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Acid-Promoted Reaction of Trimethylsilylketene Bis(ethylthio)acetal with Imines. Synthesis of γ,γ-Bis(ethylthio)allylamines

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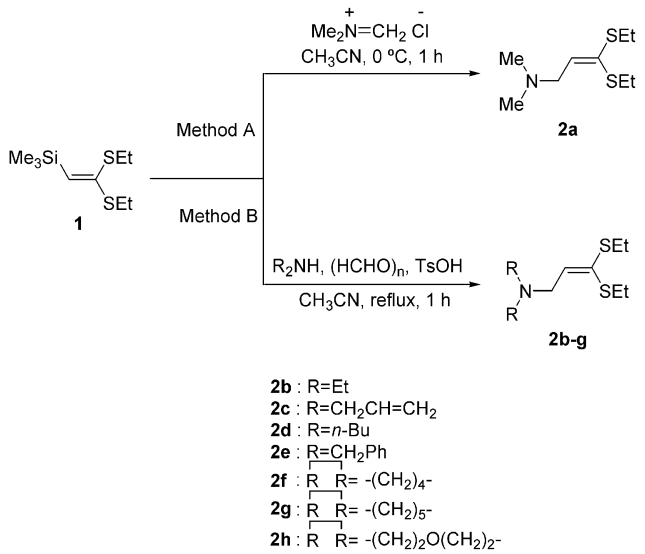
Abstract: Acid-catalyzed reaction of silylketene dithioacetal **1** with iminium salts or imines **3b**,**d**−**h** gave the corresponding γ,γ-bis(ethylthio)allylamines **2a**−**h** or **5b**,**d**−**h** in generally high yields. Similar reactions of **1** with (salicylidene)-amines **6a**−**e** afforded 4-amino-2,2-bis(ethylthio)chromans **8a**−**e** in good to moderate yields.

The reaction of allylsilanes with aldehydes and ketones in the presence of Lewis acids or fluoride ions is known as the Sakurai−Hosomi reaction,[1] which has been extensively studied and applied successfully in organic synthesis.[2] Similar treatment of imines with allylsilanes leads to homoallylamines.[3] In contrast, little is known about the reaction between their homologous vinylsilanes and carbonyl compounds or imines, except for cases using either special vinylsilanes,[2f,4] or reactive carbonyl compounds[2f,5] or imines[2h] and a few examples using vinylsilanes containing iminium functionality in the molecule.[6]

We have recently reported that highly reactive silylketene bis(ethylthio)acetal **1**, the vinylsilane family, reacted readily with a wide variety of aldehydes under the presence of Lewis acids to give deoxygenative di[β,β-bis(ethylthio)]vinylation products of aldehydes.[7] To develop further synthetic utility of silylketene dithioacetal **1**, we have become interested in investigating the reactiviy of **1** toward imino compounds.

We found acid-promoted condensation of **1** and imino compounds. We report herein β,β-bis(ethylthio)vinylation of imino compounds with **1** and synthetic application of this reaction to functionalized chromans.

SCHEME 1



Reaction of Silylketene Dithioacetal with Iminium Salts. The reaction of **1** (1 equiv) with *N*,*N*-dimethyl(methylene)iminium chloride (1.2 equiv) was carried out in CH_3CN under mild conditions (0 °C, 1 h) to afford an expected bis(ethylthio)allylamine **2a** in good yield (method A in Scheme 1, entry 1 in Table 1). To investigate the dependence of substituents of iminium salts upon this Mannich-type condensation, the reaction using a wide variety of in-situ generated iminium salts was carried out. A mixture of **1** (1 equiv), dialkylamines (2 equiv), and excess paraformaldehyde (20 equiv) in CH_3CN containing *p*-toluenesulfonic acid monohydrate (1.9 equiv) was heated at reflux for 1 h to afford the corresponding bis(ethylthio)allylamines **2b**−**g** in 67−86% yields (method B, entries 2−8). Regardless of substituents of iminium ions, reaction of iminium salts proceeded cleanly with **1** to provide allylic amines (Scheme 1).

