# *Articles*

## Electrochemical Synthesis of Functional Aryl- and Heteroarylchlorosilanes. Application to the Preparation of Donor−Acceptor or Donor−Donor Organosilicon Molecules

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A variety of functional aryl- and heteroarylchlorosilanes were prepared by electrochemical reduction of halothiophenes, halofurans, halopyridines, and substituted aryl halides in the presence of a large excess of commercial organodi- or trichlorosilanes using an undivided cell, a sacrificial Mg or Al anode, a constant current density, and tetrabutylammonium bromide as the supporting electrolyte. New structures are described, and some examples of the use of these more elaborate chlorosilanes are given, particularly as interesting precursors for the preparation of polarized D−A and D−D organosilicon models.

### Introduction

Previous work has shown interest in silicon-containing precursors in the synthesis of materials with nonlinear optical (NLO) properties.[1−6] On the other hand, some polysilane films and, particularly, polysilynes have potential applications in optical interconnect films.[2,7,8] It is now well known that second-order organic NLO chromophores require a push−pull structure, that is, a conjugated central transmitter end-functionalized by strongly electron conjugated donors (D) and acceptors (A), respectively. Such materials usually have a much higher NLO response than inorganic materials. However their NLO application is often limited by a dramatic light absorption red-shifted from the UV to the visible region.[9,10] As a consequence, Zyss[11] and Moylan et al.[12] first indicated that a partial interruption of chain conjugation by the introduction of a semiconjugated spacer might give good NLO properties as well as low absorption in this region. It then was shown that the incorporation of a central $SiMe_2$ spacer in the conjugated chain effectively allows a balance between transparency and NLO properties at the second order[13] and at the third order in the excited state.[6] A strategy to elaborate silylene spacer containing models relies on the synthesis of functional mono- or dichlorosilanes, which generally are not very easy to prepare. Classical methods of carbon−silicon bond formation,[14] i.e., coupling of organometallic nucleophiles (generated from BuLi or Mg) with dichlorosilanes, generally are not selective and necessitate further separation from the starting material and the symmetrical dithienyl silane.[13] Following our previous results,[4,5,15] we propose here an electrochemical access to a variety of aryl and

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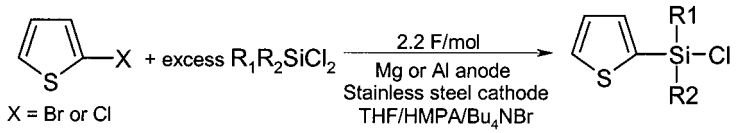
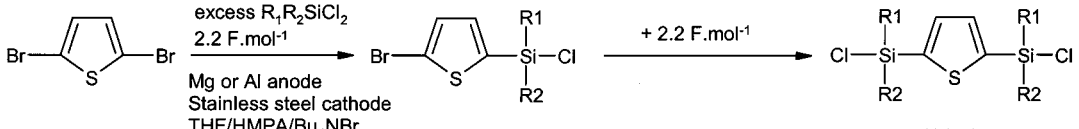
**Scheme 1. Electrochemical Synthesis of 2-Thienylmonochlorosilanes**




$R_1$,$R_2$ = Me, Me; X = Br: 88%; X = Cl: 85% (isolated)
$R_1$, $R_2$ = Me, Ph; X = Br: 64%; X = Cl: 63% (isolated)

**Scheme 2. Electrosilylation of 2,5-Dibromothiophene with Diorganodichlorosilanes in Excess**




$R_1$, $R_2$ = Me, Me 88% isolated
$R_1$, $R_2$ = Me, Ph 85% isolated

85% isolated
77% isolated

heteroaryl mono- and dichlorosilanes, some of which are new, by reductive coupling of aryl halides with di- or trichlorosilanes (in large used excess) using the intensiostatic sacrificial anode.[16] Their subsequent use for the electrochemical preparation of D−A and D−D organosilicon models is envisaged.

## Results and Discussion

**1. Electrochemical Synthesis of Functional Aryl- and Heteroarylmonochlorosilanes. 1.1. Electrochemical Synthesis of Thienyl- and Bromothienylmonochlorosilanes and 2,5-Bis(diorganochlorosilyl)thiophenes.** In previous work, we synthesized thienylmonochlorosilanes, 2-Th$SiR_1R_2Cl$ (Th = thienyl, $R_1$ = $R_2$ = Me and $R_1$ = Me, $R_2$ = Ph), from 2-halothiophenes (2-XTh) (X = Cl, Br) and 5-(2-bromothienyl)-monochlorosilanes, 2-BrT-5-$SiR_1R_2Cl$, from 2,5-dihalothiophenes (2,5-$X_2$T) (T = thienylene) by the electrochemical route involving the suitable charge (2.2 F mol$^{-1}$) under the following experimental conditions: 20:1 $R_1R_2SiCl_2$/substrate molar ratio, 20:6 (v/v) tetrahydrofuran (THF)/hexamethylphosphoramide (HMPA) as solvent/cosolvent, magnesium or aluminum anode, stainless steel cathode, $i$ = 0.1 A, $j$ = 0.1 ± 0.05 A dm$^{-2}$, 0.02 M−$Bu_4NBr$ as the supporting electrolyte (Schemes 1 and 2).[4,5]

Under these conditions, the electrolysis of 2,5-dibromothiophene, pursued up to 4.4 F mol$^{-1}$, enabled us to synthesize 2,5-bis(diorganochlorosilyl)thiophenes with excellent selectivity and in high yield of isolated product (Scheme 2). The electrochemical synthesis of such derivatives is more efficient than the usual chemical routes (51% for $R_1$, $R_2$ = Me, Me and 50% for $R_1$, $R_2$ = Me, Ph).[17] Such compounds are key intermediates for 2,5-bis[(2′-thienyl)diorganosilyl)]thiophenes, which give interesting results in NLO for the third generation harmonic.[6]

As we demonstrated previously,[4] according to the order of reduction potentials, the halothiophenes and the dichlorosilanes studied act as the substrates and the electrophiles, respectively. A great advantage of the electrochemical route lies in the achievement of the coupling reaction, not only from brominated substrates, as in the chemical route, but also from chlorinated substrates, which are less reactive and less expensive.

**Table 1. Influence of the Cosolvent Nature in the Electrochemical Synthesis of 2-Thienylmonochlorosilanes[a]**

| cosolvent | 2-BrTh conversion (%) | $ThSiMe_2Cl$, yield (%) GC | $ThSiMe_2Cl$, yield (%) isolated |
|---|---|---|---|
| HMPA | 100 | 95 | 88 |
| DMPU | 100 | 95 | 81 |
| TDA-1 | 87 | 82 | 76 |
| TMU | 64 | 58 | 43 |

[a] Mg anode, $Me_2SiCl_2$/2-BrTh = 20 (mol), THF/cosolvent = 20:6 (v:v), 2.2 F mol$^{-1}$.

Moreover, in the present work, we show that the success of the electrochemical synthesis of 2-thienylchlorosilanes does not require the use of HMPA as a cosolvent. Actually, *N*,*N*′-dimethylpropyleneurea (DMPU) and tris(3,6-dioxaheptyl)amine (TDA-1) also gave excellent results for the coupling of 2-bromothiophene with $Me_2SiCl_2$. However with tetramethylurea (TMU), the conductivity was lower and the conversion was decreased (Table 1).

