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Palladium-catalyzed carbostannylation by means of reagents containing carbon–tin–halogen inter-element linkages

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Abstract

Reagents containing carbon–tin–halogen inter-element linkages were effective for palladium-catalyzed carbostannylation. In situ generated allyltin trichlorides add to carbon–carbon double bonds of bicyclo[2.2.1]hept-2-ene (norbornene) and bicyclo[2.2.1]hepta-2,5-diene (norbornadiene), stereoselectively, under the catalysis of palladium(0) species in good yields. The regioselectivity of unsymmetrically substituted allylic reagents dramatically alters with the choice of the tin(II) salt. Aryltin trichlorides undergo palladium-catalyzed arylstannylation of norbornene, giving a mixture of products composed of that taking one norbornene and that taking two norbornenes. The product ratio is dependent on the choice of the solvent and electronic nature of the aromatic substituent.

Keywords: Palladium and compounds; Allylation; Arylation; Alkenes; Tin and compounds

1. Introduction

Organotin reagents are useful because many of them possess fairly stable carbon–tin bonds that can be selectively activated by a variety of methods. Such properties have enabled a number of selective syntheses of complex organic molecules [1–3]. We have studied the utility of carbon–tin–halogen inter-element linkages and found that carbon–tin bonds are useful for palladium-catalyzed carbostannylation.

Carbometallation of alkenes is a useful two-carbon homologation of organometallics [4,5]. It is desirable to construct a carbon–tin bond according to this protocol. Nevertheless, carbostannylation has been a rather unexplored reaction, in comparison with many other carbometallations as well as extensively studied stannylmetallations. The carbostannylation reaction was first developed by Himbert, employing combinations of nucleophilic organotin reagents and alkynes that possess a π-accepting substituent [6]. Yamaguchi et al. have widened the scope of the reaction by developing stanna-oxa-ene-type reactions via in situ generation of nucleophilic trichlorotin enolates or analogs and electrophilic alkynyltin trichloride [7,8]. Yamamoto et al. reported a Lewis acid promoted allylstannylation of non-polar terminal alkynes [9]. All those reactions required electron-deficient alkynes as substrates and highly nucleophilic organotin compounds as the reagents. Recently, Shirakawa et al. have developed transition metal-catalyzed carbostannylations of alkynes with 1-alkynyl-, 1-alkenyl-, and allyltributyltin reagents [10–12]. They realized the reaction of neutral 1-alkynyl- and 1-alkenyltin reagents by the development of electron-accepting ligands on palladium [10,11,13,14]. Unlike alkyne carbostannylations, the alkene counterpart has seldom been explored [7]. We developed a palladium-catalyzed novel stereoselective carbostannylation of norbornene utilizing an organotin reagent containing carbon–tin–halogen inter-element linkages. The present reaction provides the first example of a palladium-catalyzed *cis*-carbostannylation of

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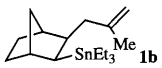
Table 1
Palladium-catalyzed carbostannylation of norbornene with allyl bromide–tin(II) chloride

Run	Solvent	Temperature (°C)	Time (h)	Yield (%) [a]
1	DMF	55	11.5	0
2	Dioxane	55	11.5	33
3	CH_2Cl_2	reflux	11.5	89
4	Toluene	55	3	98
5	Toluene	55	1	47
6	Toluene	rt	11	59
7	Toluene	rt	48	93

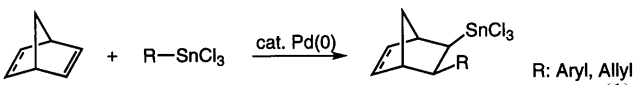
[a] Isolated yields based on tin(II) chloride used, assuming that 5 mol% is consumed to generate a catalytic Pd(0) species.

Table 2
Palladium-catalyzed carbostannylation of norbornene with allylic compounds

run	allylic compound	product	yield (%) [a]
1		**1a**	97
2		 **1b**	98
3		**1a**	59
4		**1a**	35

[a] Isolated yields.

non-polar carbon–carbon double bonds (Eq. (1)) [15,16].

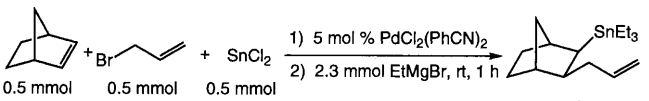


(1)

2. Results and discussion

2.1. Allylstannylation [15]

Masuyama et al. have demonstrated that allylic tin reagents can be generated in situ by treating various allylic compounds with tin(II) salts in the presence of a palladium catalyst [17,18]. Kurosawa et al. also reported on a detailed mechanistic study [19]. Following these precedents, we first attempted allylstannylation of norbornene via in situ generation of allyltin trihalide in DMF. Our first result was depressing, however. The desired adduct was not obtained at all. Nevertheless, further investigation revealed that the reaction is highly dependent on the choice of the solvent. Thus the effects of the solvent and temperature on the reaction between norbornene and the reagent derived from allyl bromide and tin(II) chloride were investigated. In order to facilitate the isolation and identification of the product, the reaction was treated with ethylmagnesium bromide (Eq. (2)). The results are summarized in Table 1.

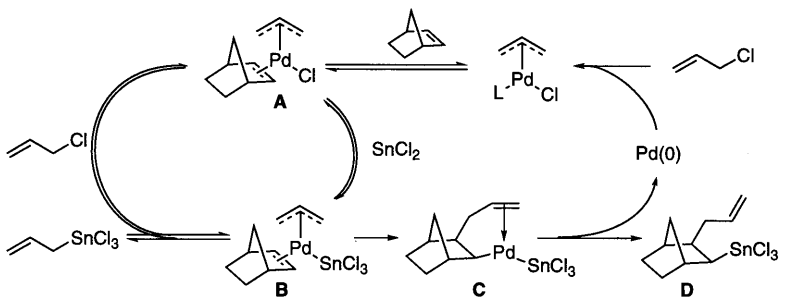


(2)

DMF, which gave desirable results in the pioneers' reaction systems, was not suitable for the present reaction (run 1). Dioxane was not very good either (run 2). On the other hand, excellent results were obtained in non-coordinating solvents, such as dichloromethane and toluene (runs 3, 4) [20]. Thus we chose toluene as the solvent for further investigation. The reaction could also be performed at room temperature (rt), although it took a few days to go to completion (runs 6, 7).

We next explored the reagent precursor that can be used for the allylstannylation. The results are summarized in Table 2. The yields were excellent with allyl and β-methallyl chloride (runs 1, 2). Not only allylic halides but also allyl acetate and allyl phenyl ether could be used, though the yields were not quite as high (runs 3, 4). On the other hand, no reaction was observed when iodobenzene was employed in place of allylic compounds. Chloroacetone was not applicable either. Both benzyl chloride and bromide gave 1,2-diphenylethane as a sole product.

Scheme 1 depicts a plausible reaction pathway. The catalytic palladium(0) species reacts with allyl chloride and norbornene to form an intermediary complex **A**

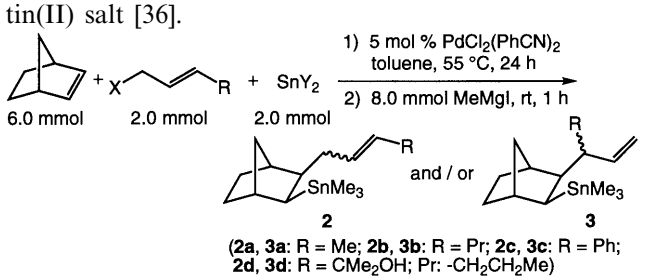


Scheme 1. A plausible reaction pathway.