Acid-Promoted Reaction of Silylketene Dithioacetal with Imines. The above results led us to investigate acid-promoted condensation of **1** and imines. First, by analogy to the reaction of **1** with carbonyl compounds,[7] silylketene dithioacetal **1** (1 equiv) was treated with (benzylidene)aniline (**3a**) (1.2 equiv) and TMSOTf (1.1 equiv) or CF_3CO_2H (1.1 equiv) in CH_3CN at 0 °C for 2−4

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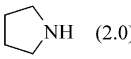
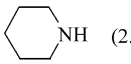
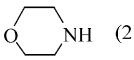
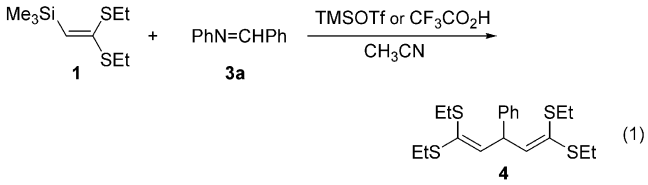
TABLE 1. Reaction of 1 with *N,N*-Dialkyl(methlene)iminium Salts[a]

entry	R_2NH (equiv)	Method	Product[b] (yield, %)
1[c]	Me_2NH (1.2)	A	**2a** (88)
2	Et_2NH (2.0)	B	**2b** (76)
3	$(CH_2{=}CHCH_2)_2NH$ (2.0)	B	**2c** (67)
4	Bu_2NH (2.0)	B	**2d** (86)
5[d]	$(PhCH_2)_2NH$ (2.0)	B	**2e** (82)
6	 (2.0)	B	**2f** (84)
7	 (2.0)	B	**2g** (85)
8	 (2.0)	B	**2h** (84)

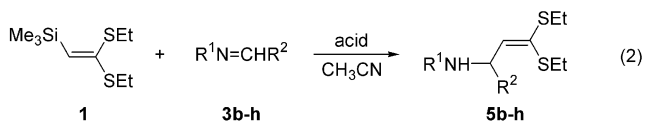
[a] All reactions were carried out using excess $(HCHO)_n$ (20 equiv) and $TsOH{\cdot}H_2O$ (1.9 equiv) at reflux for 1 h in CH_3CN unless otherwise noted. [b] Isolated yield. Yields were based on **1**. [c] The reaction was carried out at 0 °C using *N,N*-dimethyl(methylene)-iminium chloride. [d] CH_3CN/H_2O (1:1) was used as a solvent.

h. 1,1,5,5-Tetrakis(ethylthio)-3-phenyl-1,4-pentadiene **4** was obtained unexpectedly in 83% yield (eq 1), which could be produced from acid-catalyzed deaminative addition of another **1** to an initially formed allylamine derivative.



(1)

However, the reaction using (benzylidene)butylamine **3b** instead of **3a** under the same conditions [TMSOTf (1.1 equiv), 0 °C, 4 h] or similar conditions [TMSOTf (1.1 equiv), rt, 4 h] led to desired allylamine **5b** in moderate yield (40% yield) or a mixture of **5b** (12%) and **4** (82%) (eq 2) (entries 1 and 2 in Table 2). Use of Lewis acids such as $BF_3{\cdot}OEt_2$, $TiCl_4$, or $EtAlCl_2$ did not improve the yields of **5b**, and **4** was similarly obtained as a major product.



(2)

3b **5b** : R^1=*n*-Bu, R^2=Ph
3c **5c** : R^1=*t*-Bu, R^2=Ph
3d **5d** : $R^1=CH_2Ph$, R^2=Ph
3e **5e** : R^1=allyl, R^2=Ph
3f **5f** : $R^1=CH_2CH_2OH$, R^2=Ph
3g **5g** : $R^1=CH_2Ph$, R^2=*i*-Pr
3h **5h** : $R^1=CH_2Ph$, R^2=*t*-Bu

TABLE 2. Acid-Promoted Reaction of 1 with Imines 3[a]

