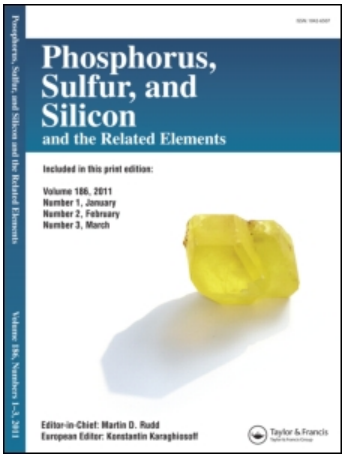

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New Syntheses of Selenolo(2,3-*b*)quinoline-2-carboxylic Ethyl Esters

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New Syntheses of Selenolo(2,3-*b*)quinoline-2-carboxylic Ethyl Esters

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*The compounds selenolo(2, 3-b)quinoline-2-carboxylic ethyl esters were synthesized in varying yields by the reaction of (**i**) 3-(2-chloro-3-quinolyl)acrylic acids, (**ii**) 3-(2-chloro-3-quinolyl)acryloyl chlorides, and (**iii**) 2-chloro-3-(1,2-dibromo-3-quinolyl)acrylic ethyl esters with sodium diselenide in ethanol under a nitrogen atmosphere.*

Keywords Bromination; chlorination; condensation; cyclization using sodium diselenide; dehydroxychlorination; esterification; hydrolysis; Vilsmeier–Haack reaction

INTRODUCTION

Recent advances in the area of organoselenium chemistry have been driven by the potential applications of selenium compounds in modern organic synthesis,[1] biochemistry,[2] photography,[3] as precursors for metal organic chemical vapor deposition of semiconducting materials,[4] ligand chemistry,[5] enzyme mimics, etc. In addition to these applications, some of the organic selenium compounds have been tested as antibacterial, antiviral, antifungal, antiparasitic, antiradiation, antiinflammatory, antihistamine, and anticancer agents.[6] Some of them also have hypnotic, analgesic, and anesthetic effects. Selenium analogs of phenothiazines (promazines) have a comparable action as tranquilizing agents.[6] Benzo[*b*]selenien-3-ylacetic acid displays auxin-like[7] activity similar to indole-3-acetic acid. The role of organoselenium compounds prompted us to explore simpler methods to synthesize selenium analogues from the appropriately functionalized quinoline systems.

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Early workers from our laboratory have synthesized selenolo (2,3-*b*)quinolines[8–10] using 2-quinolone-3-ethanols and 2-chloro-3-vinyl quinolines as the starting compounds.

We recently reported a new synthesis of selenolo(2,3-*b*)quinoline-2-carboxylic ethyl esters[11] in good yields by the reaction of 3-(2-chloro-3-quinolyl)acrylic ethyl esters, with sodium diselenide in an ethanol medium under a nitrogen atmosphere.

As part of our current studies on the development of new routes to the synthesis of selenium heterocycles, we now report the reaction of the following intermediates with sodium diselenide individually:

1. 3-(2-chloro-3-quinolyl)acrylic acids,
2. 3-(2-chloro-3-quinolyl)acryloyl chlorides, and
3. 2-chloro-3-(1,2-dibromo-3-quinolyl)acrylic ethyl esters.

RESULTS AND DISCUSSION

The role of Na_2Se_2[12] is excellent where it is used for the introduction of selenium into organic molecules. An ethanolic solution of sodium diselenide is advantageous in that it provides a superior solvent for nucleophilic displacement reactions in water-insoluble or hydrolysis-sensitive organic compounds.

Shanmugam et al.[13–15] from our laboratory were the first to synthesize selenolo(2,3-*b*)quinolines utilizing 2-quinolone-3-ethanols and 2-chloro-3-vinyl quinolines as starting compounds. However, the preparation of these reported precursors involved tedious procedures.