[21,22]. Then it is transformed into the key intermediate **B** by tin(II) chloride. This process might be reversible [19,23,24]. π-Allylpalladium chloride is indeed reported to add to norbornene to give the allylpalladation product [25]. The process is not facile, however [26]. In order to obtain the adduct in good yield, it is necessary to replace the chloride ligand by a more electron-accepting ligand such as hexafluoroacetylacetonate via the acetate [19,26–33]. Taking these facts into account, the smooth isomerization of the intermediate **B** into **C**, which is assumed to be the rate-determining step [34], could be ascribable to a weakly σ-donating and potentially π-accepting character of the trichlorostannate ligand [24]. Finally, reductive elimination provides the adduct **D** with a concomitant regeneration of the catalytic palladium(0) species.

The complex **B** may also be in equilibrium with allyltin trichloride under the reaction conditions [19]. Palladium-catalyzed reaction between allyl chloride and tin(II) chloride in the absence of norbornene gave an almost homogeneous solution in toluene, while tin(II) chloride itself appears insoluble in this solvent. The resulting reaction solution was investigated using ^{119}Sn-NMR. A sharp singlet was observed at δ −25.1 ppm. The corresponding solution obtained in THF showed a signal at δ −120.8 ppm. On the other hand, 0.5 mol dm^{-3} THF solution of tin(II) chloride showed a ^{119}Sn-NMR signal at δ −216.4 ppm. The appearance of the new signals would suggest the formation of allyltin trichloride or its complex. A significant difference of the chemical shifts from that reported by Masuyama would be attributable to the formation of a hypervalent structure of the allyltin species in such a strongly coordinating solvent as DMF [17,35]. The higher field shift observed in THF might also reflect reversible formation of such a species, though the solvent polarity would also affect it to some extent. The present result was surprising to us, because ultrasonic irradiation is necessary for Masuyama's carbonyl allylation in such a solvent as toluene [35].

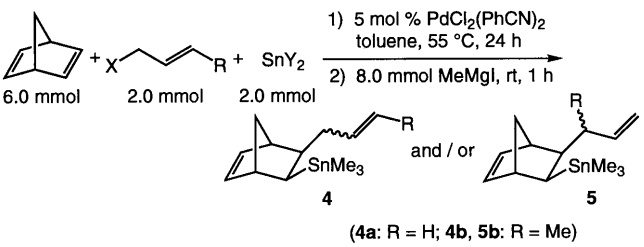
Regioselectivity was next studied with allylic reagents with a substituent at the 1- or 3-position of the allylic moiety (Eq. (3)). In the following studies, methylmagnesium iodide instead of ethylmagnesium bromide was used to trap the products. The position of carbon–carbon bond formation can be altered by changing the tin(II) salt [36].



(3)

The trend can be seen from Table 3. Crotyl and α-methallyl chloride expressed analogous regioselectivities except when tin(II) bromide was used without addition of triphenylphosphine (runs 1–8). This would suggest that the reaction of both allylic compounds proceeds through a common π-allylic palladium intermediate. In general, new carbon–carbon bond formation took place at the less hindered allylic terminus to give **2** when tin(II) chloride was used (runs 1, 5, 9, 13, 17, 23). On the contrary, exclusive production of **3** was observed in the cases that crotyl or α-methallyl chloride and tin(II) iodide were the reagent precursors (runs 4, 8). Also in the reactions of other allylic halides, formation of **3** predominated when tin(II) iodide was used (runs 12, 16, 20). The use of tin(II) bromide generally gave intermediate selectivity. The reactions with this salt usually gave the highest total yields, especially when 10 mol% of triphenylphosphine was added (runs 3, 7, 11, 15, 19). Forming a striking contrast to this, the addition of the phosphine completely suppressed the reaction when tin(II) chloride and iodide were used. Tin(II) fluoride and acetate were not quite effective (runs 21, 22). The reactions of methyl 4-bromocrotonate were different from those of other allylic halides: by changing the tin(II) salt from chloride to bromide, the yield decreased, though the adduct **2** was exclusively obtained (run 24). Addition of the phosphine disturbed the reaction (run 25). The adduct was not obtained when tin(II) iodide was used either (run 26).

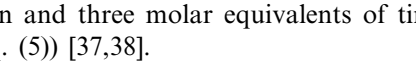
Not only norbornene but also norbornadiene could be allylstannylated (Eq. (4)). The results are indicated in Table 4.



(4)

2.2. Arylstannylation

We next examined arylstannylation with aryltin trichlorides. Following the failure in the attempt at in situ generation of aryltin trihalides from the corresponding aryl halides and tin(II) chloride, aryltin trichlorides for the present study were prepared by disproportionation between the corresponding tetraaryltin and three molar equivalents of tin(IV) chloride (Eq. (5)) [37,38].



(5)

Table 3
Allylstannylation with unsymmetrically substituted allylic compounds

Run	R	X	Y	Additive (10 mol%)	Products		
					Yield (%) [a]	**2**:**3**	Ratio [b]
1	Me	Cl	Cl		61	100:0	
2	Me	Cl	Br		74	15:85	75:25
3	Me	Cl	Br	PPh_3	97	25:75	86:14
4	Me	Cl	I		34	0:100	78:22
5	Me [c]	Cl	Cl		60	100:0	
6	Me [c]	Cl	Br		40	50:50	86:14
7	Me [c]	Cl	Br	PPh_3	79	27:73	84:16
8	Me [c]	Cl	I		42	0:100	84:16
9	Me	Br	Cl		82	100:0	
10	Me	Br	Br		68	40:60	80:20
11	Me	Br	Br	PPh_3	91	28:72	80:20
12	Me	Br	I		21	23:77	83:17
13	Pr	Br	Cl		79	100:0	
14	Pr	Br	Br		71	43:57	75:25
15	Pr	Br	Br	PPh_3	95	47:53	73:27
16	Pr	Br	I		34	48:52	84:16
17	Ph	Cl	Cl		54	100:0	
18	Ph	Cl	Br		71	95:5	77:23
19	Ph	Cl	Br	PPh_3	95	38:62	73:27
20	Ph	Cl	I		15	37:63	76:24
21	Ph	Cl	F		19	100:0	
22	Ph	Cl	OAc		21		31:6988:12
23	CO_2Me [d]	Br	Cl		66	100:0	
24	CO_2Me [d]	Br	Br		13	100:0	
25	CO_2Me [d]	Br	Br	PPh_3	0		
26	CO_2Me [d]	Br	I		0		

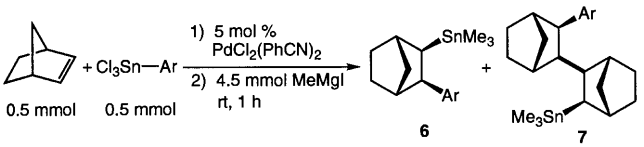
[a] Isolated yields based on tin(II) halide assuming that 5 mol% is consumed to generate Pd(0).
[b] Diastereomer ratio of **3**.
[c] α-Methallyl chloride was used instead of crotyl chloride.
[d] The ester moiety was converted to the corresponding tertiary alcohol by treatment with an excess of MeMgI when the allylstannylation was terminated.

Table 4
Allylstannylation of norbornadiene

Run	R	X	Y	Additive (10 mol%)	Product		
					Yield (%) [a]	**4**:**5**	Ratio [b]
1	H	Br	Cl		58		
2	Me	Cl	Cl		62	100:0	
3	Me	Cl	Br		53	100:0	
4	Me	Cl	Br	PPh_3	74	38:62	75:25
5	Me	Cl	I		33	0:100	73:27

[a] Isolated yields based on tin(II) halide assuming that 5 mol% is consumed to generate Pd(0).
[b] Diastereomer ratio of **5**.

