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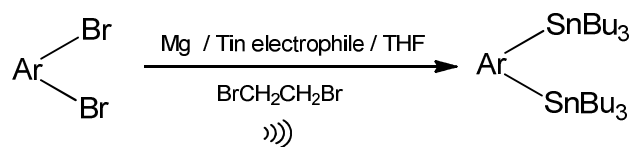
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PICTOGRAM



Tin electrophile = (*n*-Bu₃Sn)₂O; *n*-Bu₃SnCl

Ar = Disubstituted aromatic and heteroaromatic compounds = 1,2-, 1,3-, and 1,4- benzenes; 4,4'- biphenyl; 1,4- naphthalene; 2,5 and 3,5- pyridines; 2,5- thiophene; also 1,3,5-trisubstituted benzene

Synopsis

Darío C. Gerbino,[‡] Pablo M. Fidelibus, Sandra D. Mandolesi, Romina A. Ocampo, Jimena Scoccia, and Julio C. Podestá^{‡,*}

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The best reaction conditions and the syntheses of some new bis(tri-*n*-butylstannylated) aromatic and heteroaromatic compounds by means of a Barbier-like sonochemical reaction are reported. Full ¹H-, ¹³C-, and ¹¹⁹Sn-NMR data of the new organotin compounds are informed.

Sonochemical Synthesis of Bis(tri-*n*-butylstannyl)aromatic compounds *via* Barbier-like Reactions

Darío C. Gerbino,[‡] Pablo M. Fidelibus, Sandra D. Mandolesi, Romina A. Ocampo, Jimena Scoccia, and Julio C. Podestá^{‡,*}

Instituto de Química del Sur (INQUISUR), Departamento de Química, Universidad Nacional del Sur-CONICET, Av. Alem 1253, 8000, Bahía Blanca, Argentina.

* Corresponding author E-mail: jpodesta@uns.edu.ar

[‡] Member of CONICET, Argentina.

1. Introduction

The synthesis of aromatic bis(stannylated) compounds is a very important target due to their practical interest. These organotins are valuable starting materials that enable the preparation of a wide variety of organic and organometallic derivatives *via* known synthetic procedures. For example, the Stille-Migita reaction [1], i.e., the reaction between alkyl halides and aryl- or vinyltins catalyzed by Pd complexes that leads to the formation of new C-C bonds. This reaction mainly involves the use of vinyl- and aryltins bearing mostly only one organotin moiety. There are also some examples of Stille reactions using bis- and tris-trimethylstannylsubstituted benzenes and pyridines [2]. Aromatic bis(stannylated) compounds are also valuable starting material for the preparation of aryldiboronic acids *via* transmetalation with borane in THF [3]. The resulting aryldiboronic acids are widely used in polymer synthesis [4] and also as starting material for Suzuki cross-coupling reactions [5].

Some methods available for the synthesis of bis(stannylated) aromatic compounds are the following. In first place the reaction between aryl lithium or magnesium derivatives and trialkyltin halides. However, the scope of these reactions is restricted to aromatic nucleus not containing functional groups that could react with the organometallic reagents. The synthesis in 50% yield of 1,2-bis(trimethylstannyl)benzene *via* a Diels-Alder reaction between bis(trimethylstannyl)ethyne and α -pyrone, was first reported by Seyferth *et al.* in 1966 [6a] who also described in 1977 the preparation of 1,8-bis(trimethylstannyl)naphthalene by reaction of 1,8-dilithionaphthalene with trimethyltin chloride in tetraglyme [6b]. A much more straightforward approach to the synthesis of 1,2-bis(trimethylstannyl)benzene (42% yield) *via* a nucleophilic aromatic substitution reaction of Me₃SnNa with 1,2-dibromobenzene in tetraglyme was described by Kuivila *et al.* in 1977 [7]. This method was also used by Mitchell *et al.* to obtain various 1,2-bis(trimethylstannyl)disubstituted aryl- and heteroaryl compounds [8]. Jurkschat *et al.* [9] improved this method obtaining 1,2-bis(trimethylstannyl)benzene in 67% yield. In 1992 it was reported that the radical nucleophilic substitution (S_{RN}1) of *p*-dichlorobenzene with Me₃SnNa in liquid ammonia gives the disubstitution product, i.e., 1,2-bis(trimethylstannyl)benzene, in 88% yield [10]. Using the same photostimulated S_{RN}1 reaction,

in 2002 Rossi *et al.* reported the synthesis of various bis(trimethylstannyl)pyridines in high yields (80-88%), and also of 1,3,5-tris(trimethylstannyl)benzene (71%) starting from the corresponding aromatic dichloro and trichloro derivatives [11]. It should be noted that most of the photostimulated $S_{RN}1$ reactions have been performed using trimethyltin anions and a few with triphenyltin anions, and that no examples of these reactions carried out using tri-*n*-butyltin anions are found in the chemical literature. More recently, has been reported the synthesis of bis(trimethyl-) and bis(tri-*n*-butylstannylated) aromatic compounds in yields of 27-73% *via* distannylation of arynes with hexamethyl- and hexa-*n*-butyldistannanes catalyzed by palladium complexes [12].

On the other hand, in two papers published in 1996 and 1997 Lee and Dai reported the preparation of aryltributylstannanes *via* a sonochemical Barbier reaction of aryl- and heteroaryl bromides with bis(tri-*n*-butyltin) oxide (**2**) in THF [13]. Taking into account its potential for the preparation of aromatic compounds containing more than one tri-*n*-butylstannyl substituent, we considered it of interest to carry out a study in order to determine the scope of this sonochemical method.

2. Results and discussion

In order to establish the best reaction conditions, we first studied the reaction of bromobenzene (**1**) with bis(tri-*n*-butyltin) oxide (**2**). In this case, the best yields were obtained as follows. A solution of **1** (1 mmol), magnesium powder (1.1 mmol), electrophile **2** (1 mmol), 1,2-dibromoethane (0.5 mmol) in anhydrous THF (5 mL), was sonicated under an Ar atmosphere during 45 min in a commercial ultrasonic cleaning bath (Ultrasonic 104X) at medium power (43-47 kHz) keeping the temperature at around 35 °C. Under these reaction conditions, phenyltri-*n*-butyltin (**4**) was obtained in 83% yield (Scheme 1).

Scheme 1

In preliminary studies, the analysis by ^{119}Sn -NMR of the crude mixture obtained in this reaction showed the formation of **4** together with tri-*n*-butyltin bromide (**5**). However, after passing a solution of the crude product in ethyl acetate through a chromatographic column with silica gel doped with 10% of KF compound **4** was obtained pure.

On the other hand, we found that, contrary to the reports of Lee *et al.* [13], bromobenzene (**1**) reacts under the same experimental conditions with tri-*n*-butyltin chloride (**3**) leading to the substitution product **4** in 78% yield (Scheme 1). In this case, the ^{119}Sn -NMR spectrum of the crude mixture showed that the organotin species present were **4** and hexa-*n*-butyldistannane (**6**). The formation of distannane **6** in the reaction with electrophile **3** could arise from the reaction of

tri-*n*-butyltin chloride **3** with the stannylmagnesium compound (*n*-Bu₃SnMgCl) formed *via* reaction of **3** with Mg [1c].

We also found that under the same reaction conditions bis(trimethyltin) oxide, bis(trimethyltin) oxide, trimethyltin chloride, and trineophyltin chloride do not react with phenyl bromide (**1**) to give the corresponding substitution products.

We then studied the reaction of tin electrophiles **2** and **3** with 2-bromopyridine, various bromoaromatic polycyclic hydrocarbons and also with functionally substituted phenyl bromides. In all cases, the substitution reactions took place with complete regioselectivity. The results obtained are summarized in Figure 1.

Figure 1

As shown in this Figure, the reaction of 2-bromopyridine with bis(trimethyltin) oxide (**2**) led to the corresponding substitution product, 2-(tri-*n*-butylstannyl)pyridine (**7**) in 83% yield, i.e., in higher yield than that obtained by Lee *et al.* (65%) [13]. Figure 1 also shows that 2-bromopyridine reacts with tri-*n*-butyltin chloride (**3**) leading to tin compound **7** in high yield.

In order to investigate the effect of functional substituents on these reactions, we studied the reaction of substituted bromobenzenes with electrophiles **2** and **3** (Figure 1). We found that the sonicated reactions of *m*-bromoanisole and *m*-bromotoluene with bis(trimethyltin)oxide (**2**) lead in high yields to the corresponding *m*-(tri-*n*-butylstannyl)anisole (**9**) (86%) and *m*-(tri-*n*-butylstannyl)toluene (**10**) (82%) respectively. On the other hand, the reaction with *o*-bromoanisole leads to *o*-(tri-*n*-butylstannyl)anisole (**8**) in just 37% yield. Figure 1 also shows that the reactions using tri-*n*-butyltin chloride (**3**) follow the same pattern.

To establish the effect of the structure of the aryl group on these reactions, we investigated the reactions of 9-bromophenanthrene and 9-bromoanthracene with both electrophiles. As shown in Figure 1, the sonicated Barbier reactions of electrophiles **2** and **3** lead to the 9-(tri-*n*-butyl) substituted derivatives **11** and **12** respectively with yields similar to those obtained in the previous reactions (around 70-80%). The substitutions carried out using tri-*n*-tributyltin chloride (**3**) as electrophile took place in lower yields than with electrophile **2**.

