HETEROCYCLES, Vol. 76, No. 2, 2008, pp. 1103 - 1119. © The Japan Institute of Heterocyclic Chemistry
Received, 27th March, 2008, Accepted, 13th May, 2008, Published online, 15th May, 2008. COM-08-S(N)64

SYNTHESIS OF THIOCHROMANS BASED ON INDIRECT CATION POOL METHOD

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This paper is dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract – A method for the synthesis of thiochromans based on the reactions of stilbenes and alkoxycarbenium ion pools, which were generated and accumulated by the reaction of anodically generated $ArS(ArSSAr)^+$ with thioacetals, has been developed.

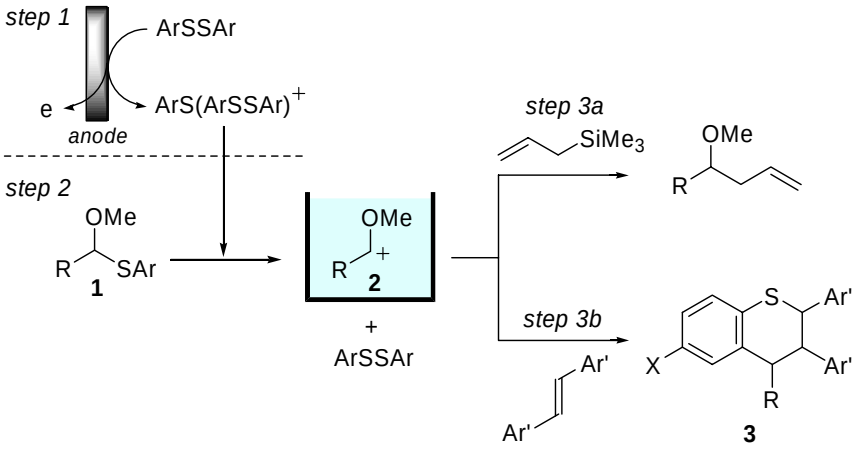
INTRODUCTION

The chemistry of thiochromans (3,4-dihydro-2*H*-1-benzothiopyrans) attracts much attention, because of their utility as synthetic intermediates as well as strong biological activity.[1] To date, many methods for the synthesis of thiochromans have been reported.[2] The cationic polar cycloaddition of phenylthionium ion with olefins developed by Ishibashi is one of the most straightforward approaches to construction of thiochroman systems.[3a-d] Katritzky reported an efficient synthesis of novel thiochromans using a similar strategy.[3e] Ishino developed an unique acid-catalyzed intermolecular cycloaddition of α,β-unsaturated aldehydes and thiophenols.[4] An efficient one-pot synthesis of thiochromans via intramolecular [4+2]cycloaddition of *o*-thiobenzoquinone methides was recently reported by Saito.[5] All these examples, however, involve a coupling process of two different components. To our knowledge, there is no method involving assembly of three different components, which should allow us to synthesize a variety of thiochroman derivatives.

We have developed the "cation pool" method,[6] in which highly reactive organic cations are generated and accumulated by the low temperature electrochemical oxidation of substrates. We have also developed the *indirect* cation pool method[7] consisting of the following three steps (Scheme 1). The highly reactive

$ArS(ArSSAr)^+$ [8] is generated and accumulated by the low temperature electrochemical oxidation of ArSSAr[9] at -78 °C (step 1), and is subsequently allowed to react with a thioacetal[10] (**1**) to generate an "alkoxycarbenium ion pool[11] (**2**) " (step 2). The cation pool of **2** thus generated is allowed to react with a carbon nucleophile such as allyltrimethylsilane to give the corresponding C-C bond formation product (step 3a). During the course of our study using various olefins as carbon nucleophiles,[12] we found that compounds having the thiochroman skeleton (**3**) were formed in the reaction with stilbene derivatives (step 3b). The reaction involves an assembly of three components, i.e., **2**, a stilbene derivative, and ArSSAr. Herein, we wish to report the details of this method for the synthesis of thiochromans based on the indirect cation pool method.

Scheme 1. Indirect generation of the alkoxycarbenium ion pools and their reactions with carbon nucleophiles

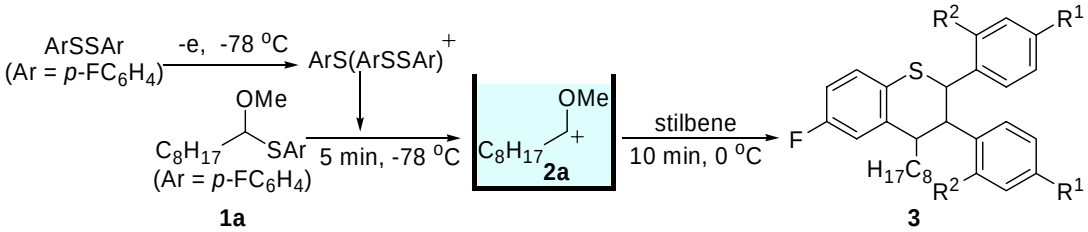


RESULTS AND DISCUSSION

We examined various reaction conditions for the reaction of alkoxycarbenium ion **2a** with *cis*-stilbene, the best result was obtained under the following conditions (Table 1, entry 1). A solution of $ArS(ArSSAr)^+ B(C_6F_5)_4^-$ [12] was generated and accumulated by the anodic oxidation of ArSSAr (1.00 mmol) in $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ at -78 °C (0.30 F/mol).[13] To the anodic solution was added thiocetal **1a** (0.30 mmol) at -78 °C, and the solution was stirred for 5 min. Then, *cis*-stilbene (0.20 mmol) was added, and the temperature was rapidly increased to 0 °C. After stirring for 10 min at the same temperature, triethylamine was added to the solution. Thiochroman **3a** was obtained in 65% yield (d.r. 2.6:1). When *trans*-stilbene was used as a carbon nucleophile, **3a** was also obtained (entry 2). Because a similar diastereoselectivity was observed in both cases, the reactions seem to proceed by a stepwise mechanism involving cationic intermediates rather than a concerted mechanism (vide infra). The reactions of other stilbene derivatives having electron-donating substituents or electron-withdrawing substituents at 4,4' or

2,2'-positions also gave thiochromans (entries 3-6). Although four diastereomers could be formed in all cases, two diastereomers were mainly obtained except for **3e**. The reactions of other alkenes such as 1,1-diphenylethene and 1,1',2,2'-tetramethylethene gave complex mixtures.