entry	**3** (equiv)	acid (equiv)	conditions *T*, °C	conditions time, h	product[b] (yield, %)
1	**3b** (1.2)	TMSOTf (1.1)	0	4	**5b** (40)
2	**3b** (1.2)	TMSOTf (1.1)	rt	4	**5b** (12), **4** (82)
3	**3b** (1.2)	CF_3CO_2H (1.1)	rt	10	**5b** (42), **4** (20)
4	**3b** (1.2)	CF_3CO_2H (1.1)	0	2	**5b** (85)
5	**3c** (1.2)	CF_3CO_2H (2.0)	0	2	no reaction
6	**3d** (1.2)	CF_3CO_2H (2.0)	0	2	**5d** (82)
7	**3e** (1.2)	CF_3CO_2H (2.0)	0	2	**5e** (86)
8	**3f** (1.2)	CF_3CO_2H (2.0)	0	2	**5f** (61), **4** (11)
9	**3g** (1.2)	CF_3CO_2H (2.0)	rt	1.5	**5g** (75)
10	**3g** (2.4)	CF_3CO_2H (4.0)	rt	2	**5g** (90)
11	**3h** (2.4)	CF_3CO_2H (4.0)	rt	10	**5h** (87)

[a] All reactions were carried out in CH_3CN. [b] Isolated yield. Yields were based on **1**.

To suppress the deaminative vinylation of **5b** with **1**, we next examined the use of protic acids.[8] The reaction of **1** (1 equiv) with **3b** (1.2 equiv) was carried out in the presence of CF_3CO_2H (1.1 equiv) at 0 °C to afford **5b** in satisfactory yield (85%) without contamination of **4** (entry 4), while the reaction at elevated temperature (room temperature) resulted in reduced yield of **5b** (42%) along with **4** (20%) (entry 3). Thus, the formation of **5b** is dependent upon acid used and reaction temperature.

To explore the scope and limitations of this CF_3CO_2H-promoted intermolecular coupling of **1** with imines, the reactions of various (benzylidene)amines **3c**−**f** and (alkylidene)amines **3g**,**h** with **1** were studied under similar conditions.

In contrast to **3b**, no reaction of (benzylidene)-*tert*-butylamine **3c** with **1** occurred to give the corresponding allylamine **5c**, but only starting materials were recovered (entry 5). This result shows that bulkiness of the N-substituent of imines plays an important role in coupling reaction with **1**. (Benzylidene)alkylamines **3d**−**f** and (alkylidene)benzylamines **3g**,**h** as well as **3b** underwent the CF_3CO_2H-promoted addition of **1** at 0 °C to room temperature to afford the corresponding allylamines **5d**−**h** in 61−90% yields (entry 6−11). On the other hand, the reaction using α,β-unsaturated imines such as (cinnamylidene)- and (crotylidene)butylamines under similar conditions did not give the expected 1,2- or 1,4-addition product either.

The above results indicate that, for the CF_3CO_2H-promoted addition of **1** to imines **3** to produce allylamines, either R^1 or R^2 in **3** must be an alkyl group and R^1 must not be a *tert*-butyl group.

Synthesis of Amino-Functionalized Benzopyranes via Condensation Reaction of (Salicylidene)-amines with Silylketene Dithioacetal. In conjunction with our continuing interest in the development of new annulating methods utilizing **1**, we investigated the reaction of **1** with (*o*-heteroatom-functionalized benzylidene)amines as well as the corresponding benzaldehydes.[7]

Treatment of (salicylidene)butylamine (**6a**) (1.2 equiv) with **1** (1.0 equiv) in the presence of CF_3CO_2H (2.0 equiv) led exclusively to 4-[2,2-bis(ethylthio)vinyl]-2,2-bis(ethylthio)chroman **7** (62%) (eq 3) (entry 1 in Table 3),

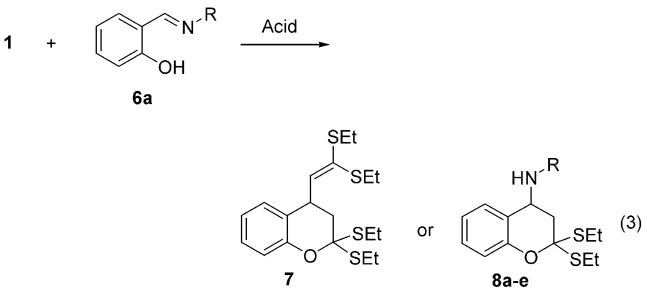
(8) Trifluoroacetic acid-promoted cyclization of imines containing the vinylsilane moiety has been reported.[6a]

