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A General Synthesis of Vinylic Silyl Hydrides Using Nickel Catalysis. Applications to the Syntheses of Silylene-Tethered Conjugated Polymers

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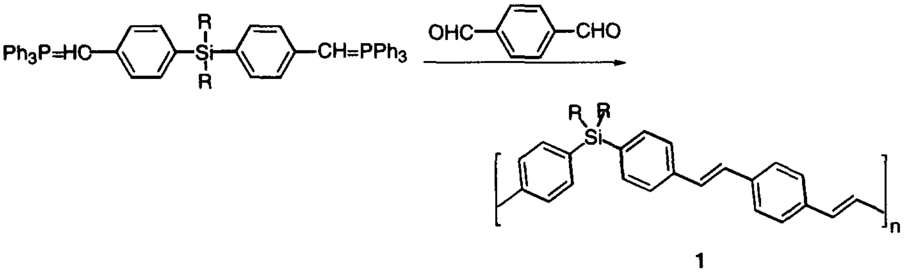
Abstract: Treatment of benzylic or allylic dithioacetals with $Me_2(^iPrO)SiCH_2MgCl$ in the presence of $NiCl_2(PPh_3)_2$ catalyst yielded the corresponding i-propoxy(vinyl)silanes which are reduced with $LiAlH_4$ to afford vinylic silyl hydrides. These hydrides serve as the precursors for the syntheses of silylene-tethered σ,π-conjugated copolymers.

Introduction

Conjugated polymers can display diverse electroactive properties such as photosensitivity,[1] conductivity,[2] as well as non-linear optical properties.[3] A polyphenylene-vinylene-based device has been shown to serve as a light emitting diode in the green light region.[4] Various model systems suggest that the photophysical properties of certain conjugated polymers can be represented by those of a short fragment of the corresponding chromophores.[5] Accordingly, there has been an increasing study on the use of spacers between well-defined conjugated moieties in the polymeric backbone that can increase the processibility and, in the meantime, the emission wavelength can be predicted.[6,7] Silylene moiety appears to be an attractive spacer for this purpose.[7] These polymers can be conveniently obtained by a displacement of silicon-halide bond with alkynyl nucleophile.[2b,6] However, the structural variety of such polymers is somewhat limited. More recently, silylene-tethered oligophenylene-vinylene lumiphores **1** were synthesized by Wittig reaction (eq 1).[7] In these



1

(1)

studies, the silylene group in **1** is linked to two aryl moieties of the backbone such that the steric environment around the silicon atom will be somewhat congested. A replacement of the aryl linkage in **1** by the vinylic ligand may release the steric hindrance at silicon. Hydrosilylation turns out to be the most promising procedure for the synthesis of polyvinylene-silylenes.[8-10] To illustrate this, platinum-catalyzed polymerization of alkynylsilanes has been used to synthesize **2** (eq 2).[9] More recently, reactions of arylene-spaced bisalkynylsilyl hydrides with bisalkynes under similar conditions can furnish the preparation of polymer **3** (eq

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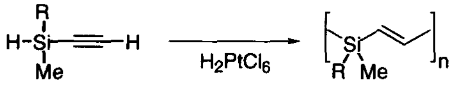
3).[10] However, these procedures are of limited success because only alkynyl silyl hydride reagents have been employed.



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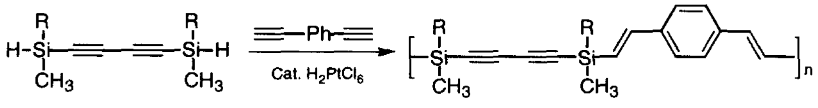


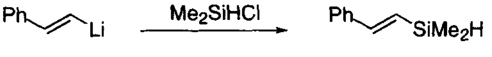
(3)

3

Recently, we were interested in investigating the photophysics of silylene tethered conjugated polymers **6**.[11] Our synthetic strategy relies on the hydrosilylation of bisalkynes **4** with vinylic bis-silyl hydrides **5** (eq 4). Accordingly, a variety of vinyl silyl hydrides is required for this purpose. To the best of our knowledge, the use of these hydrides in the transition metal-catalyzed hydrosilylation for the synthesis of silylene-tethered polymers has not been reported. It is interesting to note that not many vinylic silyl hydrides are known in the literature.[12] Chan *et al.* briefly reported the preparation of (β-styryl)dimethylsilane (**7**) from the reaction of β-styryl lithium with dimethylchlorosilane (eq 5).[12a] However, these procedures may not be easily applicable for the synthesis of **5** with different structural variety.

