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Synthesis and characterization of 3,5-lutidinyl chalcogen and -dichalcogen compounds: X-ray crystal structure of bis(3,5-dimethyl-2-pyridyl) diselenide and 2,6-bis(selenomethyl)-3,5-lutidine

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ABSTRACT

The synthesis of 3,5-lutidinyl chalcogen and -dichalcogen compounds has been described by a method involving selective mono- and dilithiation of 3,5-lutidine (**1**) ring. The selective mono- and dilithiation of **1** has been achieved by reacting BF_3-complexed 3,5-lutidine (**2**) with 1 and 2 equiv of LTMP/LDA respectively. The subsequent insertion of elemental selenium followed by aerial oxidation or quenching with iodomethane leads to the formation of bis(3,5-dimethyl-2-pyridyl) diselenide (**5**) and 2,6-bis (selenomethyl)-3,5-lutidine (**7**) respectively. In addition, sequential incorporation of sulfur and selenium atom in the same lutidine ring has been reported for the first time. Single-crystal X-ray studies of (**5**), having a rare C–Se–Se–C torsion angle of 180°(4), and (**7**) have also been reported.

1. Introduction

The chemistry of organochalcogen compounds containing at least one heterocyclic ring has gained momentum due to some unique properties of these compounds [1]. Pyridylseleno group has been found to be a better leaving group in the selenoxide-elimination reactions leading to the formation of terminal olefins [2,3]. The pyridyl metal chalcogenolates act as better single source precursors of semiconducting materials compared to its alkyl/aryl congeners [4,5]. In biochemistry, selenium derivatives of quinoline and pyridine, because of their superior redox catalytic and metal binding capabilities, act as effective and selective antioxidants when compared with the mono-functional arylselenium compounds [6]. The pyridyl and picolyl chalcogens [7–13] have been known for some time and have been extensively studied. However, it is surprising that there is no report on the chemistry of lutidinyl chalcogen compounds.

Due to the non-availability of 2-bromo-3,5-lutidine, we thought of synthesizing 3,5-lutidinyl chalcogens by utilizing direct lithiation of 3,5-lutidine ring (**1**). Selective ring lithiation of **1** has only been achieved by using 3–8 equiv of *n*-BuLi/LiDMAE complex (16 equiv of *n*-BuLi) [14]. However, our effort to follow this route for the synthesis of bis(3,5-dimethyl-2-pyridyl) diselenide met with very little success as the yields obtained were very poor (~5%). In addition, this methodology poses difficulties in the purification procedure due to the formation of highly obnoxious by products because an excess of elemental selenium is needed for quenching the excess of the base used. Therefore, we thought of developing a methodology which does not have these drawbacks. In this paper, we report an efficient and an inexpensive method which offers the titled compounds in high yields and purity. Kessar *et al.* reported the lithiation of pyridine aided by BF_3 complexation with lithium tetramethyl piperidine (LTMP).[15] However, it is for the first time that selective mono- and dilithiation of 3,5-lutidine ring has been achieved by using BF_3-complexed 3,5-lutidine with lithium diisopropylamide (LDA) or lithium tetramethyl piperidine (LTMP). Single-crystal X-ray studies of bis(3,5-dimethyl-2-pyridyl) diselenide (**5**), having a rare C–Se–Se–C torsion angle of 180°(4), and 2,6-bis(selenomethyl)-3,5-lutidine (**7**) have also been reported.

2. Results and discussion

2.1. Preparation of lutidinyl chalcogen compounds by monolithiation of *1*

Similar to Kessar's reaction on pyridine [15] complexation of $BF_3 \cdot Et_2O$ to 3,5-lutidine in dry diethyl ether at 0 °C gives the adduct **2**. This adduct undergoes lithium hydrogen abstraction reaction at −78 °C with LTMP and delivers carbanion (**3**). The carbanion **3** when reacted with elemental selenium gives the corresponding

