# Stereoselective Synthesis of (*Z*)-1-Silyl-2-stannylethene by Palladium-Catalyzed Silastannation of Ethyne and Its Synthetic Transformations

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Dedicated to Professor Teruaki Mukaiyama on the occasion of his 77th birthday with admiration for his outstanding contribution to organic synthesis.

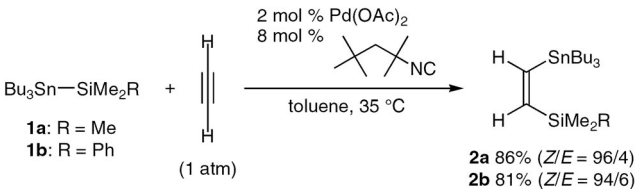
**Abstract:** (*Z*)-1-Silyl-2-stannylethenes were stereoselectively synthesized by silastannation of ethyne, catalyzed by a palladium/*tert*-alkyl isocyanide catalyst, and the synthetic utilities were demonstrated by their transformations.

**Key words:** palladium, alkyne, silylstannane, *cis*-addition, cross-coupling

Because of the widespread use of organosilicon and -tin compounds in organic synthesis,[1] it is evermore desired to establish efficient and practical methods to prepare these organometallic compounds in a regio- and stereodefined form. Compounds having both carbon–silicon and carbon–tin bonds in the molecule would allow stepwise transformations of the two carbon–metal bonds based on the difference in their intrinsic reactivities. For instance, 1-silyl-2-stannylethene is a highly useful synthetic intermediate for building olefinic compounds. (*E*)-1-Silyl-2-stannylethene can be easily prepared by hydrostannation of ethynylsilane[2] and has been used as a valuable building block.[3] On the other hand, the corresponding *Z* isomer received much less attention. Whereas the *Z* isomer can be prepared by stannylcupration of ethyne (HC≡CH),[4] *cis*-silastannation[5,6] of ethyne would provide a more straightforward approach to the *Z* isomer. However, silastannation of ethyne using $Pd(PPh_3)_4$ at 55 °C was reported to afford a mixture of *Z* and *E* isomers with the latter predominating (1:4).[5c] It is likely that the *Z* isomer initially formed isomerized to the *E* isomer, which was thermodynamically more stable.

We have reported that a palladium/*tert*-alkyl isocyanide catalyst is so active that the silastannation of mono-substituted alkynes proceeded at room temperature to give 2-substituted (*Z*)-1-silyl-2-stannylethenes.[6] Now, we report the stereoselective synthesis of (*Z*)-1-silyl-2-stannylethene with the use of the palladium/*tert*-alkyl isocyanide complex[7] as the catalyst for the silastannation of ethyne. The synthetic transformations were also examined.

When tributyl(trimethylsilyl)stannane (**1a**) was stirred for one day under a balloon pressure of ethyne in the presence of palladium(II) acetate (2 mol%) and 1,1,3,3-tetramethylbutyl isocyanide (8 mol%) in toluene at 35 °C,[8] the addition reaction proceeded to completion (Scheme 1). $^1$H NMR analysis of the crude reaction mixture revealed that (*Z*)-1-tributylstannyl-2-(trimethylsilyl)ethene (**2a**) was formed as the major product together with a small amount of bis-stannation product (<5%).[9] The pure silastannation product was obtained in 86% yield (*Z*/*E* = 96/4) by simple bulb-to-bulb distillation. The stereochemistry of the silastannation product **2a** was unambiguously confirmed by the coupling constant (*J* = 18.4 Hz for *Z*; 23.0 Hz for *E*) of the two vicinal vinylic protons in the $^1$H NMR spectrum. Dimethylphenylsilyl derivative **1b** similarly underwent the reaction with ethyne to give rise to the *Z* adduct **2b**.[10]




**Scheme 1**

Next, the silastannated products were used for further synthetic transformations to demonstrate their utilities as a building block. Lithiation of the vinylstannane moiety of **2a** with *n*-BuLi followed by the reaction with aldehydes gave γ-trimethylsilyl allylic alcohols **3** with retention of the *Z* stereochemistry (Scheme 2). Then, (*Z*)-γ-trimethylsilyl allylic alcohols **3** were subjected to the copper(I)-promoted cross-coupling reaction, developed recently by Takeda et al.[11] The cross-coupling of **3** with allyl and benzyl halides successfully took place to afford only (*Z*)-allylic alcohols **4**. The minor *E* isomer remained unchanged because the cross-coupling reaction involved intramolecular 1,4-silyl migration from the $sp^2$ carbon to oxygen.

