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# A Synthesis of (1*E*,3*E*)-TMS Dienes from Keto-Xanthates via Chugaev-Type Elimination

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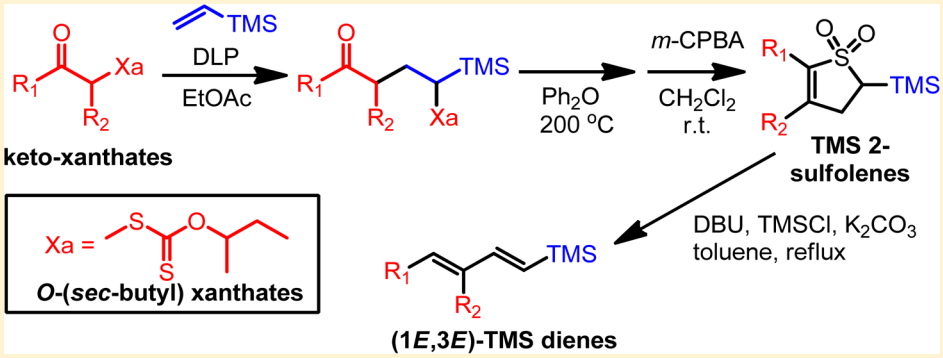
Supporting Information




**ABSTRACT:** An efficient route leading to exclusively (1*E*,3*E*)-TMS dienes is described. Radical xanthate addition of keto-xanthates to vinyltrimethylsilane followed by one-pot Chugaev elimination/cyclization and in situ oxidation with *m*-CPBA afforded the corresponding TMS 2-sulfolenes. Isomerization to 3-sulfolenes by the action of DBU with the extrusion of sulfur dioxide in refluxing toluene gave the titled (1*E*,3*E*)-TMS dienes.

1,3-Dienes are important intermediates in modern organic synthesis, in particular in relation to the Diels–Alder reaction.[1] In addition, the silane group presents an alternate and versatile functionality that can undergo various transformations to other important functionalities such as allylic alcohols[2] and aldehydes[3] or be transformed into excellent coupling partners such as iodides[4] and boronate derivatives.[5]

Classical methods for preparing such dienylsilanes include a modified Peterson olefination[6] or Horner–Wadsworth–Emmons-type reactions.[7] A more popular approach to dienylsilanes relies on palladium- or nickel-catalyzed cross-couplings. However, it is important to note that most of the coupling partners are vinyl or dienyl halides,[8] triflates,[9] tosylates, and phosphonates.[10] This limits the coupling precursors to predefined geometrical alkenyl halides or dithioacetals[11] that may not be commercially available or require tedious preparations. Organometallic reagents such as stannanes[12] and organozinc[13] or organotitanium derivatives[14] pose technical difficulties in the handling and synthesis of the reagents as well as the issue of toxicity. In addition, such methods often exhibit poor or suboptimal stereoselectivities in the formation of the dienes.[6−14]

Direct preparations of 1,3-dienes are usually plagued by polymerization upon prolonged storage and difficulties in handling. In regard to this aspect, bench-stable 2-sulfolenes can be isomerized to 3-sulfolenes,[15] which are well-known precursors to such dienes, Unfortunately, these have been largely neglected because of the lack of a convenient synthetic access. Our ongoing efforts in discovering new applications for the xanthate radical addition transfer reaction[16] prompted us to exploit the rich chemistry of xanthates to access these 2-sulfolenes as key intermediates to 1,3-dienes.[17]

Herein we report a novel and rapid method to access functionalized (1*E*,3*E*)-TMS dienes. We envisaged that heating of secondary *O*-(2-butyl) xanthate adducts **2** would initiate Chugaev elimination and cyclization followed by dehydration to give 2-dihydrothiophenes **3** (Scheme 1).[18] These would then be oxidized in situ to give 2-sulfolenes **4**, which can be easily isolated via silica gel column chromatography and stored as bench-stable solids. These 2-sulfolenes **4** can be easily isomerized to 3-sulfolenes **5** with DBU to obtain the corresponding (1*E*,3*E*)-TMS dienes **6** directly under the reaction conditions previously reported by us.[17]

Such a protocol based on the Chugaev elimination would not only effectively truncate possible tedious multistep workups to a simplified one-pot process but, more importantly, would avoid the use of acids, which may prove to be quite detrimental to certain sensitive functionalities next to the sulfone such as the trimethylsilyl (TMS) group.

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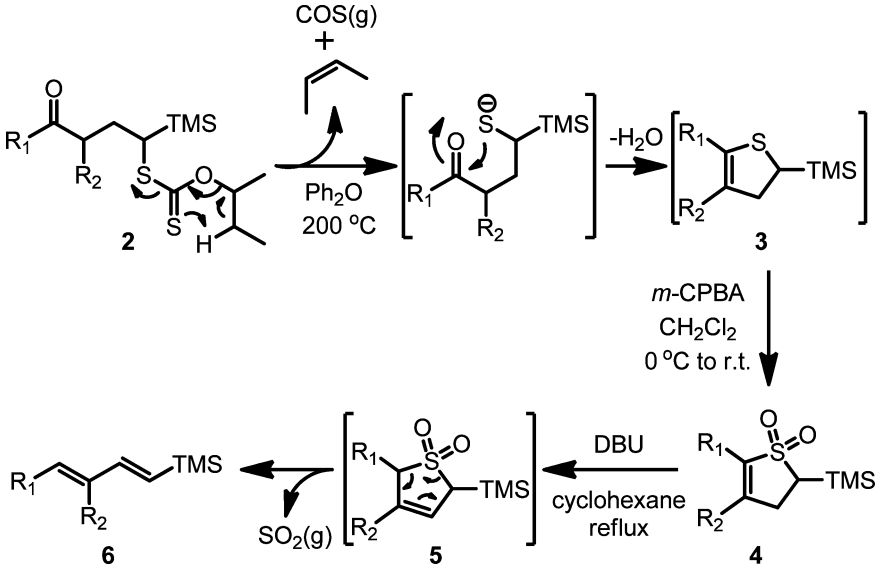
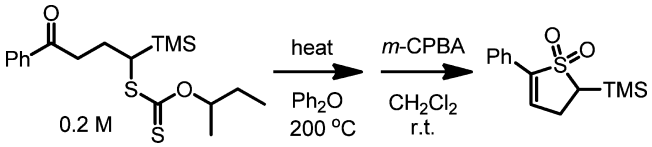
**Scheme 1. Proposed Route to 1,3-TMS Dienes from Xanthate Adducts**




A preliminary experiment of the one-pot reaction using xanthate adduct **2a** was carried out. The initial results were disheartening, as a complex mixture of products was observed and only a 20% yield of 2-sulfolene **4a** was isolated. This could have arisen from competing intermolecular reactions between the fragmented nucleophilic sulfur coproducts and the ketone or thiocarbonyl of another adduct molecule. Fortunately, this was circumvented by utilizing more dilute conditions, which greatly favored the intramolecular cyclization and effectively curtailed the intermolecular side reactions and gave the 2-sulfolene in improved yields. After a series of trials, the optimized conditions were found to be a dilution of 0.2 M and addition of *m*-CPBA at room temperature, which gave 2-sulfolene **4a** in 89% isolated yield with no desilylation observed (Scheme 2).

