Reactions of Diaminosulfoxonium Ylides with Aldehydes. Preparation of Cyclopropyldiaminosulfoxonium Salts

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(Received October 18, 1993)

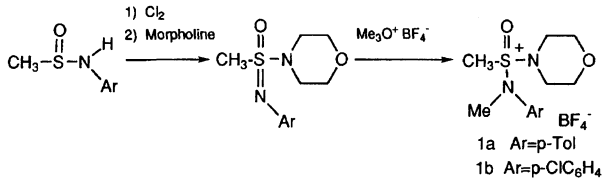
The reaction of diaminosulfoxonium ylides with aldehydes gave the corresponding cyclopropyldiaminosulfoxonium salts in good yields when 1,8-diazabicyclo[5.4.0.]undec-7-ene (DBU) was used as a base. These ylides reacted with aldehydes to give the corresponding betaines, which resulted in the formation of vinylsulfoxonium salts. The additional ylides reacted with these salts to afford cyclopropylsulfoxonium salts. The reaction of these salts with potassium hydroxide is also described.

Cyclopropylsulfonium or sulfoxonium salts are interesting compounds for their unique reactivity.[1] Methods for the preparation of cyclopropylsulfonium salts include the cyclization of (3-chloropropyl)diphenylsulfonium salts with bases[2,3] and alkylation of the corresponding sulfoximines.[4,5] The reaction of these salts with bases and carbonyl compounds afforded cyclobutanone derivatives, which were widely used for the synthesis of natural products. We have reported the synthesis and reactions of methyldiaminosulfoxonium salts (**1**) (Scheme 1).[6] These result prompted us to investigate a new synthesis of cyclopropyldiaminosulfoxonium salts (**2**) from **1**. In a previous communication, we have reported the synthesis of **2** by the reaction of **1** with aldehydes.[7] In this paper, we would like to report the full details of the formation of cyclopropyldiaminosulfoxonium salts **2**, and some reaction of these salts.

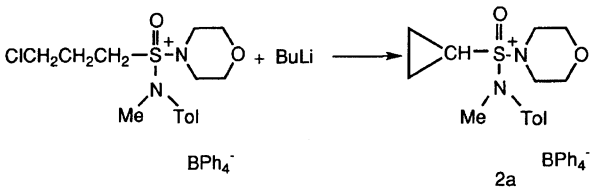
Results and Discussion

The most popular method of the preparation of cyclopropylsulfonium salts is the cyclization of the corresponding 3-haloalkylsulfonium salts by the method reported by Trost et al.[2] We have already tried the synthesis of unsubstituted **2a** by a similar method from 3-chloropropylsulfoxonium tetraphenylborate (Scheme 2).[6] However, it takes 7 steps for the synthesis of **2a** starting from 1-bromo-3-chloropropane.

Trost et al. have reported asymmetric alkylation and cyclization by the use of chiral *N*-nitrosulfoximines.[8] We have also prepared *N*-(*p*-bromophenyl)ethanesulfonimidmorpholide by the methylation of *N*-(*p*-bromophenyl)methanesulfonimidmorpholide.[9] The reaction of methylenetriphenylphosphorane with 1,2-dibromoethane or 1,3-dibromopropane and bases afforded the



Scheme 1.



Scheme 2.

corresponding cyclopropyl- or cyclobutylphosphonium salts.[10] These results prompted us to investigate the preparation of **2** by the reaction of **1** with dibromoethane followed by the addition of DBU. However, the reaction afforded the complex mixtures of unidentified products. Thus, another approach for the synthesis of **2** must be required.

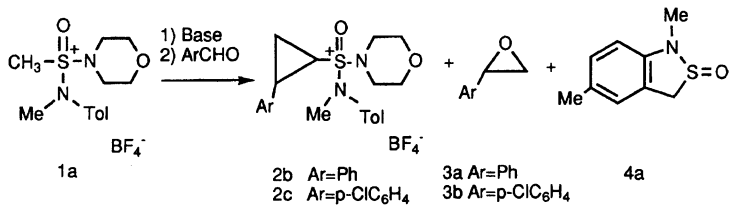
In the course of work toward the synthetic application of diaminosulfoxonium salts **1**, we found that a small amount of **2** was obtained as side products in the reaction of **1** with aldehydes. To confirm the origin of these sulfoxonium salts **2**, several conditions were studied. As shown in Table 1, good yields were observed with DBU as a base. When butyllithium or potassium *t*-butoxide was used as the base, yields of **2** were quite low, while epoxides (**3**) and the rearranged product (**4**) were obtained. When salt **1a** was treated with an equimolecular amount of benzaldehyde, the yield of **2b** was low and benzaldehyde was recovered in 35% yield. Two equivalents of **1a** must be required for this reaction (Scheme 3). By using DBU as a base, reactions of **1** with aromatic aldehydes were done (Scheme 4, Table 2).

Salts **2** were obtained as mixtures (1 : 1 by ^{1}H NMR) of *cis* and *trans* isomers. Purification was done by recrystallization from methanol. Yields were generally high and no substituent effect was observed. When paraformaldehyde was used as a substrate, salt **2a** was obtained in 88% yield.

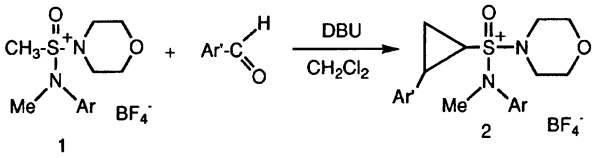
In a previous communication, we had proposed two reaction pathways as shown in Mechanism-1.[7] Route A: oxide ion of the intermediate betaine (**5**) attacked the sulfoxonium sulfur to afford the four-membered cyclic sulfoxonium salts (**6**), which was attacked by another

Table 1. Reaction of **1** with Aldehydes

Salt	Conditions				Product			
1	Aldehyde	Base	Temp/°C	Excess of ylide/%	**2**	**3**	**4a**	TolNHMe
1a	Ph	BuLi	−30	10	**2b** 7	**3a** 35	35	28
1a	p-ClC_6H_4	BuLi	−30	10	**2c** 6	**3b** 38	30	30
1a	Ph	t-BuOK	60	10	**2b** 6	**3a** 25	54	20
1a	Ph	t-BuOK	60	110	**2b** 14	**3a** 30	42	64
1a	Ph	DBU	Reflux	10	**2b** 35	**3a** 0	0	18
1a	Ph	DBU	Reflux	110	**2b** 86	**3a** 0	0	40



Scheme 3.