Table 1. Reactions of the alkoxycarbenium ion pool **2a** with stilbene derivatives.[a]

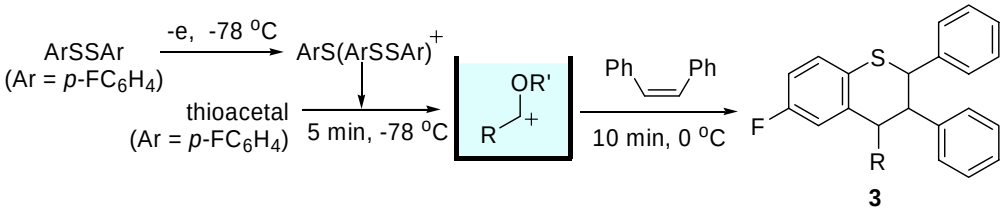


entry	stilbene	R^1	R^2	**3**	diastereomer ratio	% yield[b]
1	*cis*-stilbene	H	H	**3a**	2.6:1	65
2	*trans*-stilbene	H	H	**3a**	2.8:1	70
3	*trans*-4,4'-dimethylstilbene	Me	H	**3b**	3.3:1	77
4	*trans*-4,4'-dimethoxystilbene	OMe	H	**3c**	1.4:1	21[d]
5	*trans*-4,4'-dichlorostilbene	Cl	H	**3d**	1.9:1	43[e]
6	*trans*-2,2'-dimethoxystilbene	H	OMe	**3e**	exclusive	53[c]

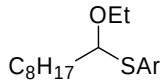
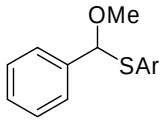
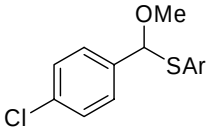
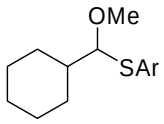
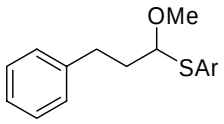
[a] ArSSAr (Ar = *p*-FC_6H_4) (1.00 mmol) was electrolyzed in 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8 mL) at -78 °C using 0.30 F/mol of electricity. The solution of thus obtained $ArS(ArSSAr)^+B(C_6F_5)_4^-$ was allowed to react with thioacetal **1a** (0.30 mmol) at -78 °C for 5 min. Then stilbene (0.20 mmol) was added and the resulting solution was stirred at 0 °C for 10 min. The reaction was quenched with Et_3N (-78 °C). [b] Isolated yield. [c] ^1H NMR yield using $Cl_2CHCHCl_2$ as an internal standard. [d] The purity of the product was ca. 85%. [e] The purity of the product was ca. 95%.

In order to test the applicability of the present method, the reactions of several alkoxycarbenium ions, which were generated from other thioacetals, with *cis*-stilbene were examined (Table 2). When the thioacetal having an ethoxy group instead of a methoxy group was used, thiochroman **3a** was also obtained in 35% yield (entry 1). The diastereoselectivity was similar to that observed in the reaction of **1a** (Table 1, entry 1). Although the reactions of the thioacetals bearing a phenyl and a 4-chlorophenyl groups gave the corresponding products (entries 2 and 3), the thioacetal having a 4-methoxyphenyl group was not effective in this reaction. Alkyl-substituted thioacetals could also be utilized for the construction of thiochromans (entries 4 and 5). NMR measurements (proton homonuclear NOE and coupling constants) of **3f**, which was carried out according to the Katritzky's procedure,[3e] showed that three phenyl groups of the major isomer of **3f** were in all trans configuration.

Table 2. Reactions of other alkoxycarbenium ion pools with *cis*-stilbene.[a]



3

entry	thioacetal	R	**3**	diastereomer ratio	% yield[b]
1		C_8H_{17}	**3a**	2.6:1	35
2		Ph	**3f**	>15:1	53
3		*p*-ClC_6H_4	**3g**	2.2:1	67
4		C_6H_{11}	**3h**	2.4:1	37
5		$PhCH_2CH_2$	**3i**	3.8:1	61

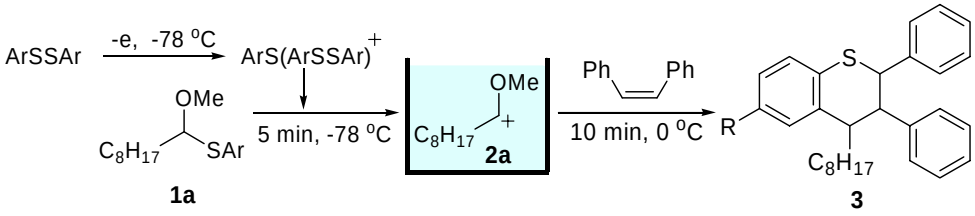
[a] ArSSAr (Ar = *p*-FC_6H_4) (1.00 mmol) was electrolyzed in 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8 mL) at -78 °C using 0.30 F/mol of electricity. The solution of thus obtained $ArS(ArSSAr)^+B(C_6F_5)_4^-$ was allowed to react with a thioacetal (0.30 mmol) at -78 °C for 5 min. Then *cis*-stilbene (0.20 mmol) was added and the resulting solution was stirred at 0 °C for 10 min. The reaction was quenched with Et_3N (-78 °C). [b] Isolated yield.

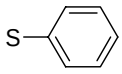
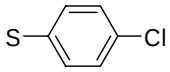
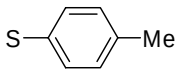
Next, the reactions using other $ArS(ArSSAr)^+$, which were generated from the corresponding ArSSAr having a different *para*-substituent on the aromatic ring, were examined. The results obtained with **2a** and *cis*-stilbene are shown in Table 3. Although $ArS(ArSSAr)^+$ bearing a chloro group on the aryl groups gave **3k** in good yield (entry 2), those without a substituent and bearing a methyl group led to the formation of the desired products in moderate yields (entries 1 and 3).

The present reaction seems to proceed by a stepwise mechanism involving cationic intermediates as shown in Scheme 2. In the first step, **2** reacts with a stilbene derivative to form cationic intermediate **I**. The formation of **3a** with similar diastereoselectivities both from *cis*- and *trans*-stilbene suggests the intermediacy of **I**. The reaction of ArSSAr with **I** gives intermediate **II**, and the formal elimination of the

methoxyl group from **II** gives rise to the formation of cationic intermediate **III**, which undergoes Friedel-Crafts reaction to give **3**.