In order to determine whether these reactions could also be of preparative interest for the synthesis of aromatic bis(trimethyltin) derivatives, we carried out similar studies using as substrates dibromo substituted aromatic molecules. The results obtained in the sonicated reactions of dibromobenzenes with electrophiles **2** and **3** using ratios dibromo derivative/electrophile = 1:3 under Barbier conditions, are summarized in Scheme 2. These reactions proceeded efficiently to give the corresponding bis(*n*-tributylstannylated) compounds in high to excellent yields (Scheme 2). In the reactions with both electrophiles, **2** and **3**, it was observed the formation of hexa-*n*-butyldistannane (**6**). The formation of ditin compound **6** could arise from the reduction of bis(trimethyltin)oxide (**2**) with Mg [14]. Using electrophile **2**, in the

^{119}Sn -NMR spectrum of the crude products before the treatment with silica gel doped with KF was also observed the formation of tri-*n*-butyltin bromide (**5**).

Scheme 2

In all these reactions was observed the formation of the reduction product, i.e., phenyltri-*n*-butyltin (**4**). In some of the reactions carried out with bis(tri-*n*-butyltin)oxide (**2**) (Scheme 2), we also determined the formation of monosubstitution's products, i.e., phenyltri-*n*-butyltin bromides **18** and **20**. The formation of aryl bromides **18** and **20** clearly indicates that these substitutions take place stepwise.

The formation of the reduction product **4** could be explained taking into account that the fragmentation of the radical anion **I**, product of the second electron transfer to **15**, would lead to the leaving group, i.e., the bromide anion and the aromatic radical σ **II** (Scheme 3). The latter could then abstract a hydrogen atom from the solvent (THF) leading to **4**. It is to note that hydrogen abstraction from the solvent by aryl radicals is a possible termination pathway when $\text{S}_{\text{RN}}1$ reactions are carried out in organic solvents [15].

Scheme 3

It should be noted that using stoichiometric amounts, i.e., ratio dibromobenzene/tin electrophile/ =1:2, the composition of the crude products changed dramatically. Thus, using stoichiometric ratios in the case of 1,2-dibromobenzene (**14**) the mixtures obtained consisted not only of compounds **4** and **16** but they also included tri-*n*-butyl-2-bromophenyltin, i.e., the product of monosubstitution. The latter is not formed using ratios **13/2** or **3** = 1:3.

The previous results indicate that these sonicated Barbier-type reactions could be extended to aryl dibromides leading to the corresponding bis(tri-*n*-butylstannylated)benzenes in very good yields. However, it should be noted the fact that in the case of the 1,2-dibromobenzene (**13**) the product of reduction **4** is formed in much higher proportion than the desired 1,2-bis(tri-*n*-butylstannyl)benzene (**16**). This might probably be connected with the existence of steric hindrance.

We then studied the reactions of methyl 2,5-dibromobenzoate (**21**) with tin electrophiles **2** and **3** (Scheme 4). The ^{119}Sn NMR spectrum of the crude product of the reaction between **21** and bis(tri-*n*-butyltin)oxide (**2**) showed two big peaks at -35.9 ppm and -36.2 ppm in a ratio 1:2 respectively, and also two very small peaks at -40.9 ppm and -41.0 ppm. In the case of the reaction of **21** with tri-*n*-tributyltin chloride (**3**), the ^{119}Sn NMR spectrum of the crude product obtained indicated the formation of three compounds with resonances at -35.9, -36.2, and -39.0 ppm with approximately the same intensity, plus very small peaks with resonances at higher field. On the other hand, mass spectra of the crude mixtures obtained in the reactions with both

electrophiles showed the formation of all the possible products of these reactions, i.e., compounds **22-26**.

Scheme 4

The only compound we were able to obtain pure *via* column chromatography separation was methyl 2-tri-*n*-butylstannyl-5-bromobenzoate (**24**). The assignment of the structure of compound **26** was done making use of its NMR characteristics specially $^nJ(^1\text{H}, ^{119}\text{Sn})$ and $^nJ(^{13}\text{C}, ^{119}\text{Sn})$ coupling constants. Although the other compounds detected by mass spectrometry were not obtained pure, taking into account that the ^{119}Sn NMR shows a peak at -36.1 ppm, i.e., very close to the one corresponding to the bromomonostannylated compound **24** (-35.9 ppm) and with the same intensity, it might be possible that this compound could have the structure **23** (Scheme 3). It should be stressed the fact that the ^1H - and ^{13}C -NMR spectra of these mixtures of organotin derivatives indicated that the COOMe group remained unaffected.

The results obtained in the sonicated reactions of some aromatic dibromosubstituted polycyclic hydrocarbons with electrophiles **2** and **3** mediated by Mg are summarized in Scheme 5. As it can be seen in Scheme 5, whereas the reaction of 4,4'-dibromobiphenyl (**27**) with bis(tri-*n*-butyltin) oxide (**2**) leads to a mixture of 4,4'-bis(tri-*n*-butylstannyl)biphenyl (**28**) and 4-(tri-*n*-butylstannyl)biphenyl (**29**) in a ratio $\mathbf{28/29} = 8.3$, the reaction of **27** with electrophile **3** leads exclusively to the bis(stannylated)biphenyl **28**. It should be noted that in the reactions with both electrophiles hexa-*n*-butyldistannane (**6**) is also formed, and that the amount of **6** which is formed using tri-*n*-butyltin chloride (**3**) is higher. However, although the yields of distannylated compound **28** obtained using electrophiles **2** and **3** are excellent, the column chromatographic separation of distannane **6** is very difficult and diminishes dramatically the yield of pure distannylated biphenyl **28**. For the same reason compound **29** could not be obtained pure.

The reaction between 1,4-dibromonaphthalene (**30**) with electrophiles **2** and **3** leads in both cases exclusively to 1,4-bis(tri-*n*-butylstannyl)naphthalene (**31**) and the compound was obtained pure in high yield by column chromatography (Scheme 5). ^{13}C NMR spectroscopy enables a quick identification of compound **31**. Thus, the ^{13}C NMR spectrum of **31** shows that the peak at 134.96 ppm attributed to carbons C-2 and C-3 shows two satellite signals corresponding to $^2J(^{119}\text{Sn}, ^{13}\text{C})$ and a $^3J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constants with values of 26.8 and 45.0 Hz, respectively. These clearly demonstrate that both carbons interact with the two tri-*n*-butylstannyl groups attached to C-1 and C-4.

Scheme 5

In the case of 9,10-dibromoanthracene (**32**), the ^{119}Sn NMR spectrum of the crude product obtained in the sonicated reaction with tri-*n*-butyltin chloride (**3**) showed it to consist of a

mixture of various organotin products, among them 9,10-distannylated compound **33** (52%) and reduction compound **12** (6%). Using bis(tri-*n*-butyltin)oxide (**2**) as electrophile, the reaction with **34** leads also to a mixture of various organotin compounds in which, unexpectedly, the reduction product **12** (36%) prevailed over the distannylated compound **33** (26%). Unfortunately, we were not able to obtain compound **33** pure from these mixtures.

It should be mentioned that we also studied the reactions of 2,4-dibromo-1-methoxynaphthalene with electrophiles **2** and **3**. The ^{119}Sn -NMR spectra of the crude product showed that these reactions lead to complex mixtures of organotin derivatives that we could neither separate nor identify.

Due to the fact that bis(organotin)pyridine derivatives are very important precursors for the synthesis of extended metallocsupramolecular assemblies and polymers with grid-like architectures [16], we also investigated Barbier sonicated reactions of some dibromo substituted aromatic heterocycles. However, it should be noted that the preparation of bis(triorganostannyl)pyridine compounds using the reaction between dibromopyridines and *n*-butyllithium followed by trialkylstannylation at low temperature has always been a difficult task, because of the time consuming purification procedures and yields as low as 17% [17]. Taking into account the previous discussion, we investigated the sonicated reactions of 3,5- (**34**) and 2,5-dibromopyridine (**35**) with electrophiles **2** and **3**. The obtained results are summarized in Scheme 6.

Scheme 6

As shown in Scheme 6, the sonicated reaction of 3,5-dibromopyridine **34** with bis(tri-*n*-butyltin)oxide (**2**) leads to a mixture of the known 3,5-bis(tri-*n*-butylstannyl)pyridine (**36**) [17] in 89% and 3-(tri-*n*-butylstannyl)pyridine (**37**) (11%), and the reaction using tri-*n*-butyltin chloride (**3**) leads exclusively to the distannylpyridine **36**. On the other hand, whereas the reaction of 2,5-dibromopyridine **35** and electrophile **2** leads to a mixture of distannylated pyridine **38** (84%) and reduction's product **37** (16%), the reaction of **35** with **3** leads to a mixture of **37** and another organotin compound. The column chromatography of the crude product of the latter reaction afforded **37** (58%) pure, and mixtures of **37** with the secondary organotin compound from which we were neither able to separate nor to identify the latter.

Another dibromosubstituted aromatic heterocyclic compound studied was 2,5-dibromothiophene (**39**). As shown in Scheme 7, the only product of substitution obtained using compound **40** and bis(tri-*n*-butyl)tin oxide (**2**) was the known 2,5-bis(tri-*n*-butylstannyl)thiophene (**41**) [19] and also some distannane **6**. Compound **40** was isolated pure in 89% yield.

