JOC Article

1,4-Silatropy of *S*-α-Silylbenzyl Thioesters: A Convenient Route to Silyl Enol and Dienol Ethers Accompanied by C−C Bond Formation via Thiocarbonyl Ylides

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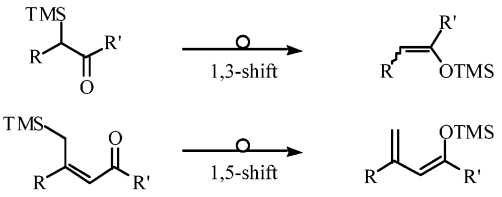
A novel convenient method for the generation of thiocarbonyl ylides from readily accessible starting materials and the first synthetic application of in situ generated ylides in the synthesis of silyl enol and dienol ethers, accompanied by C−C bond formation, is described. Under completely neutral conditions without any catalyst or additive, thermal reactions of *S*-α-silylbenzyl thioesters in sealed tubes at 180 °C provided silyl enol and dienol ethers in good to excellent yields with high stereoselectivities. This procedure consists of a multistep reaction in a one-pot process, i.e., 1,4-silatropy of *S*-α-silylbenzyl thioesters to give thiocarbonyl ylides, 1,3-electrocyclization of the ylides to give thiiranes, and the extrusion of sulfur from thiiranes to give silyl enol and dienol ethers.

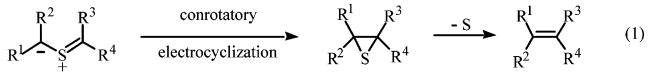
Introduction

Silyl enol and dienol ethers are well-known as key intermediates for various organic transformations including aldol condensations,[1] Diels−Alder reactions,[2] and related reactions.[3] Thus efficient preparations as well as synthetic applications of these compounds have been extensively studied over the past decades.[4] They are generally prepared via the silylation of carbonyl compounds by either kinetically[4,5] or thermodynamically[4,6] controlled enolate ions. While these methods require the addition of basic reagents, silyl migration protocols, when such precursors are readily accessible, could provide alternative and more useful routes to silyl enol ethers[7] or silyl dienol ethers[8] under neutral conditions, without the need of an additive or catalyst (Scheme 1).

SCHEME 1. A Convenient Route to Silyl Enol and Dienol Ethers via Silyl Migration



Thiocarbonyl ylides have promising synthetic potential for the stereospecific synthesis of olefins via conrotatory 1,3-dipolar electrocyclization followed by sulfur extrusion with retention of configuration (eq 1).[9] Similarily, siloxy-



(1)

tethered thiocarbonyl yildes (e.g. $R^3 = OSiMe_3$ in eq 1) have the possibility of providing silyl enol or dienol ethers. However, those applications have not received much attention due to (1) disadvantages such as the lack of available starting materials or the lack of generality

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(6) For silyl enol ethers, see: (a) Deyine, A.; Dujardin, G.; Mammeri, M.; Poirier, J.-M. *Synth. Commun.* **1998**, *28*, 1817. (b) Yamamoto, Y.; Matui, C. *Organometallics* **1997**, *16*, 2204. For silyl dienol ethers, see: (c) Moreno, M. J. S. M.; Martins, R. M. L. M.; Melo, M. L. Sa e; Neves, A. S. C. *Chem. Lett.* **1997**, 529.

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10.1021/jo026211z CCC: $25.00
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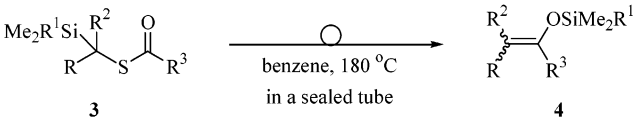
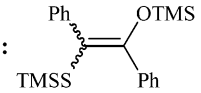
TABLE 1. Preparation of Silyl Enol Ethers 4 from *S*-α-Silylbenzyl Thioesters 3



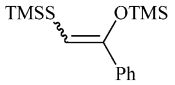
3 **4**

entry	thioester[a]	R	R^1	R^2	R^3	time (h)	yield (%)[b]	ratio of *Z*:*E*[b]
1	**3a**	Ph	CH_3	H	Ph	24	93 (**4a**)	91:9
2	**3b**	Ph	CH_3	H	*p*-$NO_2C_6H_4$	24	92 (**4b**)	91:9
3	**3c**	Ph	CH_3	H	*p*-$MeOC_6H_4$	8	91 (**4c**)	91:9
4	**3d**	Ph	CH_3	H	2-furyl	3	89 (**4d**)	96:4
5	**3e**	Ph	CH_3	H	2-thienyl	2	87 (**4e**)	93:7
6	**3f**	Ph	CH_3	H	2-(4-Cl-pyridyl)	1	52 (**4f**)	83:17
7	**3g**	Ph	CH_3	H	CH_3	64	44[c] (**4g**)	75:25
8	**3h**	Ph	Ph	H	Ph	5	87 (**4h**)	88:12
9	**3i**	Ph	CH_3	Me_3Si	Ph	1	(96)[d] (**4i**)	(11:89)[d]
10	**3j**	H	CH_3	Me_3Si	Ph	126	(58)[e] (**4j**)	(88:12)[e]

[a] All reactions were carried out with 0.05 mmol of thioesters in sealed tubes. [b] Determined by ^{1}H NMR in the presence of mesitylene as an internal standard. *Z*-Structures of the major products of **4b**,**d**,**e**,**f** were determined by difference NOE experiments, while those of **4a**,**c**,**g**,**h** were confirmed by comparison of their spectra with those of reported data (see Experimental Section). [c] Starting material (45%) remained in the reaction mixture. [d] 1,2-Diphenyl-1-trimethylsilylthio-2-(trimethylsiloxy)ethene was obtained.

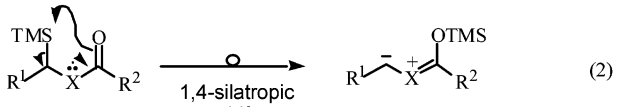
4i: 

[e] A mixture of starting material (36%) and 1-trimethylsilylthio-2-phenyl-2-(trimethylsiloxy)ethene (58%) was obtained.

4j: 

of their reactions often encountered in their chemistry[10] and (2) a number of alternative flexible routes to olefins.

We previously reported on a series of convenient routes to nitrogen-centered 1,3-dipolar species (azomethine ylides **1** and azomethine imines) via intramolecular 1,2- or 1,4-silatropic shift and their cycloaddition reactions.[11] In the same context, our continuing effort has focused on the extension of such a silatropy protocol to the generation of sulfur-centered 1,3-dipoles (eq 2), and quite



(2)

Azomethine ylides **1**: X = NR
Thiocarbonyl ylides **2**: X = S

recently in a preliminarily paper, we reported on the smooth transformation of *S*-α-silylmethyl thioesters to silyl enol ethers via siloxy-tethered thiocarbonyl ylides.[12]

From these points of view, we now present full details of a simple new approach to silyl enol and dienol ethers from readily accessible starting materials: the thermal 1,4-silatropy reaction of *S*-α-silylbenzyl thioesters to give thiocarbonyl ylides then electrocyclization to thiiranes followed by sulfur extrusion, in a one-pot process under completely neutral conditions without any catalyst or additive.

Results and Discussion

Silyl Enol Ethers. Our initial approach was to examine the behavior of thioester **3a** under thermal conditions: a benzene solution of thioester **3a** in a sealed tube was heated at 180 °C for 24 h. This simple operation, without any catalyst or additive under neutral conditions, provided silyl enol ether **4a** in high yield (93%) with a high stereoselectivitiy (*E*/*Z* = 9/91), the spectral data of which are completely consistent with those reported in the literature.[13] The formation of silyl enol ether **4a** as a major product was encouraging because the migration of a silyl group from carbon to oxygen was confirmed by this experiment, which shows good evidence for the intermediacy of a thiocarbonyl ylide in the course of the reaction as noted previously (eq 1). No sign of a dimerization product[14] was detected in the ^{1}H NMR and GCMS spectra of the crude product mixture. To examine the generality of this protocol, a series of *S*-α-silylbenzyl thioesters **3** were subjected to the same reaction conditions and the results are summarized in Table 1.

