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Note

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Tandem Esterification/1,4-Addition-Type Friedel–Crafts Alkylation Reactions of Phenols/Naphthols with Olefinic Thioazlactones: Access to Functionalized 1,2-Dihydrobenzo[*f*]chromen-3-ones and 3,4-Dihydrochromen-2-ones

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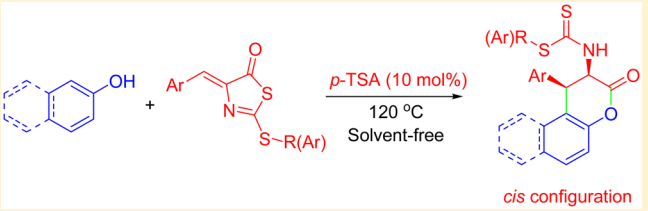
Supporting Information

ABSTRACT: An efficient approach for the synthesis of novel alkyl 2,3-dihydro-3-oxo-1-aryl-1*H*-benzo[*f*]chromen-2-ylcarbamodithioates and alkyl 3,4-dihydro-2-oxo-4-aryl-2*H*-chromen-3-ylcarbamodithioates from 2-(alkylthio)thioazlactones (thioazlactones) and phenols or naphthols catalyzed by PTSA was developed. The reaction proceeds via a domino esterification/intramolecular 1,4-addition-type Friedel–Crafts alkylation reaction to afford interesting complex molecules by a simple procedure with high yields and diastereoselectivity. An X-ray analysis was carried out to firmly establish the stereochemistry of the products.



Chromenes, chromanes, and their benzo-fused derivatives are widely present in a variety of significant natural products, and their extracts from various medicinal plants have found wide applications in the treatment of diverse ailments.[1] An example of a naturally occurring chromane is vitamin E, which acts as an antioxidant.[2] Recently, antimicrobial,[3] antiviral,[4] mutagenic,[5] antiproliferative,[6] sex hormone,[7] antitubercular,[8] anticancer,[9] and anti-HIV[10] activities of these compounds have been widely reported. Moreover they have been extensively applied to the treatment of Alzheimer's, Parkinson's, and Huntington's diseases, AIDS associated dementia, and Down syndrome as well as for the treatment of schizophrenia and myoclonus.[11]

Due to their widespread applications and importance in the structures of biologically active molecules, numerous synthetic routes for the synthesis of highly functionalized chromenes and chromanes have been reported over the past decades.[12] Among the reported methodologies for the synthesis of these compounds, the reaction of salicylaldehyde with enolates,[13] Lewis acid and transition metal catalyzed asymmetric epoxidation,[14] allylic alkylation,[15] oxidative cyclization,[16] enyne cyclization,[17] oxa-Povarov,[18] [3 + 3] cyclocoupling of phenols and allylic alcohols,[19] intramolecular arylation reactions of alkenes,[20] and organocatalytic cascade reactions such as Michael–Michael, Michael–aldol, and Michael–Henry reactions are the most salient methods.[21]

A literature survey revealed that there has been a great deal of research on the utilization of azlactones in organic transformations.[22] Recently, an enantioselective [4 + 2] cycloaddition of *o*-hydroxylstyrenes with azlactones has been established by Shi et al. for the synthesis of the biologically important dihydrocoumarin scaffold in an efficient and enantioselective style (up to 99% yield, 96:4 er) using a chiral Brønsted acid (chiral phosphoric acid) and base (chiral guanidine) catalysis (Scheme 1, eq 1).[23] In addition, Khosropour and co-workers reported the synthesis of naphtho[2,1-*b*]furan-2(1*H*)-one derivatives from the reaction of (*Z*)-4-arylidene-2-phenyl-5(4)-oxazolones (azlactones) with 2-naphthols via a domino transesterification/Mannich-type Friedel–Crafts alkylation reaction (Scheme 1, eq 2).[24]

Although the thioazlactones **1** are the thia analogues of the azlactones with similar active sites, there are only a few reports on applying these compounds as substrates for further transformations in synthetic organic chemistry.[25] For this purpose, we are encouraged to repeat the work of Khosropour et al. by using 2-(alkylthio)thioazlactones **1a** instead of azlactone and 2-naphthol under optimized reaction conditions (Scheme 1, eq 3). Surprisingly, we observed that the benzyl 2,3-dihydro-3-oxo-1-phenyl-1*H*-benzo[*f*]chromen-2-ylcarbamodithioate **3a** was obtained as the only product and no benzyl 1-benzyl-1,2-dihydro-2-oxonaphtho[2,1-*b*]furan-1-ylcarbamodithioate **4** was observed. With this surprising result, we focused our attempt on the optimization of the reaction conditions by varying the amount of *p*-TSA, reaction temperature, and time and using a solvent for the reaction. We observed that the best yield was obtained when equimolar amounts of 2-naphthol and thioazlactone **1a** were stirred in the presence of 10 mol % of *p*-TSA as catalyst under solvent-free conditions at 120 °C for 6 h. Performing the reaction in refluxing toluene, ethanol, acetonitrile, and chloroform gave no result after 2 days, and the starting materials were recovered. In addition, increasing