With these reagents, oxidative addition of the carbon–tin bond to an ordinary palladium(0) species is indispensable to the arylstannylation, while it may not be essential to the allylstannylation discussed in the previous section [10,11,13,14,39].



(**6a**, **7a**: Ar = *p*-MeC_6H_4; **6b**, **7b**: Ar = *m*-$F_3CC_6H_4$; **6c**, **7c**: Ar = *m*-FC_6H_4; **6d**, **7d**: Ar = *m*-ClC_6H_4; **6e**, **7e**: Ar = *p*-ClC_6H_4; **6f**, **7f**: Ar = *p*-FC_6H_4; **6g**, **7g**: Ar = Ph; **6h**, **7h**: Ar = *o*-MeC_6H_4; **6i**, **7i**: Ar = *p*-$MeOC_6H_4$)

(6)

Table 5
Palladium-catalyzed *p*-tolylstannylation of norbornene [a]

Run	Norbornene (mol equiv)	Catalyst (mol%)	Solvent	Temperature (°C)	Time (h)	Yield [b] (%)	Ratio **6a**:**7a**
1	3.0	5	DMF	55	2 [c]	8	88:12
2	4.0	5	$(CH_2Cl)_2$	55	2	63	29:71
3	1.5	5	THF	55	8	44	45:55
4	3.0	5	THF	55	2	46	46:54
5	3.1	5	$CHCl_3$	55	2	85	39:61
6	3.1	5	Dioxane	55	2	82	38:62
7	1.0	5	Benzene	55	2	61	72:28
8	1.5	5	Benzene	55	9	65	69:31
9	2.1	5	Benzene	55	2	77	65:35
10	3.0	5	Benzene	55	2	79	68:32
11	6.0	5	Benzene	55	2	83	65:35
12	9.0	1	Benzene	55	2	84	71:29
13	2.1	1	Benzene	rt	72	75	69:31
14	6.2	5 [d]	Benzene	55	2	84	67:33
15	3.4	0	Benzene	55	2	0	
16	6.4	5 [e]	Benzene	55	11	11	98:2
17	5.5	5 [e]	Benzene	55	24	70	95:5
18	6.2	5 [e]	Benzene	55	96	87	80:20

[a] Conditions are as described in the text unless otherwise noted.
[b] Isolated yields after GPC separation based on the tin reagent used.
[c] *p*-Tolyltrimethyltin was obtained in 65% yield.
[d] $Pd(dba)_2$ was used in place of $PdCl_2(PhCN)_2$.
[e] Triphenylphosphine (10 mol%) was added to the reaction.

Basic aspects of the reaction were first explored using *p*-tolyltin trichloride. The results are summarized in Table 5.

The reaction gave a mixture of 1:1 adduct **6** and 2:1 adduct **7** (Eq. (6)). Each product was obtained as a single isomer. The stoichiometry between the tin reagent and norbornene had no marked influence on the product ratio (runs 3, 4 and runs 7–11). A significant amount of the 2:1 adduct **7** was obtained even when only one molar equivalent of norbornene was used (run 7). No products via incorporation of the third norbornene molecule were detected in any case even when as much as nine molar equivalents of norbornene were used (run 12). On the other hand, the results were highly dependent on the solvent, although the causation between them is unknown. The trend of the solvent effect resembles that of allylstannylation, namely, the reaction gave higher yields in less coordinating solvents such as benzene, chloroform, and 1,2-dichloroethane than in a highly coordinating solvent such as DMF (runs 1, 2, 5, 10). THF gave intermediate results (3, 4). Dioxane, which is an ethereal solvent like THF but the dielectric constant of which is as low as that of benzene, gave a high yield (run 6). The amount of the catalyst could be reduced to 1 mol% (run 12). Although it takes longer, the reaction could be performed at room temperature (run 13). Not only a palladium(II) complex but also a palladium(0) complex was effective as a catalyst precursor (run 14). The palladium catalyst was indispensable to the reaction (run 15). An addition of triphenylphosphine (two molar equivalents) to the palladium catalyst had interesting effects on the reaction: although the reaction was slowed down, prolonged reaction provided the highest yield and selectivity for the production of **6** (runs 16–18).

The stereochemistry of the product was elucidated by an X-ray crystallographic analysis of the 2:1 adduct **7j** obtained by the reaction between phenyltin trichloride and norbornene and subsequent treatment of the reaction mixture with phenylmagnesium bromide. As shown in Fig. 1, both of the norbornene-insertions proceeded via an *exo-cis* fashion.

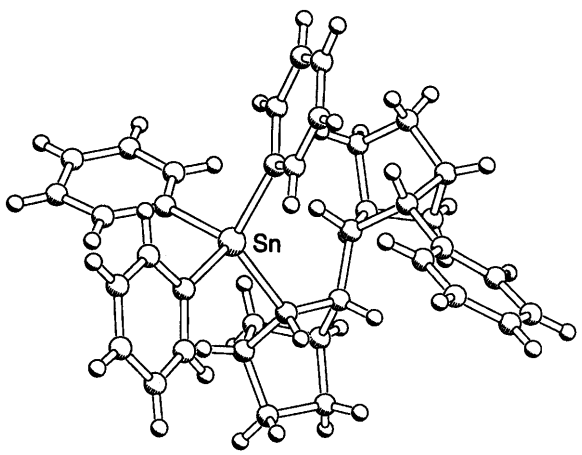
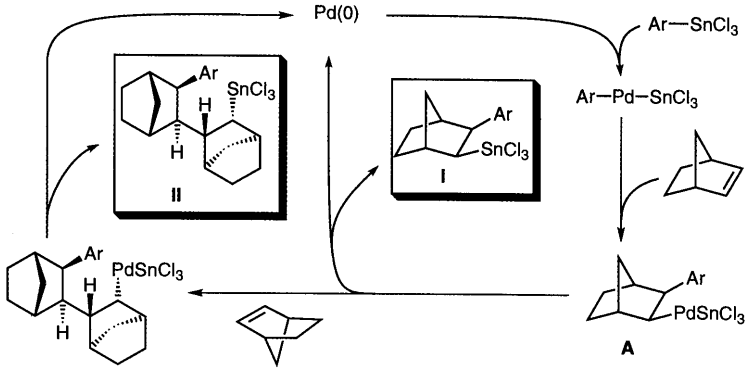


Fig. 1. The X-ray structure of **7j**.



Scheme 2. A plausible reaction pathway.

Table 6
Palladium-catalyzed arylstannylation of norbornene [a]

Run	Substituent on the Ar	Norbornene (mol equiv.)	Catalyst (mol%)	Time (h)	Yield (%) [b]	Ratio **6**:**7**
1	*m*-CF3	6.0	1	2	73	84:16
2	*m*-F	6.0	1	2	84	79:21
3	*m*-Cl	6.0	1	2	87	77:23
4	*p*-Cl	6.0	1	2	82	72:28
5	*p*-F	3.9	1	2	90	77:23
6	H	6.0	1	2	83	77:23
7	*p*-Me	6.0	1	2	83	65:35
8	*o*-Me	6.0	5	24	24	67:33
9	*p*-OMe	5	2	2	85	54:46
10 [c,d]	H	6.0	5	2	60	75:25
11 [c,d]	*p*-Me	6.0	5	2	63	67:33

[a] Conditions are as described in the text.
[b] Isolated yields after GPC separation based on the tin reagent used.
[c] The reaction mixture was treated by PhMgBr instead of MeMgI.
[d] Compound numbers for products in runs 10 and 11: run 10, **6j** and **7j**; run 11, **6k** and **7k**.

Thus, the reaction pathway could be interpreted as depicted in Scheme 2.

