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A New Regiospecific Method for the Synthesis of Substituted Phenanthridines and Benzo[j]phenanthridines via Aromatic Annelation of 1-N-Benzenesulfonyl-3-[Bis(methylthio)methylene]-1,2,3,4-tetrahydroquinoline-4-one

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Abstract: A new efficient method for the synthesis of substituted phenanthridines, benzo[*j*]phenanthridines and naphtho[2,1-*j*]phenanthridines is described. The method involves reaction of α-oxoketene dithioacetal **2** with allyl (**3a**), methallyl (**3b**), benzyl (**11a-f**) and 1-naphthylmethyl (**20**) magnesium halides followed by cyclization of the resulting carbinolacetals in the presence of $BF_3.Et_2O$ in refluxing benzene. The dihydrophenanthridines thus obtained were aromatized by treatment with a base in the presence of phase transfer catalyst. © 1998 Published by Elsevier Science Ltd. All rights reserved.

Phenanthridines and their benzo analogs have received significant attention due to their widespread occurrence in nature and broad range of biological properties[1]. The phenanthridine ring system is present in many synthetic dye-stuffs[2] and in several metabolites of plant families Fumariaceae, Papaveraceae, Rutaceae and Amaryllidaceae[3]. Among various synthetic routes for the construction of phenanthridine derivatives[1], the methods involving the creation of heterocyclic ring by (i) Bischler-Napieralsky and directed metalation based cyclization of 2-substituted biphenyls[5], (ii) cyclization of substituted 2,2'-disubstituted biphenyls[1a,6], (iii) Pschorr and related reactions[1a,7], (iv) photocyclization of benzanilides and benzylideneanilines[8], (v) cyclization of *o*-halobenzylanilines through benzyne or radical intermediates[10] (vi) cyclodehydration of 2-(anilinomethylene)cyclohexanone[1a], (vii) Beckmann and Schmidt rearrangement of fluorenones[1a,11], (viii) Pd(II) promoted ring closure of N-arylbenzamides[12], (ix) cross coupling between 2-formylbenzeneboronic acid and 2-bromoaniline[13], (x) directed orthometalation and cross coupling reaction of *o*-N-*t*-Boc arylboronic acids with *o*-bromobenzaldehydes and benzamides[14] have been well documented. On the other hand, synthetic approaches based on annelation of quinolines and isoquinolines[15] leading to phenanthridine derivatives have received scant attention, although benzoannelated phenanthridines have been synthesized starting from appropriately 3- and or 4-substituted quinolines and isoquinolines involving photolytic and other cyclizations[1a,8,16].

In continuation of our interest on α–oxoketene dithioacetals[17] and their applications in our aromatic[18] and heteroaromatic[19] annelation methodology, we became interested in developing a new general method for the synthesis of phenanthridines. We have demonstrated that the N-benzenesulfonyl-3-[bis(methylthio)methylene]-1,2,3,4-tetrahydroquinoline-4-one **2** is a versatile 3-carbon electrophilic fragment which can be reacted with allyl and benzyl anions to afford the corresponding regiospecifically substituted phenanthridines and benzo[*j*]phenanthridines in excellent yields. These results are described in this paper.

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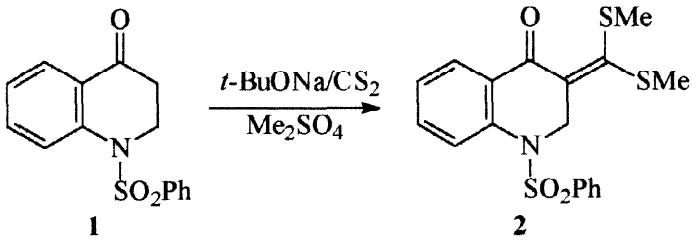
Results and Discussion

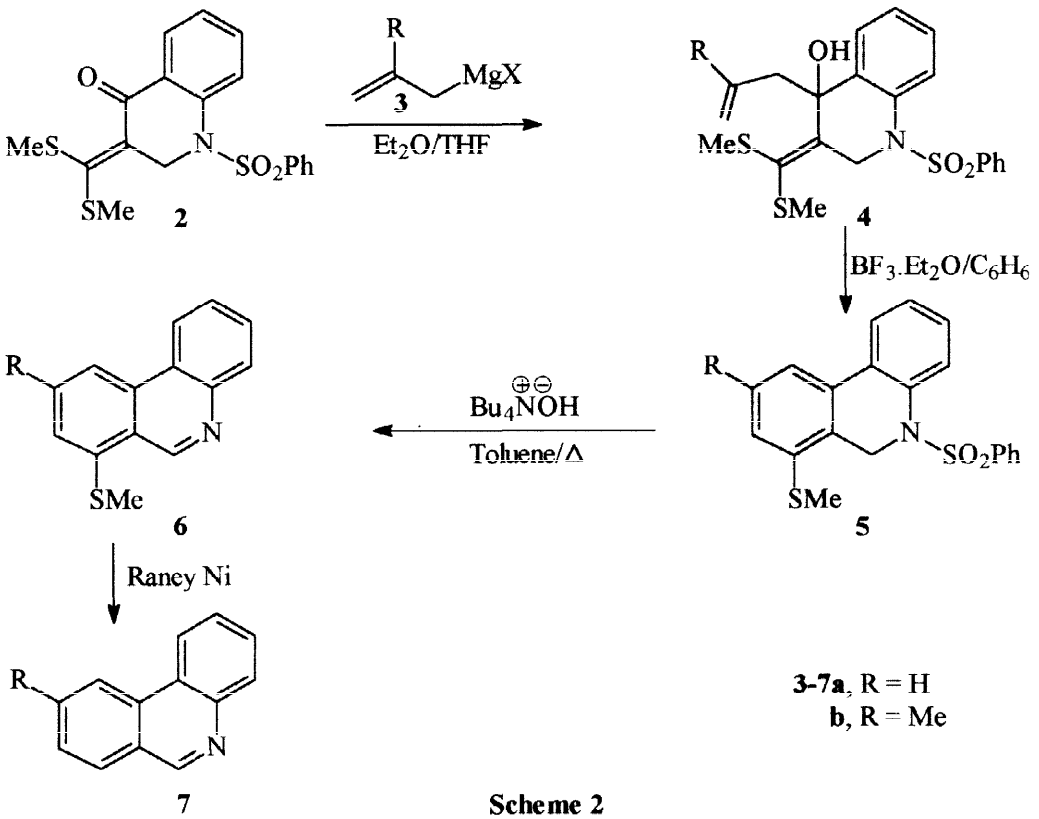
The key intermediate α–oxoketene dithioacetal **2** was prepared from the corresponding ketone **1** according to our earlier reported procedure[20] (Scheme 1). Treatment of **2** with allylmagnesium bromide **3a** in



1 **2**

Scheme 1

dry Et_2O-THF resulted in the formation of the corresponding carbinolacetal **4a** in nearly quantitative yield (TLC) (Scheme 2). The carbinolacetal **4a** was then treated with $BF_3.Et_2O$ in refluxing benzene and the reaction mixture after work-up yielded the corresponding N-benzene sulfonyl-5,6-dihydro-7-(methylthio)-