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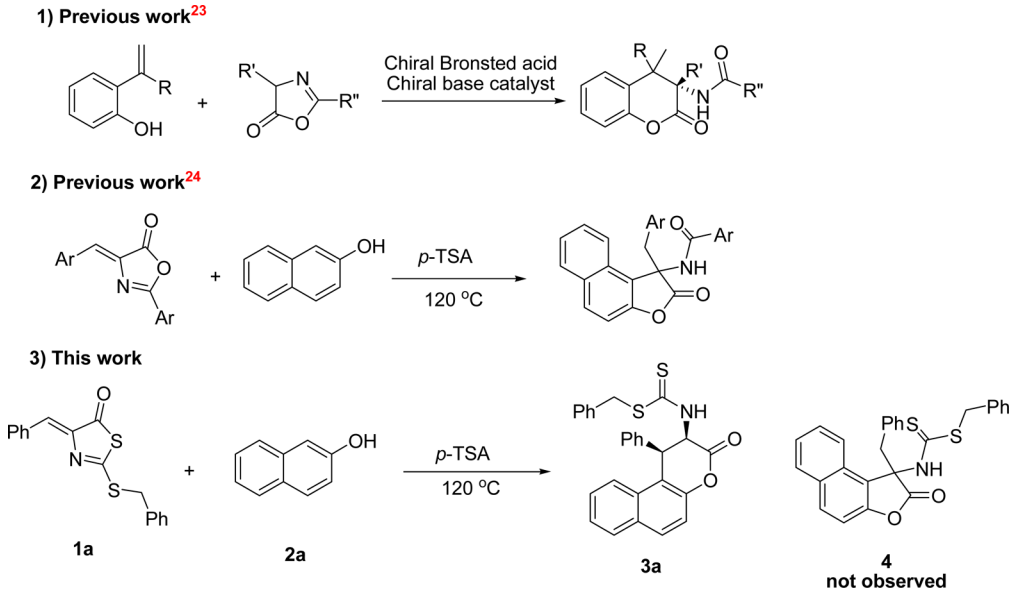
Scheme 1. Synthetic Strategies Using Azlactones and Thioazlactone



the amount of *p*-TSA from 10 to 20 mol % does not have a significant effect on the yield.

After optimization of the reaction conditions, the generality of this protocol was examined using various thioazlactones **1a**−**g** and electron-rich arenes **2a**−**e**. The results are summarized in Table 1. Electron-donating and -withdrawing groups on the aryl substituents of the thioazlactone skeleton do not have a significant effect on the reaction yield, and good to high yields were obtained in all cases. Varying the substitution pattern on the thio group of the thiazole ring in thioazlactones does not affect the yield. In addition, various electron-rich arenes such as 2-naphthol (entries 1, 8, 10, and 14), 2,7-dihydroxynaphthalene (entries 6 and 12), resorcinol (entries 2, 7, 9, and 11), 3,4,5-trimethoxyphenol (entries 3, 5, and 13), and 2,3,5-trimethylphenol (entry 4) were examined in this protocol and gave the corresponding products in good to high yields. Other electron-rich arenes such as 1-naphthol and 1,5-naphthalenediol and indole were also applied in this protocol and no reaction took place.

The structures of all products were elucidated from their IR and ^{1}H and ^{13}C NMR spectra and HRMS and CHN analyses. The ^{1}H NMR spectra of the products showed two characteristic signals between 5.00 and 6.00 ppm for the aliphatic CH resonances of the 3,4-dihydrochromen-2-one ring. The distinctive carbons of the dithiocarbamate and the ester moieties in the products were observed between 198.0 and 201.0 ppm and between 165.0 and 167.0 ppm, respectively. In addition, the two aliphatic carbons of the 3,4-dihydrochromen-2-one rings were observed between 40.0 and 43.0 ppm and between 57.0 and 60.0 ppm.