TABLE 3. Acid-Promoted Reaction of 1 with (Salicylidene)Amines 6

				conditions		
entry	**6** (equiv)	acid (equiv)	solvent[b]	*T*, °C	time, h	product[b] (yield, %)
1	**6a** (1.2)	CF_3CO_2H (2.0)	MeCN	0 to rt	10	**7** (62)
2	**6a** (1.2)	CF_3SO_3H (0.1)	MeCN	rt	40−75	**8a** (17−26)
3	**6a** (2.0)	CF_3SO_3H (0.1)	MeCN/HFIP	0	24	**8a** (43)
4	**6a** (4.0)	CF_3SO_3H (2.0)	MeCN/HFIP	0	24	**8a** (95)
5	**6b** (4.0)	CF_3SO_3H (2.0)	MeCN/HFIP	0	10	**8b** (63)
6	**6c** (4.0)	CF_3SO_3H (2.0)	MeCN/HFIP	0	11	**8c** (80)
7	**6d** (4.0)	CF_3SO_3H (2.0)	MeCN/HFIP	0	18	**8d** (45)
8	**6e** (4.0)	CF_3SO_3H (2.0)	MeCN/HFIP	0	10	**8e** (50)

[a] Isolated yield. Yields were based on silylketene dithioacetal **1**. [b] A mixed solvent of CH_3CN−HFIP (9:1) was used except for entries 1 and 2.

formation of which has been also found by the $BF_3{\cdot}OEt_2$-promoted reaction of **1** with salicylaldehyde.[7]



6a, 8a: R=CH_2Ph
6b, 8b: R=*n*-Bu
6c, 8c: R=$CH_2CH{=}CH_2$
6d, 8d: R=CH_2CH_2OH
6e, 9e: R=-$(CH_2)_3OH$

However, the use of a catalytic amount of CF_3SO_3H (0.1 equiv), instead of CF_3CO_2H, and prolonged reaction time (40−75 h) led to an expected annulation product, 4-butylamino-2,2-bis(ethylthio)chroman (**8a**), albeit in low yields (17−26%) (Table 3, entry 2).

To improve the yield of **8a**, a number of reaction conditions were examined, and representative ones are shown in Table 3. Optimum reaction conditions involved the use of excess **6a** (4 equiv) and CF_3SO_3H (2 equiv) to **1** (1 equiv) in a 9:1 mixed solvent of CH_3CN and hexafluoro-2-propanol (HFIP) at 0 °C for 24 h, and the yield of **8a** increased up to 95% (Table 3, entry 4). Various types of (salicylidene)amines **6b**−**e** were also subjected to such optimum conditions to produce the corresponding 4-amino-2,2-bis(ethylthio)chromans **8b**−**e** in good to moderate yields (Table 3, entries 5−8).

Conclusion. We note the following results from this investigation:

(1) Silylketene dithioacetal **1** reacted with iminium salts and imines in the presence of acid to produce allylamines.

(2) A new synthetic approach to 4-aminochromans was developed by the acid-promoted reaction of (salicylidene)-amines with **1**.

Experimental Section

Materials. Acetonitrile (CH_3CN) was distilled from P_2O_5 and redistilled from CaH_2. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl in a recycling still. Hexsafluoroisopropyl alcohol (HFIP) was distilled from Molecular Sieves Powder. TMSOTf was prepared from tetramethylsilane ($SiMe_4$) and trifluoromethansulfonic acid anhydride, after it was distilled. Other reagents were purified and dried by standard procedures. Silylketene dithioacetal **1**[7] and *N*,*N*-dimethyl(methylene)iminium chloride[9] were prepared according to the literature procedure.

General Methods. All reactions were carried out under nitrogen or argon atomosphere. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$, operating ^1H at 400 or 500 MHz and ^{13}C NMR at 101 or 126 MHz with $SiMe_4$ as an internal standard. IR spectra were recorded on thin films on KBr plates. Mass spectra were recorded at 70 eV. Column chromatography on silica gel was performed with Fuji Silysia BW-127ZH. Preparative TLC was performed on Wakogel B-5F/TLC-cards (20 × 20 × 0.7 cm).