Scheme 4.

Table 2. Reaction of **1** with Aldehydes by the Use of DBU as a Base

Salt	Aldehyde	Product	
1	Ar'CHO		yield/%
1a	p-ClC_6H_4	**2c**	84
1a	p-MeC_6H_4	**2d**	90
1a	p-$NO_2C_6H_4$	**2e**	90
1a	C_6H_{13}	**2f**	80
1a	PhCH=CH	**2g**	87
1b	Ph	**2h**	88
1b	p-ClC_6H_4	**2i**	90
1b	p-MeC_6H_4	**2j**	85
1b	p-$NO_2C_6H_4$	**2k**	92
1b	p-BrC_6H_4	**2l**	87

diaminosulfoxonium ylide (**7**) to give the corresponding **2**. Route B: oxide ions of the betaines **5** attacked the α-carbon of sulfoxonium sulfur to give the corresponding epoxide, which further reacted with another ylide **7** to afford salts **2** (Chart 1).

To discover which mechanism is operative, the reaction of styrene oxide with ylide **7** was done under several conditions. However, no cylopropylsulfoxonium salts **2** were obtained. *N*-Methyl-*p*-toluidine and the rearranged product **4a** were obtained (Scheme 5, Table 3). This result suggested that the reaction did not proceed through route B. Additionally, the following experiment was done. Since (3-hydroxy-3-phenylpropyl)-(*N*-methyl-*p*-tolylamino)morpholinosulfoxonium tetraphenylborate (**8**) is a proposed intermediate for route B, **8** was prepared as shown in Scheme 6. Treatment of **8** with DBU resulted in the formation of the rearranged product (**4b**) and *N*-methyl-*p*-toluidine. Salt **2** was not detected in the reaction mixture. Thus, route B is excluded (Scheme 7).

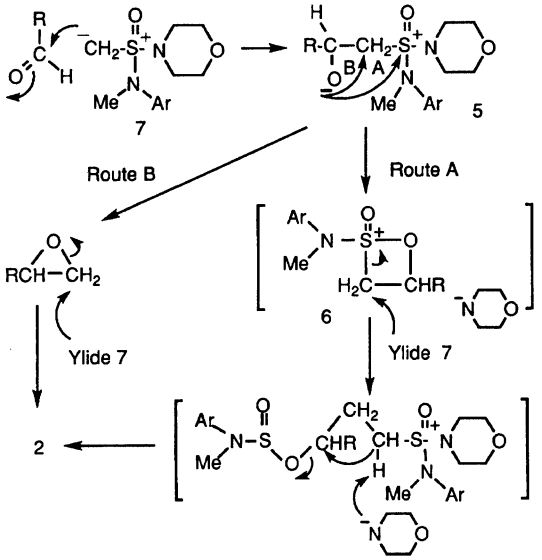
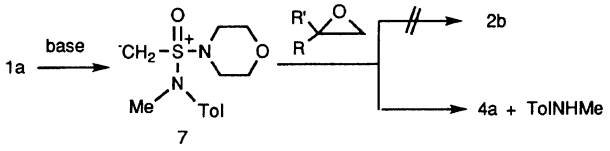


Chart 1. Mechanism-1

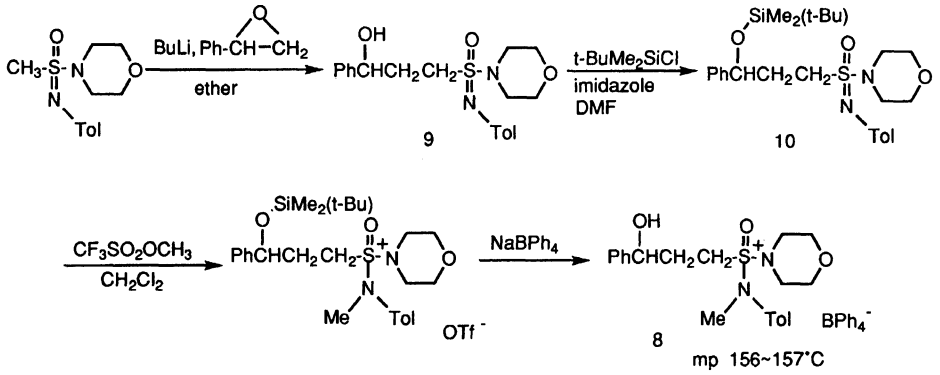


Scheme 5.

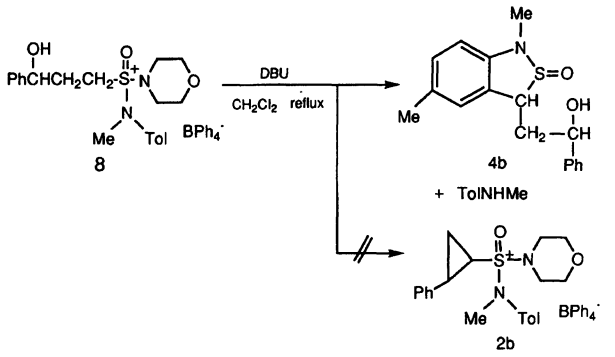
Thus, we concluded that the reaction might proceed through route A, in which four-membered cyclic sulfoxonium salts (**6**) were assumed to the intermediates.

Table 3. Reaction of **1** with Epoxides

Salt	Base	Epoxide		Temp	Solvent	Products (Yield/%)		
		R	R′	°C		**2b**	**4a**	TolNHMe
1a	DBU	Ph	H	Reflux	CH_2Cl_2	0	16	33
1a	*t*-BuOK	Ph	H	50	*t*-BuOH	0	40	35
1a	Butyllithium	Ph	H	0	THF	0	15	45
1a	CH_3SOCH_2Na	Ph	H	40	DMSO	0	30	15
1a	DBU	Ph	Ph	Reflux	CH_2Cl_2	0	30	32
1a	DBU	*p*-ClC_6H_4	H	Reflux	CH_2Cl_2	0	30	24



Scheme 6.



Scheme 7.

