Tetrahedron 66 (2010) 8615–8622

Contents lists available at ScienceDirect

Tetrahedron

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

A new domino Knoevenagel-hetero-Diels–Alder reaction: an efficient catalyst-free synthesis of novel thiochromone-annulated thiopyranocoumarin derivatives in aqueous medium

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ARTICLE INFO

Article history:
Received 30 June 2010
Received in revised form 21 August 2010
Accepted 13 September 2010
Available online 18 September 2010

Keywords:
Domino reaction
Knoevenagel-hetero-Diels–Alder
O-acrylated salicylaldehyde
Aqueous medium
3,4-Dihydrocoumarine
Thiopyran

ABSTRACT

An efficient catalyst-free synthesis of novel pentacyclic thiochromone-annulated thiopyranocoumarin derivatives is achieved via domino Knoevenagel-hetero-Diels–Alder reaction of 4-hydroxy dithiocoumarin and *O*-acrylated salicylaldehyde derivatives in H_2O as solvent. The products are formed in good yields with high regio- and stereo-selectivity.

1. Introduction

Coumarins and chromones constitute an important class of compound due to their presence as an important constituent of natural products[1] and synthetic organic chemistry. Members of this group display a broad range of applications[2] as fragrances, pharmaceuticals, food additives and cosmetics, agrochemicals, optical brightening agents, dispersal fluorescent, and tunable dye lasers[3] and biological activities like antihelminthic, hypnotic, insecticidal, and anticoagulant[4] properties.

Thiochroman-4-one and 1-thiochromone derivatives are interesting classes of heterocycles due to their broad pharmacological and medicinal importance.[5] Also, the 3,4-dihydrocoumarine system shows a wide range of biological activities,[6] such as aldose reductase inhibition,[7] antiherpetic,[8] protein kinases,[9] and a moderate estrogenic activity. These wide range of biological applications have stimulated considerable interest in evolving newer synthetic methods for the construction of polycycles of 3,4-dihydrocoumarine and thiochromone derivatives.

The hetero-Diels–Alder reaction represents an effective method for the synthesis of heterocyclic compounds, especially natural products.[10] In recent years, intramolecular hetero-Diels–Alder reactions have been used widely in numerous reactions because of their economical and stereocontrolled nature.[11] These reactions allow the formation of two or more rings in one operation, thus avoiding sequential chemical transformations. Recently, domino reactions have been used as highly efficient processes for the improvement of reaction efficiency.[12] Among these reactions, the domino Knoevenagel-hetero-Diels–Alder reaction is a very efficient process, especially in the field of heterocycles and natural products.[13] A variety of heterocyclic compounds have been synthesized by domino-Knoevenagel-hetero-Diels–Alder reaction.[13b,14] Tietze et al. extensively described the domino Knoevenagel-hetero-Diels–Alder reaction of unsaturated aromatic and aliphatic aldehydes (especially *O*-allylated salicylaldehydes) with several 1,3-dicarbonyl compounds.[12e,d,15] Furthermore, there have been some reports on domino Knoevenagel-hetero-Diels–Alder reactions of *O*-propargylated salicylaldehyde derivatives for the synthesis of polycycles with a pyran ring,[16] However, we have also reported a catalyst-free domino-Knoevenagel-hetero-Diels–Alder reaction of *O*-acrylated salicylaldehydes.[17a] In order to expand the scope of this catalyst-free methodology, we focused our attention

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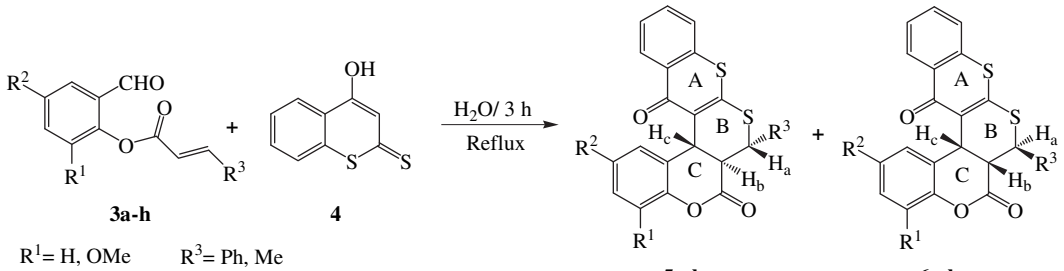
0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.09.048

on the domino-Knoevenagel-hetero-Diels–Alder reaction of *O*-acrylated salicylaldehydes with 4-hydroxy dithiocoumarin. To the best of our knowledge there are no examples of domino Knoevenagel-hetero-Diels–Alder reactions using a thioester with *O*-acrylated salicylaldehydes in the literature. In the context of our general interest in the domino-Knoevenagel-hetero-Diels–Alder reaction[17] and synthesis of sulfur-containing heterocycles,[18] we herein report a new and highly efficient reaction for the preparation of polycyclic compounds **5a**–**h** and **6a**–**h**, which consist of a thiochromone ring (A), a dihydrothiopyran ring (B) annulated to a dihydrocoumarin ring (C) (Scheme 1).



3a-h **4**

R^1= H, OMe R^3= Ph, Me

R^2= H, Br, NO_2

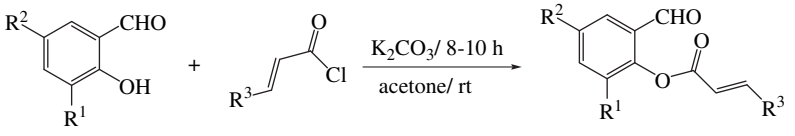
5a-h **6a-h**

Scheme 1.

2. Results and discussion

2.1. Preparation of substrates for domino Knoevenagel-hetero-Diels–Alder reaction

The *O*-acrylated salicylaldehyde derivatives **2a**–**j** were prepared from the corresponding substituted salicylaldehydes and (*E*)-acryloyl chloride derivatives (cinnamoyl chloride, crotonoyl chloride, and acryloyl chloride) using K_2CO_3 in dry acetone with high yields and excellent purity at room temperature (Scheme 2).



1a-d **2a-c** **3a-j**

R^1= H, OMe

R^2= H, Br, NO_2

R^3= Ph, Me, H

	R^1	R^2	R^3
3a	H	H	Ph
3b	OMe	H	Ph
3c	H	Br	Ph
3d	H	NO_2	Ph
3e	H	H	Me
3f	OMe	H	Me
3g	H	Br	Me
3h	H	NO_2	Me
3i	OMe	H	H
3j	H	Br	H

Scheme 2.