(10) For reviews on thiocarbonyl ylides, see: (a) Kellogg, R. M. *Tetrahedron* **1976**, *32*, 2165. (b) Huisgen, R.; Fulka, C.; Kalwinsch, I.; Li, X.; Mloston, G.; Moran, J. R.; Pröbstl, A. *Bull. Soc. Chim. Belg.* **1984**, *93*, 511. (c) Mloston, G.; Heimgartner, H. *Pol. J. Chem.* **2000**, *74*, 1503.

(11) For azomethine ylides, see: (a) Ohno, M.; Komatsu, M.; Miyata, H.; Ohshiro, Y. *Tetrahedron Lett.* **1991**, *32*, 5813. (b) Komatsu, M.; Ohno, M.; Tsuno, S.; Ohshiro, Y. *Chem. Lett.* **1990**, 575. (c) Iyoda, M.; Sultana, F.; Komatsu, M. *Chem. Lett.* **1995**, 1133. (d) Washizuka, K.-I.; Minakata, S.; Ryu, I.; Komatsu, M. *Tetrahedron* **1999**, *55*, 12969. For azomethine imines, see: (e) Washizuka, K.-I.; Nagai, K.; Minakata, S.; Ryu, I.; Komatsu, M. *Tetrahedron Lett.* **2000**, *41*, 691. (f) Washizuka, K.-I.; Nagai, K.; Minakata, S.; Ryu, I.; Komatsu, M. *Tetrahedron Lett.* **1999**, *40*, 8849.

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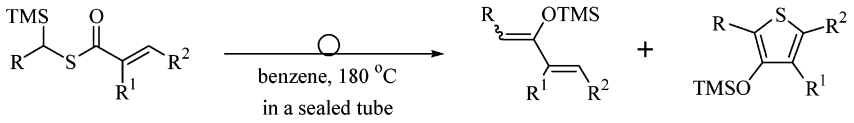
(13) Anders, E.; Stankowiak, A.; Riemer, R. *Synthesis* **1987**, 931.

(14) In the absence of effective trapping agents, thiocarbonyl ylides typically undergo 1,3-dipolar electrocyclization to thiiranes or dimerization to 1,4-dithianes. For electrocyclization, see: (a) Buter, J.; Wassenaar, S.; Kellogg, R. M. *J. Org. Chem.* **1972**, *37*, 4045. For dimerization, see: (b) Kalwinsch, I.; Li, X.; Gottstein, A.; Huisgen, R. *J. Am. Chem. Soc.* **1981**, *103*, 7032. For a review on thiocarbonyl ylides, see ref 10a.

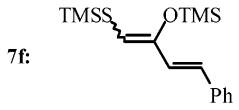
TABLE 2. Preparation of Silyl Dienol Ethers 7 from α,β-Unsaturated *S*-α-Silylbenzyl Thioesters 6



6 **7** **8**

entry	thioester **6**[a]	R	R^1	R^2	time (h)	silyl enol ether **7** yield (%)[b]	silyl enol ether **7** ratio of *Z*:*E*[b,c]	thiophene **8** yield (%)[b]
1	**6a**	Ph	H	Ph	1.5	82[d] (**7a**)	78:22	9 (**8a**)
2	**6a**	Ph	H	Ph	80[e]	6 (**7a**)	100:0	55 (**8a**)
3	**6b**	Ph	H	*p*-$NO_2C_6H_4$	2	74 (**7b**)	78:22	nd[f]
4	**6c**	Ph	H	*p*-$MeOC_6H_4$	2	79 (**7c**)	77:23	10 (**8c**)
5	**6d**	Ph	H	CH_3	1.7	67[f] (**7d**)	73:27	11 (**8d**)
6	**6e**	Ph	CH_3	H	13	nd[g] (**7e**)	nd[g]	40 (**8e**)
7	**6f**	$SiMe_3$	H	Ph	26	(72)[h] (**7f**)	(65:35)[h]	0

[a] All reactions were carried out with 0.05 mmol of thioesters in sealed tubes. [b] Determined by ^1H NMR in the presence of mesitylene as an internal standard. [c] Only one report[18] describes the synthesis of **7a** from 1,4-diphenyl-but-1-en-3-one and a silylating agent, where the configuration and the diastereomer ratio are not mentioned. The other silyl dienol ethers are unprecedented. [d] Starting material (7%) remained in the reaction mixture. [e] Prolonged reaction time under the same conditions. [f] Starting material (13%) remained in the reaction mixture. [g] Not determined. [h] 1-Trimethylsilylthio-2-trimethylsiloxy-4-phenyl-1,3-butadiene (**7f**) was obtained.



Aromatic thioesters **3** (entries 1−6 and 8) afforded the corresponding silyl enol ethers **4** in high yields with high *Z*-selectivities, the stereoselectivities of which are higher than that reported for the silylation of benzyl phenyl ketone with LDA and trimethylsilyl chloride at −78 °C.[15] Among these, the nitro group had no apparent detrimental effect on reactivity, reaction yield, and stereoselectivity (entry 2). However, in the presence of a methoxy group, thioester **3c** showed an enhanced reactivity with no loss in yield or stereoselectivity (entry 3). It would be expected that the reaction of thioester **3c** would be accelerated by an increase in the interaction between the silicon and the oxygen electron donated from the 4-methoxyphenyl group in the rate-limiting silyl migration step. Moreover, the reactions of thioesters **3d**−**f** having aromatic heterocycles smoothly proceeded with good stereoselectivities to afford the corresponding silyl enol ethers **4d**−**f**, respectively (entries 4−6). The acceleration effect of 2-furyl and 2-thienyl groups in the reactions of **3d**,**e** was similar to that of the *p*-methoxyphenyl group in the reaction of **3c**. In the case of **3f**, the reaction was stopped at its early stage, since the yield of **4f** decreased gradually by further reaction. In addition, the reaction of aliphatic thioester **3g** (entry 7), although it proceeded rather sluggishly, showed a slightly improved stereoselectivity compared to the thermodynamic reaction of benzyl methyl ketone with triethylamine and trimethylsilyl chloride.[16] Furthermore, a variation in the migrating silyl group also showed a significant effect on the reaction rate: when the dimethylphenylsilyl group (thioester **3h**) was employed, the reaction was accelerated despite its bulkiness since the partial negative charge developing on the silicon atom in the transition state could be delocalized over the phenyl ring on the silyl group (entry 8). Interestingly, when another silyl group was introduced at the α position to the sulfur atom, thioesters **3** showed quite a different reaction pathway and reactivities (entries 9 and 10). For example, the thermal reactions of α,α-bissilylated thioesters **3i** and **3j** led to the formation of silylthio-substituted silyl enol ethers via tandem silyl group migrations without the involvement of a sulfur extrusion process.[17] While the reaction of **3i** was complete within 1 h, that of **3j**, with no phenyl group on the α position of the migrating silyl group, was not complete even after 100 h (36% of the starting material remained). The observed elegant reactivity of **3i** compared to those of **3a**−**h** and **3j** can be explained partly by the relaxation of large steric repulsions among the bulky substituents at one carbon atom by the silyl migration and partly by the stabilization of the sulfonium ion by the other *β*-silyl group during the silyl migration step. The striking reactivity drop in the case of **3j** could be attributed to the generation of a nonstabilized thiocarbonyl ylide from **3j**, in contrast to the generation of the phenyl ring-stabilized thiocarbonyl ylides from **3a**−**i**.

Silyl Dienol Ethers. Encouraged by the results described above, our next interest was concentrated on the preparation of silyl dienol ethers using the same protocol, and the results are summarized in Table 2.

