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A FACILE SYNTHESIS AND REACTIONS OF AMINO SELENOLO[2,3-b]PYRIDINE CARBOXYLATE

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ABSTRACT:

Incorporating selenium metal bonded to the pyridine nucleus was achieved by the reaction of selenium metal with 2-chloropyridine carbonitrile **1** in the presence of sodium borohydride as reducing agent. The resulting non isolated selanyl sodium salt was subjected to react with various α-halogenated carbonyl compounds to afford the selenyl pyridine derivatives **3a-f** which compounds **3a-d** underwent *Thorpe-Ziegler* cyclization to give 1-amino-2-substitutedselenolo[2,3-b]pyridine compounds **4a-d**, while the other compounds **3e,f** failed to be cyclized. Basic hydrolysis of amino selenolo[2,3-b]pyridine carboxylate **4a** followed by decarboxylation furnished the corresponding amino selenolopyridine compound 6 which was used as a versatile precursor for synthesis of other heterocyclic compound **7-16**. All the newly synthesized compounds were established by elemental and spectral analysis (IR, ^{1}H NMR) in addition to mass spectra for some of them hoping these compounds afforded high biological activity.

KEYWORDS: Selenolopyridine; Pyridoselenolopyridine; Pyranoselenolopyridine; Synthesis; Reactions.

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INTRODUCTION

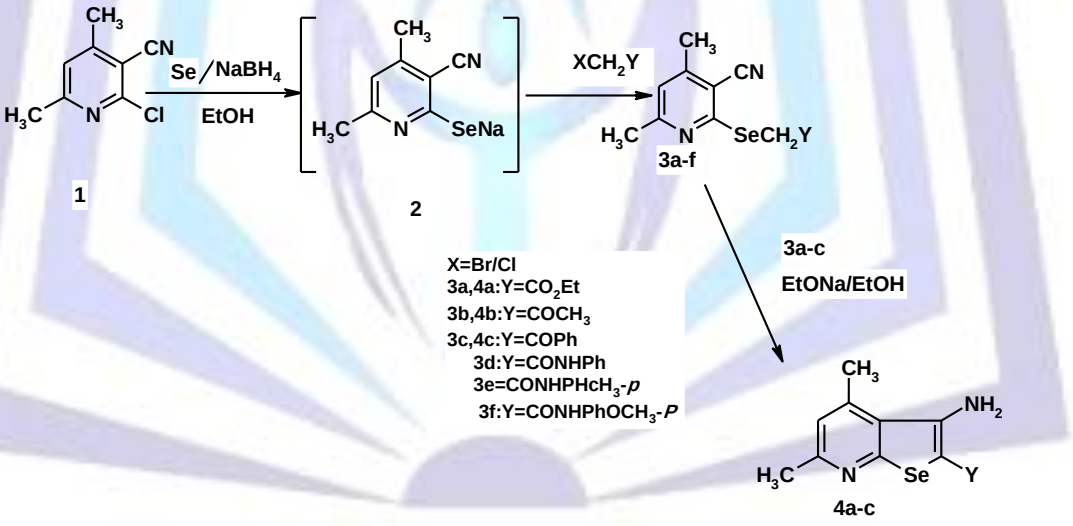
In the recent years, many exciting research results have indicated that selenium is a very important element that has attracted the attention of scientists working in a variety of fields. The interest in selenium-containing compounds has increased, not only because of their reactivates and chemical properties[1–5] but also because of their pharmaceutical applications.[6–9] Organoselenium compounds have proven to be an important class of biological active products as antioxidants, [10] antibacterial agents, [11] and catalysts[12].

Some organoselenium compounds are known as effective insecticides, microbicides[13], prooxidants[14,] and anti-mycobacterial agents[15]. On the other hand, many pyridines are reported to be useful as herbicides, [16] bactericides, [17] and fungicides, [18] as well as pharmaceuticals.[19]

In continuation of our previous work for synthesis of new pyridines and thieno[2,3-b]pyridines[20-27]. Herein, we synthesized selenolo[2,3-b]pyridine by an innovative method, through the reaction of 2-chloro-4,6-dimethyl pyridine-3-carbonitrile with selenium metal in ethanol using sodium borohydride as reducing agent. The non-isolated selanyl sodium salt was subjected to react with α-halogenated carbonyl compounds *in situ* to afford the substituted selanyl pyridine compounds **3a-f**. The latter compounds underwent *Thorpe-Zeigler*cyclization upon refluxing in ethanolic sodium ethoxide solution to give the amino-substitutedselenolo[2,3-b]pyridine compounds **4a-c.** The latter compounds were used as aversatile precursor for synthesis of other hetero cyclic compounds.

RESULTS AND DISCUSSION:

Synthesis of bi-functionally substituted selenolo[2,3-b]pyridines were achieved by incorporating selenium metal fused to pyridine ring, through reduction of selenium by sodium borohydride to afford the non-isolated intermediate sodium salt **2**, which was used to the next reaction with α-halogenated carbonyl compounds to afford the selanyl alkylated pyridine compounds **3a-f**. The chemical structure of compounds **3a-f** were established by elemental and spectral analysis. IR spectrum of compound **3a** showed absorptions band at 2215, 1745 cm^{-1} characteristics for CN and CO of ester group respectively .^{1}H NMR spectrum in $CDCl_3$ showed triplet signals at 1.34 -1.60 for CH_3 group , singlet signals at 2.50- 2.60 for $2CH_3$ group, quartet signals at 4.4 - 4.60 for CH_2 group and singlet signals at 7.10 for CH pyridine. Compounds **3a-c** underwent *Thorpe -Ziegler* cyclization upon heating in ethanolic sodium ethoxide solution to afford the selenolo[2,3-b]pyridine compounds **4a-f**. All attempts to cyclize the (*p*-substituted) phenyl selanyl acetanilide compound **3e-f** using ethanolic sodium ethoxidesolution, potassium carbonate in DMF or ethanolic sodium hydroxide, failed.



