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A straightforward synthesis of symmetrical polyendiynes by dimerization reactions of silyl derivatives

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

Dipartimento di Chimica, Università di Bari, Centro CNR di Studio sulle Metodologie Innovative di Sintesi Organiche, via Amendola 173, 70126 Bari, Italy

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Abstract

A straightforward synthesis of polyendiynes is described. The method is based upon a simple dimerization reaction of silylated enynes in the presence of copper salts. A variety of polyunsaturated compounds have been obtained in high yields and with high retention of configuration. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Silicon and compounds; Dimerization; Diynes

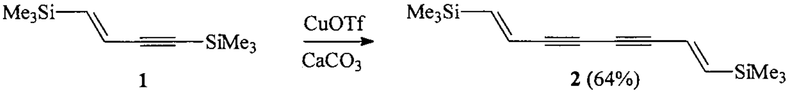
1. Introduction

In our previous studies dealing with the synthesis of stereo-defined conjugated polyenes [1–13] we reported a synthetic methodology based upon the chemoselective acylation of dienyl and trienyl bis-silylated systems [2]. The procedure was successfully applied to the synthesis of a series of natural compounds having a conjugated polyene structure [3–7].

Furthermore, during our investigation, we employed electrophiles different from acyl chlorides, in order to obtain several polyfunctional polyenyl compounds. In this respect, we found that (all *E*) 1,4-bis(trimethylsilyl)-1,3-butadiene and 1,6-bis(trimethylsilyl)-1,3,5-hexatriene react with PhSCl and PhSCOCl [8] affording conjugated dienyl and trienyl monosilylated sulfides and thioesters, compounds presenting both silicon and sulfur functionalities, which are synthetically useful.

In connection with this type of synthetic work, we considered of interest to investigate on the reactivity of other bis-silylated system, presenting different type of unsaturations, toward sulfur electrophiles.

Accordingly, we have reacted (*E*)-1,4-bis-(trimethylsilyl)-3-buten-1-yne [11,14] **1** with PhSSPh in the presence of $CaCO_3$ and CuOTf, as described in a recent work [15], with the aim of performing a chemoselective substitution, on the triple bond, of the trimethylsilyl group with the phenylthio group. Surprisingly, as a result we have not observed the formation of the expected monosilylated sulfide, but the formation of a different product, which, after appropriate analysis (GC/MS, ^{1}H-NMR) revealed to be the dimeric product **2**, according to the Eq. 1. It seemed evident that this reaction was not affected by the presence of PhSSPh. Indeed, repeating the same reaction without PhSSPh, we have obtained equally compound **2** in 64% yield.



(1)

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* Corresponding author.

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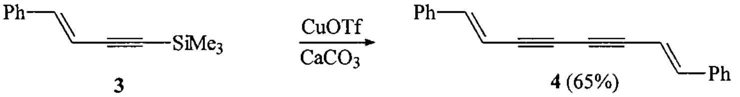
It is well known that symmetrical conjugated diynes are generally synthesized by oxidative dimerization of terminal acetylenes in the presence of a tertiary amine and copper salts, CuI [16], CuCl [17] or $Cu(OAc)_2$ [18], by self-coupling reactions of arylacetylenes in the presence of Pd(0)–CuI [19], or, more recently, by catalyzed Pd(II)–CuI self-coupling of terminal aryl- and alkylacetylenes [20].

Nevertheless, this direct dimerization of terminal silylated alkynes prompted us to investigate on the possibility of employing other silylated enynes, with the aim of synthesizing polyfunctional polyendiynes. Thus, when we subjected compound **3** to the dimerization reaction, we obtained the expected dimer **4** in 65% yield (Eq. 2):



(2)

In order to extend the synthetic utility of this methodology, we started to perform the synthesis of a series of mono-silylated enynes and now we wish to report their successfully utilization in the dimerization reaction.

2. Results and discussion

There are a number of methods available for the stereoselective synthesis of mono-silylated enynes, including coupling reactions of trimethylsilylacetylene with vinyl halides [21] in the presence of a Pd(II) catalyst, coupling reactions of trimethylsilylethynyl zinc halides [22,23], in the presence of a Pd(0) catalyst, with the appropriate vinyl halides or the Wittig reaction [24]. However, we have developed a direct and general synthethic approach to a wide range of silylated enynes.