2.2. Domino Knoevenagel-hetero-Diels–Alder reaction of *O*-acrylated salicylaldehyde derivatives with 4-hydroxy dithiocoumarin

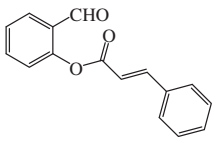
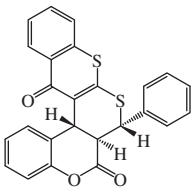
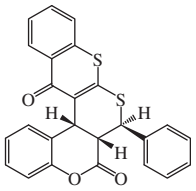
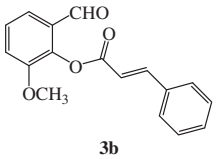
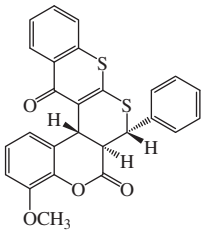
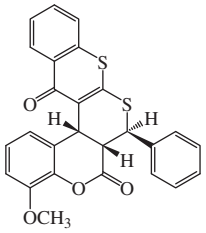
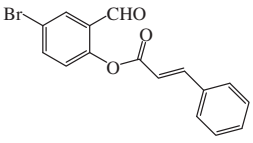
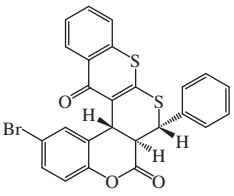
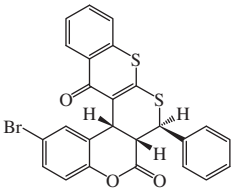
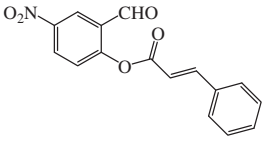
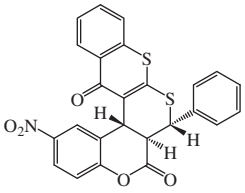
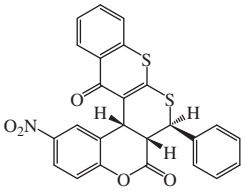
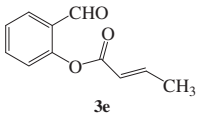
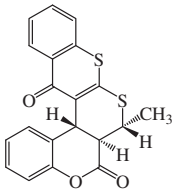
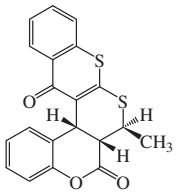
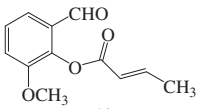
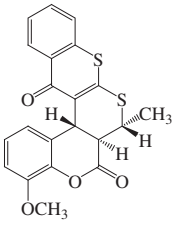
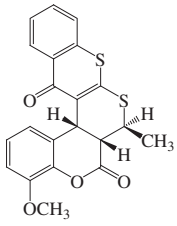
The domino Knoevenagel-hetero-Diels–Alder reaction of compound **3a** with 4-hydroxy dithiocoumarin **4** was used as a model to optimize the reaction conditions. The effect of solvent and catalyst was studied by carrying out the reaction at various conditions. The experimental results are summarized in Table 1. We first used water as solvent in the absence of any catalyst under reflux conditions for 3 h, wherein the products were obtained in 65% yield (entry 1). When the reaction was carried out in the presence of triethyl amine (1 equiv) in AcOH for 48 or 5 h at room temperature or reflux, respectively, the yield was decreased (Table 1, entries 2 and 3). According to our previous report,[17b] the effect of ZnO as Lewis acid was also studied. Using various amount of ZnO as catalyst did not give the desired product. Instead, hydrolysis of the ester moiety of the intermediate (Knoevenagel adduct) was observed, which led to low yield of the desired product. After this failure, we tried various ratios of **3a**/**4**. However, the best result was obtained when the reaction was carried out under refluxing conditions using **3a** (0.5 mmol, 1 equiv), **4** (0.6 mmol, 1.2 equiv) in H_2O (90%, entry 10). In all the cases the products were obtained as a mixture of *cis*- and *trans*-isomers and changing the reaction conditions did not significantly change the ratio of *cis*/*trans* isomers. Using these optimized conditions, we investigated the effect of substituents on the ratio of *cis*/*trans* and yield of products (Table 2). Reaction of **3a** with 1.2 equiv of **4** in refluxing aqueous medium gave the products **5a**/**6a** in 90% yield as a mixture of *trans*- and *cis*-diastereomers (59/41, respectively, Table 2, entry 1). When the same reaction was carried out with **3b**, the desired products **5b** and **6b** were obtained in 63/37, in 86% overall yield (entry 2). The diastereoselectivity varied significantly with the substituent on the R_2 position. When the reaction was carried out with **3c** and **3d**, the products **5c**/**6c** and **5d**/**6d** were obtained in 60% and 73% yield with a major *trans*-diastereoselectivity (entries 3 and 4). More contrasted results were

Table 1
Effect of catalyst and solvent on the domino Knoevenagel-hetero-Diels–Alder reaction of **3a** and **4**

Entry	Solvent	Catalyst	Ratio **3a**/**4**	Temperature	Time (h)	Yield[a] (%)	Ratio[b] *cis*/*trans*
1	H_2O	—	1/1	Reflux	3	65	59/41
2	AcOH	Et_3N	1/1	rt	48	Trace	64/36
3	AcOH	Et_3N	1/1	Reflux	5	23	62/38
4	CH_3CN	ZnO (20%)	1/1	rt	24	0	—
5	CH_3CN	ZnO (20%)	1/1	Reflux	2	0	—
6	CH_3CN	ZnO (50%)	1/1	Reflux	2	0	—
7	CH_3CN	ZnO (100%)	1/1	Reflux	2	0	—
8	H_2O	—	1.5/1	Reflux	3	68	57/43
9	H_2O	—	1/1.5	Reflux	3	90	60/40
10	H_2O	—	1/1.2	Reflux	3	90	59/41

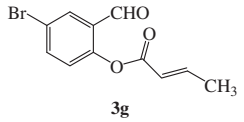
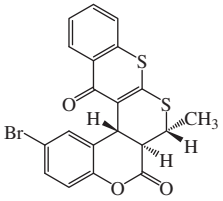
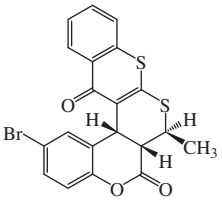
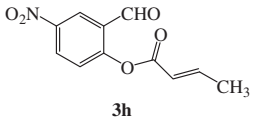
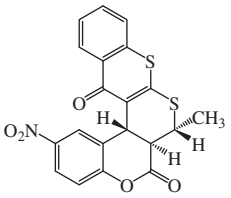
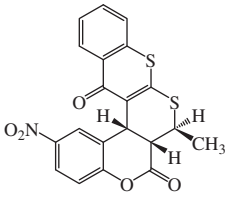
[a] Yield of isolated products.
[b] Based on ^{1}H NMR of the crude.

