Stereoselective synthesis of (*E,E*)-1-arylseleno-substituted 1,5-dien-3-ynes

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Sonogashira coupling of (*E*)-1-iodo-2-arylselenoethylenes **1** with (trimethylsilyl)acetylene gave (*E*)-1-arylseleno-4-(trimethylsilyl)but-1-en-3-ynes **2**, which underwent desilylation to afford (*E*)-1-arylselenobut-1-en-3-ynes **3** in high yields. (*E,E*)-1-Arylseleno-substituted 1,5-dien-3-ynes **5** could be synthesised stereoselectively via Sonogashira coupling of (*E*)-1-arylselenobut-1-en-3-ynes **3** with (*E*)-vinyl iodides **4**.

Keywords: (*E*)-1-iodo-2-arylselenoethylene, Sonogashira coupling, 1,5-dien-3-yne, (*E*)-1-arylselenobut-1-en-3-yne, stereoselective synthesis

Enyne systems have attracted much attention from synthetic organic chemists as they show interesting chemical and biological reactivities.[1-3] Stereo-defined conjugated polyenynes containing an internal carbon-carbon triple bond unit are widely distributed in nature and show interesting biological activities.[4,5] Recently, dienyne compounds have attracted much interest since they are important synthetic intermediates.[6-10] Uenishi and Matsui reported the stereocontrolled synthesis of dienynes by stepwise Suzuki/Sonogashira coupling reactions of 1,1-dibromoalk-1-enes.[11] Sato and coworkers reported that conjugated diynes underwent selective mono-titanation with a Ti(II) reagent to give 1 : 1 diyne-titanium alkoxide complexes, which reacted with another acetylene to give stereo-defined dienynes.[12] Otterlo *et al.* described the synthesis of dienynes from alkenes and diynes using ruthenium-mediated ring-closing metathesis.[13] Shi *et al.*[14] reported that 2-iodo-4-(phenylchalcogenyl)-1-butenes react with alkynes under $Pd(OAc)_2$ catalysis to give conjugated dienynes. Hiyama and coworkers[15] described a one-pot synthesis of conjugated dienynes by a palladium-mediated three-component cross-coupling reaction. The synthesis of dienynes containing metal or heteroatom functional groups has also attracted considerable interest in organic synthesis because many useful functional group transformations can be achieved by introduction and removal of metal or heteroatom functions. Alami and Frri[16] reported the regioselective synthesis of stannylated dienynes by the palladium-catalysed hydrostannylation of enediynes. However, to the best of our knowledge, the synthesis of 1-arylseleno-substituted 1,5-dien-3-ynes has not been described. Herein, we wish to report that (*E,E*)-1-arylseleno-substituted 1,5-dien-3-ynes can be conveniently synthesised via Sonogashira coupling of (*E*)-1-iodo-2-arylselenoethylenes with (trimethylsilyl)acetylene, followed by desilylation and then coupling with (*E*)-vinyl iodides.

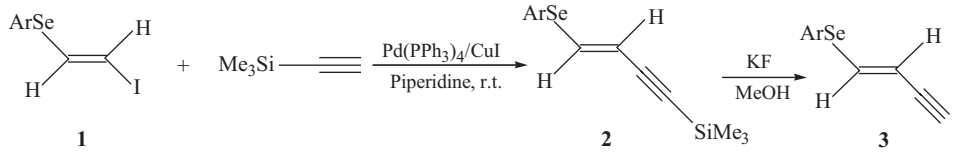
There has been a lively interest in terminal conjugated enynes, alk-3-en-1-ynes, due to their synthetic utility; the acetylenic hydrogen can be converted into various functionalities as well as undergo carbon–carbon bond formation. Furthermore, the terminal conjugated enyne is a useful building block for the synthesis of natural products in organic synthesis, owing to its presence in natural products such as laurencin,[17] dactylyne,[18] quinolizidine,[19] and histrionicotoxin.[20-22] Very recently, Hoshi *et al.*[23] reported the synthesis of terminal conjugated enynes via Cu-mediated Suzuki-Miyaura cross-coupling reaction of alkenyldialkylboranes with (trimethylsilyl)ethynyl bromide. Our methodology involves the preparation and the reactions of the building block (*E*)-1-arylselenobut-1-en-3-ynes **3** which can be conveniently obtained according to Scheme 1.