It is worth noting that this reaction was highly diastereoselective, and only a single diastereomer was formed in high purity after purification, although two stereogenic centers were generated in this reaction. In order to determine the configuration of the two newly generated stereogenic centers, single crystals of compound **3a** suitable for X-ray crystallographic analysis were prepared by recrystallization from a toluene/ethanol mixture. According to the ORTEP representations (for details of the crystal structure data of **3a** see Figure 1 and Table 1 in the Supporting Information; CCDC no. 1063155), its stereochemistry was assigned to be cis, in which the dithiocarbamate and the aryl group are in a cis configuration. The stereochemistry of the other products was assigned by analogy.

A plausible mechanism for the synthesis of benzyl 2,3-dihydro-3-oxo-1-phenyl-1*H*-benzo[*f*]chromen-2-ylcarbamodithioate is depicted in Scheme 2. According to the stereochemistry of the products, the ring opening of the activated thioazlactone with 2-naphthol is proposed as the initial step to afford the intermediate **A** after tautomerization, which is in resonance with the form **B**. Then, an intramolecular 1,4-addition-type Friedel−Crafts alkylation reaction afforded the intermediate **C**, which provided the corresponding product upon tautomerization−hydrogen transformation. The stereochemical outcome of this reaction may be dictated by the last step (tautomerization) toward thermodynamic products at high temperature. Also, according to the proposed mechanisms by us and Khosropour et al.,[24] the difference between the products may be attributed to the stability of the intermediate **A** in the enamine form in comparison to the proposed imine intermediate in the reaction of 2-naphthol with azlactones.

In summary, we have developed a domino approach for the diastereoselective synthesis of novel alkyl 2,3-dihydro-3-oxo-1-aryl-1*H*-benzo[*f*]chromen-2-ylcarbamodithioates and alkyl 3,4-dihydro-2-oxo-4-aryl-2*H*-chromen-3-ylcarbamodithioates from the reaction of naphthols and phenols with thioazlactones catalyzed by *p*-TSA. Performance of the reaction under solvent-free conditions, good isolated yields, and excellent diastereoselectivity are the main advantages of this procedure.

EXPERIMENTAL SECTION

General Considerations. All reagents and solvents were commercially available and were used as received. Thioazlactones were prepared via Erlenmeyer−Plöchl reactions according to the literature sources.[25] NMR spectra were recorded with 300 MHz spectrometers for ^{1}H NMR and 75 MHz instruments for ^{13}C NMR. Chemical shifts are reported in ppm relative to TMS or $CDCl_3$ as internal standard. Infrared spectra were recorded in potassium bromide pellets on a FT-IR spectrometer over the range 400−4000 cm^{-1}. Elemental analysis was conducted with a CHN analyzer. The high-resolution mass spectra were recorded under ESI Q-TOF

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Table 1. Diversity in the Synthesis of 1,2-Dihydrobenzo[*f*]chromen-3-one and 3,4-Dihydrochromen-2-one