The reaction would be catalyzed by a palladium(0) species, because the result with bis(dibenzylideneacetone)palladium(0) complex was similar to that with dichlorobis(benzonitrile)palladium(II) (Table 5 runs 11,14). Thus the reaction is initiated by an oxidative addition of aryltin trichloride to a catalytic palladium(0) species. Subsequent arylpalladation of the carbon–carbon double bond generates the key intermediate **A**. The following reductive elimination affords the adduct **I** with concomitant regeneration of the catalytic palladium(0) species. On the other hand, the product **II** is formed when a further carbopalladation of another norbornene molecule occurs prior to the reductive elimination. According to the X-ray crystallographic analysis, the reaction of the second norbornene proceeds in a regio- as well as stereoselective way to avoid steric interaction between the bridge methylenes of both norbornene moieties.

The reaction did not proceed at all with the corresponding tributyltin reagent, under the present conditions. It would be reasonable to expect that oxidative addition of not only aryltin trichlorides but also aryltributyltins to the catalytic palladium(0) species takes place [14,39]. The crucial difference between the trichlorotin and tributyltin reagents would therefore lie in the norbornene-insertion step. According to Kurosawa's report, the trichlorostannate ligand makes palladium highly electrophilic, allowing more efficient complexation with a nucleophilic alkene [19]. Thus the electron-accepting character of the trichlorostannate ligand must have played a decisive role in the present reaction [24].

The results with other aryltin trichlorides are given in Table 6. The reaction was successful with a wide range of aryltin reagents from that with electron-donating to

electron-withdrawing substituents. All the products obtained were single isomers, again. A certain degree of correlation was observed between the electronic character of the aromatic substituent and the product ratio, namely, the more the substituent is electron donating, the higher the proportion of the 2:1 adduct **7** was.

The observed dependence of the product distribution on the aryl substituent might reflect the stability of the key intermediate **A**. An intramolecular coordination in η^2 fashion has been reported for structurally analogous palladium iodide complexes with hydrogen or an electron-donating substituent on the aromatic ring [40,41]. This type of coordination should bring about certain stabilization of the complex **A**. Thus, a more electron-donating substituent is likely to impart more stability to the corresponding intermediate **A**, and thus, more probability of its undergoing insertion of another norbornene molecule to afford higher proportion of the adduct **II** (Scheme 1).

In conclusion, palladium-catalyzed stereoselective carbostannylation of norbornene that does not occur with the corresponding tributyltins was realized by the utilization of carbon–tin–halogen inter-element linkages. The present reaction furnishes not only a new carbon–carbon bond but also a new carbon–tin bond that may possess potential utility for further transformations [42,43].

3. Experimental

^{1}H (200 MHz) NMR spectra were recorded on a Varian Gemini 200 spectrometer. ^{13}C (125.7 MHz) and ^{119}Sn (186.4 MHz) NMR spectra were recorded on a JEOL JNM-α500 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to internal tetramethylsilane (^{1}H δ 0.00 ppm) and chloroform-*d* (^{13}C δ 77.00 ppm), respectively. ^{119}Sn shifts are referenced to external tetramethyltin (^{119}Sn δ 0.00 ppm). Mass spectra were measured at 70 eV on a Shimadzu QP2000A mass spectrometer. IR spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrophotometer. The elemental analyses were performed at the Technical Research Center for Instrumental Analysis, Gunma University. Gel permeation chromatography was performed on a liquid chromatograph LC-08 (Japan Analytical Industry Co., Ltd.) using JAIGEL-H. Melting points were measured with a Yanaco-MP apparatus. Benzene, toluene, and 1,4-dioxane were distilled under an argon atmosphere from freshly prepared sodium wire. Diethyl ether (ether), THF, and hexane were distilled under an argon atmosphere from sodium/benzophenone. Chloroform, DMF, DMSO, dichloromethane, and 1,2-dichloroethane were distilled under an argon atmosphere from calcium hydride.

3.1. Typical procedure for the allylstannylation of norbornene

To a solution (3.0 ml) of dichlorobis(benzonitrile)palladium (9.6 mg, 0.025 mmol) were added allyl bromide (60 mg, 0.5 mmol), norbornene (141 mg, 1.5 mmol), and tin(II) chloride (95 mg, 0.5 mmol) in a 10 ml Pyrex® tube equipped with a magnetic stirring bar under nitrogen, successively. The tube was cooled with a liquid nitrogen bath and sealed under vacuum, then heated at 55°C. The tube was then opened under nitrogen and the reaction mixture was treated with an ethereal solution of ethylmagnesium bromide (0.95 mol dm^{-3}, 4.5 mmol) at 0°C and stirred at rt for 1 h. The crude product was obtained by quenching with water, extraction with ether, and drying the organic layer over anhydrous sodium sulfate. Silica-gel column chromatography after concentration afforded the desired product, *exo-cis*-2-(2-propenyl)-3-triethylstannylbicyclo-[2.2.1]heptane (**1a**) as a colorless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.80 (m, 6H), 1.17 (t, $J = 7.5$ Hz, 9H), 1.05–2.21 (m, 12H), 4.95 (m, 2H), 5.75 (m, 1H). ^{13}C-NMR ($CDCl_3$): δ 1.82, 11.1, 29.7, 33.3, 35.0, 37.3, 40.1, 40.9, 44.0, 46.2, 114.9, 138.6. ^{119}Sn-NMR ($CDCl_3$): δ −10.6.

*3.1.1. exo-cis-2-(2-Methyl-2-propenyl)-3-triethylstannylbicyclo[2.2.1]heptane (**1b**)*

Colorless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.80 (m, 6H), 1.17 (t, $J = 7.5$ Hz, 9H), 1.03–2.24 (m, 15H), 4.65 (s, 1H), 4.72 (s, 1H). ^{13}C-NMR ($CDCl_3$): δ 1.85, 11.1, 22.5, 29.8, 33.4, 35.0, 37.5, 40.1, 41.0, 43.9, 48.1, 111.0, 145.3. ^{119}Sn-NMR ($CDCl_3$): δ −10.7 (s).

*3.1.2. exo-cis-2-(2-Butenyl)-3-trimethylstannylbicyclo[2.2.1]heptane (**2a**)*

Colorless oil. ^{1}H-NMR (of a 75:25 mixture of geometrical isomers, 200 MHz, $CDCl_3$): δ 0.04 (s, 6.75H), 0.07 (s, 2.25H), 0.95–2.22 (m,15H), 5.33–5.47 (m, 2H). ^{13}C-NMR (of the major isomer) ($CDCl_3$): δ −8.13, 18.0, 29.9, 33.3, 34.9, 38.8, 40.2, 40.8, 42.0, 46.8, 125.5, 131.1. ^{119}Sn-NMR ($CDCl_3$): δ −12.8 (s).

*3.1.3. exo-cis-2-(1-Methyl-2-propenyl)-3-trimethylstannylbicyclo[2.2.1]heptane (**3a**)*

Colorless oil. ^{1}H-NMR (of a 75:25 mixture of diastereomers, 200 MHz, $CDCl_3$): δ 0.02 (s, 6.75H), 0.07 (s, 2.25H), 0.96–2.29 (m,14H), 4.86–4.99 (m, 2H), 5.58–5.76 (m, 1H). ^{13}C-NMR ($CDCl_3$): δ (−7.20), −6.31, 12.5, 20.8 (21.1), 31.3, 32.5, 36.1, 39.2, 39.5 (40.1), 41.4, 42.4 (45.4), 52.3 (53.2) (112.8), 114.6, 144.6 (^{13}C chemical shifts in parentheses are assigned to that of the minor isomer). ^{119}Sn-NMR ($CDCl_3$): δ −11.8.