(4)

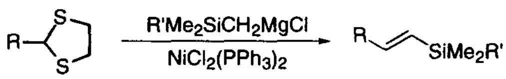
4 **5** **6**



(5)

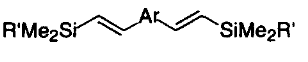
7

We recently reported a unified procedure to prepare vinylsilanes **9** from the corresponding aryl- or vinyl-substituted dithioacetals **8** (eq 6).[13,14] Bisvinylsilanes **10** can be prepared conveniently from **11**. It was felt that, when appropriate Grignard reagents are employed, this methodology can provide a convenient procedure for the preparation of various vinylic hydrosilane derivatives **12**.



(6)

8 **9**



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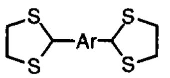
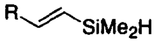


11



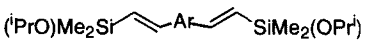
12

Results and Discussion

At the beginning of this research, HMe_2SiCH_2MgCl[15] was used to attempt the cross coupling reaction with dithioacetal **8** under the nickel-catalyzed conditions. Unfortunately, a mixture of products was obtained and the corresponding vinylic silyl hydride **12** was isolated, at most, as the minor product. An alternative route is therefore highly desirable.

It is well documented that silyl hydrides can be synthesized by reduction of the corresponding silyl halides[16] or triflates.[17] More recently, treatment of alkoxysilane moiety in polymers by $LiAlH_4$ also led to the formation of silyl hydride functionality.[18] Accordingly, it is envisaged that this methodology can be extended to the synthesis of **12**. Our strategy is therefore to adopt the reaction shown in eq 6, using $Me_2(iPrO)SiCH_2MgCl$ as the Grignard reagent.[19] The corresponding isopropoxyvinylsilanes **13** would be expected. Reduction of the Si-O bond in **13** would lead to the formation of the corresponding vinylic silyl hydrides **12**.

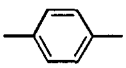
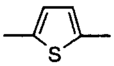
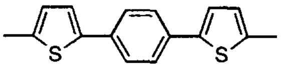
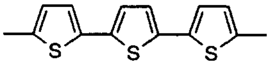
13



14

A benzene solution of dithioacetal **8** and $Me_2(^iPrO)SiCH_2MgCl$ in the presence of 5 mol % of $NiCl_2(PPh_3)_2$ was refluxed for 16 h to give, after usual workup, the corresponding vinylsilane **13** in good yield. Reactions of bisdithioacetals **11** under the same conditions yielded bisvinylsilanes **14**. The results are tabulated in Table 1. It is noteworthy that aromatic hydrocarbon solvents were essential for these cross coupling

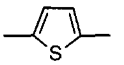
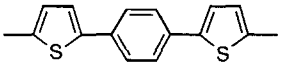
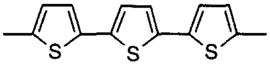
Table 1 $NiCl_2(PPh_3)_2$-Catalyzed Cross Coupling Reactions of **8** or **11** with $Me_2(^iPrO)SiCH_2MgCl$

Entry	Substrate (**8** or **11**)	Product (% Yield)
1	**8a** (R = Ph)	**13a** (85)
2	**8b** (R = 2-Thienyl)	**13b** (90)
3	**8c** (R = β-styryl)	**13c** (88)
4	**11a** (Ar = 	**14a** (58)
5	**11b** (Ar =  S	**14b** (56)
6	**11c** (Ar =  S S	**14c** (84)
7	**11d** (Ar =  S S S	**14d** (53)

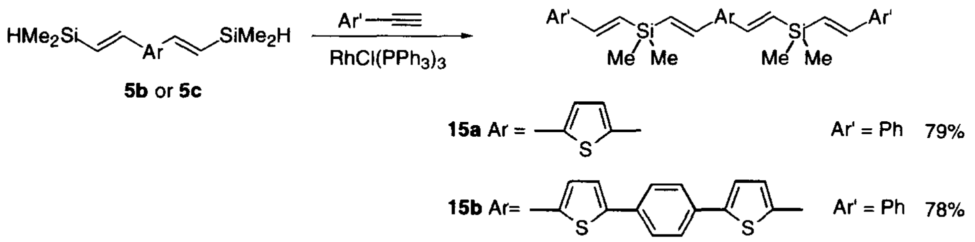
reactions when benzylic substrates **8a, b**, and **11** were employed (entries 1,2,4-7). However, allylic dithioacetal **8c** can undergo the reaction without difficulty in THF solvent (entry 3).

Reduction of the Si-O bond in **13** and **14** with $LiAlH_4$ in refluxing benzene solution for 16-18 h yielded the corresponding silylhydrides **12** and **5**, respectively. Longer reaction time was necessary when the reaction was carried out at lower temperature (e.g. in refluxing ether). The results are summarized in Table 2.

