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## A facile [4+1] type synthetic route to thiophenes from dienol silyl ethers and elemental sulfur

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Abstract—A facile method for the synthesis of thiophene derivatives via the reaction of readily accessible dienol silyl ethers with elemental sulfur is described. Dienol silyl ethers and elemental sulfur, when heated at 180 °C in the presence of MS4A, provided 3-siloxythiophene derivatives in yields up to 98%. In this reaction, thiophene derivatives might be formed through 1,2-dithiines and eight-membered cyclic tetrasulfides.

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## 1. Introduction

The thiophene ring structure is widespread in nature and many of these compounds are biologically active.<sup>1</sup> Thiophene derivatives are also widely utilized as functional materials in dyes, liquid crystals and as components of organic conducting polymers.<sup>1</sup> Because of their significance, heterocycles are important target molecules from a synthetic point of view, and a number of methods for their preparation have been reported to date.<sup>1</sup> Although the Gewald, Hinsberg and Paal syntheses are well-known procedures for the construction of the ring, new or improved methodologies have been developed more recently.<sup>1</sup> Among these procedures, [4+1] type ring formation from 4-carbon units and elemental sulfur should be practical because of the low cost sources and, in fact, one of these reactions is used in the commercial production of thiophenes.<sup>2</sup> While the thermal reaction of dienes with elemental sulfur is a simple approach to thiophene synthesis,<sup>3</sup> a high reaction temperature is required (300– 420 °C), and the efficiency is also low (up to 51%).

We previously reported on efficient methods of generation of nitrogen-centered 1,3-dipoles, azomethine ylides and azomethine imines, via an intramolecular 1,2- or 1,4silatropic shift and their cycloaddition reactions.<sup>4</sup> By applying the 1,4-silatropic protocol to the generation of thiocarbonyl ylides, we developed a convenient route for the preparation of enol and dienol silyl ethers from readily accessible starting materials, as shown in Scheme 1 for the case of dienol silyl ethers.<sup>5</sup> These reactions proceed via the generation of thiocarbonyl ylides by the thermal 1,4silatropy of *S*- $\alpha$ -silyl thioesters and electrocyclization of the thiocarbonyl ylides to give thiiranes followed by sulfur extrusion under completely neutral conditions without the need for any catalyst or additive. In these reactions, thiophene derivatives were also obtained as minor products.



Scheme 1. A convenient route to dienol silyl ethers via thiocarbonyl ylides.

Keywords: Thiophene; Dienol silyl ether; Elemental sulfur.

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In preliminary experiments, the precursors of the thiophenes were found to be the dienol silyl ethers and elemental sulfur generated in situ. This fact stimulated us to develop a new method for the synthesis of siloxythiophenes. The desired siloxythiophenes should be equivalent to hydroxythiophenes, which have been prepared only with difficulty by low yielding and/or multi-step procedures especially for simple 3-hydroxythiophenes.<sup>6</sup>

From these points of view, we present the full details of an efficient and convenient approach to siloxythiophenes from dienol silyl ethers and elemental sulfur as the  $S_1$  unit via a [4+1] type reaction.

## 2. Results and discussion

As mentioned in the introduction, to clarify the mechanism of generation of thiophene derivatives, the time course for the reaction of silylmethylthioester **1a** was monitored by <sup>1</sup>H NMR (Fig. 1). The thermal reaction of **1a** for 1.5 h provided a mixture of **2a** (82%) and **3a** (9%), which led to a mixture of **2a** (6%) and **3a** (55%) upon continued heating under the same conditions for 80 h. Thus, the formation of the thiophene **3a** must have been related to the consumption of the dienol silyl ether **2a**. Since sulfur might be generated in situ in this reaction, as shown in Scheme 1, it appears that the dienol silyl ether was consumed by a reaction with sulfur.



Figure 1. A time course for the reaction of  $\alpha$ ,  $\beta$ -unsaturated thioester 1a.

To verify the reaction pathway proposed above, an additional experiment was carried out (Eq. 1). As shown in Figure 1, the thermal treatment of thioester **1a** at 180 °C for 80 h led to the formation of thiophene **3a** in 55% yield. In the presence of elemental sulfur (5 equiv), the reaction proceeded at an increased rate and gave a higher yield of product (61%).



Based on the above results, a solution of dienol silyl ether 2a and 5 equiv of elemental sulfur in benzene was heated at 180 °C for 36 h in a sealed glass tube (Eq. 2) to give thiophene 3a in 66% yield. These results verify that a dienol silyl ether is a precursor of a thiophene.