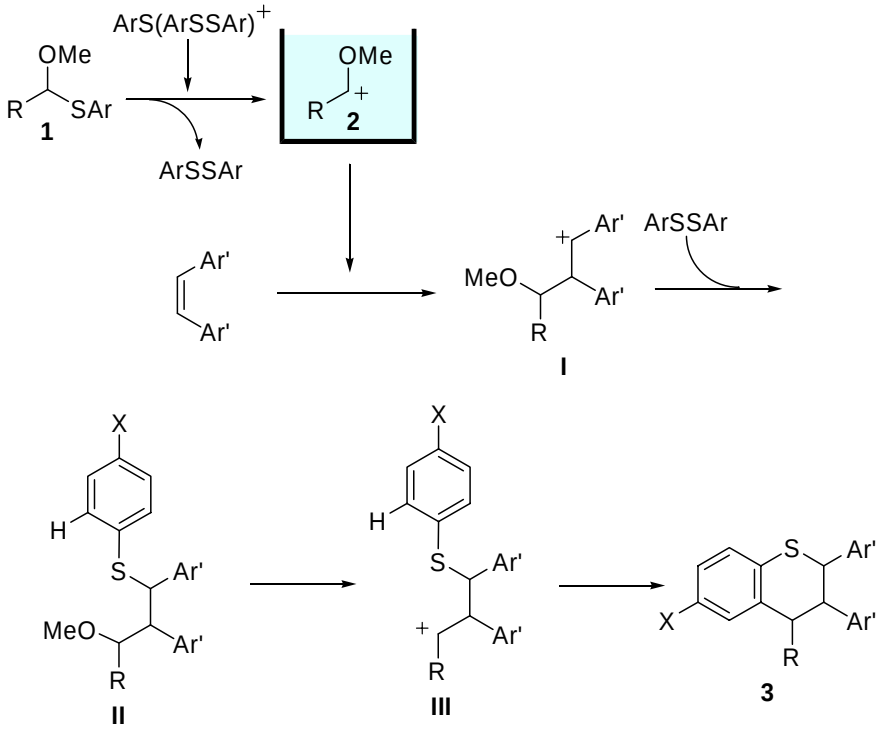
Table 3. Synthesis of thiochromans using other ArS(ArSSAr)$^{+}$.[a]



entry	SAr	R	**3**	diastereomer ratio	% yield[b]
1		H	**3j**	2.6:1	28
2		Cl	**3k**	3.1:1	74
3		Me	**3l**	2.4:1	32[c]

[a] ArSSAr (1.00 mmol) was electrolyzed in 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8 mL) at -78 °C using 0.30 F/mol of electricity. The solution of thus obtained $ArS(ArSSAr)^{+}B(C_6F_5)_4^{-}$ was allowed to react with **1a** (0.30 mmol) at -78 °C for 5 min. Then *cis*-stilbene (0.20 mmol) was added and the resulting solution was stirred at 0 °C for 10 min. The reaction was quenched with Et_3N (-78 °C). [b] Isolated yield. [c] The purity of the product was ca. 85%.

Scheme 2. Plausible mechanism



CONCLUSION

The reactions of alkoxycarbenium ion pools generated by the indirect cation pool method with a variety of stilbene derivatives led to the formation of the corresponding thiochromans. This reaction provides a versatile method for the construction of the thiochroman derivatives by assembling three different components, i.e., an alkoxycarbenium ion, a stilbene derivative, and ArSSAr. It is hoped that a variety of molecules having a thiochroman skeleton will be synthesized based on the present method.

EXPERIMENTAL

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) spectrometer with Me_4Si as an internal standard unless otherwise noted. EI mass spectra were recorded on JMS-SX102A spectrometer. FAB mass spectra were recorded on JMX-HX110A spectrometer. IR spectra were measured with a SHIMADZU FTIR 1600 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 Japan Analytical Industry LC-908 equipped with JAIGEL-1H and 2H using $CHCl_3$ as eluent. All reactions were carried out under Ar atmosphere unless otherwise noted.

Materials. $Bu_4NB(C_6F_5)_4$ was prepared from Bu_4NBr (35.1 g, 109 mmol) and aqueous solution of $NaB(C_6F_5)_4$ (10 wt%, 499 g, 71.1 mmol) in water (100 mL). The mixture was diluted with EtOAc and was washed with water. After drying over $MgSO_4$ and removal of solvent, the precipitate was recrystallized from $CHCl_3$/hexane and dried at 50 ^{o}C/1 mmHg overnight to give $Bu_4NB(C_6F_5)_4$ (65.1 g, 70.6 mmol, 99%). Dichloromethane 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. Dry THF was used as obtained (Kanto Chemical Co., Inc.). ArSSAr (Ar = *p*-FC_6H_4) was prepared according to the procedure in the literature,[14] and identified by the comparison of its spectral data with that of authentic sample.[15] *trans*-2,2'-Methoxystilbene was prepared according to the procedure in the literature,[16] and identified by the comparison of its spectral data with that of authentic sample.[17]

Thioacetals. 1-Methoxy-1-phenylthiononane, 1-methoxy-1-(4-methylphenylthio)nonane and 1-methoxy-1-(4-chlorophenylthio)nonane were prepared according to the literature procedures.[8]

1-Methoxy-1-(4-fluorophenylthio)nonane (1a). To a solution of pelargonaldehyde dimethyl acetal (4.03 g, 21.4 mmol) and *p*-fluorothiophenol (2.30 mL, 21.5 mmol) in toluene (180 mL), was added BF_3-OEt_2 (2.7 mL, 21.5 mmol) at -78 ^{o}C. The solution was stirred for 2 h. Saturated aqueous $NaHCO_3$ was added. The reaction mixture was partitioned between Et_2O and saturated aqueous $NaHCO_3$. The organic phase

was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by flash chromatography (hexane/EtOAc 30:1) to give the title compound (**1a**) (4.23 g, 14.9 mmol, 70%): TLC R_f 0.28 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3H), 1.18-1.32 (m, 10H), 1.34-1.46 (m, 2H), 1.58-1.74 (m, 2H), 3.47 (s, 3H), 4.51 (t, J = 6.4 Hz, 1H), 6.94-7.02 (m, 2H), 7.39-7.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.6, 26.2, 29.1, 29.2, 29.4, 31.8, 35.5, 55.5, 91.0, 115.8 (d, J = 21.7 Hz), 127.9 (d, J = 3.4 Hz), 136.1 (d, J = 8.0 Hz), 162.7 (d, J = 246.0 Hz); IR (neat) 2926, 1590, 1491, 830 cm^{-1}; LRMS (EI) m/z 284 (M^+), 157 (M^+-SC_6H_4F); HRMS (EI) calcd for $C_{16}H_{25}FOS$ (M^+) 284.1610, found 284.1605.

1-Ethoxy-1-(4-fluorophenylthio)nonane. To a solution of pelargonaldehyde (16 mL, 93 mmol) in EtOH (70 mL) was added BF_3-OEt_2 (12.5 mL, 99.5 mmol). Then the mixture was stirred at reflux condition overnight. Saturated aqueous $NaHCO_3$ was added. The reaction mixture was partitioned between Et_2O and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by distillation (80 ^{o}C, 1.79 mmHg) and flash chromatography (hexane/EtOAc 100:1) to give pelargonaldehyde diethyl acetal (1.91 g, 8.83 mmol, 9%). To a solution of pelargonaldehyde diethyl acetal (1.02 g, 4.70 mmol) and *p*-fluorothiophenol (0.55 mL, 5.16 mmol) in toluene (50 mL), was added BF_3-OEt_2 (0.75 mL, 5.97 mmol) at -78 ^{o}C. The solution was stirred for 2 h. Et_3N (2 mL) was added. The reaction mixture was partitioned between Et_2O and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by flash chromatography (hexane/EtOAc 50:1) to give the title compound (722 mg, 2.42 mmol, 51%): TLC R_f 0.52 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3H), 1.18-1.46 (m, 15H), 1.60-1.74 (m, 2H), 3.47 (dq, J = 9.4, 7.2 Hz, 1H), 3.95 (dq, J = 9.4, 7.2 Hz, 1H), 4.58 (t, J = 6.4 Hz, 1H), 6.94-7.02 (m, 2H), 7.40-7.45 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 14.8, 22.6, 26.2, 29.1, 29.2, 29.4, 31.8, 35.8, 63.5, 89.3, 115.7 (d, J = 21.5 Hz), 127.9, 136.2 (d, J = 8.6 Hz), 162.6 (d, J = 245.6 Hz); IR (neat) 2926, 1489, 1086 cm^{-1}; LRMS (EI) m/z 298 (M^+), 253 (M^+-OEt), 171 (M^+-SC_6H_4F), 127 (M^+-$EtOCHC_8H_{17}$); HRMS (EI) calcd for $C_{17}H_{27}FOS$ (M^+) 298.1767, found 298.1765.