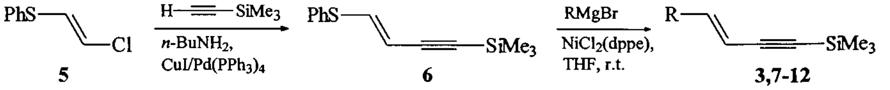
Our methodology is based upon the coupling reaction of the readily available (*E*)-1-chloro-2-phenylthioethene **5** [25] with trimethylsilylacetylene in the presence of Pd(0) [26] to afford (*E*)-4-phenylthio-1-trimethylsilyl-3-buten-1-yne **6** in 89% yield [10]. This compound represents the key intermediate for the synthesis of enynes. Indeed it is sufficient to react compound **6** with a series of Grignard reagents in the presence of $NiCl_2(dppe)$ as a catalyst to obtain the desired products (Scheme 1):

The experimental results are reported in Table 1. The mono-silylated enynes were obtained in high yields (entries 1–6, 75–96% yields) and with high retention of configuration. Indeed, for compounds **3**,**7**–**11** the observed *E*/*Z* ratio was ≥98%, as ascertained by GC analysis, whereas only the bis-silylated hexadienyne **12** (entry 7) was obtained in low yield (36%) and with a lower stereochemical purity (3*E*,5*E*/3*Z*,5*E* = 80/20) (^{1}H-NMR analysis).

Due to the availability of these substrates, we carried out the reactions of silylated enynes with CuOTf and in the presence of an excess of $CaCO_3$, in refluxing THF:dioxane (1:1), obtaining the corresponding polyendiynes in fair to good yields (Table 2). Indeed, with this procedure, we have been able to synthesize aryl polyenynes (entries 2–4, products **4**, **13** and **14**, 33–65% yields), alkyl derivatives (entries 5–7, products **15**–**17**, 46–52% yields, with product **17** presenting six unsaturations) and also a bis-silylated conjugated diendiyne (entry 1, product **2**, 64% yield), together with a bis-silylated tetraendiyne (entry 8, product **18**, 63% yield). All these dimers, apart from compound **18**, were obtained with high retention of configuration (≥ 95%, as ascertained by ^{1}H-NMR analysis). In the case of compound **18**, a predominant isomer was obtained, with all *E* configuration, together with other isomers, due to the low stereochemical purity of the starting dienyne **12**.

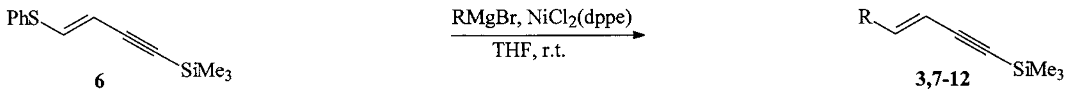
By inspection of the above results, it is clear that our procedure could be applied, in principle, to any type of functionalized silylated enyne, in spite of a few disappointing yields.

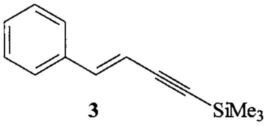
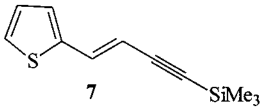
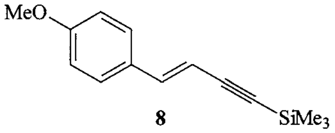
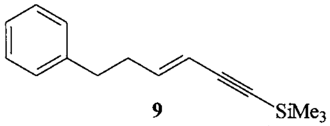
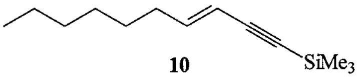
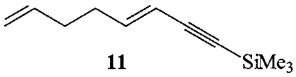
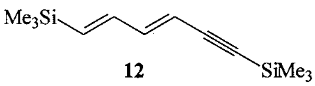
However, while this work was in progress, a recent study appeared [27] in which was realized the synthesis of polyynes, starting from aryl ethynyl and butadiynyl trimethylsilanes, by one-pot desilylation/dimerization procedure. Thus, in order to compare the two methods, we decided to repeat all the reactions in the conditions reported in the cited study. These new conditions required a different copper salt, $Cu(OAc)_2$, and K_2CO_3, both present in a significant excess (30–40 equivalents), and a different solvent (pyridine/methanol 1/1). We found that in all cases examined, (Table 3), including also the dimerization reaction of compound **6** (entry 3), the dimers were obtained with the same stereochemical purity and that there was an increase of the yields. However, it is noteworthy that our procedure is operationally simpler than the reported method, due to very mild reaction conditions. Indeed, it is not necessary a



