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Domino Synthesis of Thiochromenes through Cu-Catalyzed Incorporation of Sulfur Using Xanthate Surrogate

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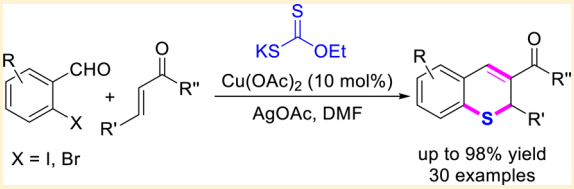
Supporting Information

ABSTRACT: An efficient domino reaction has been developed for the synthesis of thiochromenes through Cu-catalyzed in situ incorporation of sulfur. This domino method avoids the use of less accessible and unpleasant arenethiols as starting materials, instead utilizes very stable aryl halides along with potassium ethyl xanthate as an odorless sulfur surrogate. The domino methodology proceeds through $C_{(aryl)}$-S coupling, thioester cleavage, sulfa-Michael addition, aldol reaction, and elimination reaction sequences to provide thiochromenes in good yields



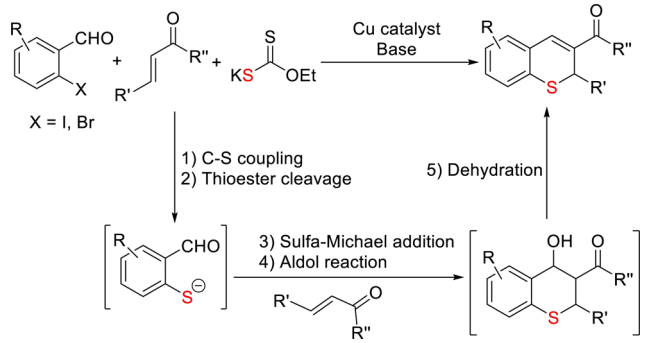
INTRODUCTION

Synthesis of sulfur-containing compounds continues to be an important task in organic chemistry because of their applications in biology, material science, and food chemistry.[1−3] Thiochromenes, the sulfur analogues of chromenes, have been testified to exhibit many pharmaceutical properties such as anticancer, antibacterial, anti-inflammatory, and antipsychiatric activities.[4] Conventionally, thiochromenes could be prepared by a four step process, such as Michael addition of thiophenol to 2-alkenoic acids followed by acid-catalyzed cyclization, reduction, and dehydration.[5] Only a handful of attempts have been made to achieve efficient method for the synthesis of thiochromenes.[6] However, most of these methods suffer from a number of drawbacks like requirement of multistep synthesis, limited substrate scope, and lower yield.

In the past years, domino sulfa-Michael-aldol reaction of 2-mercaptobenzaldehydes with α,β-unsaturated compounds has been used as an efficient tool for the synthesis of chiral thiochromanes.[7] However, very few methods utilized cascade sulfa-Michael-aldol reaction to synthesize chiral thiochromenes,[8] cascade sulfa-Michael-aldol reaction of 2-mercaptobenzaldehydes with simple chalcones has remained unexplored. Despite the progress toward synthesis of thiochromenes, all the reported methods utilize arenethiols as starting materials which are less accessible, produce unpleasant smell, and concern environmental safety. Therefore, development of a catalytic method which overcomes all above-mentioned difficulties would be highly desirable.

In recent years, considerable effort has been devoted toward transition metal catalyzed $C_{(aryl)}$-S bond formation by means of in situ generation of sulfur.[9] As a result, construction of sulfur-containing heterocyclic compounds involving concomitant formation of C−S bonds has been developed to some extent.[10] We have previously used xanthates as coupling partner with aryl halides under copper catalysis as a means of incorporating sulfur.[11] We envisioned a domino process for the synthesis of thiochromenes through Cu-catalyzed in situ incorporation of sulfur using easily available and odorless potassium ethyl xanthate as source of sulfur (Scheme 1). In this strategy, coupling of 2-halobenzaldehyde and xanthate can be achieved by copper catalyst. Thioester cleavage could occur in the presence of base to generate 2-formylbenzenethiolate which can undergo sulfa-Michael addition with chalcone followed by aldol reaction and then base can facilitate the dehydration.

Scheme 1. Our Strategy for Cu-Catalyzed Domino Synthesis of Thiochromenes



RESULTS AND DISCUSSION

Initially, 2-iodobenzaldehyde was reacted with simple chalcone in the presence of 2 equiv of potassium ethyl xanthate, 10 mol% of $Cu(OAc)_2$, and 2 equiv of NaOH in DMSO solvent at 100 °C. The reaction proceeded to completion after 14 h, and the desired thiochromene was isolated in 23% yield (Table 1, entry 1). The structure of **3a** was unambiguously confirmed by single-crystal XRD analysis (see the Supporting Information, Figure S1). Encouraged by this result, optimization of the reaction was performed with respect to Cu source, solvents, and bases.

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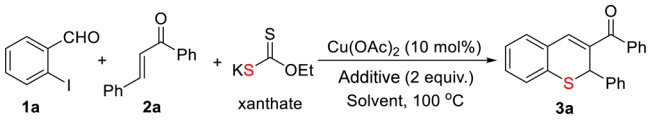
Table 1. Optimization of Reaction Conditions[a]



entry	Cu salt	additive	solvent	time (h)	yield (%)[b]
1	$Cu(OAc)_2$	NaOH	DMSO	14	23[c]
2	CuI	NaOH	DMSO	24	8[c]
3	CuCl	NaOH	DMSO	24	7[c]
4	$CuBr_2$	NaOH	DMSO	24	11[c]
5	$CuCl_2$	NaOH	DMSO	24	16[c]
6	$Cu(OAc)_2$	NaOH	PhMe	24	nd[d]
7	$Cu(OAc)_2$	NaOH	dioxane	24	nd[d]
8	$Cu(OAc)_2$	NaOH	CH_3CN	24	nd[d]
9	$Cu(OAc)_2$	NaOH	DMF	14	38[c]
10	$Cu(OAc)_2$	KOH	DMF	14	34[c]
11	$Cu(OAc)_2$	LiOH	DMF	18	25[c]
12	$Cu(OAc)_2$	Na_2CO_3	DMF	24	21[c]
13	$Cu(OAc)_2$	K_3PO_4	DMF	24	28[c]
14	$Cu(OAc)_2$	NaOAc	DMF	14	62[c]
15	$Cu(OAc)_2$	NaO^tBu	DMF	3	[e]
16	$Cu(OAc)_2$	Et_2NH	DMF	5	[e]
17	$Cu(OAc)_2$	DABCO	DMF	5	[e]
18	$Cu(OAc)_2$	AgOAc	DMF	9	79
19	**$Cu(OAc)_2$**	**AgOAc**	**DMF**	7	**92**[f]