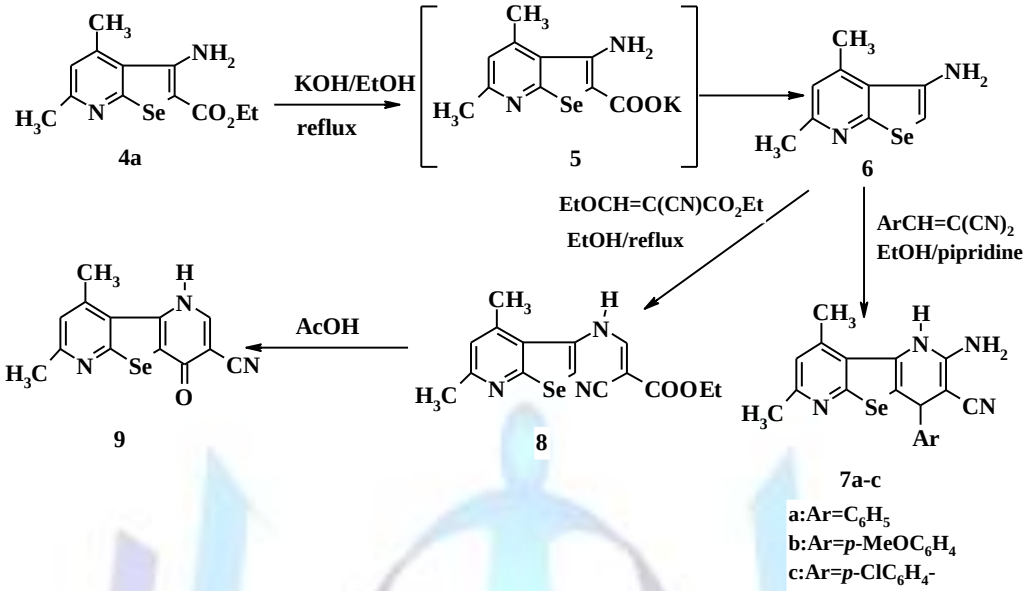
Scheme 1. Synthesis of 3-amino -2-substituted -4, 6-dimethyl selenolo[2, 3-b]pyridine**(4a-c)**

Basic hydrolysis of 3-amino-4,6-dimethyl-2-selenolo[2,3-b]pyridine-2-carboxylate **4a**[28] using ethanolic potassium hydroxide solution afforded the not isolated potassium salt **5** which underwent decarboxylation to give the amino selenolopyridine compound **6**.[29] The structure of the latter compound was elucidated by m.p, TLC, elemental and spectral data. IR spectrum revealed the disappearance of absorption band at 1667 cm^{-1} characteristic of CO ester group and appearance of bands at 3326, 3461 cm^{-1} for NH_2 group.

The 3-amino-4,6-dimethyl selenolo[2, 3-b] pyridine compound **6** was used as a versatile precursor for synthesis of other heterocyclic containing selenolopyridine moiety.

Reaction of the amino compound **6** with arylidinemalononitrile in refluxed ethanol in the presence of catalytic amount of pipridine as basic catalyst afforded the amino aryl pyridoselenopyridinecarbonitrile compounds **7a-c.** Thus, the reaction of compound **6** with ethoxymethylene ethyl cyanoacetate in ethanol afforded the corresponding ethoxy carbonyl carbonitrile compound **8** which underwent ring closure by loss of ethanol mol upon reflux in acetic acid to give the corresponding cyanopyridinone **9**.

The structure molecule of compound **9** proved by elemental and spectral analysis .IR spectrum revealed appearance of absorption band at 1694 for CO, band at 2215 for CN and appearance of band at 3331, 3441 cm^{-1} for NH.



Scheme 2. Synthesis of pyrido[2´,3´:4,5]selenolo[2,3-b]pyridine derivatives **7-9.**

Heating of amino compound **6** with orthophosphoric acid on steam bath followed by cooling and pouring on ice water mixture yielded 4,6-dimethylseleno[2,3-b]pyridin-3(2H)-one compound **10**. The structure of compounds **10** was confirmed in the basis of elemental and spectral analyses. IR spectrum of **10** revealed the disappearance of absorption bands 3470 to 3427 cm^{-1}characteristic of NH_2group in the starting material and showed the appearance absorption band at 1682 cm^{-1} corresponding to carbonyl group. ^{1}HNMR spectrum in $CDCl_3$ showed signals at 2.57 characteristic of $2CH_3$ groups and 3.91 for CH_2 and at 6.82 characteristic for CH pyridine. Mass spectrum revealed a peak at 226.63 (M^+) as a molecular ion peak and a base peak.

Furthermore, condensation of the latter compound with aromatic aldehydes in refluxing ethanol in the presence of catalytic amount of piperidine yield the corresponding Schiff´s bases **11a–d**. The latter compounds reacted with malononitrile in refluxing ethanol in the presence of triethyl amine to afford the amino arylcyanopyranoselenolopyridines**12 a-c**. Compounds **12a–c** were obtained by an alternative route, via treatment of selenone compound **10** with arylidenemalononitrile in refluxing ethanol and triethylamine as a basic catalyst. The amino pyranoseleno pyridine carbonitrile compounds **12a** were reacted with triethylorthoformate in the presence of acetic anhydride to give the corresponding ethoxymethylene amino derivative **13**.

Synthesis of the biselenedopyridinylidenedione compound **14** was achieved by reacting selenone**10** with sodium nitrite in acetic acid.Compound**14** was synthesized by an alternative route ,via reaction of the Schiffs´ base **11** with hydrazine hydrate or phenyl hydrazine .Compound **14** was synthesized by the tow routs is in an agreement in all aspects. Diazotization and coupling of selenone compound **10** with aryldiazonium chloride afforded the corresponding aryl diazoselenolopyridine compounds**15a-e**

The structure of compound **15a** was elucidated by IR, ^{1}HNMR spectra. IR spectrum showed absorption band at 1679 cm^{-1} for CO. ^{1}HNMR spectrum in ($CDCl_3$) showed tow singlet signal at 2.40- 2.60 characteristic of $2CH_3$ groups, singlet at 6.90 for CH pyridine and multiplet signals at 7.10-7.60 for aromatics (Scheme 3).