Scheme 1.

Table 1
Synthesis of silylated enynes and dienynes



Entry	R	Products[a]	Yield (%)[b]
1	Phenyl	 **3**	85
2	2-Thienyl	 **7**	79
3	*p*-Methoxyphenyl	 **8**	86
4	2-Phenylethyl	 **9**	96
5	*n*-Hexyl	 **10**	79
6	3-Butenyl	 **11**	75
7	(*E*)-2-Trimethylsilylethenyl	 **12**	36

[a] The stereochemical purity of compounds **3** and **7**–**11** was ≥98% (*E*/*Z* ratio). For compounds **12** 3*E*, 5*E*/3*Z*, 5*E* = 80/20.

[b] Yields refer to products purified by flash chromatography; all compounds exhibited spectral data consistent with the assigned structure.

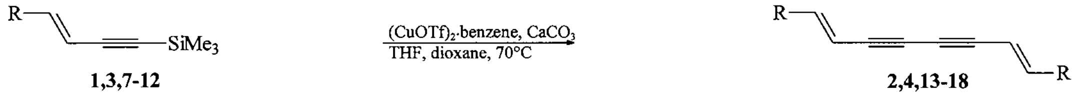
significant excess of reagent (only 0.6 equivalent of $(CuOTf)_2$benzene, instead of 40 equivalents of $Cu(OAc)_2$) and shorter reaction times (15 h, instead of 1–3 days) are required.

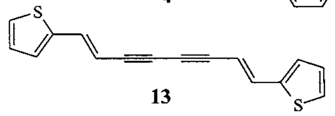
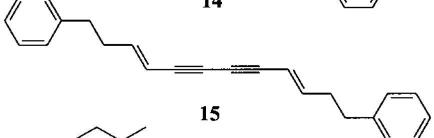
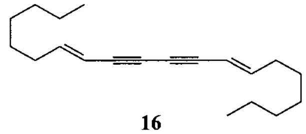
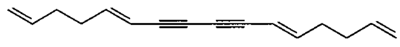
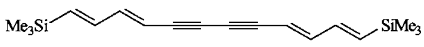
In conclusion, the procedure described here should provide various stereodefined conjugated polyendiynes with high stereospecificity. Moreover, the ready availability of functionalized enynes, together with the simplicity of the operations involved, are further attractive features of this methodology, which appears to be superior or competitive with the existing methods.

3. Experimental details

Merck silica gel (60, particle size 0.040–0.063 mm) for flash column chromatography and Merck plastic sheets with silica gel 60 F_{254} for TLC were used. GC analysis was performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a SE-30 (methylsilicone, 30 m × 0.25 mm id) capillary column. GC/mass-spectrometry analysis was performed on a Hewlett-Packard 5970A equipped with an HP-1 capillary column, 25 m, and HP MSD 5970B. ^1H-NMR

Table 2
Synthesis of polyendiynes by dimerization reactions with CuOTf



Entry	Compounds	Products	Yield (%)[a,b]
1	**1**	 **2**	64
2	**3**	 **4**	65
3	**7**	 **13**	55
4	**8**	 **14**	33
5	**9**	 **15**	52
6	**10**	 **16**	46
7	**11**	 **17**	50
8	**12**	 **18**	63

[a] Yields refer to products purified by flash chromatography; all compounds exhibited spectral data consistent with the assigned structure.
[b] Product **18** was obtained as a mixture of isomers (all *E* isomer was predominant).

