

Preliminary Communication

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Tandem hetero-Diels–Alder-hemiacetal reaction in the synthesis of new chromeno[4',3':4,5]thiopyrano[2,3-*d*]thiazoles

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Abstract: Novel *rel*-(5*aR*,6*R*,11*bS*)-6-hydroxy-3,5*a*,6,11*b*-tetrahydro-2*H*,5*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*][1,3]thiazole-2-ones were synthesized via tandem hetero-Diels-Alder-hemiacetal reaction of 5-(2-hydroxybenzylidene)-4-thioxo-2-thiazolidinones and α,β -unsaturated aldehydes. The stereochemistry of cycloadditions was confirmed by NMR spectra and a single crystal X-ray diffraction analysis.

Keywords: hetero-Diels-Alder-hemiacetal reaction; tandem reactions; thiopyrano[2,3-*d*][1,3]thiazoles; 4-thioxo-2-thiazolidinones; X-ray analysis.

Introduction

The hetero-Diels–Alder reaction has been recognized as one of the most powerful and atom-economical protocols for construction of heterocyclic compounds. Over the past decades, numerous studies have been presented involving LUMO-lowering activation of electron deficient dienophiles in the synthesis of various thiopyran derivatives [1]. Examples of this methodology are the reactions

of 5-methylidene-4-thioxo-2-thiazolidinone with different dienophiles including acrylonitrile [2], acrylic acid and its analogs [3–7], maleic and fumaric acids derivatives [8–11], nitrostyrene [12, 13], arylidene pyruvic [14] and cinnamic acids derivatives [15, 16], 2(5*H*)furanone [17] and norbornene derivatives [18–21]. α,β -Unsaturated aldehydes have been also reported as dienophiles in this reaction [2, 22].

Recently, we have reported that the reaction of 5-arylidene-4-thioxo-2-thiazolidinones with *ortho*-phenolic group at arylidene moiety with α,β -unsaturated carboxylic acid derivatives proceeds as diastereoselective tandem acylation-hetero-Diels-Alder reaction providing the 2*H*,5*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*]thiazoles (Scheme 1). Derivatives of maleic, fumaric [24], acrylic, crotonic, cinnamic [16] and itaconic [7] acids as well as 2(5*H*)furanone [17] have been studied as dienophiles in such type of heterodiene condensation. We have also established that the reaction of β,γ -unsaturated α -ketoacids with 5-(2-hydroxybenzylidene)-4-thioxo-2-thiazolidinones proceeds similarly as a tandem process with the pyran ring formation via the hemiacetal reaction yielding 6-hydroxy-2-oxo-5-phenyl-3,5*a*,6,11*b*-tetrahydro-2*H*,5*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*][1,3]thiazole-6-carboxylic acids. We have observed that the use of arylidene pyruvic acids in the hetero-Diels–Alder-hemiacetal reaction gives rise to a mixture of *rel*-(5*S*,5*aR*,11*bR*)- and *rel*-(5*R*,5*aS*,11*bR*)-annulated diastereoisomers [23].

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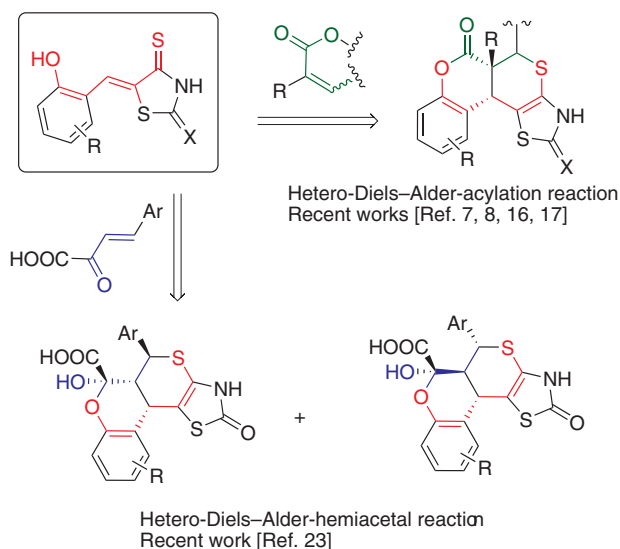
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Results and discussion