**1.2. Electrochemical Synthesis of Substituted Phenylmonochlorosilanes.** Several chemical routes involving condensation of dimethyldichlorosilane with the appropriate Grignard reagent,[18,19] thermal rearrangement of chloromethylsilanes,[20] or cleavage of bis(dimethylchloro)disilanes by a suitable acid chloride in the presence of a palladium catalyst[21] lead to aryldimethylchlorosilanes. Since the electrochemical coupling of mono- and dibromothiophenes with a large excess of diorganodichlorosilane gives the corresponding thienylmonochlorosilanes, we investigated the reduction of variously substituted halobenzenes under the same conditions.

**1.2.1. Electrochemical Reduction of *p*-Bromoanisole in the Presence of a Large Excess of $Me_2SiCl_2$: Preliminary Study.** In a first experiment at room temperature, we carried out the direct electrolysis of *p*-bromoanisole in the presence of a 20-fold molar excess of $Me_2SiCl_2$. Whatever the anode (Al, Mg), poor *p*-

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**Table 2. Electroreduction of *p*-Bromoanisole with a Large Excess of $Me_2SiCl_2$ for 2.2 F $mol^{-1}$**

| | | *p*-$MeOC_6H_4SiMe_2Cl$, (**1**), yield (%) | | byproducts, GC yield (%) | |
|---|---|---|---|---|---|
| anode metal | conversion (%) | GC | isolated | A[a] | PDMS |
| Al | 8 | 8 | | | main product |
| Mg | 13 | 13 | | | main product |
| Mg +[$Ni(bpy)Br_2$ +excess bpy] | 98 | 94 | 86 | 4 | |

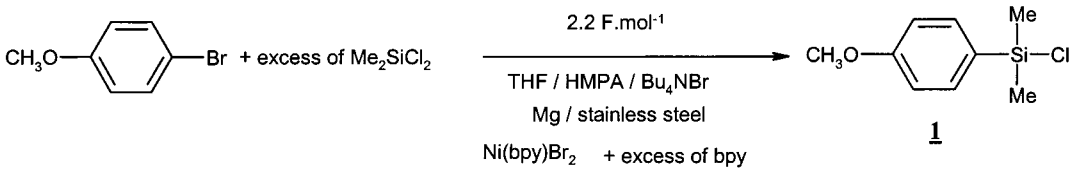
[a] (*p*-$MeOC_6H_4)_2SiMe_2$.

**Table 3. Electrochemical Ni-Catalyzed Synthesis of *p*-Substituted Arylmonochlorosilanes by Coupling of *p*-Substituted Halobenzenes with Diorganodichlorosilanes in Excess[a]**

| | | | | | *p*-$Y-C_6H_4-SiR_1R_2Cl$ | | |
|---|---|---|---|---|---|---|---|
| *p*-$Y-C_6H_4-X$, X = Cl, Br | peak potential $E_p$ (V)[b] | $R_1R_2SiCl_2$ | peak potential $E_p$ (V)[23] | conversion (%) | $R_1,R_2$ | GC yield (%) | isolated yield (%) |
| *p*-$CH_3OC_6H_4Br$ | −2.45 | $Me_2SiCl_2$ | −2.54 | 98 | Me,Me | 94 | 86 |
| | | $MeViSiCl_2$ | −2.62 | 98 | Me,Vi | 95 | 85 |
| | | $PhMeSiCl_2$ | −2.68 | 94 | Ph,Me | 90 | 77 |
| *p*-$Me_2NC_6H_4Br$ | −2.05 | $Me_2SiCl_2$ | | 70 | Me,Me | 65 | 55 |
| *p*-$FC_6H_4Br$ | −2.70 | $Me_2SiCl_2$ | | 100 | Me,Me | 94 | 83 |
| *p*-$CF_3C_6H_4Br$ | −2.40 | $Me_2SiCl_2$ | | 100 | Me,Me | 96 | 86 |
| *p*-$NO_2C_6H_4Br$ | −1.22 | $Me_2SiCl_2$ | | 100 | | 0 | |
| *p*-$NO_2C_6H_4Cl$ | −2.65 | $Me_2SiCl_2$ | | 100 | | 0 | |

[a] Mg anode, $R_1R_2SiCl_2$/*p*-$YC_6H_4X$ = 20 (mol), 2.2 F $mol^{-1}$. [b] Measured vs SCE at a 1-mm-diameter Pt disk in THF−0.1 M $Bu_4NBF_4$; sweep rate 0.2 V $s^{-1}$; voltage scan 0/1.0/-2.93/0 V.

**Scheme 3. Nickel-Catalyzed Electrochemical Synthesis of *p*-Methoxyphenyldimethylchlorosilane (1)**




bromoanisole conversion and *p*-anisyldimethylchlorosilane (**1**) formation were observed (Table 2). Polydimethylsilane (PDMS), resulting from $Me_2SiCl_2$ autocoupling,[22] was the main product formed. This result is consistent with the similar reduction potentials for *p*-bromoanisole (−2.45 V vs SCE) and $Me_2SiCl_2$ (−2.54 V vs SCE,[23] Table 3), allowing the reduction of both starting materials. Autocoupling of $Me_2SiCl_2$ is, however, favored due to its much higher concentration and higher electrophilicity.

Thus redox catalysis was necessary to favor the reduction of the aryl halide, and we chose Ni(0) catalysis using $Ni(bpy)Br_2$ [16,24] (peak potential: $E_p$ = −1.2 V vs SCE) + excess bpy (bpy = 2,2′-bipyridine), cf. Scheme 3.

Under these conditions, conversion of the substrate was complete and the selectivity (94% by GC) and the isolated yield of the expected arylchlorosilane (86%) were excellent (Table 2). A small amount of bis(*p*-methoxyphenyl)dimethylsilane (4%) was also formed due to the trapping of the aryl anion by the **1** present in the medium.

This electrochemical synthesis of **1** was performed on a larger scale (40 g) using a previously described electrochemical cell fabricated from a 500 mL Grignard reactor equipped with six cathodes and six magnesium bar anodes.[25] The conversion rate, selectivity, and yield of isolated product were comparable with those obtained in a 100 mL cell. We extended the method to the synthesis of other differently substituted arylchlorosilanes.

**1.2.2. Generalized Electrochemical Synthesis of Arylmonochlorosilanes.** Reduction peak potentials $E_p$ of several *p*-substituted halo benzenes were determined vs SCE by cyclic voltammetry (Table 3). As all the values obtained for the substrates involved (except for *p*-$Me_2NC_6H_4Br$) were of the same order as those of the chlorosilanes, nickel catalysis was necessary for the entire series.

Thus under these conditions, for a charge passed of 2.2 F per mole of *p*-substituted halobenzene, the corresponding *p*-substituted arylchlorosilanes were synthesized using an excess (20:1) of the $R_2SiCl_2$ electrophile, in high selectivity and isolated yield, except for the case of Y = $NO_2$ (Table 3).