**Scheme 2. Optimized Conditions for the One-Pot Reaction To Give 2-Sulfolene**

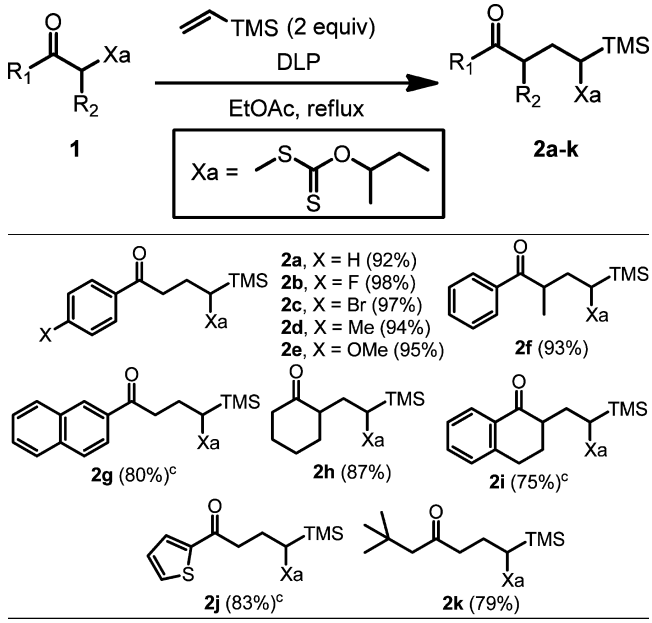



Having demonstrated the TMS group to be tolerant of this one-pot protocol, we decided to expand the scope by screening a number of TMS xanthate adducts **2a**–**k**, which were generally synthesized in good to excellent yields (75–98%) by radical addition of corresponding keto-xanthates **1** with vinyltrimethylsilane (Table 1).

Next, we attempted the one-pot conversion of the TMS xanthate adducts to the corresponding TMS 2-sulfolenes. 2-Sulfolenes bearing *para*-substituted aryls (**4a**–**e**), a methyl $\beta$ to the sulfone (**4f**), and a 2-naphthalenyl group $\alpha$ to the sulfone (**4g**) as well as cyclohexyl-fused (**4h**) and dihydronaphthalene-fused (**4i**) 2-sulfolenes were prepared in moderate to excellent yields (63–91%; Table 2). An interesting example to note was the 2-sulfolene bearing a thiophene **4j.** Use of *m*-CPBA could oxidize both the substituted thiophene and the 2-dihydrothiophene. This required careful manipulation of the reaction at a low temperature of 0 °C, allowing oxidation to occur selectively on the 2-dihydrothiophene instead of the electron-rich substituted thiophene to give the desired 2-sulfolene **4j** in a moderate yield of 58%.

Attempts to use methylene-substituted substrates were unsuccessful with this method. We reasoned that this failure is due to the favored formation of the more stable tetrasubstituted alkene instead of the desired trisubstituted 2-dihydrothiophene. In this respect, we tested the behavior of substrate **2k**, in which either external or internal elimination would lead to trisubstitution. The results showed that even in such cases,

**Table 1. Preparation of TMS Xanthate Adducts**[a,b]




[a]Conditions: To vinyltrimethylsilane (2.0 equiv) and **1** in EtOAc (1.0 M in the xanthate) heated to reflux under nitrogen was added 0.05 equiv of dilauroyl peroxide (DLP) every hour until **1** was mostly consumed as indicated by TLC. [b]Isolated yields based on **1** are shown. [c]0.10 equiv of DLP was used at hourly intervals.


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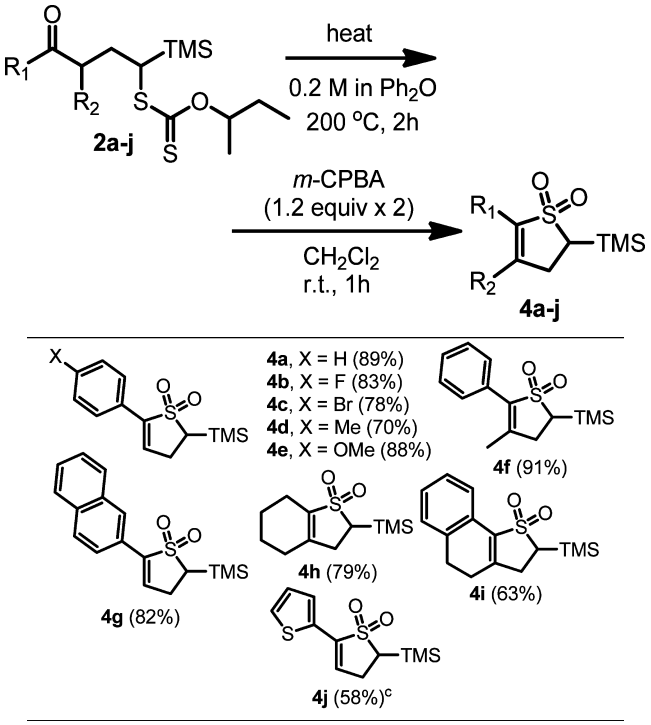
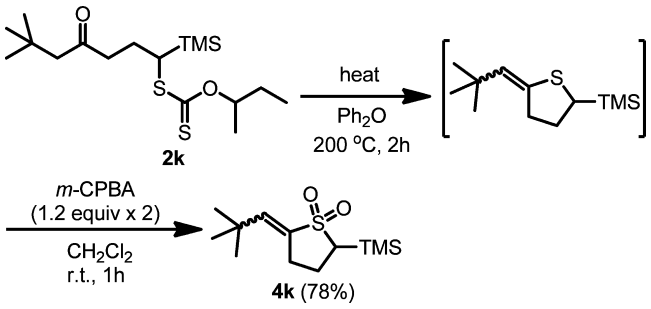
**Table 2. One-Pot Synthesis of TMS 2-Sulfolenes**[a,b]




[a]Conditions: In the first step, **2** (0.2 M in $Ph_2O$) was heated to 200 °C under nitrogen for 2 h. In the second step, the reaction mixture was cooled to room temperature and diluted with $CH_2Cl_2$ (2.0 times the volume of $Ph_2O$), and this was followed by two additions of *m*-CPBA (1.2 equiv) every 30 min. [b]Isolated yields based on **2** are shown. [c]The oxidation was done at 0 °C.

elimination to give the *exo*-alkene is favored (Scheme 3). This represents perhaps the main limitation of the present approach.

