensitivity.

3. Contrast Curves of Organotin and Organotellurium Dicarboxylates

Utilizing the reaction shown in Figure 4, thirty-one organotin and organotellurium compounds of the type $(R)_2M(O_2R')_2$ were synthesized. The compounds were dissolved in toluene (2 wt%) and spin-coated as thin films at the Paul Scherrer Institut (PSI, Switzerland). Resist films were then exposed with 13.5-nm radiation and developed with a hexanes developing solution. Exposures were performed at Paul Scherrer Institut on the XIL-II beamline using open-frame exposures to prepare contrast curves or using interference lithography[21] for dense-line patterning. Photosensitivity was quantified by finding the E_{max} (energy needed to achieve maximum thickness after development) from the contrast curves and patterning was evaluated using E_{size} (mJ/cm^2), line edge roughness (LER, nm), and resolution (nm).

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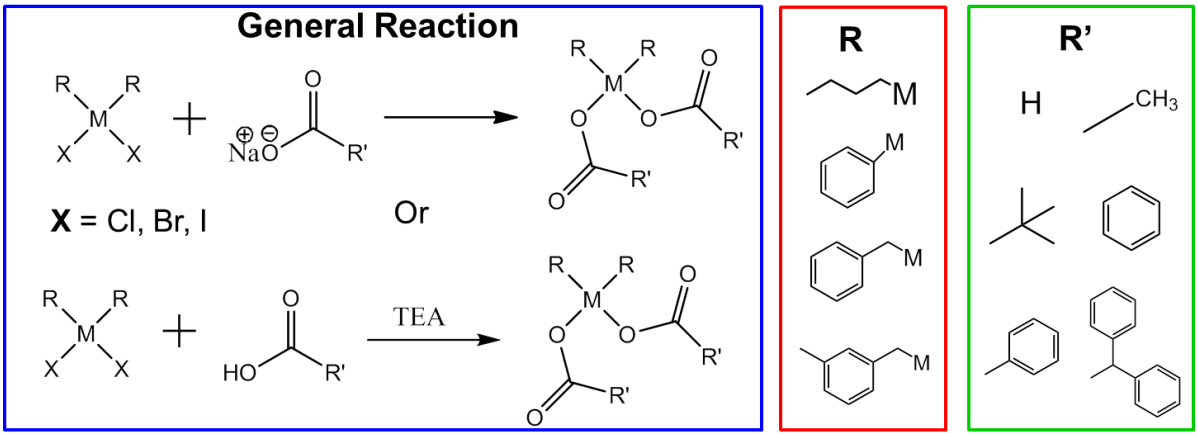

Figure 4. General reaction scheme for synthesis of tin and tellurium carboxylates.

3.1. Diphenyltin Dicarboxylates

A series of diphenyltin dicarboxylates were synthesized and analyzed for EUV lithographic performance. We expect the phenyl tin-carbon bond to be stronger than both benzyl and butyl tin-carbon bonds, which may result in worse sensitivities.[22-24] Figure 5 shows the EUV sensitivity results from four diphenyl tin compounds. A linear trend shows that E_{max} decreases with decreasing molecular weight. This relationship between E_{max} and MW may indicate that the efficiency of the negative-tone behavior (e.g. cross-linking) increases with decreasing distance between tin atoms. These compounds are roughly twice as slow as analogous dibenzyltin compounds. We were unable to print dense lines with any diphenyl tin compounds.

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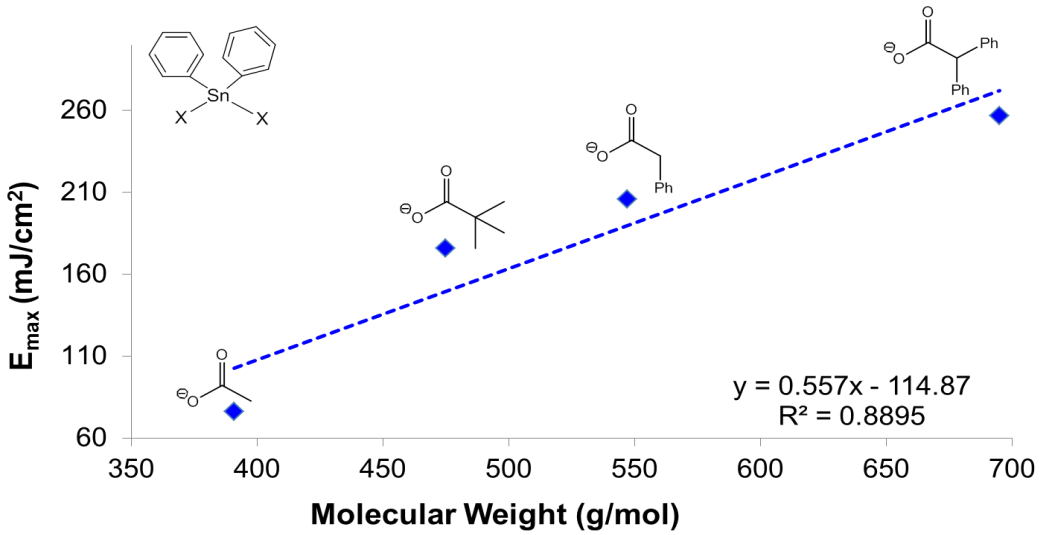

Figure 5. E_{max} (mJ/cm^2) as a function of molecular weight (g/mol) of four diphenyltin compounds show a similar linear trend as dibenzyltin compounds.

3.2. Dibutyltin Dicarboxylates

A series of dibutyltin dicarboxylates and were synthesized and analyzed for EUV lithographic performance. We expect the tin-butyl bond to be weaker than the tin-phenyl bond strength. This could lead to better sensitivities.[22-24] Figure 6 shows the results from five dibutyltin compounds that were evaluated for contrast curves. A linear trend between molecular weight and $E_{max,}$ similar to diphenyltin compounds, is observed. Most of the compounds have very good solubility and form high quality films. The films tended to crystallize or decompose over the course of a few hours, however.

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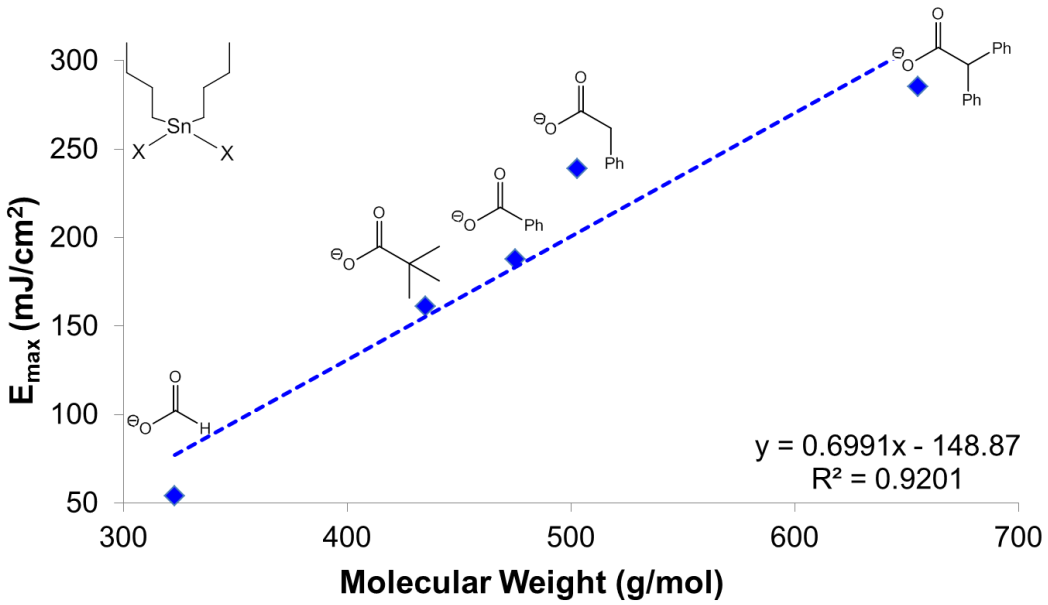

Figure 6. E_{max} (mJ/cm^2) as a function of molecular weight for five dibutyltin compounds show a similar linear trend as dibenzyl tin compounds.

3.3. Dibenzyltin Dicarboxylates

A series of dibenzyltin dicarboxylates were synthesized and analyzed for EUV lithographic performance. We expect the tin-benzyl bond to be weaker than the tin-butyl bond strength.[22-24] This could lead to better sensitivities. The benzyl functional group (Figure 7A) is known to have good free radical stability due, in part, to resonance effects (Figure 7B).[25-27] Free radical stability is inversely related to bond strength associated with covalent bonding of the benzylic carbon to another species. We postulate that the sensitivity of mononuclear tin resists can be improved by decreasing the bond strength of the tin-carbon bond after observing a similar trend with tin-oxo clusters in previous experiments by Cardineau, *et al.*[18]

Figure 8 shows a plot of the compounds developed as contrast curves. A linear trend between molecular weight and E_{max}, similar to both diphenyltin and dibutyltin compounds, is observed.

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Most of the compounds have very good solubility and form high quality films. The films tended to crystallize or decompose over the course of a few hours to days.

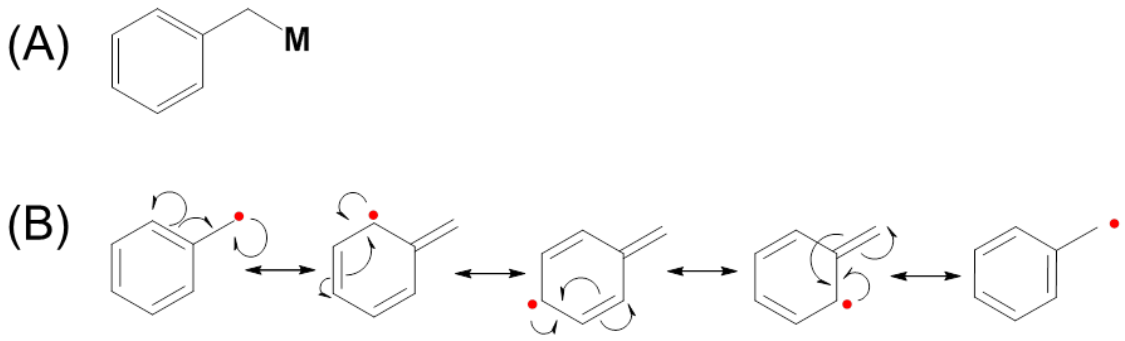

Figure 7. (A) Benzyl ligand showing how it coordinates with the metal and (B) Benzyl radical stability through resonance effects.

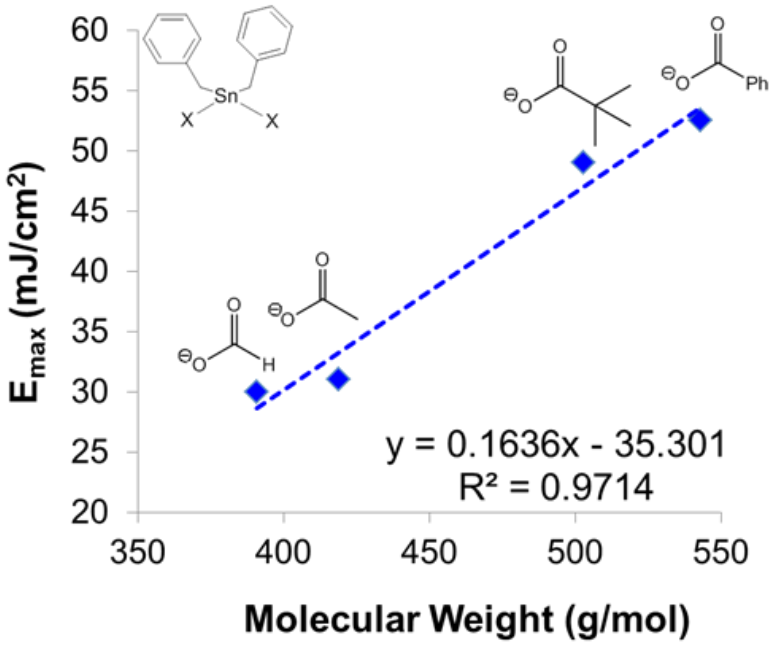

Figure 8. Dibenzyltin dicarboxylate EUV photoreactivity. E_{max} as a function of molecular weight shows a linear relationship.

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3.3.1. Effects of Tin-Carbon Bond Strength on Sensitivity

Figure 9 shows the effects of tin-carbon bond strength on the sensitivity of three resists. Here, the E_{max} is determined for compounds **1, 11,** and **17**: $R_2Sn(O_2C(C(CH_3)_3)_2$ where R = phenyl, butyl, benzyl. There are no experimental measurements available of direct bond strength between Sn-R in these cases, but the C-H bond dissociation energies have been measured.[22-24] These values were used as a measure of relative free radical stability. The inverse relation suggests that photolytic cleavage occurs at the Sn-C bond during exposure. Decreasing the Sn-C bond strength further may help improve photospeeds.

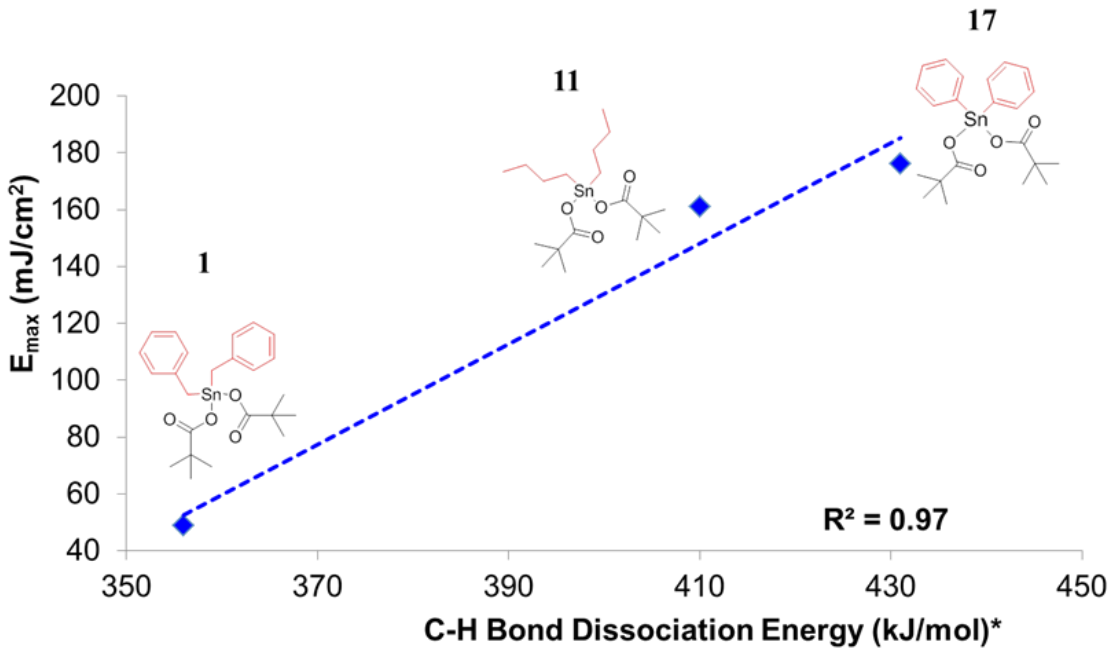

Figure 9. Variation of tin-carbon bond energy shows an inverse relationship with sensitivity. This may indicate that this bond plays an important role during photoexposure.

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3.4. Bis(m-xylil)tin Dicarboxylates

Crystallinity is a problem with some films of dibenzyltin compounds. While the dibenzyltin compounds initially form high quality films, they often crystallize after 3-40 hours. To attempt to fix this issue, a series of bis(m-xylil) tin dicarboxylates were synthesized (Figure 10A). Adding a methyl group to the meta position on the benzyl ligand may assist in breaking up the observed crystallinity in dibenzyltin films. Unfortunately, we did not notice any improvement in the films ability to resist crystallization and the photosensitivity became worse. Four compounds were developed for a contrast curve and no imaging data was obtained (Figure 10B).

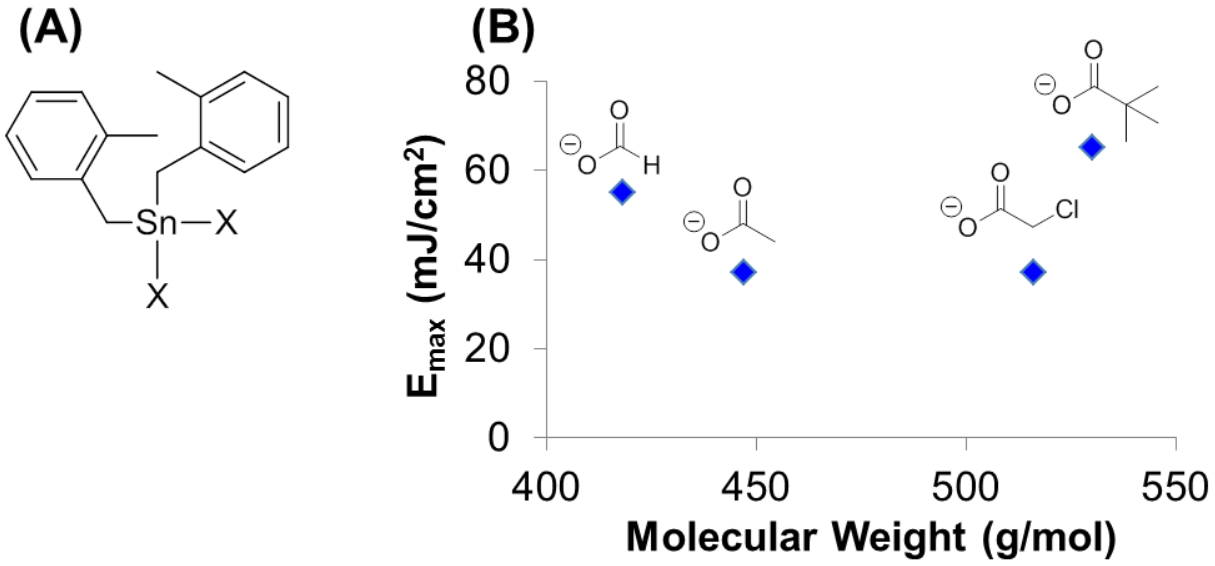

Figure 10. **(A)** Structure of bis(m-xylil)tin dicarboxylates. **(B)** Four m-xylil compounds showed worse sensitivities than benzyl compounds.