Following our previous results we applied α,β -unsaturated aldehydes as dienophiles in hetero-Diels–Alder reactions for the synthesis of novel fused thiopyrano[2,3-*d*]thiazole derivatives. The reaction of 5-(2-hydroxybenzylidene)-4-thioxo-2-thiazolidinones **1a–d** and α,β -unsaturated aldehydes (acrolein, crotonaldehyde, *trans*-cinnamaldehyde) in boiling acetic acid afforded pure tetracyclic fused 6-hydroxy-3,5*a*,6,11*b*-tetrahydro-2*H*,5*H*-chromeno[4',3':4,5]



Scheme 1 Recent results in the synthesis of chromenothiopyrano-thiazoles via tandem hetero-Diels-Alder reaction.

thiopyrano[2,3-*d*][1,3]thiazole-2-ones **2a–l**. Formation of the mixture of *rel*-(5*aR*,6*R*,11*bS*)-**2a–d** and *rel*-(5*S*,5*aR*,6*R*,11*bS*)-annulated **2e–l** diastereoisomers is regioselective and diastereoselective based on the use of α,β -unsaturated aldehydes followed by the hetero-Diels-Alder-hemiacetal tandem process (Scheme 2).

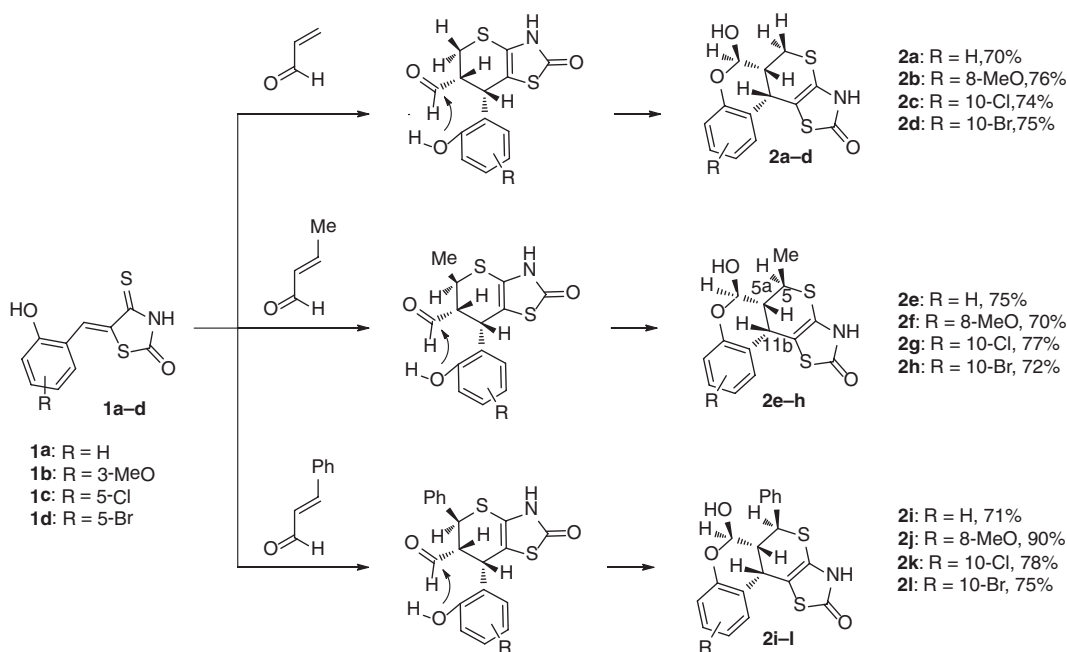
The structures and stereochemical features of final products were established by analysis of the ^1H NMR

spectra. Thus, the proton attached to the hemiacetal hydroxyl group appears as a doublet at δ 7.12–8.02 with a coupling constant of 4.9–6.8 Hz. The proton at C-6 appears as a doublet at δ 4.97–5.61 with a coupling constant of 3.8–6.5 Hz. The *cis*-configuration of the protons at positions 5 and 11*b* and *trans*-configuration at positions 5 and 5*a* was assigned based on the coupling constants ($J_{5a,11b} = 4$ Hz, $J_{5,5a} = 9$ Hz). Additionally, the structure of **2i** was obtained by single crystal X-ray crystallographic analysis (Figure 1).