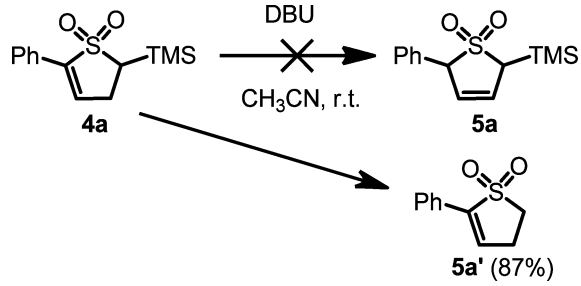
**Scheme 3. Formation of the *exo*-Alkene Is Favored during Elimination of Water**




Regardless, with a good number of TMS 2-sulfolenes in hand, we attempted the in situ DBU-induced isomerization and elimination of sulfur dioxide to generate the 1,3-dienes. Conversion to the 1,3-diene was disappointingly low with cyclohexane, and significant desilylation was observed. To monitor this desilylation, we first attempted to isomerize 2-sulfolene **4a** to 3-sulfolene **5a** with DBU in acetonitrile. To our surprise, we obtained the desilylated 2-sulfolene **5a′** in 87% yield (Scheme 4).

Presumably, hydroxide anion generated by the action of DBU with adventitious water caused the desilylation by nucleophilic attack on the TMS group. This hypothesis was proven by a series of trial experiments to remove water from the medium. This led

**Scheme 4. Desilylation of TMS 2-Sulfolene by DBU in the Presence of Water**




to a better ratio of silylated dienes and improved conversions in toluene at elevated temperatures (Table 3). However, inconsistency was observed even under the most optimized conditions (Table 3, entry 8), which depended on the extent to which the setup was kept strictly moisture-free. Further attempts to completely remove moisture remained futile, and thus, we decided to approach this problem from another perspective.

Instead of meticulous physical removal of water, we decided to introduce a sacrificial electrophile to trap the hydroxide anion.[19] Indeed, this measure worked effectively to furnish the silylated dienes with the complete absence of desilylation. 1,3-TMS dienes bearing *para*-substituted aryls (**6a**–**e**) or 3-methyl-4-phenyl (**6f**), naphthalenyl (**6g**), dihydronaphthalenyl (**6i**), or heteroaryl (**6j**) substitution were obtained in moderate to good yields of 64–88% (Table 4).[20]

Notably, the reaction was significantly slower on substrate **4f** bearing a methyl group at the 4′ position of the TMS 2-sulfolene, and poor conversion (28%) was noted. However, this was circumvented by increasing the amount of DBU to 10 equiv, which gave 1,3-TMS diene **6f** in a moderate yield of 64% (Table 4, **6f**). This sluggishness is the result of steric hindrance.

In conclusion, we have demonstrated the use of secondary *O*-(2-butyl) xanthate adducts to form 2-sulfolenes in a one-pot fashion. This eliminates tedious multistep workups and, more importantly, avoids acidic conditions, making the protocol tolerant of an acid-sensitive group (e.g., trimethylsilyl) adjacent to the sulfone, thus creating a new pathway to TMS 2-sulfolenes. In addition, we were able to convert these TMS 2-sulfolenes to the corresponding (1*E*,3*E*)-TMS dienes with the absence of desilylation. This method offers an advantage in preparation over previous methods since it starts from a simple precursor such as vinyltrimethylsilane.

## EXPERIMENTAL SECTION

**General Experimental Methods.** Proton magnetic resonance spectra ($^1$H NMR) were recorded at 400 MHz, and coupling constants ($J$) are reported to ±0.5 Hz. Chemical shifts ($\delta$) are reported in parts per million relative to the residual solvent peak at 7.26 ppm ($CDCl_3$). Carbon magnetic resonance spectra ($^{13}$C NMR) were recorded in the same instrument at 100.6 MHz, and chemical shifts are reported in parts per million relative to the signal of chloroform-*d* ($\delta$ 77.00, triplet). High-resolution mass spectra were recorded by positive electron impact ionization ($EI^+$) at 70 eV on a double-focusing high-resolution mass spectrometer. The quoted masses are accurate to ±5 ppm.

*O-sec*-Butyl xanthates **1** were prepared from the corresponding chlorides or bromides with potassium *O-sec*-butyl carbonodithioate[21] using a procedure similar to that reported in our previous publication.[22]

**General Procedure A for the Addition of Xanthates 1 to Vinyltrimethylsilane To Obtain TMS Xanthate Adducts 2.** A solution of the corresponding xanthate (5 mmol, 1.0 equiv) and vinyltrimethylsilane (2.0 equiv) in EtOAc was refluxed under a nitrogen


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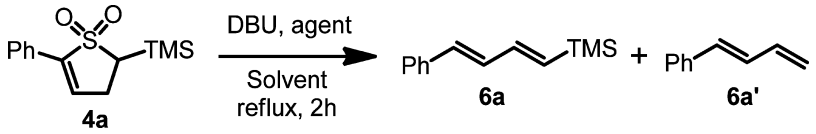
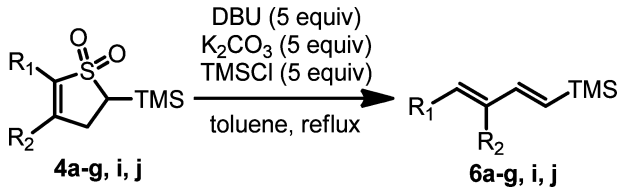
**Table 3. Screening of Conditions To Reduce Protodesilylation**

