# Stereoselective synthesis of (3*E*)-2-stannyl-1,3-dienes via palladium catalysed cross-coupling reactions

**Mingzhong Cai*, Haigen Li and Wenyan Hao**

*Department of Chemistry, Jiangxi Normal University, Nanchang 330027, P.R. China*

Hydrozirconation of terminal alkynes **1** gives (*E*)-alkenylzirconium complexes **3**, which when cross-coupled with α-iodoethenylstannanes **4** in the presence of [$Pd(PPh_3)_4$] catalyst afford stereoselectively (3*E*)-2-stannyl-1,3-dienes **5** in good yields.

**Keywords:** palladium, zirconium, tin, 1,3-diene, cross-coupling reaction

The stereoselective synthesis of 1,3-dienes is of considerable interest in organic synthesis since many natural compounds such as insect sex pheromones and Achilla amide possess the structural skeleton of 1,3-dienes.[1] The synthesis of dienes for use in the preparation of more complex targets via Diels–Alder reaction is still an important challenge in organic synthesis,[2] although other elegant uses of these compounds have been developed.[3] Conjugated dienes are usually prepared by utilising either a Wittig type approach[4] or cross-coupling reactions of stereodefined vinyl halides with vinyl organometallic compounds catalysed by transition metals.[5] The metal- or heteroatom-containing 1,3-dienes will also be useful as building blocks in organic synthesis because many useful functional group transformations can be achieved by introduction and removal of metal or heteroatom functions. The stereoselective syntheses of 1,3-dienylsilanes,[6] 1,3-dienyl sulfides,[7] and 1,3-dienyl selenides[8] have already been described in the literature. Dienylstannanes serve as valuable versatile intermediates since vinylstannanes are pivotal intermediates in a wide range of carbon–carbon bond forming reactions.[9] The stereoselective synthesis of 1-stannyl-substituted 1,3-dienes has been described,[10] however, the stereoselective syntheses of 2-stannyl-substituted 1,3-dienes has received less attention.[11]

The (*E*)-alkenylzirconium complexes, obtained by hydrozirconation of terminal alkynes, can undergo a cross-coupling reaction with alkenyl halides in the presence of a catalytic amount of [$Pd(PPh_3)_4$] or [$Ni(PPh_3)_4$] to form 1,3-butadienes.[12] Here, we report that 2-stannyl-substituted 1,3-dienes can be synthesised by cross-coupling reaction of α-iodoethenylstannanes with (*E*)-alkenylzirconium complexes in the presence of [$Pd(PPh_3)_4$] catalyst.

α-Iodoethenylstannanes **4** were conveniently prepared in good yields by the hydrozirconation of ethynyltrialkylstannanes and successive reaction with iodine.[13]

**Table 1** Synthesis of (3*E*)-2-stannyl-1,3-dienes **5a–h**

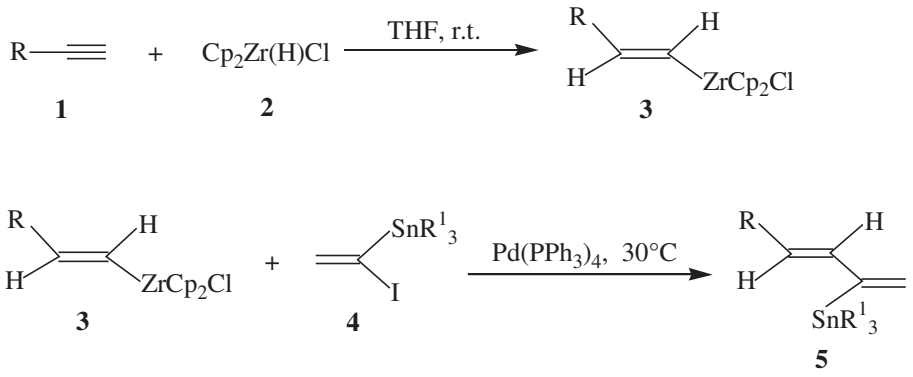
| Entry | R | $R^1$ | Product 5 | Yield /%[a] |
|---|---|---|---|---|
| 1 | *n*-$C_4H_9$ | *n*-$C_4H_9$ | **5a** | 85 |
| 2 | *n*-$C_4H_9$ | $CH_3$ | **5b** | 88 |
| 3 | Ph | *n*-$C_4H_9$ | **5c** | 75 |
| 4 | Ph | $CH_3$ | **5d** | 83 |
| 5 | *n*-$C_6H_{13}$ | *n*-$C_4H_9$ | **5e** | 82 |
| 6 | *n*- $C_6H_{13}$ | $CH_3$ | **5f** | 86 |
| 7 | $CH_3OCH_2$ | *n*-$C_4H_9$ | **5g** | 81 |
| 8 | $CH_3OCH_2$ | $CH_3$ | **5h** | 71 |

The products were identified by $^1$H NMR, IR, MS and elemental analyses.
[a]Isolated yield.