*3.1.4. exo-cis-2-(2-Hexenyl)-3-trimethylstannylbicyclo-[2.2.1]heptane (**2b**)*

Colorless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.05 (s, 9H), 0.82 (t, $J = 7.2$ Hz, 3H), 1.30 (q, $J = 7.4$ Hz, 2H), 0.93–2.16 (m, 14H). ^{13}C-NMR ($CDCl_3$): δ −8.16, 13.7, 22.7, 29.9, 33.3, 34.8, 38.8, 40.0, 40.8, 42.0, 46.9, 130.0, 191.0. ^{119}Sn-NMR ($CDCl_3$): δ −12.7.

*3.1.5. exo-cis-2-(1-Propyl-2-propenyl)-3-trimethyl-stannylbicyclo[2.2.1]heptane (**3b**)*

Colorless oil. ^{1}H-NMR (of a 75:25 mixture of diastereomers, 200 MHz, $CDCl_3$): δ 0.01 (s, 6.75H), 0.03 (s, 2.25H), 0.80–2.29 (m, 18H), 4.77–5.07 (m, 2H), 5.32–5.66 (m, 1H). ^{13}C-NMR (of the major diastereomer, $CDCl_3$): δ −6.10, 14.4, 19.3, 31.3, 32.4, 36.5, 39.2, 39.7, 41.3, 47.9, 50.6, 116.3, 142.3. ^{119}Sn-NMR ($CDCl_3$): δ −12.8.

*3.1.6. exo-cis-2-{(E)-3-Phenyl-2-propenyl}-3-trimethylstannylbicyclo[2.2.1]heptane (**2c**)*

Colorless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.09 (s, 9H), 1.06–2.25 (m, 12H), 6.18 (m, 1H), 6.34 (d, $J =$ 16.2 Hz, 1H), 7.15–7.35 (m, 5H). ^{13}C-NMR ($CDCl_3$): δ −8.07, 29.9, 33.3, 35.0, 38.8, 40.3, 40.9, 42.4, 46.8, 126.0, 126.9, 128.5, 130.5, 137.8. ^{119}Sn-NMR ($CDCl_3$): δ −12.2.

*3.1.7. exo-cis-2-(1-Phenyl-2-propenyl)-3-trimethylstannylbicyclo[2.2.1]heptane (**3c**)*

Colorless oil. ^{1}H-NMR (of a 77:23 mixture of diastereomers, 200 MHz, $CDCl_3$): δ −0.33 (s, 2.07H), 0.10 (s, 6.93H), 0.99–3.10 (m, 11H), 4.83–4.97 (m, 0.46H), 5.09–5.13 (m, 1.54H), 5.59–5.66 (m, 0.23H), 5.86–5.93 (m, 0.77H), 7.08–7.35 (m, 5H). ^{13}C-NMR ($CDCl_3$): δ (−7.58), −5.97, 31.0 (31.3) (32.4), 32.5, 35.7 (35.8) (38.8), 39.8, 40.3 (40.5) (41.8), 41.9 (48.5), 50.9, 55.4 (56.8) (112.8), 116.2, 126.1 (126.6), 128.2, 128.4 (128.8) (129.0), 141.3 (142.8) (144.5), 145.2 (^{13}C chemical shifts in parentheses are assigned to the minor isomer). ^{119}Sn-NMR ($CDCl_3$): δ −10.6.

*3.1.8. exo-cis-2-(4-Hydroxy-4-methyl-2-pentenyl)-3-trimethylstannylbicyclo[2.2.1]heptane (**2d**)*

Colorless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.05 (s, 9H), 0.95–2.16 (m, 12H), 1.24 (s, 6H), 1.34 (s, 1H), 5.50 (m, 2H). ^{13}C-NMR ($CDCl_3$): δ −8.26, 29.8, 33.2, 34.8, 38.7, 39.9, 40.7, 41.5, 46.5, 53.4, 70.6, 126.5, 138.6. ^{119}Sn-NMR ($CDCl_3$): δ −12.4.

*3.1.9. exo-cis-2-(2-Propenyl)-3-trimethylstannylbicyclo-[2.2.1]hept-5-ene (**4a**)*

Colorless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.09 (s, 9H), 1.07–2.80 (m, 8H), 4.94–5.06 (m, 2H), 5.72–5.92 (m, 1H), 5.95–6.09 (m, 2H).

*3.1.10. exo-cis-2-(2-Butenyl)-3-trimethylstannylbicyclo[2.2.1]hept-5-ene (**4b**)*

Colorless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.08 (s, 9H), 0.92–2.76 (m, 11H), 5.43 (m, 2H), 5.94 (m, 2H).

*3.1.11. exo-cis-2-(1-Methyl-2-propenyl)-3-trimethylstannylbicyclo[2.2.1]hept-5-ene (**5b**)*

Colorless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.05 (s, 9H), 1.00–2.98 (m, 10H), 4.85–5.01 (m, 2H), 5.57–5.91 (m, 2H), 6.05 (m, 2H).

3.1.12. Palladium-catalyzed reaction between allyl bromide and tin(II) chloride in the absence of norbornene

The reaction was performed in the same way as described in Section 3.1, except that norbornene was excluded. After the precipitate of tin(II) chloride had disappeared, the sealed tube was opened under argon and the reaction solution was transferred to an NMR tube under a stream of argon and investigated using ^{119}Sn-NMR.

3.2. Typical procedure for the synthesis of tetraaryltin

In a 500 ml three-necked round-bottomed flask furnished with a 300 ml dropping funnel, reflux condenser, and magnetic stir bar were charged magnesium (11.6 g, 0.48 mol) and ether (50 ml) under an argon atmosphere. An ethereal solution (200 ml) of *p*-bromotoluene (50 g, 0.29 mol) was added so that gentle reflux continued. After completion of the addition, the reaction mixture was heated under reflux for 1 h, and then tin tetrachloride (17.1 g, 66 mmol) was added dropwise via a syringe at rt. The resulting gray suspension refluxed overnight. Then it was poured into an ice-cold aqueous hydrochloric acid (1.0 mol dm^{-3}, 400 ml). After stirring for 1 h, a white cake was collected by filtration. The product was purified by recrystallization from pyridine (15.7 g, 49%). Other tetraaryltins were synthesized analogously. Colorless crystals: m.p. 211°C. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.35 (s, 12H), 7.21 (d, $J = 7.0$ Hz, 8H), 7.48 (d, $J = 7.0$ Hz, 8H). ^{119}Sn-NMR ($CDCl_3$): δ −127.4.

3.2.1. Typical procedure for the synthesis of aryltin trichloride [37,38]

In a 30 ml two-necked round-bottomed flask equipped with a reflux condenser, rubber septum, and a magnetic stir bar was charged tetra(*p*-tolyl)tin (8.37 g, 17.3 mmol). Tin(IV) chloride (6.20 ml, 53.0 mmol) was added under an argon atmosphere. The mixture was heated at 150°C for 4 h. After cooling, fractional distillation of the resulting colorless solution afforded *p*-tolyltin trichloride as a colorless oil. Other aryltin trichlorides were also prepared according to this procedure: b.p. 86.0–89.0°C/0.60 mmHg. ^{119}Sn-NMR ($CDCl_3$): δ −64.0.

