Novel stereoselective synthesis of (*Z*)-2-arylthio-substituted 1,3-enynes from (*E*)-α-stannylvinyl sulfides and 1-alkynes

Ming-Zhong Cai[a]*, Dong Wang[a] and Ping-Ping Wang[b]

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

[b]*Department of Chemistry, Jiujiang College, Jiujiang 332000, P. R. China*

(*E*)-α-Stannylvinyl sulfides **1** underwent the iododestannylation reaction with iodine to give the (*E*)-α-iodovinyl sulfides **2**, which were coupled directly with terminal alkynes **3** without isolation in the presence of $Pd(PPh_3)_4$ and CuI co-catalyst to afford stereoselectively (*Z*)-2-arylthio-substituted 1,3-enynes **4** in good yields.

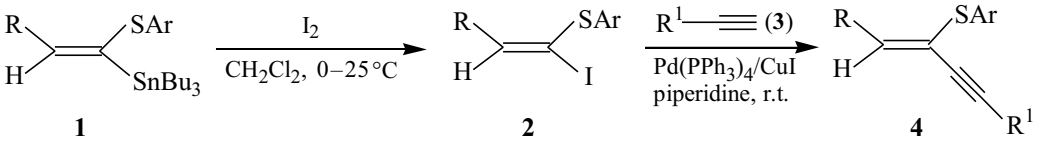
Keywords: (*E*)-α-stannylvinyl sulfide, (*E*)-α-iodovinyl sulfide, 1,3-enynylsulfide, coupling reaction, palladium catalysis

The discovery of strong antifungal agents[1] and new powerful antitumor antibiotics[2] has stimulated intense interest in the chemistry of enynes,[3] the enyne moiety being the origin of the biological properties of these substances. Conjugated enynes are also important synthetic intermediates since the conjugated enyne moiety can be readily converted in a stereospecific manner into the corresponding diene system.[4] Recently, Takahashi and coworkers described the formation of highly substituted enynes using a coupling reaction between alkenylzirconium compounds and alkynyl halides.[5] Gimeno and coworker reported the stereoselective synthesis of chiral terminal (*E*)-1,3-enynes derived from the optically active aldehydes.[6] The synthesis of 1,3-enynes containing functional groups has also been of considerable interest in recent years. The stereoselective synthesis of 1,3-enynyltellurides,[7] 1,3-enynylselenides,[8] 1,3-enynylsilanes,[9] 1,3-enynylstannanes[10] and fluoro or CF_3-substituted 1,3-enynes[11] has already been described in the literature. The synthesis of (*Z*)-2-arylthio-substituted 1,3-enynes has received less attention.[12] The transition metal-catalysed cross-coupling reaction is a highly versatile method for carbon–carbon bond formation and is a widely used synthetic tool.[13] The palladium-catalysed coupling reaction of alkenyl halides with terminal alkynes (Sonogashira reaction) provides a direct route to 1,3-enynes.[14] Herein, we report that (*Z*)-2-arylthio-substituted 1,3-enynes can be synthesised from (*E*)-α-stannylvinyl sulfides and terminal alkynes via a stereospecific iododestannylation, followed by a palladium-catalysed coupling reaction.

(*E*)-α-Stannylvinyl sulfides **1** were conveniently prepared by the palladium-catalysed hydrostannylation of alkynylsulfides according to a literature procedure.[15] (*E*)-α-Stannylvinyl sulfides **1** underwent an iododestannylation reaction with iodine at 0°C in CH_2Cl_2 for 2 h to give the corresponding (*E*)-α-iodovinyl sulfides **2** in 90–93% yields. The intermediates **2** reacted with terminal alkynes **3** in piperidine at room temperature in the presence of $Pd(PPh_3)_4$ and a CuI co-catalyst for 30 min to afford stereoselectively (*Z*)-2-arylthio-substituted 1,3-enynes **4** in high yields (Scheme 1). The typical results are summarised in Table 1. The *E*-configuration of (*E*)-1-iodo-1- phenylsulfanylhex-1-ene **2c** was confirmed by NOESY in the ^1H NMR spectrum. An enhancement of the allylic protons was observed as the vinylic proton (δ = 6.89) of **2c** was irradiated. There was no correlation between the vinylic proton and an aromatic proton. The NOE results indicate that **2c** has the expected *E*-configuration and the iododestannylation reaction of (*E*)-α-stannylvinyl sulfides **1** occurs with retention of configuration.