With nitro derivatives, the reaction was different; the products obtained were *p*-$BrC_6H_4-N{=}N-C_6H_4Br$-*p* and *p*-$ClC_6H_4-N{=}N-C_6H_4Cl$-*p* respectively from *p*-nitrobromobenzene and *p*-nitrochloro benzene. Such products are of interest as transmitter sequence of some molecules having NLO properties for the second generation harmonic. This result is consistent with the easy reduction of the $NO_2$ group, as shown by the much higher peak potential value (−1.22 V) for *p*-$NO_2C_6H_4Br$ compared with those of the other bromides. The failure of

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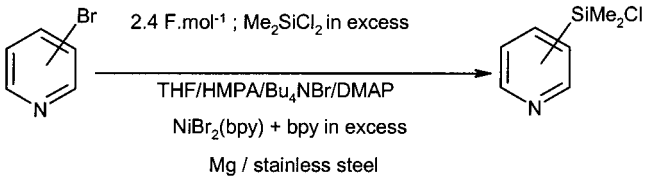
**Table 4. Electrochemical Reduction of 2- and 3-Bromopyridines in the Presence of $Me_2SiCl_2$ in Excess for a Charge of 2.4 F $mol^{-1}$**

| substrate | product | conversion (%) | yield (%) GC | yield (%) isolated | chemical route yield(%) |
|---|---|---|---|---|---|
| 2-bromopyridine | 2-pyridyldimethylchlorosilane | 100 | 98 | 76 | not isolated[30] |
| 3-bromopyridine | 3-pyridyldimethylchlorosilane | 100 | 95 | 69 | 59[30] |

**Scheme 4. Electrosynthesis of Dimethylpyridylmonochlorosilanes**




the nickel redox catalysis shows that the C−Br and C−Cl bonds are not sufficiently activated for oxidative addition to the Ni(0), compared with the ease of reduction of $NO_2$.

This mild, safe, and selective synthesis by the electrochemical route of such functionalized arylchlorosilanes is particularly interesting for trifluoromethylated aromatic compounds knowing that *p*-trifluoromethylphenyllithium[26] and the Grignard derivatives of *o*-, *m*-, and *p*-bromotrifluoromethylbenzene are explosive.[27,28]

**1.3. Electrochemical Synthesis of Pyridyldimethylmonochlorosilanes.** In the same way, we examined the reduction of 2- and 3-bromopyridines in the presence of a 20-fold excess of dimethyldichlorosilane for a charge of 2.4 F $mol^{-1}$ passed. The reduction potentials of these two substrates were determined vs SCE by cyclic voltammetry at a 1-mm-diameter Pt disk in THF−0.1 M $Bu_4NBF_4$ (sweep rate, 0.2 $Vs^{-1}$; voltage scan 0/1.0/−2.93/0 V. The peak potential values, $E_p = -2.45$ V, for 2-bromopyridine and $E_p = -2.63$ V for 3-bromopyridine, were again of the same order or more cathodic than the reduction potential of $Me_2SiCl_2$. Thus, dimethyl-2- and 3-pyridylchlorosilanes could be synthesized in high selectivities and good isolated yield from 2- and 3-bromopyridine, respectively, using Ni(0) catalysis and a slight amount of 4-(dimethylamino)-pyridine (DMAP) to enhance the electrophilic character of dimethyldichlorosilane[29] (Scheme 4 and Table 4). Comparison of the electrochemical and chemical routes[30] for the preparation of these derivatives (Table 4) shows that the sacrificial anode method is a very good alternative.

**2. Electrochemical Synthesis of Functional Aryldichlorosilanes.** Some phenyldichlorosilanes and, particularly, *p*-(trifluoromethylphenyl)methyldichlorosilane and (*p*-methoxyphenyl)methyldichlorosilane are precursors of polysilane films that are of interest for electrooptic applications.[7,8] The synthesis of this class of products is not widely described by usual chemical routes. We have exploited the versatile and efficient electrochemical route to synthesize *p*-substituted phenylorganodichlorosilanes from *p*-methoxy-, *p*-fluoro-, and *p*-trifluoromethylbromobenzenes in the presence of organotrichlorosilane in large, 20:1 excess. Because the reduction potential of methyltrichlorosilane[23] was of the same order as those of these substrates, a Ni(0) redox catalysis was required. Under standard conditions, involving a sacrificial magnesium anode, *p*-substituted phenylorganodichlorosilanes were obtained with complete conversion and selectivity (Scheme 5).

Despite their sensitivity to hydrolysis, yields of isolated chlorosilane products are good and, in any case, better than those obtained in the chemical routes. The electrosynthesis with a sacrificial magnesium anode constitutes a useful preparative method for functional mono- and dichlorosilanes and, particularly, for fluorinated methyldichlorosilanes. These also are interesting precursors of fluorinated polysiloxanes.

**3. Use of the Aryl- and Heteroarylchlorosilanes Electrochemically Synthesized.** The electrochemically prepared functionalized title compounds are interesting synthetic intermediates. Here, we report some examples of the electrosynthesis of alternating silicon−aromatic ring structures, this backbone being suitable for NLO at the excited state for the third generation harmonic.[6]

**3.1. Electrochemical Coupling of Bromofurans with 2-Thienylchlorosilanes.** Alternating furyl and thienyl ring structures have proved to be of interest because of semiconducting properties[31] and for their antifungal properties.[32] In view of the efficiency of the sacrificial anode technique for the coupling of mono- and dibromofurans with $Me_3SiCl$ and several dichlorosilanes,[33] we prepared 2-furyl-2-thienyldimethylsilane (Scheme 6) and 2,5-bis(2′-furyldimethylsilyl)thiophene (Scheme 7) by electrolysis of 2-bromofuran with dimethyl-2-thienylchlorosilane and 2,5-bis(chlorodimethylsilyl)thiophene, respectively, under stoichiometric conditions. Good yields were obtained after the passage of 2.2 or 4.4 F $mol^{-1}$, respectively.

**3.2. Electrochemical Coupling of 2-Bromo- and 2,5-Dibromothiophene with *p*-Methoxyphenyldimethylchlorosilane (1).** Under the same conditions (equimolar ratio of reactants, 2.2 F $mol^{-1}$, Mg anode, Ni(0) catalysis), the electrochemical reductive silylation of 2-bromothiophene in the presence of **1** gave, almost quantitatively, *p*-methoxyphenyl-2-thienyldimethylsilane (Scheme 8).

On the other hand, when we tried to extend the reaction to the reduction of 2,5-dibromothiophene, we obtained only the symmetrical disilane ($p$-$CH_3OC_6H_4$-$Me_2Si)_2$ in excellent yield (88%), resulting from the



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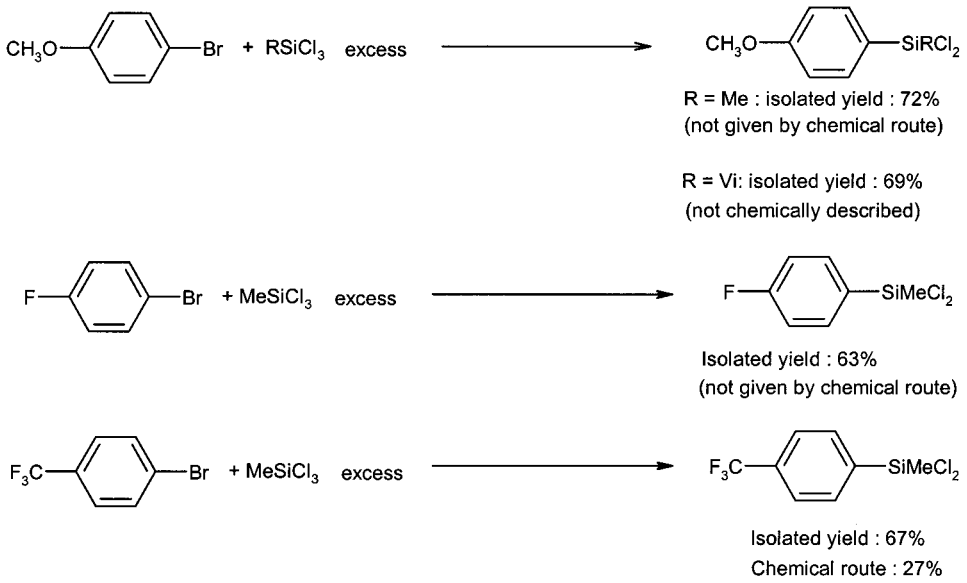
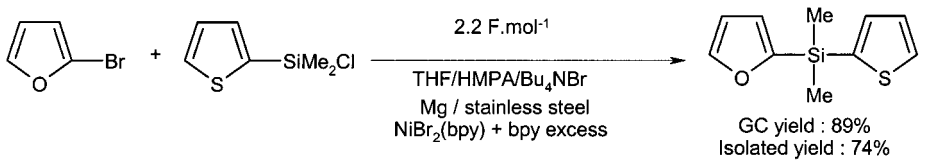
**Scheme 5. Electrosynthesis of *p*-Substituted Phenylorganodichlorosilanes[a]**