Hydrozirconation of terminal alkynes **1** at room temperature in THF gave (*E*)-alkenylzirconium complexes **3**, which were cross-coupled with α-iodoethenylstannanes **4** at 30 °C in the presence of [$Pd(PPh_3)_4$] catalyst to afford (3*E*)-2- stannyl-1,3-dienes **5** in good yields (Scheme 1). The experimental results are summarised in Table 1.

It is well documented that the cross-coupling reaction of alkenylzirconium complexes with alkenyl halides in the presence of a palladium catalyst occurs with retention of configuration.[12] The *E*-configuration of the compounds **5** has been proved by their $^1$H NMR spectra which show a doublet at δ = 6.2–7.1 with a coupling constant of 15–16 Hz, and this is also evidence of the retention of the *E*-configuration of the starting compounds **3**.

In conclusion, we have developed a direct route to (3*E*)-2-stannyl-1,3-dienes by the palladium catalysed cross-coupling reaction of α-iodoethenylstannanes with (*E*)-alkenylzirconium complexes. The method has some attractive advantages such as mild reaction conditions, a simple procedure and good yields. Investigations into the synthetic applications of (3*E*)-2-stannyl-1,3-dienes **5** are in progress.




**Scheme 1**

* Correspondent. E-mail: caimingz@tom.com

## Experimental

$^1$H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as internal standard using $CDCl_3$ as the solvent. IR spectra were determined on a Perkin-Elmer 683 spectrophotometer. Mass spectra were obtained on a Finigan 8230 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser. All reactions were carried out in pre-dried glassware (150 °C, 4 h) and cooled under a stream of dry Ar. Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl immediately before use. $[Cp_2Zr(H)Cl]$ was prepared according to the literature method.[14]

*General procedure for the synthesis of* **4**: A mixture of $[Cp_2Zr(H)Cl]$ (5 mmol) and ethynyltrialkylstannane (5 mmol) in THF (25 cm$^3$) was stirred at room temperature for 40 min to yield a clear solution. Iodine (5 mmol) was added to the resulting solution at 0° and the mixture was stirred for 30 min, then at room temperature for 30 min. The solvent was removed by rotary evaporation under reduced pressure. The mixture was diluted with diethyl ether (90 cm$^3$), filtered through a short plug of silica gel and concentrated to give a residue. The residue was purified by column chromatography on silica gel eluting with hexane.

*1-Iodo-1-tributylstannylethene* (*yield: 78%*): IR (film): ν (cm$^{-1}$) 2954, 2873, 1580, 1464, 1376. $^1$H NMR: δ 7.00(d, *J* = 1.6 Hz, 1H), 6.77 (d, *J* = 1.6 Hz, 1H), 1.59–1.51 (m, 6H), 1.38–1.28 (m, 6H), 1.02 (t, *J* = 8.2 Hz, 6H), 0.91 (t, *J* = 7.4 Hz, 9H). Anal. Found: C, 37.7; H, 6.4. $C_{14}H_{29}SnI$ Calc.: C, 37.9; H, 6.6%.

*1-Iodo-1-trimethylstannylethene* (*yield: 73%*): IR (film): ν (cm$^{-1}$) 2955, 2871, 1585, 1463, 1378. $^1$H NMR: δ 6.95 (d, *J* = 2.0 Hz, 1H), 6.77 (d, *J* = 2.0 Hz, 1H), 0.25 (s, 9H); Anal. Found: C, 18.8; H, 3.4. $C_5H_{11}SnI$ Calc.: C, 18.9; H, 3.5%.