3.2.2. Arylstannylation of norbornene

In a 20 ml two-necked round-bottomed flask furnished with a reflux condenser and septum, dichlorobis(benzonitrile)palladium(II) (9.0 mg, 0.025 mmol) was dissolved in a solvent (1 ml) at rt under an argon atmosphere. To the solution was added a norbornene solution in the same solvent (4 ml) via a syringe. Then, aryltin trichloride (0.5 mmol) was added dropwise to the resulting orange colored solution. The resulting yellow solution was heated at 55°C for the time indicated in Table 5. Then the reaction was cooled to rt and treated by methylmagnesium iodide (1 mol dm^{-3} in ether, 2.3 mmol) for 1 h. After treatment with 1 mol dm^{-3} hydrochloric acid, the reaction mixture was poured into water and extracted with ether (three times, 20 ml each). The organic layer was combined and dried over anhydrous sodium sulfate. Volatiles were evaporated off and the residue was submitted to silica-gel column chromatography to exclude the materials other than the desired adducts **6** and **7**. The adducts **6** and **7** were separated from each other by GPC (chloroform).

*3.2.3. exo-cis-2-(p-Tolyl)-3-(trimethylstannyl)-bicyclo[2.2.1]heptane (**6a**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ −0.30 (s, 9H), 1.32–1.39 (m, 3H), 1.62–1.99 (m, 4 H), 2.31 (s, 3H), 2.41–2.62 (m, 2H), 3.05 (d, $J = 10.0$ Hz, 1H), 7.01–7.10 (m, 4H). ^{13}C-NMR (125.7 MHz, $CDCl_3$): δ −9.2, 20.7, 31.0, 32.7, 37.6, 40.9, 42.1, 43.0, 50.5, 127.4, 129.2, 135.1, 145.7. ^{119}Sn-NMR (186.4 MHz, $CDCl_3$): δ −14.56. IR (neat): *v* 2948 (s), 2868 (s), 1513 (s), 1472 (m), 1451 (m), 1311 (w), 1295 (m), 1184 (m), 1172 (w), 1021 (w), 968 (w), 841 (m), 812 (s), 762 (s), 709 (m) cm^{-1}. MS (*m*/*z*): 335 (M^+ − Me, 83%), 241 (53%), 239 (39%), 165 (37%), 128 (22%), 105 (100%), 91 (23%), 67 (34%). Anal. Found: C, 57.57; H, 7.37. Calc. for $C_{17}H_{26}Sn$: C, 58.49; H, 7.51%.

*3.2.4. exo-cis-2-{exo-cis-3-(p-Tolyl)bicyclo[2.2.1]-hept-2-yl}-3-trimethylstannylbicyclo[2.2.1]heptane (**7a**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ −0.10 (s, 9H), 0.42–0.55 (m, 1H), 0.86–1.00 (m, 2H), 1.06–1.72 (m, 11H), 1.84–1.91 (m, 1H), 2.04–2.20 (m, 2H), 2.31 (s, 3H), 2.39–2.40 (m, 2H), 2.88 (d, $J = 9.2$ Hz, 1H), 7.02–7.12 (m, 4H). ^{13}C-NMR (125.7 MHz, $CDCl_3$): δ −7.8, 30.4, 30.9, 31.2, 31.9, 36.6, 37.1, 38.2, 38.5, 41.0, 42.7, 43.9, 46.3, 53.0, 58.2, 128.5, 129.0, 134.8, 144.0. ^{119}Sn-NMR (186.4 MHz, $CDCl_3$): δ −15.2. IR (neat): *v* 2947 (s), 2867 (s), 1513 (s), 1473 (m), 1452 (s), 1377 (w), 1309 (w), 1293 (m), 1255 (m), 1216 (m), 1186 (m), 1141 (w), 1110 (m), 1042 (w), 1021 (m), 950 (w), 926 (w), 908 (m), 891 (w), 842 (m), 811 (s), 758 (s), 701 (m) cm^{-1}. MS (*m*/*z*): 429 (M^+ − Me, 44%), 279 (24%), 161 (39%), 131 (31%), 105 (100%), 91 (28%), 67 (30%). Anal. Found: C, 64.45; H, 8.20. Calc. for $C_{24}H_{36}Sn$: C, 65.04; H, 8.19%.

*3.2.5. exo-cis-2-(m-Chlorophenyl)-3-(trimethylstannyl)-bicyclo[2.2.1]heptane (**6d**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ −0.29 (s, 9H), 1.31–1.53 (m, 3H), 1.62–1.96 (m, 4H), 2.32–2.55 (m, 2H), 3.05 (d), 6.99–7.22 (m, 4H). ^{13}C-NMR (125.7 MHz, CDCl3): δ −9.3, 30.9, 32.6, 37.6, 41.0, 41.8, 42.3, 50.7, 125.6, 125.8, 127.8, 129.8, 134.4, 150.7. ^{119}Sn-NMR (186.4 MHz, $CDCl_3$): δ −13.0. MS (*m*/*z*): 357 (37%), 355 (M^+ − Me, 100%), 351 (37%), 261 (43%), 165 (50%), 125 (25%), 67 (25%). Anal. Found: C, 50.85; H, 6.11. Calc. for $C_{16}H_{23}ClSn$: C, 52.01; H, 6.27%.

*3.2.6. exo-cis-2-[exo-cis-3-(m-Chlorophenyl)bicyclo-[2.2.1]hept-2-yl]-3-trimethylstannylbicyclo[2.2.1]heptane (**7d**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.11 (s, 9H), 0.36–0.53 (m, 1H), 0.80–0.96 (m, 1H), 0.98 (dm, $J = 9.2$ Hz, 1H), 1.06–1.66 (m, 11H) 1.72 (ddd, $J = 9.2$, 5.5, 1.6 Hz, 1 H), 1.85 (ddd, $J = 10.2$, 1.9, 1.9 Hz, 1H), 2.01 (br.d $J = 3.9$ Hz, 1H), 2.13 (br.d $J = 3.9$ Hz, 1H), 2.39–2.43 (m, 2H), 2.89 (br.d, $J = 9.2$ Hz, 1H), 7.05–7.27 (m, 4H). ^{13}C-NMR (125.7 MHz, CDCl3): δ −7.9, 30.3, 30.7, 31.1, 32.0, 36.6, 37.0, 38.1, 38.5, 40.9, 42.3, 43.6, 46.4, 53.2, 58.1, 125.6, 127.4, 129.0, 129.2, 133.7, 146.4. MS (*m*/*z*): 451 (9%), 449 (M^+ − Me, 24%), 197 (28%), 165 (56%), 151 (30%), 128 (31%), 125 (39%), 95 (39%), 79 (47%), 67 (100%), 43 (30%).

*3.2.7. exo-cis-2-(p-Chlorophenyl)-3-(trimethylstannyl)-bicyclo[2.2.1]heptane (**6e**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ 6.99–7.22 (m, 4H), 3.05 (d, $J = 10.2$ Hz, 1H), 2.32–2.55 (m, 2H), 1.62–1.96 (m, 4H), 1.31–1.53 (m, 3H), −0.29 (s, 9H). ^{13}C-NMR (125.7 MHz, CDCl3): δ −9.3, 30.9, 32.6, 37.6, 41.0, 41.8, 42.3, 50.7, 125.6, 125.8, 127.8, 129.8, 134.4, 150.7. ^{119}Sn-NMR (186.4 MHz, $CDCl_3$): δ −13.0. MS (*m*/*z*): 357 (37%), 355 (M^+ − Me, 100%), 351 (37%), 261 (43%), 165 (50%), 125 (25%), 67 (25%). Anal. Found: C, 51.66; H, 6.40. Calc. for $C_{16}H_{23}ClSn$: C, 52.01; H, 6.27%.