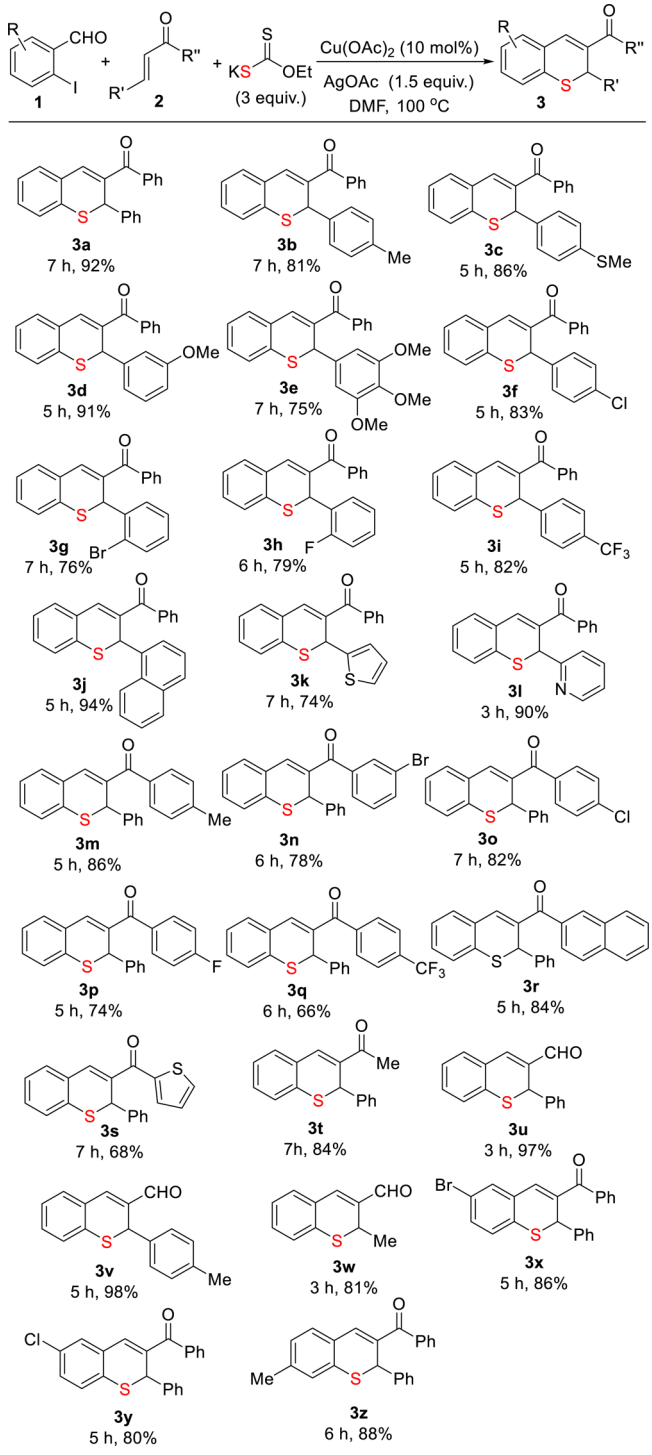
[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), xanthate (1 mmol), $Cu(OAc)_2$ (10 mol%), additive (1 mmol), solvent (2 mL), 100 °C. [b]Isolated yield. [c]The reaction generated a complex mixture from which pure product could nevertheless be isolated. [d]Starting materials remained. [e]The reaction generated a complex, inseparable mixture from which pure product could not be isolated. [f]1.5 mmol of xanthate and 0.75 mmol of AgOAc were used.

When $Cu(OAc)_2$ was replaced with other copper salts such as CuI, CuCl, $CuBr_2$, and $CuCl_2$, the yield was not improved (entries 2−5).

When the reaction was conducted in different solvents such as toluene, dioxane and acetonitrile, the thiochromene formation was not observed in these solvents (entries 6−8). Interestingly, the thiochromene was isolated in 38% yield, when the reaction was carried out in DMF solvent (entry 9). Further optimization was performed in DMF solvent, as it provided better yield than DMSO solvent. Replacement of NaOH with KOH and LiOH resulted in lower yield (entries 10 and 11). The starting materials were not consumed completely when Na_2CO_3 and K_3PO_4 were used as base (entries 12 and 13). To our delight, thiochromene was obtained in 62% yield, when NaOAc was used (entry 14). NaO^tBu, Et_2NH, and DABCO, gave inseparable complex reaction mixtures (entries 15−17). Remarkable improvement in yield (81%) was observed when AgOAc was employed as base (entry 18). After studying the reaction condition with respect to temperature, equivalents of $Cu(OAc)_2$, xanthate, and base, the domino reaction provided 92% yield for thiochromene in the presence of 10 mol% $Cu(OAc)_2$, 3 equiv of xanthate, and 1.5 equiv AgOAc in DMF at 100 °C (entry 19).

Next, substrate scope of this domino reaction was explored under the optimized reaction conditions. The domino reaction proceeded smoothly with a variety of other substrates, and the corresponding thiochromenes were isolated in good yields (Scheme 2). Electron-releasing substituents on the aryl ring that is attached to alkene part of chalcone facilitated the

Scheme 2. Scope of the Domino Reaction with Respect to 2-Iodobenzaldehyde



domino reaction, and thiochromenes **3b**−**3e** were obtained in good to excellent yields. Chalcones bearing chloro, bromo, and fluoro substituents, importantly at *ortho* position of aryl ring reacted effortlessly and provided the corresponding thiochromenes (**3f**−**3h**) in good yields.

