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Addition of ArSSAr to Carbon-Carbon Multiple Bonds Using Electrochemistry

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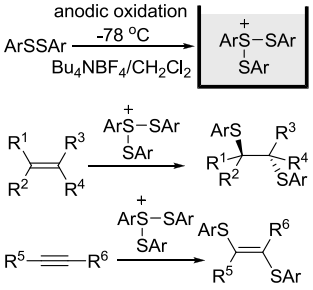

TETRAHEDRON

Addition of ArSSAr to Carbon-Carbon Multiple Bonds Using Electrochemistry

Shunsuke Fujie, Kouichi Matsumoto, Seiji Suga[1], Toshiki Nokami, and Jun-ichi Yoshida[*]

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Abstract— $ArS(ArSSAr)^+$ (arylbis(arylthio)sulfonium ions), which were generated and accumulated by the electrochemical oxidation of diaryl disulfides (ArSSAr) in CH_2Cl_2 at −78 °C, reacted with alkenes to give the corresponding diarylthio-substituted compounds in a stereospecific manner in good yields, when the reaction was quenched with a soft nucleophile such as allylsilanes, ketene silyl acetals, and triethylamine. A mechanism involving the initial formation of an episulfonium ion followed by ring-opening by the attack of ArSSAr has been suggested. The reactions of $ArS(ArSSAr)^+$ with alkynes also took place to give 1,2-diorganothio-substitued alkenes stereoselectively under similar conditions.

1. Introduction

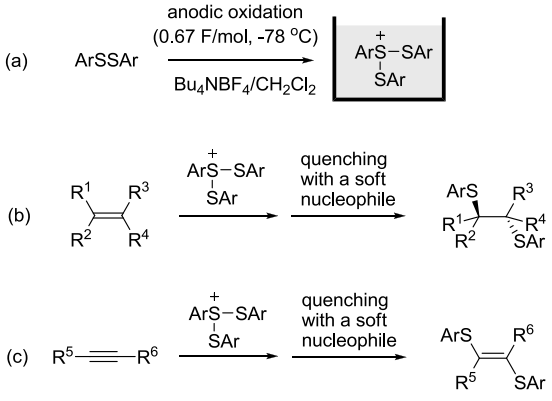
Organosulfur compounds have attracted a great deal of interest in various research fields of chemistry, and a variety of methods for their synthesis have been reported so far.[2] Among them, the addition of diorgano disulfides to carbon-carbon multiple bonds serves as a useful method. A stoichiometric or a catalytic amount of acids such as BF_3-OEt_2, $GaCl_3$, $AlCl_3$, and PhIO-OTf are effective to drive this type of transformation.[3]

ArS^+ are also effective as electrophilic reagents to introduce ArS groups into carbon-carbon multiple bonds, although some doubts have been advanced of their existence in this form in the solution phase. The reactions of "ArS^+" (ArS^+ or their equivalents)[4] with carbon-carbon multiple bonds give rise to the formation of episulfonium ions or thiirenium ions intermediates,[5] which undergo ring opening reaction by the action of quenching nucleophiles.

In addition to the chemical method, the electrochemical method[6] is also effective for generation of "ArS^+".[7] In fact, the electrochemical oxidation of ArSSAr is the most straightforward method for generating "ArS^+". The radical cation of ArSSAr produced by one electron oxidation of ArSSAr undergoes the cleavage of sulfur-sulfur bond to give ArS^+ and an ArS·. ArS· is further oxidized to give ArS^+. Thus, the electrochemical generation,in principle, does not produce any byproducts, and therefore is superior to the chemical generation which needs the use of toxic reagents and produces byproducts derived from them.

Recently, we revealed that highly reactive arylbis(arylthio)sulfonium ions ($ArS(ArSSAr)^+$)[8], which can be seen as ArS^+ stabilized by the interaction with ArSSAr, were generated and accumulated by the electrochemical oxidation[9] of ArSSAr in CH_2Cl_2 using Bu_4NBF_4 as supporting electrolyte at −78 °C (Scheme 1 (a)), and that these species served as electrophilic "ArS^+" for reactions with various nucleophiles.[10]

To the best of our knowledge, however, the addition of two ArS groups by the action of "ArS^+" to carbon-carbon multiple bonds has not yet been reported so far. Herein, we report that the reactions of electrochemically generated $ArS(ArSSAr)^+$ with alkenes and alkynes led to stereoselective addition of ArSSAr to the carbon-carbon multiple bonds when a suitable nucleophile was used as a quenching reagent (Scheme 1 (b) and (c)).



Scheme 1. Stereoselective addition of ArSSAr to carbon-carbon multiple bonds using $ArS(ArSSAr)^+$

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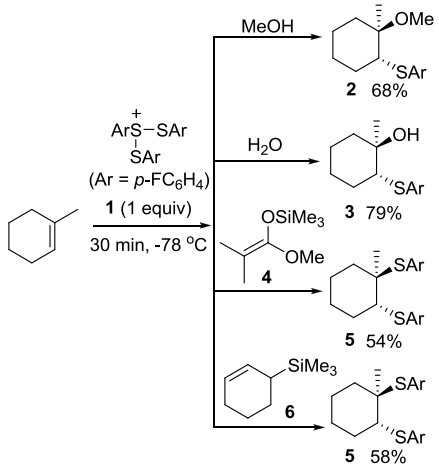
2. Results and discussion

A solution of $(ArS(ArSSAr)^+ BF_4^-)$ (**1**) (Ar = *p*-FC_6H_4) was generated by the anodic oxidation of ArSSAr (Ar = *p*-FC_6H_4) in Bu_4NBF_4/CH_2Cl_2 at −78 °C (0.67 F/mol)[11] according to the procedure reported previously (Scheme 1 (a)).[10a] First, we examined reactions of **1** with 1-methylcyclohexene using various quenching nucleophiles (Scheme 2). 1-Methylcyclohexene (1 equiv) was added to the resulting solution of **1** at −78 °C. Quenching of the reaction with MeOH as a nucleophile afforded adduct **2** (Markovnikov product) in 68% yield. A MeO group was introduced on the tertiary carbon, suggesting that MeOH attacked a partially developed carbocationic center.[12,13] It is also noteworthy that the anti addition product was obtained exclusively. These observations are quite similar to those obtained for "ArS^+" generated by other methods in the absence of ArSSAr. The use of H_2O as a quenching nucleophile led to the formation of **3** in a similar manner.