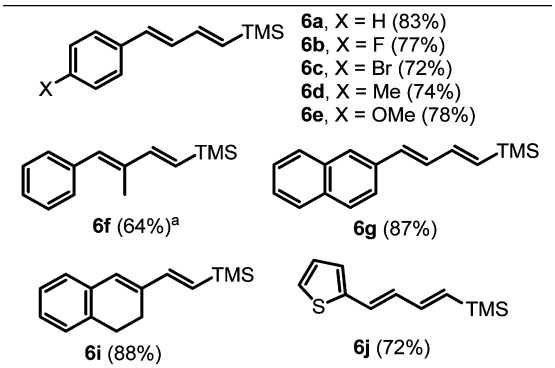



| entry | solvent | base (equiv) | drying agent/cobase | $T$ (°C) | product ratio (TMS:H)[a] |
|---|---|---|---|---|---|
| 1 | cyclohexane 3 mL | DBU (1.2) | – | 90 | 21:8 |
| 2 | cyclohexane 1 mL | DBU (1.2) | – | 90 | 16:7 |
| 3 | toluene 3 mL | DBU (1.0) | – | 120 | 43:40 |
| 4 | toluene 1 mL | DBU (1.0) | – | 120 | 39:40 |
| 5 | toluene 3 mL | DBU (0.5) | $Et_3N$ | 120 | 51:26 |
| 6 | toluene 3 mL | DBU (0.5) | DABCO | 120 | 57:34 |
| 7 | toluene 3 mL | DBU (0.5) | $MgSO_4$ | 120 | 62:27 |
| **8** | **toluene 3 mL** | **DBU (0.5)** | **$K_2CO_3$** | **120** | **87:0** |

[a]Product yield ratios were determined by $^1$H NMR analysis of isolated mixtures of compounds **6a** and **6a′**.

**Table 4. Synthesis of Functionalized (1*E*,3*E*)-TMS Dienes**




No product was observed from 2-sulfolene **4h** because of high volatility. [a]The reaction was done with DBU (10 equiv), TMSCl (10 equiv), and $K_2CO_3$ (10 equiv) in toluene (5 mL).

atmosphere for 10 min. Dilauroyl peroxide (DLP) (5 mol %) was then added every hour until complete consumption of the xanthate was indicated by TLC analysis. The resulting solution was concentrated under reduced pressure, and the crude mixture was purified by flash column chromatography (silica gel, $Et_2O$/petroleum ether = 10/90) to give the title TMS xanthate adduct.

***O-sec*-Butyl *S*-4-Oxo-4-phenyl-1-(trimethylsilyl)butyl Carbonodithioate (2a).** Yield: 1.69 g, 92%. Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): diastereomers = 1/1; $\delta$ 7.93 (d, 2H, $J$ = 7.8 Hz), 7.54 (t, 1H, $J$ = 7.4 Hz), 7.44 (t, 2H, $J$ = 7.7 Hz), 5.56–5.64 (m, 1H), 3.25–3.29 (m, 1H), 3.13–3.19 (m, 2H), 2.29–2.39 (m, 1H), 1.56–1.90 (m, 3H), 1.33 (d, 1.5H, $J$ = 6.3 Hz), 1.27 (d, 1.5H, $J$ = 6.3 Hz), 0.93 (t, 1.5H, $J$ = 7.4 Hz), 0.90 (t, 1.5H, $J$ = 7.5 Hz), 0.15 (s, 4.5H), 0.15 (s, 4.5H). $^{13}$C NMR ($CDCl_3$, 100 MHz): diastereomers = 1/1; $\delta$ 216.1, 199.8, 136.9, 133.0, 128.5, 128.0, 83.0, 37.0, 36.3, 28.5, 25.3, 18.7, 9.6, −2.6. HRMS (EI$^+$) $m/z$: calcd for [M]$^+$ $C_{18}H_{28}O_2S_2Si$ 368.1300, found 368.1305.

***O-sec*-Butyl *S*-4-(4-Fluorophenyl)-4-oxo-1-(trimethylsilyl)-butyl Carbonodithioate (2b).** Yield: 1.89 g, 98%. Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): diastereomers = 1/1; $\delta$ 7.93–7.96 (m, 2H), 7.11 (t, 2H, $J$ = 8.6 Hz), 5.55–5.64 (m, 1H), 3.26 (dd, 1H, $J$ = 11.1 Hz, $J$ = 3.5 Hz), 3.05–3.15 (m, 2H), 2.28–2.37 (m, 1H), 1.59–1.87 (m, 3H), 1.33 (d, 1.5H, $J$ = 6.3 Hz), 1.27 (d, 1.5H, $J$ = 6.3 Hz), 0.92 (t, 1.5H, $J$ = 7.5 Hz), 0.90 (t, 1.5H, $J$ = 7.5 Hz), 0.14 (s, 4.5H), 0.14 (s, 4.5H). $^{13}$C NMR ($CDCl_3$, 100 MHz): diastereomers = 1/1; $\delta$ 216.2, 198.1, 165.6 (d, $J_{CF}$ = 254.5 Hz), 133.3, 130.6 (d, $J_{CF}$ = 9.2 Hz), 115.6 (d, $J_{CF}$ = 21.8 Hz), 83.0, 36.9, 36.3, 28.5, 25.2, 18.7, 9.6, −2.6. HRMS (EI$^+$) $m/z$: calcd for [M]$^+$ $C_{18}H_{27}FO_2S_2Si$ 386.1206, found 386.1209.

***O-sec*-Butyl *S*-4-(4-Bromophenyl)-4-oxo-1-(trimethylsilyl)-butyl Carbonodithioate (2c).** Yield: 2.17 g, 97%. Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): diastereomers = 1/1; $\delta$ 7.79 (dd, 2H, $J$ = 8.4 Hz, $J$ = 1.2 Hz), 7.58 (d, 1H, $J$ = 8.6 Hz), 5.53–5.67 (m, 1H), 3.26 (dd, 1H, $J$ = 11.1 Hz, $J$ = 3.5 Hz), 3.01–3.23 (m, 2H), 2.29–2.39 (m, 1H), 1.57–1.85 (m, 3H), 1.33 (d, 1.5H, $J$ = 6.3 Hz), 1.28 (d, 1.5H, $J$ = 6.3 Hz), 0.92 (t, 1.5H, $J$ = 7.5 Hz), 0.90 (t, 1.5H, $J$ = 7.5 Hz), 0.13 (s, 4.5H), 0.13 (s, 4.5H). $^{13}$C NMR ($CDCl_3$, 100 MHz): diastereomers = 1/1; $\delta$ 216.0, 198.5, 135.4, 131.7, 129.4, 127.9, 82.9, 36.8, 36.6, 36.1, 28.4, 25.0, 24.8, 18.6, 9.5, −2.7. HRMS (EI$^+$) $m/z$: calcd for [M]$^+$ $C_{18}H_{27}BrO_2S_2Si$ 446.0405, found 446.0384.