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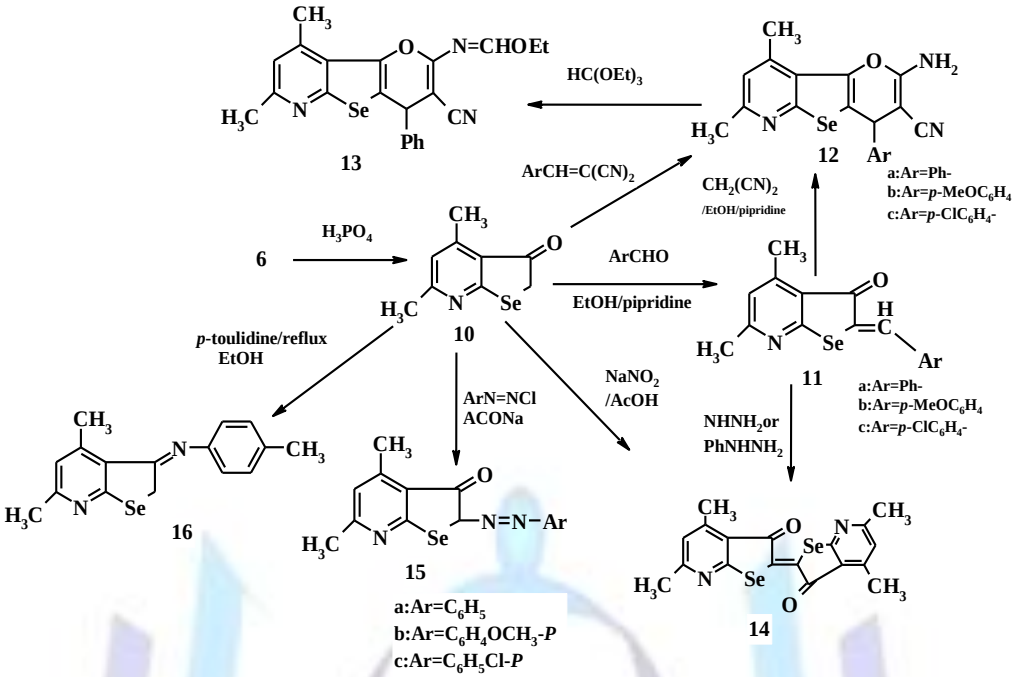

Scheme 3. Condensation reactions of selenolo[2,3-b]pyridine-3-(2H)-one to formpyrano[2´,3´:4,5] selenolo[2,3-b]pyridine compounds **12,13.**

EXPERIMENTAL

All melting points are corrected and measured on a Fisher-John apparatus. IR spectra were recorded (KBr) with a Perkin-Elmer 1430 Spectrophotometer. ^{1}HNMR spectra were obtained on a Varian EM-390 MHz (90 MHz) and Bruker (400 MHz) spectrometers in $CDCl_3$, DMSO-d_6 using Me_4Si as internal standard, and chemical shifts are expressed as ppm. Mass spectra were measured on a Joel-JMS 600 spectrometer. Analytical data were obtained on Elemental Analyze system GmbH-VarioELV.3 microanalyzer in the central lab of Assiut University.

3-Cyano-4,6-dimethyl-2-substituted selanylpyridines(3a-f)

General Procedure

To a suspension of selenium metal (4.83 g, 0.06 mol) in absolute ethanol (60 ml) in an ice bath, then sodium borohydride (3.3 g, 0.088 mol) was added in small portions till all selenium metal was dissolved. After that, the chloropyridinecarbonitrile**1** (10 g, 0.06 mol) was added to the reaction mixture with stirring for 1h. The reaction mixture was refluxed for 2 h followed by cooling. The α-halogenated carbonyl compound (0.059 mol) was added to the reaction mixture and left with stirring overnight. The solid precipitate which formed by stirring was filtered off, dried and recrystallized from ethanol.

Ethyl 2-(3-cyano-4, 6-dimethylpyridin-2-ylselanyl) acetate (3a)

Obtained by the reaction with ethylchloroacetate (8.5 ml, 0.03 mol) as the above general procedure as white crystals (90 %, 9.8 g) yield, m.p. 56-58^{o}C. The solid product was recrystallized from ethanol.IR v: 2980, 2941 cm^{-1}(CH aliphatic), 2231 cm^{-1} (CN), 1745 cm^{-1} (C=O). ^{1}H NMR (90 MHz, $CDCl_3$): *δ*= 1.34 -1.50 (t, *J*=9 Hz, 3H, CH_3 ester), 2.50, 2.60 (2s, 6H, $2CH_3$ pyridine), 4.10 (s, 2H, CH_2), 4.40-4.60 (q, *J*=7.5Hz, 2H, CH_2 ester), 7.10 (s, 1H, CH pyridine) ppm. Anal. Calcd. for: $C_{12}H_{14}N_2O_2Se$ (297.22): C, 48.49; H, 4.75; N, 9.43%. Found: C, 48.39; H, 4.85; N, 9.3 %.

3-Cyano-4, 6-dimethyl-pyridin-2-selanylacetone (3b)

Obtained by the reaction with chloroacetone (5 ml, 0.05 mol) as the above general procedure as white crystals; m.p. 58-60^{o}C in (92%, 9.00 g) yield, IR v: 2916, 2999 cm^{-1} (CH aliphatic), 2222 cm^{-1} (CN), 1724 cm^{-1} (C=O).^{1}H NMR (400MHz, $CDCl_3$): *δ*= 2.30, 2.44 (2s, 6H, $2CH_3$ pyridine), 2.50 (s, 3H, CH_3 acetyl), 4.60 (s, 2H, CH_2), 6.87 (s, 1H, CH pyridine) ppm. Anal. Calcd. for: $C_{11}H_{12}N_2OSe$ (267.19): C, 49.45; H, 4.53; N, 10.48 %. Found: C, 49.47; H, 4.50; N, 10.47 %.