Electron-withdrawing group containing chalcone was also tolerated in the domino reaction and afforded thiochromene **3i** in 82% yield. Replacement of the phenyl group that is attached to the alkene part of the chalcone with naphthyl, thiophenyl, and pyridyl groups gave the corresponding thiochromenes **3j**−

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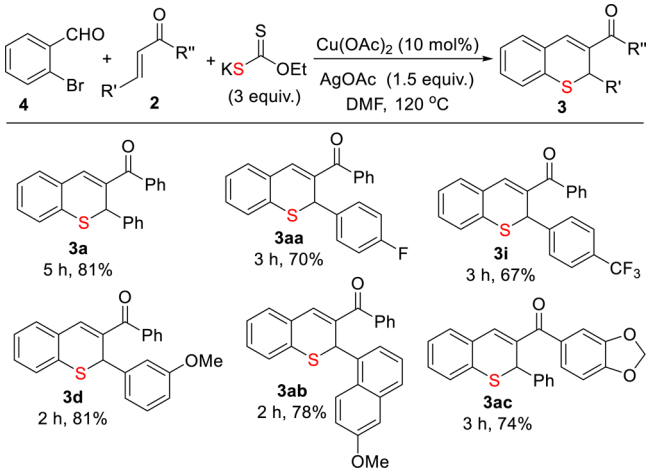
3l in good to excellent yields. Similarly, electron-releasing and electron-withdrawing substituents on the aryl ring that is attached to carbonyl part of chalcone were well tolerated in this domino reaction, and the corresponding thiochromenes **3m**–**3r** were isolated in decent yields. Chalcones having naphthyl, thiophenyl, and methyl groups attached to carbonyl part reacted easily to give thiochromene **3s**, **3t**, and **3u**. Notably, cinnamaldehydes and crotonaldehyde were found to be effective substrates for this domino reaction (**3v**–**3x**). Also, 2-iodobenzaldehyde having bromo, chloro, or methyl substituents offered thiochromenes **3y**, **3z**, and **3aa** in excellent yields.

Subsequently, the domino synthesis of thiochromenes was performed using comparatively less reactive 2-bromobenzaldehyde **4** as starting material. The domino reaction gave thiochromene in 67% yield under the standard optimized conditions. However, the yield was increased to 81% when the reaction was conducted at 120 °C (Scheme 3).

Scheme 3. Scope of the Domino Reaction with Respect to 2-Bromobenzaldehyde

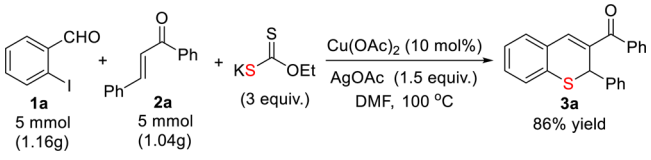


The generality of domino synthesis of thiochromenes using less reactive 2-bromobenzaldehyde **4** as starting material was explored with various substituted chalcones. All the substituents were well tolerated and the corresponding thiochromenes (**3a**, **3ab**, **3i**, **3d**, **3ac**, and **3ad**) were obtained in good yields.

In order to showcase the efficacy of domino synthesis of thiochromenes on gram scale, the reaction was performed in 5 mmol (1.16 g) scale under standard optimized condition without altering any reaction parameters (Scheme 4). The reaction proceeded smoothly and provided the thiochromene in 86% yield.

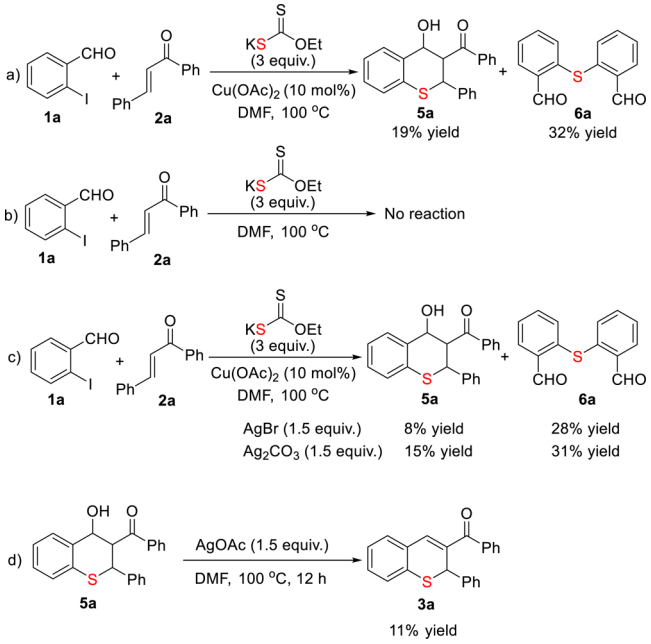
To gain insight into the possible reaction pathway, control experiments were performed. When the domino reaction was performed without AgOAc, formation of thiochromene **3a** was not observed, instead thiochromane **5a** was isolated in 19% yield as mixture of two diastereomers along with diarylsulfide

Scheme 4. Gram-Scale Synthesis



6a (32% yield) (Scheme 5a). Also, thiochromene **3a** formation was not observed in the absence of both $Cu(OAc)_2$ and AgOAc (Scheme 5b).

Scheme 5. Control Experiments



These experiments reveal that $Cu(OAc)_2$ promotes $C_{(aryl)}$-S coupling but the Lewis acidity is not adequate to activate chalcone to undergo sulfa-Michael-aldol reaction. Thus, coupling of in situ formed 2-formylbenzenethiolate with 2-iodobenzaldehyde might be responsible for the formation of diarylsulfide **6a**. In order to understand the importance of AgOAc, the domino reaction was performed with other silver salts. The domino reaction with AgBr and Ag_2CO_3 did not provide thiochromene **3a** instead thiochromane **5a** and diarylsulfide **6a** (Scheme 5c) were isolated. The dehydration of thiochromane **5a** in the presence of AgOAc gave 11% yield for product **3a** and thiochromane **5a** remained without reacting even after 12 h (Scheme 5d). These control experiments show that $Cu(OAc)_2$ and AgOAc are essential for the domino reaction to complete. From these observations, a possible reaction pathway has been proposed as shown in Scheme 6. Oxidative addition of copper acetate with 2-iodobenzaldehyde may lead to intermediate **A** which undergoes ligand exchange with potassium ethyl xanthate to generate intermediate **B**. Subsequently, reductive elimination of intermediate **B** affords intermediate **C** which may undergo thioester cleavage and the reaction of resulting thiolate with chalcone **2a** by Michael-aldol-elimination reaction sequence in the presence of AgOAc to give the product **3a**.