***O-sec*-Butyl *S*-4-Oxo-4-*p*-tolyl-1-(trimethylsilyl)butyl Carbonodithioate (2d).** Yield: 1.79 g, 94%. Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): diastereomers = 1/1; $\delta$ 7.83 (d, 2H, $J$ = 8.0 Hz), 7.24 (d, 2H, $J$ = 8.0 Hz), 5.58–5.63 (m, 1H), 3.26 (dd, 1H, $J$ = 10.9 Hz, $J$ = 3.5 Hz), 3.11–3.15 (m, 2H), 2.40 (s, 3H), 2.28–2.38 (m, 1H), 1.61–1.89 (m, 3H), 1.33 (d, 1.5H, $J$ = 6.3 Hz), 1.27 (d, 1.5H, $J$ = 6.3 Hz), 0.93 (t, 1.5H, $J$ = 7.4 Hz), 0.90 (t, 1.5H, $J$ = 7.5 Hz), 0.14 (s, 4.5H), 0.14 (s, 4.5H). $^{13}$C NMR ($CDCl_3$, 100 MHz): diastereomers = 1/1; $\delta$ 211.9, 199.4, 143.7, 134.4, 129.2, 128.1, 82.9, 36.9, 36.3, 28.5, 25.4, 25.1, 21.6, 18.7, 9.6, −2.6. HRMS (EI$^+$) $m/z$: calcd for [M]$^+$ $C_{19}H_{30}O_2S_2Si$ 382.1456, found 382.1472.

***O-sec*-Butyl *S*-4-(4-Methoxyphenyl)-4-oxo-1-(trimethylsilyl)-butyl Carbonodithioate (2e).** Yield: 1.89 g, 95%. Yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): diastereomers = 1/1; $\delta$ 7.92 (d, 2H, $J$ = 8.8 Hz), 6.92 (d, 2H, $J$ = 8.8 Hz), 5.56–5.64 (m, 1H), 3.86 (s, 3H), 3.26 (dd, 1H, $J$ = 10.9 Hz, $J$ = 3.5 Hz), 3.08–3.14 (m, 2H), 2.27–2.37 (m, 1H), 1.61–1.88 (m, 3H), 1.34 (d, 1.5H, $J$ = 6.3 Hz), 1.27 (d, 1.5H, $J$ = 6.2 Hz), 0.93 (t, 1.5H, $J$ = 7.4 Hz), 0.90 (t, 1.5H, $J$ = 7.5 Hz), 0.14 (s, 4.5H), 0.14 (s, 4.5H). $^{13}$C NMR ($CDCl_3$, 100 MHz): diastereomers = 1/1; $\delta$ 216.1, 198.3, 163.4, 130.3, 130.0, 113.7, 82.9, 55.4, 36.7, 36.4, 28.5, 25.5, 18.7, 9.6, −2.6. HRMS (EI$^+$) $m/z$: calcd for [M]$^+$ $C_{19}H_{30}O_3S_2Si$ 398.1406, found 398.1406.

***O-sec*-Butyl *S*-3-Methyl-4-oxo-4-phenyl-1-(trimethylsilyl)-butyl Carbonodithioate (2f).** Yield: 1.78 g, 93%. Yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): diastereomers = 1/1/1/1; $\delta$ 7.92–7.98 (m, 2H), 7.52–7.56 (m, 1H), 7.40–7.48 (m, 2H), 5.36–5.67 (m, 1H), 3.70–3.85 (m, 1H), 3.07–3.42 (m, 1 H), 1.92–2.52 (m, 1H), 1.41–1.90 (m, 3H), 1.35 (dd, 2H, $J$ = 15.1 Hz, $J$ = 6.3 Hz), 1.24 (dd, 2.5H, $J$ = 13.8 Hz, $J$ = 6.5 Hz), 1.17 (dd, 1.5H, $J$ = 7.2 Hz, $J$ = 1.5 Hz), 0.95 (m, 1.5H), 0.86 (t, 0.75H, $J$ = 7.4 Hz), 0.73 (t, 0.75H, $J$ = 7.5 Hz), 0.13 (s, 2.25H), 0.12 (s, 2.25H), 0.09 (s, 2.25H), 0.09 (s, 2.25H). $^{13}$C NMR ($CDCl_3$, 100 MHz): diastereomers = 1/1/1/1; $\delta$ 215.9, 215.0, 203.9, 203.4, 136.5, 135.9, 132.9, 128.6, 83.1, 82.8, 38.9, 35.2, 34.5, 34.1, 33.7, 33.0, 28.6,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28.4, 28.2, 19.5, 18.7, 18.5, 18.1, 16.6, 9.6, −3.0. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{19}H_{30}O_2S_2Si$ 382.1456, found 382.1461.

***O-sec*-Butyl *S*-4-(Naphthalen-2-yl)-4-oxo-1-(trimethylsilyl)-butyl Carbonodithioate (2g).** Yield: 1.67 g, 80%. White solid, mp 71−75 °C. $^1$H NMR ($CDCl_3$, 400 MHz): diastereomers = 1/1; $\delta$ 8.45 (s, 1H), 8.02 (dd, 1H, $J$ = 8.6 Hz, $J$ = 1.7 Hz), 7.95 (d, 1H, $J$ = 7.9 Hz), 7.87 (dd, 2H, $J$ = 8.1 Hz, $J$ = 6.1 Hz), 7.52−7.62 (m, 2H), 5.56−5.63 (m, 1H), 3.26−3.34 (m, 3H), 2.36−2.45 (m, 1H), 1.56−2.04 (m, 3H), 1.32 (d, 1.5H, $J$ = 6.3 Hz), 1.26 (d, 1.5H, $J$ = 6.2 Hz), 0.91 (t, 1.5H, $J$ = 7.5 Hz), 0.88 (t, 1.5H, $J$ = 7.5 Hz), 0.18 (s, 4.5H), 0.17 (s, 4.5H). $^{13}$C NMR ($CDCl_3$, 100 MHz): diastereomers = 1/1; $\delta$ 216.2, 199.7, 135.5, 134.2, 132.5, 129.7, 129.5, 128.3, 127.7, 126.7, 123.8, 83.0, 37.0, 36.3, 28.5, 25.4, 18.7, 9.6, −2.6. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{22}H_{30}O_2S_2Si$ 418.1456, found 418.1458.

