Low-line edge roughness extreme ultraviolet photoresists of organotin carboxylates

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Abstract. Pure thin films of organotin compounds have been lithographically evaluated using extreme ultraviolet lithography (EUVL, 13.5 nm). Twenty compounds of the type $R_2Sn(O_2CR')_2$ were spin-coated from solutions in toluene, exposed to EUV light, and developed in organic solvents. Exposures produced negative-tone contrast curves and dense-line patterns using interference lithography. Contrast-curve studies indicated that the photosensitivity is linearly related to the molecular weight of the carboxylate group bound to tin. Additionally, photosensitivity was found to be linearly related to free radical stability of the hydrocarbon group bound directly to tin (R = phenyl, butyl, and benzyl). Dense-line patterning capabilities varied, but two resists in particular show exceptionally good line edge roughness (LER). A resist composed of an amorphous film of $(C_6H_5CH_2)_2Sn(O_2CC(CH_3)_3)_2$ (**1**) achieved 1.4 nm LER at 22-nm half-pitch patterning and a resist composed of $(C_6H_5CH_2)_2Sn(O_2CC_6H_5)_2$ (**2**) achieved 1.1 nm LER at 35-nm half-pitch at high exposure doses (600 mJ/cm^2). Two photoresists that use olefin-based carboxylates, $(C_6H_5CH_2)_2Sn(O_2CCH{=}CH_2)_2$ (**3**) and $(C_6H_5CH_2)_2Sn(O_2CC(CH_3){=}CH_2)_2$ (**4**), demonstrated better photospeeds (5 mJ/cm^2 and 27 mJ/cm^2) but worse LER. © *2015 Society of Photo-Optical Instrumentation Engineers (SPIE)* [DOI: 10.1117/1.JMM.14.4.043506]

Keywords: extreme ultraviolet; organometallic; resist; photoresist; tin; line edge roughness; line width roughness.

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1 Introduction

Traditional chemically amplified photoresists have been used in the microelectronics industry for over 20 years.[1,2] These lithographic systems have enormous capability and have achieved the photolithographic performance that allowed the industry to follow Moore's law.[3] However, the cost and complexity of achieving smaller feature sizes are increasing with each new technology node. Extreme ultraviolet lithography (EUVL, 13.5 nm) continues to rely on conventional chemically amplified photoresists, but these resists may be unable to meet the needs of future technology nodes.[4,5] EUV photons (92 eV) interact with matter differently than do 193-nm photons (6.4 eV), therefore, the fundamental design of photoresists may need to change to obtain the best lithographic performance for EUVL. As film thickness decreases to compensate for smaller patterning without line collapse,[6] organic films may be unable to absorb the photons efficiently[7] which may lead to poorer sensitivity and poorer line edge roughness (LER).[8] Etch resistance may also be inadequate in these thinner, organic films.[9,10] We have previously reported on a new resist system, molecular organometallic resists (MORE for EUV), that seeks to overcome these potential obstacles. By using elements that have high-EUV optical density, we intend to create molecular films that absorb greater numbers of EUV photons than do purely organic resists and to create resists with better resolution, sensitivity, and LER.

Here, we present recent lithographic results of several MORE mononuclear tin compounds that have been spin coated as thin films on wafers and exposed to EUV light. We have synthesized a series of tin compounds of the general type $R_2Sn(O_2CR')_2$, to study the effects of increasing ligand bulk and increasing Sn–R bond energy on photosensitivity and lithographic performance. 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), LER (nm), and resolution (nm). Although the sensitivity of many of these compounds is poor (E_{size} = 50 to 600 mJ/cm^2), they are capable of good resolution and excellent LER. In particular, dibenzyltin dipivalate [**1**, Fig. 1(a)] resolves 16-nm half-pitch dense lines with 2.1-nm LER and resolves 22-nm half-pitch dense lines with 1.4-nm LER [Fig. 1(b)]. We also see a linear trend when we compare molecular weights with E_{max} within a particular compound family [Fig. 2(b)].