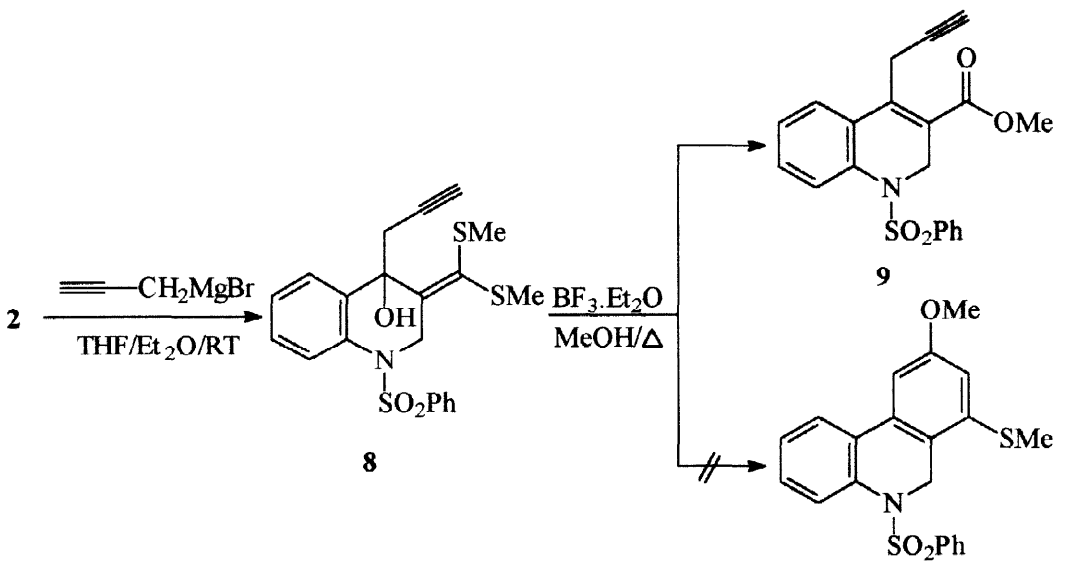


Scheme 2

phenanthridine **5a** in 82% yield. The dihydrophenanthridine **5a** was then aromatized by treatment with sodium hydroxide in refluxing toluene in the presence of phase transfer catalyst to afford the corresponding 7-(methylthio)phenanthridine **6a** in 97% yield. The parent phenanthridine **7a** was obtained in 62% yield from **6a** by subjecting it to dethiomethylation with Raney Ni. The corresponding 9-methylphenanthridine **7b** was similarly obtained by reacting **2** with methallylmagnesium chloride **3b** following the same reaction sequence outlined for compound **7a** (Scheme 2).

In the next experiment, **2** was reacted with propargylmagnesium bromide (Scheme 3) to examine whether the carbinolacetal **8** would undergo solvent assisted cyclization in the presence of $BF_3.Et_2O$ in

methanol to yield the corresponding 9-methoxyphenanthridine **10**, as observed in the case of other oxoketene dithioacetals[18d]. However, the carbinolacetal **8** on treatment with methanolic $BF_3.Et_2O$ yielded only the corresponding hydrolyzed product **9** in 90% yield and no cyclized product was detected in the reaction mixture.



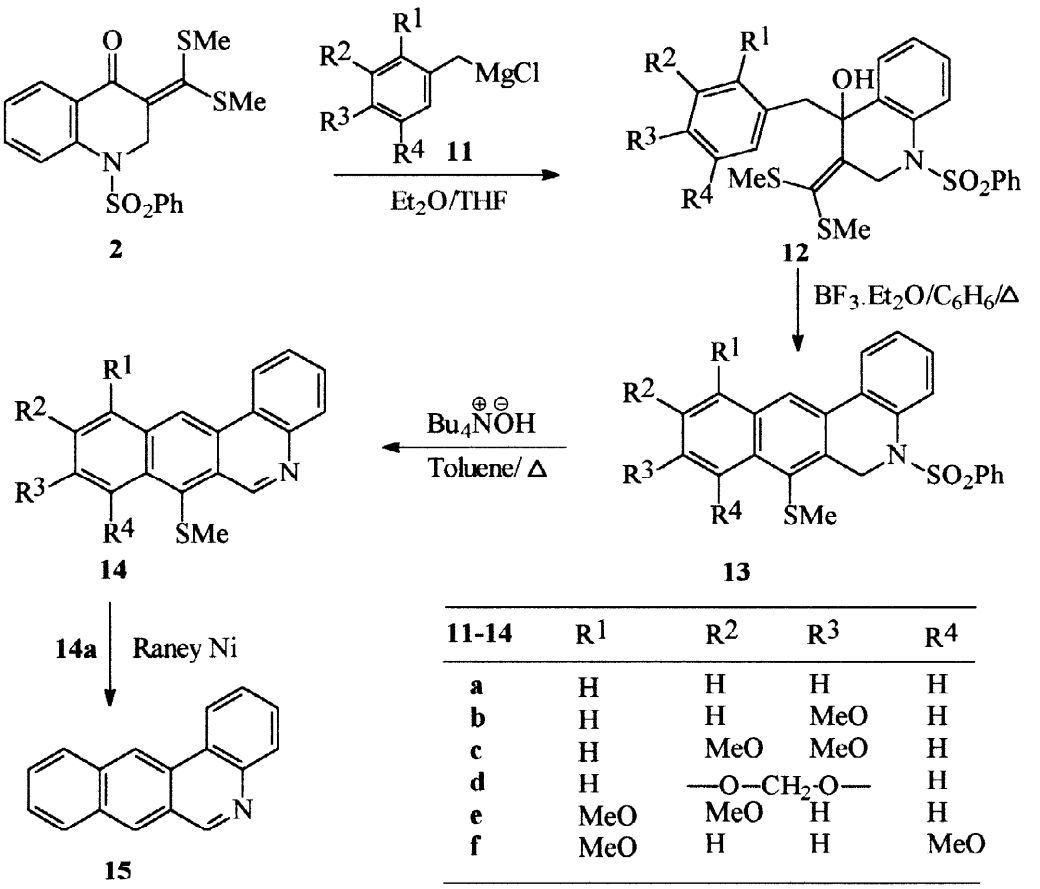
Scheme 3

The protocol was next extended for the synthesis of benzo[*j*]phenanthridines. In a typical experiment, the benzylmagnesium chloride **11a** (Scheme 4) was reacted with **2** to yield the carbinolacetal **12a** in nearly quantitative yield, which was then treated with $BF_3.Et_2O$ in refluxing benzene to afford N-benzenesulfonyl-5,6-dihydro-7-(methylthio)benzo[*j*]phenanthridine **13a** in 79% yield. Aromatization of **13a** under the reported conditions afforded the corresponding 7-(methylthio)benzo[*j*]phenanthridine **14a** in 88% yield. The parent benzo[*j*]phenanthridine **15** was obtained in 77% yield from **14a** by subjecting it to Raney Ni desulfuriztion.

Alternatively, **15** was also prepared starting from β-oxodithioacetal **16**. The required **16** was prepared from **2** following our earlier reported procedure[21] (Scheme 5). Thus, **2** was reacted with sodium borohydride in acetic acid to yield a mixture of **16** and **17** in 40 and 51% yields respectively from which **16** was separated by column chromatography. Reaction of **16** with benzylmagnesium chloride afforded the corresponding carbinolacetal **18** which when treated with $BF_3.Et_2O$ in refluxing benzene yielded N-benzenesulfonyl-5,6-dihydrobenzo[*j*]phenanthridine **19** in 87% yield (Scheme 6). Aromatization of **19** under the described reaction conditions afforded benzo[*j*]phenanthridine **15** in 98% yield, which was found to be identical with that prepared from **14a**.

