A Novel One-Step Synthesis of 2-Methoxycarbonylthieno[2,3-*b*]quinolines and 3-Hydroxy-2-methoxycarbonyl-2,3-dihydrothieno[2,3-*b*]-quinolines*

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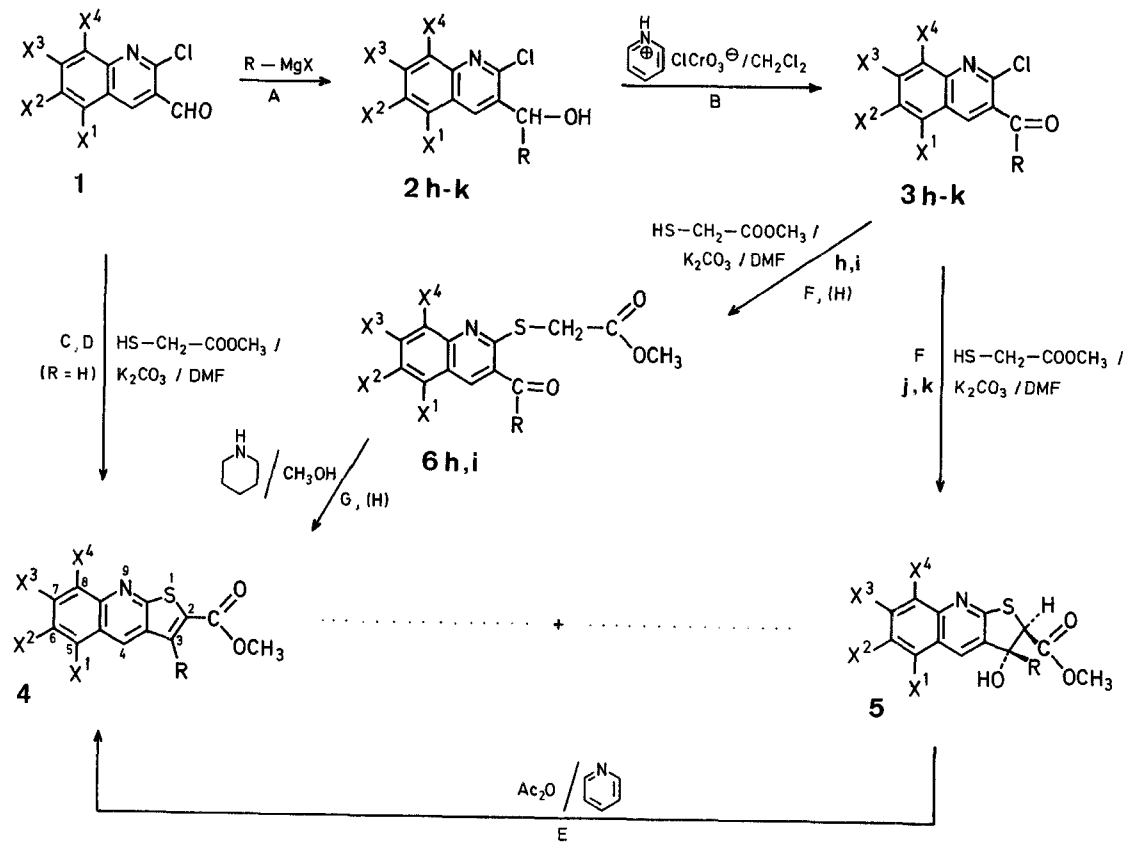
Of the various methods for the synthesis of the thieno[2,3-*b*]quinoline ring[1-4] and 2,3-dihydro derivatives[5,6], only one method[1,2] can be applied to the synthesis of 2-substituted thieno[2,3-*b*]quinolines. This method is a four-step synthesis starting with the ring cleavage of quinoline with thiocarbonyl chloride. Besides the use of the latter reagent, the method has the drawback that the starting quinolines required for the synthesis of 5,6,7- or 6,7,8-trisubstituted 2-methoxycarbonylthieno[2,3-*b*]quinolines are not readily available. Similarly, the synthesis of 2,3-dihydrothieno[2,3-*b*]-quinolines, reported earlier[5,6], involves several steps and it cannot be used to incorporate substituents at position 2 and 3. We now report a novel one-step synthesis of 2-methoxycarbonylthieno[2,3-*b*]quinolines (**4**) and 3-hydroxy-2-methoxycarbonyl-2,3-dihydrothieno[2,3-*b*]quinolines (**5**); these compounds may be substituted in the 3,5,6,7, and/or 8 positions. The synthesis of compounds **5** involves a new type of intermolecular cyclocondensation. The present investigation includes a new, convenient synthesis of 2-chloro-3-acylquinolines (**3**).