Methyl phenyl(4-fluorophenylthio)methyl ether. To a solution of benzaldehyde dimethyl acetal (1.94 g, 12.7 mmol) and *p*-fluorothiophenol (1.35 mL, 12.7 mmol) in toluene (100 mL), was added BF_3-OEt_2 (1.60 mL, 12.6 mmol) at -78 ^{o}C. The solution was stirred for 2 h. Saturated aqueous $NaHCO_3$ was added. The reaction mixture was partitioned between Et_2O and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by flash chromatography (hexane/EtOAc 100:1) to give the title compound (1.92 g, 7.73 mmol, 61%): TLC R_f 0.29 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$)

δ 3.55 (s, 3H), 5.63 (s, 1H), 6.85-6.91 (m, 2H), 7.15-7.25 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.6, 91.1, 115.4 (d, *J* = 21.4 Hz), 126.0, 127.0, 127.7, 127.8, 136.6 (d, *J* = 8.3 Hz), 138.9, 162.7 (d, *J* = 245.6 Hz); IR (neat) 1590, 1489, 1223 cm^{-1}; LRMS (EI) m/z 248 (M^+), 217 (M^+-OMe), 121 (M^+-SC_6H_4F), 77 (M^+-$MeOCHSC_6H_4F$); HRMS (EI) calcd for $C_{14}H_{13}FOS$ (M^+) 248.0671, found 248.0677.

Methyl 4-chlorophenyl(4-fluorophenylthio)methyl ether. To a solution of *p*-chlorobenzaldehyde (8.19 g, 58.3 mmol) in MeOH (55 mL) was added BF_3-OEt_2 (9.0 mL, 71.0 mmol). Then the mixture was stirred at reflux condition overnight. Saturated aqueous $NaHCO_3$ was added. The reaction mixture was partitioned between Et_2O and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. The removal of the solvent gave *p*-chlorobenzaldehyde dimethyl acetal (8.34 g), and this material was used for the subsequent reaction without further purification. To a solution of *p*-chlorobenzaldehyde dimethyl acetal (4.68 g, ca. 25 mmol) and *p*-fluorothiophenol (2.60 mL, 24.4 mmol) in toluene (150 mL), was added BF_3-OEt_2 (3.50 mL, 27.6 mmol) at -78 °C. The solution was stirred for 2 h. Et_3N (8 mL) was added. The reaction mixture was partitioned between Et_2O and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by flash chromatography (hexane/EtOAc 20:1) to give the title compound (3.58 g, 12.7 mmol, ca. 51%): TLC R_f 0.29 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (s, 3H), 5.59 (s, 1H), 6.85-6.92 (m, 2H), 7.06-7.11 (m, 2H), 7.15-7.20 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 56.5, 90.3, 115.6 (d, *J* = 21.5 Hz), 126.3, 127.4, 128.0, 133.4, 137.0 (d, *J* = 7.2 Hz), 137.8, 163.0 (d, *J* = 247.0 Hz); IR (KBr) 1588, 1489, 1219 cm^{-1}; LRMS (FAB) m/z 281 (M^+-H), 251 (M^+-OMe), 171 (M^+-C_6H_4Cl), 155 (M^+-SC_6H_4F); HRMS (FAB) calcd for $C_{14}H_{12}ClFOS$ (M^+) 282.0281, found 282.0278.

Methyl cyclohexyl(4-fluorophenylthio)methyl ether. To a solution of cyclohexanecarbaldehyde (7.38 g, 66 mmol) in MeOH (40 mL) was added BF_3-OEt_2 (10.0 mL, 78.9 mmol). Then the mixture was stirred at reflux condition overnight. Saturated aqueous $NaHCO_3$ was added. The reaction mixture was partitioned between Et_2O and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. The removal of the solvent gave cyclohexanecarbaldehyde dimethyl acetal (8.06 g), and this material was used for the subsequent reaction without further purification. To a solution of cyclohexanecarbaldehyde dimethyl acetal (2.14 g, ca. 14 mmol) and *p*-fluorothiophenol (1.5 mL, 14.0 mmol) in CH_2Cl_2 (90 mL), was added BF_3-OEt_2 (1.70 mL, 13.4 mmol) at -78 °C. The solution was stirred for 2 h. Saturated aqueous $NaHCO_3$ was added. The reaction mixture was partitioned between Et_2O and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by flash chromatography (hexane/EtOAc 50:1) to give the title

compound (1.80 g, 7.1 mmol, ca. 51%): TLC R_f 0.39 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00-1.24 (m, 5H), 1.55-1.66 (m, 2H), 1.68-1.80 (m, 2H), 1.88-2.02 (m, 2H), 3.42 (s, 3H), 4.28 (d, *J* = 7.2 Hz, 1H), 6.94-7.02 (m, 2H), 7.41-7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 26.1, 26.5, 29.5, 30.0, 42.9, 56.5, 97.9, 115.8 (d, *J* = 21.8 Hz), 129.43 (d, *J* = 3.2 Hz), 135.5 (d, *J* = 7.9 Hz), 162.2 (d, *J* = 244.7 Hz); IR (neat) 2926, 1590, 1489 cm^{-1}; LRMS (EI) m/z 254 (M^+), 223 (M^+-OMe), 171 (M^+-C_6H_{11}), 127 (M^+-SC_6H_4F), 83 (M^+-$MeOCHSC_6H_4F$); HRMS (EI) calcd for $C_{14}H_{19}FOS$ (M^+) 254.1141, found 254.1130.