Scheme 7

On the other hand, the reaction of **39** with the electrophile **3** led to a mixture of **40** and 2-(tri-*n*-butylstannyl)thiophene (**41**) together with a high amount of distannane **6**. It should be noted that although the total yield was high we were not able to obtain pure the monosubstituted compound **41** from the crude product mixture.

The reactions of some tribromo substituted benzenes with electrophiles **2** and **3** were also investigated. Thus, the reaction of 1,3,5-tribromobenzene (**42**) with electrophiles **2** and **3** leads to mixtures in which, as shown in Scheme 8, 1,3,5-tris(tri-*n*-butylstannyl)benzene (**43**) predominates largely.

Scheme 8

However, the distannane **6** formed in these reactions precluded us to obtain pure compounds **43** and **17** from the crude product mixtures. The structures of these compounds were deduced from the ^1H -, ^{13}C - and ^{119}Sn -NMR spectra and by mass spectrometry of the mixtures.

It should be mentioned that we also carried out studies on the sonicated Barbier reactions of 1,2,4-tetrabromobenzene, 2,4,6-tribromoanisole, and 1,6,8-tribromo-1-methoxynaphthalene with electrophiles **2** and **3**. However, the ^{119}Sn -NMR spectra of the crude products obtained in these reactions showed them to consist of various organotin compounds. We were unable to obtain pure any of the compounds components of these mixtures.

In order to test the chemical reactivity of the aryl- and heteroaryl-bis(tri-*n*-butylstannylated) compounds, we carried out Stille reactions with some of them. We found that the reaction between 1,4-bis(tri-*n*-butylstannyl)naphthalene (**31**) and *p*-iodotoluene (Scheme 9) in THF in the presence of catalytic amounts of palladium bis(triphenylphosphine) dichloride afforded the known 1,4-ditolyl-naphthalene (**44**) [20] in 71% yield.

Scheme 9

Similarly, the reaction of **36** with *p*-bromoanisole in the presence of the same catalyst leads to 3,5-di(*p*-anisyl)pyridine (**45**) [21] in 67% yield. These results indicate that the reactivity of the bis(tri-*n*-butylstannylated)aromatic compounds is similar to that found in other Stille reactions carried out with trimethylstannyl substituted aromatic systems [22].

In conclusion, the results obtained demonstrate that, despite initial reports indicating that tri-*n*-butyltin chloride (**3**) was not a suitable tin electrophile for the Barbier sonicated substitutions of aryl bromides, in fact in many cases it is the opposite, i.e., the use of **3** leads to bis(stannylated) products in excellent yields, even higher than those obtained with electrophile

2. As for the effect of the substituents, it was observed that in the case of aryl *o*-bromomethoxy and *o*-dibromosubstituted compounds the yields of aryl tri-*n*-butylsubstituted compounds are substantially lower. The reactions with dibromo substituted heterocycles lead to the corresponding bis(tri-*n*-butylstannylated)heterocycles with excellent yields. This is particularly important in the preparation of suitable substrates for cross-coupling reactions leading to the synthesis of extended metallosupramolecular assemblies and polymers. The method and the work up are very simple, and enable the synthesis of aromatic and heteroaromatic bis(tri-*n*-butylstannyl) substituted derivatives with, in general, high global yields.

Taking into account the previous results, we intend to carry out new studies on the best reaction conditions in order to improve the yields of the reactions of polybromo substituted aromatic compounds, and also to develop a method for a more simple and efficient separation of the hexa-*n*-butyldistannane (**6**).

3. Experimental

3.1. General methods

^1H , ^{13}C and ^{119}Sn NMR spectra were obtained in a Bruker ARX 300 instrument at 300 °K, in 5 mm diameter tubes, using 10% (w/v) solutions of the compounds and were recorded in CDCl_3 (300.1 MHz for ^1H , 75.5 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). Chemical shifts (δ) are given in ppm downfield relative to TMS (^1H and ^{13}C), Me_4Sn (^{119}Sn) and coupling constants (^nJ) are in Hz. Infrared spectra were recorded with a Nicolet Nexus FT spectrometer. Mass spectra were obtained with a GC/MS instrument (HP5-MS capillary column, 30 m/0.25 mm/0.25 μm) equipped with 5972 mass selective detector operating at 70 eV (EI). Melting points were determined in a Kofler hot stage and are uncorrected. High resolution mass spectra (HRMS) were recorded on a Finnigan Mat. 900 (HR-EI-MS). Solvents were dried and distilled in accordance with standard procedures. The reactions were performed under an argon atmosphere using a NDI ULTRASONIC 104X bath operating at 43-47 KHz at 35 °C ($\pm 1^\circ\text{C}$). They were monitored by thin-layer chromatography on silica gel plates (60F-254) and visualized under UV light and/or using 5% phosphomolybdic acid in ethanol. Column chromatography was performed over silica gel 60 (70-230 mesh) doped with 10% of potassium fluoride [23]. Except dibromo substrates **29** [24], **32** [25] and **34** [26] which were obtained by known procedures, the mono-, di-, and tri-substituted substrates used in these studies were commercially available and used as purchased.

3.2. Synthesis of Arylstannanes via Sonochemical Barbier Reactions

All the reactions were carried out under an argon atmosphere and following the same procedure. The reaction flask was located in the water bath of the ultrasonic cleaner, and the temperature of

the bath was controlled using the water circulation flow of a thermostat. One experiment is described in detail in order to illustrate the methods used.

3.2.1. Reactions with bis(*tri-n*-butyltin) oxide (**2**)

A mixture of magnesium turnings (0.027 g, 1.1 mmol), bromobenzene (0.15 g, 1 mmol), bis(*tri-n*-butyltin) oxide (0.60 g, 1 mmol) and 1,2-dibromoethane (0.094 g, 0.5 mmol) as initiator in dry THF (5 mL) was sonicated for one hour in a ultrasonic cleaning bath at around 35 °C, with monitoring of the reaction by TLC. Once the reaction finished, aqueous saturated NH₄Cl solution (40 mL) was added and extracted with ethyl acetate (3 x 20 mL). The combined extracts were washed with brine (60 mL) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography with silica gel doped with 10% of KF to retain the *tri-n*-butyltin bromide formed during the reaction. **4** eluted with 95:5 (hexane/diethyl ether) as an oil (0.304 g, 0.83 mmol, 83 %, b.p. 137-139 °C/ 0.6 mmHg, (lit [27] b.p. 125-128 °C/0.14 mmHg). ¹¹⁹Sn NMR (CDCl₃): δ -42.4 ppm.

3.2.2 Reactions with *tri-n*-butyltin chloride (**3**)

A mixture of magnesium turnings (0.036 g, 1.5 mmol), bromobenzene (0.15 g, 1 mmol), *tri-n*-butyltin chloride (0.49 g, 1.5 mmol) and 1,2-dibromoethane (0.094 g, 0.5 mmol) as initiator in dry THF (5 mL) was sonicated for one hour in a ultrasonic cleaning bath at around 35 °C, with monitoring of the reaction by TLC. Once the reaction finished, aqueous saturated NH₄Cl solution (40 mL) was added and extracted with ethyl acetate (3 x 20 mL). The combined extracts were washed with brine (60 mL) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the product was isolated by column chromatography with silica gel doped with 10% of KF to retain *tri-n*-butyltin halides formed during the reaction. **4** (0.286, 0.78 mmol, 78 %) eluted with 98:2 (hexane/diethyl ether).

3.3. Physical and spectroscopic characteristic of the aryl*tri-n*-butyltin obtained

The synthesis and physical characteristics of the following compounds have already been reported: 2-*tri-n*-butylstannylpyridine (**7**) (commercially available), 2-*tri-n*-butylstannylanisole (**8**) [28], 3-*Tri-n*-butylstannylanisole (**9**) (commercially available), 3-*Tri-n*-butylstannyltoluene (**10**) (commercially available), 9-*tri-n*-butylstannylphenanthrene (**11**) [29], 9-*tri-n*-butylstannylanthracene (**12**) [29], 1,2-bis(*tri-n*-butylstannyl)benzene (**16**) [30], 1,3-bis(*tri-n*-butylstannyl)benzene (**17**) [31], 1,4-bis(*tri-n*-butylstannyl)benzene (**20**) [32], 4-(*tri-n*-butylstannyl)biphenyl (**29**) (commercially available), 3,5-bis(*tri-n*-butylstannyl)pyridine (**36**) [17], 3-(*tri-n*-butylstannyl)pyridine (**37**) (commercially available), 2-*tri-n*-butylstannylthiophene (**41**) (commercially available), and 2,5-bis(*tri-n*-butylstannyl)thiophene (**42**) [19].

Methyl 5-bromo-2-(tri-n-butylstannyl)benzoate (24). Colorless oil. ^1H NMR (CDCl_3) δ 8.24 [d, 1H, $^4\text{J}(\text{H,H})$ 1.9]; 7.63 [dd, 1H, $^4\text{J}(\text{H,H})$ 1.9 & $^3\text{J}(\text{H,H})$ 7.8]; 7.51 (d, 1H, $^3\text{J}(\text{H,H})$ 7.8]; 3.93 (s, 3H); 1.65-0.96 (m, 18H); 0.88 [t, 9H, $^3\text{J}(\text{H,H})$ 6.9]. IR (film, cm^{-1}) 3028 (m), 2955 (s), 2910 (s), 2871 (s), 2850 (s), 1727 (s), 1600 (m), 1464 (s), 1240 (s), 1050 (s), 880 (s), 830 (m), 710 (s). HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{33}\text{BrO}_2\text{Sn}_2$ 504.0683, found 504.0678. Anal. calcd. for $\text{C}_{20}\text{H}_{33}\text{BrO}_2\text{Sn}_2$: C, 47.65; H, 6.60, found: C, 47.60; H, 6.55.