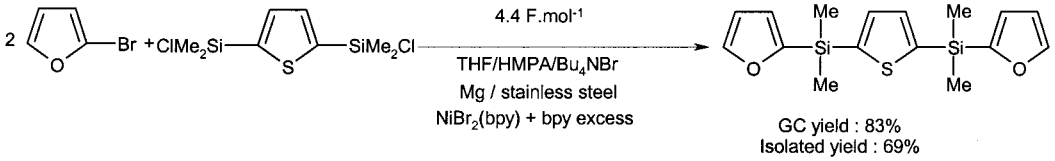



[a] Conditions: 2.2 F mol$^{-1}$, THF/HMPA/$NBu_4Br$, Mg/stainless steel, $Ni(bpy)Br_2$ + excess bpy.

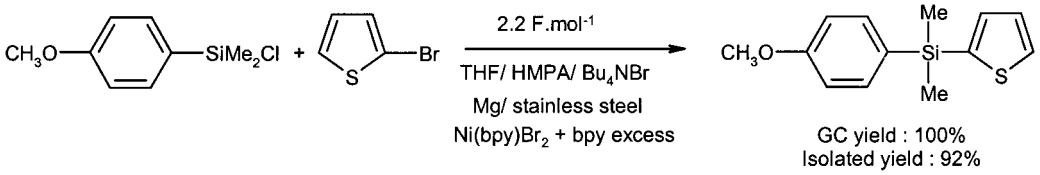
**Scheme 6. Preparation of 2-Furyl-2-thienyldimethylsilane**



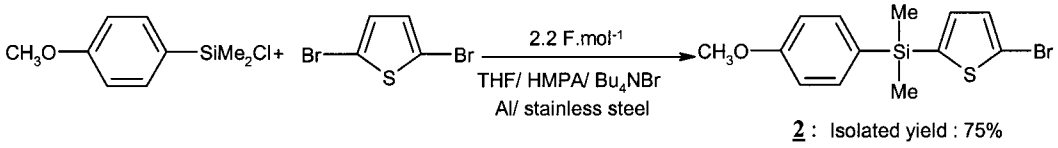

**Scheme 7. Preparation of 2,5-Bis[(2′-furyl)dimethylsilyl]thiophene**




**Scheme 8. Preparation of *p*-Methoxyphenyl-2-thienyldimethylsilane**




**Scheme 9. Preparation of 2-(5-Bromothienyl)-*p*-methoxyphenyldimethylsilane (2)**

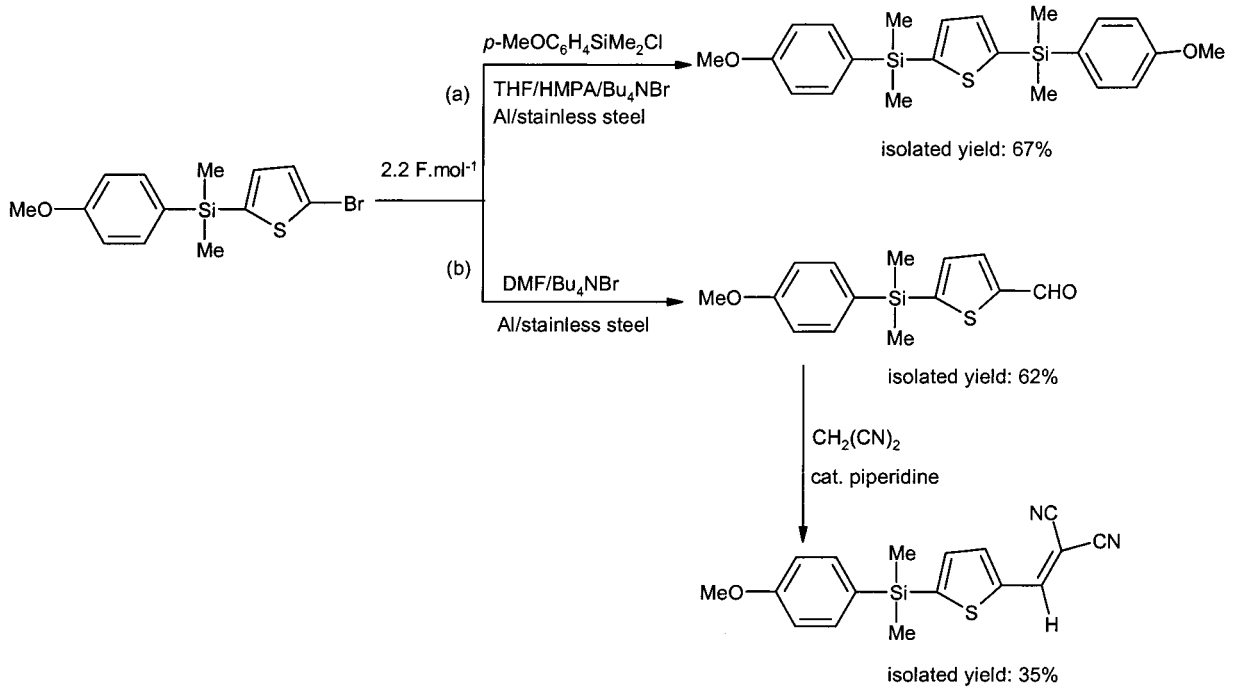



autocoupling of the chlorosilane. However, direct electrolysis using an aluminum anode and the suitable charge for reducing one $C_{thienyl}$–Br bond of the substrate (2.2 F mol$^{-1}$ ) led selectively to 2-(5-bromothienyl)-*p*-methoxyphenyldimethylsilane (**2**) (Scheme 9). Under these conditions, only a small amount (less than 10% by GC) of bis(*p*-methoxyphenyl)tetramethyldisilane was formed. The autocoupling of the arylchlorosilane observed with a magnesium anode, even in the presence of Ni(0) redox catalyst, is probably due to the competitive chemical reductive role of the anodically scoured magnesium.[4]

**4. Multi Electrochemical Step Synthesis of Molecules with Electron Donor and Acceptor Groups.** From the preliminary results detailed above, we envisaged two strategies using **2** as the substrate in electrochemical reactions (Scheme 10).