3-Cyano-4, 6-dimethyl-pyridin-2-ylselanylacetophenone (3c)

Obtained by the reaction with phencyl bromide (12 g, 0.03 mol) as the above general procedure as white crystals (95 %, 9.70 g) yield, m.p. 75-77 ^{o}C. IR v:2919, 2963 cm^{-1}(CH aliphatic), 2226 cm^{-1}(CN), 1690 cm^{-1}(C=O). ^{1}H NMR (90 MHz, $CDCl_3$): *δ*= 2.50, 2.66(2s, 6H, $2CH_3$ pyridine), 4.60 (s, 2H, CH_2), 6.80(s, 1H, CHpyridine), 7.30-7.50 (m, 5H, Ar-H) ppm. Anal. Calcd. for $C_{16}H_{14}N_2OSe$ (329.26): C, 58.37; H, 4.29; N, 8.51%. Found: C, 58.24; H, 4.35; N, 8.70%

2-(3-Cyano-4, 6-dimethylpyridin-2-ylselanyl)-N-phenylacetamide (3d)

Obtained by the reaction with chloro acetanilide (10.2 gm, 0.02 mol) as the above general procedure as white crystals (98 %, 10.4g) yield, m.p. 83-85^{o}C. IR v: 3289 cm^{-1}(NH), 3088, 3139 cm^{-1}(CH aromatic), 2916,2900 cm^{-1}(CH aliphatic), 2214 cm^{-1}(CN), 1665 cm^{-1}(C=O).^{1}H NMR (90 MHz, $CDCl_3$): δ= 2.50,2.70 (2s, 6H, 2CH_3 pyridine), 4.60 (s, 2H, CH_2), 7.20(s, 1H, CH pyridine), 7.40-7.60 (m, 5H, Ar-H),10.00(s, 1H, NH) ppm. Anal. Calcd. for $C_{16}H_{15}N_3OSe$ (344.28): C, 55.82; H, 4.39; N, 12.21%. Found: C, 55.7; H, 4.48; N, 12.14 %.

2-(3-Cyano-4,6-dimethylpyridin-2-ylselanyl)-N-p-tolylacetamide(3e)

Obtained by the reaction with *p*-methyl chloroacetanilide(11.80g, 0.03 mol) as the above general procedure as white crystals (95 %, 10 g) yield, m.p. 78-80^{o}C. IR v: 3300 cm^{-1}(NH), 3133, 3018cm^{-1}(CH aromatic), 2827,2894,2946 cm^{-1}(CH aliphatic), 2226 cm^{-1}(CN), 1680cm^{-1}(C=O).^{1}H NMR (90 MHz,$CDCl_3$): δ= 2.46 (s, 3H, CH_3acetanilide), 2.60, 2.80(2s, 6H, 2CH_3 pyridine), 4.10 (s, 2H, CH_2), 7.53-7.89 (m, 5H, Ar-H), 10.10 (s, 1H, NH) ppm. Anal. Calcd. for $C_{17}H_{17}N_3OSe$ (358.30): C, 56.99; H, 4.78; N, 11.73 %. Found: C, 56.80; H, 4.87; N, 11.90 %.

2-(3-Cyano-4,6-dimethylpyridin-2-ylselanyl)-N-p-anisylacetamide (3f)

Obtained by the reaction with p-methoxychloroacetanilide (11.86 g, 0.03 mol) as the above general procedure as white crystals in (90 %, 9.00g) yield, m.p. 63 -65^{o}C.IR v: 3265 cm^{-1}(NH), 3091, 3058cm^{-1}(CH aromatic), 2922, 3065 cm^{-1}(CH aliphatic), 2225 cm^{-1}(CN) and 1683 cm^{-1}(C=O).^{1}H NMR (90 MHz $CDCl_3$): δ= 2.00 (s, 3H, CH_3 anilide), 2.50, 2.60 (2s, 6H, 2CH_3 pyridine), 4.60 (s, 2H, CH_2),6.83-7.80 (m, 6H, Ar-H+NH). Anal. Calcd. for $C_{17}H_{17}N_3O_2Se$ (374.30): C, 54.55; H, 4.58; N, 11.23 %. Found: C, 54.61; H, 4.40; N, 11.52 %.

3-Amino-4, 6-dimethyl-2-substituted selenolo[2, 3-b]pyridine (4a-c)

General Procedure:

A solution of substituted selanyl pyridine derivative **3a-c** (10 g, 0.033 mol) in sodium ethoxide solution (prepared by 2.30 g of finely divided sodium metal in 30 absolute ethanol) was stirred for 1h .The solid product which formed by stirring was collected, filtered off, dried and recrystallized from the proper solvent .

Ethyl 3-amino-4, 6-dimethylselenolo[2,3-b] pyridine-2-carboxylate (4a)

Obtained by the reaction of compound **3a** as the above general procedure. The solid product which formed by stirring was filtered off, dried and recrystallized form ethanol as yellow needles in (75 %, 7.50 g) yield, m.p.123-125 ^{o}C.IR v: 3326, 3429 cm^{-1}(NH_2), 2977, 2917 cm^{-1}(CH aliphatic), 1667 cm^{-1} (C=O). ^{1}H NMR (400MHz, $CDCl_3$): δ= 1.38 -1.68 (t, *J*=9.00 Hz, 3H, CH_3 ester), 2.58, 2.74 (2s, 6H, 2CH_3 pyridine), 4.32 (q, *J*= 7.50 Hz, 2H, CH_2), 6.32 (s, 1H, CH pyridine), 7.28 (s, 2H, NH_2) ppm; EI-MS: *m/z (%)* = 298.39(M^+). Anal. Calcd. for $C_{12}H_{14}N_2O_2Se$ (297.22): C, 48.49; H, 4.75; N, 9.43%. Found: 48.36; H, 4.67; N, 9.35%.

2-Acetyl-3-amino-4, 6-dimethyl-2-selenolo[2, 3-b] pyridine (4b)

Obtained by the reaction of compound **3b** as the above general procedure. The solid product which formed filtered off, dried and recrystallized form ethanol as pale brown crystals(80%, 7.50g) yield. mp 149-150^{o}C.IR v: 3450, 3494 cm^{-1}(NH_2), 2975, 2901cm^{-1}(CH aliphatic), 1594 cm^{-1}(C=O). ^{1}H NMR (400MHz, $CDCl_3$): δ= 2.44 (s, 3H, CH_3 acetyl), 2.60, 2.75 (2s, 6H, 2CH_3 pyridine), 6.90 (s, 2H, NH_2), 7.26(s, 1H, CH pyridine) ppm. Anal. Calcd. For $C_{11}H_{12}N_2OSe$ (267.19): C, 49.45; H, 4.53; N, 10.48%. Found: C, 49.53; H, 4.38; N, 10.55%.