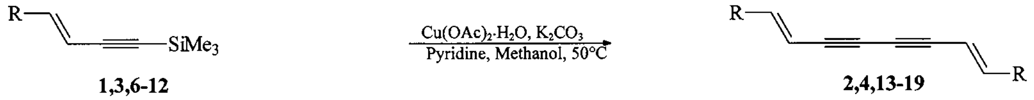
spectra were recorded in deuterochloroform on a Bruker AM 500 spectrometer at 500 MHz and on a Bruker AM 300 spectrometer at 300 MHz. Elemental analyses were recorded on a Carlo Erba EA1108 elemental analyzer. The products were purified by flash chromatography, by distillation with a Kugelrohr apparatus Büchi GKR-51 or by crystallization. Petroleum ether 40–70°C was used as eluent for chromatography. Melting points (uncorrected) were determined on a Reichert microscope.

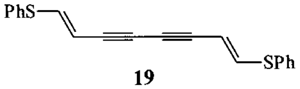
*3.1. Preparation of products **1** and **6***

*3.1.1. (3E)-1,4-Bis(trimethylsilyl)-3-buten-1-yne (**1**)*

A solution of ethynyltrimethylsilane (1.82 g, 18.53 mmol) in benzene (25 ml) was added at room temperature, under nitrogen, to a stirred mixture of (*E*)-1-bromo-2-trimethylsilylethene (3.32 g, 18.53 mmol), *n*-butylamine (2.03 g, 27.80 mmol), CuI (0.177 g, 0.93 mmol) and $Pd(PPh_3)_4$ (0.323 g, 0.28 mmol) in benzene (30 ml). The reaction mixture was stirred for 1 h, quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by distillation (Kugelrohr oven temperature 70°C/1 mmHg) affording 2.91 g (80% yield) of **1** as a colorless oil [11]. ^1H-NMR (500 MHz, $CDCl_3$): δ 0.05 (s, 9H), 0.16 (s, 9H), 5.94 (d, $J = 19.3$ Hz, 1H), 6.49 (d, $J = 19.3$ Hz, 1H) ppm. MS *m*/*e* 196 (M^+, 17), 181 (100), 155 (67), 141 (10), 123 (16), 122 (15), 97 (21), 83 (13), 73 (53), 70 (9).

Table 3
Synthesis of polyendiynes by dimerization reactions with $Cu(OAc)_2$



Entry	Compounds	Products	Yield (%)[a]
1	**1**	**2**	86
2	**3**	**4**	82
3	**6**	 **19**	71
4	**7**	**13**	97
5	**8**	**14**	67
6	**9**	**15**	98
7	**10**	**16**	74
8	**11**	**17**	95
9	**12**	**18**	94

[a] Yields refer to products purified by flash chromatography.

3.1.2. (3E)-4-Phenylthio-1-trimethylsilyl-3-buten-1-yne (6)

A solution of ethynyltrimethylsilane (1.42 g, 14.47 mmol) in benzene (20 ml) was added at room temperature, under nitrogen, to a mixture of (*E*)-1-phenylthio-2-chloroethene 5 (2.47 g, 14.47 mmol), *n*-butylamine (1.59 g, 21.70 mmol), CuI (0.137 g, 0.72 mmol) and $Pd(PPh_3)_4$ (0.254 g, 0.22 mmol) in benzene (30 ml). The reaction mixture was stirred for 3 h (reaction completion), quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by distillation (Kugelrohr oven temperature 175°C/1 mmHg) leading to compound **6** as a yellow oil (2.99 g, 89%). The spectral data are in according with those reported [10].

3.2. General procedure for the synthesis of mono-silylated enynes

A freshly prepared THF solution of Grignard reagent (three equivalents) was added at room temperature, under nitrogen, to a stirred THF solution of **6** (one equivalent) and $NiCl_2$ (dppe) (0.09 equivalents). After reaction completion (15 h), the mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic extracts were dried (Na_2SO_4) and concentrated. The crude material was purified by flash chromatography leading to compounds **3** [22], **7** [22], **8** [21], **9** [24], **10** [23], **11** and **12**. The spectral and physical data of unknown compounds are as follows.

