Regioselective synthesis of biologically interesting pentacyclic polyheterocycles by sequential thio-Claisen and $AlCl_3$ catalyzed oxy-Claisen rearrangement of 4-(4′-aryloxybut-2′-ynylthio)-1-phenyl-1,8-naphthyridin-2(1*H*)-one

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Abstract: A number of 4-aryloxymethyl-6-phenyl-2*H*-thiopyrano[3,2-*c*][1,8]naphthyridin-5(6*H*)-ones were regioselectively synthesized in 82%–95% yields by the thermal Claisen rearrangement of 4-(4′-aryloxybut-2′-ynylthio)-1-phenyl-[1,8]naphthyridin-2(1*H*)-ones. These products were then subjected to a second Claisen rearrangement in the presence of a Lewis acid catalyst, anhyd. $AlCl_3$, to give hitherto unreported pentacyclic heterocycles in 75%–90% yields. The same final products were also obtained in low yield upon refluxing 4-aryloxymethyl-6-phenyl-2*H*-thiopyrano-[3,2-*c*][1,8]naphthyridin-5(6*H*)-ones in *N,N*-diethyl aniline for 12–14 h. This method was found to be more effective than thermal Claisen rearrangement.

Key words: [3,3] sigmatropic rearrangement, regioselective synthesis, phase transfer catalysis, sequential Claisen rearrangement, Lewis acid catalyzed Claisen rearrangement, single crystal X-ray.

Résumé : On a réalisé des synthèses régiosélectives de 4-aryloxyméthyl-6-phényl-2*H*-thiopyrano[3,2-*c*][1,8]naphtyridin-5(6*H*)-ones, avec des rendements allant de 82 % à 95 %, en soumettant des 4-(4'-aryloxybut-2'-ynylthio)-1-phényl[1,8]naphtyridin-2(1*H*)-ones à un réarrangement de Claisen thermique. Ces produits ont ensuite été soumis à un deuxième réarrangement de Claisen, en présence d'un acide de Lewis comme catalyseur, le trichlorure d'aluminium, pour conduire à la formation d'hétérocycles pentacycliques non rapportés jusqu'à maintenant, avec des rendements allant de 75 % à 90 %. On a aussi obtenu ces produits avec de faibles rendements en portant les 4-aryloxyméthyl-6-phényl-2*H*-thiopyrano[3,2-*c*][1,8]naphtyridin-5(6*H*)-ones au reflux dans la *N,N*-diéthylaniline pendant 12 à 14 h. On a trouvé que cette méthode est plus efficace que le réarrangement thermique de Claisen.

Mots clés : réarrangement sigmatropique [3,3], synthèse régiosélective, catalyse par transfert de phase, réarrangements de Claisen séquentiels, réarrangement de Claisen catalysé par un acide de Lewis, diffraction des rayons X par un cristal unique.

[Traduit par la Rédaction]

Introduction

1,8-Naphthyridinones and their derivatives have attracted considerable attention primarily because the 1,8-naphthyridine skeleton is present in many compounds that have been isolated from natural substances and exhibited various medicinal and biological activities (1, 2). 4-Hydroxy-1-phenyl-1,8-naphthyridin-2(1*H*)-one and its derivatives have been used as inhibitors of sulfidopeptide leukotrienes, the major component of SRS-A release (3). 2-Oxo-1,8-naphthyridin-3-carboxylic acid derivatives possess potent gastric antisecretary properties and anti-inflammatory activities (4–6). A series of novel imidazo[4,5-*c*][1,8]naphthyridin-4(5*H*)-ones exhibited potent bronchodilator activity (7). The attractive bioactivities of these 1,8-naphthyidinones, such as the cytoprotective, anti-inflammatory, and antiallergic activity of some 2,3-fused and 3,4-fused furo- and pyrano-tricyclic compounds, justify the great interest in the naphthyridinone moiety as a target in organic synthesis. It is well-documented that the Claisen rearrangement (8) is an excellent method for carbon–carbon bond formation and has been successfully employed for the synthesis of a number of potentially bioactive thieno[3,2-*d*]pyrimidinone and dihydrothieno[3,2-*d*]pyrimidinone derivatives (9). We have previously reported the sequential [3,3] sigmatropic rearrangement of suitably substituted but-2-ynes to give interesting results, e.g., easy access to [6,6] and [6,5] fused polyhetrocycles (10). In view of the medicinal importance of 1,8-

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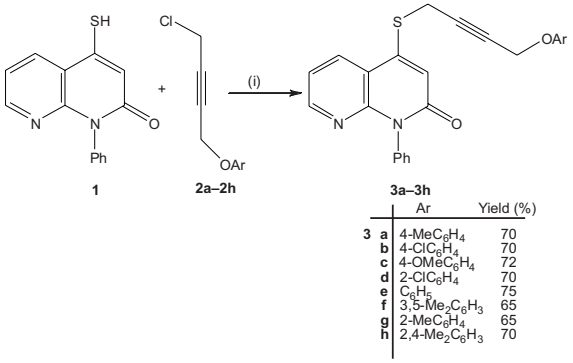
Scheme 1. Reagent and conditions: (*i*) BTEAC, $CHCl_3$, 1% aq. NaOH, 8–10 h, stirring, RT.



		Ar	Yield (%)
3	a	4-MeC_6H_4	70
	b	4-ClC_6H_4	70
	c	4-$OMeC_6H_4$	72
	d	2-ClC_6H_4	70
	e	C_6H_5	75
	f	3,5-$Me_2C_6H_3$	65
	g	2-MeC_6H_4	65
	h	2,4-$Me_2C_6H_3$	70

naphthyridine and its derivatives, we became interested in synthesizing a number of polyheterocycles derived from 4-hydroxy-1-phenyl-1,8-naphthyridin-2(1*H*)-one. Here, we report our focused attention on the synthesis of furothiopyrano heterocyclic ring-fused 1,8-napthyridin-2(1*H*)-one by the application of thio-Claisen and oxy-Claisen rearrangement.

Results and discussion

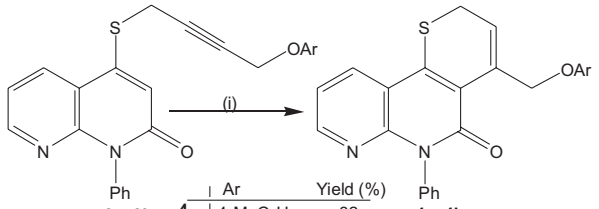
The starting materials, 4-(4′-aryloxybut-2′-ynylthio)-1-phenyl-[1,8]naphthyridin-2(1*H*)-ones (**3a**–**3h**) were synthesized by phase transfer catalyzed alkylation (11) of 4-mercapto-1-phenyl-1,8-naphthyridin-2(1*H*)-one (**3**) with 1-aryloxy-4-chlorobut-2-ynes (**2a**–**2h**) in 65%–75% yield. 4-Mercapto-1-phenyl-1,8-naphthyridin-2(1*H*)-one (**1**) was prepared according to published procedure (12) (Scheme 1).