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3.5. Diphenyltellurium Dicarboxylates

A series of diphenyl tellurium dicarboxylates were synthesized and analyzed for lithographic performance. All of the compounds have very good solubility and film quality. A linear relation between E_{max} and molecular weight is observed for these compounds. Figure 11 shows a comparison between diphenyltellurium compounds and analogous tin compounds.

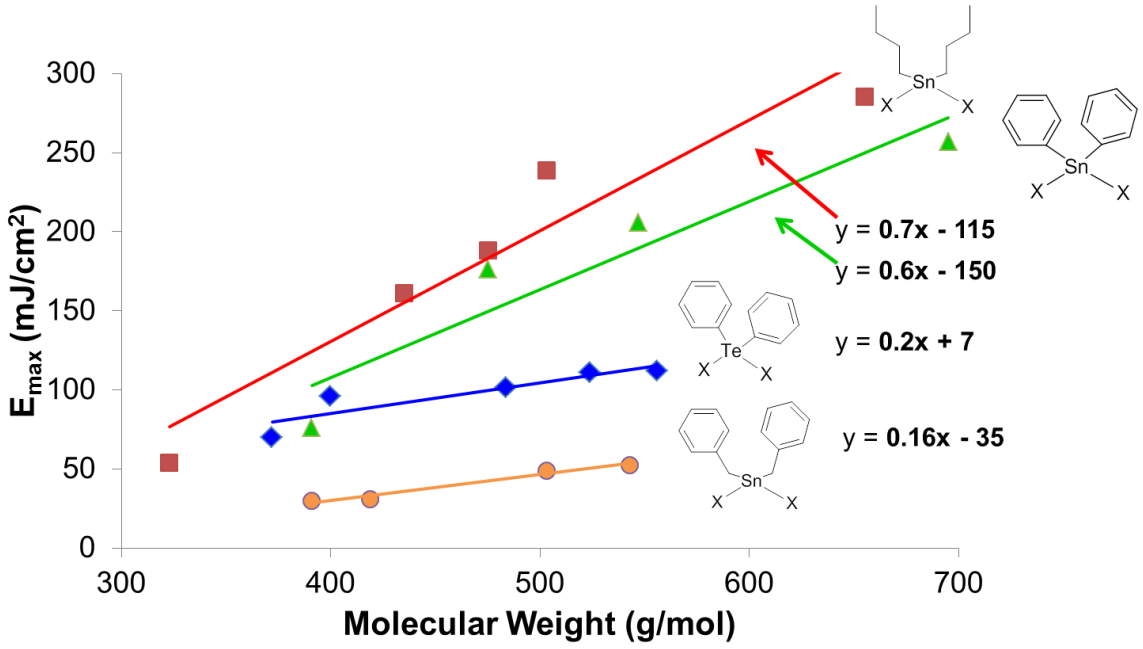

Figure 11. E_{max} (mJ/cm^2) as a function of molecular weight (g/mol) of various tin and tellurium compounds. Each family of resists show a similar linear trend.

4. Dense-Line Patterning Performance

4.1. Diphenyltellurium Dicarboxylates

Only two diphenyltellurium dicarboxylates showed dense-line patterning after exposure and development. They both required high doses and had poor patterning capabilities.

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Diphenyltellurium dibenzoate (**22**) resolved 40-nm dense lines with 400 mJ/cm^2 exposure dose, and diphenyltellurium dipivalate (**21**) printed 35-nm dense lines with 610 mJ/cm^2 (Figure 12).

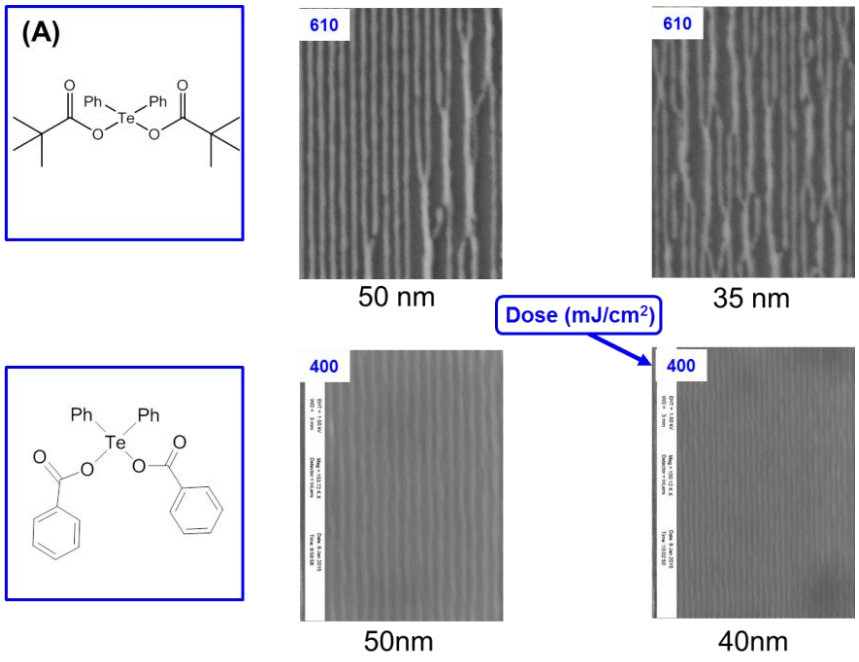

Figure 12. Two diphenyltellurium dicarboxylates were imaged at PSI. They both required high exposure doses and had poor quality patterning.

4.2 Dibutyltin Dicarboxylates

Three dibutyltin dicarboxylates were developed for dense-line patterning (Figure 13). An interesting phenomenon is observed with all of these compounds after development. Figure 14 shows dibutyltin diacetate at increasing magnification factors. The origins of these droplets are unknown, but may be due to phase segregation from impurities. These phenomena led to a very "wavy" film that was seen with all dibutyltin compounds.

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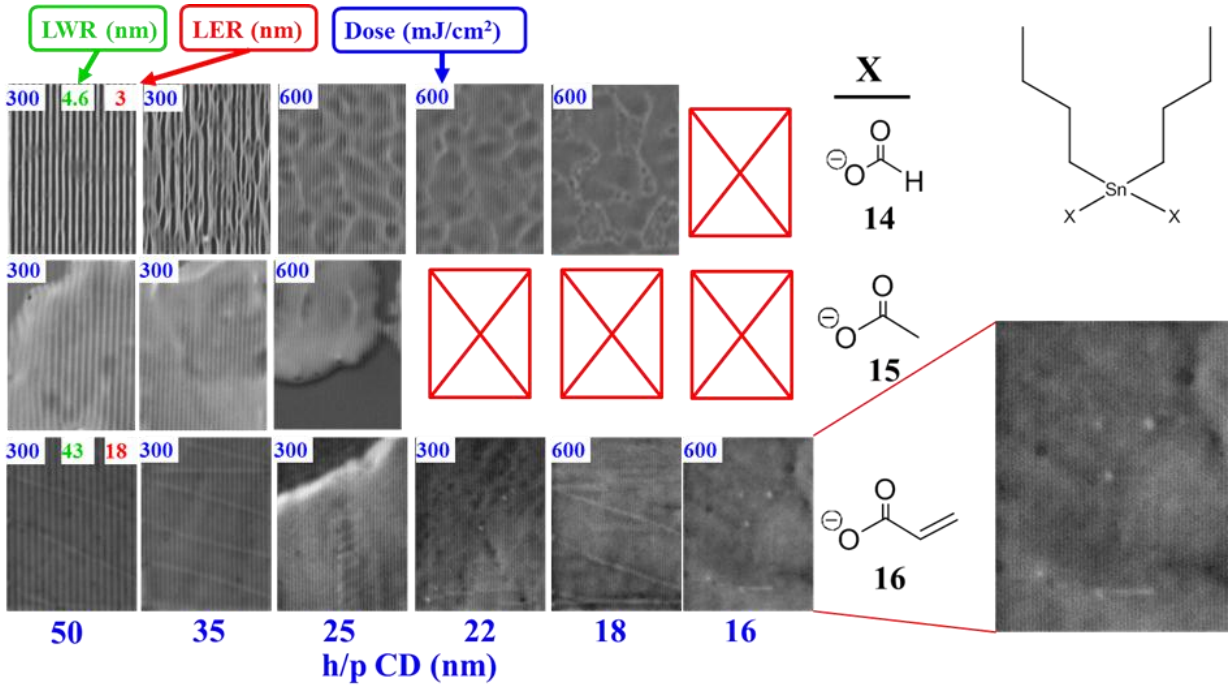

Figure 13. Dibutyltin dicarboxylates imaged at PSI. All compounds required high exposure dose with poor film quality after development.

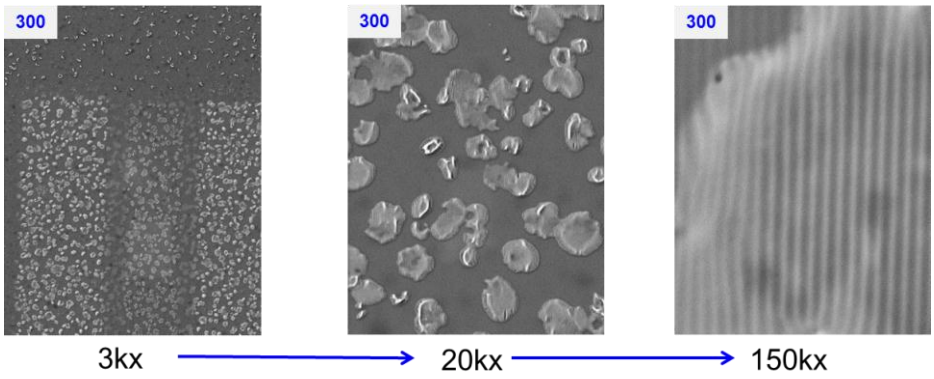

Figure 14. Interesting phenomena after exposure and development of dibutyltin diacetate. Patterning is only occurring on the droplets. This may be due to impurities associated with synthesis.

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4.3. Dibenzyltin Dicarboxylates

Five dibenzyltin dicarboxylates were developed for dense-line patterning (Figure 15). A very wide range of photoresponse (5-600 mJ/cm^2) and lithographic capabilities is observed. Dibenzyltin dipivalate (**1**) has achieved 16-nm dense line patterning at a high exposure dose of 600 mJ/cm^2. The most remarkable quality of two of these dibenzyl tin resists is the extremely low LER, 1.4 nm (dibenzyltin dipivalate, **1**) and 1.1 nm (dibenzyltin dibenzoate, **2**).

Figure 16 shows a plot of E_{size} *vs.* molecular weight that shows linearity with alkyl and aryl substituents. Interestingly, dibenzyltin diacrylate (**3**) and dibenzyltin dimethacrylate (**4**) deviated from this linear trend and are much more sensitive than would be predicted based on molecular weight arguments alone. In this case, the deviation may be attributed to a different and more efficient mechanism of exposure, similar to olefin containing resists reported by Passarelli, *et al.*[28]

Further roughness analysis of dibenzyltin dipivalate shows not only excellent roughness down to 22 nm, but also a deviation from theoretical predictions. In this case, LWR (line width roughness) continues to improve with decreasing feature size while holding the dose constant (Figure 17). Typically, smaller feature size would lead to worse roughness. This reason for this deviation is unknown.

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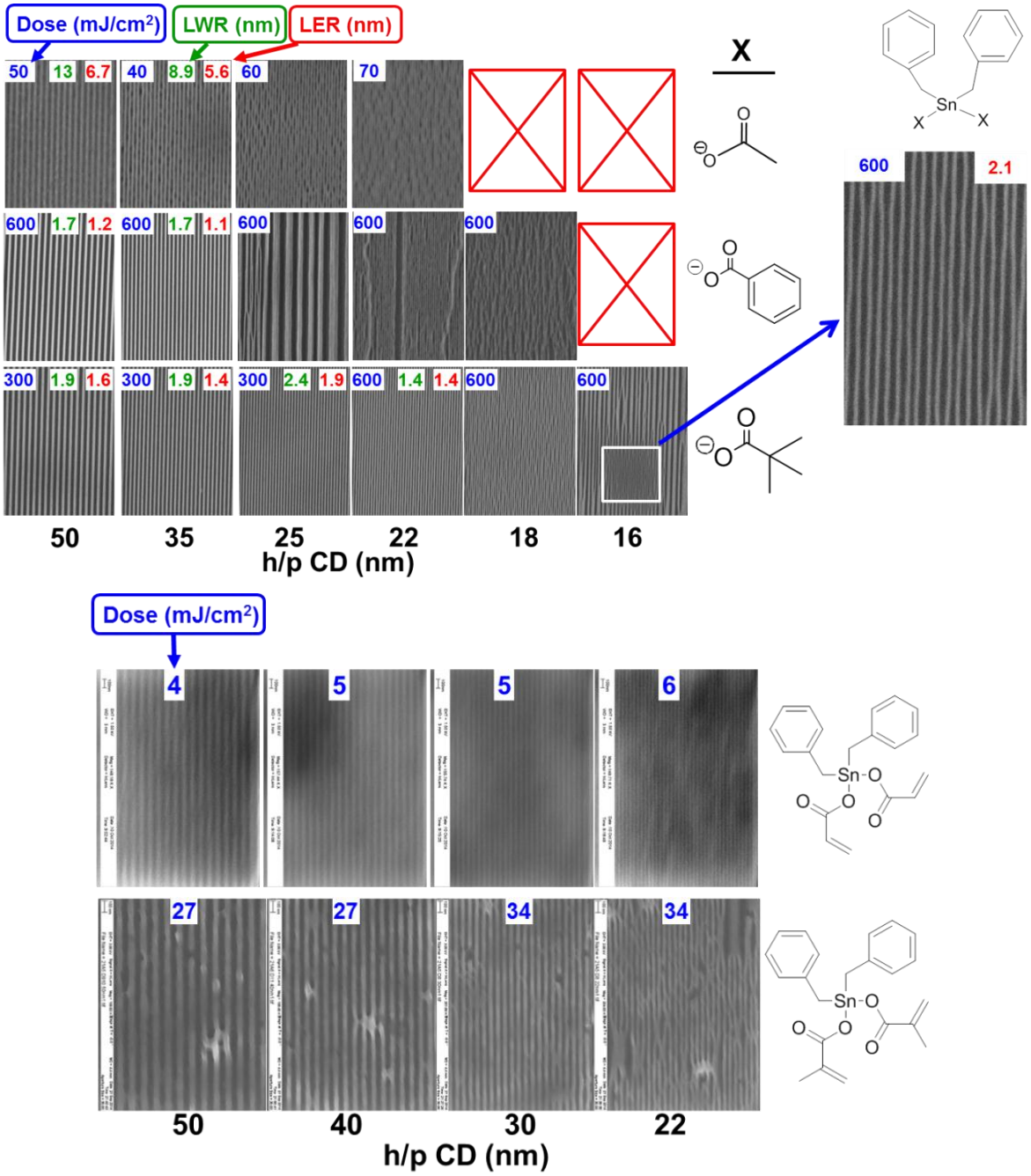

Figure 15. Dibenzyltin dicarboxylates imaged at PSI. Note the RLS tradeoff between speed and LER. Our best imaging came from dibenzyltin dipivalate, achieving 16-nm dense line patterning and fantastic LER at larger feature sizes. Photospeed is drastically improved when ligands contain olefins.

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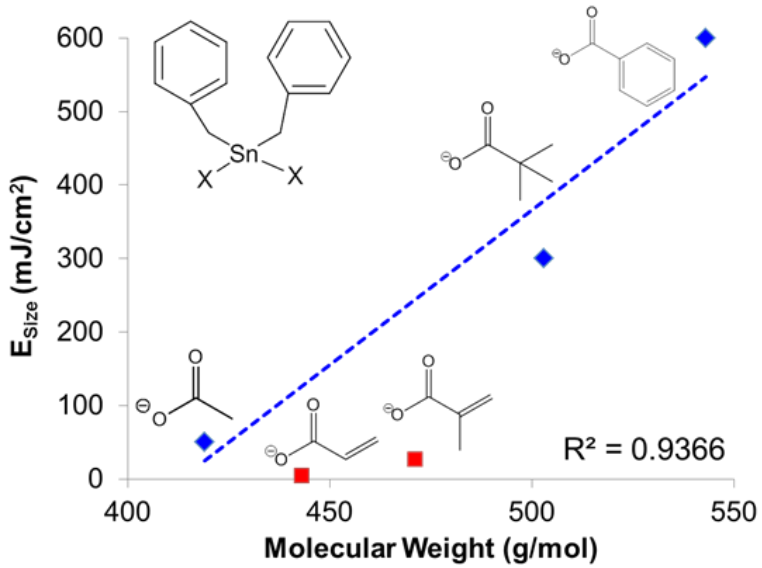

Figure 16. E_{size} as a function of molecular weight shows deviation from linearity with acrylate and methacrylate systems.

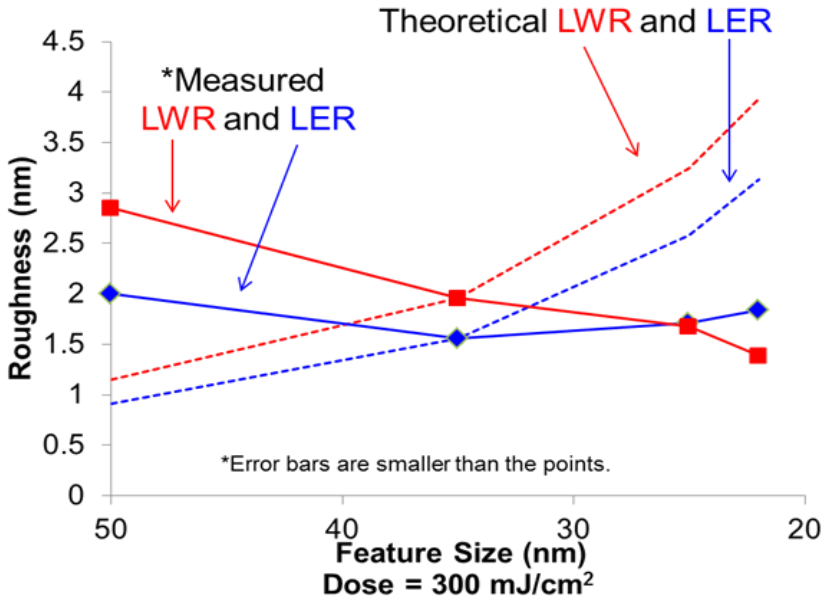

Figure 17. Roughness analysis of dibenzyltin dipivalate shows measured LER and LWR that do not follow theoretical predictions with decreasing feature size.