Interestingly, it must be noted that the benzylmagnesium chloride reacted with **2** in 1,2-fashion exclusively instead of following sequential 1,4- and 1,2-addition mode as observed with other oxoketene dithioacetals[18c-d]. This regioselective addition of **11a** to **2** is unusual and this is the first example to have followed exclusive 1,2-addition mode.

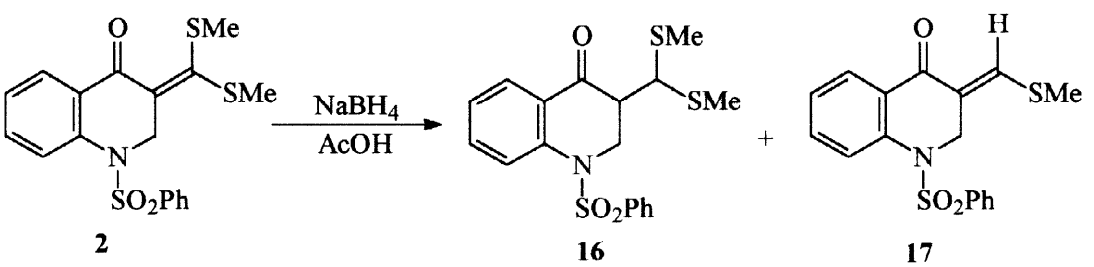
The reaction of alkoxybenzyl Grignard reagents **11b-f** with **2** were next examined with a view to synthesizing oxygenated benzo[*j*]phenanthridines (Scheme 4). The regiobehaviour of alkoxybenzyl Grignard reagents has been extensively investigated in our laboratory[22] and they display exclusive 1,2-preference in their addition reaction to various α–oxoketene dithioacetals. Thus, 4-methoxy benzylmagnesium chloride **11b** was reacted with **2** to yield the corresponding carbinolacetal **12b**, which was then cyclized under the described



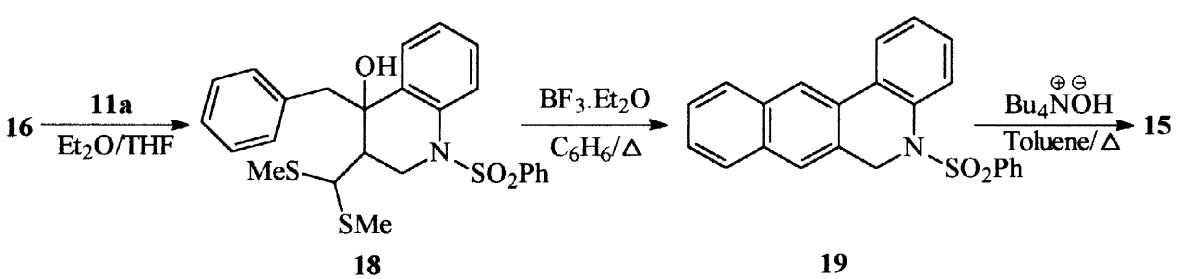
11-14	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	H	MeO	H
c	H	MeO	MeO	H
d	H	—O—CH_2-O—		H
e	MeO	MeO	H	H
f	MeO	H	H	MeO

Scheme 4

reaction conditions to afford the corresponding **13b** in 65% yield. Compound **13b** was then treated with 50% aqueous NaOH in the presence of phase transfer catalyst in toluene to yield the aromatized compound **14b** in 94% yield. Similarly the other dialkoxybenzylmagnesium chloride **11c-f** were reacted with **2** to yield the



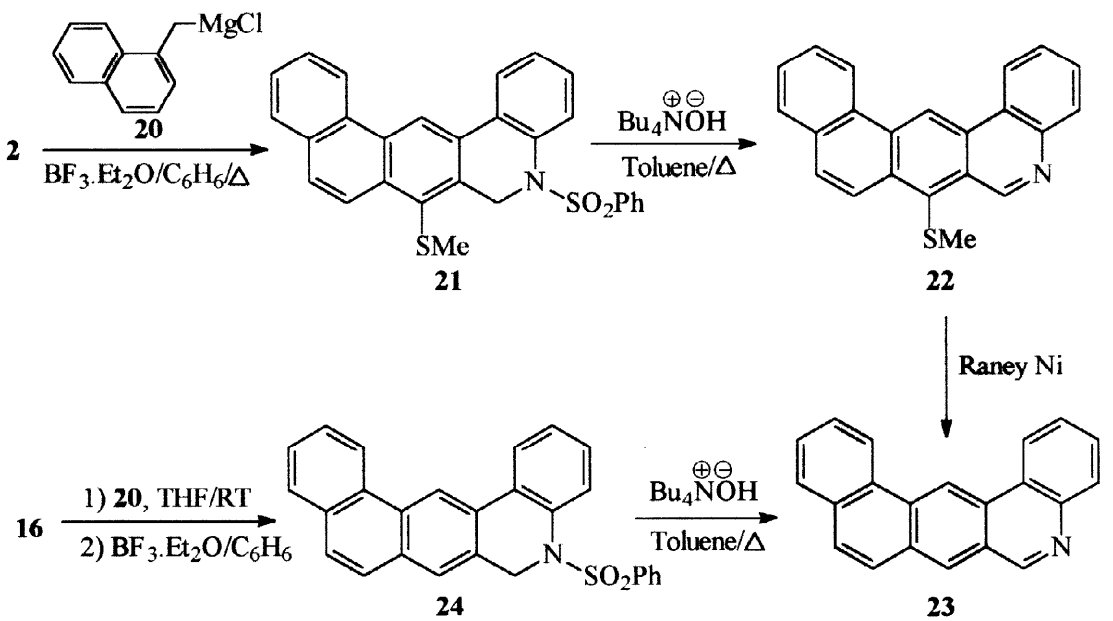
Scheme 5



Scheme 6

corresponding carbinolacetal **12c-f** which were then cyclized and aromatized as described above to afford alkoxysubstituted benzo[*j*]phenanthridines **14c-f** in overall good yields (Scheme 4). The regiospecificity of the cyclization is proved on the basis of NMR data.

The method was successfully extended for the construction of hitherto unreported naphtho[2,1-*j*]phenanthridine ring system as formulated in Scheme 7. Thus, α-naphthylmethylmagnesium chloride **20** was reacted with **2** to yield the corresponding N-benzenesulfonyl-5,6-dihydro-7-(methylthio) naphtho[2,1-*j*]phenanthridine **21**. The parent naphtho[2,1-*j*]phenanthridine **23** was subsequently obtained in 72% yield by aromatization and dethiomethylation of **21** as described earlier. Also, **23** was prepared alternatively by reacting **20** with **16** under the described reaction conditions in 80% overall yield.