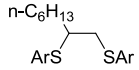
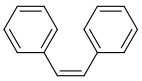
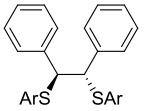
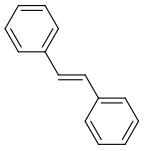
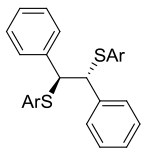
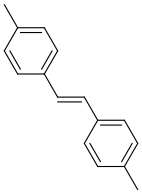
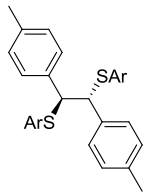
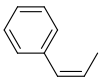
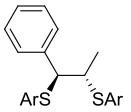
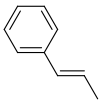
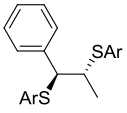


Scheme 2. The reactions of $ArS(ArSSAr)^+$ (**1**) (Ar = *p*-FC_6H_4) with 1-methylcyclohexene followed by addition of a quenching nucleophile

However, it was surprising that use of ketene silyl acetal **4** as a quenching nucleophile led to anti addition of two ArS groups to give compound **5**.[14] No appreciable carbon-carbon bond formation took place. The formation of **5** indicated that ArSSAr attacked the episulfonium ion as a nucleophile. Use of an allylsilane such as **6** as a quenching nucleophile also gave rise to the formation of **5**. The reactions of other alkenes using **4** or **6** as a quenching nucleophile also gave the corresponding diarylthio-substituted compounds as depicted in Table 1. Et_3N was also found to be an effective quenching nucleophile for formation of diarylthio-substituted compounds.

The reactions of (*Z*)- and (*E*)-diphenylethene were carried out to examine the stereoselectivity of the present reaction (Table 1). The stereochemistry of the products was determined by X-ray crystallographic analysis (Figure 1).[15] The reaction with (*Z*)-diphenylethene exclusively gave the *dl* product (**9**) and (*E*)-diphenylethene exclusively gave *meso* product (**10**), indicating that the reactions are stereospecific and anti-selective.

Table 1. Reactions of $ArS(ArSSAr)^+$ (**1**) (Ar = *p*-FC_6H_4) with Alkenes [a]

Alkene	Product	Yield (%) [b] Quenching nucleophile **4**	**6**	Et_3N
	 **7**	64	36	72[c]
	 **8**	35	42	66[c]
	 **9**	68	71[d]	84[c]
	 **10**	54	53[d]	trace
	 **11**	56[d]	30[d]	0
	 **12**	31[d]	51[d]	73[c,d]
	 **13**	41[d]	60[d]	3[c,d]

a) Typical procedure: ArSSAr (Ar = *p*-FC_6H_4; 0.40 mmol) was electrochemically oxidized in 0.3 M Bu_4NBF_4/CH_2Cl_2 (8 mL) at −78 °C using 0.67 F/mol of electricity. The solution of **1** (ca. 0.27 mmol) thus obtained was allowed to react with an alkene (0.27 mmol, 1 equiv) at −78 °C for 30 min. A quenching nucleophile (3 equiv) was added and the mixture was stirred for 30 min at the same temperature. Then, Et_3N (1 mL) was added to quench the reaction. b) Yields of isolated products. c) 3 equiv of **1** was used. d) Yields determined by NMR.

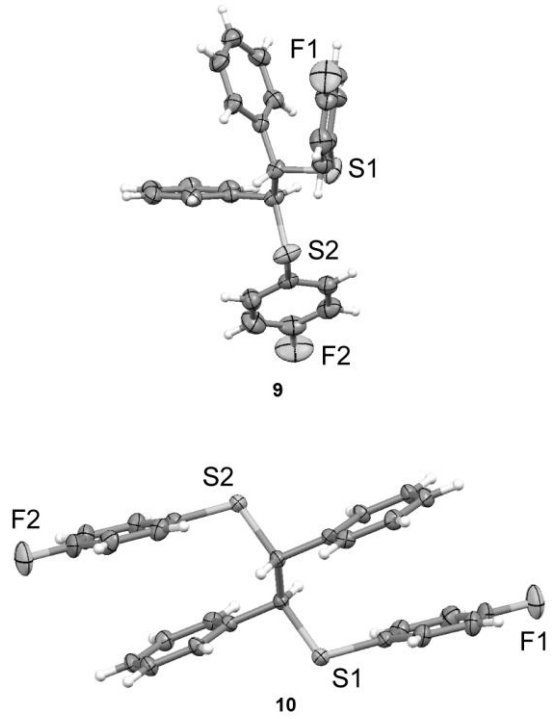
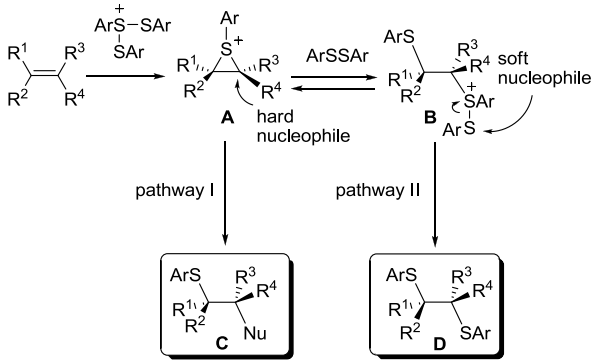