CONCLUSION

In summary, we have accomplished the domino synthesis of thiochromenes using Cu-catalyzed in situ incorporation of sulfur as a key step. Stable and odorless potassium ethyl xanthate has been utilized as an efficient sulfur source. The domino methodology proceeds through $C_{(aryl)}$-S coupling, thioester cleavage, sulfa-Michael addition, aldol reaction, and elimination reaction sequences to provide thiochromenes in good yields. A variety of thiochromenes have been synthesized

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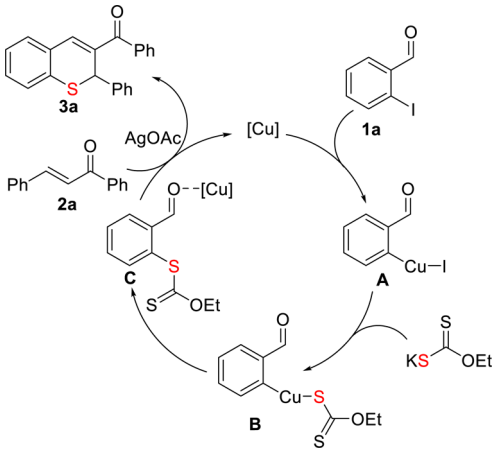
Scheme 6. Possible Reaction Pathway



in good to excellent yields from commercially available and easily accessible starting materials and catalyst. The gram scale synthesis and avoidance of foul-smelling arenethiols make this domino process practical and environmentally friendly.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in oven-dried reaction tubes. Reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 F_{254} precoated plates (0.25 mm) and visualized by UV fluorescence. Column chromatography was performed using Silica gel (particle size: 100−200 mesh) and eluted with hexanes/ethyl acetate mixture. All the reactions were carried out in temperature controlled magnetic stirrers. ^{1}H and ^{13}C NMR spectra were recorded on 400 and 500 MHz (100 and 125 MHz for ^{13}C) instrument. ^{1}H NMR spectra were reported relative to residual $CDCl_3$ (δ 7.26 ppm). When the residual peak is overlapping with compound, spectra reported to residual TMS. ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.16 ppm). Chemical shifts were reported in parts per million and coupling constants (J) are reported in Hertz. Melting points were recorded on melting point apparatus and are corrected with benzoic acid as reference. Infrared spectra were recorded on a FTIR 4000 Series spectrometer using dry KBr pellet. The wave numbers of recorded IR signals are quoted in cm^{-1}. High-resolution mass spectra (HRMS) were recorded on Q-TOF Micro mass spectrometer. $Cu(OAc)_2$ and potassium ethyl xanthogenate were obtained from commercial source and used directly as received.

General Procedure for the Synthesis of Thiochromenes. A oven-dried reaction tube was loaded with 2-iodobenzaldehyde (0.5 mmol), chalcone (0.5 mmol), potassium ethyl xanthate (1.5 mmol), AgOAc (1.5 mmol), and $Cu(OAc)_2$ (0.05 mmol) and then DMF (2 mL) was added. The reaction tube was closed with glass-stopper and stirred at 100 °C (120 °C in case of 2-bromobenzaldehyde) for recommended time. The reaction mixture was brought to room temperature and diluted with ethyl acetate and then washed with brine. The aqueous layer was extracted twice with ethyl acetate and the combined organic extractions were dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the residue was purified by silica gel column using hexanes/ethyl acetate (90:10, v/v) mixture to afford the thiochromene.

[2-(Phenyl)-2H-thiochromen-3-yl](phenyl)methanone (***3a***). 152 mg, 92% yield; pale yellow solid; mp 156−158 °C; R_f 0.52 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.48 (s, 1H), 7.10−7.15 (m, 1H), 7.17−7.30 (m, 8H), 7.39 (s, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.56 (tt, J = 7.6 Hz, 2.4 Hz, 1H), 7.69 (d, J = , 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.3, 125.8, 126.7, 127.8, 127.9, 128.5, 128.8, 129.3, 130.5, 130.9, 131.2, 132.0, 132.8, 133.3, 138.2, 140.1, 142.0, 195.8; FTIR (KBr) 3056, 1644, 1586, 1559, 1490, 758 cm^{-1}; HRMS (m/z) calculated for $C_{22}H_{17}OS$ $[M+H]^+$: 329.1000; found: 329.1018.

[2-(p-Tolyl)-2H-thiochromen-3-yl](phenyl)methanone (***3b***). 139 mg, 81% yield; pale yellow solid; mp 117−119 °C; R_f 0.41 (5% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.17 (s, 3H), 5.36 (s, 1H), 6.93 (d, J = 6.4 Hz, 2H), 7.04 (td, J = 6.2 Hz, 1.2 Hz, 1H), 7.08 (d, J = 6.4 Hz, 2H), 7.13−7.18 (m, 3H), 7.30 (s, 1H), 7.38 (t, J = 6.4 Hz, 2H), 7.48 (tt, J = 6.0 Hz, 1.6 Hz, 1H), 7.62 (d, J = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 40.1, 125.7, 126.6, 127.8, 128.5, 129.3, 129.5, 130.5, 130.9, 131.1, 132.0, 132.8, 133.5, 137.5, 138.2, 139.1, 140.0, 195.9; FTIR (KBr) 3054, 1641, 1507, 1441, 754 cm^{-1}; HRMS (m/z) calculated for $C_{23}H_{19}OS$ $[M+H]^+$: 343.1157; found: 343.1135.

[2-(4-(Methylthio)phenyl)-2H-thiochromen-3-yl](phenyl)-methanone (***3c***). 162 mg, 86% yield; yellowish viscous liquid; R_f 0.39 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 5.42 (s, 1H), 7.08 (d, J = 8.4 Hz, 2H), 7.13 (dd, J = 6.6 Hz, 2.4 Hz, 1H), 7.19 (d, J = 8.4 Hz, 2H), 7.22−7.28 (m, 3H), 7.38 (s, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.69 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.8, 39.9, 125.8, 126.8, 127.2, 127.8, 128.5, 129.3, 130.5, 130.9, 131.2, 132.0, 132.6, 133.2, 138.0, 138.1, 138.8, 140.1, 195.8; FTIR (KBr) 3059, 1642, 1583, 1486, 1556, 754 cm^{-1}; HRMS (m/z) calculated for $C_{23}H_{18}ONaS_2$ $[M+Na]^+$: 397.0698; found: 397.0691.