We have also investigated a one-pot synthesis of (*Z*)-2-arylthio-substituted 1,3-enynes from (*E*)-α-stannylvinyl sulfides **1**, iodine and terminal alkynes **3**. We found that, after the iododestannylation reaction of (*E*)-α-stannylvinyl sulfides **1** using iodine in CH_2Cl_2 at 0°C for 2 h, solvent removal under reduced pressure and stirring of the residue with piperidine, terminal alkynes **3**, 5 mol% $Pd(PPh_3)_4$ and 10 mol% CuI at room temperature for 30 min, the (*Z*)-2-arylthio-substituted 1,3-enynes **4** were obtained in good yields. The experimental results are summarised in Table 2.

In summary, we have developed a novel stereoselective synthesis of (*Z*)-2-arylthio-substituted 1,3-enynes from (*E*)-α-stannylvinyl sulfides and terminal alkynes. The present



Scheme 1

Table 1 Synthesis of (*Z*)-2-arylthio-substituted 1,3-enynes **4a–i** from **2** and **3**

Entry	R	Ar	R^1	Product	Yield[a]/%
1	Ph	Ph	$SiMe_3$	**4a**	86
2	Ph	Ph	*n*-C_4H_9	**4b**	85
3	Ph	Ph	Ph	**4c**	89
4	CH_3OCH_2	Ph	*n*-C_4H_9	**4d**	83
5	CH_3OCH_2	Ph	Ph	**4e**	85
6	CH_3OCH_2	Ph	CH_3OCH_2	**4f**	80
7	*n*-C_4H_9	Ph	*n*-C_4H_9	**4g**	87
8	*n*-C_4H_9	Ph	Ph	**4h**	88
9	*n*-C_4H_9	Ph	CH_3OCH_2	**4i**	82

[a]Isolated yield based on the (*E*)-α-iodovinyl sulfide **2** used.

* Correspondent. E-mail: caimzhong@163.com

Table 2 One-pot synthesis of (*Z*)-2-arylthio-substituted 1,3-enynes from **1**, I_2 and **3**

Entry	R	Ar	R^1	Product	Yield[a]/%
1	Ph	Ph	$SiMe_3$	**4a**	72
2	Ph	Ph	*n*-C_4H_9	**4b**	70
3	Ph	Ph	Ph	**4c**	76
4	CH_3OCH_2	Ph	*n*-C_4H_9	**4d**	65
5	CH_3OCH_2	Ph	Ph	**4e**	71
6	CH_3OCH_2	Ph	CH_3OCH_2	**4f**	67
7	*n*-C_4H_9	Ph	*n*-C_4H_9	**4g**	73
8	*n*-C_4H_9	Ph	Ph	**4h**	75
9	*n*-C_4H_9	Ph	CH_3OCH_2	**4i**	68

[a]Isolated yield based on the (*E*)-α-stannylvinyl sulfide **1** used.

method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and good yields.

Experimental

IR spectra were obtained on a Perkin-Elmer 683 instrument using neat films. ^{1}H NMR spectra were recorded on a Bruker AC-400 (400 MHz) spectrometer using $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded on a Bruker AC-400 (100 MHz) spectrometer using $CDCl_3$ as solvent. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Microanalyses were carried out using a Yanaco MT-3 CHN microelemental analyser. CH_2Cl_2 was distilled from P_2O_5, and piperidine was dried over KOH and distilled before use.

General procedure for the synthesis of (E)-α-iodovinyl sulfides **2a–c**
A solution of iodine (1.7 mmol) in dry CH_2Cl_2 (10 ml) was added dropwise to a solution of (*E*)-α-stannylvinyl sulfide (1.5 mmol) in dry CH_2Cl_2 (10 ml) over 30 min at 0°C under Ar. After stirring for 30 min, the mixture was stirred for 1 h at room temperature and quenched with sat. aq. $Na_2S_2O_3$ (10 ml). The organic layer was washed with sat. aq. $Na_2S_2O_3$ (10 ml) and water (3 × 10 ml) and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography on silica gel using light petroleum as eluent.