2 Results and Discussion

A series of compounds of the type $R_2Sn(O_2CR')_2$ have been prepared using procedures modified from experimental methods found in literature.[11,12] Toluene solutions of these compounds were spin-coated onto silicon wafers as thin films. The resists were then exposed to EUV light at the Paul Scherrer Institut (PSI) for evaluation of both contrast curves and dense line and space patterning. The exposed wafers were developed in hexanes for 5 to 25 s revealing negative-tone imaging. Although toluene and hexanes are

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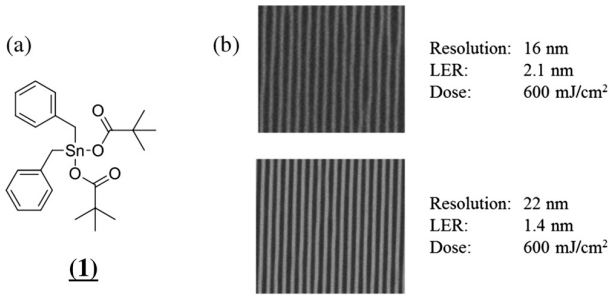

Fig. 1 (a) Structure of compound **1**, $(C_6H_5CH_2)_2Sn(O_2C(C(CH_3)_3))_2$ and (b) dense-line patterning capabilities of compound **1** exhibiting low line edge roughness (LER).

not traditional solvents used by the microelectronics industry, spin-coating from toluene created the highest quality films and developing with hexanes led to the best dissolution contrast when compared to traditional industrial solvents.

2.1 *Dependence of Molecular Weight on Photosensitivity (E_{max})*

Contrast curve exposures of resists at PSI give a good measure of their relative photosensitivities. Previously, Cardineau et al.,[13] reported that the sensitivities of tin-oxo clusters improve as the molecular weight of the counter ions decreases. We have lithographically evaluated a series of mononuclear $R_2Sn(carboxylate)_2$ compounds and found little correlation when plotting E_{max} versus molecular weight of the compounds [Fig. 2(a)]. However, when plotting E_{max} versus carboxylate variations with R held constant [Fig. 2(b)], we observe a molecular weight dependence with good correlation. 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.

2.2 *E_{size} Dependence on Molecular Weight*

We patterned dense lines with interference lithography at PSI and found that the same linear dependence held between molecular weight and E_{size} with dibenzyltin dicarboxylates that are nonacrylate based (Fig. 3). 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

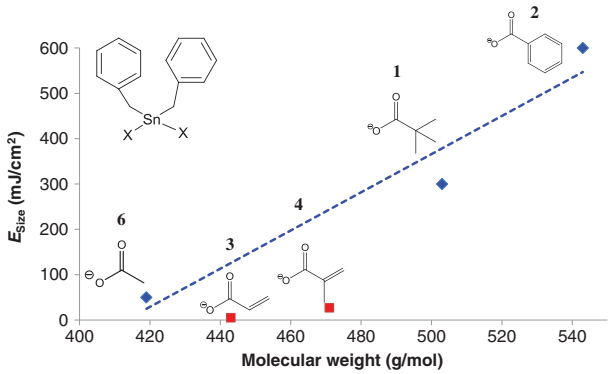

Fig. 3 50-nm dense-line patterning shows the same linear dependence with a significant deviation when analyzing acrylate-based resists.

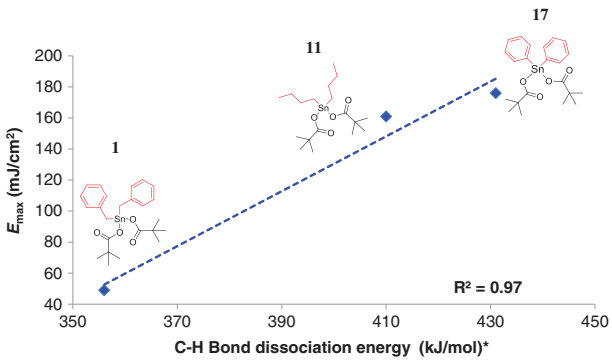

Fig. 4 Variation of C—H bond strength shows an inverse relationship with sensitivity. This may indicate that this bond strength plays an important role during photoexposure.

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.,[14] in which crosslinking occurs through free-radical polymerization.

