



A Straightforward Route to Polyenylsilanes by Palladium- or Nickel-Catalyzed Cross-Coupling Reactions

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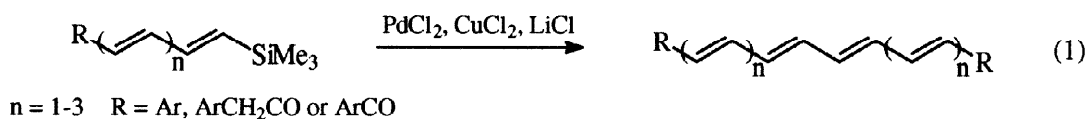
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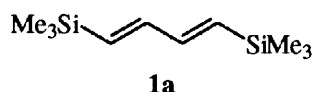
Abstract: An efficient conversion of bis-silylated dienes and trienes into polyenylsilanes by cross-coupling reactions is described. The aryl substituted polyenes are synthesized by *ipso*-borodesilylation with BCl_3 followed by Pd-catalyzed coupling reactions of the resulting boron derivative with aryl halides, whereas the synthesis of alkyl substituted polyenes requires the conversion of the boron intermediate into iodo-derivative and the subsequent coupling with alkyl Grignard reagents in the presence of a Ni(II) catalyst.

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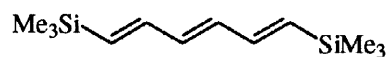
In the last few years work performed in these¹ and other laboratories² has shown the synthetic versatility of polyenylsilanes. Indeed, the synthesis of a variety of natural compounds presenting a backbone of conjugated double bonds (*e.g.* ostopanic acid,^{1b} parinaric acid,^{1c} leukotriene B₃,^{1b} SM-9064,^{1d} various dienyl amides^{1f}) has been made possible by using such a type of compounds as starting materials or intermediates. More recently, we have shown that polyenylsilanes can undergo an easy homocoupling reaction¹ⁱ (eq. 1) which, by doubling the number of double bonds in one step, permits to obtain polyenes of potential interest in the field of electroactive materials³ or materials with nonlinear optical (NLO) properties.⁴



With this background, we became interested in seeking new routes to polyenylsilanes and, therefore, we evaluated the possibility of operating a chemoselective substitution with an appropriate reagent of one of the trimethylsilyl groups of (1*E*,3*E*)-1,4-bis(trimethylsilyl)-1,3-butadiene **1a** and (1*E*,3*E*,5*E*)-1,6-bis(trimethylsilyl)-1,3,5-hexatriene **1b**.



1a



1b

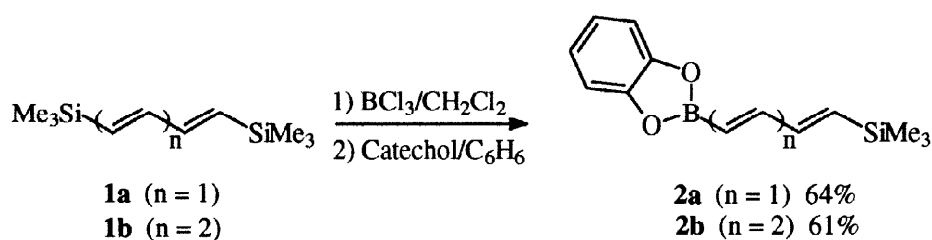
In principle, the above bis-silylated compounds could be transformed into a mono-silylated system by reaction with organometallic reagents in the presence of transition metals.⁵ However, it is worth noting that, until recently, alkenyl silicon compounds, if compared with other organometallics, have not been considered synthetically useful for transition metals-catalyzed cross-coupling reactions, with respect to generality, efficiency and selectivity. In particular, the major drawback of the trimethylsilyl derivatives has been their inability to undergo general carbon-carbon bond forming reactions, due to the extremely low polarity of the carbon-silicon bond. As a consequence, only some cases are reported in the literature, in which trimethylsilyl derivatives are coupled with aryl or vinyl halides.⁵ Examples of the failure of the process are also known,⁶ whereas the use of silicon groups containing atoms of higher electronegativity appear to be of more general scope.^{5,7}

We have recently overcome the above limitation, disclosing a novel and efficient method⁸ for a simple and rapid conversion of 1-alkenyl-trimethylsilanes into substituted alkenes, by *ipso*-borodesilylation with BCl₃ and subsequent palladium-catalyzed coupling reactions of the resulting haloborane with organic halides.