Table 1 Coupling reaction of **1** with (trimethylsilyl)acetylene[a] and desilylation of **2**[b]

Entry	Ar	Product	Yield/%[c]
1	Ph	**2a**	89
2	4-MeC_6H_4	**2b**	90
3	4-ClC_6H_4	**2c**	87
4	Ph	**3a**	90
5	4-MeC_6H_4	**3b**	91
6	4-ClC_6H_4	**3c**	88

[a]The reaction of **1** (1.0 mmol) with (trimethylsilyl)acetylene (1.5 mmol) was carried out using $Pd(PPh_3)_4$ (0.05 mmol), CuI (0.1 mmol) and piperidine (3 ml) at room temperature for 2 h.
[b]The desilylation reaction of **2** (1 mmol) with KF (10 mmol) was performed in methanol (4 ml) at 70°C for 5 h.
[c]Isolated yield of **2** based on the **1** used.

Sonogashira coupling of alkenyl iodides with terminal alkynes provides a simple and general route for the synthesis of conjugated enynes.[24,25] (*E*)-1-Iodo-2-arylselenoethylenes **1** were easily prepared by the hydrozirconation of arylselenoacetylenes, followed by the reaction with iodine according to a literature procedure.[26] (*E*)-1-Iodo-2-arylselenoethylenes **1** are difunctional group reagents in which two synthetically versatile groups are linked to the olefinic carbon atoms and can be considered both as vinylic selenides and as vinylic iodides. Vinylic selenides are important synthetic intermediates since vinylic selenides are synthetically equivalent to carbonyls and can be stereospecifically converted into alkenes by nickel-catalysed coupling reactions with Grignard reagents.[27-29] We observed that reaction of (*E*)-1-iodo-2-arylselenoethylenes **1** with (trimethylsilyl)acetylene in piperidine at room temperature using $Pd(PPh_3)_4$ and CuI as a co-catalyst, proceeded fairly rapidly to afford stereoselectively the desired (*E*)-1-arylseleno-4-(trimethylsilyl)but-1-en-3-ynes **2** in high yields; typical results are summarised in Table 1. We next investigated the desilylation reaction of (*E*)-1-arylseleno-4-(trimethylsilyl)but-1-en-3-ynes **2** with KF in methanol in order to prepare (*E*)-1-



1 **2** **3**

Scheme 1

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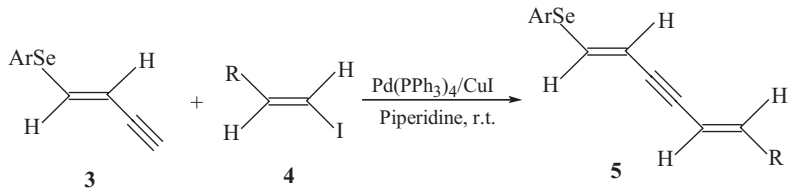

Scheme 2

arylselenobut-1-en-3-ynes **3**. We found that the desilylation reaction of (*E*)-1-arylseleno-4-(trimethylsilyl)but-1-en-3-ynes **2** with KF proceeded smoothly in methanol at 70°C to give the desired (*E*)-1-arylselenobut-1-en-3-ynes **3** in high yields. Typical results are also summarised in Table 1.

(*E*)-1-Arylselenobut-1-en-3-ynes **3** were coupled with a variety of (*E*)-vinyl iodides **4** (Scheme 2); typical results are summarised in Table 2. As shown in Table 2, the Sonogashira coupling reaction of (*E*)-1-arylselenobut-1-en-3-ynes **3** with a variety of (*E*)-vinyl iodides **4** proceeds smoothly in piperidine at room temperature using $Pd(PPh_3)_4$ and CuI as a co-catalyst, to afford the desired (*E,E*)-1-arylseleno-substituted 1,5-dien-3-ynes **5** in good yields. The stereochemistry of compounds **5** was easily established since their ^{1}H NMR spectra give rise to three or four doublets at δ = 7.14–5.55 with a coupling constant of 15.6–19.2 Hz, which indicated that the Sonogashira coupling reactions of (*E*)-1-arylselenobut-1-en-3-ynes **3** with a variety of (*E*)-vinyl iodides **4** occurred with the retention of configuration.