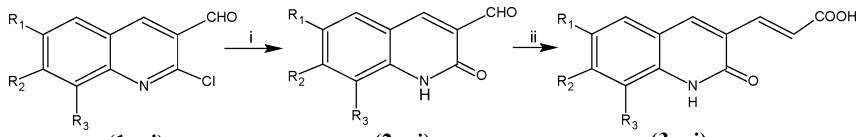
Herein, we report simple and convenient methods to synthesize selenolo(2,3-*b*)quinolines from the readily accessible precursors 2-chloro-3-formyl quinoline and its derivatives (Scheme 1).

2-chloro-3-formyl quinolines were in turn prepared by reacting acetanilides with Vilsmeir reagent ($POCl_3$/DMF).[16] This pocedure involves the conversion of acetanilides into 2-chloro-3-formyl quinolines using a Vilsmeier reagent.

2-chloro-3-formyl quinolines (**1**) were converted to the oxo compounds (**2**) by refluxing with 4M of HCl. These were then treated with malonic acid, pyridine, and piperidine to furnish 3-(2-oxo-1, 2-dihydro-3-quinolyl)acrylic acids[17] (**3**).

(**i**). Compound (**4a**) was synthesized by the dehydroxychlorination of 3-(2-oxo-1,2-dihydro-3-quinolyl)acrylic acid (**3a**) with freshly distilled phosphorus oxychloride. The structure of the resulting compound was attested through the following spectral values.

The IR spectrum of the solid displayed bands for (—C═O) at 1690 cm^{-1}, (—C═Cl) at 1010 cm^{-1}, and (—OH) at 3401 cm^{-1}. Its ^1H



(1a–i) **(2a–i)** **(3a–i)**

(**a**) R_1=R_2=R_3=H, (**b**) R_1=CH_3, R_2=R_3=H, (**c**) R_1=R_3=H, R_2=CH_3, (**d**) R_1=R_2=H, R_3=CH_3, (**e**) R_1=OCH_3, R_2=R_3=H, (**f**) R_1=R_3=H, R_2=OCH_3, (**g**) R_1=R_2=H, R_3=OCH_3, (**h**) R_1=R_3=CH_3, R_2=H, (**i**) R_1=H, R_2=R_3= –CH=CH–CH=CH–.

SCHEME 1 (i) 4M HCl (ii) Malonic acid, pyridine, piperidine.

NMR spectra showed a singlet at 8.38 δ for C_4—H; —COOH peak at 12.95δ; doublets for vinyl protons at 6.54δ, 8.09δ with J = 16Hz typical of a trans configuration; and a multiplet for C_5, C_6, C_7, and C_8—H at 7.63δ–7.84 δppm. Its mass spectra with the m/e value at 233(M^+) and 235(M+2) (one third the intensity of the parent peak); the elemental analysis (C, 61.71; H, 3.11; N, 5.67%) corroborated with the molecular formula $C_{12}H_8ClNO_2$. Thus, the structure of (**4a**) was confirmed as 3-(2-chloro-3-quinolyl)acrylic acid (**4a**) (Scheme 2).

(**4a**) was then refluxed with sodium diselenide to give rise to the expected product, selenolo(2,3-*b*)quinoline-2-carboxylic acid (**9**).

The resulting yellow-colored crystals exhibited IR absorption bands at 1726 cm^{-1} and 1191 cm^{-1} characteristic of (—C=O), and (—C—O) of ester with the disappearance of an acid peak at 1690 cm^{-1}, (—OH) peak at 3401 cm^{-1}, and (—C=Cl) at 1010 cm^{-1}.