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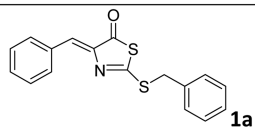
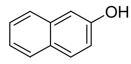
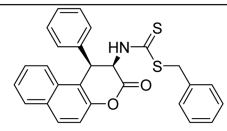
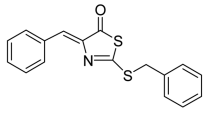
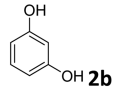
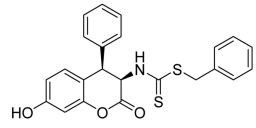
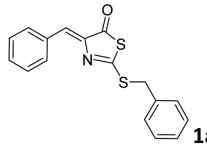
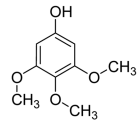
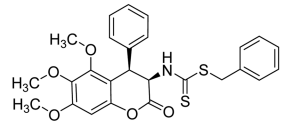
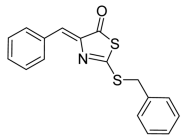
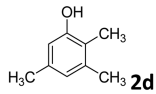
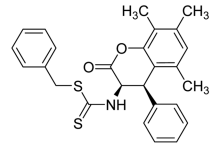
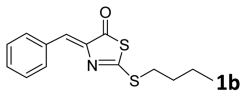
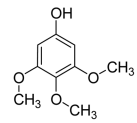
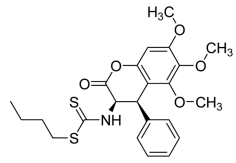
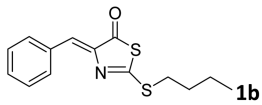
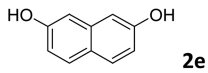
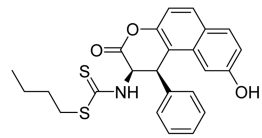
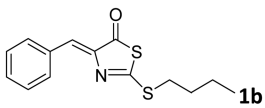
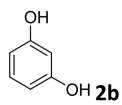
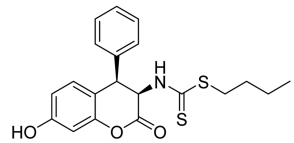
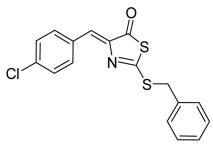
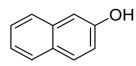
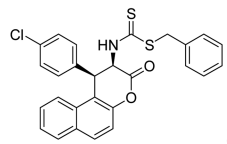
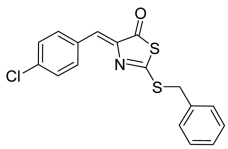
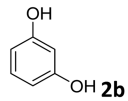
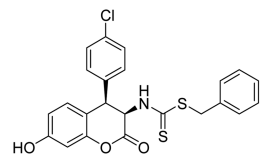
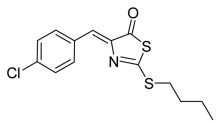
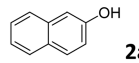
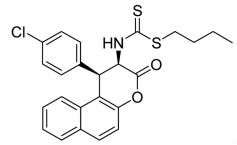
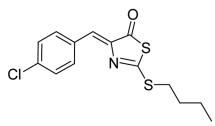
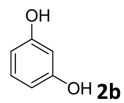
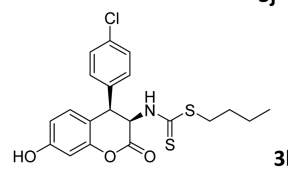
1	 1a	 2a	 3a	69%
2	 1a	 2b	 3b	60%
3	 1a	 2c	 3c	60%
4	 1a	 2d	 3d	60%
5	 1b	 2c	 3e	68%
6	 1b	 2e	 3f	51%
7	 1b	 2b	 3g	62%
8	 1c	 2a	 3h	66%
9	 1c	 2b	 3i	59%
10	 1d	 2a	 3j	61%
11	 1d	 2b	 3k	61%

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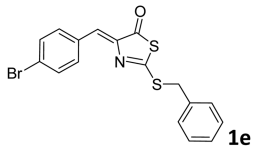
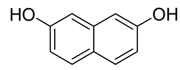
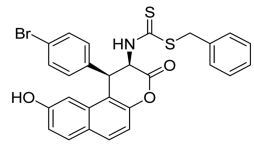
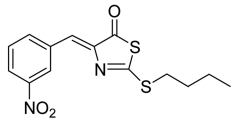
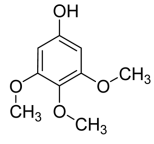
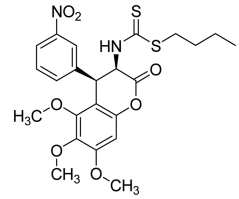
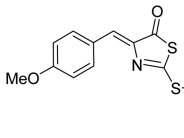
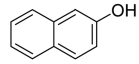
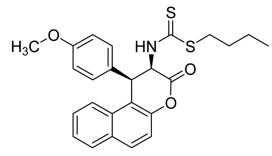
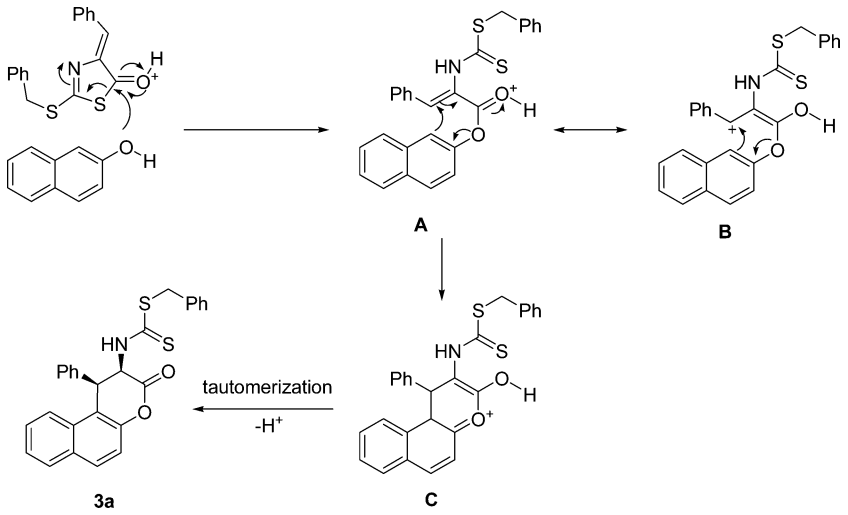
Table 1. continued

Entry	Thioazlactone	Phenol/naphthol	Product	Yield (%)[a]
12	 **1e**	 **2e**	 **3l**	48%
13	 **1f**	 **2c**	 **3m**	72%
14	 **1g**	 **2a**	 **3n**	59%

[a]Isolated yield after column chromatography.