Table 2 Reduction of **13** or **14** with $LiAlH_4$

Entry	Substrate (**13** or **14**)	Product (%Yield)
8	**13a** (R = Ph)	**12a** (75)
9	**13b** (R = 2-Thienyl)	**12b** (74)
10	**13c** (R = β-styryl)	**12c** (65)
11	**14a** (Ar = 	**5a** (75)
12	**14b** (Ar = 	**5b** (74)
13	**14c** (Ar = 	**5c** (73)
14	**14d** (Ar = 	**5d** (67)

As evident in Table 2, vinyl silyl hydrides **5** and **12** can be conveniently prepared in two steps in satisfactory yield. Since the aryl group in **8** and **11** can be easily modified, a wide range of different structural variety of vinylic silyl hydrides **5** and **12** can thus be synthesized. It is noteworthy that these hydrides **5** have served as a useful entity for the synthesis of silylene-tethered conjugated oligomers **15** and polymers **6**.[11] To illustrate this, phenylacetylene was allowed to react with **5b** in the presence of 0.5 mol % of $RhCl(PPh_3)_3$ to afford **15a** (eq 7). Oligomer **15b** was prepared in a similar manner. Alternatively, **12b** was employed to add onto 1,4-diethynylbenzene to yield **15c** (eq 8). When bis-alkynes **4** and bis-silyl hydrides **5** were allowed to react under similar conditions, the silylene tethered σ-π conjugated polymers **6** were thus obtained (eq 9).



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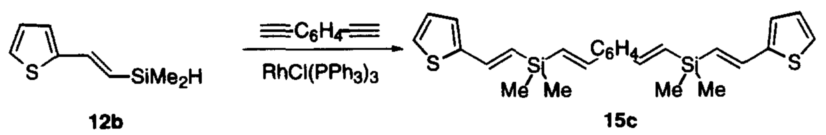

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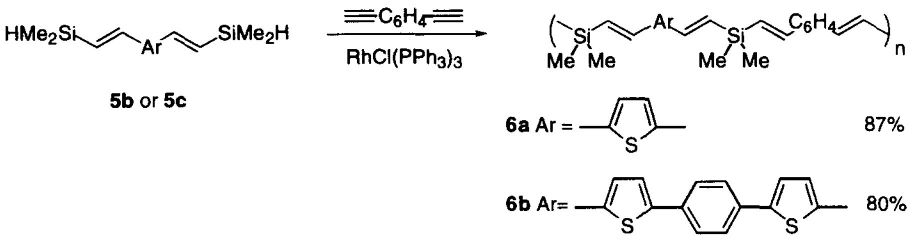

(9)

In summary, we have demonstrated a convenient two-step synthesis of a variety of vinylic silyl hydrides from the corresponding dithioacetals. These hydrides can be extended to the synthesis of a wide range of silylene-tethered conjugated oligomers and polymers. The investigation of the photophysical properties of these oligomers as well as polymers is in progress in our laboratory.

Experimental Section

General Procedure for the Preparation of Bisdithioacetals 11. - A chloroform solution of the dialdehyde (1 equiv), $BF_3{\bullet}Et_2O$ (10 mol%) and 1,2-ethanedithiol (3.0 equiv) was stirred at room temperature for 4 h. The mixture was poured into 10% NaOH and the two layers were separated. The organic layer was washed with brine (20 mL), and dried ($MgSO_4$). The solvent was removed in vacuo to give **11**.

11b (99%); mp 68-70 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.26-3.47 (m, 8 H), 5.79 (s, 2 H), 6.80 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 39.9, 50.9, 124.9, 147.2; MS m/z (rel intensity) 292 (M^+, 100), 264 (41), 172 (28), 127 (26), 105 (12), 59 (7); HRMS Calcd for $C_{10}H_{12}S_5$: 291.9542; Found: 291.9537.

11c (92%); mp 195-197°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.35-3.52 (m, 8 H), 5.89 (s, 2 H), 7.00 (d, J = 3.7 Hz, 2 H), 7.08 (d, J = 3.7 Hz, 2 H), 7.52 (s, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 39.9, 50.9, 122.5, 125.9, 126.0, 126.5, 143.8, 146.6; MS m/z (rel intensity) 450 (M^+, 100), 422 (43), 361 (19), 328 (35), 285 (14), 242 (121), 196 (7), 183 (7), 124 (26); HRMS Calcd for $C_{20}H_{18}S_6$: 449.9733; Found: 449.9728.