2-Chloro-3-formylquinolines (**1a–g**) are prepared according to Ref.[7,8]. The reaction of compounds **1a–g** with methyl mercaptoacetate in dimethylformamide in the presence of anhydrous potassium carbonate affords 2-methoxycarbonylthieno[2,3-*b*]quinolines (**4a–g**) in 70–80% yields along with 3-hydroxy-2-methoxycarbonyl-2,3-dihydrothieno[2,3-*b*]quinolines (**5a–g**) which can be isolated in 10–15% yields by column chromatography. On the other hand, when the reaction of compounds **1a–g** with methyl mercaptoacetate is performed in dimethylformamide/water (9/1) in the presence of potassium carbonate, compounds **5a–g** are obtained in 60–80% yields along with compounds **4a–g** in 10–12% yields.

The I.R. carbonyl absorption band of 3-hydroxy-2-methoxycarbonyl-2,3-dihydrothieno[2,3-*b*]quinolines (**5a–g**) appears between 1735 and 1745 cm^{-1}, which indicates that the hydroxy group is not involved in hydrogen bonding. Further, the coupling constant of the methine protons ($J_{2,3}$) ranged between 8.5 and 9.0 Hz. Based on these observations, the stereochemistry of compounds **5a–g** may be assigned as *trans*. Reaction of compounds **5a–g** with acetic anhydride/pyridine affords the dehydration products **4a–g** in almost quantitative yield.

The reaction of aldehydes **1a** and **1c** with methyl- and phenylmagnesium halides affords the secondary alcohols **2h–k**. Oxidation of these alcohols with pyridinium chlorochromate gives the corresponding 2-chloro-3-acylquinolines (**3h–k**) in nearly quantitative yields. Of these, only quin-



1-6	X¹	X²	X³	X⁴	R (for 2-6 only)
a	H	H	H	H	H
b	H	OCH_3	H	H	H
c	H	OCH_3	OCH_3	H	H
d	OCH_3	OCH_3	OCH_3	H	H
e	H	OC_2H_5	OC_2H_5	H	H
f	H	OCH_3	OCH_3	NO_2	H
g	H	OC_2H_5	OC_2H_5	NO_2	H
h	H	H	H	H	CH_3
i	H	OCH_3	OCH_3	H	CH_3
j	H	H	H	H	C_6H_5
k	H	OCH_3	OCH_3	H	C_6H_5

Table 1. 2-Chloro-3-(1-hydroxyalkyl)-quinolines (**2**) and 2-Chloro-3-acylquinolines (**3**) prepared

