Regioselective synthesis of 7-acetyl-11c-methyl-4b,5,7,11c-tetrahydro[1]benzofuro[2',3':4,5]thiopyrano[2,3-*b*]indoles by sequential Claisen rearrangement of 2-(4'-aryloxybut-2'-ynylthio)-1-acetylindoles

K.C. Majumdar* and S. Alam

Department of Chemistry, University of Kalyani, Kalyani 741 235, W. B., India

Hitherto unreported indole-annulated pentacyclic heterocycles containing oxygen, nitrogen and sulfur have been synthesised by thermal Claisen rearrangement followed by Lewis acid catalysed Claisen rearrangement. 9-Acetyl-4-aryloxymethyl-2,9-dihydrothiopyrano[2,3-*b*]indoles are regioselectively synthesised in 80–85 % yield by thermal rearrangement of 2-(4'-aryloxybut-2'-ynylthio)-1-acetylindoles. A second, Lewis acid catalysed, rearrangement gave 7-acetyl-11c-methyl-4b,5,7,11c-tetrahydro[1]benzofuro[2',3': 4,5]thiopyrano[2,3-*b*]indoles in yields of 85–90 %. The thermal Claisen rearrangement in refluxing *N,N*-diethylaniline for 3 h gave the same products in lower yield (50–54 %).

Keywords: Claisen rearrangement, fused indoles, fused thiophenes, indoline-2-thione

Indole subunits are frequently present in biologically active compounds.[1] Nitrogen containing heterocycles recognised as pharmacophores have received great attention in drug discovery and lead optimisation. The 2,3-substituted indole moiety present in the β-carboline skeleton shows important bioactivity.[1g] Some indole derivatives have been found to possess high antitumor activity;[2] some cause inflammation and vesication to human skin.[3] Pyrido[4,3-*b*]indole derivatives are biologically important molecules[1j] and the thiopyranoindole moiety are closely analogous. Indoline-2-thiones are important starting material in the synthesis of thiopyranoindole heterocyclic compounds and have found some use in the synthesis of biologically active compounds.[4] Reserpine, yohimbine, rauniticine[1k] and aspidospermine[1a] are [6,6]-fused pentacyclic indole alkaloids having extensive bioactivity. This familiar bioactivity of various indole derivatives has drawn our interest to this area, and we planned to synthesise the [6,5]-fused pentacyclic indole derivative in which the bioactive thiopyranoindole moiety is fused with a benzofuran moiety.

Strategies involving Claisen rearrangements have become important tools in the synthesis of various heterocyclic compounds. Since 1912 several classes of organic compound have been synthesised by the Claisen rearrangement and many of them are biologically active.[5] Claisen rearrangements can be performed thermally as well as catalytically in presence of various types of catalyst.[5,6] Earlier studies in the synthesis of different oxygen, sulfur and nitrogen heterocycles by the application of sequential [3,3] sigmatropic rearrangement of suitably tailored 1,4-disubstituted but-2-ynes have led to the synthesis of new heterocyclic compounds derived from 5-hydroxyuracil and 3-hydroxycoumarin.[7] Both the first and second Claisen rearrangements were achieved thermally. These results encouraged us to undertake a study on the sequential [3,3] sigmatropic rearrangement of 1-acetyl-2-(4'-aryloxybut-2′-ynylthio)indole. Here we report the results of our study.

Results and discussion

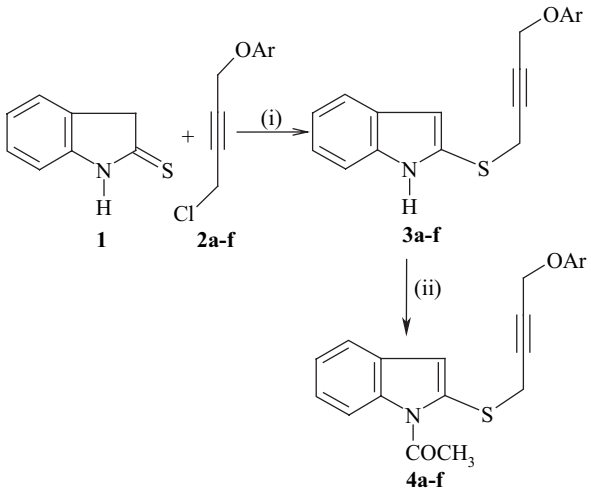
The required precursors for our present study, 1-acetyl-2-(4′-aryloxybut-2'-ynylthio)indoles (**4a–f**) were synthesised in 85–90 % yields by the reaction of indoline-2-thione (**1**) with 1-aryloxy-4-chlorobut-2-yne (**2a–f**) and acetyl chloride by two successive phase transfer catalysed reactions. Compounds **3a–f** were prepared in excellent yield (95–98 %) by the phase transfer catalysed alkylation of **1** by **2a–f** using benzyltriethylammonium chloride (BTEAC) as phase-transfer catalyst in 1 % aqueous NaOH–CH_2Cl_2 for 15 minutes at room temperature.

In order to obtain the appropriate substrates for the second Claisen rearrangement it was necessary to introduce an electron-withdrawing group at the nitrogen atom of the indole moiety of **3a–f**.[4a] Therefore we acetylated them, using acetyl chloride at 0 °C and tetrabutylammonium hydrogen sulfate as phase-transfer catalyst in dry CH_2Cl_2 in the presence of NaOH (powder) for 1 h, to give compounds **4a–f** (Scheme 1). Compounds **3a–f** and **4a–f** were characterised by their spectral data and elemental analyses.

Compounds **4a–f** contain the (but-2-ynylthio)indole moiety as well as the aryl prop-2-ynylether moiety, and thus offer scope for two different [3,3]-sigmatropic rearrangements.

Table 1 Substituents, and yields of compounds **3a–f**, **4a–f**, **5a–f** and **9a–f**

Ar	Yield/ %			
	3	**4**	**5**	**9**
a 4-MeC_6H_4	98	90	84	90
b 2-MeC_6H_4	96	85	83	88
c C_6H_5	96	88	80	89
d 4-$MeOC_6H_4$	98	90	85	90
e 2,4-$Me_2C_6H_3$	97	86	83	85
f 2,3-$Me_2C_6H_3$	95	85	82	86



Scheme 1 Reagents and conditions: (i) 1 % aq. NaOH soln., CH_2Cl_2, BTEAC, stirring, 15 min, rt. (ii) CH_3COCl, Dry CH_2Cl_2, $^nBu_4NHSO_4$, NaOH (powder), stirring 1 h, 0 °C.