3.2.1. (3E)-1-Trimethylsilyl-3,7-octadien-1-yne (**11**).

Compound **11** was prepared from **6** (0.5 g, 2.16 mmol) in accordance with general procedure. Purification by flash chromatography (petroleum ether) gave **11** (0.288 g, 75% yield) as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.16 (s, 9H), 2.10–2.22 (m, 4H), 4.95–5.04 (m, 2H), 5.51 (dt, $J = 15.9$, 1.6 Hz, 1H), 5.77 (ddt, $J = 17.0$, 10.3, 6.4 Hz, 1H), 6.19 (dt, $J = 15.9$, 6.7 Hz, 1H) ppm. MS *m/e* 178 (M^+, 8), 164 (17), 163 (100), 137 (11), 135 (11), 122 (26), 109 (32), 107 (20), 95 (16), 83 (25), 73 (38), 59 (98).

3.2.2. 1,6-Bis(trimethylsilyl)-3,5-hexadien-1-yne (**12**)

Compound **12**, as a mixture of two isomers, (3*E*, 5*E*/3*Z*, 5*E* = 80/20), was prepared from **6** (0.5 g, 2.15 mmol), in accordance with general procedure, and obtained as a colorless oil in 36% yield (0.172 g) after flash chromatography (petroleum ether).

(3*E*, 5*E*)-isomer-^{1}H-NMR data (500 MHz, $CDCl_3$): δ 0.06 (s, 9H), 0.17 (s, 9H), 5.60 (d, $J = 15.5$ Hz, 1H), 5.97 (dd, $J = 18.1$, 0.7 Hz, 1H), 6.48 (dd, $J = 18.1$, 10.4 Hz, 1H), 6.59 (ddd, $J = 15.5$, 10.4, 0.7 Hz, 1H) ppm. MS; *m/e* 222 (M^+, 14), 207 (34), 192 (8), 191 (39), 175 (6), 163 (6), 149 (53), 135 (19), 133 (18), 119 (10), 83 (16), 73 (100), 59 (38).

(3*Z*, 5*E*)-isomer-^{1}H-NMR data (500 MHz, $CDCl_3$): δ 0.09 (s, 9H), 0.20 (s, 9H), 5.44 (d, $J = 10.6$ Hz, 1H), 6.07 (d, $J = 18.5$ Hz, 1H), 6.39 (dt, $J = 10.6$, 0.9 Hz, 1H), 7.06 (ddd, $J = 18.5$, 10.6, 0.9 Hz, 1H). MS *m/e* 222 (M^+, 5), 207 (16), 192 (17), 191 (84), 175 (7), 163 (5), 149 (45), 135 (23), 133 (18), 119 (17), 83 (13), 73 (100), 59 (28).

3.3. Dimerization reactions of enynes with CuOTf: general procedure

A solution of the complex $(CF_3SO_2Cu)_2$benzene (0.6 equivalents) in THF/1,4-dioxane (1:1 v:v) was added at 70°C, under nitrogen, to a stirred suspension of $CaCO_3$ (four equivalents) and enynes in THF/1,4-dioxane (1:1 v/v). The mixture was reacted at the same temperature for 15 h, then quenched with NH_4Cl, extracted with ethyl acetate and dried (Na_2SO_4). After removal of the solvent, the residue was purified by flash chromatography leading to products **2**,**4** and **13**–**18**.

3.4. Dimerization reactions of enynes with $Cu(OAc)_2$: general procedure

A methanol solution of enynes was added to a stirred suspension of $Cu(OAc)_2H_2O$ (40 equivalents) and K_2CO_3 (30 equivalents) in pyridine/methanol (1:1 v/v) and the resulting mixture warmed at 50°C. After reaction completion (1–3 days), the usual workup afforded a residue which was purified by flash chromatography and led to compounds **2**, **4** and **13**–**19**.

