Tetrahedron 69 (2013) 2430–2435

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Catalyst-free C–S/C–O bond formation: synthesis of novel 4-thio-substituted 2-aryl-4*H*-chromenes from easily available 2-hydroxychalcones

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ARTICLE INFO

Article history:
Received 1 November 2012
Received in revised form 12 January 2013
Accepted 15 January 2013
Available online 26 January 2013

Keywords:
Domino reaction
2-Hydroxychalcones
Thio-substituted
4*H*-Chromenes
Catalyst-free

ABSTRACT

An efficient catalyst-free synthesis of novel functionalized 4-thio-substituted 2-aryl-4*H*-chromenes from easily available 2-hydroxychalcone derivatives is described. This domino reaction enables successful assembly of two new C–S and C–O sigma bonds in a one-pot operation.

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1. Introduction

Chromenes and chromans are important classes of heterocyclic compounds, which constitute the key cores of various natural products. For example, 4-thio-substituted chromans 4β-benzylthioether-epicatechin (**1**), 4β-2-aminoethylthiolepicatechin (**2**), and 4β-2-hydroxyethylthioepicatechin (**3**) are widely present in plants, including edible vegetables and fruits (Fig. 1).[1] They also exhibit a wide of range of biological activities.[2] In recent years, functionalized chromenes and chromans have played an ever-increasing role in the synthetic approaches toward promising compounds in the field of medicinal chemistry.[3–7] To data, only few examples for the synthesis of 4-thio-substituted chromenes have been reported.[8] Magedov described an efficient method for the synthesis of 2-amino-4-(phenylthio)-4*H*-chromene-3-carbonitriles by a Michael addition reaction of iminochromene with thiophenols (Scheme 1a).[9] Singh found that this transformation could be achieved by a one-pot three-component reaction of salicylaldehyde, malononitrile, and thiophenols in ionic liquid.[10] Recently, Zhu also developed a route for the synthesis of thio-substituted chromenes by the reaction of 2-(trifluoromethyl)-2-hydroxy-2*H*-chromenes with thiophenols promoted by Lewis acid (Scheme 1b).[11] However, thio-substituted chromenes with an aryl group at C-2 position are not easily accessible by currently existing routes. Consequently, in order to expand the chromene library, the development of new and more general methods for their preparation is of significant interest. In addition, catalyst-free synthetic methods have attracted much interest owing to reduced pollution, mild conditions, ease of purification, and lower costs. Encouraged by the synthesis of flavones involving the intramolecular cyclization of 2-hydroxyphenyl-3-phenylpropane-1,3-dione intermediate[12] and as a continuation of our efforts toward the development of new synthetic protocols for the construction of heterocyclic frameworks,[13] we herein report an efficient strategy for the preparation of novel 4-thio-substituted 2-aryl-4*H*-chromenes from easily available starting materials 2-hydroxychalcones without any catalyst (Scheme 1c).

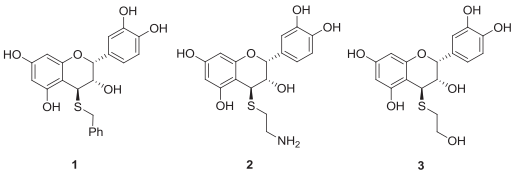

Fig. 1. Examples of natural products.

2. Results and discussion

Initially, 2-hydroxychalcone derivatives (**4**) were synthesized according to the known methods.[14] Next, an attempted reaction of

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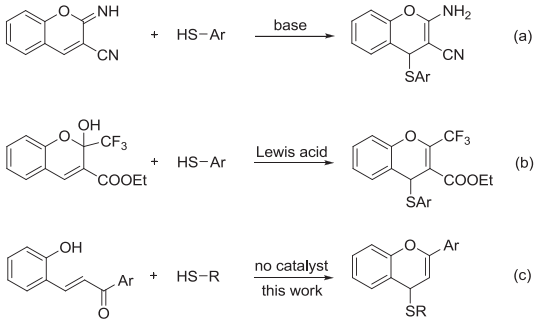
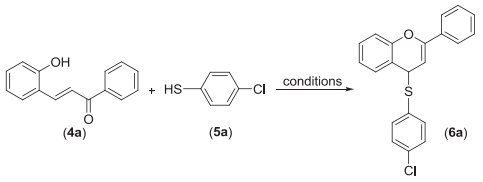
http://dx.doi.org/10.1016/j.tet.2013.01.047



Scheme 1. Strategies for the synthesis of thio-substituted chromenes.

2-hydroxychalcone (**4a**) with 4-chlorobenzenethiol (**5a**) was carried out to gain the desired product 4-(4-chlorophenylthio)-2-phenyl-4*H*-chromene (**6a**) in various solvents under catalyst-free conditions. Preliminary experiment indicated that in refluxing THF, MeCN, and MeOH, product **6a** was not observed (Table 1, entries 1–3). No reactions occurred in DMSO and DMF at 100 °C (Table 1, entries 4, 5). The reaction gave **6a** in 40% yield using EtOH as the solvent (Table 1, entry 6). When *n*-PrOH, *t*-BuOH, benzene, and 1,2-dichloroethane (DCE) were employed, the reactions delivered the product in a low yield (Table 1, entries 7–10). We were pleased to find that the reaction proceeded smoothly in refluxing toluene for 6 h to provide product **6a** in 76% yield (Table 1, entry 11). The yield increased to 80% when 1.1 equiv of **5a** was used (Table 1, entry 12), but it could not be further improved as increasing the ratio of **4a**/**5a** to 1.5 (Table 1, entry 13). While the temperature decreased to 80 °C, the similar result was obtained as in refluxing benzene (Table 1, entry 14).