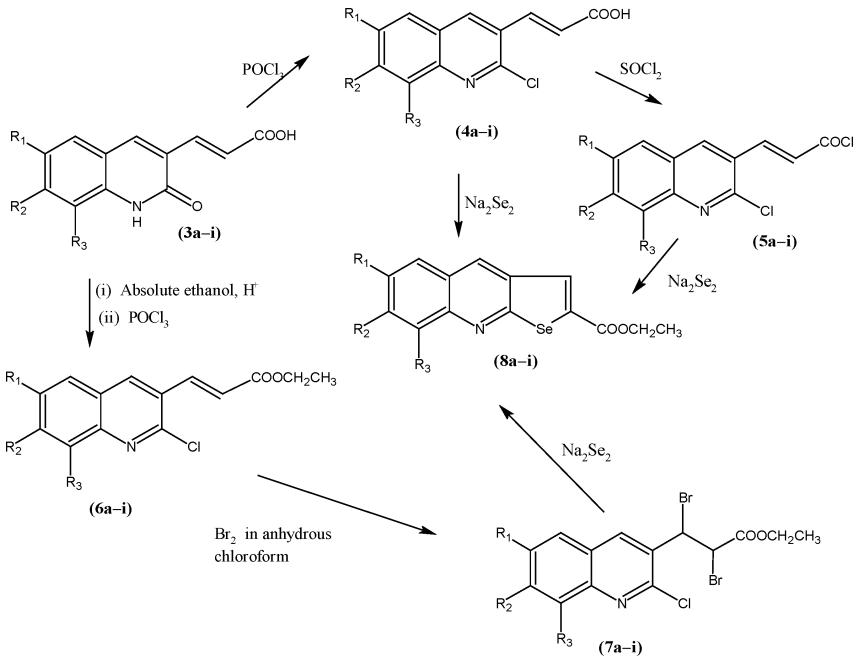
The ^{1}H NMR spectrum of the product exhibited multiplet for 6 protons at 7.28–8.01δ(C_3, C_4, C_5, C_6, C_7, C_8—H), a 2-proton quartet at 4.30δ(J = 7Hz, $-OCH_2$) and a 3-proton triplet at 1.40δ (J = 7Hz, $-CH_3$ of ester).

The NMR data clearly showed the disappearance of —CH=CH— and —COOH groups. The mass spectrum of the product showed the molecular ion peak at m/z = 304. The elemental analysis (C, 54.95; H, 3.32; N, 4.49%) agreed with the molecular formula $C_{14}H_{11}NO_2$ Se attesting the structure of the product as selenolo(2,3-*b*)quinoline-2-carboxylic ethyl ester (**8a**), thus attesting the esterification of the acid group.

(**ii**). The next intermediate compound (**5a**) was synthesized by refluxing 3-(2-chloro-3-quinolyl)acrylic acid (**4a**) with thionyl chloride. The structure of the recrystallized product was identified on the basis of the following spectral and analytical data.

In IR spectrum —COCl peak appeared at 1780 cm^{-1}; —C=Cl at 1020 cm^{-1}.

In the ^{1}H NMR spectrum, the doublets appeared at 6.78δ (J = 16Hz, —CH=C<u>H</u>—) and 8.23δ (J = 16Hz, —C<u>H</u>=CH—); and multiplets appeared



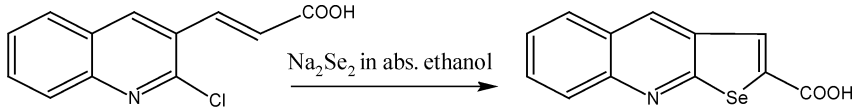
(**a**) R_1=R_2=R_3=H, (**b**) R_1=CH_3, R_2=R_3=H, (**c**) R_1=R_3=H , R_2=CH_3, (**d**) R_1=R_2=H, R_3=CH_3, (**e**) R_1=OCH_3, R_2=R_3=H, (**f**) R_1=R_3=H, R_2=OCH_3, (**g**) R_1=R_2=H, R_3=OCH_3, (**h**) R_1=R_3=CH_3, R_2=H, (**i**) R_1=H, R_2=R_3=—CH=CH—CH=CH—.

SCHEME 2

at 7.59–7.92δ for C_5, C_6, C_7, and C_8—H; and a singlet appeared at 8.48δ (C_4—H).