(E)-1-Iodo-1-phenylsulfanyl-2-phenylethene (**2a**): Yield 93%; colourless oil; IR (film): ν (cm^{-1}) 3056, 1716, 1582, 1490, 1476, 866, 740, 688; ^{1}H NMR ($CDCl_3$): δ 7.81 (s, 1H), 7.62–7.53 (m, 2H), 7.38–7.29 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 149.5, 137.0, 136.0, 130.6, 129.3, 129.0, 128.6, 128.4, 127.8, 88.8; MS: *m/z* 338 (M^+, 36), 211 (100), 178 (67), 167 (27), 134 (43), 77 (32); Anal. Found: C, 49.5; H, 3.05. $C_{14}H_{11}SI$ Calc.: C, 49.7; H, 3.25%.

(E)-1-Iodo-1-phenylsulfanyl-3-methoxyprop-1-ene (**2b**): Yield 90%; colourless oil; IR (film): ν (cm^{-1}) 3058, 1714, 1582, 1491, 1474, 1190, 1107, 786, 741, 689; ^{1}H NMR ($CDCl_3$): δ 7.36–7.30 (m, 5H), 6.95 (t, *J* = 6.4 Hz, 1H), 4.14 (d, *J* = 6.4 Hz, 2H), 3.37 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 148.4, 134.9, 130.8, 129.2, 127.9, 88.8, 71.4, 58.3; MS: *m/z* 306 (M^+, 4.3), 288 (74), 275 (48), 177 (33), 147 (100), 115 (28), 91 (31), 69 (46); Anal. Found: C, 39.1; H, 3.4. $C_{10}H_{11}OSI$ Calc.: C, 39.2; H, 3.6%.

(E)-1-Iodo-1-phenylsulfanylhex-1-ene (**2c**): yield 92%; Colourless oil; IR (film): ν (cm^{-1}) 3056, 2956, 1715, 1583, 1490, 1440, 785, 740, 688; ^{1}H NMR ($CDCl_3$): δ 7.35–7.28 (m, 5H), 6.89 (t, *J* = 7.2 Hz, 1H), 2.36–2.30 (m, 2H), 1.44–1.32 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 153.7, 135.0, 129.3, 128.7, 126.7, 83.9, 32.7, 30.3, 21.8, 13.4; Anal. Found: C, 45.05; H, 4.5. $C_{12}H_{15}SI$ Calc.: C, 45.3; H, 4.7%.

General procedure for the synthesis of (Z)-2-arylthio-substituted 1,3-enynes **4a–i**
Terminal alkyne **3** (2.0 mmol) and CuI (0.1 mmol) were added to a solution of (*E*)-α-iodovinyl sulfide **2** (1.0 mmol) and $Pd(PPh_3)_4$ (0.05 mmol) in piperidine (6 ml) at room temperature under Ar. The mixture was stirred for 30 min, quenched with sat. aq. NH_4Cl (10 ml) and extracted with diethyl ether (2 × 30 ml). The ethereal solution was washed with water (2 × 10 ml) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography on silica gel using light petroleum as eluent.

General procedure for on-pot synthesis of (Z)-2-arylthio-substituted 1,3-enynes **4a–i**
A solution of iodine (1.7 mmol) in dry CH_2Cl_2 (10 ml) was added dropwise to a solution of (*E*)-α-stannylvinyl sulfide **1** (1.5 mmol) in dry CH_2Cl_2 (10 ml) over 30 min at 0°C under Ar. After stirring for 30 min, the mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was dissolved in piperidine (9 ml). Then terminal alkyne **3** (3.0 mmol), $Pd(PPh_3)_4$ (0.075 mmol) and CuI (0.15 mmol) were added and the mixture was stirred at room temperature for 30 min, quenched with sat. aq. NH_4Cl (15 ml) and extracted with diethyl ether (2 × 30 ml). The ethereal solution was washed with water (2 × 10 ml) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography on silica gel using light petroleum as eluent.

