Pergamon

Tetrahedron, Vol. 52, No. 15, pp. 5495-5504, 1996

0040-4020/96 $15.00 + 0.00

S0040-4020(96)00240-2

Sequential Catalytic Synthesis of Rod-like Conjugated Poly-ynes

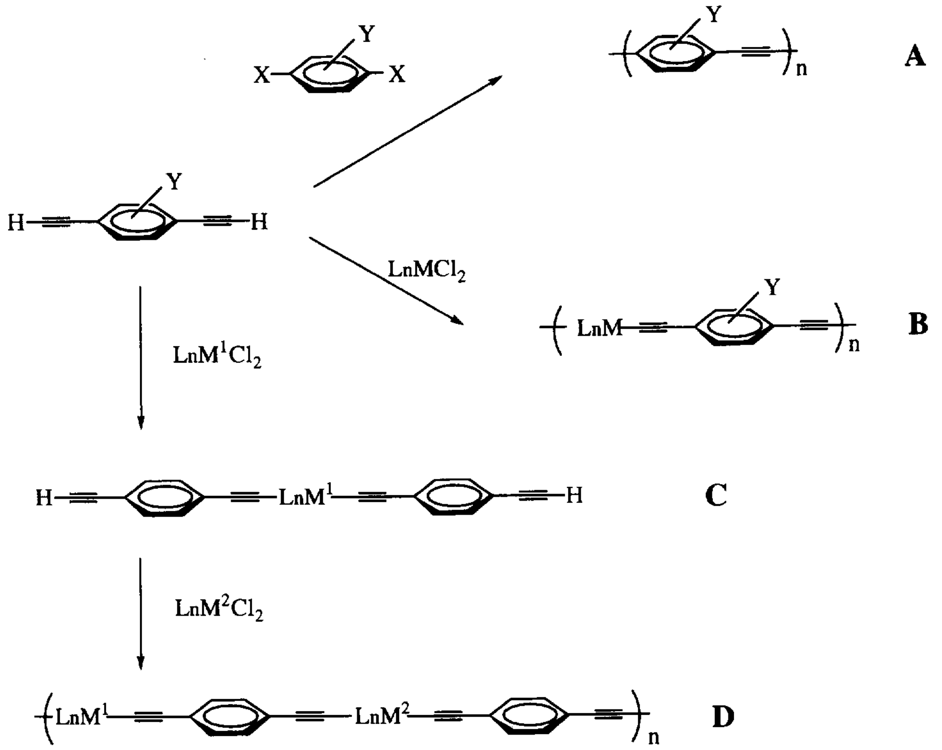
Olivier Lavastre, Laurence Ollivier, Pierre H. Dixneuf *
Laboratoire de Chimie de Coordination Organique, URA CNRS 415, Campus de Beaulieu, Université de Rennes I, F-35042 Rennes, France.
Sourisak Sibandhit
Centre Régional de Mesures Physiques de l'Ouest, Campus de Beaulieu, Université de Rennes I, F-35042 Rennes, France.

ABSTRACT : Several poly-ynes $X-[C\equiv C-C_6H_4-]_nC\equiv C-Si^iPr_3$ (X = H, $SiMe_3$) with controlled length (n = 1, 2, 3, 4) have been prepared from the easily accessible 4-trimethylsilylethynyl iodobenzene by using iterative and convergent methods based on both Pd/Cu catalysed C-C cross-coupling and selective desilylation reactions. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Carbon-rich polymers containing extended π-systems[1] have attracted considerable attention due to their applications in material science. For example organic polymers containing an arylene-alkynylene unit have shown interesting photoluminescence[2-4] or conduction[5] properties. Conjugated polymers containing metals and π-conjugated bridges have also shown optical non-linearity properties[6-7], induced by metal to conjugated ligand dπ-pπ* interaction, liquid crystal properties[8-9] or have been used as ceramic precursors[10]. These polymers are usually obtained by the coupling of monomeric rod-like molecules such as diethynylbenzene derivatives with dihaloarenes by Pd-catalyzed polycondensation[2-4,7a,11,12] or with metal complexes[9,13]. Thus, polymers **A** and **B** are directly built from organic diethynyl derivatives whereas mixed metal polymers **D** are synthesized *via* the corresponding organometallic monomers **C**[14] (Scheme 1).

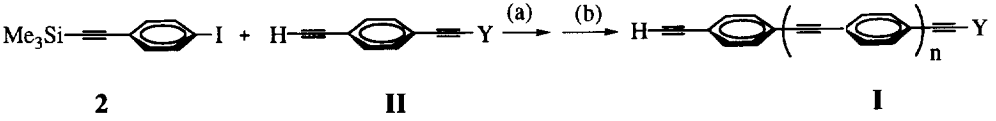
The modification of the unsaturated molecule is essential to improve the desired properties of the corresponding materials (solubility, structure, HOMO-LUMO gap, ...). Especially, it becomes necessary to be able to increase step by step the length of the conjugated organic bridge in organometallic polymers **B** and **D** to modify their properties and thus to find general methods of building rigid unsaturated molecules with different length. We now report an easy access to several poly-ynes $H-[C\equiv C-C_6H_4-]_nC\equiv C-Y$ with controlled length n = 1, 2, 3, 4 derived from diethynyl benzene by using: i) the amino functionality as masking group for aryl iodide via the Sandmeyer reaction, ii) 4-trimethylsilylethynyl iodobenzene **2** as building block and iii) iterative and convergent chain growing methods using both Pd-catalyzed C-C cross-coupling and selective desilylation reactions.