The X-ray diffraction study of **2i** showed that dihydrothiopyran and dihydropyran rings are fused in a *cis*-decalin mode. Moreover, the H atom pairs at the stereogenic centers C7 and C8 as well as at C7 and C16 centers are in *cis* configuration while protons at C6 and C7 centers are *trans* to each other. The torsion angles H7–C7–C8–H8, H7–C7–C16–H16 and H6–C6–C7–H7 amount to 60, 52 and 170°, respectively.

Conclusion

In summary, it was established that 5-arylideneisorhodanines with an *ortho*-phenolic group at arylidene moiety undergo a diastereoselective tandem hetero-Diels-Alder-hemiacetal reaction providing novel *rel*-(5*aR*,6*R*,11*bS*)-6-hydroxy-3,5*a*,6,11*b*-tetrahydro-2*H*,5*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*][1,3]thiazole-2-ones.



Scheme 2 Synthesis of *rel*-(5*aR*,6*R*,11*bS*)-6-hydroxy-3,5*a*,6,11*b*-tetrahydro-2*H*,5*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*][1,3]thiazole-2-ones **2a–l**.

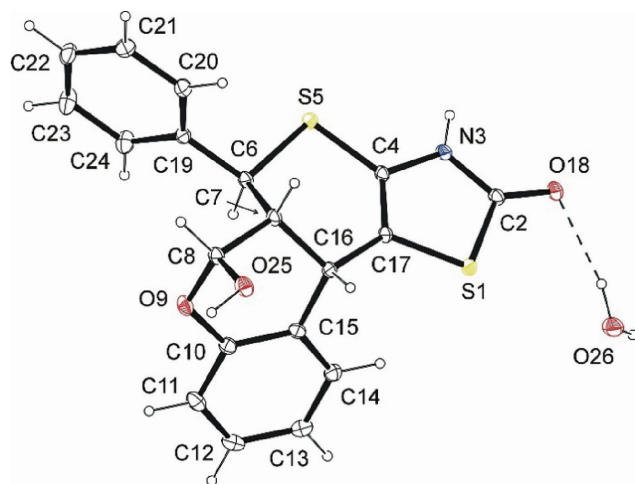


Figure 1 ORTEP view of **2i** showing displacement ellipsoids at the 30% probability level. Hydrogen atoms are shown as spheres of an arbitrary radius.

Experimental

All materials were purchased from commercial sources and used without purification. Melting points were measured in open capillary tubes and were uncorrected. The elemental analyses were performed using a Perkin–Elmer 2400 CHN analyzer. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Varian Gemini 400 in $\text{DMSO-}d_6$ using tetramethylsilane as an internal standard. Mass spectra were obtained using electrospray ionization (ESI) technique on an Agilent 1100 Series LC-MS instrument. The purity of all compounds was checked by TLC. The starting 4-thioxo-2-thiazolidinone was obtained according to method described previously [25]. 5-Arylidene-4-thioxo-2-thiazolidinones **1a–d** were prepared by Knoevenagel condensation: a mixture of 4-thioxo-2-thiazolidinone (10 mmol), an aldehyde (10 mmol) and a catalytic amount of EDDA in ethanol 10 mL was heated under reflux for 10 min. The resultant solid product was filtered and used without further purification.

General procedure of hetero-Diels-Alder-hemiacetal reaction affording **2a–l**

A mixture of a 5-(2-hydroxybenzylidene)-4-thioxo-2-thiazolidinone (10 mmol) and a dienophile (11 mmol) was heated under reflux for 1 h in 10 mL of glacial acetic acid. The mixture contained a catalytic amount of hydroquinone (2–3 mg) for preventing polymerization processes. After completion of the reaction, as determined by TLC analysis, the mixture was poured into water and the precipitated crystals were filtered off, washed with ethanol, and crystallized from solvent indicated below.

