New Polymer-Supported Organosilicon Reagents

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New polymer-supported organosilanes have been prepared using two different strategies. These involved the synthesis of soluble and insoluble supports through the copolymerization of styrene and monomers containing a thiophene ring. Selective metallation of the thiophene ring followed by silylation allowed the introduction of various functionalized organosilanes onto the polymer with a high degree of substitution. These supports can be used for solid-phase organic synthesis, the product being released through a Tamao–Fleming oxidation, which generates an additional hydroxy group during the cleavage along with the recycled support.

Introduction

Solid-phase synthesis, which now encompasses not only peptide chemistry but also the combinatorial synthesis of a large range of small organic molecules, has recently enjoyed considerable interest.[1] The effect of the nature of the linker used to graft the functionable moiety to the polymer fragment has been studied in depth. The linker is particularly important in that it must be stable to the conditions used throughout the synthesis but has to be cleaved or removed without the undesired transformation of the final product. In this context, the use of silicon linkers is widespread as they can be removed under numerous orthogonal conditions.[2] Many silicon linkers are very often traceless, leaving in the medium only silicates that are easily removed by simple aqueous treatment. Two main strategies have been developed to incorporate a silylated moiety onto a support: either a silylated monomer is synthesized and copolymerized to give the support or a polymeric support is chemically modified in order to introduce the silyl group. In the literature, examples illustrating the direct method of introduction of silicon by copolymerization are rather scarce. Among them, one can mention the work of Nakahama and co-workers on the synthesis of vinyl monomers bearing hydrosilane functions.[3] Fréchet and co-workers have also synthesized a vinyl monomer containing a silylated group that was then copolymerized with styrene and divinylbenzene to give an insoluble support.[4] Polymerization by hydrosilylation was developed by Itsuno et al. to introduce silyl functions onto a support.[5] Lastly, a new kind of support, named "rasta silanes", was recently developed by Hodges et al.[6] The principal method used to introduce a silyl group onto a preformed support involves the metallation of an aromatic nucleus. Generally, a polymer containing a styrene moiety is deprotonated using strong bases (*n*BuLi/TMEDA) before the addition of the desired electrophilic silyl reagent.[7] Various polymer-supported organosilicon compounds have thus been prepared by using this approach, although metallation is sometimes tedious and only partial.

In the course of our research into the use of organosilicon intermediates in organic synthesis, we have developed new organosilicon-based building blocks and studied various functionalizations of chiral organosilanes by using the silicon group both to control the stereochemistry of new stereogenic centres[8] and as a masked hydroxy group.[9] We thus planned to extend part of this chemistry to organosilanes (vinyl- and allylsilanes) grafted onto a polymer support, taking advantage of the polymer to access a larger range of target molecules.

Our strategy is based on the utilization of a home-made polystyrene-based polymer having an arylsilyl linker. The choice of such a linker was dictated by pioneering studies by Fleming and co-workers who showed that an arylsilyl group can be converted into an OH group under mild oxidative conditions.[10] Consequently, the arylsilyl group can be considered a masked hydroxy group. Such a transformation is now extensively used in organic synthesis and has found many applications in the total synthesis of natural products.[9] We envisioned extending such an approach to solid-phase synthesis. It was anticipated that an arylsilyl linker would be particularly well adapted for solid-phase synthesis, being stable to a variety of conditions but easily removable through a mild oxidative treatment. Functionalization of the aryl moiety should be carried out through

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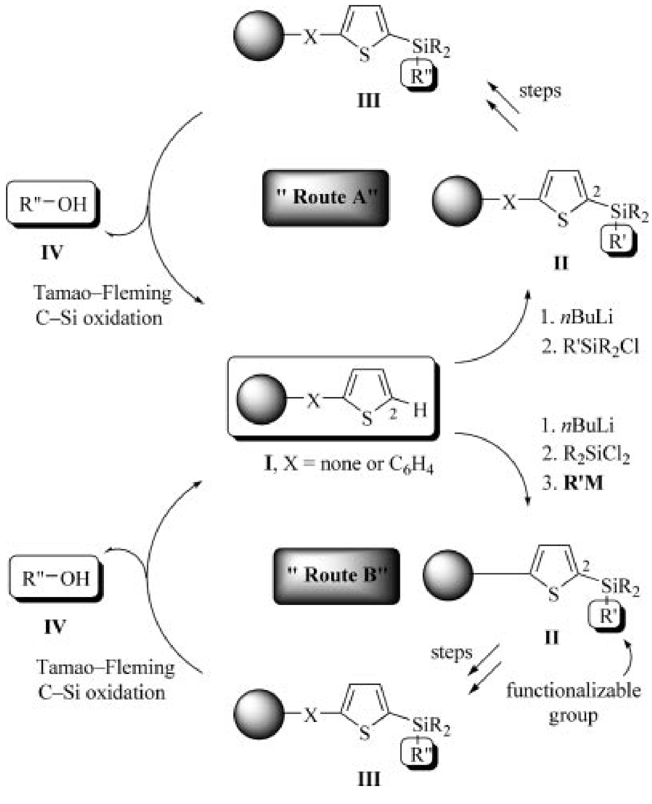
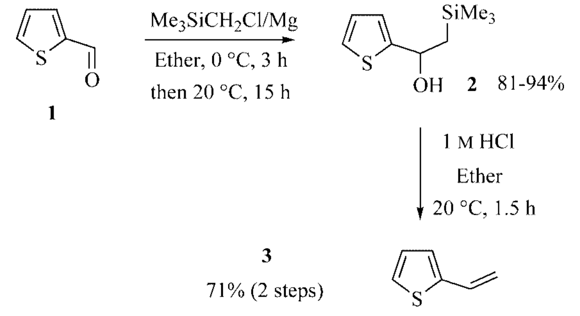
metallation then silylation (i.e. **I** → **II**, Scheme 1). As mentioned above, many aryl groups can be metallated by using strong bases but precedent in the literature has shown that such functionalizations are often tedious allowing only low polymer loading.[11] We thus turned our attention to thiophene-based polymers which should be easier to functionalize. The acidity of the thiophene C-2 proton is relatively high compared with the acidity of other aromatic protons, thus allowing easier metallation of thiophenes than of phenyl analogues.[12] Moreover, we have previously shown that a thienyldimethylsilyl group could be used as a latent hydroxy group.[13] Note that, with this silyl group, the removal of the aromatic group of the arylsilyl moiety, which precedes the oxidation step, can be carried out under either electrophilic (protodesilylation) or nucleophilic conditions. This point is crucial if one considers that the silicon group will be unmasked on substrates possessing functionalities that may be sensitive to electrophiles or nucleophiles. Two different routes can be envisioned depending on the nature of the target silane. A few functionalized chlorosilanes ($R'R_2SiCl$) are commercially available. These can be easily introduced after metallation of the thiophene ring, following route **A**.[14] However, although this approach is straightforward, it is limited by the number of chlorosilanes available. Therefore, a second approach (route **B**) was envisaged which should offer access to a broader range of organosilanes. This strategy involves the reaction of the metallated thiophene moiety with a dichlorosilane to produce "in situ" the corresponding chlorosilane which can then react with a second organometallic species R′M to produce **II**. Subsequent elaboration of the carbon framework in **II** (R′) would provide **III** (R′′) which would then be submitted to Tamao–Fleming oxidation,[9] releasing alcohol **IV** as well as the recovered polymer **I** which should thus be reusable. The release of the organic compound from the polymer would thus be accompanied by the introduction of an additional OH group (i.e. **IV**). Note that oxidation of a C–Si bond to the corresponding C–OH bond has never been used to the best of our knowledge in solid-phase synthesis as silicon linkers are usually simply replaced by a proton through protodesilylation.[2] We report herein our preliminary studies on the preparation of polymer-supported organosilane reagents of type **I** and evaluate their use in the multi-step synthesis of a model alcohol.



Scheme 1.

Results and Discussion

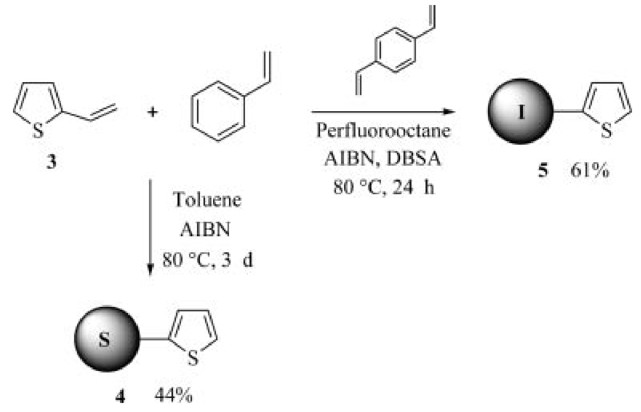
Our first polymer was prepared from the copolymerization of styrene with vinylthiophene **3**. The latter was prepared in two steps following a method recently reported by O'Doherty and co-workers[15] for the preparation of vinylfuran. Addition of the Grignard derivative of (chloromethyl)trimethylsilane to thiophene-2-carboxaldehyde led to β-hydroxysilane **2** in a good and reproducible yield (Scheme 2). β-Hydroxysilane **2** was then treated, without further purification, with acid to provide, after Peterson elimination, the desired 2-vinylthiophene[16] in a 71% purified yield.



Scheme 2.