**4.1. Electrochemical Synthesis of a Bis(Electron Donor Substituted) Molecule.** We reacted **2** with an equimolar quantity of **1** taken as the electrophile under

**Scheme 10. Electrochemical Synthesis of Electron Di-donor and Donor−Acceptor Silicon Molecules**




our standard electrolytic conditions with a sacrificial aluminum anode to synthesize 2,5-bis(*p*-methoxyphenyldimethylsilyl)thiophene. After the passage of 2.2 F $mol^{-1}$ of charge this product was obtained in 80% selectivity and 67% isolated yield (Scheme 10a). This access to a two-electron-donor molecule seems to be attractive for NLO in reference to a systematic study of the influence of substituents and chain length of polyenes on the $\gamma$ value.[34]

**4.2. Electrochemical Synthesis of Electron Donor−Acceptor Substituted Molecules.** We reacted **2** in *N*,*N*-dimethylformamide (DMF), used both as the solvent and the electrophile,[35] under our standard electrolytic conditions with an aluminum sacrificial anode. 2-(*p*-Methoxyphenyldimethylsilyl)thienyl-5-carbaldehyde (Scheme 10b) was obtained after the passage of 2.2 F $mol^{-1}$ of charge, in 85% selectivity and 62% isolated yield.

To enhance the electron-withdrawing character of the attractor substituent, we chemically treated the molecule with dicyanomethane in the presence of piperidine to obtain the corresponding 1,1′-dicyanovinyl product, which was isolated in 35% yield.

## Conclusion

A selective and efficient method for the synthesis of functionalized mono- and dichlorosilanes as key intermediates for polarized organosilicon molecules that are interesting for NLO applications is reported. The electrosynthetic route is especially advantageous, due to its selectivity and versatility, for the preparation of new organosilicon models. Compared with chemical routes, the electrosynthetic method gives better results and, moreover, is the only synthetic alternative to some structures. The larger scale electrosynthesis makes the sacrificial anode method a real synthetic tool for functionalized arylchlorosilanes.

## Experimental Section

**Materials.** Aryl halides (Acros) and $Bu_4NBr$ (Aldrich) were used without purification. THF (SDS) and HMPA (Aldrich) were dried by distillation over sodium benzophenone ketyl and $CaH_2$, respectively, while dichlorosilanes were distilled over Mg powder just before use. 2-Bromofuran was chemically prepared as described in the literature.[36]

**General Methods.** Gas chromatography was performed with a temperature-programmable Hewlett-Packard 5890A apparatus equipped with a 25 m × 0.25 $\mu$m CP-Sil 5CB capillary column. $^1H$ and $^{13}C$ NMR spectra were recorded of $CDCl_3$ solutions on a Bruker AC 250 spectrometer, using residual $CHCl_3$ as the internal standard. $^{29}Si$ NMR spectra of $CDCl_3$ solutions were recorded on a Bruker AC 200 spectrometer. Electron impact mass spectra were measured at 70 eV on a VG Micromass 16F spectrometer coupled with a gas chromatograph equipped with a 25 m × 0.25 $\mu$m CP-Sil 5CB capillary column. IR spectra were recorded with a Perkin-Elmer 1420 spectrophotometer of pure liquid films (NaCl or KBr plates). Elemental analyses were performed by the "Service Central de Microanalyse" du CNRS (France).

**Voltammetry.** Cyclic voltammetry was carried out under argon in THF (20 mL) solutions containing the substrate (2 mM) and 0.1 M $Bu_4NBF_4$, using a 1 mm diameter Pt or glassy carbon disk as the working electrode and an aqueous saturated calomel reference electrode (Tacussel XR 110) separated from the medium by a Tacussel AL 120 junction filled with the same electrolytic solution. For measurements with Pt disk working electrode, ferrocene ($10^{-3}$ M) was used as the internal standard ($E_{pa}$ = 0.63 V, $E_{pc}$ = 0.56 V). The solution resistance was compensated for with a positive feedback device. The potentiostat used (Sirius) was previously described.[25] The sweep rate was 0.2 V $s^{-1}$, and the voltage scan was 0/1.0/−3/0 V.

**General Procedure for Electrolysis.** Electrolysis was performed in an undivided cell (100 mL) described else-

(34) Puccetti, G.; Blanchard-Desce, M.; Ledoux, I.; Lehn, J.-M.; Zyss, J. *J. Phys. Chem.* **1993**, *97*, 9385.

(35) Saboureau, C.; Troupel, M.; Sibille, S.; D'Incan, E.; Périchon, J. *J. Chem. Soc., Chem. Commun.* **1989**, 895.

(36) Keegztra, M. A.; Klomp, A. J. A.; Brandsma, L. *Synth. Commun.* **1990**, *20*, 3371.

where[4,25] equipped with a sacrificial cylindrical aluminum or magnesium bar (1 cm diameter) as the anode and a concentric stainless steel grid or carbon ($1.0 \pm 0.2$ dm$^2$) as the cathode. A constant current (0.1 A, density $0.1 \pm 0.05$ A dm$^{-2}$) was provided by a Sodilec EDL 36-07 regulated dc power supply. To the dried cell, containing a magnetic spin bar, was added $Bu_4NBr$ (0.5 g, 1.6 mmol) as the supporting electrolyte. The cell then was twice deaerated under vacuum and flushed with dry nitrogen. THF (20 mL), HMPA, or other cosolvent (6 mL) and the di- or trichlorosilane (40 to 60 mL) were introduced through a septum by syringe. The solution was degassed by bubbling nitrogen through it for 10 min. HCl resulting from the reaction of the chlorosilane with traces of water was removed by pre-electrolyzing the solution ($i = 0.1$ A). The siloxane formed is electrochemically inert. When evolution of $H_2$ had ceased, the substrate (20 mmol) and, if necessary, the nickel catalyst $NiBr_2$(bpy) (0.45 g, 1.2 mmol) and an excess of 2,2′-bipyridine (0.78 g, 5 mmol) were introduced. The electrolysis ($i = 0.1$ A) was performed until the theoretically required charge had been passed. The reaction was monitored by gas chromatography. After precipitation of the major part of the salts from the resulting solution by addition of anhydrous pentane ($2 \times 50$ mL) and subsequent filtration, solvents and excess di- or trichlorosilane were evaporated at reduced pressure. The crude product was analyzed by GC and then distilled under vacuum or eluted with pentane on a silica gel column. If needed, unconverted $PhMeSiCl_2$ and $ViSiCl_3$ starting material can be easily recovered as pure products by distillation; recovery of $Me_2SiCl_2$ and $MeSiCl_3$ is done as a solution in THF, which can be recycled in a new experiment.

**2-Thienyldimethylchlorosilane:** CAS registry no. (RN) 119708-77-9; yield 88%; bp 38 °C/0.5 mmHg. Spectral data agree with those reported in ref 4.

**2-Thienylmethylphenylchlorosilane:** yield 64%; bp 131 °C/1 mmHg. Spectral data agree with those reported in ref 4.

**5-(2-Bromothienyl)dimethylchlorosilane:** yield 88%; bp 82 °C/0.5 mmHg; $^1$H NMR $\delta$ 0.54 (s, 6H), 6.95 (d, 1H, $C_{thienyl}H$, $^3J = 3.5$), 6.98 (d, 1H, $C_{thienyl}H$, $^3J = 3.5$). Other spectral data agree with those reported in ref 4.

**2,5-Bis(chlorodimethylsilyl)thiophene:** RN 4414-24-8; yield 85%; bp 112−114 °C/14 mmHg. Spectral data agree with those reported in refs 5 and 17.