Reaction of 1 with *N*,*N*-Dimethyl(methylene)iminium Chloride. To a solution of *N*,*N*-dimethyl(methylene)iminium chloride (51.0 mg, 0.55 mmol) in CH_3CN (3.0 mL) was added a solution of **1** (0.45 mmol) in CH_3CN (2.0 mL) at 0 °C, and then the mixture was stirred at this temperature for 1.0 h. The reaction was quenched with the addition of aqueous $NaHCO_3$. The mixture was extracted with $CHCl_3$, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on preparative TLC (silica gel, AcOEt/ hexane = 1:10) to afford 3-(dimethyamino)-1,1-bis(ethylthio)-1-propene (**2a**) (81.3 mg, 0.40 mmol, 88%) as a yellow oil: IR (neat) 2969, 2925 1454, 1259, 1025 cm^{-1}; ^1H NMR (400 MHz) δ 1.22 (3H, t, J = 7.3 Hz), 1.25 (3H, t, J = 7.3 Hz), 2.26 (6H, s), 2.74 (2H, q, J = 7.3 Hz), 3.26 (4H, d, J = 6.6 Hz), 6.13 (1H, t, J = 6.6 Hz); ^{13}C NMR (400 MHz) δ 14.2, 15.2, 27.0, 27.3, 45.2, 58.7, 132.5, 134.8. Anal. Calcd for $C_9H_{19}NS_2$: C, 52.63; H, 9.32; N, 6.82. Found: C, 52.90; H, 9.31; N, 6.55.

General Procedure for the Synthesis of Bis(ethylthio)-allylamines 2b−h. To a suspension of $(HCHO)_n$ (190.7 mg, 6.35 mmol) and $TsOH{\cdot}H_2O$ (0.61 mmol) in CH_3CN (1.0 mL) was added a solution of **1** (0.32 mmol) and a secondary amine (125 mg, 0.64 mmol) in CH_3CN (1.0 mL) at room temperature, and the mixture was stirred under reflux for 1.5 h. The reaction was quenched with the addition of aqueous $NaHCO_3$. The reaction mixture was extracted with AcOEt, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on preparative TLC (silica gel, AcOEt/ hexane = 1:10) to afford bis(ethylthio)allylamines **2b**−**h**. The reaction conditions and yield of **2b**−**h** are summarized in Table 1. The compounds **2a**−**d** had the following properties. The properties for compounds **2e**−**h** are provided in the Supporting Information.

3-(Diethylamino)-1,1-bis(ethylthio)-1-propene (2b): yellow oil; IR (neat) 1448, 1373, 1259, 1054, 968 cm^{-1}; ^1H NMR (400 MHz) δ 1.05 (6H, t, J = 7.2 Hz), 1.22 (3H, t, J = 7.3 Hz), 1.24 (3H, t, J = 7.3 Hz), 2.54 (4H, q, J = 7.2 Hz), 2.73 (2H, q, J = 7.3 Hz), 2.79 (2H, q, J = 7.3 Hz), 3.43 (2H, d, J = 6.5 Hz), 6.16 (1H, t, J = 6.5 Hz); ^{13}C NMR (400 MHz) δ 11.8, 14.1, 15.0, 26.7, 27.1, 46.8, 52.0, 131.3, 135.4. Anal. Calcd for $C_{11}H_{23}NS_2$: C, 56.60; H, 9.93; N, 6.00. Found: C, 56.26; H, 9.76; N, 5.87.

3-(Diallylamino)-1,1-bis(ethylthio)-1-propene (2c): yellow oil; IR (neat) 1446, 1259, 1118, 995, 917 cm^{-1}; ^1H NMR (400

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MHz) δ 1.21 (3H, t, J = 7.3 Hz), 1.24 (3H, t, J = 7.3 Hz), 2.73 (2H, q, J = 7.3 Hz), 2.78 (2H, q, J = 7.3 Hz), 3.09 (4H, d, J = 6.5 Hz), 3.40 (2H, q, J = 6.5 Hz), 5.13−5.20 (4H, m), 5.81−5.91 (2H, m), 6.14 (1H, t, J = 6.5 Hz); ^{13}C NMR (400 MHz) δ 14.1, 15.1, 26.8, 27.2, 52.8, 56.7, 117.7, 131.9, 135.4, 135.5. Anal. Calcd for $C_{13}H_{23}NS_2$: C, 60.65; H, 9.00; N, 5.44. Found: C, 60.28; H, 8.97; N, 5.28.

