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# Free Radical Hydrostannylation of Unactivated Alkenes with Chiral Trialkylstannanes

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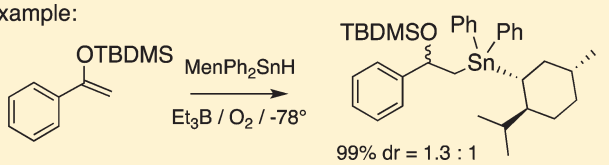
**ABSTRACT:** Free radical hydrostannylation of olefins with differing steric and electronic demands have been carried out using the chiral, nonracemic stannanes (1*R*,2*S*,5*R*)-menthyldiphenyltin hydride (**7**), bis[(1*R*,2*S*,5*R*)-menthyl]phenyltin hydride (**8**), and tris[(1*R*,2*S*,5*R*)-menthyl]tin hydride (**9**). These reactions resulted in adducts **16**−**18** with yields that were found to depend on the nature of the substituents on both alkene and stannane and could be carried out at low temperature initiated by triethylborane and oxygen; $MenPh_2SnH$ (**7**) reacted with *tert*-butyldimethyl(1-phenylvinyloxy)silane (**1**) at −78 °C to afford adduct **19** in near-quantitative yield. Somewhat surprisingly, addition of small quantities of diphenyl diselenide to these reactions failed to improve the outcome under any circumstances.

Example:




## INTRODUCTION

Single-enantiomer drug candidates are important to many pharmaceutical companies, and as a consequence, new methods for the preparation of enantiopure compounds are critical for the development of next-generation pharmaceutical products.[1] While motifs may vary, many of these candidates require chiral benzylic alcohols as synthetic starting materials or intermediates; a recent preparation of the antidepressant drug fluoxetine (Prozac) is an example of this chemistry (Scheme 1).[2] The critical step in the example provided in Scheme 1 involves access to ethyl (*R*)-3-hydroxy-3-phenylpropanoate, and this has traditionally been achieved through chiral resolution techniques[2] or through chiral reduction.[3]

We considered the possibility of carrying out asymmetric free radical hydrostannylation chemistry on an appropriately constructed alkene to give a chiral building block suitable for further elaboration (Scheme 2). To our disappointment, initial attempts to hydrostannylate the enol ether **1** with tris[(1*R*,2*S*,5*R*)-menthyl]tin hydride (tris[(1*R*,2*S*,5*R*)-2-(1-methylethyl)-5-methylcyclohexyl]tin hydride) under radical conditions resulted in returned starting material, even in the presence of benzeneselenol as a polarity reversal catalyst.[4,5] In contrast, triphenylstannane afforded the product **2** in 20% yield and this could be improved to 95% in the presence of benzeneselenol.[5]

Chiral free radical hydrostannylation reactions have been reported on a number of occasions; these reactions proceed most readily with electron-deficient alkenes, which is largely a consequence of the nucleophilicty of the stannyl radical.[6−12] For example, Podestá reported that reactions of (1*R*,2*S*,5*R*)-menthyldimethylstannane with diphenylpropenoates and propenenitriles (e.g., **3**) take place with high levels of diastereoselectivity (Scheme 3),[10] while the addition of achiral trialkylstannanes to (1*R*,2*S*,5*R*)-menthyl crotonate (**4**) affords chiral tetraorganotin compounds with moderate diastereoselectivity (Scheme 3).[11,12]

Roberts demonstrated that trialkylsilanes, in the presence of a catalytic amount of a thiol, are capable of reducing alkyl halides and other precursors.[13] Now known as "polarity reversal catalysis", the success of this chemistry has been attributed to favorable polar effects in the transition state for hydrogen atom transfer from a sulfur- to a carbon-centered radical (e.g., **5**) over the less favorable transition state (e.g., **6**), and this hypothesis has been supported by computational chemistry;[14] this technique has been applied to the free radical hydrosilylation of alkenes.[15,16] A similar catalytic phenomenon has been described by Crich for reactions involving stannanes and benzeneselenol, a technique that effectively extends the kinetic range of stannane-mediated reactions.[4] Importantly, benzeneselenol can be conveniently prepared in situ by the reaction of diphenyl diselenide with trialkyltin hydrides (Scheme 4).[4]

Computational chemistry suggests that polarity reversal catalysis involving stannanes should be possible using a thiol as catalyst.[17] We were surprised that, given this history, we were only able to locate one report that utililized $Bu_3SnH$/ArSH to hydrostannylate, and this chemistry involved terminal alkynes such as phenylacetylene (Scheme 4).[18]

As part of an ongoing program of work aimed at developing free radical methods for the preparation of chiral intermediates,[5,19−25] we have explored the use of chiral free radical hydrostannylation chemistry to the synthesis of enantiopure intermediates for use in the preparation of pharmaceutical products. We now report that hydrostannylation of substituted alkenes with (1*R*,2*S*,5*R*)-menthyldiphenyltin hydride[25] (**7**), bis[(1*R*,2*S*,5*R*)-menthyl]phenyltin hydride[25] (**8**), and tris[(1*R*,2*S*,5*R*)-menthyl]tin hydride[26] (**9**) proceeds in yields that depend on the substituent on the alkene. Somewhat surprisingly, addition of

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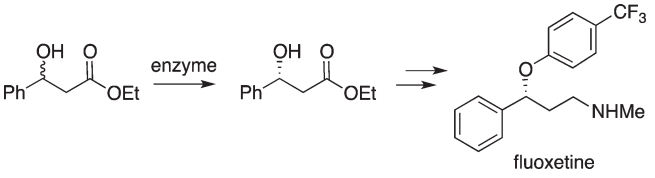
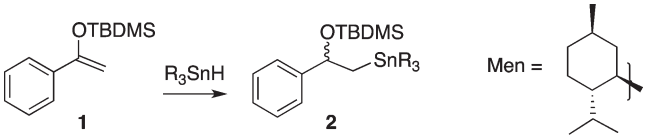
**Scheme 1**



