

Stereoselective synthesis of (*E*)- α -aryltellurenylvinylsilanes via hydromagnesiation reaction of alkynylsilanes

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Abstract

(*E*)- α -Aryltellurenylvinylsilanes have been synthesized stereoselectively via the hydromagnesiation of alkynylsilanes, followed by the reaction with aryltellurenyl iodides. (*E*)- α -Aryltellurenylvinylsilanes can undergo the cross coupling reaction with Grignard reagents in the presence of Ni(PPh₃)₂Cl₂ catalyst to afford (*Z*)-1,2-disubstituted vinylnilanes in good yields.

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1. Introduction

The trisubstituted alkene moiety is incorporated in many biologically active compounds occurring in nature and the stereoselective synthesis of trisubstituted alkenes is of considerable interest in organic chemistry [1]. Difunctional group reagents, which have two different functional groups linked to the olefinic carbon atoms, for example, Sn–Si [2], Se–Si [3], Zr–Si [4], Te–Zr [5] and Te–Br [6] combinations, play an important role in organic synthesis, especially in developing many convenient methods for stereoselective preparation of trisubstituted alkenes. Vinylnilanes are important synthetic intermediates and have numerous uses in organic synthesis owing to the versatile reactivity of the silyl group and the carbon–carbon double bond [7]. Vinylic tellurides are also important intermediates because the tellurium moiety can be replaced by different organic groups always with total retention of the configuration [8]. However, to date, the difunctional group reagent containing silicon and tellurium has rarely aroused attention. Kambe and co-workers [9] described that trimethylsilylacetylene underwent the photo-promoted

carbottelluration with tellurides to give (*Z*)- α -silylvinylnil tellurides in moderate yields. Recently, Fujiwara et al. [10] reported that trimethylsilylacetylene underwent the photoinduced addition with carbamotelluroates to afford (*E*)- β -telluro- β -trimethylsilylacrylamides, but the yields and stereoselectivity were poor. Hydromagnesiation is one of the most promising organometallic technique used in organic synthesis and has emerged as a unique hydrometallation with some attractive features, such as the high regioselectivity and stereoselectivity observed with alkynylsilanes [11]. We now wish to report that (*E*)- α -aryltellurenylvinylnilanes could be synthesized by hydromagnesiation of alkynylsilanes, followed by treatment with aryltellurenyl iodides.

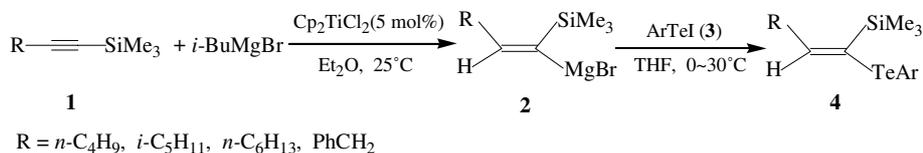
2. Results and discussion

Alkynylsilanes **1** were prepared according to the literature procedure [12]. Hydromagnesiation of alkynylsilanes **1** at 25 °C in diethyl ether for 6 h gave (*Z*)- α -silylvinylnil Grignard reagents **2**, which reacted with aryltellurenyl iodides **3** in THF to afford (*E*)- α -aryltellurenylvinylnilanes **4** in good yields (Scheme 1). The typical results are summarized in Table 1.

The hydromagnesiation of alkynylsilanes **1** at 25 °C in ether is almost 100% regio- and stereoselective as

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Scheme 1.

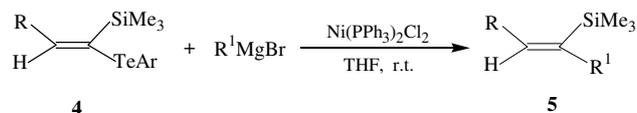
Table 1
Synthesis of (*E*)- α -aryltellurenylvynylsilanes **4**