4,4'-Bis(tri-n-butylstannyl)biphenyl (28). Colorless oil. ^1H NMR (CDCl_3): δ 7.47 (m, 8H); 1.49 (m, 12H), 1.16 (m, 24H), 0.82 [t, 18H, $^3\text{J}(\text{H,H})$ 7.1]. IR (film, cm^{-1}) 3025 (m), 2960 (s), 2920 (s), 2870 (s), 2851 (s), 1605 (m), 1460 (s), 803 (s). HRMS (EI) calcd for $\text{C}_{36}\text{H}_{62}\text{Sn}_2$ 734.2895, found 734.2889. Anal. calcd for $\text{C}_{36}\text{H}_{62}\text{Sn}_2$: C, 59.05; H, 8.53, found: C, 59.09; H, 8.57.

1,4-Bis(tri-n-butylstannyl)naphthalene (31). Colorless oil. ^1H NMR (CDCl_3): δ 7.89 (m, 2H), 7.58 (m, 4H), 1.68(m, 12H), 1.38 (m, 24H); 0.98 [t, 18H, $^3\text{J}(\text{H,H})$ 7.2]. IR (film, cm^{-1}) 3031 (m), 2955 (s), 2915 (s), 2880 (s), 2850 (s), 1600 (m), 1455 (s), 805 (s). HRMS (EI) calcd for $\text{C}_{34}\text{H}_{60}\text{Sn}_2$ 708.2739, found 708.2734. Anal. calcd for $\text{C}_{34}\text{H}_{60}\text{Sn}_2$: C, 57.82; H, 8.56, found: C, 57.86; H, 8.60.

2,5-Bis(tri-n-butylstannyl)pyridine (38). Colorless oil. ^1H NMR (CDCl_3) δ 8.25 [dd, 1H, ^4J H,H) 0.8 & ^3J H,Sn) 18.5]; 7.51 [dd, 1H, $^3\text{J}(\text{H,H})$ 7.6 & $^3\text{J}(\text{H,Sn})$ 34.1]; 7.35 [dd, 1H, ^4J H,H) 0.8 & $^3\text{J}(\text{H,H})$ 7.6 &]; 1.56 (m, 12H); 1.26 (m, 24H); 0.85 [t, 18H, $^3\text{J}(\text{H,H})$ 7.2]. IR (film, cm^{-1}) 3032 (m), 2962 (s), 2915 (s), 2880 (s), 2848 (s), 1573 (m), 1603 (m), 1460 (s), 850 (s), 713 (s). HRMS (EI) calcd for $\text{C}_{29}\text{H}_{57}\text{NSn}_2$ 659.2535, found 659.2542. Anal. calcd for $\text{C}_{29}\text{H}_{57}\text{NSn}_2$: C, 53.00; H, 8.74, found: C, 53.06; H, 8.67.

1,3,5-Tris(tri-n-butylstannyl)benzene (43). Clear oil. ^1H NMR (CDCl_3): δ 7.39 (s, $J = 37.5$ Hz, 3H), 1.64-1.58 (m, 36H), 1.45-1.33 (m, 18H), 0.91 (t, $J = 8.0$ Hz, 27H). ^{13}C NMR (CDCl_3): δ 144.4 (27.9), 141.1 (28.7 and 381.1), 29.2 (19.1), 27.4 (60.0), 13.7, 9.9 (360.7). ^{119}Sn NMR (CDCl_3): δ -44.4. IR (film, cm^{-1}) 3027 (m), 2961 (s), 2910 (s), 2885 (s), 2850 (s), 1600 (m), 1462 (s), 865 (s), 820 (s), 710 (s).

Acknowledgements

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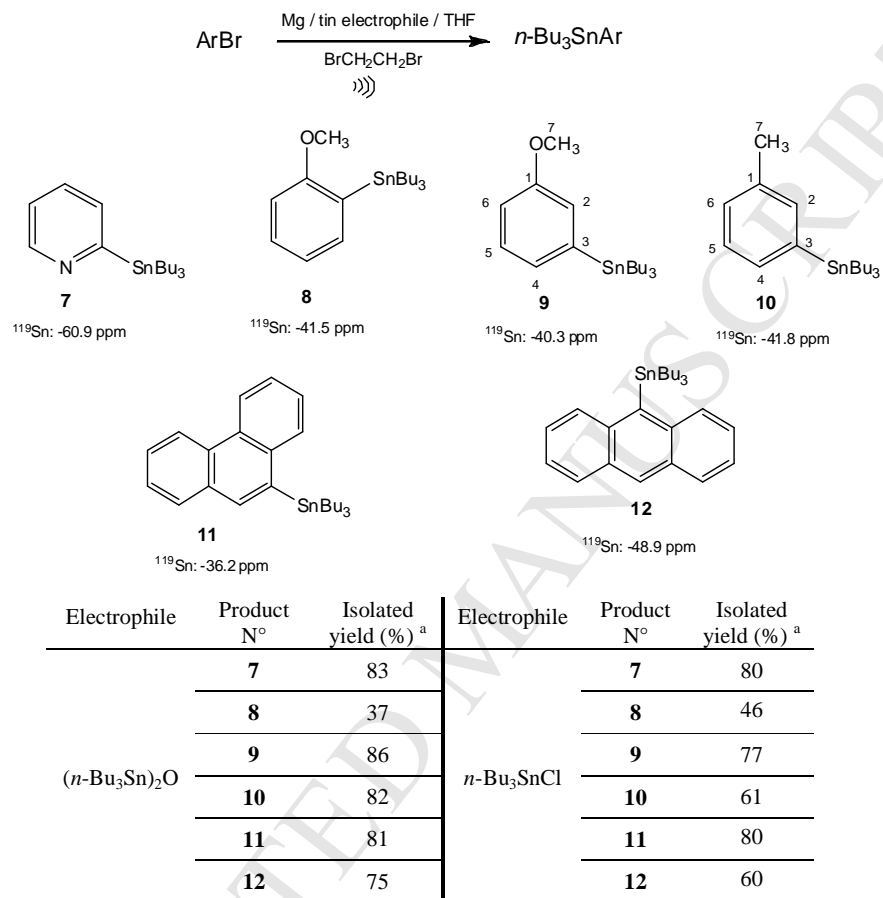
References