In summary, we have developed a highly stereoselective and general route to (*E,E*)-1-arylseleno-substituted 1,5-dien-3-ynes **5** via Sonogashira coupling of (*E*)-1-iodo-2-arylselenoethylenes with (trimethylsilyl)acetylene, followed by a desilylation reaction and then coupling with (*E*)-vinyl iodides. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions, high stereoselectivity and good yields. Investigations into the synthetic applications of compounds **5** are currently in progress.

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 Finigan 8239 mass spectrometer. Microanalyses were determined 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. For some AA'XX' systems in ^{1}H NMR $J^* = J_{23} + J_{25}$.

General procedure for the synthesis of (E)-1-arylseleno-4-(trimethylsilyl)but-1-en-3-ynes **2a–c**

(*E*)-1-Iodo-2-arylselenoethylene **1** (1.0 mmol), $Pd(PPh_3)_4$ (0.05 mmol), piperidine (3 ml), and CuI (0.1 mmol) were added to a flask under argon, and the resulting mixture was stirred at room temperature for 5 min. To this solution was added (trimethylsilyl)acetylene (1.5 mmol), and the reaction mixture was stirred at room temperature for 2 h, quenched with sat. NH_4Cl aq. solution (10 ml) at 0°C and extracted with Et_2O (2 × 20 ml). The ethereal solution was washed with water (2 × 10 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel eluting with light petroleum ether (b.p. 30–60°C).

(E)-1-Phenylseleno-4-trimethylsilylbut-1-en-3-yne (**2a**): Colourless oil; IR (film): ν (cm^{-1}) 3059, 2958, 2142, 1712, 1578, 1250, 844, 760, 690; ^{1}H NMR ($CDCl_3$): δ 7.54–7.51 (m, 2H), 7.34–7.32 (m, 3H), 7.21 (d, *J* = 16.0 Hz, 1H), 5.71 (d, *J* = 16.0 Hz, 1H), 0.16 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 136.4, 134.1, 129.6, 128.3, 127.8, 111.7, 103.3, 95.2, –0.1; MS: *m/z* 279 (M$^+$, 12), 250 (55), 78 (44), 73 (100); Anal. Found: C, 55.7; H, 5.6. $C_{13}H_{16}SiSe$ Calc.: C, 55.89; H, 5.77%.

(E)-1-(4-Methylphenyl)seleno-4-trimethylsilylbut-1-en-3-yne (**2b**): Colourless oil; IR (film): ν (cm^{-1}) 3033, 2961, 2163, 1704, 1563, 1251, 844, 803, 760; ^{1}H NMR ($CDCl_3$): δ 7.43–7.41 (m, 2H), 7.19 (d, *J* = 15.6 Hz, 1H), 7.14 (d, *J** = 8.0 Hz, 2H), 5.64 (d, *J* = 15.6 Hz, 1H), 2.35 (s, 3H), 0.16 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 138.8, 137.1, 134.7, 130.5, 123.9, 111.1, 103.6, 95.1, 21.3, 0.1; MS: *m/z* 294 (M$^+$, 14), 263 (33), 91 (35), 73 (100); Anal. Found: C, 57.6; H, 6.3. $C_{14}H_{18}SiSe$ Calc.: C, 57.31; H, 6.18%.

(E)-1-(4-Chlorophenyl)seleno-4-trimethylsilylbut-1-en-3-yne (**2c**): Colourless oil; IR (film): ν (cm^{-1}) 3031, 2957, 2166, 1706, 1556, 1473, 1254, 842, 824, 760; ^{1}H NMR ($CDCl_3$): δ 7.46–7.43 (m, 2H), 7.31–7.28 (m, 2H), 7.15 (d, *J* = 15.6 Hz, 1H), 5.73 (d, *J* = 15.6 Hz, 1H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 135.5, 135.4, 134.9, 129.9, 126.2, 112.6, 103.1, 95.8, 0.0; MS: *m/z* 314 (M$^+$, ^{35}Cl, 32), 191 (100), 189 (56), 156 (50), 73 (33); Anal. Found: C, 49.5; H, 4.6. $C_{13}H_{15}SiSeCl$ Calc.: C, 49.75; H, 4.82%.

