Synthesis of Novel Polycyclic Indole-Annulated Thiopyranocoumarin Derivatives *via* Domino *Knoevenagel*–Hetero-*Diels*–*Alder* Reaction in Aqueous Media

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An efficient synthesis of polycyclic indole derivatives is achieved *via* domino *Knoevenagel*–hetero-*Diels*–*Alder* reaction of *O*-acrylated salicylaldehyde derivatives with dihydroindole-2-thiones in H_2O as solvent. The products are formed in good-to-excellent yields with high regio- and stereoselectivity.

Introduction. – Heterocycles have popularly been utilized as pharmacophores for preparing drugs [1]. Among them, the indole moiety is frequently encountered in medicinal chemistry and is considered to be a privileged scaffold [2]. However, polycyclic annulated indole compounds continue to be of extensive synthetic interest, partly because there are many biologically active natural products of this type, and also because the polycyclic frameworks lead to relatively rigid structures that might be expected to show substantial selectivity in their interactions with enzymes or receptors [3]. On the other hand, coumarins and their derivatives are very important organic compounds. They constitute the structural scaffold of several natural products [4]. Their applications range from pharmaceuticals [5], optical brighteners, and laser dyes [6]. Also coumarins and functionalized coumarins have shown activity as antimicrobials and chemotherapeutics [7].

An important objective in organic synthesis is the development of highly efficient synthetic procedures toward complex molecules. The hetero-*Diels*–*Alder* reaction represents an effective method for the synthesis of heterocyclic compounds, especially natural products [8]. In recent years, intramolecular hetero-*Diels*–*Alder* reactions have widely been used in numerous reactions because of their economical and stereocontrolled nature [9]. These reactions allow the formation of two or more rings in one operation, thus avoiding sequential chemical transformations. However, it is prerequisite that activating groups have to be built into dienophiles to achieve the desired reactivity [10].

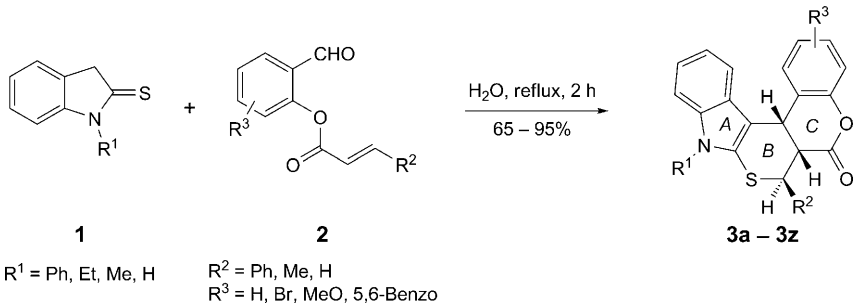
Recently, domino reactions have been used as highly efficient processes for the improvement of reaction efficiency [11]. Among these reactions, the domino *Knoevenagel*–hetero-*Diels*–*Alder* reaction is a very efficient process, especially in the field of heterocycles and natural products [12].

Tietze et al. extensively described the domino *Knoevenagel*–hetero-*Diels*–*Alder* reaction (DKHDA) of unsaturated aromatic and aliphatic aldehydes (especially *O*-

allylated salicylaldehydes) with several 1,3-dicarbonyl compounds [13], and recently *Balalaie* and co-workers described this type of reaction with *O*-propargylated salicylaldehyde derivatives for synthesis of tetracycles with a pyran ring [14], but DKHDA reactions of *O*-acrylated salicylaldehydes are rare [15].

In the context of our general interest in the synthesis of heterocyclic compounds using thioamides [16], we herein report a new and highly efficient reaction for the preparation of polycyclic compounds **3a** – **3z**, which consist of an indole ring (*A*) and a dihydrothiopyran ring (*B*) annulated to a dihydrocoumarin ring (*C*; *Scheme 1*).

Scheme 1. *One-Pot Synthesis of Polycyclic Indole Derivatives*



1 **2** **3a – 3z**

R^1 = Ph, Et, Me, H

R^2 = Ph, Me, H

R^3 = H, Br, MeO, 5,6-Benzo

Results and Discussion. – The *O*-acrylated salicylaldehyde derivatives **2** were prepared in high yields and excellent purity *via* reaction of substituted salicylaldehydes and (*E*)-acryloyl chloride derivatives using anhydrous K_2CO_3 in dry acetone. Our first experiment showed that no catalyst is required for DKHDA reaction. The effect of solvent was studied by carrying out the reaction at various solvents such as toluene, MeCN, and H_2O. Hydrolysis of the ester moiety of intermediate **4** (*cf. Scheme 2*) in organic solvents led to low yields. Surprisingly, the hydrolysis did not occur in H_2O. However, high yields with short reaction times were observed in refluxing H_2O. The catalyst-free DKHDA reaction of dihydroindole-2-thiones **1** and *O*-acrylated salicylaldehyde derivatives **2** in H_2O led to compounds **3a** – **3z** in good-to-excellent yields. The reaction is highly stereoselective, leading exclusively to the *cis*-fused compounds. It is highly desirable to develop environmentally benign processes that can be conducted in aqueous media. Furthermore, using H_2O as a solvent has advantages, such as low cost and safety, and it is part of the biosphere [17]. To generalize our method, we used a series of dihydroindole-2-thione derivatives **1** and *O*-acrylated salicylaldehyde derivatives **2** to obtain the corresponding products **3a** – **3z** in high yields (*Table*).

The structures of compounds **3a** – **3z** have been determined by spectroscopic methods (^{1}H- and ^{13}C-NMR, and DEPT) and elemental analysis. The relative configurations were determined from the coupling constants of the relevant H-atoms and NOE experiments. For instance, in compound **3k**, H_a and H_b ($J = 9.5$ Hz) are in *trans*-relation, and H_b and H_c ($J = 4.5$ Hz) are in a *cis*-arrangement. NOE Measurements on compound **3k** confirmed the *cis*-orientation of H_b and H_c (*Fig.*). In all the cases, the relative orientation of the ring junction H-atoms was found to be same.