Scheme 7

In conclusion, we have demonstrated a new efficient method for the synthesis of phenanthridines, benzo[*j*]phenanthridines and naphtho[2,1-*j*]phenanthridines. The overall transformation describes annelation of quinoline with benzene, naphthalene and phenanthrene in highly regiospecific manner. It may be noted here that the benzo[*j*]phenanthridines are virtually unexplored in the literature probably due to the lack of suitable methods for their synthesis. To our knowledge, this is the first general method for the synthesis of benzo[*j*]phenanthridine in high yield. The only method described in the literature[23] involves the Schmidt rearrangement of benzo[*b*]fluoren-11-one or Beckmann rearrangement of its oxime to yield a mixture of benzo[*b*]- and benzo[*j*]phenanthridones from which the desired benzo[*j*]phenanthridine was isolated by separation, reduction and dehydrogenation in 12% overall yield. Thus, the present synthesis of benzo[*j*]phenanthridines will serve as an exclusive method of preparative importance for this class of compounds. We are currently engaged in the application of this strategy for the synthesis of phenanthridine containing natural products as well as other heterocyclic ring systems.

Experimental Section

General. Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. ^{1}H NMR (300 MHz), ^{13}C NMR (75.43 MHz) spectra were recorded on Bruker ACF-300 spectrometer. A few ^{1}H NMR spectra were

recorded on Varian EM-390 (90 MHz) spectrometer. The chemical shifts are reported in δ (ppm) relative to TMS and the coupling constant (J) are given in Herz (Hz). Mass spectra were obtained on a Jeol JMS-D-300 Mass spectrometer. Elemental analyses were carried out on a Heraeus CHN-O-Rapid analyzer.

All reactions were conducted in oven dried (120°C) glassware under a dry argon or nitrogen atmosphere. All reactions were monitored by analytical TLC on glass plates coated with silica gel (Acme's) containing 13% calcium sulfate as binder and visualization of spots was accomplished by exposure to iodine vapour or by spraying acidic potassium permanganate solution. Column chromatography was carried out using silica gel (Acme's, 60-120 mesh) and eluted with mixture of hexane and ethylacetate.

Diethyl ether was dried by keeping over fused calcium chloride and then over sodium wire. THF was freshly distilled from benzophenone ketyl prior to use. Magnesium turnings (Sisco), sodium borohydride (Aldrich), allyl bromide (Spectrochem), 3-chloro-2-methyl-1-propene (Aldrich), benzyl chloride (SD's), 1-chloromethyl naphthalene (Aldrich) were used as supplied. The alkoxybenzyl chlorides were prepared from their corresponding alkoxy benzaldehydes as per the reported methods.

Raney Nickel (W2)[24] and N-benzenesulfonyl-1,2,3,4-tetrahydroquinolin-4-one (**1**)[25] were prepared according to the literature procedure.

N-Benzenesulfonyl-3-[bis(methylthio)methylene]-1,2,3,4-tetrahydroquinolin-4-one (2). To an ice cooled and well stirred suspension of sodium-*t*-butoxide (100 mmol) in dry benzene (150 mL), a mixture of N-benzenesulfonyl-1,2,3,4-tetrahydroquinolin-4-one **1** (14.35 g, 50 mmol) and carbon disulfide 3 mL (50 mmol) in dry benzene (100 mL) was added and the reaction mixture was stirred for 5 h. Methyl iodide (15 g, 100 mmol) was then slowly added at 0°C and the reaction mixture was further stirred for 6 h at rt. The reaction mixture was then poured into ice cooled water (500 mL), extracted with benzene (2 × 100 mL) and the combined benzene extracts were washed thoroughly with water (3 × 150 mL), dried (Na_2SO_4) and solvent evaporated to give a residue which on trituration with hexane-benzene afforded 15.3 g of **2** as light yellow crystals; yield 78 %; mp 111-112°C; IR (KBr): 1620 cm^{-1}; ^1H NMR (90 MHz): δ 2.29 (s, 3H), 2.47 (s, 3H), 5.19 (s, 2H), 7.30-8.30 (m, 9H). Anal. Calcd for $C_{18}H_{17}NO_3S_3$ (391.534): C, 55.22; H, 4.38; N, 3.58%. Found: C, 55.42; H, 4.26; N, 3.51%.

N-Benzenesulfonyl-3-[bis(methylthio)methyl]-1,2,3,4-tetrahydroquinolin-4-one (16) and N-benzenesulfonyl-3-(methylthio)methylene-1,2,3,4-tetrahydroquinolin-4-one (17). To a well stirred solution of **2** (3.91 g, 10 mmol) in glacial acetic acid (50 mL), sodium borohydride 1.5 g (40 mmol) was added in small portions over a period of 30 min at 5-10°C. The reaction mixture was further stirred at rt for 3 h (monitored by TLC) and then poured onto crushed ice (100 g), followed by extraction with chloroform (3 × 50 mL). The combined chloroform extracts were washed with water (3 × 100 mL), dried (Na_2SO_4) and solvent evaporated to give viscous residue, which on column chromatography over silica gel (hexane-EtOAc, 19:1) gave **16** (1.5 g, 40%) and **17** (1.7 g, 51%) as light yellow crystals.

16: mp 80-81°C; IR (KBr): 1680 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.12 (s, 3H), 2.14 (s, 3H), 2.65 (dd, J = 3.6, 12.9 Hz, 1H), 3.98 (t, J = 15 Hz, 1H), 4.30 (brs, 1H), 4.63 (dd, J = 3.6, 14.7 Hz, 1H), 7.24 (brt, J = 7.2 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.54-7.56 (m, 2H), 7.70 (d, J = 7.5 Hz, 2H), 7.83 (d, J = 8 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.33, 16.69, 47.03, 49.93, 52.14, 124.08, 125.26, 126.77, 127.01; 127.50, 127.98, 128.31, 129.22, 133.02, 134.35, 139.84, 141.97. Anal. Calcd for $C_{18}H_{19}NO_3S_3$ (393.550): C, 54.94; H, 4.87; N, 3.56%. Found: C, 54.76; H, 4.78; N, 3.62%.

17: mp 164-166°C; IR (KBr): 1651 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 2.51 (s, 3H), 4.63 (s, 2H), 7.30-8.10 (m, 10H). Anal. Calcd for $C_{17}H_{15}NO_3S_2$ (345.442): C, 59.11; H, 4.38; N, 4.05%. Found: C, 58.93; H, 4.45; N, 4.10%.

General procedure of the reaction of dithioacetal 2 with allyl, methallyl, benzyl, alkoxy substituted benzyl and 1-(naphthylmethyl)magnesium halides. To an ice cooled solution of appropriate Grignard reagent (prepared from the corresponding halide, 10 mmol) in dry ether (100 mL), the oxoketene dithioacetal **2** (5 mmol) in dry THF (50 mL) was added drop wise and the reaction mixture was further stirred for 1.5 h at rt. The reaction mixture was then poured into saturated aqueous NH_4Cl solution (200 mL), extracted with benzene (2 × 100 mL) and then the combined benzene extracts were washed with water (2 × 100 mL), dried (Na_2SO_4) and solvent evaporated to give the crude carbinolacetals (TLC).

The reaction of β-oxodithioacetal **16** with benzyl and 1-(naphthylmethyl)magnesium chloride was carried out in the similar manner and all the crude carbinolacetals were subjected to cycloaromatization without further purification.

General procedure of $BF_3.Et_2O$ induced cycloaromatization of carbinolacetals. To a solution of crude carbinolacetal (5 mmol) in dry benzene (50 mL), $BF_3.Et_2O$ (1.5 g) was added and the reaction mixture was refluxed for 45 min. The mixture was then ice cooled, poured into saturated aqueous $NaHCO_3$ solution (100 mL), extracted with chloroform (2 × 100 mL), washed with water (2 × 100 mL), dried (Na_2SO_4) and solvent evaporated. Purification of the residue by column chromatography over silica gel (hexane-ethylacetate as the eluent) afforded the cyclized compound and the spectral and analytical data are given below.