Scheme 1

DISCUSSION

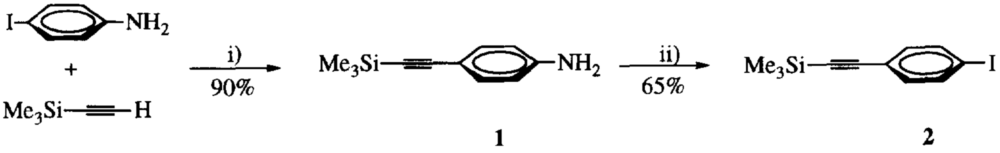
In order to produce poly-yne systems of type **I** (Scheme 2) the adopted strategy was based on a convergent method involving the cross-coupling reaction (a) of the 4-trimethylsilylethynyl iodobenzene **2** with a terminal alkyne of type **II** and subsequent selective elimination of the trimethylsilylgroup (b).



Scheme 2

The synthesis of the key starting derivative 4-trimethylsilylethynyl iodobenzene **2** was first achieved from 4-trimethylsilylethynyl aniline **1**, via formation of the corresponding diazoic salt (Scheme 3). The derivative **1** was obtained in 90 % yield from Pd/Cu catalysed carbon-carbon cross-coupling of 4-iodoaniline and trimethylsilylacetylene using the straightforward catalytic methods reported by S. Takahashi et al[15] .

The aniline derivative **1** in concentrated hydrochloric acid was reacted with sodium nitrite at 0 °C and the intermediate diazoic salt on reaction with KI led to the formation of **2** isolated in 65 % yield. The same derivative **2** has just been prepared by another route from 4-bromoiodobenzene via catalytic cross-coupling reaction with trimethylsilylethyne leading to 4-trimethylsilylethynyl bromobenzene followed by its reaction with t-BuLi and then iodine[16].



Legend : i) $PdCl_2(PPh_3)_2$ (1 mol %), CuI (1 mol %), NEt_3 (solvent), r.t., 18 h
ii) HCl 12N, $NaNO_2$; 0°C, KI.

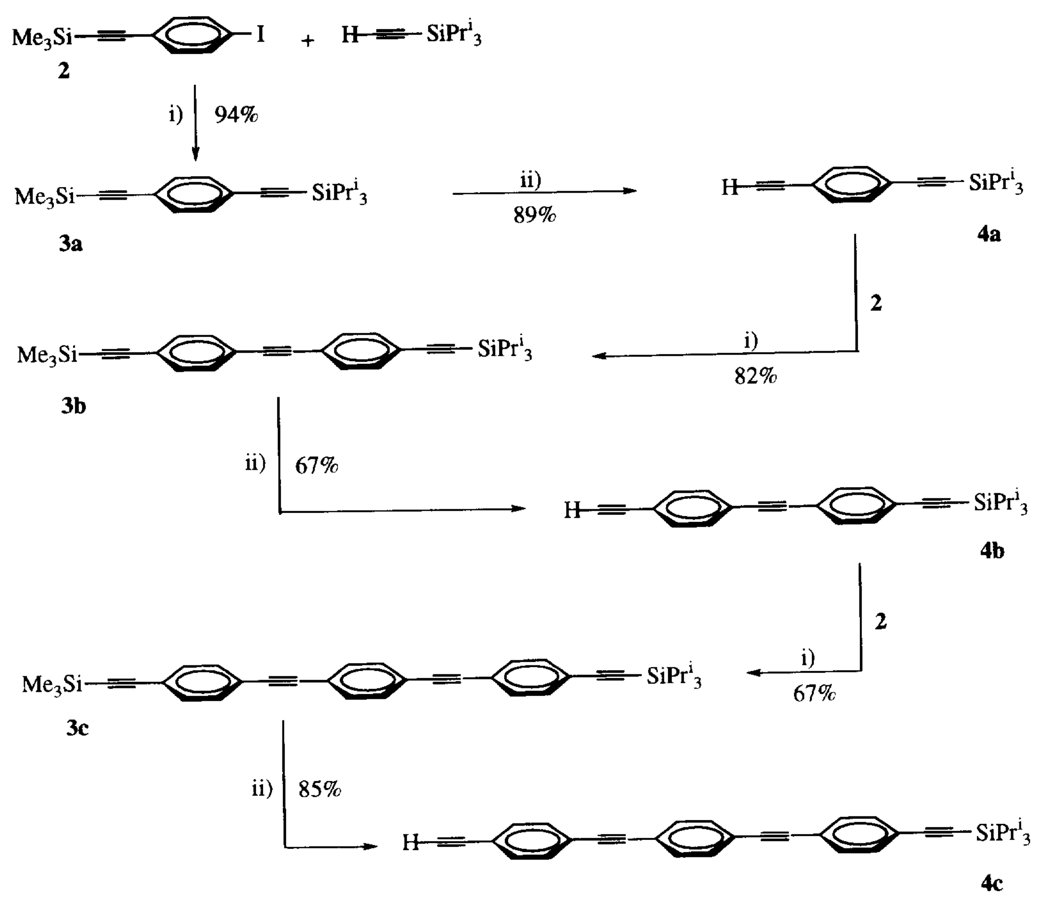
Scheme 3

In order to produce a terminal alkyne of type **II** we considered the possibility to prepare $HC{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}C\text{-}Si^iPr_3$ **4a**. Indeed the monodesilylation conditions of $Me_3Si\text{-}(C{\equiv}C)_2\text{-}SiMe_3$[17] applied to $Me_3SiC{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CSiMe_3$ led to a mixture of compounds[18].