Table. *Synthesis of Polycyclic Indole Derivatives*[a])

Entry	R^1	R^2	R^3	Product	Yield [%][b])	*Entry*	R^1	R^2	R^3	Product	Yield [%][b])
1	H	Ph	H	**3a**	88	*14*	Et	Ph	5-Br	**3n**	85
2	H	Ph	5-Br	**3b**	80	*15*	Et	Ph	3-MeO	**3o**	92
3	H	Ph	3-MeO	**3c**	94	*16*	Et	Ph	5,6-Benzo	**3p**	70
4	H	Me	3-MeO	**3d**	94	*17*	Et	Me	3-MeO	**3q**	87
5	H	H	5-Br	**3e**	85	*18*	Et	Me	5-Br	**3r**	93
6	H	H	H	**3f**	90	*19*	Et	H	H	**3s**	85
7	Me	Ph	H	**3g**	80	*20*	Ph	Ph	H	**3t**	92
8	Me	Ph	3-MeO	**3h**	88	*21*	Ph	Ph	5-Br	**3u**	88
9	Me	Ph	5-Br	**3i**	83	*22*	Ph	Ph	3-MeO	**3v**	82
10	Me	Ph	5,6-Benzo	**3j**	74	*23*	Ph	Ph	5,6-Benzo	**3w**	65
11	Me	Me	5-Br	**3k**	95	*24*	Ph	Me	5-Br	**3x**	83
12	Me	H	5-Br	**3l**	92	*25*	Ph	Me	3-MeO	**3y**	90
13	Et	Ph	H	**3m**	83	*26*	Ph	H	5-Br	**3z**	85

[a]) All the reactions were carried out in H_2O under reflux for 2 h, molar ratio **1/2** 1 : 1. [b]) Isolated product.

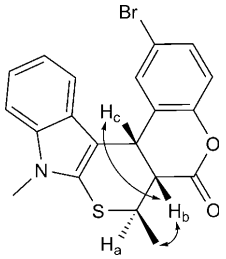
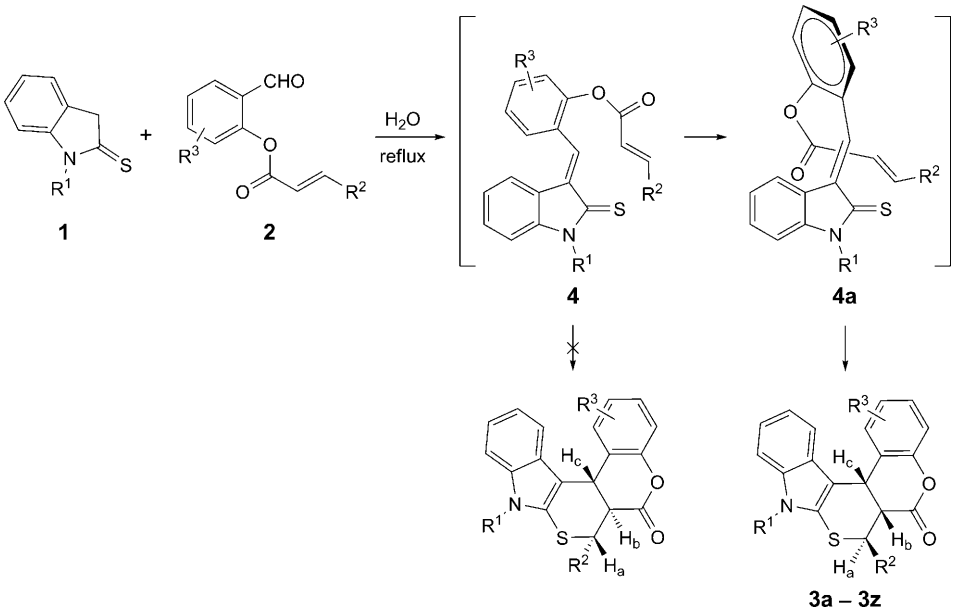


Figure. *Selected NOE enhancements of* **3k**

A plausible mechanism for the intramolecular DKHDA reaction to produce stereoselectively products **3a**–**3z** is proposed in *Scheme 2*. Dihydroindole-2-thiones **1** undergo a *Knoevenagel* condensation with aldehydes **2** in refluxing H_2O to afford the 'heterodienes' **4**, the stereochemistry of the final *Diels–Alder* reaction depends on the '*endo*'- and '*exo*'-orientation of the dienophile in the transition state. All efforts to isolate the intermediates **4** failed. The intermediates **4** may undergo rotation around single bond to assume the structures **4a**, which may then undergo [4 + 2] cyclization with '*endo*'-selectivity to give desired products **3a**–**3z**.

Conclusions. – We have reported a highly efficient stereoselective method for the synthesis of novel heteropolycyclic compounds through a DKHDA reaction in aqueous media. The major advantage of this reaction is the ease of the workup, since the products can be isolated without chromatography. This reaction also offers other advantages such as clean reactions, high yields of products, short reaction time, and no need of a catalyst, which make it a useful and attractive procedure for the synthesis of pentacyclic indole derivatives. Further studies to extend the scope and synthetic utility of dihydroindole-2-thiones and dihydroindole-2-ones in DKHDA reactions are in progress in our laboratory.

Scheme 2. *A Plausible Mechanism for the Formation of Compounds* **3a**–**3z**



We would like to acknowledge the *Islamic Development Bank* (*IDB*) for granting a loan in 1993 for purchasing a 500-MHz *Bruker* NMR spectrometer.

Experimental Part

General. Commercially available materials were purchased from *Sigma–Aldrich* and *Merck*, and were used without any additional purification. TLC: Silica-gel plates *60 F_{254}* (SiO_2; *Merck*). M.p.: *Büchi* melting point *B-540* apparatus; in sealed capillaries; uncorrected. ^{1}H- and ^{13}C-NMR Spectra: *Bruker* (*DRX-500 Avance*) spectrometer at 500 (^{1}H) and 125 (^{13}C) MHz, in $CDCl_3$ and (D_6)DMSO solns., at ambient temp.; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. Signals of the ^{13}C-NMR spectra corresponding to CH, CH_2, or Me groups are assigned from DEPT. Elemental analysis: *Perkin-Elmer 2004 (II)* CHN analyzer.

General Procedure for Preparation of the O*-Acrylated Salicylaldehyde Derivatives* **2**. A mixture of a salicylaldehyde derivative (10 mmol), and acryloyl chloride or its derivative (12 mmol) was stirred in acetone (10 ml) in the presence of K_2CO_3 (1.38–1.66 g, 10–12 mmol) for 8–10 h at r.t. After completion of the reaction (monitored by TLC), ice-cold H_2O (50 ml) was added to the mixture with vigorous stirring to afford a light precipitate that was filtered, washed with H_2O, and air-dried.

General Procedure for Domino Knoevenagel-*Hetero*-Diels–Alder (DKHDA) *Reaction* (**3a**–**3z**). Dihydroindole-2-thiones **1** were prepared according to the procedure described in [18]. A mixture of **1** (1 mmol) and an *O*-acrylated salicylaldehyde derivative **2** (1 mmol) in H_2O (8 ml) was refluxed. The progress of the reaction was monitored by TLC (mini-extraction with AcOEt carried out for TLC). After completion (2 h), the mixture was cooled, and the solid precipitate was filtered, washed with H_2O, air dried, and recrystallized from EtOH.