Scheme 2. Proposed Mechanism for the Preparation of the Products 3



conditions. Melting points were measured on a capillary melting point apparatus and are uncorrected.

General Procedure for the Synthesis of Alkyl 2,3-Dihydro-3-oxo-1-aryl-1*H*-benzo[*f*]chromen-2-ylcarbamodithioates and Alkyl 3,4-Dihydro-2-oxo-4-aryl-2*H*-chromen-3-ylcarbamodithioates. In a test tube equipped with a magnetic stir bar were placed a thioazlactone **2a–g** (1 mmol), a phenol or naphthol derivative **1a–e** (1 mmol), and *p*-TSA (10 mol %) and the mixture was stirred at 120 °C for 6 h. The progress of reaction was monitored by TLC (ethyl acetate/petroleum ether, 1/4). The mixture was cooled to room temperature and quenched with water (10 mL). The product was extracted with ethyl acetate (2 × 10), and the combined organic phases were washed with water (10 mL) three times to remove the *p*-TSA. The organic phase was then evaporated to give the crude product. Purifications have been done by column chromatography using silica gel and ethyl acetate/hexane (1/15).

*Benzyl 2,3-dihydro-3-oxo-1-phenyl-1H-benzo[f]chromen-2-ylcarbamodithioate (**3a**):* white solid (314 mg, 69% yield); mp 166–168 °C; IR (KBr) ν 3334, 1769, 1625, 1494, 1354, 1222, 1137, 813, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 4.57 (2H, AB-q, J = 13.8 Hz), 5.85–5.91 (2H, m), 7.05 (2H, m), 7.24–7.28 (3H, m), 7.32–7.52 (9H, m), 7.79–7.95 (3H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 40.1, 40.2, 58.9, 116.8, 117.3, 123.2, 125.7, 127.6, 127.8, 128.2, 128.3, 128.6, 128.7, 129.0, 129.2, 130.6, 131.0, 131.3, 135.4, 136.0, 148.3, 166.6, 198.6 ppm. Anal. Calcd for $C_{27}H_{21}NO_2S_2$ (455.6): C, 71.18; H, 4.65; N, 3.07. Found: C, 71.28; H, 4.52; N, 2.97.

*Benzyl 3,4-dihydro-5-hydroxy-2-oxo-4-phenyl-2H-chromen-3-ylcarbamodithioate (**3b**):* white solid (253 mg, 60% yield); mp 136–168 °C; IR (KBr) ν 3324, 1760, 1625, 1493, 1330, 1151, 970, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 4.52 (2H, AB-q, J = 13.8 Hz), 5.12 (1H, d, J = 6.8 Hz), 5.21 (1H, br s), 5.71(1H, t, J = 6.6 Hz), 6.65–6.72(2H, m), 6.86–6.91(2H, m), 7.08 (1H, d, J = 8.3 Hz), 7.21–7.39 (9H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 40.1, 42.7, 59.1, 104.2, 110.0, 113.0, 115.9, 127.7, 128.0, 128.1, 128.6, 129.0, 130.5, 135.9, 136.4, 151.2, 156.5, 166.5, 198.4 ppm; HRMS (ES$^+$) calcd for $C_{23}H_{20}NO_3S_2$ [M + H]$^+$ 422.0879, found 422.0884.

*Benzyl 3,4-dihydro-5,6,7-trimethoxy-2-oxo-4-phenyl-2H-chromen-3-ylcarbamodithioate (**3c**):* white solid (297 mg, 60% yield); mp 125–128 °C; IR (KBr) ν 3315, 1770, 1616, 1491, 1466, 1347, 1128, 1091, 1032, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 3.62 (3H, s), 3.83 (3H, s), 3.89 (3H, s), 4.52 (2H, AB-q, J = 13.8 Hz), 5.35 (1H, d, J = 6.9 Hz), 5.67 (1H, t, J = 6.8 Hz), 6.55 (1H, s), 6.94–6.98 (2H, m), 7.22–7.38 (9H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 38.7, 40.1, 56.2, 58.9, 61.0, 61.2, 96.6, 110.5, 127.6, 128.0 (2C), 128.6, 128.9,

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129.0, 135.9, 136.5, 139.7, 146.3, 150.9, 154.2, 166.6, 198.4 ppm; HRMS (ES$^+$) calcd for $C_{26}H_{26}NO_5S_2$ [M + H]$^+$ 496.1252, found 496.1256.

