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Elucidation of the Stereochemistry of Thiirane Formation from a 1λ^4,2-Dithietane Bearing Two Chiral Carbon Centers

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ABSTRACT: *A tetracoordinated sulfurane bearing a 1λ^4,2-dithietane moiety, whose 3- and 4-positions were chiral carbon centers, was synthesized. Its thermolysis gave the corresponding thiirane as a single diastereomer, whose configuration and stereochemistry were determined.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:412–417, 2010; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20630

INTRODUCTION

Tetracoordinated sulfuranes are usually thermally unstable and easily reduced to divalent sulfur compounds with the loss of two ligands. In general, two mechanisms are considered for such a reaction. One is a concerted reductive elimination of two ligands, which is called a ligand coupling. The other is ligand dissociation to form a sulfonium salt followed by a nucleophilic attack on another ligand by the dissociated ligand. Although the ligand-coupling mechanism is common in the chemistry of hypervalent organosulfur compounds [1], some reactions have been reported to proceed via the latter reaction mechanism [2]. We reported previously that the thermolysis of a 1,2λ^6-oxathietane, a pentacoordinated sulfurane bearing the Martin ligand [3] and a four-membered ring, gave the oxirane with retention of the relative configuration, suggesting the ligand-coupling mechanism [2]. In contrast, the oxirane with inversion of configuration was obtained upon heating in the presence of lithium bromide, which induced a heterolytic cleavage of the S(IV)—O bond [2].

We also reported the synthesis of the sulfur-substituted sulfurane **1** bearing a 1λ^4,2-dithietane moiety, whose thermolysis gave the corresponding cyclic sulfenate and triphenylthiirane [4] (Scheme 1).

This reaction seems to proceed via the ligand-coupling mechanism. However, this is not certain because the product is the same as that from the other reaction mechanism. In addition, it might proceed via the latter reaction mechanism considering the polarized apical bonds.

The reaction mechanism can be determined by ascertaining whether the relative configuration of the resulting thiirane is retained or inverted. To distinguish between the two mechanisms, it is necessary to introduce another chiral center to the 3-position. In this paper, we wish to report the synthesis and thermolysis of 1λ^4,2-dithietane bearing chiral carbon centers at both the 3- and 4-positions.

RESULTS AND DISCUSSION

A tetracoordinated 1λ^4,2-dithietane bearing the Martin ligand and two chiral carbon centers at the 3- and 4-positions was synthesized from benzyl sulfide **4**, according to the method reported previously [4],

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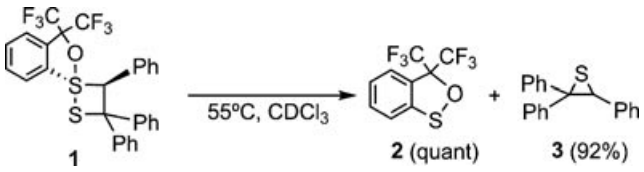


SCHEME 1 Thermolysis of 1λ⁴,2-dithietane **1**.

and obtained as a mixture of two diastereomers, **9a** and **9b** (Scheme 2).

A single diastereomer of β-(acetylthio)alkyl sulfide **6b** was successfully separated by repeated recrystallization of the diastereomer mixture from pentane and methanol, and its configuration was determined by X-ray crystallographic analysis (Fig. 1; Table 1). The configuration of the α- and β-positions of the alkyl group of **6b** was (*S,R*) or (*R,S*), both of which existed in the unit cell of a single crystal as two independent molecules.

1λ⁴,2-Dithietane **9b** was synthesized from **6b** as a single diastereomer by the same method as that shown in Scheme 2. In the synthetic scheme from **6–9**, the relative stereochemistry of all the reactions must be retained, and thus the configuration of **9b** must be identical to that of **6b**.