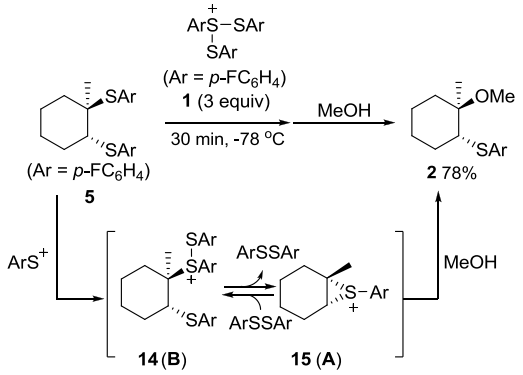
Figure 1. X-ray structures of **9** and **10**

Although the reaction mechanism has not yet been fully clarified, the following mechanistic arguments seem to be reasonable (Scheme 3). In the first step, episulfonium ion intermediate[5] **A** is generated by the reaction of $ArS(ArSSAr)^+$ with an alkene. Nucleophilic attack of ArSSAr on **A** opens the three-membered ring to give sulfonium intermediate **B**. There is an equilibrium between **A** and **B**.[16] A hard quenching nucleophile such as MeOH or H_2O selectively attacks **A** to give the corresponding product **C** (pathway I). On the other hand, a soft quenching nucleophile such as ketene silyl acetal **4**, allylsilane **6** and triethylamine selectively attacks **B** to cleave the S-S bond giving diarylthio-substituted compound **D** as the final product (pathway II).



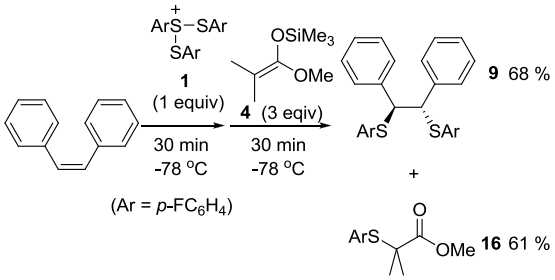
Scheme 3. Plausible reaction mechanism

The existence of the equilibrium between **A** and **B** is supported by the fact that the treatment of diarylthio-substituted product **5** with **1** followed by quenching with MeOH gave compound **2** stereoselectively (Scheme 4). Presumably, the reaction of **5** with ArS^+ gave **14** (**B**). The ring-closing to episulfonium ion **15** (**A**) followed by nucleophilic attack by MeOH gave **2**.



Scheme 4. Existence of the equilibrium

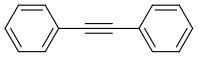
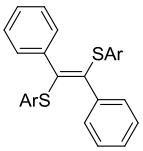
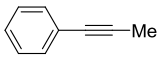
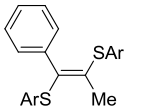
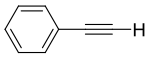
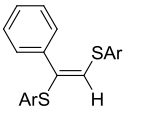
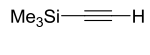
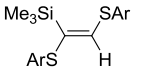
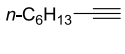
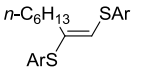
The attack of a soft nucleophile on **B** is supported by the experiment shown in Scheme 5. When (*Z*)-diphenylethene was reacted with **1** and the resulting mixture was treated with a ketene silyl acetal **4**, ArS substituted ester **16** and ArSSAr addition product **9** were obtained in equal amounts.[17]



Scheme 5. Evidence of the attack of a soft nucleophile

It was also found that the reactions of $ArS(ArSSAr)^+$ (**1**) (Ar = p-FC_6H_4) with alkynes gave the corresponding diarylthio-substituted compounds, when a soft nucleophile such as allylsilane **6** and triethylamine was used as a quenching nucleophile (Table 2). The reactions were highly stereoselective (except for formation of **19**), and the stereochemistry of the products were identified as *E*-isomers by comparison of the NMR spectra with those reported in the literature.[18]

Table 2. Reactions of ArS(ArSSAr)$^+$ (**1**) (Ar = *p*-FC_6H_4) with Alkynes

Alkyne	Product	Yield (%)[a] Quenching nucleophile **6**[b]	Yield (%)[a] Quenching nucleophile Et_3N[c]
	 **17**	99	80
	 **18**	77 (E/Z = 94:6)	95 (E/Z = 92:8)
	 **19**	62[d] (E/Z = 59:41)	57 (E/Z = 85:15)
	 **20**	34	62
	 **21**	49[d]	33[d]

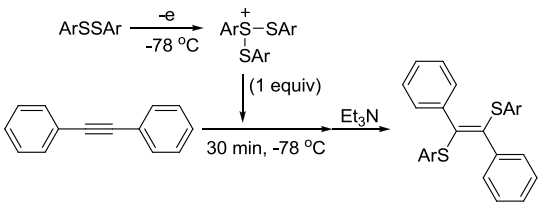
a) Yields of isolated products. b) 1 eq of ArS(ArSSAr)$^+$ was used. c) 3 eq of ArS(ArSSAr)$^+$ was used. d) Yields determined by NMR.

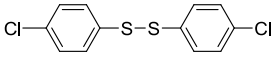
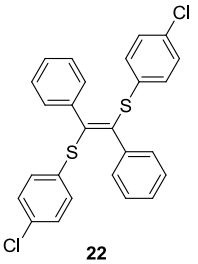
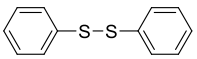
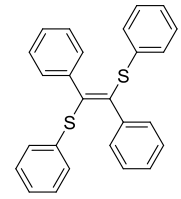
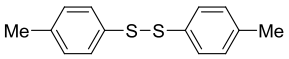
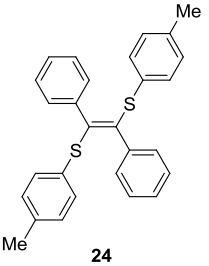
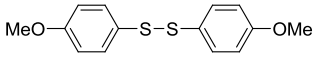
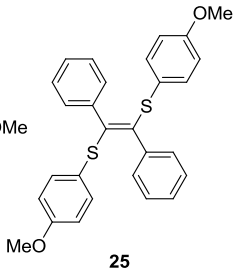
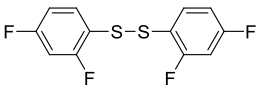
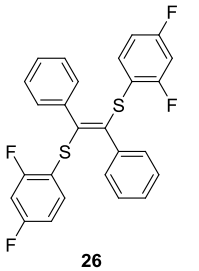
ArS(ArSSAr)$^+$ having various substituent(s) on the aromatic ring could also be generated and accumulated by the electrochemical oxidation of the corresponding ArSSAr in CH_2Cl_2 at −78 °C. Their reactions with diphenylethyne took place smoothly to give the corresponding (*E*)-1,2-diarylthio-1,2-diphenylethenes (Table 3). The reactions were highly stereoselective and only a single stereoisomer was obtained. Therefore, the present method serves as an efficient method for synthesizing diarylthio-substituted alkenes bearing various substituents on the aromatic rings.