The substrates **3a**–**3h** contain the propynylthio-1,8-naphthyridinone moiety as well as the aryl prop-2-ynyl ether moiety, which suggests two different possible [3,3] sigmatropic rearrangements. The aliphatic Claisen rearrangement has the lower activation energy since the aromatic counterpart has to disturb its aromatic sextet in the transition state. Substrate **3a** was heated in chlorobenzene (132 °C) and the reaction was monitored by TLC until complete conversion. Complete conversion was achieved in 4 h giving a white solid in 95% yield. The product **4a** was characterized from elemental analysis and spectroscopic data as 4-(4′-methylphenoxymethyl)-6-phenyl-2*H*-thiopyrano[3,2-*c*][1,8]naphthyridin-5(6*H*)-one. Its ^{1}H NMR spectrum (600 MHz) showed two two-proton doublets at δ: 3.43 (J = 5.4 Hz, -SCH_2), 5.17 (J = 1.2 Hz, -OCH_2) respectively, one proton triple triplet (tt) at δ: 6.28–6.31 (J = 1.8 Hz, 6 Hz, =CH), and a multiplet for twelve aromatic protons at δ: 6.83–8.43. Substrates **3b**–**3h** under similar treatment afforded compounds **4b**–**4h** in 82%–90% yield (Scheme 2).

The formation of products **4a**–**4h** from the substrates **3a**–**3h** is easily rationalized by the initial [3,3] sigmatropic rearrangement of the sulfides **3a**–**3h** to give **5.** This was followed by enolization to **6** and subsequent [1,5] hydrogen shift and electrocyclic ring closure (ECR) to give products **4a**–**4h** (Scheme 3).

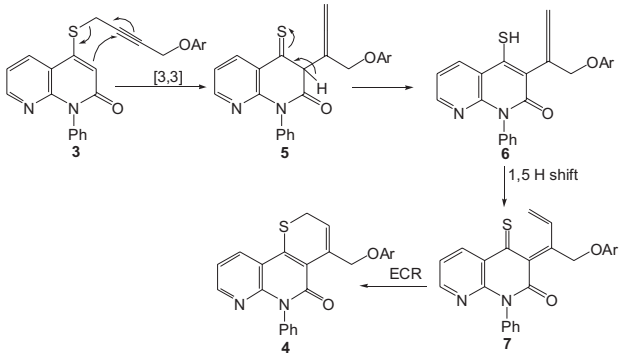
Compounds **4a**–**4h** contain allyl aryl ether moieties favourable for a further [3,3] sigmatropic rearrangement. Compounds **4a**, **4d**, and **4f** were refluxed in *N*,*N*-diethyl aniline to perform Claisen rearrangement of allyl aryl ether to

Scheme 2. Reagent and conditions: (*i*) Chlorobenzene, reflux, 4–6 h.

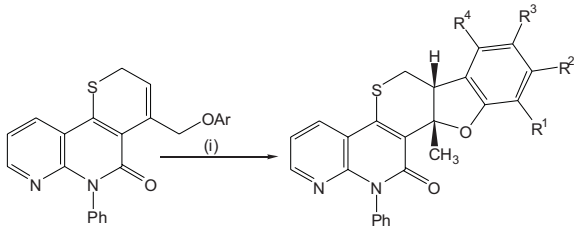


		Ar	Yield (%)
4	a	4-MeC_6H_4	82
	b	4-ClC_6H_4	82
	c	4-$OMeC_6H_4$	90
	d	2-ClC_6H_4	95
	e	C_6H_5	85
	f	3,5-$Me_2C_6H_3$	85
	g	2-MeC_6H_4	90
	h	2,4-$Me_2C_6H_3$	85

Scheme 3.



Scheme 4. Reagent and conditions: (*i*) *N*,*N*-Diethyl aniline, reflux, 12–14 h.



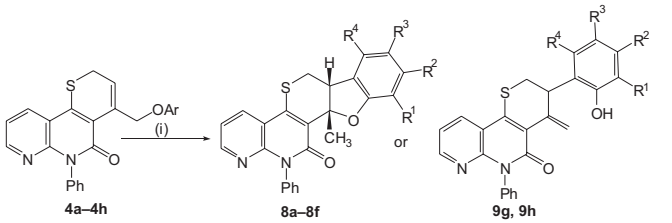
		R^1	R^2	R^3	R^4	Yield (%)
8	a	H	H	CH_3	H	30
	d	Cl	H	H	H	25
	f	H	CH_3	H	CH_3	28

afford the cyclized products in 25% to 30% yields. The products were characterized as **8a**, **8d**, and **8f** from their elemental analyses and spectroscopic data (Scheme 4).

The thermal rearrangement required very high temperature and afforded products in poor yield because of decomposition, so we attempted Lewis acid catalyzed Claisen rearrangement. Among different catalysts reported in literature (13), $AlCl_3$ and its derivatives are known to be efficient for Claisen rearrangement.

Substrate **4a**, upon treatment with anhyd. $AlCl_3$ in dry dichloromethane at RT for 1 h, afforded the cyclized product **8a** in 90% yield. Compound **8a** was characterized from elemental analysis and spectroscopic data. The ^{1}H NMR (500 MHz) spectrum showed δ_H: 1.86 (s, 3H, CH_3 of ring junction), 2.31 (s, 3H, $ArCH_3$), 2.84–2.89 (t, 1H, J =

Scheme 5. Reagent and conditions: (*i*) $AlCl_3$ (1 equiv.), Dry CH_2Cl_2, stirring, 2 h, RT.



		R^1	R^2	R^3	R^4	Yield(%)
8	a	H	H	CH_3	H	90
	b	H	H	Cl	H	88
	c	H	H	OCH_3	H	80
	d	Cl	H	H	H	85
	e	H	H	H	H	85
	f	H	CH_3	H	CH_3	90

		R^1	R^2	R^3	R^4	Yield(%)
9	g	CH_3	H	H	H	87
	h	CH_3	H	CH_3	H	75

Scheme 6.