*N-(3,4-Dihydro-5,7,8-trimethyl-2-oxo-4-phenyl-2H-chromen-3-yl)-2-phenylethanethioamide (**3d**):* white solid (268 mg, 60% yield); mp 147−149 °C; IR (KBr) ν 3324, 1763, 1602, 1493, 1453, 1175, 1086, 976, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 2.10 (3H, s), 2.28 (3H, s), 2.30 (3H, s), 4.53 (2H, AB-q, J = 13.8 Hz), 5.26 (1H, d, J = 6.8 Hz), 5.62 (1H, t, J = 6.4 Hz), 6.86 (1H, s), 6.93 (2H, m), 7.21−7.40 (9H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 11.8, 18.3, 19.8, 40.0, 40.6, 59.0, 120.0, 122.3, 127.6, 128.0, 128.3, 128.4, 128.6, 128.9, 129.0, 133.9, 135.3, 136.0, 138.1, 148.9, 166.9, 198.2 ppm. Anal. Calcd for $C_{26}H_{25}NO_2S_2$ (447.13): C, 69.77; H, 5.63; N, 3.13. Found: C, 69.75; H, 5.35; N, 3.10.

*Butyl 3,4-dihydro-5,6,7-trimethoxy-2-oxo-4-phenyl-2H-chromen-3-ylcarbamodithioate (**3e**):* viscous oil (313 mg, 68% yield); IR (KBr) ν 3248, 1774, 1617, 1494, 1460, 1358, 1160, 1089 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 0.94 (3H, t, J = 7.3 Hz), 1.42 (2H, m), 1.66 (2H, m), 3.24 (2H, t, J = 7.2 Hz), 3.62 (3H, s), 3.82 (3H, s), 3.88 (3H, s), 5.35 (1H, d, J = 6.9 Hz), 5.70 (1H, t, J = 6.8 Hz), 6.55 (1H, s), 6.97−6.99 (2H, m), 7.21−7.28 (4H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 13.6, 21.9, 30.8, 35.2, 38.2, 56.2, 58.7, 61.0, 61.2, 96.5, 110.5, 127.9, 128.0, 128.9, 136.5, 139.7, 146.3, 150.8, 154.1, 166.7, 199.3 ppm. Anal. Calcd for $C_{23}H_{27}NO_5S_2$ (461.59): C, 59.85; H, 5.90; N, 3.03. Found: C, 60.01; H, 5.98; N, 3.08.

*Butyl 2,3-dihydro-9-hydroxy-3-oxo-1-phenyl-1H-benzo[f]-chromen-2-ylcarbamodithioate (**3f**):* viscous oil (223 mg, 51% yield); IR (KBr) ν 3342, 1768, 1625, 1491, 1354, 1154, 1014, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 0.95 (3H, t, J = 7.3 Hz), 1.45 (2H, m), 1. 69 (2H, m), 3.27 (2H, t, J = 7.3 Hz), 5.68 (1H, br s), 5.71 (1H, d, J = 7.1 Hz), 5.84 (1H, t, J = 6.7 Hz), 7.02−7.07 (4H, m), 7.20−7.37 (5H, m), 7.72−7.82 (2H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 13.6, 21.9, 29.7, 35.3, 40.3, 58.7, 105.8, 114.2, 115.7, 117.5, 126.6, 128.2, 128.3, 129.1, 130.3, 130.7, 132.6, 135.4, 149.0, 155.2, 166.8, 199.5 ppm; HRMS (ES$^+$) calcd for $C_{24}H_{23}NO_3S_2$ [M + H]$^+$ 438.1198, found 438.1192.