3. Conclusions

We found that ArS(ArSSAr)$^+$ generated and accumulated by the electrochemical oxidation of ArSSAr in CH_2Cl_2 at −78 °C reacted with alkenes and alkynes giving rise to stereoselective addition of ArSSAr to a carbon-carbon multiple bond when a soft nucleophile such as allylsilanes, ketene silyl acetals, and triethylamine was used as a quenching nucleophile. The present method serves as an efficient and convenient method for highly stereoselective synthesis of organosulfur compounds.

Table 3. Reactions of ArS(ArSSAr)$^+$ with diphenylethyne [a]



ArSSAr	Product	Yield (%)[b]
	 **22**	71[c]
	 **23**	53
	 **24**	56 81[d]
	 **25**	32 50[d]
	 **26**	62 79[d]

a) 1 eq of ArS(ArSSAr)$^+$ was used and Et_3N was used as quenching nucleophile. b) Yields of isolated products. c) **6** was used as quenching nucleophile. d) The reaction was carried out for 90 min.

4. Experimental section

4.1. General Remarks

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 2000 (^{1}H 300 MHz, ^{13}C 75 MHz), Varian MERCURY plus-400 (^{1}H 400 MHz, ^{13}C 100 MHz), or JEOL ECA-600P (^{1}H 600 MHz, ^{13}C 150 MHz) with Me_4Si as an internal standard unless otherwise noted. Mass spectra were obtained on a JEOL JMS-SX102A mass spectrometer, JEOL JMS-HX110A mass spectrometer, JEOL MS-BU250 mass spectrometer, or JEOL JMS-MS700 mass spectrometer. Thin-layer chromatography (TLC) was carried out by using Merck precoated silica gel F_{254} plates (thickness 0.25 mm). Flash chromatography was carried out on a column of silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40-100 μm). Gel permeation chromatography (GPC) was carried out on a Japan Analytical Industry LC-9201 equipped with JAIGEL-1H and 2H using $CHCl_3$ as eluent. X-ray single crystal structure analysis was performed on RIGAKU R-AXIS RAPID. All reactions were carried out under Ar atmosphere unless otherwise noted.

4.2. Materials

Dichloromethane (CH_2Cl_2) was washed with water, distilled from P_2O_5, redistilled from dried K_2CO_3 to remove a trace amount of acid, and stored over molecular sieves 4A. Trifluoromethanesulfonic acid (TfOH) was purchased from Nacalai and was used without further purification. ArSSAr (Ar = *p*-FC_6H_4) was prepared according to the procedures in the literatures,[19] and identified by the comparison of its spectral data with that of authentic sample.[20]

4.2.1. Bis(2,4-difluoropheny) disulfide. To a solution of 2,4-difluorobenzenethiol (4.49 g, 31 mmol) in CH_2Cl_2 (10 mL) was added a solution of SO_2Cl_2 (2.28 g, 16.9 mmol) in 10 mL of CH_2Cl_2 at 0 °C.[21] Then, the mixture was heated to room temperature and stirred for additional 7 h. The reaction was quenched with water (15 mL) and the resulted mixture was extracted with Et_2O (2 x 20 mL). The combined extracts were washed with saturated $NaHCO_3$ (20 mL), and brine (25 mL) and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography (hexane/EtOAc 100:1) to obtain the title compound (4.01 g, 90%): TLC R_f 0.33 (hexane/EtOAc 100:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81-6.88 (m, 4H), 7.47-7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.7 (t, *J* = 26.0 Hz), 112.1 (dd, *J* = 18.3, 4.0 Hz), 119.2 (dd, *J* = 18.3, 4.0 Hz), 134.7 (dd, *J* = 9.5, 2.0 Hz), 161.7 (dd, *J* = 249.1, 12.3 Hz), 163.6 (dd, *J* = 250.5, 11.3 Hz); LRMS (EI) m/z 290 (M^+), 145 (M^+-$SC_6H_3F_2$); HRMS (EI) calcd for $C_{12}H_6F_4S_2$ 289.9847, found 289.9848.

4.3. Electrochemical Generation and Accumulation of ArS(ArSSAr)$^+$ (Ar = *p*-FC_6H_4) (1).

The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 320 mg, dried at 250 °C/1 mmHg for 2 h before use) and a platinum plate cathode (40 mm x 20 mm). In the anodic chamber was placed a solution of ArSSAr (Ar = *p*-FC_6H_4) (104.2 mg, 0.410 mmol) in 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL). In the cathodic chamber were placed 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL) and trifluoromethanesulfonic acid (44.6 mg, 0.297 mmol). The constant current electrolysis (8 mA) was carried out at −78 °C with magnetic stirring until 0.67 F/mol of electricity[11] was consumed. The solution of **1** (0.038 M at −78 °C) thus obtained was used for the subsequent reaction.