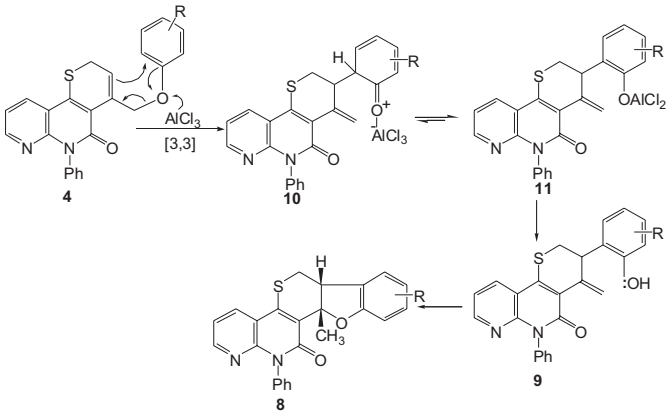
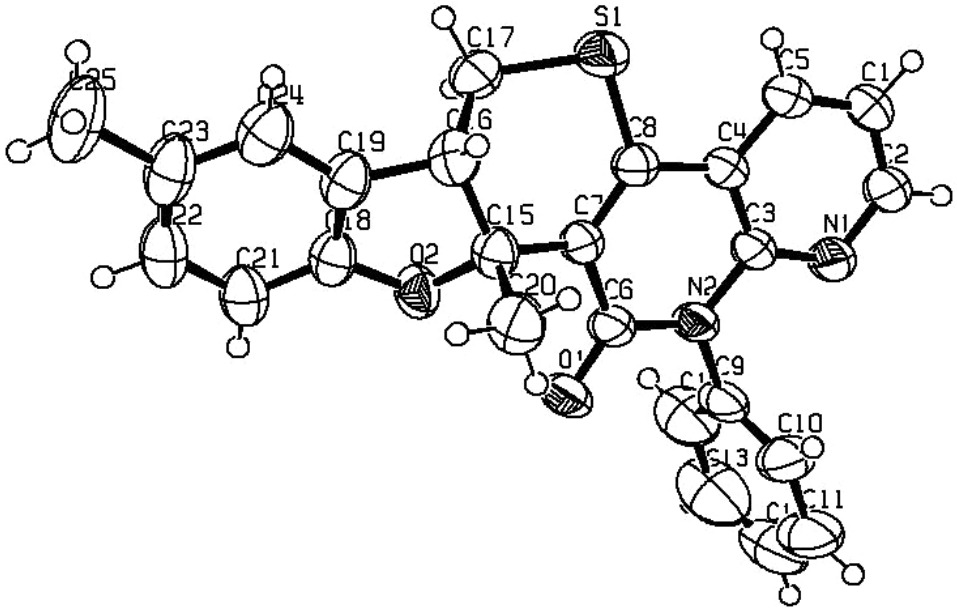


Fig. 1. Single crystal X-ray structure of compound **8a**.



12.3 Hz, SC**H**$_2$), 3.11–3.15 (dd, 1H, *J* = 3.7 Hz, 13.2 Hz, SCH_2), 3.46–3.49 (dd, 1H, *J* = 3.7 Hz, 11.2 Hz, ring juncture H), 6.84–6.85 (d, 1H, *J* = 8.1 Hz, ArH), 6.97–6.99 (d, 1H, *J* = 7.9 Hz, ArH), 7.09 (s, 1H, ArH), 7.14–7.16 (dd, 1H, *J* = 4.6 Hz, 7.8 Hz, ArH), 7.29–7.30 (d, 2H, *J* = 7.5 Hz, ArH), 7.44–7.47 (t, 1H, *J* = 7.4 Hz, ArH), 7.53–7.55 (m, 2H, ArH), 8.26–8.27 (d, 1H, *J* = 7 Hz, ArH), 8.43–8.44 (d, 1H, *J* = 3.3 Hz, ArH). Compounds **4b**–**4h** were also similarly treated to give products **8a**–**8f**, **9g**, and **9h** in 75%–90% yields (Scheme 5). The products were characterized from their elemental analyses and spectroscopic data.

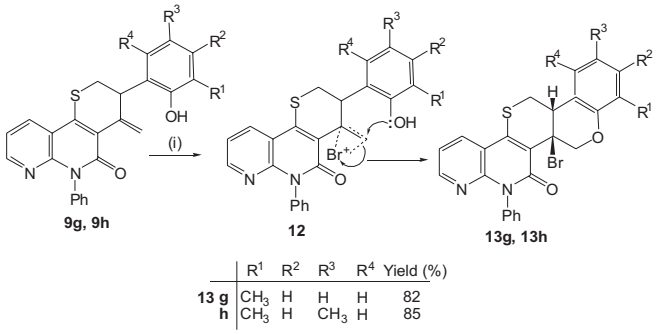
We also examined whether the charge accelerated [3,3] sigmatropic rearrangement is applicable to the sulfides **3a**–**3f**. The substrates **3a**–**3f**, when treated with anhyd. $AlCl_3$ in dichloromethane at RT, showed a tendency to decompose and no traceable product was obtained, although they are quite stable in dichloromethane at RT.

The formation of products **8a**–**8f**, **9g,** and **9h** from **4a**–**4h** is shown in Scheme 6. The isolation of the intermediate **9g** and **9h** indicates that the formation of both the thermal and catalytic rearrangement may follow the [3,3] sigmatropic rearrangement pathway. The use of a Lewis acid catalyst avoids the problem of high temperature that led to decomposition. The formation of products **8** from **4** can be rationalized by a series of steps involving an initial charge accelerated [3,3] sigmatropic rearrangement to give **10,** an ether–oxygen–$AlCl_3$ complex that may pass through a charge-delocalized transition state followed by rapid tautomerization to intermediate **11**, and proton exchange to give the intermediate **9**, which on *5-exo*-cyclization gives the products **8**, analogous to the product usually obtained in the thermal rearrangement (Scheme 6). The single crystal X-ray analysis of **8a** showed the cis stereochemistry at the ring juncture (Fig. 1).

The compounds **9g** and **9h**, upon treatment with pyridine hydrotribromide in chloroform, afforded compounds **13g** and **13h**. The formation of products **13g** and **13h** is thought to occur through the intermediate bromonium ion followed by a "6-endo" attack of the phenolic OH on the bromonium ion **12** (Scheme 7) (10*b*).

In summary, it has been possible to successfully perform the sequential Claisen rearrangement of 4-(4′-aryloxybut-2′-

Scheme 7. Reagent and conditions: (*i*) $PyHBr_3$, $CHCl_3$, 1 h, RT.



	R^1	R^2	R^3	R^4	Yield (%)
13 g	CH_3	H	H	H	82
h	CH_3	H	CH_3	H	85

ynylthio)-1-phenyl-1,8-naphthyridin-2(1*H*)-ones. The method is facile, operationally simple, and allows rapid access to two complex biologically significant heterocyclic systems.

Experimental[2]

Melting points were determined in an open capillary and are uncorrected. IR spectra were recorded on a PerkinElmer L 120–000A spectrometer (ν_{max} in cm^{-1}) on KBr disks. UV absorption spectra were recorded in EtOH on a Shimadzu UV-2401PC spectrophotometer (λ_{max} in nm). ^1H NMR (300 MHz, 400 MHz, 500 MHz, 600 MHz) and ^{13}C NMR (75.5 MHz, 125.7 MHz) spectra were recorded on a Bruker DPX-300, Varian-400 FT-NMR, Bruker DPX-500, and Varian-600 MHz spectrometers in $CDCl_3$ (chemical shifts in δ) with TMS as internal standard. Elemental analyses and mass spectra were recorded on a Leco 932 CHNS analyzer and on a JEOL JMS-600 instrument, respectively. ^1H NMR and ^{13}C NMR spectra were recorded at the Indian Institute of Chemical Biology, Kolkata, and Bose Institute, Kolkata. Silica gel [60–120 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 between 60–80 °C.

The 1-aryloxy-4-chlorobut-2-ynes (**2a**–**2f**) were prepared according to published procedures (14–16).

