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A convenient synthesis of amides and nitriles with a branched and conjugated dienyne structure

Vito Fiandanese,* Francesco Babudri, Giuseppe Marchese and Angela Punzi

Dipartimento di Chimica, C.N.R. ICCOM, Università di Bari, via Orabona 4, 70126 Bari, Italy

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Abstract—An efficient and stereoselective synthetic approach to a variety of amides and nitriles with a branched and conjugated dienyne structure has been developed, starting from a readily available mono-silylated unsaturated amide and nitrile with an enyne structure. A nucleophilic hydrohalogenation of the triple bond of the enynes with NaI afforded a *Z*,*E*-iododienamide and a *Z*,*E*-iododienenitrile that, subjected to palladium-catalyzed cross-coupling reactions with a variety of terminal alkynes, led directly to the title compounds.

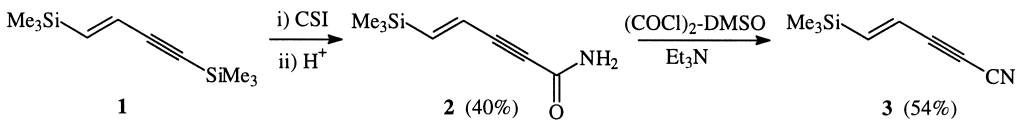
1. Introduction

In our previous studies on the synthesis of stereodefined polyenes[1] we have devised new methodologies for the synthesis of a series of natural compounds[2–7]with a conjugated polyunsaturated structure, starting from unsaturated *bis*-silyl derivatives. As part of our studies on the development of novel approaches to these polyunsaturated systems, we now report an efficient and convenient synthesis of a variety of amides and nitriles with a conjugated and branched dienyne structure, which can be successfully elaborated for the construction of the above natural compounds.

Previously,[8] using our methodology, we devised the synthesis of a monosilylated amide **2** and nitrile **3**, starting from an easily available *bis*-silylated precursor **1**[9] (Scheme 1).

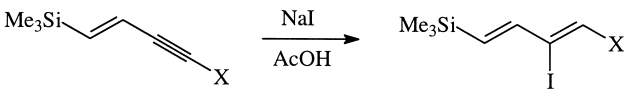
Both compounds **2** and **3** have now been further elaborated. Indeed, several years ago the nucleophilic regio- and stereospecific hydrohalogenation reaction of 2-propynoic acid and its derivatives with lithium halides in AcOH was reported, affording (*Z*)-3-halopropenoic acids.[10] More recently[11] the same hydrohalogenation reaction was performed with NaI in AcOH on trifluoromethyl alkynoic esters, leading regio- and stereoselectively to (*Z*)-3-haloalkenoic esters. Thus, when we applied this procedure to our substrates, we found that the reaction of compound **2** and compound **3** with NaI in AcOH led, respectively, to the iododienamide **4** and to the iododienenitrile **5** (Scheme 2).

This result allowed us to extend the synthetic utility of these iodo-derivatives, and we started to perform the synthesis of a series of amides and nitriles with a conjugated and branched dienyne structure. Such highly unsaturated compounds represent useful intermediates in organic synthesis, and only a few examples of branched dienynes have been reported.[12–16]



1 **2** (40%) **3** (54%)

Scheme 1.



2 X = $CONH_2$
3 X = CN

4 X = $CONH_2$ (54%)
5 X = CN (89%)

Scheme 2.

Keywords: silicons and compounds; dienynes; amides; nitriles.

* Corresponding author. Tel.: +39-80-5442075; fax: +39-80-5442129; e-mail: fianda@chimica.uniba.it

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2. Results and discussion

When the *E*-amide **2** was subjected to the addition reaction with NaI in AcOH the iododienamide **4** was obtained as a mixture of stereoisomers (*Z*,*E*/*E*,*E*=70/30) (Scheme 3). Both the *Z*,*E*- and *E*,*E*-stereoisomers were easily separated by column chromatography, and the assignment of the configuration was performed by ^{1}H NMR spectroscopy. Indeed, the chemical shift of the single olefinic proton of the *Z*,*E*-isomer (δ=6.72) was higher than the chemical shift of the olefinic proton of the *E*,*E*-isomer (δ=6.59), in accordance with those calculated by using the substituent shielding constants.[17]

On the contrary, the *E*-nitrile **3** reacted with NaI in a stereoselective manner, leading only to the *Z*,*E* stereoisomer **5** (*Z*,*E*≥98%) (Scheme 4).