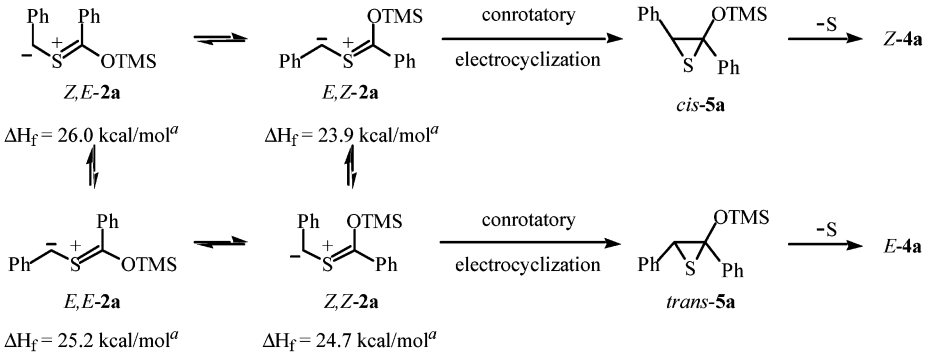
The thermal reaction of α,*β*-unsaturated thioester **6a** afforded silyl dienol ether **7a** in good yield with a moderate stereoselectivity, the structure of which was assigned on the basis of ^1H NMR, ^{13}C NMR, GCMS, and HRMS analyses. The stereochemistry was determined by a difference nOe experiment on the crude reaction mixture. In C_6D_6, two singlet signals of the diagnostic vinyl protons (H_a) of *E*- and *Z*-**7a** appeared at *δ* 6.23 and

(15) Lesséne, G.; Tripoli, R.; Cazeau, P.; Biran, C.; Bordeau, M. *Tetrahedron Lett.* **1999**, *40*, 4037.

(16) Bonafoux, D.; Bordeau, M.; Biran, C.; Dunogués, J. *J. Organomet. Chem.* **1995**, *493*, 27.

(17) Both of the two silyl groups participated in the migration. Although an initial 1,4-silyl migration, followed by 1,3-electrocyclization affording thiiranes **10** is conceivable, the mechanism of this multistep reaction is under investigation and will be published elsewhere.

SCHEME 2. The Reaction Mechanism



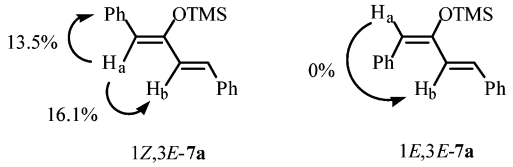


FIGURE 1. Determination of stereochemistry by difference NOE experiment.

5.81 with the major peak at a higher field. Irradiation of the vinyl H_a δ 5.81 resulted in an enhancement in the vinyl H_b signal (16.1%) and the aromatic region signals (13.5%), establishing the 1*Z*,3*E* configuration for the major isomer **7a** (Figure 1). (Irradiation of the vinyl H_a at δ 6.23 was unsuccessful: neither the vinyl H_b signal nor the aromatic region signals increased.)

More interestingly, the reaction of α,*β*-unsaturated thioester **6a** provided the siloxythiophene derivative **8a** as a minor product.[19] In a survey of the reaction conditions, the observed yields of silyl dienol ether **7a** and thiophene **8a** were found to be time-dependent. For example, the reaction of **6a** for 90 min provided a mixture of **7a** (82%) and **8a** (9%) (entry 1), which led to a mixture of **7a** (6%) and **8a** (55%) upon continued heating under the same conditions for 80 h (entry 2). In this respect, it is understandable that the observed reaction yield and stereoselectivity of **6a** were somewhat lower than those of thioesters **3** owing to the involvement of the thiophene formation process.[20] The α,*β*-unsaturated thioesters **6a**−**c** exhibited further enhanced silatropic reactivities probably due to the increased electron density at the carbonyl oxygen compared to those of the aromatic or aliphatic thioesters **3**: the reactions were usually complete within 2 h with no significant adverse effect on the reactivity by changing the substituent (R^2) at the *β*-position of the α,*β*-unsaturated moiety (entries 1, 3, and 4). Because of their inherent instability, the reactions of thioesters **6d** and **6e** gave complex mixtures with silyl dienol ether **7d** and thiophene **8e** as the major products, respectively. Changing the reaction temperature had no effect on the results. For example, the reaction of **6d** at 140 °C for 24 h afforded a mixture of **7d** (54%, *Z*/*E* = 74/26) and **8d** (14%). Similarly to **3f** and **3g** (Table 1), α,α-bissilylated thioester **6f** also provided the silylthio-substituted analogue of silyl dienol ether **7f** under the same conditions (entry 7). On the basis of the wide range of reactivity discussed above, it would be expected that the reactivity of thioester **6f** would lie between those of **6a** and **3g**. Indeed, the low reactivity of **3g** (entry 7 in Table 1) was greatly improved when the phenyl ring was replaced by a vinyl group (entry 7). However, **6f** did not exceed **6a** in either reactivity, due to the absence of the carbanion-stabilizing phenyl group at the α position of the migrating silyl group, or stereoselectivity.[21]

Mechanistic considerations. On the basis of our earlier findings on the generation of azomethine ylides from *N*-(α-silylbenzyl)amides via 1,4-silatropy[11] (eq 2) and the general feature of thiocarbonyl ylides chemistry (eq 1), the reaction mechanism of this protocol can be explained by a sequence of multistep reactions: (1) thermal 1,4-silatropy of thioesters **3** to give thiocarbonyl ylides **2**, (2) conrotatory electrocyclic ring closure of ylides **2** to give thiiranes **5**, and (3) thermal desulfurization of thiiranes **5** with retention of configuration to give silyl enol ethers **4** or silyl dienol ethers **7** (Scheme 2). In addition, the observed reactivities, described in Tables 1 and 2, provide strong support for the rate-determining step being the silyl migration step.

The stereochemical aspect, outlined in Scheme 2, provides additional support for the proposed mechanism of this sequence of reactions. For example, four geometries of thiocarbonyl ylide **2a** are possible in the silatropic reaction of thioester **3a**. Both *Z*,*E*-**2a** and *E*,*Z*-**2a** conformations would give *Z*-silyl enol ether **4a** via *cis*-thiirane **5a**, while the other two conformations would lead to the *E*-isomer **4a** via *trans*-thiirane **5a**. Among these, the *Z*,*E*-**2a** and *Z*,*Z*-**2a** conformations are disfavored by "Ph//Ph" and "TMSO//Ph" steric hindrance, respectively, which is minimized in the case of the *E*,*Z*-**2a** and *E*,*E*-**2a** conformations. However, the *E*,*E*-**5** conformation is also disfavored by Ph//H interaction, which is larger than the TMSO//H interaction in the *E*,*Z*-**2a** conformation. Thus, the *E*,*Z*-**2a** conformation is preferred, due to the relief of steric interactions, which is well supported

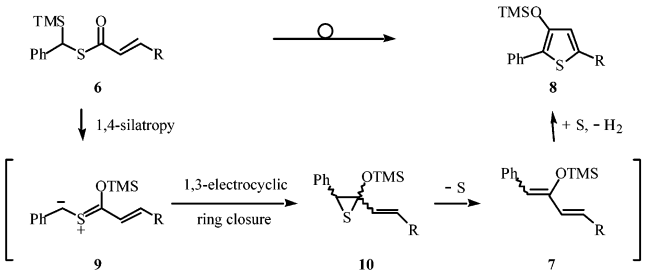
(18) Guemra, K.; Mansri, A.; Casals, P. F.; Montheard, J. P. *Eur. Polym. J.* **1996**, 32, 185−91.

(19) The regiochemistry of product **8a** was determined by a difference NOE experiment. Irradiation of the *o*-aromatic protons at δ 7.51 (in C_6D_6) in product **8a** resulted in an enhancement in the thiophene H-4 signal (15.8%) with no enhancement in the other *o*-aromatic proton signals, thus establishing the 2,5-diphenyl-substituted thiophene as **8a**. A 4,5-diphenyl-substituted thiophene will show NOE between the *o*-aromatic protons at thiophene-C4 and C5. In our previous paper,[12] 4-substituted 2-trimethylsiloxy-5-phenylthiophenes, byproducts in the preparation of silyl enol ethers, were incorrectly proposed.

(20) For sulfuration of conjugated dienes and strained olefins, see: Rys, A. Z.; Harpp, D. N. *Tetrahedron Lett.* **1997**, *38*, 4931 and references cited therein.