*3.2.8. exo-cis-2-{exo-cis-3-(p-Chlorophenyl)-bicyclo[2.2.1]hept-2-yl}-3-trimethylstannylbicyclo[2.2.1]-heptane (**7e**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.11 (s, 9H), 0.40–0.51 (m, 1H), 0.83–1.00 (m, 2H), 1.06–1.86 (m, 12H), 1.95–2.05 (m, 1H), 2.07–2.15 (m, 1H), 2.37–2.41 (m, 2H), 2.88 (br.d $J = 9.2$ Hz, 1H), 7.09–7.27 (m, 4H). ^{13}C-NMR (125.7 MHz, CDCl3): δ −7.8, 30.3, 30.7, 31.2, 31.9, 36.5, 37.0, 38.1, 38.5, 40.9, 42.5, 43.7, 46.4, 52.8, 58.1, 127.9, 130.5, 131.1, 142.7. MS (*m*/*z*): 451 (11%), 449 (M^+ − Me, 26%), 165 (72%), 151 (35%), 128 (28%), 125 (66%), 85 (40%), 79 (47%), 67 (100%), 43 (31%).

*3.2.9. exo-cis-2-(p-Fluorophenyl)-3-(trimethylstannyl)-bicyclo[2.2.1]heptane (**6f**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ −0.30 (s, 9H), 1.31–1.39 (m, 3H), 1.62–1.97 (m, 4H), 2.32–2.53 (m, 2H), 3.06 (d, J = 10.2 Hz, 1H), 6.94 (tt, J = 8.8 Hz, 2H), 7.11 (ddt, J = 4.0 Hz, 2H). ^{13}C-NMR (125.7 MHz, CDCl3): δ −9.2, 31.0, 32.6, 37.5, 41.0, 44.2, 42.6, 50.2, 114.9, 115.3, 128.8, 128.9, 144.5, 163.6. ^{119}Sn-NMR (186.4 MHz, $CDCl_3$): δ −13.7. MS (m/z): 339 (M^+ − Me, 97%), 337 (70%), 245 (69%), 165 (74%), 133 (33%), 109 (100%), 67 (35%).

*3.2.10. exo-cis-2-Phenyl-3-(trimethylstannyl)bicyclo-[2.2.1]heptane (**6g**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ −0.31 (s, 9H), 1.33–1.40 (m, 3H), 1.63–1.99 (m, 4H), 2.33–2.59 (m, 2H), 3.09 (d, J = 10.4 Hz, 1H), 7.13–7.30 (m, 5H). ^{13}C-NMR (125.7 MHz, $CDCl_3$): δ −9.3, 31.0, 32.7, 37.6, 41.1, 41.9, 42.7, 50.9, 125.7, 127.5, 127.6, 128.5, 128.6, 148.6. ^{119}Sn-NMR (186.4 MHz, $CDCl_3$) δ −13.9. MS (m/z): 321 (M^+ − Me, 77%), 227 (43%), 225 (31%), 165 (54%), 135 (21%), 115 (24%), 91 (100%), 67 (44%). Anal. Found: C, 57.57; H, 7.37. Calc. for $C_{16}H_{24}Sn$: C, 57.36; H, 7.22%.

*3.2.11. exo-cis-2-(exo-cis-3-Phenylbicyclo[2.2.1]-hept-2-yl)-3-trimethylstannylbicyclo[2.2.1]heptane (**7g**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.10 (s, 9H), 0.34–0.47 (m, 1H), 0.78–0.97 (m, 2H), 1.05–1.75 (m, 11H), 1.81–1.92 (m, 1H), 2.00–2.19 (m, 2H), 2.41 (m, 2H), 2.91 (d, J = 9.2 Hz, 1H), 7.09–7.29 (m, 5H). ^{13}C-NMR (125.7 MHz, $CDCl_3$): δ −7.8, 30.4, 30.8, 31.2, 31.9, 36.6, 37.0, 38.1, 38.5, 40.9, 42.4, 43.8, 53.3, 46.4, 58.1, 111.9, 125.5, 127.8, 129.2, 144.1. MS (m/z): 415 (M^+ − Me, 83%), 265 (36%), 161 (45%), 143 (22%), 117 (40%), 91 (100%), 79 (31%), 67 (48%). Anal. Found: C, 64.72; H, 8.18. Calc. for $C_{17}H_{26}Sn$: C, 64.36%, H: 7.99%.

*3.2.12. exo-cis-2-(o-Tolyl)-3-(trimethylstannyl)bicyclo-[2.2.1]heptane (**6h**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ −0.34 (s, 9H), 1.35–1.40 (m, 3H), 1.54–2.08 (m, 4H), 2.26 (s, 3H), 2.34–2.55 (m, 2H), 3.14 (d, J = 10.0 Hz, 1H), 6.99–7.26 (m, 4H). ^{13}C-NMR (125.7 MHz, $CDCl_3$): δ −9.2, 20.3, 31.7, 32.4, 37.8, 41.1, 41.4, 42.0, 46.9, 125.3, 125.7, 126.3, 130.5, 135.8, 146.5. ^{119}Sn-NMR (186.4 MHz, $CDCl_3$): δ −12.1. MS (m/z): 335 (M^+ − Me, 87%), 241 (57%), 239 (43%), 165 (55%), 128 (23%), 115 (22%), 105 (100%), 91 (29%), 77 (21%), 67 (35%). Anal. Found: C, 57.10; H, 7.30. Calc. for $C_{17}H_{26}Sn$: C, 58.49; H, 7.51%.

*3.2.13. exo-cis-2-{exo-cis-3-(o-tolyl)bicyclo-[2.2.1]hept-2-yl}-3-trimethylstannylbicyclo[2.2.1]heptane (**7h**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ −0.20–0.00 (m, 1H), 0.11 (s, 9H), 0.78–0.94 (m, 3H), 1.16–1.46 (m, 6H), 1.55–1.66 (m, 2H), 1.81–1.91 (m, 2H), 1.98–2.05 (m, 2H), 2.11–2.19 (m, 1H), 2.23 (s, 3H), 2.31–2.39 (m, 1H), 2.51 (m, 1H), 2.98 (br.d, J = 9.4 Hz, 1H), 7.06–7.15 (m, 3H), 7.30–7.34 (m, 1H). ^{13}C-NMR (125.7 MHz, $CDCl_3$): δ −8.2, 20.5, 30.8, 30.9, 31.2, 32.4, 37.1, 37.2, 37.4, 38.2, 40.1, 40.9, 43.4, 45.9, 50.4, 55.7, 125.5, 125.7, 126.2, 129.6, 137.2, 142.3. MS (m/z): 429 (M^+ − Me, 36%), 278 (22%), 161 (48%), 131 (33%), 105 (100%), 91 (32%), 79 (34%).

*3.2.14. exo-cis-2-(p-methoxyphenyl)-3-(trimethyl-stannyl)bicyclo[2.2.1]heptane (**6i**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ −0.31 (s, 9H), 1.30–1.37 (m, 3H), 1.60–1.96 (m, 4H), 2.30–2.55 (m, 2H), 3.02 (d, J = 10.0 Hz, 1H), 3.78 (s, 3H), 6.79 (dt, J = 9.0 Hz, 2H), 7.06 (dt, J = 8.6 Hz, 2H). ^{13}C-NMR (125.7 MHz, $CDCl_3$): δ −9.2, 31.0, 32.7, 37.5, 40.9, 42.2, 43.0, 50.1, 55.2, 113.8, 128.4, 141.1, 157.7. ^{119}Sn-NMR (186.4 MHz, $CDCl_3$): δ −15.0. MS (m/z): 351 (M^+ − Me, 100%), 257 (99%), 253 (42%), 201 (26%), 165 (33%), 121 (68%). Anal. Found: C, 55.68; H, 7.18. Calc. for $C_{17}H_{26}Sn$: C, 55.93; H, 7.18%.