Although sufficient amounts of a single diastereomer of **9b** could not be prepared, the other diastereomer, 1λ⁴,2-dithietane **9a**, was successfully separated by repeated recrystallization of a diastereomeric mixture from carbon tetrachloride and hexane. Thiirane **10a** was obtained and isolated with 94% yield in the thermolysis of **9a** in toluene (Scheme 3). Formation of thiirane **10a** was confirmed by comparison of its ^{1}H NMR spectrum with that of one of the two diastereomers, which were synthesized as authentic samples from 4-(*tert*-butyl)thiobenzophenone and phenyldiazomethane [5].

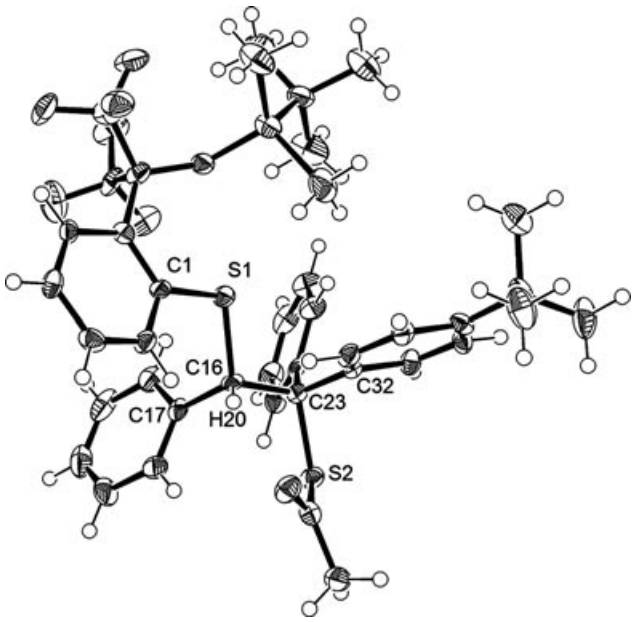
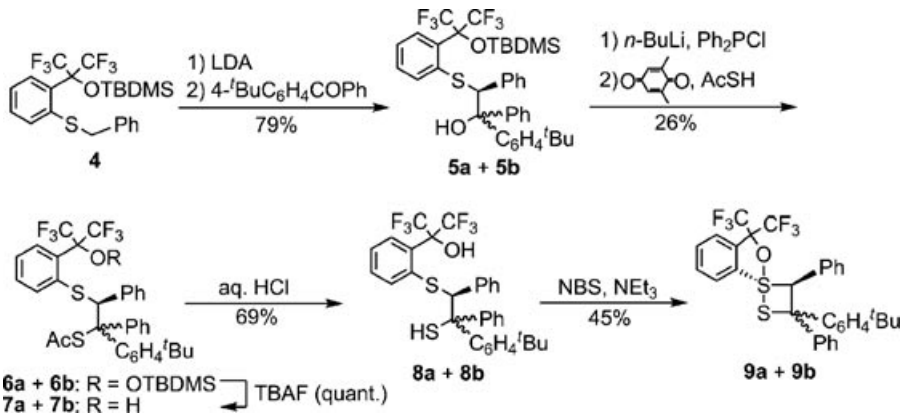


FIGURE 1 ORTEP drawing of **6b** (thermal ellipsoid plot with 50% probability)

Because it was difficult to determine the configuration of **10a** spectroscopically, we determined the configuration as follows: To begin, a thiirane was stereospecifically converted to the corresponding olefin. Next, the geometry of the olefin was determined. That is, thiirane **10a** was converted to olefin **11a** in good yield by reaction with triirondodecacarbonyl (Scheme 3), which is known to proceed with retention of configuration [6]. The geometry of the olefin was determined to be the *E*-configuration by comparison of its ^{1}H and ^{13}C NMR spectra with that of an authentic sample of (*E*)-1-(4-(*tert*-butyl)phenyl)-1,2-diphenylethylene



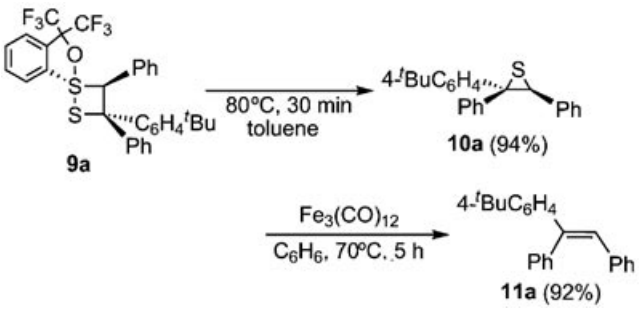
SCHEME 2 Synthetic pathway for 1λ⁴,2-dithietane **9**.