[2-(3-Methoxyphenyl)-2H-thiochromen-3-yl](phenyl)methanone (***3d***). 164 mg, 91% yield; yellow solid; mp 147−149 °C; R_f 0.36 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.68 (s, 3H), 5.45 (s, 1H), 6.71 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 6.82 (s, 1H), 6.87 (d, J = 8.0 Hz, 1H), 7.08−7.15 (m, 2H), 7.19−7.27 (m, 3H), 7.38 (s, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.69 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.2, 55.2, 112.6, 113.1, 119.1, 125.8, 127.7, 128.5, 129.3, 129.8, 130.5, 130.9, 131.2, 132.0, 132.8, 133.3, 138.2, 140.2, 143.5, 159.8, 195.8; FTIR (KBr) 3056, 2834, 1641, 1600, 1556, 1487, 755 cm^{-1}; HRMS (m/z) calculated for $C_{23}H_{19}O_2S$ $[M+H]^+$: 359.1106; found: 359.1125

[2-(3,4,5-Trimethoxyphenyl)-2H-thiochromen-3-yl](phenyl)-methanone (***3e***). 157 mg, 75% yield; brownish viscous liquid; R_f 0.54 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.67 (s, 6H), 3.76 (s, 3H), 5.40 (s, 1H), 6.51 (s, 2H), 7.12−7.17 (m, 1H), 7.26−7.29 (m, 2H), 7.32 (d, J = 7.2 Hz, 1H), 7.39 (s, 1H), 7.48 (t, J = 8.0 Hz, 2H), 7.58 (tt, J = 7.6 Hz, 1.6 Hz, 1H), 7.71 (dd, J = 8.4 Hz, 1.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.6, 56.0, 60.9, 103.7, 125.9, 127.9, 128.6, 129.3, 130.6, 131.2, 132.1, 132.9, 133.8, 137.5, 137.6, 138.1, 139.9, 153.2, 195.9; FTIR (KBr) 3051, 2862, 1647, 1592, 1541, 1436, 751 cm^{-1}; HRMS (m/z) calculated for $C_{25}H_{22}O_4NaS$ $[M+Na]^+$: 441.1137; found: 441. 1153.

[2-(4-Chlorophenyl)-2H-thiochromen-3-yl](phenyl)methanone (***3f***). 151 mg, 83% yield; yellow viscous liquid; R_f 0.65 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.41 (s, 1H), 7.13−7.23 (m, 5H), 7.24−7.27 (m, 3H), 7.41 (s, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.57 (tt, J = 7.6 Hz, 2.0 Hz, 1H), 7.69 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.8, 126.0, 127.8, 128.1, 128.6, 128.9, 129.3, 130.4, 131.0, 131.4, 132.1, 132.4, 133.0, 133.6, 138.0, 140.4, 140.5, 195.7; FTIR (KBr) 3038, 1651, 1613, 1578, 1476, 818, 757 cm^{-1}; HRMS (m/z) calculated for $C_{22}H_{15}OClNaS$ $[M+Na]^+$: 385.0424; found: 385.0432.

[2-(2-Bromophenyl)-2H-thiochromen-3-yl](phenyl)methanone (***3g***). 155 mg, 76% yield; pale yellow solid; mp 148−150 °C; R_f 0.38 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.86 (s, 1H), 7.00−7.08 (m, 3H), 7.11−7.23 (m, 3H), 7.29 (d, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.54−7.62 (m, 3H), 7.72 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.0, 122.9, 126.0, 127.6, 127.7, 128.2, 128.6, 129.1, 129.3, 130.5, 131.0, 131.4, 132.1, 132.2, 132.5, 133.8, 137.9, 139.6, 141.8, 195.2; FTIR (KBr) 3059, 1641, 1585, 1556, 1461, 1109, 754 cm^{-1}; HRMS (m/z) calculated for $C_{22}H_{15}OBrNaS$ $[M+Na]^+$: 428.9919; found: 428.9929.

[2-(2-Fluorophenyl)-2H-thiochromen-3-yl](phenyl)methanone (***3h***). 137 mg, 79% yield; yellowish viscous liquid; R_f 0.41 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.77 (s, 1H), 6.88 (t, J = 7.6 Hz, 1H), 7.00−7.07 (m, 2H), 7.10−7.16 (m, 2H), 7.18−7.23 (m, 2H), 7.27 (d, J = 7.0 Hz, 1H), 7.43−7.52 (m, 3H), 7.56 (t, J = 7.6 Hz, 1H), 7.72 (d, J = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ

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33.3 (d, J = 3.9 Hz), 116.0 (d, J = 21.6 Hz), 124.1(d, J = 3.7 Hz), 125.9, 127.7 (d, J = 3.0 Hz), 127.9, 128.5, 128.6 (d, J = 11.5 Hz), 129.3 (d, J = 7.8 Hz), 129.4, 130.4, 130.9, 131.3, 131.7, 132.1, 132.6, 137.9, 141.3, 159.1(d, J = 246.9 Hz), 195.2; FTIR (KBr) 3056, 1641, 1598, 1583, 1436, 1264, 754 cm^{-1}; HRMS (m/z) calculated for $C_{22}H_{15}OFNaS$ $[M+Na]^+$: 369.0725; found: 369.0722.

*[2-(4-(Trifluoromethyl)phenyl)-2H-thiochromen-3-yl](phenyl)-methanone (**3i**).* 140 mg, 82% yield; yellowish viscous liquid; R_f 0.46 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.39 (s, 1H), 7.06−7.12 (m, 1H), 7.18−7.21 (m, 3H), 7.32 (d, J = 8.4 Hz, 2H), 7.37−7.44 (m, 5H), 7.51 (tt, J = 7.6 Hz, 2.4 Hz, 1H), 7.63 (dd, J = 8.2 Hz, 1.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.0, 124.1 (q, J = 270.2 Hz), 125.7 (q, J = 3.7 Hz), 126.1, 127.1, 127.8, 128.6, 129.3, 129.8 (q, J = 32.2 Hz), 130.4, 131.1, 131.5, 132.16, 132.19, 132.6, 137.9, 140.8, 145.8, 195.5; FTIR (KBr) 3064, 1641, 1617, 1597, 1446, 1325, 1120, 754 cm^{-1}; HRMS (m/z) calculated for $C_{23}H_{15}OSNaF_3$ $[M+Na]^+$: 419.0693; found: 419.0705.