Table 1
Optimization of the reaction conditions for the synthesis of **6a**

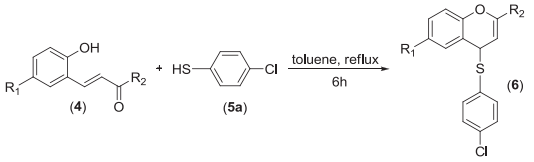


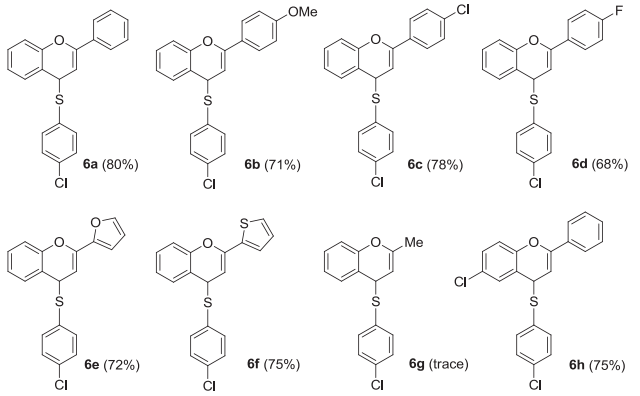
Entry[a]	Solvent	Temp (°C)	**4a**/**5a**[b]	Yield[c] (%)
1	THF	Reflux	1:1	—
2	MeCN	Reflux	1:1	—
3	MeOH	Reflux	1:1	—
4	DMSO	100	1:1	—
5	DMF	100	1:1	—
6	EtOH	Reflux	1:1	40
7	*n*-PrOH	Reflux	1:1	8
8	*t*-BuOH	Reflux	1:1	12
9	DCE	Reflux	1:1	10
10	Benzene	Reflux	1:1	20
11	Toluene	Reflux	1:1	76
12	Toluene	Reflux	1:1.1	80
13	Toluene	Reflux	1:1.5	80
14	Toluene	80	1:1	20

[a] All reactions were performed using **4a** (0.5 mmol) in solvent (3.0 mL) for 6 h.
[b] Molar ratio of **4a**/**5a**.
[c] Isolated yield.

With the optimal reaction conditions (1.1 equiv of thiol, toluene, at reflux) in hand, the reactions of **5a** with various 2-hyroxychalcone derivatives were explored to gauge the generality of this process (Table 2). For the substrates bearing electron-donating (–OMe) and electron-withdrawing groups (–Cl, –F) on the phenyl ring (R_2), the reactions proceeded smoothly to give the corresponding 4-thio-substituted 4*H*-chromenes **6b**–**d** in 68–78% yields. The structure of

Table 2
Synthesis of 4-(4-chlorophenylthio)-substituted 4*H*-chromenes





[a] All reactions were performed using **4** (0.5 mmol), **5a** (0.55 mmol) in toluene (3.0 mL).
[b] Isolated yield.

6d was further confirmed by X-ray diffraction analysis (Fig. 2).[15] This transformation was also suitable for heterocyclic substrates (furan and thiophene), furnishing **6e** and **6f** in 72% and 75% yields, respectively. However, the alkyl group ($-CH_3$) substrate resulted in a complex reaction mixture and a trace amount of product **6g** was not isolated. Moreover, the reaction of (*E*)-3-(5-chloro-2-hydroxyphenyl)-1-phenylprop-2-en-1-one (R_1=Cl) with **5a** also gave rise to **6h** in 75% yield.

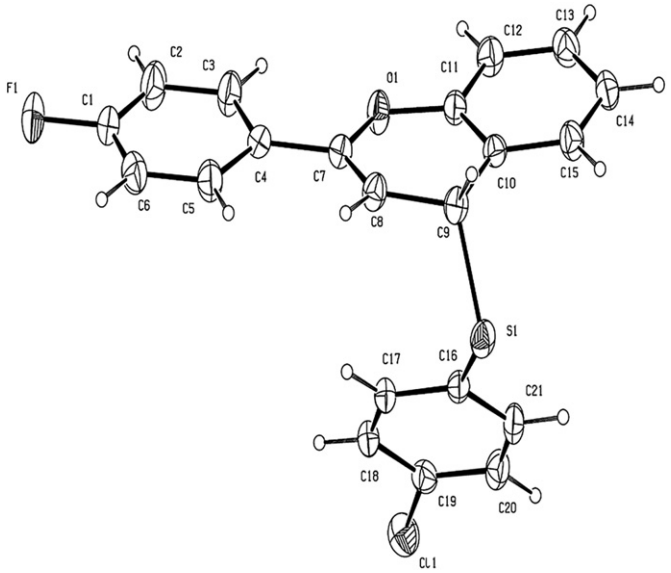
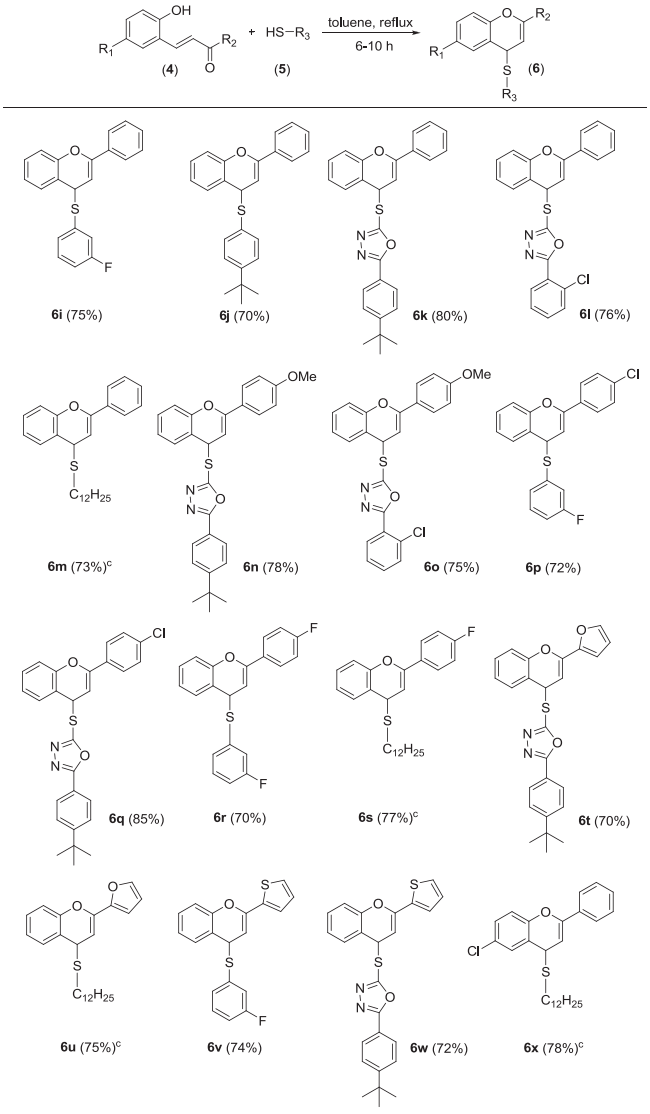