- [1] (a) T. N. Mitchell, *Organotin Reagents in Cross-Coupling Reactions*, F. Diederich, P. J. Stang, (Eds.), *Metal-catalyzed Cross-coupling*; Wiley-VCH: Weinheim, Germany, 1998, pp 167-202. (b) V. Farina, V. Krishnamurthy, W. J. Scott, *The Stille Reaction*, John Wiley & Sons Ltd, New York, 1998. (c) A. Davies, *Organotin Chemistry*, VCH, Weinheim, Germany, 2004. (d) A. G. Davies, M. Gielen, K. Pannell and E. Tiekink, *Tin Chemistry: Fundamentals, Frontiers and Applications*, 1st Edition, John Wiley & Sons, Ltd, West Sussex, United Kingdom, 2008. (e) P. J. Smith, Ed., *Chemistry of Tin*, 2nd Edition, Blackie Academic & Professional, London, 1998.
- [2] (a) Y. Yang, H. N. C. Wong *Tetrahedron* 50 (1994) 9583-9608. (b) Y. Yamamoto, Y. Azuma, H. Mitoh *Synthesis* (1986) 564-565. (c) S. Gronowitz, D. Peters *Heterocycles* 30 (1990) 645-658. (d) T. Otsubo, Y. Kono, N. Hozo, H. Miyamoto, Y. Aso, F. Ogura, T. Tanaka, M. Sawada *Bull. Chem. Soc. Jpn.* 66 (1993) 2033-2041. (e) J. J. S. Lamba, J. M. Tour *J. Am. Chem. Soc.* 116 (1994) 11723-11726. (f) E. F. Córscico, R. A. Rossi *Synlett* (2000) 230-232. (g) A. N. Santiago, S. M. Basso, J. P. Montañez, R. A. Rossi *J. Phys. Org. Chem.* 19 (2006) 829-835.
- [3] (a) M. B. Faraoni, L. C. Koll, S. D. Mandolesi, A. E. Zúñiga, J. C. Podestá *J. Organomet. Chem.* 613 (2000) 236-238. (b) S. D. Mandolesi, S. E. Vaillard, J. C. Podestá, R. A. Rossi *Organometallics* 21 (2002) 4886-4888.
- [4] (a) T. M. Miller, T. X. Neenan, R. Zayas, H. E. Bair *J. Am. Chem. Soc.* 114 (1992) 1018-1025. (b) J. M. Tour, J. J. S. Lamba *J. Am. Chem. Soc.* 115 (1993) 4935-4936. (c) A. B. Morgan, J. L. Jurs, J. M. Tour *J. Appl. Polym. Sci.* 76 (2000) 1257-1268.
- [5] P. M. Fidelibus, G. F. Silbestri, M. T. Lockhart, S. D. Mandolesi, A. B. Chopa, J. C. Podestá, *Appl. Organometal. Chem.* 21 (2007) 682-687.
- [6] (a) A. B. Evin, D. Seyferth, *J. Am. Chem. Soc.* 89 (1967) 952-959. (b) D. Seyferth, S. C. Vick, *J. Organomet. Chem.* 141 (1977) 173-187.
- [7] (a) K. R. Wursthorn, H. G. Kuivila, G. F. Smith *J. Am. Chem. Soc.* 100 (1977) 2779-2789. (b) K. R. Wursthorn, H. G. Kuivila *J. Organomet. Chem.* 140 (1977) 29-39.
- [8] T. N. Mitchell, K. Böttcher, P. Bleckmann, B. Costisella, Ch. Schwittek *Eur. J. Org. Chem.* (1999) 2413-2417.
- [9] R. Altmann, K. Jurkschat, M. Schürmann, D. Dakternieks, A. Duthie *Organometallics* 17 (1998) 5858-5866.
- [10] C. C. Yammal, J. C. Podestá, R. A. Rossi *J. Org. Chem.* 57 (1992) 5720-5725.
- [11] E. F. Córscico, R. A. Rossi *Synlett* (2000) 227-229.
- [12] H. Yoshida, K. Tanino, J. Ohshita, A. Kunai *Angew. Chem. Int. Ed.* 43 (2004) 5052-5055.
- [13] (a) A. S.-Y. Lee, W.-Ch. Dai *Tetrahedron Lett.* 37 (1996) 495-498. (b) A. S.-Y. Lee, W.-Ch. Dai *Tetrahedron* 53 (1997) 859-868.
- [14] B. Jousseume, E. Chanson, M. Pereyre *Organometallics*, 5 (1986) 1271-1272.
- [15] R. A. Rossi, A. Pierini, A. N. Santiago, *Org. Reactions*, 54 (1999) 1-271.
- [16] (a) J. A. Joule and K. Mills *Heterocyclic Chemistry*, 5th ed., Wiley-VCH, Weinheim, 2010. (b) J. Jack Li and G. W. Gribble *Palladium in Heterocyclic Chemistry: A Guide for the Synthetic Chemist*, 2nd Ed., Elsevier, Oxford, 2007.
- [17] M. V. Nora de Souza, R. H. Dodd *Heterocycles* 47 (1998), 811-827.
- [18] G. S. Hanan, U. S. Schubert, D. Volkmer, E. Riviere, J.-M. Lehn, N. Kyritsakas, J. Fischer *Can. J. Chem.* 75 (1997) 169-182.
- [19] (a) J. Hou, Z. Tan, Y. Yan, Y. He, Ch. Yang, Y. Li *J. Am. Chem. Soc.* 128 (2006) 4911-4916. (b) X. Guo, M. D. Watson *Org. Lett.* 10 (2008) 5333-5336.
- [20] P. M. Fidelibus, G. F. Silbestri, M. T. Lockhart, S. D. Mandolesi, A. B. Chopa, J. C. Podestá, *Appl. Organometal. Chem.* 21 (2007) 682-687.
- [21] B. Balasubrahmanyam, I. Jeyashri, N. Namboothiri, *Tetrahedron* 50 (1994) 8127-8142.
- [22] (a) J.K. Stille, *Angew. Chem., Int. Ed. Engl.* 25 (1986) 508-524. (b) V. Farina, V. Krishnamurthy, W.J. Scott, *Organic Reactions* 50 (1997) 1-652.
- [23] E. Ferrer Flegeau, M. E. Popkin, M. F. Greaney, *J. Org. Chem.* 73 (2008) 3303-3306.
- [24] R. S. Schreiber, W. Bradley Reid, Jr, R. W. Jackson *Organic Syntheses, Coll. Vol. 4*, (1963) 256-257.

- [25] O. Cakmak, I. Demirtas, H. T. Balaydin Tetrahedron 58 (2002) 5603-5609.
- [26] H. T. Clarke, T. F. Murray Organic Syntheses, Coll. Vol. 1, (1941) 207-208.
- [27] H. Gilman and S. D. Rosenberg J. Am. Chem. Soc. 75 (1953) 2507-2509.
- [28] C. Bolm, M. Ewald, M. Felder, G. Schingloff Chem. Ber. 125 (1992) 1169-1173
- [29] (a) Weisemann, G. Schmidtberg, H.-A. Brune J. Organomet. Chem. 365 (1989) 403-412.
(b) H. Nierengarten, J. Rojo, E. Leize, J.-M. Lehn, A. Van Dorsselaer Eur. J. Inorg. Chem. (2002) 573-579.
- [30] H. Yoshida, K. Tanino, J. Ohshita, A. Kunai, Angew. Chem. Int. Ed. 43 (2004) 5052-5055
- [31] (a) S. Kool, L. S. Liebeskind. J. Am. Chem. Soc. 117 (1995) 3389-3404. (b) M. E. Wright Organometallics 8 (1989) 407-411.
- [32] S. M. Moerlein J. Organomet. Chem. 319 (1987) 29-39.

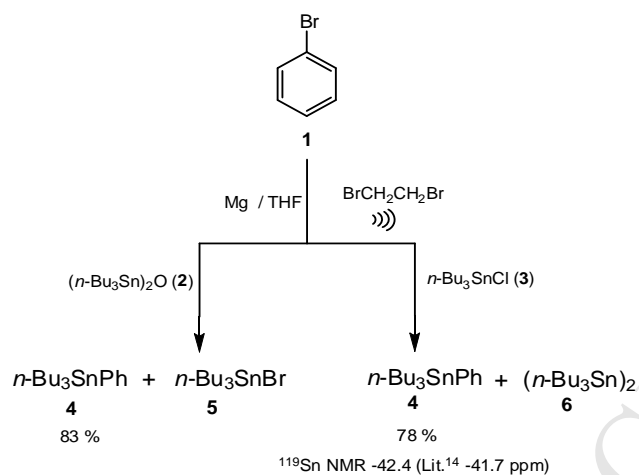
Research highlights

- Synthesis of new Aryl- and Heteroaryl bis(tri-*n*-butylstannylated) compounds
- Sonochemical Barbier-like synthesis of bis(tri-*n*-butylstannylated) aromatic compounds mediated by Mg.
- Use of bis(tri-*n*-butyltin) oxide and tri-*n*-butyltin chloride electrophiles for the synthesis of aryl tri-*n*-butyltin compounds.

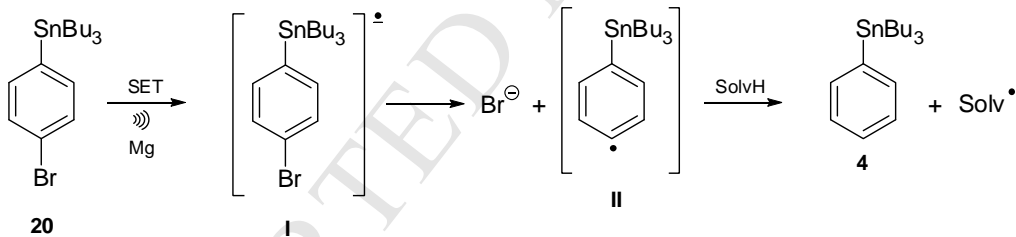


^a Pure compound after column chromatography

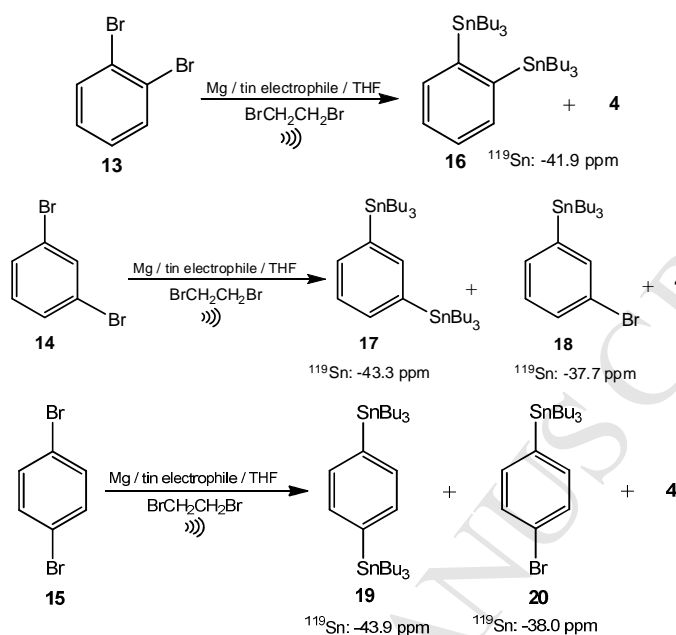
Figure 1. Aryltri-*n*-butyltin products obtained in the sonicated reactions with tin electrophiles **2** and **3**.



Scheme 1. Reaction of **1** with bis(tri-*n*-butyltin) oxide (**2**) and tri-*n*-butyltin chloride (**3**).



Scheme 2. Mechanism of the reduction of compound **20**.