Both vinylsilanes and -stannanes are known to react with an iodonium source to produce vinyl iodides. However, treatment of **2a** with iodine (1.15 equiv) gave (*Z*)-1-iodo-2-(trimethylsilyl)ethene (**5**) in 42% isolated yield via chemoselective and stereospecific replacement of the stannyl group with an iodo group (Scheme 3). It is of note that the stereoselective synthesis of the iodide **5** was unprecedented.[12]

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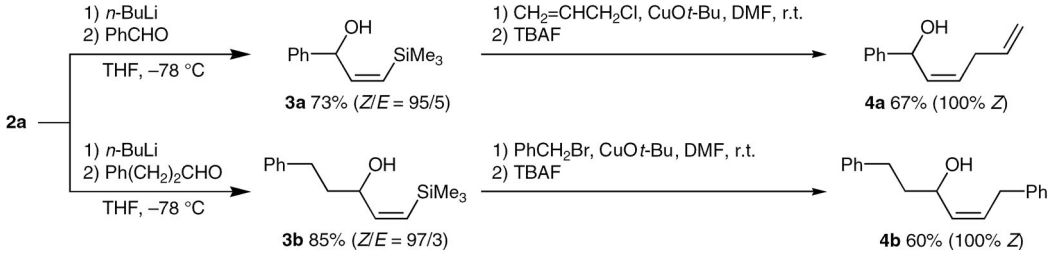
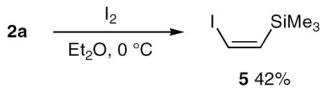
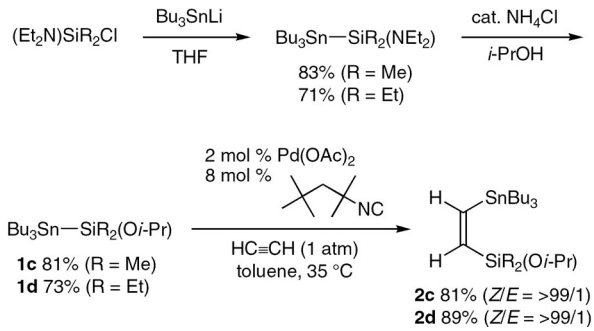



**Scheme 2**




**Scheme 3**

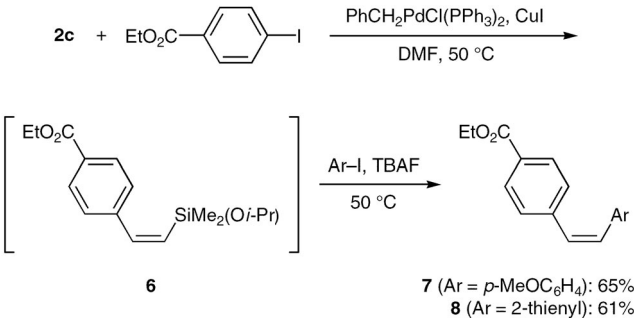
Various synthetic transformations, like a cross-coupling reaction, can be carried out much easier with an isopropoxydimethylsilyl group than with trimethylsilyl and dimethylphenylsilyl groups. On the other hand, an isopropoxydimethylsilyl group is adequately stable against hydrolysis. Thus, we next examined the silastannation using silylstannanes having an isopropoxy group on the silicon (**1c** and **1d**). Silylstannanes **1c** and **1d** were prepared from the corresponding aminochlorosilanes[13] as shown in Scheme 4. The silastannation reaction of **1c** and **1d** also took place under the same conditions. In addition, a complete *cis*-stereoselectivity was observed in the products (**2c** and **2d**).




**Scheme 4**

The silastannated product **2c**, having an isopropoxydimethylsilyl group, has a broader scope as a building block. For example, the successive cross-coupling of **2c** can be carried out in one-pot reaction. In the presence of a palladium/copper catalyst,[14] **2c** was treated with ethyl *p*-iodobenzoate to give (*Z*)-β-silylstyrene derivative **6**. Addition of *p*-iodoanisole and tetrabutylammonium fluoride (TBAF) to the reaction mixture afforded the stilbene derivative **7** without loss of the *Z* stereochemistry (Scheme 5).[15] Likewise, the coupling of **6** with 2-thienyl iodide took place in a similar manner to give **8**.