3-(Dibutylamino)-1,1-bis(ethylthio)-1-propene (2d): yellow oil; IR (neat) 1456, 1373, 1259, 1087, 968 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.83 (6H, t, J = 7.3 Hz), 1.15 (3H, t, J = 7.3 Hz), 1.17 (3H, t, J = 7.3 Hz), 1.18−1.27 (4H, m), 1.33−1.40 (4H, m), 2.33−2.37 (4H, m), 2.65 (2H, q, J = 7.3 Hz), 2.71 (2H, q, J = 7.3 Hz), 3.30 (2H, d, J = 6.5 Hz), 6.10 (1H, t, J = 6.5 Hz); ^{13}C NMR (400 MHz) δ 14.0, 14.2, 15.0, 20.6, 26.8, 27.1, 29.3, 53.2, 53.7, 131.0, 136.3. Anal. Calcd for $C_{15}H_{31}NS_2$: C, 62.22; H, 10.79; N, 4.84. Found: C, 62.61; H, 10.51; N, 4.54.

Reaction of 1 with Imines 3. General Procedure. To a solution of **1** (100 mg, 0.45 mmol) and an imine (0.55 mmol) in CH_3CN (5.0 mL) was added CF_3CO_2H (0.91 mmol) at 0 °C or room temperature, and the mixture was stirred for 2 h. The reaction was quenched with the addition of Et_3N (ca. 1 mL) followed by aqueous $NaHCO_3$. After similar workup, the residue was chromatographed on preparative TLC (silica gel, AcOEt/ hexane = 1:10) to afford allylamines **5b**,**d**−**h**. The reaction conditions and yield of **5b**,**d**−**h** are summarized in Table 2. The compounds **5b**,**d**,**e** had the following properties. The properties for compounds **5f**−**h** are provided in the Supporting Information.

3-(Butylamino)-1,1-bis(ethylthio)-3-phenyl-1-propene (5b): yellow oil; IR (neat) 1454, 1261, 1118, 757, 700 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.89 (3H, t, J = 7.3 Hz), 1.18 (3H, t, J = 7.3 Hz), 1.23 (3H, t, J = 7.3 Hz), 1.33 (1H, tt, J = 7.3 Hz, J = 7.3 Hz), 1.40−1.52 (3H, m), 2.50−2.65 (2H, m), 2.69−2.88 (4H, m), 4.99 (1H, d, J = 8.7 Hz), 6.12 (1H, d, J = 8.7 Hz), 7.20−7.23 (1H, m), 7.29−7.32 (2H, m), 7.37−7.39 (2H, m); ^{13}C NMR (400 MHz) δ 13.9, 14.0, 15.2, 20.4, 26.8, 27.2, 32.3, 47.3, 61.9, 127.0, 127.1, 128.4, 131.0, 140.6, 143.1. Anal. Calcd for $C_{17}H_{27}NS_2$: C, 65.96; H, 8.79; N, 4.53. Found: C, 66.09; H, 8.79; N, 4.42.

3-(Benzylamino)-1,1-bis(ethylthio)-3-phenyl-1-propene (5d): yellow oil; IR (neat) 1600, 1452, 1261, 1027, 700 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.18 (3H, t, J = 7.3 Hz), 1.19 (3H, t, J = 7.3 Hz), 1.63 (1H, s), 2.64−2.84 (4H, m), 3.73 (2H, d, J = 6.8 Hz), 5.06 (1H, d, J = 8.8 Hz), 6.16 (1H, d, J = 8.8 Hz), 7.20−7.25 (2H, m), 7.27−7.33 (6H, m); ^{13}C NMR (400 MHz) δ 14.0, 15.1, 17.2, 26.8, 51.4, 61.5, 127.0, 127.2, 128.1, 128.2, 128.5, 131.6, 140.1, 140.4, 142.8. Anal. Calcd for $C_{20}H_{25}NS_2$: C, 69.92; H, 7.33; N, 4.08. Found: C, 69.82; H, 7.39; N, 4.02.

3-(Allylamino)-1,1-bis(ethylthio)-3-phenyl-1-propene (5e): yellow oil; IR (neat) 1490, 1454, 1263, 917, 759 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.18 (3H, t, J = 7.3 Hz), 1.21 (3H, t, J = 7.3 Hz), 1.49 (1H, s), 2.57−2.85 (4H, m), 3.15−3.27 (2H, m), 5.03 (1H, d, J = 8.9 Hz), 5.09 (1H, dd, J = 5.9 Hz, J = 10.3 Hz), 6.13 (1H, d, J = 8.9 H), 7.20−7.24 (1H, m), 7.28−7.32 (2H, m), 7.38−7.40 (2H, m); ^{13}C NMR (400 MHz) δ 14.0, 15.1, 26.8, 27.1, 49.9, 51.2, 115.8, 127.0, 127.1, 128.4, 131.5, 136.7, 142.8. Anal. Calcd for $C_{16}H_{23}NS_2$: C, 65.50; H, 7.90; N, 4.77. Found: C, 65.35; H, 7.96; N, 4.75.