* Correspondent. E-mail: kcm_ku@yahoo.co.in

However, the thio-Claisen rearrangement in the (but-2-ynylthio)indole moiety may be expected to require a lower activation energy than the corresponding rearrangement of the (alk-2-ynyloxy)arene moiety as the aromatic sextet would be disturbed in the transition state of the latter.

The substrate **4a** was refluxed in chlorobenzene (132 °C) and the reaction was monitored. Complete conversion was achieved in 1 h, giving a greenish yellow solid in 84 % yield. The product **5a** was characterised from its elemental analysis and spectroscopic data as 9-acetyl-4-(4'-methylphenyloxymethyl)-2,9-dihydrothiopyrano[2,3-*b*]indole. Compounds **4b–f** on similar treatment furnished the products **5b–f** in 80–85 % yield (Scheme 2).

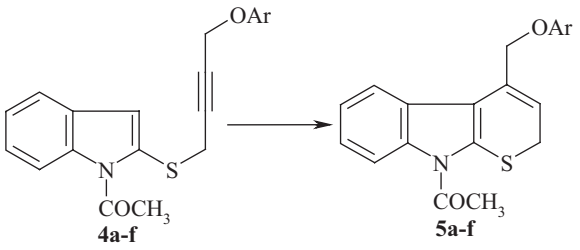
The formation of products **5a–f** from the substrates **4a–f** may be explained by an initial [3,3] sigmatropic rearrangement in substrates **4a–f** followed by rapid enolisation to give the allenylene–thiol intermediate (**7**) followed by [1,5] hydrogen shift and 6π-electrocyclic ring closure (ECR) to give finally the products **5a–f** (Scheme 3).

The product **5a** is an allyl–aryl ether and therefore a suitable substrate for the occurrence of a second Claisen rearrangement. However, this would require higher temperature than the first [3,3] sigmatropic rearrangement of compound **4a** as during this rearrangement the aromaticity of the aryl part will be disturbed.

At higher temperature in refluxing *N*,*N*-diethylaniline (216 °C) for 3 h compound **5a** underwent [3,3] sigmatropic rearrangement[7] and the product **9a** was obtained as a white solid in moderate yield (0.072 g, 52 %). The product was characterised as 7-acetyl-11c-methyl-4b,5,7,11c-tetrahydro [1]benzofuro[2',3':4,5]thiopyrano[2,3-*b*]indole from its elemental analysis and spectral data. To improve the yield the reaction was carried out in the presence of Lewis acid catalyst anhydrous $AlCl_3$[6a] in dry dichloromethane solution at room temperature and the same product **9a** was obtained in excellent yield (90 %) (Scheme 4). Encouraged by this initial success, substrates **5b–f** were similarly treated and the corresponding products **9b–f** were obtained in 85–90 % yield. Thermal rearrangement of **5b,c** afforded the same compounds **9b** and **9c** in 50 % and 54 % yield respectively. The stereochemistry of the furothiopyrano ring juncture of **9** can only be surmised from the molecular model (Dreiding model) of the molecule, which show a strain free *cis* arrangement (Scheme 4). The formation of the products **9a–f** may be mechanistically explained by an initial [3,3]-sigmatropic rearrangement in **5a–f** to give dienone intermediates **10**, which then enolise to give **11**. Intermediate **11** may undergo 5-*exo* cyclisation to give the final products **9**. In the case of the catalysed Claisen rearrangement the reaction is rationalised by the steps involving an initial charge-accelerated [3,3] sigmatropic rearrangement of **5** to **14** *via* ether oxygen–$AlCl_3$ complex **13** followed by rapid tautomerisation and proton exchange to give intermediate **11** which may then undergo 5-*exo* cyclisation leading to products **9a–f** (Scheme 5).

Previously [6,6] fused products were obtained, where intermediates similar to **11** were isolated. These were then reacted with pyridinium hydrotribromide[7b] ($PyHBr_3$) to give cyclised products. However, we could not isolate intermediate **11**. Only [6,5] fused products **9a–f** were obtained under thermal and catalysed conditions.

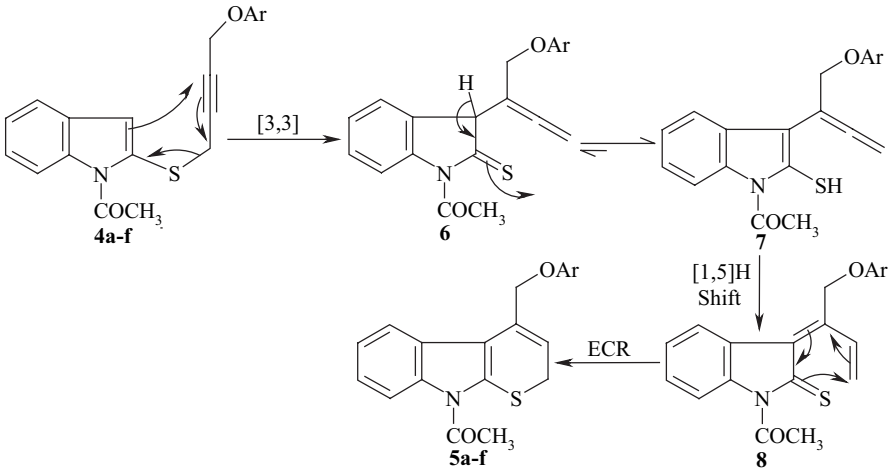
In conclusion, we have successfully performed the sequential Claisen rearrangement, a thio-Claisen rearrangement of the propynyl vinyl sulfide followed by an oxy-Claisen rearrangement of allyl aryl ether moiety in substrates **4a–f**. This methodology displays appreciable regioselectivity and it is a novel approach for the construction of the furothiopyrano ring system. It represents a protocol for the synthesis of pentacyclic heterocyclic compounds, *e.g.* 7-acetyl-11c-methyl-4b,5,7,11c-tetrahydro[1]benzofuro[2',3':4,5]thiopyrano[2,3-*b*] indole from 2-(4'-aryloxybut-2′-ynylthio)-1-acetylindole.



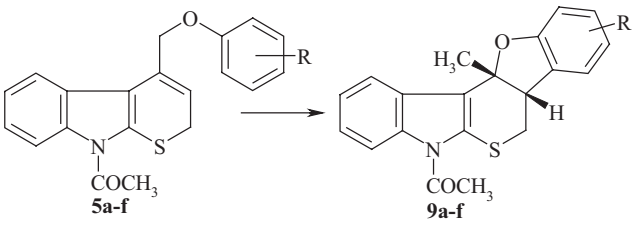
Scheme 2 Reagents and conditions: chlorobenzene, reflux, 1 h.