11d (68%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.31-3.52 (m, 8 H), 5.89 (s, 2 H), 6.91 (d, J = 3.6 Hz, 2 H), 6.93 (d, J = 3.6 Hz, 2 H), 6.99 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 39.9, 50.9, 123.0, 124.2, 126.2, 136.2, 137.2, 146.5; MS m/z (rel intensity) 456 (M^+, 14), 369 (15), 380 (13), 277 (100), 264 (10), 184 (18), 124 (53), 64 (30); HRMS Calcd for $C_{18}H_{16}S_7$: 455.9297; Found: 455.9292.

General Procedure for the $NiCl_2(PPh_3)_2$-Catalyzed Reactions of Dithioacetals 8 or 11 with $Me_2(^i PrO)SiCH_2MgCl$. A THF solution of $Me_2(^i PrO)SiCH_2MgCl$ (5-10 equiv) was evacuated as much as possible and then dissolved in benzene. Dithioacetal **8** or **11** and $NiCl_2(PPh_3)_2$ (0.1 equiv) were then introduced. The mixture was refluxed under N_2 for 16 h and then poured into saturated NH_4Cl. The organic layer was separated and the aqueous layer was extracted twice (2 x 20 mL) with ether. The combined organic portions were washed twice (2 x 20 mL) with 10% NaOH and with brine (20 mL), and dried ($MgSO_4$). The solvent was removed in vacuo and the residue was distilled under reduced pressure or triturated with MeOH to give compound **13** or **14**.

Dimethyl(i-propoxy)(β-styryl)silane (13a). In a manner similar to that described in the general procedure, a mixture of **8a** (1.82 g, 10.0 mmol) and $NiCl_2(PPh_3)_2$ (0.70 g, 1.0 mmol) was treated with $Me_2(^iPrO)SiCH_2MgCl$ (50.0 mmol) in benzene (50 mL) to give **13a** (1.55 g, 85%): bp 64 °C (0.5 mm). ^1H NMR ($CDCl_3$, 200 MHz) δ 0.26 (s, 6 H), 1.17 (d, J = 5.7 Hz, 6 H), 4.03 (sept, J = 5.7 Hz, 1 H), 6.43 (d, J = 19.3 Hz, 1 H), 6.97 (d, J = 19.3 Hz, 1 H), 7.27-7.46 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -1.1, 25.7, 65.1, 126.5, 127.1, 128.3, 128.5, 138.0, 145.2; MS m/z (rel intensity) 220 (M^+, 34), 189 (86), 162 (68), 147 (100), 131 (42), 117 (40), 75 (42), 59 (14); HRMS Calcd for $C_{13}H_{20}SiO$: 220.1283; Found: 220.1290.

Dimethyl(i-propoxy)(β-thienylvinyl)silane (13b). In a manner similar to that described in the general procedure, a mixture of **8b** (1.88 g, 10.0 mmol), $NiCl_2(PPh_3)_2$ (0.70 g, 1.0 mmol) and $Me_2(^iPrO)SiCH_2MgCl$ (50.0 mmol) in benzene (50 mL) was transformed into **13b** (1.69 g, 90%): bp 62 °C (0.5 mm) ^1H NMR ($CDCl_3$, 200 MHz) δ 0.24 (s, 6 H), 1.16 (d, J = 6.1 Hz, 6 H), 4.03 (sept, J = 6.1 Hz, 1 H), 6.17 (d, J = 18.9 Hz, 1 H), 6.94- 7.09 (m, 3 H), 7.18 (d, J = 4.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -1.2, 25.7, 65.1, 125.1, 126.2, 126.6, 127.4, 137.6, 144.9; MS m/z (rel intensity) 226 (M^+, 15), 211 (7), 189 (7), 168 (100), 151 (66), 143 (32), 133 (20), 75 (36), 59 (17); HRMS Calcd for $C_{11}H_{18}SiOS$: 226.0847; Found: 226.0855.

1,4-Bis{[dimethyl(i-propoxy)silyl]vinyl}benzene (14a). In a manner similar to that described in the general procedure, a mixture of **11a** (1.43 g, 5.0 mmol) and $NiCl_2(PPh_3)_2$ (0.35 g, 0.5 mmol) was treated with $Me_2(^iPrO)SiCH_2MgCl$ (50.0 mmol) in benzene (50 mL) was converted to **14a** (1.05 g, 58%); bp 88 °C (0.5 mm) ^1H NMR ($CDCl_3$, 300 MHz) δ 0.25 (s, 12 H), 1.17 (d, J = 5.8 Hz, 12 H), 4.03 (sept, J = 5.8 Hz, 2 H), 6.43 (d, J = 19.2 Hz, 2 H), 6.95 (d, J = 19.2 Hz, 2 H), 7.41 (s, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ -1.1, 25.7, 65.1, 126.8, 133.5, 133.9, 144.7; MS m/z (rel intensity) 362 (M^+, 34), 347 (14), 304 (100), 261 (78), 219 (11), 189 (38), 147 (19), 133 (26), 117 (58), 75 (19); HRMS Calcd for $C_{20}H_{34}Si_2O_2$: 362.2097; Found: 362.2103.