Fig. 2. X-ray crystal structure of compound **6d**.

Then, we further extended the substrates to a variety of thiols for the preparation of structurally diverse and functionalized 4-thio-substituted 4*H*-chromenes (Table 3). The experimental results indicated that the treatments of **4a** with aryl thiols including electron-deficient 3-fluorobenzenethiol and electron-rich 4-*tert*-butylbenzenethiol could give the corresponding products **6i** and **6j** in 75% and 70% yields, respectively. In addition, heteroaryl thiols,

Table 3
Synthesis of various 4-thio-substituted 2-aryl-4*H*-chromenes **6**[a,b]



[a] All reactions were performed using **4** (0.5 mmol), **5** (0.55 mmol) in toluene (3.0 mL).
[b] Isolated yields. [c] *n*-Dodecane-1-thiol (1.0 mmol) was employed for 10 h.

such as 5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole-2-thiol and 5-(2-chlorophenyl)-1,3,4-oxadiazole-2-thiol also afforded **6k** and **6l** in good yields. Nevertheless, the reaction of **4a** with aliphatic thiol (*n*-dodecane-1-thiol) was slower than those aromatic substrates. When 2.0 equiv of *n*-dodecane-1-thiol was used and the reaction time was prolonged to 10 h, **6m** was isolated in 73% yield. This probably reflected the lower nucleophilicity of the aliphatic thiol. In addition, other 2-hyroxychalcone derivatives (**4**) could also react with various thiols, furnishing the desired products **6n**–**x** in 70–85% yields.

The possible reaction mechanism was proposed using **4a** as an example, as shown in Fig. 3. First, under catalyst-free reaction conditions, **4a** reacted with 4-chlorobenzenethiol (**5a**) via a Michael addition reaction to form the saturated intermediate thio-substituted ketone (**6aa**),[16] which was successfully isolated from the reaction mixture in refluxing toluene for 15 min. Then isomerization of **6aa** gave rise to the formation of the chroman ring (hemiketal) **6ab**. It was notably that ^{1}H NMR spectroscopy showed up as a mixture of ketone and hemiketal with an approximate molar ratio of 20:1 in $CDCl_3$[17] and only ketone form was observed in DMSO-d_6

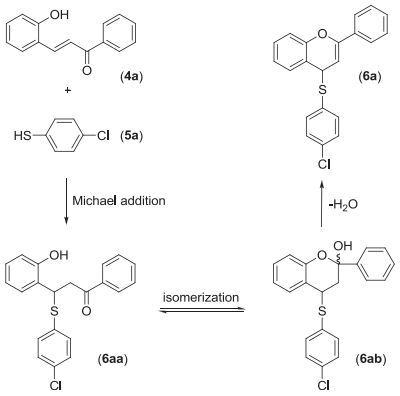


Fig. 3. Possible reaction pathway for the present reaction.

(see Supplementary data). Subsequently, the expected thio-substituted 4*H*-chromene **6a** was obtained after loss of water of **6ab**.

3. Conclusion

In summary, we have developed an efficient, catalyst-free synthesis of novel 4-thio-substituted-2-aryl-4*H*-chromenes by the reactions of 2-hydroxychalcone derivatives with various thiols. This domino reaction enables successful assembly of two new C–S and C–O sigma bonds in a one-pot operation. Moreover, due to easily accessible starting materials, wide scope of substrates, and good yields, we believe that this new synthetic approach has potential in the synthesis of various functionalized 4*H*-chromenes, which are of considerable interest as potential biologically active compounds or pharmaceuticals.

4. Experimental

4.1. General method

All chemicals were commercial and used without further purification. All organic solvents were dried and freshly distilled before use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 300 MHz spectrometers using $CDCl_3$ as the solvent. Chemical shifts are reported relative to TMS (internal standard). IR spectra were obtained as KBr, cm^{-1} pellet samples on a Nicolet 5700 FTIR spectrometer. The X-ray crystal structure determinations of compounds were obtained on a Bruker SMART APEX CCD system. Flash column chromatography was performed on silica gel (200–300 mesh). High-resolution mass spectra were recorded on Bruker micrOTOF-QII (ESI) and Waters GCT Premier (EI and CI). After careful attempt of different ion sources, such as ESI, EI, CI and APCI (Thermo LCQ TM Deca XP plus), the C–S bond (chromenes-C4) cleavages were still observed for some compounds. HRMS (CI) data of two fragments for those C–S bond cleavage compounds were given.