N-Benzenesulfonyl-5,6-dihydro-7-(methylthio)phenanthridine (5a). Colourless crystals (ether); mp 160-161°C; yield 82%; IR (KBr): 1573, 1439 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.49 (s, 3H), 4.97 (s, 2H), 6.89-6.94 (m, 3H), 7.01-7.07 (m, 3H), 7.11-7.17 (m, 2H), 7.30-7.42 (m, 2H), 7.55 (dd, J = 9, 3 Hz, 1H), 7.79 (dd, J = 9, 3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.41, 46.17, 120.20, 124.07, 125.89, 126.67, 127.50, 127.80, 128.00, 128.18, 128.53, 129.67, 130.35, 131.29, 132.23, 135.44, 135.63, 137.58; MS (*m/z*, %): 367 (M^+, 30.8), 368 (7.3), 226 (100). Anal. Calcd for $C_{20}H_{17}NO_2S_2$ (367.491): C, 65.37; H, 4.66; N, 3.81%. Found: C, 65.12; H, 4.66; N, 3.81%.

N-Benzenesulfonyl-5,6-dihydro-9-methyl-7-(methylthio)phenanthridine (5b). Colourless crystals (ether); mp 139-140°C; yield 86%; IR (KBr): 2920, 1598, 1556, 1427 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.19 (s, 3H), 2.46 (s, 3H), 4.90 (s, 2H), 6.81-6.92 (m, 4H), 7.10-7.17 (m, 3H), 7.26-7.39 (m, 2H), 7.52 (dd, J = 1.6, 7.5 Hz, 1H), 7.76 (dd, J = 1.5, 7.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.45, 21.19, 46.07, 121.11, 124.01, 126.66, 127.05, 127.45, 127.73, 128.06, 128.30, 130.60, 131.13, 131.83, 135.04, 135.69, 137.49, 137.61. Anal. Calcd for $C_{21}H_{19}NO_2S_2$ (381.518): C, 66.11; H, 5.02; N, 3.67%. Found: C, 65.92; H, 4.88; N, 3.61%.

N-Benzenesulfonyl-5,6-dihydro-7-(methylthio)benzo[*j*]phenanthridine (13a). Colourless crystals (hexane-ether); mp 150-151°C; yield 79%; IR (KBr): 2919, 1580, 1487 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H), 5.38 (s, 2H), 6.59-6.65 (m, 2H), 6.80-6.86 (m, 1H), 7.01-7.05 (m, 2H), 7.32-7.46 (m, 3H), 7.51-7.57 (m, 1H), 7.64-7.71 (m, 3H), 7.82 (dd, J = 1.6, 7.8 Hz, 1H), 8.54 (d, J = 8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.32, 48.71, 123.67, 124.44, 126.07, 126.35, 126.75, 127.29, 127.60, 127.64, 128.00, 128.61, 128.65, 129.16, 130.63, 130.83, 132.01, 133.11, 133.72, 134.93, 136.27, 137.29. Anal. Calcd for $C_{24}H_{19}NO_2S_2$ (417.530): C, 69.04; H, 4.59; N, 3.36%. Found: C, 68.77; H, 4.48; N, 3.33%.

N-Benzenesulfonyl-5,6-dihydro-9-methoxy-7-(methylthio)benzo[*j*]phenanthridine (13b). Light yellow crystals (ether); mp 191°C; yield 65%; IR (KBr): 1496 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 4.01 (s, 3H), 5.41 (s, 2H), 6.65-6.71 (m, 2H), 6.87-6.92 (m, 1H), 7.02-7.05 (m, 2H), 7.12 (dd, J = 2.5, 9 Hz, 1H), 7.34-7.45 (m, 2H), 7.58 (s, 1H), 7.59 (d, J = 8.7 Hz, 1H), 7.67 (dd, J = 3, 9 Hz, 1H), 7.82 (dd, J = 3, 9 Hz, 1H), 7.91 (d, J = 3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.95, 48.85, 55.38, 104.38, 119.08, 123.42, 124.01, 126.80, 127.15, 127.54, 128.09, 128.26, 128.48, 129.05, 130.17, 131.07, 131.93, 135.46, 135.52,

135.99, 137.33, 158.93; MS (*m/z*, %): 447 (M^+, 24.8), 306 (57.4). Anal. Calcd for $C_{25}H_{21}NO_3S_2$ (447.570): C, 67.09; H, 4.73; N, 3.13%. Found: C, 66.87; H, 4.69; N, 3.08%.

N-Benzenesulfonyl-5,6-dihydro-9,10-dimethoxy-7-(methylthio)benzo[*j*]phenanthridine (13c). Light yellow crystals (ether); mp 192°C; yield 67%; IR (KBr): 1497, 1488 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.99 (s, 3H), 4.08 (s, 3H), 5.36 (s, 2H), 6.66-6.71 (m, 2H), 6.88-6.94 (m, 1H), 6.98 (s, 1H), 7.04 (dd, J = 1, 7.5 Hz, 2H), 7.32-7.42 (m, 2H), 7.52 (s, 1H), 7.66 (dd, J = 1.8, 6 Hz, 1H), 7.81 (dd, J = 1.8, 6 Hz, 1H), 7.90 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.05, 48.68, 55.88, 55.97, 104.97, 106.84, 122.11, 124.03, 126.79, 127.53, 127.56, 127.68, 128.02, 128.18, 128.75, 128.84, 130.17, 131.18, 131.90, 133.06, 135.98, 137.41, 149.63, 150.58; MS (*m/z*, %): 477 (M^+, 10.7), 336 (13.1). Anal. Calcd for $C_{26}H_{23}NO_4S_2$ (477.603): C, 65.39; H, 4.85; N, 2.93%. Found: C, 65.23; H, 4.78; N, 3.01%.

N-Benzenesulfonyl-5,6-dihydro-9,10-methylenedioxy-7-(methylthio)benzo[*j*]phenanthridine (13d). Light yellow crystals (ether); mp 199-200°C; yield 73%; IR (KBr): 1489, 1460 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H), 5.35 (s, 2H), 6.07 (s, 2H), 6.68-6.73 (m, 2H), 6.89-6.91 (m, 1H), 6.94 (s, 1H), 7.03 (dd, J = 1, 7.5 Hz, 2H), 7.35-7.40 (m, 2H), 7.45 (s, 1H), 7.64 (dd, J = 1.8, 6 Hz, 1H), 7.81 (dd, J = 1.8, 6 Hz, 1H), 7.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.17, 48.68, 101.40, 102.86, 104.25, 122.70, 124.03, 126.82, 127.54, 127.59, 127.92, 128.06, 128.33, 129.47, 130.26, 130.97, 131.85, 131.93, 133.44, 136.08, 137.47, 147.78, 149.13; MS (*m/z*, %): 461 (M^+, 49.7), 320 (80.8), 273 (100). Anal. Calcd for $C_{25}H_{19}NO_4S_2$ (461.560): C, 65.06; H, 4.15; N, 3.03%. Found: C, 64.89; H, 4.10; N, 2.97%.