*Butyl 3,4,5,6-tetrahydro-5-hydroxy-2-oxo-4-phenyl-2H-chromen-3-ylcarbamodithioate (**3g**):* viscous oil (240 mg, 62% yield); IR (KBr) ν 3354, 1768, 1627, 1493, 1340, 1154, 699 cm^{-1}: ^{1}H NMR (300 MHz, $CDCl_3$) 0.94 (3H, t, J = 7.3 Hz), 1.45 (2H, m), 1.67 (2H, m), 3.25 (2H, t, J = 7.2 Hz), 5.12 (1H, d, J = 6.8 Hz), 5.52 (1H, br s), 5.74 (1H, t, J = 6.6 Hz), 6.65−6.73 (2H, m), 6.91−6.94 (2H, m), 7.08 (1H, d, J = 8.3 Hz), 7.25−7.28 (4H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 13.6, 21.9, 30.8, 35.3, 42.8, 59.0, 104.2, 113.1, 115.9, 128.1, 129.0, 130.4, 130.9, 136.6, 151.2, 156.6, 166.8, 199.4 ppm; HRMS (ES$^+$) calcd for $C_{20}H_{22}NO_3S_2$ [M + H]$^+$ 388.1036, found 388.1039.

*Benzyl 1-(4-chlorophenyl)-2,3-dihydro-3-oxo-1H-benzo[f]-chromen-2-ylcarbamodithioate (**3h**):* viscous oil (323 mg, 66% yield); IR (KBr) ν 3337, 1772, 1626, 1491, 1352, 1222, 1139, 813, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 4.50 (2H, AB-q, J = 14.0 Hz), 5.77 (1H, t, J = 7.1 Hz), 5.90 (1H, d, J = 7.1 Hz), 6.91(2H, d, J = 8.4 Hz), 7.17(2H, d, J = 8.4 Hz), 7.30−7.52 (9H, m), 7.72 (1H, m), 7.86−7.94 (2H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 39.4, 40.1, 58.7, 116.7, 123.0, 125.8, 127.7, 127.9, 128.7, 128.8(2C), 129.0(2C), 129.4, 129.5, 130.8, 131.4, 133.9, 134.3, 135.9, 148.3, 166.4, 198.6 ppm; HRMS (ES$^+$) calcd for $C_{27}H_{21}ClNO_2S_2$ [M + H]$^+$ 490.0697, found 490.0704.

*Benzyl 4-(4-chlorophenyl)-3,4-dihydro-5-hydroxy-2-oxo-2H-chromen-3-ylcarbamodithioate (**3i**):* white solid (269 mg, 59% yield); mp 140−142 °C; IR (KBr) ν 3332, 1769, 1626, 1491, 1261, 1102, 803, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 4.51(2H, AB-q, J = 14.8 Hz), 5.15 (1H, d, J = 6.8 Hz), 5.62 (1H, t, J = 6.8 Hz), 6.68−6.80 (4H, m), 7.03 (1H, m), 7.15 (2H, d, J = 8.4 Hz), 7.25−7.37 (7H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 40.1, 41.9, 59.1, 104.2, 113.3, 114.8, 127.7, 128.7, 129.0, 129.1, 129.4, 130.3, 134.0, 135.0, 135.9, 151.0, 157.4, 166.5, 198.3 ppm; HRMS (ES$^+$) calcd for $C_{23}H_{19}ClNO_3S_2$ [M + H]$^+$ 456.0489, found 456.0494.

*Butyl 2,3-dihydro-3-oxo-1H-benzo[f]chromen-2-ylcarbamodithioate (**3j**):* viscous oil (278 mg, 61% yield); IR (KBr) ν 3305, 1768, 1625, 1490, 1350, 1222, 1140, 976, 812 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 0.97 (3H, t, J = 7.5 Hz), 1.47 (2H, m), 1.70 (2H, m), 3.29 (2H, t, J = 7.4 Hz), 5.81(1H, d, J = 6.0 Hz), 5.89 (1H, d, J = 7.1 Hz), 6.98 (2H, d, J = 8.4 Hz), 7.23−7.26 (2H, m), 7.36 (2H, d, J = 8.9 Hz), 7.44−7.53 (2H, m), 7.72 (1H, m), 7.86−7.94 (2H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 13.6, 22.0, 30.9, 35.4, 39.5, 58.5, 116.8 (2C), 123.1, 125.9, 127.9, 128.8, 129.4, 129.6, 130.8, 130.9, 131.4, 134.1, 134.3, 148.3, 166.6, 199.7 ppm; HRMS (ES$^+$) calcd for $C_{24}H_{23}ClNO_2S_2$ [M + H]$^+$ 456.0853, found 456.0851.