In summary, highly stereoselective *cis*-silastannation of ethyne catalyzed by a palladium/*tert*-alkyl isocyanide complex was achieved, and the usefulness of the products




**Scheme 5**

was demonstrated by their synthetic transformations. The *Z* olefinic geometries were kept during the transformations shown in Schemes 2, 3, and 5. Thus, the (*Z*)-1-silyl-2-stannylethenes offer a versatile synthetic platform for the *cis*-disubstituted -CH=CH- skeleton.

Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used as received. All reactions were carried out under a nitrogen atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 $PF_{254}$ (Merck). $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian Gemini 2000 ($^1H$ at 300.07 MHz and $^{13}C$ at 75.46 MHz) spectrometer or a Varian Mercury 400 ($^1H$ at 400.44 MHz). Proton chemical shifts are referenced to residual $CHCl_3$. Carbon chemical shifts are referenced to $CDCl_3$. $^{29}Si$ and $^{119}Sn$ NMR spectra were recorded on a JEOL JNM-A400 spectrometer ($^{29}Si$ at 79.30 MHz and $^{119}Sn$ at 148.95 MHz). Silicon and tin chemical shifts are referenced to external standards $Me_4Si$ and $Me_4Sn$, respectively. High resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. Chloro(diethylamino)dimethylsilane was prepared according to the literature method.

**Preparation of Silylstannanes**

**Isopropoxy(dimethyl)(tributylstannyl)silane (1c)**

To a THF solution (150 mL) of $Bu_3SnLi$, which was prepared from $Bu_3SnH$ (43.7 g, 150 mmol) and LDA, was added $(Et_2N)Me_2SiCl$ (26.1 g, 158 mmol) dropwise at 0 °C, and the reaction mixture was allowed to warm to r.t. overnight. The reaction mixture was diluted with hexane, filtered through Celite®, and concentrated. Further filtration through Celite® (hexane–$Et_2O$, 3:1) followed by distillation (138 °C/0.9 mmHg) gave $Bu_3Sn$–$SiMe_2(NEt_2)$ (52.6 g, 83%) as a pale yellow oil. A mixture of $Bu_3Sn$–$SiMe_2(NEt_2)$ (25.2 g, 60 mmol) and $NH_4Cl$ (1.5 g) in *i*-PrOH (120 mL) was stirred at r.t. overnight. The reaction mixture was diluted with hexane, filtered through Celite®, and concentrated. Further filtration through Celite® (hexane–$Et_2O$, 3:1) followed by distillation (120 °C/0.4 mmHg) gave **1c** (19.8 g, 81%) as a pale yellow oil.

$^1$H NMR (300 MHz): δ = 0.37 (s, $^3J_{Sn–H}$ = 19.5 Hz, 6 H), 0.77−0.95 (m, 15 H), 1.16 (d, *J* = 6.1 Hz, 6 H), 1.24−1.38 (m, 6 H), 1.42−1.57 (m, 6 H), 3.90 (sept, *J* = 6.1 Hz, 1 H).

$^{13}$C NMR: δ = 4.5 ($^2J_{Sn–C}$ = 83.5 Hz), 8.2 ($^1J_{Sn–C}$ = 252.9, 241.5 Hz), 13.7, 25.7, 27.6 ($^2J_{Sn–C}$ = 51.0 Hz), 30.3 ($^3J_{Sn–C}$ = 17.4 Hz), 66.8.

$^{29}$Si NMR ($CDCl_3$): δ = 21.6.

$^{119}$Sn NMR ($CDCl_3$): δ = –141.1.

HRMS (EI): *m*/*z* calcd for $C_{17}H_{40}OSiSn$ ($M^+$), 408.1870; found, 408.1872.

Anal. Calcd for $C_{17}H_{40}OSiSn$: C, 50.13; H, 9.90. Found: C, 50.37; H, 9.63.

**Diethyl(isopropoxy)(tributylstannyl)silane (1d)**

According to the procedure analogous to that described for **1c**, **1d** was prepared as a pale yellow oil.