3-Amino-2-benzoyl-4,6-dimethylselenolo[2, 3-b]pyridine (4c)

Obtained by the reaction of compound **3c** as the above general procedure. The solid product which formed filtered off, dried and recrystallized form ethanol as brown crystals (85%, 8.50 g) yield, m.p. 118–120^{o}C. IR v: 3422, 3499cm^{-1} (NH_2), 2981, 2975 cm^{-1}(CH aliphatic), 1600 cm^{-1}(C=O). ^{1}H NMR (400MHz, $CDCl_3$): δ= 2.50, 2.80 (2s, 6H, 2CH_3 pyridine), 7.10(s, 2H, NH_2), 7.50-7.90 (m, 5H, Ar-H), 8.60 (s, 1H, CH pyridine) ppm. Anal. Calcd. for$C_{16}H_{14}N_2OSe$ (329.26): C, 58.37; H, 4.29; N, 8.51%. Found: C, 58.51; H, 4.48; N, 8.62%.

3-Amino-4,6-dimethylselenolo[2, 3-b]pyridine (6)

Amino ester compound **4a** (5 g, 0.017mol) was refluxed in alcoholic potassium hydroxide solution(prepared by dissolving potassium hydroxide (3 g) in ethanol (60 ml)) for 1 h, then the mixture was cooled and added to diluted HCl solution (10%). The solid precipitate which formed by adding HCl was filtered off, dried and recrystallized from ethanol as yellow white crystals in (80 %,4.00 g) yield.mp 168-170 ^{o}C.IR v: 3323, 3461cm^{-1}(NH_2), 2850, 2922 cm^{-1}(CH aliphatic). ^{1}H NMR (90 MHz, DMSO-d_6): δ= 2.40, 2.70 (2s, 6H, 2CH_3 pyridine), 4.00 (s, 1H, CH selenophene), 6.50 (s, 2H, NH_2) and 7.40 (s, 1H, CH aromatic) ppm. Anal. Calcd. for $C_9H_{10}N_2Se$ (225.15): C, 48.01; H, 4.48; N, 12.44%. Found: C, 48.22; H, 4.57; N, 12.55 %.

2-Amino-1,4-dihydro-7,9-dimethyl-4-arylpyrido[2',3':4,5]selenolo[2,3-b]pyridine-3-carbonitrile(7a-c)

General procedure:

A mixture of amino selenolopyridine compound **6** (1 g, 0.004 mol) and arylidenemalononitrile (1g, 6 mmol) in ethanol (30 ml), was refluxed in the presence of few drops of piperidine for 3 h. The solid product which formed upon heating during reflux was collected and recrystallized from the proper solvent.

2-Amino-1,4-dihydro-7,9-dimethyl-4-phenylpyrido[2',3':4,5]selenolo[2,3-b]pyridine-3-carbonitrile(7a)

Obtained by the reaction with benzylidene malononitrile (0.68 g, 4.00mmol)as yellow crystals in (85%,0.85 g) yield. mp 236-238 ^{o}C.IR v: 3328 -3560 cm^{-1}(NH, NH_2), 2848, 2917 cm^{-1} (CH aliphatic), 2198cm^{-1}(CN). ^{1}H NMR (400 MHz, DMSO-d_6): δ= 2.40, 2.50 (2s, 6H, $2CH_3$ pyridine), 6.90 (s, 2H, NH_2), 7.30-7.70 (m, 7H, Ar-H+ 2CH pyridine), 8.40 (s, 1H, NH) ppm. Anal. Calcd. for: $C_{19}H_{16}N_4Se$ (379.33): C, 60.16; H, 4.25; N, 14.77; Se, 20.82 %. Found: C, 60.21; H, 4.08; N, 14.82 %.

2-Amino-1,4-dihydro-7,9-dimethyl-4-(p-anisyl)pyrido[2',3':4,5]selenolo[2,3-b]pyridine-3-carbonitrile(7b).

Obtained by the reaction with *p*-methoxybenzylidene malononitrile as yellow crystals in (90 %, 0.9 g) yield,m.p. 218-220^{o}C. IR v: 3363-3400 cm^{-1}(NH- NH_2), 2848, 2917cm^{-1}(CH aliphatic), 2205 cm^{-1} (CN). ^{1}H NMR (400 MHz, DMSO-d_6): δ= 2.45, 2.54 (2s, 6H, $2CH_3$ pyridine), 2.75(s, 3H, OCH_3), 6.80 (s, 2H, NH_2), 7.35-7.65 (m, 6H, Ar-H+ 2CH pyridine), 7.90 (s, 1H, NH) ppm. Anal. Calcd. for: $C_{20}H_{18}N_4OSe$ (409.35): C, 58.68; H, 4.43; N, 13.69 %. Found: C, 58.79; H, 4.34; N, 13.77 %.

2-Amino-4-(p-chlorophenyl)-1,4-dihydro-7,9-dimethyl)pyrido[2',3':4,5]selenolo[2,3-b]pyridine-3-carbonitrile(7c).

Obtained by the reaction with *p*-chlorobenzylidene malononitrile as yellow crystals in (82 %, 0.85 g) yield,m.p. 238-240^{o}C.IR v: 3244 – 3466 cm^{-1}(NH_2, NH), 2848, 2917 cm^{-1}(CH aliphatic), 2214 cm^{-1} (CN). ^{1}H NMR (90 MHz, $CDCl_3$): δ= 2.45, 2.50 (2s, 6H, $2CH_3$ pyridine), 6.50 (s, 2H, NH_2), 6.70-7.10 (m, 4H, ArH), 7.20, 7.25 (2s, 2H, 2CH pyridine), 7.80 (s, 1H, NH) ppm. Anal. Calcd. for: $C_{19}H_{15}Cl\ N_4Se$ (413.77): C, 55.15; H, 3.65; N, 13.54; Cl, 8.57 %. Found: C, 55.22; H, 3.46; N, 13.79; Cl, 8.49 %.