Entry	R	Ar	Product	Yield ^a (%)
1	<i>n</i> -C ₄ H ₉	Ph	4a	78
2	<i>n</i> -C ₄ H ₉	4-ClC ₆ H ₄	4b	82
3	<i>n</i> -C ₄ H ₉	4-CH ₃ C ₆ H ₄	4c	75
4	<i>i</i> -C ₅ H ₁₁	Ph	4d	79
5	<i>i</i> -C ₅ H ₁₁	4-ClC ₆ H ₄	4e	81
6	<i>i</i> -C ₅ H ₁₁	4-CH ₃ C ₆ H ₄	4f	73
7	<i>n</i> -C ₆ H ₁₃	Ph	4g	77
8	<i>n</i> -C ₆ H ₁₃	4-ClC ₆ H ₄	4h	80
9	<i>n</i> -C ₆ H ₁₃	4-CH ₃ C ₆ H ₄	4i	72
10	PhCH ₂	Ph	4j	68

^a Isolated yield based on the alkynylsilane **1** used.

previously described [11]. We observed that the Mg/Te exchange reaction on intermediates **2** occurs with total retention of the configuration. Investigations of the crude products **4** by ¹H NMR spectroscopy (400 MHz) showed their isomeric purities to be more than 98%, one olefinic proton signal of **4a–j** splits characteristically into one triplet with a coupling constant of ²*J*(2H) = 6.4–7.5 Hz, which indicated that the hydromagnesiation of alkynylsilanes had taken place with strong preference for the addition of the magnesium atom at the carbon adjacent to the silyl group. The stereochemistry for the obtained compounds **4** was confirmed by the NOESY in the ¹H NMR spectra. An enhancement of the aromatic protons next to tellurium was observed as the vinylic proton of **4a** was irradiated. There was no correlation between the vinylic proton and CH₃ bonded to the silicon atom. The correlation between the allylic hydrogens and CH₃ bonded to the silicon atom was also observed. The NOE results indicate that **4a** has the expected *E* configuration.

(*E*)- α -Aryltellurenylvynylsilanes **4** are new difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinylsilanes and vinylic tellurides. Vinylic tellurides have been employed to effect



Scheme 2.

Table 2
Synthesis of (*Z*)-1,2-disubstituted vinylsilanes **5** according to Scheme 2

Entry	R	Ar	R ¹	Product	Yield ^a (%)
1	<i>n</i> -C ₄ H ₉	Ph	<i>n</i> -C ₄ H ₉	5a	74
2	<i>n</i> -C ₄ H ₉	4-ClC ₆ H ₄	Ph	5b	81
3	<i>i</i> -C ₅ H ₁₁	Ph	<i>n</i> -C ₄ H ₉	5c	75
4	<i>n</i> -C ₆ H ₁₃	4-ClC ₆ H ₄	Ph	5d	77
5	PhCH ₂	Ph	<i>n</i> -C ₄ H ₉	5e	65

^a Isolated yield based on the **4** used.

Ni(0)-catalyzed cross coupling reactions with Grignard reagents [13]. Therefore, we carried out the nickel catalyzed cross coupling reaction of compounds **4** with Grignard reagents in the presence of catalytic amount of Ni(PPh₃)₂Cl₂ in THF at room temperature, the corresponding (*Z*)-1,2-disubstituted vinylsilanes **5** were obtained in good yields according to the Scheme 2 and Table 2.

In conclusion, we have developed a direct route to the stereoselective synthesis of (*E*)- α -aryltellurenylvynylsilanes by the hydromagnesiation of the alkynylsilanes. The present method has some attractive advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and good yields. The investigation of the synthetic applications of (*E*)- α -aryltellurenylvynylsilanes **4** is in progress.

3. Experimental

Tetrahydrofuran (THF) was distilled from sodium–benzophenone immediately prior to use. (Ph₃P)₂NiCl₂ was prepared according to literature [14]. IR spectra were obtained on a Perkin–Elmer 683 instrument as neat films. ¹H NMR spectra were recorded on a Bruker AC-400 (400 MHz) spectrometer using CDCl₃ as solvent. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer.

3.1. General procedure for the synthesis of (*E*)- α -aryltellurenylvynylsilanes (**4a–j**)

To a solution of isobutylmagnesium bromide (4.5 mmol) in diethyl ether (7 ml) was added Cp₂TiCl₂ (50 mg, 0.2 mmol) at 0 °C under Ar, and the mixture was

stirred for 30 min at that temperature. To this solution was added alkynylsilane **1** (4.0 mmol), and the mixture was stirred for 6 h at 25 °C. After removal of the ether under reduced pressure (2 h, r.t./2 Torr), the residue was dissolved in THF (5 ml), cooled to 0 °C, and a solution of aryltellurenyl iodide **3** (5.0 mmol) in THF (8 ml) was added dropwise over 30 min with stirring. The reaction mixture was brought to 30 °C gradually and stirred for 4 h, quenched with sat. aq NH₄Cl (25 ml) and extracted with Et₂O (2 × 30 ml). The organic layer was washed with sat. aq Na₂S₂O₃ (20 ml) and water (3 × 30 ml) and dried (MgSO₄). Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography on silica gel using light petroleum as eluent.