*[2-(Naphthalen-1-yl)-2H-thiochromen-3-yl](phenyl)methanone (**3j**).* 178 mg, 94% yield; yellow viscous liquid; R_f 0.40 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 6.34 (s, 1H), 7.09−7.25 (m, 5H), 7.34 (dd, J = 7.2 Hz, 1.6 Hz, 1H), 7.46−7.61 (m, 4H), 7.62−7.68 (m, 2H), 7.70 (d, J = 7.0 Hz, 1H), 7.77 (d, J = 7.6 Hz, 2H), 7.85 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.8, 123.4, 124.4, 125.2, 125.88, 125.93, 126.7, 128.2, 128.5, 128.6, 129.2, 129.4, 129.7, 130.4, 131.1, 131.2, 132.0, 132.8, 133.2, 134.7, 135.7, 138.2, 141.6, 195.5; FTIR (KBr) 3056, 1641, 1594, 1554, 1441, 754 cm^{-1}; HRMS (m/z) calculated for $C_{26}H_{18}ONaS$ $[M+Na]^+$: 401.0971; found: 401.0973.

*[2-(Thiophen-2-yl)-2H-thiochromen-3-yl](phenyl)methanone (**3k**).* 125 mg, 74% yield; brownish viscous liquid; R_f 0.35 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.76 (s, 1H), 6.81 (t, J = 3.6 Hz, 1H), 6.91 (d, J = 2.4 Hz, 1H), 7.04 (d, J = 5.2 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.24−7.30 (m, 2H), 7.31−7.36 (m, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.73 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.7, 124.8, 125.0, 126.0, 126.8, 128.1, 128.5, 129.4, 130.4, 131.1, 131.2, 132.1, 132.5, 133.8, 138.1, 139.8, 145.4, 195.4; FTIR (KBr) 3059, 1640, 1590, 1553, 1445, 754 cm^{-1}; HRMS (m/z) calculated for $C_{20}H_{14}ONaS_2$ $[M+Na]^+$: 357.0378; found: 357.0381.

*[2-(Pyridin-2-yl)-2H-thiochromen-3-yl](phenyl)methanone (**3l**).* 148 mg, 90% yield; brownish viscous liquid; R_f 0.41 (20% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.57 (s, 1H), 7.05−7.13 (m, 2H), 7.19 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.22−7.28 (m, 3H), 7.43 (s, 1H), 7.45−7.54 (m, 3H), 7.57 (tt, J = 7.2 Hz, 2.0 Hz, 1H), 8.48 (ddd, J = 4.8 Hz, 1.6 Hz, 0.8 Hz, 1H), 7.79 (dd, J = 8.2 Hz, 1.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 42.4, 121.0, 122.3, 125.8, 127.6, 128.5, 129.6, 130.7, 130.9, 131.0, 132.1, 132.5, 132.9, 136.8, 138.1, 140.6, 149.7, 160.2, 195.9; FTIR (KBr) 3056, 1641, 1585, 1465, 751 cm^{-1}; HRMS (m/z) calculated for $C_{21}H_{15}ONNaS$ $[M+Na]^+$: 352.0767; found: 352.0772.

*(2-Phenyl-2H-thiochromen-3-yl)(p-tolyl)methanone (**3m**).* 147 mg, 86% yield; yellow viscous liquid; R_f 0.36 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 3H), 5.46 (s, 1H), 7.12 (td, J = 6.0 Hz, 1.2 Hz, 1H), 7.16−7.22 (m, 3H), 7.23−7.29 (m, 7H), 7.38 (s, 1H), 7.62 (d, J = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 40.5, 125.8, 126.7, 127.72, 127.74, 128.8, 129.2, 129.6, 130.6, 130.8, 131.0, 132.7, 133.5, 135.4, 139.5, 142.1, 142.8, 195.6; FTIR (KBr) 3046, 1642, 1596, 1543, 1472, 753 cm^{-1}; HRMS (m/z) calculated for $C_{23}H_{18}ONaS$ $[M+Na]^+$: 365.0976; found: 365.0965.

*(2-Phenyl-2H-thiochromen-3-yl)(3-bromophenyl)methanone (**3n**).* 159 mg, 78% yield; brownish viscous liquid; R_f 0.45 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.43 (s, 1H), 7.11−7.16 (m, 1H), 7.17−7.22 (m, 3H), 7.23−7.28 (m, 5H), 7.33 (t, J = 6.0 Hz, 1H), 7.38 (s, 1H), 7.58 (d, J = 6.0 Hz, 1H), 7.67 (d, J = 6.4 Hz, 1H), 7.80 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.2, 122.8, 125.9, 126.7, 127.7, 127.8, 127.9, 128.8, 130.0, 130.3, 131.1, 131.5, 132.0, 132.9, 133.0, 134.8, 140.1, 140.8, 141.8, 194.2; FTIR (KBr) 3059, 1643, 1617, 1557, 1436, 1112, 758 cm^{-1}; HRMS (m/z) calculated for $C_{22}H_{16}OBrS$ $[M+H]^+$: 407.0100; found: 407.0103.

*(2-Phenyl-2H-thiochromen-3-yl)(4-chlorophenyl)methanone (**3o**).* 150 mg, 82% yield; yellow solid; mp 144−146 °C; R_f 0.48 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.43 (s, 1H), 7.13 (td, J = 8.4 Hz, 2.4 Hz, 1H), 7.16−7.23 (m, 3H), 7.23−7.28 (m, 5H), 7.35 (s, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.3, 125.9, 126.7, 127.8, 127.9, 128.8, 130.3, 130.7, 131.0, 131.4, 132.9, 133.1, 136.5, 138.4, 140.1, 141.9, 194.6; FTIR (KBr) 3060, 1648, 1616, 1586, 1487, 828, 761 cm^{-1}; HRMS (m/z) calculated for $C_{22}H_{15}OClNaS$ $[M+Na]^+$: 385.0424; found: 385.0429.

*(2-Phenyl-2H-thiochromen-3-yl)(4-fluorophenyl)methanone (**3p**).* 129 mg, 74% yield; yellow viscous liquid; R_f 0.45 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.35 (s, 1H), 7.01−7.07 (m, 3H), 7.07−7.13 (m, 3H), 7.14−7.20 (m, 5H), 7.26 (s, 1H), 7.61−7.67 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.5, 115.7 (d, J = 21.7 Hz), 125.8, 126.7, 127.7, 127.8, 128.8, 130.4, 130.9, 131.2, 131.8 (d, J = 9.0 Hz), 132.8, 133.2, 134.3 (d, J = 3.3 Hz), 139.7, 141.9, 165.1 (d, J = 251.8 Hz), 194.4; FTIR (KBr) 3054, 1643, 1560, 1421, 751 cm^{-1}; HRMS (m/z) calculated for $C_{22}H_{15}OFNaS$ $[M+Na]^+$: 369.0725; found: 369.0727.

