Bicyclic allyltin derivatives through selective “one pot” hydrostannation - Diels-Alder reaction

Romina A. Ocampo, Sandra D. Mandolesi,* and Liliana C. Koll*

Departamento de Química and INQUISUR (UNS-CONICET), Universidad Nacional del Sur, Avda. Alem 1253, 8000 Bahía Blanca, Argentina
E-mail: lckoll@criba.edu.ar

Dedicated to the Argentinean professors Rita H. Rossi, Julio C. Podestá, Manuel González Sierra and Oscar S. Giordano in recognition of their achievements in organic chemistry and their contributions in the development of the field in our country

Abstract
In this paper we report a simple "one pot" procedure to functionalized allyltin derivatives from 1-ethynylcyclohexene. Radical addition of trineophyltin hydride gives quantitatively to (*Z,E*)-1-(2-trineophylstannylvinyl)cyclohexene, a conjugated dienyl-stannane that, *via* a [4+2] cycloaddition reaction (Diels-Alder) with activated dienophiles, affords substituted bicyclic unsaturated products with specific stereochemistry and a trialkylstannyl group in allylic position. The Stille reaction of the allyltin compound enables the synthesis of aryl substituted bicyclic compounds in moderate to good yields (48-85%).

Keywords: Bicyclic allyltin, hydrostannation, hydrostannylation, Diels-Alder reaction, Stille coupling

Introduction

The Diels-Alder reaction is one of the most commonly used organic reactions to construct, in a regio- and stereocontrolled way, a six membered ring with up to four stereogenic centers.[1] The widespread utility of the reaction rests on its ability to form otherwise difficult to access molecules such as bridged bicyclic compounds and also more complex structures due to its potential to form carbon-carbon, carbon-heteroatom and heteroatom-heteroatom bonds. The synthesis of stereodefined conjugated dienylstannanes is an area of interest as they are very useful synthetic intermediates. We are interested in developing a fast route to obtain these types of precursors in order to study them as dienes in a “one pot” Diels-Alder reaction. Furthermore, allyltin reagents are very important in organic and asymmetric synthesis,[2] as shown, for instance,

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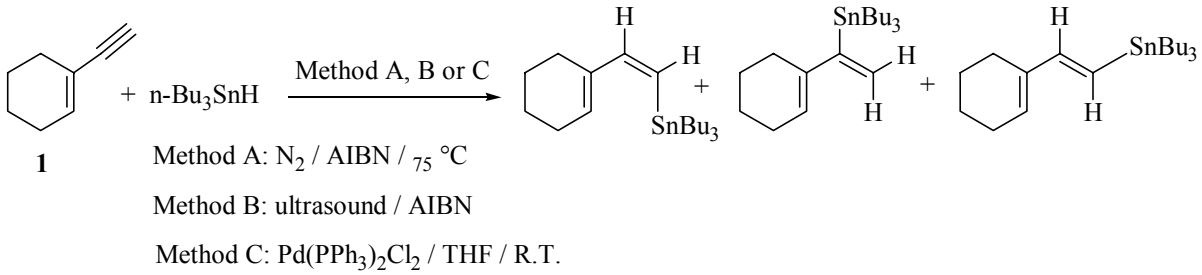
in reactions of allystannanes with aldehydes in the presence of chiral non-racemic ligands coordinated with Lewis acids.[3] We now report the synthesis of a variety of functionalized compounds containing allyltin structures *via* a "one pot" hydrostannation Diels-Alder reaction. These compounds could be suitable building blocks of non-steroidal compounds which are selective modulators (*i.e.*, agonists and antagonists) of a steroid receptor, specifically, the glucocorticoid receptor. Such receptors are useful to treat diseases such as obesity, diabetes, inflammation and others.[4] Thus, the possibility of synthesizing such precursors through a "one pot" protocol was the main target of this study. The allyltin compounds obtained are being tested in palladium catalyzed C-C Stille coupling reactions with the aim to obtain tin free non-steroidal analogs.

Results and Discussion

Initially the hydrostannation of 1-ethynylcyclohexene (**1**) was performed with the easy to handle and commercially available tri-*n*-butyltin hydride under three different reaction conditions: Method A: free radical conditions and photochemical initiation, nitrogen atmosphere, azobisisobutyronitrile (AIBN) (0.01 equiv), without solvent, at 75 °C; Method B: free radical conditions using ultrasound,[5] nitrogen atmosphere, r.t., AIBN (0.01 equiv), without solvent and Method C: under catalyzed conditions bis(triphenylphosphine)palladium (II) chloride (2 mol%), r.t. in THF (Scheme 1).



Scheme 1. Addition of tri-*n*-butyltin hydride to 1-ethynylcyclohexene **1**.

The ^{119}Sn NMR spectra of the crude products resulting from these additions clearly showed that mixtures of at least three dienyltin adducts were obtained. In previous studies with mono- and disubstituted alkynes,[6] we demonstrated that it was possible to improve the selectivity of this reaction using organotin hydrides with bulky organic ligands. In view of the poor regio- and stereoselectivity of the present hydrostannylation (Scheme 1), we considered the alternative addition of the more sterically demanding trineophyltin hydride **2** (neophyl –Neph- is 2-methyl-2-phenylpropyl) to enyne **1** under similar reaction conditions. As shown in Scheme 2, the results obtained were substantially different. In the case of Methods A and B under free radical conditions, [(1*Z*)-2-cyclohexenylvinyl]trineophylstannane **3** resulting from an *anti* attack, was

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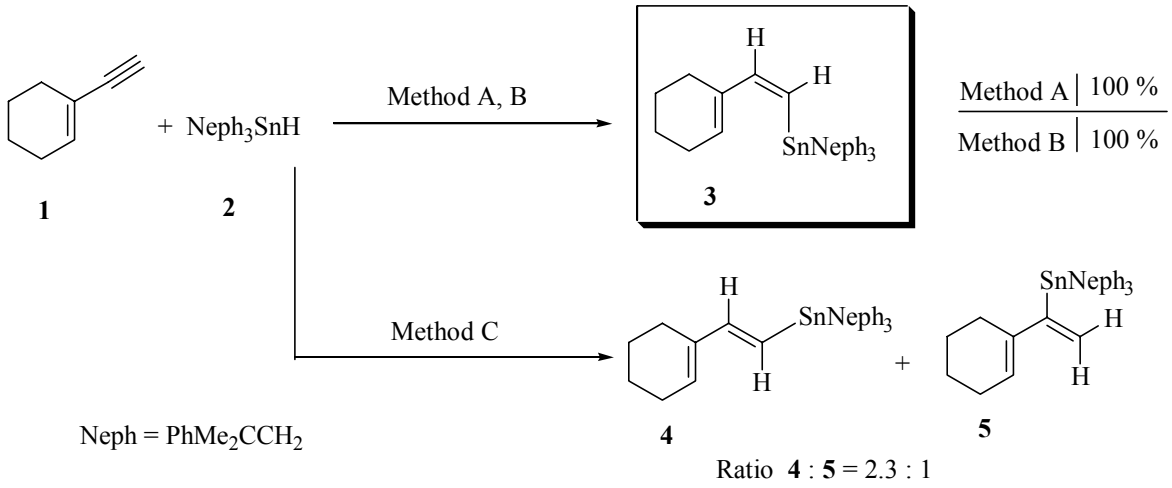
the only product obtained in quantitative yield after 1 h (Method A) and 40 min (Method B) of reaction, respectively.



Scheme 2. Addition of trineophylstannyl hydride **2** to 1-ethynylcyclohexene **1**.