*(6a*R**,7*S**,13c*S**)-6a,7,9,13c-Tetrahydro-7-phenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3a**). Yellow solid. Yield: 168 mg (88%). M.p. 267–268°. ^{1}H-NMR ($CDCl_3$/(D_6)DMSO 1:10): 3.39 (*dd*, *J* = 8.7, 4.5, H–C(6a)); 4.49–4.52 (*m*, H–C(7), H–C(13c)); 6.83 (*t*, *J* = 7.4, 1 H); 6.84–6.93 (*m*, 3 H); 7.08–7.18 (*m*, 9 H); 10.45 (*s*, NH). ^{13}C-NMR ($CDCl_3$/(D_6)DMSO 1:10): 33.14 (CH); 43.46

(CH); 47.52 (CH); 103.39 (C); 111.09 (CH); 116.95 (CH); 116.97 (CH); 119.94 (CH); 121.16 (CH); 125.10 (CH); 126.18 (C); 128.06 (C); 128.47 (C); 128.70 (CH); 129.08 (CH); 129.17 (CH); 129.24 (CH); 129.76 (CH); 136.84 (C); 137.56 (C); 150.13 (C); 167.44 (C). Anal. calc. for $C_{24}H_{17}NO_2S$ (383.46): C 75.17, H 4.47, N 3.65; found: C 74.92, H 4.42, N 3.68.

*(6a*R*,7*S*,13c*S*)-2-Bromo-6a,7,9,13c-tetrahydro-7-phenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3b**). Pale-yellow solid. Yield: 185 mg (80%). M.p. 245 – 247°. ^{1}H-NMR ((D$_6$)DMSO): 3.81 (*dd*, *J* = 8.2, 4.6, H–C(6a)); 4.77 (*d*, *J* = 8.0, H–C(7)); 4.84 (*d*, *J* = 4.6, H–C(13c)); 6.98 (*t*, *J* = 7.4, 1 H); 7.06 (*t*, *J* = 7.5, 1 H); 7.13 (*d*, *J* = 8.6, 1 H); 7.24 (*d*, *J* = 7.5, 1 H); 7.31 (*d*, *J* = 8.0, 1 H); 7.34 – 7.46 (*m*, 6 H); 7.55 (*d*, *J* = 8.5, 1 H); 11.52 (*s*, NH). ^{13}C-NMR ((D$_6$)DMSO): 32.53 (CH); 43.28 (CH); 46.09 (CH); 103.22 (C); 111.55 (CH); 117.20 (C); 117.37 (CH); 119.79 (CH); 120.32 (CH); 121.57 (CH); 128.42 (C); 128.52 (C); 129.38 (CH); 129.38 (C); 129.53 (2 CH); 132.35 (CH); 132.53 (CH); 136.96 (C); 138.37 (C); 149.88 (C); 166.83 (C). Anal. calc. for $C_{24}H_{16}BrNO_2S$ (462.36): C 62.35, H 3.49, N 3.03; found: C 62.05, H 3.42, N 2.98.

*(6a*R*,7*S*,13c*S*)-6a,7,9,13c-Tetrahydro-4-methoxy-7-phenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3c**). Yellow solid. Yield: 194 mg (94%). M.p. 253 – 255°. ^{1}H-NMR ((D$_6$)DMSO): 3.75 (*dd*, *J* = 7.0, 4.7, H–C(6a)); 3.82 (*s*, MeO); 4.56 (*d*, *J* = 4.7, H–C(13c)); 4.83 (*d*, *J* = 6.7, H–C(7)); 6.87 (*t*, *J* = 7.5, 1 H); 6.92 (*d*, *J* = 6.9, 1 H); 7.00 (*t*, *J* = 7.5, 1 H); 7.08 – 7.15 (*m*, 3 H); 7.27 (*d*, *J* = 8.0, 1 H); 7.33 – 7.40 (*m*, 3 H); 7.43 (*d*, *J* = 7.0, 2 H); 11.44 (*s*, NH). ^{13}C-NMR ((D$_6$)DMSO): 32.48 (CH); 43.32 (CH); 46.08 (CH); 56.78 (Me); 103.79 (C); 111.31 (CH); 112.96 (CH); 117.79 (CH); 119.98 (CH); 121.30 (CH); 121.40 (CH); 125.31 (CH); 127.69 (C); 128.08 (C); 128.48 (C); 129.14 (CH); 129.21 (CH); 129.53 (CH); 136.94 (C); 139.26 (C); 139.66 (C); 148.06 (C); 167.26 (C). Anal. calc. for $C_{25}H_{19}NO_3S$ (413.49): C 72.62, H 4.63, N 3.39; found: C 72.32, H 4.56, N 3.33.

*(6a*R*,7*R*,13c*S*)-6a,7,9,13c-Tetrahydro-4-methoxy-7-methyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3d**). Yellow solid. Yield: 165 mg (94%). M.p. 205 – 208°. ^{1}H-NMR ((D$_6$)DMSO): 1.49 (*d*, *J* = 6.7, Me); 3.29 (*dd*, *J* = 4.7, 3.7, H–C(6a)); 3.72 – 3.75 (*m*, H–C(7)); 3.85 (*s*, MeO); 4.77 (*d*, *J* = 3.7, H–C(13c)); 6.87 (*t*, *J* = 7.2, 1 H); 6.98 (*d*, *J* = 6.4, 2 H); 7.06 (*d*, *J* = 7.7, 1 H); 7.11 – 7.17 (*m*, 2 H); 7.26 (*d*, *J* = 7.8, 1 H); 10.93 (*s*, NH). ^{13}C-NMR ((D$_6$)DMSO): 21.27 (Me); 32.19 (CH); 34.13 (CH); 45.87 (CH); 56.75 (Me); 103.37 (C); 111.14 (CH); 112.89 (CH); 117.75 (CH); 119.79 (CH); 121.00 (CH); 121.57 (CH); 125.19 (CH); 127.87 (C); 127.98 (C); 128.47 (C); 137.05 (C); 139.84 (C); 148.07 (C); 167.98 (C). Anal. calc. for $C_{20}H_{17}NO_3S$ (351.42): C 68.36, H 4.88, N 3.99; found: C 68.51, H 4.82, N 3.93.

*(6a*R*,13c*S*)-2-Bromo-6a,7,9,13c-tetrahydro-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3e**). Light yellow solid. Yield: 164 mg (85%). M.p. 248 – 250°. ^{1}H-NMR ((D$_6$)DMSO): 3.23 – 3.37 (*m*, 2 H–C(7)); 3.58 (*m*, H–C(6a)); 4.86 (*d*, *J* = 4.2, H–C(13c)); 6.92 (*t*, *J* = 7.3, 1 H); 7.01 (*t*, *J* = 7.4, 1 H); 7.10 – 7.14 (*m*, 2 H); 7.26 (*d*, *J* = 7.9, 1 H); 7.53 (*s*, 1 H); 7.54 (*d*, *J* = 7.9, 1 H); 11.41 (*s*, NH). ^{13}C-NMR ((D$_6$)DMSO): 25.22 (CH$_2$); 30.30 (CH); 39.51 (CH); 103.28 (C); 111.33 (CH); 117.10 (C); 117.24 (CH); 119.91 (CH); 120.12 (CH); 121.33 (CH); 127.85 (C); 128.54 (C); 129.56 (C); 132.36 (CH); 132.44 (CH); 136.87 (C); 150.13 (C); 168.51 (C). Anal. calc. for $C_{18}H_{12}BrNO_2S$ (386.26): C 55.97, H 3.14, N 3.63; found: C 56.12, H 3.18, N 3.68.