General procedure for the synthesis of (E)-1-arylselenobut-1-en-3-ynes **(3a–c)**

A mixture of (*E*)-1-arylseleno-4-(trimethylsilyl)-1-buten-3-yne **2** (1 mmol) and anhydrous KF (10 mmol) in methanol (4 ml) was heated at reflux for 5 h. After removal of the solvent under reduced pressure, the mixture was extracted with diethyl ether (2 × 20 ml). The ethereal solution was washed with water (2 × 10 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel eluting with light petroleum ether (b.p. 30–60°C).

(E)-1-Phenylselenobut-1-en-3-yne (**3a**): Colourless oil; IR (film): ν (cm^{-1}) 3296, 2962, 2096, 1699, 1564, 1403, 1261, 1093, 930, 800; ^{1}H NMR ($CDCl_3$): δ 7.56–7.52 (m, 2H), 7.35–7.32 (m, 3H), 7.25 (d, *J* = 15.6 Hz, 1H), 5.68 (d, *J* = 15.6 Hz, 1H), 2.97 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 137.0, 134.0, 129.6, 128.4, 127.7, 110.6, 82.0, 77.9; MS: *m/z* 208 (M$^+$, 18), 157 (100), 154 (69), 78 (67), 77 (82); Anal. Found: C, 58.1; H, 4.2. $C_{10}H_8Se$ Calc.: C, 57.98; H, 3.89%.

(E)-1-(4-Methylphenyl)selenobut-1-en-3-yne (**3b**): Colourless oil; IR (film): ν (cm^{-1}) 3288, 3032, 2920, 2096, 1674, 1564, 1489, 1097, 929, 803; ^{1}H NMR ($CDCl_3$): δ 7.44–7.41 (m, 2H), 7.23 (d, *J* = 15.6 Hz, 1H), 7.15 (m, *J** = 8.4 Hz, 2H), 5.61 (d, *J* = 15.6 Hz, 1H), 2.95 (s, 1H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 138.7, 137.7, 134.5, 130.4, 123.6, 109.8, 82.2, 77.6, 21.2; MS: *m/z* 222 (M$^+$, 57), 171 (85), 169 (73), 91 (100); Anal. Found: C, 59.5; H, 4.3. $C_{11}H_{10}Se$ Calc.: C, 59.73; H, 4.56%.

(E)-1-(4-Chlorophenyl)selenobut-1-en-3-yne (**3c**): Colourless oil; IR (film): ν (cm^{-1}) 3300, 2963, 2097, 1566, 1403, 1261, 1092, 928, 814; ^{1}H NMR ($CDCl_3$): δ 7.47–7.44 (m, 2H), 7.32–7.30 (m, 2H), 7.19 (d, *J* = 16.0 Hz, 1H), 5.69 (d, *J* = 16.0 Hz, 1H), 2.99 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 136.4, 135.4, 135.0, 130.0, 126.1, 111.5, 81.9, 78.4; MS: *m/z* 242 (M$^+$, ^{35}Cl, 8.6), 191 (100), 156 (65), 112 (50), 75 (43); Anal. Found: C, 49.4; H, 2.8. $C_{10}H_7SeCl$ Calc.: C, 49.70; H, 2.92%.

Table 2 Synthesis of (*E,E*)-1-arylseleno-substituted 1,5-dien-3-ynes **5**[a]

Entry	Ar	R	Product	Yield/%[b]
1	Ph	*n*-C_4H_9	**5a**	81
2	Ph	CH_3OCH_2	**5b**	87
3	Ph	Me_3Si	**5c**	89
4	4-ClC_6H_4	*n*-C_4H_9	**5d**	84
5	4-ClC_6H_4	Me_3Si	**5e**	90
6	4-$CH_3C_6H_4$	*n*-C_6H_{13}	**5f**	85
7	4-$CH_3C_6H_4$	Me_3Si	**5g**	83

[a]The reactions were performed with 1.5 mmol of **3**, 1.0 mmol of **4**, 0.05 mmol of $Pd(PPh_3)_4$ and 0.1 mmol of CuI in piperidine (3 ml) under Ar at room temperature.
[b]Isolated yield based on the **4** used.