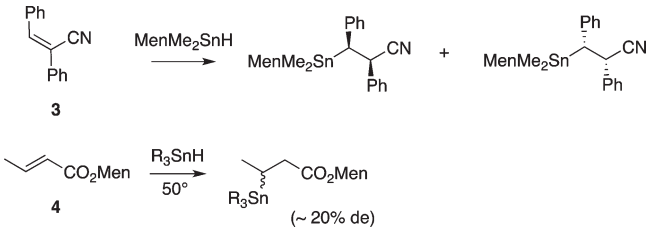

**Scheme 2**



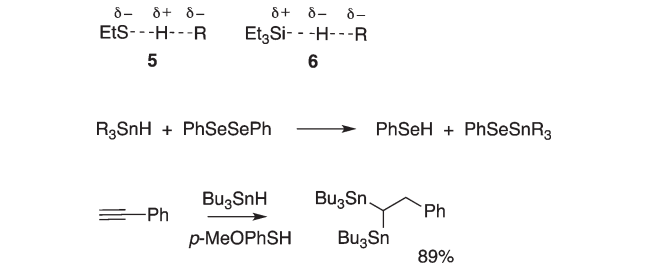

**Scheme 2**

0% (R = Men)
20% (R = Ph)

**Scheme 3**




**Scheme 4**

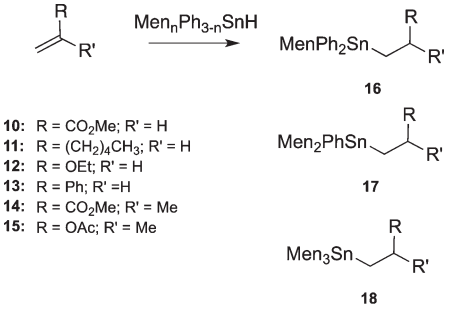



catalytic amounts of diphenyl diselenide appears to have little effect on the outcomes of these reactions.

## RESULTS AND DISCUSSION

**Reactions of Chiral Stannanes with a Variety of Substrates.** Despite the results depicted in Scheme 3, Podestá reported that some menthyl-substituted stannanes fail to react with methyl 1,2-diphenylacrylate under radical conditions,[7] and this was of some concern to us. We therefore chose to begin this study by exploring the hydrostannylation chemistry of chiral stannanes (**7**−**9**) with a variety of substrates (**10**−**15**) under the "standard" radical hydrostannylation conditions reported previously by us (Scheme 5).[5] To that end, each substrate was

**Scheme 5**




**10:** R = $CO_2Me$; R' = H
**11:** R = $(CH_2)_4CH_3$; R' = H
**12:** R = OEt; R' = H
**13:** R = Ph; R' =H
**14:** R = $CO_2Me$; R' = Me
**15:** R = OAc; R' = Me

**Table 1. Reactions of Stannanes 7− 9 (1.0 equiv) with Substrates 10−15 at 80 °C (AIBN) in the Absence of Solvent or in 1.85 M Benzene Solution**[a]

| entry | substrate | stannane | amt of **16**−**18**, %[b] | $^{119}$Sn NMR,[c] δ |
|---|---|---|---|---|
| 1 | **10** | **7** | 95 (52) | −89.9 |
| 2 | | **8** | 93 (67) | −79.3 |
| 3 | | **9** | 99 (62) | −70.3 |
| 4 | **11** | **7** | 94d (65) | −92.5 |
| 5 | | **8** | n.r.[e] | |
| 6 | | **9** | n.r.[e] | |
| 7 | **12** | **7** | 73[d] (35) | −97.0 |
| 8 | | **8** | n.r.[e] | |
| 9 | | **9** | n.r.[e] | |
| 10 | **13** | **7** | 99 (84) | −91.8 |
| 11 | | **8** | 99 (70) | −79.3 |
| 12 | | **9** | 97 (22) | −72.6 |
| 13 | **14** | **7** | 93 (79) | −94.5/−94.7[f] |
| 14 | | **8** | 88 (33) | −98.7/−98.8[f] |
| 15 | | **9** | n.r.[e] | |
| 15 | **15** | **7** | n.r.[e] | |
| 17 | | **8** | n.r.[e] | |
| 18 | | **9** | n.r.[e] | |

[a] See text. All reaction mixtures were stirred at 80 ± 3 °C for 2.5 h. [b] $^1$H NMR estimated conversions (isolated yields in parentheses). [c] $CDCl_3$. [d] Conversion based on unreacted stannane. [e] No reaction. [f] 1:1 mixture of diastereoisomers.

treated with 1.0 equiv of **7** at 80 °C in the absence of solvent (AIBN initiation), for 2.5 h. Due to viscosity issues, reactions involving **8** or **9** were carried out in benzene at 1.85 M concentration. All reactions were carried out under an atmosphere of argon. Percentage conversions were estimated from the $^1$H NMR spectrum of each crude reaction mixture before chromatographic separation yielded the tetraorganotin products (**16**−**18**). The results of these studies are summarized in Table 1.