The selective desilylation of the trimethylsilyl group, with respect to the bulkier triisopropylsilyl group, in poly-yne molecules has been recently observed[19]. Thus, the synthesis of the diyne **3a** containing both $SiMe_3$ and Si^iPr_3 groups was attempted as a step in the route to the terminal alkyne **4a** of the type **II**.

The Pd/Cu catalysed cross-coupling of triisopropylsilylacetylene with compound **2** led to 1-trimethylsilylethynyl, 4-triisopropylsilylethynylbenzene **3a** in excellent yield (94 %) as a colourless oil (Scheme 4). Compound **3a** was reacted with sodium hydroxide in ethanol-tetrahydrofuran at room temperature and the monodesilylated diyne **4a** was selectively formed and isolated in 89 % yield.

The high yields obtained in the selective transformations **2** → **3a** → **4a** and the straightforward access to the key product **2** led us to consider that the repetition of these two steps could lead to an iterative method of access of oligomers of type **I**. Indeed derivative **4a** was coupled with **2** to give **3b** in 82 % yield (Scheme 4) and the latter by selective desilylation afforded **4b** isolated in 67 % yield. The catalytic cross-coupling of **2** and **4b** led to **3c** in 67 % yield which afforded the oligomer **4c** in 85 % yield on selective desilylation. Thus this iterative method should be used to reach higher oligomers step by step as long as the terminal poly-yne **4** is obtained with a high purity which is easily checked by NMR.

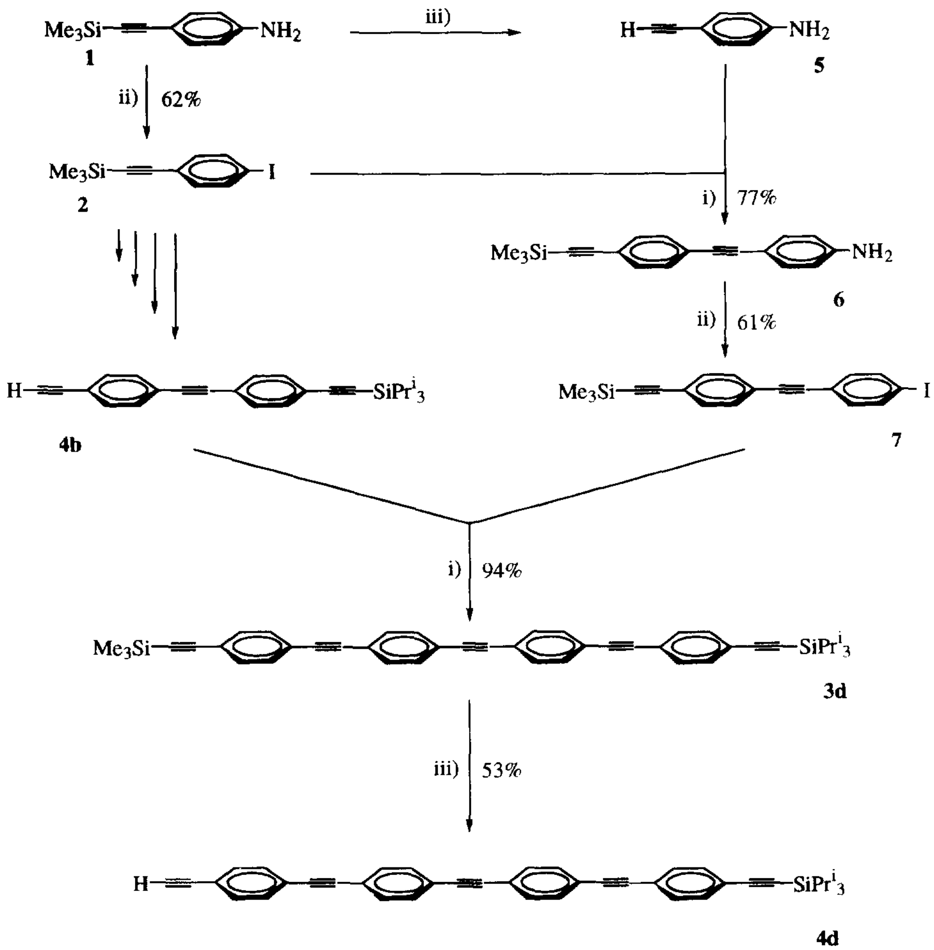


Legend : i) $PdCl_2(PPh_3)_2$ (1 mol %), CuI (1 mol %), NEt_3 (solvent), r.t., 18 h
ii) EtOH, NaOH in THF, 30 min.