*(2-Phenyl-2H-thiochromen-3-yl)[4-(trifluoromethyl)phenyl]-methanone (**3q**).* 132 mg, 66% yield; yellow viscous liquid; R_f 0.48 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.39 (s, 1H), 7.05−7.10 (m, 1H), 7.11−7.17 (m, 3H), 7.18−7.21 (m, 5H), 7.28 (s, 1H), 7.64−7.72 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 40.0, 123.7 (q, J = 270.9 Hz), 125.5 (q, J = 3.6 Hz), 125.9, 126.6, 127.7, 127.9, 128.8, 129.4, 130.1, 131.1, 131.6, 132.8, 132.9,133.2 (q, J = 32.5 Hz), 141.1, 141.4, 141.8, 194.5; FTIR (KBr) 3058, 1647, 1617, 1585, 1406, 1324, 1129, 752 cm^{-1}; MS (m/z): HRMS (m/z) calculated for $C_{23}H_{15}OF_3NaS$ $[M+Na]^+$: 419.0688; found: 419.0693.

*(2-Phenyl-2H-thiochromen-3-yl) (naphthalen-2-yl)methanone (**3r**).* 160 mg, 84% yield; yellow viscous liquid; R_f 0.70 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.51 (s, 1H), 7.08 (t, J = 7.2 Hz, 1H), 7.15−7.27 (m, 6H), 7.32 (d, J = 7.2 Hz, 2H), 7.45 (s, 1H), 7.49−7.59 (m, 2H), 7.76 (d, J = 8.4 Hz, 1H), 7.84−7.92 (m, 3H), 8.18 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.5, 125.6, 125.8, 126.7, 126.9, 127.7, 127.8, 127.9, 128.2, 128.5, 128.8, 129.3, 130.2, 130.5, 130.9, 131.1, 132.4, 132.8, 133.5, 135.0, 135.4, 140.1, 142.0, 195.7; FTIR (KBr) 3056, 1640, 1584, 1555, 1490, 758 cm^{-1}; HRMS (m/z) calculated for $C_{26}H_{19}OS$ $[M+H]^+$: 379.1157; found: 379.1164.

*(2-Phenyl-2H-thiochromen-3-yl) (thiophen-2-yl)methanone (**3s**).* 115 mg, 68% yield; yellow viscous liquid; R_f 0.40 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.38 (s, 1H), 7.12−7.20 (m, 5H), 7.22−7.29 (m, 4H), 7.33 (d, J = 7.6 Hz, 1H), 7.65 (dd, J = 5.0 Hz, 1.2 Hz, 1H), 7.68 (s, 1H), 7.71 (dd, J = 3.6 Hz, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.9, 125.9, 126.8, 127.8, 127.9, 128.8, 130.5, 130.7, 131.0, 132.6, 133.4, 133.6, 133.7, 137.8, 141.8, 143.1, 186.7; FTIR (KBr) 3058, 1617, 1584, 1553, 1411, 759 cm^{-1}; HRMS (m/z) calculated for $C_{20}H_{15}OS_2$ $[M+H]^+$: 335.0564; found: 335.0557.

*1-(2-Phenyl-2H-thiochromen-3-yl)ethan-1-one (**3t**).* 112 mg, 84% yield; yellow viscous liquid; R_f 0.42 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.48 (s, 3H), 5.36 (s, 1H), 7.14−7.20 (m, 6H), 7.23−7.26 (m, 2H), 7.37 (d, J = 7.2 Hz, 1H), 7.67 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.7, 38.9, 125.8, 126.7, 127.7, 127.8, 128.7, 130.6, 130.9, 131.2, 133.0, 134.1, 137.5, 142.1, 196.6; FTIR (KBr) 3058, 2924, 1659, 1622, 1584, 1438, 754 cm^{-1}; HRMS (m/z) calculated for $C_{17}H_{14}ONaS$ $[M+Na]^+$: 289.0663; found: 289.0687.

*2-Phenyl-2H-thiochromene-3-carbaldehyde (**3u**).*[8a] 123 mg, 97% yield; pale yellow viscous liquid; R_f 0.44 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.21 (s, 1H), 7.16−7.22 (m, 6H), 7.27 (t, J = 7.2 Hz, 2H), 7.41 (d, J = 7.6 Hz, 1H), 7.46 (s, 1H), 9.67 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 38.5, 126.0, 126.6, 127.8, 128.0, 128.8, 130.0, 131.1, 131.9, 134.3, 135.0, 141.8, 145.3, 191.3; FTIR (KBr) 3058, 1668, 1583, 1554, 1437, 751 cm^{-1}; HRMS (m/z) calculated for $C_{16}H_{12}OKS$ $[M+K]^+$: 291.0246; found: 291.0245.

*2-Phenyl-2H-thiochromene-3-carbaldehyde (**3v**).* 131 mg, 98% yield; yellow viscous liquid; R_f 0.47 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.16 (s, 3H), 5.10 (s, 1H), 6.92 (d, J = 7.6 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 7.08−7.13 (m, 1H), 7.16−7.21 (m, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.37 (s, 1H), 9.58 (s, 1H); ^{13}C NMR

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($CDCl_3$, 100 MHz) δ 21.2, 38.3, 125.9, 126.5, 127.8, 129.5, 130.0, 131.1, 131.8, 134.3, 135.0, 137.8, 138.9, 145.2, 191.4; FTIR (KBr) 3056, 2934, 1665, 1593, 1564, 1427, 753 cm^{-1}; HRMS (m/z) calculated for $C_{17}H_{14}ONaS$ $[M+Na]^+$: 289.0663; found: 289.0670.

*2-Methyl-2H-thiochromene-3-carbaldehyde (**3w**).* 77 mg, 81% yield; yellow viscous liquid; R_f 0.50 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.29 (d, J = 7.2 Hz, 3H), 4.08 (q, J = 7.2 Hz, 1H), 7.18 (td, J = 7.4 Hz, 1.2 Hz, 1H), 7.23 (s, 1H), 7.30 (td, J = 7.2 Hz, 1.6 Hz, 1H), 7.33−7.37 (m, 2H), 9.61 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.3, 30.4, 125.8, 128.4, 130.0, 131.0, 131.5, 134.2, 138.0, 144.3, 191.3; FTIR (KBr) 3057, 2813, 1673, 1584, 1556, 1439, 751 cm^{-1}; HRMS (m/z) calculated for $C_{11}H_{10}ONaS$ $[M+Na]^+$: 213.0350; found: 213.0348.