2.3 *Tin–Carbon Bond Strength and E_{max} Dependence*

We wanted to explore the effect of the tin–carbon bond strength on the sensitivity of three resists. However, there are no experimental measurements available of direct

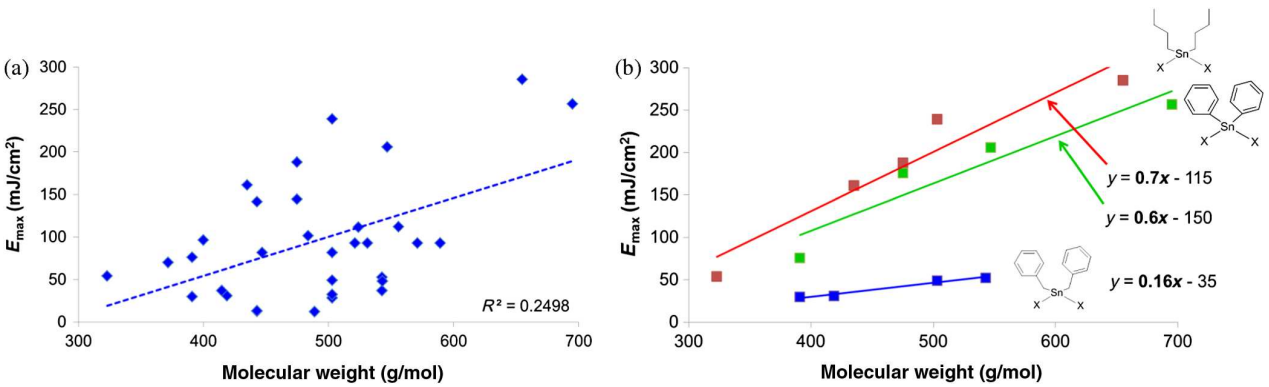

Fig. 2 (a) Comparing a wide variety of organotin carboxylates shows little correlation of data. However (b) strong correlations exist when comparing a particular family of compounds.

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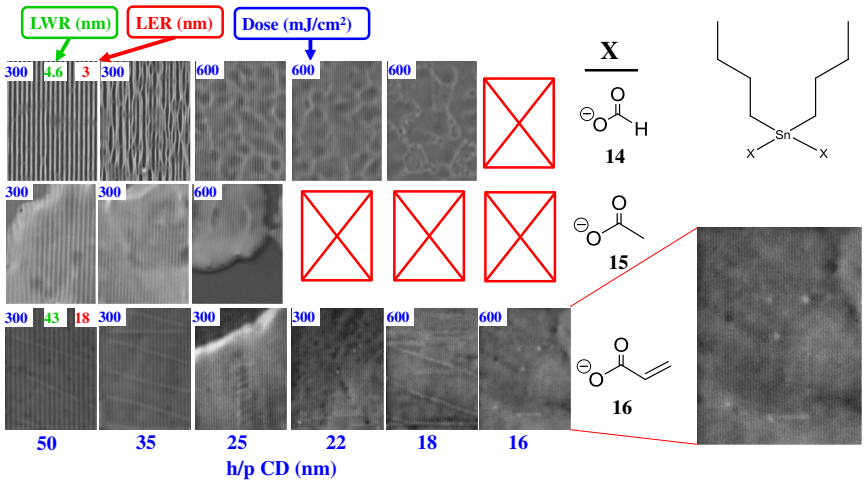

Fig. 5 Dense-line patterning capabilities of dibutyltin dicarboxylates. All of the films exhibited poor film quality after development.

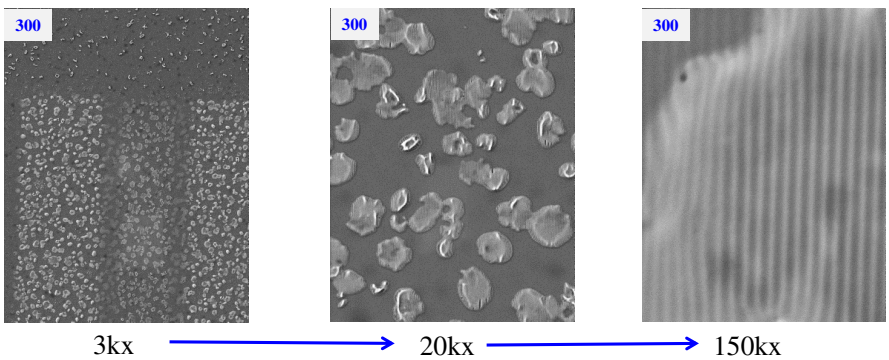

Fig. 6 Strange patterning phenomenon of dibutyltin diacetate (**15**). Each island shows patterning with no patterning in the spaces.