Scheme 4

A related method, but a convergent one, was used for the access to oligomers $X\text{-}(C{\equiv}C\text{-}C_6H_4\text{-})_4C{\equiv}C\text{-}Si^iPr_3$ (X = Me_3Si, H) by C-C coupling of two fragments containing two aryl groups (Scheme 5).

The synthesis of the 4-diynyliodobenzene **7** was achieved in the following way. 4-trimethylsilylethynyl aniline **1** was desilylated to give **5** which was catalytically coupled with the iodoarene **2** to afford **6** in 77 % yield. The Sandmeyer reaction applied to **6** afforded compound **7** (61 %). The cross-coupling of reaction of **7** with **4b** led to the pentayne **3d** (94 %) disymmetrically protected at both ends. Its treatment with NaOH/EtOH led to the mono desilylated pentayne **4d** (53 %).



Legend : i) $PdCl_2(PPh_3)_2$ (1 mol %), CuI (1 mol %), NEt_3 (solvent), r.t., 18 h
ii) HCl 12N, $NaNO_2$; 0°C, KI.
iii) EtOH, NaOH in THF, 30 min.

Scheme 5

SPECTROSCOPIC CHARACTERIZATION

The poly-ynes thus prepared were characterized by analysis and spectroscopy. Compounds **3a-d** showed in IR only one $C\equiv C$ vibration between 2160 and 2150 cm^{-1}. Terminal alkynes **4a-d** presented expected vibrations for trialkylsilylethynyl group $C\equiv CSi$ near 2151 cm^{-1} and for terminal acetylenic ends near 3300 cm^{-1} ($\equiv C$-H) and 2110 cm^{-1} ($C\equiv CH$).

All compounds **3a-d** and **4a-d** were characterized by ^{13}C NMR spectroscopy. Complete assignements were established on the basis of ^{1}H decoupling or ^{1}H selective decoupling technics. The ethynyl groups $C\equiv CSiR_3$ of the compounds **3a-d** gave four signals with a small difference when R is Me or ^{i}Pr. Terminal alkynes **4a-d** gave two signals for the silylacetylene group C≡CSi near 106 and 93 ppm and two other signals for the terminal acetylenic end near 83 ppm (*C*≡CH, $^2J_{CH}$ = 50 Hz) and 79 ppm (C≡*C*H, $^1J_{CH}$ = 251 Hz). The main characteristic of these compounds **3** and **4** is the unusual chemical shift for the carbon atoms of methyl groups (18 ppm) and the shielded CH group (11 ppm) of the isopropyl moiety. The shielding of this CH group induced an unexpected effect in ^{1}H NMR spectroscopy. For all compounds **3** and **4**, we did not observed the classical first order septuplet (CH) - doublet (CH_3) system for an isopropyl group but a system of the type AA'_6 was shown (Figure 1). We have used the NMR simulation software PANIC[20] to confirm this system. Chemical shifts of 1.10 ppm for CH and 1.16 ppm for Me with $^3J_{HH}$ = 7.00 Hz were found in accordance with the experimental spectrum (Figure 1). The shielded signal for the proton of CH group could be attributed to the presence of silicon atom, as observed in ^{13}C NMR spectroscopy.

All poly-ynes thus prepared were obtained pure as shown by analysis and NMR spectroscopy. Especially the latter was efficient to show that no starting products were present with the coupled product or the monodesilylated product.

CONCLUSION

The efficiency of the Pd/Cu catalysed C-C cross-coupling and selective desilylation reactions associated to 4-trimethylsilylethynyl iodobenzene as building block gives a simple access to several poly-ynes derived from 1,4-diethynylbenzene. The high yield and selectivity of these reactions allow the step by step synthesis of conjugated poly-ynes with controlled length, which are potentially new precursors to establish extended π-conjugated rigid systems in organic polymers or bridges between metals.

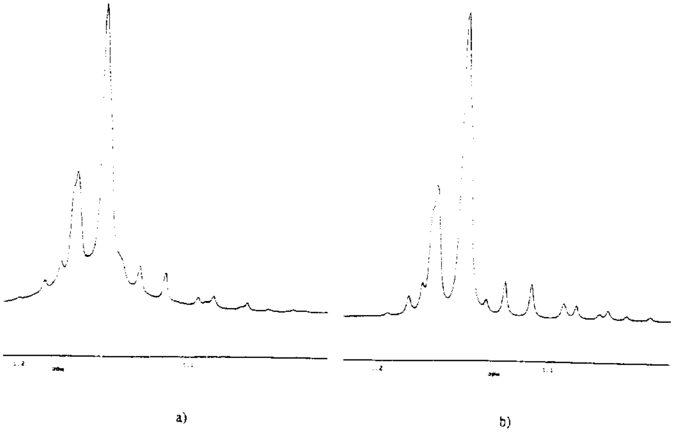


Figure 1 : ^{1}H NMR spectrum of **4a**, for the $SiCH(CH_3)_2$ group region ; a) Experimental spectrum (C_6D_6, 300MH$_z$) ; b) Simulated AA'_6 spectrum, δ ppm : 1.10 CH, 1.16 CH_3, $^3J_{HH}$ = 7.00 Hz.