Experimental

Melting points were determined in open capillaries. IR spectra were recorded on a Perkin-Elmer L 120-000A spectrometre (ν_{max} in cm^{-1}) on KBr discs. UV absorption spectra were recorded in EtOH on a Shimadzu UV-2401PC spectrophotometre (λ_{max} in nm). ^1H NMR (300 MHz, 400 MHz, 500 MHz) and ^{13}C NMR (125.7 MHz) spectra were recorded on a Bruker DPX-300, Varian-400 and Bruker DPX-500 spectrometres in $CDCl_3$ (chemical shift in δ) with TMS as internal standard. Mass spectra were recorded on a JEOL JMS600 instrument and elemental analyses were recorded on a Leco CHNS-932 analyser. Silica gel [(230–400 mesh), Spectrochem, India] was used for chromatographic separation. Silica gel G [E-Merck (India)] was used for TLC. Petroleum ether refers to the fraction boiling



Scheme 3



Scheme 4 Reagents and conditions: anhyd. $AlCl_3$ (1 equiv.), dry CH_2Cl_2, stirring, 30 min, rt.

60–80 °C. The 1-aryloxy-4-chlorobut-2-ynes were prepared according to the published procedure.[8]

2-(4′-Aryloxybut-2′-ynylthio)indoles (**3a–f**): To a mixture of indoline-2-thione (**1**) (0.45 g, 3 mmol) and 1-(4′-methyl)aryloxy-4-chlorobut-2-yne (**2a**) (0.58 g, 3 mmol) in dichloromethane (20 ml) was added a solution of benzyltriethylammonium chloride (BTEAC, 0.5 g, 1.8 mmol) in 1 % aqueous NaOH (20 ml) and the mixture was stirred at room temperature for 15 minutes. The reaction mixture was then washed with water (2 × 20 ml), brine (20 ml) and dried over Na_2SO_4. The compound was purified by column chromatography; elution with petroleum ether-ethyl acetate (9:1) on silica gel (230–400 mesh) afforded **3a**. Similarly the compounds **3b–f** were prepared.

4′-p-Tolyl compound (**3a**): White solid (0.90 g, 98 %), m.p. 96–98 °C. IR (KBr): ν_{max} 3393 (N-H), 2918 (ν_{CH}), 2226 ($\nu_{C\equiv C}$), 1441 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 219 (log ε 3.97), 284 (log ε 4.18) nm. ^1H NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 3H, $ArCH_3$), 3.49 (s, 2H, SCH_2), 4.67 (s, 2H, OCH_2), 6.68 (s, 1H, =CH), 6.87–7.55 (m, 8H, ArH), 8.18 (br s, 1H, NH). MS: *m/z* 308 (M^+ + 1, 6 %), 307 (M^+, 16), 266 (30), 250 (40), 199 (54), 149 (22), 148 (27), 129 (100). Anal. Calcd for $C_{19}H_{17}NOS$: C, 74.23; H, 5.57; N, 4.56 %. Found C, 74.43; H, 5.74; N, 4.45 %.

4′-o-Tolyl compound (**3b**): White solid (0.88 g, 96 %), m.p. 92–94 °C. IR (KBr): ν_{max} 3396 (ν_{NH}), 2921 (ν_{CH}), 2227 ($\nu_{C\equiv C}$), 1472 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 220 (log ε 3.95), 278 (log ε 4.12), 290 (log ε 4.10) nm. ^1H NMR (400 MHz, $CDCl_3$): δ 2.24 (s, 3H, $ArCH_3$), 3.50 (s, 2H, SCH_2), 4.73 (s, 2H, OCH_2), 6.69 (s, 1H, =CH), 6.91–7.55 (m, 8H, ArH), 8.08 (br s, 1H, NH). MS: *m/z* 308 (M^+ + 1, 5 %), 307 (M^+, 15), 266 (31), 248 (19), 205 (26), 199 (53), 185 (18), 149 (23), 148 (27), 129 (100). Anal. Calcd for $C_{19}H_{17}NOS$: C, 74.23; H, 5.57; N, 4.56. Found C, 74.41; H, 5.66; N, 4.68 %.

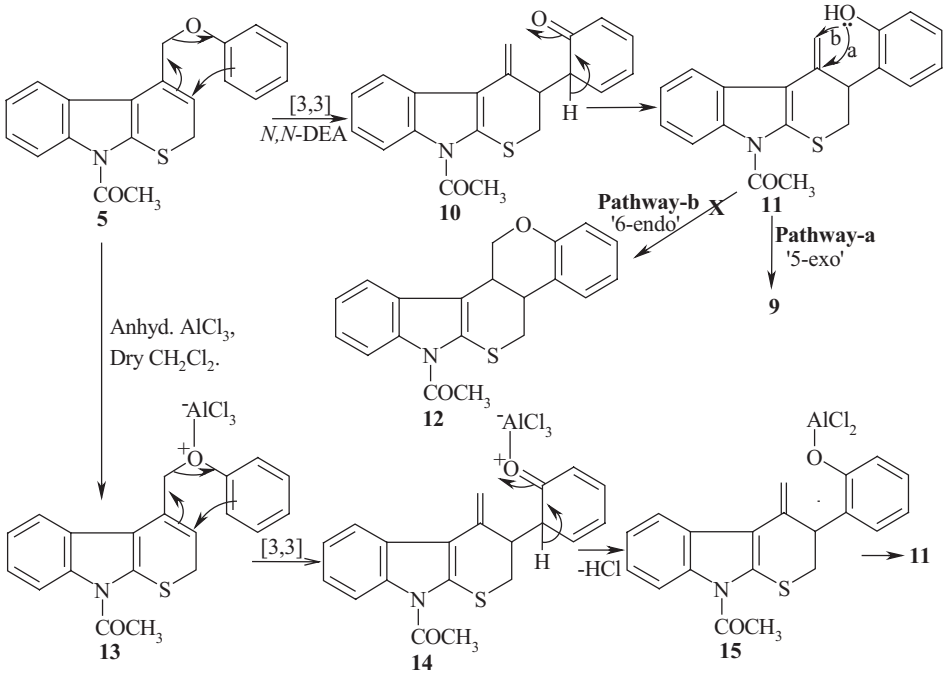
4′-Phenyl compound (**3c**): White solid (0.84 g, 96 %), m.p. 88–90 °C. IR (KBr): ν_{max} 3405 (N-H), 2911 (ν_{CH}), 2226 ($\nu_{C\equiv C}$), 1508 cm^{-1} (δ_{CH}). UV (EtOH): λ_{max} 225 (log ε 3.93), 277 (log ε 4.12), 290 (log ε 4.11) nm. ^1H NMR (300 MHz, $CDCl_3$): δ 3.50 (s, 2H, SCH_2), 4.70 (s, 2H, OCH_2), 6.68 (s, 1H, =CH), 6.79–7.55 (m, 9H, ArH), 8.14 (br s, 1H, NH). MS: *m/z* 294 (M^+ + 1, 5 %), 293 (M^+, 6), 260 (13), 255 (15), 199 (24), 198 (100), 166 (16), 147 (20), 148 (46), 129 (4). Anal. Calcd for $C_{18}H_{15}NOS$: C, 73.69; H, 5.15; N, 4.77. Found C, 73.55; H, 5.27; N, 4.93 %.