Now we wish to report our successful attempts to extend the novel methodology to bis-silylated systems, thus providing a new and general procedure for the synthesis of polyenyl derivatives.

With this aim, the silanes **1a,b** were subjected to reaction with boron trichloride in methylene chloride and we found that also for these conjugated systems an easy selective *ipso*-borodesilylation occurred, involving only one trimethylsilyl group. In the case of trienyl silane **1b** an extensive protodesilylation reaction was found to take place as a competing process. However, such a drawback was avoided by adding the boron trichloride to the solution of **1b** containing 2–4 equiv of sodium carbonate. Moreover, we found that the boronic esters **2a,b** could be obtained in good yields provided that the intermediate boron derivative was added to catechol in benzene⁹ at room temperature (Scheme 1).

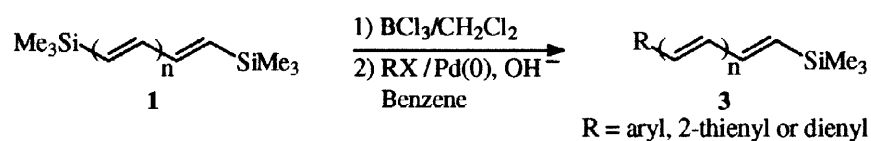
Scheme 1



It is noteworthy that polyunsaturated boronic esters are usually prepared by hydroboration of enynes with catecholborane.¹⁰ Therefore, our approach should represent an efficient and alternative choice for the synthesis of these derivatives, starting from readily accessible bis-silylated polyenes.

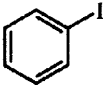
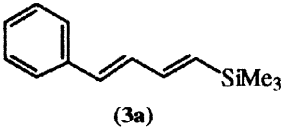
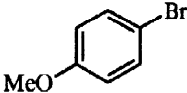
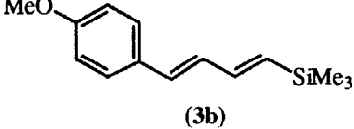
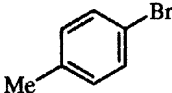
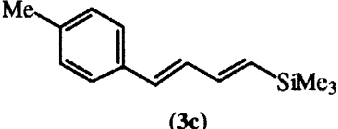
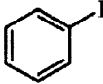
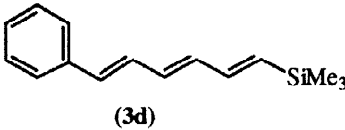
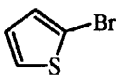
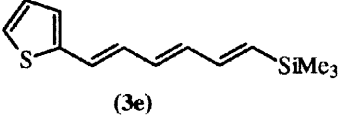

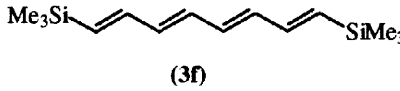
Obviously, the boronates could serve as useful starting materials for the Suzuki-Miyaura cross-coupling reaction.¹¹ However, we were able to set up a more simple cross-coupling procedure using directly the intermediate deriving from the transmetalation step, as depicted in Scheme 2.

Scheme 2



The representative results are reported in Table 1. Dienyl, trienyl and tetraenylsilanes were obtained in fair to good yields. In the case of the dienyl compound **1a**, after the transmetalation step, methylene chloride was evaporated and the intermediate boron derivative was dissolved in the new solvent (Table 1, entries 1-3). In the synthesis of the trienyl and tetraenyl systems (Table 1, entries 4-6), in order to obtain fair to good yields of the coupling product, it was found convenient to add 2-4 equiv of Na_2CO_3 to the solution of **1** before treating with BCl_3 . The intermediate resulting from the treatment with BCl_3 was then reacted with an aqueous solution of sodium carbonate and finally the cross-coupling step was performed in the usual conditions.