To improve the efficiency of the reaction, the effect of additives was examined (Table 1). Although triethylamine and tri-n-butylphosphine are well known activators of elemental sulfur,<sup>7</sup> the use of these reagents had no effect on the results (entries 2 and 3). Lewis acids were also ineffective because of their tendency to cause the polymerization of dienol silvl ether 2a (entries 4, 5, 6 and 7). Interestingly, when molecular sieves 4Å (MS4A) were employed as an additive, the desired thiophene was obtained in almost quantitative yield (entry 8). To clarify the effect of MS4A, reactions using other porous inorganic materials and dehydrating agents were examined. Porous inorganic materials, such as zeolite, silica gel and alumina (entries 9, 10 and 11) and a dehydrating agent, sodium sulfate (entry 12) were ineffective except for potassium carbonate, which gave a quantitative yield (entry 13). Even when the reaction was carried out without these additives, the hydrolysis of starting dienol silyl ether did not occur, suggesting that MS4A does not function as a dehydrating reagent. Since the presence of potassium carbonate requires a longer reaction time than that with MS4A, the following experiments were carried out using MS4A as an additive.

Reactions of dienol silyl ethers **2b–e** with elemental sulfur in the presence of MS4A were carried out (Table 2). The starting dienol silyl ether **2b**, in which the substituent  $R^1$  is a methyl group, was efficiently converted to the corresponding thiophene (entry 1). Thiophene derivative **3c** possessing no substituent at the 2-position was also obtained in good yield from dienol silyl ether **2c** (entry 2). Dialkyl substituted dienol silyl ether **2d** having no aromatic substituent reacted to give 2,5-dialkyl substituted thiophene **3d** (entry 3). Although improvements in the efficiency are needed, 2,5-unsubstituted thiophene **3e** was synthesized from the unsubstituted dienol silyl ether **2e** (entry 4). The low yield might be because of the condensation polymerization of **2e**.

The present method was applicable to other types of dienol silyl ethers.

Thermal reaction of 2,3-bis(trimethylsilyloxy)-1,3butadiene **2f** with elemental sulfur gave 3,4-

<b>Table 1.</b> Effect of additives on the formation of thiophene <b>3a</b> from dienol silvl ether <b>2a</b> and elemental sulf
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	OSiMe <sub>3</sub> Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph				
Entry	Additive		Time (h)	Yield (%) <sup>a</sup>	
1	No	ne	36	66	
2	Et <sub>3</sub> N	(1 equiv)	40	27 <sup>b</sup>	
3	<i>n</i> -Bu <sub>3</sub> P	(1 equiv)	40	54	
4	BF <sub>3</sub> ·OEt <sub>2</sub>	(1 equiv)	6	0	
5	AgOTf	(1 equiv)	1	0	
6	Mg(OTf) <sub>2</sub>	(1 equiv)	24	28	
7	Zn(OTf) <sub>2</sub>	(1 equiv)	18	20	
8	MS4A	(10 mg)	48	98 (87) <sup>c</sup>	
9	Zeolite <sup>d</sup>	(10 mg)	84	57	
10	Silica gel <sup>e</sup>	(10 mg)	40	66	
11	Alumina <sup>f</sup>	(10 mg)	63	37	
12	Na <sub>2</sub> SO <sub>4</sub>	(1 equiv)	39	40	
13	$K_2CO_3$	(1 equiv)	90	98	

<sup>a</sup> Determined by <sup>1</sup>H NMR.

Entry

1 2

3

4

<sup>b</sup> Dienol silyl ether **2a** (37%) was recovered.

<sup>c</sup> Isolated yield. 2,5-Diphenyl-3-hydroxythiophene was also obtained in 8% yield as a result of hydrolysis of **3a** on work up.

<sup>d</sup> Zeolite A-4 from Wako Pure Chem. Ind.

<sup>e</sup> Silica gel 60 from Merck Co.

<sup>f</sup> Aluminium oxide 90 active basic from Merck Co.

2b

2c

2d

2e

Table 2. Reactions of dienol silyl ethers with elemental sulfur



20

10

Me

Η

<sup>a</sup> Isolated yield. <sup>1</sup>H NMR yields before purification are presented in the parenthesis.

Н

Me

Н

bis(trimethylsilyloxy)thiophene **3f** in 29% yield (Eq. 3).



Since Danishefsky's diene 2g should be a good candidate for synthesis of a functionalized thiophene, the reaction of 2g with elemental sulfur was carried out, unexpectedly affording 5-unsubstituted thiophene **3e** in 51% yield (Eq. 4). Although the reaction mechanism is unclear at present, Danishefsky's diene is a better starting material rather than **2e** for the formation of 2,5-unsubstituted thiophene **3e**.