4′-p-Methoxyphenyl compound (**3d**): White solid (0.95 g, 98 %), m.p. 100–102 °C. IR (KBr): ν_{max} 3392 (ν_{NH}), 2955 (ν_{CH}), 2227 ($\nu_{C\equiv C}$), 1470 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 221 (log ε 3.91), 290 (log ε 4.07) nm. ^1H NMR (300 MHz, $CDCl_3$): δ 3.51 (s, 2H, SCH_2), 3.75 (s, 3H, OCH_3), 4.66 (s, 2H, OCH_2), 6.70 (s, 1H, =CH), 6.76–7.56 (m, 8H, ArH), 8.21 (br s, 1H, NH). MS: *m/z* 324 (M^+ + 1, 7 %), 323 (M^+, 8), 255 (48), 199 (39), 198 (100), 147 (11), 148 (37), 129 (4). Anal. Calcd for $C_{19}H_{17}NO_2S$: C, 70.56; H, 5.30; N, 4.33. Found C, 70.72; H, 5.45; N, 4.47 %.

4′-(2,4-Dimethylphenyl) compound (**3e**): Viscous liquid (0.93 g, 97 %). IR (neat): ν_{max} 3398 (ν_{NH}), 2922 (ν_{CH}), 2226 ($\nu_{C\equiv C}$), 1448 cm^{-1} (δ_{CH}). UV (EtOH): λ_{max} 218 (log ε 3.96), 291 (log ε 4.14) nm. ^1H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 3H, $ArCH_3$), 2.26 (s, 3H, $ArCH_3$), 3.49 (s, 2H, SCH_2), 4.70 (s, 2H, OCH_2), 6.68 (s, 1H, =CH), 6.85–7.55 (m, 7H, ArH), 8.10 (br s, 1H, NH). MS: *m/z* 322 (M^+ + 1, 22 %), 321 (M^+, 18), 246 (37), 242 (58), 200 (100), 199 (41), 186 (44), 148 (4). Anal. Calcd for $C_{20}H_{19}NOS$: C, 74.73; H, 5.96; N, 4.36. Found C, 74.90; H, 5.77; N, 4.48 %.

4′-(3,4-Dimethylphenyl) compound (**3f**): Viscous liquid (0.91 g, 95 %). IR (neat): ν_{max} 3396 (ν_{NH}), 2920 (ν_{CH}), 2227 ($\nu_{C\equiv C}$), 1450 cm^{-1} (δ_{CH}). UV (EtOH): λ_{max} 220 (log ε 3.93), 279 (log ε 4.12), 290 (log ε 4.06) nm. ^1H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 3H, $ArCH_3$), 2.27 (s, 3H, $ArCH_3$), 3.50 (s, 2H, SCH_2), 4.71 (s, 2H, OCH_2), 6.68 (s, 1H, =CH), 6.82–7.54 (m, 7H, ArH), 8.10 (br s, 1H, NH). MS: *m/z* 322 (M^+ + 1, 14 %), 321 (M^+, 15), 320 (17), 264 (8), 246 (100), 214 (25), 199 (29), 186 (64), 148 (5), 129 (7). Anal. Calcd for $C_{20}H_{19}NOS$: C, 74.73; H, 5.96; N, 4.36. Found C, 74.58; H, 6.12; N, 4.45 %.

2-(4′-Aryloxybut-2′-ynylthio)-1-acetylindoles (**4a–f**): *n*-Bu_4NHSO_4 (10 mg, 0.01 eq.) and NaOH (0.20 g, powder) were added to a dichloromethane solution of **3a** (0.77 g, 2.5 mmol) at ice-bath temperature. Acetyl chloride (0.30 g, 1.5 eq.) in dry dichloromethane (10 ml) was added dropwise. The mixture was stirred for 1 h at the same temperature and then filtered. The filtrate was washed with saturated $NaHCO_3$ solution (2 × 25 ml), water (25 ml), brine (25 ml) and dried (Na_2SO_4) and then evaporated. The residue was subjected to column chromatography. Elution of the column with petroleum ether–ethyl acetate (10:1) on silica gel (60–120 mesh) afforded compound **4a**. Compounds **4b–f** were also obtained by the same procedure.



Scheme 5

Compound **4a**: White solid (0.79 g, 90 %), m.p. 98–100 °C. IR (KBr): ν_{max} 2921 (ν_{CH}), 2226 ($\nu_{C\equiv C}$), 1697 ($\nu_{C=O}$), 1453, 1375 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 245 (log ε 4.16), 252 (log ε 4.11), 261 (log ε 4.09), 285 (log ε 4.06), 293 (log ε 4.03) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H, $ArCH_3$), 2.83 (s, 3H, $COCH_3$), 3.65–3.66 (t, 2H, *J* = 2 Hz, SCH_2), 4.63–4.64 (t, 2H, *J* = 2 Hz, OCH_2), 6.58 (s, 1H, =CH), 6.79–7.80 (m, 8H, ArH). MS: *m/z* 372 (100 %), 350 (M^+ + 1, 39), 349 (M^+, 32), 308 (18), 191 (9), 190 (20), 159 (8). Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found C, 72.34; H, 5.39; N, 4.16 %.

Compound **4b**: White solid (0.74 g, 85 %), m.p. 96–98 °C. IR (KBr): ν_{max} 2918 (ν_{CH}), 2225 ($\nu_{C\equiv C}$), 1694 ($\nu_{C=O}$), 1453, 1375 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 245 (log ε 4.11), 252 (log ε 4.10), 261 (log ε 4.08), 294 (log ε 4.04) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 3H, $ArCH_3$), 2.83 (s, 3H, $COCH_3$), 3.65–3.66 (t, 2H, *J* = 2 Hz, SCH_2), 4.64–4.65 (t, 2H, *J* = 2 Hz, OCH_2), 6.59 (s, 1H, =CH), 6.84–7.80 (m, 8H, ArH). MS: *m/z* 372 (100 %), 350 (M^+ + 1, 38), 349 (M^+, 30), 308 (17), 191(10), 190 (21), 159 (9). Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found C, 72.37; H, 5.59; N, 3.95 %.

