Stereoselective synthesis of difunctionalised 1,3-dienes containing silicon and sulfur via palladium catalysed cross-coupling reactions

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Hydromagnesiation of alkynylsilanes **1** in diethyl ether gave (*Z*)-α-silylvinyl Grignard reagents **2**, which underwent a cross-coupling reaction with (*E*)-α-iodovinyl sulfides **3** in the presence of $Pd(PPh_3)_4$ as catalyst to afford stereoselectively (*Z,Z*)-2-silyl-3-arylsulfanyl-substituted 1,3-dienes **4** in good yields.

Keywords: hydromagnesiation, (*E*)-α-iodovinyl sulfide, 1,3-diene, cross-coupling reaction, palladium catalysis

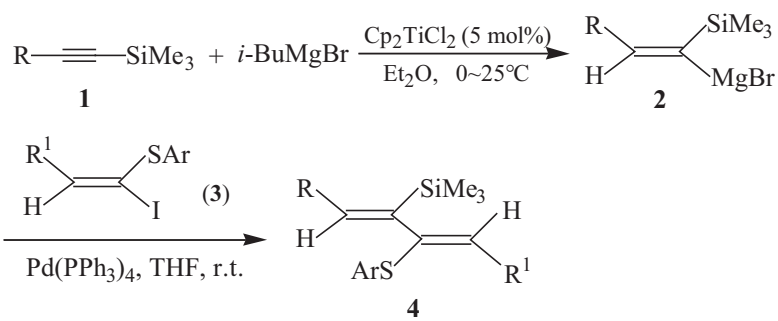
The stereocontrolled synthesis of 1,3-dienes containing metal or heteroatom functional groups has received much attention in organic synthesis because many useful functional group transformations can be achieved by introduction and removal of metal or heteroatom functions. The stereoselective syntheses of 1,3-dienyl sulfides,[1] 1,3-dienyl selenides,[2-5] 1,3-dienylsilanes[6-8] and 1,3-dienylstannanes[9-11] have already been described in the literature. Recently, the synthesis of difunctionalised 1,3-dienes has also attracted great interest in organic synthesis since such dienes may find use as synthetic building blocks.[12-20] In addition, difunctionalised 1,3-dienes containing heteroatoms can control both regio- and stereoselectivity and play a very important role in cycloadditions.[21-25] Jin *et al*.[26] reported the stereoselective synthesis of 2-alkoxy-3-alkyl(aryl)thiobuta-1,3-dienes by a Negishi coupling reaction between α-alkyl(aryl)thio vinyl zinc chloride and α-bromo vinyl ether. Very recently, Coleman and Walczak[27] described the stereoselective synthesis of (*E,E*)-1-tributylstannyl-4-borylbuta-1,3-diene and its use as an orthogonal Stille and Suzuki–Miyaura coupling partner. However, to the best of our knowledge, no well-established method is available to prepare stereoselectively (*Z,Z*)-2-silyl-3-arylsulfanyl-substituted 1,3-dienes. Hydromagnesiation has emerged as a unique hydrometallation with some attractive features such as the high regioselectivity and stereoselectivity observed with alkynylsilanes.[28,29] Recently, we have reported the stereoselective synthesis of 2-silyl-1,3-alkadienes via hydromagnesiation of alkynylsilanes, followed by treatment with alkenyl halides in the presence of $Pd(PPh_3)_4$ as catalyst.[30] Here we report that (*Z,Z*)-2-silyl-3-arylsulfanyl-substituted 1,3-dienes could be conveniently synthesised by the hydromagnesiation of alkynylsilanes, followed by the cross-coupling reaction with (*E*)-α-iodovinyl sulfides in the presence of $Pd(PPh_3)_4$ as catalyst (Scheme 1).