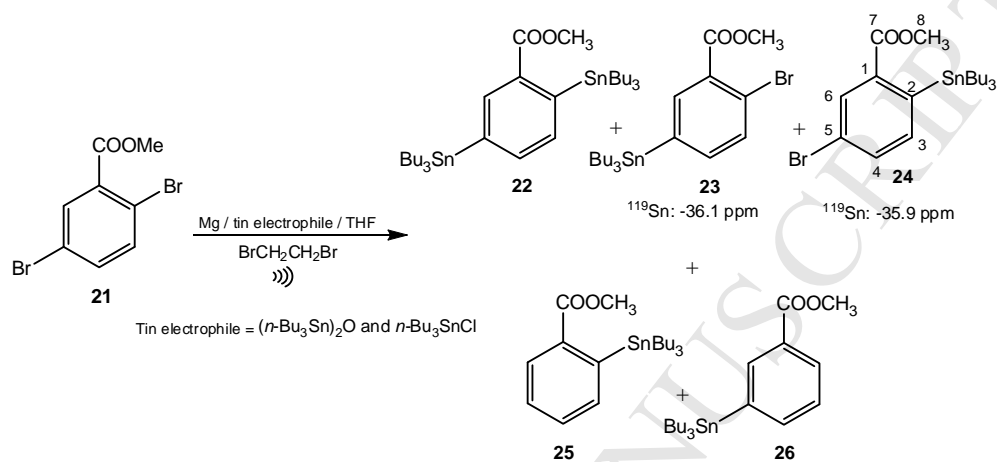


Electrophile	Dibromide N°	Product N° (%) ^a	Isolated Yield (%) ^b	Electrophile	Product N° (%) ^a	Isolated Yield (%) ^b
<i>(n</i> -Bu ₃ Sn) ₂ O	13	16 (14)	--	<i>n</i> -Bu ₃ SnCl	16 (21)	16
		4 (86)	62		4 (79)	60
	14	17 (65)	60		17 (94)	77
		18 (28)	20		--	--
		4 (7)	--		4 (6)	--
	15	19 (73)	66		19 (94)	75
20 (19)		15	--	--		
		4 (8)	--	4 (6)	--	

^a From ¹¹⁹Sn NMR spectrum. ^b Pure compound after column chromatography.

Reactions with *(n*-Bu₃Sn)₂O: substrate (1 mmol), Mg (3.3 mmol), *(n*-Bu₃Sn)₂O (3 mmol), 1,2-dibromoethane (0.5 mmol) in 5 ml of dry THF was sonicated 4 h. at r.t. under argon. **Reactions with *n*-Bu₃SnCl:** substrate (1 mmol), Mg (3.3 mol), *n*-Bu₃SnCl (3 mmol), 1,2-dibromoethane (0.5 mmol) in 5 ml of dry THF was sonicated 4 h. at r.t. under argon.

Scheme 3. Barbier sonicated reactions of dibromobenzenes



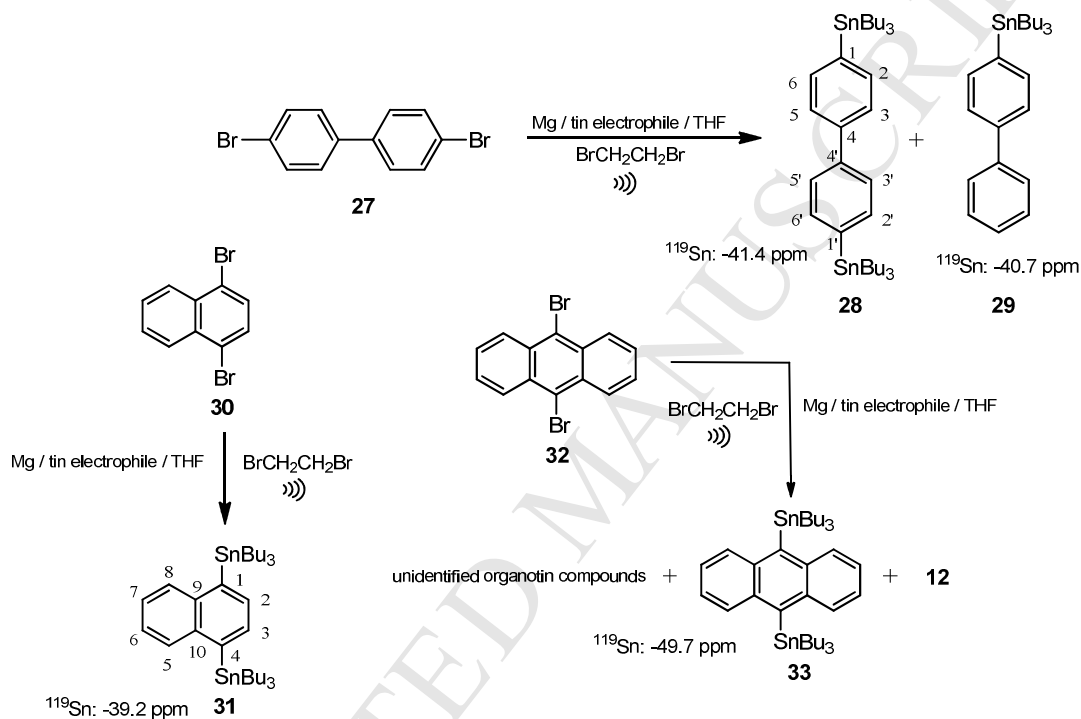
¹³ C-NMR data ^a								
Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
24	145.9	122.7	138.5	134.71	137.4	132.8	167.9	52.6
	(NO)	(NO)	(31.1)	(39.3)		(27.2)	(4.5)	b

^a In CDCl₃; ¹³C chemical shifts, δ, in ppm with respect to the central peak of CHCl₃ (¹³C spectra); ^b ⁿJ(¹³C, ¹¹⁹Sn) coupling constants in Hz (in brackets). ^b *n*-Butyl groups chemical shifts (coupling constants): 29.3 (20.1); 27.5 (58.3); 13.8; 11.27 (363.6).

Scheme 4. Barbier sonicated reactions of methyl 2,5-dibromobenzoate (**21**) and ¹³C-NMR characteristics of compound **24**.

Electrophile	Dibromide N°	Product N° (%) ^a	Isolated yield (%) ^b	Electrophile	Product N° (%) ^a	Isolated yield (%) ^b
<i>(n</i> -Bu ₃ Sn) ₂ O	27	28 (89)	55	<i>n</i> -Bu ₃ SnCl	28 (100)	82
		29 (11)	--		--	--
	30	31 (100)	84		31 (100)	86
		32	33 (22)		-- ^c	33 (52)
		12 (61)	-- ^c	12 (6)	-- ^c	

^a From ¹¹⁹Sn NMR spectrum. ^b Pure compound after column chromatography. ^c Could not be separated pure.



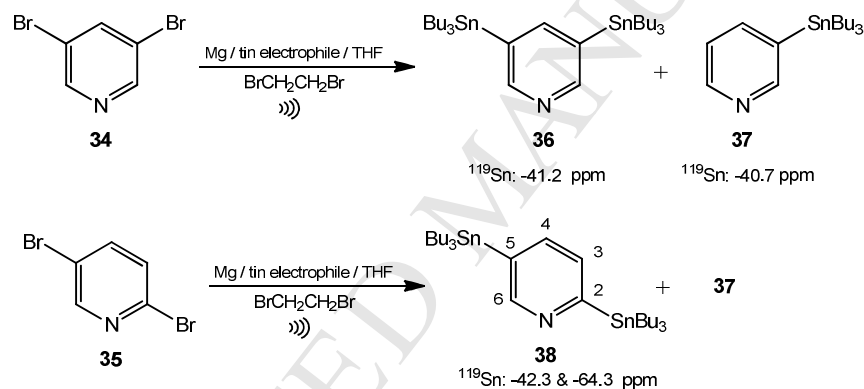
Compound	¹³ C-NMR data ^a	Compound	¹³ C-NMR data ^a
28		31	
C-1 & C-1'	140.90 (387.6)	C-1 & C-4	143.54 (386.5)
C-2, C-2', C-6. & C-6'	137.02 (30.5)	C-2 & C-3	134.96 (26.8 & 45.0)
C-3, C-3', C-5 & C-5'	126.72 (40.9)	C-5 & C-8	131.42 (28.3)
C-4 & C-4'	141.03 (29.2)	C-6 & C-7	125.32
<i>n</i> -Bu	9.84 (343.1); 13.83; 27.20 (56.2); 29.31 (20.3).	C-9 & C-10	139.62 (27.5)
		<i>n</i> -Bu	10.68 (338.8); 13.77; 27.69 (56.6); 29.42 (18.4)

^a In CDCl₃; ¹³C chemical shifts, δ , in ppm with respect to the central peak of CHCl₃ (¹³C spectra); ⁿJ(¹³C, ¹¹⁹Sn) coupling constants in Hz (in brackets).

Scheme 5. Barbier sonicated reactions of 4,4'-dibromobiphenyl (**27**), 1,4-dibromonaphthalene (**30**) and 9,10-dibromanthracene (**32**), and ¹³C NMR characteristics of the new compounds **28** and **31**.

Electrophile	Dibromide N°	Product N° (%) ^a	Isolated yield (%) ^b	Electrophile	Product N° (%) ^a	Isolated yield (%) ^b
<i>(n</i> -Bu ₃ Sn) ₂ O	34	36 (89)	65	<i>n</i> -Bu ₃ SnCl	36 (100)	55
		37 (11)	--		37	--
	35	38 (84)	70		38	--
		37 (16)	--		37 ^c	58

From ¹¹⁹Sn NMR spectrum.^b Pure compound after column chromatography.^c Plus other unidentified organotin compound.