3-(4,6-Dimethylselenolo[2,3-b]pyridine-3-ylamino)-2-ethoxyacrylo nitrile (8)

A mixture ofaminoselenolopyridinecompound **6** (1.7 g, 7 mmol) and ethyl 2-cyano-3-ethoxyacrylate (1 g, 6 mmol) in ethanol (30 ml) was refluxed for 2 h.in presence of catalytic drops of acetic acid. The solid precipitate which formed upon heating during reflux was filtered off, dried and recrystallized from ethanol: acetic acid mixture as yellowish crystals in (85 %,0.90 g) yield,m.p. 268-270^{o}C.IR v: 3468 cm^{-1}(NH), 2981, 2992 cm^{-1}(CH aliphatic), 2194 cm^{-1}(CN),1698 cm^{-1}(C=O ester).^{1}H NMR (400 MHz, DMSO-d_6): δ= 1.21-1.25 (t, *J*= 7.00 Hz, 3H, CH_3 ester), 1.93, 2.65 (2s, 6H, $2CH_3$ pyridine), 4.20-4.26 (q, *J*= 4.20 Hz, 2H, CH_2), 7.00, (2s, 2H, CH pyridine+ CH acrylate), 7.28 (s, 1H, NH) ppm. Anal. Calcd. for: $C_{15}H_{15}N_3O_2Se$ (348.27): C, 51.73; H, 4.34; N, 12.07 %. Found: C, 51.81; H,4.27; N, 12.21 %.

7,9-Dimethyl-4-oxo-1,4-dihydropyrido[2`,3`:4,5]selenolo[2,3-b]pyridine-3-carbo- nitrile (9)

A solution of ethoxy acrylonitrile compound **8** (1.33 g, 5 mmol) in acetic acid (10 ml) was heated under reflux for 3 h. The solid precipitate which formed upon heating during reflux was filtered off, dried and recrystallized from dioxane as yellow crystals in (65%,0.75g) yield, m.p. 268-270 ^{o}C.IR v:3441 cm^{-1}(NH), 2917, 2950 cm^{-1}(CH aliphatic), 3050, 3070 cm^{-1}(CH aromatic), 2215 cm^{-1}(CN), 1660 cm^{-1}(C=O). ^{1}H NMR (400 MHz, DMSO-d_6): δ= 2.40, 2.52 (2s, 6H, $2CH_3$ pyridine), 6.95(s, 2H, 2CH pyridine), 9.05(s, 1H, NH) ppm. Anal. Calcd. for $C_{13}H_9N_3OSe$ (302.20): C, 51.67; H, 3.00; N, 13.90 %. Found: C, 51.76; H, 2.89; N, 14.10 %.

4, 6-Dimethylselenolo[2, 3-b]pyridin-3(2H)-one (10)

A mixture of amino-4,6-dimethyl-2-ethylselenolo[2,3-b]pyridinecompound **(6)**(3g,0.01mol) and ortho-phosphoric acid (4 ml) was heated on steam bath for 1 h. The solid precipitate which formed by pouring the reaction mixture into an ice-water bath, was filtered off, dried and recrystallized from ethanolaswhite crystals in(75%,1.8g) yield, m.p. 118-120 ^{o}C.IR v: 2972, 2924 cm^{-1}(CH aliphatic), 1682 cm^{-1}(C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.57 (s, 3H, CH_3 pyridine), 2.80(s, 3H, CH_3 pyridine), 3.90(s, 2H, CH_2selenophene), 6.82(s, H, CH pyridine) ppm.EI-MS: *m/z(%)* = 226.63 (M^{+1}).Anal. Calcd. for: C_9H_9NOSe (226.14): C, 47.80; H, 4.01; N, 6.19 %. Found: C, 47.70; H, 4.11; N, 6.22% .

Arylidene-4, 6-dimthyl-1,2-dihydroselenolo[2,3- b]pyridin-3-one (11a-c)

Generalprocedure:

A mixture of selenolopyridinone**10** (1 g, 0.004 mol) and aromatic aldehyde (0.01 mol)in ethanol (30 ml), in presence of catalytic drops of piperidinewas heated under reflux for 2 h. The solid product which formed upon heating during reflux was collected and recrystallized from ethanol.

2-Benzylidene-4,6-dimethyl-1,2-dihydroselenolo[2,3-b]pyridin-3-one (11a).

Obtained by the reaction with benzaldehyde as white crystals in (85%,0.58g) yield, m.p. 158-160^{o}C.IR v:3040 cm^{-1}(CH aromatic), 2900, 2917cm^{-1}(CH aliphatic), 1669 cm^{-1}(C=O). ^{1}H NMR (90MHz, $CDCl_3$): δ= 1.93, 2.62 (2s, 6H, $2CH_3$ pyridine), 6.24-6.91 (m, 5H, Ar-H), 7.10, 7.30 (2s, 2H, CH benzylidene+ CH pyridine) ppm. Anal. Calcd. for $C_{16}H_{13}NOSe$ (314.25): C, 61.15; H, 4.17; N, 4.46 %. Found: C, 61.1; H, 4.19; N, 4.48% .

4,6-Dimethyl-1,2-dihydro-2-(p-methoxybenzylidene)selenolo[2,3-b]pyridin-3-one (11b)

Obtained by the reaction with *p*-anisaldehyde as yellow crystals in (76%, 0.70 g) yield, m.p. 258-260 ^{o}C.IR v: 3043 cm^{-1}(CH aromatic), 2814, 2926 cm^{-1}(CH aliphatic), 1654 cm^{-1}(CO). ^{1}H NMR (90 MHz, $CDCl_3$): δ= 2.30, 2.50 (2s, 6H, $2CH_3$ pyridine), 2.80 (s, 3H, OCH_3), 6.50-7.00(m,4H, Ar-H), 7.20, 7.30 (2s, 2H, CH pyridine+ CH benzylidene) ppm. Anal. Calcd. for $C_{16}H_{13}NO_2Se$ (344.27): C, 59.31; H, 4.39; N, 4.07 %. Found: C, 59.50; H, 4.24; N, 4.00%.

2-(4-Chlorobenzylidene)-4,6-dimethyl-1,2-dihydroselenolo[2,3-b]pyridin-3-one (11c)

Obtained by the reaction with *p*-chlorobenzaldehyde as yellowish white needles in (85%, 0.80g) yield, m.p. 175-180 ^{o}C.IR v: 3042 cm^{-1}(CH aromatic), 2848, 2916 cm^{-1}(CH aliphatic), 1659 cm^{-1}(CO). ^{1}H NMR (400MHz, $CDCl_3$): δ=2.35, 2.56 (2s, 6H, $2CH_3$ pyridine), 7.20-7.60 (m, 7H, Ar-H+ CH pyridine+ CH benzylidene) ppm. Anal. Calcd. for: $C_{16}H_{12}ClNOSe$ (348.69): C, 55.11; H, 3.47; Cl, 10.17, N, 4.02 %. Found: C, 55.23; H, 3.34; Cl, 10.35, N, 3.91%.