To expand the utility of the system, a 1,3-butadiene having trimethylsiloxy group at 1-position was evaluated in the reaction. 1-Trimethylsilyloxy-1,3-butadiene 2h was found to function as a starting dienol silvl ether to afford 2-siloxythiophene **3h** (Eq. 5).

3c

3d

3e

Yield (%)<sup>a</sup>

80 (82)

77 (76)

44 (51)

14 (15)

These results present the potential for applying this reaction to synthesis of a variety of thiophene derivatives.

While no by-products were observed in the synthesis of thiophene from dienol silyl ethers except for 2e, 1,2-dithiine 4e (5%) and the eight-membered cyclic tetrasulfide **5e** (2%) were obtained after 10 h in the case of the reaction of dienol silvl ether 2e. To clarify the route of formation of the thiophene derivative, the reaction of 2e with sulfur was followed by 'H NMR and the time course is illustrated in Figure 2. Even after the complete consumption of dienol silvl ether 2e, the amount of thiophene 3e increased with the decrease in the amounts of 4e and 5e. Thus, it is conceivable that the cyclic polysulfides

could be precursors of the thiophene derivative in this reaction. In practice, examples of the formation of thiophene derivatives from 1,2-dithiine have been reported.<sup>8</sup>



Figure 2. Time course for the reaction of dienol silyl ether 2e with elemental sulfur.

To confirm that thiophene derivative **3e** was formed via **4e** and **5e**, these compounds were treated under the same conditions as were used for the formation of thiophene from **2e**, respectively (Scheme 2). As a result, the reaction of 1,2-dithiine **4e** gave thiophene derivative **3e** in 19%. In the case of **5e**, **4e** was also formed in situ and was gradually converted to the thiophene derivative. These results suggest that dienol silyl ether **2e** was initially converted to a mixture of cyclic polysulfides **4e** and **5e**, which were then altered to thiophene derivative **3e** in equilibrium between 1,2-dithiines and cyclic tetrasulfides have been reported,<sup>9</sup> a fact that also supports the proposed reaction pathway.



Scheme 2. Thermal treatment of 4e and 5e leading to thiophene 3e.

A plausible path for the formation of a thiophene derivative from a dienol silyl ether and elemental sulfur is proposed on the basis of the above results (Scheme 3). A nucleophilic attack on elemental sulfur by the carbon of the 1-position of the dienol silyl ether occurs, and the  $S_8$  ring is opened. The elimination of  $S_6$  followed by an attack of sulfur at the  $\beta$ -position of the generated carboxonium group gives the 1,2-dithiine skeleton. The elimination of hydrogen sulfide from the 1,2-dithiine then gives the thiophene derivative. Indeed, the generation of hydrogen sulfide was confirmed by using CuSO<sub>4</sub> test paper. Based on this fact, it is presumed that the effect of MS4A or potassium carbonate is to act as a scavenger of hydrogen sulfide.



**Scheme 3.** Plausible reaction mechanism for the generation of a thiophene derivative from a dienol silyl ether and elemental sulfur.

#### **3.** Conclusions

A convenient route to 3-siloxythiophene derivatives from readily accessible dienol silyl ethers and elemental sulfur is described. The presence of MS4A improved the efficiency of the reaction, providing thiophene derivatives in up to 98% yield. Furthermore, the isolation of a 1,2-dithiine derivative and an eight-membered cyclic tetrasulfide and a study of the reaction profile suggest that the reaction proceeds via these intermediates to form the thiophene derivatives. Further studies in this area are currently underway in our laboratory.

#### 4. Experimental

## 4.1. General experimental methods

IR spectra were obtained on a Jasco FT/IR-410 infrared spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL FT NMR JNM EX 270 spectrometer (<sup>1</sup>H NMR, 270 MHz; <sup>13</sup>C NMR, 68 MHz). Chemical shifts are reported in parts per million ( $\delta$ ), relative to internal TMS at 0.00 for <sup>1</sup>H NMR and chloroform at 77.0 for <sup>13</sup>C NMR. Mass spectra were obtained with a Shimadzu Model GC-MS-QP5000 spectrometer. High-resolution mass spectral data were obtained on a JEOL DX-303 mass spectrometer. All reactions were performed under an atmosphere of argon. Organic solvents were dried and distilled prior to use. Column chromatography was performed using silica gel 60, spherical, neutrality (Nacalai Tesque), which was dried at 140 °C under reduced pressure for 3 h prior to use. Because of high moisture sensitivity, high-resolution mass spectral (HRMS) data are given for the products instead of elemental analyses.