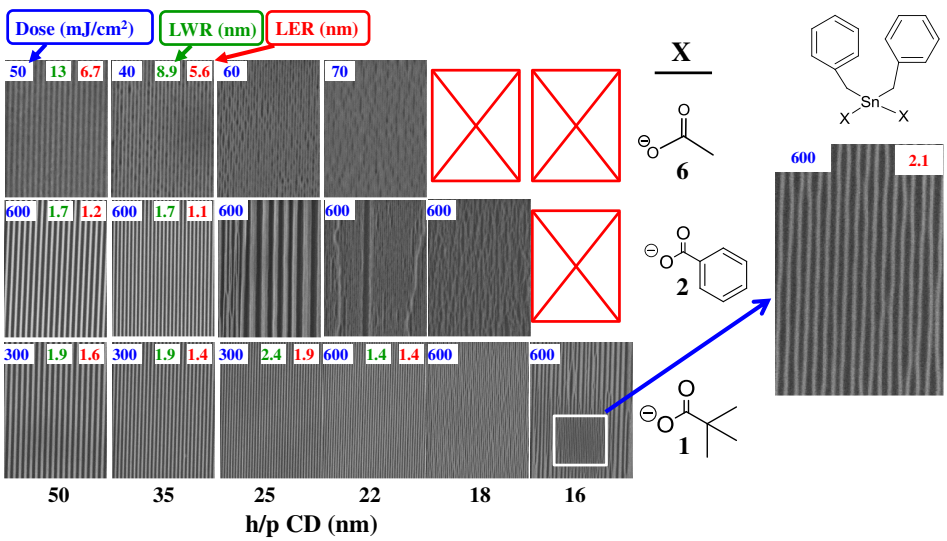

Fig. 7 Dense-line patterning capabilities of dibenzyltin dicarboxylates. These resists achieved the highest resolution and lowest LER of any metal based resist evaluated by our group.

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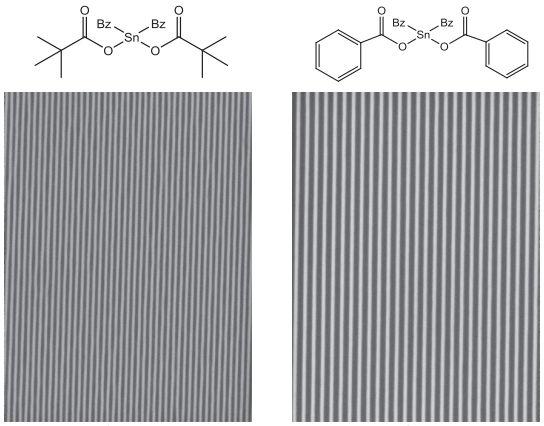

Compound:	**1**	**2**
CD:	22 nm	35 nm
LER:	1.4 nm	1.1 nm
LWR:	1.4 nm	1.7 nm

Fig. 8 Compounds **1** and **2** display high resolution patterning with extremely low LER.

bond dissociation energies between Sn–R in these cases, but the C—H bond dissociation energies have been measured[15–17] and we used these values as a measure of relative bond strength between Sn–R. Figure 4 shows the E_{max} of compounds **1**, **11**, and **17**: $R_2Sn(O_2C(C(CH_3)_3)_2$ where R = phenyl, butyl, benzyl plotted as a function of C—H bond-strength. 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.

2.4 *Imaging of Tin Dicarboxylates*

Imaging was performed at the Swiss Light Source (SLS) at PSI using interference lithography.[18] Figure 5 shows dense line/space patterns of three dibutyltin compounds. Although these resists exhibit pattern modulation to 16 nm, the film quality is poor. Figure 6 shows $(Bu)_2Sn(O_2CCH_3)_2$ (**15**) at increasing levels of magnification. At low magnification, many light-colored spots are present in the exposed areas. At higher magnification, dense-line patterns are visible. All of the dibutyltin complexes required high exposures and had poor LER.

Figure 7 shows dense line/space patterning capabilities of various dibenzyl tin compounds. The sensitivities show a large range of values (50 to 600 mJ/cm^2) corresponding to a wide range of resolution capabilities. Dibenzyltin dipivalate (**1**) has achieved 16-nm dense 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**) (Fig. 8).