(21) The reason for the obtained low stereoselectivity was not investigated further.

SCHEME 3. The Plausible Route to Thiophenes



by computational calculation: on the basis of the result of the heat of formation analysis by MO calculation with MOPAC PM3, the *E*,*Z*-**2a** conformation is energetically the most favored (ΔH_f = 23.9 kcal/mol). In this regard, the formation of the *Z*-silyl enol ether **4a** via the thiocarbonyl ylide *E*,*Z*-**2a** conformation could be considered to be the major route in this reaction, which is in good agreement with our experimental results. However, the possibility of kinetic control of the reactions cannot be excluded at the moment.

Scheme 3 suggests a plausible hypothesis for the generation of thiophenes **8**: following the same pathway as that for thioesters **3** (Scheme 2), the reactions of thioesters **6** initially provide a mixture of silyl dienol ethers **7** and elemental sulfur. Their further in situ reactions at ambient temperature lead to the formation of thiophenes **8**.[20] It is noteworthy that the electrocyclization of thiocarbonyl ylides **9** does not proceed in a 1,5-manner but exclusively in a 1,3-manner.

To verify the mechanism proposed above, an additional experiment was carried out. First, silyl dienol ether **7a** was isolated by rapid column chromatography on silica gel (54%, *E*/*Z* = 1/9).[22] A benzene-d_6 solution of **7a** and elemental sulfur (5 equiv) was then heated in a sealed tube at 180 °C for 36 h. The reaction, although proceeding rather sluggishly, provided thiophene **8a** in moderate yield (66%). However, in the absence of elemental sulfur, a change in the *E*/*Z* ratio (from 1/9 to 25/75) of silyl dienol ether **7a** was observed under the same conditions. Probably due to the observed isomerization and the involvement of thiophenes in the course of the reaction, these α,β-unsaturated thioesters **6** showed rather lower stereoselectivities compared to those of thioesters **3**. Further development of this methodology for thiophene synthesis will be reported in a future report.

Conclusions

A convenient route to silyl enol ethers **4** and silyl dienol ethers **7** from readily accessible *S*-α-silylbenzyl thioesters **3** and **6** without any catalyst or additive under completely neutral conditions is described. The key to this methodology involves a convenient method for the generation of thiocarbonyl ylides **2** by 1,4-silatropy of *S*-α-silylbenzyl thioesters **3** and **6** and synthetic applications of the in situ generated ylides to the preparation of silyl enol and dienol ethers via the formation of a C−C bond. Furthermore, the observed results provide a facile new route to ene thiol ethers **4f**,**g** and **7f**, and thiophenes derivatives **8**, depending on the starting materials in this procedure. Further study on synthetic applications of the thiocarbonyl ylides **2** in the construction of heterocyclic targets, such as 1,3-dipolar cycloaddition, is in progress.

(22) Silyl dienol ether **7a** is unstable under the purification conditions; the desilylated compound was also isolated (27%).

Experimental Section

Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. Because of high moisture sensitivity, high-resolution mass spectral (HRMS) data are given for the products except for **3a**,**b**,**h** and **6a**−**c**,**f** instead of elemental analyses. Chemical shifts are reported in parts per million (δ), relative to internal TMS at 0.00 for ^{1}H NMR and chloroform at 77.0 for ^{13}C NMR. All reactions were carried out under an atmosphere of nitrogen. Organic solvents were dried and distilled prior to use.

General Procedure for the Preparation of Thioesters 3a−j. A mixture of acyl chloride (1.12 mmol) in ether (5 mL) was added to a mixture of α-silylmethylthiol (1.02 mmol) and Et_3N (170 μL, 1.22 mmol) in ether (10 mL) at 0−5 °C over 30 min and then stirred at the same temperature for 1 h and at room temperature for 30 min. The reaction mixture was washed with 0.5 N HCl, a saturated $NaHCO_3$ solution, and brine, dried over $MgSO_4$, and concentrated in vacuo. Purification by flash chromatography on silica gel afforded thioester **3**.

***S*-α-Trimethylsilylbenzyl Thiobenzoate (3a).** A white solid (285 mg, 93%): mp 94.5−95.5 °C; IR (KBr) 1688 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9H), 4.24 (s, 1H), 7.14 (m, 1H), 7.22−7.27 (m, 4H), 7.42 (m, 2H), 7.52 (m, 1H), 7.96 (br d, 2H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ −2.4, 35.6, 125.5, 127.2, 127.8, 128.1, 128.4, 133.1, 136.8, 141.3, 191.3; MS (EI) *m*/*z* (rel intensity) 300 (M^+, 6), 285 (2), 195 (33), 121 (20), 105 (47), 73 (100). Anal. Calcd for $C_{17}H_{20}OSSi$: C, 67.95; H, 6.71; S, 10.67. Found: C, 67.97; H, 6.74; S, 10.62.

***S*-α-Trimethylsilylbenzyl 4-Nitrothiobenzoate (3b).** A yellow solid (299 mg, 85%): mp 118.0−119.5 °C; IR (KBr) 1668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9H), 4.26 (s, 1H), 7.16 (m, 1H), 7.24−7.28 (m, 4H), 8.10 (br d, 2H, *J* = 8.6 Hz), 8.27 (br d, 2H, *J* = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ −2.4, 36.3, 123.7, 125.8, 127.8, 128.20, 128.23, 140.6, 141.4, 150.3, 189.9; MS (EI) *m*/*z* (rel intensity) 345 (M^+, 35), 330 (22), 223, (13), 195 (100), 150 (11), 122 (2), 73 (82); HRMS (EI) calcd for $C_{17}H_{19}NO_3SSi$ (M^+) 345.0855, found 345.0866. Anal. Calcd for $C_{17}H_{19}NO_3SSi$: C, 59.10; H, 5.54; N, 4.05; S, 9.28. Found: C, 58.90; H, 5.41; N, 4.03; S, 9.26.

***S*-α-Trimethylsilylbenzyl 4-Methoxythiobenzoate (3c).** A colorless oil (269 mg, 80%): IR (neat) 1662 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9H), 3.85 (s, 3H), 4.22 (s, 1H), 6.89 (br d, 2H, *J* = 9.2 Hz), 7.12 (m, 1H), 7.21−7.27 (m, 4H), 7.94 (br d, 2H, *J* = 9.2 Hz); ^{13}C NMR ($CDCl_3$) δ −2.4, 35.4, 55.5, 113.6, 125.4, 127.8, 128.0, 129.4, 129.7, 141.6, 163.5, 189.7; MS (EI) *m*/*z* (rel intensity) 330 (M^+, 37), 315 (14), 195 (24), 135 (100), 73 (24); HRMS (EI) calcd for $C_{18}H_{22}O_2SSi$ (M^+) 330.1110, found 330.1118.

***S*-α-Trimethylsilylbenzyl 2-Furancarbothioate (3d).** A colorless solid (180 mg, 50%): mp 43.0−44.0 °C; IR (KBr) 1664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9H), 4.23 (s, 1H), 6.49 (dd, 1H, *J* = 3.6, 1.8 Hz), 7.09−7.16 (m, 2H), 7.30−7.35 (m, 4H), 7.54−7.55 (m, 1H); ^{13}C NMR ($CDCl_3$) δ −2.5, 34.5, 112.0, 115.2, 125.4, 127.9, 128.0, 141.1, 145.8, 150.5, 179.9; MS (EI) *m*/*z* (rel intensity) 290 (M^+, 68), 275 (22), 195 (100), 95 (50), 73 (99); HRMS (EI) calcd for $C_{15}H_{18}O_2SSi$ (M^+) 290.0796, found 290.0794.

***S*-α-Trimethylsilylbenzyl 2-Thiophenecarbothioate (3e).** A colorless oil (54 mg, 17%): IR (KBr) 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9H), 4.23 (s, 1H), 7.06−7.23 (m, 6H), 7.57 (dd, 1H, *J* = 4.0, 1.2 Hz), 7.81 (dd, 1H, *J* = 3.9, 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ −2.4, 35.9, 125.6, 127.7, 127.8, 128.1, 130.9, 132.4, 141.2, 141.7, 183.4; MS (EI) *m*/*z* (rel intensity) 306 (M^+, 67), 291 (20), 195 (100), 111 (40), 73 (77); HRMS (EI) calcd for $C_{15}H_{18}OS_2Si$ (M^+) 306.0567, found 306.0572.