The geometry of compound **3** was assigned on the basis of the large $^{3}J_{(Sn,H)}$ coupling constant of 151.3 Hz that indicated the existence of *trans* H-C-C-Sn linkages. The absence of the signal corresponding to a terminal vinyl methylene in the ^{13}C NMR spectra supported that the tin atom was not attached to the cyclohexenyl moiety. The structure was confirmed by other ^{1}H, ^{13}C and ^{119}Sn NMR data (see Experimental Section). When the reaction was performed under palladium catalyzed conditions and after 45 min (Method C), a mixture of [(1*E*)-2-cyclohexenylvinyl]-trineophylstannane **4** and (1-cyclohexenylvinyl)trineophylstannane **5 (4:5**, 2.3:1**)** was obtained. The ratio of isomers was determined through the corresponding ^{119}Sn NMR spectrum of the crude product. These adducts were the result of the corresponding *syn* addition of the trineophyltin hydride. No addition to the double bond of enyne **1** was observed in any case. Although the mixture of regioisomers **4** and **5** could not be separated, we were able to obtain enriched mixtures from which useful NMR data could be obtained. The stereochemistry of **4** and **5** was assigned taking into account that the $^{3}J_{(Sn,H)}$ coupling constant value of 69.8 Hz extracted from the ^{1}H NMR spectrum lies in the range 65-85 Hz, and indicated a *cis* arrangement between the proton attached to the same vinyl carbon as the cyclohexenyl moiety and the stannyl group in stereoisomer **4**. Furthermore, the $^{3}J_{(H,H)}$ of 19.1 Hz indicated *trans* H-C-C-H linkages around the vinyl group in the same adduct. In the case of compound **5**, the $^{2}J_{(Sn,C)}$ coupling constant of 28.2 Hz corresponded to a CH_2 at 123.41 ppm in the ^{13}C NMR spectra together with $^{2}J_{(H,H)}$ and $^{3}J_{(Sn,H)}$ coupling constants values of 2.3 Hz and 67.5 Hz, respectively, confirmed both the existence of a terminal sp^2 carbon and cyclohexenyl- and trineophyltin groups attached to the same vinyl carbon. Other ^{1}H, ^{13}C and ^{119}Sn NMR data also confirmed the assigned structures (see Experimental Section).

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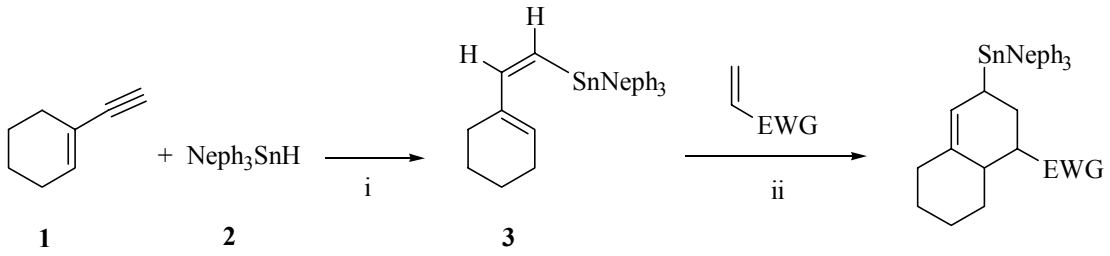
As we were looking for the best conditions for a "one pot" hydrostannation Diels-Alder reaction, we selected the addition of $Neph_3SnH$ **2** to **1** using Method B (Scheme 3).



Reagents and conditions: i) Method B: ultrasound, AIBN (100%); ii) Method D: CH_2Cl_2, $AlCl_3$, -78 °C; Method E: PhH, hydroquinone, 80 °C; Method F: PhH, hydroquinone, 40 °C, ultrasound.

Scheme 3. "One pot" hydrostannation Diels-Alder reactions.

Since the trialkylstannyl group was known to have a small electron-donating inductive effect[7] when attached to a dienic sp^2 carbon atom, it could react readily with electron-poor dienophiles. The adducts obtained in these reactions should reflect the stereochemistry of the starting compounds. So, without further purification, the dienylstannane **3** was used as the conjugated diene precursor for the Diels-Alder reaction performed under three different experimental conditions with several activated dienophiles: Method D: methylene dichloride, aluminum trichloride, -78 °C; Method E: benzene, hydroquinone (as polymerization inhibitor), 80 °C and Method F: benzene, hydroquinone, 40 °C, ultrasound (Table 1).

The formation of the *"ortho* or *meta"* adducts in the Diels-Alder reaction in most cases can be explained in terms of Frontier Orbital Theory and it was possible to predict the regiochemistry of these [4*n* + 2] cycloadditions. Thus, the strongest interaction will be between the centers on the frontier orbitals having the largest orbital coefficients, which are, in this case, the HOMO of the diene with an electron releasing group (ERG) at C_1 that reacts with the LUMO of the dienophile with an electron withdrawing group (EWG). The most favored regioisomer that should be expected is the "*ortho*" adduct (Scheme 4, a).

However, when the diene was substituted at C_1 with a weak ERG such as the trineophyl-stannyl group, its contribution to the distortion effect on the size of the orbital was very small so the coefficients of C_1 and C_4 were expected to be very similar. Because of this, in the determination of the regiochemistry, the predominant effect was steric and as such the preferred product was expected be the "*meta*" adduct (Scheme 4, b). This structural hypothesis was confirmed through the spectroscopic analyses of the products obtained in the corresponding "one pot" reactions.

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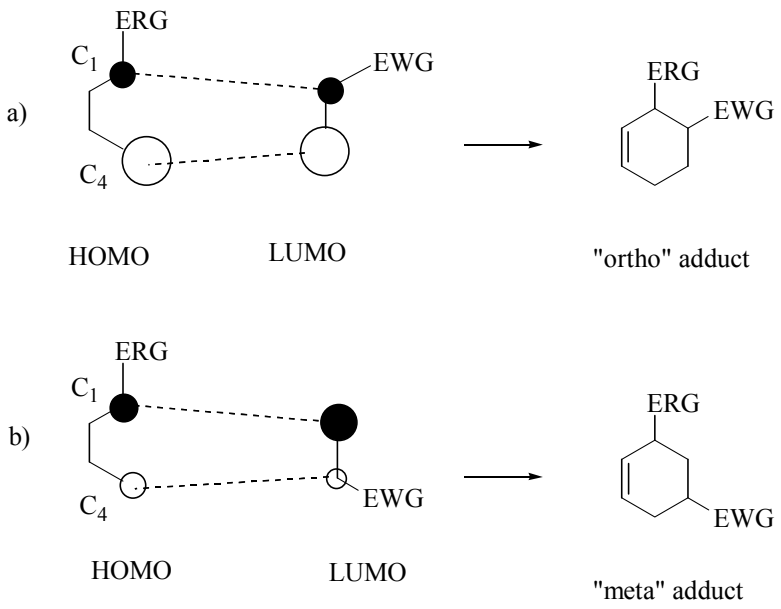

Scheme 4. Relative coefficients of interacting frontier orbitals.