### 4.2. Synthesis of starting dienol silyl ethers

Starting dienol silyl ethers 2b,<sup>10</sup>  $2c^{11}$  and  $2d^{10}$  were prepared according to the published procedures except for dienol silyl ether 2a.<sup>5</sup>

4.2.1. 1,4-Diphenyl-2-(trimethylsilyloxy)-1,3-butadiene (2a). trans-1,4-Dipehnyl-but-3-en-2-one<sup>12</sup> (267 mg,1.20 mmol), DBU (237 mg, 1.56 mmol) and trimethylsilyl chloride (156 mg, 1.40 mmol) were placed in a 20 mL round bottom flask and was refluxed in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) for 12 h. After being cooled to room temperature, hexane (20 mL) was added to the reaction mixture and washed twice with saturated aqueous Na<sub>2</sub>CO<sub>3</sub> (10 mL). The organic layer was dried over MgSO<sub>4</sub>, and filtered. Removal of the solvent and purification by rapid column chromatography on dried neutral silicagel afforded dienol silvl ether 2a as a pale yellow oil. Yield: 248 mg (84%). (1Z,3E)-2a/(1E,3E)-2a = 96/4. (12,3*E*)-2a: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.57 (br d, 2H, J=7.3 Hz, o-aromatic H), 7.44 (br d, 2H, J=7.3 Hz, o-aromatic H), 7.37-7.14 (m, 6H, aromatic H), 6.82 (d, 1H, J = 15.8 Hz, vinyl H-4), 6.72 (d, 1H, J = 15.8 Hz, vinyl H-3), 5.90 (s, 1H, vinyl H-1), 0.15 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>]; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  149.8, 136.8, 136.3, 128.9, 128.8, 128.6, 128.0, 127.8, 127.5, 126.5, 126.2, 115.4, 0.9; MS (EI) m/z (relative intensity): 294 (M<sup>+</sup>, 15), 203 (21), 131 (96), 73  $(Me_3Si^+, 100)$ ; HRMS (EI) calcd for  $C_{19}H_{20}OSi$  (M<sup>+</sup>) 294.1440, found 294.1424. Key spectra of the minor compound (1E, 3E)-2a obtained from the mixture of 2a: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  6.23 (s, 1H, vinyl H-1), 0.28 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>]. Only distinct signals are listed.

# **4.3.** General procedure for the reaction of dienol silyl ether with elemental sulfur

Molecular sieves 4Å (50.0 mg) were placed in a 10 mL glass tube, which was flame-dried under reduced pressure. Elemental sulfur (48.1 mg, 1.50 mmol), dienol silvl ether 2 (0.300 mmol) and benzene (3 mL) were added to the tube and the solution was freeze-dried twice. The glass tube was then sealed and the mixture was heated at 180 °C until the amount of thiophene derivative reached a constant value. Reactions were monitored by <sup>1</sup>H NMR using benzene- $d_6$  as a solvent in one-fifth scale of the procedure described above with mesitylene as an internal standard. The yields of thiophene derivatives 3 listed in Tables 1 and 2 were determined by <sup>1</sup>H NMR of the crude reaction mixture based on the added mesitylene. The reaction mixture was concentrated in vacuo and the residue was purified by column chromatography on dried neutral silica gel, to afford thiophene 3. Cyclic polysulfides 4e and 5e were also produced in the reaction of dienol silyl ether 2e. Thiophenes **3a**, <sup>5</sup> **3e**<sup>13</sup>, **3h**<sup>14</sup> and 2,5-diphenyl-3-hydroxythiophene<sup>5</sup> are known compounds.

**4.3.1.** 2-Methyl-5-phenyl-3-(trimethylsilyloxy)thiophene (**3b**). IR (neat) 2958, 1568, 1502, 1252 and 847 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.51 (d, 2H, *J*=7.3 Hz, *o*-aromatic H at thiphene-C5), 7.35 (dd, 2H, *J*=7.3 Hz, *m*-aromatic H), 7.25 (d, 1H, *J*=7.3 Hz, *p*-aromatic H), 6.82 (s, 1H, 4-position in thiophene), 2.27 (s, 3H, Me), 0.28 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>]; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  148.1, 136.9, 134.5, 128.7, 126.9, 124.7, 118.6, 117.8, 11.3, 0.35; MS (EI) *m*/*z* (relative intensity): 262 (M<sup>+</sup>, 54), 247 (M<sup>+</sup> – Me, 15), 173 (10), 73 (Me<sub>3</sub>Si<sup>+</sup>, 100), 59 (96); HRMS (EI) calcd for C<sub>10</sub>H<sub>18</sub>OSSi (M<sup>+</sup>) 262.0848, found 262.0846.