Both compounds were then subjected to a series of palladium-catalyzed cross-coupling reactions[18] with terminal alkynes **6** according to Scheme 5.

The overall results are reported in Table 1. Several terminal alkynes **6** bearing different R groups (alkyl, aryl, 2-pyridyl) were used (entries 1–9). All reactions proceeded in good yields (61–84%) and with high stereoselectivity. In all the amides **7**–**12**, we evaluated the stereoselectivity in the range of 95–98% by means of ^{1}H NMR analysis of the crude reaction products. It is worth noting that the same crude samples analyzed by gas chromatography revealed the presence of a discrete amount of the other stereoisomer, certainly due to an isomerization occurring during this type of analysis. On the contrary, when analysing the nitriles **13**–**15**, the GC analyses were consistent with the ^{1}H NMR analyses of the reaction products, and the stereoselectivity was evaluated in the range of 92–98%.

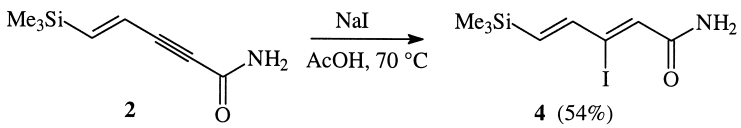
In conclusion, the procedure described here appears to be a useful route to stereodefined amides and nitriles with a branched and conjugated dienyne structure, starting from easily available precursors. Moreover, for the mild reaction conditions and the simplicity of the operations involved the methodology is very promising.

3. Experimental

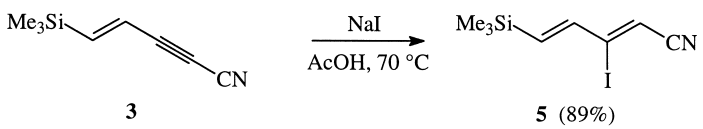
Macherey–Nagel silica gel (60, particle size 0.040–0.063 mm) for column chromatography and Macherey–Nagel aluminum sheets with silica gel 60 F_{254} for TLC were used. GC/mass-spectrometry analysis was performed on a Shimadzu GCMS-QP5000 gas chromatograph-mass spectrometer equipped with a MDN-1 capillary column (methylsilicone, 30 m×0.25 mm id). IR spectra were recorded on a Perkin–Elmer FT-IR 1710 spectrometer. ^{1}H NMR spectra were recorded in deuterochloroform on a Bruker AM 500 spectrometer at 500 MHz. ^{13}C NMR spectra were recorded in deuterochloroform on a Bruker AM 500 spectrometer at 125.7 MHz. Elemental analyses were recorded on a Carlo Erba EA 1108 elemental analyzer. Acetonitrile was distilled over molecular sieves. Melting points (uncorrected) were determined on an Electrothermal 9100 instrument.

3.1. Synthesis of compounds 4 and 5

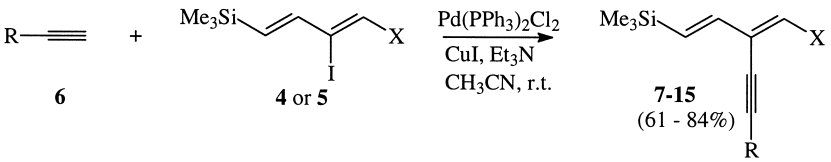
3.1.1. (2*Z*,4*E*)-3-Iodo-5-trimethylsilyl-2,4-pentadienamide (4). In a tightly stoppered flask were introduced compound **2** (1.01 g, 6.03 mmol), NaI (4.53 g, 30.16 mmol) and acetic acid (20 mL), then the resulting mixture was stirred at 70°C. After reaction completion (24 h), the mixture was quenched with water (100 mL), neutralized with solid K_2CO_3 and extracted with ethyl acetate (3×100 mL). The organic extracts were washed with a 10% aqueous solution of sodium thiosulfate (100 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum.