***S*-α-Trimethylsilylbenzyl 2-(4-Chloropyridine)carbothioate (3f).** A colorless oil (65 mg, 21%): IR (KBr) 1668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 9H), 4.17 (s, 1H), 7.09−7.16 (m, 1H), 7.21−7.31 (m, 4H), 7.48 (dd, 1H, J = 5.1, 2.0 Hz), 7.89 (d, 1H, J = 2.0 Hz), 8.59 (d, 1H, J = 5.1 Hz); ^{13}C NMR ($CDCl_3$) δ −2.5, 35.4, 120.9, 125.4, 127.4, 127.7, 127.9, 141.0, 145.5, 149.7, 152.9, 191.6. MS (EI) *m*/*z* (rel intensity) 337 (M^+ + 2, 15), 335 (M^+, 35), 320 (27), 195 (100), 185 (23), 73 (70); HRMS (EI) calcd for $C_{16}H_{18}ClNOSSi$ (M^+) 335.0566, found 335.0564.

***S*-α-Trimethylsilylbenzyl Thioacetate (3g).** A colorless oil (1.69 g, 67%): IR (neat) 1692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (s, 9H), 2.30 (s, 3H), 4.03 (s, 1H), 7.10−7.28 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −2.4, 30.2, 36.0, 125.6, 127.8, 128.2, 141.4, 195.2; MS (EI) *m*/*z* (rel intensity) 238 (M^+, 47), 223, (20), 195 (100), 73 (68); HRMS (EI) calcd for $C_{12}H_{18}OSSi$ (M^+) 238.0848, found 238.0842.

***S*-α-(Dimethylphenylsilyl)benzyl Thiobenzoate (3h).** A white solid (6.10 g, 81%): mp 84.0−85.0 °C; IR (KBr) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.35 (s, 3H), 0.39 (s, 3H), 4.43 (s, 1H), 7.06−7.21 (m, 5H), 7.28−7.44 (m, 7H), 7.52 (m, 1H), 7.92 (br d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ −4.1, −3.7, 35.2, 125.6, 127.2, 127.6, 127.9, 128.1, 128.4, 129.5, 133.1, 134.2, 135.4, 136.7, 140.7, 191.0; MS (EI) *m*/*z* (rel intensity) 362 (M^+, 26), 347 (5), 285 (9), 257 (66), 135 (100), 105 (23). Anal. Calcd for $C_{22}H_{22}OSSi$: C, 72.88; H, 6.12; S, 8.84. Found: C, 73.06; H, 6.17; S, 8.83.

***S*-α,α-Bis(trimethylsilyl)benzyl Thiobenzoate (3i).** DMAP (10 mol %) was used as a catalyst. A white solid (420 mg, 92%): mp 94.0−96.5 °C; IR (KBr) 1666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 18H), 7.09 (m, 1H), 7.20−7.33 (m, 4H), 7.44 (m, 2H), 7.56 (m, 1H), 8.01 (br d, 2H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 1.4, 37.2, 124.4, 127.2, 127.3, 127.5, 128.4, 132.9, 137.4, 139.8, 191.7; MS (EI) *m*/*z* (rel intensity) 372 (M^+, 100), 357 (36), 299 (10), 267 (68), 225 (13), 179 (19), 163 (29), 135 (27), 105 (37), 73 (63); HRMS (EI) calcd for $C_{20}H_{28}OSSi_2$ (M^+) 372.1399, found 372.1398.

***S*-α,α-Bis(trimethylsilyl)methyl Thiobenzoate (3j).** A colorless oil (400 mg, 54%); IR (neat) 1659 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 18H), 2.37 (s, 1H), 7.44 (m, 2H), 7.56 (m, 1H), 8.00 (br d, 2H, J = 7.02 Hz); ^{13}C NMR ($CDCl_3$) δ −0.3, 13.8, 127.0, 128.4, 132.8, 137.1, 192.2; MS (EI) *m*/*z* (rel intensity) 296 (M^+, 39), 281 (59), 191 (27), 163 (78), 149 (30), 105 (100), 73 (88); HRMS (EI) calcd for $C_{14}H_{24}OSSi_2$ (M^+) 296.1086, found 296.1077.

General Procedure for the Preparation of Thioesters 6a−f. DCC (580 mg, 2.81 mmol) was added to a mixture of α-silylmethylthiol (2.55 mmol), α,*β*-unsaturated carboxylic acid (2.71 mmol), and DMAP (20 mg, 0.16 mmol) in CH_2Cl_2 (50 mL) at 0 °C, and the reaction mixture was stirred at the same temperature for 2 h and then at room temperature for 1 h. The precipitated dicyclohexylurea was removed by filtration. The filtrate was washed with 0.5 N HCl, a saturated $NaHCO_3$ solution, and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give thioester **6**.

***S*-α-Trimethylsilylbenzyl (*E*)-Thiocinnamate (6a).** A white solid (732 mg, 88%): mp 46.5−47.5 °C; IR (KBr) 1672 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (s, 9H), 4.20 (s, 1H), 6.71 (d, 1H, J = 15.7 Hz), 7.15 (m, 1H), 7.24−7.31 (m, 4H), 7.37−7.42 (m, 3H), 7.53 (m, 2H), 7.58 (d, 1H, J = 15.7 Hz); ^{13}C NMR ($CDCl_3$) δ −2.4, 35.8, 124.6, 125.5, 127.8, 128.1, 128.2, 128.8, 130.4, 134.1, 140.3, 141.3, 189.1; MS (EI) *m*/*z* (rel intensity) 326 (M^+, 27), 311 (16), 195 (100), 131 (51), 103 (20), 73 (72); HRMS (EI) calcd for $C_{19}H_{22}OSSi$ (M^+) 326.1161, found 326.1176. Anal. Calcd for $C_{19}H_{22}OSSi$: C, 69.89; H, 6.79; S, 9.82. Found: C, 69.96; H, 6.73; S, 9.85.

***S*-α-Trimethylsilylbenzyl (*E*)-4-Nitrothiocinnamate (6b).** A yellow solid (320 mg, 33%): mp 125.5−127.0 °C; IR (KBr) 1657 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.09 (s, 9H), 4.21 (s, 1H), 6.79 (d, 1H, J = 15.9 Hz), 7.15 (m, 1H), 7.21−7.30 (m, 4H), 7.54 (d, 1H, J = 15.9 Hz), 7.65 (br d, 2H, J = 8.9 Hz), 8.24 (br d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ −2.5, 36.2, 124.1, 125.7, 127.7, 128.2, 128.3, 128.7, 137.0, 140.3, 140.9, 148.4, 188.6; MS (EI) *m*/*z* (rel intensity) 371 (M^+, 27), 356 (20), 249 (25), 195 (100), 73 (99); HRMS (EI) calcd for $C_{19}H_{21}NO_3SSi$ (M^+) 371.1011, found 371.1010. Anal. Calcd for $C_{19}H_{21}NO_3SSi$: C, 61.42; H, 5.70; N, 3.77; S, 8.63. Found: C, 61.13; H, 5.60; N, 3.77; S, 8.51.

***S*-α-Trimethylsilylbenzyl (*E*)-4-Methoxythiocinnamate (6c).** A bright yellow solid (815 mg, 88%): mp 107.5−108.5 °C; IR (KBr) 1653 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 3.83 (s, 3H), 4.19 (s, 1H), 6.59 (d, 1H, J = 15.8 Hz), 6.89 (br d, 2H, J = 8.9 Hz), 7.13 (m, 1H), 7.21−7.30 (m, 4H), 7.46 (br d, 2H, J = 8.9 Hz), 7.54 (d, 1H, J = 15.8 Hz); ^{13}C NMR ($CDCl_3$) δ −2.4, 35.7, 55.4, 114.3, 122.3, 125.4, 126.8, 127.8, 128.1, 130.0, 140.1, 141.5, 161.4, 189.0; MS (EI) *m*/*z* (rel intensity) 356 (M^+, 19), 341 (5), 281 (3), 195 (10), 161 (100), 133 (13), 73 (23); HRMS (EI) calcd for $C_{20}H_{24}O_2SSi$ (M^+) 356.1266, found 356.1263. Anal. Calcd for $C_{20}H_{24}O_2SSi$: C, 67.37; H, 6.78; S, 8.99. Found: C, 67.40; H, 6.82; S, 8.91.