Product	Method	Yield [%]	m.p. [°C]	Molecular Formula[a]	M.S. (M^+) *m/e*	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS_{int}) δ [ppm]
2h	A	90	72–73°	$C_{11}H_{10}ClNO$ (207.7)	207	3350 (OH)	1.40–1.50 (d, 3H, —CH$_3$, J = 9.0 Hz); 3.30 (br.s, 1H, OH); 5.05–5.40 (q, 1H, —CH—OH); 7.1–8.0 (m, 4H$_{arom}$); 8.30 (s, 1H, 4-H)
2i	A	96	172–173°	$C_{13}H_{14}ClNO_3$ (267.7)	267	3500 (OH)	1.98–2.05 (d, 3H, CH—CH$_3$, J = 6.3 Hz); 2.60 (br.s, 1H, OH); 3.90, 3.95 (2s, 6H, 2OCH$_3$); 5.15–5.35 (q, 1H, CH—OH); 6.88 (s, 1H, 8-H); 7.28 (s, 1H, 5-H); 8.08 (s, 1H, 4-H)
2j	A	90	89–90°	$C_{16}H_{12}ClNO$ (269.7)	269	3400 (OH)	3.32 (br.s, 1H, OH); 6.10 (s, 1H, CH); 6.9–7.9 (m, 9H$_{arom}$); 8.30 (s, 1H, 4-H)
2k	A	91	152–153°	$C_{18}H_{16}ClNO_3$ (329.8)	329	3300 (OH)	3.52 (br.s, 1H, OH); 3.88 (s, 6H, 2OCH$_3$); 6.18 (s, 1H, CH—OH); 6.88 (s, 1H, 8-H); 7.0–7.45 (m, 6H, 5-H and 5H$_{arom}$); 8.11 (s, 1H, 4-H)
3h	B	97	75–76°	$C_{11}H_8ClNO$ (205.6)	205	1705 ($COCH_3$)	2.70 (s, 3H, CO—CH$_3$); 7.00–8.05 (m, 4H$_{arom}$); 8.25 (s, 1H, 4-H)
3i	B	96	172°	$C_{13}H_{12}ClNO_3$ (265.7)	265	1665 ($COCH_3$)	2.72 (s, 3H, CO—CH$_3$); 3.94, 3.99 (2s, 6H, 2OCH$_3$); 6.99 (s, 1H, 8-H); 7.26 (s, 1H, 5-H); 8.19 (s, 1H, 4-H)
3j	B	92	82–83°	$C_{16}H_{10}ClNO$ (267.7)	267	1685 ($COCH_3$)	6.9–8.0 (m, 9H$_{arom}$); 8.12 (s, 1H, 4-H)
3k	B	97	142–144°	$C_{18}H_{14}ClNO_3$ (327.8)	327	1670 ($COCH_3$)	3.92, 3.98 (2s, 6H, 2OCH$_3$); 7.01 (s, 1H, 8-H); 7.28 (m, 4H, 5-H, 3′-H, 4′-H, 5′-H); 7.72–7.84 (dd, 2H, 2′-H, 6′-H, J_o = 8.10 Hz, J_m = 2.7 Hz); 7.99 (s, 1H, 4-H)

[a] The microanalyses showed the following maximum deviations from the calculated values: C ±0.39; H ±0.36; N ±0.36.