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5. Photomechanism of EUV Exposure of Dibenzyltin Dicarboxylates

Dibenzyltin compounds were analyzed in greater detail because they have the most potential to act as high resolution and low LER resists. It is very important to understand these systems so we can attempt to improve them. Figures 18 and 19 show nine likely mechanistic paths and photoproducts that may result from EUV exposure. Through careful analysis of volatile species that are generated through e-beam outgassing combined with x-ray photoelectron spectroscopy (XPS) of the film that remains on the wafer after exposure and development, we propose that we can determine the photoproduct and most likely photomechanism.

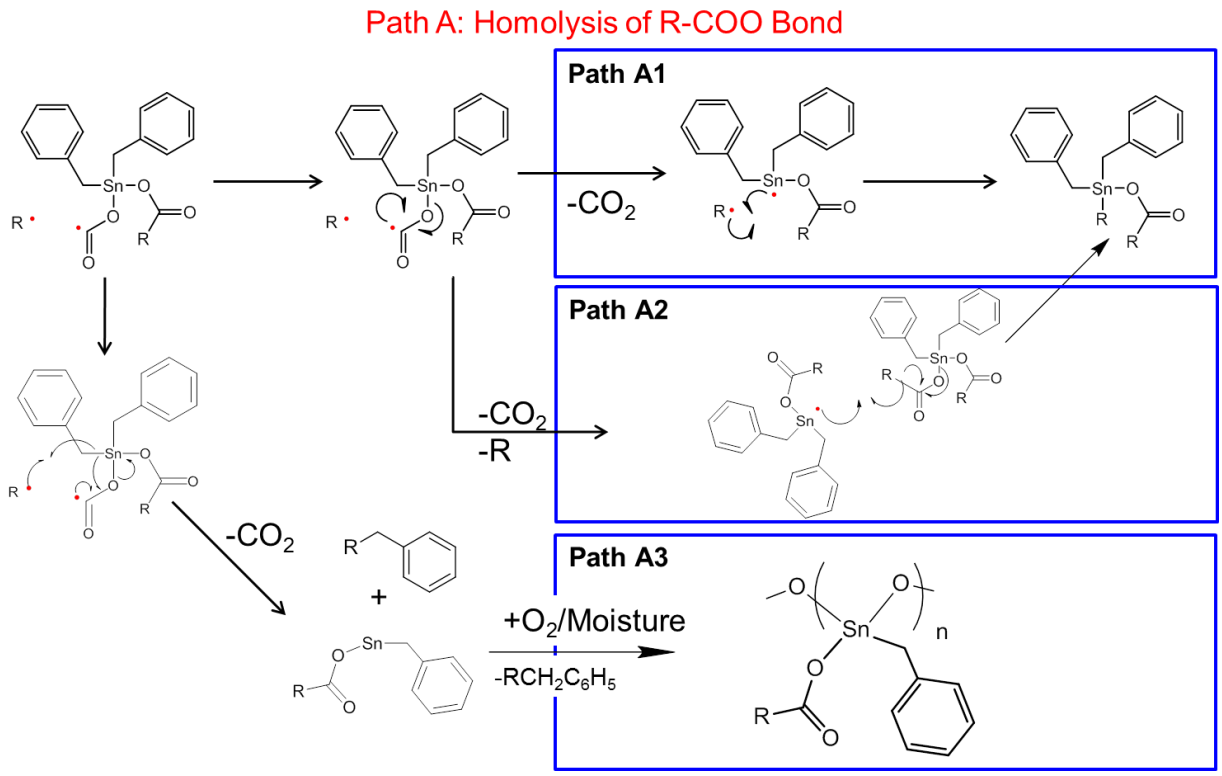

Figure 18. Three potential mechanistic paths of EUV exposure of dibenzyltin dicarboxylates through homolysis of the R-COO bond.

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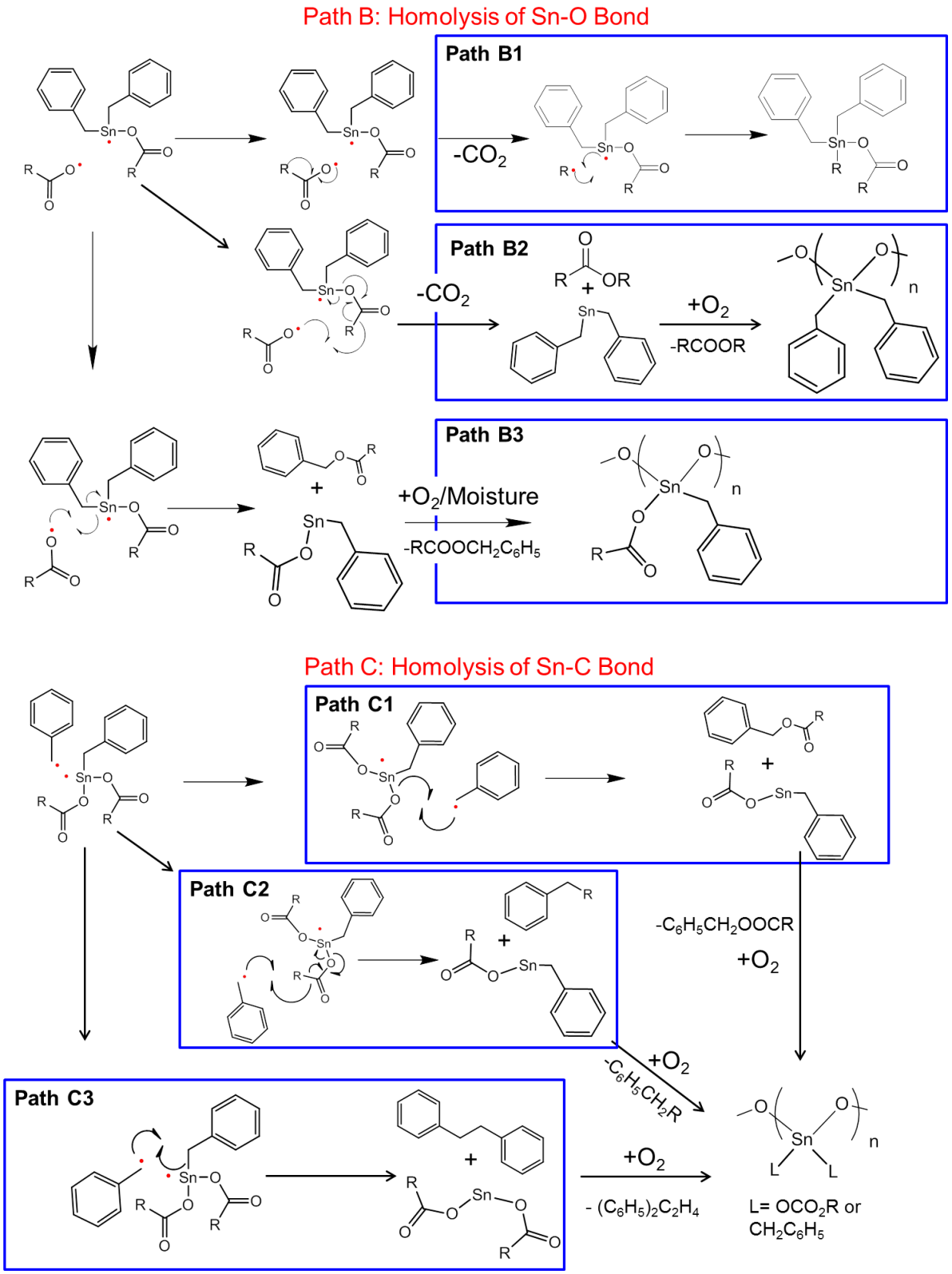

Figure 19. Six more potential mechanistic paths of EUV exposure of dibenzyltin dicarboxylates.

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5.1. E-beam Outgassing and Mass Spectral Analysis

One major component of resist exposure is the generation of volatile compounds. The composition of these species is very important to characterize due to potential contamination of the EUV optics. We can also use this data to help deduce the photochemical mechanism of exposure. With the help of the Denbeaux group, we have exposed a number of resists in the ERIC (Electron Resist Interaction Chamber). Here, we expose resists that have been spin coated into thin films on a silicon substrate with an electron gun emitting two-keV electrons and analyzed the resulting volatile species with a mass spectrometer.

Figure 20 shows the mass spectral data collected during the e-beam exposure of dibenzyltin dipivalate (**1**) and dibenzyltin dibenzoate (**2**). The major species that were outgassed are located at Z = 28 (CO, N_2, or C_2H_4) and Z = 182 (bibenzyl) and subsequent fragmentation.[29] E-beam outgassing of four other resists shows similar mass spectral characteristics.

Previous experimentation by Hossenlopp, *et al.*, demonstrated a loss of CO_2 during 230-nm excitation of dibutyltin diacetate.[34] We observe CO_2 outgasses ten times less than bibenzyl and toluene in dibenzyltin systems. This suggests dibenzyltin dicarboxylates undergo a different exposure mechanism than dibutyltin dicarboxylates.

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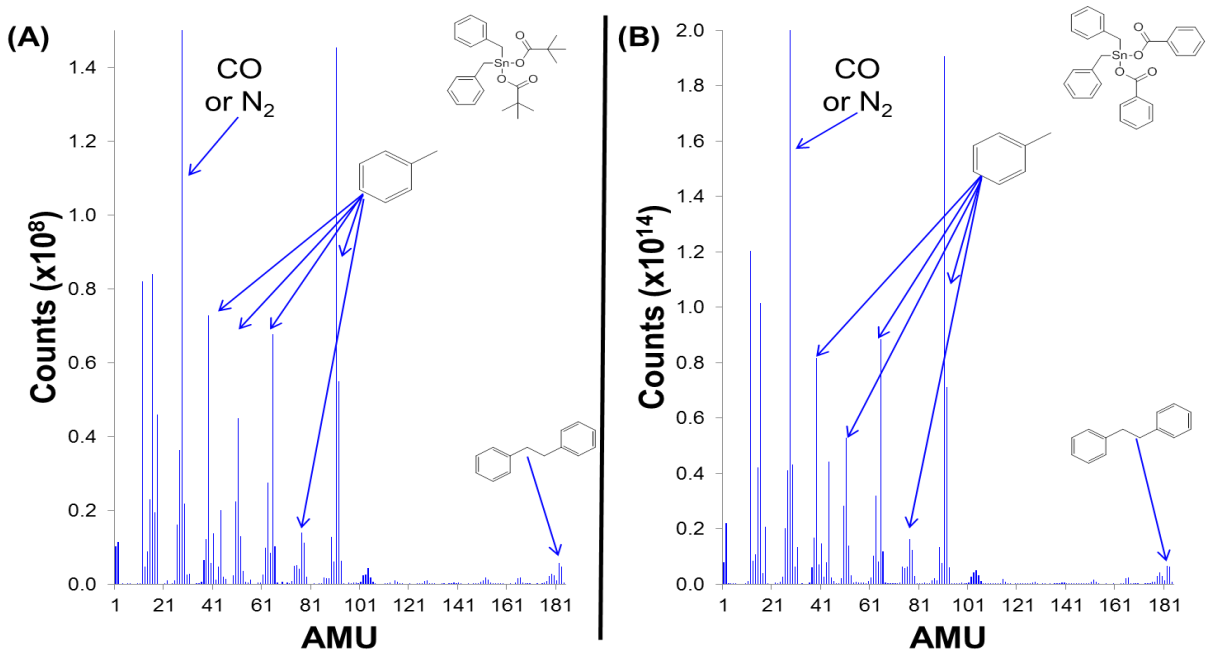

Figure 20. Mass spectral analysis of volatile material from films of (A) dibenzyltin dipivalate and (B) dibenzyltin dibenzoate through e-beam exposure.

5.2. X-Ray Photoelectron Spectroscopy

It is important to analyze the composition of the residue that remains on the wafer after exposure and development. Characterization of this residue can help determine a likely mechanism of exposure. XPS is a highly sensitive spectroscopic technique that uses high energy photons (λ = 1486 eV) to perturb electrons in atoms. Ejected electrons are collected and the kinetic energies are measured. The binding energy of the electrons can then be calculated (Equation 1). Each element, as well as different bonding between elements, has unique binding energy values. Vast databases exist which can be used to characterize materials based on measured electron kinetic energies.

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$$E_{binding} = E_{photon} - E_{kinetic}$$

Equation 1. Equation to determine the binding energy of collected electrons that have been ejected from a sample.

Dibenzyltin dipivalate was coated onto a 4-inch wafer and cleaved into 2x2 cm chips. Seven chips were exposed to EUV light at PSI as broadfield exposures. A 3x3 mm open frame was used to expose the chips such that one large square (1.5x1.5 cm) of exposed film was surrounded by unexposed film. The chip was developed immediately and analyzed by XPS one week after development.

High resolution XPS scans were obtained for three ranges of binding energy. These scans were chosen based on starting material and likely photoproducts: C1s (280–295 eV), O1s (520–540 eV), and Sn3d (480–500 eV). Through careful analysis of the resulting data, the following was determined: (1) Coalescence of the O1s peaks from two to one after exposure indicates that there is a reduction in C=O concentration, an increase in Sn-O concentration, or both (Figure 21A). (2) The Sn:C roughly doubles from unexposed to exposed film. (3) The Sn3d peak shifts from 487.0 eV to 487.4 eV when comparing unexposed and exposed film (Figure 21B). This suggests that the tin center is surrounded by more electronegative species.

The increased Sn:C agrees with outgassing data that shows high concentrations of R_2 during exposure. We would expect the relative amount of tin to increase in the film after exposure. The coalescence of the two peaks in O1s analysis is a bit more difficult to interpret on its own. However, when we also take into account the shift in binding energy of Sn3d, it is possible that the coalescence is due to an increase in Sn-O, since oxygen is more electronegative than carbon.

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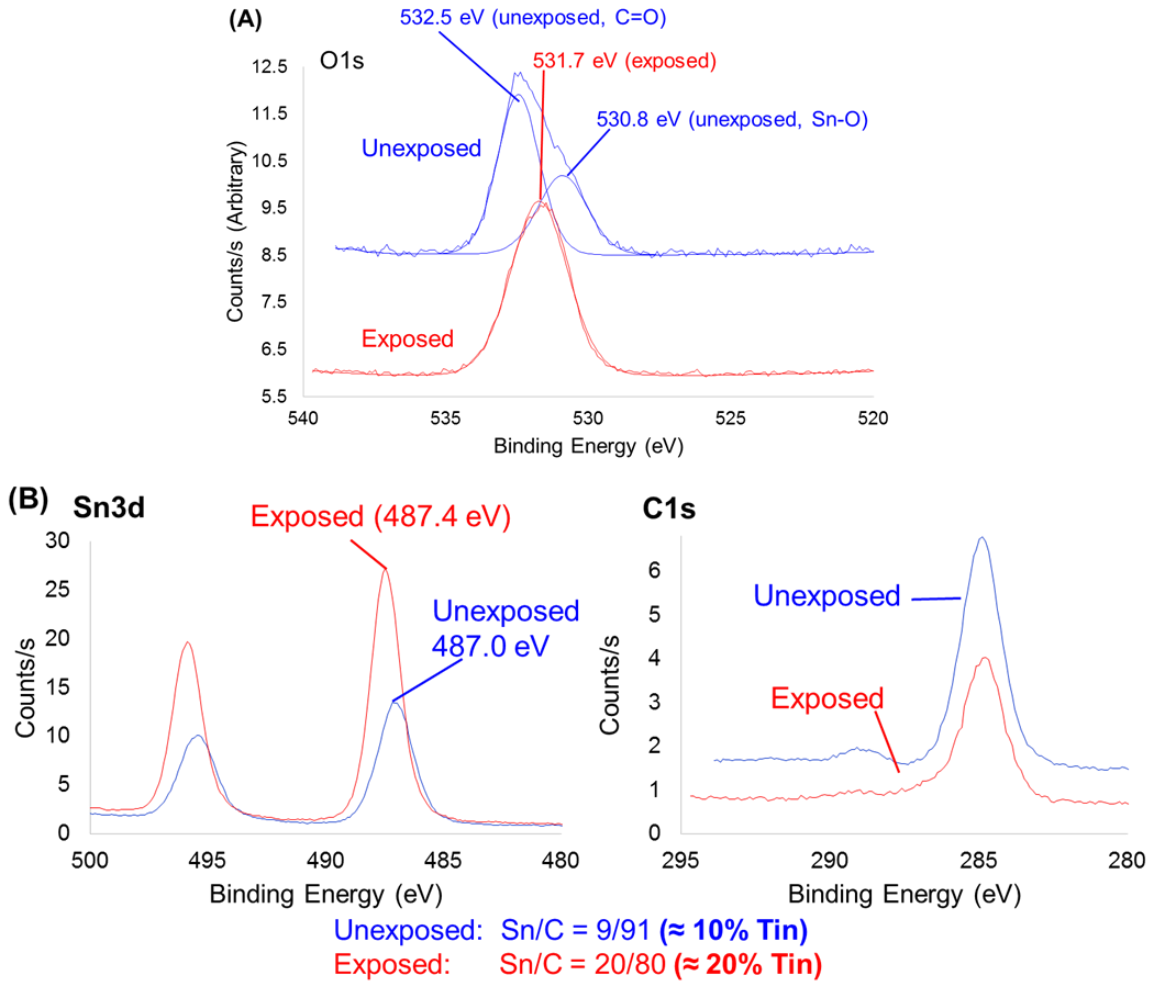

Figure 21. XPS analysis of an unexposed and exposed film of dibenzyltin dipivalate. Here, we show detailed results obtained at the binding energies for (A) O1s and (B) Sn3d and C1s.

5.3. Post Exposure Delay

To test for the possibility of post exposure chemistry occurring, a series of exposures were performed with post exposure delay. Historically, post exposure delay (PED) was detrimental to overall resist performance.[30-32] If PED occurred, the acids generated during exposure would be quenched by bases in the surrounding environment. This would lead to a phenomenon called t-topping, a bridging of the photoresist near the top of the resist film.