4.2. General experimental procedure for the synthesis of 4-thio-substituted-4*H*-chromenes (6)

A mixture of **4** (0.5 mmol) and thiols (**5**) (0.55 mmol) was heated at reflux in anhydrous toluene (3.0 mL). After the reactant disappeared (6–10 h, monitored by thin layer chromatography), the mixture was cooled to room temperature. The reaction mixture was directly added to the column chromatography using petroleum ether as the eluent to remove toluene, then eluting with petroleum ether or petroleum ether/ethyl acetate to give the expected compounds **6**.

4.3. Characterization data

*4.3.1. 4-(4-Chlorophenylthio)-2-phenyl-4H-chromene (**6a**).* Mp 87–88 °C; IR (KBr, cm^{-1}) 2358, 1230, 1086, 816, 679; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.58–7.54 (m, 2H), 7.41–7.36 (m, 4H), 7.19–6.99 (m, 6H), 6.87 (d, J=8.1 Hz, 1H), 5.62 (d, J=5.0 Hz, 1H), 5.15 (d, J=5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 152.1, 150.9, 137.5, 135.1, 133.6, 129.7, 129.5, 128.9, 128.41, 128.40, 128.3, 124.8, 123.8, 119.9, 116.4, 97.1, 45.9; HRMS-EI: m/z calcd for $C_{21}H_{15}ClOS$: 350.0532, found: 350.0528.

*4.3.2. 4-(4-Chlorophenylthio)-2-(4-methoxyphenyl)-4H-chromene (**6b**).* Mp 63–64 °C; IR (KBr, cm^{-1}) 2358, 1647, 1610, 1244, 1026, 817, 649; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.50 (d, J=6.9 Hz, 2H), 7.37 (d, J=7.5 Hz, 1H), 7.18–7.00 (m, 6H), 6.91–6.85 (m, 3H), 5.51 (d, J=5.0 Hz, 1H), 5.14 (d, J=5.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 160.2, 152.1, 150.9, 137.4, 135.0, 129.9, 129.5, 128.4, 128.3, 126.3, 126.2, 123.7, 120.0, 116.4, 113.7, 95.5, 55.3, 46.1; HRMS-EI: m/z calcd for $C_{22}H_{17}ClO_2S$: 380.0638, found: 380.0632.

*4.3.3. 2-(4-Chlorophenyl)-4-(4-chlorophenylthio)-4H-chromene (**6c**).* Mp 72–73 °C; IR (KBr, cm^{-1}) 2358, 1646, 1231, 1006, 825, 665; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.49 (d, J=8.6 Hz, 2H), 7.41–7.33 (m, 3H), 7.22–7.05 (m, 4H), 6.98 (d, J=8.3 Hz, 2H), 6.86 (d, J=8.1 Hz, 1H), 5.60 (d, J=5.0 Hz, 1H), 5.12 (d, J=5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 151.9, 149.9, 137.5, 135.2, 134.8, 132.0, 129.5, 128.6, 128.5, 128.4, 126.0, 124.0, 119.7, 116.4, 97.5, 45.7; HRMS-EI: m/z calcd for $C_{21}H_{14}Cl_2OS$: 384.0142, found: 384.0146.

*4.3.4. 4-(4-Chlorophenylthio)-2-(4-fluorophenyl)-4H-chromene (**6d**).* Mp 85–87 °C; IR (KBr, cm^{-1}) 2358, 1651, 1224, 1005, 812, 655; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.55–7.50 (m, 2H), 7.38 (d, J=8.8 Hz, 1H), 7.24–6.98 (m, 8H), 6.86 (d, J=8.1 Hz, 1H), 5.54 (d, J=5.0 Hz, 1H), 5.11 (d, J=5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 163.1 (d, $^1J_{C-F}$=247.1 Hz), 152.0, 150.1, 137.4, 135.1, 129.7 (d, $^4J_{C-F}$=3.3 Hz), 129.6, 129.5, 128.4, 126.6 (d, $^3J_{C-F}$=8.3 Hz), 123.9, 119.8, 116.4, 115.3 (d, $^2J_{C-F}$=21.7 Hz), 96.8 (d, $^5J_{C-F}$=1.6 Hz), 45.8; HRMS-EI: m/z calcd for $C_{21}H_{14}ClFOS$: 368.0438, found: 368.0450.

*4.3.5. 4-(4-Chlorophenylthio)-2-(furan-2-yl)-4H-chromene (**6e**).* Yellow oil; IR (KBr, cm^{-1}) 2359, 1635, 1230, 1011, 815, 694; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.40–7.34 (m, 2H), 7.23–7.01 (m, 6H), 6.82 (d, J=8.1 Hz, 1H), 6.50 (d, J=3.4 Hz, 1H), 6.41 (dd, J_1=3.4 Hz, J_2=1.8 Hz, 1H), 5.65 (d, J=5.0 Hz, 1H), 5.09 (d, J=5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 151.6, 147.9, 143.6, 142.7, 137.2, 135.0, 129.8, 129.6, 128.42, 128.39, 123.8, 119.9, 116.3, 111.3, 107.3, 95.9, 45.2; HRMS-EI: m/z calcd for $C_{19}H_{13}ClO_2S$: 340.0325, found: 340.0333.