$^1$H NMR (300 MHz): δ = 0.75−0.93 (m, 19 H), 0.95−1.13 (m, 6 H), 1.16 (d, *J* = 6.0 Hz, 6 H), 1.25−1.38 (m, 6 H), 1.42−1.55 (m, 6 H), 3.89 (sept, *J* = 6.0 Hz, 1 H).

$^{13}$C NMR: δ = 7.3, 8.6 ($^1J_{Sn–C}$ = 248.2, 236.6 Hz), 10.4 ($^2J_{Sn–C}$ = 77.7 Hz), 13.7, 25.7, 27.7 ($^2J_{Sn–C}$ = 52.2 Hz), 30.3 ($^3J_{Sn–C}$ = 17.4 Hz), 67.1.

HRMS (EI): *m*/*z* calcd for $C_{15}H_{35}OSiSn$ ($M^+$ – Bu), 379.1479; found, 379.1478.

Anal. Calcd for $C_{19}H_{44}OSiSn$: C, 52.42; H, 10.19. Found: C, 52.69; H, 10.45.

**Silastannation of Ethyne**

**Trimethyl[(*Z*)-2-(tributylstannyl)vinyl]silane (2a)**

To a flask containing $Pd(OAc)_2$ (4.5 mg, 0.020 mmol) and 1,1,3,3-tetramethylbutyl isocyanide (11 mg, 0.080 mmol) were added successively toluene (10 mL) and silylstannane **1a** (362 mg, 1.00 mmol) at r. t. A balloon filled with gaseous ethyne was then attached to the flask via a three-way joint. The flask was then evacuated and refilled with ethyne from the balloon four times and the mixture was stirred for 1 day at 35 °C in the dark. The volatile materials were removed under reduced pressure, and the residue was filtered through a plug of Florisil® (hexane) and concentrated. The residue was subjected to bulb-to-bulb distillation (97–99 °C/1 mmHg) to afford **2a** (332 mg, 86%) as a pale yellow oil.

$^1$H NMR (300 MHz): δ = 0.10 (s, 9 H), 0.84–0.97 (m, 15 H), 1.23–1.39 (m, 6 H), 1.43–1.57 (m, 6 H), 7.00 (d, *J* = 18.6 Hz, 1 H), 7.12 (d, *J* = 18.6 Hz, 1 H).

$^{13}$C NMR: δ = –0.5, 11.1 ($^1J_{Sn–C}$ = 334.0, 320.1 Hz), 13.7, 27.4 ($^2J_{Sn–C}$ = 56.8 Hz), 29.2 ($^3J_{Sn–C}$ = 19.7 Hz), 151.0, 153.7 ($^2J_{Sn–C}$ = 29.1 Hz).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{29}SiSn$ ($M^+$ – Bu), 333.1061; found, 333.1065.

**Dimethyl(phenyl)[(*Z*)-2-(tributylstannyl)vinyl]silane (2b)**

According to the procedure analogous to that described for **2a**, **2b** (396 mg, 90%) was prepared from **1b** (415 mg, 0.98 mmol).

$^1$H NMR (300 MHz): δ = 0.36 (s, 6 H), 0.77−0.94 (m, 15 H), 1.20−1.33 (m, 6 H), 1.38−1.54 (m, 6 H), 7.16 (d, *J* = 18.9 Hz, 1 H), 7.29 (d, *J* = 18.9 Hz, 1 H), 7.31−7.38 (m, 3 H), 7.51−7.57 (m, 2 H).

$^{13}$C NMR: δ = –1.5, 11.0 ($^1J_{Sn–C}$ = 335.2, 321.3 Hz), 13.7, 27.3 ($^2J_{Sn–C}$ = 56.9 Hz), 29.1 ($^3J_{Sn–C}$ = 19.7 Hz), 127.7, 128.9, 134.0, 139.1, 151.2, 153.8.

$^{29}$Si NMR ($CDCl_3$): δ = –13.7.

$^{119}$Sn NMR ($CDCl_3$): δ = –68.0.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{31}SiSn$ ($M^+$ – Bu), 395.1217; found, 395.1220.