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Organotin compounds acting as photoresists could potentially benefit from PED. Outgassing data suggest that exposure of $R_2Sn(IV)$ $(carboxylate)_2$ eliminates R_2 reducing Sn(IV) to Sn(II). Sn(II) is relatively unstable in air. EUV exposures are performed under high vacuum. Upon exposure to air and moisture, Sn(II) could oxidize to Sn(IV) through hydroxide addition. Tin hydroxides readily eliminate water and form stannoxane, -Sn-O-Sn-.[33]

Five wafer chips coated with dibenzyltin dipivalate (**1**) was exposed to EUV light as a contrast curve. Each chip was developed after a set amount of time (0, 0.25, 1, 3, 24 hours) and E_{max} was determined. Figure 22 shows that increasing PED leads to improved E_{max}. Similar experiments with compounds **2, 4,** and **6** all show the same effect (Figure 23). This may indicate post exposure chemistry occurs after an exposed resist is removed from the high vacuum of the EUV exposure chamber.

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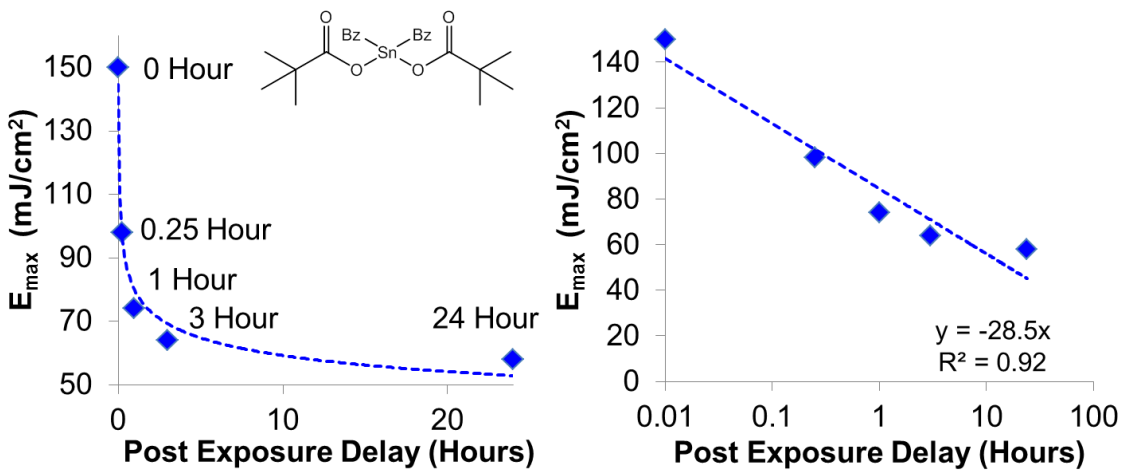

Figure 22. Post exposure delay effects on dibenzyltin dipivalate. A significant improvement in photospeed occurs as post exposure delay increases. After 24 hours, we see roughly 3x improvement.

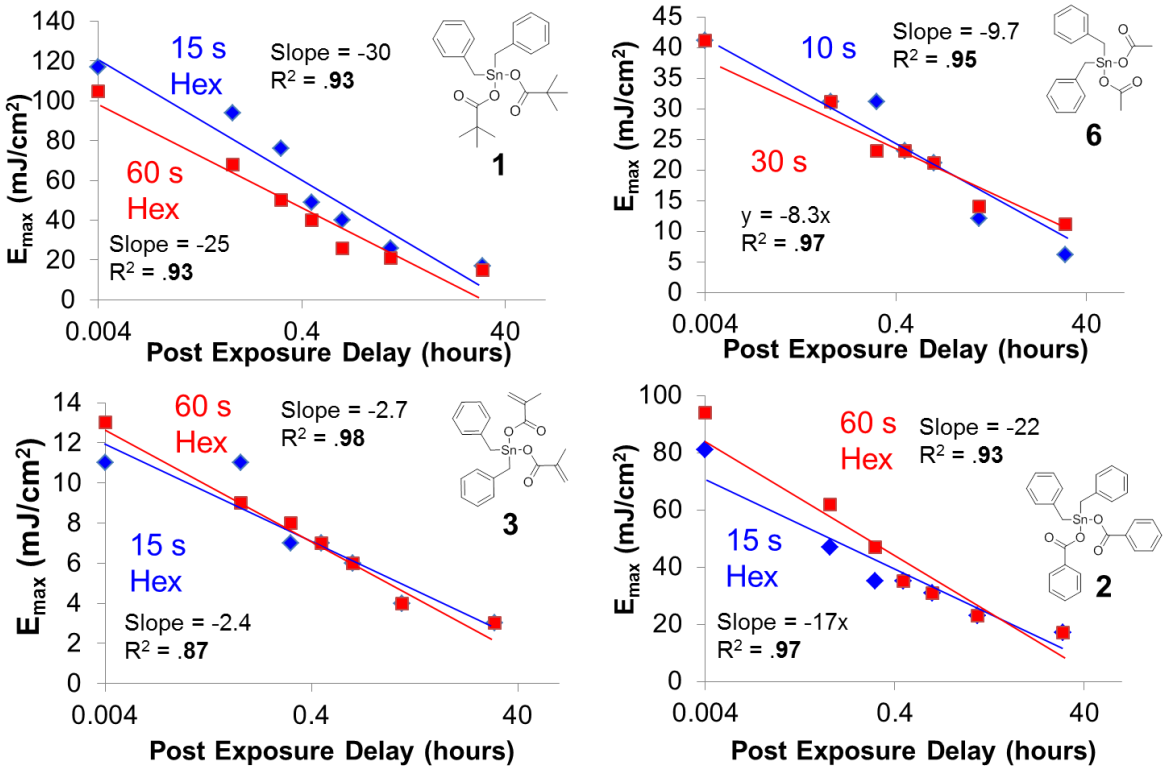

Figure 23. All compounds tested show enhanced sensitivities after PED. Resists were developed at two different development times and show similar trends. Reported slope is in units mJ/(cm^2 · hours).

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5.4. Proposed Mechanism of EUV Exposure of Dibenzyltin Dipivalate

Cardineau[19] proposed that dibutyltin carboxylates likely undergo a decarboxylation event with a recombination of radicals to generate a tin hydride or alkyltin group.[39,40] Experiments performed by Hossenlopp, *et al*. demonstrated loss of CO_2 in such systems using 230-nm excitation,[34] so we initially proposed a similar mechanism for the dibenzyltin dicarboxylate systems.

Data suggests that the dibenzyltin systems undergo a different photomechanism from decarboxylation and radical recombination. Comparing e-beam outgassing data of compound **1** and **2**, we see very minute differences between the two, which suggests they are following similar mechanisms. Pathways A1, A2, and B1 (Figure 18) can be eliminated because the photoproduct would not shift the solubility parameters much, if at all. This would lead to poor developer dissolution contrast. We found that the exposed areas were extremely resistant to aggressive developers such as dichloromethane and acetone while the unexposed areas cleared immediately, indicating a significant solubility shift. Outgassing data showed that the major outgassed species were carbon monoxide (CO), nitrogen (N_2), or ethane (C_2H_4), and bibenzyl ($C_{14}H_{14}$). Mechanism B2 would probably not outgas toluene and can be eliminated from consideration.

Analysis of an unexposed and exposed film with XPS gives a much clearer picture into the composition of the photoproduct. PED studies coupled with tin chemistry literature seem to indicate post exposure chemistry occurs. We therefore propose the following mechanism of EUV photoexposure (Figure 24): Exposure of dibenzyl tin dipivalate to EUV light causes both toluene ligands to reductively eliminate and form bibenzyl. This material outgasses into the exposure chamber leaving behind Sn(II) $(carboxylate)_2$, a reactive intermediate. When the film

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is introduced to standard atmospheric conditions, oxygen and/or water is able to diffuse through the film and react with the Sn(II) molecules. Intermolecular interactions occur that form stannoxanes, which would be very insoluble in most solvents.

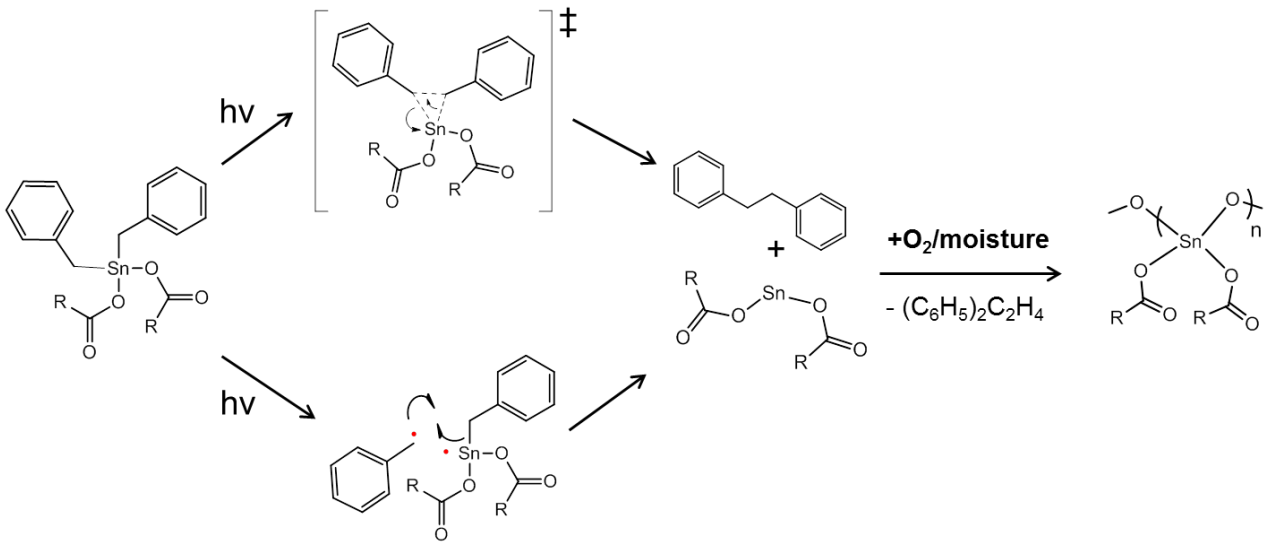

Figure 24. Proposed mechanism of EUV exposure of dibenzyltin dipivalate.

6. Discussion

We set out to design a series of photoresists that were comprised of high EUV optically dense elements. An increase in the resist optical density should directly increase photon absorption and potentially create resists that have improved photospeeds. We developed and answered three questions that were investigated during the course of this work on Molecular Organometallic Resists for EUV (MORE):

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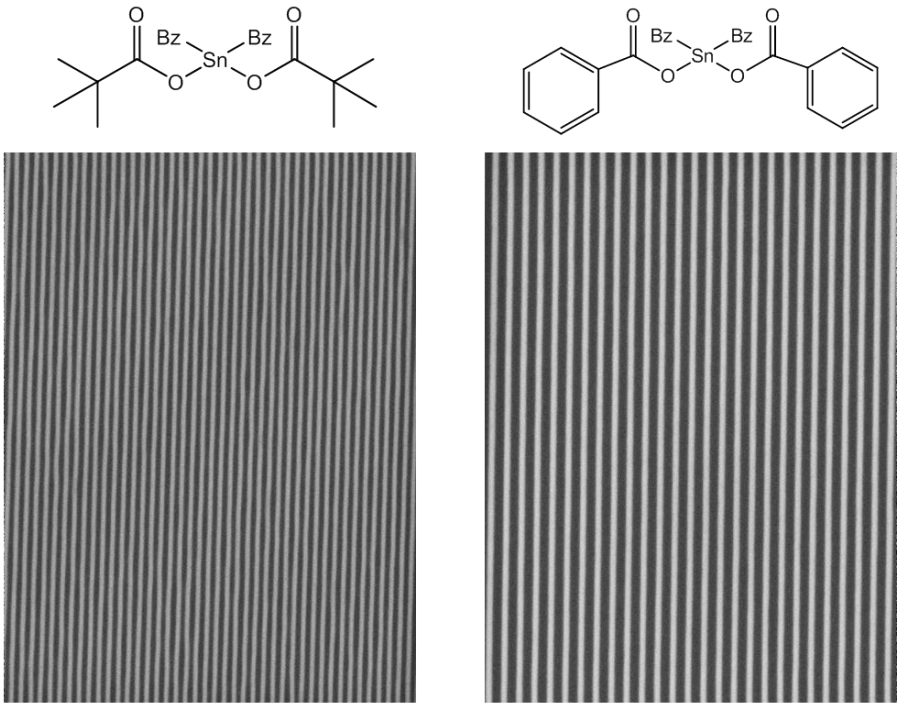
Can mononuclear tin and tellurium compounds act as high resolution and low-LER EUV photoresists?

Yes. We synthesized many compounds of the type $R_2M(OOCR')_2$ (M = tin, tellurium) and examined the effects of systematic molecular modification on EUV lithographic performance. Although the sensitivity of many of these compounds is poor (E_{size} = 50-600 mJ/cm^2), they are capable of good resolution and excellent LER. In particular, dibenzyltin dipivalate, **1,** resolves 22-nm half-pitch dense lines with an LER of 1.4 nm and dibenzyltin dibenzoate resolves 35-nm half-pitch dense lines with an LER or 1.1 nm (Figure 25).



Compound:	1	2
CD:	22 nm	35 nm
LER:	1.4 nm	1.1 nm
LWR:	1.4 nm	1.7 nm

Figure 25. Compounds 1 and 2 display high resolution patterning with extremely low LER.

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Can resist sensitivity be improved by selecting better ligands?

Yes. We discovered that we could improve resist sensitivity in three ways: (1) Decreasing Sn-C bond strength; (2) Using carboxylate ligands with olefin groups and (3) Using smaller carboxylate ligands.

It is observed that there is an improvement in resist sensitivity when alkyl groups with more free radical stability are used. Relatively small changes in the relative bond strength (350–430 kJ/mol) resulted in large changes in photospeed (50–180 mJ/cm^2). This trend suggests that photolytic cleavage is occurring at the Sn-C during exposure. Decreasing the Sn-C bond strength may be necessary to achieve reasonable photospeeds.

Two molecules that contained two olefin groups (dibenzyl tin diacrylate, **3**, and dibenzyl tin dimethacrylate, **4**) required much lower exposure doses than would be predicted (5 mJ/cm^2, 27 mJ/cm^2) to print dense lines. We propose that these molecules undergo a more efficient exposure mechanism, possibly utilizing a free radical polymerization after an initiation event.

Can a photomechanism be proposed that is consistent with all experimental data?

Although it is not possible to prove a mechanism, utilizing a combination of mass spectroscopy and XPS gave us many clues as to the volatile and non-volatile products. An important discovery was the post exposure delay effect that showed up to three times improvement in photospeed. Although it is not known precisely what happens when these films are exposed to EUV light, a photomechanism has been proposed that is supported by the experimental data. More work must be performed before we can reach a more definitive answer. Future analysis by NMR and FTIR may provide important data.

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How can we modify molecules to improve resist performance?

When comparing resists of a family, the photospeed is linearly-related to the molecular weight. The observed sensitivity dependence on carboxylate molecular weight provides insight into the possible role of this ligand. As the molecular weight of the carboxylate ligand is increased, the molecular volume of the molecule is increased. This could potentially have two effects: (1) Intermolecular interactions after exposure that caused a reduction in solubility are physically hindered and thus slower. (2) The increased molecular volume decreased the films mass density and thus decreased the film's overall photon absorption leading to worse sensitivities. It has also been determined that decreasing Sn-C bond strength creates a more sensitive resist.

I propose that we must both decrease Sn-C bond strength and increase a film's mass density to simultaneously maintain low LER and improve photospeed. This approach presents significant synthetic challenges, but literature suggests that it is possible.[46-49] Decreasing Sn-C bond strength can be accomplished most simply by using ligands with greater free radical stability. Figure 26 shows a few examples of ligands that would have lower bond strength than the benzyl ligand. Increasing mass density may be accomplished by creating molecules with multiple metals. Short chain oligomers may be possible by reacting a diacid with precise concentrations of dialkyltin dihalide and trialkyltin halide (Figure 27A) or reacting different digrignard reagents with Sn powder (Figure 27B).

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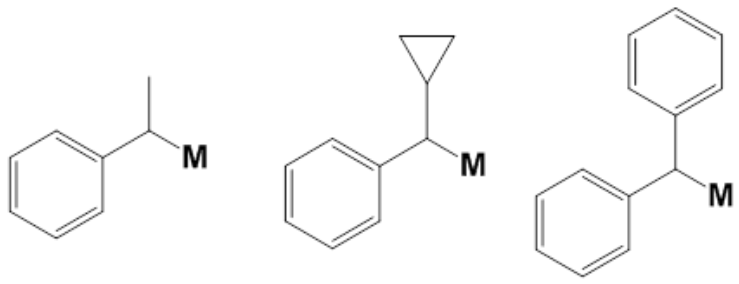

Figure 26. Examples of ligands that have lower bond strength than benzyl ligand.

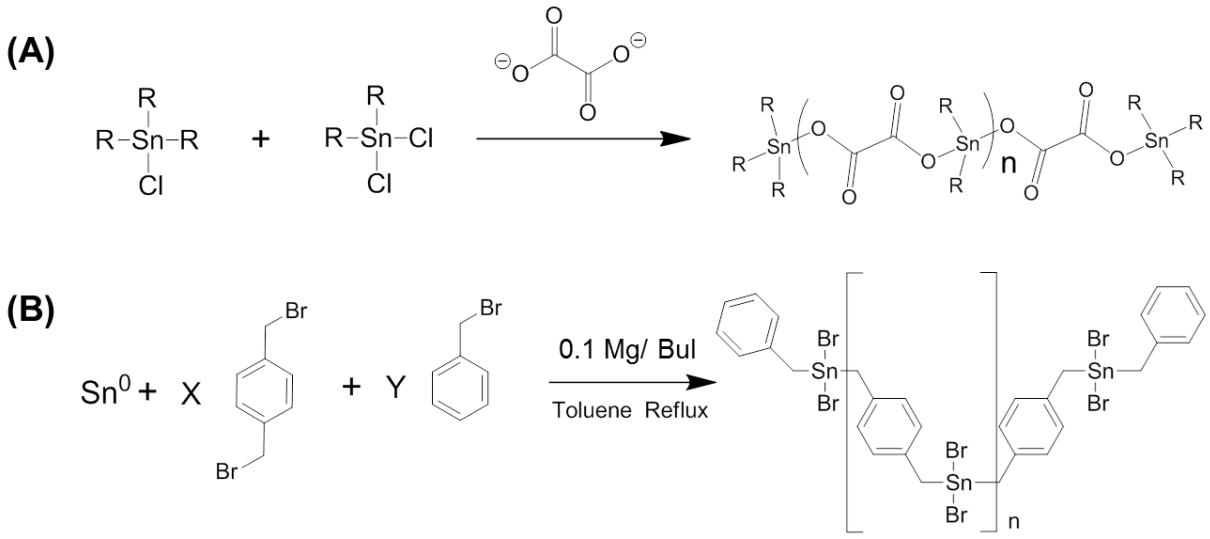

Figure 27. Possibly create films with greater mass density by reacting (A) Diacid with trialkyltin and dialkyltin halides or (B) Digrignard reagents with tin powder.