N-Benzenesulfonyl-5,6-dihydro-10,11-dimethoxy-7-(methylthio)benzo[*j*]phenanthridine (13e). Colourless crystals (ether); mp 164°C; yield 75%; IR (KBr): 1598, 1463 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H), 3.93 (s, 3H), 4.01 (s, 3H), 5.37 (s, 2H), 6.64-6.69 (m, 2H), 6.86-6.91 (m, 1H), 7.03 (dd, J = 1.2, 9 Hz, 2H), 7.35 (d, J = 9 Hz, 1H), 7.37-7.46 (m, 2H), 7.78 (dd, J = 2, 6 Hz, 1H), 7.82 (dd, J = 2, 6 Hz, 1H), 7.95 (s, 1H), 8.32 (d, J = 9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.40, 48.76, 56.50, 61.11, 115.60, 116.92, 122.63, 124.71, 126.80, 127.57, 127.60, 128.00, 129.50, 130.66, 131.30, 131.80, 133.21, 136.40, 137.46, 142.91, 148.46; MS (*m/z*, %): 477 (M^+, 97.9), 336 (87.0), 289 (100). Anal. Calcd for $C_{26}H_{23}NO_4S_2$ (477.603): C, 65.39; H, 4.85; N, 2.93%. Found: C, 65.21; H, 4.78; N, 2.87%.

N-Benzenesulfonyl-5,6-dihydro-8,11-dimethoxy-7-(methylthio)benzo[*j*]phenanthridine (13f). Yellow crystals (ether); mp 160-161°C; yield 78%; IR (KBr): 1613, 1489 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.92 (s, 3H), 3.95 (s, 3H), 5.42 (s, 2H), 6.66-6.71 (m, 3H), 6.85-6.92 (m, 2H), 7.03-7.07 (m, 2H), 7.33-7.44 (m, 2H), 7.75 (dd, J = 1.5, 9 Hz, 1H), 7.81 (dd, J = 1.5, 9 Hz, 1H), 8.07 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.97, 48.76, 55.82, 57.38, 104.01, 109.33, 117.50, 124.67, 126.62, 126.79, 126.84, 127.47, 127.65, 127.85, 128.50, 128.66, 129.43, 131.21, 131.88, 135.81, 136.33, 137.37, 150.02, 150.48; MS (*m/z*, %): 477 (M^+, 32.2), 336 (98.0). Anal. Calcd for $C_{26}H_{23}NO_4S_2$ (477.603): C, 65.39; H, 4.85; N, 2.93%. Found: C, 65.21; H, 4.92; N, 2.89%.

N-Benzenesulfonyl-5,6-dihydrobenzo[*j*]phenanthridine (19). Colourless crystals (hexane-ether); mp 141°C; yield 87%; IR (KBr): 1443, 1345 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.93 (s, 2H), 6.59 (dd, J = 2, 7.5 Hz, 2H), 6.82 (dd, J = 2, 7.5 Hz, 1H), 7.01 (dd, J = 0.9, 7.5 Hz, 2H), 7.33-7.43 (m, 4H), 7.46 (s, 1H), 7.60 (s, 1H), 7.61-7.64 (m, 1H), 7.70 (d, J = 7.5 Hz, 2H), 7.82 (dd, J = 0.9, 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.40, 122.21, 124.25, 124.54, 126.07, 126.40, 127.03, 127.20, 127.48, 127.67, 127.85, 128.18, 128.46, 128.73, 129.38, 130.78, 131.91, 132.49, 132.87, 136.22, 137.06; MS (*m/z*, %): 371 (M^+, 32.4), 230 (100). Anal. Calcd for $C_{23}H_{17}NO_2S$ (371.458): C, 74.37; H, 4.61; N, 3.77%. Found: C, 74.21; H, 4.52; N, 3.68%.

N-Benzenesulfonyl-5,6-dihydro-7-(methylthio)naphtho[2,1-*j*]phenanthridine (21). Light yellow crystals (ether); mp 184-186°C; yield 69%; IR (KBr): 1508, 1436 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H), 5.37 (s, 2H), 6.52-6.57 (m, 1H), 6.67-6.72 (m, 1H), 6.99-7.08 (m, 2H), 7.34-7.43 (m, 2H), 7.52-7.61 (m, 3H), 7.73-7.76 (m, 2H), 7.81-7.85 (m, 2H), 8.41 (s, 1H), 8.48-8.52 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.48, 48.55, 116.40, 118.02, 122.35, 124.30, 126.67, 126.76, 126.93, 127.48, 127.54, 128.04, 128.29, 128.42, 128.52, 128.63, 129.43, 130.06, 130.09, 131.08, 131.62, 132.78, 135.21, 136.34, 137.27; MS (*m/z*, %): 467 (M^+, 18.2), 326 (53.7), 279 (100). Anal. Calcd for $C_{28}H_{21}NO_2S_2$ (467.611): C, 71.92; H, 4.53; N, 3.00%. Found: C, 71.77; H, 4.32; N, 2.81%.

N-Benzenesulfonyl-5,6-dihydronaphtho[2,1-*j*]phenanthridine (24). Colourless crystals (ether); mp 209-210°C; yield 85%; IR (KBr): 3015, 1676,1658, 1595, 1472 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.99 (s, 2H), 6.55-6.58 (m, 2H), 6.71-6.77 (m, 1H), 7.00-7.06 (m, 2H), 7.39-7.44 (m, 2H), 7.50 (s, 1H), 7.57-7.70 (m, 4H), 7.81-7.88 (m, 3H), 8.42 (s, 1H), 8.53 (dd, J = 1.7, 9.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.10, 117.05, 122.34, 124.18, 125.37, 126.09, 126.69, 126.73, 126.99, 127.52, 127.56, 127.73, 128.31, 128.57, 128.71, 129.03, 129.17, 129.97, 131.03, 131.33, 131.84, 131.95, 136.25, 137.03. Anal. Calcd for $C_{27}H_{19}NO_2S$ (421.518): C, 76.94; H, 4.54; N, 3.32%. Found: C, 76.68; H, 4.23; N, 3.27%.

General procedure for aromatization of dihydrophenanthridines. To a solution of dihydrophenanthridine (3 mmol) in toluene (20 mL), were added catalytic amount of tetrabutyl ammonium bromide and 50% aqueous NaOH (15 mL). The mixture was heated to reflux for 10 h. The reaction mixture was cooled to rt and diluted with water (200 mL), extracted with dichloromethane (3 × 50 mL), dried (Na_2SO_4) and solvent evaporated. The residue on trituration with hexane-ether afforded nearly quantitative yields of the corresponding phenanthridines whose spectral and analytical data are given below.

7-(Methylthio)phenanthridine (6a). Colourless crystals (ether); mp 123-124°C; yield 97%; IR (KBr): 1595, 1563 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.53 (s, 3H), 7.35 (d, J = 7.8 Hz, 1H), 7.57-7.62 (m, 2H), 7.67-7.72 (m, 1H), 8.15 (dd, J = 1.2, 8 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.41 (d, J = 9 Hz, 1H), 9.69 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.93, 118.66, 122.41, 123.68, 123.73, 124.32, 127.02, 128.77, 129.91, 130.53, 133.02, 138.72, 144.13, 149.45; MS (*m/z*, %): 225 (M^+, 100), 226 (22.9). Anal. Calcd for $C_{14}H_{11}NS$ (225.314): C, 74.63; H, 4.92; N, 6.22%. Found: C, 74.37; H, 4.83; N, 6.18%.