**Isopropoxy(dimethyl)[(*Z*)-2-(tributylstannyl)vinyl]silane (2c)**

A mixture of $Pd(OAc)_2$ (27 mg, 0.12 mmol), 1,1,3,3-tetramethylbutyl isocyanide (65 mg, 0.46 mmol), and silylstannane **1b** (2.23 g, 5.48 mmol) in toluene (48 mL) was stirred under a balloon pressure of ethyne for 2 h at 35 °C in the dark. The reaction mixture was passed through a plug of Florisil® ($Et_2O$), and the volatile materials were evaporated. Bulb-to-bulb distillation (140 °C/0.3 mmHg) afforded **2c** (1.94 g, 81%) as a yellow oil.

$^1$H NMR (300 MHz): δ = 0.18 (s, 6 H), 0.77−1.06 (m, 15 H), 1.17 (d, *J* = 6.3 Hz, 6 H), 1.24−1.37 (m, 6 H), 1.44−1.56 (m, 6 H), 4.02 (sept, *J* = 6.3 Hz, 1 H), 6.91 (d, *J* = 18.9 Hz, $^3J_{Sn–H}$ = 179.3, 171.0 Hz, 1 H), 7.18 (d, *J* = 18.9 Hz, $^2J_{Sn–H}$ = 84.5, 80.6 Hz, 1 H).

$^{13}$C NMR: δ = –0.2, 11.1, 13.8, 25.8, 27.4, 29.2, 65.1, 150.9, 153.3.

HRMS (EI): *m*/*z* calcd for $C_{15}H_{33}OSiSn$ ($M^+$ – Bu), 377.1323; found, 377.1322.

**Diethyl(isopropoxy)[(*Z*)-2-(tributylstannyl)vinyl]silane (2d)**

According to the procedure analogous to that described for **2c**, **2d** (2.09 g, 89%) was prepared from **1d** (2.21 g, 5.07 mmol).

$^1$H NMR (400 MHz): δ = 0.61−0.69 (m, 4 H), 0.86−1.10 (m, 21 H), 1.18 (d, *J* = 6.0 Hz, 6 H), 1.26−1.36 (m, 6 H), 1.46−1.54 (m, 6 H), 4.03 (sept, *J* = 6.0 Hz, 1 H), 6.83 (d, *J* = 18.8 Hz, $^3J_{Sn–H}$ = 181.0, 173.0 Hz, 1 H), 7.24 (d, *J* = 18.8 Hz, $^2J_{Sn–H}$ = 84.8, 81.6 Hz, 1 H)

$^{13}$C NMR: δ = 6.2, 7.1, 11.1, 13.8, 25.8, 27.5, 29.2, 65.1, 148.3, 154.4.

HRMS (EI): *m*/*z* calcd for $C_{17}H_{37}OSiSn$ ($M^+$ – Bu), 405.1636; found, 405.1644.

**Synthesis of (*Z*)-Allylic Alcohols 3**

**(*Z*)-1-Phenyl-3-(trimethylsilyl)prop-2-en-1-ol (3a)**

To a solution of **2a** (1.97 g, 5.1 mmol) in THF (25 mL) was added *n*-BuLi (1.56 M in hexane, 3.9 mL, 6.1 mmol) at –78 °C, and the reaction mixture was stirred for 2 h at –78 °C. Benzaldehyde (806 mg, 7.6 mmol) was added, and then the mixture was gradually warmed to r.t. After evaporating the solvents, the residue was extracted with $Et_2O$ (3 ×), and the organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane−EtOAc, 6:1) to give **3a** (763 mg, 73%, *Z*/*E* = 95/5).

$^1$H NMR (300 MHz): δ = 0.20 (s, 9 H), 1.87 (br s, 1 H), 5.33 (d, *J* = 9.0 Hz, 1 H), 5.75 (dd, *J* = 13.9, 0.6 Hz, 1 H), 6.41 (dd, *J* = 13.9, 9.0 Hz, 1 H), 7.23−7.42 (m, 5 H).

$^{13}$C NMR: δ = 0.6, 74.1, 126.0, 127.6, 128.5, 132.2, 142.7, 148.5.

$^{29}$Si NMR ($CDCl_3$): δ = –9.8.

HRMS (EI): *m*/*z* calcd for $C_{12}H_{18}OSi$ ($M^+$), 206.1127; found, 206.1130.

For the *E* isomer:

$^1$H NMR (300 MHz): δ = 0.07 (s, 9 H), 5.17 (d, *J* = 5.3 Hz, 1 H), 5.99 (dd, *J* = 18.7, 1.1 Hz, 1 H), 6.19 (dd, *J* = 18.7, 5.3 Hz, 1 H), 7.23−7.42 (m, 5 H).