Inspection of Table 1 reveals that the substrates are divided into two classes: those that add normally to substrates **10**−**15** and those that will not add. In each reacting substrate the conversions are observed to be high, with isolated yields often somewhat lower, reflecting difficulties in product isolation. The unreacting substrates typically contain electron-donating groups that are not well matched with the nucleophilic properties of the incipient stannyl radical.[5] It is particularly noteworthy that the more sterically incumbered stannanes (**8**, **9**) are more sensitive to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electronic demand and steric environment of the alkene. For example, while the monomenthyl-substituted stannane **7** reacts well with all substrates with the exception of vinyl acetate (**15**; entry 16), the dimenthylstannane **8** begins to exhibit substrate selectivity in failing to react with the mildly electron-rich alkene 1-heptene (**11**; entry 5) and the remaining electron-rich systems (**12** and **15**, entries 8 and 17). On the other hand, trimenthylstannane (**9**) reacts only with the sterically unencumbered alkenes that are also electron-deficient (**10** and **13**, entries 3 and 12). This phenomenon of bulky stanannes performing either well or not at all has been reported previously by Podestá.[7,27]

It it interesting to note (and somewhat disappointing) that the prochiral alkene methyl methacrylate failed to show any stereoselectivity in its reaction with either **7** or **8**; products **16** and **17** (R = $CO_2$Me; R′ = Me) were isolated as a 1:1 mixture of diastereoisomers, as evidenced by NMR spectroscopy (entries 13 and 14).

In order to improve on these reaction conditions, and in an attempt to "encourage" the unreactive systems to undergo hydrostannylation, we repeated each of the reactions listed in Table 1 in the presence of catalytic amounts of diphenyl diselenide as described in our earlier publication.[5] Unfortunately, under no circumstance did we observe an improved outcome and, more importantly, the unreactive alkenes still failed to react under these conditions.

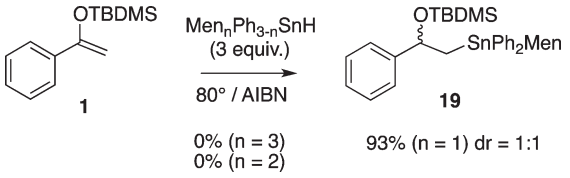
**Reactions of Chiral Stannanes with *tert*-Butyldimethylsilyloxystyrene (1).** We next turned our attention to the reactions of the silyl enol ether **1** with chiral stannanes **7**−**9**. We had previously shown that **1** fails to react with tris[(1*R*,2*S*,5*R*)-menthyl]tin hydride (**9**) under "standard" or "polarity reversal catalyzed" conditions.[5] It came as no surprise, therefore, that bis[(1*R*,2*S*,5*R*)-menthyl]phenyltin hydride (**8**) also failed to react under these conditions (Scheme 6).

To our (unexpected) delight, (1*R*,2*S*,5*R*)-menthyldiphenyltin hydride (**7**) did react with **1** under the conditions detailed in Table 1 (80°, neat, AIBN) to afford the adduct **19** in low yield; however, when the amount of stannane was increased to 3 equiv, **19** was isolated in 93% yield. Interestingly, as was observed for **14** (Table 1, entry 13), this reaction proceeded without stereoselectivity.

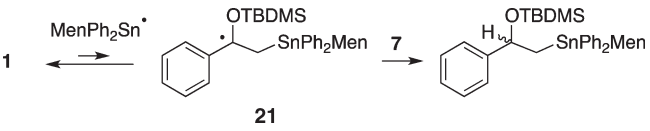
The reactivities of stannanes **7**−**9** toward the enol ether **1** can be attributed to steric congestion resulting from the interactions of (multiple) menthyl substituents on the reagent with the bulky *tert*-butyldimethylsilyl group on the oxygen atom in **1**. This congestion disfavors the equilibrium to form adduct radical **21** (Scheme 7), and as a consequence, high concentrations and multiple equivalents of **7** are required for a successful outcome. For the remaining chiral reagents, these unfavorable interactions would appear to be too strong to be overcome through adjustment of these parameters.

**Low-Temperature Hydrostannylations.** In an attempt to induce stereoselectivity in this reaction, we considered carrying out the radical hydrostannylation at reduced temperatures. While there are a number of methods for initiating radical reactions at low temperature,[28] the method of choice from our perspective involves the use of triethylborane and oxygen because of its ease of application.[29] To the best of our knowledge, low-temperature radical hydrostannylation of alkenes employing this method of initiation has not been reported previously; however, Oshima reported the use of triethylborane as an initiator for the hydrostannylation of alkynes.[30] As a consequence, we chose to explore

**Scheme 6**




**Scheme 7**




**Scheme 8**

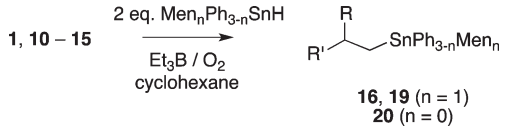



**Table 2. Reactions of Stannanes $Ph_3SnH$ and 7 (2.0 equiv) with Substrates 1 and 10 — 15 at Room Temperature Initiated by $Et_3B/O_2$ (See Text)[a]**

| entry | substrate | stannane | amt of **16**, **19**, or **20**, %[b] | $^{119}$Sn NMR[c] δ |
|---|---|---|---|---|
| 1 | **1** | $Ph_3SnH$ | >99[e] (99) [20] | −124.8 |
| 2 | | **7** | >99[e](99) | −94.5/−94.6[d] |
| 3 | **10** | $Ph_3SnH$ | >99[e] [97] | −109.4 |
| 4 | | **7** | >99[e] | −89.9 |
| 5 | **11** | $Ph_3SnH$ | 77 [93] | −110.3 |
| 6 | | **7** | 83 | −92.5 |
| 7 | **12** | $Ph_3SnH$ | 70 {77}[f] | −112.3 |
| 8 | | **7** | 98 | −97.0 |
| 9 | **13** | $Ph_3SnH$ | >99[e] [63] | −111.1 |
| 10 | | **7** | >99[e] | −91.8 |
| 11 | **14** | $Ph_3SnH$ | >99[e] {56}[f] | −117.2 |
| 12 | | **7** | >99[e] | −94.5/−94.7[d] |
| 13 | **15** | $Ph_3SnH$ | >99[e] [44] | −119.8 |
| 14 | | **7** | n.r.[g] | |

[a] See text. All reaction mixtures were kept at 23 °C for 3 h. [b] $^1$H NMR estimated conversions: isolated yields are given in parentheses and isolated yields from ref 5 in brackets (see text). [c] $CDCl_3$. [d] 1:1 mixture of diastereoisomers. [e] Quantitative. [f] Reference 31. [g] No reaction.

the feasibility of this chemistry using a model stannane: namely, triphenyltin hydride.