2,5-Bis{β-[dimethyl(i-propoxy)silyl]vinyl}thiophene (14b). In a manner similar to that described in the general procedure, a mixture of **11b** (1.46 g, 5.0 mmol) and $NiCl_2(PPh_3)_2$ (0.35 g, 0.5 mmol) was treated with $Me_2(^iPrO)SiCH_2MgCl$ (50.0 mmol) in benzene (50 mL) to give **14b** (1.03 g, 56%); bp 92 °C (0.5 mm) ^1H NMR ($CDCl_3$, 200 MHz) δ 0.23 (s, 12 H), 1.17 (d, J = 5.9 Hz, 12 H), 4.99 (sept, J = 5.9 Hz, 2 H), 6.15 (d, J = 18.8 Hz, 2 H), 6.85 (s, 2 H), 6.96 (d, J = 18.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.2, 25.7, 65.2, 126.9, 127.5, 137.7, 144.5; MS m/z (rel intensity) 368 (M^+, 45), 354 (10), 278 (100), 189 (41), 147 (15), 108 (32), 75 (55); HRMS Calcd for $C_{18}H_{32}Si_2O_2S$: 368.1661 Found: 368.1664.

2,2'-*p*-Phenylene-bis-5-[β-dimethyl(i-propoxy)silylvinyl]thiophene (14c). In a manner similar to that described in the general procedure, a mixture of **11c** (2.25 g, 5.0 mmol), $NiCl_2(PPh_3)_2$ (0.35 g, 0.5 mmol) and $Me_2(^iPrO)SiCH_2MgCl$ (50.0 mmol) in benzene (50 mL) was transformed into **14c** (2.21 g, 84%); mp 102-103 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.25 (s, 12 H), 1.17 (d, J = 6.0 Hz, 12 H), 4.03 (sept, J = 6.0 Hz, 2 H), 6.18 (d, J = 18.9 Hz, 2 H), 6.96 (d, J = 3.7 Hz, 2 H), 7.01 (d, J = 18.9 Hz, 2 H), 7.21 (d, J = 3.7 Hz, 2 H), 7.58 (s,4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.1, 25.8, 65.2, 123.6, 126.0, 127.0, 127.6, 133.4, 137.6, 143.3,144.4; MS m/z (rel intensity) 526 (M^+, 47), 468 (14), 410 (32), 352 (14), 256 (21), 213 (10), 185 (15), 171 (10), 129 (45), 97 (60), 85 (49), 73 (100); HRMS Calcd for $C_{28}H_{38}Si_2O_2S_2$: 526.1851;

Found: 526.1854.

5,5"-Bis{[β-dimethyl(i-propoxy)silyl]vinyl}-2,2';5'2"-terthiophene (14d). In a manner similar to that described in the general procedure, a mixture of **11d** (1.82 g, 4.0 mmol) and $NiCl_2(PPh_3)_2$ (0.28 g, 0.4 mmol) was treated with $Me_2(^iPrO)SiCH_2MgCl$ (40.0 mmol) in benzene (40 mL) to give **14d** (1.13 g, 53%); ^1H NMR ($CDCl_3$, 200 MHz) δ 0.24 (s,12 H), 1.16 (d, *J* = 6.1 Hz, 12 H), 4.03 (sept, *J* = 6.1 Hz, 2 H), 6.13 (d, *J* = 18.8 Hz, 2 H), 6.89 (d, *J* = 3.7 Hz, 2 H), 6.97 (d, *J* = 18.8 Hz, 2 H), 7.03 (d, *J* = 3.7 Hz, 2 H), 7.06 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ –1.2, 25.7, 65.2, 124.0, 124.5, 127.2, 127.3, 136.4, 136.6, 137.4, 143.9; MS m/z (rel intensity) 532 (M^+, 10), 475 (5), 430 (22), 355 (8), 277 (65), 207 (100), 147 (38), 171 (10), 73 (30); HRMS Calcd for $C_{26}H_{36}Si_2O_2S_3$: 532.1416; Found: 532.1420.