(Z)-1-Phenyl-2-phenylsulfanyl-4-trimethylsilyl-but-1-en-3-yne (**4a**): Colourless oil; IR (film): ν (cm^{-1}) 3059, 2137, 1716, 1583, 1249, 844, 750, 690; ^{1}H NMR ($CDCl_3$): δ 7.63–7.29 (m, 10H), 7.10 (s, 1H), –0.01 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 136.2, 135.7, 134.2, 132.8, 129.7, 128.7, 128.3, 128.1, 119.4, 103.1, 97.6, –0.4; MS: *m/z* 308 (M^+, 100), 293 (17), 277 (25), 183 (28), 167 (41), 97 (48), 73 (53), 59 (28); Anal. Found: C, 73.8; H, 6.3. $C_{19}H_{20}SiS$ Calc.: C, 74.0; H, 6.5%.

(Z)-1-Phenyl-2-phenylsulfanyloct-1-en-3-yne (**4b**): Colourless oil; IR (film): ν (cm^{-1}) 3058, 2957, 2213, 1716, 1583, 1477, 1440, 860, 747, 690; ^{1}H NMR ($CDCl_3$): δ 7.59–7.24 (m, 10H), 7.00 (s, 1H), 2.09 (t, *J* = 6.4 Hz, 2H), 1.23–1.11 (m, 4H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 135.9, 135.3, 133.4, 133.3, 129.5, 128.5, 128.2, 127.7, 119.4, 93.6, 79.9, 30.3, 21.8, 18.9, 13.6; MS: *m/z* 292 (M^+, 100), 235 (43), 167 (26), 141 (47), 115 (49), 91 (26), 77 (18); Anal. Found: C, 82.1; H, 6.6. $C_{20}H_{20}S$ Calc.: C, 82.2; H, 6.85%.

(Z)-1-Phenyl-2-phenylsulfanyl-4-phenylbut-1-en-3-yne (**4c**): Colourless oil; IR (film): ν (cm^{-1}) 3058, 2128, 1594, 1487, 755, 707, 689; ^{1}H NMR ($CDCl_3$): δ 7.66–6.98 (m, 16H); ^{13}C NMR ($CDCl_3$): δ 135.8, 135.5, 134.0, 131.3, 129.6, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 122.6, 119.3, 92.4, 88.6; MS: *m/z* 312 (M^+, 44), 311 (M^+-1, 63), 235 (49), 202 (100), 77 (25); Anal. Found: C, 84.4; H, 5.2. $C_{22}H_{16}S$ Calc.: C, 84.6; H, 5.1%.

(Z)-1-Methoxy-3-phenylsulfanylnon-2-en-4-yne (**4d**): Colourless oil; IR (film): ν (cm^{-1}) 3059, 2211, 1702, 1582, 1440, 1378, 1112, 746, 691; ^{1}H NMR ($CDCl_3$): δ 7.42–7.21 (m, 5H), 6.23 (t, *J* = 6.4 Hz, 1H), 4.24 (d, *J* = 6.4 Hz, 2H), 3.37 (s, 3H), 2.09 (t, *J* = 6.8 Hz, 2H), 1.25–1.12 (m, 4H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 135.8, 133.3, 132.1, 128.6, 127.4, 120.9, 92.4, 78.4, 69.4, 58.2, 30.3, 21.7, 18.8, 13.5; MS: *m/z* 260 (M^+, 18), 150 (15), 121 (34), 91 (27), 77 (20), 60 (22), 45 (100); Anal. Found: C, 73.6; H, 7.5. $C_{16}H_{20}OS$ Calc.: C, 73.9; H, 7.7%.

(Z)-1-Methoxy-3-phenylsulfanyl-5-phenylpent-2-en-4-yne (**4e**): Colourless oil; IR (film): ν (cm^{-1}) 3059, 2201, 1717, 1668, 1581, 1489, 1478, 1118, 1024, 756, 690; ^{1}H NMR ($CDCl_3$): δ 7.51–7.04 (m, 10H), 6.38 (t, *J* = 6.4 Hz, 1H), 4.31 (d, *J* = 6.4 Hz, 2H), 3.41 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 136.3, 132.9, 131.4, 128.8, 128.4, 128.3, 128.1, 127.8, 122.5, 120.8, 91.1, 86.9, 69.4, 58.3; MS: *m/z* 280 (M^+, 3.8), 265 (48), 105 (91), 77 (76), 45 (100); Anal. Found: C, 76.9; H, 5.5. $C_{18}H_{16}OS$ Calc.: C, 77.1; H, 5.7%.