*Butyl 4-(4-chlorophenyl)-3,4-dihydro-5-hydroxy-2-oxo-2H-chromen-3-ylcarbamodithioate (**3k**):* viscous oil (256 mg, 61% yield); IR (KBr) ν 3309, 1765, 1626, 1491, 1454, 1329, 1154, 1102, 904, 815 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 0.95 (3H, t, J = 7.2 Hz), 1.43 (2H, m), 1.67 (2H, m), 3.26 (2H, td, J = 7.2, 1.4 Hz), 5.18 (1H, d, J = 6.8 Hz), 5.38 (1H, br s), 5.67 (1H, t, J = 6.5 Hz), 6.65−6.73 (2H, m), 6.83 (2H, d, J = 8.4 Hz), 7.07 (1H, d, J = 8.3 Hz), 7.23−7.31 (3H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 13.6, 21.9, 30.8, 35.4, 42.0, 58.9, 104.3, 113.2, 115.4, 129.1, 129.4, 130.4, 134.1, 135.1, 151.1, 156.7, 166.6, 199.5 ppm. Anal. Calcd for $C_{20}H_{20}ClNO_3S_2$ (422.0): C, 56.93; H, 4.78; N, 3.32. Found: C, 56.72; H, 4.55; N, 3.19.

*Benzyl 1-(4-bromophenyl)-2,3-dihydro-9-hydroxy-3-oxo-1H-benzo[f]chromen-2-ylcarbamodithioate (**3l**):* white solid (264 mg, 48% yield); mp 166−168 °C; IR (KBr) ν 3314, 1766, 1626, 1487, 1357, 1230, 1135, 1072, 911, 833, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 4.53 (2H, AB-q, J = 15.0 Hz), 5.28 (1H, br s), 5.73−5.73 (2H, m), 6.82 (2H, d, J = 8.4 Hz), 6.96 (1H, s), 7.04(1H, m), 7.19−7.43 (9H, m), 7.75−7.84 (2H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 39.5, 40.1, 58.7, 105.6, 114.3, 115.1, 117.6, 122.5, 126.7, 127.7, 128.7, 129.0, 129.8, 130.6, 130.8, 132.3, 132.5, 134.3, 135.9, 148.9, 155.2, 166.4, 198.6 ppm; HRMS (ES$^+$) calcd for $C_{27}H_{20}BrNNaO_3S_2$ [M + Na]$^+$ 571.9966, found 571.9972.

*Butyl 3,4-dihydro-5,6,7-trimethoxy-4-(3-nitrophenyl)-2-oxo-2H-chromen-3-ylcarbamodithioate (**3m**):* white solid (364 mg, 72% yield); mp 140−141 °C; IR (KBr) ν 3258, 1771, 1618, 1530, 1490, 1348, 1138, 1086 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 0.98 (3H, m), 1.48 (2H, m), 1.73 (2H, m), 3.32 (2H, m), 3.77 (3H, s), 3.84 (3H, s), 3.95 (3H, s), 5.66 (2H, m), 6.62 (1H, s), 7.34 (2H, m), 7.50 (1H, m), 7.88 (1H, s), 8.16 (1H, m) ppm: ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.4, 31.3, 35.9, 37.9, 56.71, 58.9, 61.5, 61.7, 97.2, 109.1, 123.5, 123.6, 130.3, 134.6, 139.4, 140.1, 146.7, 149.0, 151.2, 155.3, 166.8, 200.4 ppm; HRMS (ES$^+$) calcd for $C_{23}H_{27}N_2O_7S_2$ [M + H]$^+$ 507.1260, found 507.1272.

*Butyl 2,3-dihydro-1-(4-methoxyphenyl)-3-oxo-1H-benzo[f]-chromen-2-ylcarbamodithioate (**3n**):* white solid (266 mg, 59% yield); mp 118−120 °C; IR (KBr) ν 3418, 1775, 1608, 1512, 1463, 1353, 1255, 1211 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 0.97 (3H, t, J = 7.3 Hz), 1.52 (2H, m), 1.74 (2H, m), 3.33 (2H, t, J = 7.3 Hz), 3.75 (3H, s), 5.79−5.87 (2H, m), 6.79 (2H, d, J = 8.6 Hz), 6.98 (2H, d, J = 8.6 Hz), 7.36−7.52 (4H, m), 7.78−7.92 (3H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 13.6, 22.0, 30.9, 35.3, 39.5, 55.2, 58.8, 114.5, 116.8, 117.6, 123.3, 125.7, 127.3, 127.8, 128.6, 129.3, 130.4, 131.0, 131.3, 148.2, 159.4, 166.9, 199.4 ppm. Anal. Calcd for $C_{25}H_{25}NO_3S_2$ (451.6): C, 66.49; H, 5.58; N, 3.10. Found: C, 66.25; H, 5.50; N, 3.14.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00740.

X-ray data for **3a** (CIF)

^{1}H and ^{13}C NMR spectra for all compounds and X-ray data for **3a** (PDF)

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Notes

The authors declare no competing financial interest.

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