General Procedure for the reduction of 13 or 14 with $LiAlH_4$. A slurry of **13** or **14** and $LiAlH_4$ (2-4 equiv) was refluxed under N_2 for 18 h and cooled to rt. The mixture was then quenched with water. After filtration, the organic layer was separated, dried and the solvent was removed in vacuo to give the residue which was chromatographed on silica gel (hexane) to afford **12** or **5**.

Dimethyl(β-styryl)silane (12a). In a manner similar to that described in the general procedure, a mixture of **13a** (2.20 g, 10.0 mmol) and $LiAlH_4$ (0.8 g, 20.0 mmol) in benzene (25 mL) was transformed into **12a** (1.21 g, 75%): ^1H NMR ($CDCl_3$, 300 MHz) δ 0.25 (d, *J* = 3.7 Hz, 6 H), 4.22 (doublet of septet, *J* = 3.7, 2.4 Hz, 1 H), 6.46 (dd, *J* = 19.1, 2.4 Hz, 1 H), 6.98 (d, *J* = 19.1 Hz, 1 H), 7.26-7.36 (m, 3 H), 7.44 (d, *J* = 7.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ –4.0, 126.1, 126.4, 128.1, 128.5, 138.1, 145.3; MS m/z (rel intensity) 162 (M^+, 100), 147 (74), 131 (65), 117 (15), 75 (14); HRMS Calcd for $C_{10}H_{14}Si$: 162.0865; Found: 162.0848.

Dimethyl[β-(2-thienyl)vinyl]silane (12b). In a manner similar to that described in the general procedure, a mixture of **13b** (2.26 g, 10.0 mmol) and $LiAlH_4$ (0.8 g, 20.0 mmol) in benzene (25 mL) was allowed to react to give **12b** (1.24 g, 74%):^1H NMR ($CDCl_3$, 300 MHz) δ 0.23 (d, *J* = 3.7 Hz, 6 H), 4.01 (doublet of septet, *J* = 3.7, 2.3 Hz, 1 H), 6.22 (dd, *J* = 18.7, 2.3 Hz, 1 H), 6.96-6.98 (m, 2 H), 7.05 (d, *J* = 18.7 Hz, 1 H), 7.18 (d, *J* = 4.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ –4.1, 125.0, 125.7, 125.8, 127.4, 137.8, 144.9; MS m/z (rel intensity) 168 (M^+, 48), 153 (100), 141 (1.0), 127 (41), 75 (1.0); HRMS Calcd for $C_8H_{12}SiS$: 168.0429; Found: 168.0433.

Dimethyl[4-phenyl-(1*E*,3*E*)-butadien-1-yl]silane (12c). In a manner similar to that described in the general procedure, a mixture of **13c** (2.46 g, 10.0 mmol) was treated with $LiAlH_4$ (0.8 g, 20.0 mmol) in benzene (25 mL) to give **12c** (0.94 g, 65%):^1H NMR ($CDCl_3$, 200 MHz) δ 0.21 (d, *J* = 3.5 Hz, 6 H), 4.17 (doublet of septet, *J* = 3.5, 2.4 Hz, 1 H), 5.99 (dd, *J* = 17.2, 2.4 Hz, 1 H), 6.56-6.83 (m, 3 H), 7.23--7.44 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ –4.0, 126.6, 127.8, 128.6, 131.2, 131.3, 133.4, 137.1, 145.8; MS m/z (rel intensity) 188 (M^+, 70), 173 (100), 160 (8), 145 (68), 128 (50), 121 (22), 105 (20); HRMS Calcd for $C_{12}H_{16}Si$: 188.1021; Found: 188.1038.

1,4-Bis[β-(dimethylsilyl)vinyl]benzene (5a). In a manner similar to that described in the general procedure, a mixture of **14a** (1.81 g, 5.0 mmol) was treated under N_2 with $LiAlH_4$ (0.8 g, 20.0 mmol) in benzene (25 mL) to give **5a** (0.92 g, 75%): ^1H NMR ($CDCl_3$, 200 MHz) δ 0.23 (d, *J* = 3.8 Hz, 12 H), 4.19 (doublet of septet, *J* = 3.8, 2.7 Hz, 2 H), 6.45 (dd, *J* = 19.2, 2.7 Hz, 2 H), 6.95 (d, *J* = 19.2 Hz, 2 H), 7.39 (s, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ –4.0, 126.3, 126.7, 137.9, 144.9; MS m/z (rel intensity) 246 (M^+, 16), 218 (10), 171 (25), 145 (24), 116 (13), 85 (11), 73 (15), 59 (100); HRMS Calcd for $C_{14}H_{22}Si_2$:

246.1260; Found: 246.1254.