Thus, the reaction of diene **3** and methyl acrylate **6** (entry 1, Table 1), gave exclusively methyl-4-trineophylstannylbicyclo[4.4.0]dec-5-ene-2-carboxylate **14** in 92% yield (Method E) and 75% yield in the presence of Lewis acid at -78 °C (Method D). Only starting material was recovered when the ultrasound was used (Method F). The absence of Sn, C coupling constants between the tin atom and the carbonyl group and the signals at δ 24.41 [$^{2}J_{(Sn,C)}$ = 15.2 Hz] corresponding to a methylene group (C_3), clearly showed that **14** was the "*meta*" adduct together with the observed $^{3}J_{(Sn\text{-}C4\text{-}C3\text{-}C2)}$ = 11.2 Hz, that, according to previous work and the graph of the Karplus equation,[8] corresponded to a dihedral angle close to 110º which supported a *trans* relation between the methoxycarbonyl group and the tin moiety. As expected, 4-trineophyl-stannyl-1,3,3a,4,6,7,8,9,9a,9b-decahydrobenzo[*e*]isobenzofuran-1,3-dione **15** was the only cycloaddition product in the reaction between **3** and the symmetric maleic anhydride **7** (entry 2, Table 1). The *trans* geometric relationship between the tin atom and the nearest carbonyl group (C_3) was determined through the $^{3}J_{(Sn\text{-}C4\text{-}C3a\text{-}C3=O)}$ coupling constant value of 64.6 Hz extracted from ^{13}C NMR spectra that gave a 150-180° dihedral angle between C_4-Sn bond and C_3=O group. This hypothesis was confirmed by considering the observed $^{3}J_{(H,H)}$ coupling constant value between H-3a and H-9b which was about 2.3 Hz consistent with a *cis* conformation. Once again, the highest yield of 95% for adduct **15** occurred under the experimental conditions given by Method E. A similar analysis allowed us to determine the structure of 8-trineophylstannyl-tricyclo[8.4.0.0^{2,7}]tetradeca-4,9-diene-3,6-dione **16**, obtained from the reaction between **3** and *p*-benzoquinone **8** (entry 3, Table 1).

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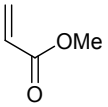
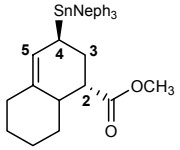
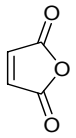
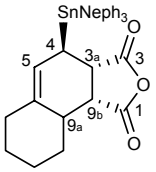
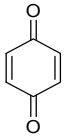
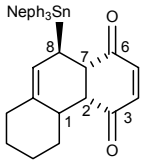
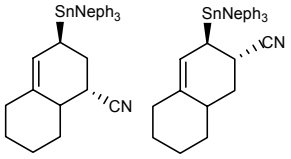
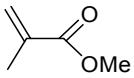
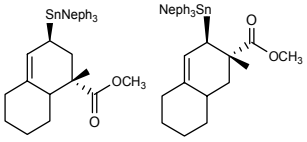
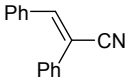
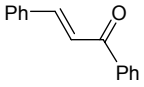
Table 1. Diels-Alder reactions between adduct **3** and activated dienophiles **6–12**

Entry	Dienophile	Method [a] /(time, h)	Yield (%) [b]	Product
1	 **6**	D / (48)	75	 **14**
		E / (22)	92	
		F / (22)	[c]	
2	 **7**	D / (48)	70	 **15**
		E / (20)	95	
		F / (12)	30	
3	 **8**	D / (10)	35	 **16**
		E / (6)	91	
		F / (11)	87	
4	 **9**	D / (48)	[c]	 **17** **17´**
		E / (20)	70[d]	
		F / (72)	[c]	
5	 **10**	D / (48)	[c]	 **18** **18´**
		E / (20)	20[d]	
		F / (72)	[c]	
6	 **11**	D / (48)	[c]	----------
		E / (20)	[c]	
		F / (72)	[c]	
7	 **12**	D / (48)	[c]	----------
		E / (20)	[c]	
		F / (72)	[c]	

[a] Method D: CH_2Cl_2, $AlCl_3$, -78 ºC; Method E: PhH, hydroquinone, 80 ºC; Method F: PhH, hydroquinone, 40 ºC, ultrasound. [b] After chromatographic purification. [c] Starting material was recovered. [d] As a mixture of two regioisomers

The value of $^3J_{(Sn,C)}$ = 53.8 Hz among the trineophyltin group attached to C_8 and the carbonyl group (C_6) indicated a dihedral angle close to 150º. Following the same analysis as before, $^3J_{(H,H)}$ coupling constant value between H_2 and H_7 of 3.0 Hz supported a *cis* conformation.

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In this case, both Methods E and F gave **16** in 91 and 87% yield, respectively. When the reaction was performed using acrylonitrile as the starting dienophile **9** (entry 4, Table 1), and benzene and hydroquinone were used (Method E) the formation of two adducts was observed in a 7.3:1 ratio, respectively according to ^{119}Sn spectra of the crude product. Only starting material was recovered under the other two reaction conditions. Column chromatography purification was very difficult because of the very similar interaction of both adducts with silica gel or alumina.

However, 4-trineophylstannylbicyclo[4.4.0]dec-5-en-2-yl cyanide **17** could be isolated and for **17´** characterization of an enriched mixture was used. Analysis of the ^{1}H and ^{13}C NMR spectra showed that the "*meta"* adduct **17** was the predominant regioisomer and the *"ortho"* adduct, 4-trineophylstannylbicyclo[4.4.0]dec-5-en-3-yl cyanide **17´** was the minor one. The conclusions about each structure were based on the fact that there was a CH_2 signal at 34.13 ppm with $^{2}J_{(Sn,C)}$ of 10.3 Hz coupling constant value in the case of **17** and a CH signal at 39.26 ppm with $^{2}J_{(Sn,C)}$ of 11.2 Hz for **17´**. Furthermore, there was a $^{3}J_{(Sn\text{-}C\text{-}C\text{-}CN)}$ of 24.7 Hz that was consistent with a dihedral angle of about 120º indicating a *trans* relation between the nitrile group and the tin moiety in compound **17´**. The absence of any coupling constant between the same groups in **17**, supported the *meta* arrangement proposed for this adduct. Nevertheless, *α*-substituted dienophiles gave very different results. Only a 20% yield was observed in the cycloaddition reaction when methyl 2-methylacrilate was used **10** (entry 5, Table 1). Under the conditions fixed by Method E (benzene/hydroquinone), a mixture of two regioisomers, methyl 2-methyl-4-trineophylstannylbicyclo [4.4.0]dec-5-ene-2-carboxylate **18** and methyl 3-methyl-4-trineophylstannylbicyclo[4.4.0]dec-5-ene-3-carboxylate **18´** were obtained in a 3 : 1 ratio, respectively according to the ^{119}Sn NMR spectrum of the crude product. No reaction was detected in other cases (Method D and F, see Table 1). Purification by column chromatography on silica-gel 60 only gave enriched fractions of each adduct and according to their spectral data (^{1}H and ^{13}C) we were able to analyze their possible structures. The absence of the ^{3}J coupling constant between the trineophyltin group and the carbonyl group in **18** possibly indicated that, once again, the major product was the "*meta"* adduct. While, the observed $^{3}J_{(Sn,C=O)}$ = 12.3 Hz, corresponding to a dihedral angle close to 110º, supported a *trans* relation between the carboximethyl group and the tin moiety in the *"ortho"* adduct **18´**.

Comparing methyl acrylate **6** with methyl-2-methylacrylate **10**, the methyl group in C_2 seems to change dramatically the yield of the reaction (entries 1 and 5, Table 1) probably due to both steric hindrance and the weak electron-releasing capacity of this group that diminished the electron-withdrawing effect of the carbonyl moiety. It is important to note that no cycloaddition product at all was obtained in the reactions conducted with dienophiles **11** and **12** (entry 6 and 7, Table 1). Presumably and in spite of the conjugating effect of the phenyl group, there was an important steric factor that prevented the reaction.