4.4. Reaction of ArS(ArSSAr)$^+$ with Alkenes

*4.4.1 (1RS,2RS)-1-(4-Fluorophenylthio)-2-methoxy-2-methylcyclohexane (**2**) (a typical procedure for the reaction with alkenes using a hard quenching nucleophile).* To the solution of **1** (0.038 M at −78 °C, 8.0 mL, 0.304 mmol) was added 1-methylcyclohexene (28.7 mg, 0.298 mmol) at −78 °C and the reaction mixture was stirred for 30 min. The reaction was quenched by addition of MeOH (1 mL) and the mixture was stirred for 30 min at the same temperature. Then, Et_3N (1 mL) was added to complete the quenching and the mixture was warmed to room temperature. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (5 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with ether (70 mL). The combined filtrate was concentrated in *vacuo* and the crude product thus obtained was purified via flash chromatography (hexane/EtOAc 30:1) and GPC to give the title compound (**2**) (52.3 mg, 68% yield): TLC R_f 0.32 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24-1.31 (m, 2H), 1.28 (s, 3H), 1.32-1.43 (m, 1H), 1.48-1.76 (m, 6H), 1.92-2.00 (m, 1H), 3.18 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.22 (s, 3H), 6.94-7.00 (m, 2H), 7.41-7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 22.2, 23.5, 29.6, 34.2, 76.6, 115.7 (d, *J* = 21.4 Hz), 131.1 (d, *J* = 3.6 Hz), 134.5 (d, *J* = 8.0 Hz), 161.9 (d, *J* = 245.2 Hz); LRMS (EI) m/z 254 (M^+), 239 (M^+-Me), 223 (M^+-OMe); HRMS (EI) calcd for $C_{14}H_{19}FOS$ 254.1141, found 254.1139.

*4.4.2. (1RS,2RS)-1-(4-Fluorophenylthio)-2-methyl-2-cyclohexanol (**3**).* TLC R_f 0.06 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18-1.28 (m, 2H), 1.28 (s, 3H), 1.33-1.60 (m, 3H), 1.64-1.76 (m, 2H), 1.82-1.88 (m, 1H), 2.03 (dddd, *J* = 13.7, 1.7, 1.7, 1.7 Hz, 1H), 2.60 (s, 1H), 2.97 (dd, *J* = 12.2, 4.2 Hz, 1H), 6.95-7.02 (m, 2H), 7.43-7.48 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.7, 23.2, 26.0, 32.1, 39.7, 62.7, 72.6, 116.0 (d, *J* = 21.7 Hz), 130.6 (d, *J* = 3.6 Hz), 134.6 (d, *J* = 8.4 Hz), 162.2 (d, *J* = 245.1 Hz); LRMS (EI) m/z 240 (M^+); HRMS (EI) calcd for $C_{13}H_{17}FOS$ 240.0984, found 240.0985.

*4.4.3. (1RS,2RS)-1,2-Bis(4-fluorophenylthio)-1-methylcyclohexane (**5**) (a typical procedure for the reaction with alkenes using a soft quenching nucleophile).* To the solution of **1** (0.038 M at −78 °C, 8.0 mL, 0.304 mmol) was added 1-methylcyclohexene (29.3 mg, 0.305 mmol) at −78 °C and the reaction mixture was stirred for 30 min. The reaction was quenched with 3-(trimethylsilyl)cyclohexene(140.0 mg, 0.907 mmol) and the mixture was stirred for 30 min at the same temperature. Then, Et_3N (1 mL) was added to complete the quenching and the mixture was warmed to room temperature. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (5 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with ether (70 mL). The combined filtrate was concentrated in *vacuo* and the crude product was obtained. The yield of title compound (**5**) was determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard (61.7 mg, 58%):TLC R_f 0.25

(hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10-1.21 (m, 1H), 1.36 (s, 3H), 1.36-1.47 (m, 1H), 1.56-1.69 (m, 4H), 1.93-2.01 (m, 1H), 3.04 (dd, *J* = 10.0, 4.0 Hz, 1H), 6.95-7.05 (m, 4H), 7.35-7.40 (m, 2H), 7.53-7.58 (m, 2H); ^{13}C NMR(150 MHz, $CDCl_3$) δ 22.2, 22.3, 30.1, 39.2, 53.5, 56.7, 115.6 (d, *J* = 20.5 Hz), 116.0 (d, *J* = 21.7 Hz), 126.5 (d, *J* = 3.6 Hz), 130.7 (d, *J* = 2.4 Hz), 134.5 (d, *J* = 7.2 Hz),139.6 (d, *J* = 8.5 Hz), 162.1 (d, *J* = 245.1 Hz), 163.5 (d, *J* = 248.8 Hz); LRMS (EI) m/z 350 (M^+),223 (M^+-SC_6H_4*p*-F); HRMS (EI) calcd for $C_{19}H_{20}F_2S_2$ 350.0974, found 350.0969.

*4.4.4. (1RS,2RS)-1,2-Bis(4-fluorophenylthio)cyclohexane (**7**).* TLC R_f 0.28 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31-1.38 (m, 2H), 1.51-1.59 (m, 2H), 1.59-1.67 (m, 2H), 2.11-2.19 (m, 2H), 3.02-3.07 (m, 2H), 6.89-6.98 (m, 4H), 7.28-7.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.8, 30.5, 50.7, 115.8 (d, *J* = 21.4 Hz), 129.1 (d, *J* = 3.1 Hz), 135.1 (d, *J* = 7.9 Hz), 162.1 (d, *J* = 245.5 Hz); LRMS (CI) m/z 336 (M^+), 209 (M^+-SC_6H_4*p*-F); HRMS (CI) calcd for $C_{18}H_{18}F_2S_2$ 336.0818, found 336.0804.

*4.4.5. 1,2-Bis(4-fluorophenylthio)octane (**8**).* TLC R_f 0.30 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.21-1.36 (m, 6H), 1.36-1.60 (m, 3H), 1.85-1.95 (m, 1H), 2.83 (dd, *J* = 9.2, 13.2 Hz, 1H), 2.92-2.99 (m, 1H), 3.10 (dd, *J* = 4.0, 13.2 Hz, 1H), 6.88-6.98 (m, 4H), 7.14-7.20 (m, 2H), 7.25-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 26.8, 29.1, 31.7, 32.6, 40.6, 49.3, 115.9 (d, *J* = 21.4 Hz), 128.9 (d, *J* = 3.2 Hz), 130.5 (d, *J* = 3.2 Hz), 132.5 (d, *J* = 7.9 Hz), 135.2 (d, *J* = 8.0 Hz), 161.6 (d, *J* = 244.3 Hz), 162.2 (d, *J* = 245.9 Hz); LRMS (CI) m/z 366 (M^+), 239 (M^+-SC_6H_4*p*-F); HRMS (CI) calcd for $C_{20}H_{24}F_2S_2$ 366.1287, found 366.1275.