2,5-Bis[β-(dimethylsilyl)vinyl]thiophene (5b). In a manner similar to that described in the general procedure, a mixture of **14b** (2.26 g, 10.0 mmol) was treated with $LiAlH_4$ (1.6 g, 40.0 mmol) in benzene (50 mL) to give **5b** (1.24 g, 74%): ^1H NMR ($CDCl_3$, 300 MHz) δ 0.23 (d, *J* = 3.7 Hz, 12 H), 4.01 (doublet of septet, *J* = 3.7, 2.3 Hz, 1 H), 6.22 (dd, *J* = 18.7, 2.3 Hz, 1 H), 6.96-6.98 (m, 2 H), 7.05 (d, *J* = 18.7 Hz, 1 H), 7.18 (d, *J* = 4.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -4.1, 126.4, 126.6, 137.9, 144.3 ; MS m/z (rel intensity) 168 (M^+, 48), 153 (100), 141 (1.0), 127 (41), 75 (1.0); HRMS Calcd for $C_{12}H_{20}Si_2S$: 252.0824; Found: 252.0826.

2,2'-*p*-Phenylene-bis-5-[β-(2-dimethylsilyl)vinyl]thiophene (5c). In a manner similar to that described in the general procedure, a mixture of **14c** (1.32 g, 2.5 mmol) was treated with $LiAlH_4$ (0.4 g, 10.0 mmol) to give **5c** (0.75 g, 73%): mp 170-181 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.22 (d, *J* = 3.8 Hz, 12 H), 4.18 (doublet of septet, *J* = 3.8, 2.7 Hz, 2 H), 6.19 (dd, *J* = 18.9, 2.7 Hz, 2 H), 6.94 (d, *J* = 3.9 Hz, 2 H), 7.00 (d, *J* = 18.9 Hz, 2 H), 7.20 (d, *J* = 3.9 Hz, 2 H), 7.57 (s, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -4.0, 123.5, 126.0, 126.1, 127.2, 133.4, 137.8, 143.1, 144.4; MS m/z (rel intensity) 410 (M^+, 100), 395 (19), 352 (11), 337 (10), 320 (21), 305 (27), 59 (32); HRMS Calcd for $C_{22}H_{26}Si_2S_2$: 410.1014; Found: 410.1019.

5,5''-Bis[β-(2-dimethylsilyl)vinyl]-2,2';5'2''-terthiophene (5d). In a manner similar to that described in the general procedure, a mixture of **14d** (1.33 g, 2.5 mmol) was treated under N_2 with $LiAlH_4$ (0.4 g, 10.0 mmol) to give **5d** (0.69 g, 67%): mp 157-158 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.21 (d, *J* = 3.6 Hz, 12 H), 4.16 (doublet of septet, *J* = 3.6, 2.7 Hz, 2 H), 6.14 (dd, *J* = 18.7, 2.7 Hz, 2 H), 6.86 (d, *J* = 3.7 Hz, 2 H), 6.96 (d, *J* = 18.7 Hz, 2 H), 7.02 (d, *J* = 3.7 Hz, 2 H), 7.05 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -4.0, 124.0, 124.3, 124.4, 126.3, 127.0, 136.4, 137.5, 143.9; MS m/z (rel intensity) 416 (M^+, 100), 326 (21), 311 (10), 268 (22), 236 (81); HRMS Calcd for $C_{20}H_{24}Si_2S_3$: 416.0578; Found: 416.0576.

2,5-Bis{β-[dimethyl(β'-styryl)silyl]vinyl}thiophene (15a). A mixture of **5b** (0.25 g, 1.0 mmol), phenylacetylene (0.20 g, 2.0 mmol) and $RhCl(PPh_3)_3$ (4.6 mg, 0.5 mol %) in THF (5 mL) was stirred under N_2 at 50 °C for 4 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel (hexane) to give the product **15a** (0.36 g, 79%); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.29 (s, 12 H), 6.22 (d, *J* = 18.7 Hz, 2 H), 6.48 (d, *J* = 19.3 Hz, 2 H), 6.83 (s, 2 H), 6.89-6.97 (m, 4 H), 7.22-7.34 (m, 6 H), 7.44 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -2.6, 126.4, 126.6, 127.0, 127.7, 128.1, 128.5, 137.9,138.1, 144.5, 145.0; MS m/z (rel intensity) 456 (M^+, 32), 365 (14), 306 (12), 161 (40), 145 (65); 135 (42), 59 (100); HRMS Calcd for $C_{28}H_{32}Si_2S$: 456.1763; Found: 456.1757.