***S*-α-Trimethylsilylbenzyl (*E*)-Thiocrotonate (6d).** A colorless oil (209 mg, 78%): IR (neat) 1674 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H), 1.85 (dd, 3H, J = 1.6, 7.0 Hz), 4.11 (s, 1H), 6.13 (dq, 1H, J = 1.6, 15.4 Hz), 6.88 (dq, 1H, J = 7.0, 15.4 Hz), 7.12 (m, 1H), 7.14−7.27 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −2.5, 18.1, 35.3, 125.4, 127.7, 128.0, 129.7, 140.6, 141.4, 189.1; MS (EI) *m*/*z* (rel intensity) 264 (M^+, 2), 249 (23), 195 (42), 73 (100), 69 (74); HRMS (EI) calcd for $C_{14}H_{20}OSSi$ (M^+) 264.1004, found 264.1005.

***S*-α-Trimethylsilylbenzyl Thiomethacrylate (6e).** A colorless oil (200 mg, 74%): IR (neat) 1666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H), 1.94 (d, 3H, J = 1.4 Hz), 4.05 (s, 1H), 5.56 (q, 1H, J = 1.4 Hz), 6.10 (s, 1H), 7.12 (m, 1H), 7.19−7.25 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −2.4, 18.3, 35.5, 123.0, 125.4, 127.8, 128.0, 141.4, 143.5, 192.7; MS (EI) *m*/*z* (rel intensity) 264 (M^+, 12), 249 (5), 195 (57), 73 (100), 69 (43); HRMS (EI) calcd for $C_{14}H_{20}OSSi$ (M^+) 264.1004, found 264.0997.

***S*-α,α-Bis(trimethylsilyl)benzyl (*E*)-Thiocinnamate (6f)**. A bright yellow solid (540 mg, 68%): mp 61.0−62.5 °C; IR (KBr) 1657 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 18H), 2.30 (s, 1H), 6.76 (d, 1H, J = 15.5 Hz), 7.38 (m, 3H), 7.54 (m, 2H), 7.60 (d, 1H, J = 15.5 Hz); ^{13}C NMR ($CDCl_3$) δ −0.3, 14.1, 124.5, 128.2, 128.8, 130.2, 134.2, 139.1, 189.9; MS (EI) *m*/*z* (rel intensity) 322 (M^+, 25), 307 (54), 249 (11), 163 (30), 131 (100), 103 (29), 73 (53); HRMS (EI) calcd for $C_{16}H_{26}OSSi_2$ (M^+) 322.1243, found 322.1248. Anal. Calcd for $C_{16}H_{26}OSSi_2$: C, 59.57; H, 8.12; S, 9.94. Found: C, 59.37; H, 7.95; S, 9.90.

Thermal 1,4-Silatropic Reactions of Thioesters 3a−f and 6a−f. *S*-α-Trimethylsilylbenzyl thioester **3** or **6** (0.05 mmol) and mesitylene (4.5 μmol) in benzene-d_6 (0.5 mL) were heated in a sealed NMR tube at 180 °C until the disappearance of the starting material. The reaction was monitored by ^1H NMR. The yields of (*E*)- and (*Z*)-silyl enol and dienol ethers (**4** and **7**) and thiophenes (**8**), presented in Tables 1 and 2, were determined by comparison of diagnostic vinyl proton signals on ^1H NMR of the crude reaction mixture, based on the added mesitylene as an internal standard. The reaction mixture was concentrated in vacuo and separated by column chromatography on silica gel.[23] Silyl enol ethers **4a**,[24] **4c**,[25] **4g**,[24,26] and **4h**[27] are known compounds.

1-(4-Nitrophenyl)-1-trimethylsiloxy-2-phenylethene (4b). Key spectra of **4b** obtained from the crude product mixture (*Z*/*E* 91:9): ^1H NMR (C_6D_6) δ 0.07 (s, 8.2H), 0.11 (s, 0.8H), 6.10 (s, 0.9H), 6.23 (s, 0.1H), 7.00−8.00 (m, 9H). ***Z*-4b:** ^{13}C NMR (C_6D_6) δ 0.70, 114.1, 123.6, 126.3, 127.4, 128.6, 129.4,

(23) Attempts to separate the isomeric products by distillation or GPC were unsuccessful.

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136.1, 145.4, 147.5, 148.8; GCMS (EI) *m*/*z* (rel intensity) 313 (M^+, 100), 298 (38), 73 (72); HRMS (EI) calcd for $C_{17}H_{19}NO_3Si$ (M^+) 313.1134, found 313.1137. ***E*-4b:** GCMS (EI) *m*/*z* (rel intensity) 313 (M^+, 100), 298 (29), 73 (68); HRMS (EI) calcd for $C_{17}H_{19}NO_3Si$ (M^+) 313.1134, found 313.1137. Isolation by column chromatography on silica gel provided a desilylated compound, α-phenyl-*p*-nitroacetophenone, the spectral data of which are completely consistent with literature data.[27]

1-(2-Furyl)-1-trimethylsiloxy-2-phenylethene (4d). *Z*-4d: ^{1}H NMR (C_6D_6) δ 0.04 (s, 9H), 6.06 (dd, 1H, J = 3.3, 1.8 Hz), 6.38 (d, 1H, J = 3.3 Hz), 6.55 (s, 1H), 6.94−7.03 (m, 2H), 7.13−7.27 (m, 2H), 7.63−7.67 (m, 2H); ^{13}C NMR (C_6D_6) δ 0.8, 107.9, 109.4, 111.6, 126.6, 128.4, 129.3, 136.5, 142.1, 142.3, 153.3; MS (EI) *m*/*z* (rel intensity) 258 (M^+, 1.6), 186 (77), 95 (100), 91 (43); HRMS (EI) calcd for $C_{15}H_{18}O_2Si$ (M^+) 258.1075, found 258.1069. Key spectra of the minor compound ***E*-4d** obtained from the crude product mixture: ^{1}H NMR (C_6D_6) δ 0.18 (s, 9H), 5.92 (dd, 1H, J = 3.2, 1.6 Hz). Only distinct signals were listed.

1-Trimethylsiloxy-2-phenyl-1-(2-thienyl)ethene (4e). *Z*-4e: ^{1}H NMR (C_6D_6) δ 0.07 (s, 9H), 6.35 (s, 1H), 6.68 (dd, 1H, J = 5.0, 3.6 Hz), 6.75 (dd, 1H, J = 5.0, 1.3 Hz), 6.98−7.04 (m, 4H), 7.59−7.64 (m, 2H); ^{13}C NMR (C_6D_6) δ 0.9, 110.4, 124.8, 125.0, 126.6, 127.3, 127.4, 129.3, 136.6, 144.1, 145.8; MS (EI) *m*/*z* (rel intnesity) 274 (M^+, 100), 183 (34), 111 (83), 73 (27); HRMS (EI) calcd for $C_{15}H_{18}OSSi$ (M^+) 274.0847, found 274.0856. Key spectra of the minor compound ***E*-4e** obtained from the crude product mixture: ^{1}H NMR (C_6D_6) δ 0.22 (s, 9H), 6.18 (br s, 1H). Only distinct signals were listed.