7. Experimental Methods

General. All reactions were carried out under a nitrogen environment. The reagents n-dibutyltin dichloride, n-dibutyltin hydroxide oxide, and diphenyltin dichloride were purchased from Alfa Aesar. All other reagents were purchased from Sigma Aldrich. All reagents were used as received unless specified. Dibenzyltin dibromide (**32**) was prepared through a literature procedure.[35]

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Instruments. ^{1}H NMR (Nuclear Magnetic Resonance) spectra were measured with Bruker 400 MHz spectrometer using TMS (tetramethyl silane) as an internal reference. All chemical shifts are reported as parts per million (ppm). Tin-H coupling constants are written in the as $J_{H\text{-}Sn}$. All other reported coupling constants are H-H.

Resist Formulation and Imaging. Resist formulations were made by dissolving solids in toluene and filtering through a 0.2 μm PTFE filter. Formulations were spin-coated onto a custom underlayer (crosslinked hydroxyethyl methacrylate/methyl methacrylate copolymers) on 4-inch silicon wafers. 40-nm to 60-nm thick resist films were made by adjusting spin-speed and formulation concentration. Resist films were then exposed with 13.5-nm radiation and developed with a hexanes developing solution. Exposures were performed at Paul Scherrer Institut on the XIL-II beamline using open-frame exposures to prepare contrast curves or using interference lithography for dense lines patterning. Photosensitivity was quantified by finding the E_{max} (energy needed to achieve maximum thickness after development) from the contrast curves and patterning was evaluated using E_{size} (mJ/cm^2), line edge roughness (LER, nm), and resolution (nm).

SEM Metrology. Scanning electron microscope micrographs were collected at Paul Scherrer Institut on a Zeiss Supra VP55. Accelerating voltage was set between 1-2 keV and the working distance was 4 mm. All images were at either 150 kX or 200 kX magnification.

LER Analysis. All LER and LWR values were obtained from the analysis of the SEM micrographs in SuMMIT Lithography Image Analysis software.

General Synthetic Procedure for Compounds 1 through 24. The general procedure was adapted from procedures found in the chemistry literature [35-37] **Method A.** R_2MX_2 (R = phenyl, benzyl; M = tin, tellurium; X = Cl, Br) (2 mmol) was combined with the sodium salt of the acid

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(4 mmol) in dichloromethane or hexanes (20 mL) in a 50-mL round-bottom flask, equipped with a stir bar and reflux condenser. The mixture was refluxed for 3 hours, cooled, and filtered through a small pore glass frit. The filtrate was evaporated to dryness at reduced pressure to a white powder and was used as is.

Method B. The acid (4 mmol) was combined with dichloromethane (10 mL) in a 50-mL round-bottom flask equipped with a stir bar. Triethylamine (0.56 mL, 4 mmol) was added slowly to the stirring solution. After 5 minutes of mixing, R_2MX_2 (0.744 g, 2 mmol) in dichloromethane (10 mL) was added to the reaction mixture. The solution was mixed until the reaction was completed, generally 0.5-3 hours. The reaction mixture was filtered through a small pore glass frit and the filtrate was evaporated under reduced pressure to approximately 5 mL. The mixture was extracted with benzene and any impurities were filtered off. The filtrate was evaporated under reduced pressure to a powder which was used as is.

Dibenzylstannanediyl bis(2,2-dimethylpropanoate) (1). Trimethylacetic acid (0.409 g, 4 mmol) was used as the acid. 0.32 grams were obtained (32% yield). ^{1}H NMR (Chloroform-*d*) δ 7.23–7.13 (m, 4H), 7.12 – 7.02 (m, 6H), 2.95 (s, $J_{H\text{-}Sn}$ = 84.8, 88.9, 136.6 Hz, 4H), 1.02 (s, 18H).

Dibenzylstannanediyl dibenzoate (2). Benzoic acid (0.488 g, 4 mmol) was used as the acid. 0.83 grams were obtained (76% yield). ^{1}H NMR (Chloroform-*d*) δ 7.98 (d, *J* = 7.7 Hz, 4H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 4H), 7.29–6.66 (m, 10H), 3.14 (s, $J_{H\text{-}Sn}$ = 89.5, 93.6, 137.3 Hz, 4H).

Dibenzylstannanediyl diacrylate (3). Acrylic acid (0.288 g, 4 mmol) was used as the acid. 0.52 grams were obtained (59% yield). ^{1}H NMR (Chloroform-*d*) δ 7.30–6.90 (m, 10H), 6.33 (d, *J* = 17.3 Hz, 2H), 6.02 (dd, *J* = 17.2, 10.3 Hz, 2H), 5.81 (d, *J* = 10.3 Hz, 2H), 3.02 (s, $J_{H\text{-}Sn}$ = 88.9, 92.9, 139.1 Hz, 4H).

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Dibenzylstannanediyl bis(2-methylacrylate) (4). Methacrylic acid (0.344 g, 4 mmol) was used as the acid. 0.51 grams were obtained (54% yield). ^{1}H NMR (Chloroform-*d*) δ 7.37–6.93 (m, 10H), 6.03 (s, 2H), 5.48 (d, *J* = 2.1 Hz, 2H), 3.02 (s, $J_{H\text{-}Sn}$ = 89.1, 93.4, 137 Hz, 4H), 1.80 (s, 6H).

Dibenzylstannanediyl diformate (5). Formic acid (0.184 g, 4 mmol) was used as the acid. 0.32 grams were obtained (41% yield). ^{1}H NMR (Chloroform-*d*) δ 8.2 (s, 2H), 7.61–6.48 (m, 11H), 3.21 (s, $J_{H\text{-}Sn}$ = 73.9, 154.8 Hz, 4H).

Dibenzylstannanediyl diacetate (6). Acetic acid (0.24 g, 4 mmol) was used as the acid. 0.5 grams were obtained (60% yield). ^{1}H NMR (Chloroform-*d*) δ 7.51–6.64 (m, 10H), 2.98 (s, $J_{H\text{-}Sn}$ = 89.2, 137.2 Hz, 4H), 1.87 (s, 6H).

Dibenzylstannanediyl bis(2-phenylacetate) (7). Phenylacetic acid (0.545 g, 4 mmol) was used as the acid. 0.68 grams were obtained (59% yield). ^{1}H NMR (Chloroform-*d*) δ 7.39–7.20 (m, 6H), 7.20 – 6.99 (m, 10H), 6.99 – 6.83 (m, 4H), 3.40 (s, 4H), 2.95 (s, $J_{H\text{-}Sn}$ = 86.8, 137.5 Hz, 4H).

Dibenzylstannanediyl bis(2,2-diphenylacetate) (8). Diphenylacetic acid (0.849 g, 4 mmol) was used as the acid. The compound was crystallized in hexanes. 0.96 grams were obtained (66% yield). ^{1}H NMR (Chloroform-*d*) δ 7.31–7.13 (m, 20H), 7.07–6.94 (m, 6H), 6.85–6.73 (m, 4H), 4.86 (s, 2H), 2.94 (s, $J_{H\text{-}Sn}$ = 84.4, 137.6 Hz, 4H).

Diphenylstannanediyl diacetate (9). Acetic acid (0.24 g, 4 mmol) was used as the acid. 0.26 grams were obtained (33% yield). ^{1}H NMR (Chloroform-*d*) δ 8.12–6.55 (m, 10H), 2.62–0.53 (m, 6H).

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Diphenylstannanediyl diacrylate (10). Acrylic acid (0.288 g, 4 mmol) was used as the acid. 0.45 grams were obtained (54% yield). ^{1}H NMR (Chloroform-*d*) δ 7.96–7.31 (m, 10H), 6.44 (d, *J* = 17.3 Hz, 2H), 6.22 (dd, *J* = 17.3, 10.2 Hz, 2H), 5.83 (d, *J* = 10.3 Hz, 2H).

Diphenylstannanediyl bis(2,2-dimethylpropanoate) (11). Trimethylacetic acid (0.409 g, 4 mmol) was used as the acid. 0.2 grams were obtained (21% yield). ^{1}H NMR (Chloroform-*d*) δ 7.88–6.70 (m, 10H), 1.17 (s, 18H).

Diphenylstannanediyl bis(2-phenylacetate) (12). Phenylacetic acid (0.545 g, 4 mmol) was used as the acid. 0.31 grams were obtained (28% yield). ^{1}H NMR (Chloroform-*d*) δ 7.77–6.86 (m, 20H), 3.59 (s, 4H).

Diphenylstannanediyl bis(2,2-diphenylacetate) (13). Diphenylacetic acid (0.849 g, 4 mmol) was used as the acid. 0.31 grams were obtained (28% yield). ^{1}H NMR (Chloroform-*d*) δ 7.66–7.06 (m, 33H), 5.15 (s, 2H).

Bis(2-methylbenzyl)stannanediyl diformate (14). Formic acid (0.184 g, 4 mmol) was used as the acid. The compound was crystallized in 1:9 dichloromethane:hexanes. 0.15 grams were obtained (18% yield). ^{1}H NMR (Chloroform-*d*) δ 7.58–6.31 (m, 8H), 3.36–2.80 (m, 4H), 2.47–1.88 (m, 6H), 1.25 (q, *J* = 6.0, 5.0 Hz, 2H).

Bis(2-methylbenzyl)stannanediyl diacetate (15). Acetic acid (0.24 g, 4 mmol) was used as the acid. The final product was crystallized from hexanes. 0.13 grams were obtained (15% yield). ^{1}H NMR (Chloroform-*d*) δ 7.42–6.55 (m, 8H), 3.10 (s, 4H), 2.60–1.95 (m, 6H).

Bis(2-methylbenzyl)stannanediyl bis(2,2-dimethylpropanoate) (16). Trimethylacetic acid (0.409 g, 4 mmol) was used as the acid. The compound was crystallized in 1:9 dichloromethane:hexanes. 0.18 grams were obtained (17% yield). ^{1}H NMR (Chloroform-*d*) δ 7.40-6.47 (m, 8H), 2.94 (s, 4H), 2.23 (s, 6H), 1.02 (s, 18H).

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Diphenyltellurium diformate (17). Formic acid (0.184 g, 4 mmol) was used as the acid. The compound was crystallized from ethyl acetate. 0.3 grams were obtained (40% yield). ^{1}H NMR (Chloroform-*d*) δ 10.1 (s, 2H), 8.09–7.33 (m, 10H).

Diphenyltellurium diacetate (18). Acetic Acid (0.24 g, 4 mmol) was used as the acid. 0.26 grams were obtained (33% yield). ^{1}H NMR (Chloroform-*d*) δ 8.11–7.31 (m, 10H), 1.94 (d, *J* = 1.0 Hz, 6H).

Diphenyltellurium diacrylate (19). Acrylic acid (0.288 g, 4 mmol) was used as the acid. The compound was crystallized in ethyl acetate. 0.4 grams were obtained (47% yield). ^{1}H NMR (Chloroform-*d*) δ 8.2–7.26 (m, 10H), 6.3-5.6 (m, 6H).

Diphenyltellurium dimethacrylate (20). Methacrylic acid (x g, 4 mmol) was used as the acid. The compound was crystallized from hexanes. 0.33 grams were obtained (37% yield). ^{1}H NMR (Chloroform-*d*) δ 8.3–7.41 (m, 10H), 6.4-6.2 (m, 4H), 2.1 (s, 2H).

Diphenyltellurium bis(2,2-dimethylpropanoate) (21). Trimethylacetic acid (0.409 g, 4 mmol) was used as the acid. The compound was crystallized in hexanes. 0.24 grams were obtained (25% yield). ^{1}H NMR (Chloroform-*d*) δ 8.09 – 7.29 (m, 10H), 1.07 (s, 18H).

Diphenyltellurium dibenzoate (22). Benzoic acid (0.488 g, 4 mmol) was used as the acid. The compound was crystallized in hexanes. 0.48 grams were obtained (47% yield). ^{1}H NMR (Chloroform-*d*) δ 8.27–7.74 (m, 8H), 7.74–7.42 (m, 8H), 7.36 (t, *J* = 7.6 Hz, 4H).

Diphenyltellurium bis(2-phenylacetate) (23). Phenylacetic acid (0.545 g, 4 mmol) was used as the acid. The compound was crystallized in hexanes. 0.31 grams were obtained (28% yield). ^{1}H NMR (Chloroform-*d*) δ 7.6–6.85 (m, 20H), 3.3 (s, 2H).

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Diphenyltellurium bis(2,2-phenylacetate) (24). Diphenylacetic acid (0.849 g, 4 mmol) was used as the acid. The compound was crystallized in 1:9 dichloromethane:hexanes. 0.63 grams were obtained (46% yield). ^{1}H NMR (Chloroform-*d*) δ 7.7–6.91 (m, 30H), 4.95 (s, 2H).

General Synthetic Procedure for Compounds 25 through 31. Method A.[41-44] Dibutyltin Dichloride (0.5 g, 2 mmol) was combined with the acid (4 mmol) and toluene (20 mL) in a 50-mL round-bottom flask equipped with a stir bar, dean stark water trap, and reflux condenser. The solution was heated and allowed to reflux for 1 hour and then filtered through a fine pore glass frit. The filtrate was evaporated under reduced pressure to form a white powder. The final product was obtained through crystallization using hexanes, if possible.

Method B. The acid (4 mmol) and dichloromethane (10 mL) was added to a 50-mL round-bottom flask equipped with a stir bar. Triethylamine (0.56 g, 4 mmol) was added slowly to the stirring solution. After 5 minutes of mixing, n-dibutyltin dichloride (0.5 g, 2 mmol) in dichloromethane (10 mL) was added to the reaction mixture. The solution was mixed until the reaction was completed, generally 1-3 hours. The reaction mixture was then filtered through a small pore glass frit and the filtrate was evaporated under reduced pressure to approximately 5 mL. The mixture was extracted with a saturated sodium bicarbonate solution three times. The organic layer was dried on sodium sulfate and the final product was crystallized from hexanes or dichloromethane/hexanes.

Dibutylstannanediyl diformate (25). Formic acid (0.184 g, 4 mmol) was used as the acid. The final product was an oil and crystallization was not possible. 0.15 grams were obtained (23% yield). ^{1}H NMR (Chloroform-*d*) δ 8.44 (s, 2H), 1.70–1.56 (m, 4H), 1.30 (dt, J = 30.1, 7.2 Hz, 8H), 0.87 (t, J = 7.2 Hz, 6H).

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Dibutylstannanediyl diacetate (26). Acetic acid (0.24 g, 4 mmol) was used as the acid. The final product was an oil and crystallization was not possible. 0.32 grams were obtained (45% yield). ^{1}H NMR (Chloroform-*d*) δ 2.06 (s, 6H), 1.81–1.44 (m, 8H), 1.35 (hd, *J* = 7.9, 7.3, 4.5 Hz, 4H), 0.88 (t, *J* = 7.3 Hz, 6H).

Dibutylstannanediyl diacrylate (27). Acrylic acid (0.288 g, 4 mmol) was used as the acid. The compound was crystallized in hexanes. 0.25 grams were obtained (33% yield). ^{1}H NMR (Chloroform-*d*) δ 6.55 – 5.66 (m, 6H), 1.87–1.45 (m, 8H), 1.43–1.14 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H).

Dibutylstannanediyl bis(2,2-dimethylpropanoate) (28). Trimethylacetic acid (0.409 g, 4 mmol) was used as the acid. The compound was crystallized in hexanes. 0.64 grams were obtained (74% yield). ^{1}H NMR (Chloroform-*d*) δ 1.75–1.41 (m, 8H), 1.39–1.26 (m, 4H), 1.19 (s, 18H), 0.85 (t, *J* = 7.4 Hz, 6H).

Dibutylstannanediyl dibenzoate (29). Benzoic acid (0.488 g, 4 mmol) was used as the acid. The compound was crystallized in 1:9 dichloromethane: hexanes. 0.12 grams were obtained (13% yield). ^{1}H NMR (Chloroform-*d*) δ 8.45–6.73 (m, 10H), 1.95–0.77 (m, 18H).

Dibutylstannanediyl bis(2-phenylacetate) (30). Phenylacetic acid (0.545 g, 4 mmol) was used as the acid. The final product was an oil and was used as is. 0.69 grams were obtained (68% yield). ^{1}H NMR (Chloroform-*d*) δ 7.44–7.05 (m, 10H), 3.63 (s, 4H), 1.84–0.36 (m, 18H).

Dibutylstannanediyl bis(2,2-diphenylacetate) (31). Diphenylacetic acid (0.849 g, 4 mmol) was used as the acid. The final product was an oil and was used as is. 0.77 grams were obtained (59% yield). ^{1}H NMR (Chloroform-*d*) δ 7.40–7.13 (m, 20H), 5.07 (s, 2H), 1.73–0.64 (m, 18H).

Dibenzyldibromostannane (32). The general procedure was adapted from procedures found in the chemistry literature.[35] Tin powder (10 g, 84 mmol) and anhydrous toluene (100 mL) were

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added to a 250-mL three necked round-bottom flask equipped with a stir bar and reflux condenser. The mixture was heated to 105 ºC in an oil bath. 1 mL water was added to the mixture to initiate reflux. Benzyl bromide (14.37 g, 84 mmol) was added to the refluxing solution over 10 minutes. The reflux was maintained for 3 hours. Unreacted tin was filtered off and white fluffy needles formed upon cooling of the reaction mixture. The solids were washed with cold toluene and dried overnight on high vacuum. 20 grams were obtained (52% yield). ^{1}H NMR (Chloroform-*d*) δ 7.27–7.18 (m, 4H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.09–6.96 (m, 4H), 3.21 (s, $J_{H\text{-}Sn}$ = 85.4, 88.8, 136.3, 4H).