(*E*)-α-Iodovinyl sulfides **3** were conveniently prepared by the hydrostannylation of alkynylsulfides and the successive reaction with iodine.[31] We found that, hydromagnesiation of alkynylsilanes **1** with isobutylmagnesium bromide using 5 mol% Cp_2TiCl_2 at 25°C in diethyl ether for 6 h, followed by solvent exchange (to THF) and subsequent reaction with (*E*)-α-iodovinyl sulfides **3** and 5 mol% $Pd(PPh_3)_4$, gave the (*Z,Z*)-2-silyl-3-arylsulfanyl-substituted 1,3-dienes **4** in good yields. As can be seen from the experimental results summarised in Table 1, the tandem hydromagnesiation/

Table 1 Synthesis of (*Z,Z*)-2-silyl-3-arylsulfanyl-substituted 1,3-dienes **4a–j**

Entry	R	R^1	Ar	Product[a]	Yield/%[b]
1	*n*-C_4H_9	*n*-C_4H_9	Ph	**4a**	75
2	*n*-C_6H_{13}	*n*-C_4H_9	Ph	**4b**	83
3	*n*-C_4H_9	Ph	Ph	**4c**	83
4	*n*-C_6H_{13}	Ph	Ph	**4d**	85
5	*n*-C_4H_9	CH_3OCH_2	Ph	**4e**	76
6	*i*-C_5H_{11}	CH_3OCH_2	Ph	**4f**	75
7	*n*-C_6H_{13}	CH_3OCH_2	Ph	**4g**	81
8	*n*-C_4H_9	*n*-C_4H_9	4-MeC_6H_4	**4h**	81
9	*n*-C_4H_9	*n*-C_4H_9	4-ClC_6H_4	**4i**	77
10	$PhCH_2$	*n*-C_4H_9	Ph	**4j**	79

[a]All the compounds were characterised using ^1H NMR, ^{13}C NMR, IR, MS and elemental analyses.
[b]Isolated yield based on compound **3** used.



Scheme 1

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cross-coupling reaction of a variety of alkynylsilanes with isobutylmagnesium bromide and (*E*)-α-iodovinyl sulfides proceeded smoothly, under very mild conditions, to afford the corresponding (*Z,Z*)-2-silyl-3-arylsulfanyl-substituted 1,3-dienes **4** stereoselectively.

The hydromagnesiation of alkynylsilanes **1** is 100% regio- and stereoselective as previously described.[28,29] It is well documented that the cross-coupling reaction of vinyl Grignard reagents with alkenyl halides in the presence of a palladium catalyst occurs with the configuration retention of both the starting vinyl Grignard reagents and the alkenyl halides.[32-34] In addition, the (2*Z*,4*Z*)-configuration of compound **4e** was confirmed by NOESY experiments. There was a correlation between the allylic protons (δ = 2.08–1.98 ppm) of the *n*-butyl group and the methyl protons of trimethylsilyl. A correlation between the aromatic protons and the allylic protons (δ = 4.31 ppm) of the methoxymethyl group was also observed. The NOE results indicate that **4e** has the expected (2*Z*,4*Z*)-configuration.

In summary, we have developed a direct route to the stereoselective synthesis of (*Z,Z*)-2-silyl-3-arylsulfanyl-substituted 1,3-dienes by the hydromagnesiation of alkynylsilanes followed by the cross-coupling with (*E*)-α-iodovinyl sulfides in the presence of a palladium catalyst. The method has some advantages such as readily available starting materials, straightforward and simple procedures, mild reaction conditions and good yields. Investigations into the synthetic applications of (*Z,Z*)-2-silyl-3-arylsulfanyl-substituted 1,3-dienes are in progress in our laboratory.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer using $CDCl_3$ as the solvent. IR spectra were determined on an FTS-185 instrument as neat films. Mass spectra were obtained on a Finnigan 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 N_2. THF was freshly distilled from sodium-benzophenone prior to use. Diethyl ether was treated with lithium aluminum hydride and distilled before use. $Pd(PPh_3)_4$ was prepared according to a literature procedure.[35]

General procedure for (Z,Z)-2-silyl-3-arylsulfanyl-substituted 1,3-dienes **4a–j**