TABLE 1 Crystal Data and Refinement Details for **6b**

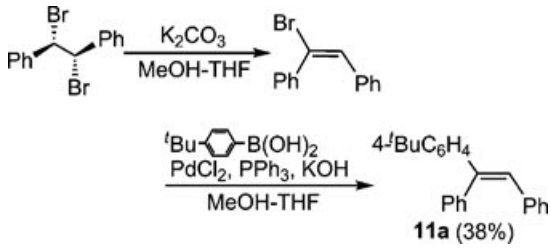
Empirical formula	$C_{41}H_{46}F_6O_2S_2Si$
Formula weight	776.99
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	
a (Å)	12.661(4)
b (Å)	12.899(4)
c (Å)	26.178(7)
α (°)	71.504(14)
β (°)	74.200(15)
γ (°)	78.597(16)
V (Å^3)	3872(2)
Z	4
*D*c (mg m^{-3})	1.333
Absorption coefficient (mm^{-1})	0.232
F (0 0 0)	1632
Crystal size (mm)	0.30 × 0.10 × 0.10
θ range (°)	3.08–25.00
Reflections collected	25449
Independent reflections	13307
Data/restraint/parameter	13307/0/955
Goodness-of-fit on F^2	0.983
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0647$, $wR2 = 0.1238$
R indices (all data)	$R1 = 0.1628$, $wR2 = 0.1788$

11a, which was synthesized alternatively by Suzuki coupling using (*E*)-diphenylbromoethylene and 4-(*tert*-butyl)phenylboronic acid (Scheme 4) [7]. Therefore, it was shown that the relative stereochemistry was retained in the formation of thiirane **10a** from 1λ^4,2-dithietane **9a**, indicating that the thiirane formation proceeded via the ligand-coupling mechanism.

In conclusion, we achieved the synthesis of 1λ^4,2-dithietane **9**, whose relative stereochemistry was retained in its thermolysis. This result indicates that the reaction mechanism for the thermolysis of **9** is ligand coupling. It is interesting that the sulfuranes featuring the four-membered structure showed the same reactivity, ligand coupling, despite a change in the contained heteroatom, even though the hypervalent S(IV)–S(II) bond is very labile [8].



SCHEME 3 Thermolysis of **9a** and desulfurization of **10a**.



SCHEME 4 Alternative synthesis of **11a**.

EXPERIMENTAL

All reactions were performed under argon atmosphere unless otherwise noted. Solvents were dried by standard methods and freshly distilled prior to use. Preparative gel permeation liquid chromatography (GPC) was performed by LC-908-C60 with JAIGEL 1H and 2H columns (Japan Analytical Industry) with chloroform as solvent. Silica-gel wet column chromatography was performed by Wakogel C-200. The melting point was determined on a Yanaco micromelting point apparatus and was uncorrected. ^{1}H (400 MHz) and ^{19}F (376 MHz) NMR spectra were recorded on a JEOL JNM-AL400 spectrometer using tetramethylsilane as an internal standard and trifluoroacetic acid as an external standard, respectively.^{13}C (126 MHz) NMR spectra were recorded on a Bruker-DRX500 spectrometer using residual chloroform as an internal standard. High-resolution mass spectral data were recorded on a JEOL JMS-700MS station mass spectrometer. X-ray crystallographic analysis was performed by Rigaku MERCURY CCD spectrometer. Elemental analysis was carried out at the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo.