General procedure for the synthesis of (12a-c)

Method A

A mixture of 2-substituted benzyledine derivatives**11a-c** (0.01 mmol), malononitrile (0.01 mmol), and few drops of piperidine in ethanol (30 ml), was heated under reflux for 2 h, then the mixture was allowed to cool. The solid product which formed on cooling, was collected and recrysallized from ethanol.

Method *B*

Amixture of selenolone compound **10** (1.76 g, 0.01 mol) and arylidene malononitrile (0.01mol) and few drops of triethyl amine in ethanol (30 ml) was heated under reflux for 3 h, then allowed to cooled .The solid product was collected and recrystallized from ethanol .

2-Amino-7,9-dimethyl-4[H]-4-pheyl-pyrano[2`,3`:4,5]selenolo[2,3-b]pyridine-3-carbonitrile (12a).

Obtainedbythe reaction of selenolone compound **10** with benzylidenemalononitrileas yellow crystals (85%,0.80 g) yield, m.p. 248- 250 ^{o}C.IR v: 3455, 3440 cm^{-1}(NH_2),3042 cm^{-1}(CH aromatic), 2846, 2918 cm^{-1} (CH aliphatic), 2202 cm^{-1}(CN). ^{1}H NMR (400MHz, $CDCl_3$): δ= 2.48, 2.51 (2s, 6H, $2CH_3$ pyridine), 4.84(s, H, CH pyrane), 6.50(s, 2H, NH_2), 6.70(s, H, CH pyridine), 6.91-7.20(m, 5H, Ar-H) ppm. Anal. Calcd. for: $C_{19}H_{15}N_3OSe$ (380.31): C, 60.01; H, 3.98; N, 11.05%. Found: C, 60.06; H, 3.95; N, 11.03 %.

2-Amino-7,9-dimethyl-4H-4-(p-anisyl)pyrano[2`,3`:4,5]selenolo[2,3-b]pyridine-3-carbonitrile (12b).

Obtained by the reaction of selenolone compound **10** with *p*-methoxybenzylidenemalononitrile as the above general procedure as pale yellow crystals in (75%, 0.75 g) yield, m.p. 272-274 ^{o}C.IR v: 3328, 3403 cm^{-1} (NH_2), 3043 cm^{-1} (CH aromatic), 2848, 2917 cm^{-1}(CH aliphatic), 2191 cm^{-1}(CN). ^{1}H NMR (90 MHz, $CDCl_3$): δ= 2.48 (s, 3H, CH_3 pyridine), 2.51(s, 3H, CH_3 pyridine), 2.67 (s, 3H, CH_3 pyridine), 5.14(s, 1H, CH pyrane), 6.81(s, 2H, NH_2), 6.91(s, 1H, CH pyridine), 7.24-6.91 (m, 4H, Ar-H) ppm. Anal. Calcd. for: $C_{20}H_{17}N_3O_2Se$ (410.34): C, 58.54; H, 4.18; N, 10.24 %. Found: C, 58.66; H, 4.25; N, 10.03 %.

2-Amino-4H-4-[p-chloropheyl)-7,9-dimethylpyrano[2`,3`:4,5]selenolo[2,3-b]pyridine-3-carbonitrile (12c)

Obtained by the reaction of selenolone compound **10** with *p*-chlorobenzylidenemalononitrile as the above general procedure. The solid product was collected and recrystallized from ethanol as yellow crystals in (90 %,0.90 g) yield, m.p. 282-284^{o}C.IR v: 3329, 3471 cm^{-1}(NH_2), 3040 cm^{-1}(CH aromatic), 2849, 2917 cm^{-1}(CH aliphatic), 2195 cm^{-1}(CN). ^{1}H NMR (90 MHz, $CDCl_3$): δ= 2.38 (s, 3H, CH_3 pyridine), 2.41(s, 3H, CH_3 pyridine), 4.83(s, H, CH pyrane), 6.55(s, 2H, NH_2), 7.10(s, H, CH pyridine), 7.23-7.64 (m, 4H, Ar-H) ppm. Anal. Calcd. for: $C_{19}H_{14}ClN_3OSe$ (414.76): C, 55.02; H, 3.40; Cl, 8.55, N, 10.13%. Found: C, 55.15; H, 3.31; Cl, 8.72; N, 10.05 %.

2-Ethoxymethyleneamino-4H-4-pheyl-7,9-dimethylpyrano[2`,3`:4,5] selenolo[2,3-b]pyridine-3-carbonitrile (13).

A mixture of amino carbonitrile compound **12a** (3.3 g, 0.01 mol) and triethylorthoformate (0.02 mmol) in acetic anhydride (1 ml) was heated under reflux for 2 h, then allowed to cool .The solid product which formed on cooling was collected and recrystallized from ethanol as white crystals (75 %,0.70 g) yield,m.p.228-230^{o}C.IR v: 3042 cm^{-1}(CH aromatic), 2969, 2849 cm^{-1}(CH aliphatic), 2220 cm^{-1}(CN). ^{1}H NMR (400MHz, $CDCl_3$): δ= 1.37 -1.41 (t, *J*= 12.00 Hz, 3H, CH_3 ester), 2.38(s, 3H, CH_3 pyridine), 2.50 (s, 3H, CH_3 pyridine), 4.50-4.68 (q, *J*= 6.80 Hz, 2H, CH_2 ester), 5.10 (s, 1H, CH pyrane), 6.80 (s ,H, CH pyridine), 6.88- 6.95(m,5H, ArH),7.64(s, 1H, N=CH) ppm. Anal. Calcd. for: $C_{22}H_{19}N_3O_2Se$ (436.38): C, 60.55; H, 4.39; N, 9.63 %. Found: C, 60.43; H, 4.58; N, 9.79 %.

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4,6,4',6'-Tetramethyl-2-(oxoselenolo]2,3-b]pyridinylidene)-3(2H)-one(14)

Method A

A mixture of compound **11** (2.67 g, 0.01 mmol) and phenyl hydrazine (1.08 g, 1.0 mmol) in ethanol (30 ml) was heated under reflux for 3 h. The red crystals which precipitated while heating was filtered off, dried and recrystallized from dioxane in 75% yield.