Table 2
Domino Knoevenagel-hetero-Diels–Alder reactions of **3a**–**h** with **4**[a]

Entry	Aldehyde	Products	Yield[b]	Ratio[c] 5/6
1	 **3a**	 **5a**  **6a**	90	59/41
2	 **3b**	 **5b**  **6b**	86	63/37
3	 **3c**	 **5c**  **6c**	60	97/03
4	 **3d**	 **5d**  **6d**	73	92/08
5	 **3e**	 **5e**  **6e**	73	07/93
6	 **3f**	 **5f**  **6f**	80	06/94

(*continued on next page*)

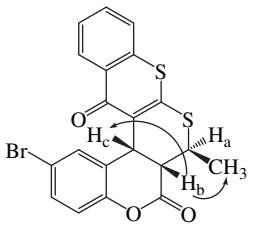
Table 2 (*continued*)

Entry	Aldehyde	Products	Yield[b]	Ratio[c] 5/6
7	 **3g**	 **5g**  **6g**	82	04/96
8	 **3h**	 **5h**  **6h**	75	05/95

[a] All the reactions were carried out in H_2O at reflux for 3 h, molar ratio **3**/**4** 1:1.2.
[b] Isolated products.
[c] Based on ^1H NMR of the crude.

obtained with the *O*-crotonoylated salicylaldehyde derivatives (**3e**–**h**), which showed a good reactivity with **4**, leading to the corresponding adducts, but with an unexpected selectivity (entries 5–8). Thus, under the same conditions, whereas the *trans*-isomer of **5a**–**d** (entries 1–4) predominated as product for the *O*-cinnamoylated salicylaldehyde derivatives (**3a**–**d**), the products **6e**–**h** were formed with the predominance of the *cis*-isomers (entry 5–8). We also attempted the reaction of *O*-acrylated salicylaldehyde derivatives **3i**–**j** with 4-hydroxy dithiocoumarin **4**. But a mixture of inseparable products was obtained.

The structures and the ratio of the products **5a**–**h** and **6a**–**h** were established on the basis of their spectroscopic data (^1H, ^{13}C NMR, and DEPT) and elemental analyses. The relative configurations were determined from the coupling constants of the relevant H-atoms, NOE experiments and also by direct comparison with the reported data in the literature.[19] In the ^1H NMR spectra, there are two distinct groups of peaks with different intensities proportional to the ratio of products. For instance, the characteristic peaks for **5a** and **6a** in the ^1H NMR spectra are a doublet of doublet (**5a**, J=13.6, 11.0 Hz and **6a**, J=11.7, 3.8 Hz) for the H_b followed closely by two doublets for H_a (**5a**, J=11.0 Hz and **6a**, J=11.7 Hz, both in *trans*-relation with H_b) and H_c (for **5a**, the J=13.6 Hz in *trans*-relation with H_b and for **6a**, J=3.8 Hz in *cis*-relation with H_b). Also, NOE measurements on compound **6g** confirmed the *cis*-orientation of H_b and H_c and *trans*-orientation of H_a and H_b (Fig. 1).



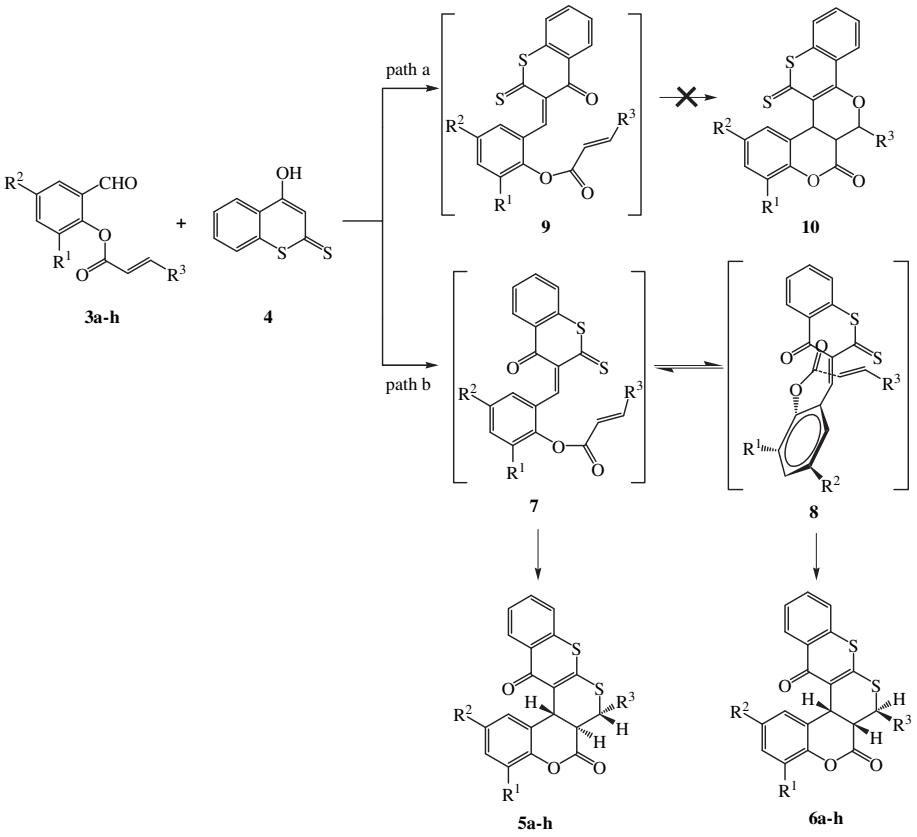
6g

Fig. 1. Selected NOE enhancements on **6g**.

A plausible mechanism for the domino-Knoevenagel-hetero-Diels–Alder reaction to produce **5a**–**h** and **6a**–**h** is proposed in Scheme 3. Aldehydes **3** undergo a Knoevenagel condensation with 4-hydroxy dithiocoumarin **4** in H_2O at reflux to afford an alkene intermediate, which has not been isolated. The alkene intermediate provides two different heterodiene fragments and therefore, two pathways can be imagined for the hetero Diels–Alder reaction. In one case, the keto carbonyl group (intermediates **9**) could be involved in the cycloaddition reaction leading to the compound **10** (path a). In another form, the thiocarbonyl group of the thioester could be reacted; affording compounds **5** and **6** (path b). The reaction does not occur via 'path a' to afford the product **10**. Here only the products **5a**–**h** and **6a**–**h** were isolated, which shows that the reaction precedes via 'path b'. However, in contrast to the homologous oxygenated substrates, α,β-unsaturated thiocarbonyls generally present very low stability.[20] Indeed, except for conveniently substituted thiocarbonyl compounds, the polymerization or dimerization of these products have been observed.[21] In most cases, these highly reactive thiocompounds are not isolated, but are generated and trapped in situ.[22]

The stereochemistry of the final products depends on the *endo*- and *exo*-orientation of the dienophile in the transition state. We could assume that the *trans*-cycloadducts **5a**–**h** were formed via an *exo*-transition state (path b, intermediates **7**), whereas the *cis*-isomers **6a**–**h** resulted from an *endo*-transition state (path b, intermediates **8**), as represented in Scheme 3. In the case of compounds with a cinnamoyl moiety **3a**–**d** we observed *exo*-transition states with the predominance of the *trans*-isomers. In crotonoyl derivatives **3e**–**h**, due to secondary orbital interactions, *endo*-transition states occurred and the *cis*-isomers were in predominance.