Synthesis of β-Alkoxyalkyl Sulfide **5**

Lithium diisopropylamide (LDA) was prepared from diisopropylamine (3.0 mL, 20 mmol) and *n*-butyllithium (1.57 M in hexane, 15 mL, 24 mmol) in THF (10 mL) at −78°C, which was added dropwise to a THF solution (30 mL) of benzyl sulfide **4** [3] (10.0 g, 20.8 mmol) at −78°C, and it was stirred for 10 min. A THF solution (10 mL) of 4-(*tert*-butyl)benzophenone [9] (5.2 g, 22 mmol) was added to the reaction mixture and further stirred for 30 min. After quenching with aqueous ammonium chloride, the solution was warmed to room temperature, extracted with chloroform, and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, separation of the

crude material with silica-gel column chromatography (hexane:chloroform = 3:1) gave a 10:9 diastereomer mixture of **5a** and **5b** (11.8 g, 79%).

5. mp. 136.5–138.5°C; Anal. Calcd for $C_{39}H_{44}F_6O_2SSi$: C, 65.16; H, 6.17. Found; C, 65.21; H, 6.43%.

5a. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.14 (s, 3H), 0.18 (s, 3H), 0.75 (s, 9H), 1.30 (s, 9H), 3.08 (s, 1H), 5.37 (s, 1H), 6.88–7.46 (m, 16H), 7.55 (d, J = 8.6 Hz, 2H);^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: −2.09 (s), −1.49 (s), 14.12 (s), 19.49 (s), 26.16 (s), 31.31 (s), 61.88 (s), 80.69 (s), 83.10 (sept, $^2J_{CF}$ = 29.6 Hz), 122.79 (q, $^1J_{CF}$ = 291.0 Hz), 122.95 (q, $^1J_{CF}$ = 291.2 Hz), 123.72 (s), 125.03 (s), 125.80 (s), 126.24 (s), 126.80 (s), 127.24 (s), 127.30 (s), 127.48 (s), 128.30 (br s), 128.92 (s), 129.45 (s), 129.94 (s), 130.46 (s), 137.01 (s), 137.59 (s), 141.83 (s), 144.57 (s), 149.93 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −72.29 (q, $^4J_{FF}$ = 8.6 Hz, 3F), −71.37 (q, $^4J_{FF}$ = 8.6 Hz, 3F).

5b.^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.10 (s, 3H), 0.17 (s, 3H), 0.79 (s, 9H), 1.20 (s, 9H), 3.09 (s, 1H), 5.24 (s, 1H), 6.88–7.46 (m), 7.59 (d, J = 7.8 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: −2.13 (s), −1.63 (s), 19.49 (s), 22.65 (s), 26.19 (s), 31.23 (s), 62.43 (s), 80.98 (s), 83.62 (sept, $^2J_{CF}$ = 29.6 Hz), 123.69 (s), 124.42 (s), 125.57 (s), 126.42 (s), 126.86 (s), 126.93 (s), 127.13 (s), 127.98 (s), 128.40 (br s), 128.74 (s), 129.16 (s), 129.71 (s), 130.35 (s), 137.42 (s), 138.18 (s), 141.44 (s), 144.78 (s), 149.49 (s). Peaks of $\underline{C}F_3$ could not be assigned due to overlapping of the peaks of **5a**; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −71.94 (m, 3F), −71.82 (m, 3F).

Synthesis of β-(Acetylthio)alkyl Sulfide **6**

To a THF solution (30 mg) of **5** (6.7 g, 9.3 mmol), *n*-butyllithium (1.57 M in hexane, 6.1 mL, 9.6 mmol) and chlorodiphenylphosphine (1.7 mL, 9.3 mmol) were added dropwise at −78 °C, and the solution was stirred for 14 h with gradual warming to room temperature. Solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane (30 mL), treated with 2,6-dimethyl-1,4-benzoquinone (1.27 g, 9.3 mmol), and stirred for 10 h. Thioacetic acid (1.7 mL, 18 mmol) was added to the solution at 0°C, and the solution was stirred for 2 days at room temperature. The reaction mixture was quenched with aqueous sodium hydrocarboxylate, extracted with chloroform, and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, separation by silica-gel column chromatography (hexane:chloroform = 2:1) and then by GPC gave a 10:9 diastereomer mixture of **6a** and **6b** (1.85 g, 26%).