*4.4.6. (1RS,2RS)-1,2-Bis(4-fluorophenylthio)-1,2-bisphenylethane (**9**).* TLC R_f 0.34 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (s, 2H), 6.82-6.86 (m, 4H), 6.91-6.93 (m, 4H), 7.02-7.05 (m, 6H), 7.17-7.21 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 59.4, 115.7 (d, *J* = 21.4 Hz), 127.1, 127.6, 128.8, 129.1 (d, *J* = 3.5 Hz), 135.7 (d, *J* = 8.0 Hz), 138.6, 162.4 (d, *J* = 245.9 Hz); LRMS (CI) m/z 434 (M^+), 307 (M^+-SC_6H_4*p*-F); HRMS (CI) calcd for $C_{26}H_{20}F_2S_2$ 434.0974, found 434.0966. X-ray data for **9**: $C_{26}H_{20}F_2S_2$, *M* = 434.56, monoclinic, space group C2/c (No. 15), *a* = 25.319(13) Å, *b* = 8.637(11) Å, *c* = 10.397(8) Å, β = 101.10(3)°, *V* = 2231.1(21) Å^3, *Z* = 4, D_c = 1.294 g/cm^3, μ = 2.649 cm^{-1}. Intensity data were measured on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation. The data were collected at 23±1 °C to maximum 2θ value of 55.0°. A total of 10640 reflections were collected. The structure was solved by SHELX-97[22] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 2561 observed reflections ($I > 2.00\sigma(I)$) and 136 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of R = 0.041 (R_w = 0.120). All calculations were performed using the Yadokari-XG crystallographic software package.

*4.4.7. (1RS,2SR)-1,2-Bis(4-fluorophenylthio)-1,2-bisphenylethane (**10**).* TLC R_f 0.33 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48 (s, 2H), 6.73-6.78 (m, 4H), 6.96-7.01 (m, 4H), 7.13-7.16 (m, 4H), 7.20-7.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 60.3, 115.5 (d, *J* = 21.8 Hz), 127.5, 128.0, 128.5, 129.1 (d, *J* = 3.1 Hz), 135.8 (d, *J* = 8.4 Hz), 139.3, 162.3 (d, *J* = 245.6 Hz); LRMS (FAB) m/z 434 (M^+), 307 (M^+-SC_6H_4*p*-F); HRMS (FAB) calcd for $C_{26}H_{20}F_2S_2$ 434.0974, found 434.0992. X-ray data for **10**: $C_{26}H_{20}F_2S_2$, *M* = 434.56, monoclinic, space group $P2_1/c$ (No. 14), *a* = 12.8076(10) Å, *b* = 5.6338(4) Å, *c* = 15.6116(13) Å, β = 108.543(8)°, *V* = 1067.98(14) Å^3, *Z* = 2, D_c = 1.351 g/cm^3, μ = 2.767 cm^{-1}. Intensity data were measured on a Rigaku RAXIS imaging plate area detector with graphite- monochromated Mo-Kα radiation. The data were collected at 20±1 °C to maximum 2θ value of 50.6°. A total of 8146 reflections were collected. The structure was solved by SHELX-97[22] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 1945 observed reflections ($I > 2.00\sigma(I)$) and 137 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of R = 0.036 (R_w = 0.074). All calculations were performed using the CrystalStructure crystallographic software package.

*4.4.8. (1RS,2SR)-1,2-Bis(4-fluorophenylthio)-1,2-bis(4-methylphenyl)ethane (**11**).* TLC R_f 0.31 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 6H), 4.44 (s, 2H), 6.73-6.79 (m, 4H), 6.97-7.05 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 60.0,115.5 (d, *J* = 21.5 Hz), 128.5, 128.8, 129.5 (d, *J* = 3.2 Hz), 135.8 (d, *J* = 8.4 Hz), 136.5,137.3, 162.4 (d, *J* = 245.9 Hz); LRMS (FAB) m/z 461 (M^+-H), 335 (M^+-SC_6H_4*p*-F); HRMS (FAB) calcd for $C_{28}H_{24}F_2S_2$ 462.1287, found 462.1304.

*4.4.9. (1RS,2RS)-1,2-Bis(4-Fluorophenylthio)-1-phenylpropane (**12**).* TLC R_f 0.25 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, *J* = 6.8 Hz, 3H), 3.50 (dq, *J* = 6.9, 6.7 Hz, 1H), 4.14 (d, *J* = 6.0 Hz, 1H), 6.83-6.88 (m, 2H), 6.94-7.00 (m, 2H), 7.16-7.27 (m, 7H), 7.30-7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 48.3, 58.8, 115.8 (d, *J* = 21.4 Hz), 116.0 (d, *J* = 21.8 Hz), 127.5, 127.87, 127.88, 129.1 (d, *J* = 3.2 Hz), 129.4 (d, *J* = 3.2 Hz), 134.8 (d, *J* = 8.0 Hz), 135.3 (d, *J* = 8.3 Hz), 137.9, 162.2 (d, *J* = 245.6 Hz), 162.3 (d, *J* = 246.0 Hz); LRMS (EI) m/z 366 (M^+), 239 (M^+-SC_6H_4*p*-F); HRMS (EI) calcd for $C_{21}H_{18}F_2S_2$ 372.0818, found 372.0816.