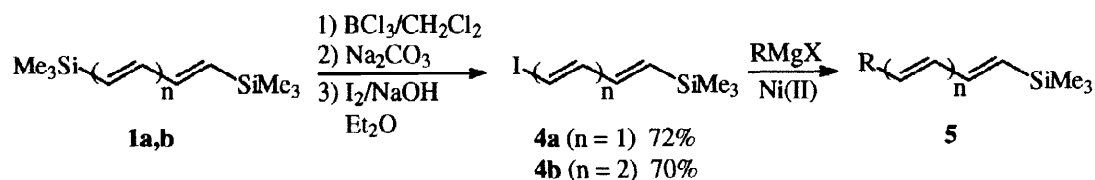
Table 1. Polyenyilsilanes by Suzuki-Miyaura Cross-Coupling Reactions.

Entry	Compound 1	Halide	Product 3	Yields ^a (%)
1	1a		 (3a)	98
2	1a		 (3b)	61
3	1a		 (3c)	73
4	1b ^{b,c}		 (3d)	45
5	1b ^{b,c}		 (3e)	38
6	1a ^{c,d}		 (3f)	70

^a Yields refer to isolated products; ^b BCl_3 was added to a solution of **1b** containing 2-4 equiv of Na_2CO_3 ; ^c The boron derivative was reacted with a 2 M aqueous solution of Na_2CO_3 ; ^d The coupling reaction was performed in toluene:MeOH (1:1) as solvent.

In view of the fact that alkyl halides having β -hydrogen atoms find a limited use in the Suzuki-Miyaura cross-coupling reactions,¹² the synthesis of alkyl substituted polyenes required a variation of our strategy, as shown in Scheme 3.

Scheme 3



Indeed, following the procedure reported for vinyl boronic acids,¹³ we found that a formal electrophilic substitution of one silyl group with iodine occurred leading to the (1*E*,3*E*)-iododerivative 4a^{1f} and to (1*E*,3*E*,5*E*)-4b, simply by reaction of the intermediate haloborane with a 2 M aqueous solution of Na₂CO₃ and treating an ethereal solution of the resulting boron derivative with iodine in the presence of NaOH. To complete the synthesis of alkyl polyenylsilanes, the iododerivatives were subjected to simple coupling reactions with Grignard reagents in the presence of a Ni(II) catalyst. Some representative examples are reported in Table 2.

Table 2. Conjugated Dienyl- and Trienyl-Silanes by Coupling Reactions with Grignard Reagents.

Iodide 4	R	Product 5	Yields ^a (%)
4a	Cy	 5a	47
4a	<i>n</i> -C ₁₀ H ₂₁	 5b	72
4b	<i>n</i> -C ₄ H ₉	 5c	70

^a Yields refer to purified products.

In conclusion, the procedure described here should provide a highly stereospecific route to a series of polyenyl silanes, (*e.g.* boronic esters, iododerivatives, alkyl and aryl substituted compounds), starting from the same readily available precursors. Moreover, taking also into account the simplicity of the operations involved, we believe that the present method compares favourably with alternative methodologies.¹⁴

EXPERIMENTAL

Merck silica gel (60, particle size 0.040–0.063 mm) for flash column chromatography and Merck plastic sheets with silica gel 60 F₂₅₄ 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 x 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 spectra were recorded in deuteriochloroform on a Bruker AM 500 spectrometer at 500 MHz and on a Varian XL 200 spectrometer at 200 MHz. The products were purified by flash chromatography or by distillation with a Kugelrohr apparatus Büchi GKR-51. In order to obtain reproducible results, it is recommended to store commercial (Aldrich) 1 M solutions of BCl₃ in methylene chloride under nitrogen in a cold room and over solid anhydrous Na₂CO₃.