Dibenzyldiiodostannane (33). Compound **32** (1g, 2.2 mmol) and acetone (10 mL) were added to a 50 mL round bottom flask equipped with a stir bar. Sodium Iodide (1.32 g, 8.8 mmol) in acetone (10 mL) was added to the mixing solution. The resulting solution was filtered and evaporated to a solid. Dissolve solid in dichloromethane and extract with water. Collected and dried the organic layer with sodium sulfate and evaporated to solid. The product was crystallized in dichloromethane. 0.6 grams were obtained (54% yield) ^{1}H NMR (Chloroform-*d*) δ 7.71–6.44 (m, 10H), 3.34 (s, 4H).

Dichlorobis(2-methylbenzyl)stannane (34). The general procedure was adapted from procedures found in the chemistry literature.[35] Followed preparation for making compound **32**. White solids were isolated upon final workup. 2.2 grams were obtained (45% yield). ^{1}H NMR (Chloroform-*d*) δ 7.64–6.40 (m, 8H), 4.72–2.52 (m, 4H), 2.58–1.75 (m, 6H).

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Appendix – Selected ^{1}H NMR Spectra

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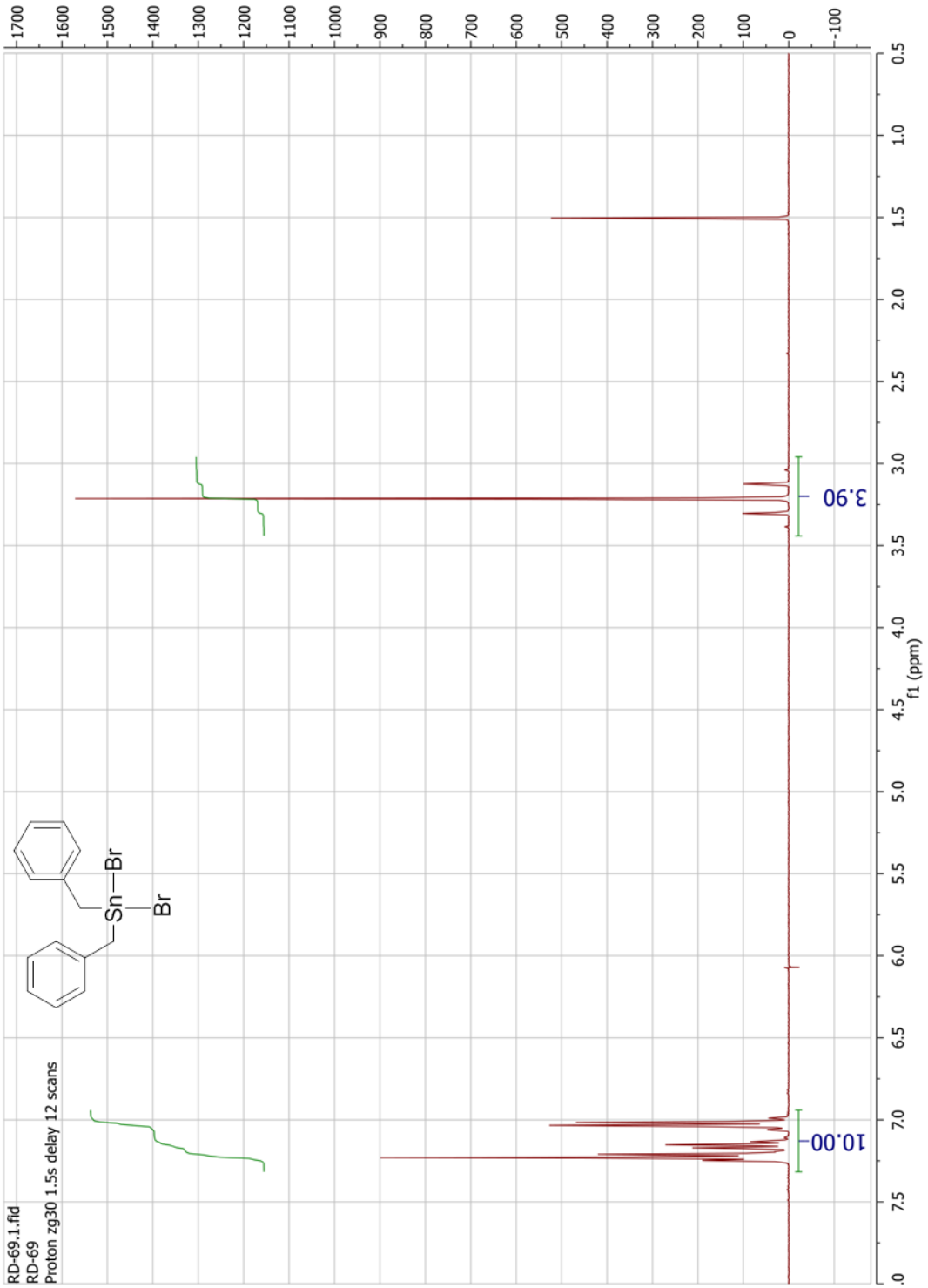

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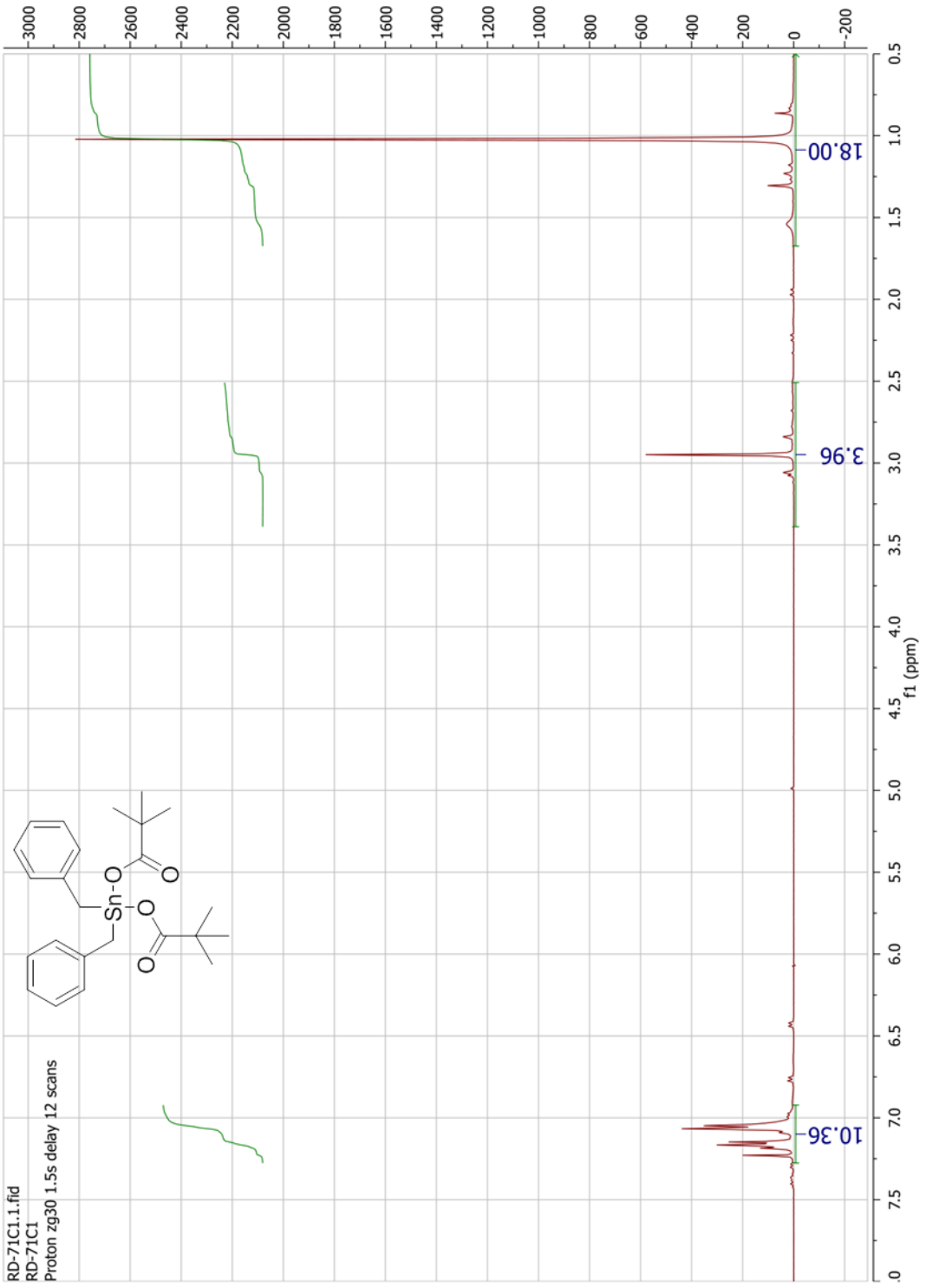

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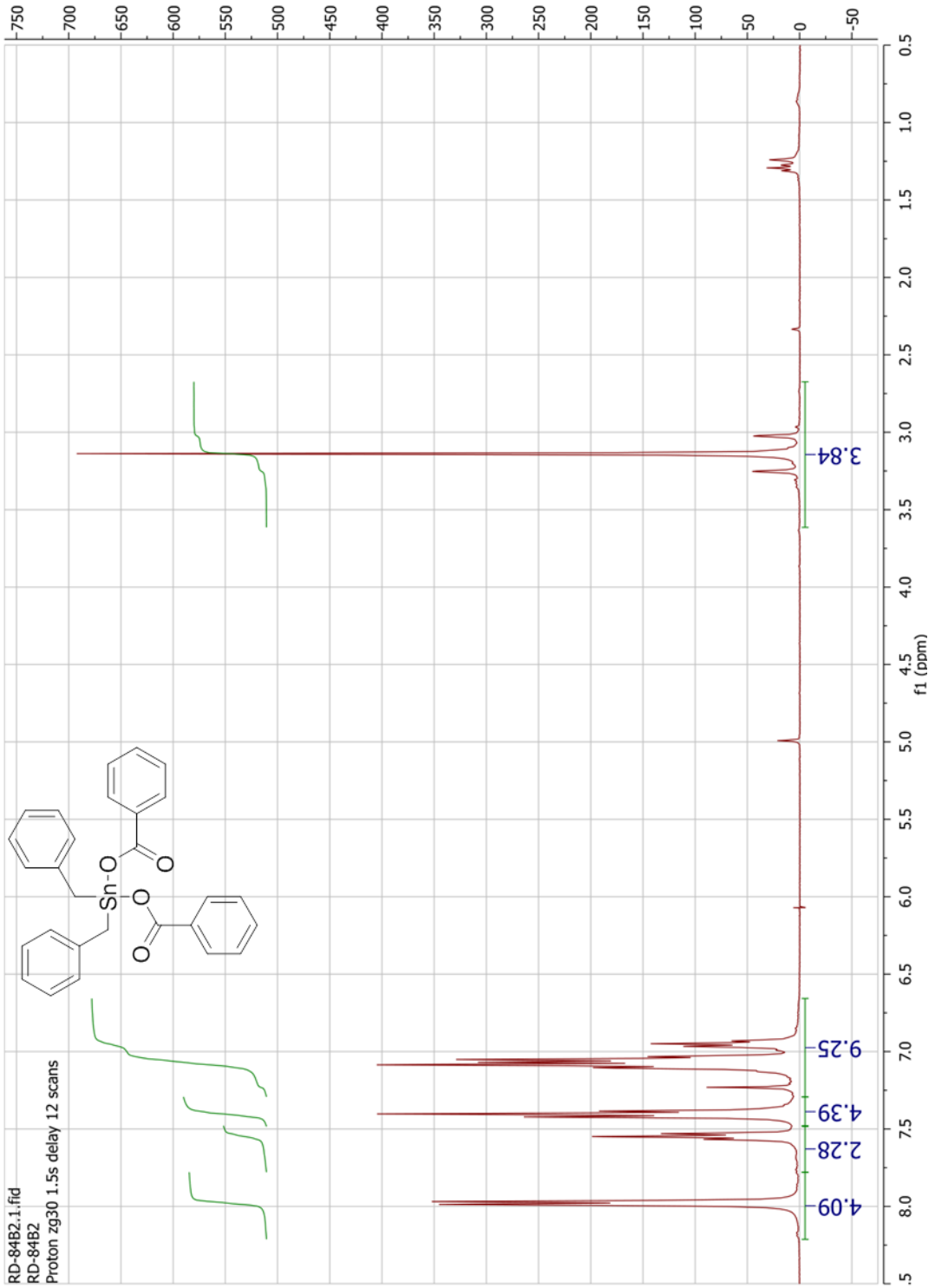

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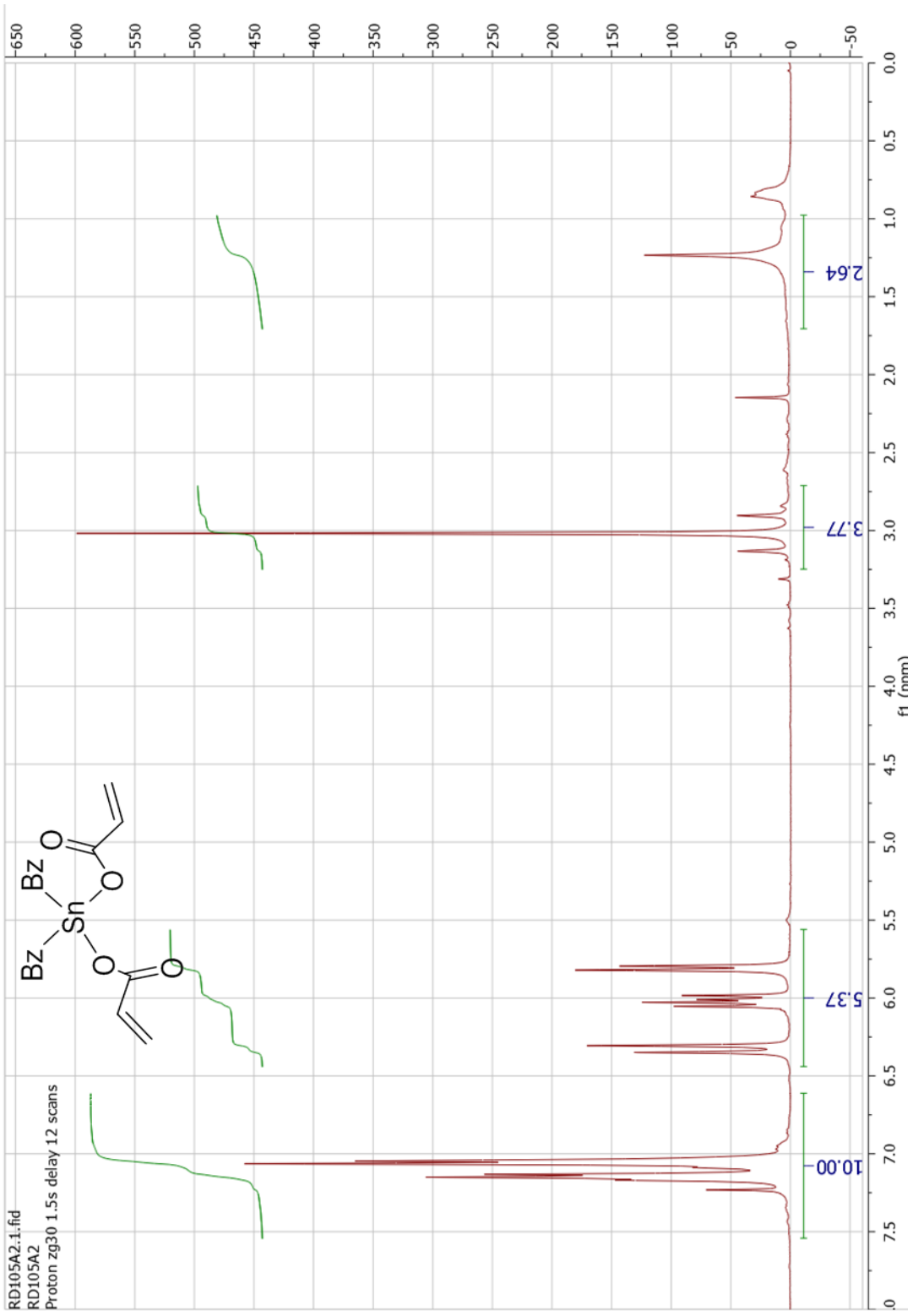