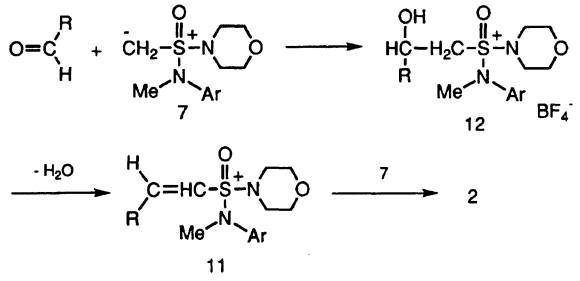
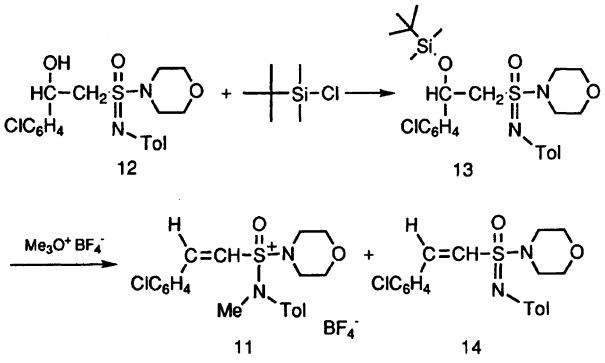


Chart 2. Mechanism-2

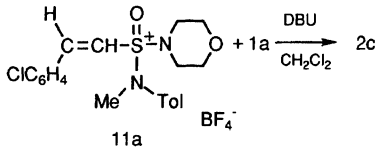


Scheme 8.

However, this conclusion left some questions, because four-membered cyclic intermediates **6** seem unusual and unstable for their strain energy. Thus, another mechanism is required for the formation of salts **2**.

We have reported a convenient synthesis of vinylphosphonium salts from 2-hydroxyalkylphosphonium salts.[11] In this reaction, an acid catalyst is essential for the dehydration process. Additionally, basic dehydration of these salts is also done for the synthesis of vinylphosphonium salts. This result prompted us to try the formation of vinylsulfoxonium salts (**11**) as plausible intermediates (Chart 2). To confirm this possibility, diaminovinylsulfoxonium tetrafluoroborate **11** was prepared according to the following Scheme 8 starting from 2-hydroxy-2-*p*-chlorophenylethyl-*N*-(*p*-tolyl)-ethanesulfonimidomorpholide (**12**). The reaction of **11** with ylide **7** derived from salt **1a** afforded the desired cyclopropylsulfoxonium salts **2c** in 76% yield. Thus, the reaction would proceed through vinylsulfoxonium salt intermediates (Scheme 9).

Dichloromethane and benzene are well-known solvents for the azeotropic separation of water. Under these conditions, we thought that dehydration might be a key step for the snythesis of **2**. Dichloromethane is much more favorable than other solvents for de-



Scheme 9.

hydration. Another reason for the formation of cyclopropyl salts might be the use of DBU as a base, since it is weaker than the other (Table 1). As shown in Scheme 10, strong bases such as potassium-butoxide and butyllithium will afford epoxides, the normal reaction products. On the other hand, DBU : HBF_4 will afford a proton source of betaine intermediates **5**, which resulted in the formation of 2-hydroxylalkylsulfoxonium salts (**12**). Dehydration of these salts **12** produced vinylsulfoxonium salts **11**, which further reacted with ylide **7** to give the corresponding **2**.

Reaction of Cyclopropyldiaminosulfoxonium Salts 2. Cyclopropyldiphenylsulfonium tetrafluoroborate was found to react with bases and ketones to give the corresponding spiroketones.[3,4] Aminosulfoxonium salts were also found to react with bases and ketones to give cyclobutanones via spiroketone intermediates.[5] In view of these results, we then tried the reaction of a cyclopropyldiaminosulfoxonium salt, **2a**, with bases. The reactions were done under several conditions, but the products obtained were *N*-methyl-*p*-toluidine and the rearranged product (**4c**) (Scheme 11). Thus, the reaction of **2a** with ketones affords only the internally rearranged product, **4c**. Then, the reaction of these salts with benzaldehyde was done. However, only the same product, **4c**, was obtained. Thus, the intramolecular rearrangement might be much faster than intermolecular reaction in this case.

In summary, the reaction of methyldiaminosulfoxonium salts **1** with aldehydes in the presence of DBU afforded the corresponding **2** in good yields. The reaction of **2a** with potassium hydroxide afforded the corresponding tricyclic product **4c**.

Experimental

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were obtained with a JEOL FX-90Q or JEOL GX-400 spectrometer. Chemical shifts are given in ppm units downfiled from tetramethylsilane. TLC analyses were done using Merck Silica gel 60 F254 aluminum plates.

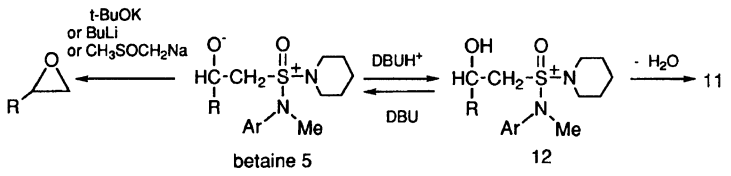
Materials. *t*-Butyldimethylchlorosilane was kindly donated by Chisso Corporation. Diaminosulfoxonium tetrafluoroborates, **1** were prepared by the method in the literature.[6] Sodium tetraphenylborate was purchased from Dojin Chem. Other reagents were purchased from Nacalai Tesque.