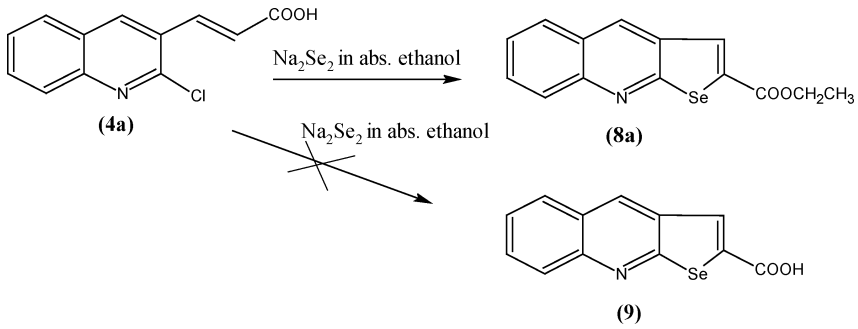
In mass spectrum, the molecular ion peak appeared at m/e 252(M^+), 254(M+2), and 256(M+4).

The elemental analysis (C, 56.91; H, 2.65; N, 5.23%) was compatible with the molecular formula $C_{12}H_7Cl_2NO$, attesting the structure as 3-(2-chloro-3-quinolyl)acryloyl chloride (**5a**) (Scheme 2).



(**4a**) (**9**)

SCHEME 3



SCHEME 4

To a freshly prepared solution of sodium diselenide in abs. ethanol, 3-(2-chloro-3-quinolyl)acryloyl chloride (**5a**) was added and refluxed. The pasty mass of the first product was left as an unidentified one.

The spectral and analytical data of the second product is given below.

IR absorption bands of the solid displayed bands at 1726 cm^{-1} and 1192 cm^{-1}, with the disappearance of —COCl peak at 1780 cm^{-1} and —C=Cl at 1020 cm^{-1}.

Multiplet at 7.28–8.01δ (m, 6H, C_3, C_4, C_5, C_6, C_7, C_8—H), 2 proton quartet at 4.30δ (J = 7Hz, —OCH_2), and 3 proton triplet at 1.40 δ (J = 7Hz, —CH_3 of ester) in the ^{1}H NMR spectrum. The molecular ion peak at m/z 304, with the elemental analysis (C, 54.95; H, 3.42; N 4.31%) corroborated with the molecular formula $C_{14}H_{11}NO_2Se$, finally confirming the structure as selenolo(2,3-*b*)quinoline-2-carboxylic ethyl ester (**8a**) (Scheme 2).

(**iii**). To synthesize the trihalo intermediate, 3-(2-chloro-3-quinolyl)acrylic ethyl ester (**6a**) was brominated with anhydrous

TABLE I The Physical and IR Data of 4a–i

Compound	Yield (%)	M.P. (°C)	IR (cm^{-1})	Mass m/e
4a	72	188–189	1690, 3401, 1010	233, 235
4b	68	192–193	1692, 3400, 1020	247, 249
4c	68	108–109	1689, 3392, 1012	247, 249
4d	79	207–208	1695, 3393, 1015	247, 249
4e	79	222–223	1698, 3405, 1021	263, 265
4f	69	231–232	1698, 3401, 1025	263, 265
4g	60	198–199	1695, 3400, 1021	263, 265
4h	58	170–171	1678, 3375, 1010	261, 263
4i	64	260–261	1701, 3415, 1032	283, 285

TABLE II The Physical and IR Data of 5a–i*

Compound	Yield (%)	M.P. (°C)	IR (cm^{-1})
5a	75	150–151	1780, 1020
5b	78	161–162	1780, 1020
5c	80	120–121	1783, 1025
5d	82	174–175	1775, 1015
5e	70	182–183	1786, 1023
5f	71	190–191	1790, 1029
5g	60	169–170	1790, 1027
5h	60	194–195	1790, 1029
5i	73	201–202	1790, 1029

*Recrystallized from chloroform.

chloroform. The structure of the resulting compound was established from the following spectral and analytical data.

IR (KBr, cm^{-1}) = 1721 (—C=O), 1064(—C=Cl).

^{1}H-NMR($CDCl_3$)δ ppm = 1.34(J = 7Hz, CH_3 of ester), a 2 proton quartet at 4.25(J = 7Hz, —CH_2 of ester), multiplet at 7.43–7.92 (4H, C_5 to C_8—H), 5.02(s, 2H,—CHBr—CHBr—), 8.25(s, C_4—H).