Methyl 2-phenylethyl(4-fluorophenylthio)methyl ether. To a solution of 3-phenylpropionaldehyde (7.88 g, 59 mmol) in MeOH (100 mL) was added BF_3-OEt_2 (10.0 mL, 78.9 mmol). Then, the mixture was stirred at reflux condition overnight. Saturated aqueous $NaHCO_3$ was added. The reaction mixture was partitioned between Et_2O and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. The removal of the solvent gave 3-phenylpropionaldehyde dimethyl acetal (9.34 g), and this material was used for the subsequent reaction without further purification. To a solution of 3-phenylpropionaldehyde dimethyl acetal (1.53 g, ca. 8.5 mmol) and *p*-fluorothiophenol (1.0 mL, 9.4 mmol) in toluene (80 mL), was added BF_3-OEt_2 (1.1 mL, 8.7 mmol) at -78 ^{o}C. The solution was stirred for 2 h. Saturated aqueous $NaHCO_3$ was added. The reaction mixture was partitioned between Et_2O and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by flash chromatography (hexane/EtOAc 20:1) to give the title compound (1.96 g, 7.10 mmol, ca. 84%): TLC R_f 0.35 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90-2.06 (m, 2H), 2.66-2.80 (m, 2H), 3.48 (s, 3H), 4.44 (t, *J* = 6.6 Hz, 1H), 6.95-7.01 (m, 2H), 7.10-7.20 (m, 3H), 7.23-7.28 (m, 2H), 7.39-7.45 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.3, 37.1, 55.6, 89.6, 115.8 (d, *J* = 21.5 Hz), 126.0, 127.3, 128.4, 128.5, 136.3 (d, *J* = 7.2 Hz), 141.0, 162.7 (d, *J* = 247.0 Hz); IR (neat) 1590, 1489, 1455 cm^{-1}; LRMS (EI) m/z 276 (M^+), 149 (M^+-SC_6H_4F); HRMS (EI) calcd for $C_{16}H_{17}FOS$ (M^+) 276.0984, found 276.0981.

Reactions of Indirect Generated Alkoxycarbenium Ion with Stilbenes.

6-Fluoro-4-octyl-2,3-diphenylthiochroman (3a): (Typical Procedure). The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode 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) (254.4 mg, 1.00 mmol) in 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL). In the cathodic chamber were placed 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL) and trifluoromethanesulfonic acid (52.6 mg, 0.351 mmol). The constant current electrolysis (8 mA) was carried out at -78 ^{o}C with magnetic stirring until 0.30 F/mol of electricity was consumed. To the anodic chamber containing electrogenerated $ArS(ArSSAr)^+B(C_6F_5)_4^-$,

was added 1-methoxy-1-(4-fluorophenylthio)nonane (**1a**) (85.2 mg, 0.300 mmol) and the mixture was stirred for 5 min at -78 °C. Then, to thus generated alkoxycarbenium ion pool was added *cis*-stilbene (36.6 mg, 0.203 mmol) and the reaction mixture was stirred for 10 min at 0 °C. The reaction was quenched with Et_3N (1 mL) at -78 °C. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 x 3 cm) of silica gel to remove $Bu_4NB(C_6F_5)_4$. The silica gel was washed with Et_2O (150 mL). The crude product was purified by flash chromatography (hexane/ EtOAc 100:1) (56.7 mg, 65%). This compound was characterized as a mixture of two diastereomers (2.6:1 by ^{1}H NMR analysis): TLC R_f 0.45 (hexane/EtOAc 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.81-0.90 (m, 3H), 1.00-1.48 (m, 14H), 3.11 (t, J = 10.3 Hz, 1H, minor diastereomer), 3.37 (t, J = 3.1 Hz, 1H, major diastereomer), 3.41-3.48 (m, 1H, major diastereomer), 3.53-3.59 (m, 1H, minor diastereomer), 4.21 (d, J = 10.3 Hz, 1H, minor diastereomer), 4.38 (d, J = 3.1 Hz, 1H, major diastereomer), 6.42 (dd, J = 10.3, 2.0 Hz, 1H, minor diastereomer), 6.68 (dd, J = 9.6, 2.8 Hz, 1H, major diastereomer), 6.78-7.30 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) major diastereomer: δ 14.0, 22.6, 27.1, 29.1, 29.2, 29.3, 31.7, 32.3, 40.5, 50.6, 51.4, 114.6 (d, J = 22.5 Hz), 118.5 (d, J = 20.9 Hz), 126.6, 127.0, 127.4 (d, J = 8.0 Hz), 128.1, 128.2, 128.5, 128.6, 129.2, 135.7 (d, J = 6.4 Hz), 140.5, 146.0, 160.2 (d, J = 241.0 Hz), and minor diastereomer (selected): δ 14.1, 26.3, 31.6, 31.8, 33.8, 46.9, 54.7, 56.0, 113.8 (d, J = 20.9 Hz), 117.3 (d, J = 22.5 Hz), 128.3, 129.3, 130.0, 140.8, 142.6, 143.4; IR (neat) 2926, 1601, 1478 cm^{-1}; LRMS (EI) m/z 432 (M^+); HRMS (EI) calcd for $C_{29}H_{33}FS$ (M^+) 432.2287, found 432.2286.

6-Fluoro-4-octyl-2,3-di-*p*-tolylthiochroman (3b). Prepared from ArSSAr (Ar = *p*-FC_6H_4) (257.9 mg, 1.01 mmol), 1-methoxy-1-(4-fluorophenylthio)nonane (**1a**) (87.0 mg, 0.306 mmol) and *trans*-4,4'-dimethylstilbene (38.1 mg, 0.183 mmol) and purified by flash chromatography (hexane/EtOAc 20:1) and purified by GPC (65.1 mg, 77%). This compound was characterized as a mixture of two diastereomers (3.3:1 by ^{1}H NMR analysis): TLC R_f 0.44 (hexane/EtOAc 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.82-0.90 (m, 3H), 1.05-1.48 (m, 14H), 2.23 (s, 3H, minor diastereomer), 2.25 (s, 3H, minor diastereomer), 2.29 (s, 3H, major diastereomer), 2.31 (s, 3H, major diastereomer), 3.06 (t, J = 10.7 Hz, 1H, minor diastereomer), 3.31 (t, J = 3.1 Hz, 1H, major diastereomer), 3.40-3.52 (m, 1H), 4.16 (d, J = 10.7 Hz, 1H, minor diastereomer), 4.32 (d, J = 3.1 Hz, 1H, major diastereomer), 6.40-7.22 (m, 11H); ^{13}C NMR (150 MHz, $CDCl_3$) major diastereomer: δ 14.1, 20.98, 21.01, 22.6, 27.2, 29.1, 29.28, 29.32, 31.8, 32.5, 40.5, 50.2, 51.2, 114.5 (d, J = 23.0 Hz), 118.5 (d, J = 21.5 Hz), 127.4 (d, J = 7.2 Hz), 128.0, 128.5, 128.8, 129.1, 129.2, 135.9 (d, J = 5.7 Hz), 136.1, 136.5, 137.6, 143.2, 160.2 (d, J = 242.7 Hz), and minor diastereomer (selected): δ 26.4, 31.8, 33.9, 47.2, 54.2, 55.7, 113.7 (d, J = 21.6 Hz), 117.2 (d, J = 23.0 Hz), 139.7, 140.4, 160.3 (d, J = 251.3 Hz); IR (neat) 1514, 1478, 1266 cm^{-1}; LRMS (EI) m/z 460 (M^+); HRMS (EI) calcd for $C_{31}H_{37}FS$ (M^+) 460.2600, found 460.2589.