*(6a*R*,13c*S*)-6a,7,9,13c-Tetrahydro-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3f**). Yellow solid. Yield: 138 mg (90%). M.p. 227 – 229°. ^{1}H-NMR (CDCl$_3$/(D$_6$)DMSO 1:10): 2.88 (*dd*, *J* = 12.4, 2.4, 1 H–C(7)); 3.02 (*dd*, *J* = 12.4, 10.2, 1 H–C(7)); 3.15 – 3.18 (*m*, H–C(6a)); 4.48 (*d*, *J* = 4.8, H–C(13c)); 6.74 (*t*, *J* = 7.4, 1 H); 6.79 – 6.83 (*m*, 3 H); 6.99 – 7.06 (*m*, 4 H); 10.43 (*s*, NH). ^{13}C-NMR (CDCl$_3$/(D$_6$)DMSO (10%)): 24.85 (CH$_2$); 32.85 (CH); 40.47 (CH); 103.37 (C); 110.90 (CH); 116.74 (CH); 117.01(CH); 119.80 (CH); 121.03 (CH); 125.17 (CH); 125.87 (C); 126.79 (C); 128.66 (C); 128.94 (CH); 129.58 (CH); 136.70 (C); 150.05 (C); 169.26 (C). Anal. calc. for $C_{18}H_{13}NO_2S$ (307.37): C 70.34, H 4.26, N 4.56; found: C 70.04, H 4.31, N 4.51.

*(6a*R*,7*S*,13c*S*)-6a,7,9,13c-Tetrahydro-9-methyl-7-phenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3g**). Yellow solid. Yield: 154 mg (80%). M.p. 247 – 250°. ^{1}H-NMR (CDCl$_3$): 3.57 (*dd*, *J* = 8.7, 4.5, H–C(6a)); 3.66 (*s*, MeN); 4.71 – 4.73 (*m*, H–C(7), H–C(13c)); 7.08 – 7.12 (*m*, 3 H); 7.20 (*t*, *J* = 7.6, 1 H); 7.27 (*d*, *J* = 7.8, 1 H); 7.31 (*d*, *J* = 7.9, 2 H); 7.33 – 7.38 (*m*, 6 H). ^{13}C-NMR (CDCl$_3$): 30.43 (Me); 33.47 (CH); 43.79 (CH); 47.45 (CH); 103.11 (C); 108.96 (CH); 117.13 (CH); 117.47 (CH); 120.38 (CH); 121.37 (CH); 125.26 (CH); 126.26 (C); 128.46 (C); 128.82 (CH); 129.41 (3 CH); 129.88 (CH);

130.61 (C); 137.39 (C); 137.80 (C); 150.29 (C); 167.54 (C). Anal. calc. for $C_{25}H_{19}NO_2S$ (397.49): C 75.54, H 4.82, N 3.52; found: C 75.31, H 4.86, N 3.44.

*(6a*R*,7*S*,13c*S*)-6a,7,9,13c-Tetrahydro-4-methoxy-9-methyl-7-phenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3h**). Light yellow solid. Yield: 188 mg (88%). M.p. 259–261°. ^{1}H-NMR ((D$_6$)DMSO): 3.64 (*s*, MeN); 3.76 (*dd*, *J* = 5.7, 4.4, H–C(6a)); 3.82 (*s*, MeO); 4.60 (*d*, *J* = 4.4, H–C(13c)); 4.87 (*d*, *J* = 5.7, H–C(7)); 6.91–6.95 (*m*, 2 H); 7.09–7.14 (*m*, 3 H); 7.19 (*d*, *J* = 7.4, 1 H); 7.36–7.44 (*m*, 6 H). ^{13}C-NMR ((D$_6$)DMSO): 30.68 (Me); 32.62 (CH); 43.43 (CH); 45.84 (CH); 56.80 (Me); 103.34 (C); 109.84 (CH); 113.02 (CH); 117.92 (CH); 120.27 (CH); 121.30 (CH); 121.40 (CH); 125.37 (CH); 127.59 (C); 128.12 (C); 129.23 (2 CH); 129.56 (CH); 130.25 (C); 137.78 (C); 138.92 (C); 139.60 (C); 148.06 (C); 167.18 (C). Anal. calc. for $C_{26}H_{21}NO_3S$ (427.51): C 73.04, H 4.95, N 3.28; found: C 72.83, H 4.88, N 3.34.

*(6a*R*,7*S*,13c*S*)-2-Bromo-6a,7,9,13c-tetrahydro-9-methyl-7-phenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3i**). Yellow solid. Yield: 197 mg (83%). M.p. 260–263°. ^{1}H-NMR ($CDCl_3$): 3.60 (*dd*, *J* = 9.0, 4.4, H–C(6a)); 3.71 (*s*, MeN); 4.72 (*d*, *J* = 9.0, H–C(7)); 4.75 (*d*, *J* = 3.8, H–C(13c)); 7.02 (*d*, *J* = 8.6, 1 H); 7.18 (*t*, *J* = 7.4, 1 H); 7.26 (*t*, *J* = 7.6, 1 H); 7.36–7.42 (*m*, 8 H); 7.48 (*dd*, *J* = 8.6, 2.1, 1 H). ^{13}C-NMR ($CDCl_3$): 30.47 (Me); 33.52 (CH); 43.78 (CH); 47.13 (CH); 102.20 (C); 109.11 (CH); 117.17 (CH); 118.05 (C); 119.09 (CH); 120.71 (CH); 121.58 (CH); 128.23 (C); 128.56 (C); 128.78 (CH); 129.49 (CH); 129.60 (CH); 130.81 (C); 132.51 (CH); 132.56 (CH); 136.96 (C); 137.85 (C); 149.37 (C); 166.81 (C). Anal. calc. for $C_{25}H_{18}BrNO_2S$ (476.38): C 63.03, H 3.81, N 2.94; found: C 63.32, H 3.75, N 2.98.