1-Trimethylsiloxy-2-phenyl-1-[2-(4-chloropyridyl)]-ethene (4f). *Z*-4f: ^{1}H NMR (C_6D_6) δ 0.08 (s, 9H), 6.58 (dd, 1H, J = 5.1, 2.0 Hz), 6.97−7.38 (m, 4H), 7.57 (d, 1H, J = 2.0 Hz), 7.77−7.74 (m, 2H), 8.05 (d, 1H, J = 5.1 Hz). Key spectra of the minor compound ***E*-4f** obtained from the crude product mixture: ^{1}H NMR (C_6D_6) δ 0.17 (s, 9H). Only distinct signals were listed. Purification by preparative gel permeation liquid chromatography (eluent: chloroform) afforded desilylated compound, 4-chloro-2-phenacylpyridine (44%): ^{1}H NMR ($CDCl_3$) δ 4.36 (s, 2H), 7.04−7.30 (m, 6H), 7.31 (dd, 1H, J = 5.4, 1.6 Hz), 7.87 (d, 1H, J = 1.6 Hz), 8.45 (d, 1H, J = 5.4 Hz); ^{13}C NMR ($CDCl_3$) δ 44.2, 122.8, 126.8, 127.2, 128.4, 129.8, 134.1, 145.4, 149.7, 154.1, 197.8; MS (EI) *m*/*z* (rel intnesity) 233 (M^+ + 2, 33), 231 (M^+, 100), 202 (26), 140 (39), 112 (57), 91 (61).

1,2-Diphenyl-1-trimethylsilylthio-2-(trimethylsiloxy)-ethene (4i). *E*-4i: ^{1}H NMR (C_6D_6) δ −0.19 (s, 9H), −0.05 (s, 9H), 7.02−7.08 (m, 2H), 7.15−7.23 (m, 4H), 7.78 (br d, 2H, J = 7.8 Hz), 7.88 (br d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 0.29, 0.94, 111.3, 126.2, 127.2, 127.3, 127.8, 129.8, 130.2, 138.9, 141.6, 151.7; MS (EI) *m*/*z* (rel intnesity) 372 (M^+, 100), 284 (11), 268 (9), 147 (57), 73 (59); HRMS (EI) calcd for $C_{20}H_{28}OSSi_2$ (M^+) 372.1399, found 372.1395. Key spectra of the minor compound ***Z*-4i** obtained from the crude product mixture: ^{1}H NMR (C_6D_6) δ 0.17 (s, 9H), 0.22 (s, 9H), 6.87−6.94 (m, 6H), 7.37 (m, 2H). Only distinct signals were listed; GCMS (EI) *m*/*z* (rel intnesity) 372 (M^+, 100), 284 (11), 268 (9), 147 (68), 73 (75); HRMS (EI) calcd for $C_{20}H_{28}OSSi_2$ (M^+) 372.1399, found 372.1423. The structure of **4i** was further verified by hydrolysis with TFA (2 equiv) to thiobenzoin, the spectral data of which are consistent with literature data.[28]

1-Trimethylsilylthio-2-phenyl-2-(trimethylsiloxy)-ethene (4j). Key spectra of the major compound ***Z*-4j** obtained from the crude product mixture: ^{1}H NMR (C_6D_6) δ 0.24 (s, 9H), 0.30 (s, 9H), 5.87 (s, 1H), 7.04−7.14 (m, 3H), 7.51 (br d, 2H, J = 6.8 Hz); ^{13}C NMR (C_6D_6) δ 0.99, 1.25, 98.2, 125.4, 128.5, 138.6, 153.9. Only distinct signals were listed; GCMS (EI) *m*/*z* (rel intnesity) 296 (M^+, 100), 208 (8), 193 (8), 191 (8), 177(6), 147 (59), 73 (69); HRMS (EI) calcd for $C_{14}H_{24}OSSi_2$ (M^+) 296.1086, found 296.1095. ***E*-4j:** Spectral data of this minor product remained unassigned. Isolation of the crude product mixture by rapid column chromatography on silica gel provided a partially desilylated compound, 2-phenyl-2-(trimethylsiloxy)-ethene-1-thiol (overall 72%): ^{1}H NMR ($CDCl_3$) δ 0.21 (s, 9H), 3.02 (d, 1H, J = 9.5 Hz), 5.75 (d, 1H, J = 9.5 Hz), 7.24−7.45 (m, 5H); ^{13}C NMR (C_6D_6) δ 0.90, 96.3, 124.9, 127.6, 128.1, 137.5, 149.5.

1,4-Diphenyl-2-trimethylsiloxy-1,3-butadiene (7a).(1*Z*,3*E*)-7a: ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9H), 5.90 (s, 1H), 6.72 (d, 1H, J = 15.8 Hz), 6.82 (d, 1H, J = 15.8 Hz), 7.14−7.37 (m, 6H), 7.44 (br d, 2H, J = 7.3 Hz), 7.57 (br d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 0.9, 115.4, 126.2, 126.5, 127.5, 127.8, 128.0, 128.6, 128.8, 128.9, 136.3, 136.8, 149.8; MS (EI) *m*/*z* (rel intnesity) 294 (M^+, 15), 203 (21), 131 (96), 73 (100); HRMS (EI) calcd for $C_{19}H_{22}OSi$ (M^+) 294.1440, found 294.1424. Key spectra of the minor compound **(1*E*,3*E*)-7a** obtained from the crude product mixture: ^{1}H NMR (C_6D_6) δ 0.28 (s, 9H), 6.23 (s, 1H). Only distinct signals were listed.

2,5-Diphenyl-3-(trimethylsiloxy)thiophene (8a). ^{1}H NMR (C_6D_6) δ 0.10 (s, 9H), 6.98 (s, 1H), 7.02−7.24 (m, 6H), 7.51 (br d, 2H, J = 7.3 Hz), 7.92 (br d, 2H, J = 7.3 Hz); MS (EI) *m*/*z* (rel intnesity) 324 (M^+, 100), 293 (16), 146 (24), 73 (55); HRMS (EI) calcd for $C_{19}H_{20}OSSi$ (M^+) 324.1004, found 324.1025. Purification by preparative gel permeation liquid chromatography (eluent: chloroform) afforded desilylated compound, 2,5-diphenyl-3-hydroxythiophene:[29] IR (KBr) 3200−3700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.19 (br s, 1H), 6.99 (s, 1H), 7.28−7.46 (m, 6H), 7.58 (br d, 2H, J = 7.3 Hz), 7.65 (br d, 2H, J = 6.8 Hz); ^{13}C NMR (CD_3CN) δ 117.3, 117.7, 125.3, 126.6, 128.3, 129.1, 129.2, 129.5, 134.0, 134.2, 140.0, 151.1; MS (EI) *m*/*z* (rel intnesity) 252 (M^+, 100), 223 (9), 191 (5), 121 (19), 102 (9), 77 (8); HRMS (EI) calcd for $C_{16}H_{12}OS$ (M^+) 252.0609, found 252.0608.

1-Phenyl-2-trimethylsiloxy-4-(4-nitrophenyl)-1,3-butadiene (7b). (1*Z*,3*E*)-7b: ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9H), 6.01 (s, 1H), 6.82 (d, 1H, J = 15.8 Hz), 6.89 (d, 1H, J = 15.8 Hz), 7.21 (m, 1H), 7.33 (m, 2H), 7.51−7.60 (m, 4H), 8.19 (br d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 0.8, 118.4, 124.1, 126.4, 126.8, 127.0, 128.1, 129.0, 132.4, 135.8, 143.3, 146.6, 149.1; MS (EI) *m*/*z* (rel intnesity) 339 (M^+, 13), 324 (3), 176 (100), 146 (60), 130 (43), 102 (49), 91(73), 73 (65); HRMS (EI) calcd for $C_{19}H_{21}NO_3Si$ (M^+) 339.1291, found 339.1299. Key spectra of the minor compound **(1*E*,3*E*)-7b** obtained from the crude product mixture: ^{1}H NMR (C_6D_6) δ 0.27 (s, 9H), 6.27 (s, 1H). Only distinct signals were listed.