Taking into account that allyltin compounds can be used as Stille coupling substrates,[9] we tested the cited reaction with compound **14** and **16** and three substituted aryl halides: 4-iodo-anisole, 2-bromopyridine and 2-bromo-6-methylquinoline (Scheme 5) according to previous experimental reaction conditions.[10] New compounds **19-24** were purified by column

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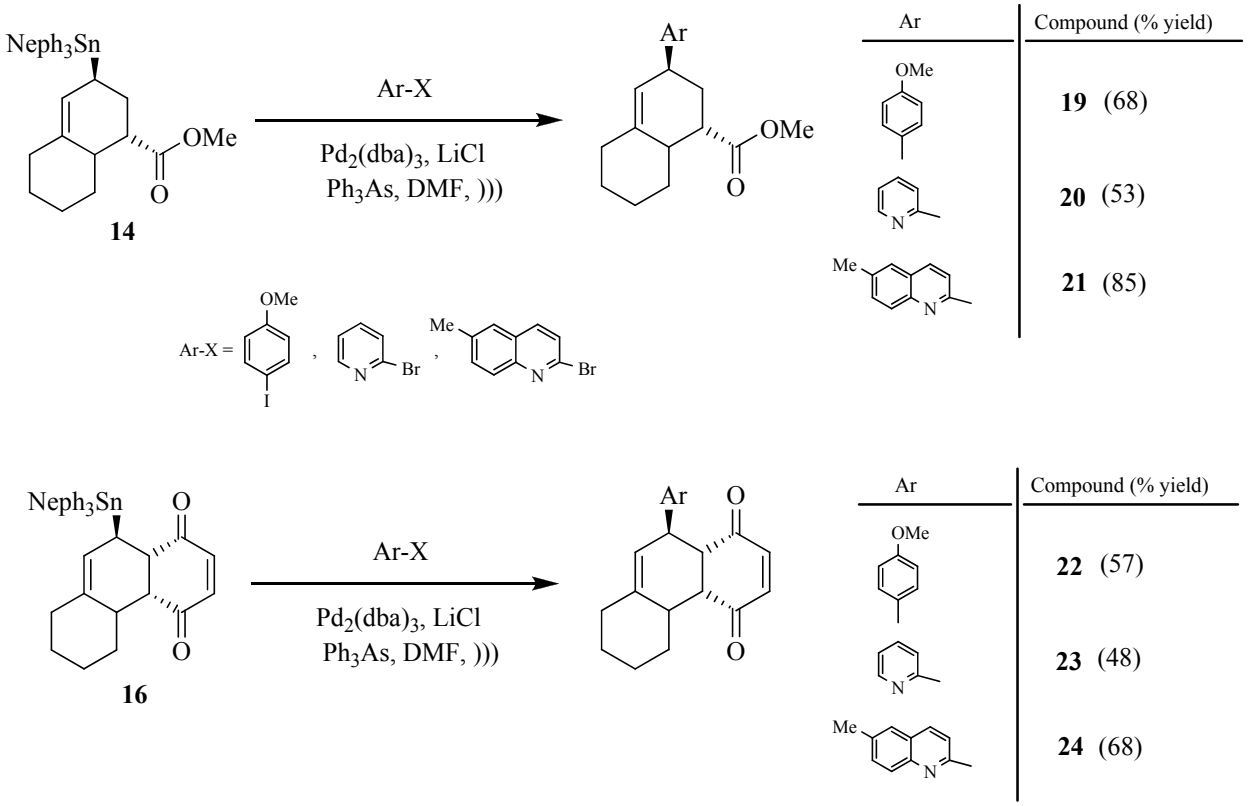
chromatography and obtained in moderate to good yields (48-85%). The stationary phase (neutral alumina) was previously treated with with 10% KF to retain the trineophyltinhalides formed in the reaction. From the NMR spectra of these compounds, it seemed that there was absolute retention of configuration in the carbon attached to the new aryl moiety.



Scheme 5. Stille coupling between **14** and **16** with some substituted aryl halides.

From these studies, we showed that, in the presence of suitably activated dienophiles, it was possible to carry out "one-pot hydrostannation Diels-Alder" reactions to obtain allylstannyl compounds in very high yields that were easily purified by column chromatography. These allylstannyl substrates are important precursor intermediates for Stille coupling reactions leading to bicyclic aryl compounds. In view of these preliminary results, we intend to optimize the method (improve yields and reaction time) with the aim of generalizing the Stille coupling for substrates **14** and **16**.

Experimental Section

General. All reactions were carried out under argon or nitrogen atmosphere. ^{1}H, ^{13}C, COSY and ^{119}Sn NMR spectra were recorded on a Bruker ARX 300 Multinuclear instrument and calibrated

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by using signals from solvents referenced to $SiMe_4$ (^1H, ^{13}C, COSY) and with respect to Me_4Sn in the case of ^{119}Sn-NMR spectra and chemical shifts are reported in ppm. Infrared spectra were recorded with a Nicolet Nexus FT spectrometer. The reactions under ultrasonic conditions were performed in an ULTRASONIC 104X bath. Elemental analyses (C, H) were performed in an EXETER CE-440 instrument at UMYMFOR (Argentina). High-resolution mass spectra (HRMS) were recorded on a BRUKER micrOTOF-Q II spectrometer (HR-ESI-MS) at UMYMFOR (Argentina). Melting points were determined with a Koefler Hot-Stage apparatus and are uncorrected. All the solvents and reagents were analytical grade. Solvents were dried using standard procedures. Trineophyltin hydride was prepared as described previously.[11]

Addition of trineophyltin hydride (2) to 1-ethynylcyclohexene (1) under radical conditions. General synthetic procedure. Synthesis of (*Z*)-2-(1-cyclohexenyl)-1-ethenyl(trineophyl) stannane (3)

Method A. 1-Ethynylcyclohexene **1**, (0.405 mL, 2.5 mmol) was treated for 1 h. with trineophyltin hydride **2** (1.305 g, 2.5 mmol) under nitrogen atmosphere at 75 ºC and with AIBN as a catalyst (this optimal time of reaction was monitored by taking samples and observing the disappearance of the Sn-H absorption by IR and products formation by ^1H NMR). The ^{119}Sn NMR spectrum of the crude product showed that only adduct **3** was obtained in quantitative yield as a colorless oil that was used without further purification. ^1H NMR (300 MHz, $CDCl_3$) δ_H 1.35 (s, 6H), 1.51 (s, 18H), 1.80-1.97 (m, 4H), 2.27 (m, 2H), 2.35 (m, 2H), 5.57 (d, 1H, $^3J_{(H,H)}$ 13.4 Hz), 5.77 (m, 1H), 6.91 (d, 1H, $^3J_{(H,H)}$ 13.5 Hz, $^3J_{(Sn,H)}$ 151.3 Hz), 7.61-7.36 (m, 15H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 22.7, 23.1, 26.0, 28.6, 33.1 ($^1J_{(Sn,C)}$ 332.2 Hz), , 33.5 ($^3J_{(Sn,C)}$ 34.0 Hz), , 38.7 ($^2J_{(Sn,C)}$ 18.8 Hz), 125.3, 125.8 ($^2J_{(Sn,C)}$ 7.10 Hz), 125.9, 128.5, 130.3 ($^1J_{(Sn,C)}$ 372.2 Hz), 139.9 ($^3J_{(Sn,C)}$ 28.2 Hz), 148.7, 152.1 ($^3J_{(Sn,C)}$ 24.1 Hz); ^{119}Sn NMR (111.8 MHz, $CDCl_3$): δ_{Sn} -89.69 ppm; HR-MS (EI): calcd for $C_{38}H_{50}Sn$ 625.5136, found 625.5139. Anal. Calcd for $C_{38}H_{50}Sn$: C, 72.9; H, 8.4. Found: C, 72.8; H, 8.3%.

Method B. 1-Ethynylcyclohexene **1**, (0.405 mL, 2.5 mmol), was treated with trineophyltin hydride **2** (1.305 g, 2.5 mmol) and AIBN as a catalyst under argon atmosphere in an ultrasonic bath during 40 min. The reaction was monitored as mentioned above. The ^{119}Sn NMR spectrum of the crude product showed that only adduct **3** was obtained in quantitative yield as a colorless oil that was used without further purification.