***O-sec*-Butyl *S*-2-(2-Oxocyclohexyl)-1-(trimethylsilyl)ethyl Carbonodithioate (2h).** Yield: 1.51 g, 87%. Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): diastereomers = 1/1/1/1; $\delta$ 5.58−5.66 (m, 1H), 3.15−3.30 (m, 1H), 2.26−2.46 (m, 4H), 1.53−2.09 (m, 7H), 1.22−1.46 (m, 4H), 0.79−1.03 (m, 4H), 0.12 (s, 2.25H), 0.12 (s, 2.25H), 0.09 (s, 2.25H), 0.09 (s, 2.25H). $^{13}$C NMR ($CDCl_3$, 100 MHz): diastereomers = 1/1/1/1; $\delta$ 213.3, 212.8, 194.8, 82.8, 48.9, 48.2, 42.7, 42.2, 35.8, 35.5, 33.4, 33.2, 31.2, 30.9, 28.6, 27.9, 25.6, 25.2, 18.7, 9.6, −2.9. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{16}H_{30}O_2S_2Si$ 346.1456, found 346.1456.

***O-sec*-Butyl *S*-2-(1-Oxo-1,2,3,4-tetrahydronaphthalen-2-yl)-1-(trimethylsilyl)ethyl Carbonodithioate (2i).** Yield: 1.50 g, 75%. Yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): diastereomers = 1/1/1/1; $\delta$ 8.00 (t, 1H, $J$ = 7.5 Hz), 7.44 (t, 1H, $J$ = 7.4 Hz), 7.21−7.35 (m, 1H), 7.22 (d, 1H, $J$ = 7.6 Hz), 5.53−5.65 (m, 1H), 3.32−3.63 (m, 1H), 2.95−3.11 (m, 2H), 2.59−2.75 (m, 1H), 2.40−2.56 (m, 2H), 1.63−2.17 (m, 4H), 1.28−1.36 (m, 3H), 0.89−0.95 (m, 3H), 0.16 (s, 2.25H), 0.16 (s, 2.25H), 0.13 (s, 2.25H), 0.13 (s, 2.25H). $^{13}$C NMR ($CDCl_3$, 100 MHz): diastereomers = 1/1/1/1; $\delta$ 216.8, 200.4, 144.0, 143.7, 133.1, 132.8, 132.5, 128.6, 127.3, 126.4, 83.0, 82.6, 46.1, 45.5, 35.5, 33.7, 32.5, 32.1, 30.6, 29.5, 28.9, 28.5, 18.7, 9.6, −2.8. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{20}H_{30}O_2S_2Si$ 394.1456, found 394.1464.

***O-sec*-Butyl *S*-4-Oxo-4-(thiophen-2-yl)-1-(trimethylsilyl)butyl Carbonodithioate (2j).** Yield: 1.55 g, 83%. Yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): diastereomers = 1/1; $\delta$ 7.68 (ddd, 1H, $J$ = 3.6 Hz, $J$ = 2.3 Hz, $J$ = 1.1 Hz), 7.61 (dd, 1H, $J$ = 4.9 Hz, $J$ = 1.0 Hz), 7.10−7.12 (m, 1H), 5.56−5.64 (m, 1H), 3.25 (dd, 1H, $J$ = 11.1 Hz, $J$ = 3.4 Hz), 3.07−3.13 (m, 2H), 2.29−2.37 (m, 1H), 1.58−1.90 (m, 3H), 1.33 (d, 1.5H, $J$ = 6.3 Hz), 1.27 (d, 1.5H, $J$ = 6.3 Hz), 0.93 (t, 1.5H, $J$ = 7.5 Hz), 0.90 (t, 1.5H, $J$ = 7.5 Hz), 0.14 (s, 4.5H), 0.13 (s, 4.5H). $^{13}$C NMR ($CDCl_3$, 100 MHz): diastereomers = 1/1; $\delta$ 215.9, 192.7, 144.2, 133.4, 131.8, 128.0, 83.0, 37.7, 36.2, 28.5, 25.5, 18.7, 9.6, −2.7. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{16}H_{26}O_2S_3Si$ 374.0864, found 374.0868.

***O-sec*-Butyl *S*-6,6-Dimethyl-4-oxo-1-(trimethylsilyl)heptyl Carbonodithioate (2k).** Yield: 1.43 g, 79%. Yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): diastereomers = 1/1; $\delta$ 5.55−5.63 (m, 1H), 3.08−3.12 (m, 1H), 2.50−2.54 (m, 2H), 2.24 (s, 2H), 2.04−2.12 (m, 1H), 1.55−1.81 (m, 3H), 1.31 (d, 1.5H, $J$ = 6.3 Hz), 1.31 (d, 1.5H, $J$ = 6.3 Hz), 0.95 (s, 9H), 0.91 (t, 1.5H, $J$ = 7.4 Hz), 0.90 (t, 1.5H, $J$ = 7.5 Hz), 0.06 (s, 4.5H), 0.06 (s, 4.5H). $^{13}$C NMR ($CDCl_3$, 100 MHz): diastereomers = 1/1; $\delta$ 216.1, 210.1, 82.7, 55.0, 43.1, 36.0, 30.8, 29.6, 28.5, 24.3, 18.7, 9.5, −2.7. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{17}H_{34}O_2S_2Si$ 362.1769, found 362.1774.

**General Procedure B for the One-Pot Synthesis of 2-Sulfolenes 4.** TMS xanthate adduct (2 mmol, 1.0 equiv) in $Ph_2O$ (10 mL) under a nitrogen atmosphere was heated to 200−210 °C for 2 h and then cooled to room temperature. $CH_2Cl_2$ (20 mL) was added, followed by two successive additions of *m*-CPBA (1.2 equiv, 70−75%) every 30 min at room temperature (with the exception of substrate **2j**), and then the mixture was quenched with $Na_2S_2O_3$ and extracted with $CH_2Cl_2$. The combined organic layers were washed with $NaHCO_3$, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure, and purification with flash column chromatography (silica gel, EtOAc-petroleum ether =25/75) gave the title 2-sulfolene.