Synthesis of Boronic Esters (2)

2-[(1*E*,3*E*)-4-trimethylsilyl-buta-1,3-dienyl]-1,3,2-benzodioxaborole (2a)

A 1 M methylene chloride solution of BCl₃ (1.7 mL, 1.7 mmol) was added dropwise, under a nitrogen atmosphere, to **1a** (0.20 g, 1.01 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 3 h. The solvent was then evaporated at reduced pressure and the crude product (a yellow oil), dissolved in benzene (5 mL), was added dropwise to a stirred suspension of catechol (0.11 g, 1.00 mmol) in benzene (10 mL) at room temperature. The reaction mixture was stirred until complete dissolution of catechol (1 h). The solvent was then removed at reduced pressure and the crude product was dissolved in hexane and filtered to eliminate traces (if any) of unreacted catechol. After evaporation of hexane 0.16 g (64% yield) of a colourless oil were obtained. (Kugelrohr distillation, oven temp. 125 °C, 10⁻² mbar). **2a**: ¹H-NMR (500 MHz): δ = 0.10 (s, 9H), 5.88 (d, *J* = 17.7 Hz, 1H), 6.24 (d, *J* = 18.3 Hz, 1H), 6.68 (dd, *J* = 10.0, 18.3 Hz, 1H), 7.04–7.10 (m, 2H), 7.20–7.25 (m, 2H), 7.32 (dd, *J* = 10.0, 17.7 Hz, 1H) ppm; MS *m/z* 244 (M⁺, 46), 229 (100), 170 (8), 166 (9), 161 (10), 144 (17), 137 (11), 109 (38), 95 (48), 73 (17), 59 (72), 45 (20), 43 (24).

2-[(1*E*,3*E*,5*E*)-6-trimethylsilyl-hexa-1,3,5-trienyl]-1,3,2-benzodioxaborole (2b)

Product **2b** was prepared starting from **1b** (0.22 g, 0.98 mmol), dissolved in 1.5 mL of methylene chloride containing anhydrous sodium carbonate (0.21 g, 1.98 mmol), and using 1 mL (1 mmol) of the BCl₃ solution. The reaction was carried out under a nitrogen atmosphere at -30 °C. After disappearance of the starting compound **1b** (GC, 0.5 h), the sodium carbonate was removed by filtration and the resulting solution added dropwise to a stirred suspension of catechol (0.11 g, 1.00 mmol) and anhydrous Na₂CO₃ (0.42 g, 3.96 mmol) in benzene (5 mL) under a nitrogen atmosphere at room temperature. After reaction completion (0.5 h) the solvent was removed at reduced pressure from the same reaction flask, operating under a nitrogen atmosphere. The usual workup led to 0.16 g (61% yield) of **2b**. (Kugelrohr distillation, oven temp. 175° C, 4.5 x 10⁻³ mbar). **2b**: ¹H-NMR (200 MHz): δ = 0.10 (s, 9H), 5.90 (d, *J* = 17.8 Hz, 1H), 6.08 (d, *J* = 17.5 Hz, 1H), 6.30–6.90 (m, 3H), 7.00–7.13 (m, 2H), 7.15–7.30 (m, 2H), 7.37 (dd, *J* = 9.6, 17.7 Hz, 1H) ppm; MS *m/z* 270

(M^+ , 87), 269 (25), 255 (56), 196 (23), 166 (34), 135 (21), 123 (15), 89 (33), 73 (64), 59 (100), 45 (16), 43 (16).