6-Fluoro-2,3-bis-(4-methoxyphenyl)-4-octylthiochroman (3c). Prepared from ArSSAr (Ar = *p*-FC_6H_4) (255.3 mg, 1.00 mmol), 1-methoxy-1-(4-fluorophenylthio)nonane (**1a**) (87.4 mg, 0.307 mmol) and *trans*-4,4'-dimethoxystilbene (47.4 mg, 0.197 mmol) and purified by flash chromatography (hexane/EtOAc 20:1) and purified by GPC (20.4 mg, 21%, purity ca. 85%). This compound was characterized as a mixture of two diastereomers (1.4:1 by ^{1}H NMR analysis): TLC R_f 0.25 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80-0.90 (m, 3H), 1.00-1.50 (m, 14H), 3.01 (t, J = 10.0 Hz, 1H, major diastereomer), 3.27 (t, J = 3.6 Hz, 1H, minor diastereomer), 3.38-3.44 (m, 1H, minor diastereomer), 3.44-3.52 (m, 1H, major diastereomer), 3.72 (s, 3H, major diastereomer), 3.73 (s, 3H, major diastereomer), 3.75 (s, 3H, minor diastereomer), 3.77 (s, 3H, minor diastereomer), 4.11 (d, J = 10.0 Hz, 1H, major diastereomer), 4.28 (d, J = 3.6 Hz, 1H, minor diastereomer), 6.38-7.20 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) major diastereomer: δ 14.3, 22.8, 26.5, 29.26, 29.34, 29.44, 31.9, 34.0, 47.1, 54.0, 55.1, 55.1, 55.3, 113.3, 113.5, 113.6, 113.7, 117.1 (d, J = 22.2 Hz), 128.1 (d, J = 7.9 Hz), 128.9, 130.1, 134.6, 135.5, 141.2 (d, J = 6.7 Hz), 157.6, 157.7, 160.0 (d, J = 240.8 Hz), and minor diastereomer (selected): δ 27.3, 31.9, 32.6, 40.7, 49.9, 51.0, 55.2, 129.4, 132.5, 138.2, 157.9, 158.2; IR (neat) 2926, 1611, 1512 cm^{-1}; LRMS (EI) m/z 492 (M^+); HRMS (EI) calcd for $C_{31}H_{37}FO_2S$ (M^+) 492.2498, found 492.2500.

2,3-Bis-(4-chlorophenyl)-6-fluoro-4-octylthiochroman (3d). Prepared from ArSSAr (Ar = *p*-FC_6H_4) (267.1 mg, 1.05 mmol), 1-methoxy-1-(4-fluorophenylthio)nonane (**1a**) (86.4 mg, 0.304 mmol) and *trans*-4,4'-dichlorostilbene (48.1 mg, 0.193 mmol) and purified by flash chromatography (hexane/EtOAc 10:1) and purified by GPC (42.0 mg, 43%, purity ca. 95%). This compound was characterized as a mixture of two diastereomers (1.9:1 by ^{1}H NMR analysis): TLC R_f 0.47 (hexane/EtOAc 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.82-0.90 (m, 3H), 1.05-1.46 (m, 14H), 3.05 (t, J = 10.6 Hz, 1H, minor diastereomer), 3.31 (t, J = 3.4 Hz, 1H, major diastereomer), 3.33-3.38 (m, 1H, major diastereomer), 3.45-3.53 (m, 1H, minor diastereomer), 4.15 (d, J = 10.6 Hz, 1H, minor diastereomer), 4.30 (d, J = 3.4 Hz, 1H, major diastereomer), 6.36 (dd, J = 10.3, 2.4 Hz, 1H, minor diastereomer), 6.63 (dd, J = 9.6, 2.8 Hz, 1H, major diastereomer), 6.76-7.28 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) major diastereomer: δ 14.1, 22.6, 27.1, 29.1, 29.2, 29.3, 31.7, 32.1, 40.5, 50.0, 50.7, 115.0 (d, J = 21.6 Hz), 118.4 (d, J = 21.5 Hz), 127.7 (d, J = 7.2 Hz), 128.3, 128.6, 128.8, 129.9, 130.5, 132.6, 133.0, 134.8 (d, J = 5.7 Hz), 138.6, 143.9, 160.2 (d, J = 242.7 Hz), and minor diastereomer (selected): δ 26.2, 29.1, 31.8, 33.7, 46.5, 54.0, 55.5, 114.2 (d, J = 23.0 Hz), 117.1 (d, J = 23.0 Hz), 128.5 (d, J = 7.2 Hz), 129.3, 129.7, 132.4 (d, J = 10.1 Hz), 139.7 (d, J = 5.7 Hz), 140.8, 141.7; IR (neat) 2926, 1491, 1094 cm^{-1}; LRMS (EI) m/z 500 (M^+); HRMS (EI) calcd for $C_{29}H_{31}Cl_2FS$ (M^+) 500.1508, found 500.1509.

6-Fluoro-2,3-bis-(2-methoxyphenyl)-4-octylthiochroman (3e). Prepared from ArSSAr (Ar = *p*-FC_6H_4)

(256.4 mg, 1.01 mmol), 1-methoxy-1-(4-fluorophenylthio)nonane (**1a**) (87.5 mg, 0.308 mmol) and *trans*-2,2'-dimethoxystilbene (47.8 mg, 0.199 mmol). The ^{1}H NMR analysis of the crude product indicated that the title compound was formed in 53% yield ($Cl_2CHCHCl_2$ was used as an internal standard): TLC R_f 0.33 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, J = 6.8 Hz, 3H), 1.00-1.58 (m, 14H), 3.35-3.41 (m, 1H), 3.81 (s, 3H), 3.86 (s, 3H), 4.19 (dd, J = 4.8, 3.6 Hz, 1H), 4.75 (d, J = 4.8 Hz, 1H), 6.58 (dd, J = 10.2, 2.4 Hz, 1H), 6.72-6.90 (m, 6H), 7.11-7.18 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 27.6, 29.3, 29.49, 29.51, 31.4, 31.9, 38.7, 42.2, 42.6, 55.4, 55.6, 110.2, 110.3, 113.9 (d, J = 21.9 Hz), 118.1 (d, J = 21.4 Hz), 120.1, 120.3, 127.2, 127.3, 127.4, 129.1, 129.6, 129.8 (d, J = 2.8 Hz), 129.9, 134.1, 137.2 (d, J = 6.7 Hz), 156.1, 157.1, 159.9 (d, J = 240.0 Hz); IR (neat) 2926, 1599, 1242 cm^{-1}; LRMS (EI) m/z 492 (M^+); HRMS (EI) calcd for $C_{31}H_{37}FO_2S$ (M^+) 492.2498, found 492.2494.