2.5 *Fast Resists with Ligands Containing Olefins*

Although the exposure doses of most tin carboxylate photoresists were very high, we discovered two molecules (dibenzyltin diacrylate, **3** and dibenzyltin dimethacrylate, **4**) that required much lower exposure doses (5, 27 mJ/cm^2) to

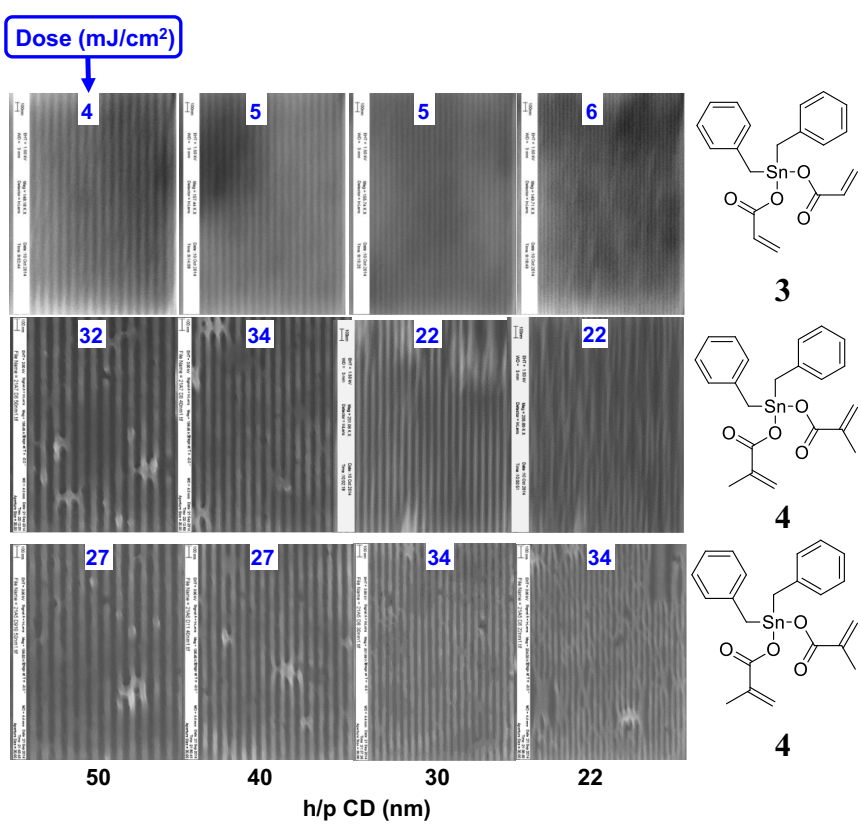

Fig. 9 Dibenzyltin acrylates displayed much better photospeeds at a cost of resolution and LER.

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print dense lines (Fig. 9). We propose that these molecules undergo a more efficient exposure mechanism, possibly utilizing a free radical polymerization after an initiation event. These free-radical polymerization reactions should crosslink the film, thereby decreasing the dissolution rate in the exposed areas.

3 Conclusions

We have evaluated the EUV lithographic capabilities of 20 organotin dicarboxylates. We systematically evaluated the imaging capabilities of these compounds as a function of the identity of the alkyl and carboxylic acid groups. We discovered a general trend within three classes of compounds (R = phenyl, butyl, benzyl) that showed improving sensitivities with decreasing molecular weight. Variations of the organic substituent bound directly to tin (phenyl, butyl, benzyl) showed a correlation between resist sensitivity and the stability of the corresponding organic free radical. We concluded that the alkyl-tin bond strength is very important in determining the ultimate sensitivity and is the most likely bond cleaved during exposure. Increased molecular weight due to carboxylate variations may affect the resist sensitivity by either reducing the film's mass density and EUV optical density or by acting as physical spacers that reduce intermolecular interactions after exposure.

We have printed dense lines of some of these compounds and have resolved features to 16 nm with significant pattern collapse at high-exposure doses (600 mJ/cm^2). Perhaps the most remarkable quality observed is the extremely low LER of two resists (1.4 and 1.1 nm, Fig. 8). When we introduced ligands that contained olefins to dibenzyl tin systems (**3**, **4**), we found that a much lower exposure dose (5, 27 mJ/cm^2, respectively) was needed to print dense lines (Fig. 9). These molecules may be capable of polymerizing through a free radical mechanism, leading to more efficient crosslinking in the film.