The results can be understood in terms of frontier molecular orbital (FMO) theory. According to FMO theory, the reactions having small HOMO–LUMO gaps manifest faster rates. It seems that the effective interaction takes place between the LUMO of the acryloyl moiety and the HOMO of the diene and thus we are dealing with a normal Diels–Alder reaction. Similarly, chemoselectivity observed in this reaction can be explained in frontier orbital terms. It seems that two important factors control the synthesis of products **5** and **6** that could be classified as (a) a more efficient



Scheme 3. A plausible mechanism for the formation of compounds **5**and **6**.

HOMO–LUMO interaction for α,β-unsaturated thioester as diene and acryloyl moiety as dienophile in the intermediate **7** and **8** than compared to intermediate **9**. The reactivity could be explained by considering the presence of a soft sulfur atom in the diene moiety of the substrates. (b) More steric hinderance in the intermediate **8** compared to **7**. The steric hinderance is much more when the cinnamoyl moiety acts as the dienophile compared to the crotonoyl group and so **7** is favored.

3. Conclusion

We have reported a highly efficient and catalyst-free method for the synthesis of novel heteropolycyclic compounds through a domino Knoevenagel-hetero-Diels–Alder reaction of *O*-acrylated salicylaldehydes **3a**–**h** with 4-hydroxy dithiocoumarin in aqueous medium. Using H_2O as a solvent has advantages, such as safety, environmentally friendly, and low cost. This reaction also offers other advantages such as high yields of products, short reaction time, clean reactions, ease of workup, and no need of a catalyst, which make it a useful and attractive procedure for the synthesis of pentacyclic 3,4-dihydrocoumarine derivatives.

4. Experimental section

4.1. General

Commercially available materials were used without any additional purification. 4-Hydroxy dithiocoumarin **4** was prepared according to the previously reported procedure.[23] Melting points were determined on a Büchi melting point B-540 apparatus and were uncorrected. IR spectra were taken films KBr pellets on a Nicolet spectrometer (Magna 550). ^{1}H NMR and ^{13}C NMR Spectra were run on Bruker (DRX-500 Avance) spectrometer at 500 (^{1}H NMR) and 125 (^{13}C NMR and DEPT) MHz, in $CDCl_3$ and DMSO-d_6 as solvents. Chemical shift have been expressed in parts per million rel to Me_4Si as internal standard. Signals of the ^{13}C NMR spectra corresponding to CH, CH_2, or CH_3 groups are assigned from DEPT (135 and 90). Elemental analysis was obtained using a Perkin–Elmer 2004 (II) CHN analyzer.

4.2. General procedure for preparation of the *O*-acrylated salicylaldehyde derivatives 3a–j

To a stirred solution of salicylaldehyde derivative (5 mmol) and acryloyl chloride or its derivative (6 mmol) in acetone (10 mL) was added K_2CO_3 (0.69 g, 6 mmol). After stirring for 8–10 h at room temperature, ice-cold water (50 mL) was added to the mixture with vigorous stirring to afford a light precipitate that was filtered, washed with water, and air-dried.

*4.2.1. 2-Formylphenyl (2E)-3-phenylacrylate (**3a**).* White solid, yield 95% (1.20 g), mp: 74–76 °C; IR (KBr): 1743, 1707, 1640, 1599, 1202, 1125, 759 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.70 (1H, d, J=16.0 Hz), 7.28 (1H, d, J=8.1 Hz, Ar–H), 7.39 (1H, t, J=7.5 Hz, Ar–H), 7.41–7.46 (3H, m, Ar–H), 7.59–7.61 (2H, m, Ar–H), 7.64 (1H, t, J=7.8 Hz, Ar–H), 7.93 (2H, m), 10.01 (1H, s, HC=O); ^{13}C NMR (125 MHz, $CDCl_3$): δ 116.7 (CH), 123.9 (CH), 126.8 (CH), 128.7 (C), 128.9 (CH), 129.5 (CH), 130.5 (CH), 131.5 (CH), 134.4 (C), 135.7 (CH), 148.2 (CH), 152.6 (C), 165.5 (C, O–C=O), 188.9 (CH, HC=O). Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79%. Found: C, 76.04; H, 4.76%.

*4.2.2. 2-Formyl-6-methoxyphenyl (2E)-3-phenylacrylate (**3b**).* Pale white solid, yield 93% (1.32 g), mp: 106–108 °C; IR (KBr): 1732, 1696, 1630, 1583, 1480, 1006, 769 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87 (3H, s, OCH_3), 6.73 (1H, d, J=16.0 Hz), 7.25 (1H, d, J=7.7 Hz, Ar–H), 7.34 (1H, t, J=7.6 Hz, Ar–H), 7.43–7.44 (3H, m, Ar–H), 7.51

(1H, d, *J*=7.8 Hz, Ar–H), 7.60–7.62 (2H, m, Ar–H), 7.94 (1H, d, *J*=16.0 Hz), 10.21 (1H, s, HC=O); ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.8 (OCH_3), 116.5 (CH), 118.3 (CH), 120.9 (CH), 127.2 (CH), 128.9 (CH), 129.5 (CH), 129.9 (C), 131.4 (CH), 134.5 (C), 142.5 (C), 148.1 (CH), 152.3 (C), 165.0 (C, O–C=O), 189.0 (CH, HC=O). Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00%. Found: C, 72.22; H, 5.05%.

*4.2.3. 4-Bromo-2-formylphenyl (2E)-3-phenylacrylate (**3c**).* White solid, yield 90% (1.49 g), mp: 135–137 °C; IR (KBr): 1738, 1681, 1238, 1197 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.67 (1H, d, *J*=16.0 Hz), 7.20 (1H, d, *J*=8.6 Hz, Ar–H), 7.44–7.46 (3H, m, Ar–H), 7.60–7.62 (2H, m, Ar–H), 7.75 (1H, dd, *J*=8.6, 2.5 Hz, Ar–H), 7.93 (1H, d, *J*=16.0 Hz), 8.04 (1H, d, *J*=2.5 Hz, Ar–H), 10.14 (1H, s, HC=O); ^{13}C NMR (125 MHz, $CDCl_3$): δ 116.2 (CH), 120.2 (C), 125.8 (CH), 129.0 (CH), 129.5 (CH), 129.9 (C), 131.7 (CH), 132.8 (CH), 134.2 (C), 138.4 (CH), 148.8 (CH), 151.7 (C), 165.2 (C, O–C=O), 187.4 (CH, HC=O). Anal. Calcd for $C_{16}H_{11}BrO_3$: C, 58.03; H, 3.35%. Found: C, 57.94; H, 3.31%.