*4.4.10. (1RS,2SR)-1,2-Bis(4-fluorophenylthio)-1-phenylpropane (**13**).* TLC R_f 0.30 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (d, *J* = 6.8 Hz, 3H), 3.55 (quintet, *J* = 6.8 Hz, 1H), 4.16 (d, *J* = 6.8 Hz, 1H), 6.80-6.86 (m, 2H), 6.92-6.97 (m, 2H), 7.11-7.16 (m, 2H), 7.16-7.25 (m, 5H), 7.30-7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 50.5, 60.7, 115.7 (d, *J* = 21.8 Hz), 115.9 (d, *J* = 21.4 Hz), 127.3, 128.0, 128.5, 129.48 (d, *J* = 2.4 Hz), 129.51 (d, *J* = 3.2 Hz), 134.8 (d, *J* = 8.4 Hz), 135.5 (d, *J* = 7.9 Hz), 139.7, 162.1 (d, *J* = 245.1 Hz), 162.3 (d, *J* = 245.6 Hz); LRMS (EI) m/z 372 (M^+), 245 (M^+-SC_6H_4*p*-F), 217 (M^+-(SC_6H_4*p*-F)-$CHCH_3$); HRMS (EI) calcd for $C_{21}H_{18}F_2S_2$ 372.0818, found 372.0823.

*4.4.11. 2-(4-Fluorophenylthio)-2-methylpropionic acid methyl ester (**16**).* TLC R_f 0.26 (hexane/EtOAc, 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (s, 6H), 3.67 (s, 3H), 6.97-7.07 (m, 2H), 7.39-7.47 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.6, 51.1, 52.2, 115.8 (d, *J* = 27.5 Hz), 126.7 (d, *J* = 3.5 Hz), 138.8 (d, *J* = 9.2 Hz), 163.7 (d, *J* = 249.4 Hz), 174.1; LRMS (CI) m/z

228(M^+), 209 (M^+-F); HRMS (CI) calcd for $C_{11}H_{13}FO_2S$ (M^+) 228.0620, found 228.0620.

4.5. Reaction of ArS(ArSSAr)$^+$ with Alkynes

*4.5.1. (E)-1,2-Bis(4-fluorophenylthio)-1,2-bisphenylethene (**17**) (a typical procedure for the reaction with alkynes using a soft quenching nucleophile).* To the solution of **1** (0.038 M at −78 °C, 7.1 mL, 0.270 mmol) was added diphenylethyne (47.7 mg, 0.268 mmol) at −78 °C and the reaction mixture was stirred for 30 min. The reaction was quenched with 3-(trimethylsilyl)cyclohexene(149.2 mg, 0.967 mmol) and the mixture was stirred for 30 min at the same temperature. Then, Et_3N (1 mL) was added to complete the quenching and the mixture was warmed to room temperature. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (5 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with ether (70 mL). The combined filtrate was concentrated in *vacuo* and the crude product was purified with flash chromatography (hexane/EtOAc 20:1) (114.9 mg, 99%): TLC R_f 0.30 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.70-6.76 (m, 4H), 7.03-7.08 (m, 4H), 7.14-7.18 (m, 2H), 7.19-7.24 (m, 4H), 7.31-7.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.4 (d, *J* = 21.9 Hz), 127.60, 127.62, 129.0 (d, *J* = 3.6 Hz), 129.8, 134.3 (d, *J* = 7.9 Hz), 136.8, 138.3, 161.8 (d, *J* = 245.2 Hz); LRMS (FAB) m/z 432 (M^+), 305 (M^+-SC_6H_4*p*-F); HRMS (FAB) calcd for $C_{26}H_{18}F_2S_2$ 432.0818, found 432.0812.

*4.5.2. 1,2-Bis(4-fluorophenylthio)-1-phenylpropene (**18**).* This compound was characterized as the mixture of two geometrical isomers (*E*/*Z* = 94:6 by ^{1}H NMR analysis, in case of use of **6**): TLC R_f 0.31 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) *E* isomer; δ 2.23 (s, 3H), 6.77-6.84 (m, 2H), 6.95-7.01 (m, 2H), 7.10-7.23 (m, 7H), 7.26-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *E* isomer; δ 22.2, 115.6 (d, *J* = 21.8 Hz), 116.0 (d, *J* = 21.4 Hz), 127.5, 127.7, 129.3 (d, *J* = 3.2 Hz), 129.4 (d, *J* = 3.1 Hz), 129.7, 133.6 (d, *J* = 8.3 Hz), 134.2, 134.3, 134.4 (d, *J* = 8.3 Hz), 139.0, 162.0 (d, *J* = 245.5 Hz), 162.4 (d, *J* = 248.4 Hz); LRMS (CI) m/z 370 (M^+), 351 (M^+-F), 243 (M^+-SC_6H_4F); HRMS (CI) calcd for $C_{21}H_{16}F_2S_2$ 370.0661, found 370.0660.

*4.5.3. 1,2-Bis(4-fluorophenylthio)-1-phenylethene (**19**).* This compound was characterized as a mixture of two geometrical isomers (*E*/*Z* = 85:15 by GC analysis, in case of use of Et_3N): TLC R_f 0.28 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1H), 6.87-6.92 (m, 2H), 6.98-7.04 (m, 2H), 7.26-7.34 (m, 7H), 7.49-7.52 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) *E* isomer; δ 116.0 (d, *J* = 21.9 Hz), 116.2 (d, *J* = 21.8 Hz), 128.1, 128.3, 128.6, 128.9, 129.5 (d, *J* = 3.6 Hz), 130.6 (d, *J* = 3.5 Hz), 131.9 (d, *J* = 8.0 Hz), 132.7 (d, *J* = 7.9 Hz), 133.0, 136.6, 161.9 (d, *J* = 245.2 Hz), 162.1 (d, *J* = 245.6 Hz); LRMS (CI) m/z 357 (MH^+), 337 (M^+-F), 229 (M^+-SC_6H_4*p*-F); HRMS (CI) calcd for $C_{20}H_{14}F_2S_2$ 356.0505, found 356.0507.