*4.3.6. 4-(4-Chlorophenylthio)-2-(thiophen-2-yl)-4H-chromene (**6f**).* Yellow oil; IR (KBr, cm^{-1}) 2357, 1631, 1234, 1008, 817, 685; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.36 (d, J=8.8 Hz, 1H), 7.28–7.24 (m, 2H), 7.20–7.00 (m, 7H), 6.85 (d, J=8.1 Hz, 1H), 5.55 (d, J=5.0 Hz, 1H), 5.09 (d, J=5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 151.8, 146.7, 137.5, 137.1, 135.2, 129.5, 128.44, 128.42, 127.9, 125.5, 124.1, 123.9, 119.8, 116.4, 96.5, 45.7; HRMS-EI: m/z calcd for $C_{19}H_{13}ClO_2S$: 356.0096, found: 356.0101.

*4.3.7. 6-Chloro-4-(4-chlorophenylthio)-2-phenyl-4H-chromene (**6h**).* Mp 105–106 °C; IR (KBr, cm^{-1}) 1647, 1228, 1006, 876, 692; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.55–7.52 (m, 2H), 7.39–7.37 (m, 4H), 7.16–7.02 (m, 5H), 6.80 (d, J=8.7 Hz, 1H), 5.61 (d, J=5.0 Hz, 1H), 5.05 (d, J=5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 150.9, 150.6, 137.6, 135.4, 133.2, 129.1, 129.0, 128.54, 128.51, 128.43, 128.40, 124.7, 121.5, 117.9, 96.8, 45.5; HRMS-CI: m/z $[M+H]^+$, calcd for $C_{15}H_{11}ClO+C_6H_4ClS$, 242.0498+142.9722, found: 242.0513+142.9725.

*4.3.8. 4-(3-Fluorophenylthio)-2-phenyl-4H-chromene (**6i**).* Yellow oil; IR (KBr, cm^{-1}) 2354, 1641, 1226, 1003, 876, 686; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.57–7.53 (m, 2H), 7.38–7.32 (m, 4H), 7.19–7.06 (m, 3H), 6.92–6.81 (m, 4H), 5.61 (d, J=5.0 Hz, 1H), 5.17 (d, J=5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.0 (d, $^1J_{C-F}$=247.2 Hz), 152.0, 150.9, 133.7 (d, $^3J_{C-F}$=7.7 Hz), 133.6, 131.4 (d, $^4J_{C-F}$=3.0 Hz), 129.4, 129.3 (d, $^3J_{C-F}$=8.3Hz), 128.9, 128.5, 128.3, 124.8, 123.8, 122.3 (d, $^2J_{C-F}$=21.2 Hz), 119.8, 116.4, 115.4 (d, $^2J_{C-F}$=20.9 Hz), 97.1, 45.8; HRMS-EI: m/z calcd for $C_{21}H_{15}FOS$: 334.0828, found: 334.0811.

*4.3.9. 4-(4-tert-Butylphenylthio)-2-phenyl-4H-chromene (**6j**).* Yellow oil; IR (KBr, cm^{-1}) 2959, 1638, 1231, 1013, 825, 691; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.81–7.74 (m, 4H), 7.50–7.35 (m, 7H), 7.26–7.24 (m, 1H), 7.13 (t, J=7.5 Hz, 1H), 6.95 (d, J=4.7 Hz, 1H), 5.71 (d, J=4.7 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 175.6, 159.7, 156.0, 153.1, 151.7, 133.3, 130.0, 129.6, 128.8, 128.5, 126.5, 125.9, 125.3, 124.3, 119.6, 117.2, 116.8, 93.0, 53.0, 35.1, 31.0; HRMS-EI: m/z calcd for $C_{25}H_{24}OS$: 372.1548, found: 372.1555.

*4.3.10. 2-(4-tert-Butylphenyl)-5-(2-phenyl-4H-chromen-4-yl-thio)-1,3,4-oxadiazole (**6k**).* Mp 75–76 °C; IR (KBr, cm^{-1}) 2960, 1626, 1456, 1241, 1014, 835, 692; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.54–7.51 (m, 2H), 7.38–7.35 (m, 4H), 7.19–7.06 (m, 6H), 6.86 (d, J=7.3 Hz, 1H), 5.61 (d, J=5.0 Hz, 1H), 5.12 (d, J=5.0 Hz, 1H), 1.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 152.0, 151.8, 150.5, 135.7, 133.9, 129.6, 128.7, 128.2, 128.1, 125.4, 124.8, 123.6, 120.5, 116.3, 97.5, 45.7, 34.5, 31.2; HRMS-CI: m/z $[M+H]^+$, calcd for $C_{15}H_{11}O+C_{12}H_{14}N_2OS$, 207.0810+234.0827, found: 207.0817+234.0843.

*4.3.11. 2-(2-Chlorophenyl)-5-(2-phenyl-4H-chromen-4-yl-thio)-1,3,4-oxadiazole (**6l**).* Mp 179–181 °C; IR (KBr, cm^{-1}) 1634, 1486, 1243, 1031, 752, 684; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.79–7.75 (m, 3H), 7.52 (d, J=7.8Hz, 1H), 7.42–7.24 (m, 8H), 7.15 (t, J=7.5 Hz, 1H), 6.93 (d, J=4.8 Hz, 1H), 5.73 (d, J=4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 175.4, 157.5, 153.4, 151.8, 133.2, 132.7, 131.3, 130.5, 130.0, 129.6, 128.8, 128.5, 126.9, 125.4, 124.3, 121.5, 117.2, 116.7, 92.8, 53.2; HRMS-CI: m/z $[M+H]^+$, calcd for $C_{15}H_{11}O+C_8H_5N_2OSCl$, 207.0810+211.9811, found: 207.0811+211.9808.