3.1.1. (*E*)-1-Trimethylsilyl-1-phenyltelluro-1-hexene (**4a**)

IR (film): ν (cm⁻¹) 3065, 2955, 2857, 1574, 1473, 1433, 1377, 1248, 838, 729, 691. ¹H NMR: δ 7.57–7.04 (m, 5H), 6.36 (t, J = 6.5 Hz, 1H), 2.46–2.23 (m, 2H), 1.38–1.19 (m, 4H), 0.86 (t, J = 7.2 Hz, 3H), 0.08 (s, 9H). MS: m/z 360 (M⁺, 6.4), 77 (9.5), 74 (9.6), 73 (100), 45 (9.9). Anal. Found: C, 49.76; H, 6.52. C₁₅H₂₄SiTe Calc.: C, 50.00; H, 6.67%.

3.1.2. (*E*)-1-Trimethylsilyl-1-(4-chlorophenyltelluro)-1-hexene (**4b**)

IR (film): ν (cm⁻¹) 3068, 2956, 2858, 1629, 1570, 1470, 1381, 1248, 1089, 1009, 838, 808, 755. ¹H NMR: δ 7.46 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 6.45 (t, J = 6.4 Hz, 1H), 2.43–2.38 (m, 2H), 1.48–1.25 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H), 0.11 (s, 9H). MS: m/z 394 (M⁺, 3.4), 81 (11), 74 (10), 73 (100), 45 (10). Anal. Found: C, 45.43; H, 5.67. C₁₅H₂₃SiClTe Calc.: C, 45.69; H, 5.84%.

3.1.3. (*E*)-1-Trimethylsilyl-1-(4-methylphenyltelluro)-1-hexene (**4c**)

IR (film): ν (cm⁻¹) 3065, 3014, 2955, 2871, 1579, 1486, 1246, 836, 796. ¹H NMR: δ 7.39 (d, J = 7.9 Hz, 2H), 6.95 (d, J = 7.9 Hz, 2H), 6.33 (t, J = 6.5 Hz, 1H), 2.38–2.27 (m, 2H), 2.25 (s, 3H), 1.39–1.21 (m, 4H), 0.81 (t, J = 7.0 Hz, 3H), 0.02 (s, 9H). MS: m/z 374 (M⁺, 3.7), 91 (11), 74 (9.4), 73 (100), 45 (10). Anal. Found: C, 51.14; H, 6.78. C₁₆H₂₆SiTe Calc.: C, 51.39; H, 6.96%.

3.1.4. (*E*)-1-Trimethylsilyl-1-phenyltelluro-5-methyl-1-hexene (**4d**)

IR (film): ν (cm⁻¹) 3066, 2954, 2869, 1574, 1473, 1433, 1384, 1366, 1248, 838, 729, 691. ¹H NMR: δ 7.67–7.20 (m, 5H), 6.84 (t, J = 6.5 Hz, 1H), 2.31–2.18 (m, 2H), 1.61–1.21 (m, 3H), 0.89 (d, J = 6.6 Hz, 6H), 0.19 (s, 9H). MS: m/z 374 (M⁺, 7.6), 117 (10), 77 (11.8), 74 (10), 73 (100). Anal. Found: C, 51.17; H, 6.83. C₁₆H₂₆SiTe Calc.: C, 51.39; H, 6.96%.

3.1.5. (*E*)-1-Trimethylsilyl-1-(4-chlorophenyltelluro)-5-methyl-1-hexene (**4e**)

IR (film): ν (cm⁻¹) 3069, 2955, 2869, 1629, 1568, 1470, 1383, 1367, 1248, 1089, 1009, 838, 808, 757, 720. ¹H NMR: δ 7.56 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 7.2 Hz, 1H), 2.29–2.18 (m, 2H), 1.59–1.51 (m, 1H), 1.33–1.24 (m, 2H), 0.89 (d, J = 6.5 Hz, 6H), 0.18 (s, 9H). MS: m/z 408 (M⁺, 2.8), 74 (10), 73 (100), 45 (9). Anal. Found: C, 46.89; H, 6.05. C₁₆H₂₅SiClTe Calc.: C, 47.06; H, 6.13%.