Scheme 3.

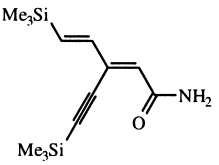
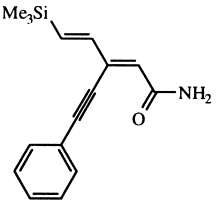
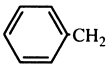
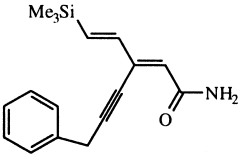
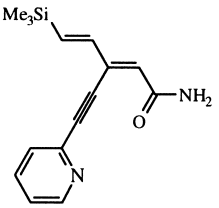
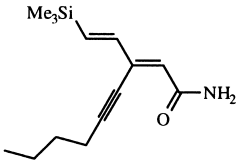
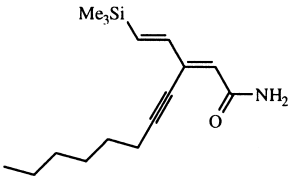
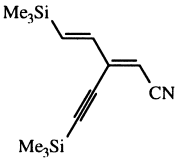
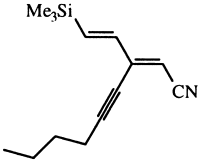
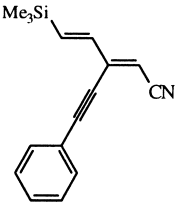


Scheme 4.



Scheme 5.

Table 1. Synthesis of conjugated dienynes

Entry	R	**4**,**5**	Products **7**–**15**		Yield (%)
1	Me_3Si	**4**		**7**	82
2		**4**		**8**	80
3		**4**		**9**	66
4		**4**		**10**	70
5	$CH_3(CH_2)_3$	**4**		**11**	84
6	$CH_3(CH_2)_5$	**4**		**12**	68
7	Me_3Si	**5**		**13**	61
8	$CH_3(CH_2)_3$	**5**		**14**	67
9		**5**		**15**	63

The mixture of stereoisomers (*Z*,*E*/*E*,*E*=70/30) was separated by column chromatography (50% ethyl acetate/petroleum ether) to give title compound **4** with a *Z*,*E* configuration, (0.97 g, 54% yield). After washing with cold petroleum ether, it obtained as a white solid (mp 116–117°C). [Found: C, 32.48; H, 4.79; N, 4.73. $C_8H_{14}INOSi$ requires C, 32.55; H, 4.78; N, 4.75%]; ν_{max} (KBr) 3376, 3193, 2954, 1650, 1616, 1588, 1555, 1391, 1307, 1248, 1205, 1058, 980, 865, 839 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.18 (1H, d, *J*=17.5 Hz), 6.72 (1H, s), 6.34 (1H, d, *J*=17.5 Hz), 6.06 (1H, br. s), 5.74 (1H, br. s), 0.12 (9H, s); δ_C (125.7 MHz, $CDCl_3$) 166.3, 149.6, 139.7, 132.0, 124.2, −1.3; MS *m*/*z* 280 (M^+−15, 2), 262 (2), 222 (63), 206 (6), 185 (12), 168 (91), 152 (10), 127 (7), 109 (12), 95 (41), 83 (77), 79 (21), 75 (70), 73 (100), 59 (65), 53 (26), 45 (60), 44 (67), 43 (62%).