Table 2. 2-Methoxycarbonylthieno[2,3-*b*]quinolines (**4**) prepared

Product	Method	Yield [%]	m.p. [°C]	Molecular formula[a]	M.S. (M^+) *m/e*	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS_{int}, if not stated otherwise) δ [ppm]
4a	C E	85 97	155°	$C_{13}H_9NO_2S$ (243.4)	243	1715 ($COOCH_3$)	3.95 (s, 3H, COOCH$_3$); 7.45–8.12 (m, 5H$_{arom}$); 8.50 (s, 1H, 3-H)
4b	C E	87 95	183–184°	$C_{14}H_{11}NO_3S$ (273.3)	273	1720 ($COOCH_3$)	(TFA/$TMS_{int.}$): 3.60, 3.70 (2s, 6H, OCH$_3$, COOCH$_3$); 7.10 (br.s, 1H, 5-H); 7.50–7.65 (d, 2H, 7-H, 8-H, J_o = 9 Hz); 8.00 (s, 1H, 4-H); 8.93 (s, 1H, 3-H)
4c	C E	80 98	192	$C_{15}H_{13}NO_4S$ (303.3)	303	1720 ($COOCH_3$)	($CDCl_3$/DMSO-d_6/TMS_{int}): 3.70, 3.86, 4.00 (3s, 9H, 2OCH$_3$, COOCH$_3$); 7.20 (s, 1H, 8-H); 7.27 (s, 1H, 5-H); 8.01 (s, 1H, 4-H); 8.54 (s, 1H, 3-H)
4d	C E	85 96	177–178°	$C_{16}H_{15}NO_5S$ (333.4)	333	1715 ($COOCH_3$)	3.92, 3.97, 4.00 (3s, 9H, 3OCH$_3$); 4.10 (s, 3H, COOCH$_3$); 7.20 (s, 1H, 8-H); 8.00 (s, 1H, 4-H); 8.76 (s, 1H, 3-H)
4e	C E	78 96	199	$C_{17}H_{17}NO_4S$ (331.4)	331	1720 ($COOCH_3$)	1.42–1.60 (t, 6H, 2O—CH$_2$—CH$_3$); 3.90 (s, 3H, COOCH$_3$); 4.12–4.34 (q, 4H, 2O—CH$_2$—CH$_3$); 7.05 (s, 1H, 8-H); 7.30 (s, 1H, 5-H); 7.91 (s, 1H, 4-H); 8.30 (s, 1H, 3-H)
4f	C E	79 98.5	195–196°	$C_{15}H_{12}N_2O_6S$ (348.3)	348	1720 ($COOCH_3$); 1520, 1340 (NO_2)	[b]
4g	C E	76 98	154–155°	$C_{17}H_{16}N_2O_6S$ (376.4)	376	1715 ($COOCH_3$); 1520, 1340 (NO_2)	1.45–1.63 (m, 6H, 2O—CH$_2$—CH$_3$); 3.90 (s, 3H, COOCH$_3$); 4.05–4.43 (m, 4H, 2O—CH$_2$—CH$_3$); 7.46 (s, 1H, 5-H); 7.95 (s, 1H, 4-H); 8.34 (s, 1H, 3-H)
4h	H G	85 92	159	$C_{14}H_{11}NO_2S$ (257.3)	257	1720 ($COOCH_3$)	2.72 (s, 3H, CH$_3$); 3.88 (s, 3H, COOCH$_3$); 7.32–8.19 (m, 4H$_{arom}$); 8.39 (s, 1H, 4-H)
4i	H G	90 88	241–242°	$C_{16}H_{15}NO_4S$ (317.4)	317	1725 ($COOCH_3$)	2.74 (s, 3H, CH$_3$); 3.96, 3.98, 4.00 (3s, 9H, 3OCH$_3$); 7.02 (s, 1H, 8-H); 8.20 (s, 1H, 4-H)
4j	C E	87 95	201–202°	$C_{19}H_{13}NO_2S$ (319.4)	319	1730 ($COOCH_3$)	3.78 (s, 3H, COOCH$_3$); 7.30–8.15 (m, 9H$_{arom}$); 8.23 (s, 1H, 4-H)
4k	C E	84 93	204°	$C_{21}H_{17}NO_4S$ (379.4)	379	1730 ($COOCH_3$)	3.76 (s, 3H, COOCH$_3$); 3.90 4.00 (2s, 6H, 2OCH$_3$); 7.00 (s, 1H, 8-H); 7.38–7.48 (m, 6H, 5-H) + 4H$_{arom}$)

[a] The microanalyses showed the following maximum deviations from the calculated values: C ±0.37; H ±0.33, N ±0.38.

[b] The ^{1}H-N.M.R. spectrum could not be recorded because the poor solubility of compound **4f** in the usual N.M.R. solvents.

Table 3. 3-Hydroxy-2-methoxycarbonyl-2,3-dihydrothieno[2,3-*b*]quinolines (**5**) prepared