EXPERIMENTAL

General data. Solvents were dried by standard methods and all reactions involving palladium complexes were conducted under nitrogen by standard Schlenk tube techniques. Elemental analyses were performed by the

CNRS analysis laboratory, Villeurbanne (France). NMR spectra were recorded on a Bruker AM 300 P operating at 300.131 MHz for ^1H, 75.469 MHz for ^{13}C. Mass spectra were obtained on a Varian Mat 311 spectrometer (Electronic ionisation mode). Compounds **1** and **3** were prepared by previously described procedures[15]. Triisopropylsilylacetylene and *para*-iodoaniline were purchased from Janssen.

Procedure for the preparation of para-iododerivatives from the corresponding amino compounds.

A slight excess of sodium nitrite dissolved in water was added to a slurry of the amino compound in concentrated hydrochloric acid at 0 °C to give an orange mixture. After 45 min, the reaction mixture was added dropwise into a solution of potassium iodide in water at 0 °C. The reaction mixture was allowed to reach the room temperature and stirred overnight. The aqueous layer was extracted twice with diethylether. The combined organic layers were washed with brine and dried with magnesium sulfate. After evaporation of the solvent, the brown crude product was purified by column chromatography on alumina with pentane as eluent.

2 white solid ; 62 % yield from 8.50 g (45 mmol) of **1**, 3.25 g (47 mmol) of $NaNO_2$ and 9.68 g (58 mmol) of KI ; IR (KBr) ν/cm^{-1} 2157 (m, C≡C) ; ^1H NMR δ (300.131 MHz, $CDCl_3$, 297 K) 7.44 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8.4 Hz), 6.99 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8.4 Hz), 0.05 (s, 9 H, $SiMe_3$) ; $^{13}C\{^1H\}$ NMR δ (75.469 MHz, $CDCl_3$, 297 K) 137.41 and 133.47 (CH of C_6H_4), 122.69 (*C*-C≡C), 104.02 (*C*≡C-Si), 95.94 (C≡*C*-Si), 94.48 (C-I), - 0.08 ($SiMe_3$) ; Elemental analysis calcd for $C_{11}H_{13}ISi$ (found) C : 44.01 (44.65), H : 4.36 (4.56).

7 yellow solid ; 61 % yield from 0.845 g (2.9 mmol) of **6**, 0.209 g (3.0 mmol) of $NaNO_2$ and 0.631 g (3.8 mmol) of KI ; IR (KBr) ν/cm^{-1} 2207 (w, C≡C), 2159 (m, C≡CSi) ; ^1H NMR δ (300.131 MHz, $CDCl_3$, 297 K) 7.68 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8.3 Hz), 7.45 (s, 4 H, C_6H_4), 7.23 (d, 2 H, C_6H_4, $^3J_{HH}$ = 8.3 Hz), 0.05 (s, 9 H, $SiMe_3$) ; $^{13}C\{^1H\}$ NMR δ (75.469 MHz, $CDCl_3$, 297 K) 137.66 and 133.16 (CH of IC_6H_4), 131.98 and 131.47 (CH of -C_6H_4-), 123.26, 123.00 and 122.59 (*C*-C≡C), 104.61 (*C*≡C-Si), 96.58 (C≡*C*-Si), 94.51 (C-I), 90.49 and 90.40 (*C*≡*C*), 0.05 ($SiMe_3$) ; Elemental analysis calcd for $C_{19}H_{17}ISi$ (found) C : 57.00 (58.31), H : 4.28 (4.37) ; HRMS m/z calcd (found) M^+ : 400.0144 (400.013).

General synthesis of derivatives 3a-d *via* Pd-catalyzed C-C coupling between *para*-iododerivatives and terminal alkynes.

A slight excess of the terminal alkyne was added to a solution of iododerivatives in deoxygenated diethylamine with 1 mol% of $PdCl_2(PPh_3)_2$ and 1 mol% of CuI. After stirring for 16 h at room temperature, the solvent was evaporated and the residue was extracted with diethylether. After evaporation the crude product was purified by column chromatography on alumina with pentane as eluent.

3a colorless oil ; 94 % yield from 7.29 g (24.3 mmol) of **2**, 5.31 g (29.2 mmol) of triisopropylsilylacetylene, 46 mg (0.24 mmol) of CuI and 170 mg (0.24 mmol) of Pd $Cl_2(PPh_3)_2$; IR (film) ν/cm^{-1} 2159 (m, C≡C) ; ^1H NMR δ (300.131 MHz, $CDCl_3$, 297 K) 7.39 (s, 4 H, C_6H_4)), 1.12 (m, 21 H, ^{i}Pr), 0.25 (s, 9 H, $SiMe_3$) ;

$^{13}C\{^1H\}$ NMR δ (75.469 MHz, $CDCl_3$, 297 K) 131.86 and 131.76 (CH of C_6H_4), 123.59 (*C*-C≡C-$SiMe_3$), 122.99 (*C*-C≡C-Si^iPr_3), 106.61 (*C*≡C-Si^iPr_3), 104.67 (*C*≡C-$SiMe_3$), 96.16 (C≡*C*-$SiMe_3$), 92.81 (C≡*C*-Si^iPr_3), 18.71 (CH*Me*), 11.33 (*C*H), - 0.03 ($SiMe_3$) ; Elemental analysis calcd for $C_{22}H_{34}Si_2$ (found) C : 74.53 (74.26), H : 9.67 (9.71) ; HRMS m/z calcd (found) M^+ : 354.219 (354.218).