Single crystal X-ray study was performed on a Bruker APEX CCD diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected using monochromated Mo Kα radiation (λ_a = 0.710 69 Å). The frames were integrated in the Bruker SAINT Software package and the data were corrected for absorption using the SADABS program. The structure was solved and refined with the SHELX suite of programs. ORTEP-III was used to produce the diagram. Pertinent crystallographic data for compound **8a** is summarized in Table 1.

Table 1. Crystallographic data for compound **8a**.

Compound	**8a**
Empirical formula	$C_{25}H_{20}N_2O_2S$
Formula weight	412.5
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	8.4181(2)
b (Å)	20.3559 (6)
c (Å)	14.1321 (4)
α (°)	90
β (°)	95.269 (2)
γ (°)	90
V ($Å^3$)	2411.42 (11)
Z	5
ρ_{calcd} (g cm^{-3})	1.424
μ (mm^{-1})	0.194
F(000)	1085
Reflections collected	20 896
Reflections independent	5886
Goodness-of-fit	1.257
Final *R* indices [$I > 2\sigma(I)$][a]	*R*1 = 0.0950, *wR*2 = 0.3021

General procedure for the preparation of 4-(4′-aryloxy-2′-but-ynylthio)-1-phenyl-1,8-naphthyridin-2 (1*H*)-one (3a–3f)

To a mixture of 4-mercapto-1-phenyl-1,8-naphthyridin-2(1*H*)-one **1** (0.50 g, 2 mmol) and 1-aryloxy-4-chloro-2-butyne **2a**–**2f** (2.4 mmol) was added a solution of benzyl triethyl ammonium chloride (BTEAC) in 1% aq. NaOH (50 mL) and the mixture was stirred at RT for 8–10 h. The reaction mixture was then diluted with water (100 mL) and the organic layer was extracted with chloroform (3 × 25 mL). The organic layer was repeatedly washed with saturated brine and dried (Na_2SO_4). The solvent was removed and the viscous mass was chromatographed over silica gel using petroleum ether – ethyl acetate (3:1) as eluant to afford the products **3a**–**3f.**

Compounds **3d**–**3h** have already been reported (12).

Compound 3a

Yield 70%; solid; mp 112–114 °C. UV–vis (EtOH) λ_{max} (nm): 205, 222, 309, 327. IR (KBr, cm^{-1}) ν_{max}: 2918, 1655, 1578, 1509, 1436. ^1H NMR (600 MHz, $CDCl_3$) δ_H: 2.26 (s, 3H, CH_3), 3.86–3.87 (t, 2H, *J* = 1.8 Hz, SCH_2), 4.68–4.69 (t, 2H, *J* = 1.8 Hz, OCH_2), 6.73 (s, 1H, =CH), 6.83–6.85 (m, 2H, ArH), 7.06–7.07 (d, 1H, *J* = 8.4 Hz, ArH), 7.14–7.17 (dd, 1H, *J* = 4.2 Hz, 7.8 Hz, ArH), 7.26–7.28 (m, 3H, ArH), 7.48–7.51 (t, 1H, *J* = 7.8 Hz, ArH), 7.56–7.59 (t, 2H, *J* = 7.8 Hz, ArH), 8.11–8.12 (dd, 1H, *J* = 1.8 Hz, 7.8 Hz, ArH), 8.45–8.46 (dd, 1H, *J* = 1.8 Hz, 4.2 Hz, ArH). MS *m*/*z*: 412 (M^+). Anal. calcd. for $C_{25}H_{20}N_2O_2S$: C 72.81, H 4.85, N 6.79; found: C 73.04, H 4.60, N 6.96.

Compound 3b

Yield 70%; solid; mp 148–150 °C. UV–vis (EtOH) λ_{max} (nm): 200, 223, 327. IR (KBr, cm^{-1}) ν_{max}: 2921, 1662, 1578, 1488, 1435. ^1H NMR (300 MHz, $CDCl_3$) δ_H: 3.86 (t, 2H, *J* = 1.8 Hz, SCH_2), 4.69 (t, 2H, *J* = 1.8 Hz, OCH_2), 6.72 (s, 1H, =CH), 6.86–6.89 (m, 2H, ArH), 7.14–7.29 (m, 5H, ArH),

[2] Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5113. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 627102 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

7.47–7.60 (m, 3H, ArH), 8.09–8.12 (dd, 1H, *J* = 1.5 Hz, 7.8 Hz, ArH), 8.45–8.47 (dd, 1H, *J* = 1.6 Hz, 4.6 Hz, ArH). MS *m/z*: 432, 434 (M^+). Anal. calcd. for $C_{24}H_{17}N_2O_2SCl$: C 66.58, H 3.93, N 6.47; found: C 66.78, H 3.75, N 6.23.

Compound 3c

Yield 72%; solid; mp 155–157 °C. UV–vis (EtOH) λ_{max} (nm): 222, 298, 327. IR (KBr, cm^{-1}) ν_{max}: 2962, 1647, 1582, 1512, 1432. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 3.72 (s, 3H, OCH_3), 3.86 (t, 2H, *J* = 2 Hz, SCH_2), 4.66 (t, 2H, *J* = 2 Hz, OCH_2), 6.72 (s, 1H, =CH), 6.79–6.81 (d, 2H, *J* = 8.8 Hz, ArH), 6.88–6.90 (d, 1H, *J* = 8.8 Hz, ArH), 7.14–7.17 (dd, 1H, *J* = 4.4 Hz, 8.4 Hz, ArH), 7.25–7.28 (m, 3H, ArH), 7.47–7.51 (t, 1H, *J* = 7.6 Hz, ArH), 7.55–7.59 (t, 2H, *J* = 7.6 Hz, ArH), 8.10–8.12 (d, 1H, *J* = 8.4 Hz, ArH), 8.45–8.46 (d, 1H, *J* = 3.6 Hz, ArH). MS *m/z*: 428 (M^+). Anal. calcd. for $C_{25}H_{20}N_2O_3S$: C 70.09, H 4.67, N 6.54; found: C 70.32, H 4.88, N 6.36.

General procedure for the preparation of compounds 4a–4h

Compounds **3a**–**3h** (1 mmol) were refluxed in chlorobenzene (5 mL) for 4–6 h. The reaction was monitored by TLC. The chlorobenzene was removed at reduced pressure and the residual mass was chromatographed over silica gel. Elution of the column with petroleum ether removed residual chlorobenzene and the rearranged products **4a**–**4h** were obtained by eluting the column with petroleum ether – ethyl acetate (4:1).