To a solution of isobutylmagnesium bromide (4.5 mmol) in diethyl ether (7 ml) was added Cp_2TiCl_2 (50 mg, 0.2 mmol) at 0°C, 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 (6 ml), cooled to 0°C, and $Pd(PPh_3)_4$ (0.232 g, 0.2 mmol) and (*E*)-α-iodovinyl sulfide **3** (3.6 mmol) were added with stirring. The reaction mixture was brought to 30°C gradually and stirred for 8 h, quenched with sat. aq. NH_4Cl (25 ml) and extracted with Et_2O (2 × 40 ml). The organic layer was washed with sat. aq. NH_4Cl (20 ml) and water (3 × 30 ml) and dried ($MgSO_4$). Removal of solvent under reduced pressure gave an oil, which was purified by column chromatography on silica gel using light petroleum ether (b.p. 30–60°C) as eluent.

(5Z,7Z)-7-Phenylsulfanyl-6-trimethylsilyldodeca-5,7-diene **(4a):** Oil. IR (film): ν (cm^{-1}) 2957, 2927, 1622, 1587, 1465, 1379, 1247, 837, 739; ^{1}H NMR ($CDCl_3$): δ 7.24–7.13 (m, 5H), 5.67 (t, *J* = 7.6 Hz, 1H), 5.50 (t, *J* = 7.6 Hz, 1H), 2.46–2.37 (m, 2H), 2.09–2.01 (m, 2H), 1.43–1.20 (m, 8H), 0.95–0.81 (m, 6H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 142.97, 142.79, 135.24, 134.56, 133.0, 131.43, 128.30, 126.27, 31.99, 31.77, 30.14, 29.44, 22.65, 22.40, 14.05, 14.03, -0.74; MS: *m/z* 346 (M$^+$, 48), 162 (58), 73 (100); Anal. Calc. for $C_{21}H_{34}SiS$: C, 72.76; H, 9.89. Found: C, 72.5; H, 10.1%.

(5Z,7Z)-6-Phenylsulfanyl-7-trimethylsilyltetradeca-5,7-diene **(4b):** Oil. IR (film): ν (cm^{-1}) 2958, 2927, 1621, 1585, 1465, 1378, 1248, 838, 739, 690; ^{1}H NMR ($CDCl_3$): δ 7.22–7.12 (m, 5H), 5.71 (t, *J* = 7.6 Hz, 1H), 5.44 (t, *J* = 7.6 Hz, 1H), 2.43–2.34 (m, 2H), 2.06–1.95 (m, 2H), 1.44–1.22 (m, 12H), 0.91–0.84 (m, 6H), 0.02 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 147.05, 140.77, 139.66, 135.16, 133.09, 131.62, 128.24, 126.05, 31.91, 31.86, 31.77, 29.64, 29.40, 28.86, 22.56, 22.40, 14.10, 14.03, 0.42; MS: *m/z* 374 (M$^+$, 36), 190 (45), 73 (100); Anal. Calc. for $C_{23}H_{38}SiS$: C, 73.73; H, 10.22. Found: C, 73.45; H, 10.0%.

(1Z,3Z)-1-Phenyl-2-phenylsulfanyl-3-trimethylsilylocta-1,3-diene **(4c):** Oil. IR (film): ν (cm^{-1}) 3059, 3021, 2956, 2928, 1625, 1583, 1477, 1440, 1248, 839, 748; ^{1}H NMR ($CDCl_3$): δ 7.61–7.56 (m, 2H), 7.35–7.14 (m, 8H), 6.51 (s, 1H), 6.05 (t, *J* = 7.6 Hz, 1H), 2.05–1.97 (m, 2H), 1.20–1.14 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 147.80, 142.12, 137.03, 132.99, 129.21, 128.94, 128.85, 128.63, 128.35, 128.06, 127.97, 126.81, 31.75, 30.34, 22.65, 14.09, 0.05; MS: *m/z* 366 (M$^+$, 75), 184 (64), 73 (100); Anal. Calc. for $C_{23}H_{30}SiS$: C, 75.35; H, 8.25. Found: C, 75.5; H, 8.4%.