*General procedure for the synthesis of* **5a–h**: A mixture of $[Cp_2Zr(H)Cl]$ (1 mmol) and terminal alkyne (**1**) (1 mmol) in THF (6 cm$^3$) was stirred at r.t. for 30 min to yield a clear solution. Into the resulting solution were added $[Pd(PPh_3)_4]$ (0.05 mmol) and α-iodoethenylstannane (**4**) (1 mmol), and the mixture was stirred at 30°C for 24 h. The mixture was diluted with diethyl ether (40 cm$^3$) and the mixture was filtered through a short plug of silica gel and concentrated to give a residue. The residue was purified by flash chromatography on silica gel, eluting with hexane.

*(3E)-2-Tributylstannyl-1,3-octadiene* (**5a**): IR (film): ν (cm$^{-1}$) 2958, 2929, 2873, 2857, 1465, 1377, 961, 787. $^1$H NMR: δ 6.29 (d, *J* = 15.2 Hz, 1H), 5.76 (d, *J* = 2.4 Hz, 1H), 5.52 (m, 1H), 5.17 (d, *J* = 2.4 Hz, 1H), 2.12–2.07 (m, 2H), 1.55–1.26 (m, 16H), 1.03–0.87 (m, 18H). MS: *m/z* 399 [M$^+$, 1.9], 343 (84), 342 (34.8), 341 (63.9), 339 (37.3), 291 (19.41), 235 (37.2), 179 (51.4), 177 (100), 175 (75), 121 (30.6), 67 (20), 57 (18.5). Anal. Found: C, 59.9; H, 10.0. $C_{20}H_{40}Sn$ Calc.: C, 60.2; H, 10.0%.

*(3E)-2-Trimethylstannyl-1,3-octadiene* (**5b**): IR (film): ν (cm$^{-1}$) 2959, 2929, 2873, 2857, 1466, 1379, 962, 912, 744. $^1$H NMR: δ 6.28 (d, *J* = 15.6 Hz, 1H), 5.74 (d, *J* = 2.8 Hz, 1H), 5.56 (m, 1H), 5.20 (d, *J* = 2.8 Hz, 1H), 2.13–2.04 (m, 2H), 1.40–1.25 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.19 (s, 3H). MS: *m/z* 273 [M$^+$, 3.8], 165 (28.1), 109 (11), 85 (37.1), 81 (32.5), 73 (53.4), 67 (32.1), 57 (88.3), 55 (82.1), 43 (91.4), 41 (100). Anal. Found: C, 48.1; H, 7.9. $C_{11}H_{22}Sn$ Calc.: C, 48.4; H, 8.1%.

*(3E)-2-Tributylstannyl-4-phenyl-1,3-butadiene* (**5c**): IR (film): ν (cm$^{-1}$) 3057, 3025, 2956, 2928, 2871, 2854, 1617, 1598, 1495, 1463, 1376, 955, 904, 753, 693. $^1$H NMR: δ 7.41–7.22 (m, 5H), 7.05 (d, *J* = 16.0 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.00 (d, *J* = 2.4 Hz, 1H), 5.38 (d, *J* = 2.4 Hz, 1H), 1.58–1.51 (m, 6H), 1.38-1.29 (m, 6H), 1.03 (t, *J* = 8.2 Hz, 6H), 0.89 (t, *J* = 7.2 Hz, 9H). MS: *m/z* 419 [M$^+$, 1.5], 363 (24.6), 362 (9.8), 291 (14.1), 279 (48.8), 233 (23.5), 177 (43.6), 146 (46.3), 131 (100), 128 (21.6), 103 (43.8), 77 (23.7), 57 (10.5). Anal. Found: C, 62.8; H, 8.5. $C_{22}H_{36}Sn$ Calc.: C, 63.0; H, 8.6%.

*(3E)-2-Trimethylstannyl-4-phenyl-1,3-butadiene* (**5d**): IR (film): ν (cm$^{-1}$) 3058, 3026, 2975, 2930, 1619, 1598, 1576, 1495, 1448, 956, 910, 736, 695. $^1$H NMR: δ 7.42–7.20 (m, 5H), 7.04 (d, *J* = 16.0 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.98 (s, 1H), 5.41 (s, 1H), 0.28 (s, 9H). MS: *m/z* 293 [M$^+$, 1.9], 279 (38.9), 278 (19), 277 (32.3), 165 (46.8), 164 (20.5), 163 (38.9), 135 (10.6), 129 (97.4), 128 (100), 103 (11.5), 77 (17.7). Anal. Found: C, 53.1; H, 6.0. $C_{13}H_{18}Sn$ Calc.: C, 53.2; H, 6.1%.