Spectral data of the *E*,*E*-isomer *(2E,4E)-3-iodo-5-trimethylsilyl-2,4-pentadienamide*. ν_{max} (KBr) 3459, 3381, 3319, 3189, 2952, 1657, 1629, 1588, 1248, 970, 865, 838 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 6.81 (1H, br. s), 6.59 (1H, s), 6.43 (1H, d, *J*=17.5 Hz), 6.41 (1H, br. s), 5.79 (1H, d, *J*=17.5 Hz), 0.09 (9H, s); δ_C (125.7 MHz, $CDCl_3$) 167.6, 145.2, 144.4, 130.6, 115.3, −1.3; MS *m*/*z* 295 (M^+, 4), 280 (13), 222 (46), 185 (18), 168 (75), 152 (12), 127 (10), 109 (24), 99 (10), 83 (39), 75 (56), 74 (62), 73 (88), 59 (93), 45 (60), 44 (100), 43 (73%).

3.1.2. (2*Z*,4*E*)-3-Iodo-5-trimethylsilyl-2,4-pentadienenitrile (5). In a tightly stoppered flask were introduced compound **3** (0.53 g, 3.55 mmol), NaI (2.66 g, 17.75 mmol) and acetic acid (10 mL), then the resulting mixture was stirred at 70°C. After reaction completion (24 h), the mixture was quenched with water (30 mL), neutralized with solid K_2CO_3 and extracted with ethyl acetate (3×50 mL). The organic extracts were washed with a 10% aqueous solution of sodium thiosulfate (50 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated at reduced pressure and the residue was isolated by filtration on a florisil column (5% ethyl acetate/petroleum ether) leading to the title compound **5** (0.876 g, 89% yield). The residual solid was crystallized from petroleum ether (pale yellow solid, mp 56–57°C). [Found: C, 34.61; H, 4.33; N, 5.01. $C_8H_{12}INSi$ requires C, 34.67; H, 4.36; N, 5.05%]; ν_{max} (KBr) 3017, 2950, 2895, 2210, 1549, 1413, 1245, 1191, 1118, 963, 844, 781 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 6.48 (1H, d, *J*=17.2 Hz), 6.29 (1H, s), 5.95 (1H, d, *J*=17.2 Hz), 0.13 (9H, s); δ_C (125.7 MHz, $CDCl_3$) 151.1, 142.2, 129.0, 118.7, 109.6, −1.5; MS *m*/*z* 262 (M^+−15, 24), 196 (5), 185 (69), 150 (58), 123 (20), 94 (16), 84 (21), 73 (28), 67 (16), 66 (31), 59 (76), 58 (22), 45 (45), 44 (14), 43 (100%).

3.2. General procedure for the synthesis of products 7–15

A CH_3CN solution (2 mL) of alkyne (0.51–0.54 mmol) was added at room temperature, under nitrogen, to a stirred mixture of compound **4** (0.34 mmol) or compound **5** (0.36 mmol), Et_3N (10.17–10.35 mmol), $Pd(PPh_3)_2Cl_2$ (2 mol%) and CuI (4 mol%) in CH_3CN (1 mL). After reaction completion (1 h), the mixture was quenched with a saturated aqueous solution of NH_4Cl (10 mL), and extracted with ethyl acetate (3×20 mL). The organic extracts were washed with water (3×10 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The compounds **7**–**15** were purified by column chromatography and/or by crystallization.

3.2.1. (*Z*)-3-[(*E*)-2-Trimethylsilylethenyl)]-5-trimethylsilyl-2-penten-4-ynamide (7). Compound **7** was prepared from **4** (0.10 g, 0.34 mmol) in accordance with general procedure. Column chromatography (40% ethyl acetate/petroleum ether) afforded 0.074 g of **7** (82% yield). The residue was cristallyzed from petroleum ether giving white crystals of **7** (mp 130–132°C). [Found: C, 58.75; H, 8.78; N, 5.25. $C_{13}H_{23}NOSi_2$ requires C, 58.81; H, 8.73; N, 5.28%]; ν_{max} (KBr) 3450, 3303, 3192, 2957, 2154, 1659, 1599, 1563, 1327, 1250, 997, 867, 843 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.84 (1H, d, *J*=18.7 Hz), 6.67 (1H, d, *J*=18.7 Hz), 6.06 (1H, s), 5.83 (1H, br. s), 5.56 (1H, br. s), 0.21 (9H, s), 0.11 (9H, s); δ_C (125.7 MHz, $CDCl_3$) 167.1, 142.1, 137.1, 135.4, 124.7, 102.1, 100.2, 0.0, −1.5; MS *m*/*z* 265 (M^+, 7), 250 (10), 192 (100), 177 (4), 176 (5), 160 (4), 147 (5), 97 (5), 83 (8), 75 (26), 74 (31), 73 (70), 59 (11), 45 (50), 44 (15), 43 (22%).