*4.3.12. 4-(Dodecylthio)-2-phenyl-4H-chromene (**6m**).* Yellow oil; IR (KBr, cm^{-1}) 2924, 1642, 1458, 1231, 1062, 911, 689; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.75 (d, J=8.1 Hz, 2H), 7.45–7.35 (m, 4H), 7.22 (t, J=8.1 Hz, 1H), 7.13–7.04 (m, 2H), 5.62 (d, J=4.8 Hz, 1H), 4.83 (d, J=4.8 Hz, 1H), 2.50–2.24 (m, 2H), 1.42–1.15 (m, 20H), 0.88 (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 152.1, 150.2, 133.7, 129.7, 128.8, 128.4, 128.1, 124.7, 123.9, 120.9, 116.3, 98.1, 39.9, 31.9, 29.6, 29.5, 29.44, 29.39, 29.3, 29.1, 29.0, 27.9, 22.7, 14.1; HRMS-EI: m/z calcd for $C_{27}H_{36}OS$: 408.2487, found: 408.2490.

*4.3.13. 2-(4-tert-Butylphenyl)-5-(2-(4-methoxyphenyl)-4H-chromen-4-ylthio)-1,3,4-oxadiazole (**6n**).* Mp 96–97 °C; IR (KBr, cm^{-1}) 2959, 2357, 1622, 1456, 1247, 1027, 829, 611; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.77–7.71 (m, 4H), 7.49–7.35 (m, 4H), 7.24 (d, J=8.1 Hz, 1H), 7.12 (t, J=7.5 Hz, 1H), 6.97–6.92 (m, 3H), 5.60 (d, J=4.6 Hz, 1H), 3.85 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 175.6, 160.7, 159.7, 156.0, 153.0, 151.7, 129.9, 128.8, 126.8, 126.4, 125.9, 125.8, 124.2, 119.6, 117.1, 116.9, 113.9, 91.3, 55.4, 53.1, 35.1, 31.0; HRMS-CI: m/z $[M+H]^+$, calcd for $C_{16}H_{13}O_2+C_{12}H_{14}N_2OS$, 237.0916+234.0827, found: 237.0918+234.0836.

*4.3.14. 2-(2-Chlorophenyl)-5-(2-(4-methoxyphenyl)-4H-chromen-4-ylthio)-1,3,4-oxadiazole (**6o**).* Mp 167–168 °C; IR (KBr, cm^{-1}) 1634,

1465, 1248, 1030, 828, 614; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.78–7.70 (m, 3H), 7.52 (d, J=7.8 Hz, 1H), 7.44–7.22 (m, 5H), 7.14 (t, J=7.5 Hz, 1H), 6.96–6.90 (m, 3H), 5.62 (d, J=4.6 Hz, 1H); 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 175.4, 160.7, 157.5, 153.3, 151.8, 133.2, 132.6, 131.3, 130.5, 130.0, 128.8, 126.9, 126.8, 125.8, 124.2, 121.6, 117.2, 116.8, 113.8, 91.2, 55.3, 53.4; HRMS-CI: m/z $[M+H]^+$, calcd for $C_{16}H_{13}O_2$+$C_8H_5ClN_2OS$, 237.0916+211.9811, found: 237.0918+211.9815.

*4.3.15. 2-(4-Chlorophenyl)-4-(3-fluorophenylthio)-4H-chromene (**6p**).* Yellow oil; IR (KBr, cm^{-1}) 3071, 2923, 1638, 1223, 1006, 874, 677; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.50–7.48 (m, 2H), 7.40–7.35 (m, 3H), 7.32–7.04 (m, 3H), 6.97–6.78 (m, 4H), 5.61 (d, J=5.0 Hz, 1H), 5.17 (d, J=5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.0 (d, $^1J_{C-F}$=247.1 Hz), 151.9, 149.9, 134.7, 133.4 (d, $^3J_{C-F}$=7.7 Hz), 132.0, 131.4 (d, $^4J_{C-F}$=2.9 Hz), 129.5, 129.3 (d, $^3J_{C-F}$=8.3 Hz), 128.6, 126.0, 124.0, 122.3 (d, $^2J_{C-F}$=21.2 Hz), 119.7, 116.4, 115.6 (d, $^2J_{C-F}$=20.9 Hz), 97.5, 45.7; HRMS-EI: m/z calcd for $C_{21}H_{14}ClFOS$: 368.0438, found: 368.0437.

*4.3.16. 2-(4-tert-Butylphenyl)-5-(2-(4-chlorophenyl)-4H-chromen-4-ylthio)-1,3,4-oxadiazole (**6q**).* Mp 84–85 °C; IR (KBr, cm^{-1}) 2962, 1626, 1492, 1242, 1011, 829, 629; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.77–7.70 (m, 4H), 7.48 (d, J=7.5 Hz, 1H), 7.42–7.35 (m, 5H), 7.24 (d, J=7.5 Hz, 1H), 7.14 (t, J=7.5 Hz, 1H), 6.93 (d, J=4.6 Hz, 1H), 5.70 (d, J=4.6 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 175.7, 159.8, 156.1, 152.2, 151.5, 135.4, 131.7, 130.1, 128.8, 128.7, 126.6, 126.5, 125.9, 124.5, 119.5, 117.2, 116.7, 93.4, 52.8, 35.1, 31.0; HRMS-CI: m/z $[M+H]^+$, calcd for $C_{15}H_{10}ClO$+$C_{12}H_{14}N_2OS$, 241.0420+234.0827, found: 241.0430+234.0829.