(1Z,3Z)-1-Phenyl-2-phenylsulfanyl-3-trimethylsilyldeca-1,3-diene **(4d):** Oil. IR (film): ν (cm^{-1}) 3060, 2924, 2854, 1627, 1584, 1477, 1440, 1248, 839, 748, 691; ^{1}H NMR ($CDCl_3$): δ 7.61–7.55 (m, 2H), 7.36–7.16 (m, 8H), 6.49 (s, 1H), 6.04 (t, *J* = 7.6 Hz, 1H), 2.03–1.95 (m, 2H), 1.36–1.14 (m, 8H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 147.81, 142.08, 137.04, 132.96, 129.19, 128.90, 128.75, 128.63, 128.32, 128.01, 127.91, 126.80, 31.98, 31.76, 29.55, 28.95, 22.56, 14.09, 0.31; MS: *m/z* 394 (M$^+$, 49), 212 (31), 73 (100); Anal. Calc. for $C_{25}H_{34}SiS$: C, 76.08; H, 8.68. Found: C, 76.2; H, 8.9%.

(2Z,4Z)-1-Methoxy-3-phenylsulfanyl-4-trimethylsilylnona-2,4-diene **(4e):** Oil. IR (film): ν (cm^{-1}) 3061, 2957, 2929, 1668, 1584, 1440, 1247, 1119, 1096, 838, 744; ^{1}H NMR ($CDCl_3$): δ 7.30–7.21 (m, 5H), 5.69 (t, *J* = 7.6 Hz, 1H), 5.55 (t, *J* = 6.4 Hz, 1H), 4.31 (d, *J* = 6.4 Hz, 2H), 3.39 (s, 3H), 2.08–1.98 (m, 2H), 1.26–1.15 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H), 0.03 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 143.90, 141.91, 137.84, 133.87, 132.44, 128.71, 128.46, 127.07, 69.81, 57.98, 31.79, 30.33, 22.62, 14.11, –0.78; MS: *m/z* 334 (M$^+$, 18), 302 (33), 277 (21), 73 (100); Anal. Calc. for $C_{19}H_{30}SiSO$: C, 68.20; H, 9.04. Found: C, 68.5; H, 9.15%.

(2Z,4Z)-1-Methoxy-8-methyl-3-phenylsulfanyl-4-trimethylsilylnona-2,4-diene **(4f):** Oil. IR (film): ν (cm^{-1}) 2956, 2926, 2872, 1658, 1594, 1464, 1377, 1248, 1120, 837, 690; ^{1}H NMR ($CDCl_3$): δ 7.33–7.22 (m, 5H), 5.68 (t, *J* = 7.6 Hz, 1H), 5.56 (t, *J* = 6.4 Hz, 1H), 4.32 (d, *J* = 6.4 Hz, 2H), 3.38 (s, 3H), 2.12–1.99 (m, 2H), 1.46–1.12 (m, 3H), 0.87 (d, *J* = 6.8 Hz, 6H), 0.05 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 143.93, 141.89, 137.88, 133.85, 132.47, 128.81, 128.54, 127.12, 69.83, 57.92, 39.39, 30.03, 27.82, 22.51, –0.38; MS: *m/z* 348 (M$^+$, 23), 316 (37), 73 (100); Anal. Calc. for $C_{20}H_{32}SiSO$: C, 68.90; H, 9.25. Found: C, 68.6; H, 9.1%.

(2Z,4Z)-1-Methoxy-3-phenylsulfanyl-4-trimethylsilylundeca-2,4-diene **(4g):** Oil. IR (film): ν (cm^{-1}) 3060, 2958, 2930, 1661, 1580, 1440, 1249, 1124, 1096, 843, 741; ^{1}H NMR ($CDCl_3$): δ 7.30–7.18 (m, 5H), 5.94 (t, *J* = 7.6 Hz, 1H), 5.68 (t, *J* = 6.4 Hz, 1H), 4.26 (d, *J* = 6.4 Hz, 2H), 3.39 (s, 3H), 2.07–1.93 (m, 2H), 1.29–1.15 (m, 8H), 0.87 (t, *J* = 7.2 Hz, 3H), 0.07 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 154.96, 140.40, 135.24, 132.16, 131.85, 129.85, 128.51, 126.07, 70.68, 58.26, 33.70, 31.75, 29.48, 29.21, 22.63, 14.08, –0.06; MS: *m/z* 362 (M$^+$, 14), 330 (37), 73 (100); Anal. Calc. for $C_{21}H_{34}SiSO$: C, 69.55; H, 9.45. Found: C, 69.3; H, 9.2%.