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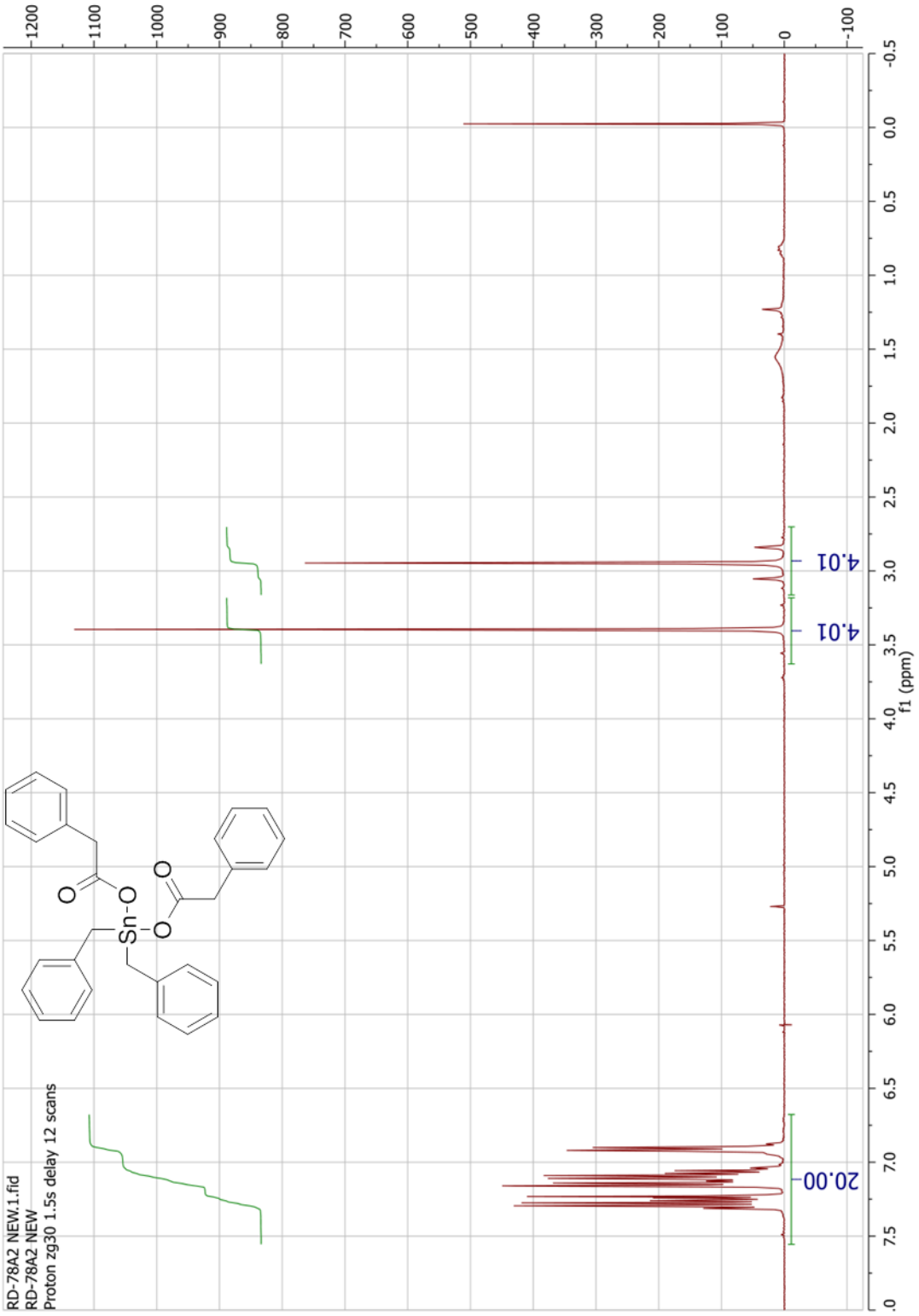

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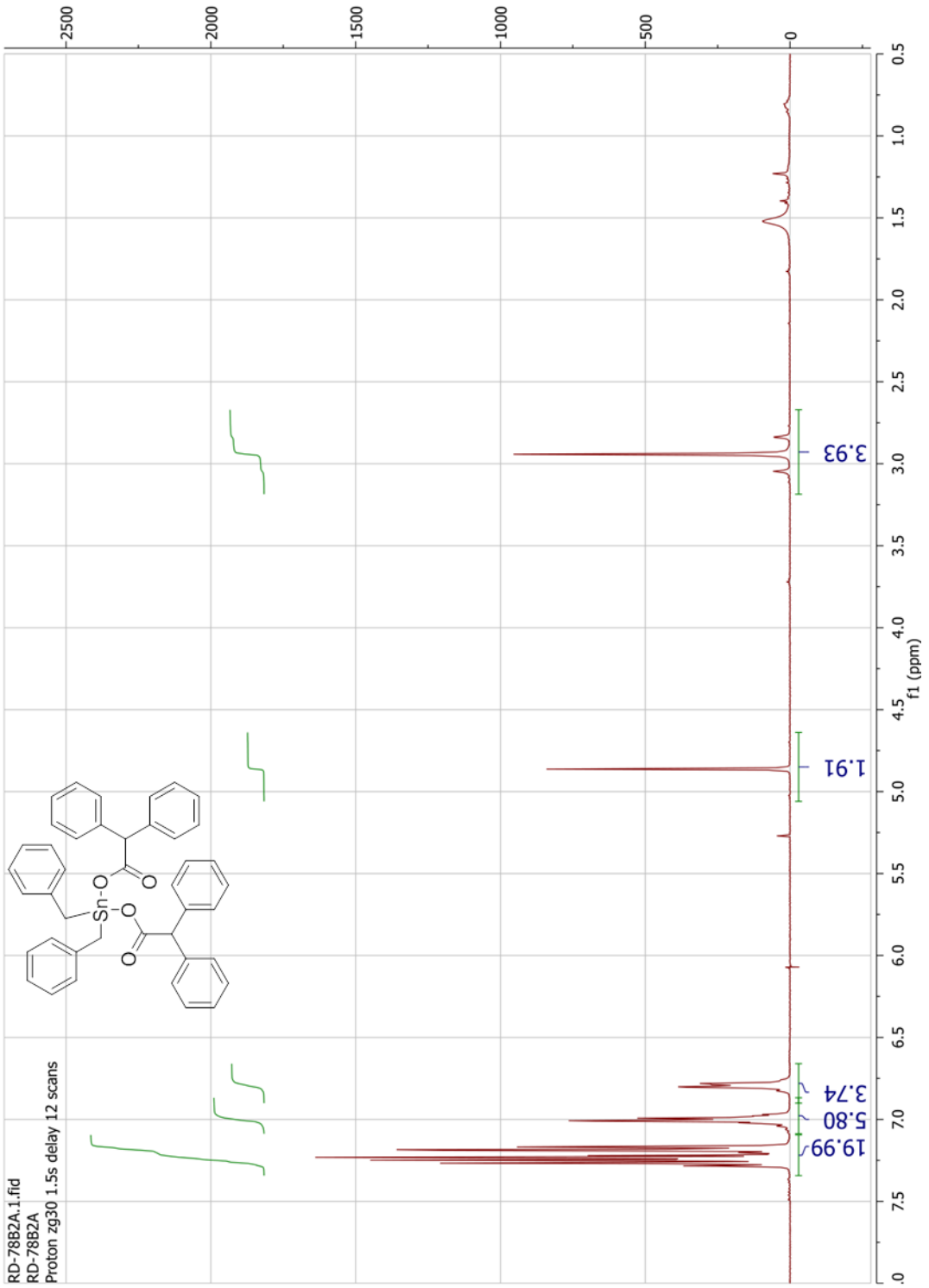

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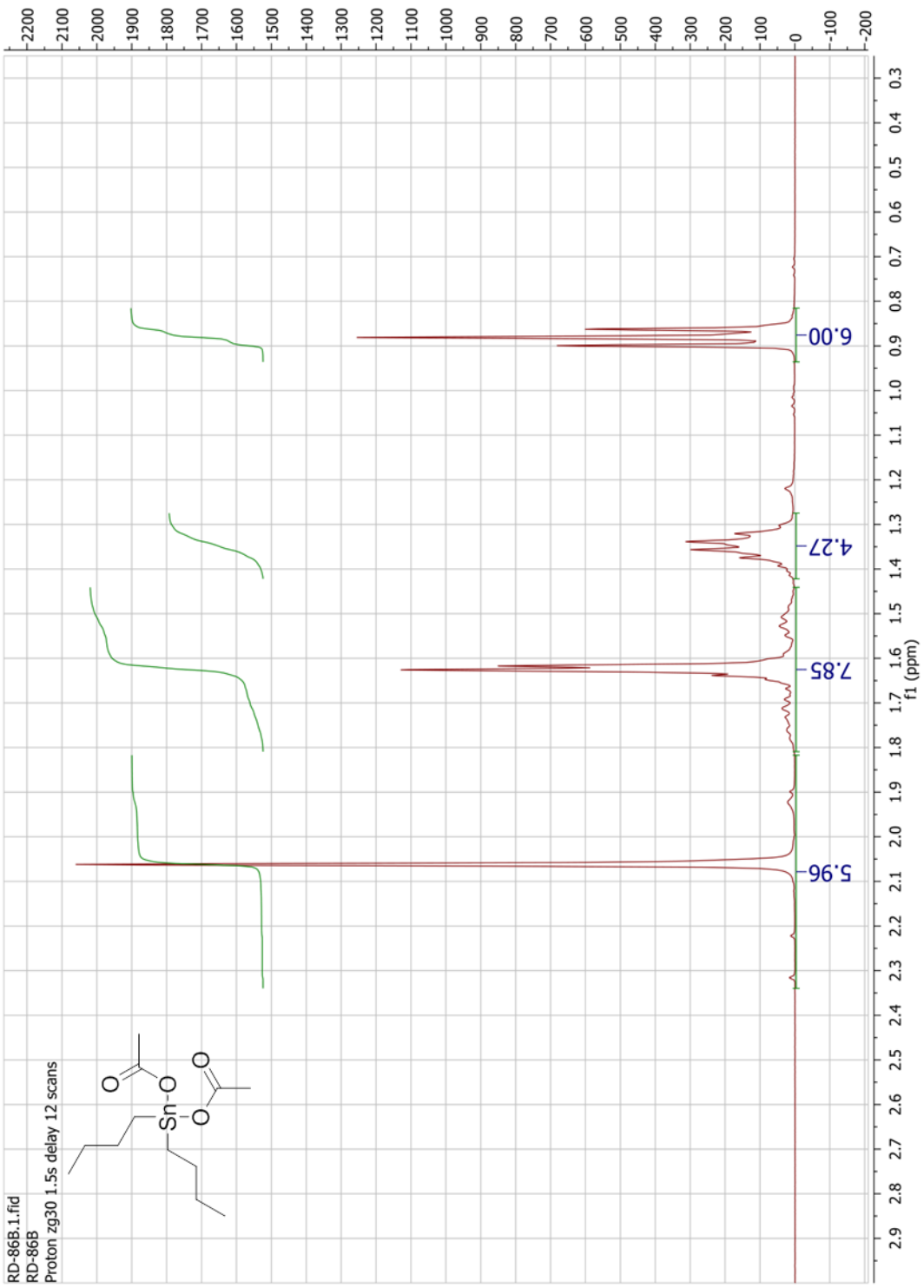

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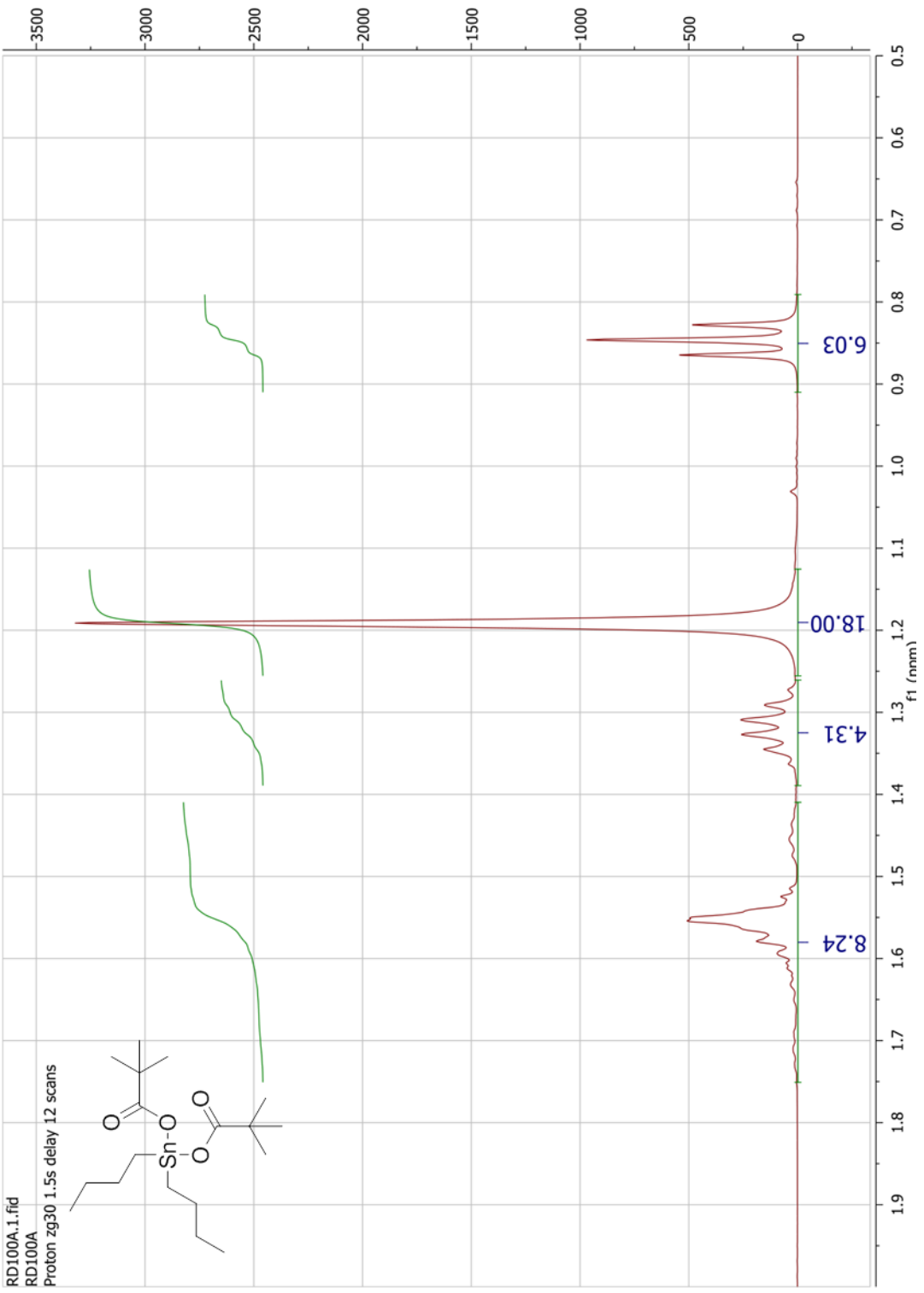

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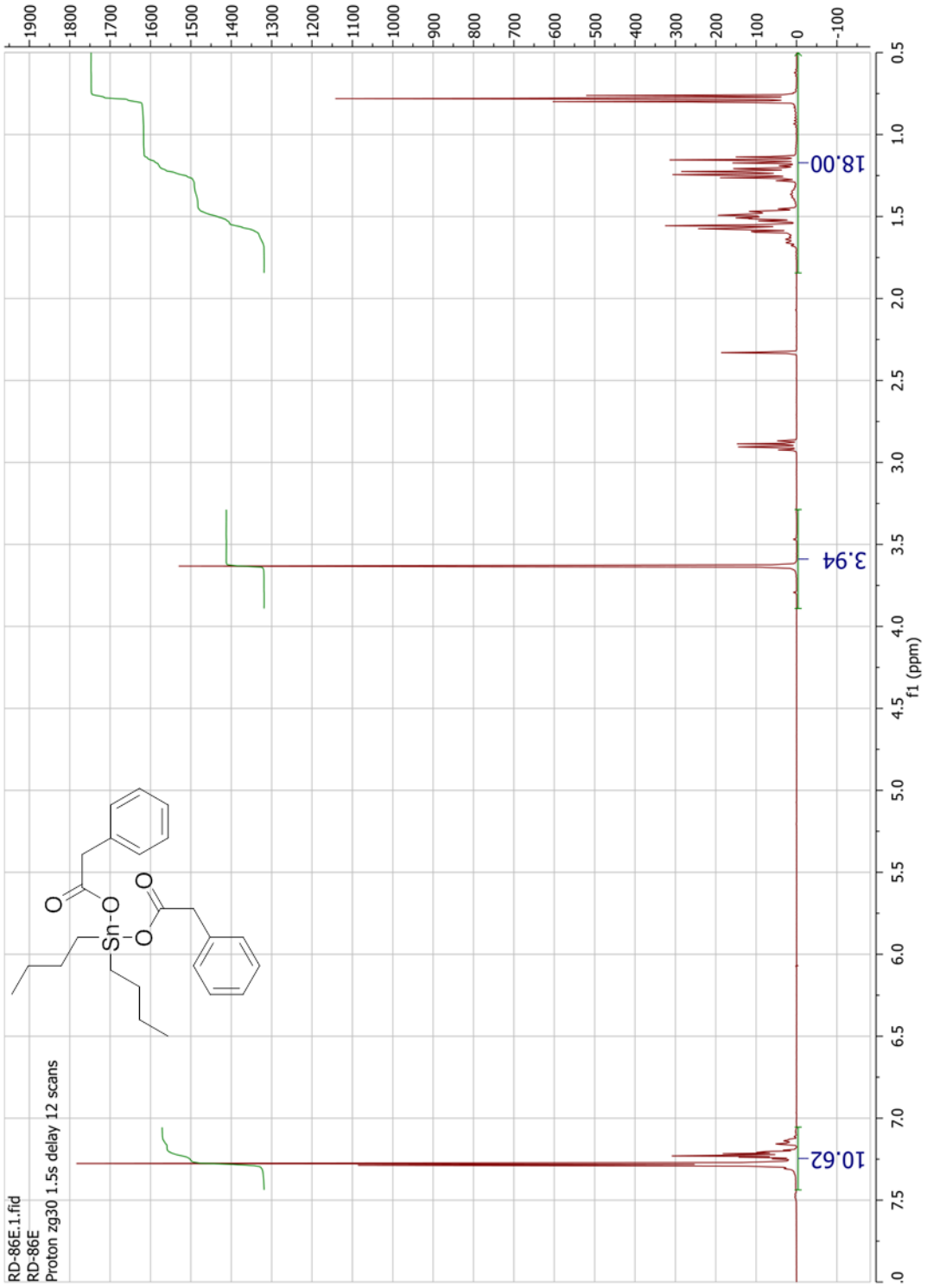