*4.2.4. 2-Formyl-4-nitrophenyl (2E)-3-phenylacrylate (**3d**).* Light yellow solid, yield 95% (1.41 g), mp: 152–154 °C; IR (KBr): 1738, 1686, 1614, 1527, 1351, 1182 cm^{-1}; ^{1}H NMR (500 MHz, CDCl3): δ 6.76 (1H, d, *J*=16.0 Hz), 7.47–7.55 (3H, m, Ar–H), 7.60 (1H, d, *J*=8.9 Hz, Ar–H), 7.66–7.68 (2H, m, Ar–H), 8.03 (1H, d, *J*=16.0 Hz), 8.55 (1H, dd, *J*=8.9, 2.7 Hz, Ar–H), 8.84 (1H, d, *J*=2.8 Hz, Ar–H), 10.31 (1H, s, HC=O); ^{13}C NMR (125 MHz, CDCl3): δ 115.5 (CH), 125.3 (CH), 125.7 (CH), 129.0 (C), 129.1 (CH), 129.5 (C), 129.6 (CH), 129.9 (CH), 132.0 (CH), 134.0 (C), 149.8 (CH), 156.8 (C), 164.5 (C, O–C=O), 186.6 (CH, HC=O). Anal. Calcd for $C_{16}H_{11}NO_5$: C, 64.65; H, 3.73; N, 4.71%. Found: C, 64.60; H, 3.70; N, 4.68%.

*4.2.5. 2-Formylphenyl (2E)-but-2-enoate (**3e**).* Colorless oil, yield 75% (0.71 g); IR (KBr): 1748, 1707, 1666, 1599, 1398, 1213, 1165, 1104, 976, 764 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.05 (3H, d, *J*=6.9 Hz, CH_3), 6.16 (1H, d, *J*=15.4 Hz), 7.25–7.34 (2H, m), 7.41 (1H, t, *J*=7.6 Hz, Ar–H), 7.67 (1H, t, *J*=7.8 Hz, Ar–H), 7.95 (1H, d, *J*=7.7 Hz, Ar–H), 10.20 (1H, s, HC=O); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.8 (CH_3), 121.6 (CH), 123.9 (CH), 126.7 (CH), 128.6 (C), 130.4 (CH), 135.7 (CH), 148.9 (CH), 152.6 (C), 164.9 (C, O–C=O), 189.0 (CH, HC=O). Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30%. Found: C, 69.39; H, 5.27%.

*4.2.6. 2-Formyl-6-methoxyophenyl (2E)-but-2-enoate (**3f**).* Pale white, yield 90% (0. 99 g), mp: 77–79 °C; IR (KBr): 1748, 1692, 1651, 1584, 1480, 1274, 1090, 1063, 769 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.04 (3H, d, *J*=6.9 Hz, CH_3), 3.89 (3H, s, OCH_3), 6.18 (1H, d, *J*=15.5 Hz), 7.24–7.37 (3H, m), 7.51 (1H, d, *J*=7.7 Hz, Ar–H), 10.19 (1H, s, HC=O); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.8 (CH_3), 56.8 (OCH_3), 118.3 (CH), 120.8 (CH), 121.4 (CH), 127.1 (CH), 129.9 (C), 142.5 (C), 148.7 (CH), 152.3 (C), 164.3 (C, O–C=O), 189.1 (CH, HC=O). Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49%. Found: C, 65.38; H, 5.45%.

*4.2.7. 4-Bromo-2-formylphenyl (2E)-but-2-enoate (**3g**).* Pale white solid, yield 88% (1.18 g), mp: 79–81 °C; IR (KBr): 1743, 1681, 1650, 1470, 1295, 1207, 1140, 965 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.05 (3H, d, *J*=6.6 Hz, CH_3), 6.14 (1H, d, *J*=15.5 Hz), 7.17 (1H, d, *J*=8.6 Hz, Ar–H), 7.28–7.33 (1H, m), 7.76 (1H, d, *J*=8.5 Hz, Ar–H), 8.04 (1H, s, Ar–H), 10.12 (1H, s, HC=O); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.9 (CH_3), 120.0 (C), 121.3 (CH), 125.8 (CH), 129.9 (C), 132.6 (CH), 138.3 (CH), 149.5 (CH), 151.7 (C), 164.5 (C, O–C=O), 187.4 (CH, HC=O). Anal. Calcd for $C_{11}H_9BrO_3$: C, 49.10; H, 3.37%. Found: C, 48.98; H, 3.42%.

*4.2.8. 2-Formyl-4-nitrophenyl (2E)-but-2-enoate (**3h**).* Pale white solid, yield 85% (1.00 g), mp: 102–104 °C; IR (KBr): 1738, 1697, 1650, 1527, 1352, 1146, 1094, 970 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.10 (3H, d, *J*=6.9 Hz, CH_3), 6.18 (1H, d, *J*=15.6 Hz), 7.36–7.40 (1H, m), 7.53 (1H, d, *J*=8.9 Hz, Ar–H), 8.52 (1H, dd, *J*=8.9, 2.8 Hz, Ar–H), 8.81 (1H, d, *J*=2.8 Hz, Ar–H), 10.25 (1H, s, HC=O); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.0 (CH_3), 120.8 (CH), 125.3 (CH), 125.5 (CH), 129.1 (C), 129.9 (CH), 150.8 (CH), 152.7 (C), 156.8 (C), 163.8 (C, O–C=O), 186.6 (CH, HC=O). Anal. Calcd for $C_{11}H_9NO_5$: C, 56.17; H, 3.86; N, 5.96%. Found: C, 56.12; H, 3.82; N, 5.93%.

*4.2.9. 2-Formyl-6-methoxyphenyl acrylate (**3i**).* White solid, yield 85% (0.88 g), mp: 67–69 °C; IR (KBr): 1748, 1692, 1486, 1274, 1135, 790 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.90 (3H, s, OCH_3), 6.13 (1H, d, *J*=10.5 Hz), 6.44 (1H, dd, *J*=17.3, 10.5 Hz), 6.71 (1H, d, *J*=17.3 Hz), 7.26 (1H, d, *J*=8.0 Hz, Ar–H), 7.38 (1H, t, *J*=8.0 Hz, Ar–H), 7.52 (1H, d, *J*=7.6 Hz, Ar–H), 10.19 (1H, s, HC=O); ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.8 (OCH_3), 118.3 (CH), 121.1 (CH), 127.2 (CH), 127.3 (CH), 129.7 (C), 134.0 (CH_2), 142.2 (C), 152.2 (C), 164.1 (C, O–C=O), 188.9 (CH, HC=O). Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89%. Found: C, 64.10; H, 4.83%.