3.4.1. (1E, 7E)-1,8-Bis(trimethylsilyl)-1,7-octadien-3,5-diyne (**2**)

Product **2** was obtained from **1** (0.2 g, 1.02 mmol) as a pale yellow oil, after purification by flash chromatography (petroleum ether) (0.108 g, 86% yield). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.07 (s, 18H), 5.98 (d, $J = 19.0$ Hz, 2H), 6.61 (d, $J = 19.0$ Hz, 2H) ppm. MS *m/e* 246 (M^+, 22), 231 (51), 205 (51), 179 (19), 173 (10), 147 (12), 145 (10), 131 (17), 123 (18), 83 (10), 73 (100), 59 (49). Elemental analysis: Found C, 67.98; H, 8.87. Calculated for $C_{14}H_{22}Si_2$: C, 68.21; H, 9.00.

3.4.2. (1E, 7E)-1,8-Diphenyl-1,7-octadien-3,5-diyne (**4**)

Product **4** was prepared from **3** (0.1 g, 0.5 mmol). Purification by flash chromatography (petroleum ether/AcOEt 9.5/0.5) afforded **4** as a pale yellow solid (m.p. 135–136°C; lit. 135–135.5°C) [28] (0.052 g, 82% yield). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.26 (d, $J = 16.0$ Hz, 2H), 7.09 (d, $J = 16.0$ Hz, 2H), 7.27–7.42 (m, 10H) ppm. MS *m/e* 254 (M^+, 59), 253 (67), 252 (100), 250 (24), 239 (8), 226 (9), 151 (8), 150 (11), 139 (31), 126 (27), 125 (11), 115 (21), 113 (15). Elemental analysis: Found C, 94.37; H, 5.48; calculated for $C_{20}H_{14}$: C, 94.45; H, 5.55.

3.4.3. (1E, 7E)-1,8-Bis(2-thienyl)-1,7-octadien-3,5-diyne (**13**)

Product **13** was prepared from **7** (0.1 g, 0.485 mmol) and purified by flash chromatography (petroleum ether/AcOEt 9.5/0.5) (0.063 g, 97% yield). The residual solid was washed with ethyl acetate giving yellow crystals of **13** (m.p. 150–151°C). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.04 (d, $J = 15.7$ Hz, 2H), 6.96–7.08 (m, 4H), 7.16 (d, $J = 15.7$ Hz, 2H), 7.20–7.25 (m, 2H) ppm. MS *m/e* 266 (M^+, 100), 265 (54), 264 (78), 232 (22), 221 (54), 208 (10), 189 (15), 132 (12), 114 (12), 110 (12), 108 (10), 69 (16). Elemental analysis: Found C, 71.83; H, 3.94; S, 23.80; calculated for $C_{16}H_{10}S_2$: C, 72.14; H, 3.79; S, 24.07.

3.4.4. (1E, 7E)-1,8-Bis(p-methoxyphenyl)-1,7-octadien-3,5-diyne (**14**)

Product **14** was prepared from **8** (0.1 g, 0.43 mmol) and purified by flash chromatography (petroleum ether/AcOEt 7/3) (0.046 g, 67% yield). The residual solid was washed with ethyl acetate giving yellow crystals of **14** (m.p. 164–165°C). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.80 (s, 6H), 6.09 (d, $J = 15.9$ Hz, 2H), 6.85 (br d, $J = 8.7$ Hz, 4H), 7.02 (d, $J = 15.9$ Hz, 2H), 7.32 (br d, $J = 8.7$ Hz, 4H) ppm. MS *m/e* 314 (M^+, 100), 299 (39), 284 (11), 283 (16), 271 (21), 268 (15), 256 (20), 255 (22), 240 (20), 239 (44), 228 (25), 227 (29), 226 (39), 169 (11), 145 (21), 119 (15), 113 (23), 101 (14). Elemental analysis: Found C, 83.89; H, 5.71; calculated for $C_{22}H_{18}O_2$: C, 84.05; H, 5.78.