*4.3.17. 2-(4-Fluorophenyl)-4-(3-fluorophenylthio)-4H-chromene (**6r**).* Yellow oil; IR (KBr, cm^{-1}) 2915, 2351, 1634, 1228, 1010, 759, 675; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.56–7.51 (m, 2H), 7.38 (dd, J_1=7.8 Hz, J_2=1.8 Hz, 1H), 7.24–7.02 (m, 5H), 6.96–6.79 (m, 4H), 5.56 (d, J=5.0 Hz, 1H), 5.18 (d, J=5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 163.0 (d, $^1J_{C-F}$=247.1 Hz), 161.9 (d, $^1J_{C-F}$=247.1 Hz), 151.8, 150.0, 133.5 (d, $^3J_{C-F}$=7.7 Hz), 131.3 (d, $^4J_{C-F}$=2.9 Hz), 129.7 (d, $^4J_{C-F}$=3.2 Hz), 129.4, 129.2 (d, $^3J_{C-F}$=8.3 Hz), 128.5, 126.5 (d, $^3J_{C-F}$=8.2 Hz), 123.9, 122.2 (d, $^2J_{C-F}$=21.2 Hz), 119.7, 116.3, 115.4 (d, $^2J_{C-F}$=20.9 Hz), 115.3 (d, $^2J_{C-F}$=21.6 Hz), 96.7, 45.6; HRMS-CI: m/z $[M+H]^+$, calcd for $C_{15}H_{11}FO$+C_6H_4FS, 225.0716+127.0018, found: 225.0708+127.0017.

*4.3.18. 4-(Dodecylthio)-2-(4-fluorophenyl)-4H-chromene (**6s**).* Yellow oil; IR (KBr, cm^{-1}) 2924, 1649, 1230, 1063, 811, 616; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.72–7.67 (m, 2H), 7.43 (d, J=7.8 Hz, 1H), 7.21 (d, J=7.5 Hz, 1H), 7.13–7.02 (m, 4H), 5.55 (d, J=4.8 Hz, 1H), 4.82 (d, J=4.8 Hz, 1H), 2.51–2.24 (m, 2H), 1.42–1.15 (m, 20H), 0.88 (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 163.1 (d, $^1J_{C-F}$=246.9 Hz), 151.9, 149.4, 129.8 (d, $^4J_{C-F}$=3.2 Hz), 129.7, 128.2, 126.6 (d, $^3J_{C-F}$=8.2 Hz), 124.0, 120.8, 116.2, 115.3 (d, $^2J_{C-F}$=21.6 Hz), 97.9 (d, $^5J_{C-F}$=1.6 Hz), 39.8, 31.9, 29.6, 29.5, 29.44, 29.40, 29.3, 29.1, 29.0, 28.0, 22.7, 14.1; HRMS-ESI: m/z $[M+Na]^+$ calcd for $C_{27}H_{35}FOSNa$: 449.2285, found: 449.2288.

*4.3.19. 2-(4-tert-Butylphenyl)-5-(2-(furan-2-yl)-4H-chromen-4-ylthio)-1,3,4-oxadiazole (**6t**).* Mp 75–76 °C; IR (KBr, cm^{-1}) 2960, 2354, 1624, 1491, 1244, 1007, 831, 685; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.76 (d, J=8.4 Hz, 2H), 7.49–7.33 (m, 5H), 7.20 (d, J=8.0 Hz, 1H), 7.12 (t, J=7.5 Hz, 1H), 6.91 (d, J=4.7 Hz, 1H), 6.81 (d, J=3.4 Hz, 1H), 6.50 (dd, J_1=3.4 Hz, J_2=1.8 Hz, 1H), 5.72 (d, J=4.7 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 175.7, 159.7, 156.0, 151.2, 147.6, 145.8, 143.3, 130.0, 128.9, 126.4, 125.9, 124.4, 119.5, 117.1, 117.0, 111.5, 108.6, 91.7, 52.3, 35.1, 31.0; HRMS-CI: m/z $[M+H]^+$, calcd for $C_{13}H_9O_2$+$C_{12}H_{14}N_2OS$, 197.0603+234.0827, found: 197.0609+234.0841.

*4.3.20. 4-(Dodecylthio)-2-(furan-2-yl)-4H-chromene (**6u**).* Yellow oil; IR (KBr, cm^{-1}) 2924, 2352, 1633, 1233, 1008, 893, 673; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.43–7.41 (m, 2H), 7.18 (t, J=7.5 Hz, 1H), 7.09 (t, J=7.5 Hz, 1H), 7.00 (d, J=8.1 Hz, 1H), 6.64 (d, J=3.3 Hz, 1H), 6.46 (dd, J_1=3.3 Hz, J_2=1.8 Hz, 1H), 5.63 (d, J=4.8 Hz, 1H), 4.80 (d, J=4.8 Hz, 1H), 2.54–2.26 (m, 2H), 1.40–1.16 (m, 20H), 0.88 (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 151.6, 148.1, 143.2, 142.7, 129.8, 128.2, 124.0, 120.9, 116.2, 111.3, 107.1, 97.0, 39.1, 31.9, 29.6, 29.5, 29.39, 29.37, 29.3, 29.1, 29.0, 28.0, 22.7, 14.1; HRMS-ESI: m/z $[M+Na]^+$ calcd for $C_{25}H_{34}O_2SNa$: 421.2172, found: 421.2176.