3.1.6. (*E*)-1-Trimethylsilyl-1-(4-methylphenyltelluro)-5-methyl-1-hexene (**4f**)

IR (film): ν (cm⁻¹) 3065, 3014, 2954, 2869, 1579, 1486, 1467, 1384, 1366, 1246, 878, 836, 796, 752, 690. ¹H NMR: δ 7.46 (d, J = 7.8 Hz, 2H), 6.98 (d, J = 7.8 Hz, 2H), 6.38 (t, J = 6.5 Hz, 1H), 2.45–2.32 (m, 2H), 2.31 (s, 3H), 1.56–1.47 (m, 1H), 1.34–1.23 (m, 2H), 0.86 (d, J = 6.6 Hz, 6H), 0.07 (s, 9H). MS: m/z 388 (M⁺, 3.6), 91 (8.3), 74 (9.3), 73 (100), 45 (8.7). Anal. Found: C, 52.37; H, 7.15. C₁₇H₂₈SiTe Calc.: C, 52.58; H, 7.22%.

3.1.7. (*E*)-1-Trimethylsilyl-1-phenyltelluro-1-octene (**4g**)

IR (film): ν (cm⁻¹) 3066, 2926, 2856, 1574, 1473, 1434, 1248, 839, 729, 691. ¹H NMR: δ 7.69–7.63 (m, 2H), 7.28–7.09 (m, 3H), 6.96 (t, J = 7.5 Hz, 1H), 2.27–2.20 (m, 2H), 1.40–1.25 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H), 0.18 (s, 9H). MS: m/z 388 (M⁺, 2.7), 77 (4.8), 74 (9.8), 73 (100), 45 (6). Anal. Found: C, 52.34; H, 7.07. C₁₇H₂₈SiTe Calc.: C, 52.58; H, 7.22%.

3.1.8. (*E*)-1-Trimethylsilyl-1-(4-chlorophenyltelluro)-1-octene (**4h**)

IR (film): ν (cm⁻¹) 3069, 2955, 2855, 1629, 1571, 1470, 1381, 1248, 1009, 839, 808, 757, 721. ¹H NMR: δ 7.56 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.97 (t, J = 7.5 Hz, 1H), 2.29–2.18 (m, 2H), 1.42–1.27 (m, 8H), 0.89 (t, J = 6.2 Hz, 3H), 0.18 (s, 9H). MS: m/z 422 (M⁺, 1.9), 109 (5.3), 74 (10), 73 (100), 45 (8.8). Anal. Found: C, 48.17; H, 6.41. C₁₇H₂₇SiClTe Calc.: C, 48.34; H, 6.40%.

3.1.9. (*E*)-1-Trimethylsilyl-1-(4-methylphenyltelluro)-1-octene (**4i**)

IR (film): ν (cm⁻¹) 3065, 3014, 2925, 2855, 1575, 1486, 1456, 1378, 1248, 928, 838, 798, 756. ¹H NMR: δ 7.75 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 6.85 (t, J = 6.9 Hz, 1H), 2.40–2.15 (m, 5H), 1.58–1.21 (m, 8H), 0.89 (t, J = 6.5 Hz, 3H), 0.19 (s, 9H). MS: m/z 402 (M⁺, 2.6), 91 (10), 74 (9.7), 73 (100), 45 (9.3). Anal. Found: C, 53.50; H, 7.22. C₁₈H₃₀SiTe Calc.: C, 53.73; H, 7.46%.

3.1.10. (*E*)-1-Trimethylsilyl-1-phenyltelluro-3-phenyl-1-propene (**4j**)

IR (film): ν (cm⁻¹) 3068, 3019, 2955, 1595, 1574, 1473, 730, 690. ¹H NMR: δ 7.57–6.93 (m, 10H), 6.87 (t, J = 7.0

Hz, 1H), 3.49 (d, $J = 6.8$ Hz, 2H), 0.19 (s, 9H). MS: m/z 394 (M^+ , 3.7), 77 (13), 74 (11), 73 (100). Anal. Found: C, 54.61; H, 5.43. $C_{18}H_{22}SiTe$ Calc.: C, 54.88; H, 5.59%.