*3.2.15. exo-cis-2-{exo-cis-3-(p-methoxyphenyl)-bicyclo[2.2.1]hept-2-yl}-3-trimethylstannylbicyclo[2.2.1]-heptane (**7i**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.10 (s, 9H), 0.42–0.58 (m, 1H), 0.82–1.00 (m, 2H), 1.06–1.70 (m, 11H), 1.82–1.89 (m, 1H), 2.03–2.10 (m, 2H), 2.16–2.38 (m, 2H), 2.87 (d, J = 9.0 Hz, 1H), 3.79 (s, 3H), 6.80 (dt, J = 8.8 Hz, 2H), 7.12 (dt, J = 8.8 Hz, 2H). ^{13}C-NMR (125.7 MHz, $CDCl_3$): δ −7.8, 30.3, 30.8, 31.3, 31.9, 36.5, 37.0, 38.2, 38.5, 40.9, 42.8, 43.9, 46.4, 52.6, 55.1, 58.2, 113.2, 130.0, 136.3, 157.6. MS (m/z): 460 (M^+, 1%), 445 (69%), 295 (41%), 161 (26%), 121 (100%), 91 (22%), 67 (24%). Anal. Found: C, 62.11; H, 7.98. Calc. for $C_{24}H_{36}Sn$: C, 62.77; H, 7.90%.

*3.2.16. exo-cis-2-Phenyl-3-(triphenylstannyl)-bicyclo[2.2.1]heptane (**6j**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.35–1.88 (m, 6H), 2.43–2.53 (m, 1H), 2.72 (dd, J = 10.1, 2.5 Hz, 1H), 2.75–2.80 (m, 1H), 3.19 (d, J = 10.1 Hz, 1H), 6.90–7.02 (m, 5H), 7.18–7.34 (m, 15H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 31.0, 32.7, 37.7, 41.3, 43.0, 44.8, 51.5, 126.1, 127.7, 128.09, 128.13, 128.3, 128.37, 128.47, 128.56, 128.62, 136.9, 137.6, 140.6, 148.4. ^{119}Sn-NMR (186.4 MHz, $CDCl_3$): δ 179.4. MS (m/z): 522 (M^+, 0.3%), 519 (0.2%), 445 (M^+ − Ph, 0.4%), 351 (100%), 197 (24%), 120 (21%), 91 (34%), 67 (18%). Anal. Found: C, 71.36; H, 5.80. Calc. for $C_{31}H_{30}Sn$: C, 71.43; H, 5.80%.

*3.2.17. exo-cis-2-{exo-cis-3-Phenylbicyclo[2.2.1]-hept-2-yl}-3-triphenylstannylbicyclo[2.2.1]heptane (**7j**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.46–0.61 (m, 1H), 0.82–1.15 (m, 3H), 1.10–1.68 (m, 8H), 1.73–1.83 (m, 1H), 1.87–2.01 (m, 1H), 2.07 (dd, $J = 9.2$, 2.4 Hz, 1H), 2.10–2.18 (m, 1H), 2.24–2.48 (m, 3H), 2.59 (d, $J = 9.0$ Hz, 1H), 6.96–7.02 (m, 2H), 7.10–7.21 (m, 3H), 7.32–7.42 (m, 9H), 7.56–7.64 (m, 6H). MS (m/z): 539 ($M^+ - Ph$, 32%), 351 (100%), 347 (43%), 264 (29%), 197 (41%), 117 (26%), 91 (55%), 67 (29%). Anal. Found: C, 73.66; H, 6.65. Calc. for $C_{38}H_{40}Sn$: C, 74.17; H, 6.55%. X-ray crystal structure analysis: the single crystals were obtained by recrystallization from chloroform. $C_{38}H_{40}Sn$, FW = 615.42, monoclinic, space group $P2_1/n$ (# 4), $a = 10.014(2)$, $b = 10.253(2)$, $c = 15.650(3)$ Å, $\beta = 117.91(2)°$, $V = 1529.0(6)$ Å^3, $Z = 4$, $D_{calc} = 2.673$ g cm^{-3}, μ(Mo–K_α) = 17.19 cm^{-1}, number of reflections measured total 3925, unique 3720 ($R_{int} = 0.053$), $R = 0.045$, $R_w = 0.034$ and GOF = 1.43. All measurements were made at 20 ± 1°C on a Rigaku AFC7S diffractometer with graphite monochromated Mo–K_α radiation ($\lambda = 0.71069$ Å), using an ω–2θ scan technique to a maximum 2θ value of 55.0°. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient 6.76500×10^{-8}). The structure was solved by direct methods (SIR92) [44] and expanded using Fourier techniques (DIRDIF94) [45]. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were included in fixed positions. The final cycle of full-matrix least-squares refinement was based on 2257 observed reflections ($I > 3.00\sigma(I)$) and 461 variable parameters. The max./min. peaks on the final difference Fourier map corresponded to 0.59/−0.51 e Å^{-3}, respectively. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation (1985 and 1992).

*3.2.18. exo-cis-2-(p-Tolyl)-3-(triphenylstannyl)bicyclo-[2.2.1]heptane (**6k**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.30 (dm, $J = 10.1$ Hz, 1H), 1.38–88 (m, 5H), 2.18 (s, 3H), 2.46 (dm, $J = 2.8$ Hz, 1H), 2.74 (dd, $J = 9.8$, 2.3 Hz, 1H), 2.55–3.02 (m, 1H), 3.15 (d, $J = 9.8$ Hz, 1H), 6.70 (d, $J = 8.2$ Hz, 1H), 6.88 (d, $J = 8.2$ Hz, 1H), 7.20–7.32 (m, 15H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 20.7, 31.0, 32.6, 37.8, 41.3, 42.9, 45.6, 51.0, 127.6, 127.7, 128.1, 128.3, 128.5, 129.2, 135.4, 137.2, 140.6, 145.8. MS (m/z): 459 ($M^+ -$ Ph, 7%), 352 (21%), 351 (100%), 197 (29%), 120 (26%), 105 (52%), 67 (22%). Anal. Found: C, 71.91; H, 6.10. Calc. for $C_{32}H_{32}Sn$: C, 71.80; H, 6.03%.

*3.2.19. exo-cis-2-{exo-cis-3-(p-Tolyl)bicyclo[2.2.1]-hept-2-yl}-3-triphenylstannylbicyclo[2.2.1]heptane (**7k**)*

^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.51–0.67 (m, 1H), 0.81–1.10 (m, 3H), 1.10–1.58 (m, 10H), 1.61 (dd, $J =$ 8.9, 5.9 Hz, 1H), 1.75 (dm, $J = 10.1$ Hz, 1H), 1.90 (dd, $J = 8.9$, 5.9 Hz, 1H), 2.05 (dd, $J = 9.1$, 2.1 Hz, 1H), 2.15 (br.d, $J = 3.8$ Hz, 1H), 2.22 (br.s, 1H), 2.29 (s, 3H), 2.37 (br.s, 1H), 2.43 (br.d, $J = 3.8$ Hz, 1H), 2.51 (d, $J = 9.1$ Hz, 1H), 6.84 (d, $J = 8.0$ Hz, 2H), 6.96 (d, $J = 8.0$ Hz, 2H), 7.28–7.42 (m, 9H), 7.53–7.64 (m, 6H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 20.8, 29.9, 30.6, 30.9, 31.9, 36.9, 37.4, 38.4, 38.5, 41.3, 42.7, 46.2, 46.9, 52.8, 60.7, 128.0, 128.4, 128.6, 128.7, 128.9, 134.8, 137.5, 141.0, 141.3. MS (m/z): 553 ($M^+ -$ Ph, 13%), 351 (100%), 278 (78%), 211 (39%), 197 (34%), 161 (34%), 131 (31%), 120 (30%), 105 (98%), 91 (29%), 67 (42%). **4.**

Supplementary material

Complete lists of bond lengths and angles, hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, CCDC no. 137553 for **7j**. Copies of the data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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