*(4a*R*,5*S*,11c*S*)-4a,5,7,11c-Tetrahydro-7-methyl-5-phenyl-4*H*-naphtho[1″,2″:5′,6′]pyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-4-one* (**3j**). Light brown solid. Yield: 164 mg (74%). M.p. 204–207°. ^{1}H-NMR ((D$_6$)DMSO): 3.69 (*s*, MeN); 3.91 (*dd*, *J* = 3.9, 2.0, H–C(4a)); 4.70 (*d*, *J* = 3.9, H–C(5)); 5.39 (*d*, *J* = 2.0, H–C(11c)); 5.83 (*d*, *J* = 8.0, 1 H); 6.38 (*t*, *J* = 7.4, 1 H); 6.87 (*t*, *J* = 7.4, 1 H); 7.32–7.38 (*m*, 3 H); 7.43 (*t*, *J* = 7.2, 2 H); 7.54–7.58 (*m*, 3 H); 7.63 (*t*, *J* = 7.4, 1 H); 7.97 (*d*, *J* = 8.4, 1 H); 8.02 (*d*, *J* = 8.8, 1 H); 8.07 (*d*, *J* = 8.0, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 27.31 (CH); 30.78 (Me); 43.34 (CH); 45.27 (CH); 102.93 (C); 109.71 (CH); 117.55 (CH); 118.17 (CH); 119.79 (CH); 120.03 (C); 120.84 (CH); 123.72 (CH); 126.31 (CH); 126.93 (C); 128.72 (2 CH); 128.95 (CH); 129.58 (CH); 129.98 (CH); 130.62 (CH); 130.90 (C); 131.13 (C); 132.28 (C); 137.71 (C); 141.67 (C); 149.55 (C); 168.09 (C). Anal. calc. for $C_{29}H_{21}NO_2S$ (447.55): C 77.83, H 4.73, N 3.13; found: C 77.01, H 4.61, N 3.19.

*(6a*R*,7*R*,13c*S*)-2-Bromo-6a,7,9,13c-tetrahydro-7,9-dimethyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3k**). Yellow solid. Yield: 219 mg (95%). M.p. 245–247°. ^{1}H-NMR ($CDCl_3$): 1.56 (*d*, *J* = 6.1, Me); 3.18 (*dd*, *J* = 9.5, 4.5, H–C(6a)); 3.59–3.63 (*m*, H–C(7)); 3.68 (*s*, MeN); 4.82 (*d*, *J* = 4.3, H–C(13c)); 7.01 (*d*, *J* = 8.6, 1 H); 7.18 (*t*, *J* = 7.4, 1 H); 7.24 (*t*, *J* = 7.6, 1 H); 7.31–7.35 (*m*, 2 H); 7.40–7.44 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 19.59 (Me); 30.41 (Me); 33.42 (CH); 33.45 (CH); 47.16 (CH); 102.00 (C); 109.04 (CH); 116.92 (CH); 118.14 (C); 119.01 (CH); 120.64 (CH); 121.46 (CH); 128.33 (C); 128.66 (C); 130.55 (C); 132.25 (CH); 132.27 (CH); 137.85 (C); 149.17 (C); 167.69 (C). Anal. calc. for $C_{20}H_{16}BrNO_2S$ (414.32): C 57.98, H 3.89, N 3.38; found: C 57.58, H 3.74, N 3.31.

*(6a*R*,13c*S*)-2-Bromo-6a,7,9,13c-tetrahydro-9-methyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3l**). Light yellow solid. Yield: 184 mg (92%). M.p. 255–257°. ^{1}H-NMR ($CDCl_3$): 3.21 (*dd*, *J* = 12.5, 2.4, 1 H–C(7)); 3.28 (*dd*, *J* = 12.4, 10.7, H–C(7)); 3.41–3.45 (*m*, H–C(6a)); 3.70 (*s*, MeN); 4.80 (*d*, *J* = 4.6, H–C(13c)); 7.01 (*d*, *J* = 8.6, 1 H); 7.18 (*t*, *J* = 7.2, 1 H); 7.24 (*t*, *J* = 7.2, 1 H); 7.33 (*s*, 1 H); 7.34 (*d*, *J* = 8.0, 1 H); 7.41 (*d*, *J* = 7.8, 1 H); 7.44 (*dd*, *J* = 8.5, 2.0, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 25.28 (CH_2); 30.59 (Me); 33.36 (CH); 39.35 (CH); 102.82 (C); 109.84 (CH); 117.14 (C); 117.36 (CH); 119.91 (CH); 120.38 (CH); 121.30 (CH); 128.16 (C); 129.42 (C); 130.09 (C); 132.36 (CH); 132.44 (CH); 137.69 (C); 150.05 (C); 168.40 (C). Anal. calc. for $C_{19}H_{14}BrNO_2S$ (400.29): C 57.01, H 3.53, N 3.50; found: C 56.64, H 3.35, N 3.43.

*(6a*R*,7*S*,13c*S*)-9-Ethyl-6a,7,9,13c-tetrahydro-7-phenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3m**). White solid. Yield: 170 mg (83%). M.p. 253–256°. ^{1}H-NMR ($CDCl_3$): 1.39 (*t*, *J* = 7.2, Me); 3.60 (*dd*, *J* = 8.9, 4.5, H–C(6a)); 4.08–4.14 (*m*, CH_2N); 4.70 (*d*, *J* = 8.9, H–C(7)); 4.75 (*d*, *J* = 4.2, H–C(13c)); 7.09 (*t*, *J* = 6.8, 3 H); 7.18 (*t*, *J* = 7.4, 1 H); 7.27–7.38 (*m*, 9 H). ^{13}C-NMR ($CDCl_3$): 15.35 (Me); 33.55 (CH); 39.26 (CH_2); 43.76 (CH); 47.50 (CH); 103.16 (C); 109.04 (CH); 117.28 (CH); 117.54 (CH); 120.30 (CH); 121.30 (CH); 125.26 (CH); 126.26 (C); 128.72 (C); 128.82 (CH); 129.41

(2 CH); 129.44 (CH); 129.69 (C); 129.88 (CH); 136.72 (C); 137.27 (C); 150.26 (C); 167.52 (C). Anal. calc. for $C_{26}H_{21}NO_2S$ (411.52): C 75.89, H 5.14, N 3.40; found: C 75.59, H 5.03, N 3.48.