Aryl Substituted Polyenylsilanes (3)

(1*E*,3*E*)-1-phenyl-4-trimethylsilyl-1,3-butadiene (3a)¹⁴

A 1 M solution of BCl_3 in methylene chloride (1.7 mL, 1.7 mmol) was added dropwise and stirring to diene **1a** (0.20 g, 1.01 mmol) at 0 °C under a nitrogen atmosphere. The resulting mixture was stirred at the same temperature until the starting compound **1a** disappeared (GC, 3 h). The solvent was then evaporated under reduced pressure and the crude oil obtained was dissolved in benzene (10 mL). The resulting solution was added to a stirred solution of iodobenzene (0.21 g, 1.03 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.035 g, 0.03 mmol) in benzene (8 mL). After a few minutes, a 2 M solution of NaOH was added (1.0 mL, 2.0 mmol) and the resulting mixture was refluxed for 6 h. The mixture was then diluted with water and extracted with ethyl acetate. The organic extracts were dried over anhydrous sodium sulphate and concentrated. The product obtained was purified on a Florisil column (elution with petroleum ether) and, after evaporation of the solvent, 0.20 g of compound **3a** were obtained (98% yield). The spectral data were consistent with those reported.^{14b}

(1*E*,3*E*)-1-(4-methoxyphenyl)-4-trimethylsilyl-1,3-butadiene (3b)^{14c}

The synthesis of **3b** was performed following the procedure described for compound **3a**, starting from **1a** (0.20 g, 1.01 mmol) and a 1 M BCl_3 solution in methylene chloride (1.7 mL, 1.7 mmol). The coupling reaction was performed in 18 mL of benzene (in the dark), using 1-bromo-4-methoxybenzene (0.19 g, 1.02 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.035 g, 0.03 mmol) and 1.0 mL of a 2 M solution of NaOH (14 h reaction time). After the usual workup, the crude product was purified by percolation on a Florisil column (petroleum ether as eluent), followed by flash chromatography (elution with petroleum ether). 0.14 g of a white solid (m.p. 75–76.5 °C, from MeOH) were isolated (61% yield). **3b**: $^1\text{H-NMR}$ (500 MHz): δ = 0.10 (s, 9H), 3.80 (s, 3H), 5.91–5.98 (m, 1H), 6.49–6.57 (m, 1H), 6.62–6.70 (m, 2H), 6.83–6.90 (m, 2H), 7.31–7.38 (m, 2H) ppm; MS m/z 232 (M^+ , 74), 217 (48), 202 (50), 175 (23), 159 (46), 158 (42), 128 (37), 115 (28), 89 (46), 73 (64), 59 (100), 45 (18), 43 (18).

(1*E*,3*E*)-1-(4-methylphenyl)-4-trimethylsilyl-1,3-butadiene (3c)

The product **3c** was prepared by the same procedure described above, starting from **1a** (0.20 g, 1.01 mmol), a 1 M BCl_3 solution in CH_2Cl_2 (1.7 mL, 1.7 mmol), *p*-bromotoluene (0.17 g, 1.00 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.035 g, 0.03 mmol), and 1.0 mL of a 2 M NaOH solution (18 h reaction time for the coupling reaction). The crude product was purified by flash chromatography (elution with petroleum ether) to obtain 0.16 g (73% yield) of **3c**: $^1\text{H-NMR}$ (500 MHz): δ = 0.10 (s, 9H), , 2.33 (s, 3H), 5.96 (d, J = 17.7 Hz, 1H), 6.56 (d, J = 15.2 Hz, 1H), 6.67 (dd, J = 10.1, 17.8 Hz, 1H), 6.74 (dd, J = 10.1, 15.2 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H),

7.30 (d, $J = 8.0$ Hz, 2H) ppm; MS m/z 216 (M^+ , 31), 201 (22), 173 (11), 159 (22), 142 (62), 115 (9), 73 (52), 59 (100).