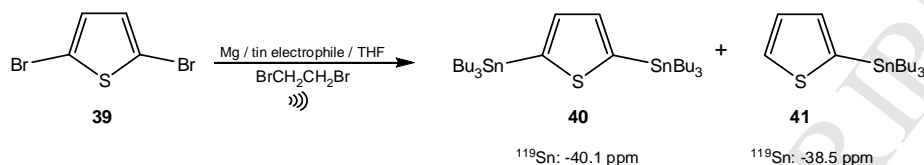
¹³ C-NMR data ^a						
Compound	C-2	C-3	C-4	C-5	C-6	<i>n</i> -Bu
38	172.91 (504.5)	157.89 (30.8 & 57.2)	141.49 (21.8 & 29.4)	137.41 (NO)	132.67 (24.4)	9.71 (346.4); 9.81 (349.2); 13.58; 13.62; 27.29 (57.9); 27.32 (55.2); 29.00 (21.2); 29.06 (22.9).

^a In CDCl₃; ¹³C chemical shifts, δ, in ppm with respect to the central peak of CHCl₃ (¹³C spectra); ⁿJ(¹³C, ¹¹⁹Sn) coupling constants in Hz (in brackets).

Scheme 6. Barbier sonicated reactions of 3,5-dibromopyridine (**34**) and 2,5-dibromopyridine (**35**), and ¹³C-NMR characteristics of compound **38**.

Electrophile	Product N° (%) ^a	Isolated yield (%) ^b	Electrophile	Product N° (%) ^a	Isolated yield (%) ^b
$(n\text{-Bu}_3\text{Sn})_2\text{O}$	40 (100)	89	$n\text{-Bu}_3\text{SnCl}$	40 (61)	55
				41 (39)	-

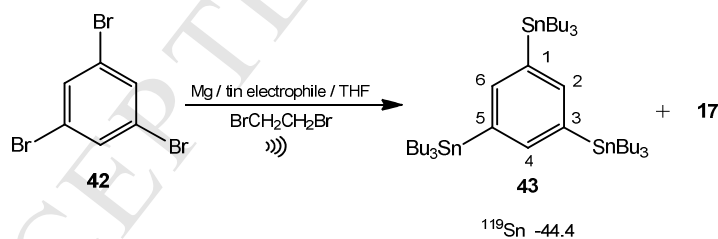
^a From ¹¹⁹Sn NMR spectrum. ^b Pure compound after column chromatography.



Scheme 7. Barbier sonicated reactions of 2,5-dibromothiophene (**39**) with electrophiles **2** and **3**.

Electrophile	Product N° (%) ^a	Electrophile	Product N° (%) ^a
$(n\text{-Bu}_3\text{Sn})_2\text{O}$	43 (93)	$n\text{-Bu}_3\text{SnCl}$	43 (88)
	17 (7)		17 (12)

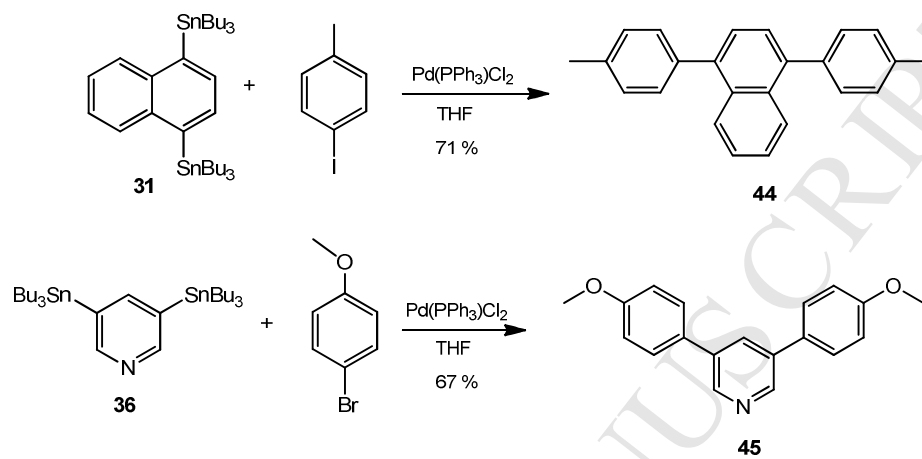
^a From ¹¹⁹Sn NMR spectrum..



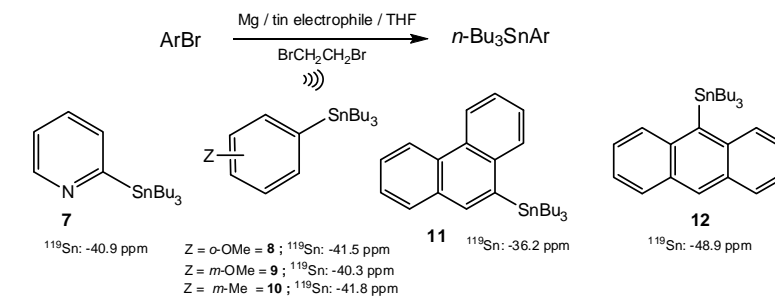
Compound	¹³ C-NMR data ^a		
	C-1, C-3, & C-5C-4	C-2, C-4, & C-6	<i>n</i> -Bu
43	141.25 (27.2 & 376.9)	144.56 (27.8)	9.83 (313.2); 13.88; 27.63 (54.4); 29.41 (20.5)

^a In CDCl₃; ¹³C chemical shifts, δ , in ppm with respect to the central peak of CHCl₃ (¹³C spectra); ⁿJ(¹³C, ¹¹⁹Sn) coupling constants in Hz (in brackets).

Scheme 8. Barbier sonicated reactions of 1,3,5-tribromobenzene (**42**) with electrophiles **2** and **3**, and ¹³C-NMR characteristics of compound **38**



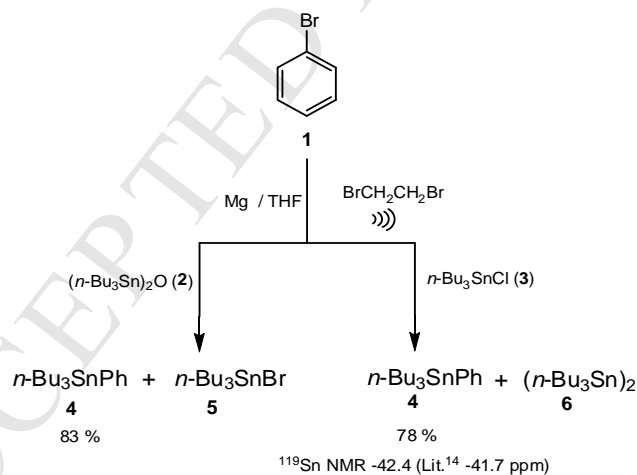
Scheme 9. Barbier sonicated reactions of 1,3,5-tribromobenzene (**42**) with electrophiles **2** and **3**.



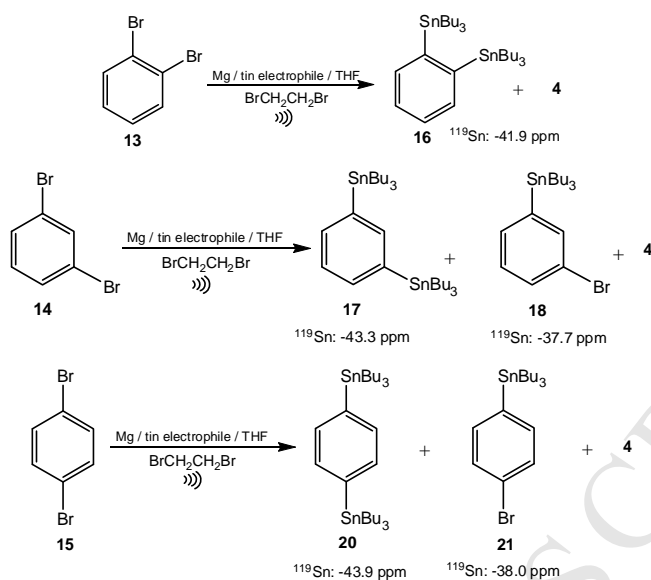
Electrophile	Product N°	Isolated yield (%) ^a	Electrophile	Product N°	Isolated yield (%) ^a
$(n\text{-Bu}_3\text{Sn})_2\text{O}$	7	83	$n\text{-Bu}_3\text{SnCl}$	7	80
	8	37		8	46
	9	86		9	77
	10	82		10	61
	11	81		11	80
	12	75	12	60	

^a Pure compound after column chromatography

Figure 1. Aryltri-*n*-butyltin products obtained in the sonicated reactions with tin electrophiles **2** and **3**.



Scheme 1. Reaction of **1** with bis(tri-*n*-butyltin) oxide (**2**) and tri-*n*-butyltin chloride (**3**).