6. White solid: mp 143.0–144.5°C (decomp); Anal. Calcd for $C_{41}H_{46}F_6O_2S_2Si$: C, 63.38; H, 5.97. Found; C, 63.30; H, 6.06%.

6a. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.05 (s, 3H), 0.09 (s, 3H), 0.83 (s, 9H), 1.28 (s, 9H), 2.14 (s, 3H), 6.24 (s, 1H), 6.86–7.40 (m, 16H), 7.55 (d, J = 8.6 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: −2.47 (s), −2.36 (s), 19.39 (s), 26.22 (s), 31.09 (s), 31.23 (s), 34.34 (s), 56.79 (s), 69.00 (s), 83.00 (sept, $^2J_{CF}$ = 30.3 Hz), 122.70 (q, $^1J_{CF}$ = 291.0 Hz), 122.76 (q, $^1J_{CF}$ = 290.4 Hz), 123.45 (s), 123.76 (s), 126.76 (s), 126.91 (s), 127.34 (s), 127.76 (s), 128.42 (s), 129.07 (br s), 129.60 (s), 130.07 (s), 130.34 (s), 130.90 (s), 131.37 (s), 138.78 (s), 138.92 (s), 139.11 (s), 149.36 (s), 194.26 (s). Two peaks of quaternary carbons overlapped at δ 138.92; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −70.92 (br q, $^4J_{FF}$ = 9.8 Hz, 3F), −70.60 (br s, 3F).

6b.^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.03 (s, 3H), 0.08 (s, 3H), 0.82 (s, 9H), 1.33 (s, 9H), 2.11 (s, 3H), 6.16 (s, 1H), 6.86–7.40 (m, 16H), 7.59 (d, J = 8.6 Hz, 2H);^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: −2.36 (s), −2.29 (s), 19.43 (s), 26.29 (s), 31.18 (s), 31.28 (s), 34.49 (s), 56.64 (s), 68.68 (s), 83.27 (sept, $^2J_{CF}$ = 30.3 Hz), 122.70 (q, $^1J_{CF}$ = 291.0 Hz), 122.80 (q, $^1J_{CF}$ = 291.0 Hz), 123.77 (s), 123.97 (s), 126.41 (s), 126.62 (s), 126.84 (s), 127.39 (s), 128.15 (s), 129.05 (br s), 130.20 (s), 130.78 (s), 130.48 (s), 130.66 (s), 131.41 (s), 135.74 (s), 139.27 (s), 139.48 (s), 142.68 (s), 150.76 (s), 194.53 (s);^{19}F NMR (376 MHz, $CDCl_3$) δ: −70.48 (br s, 3F), −71.11 (q, $^4J_{FF}$ = 9.6 Hz, 3F).

Deprotection of the TBDMS Group of **7**

To a THF solution (10 mL) of **6** (1.00 g, 1.28 mmol), tetrabutylammonium fluoride (1 M in THF, 1.30 mL, 1.30 mmol) was added and the solution was stirred at 0°C for 15 min. The reaction mixture was quenched with aqueous ammonium chloride, extracted with chloroform, and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, separation by silica-gel column chromatography (chloroform) gave **7** (0.85 g, 100%) as a diastereomer mixture.

7. White solid: mp 157.0–159.0°C (decomp); Anal. Calcd for $C_{35}H_{32}F_6O_2S_2$: C, 63.43; H, 4.87. Found; C, 63.27; H, 5.07%.