(1E,3E,5E)-1-phenyl-6-trimethylsilyl-1,3,5-hexatriene (3d)^{14b,15}

A 1 M solution of BCl_3 (0.9 mL, 0.9 mmol) was added dropwise to a stirred suspension of **1b** (0.20 g, 0.89 mmol) and anhydrous sodium carbonate (0.38 g, 3.58 mmol) in 2 mL of freshly distilled methylene chloride under a nitrogen atmosphere at -30°C . After disappearance of the starting product **1b** (0.5 h), as revealed by GC, the mixture was warmed to room temperature and 2.3 mL of a 2 M solution of sodium carbonate were slowly added. A solution of iodobenzene (0.18 g, 0.88 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.031 g, 0.027 mmol) in 10 mL of benzene was then added, followed by the addition of a 2 M NaOH solution (0.9 mL). The mixture was then refluxed for 12 h. After the usual workup and purification by flash chromatography, 0.09 g (45% yield) of a white solid (m.p. $85\text{--}88^\circ\text{C}$, lit.^{14b} $84\text{--}87^\circ\text{C}$) were isolated. (Kugelrohr distillation, oven temp. 175°C , 2.5×10^{-4} mbar). The spectral data were consistent with those reported.^{14b}

(1E,3E,5E)-1-(2-thienyl)-6-trimethylsilyl-1,3,5-hexatriene (3e)¹⁶

The procedure was identical to that described for **3d** starting from **1b** (0.30 g, 1.34 mmol) in the presence of anhydrous sodium carbonate (0.57 g, 5.38 mmol) in 3 mL of freshly distilled methylene chloride and using 1.35 mL of the 1 M solution of BCl_3 . The hydrolysis was performed with 3.5 mL of a 2 M aqueous solution of sodium carbonate. The coupling reaction with 2-bromothiophene (0.22 g, 1.35 mmol) required $\text{Pd}(\text{PPh}_3)_4$ as a catalyst (0.046 g, 0.04 mmol), 1.30 mL of a 2 M solution of NaOH and 15 mL of anhydrous benzene as a solvent (12 h reaction time). After the usual workup and purification by percolation on a Florisil column, 0.12 g of a yellow solid (m.p. $148\text{--}151^\circ\text{C}$) were isolated (38% yield). (Kugelrohr distillation, oven temp. 125°C , 3.0×10^{-4} mbar). **3e**: $^1\text{H-NMR}$ (500 MHz): $\delta = 0.09$ (s, 9H), 5.91 (d, $J = 18.3$ Hz, 1H), 6.28–6.33 (m, 2H), 6.57 (dd, $J = 9.5, 18.3$ Hz, 1H), 6.61 (dd, $J = 9.5, 15.3$ Hz, 1H), 6.69 (d, $J = 15.3$ Hz, 1H), 6.93–6.98 (m, 2H), 7.12–7.17 (m, 1H) ppm; MS m/z 234 (M^+ , 18), 160 (13), 141 (18), 73 (100), 59 (23), 45 (13), 43 (9).

(1E,3E,5E,7E)-1,8-bis-(trimethylsilyl)-1,3,5,7-octatetraene (3f)

The 1 M solution of BCl_3 (21.4 mL, 21.4 mmol) was added dropwise to diene **1a** (2.50 g, 12.59 mmol) dissolved in 56 mL of freshly distilled methylene chloride under a nitrogen atmosphere, at 0°C , and the mixture was stirred until disappearance of the starting product (GC, 3 h). The reaction mixture was then quenched with 33 mL of a 2 M solution of sodium carbonate and extracted with ethyl acetate. The organic extracts were dried over anhydrous sodium sulphate and concentrated to give 2.14 g of a white solid. The crude product and **4a** (2.55 g, 10.11 mmol) were dissolved in 468 mL of toluene/methanol 1/1 mixture and $\text{Pd}(\text{PPh}_3)_4$ (1.17 g, 1.01 mmol) was added. The mixture was stirred for a few minutes and, after adding dropwise 127 mL of a 2M solution of sodium carbonate, was refluxed for 1 h, then diluted with water and extracted with ethyl acetate. The organic extracts were washed with water and dried over anhydrous sodium sulphate. After evaporation of

the solvent at reduced pressure, the crude product was purified by percolation on Florisil column (petroleum ether as eluent) followed by distillation with a Kugelrohr apparatus (oven temp. 100 °C, 1 mbar). 2.21 g of compound **3f** were obtained (70% yield). **3f**: $^1\text{H-NMR}$ (200 MHz): δ = 0.10 (s, 18H), 5.90 (d, J = 18.1 Hz, 2H), 6.22–6.33 (m, 4H), 6.48–6.67 (m, 2H) ppm; MS m/z 250 (M^+ , 14), 162 (17), 161 (7), 147 (39), 74 (8), 73 (100), 59 (16), 45 (11).