**2,5-Bis(chloromethylphenylsilyl)thiophene:** RN 132440-06-3; yield 77%; bp 194 °C/1 mmHg. Spectral data agree with those reported in refs 5 and 17.

**2-Pyridyldimethylchlorosilane:** RN 108094-01-5; yield 76%; bp 38 °C/1 mmHg; $^1$H NMR $\delta$ 0.36 (s, 6H), 7.48 (m, 1H), 7.52 (m, 2H), 7.70 (d, 1H); $^{13}$C NMR $\delta$ 0.1 ($Si(CH_3)_2$), 122.9 ($C_5$), 128.9 ($C_3$), 133.9 ($C_4$), 150.4 ($C_6$), 169.6 ($C_2$); MS *m*/*z* (rel intensity, %) 173 (8), 171 (24, M), 158 (50), 157 (16), 156 (100, M-$CH_3$); IR (neat KBr) 2959, 2908, 1265, 1065, 908, 852, 759, 705, 550, 450 cm$^{-1}$. Spectral data agree with those reported in the literature.[30]

**3-Pyridyldimethylchlorosilane:** RN 108O94-02-6; yield 69%; bp 45 °C/0.5 mmHg; $^1$H NMR $\delta$ 0.27 (s, 6H), 7.45 (m, 2H), 8.48 (d, 1H), 8.74 (s, 1H); $^{13}$C NMR $\delta$ 0.2 ($Si(CH_3)_2$), 128.8 ($C_5$), 135.1 ($C_3$), 148.1 ($C_4$), 150.0 ($C_2$), 150.1 ($C_6$); IR (neat KBr) 2961, 2906, 1262, 1060, 907, 850, 758, 703, 550, 445 cm$^{-1}$. Spectral data agree with those reported in the literature.[30]

***p*-Methoxyphenyldimethylchlorosilane:** RN 2372-33-0; yield 86%; bp 80 °C/1 mmHg; $^1$H NMR $\delta$ 0.62 (s, 6H), 3.75 (s, 3H), 6.90 (d, 2H, $^3J = 8$), 7.51 (d, 2H, $^3J = 8$); $^{13}$C NMR $\delta$ 2.3 ($Si(CH_3)_2$), 55.1 (OMe), 113.9 (T), 134.8 (T), 139.9 (Q), 161.5 (Q); MS *m*/*z* (rel intensity, %) 202 (8), 200 (23, M), 187 (38), 185 (100, M − $CH_3$), 95 (1.5), 93 (5), 63 (12); IR (neat KBr) 3072, 3004, 2958, 2836, 1578, 1489, 1461, 1441, 1404, 1290, 1259, 1247, 1171, 1113, 1100, 1072, 1033, 1002, 821, 791, 750, 696, 601, 496 cm$^{-1}$. Spectral data agree with those reported in the literature.[21]

***p*-Methoxyphenylmethylvinylchlorosilane:** yield 85%; bp 98 °C/1 mmHg; $^1$H NMR $\delta$ 0.68 (s, 3H, SiMe), 3.75 (s, 3H, $OCH_3$), 5.93−6.29 (m, 3H, $H_{vinyl}$), 6.90 (d, 2H, $^3J = 8.5$, $H_{arom}$), 7.51 (d, 2H, $^3J = 8.5$, $H_{arom}$); $^{13}$C NMR $\delta$ 0.9 ($SiCH_3$), 55.1 ($OCH_3$), 114.0 (T), 129.6 (S), 134.8 (T), 135.5 (T), 136.5 (Q), 161.5 (Q); MS *m*/*z* (rel intensity, %) 214 (2), 212 (5, M), 210 (10), 197 (11), 195 (14), 107 (11), 105 (36), 97 (100), 96 (39), 85 (12), 81(12), 79 (29), 71 (10); IR (neat KBr) 3002, 2949, 2833, 1575, 1489, 1459, 1439, 1288, 1259, 1249, 1169, 1111, 1099, 1070, 1033, 1001, 823, 790, 750, 698, 600, 501 cm$^{-1}$. Anal. Calcd for $C_{10}H_{13}ClOSi$: C, 56.6; H, 6.1; O, 7.5. Found: C, 56.7; H, 6.05; O, 7.55.

***p*-Methoxyphenylmethylphenylchlorosilane:** yield 77%; bp 141 °C/3 mmHg; $^1$H NMR $\delta$ 0.86 (s, 3H), 3.81 (s, 3H), 6.99 (d, 2H, $^3J = 8.5$), 7.47 (m, 3H), 7.58 (d, 2H, $^3J = 8.5$), 7.74 (m, 2H); $^{13}$C NMR $\delta$ 1.4 ($SiCH_3$), 55.2 ($OCH_3$), 114.1 (T), 128.3 (T), 128.6 (T), 131.9 (T), 133.9 (Q), 136.0 (Q), 134.2 (T), 161,8 (Q); MS *m*/*z* (rel intensity, %) 264 (3), 262 (9, M), 249 (30), 247 (100, M − $CH_3$); IR (neat KBr) 3001, 2948, 2834, 1573, 1492, 1459, 1440, 1285, 1262, 1249, 1171, 1110, 1100, 1068, 1031, 1000, 824, 786, 750, 696, 600, 505 cm$^{-1}$. Anal. Calcd for $C_{14}H_{15}ClOSi$: C, 64.12; H, 5.72; O, 6.1. Found: C, 64.15; H, 5.74; O, 6.08.

**(*p*-Dimethylamino)phenyldimethylchlorosilane:** yield 55%; bp 158 °C/1 mmHg; $^1$H NMR $\delta$ 0.64 (s, 6H), 2.88 (s, 6H), 6.65 (d, 2H, $^3J = 8.5$), 7.58 (d, 2H, $^3J = 8.5$); $^{13}$C NMR $\delta$ 1.1 ($SiMe_2$), 41.8 ($NMe_2$), 116.3 (T), 133.6 (T), 138.9 (Q), 151.3 (Q); MS *m*/*z* (rel intensity, %) 215 (27), 214 (18), 213 (77, M), 212 (19), 200 (37), 199 (17), 198 (100, M − $CH_3$), 182 (14), 134 (17), 99 (16); IR (neat KBr) 2884, 2806, 1597, 1499, 1445, 1353, 1285, 1262, 1228, 1190, 1166, 1080, 1063, 947, 786, 778, 495 cm$^{-1}$. Anal. Calcd for $C_{10}H_{16}ClNSi$: C, 56.33; H, 7.5; N, 6.57. Found: C, 56.35; H, 7.45; N, 6.55.

***p*-Fluorophenyldimethylchlorosilane:** RN 2855-86-4; yield 83%; bp 67 °C/1 mmHg; $^1$H NMR $\delta$ 0.6 (s, 6H), 7.14 (m, 2H), 7.63 (m, 2H); $^{13}$C NMR $\delta$ 0.9 ($SiMe_2$), 117.3 (T), 138.6 (T), 139.8 (Q), 165.4 (Q); MS *m*/*z* (rel intensity, %) 190 (22), 188 (76, M), 175 (35), 173 (100, M − $CH_3$); IR (neat KBr) 3098, 3072, 1877, 1750, 1627, 1586, 1485, 1428, 1401, 1289, 1258, 1231, 1192, 1156, 1089, 1065, 1014, 931, 823, 596, 504 cm$^{-1}$.