rel-(5a*R*,6*R*,11*B*S)-6-Hydroxy-3,5a,6,11*b*-tetrahydro-2*H*,5*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*][1,3]thiazole-2-one (2a) Yield 70%; mp 168–170°C (EtOH); ^1H NMR: δ 2.37 (m, 1H, 5-H), 2.87 (dd, 1H, $J=8.2, 12.4$ Hz, 5-H), 3.22 (m, 1H, 5a-H), 4.03 (d, 1H, $J=5.0$ Hz, 11b-H), 5.46 (t, 1H, $J=4.6$ Hz, 6-H), 6.75 (d, 1H, $J=8.0$ Hz, arom.), 6.88 (t, 1H, $J=7.5$ Hz, arom.), 7.13 (t, 1H, $J=7.5$ Hz, arom.), 7.24 (d, 1H, $J=7.5$ Hz, arom.), 7.53 (d, 1H, $J=5.2$ Hz, OH), 11.41 (s, 1H, NH); ^{13}C NMR:

δ 25.9, 31.6, 36.0, 92.9, 104.6, 117.3, 119.7, 121.2, 123.5, 128.9, 129.2, 151.2, 170.9; ESI-MS: m/z 294 (M+H) $^+$. Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_3\text{S}_2$: C, 53.23; H, 3.78; N, 4.77. Found: C, 53.21; H, 3.77; N, 4.75.

rel-(5a*R*,6*R*,11*B*S)-6-Hydroxy-8-methoxy-3,5a,6,11*b*-tetrahydro-2*H*,5*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*][1,3]thiazole-2-one (2b) Yield 76%; mp 202–204°C (EtOH); ^1H NMR: δ 2.37 (m, 1H, 5-H), 2.67 (m, 1H, 5-H), 3.02 (m, 1H, 5-H), 3.78 (s, 3H, CH_3O), 4.00 (d, 1H, $J=4.2$ Hz, 11b-H), 5.48 (t, 1H, $J=5.1$ Hz, 6-H), 6.78–6.88 (m, 3H, arom.) 7.46 (d, 1H, $J=5.2$ Hz, OH), 11.21 (s, 1H, NH); ^{13}C NMR: δ 26.1, 31.9, 35.8, 55.9, 92.9, 104.9, 111.2, 119.6, 120.7, 123.8, 140.8, 148.7, 171.0; ESI-MS: m/z 324 (M+H) $^+$. Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_4\text{S}_2$: C, 52.00; H, 4.05; N, 4.33. Found: C, 52.02; H, 4.07; N, 4.35.

rel-(5a*R*,6*R*,11*B*S)-10-Chloro-6-hydroxy-3,5a,6,11*b*-tetrahydro-2*H*,5*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*][1,3]thiazole-2-one (2c) Yield 74%; mp 102–104°C (EtOH); ^1H NMR: δ 2.90 (m, 1H, 5-H), 3.26 (m, 1H, 5-H), 3.31 (m, 1H, 5a-H) 4.09 (d, 1H, $J=4.8$ Hz, 11b-H), 5.49 (t, 1H, $J=5.1$ Hz, 6-H), 6.84 (d, 1H, $J=8.4$ Hz, arom.), 7.20 (d, 1H, $J=9.2$ Hz, arom.), 7.30 (s, 1H, arom.), 7.67 (d, 1H, $J=5.2$ Hz, OH), 11.51 (s, 1H, NH). ^{13}C NMR: δ 25.7, 31.1, 35.7, 93.2, 103.5, 119.3, 120.3, 124.6, 125.6, 128.8, 129.4, 150.1, 170.9; ESI-MS: m/z 328/330 (M+H) $^+$. Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{ClNO}_3\text{S}_2$: C, 47.63; H, 3.07; N, 4.27. Found: C, 47.62; H, 3.09; N, 4.25.