The mass spectrum showed its molecular ion peak at 421(M^+), 423(M+2), 425(M+4), and 427(M+6). The elemental analysis (C, 39.52; H, 2.61; N, 3.19%) was compatible with the molecular formula $C_{14}H_{12}Br_2ClNO_2$ confirming the structure of the compound as 2-chloro-3-(1,2-dibromo-3-quinolyl)acrylic ethyl ester (**6a**) (Scheme 2).

The reaction of 2-chloro-3-(1,2-dibromo-3-quinolyl)acrylic ethyl ester (**6a**) with sodium diselenide under a reflux temperature furnished yellow needle-shaped crystals.

TABLE III The Physical and IR Data of 7a–i*

Compound	Yield (%)	M.P. (°C)	IR (cm^{-1})
7a	75	151–152	1721, 1064
7b	70	174–175	1720, 1060
7c	72	125–126	1720, 1060
7d	72	155–156	1715, 1057
7e	70	105–106	1726, 1067
7f	71	140–141	1730, 1069
7g	68	137–138	1733, 1071
7h	70	164–165	1715, 1041
7i	74	182–183	1735, 1075

*Recrystallized from pet. ether:benzene (4:1v/v).

It exhibited the following spectral and analytical data: an appearance of a peak at 1726 cm^{-1} and 1191 cm^{-1} in IR spectrum, a triplet at 1.40δ (J = 7Hz, $-CH_3$ of ester), a quartet at 4.30δ (J = 7Hz, 2H, $-OCH_2$), and a multiplet at 7.28–8.01δ (m, 6H, C_3, C_4, C_5, C_6, C_7, C_8—H) in ^{1}H NMR spectrum.

A molecular ion peak at m/z 304 and elemental analysis (C, 54.91; H, 3.51; N, 4.45%) further advocated the proposed molecular formula $C_{14}H_{11}NO_2Se$, augmenting the structure of the compound as selenolo(2,3-*b*)quinoline-2-carboxylic ethyl ester (**8a**) (Scheme 2).

A series of similar compounds (**8b–i**) were realized from (**4b–i**), (**5b–i**), and (**7b–i**) in varying yields.

EXPERIMENTAL

Melting points were determined using a Raaga melting point apparatus and were uncorrected. IR spectra were recorded on FTIR 8201(PC)S spectrometer as KBr pellets, and the absorption frequencies are expressed in reciprocal centimeters (cm^{-1}). Proton NMR spectra were recorded on a Gemini-200MHz or on a Varian AMX 400 spectrometer in $CDCl_3$. Chemical shifts were expressed in δ(ppm) downfield from tetramethylsilane as an internal standard. Elemental analysis was performed by Perkin-Elmer model 240B CHN analyzer, and the values are within the permissible limits ($\pm$0.5). Mass spectra were recorded by an EIMS technique on an Autospec mass spectrometer. Crude products were checked by TLC and purified by column chromatography using silica gel (60–120 mesh).

The Preparation of 3-(2-chloro-3-quinolyl)acrylic Acids (4a–i): General Procedure

3-(2-oxo-1,2-dihydro-3-quinolyl)acrylic acid (**3a–i**) (1.56 g, 0.008 mole) was refluxed with phosphoryl chloride 8 mL (excess) in an oil bath for 2–21/2 h. The mixture was then cooled and poured into crushed ice. The separated solid was filtered , washed with water, and purified by column chromatography over silica gel using pet. ether: ethyl acetate (10:1) as the eluent.

The Preparation of Selenolo(2,3-*b*)quinoline-2-carboxylic Ethyl Esters (8a–i) from 3-(2-Chloro-3-quinolyl)acrylic Acids (4a–i): General Procedure

To a freshly prepared solution of sodium diselenide [selenium powder (1.069 g, 0.0136 mole) and sodium borohydride (0.358 g, 0.0095 mole)

in abs. ethanol], 3-(2-chloro-3-quinolyl)acrylic acid (**4a–i**) (1 g, 0.0043 mole) was added and heated under reflux temperature for 15 h on a steam bath. Thereafter, the solution was evaporated, and the residue was dissolved in 50 mL of chloroform followed by washing with 70 mL of water. The organic extract was dried and evaporated. Column chromatography was used to purify the crude product using pet. ether as the eluent. The first product was left as an unidentified one since it was a pasty mass.