To our delight, reaction of all substrates **1** and **10**−**15** with 2 equiv of triphenyltin hydride in cyclohexane (1 M), initiated by $Et_3B/O_2$, proceeded with excellent conversion at room temperature (23 °C) to afford stannanes **20** (Scheme 8, Table 2). It should be noted that even isoprenyl acetate (**15**) reacts with $Ph_3SnH$ in quantitative yield under these conditions (entry 13). These data are to be compared with the yields reported previously for the analogous reaction carried out under "standard"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conditions (AIBN/80 °C);[5,31] this comparison reveals that the $Et_3B/O_2$ initiated reactions appear, on face value, to provide superior outcomes (Table 2).

When these reactions were repeated with (1*R*,2*S*,5*R*)-menthyldiphenyltin hydride (**7**), with the exception of **15**, which failed to react, high conversions to stannanes **16** and **19** were observed by $^1$H NMR spectroscopy of the crude reaction mixtures. In the case of the silylated substrate **1**, the required product **19** was isolated in 99% yield; unfortunately, no diastereoselectivity was observed.

In a further attempt to induce diastereoselectivity, the reaction of **1** with **7** was repeated at −78 °C; in this case a reaction time of 5 h was required. To our delight, high conversion to the required product was observed under these conditions, with **19** isolated in 99% yield. Unfortunately, only moderate (1.3:1) diastereoselectivity was observed and the diastereoisomers of **19** could not be separated by chromatography.

## CONCLUSIONS

Free radical hydrostannylations of olefins of differing steric and electronic demand have been carried out using the chiral, nonracemic stannanes (1*R*,2*S*,5*R*)-menthyldiphenyltin hydride (**7**), bis[(1*R*,2*S*,5*R*)-menthyl]phenyltin hydride (**8**), and tris-[(1*R*,2*S*,5*R*)-menthyl]tin hydride (**9**). These reactions resulted in adduct yields (**16**−**18**) that were found to depend on the nature of the substituents on both alkene and stannane. For alkenes bearing electron-withdrawing groups, excellent yields of hydrostannylated products (**16**−**18**) were obtained irrespective of stannane. For alkenes bearing electon-donating groups, the bulkier stannanes (**8** and **9**) failed to react, while $MenPh_2SnH$ (**7**) reacted with all substrates with good to excellent conversions, except for vinyl acetate, which failed to react under all circumstances.

This work also demonstrated the feasibility of low-temperature hydrostannylation initiated by triethylborane and oxygen; $MenPh_2SnH$ (**7**) reacted with *tert*-butyldimethyl(1-phenylvinyloxy)silane (**1**) at −78 °C to afford adduct **19** in near-quantitative yield. Despite being carried out at low temperature, little diastereoselectivity was observed in this reaction.

Somewhat surprisingly, addition of small quantities of diphenyl diselenide to these reactions failed to improve the outcome in each case.

## EXPERIMENTAL SECTION

(1*R*,2*S*,5*R*)-Menthyldiphenyltin hydride (**7**), bis[(1*R*,2*S*,5*R*)-menthyl]phenyltin hydride (**8**), and tris[(1*R*,2*S*,5*R*)-menthyl]tin hydride (**9**) were prepared following literature procedures.[25,26]

**General Methods.** *tert-Butyldimethyl(1-phenylvinyloxy)silane.*[32] To a solution of acetophenone (2.16 g, 18 mmol) in $CH_2Cl_2$ was added triethylamine (2.5 mL, 20 mmol) at room temperature. After 1 h *tert*-butyldimethylsilyl trifluoromethanesulfonate (5 g, 19 mmol) was added and the resulting mixture was stirred at this temperature for a further 2 h. To this solution was added cold phosphate buffer (pH 7, 30 mL), with stirring, and the mixture was washed with $CH_2Cl_2$. The organic phases were combined, dried ($MgSO_4$), and concentrated in vacuo to yield the title compound as a clear oil (4.2 g, 99%), which could be used directly or purified by column chromatography (petroleum spirits, 1% $Et_3N$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.23 (6H, s), 1.06 (s, 9H), 4.43 (1H, d, $J$ = 1.6 Hz), 4.85 (1H, d, $J$ = 1.6 Hz), 7.29−7.40 (3H, m), and 7.60−7.63 (2H, m). $^{13}$C NMR $\delta$ (125 MHz, $CDCl_3$): −4.6, 18.3, 25.8, 90.9, 125.3 128.0 128.1, 137.8, and 156.0.

*General Procedure A for Hydrostannylation Reactions at 80 °C.* A few crystals of AIBN were added to a homogeneous mixture of stannane (1.0 equiv) and olefin (1.0 equiv) in the absence of solvent (**7** or $Ph_3SnH$) or in benzene (1.85 M, **8** or **9**) under an inert atmosphere. The mixture was heated at 80 °C for 2.5 h and cooled, the solvent removed in vacuo (where appropriate), and the residue separated by flash column chromatography (20/1 hexanes/EtOAc, 1% $Et_3N$) to afford the hydrostannylated product **16**−**20** as detailed below.