2,2'-*p*-Phenylene-bis-5-{[β-dimethyl(β-styryl)silyl]vinyl}thiophene (15b). In a manner similar to that described above, a mixture of **5c** (0.21 g, 0.5 mmol), phenylacetylene (0.10 g, 1.0 mmol) and $RhCl(PPh_3)_3$ (2.3 mg, 0.5 mol %) in THF (5 mL) was transformed into **15b** (0.24 g, 78%): ^1H NMR ($CDCl_3$, 300 MHz) δ 0.32 (s, 12 H), 6.28 (d, *J* = 18.8 Hz, 2 H), 6.52 (d, *J* = 19.0 Hz, 2 H), 6.97 (d, *J* = 19.0 Hz, 2 H), 6.96 (d, *J* = 3.7 Hz, 2 H), 7.00 (d, *J* = 18.8 Hz, 2 H), 7.21 (d, *J* = 3.7 Hz, 2 H), 7.26- 7.37 (m, 6 H), 7.47 (d, *J* =7.8 Hz, 4 H), 7.59 (s, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ -2.6, 123.5, 125.9, 126.5, 127.0, 127.2, 127.4, 128.1, 128.4, 128.5, 137.4, 138.1, 143.0, 144.6, 145.1; MS m/z (rel intensity) 614 (M^+, 86), 441 (23), 211 (12), 161 (11), 145 (100), 135 (34), 73 (28), 59 (73); HRMS Calcd for $C_{38}H_{38}Si_2S_2$: 614.1953; Found: 614.1958.

1,4-Bis{β-{dimethyl[β'-(2-thienyl)vinyl]silyl}vinyl}benzene (15c). In a manner similar to that described above, a mixture of **12b** (0.67 g, 4.0 mmol), 1,4-diethynylbenzene (0.25 g, 2.0 mmol) and $RhCl(PPh_3)_3$ (18.5 mg, 0.5 mol %) in THF (20 mL) was converted to **15c** (0.74 g, 80%): ^1H NMR ($CDCl_3$, 300 MHz) δ 0.28 (s, 12 H), 6.23 (d, *J* = 18.9 Hz, 2 H), 6.48 (d, *J* = 19.1 Hz, 2 H), 6.91 (d, *J* = 19.1 Hz, 2 H), 6.95-7.03 (m, 6 H), 7.17 (br d, *J* = 4.7 Hz, 2 H), 7.41 (s, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -2.6, 124.9, 125.9, 126.4, 126.7, 127.0, 127.3, 127.5, 137.4, 138.0, 144.5; MS m/z (rel intensity) 462 (M^+, 5), 365 (14), 350 (4), 283 (20), 242 (19), 199 (28), 167 (68), 141 (100), 73 (55), 59 (53); HRMS Calcd for $C_{26}H_{30}Si_2S_2$: 462.1327; Found: 462.1327.

Poly(1,4-divinylbenzene-dimethylsilylene-2,5-divinylthiophene-dimethylsilylene) (6a). A mixture of **5b** (0.25 g, 1.0 mmol), 1,4-diethynylbenzene (0.13 g, 1.0 mmol) and $RhCl(PPh_3)_3$ (4.6 mg, 0.5 mol %) in THF (5 mL) was stirred at 50 °C for 4 h. After cooling, methanol was added to precipitate the crude polymer. After filtration, the solid was washed twice with methanol and dried to give **6a** (0.32 g, 87%); M_n = 5535 (polydispersity 2.4); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.27 (br s, 12 H), 6.21 (br d, *J* = 18.7 Hz, 2 H), 6.47 (br d, *J* =19.2 Hz, 2 H), 6.82 (br, 2 H), 6.90 (br d, *J* =19.2 Hz, 2 H), 6.92 (br d, *J* = 18.7 Hz, 2 H), 7.40 (br, 4 H).

Poly(1,4-divinylbenzene-dimethylsilylene-2,2'-p-phenylene-bis-(5-vinylthiophene)-dimethylsilylene (6b). In a manner similar to that described above, a mixture of **5c** (0.21 g, 0.5 mmol), 1,4-diethynylbenzene (63 mg, 0.5 mmol) and $RhCl(PPh_3)_3$ (2.3 mg, 0.5 mol %) in THF (2.5 ml) was transformed into **6b** (0.21 g, 80%): M_n = 6167 (polydispersity 2.0); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.31 (br s, 12 H), 6.26 (br d, *J* =18.2 Hz, 2 H), 6.51 (br d, *J* =19.2 Hz, 2 H), 6.59 (br, 6 H), 7.20-7.24 (br, 4 H), 7.43- 7.58 (br, 8 H).

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