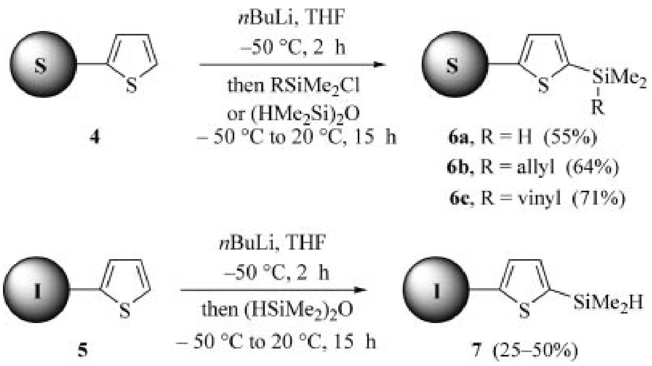
The soluble support based on styrene ($x = 0.9$) and 2-vinylthiophene **3** ($y = 0.1$) was synthesized in toluene at 80 °C by radical copolymerization using AIBN as the initiator. The copolymerization reactivity ratio of styrene and 2-vinylthiophene reported in the literature is 0.35 and 3.10, respectively, showing that 2-vinylthiophene reacts more rapidly than styrene.[17] Therefore, the copolymers obtained are probably not strictly statistical. However, the degree of sulfur incorporation ($mmol\,g^{-1}$) obtained is close to that expected, based on monomer feed composition. A reasonable yield of the soluble thiophene-based polymer **4** was thus obtained (Scheme 3). We also prepared an insoluble version of the above polymer through the copolymerization of styrene, divinylbenzene (DVB) and **3**. Such polymers are commonly used as they facilitate handling and recovery of the support. We chose to prepare gel-type beads through suspension polymerization using DVB as a crosslinking agent

(2%) and styrene as the chain dilutant (Scheme 3). In our first attempt, an aqueous phase was used as the suspending medium. However, whatever the stabiliser used [acacia gum or poly(vinyl alcohol) (PVA)], we were unable to obtain beads in a satisfactory yield. The high solubility of 2-vinylthiophene in water was identified as a possible drawback and, therefore, water was replaced by a perfluorous medium such as perfluorooctane.[18] Under these conditions, beads of **5** of a satisfactory size and shape were obtained in a good yield.



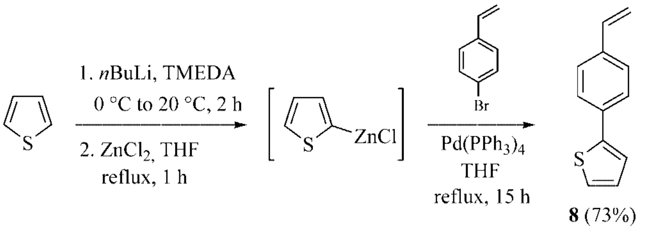
Scheme 3.

Having prepared the polymers, we then investigated the functionalization step (**I** → **II**, Route **A**, Scheme 1). Lithiation of the soluble polymer **4** was easily carried out with *n*BuLi at –50 °C, followed by the addition of the desired chlorosilanes (Scheme 4). Polymer-supported silanes **6a–c** were thus obtained in good yields after precipitation from MeOH and showed excellent levels of substitution (50–70%).[19] ^{1}H NMR and elemental analyses unambiguously indicated the incorporation of the silane moiety onto the polymer. Note that much lower degrees of substitution (DS),[19] ranging between 6 and 10%, were observed with the analogous soluble polystyrene under drastic conditions (*n*BuLi/TMEDA at 65 °C in cyclohexane for 4 hours). The insoluble support was also metallated under similar conditions, then silylated with tetramethyldisiloxane to give **7** with a good degree of substitution. IR experiments and elemental analysis were used to prove the presence of the Si–H bond and thus the grafting of the silane moiety onto the polymer. As a comparison, metallation then silylation of commercially available Amberlite XE 305 resin (styrene and divinylbenzene resin, 2% crosslinking) using chlorodimethylsilane and allylchlorodimethylsilane led to degrees of substitution of 19 and 26%, respectively.[20] This is in good agreement with previous reports by Farrall and Fréchet[11] who claimed a maximum degree of substitution of 23% under conditions similar to those described above and using carbon dioxide as an electrophile. To summarize, metallation of our thiophene-based polymers is, as expected, much easier and allows a high degree of substitution under conditions compatible with the resin structure.



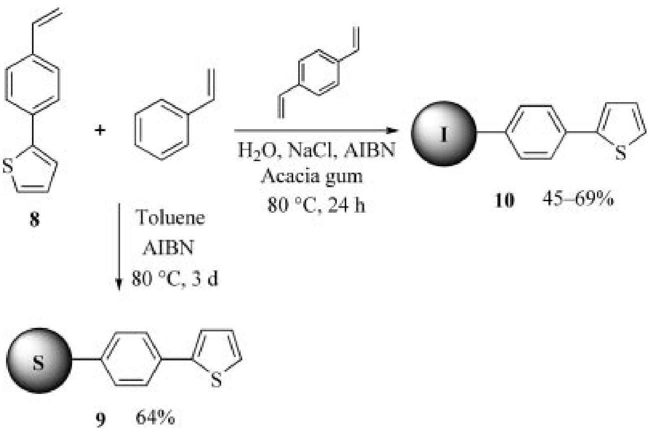
Scheme 4.

As mentioned above, the high solubility of vinylthiophene **3** made the preparation of the insoluble support **5** rather troublesome. Therefore, it was envisioned that a more lipophilic monomer such as **8**,[21] possessing both a styrene-based structure and a thiophene moiety, would facilitate the preparation of an insoluble support with a reactivity close to that of styrene. Monomer **8** was prepared in good yield through the palladium-mediated Negishi coupling of thiophene and *p*-bromostyrene (Scheme 5).[22]



Scheme 5.

The soluble support **9** was prepared through the copolymerization of styrene ($x = 0.85$) and **8** ($y = 0.15$) in toluene at 80 °C under radical conditions using AIBN as the initiator (Scheme 6). Polymer **9** was thus obtained after 3 days in a satisfying 64% yield. The insoluble analogue **10** was prepared, as above, through the suspension copolymerization of styrene ($x = 0.87$), **8** ($y = 0.11$) and divinylbenzene ($z = 0.02$) in an aqueous medium. This led to gel-type beads of **10** in good yields of 45–69%.



Scheme 6.

Several typical features of **10** were determined such as bead size and swelling (Tables 1 and 2).[1a] Swelling has been measured in beads that have a diameter of 0.8–1 mm in various solvents. The resin absorbs solvents to a certain extent which provides information on site accessibility and consequently on the functionalization of the resin.[23] As shown in Table 2, swelling of **10** is reasonable in THF, benzene, toluene and chlorinated solvents, but is usually lower than that exhibited by 1% crosslinked styrene/divinylbenzene copolymer (PS/DVB-1). However, this indicates that our polymer should be useful with most organic solvents and particularly in THF, in which lithiation reactions are usually carried out, thus mimicking to a certain extent solution-phase conditions.

Table 1. Distribution of bead size of polymer **10** (see Scheme 6).

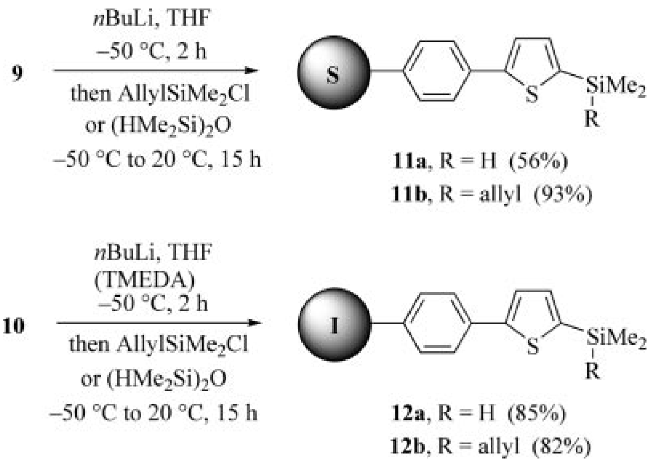
Diameter [mm]	Distribution [%]
>1	35
0.8–1	49
0.5–0.8	12
<0.5	4

Table 2. Swelling of **10** and PS/DVB-1 in different solvents (see Scheme 6).

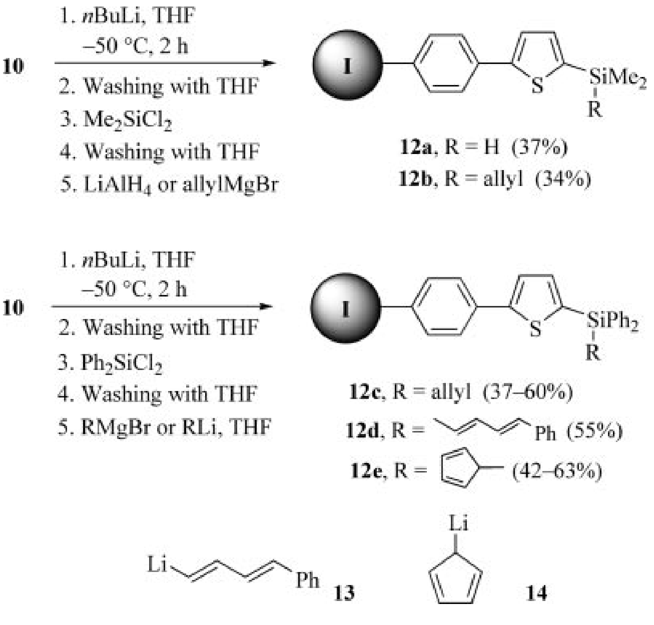
Solvent	Volume of swollen resin **10** [mL g^{1}]	Volume of swollen resin, PS/DVB-1 [mL g^{1}]
THF	4.8	8.8
Benzene	4.8	–
Toluene	4.6	8.5
CH_2Cl_2	4.2	8.3
CCl_4	4.2	–
DMF	2.8	5.6
MeOH	<0.3	1.6

Support **9** was functionalized under the same conditions as described above for the functionalization of support **4**. A slight excess of *n*BuLi was used and then tetramethyldisiloxane or allylchlorodimethylsilane were added to provide resin-bound organosilanes **11a** or **11b** with a degree of substitution of 56% and 93%, respectively (Scheme 7). Metallation of support **10** was carried out under the following optimized conditions: *n*BuLi (4 equiv.) in THF with a 0.04 M concentration at –50 °C over 2 hours. Addition of TMEDA (4 equiv.) generally improves the degree of substitution. Higher or lower temperatures led to a decrease in DS. Similarly, lithiation over a shorter period of time led to incomplete metallation while a longer period led to low DS. Lithiation of insoluble resin **10** then silylation under these optimized conditions led to **12a**,**b** with degrees of substitution of 85 and 82%, respectively.