*4.2.10. 4-Bromo-2-formylphenyl acrylate (**3j**).* White solid, yield 83% (1.06 g), mp: 70–72°C; IR (KBr): 1753, 1686, 1470, 1398, 1207, 1161, 1109, 883 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.17 (1H, d, *J*=10.4 Hz), 6.41 (1H, dd, *J*=17.3, 10.5 Hz), 6.72 (1H, d, *J*=17.3 Hz), 7.20 (1H, d, *J*=8.6 Hz, Ar–H), 7.78 (1H, d, *J*=8.5 Hz, Ar–H), 8.06 (1H, s, Ar–H), 10.12 (1H, s, HC=O); ^{13}C NMR (125 MHz, $CDCl_3$): δ 120.3 (C), 125.6 (CH), 127.2 (CH), 129.8 (C), 133.1 (CH), 134.7 (CH_2), 138.4 (CH), 151.3 (C), 164.3 (C, O–C=O), 187.3 (CH, HC=O). Anal. Calcd for $C_{10}H_7BrO_3$: C, 47.09; H, 2.77%. Found: C, 47.00; H, 2.74%.

4.3. General procedure for domino Knoevenagel-hetero-Diels–Alder reaction

A mixture of an *O*-acrylated salicylaldehyde derivative **3** (0.5 mmol) and 4-hydroxy dithiocoumarin **4** (0.6 mmol) in water (7 mL) was stirred at reflux temperature. The progress of the reaction was monitored by TLC (mini-extraction with CH_2Cl_2 carried out for TLC) using petroleum ether–ethyl acetate mixture (2:1) as eluent. After completion (3 h), the solid precipitate was filtered, washed with hot water, dried, and recrystallized from EtOH. Compounds **5** and **6** have the same polarity; therefore our attempt to separate these compounds using different solid supports and solvents was not successful.

*4.3.1. Mixture of **5a** and **6a**.* Following the general procedure the reaction afforded a mixture of **5a** and **6a** (59:41, 193 mg, 90%) as a yellow solid; R_f: 0.64; mp: 282–284 °C; IR (KBr): 1759, 1625, 1527, 1223, 1105, 759 cm^{-1}. Anal. Calcd for $C_{25}H_{16}O_3S_2$: C, 70.07; H, 3.76%. Found: C, 69.95; H, 3.71%.

4.3.1.1. (6aR,7S*,14bR*)-7-Phenyl-6a,14b-dihydro-6H,7H,14H-thiochromeno [3′,2′:5,6]thiopyrano[3,4-c]chromene-6,14-dione (**5a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.75 (1H, dd, *J*=13.6, 11.0 Hz, H_b), 4.73 (1H, d, *J*=11.0 Hz, H_a), 4.59 (1H, d, *J*=13.6 Hz, H_c), 6.74 (1H, d, *J*=7.8 Hz, Ar–H), 7.06 (1H, t, *J*=7.6 Hz, Ar–H), 7.12–7.16 (1H, m, Ar–H), 7.31–7.45 (6H, m, Ar–H), 7.54–7.71 (3H, m, Ar–H), 8.51 (1H, d, *J*=7.8 Hz, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 38.9 (CH), 47.5 (CH), 50.4 (CH), 117.5 (CH), 124.4 (C), 124.7 (CH), 125.5 (CH), 125.6 (CH), 128.2 (C), 128.3 (CH), 128.5 (CH), 129.0 (CH), 129.4 (CH), 129.7 (CH), 130.2 (CH), 131.5 (C), 132.3 (CH), 136.2 (C), 136.3 (C), 151.3 (C), 151.7 (C), 167.7 (C, O–C=O), 178.1 (C, C=O).

4.3.1.2. (6aS,7R*,14bR*)-7-Phenyl-6a,14b-dihydro-6H,7H,14H-thiochromeno [3′,2′:5,6]thiopyrano[3,4-c]chromene-6,14-dione (**6a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.55 (1H, dd, *J*=11.7, 3.8 Hz, H_b), 4.47 (1H, d, *J*=11.7 Hz, H_a), 5.49 (1H, d, *J*=3.8 Hz, H_c), 6.86 (1H, d, *J*=7.6 Hz, Ar–H), 7.12–7.16 (2H, m, Ar–H), 7.31–7.45 (6H, m, Ar–H), 7.54–7.71 (3H, m, Ar–H), 8.61 (1H, d, *J*=7.9 Hz, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 35.1 (CH), 44.6 (CH), 46.1 (CH), 117.3 (CH), 122.9 (C), 124.7

(CH), 125.5 (CH), 125.9 (CH), 128.5 (CH), 128.7 (CH), 128.8 (CH), 129.3 (CH), 129.4 (CH), 129.8 (CH), 130.3 (C), 132.4 (CH), 134.5 (C), 136.2 (C), 136.3 (C), 150.4 (C), 152.3 (C), 166.0 (C, O–C=O), 176.8 (C, C=O).

*4.3.2. Mixture of **5b** and **6b**.* Following the general procedure the reaction afforded a mixture of **5b** and **6b** (63:37, 198 mg, 86%) as a yellow solid; R_f: 0.53; mp: 244–246 °C; IR (KBr): 1753, 1614, 1589, 1480, 1440, 1346, 1202, 1175, 1065, 759 cm^{-1}. Anal. Calcd for $C_{26}H_{18}O_4S_2$: C, 68.10; H, 3.96%. Found: C, 67.99; H, 3.91%.

4.3.2.1. (6aR,7S*,14bR*)-4-Methoxy-7-phenyl-6a,14b-dihydro-6H,7H,14H-thiochromeno[3′,2′:5,6]thiopyrano[3,4-c]chromene-6,14-dione (**5b**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.76 (1H, dd, *J*=13.6, 11.0 Hz, H_b), 3.91 (3H, s, OCH_3), 4.70 (1H, d, *J*=11.0 Hz, H_a), 4.99 (1H, d, *J*=13.6 Hz, H_c), 6.33 (1H, d, *J*=7.8 Hz, Ar–H), 6.91 (1H, d, *J*=8.2 Hz, Ar–H), 6.99 (1H, t, *J*=8.1 Hz, Ar–H), 7.34–7.43 (5H, m, Ar–H), 7.52–7.68 (3H, m, Ar–H), 8.49 (1H, d, *J*=7.2 Hz, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.0 (CH), 47.5 (CH), 50.2 (CH), 56.6 (OCH_3), 111.9 (CH), 117.3 (CH), 124.5 (C), 124.8 (CH), 125.5 (CH), 128.4 (CH), 129.1 (CH), 129.4 (CH), 129.6 (CH), 129.7 (C), 129.8 (CH), 131.5 (C), 132.4 (CH), 136.2 (2C), 140.9 (C), 148.3 (C), 151.1 (C), 167.2 (C, O–C=O), 178.1 (C, C=O).