Compound **4c**: White solid (0.74 g, 88 %), m.p. 92–94 °C. IR (KBr): ν_{max} 2932 (ν_{CH}), 2225 ($\nu_{C\equiv C}$), 1692 ($\nu_{C=O}$), 1453, 1379 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 238 (log ε 4.11), 252 (log ε 4.08), 261 (log ε 4.05), 277 (log ε 4.01), 284 (log ε 4.00) nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.83 (s, 3H, $COCH_3$), 3.66–3.67 (t, 2H, *J* = 2 Hz, SCH_2), 4.67–4.68 (t, 2H, *J* = 2 Hz, OCH_2), 6.59 (s, 1H, =CH), 6.90–7.81 (m, 9H, ArH). MS: *m/z* 336 (M^+ + 1, 13 %), 335 (M^+, 14), 307 (16), 207 (44), 201 (27), 200 (100), 191 (12), 190 (16), 159 (47). Anal. Calcd for $C_{20}H_{17}NO_2S$: C, 71.62; H, 5.11; N, 4.18. Found C, 71.49; H, 5.12; N, 4.28 %.

Compound **4d**: White solid (0.82 g, 90 %), m.p. 88–90 °C. IR (KBr): ν_{max} 2930 (ν_{CH}), 2226 ($\nu_{C\equiv C}$), 1694 ($\nu_{C=O}$), 1431, 1376 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 244 (log ε 4.10), 252 (log ε 4.08), 261 (log ε 4.05), 294 (log ε 4.01) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.83 (s, 3H, $COCH_3$), 3.65 (s, 2H, -SCH_2), 3.72 (s, 3H, OCH_3), 4.61 (s, 2H, OCH_2), 6.58 (s, 1H, =CH), 6.72–7.85 (m, 8H, ArH). MS: *m/z* 366 (M^+ + 1, 17 %), 365 (M^+, 22), 322 (20), 202 (25), 200 (100), 199 (40), 191 (6), 159 (8). Anal. Calcd for $C_{21}H_{19}NO_3S$: C, 69.02; H, 5.24; N, 3.83. Found C, 70.07; H, 5.36; N, 3.66 %.

Compound **4e**: White solid (0.78 g, 86 %), m.p. 94–96 °C. IR (KBr): ν_{max} 2927 (ν_{CH}), 2225 ($\nu_{C\equiv C}$), 1689 ($\nu_{C=O}$), 1454, 1378 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 246 (log ε 4.10), 253 (log ε 4.06), 261 (log ε 4.03), 285 (log ε 4.02), 294 (log ε 4.01) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.16 (s, 3H, $ArCH_3$), 2.23 (s, 3H, $ArCH_3$), 2.83 (s, 3H, $COCH_3$), 3.65–3.66 (t, 2H, *J* = 2 Hz, SCH_2), 4.65–4.66 (t, 2H, *J* = 2 Hz, OCH_2), 6.59 (s, 1H, =CH), 6.73–7.81 (m, 7H, ArH). MS: *m/z* 386 (85 %), 364 (M^+ + 1, 83), 363 (M^+, 23), 322 (52), 205 (23), 200 (83), 199 (100), 191 (27), 190 (22), 177 (77). Anal. Calcd for $C_{22}H_{21}NO_2S$: C, 72.70; H, 5.82; N, 3.85. Found C, 72.58; H, 5.76; N, 3.80 %.

Compound **4f:** White solid (0.77 g, 85 %), m.p. 84–86 °C. IR (KBr): ν_{max} 2920 (ν_{CH}), 2225 ($\nu_{C\equiv C}$), 1694 ($\nu_{C=O}$), 1453, 1375 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 245 (log ε 4.09), 252 (log ε 4.08), 261 (log ε 4.05), 295 (log ε 4.04) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.11 (s, 3H, $ArCH_3$), 2.24 (s, 3H, $ArCH_3$), 2.83 (s, 3H, $COCH_3$), 3.65–3.66 (t, 2H, *J* = 2 Hz, SCH_2), 4.66–4.67 (t, 2H, *J* = 2 Hz, OCH_2), 6.59 (s, 1H, =CH), 6.73–7.81 (m, 7H, ArH). MS: *m/z* 386 (89), 364 (M^+ + 1, 100), 363 (M^+, 27), 322 (36), 200 (18), 191 (20), 173 (41). Anal. Calcd for $C_{22}H_{21}NO_2S$: C, 72.70; H, 5.82; N, 3.85. Found C, 72.88; H, 5.97; N, 3.93 %.

9-Acetyl-4-aryloxymethyl-2,9-dihydrothiopyrano[2,3-b]indoles (**5a–f**): Compound **4a** (0.52 g, 1.5 mmol) was refluxed in chlorobenzene (15 ml) for 1 h. Then the reaction mixture was subjected to column chromatography over silica gel (60–120 mesh). Elution of the column with petroleum ether followed by petroleum ether – ethyl acetate (9:1) gave compound **5a** as a greenish yellow solid. Compounds **5b–f** were similarly synthesised. These compounds were recrystalised from ethyl acetate-petroleum ether.

Compound **5a**: greenish-yellow crystalline solid (0.44 g, 84 %), m.p. 128–130 °C. IR (KBr): ν_{max} 2901 (ν_{CH}), 1685 ($\nu_{C=O}$), 1431, 1373 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 224 (log ε 4.33), 272 (log ε 4.21), 343 (log ε 3.66) nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.30 (s, 3H, $ArCH_3$), 2.83 (s, 3H, $COCH_3$), 3.44–3.45 (d, 2H, *J* = 5.6 Hz, SCH_2), 4.92 (s, 2H, OCH_2), 5.77–5.80 (t, 1H, *J* = 5.6 Hz, =CH), 6.85–7.86 (m, 8H, ArH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 20.9, 27.2, 28.5, 69.5, 114.0, 114.4, 115.3, 117.4, 120.0, 123.7, 124.2, 128.6, 130.4, 130.9, 132.9, 134.5, 135.8, 156.6, 169.2. MS: *m/z* 350 (M^+ + 1, 18 %), 349 (M^+, 16), 309 (100), 308 (70), 292 (38), 231 (46), 230 (38), 214 (20), 200 (10), 138 (32), 129 (49). Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found C, 72.35; H, 5.52; N, 4.12 %.