(Z)-1,6-Dimethoxy-3-phenylsulfanylhex-2-en-4-yne (**4f**): Colourless oil; IR (film): ν (cm^{-1}) 3060, 2987, 2207, 1715, 1583, 1187, 1098, 745, 690; ^{1}H NMR ($CDCl_3$): δ 7.42–7.28 (m, 5H), 6.37 (t, *J* = 6.2 Hz, 1H), 4.26 (d, *J* = 6.2 Hz, 2H), 4.01 (s, 2H), 3.38 (s, 3H), 3.09 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 138.0, 132.5, 131.5, 128.3, 127.1, 119.1, 85.7, 83.5, 68.9, 59.4, 57.9, 56.7; MS: *m/z* 248 (M^+, 14), 218 (31), 185 (30), 147 (25), 121 (32), 109 (100), 65 (93), 51 (99); Anal. Found: C, 67.5; H, 6.3. $C_{14}H_{16}O_2S$ Calc.: C, 67.7; H, 6.45%.

(Z)-6-Phenylsulfanyldodec-5-en-7-yne (**4g**): Colourless oil; IR (film): ν (cm^{-1}) 3060, 2959, 2212, 1707, 1582, 1465, 1379, 745, 690; ^{1}H NMR ($CDCl_3$): δ 7.39–7.18 (m, 5H), 6.22 (t, *J* = 7.6 Hz, 1H), 2.41–2.35 (m, 2H), 2.11 (t, *J* = 6.8 Hz, 2H), 1.42–1.13 (m, 8H), 0.93–0.76 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 142.2, 134.4, 131.2, 128.5, 126.7, 117.1, 89.9, 79.4, 31.1, 30.4, 29.7, 22.4, 21.7, 18.8, 13.9,

13.6; MS: *m/z* 272 (M^+, 74), 245 (24), 229 (70), 147 (35), 109 (42), 91 (74), 85 (100), 77 (62), 57 (85); Anal. Found: C, 79.15; H, 8.7. $C_{18}H_{24}S$ Calc.: C, 79.4; H, 8.8%.

(Z)-6-Phenylsulfanyl-8-phenyloct-5-en-7-yne (**4h**): Colourless oil; IR (film): ν (cm^{-1}) 3059, 2957, 2202, 1716, 1583, 1478, 1440, 754, 689; ^1H NMR ($CDCl_3$): δ 7.48–7.07 (m, 10H), 6.37 (t, J = 7.6 Hz, 1H), 2.47–2.42 (m, 2H), 1.49–1.36 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 142.9, 134.0, 132.0, 131.4, 128.7, 128.1, 128.0, 127.2, 123.0, 117.3, 89.1, 88.1, 31.0, 29.9, 22.4, 14.0; MS: *m/z* 292 (M^+, 100), 249 (70), 215 (26), 183 (32), 155 (63), 141 (73), 115 (74), 91 (30), 77 (17); Anal. Found: C, 82.3; H, 6.7. $C_{20}H_{20}S$ Calc.: C, 82.2; H, 6.85%.

(Z)-6-Phenylsulfanyl-9-methoxynon-5-en-7-yne (**4i**): Colourless oil; IR (film): ν (cm^{-1}) 3059, 2213, 1715, 1583, 1439, 1187, 1099, 742, 690; ^1H NMR ($CDCl_3$): δ 7.38–7.21 (m, 5H), 6.37 (t, J = 7.6 Hz, 1H), 4.02 (s, 2H), 3.10 (s, 3H), 2.42–2.37 (m, 2H), 1.45–1.32 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 145.1, 134.1, 131.0, 128.7, 126.8, 116.1, 85.2, 84.1, 60.0, 57.2, 30.9, 29.8, 22.4, 13.9; MS: *m/z* 260 (M^+, 100), 217 (33), 185 (60), 91 (67), 65 (68), 51 (58); Anal. Found: C, 73.9; H, 7.6. $C_{16}H_{20}OS$ Calc.: C, 73.85; H, 7.7%

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