3.2. General procedure for the synthesis of (*Z*)-1,2-disubstituted vinylsilanes (**5a–e**)

To a stirred suspension of $Ni(PPh_3)_2Cl_2$ (0.05 mmol) and (*E*)- α -aryltellurenyl-vinylsilanes **4** (1 mmol) in THF (5 ml) was added a solution of R^1MgBr (4 mmol) in THF (6 ml) under nitrogen at room temperature and the mixture was stirred for 48 h. The mixture was treated with sat. aq NH_4Cl (10 ml) and extracted with ether (2×30 ml). The ethereal solution was washed with water (3×20 ml) and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography on silica gel eluting with light petroleum.

3.2.1. (*Z*)-5-Trimethylsilyl-5-decene (**5a**)

IR (film): ν (cm^{-1}) 2954, 2860, 1613, 1465, 1248, 849. 1H NMR: δ 5.83 (t, $J = 7.0$ Hz, 1H), 2.37–1.82 (m, 4H), 1.59–1.11 (m, 8H), 1.08–0.67 (m, 6H), 0.11 (s, 9H). MS: m/z 212 (M^+ , 5.2), 73 (100). Anal. Found: C, 73.40; H, 13.13. $C_{13}H_{28}Si$ Calc.: C, 73.58; H, 13.21%.

3.2.2. (*Z*)-1-Trimethylsilyl-1-phenyl-1-hexene (**5b**)

IR (film): ν (cm^{-1}) 2956, 2858, 1602, 1249, 839. 1H NMR: δ 7.39–6.83 (m, 5H), 6.02 (t, $J = 7.0$ Hz, 1H), 2.42–2.12 (m, 2H), 1.62–1.21 (m, 4H), 0.90 (t, $J = 5.4$ Hz, 3H), 0.12 (s, 9H). MS: m/z 232 (M^+ , 3.8), 73 (100). Anal. Found: C, 77.31; H, 10.25. $C_{15}H_{24}Si$ Calc.: C, 77.59; H, 10.34%.

3.2.3. (*Z*)-2-Methyl-6-trimethylsilyl-5-decene (**5c**)

IR (film): ν (cm^{-1}) 2955, 2871, 1612, 1466, 1384, 1366, 1249, 835. 1H NMR: δ 5.83 (t, $J = 7.0$ Hz, 1H), 2.37–1.93 (m, 4H), 1.59–1.09 (m, 7H), 1.05–0.79 (m, 9H), 0.12 (s, 9H). MS: m/z 226 (M^+ , 4.2), 73 (100). Anal. Found: C, 74.19; H, 13.06. $C_{14}H_{30}Si$ Calc.: C, 74.34; H, 13.27%.

3.2.4. (*Z*)-1-Trimethylsilyl-1-phenyl-1-octene (**5d**)

IR (film): ν (cm^{-1}) 2955, 2855, 1602, 1573, 1488, 1249, 837. 1H NMR: δ 7.34–6.80 (m, 5H), 5.98 (t, $J = 7.0$ Hz, 1H), 2.46–2.02 (m, 2H), 1.72–1.17 (m, 8H), 0.90 (t, $J = 5.4$ Hz, 3H), 0.11 (s, 9H). MS: m/z 260 (M^+ , 3.2), 73 (100). Anal. Found: C, 78.22; H, 10.53. $C_{17}H_{28}Si$ Calc.: C, 78.46; H, 10.77%.

3.2.5. (*Z*)-1-Phenyl-3-trimethylsilyl-2-heptene (**5e**)

IR (film): ν (cm^{-1}) 2956, 2859, 1601, 1494, 1453, 1248, 838. 1H NMR: δ 7.42–6.88 (m, 5H), 5.87 (t, $J = 7.0$ Hz, 1H), 3.53 (d, $J = 7.2$ Hz, 2H), 2.41–2.06 (m, 2H), 1.62–1.18 (m, 4H), 0.89 (t, $J = 5.4$ Hz, 3H), 0.12 (s, 9H). MS: m/z 246 (M^+ , 4.5), 73 (100). Anal. Found: C, 77.82; H, 10.43. $C_{16}H_{26}Si$ Calc.: C, 78.05; H, 10.57%.

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