1-Phenyl-2-trimethylsiloxy-4-(4-methoxyphenyl)-1,3-butadiene (7c). Key spectra of **7c** obtained from the crude reaction mixture (*Z*:*E* 77:23): ^{1}H NMR (C_6D_6) δ 0.16 (s, 6.9H), 0.30 (s, 2.1H), 3.25 (s, 0.7H), 3.32 (s, 2.3H), 5.83 (s, 0.8H), 6.20 (s, 0.2H), 6.57 (d, 0.8H, J = 15.7 Hz), 6.63−7.30 (m, 8.7H), 7.69 (br d, 1.5H, J = 7.3 Hz). **(1*Z*,3*E*)-7c:** GCMS (EI) *m*/*z* (rel intnesity) 324 (M^+, 13), 293 (9), 161 (13), 73 (100); HRMS (EI) calcd for $C_{20}H_{24}O_2Si$ (M^+) 324.1546, found 324.1537. **(1*E*,3*E*)-7c:** GCMS (EI) *m*/*z* (rel intnesity) 324 (M^+, 6), 293 (4), 161 (100), 73 (44); HRMS (EI) calcd for $C_{20}H_{24}O_2Si$ (M^+) 324.1546, found 324.1525. In a separate experiment, treatment of the crude product mixture by column chromatography on silica gel (eluent: hexane/ethyl acetate 10/1) gave desilylated compound, *trans*-1-phenyl-4-(4-methoxyphenyl)-3-buten- 2-one (85%), the spectral data of which are consistent with literature data.[30]

2-Phenyl-3-trimethylsiloxy-5-(4-methoxyphenyl)-thiophene (8c). ^{1}H NMR (C_6D_6) δ 0.13 (s, 9H), 3.29 (s, 3H), 6.73 (br d, 2H, J = 8.9 Hz), 6.93 (s, 1H), 7.04−7.26 (m, 3H), 7.47 (br d, 2H, J = 8.9 Hz), 7.95 (br d, 2H, J = 7.3 Hz); MS (EI) *m*/*z* (rel intnesity) 354 (M^+, 84), 339 (33), 161 (17), 140

(28) Reitz, D. B.; Beak, P.; Farney, R. F.; Helmick, L. S. *J. Am. Chem. Soc.* **1978**, *100*, 5428.

(29) Although the desilylated compound of **8a**, 3-hydroxy-2,5-diphenylthiophene, is known (Witzel, B. E.; Allison, D. L.; Caldwell, C. G.; Rupprecht, K. Eur. Pat. Appl. EP 318,066, 1988; *Chem. Abstr.* **1990**, 112, 151861p), the patent includes no spectral data. Thus the spectra of the desilylation product could not be compared with those of the corresponding compound in this patent.

(30) Fine, S. A.; Pulaski, P. D. *J. Org. Chem.* **1973**, *38*, 1747.

(24), 121 (31), 73 (100); HRMS (EI) calcd for $C_{20}H_{22}O_2SSi$ (M^+) 354.1110, found 354.1111.

1-Phenyl-2-trimethylsiloxy-1,3-pentadiene (7d). (1*Z*,3*E*)-7d: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9H), 1.82 (d, 3H, J = 5.7 Hz), 5.64 (s, 1H), 5.94 (dq, 1H, J = 5.7, 15.4 Hz), 6.03 (d, 1H, J = 15.4 Hz), 7.12 (m, 1H), 7.28 (m, 2H), 7.50 (br d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 0.8, 17.9, 122.1, 125.7, 126.4, 127.9, 128.6, 130.5, 136.6, 149.5; MS (EI) *m*/*z* (rel intnesity) 232 (M^+, 20), 217 (14), 141 (18), 115 (9), 73 (100); HRMS (EI) calcd for $C_{14}H_{20}OSi$ (M^+) 232.1283, found 232.1285. **(1*E*,3*E*)-7d:** ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 9H), 1.79 (dd, 3H, J = 1.6, 7.0 Hz), 5.88 (s, 1H), 6.14 (dq, 1H, J = 7.0, 15.1 Hz), 6.40 (dq, 1H, J = 1.6, 15.1 Hz), 7.15−7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 0.4, 18.1, 111.4, 125.3, 125.7, 128.0, 128.8, 129.0, 136.6, 149.6; MS (EI) *m*/*z* (rel intnesity) 232 (M^+, 100), 217 (84), 201 (27), 141 (42), 115 (20), 73 (90).

2-Phenyl-3-trimethylsiloxy-5-methylthiophene (8d). ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9H), 2.42 (d, 3H, J = 1.1 Hz), 6.39 (q, 1H, J = 1.1 Hz), 7.17 (m, 1H), 7.29−7.35 (m, 2H), 7.66 (br d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 0.2, 16.0, 120.2, 121.3, 125.8, 126.6, 128.3, 134.0, 135.7, 147.1; MS (EI) *m*/*z* (rel intnesity) 262 (M^+, 60), 247 (19), 231 (28), 115 (19), 73 (100); HRMS (EI) calcd for $C_{14}H_{18}OSSi$ (M^+) 262.0848, found 262.0846.

2-Phenyl-3-trimethylsiloxy-4-methylthiophene (8e). Key spectra of **8e** obtained from the crude product mixture: ^{1}H NMR (C_6D_6) δ 0.03 (s, 9H), 1.97 (d, 3H, J = 1.0 Hz), 6.48 (q, 1H, J = 1.0 Hz), 7.00−7.19 (m, 3H), 7.72 (br d, 2H, J = 7.1 Hz); MS (EI) *m*/*z* (rel intnesity) 262 (M^+, 100), 247 (60), 231 (44), 73 (85); HRMS (EI) calcd for $C_{14}H_{18}OSSi$ (M^+) 262.0848, found 262.0846. Column chromatography on silica gel (eluent: hexane/ethyl acetate 10/1) gave desilylated compound (35%), 2-phenyl-3-hydroxy-4-methylthiophene: ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 3H), 5.06 (br s, 1H), 6.61 (s, 1H), 7.27 (m, 1H), 7.41 (m, 2H), 7.58 (br d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 13.1, 117.5, 118.0, 126.8, 127.2, 129.0, 129.1, 133.3, 147.4; MS (EI) *m*/*z* (rel intnesity) 190 (M^+, 100), 161 (14), 122 (46), 121 (74).

Trimethylsilylthio-2-trimethylsiloxy-4-phenylbutadiene (7f). Key spectra of **7f** obtained from the crude product mixture (*Z*:*E* 65:35): ^{1}H NMR (C_6D_6) δ 0.20 (s, 3.2H), 0.25 (s, 5.9H), 0.26 (s, 3.2H), 0.42 (s, 5.9H), 5.47 (s, 0.7H), 5.57 (s, 0.4H), 6.60 (d, 0.7H, J = 15.4 Hz), 6.90 (d, 0.7H, J = 15.4 Hz), 7.86 (d, 0.4H, J = 15.7 Hz), 6.87−7.42 (m, 5.4H). **(1*Z*,3*E*)-7f:** GCMS (EI) *m*/*z* (rel intnesity) 322 (M^+, 97), 248 (11), 233 (9), 217 (57), 201 (46), 147 (46), 73 (100.0); HRMS (EI) calcd for $C_{16}H_{26}OSSi_2$ (M^+) 322.1243, found 322.1230. **(1*E*,3*E*)-7f:** GCMS (EI) *m*/*z* (rel intnesity) 322 (M^+, 77), 248 (13), 233 (9), 217 (49), 201 (40), 147 (49), 73 (100.0); HRMS (EI) calcd for $C_{16}H_{26}OSSi_2$ (M^+) 322.1243, found 322.1224. Under silica gel column chromatography conditions (eluent: hexane/ethyl acetate 10/1), silylthio compound was hydrolyzed to enethiol, (1*Z*,2*E*)-2-trimethylsiloxy-4-phenylbutadiene-1-thiol (38%): ^{1}H NMR δ 0.34 (s, 9H), 3.00 (d, 1H, J = 9.7 Hz), 5.51 (d, 1H, J = 9.7 Hz), 6.57 (s, 2H), 6.87−7.05 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 1.0, 101.6, 125.0, 126.3, 126.4, 127.4, 128.5, 136.7, 149.5.

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Supporting Information Available: Spectral data for thioesters and products. This material is available free of charge via the Internet at http://pubs.acs.org.

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