7a. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.35 (s, 9H), 2.10 (s, 3H), 6.16 (s, 1H), 6.73 (d, J = 7.4 Hz, 2H), 7.02–7.61 (m, 16H), 7.74 (s, 1H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 31.26 (s), 34.55 (s), 61.64 (s), 68.19 (s), 124.18 (s), 127.17 (s), 127.30 (s), 127.53 (s), 127.96 (s), 128.16 (s), 128.80 (s), 129.07 (br s), 129.88 (s), 130.37 (s), 131.03 (s), 133.64 (s), 135.07 (s), 136.33 (s), 137.66 (s), 141.61 (s), 151.38 (s), 193.76 (s). The $\underline{C}(CF_3)_2$ and $\underline{C}F_3$ peaks could not be

assigned due to overlapping with the peaks of **7b**. Two peaks at δ 130.37 were overlapped. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −76.51 (q, $^4J_{FF}$ = 8.6 Hz, 3F), −76.24 (q, $^4J_{FF}$ = 8.6 Hz,3F).

7b. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.33 (s, 9H), 2.12 (s, 3H), 6.21 (s, 1H), 6.72 (d, J = 7.4 Hz, 2H), 7.02–7.38 (m, 13H), 7.45 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 7.3 Hz, 1H), 7.67 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 31.16 (s), 31.20 (s), 34.47 (s), 61.53 (s), 68.21(s), 80.53 (sept, $^2J_{CF}$ = 29.6 Hz), 122.60 (q, $^1J_{CF}$ = 287.9 Hz), 122.80 (q, $^1J_{CF}$ = 286.6 Hz), 124.18 (s), 127.25 (s), 127.30 (s), 127.95 (s), 128.10 (s), 128.26 (s), 128.63 (s), 129.10 (br s), 129.85 (s), 130.01 (s), 130.72 (s), 130.92 (s), 134.00 (s), 135.92 (s), 137.71 (s), 138.30 (s), 138.40 (s), 150.35 (s), 193.75 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −76.56 (q, $^4J_{FF}$ = 8.7 Hz, 3F), −76.10 (q, $^4J_{FF}$ = 8.7 Hz, 3F).

Synthesis of β-Mercaptoalkyl Sulfide **8**

To a methanol solution (50 mL) of **7** (0.85 g, 1.3 mmol), 12 M HCl (15 mL) was added and the solution was stirred at 95°C for 5 h. After removal of the solvent under reduced pressure, purification by GPC gave **8** (0.55 g, 69%) as a diastereomer mixture.

8. mp. 125.4–126.5°C; MS (FAB$^+$, matrix = *m*-nitrobenzyl alcohol) *m*/*z* 587 [M – SH].

8a. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.28 (s, 9H), 2.73 (s, 1H), 5.42 (s, 1H), 6.86 (d, J = 7.8 Hz, 2H), 6.98–7.62 (m, 16H), 7.77 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 31.17 (s), 34.39 (s), 62.76 (s), 67.68 (s), 80.56 (sept, $^2J_{CF}$ = 29.6 Hz), 122.63 (q, $^1J_{CF}$ = 288.2 Hz), 122.82 (q, $^1J_{CF}$ = 287.5 Hz), 125.06 (s), 127.41 (s), 127.63 (s), 127.83 (s), 127.93 (s), 128.17 (s), 128.90 (s), 129.17 (s), 130.29 (s), 129.89 (s), 131.17 (s), 133.96 (s), 136.37 (s), 137.03 (s), 140.98 (s), 141.67 (s), 150.41 (s). One aromatic carbon peak could not be assigned due to overlapping. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −76.61 (q, $^4J_{FF}$ = 8.7 Hz, 3F), −76.08 (q, $^4J_{FF}$ = 8.7 Hz,3F).

8b. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.37 (s, 9H), 2.74 (s, 1H), 5.39 (s, 1H), 6.91 (d, J = 7.3 Hz, 2H), 6.98–7.62 (m, 16H), 7.82 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 31.26 (s), 34.50 (s), 62.99 (s), 67.82 (s), 80.59 (sept, $^2J_{CF}$ = 29.4 Hz), 122.65 (q, $^1J_{CF}$ = 288.2 Hz), 122.84 (q, $^1J_{CF}$ = 287.7 Hz), 124.76 (s), 127.25 (s), 127.45 (s), 127.74 (s), 127.84 (s), 128.25 (s), 128.96 (s), 129.15 (s), 129.41 (s), 129.82 (s), 131.08 (s), 133.91 (s), 136.55 (s), 137.17 (s), 139.33 (s), 144.07 (s), 150.75 (s). One peak could not be assigned due to overlapping. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −76.68 (q, $^4J_{FF}$ = 8.3 Hz, 3F), −75.67 (q, $^4J_{FF}$ = 8.3 Hz,3F).