Compound **5b**: Greenish-yellow crystalline solid (0.43 g, 83 %), m.p. 116–118 °C. IR (KBr): ν_{max} 2926 (ν_{CH}), 1698 ($\nu_{C=O}$), 1440, 1370 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 226 (log ε 4.31), 271 (log ε 4.20), 332 (log ε 3.72) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.11 (s, 3H, $ArCH_3$), 2.84 (s, 3H, $COCH_3$), 3.45–3.46 (d, 2H, *J* = 5.6 Hz, SCH_2), 4.97 (s, 2H, OCH_2), 5.78–5.81 (t, 1H, *J* = 5.6 Hz, =CH), 6.87–7.86 (m, 8H, ArH). MS: *m/z* 350 (M^+ + 1, 34 %), 349 (M^+, 30), 293 (9), 216 (31), 214 (89), 200 (20), 186 (22), 179 (39), 152 (56), 137 (100). Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found C, 72.04; H, 5.61; N, 3.92 %.

Compound **5c**: Green crystalline solid (0.40 g, 80 %), m.p. 122–124 °C. IR (KBr): ν_{max} 2898 (ν_{CH}), 1683 ($\nu_{C=O}$), 1431, 1373 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 222 (log ε 4.34), 270 (log ε 4.33), 346 (log ε 3.72) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.83 (s, 3H, $COCH_3$), 3.44–3.45 (d, 2H, *J* = 5.6 Hz, SCH_2), 4.94 (s, 2H, OCH_2), 5.78–5.80 (t, 1H, *J* = 5.6 Hz, =CH), 6.95–7.85 (m, 9H, ArH). MS: *m/z* 336 (M^+ + 1, 80 %), 335 (M^+, 100), 320 (26), 308 (21), 307 (90), 292 (33), 274 (51), 230 (8), 214 (7), 200 (29). Anal. Calcd for $C_{20}H_{17}NO_2S$: C, 71.62; H, 5.11; N, 4.18. Found C, 71.71; H, 5.21; N, 3.99 %.

Compound **5d**: Greenish-yellow crystalline solid (0.47 g, 85 %), m.p. 118–120 °C. IR (KBr): ν_{max} 2926 (ν_{CH}), 1683 ($\nu_{C=O}$), 1431, 1373 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 226 (log ε 4.25), 273 (log ε 4.12), 344 (log ε 3.57) nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.83 (s, 3H, $COCH_3$), 3.43–3.44 (d, 2H, *J* = 5.6 Hz, SCH_2), 3.77 (s, 3H, OCH_3), 4.89 (s, 2H, OCH_2), 5.75–5.77 (t, 1H, *J* = 5.6 Hz, =CH), 6.83–7.86 (m, 8H, ArH). MS: *m/z* 388 (56 %), 366 (M^+ + 1, 18), 365 (M^+, 23), 364 (30), 322 (22), 246 (37). 242 (58), 200 (100), 186 (44). Anal. Calcd for $C_{21}H_{19}NO_3S$: C, 69.02; H, 5.24; N, 3.83. Found C, 68.90; H, 5.08; N, 3.96 %.

Compound **5e**: White solid (0.45 g, 83 %), m.p. 124–126 °C. IR (KBr): ν_{max} 2921 (ν_{CH}), 1698 ($\nu_{C=O}$), 1450, 1370 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 222 (log ε 4.31), 271 (log ε 4.28), 333 (log ε 3.68) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.11 (s, 3H, $ArCH_3$), 2.25 (s, 3H, $ArCH_3$), 2.83 (s, 3H, $COCH_3$), 3.43–3.44 (d, 2H, *J* = 5.6 Hz, SCH_2), 4.96 (s, 2H, OCH_2), 5.76 –5.79 (t, 1H, *J* = 5.6 Hz, =CH), 6.77–7.85 (m, 7H, ArH). MS: *m/z* 386 (10 %), 380 (70), 364 (M^+ + 1, 11), 363 (M^+, 10), 362 (16), 322 (13), 246 (82), 242 (33), 216 (30), 200 (46), 186 (100). Anal. Calcd for $C_{22}H_{21}NO_2S$: C, 72.70; H, 5.82; N, 3.85. Found C, 72.88; H, 5.92; N, 3.91 %.

Compound **5f**: White solid (0.44 g, 82 %), m.p. 132–134 °C. IR (KBr): ν_{max} 2920 (ν_{CH}), 1698 ($\nu_{C=O}$), 1450, 1370 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 222 (log ε 4.29), 269 (log ε 4.27), 328 (log ε 3.73) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3H, $ArCH_3$), 2.26 (s, 3H, $ArCH_3$), 2.84 (s, 3H, $COCH_3$), 3.45–3.46 (d, 2H, *J* = 5.5 Hz, SCH_2), 4.95 (s, 2H, OCH_2), 5.78–5.81 (t, 1H, *J* = 5.5 Hz, =CH), 6.78– 7.86 (m, 7H, ArH). MS: *m/z* 386 (9 %), 380 (71), 364 (M^+ + 1, 11 %), 363 (M^+, 12), 362 (17), 320 (40), 246 (84), 242 (33), 214 (44), 200 (48), 186 (100), 174 (44). Anal. Calcd for $C_{22}H_{21}NO_2S$: C, 72.70; H, 5.82; N, 3.85. Found C, 72.58; H, 5.89; N, 3.71 %.

5-Acetyl-12a-methyl-5,7,7a,12a-tetrahydro[1]benzofuro[2',3':4,5]thiopyrano[2,3-b]indoles (**9a–f**): Anhydrous $AlCl_3$ (0.05 g, 1 eq.) was added to **5a** (0.14 g, 0.4 mmol) in dry dichloromethane (10 ml) and stirred at room temperature for 30 minutes. Then crushed ice was added to the reaction mixture. Dichloromethane layer was washed with water (2 × 10 ml), brine (10 ml) and dried (Na_2SO_4). The solvent was distilled off and the residue was subjected to column chromatography. Elution of the column with petroleum ether-ethyl acetate (8:1) on silica gel (60–120 mesh) afforded compound **9a** as white solid. It was recrystalised from ethyl acetate-petroleum ether. Compounds **9b–f** were similarly synthesised and recrystalised following the same procedure. For thermal rearrangement compounds **5a–c** (0.14 g, 0.4 mmol) was refluxed in *N,N*-diethylaniline (5 ml) for 3 h. The reaction mixture was then cooled, poured into ice cold 6N HCl (20 ml) and extracted with chloroform (20 ml). The chloroform layer was washed with water and dried over Na_2SO_4. After removal of the chloroform the products **9a–c** were purified similarly.