**5-Phenyl-2-(trimethylsilyl)-2,3-dihydrothiophene 1,1-Dioxide (4a).** Yield: 474 mg, 89%. White solid, mp 113−114 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.66−7.69 (m, 2H), 7.38−7.41 (m, 3H), 6.77 (t, 1H, $J$ = 3.0 Hz), 2.82−3.03 (m, 2H), 2.75−2.79 (m, 1H), 0.30 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 144.8, 132.0, 129.3, 128.7, 127.8, 126.6, 50.1, 27.1, −2.9. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{13}H_{18}O_2SSi$ 266.0797, found 266.0792.

**5-(4-Fluorophenyl)-2-(trimethylsilyl)-2,3-dihydrothiophene 1,1-Dioxide (4b).** Yield: 472 mg, 83%. White solid, mp 138−140 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.66 (dd, 2H, $J$ = 8.7 Hz, $J$ = 5.3 Hz), 7.08 (t, 2H, $J$ = 8.7 Hz), 6.72 (t, 1H, $J$ = 2.9 Hz), 2.91−3.02 (m, 2H), 2.76−2.83 (m, 1H), 0.29 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 163.4 (d, $J_{CF}$ = 249.9 Hz), 144.2, 131.7, 128.8 (d, $J_{CF}$ = 8.4 Hz), 124.1 (d, $J_{CF}$ = 3.4 Hz), 116.0 (d, $J_{CF}$ = 21.9 Hz), 50.1, 27.2, −2.7. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{13}H_{17}FO_2SSi$ 284.0703, found 284.0704.

**5-(4-Bromophenyl)-2-(trimethylsilyl)-2,3-dihydrothiophene 1,1-Dioxide (4c).** Yield: 539 mg, 78%. Yellow solid, mp 167−170 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.50−7.55 (m, 4H), 6.77−6.78 (m, 1H), 2.91−3.01 (m, 2H), 2.73−2.82 (m, 1H), 0.29 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 144.2, 132.4, 132.1, 128.2, 126.9, 123.8, 50.2, 27.3, −2.7. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{13}H_{17}BrO_2SSi$ 343.9902, found 343.9898.

**5-(*p*-Tolyl)-2-(trimethylsilyl)-2,3-dihydrothiophene 1,1-Dioxide (4d).** Yield: 393 mg, 70%. White solid, mp 135−140 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.57 (d, 2H, $J$ = 8.2 Hz), 7.20 (d, 2H, $J$ = 7.9 Hz), 6.72 (t, 1H, $J$ = 3.1 Hz), 2.91−3.01 (m, 2H), 2.72−2.86 (m, 1H), 2.36 (s, 3H), 0.30 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 145.1, 139.6, 130.8, 129.6, 126.6, 125.0, 50.2, 27.1, 21.3, −2.7. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{14}H_{20}O_2SSi$ 280.0953, found 280.0952.

**5-(4-Methoxyphenyl)-2-(trimethylsilyl)-2,3-dihydrothiophene 1,1-Dioxide (4e).** Yield: 522 mg, 88%. Yellow solid, mp 117−122 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.59 (d, 2H, $J$ = 8.5 Hz), 6.88 (d, 2H, $J$ = 8.5 Hz), 6.63 (s, 1H), 3.77 (s, 3H), 2.87−2.96 (m, 2H), 2.72−2.79 (m, 1H), 0.26 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 160.4, 144.4, 129.8, 128.0, 120.2, 114.2, 55.2, 50.0, 26.9, −2.8. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{14}H_{20}O_3SSi$ 296.0902, found 296.0907.

**4-Methyl-5-phenyl-2-(trimethylsilyl)-2,3-dihydrothiophene 1,1-Dioxide (4f).** Yield: 511 mg, 91%. White solid, mp 127−128 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.39−7.44 (m, 5H), 2.87−2.90 (m, 2H), 2.67−2.74 (m, 1H), 1.95 (s, 3H), 0.29 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 143.6, 139.1, 129.4, 128.9, 128.5, 128.0, 49.5, 32.7, 17.2, −2.7. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{14}H_{20}O_2SSi$ 280.0953, found 280.0943.

**5-(Naphthalen-2-yl)-2-(trimethylsilyl)-2,3-dihydrothiophene 1,1-Dioxide (4g).** Yield: 519 mg, 82%. White solid, mp 132−135 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.29 (s, 1H), 7.82−7.88 (m, 3H), 7.66 (dd, 1H, $J$ = 8.6 Hz, $J$ = 1.6 Hz), 7.46−7.52 (m, 2H), 6.90 (t, 1H, $J$ = 3.0 Hz), 2.95−3.01 (m, 2H), 2.77−2.85 (m, 1H), 0.33 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 145.2, 133.5, 133.1, 131.9, 128.7, 128.7, 127.6, 126.9, 126.6, 126.2, 125.1, 124.0, 50.3, 27.3, −2.7. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{17}H_{20}O_2SSi$ 316.0953, found 316.0955.

**2-(Trimethylsilyl)-2,3,4,5,6,7-hexahydrobenzo[*b*]thiophene 1,1-Dioxide (4h).** Yield: 386 mg, 79%. White solid, mp 89−90 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 2.70−2.74 (m, 2H), 2.50−2.60 (m, 1H), 2.35 (s, 2H), 2.14 (s, 2H), 1.69−1.76 (m, 4H), 0.25 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 144.3, 136.6, 48.7, 31.4, 27.1, 21.2, 21.0, 17.9, −3.0. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{11}H_{20}O_2SSi$ 244.0953, found 244.0961.

**2-(Trimethylsilyl)-2,3,4,5-tetrahydronaphtho[1,2-*b*]thiophene 1,1-Dioxide (4i).** Yield: 369 mg, 63%. Light-yellow solid, mp 138−141 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.71−7.73 (m, 1H), 7.16−7.26 (m, 3H), 2.90−2.99 (m, 4H), 2.73−2.80 (m, 1H), 2.49 (t, 2H, $J$ = 8.2 Hz), 0.29 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 145.7, 136.6, 134.5, 128.7, 127.9, 127.0, 125.6, 122.8, 50.8, 31.0, 27.3, 26.3, −2.7. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{15}H_{20}O_2SSi$ 292.0953, found 292.0952.