The Preparation of 3-(2-Chloro-3-quinolyl)acryloyl Chloride (5a–i): General Procedure

3-(2-chloro-3-quinolyl)acrylic acid (**4a–i**) (1 g, 0.043 mole) was refluxed with thionyl chloride (1.56 mL, 0.0214 mole) for 1 h. Excess thionyl chloride was removed by co-distillation with benzene, and the resulting acid chloride was recrystallized from chloroform.

The Preparation of Selenolo(2,3-*b*)quinoline-2-carboxylic Ethyl Esters (8a–i) from 3-(2-Chloro-3-quinolyl)acryloyl Chloride (5a–i): General Procedure

To a freshly prepared solution of sodium diselenide [selenium powder (0.991 g, 0.0131 mole) and sodium borohydride (0.332 g, 0.0088 mole) in abs. ethanol], 3-(2-chloro-3-quinolyl)acryloyl chloride (**5a–i**) (1 g, 0.0043 mole) was added and heated under reflux temperature for 15 h on a steam bath. Thereafter, the solution was evaporated, and the residue was dissolved in 40 mL of chloroform followed by washing with 70 mL of water. The organic extract was dried and evaporated. Column chromatography was used to purify the crude product using pet. ether as the eluent. The pasty mass of the first product was left as an unidentified one. The second product was identified as selenolo(2,3-*b*)quinoline-2-carboxylic ethyl ester.

The Preparation of 2-Chloro-3-(1,2-dibromo-3-quinolyl)-acrylic Ethyl Ester (7a–i): General Procedure

Bromine (0.18 mL, 0.0036 mole) in 10 mL of anhydrous chloroform was added in a dropwise manner to a cooled, stirred suspension of 3-(2-chloro-3-quinolyl)acrylic ethyl ester (**6a**) (0.9 g, 0.0033 mole) in 20 mL of anhydrous chloroform, for about 30 min.

Stirring and cooling was continued for another 3 h. A light brown yellow powder resulted from distilling out the solvent together with

excess bromine. It was then recrystallized from pet. ether:benzene (4:1 v/v) to yield creamy white needles.

The Preparation of Selenolo(2,3-*b*)quinoline-2-carboxylic Ethyl Esters (8a–i) from 2-Chloro-3-(1,2-dibromo-3-quinolyl)acrylic Ethyl Ester (7a–i): General Procedure

To a freshly prepared solution of sodium diselenide [selenium powder (0.593 g, 0.0075 mole,) and sodium borohydride (0.198 g, 0.0053 mole) in abs. ethanol], 2-chloro-3-(1,2-dibromo-3-quinolyl)acrylic ethyl ester (**7a–i**) (1 g, 0.0024 mole) was added and heated under reflux temperature for 15 h on a steam bath. Thereafter, the solution was evaporated and the residue was dissolved in 40 mL of chloroform followed by washing with 70 mL of water. The organic extract was dried and evaporated. The residue was then chromatographed over silicagel with pet. ether as the eluent. The first product was left as an unidentified one since it was a pasty mass. The second product was identified as selenolo(2,3-*b*)quinoline-2-carboxylic ethyl ester.

Physical and Spectroscopic Data of (8a–i)

Selenolo(2,3-b)-quinoline-2-carboxylic Ethyl Ester (8a)

Light-yellow needle-shaped crystals, Yield = 65%, m.p. = 194–196°C, Lit.[11] m.p. 194–196°C (Cal: C, 55.20; H, 3.64; N, 4.62; Found: C, 55.4; H, 3.50; N, 4.59), IR (KBr, cm^{-1}) = 1726(—C═O of ester), 1192 (—C—O of ester), ^{1}H NMR ($CDCl_3$)δ ppm: 1.40 (t, J = 7 Hz, —CH_3 of ester), 4.30 (q, J = 7 Hz, —OCH_2 of ester), 7.28–8.01 (m, 6H, C_3, C_4, C_5, C_6, C_7, C_8—H), M F = $C_{14}H_{11}NO_2Se$, Mass (m/z)M^+ = 304.