Addition of trineophylstannyl hydride (2) to 1-ethynylcyclohexene (1) catalyzed by bis(triphenylphosphine)palladium(II) chloride. Synthesis of (*E*)-2-(1-cyclohexenyl)-1-ethenyl(trineophyl)stannane (4) and 1-(1-cyclohexenyl)vinyl(trineophyl)stannane (5)

Method C. To a solution of 1-ethynylcyclohexene **1** (0.405 mL, 2.5 mmol) and bis(triphenylphosphine)palladium(II) chloride (0.07 g; 0.05 mmol) in dry THF (7 mL) under nitrogen atmosphere was added trineophylstannyl hydride **2**, (1.305 g; 2.5 mmol), and the mixture was stirred at room temperature during 45 min. Dry hexane (10 mL) was added and cooled over 10 min at 0 ºC. The resultant residue of catalyst was filtered through porous plate and the solvent was distilled off under reduced pressure. The ^{119}Sn NMR spectrum showed two

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signals corresponding to adducts **4** and **5** in a ratio 7:3, respectively. The mixture of isomers could not be separated. However, enriched mixtures of **4** and **5** obtained by column chromatography on silica gel 60 eluted with 9:1 (hexane/Et_2O) were used for structural analysis. **Compound (4).** ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 1.10 (s, 2H, $^2J_{(Sn,H)}$ 12.2 Hz), 1.29 (s, 18H), 2.05-1.96 (m, 4H), 2.27-2.06 (m, 4H), 5.50 (d, 1H, $^3J_{(H,H)}$ 19.1, $^3J_{(Sn,H)}$ 76.4 Hz), 5.70 (t, 1H, $^3J_{(H,H)}$ 7.0 Hz), 6.28 (d, 1H, $^3J_{(H,H)}$ 19.1 Hz, $^3J_{(Sn,H)}$ 69.8 Hz), 7.61-7.06 (m, 15H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 23.0, 23.2, 24.3, 26.3, 32.3 ($^1J_{(Sn,C)}$ 321.4 Hz), 33.5 ($^3J_{(Sn,C)}$ 34.2 Hz), 38.6 ($^2J_{(Sn,C)}$ 17.6 Hz), 125.8, 126.0, 127.3 ($^1J_{(Sn,C)}$ 411.6 Hz), 129.2, 128.4, 148.3 ($^2J_{(Sn,C)}$ 11.2 Hz), 152.1 ($^3J_{(Sn,C)}$ 24.8 Hz), 159.0 ($^3J_{(Sn,C)}$ 74.0 Hz); ^{119}Sn NMR (111.8 MHz, $CDCl_3$): δ -80.37 ppm. **Compound (5).** ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 1.16 (s, 2H, $^2J_{(Sn,H)}$ 13.4 Hz), 1.27 (s, 18H), 2.05-1.96 (m, 4H), 2.27-2.06 (m, 4H), 5.18 (d, 1H, $^2J_{(H,H)}$ 2.3 Hz, $^3J_{(Sn,H)}$ 67.5 Hz), 5.35 (t, 1H, $^3J_{(H,H)}$ 8.0 Hz), 5.76 (d, 1H, $^2J_{(H,H)}$ 2.0 Hz), 7.61-7.06 (m, 15H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 23.0, 23.4, 26.1, 27.9 ($^3J_{(Sn,C)}$ 17.4 Hz), 31.9 ($^1J_{(Sn,C)}$ 336.0 Hz), 33.5 ($^3J_{(Sn,C)}$ 34.4 Hz), 38.5 ($^2J_{(Sn,C)}$ 18.6 Hz), 123.4 ($^2J_{(Sn,C)}$ 28.2 Hz), 125.8, 125.9, 127.0 ($^3J_{(Sn,C)}$ 26.9 Hz), 128.4, 138.2 ($^2J_{(Sn,C)}$ 34.4 Hz), 141.6 ($^1J_{(Sn,C)}$ 310.4 Hz), 151.9 ($^3J_{(Sn,C)}$ 22.2 Hz); ^{119}Sn NMR (111.8 MHz, $CDCl_3$): δ_{Sn} -81.50 ppm.

"One pot" cycloaddition reaction between 3 and activated dienophiles. General synthetic procedure. Synthesis of 4-trineophylstannyl-1,3,3a,4,6,7,8,9,9a,9b-decahydrobenzo[e]iso benzofuran-1,3-dione (15)

Method D. In the same flask where stannyl diene **3** (1.56 g; 2.5 mmol) was obtained as mentioned above, dry dichloromethane (4.5 mL) was added and the solution was cooled to -78 °C in argon atmosphere. Aluminum trichloride (0.07 g; 0.5 mmol) and maleic anhydride (0.25 g; 2.5 mmol) were added. The resulting mixture was allowed to warm to 0 °C over a period of 1 h and left stirring 48 h. at room temperature. Then, the reaction mixture was poured into water (10 mL) and extracted with dichloromethane (3 × 15 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography with silica-gel 60 and pure compound **15** eluted with 95:5 (hexane/Et_2O) as a clear yellow oil. (1.75 mmol; 70%). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 0.94 (s, 6H, $^2J_{(Sn,H)}$ 30.7 Hz), 1.14 (s, 18H), 1.68 (dd, 1H, $^3J_{(H,H)}$ 8.7 Hz), , 1.78-1.55 (m, 6H), 1.92 (td, 2H, $^3J_{(H,H)}$ 12.4 Hz, $^3J_{(H,H)}$ 3.6 Hz), 2.08 (m, 1H), 2.10 (dd, 1H, $^3J_{(H,H)}$ 8.6Hz, $^3J_{(H,H)}$ 2.3 Hz), 2.73 (dd, 1H, $^3J_{(H,H)}$ 8.7Hz, $^3J_{(H,H)}$ 2.3Hz), 5.00 (d, 1H, $^3J_{(H,H)}$ 5.4 Hz, $^3J_{(Sn,H)}$ 17.8 Hz), 7.36-6.93 (m, 15H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 25.6, 26.4, 30.5, 30.6 ($^1J_{(Sn,C)}$ 298.1 Hz), 32.4 ($^1J_{(Sn,C)}$ 233.0 Hz), 32.7, 32.8 ($^3J_{(Sn,C)}$ 40.4 Hz), 35.2, 37.1 ($^2J_{(Sn,C)}$ 19.4 Hz), 40.3 ($^2J_{(Sn,C)}$ 13.6 Hz), 42.5 ($^3J_{(Sn,C)}$ 46.6 Hz), 120.3 ($^2J_{(Sn,C)}$ 33.5 Hz), 124.2, 125.0, 127.4, 131.6 ($^3J_{(Sn,C)}$ 42.3 Hz), 149.9 ($^3J_{(Sn,C)}$ 14.1 Hz), 170.6, 173.3 ($^3J_{(Sn,C)}$ 64.6 Hz); ^{119}Sn NMR (111.8 MHz, $CDCl_3$): δ_{Sn} -32.15 ppm; HR-MS (EI): calcd for $C_{42}H_{52}O_3Sn$ 723.5782, found 723.5789. Anal. Calcd for $C_{42}H_{52}O_3Sn$: C, 69.7; H, 7.5. Found: C, 69.7; H, 7.6%.

Method E. Over a solution of **3** (1.56 g; 2.5 mmol) and dry benzene (4.5 mL) in argon atmosphere, *p*-hydroquinone (20 mg, 0.18 mmol) and maleic anhidride (0.25 g; 2.5 mmol) were

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added. The solution was heated at 80 °C for 20 h, the solvent was removed *in vacuo* and the product was isolated by column chromatography with neutral aluminum oxide and compound **15** eluted with 95:5 (hexane/Et_2O), 2.38 mmol; 95%.