Compound 4a

Yield 82%; solid; mp 175–177 °C. UV–vis (EtOH) λ_{max} (nm): 204, 225, 343. IR (KBr, cm^{-1}) ν_{max}: 2925, 1646, 1629, 1582, 1509, 1443. ^1H NMR (600 MHz, $CDCl_3$) δ_H: 2.26 (s, 3H, CH_3), 3.43–3.44 (d, 2H, *J* = 5.4 Hz, SCH_2), 5.17 (d, 2H, *J* = 1.2 Hz, OCH_2), 6.28–6.31 (tt, 1H, *J* = 1.8 Hz, 6 Hz, =CH), 6.83–6.85 (m, 2H, ArH), 7.02–7.04 (d, 1H, *J* = 8.4 Hz, ArH), 7.17–7.20 (dd, 1H, *J* = 4.8 Hz, 7.8 Hz, ArH), 7.26–7.28 (m, 3H, ArH), 7.48–7.50 (tt, 1H, *J* = 1.2 Hz, 4.8 Hz, ArH), 7.56–7.58 (m, 2H, ArH), 8.30–8.31 (dd, 1H, *J* = 1.8 Hz, 7.8 Hz, ArH), 8.42–8.43 (dd, 1H, *J* = 1.8 Hz, 4.8 Hz, ArH). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_c: 20.87, 24.95, 69.02, 115.34, 115.44, 117.54, 118.61, 125.54, 128.97, 129.29, 129.95, 130.19, 130.31, 134.16, 136.95, 137.51, 146.18, 149.36, 150.69, 156.90, 160.45. MS *m/z*: 412 (M^+). Anal. calcd. for $C_{25}H_{20}N_2O_2S$: C 72.81, H 4.85, N 6.79; found: C 73.07, H 5.02, N 6.58.

Compound 4b

Yield 82%; solid; mp 204–206 °C. UV–vis (EtOH) λ_{max} (nm): 205, 226, 342. IR (KBr, cm^{-1}) ν_{max}: 2961, 2921, 1646, 1576, 1491, 1443. ^1H NMR (500 MHz, $CDCl_3$) δ_H: 3.43 (d, 2H, *J* = 6 Hz, SCH_2), 5.17 (s, 2H, OCH_2), 6.25–6.27 (t, 1H, *J* = 6 Hz, =CH), 6.85–6.87 (d, 2H, *J* = 8.8 Hz, ArH), 7.17–7.20 (m, 3H, ArH), 7.24–7.25 (m, 2H, ArH), 7.47–7.50 (t, 1H, *J* = 7.4 Hz, ArH), 7.55–7.58 (t, 2H, *J* = 7.4 Hz, ArH), 8.30–8.31 (dd, 1H, *J* = 1.3 Hz, 7.9 Hz, ArH), 8.43–8.44 (dd, 1H, *J* = 1.3 Hz, 4.5 Hz, ArH). MS *m/z*: 432, 434 (M^+). Anal. calcd. for $C_{24}H_{17}N_2O_2SCl$: C 66.58, H 3.93, N 6.47; found: C 66.35, H 4.12, N 6.64.

Compound 4c

Yield 90%; solid; mp 180–182 °C. UV–vis (EtOH) λ_{max} (nm): 204, 226, 344. IR (KBr, cm^{-1}) ν_{max}: 2928, 1645, 1578, 1508, 1442. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 3.43 (d, 2H, *J* = 6 Hz, SCH_2), 3.73 (s, 3H, OCH_3), 5.14 (d, 2H, *J* = 2 Hz, OCH_2), 6.28–6.31 (t, 1H, *J* = 6 Hz, =CH), 6.76–6.79 (dd, 2H, *J* = 2.4 Hz, 6.8 Hz, ArH), 6.86–6.88 (dd, 2H, *J* = 2.4 Hz, 6.8 Hz, ArH), 7.17–7.20 (dd, 1H, *J* = 4.4 Hz, 7.6 Hz, ArH), 7.25–7.27 (m, 2H, ArH), 7.46–7.50 (t, 1H, *J* = 8 Hz, ArH), 7.55–7.58 (t, 2H, *J* = 8 Hz, ArH), 8.29–8.31 (dd, 1H, *J* = 1.6 Hz, 7.6 Hz, ArH), 8.42–8.43 (dd, 1H, *J* = 1.6 Hz, 4.4 Hz, ArH). MS *m/z*: 428 (M^+). Anal. calcd. for $C_{25}H_{20}N_2O_3S$: C 70.09, H 4.67, N 6.54; found: C 69.91, H 4.91, N 6.76.

Compound 4d

Yield 95%; solid; mp 212–214 °C. UV–vis (EtOH) λ_{max} (nm): 204, 223, 343. IR (KBr, cm^{-1}) ν_{max}: 2924, 1651, 1579, 1485, 1444. ^1H NMR (600 MHz, $CDCl_3$) δ_H: 3.46 (d, 2H, *J* = 6 Hz, SCH_2), 5.26 (d, 2H, *J* = 1.8 Hz, OCH_2), 6.43–6.45 (tt, 1H, *J* = 1.8 Hz, 6 Hz, =CH), 6.84–6.87 (dt, 1H, *J* = 1.2 Hz, 7.8 Hz, ArH), 6.98–6.99 (dd, 1H, *J* = 1.2 Hz, 8.4 Hz, ArH), 7.13–7.16 (dt, 1H, *J* = 1.8 Hz, 8.4 Hz, ArH), 7.18–7.20 (dd, 1H, *J* = 4.2 Hz, 7.8 Hz, ArH), 7.28–7.29 (m, 2H, ArH), 7.33–7.34 (dd, 1H, *J* = 1.2 Hz, 7.8 Hz, ArH), 7.48–7.50 (t, 1H, *J* = 7.8 Hz, ArH), 7.56–7.59 (m, 2H, ArH), 8.31–8.32 (dd, 1H, *J* = 1.8 Hz, 7.8 Hz, ArH), 8.43–8.44 (dd, 1H, *J* = 1.8 Hz, 4.8 Hz, ArH). MS *m/z*: 432, 434 (M^+). Anal. calcd. for $C_{24}H_{17}N_2O_2SCl$: C 66.58, H 3.93, N 6.47; found: C 66.80, H 3.68, N 6.26.

Compound 4e

Yield 85%; solid; mp 186–188 °C. UV–vis (EtOH) λ_{max} (nm): 206, 222, 337. IR (KBr, cm^{-1}) ν_{max}: 2921, 1655, 1574, 1443. ^1H NMR (400 MHz, $CDCl_3$) δ_H: 3.43 (d, 2H, *J* = 6 Hz, SCH_2), 5.19 (s, 2H, OCH_2), 6.28–6.31 (t, 1H, *J* = 6 Hz, =CH), 6.91–6.94 (m, 3H, ArH), 7.17–7.27 (m, 5H, ArH), 7.46–7.50 (t, 1H, *J* = 8 Hz, ArH), 7.54–7.58 (t, 2H, *J* = 8 Hz, ArH), 8.29–8.31 (dd, 1H, *J* = 1.6 Hz, 8 Hz, ArH), 8.42–8.43 (dd, 1H, *J* = 1.6 Hz, 4.4 Hz, ArH). MS *m/z*: 398 (M^+). Anal. calcd. for $C_{24}H_{18}N_2O_2S$: C 72.36, H 4.52, N 7.03; found: C 72.57, H 4.35, N 7.22.