Method B

To a stirred solution of compound **10** (1.79 g, 0.01 mmol) in acetic acid (20 ml), sodium nitrite solution (0.02 mmol) in water (5 ml) was added dropwise over 10 min. The solid product was collected and recrystallized from dioxane in (78%, 1.20 g) yield, m.p. >300 ^{o}C.IR v: 2926, 2913 cm^{-1} (CH aliphatic), 1706 cm^{-1}(C= O).^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.38 (s, 6H, $2CH_3$ pyridine), 2.50(s, 6H, $2CH_3$ pyridine), 6.82 (s, 2H, 2CH pyridine) ppm.Anal. Calcd. for $C_{18}H_{14}N_2O_2Se_2$ (448.24): C, 48.23; H, 3.15; N, 7.14. Found: C, 48.11; H, 3.27; N, 7.35.

2-Arylazo-4, 6-dimethylselenolo[2, 3-b]pyridin-3-one (15a-e)

General Procedure:

To a solution of 4, 6-dimethylselenolo[2,3-b]pyridin-3(2H)-one **10** (1.79 g, 0.01 mol) in ethanol containing sodium acetate (4.10 g, 0.05 mmol), a solution of diazotized aromatic amine (0.01 mol) wasaddeddropwise with stirring at 5^{o}C for 15 minutes. After addition was finished the stirring was continued for 1h, and then allowed to stand for 2h. The solid product was collected and recrystallized from ethanol.

4, 6-Dimethyl-2-phenylazoselenolo [2, 3-b] pyridin-3-one (15a)

Obtained by the reaction of **10** with aniline as the above general procedure as red crystals in (81 %,0.80 g) yield. m.p.98-100 ^{o}C.IR v:3430 cm^{-1}(NH), 3045 cm^{-1}(CH aromatic), 2988, 2938cm^{-1}(CH aliphatic), 1668 cm^{-1}(C=O). ^{1}H NMR (90 MHz, $CDCl_3$) δ =2.40(s, 3H, CH_3 pyridine), 2.60 (s, 3H, CH_3 pyridine), 3.50 (s, 1H, CH selenophene), 6.90 (s, 1H, CH pyridine), 7.30-7.55 (m, 5H, Ar-H) ppm. Anal. Calcd. for: $C_{15}H_{13}N_3OSe$ (330.25): C, 54.55; H, 3.97; N, 12.72 %. Found: C, 54.69; H, 3.82; N, 12.51 %.

4,6-Dimethyl-2-(p-methoxyphenyl)azoselenolo[2,3-b]pyridin-3-one (15b)

Obtained by the reaction with *p*-anisidine as the above general procedure as red crystals (85 %, 0.80 g) yield, m.p.168-170^{o}C.IR v: 3421 cm^{-1}(NH), 3042 cm^{-1} (CH aromatic), 2988, 2938 cm^{-1}(CH aliphatic), 1637.22 cm^{-1}(C=O). ^{1}H NMR (90 MHz, DMSO-d_6): δ =2.30, 2.45 (2s, 6H, $2CH_3$ pyridine), 2.80 (s, 3H, OCH_3),3.70 (s, 1H, CH selenophene), 6.80(s, 1H, CH pyridine), 7.40-7.60 (dd, 4H, Ar-H *p*-sub) ppm. Anal. Calcd. for: $C_{16}H_{15}N_3O_2Se$ (360.28): C, 53.34; H, 4.20; N, 11.66 %. Found: C, 53.51; H, 4.02; N, 11.47%.

2-(p-Chlorophenyl)-4,6-dimethyl-2-azoselenolo[2,3-b]pyridin-3-one (15c)

Obtained by the reaction with *p*-chloro aniline as the above general procedure as red crystals (90 %,0.90 g) yield.m.p.198-200 ^{o}C.IR v: 3421 cm^{-1}(NH),3043 cm^{-1}(CH aromatic), 2988, 2938 cm^{-1}(CH aliphatic), 1659.47 cm^{-1}(C=O) ppm.^{1}H NMR (400MHz,$CDCl_3$) δ =2.30, 2.46 (2s, 6H, $2CH_3$ pyridine), 3.70 (s, 1H, CH selenophene), 6.86(s, 1H, CH pyridine), 7.60-7.86 (dd, 4H, ArH*p*-sub) ppm. Anal. Calcd. for: $C_{15}H_{12}Cl\ N_3OSe$ (364.70): C, 49.40; H, 3.32; Cl, 9.72; N, 11.52 %. Found: C, 49.54; H, 3.23; Cl, 9.91; N, 11.35 %.

N-(4, 6-Dimethyl selenolo[2,3-b]pyridine-3(2H)ylidene)toluidine (16)

Selenopyridinone compound **10** (1 g, 0.004 mol), *p*-toulidine (0.01 mol)was refluxed in ethanol (30 ml) for 2 h in the presence of few drops of piperidine. The solid product which formed on heating was collected then allowed to cool, filtered off and recrystallized from ethanol in (80 %,0.8 g) yield, m.p. 155 ^{o}C.IR v: 3044 cm^{-1}(CH aromatic), 2913, 2800cm^{-1}(CH aliphatic). ^{1}H NMR (400 MHz, DMSO) δ =2.35, 2.42 (2s, 6H, $2CH_3$*p*-toulidine), 2.48 (s, 3H, CH_3 pyridine), 4.80(s, 2H, CH_2), 6.75(s, 1H, CH pyridine), 7.14-6.88 (dd, 4H, Ar-H *p*-substituted) ppm. Anal. Calcd. for: $C_{16}H_{16}N_2Se$ (375.25): C, 60.95; H, 5.12; N, 8.89%. Found: C, 60.81; H, 5.01; N, 8.90%.

CONCLUSION:

The previously discussed reactions described a facile synthesis of 3-amino -2-substituted -4,6-dimethyl selenolo[2,3-b]pyridine **(4a-c)** and reactions of its amino-ester **4a** forming pyridoselenolo[2,3-b] pyridines **7, 9** and pyranoselenolo[2,3-b]pyridines **12**, **13** respectively.

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