**5-(Trimethylsilyl)-4,5-dihydro[2,2′-bithiophene] 1,1-Dioxide (4j).** Yield: 316 mg, 58%. Yellowish-green solid, mp 119−121 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.55 (d, 1H, $J$ = 3.2 Hz), 7.34 (d, 1H, $J$ = 5.0 Hz), 7.04−7.06 (m, 1H), 6.64 (t, 1H, $J$ = 3.3 Hz), 2.89−3.02 (m, 2H), 2.76−2.82 (m, 1H), 0.29 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 139.8, 129.8, 129.1, 128.0, 126.9, 126.7, 49.9, 27.5, −2.7. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{11}H_{16}O_2S_2Si$ 272.0361, found 272.0357.

**2-(2,2-Dimethylpropylidene)-5-(trimethylsilyl)tetrahydrothiophene 1,1-Dioxide (4k).** Yield: 406 mg, 78%. White solid, mp 103−105 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 6.33 (s, 1H), 2.77−2.87 (m, 1H), 2.58−2.68 (m, 2H), 2.27, 2.20 (ABq, 2H, $J_{AB}$ = 14.9 Hz), 0.95 (s, 9H), 0.20 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 143.8, 134.0, 48.1, 37.3, 30.9, 29.5, 27.3, −2.9. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{12}H_{24}O_2SSi$ 260.1266, found 260.1265.

**General Procedure C for the Synthesis of TMS Dienes 6.** A mixture of $K_2CO_3$ (5.0 equiv) and DBU (5.0 equiv) in toluene (5 mL) was refluxed under nitrogen. Trimethylsilyl chloride (5.0 equiv) was added to the refluxing mixture, followed by 2-sulfolene (0.5 mmol, 1.0 equiv), and the mixture was stirred for 1 h. The crude reaction mixture was cooled to room temperature and passed through a short silica plug. After a wash with petroleum ether (60 mL), the filtrate was concentrated under reduced pressure to afford the titled TMS diene.

**Trimethyl((1*E*,3*E*)-4-phenylbuta-1,3-dienyl)silane (6a).**[11] Yield: 84 mg, 83%.

**((1*E*,3*E*)-4-(4-Fluorophenyl)buta-1,3-dienyl)trimethylsilane (6b).**[23] Yield: 85 mg, 77%.

**((1*E*,3*E*)-4-(4-Bromophenyl)buta-1,3-dienyl)trimethylsilane (6c).** Yield: 102 mg, 72%. Yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.45 (d, 2H, $J$ = 8.4 Hz), 7.27 (d, 2H, $J$ = 8.4 Hz), 6.78 (dd, 1H, $J$ = 15.3 Hz, $J$ = 10.1 Hz), 6.68 (dd, 1H, $J$ = 17.9 Hz, $J$ = 10.1 Hz), 6.51 (d, 1H, $J$ = 15.3 Hz), 6.05 (d, 1H, $J$ = 17.8 Hz), 0.15 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 143.7, 136.1, 135.9, 132.3, 131.7, 131.4, 127.9, 121.3, −1.3. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{13}H_{17}BrSi$ 280.0283, found 280.0286.

**Trimethyl((1*E*,3*E*)-4-*p*-tolylbuta-1,3-dienyl)silane (6d).**[24] Yield: 80 mg, 74%.

**((1*E*,3*E*)-4-(4-Methoxyphenyl)buta-1,3-dienyl)trimethylsilane (6e).**[24] Yield: 90 mg, 78%.

**Trimethyl((1*E*,3*E*)-3-methyl-4-phenylbuta-1,3-dienyl)silane (6f).**[11] Yield: 69 mg, 64%.

**Trimethyl((1*E*,3*E*)-4-(naphthalen-2-yl)buta-1,3-dienyl)silane (6g).** Yield: 110 mg, 87%. Yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.78−7.81 (m, 4H), 7.64 (dd, 1H, $J$ = 8.6 Hz, $J$ = 1.5 Hz), 7.42−7.49 (m, 2H), 6.94 (dd, 1H, $J$ = 15.6 Hz, 9.9 Hz), 6.73−6.80 (m, 2H), 6.08 (d, 1H, $J$ = 18.6 Hz), 0.16 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 144.1, 135.2, 134.7, 133.6, 133.0, 133.0, 132.0, 128.2, 128.0, 127.7, 126.7, 126.3, 125.9, 123.5, −1.2. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{17}H_{20}Si$ 252.1334, found 252.1326.

**(*E*)-(2-(3,4-Dihydronaphthalen-2-yl)vinyl)trimethylsilane (6i).** Yield: 100 mg, 88%. Colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.10−7.20 (m, 4H), 6.78 (d, 1H, $J$ = 19.0 Hz), 6.52 (s, 1H), 6.06 (d, 1H, $J$ = 18.9 Hz), 2.89 (t, 1H, $J$ = 8.1 Hz), 2.52 (t, 1H, $J$ = 8.1 Hz), 0.18 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 145.3, 138.7, 135.8, 134.7, 128.7, 128.2, 127.2, 127.0, 126.6, 126.5, 27.8, 22.4, −1.1. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{15}H_{20}Si$ 228.1334, found 228.1328.

**Trimethyl((1*E*,3*E*)-4-(thiophen-2-yl)buta-1,3-dienyl)silane (6j).** Yield: 75 mg, 72%. Yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.17 (d, 1H, $J$ = 4.3 Hz), 6.97−7.00 (m, 2H), 6.58−6.74 (m, 3H), 5.96−6.03 (m, 1H), 0.13 (s, 9H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 143.5, 142.6, 134.9, 131.4, 127.6, 126.2, 125.6, 124.6, −1.3. HRMS (EI$^+$) $m/z$: calcd for $[M]^+$ $C_{11}H_{16}SSi$ 208.0742, found 208.0747.

## ■ ASSOCIATED CONTENT

### Supporting Information

$^1$H and $^{13}$C NMR spectra of the compounds potassium *O*-*sec*-butyl carbonodithioate, **2a**−**k**, **4a**−**k**, **6a**−**g**, **6i**, and **6j** and the NOESY spectrum of **6f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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(18) In practically all of the previous studies, *O*-ethyl xanthates were used. The adducts, however, do not undergo the Chugaev elimination at reasonable temperatures. Hence, the use of *O*-(2-butyl) xanthates **2** was required in the present approach.

(19) Trimethylsilyl chloride, TMSCl, should react rapidly with residual water, and the released HCl can be irreversibly neutralized with excess anhydrous potassium carbonate. The latter reagent is also a good dehydrating agent in its own right.

(20) Use of an excess amount of reagents (5 equiv) was required to drive the reaction to completion within 45 min to 1 h as well as to safeguard against possible desilylation at prolonged reaction times.

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