*(6a*R*,7*S*,13c*S*)-2-Bromo-9-ethyl-6a,7,9,13c-tetrahydro-7-phenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3n**). Light yellow solid. Yield: 208 mg (85%). M.p. 267–270°. ^{1}H-NMR ($CDCl_3$): 1.45 (*t*, *J* = 7.2, Me); 3.63 (*dd*, *J* = 9.1, 4.4, H–C(6a)); 4.14–4.20 (*m*, CH_2N); 4.70 (*d*, *J* = 9.1, H–C(7)); 4.78 (*d*, *J* = 4.1, H–C(13c)); 7.02 (*d*, *J* = 8.6, 1 H); 7.18 (*t*, *J* = 7.8, 1 H); 7.24 (*t*, *J* = 7.3, 1 H); 7.38–7.42 (*m*, 8 H); 7.48 (*dd*, *J* = 8.6, 2.3, 1 H). ^{13}C-NMR ($CDCl_3$): 15.35 (Me); 33.61 (CH); 39.33 (CH_2); 43.76 (CH); 47.18 (CH); 102.22 (C); 109.16 (CH); 117.23 (CH); 118.05 (C); 119.06 (CH); 120.62 (CH); 121.51 (CH); 128.48 (C); 128.53 (C); 128.79 (CH); 129.47 (CH); 129.59 (CH); 129.90 (C); 132.49 (CH); 132.55 (CH); 136.79 (C); 137.34 (C); 149.36 (C); 166.80 (C). Anal. calc. for $C_{26}H_{20}BrNO_2S$ (490.41): C 63.68, H 4.11, N 2.86; found: C 64.05, H 4.04, N 2.91.

*(6a*R*,7*S*,13c*S*)-9-Ethyl-6a,7,9,13c-tetrahydro-4-methoxy-7-phenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3o**). Light yellow solid. Yield: 203 mg (92%). M.p. 268–270°. ^{1}H-NMR ((D_6)DMSO): 1.26 (*t*, *J* = 7.0, Me); 3.79 (*dd*, *J* = 6.8, 4.8, H–C(6a)); 3.82 (*s*, MeO); 4.08–4.18 (*m*, CH_2N); 4.61 (*d*, *J* = 4.8, H–C(13c)); 4.88 (*d*, *J* = 6.9, H–C(7)); 6.89–6.94 (*m*, 2 H); 7.06–7.14 (*m*, 3 H); 7.19 (*d*, *J* = 7.7, 1 H); 7.36–7.40 (*m*, 3 H); 7.43–7.47 (*m*, 3 H). ^{13}C-NMR ((D_6)DMSO): 15.58 (Me); 32.64 (CH); 39.12 (CH_2); 43.38 (CH); 45.86 (CH); 56.80 (Me); 103.56 (C); 109.82 (CH); 113.02 (CH); 118.05 (CH); 120.24 (CH); 121.32 (CH); 121.40 (CH); 125.37 (CH); 127.59 (C); 128.39 (C); 129.23 (2 CH); 129.56 (CH); 129.56 (C); 136.70 (C); 138.94 (C); 139.60 (C); 148.06 (C); 167.16 (C). Anal. calc. for $C_{27}H_{23}NO_3S$ (441.54): C 73.45, H 5.25, N 3.17; found: C 73.05, H 5.25, N 3.11.

*(4a*R*,5*S*,11c*S*)-7-Ethyl-4a,5,7,11c-tetrahydro-5-phenyl-4*H*-naphtho[1″,2″:5′,6′]pyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-4-one* (**3p**). Light brown solid. Yield: 161 mg (70%). M.p. 211–214°. ^{1}H-NMR ((D_6)DMSO): 1.29 (*t*, *J* = 6.9, Me); 3.91 (*dd*, *J* = 4.3, 2.0, H–C(4a)); 4.15–4.21 (*m*, CH_2N); 4.70 (*d*, *J* = 4.3, H–C(5)); 5.39 (*d*, *J* = 2.0, H–C(11c)); 5.83 (*d*, *J* = 8.1, 1 H); 6.38 (*t*, *J* = 7.6, 1 H); 6.87 (*t*, *J* = 7.6, 1 H); 7.34–7.38 (*m*, 3 H); 7.43 (*t*, *J* = 7.4, 2 H); 7.54–7.58 (*m*, 3 H); 7.63 (*t*, *J* = 7.5, 1 H); 7.97 (*d*, *J* = 8.3, 1 H); 8.02 (*d*, *J* = 8.8, 1 H); 8.07 (*d*, *J* = 8.0, 1 H). ^{13}C-NMR ((D_6)DMSO): 15.48 (Me); 27.35 (CH); 39.13 (CH_2); 43.28 (CH); 45.37 (CH); 103.18 (C); 109.67 (CH); 117.72 (CH); 118.17 (CH); 119.76 (CH); 120.06 (C); 120.88 (CH); 123.79 (CH); 126.31 (CH); 127.20 (C); 128.72 (2 CH); 128.92 (CH); 129.61 (CH); 129.89 (C); 129.96 (CH); 130.62 (CH); 131.13 (C); 132.28 (C); 136.62 (C); 141.67 (C); 149.55 (C); 168.07 (C). Anal. calc. for $C_{30}H_{23}NO_2S$ (461.57): C 78.07, H 5.02, N 3.03; found: C 78.27, H 5.06, N, 3.05.

*(6a*R*,7*R*,13c*S*)-9-Ethyl-6a,7,9,13c-tetrahydro-4-methoxy-7-methyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3q**). Yellow solid. Yield: 165 mg (87%). M.p. 173–176°. ^{1}H-NMR ((D_6)DMSO): 1.21 (*t*, *J* = 7.0, Me); 1.47 (*d*, *J* = 6.9, Me); 3.40 (*dd*, *J* = 5.7, 5.6, H–C(6a)); 3.79–3.81 (*m*, 4 H); 4.03–4.09 (*m*, CH_2N); 4.78 (*d*, *J* = 4.6, H–C(13c)); 6.88 (*t*, *J* = 7.8, 1 H); 7.01–7.09 (*m*, 3 H); 7.13–7.19 (*m*, 2 H); 7.40 (*d*, *J* = 8.1, 1 H). ^{13}C-NMR ((D_6)DMSO): 15.48 (Me); 21.34 (Me); 32.19 (CH); 34.31 (CH); 38.94 (CH_2); 45.54 (CH); 56.66 (Me); 103.07 (C); 109.62 (CH); 112.78 (CH); 118.05 (CH); 120.03 (CH); 121.03 (CH); 121.55 (CH); 125.26 (CH); 127.82 (C); 128.29 (C); 129.07(C); 136.69 (C); 139.69 (C); 148.02 (C); 167.93 (C). Anal. calc. for $C_{22}H_{21}NO_3S$ (379.47): C 69.63, H 5.58, N 3.69; found: C 69.25, H 5.55, N 3.74.