9-Methyl-7-(methylthio)phenanthridine (6b). Colourless crystals (ether); mp 103-104°C; yield 84%; IR (KBr): 1563, 1540 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.58 (s, 3H), 2.59 (s, 3H), 7.29 (s, 1H), 7.60-7.75 (m, 2H), 8.12 (s, 1H), 8.16 (dd, J = 1.2, 9 Hz, 1H), 8.50 (dd, J = 1.2, 9 Hz, 1H), 9.69 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.26, 22.49, 118.81, 122.27, 122.45, 123.72, 126.57, 126.88, 128.73, 129.93, 133.12, 138.44, 141.14, 144.38, 149.95; MS (*m/z*, %): 239 (M^+, 100), 224 (78.6). Anal. Calcd for $C_{15}H_{13}NS$ (239.341): C, 75.28; H, 5.47; N, 5.85%. Found: C, 74.80; H, 5.32; N, 5.78%.

7-(Methylthio)benzo[*j*]phenanthridine (14a). Colourless crystals (ether); mp 128-129°C; yield 88%; IR (KBr): 1596, 1552, 1487 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H), 7.41-7.51 (m, 3H), 7.57-7.62 (m, 1H), 7.74-7.78 (m, 1H), 8.05 (dd, J = 1.2, 8.1 Hz, 1H), 8.30 (dd, J = 1.2, 8.1 Hz, 1H), 8.57 (s, 1H), 8.68-8.71 (m, 1H), 10.13 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.92, 122.03, 123.28, 125.78, 126.58, 127.10, 127.45, 128.59, 128.84, 128.96, 129.79, 133.61, 135.09, 142.78, 153.38. Anal. Calcd for $C_{18}H_{13}NS$ (275.374): C, 78.51; H, 4.76; N, 5.09%. Found: C, 78.32; H, 4.65; N, 4.95%.

9-Methoxy-7-(methylthio)benzo[*j*]phenanthridine (14b). Light yellow crystals (ether); mp 175°C; yield 94%; IR (KBr): 1619, 1490 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H), 3.93 (s, 3H), 7.18 (dd, J = 2.4, 9 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 7.76 (d, J = 9 Hz, 1H), 7.98 (s, 1H), 8.09 (d, J = 7.8 Hz, 1H), 8.40 (d, J = 7.8 Hz, 1H), 8.65 (s, 1H), 10.17 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.40,

55.36, 103.18, 121.83, 121.97, 122.03, 123.68, 126.21, 127.14, 127.55, 128.20, 129.87, 130.09, 130.54, 132.34, 135.44, 142.68, 153.36, 158.81; MS (*m/z*, %): 305 (M^+, 100), 306 (22.5), 290 (76). Anal. Calcd for $C_{19}H_{15}NOS$ (305.400): C, 74.72; H, 4.95; N, 4.59%. Found: C, 74.58; H, 5.01; N, 4.63%.

9,10-Dimethoxy-7-(methylthio)benzo[*j*]phenanthridine (14c). Light yellow crystals (ether); mp 179-180°C; yield 92%; IR (KBr): 1619, 1482 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 3H), 3.99 (s, 3H), 4.02 (s, 3H), 6.96 (s, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.91 (s, 1H), 8.06 (d, J = 7.8 Hz, 1H), 8.32 (d, J = 7.8 Hz, 1H), 8.41 (s, 1H), 10.05 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.44, 55.78, 104.01, 105.71, 119.58, 121.62, 123.42, 124.42, 126.71, 128.00, 128.07, 129.69, 130.68, 131.79, 142.67, 150.98, 151.07, 152.92; MS (*m/z*, %): 335 (M^+, 100), 336 (23.2). Anal. Calcd for $C_{20}H_{17}NO_2S$ (335.425): C, 71.62; H, 5.11; N, 4.18%. Found: C, 71.48; H, 5.04; N, 4.11%.

9,10-Methylenedioxy-7-(methylthio)benzo[*j*]phenanthridine (14d). Colourless crystals (ether); mp 235°C; yield 93%; IR (KBr): 1612, 1592 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H), 6.12 (s, 2H), 7.25 (s, 1H), 7.63-7.73 (m, 2H), 8.15 (d, J = 7.8 Hz, 1H), 8.21 (s, 1H), 8.58 (d, J = 8 Hz, 1H), 8.76 (s, 1H), 10.25 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.75, 101.75, 102.36, 103.65, 120.92, 121.99, 123.57, 125.13, 127.13, 128.46, 128.70, 129.93, 132.57, 132.72, 133.20, 143.05, 149.47, 149.80, 153.44; MS (*m/z*, %): 319 (M^+, 100), 320 (22.9). Anal. Calcd for $C_{19}H_{13}NO_2S$ (319.383): C, 71.45; H, 4.10; N, 4.39%. Found: C, 71.38; H, 4.02; N, 4.43%.

10,11-Dimethoxy-7-(methylthio)benzo[*j*]phenanthridine (14e). Colourless crystals (ether); mp 143°C; yield 93%; IR (KBr): 1530, 1384 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.47 (s, 3H), 4.08 (s, 3H), 4.13 (s, 3H), 7.51 (t, J = 7.5 Hz, 1H), 7.64-7.74 (m, 2H), 8.13 (d, J = 9 Hz, 1H), 8.75 (dd, J = 3, 9 Hz, 2H), 9.36 (s, 1H), 10.26 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.12, 56.70, 61.14, 115.29, 117.09, 122.40, 123.60, 123.80, 125.00, 127.10, 127.20, 128.70, 129.70, 129.80, 129.90, 130.31, 143.23, 148.76, 153.56; MS (*m/z*, %): 335 (M^+, 100), 320 (47.4). Anal. Calcd for $C_{20}H_{17}NO_2S$ (335.425): C, 71.62; H, 5.11; N, 4.18%. Found: C, 71.32; H, 5.01; N, 4.20%.

8,11-Dimethoxy-7-(methylthio)benzo[*j*]phenanthridine (14f). Light yellow crystals (ether); mp 169-170°C; yield 98%; IR (KBr): 1615, 1594 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.48 (s, 3H), 3.98 (s, 3H), 4.00 (s, 3H), 6.47-6.82 (m, 2H), 7.63-7.72 (m, 2H), 8.12 (d, J = 9 Hz, 1H), 8.68 (d, J = 9 Hz, 1H), 9.36 (s, 1H), 10.30 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.15, 55.81, 56.75, 104.02, 107.36, 115.77, 122.67, 123.92, 126.45, 127.14, 127.40, 128.24, 128.72, 129.28, 129.69, 135.85, 143.05, 149.62, 151.15, 153.99; MS (*m/z*, %): 335 (M^+, 100), 320 (52.4). Anal. Calcd for $C_{20}H_{17}NO_2S$ (335.425): C, 71.62; H, 5.11; N, 4.18%. Found: C, 71.38; H, 5.04; N, 4.21%.

Benzo[*j*]phenanthridine (15). Colourless crystals (hexane-ether); mp 143-144°C (Lit[23] 143°C); yield 98%; IR (KBr): 1622, 1603 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.53-7.73 (m, 4H), 8.03-8.06 (m, 2H), 8.12 (dd, J = 1.6, 7.8 Hz, 1H), 8.44 (s, 1H), 8.60 (dd, J = 1.6, 7.8 Hz, 1H), 8.92 (s, 1H), 9.29 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 120.17, 123.67, 124.34, 125.95, 126.86, 127.29, 127.98, 128.27, 128.34, 129.85, 131.51, 133.81, 143.13, 154.51. Anal. Calcd for $C_{17}H_{11}N$ (229.281): C, 89.06; H, 4.84; N, 6.11%. Found: C, 89.24; H, 4.78; N, 6.05%.