4.3.2.2. (6aS,7R*,14bR*)-4-Methoxy-7-phenyl-6a,14b-dihydro-6H,7H,14H-thiochromeno[3′,2′:5,6]thiopyrano[3,4-c]chromene-6,14-dione (**6b**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.53 (1H, dd, *J*=11.7, 3.9 Hz, H_b), 3.93 (3H, s, OCH_3), 4.52 (1H, d, *J*=11.7 Hz, H_a), 5.48 (1H, d, *J*=3.8 Hz, H_c), 6.44 (1H, d, *J*=7.7 Hz, Ar–H), 6.96 (1H, d, *J*=8.3 Hz, Ar–H), 7.07 (1H, t, *J*=8.0 Hz, Ar–H), 7.34–7.43 (5H, m, Ar–H), 7.52–7.68 (3H, m, Ar–H), 8.59 (1H, d, *J*=7.1 Hz, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 35.1 (CH), 44.5 (CH), 45.8 (CH), 56.8 (OCH_3), 112.5 (CH), 120.0 (CH), 123.0 (C), 125.4 (C), 125.5 (CH), 125.7 (CH), 128.3 (CH), 128.5 (CH), 129.2 (CH), 130.1 (CH), 130.2 (CH), 130.3 (C), 132.2 (CH), 134.6 (C), 136.3 (C), 139.5 (C), 148.1 (C), 152.2 (C), 165.3 (C, O–C=O), 176.6 (C, C=O).

4.3.3. (6aR,7S*,14bR*)-2-Bromo-7-phenyl-6a,14b-dihydro-6H,7H,14H-thiochromeno[3′,2′:5,6]thiopyrano[3,4-c]chromene-6,14-dione (**5c**).* Following the general procedure the reaction afforded a mixture of **5c** and **6c** (97:03, 153 mg, 60%) as a yellow solid; R_f: 0.69; mp: 279–281 °C; IR (KBr): 1779, 1615, 749 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.70 (1H, dd, *J*=13.6, 11.0 Hz, H_b) {for **6c**, 3.53 (1H, dd, *J*=11.8, 3.9 Hz, H_b)}, 4.71 (1H, d, *J*=11.0 Hz, H_a) {for **6c**, 4.45 (1H, d, *J*=11.8 Hz, H_a)}, 4.96 (1H, d, *J*=13.7 Hz, H_c) {for **6c**, 5.52 (1H, d, *J*=3.9 Hz, H_c)}, 6.82 (1H, s, Ar–H), 7.03 (1H, d, *J*=8.6 Hz, Ar–H), 7.38–7.47 (6H, m, Ar–H), 7.58 (1H, d, *J*=7.9 Hz, Ar–H), 7.64 (1H, t, *J*=7.5 Hz, Ar–H), 7.70 (1H, t, *J*=7.2 Hz, Ar–H), 8.51 (1H, d, *J*=7.9 Hz, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 38.9 (CH), 47.4 (CH), 50.1 (CH), 117.7 (C), 119.2 (CH), 123.7 (C), 125.5 (CH), 128.4 (CH), 128.7 (CH), 128.8 (CH), 129.4 (CH), 129.5 (CH), 129.8 (CH), 130.4 (C), 131.4 (C), 131.7 (CH), 132.5 (CH), 136.0 (C), 136.1 (C), 150.7 (C), 152.0 (C), 167.0 (C, O–C=O), 177.8 (C, C=O). Anal. Calcd for $C_{25}H_{15}BrO_3S_2$: C, 59.18; H, 2.98%. Found: C, 59.09; H, 2.93%.

4.3.4. (6aR,7S*,14bR*)-2-Nitro-7-phenyl-6a,14b-dihydro-6H,7H,14H-thiochromeno [3′,2′:5,6]thiopyrano[3,4-c]chromene-6,14-dione (**5d**).* Following the general procedure the reaction afforded a mixture of **5d** and **6d** (92:08, 173 mg, 73%) as a yellow solid; R_f: 0.61; mp: 252–254 °C; IR (KBr): 1779, 1619, 1522, 1346, 1073, 749 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.73 (1H, dd, *J*=13.8, 11.1 Hz, H_b) {for **6d**, 3.64 (1H, dd, *J*=11.7, 3.7 Hz, H_b)}, 4.75 (1H, d, *J*=11.0 Hz, H_a) {for **6d**, 4.40 (1H, d, *J*=11.7 Hz, H_a)}, 5.01 (1H, d, *J*=13.8 Hz, H_c) {for **6d**, 5.51 (1H, d, *J*=3.7 Hz, H_c)}, 7.27 (1H, d, *J*=8.8 Hz, Ar–H), 7.40–7.44 (5H, m, Ar–H), 7.58–7.67 (3H, m, Ar–H), 7.73 (1H, t, *J*=7.6 Hz, Ar–H), 8.22 (1H, dd, *J*=8.8, 2.5 Hz, Ar–H), 8.51 (1H, d, *J*=8.0 Hz, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 38.9 (CH), 47.3 (CH), 49.8 (CH), 118.3 (CH), 122.3 (CH), 122.9 (C), 124.7 (CH), 125.6 (CH), 128.4 (CH), 129.0 (CH), 129.5 (C), 129.6 (CH), 129.8 (CH), 129.9 (CH), 131.3 (C), 132.8 (CH), 135.6 (C), 136.1 (C), 144.6 (C), 152.9 (C), 156.0 (C), 165.9 (C, O–C=O), 177.0 (C, C=O). Anal. Calcd for $C_{25}H_{15}NO_5S_2$: C, 63.41; H, 3.19; N, 2.96%. Found: C, 63.49; H, 3.22; N, 2.92%.

4.3.5. (6aS,7S*,14bR*)-7-Methyl-6a,14b-dihydro-6H,7H,14H-thiochromeno [3′,2′:5,6]thiopyrano[3,4-c]chromene-6,14-dione (**6e**).* Following the general procedure the reaction afforded a mixture of **5e** and **6e** (07:93, 134 mg, 73%) as a yellow solid; R_f: 0.66; mp: 227–229 °C; IR (KBr): 1759, 1609, 1527, 1449, 1187, 735 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.49 (3H, d, *J*=6.7 Hz, CH_3) {for **5e**, 1.75 (3H, d, *J*=6.5 Hz, CH_3)}, 3.01 (1H, dd, *J*=11.4, 3.9 Hz, H_b), 3.40–3.47 (1H, m, H_a) {for **5e**, 3.72–3.76 (1H, m, H_a)}, 5.37 (1H, d, *J*=3.9 Hz, H_c) {for **5e**, 4.79 (1H, d, *J*=13.6 Hz, H_c)}, 6.76 (1H, d, *J*=7.6 Hz, Ar–H), 7.07 (1H, t, *J*=7.5 Hz, Ar–H), 7.11 (1H, d, *J*=8.0 Hz, Ar–H), 7.27 (1H, t, *J*=9.2 Hz, Ar–H), 7.52 (1H, d, *J*=8.0 Hz, Ar–H), 7.57 (1H, t, *J*=7.4 Hz, Ar–H), 7.64 (1H, t, *J*=7.1 Hz, Ar–H), 8.56 (1H, d, *J*=7.9 Hz, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.9 (CH_3), 34.4 (CH), 34.6 (CH), 46.4 (CH), 117.2 (CH), 123.1 (C), 124.4 (C), 125.4 (CH), 125.7 (CH), 128.2 (CH), 128.5 (CH), 129.1 (CH), 130.2 (CH), 130.3 (C), 132.1 (CH), 136.3 (C), 150.4 (C), 151.8 (C), 166.7 (C, O–C=O), 176.5 (C, C=O). Anal. Calcd for $C_{20}H_{14}O_3S_2$: C, 65.55; H, 3.85%. Found: C, 65.43; H, 3.81%.