*(6a*R*,7*S*,13c*S*)-2-Bromo-9-ethyl-6a,7,9,13c-tetrahydro-7-methyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3r**). Pale-yellow solid. Yield: 200 mg (93%). M.p. 238–240°. ^{1}H-NMR ($CDCl_3$): 1.43 (*t*, *J* = 7.2, Me); 1.56 (*d*, *J* = 6.8, Me); 3.19 (*dd*, *J* = 9.6, 4.6, H–C(6a)); 3.58–3.62 (*m*, H–C(7)); 4.08–4.19 (*m*, CH_2N); 4.84 (*d*, *J* = 4.4, H–C(11c)); 7.01 (*d*, *J* = 8.6, 1 H); 7.18 (*t*, *J* = 7.4, 1 H); 7.24 (*t*, *J* = 7.5, 1 H); 7.31 (*s*, 1 H); 7.37 (*d*, *J* = 8.1, 1 H); 7.41–7.44 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 15.33 (Me); 19.52 (Me); 33.39 (CH); 33.49 (CH); 39.26 (CH_2); 47.24 (CH); 102.04 (C); 109.11 (CH); 117.00 (CH); 118.14 (C); 118.99 (CH); 120.56 (CH); 121.40 (CH); 128.58 (C); 128.66 (C); 129.64 (C); 132.26 (2 CH); 136.79 (C); 149.17 (C); 167.69 (C). Anal. calc. for $C_{21}H_{18}BrNO_2S$ (428.34): C 58.89, H 4.24, N 3.27; found: C 58.63, H 4.18, N 3.21.

*(6a*R*,13c*S*)-9-Ethyl-6a,7,9,13c-tetrahydro-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3s**). Yellow solid. Yield: 142 mg (85%). M.p. 231–233°. ^{1}H-NMR ($CDCl_3$): 1.37 (*t*, *J* = 7.2, Me); 3.16 (*dd*, *J* = 11.9, 2.0, 1 H–C(7)); 3.28 (*dd*, *J* = 12.3, 10.8, H–C(7)); 3.41–3.44 (*m*, H–C(6a)); 4.04–4.14 (*m*, CH_2N); 4.78 (*d*, *J* = 4.8, H–C(11c)); 7.06 (*t*, *J* = 7.5, 1 H); 7.10 (*t*, *J* = 8.1, 2 H); 714–7.22 (*m*, 2 H); 7.28–7.32 (*m*, 2 H); 7.39 (*d*, *J* = 7.8, 1 H). ^{13}C-NMR ((D_6)DMSO): 15.30 (Me); 24.98 (CH_2); 32.90 (CH); 39.18

(CH_2); 40.64 (CH); 103.21 (C); 108.95 (CH); 117.32 (CH); 117.36 (CH); 120.27 (CH); 121.30 (CH); 125.47 (CH); 125.89 (C); 128.38 (C); 129.02 (C); 129.14 (CH); 129.76 (CH); 136.64 (C); 150.15 (C); 169.62 (C). Anal. calc. for $C_{20}H_{17}NO_2S$ (335.42): C 71.62, H 5.11, N 4.18; found: C 71.15, H 5.04, N 4.16.

*(6a*R*,7*S*,13c*S*)-6a,7,9,13c-Tetrahydro-7,9-diphenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3t**). White solid. Yield: 211 mg (92%). M.p. 250–252°. ^{1}H-NMR ($CDCl_3$): 3.67 (*dd*, *J* = 9.4, 4.5, H–C(6a)); 4.63 (*d*, *J* = 9.4, H–C(7)); 4.87 (*d*, *J* = 4.2, H–C(11c)); 7.11–7.17 (*m*, 4 H); 7.24–7.27 (*m*, 1 H); 7.32–7.35 (*m*, 7 H); 7.42–7.57 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 33.74 (CH); 44.03 (CH); 47.46 (CH); 104.91 (C); 110.27 (CH); 117.33 (CH); 117.48 (CH); 121.23 (CH); 122.07 (CH); 125.35 (CH); 126.06 (C); 127.60 (CH); 128.76 (CH); 128.88 (CH); 128.97 (C); 129.34 (CH); 129.45 (CH); 129.49 (CH); 129.85 (CH); 129.85 (C); 130.08 (CH); 131.07 (C); 136.84 (C); 138.22 (C); 150.23 (C); 167.41 (C). Anal. calc. for $C_{30}H_{21}NO_2S$ (459.56): C 78.41, H 4.61, N 3.05; found: C 77.95, H 4.72, N 3.15.

*(6a*R*,7*S*,13c*S*)-2-Bromo-6a,7,9,13c-tetrahydro-7,9-diphenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3u**). Yellow solid. Yield: 237 mg (88%). M.p. 228–230°. ^{1}H-NMR ($CDCl_3$): 3.70 (*dd*, *J* = 9.5, 4.4, H–C(6a)); 4.63 (*d*, *J* = 9.5, H–C(7)); 4.90 (*d*, *J* = 3.6, H–C(13c)); 7.05 (*d*, *J* = 8.5, 1 H); 7.21–7.26 (*m*, 2 H); 7.31–7.38 (*m*, 6 H); 7.49–7.51 (*m*, 4 H); 7.55–7.60 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 33.80 (CH); 44.03 (CH); 47.14 (CH); 103.98 (C); 110.41 (CH); 117.15 (CH); 118.16 (C); 119.12 (CH); 121.55 (CH); 122.30 (CH); 127.62 (CH); 128.34 (C); 128.71 (C); 128.86 (2 CH); 129.41 (CH); 129.60 (CH); 130.13 (CH); 131.29 (C); 132.53 (CH); 132.61 (CH); 136.45 (C); 136.74 (C); 138.29 (C); 149.33 (C); 166.68 (C). Anal. calc. for $C_{30}H_{20}BrNO_2S$ (538.45): C 66.92, H 3.74, N 2.60; found: C 66.55, H 3.66, N 2.60.

*(6a*R*,7*S*,13c*S*)-6a,7,9,13c-Tetrahydro-4-methoxy-7,9-diphenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3v**). White solid. Yield: 201 mg (82%). M.p. 262–265°. ^{1}H-NMR ((D_6)DMSO): 3.82–3.84 (*m*, 4 H); 4.76–4.80 (*m*, 2 H); 6.93 (*d*, *J* = 6.5, 1 H); 7.02–7.17 (*m*, 5 H); 7.31–7.38 (*m*, 4 H); 7.42 (*d*, *J* = 6.8, 2 H); 7.50 (*d*, *J* = 7.6, 3 H); 7.60 (*t*, *J* = 7.6, 2 H). ^{13}C-NMR ((D_6)DMSO): 32.84 (CH); 43.69 (CH); 45.92 (CH); 56.83 (Me); 105.49 (C); 110.18 (CH); 113.07 (CH); 118.28 (CH); 121.26 (CH); 121.32 (CH); 122.32 (CH); 125.49 (CH); 127.37 (C); 127.76 (2 CH); 128.81 (C); 129.29 (2 CH); 129.52 (CH); 130.37 (C); 130.50 (C); 130.74 (CH); 136.71 (C); 137.98 (C); 139.53 (C); 148.11 (C); 166.96 (C). Anal. calc. for $C_{31}H_{23}NO_3S$ (489.58): C 76.05, H 4.73, N 2.86; found: C 75.65, H 4.62, N 2.92.