While these results (Schemes 4 and 7) were satisfying in terms of the degree of substitution, it was still necessary to extend the method to a broader class of polymer-bound organosilanes. One limitation of approach **A** is the poor availability of functionalized chlorosilanes. To increase the diversity of supported organosilane reagents, it was thus necessary to have in hand differently substituted chlorosilanes. As these are often difficult to prepare owing to their sensitivity to moisture, we considered the alternative approach **B** (Scheme 1) which should allow a larger range of silicon substituents. In this strategy, the sensitive chlorosilane intermediate is generated in situ and is simply washed before the addition of the second functionalized organometallic reagent R′M.[24] The chlorosilane is prepared through the reaction of the supported lithiated thiophene with a suitable dichlorosilane.[25] Variability is thus afforded both by the choice of dichlorosilane R_2SiCl_2 and by the organometallic reagents R′M. It is important to note that this strategy cannot be applied to soluble supports as crosslinking between the macromolecular chains generally occurs leading to gelatinous and unusable supports. Therefore, we limited our study to insoluble support **10** in which crosslinking should be more limited. This was first tested by synthesizing the supported organosilane reagents **12a** and **12b** (Scheme 8).



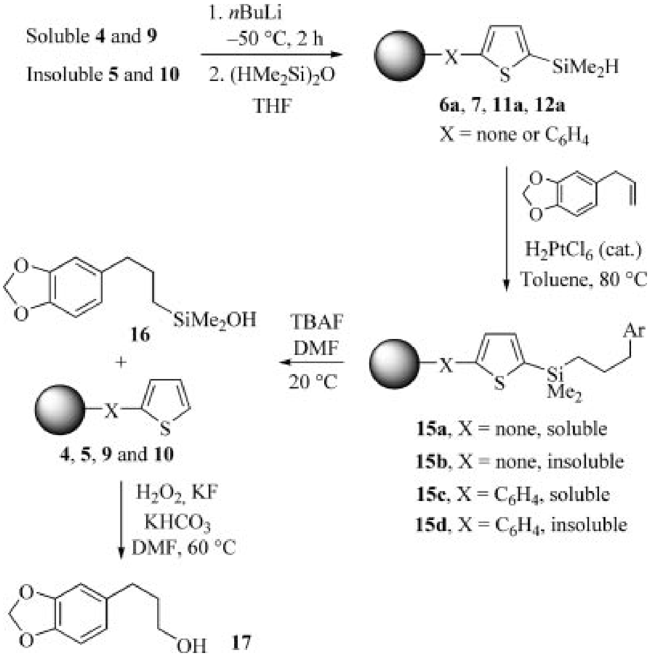
Scheme 7.



Scheme 8.

To estimate the degree of substitution of the support, we made the assumption that the chlorosilane intermediate formed does not undergo any partial in situ hydrolysis and reacts completely with the organometallic species RMgBr or RLi. We could then observe a significant decrease in the degree of substitution in compounds **12a**,**b** obtained through route **B** compared with those obtained through route **A** (Scheme 7). However, this strategy allows such a variation of the substituents at silicon that we chose to continue our study by introducing new silylated functions onto the insoluble support **10**. Ph_2SiCl_2 was added after lithiation of **10** with an excess of *n*BuLi (4 equiv.) to generate the chlorosilane intermediate which was finally quenched with phenylbutadienyllithium (**13**)[26] (2.5 equiv.) or cyclopentadienyllithium (**14**)[27] (4 equiv.) to give, respectively, supported dienylsilanes **12d** and **12e** with good degrees of substitution. These last two examples illustrate the flexibility of route **B**, which allows functionalized organosilanes to be grafted in a single pot. Washing is generally required in order to discard excess reagents. Commercially available Ph_2SiCl_2 was selected as a dichlorosilane as it often provides better yields than Me_2SiCl_2.

With our supported organosilanes in hand, we then tested the validity of the approach summarized in Scheme 1. A simple four-step sequence was studied as a test case. This involved the introduction of a $SiMe_2H$ group onto the support through silylation (generating silanes **6a**, **7**, **11a** and **12a**), followed by platinum-mediated hydrosilylation[28] of safrole to give **15a**–**d**, cleavage from the resin to release silanol **16** and Tamao–Fleming oxidation[9,29] of the latter to release the desired alcohol **17** (Scheme 9). The sequence was carried out with soluble supports **4** and **9** and insoluble supports **5** and **10**. The results are summarized in Table 3. The complete sequence was successful with the four supports, with the overall yield varying with the nature of the support. The best results were obtained with the insoluble support **10**, with both a high degree of substitution achieved during the silylation process and an overall yield of 39% in alcohol **17**[30] (entry 4, Table 3).



Scheme 9.

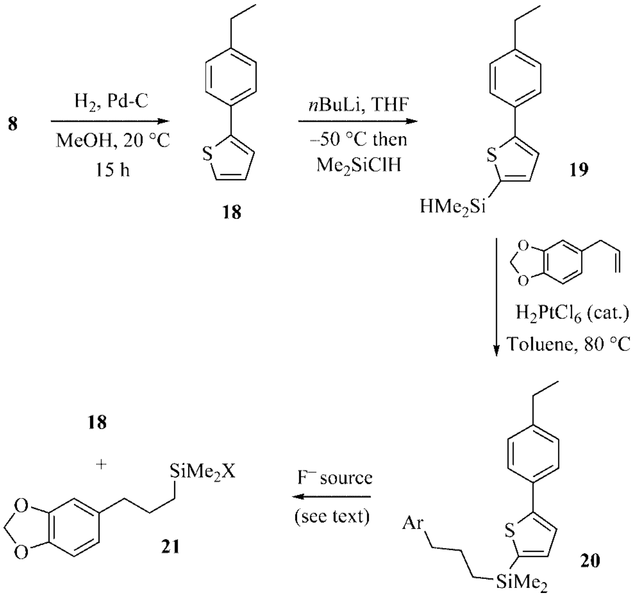
Table 3. Solid-support synthesis of alcohol **17** (see Scheme 9).

Entry	Support	DS of supported silane [%][a]	Yield [%][b]
1	**4**	55	20
2	**5**	47	16
3	**9**	56	26
4	**10**	81	39

[a] DS calculated following ref.[19]. [b] Isolated yield.

In each case the support was recovered after desilylation under nucleophilic conditions (TBAF, DMF). These preliminary results confirm that our home-made polymer can be used for solid-phase synthesis.

As cleavage from the resin and oxidation of the silicon group are the key steps of the sequence, the use of sources of fluoride other than TBAF were evaluated using compound **20** as a model by estimating the yield of the arylthiophene **18** recovered after desilylation (Scheme 10). Most of the fluoride sources tested led to high yields of **18**. Note that TBAF gave similar results in THF and DMF (1.45 h and 1.5 h at 20 °C and 83 and 91% yields, respectively) and led to a faster reaction than CsF in DMF (20 °C). $nBu_4N(SnPh_3F_2)$[31] in THF and $(Me_2N)_3S(Me_3SiF_2)$ (TAS-F)[32] in DMF reacted more slowly (22 h under reflux and 4.5 h at 20 °C, respectively) to provide **18** in 88 and 90% yields, respectively. HF/pyridine in THF led essentially to degradation. Therefore, TBAF in DMF at 20 °C appear to be the best conditions for the desilylation process in solid-support synthesis.



Scheme 10.

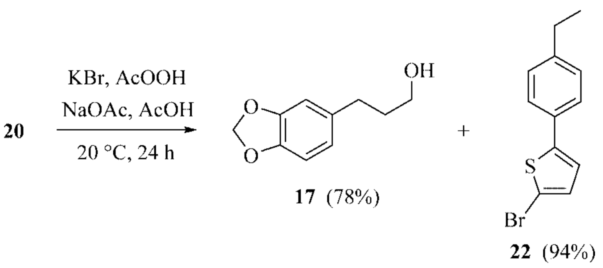
As mentioned above, oxidation of the C–Si bond occurs in two distinct steps: first, nucleophilic cleavage of the target

Table 4. Recycling of solid supports.