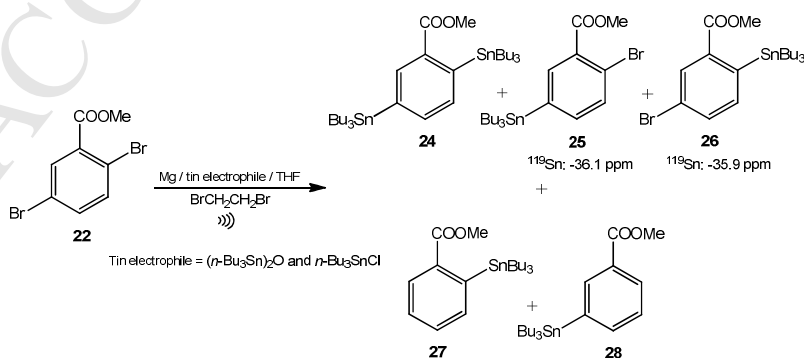


Electrophile	Product N° (%) ^a	Isolated yield (%) ^b	Electrophile	Product N° (%) ^a	Isolated yield (%) ^b
<i>(n</i> -Bu ₃ Sn) ₂ O	16 (14)	-	<i>n</i> -Bu ₃ SnCl	16 (21)	16
	4 (86)	62		4 (79)	60
	17 (65)	60		17 (94)	77
	18 (28)	20		4 (6)	-
	4 (7)	-		20 (94)	75
	21 (19)	15		4 (6)	-
	4 (8)	-			

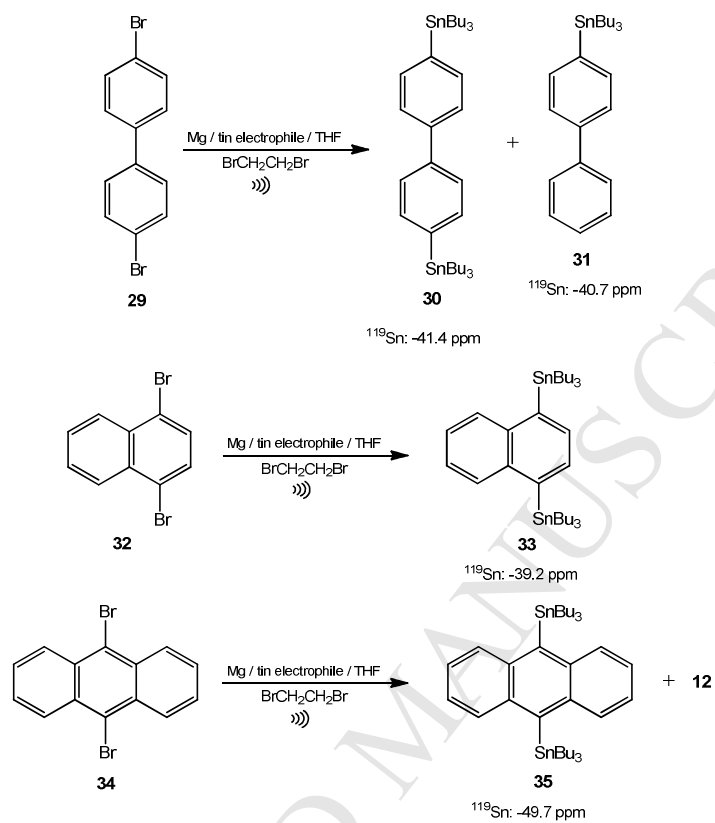
^a From ¹¹⁹Sn NMR spectrum. ^b Pure compound after column chromatography.

Reactions with *(n*-Bu₃Sn)₂O: substrate (1 mmol), Mg (3.3 mmol), *(n*-Bu₃Sn)₂O (3 mmol), 1,2-dibromoethane (0.5 mmol) in 5 ml of dry THF was sonicated 4 h. at r.t. under argon. Reactions with *n*-Bu₃SnCl: substrate (1 mmol), Mg (3.3 mol), *n*-Bu₃SnCl (3 mmol), 1,2-dibromoethane (0.5 mmol) in 5 ml of dry THF was sonicated 4 h. at r.t. under argon.

Scheme 2. Barbier sonicated reactions of dibromobenzenes



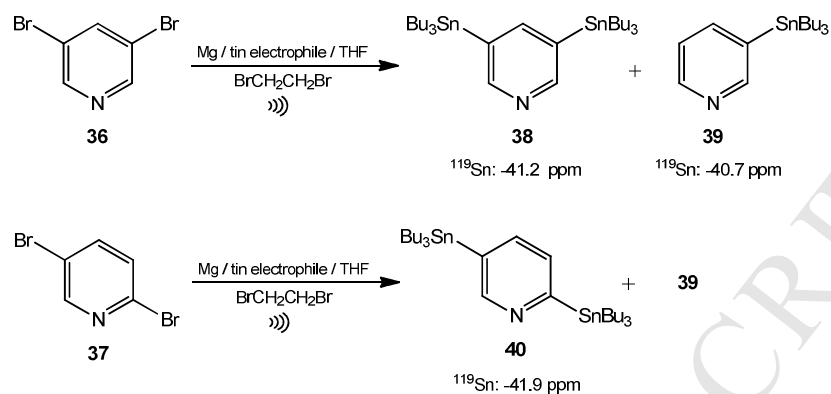
Scheme 3. Barbier sonicated reactions of methyl 2,5-dibromobenzoate (**22**)



Electrophile	Product N° (%) ^a	Isolated yield (%) ^b	Electrophile	Product N° (%) ^a	Isolated yield (%) ^b
$(n\text{-Bu}_3\text{Sn})_2\text{O}$	30 (89)	55	$n\text{-Bu}_3\text{SnCl}$	30 (100)	82
	31 (11)	-		-	-
	32 (100)	84		32 (100)	86
	35 (39)	15		35 (91)	82
	12 (61)	37		12 (9)	-

^a From ^{119}Sn NMR spectrum. ^b Pure compound after column chromatography.

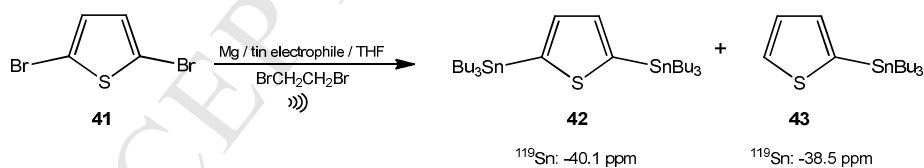
Scheme 4. Barbier sonicated reactions of 4,4'-dibromobiphenyl (**29**), 1,4-dibromonaphthalene (**32**) and 9,10-dibromanthracene (**35**).



Electrophile	Product N° (%) ^a	Isolated yield (%) ^b	Electrophile	Product N° (%) ^a	Isolated yield (%) ^b
<i>(n</i> -Bu ₃ Sn) ₂ O	38 (89)	65	<i>n</i> -Bu ₃ SnCl	38 (100)	55
	39 (11)	-		-	-
	40 (84)	70		40 (91)	58
	39 (16)	-		39 (9)	-

^a From ¹¹⁹Sn NMR spectrum. ^b Pure compound after column chromatography

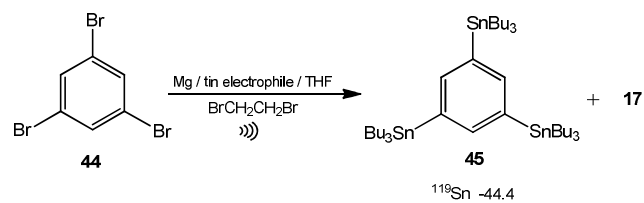
Scheme 5. Barbier sonicated reactions of 3,5-dibromopyridine (**36**) and 2,5-dibromopyridine (**37**).



Electrophile	Product N° (%) ^a	Isolated yield (%) ^b	Electrophile	Product N° (%) ^a	Isolated yield (%) ^b
<i>(n</i> -Bu ₃ Sn) ₂ O	43 (100)	89	<i>n</i> -Bu ₃ SnCl	43 (61)	55
				44 (39)	-

^a From ¹¹⁹Sn NMR spectrum. ^b Pure compound after column chromatography.

Scheme 6. Barbier sonicated reactions of 2,5-dibromothiophene (**41**) with electrophiles **2** and **3**.

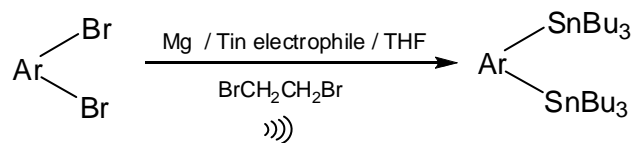


Electrophile	Product N° (%) ^a	Electrophile	Product N° (%) ^a
<i>n</i> -Bu ₃ Sn) ₂ O	45 (93)	<i>n</i> -Bu ₃ SnCl	45 (88)
	17 (7)		17 (12)

^a From ¹¹⁹Sn NMR spectrum..

Scheme 7. Barbier sonicated reactions of 1,3,5-tribromobenzene (**44**) with electrophiles **2** and **3**.

PICTOGRAM



Tin electrophile = $(n\text{-Bu}_3\text{Sn})_2\text{O}$; $n\text{-Bu}_3\text{SnCl}$

Ar = Disubstituted aromatic and heteroaromatic compounds =
1,2-, 1,3-, and 1,4- benzenes; 4,4'- biphenyl; 1,4- naphthalene;
9,10- anthracene; 2,5 and 3,5- pyridines; 2,5- thiophene; also
1,3,5-trisubstituted benzene

Synopsis

Darío C. Gerbino,[‡] Pablo M. Fidelibus, Sandra D. Mandolesi, Romina A. Ocampo, Jimena Scoccia, and Julio C. Podestá^{‡,*}

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The best reaction conditions and the syntheses of some new bis(tri-*n*-butylstannylated) aromatic and heteroaromatic compounds by means of a Barbier-like sonochemical reaction are reported. Full ¹H-, ¹³C-, and ¹¹⁹Sn-NMR data are informed.