3b pale yellow solid ; 82 % yield from 0.318 g (1.1 mmol) of **2**, 0.300 g (1.1 mmol) of **4a** ; IR (KBr) ν/cm^{-1} 2156 (s, C≡C) ; ^1H NMR δ (300.131 MHz, $CDCl_3$, 297 K) 7.44 (s, 8 H, C_6H_4), 1.12 (m, 21 H, ^iPr), 0.25 (s, 9 H, $SiMe_3$) ; $^{13}C\{^1H\}$ NMR δ (75.469 MHz, $CDCl_3$, 297 K) 132.09, 132.01, 131.48 and 131.46 (CH of C_6H_4), 123.64, 123.18, 123.15 and 122.90 (C ipso), 106.67 (*C*≡C-Si^iPr_3), 104.67 (*C*≡C-$SiMe_3$), 96.47 (C≡*C*-$SiMe_3$), 93.01 (C≡*C*-Si^iPr_3), 91.03 and 90.84 (*C*≡*C*), 18.76 (CH*Me*), 11.39 (*C*H), 0.03 ($SiMe_3$) ; Elemental analysis calcd for $C_{30}H_{38}Si_2$ (found) C : 79.25 (79.68), H : 8.43 (8.35).

3c pale yellow solid ; 67 % yield from 0.314 g (1.05 mmol) of **2**, 0.400 g (1.05 mmol) of **4b** ; IR (KBr) ν/cm^{-1} 2154 (s, C≡C) ; ^1H NMR δ (300.131 MHz, $CDCl_3$, 297 K) 7.49 and 7.45 (m, 12 H, C_6H_4), 1.12 (m, 21 H, ^iPr), 0.24 (s, 9 H, $SiMe_3$) ; $^{13}C\{^1H\}$ NMR δ (75.469 MHz, $CDCl_3$, 297 K) 132.09, 132.02, 131.66, 131.49 and 131.48 (CH of C_6H_4), 123.66, 123.23, 123.15, 123.11, 123.07 and 122.90 (C ipso), 106.66 (*C*≡C-Si^iPr_3), 104.65 (*C*≡C-$SiMe_3$), 96.52 (C≡*C*-$SiMe_3$), 93.05 (C≡*C*-Si^iPr_3), 91.15, 91.06, 91.00 and 90.89 (*C*≡*C*), 18.75 (CH*Me*), 11.39 (*C*H), 0.00 ($SiMe_3$) ; HRMS m/z calcd for $C_{38}H_{42}Si_2$ (found) M^+ : 554.2825 (554.282).

3d pale yellow solid ; 94 % yield from 0.191 g (0.5 mmol) of **4b**, 0.200 g (0.5 mmol) of **7** ; IR (KBr) ν/cm^{-1} 2153 (s, C≡C) ; ^1H NMR δ (300.131 MHz, $CDCl_3$, 297 K) 7.50 to 7.43 (m, 16 H, C_6H_4), 1.06 (m, 21 H, ^iPr), 0.18 (s, 9 H, $SiMe_3$) ; $^{13}C\{^1H\}$ NMR δ (75.469 MHz, $CDCl_3$, 297 K) 132.05, 131.97, 131.63 and 131.44 (CH of C_6H_4), 123.63, 123.19, 123.13, 123.06, 123.03 and 122.85 (C ipso), 106.63 (*C*≡C-Si^iPr_3), 104.61 (*C*≡C-$SiMe_3$), 96.53 (C≡*C*-$SiMe_3$), 93.06 (C≡*C*-Si^iPr_3), 91.18, 91.13, 91.08, 90.98 and 90.89 (*C*≡*C*), 18.76 (CH*Me*), 11.39 (*C*H), 0.02 ($SiMe_3$) ; HRMS m/z calcd for $C_{46}H_{46}Si_2$ (found) M^+ : 654.3179 (654.318)

6 pale yellow solid ; 77 % yield from 0.651 g (2.2 mmol) of **2**, 0.254 g (2.2 mmol) of **5** ; IR (KBr) ν/cm^{-1} 2209 (s, C≡C), 2153 (s, C≡CSi) ; ^1H NMR δ (300.133 MHz, $CDCl_3$, 297 K) 7.41 (s, 4 H, C_6H_4), 7.32 and 6.62 (d, 2 H, $C_6H_4NH_2$, $^3J_{HH}$ = 5 Hz), 3.82 (broad s, 2 H, NH_2), 0.25 (s, 9 H, $SiMe_3$) ; $^{13}C\{^1H\}$ NMR δ (75.469 MHz, $CDCl_3$, 297 K) 146.92 (C-NH_2), 133.09, 131.89 and 131.15 (CH of C_6H_4), 124.13 and 122.21 (C ipso, C_6H_4), 114.79 (*C*H-C-NH_2), 112.33 (C ipso, $C_6H_4NH_2$), 104.91 (*C*≡C-Si), 95.90 (C≡*C*-Si), 92.30 and 87.18 (*C*≡*C*), 0.00 ($SiMe_3$) ; Elemental analysis calcd for $C_{19}H_{19}NSi$ (found) C : 78.86 (78.56), H : 6.62 (6.48) ; HRMS m/z calcd (found) M^+ : 289.1287 (289.128).