*(3E)-2-Tributylstannyl-1,3-decadiene* (**5e**): IR (film): ν (cm$^{-1}$) 2957, 2927, 2872, 2856, 1464, 1377, 961, 907, 787. $^1$H NMR: δ 6.28 (d, *J* = 15.2 Hz, 1H), 5.76 (d, *J* = 2.8 Hz, 1H), 5.53 (m, 1H), 5.17 (d, *J* = 2.8 Hz, 1H), 2.10–2.03 (m, 2H), 1.53–1.21 (m, 20H), 0.96–0.81 (m, 18H). MS: *m/z* 427 [M$^+$, 1.3], 371 (99.8), 370 (42.7), 369 (76.6), 368 (33.1), 367 (44.1), 291 (22), 259 (28.3), 235 (37.3), 179 (52.4), 177 (100), 175 (74.1), 121 (28.9), 67 (46), 57 (15.5). Anal. Found: C, 61.6; H, 10.1. $C_{22}H_{44}Sn$ Calc.: C, 61.8; H, 10.3%.

*(3E)-2-Trimethylstannyl-1,3-decadiene* (**5f**): IR (film): ν (cm$^{-1}$) 2959, 2929, 2873, 2857, 1466, 1379, 962, 912, 744. $^1$H NMR: δ 6.28 (d, *J* = 15.6 Hz, 1H), 5.74 (d, *J* = 2.4 Hz, 1H), 5.57 (m, 1H), 5.20 (d, *J* = 2.4 Hz, 1H), 2.19–2.05 (m, 2H), 1.41–1.25 (m, 8H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.20 (s, 9H). MS: *m/z* 301 [M$^+$, 2.3], 222 (24.8), 165 (17.1), 110 (33.6), 109 (27.5), 95 (50.4), 81 (72.9), 67 (100), 55 (47.3), 43 (46.3), 41 (55.9). Anal. Found: C, 51.6; H, 8.45. $C_{13}H_{26}Sn$ Calc.: C, 51.8; H, 8.6%.

*(3E)-2-Tributylstannyl-5-methoxy-1,3-pentadiene* (**5g**): IR (film): ν (cm$^{-1}$) 2957, 2926, 2873, 2855, 1637, 1464, 1376, 1122, 1072, 963, 910, 787. $^1$H NMR: δ 6.48 (d, *J* = 15.2 Hz, 1H), 5.88 (d, *J* = 2.4 Hz, 1H), 5.60 (m, 1H), 5.31 (d, *J* = 2.4 Hz, 1H), 3.98 (d, *J* = 6.4 Hz, 2H), 3.32 (s, 3H), 1.54–1.21 (m, 12H), 1.00–0.83 (m, 15H). MS: *m/z* 387 [M$^+$, 1.4], 361 (77.9), 359 (61.5), 331 (30.2), 330 (13.1), 305 (47.3), 291 (29.5), 267 (60.6), 265 (98.8), 235 (39.9), 179 (59.4), 177 (81.4), 175 (57.7), 151 (25.7), 121 (31.9), 57 (58.4), 41 (100). Anal. Found: C, 55.5; H, 9.1. $C_{18}H_{36}OSn$ Calc.: C, 55.8; H, 9.3%.

*(3E)-2-Trimethylstannyl-5-methoxy-1,3-pentadiene* (**5h**): IR (film): ν (cm$^{-1}$) 2979, 2930, 2875, 1637, 1449, 1383, 1112, 965, 912, 736. $^1$H NMR: δ 6.48 (d, *J* = 15.2 Hz, 1H), 5.86 (d, *J* = 2.4 Hz, 1H), 5.64 (m, 1H), 5.34 (d, *J* = 2.4 Hz, 1H), 3.98 (d, *J* = 6.0 Hz, 2H), 3.33 (s, 3H), 0.22 (s, 9H). MS: *m/z* 261 [M$^+$, 3.8], 165 (21.7), 149 (19.2), 97 (12.7), 72 (54), 71 (33.1), 59 (100), 55 (53.5), 45 (79.4), 43 (54). Anal. Found: C, 41.1; H, 6.8. $C_9H_{18}OSn$ Calc.: C, 41.4; H, 6.9%.

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