3.2.2. (*Z*)-3-[(*E*)-2-Trimethylsilylethenyl)]-5-phenyl-2-penten-4-ynamide (8). Compound **8** was prepared from **4** (0.10 g, 0.34 mmol) in accordance with general procedure. Column chromatography (30% petroleum ether/ethyl acetate) led to **8** (0.073 g, 80% yield) that was crystallized from petroleum ether (white solid, mp 121–122°C). [Found: C, 71.25; H, 7.15; N, 5.18. $C_{16}H_{19}NOSi$ requires C, 71.33; H, 7.11; N, 5.20%]; ν_{max} (KBr) 3381, 3192, 3053, 2954, 2200, 1650, 1619, 1598, 1556, 1391, 1343, 1248, 997, 864, 841 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.96 (1H, d, *J*=18.7 Hz), 7.56–7.45 (2H, m), 7.38–7.29 (3H, m), 6.78 (1H, d, *J*=18.7 Hz), 6.14 (1H, s), 5.82 (1H, br. s), 5.68 (1H, br. s), 0.14 (9H, s); δ_C (125.7 MHz, $CDCl_3$) 167.3, 141.9, 137.4, 135.7, 131.8, 128.9, 128.4, 124.1, 122.4, 94.4, 86.8, −1.4; MS *m*/*z* 269 (M^+, 5), 268 (3), 254 (14), 196 (100), 180 (11), 167 (5), 152 (6), 141 (5), 128 (11), 126 (7), 75 (22), 74 (35), 73 (58), 59 (11), 45 (47), 44 (27), 43 (35%).

3.2.3. (*Z*)-3-[(*E*)-2-Trimethylsilylethenyl)]-6-phenyl-2-exen-4-ynamide (9). Compound **9** was prepared from **4** (0.10 g, 0.34 mmol) in accordance with general procedure and isolated by column chromatography (40% ethyl acetate/petroleum ether) obtaining 0.063 g of **9** (66% yield). The residue was crystallized from petroleum ether (white solid, mp 73–75°C). [Found: C, 72.01; H, 7.40; N, 4.90. $C_{17}H_{21}NOSi$ requires C, 72.04; H, 7.47; N, 4.94%]; ν_{max} (KBr) 3376, 3201, 2953, 1664, 1620, 1595, 1562, 1401, 1330, 1245, 989, 865, 841 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.90 (1H, d, *J*=18.7 Hz), 7.38–7.20 (5H, m), 6.72 (1H, *J*=18.7 Hz), 6.03 (1H, s), 5.82 (1H, br. s), 5.57 (1H, br s), 3.82 (2H, s), 0.12 (9H, s); δ_C (125.7 MHz, $CDCl_3$) 167.4, 141.8, 137.7, 136.1, 136.0, 128.6, 127.9, 126.8, 123.8, 93.2, 80.3, 25.7, −1.5; MS *m*/*z* 283 (M^+, 3), 282 (3), 268 (6), 210 (54), 194 (22), 192 (100), 165 (23), 152 (10), 139 (6), 128 (7), 115 (9), 91 (11), 77 (7), 75 (40), 74 (45), 73 (91), 59 (19), 45 (60), 44 (29), 43 (34%).