General synthesis of compounds 4a-d *via* selective deprotection of trimethylsilyl versus triisopropylsilyl acetylene derivatives.

An equimolar amount of aqueous sodium hydroxyde (1 M) was added to a stirred solution of the silylated product **3a-d** dissolved in a 1/1 ethanol/THF mixture. After 30 min the solvents were removed under reduced pressure (10 mm Hg). The residue was extracted with diethyl ether. After drying of the organic layer with magnesium sulfate and evaporation of the solvent, the crude product was purified by column chromatography on alumina with pentane as eluent.

4a white solid ; 89 % yield from 8 g of **3a**. IR (KBr) ν/cm^{-1} 3293 (C≡CH), 2151 (C≡CSi), 2109 (C≡C) ; ^{1}H NMR δ ppm (300.131 MHz, $CDCl_3$, 297 K) 7.41 (s, 4 H, C_6H_4), 3.15 (s, 1 H, C≡CH), 1.12 (m, 21 H, ^{i}Pr) ; ^{13}C{^{1}H} NMR δ (75.469 MHz, $CDCl_3$, 297 K) 131.94 (CH of C_6H_4), 124.03 (*C*-C≡CSi), 121.93 (*C*-C≡CH), 106.41 (*C*≡C-Si), 93.03 (C≡*C*-Si), 83.31 (*C*≡CH), 78.9 (C≡*C*H), 18.70 (Me), 11.32 (CH) ; ^{13}C NMR δ (75.469 MHz, $CDCl_3$, 297 K) 131.94 (d, CH of C_6H_4, $^{1}J_{CH}$ = 165.3 Hz), 83.31 (dt, *C*≡CH, $^{2}J_{CH}$ = 49.8 Hz, $^{3}J_{CH}$ = 2.9 Hz), 78.9 (d, C≡*C*H, $^{1}J_{CH}$ = 251.6 Hz), 18.70 (q, CH_3, $^{1}J_{CH}$ = 126.6 Hz), 11.32 (dm, CH, $^{1}J_{CH}$ = 119.50 Hz) ; Elemental analysis calcd for $C_{19}H_{26}Si$ (found) C : 80.80 (81.08), H : 9.29 (9.27) ; HRMS m/z calcd (found) M^{+} : 282.1804 (282.181).

4b white solid ; 67 % yield from **3b**. IR (KBr) ν/cm^{-1} 3304 (C≡CH), 2151 (C≡CSi), 2110 (C≡C) ; ^{1}H NMR δ ppm (300.131 MHz, $CDCl_3$, 297 K) 7.46 and 7.45 (m, 8 H, C_6H_4), 3.17 (s, 1 H, C≡CH), 1.11 (m, 21 H, ^{i}Pr) ; ^{13}C{^{1}H} NMR δ ppm (75.469 MHz, $CDCl_3$, 297 K) 132.12, 132.04, 131.50 and 131.42 (CH of C_6H_4), 123.66, 123.55, 122.79 and 122.11 (C ipso), 106.61 (*C*≡C-Si), 93.06 (C≡*C*-Si), 91.12 and 90.64 (C≡C), 83.25 (*C*≡CH), 79.06 (C≡*C*H), 18.70 (Me), 11.33 (CH) ; ^{13}C NMR δ (75.469 MHz, $CDCl_3$, 297 K) 131.08 and 131.46 (d, CH of C_6H_4, $^{1}J_{CH}$ = 161.6 Hz), 83.25 (d, *C*≡CH, $^{2}J_{CH}$ = 49.8 Hz), 79.06 (d, C≡*C*H, $^{1}J_{CH}$ = 251.7 Hz), 18.70 (q, Me, $^{1}J_{CH}$ = 126.5 Hz), 11.33 (d, CH, $^{1}J_{CH}$ = 119.6 Hz) ; Elemental Analysis calcd for $C_{27}H_{30}Si$ (found) C : 84.77 (84.47), H : 7.91 (8.44).

4c pale yellow solid ; 85 % yield from **3c** ; IR (KBr) ν/cm^{-1} 3301 (C≡C-H), 2152 (C≡CSi), 2107 (C≡C) ; ^{1}H NMR δ (300.131 MHz, $CDCl_3$, 297 K) 7.50 to 7.45 (m, 12 H, C_6H_4), 3.24 (s, 1 H, C≡CH), 1.19 (m, 21 H, ^{i}Pr) ; ^{13}C{^{1}H} NMR δ (75.469 MHz, $CDCl_3$, 297 K) 132.15, 132.05, 131.62, 131.53 and 131.43 (CH of C_6H_4), 123.63, 123.53, 123.17, 122.96, 122.85 and 122.15 (C ipso), 106.63 (*C*≡C-Si), 93.06 (C≡*C*-Si), 91.20, 91.08, 90.87 and 90.84 (C≡C), 83.25 (*C*≡CH), 79.11 (C≡*C*H), 18.71 (Me), 11.34 (CH) ; Elemental analysis calcd for $C_{35}H_{34}Si$ (found) C : 87.09 (87.01), H : 7.11 (7.41).