*4.3.21. 4-(3-Fluorophenylthio)-2-(thiophen-2-yl)-4H-chromene (**6v**).* Yellow oil; IR (KBr, cm^{-1}) 2924, 2352, 1632, 1227, 1052, 870, 711; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.36 (dd, J_1=7.5 Hz, J_2=1.8 Hz, 1H), 7.28–7.16 (m, 2H), 7.13–6.82 (m, 7H), 5.56 (d, J=5.0 Hz, 1H), 5.15 (d, J=5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.0 (d, $^1J_{C-F}$=247.1 Hz), 151.7, 146.7, 137.1, 133.4 (d, $^3J_{C-F}$=7.6 Hz), 131.5 (d, $^4J_{C-F}$=3.0 Hz), 129.5, 129.4 (d, $^3J_{C-F}$=7.6 Hz), 128.5, 127.4, 125.6, 124.2, 124.0, 122.4 (d, $^2J_{C-F}$=21.2 Hz), 119.8, 116.4, 96.4, 45.7; HRMS-CI: m/z, calcd for $C_{13}H_9OS$+C_6H_4FS, 213.0374+127.0018, found: 213.0393+127.0008.

*4.3.22. 2-(4-tert-Butylphenyl)-5-(2-(thiophen-2-yl)-4H-chromen-4-ylthio)-1,3,4-oxadiazole (**6w**).* Mp 139–140 °C; IR (KBr, cm^{-1}) 2962, 2352, 1661, 1620, 1245, 1022, 832, 710; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.75 (d, J=8.5 Hz, 2H), 7.49–7.34 (m, 6H), 7.25–7.07 (m, 3H), 6.90 (d, J=4.7 Hz, 1H), 5.62 (d, J=4.7 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 175.7, 159.7, 156.0, 151.2, 147.6, 145.8, 143.3, 130.0, 128.9, 126.4, 125.9, 124.4, 119.5, 117.1, 117.0, 111.5, 108.6, 91.7, 52.3, 35.1, 31.0; HRMS-CI: m/z $[M+H]^+$, calcd for $C_{13}H_9OS$+$C_{12}H_{14}N_2OS$, 213.0374+234.0827, found: 213.0372+234.0834.

*4.3.23. 6-Chloro-4-(dodecylthio)-2-phenyl-4H-chromene (**6x**).* Yellow oil; IR (KBr, cm^{-1}) 2940, 1652, 1235, 1007, 877, 692; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.72–7.68 (m, 2H), 7.43–7.39 (m, 4H), 7.17 (dd, J_1=8.8 Hz, J_2=2.5 Hz, 1H), 7.00 (d, J=8.8 Hz, 2H), 5.60 (d, J=4.8 Hz, 1H), 4.77 (d, J=4.8 Hz, 1H), 2.47–2.24 (m, 2H), 1.42–1.16 (m, 20H), 0.88 (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 150.6, 150.2, 133.3, 129.3, 129.0, 128.6, 128.4, 128.3, 124.7, 122.6, 117.7, 97.7, 39.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 29.0, 27.9, 22.7, 14.1; HRMS-EI: m/z calcd for $C_{27}H_{35}ClOS$: 442.2097, found: 442.2099.

*4.3.24. 3-(4-Chlorophenylthio)-3-(2-hydroxyphenyl)-1-phenylpropan-1-one (**6aa**).* Mp 127–128 °C; IR (KBr, cm^{-1}) 3416, 2355, 1662, 1602, 1229, 1084, 975, 672; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.90 (d, J=8.8 Hz, 2H), 7.58–7.54 (m, 1H), 7.45–7.06 (m, 9H), 6.90–6.82 (m, 2H), 5.20 (dd, J_1=9.3 Hz, J_2=4.5 Hz, 1H), 3.76 (dd, J_1=18.0 Hz, J_2=9.3 Hz, 1H), 3.62 (dd, J_1=18.0 Hz, J_2=4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 198.7, 153.8, 135.8, 133.9, 133.5, 132.8, 132.4, 129.1, 128.9, 128.7, 128.4, 128.3, 127.5, 121.4, 118.1, 45.0, 41.8; ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 9.75 (s, 1H), 7.96 (d, J=7.5 Hz, 2H), 7.62 (t, J=7.5 Hz, 1H), 7.49–7.46 (m, 2H), 7.34–7.26 (m, 5H), 7.06–7.00 (m, 1H), 6.80 (d, J=7.7 Hz, 1H), 6.71 (d, J=7.5 Hz, 1H), 5.29 (d, J=7.2 Hz, 1H), 3.78–3.59 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 197.1, 154.5, 136.4, 134.4, 133.3, 132.2, 131.4, 128.8, 128.7, 128.2, 128.0, 126.9, 119.0, 115.2, 43.3, 41.4; HRMS-ESI: m/z $[M+Na]^+$ calcd for $C_{21}H_{17}ClO_2SNa$: 391.0530, found: 391.0537.

Acknowledgements

We gratefully acknowledge support from the National Natural Science Foundation of China (Grant 21102042) and the Science and

Technology Foundation for Creative Research Group of HBDE (2013).

Supplementary data

^{1}H NMR and ^{13}C NMR spectra for all new compounds. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.01.047. These data include MOL files and InChiKeys of the most important compounds described in this article.

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15. Crystal data for **6d**: CCDC number 898680, $C_{21}H_{14}ClFOS$, triclinic, space group P−1, a=6.317(3), b=10.243(4), c=13.759(6) Å, α=85.000(5)°, β=88.210(5)°, γ=79.592(5)°, U=872.2(6) Å^3, Z=2, specimen: 0.21×0.20×0.16 mm^3, T=296(2) K, absorption coefficient 0.354 mm^{-1}, reflections collected 4994, independent reflections 3051 [$R_{(int)}$=0.0158], refinement by full-matrix least-squares on F^2, data/restraints/parameters 3051/0/226, goodness-of-fit on F^2=1.019, final R indices [$I>2s(I)$] $R1$=0.0396, $wR2$=0.0866, R indices (all data) $R1$=0.0641, $wR2$=0.0985, largest diff. peak and hole 0.177 and −0.204 e Å^{-3}.
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