Compound 4f

Yield 85%; solid; mp 165–167 °C. UV–vis (EtOH) λ_{max} (nm): 206, 224, 341. IR (KBr, cm^{-1}) ν_{max}: 2913, 1663, 1583, 1448. ^1H NMR (600 MHz, $CDCl_3$) δ_H: 2.25 (s, 6H, CH_3), 3.44–3.45 (d, 2H, *J* = 6 Hz, SCH_2), 5.15 (d, 2H, *J* = 2 Hz, OCH_2), 6.31–6.33 (t, 1H, *J* = 6 Hz, =CH), 6.57 (s, 1H, ArH), 6.58 (s, 1H, ArH), 7.18–7.20 (dd, 1H, *J* = 4.8 Hz, 7.8 Hz, ArH), 7.27–7.28 (m, 3H, ArH), 7.48–7.50 (t, 1H, *J* = 7.2 Hz, ArH), 7.56–7.59 (t, 2H, *J* = 7.8 Hz, ArH), 8.30–8.31 (dd, 1H, *J* = 1.2 Hz, 7.8 Hz, ArH), 8.42–8.43 (dd, 1H, *J* = 1.2 Hz, 4.8 Hz, ArH). MS *m/z*: 426 (M^+). Anal. calcd. for $C_{26}H_{22}N_2O_2S$: C 73.23, H 5.16, N 6.57; found: C 73.04, H 5.39, N 6.78.

Compound 4g

Yield 90%; solid; mp 195–197 °C. UV–vis (EtOH) λ_{max} (nm): 204, 223, 339. IR (KBr, cm^{-1}) ν_{max}: 2924, 1653, 1575, 1492, 1443. ^1H NMR (600 MHz, $CDCl_3$) δ_H: 2.26 (s, 3H,

CH_3), 3.45–3.46 (d, 2H, J = 6 Hz, SCH_2), 5.20 (d, 2H, J = 1.2 Hz, OCH_2), 6.34–6.36 (tt, 1H, J = 1.8 Hz, 6 Hz, =CH), 6.81–6.87 (m, 1H, ArH), 7.07–7.12 (m, 2H, ArH), 7.18–7.20 (dd, 1H, J = 4.8 Hz, 7.8 Hz, ArH), 7.26–7.28 (m, 3H, ArH), 7.48–7.51 (m, 1H, ArH), 7.56–7.59 (m, 2H, ArH), 8.31–8.32 (dd, 1H, J = 1.8 Hz, 7.8 Hz, ArH), 8.43–8.44 (dd, 1H, J = 1.8 Hz, 4.8 Hz, ArH). MS m/z: 412 (M^+). Anal. calcd. for $C_{25}H_{20}N_2O_2S$: C 72.81, H 4.85, N 6.79; found: C 72.55, H 5.02, N 7.02.

Compound 4h

Yield 85%; solid; mp 178–180 °C. UV–vis (EtOH) λ_{max} (nm): 200, 226, 341. IR (KBr, cm^{-1}) ν_{max}: 2918, 1651, 1579, 1503, 1444. ^1H NMR (300 MHz, $CDCl_3$) δ_H = 2.22 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 3.43 (d, 2H, J = 6 Hz, SCH_2), 5.16 (s, 2H, OCH_2), 6.32–6.36 (t, 1H, J = 6 Hz, =CH), 6.74–6.93 (m, 3H, ArH), 7.16–7.28 (m, 3H, ArH), 7.47–7.60 (m, 3H, ArH), 8.30–8.32 (d, 1H, J = 7.8 Hz, ArH), 8.42–8.44 (dd, 1H, J = 1.2 Hz, 4.4 Hz, ArH). MS m/z: 426 (M^+). Anal. calcd. for $C_{26}H_{22}N_2O_2S$: C 73.23, H 5.16, N 6.57; found: C 73.49, H 5.40, N 6.38.

General procedure for the preparation of 8a–8f, 9g, and 9h

Compound **4a**–**4f** (0.5 mmol) was dissolved in dry dichloromethane (10 mL) and anhyd. $AlCl_3$ (0.06 g, 0.5 mmol) was added. The reaction mixture was stirred at RT for 0.5–2.0 h. Crushed ice was added to the reaction mixture and was extracted with dichloromethane. The combined extracts were washed with water (20 mL), brine (20 mL), and dried (Na_2SO_4). The solvent was removed and the residual viscous mass was chromatographed over silica gel using petroleum ether – ethyl acetate (3:1) as eluant to afford the products **8a**–**8f**, **9g**, and **9h**.

Compound 8a

Yield 90%; solid; mp 150–152 °C. UV–vis (EtOH) λ_{max} (nm): 206, 224, 296, 320, 332. IR (KBr, cm^{-1}) ν_{max}: 2924, 1655, 1583, 1488, 1441. ^1H NMR (500 MHz, $CDCl_3$) δ_H: 1.86 (s, 3H, CH_3 of ring junction), 2.31 (s, 3H, $ArCH_3$), 2.84–2.89 (t, 1H, J = 12.3 Hz, SCH_2), 3.11–3.15 (dd, 1H, J = 3.7 Hz, 13.2 Hz, SCH_2), 3.46–3.49 (dd, 1H, J = 3.7 Hz, 11.2 Hz, ring juncture H), 6.84–6.85 (d, 1H, J = 8.1 Hz, ArH), 6.97–6.99 (d, 1H, J = 7.9 Hz, ArH), 7.09 (s, 1H, ArH), 7.14–7.16 (dd, 1H, J = 4.6 Hz, 7.8 Hz, ArH), 7.29–7.30 (d, 2H, J = 7.5 Hz, ArH), 7.44–7.47 (t, 1H, J = 7.4 Hz, ArH), 7.53–7.55 (m, 2H, ArH), 8.26–8.27 (d, 1H, J = 7 Hz, ArH), 8.43–8.44 (d, 1H, J = 3.3 Hz, ArH). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_c: 21.26, 24.75, 29.28, 52.04, 86.05, 111.26, 114.83, 118.30, 125.10, 127.08, 128.68, 128.81, 129.68, 129.71, 130.14, 130.38, 134.30, 137.53, 145.85, 149.45, 151.03, 155.71, 160.56. MS m/z: 412 (M^+). Anal. calcd. for $C_{25}H_{20}N_2O_2S$: C 72.81, H 4.85, N 6.79; found: C 72.58, H 4.64, N 6.98.

Compound 8b

Yield 88%; solid; mp 260–262 °C. UV–vis (EtOH) λ_{max} (nm): 205, 224, 301, 321, 332. IR (KBr, cm^{-1}) ν_{max}: 2921, 1652, 1583, 1470, 1442. ^1H NMR (500 MHz, $CDCl_3$) δ_H: 1.88 (s, 3H, CH_3 of ring junction), 2.85–2.90 (t, 1H, J = 12.2 Hz, SCH_2), 3.12–3.15 (dd, 1H, J = 2.6 Hz, 13 Hz, SCH_2), 3.52–3.54 (d, 1H, J = 8.5 Hz, ring juncture H), 6.87–6.88 (d, 1H, J = 8.3 Hz, ArH), 7.13–7.17 (m, 2H, ArH), 7.25–7.30 (m, 3H, ArH), 7.41–7.55 (m, 3H, ArH), 8.25–8.27 (d, 1H, J = 7.4 Hz, ArH), 8.45–8.46 (m, 1H, ArH). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_c: 24.75, 29.03, 51.92, 86.99, 112.72, 114.70, 118.39, 124.77, 125.71, 126.55, 128.63, 128.74, 129.49, 129.69, 130.62, 134.30, 137.42, 145.97, 149.45, 151.22, 156.58, 160.44. MS m/z: 432, 434 (M^+). Anal. calcd. for $C_{24}H_{17}N_2O_2SCl$: C 66.58, H 3.93, N 6.47; found: C 66.84, H 4.14, N 6.69.