6-Methyl Selenolo(2,3-b)quinoline-2-carboxylic Ethyl Ester (8b)

Light-yellow needle-shaped crystals, Yield = 60%, m.p. = 159–161°C, Lit.[11] m.p. 159–161°C (Cal: C, 56.59; H, 4.12; N, 4.42; Found: C, 56.50; H, 4.10; N, 4.40), IR (KBr, cm^{-1}) = 1709 (C═O of ester), 1251 (—C—O of ester), ^{1}H NMR($CDCl_3$) δ ppm: 1.43 (t, J = 7 Hz, —CH_3 of ester), 4.42 (q, J = 7 Hz, —OCH_2 of ester), 2.57 (s, 3H, —CH_3), 8.26 (s, 1H, C_4—H), 8.53 (s, C_3—H), 8.13 (d, J = 2 Hz, C_5—H), 8.03 (s, C_7—H), 7.64 (d, C_8—H, J = 8.2 Hz). M.F = $C_{15}H_{13}NO_2Se$, Mass (m/z)M^+ = 318.

7-Methyl Selenolo(2,3-b)quinoline-2-carboxylic Ethyl Ester (8c)

Light-yellow needle-shaped crystals, Yield = 66%, m.p. = 178–180°C, Lit.[11] m.p. 178–180°C (Cal: C, 56.59; H, 4.12; N, 4.42; Found: C, 56.60;

H, 4.12; N, 4.50), IR (KBr, cm^{-1}) = 1712 (C=O of ester), 1251 (—C—O of ester), ^{1}HNMR($CDCl_3$)δ ppm: 1.42 (t, J = 6.6 Hz, —CH_3 of ester), 4.44 (q, J = 6.8 Hz,—OCH_2 of ester), 2.61 (s, 3H, —CH_3), 8.25 (s, 1H, C_4—H), 8.56 (s, C_3-H) 7.39–7.92 (m, 3H, C_5, C_6, C_8—H). M.F = $C_{15}H_{13}NO_2Se$, Mass (m/z)M^+ = 318.

8-Methyl Selenolo(2,3-b)quinoline-2-carboxylic Ethyl Ester (8d)

Light-yellow needle-shaped crystals, Yield = 75%, m.p. = 164–166°C, Lit.[11] m.p. 164–166°C (Cal: C, 56.59; H, 4.12; N, 4.42; Found: C, 56.60; H, 4.12; N, 4.50), IR (KBr, cm^{-1}) = 1724 (C=O of ester), 1254 (—C—O of ester), ^{1}H NMR($CDCl_3$) δ ppm: 8.25 (s, C_4—H), 8.56 (s, C_3—H), 7.45 (t, J = 7.4 Hz, C_6—H), 7.79 (d, J = 8 Hz, C_5—H), 7.63 (d, J = 7 Hz, C_7—H), 2.86 (s, 3H, CH_3), 1.44 (t, J = 7 Hz, 3H, CH_3 (of ester)), 4.43 (q, J = 7 Hz, 2H, —OCH_2). M.F = $C_{15}H_{13}NO_2Se$, Mass (m/z) M^+ = 318.

6-Methoxy Selenolo(2,3-b)quinoline-2-carboxylic Ethyl Ester (8e)

Light-yellow needle-shaped crystals, Yield = 66%, m.p. = 145–147°C, Lit.[11] m.p. 145–147°C (Cal: C, 53.88; H, 3.92; N, 4.21; Found: C, 53.80; H, 3.99; N, 4.21), IR (KBr, cm^{-1}) = 1718 (C=O of ester), 1242 (—C—O of ester), ^{1}H NMR($CDCl_3$)δ ppm: 8.28 (s, C_4—H), 8.54 (s, C_3-H), 7.51–7.93 (m, 3H, C_5, C_7, C_8—H), 4.47 (q, J = 7.6 Hz, 2H, —OCH_2), 3.99 (s, 3H, —OCH_3), 1.46 (t, J = 6.4 Hz, 3H,—CH_3) M.F = $C_{15}H_{13}NO_3Se$, Mass (m/z)M^+ = 334.