Reaction of Sulfoxonium Ylides with Aldehydes. By Using Butyllithium as a Base. To a solution of **1a** (1.17 g, 3.3 mol) in THF (30 mL) was added at −30 °C a solution of butyllithium (10% w/v, 2.3 mL, 3.5 mmol) in hexane. After this was stirred for 1 h, benzaldehyde (0.32 g, 3.0 mmol) in THF (5 mL) was added to this solution at this temperature. After this was stirred for 8 h, the reaction mixture was warmed up to r.t., poured into water (50 mL), and extracted with dichloromethane (15 mL×3). The combined extract was dried over magnesium sulfate and filtered. The resulting filtrate was evaporated to give a yellow oil, which was chromatographed over silica gel by elution successively with hexane, dichloromethane, and dichloromethane–ethyl acetate. The hexane eluant was evaporated to give styrene oxide (0.13 g, 1.1 mmol, 31%) and *N*-methyl-*p*-toluidine (0.10 g, 0.84 mmol, 28%). The dichloromethane eluant was evaporated to give **4a** (0.19 g, 105 mmol, 35%). Mp 160—161 °C (lit,[6] mp 160—161 °C) The dichloromethane–ethyl acetate eluant was evaporated to give salt **2b** (0.10 g, 0.21 mmol, 7%). Trans isomer was isolated. **2b** (*trans*) : Mp 172—173 °C. ^1H NMR ($CDCl_3$) δ=1.81—1.94 (m, 2H, CH_2), 2.25 (s, 3H, TolMe), 2.57—2.62 (m, 1H, PhCH), 3.40 (s, 3H, NMe), 3.61—3.73 (m, 4H, NCH_2), 3.74—3.87 (m, 4H, OCH_2), 3.96—3.97 (m, 1H, SCH), 6.94 (d, 2H, Ar), 7.10 (d, 2H, Ar), 7.20—7.26 (m, 3H, Ar), 7.34 (d, 2H, Ar). Found: C, 54.89; H, 6.05; N, 5.99%. Calcd for $C_{21}H_{27}BF_4N_2O_2S$: C, 55.02; H, 5.90; N, 6.11%

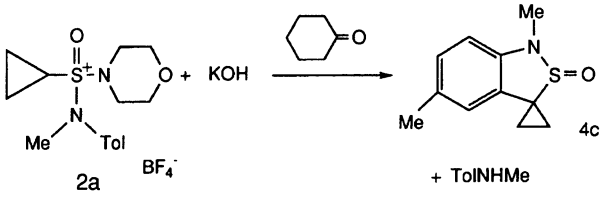
By Using Potassium *t*-Butoxide as a Base. To a solution of **1a** (1.17 g, 3.3 mmol) in *t*-butyl alcohol (20 mL) was added potassium *t*-butoxide (0.37 g, 3.4 mmol) at 50 °C. After this was stirred for 1 h at this temperature, a solution of benzaldehyde (0.32 g, 3.0 mmol) in *t*-butyl alcohol (10 mL) was added to this solution. After this was stirred for 6 h at this temperature, the reaction mixture was condensed to 10 mL and poured into water (100 mL). The resulting mixture was extracted first with hexane (10 mL×3) and then dichloromethane (10 mL×3). The combined hexane extract was dried over magnesium sulfate and evaporated to give a pale yellow oil, which was chromatographed over silica gel by elution with hexane to afford styrene oxide (0.09 g, 0.75 mmol, 25%), *N*-methyl-*p*-toluidine (0.07 g, 0.6 mmol, 20%), and recovered benzaldehyde (0.11 g, 1.05 mmol, 35%). The combined dichloromethane extract was dried over magnesium sulfate and evaporated to give pale orange oily crystals, which was chromatographed over silica gel by stepwise elution with dichloromethane and dichloromethane–ethyl acetate. The dichloromethane eluant was evaporated to give the rearranged product **4a** (0.29 g, 1.62 mmol, 54%). The dichloromethane–ethyl acetate eluant was evaporated to afford to the salt **2b** (0.08 g, 0.18 mmol, 6%).

By Using DBU as a Base. To a solution of **1a** (3.92 g, 11 mmol) in dichloromethane was added a solution of DBU (1.68 g, 11 mmol) in dichloromethane (20 mL). After this was stirred for 30 min, benzaldehyde (0.54 g, 5.0 mmol) in dichloromethane (10 mL) was added to this solution and refluxed for 3 h. The reaction mixture was treated with water (20 mL), 5% HCl solution, and dried over magnesium sulfate. The filtrate was evaporated to give a cis and trans mixture of cyclopropyldiaminosulfoxonium salts of **2b** (2.01 g, 4.4 mmol, 88%). Recrystallization from methanol gave colorless crystals of trans **2b** (35%). Other reactions were done in a similar manner.

2c (*trans*) : Mp 204—205 °C. ^1H NMR ($CDCl_3$) δ=1.83—1.95 (m, 2H, CH_2), 2.20 (s, 3H, TolMe), 2.46—2.52 (m, 1H, ArCH), 3.39 (s, 3H, NMe), 3.62—3.74 (m, 4H, NCH_2), 3.75—3.90 (m, 5H, OCH_2 and SCH), 6.84



Scheme 10.



Scheme 11.

(d, 2H, Ar), 7.08 (d, 2H, Ar), 7.18 (d, 2H, Ar), 7.32 (d, 2H, Ar). Found: C, 50.90; H, 5.24; N, 5.50%. Calcd for $C_{21}H_{26}BClF_4N_2O_2S$: C, 51.17; H, 5.28; N, 5.69%.

2d (*trans*) : Mp 199—200 °C; ^{1}H NMR ($CDCl_3$) δ=1.80—1.94 (m, 2H, CH_2), 2.29 (s, 3H, TolMe), 2.56—2.62 (m, 1H, ArCH), 3.40 (s, 3H, NMe), 3.60—3.71 (m, 4H, NCH_2), 3.74—3.89 (m, 5H, OCH_2 and SCH), 6.82 (d, 2H, Ar), 7.05 (d, 2H, Ar), 7.11 (d, 2H, Ar), 7.33 (d, 2H, Ar). Found: C, 55.89; H, 6.05; N. 5.96%. Calcd for $C_{22}H_{29}BF_4N_2O_2S$: C, 55.93; H, 6.14; N, 5.93%.

2e (*trans*) : Mp 154—155 °C. ^{1}H NMR (CD_3SOCD_3) δ=2.04—2.12 (m, 2H, CH_2), 2.06 (s, 3H, TolMe), 2.78—2.84 (m, 1H, ArCH), 3.36 (s, 3H NMe), 3.62—3.73 (m, 4H, NCH_2), 3.77—3.90 (m, 4H, OCH_2), 3.95—3.98 (m, 1H, SCH), 7.06 (d, 2H, Ar), 7.13 (d, 2H, Ar), 7.13 (d, 2H, Ar), 7.37 (d, 2H, Ar), 8.05 (d, 2H, Ar). Found: C, 49.79; H, 5.08; N, 8.27%. Calcd for $C_{21}H_{26}BF_4N_3O_4S$: C, 50.10; H, 5.17; N, 8.35%.