Entry	Support	Supported silane (1st cycle)		Supported silane (2nd cycle)	
		DS [%][a]	S [mmol g^{-1}][b]	DS [%][a]	S [mmol g^{-1}][b]
1	**4**	55	0.9	79	0.6
2	**5**	47	1.1	22	0.9
3	**9**	56	1.4	95	1.4
4	**10**	81	1.2	67	1

[a] DS calculated following ref.[19]. [b] Sulfur content estimated through elemental analysis.

molecule from the support, then oxidation of the organosilane in solution. Precedent in the laboratory has shown that these two steps may be carried out in a single pot under solution-phase conditions. Unfortunately, we have been unable to extend these conditions to the solid-phase synthesis of **17**. It is also important to mention that our efforts to oxidize the C–Si bond under electrophilic "one-pot" conditions[10] have also failed under solid-phase conditions, while they provided excellent yields of alcohol **17** and bromide **22** when applied to model compound **20** (Scheme 11). This may be indicative of the difficulty of sterically hindered reagents such as bromine to access the reactive function (here the thiophene ring for an *ipso* substitution).



Scheme 11.

Recycling of the support was also studied by submitting the recovered polymers **4**, **5**, **9** and **10** to a second lithiation/silylation sequence. The results summarized in Table 4 indicate that a second lithiation did occur, demonstrating that our supports may be recycled. However, the level of incorporation of the silane (DS) varies from one support to another. For instance, in entries 2 and 4, the degree of substitution is lower on the second run. Elemental analysis of the support after the synthesis of alcohol **17** indicates that silicon content in the support is very low (0.07 mmol Si per g support), thus eliminating the hypothesis of an incomplete desilylation upon TBAF treatment. In contrast, partial degradation of the insoluble supports (entries 2 and 4) is likely as shown by the slightly lower sulfur content in the support after the second silylation. Finally, soluble supports **4** and **9** (entries 1 and 3) exhibit a higher incorporation of silicon after the second silylation with a slightly lower sulfur content. This surprising result is probably due to the sensitivity of the lithiation/silylation sequence toward moisture, leading to reproducibility problems.

Conclusions

In conclusion, we have prepared a series of soluble and insoluble supported organosilanes for solid-phase organic synthesis (SPOS). The high acidity of the thiophene ring allows easy metallation which leads to high levels of organosilane-functionalized intermediates, in contrast to the low degree of substitution found in polystyrene-based polymers. The thiophene ring also allows cleavage of the product from the resin under mild nucleophilic conditions (TBAF). We also report here the first application of the Tamao–Fleming oxidation reaction to selectively cleave and subsequently oxidize an organosilane supported on a polymeric matrix. Release of the product under oxidative conditions not only leads to an additional hydroxy group, but also allows the support to be recycled. Finally, we have been able to incorporate functionalized organosilanes onto the polymer support using a short one-pot sequence (route **B**).[33] This considerably extends the number of supported organosilanes that are available, the variability of the substituents on the silicon centre leading to further applications of this strategy in polymer-supported organic synthesis. Functionalization of these supports is currently underway and will be reported in due course.

Experimental Section

General Remarks: NMR analyses were carried out with Bruker AC-200 FT (200 MHz for proton, 50.4 MHz for carbon), Bruker AC-250 FT (250 MHz for proton, 63 MHz for carbon) and Bruker DPX-300 (300 MHz for proton, 75.5 MHz for carbon) spectrometers using deuteriated chloroform as the solvent. The ^{1}H and ^{13}C chemical shifts (δ) are given relative to the internal reference (TMS) and are expressed in ppm. The coupling constants (J) are expressed in Hertz. The following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quadruplet), dd (doublet of doublets), m (multiplet) and br. ("broad peak"). Gas chromatography was carried out with a Hewlett Packard HP 4890A instrument. Some mass spectra (low resolution) were obtained using a Thermo Quest Finnigan Trace GC-MS apparatus with electronic impact ionization (ionization potential: 70 eV). Other mass spectra (low and high resolution) were obtained with a Micromass autospec-Q spectrometer. The electronic impact (ionization potential: 70 eV) and LSIMS modes [potential of ionization: 35 keV, matrix: (3-nitrophenyl) methanol] were used to achieve ionization. IR spectra were obtained with a Perkin–Elmer Paragon 1000 FT-IR spectrometer as a liquid film on NaCl crystal or as a powder with KBr. The wavelengths (ν) are expressed in cm^{-1}. Elemental analyses were performed by the Service Central d'Analyses, Vernaison, France; results are expressed in weight percent (wt.-%). The sulfur content in the polymer is denoted as S_{cont} and given in mmol S per g. The silicon content in the polymer is denoted as Si_{cont} and given in mmol Si per g.

1-(2-Thienyl)-2-(trimethylsilyl)ethanol (2): Magnesium turnings (2.85 g, 117.3 mmol) were placed in a dry three-necked flask equipped with a reflux condenser, a thermometer, an inlet for nitrogen and a septum. A few drops of a solution of (chloromethyl) dimethylsilane (13.62 mL, 97.6 mmol) in diethyl ether (57 mL) were added. The reaction was initiated by adding few drops of 1,2-dibromoethane and gentle heating. After (chloromethyl)dimethylsilane in diethyl ether had been added, the mixture was refluxed for 1 h and then cooled to 0 °C. Thiophene-2-carbaldehyde (**1**) (8 mL, 85.6 mmol) in diethyl ether (86 mL) was slowly added. The mixture was stirred at 0 °C for 3 hours, then at room temperature for 18 hours. After quenching with a saturated solution of NH$_4$Cl, the aqueous layer was extracted with diethyl ether. The combined extracts were washed with saturated solutions of NaHCO$_3$ and NaCl, dried with MgSO$_4$ and the solvents evaporated under vacuum to afford **2** as a yellow oil (16.1 g, 94%). IR (film, NaCl): $\tilde{\nu}$ = 3362, 2952, 2895, 1439, 1416, 1314, 1248, 1202, 1175, 1038, 1014, 976, 947, 846, 697 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.23 (dd, J = 1.2, 4.9 Hz, 1 H, H$_{\text{arom}}$), 6.97–6.92 (m, 2 H, H$_{\text{arom}}$), 5.11 (m, 1 H, CH), 1.88 (d, J = 4.3 Hz, 1 H, OH), 1.32 (dd, J = 4.3, 7.3 Hz, 2 H, CH$_2$), –0.03 (s, 9 H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ = 151.0 (CH$_{\text{arom}}$), 126.4 (CH$_{\text{arom}}$), 124.5 (CH$_{\text{arom}}$), 123.3 (CH$_{\text{arom}}$), 68.3 (CH), 28.9 (CH$_2$), –1.24 (CH$_3$) ppm.

2-Vinylthiophene (3):[16] A 1 M aqueous solution of HCl (62 mL, 62 mmol) was added to a solution of **2** (6.23 g, 31.2 mmol) in diethyl ether (15.5 mL). The biphasic solution was vigorously stirred at room temperature for 1.5 h. The layers were separated and the aqueous layer was extracted with diethyl ether. The combined extracts were washed with a saturated solution of NaHCO$_3$, dried with MgSO$_4$ and the solvent evaporated. The yellow crude product was distilled under reduced pressure to afford **3** as a colorless oil (2.41 g, 71%, two steps). IR (film, NaCl): $\tilde{\nu}$ = 3088, 2954, 1795, 1621, 1519, 1440, 1406, 1240, 1201, 1046, 977, 897, 851, 828, 699 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.17 (m, 1 H, H$_{\text{arom}}$), 6.97 (m, 2 H, H$_{\text{arom}}$), 6.82 (dd, J = 11.0, 17.4 Hz, 1 H, CH=CH$_2$), 5.57 (d, J = 17.4 Hz, 1 H, =CH$_2$), 5.15 (d, J = 11 Hz, 1 H, =CH$_2$) ppm. ^{13}C NMR (CDCl$_3$): δ = 143.0 (C$_{\text{q,arom}}$), 129.8 (CH=CH$_2$), 127.3 (CH$_{\text{arom}}$), 125.7 (CH$_{\text{arom}}$), 124.3 (CH$_{\text{arom}}$), 113.2 (=CH$_2$) ppm.

Soluble Support Styrene/2-Vinylthiophene (4): 2-Vinylthiophene (4 g, 36.4 mmol) and AIBN (1.8 g, 11 mmol) were added to a solution of styrene (32 g, 307.7 mmol) in toluene (216 mL). The solution was degassed and stirred for 3 days at 80 °C. The solvent was then evaporated. The residue was dissolved in THF, precipitated in cold methanol (–30 °C) and the filtered to afford the copolymer styrene/2-vinyl-thiophene **4** as a pale yellow solid (15.71 g, 44%). IR (solution, CH$_2$Cl$_2$): $\tilde{\nu}$ = 3082, 3060, 3026, 2925, 2850, 1601, 1493, 1453, 1266, 1029, 909, 737, 699, 539 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.50–6.10 (br., H$_{\text{arom}}$), 2.80–0.70 (br., CH and CH$_2$) ppm. S$_{\text{cont}}$ = 3.61 (1.1 mmol S per g).

Insoluble Support Styrene/2-Vinylthiophene/Divinylbenzene (5): Perfluorooctane (PFO, 160 mL) was placed in a double-coated reactor equipped with a mechanical stirrer. An organic phase consisting of styrene (13.68 g, 131.6 mmol), 2-vinylthiophene **3** (1.83 g, 16.6 mmol), divinylbenzene (491 mg, 3 mmol), AIBN (800 mg, 4.9 mmol) and dodecylbenzenesulfonic acid, sodium salt [DBSA, 320 mg (200 mg DBSA per 100 mL PFO)] was added to PFO. The mixture was polymerized at 80 °C for 24 h whilst stirring at a speed of 700 rounds per minute. The resulting beads were placed in a Soxhlet apparatus and washed with THF for 24 h. They were then dried under vacuum to afford resin **5** as yellow beads (9.71 g, 61%). IR (KBr): $\tilde{\nu}$ = 3025, 2923, 2850, 1601, 1493, 1452, 1068, 1028, 758, 698, 538 cm^{-1}. S$_{\text{cont}}$ = 3.52 (1.1 mmol S per g).