4.3.6. (6aS,7S*,14bR*)-4-Methoxy-7-methyl-6a,14b-dihydro-6H,7H,14H-thiochromeno[3′,2′:5,6]thiopyrano[3,4-c]chromene-6,14-dione (**6f**).* Following the general procedure the reaction afforded a mixture of **5f** and **6f** (06:94, 159 mg, 80%) as a Pale yellow solid; R_f: 0.47; mp: 263–265 °C; IR (KBr): 1764, 1624, 1485, 1459, 1274, 744 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.48 (3H, d, *J*=6.6 Hz, CH_3) {for **5f**, 1.71 (3H, d, *J*=6.5 Hz, CH_3)}, 2.99 (1H, dd, *J*=11.4, 4.0 Hz, H_b), 3.44–3.50 (1H, m, H_a) {for **5f**, 3.86–3.91 (1H, m, H_a)}, 3.91 (3H, s, OCH_3), 5.37 (1H, d, *J*=3.7, H_c) {for **5f**, 4.80 (1H, d, *J*=13.8 Hz, H_c)}, 6.34 (1H, d, *J*=7.7 Hz, Ar–H), 6.89 (1H, d, *J*=8.1 Hz, Ar–H), 6.99 (1H, t, *J*=7.9 Hz, Ar–H), 7.51 (1H, d, *J*=8.0 Hz, Ar–H), 7.56 (1H, t, *J*=7.5 Hz, Ar–H), 7.63 (1H, t, *J*=6.9 Hz, Ar–H), 8.55 (1H, d, *J*=7.9 Hz, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.1 (CH_3), 34.4 (CH), 34.7 (CH), 46.1 (CH), 56.6 (OCH_3), 112.1 (CH), 119.7 (CH), 123.0 (C), 125.4 (C), 125.5 (CH), 125.6 (CH), 128.2 (CH), 130.1 (CH), 130.2 (C), 132.1 (CH), 136.3 (C), 139.5 (C), 147.9 (C), 152.0 (C), 166.4 (C, O–C=O), 176.6 (C, C=O). Anal. Calcd for $C_{21}H_{16}O_4S_2$: C, 63.62; H, 4.07%. Found: C, 63.74; H, 4.12%.

4.3.7. (6aS,7S*,14bR*)-2-Bromo-7-methyl-6a,14b-dihydro-6H,7H,14H-thiochromeno[3′,2′:5,6]thiopyrano[3,4-c]chromene-6,14-dione (**6g**).* Following the general procedure the reaction afforded a mixture of **5g** and **6g** (04:96, 182 mg, 82%) as a Pale yellow solid; R_f: 0.69; mp: 275–278 °C; IR (KBr): 1764,1612, 1527, 1475, 1192, 1171, 738 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.48 (3H, d, *J*=6.5 Hz, CH_3) {for **5g**, 1.73 (3H, d, *J*=6.5 Hz, CH_3)}, 3.01 (1H, dd, *J*=11.4, 3.9 Hz, H_b), 3.37–3.42 (1H, m, H_a) {for **5g**, 3.74–3.79 (1H, m, H_a)}, 5.35 (1H, d, *J*=3.7, H_c) {for **5g**, 4.76 (1H, d, *J*=13.7 Hz, H_c)}, 6.83 (1H, s, Ar–H), 7.00 (1H, d, *J*=8.5 Hz, Ar–H), 7.41 (1H, d, *J*=8.0 Hz, Ar–H), 7.54 (1H, d, *J*=8.0 Hz, Ar–H), 7.59 (1H, t, *J*=7.6 Hz, Ar–H), 7.66 (1H, t, *J*=7.5 Hz, Ar–H), 8.56 (1H, d, *J*=8.0 Hz, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.0 (CH_3), 34.4 (CH), 34.6 (CH), 46.0 (CH), 118.6 (C), 119.0 (CH), 122.2 (C), 125.5 (CH), 126.7 (C), 128.3 (CH), 130.1 (C), 130.2 (CH), 131.3 (CH), 132.2 (CH), 132.3 (CH), 136.3 (C), 149.5 (C), 152.6 (C), 166.3 (C, O–C=O), 176.5 (C, C=O). Anal. Calcd for $C_{20}H_{13}BrO_3S_2$: C, 53.94; H, 2.94%. Found: C, 53.82; H, 2.89%.

4.3.8. (6aS,7S*,14bR*)-7-Methyl-2-nitro-6a,14b-dihydro-6H,7H,14H-thiochromeno [3′,2′:5,6]thiopyrano[3,4-c]chromene-6,14-dione (**6h**).* Following the general procedure the reaction afforded a mixture of **5h** and **6h** (05:95, 155 mg, 75%) as an orange solid; R_f: 0.63; mp: 271–273 °C; IR (KBr): 1779, 1588, 1522, 1346, 1187, 749 cm^{-1}; ^{1}H NMR

(500 MHz, DMSO-d_6): δ 1.34 (3H, d, J=6.4 Hz, CH_3) {for **5h**, 1.77 (3H, d, J=6.6 Hz, CH_3)}, 3.26 (1H, dd, J=11.4, 4.1 Hz, H_b) {for **5h**, 3.05 (1H, dd, J=13.9, 11.0 Hz, H_b)}, 3.42–3.50 (1H, m, H_a) {for **5h**, 3.72–3.76 (1H, m, H_a)}, 5.41 (1H, d, J=3.7 Hz, H_c) {for **5h**, 4.84 (1H, d, J=13.9 Hz, H_c)}, 7.42 (1H, d, J=8.9 Hz, Ar–H), 7.46 (1H, s, Ar–H), 7.64 (1H, t, J=7.2 Hz, Ar–H), 7.76 (1H, t, J=7.2 Hz, Ar–H), 7.81 (1H, d, J=8.0 Hz, Ar–H), 8.21 (1H, d, J=7.2 Hz, Ar–H), 8.38 (1H, d, J=7.8 Hz, Ar–H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 19.2 (CH_3), 34.6 (CH), 34.8 (CH), 45.0 (CH), 119.2 (CH), 122.5 (C), 124.4 (CH), 125.3 (C), 125.6 (CH), 126.3 (C), 126.7 (CH), 129.2 (CH), 129.5 (CH), 133.2 (CH), 136.1 (C), 154.0 (C), 152.4 (C), 155.3 (C), 165.6 (C, O–C=O), 176.3 (C, C=O). Anal. Calcd for $C_{20}H_{13}NO_5S_2$: C, 58.38; H, 3.18; N, 3.40%. Found: C, 58.46; H, 3.21; N, 3.36%.

Acknowledgements

We gratefully acknowledge partial financial support from the Research Council of Sharif University of Technology.

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