3.2.4. (*Z*)-3-[(*E*)-2-Trimethylsilylethenyl)]-5-(2-pyridyl)-2-penten-4-ynamide (10). Compound **10** was prepared from **4** (0.10 g, 0.34 mmol) in accordance with general

procedure and isolated by column chromatography (20% petroleum ether/ethyl acetate) giving 0.064 g of **10** (70% yield). By crystallization from petroleum ether white crystals of **10** were obtained (mp 112–114°C). [Found: C, 66.55; H, 6.75; N, 10.43. $C_{15}H_{18}N_2OSi$ requires C, 66.63; H, 6.71; N, 10.36%]; ν_{max} (KBr) 3291, 3127, 2954, 1678, 1639, 1585, 1561, 1464, 1386, 1246, 996, 865, 843 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 8.58 (1H, d, J=4.7 Hz), 7.93 (1H, d, J=18.7 Hz), 7.66 (1H, t, J=7.6 Hz), 7.48 (1H, d, J=7.6 Hz), 7.24 (1H, dd, J=7.6, 4.7 Hz), 6.77 (1H, d, J=18.7 Hz), 6.26 (1H, s), 6.21 (1H, br. s), 6.01 (1H, br. s), 0.11 (9H, s); δ_C (125.7 MHz, $CDCl_3$) 167.1, 150.0, 142.6, 142.0, 136.9, 136.3, 134.6, 127.6, 125.9, 123.3, 92.6, 86.5, −1.5; MS *m/z* 270 (M^+, 27), 255 (25), 237 (22), 226 (38), 197 (100), 181 (22), 170 (9), 169 (12), 168 (10), 128 (13), 106 (11), 83 (12), 78 (37), 75 (51), 74 (51), 73 (89), 59 (25), 55 (15), 53 (21), 52 (11), 51 (28), 45 (93), 44 (35), 43 (54%).

3.2.5. (*Z*)-3-[(*E*)-2-Trimethylsilylethenyl)]-2-nonen-4-ynamide (11). Compound **11** was prepared from **4** (0.10 g, 0.339 mmol) in accordance with general procedure. Purification by column chromatography (40% ethyl acetate/petroleum ether) led to compound **11** (0.071 g, 84% yield) as a pale yellow solid (mp 61–64°C). [Found: C, 67.41; H, 9.35; N, 5.55. $C_{14}H_{23}NOSi$ requires C, 67.42; H, 9.29; N, 5.62%]; ν_{max} (KBr) 3376, 3201, 2958, 2932, 2233, 1661, 1620, 1596, 1561, 1392, 1335, 1246, 989, 865, 840 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.86 (1H, d, J=18.7 Hz), 6.67 (1H, d, J=18.7 Hz), 6.00 (1H, br. s), 5.97 (1H, s), 5.66 (1H, br. s), 2.37 (2H, t, J=7.0 Hz), 1.58–1.49 (2H, m), 1.48–1.36 (2H, m), 0.91 (3H, t, J=7.4 Hz), 0.09 (9H, s); δ_C (125.7 MHz, $CDCl_3$) 167.7, 141.3, 137.9, 136.3, 123.5, 96.3, 78.2, 30.5, 21.9, 19.1, 13.5, −1.5; MS *m/z* 249 (M^+, <1), 234 (5), 207 (8), 192 (8), 176 (100), 160 (6), 134 (5), 133 (5), 131 (5), 118 (14), 91 (5), 75 (23), 74 (24), 73 (43), 59 (12), 45 (33), 44 (17), 43 (20%).

3.2.6. (*Z*)-3-[(*E*)-2-Trimethylsilylethenyl)]-2-undecen-4-ynamide (12). Compound **12** was obtained from **4** (0.15 g, 0.51 mmol) in accordance with general procedure. Purification by column chromatography (40% ethyl acetate/petroleum ether) afforded 0.096 g of **12**, (68% yield) as a pale yellow solid (mp 44–47°C). [Found: C, 69.11; H, 9.75; N, 5.00. $C_{16}H_{27}NOSi$ requires C, 69.26; H, 9.81; N, 5.05%]; ν_{max} (KBr) 3383, 3190, 2955, 2930, 2856, 2229, 1644, 1595, 1560, 1395, 1335, 1246, 1002, 867, 843 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.86 (1H, d, J=18.7 Hz), 6.64 (1H, d, J=18.7 Hz), 6.10 (1H, br. s), 5.97 (1H, s), 5.71 (1H, br. s), 2.36 (2H, t, J=7.0 Hz), 1.58–1.50 (2H, m), 1.44–1.36 (2H, m), 1.33–1.22 (4H, m), 0.86 (3H, t, J=6.9 Hz), 0.09 (9H, s); δ_C (125.7 MHz, $CDCl_3$) 167.7, 141.2, 137.9, 136.2, 123.6, 96.3, 78.2, 31.2, 28.5, 28.4, 22.5, 19.4, 14.0, −1.5; MS *m/z* 277 (M^+, <1), 262 (5), 220 (3), 207 (10), 204 (100), 192 (9), 148 (5), 134 (6), 133 (7), 118 (25), 106 (5), 105 (5), 91 (6), 75 (28), 74 (33), 73 (70), 59 (20), 45 (30), 44 (14), 43 (21%).