Styrene/Dimethyl(5-vinyl-2-thienyl)silane (6a): A solution of copolymer styrene/2-vinylthiophene **4** (1.01 g, 0.87 mmol functions of S) in THF (23 mL) was placed in a dry three-necked flask equipped with a magnetic stirrer, a thermometer, an inlet for nitrogen and a septum. This solution was cooled to –50 °C. A 2.5 M solution of *n*BuLi in hexanes (1.03 mL, 2.6 mmol) was slowly added. The resulting red-brown solution was stirred at –50 °C for 2 h. 1,1,3,3-Tetramethyldisiloxane (0.46 mL, 2.6 mmol) was then added. The resulting mixture was allowed to warm slowly. After evaporation of the solvent, the residue was dissolved in THF, precipitated in cold methanol (–30 °C) and filtered to afford the copolymer **6a** as a pale yellow solid (789 mg, DS = 55%). IR (solution, CH$_2$Cl$_2$): $\tilde{\nu}$ = 3082, 3060, 3026, 2925, 2851, 2123 (SiH), 1601, 1493, 1452, 1265, 875, 759, 739, 699, 539 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.50–5.80 (br., H$_{\text{arom}}$), 4.51 (br., SiH), 2.70–0.50 (br., CH and CH$_2$), 0.35 (br., CH$_3$) ppm. Si$_{\text{cont}}$ = 1.30 (0.5 mmol Si per g).

Styrene/Allyldimethyl(5-vinyl-2-thienyl)silane (6b): Following the general procedure described above for the preparation of **6a**, copolymer **6b** was obtained from **4** (1.104 g, 0.95 mmol functions of S) as a pale yellow solid (953 mg, DS = 64%). IR (solution, CH$_2$Cl$_2$): $\tilde{\nu}$ = 3082, 3060, 3026, 2930, 2851, 1629 (C=C allylsilane), 1601, 1493, 1453, 1266, 1029, 739, 698, 539 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.70–5.80 (br., H$_{\text{arom}}$), 5.77 (br., =CH), 4.88 (br., =CH$_2$), 2.80–0.60 (br., CH and CH$_2$), 0.26 (br., CH$_3$) ppm. Si$_{\text{cont}}$ = 1.45 (0.5 mmol Si per g).

Styrene/Dimethyl(vinyl)(5-vinyl-2-thienyl)silane (6c): Following the general procedure described above for the preparation of **6a**, copolymer **6c** was obtained from **4** (6.09 g, 10.3 mmol functions of S) as a pale yellow solid (6.86 g, DS = 71%). IR (solution, CH$_2$Cl$_2$): $\tilde{\nu}$ = 3417, 3082, 3060, 3026, 2926, 2851, 1601, 1493, 1453, 1265, 1249, 837, 813, 776, 761, 739, 699 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.60–5.50 (br., H$_{\text{arom}}$, =CH and =CH$_2$), 3.10–0.60 (br., CH and CH$_2$), 0.34 (br., CH$_3$) ppm. Si$_{\text{cont}}$ = 3.09 (1.1 mmol Si per g).

Supported Reagent Styrene/Dimethyl(5-vinyl-2-thienyl)silane (7): Some beads of resin **5** (2.05 g, 2.2 mmol functions of S) were suspended in THF (56 mL) in a dry three-necked flask equipped with a magnetic stirrer, a thermometer, an inlet for nitrogen and a septum. The suspension was cooled to –50 °C. A 1.97 M solution of *n*BuLi in hexanes (1.62 mL, 3.2 mmol) was slowly added. The mixture was stirred at –50 °C for 2 h and then 1,1,3,3-tetramethyldisiloxane (0.56 mL, 3.2 mmol) was added. The suspension was allowed to warm slowly to room temperature over 15 h. After filtration, the beads were washed with THF and then dried under vacuum to afford resin **7** as orange beads (2.075 g, DS = 47%). IR (KBr): $\tilde{\nu}$ = 3026, 2924, 2851, 2122 (SiH), 1601, 1493, 1452, 1068, 1029, 759, 698, 539 cm^{-1}. Si$_{\text{cont}}$ = 1.40 (0.5 mmol Si per g).

2-(4-Vinylphenyl)thiophene (8):[21] THF (114 mL), thiophene (3.67 mL, 45.9 mmol) and TMEDA (6.92 mL, 45.9 mmol) were placed in a dry three-necked flask equipped with a magnetic stirrer, a thermometer, an inlet for nitrogen and a septum. The solution was cooled to 0 °C. A 2.5 M solution of *n*BuLi in hexanes (18.36 mL, 45.9 mmol) was added dropwise. The resulting yellow mixture was stirred at room temperature for 2 h. Zinc chloride (7.81 g, 57.4 mmol) and THF (114 mL) were placed in another three-necked flask equipped with a magnetic stirrer, a refluxing condenser, an inlet for nitrogen and a septum. The 2-thienyllithium solution was slowly added to this mixture. The solution was refluxed for 1 h and then cooled to room temperature. Tetrakis(triphenylphosphane)palladium (265 mg, 0.23 mmol), *p*-bromostyrene (3 mL, 22.9 mmol) and THF (57 mL) were placed in another three-necked flask equipped with a magnetic stirrer, a refluxing condenser, an inlet for nitrogen and a septum. The 2-thienylzinc chloride solution was slowly added to this mixture and the solution was refluxed for 15 h. After cooling, the solution was poured into a saturated solution of NH_4Cl (150 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with water (2 × 60 mL), 10% HCl (3 × 60 mL) and a saturated solution of NaCl (2 × 60 mL). The organic layer was dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography through silica gel (petroleum ether) to afford **8** as a white solid (3.11 g, 73%). R_f (petroleum ether) = 0.43. M.p. 107–108 °C. IR (KBr): ṽ = 3442, 3070, 3000, 1626, 1499, 1428, 1406, 1122, 991, 905, 852, 843, 822, 694 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.62 (d, J = 8.2 Hz, 2 H, H_{arom}), 7.46 (d, J = 8.2 Hz, 2 H, H_{arom}), 7.36 (d, J = 3.0 Hz, 1 H, H_{arom}), 7.31 (d, J = 4.9 Hz, 1 H, H_{arom}), 7.13 (d, J = 3.6 Hz, 1 H, H_{arom}), 6.77 (dd, J = 11.0, 17.7 Hz, 1 H, =CH), 5.82 (d, J = 17.4 Hz, 1 H, =C*H*H′), 5.31 (d, J = 11 Hz, 1 H, =CH*H′*) ppm. ^{13}C NMR ($CDCl_3$): δ = 144.0 (thiophene C_q), 136.6 (phenyl C_q), 136.2 (vinylic CH), 133.7 (phenyl C_q), 128.0 (thiophene CH), 126.6 (phenyl CH), 125.9 (phenyl CH), 124.8 (thiophene CH), 123.0 (thiophene CH), 113.8 (vinylic CH_2) ppm. MS (EI): *m*/*z* (%) = 188 (5), 187 (13), 186 (100), 184 (14), 171 (6), 152 (11), 115 (10), 93 (6), 63 (3). $C_{12}H_{10}S$ (186.28): calcd. C 77.38, H 5.41, S 17.21; found C 77.33, H 5.24, S 17.60.

Synthesis of Soluble Support Styrene/2-(4-Vinylphenyl)thiophene (9): Compound **8** (514 mg, 2.8 mmol) and AIBN (104 mg, 0.63 mmol) were added to a solution of styrene (1.56 g, 15 mmol, 1 equiv.) in toluene (11 mL). The solution was degassed and stirred for 3 days at 80 °C. The solvent was then evaporated. The residue was dissolved in THF, precipitated in cold methanol (–30 °C) and filtered to afford the copolymer **9** as a pale yellow solid (1.32 g, 64%). IR (solution, CH_2Cl_2): ṽ = 3083, 3060, 3026, 2925, 2851, 1601, 1493, 1452, 1028, 820, 758, 699 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.80–5.90 (br., H_{arom}), 2.80–0.50 (br., CH and CH_2) ppm. S_{cont} = 4.30 (1.3 mmol S per g).

Insoluble Support Styrene/2-(4-Vinylphenyl)thiophene/Divinylbenzene (10): An aqueous solution of water (350 mL), acacia powder (14 g) and sodium chloride (8.8 g) was placed in a double-coated reactor equipped with a mechanical stirrer. An organic phase consisting of styrene (7.96 g, 76.5 mmol), 2-(4-vinylphenyl)thiophene (1.8 g, 9.7 mmol), divinylbenzene (286 mg, 1.8 mmol) and AIBN (502 mg, 3.1 mmol) was suspended in the aqueous solution. The mixture was polymerized at 80 °C for 24 h whilst stirring at a speed of 600 rounds per minute with a magnetic stirrer. The resulting beads were placed in a Soxhlet apparatus and were washed with THF for 24 h. They were then dried under vacuum to afford resin **10** as yellow beads (6.36 g, 63%). IR (KBr): ṽ = 3025, 2922, 2850, 1601, 1493, 1452, 1067, 1028, 819, 757, 698, 541 cm^{-1}. S_{cont} = 4.47 (1.4 mmol S per g).