*General Procedure B for Hydrostannylation Reactions at 23 °C.* To the required olefin (1.0 equiv) was added stannane ($Ph_3SnH$ or **7**, 2.0 equiv) followed by $Et_3B$ in cyclohexane (1 M, 1.0 equiv). The mixture was stirred open to the atmosphere for 3 h and concentrated in vacuo and the residue separated by flash chromatography (20/1 hexanes/EtOAc, 1% $Et_3N$) to afford the hydrostannylated product **16**−**20** as detailed below.

*Methyl 3-[((1R,2S,5R)-Menthyl)diphenylstannyl]propanoate (**16**; R = $CO_2Me$, R′ = H).* Following general procedure A. Isolated as a colorless oil (52%). $[\alpha]_D^{27}$ = −18.15° ($c$ = 5.35, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.73 (3H, d, $J$ = 7.0 Hz), 0.81 (3H, d, $J$ = 7.0 Hz), 0.85 (3H, d, $J$ = 6.0 Hz), 0.95 (1H, qd, $J$ = 3.0 Hz, 12.5 Hz), 1.05 (1H, qd, $J$ = 3.0, 12.5 Hz), 1.28−1.36 (2H, m), 1.42−1.52 (3H, m), 1.63−1.70 (2H, m), 1.75−1.78 (1H, m), 1.99 (1H, td, $J$ = 3.0, 12.5 Hz), 2.07 (3H, dt, $J$ = 3.0, 8.5 Hz), 2.06−2.08 (1H, m), 2.46−2.61 (2H, m), 3.59 (3H, s), 7.33−7.39 (6H, m), 7.45−7.57 (4H, m). $^{13}$C NMR (125 MHz): $\delta$ 5.1, 15.8, 21.8, 22.5, 26.7, 30.9, 34.1, 35.0, 35.2, 35.3, 41.2, 46.4, 51.5, 128.1, 128.2, 128.3, 137.0, 137.1, 139.7, 139.8, 175.6. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −89.9. IR (neat) $\nu_{max}$ 3064, 1729 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{26}H_{36}O_2Sn$ 607.078 27 (M + $Ag^+$), found 607.077 86.

*Methyl 3-[Bis((1R,2S,5R)-menthyl)phenylstannyl]propanoate (**17**; R = $CO_2Me$, R′ = H).* Following general procedure A. Isolated as a colorless oil (67%). $[\alpha]_D^{27}$ = −38.40° ($c$ = 18.9, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.74 (3H, d, $J$ = 7.0 Hz), 0.76 (3H, d, $J$ = 7.0 Hz), 0.83−1.05 (16H, m), 1.20−1.46 (8H, m), 1.54−1.61 (2H, m), 1.67 (2H, td, $J$ = 3.0, 12.0 Hz), 1.73−1.80 (4H, m), 1.96−2.02 (2H, m), 2.42−2.52 (2H, m), 3.63 (3H, s), 7.25−7.34 (3H, m), 7.38−7.45 (3H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 51.2, 16.1, 16.2, 21.8, 21.9, 22.4, 22.5, 26.7, 26.8, 31.2, 34.0, 35.0, 35.1, 35.26, 35.28, 35.33, 35.34, 41.4, 41.5, 46.5, 46.6, 51.3, 127.6, 127.7, 136.7, 143.3, 175.6. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −79.3. IR (neat): $\nu_{max}$ 2952, 1734 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{30}H_{50}O_2Sn$ 669.187 82 (M + $Ag^+$), found 669.187 35.

*Methyl 3-[Tris((1R,2S,5R)-menthyl)stannyl]propanoate (**18**; R = $CO_2Me$, R′ = H).* Following general procedure A. Isolated as a white solid (62%). $[\alpha]_D^{27}$ = +57.7° ($c$ = 17.4, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.79 (9H, dd, $J$ = 1.5, 6.5 Hz), 0.86 (9H, d, $J$ = 4.5 Hz), 0.89−1.03 (6H, m), 0.97 (9H, dd, $J$ = 1.5, 6.5 Hz), 1.07−1.13 (2H, m), 1.19−1.27 (6H, m), 1.39−1.48 (3H, m), 1.52−1.63 (3H, m), 1.70 (3H, d, $J$ = 12.0 Hz), 1.76 (3H, d, $J$ = 12.5 Hz), 1.88−1.94 (3H, m), 2.46−2.58 (2H, m), 3.70 (3H, d, $J$ = 2.0 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 7.33, 16.7, 22.2, 22.7, 27.1, 31.9, 33.9, 35.4, 35.5, 35.6, 41.8, 46.7, 51.5, 176.1. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −70.3. IR (neat): $\nu_{max}$ 2947, 1743 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{34}H_{64}O_2Sn$ 715.302 46 (M+$Ag^+$); found 715.299 57.

*Synthesis of Heptyl((1S,2S,5R)-menthyl)diphenylstannane (**16**; R = $(CH_2)_4CH_3$, R′ = H).* Following general procedure A. Isolated as a colorless oil (65%). $[\alpha]_D^{25}$ = −18.73° ($c$ = 4.15, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.68 (3H, d, $J$ = 6.5 Hz), 0.80 (3H, d, $J$ = 6.5 Hz), 0.82 (3H, d, $J$ = 6.5 Hz), 0.82 (3H, t, $J$ = 7. Hz), 0.89−1.06 (4H, m), 1.18−1.35 (13H, m), 1.44 (1H, tt, $J$ = 2.5, 12.0 Hz), 1.55−1.61 (2H, m), 1.87 (1H, td, $J$ = 3.0, 12.0 Hz), 2.01 (1H, dt, 2.5, 9.5 Hz), 7.31−7.36 (6H, m) and 7.46−7.51 (4H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 10.9, 14.1, 15.8, 21.7, 22.5, 22.6, 26.7, 26.8, 28.7, 31.8, 33.9, 34.4, 34.5, 35.3, 35.4, 41.4, 46.6, 128.0, 128.1, 137.0, 140.7, 140.8. $^{119}$Sn NMR $\delta$ (187 MHz, $CDCl_3$): −92.5. IR (neat): $\nu_{max}$ 2954 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{29}H_{44}OSn$ 619.151 04 (M + $Ag^+$), found 619.150 52.