2f (*trans*) (BPh_4) : Mp 184—185 °C. ^{1}H NMR (CD_3COCD_3) δ=0.84—0.88 (t, 3H, J=7.3 Hz, CH_3), 1.15—1.49 (m, 10H, CH_2), 1.64—1.70 (m, 2H, CH_2), 2.40 (s, 3H, TolMe), 3.17—3.20 (m, 1H, CH), 3.31—3.34 (m, 1H, SCH), 3.53 (s, 3H, NMe), 3.65—3.71 (m, 4H, NCH_2), 3.82—3.86 (m, 4H, OCH_2), 6.75—7.34 (m, 20H, Ar), 7.39—7.41 (d, 2H, Ar), 7.48—7.50 (d, 2H, Ar). Found: C, 77.19; H, 8.04; N, 4.05%. Calcd for $C_{45}H_{59}BN_2O_2S$: C, 77.36; H, 7.88; N, 4.01%.

2g PhCH=CH (*trans*) (BPh_4) : Mp 224—225 °C. ^{1}H NMR (CD_3COCD_3) δ=1.84—1.98 (m, 2H, CH_2), 2.41 (s, 3H, TolMe), 2.74—2.77 (m, 1H, CH), 3.52 (s, 3H, NMe), 3.70—3.79 (m, 4H, NCH_2), 3.82—3.93 (m, 5H, OCH_2 and SCH), 5.37—5.43 (m, 1H, CH), 6.33—6.37 (d, 1H, J=15.9 Hz, PhCH), 6.76—7.36 (m, 25H, Ar), 7.22—7.24 (d, 2H, Ar), 7.53—7.55 (d, 2H, Ar). Found: C, 78.64; H, 6.93; N, 6.25%. Calcd for $C_{48}H_{47}BN_2O_2S$: C, 78.77; H, 6.84; N, 5.93%.

2h (*trans*) : Mp 182—183 °C. ^{1}H NMR ($CDCl_3$) δ=1.83—1.86 (m, 2H, CH_2), 2.42—2.48 (m, 1H, ArCH), 3.45 (s, 3H, NMe), 3.49—3.58 (m, 8H, NCH_2 and OCH_2), 3.69—3.73 (m, 1H, SCH), 6.93 (d, 2H, Ar), 7.07 (d, 2H, Ar), 7.13—7.79 (m, 5H, Ar). Found. C, 49.86; H, 5.12; N, 5.58%. Calcd for $C_{20}H_{24}BClF_4N_2O_2S$: C, 50.10; H, 5.01; N, 5.85%.

2i (*trans*) : Mp 136—137 °C. ^{1}H NMR ($CDCl_3$) δ=1.81—1.89 (m, 2H, CH_2), 2.71—2.75 (m, 1H, ArCH), 3.33 (s, 3H, NMe), 3.56—3.68 (m, 4H, NCH_2), 3.71—3.80 (m, 4H, OCH_2), 4.04—4.08 (m, 1H, SCH), 6.76 (d, 2H, Ar), 6.90 (d, 2H, Ar), 7.12 (d, 2H, Ar), 7.50 (d, 2H, Ar). Found: C, 46.57; H, 4.16; N, 5.00%. Calcd for $C_{20}H_{23}BCl_2F_4N_2O_2S$: C, 46.78; H, 4.31; N, 5.25%.

2j (*trans*) : Mp 204—205 °C. ^{1}H NMR ($CDCl_3$) δ=1.81—1.96 (m, 2H, CH_2), 2.30 (s, 3H, ArMe), 2.54—2.60 (m, 1H, ArCH), 3.49 (s, 3H, NMe), 3.63—3.73 (m, 4H, NCH_2), 3.76—3.87 (m, 2H, OCH_2), 3.89—3.92 (m, 1H, SCH), 6.81 (d, 2H, Ar), 7.10 (d, 2H, Ar), 7.28 (d, 2H, Ar), 7.43 (d, 2H, Ar). Found: C, 51.65; H, 5.35; N, 5.60%. Calcd for $C_{21}H_{26}BClF_4N_2O_2S$: C, 51.17; H, 5.28; N, 5.69%.

2k (*trans*) : Mp 215—216 °C. ^{1}H NMR (CD_3SOCD_3) δ=2.06—2.17 (m, 2H, CH_2), 2.82—2.87 (m, 1H, ArCH), 3.38 (s, 3H, NMe), 3.65—3.74 (m, 4H, NCH_2), 3.77—3.87 (m, 4H, OCH_2), 4.00—4.04 (m, 1H, SCH), 7.18 (d, 2H, Ar), 7.32 (d, 2H, Ar), 7.54 (d, 2H, Ar), 8.08 (d, 2H, Ar). Found: C, 45.87; H, 4.48; N, 8.12%. Calcd for $C_{20}H_{23}BClF_4N_3O_4S$: C, 45.85; H, 4.39; N, 8.02%.

2l (*trans*) : Mp 188—189 °C. ^{1}H NMR ($CDCl_3$) δ=2.01—2.12 (m, 2H, CH_2), 2.71—2.77 (m, 1H, ArCH), 3.44 (s, 3H, NMe), 3.68—3.78 (m, 4H, NCH_2), 3.81—3.89 (m, 4H, OCH_2), 3.91—3.94 (m, 1H, SCH), 6.92 (d, 2H, Ar), 7.42 (d, 2H, Ar), 7.46 (d, 2H, Ar), 7.59 (d, 2H, Ar). Found: C, 42.70; H, 3.99; N, 4.91%. Calcd for $C_{20}H_{23}BBrClF_4N_2O_2S$: C, 43.05; H, 4.13; N, 5.02%.