Compound 8c

Yield 80%; solid; mp 226–228 °C. UV–vis (EtOH) λ_{max} (nm): 204, 224, 333. IR (KBr, cm^{-1}) ν_{max}: 2938, 1650, 1582, 1484, 1441. ^1H NMR (500 MHz, $CDCl_3$) δ_H: 1.87 (s, 3H, CH_3 of ring junction), 2.86–2.91 (dd, 1H, J = 11.5 Hz, 13 Hz, SCH_2), 3.13–3.16 (dd, 1H, J = 3.8 Hz, 13 Hz, SCH_2), 3.48–3.51 (dd, 1H, J = 3.8 Hz, 11.3 Hz, ring juncture H), 3.78 (s, 3H, OCH_3), 6.71–6.71 (dd, 1H, J = 2.5 Hz, 8.7 Hz, ArH), 6.86–6.92 (m, 2H, ArH), 7.14–7.16 (dd, 1H, J = 4.6 Hz, 7.9 Hz, ArH), 7.29–7.30 (d, 2H, J = 7.4 Hz, ArH), 7.44–7.47 (t, 1H, J = 7.4 Hz, ArH), 7.50–7.60 (m, 2H, ArH), 8.25–8.27 (dd, 1H, J = 1.4 Hz, 7.9 Hz, ArH), 8.43–8.44 (dd, 1H, J = 1.4 Hz, 4.5 Hz, ArH). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ_c: 24.72, 29.12, 52.35, 56.45, 86.18, 111.08, 111.69, 114.35, 118.30, 126.94, 127.05, 128.68, 129.67, 129.74, 134.27, 137.51, 145.76, 149.45, 151.04, 151.91, 154.65, 160.53. MS m/z: 428 (M^+). Anal. calcd. for $C_{25}H_{20}N_2O_3S$: C 70.09, H 4.67, N 6.54; found: C 69.85, H 4.48, N 6.72.

Compound 8d

Yield 85%; solid; mp 162–164 °C. UV–vis (EtOH) λ_{max} (nm): 206, 224, 290, 321, 332. IR (KBr, cm^{-1}) ν_{max}: 2926, 1655, 1584, 1444. ^1H NMR (600 MHz, $CDCl_3$) δ_H: 1.92 (s, 3H, CH_3 of ring junction), 2.90–2.94 (dd, 1H, J = 11.4 Hz, 13.2 Hz, SCH_2), 3.13–3.16 (dd, 1H, J = 3.6 Hz, 13.2 Hz, SCH_2), 3.58–3.61 (dd, 1H, J = 3.6 Hz, 11.4 Hz, ring juncture H), 6.84–6.86 (t, 1H, J = 7.8 Hz, ArH), 7.13–7.16 (dd, 1H, J = 4.8 Hz, 7.8 Hz, ArH), 7.17–7.19 (m, 2H, ArH), 7.29–7.30 (d, 2H, J = 6.6 Hz, ArH), 7.45–7.48 (t, 1H, J = 8.4 Hz, ArH), 7.55–7.57 (t, 2H, J = 8.4 Hz, ArH), 8.24–8.25 (dd, 1H, J = 1.8 Hz, 7.8 Hz, ArH), 8.43–8.44 (dd, 1H, J = 1.8 Hz, 4.8 Hz, ArH). MS m/z: 432, 434 (M^+). Anal. calcd. for $C_{24}H_{17}N_2O_2SCl$: C 66.58, H 3.93, N 6.47; found: C 66.32, H 4.15, N 6.66.

Compound 8e

Yield 85%; solid; mp 214–216 °C. UV–vis (EtOH) λ_{max} (nm): 203, 224, 287, 332. IR (KBr, cm^{-1}) ν_{max}: 2919, 1644, 1583, 1461, 1443. ^1H NMR (500 MHz, $CDCl_3$) δ_H: 1.88 (s, 3H, CH_3 of ring junction), 2.85–2.89 (t, 1H, J = 12.3 Hz, SCH_2), 3.13–3.16 (d, 1H, J = 10.5 Hz, SCH_2), 3.52 (d, 1H, J = 8.8 Hz, ring juncture H), 6.90–6.97 (m, 2H, ArH), 7.15–7.20 (m, 2H, ArH), 7.25–7.30 (m, 3H, ArH), 7.46–7.55 (m, 3H, ArH), 8.26–8.27 (d, 1H, J = 7.5 Hz, ArH), 8.44 (d, 1H, J = 2.1 Hz, ArH). MS m/z: 398 (M^+). Anal. calcd. for $C_{24}H_{18}N_2O_2S$: C 72.36, H 4.52, N 7.03; found: C 72.54, H 4.77, N 6.81.

Compound 8f

Yield 90%; solid; mp 284–286 °C. UV–vis (EtOH) λ_{max}

(nm): 207, 224, 288, 320, 332. IR (KBr, cm^{-1}) ν_{max}: 2925, 1655, 1584, 1441. ^1H NMR (500 MHz, $CDCl_3$) δ_H: 1.79 (s, 3H, CH_3 of ring junction), 2.26 (s, 3H, $ArCH_3$), 2.36 (s, 3H, $ArCH_3$), 2.68–2.74 (t, 1H, J = 12.6 Hz, SCH_2), 3.07–3.11 (dd, 1H, J = 3.8 Hz, 13.1 Hz, SCH_2), 3.39–3.43 (dd, 1H, J = 3.8 Hz, 12.4 Hz, ring juncture H), 6.55 (s, 1H, ArH), 6.62 (s, 1H, ArH), 7.15–7.17 (dd, 1H, J = 4.6 Hz, 7.9 Hz, ArH), 7.30–7.31 (d, 2H, J = 7.4 Hz, ArH), 7.45–7.48 (t, 1H, J = 7.4 Hz, ArH), 7.53–7.57 (t, 2H, J = 7.8 Hz, ArH), 8.28–8.30 (dd, 1H, J = 1.6 Hz, 7.9 Hz, ArH), 8.44–8.45 (dd, 1H, J = 1.6 Hz, 4.6 Hz, ArH). MS m/z: 426 (M^+). Anal. calcd. for $C_{26}H_{22}N_2O_2S$: C 73.23, H 5.16, N 6.57; found: C 73.47, H 4.97, N 6.35.