7-(Methylthio)naphtho[2,1-*j*]phenanthridine (22). Light yellow crystals (ether); mp 196-197°C; yield 91%; IR (KBr): 1635, 1505 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.61-7.84 (m, 6H), 8.19 (dd, J = 1.26, 9.02 Hz, 1H), 8.67-8.78 (m, 3H), 9.69 (s, 1H), 10.28 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.13, 114.71, 116.49, 122.08, 122.80, 123.18, 123.75, 124.69, 125.90, 126.01, 126.45, 127.17, 127.24, 128.08, 128.68, 128.82, 128.92, 132.21, 133.40, 135.17. MS (*m/z*, %): 325 (M^+, 17.4), 310 (13.6). Anal. Calcd for $C_{22}H_{15}NS$ (325.434): C, 81.20; H, 4.65; N, 4.30%. Found: C, 80.84; H, 4.52; N, 4.21%.

Naphtho[2,1-*j*]phenanthridine (23). Colourless crystals (ether); mp 188-190°C; yield 91%; IR (KBr): 3011, 1619, 1602, 1571, 1453 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.43-7.69 (m, 7H), 7.98 (s, 1H), 8.08 (d, J = 8 Hz, 1H), 8.41 (d, J = 8 Hz, 1H), 8.54 (dd, J = 3, 6 Hz, 1H), 9.07 (s, 1H), 9.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.86, 121.95, 122.91, 123.94, 124.42, 126.46, 126.81, 126.93, 127.58, 127.65, 128.10, 128.40, 128.59, 129.07, 129.60, 129.99, 130.68, 131.59, 132.31, 143.57, 153.83. Anal. Calcd for $C_{21}H_{13}N$ (279.341): C, 90.30; H, 4.69; N, 5.01%. Found: C, 90.11; H, 4.60; N, 4.97%.

General procedure for the dethiomethylation of 6a-b, 14a and 22. To a solution of methylthiophenanthridine (2 mmol) in ethanol (25 mL), Raney nickel (W2, 4 times by weight) was added and refluxed for 5 h. The reaction mixture was cooled to rt and filtered through G-3 cintered funnel. The residue was washed with ethanol (20 mL). The bulk of the ethanol was distilled off and chloroform (50 mL) was added. The solution was washed with water (2 × 50 mL), dried (Na_2SO_4) and solvent evaporated. Analytically pure compounds **7a-b**, **15** and **23** were obtained by passing through a short length silica gel column.

Phenanthridine (7a). Colourless crystals (ether); mp 106-107°C (lit.[26] 107-109°C); yield 62%; IR (KBr): 3025, 1608, 1590 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.59-7.81 (m, 4H), 7.96 (d, J = 7.86 Hz, 1H), 8.17 (dd, J = 1.32, 8 Hz, 1H), 8.49 (t, J = 9 Hz, 2H), 9.23 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.73, 122.10, 123.99, 126.27, 126.97, 127.35, 128.59, 128.63, 130.04, 130.87, 132.43, 144.34, 153.39. Anal. Calcd for $C_{13}H_9N$ (179.221): C, 87.12; H, 5.06; N, 7.82%. Found: C, 86.91; H, 4.98; N, 7.78%.

9-Methylphenanthridine (7b). Low melting crystals; (lit.[27] bp 155-160°C/1 mm); yield 78%; IR (KBr): 3064, 2953, 1620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.23 (dd, J = 1.2, 8.1 Hz, 1H), 7.46-7.52 (m, 1H), 7.58-7.64 (m, 2H), 8.02 (s, 1H), 8.12 (dd, J = 1.2, 8.1 Hz, 1H), 8.28 (dd, J = 1.3, 8.2 Hz, 1H), 9.05 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.20, 121.13, 122.01, 123.74, 124.23, 126.59, 128.22, 128.30, 128.91, 129.75, 132.27, 141.18, 144.25, 152.98. Anal. Calcd for $C_{14}H_{11}N$ (193.248): C, 87.01; H, 5.74; N, 7.25%. Found: C, 86.85; H, 5.68; N, 7.14%.

N-Benzenesulfonyl-3-[bis(methylthio)methylene]-4-hydroxy-4-propargyl-1,2,3,4-tetrahydroquinoline (8). To an ice cold solution of propargylmagnesium bromide (prepared from propargyl bromide 1 g, 8 mmol, magnesium turnings 0.5 g and catalytic amount of $HgCl_2$) in dry ether (80 mL), the oxoketene dithioacetal **2** (1.96 g, 5 mmol) in dry THF (40 mL) was added dropwise and the reaction mixture was further stirred for 1.5 h at room temperature. The reaction mixture was then poured into saturated aqueous NH_4Cl solution (200 mL), extracted with benzene (2 × 100 mL) and the combined benzene extracts were washed with water (2 × 100 mL), dried (Na_2SO_4) and solvent evaporated to give a residue, which on trituration with hexane-ether afforded carbinolacetal **8** as colourless crystals, mp 144°C; yield 1.8 g (87%); IR (KBr): 2976, 1578, 1441 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.84 (t, J = 3 Hz, 1H), 2.27 (s, 3H), 2.36 (s, 3H), 2.79 (qd, J = 3, 18 Hz, 2H), 4.39 (s, 1H), 4.59 (d, J = 16.3 Hz, 1H), 5.36 (d, J = 16.3 Hz, 1H), 7.24-7.38 (m, 4H), 7.46-7.57 (m, 4H), 7.67 (dd, J = 1.8, 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.96, 17.69, 33.87, 52.27, 71.52, 74.18, 79.44, 124.68, 126.49, 127.23, 127.41, 128.27, 128.70, 132.78, 134.59, 136.28, 139.09, 143.41. Anal. Calcd for $C_{21}H_{21}NO_3S_3$ (431.599): C, 58.44; H, 4.90; N, 3.25%. Found: C, 58.25; H, 4.95; N, 3.31%.

N-Benzenesulfonyl-1,2-dihydro-3-methoxycarbonyl-4-propargylquinoline (9). To a solution of **8** (1.30 g, 3 mmol) in methanol (20 mL), was added $BF_3.Et_2O$ (0.5 g, 5 mmol). The reaction mixture was refluxed for 2 h, cooled to room temperature and poured into saturated aq. $NaHCO_3$ solution (200 mL). The reaction mixture was then extracted with chloroform (2 × 50 mL), washed with water (2 × 75 mL), dried (Na_2SO_4) and solvent evaporated. Column chromatography of the residue obtained over silica gel with hexane-ethylacetate (9:1) afforded **9** as colourless crystals (ether), mp 107-108°C; yield 1 g (90%); IR (KBr): 2952, 1718 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.88 (t, J = 3 Hz, 2H), 3.36 (d, J = 3 Hz, 2H), 3.82 (s, 3H),

4.63 (s, 2H), 7.22-7.47 (m, 7H), 7.60 (dd, J = 1.5, 8 Hz, 1H), 7.76 (dd, J = 1.3, 8 Hz, 1H). Anal. Calcd for $C_{20}H_{17}NO_4S$ (367.423): C, 65.38; H, 4.66; N, 3.81%. Found: C, 65.13; H, 4.58; N, 3.79%.

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