*(4a*R*,5*S*,11c*S*)-4a,5,7,11c-Tetrahydro-5,7-diphenyl-4*H*-naphtho[1″,2″:5′,6′]pyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-4-one* (**3w**). Light brown solid. Yield: 165 mg (65%). M.p. 241–244°. ^{1}H-NMR ((D_6)DMSO): 3.96 (*dd*, *J* = 4.5, 2.2, H–C(4a)); 4.76 (*d*, *J* = 4.5, H–C(5)); 4.31 (*d*, *J* = 2.2, H–C(11c)); 5.90 (*d*, *J* = 8.1, 1 H); 6.46 (*t*, *J* = 7.5, 1 H); 6.84 (*t*, *J* = 7.6, 1 H); 7.00 (*d*, *J* = 8.2, 1 H); 7.34–7.38 (*m*, 2 H); 7.43 (*t*, *J* = 7.4, 2 H); 7.54–7.56 (*m*, 6 H); 7.64–7.67 (*m*, 3 H); 8.01 (*d*, *J* = 8.4, 1 H); 8.06 (*d*, *J* = 8.9, 1 H); 8.10 (*d*, *J* = 8.0, 1 H). ^{13}C-NMR ((D_6)DMSO): 27.35 (CH); 43.55 (CH); 45.43 (CH); 104.83 (C); 110.01 (CH); 117.91 (CH); 118.21 (CH); 119.79 (C); 120.72 (CH); 121.78 (CH); 123.76 (CH); 126.38 (CH); 128.29 (CH); 128.56 (C); 128.69 (CH); 128.84 (CH); 128.98 (CH); 129.61 (2 CH); 130.02 (CH); 130.82 (2 CH); 131.07 (C); 131.30 (C); 132.32 (C); 136.69 (C); 138.09 (C); 141.59 (C); 149.67 (C); 167.41 (C). Anal. calc. for $C_{34}H_{23}NO_2S$ (509.62): C 80.13, H 4.55, N 2.75; found: C 79.07, H 4.48, N 2.71.

*(6a*R*,7*S*,13c*S*)-2-Bromo-6a,7,9,13c-tetrahydro-7-methyl-9-phenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3x**). Pale-yellow solid. Yield: 198 mg (83%). M.p. 231–234°. ^{1}H-NMR ($CDCl_3$): 1.50 (*d*, *J* = 6.8, Me); 3.24 (*dd*, *J* = 9.8, 4.5, H–C(6a)); 3.53–3.56 (*m*, H–C(7)); 4.42 (*d*, *J* = 4.1, H–C(13c)); 7.04 (*d*, *J* = 8.5, 1 H); 7.19–7.25 (*m*, 2 H); 7.29 (*d*, *J* = 8.0, 1 H); 7.40 (*s*, 1 H); 7.45–7.54 (*m*, 5 H); 7.60 (*t*, *J* = 7.6, 2 H). ^{13}C-NMR ($CDCl_3$): 19.30 (Me); 33.52 (CH); 33.61 (CH); 47.28 (CH); 103.83 (C); 110.34 (CH); 116.95 (CH); 118.21 (C); 119.07 (CH); 121.48 (CH); 122.19 (CH); 127.61 (CH); 128.42 (C); 128.78 (C); 128.84 (CH); 130.10 (CH); 130.95 (C); 132.24 (CH); 132.35 (CH); 136.83 (C); 138.31 (C); 149.19 (C); 167.61 (C). Anal. calc. for $C_{25}H_{18}BrNO_2S$ (476.38): C 63.03, H 3.81, N 2.94; found: C 62.45, H 3.71, N 2.90.

*(6a*R*,7*S*,13c*S*)-6a,7,9,13c-Tetrahydro-4-methoxy-7-methyl-9-phenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3y**). Yellow solid. Yield: 192 mg (90%). M.p. 214–216°. ^{1}H-NMR ((D_6)DMSO): 1.42 (*d*, *J* = 6.8, Me); 3.41 (*dd*, *J* = 6.1, 5.2, H–C(6a)); 3.68–3.71 (*m*, H–C(7)); 3.83 (*s*, MeO); 4.91 (*d*, *J* = 4.5, H–C(11c)); 6.98 (*t*, *J* = 7.3, 1 H); 7.03 (*t*, *J* = 7.4, 1 H); 7.07–7.11 (*m*, 3 H); 7.19 (*t*, *J* = 7.9, 1 H); 7.27 (*d*, *J* = 7.6, 1 H); 7.44 (*d*, *J* = 7.7, 2 H); 7.52 (*t*, *J* = 7.3, 1 H); 7.60 (*t*, *J* = 7.6, 2 H). ^{13}C-NMR

((D$_6$)DMSO): 21.01 (Me); 32.31 (CH); 34.41 (CH); 45.69 (CH); 56.71 (Me); 105.01 (C); 110.03 (CH); 112.88 (CH); 118.29 (CH); 121.12 (CH); 121.45 (CH); 122.06 (CH); 125.44 (CH); 127.57 (C); 127.84 (CH); 128.67 (C); 129.27 (CH); 130.35 (C); 130.71 (CH); 136.78 (C); 138.01 (C); 139.64 (C); 148.07 (C); 167.85 (C). Anal. calc. for $C_{26}H_{21}NO_3S$ (427.51): C 73.05, H 4.95, N 3.28; found: C 72.57, H 4.91, N 3.17.

*(6a*R**,13c*S**)-2-Bromo-6a,7,9,13c-tetrahydro-9-phenyl-6*H*-[1]benzopyrano[4′,3′:4,5]thiopyrano[2,3-*b*]indol-6-one* (**3z**). Yellow solid. Yield: 196 mg (85%). M.p. 231–234°. ^{1}H-NMR ($CDCl_3$): 3.14 (*d*, *J* = 11.0, 1 H–C(7)); 3.24 (*dd*, *J* = 12.3, 11.2, 1 H–C(7)); 3.47–3.50 (*m*, H–C(6a)); 4.88 (*d*, *J* = 4.4, H–C(13c)); 7.04 (*d*, *J* = 8.5, 1 H); 7.19–7.29 (*m*, 3 H); 7.44–7.56 (*m*, 6 H); 7.60 (*t*, *J* = 7.5, 2 H). ^{13}C-NMR ($CDCl_3$): 25.15 (CH_2); 32.90 (CH); 40.35 (CH); 103.99 (C); 110.29 (CH); 116.95 (CH); 118.34 (C); 119.25 (CH); 121.48 (CH); 122.28 (CH); 127.67 (CH); 127.92 (C); 128.89 (CH); 128.90 (C); 129.92 (C); 130.11 (CH); 132.38 (CH); 132.35 (CH); 136.45 (C); 136.74 (C); 149.27 (C); 168.87 (C). Anal. calc. for $C_{24}H_{16}BrNO_2S$ (462.36): C 62.35, H 3.49, N 3.03; found: C 61.92, H 3.40, N 3.07.

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