Compound **9a**: White solid (0.13 g, 90 %), m.p. 164–166 °C. IR (KBr): ν_{max} 2926 (ν_{CH}), 1700 ($\nu_{C=O}$), 1435, 1369 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 231 (log ε 4.11), 255 (log ε 4.01), 264 (log ε 3.97), 292 (log ε 4.05) nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.72 (s, 3H, 12a-CH_3), 2.31 (s, 3H, $ArCH_3$), 2.66–2.71 (t, 1H, *J* = 12.5 Hz, SCH_2), 2.80 (s, 3H, $COCH_3$), 2.95–2.98 (dd, 1H, *J* = 3.8, 12.5 Hz, SCH_2), 3.42–3.46 (dd, 1H, *J* = 3.8, 12.5 Hz, 7a-H), 6.75–7.93 (m, 7H, ArH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 15.5, 27.0, 27.1, 33.6, 52.0, 84.5, 114.4, 118.9, 120.8, 121.0, 121.1, 122.6, 123.9, 124.0, 128.0, 130.0, 130.6, 132.4, 136.0, 156.4, 169.9. MS: *m/z* 350 (M^+ + 1, 24 %), 349

(M^+, 100), 334 (12), 307 (31), 292 (77), 274 (36), 200 (13), 168 (13). Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found C, 72.37; H, 5.53; N, 3.90 %.

Compound **9b**: White solid (0.12 g, 88 %), m.p. 174–176 °C. IR (KBr): ν_{max} 2928 (ν_{CH}), 1701 ($\nu_{C=O}$), 1454, 1367 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 230 (log ε 4.12), 255 (log ε 4.03), 263 (log ε 3.95), 287 (log ε 4.06) nm. ^1H NMR (500 MHz, $CDCl_3$): δ 1.73 (s, 3H, 12a-CH_3), 2.25 (s, 3H, $ArCH_3$), 2.67–2.72 (t, 1H, J = 12.5 Hz, SCH_2), 2.80 (s, 3H, $COCH_3$), 2.97–3.01 (dd, 1H, J = 3.9, 12.5 Hz, -SCH_2), 3.49–3.52 (dd, 1H, J = 3.9, 12.5 Hz, 7a-H), 6.81–7.95 (m, 7H, ArH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.2, 26.7, 27.1, 33.5, 51.7, 84.9, 110.5, 114.3, 118.6, 120.8, 123.9, 124.0, 125.9, 128.9, 129.9, 129.9, 130.4, 132.5, 135.9, 155.9, 169.9. MS: *m/z* 350 (M^+ + 1, 22 %), 349 (M^+, 100), 334 (14), 306 (20), 307 (30), 293 (18), 292 (78), 200 (13), 187 (11), 168 (14). Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found C, 72.35; H, 5.34; N, 3.93 %.

Compound **9c**: White solid (0.12 g, 89 %), m.p. 168–170 °C. IR (KBr): ν_{max} 2906 (ν_{CH}), 1703 ($\nu_{C=O}$), 1454, 1374 (δ_{CH}) cm^1. UV (EtOH): λ_{max} 228 (log ε 4.09), 255 (log ε 4.05), 263 (log ε 3.93), 288 (log ε 4.01) nm. ^1H NMR (300 MHz, $CDCl_3$): δ 1.73 (s, 3H, 12a-CH_3), 2.64–2.73 (t, 1H, J = 12.5 Hz, SCH_2), 2.81 (s, 3H, $COCH_3$), 2.95–3.01 (dd, 1H, J = 3.4, 12.5 Hz, SCH_2), 3.47–3.52 (dd, 1H, J = 3.4, 12.5 Hz, 7a-H), 6.85–7.95 (m, 8H, ArH). MS: *m/z* 336 (M^+ + 1, 26 %), 335 (M^+, 100), 320 (12), 293 (48), 292 (25), 278 (94), 260 (28), 200 (17), 168 (11). Anal. Calcd for $C_{20}H_{17}NO_2S$: C, 71.62; H, 5.11; N, 4.18. Found C, 71.78; H, 5.01; N, 4.32 %.

Compound **9d**: White solid (0.13 g, 90 %), m.p. 160–162 °C. IR (KBr): ν_{max} 2918 (ν_{CH}), 1697 ($\nu_{C=O}$), 1488, 1371 (δ_{CH}) cm^1. UV (EtOH): λ_{max} 232 (log ε 4.20), 255 (log ε 4.11), 262 (log ε 3.96), 296 (log ε 4.08) nm. ^1H NMR (500 MHz, $CDCl_3$): δ 1.73 (s, 3H, 12a-CH_3), 2.68–2.73 (t, 1H, J = 12.5 Hz, SCH_2), 2.80 (s, 3H, $COCH_3$), 2.96–3.00 (dd, 1H, J = 3.8, 12.5 Hz, SCH_2), 3.43–3.47 (dd, 1H, J = 3.8, 12.5 Hz, 7a-H), 3.78 (s, 3H, OCH_3), 6.72–7.92 (m, 7H, ArH). MS: *m/z* 388 (65 %), 366 (M^+ + 1, 100), 365 (M^+, 22), 324 (73), 290 (13), 260 (13), 200 (14). Anal. Calcd for $C_{21}H_{19}NO_3S$: C, 69.02; H, 5.24; N, 3.83. Found C, 68.89; H, 5.42; N, 3.74 %.

Compound **9e**: White solid (0.12 g, 85 %), m.p. 168–170 °C. IR (KBr): ν_{max} 2926 (ν_{CH}), 1700 ($\nu_{C=O}$), 1435, 1367 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 231 (log ε 4.13), 255 (log ε 4.02), 263 (log ε 3.98), 288 (log ε 4.06) nm. ^1H NMR (500 MHz, $CDCl_3$): δ 1.73 (s, 3H, 12a-CH_3), 2.16 (s, 3H, $ArCH_3$), 2.25 (s, 3H, $ArCH_3$), 2.67–2.72 (t, 1H, J = 12.5 Hz, SCH_2), 2.80 (s, 3H, $COCH_3$), 2.97–3.01 (dd, 1H, J = 3.9, 12.5 Hz, SCH_2), 3.49–3.52 (dd, 1H, J = 3.9, 12.5 Hz, 7a-H), 6.81–7.95 (m, 6H, ArH). MS: *m/z* 386 (89 %), 364 (M^+ + 1, 100), 363 (M^+, 27), 324 (16), 289 (18), 260 (12), 200 (18). Anal. Calcd for $C_{22}H_{21}NO_2S$: C, 72.70; H, 5.82; N, 3.85. Found C, 72.85; H, 5.89; N, 3.69 %.