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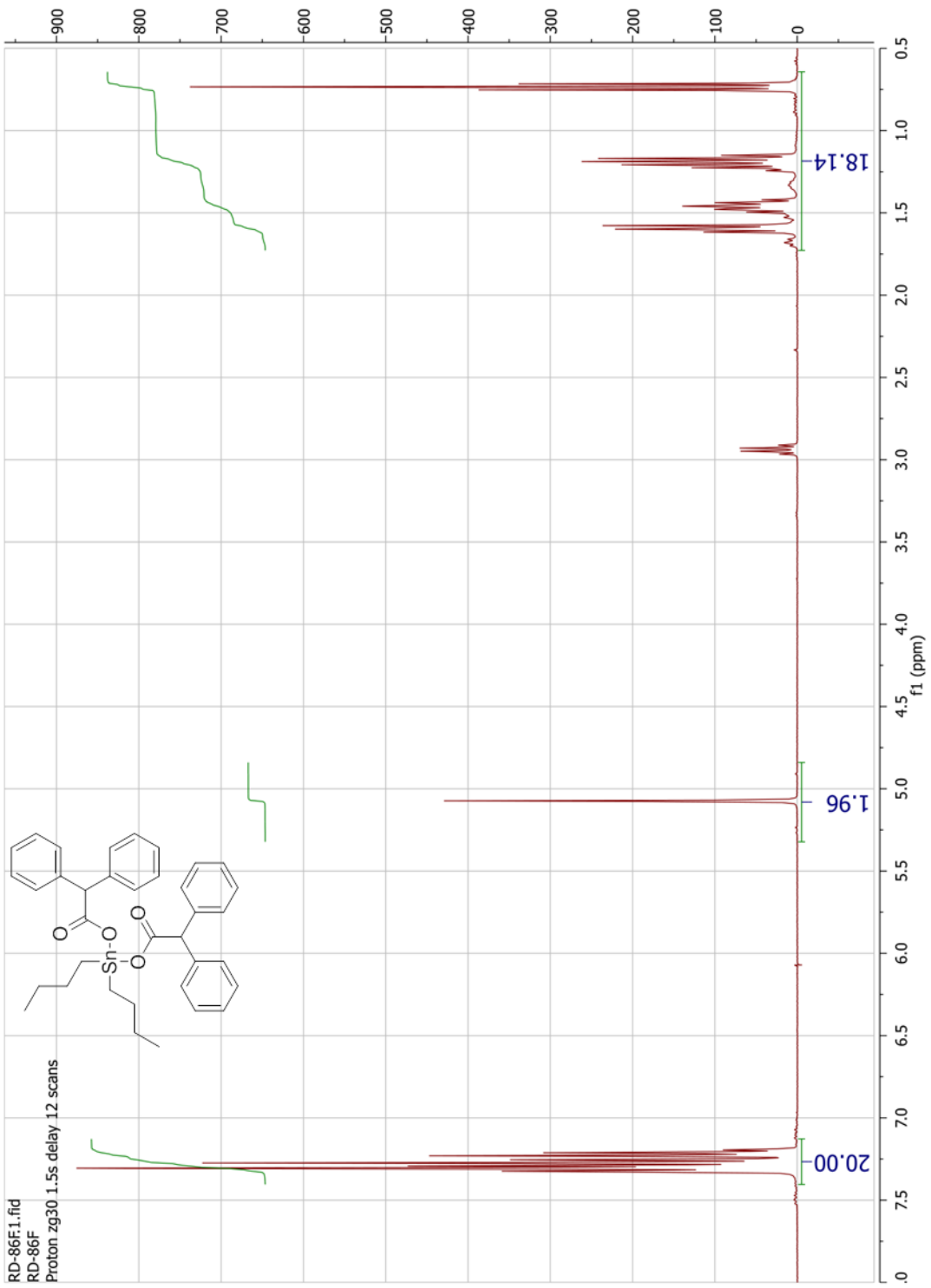

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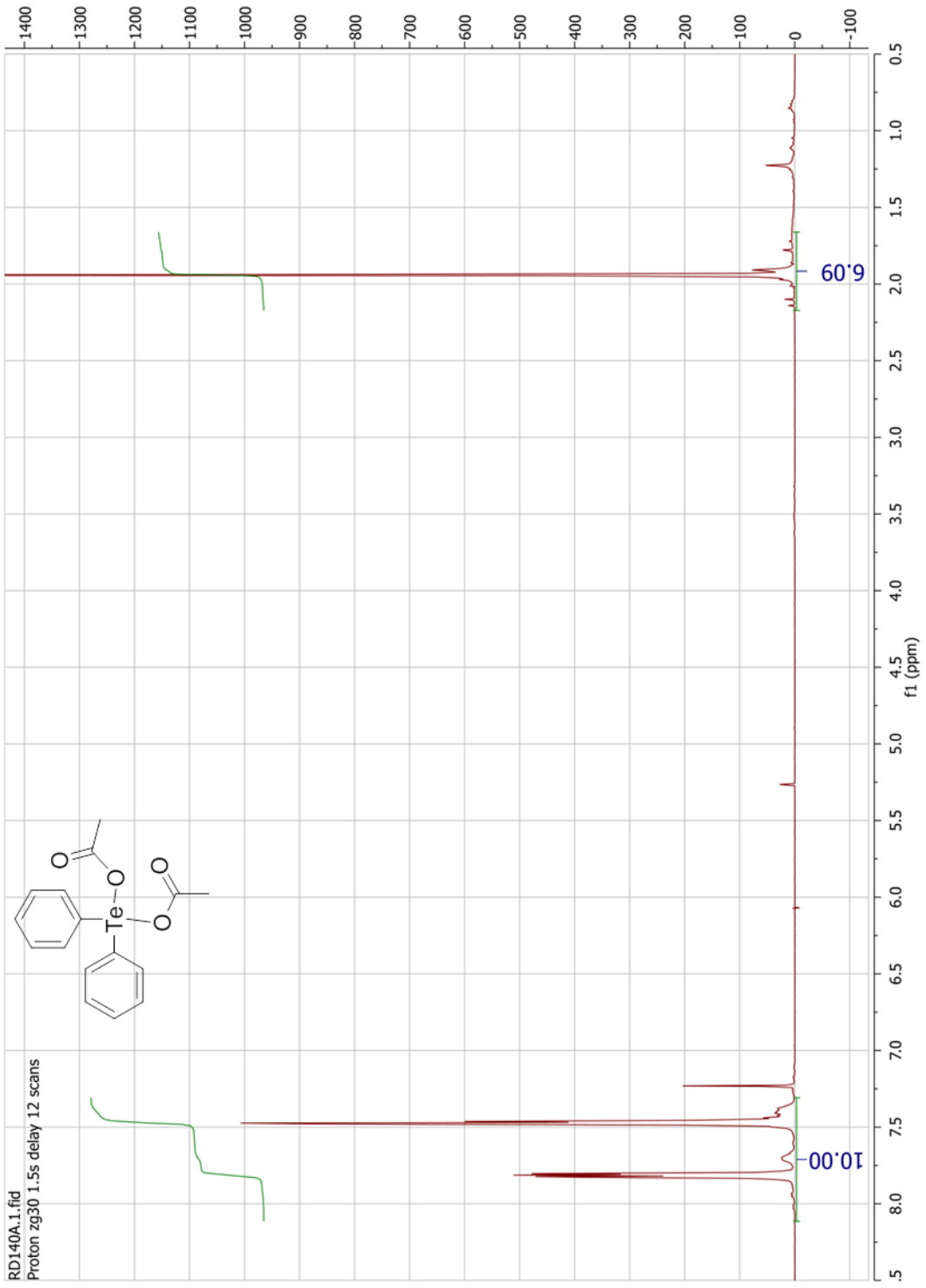

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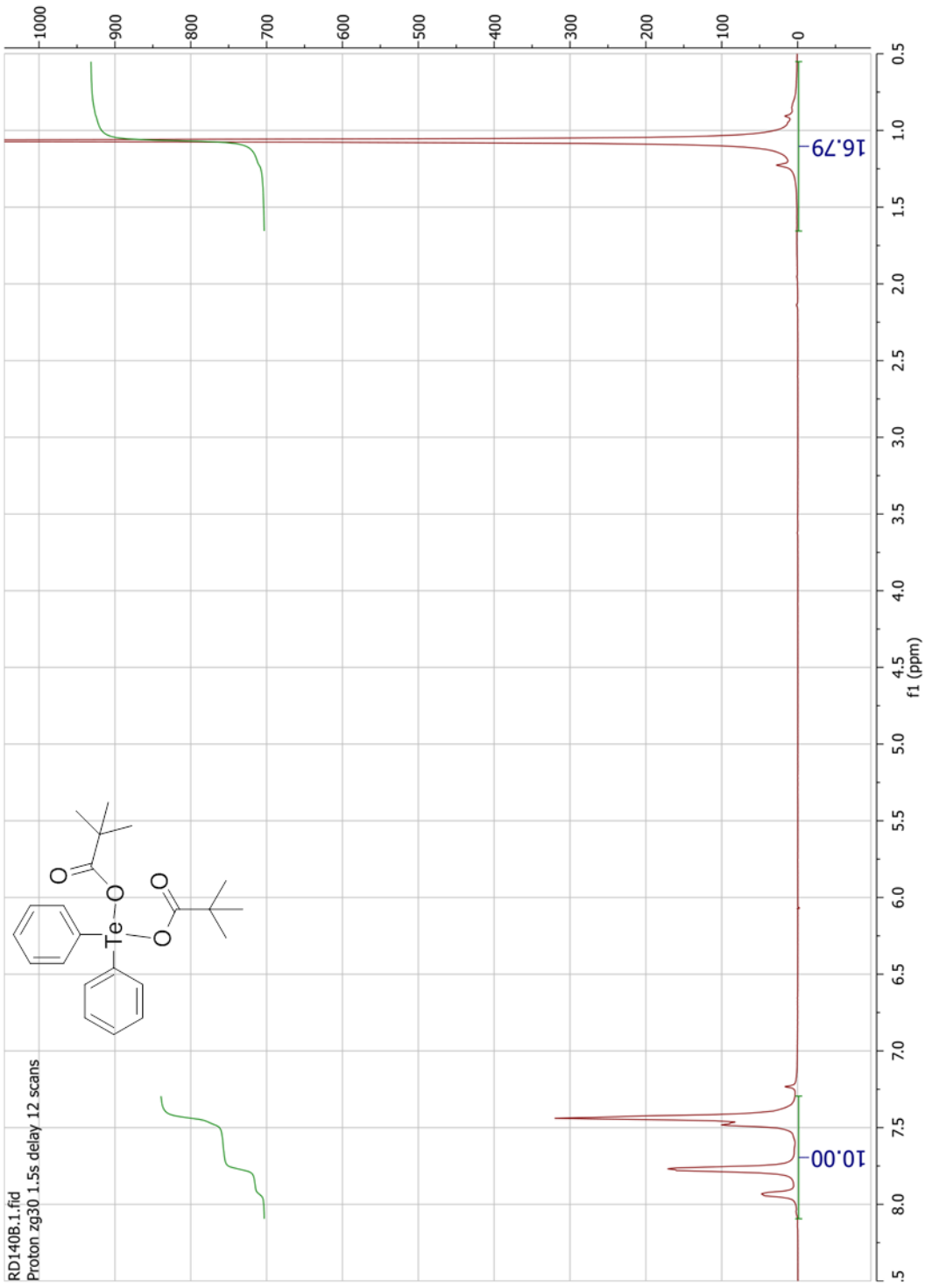

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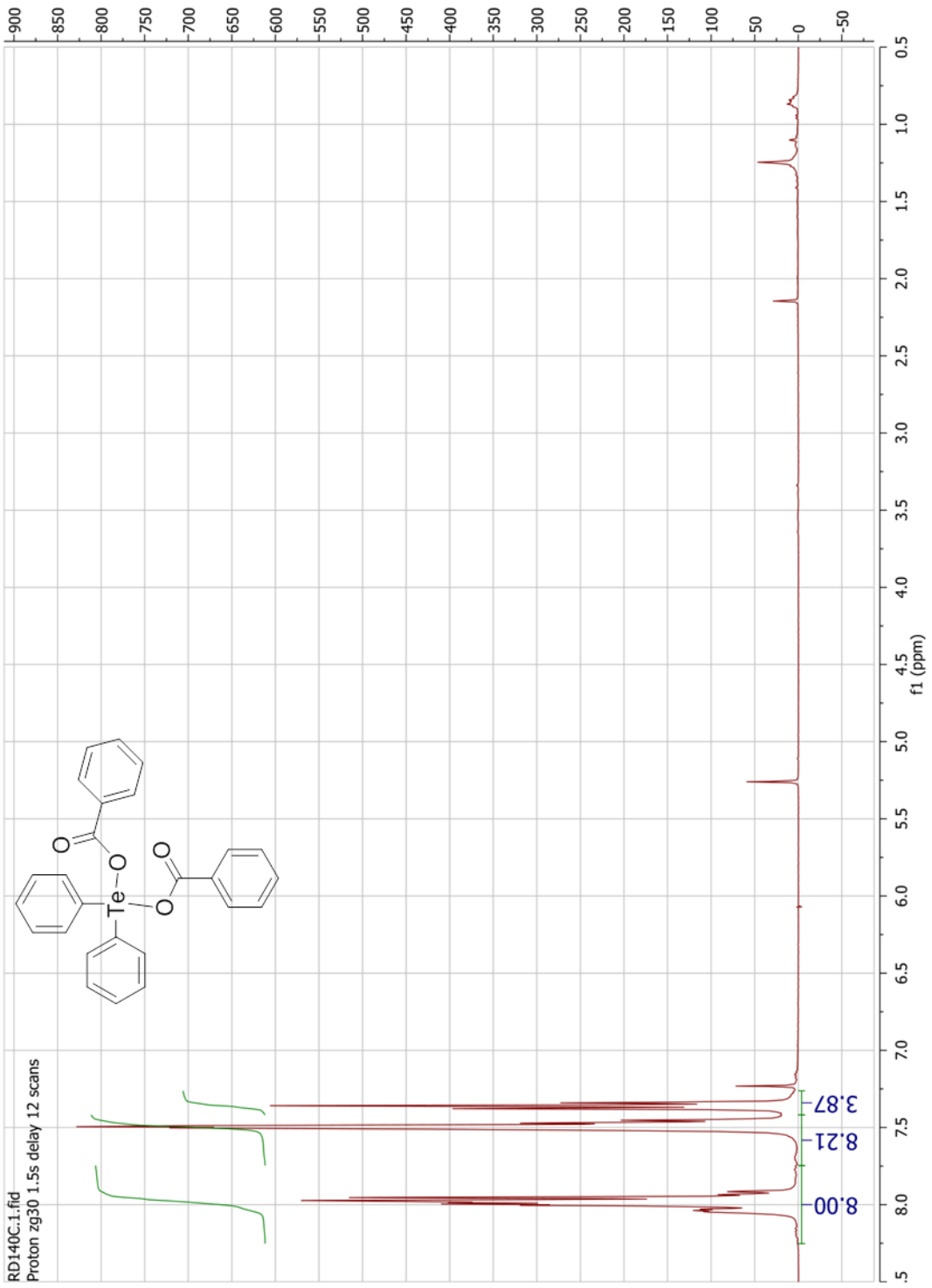

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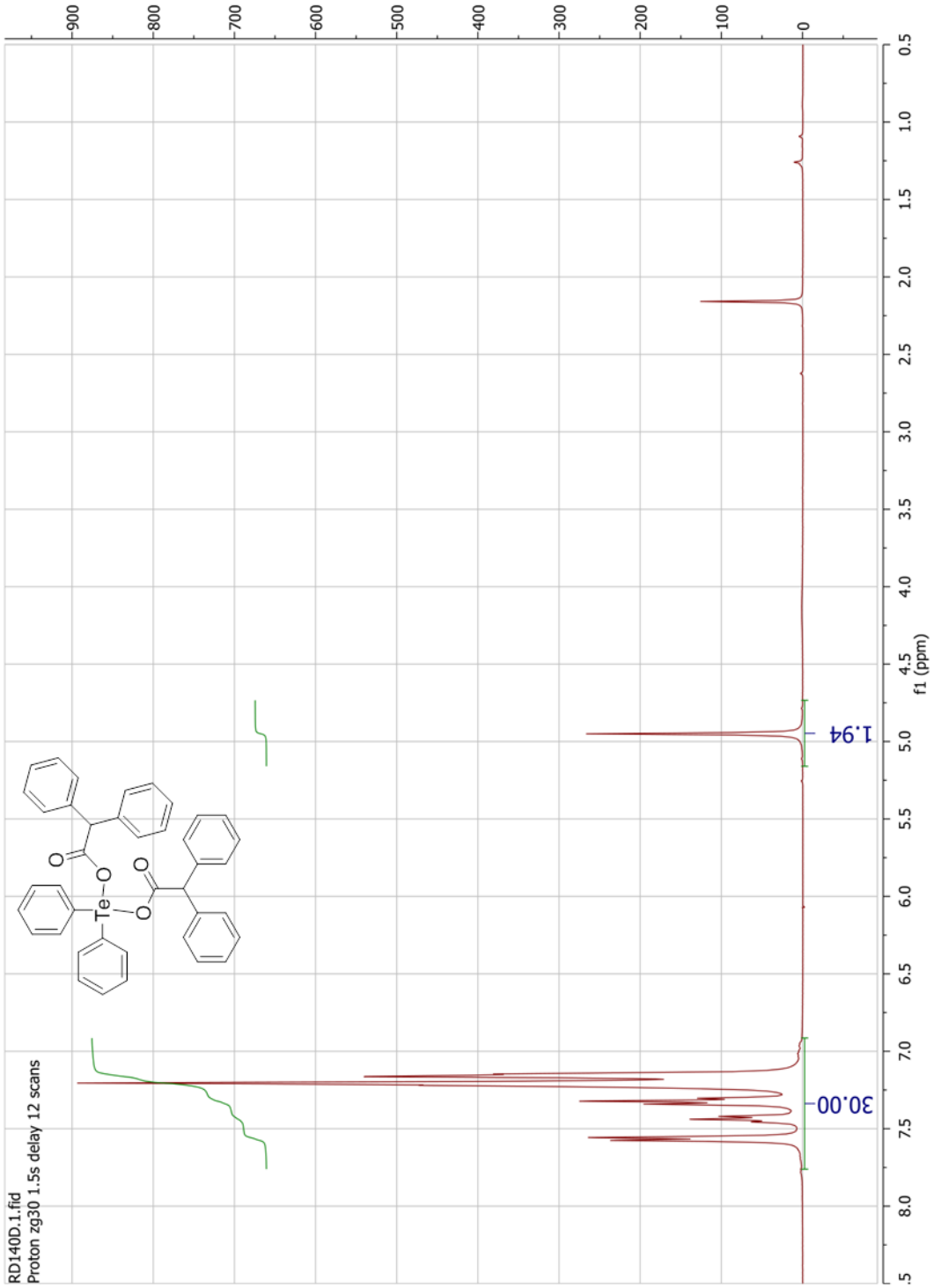

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