*(2-Ethoxyethyl)((1S,2S,5R)-menthyl)diphenylstannane (**16**; R = OEt, R′ = H).* Following general procedure A. Isolated as a colorless oil (35%). $[\alpha]_D^{27} = -19.4°$ ($c$ = 6.5, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.67 (3H, d, $J$ = 6.5 Hz), 0.79 (3H, d, $J$ = 7.0 Hz), 0.83 (3H, d, $J$ = 6.5 Hz), 0.91−1.06 (2H, m), 1.18 (3H, t, $J$ = 7.0 Hz), 1.26−1.35 (2H, m), 1.46 (1H, t, $J$ = 3.0, 12.0 Hz), 1.58−1.68 (4H, m), 1.73−1.76 (1H, m), 1.92 (1H, td, $J$ = 3.0, 12.0 Hz), 2.01−2.04 (1H, m), 3.42 (2H, q, $J$ = 7.02 Hz), 3.58−3.71 (2H, m), 7.32−7.36 (6H, m), 7.47−7.57 (4H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 12.7, 15.3, 15.8, 21.8, 22.5, 26.7, 33.9, 35.0, 35.3, 35.4, 41.1, 46.4, 65.5, 66.7, 128.0, 128.1, 128.2, 137.0, 137.6, 140.3, 140.4. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −97.0. IR (neat): $\nu_{max}$ 3063 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{26}H_{38}OSn$ 593.098 76 (M + Ag$^+$, 100%), found 593.099 01.

*((1R,2S,5R)-Menthyl)(phenethyl)diphenylstannane (**16**; R = Ph, R′ = H).* Following general procedure A. Isolated as a colorless oil (84%). $[\alpha]_D^{27} = -10.2°$ ($c$ = 43.25, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.67 (3H, d, $J$ = 6.5 Hz), 0.77−0.80 (6H, m), 0.82−1.04 (2H, m), 1.20−1.29 (2H, m), 1.41 (1H, tt, $J$ = 2.5, 11.5 Hz), 1.55 (2H, t, $J$ = 8.5 Hz), 1.59−1.73 (3H, m), 1.85 (1H, td, $J$ = 3.0, 12.5 Hz), 1.92−1.99 (1H, m), 2.77−2.87 (2H, m), 7.14−7.16 (3H, m), 7.23−7.26 (2H, m), 7.32−7.35 (6H, m), 7.43−7.54 (4H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 12.8, 15.9, 21.9, 22.5, 26.7, 32.8, 34.0, 34.7, 35.3, 41.3, 46.5, 125.7, 127.7, 128.2, 128.3, 128.4, 137.0, 140.1, 140.2, 145.5. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −91.8. IR (neat): $\nu_{max}$ 3063 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{30}H_{38}Sn$ 625.104 09 (M + Ag$^+$, 38%), found 625.104 023.

*Bis((1R,2S,5R)-menthyl)(phenethyl)phenylstannane (**17**; R = Ph, R′ = H).* Following general procedure A. Isolated as a colorless oil (70%). $[\alpha]_D^{27} = -39.6°$ ($c$ = 15.75, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.97 (6H, d, $J$ = 7.0 Hz), 1.03 (6H, d, $J$ = 5.0 Hz), 1.05−1.24 (3H, m), 1.06 (3H, d, $J$ = 7.5 Hz), 1.10 (3H, d, $J$ = 7.0 Hz), 1.42−1.67 (9H, m), 1.83−1.98 (8H, m), 2.16−2.22 (2H, m), 2.98−3.09 (2H, m), 7.32−7.35 (1H, m), 7.37−7.39 (2H, m), 7.45−7.53 (5H, m), 7.64−7.72 (2H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 13.3, 16.3, 16.4, 22.0, 22.1, 22.6, 33.3, 34.0, 34.1, 35.0, 35.1, 35.3, 35.4, 41.5, 41.7, 46.7, 127.7, 127.9, 128.3, 136.9, 142.1, 146.3. $^{119}$Sn NMR $\delta$ (187 MHz, $CDCl_3$): $\delta$ −79.3 . IR (neat): $\nu_{max}$ 3062 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{34}H_{52}Sn$ 687.213 64 (M + Ag$^+$, 100%), found 687.212 95.

*Tris((1R,2S,5R)-menthyl)(phenethyl)stannane (**18**; R = Ph, R′ = H).* Following general procedure A. Isolated as a white solid (22%). $[\alpha]_D^{27}$ = +37.37° ($c$ = 3.7, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.82 (9H, d, $J$ = 6.5 Hz), 0.87 (9H, d, $J$ = 6.0 Hz), 0.92−1.06 (5H, m), 0.99 (9H, d, $J$ = 6.0 Hz), 1.31−1.81 (3H, m), 1.27−1.33 (6H, m), 1.47−1.54 (3H, m), 1.59−1.65 (6H, m), 1.72 (3H, dd, $J$ = 2.5, 12.5 Hz), 1.77−1.79 (3H, m), 1.95−1.97 (3H, m), 2.84−2.92 (2H, m), 7.17−7.23 (3H, m), 7.29−7.33 (2H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 15.8, 16.8, 22.3, 22.7, 27.2, 33.8, 33.9, 35.1, 35.5, 35.7, 41.9, 46.9, 125.5, 127.6, 128.4, 146.7. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −72.6. IR (neat): $\nu_{max}$ 2945 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{38}H_{66}Sn$ 749.322 83 (M + Ag$^+$, 100%), found 749.323 19.