Product	Method	Yield [%]	m.p. [°C]	Molecular Formula[a]	M.S. (M^+) *m/e*	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. (solvent/TMS_{int}) δ [ppm]
5a	D	75	147°	$C_{13}H_{11}NO_3S$ (261.3)	261	3300 (OH); 1735 ($COOCH_3$)	($CDCl_3$/DMSO-d_6): 3.60 (br.s, 1H, CH—OH); 3.76 (s, 3H, $COOCH_3$); 4.38–4.48 (d, 1H, CH—OH, J = 9 Hz); 5.14–5.24 (d, 1H, CH—$COOCH_3$, J = 9 Hz); 7.3–8.0 (m, $5H_{arom}$)
5b	D	75	189°	$C_{14}H_{13}NO_4S$ (291.3)	291	3350 (OH); 1740 ($COOCH_3$)	($CDCl_3$/DMSO-d_6): 3.60 (br.s, 1H, CH—OH); 3.70 (s, 3H, $COOCH_3$); 3.78 (s, 3H, OCH_3); 4.32–4.42 (d, 1H, CH—OH, J = 9 Hz); 5.26–5.36 (d, 1H, CH—$COOCH_3$, J = 9 Hz); 7.25 (br.s, 1H, 5-H); 7.46 (br.s, 1H, 7-H); 7.56 (br.s, 1H, 8-H); 8.04 (s, 1H, 4-H)
5c	D	80	195°	$C_{15}H_{15}NO_5S$ (321.4)	321	3300 (OH); 1740 ($COOCH_3$)	[b]
5d	D	73	165–166°	$C_{16}H_{17}NO_6S$ (351.4)	351	3400 (OH); 1735 ($COOCH_3$)	($CDCl_3$): 3.72 (br.s, 4H, CH—OH, $COOCH_3$); 3.82, 3.90, 3.98 (3s, 9H, $3OCH_3$); 4.39–4.48 (d, 1H, CH—OH, J = 8.5 Hz); 5.69–5.78 (d, 1H, CH—$COOCH_3$, J = 8.5 Hz); 7.06 (s, 1H, 8-H); 8.15 (s, 1H, 4-H)
5e	D	65	120–121°	$C_{17}H_{19}NO_5S$ (349.4)	349	3350 (OH); 1735 ($COOCH_3$)	($CDCl_3$): 1.44–1.62 (t, 6H, $2O—CH_2—CH_3$); 3.67 (br.s, 1H, CH—OH); 3.75 (s, 3H, $COOCH_3$); 4.25–4.46 (m, 5H, $2O—CH_2—CH_3$, CH—OH); 5.51–5.61 (d, 1H, CH—$COOCH_3$, J = 9 Hz); 7.18 (s, 1H, 8-H); 7.35 (s, 1H, 5-H); 8.00 (s, 1H, 4-H)
5f	D	74	207–208°	$C_{15}H_{14}N_2O_7S$ (366.35)	366	3400 (OH); 1740 ($COOCH_3$); 1520, 1335 (NO_2)	[b]
5g	D	76	178–179°	$C_{17}H_{18}N_2O_7S$ (394.4)	394	3380 (OH); 1740 ($COOCH_3$); 1510, 1340 (NO_2)	($CDCl_3$/DMSO-d_6): 1.2–1.6 (m, 6H, $2O—CH_2—CH_3$); 3.65 (br.s, 1H, CH—OH); 3.73 (s, 3H, $COOCH_3$); 4.00–4.43 (m, 5H, $2O—CH_2—CH_3$, CH—OH); 5.54–5.68 (d, 1H, CH—$COOCH_3$, J = 8.5 Hz); 7.40 (s, 1H, 5-H); 7.95 (s, 1H, 4-H)
5j	D	80	194°	$C_{19}H_{15}NO_3S$ (337.4)	337	3250 (OH); 1745 ($COOCH_3$)	($CDCl_3$): 3.69 (s, 3H, $COOCH_3$); 3.83 (s, 1H, OH); 4.60 (s, 1H, CH—$COOCH_3$); 7.25–7.93 (m, $10H_{arom}$)
5k	D	81	181	$C_{21}H_{19}NO_5S$ (397.45)	397	3300 (OH); 1740 ($COOCH_3$)	($CDCl_3$/DMSO-d_6): 3.63 (s, 3H, $COOCH_3$); 3.82 (br.s, 4H, OCH_3, OH); 3.90 (s, 3H, OCH_3); 4.70 (s, 1H, CH—$COOCH_3$); 6.90 (s, 1H, 8-H); 7.0–7.6 (m, 7H, 5-H, 4-H, $5H_{arom}$)

[a] The microanalyses showed the following maximum deviations from the calculated values: C ±0.29; H ±0.32; N ±0.38.