Styrene/Dimethyl[5-(4-vinylphenyl)-2-thienyl]silane (11a): A solution of copolymer **9** (1.051 g, 1.4 mmol functions of S, 1 equiv.) in THF (37 mL) was placed in a dry three-necked flask equipped with a magnetic stirrer, a thermometer, an inlet for nitrogen and a septum. This solution was then cooled to –50 °C. A 2.5 M solution of *n*BuLi in hexanes (0.84 mL, 2.1 mmol, 1.5 equiv.) was slowly added. The resulting red-brown solution was stirred at –50 °C for 2 h and then 1,1,3,3-tetramethyldisiloxane (0.37 mL, 2.1 mmol, 1.5 equiv.) was added. The resulting mixture was allowed to warm slowly to room temperature. After evaporation of the solvent, the residue was dissolved in THF, precipitated in cold methanol (–30 °C) and filtered to afford the copolymer **11a** as a brown solid (975 mg, DS = 56%). IR (solution, CH_2Cl_2): ṽ = 3419, 3025, 2925, 2125 (SiH), 1601, 1493, 1452, 1253, 1074, 1000, 874, 760, 699 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.80–5.90 (br., H_{arom}), 4.61 (br., SiH), 2.80–0.60 (br., CH and CH_2), 0.44 (br., CH_3) ppm. Si_{cont} = 2.02 (0.7 mmol Si per g).

Styrene/Allyldimethyl[5-(4-vinylphenyl)-2-thienyl]silane (11b): Following the general procedure described above for the preparation of **11a**, copolymer **11b** was obtained from **9** (1.408 g, 1.8 mmol functions S, 1 equiv.) as a brown solid (1.45 g, DS = 93%). IR (solution, CH_2Cl_2): ṽ = 3419, 3026, 2924, 1629 (C=C allylsilane), 1601, 1493, 1452, 1265, 1250, 996, 835, 803, 758, 739, 699 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.80–6.05 (br., H_{arom}), 5.83 (br., =CH), 4.90 (br., =CH_2), 2.90–0.60 (br., CH and CH_2), 0.37 (br., CH_3) ppm. Si_{cont} = 3.10 (1.1 mmol Si per g).

Styrene/Dimethyl[5-(4-vinylphenyl)-2-thienyl]silane (12a) Following Route A: Beads of resin **10** (624 mg, 0.66 mmol functions S) were suspended in THF (17 mL) in a dry three-necked flask equipped with a magnetic stirrer, a thermometer, an inlet for nitrogen and a septum. TMEDA (0.4 mL, 2.6 mmol) was then added to the suspension. The mixture was then cooled to –50 °C. A 1.9 M solution of *n*BuLi in hexanes (1.39 mL, 2.6 mmol) was slowly added. The resulting mixture was stirred at –50 °C for 2 h and then 1,1,3,3-tetramethyldisiloxane (0.47 mL, 2.7 mmol) was added. The suspension was allowed to warm slowly to room temperature over 15 h. After filtration, the beads were washed with THF and then dried under vacuum to afford resin **12a** as yellow beads (683 mg, DS = 85%). IR (KBr): ṽ = 3025, 2922, 2855, 2123 (SiH), 1601, 1493, 1452, 1251, 1069, 1028, 999, 873, 757, 697, 538 cm^{-1}. Si_{cont} = 2.41 (0.9 mmol Si per g).

Styrene/Allyldimethyl[5-(4-vinylphenyl)-2-thienyl]silane (12b). Route A: Following the general procedure described above for the preparation of **12a**, polymer **12b** was obtained from resin **10** (1.092 g, 1.5 mmol functions of S) and allylchlorodimethylsilane (0.33 mL, 2.3 mmol) as yellow beads (1.19 g, DS = 82%). IR (KBr): ṽ = 3025, 2923, 2852, 1629 (C=C allylsilane), 1601, 1493, 1452, 1069, 1028, 996, 820, 800, 757, 698, 542 cm^{-1}. Si_{cont} = 2.88 (1 mmol Si per g).

Styrene/Allyldiphenyl[5-(4-vinylphenyl)-2-thienyl]silane (12c). Route B: Beads of resin **10** (1.115 g, 1.4 mmol functions of S) were suspended in THF (37 mL) in a dry three-necked flask equipped with a magnetic stirrer, a thermometer, an inlet for nitrogen and a septum. The suspension was then cooled to –50 °C and a 1.9 M solution of *n*BuLi in hexanes (2.98 mL, 5.7 mmol) was slowly added. The resulting mixture was stirred at –50 °C for 2 h and then allowed to warm rapidly to 10 °C. The beads turned dark green. These were washed with THF (3 × 10 mL) under an inert atmosphere. The beads were then suspended in THF (37 mL) and cooled to –50 °C and dichlorodiphenylsilane (1.19 mL, 5.7 mmol) was added. This mixture was stirred at –50 °C for 1 h and then allowed to warm rapidly to 10 °C. The beads turned orange and were washed with THF (3 × 10 mL) under an inert atmosphere. The beads were then suspended in THF (37 mL) and cooled to –50 °C. Then a 1 M solution of allylmagnesium bromide in diethyl ether (5.7 mL, 5.7 mmol) was added. The resulting mixture was stirred at –50 °C for 0.5 h and then allowed to warm slowly to room temperature over 15 h. The formation of salts was observed and the beads turned brown. After filtration, the beads were washed with THF and then dried under vacuum to afford resin **12c** as dark brown beads (1.403 g, DS = 60%). IR (KBr): ṽ = 3023, 2921, 1628 (C=C allylsilane), 1600, 1492, 1452, 1428, 1111, 1067, 1028, 997, 759, 698, 534 cm^{-1}. Si_{cont} = 1.83 (0.7 mmol Si per g).

Styrene/Diphenyl(4-phenylbuta-1,3-dienyl)[5-(4-vinylphenyl)-2-thienyl]silane (12d): Following the general procedure described above for the preparation of **12c**, polymer **12d** was obtained from resin **10** (1.104 g, 1.4 mmol functions of S), dichlorodiphenylsilane (1.18 mL, 5.6 mmol) and 4-phenylbuta-1,3-dienyllithium as green beads (1.325 g, DS = 55%). IR (KBr): ṽ = 3023, 2920, 1653, 1635, 1600, 1492, 1452, 1429, 1112, 1067, 1028, 757, 698, 536, 517 cm^{-1}. Si$_{cont}$ = 1.60 (0.6 mmol Si per g).

Styrene/Cyclopenta-2,4-dienyldiphenyl[5-(4-vinylphenyl)-2-thienyl]silane (12e): Beads of resin **10** (1.113 g, 1.4 mmol functions S) were suspended in THF (37 mL) in a dry three-necked flask equipped with a magnetic stirrer, a thermometer, an inlet for nitrogen and a septum. The suspension was cooled to –50 °C and then a 2.22 M solution of *n*BuLi in hexanes (2.55 mL, 5.6 mmol) was slowly added. The mixture was stirred at –50 °C for 2 h and then allowed to warm rapidly to 10 °C. The beads turned dark green. They were washed with THF (3 × 10 mL) under an inert atmosphere, then suspended in THF (37 mL) and cooled to –50 °C. Then dichlorodiphenylsilane (1.19 mL, 5.6 mmol) was added. The resulting mixture was stirred at –50 °C for 1 h and then allowed to warm rapidly to 10 °C. The beads turned orange. They were washed with THF (3 × 10 mL) under an inert atmosphere. The beads were then suspended in THF (20 mL) and cooled to –78 °C and a solution of cyclopentadienyllithium in THF was added [5.6 mmol; prepared from freshly distilled cyclopentadiene (0.46 mL, 5.6 mmol) and a 2.22 M solution of *n*BuLi in hexanes (2.82 mL, 6.3 mmol) in THF (16.9 mL) at –78 °C for 1 h]. The resulting mixture was stirred at –78 °C for 1 h and then allowed to warm slowly to room temperature over 15 h. After filtration, the beads were washed with THF and dried under vacuum to afford resin **12e** as brown beads (1.384 g, DS = 63%). IR (KBr): $\tilde{\nu}$ = 3024, 2922, 1630 (C=C allylsilane), 1601, 1493, 1452, 1429, 1112, 1067, 1028, 998, 757, 698, 537 cm^{-1}. Si$_{cont}$ = 1.88 (0.7 mmol Si per g).