4d orange solid ; 53 % yield from **3d**. IR (KBr) ν/cm^{-1} 3304 (C≡C-H), 2151 (C≡CSi), 2108 (C≡C) ; ^{1}H NMR δ (300.131 MHz, CD_2Cl_2, 297 K) 7.51 to 7.46 (m, 16 H, C_6H_4), 3.17 (s, 1 H, C≡CH), 1.11 (m, 21 H, ^{i}Pr) ; ^{13}C{^{1}H} NMR δ (75.469 MHz, CD_2Cl_2, 297 K) 132.55, 132.37, 132.04, 131.94 and 131.86 (CH of C_6H_4), 124.02, 123.89, 123.79, 123.53, 123.43, 123.27 and 122.58 (C ipso), 106.90 (*C*≡C-Si), 93.54 (C≡*C*-Si), 91.36, 91.28, 91.15 and 91.08 (C≡C), 83.40 (*C*≡CH), 79.41 (C≡*C*H), 18.84 (Me), 11.74 (CH) ; HRMS m/z calcd for $C_{43}H_{38}Si$ (found) M^+ : 582.2743 (582.273).

ACKNOWLEDGEMENTS

The authors wish to thank the CNRS for financial support and P. Guenot (CRMPO, Université de Rennes I, France) for HRMS measurements.

REFERENCES

1 (a) Diederich, F.; Rubin, Y. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1101-1123 ; *Angew. Chem.* **1992**, *104*, 1123. (b) Bunz, U. H. F. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1073-1076 ; *Angew. Chem.* **1992**, *106*, 1127.

2 Mangel, T.; Eberhardt, A.; Scherf, U.; Bunz, U. H. F.; Müllen, K. *Macromol. Rapid Commun.* **1995**, *16*, 571-580.

3 Davey, A. P.; Elliott, S.; O'Connor, O.; Blau, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1433-1434.

4 Yamamoto, T.; Takagi, M.; Kizu, K.; Maruyama, T.; Kubota, K.; Kanbara, H.; Kurihara, T.; Kaino, T. *J. Chem. Soc., Chem. Commun.* **1993**, 797-798.

5 Ofer, D.; Swager, T. M.; Wrighton, M. S. *Chem. Mater.* **1995**, *7*, 418-425.

6 (a) Frazier, C. C.; Guha, S.; Chen, W. P.; Cockerham, M. P.; Porter, P. L. *Polymer* **1987**, *28*, 553-555. (b) Fyfe, H. B.; Mlekuz, M.; Stringer, G.; Taylor, N. J.; Marder, T. B. in *Inorganic and Organometallic Polymers with Special Properties* **1992**, 331-344.

7 (a) Corriu, R. J.-P.; Douglas, W. E.; Yang, Z.; Karakus, Y.; Cross, G.; Bloor, D. *J. Organomet. Chem.* **1993**, *455*, 69-76. (b) Long, N. J. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21-38.

8 (a) Altmann, M.; Enkelmann, V.; Lieser, G.; Bunz, U. H. F. *Adv. Mater.* **1995**, *7*, 726-728. (b) Altmann, M.; Bunz, U. H. F. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 569-571.

9 (a) Takahashi, S.; Kariya, M.; Yatake, T.; Sonogashira, K.; Hagihara, N. *Macromolecules* **1978**, *11*, 1063-1066. (b) Faulkner, C.; Ingham, S.; Khan, M.; Lewis, J.; Long, N.; Raithby, P. *J. Organomet. Chem.* **1994**, *482*, 139-145.

10 Corriu, R. J.-P.; Gerbier, P.; Guérin, C.; Henner, B. J. L.; Jean, A.; Mutin, P. H. *Organometallics* **1992**, *11*, 2507-2513.

11 Corriu, R. J.-P.; Douglas, W. E.; Yang, Z. *J. Organomet. Chem.* **1993**, *456*, 35-39.

12 Wright, M. E. *Macromolecules* **1989**, *22*, 3256-3259.

13 Nishihara, H.; Shimura, T.; Ohkubo, A.; Matsuda, N.; Aramaki, K. *Adv. Mater.* **1993**, *5*, 752-754.

14 Lavastre, O.; Even, M.; Pacreau, A.; Vairon, J.P.; Dixneuf, P. H. *Organometallics* **1996**, in press.

15 Takahashi, S.; Kuroyama, Y.; Sonogashira, KK.; Hagihara, N. *Synthesis* **1980**, 627-630.

16 Hsung, R. P.; Chidsey, C. E. D.; Sita, L. R. *Organometallics* **1995**, *14*, 4808-4815.

17 Holmes, A. B.; Jennings-White, C. L. D.; Schulthess, A. H.; Akinde, B.; Walton, D. R. M. *J. Chem. Soc. Chem. Comm.* **1979**, 840-842.

18 Ghose, B. N. *Synth. React. Inorg. Met.-Org. Chem.*, *24*, **1994**, 29-52.

19 Faust, R.; Diederich, F.; Volker, G.; Seiler, P. *Chem. Eur. J.* **1995**, *1*, 111-117.

20 NMR simulation software PANIC85 (Parameters Adjustement in NMR by Iterative Calculation) available on Bruker spectrometer.

(*Received in Belgium* 29 *January* 1996; *accepted* 26 *February* 1996)