Method F. Over a solution of **3** (1.56 g; 2.5 mmol) and dry benzene (4.5 mL) in argon atmosphere in an ultrasonic bath, *p*-hydroquinone (20 mg, 0.18 mmol) and maleic anhydride (0.25 g; 2.5 mmol) were added. The temperature was maintained below 40 °C for 12 h. The solvent was distilled off under reduced pressure and product **15** was isolated as mentioned above (0.75 mmol; 30%).

Methyl-4-trineophylstannylbicyclo[4.4.0]dec-5-ene-2-carboxylate (14). Yellowish oil. ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 0.90 (s, 6H, $^3J_{(Sn,H)}$ 37.5 Hz), 1.32-1.29 (m, 2H), 1.10 (s, 18H), 1.37-1.30 (m, 2H), 1.78-1.59 (m, 3H), 1.87 (dd, 2H, $^3J_{(H,H)}$ 5.2 Hz, $^3J_{(H,H)}$ 5.3 Hz), 1.93 (t, 2H, $^3J_{(H,H)}$ 12.4 Hz), 2.23 (dt, 1H, $^3J_{(H,H)}$ 2.8 Hz, $^3J_{(H,H)}$ 5.7 Hz), 2.43 (dt, 1H, $^3J_{(H,H)}$ 2.8 Hz, $^3J_{(H,H)}$ 5.7 Hz), 3.62 (s, 3H), 4.97 (d, 1H, $^3J_{(H,H)}$ 5.6 Hz, $^3J_{(Sn,H)}$ 49.5 Hz), 7.25-6.98 (m, 15H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 24.4 ($^2J_{(Sn,C)}$ 15.2 Hz), 25.9, 27.31, 27.8 ($^1J_{(Sn,C)}$ 369.2 Hz,), 29.6 ($^1J_{(Sn,C)}$ 284.7 Hz), 29.9, 31.0 ($^3J_{(Sn,C)}$ 34.0 Hz), 31.3 ($^3J_{(Sn,C)}$ 34.6 Hz), 35.4, 37.1 ($^2J_{(Sn,C)}$ 18.2 Hz), 38.5 ($^3J_{(Sn,C)}$ 12.0 Hz), 42.6 ($^3J_{(Sn,C)}$ 11.2 Hz), 51.5, 122.5 ($^2J_{(Sn,C)}$ 37.6 Hz), 124.4, 124.4, 127.1, 135.3 ($^3J_{(Sn,C)}$ 46.7 Hz), 150.3 ($^3J_{(Sn,C)}$ 17.6 Hz), 175.4, ^{119}Sn NMR (111.8 MHz, $CDCl_3$): δ_{Sn} -46.25 ppm. HR-MS (EI): calcd for $C_{42}H_{56}O_2Sn$ 711.6063, found 711.6059. Anal. Calcd for $C_{42}H_{56}O_2Sn$: C, 70.8; H, 8.3. Found: C, 70.6; H, 8.2%.

8-Trineophylstannyltricyclo[8.4.0.0^{2,7}]tetradeca-4,9-diene-3,6-dione (16). Yellow oil. ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 0.99 (s, 6H, $^3J_{(Sn,H)}$ 30.0 Hz), 1.18 (s, 18H), 1.68 (m, 2H), 1.65-1.63 (m, 4H), 1.95 (t, 2H, ($^3J_{(H,H)}$ 10.8 Hz), 2.22 (d, 1H, $^3J_{(H,H)}$ 5.9 Hz), 2.34 (dd, 1H, $^3J_{(H,H)}$ 6.8Hz, $^3J_{(H,H)}$ 3.0 Hz), 2.51 (dd, 1H, $^3J_{(H,H)}$ 5.3Hz, $^2J_{(Sn,H)}$ 73.1 Hz), 3.09 (dd, 1H, $^3J_{(H,H)}$ 6.8 Hz, $^3J_{(H,H)}$ 3.1 Hz), 5.13 (d, 1H, $^3J_{(H,H)}$ 5.4 Hz), 6.49 (d, 1H, $^3J_{(H,H)}$ 10.3 Hz), 6.59 (d, 1H, $^3J_{(H,H)}$ 10.3 Hz), 7.42-6.97 (m, 15H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 24.1 ($^1J_{(Sn,C)}$ 267.3 Hz), 27.2, 27.9, 29.3, 31.5 ($^1J_{(Sn,C)}$ 293.3 Hz), 34.1 ($^3J_{(Sn,C)}$ 36.7 Hz), 37.1, 38.4 ($^2J_{(Sn,C)}$ 18.5 Hz), 40.1 ($^2J_{(Sn,C)}$ 12.3 Hz), 47.7, 51.0 ($^3J_{(Sn,C)}$ 16.4 Hz), 125.7, 126.2, 128.8, 121.7 ($^2J_{(Sn,C)}$ 36.5 Hz), 133.9 ($^3J_{(Sn,C)}$ 44.2 Hz), 140.6, 142.1, 151.3 ($^3J_{(Sn,C)}$ 15.0 Hz), 199.6 ($^3J_{(Sn,C)}$ 53.8 Hz), 202.7; ^{119}Sn NMR (111.8 MHz, $CDCl_3$): δ_{Sn} -39.77 ppm. HR-MS (EI): calcd for $C_{44}H_{54}O_2Sn$ 733.6083, found 733.6072. Anal. Calcd for $C_{44}H_{54}O_2Sn$: C, 72.0; H, 7.7. Found: C, 71.8; H, 7.5%.

4-Trineophylstannylbicyclo[4.4.0]dec-5-en-2-yl cyanide (17). Yellowish oil. ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 0.90 (s, 6H, $^2J_{(Sn,H)}$ 43.1 Hz), 1.10 (s, 18H), 1.66-1.60 (m, 2H), 1.52-1.58 (m, 2H), 1.70-1.68 (m, 2H), 1.82-1.71 (m, 4H), 2.14 (dd, 2H, $^3J_{(H,H)}$ 16.0 Hz, $^3J_{(H,H)}$ 14.5 Hz), 2.64 (dt, 1H, $^3J_{(H,H)}$ 4.8 Hz, $^3J_{(H,H)}$ 11.0 Hz), 5.03 (d, 1H, $^3J_{(Sn,H)}$ 28.6 Hz, $^3J_{(H,H)}$ 3.5 Hz), 7.26-6.99 (m, 15H), ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 24.8, 25.9, 27.5, 29.5 ($^1J_{(Sn,C)}$ 300.8 Hz), 31.2 ($^1J_{(Sn,C)}$ 246.4 Hz), 30.4, 32.0, 32.4 ($^3J_{(Sn,C)}$ 35.0 Hz), 32.5 ($^3J_{(Sn,C)}$ 35.0 Hz), 34.1 ($^2J_{(Sn,C)}$ 10.3 Hz), 36.8 ($^3J_{(Sn,C)}$ 11.8 Hz), 36.9 ($^2J_{(Sn,C)}$ 18.2 Hz), 119.9, 123.2 ($^2J_{(Sn,C)}$ 33.2 Hz), 124.3, 124.6, 127.2, 132.2 ($^3J_{(Sn,C)}$ 43.2 Hz), 150.1 ($^3J_{(Sn,C)}$ 17.2 Hz); ^{119}Sn NMR (111.8 MHz, $CDCl_3$): δ_{Sn} -38.80 ppm. HR-MS (EI): calcd for $C_{41}H_{53}NSn$ 679.1538, found 679.1525. Anal. Calcd for $C_{41}H_{53}NSn$: C, 72.4; H, 7.9. Found: C, 72.3; H, 7.7%.