4-Phenylbuta-1,3-dienyllithium (13):[26b] THF (5.05 mL) and dicyclohexylamine (1.26 mL, 6.3 mmol) were placed in a dry three-necked flask equipped with a thermometer, an inlet for nitrogen and a septum. The solution was then cooled to –78 °C and a 1.85 M solution of *n*BuLi in hexanes (3.43 mL, 6.3 mmol) was slowly added. The mixture turned yellow and was stirred at –78 °C for 15 min. THF (3.8 mL), dibromomethane (0.45 mL, 6.3 mmol) and cinnamaldehyde (0.4 mL, 3.2 mmol) were placed in another dry three-necked flask equipped with a thermometer, an inlet for nitrogen and a septum. The resulting solution was cooled to –78 °C and the solution of lithium dicyclohexylamide was added slowly to the second solution. The mixture turned yellow, then orange and was stirred at –78 °C for 1.5 h. The reaction mixture was then quenched with a 10% aqueous solution of HCl (5 mL) at –78 °C. After filtration, the aqueous phase was extracted with diethyl ether (3 × 5 mL) and the combined organic phases were washed with a saturated solution of NaCl (3 × 15 mL), dried with MgSO$_4$ and concentrated under vacuum. The residue was purified by chromatography through silica gel (petroleum ether/EtOAc, 92:8) to afford 1,1-dibromo-4-phenylbut-3-en-2-ol as a yellow oil (429 mg, 44%). R_f (petroleum ether/EtOAc, 9:1) = 0.21. IR (film, NaCl): $\tilde{\nu}$ = 3396 (OH), 3058, 3026, 1651, 1494, 1449, 1150, 1071, 1028, 966, 752, 718, 693 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.37–7.19 (m, 5 H, H$_{arom}$), 6.73 (d, *J* = 15.8 Hz, 1 H, Ph-C*H*=), 6.23 (dd, *J* = 6, 15.8 Hz, 1 H, =C*H*-CHOH), 5.66 (d, *J* = 3.7 Hz, 1 H, CHBr$_2$), 4.52 (m, 1 H, C*H*OH) ppm. ^{13}C NMR (CDCl$_3$): δ = 135.8 (C$_{q,arom}$), 134.8 (Ph-*C*H=), 128.7 (CH$_{arom}$), 128.4 (CH$_{arom}$), 126.8 (CH$_{arom}$), 125.4 (=*C*H-CHOH), 77.2 (CHOH), 51.4 (CHBr$_2$) ppm. Activated zinc (4.18 g, 63.9 mmol) was added to a solution of this alcohol (3.9 g, 12.8 mmol) in dichloromethane (41 mL). The resulting mixture was cooled to 0 °C and acetic acid (2.93 mL, 51.1 mmol) was slowly added. The solution was stirred vigorously at room temperature for 21 h. Water (5 mL) and K$_2$CO$_3$ were added until the pH = 7. After filtration, the aqueous phase was extracted with CH$_2$Cl$_2$. The organic layer was dried with MgSO$_4$ and concentrated under vacuum. The residue was purified by chromatography through silica gel (petroleum ether) to afford (4-bromobuta-1,3-dienyl)benzene as a yellow solid (984 mg, 37%). R_f (petroleum ether) = 0.41. ^{1}H NMR (CDCl$_3$): δ = 7.60–6.10 (m, 9 H). ^{13}C NMR (CDCl$_3$): δ = 137.6, 136.6 (C$_{q,arom\text{–}E}$), 136.5 (C$_{q,arom\text{–}Z}$), 136.0 (s), 133.3 (s), 132.7 (s), 128.7 (s), 128.3 (s), 128.0 (s), 126.8 (s), 126.5 (s), 126.0 (s), 124.3 (s), 108.9 (s, =CHBr-*E*), 108.5 (s, =CHBr-*Z*) ppm. This dienyl bromide (0.73 g, 3.5 mmol) and diethyl ether (24 mL) were placed in a dry three-necked flask equipped with a thermometer, an inlet for nitrogen and a septum. The yellow solution was cooled to –90 °C and a 1.38 M solution of *t*BuLi in pentane (5.07 mL, 7 mmol) was slowly added. The mixture turned dark brown and was stirred at –90 °C for 1.5 h to afford crude 4-phenylbuta-1,3-dienyllithium, which was used directly in the preparation of **12d**.

Styrene/(3-Benzo[1,3]dioxol-5-ylpropyl)dimethyl(5-vinyl-2-thienyl)silane (15a): Safrole (0.44 mL, 3 mmol) and a 10% solution of hexachloroplatinic acid (75 µL) were added to a solution of copolymer **6a** (677 mg, 0.3 mmol functions of Si) in toluene (35 mL). The resulting mixture was heated at 80 °C until completion of the reaction. The reaction was monitored by IR spectroscopy (disappearance of the Si–H band at 2114 cm^{-1}). After evaporation of the solvent, the residue was dissolved in THF, precipitated in cold methanol (–30 °C) and filtered to afford copolymer **15a** as a grey solid (633 mg). IR (solution, CH$_2$Cl$_2$): $\tilde{\nu}$ = 3027, 2921, 1698, 1602, 1494, 1454, 1368, 1265, 1069, 1029, 909, 746, 697 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.80–5.90 (br., H$_{arom}$), 5.87 (br., OCH$_2$O), 2.70–0.20 (br., CH, CH$_2$, CH$_3$) ppm.

Styrene/(3-Benzo[1,3]dioxol-5-ylpropyl)dimethyl(5-vinyl-2-thienyl)silane (15b): Safrole (1.2 mL, 8.1 mmol) and a 10% solution of hexachloroplatinic acid (105 µL) were added to a suspension of beads of resin **7** (1.556 g, 0.78 mmol functions of Si) in toluene (43 mL). The mixture was stirred at 80 °C for 24 h. After filtration, the beads were washed with THF and then dried under vacuum to afford resin **15b** as brown beads (1.596 g). IR (KBr): $\tilde{\nu}$ = 3026, 2923, 2851, 1602, 1493, 1452, 1249, 1068, 1029, 907, 803, 758, 698, 539 cm^{-1}.

Styrene/(3-Benzo[1,3]dioxol-5-ylpropyl)dimethyl[5-(4-vinylphenyl)-2-thienyl]silane (15c): Safrole (0.93 mL, 6.3 mmol) and a 10% solution of hexachloroplatinic acid (127 µL) were added to a solution of copolymer **11a** (936 mg, 0.67 mmol functions of Si) in toluene (33 mL). The resulting mixture was stirred at 80 °C until completion of the reaction. The reaction was monitored by IR spectroscopy (disappearance of the Si–H band at 2126 cm^{-1}). After evaporation of the solvent, the residue was dissolved in THF, precipitated in cold methanol (–30 °C) and filtered to afford the copolymer **15c** as a grey solid (954 mg). IR (solution, CH$_2$Cl$_2$): $\tilde{\nu}$ = 3026, 2925, 1601, 1492, 1452, 1264, 1250, 1073, 1040, 999, 804, 759, 737, 700 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.75–6.05 (br., H$_{arom}$), 5.88 (br., OCH$_2$O), 2.90–0.10 (br., CH, CH$_2$, CH$_3$) ppm.

Styrene/(3-Benzo[1,3]dioxol-5-ylpropyl)dimethyl[5-(4-vinylphenyl)-2-thienyl]silane (15d): Safrole (0.73 mL, 4.9 mmol) and a 10% solution of hexachloroplatinic acid (120 µL) were added to a suspension of beads of resin **12a** (893 mg, 0.83 mmol functions of Si) in toluene (26 mL). The mixture was stirred at 80 °C for 24 h. After filtration, the beads were washed with THF and then dried under vacuum to afford resin **15d** as brown beads (954 mg). IR (KBr): $\tilde{\nu}$ = 3025, 2922, 2850, 1601, 1493, 1452, 1250, 1069, 1029, 999, 819, 803, 757, 698, 540 cm^{-1}.

(3-Benzo[1,3]dioxol-5-ylpropyl)dimethylsilanol (16) from 15a: A 1 M solution of TBAF in THF (1.1 mL, 1.1 mmol) was added to a solution of copolymer **15a** (617 mg) in DMF (3.9 mL). The mixture was stirred at room temperature for 24 h. After evaporation of the solvent, the residue was dissolved in THF, precipitated in cold methanol (–30 °C) and filtered to afford the copolymer **4**. The filtrate was evaporated, dissolved in EtOAc and then washed with water. The organic layer was dried with $MgSO_4$ and concentrated under vacuum to afford silanol **16** as a brown oil (76 mg), which used in the next step without further purification. R_f (petroleum ether/EtOAc, 98:2) = 0.14. IR (film, NaCl): $\tilde{\nu}$ = 2953, 2925, 1503, 1490, 1443, 1251, 1188, 1042, 938, 839, 801 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 6.68 (m, 3 H, H_{arom}), 5.92 (s, 2 H, OCH_2O), 2.54 (t, J = 7.6 Hz, 2 H, CH_2Ar), 1.59 (m, 2 H, CH_2-CH_2-CH_2), 0.54 (m, 2 H, $SiCH_2$), 0.04 (s, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 147.4 ($C_{q,arom}$), 145.4 ($C_{q,arom}$), 136.6 ($C_{q,arom}$), 121.1 (CH_{arom}), 108.9 (CH_{arom}), 108.0 (CH_{arom}), 100.6 (OCH_2O), 39.3 (CH_2Ar), 25.6 (CH_2-CH_2-CH_2), 18.0 ($SiCH_2$), 0.3 (s, CH_3) ppm.

[3-(Benzo[1,3]dioxol-5-yl)propyl]dimethylsilanol (16) from 15b: Following the general procedure described above for the preparation of **16** from **15a**, treatment of resin **15b** (1.563 g) with a 1 M solution of TBAF in THF (1.7 mL, 1.7 mmol) afforded silanol **16** as a brown oil (204 mg).

16 from 15c: Following the general procedure described above for the preparation of **16** from **15a**, treatment of copolymer **15c** (950 mg) with a 1 M solution of TBAF in THF (1.3 mL, 1.3 mmol) afforded silanol **16** as a brown oil (192 mg).

16 from 15d: Following the general procedure described above for the preparation of **16** from **15a**, treatment of resin **15d** (940 mg) with a 1 M solution of TBAF in THF (1.2 mL, 1.2 mmol) afforded silanol **16** as a brown oil (124 mg).