4 Experimental Methods

4.1 *Instruments*

^{1}H nuclear magnetic resonance (NMR) spectra were measured with a Bruker 400 MHz spectrometer using tetramethyl silane as an internal reference. All chemical shifts are reported as parts per million. Tin–H coupling constants are written in the as J_{H-Sn}. All other reported coupling constants are H—H.

4.2 *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 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 solvent. Exposures were performed at PSI on the XIL-II beamline using open-frame exposures to prepare contrast curves or using interference lithography for dense-line patterning.

4.3 *Scanning Electron Microscope Metrology*

Scanning electron microscope micrographs were collected at PSI on a Zeiss Supra VP55. Accelerating voltage was set between 1 and 2 KeV and the working distance was 4 mm. All images were at either 150 kX or 200 kX magnification.

4.4 *Line Edge Roughness Analysis*

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

4.5 *General Synthetic Procedure*

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 (**21**) was prepared by a procedure found in the literature.[19]

4.5.1 *Synthetic procedure for compounds 1 through 13*

The general procedure was adapted from procedures found in the chemistry literature.[11,12,19]

Method A. R_2SnX_2 (R = Phenyl, Benzyl; X = Cl, Br) (2 mmol) was combined with the sodium salt of the acid (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 h, 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 min 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 to 3 h. 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 g were obtained (32% yield). ^{1}H NMR (Chloroform-*d*) δ 7.28–6.92 (m, 10H), 2.95 (s, J_{H-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 g 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-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 g were obtained

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(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, $J_{H-Sn} = 88.9$, 92.9, 139.1 Hz, 4H).

Dibenzylstannanediyl bis(2-methylacrylate) (**4**). methacrylic acid (0.344 g, 4 mmol) was used as the acid. 0.51 g 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, $J_{H-Sn} = 89.1$, 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 g were obtained (41% yield). ^{1}H NMR (Chloroform-*d*) δ 8.2 (s, 2H), 7.61–6.48 (m, 11H), 3.21 (s, $J_{H-Sn} = 73.9$, 154.8 Hz, 4H).

Dibenzylstannanediyl diacetate (**6**). acetic acid (0.24 g, 4 mmol) was used as the acid. 0.5 g were obtained (60% yield). ^{1}H NMR (Chloroform-*d*) δ 7.51–6.64 (m, 10H), 2.98 (s, $J_{H-Sn} = 89.2$, 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 g 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, $J_{H-Sn} = 86.8$, 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 g 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, $J_{H-Sn} = 84.4$, 137.6 Hz, 4H).

Diphenylstannanediyl diacetate (**9**). acetic acid (0.24 g, 4 mmol) was used as the acid. 0.26 g were obtained (33% yield). ^{1}H NMR (Chloroform-*d*) δ 8.12–6.55 (m, 11H), 2.62–0.53 (m, 6H).

Diphenylstannanediyl diacrylate (**10**). acrylic acid (0.288 g, 4 mmol) was used as the acid. 0.45 g 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 g 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 g 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. 0.63 g were obtained (45% yield). ^{1}H NMR (Chloroform-*d*) δ 7.66–7.06 (m, 33H), 5.15 (s, 2H).

4.5.2 *Synthetic procedure for compounds 14 through 20*

Method A. 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 h 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 min 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 to 3 h. 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 (**14**). 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 g 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).

Dibutylstannanediyl diacetate (**15**). 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 g 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 (**16**). acrylic acid (0.288 g, 4 mmol) was used as the acid. The compound was crystallized in hexanes. 0.25 g 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) (**17**). trimethylacetic acid (0.409 g, 4 mmol) was used as the acid. The compound was crystallized in hexanes. 0.64 g 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 (**18**). benzoic acid (0.488 g, 4 mmol) was used as the acid. The compound was crystallized in 1:9 dichloromethane: hexanes. 0.12 g 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) (**19**). 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 g 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) (**20**). 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 g 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 (**21**). this procedure was adapted from the literature.[19] Tin powder (10 g, 84 mmol) and anhydrous toluene (100 mL) were added to a 250-mL three necked round-bottom flask equipped with a stir bar and reflux condenser. The mixture was heated to

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105°C 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 min. The reflux was maintained for 3 h. 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 g were obtained (52% yield). ^{1}H NMR (Chloroform-*d*) δ 7.32–6.94 (m, 10H), 3.21 (s, 4H).

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