***p*-(Trifluoromethyl)phenyldimethylchlorosilane:** yield 86%; bp 76 °C/1 mmHg; $^1$H NMR $\delta$ 0.43 (s, 6H), 7.37 (d, 2H), 7.58 (d, 2H); $^{13}$C NMR $\delta$ 1.2 ($SiMe_2$), 120.8 ($CF_3$), 124.3 (T), 132.0 (T), 133.3 (Q), 138.6 (Q); MS *m*/*z* (rel intensity, %) 240 (17), 238 (60, M), 225 (33), 223 (100, M − $CH_3$); IR (neat KBr) 1911, 1656, 1603, 1581, 1490, 1402, 1325, 1261, 1170, 1131, 1103, 1075, 1063, 1013, 950, 830, 775, 720, 503 cm$^{-1}$. Anal. Calcd for $C_9H_{10}ClF_3Si$: C, 45.37; H, 4.02. Found: C, 45.35; H, 4.09.

***p*-Methoxyphenylmethyldichlorosilane:** RN 18236-55-0; yield 72%; bp 81 °C/1 mmHg; $^1$H NMR $\delta$ 0.76 (s, 3H), 3.84 (s, 3H), 6.98 (d, 2H, $^3J = 9$), 7.68 (d, 2H, $^3J = 9$); $^{13}$C NMR $\delta$ 1.3 ($SiCH_3$), 55.4 ($OCH_3$), 115.8 (T), 135.6 (T), 140.3 (Q), 158.8 (Q); MS *m*/*z* (rel intensity, %) 224 (4), 222 (20), 220 (35, M), 210 (12), 208 (56), 205 (100, M − $CH_3$); IR (neat KBr) 3069, 3001, 2962, 2839, 1579, 1486, 1459, 1440, 1404, 1287, 1259, 1245, 1176, 1110, 1100, 1071, 1035, 1000, 820, 794, 750, 698, 600, 503 cm$^{-1}$. Spectral data agree with those reported in the literature.[21]

***p*-Methoxyphenylvinyldichlorosilane:** yield 69%; bp 104 °C/1 mmHg; $^1$H NMR $\delta$ 3.85 (s, 3H, $OCH_3$), 6.21−6.35 (m, 3H, $H_{vinyl}$), 6.97 (d, 2H, $^3J = 9$, $H_{arom}$), 7.66 (d, 2H, $^3J = 9$, $H_{arom}$); $^{13}$C NMR $\delta$ 55.5 ($OCH_3$), 115.7 (T), 132.2, (S), 135.3 (T), 139.4 (T), 140,1 (Q), 158.5 (Q); MS *m*/*z* (rel intensity, %) 236 (2), 234 (16), 232 (29, M), 222 (16), 220 (55), 217 (100, M − $CH_3$); IR (neat KBr) 3000, 2945, 2837, 1572, 1484, 1462, 1430, 1285, 1255, 1263, 1167, 1110, 1100, 1063, 1033, 1000, 820, 788, 750, 695, 600, 504 cm$^{-1}$. Anal. Calcd for $C_9H_{10}Cl_2OSi$: C, 46.35; H, 4.29; O, 6.86. Found: C, 46.35; H, 4.33; O, 6.83.

***p*-Fluorophenylmethyldichlorosilane:** RN 2355-86-4; yield 63%; bp 78 °C/1 mmHg; $^1$H NMR $\delta$ 0.72 (s, 3H), 7.19 (m, 2H), 7.68 (m, 2H); $^{13}$C NMR $\delta$ 1.2 (SiMe), 118.2 (T), 138.8 (T), 140.0 (Q), 166.3 (Q); MS *m*/*z* (rel intensity, %) 212 (4), 210 (25),

208 (36, M), 198 (10), 196 (61), 193 (100, M − $CH_3$); IR (neat KBr) 3099, 3070, 1863, 1752, 1631, 1580, 1423, 1400, 1285, 1268, 1230, 1190, 1150, 1088, 1064, 1013, 930, 822, 576, 511 $cm^{-1}$.

***p*-Trifluoromethylphenylmethyldichlorosilane:** RN 339-57-1; yield 67%; bp 88 °C/1 mmHg; $^1H$ NMR $\delta$ 0.96 (s, 3H), 7.73 (d, 2H, $^3J = 8$), 7.88 (d, 2H, $^3J = 8$); $^{13}C$ NMR $\delta$ 1.4 (SiMe), 121.0 ($CF_3$), 124.6 (T), 132.1 (T), 133.6 (Q), 138.9 (Q); MS *m/z* (rel intensity, %) 262 (1), 260 (16), 258 (28, M), 248 (11), 246 (59), 243 (100, M-$CH_3$); IR (neat KBr) 1654, 1600, 1575, 1492, 1400, 1322, 1265, 1162, 1127, 1100, 1073, 1060, 1015, 948, 832, 773, 720, 535, 503 $cm^{-1}$. Spectral data agree with those reported in the literature.[27]

***p*-Methoxyphenyl-2-thienyldimethylsilane:** yield 92%; $^1H$ NMR $\delta$ 0.86 (s, 6H, $SiMe_2$), 3.98 (s, 3H, $OCH_3$), 7.15 (d, 2H, $^3J = 8.5$, $H_{phenyl}$), 7.41 (m, 1H, $H_{thienyl}$), 7.54 (d, 1H, $^3J = 3.3$, $H_{thienyl}$), 7.76 (d, 2H, $^3J = 8.5$, $H_{phenyl}$), 7.81 (d, 1H, $^3J = 4.5$, $H_{thienyl}$); $^{13}C$ NMR $\delta$ −0.7 ($Si(CH_3)_2$), 55.1 ($OCH_3$), 114.0 (T), 128.5 (T), 131.3 (T), 135.5 (Q), 135.6 (T), 135.7 (T), 138.5 (Q), 161.0 (Q); $^{29}Si$ NMR $\delta$ −11.46; MS *m/z* (rel intensity, %) 248 (27, M), 234 (19), 233 (100, M − $CH_3$); IR (neat NaCl) 3079, 1593, 1564, 1502, 1463, 1440, 1405, 1397, 1311, 1279, 1249, 1213, 1182, 1113, 1083, 1032, 991, 852, 834, 807, 776, 709, 677, 606, 524, 487 $cm^{-1}$. Anal. Calcd for $C_{13}H_{16}OSSi$: C, 62.90; H, 6.45; S, 12.9. Found: C, 62.80; H, 6.51; S, 12.75.

**2-Furyl-2-thienyldimethylsilane:** yield 74%; bp 115 °C/20 mmHg; $^1H$ NMR $\delta$ 0.48 (s, 6H, $SiMe_2$), 6.21 (m, 1H, $H_{furyl}$), 6.57 (d, 1H, $^3J = 3.3$, $H_{furyl}$), 7.01 (m, 1H, $H_{thienyl}$), 7.22 (d, 1H, $^3J = 3.5$, $H_{thienyl}$), 7.44 (d, 1H, $^3J = 4.5$, $H_{thienyl}$), 7.56 (d, 1H, $^3J = 1.5$, $H_{furyl}$); $^{13}C$ NMR $\delta$ −2.7 ($Si(CH_3)_2$), 111.4 (T), 121.3 (T), 128.3 (T), 131.4 (T), 135.5 (T), 141,7 (T), 147.2 (Q), 157.5 (Q); MS *m/z* (rel intensity, %) 208 (51, M), 193 (100, M − $CH_3$), 167 (22); IR (neat KBr) 3115, 2968, 1550, 1494, 1409, 1259, 1213, 1108, 998, 812, 783, 744, 706 $cm^{-1}$. Anal. Calcd for $C_{10}H_{12}OSSi$: C, 57.69; H, 5.76; S, 15.38. Found: C, 57.61; H, 5.71; S, 15.35.