*(6-Bromo-2-phenyl-2H-thiochromen-3-yl) (phenyl)methanone (**3x**).* 176 mg, 86% yield; yellow viscous liquid; R_f 0.58 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.44 (s, 1H), 7.09 (d, J = 8.4 Hz, 1H), 7.15−7.23 (m, 5H), 7.26 (s, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.37 (s, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.4, 118.8, 126.7, 128.0, 128.6, 128.8, 128.9, 129.1, 129.3, 131.8, 132.3, 133.1, 133.7, 134.5, 137.9, 138.4, 141.5, 195.6; FTIR (KBr) 3057, 1643, 1537, 1491, 1448, 1084, 728 cm^{-1}; HRMS (m/z) calculated for $C_{22}H_{15}OBrNaS$ $[M+Na]^+$: 428.9925; found: 428.9945.

*(6-Chloro-2-phenyl-2H-thiochromen-3-yl) (phenyl)methanone (**3y**).* 146 mg, 80% yield; yellow viscous liquid; R_f 0.32 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.48 (s, 1H), 7.18−7.29 (m, 8H), 7.31 (s, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.56 (tt, J = 7.6 Hz, 2.4 Hz, 1H), 7.68 (dd, J = 8.2 Hz, 1.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.4, 126.7, 128.0, 128.6, 128.8, 128.9, 129.3, 130.2, 130.8, 131.1, 131.2, 131.9, 132.3, 134.5, 137.8, 138.6, 141.4, 195.6; FTIR (KBr) 3054, 1641, 1564, 1501, 1468, 821, 736 cm^{-1}; HRMS (m/z) calculated for $C_{22}H_{15}OClNaS$ $[M+Na]^+$: 385.0430; found: 385.0449.

*(7-Methyl-2-phenyl-2H-thiochromen-3-yl) (phenyl)methanone (**3z**).* 151 mg, 88% yield; yellow viscous liquid; R_f 0.62 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.19 (s, 3H), 5.37 (s, 1H), 6.94−7.00 (m, 2H), 7.03−7.13 (m, 4H), 7.20 (d, J = 7.2 Hz, 2H), 7.28 (s, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.46 (t, J = 6.8 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9, 40.3, 126.7, 127.6, 127.7, 128.4, 128.7, 129.2, 129.3, 130.4, 131.5, 131.9, 132.16, 133.4, 135.5, 138.2, 140.5, 142.0, 195.9; FTIR (KBr) 3052, 2920, 1673, 1584, 1555, 1438, 751 cm^{-1}; HRMS (m/z) calculated for $C_{23}H_{19}OS$ $[M+H]^+$: 343.1157; found: 343.1129.

*[2-(4-Fluorophenyl)-2H-thiochromen-3-yl](phenyl)methanone (**3aa**).* 122 mg, 70% yield; yellow viscous liquid; R_f 0.50 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.36 (s, 1H), 6.80 (tt, J = 10.8 Hz, 2.4 Hz, 2H), 7.03−7.08 (m, 1H), 7.13−7.19 (m, 5H), 7.32 (s, 1H), 7.39 (t, J = 7.2 Hz, 2H), 7.48 (tt, J = 7.2 Hz, 1.2 Hz, 1H), 7.61 (dd, J = 8.2 Hz, 1.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.7, 115.6 (d, J = 21.4 Hz), 125.9, 127.8, 128.4 (d, J = 8.1 Hz), 128.5, 129.3, 130.4, 131.0, 131.3, 132.1, 132.5, 133.3, 137.9 (d, J = 3.2 Hz), 138.1, 140.2, 162.3 (d, J = 244.7 Hz), 195.8; FTIR (KBr) 3053, 1648, 1598, 1564, 1423, 1198, 751 cm^{-1}; HRMS (m/z) calculated for $C_{22}H_{15}OFNaS$ $[M+Na]^+$: 369.0720; found: 369.0721.

*[2-(6-Methoxynaphthalen-1-yl)-2H-thiochromen-3-yl](phenyl)-methanone (**3ab**).* 159 mg, 78% yield; brownish viscous liquid; R_f 0.32 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.78 (s, 3H), 5.53 (s, 1H), 6.93−7.01 (m, 2H), 7.05 (td, J = 6.8 Hz, 1.6 Hz, 1H), 7.11−7.17 (m, 2H), 7.21(d, J = 7.6 Hz, 1H), 7.31−7.41 (m, 4H), 7.44−7.55 (m, 4H), 7.63 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.5, 55.4, 105.7, 118.9, 125.2, 125.76, 125.79, 127.7, 127.8, 128.5, 128.7, 129.3, 129.7, 130.5, 131.0, 131.2, 132.0, 132.8, 133.2, 134.2, 136.9, 138.2, 140.2, 157.9, 195.9; FTIR (KBr) 3056, 2933, 1638, 1505, 1481, 1441, 754 cm^{-1}; HRMS (m/z) calculated for $C_{27}H_{20}O_2NaS$ $[M+Na]^+$: 431.1082; found: 431.1079.

*(2-Phenyl-2H-thiochromen-3-yl)(benzo[d][1,3]dioxol-5-yl)-methanone (**3ac**).* 138 mg, 74% yield; brownish viscous liquid; R_f 0.35 (10% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.34 (s, 1H), 5.98 (q, J = 0.8 Hz, 2H), 6.80 (d, J = 6.4 Hz, 1H), 7.07 (td, J = 5.8 Hz, 1.2 Hz, 1H), 7.10−7.15 (m, 3H), 7.15−7.20 (m, 6H), 7.25 (dd, J = 6.4 Hz, 1.2 Hz, 1H), 7.29 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.8, 101.9, 108.0, 109.7, 125.5, 125.8, 126.7, 127.7, 127.8, 128.8, 130.5, 130.7, 131.0, 132.3, 132.6, 133.5, 138.7, 142.0, 148.0, 151.3, 194.2; FTIR (KBr) 3064, 2920, 1636, 1605, 1503, 1439, 761 cm^{-1}; HRMS (m/z) calculated for $C_{23}H_{17}O_3S$ $[M+H]^+$: 373.0898; found: 373.0879.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02740.

^1H and ^{13}C NMR spectra (PDF)

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

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Notes

The authors declare no competing financial interest.

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