Reaction of 1a with DBU Followed by the Addition of Paraformaldehyde. To a solution of **1a** (3.92 g, 11 mmol) in dichloromethane was added a solution of DBU (1.68 g, 11 mmol) in dichloromethane (20 mL). After this was stirred for 30 min, paraformaldehyde (0.15 g, 5.0 mmol) in dichloromethane (10 mL) was added to this solution and refluxed for 3 h. The reaction mixture was evaporated to give a pale orange oil, which was chromatographed over silica gel by elution with dichloromethane-ethyl acetate to afford **2a** (88%). Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ=1.29—1.61 (m, 2H, CH_2), 2.42 (s, 3H, TolMe), 3.43—3.46 (m, 1H, SCH), 3.51 (s, 3H, NMe), 3.58—3.61 (m, 4H, NCH_2), 3.75—3.78 (m, 4H, OCH_2), 7.33 (d, 2H, Ar), 7.42 (d, 2H, Ar). Salt **2a** was changed into its tetraphenylborate. Mp 138—139 °C. (lit, Mp 134—135 °C[6]) ^{1}H NMR (CD_3COCD_3) δ=1.31—1.36 (m, 2H, CH_2), 1.56—1.61 (m, 2H, CH_2), 2.41 (s, 3H, TolMe), 3.41—3.43 (m, 1H, SCH), 3.58 (s, 3H, NMe), 3.71—3.75 (m, 4H, NCH_2), 3.82—3.85 (m, 4H, OCH_2), 6.76—6.80 (m, 4H, Ar), 6.90—6.94 (m, 8H, Ar), 7.34—7.41 (m, 8H, Ar), 7.42 (d, 2H, Ar), 7.53 (d, 2H, Ar).

Reaction of Ylide 7 with Epoxide. A) By Using DBU as a Base: To a solution of **1a** (0.40 g, 1.1 mmol) in dichloromethane (20 mL) was added DBU (0.17 g, 1.1 mmol) at r.t. After this was stirred for 30 min, a solution of styrene oxide (0.12 g, 1.0 mmol) in dichloromethane (15 mL) was added to this solution at r.t. After refluxing for 8 h, the solution was washed with water and dried over magnesium sulfate. The filtrate was evaporated to give a pale brown oil,

which was chromatographed over silica gel by elution with dichloromethane to give *N*-methyl-*p*-toluidine (0.040 g, 0.33 mmol, 33%), recovered styrene oxide (0.06 g, 0.5 mmol) and **4a** (0.025 g, 0.16 mmol, 16%).

B) By Using Potassium *t*-Butoxide as a Base: To a solution of **1a** (0.40 g, 1.1 mmol) in *t*-butyl alcohol (20 mL) was added potassium *t*-butoxide (0.12 g, 1.1 mmol) in one portion at 50 °C. After this was stirred for 1 h, a solution of styrene oxide (0.12 g, 1.0 mmol) in *t*-butyl alcohol (10 mL) was added. After being stirred for 15 h at this temperature, the reaction mixture was condensed to 10 mL, poured into water (100 mL), and extracted with dichloromethane (15 mL×3). The combined extracts were dried over magnesium sulfate. The resulting filtrate was evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with hexane–dichloromethane to afford *N*-methyl-*p*-toluidine (0.042 g, 0.35 mmol, 35%), recovered styrene oxide (0.048 g, 0.4 mmol), and **4a** (0.072 g, 0.40 mmol 40%).

C) By Using Butyllithium as a Base: To a solution of **1a** (0.80 g, 2.2 mmol) in THF (25 mL) was added a solution of butyllithium (10% w/v, 1.4 mL, 2.2 mmol) in hexane at 0 °C. After being stirred for 1 h, a solution of styrene oxide (0.24 g, 2.0 mmol) in THF (10 mL) was added to this solution at this temperature. After this was stirred for 15 h, the reaction mixture was poured into water (100 mL), extracted with dichloromethane (15 mL×3). The combined extract was dried over magnesium sulfate and evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with hexane–dichloromethane to give *N*-methyl-*p*-toludine (0.11 g, 0.90 mmol, 45%), recovered styrene oxide (0.12 g, 1 mmol), and **4a** (0.48 g, 0.30 mmol, 15%).

D) By Using Dimsyl Sodium as a Base: To a solution of dimsylsodium (2.2 mmol, prepared from sodium hydride and dimethyl sulfoxide) in dimethyl sulfoxide (5 mL) was added **1a** (0.80 g, 2.2 mmol) in one portion. After this was stirred for 1 h, a solution of styrene oxide (0.24 g, 2.0 mmol) in dimethyl sulfoxide (5 mL) was added to this solution at 40 °C. After being stirred for 8 h, the reaction mixture was poured into water (50 mL) and extracted with hexane (10 mL×3) and dichloromethane (10 mL×3). The combined hexane extract was washed with water, dried over magnesium sulfate, and evaporated to give a pale yellow oil. This oil was chromatographed over silica gel by elution with hexane to afford styrene oxide (0.18 g, 1.3 mmol, 66%) and *N*-methyl-*p*-toluidine (0.36 g, 0.3 mmol, 15%). The combined dichloromethane extract was washed with water, dried over magnesium sulfate, and evaporated to give a brown oil. This oil was chromatographed over silica gel by elution with dichloromethane-ethyl acetate to afford **4a** (0.93 g, 0.6 mmol, 30%).

Reaction of *N*-(*p*-Tolyl)methanesulfonimidomorpholide with Butyllithium and Styrene Oxide. Preparation of 9. To a solution of amide (3.4 g, 13.5 mmol) in ether (100 mL) was added a hexane solution of butyllithium (12.9 mL, 10% w/v, 20.3 mmol) at room temperature. After being stirred for 30 min, a solution of styrene oxide (2.4 g 20.3 mmol) in ether (40 mL) was added to this solution. After this was stirred for 12 h, the reaction mixture was washed with water (20 mL×3), dried over magnesium sulfate, and evaporated to give a pale brown oil. The resulting oil was chromatographed over silica gel by elution of dichloromethane–ethyl acetate (2:1) to give a pale orange oil of *N*-(*p*-tolyl)-3-hydroxy-3-phenylpropanesulfonimidomorpholide (**9**) (2.40 g, 6.41 mmol, 47%); ^{1}H NMR ($CDCl_3$) δ=2.12—2.31 (m, 2H, CH_2), 2.24 (s, 3H, TolMe), 3.04—3.16 (m, 4H, NCH_2), 3.41—3.53 (m, 4H, OCH_2), 4.23 (s, 1H, OH), 4.81—4.86 (dm, 1H, CH), 6.95 (br m, 4H, Tol), 7.20—7.30 (m, 5H, Ph). Found: *m/z* 374.1668. Calcd for $C_{20}H_{26}N_2O_3S$: M, 374.1664.