6-Fluoro-2,3,4-triphenylthiochroman (3f). Prepared from ArSSAr (Ar = *p*-FC_6H_4) (255.8 mg, 1.01 mmol), methyl phenyl(4-fluorophenylthio)methyl ether (77.9 mg, 0.314 mmol) and *cis*-stilbene (35.1 mg, 0.195 mmol) and purified by flash chromatography (hexane/EtOAc 20:1) and purified by GPC (41.2 mg, 53%). This compound was characterized as a mixture of two diastereomers (>15:1 by ^{1}H NMR analysis): TLC R_f 0.39 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (t, J = 10.8 Hz, 1H), 4.41 (d, J = 10.8 Hz, 1H), 4.66 (d, J = 10.8 Hz, 1H), 6.49 (ddd, J = 10.6, 2.6, 1.2 Hz, 1H), 6.72-7.20 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$) major diastereomer: δ 51.3, 54.9, 56.4, 113.9 (d, J = 22.3 Hz), 117.5 (d, J = 22.3 Hz), 126.0, 126.3, 127.3, 127.6 (d, J = 7.5 Hz), 127.8, 128.12, 128.15, 128.19, 128.19, 129.1, 129.3 (d, J = 2.7 Hz), 139.2, 140.4 (d, J = 6.7 Hz), 141.2, 143.2, 160.0 (d, J = 241.2 Hz); IR (KBr) 1601, 1474, 696 cm^{-1}; LRMS (EI) m/z 396 (M^+); HRMS (EI) calcd for $C_{27}H_{21}FS$ (M^+) 396.1348, found 396.1349.

4-(4-Chlorophenyl)-6-fluoro-2,3-diphenylthiochroman (3g). Prepared from ArSSAr (Ar = *p*-FC_6H_4) (256.6 mg, 1.01 mmol), methyl 4-chlorophenyl(4-fluorophenylthio)methyl ether (88.9 mg, 0.314 mmol) and *cis*-stilbene (36.9 mg, 0.205 mmol) and purified by flash chromatography (hexane/EtOAc 20:1) and purified by GPC (59.5 mg, 67%). This compound was characterized as a mixture of two diastereomers (2.2:1 by ^{1}H NMR analysis): TLC R_f 0.32 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (t, J = 10.8 Hz, 1H), 4.41 (d, J = 10.8 Hz, 1H), 4.67 (d, J = 10.8 Hz, 1H), 6.46-7.22 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$) major diastereomer: δ 50.6, 54.8, 56.4, 114.0 (d, J = 21.8 Hz), 117.6 (d, J = 22.2 Hz), 126.3, 126.4, 127.5 (d, J = 7.5 Hz), 128.0, 128.09, 128.16, 128.19, 128.3, 129.1, 129.5, 130.4, 132.9, 137.8, 140.9, 143.0, 160.1 (d, J = 241.6 Hz), and minor diastereomer (selected): δ 51.2, 54.3, 56.5, 114.1 (d, J = 21.8 Hz), 117.4 (d, J = 22.2 Hz), 128.4, 138.9, 140.28, 140.35, 160.0 (d, J = 241.6 Hz); IR (KBr) 1601, 1453, 698 cm^{-1}; LRMS (EI) m/z 430 (M^+); HRMS (EI) calcd for $C_{27}H_{20}ClFS$ (M^+) 430.0958, found 430.0955.

4-Cyclohexyl-6-fluoro-2,3-diphenylthiochroman (3h). Prepared from ArSSAr (Ar = *p*-FC_6H_4) (255.4

mg, 1.00 mmol), methyl cyclohexyl(4-fluorophenylthio)methyl ether (77.7 mg, 0.305 mmol) and *cis*-stilbene (36.2 mg, 0.201 mmol) and purified by flash chromatography (hexane/EtOAc 20:1) and purified by GPC (30.0 mg, 37%). This compound was characterized as a mixture of two diastereomers (2.4:1 by ^{1}H NMR analysis): TLC R_f 0.38 (hexane/EtOAc 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.65-1.88 (m, 1H), 3.22-3.30 (m, 1H), 3.53-3.60 (m, 1H), 4.21 (d, J = 10.7 Hz, 1H, major diastereomer), 4.30 (d, J = 2.0 Hz, 1H, minor diastereomer), 6.40 (dd, J = 10.3, 2.8 Hz, 1H, major diastereomer), 6.65 (dd, J = 9.6, 2.8 Hz, 1H, minor diastereomer), 6.79-7.33 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) major diastereomer: δ 26.0, 26.3, 26.3, 26.5, 32.1, 39.9, 53.0, 53.9, 55.0, 113.8 (d, J = 21.5 Hz), 116.8 (d, J = 21.5 Hz), 126.3, 128.15, 128.20, 128.25, 128.3, 128.5, 129.3, 129.4, 142.8, 142.9, 160.3 (d, J = 241.3 Hz), and minor diastereomer (selected): δ 25.5, 25.7, 26.2, 30.7, 31.1, 38.6, 45.7, 46.8, 53.3, 114.7 (d, J = 21.6 Hz), 118.4 (d, J = 21.6 Hz), 130.9, 134.6, 140.8, 145.3, 160.1 (d, J = 241.3 Hz); IR (KBr) 1476, 1264, 700 cm^{-1}; LRMS (EI) m/z 402 (M^+); HRMS (EI) calcd for $C_{27}H_{27}FS$ (M^+) 402.1818, found 402.1819.

6-Fluoro-2,3-diphenyl-4-(2-phenylethyl)thiochroman (3i). Prepared from ArSSAr (Ar = *p*-FC_6H_4) (254.4 mg, 1.00 mmol), methyl 2-phenylethyl(4-fluorophenylthio)methyl ether (83.2 mg, 0.301 mmol) and *cis*-stilbene (36.4 mg, 0.202 mmol) and purified by flash chromatography (hexane/EtOAc 20:1) and purified by GPC (52.1 mg, 61%). This compound was characterized as a mixture of two diastereomers (3.8:1 by ^{1}H NMR analysis): TLC R_f 0.39 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50-1.66 (m, 1H), 1.72-1.84 (m, 1H), 2.52-2.84 (m, 2H), 3.15 (t, J = 10.4 Hz, 1H, minor diastereomer), 3.40-3.50 (m, 2H, major diastereomer), 3.54 (dt, J = 10.4, 3.2 Hz, 1H, minor diastereomer), 4.17 (d, J = 10.4 Hz, 1H, minor diastereomer), 4.39 (d, J = 3.6 Hz, 1H, major diastereomer), 6.38-7.30 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$) major diastereomer: δ 33.3, 34.0, 39.9, 50.4, 51.3, 114.5 (d, J = 22.2 Hz), 118.4 (d, J = 21.4 Hz), 125.7, 126.5, 127.0, 127.4 (d, J = 7.6 Hz), 128.1, 128.2, 128.4, 128.5, 129.1, 135.4, 135.6, 140.1, 140.8, 141.0, 145.6, 160.0 (d, J = 241.6 Hz), and minor diastereomer (selected): δ 32.5, 35.6, 54.7, 55.9, 113.8 (d, J = 21.9 Hz), 117.2 (d, J = 22.2 Hz), 126.3, 128.2, 129.2, 143.1, 143.0; IR (neat) 3004, 1601, 1495 cm^{-1}; LRMS (EI) m/z 424 (M^+); HRMS (EI) calcd for $C_{29}H_{25}FS$ (M^+) 424.1661, found 424.1661.