General procedure for the synthesis of (E,E)-1-arylseleno-substituted 1,5-dien-3-ynes (**5a–g**)

(*E*)-Vinyl iodide **4** (1.0 mmol), $Pd(PPh_3)_4$ (0.05 mmol), piperidine (3 ml), and CuI (0.1 mmol) were added to a flask under argon, and the resulting mixture was stirred at room temperature for 5 min. To this solution was added (*E*)-1-arylselenobut-1-en-3-yne **3** (1.5 mmol), and the reaction mixture was stirred at room temperature for 2 h, quenched with sat. NH_4Cl aq. solution (10 ml) at 0°C and extracted with Et_2O (2 × 20 ml). The ethereal solution was washed with water (2 × 10 ml) and dried over $MgSO_4$. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel eluting with light petroleum ether (b.p. 30–60°C).

(1E,5E)-1-Phenylselenodeca-1,5-dien-3-yne (**5a**): Colourless oil; IR (film): ν (cm^{-1}) 3018, 2957, 2927, 2174, 1578, 1477, 1438, 926, 735, 690; ^1H NMR ($CDCl_3$): δ 7.53–7.51 (m, 2H), 7.34–7.26 (m, 3H), 7.08 (d, *J* = 16.0 Hz, 1H), 6.13 (dt, *J* = 16.0, 7.2 Hz, 1H), 5.89 (d, *J* = 16.0 Hz, 1H), 5.56 (d, *J* = 16.0 Hz, 1H), 2.12–2.08 (m, 2H), 1.39–1.30 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 145.1, 133.5, 133.2, 129.5, 129.3, 128.0, 113.0, 109.4, 89.4, 86.4, 32.9, 30.8, 22.1, 13.9; MS: *m/z* 290 (M^+, 43), 233 (32), 165 (100), 128 (53), 78 (84), 77 (66); Anal. Found: C, 66.2; H, 6.1. $C_{16}H_{18}Se$ Calc.: C, 66.42; H, 6.27%.

(1E,5E)-1-Phenylseleno-7-methoxyhepta-1,5-dien-3-yne (**5b**): Colourless oil; IR (film): ν (cm^{-1}) 3054, 2924, 2175, 1578, 1554, 1477, 1438, 1120, 928, 738, 690; ^1H NMR ($CDCl_3$): δ 7.54–7.52 (m, 2H), 7.35–7.32 (m, 3H), 7.14 (d, *J* = 15.6 Hz, 1H), 6.13 (dt, *J* = 15.6, 5.6 Hz, 1H), 5.86 (d, *J* = 15.6 Hz, 1H), 5.82 (d, *J* = 15.6 Hz, 1H), 3.96 (d, *J* = 5.6 Hz, 2H), 3.34 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 139.1, 134.6, 133.7, 129.6, 129.5, 128.2, 112.1, 111.6, 88.5, 88.2, 72.3, 58.2; MS: *m/z* 278 (M^+, 57), 165 (100), 152 (51), 121 (45), 78 (87), 77 (99), 63 (65); Anal. Found: C, 60.4; H, 4.9. $C_{14}H_{14}OSe$ Calc.: C, 60.65; H, 5.09%.

(1E,5E)-1-Phenylseleno-6-trimethylsilylhexa-1,5-dien-3-yne (**5c**): Colourless oil; IR (film): ν (cm^{-1}) 3059, 2955, 2178, 1578, 1548, 1248, 926, 865, 736, 690; ^1H NMR ($CDCl_3$): δ 7.55–7.52 (m, 2H), 7.35–7.32 (m, 3H), 7.14 (d, *J* = 15.6 Hz, 1H), 6.41 (d, *J* = 19.2 Hz, 1H), 6.03 (d, *J* = 19.2 Hz, 1H), 5.87 (d, *J* = 15.6 Hz, 1H), 0.08 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 145.6, 134.7, 133.7, 131.5, 129.6, 128.2, 123.1, 112.3, 90.6, 88.3, –1.7; MS: *m/z* 306 (M^+, 100), 304 (69), 153 (42), 123 (30), 73 (53); Anal. Found: C, 58.7; H, 5.7. $C_{15}H_{18}SiSe$ Calc.: C, 58.99; H, 5.94%.