**2,5-Bis(2-furyldimethylsilyl)thiophene:** yield 69%; $^1H$ NMR $\delta$ 0.66 (s, 12H, $SiMe_2$), 6.45 (m, 2H, $H_{furyl}$), 6.79 (d, 2H, $^3J = 3.3$, $H_{furyl}$), 7.48 (s, 2H, $H_{thienyl}$), 7.73 (d, 2H, $^3J = 1.5$, $H_{furyl}$); $^{13}C$ NMR $\delta$ −2.7 ($Si(CH_3)_2$), 109.6 (T), 121.3 (T), 136.6 (Q), 143.0 (T), 147.3 (T), 157.5 (Q); MS *m/z* (rel intensity, %) 332 (47, M), 317 (100, M-$CH_3$); IR (neat KBr) 3149, 3111, 3081, 2964, 1550, 1494, 1455, 1409, 1327, 1257, 1213, 1148, 1108, 1059, 998, 811, 785, 744, 705, 679 $cm^{-1}$. Anal. Calcd for $C_{16}H_{20}O_2SSi_2$: C, 57.83; H, 3.61; S, 9.6. Found: C, 57.78; H, 3.64; S, 9.55.

**2-(5-Bromothienyl)-*p*-methoxyphenyldimethylsilane (*2*):** yield 75%; $^1H$ NMR $\delta$ 0.55 (s, 6H, $SiMe_2$), 3.78 (s, 3H, $0CH_3$), 6.90 (d, 2H, $^3J = 8.5$, $H_{phenyl}$), 6.97 (d, 1H, $^3J = 3.5$, $H_{thienyl}$), 7.06 (d, 1H, $^3J = 3.5$, $H_{thienyl}$), 7.50 (d, 2H, $^3J = 8.5$, $H_{phenyl}$); $^{13}C$ NMR $\delta$ −1.1 ($Si(CH_3)_2$), 55.1 ($OCH_3$), 113.8 (T), 117.6 (Q), 131.4 (T), 134.7 (T), 135.3 (T), 135.8 (Q), 141.5 (Q), 161.0 (Q); MS *m/z* (rel intensity, %) 329 (5), 328 (30), 327 (6), 326 (28, M), 315 (9), 314 (20), 313 (97), 312 (17), 311 (100, M − $CH_3$), 231 (15), 229 (16); IR (neat KBr) 3001, 2957, 2901, 1594, 1564, 1502, 1462, 1441, 1404, 1310, 1279, 1250, 1204, 1182, 1114, 1067, 1033, 1000, 953, 835, 807, 777, 738, 677, 608, 566, 524, 487, 443 $cm^{-1}$. Anal. Calcd for $C_{13}H_{15}BrOSSi$: C, 47.70; H, 4.58; S, 9.78. Found: C, 47.65; H, 4.65; S, 9.75.

**2,5-Bis(*p*-methoxyphenyldimethylsilyl)thiophene:** yield 67%; $^1H$ NMR $\delta$ 0.91 (s, 12H, $SiMe_2$), 3.97 (s, 6H, $0CH_3$), 7.16 (d, 4H, $^3J = 8.5$, $H_{phenyl}$), 7.14 (s, 2H, $H_{thienyl}$), 7.74 (d, 4H, $^3J = 8.5$, $H_{phenyl}$); $^{13}C$ NMR $\delta$ −0.7 ($Si(CH_3)_2$), 55.1 ($OCH_3$), 116.9 (T), 135.4 (T), 136.8 (T), 139.4 (Q), 142,3 (Q), 161.3 (Q); $^{29}Si$ NMR $\delta$ −12.13; MS *m/z* (rel intensity, %) 412 (26, M), 398 (16), 397 (100, M − $CH_3$); IR (neat KBr) 3082, 1591, 1563, 1501, 1462, 1403, 1398, 1281, 1248, 1213, 1180, 1111, 1083, 1030, 991, 834, 805, 774, 709, 677, 522, 485, 412 $cm^{-1}$. Anal. Calcd for $C_{22}H_{28}O_2SSi_2$: C, 64.07; H, 6.79; S, 7.76. Found: C, 64.1; H, 6.81; S, 7.68.

**[2-(*p*-Methoxyphenyldimethylsilyl)thienyl]-5-carbaldehyde:** yield 62%; $^1H$ NMR $\delta$ 0.59 (s, 6H, $SiMe_2$), 3.77 (s, 3H, $0CH_3$), 6.93 (d, 2H, $^3J = 8.5$, $H_{phenyl}$), 7.02 (d, 1H, $^3J = 3.5$, $H_{thienyl}$), 7.08 (d, 1H, $^3J = 3.5$, $H_{thienyl}$), 7.55 (d, 2H, $^3J = 8.5$, $H_{phenyl}$), 9.94 (s, 1H, CHO); $^{13}C$ NMR $\delta$ −1.6 ($Si(CH_3)_2$), 56.0 ($OCH_3$), 114.1 (T), 128.5 (T), 129.5 (T), 136.7 (T), 132.4 (Q), 136.8 (Q), 145.5 (Q), 162.0 (Q), 183.7 (T); MS *m/z* (rel intensity, %) 276 (13, M), 261 (100, M − $CH_3$); IR (neat KBr) 3005, 1700, 1594, 1564, 1502, 1462, 1404, 1282, 1245, 1188, 1105, 1033, 948, 837, 807 $cm^{-1}$. Anal. Calcd for $C_{14}H_{16}O_2SSi$: C, 60.86; H, 5.79; S, 11.59. Found: C, 60.59; H, 5.69; S, 11.78.

**2-(5-*gem*-Dicyanovinyl)thienyl-(*p*-methoxyphenyldimethylsilane):** yield 35%; F 87 °C; $^1H$ NMR $\delta$ 0.56 (s, 6H, $SiMe_2$), 3.75 (s, 3H, $0CH_3$), 6.88 (d, 2H, $^3J = 8.5$, $H_{phenyl}$), 6.92 (d, 1H, $^3J = 3.5$, $H_{thienyl}$), 7.11 (d, 1H, $^3J = 3.5$, $H_{thienyl}$), 7.46 (s, 1H, CH═$(CN)_2$), 7.56 (d, 2H, $^3J = 8.5$, $H_{phenyl}$); $^{13}C$ NMR $\delta$ −1.9 ($Si(CH_3)_2$), 55.8 ($OCH_3$), 82.1 (Q), 113.4 (T), 117.2 (Q), 126.4 (T), 127.8 (T), 133.4 (T), 132.8 (Q), 136.6 (Q), 137.8 (Q), 162.2 (Q), 165.3 (Q); MS *m/z* (rel intensity, %) 324 (100, M); IR (neat KBr) 2997, 2230, 1657, 1579, 1558, 1459, 1404, 1278, 1251, 1165, 1101, 1027, 948, 887, 852 $cm^{-1}$. Anal. Calcd for $C_{17}H_{16}N_2OSSi$: C, 62.96; H, 4.93; N, 8.64; S, 9.87. Found: C, 62.92; H, 4.81; N, 8.58; S, 9.75.

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