*4.5.4. (E)-1,2-Bis(4-fluorophenylthio)-1-(trimethylsilyl)ethene (**20**).* TLC R_f 0.30 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, 9H), 6.56 (s, 1H), 6.96-7.04 (m, 4H), 7.17-7.22 (m, 2H), 7.31-7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.2, 116.1 (d, *J* = 21.8 Hz), 116.3 (d, *J* = 21.8 Hz), 129.9 (d, *J* = 3.2 Hz), 130.8 (d, *J* = 7.9 Hz), 131.2 (d, *J* = 3.2 Hz), 133.6 (d, *J* = 8.0 Hz), 135.8, 137.6, 161.8 (d, *J* = 244.7 Hz), 162.1 (d, *J* = 245.6 Hz); LRMS (CI) m/z 352 (M^+), 337 (M^+-CH_3); HRMS (CI) calcd for $C_{17}H_{18}F_2S_2Si$ 352.0587, found 352.0576.

*4.5.5. (E)-1,2-Bis(4-fluorophenylthio)-1-octene (**21**).* TLC R_f 0.36 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.24-1.34 (m, 6H), 1.51-1.58 (m, 2H), 2.34-2.38 (m, 2H), 6.13 (s, 1H), 6.94-7.04 (m, 4H), 7.23-7.26 (m, 2H), 7.35-7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 28.2, 28.9, 31.7, 32.7, 116.1 (d, *J* = 21.9 Hz), 116.2 (d, *J* = 21.4 Hz), 123.0, 128.4 (d, *J* = 3.6 Hz), 130.8 (d, *J* = 7.9 Hz), 130.9, 134.0 (d, *J* = 7.9 Hz), 138.7, 161.6 (d, *J* = 244.3 Hz), 162.3 (d, *J* = 245.6 Hz); LRMS (CI) m/z 365 (MH^+), 345 (M^+-F), 237 (M^+-SC_6H_4*p*-F); HRMS (CI) calcd for $C_{20}H_{22}F_2S_2$ 364.1131, found 364.1129.

*4.5.6. (E)-1,2-Bis(4-chlorophenylthio)-1,2-bisphenylethene (**22**).* TLC R_f 0.43(hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (brs, 8H), 7.17-7.22 (m, 6H),7.38-7.39 (m, 4H); ^{13}C NMR (100 MHz, CDCl3) δ 127.8, 128.0, 128.6, 129.9, 132.7, 132.9, 133.0, 137.2, 138.4; LRMS (FAB) m/z 464 (M^+), 321 (M^+-SC_6H_4*p*-Cl); HRMS (FAB) calcd for $C_{26}H_{18}Cl_2S_2$ 464.0227, found 464.0222.

*4.5.7. (E)-1,2-Bis(phenylthio)-1,2-bisphenylethene (**23**).* TLC R_f 0.31 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00-7.07 (m, 6H), 7.10-7.15 (m, 6H), 7.17-7.21 (m, 4H), 7.40-7.43 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.6, 127.5, 128.2, 129.8, 131.5, 134.2, 137.2, 138.7; LRMS (EI) m/z 396 (M^+), 287 (M^+-SC_6H_5), 210 (M^+-SC_6H_5-C_6H_5); HRMS (EI) calcd for $C_{26}H_{20}S_2$ 396.1006, found 396.1009.

*4.5.8. (E)-1,2-Bis(4-methylphenylthio)-1,2-bisphenylethene (**24**).* TLC R_f 0.34 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 6H), 6.84 (d, *J* = 7.6 Hz, 4H), 6.97-7.00 (m, 4H), 7.10-7.14 (m, 2H), 7.16-7.21 (m, 4H), 7.38-7.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 127.3, 127.4, 129.0, 129.8, 130.6, 131.8, 136.6, 137.2, 138.9; LRMS (FAB) m/z 424 (M^+), 301 (M^+-SC_6H_4*p*-CH_3); HRMS (FAB) calcd for $C_{28}H_{24}S_2$ 424.1319, found 424.1325.

*4.5.9. (E)-1,2-Bis(4-methoxyphenylthio)-1,2-bisphenylethene (**25**).* TLC R_f 0.21 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 6H), 6.54-6.59 (m, 4H), 6.98-7.02 (m, 4H), 7.11-7.16 (m, 2H), 7.18-7.22 (m, 4H), 7.31-7.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 113.8, 124.5, 127.2, 127.5, 129.8, 134.4, 136.7, 138.8, 158.8; LRMS (EI) m/z 456 (M^+), 317 (M^+-SC_6H_4*p*-OCH_3); HRMS (EI) calcd for $C_{28}H_{24}O_2S_2$ 456.1218, found 456.1217.

*4.5.10. (E)-1,2-Bis(2,4-difluorophenylthio)-1,2-bisphenylethene (**26**).* TLC R_f 0.31 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53-6.60 (m, 4H), 7.04-7.10 (m, 2H), 7.12-7.17 (m, 2H), 7.19-7.23 (m, 4H), 7.35-7.38 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 104.0 (t, *J* = 26.2 Hz), 111.3 (dd, *J* = 4.0, 21.0 Hz), 116.2 (dd, *J* = 3.9, 17.7 Hz), 127.87, 127.91, 129.6, 135.0, 136.4 (dd, *J* = 2.3, 9.1 Hz), 138.0, 162.2 (dd, *J* = 12.0, 248.8 Hz), 162.9 (dd, *J* = 11.4, 249.4 Hz); LRMS (FAB) m/z 468 (M^+), 323 (M^+-$SC_6H_3F_2$); HRMS (FAB) calcd for $C_{26}H_{16}F_4S_2$ 468.0630, found 468.0648.

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16. Although we tried to observe the intermediate **A** or **B** in Scheme 3 using the reaction of 1-octene and $ArS(ArSSAr)^+$ (Ar = *p*-FC_6H_4) by the low temperature NMR measurement at -80 ^oC extensively, we could not observe definite signals of the intermediates. Only a complex signals including broad peaks were observed, presumably because of the equilibrium between **A** and **B**. By increasing the temperature, signals due to thiofluorinated compound (ArS-C-C-F) appeared. See also ref 10(d).
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