Synthesis of 1λ^4,2-Dithietane **9**

To a carbon tetrachloride solution (20 mL) of **8** (0.55 g, 0.89 mmol), a carbon tetrachloride suspension (10 mL) of NBS (0.16 g, 0.90 mmol) and then triethylamine (0.13 mL, 0.93 mmol) were sequentially added at 0 °C. The reaction mixture was stirred for 5 min and filtered through Celite. Recrystallization from carbon tetrachloride and hexane gave **9** (0.25 g, 45%) as a diastereomer mixture.

9. mp. 88.8–89.8°C (decomp); HRMS (FAB$^+$, matrix = PEG600 and *m*-nitrobenzyl alcohol) *m*/*z* calcd for $C_{33}H_{29}F_6OS_2$[M + H$^+$] 619.1564, found: 619.1566.

9a. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.22 (s, 9H), 6.80 (s, 1H), 7.0–7.7 (m, 17H), 8.31 (d, J = 8.0 Hz, 1H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 31.15 (s), 34.22 (s), 60.09 (s), 95.32 (s), 122.86 (q, $^1J_{CF}$ = 289.0 Hz), 122.91 (q, $^1J_{CF}$ = 289.1 Hz), 124.43 (s), 126.39 (s), 126.44 (s), 126.79 (s), 127.67 (s), 128.00 (s), 128.55 (s), 128.96 (s), 130.46 (s), 130.58 (s), 132.18 (s), 132.58 (s), 132.75 (s), 134.50 (s), 134.93 (s), 140.01 (s), 148.07 (s), 149.68 (s). The peak of $\underline{C}(CF_3)_2$ could not be observed due to low intensity of the peak. ^{19}F NMR (376 MHz) δ −78.50 (q, $^4J_{FF}$ = 8.7 Hz, 3F), −76.54 (q, $^4J_{FF}$ = 8.7 Hz, 3F).

9b. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (s, 9H), 6.85 (s, 1H), 7.0–7.7 (m, 17H), 8.39 (d, J = 8.0 Hz, 1H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 31.17 (s), 34.24 (s), 59.07 (s), 94.72 (s), 124.83 (s), 127.57 (s), 128.44 (s), 129.22 (s), 130.13 (s), 132.27 (s), 132.47 (s), 134.11 (s), 134.99 (s), 143.49 (s), 144.76 (s), 149.15 (s). Other peaks could not be assigned due to overlapping with the peaks of **1a**.^{19}F NMR (376 MHz) δ −78.54 (q, $^4J_{FF}$ = 8.7 Hz, 3F), −76.77 (q, $^4J_{FF}$ = 8.7 Hz, 3F).

Thermolysis of 1λ^4,2-Dithietane **9a**

A $CDCl_3$ solution (0.5 mL) of **9a** (4 mg, 6.5 μmol) with a few amounts of mesitylene as an internal standard in an NMR tube was degassed by freeze–pump–thaw cycle for five times and then sealed. The NMR tube was heated at 55°C for 110 min. NMR measurements were conducted after cooling down to room temperature. Cyclic sulfenic ester **2** and **10a** was observed at 91% and 88% yields, respectively. The yield for **2** was calculated from an integral ratio of the peak of **2** with those of all measurable peaks in ^{19}F NMR, and the yield of **10a** was calculated from comparison of the peak integration of **10a** with that of an aromatic peak of mesitylene.

Alternatively, a toluene (5 mL) solution of **9a** (25 mg, 40 mmol) was heated at 80°C for 30 min, and then the solvent was removed. Purification of the residue by silica-gel column chromatography (hexane:chloroform = 2:1) gave **10a** (13 mg, 94%).