Iododerivatives (4)

(1E,3E)-1-Iodo-4-trimethylsilyl-1,3-butadiene (4a)^{1f}

A 1 M methylene chloride solution of BCl_3 (1.70 mL, 1.70 mmol) was added dropwise to diene **1a** (0.20 g, 1.01 mmol) at 0 °C under a nitrogen atmosphere and the mixture was stirred for 3 h, then quenched with a 2 M aqueous solution of sodium carbonate (9.2 mmol) and extracted with ethyl acetate. The organic extracts were dried over anhydrous sodium sulphate and concentrated to give 0.17 g of a white solid. The crude product was dissolved in 5 mL of diethyl ether and a 3 M solution of NaOH (1.20 mL, 3.6 mmol) was added under stirring at 0 °C. The addition of the base was followed by the dropwise addition of a solution of iodine (0.60 g, 2.36 mmol) in diethyl ether (4 mL) at the same temperature. After reaction completion (0.5 h, TLC, GC analysis) the reaction mixture was quenched with a 10% aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ and extracted with ethyl acetate. The organic extracts were dried over anhydrous sodium sulphate and concentrated to give 0.18 g (72% yield) of a yellow oil (Kugelrohr distillation, oven temp. 75 °C, 1 mbar).^{1f} The spectral data were consistent with those previously reported.^{1f}

(1E,3E,5E)-1-Iodo-6-trimethylsilyl-1,3,5-hexatriene (4b)

Triene **1b** (0.75 g, 3.34 mmol), dissolved in 8 mL of methylene chloride containing anhydrous sodium carbonate (1.43 g, 13.49 mmol), was reacted with a 1 M solution of BCl_3 in the same solvent (3.4 mL, 3.4 mmol) at -30 °C. The reaction mixture was quenched with 15 mL of a 2 M solution of sodium carbonate, and the solid product, isolated by following the usual workup, was dissolved in 13 mL of diethyl ether. After cooling at 0 °C and treating with 3 M aqueous NaOH (3.8 mL, 11.4 mmol), a solution of iodine (0.86 g, 3.39 mmol) in 13 mL of diethyl ether was then added dropwise and slowly at 0 °C, in the dark. The reaction mixture was quenched with a 10% aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ and extracted with cold petroleum ether. The organic extracts were dried over anhydrous sodium sulphate and the solvent was removed at 0 °C under reduced pressure and in the dark. 0.65 g (70% yield) of **4b** were isolated. **4b**: $^1\text{H-NMR}$ (200 MHz): δ = 0.10 (s, 9H), 6.00 (d, J = 18.2 Hz, 1H), 6.08–6.29 (m, 2H), 6.34 (d, J = 14.5 Hz, 1H), 6.47 (dd, J = 9.3, 18.2 Hz, 1H), 7.04 (dd, J = 10.1, 14.5 Hz, 1H) ppm; MS m/z 278 (M^+ , 32), 263 (8), 185 (100), 151 (14), 123 (36), 73 (90), 59 (69), 58 (16), 45 (15), 43 (30).

Alkyl Substituted Polyenyilsilanes (5)**(1E,3E)-1-cyclohexyl-4-trimethylsilyl-1,3-butadiene (5a)**