Reaction of *N*-(*p*-Tolyl)-3-hydroxy-3-phenyl-1-propanesulfonimidomorpholide 9 with *t*-Butyldimethylchlorosilane. Preparation of 10. To a solution of this imide (1.89 g, 5.1 mmol) and imidazole (0.84 g, 12.4 mmol) in DMF (5 mL) was added *t*-butyldimethylchlorosilane (0.91 g, 6.1 mmol) in one portion. After being stirred for 2 d at 45 °C, the reaction mixture was poured into water (100 mL) and extracted with ether (15 mL×3). The combined extracted was washed with water, dried over magnesium sulfate, and evaporated to give a pale brown oil. This oil was chromatographed over silica gel by elution with dichloromethane–ethyl acetate (5:1) to give pale yellow oil of silyl ether (**10**) (2.24 g, 43.6 mmol, 91%); ^{1}H NMR ($CDCl_3$) δ=0.00 (s, 3H, MeSi), 0.19 (s, 3H, MeSi), 1.03 (s, 9H, Me_3C), 2.26—2.47 (m, 2H, CH_2), 2.37 (s, 3H, TolMe), 3.10—3.26 (m, 2H, SCH_2), 3.23—3.40 (m, 4H, NCH_2), 3.61—3.74 (m, 4H, OCH_2), 5.02—5.37 (dd, 1H, CH), 7.03—7.12 (dd, 4H, Tol), 7.36—7.46 (m, 5H, Ph). Found: *m/z* 488.2598. Calcd for $C_{26}H_{40}N_2O_3SSi$: M, 488.2528.

Methylation of *t*-Butyldimethylsilylated Imidamide 10. Preparation of 8. To a solution of this imidamide **10** (0.56 g, 1.15 mmol) in dichloromethane (10 mL) was added methyl trifluoromethanesulfonate (0.23 g, 1.4 mmol) in one portion at r.t. After being stirred for 3 d, the reaction mixture was evaporated to give a pale brown oil (0.75 g, 1.15 mmol) of sulfoxonium trifluoromethanesulfonate. This oil was dissolved in acetone (15 mL) and sodium tetraphenylborate (0.44 g, 1.29 mmol) in acetone was added. Ether (30 mL) was added to this solution to give colorless precipitates of the corresponding tetraphenylborate. Recrystallization from methanol gave the colorless crystals of (3-hydroxy-3-phenylpropyl)(*N*-methyl-*p*-tolylamino)morpholinosulfoxonium tetraphenylborate (**8**) (0.31 g, 0.44 mmol, 39%). Mp 156—157 °C. ^{1}H NMR (CD_3COCD_3) δ=2.10—2.20 (m, 2H, CH_2), 2.42 (s, 3H, TolMe), 3.52 (s, 3H, NMe), 3.69—3.72 (m, 4H, NCH_2), 3.79—3.81 (m, 4H, OCH_2), 4.02—4.21 (m, 2H, SCH_2), 4.75—4.79 (m, 1H, CH), 4.86—4.87 (m, 1H, OH), 6.76—7.36 (m, 25H, Ar), 7.40—7.55 (dd, 4H, Tol). Found: C, 76.38; H, 6.71; N, 4.04%. Calcd for $C_{45}H_{49}BN_2O_3S$: C, 76.32; H, 6.98; N, 3.96%.

Reaction of 3-Hydroxy-3-phenylpropylsulfoxonium Tetraphenylborate 8 with DBU. To a solution of salt **8** (0.40 g, 0.57 mmol) in dichloromethane (15 mL) was added DBU (0.10 g, 0.68 mmol) at r.t. After being refluxed for 5 h, the reaction mixture was poured into water and extracted with dichloromethane (10 mL×2) and ethyl acetate (10 mL×3). The combined dichloromethane extract was dried over magnesium sulfate and evaporated to give a pale orange oil, which was chromatographed over silica gel by elution with dichloromethane to afford *N*-methyl-*p*-toluidine (0.024 g, 0.20 mmol, 35%). The combined ethyl acetate extract was dried over magnesium sulfate and evaporated to give a brown oil, which was chromatographed over silica gel by elution with dichloromethane–ethyl acetate to afford the

rearranged product, **4b** (0.030 g, 0.09 mmol, 15%). Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ=2.22 (s, 3H, TolMe), 2.45 (d, 1H, OH), 2.51—2.55 (m, 2H, CH_2), 3.23 (s, 3H, NMe), 4.15—4.18 (q, 1H, SCH), 5.12 (br s, 1H, PhCH), 6.54 (d, 1H, Ar), 6.89 (s, 1H, Ar), 7.00 (d, 1H, Ar), 7.32—7.35 (m, 3H, Ar), 7.44 (d, 2H, Ar). Found: *m/z* 301.1148. Calcd for $C_{17}H_{19}NO_2S$: M, 301.1136.

Preparation of *N*-(*p*-Tolyl)-2-hydroxy-2-(*p*-chlorophenyl)ethanesulfonimidomorpholide (12). To a solution of *N*-(*p*-tolyl)methanesulfonimidomorpholide (5.0 g, 19.8 mmol) in ether (100 mL) was added butyllithium (1.6 M in hexane, 19.1 mL, 29.8 mmol) at 0 °C (1 M=1 mol dm^{-3}). After this was stirred for 1 h, *p*-chlorobenzaldehyde (2.8 g, 19.8 mmol) in ether (50 mL) was added to it. After being stirred for 8 h, the resulting mixture was washed with water (25 mL) three times. The ether solution was dried over $MgSO_4$, and evaporated to give the crude sulfonimidomorpholide, which was chromatographed over silica gel by elution with dichloromethane–hexane to give pure *N*-(*p*-tolyl)-2-hydroxy-2-(*p*-chlorophenyl)ethanesulfonimidomorpholide (**12**) in 65% yield. (5.1 g, 12.9 mmol). Mp. 189—190 °C. ^{1}H NMR ($CDCl_3$) δ=2.12 (s, 3H, TolMe), 3.24—3.38 (m, 6H, NCH_2 and SCH_2), 3.51—3.65 (m, 4H, OCH_2), 5.27 (d, 1H, J=8.1 Hz, CH), 5.40 (s, 1H, OH), 6.99—7.04 (br m, 4H, Tol), 7.33 (s, 4H, PhCl). ^{13}C NMR ($CDCl_3$) δ=20.64 (TolMe), 46.62 (NCH_2), 58.99 (CH_2), 66.39 (OCH_2), 68.31 (CH), 122.94, 129.67, 127.05, 128.79, 131.88, 133.82, 139.56, 139.87 (Ar). Found: C, 57.56; H, 6.18; N, 6.93%. Calcd for $C_{19}H_{23}N_2O_3SCl$: C, 57.60; H, 6.05; N, 7.00%.