[b] The ^{1}H-N.M.R. spectrum could not be recorded because of the poor solubility of the compound in the usual N.M.R. solvents.

olines **3j** and **3k** undergo intermolecular cyclocondensation with methyl mercaptoacetate to give compounds **4j, k** and **5j, k** whereas under the same conditions quinolines **3h** and **3i** undergo a substitution reaction to give the 2-methoxycarbonylmethylthio-3-acylquinolines **6h** and **6i**, respectively. Addition of piperidine to the methanolic solution of compounds **6h, i** leads to intramolecular cyclocondensation to give the 2-methoxycarbonylthieno[2,3-*b*]quinolines **4h, i**. Compounds **4h, i** can also be obtained from quinolines **3h, i** in a one-pot reaction with methyl mercaptoacetate in the presence of piperidine.

Melting points were measured in a sulfuric acid bath and are uncorrected. Mass spectra were recorded on a JEOL-JMS-D 300 mass spectrometer. ^{1}H-N.M.R. spectra were recorded on a Perkin-Elmer R-32 instrument except for compounds **2b**, **2g**, and **3g** the spectra of which were recorded on a Varian EM-360 L spectrometer. Typical working procedures are given in the following.

2-Chloro-3-(1-hydroxyethyl)-6,7-dimethoxyquinoline (2i):

Method A: A solution of methylmagnesium iodide is prepared from magnesium turnings (0.9 g, 0.04 mol) and methyl iodide (5.6 g, 0.04 mol) in ether (50 ml). To this solution is added, dropwise and with stirring, a solution of 2-chloro-3-formyl-6,7-dimethoxyquinoline (**1c**; 5.0 g, 0.02 mol) in tetrahydrofuran (50 ml) and the mixture is stirred at 30°C for 10 min. Aqueous 10% ammonium chloride (100 ml) is then added and the organic material is extracted with ethyl acetate (2 × 100 ml). The extract is dried with sodium sulphate and evaporated. Addition of petroleum ether to the residue leads to formation of a solid. This product is isolated by suction and recrystallized from chloroform/petroleum ether (30/70).

3-Acetyl-2-chloro-6,7-dimethoxyquinoline (3i):

Method B: To a well stirred solution of compound **2i** (5.3 g, 0.02 mol) in dry dichloromethane (50 ml) is added pyridinium chlorochromate (6.6 g, 0.03 mol) and the mixture is stirred at room temperature (31°C) for 45 min. The suspension is extracted with ether (3 × 100 ml), the extract dried with sodium sulphate and evaporated. The residue is passed through a short band of Florisil® using chloroform/ethyl acetate (9/1) as eluent. Removal of the solvent gives a solid which is recrystallized from methanol.

2-Methoxycarbonylthieno[2,3-*b*]quinoline (4a):

Method C: A mixture of 2-chloro-3-formylquinoline (**1a**; 15 g, 0.07 mol), methyl mercaptoacetate (8 g, 0.07 mol), anhydrous potassium carbonate (11.5 g, 0.08 mol), and dry tetrahydrofuran (75 ml)

is stirred at room temperature (30–35 °C) for 3 h. Addition of water (250 ml) then leads to the formation of a solid which is isolated by suction and washed with cold water (250 ml). The solid product is purified by column chromatography on silica gel using chloroform as eluent. The eluate is evaporated and the residual product **4a** recrystallized from petroleum ether/chloroform (80/20).

3-Hydroxy-2-methoxycarbonyl-2,3-dihydrothieno[2,3-*b*]quinoline (5a):

Method D: A mixture of 2-chloro-3-formylquinoline (**1a**; 16 g, 0.08 mol), methyl mercaptoacetate (9.6 g, 0.09 mol), potassium carbonate (12.4 g, 0.09 mol), dimethylformamide (72 ml), and water (8 ml) is stirred at room temperature (30–35 °C) for 4–5 h. Dilution of the mixture with water (300 ml) then leads to precipitation of a solid which is isolated by suction, dried, and purified by column chromatography on silica gel using chloroform and chloroform/methanol (70/30) as eluents. Elution with chloroform gives product **4a**; product **5a** is obtained by elution with chloroform/methanol. Compound **4a** is recrystallized from petroleum ether/chloroform (80/20) and compound **5a** from methanol.