Compound **4a** (0.18 g, 0.71 mmol) in 5 mL of freshly distilled THF was reacted at 0 °C with a 0.86 M solution of cyclohexylmagnesium bromide in THF (1.5 mL, 1.29 mmol) in the presence of NiCl₂(dppe) (0.013 g, 0.025 mmol). After reaction completion (2 h, GC), the mixture was quenched with saturated aqueous NH₄Cl and extracted with ethyl acetate. The organic extracts were dried over Na₂SO₄ and evaporated to give a crude product which was purified by flash chromatography (petroleum ether as eluent) followed by distillation with a Kugelrohr apparatus (oven temp. 150 °C, 25 mbar). 0.07 g (47% yield) of a colourless oil were obtained. **5a**: ¹H-NMR (500 MHz): δ = 0.08 (s, 9H), 1.00–1.35 (m, 6H), 1.56–1.80 (m, 4H), 1.95–2.05 (m, 1H), 5.68 (dd, *J* = 7.0, 15.4 Hz, 1H), 5.72 (d, *J* = 18.4 Hz, 1H), 6.02 (dd, *J* = 10.0, 15.4 Hz, 1H), 6.48 (dd, *J* = 10.0, 18.4 Hz, 1H) ppm; MS *m/z* 208 (M⁺, 7), 193 (9), 134 (20), 125 (5), 111 (33), 109 (7), 99 (5), 91 (12), 83 (9), 73 (100), 59 (59), 55 (14), 45 (18), 43 (20), 41 (24).

(1E,3E)-1-trimethylsilyl-1,3-tetradecadiene (5b)

The same procedure described above was followed using **4a** (0.17 g, 0.67 mmol), a 0.82 M solution of *n*-decylmagnesium bromide (0.9 mL, 0.74 mmol) and NiCl₂(dppe) (0.012 g, 0.023 mmol) as a catalyst in 5 mL of anhydrous THF. After the usual workup and purification by chromatography (petroleum ether as eluent), 0.13 g (72 % yield) of a colourless oil were obtained. (Kugelrohr distillation, oven temp. 150 °C, 25 mbar). **5b**: ¹H-NMR (500 MHz): δ = 0.06 (s, 9H), 0.87 (t, *J* = 6.9 Hz, 3H), 1.18–1.45 (m, 16H), 2.07 (q, *J* = 7.1 Hz, 2H), 5.70 (d, *J* = 18.4 Hz, 1H), 5.73 (dt, *J* = 7.1, 15.2 Hz, 1H), 6.05 (dd, *J* = 10.0, 15.2 Hz, 1H), 6.48 (dd, *J* = 10.0, 18.4 Hz, 1H) ppm; MS *m/z* 266 (M⁺, 15), 251 (43), 192 (5), 127 (23), 126 (32), 125 (34), 112 (25), 111 (43), 73 (100), 59 (98), 43 (34), 41 (25).

(1E,3E,5E)-1-trimethylsilyl-1,3,5-decatriene (5c)

The coupling reaction was performed starting from **4b** (1.01 g, 3.63 mmol), a 0.80 M solution of *n*-butylmagnesium bromide (9.0 mL, 7.2 mmol) and NiCl₂(dppe) (0.12 g, 0.23 mmol) in 50 mL of anhydrous THF (3 h reaction time). After the usual workup, 0.53 g (70% yield) of a colourless oil were obtained. (Kugelrohr distillation, oven temp. 110 °C, 1.0 x 10⁻³ mbar). **5c**: ¹H-NMR (500 MHz): δ = 0.07 (s, 9H), 0.88 (t, *J* = 7.0 Hz, 3H), 1.19–1.41 (m, 4H), 2.09 (q, *J* = 7.2 Hz, 2H), 5.73 (dt, *J* = 7.0, 15.0 Hz, 1H), 5.81 (d, *J* = 18.3 Hz, 1H), 6.05 (ddt, *J* = 1.4, 10.4, 15.0 Hz, 1H), 6.11 (dd, *J* = 10.0, 14.9 Hz, 1H), 6.20 (dd, *J* = 10.4, 14.9 Hz, 1H), 6.51 (dd, *J* = 10.0, 18.3 Hz, 1H) ppm; MS *m/z* 208 (M⁺, 19), 193 (7), 152 (4), 151 (5), 137 (10), 123 (29), 109 (8), 99 (4), 95 (11), 85 (7), 73 (100), 59 (65), 45 (14), 43 (14).

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