**(*Z*)-5-Phenyl-1-(trimethylsilyl)pent-1-en-3-ol (3b)**

According to the procedure described for **3a**, **3b** (991 mg, 85%, *Z*/*E* = 97/3) was prepared from **2a** (1.94 g, 4.97 mmol) and 3-phenylpropanal (1.00 g, 7.45 mmol).

$^1$H NMR (300 MHz): δ = 0.05 (s, 9 H), 1.49 (br s, 1 H), 1.66−1.97 (m, 2 H), 2.60−2.80 (m, 2 H), 4.22 (dt, *J* = 5.2, 8.5 Hz, 1 H), 5.66 (d, *J* = 14.1, 0.8 Hz, 1 H), 6.27 (dd, *J* = 14.1, 8.5 Hz, 1 H), 7.13−7.31 (m, 5 H).

$^{13}$C NMR: δ = 0.3, 31.7, 38.7, 71.6, 125.8, 128.35, 128.43, 132.1, 141.7, 149.7.

HRMS (EI): *m*/*z* calcd for $C_{14}H_{22}OSi$ ($M^+$), 234.1440; found, 234.1439.

**Copper-Promoted Cross-Coupling of 3 (*Z*)-1-Phenylhexa-2,5-dien-1-ol (4a)**

To a DMF suspension (9 mL) of CuI (524 mg, 2.75 mmol) was added *t*-BuOLi (240 mg, 3.00 mmol) at 0 °C. After the mixture was stirred for 20 min at r.t., a DMF solution (8 mL) of **3a** (514 mg, 2.49 mmol) and a DMF solution (8 mL) of allyl chloride (230 mg, 3.01 mmol) were successively added to the mixture. After being stirred for 2 h at r.t., the reaction mixture was quenched by addition of an aq $NH_3$ solution (3.5%). The organic materials were extracted with $Et_2O$, dried over $Na_2SO_4$, and concentrated. The residue was dissolved in THF (25 mL), and TBAF (1.0 M in THF, 2.5 mL, 2.5 mmol) was added to the solution. The mixture was stirred at r.t. and diluted with $H_2O$. The organic materials were extracted with EtOAc, washed with 1 M HCl and then with $H_2O$, dried over $Na_2SO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane−EtOAc, 6:1) to afford **4a** (290 mg, 67%).

$^1$H NMR (300 MHz): δ = 1.90 (s, 1 H), 2.87−3.07 (m, 2 H), 5.02 (dq, *J* = 9.8, 1.6 Hz, 1 H), 5.07 (dq, *J* = 17.0, 1.7 Hz, 1 H), 5.49−5.65 (m, 2 H), 5.66−5.71 (m, 1 H), 5.83 (ddt, *J* = 17.1, 10.2, 6.4 Hz, 1 H), 7.22−7.41 (m, 5 H).

$^{13}$C NMR: δ = 31.9, 69.7, 115.5, 125.9, 127.5, 128.5, 129.0, 133.0, 136.0, 143.4.

HRMS (EI): *m*/*z* calcd for $C_{12}H_{14}O$ ($M^+$), 174.1045; found, 174.1051.

**(*Z*)-1,6-Diphenylhex-4-en-3-ol (4b)**

According to the procedure analogous to that described for **4a**, **4b** (387 mg, 60%) was prepared from **3b** (596 mg, 2.54 mmol) and benzyl bromide (856 mg, 5.00 mmol).

$^1$H NMR (300 MHz): δ = 1.59 (s, 1 H), 1.82 (dddd, *J* = 13.6, 9.5, 6.8, 5.9 Hz, 1 H), 1.91−2.06 (m, 1 H), 2.64−2.82 (m, 2 H), 3.38 (dd, *J* = 15.5, 7.5 Hz, 1 H), 3.46 (dd, *J* = 15.5, 7.5 Hz, 1 H), 4.59 (dt, *J* = 6.6, 7.5 Hz, 1 H), 5.58 (ddt, *J* = 10.8, 8.7, 1.5 Hz, 1 H), 5.73 (ddt, *J* = 10.8, 0.9, 7.5 Hz, 1 H), 7.14−7.25 (m, 6 H), 7.26−7.34 (m, 4 H).