(1E,5E)-1-(4-Chlorophenyl)selenodeca-1,5-dien-3-yne (**5d**): Colourless oil; IR (film): ν (cm^{-1}) 3020, 2957, 2928, 2183, 1558, 1474, 1387, 1090, 926, 814, 730; ^1H NMR ($CDCl_3$): δ 7.47–7.43 (m, 2H), 7.31–7.26 (m, 2H), 7.02 (d, *J* = 16.0 Hz, 1H), 6.14 (dt, *J* = 15.6, 7.2 Hz, 1H), 5.89 (d, *J* = 15.6 Hz, 1H), 5.56 (d, *J* = 16.0 Hz, 1H), 2.14–2.09 (m, 2H), 1.41–1.25 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 145.5, 144.5, 134.7, 132.3, 129.7, 126.8, 113.8, 109.3, 89.8, 86.1, 32.9, 30.8, 22.1, 13.9; MS: *m/z* 324 (M^+, ^{35}Cl, 84), 232 (39), 165 (100), 152 (35); Anal. Found: C, 59.5; H, 5.5. $C_{16}H_{17}SeCl$ Calc.: C, 59.35; H, 5.29%.

(1E,5E)-1-(4-Chlorophenyl)seleno-6-trimethylsilylhexa-1,5-dien-3-yne (**5e**): Colourless oil; IR (film): ν (cm^{-1}) 3034, 2956, 2179, 1576, 1549, 1474, 1249, 1090, 926, 865, 814, 730; ^1H NMR ($CDCl_3$): δ 7.43–7.40 (m, 2H), 7.32–7.30 (m, 2H), 7.08 (d, *J* = 16.0 Hz, 1H), 6.42 (d, *J* = 19.2 Hz, 1H), 6.03 (d, *J* = 19.2 Hz, 1H), 5.89 (d, *J* = 16.0 Hz, 1H), 0.10 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 146.0, 134.9, 133.8, 129.7, 129.1, 126.5, 123.0, 113.1, 90.9, 88.0, -1.7; MS: *m/z* 340 (M^+, ^{35}Cl, 28), 112 (32), 73 (100); Anal. Found: C, 52.8; H, 4.8. $C_{15}H_{17}SiSeCl$ Calc.: C, 53.01; H, 5.04%.

(1E,5E)-1-(4-Methylphenyl)selenododeca-1,5-dien-3-yne (**5f**): Colourless oil; IR (film): ν (cm^{-1}) 3020, 2956, 2926, 2182, 1645, 1559, 1490, 926, 803; ^1H NMR ($CDCl_3$): δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.13 (m, *J** = 8.0 Hz, 2H), 7.06 (d, *J* = 16.0 Hz, 1H), 6.11 (dt, *J* = 16.0, 7.2 Hz, 1H), 5.80 (d, *J* = 16.0 Hz, 1H), 5.55 (d, *J* = 16.0 Hz, 1H), 2.34 (s, 3H), 2.14–2.05 (m, 2H), 1.39–1.25 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 145.0, 138.3, 134.0, 133.9, 130.3, 124.5, 112.1, 109.5, 89.2, 86.5, 33.2, 31.7, 28.8, 28.7, 22.6, 21.2, 14.1; MS: *m/z* 332 (M^+, 81), 247 (59), 181 (64), 165 (100), 91 (91); Anal. Found: C, 68.6; H, 7.1. $C_{19}H_{24}Se$ Calc.: C, 68.86; H, 7.30%.

(1E,5E)-1-(4-Methylphenyl)seleno-6-trimethylsilylhexa-1,5-dien-3-yne (**5g**): Colourless oil; IR (film): ν (cm^{-1}) 2956, 2179, 1548, 1490, 1249, 925, 865, 802; ^1H NMR ($CDCl_3$): δ 7.43–7.41 (m, 2H), 7.15–7.08 (m, 3H), 6.39 (d, *J* = 19.2 Hz, 1H), 6.02 (d, *J* = 19.2 Hz, 1H), 5.80 (d, *J* = 15.6 Hz, 1H), 2.35 (s, 3H), 0.08 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 145.3, 138.5, 135.4, 134.1, 130.4, 124.2, 123.2, 111.5, 88.5, 79.9, 21.2, -1.7; MS: *m/z* 320 (M^+, 29), 246 (22), 167 (34), 91 (65), 73 (100); Anal. Found: C, 60.4; H, 6.5. $C_{16}H_{20}SiSe$ Calc.: C, 60.16; H, 6.31%.

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