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4-Trineophylstannylbicyclo[4.4.0]dec-5-en-3-yl cyanide (17′). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 0.87 (s, 6H, $^{2}J_{(Sn,H)}$ 42.3 Hz), 1.11 (s, 18H), 1.42-1.22 (m, 4H), 1.78-1.56 (m, 3H), 2.29-1.89 (m, 4H), 2.64 (tt, 1H, $^{3}J_{(H,H)}$ 6.0Hz, $^{3}J_{(H,H)}$ 11.4 Hz), 2.86 (dt, 1H, $^{3}J_{(H,H)}$ 6.4 Hz, $^{3}J_{(H,H)}$ 12.8 Hz), 4.99 (d, 1H, $^{3}J_{(Sn,H)}$ 36.2 Hz, $^{3}J_{(H,H)}$ 3.4 Hz), 7.41-6.86 (m, 15H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 25.4, 26.7, 28.4, 29.4 ($^{1}J_{(Sn,C)}$ 328.9 Hz), 32.4 ($^{3}J_{(Sn,C)}$ 34.6 Hz), 32.5 ($^{3}J_{(Sn,C)}$ 34.6 Hz), 34.7 ($^{3}J_{(Sn,C)}$ 11.7 Hz), 34.8 ($^{1}J_{(Sn,C)}$ 239.0 Hz), 35.0, 36.9 ($^{2}J_{(Sn,C)}$ 19.4 Hz), 39.3 ($^{2}J_{(Sn,C)}$ 11.2 Hz), 39.6, 119.8 ($^{3}J_{(Sn,C)}$ 24.7 Hz), 122.8 ($^{2}J_{(Sn,C)}$ 31.7 Hz), 125.2, 125.5, 128.0, 134.4 ($^{3}J_{(Sn,C)}$ 41.1 Hz), 151.0 ($^{3}J_{(Sn,C)}$ 16.4 Hz); ^{119}Sn NMR (111.8 MHz, $CDCl_3$): δ_{Sn} -37.72 ppm.

Methyl-2-methyl-4-trineophylstannylbicyclo[4.4.0]dec-5-ene-2-carboxilate (18). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 0.88 (s, 6H), 1.04 (m, 1H), 1.08 (s, 18H), 1.32 (d, 2H), 1.49 (s, 3H), 1.63-1.42 (m, 6H), 1.98 (t, 2H, $^{3}J_{(H,H)}$ 11.6 Hz), 2.16 (t, 1H, $^{3}J_{(H,H)}$ 13.9 Hz), 3.52 (s, 3H), 5.15 (d, 1H, $^{3}J_{(H,H)}$ 6.1 Hz, $^{3}J_{(Sn,H)}$ 36.1 Hz), 7.25-7.13 (m, 15H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 24.3, 24.9, 25.8, 26.7, 29.2 ($^{1}J_{(Sn,C)}$ 292.9 Hz), 33.5 ($^{3}J_{(Sn,C)}$ 34.6 Hz), 34.3, 36.9 ($^{2}J_{(Sn,C)}$ 18.2 Hz), 37.1 ($^{2}J_{(Sn,C)}$ 10.6 Hz), 41.4, 41.5 ($^{1}J_{(Sn,C)}$ 245.9 Hz), 44.3 ($^{3}J_{(Sn,C)}$ 16.9 Hz), 51.7, 122.4 ($^{3}J_{(Sn,C)}$ 34.1 Hz), 124.4, 124.5, 127.1, 133.5, 150.5 ($^{3}J_{(Sn,C)}$ 18.6 Hz), 174.7; ^{119}Sn NMR (111.8 MHz, $CDCl_3$): δ_{Sn} -36.43 ppm.

Methyl-3-methyl-4-trineophylstannylbicyclo[4.4.0]dec-5-ene-3-carboxilate (18′). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 0.85 (s, 6H), 1.07 (m, 2H), 1.08 (s, 18H), 1.49 (s, 3H), 1.63-1.52 (m, 6H), 1.91-1.80 (m, 1H), 1.98 (t, 2H, $^{3}J_{(H,H)}$ 11.6 Hz), 2.40 (d, 1H, $^{3}J_{(H,H)}$ 10.0 Hz), 3.59 (s, 3H), 4.93 (d, 1H, $^{3}J_{(H,H)}$ 5.7 Hz, $^{3}J_{(Sn,H)}$ 37.0 Hz), 7.12-6.96 (m, 15H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 23.4, 25.6, 26.0, 27.3, 30.1 ($^{1}J_{(Sn,C)}$ 292.8 Hz), 33.4 ($^{3}J_{(Sn,C)}$ 34.0 Hz), 34.3, 36.9 ($^{2}J_{(Sn,C)}$ 18.2 Hz), 38.1, 44.3 ($^{2}J_{(Sn,C)}$ 9.8 Hz), 45.1, 49.9 ($^{1}J_{(Sn,C)}$ 245.3 Hz), 50.9, 121.6 ($^{3}J_{(Sn,C)}$ 32.9 Hz), 124.4, 124.5, 127.1, 133.5, 150.4 ($^{3}J_{(Sn,C)}$ 18.6 Hz), 178.1 ($^{3}J_{(Sn,C)}$ 12.3 Hz); ^{119}Sn NMR (111.8 MHz, $CDCl_3$): δ_{Sn} -40.48 ppm.

Stille coupling of methyl-4-trineophylstannylbicyclo[4.4.0]dec-5-ene-2-carboxylate (14) with 4-iodoanisole. General synthetic procedure

Synthesis of methyl 4-(4-methoxy-phenyl)bicyclo[4.4.0]dec-5-ene-2-carboxylate (19). A solution of **14** (0.15 g, 0.2 mmol), $Pd_2(dba)_3$ (3 mg, 0.005 mmol), Ph_3As (3 mg, 0.01 mmol), LiCl (12.5 mg, 0.3 mmol), 4-iodoanisole (24 mg, 0.2 mmol) and DMF (0.4 mL) under argon atmosphere was maintained in an ultrasonic bath. After 18 h the reaction was complete and no starting product was observed by TLC (SiO_2). The crude product was filtered through celite to separate the inorganic insolubles salts together with the catalyst. The solvent was distilled off under reduced pressure and product **19** was isolated by column chromatography with alumina treated with 10% of KF to retain trineophyltinhalides formed during the reaction. **19** eluted with 98:2 (hexane/Et_2O) as clear yellowish oil. (36 mg, 68%). IR (ν_{max} cm^{-1}): 1744 (C=O); ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 1.46-1.50 (4H, m), 1.61 (2H, m), 2.02-2.08 (2H, m), 2.23 (dt, 1H, $^{3}J_{(H,H)}$ 2.7 Hz, $^{3}J_{(H,H)}$ 5.8 Hz), 2.50 (2H, dd, $^{3}J_{(H,H)}$ 5.1 Hz, $^{3}J_{(H,H)}$ 5.2 Hz), 2.65 (dt, 1H, $^{3}J_{(H,H)}$ 2.6 Hz, $^{3}J_{(H,H)}$ 5.4 Hz), 3.39 (dt, 1H, $^{3}J_{(H,H)}$ 3.4 Hz, $^{3}J_{(H,H)}$ 5.9 Hz), 3.63 (s, 3H), 3.66 (s, 3H), 5.55 (d, 1H, $^{3}J_{(H,H)}$ 3.5 Hz), 6.96-7.15 (m, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 26.4, 27.2, 28.8, 30.6, 35.8,

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38.1, 45.8, 46.9, 50.3, 54.7, 112.8, 126.3, 129.6, 140.1, 142.8, 158.4, 174.6; Anal. Calcd for $C_{19}H_{24}O_3$ (300.1725) C, 76.0; H, 8.1. Found: C, 75.9; H, 8.0%.