*Methyl (2R/2S)-3-[((1S,2S,5R)-Menthyl)diphenylstannyl]-2-methylpropanoate (**16**; R = $CO_2$Me, R′ = Me).* Following general procedure A. Isolated as a clear oil as a 1:1 mixture of diastereoisomers (79%). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.69 (3H, d, $J$ = 7.0 Hz), 0.71 (3H, d, $J$ = 6.5 Hz), 0.76 (3H, d, $J$ = 6.5 Hz), 0.83−0.85 (6H, m), 0.89−0.91 (3H, m), 0.98−1.06 (3H, m), 1.16−1.18 (3H, m), 1.23−1.44 (4H, m), 1.54−1.66 (3H, m), 1.73−1.74 (1H, m), 1.92−1.98 (1H, m), 2.03−2.07 (1H, m), 2.63−2.68 (1H, m), 3.45/3.46 (3H, s × 2), 7.33−7.36 (6H, m), 7.45−7.54 (4H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 15.8, 16.0, 21.2, 21.3, 21.8, 25.5, 26.4, 33.6, 33.9, 34.8, 34.9, 35.2, 35.3, 37.2, 41.0, 41.1, 46.2, 46.3, 51.5, 128.0, 128.11, 128.12, 128.2, 128.3, 137.0, 137.10, 137.13, 139.8, 140.1, 140.2, 140.4. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −94.5, −94.7. IR (neat): $\nu_{max}$ 3063, 1733 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{27}H_{38}O_2Sn$ 621.093 92 (M + Ag$^+$), found 621.093 47.

*Methyl (2R/2S)-3-[Bis((1S,2S,5R)-menthyl)phenylstannyl]-2-methylpropanoate (**17**; R = $CO_2$Me, R′ = Me).* Following general procedure A. Isolated as a clear oil and as a 1:1 mixture of diastereoisomers (33%). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.74 (3H, d × 2, $J$ = 7.0 Hz), 0.79 (3H, dd, $J$ = 2.5, 7.0 Hz), 0.83−0.89 (14H, m), 0.90−1.10 (3H, m), 1.17 (3H, d × 2, $J$ = 7.0 Hz), 1.19−1.31 (4H, m), 1.37−1.47 (3H, m), 1.55−1.63 (2H, m), 1.65−1.71 (2H, m), 1.75−1.82 (4H, m), 1.97−2.08 (2H, m), 2.54−2.65 (1H, m), 3.51 (3H, s × 2), 7.13−7.24 (3H, m), 7.44−7.46 (2H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 16.20, 16.23, 16.28, 16.3, 16.34, 16.5, 21.0, 21.5, 21.91, 21.93, 21.97, 22.0, 22.59, 22.62, 22.64, 26.9, 33.84, 33.85, 33.9, 34.1, 35.32, 35.35, 35.38, 35.4, 35.5, 37.3, 37.4, 41.4, 41.5, 46.5, 46.7, 46.8, 51.4, 127.6, 127.62, 127.69, 127.7, 136.87, 136.88, 142.0, 142.1, 178.1, 178.3. $^{119}$Sn NMR $\delta$ (187 MHz, $CDCl_3$): $\delta$ −98.7, −98.8. IR (neat): $\nu_{max}$ 2952, 1734 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{31}H_{52}O_2Sn$ 615.262 09 (M + K$^+$), found 615.262 02.

*Methyl 3-(Triphenylstannyl)propanoate[33] (**20**; R = $CO_2$Me, R′ = H).* Following general procedure A. Isolated as a white solid (97%). Mp: 46−47 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.73 (2H, t, $J$ = 7.5 Hz), 2.74 (2H, t, $J$ = 7.5 Hz), 3.52 (3H, s), 7.39−7.44 (9H, m), 7.55−7.67 (6H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 5.5, 30.7, 51.5, 128.5, 128.8, 137.0, 138.5, 175.1. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −109.4. IR (neat) $\nu_{max}$ 3063, 1729 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{22}H_{22}O_2Sn$ 544.968 72 (M + Ag$^+$), found 544.968 51.

*Heptyltriphenylstannane[34] (**20**; R = $(CH_2)_4CH_3$, R′ = H).* Following general procedure A. Isolated as a colorless oil that crystallized on standing (93%). Mp: 55−56 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.87 (3H, t, $J$ = 7.0 Hz), 1.18−1.31 (6H, m), 1.37 (2H, quin, $J$ = 7.5, 15.0 Hz), 1.53−1.54 (2H, m), 1.75 (2H, quin, 7.5, 15.0), 7.37−7.41 (9H, m) and 7.52−7.62 (6H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 11.1, 14.0, 22.5, 26.6, 28.7, 31.7, 34.2, 128.4, 128.7, 137.0, 139.2 ppm. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −110.3. IR (neat): $\nu_{max}$ 3063 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{25}H_{30}Sn$ 557.041 49 (M + Ag$^+$), found 557.041 07.

*(2-Ethoxyethyl)triphenylstannane (**20**; R = OEt, R′ = H).* Following general procedure A. Isolated as a colorless oil (77%). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.11 (3H, t, $J$ = 7.0 Hz), 1.89 (2H, t, $J$ = 7.5 Hz), 3.39 (2H, q, $J$ = 7.0 Hz), 3.79 (2H, t, $J$ = 7.5 Hz), 7.30−7.43 (9H, m), 7.54−7.67 (6H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 13.6, 15.1, 65.6, 67.9, 128.3, 128.7, 137.1, 139.1. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −112.3. IR (neat): $\nu_{max}$ 3063 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{22}H_{24}OSn$ 530.989 46 (M + Ag$^+$), found 530.989 01.