(5Z,7Z)-7-(4-Methylphenyl)sulfanyl-6-trimethylsilyldodeca-5,7-diene **(4h):** Oil. IR (film): ν (cm^{-1}) 2957, 2926, 1618, 1593, 1492, 1465, 1248, 838, 808; ^{1}H NMR ($CDCl_3$): δ 7.10–7.08 (m, 2H), 7.03–7.01 (m, 2H), 5.79 (t, *J* = 7.6 Hz, 1H), 5.54 (t, *J* = 7.6 Hz, 1H), 2.40–2.32 (m, 2H), 2.29 (s, 3H), 1.98–1.90 (m, 2H), 1.45–1.22 (m, 8H), 0.94–0.86 (m, 6H), 0.07 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 146.81, 140.79, 140.16, 136.07, 133.50, 132.17, 131.37, 129.02, 31.95, 31.88, 31.57, 29.31, 22.40, 22.16, 21.03, 14.08, 14.03, 0.40; MS: *m/z* 360 (M$^+$, 11), 91 (35), 73 (100); Anal. Calc. for $C_{22}H_{36}SiS$: C, 73.26; H, 10.06. Found: C, 73.1; H, 9.85%.

(5Z,7Z)-7-(4-Chlorophenyl)sulfanyl-6-trimethylsilyldodeca-5,7-diene **(4i):** Oil. IR (film): ν (cm^{-1}) 2956, 2926, 1620, 1592, 1475, 1248, 838, 819, 758; ^{1}H NMR ($CDCl_3$): δ 7.20–7.16 (m, 2H), 7.12–7.10 (m, 2H), 5.82 (t, *J* = 7.6 Hz, 1H), 5.63 (t, *J* = 7.6 Hz, 1H), 2.39–2.31 (m, 2H), 1.99–1.92 (m, 2H), 1.44–1.23 (m, 8H), 0.95–0.88 (m, 6H), 0.07 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 147.27, 140.67, 139.28, 133.86, 132.71, 132.56, 132.02, 128.40, 31.90, 31.59, 30.15, 29.42, 22.41, 22.22, 14.09, 14.06, 0.43; MS: *m/z* 382 (M$^+$, ^{37}Cl, 12), 380 (M$^+$, ^{35}Cl, 35), 163 (56), 162 (45), 73 (100); Anal. Calc. for $C_{21}H_{33}SiSCl$: C, 66.18; H, 8.73. Found: C, 66.4; H, 8.9%.

(2Z,4Z)-1-Phenyl-4-phenylsulfanyl-3-trimethylsilylnona-2,4-diene **(4j):** Oil. IR (film): ν (cm^{-1}) 3057, 2956, 2928, 1643, 1597, 1467, 1249, 837, 740; ^{1}H NMR ($CDCl_3$): δ 7.39–7.15 (m, 10H), 5.78 (t, *J* = 7.6 Hz, 1H), 5.63 (t, *J* = 7.6 Hz, 1H), 3.58 (d, *J* = 7.6 Hz, 2H), 2.15–2.03 (m, 2H), 1.28–1.16 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.08 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 153.87, 140.78, 138.45, 135.79, 133.49, 132.53, 131.68, 130.28, 129.54, 129.13, 128.42, 126.13, 39.61, 31.78, 29.54, 22.43, 14.02, 0.41; MS: *m/z* 380 (M$^+$, 23), 196 (38), 73 (100); Anal. Calc. for $C_{24}H_{32}SiS$: C, 75.73; H, 8.47. Found: C, 75.5; H, 8.2%.

We thank the Natural Science Foundation of Jiangxi Province (Project No. 2007GZW0172) for financial support.

Received 26 March 2008; accepted 23 April 2008
Paper 08/5181 doi: 10.3184/030823408X320656

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