Methyl 4-(2-pyridyl)bicyclo[4.4.0]dec-5-ene-2-carboxylate (20). Yellowish oil. Yield: 53%. IR (ν_{max} cm^{-1}): 1746 (C=O); ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 1.47-1.52 (4H, m), 1.63 (2H, m), 2.05-2.09 (2H, m), 2.51 (dd, 2H, $^3J_{(H,H)}$ 5.0 Hz, $^3J_{(H,H)}$ 5.2 Hz), 2.63 (dt, 1H, $^3J_{(H,H)}$ 1.9 Hz, $^3J_{(H,H)}$ 6.3 Hz), 2.68 (dt, 1H, $^3J_{(H,H)}$ 1.9 Hz, $^3J_{(H,H)}$ 5.4 Hz), 3.37 (dt, 1H, $^3J_{(H,H)}$ 3.5 Hz, $^3J_{(H,H)}$ 5.8 Hz), 3.66 (s, 3H), 5.56 (d, 1H, $^3J_{(H,H)}$ 3.5 Hz), 7.06-7.46 (m, 3H), 8.46 (d, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 26.6, 27.0, 28.9, 30.6, 35.9, 42.2, 43.5, 46.9, 50.3, 120.4, 121.7, 128.0, 135.8, 141.3, 149.5, 162.3, 174.7; Anal. Calcd for $C_{17}H_{21}NO_2$ (271.1572) C, 75.3; H, 7.8; N, 5.2. Found: C, 75.3; H, 7.9; N, 5.0%.

Methyl 4-(6-methyl-2-quinolyl)bicyclo[4.4.0]dec-5-ene-2-carboxylate (21). Yellowish oil. Yield: 85%. IR (ν_{max} cm^{-1}): 1741 (C=O); ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 1.46-1.50 (4H, m), 1.62 (2H, m), 2.04-2.10 (2H, m), 2.35 (s, 3H), 2.52 (dd, 2H, $^3J_{(H,H)}$ 4.9 Hz, $^3J_{(H,H)}$ 5.2 Hz), 2.65 (dt, 1H, $^3J_{(H,H)}$ 1.9 Hz, $^3J_{(H,H)}$ 6.0 Hz), 2.67 (dt, 1H, $^3J_{(H,H)}$ 1.9 Hz, $^3J_{(H,H)}$ 5.3 Hz), 3.35 (dt, 1H, $^3J_{(H,H)}$ 3.6 Hz, $^3J_{(H,H)}$ 5.9 Hz), 3.67 (s, 3H), 5.37 (d, 1H, $^3J_{(H,H)}$ 3.6 Hz), 7.25-7.57 (m, 4H), 7.78 (d, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 21.4, 26.4, 27.2, 27.6, 28.8, 35.8, 42.2, 43.3, 46.9, 50.3, 120.13, 126.4, 128.0, 128.1, 129.9, 131.5, 135.2, 135.3, 141.3, 149.5, 160.8, 174.6; Anal. Calcd for $C_{22}H_{25}NO_2$ (335.1885) C, 78.8; H, 7.5; N, 4.2. Found: C, 78.7; H, 7.6; N, 4.2%.

8-(4-Methoxyphenyl)tricyclo[8.4.0.0^{2,7}]tetradeca-4,9-diene-3,6-dione (22). Clear yellowish oil. Yield: 57%. IR (ν_{max} cm^{-1}): 1686 and 1666 (C=O); ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 1.50 (2H, m), 1.60 (2H, m), 1.82 (2H, m), 2.24 (2H, t, $^3J_{(H,H)}$ 6.8 Hz), 2.96 (1H, m,), 3.38 (1H, m), 3.69 (1H, dd, $^3J_{(H,H)}$ 2.5 Hz, $^3J_{(H,H)}$ 11.5 Hz), 3.80 (3H, s), 4.16 (1H, dd, $^3J_{(H,H)}$ 3.5 Hz, $^3J_{(H,H)}$ 11.6 Hz), 5.65 (1H, d, $^2J_{(H,H)}$ 3.6 Hz), 6.47 (1H, d, $^3J_{(H,H)}$ 10.5 Hz), 6.56 (1H, d, $^3J_{(H,H)}$ 10.5 Hz), 6.97-7.17 (4H, m); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 25.8, 27.2, 29.8, 35.2, 43.8, 45.8, 48.0, 50.5, 51.1, 55.4, 121.1, 125.7, 126.0, 129.9, 137.3, 146.0, 147.1, 148.1, 159.3, 193.5, 193.4; Anal. Calcd. for $C_{21}H_{22}O_3$ (322.1569) C, 78.2; H, 6.9. Found: C, 78.2; H, 6.9%.

8-(2-Pyridyl)tricyclo[8.4.0.0^{2,7}]tetradeca-4,9-diene-3,6-dione (23). Clear yellowish oil. Yield: 48%. IR (ν_{max} cm^{-1}): 1681 and 1669 (C=O); ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 1.48 (2H, m), 1.59 (2H, m), 1.86 (2H, m), 2.22 (2H, t $^3J_{(H,H)}$ 6.5 Hz), 2.97 (1H, m), 3.38 (1H, m), 3.70 (1H, dd, $^3J_{(H,H)}$ 2.7 Hz, $^3J_{(H,H)}$ 11.6 Hz), 4.17 (1H, dd, $^3J_{(H,H)}$ 3.6 Hz, $^3J_{HH}$ = 11.6 Hz), 5.65 (1H, d, $^2J_{(H,H)}$ 3.6 Hz), 6.46 (1H, d, $^3J_{(H,H)}$ 10.6 Hz), 6.58 (1H, d, $^3J_{(H,H)}$ 10.6 Hz), 7.11-7.15 (3H, m), 8.58-8.60 (1H, m); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 25.8, 27.2, 29.8, 35.2, 43.8, 43.9, 44.4, 51.2, 120.1, 121.4, 128.5, 135.8, 145.2, 146.3, 147.4, 149.5, 160.5, 192.7, 193.9; Anal. Calcd. for $C_{19}H_{19}NO_2$ (293.1416) C, 77.8; H, 6.5; N, 4.8. Found: C, 77.8; H, 6.5; N, 4.7%.

8-(6-Methyl-2-quinolyl)tricyclo[8.4.0.0^{2,7}]tetradeca-4,9-diene-3,6-dione (24). Clear yellowish oil. Yield: 68%. IR (ν_{max} cm^{-1}): 1678 and 1667 (C=O). ^{1}H NMR (300.0 MHz, $CDCl_3$) δ_H 1.49 (2H, m), 1.58 (2H, m), 1.85 (2H, m), 2.15 (2H, t, $^3J_{(H,H)}$ 6.9 Hz), 2.59 (3H, s), 2.96 (1H, m), 3.37 (1H, m), 3.67 (1H, dd, $^3J_{(H,H)}$ 2.6 Hz, $^3J_{(H,H)}$ 11.5 Hz), 4.24 (1H, dd, $^3J_{(H,H)}$ 3.5 Hz, $^3J_{(H,H)}$ 11.5 Hz), 5.63 (1H, d, $^2J_{(H,H)}$ 3.7 Hz), 6.45 (1H, d, $^3J_{(H,H)}$ 10.5 Hz), 6.56 (1H, d, $^3J_{(H,H)}$ 10.5 Hz), 6.98-7.15 (4H, m), 7.90-8.01 (1H, m); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ_C 25.2, 25.8, 27.2, 29.8, 35.2,

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43.8, 45.8, 48.0, 51.1, 121.9, 123.5, 126.7, 128.4, 129.6, 130.0, 135.1, 142.9, 146.0, 147.4, 147.5, 148.1, 157.9, 193.4, 193.5. Anal. Calcd for $C_{24}H_{23}NO_2$ (357.4449) C, 80.6; H, 6.5; N, 3.9. Found: C, 80.6; H, 6.5; N, 3.9%.

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