*(Phenethyl)triphenylstannane[33] (**20**; R = Ph, R′ = H).* Following general procedure A. Isolated as a while solid (63%). Mp: 127−128 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.83 (2H, td, $J$ = 1.0, 8.5 Hz), 2.99 (2H, t, $J$ = 8.5 Hz), 7.13−7.17 (3H, m), 7.22−7.25 (2H, m), 7.33−7.37 (6H, m), 7.45−7.55 (9H, m). $^{13}$C NMR $\delta$ (125 MHz, $CDCl_3$): 12.9, 32.5, 125.8, 127.8, 128.4, 128.5, 128.8, 138.6, 144.7. $^{119}$Sn NMR $\delta$ (187 MHz, $CDCl_3$): −111.1. IR (neat): $\nu_{max}$ 3060 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{26}H_{24}Sn$ 562.994 54 (M + Ag$^+$), found 562.994 13.

*(±)-Methyl 2-Methyl-3-(triphenylstannyl)propanoate (**20**; R = $CO_2$Me, R′ = Me).* Following general procedure A. Isolated as a colorless oil (56%). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.27 (3H, dd, $J$ = 2.0, 7.0 Hz), 1.66−1.71 (1H, m), 1.78−1.84 (1H, m), 2.86−2.94 (1H, m), 3.38 (1H, s), 7.38−7.39 (9H, m), 7.57−7.60 (6H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 16.5, 21.3, 37.1, 51.5, 128.4, 128.8, 137.0, 138.9, 177.5. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −117.2. IR (neat): $\nu_{max}$ 3063, 1725 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{23}H_{24}O_2Sn$ 558.984 37 (M + Ag$^+$), found 558.984 01.

*(±)-1-(Triphenylstannyl)propan-2-yl acetate (**20**; R = OAc, R′ = Me).* Following general procedure A. Isolated as a colorless oil (44%). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.32 (3H, d, $J$ = 7.0, 13.0 Hz), 1.69 (3H, s), 1.90 (1H, dd, $J$ = 7.0 Hz), 1.95 (1H, dd, $J$ = 7.0 Hz, $CH_2$), 5.33 (1H, q, $J$ = 7.0 Hz), 7.38−7.43 (9H, m), 7.53−7.64 (6H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 19.9, 20.9, 23.6, 70.6, 128.5, 128.9, 136.9, 138.5, 170.4. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −119.8 ppm. IR (neat): $\nu_{max}$ 3015, 1731 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{23}H_{24}O_2Sn$ 558.984 37 (M + Ag$^+$), found 558.983 95.

*[2-(tert-Butyldimethylsilyloxy)-2-phenylethyl]triphenylstannane (**20**; R = OTBDMS, R′ = Ph).* Following general procedure B. Isolated as a colorless oil (99%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.77 (3H, s), −0.81 (3H, s), 0.74 (9H, s), 2.10 (1H, dd, $J$ = 12.8, 7.6 Hz), 2.19 (1H, dd, $J$ = 13.2, 4.8 Hz), 5.21 (1H, dd, $J$ = 7.2, 5.2 Hz), 7.17−7.20 (4H, m), 7.27−7.20 (15H, m), 7.60−7.63 (5H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ −4.9, −4.7, 18.3, 25.9, 26.6, 73.8, 126.0, 127.0, 128.2, 128.3, 128.5, 137.0, 139.4, 146.6. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −124.8. IR (neat): $\nu_{max}$ 3064 cm$^{-1}$. Anal. Calcd for $C_{32}H_{38}OSiSn$: C, 65.65; H, 6.54; Sn, 20.28. Found: C, 65.68; H, 6.53; Sn, 20.35.

*[(2R/2S)-(tert-Butyldimethylsilyloxy)-2-phenylethyl][(1R,2S,5R)-menthyl)diphenylstannane (**19**).* To silyl enol ether **1** (0.23 g, 1 mmol) was added $MenPh_2SnH$ (**7**; 1 g, 1.9 mmol), followed by $Et_3B$ (1 mL, 1 mmol). The mixture was stirred open to the atmosphere at −78 °C for 5 h, concentrated in vacuo, and purified by column chromatography (petroleum spirits, 1% $Et_3N$) to give the title compound as a clear oil and as a 1.3:1 mixture of diastereoisomers (99%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.27 (3H, s), −0.24 (3H, s), −0.19 (3H, s), −0.13 (3H, s), 0.59−1.31 (42H, m), 1.55−1.69 (12H, m), 1.80−1.97 (6H, m), 4.96 (1H, dd, $J$ = 5.5, 9.2 Hz), 5.06 (1H, dd, $J$ = 5.5, 7.6 Hz), 7.16−7.42 (30H, m). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ −4.8, −4.7, 15.9, 16.0, 18.2, 21.7, 22.4, 22.5, 25.4, 25.5, 25.9, 26.6, 33.6, 33.7, 34.4, 34.8, 35.1, 35.2, 35.3, 40.8, 41.0, 46.0, 46.1, 74.4, 74.5, 125.8, 125.9, 126.9, 127.0, 127.8, 127.95, 127.97, 128.00, 128.01, 128.09, 128.1, 137.0, 137.1, 140.1, 140.5, 146.9, 147.2. $^{119}$Sn NMR (187 MHz, $CDCl_3$): $\delta$ −94.5, −94.6. IR (neat): $\nu_{max}$ 3063 cm$^{-1}$. HRMS: $m/z$ calcd for $C_{36}H_{52}OSiSn$ 755.185 48 ($M + Ag^+$), found 755.185 12.

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