rel-(5a*R*,6*R*,11*B*S)-10-Bromo-6-hydroxy-3,5a,6,11*b*-tetrahydro-2*H*,5*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*][1,3]thiazole-2-one (2d) Yield 75%; mp 131–133°C (EtOH); ^1H NMR: δ 2.37 (m, 1H, 5-H), 2.91 (dd, 1H, $J=8.9, 12.9$ Hz, 5-H), 3.26 (m, 1H, 5a-H), 4.10 (d, 1H, $J=4.8$ Hz, 11b-H), 5.48 (t, 1H, $J=4.9$ Hz, 6-H), 6.78 (d, 1H, $J=8.6$ Hz, arom.), 7.34 (d, 1H, $J=8.6$ Hz, arom.), 7.42 (s, 1H, arom.), 7.67 (d, 1H, $J=5.2$ Hz, OH), 11.50 (s, 1H, NH); ^{13}C NMR: δ 31.0, 33.4, 35.7, 93.2, 103.5, 112.3, 119.8, 126.7, 129.4, 131.6, 150.5, 170.9; ESI-MS: m/z 372/374 (M+H) $^+$. Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{BrNO}_3\text{S}_2$: C, 41.94; H, 2.71; N, 3.76. Found: C, 41.92; H, 2.73; N, 3.75.

rel-(5*S*,5a*R*,6*R*,11*B*S)-6-Hydroxy-5-methyl-3,5a,6,11*b*-tetrahydro-2*H*,5*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*][1,3]thiazole-2-one (2e) Yield 75%; mp 191–193°C (PhMe); ^1H NMR: δ 1.55 (d, 3H, $J=7.1$ Hz, CH_3), 2.13 (m, 1H, 5a-H), 3.55 (m, 1H, 5-H), 4.95 (d, 1H, $J=6.0$ Hz, 11b-H), 5.33 (t, 1H, $J=6.0$ Hz, 6-H), 6.74 (d, 1H, $J=7.8$ Hz, arom.), 6.86 (t, 1H, $J=7.1$ Hz, arom.), 7.06–7.13 (m, 2H, arom.), 7.33 (d, 1H, $J=5.1$ Hz, OH), 11.10 (s, 1H, NH); ^{13}C NMR: δ 21.0, 30.7, 35.4, 41.2, 93.0, 104.7, 117.0, 118.5, 120.9, 125.3, 129.0, 130.1, 152.3, 171.0; ESI-MS: m/z 308 (M+H) $^+$. Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_3\text{S}_2$: C, 54.70; H, 4.26; N, 4.56. Found: C, 54.71; H, 4.24; N, 4.57.

rel-(5*S*,5a*R*,6*R*,11*B*S)-6-Hydroxy-8-methoxy-5-methyl-3,5a,6,11*b*-tetrahydro-2*H*,5*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*][1,3]thiazole-2-one (2f) Yield 70%; mp 202–204°C (PhMe); ^1H NMR: δ 1.49 (d, 3H, $J=6.5$ Hz, CH_3), 2.13 (dd, 1H, $J=4.9, 11.6$ Hz, 5a-H), 3.54 (m, 1H, 5-H), 3.77 (s, 3H, CH_3O), 3.93 (d, 1H, $J=4.2$ Hz, 11b-H), 5.33 (t, 1H, $J=6.2$ Hz, 6-H), 6.80 (t, 1H, $J=7.2$ Hz, arom.), 7.12 (d, 1H, $J=7.2$ Hz, OH), 7.19 (d, 1H, $J=7.2$ Hz, arom.), 7.50 (t, 1H, $J=7.2$ Hz, arom.), 11.13 (s, 1H, NH); ^{13}C NMR: δ 21.1, 30.7, 35.4, 41.0, 55.9, 93.2, 104.8, 111.4, 118.4, 120.5, 123.4, 129.4, 141.8, 148.5, 171.0; ESI-MS: m/z 338 (M+H) $^+$. Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_4\text{S}_2$: C, 53.40; H, 4.48; N, 4.15. Found: C, 53.41; H, 4.47; N, 4.16.

rel-(5*S*,5a*R*,6*R*,11*B*S)-10-Chloro-6-hydroxy-5-methyl-3,5a,6,11*b*-tetrahydro-2*H*,5*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*][1,3]thiazole-2-one (2g) Yield 77%; mp 142–144°C (PhMe); ^1H NMR: δ 1.14 (d, 3H, $J=6.9$ Hz, CH_3), 2.20 (dd, 1H, $J=5.4, 12.0$ Hz, 5a-H), 2.30