3.4.5. *(3E, 9E)-1,12-Diphenyl-3,9-dodecadien-5,7-diyne* ***(15)***

Product **15** was prepared from **9** (0.1 g, 0.438 mmol). Purification by flash chromatography (petroleum ether/AcOEt 9.5/0.5) afforded 0.067 g of **15** (98% yield). Washing with petroleum ether gave white crystals of **15** (m.p. 90–91°C). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.41–2.49 (m, 4H), 2.71 (t, $J = 7.7$ Hz, 4H), 5.56 (d, $J = 15.6$ Hz, 2H), 6.31 (dt, $J = 15.6$, 7.1 Hz, 2H), 7.12–7.25 (m, 10H) ppm. MS *m/e* 310 (M^+, 10), 219 (9), 204 (18), 203 (27), 202 (10), 191 (15), 178 (15), 141 (13), 117 (13), 115 (14), 91 (100), 65 (16). Elemental analysis: Found C, 92.53; H, 6.98; calculated for $C_{24}H_{22}$: C, 92.85; H, 7.15.

3.4.6. *(7E, 13E)-7,13-eicosadien-9,11-diyne* ***(16)***

Product **16** was prepared from **10** (0.1 g, 0.48 mmol). Purification by flash chromatography (petroleum ether) gave 0.048 g of **16** as a pale yellow oil (74% yield).^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.86 (t, $J = 6.9$ Hz, 6H), 1.19–1.31 (m, 12H), 1.32–1.41 (m, 4H), 2.06–2.15 (m, 4H), 5.52 (d, $J = 15.6$ Hz, 2H), 6.27 (dt, $J = 15.6$, 7.2 Hz, 2H) ppm. MS *m/e* 270 (M^+, 98), 213 (11), 199 (21), 186 (22), 157 (24), 143 (49), 141 (27), 129 (89), 128 (78), 127 (30), 117 (29), 115 (100), 105 (19), 102 (76), 91 (48), 79 (23), 77 (23), 67 (22), 55 (30).

3.4.7. *(5E, 11E)-1,5,11,15-hexadecatetraen-7,9-diyne* ***(17)***

A total of 0.056 g of a pale yellow oil (95% yield) were obtained from **11** (0.1 g, 0.56 mmol), after purification by flash chromatography (petroleum ether).^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.10–2.17 (m, 4H), 2.18–2.25 (m, 4H), 4.95–5.04 (m, 4H), 5.55 (d, $J = 15.6$ Hz, 2H), 5.76 (ddt, $J = 17.0$, 10.3, 6.4 Hz, 2H), 6.27 (dt, $J = 15.6$, 7.0 Hz, 2H) ppm. MS *m/e* 210 (M^+, 22), 182 (11), 169 (65), 167 (21), 154 (33), 153 (82), 152 (32), 141 (62), 129 (25), 128 (98), 127 (49), 115 (100), 102 (44), 91 (41), 89 (30), 77 (26), 76 (21), 75 (31), 65 (23), 63 (34).

3.4.8. *1,12-Bis(trimethylsilyl)-1,3,9,11-dodecatetraen-5,7-diyne* ***(18)***

Product **18**, as a mixture of isomers, was prepared from **12** (0.15 g, 0.68 mmol). Purification by flash chromatography (petroleum ether) gave **18** as an orange oil (0.095 g, 94% yield). All *E*-isomer ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.08 (s, 18H), 5.68 (d, $J = 15.2$ Hz, 2H), 6.05 (d, $J = 18.2$ Hz, 2H), 6.52 (dd, $J = 18.2$, 10.5 Hz, 2H), 6.67 (dd, $J = 15.2$, 10.5 Hz, 2H) ppm. MS *m/e* 298 (M^+, 15), 210 (3), 209 (4), 195 (20), 165 (4), 73 (100), 59 (7), 45 (11).

3.4.9. *(1E, 7E)-1,8-Bis(phenylthio)-1,7-octadien-3,5-diyne* ***(19)***

Product **19** was prepared from **6** (0.551 g, 2.37 mmol). Purification by flash chromatography (petroleum ether/AcOEt 9/1) gave **19** as a yellow solid (0.27 g, 71% yield). Further crystallization from petroleum ether/ethyl acetate afforded yellow crystals of **19** (m.p. 73–74 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.55 (d, $J = 15.8$ Hz, 2H), 6.97 (d, $J = 15.8$ Hz, 2H), 7.28–7.45 (m, 10H) ppm.

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