7-Methoxy Selenolo(2,3-b)quinoline-2-carboxylic Ethyl Ester (8f)

Light-yellow needle-shaped crystals, Yield = 58%, m.p. = 154–156°C, Lit.[11] m.p. 154–156°C (Cal: C, 53.88; H, 3.92; N, 4.21; Found: C, 53.89; H, 3.99; N, 4.15), IR (KBr, cm^{-1}) = 1700 (C=O of ester), 1245 (—C—O of ester), ^{1}H NMR($CDCl_3$)δ ppm: 8.23 (s, C_4—H), 8.50 (s, C_3—H), 7.24–7.84 (m, 3H, C_5, C_6, C_8—H), 3.97 (s, 3H, —OCH_3), 1.45 (t, 3H, —CH_3), 4.40 (q, J = 6.2 Hz, —OCH_2) M.F = $C_{15}H_{13}NO_3Se$, Mass (m/z) M^+ = 334.

8-Methoxy-selenolo(2,3-b)quinoline-2-carboxylic Ethyl Ester (8g)

Light-yellow needle-shaped crystals, Yield = 49%, m.p. = 161–162°C, (Cal: C, 53.88; H, 3.92; N, 4.21; Found: C, 53.89; H, 3.99; N, 4.15), IR(KBr, cm^{-1}) = 1720(C=O of ester), 1241 (—C—O of ester), ^{1}H NMR($CDCl_3$)δppm: 8.30(s, C_4—H), 8.54(s, C_3—H), 7.28–7.91(m, 3H, C_5,

C_6, C_7—H), 4.01(s, 3H, —OCH_3), 1.47(t, 3H, —CH_3), 4.48(q, J = 6.2 Hz, —OCH_2). M.F = $C_{15}H_{13}NO_3Se$, Mass (m/z) $M^+ = 334$.

6,8-Dimethyl-selenolo(2,3-b)quinoline-2-carboxylic Ethyl Ester (8h)

Light-yellow-needle-shaped crystals, Yield = 56%, m.p. = 184–185°C, (Cal: C, 57.84; H, 4.55; N, 4.22; Found: C, 57.56; H, 4.25; N, 4.02), IR (KBr, cm^{-1}) = 1709 (C=O of ester), 1219 (—C—O of ester), ^1H NMR($CDCl_3$)δ ppm: 2.40, 2.55 (s_{each}, —CH_3), 8.18 (s, C_4—H), 8.48 (s, C_3—H), 7.20 (s, C_7—H), 7.41 (s, C_5—H), 1.39 (t, 3H, —CH_3), 4.41 (q, J = 6.2 Hz, —OCH_2). M.F = $C_{16}H_{15}NO_2Se$, Mass (m/z)$M^+ = 332$.

Benzo(h) Selenolo(2,3-b)quinoline-2-carboxylic Ethyl Ester (8i)

Light-yellow needle-shaped crystals, Yield = 60%, m.p. = 191–192°C, (Cal: C, 61.03; H, 3.70; N, 3.95; Found: C, 60.92; H, 3.35; N, 3.51), IR (KBr, cm^{-1}) = 1735(C=O of ester), 1246 (—C—O of ester), ^1H NMR($CDCl_3$)δ ppm: 1.52(t, J = 7.2 Hz, —CH_3 of ester), 4.48 (q, J = 7.2 Hz, —OCH_2 of ester), 7.49–9.51 (m, 8H, C_3, C_4, C_5, C_6, C_7, C_8, C_9, C_{10}—H). M.F = $C_{18}H_{13}NO_2Se$, Mass (m/z) $M^+ = 354$

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