(3-Benzo[1,3]dioxol-5-yl)propan-1-ol (17):[30] A mixture of silanol **16** (192 mg, 0.8 mmol), potassium fluoride (221 mg, 3.8 mmol) and potassium hydrogencarbonate (381 mg, 3.8 mmol) was placed under nitrogen in a round flask. DMF (9.3 mL) was added. This mixture was cooled to 0 °C and a 35% aqueous solution of H_2O_2 (2.22 mL, 25.4 mmol) was slowly added and the resulting solution stirred at 60 °C for 24 h. The reaction was quenched with solid sodium thiosulfate. After evaporation of the solvent, the residue was dissolved in EtOAc and washed with water. The organic phase was dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography through silica gel (petroleum ether/EtOAc, 7:3) to afford alcohol **17** as a pale yellow oil (56 mg, 24%, four steps). R_f (petroleum ether/EtOAc, 7:3) = 0.34. ^1H NMR ($CDCl_3$): δ = 6.69 (m, 3 H, H_{arom}), 5.92 (s, 2 H, OCH_2O), 3.66 (t, J = 6.4 Hz, 2 H, CH_2OH), 2.63 (t, J = 7.6 Hz, 2 H, CH_2Ar), 1.85 (m, 2 H, CH_2-CH_2-CH_2), 1.32 (s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 147.5 ($C_{q,arom}$), 145.5 ($C_{q,arom}$), 135.6 ($C_{q,arom}$), 121.0 (CH_{arom}), 108.8 (CH_{arom}), 108.1 (CH_{arom}), 100.7 (OCH_2O), 61.9 (CH_2OH), 34.3 (CH_2-CH_2-CH_2), 31.7 (CH_2Ar) ppm.

2-(4-Ethylphenyl)thiophene (18): A solution of 2-(4-vinylphenyl) thiophene (**8**) (1.15 g, 6.18 mmol, 1 equiv.) and palladium [10 wt.-% on activated carbon (1.15 g)] in methanol (12.5 mL) was vigorously stirred under hydrogen at room temperature for 15 h. After filtration through Celite, the residue was concentrated under vacuum. The residue was purified by chromatography through silica gel (petroleum ether) to afford **18** as a white solid (1.012 g, 87%). R_f (petroleum ether) = 0.44. M.p. 40–41 °C. IR (KBr): $\tilde{\nu}$ = 2960, 2926, 1501, 1429, 1119, 1053, 851, 819, 704 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.60 (d, J = 8.3 Hz, 2 H, H_{arom}), 7.31 (m, 4 H, H_{arom}), 7.13 (m, 1 H, H_{arom}), 2.73 (q, J = 7.5 Hz, 2 H, CH_2), 1.33 (t, J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 144.5 ($C_{q,arom}$), 143.6 ($C_{q,arom}$), 131.9 ($C_{q,arom}$), 128.3 (CH_{arom}), 127.9 (CH_{arom}), 125.9 (CH_{arom}), 124.2 (CH_{arom}), 122.6 (CH_{arom}), 28.5 (CH_2), 15.5 (CH_3) ppm. MS (EI): m/z (%) = 189 (5), 188 (42), 173 (100), 171 (9), 128 (16), 115 (16), 102 (7), 58 (10), 45 (12). $C_{12}H_{12}S$ (188.29): calcd. C 76.55, H 6.42, S 17.03; found C 75.92, H 6.58, S 16.99.

[5-(4-Ethylphenyl)-2-thienyl]dimethylsilane (19): A solution of 2-(4-ethylphenyl)thiophene (**18**) (230 mg, 1.2 mmol) in THF (2.5 mL) was placed in a dry three-necked flask equipped with a thermometer, an inlet for nitrogen and a septum and cooled to –50 °C. A 1.89 M solution of *n*BuLi in hexanes (0.72 mL, 1.4 mmol) was slowly added. The resulting mixture turned dark green then pale green. The solution was stirred at –50 °C for 2 h and then chlorodimethylsilane (0.2 mL, 1.8 mmol) was added. The solution was allowed to warm rapidly to 0 °C and turned yellow. The reaction was quenched with a saturated solution of NH_4Cl (5 mL). The aqueous layer was extracted with diethyl ether (3 × 5 mL) and the combined organic phases were washed with water (3 × 15 mL), dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography through silica gel (petroleum ether) to afford **19** as a white solid (235 mg, 78%). R_f (petroleum ether) = 0.51. M.p. 31 °C. IR (KBr): $\tilde{\nu}$ = 2963, 2125 (SiH), 1434, 1250, 1000, 951, 873, 833, 802, 766 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.55 (d, J = 8.2 Hz, 2 H, H_{arom}), 7.34 (d, J = 3.4 Hz, 1 H, H_{arom}), 7.23 (m, 3 H, H_{arom}), 4.59 (m, 1 H, SiH), 2.67 (q, J = 7.6 Hz, 2 H, CH_2), 1.27 (t, J = 7.6 Hz, 3 H, CH_3-CH_2), 0.42 [d, J = 3.7 Hz, 6 H, $Si(CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 150.5 ($C_{q,arom}$), 143.8 ($C_{q,arom}$), 136.1 (CH_{arom}), 135.5 ($C_{q,arom}$), 128.3 (CH_{arom}), 126.0 (CH_{arom}), 124.0 (CH_{arom}), 28.6 (CH_2), 15.5 (CH_3-CH_2), –2.8 [$Si(CH_3)_2$] ppm. MS (EI): m/z (%) = 247 (8), 246 (41), 231 (100), 205 (15), 188 (22), 173 (65), 171 (16), 128 (28), 115 (67), 89 (16), 77 (29), 58 (38), 43 (45), 40 (61). HRMS $C_{14}H_{18}SSi$: calcd. 246.0897; found 246.0898.

[3-(Benzo[1,3]dioxol-5-yl)propyl][5-(4-ethylphenyl)-2-thienyl]dimethylsilane (20): Safrole (0.75 mL, 5.1 mmol) and a 10% solution of hexachloroplatinic acid (0.11 mL) were added to a solution of **19** (1.236 g, 5 mmol) in toluene (10 mL) under an inert atmosphere. The solution was stirred at 80 °C for 3.5 h. After evaporation of the solvent, the residue was dissolved in EtOAc (40 mL) and washed with water (3 × 15 mL). The organic layer was dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography through silica gel (petroleum ether/EtOAc, 99:1) to afford **20** as a pale blue oil (325 mg, 16%). R_f (petroleum ether/EtOAc, 98:2) = 0.41. IR (film, NaCl): $\tilde{\nu}$ = 2962, 2927, 1502, 1489, 1443, 1249, 1107, 1041, 997, 950, 834, 804, 778 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.59 (d, J = 7.9 Hz, 2 H, H_{arom}), 7.37 (d, J = 3.4 Hz, 1 H, H_{arom}), 7.24 (m, 3 H, H_{arom}), 6.70 (m, 3 H, H_{arom}), 5.94 (s, 2 H, OCH_2O), 2.70 (q, J = 7.5 Hz, 2 H, CH_3-CH_2), 2.60 (t, J = 7.5 Hz, 2 H, CH_2-CH_2Ar), 1.71 (m, 2 H, CH_2-CH_2-CH_2), 1.30 (t, J = 7.5 Hz, 3 H, CH_3-CH_2), 0.86 (m, 2 H, $SiCH_2$), 0.37 [s, 6 H, $Si(CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 149.9 ($C_{q,arom}$), 147.4 ($C_{q,arom}$), 145.5 ($C_{q,arom}$), 143.6 ($C_{q,arom}$), 138.1 ($C_{q,arom}$), 136.3 ($C_{q,arom}$), 135.2 (s, CH_{arom}), 131.9 ($C_{q,arom}$), 128.3 (CH_{arom}), 126.0 (CH_{arom}), 123.9 (CH_{arom}), 121.2 (CH_{arom}), 108.9 (CH_{arom}), 108.0 (CH_{arom}), 100.6 (OCH_2O), 39.3 (CH_2-CH_2Ar), 28.5 (CH_3-CH_2), 26.1 (CH_2-CH_2-CH_2), 16.2 ($SiCH_2$), 15.4 (CH_3-CH_2), –1.9 [$Si(CH_3)_2$] ppm. MS (LSIMS): m/z (%) = 407 (26), 393 (6), 245 (42), 221 (100), 201 (30), 179 (8), 135 (10).

Desilylation of Silane 20 with TBAF: A 1 M solution of TBAF in THF (0.4 mL, 0.4 mmol) was added to a solution of silane **20** (161 mg, 0.39 mmol) in DMF (10 mL) and the solution was stirred at room temperature for 1.5 h. After evaporation of the solvents, the residue was dissolved in EtOAc and washed with water. The organic layer was dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography through silica gel (petroleum ether) to afford **18** as a white solid (67 mg, 91%), spectroscopically identical to that prepared above.

2-Bromo-5-(4-ethylphenyl)thiophene (22): Peracetic acid (0.12 mL, 1.9 mmol) was slowly added to a cooled solution of silane **20**

(153 mg, 0.37 mmol), KBr (53 mg, 0.45 mmol) and sodium acetate (88 mg, 1.1 mmol) in AcOH (1.9 mL). The mixture was allowed to warm to room temperature and then cooled to 0 °C again. More sodium acetate (264 mg, 3.2 mmol) and peracetic acid (0.37 mL, 5.6 mmol) were then slowly added and the solution was stirred at room temperature for 24 h. The reaction was quenched with a 25% aqueous solution of sodium thiosulfate (8 mL), EtOAc was added and the layers were separated. The aqueous layer was extracted with EtOAc. The organic layer was washed with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography through silica gel (petroleum ether, then petroleum ether/EtOAc, 7:3) to afford alcohol **17** as a pale yellow oil (52 mg, 78%) and **22** as a white solid (93 mg, 94%). Compound **22**: ^{1}H NMR ($CDCl_3$): δ = 7.45 (d, J = 8.2 Hz, 2 H, H_{arom}), 7.22 (d, J = 8.2 Hz, 2 H, H_{arom}), 7.02 (m, 2 H, H_{arom}), 2.68 (q, J = 7.6 Hz, 2 H, CH_2), 1.27 (t, J = 7.6 Hz, 3 H, CH_3) ppm.

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