(m, 1H, 5-H), 4.08 (d, 1H, $J=4.8$ Hz, 11b-H), 5.32 (t, 1H, $J=6.3$ Hz, 6-H), 6.85 (d, 1H, $J=8.7$ Hz, arom.), 7.22–7.31 (m, 2H, arom.), 7.71 (d, 1H, $J=6.0$ Hz, OH), 11.40 (s, 1H, NH); ^{13}C NMR: δ 20.8, 30.5, 35.4, 93.2, 103.8, 118.9, 119.1, 124.4, 125.1, 128.7, 129.0, 129.4, 151.2, 170.9; ESI-MS: m/z 342 (M+H) $^+$. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{ClNO}_3\text{S}_2$: C, 49.19; H, 3.54; N, 4.10. Found: C, 49.22; H, 3.55; N, 4.12.

rel-(5S,5aR,6R,11bS)-10-Bromo-6-hydroxy-5-methyl-3,5a,6,11b-tetrahydro-2H,5H-chromeno[4',3':4,5]thiopyrano[2,3-d][1,3]thiazole-2-one (2h) Yield 72%; mp 182–184°C (PhMe); ^1H NMR: δ 1.43 (d, 3H, $J=6.9$ Hz, CH_3), 2.19 (dd, 1H, $J=5.1, 11.6$ Hz, 5a-H), 3.52 (m, 1H, 5-H), 4.08 (d, 1H, $J=5.0$ Hz, 11b-H), 5.31 (t, 1H, $J=6.0$ Hz, 6-H), 6.79 (d, 1H, $J=8.7$ Hz, arom.), 7.33 (d, 1H, $J=8.5$ Hz, arom.), 7.42 (s, 1H, arom.), 7.70 (d, 1H, $J=6.3$ Hz, OH), 11.40 (s, 1H, NH); ^{13}C NMR: δ 20.7, 30.6, 35.4, 93.2, 103.8, 111.9, 125.7, 125.8, 128.7, 129.4, 131.9, 151.7, 170.9. ESI-MS m/z 386/388 (M+H) $^+$. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{BrNO}_3\text{S}_2$: C, 43.53; H, 3.13; N, 3.63. Found: C, 43.54; H, 3.14; N, 3.65.

rel-(5S,5aR,6R,11bS)-6-hydroxy-5-phenyl-3,5a,6,11b-tetrahydro-2H,5H-chromeno[4',3':4,5]thiopyrano[2,3-d][1,3]thiazole-2-one (2i) Yield 71%; mp 188–190°C (PhMe); ^1H NMR (400 MHz, DMSO- d_6): δ 2.59 (dd, 1H, $J=4.3, 8.7$ Hz, 5a-H), 3.98 (d, 1H, $J=3.6$ Hz, 11b-H), 4.38 (d, 1H, $J=8.8$ Hz, 5-H), 5.01 (t, 1H, $J=3.9$ Hz, 6-H), 6.76 (d, 1H, $J=8.1$ Hz, arom.), 6.66 (t, 1H, $J=7.4$ Hz, arom.), 7.08–7.14 (m, 2H, arom.), 7.49 (d, 1H, $J=4.9$ Hz, OH), 11.32 (s, 1H, NH); ^{13}C NMR: δ 30.3, 41.6, 44.0, 91.4, 103.6, 117.4, 120.3, 121.4, 123.4, 125.8, 128.7, 128.8, 128.9, 129.4, 138.3, 150.1, 171.1; ESI-MS: m/z 370 (M+H) $^+$. Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_3\text{S}_2$: C, 61.77; H, 4.09; N, 3.79. Found: C, 61.75; H, 4.07; N, 3.80.

rel-(5S,5aR,6R,11bS)-6-Hydroxy-8-methoxy-5-phenyl-3,5a,6,11b-tetrahydro-2H,5H-chromeno[4',3':4,5]thiopyrano[2,3-d][1,3]thiazole-2-one (2j) Yield 90%; mp 170–172°C (PhMe); ^1H NMR: δ 2.33 (m, 1H, 5a-H), 3.77 (s, 3H, CH_3O), 3.90 (m, 1H, 11b-H), 4.41 (d, 1H, $J=9.2$ Hz, 5-H), 5.08 (t, 1H, $J=3.9$ Hz, 6-H), 6.80–6.87 (m, 3H, arom.), 7.34–7.40 (m, 6H, arom., OH), 11.35 (s, 1H, NH); ^{13}C NMR: δ 30.5, 41.5, 43.9, 56.0, 91.5, 103.9, 111.5, 120.2, 120.4, 120.9, 123.7, 128.7, 128.8, 129.4, 138.6, 140.6, 148.7, 171.2; ESI-MS: m/z 400 (M+H) $^+$. Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{NO}_4\text{S}_2$: C, 60.13; H, 3.29; N, 3.51. Found: C, 60.12; H, 3.28; N, 3.53.