Compound **9f**: Viscous liquid (0.12 g, 86 %). IR (neat): ν_{max} 2915 (ν_{CH}), 1702 ($\nu_{C=O}$), 1473, 1376 (δ_{CH}) cm^{-1}. UV (EtOH): λ_{max} 233 (log ε 4.12), 256 (log ε 4.03), 264 (log ε 3.97), 294 (log ε 4.05) nm. ^1H NMR (400 MHz, $CDCl_3$): δ 1.71 (s, 3H, 12a-CH_3), 2.16 (s, 3H, $ArCH_3$), 2.24 (s, 3H, $ArCH_3$), 2.63–2.70 (t, 1H, J = 12.5 Hz, SCH_2), 2.79 (s, 3H, $COCH_3$), 2.94–2.98 (dd, 1H, J = 3.8, 12.5 Hz, SCH_2), 3.45–3.48 (dd, 1H, J = 3.8, 12.5 Hz, 7a-H), 6.71–7.95 (m, 6H, ArH). MS: *m/z* 386 (88 %), 364 (M^+ + 1, 100), 363 (M^+, 26), 324 (17), 320 (15), 289 (20), 260 (12), 200 (17), 173 (41). Anal. Calcd for $C_{22}H_{21}NO_2S$: C, 72.70; H, 5.82; N, 3.85. Found C, 72.90; H, 5.96; N, 4.02 %.

We thank the CSIR (New Delhi) for financial assistance. One of us (S.A) is grateful to the UGC (New Delhi) for a fellowship. We also thank the DST (New Delhi) for providing UV-VIS and FT-IR spectra under the FIST programme, and the University of Kalyani for laboratory facilities.

Received 30 September 2005; accepted 21 November 2005
Paper 05/3519

References

1 (a) Y. Sendo, I. Iijima and Y. Ban, *Tetrahedron Lett.*, 1969, **30**, 2527; (b) R.J. Sundberg, *The Chemistry of Indoles*, Academic Press, New York, 1970. pp 438–439; (c) J.E. Saxton, *Indoles*, Wiley-Interscience, New York, 1983, Part 4; (d) M. Taniguchi, T. Anjiki, M. Nakagawa and T. Hino, *Chem. Pharm. Bull*., 1984, **32**, 2544; (e) J.S. Carle and C. Christophersen, *J. Org. Chem.*, 1980, **45**, 1586; (f) Y. Nakashima, Y. Kawashima, F. Amanuma, K. Sota, A. Tanaka and T. Kameyama, *Chem. Pharm. Bull.,* 1984, **32**, 4271; (g) T. Ohmoto and K. Koike, *Chem. Pharm. Bull*., 1984, **32**, 170 (h) M. Shimizu, M. Ishikawa, Y. Komoda, T. Nkajima, K. Yamaguchi and N. Yoneda, *Chem. Pharm. Bull.,* 1984, **32**, 463; (i) S. Kamijo and Y. Yamamoto, *J. Org. Chem.,* 2003, **68**, 4764; (j) Y. Hashimoto, K. Shudo and T. Okamoto, *Chem. Pharm. Bull.,* 1984, **32**, 4300; (k) E. Yamanaka, M. One, S. Kasamatsu, N. Aimi and S. Sakai, *Chem. Pharm. Bull.,* 1984, **32**, 818.

2 (a) N. Haider and E. Sotero, *Chem. Pharm. Bull.*, 2002, **50**, 1479; (b) C. Guillonneare, A. Pierre, Y. Charton, N. Guilbaud, I. Kraus-Berthier, S. Leonce, A. Michel, I. Bisagni and G. Atassi, *J. Med. Chem.*, 1999, **42**, 2191.

3 (a) S. Sakai, N, Aimi, K. Yamaguchi, Y. Hitotsuyonagi, C. Watanabe, K. Yokose, Y. Koyama, K. Shudo and A. Itai, *Chem. Pharm. Bull.,* 1984, **32**, 354; (b) Y. Endo, K. Shudo, K. Furuhata, H. Ogura, S. Sakai, N. Aimi, Y. Hitotsuyanagi and Y. Koyama, *Chem. Pharm. Bull.,* 1984, **32**, 358.

4 (a) S. Takada and Y. Makisumi, *Chem. Pharm. Bull.,* 1984, **32**, 872; (b) S. Takada, N. Ishizuka, T. Sasatani, Y. Makisumi, H. Jyoyama, H. Hatakeyama, F. Asanuma and K. Hirose, *Chem. Pharm. Bull.,* 1984, **32**, 877.

5 (a) B.S. Thyagarajan, *Adv. Heterocyclic Chem*., 1967, **8**, 143; (b) J.E. Macor, O.D. Langer, J.Z. Gougoutas, M.F. Melley and L.A.M. Cornelius, *Tetrahedron Lett.,* 2000, **41**, 3541; (c) S.C. Ghosh and A. De, *J. Chem. Soc. Perkin Trans. 1*, 1999, **24**, 3705; (d) E.W. Baxter, D. Labaree, H.L. Ammon and P.S. Mariano, *J. Am. Chem. Soc.,* 1990, **112**, 7682; (e) Y. Tamaru, T. Harada, Y. Toshiro and Z. Yoshida, *J. Am. Chem. Soc.,* 1980, **102**, 2392; (f) R.M. Lemieux and A.I. Meyers, *J. Am. Chem. Soc.,* 1998, **120**, 5453; (g) D.C. Smith and P.L. Fuchs, *J. Org. Chem.,* 1995, **60**, 2692; (h) S. Takano, M. Hirama and K. Ogasawara, *Tetrahedron Lett.,* 1982, **23**, 881.

6 (a) D.K. Bates and M.W. Janes, *J. Org. Chem.*, 1978, **43**, 3856; (b) P.L. Raymond, *Chem. Rev.,* 1984, **84**, 205; (c) N. Katsumasa, B. Hiroshi, M. Keiji and Y. Hisashi, *J. Am. Chem. Soc.,* 1990, **112**, 316; (d) F. Zulfiqar and T. Kitazume, *Green Chem.,* 2000, **2**, 296.

7 (a) K.C. Majumdar, P. Chatterjee and S. Saha, *Tetrahedron Lett.,* 1998, **39**, 7147; (b) K.C. Majumdar, U.K. Kundu and S.K. Ghosh, *Org. Lett*., 2002, **4**, 2629; (c) K.C. Majumdar and U. Das, *J. Org. Chem*., 1998, **63**, 9997.

8 (a) K.C. Majumdar and B.S. Thyagarajan, *Int. J. Sulfur Chem.*, 1972, **2A**, 93; 1972, **2A**, 153; (b) J.B. Hillard, K.V. Reddy, K.C. Majumdar and B.S. Thyagarajan, *J. Heterocyclic Chem.*, 1974, **11**, 369.