$^{13}$C NMR: δ = 31.7, 33.9, 39.0, 67.0, 125.8, 126.1, 128.2, 128.4 [overlapping], 128.5, 130.6, 133.1.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{18}$ ($M^+ - H_2O$), 234.1409; found, 234.1406.

**Iododestannation of 2a [(*Z*)-2-Iodovinyl](trimethyl)silane (5)[12]**

To a solution of **2a** (778 mg, 2.00 mmol) in $Et_2O$ (6 mL) was added a solution of $I_2$ (583 mg, 2.30 mmol) in $Et_2O$ (6 mL) dropwise at 0 °C. After the mixture was stirred for 1 h at 0 °C, 0.5 M aq solution of $Na_2S_2O_3$ and sat. aq solution of KF were successively added to the reaction mixture. The organic materials were extracted with $Et_2O$, and the solvent was evaporated (200 mmHg). The residue was subjected to bulb-to-bulb distillation (90 °C/20 mmHg) to afford **5** (193 mg, 42%).

**Palladium-Catalyzed Successive Cross-Coupling of 2c Ethyl 4-[(*Z*)-2-(4-Methoxyphenyl)vinyl]benzoate (7)**

A mixture of **2c** (433 mg, 1.00 mmol), ethyl 4-iodobenzoate (248 mg, 0.90 mmol), $PhCH_2PdCl(PPh_3)_2$ (36 mg, 0.048 mmol), and CuI (19 mg, 0.10 mmol) in DMF (3 mL) was stirred for 30 min at r.t., and then for 3 h at 50 °C. 4-Iodoanisole (210 mg, 0.90 mmol) and TBAF (1.0 M in THF, 2.5 mL, 2.5 mmol) were added to the reaction mixture at 0 °C. After the mixture was stirred for 8 h at 50 °C, sat. aq solution of KF was added to the mixture. The organic materials were extracted with EtOAc, passed through a plug of Florisil® (EtOAc), and concentrated. The residue was purified by column chromatography on silica gel (hexane−EtOAc, 10:1) to afford **7** (166 mg, 65%).

$^1$H NMR (300 MHz): δ = 1.39 (t, *J* = 7.1 Hz, 3 H), 3.79 (s, 3 H), 4.37 (q, *J* = 7.1 Hz, 2 H), 6.51 (d, *J* = 12.3 Hz, 1 H), 6.63 (d, *J* = 12.3 Hz, 1 H), 6.73−6.79 (m, 2 H), 7.13−7.20 (m, 2 H), 7.31−7.36 (m, 2 H), 7.89−7.95 (m, 2 H).

$^{13}$C NMR: δ = 14.3, 55.1, 60.8, 113.6, 127.6, 128.7, 129.0, 129.4, 130.1, 131.6, 142.3, 158.9, 166.3 [one carbon signal is missing due to overlapping].

HRMS (EI): *m*/*z* calcd for $C_{18}H_{18}O_3$, 282.1256; found, 282.1255.

**Ethyl 4-[(*Z*)-2-(2-Thienyl)vinyl]benzoate (8)**

According to the procedure analogous to that described for **7**, **8** (157 mg, 61%) was prepared from **2c** (433 mg, 1.00 mmol), ethyl 4-iodobenzoate (248 mg, 0.90 mmol), and 2-thienyl iodide (189 mg, 0.90 mmol).

$^1$H NMR (300 MHz): δ = 1.4 (t, *J* = 7.1 Hz, 3 H), 4.39 (q, *J* = 7.1 Hz, 2 H), 6.56 (d, *J* = 12.2 Hz, 1 H), 6.76 (d, *J* = 12.2 Hz, 1 H), 6.89 (dd, *J* = 5.0, 3.5 Hz, 1 H), 6.97 (d, *J* = 3.5 Hz, 1 H), 7.12 (dd, *J* = 5.0, 1.2 Hz, 1 H), 7.44 (d, *J* = 8.0 Hz, 2 H), 8.03 (dt, *J* = 8.0, 1.8 Hz, 2 H).

$^{13}$C NMR: δ = 14.3, 60.9, 124.4, 125.8, 126.5, 127.7, 128.5, 128.7, 129.4, 129.7, 139.1, 142.0, 166.3.

HRMS (EI): *m*/*z* calcd for $C_{15}H_{14}O_2S$, 258.0715; found, 258.0721.

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