rel-(5S,5aR,6R,11bS)-10-Chloro-6-hydroxy-5-phenyl-3,5a,6,11b-tetrahydro-2H,5H-chromeno[4',3':4,5]thiopyrano[2,3-d][1,3]thiazole-2-one (2k) Yield 78%, mp 190–192°C (PhMe); ^1H NMR: δ 2.75 (dd, 1H, $J=4.8, 9.6$ Hz, 5a-H), 4.10 (d, 1H, $J=4.8$ Hz, 11b-H), 4.36 (d, 1H, $J=9.4$ Hz, 5-H), 4.98 (t, 1H, $J=4.6$ Hz, 6-H), 6.87 (d, 1H, $J=8.7$ Hz, arom.), 7.12–7.20 (m, 2H, arom.), 7.65 (d, 1H, $J=4.6$ Hz, OH), 11.44 (s, 1H, NH). ^{13}C NMR: δ 30.2, 41.0, 43.9, 91.4, 102.6, 119.4, 121.0, 124.9, 125.8, 128.4, 128.6, 128.7, 128.9, 129.4, 137.8, 149.8, 171.1; ESI-MS: m/z 404/406 (M+H) $^+$. Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{ClNO}_3\text{S}_2$: C, 56.50; H, 3.49; N, 3.47. Found: C, 56.52; H, 3.51; N, 3.46.

rel-(5S,5aR,6R,11bS)-10-Bromo-6-hydroxy-5-phenyl-3,5a,6,11b-tetrahydro-2H,5H-chromeno[4',3':4,5]thiopyrano[2,3-d][1,3]thiazole-2-one (2l) Yield 75%, mp 217–219°C (PhMe); ^1H NMR: δ 2.62 (dd, 1H, $J=5.6, 10.9$ Hz, 5a-H), 4.03 (m, 1H, 11b-H), 4.31 (d, 1H, $J=9.5$ Hz, 5-H), 4.97 (m, 1H, 6-H), 6.74 (d, 1H, $J=8.4$ Hz, arom.), 7.26 (d, 1H, $J=7.6$ Hz, arom.), 7.31–7.51 (m, 2H, OH, arom.), 11.44 (s, 1H, NH); ^{13}C NMR: δ 30.1, 41.0, 43.9, 91.4, 102.5, 112.6, 119.9, 121.0, 126.2, 128.9, 129.4, 131.3, 131.6, 178, 150.3, 171.1; ESI-MS: m/z 448/450 (M+H) $^+$. Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{BrNO}_3\text{S}_2$: C, 50.90; H, 3.15; N, 3.12. Found: C, 50.91; H, 3.13; N, 3.14.

X-ray crystallographic study

Crystallographic data for **2i**: Empirical formula $\text{C}_{19}\text{H}_{15}\text{NO}_3\text{S}_2 \cdot \text{H}_2\text{O}$, formula weight 387.45, light-brown block crystals, crystal system monoclinic, space group $P2_1/c$, $a=10.9127(4)$, $b=15.1717(4)$, $c=11.2980(4)$ Å, $\beta=111.457(4)^\circ$, $V=1740.90(11)$ Å 3 , $Z=4$, $D_{\text{calc}}=1.478$ g/cm 3 . A light-brown crystal (benzene-acetone) ($0.17 \times 0.13 \times 0.07$ mm) was used to record 17 948 (CuK α -radiation, $\theta_{\text{max}}=76.38^\circ$) intensities on a Super Nova diffractometer. The supplementary crystallographic data of **2i** have been deposited at the Cambridge Crystallography Data Centre (CCDC) as supplementary publication CCDC 1497433. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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