4-Octyl-2,3-diphenylthiochroman (3j). Prepared from PhSSPh (222.4 mg, 1.02 mmol), 1-methoxy-1-phenylthiononane (83.2 mg, 0.312 mmol) and *cis*-stilbene (36.6 mg, 0.203 mmol) and purified by flash chromatography (hexane/EtOAc 20:1) and purified by GPC (23.4 mg, 28%). This compound was characterized as a mixture of two diastereomers (2.6:1 by ^{1}H NMR analysis): TLC R_f 0.37 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, J = 7.2 Hz, 3H, major diastereomer), 0.85 (t, J = 6.8 Hz, 3H, minor diastereomer), 1.00-1.48 (m, 14H), 3.15 (t, J = 10.4 Hz, 1H, minor diastereomer), 3.60 (t, J = 3.2 Hz, 1H, major diastereomer), 3.42-3.50 (m, 1H, major diastereomer), 3.56-3.64 (m, 1H,

minor diastereomer), 4.25 (d, J = 10.4 Hz, 1H, minor diastereomer), 4.41 (d, J = 3.2 Hz, 1H, major diastereomer), 6.65-7.29 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) major diastereomer: δ 14.2, 22.8, 27.3, 29.2, 29.42, 29.44, 31.9, 32.7, 40.2, 50.8, 51.4, 124.3, 126.0, 126.2, 126.6, 126.7, 127.9, 128.3, 128.6, 129.2, 132.1, 133.4, 134.9, 140.6, 146.6, and minor diastereomer (selected): δ 26.4, 29.3, 29.4, 31.9, 33.8, 46.5, 54.6, 56.2, 124.2, 125.9, 126.1, 126.2, 127.9, 128.10, 128.12, 129.2, 130.7, 138.3, 142.5, 144.2; IR (neat) 2926, 1453, 700 cm^{-1}; LRMS (EI) m/z 414 (M^+); HRMS (EI) calcd for $C_{29}H_{34}S$ (M^+) 414.2381, found 414.2379.

6-Chloro-4-octyl-2,3-diphenylthiochroman (3k). Prepared from ArSSAr (Ar = p-ClC_6H_4) (287.9 mg, 1.00 mmol), 1-methoxy-1-(4-chlorophenylthio)nonane (90.9 mg, 0.302 mmol) and *cis*-stilbene (35.9 mg, 0.199 mmol) and purified by flash chromatography (hexane/EtOAc 20:1) and purified by GPC (66.4 mg, 74%). This compound was characterized as a mixture of two diastereomers (3.1:1 by ^{1}H NMR analysis): TLC R_f 0.29 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81-0.87 (m, 3H), 1.00-1.50 (m, 14H), 3.11 (t, J = 10.4 Hz, 1H, minor diastereomer), 3.34 (t, J = 3.2 Hz, 1H, major diastereomer), 3.40-3.48 (m, 1H, major diastereomer), 3.52-3.60 (m, 1H, minor diastereomer), 4.19 (d, J = 10.4 Hz, 1H, minor diastereomer), 4.36 (d, J = 3.2 Hz, 1H, major diastereomer), 6.65-7.30 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) major diastereomer: δ 14.2, 22.7, 27.2, 29.2, 29.3, 29.4, 31.86, 31.91, 32.6, 40.3, 50.4, 51.4, 126.5, 126.9, 127.0, 127.2, 128.0, 128.4, 128.5, 129.1, 129.6, 131.7, 133.6, 135.2, 140.23, 145.8, and minor diastereomer (selected): δ 26.3, 29.3, 31.9, 33.8, 46.7, 54.5, 56.0, 126.2, 126.36, 126.39, 128.1, 128.2, 129.1, 129.8, 130.3, 132.1, 140.2, 142.2, 143.2; IR (neat) 2926, 1468, 1103 cm^{-1}; LRMS (EI) m/z 448 (M^+); HRMS (EI) calcd for $C_{29}H_{33}ClS$ (M^+) 448.1992, found 448.1981.

6-Methyl-4-octyl-2,3-diphenylthiochroman (3l). Prepared from ArSSAr (Ar = p-MeC_6H_4) (250.7 mg, 1.02 mmol), 1-methoxy-1-(4-methylphenylthio)nonane (82.4 mg, 0.294 mmol) and *cis*-stilbene (36.0 mg, 0.200 mmol) and purified by flash chromatography (hexane/EtOAc 20:1) and purified by GPC (27.6 mg, 32%, purity ca. 85%). This compound was characterized as a mixture of two diastereomers (2.4:1 by ^{1}H NMR analysis): TLC R_f 0.36 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80-0.88 (m, 3H), 1.00-1.48 (m, 14H), 2.10 (s, 3H, minor diastereomer), 2.17 (s, 3H, major diastereomer), 3.12 (t, J = 10.0 Hz, 1H, minor diastereomer), 3.32 (t, J = 2.8 Hz, 1H, major diastereomer), 3.42-3.48 (m, 1H, major diastereomer), 3.50-3.58 (m, 1H, minor diastereomer), 4.21 (d, J = 10.0 Hz, 1H, minor diastereomer), 4.36 (d, J = 2.8 Hz, 1H, major diastereomer), 6.51 (br s, 1H, minor diastereomer), 6.73-6.76 (m, 1H, major diastereomer), 6.80-7.30 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) major diastereomer: δ 14.2, 21.0, 22.8, 27.2, 29.2, 29.40, 29.44, 31.9, 32.9, 40.0, 50.9, 51.5, 125.8, 126.1, 126.7, 127.7, 127.9, 128.1, 128.2, 128.6, 129.2, 132.7, 133.1, 133.8, 140.7, 146.8, and minor diastereomer (selected): δ 21.0, 26.5, 29.3, 29.4, 29.8, 31.9, 33.8, 46.7, 54.7, 56.9, 125.8, 126.2, 126.9, 127.1, 127.8, 129.2, 130.0, 131.2, 131.3,

133.9, 138.2, 142.8, 144.3; IR (neat) 2924, 1453, 700 cm^{-1}; LRMS (EI) m/z 428 (M^+); HRMS (EI) calcd for $C_{30}H_{36}S$ (M^+) 428.2538, found 428.2537.

ACKNOWLEDGEMENTS

This work was financially supported in part by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science. We are also grateful to Nippon Shokubai Co. and Nippoh Chemicals Co. for providing sodium tetrakis(pentafluorophenyl)borate as a precursor of $Bu_4NB(C_6F_5)_4$.

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