Reaction of 12 with *t*-Butyldimethylchlorosilane. Preparation of 13. To a solution of **12** (2.86 g, 7.24 mmol) and imidazole (1.23 g, 18.1 mmol) in DMF (5 mL) was added *t*-butyldimethylchlorosilane (2.18 g, 14.5 mmol) in one portion. After being stirred for 2 d at 45 °C, the reaction mixture was poured into water (100 mL) and extracted with ether (15 mL×3). The combined extracts were washed with water, dried over magnesium sulfate, and evaporated to give a pale brown oil. This oil was chromatographed over silica gel by elution with dichloromethane–ethyl acetate (5 : 1) to give a pale yellow oil of silyl ether (**13**). (3.36 g, 6.59 mmol, 91%). ^{1}H NMR ($CDCl_3$) δ=0.00 (s, 3H, MeSi), 0.22 (s, 3H, MeSi), 0.97 (s, 9H, Me_3C), 3.19—3.32 (m, 6H, CH_2 and NH_2), 3.66—3.72 (m, 4H, OCH_2), 5.58—5.59 (m, 1H, CH), 7.09—7.14 (br m, 4H, Tol), 7.44—7.51 (br m, 4H, ClPh). Found: *m/z* 508.1937. Calcd for $C_{25}H_{37}ClN_2O_3SSi$: M, 508.1983.

Preparation of Vinyl Salt (11a): Methylation of *t*-Butyldimethylsililated Sulfonimidomorpholide 13. To a solution of sulfonimidomorpholide **13** (0.69 g, 1.36 mmol) in dichloromethane (20 mL) was added trimethyloxonium tetrafluoroborate (0.26 g, 1.8 mmol) in one portion. The reaction mixture was refluxed for 3 h. The resulting solution was evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with dichloromethane to give *trans*-*N*-(*p*-tolyl)-2-(*p*-chlorophenyl)ethenesulfonimidomorpholide (**14**) (0.10 g, 0.27 mmol) in 20% yield. Mp 142—143 °C. ^{1}H NMR ($CDCl_3$) δ=2.29 (s, 3H, TolMe), 3.15—3.27 (m, 4H, NCH_2), 3.61—3.73 (m, 4H, OCH_2), 6.78 (d, 1H, J=15.4 Hz, =CH), 7.04 (d, 2H, Ar), 7.39 (d, 2H, Ar), 7.43 (d, 2H, Ar), 7.48 (d, 1H, J=15.4 Hz, =CH). ^{13}C NMR ($CDCl_3$) δ=20.67 (TolMe), 46.44 (NCH_2), 66.25 (OCH_2), 122.30 (=CH), 123.29, 129.07, 129.29, 129.41, 129.60, 131.02, 131.48 136.75 (Ar), 141.48 (=CH). Found: C, 60.75; H, 5.22; N, 7.19%. Calcd for $C_{19}H_{21}N_2O_2SCl$: C, 60.55; H, 5.62; N, 7.43%. The dichloromethane–ethyl acetate fraction was evaporated to afford the desired [*trans*-2-(*p*-chlorophenyl)ethenyl](*N*-methyl-*p*-tolylamino)morpholinosulfoxonium tetrafluoroborate (**11a**). (0.067 g, 0.14 mmol, 10%) Mp 189—190 °C. ^{1}H NMR ($CDCl_3$) δ=2.38 (s, 3H, TolMe), 3.49 (s, 3H, NMe), 3.53—3.63 (m, 4H, NCH_2), 3.66—3.70 (m, 4H, OCH_2), 7.28 (d, 2H, Ar), 7.43—7.61 (br m, 4H, Ar), 7.74—7.84 (br m, 4H, J=14.7 Hz, Ar and =CH). ^{13}C NMR ($CDCl_3$) δ= 21.19 (TolMe), 40.35 (NMe), 46.09 (NCH_2), 65.59 (OCH_2), 113.21 (=CH), 127.42, 129.21, 129.93, 131.21. 131.75, 134.59, 140.20, 140.86, 153.02 (Ar and =CH). Found: C, 50.25; H, 4.54; N, 5.56%. Calcd for $C_{20}H_{24}BClF_4N_2O_2$: C, 50.18; H, 5.05; N, 5.85%.

Reaction of 11a with Salt 1a in the Presence of DBU. To a solution of **11a** (0.031 g, 0.065 mmol) and DBU (0.12 g, 0.078 mmol) in dichloromethane (10 mL) was added salt **1a** (0.023 g, 0.065 mmol) in one portion and refluxed for 5 h. The resulting mixture was washed with water (10 mL) and 1 M HCL (5 mL) three times. The dichloromethane layer was dried over magnesium sulfate and filtered. The filtrate was evaporated to give pale yellow crystals of salts **2c** (0.022 g, 0.046 mmol) in 65% yield.

Reaction of Salt 2a with Potassium Hydroxide and Cyclohexanone. To a solution of **2a** (0.40 g, 1.05 mmol) and cyclohexanone (0.08 g, 0.84 mmol) in dimethyl sulfoxide (3 mL) was added potassium hydroxide (0.09 g, 1.7 mmol) at r.t. After this was stirred for 4 h, a solution of HBF_4 (1 M, 2.1 mL) was added to the reaction mixture and extracted with ether (15 mL×3). The combined extract was dried over magnesium sulfate and evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with hexane–dichloromethane to give *N*-methyl-*p*-toluidine (0.038 g, 0.32 mmol, 30%) and the rearranged product **4c** (0.010 g, 0.03 mmol, 5%).

4c: Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ=1.16—1.25 (m, 1H, CH_2), 1.60—1.67 (m, 1H, CH_2), 1.76—1.94 (m, 2H, CH_2), 2.30 (s, 3H, TolMe), 3.35 (s, 3H, NMe), 6.60 (s, 1H, Ar), 6.66 (d, 1H, Ar), 7.06 (d, 1H, Ar). Found: *m/z* 207.0754. Calcd for $C_{11}H_{13}NOS$: M, 207.0718.

This work was partly supported by the Central Research Institute of Fukuoka University. We are grateful to Professor Haruo Matsuyama at Tokyo Metropolitan University for the high-resolution mass spectroscopic analysis.

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