Synthesis of 4-Aminochroman Derivatives 8a−e from (Salicylidene)amines 6a−e and 1. General Procedure. To a solution of **1** (50 mg, 0.23 mmol) and (salicylidene)amine **6** (0.91 mmol) in CH_3CN (2.7 mL) was added a solution of CF_3SO_3H (0.45 mmol) in HFIP at 0 °C, and the mixture was stirred for 10−24 h. The reaction was quenched with the addition of aqueous $NaHCO_3$. After similar workup, the residue was chromatographed on preparative TLC (silica gel, AcOEt/ hexane = 1:10) to afford 4-aminochromans **8a**−**e**. The reaction conditions and yield of **8a**−**e** are summarized in Table 3. The compounds **8a**,**d** had the following properties. The properties for compounds **8b**,**c**,**e** are provided in the Supporting Information.

4-(Butylamino)-2,2-bis(ethylthio)chroman (8a): yellow oil; IR (neat) 1583, 1483, 1454, 1218, 912 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.93 (3H, t, J = 7.3 Hz), 1.22 (3H, t, J = 7.5 Hz), 1.28 (3H, t, J = 7.5 Hz), 1.34−1.45 (3H, m,), 1.47−1.57 (2H, m), 2.38 (1H, dd, J = 9.1 Hz, J = 13.9 Hz), 2.61−2.69 (2H, m,), 2.74−2.89 (5H,m), 4.16 (1H, dd, J = 6.0 Hz, J = 9.1 Hz), 6.84 (1H, d, J = 8.1 Hz), 6.99 (1H, t, J = 7.6 Hz), 7.16 (1H, t, J = 8.1 Hz), 7.53 (1H, d, J = 7.6 Hz); ^{13}C NMR (400 MHz) δ 14.0, 14.5, 14.6, 20.5, 24.2, 24.6, 32.7, 40.2, 46.0, 50.8, 94.4, 117.1, 121.8, 125.0, 127.8, 128.3, 152.2. Anal. Calcd for $C_{17}H_{27}NOS_2$: C, 62.72; H, 8.36; N, 4.30. Found: C, 62.59; H, 8.32; N, 4.30.

2,2-Bis(ethylthio)-4-(hydroxyethylamino)chroman (8d): yellow oil; IR (neat) 3434, 1583, 1452, 1218, 916 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.22 (3H, t, J = 7.5 Hz), 1.27 (3H, t, J = 7.5 Hz), 2.27 (NH, s), 2.41 (1H, dd, J = 8.4, 14.0 Hz), 2.67 (1H, dd, J = 6.4, 14.0 Hz), 2.73−2.85 (5H, m), 2.98 (1H, ddd, J = 3.6, 6.0, 12.0 Hz), 3.64 (1H, ddd, J = 4.0, 6.8, 10.8 Hz), 3.71 (1H, ddd, J = 4.0, 6.4, 10.4 Hz), 4.15 (1H, dd, J = 6.2, 8.3 Hz), 6.86 (1H, d, J = 8.1 Hz), 7.00 (1H, t, J = 7.3 Hz), 7.18 (1H, t, J = 8.0 Hz), 7.51 (1H, d, J = 7.6 Hz); ^{13}C NMR (101 MHz) δ 14.4, 14.5, 24.3, 24.6, 40.1, 47.7, 50.7, 61.3, 94.1, 117.3, 121.9, 124.3, 128.0, 128.6, 152.1. Anal. Calcd for $C_{15}H_{23}NO_2S_2$: C, 57.47; H, 7.40; N, 4.47. Found: C, 57.74, H, 7.50, N, 4.35.

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Supporting Information Available: Experimental procedures and spectral and analytical data for compounds **2e**−**h**, **5f**−**h**, **7**, and **8b**,**c**,**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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