Compound 9g

Yield 87%; solid; mp 128–130 °C. UV–vis (EtOH) λ_{max} (nm): 205, 224, 337. IR (KBr, cm^{-1}) ν_{max}: 3475, 2921, 1638, 1579, 1444, 1281. ^1H NMR:(300 MHz, $CDCl_3$) δ_H: 2.27 (s, 3H, $ArCH_3$), 3.39–3.44 (dd, 1H, J = 3.3 Hz, 12.2 Hz, SCH_2), 3.66–3.73 (dd, 1H, J = 8.4 Hz, 12.3 Hz, SCH_2), 4.33–4.36 (dd, 1H, J = 3.1 Hz, 5 Hz, ring juncture H), 5.02 (s, 1H, OH), 5.41 (s, 1H, $=CH_2$), 6.70 (s, 1H, $=CH_2$), 6.79–6.84 (t, 1H, J = 7.3 Hz, ArH), 6.95–7.15 (m, 3H, ArH), 7.26–7.31 (m, 2H, ArH), 7.48–7.60 (m, 3H, ArH), 8.21–8.24 (d, 1H, J = 8.1 Hz, ArH), 8.42–8.43 (d, 1H, J = 3.2 Hz, ArH). MS m/z: 412 (M^+). Anal. calcd. for $C_{25}H_{20}N_2O_2S$: C 72.81, H 4.85, N 6.79; found: C 72.99, H 5.10, N 6.55.

Compound 9h

Yield 75%; solid; mp 230–232 °C. UV–vis (EtOH) λ_{max} (nm): 205, 224, 337, 344. IR (KBr, cm^{-1}) ν_{max}: 3475, 2921, 1640, 1579, 1444, 1281. ^1H NMR (300 MHz, $CDCl_3$) δ_H: 2.11 (s, 3H, $ArCH_3$), 2.22 (s, 3H, $ArCH_3$), 3.35–3.59 (d, 1H, J = 11 Hz, -SCH_2) 3.65–3.72 (t, 1H, J = 9.8 Hz, SCH_2), 4.28–4.30 (d, 1H, J = 6.5 Hz, ring juncture H) 4.84 (s, 1H, OH), 5.37 (s, 1H, $=CH_2$), 6.65 (s, 1H, $=CH_2$), 6.77 (s, 1H, ArH), 6.88 (s, 1H, ArH), 7.13–7.15 (m, 1H, ArH), 7.26–7.30 (m, 2H, ArH), 7.48–7.58 (m, 3H, ArH), 8.22–8.24 (d, 1H, J = 7.9 Hz, ArH), 8.43–8.44 (d, 1H, J = 3.1 Hz, ArH). MS m/z: 426 (M^+). Anal. calcd. for $C_{26}H_{22}N_2O_2S$: C 73.23, H 5.16, N 6.57; found: C 73.09, H 5.33, N 6.71.

General procedure for the preparation of compounds 8a, 8d, and 8f

A mixture of compounds **4a**, **4d**, and **4f** (1 mmol) in *N,N*-diethylaniline (5 mL) was refluxed for 12–14 h. The reaction mixture was cooled, poured into ice-cold 6 (N) HCl (30 mL), and extracted with $CHCl_3$ (3 × 20 mL). The $CHCl_3$ layer was washed with water and dried over Na_2SO_4. Removal of $CHCl_3$ gave a viscous liquid, which was chromatographed over silica gel. Elution of the column with petroleum ether – ethyl acetate (4:1) furnished products **10a**, **10d**, and **4f**.

General procedure for the cyclization of the compounds 9g and 9h

The brominating agent, solid pyridine hydrobromide perbromide (0.16 g, 0.5 mmol), was added to a chloroform solution (20 mL) of the compounds **9g** and **9h** (0.5 mmol). The reaction mixture was then stirred for 1 h on a magnetic stirrer at 0–5 °C. After the completion of the reaction (monitored by TLC), the mixture was washed with 5% aq. $NaHCO_3$ (3 × 25 mL) and water (3 × 25 mL), and dried (Na_2SO_4). The residual mass after removal of the solvent was subjected to column chromatography over silica gel using petroleum ether – ethyl acetate (6:1) as eluant to give cyclized products **13g** and **13h**.

Compound 13g

Yield 82%; solid; mp 146–148 °C. UV–vis (EtOH) λ_{max} (nm): 207, 224, 286, 323, 334. IR (KBr, cm^{-1}) ν_{max}: 2923, 1651, 1584, 1443. ^1H NMR (300 MHz, $CDCl_3$) δ_H: 2.22 (s, 3H, $ArCH_3$), 2.82 (t, 1H, J = 12.6 Hz, SCH_2), 3.18–3.23 (dd, 1H, J = 4 Hz, 13 Hz, SCH_2), 3.54–3.57 (d, 1H, J = 9.5 Hz, OCH_2), 3.97–4.02 (dd, 1H, J = 4 Hz, 13 Hz, ring juncture H), 4.89–4.92 (d, 1H, J = 9.5 Hz, OCH_2), 6.58–6.90 (t, 1H, J = 7.3 Hz, ArH), 7.01–7.04 (d, 1H, J = 7.3 Hz, ArH), 7.14–7.33 (m, 4H, ArH), 7.49–7.61 (m, 3H, ArH), 8.30–8.33 (d, 1H, J = 8.1 Hz, ArH), 8.46–8.47 (d, 1H, J = 2.8 Hz, ArH). MS m/z: 490, 492 (M^+). Anal. calcd. for $C_{25}H_{19}N_2O_2SBr$: C 61.09, H 3.86, N 5.70; found: C 61.27, H 4.07, N 5.86.

Compound 13h

Yield 85%; solid; mp 140–142 °C. UV–vis (EtOH) λ_{max} (nm): 207, 224, 294, 334. IR (KBr, cm^{-1}) ν_{max}: 2924, 1655, 1584, 1443. ^1H NMR (500 MHz, $CDCl_3$) δ_H: 2.18 (s, 3H, $ArCH_3$), 2.29 (s, 3H, $ArCH_3$), 2.83–2.88 (dd, 1H, J = 12.4 Hz, 13 Hz, SCH_2), 3.17–3.20 (dd, 1H, J = 4.2 Hz, 13.2 Hz, SCH_2), 3.54–3.56 (d, 1H, J = 9.6 Hz, OCH_2), 3.93–3.96 (dd, 1H, J = 4.2 Hz, 12.2 Hz, ring juncture H), 4.89–4.91 (d, 1H, J = 9.6 Hz, OCH_2), 6.84 (s, 1H, ArH), 6.95 (s, 1H, ArH), 7.16–7.18 (dd, 1H, J = 4.6 Hz, 8 Hz, ArH), 7.28–7.32 (m, 2H, ArH), 7.46–7.50 (m, 1H, ArH), 7.56–7.59 (t, 2H, J = 7.8 Hz, ArH), 8.30–8.32 (dd, 1H, J = 1.6 Hz, 7.9 Hz, ArH), 8.45–8.47 (dd, 1H, J = 1.6 Hz, 4.6 Hz, ArH). MS m/z: 504, 506 (M^+). Anal. calcd. for $C_{26}H_{21}N_2O_2SBr$: C 61.78, H 4.15, N 5.54; found: C 61.57, H 4.38, N 5.36.

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