The similarly prepared compounds **5b, f, g** are recrystallized from dimethylformamide and compounds **5c, d, e, j, k** from methanol.

2-Methoxycarbonylthieno[2,3-*b*]quinoline (4a):

Method E: A mixture of compound **5a** (12 g, 0.04 mol), acetic anhydride (10 ml), and pyridine (0.5 ml) is stirred at 50 °C for 30 min. Addition of water (100 ml) then leads to precipitation of a solid which is isolated by suction, washed with water (500 ml), dried, and cyrstallized from petroleum ether/chloroform (80/20) to afford **4a** in quantitative yield.

3-Acetyl-2-(methoxycarbonylmethylthio)-quinoline (6h):

Method F: A mixture of 3-acetyl-2-chloroquinoline (**3h**; 2.05 g, 0.01 mol), methyl mercaptoacetate (1.06 g, 0.01 mol), potassium carbonate (1.38 g, 0.01 mol), and dry dimethylformamide (20 ml) is stirred at room temperature (30 °C) for 2.5 h. Water (75 ml) is then added, the resultant solid product isolated by suction, and recrystallized from chloroform/methanol (20/80); yield of **6h**: 2.5 g (91 %); m.p. 140–141 °C.

$C_{14}H_{13}NO_3S$	calc.	C 61.09	H 4.72	N 5.09
(275.3)	found	61.05	5.06	5.00

M.S.: m/e = 275 (M^+).

I.R. (KBr): ν = 1740 ($COOCH_3$); 1680 cm^{-1} (CO—CH_3).

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 2.62 (s, 3H, CO—CH_3); 3.65 (s, 3H, $COOCH_3$); 3.88 (s, 2H, S—CH_2—$COOCH_3$); 7.30–7.77 (m, 4H_{arom}); 8.43 ppm (s, 1H, 4—H).

3-Acetyl-6,7-dimethoxy-2-(methoxycarbonylmethylthio)-quinoline (6i):

Method F is used as above; yield of **6i**: 95 %; m.p. 170 °C.

$C_{16}H_{17}NO_5S$	calc.	C 57.31	H 5.07	N 4.17
(335.2)	found	57.27	4.96	4.41

M.S.: m/e = 335 (M^+).

I.R. (KBr): ν = 1745 ($COOCH_3$); 1675 cm^{-1} (CO—CH_3).

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 2.61 (s, 3H, CO—CH_3); 3.70 (s, 3H, S—CH_2—$COOCH_3$); 3.92 (s, 2H, S—CH_2—$COOCH_3$); 3.97, 4.00 (2s, 6H, 2OCH_3); 7.00 (s, 1H, 8-H); 7.10 (s, 1H, 5-H); 8.30 ppm (s, 1H, 4-H).

2-Methoxycarbonyl-3-methylthieno[2,3-*b*]quinoline (4h):

Method G: A solution of compound **6h** (2.75 g, 0.01 mol) and piperidine (0.85 g, 0.01 mol) in methanol (25 ml) is stirred at room temperature (30–33 °C) for 3.5 h. Removal of methanol under reduced pressure followed by addition of water (75 ml) to the residue affords product **4h** which is recrystallized from petroleum ether/chloroform (80/20); yield: 2.36 g (92 %).

2-Methoxycarbonyl-3-methylthieno[2,3-*b*]quinoline (4h):

Method H: A mixture of 2-chloro-3-acetylquinoline (**3h**; 4.1 g, 0.02 mol), piperidine (1.6 g, 0.02 mol), methyl mercaptoacetate (2.1 g, 0.02 mol), and dry dimethylformamide (30 ml) is stirred at room temperature (30–32 °C) for 2.5 h. Water (75 ml) is then added and the resultant solid product isolated by suction, dried, and recrystallized from petroleum ether/chloroform (80/20); yield of **4h**: 2.18 g (85 %).

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