3.2.7. (*Z*)-3-[(*E*)-2-Trimethylsilylethenyl)]-5-trimethylsilyl-2-penten-4-ynenitrile (13). Compound **13** was prepared from **5** (0.10 g, 0.36 mmol) in accordance with general procedure. Purification by column chromatography (5% ethyl acetate/petroleum ether) afforded 0.055 g of **13** (61% yield) as a pale yellow oil. [Found: C, 63.15; H, 8.60; N, 5.80. $C_{13}H_{21}NSi_2$ requires C, 63.09; H, 8.55; N, 5.66%]; ν_{max} (neat) 3042, 2956, 2900, 2214, 2155, 1553, 1251, 1202, 982, 892, 872, 839 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 6.69 (1H, d, J=18.5 Hz), 6.43 (1H, d, J=18.5 Hz), 5.48 (1H, s), 0.26 (9H, s), 0.11 (9H, s); δ_C (125.7 MHz, $CDCl_3$) 144.3, 142.5, 139.2, 116.9, 109.1, 103.5, 97.4, −0.4, −1.7; MS *m/z* 247 (M^+, 6), 246 (10), 232 (40), 216 (5), 205 (6), 174 (7), 155 (9), 148 (10), 133 (14), 109 (16), 94 (7), 83 (10), 73 (100), 59 (34), 45 (71), 44 (8), 43 (45%).

3.2.8. (*Z*)-3-[(*E*)-2-Trimethylsilylethenyl)]-2-nonen-4-ynenitrile (14). Compound **14** was prepared from **5** (0.10 g, 0.36 mmol) in accordance with general procedure. Purification by column chromatography (3% ethyl acetate/petroleum ether) gave compound **14** (0.056 g, 67% yield) as a pale yellow oil. [Found: C, 72.49; H, 9.07; N, 6.00. $C_{14}H_{21}NSi$ requires C, 72.66; H, 9.15; N, 6.05%]; ν_{max} (neat) 3044, 2958, 2933, 2873, 2210, 1554, 1461, 1450, 1428, 1250, 1205, 982, 867, 838 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 6.67 (1H, d, J=18.3 Hz), 6.44 (1H, d, J=18.3 Hz), 5.41 (1H, s), 2.49 (2H, t, J=7.0 Hz), 1.65–1.57 (2H, m), 1.52–1.43 (2H, m), 0.93 (3H, t, J=7.4 Hz), 0.11 (9H, s); δ_C (125.7 MHz, $CDCl_3$) 143.6, 143.4, 140.0, 117.4, 104.7, 102.0, 74.5, 30.3, 21.9, 19.4, 13.5, −1.7; MS *m/z* 231 (M^+, 6), 216 (20), 202 (8), 189 (15), 174 (13), 147 (12), 131 (7), 105 (7), 84 (10), 83 (10), 73 (39), 59 (100), 45 (42), 44 (8), 43 (47%).