**4.3.2. 2-Phenyl-4-(trimethylsilyloxy)thiophene** (3c). IR (neat) 2962, 1552, 1497 and 847 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 

7.56 (d, 2H, J=7.3 Hz, *o*-aromatic H at thiphene-C2), 7.37 (dd, 2H, J=7.3 Hz, *m*-aromatic H), 7.29 (d, 1H, J=7.3 Hz, *p*-aromatic H), 6.93 (d, 1H, J=1.6 Hz, 3-position in thiophene), 6.32 (d, 1H, J=1.6 Hz, 5-position in thiophene), 0.30 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>]; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  152.4, 141.8, 134.3, 128.7, 127.4, 125.1, 118.3, 104.1, 0.13; MS (EI) *m*/*z* (relative intensity): 248 (M<sup>+</sup>, 100), 233 (M<sup>+</sup> – Me, 46), 205 (30), 173 (7), 115 (14), 73 (Me<sub>3</sub>Si<sup>+</sup>, 17); HRMS (EI) calcd for C<sub>13</sub>H<sub>16</sub>OSSi (M<sup>+</sup>), 248.0691, found 248.0706.

**4.3.3. 2,5-Dimethyl-3-(trimethylsilyloxy)thiophene (3d).** IR (neat) 2962, 1578, 1254 and 845 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.26 (s, 1H, 4-position in thiophene), 2.34 (s, 3H, Me), 2.17 (s, 3H, Me), 0.22 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>]; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  146.7, 133.0, 120.1, 115.6, 15.8, 10.8, 0.17; MS (EI) *m/z* (relative intensity): 200 (M<sup>+</sup>, 100), 185 (M<sup>+</sup> – Me, 52), 111 (19), 73 (Me<sub>3</sub>Si<sup>+</sup>, 44); HRMS (EI) calcd for C<sub>9</sub>H<sub>16</sub>OSSi (M<sup>+</sup>), 200.0691, found 200.0699.

**4.3.4. 3,4-Bis(trimethylsilyloxy)thiophene (3f).** IR (neat) 2960, 1493, 1254 and 845 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.26 (s, 2H, 2- and 5-position in thiophene), 0.26 [s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>]; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  144.4, 103.0, 0.18; MS (EI) *m/z* (relative intensity): 260 (M<sup>+</sup>, 43), 245 (M<sup>+</sup> – Me, 14), 73 (Me<sub>3</sub>Si<sup>+</sup>, 100); HRMS (EI) calcd for C<sub>10</sub>H<sub>20</sub>O<sub>2</sub>SSi<sub>2</sub> (M<sup>+</sup>), 260.0723 found 260.0748.

**4.3.5. 4-Trimethylsilyloxy-3***H***,6***H***-1,2-dithiine (4e). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 270 MHz) \delta 5.02–4.98 (tt,** *J***=4.6, 1.4 Hz, 1H, C=CH), 3.07–3.02 (m, 4H, C=CH–CH<sub>2</sub> and CH<sub>2</sub>–C=CH), 0.09 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>]; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 68 MHz) \delta 149.7, 104.9, 33.3, 31.5, 0.90; MS (EI)** *m/z* **(%) 206 (M<sup>+</sup>, 87), 143 (23), 142 (M<sup>+</sup> – 2S, 68), 127 (100), 85 (18), 75 (54), 73 (Me<sub>3</sub>Si<sup>+</sup>, 54); HRMS (EI)** *m/z* **calcd for C<sub>7</sub>H<sub>14</sub>OS<sub>2</sub>Si 206.0255, found 206.0253.** 

**4.3.6. 1,2,3,4-Tetrathia-6-trimethylsilyloxy-6-cyclooctene** (5e). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 270 MHz)  $\delta$  4.61 (t, J= 9.0 Hz, 1H, C=CH), 3.07 (s, 2H, CH<sub>2</sub>-C=CH), 2.97 (d, J=9.0 Hz, 2H, C=CH-CH<sub>2</sub>), 0.21 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>]; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 68 MHz)  $\delta$  154.2, 103.8, 41.0, 35.6, 0.66; MS (EI) m/z (%) 270 (M<sup>+</sup>, 16), 206 (M<sup>+</sup> - 2S, 100), 173 (21), 159 (16), 142 (M<sup>+</sup> - 4S, 59), 127 (58), 75 (39), 73 (Me<sub>3</sub>Si<sup>+</sup>, 40); HRMS (EI) m/z calcd for C<sub>7</sub>H<sub>14</sub>OS<sub>4</sub>Si 269.9697, found 269.9698.

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