Alternative Synthesis of a Diastereomer Mixture of Thiiranes **10a** *and* **10b**

A toluene (20 mL) solution of 4-(*tert*-butyl) benzophenone (1.32 g, 5.59 mmol) and the Lawesson's reagent (1.50 g, 3.71 mmol) was stirred at 85°C for 4.5 h. After removal of the solvent, purification by silica-gel column chromatography (hexane:chloroform = 2:1) gave 4-(*tert*-butyl) thiobenzophenone (1.37 g, <99%), which was used without further purification.

A toluene (15 mL) solution of 4-(*tert*-butyl)thiobenzophenone (1.02 g, 4.02 mmol) was treated with a toluene (60 mL) solution of phenyldiazomethane at 85°C for 30 min, which was prepared by reported procedure [10] from sodium hydroxide (2.0 g, 50 mmol), benzyltrimethylammonium chloride (20 mg, 0.18 mmol), and benzaldehyde tosylhydrazone (1.57 g, 5.75 mmol). After removal of the solvent under reduced pressure, purification from silica-gel column chromatography (hexane:chloroform = 2:1) gave a 1:1 diastereomer mixture of thiiranes **10a** and **10b** (1.18 g, 85%).

10. mp. 135.0–137.0°C (decomp).

10a. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.29 (s, 9H), 4.66 (s, 1H), 7.05–7.38 (m, 14H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 31.26 (s), 34.44 (s), 50.92 (s), 60.31 (s), 125.26 (s), 126.97 (s), 127.24 (s), 127.33 (s), 127.40 (s), 127.67 (s), 129.04 (s), 131.01 (s), 135.76 (s), 138.37 (s), 141.67 (s), 150.14 (s).

10b. ^{1}H NMR (400 MHz) δ: 1.21 (s, 9H), 4.62 (s, 1H), 7.00–7.48 (m, 14H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 31.23 (s), 34.34 (s), 50.94 (s), 60.35 (s), 124.30 (s), 127.11 (s), 127.21 (s), 127.59 (s), 127.86 (s), 128.26 (s), 129.08 (s), 130.41 (s), 135.20 (s), 135.79 (s), 144.96 (s), 149.89 (s).

Desulfurization of Thiirane **10a**

Thiirane **10a** (18 mg, 52 μmol) and triirondodecacarbonyl (10 mg, 20 μmol) were dissolved in benzene (5 mL) and stirred at 70°C for 5 h. After removal of the solvent under reduced pressure, purification by silica-gel column chromatography (hexane) gave **11a** (15 mg, 92%).

Alternative Synthesis of (E)-1-(4-(Tert-butyl)phenyl)-1,2-diphenylethylene **11a**

To a 1:1 methanol-THF (10 mL) solution of *meso*-1,2-dibromo-1,2-diphenylethane (0.12 g, 3.5 mmol), potassium carboxylate (0.10 g, 7.2 mmol) at room temperature was added and the solution was stirred for 14 h. The reaction mixture was filtered off, treated with 4-(*tert*-butyl)phenylboronic acid (68 mg, 3.8 mmol), potassium hydroxide (50 mg, 89 mmol), triphenylphosphine (4.5 mg, 17 μmol), and $PdCl_2$ (3.5 mg, 20 μmol), and the reaction mixture was stirred at room temperature for 1 h. It was extracted with ether, washed with aqueous potassium hydroxide, and dried over anhydrous magnesium sulfate. After removal of the solvent, purification by silica-gel column chromatography (hexane) gave **11a** (41 mg, 38%).

11a. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.34 (s, 9H), 6.97 (s, 1H), 6.99–7.38 (m, 14H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 31.29 (s), 34.52 (s), 125.11 (s), 126.56 (s), 127.12 (s), 127.29 (s), 127.43 (s), 127.91 (s), 128.58 (s), 129.48 (s), 130.33 (s), 137.46 (s), 140.36 (s), 140.42 (s), 142.29 (s), 150.58 (s).

Crystallographic data for **6b** have been deposited with Cambridge Crystallographic Data Center (CCDC) as supplementary crystallographic number CCDC 773607. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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