3.2.9. (*Z*)-3-[(*E*)-2-Trimethylsilylethenyl)]-5-phenyl-2-penten-4-ynenitrile (15). Compound **15** was prepared from **5** (0.10 g, 0.36 mmol) in accordance with general procedure. Purification by column chromatography (5% ethyl acetate/petroleum ether) led to compound **15** (0.057 g, 63% yield) as a yellowish oil. [Found: C, 76.39; H, 6.78; N, 5.60. $C_{16}H_{17}NSi$ requires C, 76.44; H, 6.82; N, 5.57%]; ν_{max} (neat) 3052, 2956, 2265, 2215, 1598, 1548, 1490, 1443, 1380, 1249, 1200, 1161, 981, 865, 837 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.62–7.58 (2H, m), 7.42–7.34 (3H, m), 6.81 (1H, d, J=18.5 Hz), 6.53 (1H, d, J=18.5 Hz), 5.53 (1H, s), 0.15 (9H, s); δ_C (125.7 MHz, $CDCl_3$) 144.1, 142.7, 139.4, 132.3, 129.7, 128.4, 121.5, 117.2, 102.5, 102.0, 82.8, −1.6; MS *m/z* 251 (M^+, 22), 250 (15), 236 (52), 220 (20), 209 (20), 167 (8), 165 (11), 159 (75), 152 (7), 118 (12), 105 (8), 84 (10), 73 (25), 59 (100), 45 (46), 44 (11), 43 (66%).

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References

1. For reviews, see: (a) Fiandanese, V. *Pure Appl. Chem.* **1990**, *62*, 1987–1992. (b) Fiandanese, V. Conjugated Polyunsaturated Silanes as Versatile Building Blocks in Organic Synthesis. In *Recent Research Developments in Organic Chemistry*. Pandalai, S. G., Ed.; Transworld Research Network: India, 1999; Vol. 3, pp 177–194.

2. Babudri, F.; Fiandanese, V.; Naso, F.; Punzi, A. *Synlett* **1992**, 221–223.
3. Babudri, F.; Fiandanese, V.; Naso, F.; Punzi, A. *Tetrahedron Lett.* **1994**, *35*, 2067–2070.
4. Babudri, F.; Fiandanese, V.; Marchese, G.; Punzi, A. *Synlett* **1995**, 817–818.
5. Babudri, F.; Fiandanese, V.; Hassan, O.; Punzi, A.; Naso, F. *Tetrahedron* **1998**, *54*, 4327–4336.
6. Babudri, F.; Fiandanese, V.; Marchese, G.; Punzi, A. *Tetrahedron* **2000**, *56*, 327–331.
7. Fiandanese, V.; Bottalico, D.; Marchese, G. *Tetrahedron* **2001**, *57*, 10213–10218.
8. De Girolamo, A.; Fiandanese, V.; Marchese, G.; Punzi, A. *Tetrahedron* **1998**, *54*, 12399–12408.
9. Fiandanese, V.; Marchese, G.; Punzi, A.; Ruggieri, G. *Tetrahedron Lett.* **1996**, *37*, 8455–8458.
10. Ma, S.; Lu, X.; Li, Z. *J. Org. Chem.* **1992**, *57*, 709–713.
11. Qing, F.-L.; Zhang, Y. *Tetrahedron Lett.* **1997**, *38*, 6729–6732.
12. Hoshi, M.; Arase, A. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2693–2700.
13. Karabelas, K.; Halberg, A. *J. Org. Chem.* **1988**, *53*, 4909–4914.
14. Bujard, M.; Ferri, F.; Alami, M. *Tetrahedron Lett.* **1998**, *39*, 4243–4246.
15. Uenishi, J.; Matsui, K. *Tetrahedron Lett.* **2001**, *42*, 4353–4355.
16. Maciagiewicz, I.; Dybowsky, P.; Skowrońska, A. *J. Organomet. Chem.* **2002**, *643–644*, 501–503.
17. Matter, U. E.; Pascual, C.; Pretsch, E.; Pross, A.; Simon, W.; Sternhell, S. *Tetrahedron* **1969**, *25*, 691–697.
18. Sonogashira, K. In *Metal Catalyzed Cross-coupling Reactions*. Stang, P. J., Diederich, F., Eds.; Wiley-VCH: Weinheim, 1998; pp 203–229.