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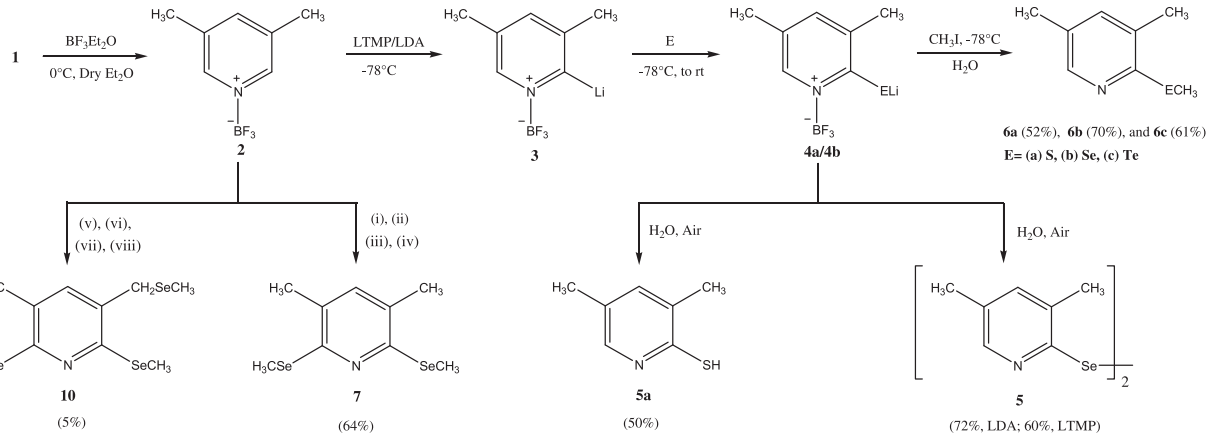
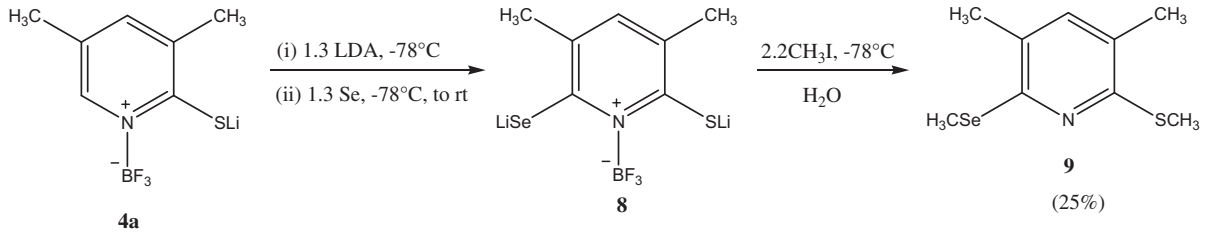


Scheme 1. Preparation of 3,5-lutidinyl chalcogen compounds by monolithiation and dilithiation of BF_3-complexed 3,5-lutidine: (i) LDA (2.2 equiv), (ii) Se (2.2 equiv), (iii) CH_3I (2.2 equiv), −78 °C, (iv) H_2O; (v) LDA (3.3 equiv), (vi) Se (3.3 equiv), (vii) CH_3I (3.3 equiv), −78 °C, (viii) H_2O.



Scheme 2. Preparation of 6-selenomethyl-2-thiomethyl-3,5-lutidine.

selenolate anion **4b**. This anion, upon hydrolysis and subsequent aerial oxidation, offers bis(3,5-dimethyl-2-pyridyl) diselenide in good yield (Scheme 1). The insertion of elemental sulfur instead of selenium in the above reaction gives 3,5-lutidin-2-thiol (**5a**) in a moderate yield.

TMP being an expensive reagent, it was thought to bring about the lithiation of **1** with less expensive LDA. We are happy to report here that in addition to being cheaper than LTMP, LDA gives better yield of **5** (72%). In light of this finding, all subsequent reactions were carried out using LDA as the lithiating reagent. This technique was further utilized for the synthesis of unsymmetrical chalcogenides. In a representative example, iodomethane was reacted with **4a**/**4b** at −78 °C followed by hydrolysis to give 2-thio- and 2-selenomethyl-3,5-lutidine (**6a** and **6b**) in 52% and 70% yields respectively. The effort to synthesize the corresponding telluromethane was not successful initially, as large amount of tellurium remained unreacted due to its surface oxidation. However, when a freshly activated tellurium was used it readily got dissolved in the reaction mixture to give a red solution of the tellurolate anion. This anion when reacted with iodomethane gave 2-telluromethyl-3,5-lutidine (**6c**) in good yield.

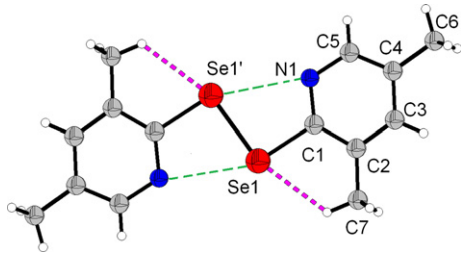


Fig. 1. Ortep diagram of bis(3,5-dimethyl-2-pyridyl) diselenide (**5**) showing Se···H and Se···N intramolecular non-bonded interactions.

2.2. Preparation of 2,6-bis(selenomethyl)-3,5-lutidine (**7**)

In as much as the organoselenium compounds having two selenium atoms show better antioxidant activity by providing two redox active centers, we decided to synthesize bis(selenoalkyl) derivative of **1** where two selenium atoms are attached at two different positions of the lutidine ring. The BF_3—lutidine adduct was treated with 2.2 equiv of LDA to give the dilithiated species. The addition of elemental selenium (2.2 equiv) to this species and subsequently its reaction with iodomethane (2.2 equiv) gives hitherto unknown 2,6-bis(selenomethyl)-3,5-lutidine (**7**) as a white solid (foul smelling) in 64% yield (Scheme 1). No compound corresponding to the side-chain lithiation of **1** was noticed in this reaction, indicating the effectiveness of this methodology for achieving the dilithiation of the 3,5-lutidine ring at the two α-positions.

2.3. Preparation of 6-selenomethy-2-thiomethyl-3,5-lutidine (**9**)

Our next attempt was aimed at the sequential incorporation of sulfur and selenium in the same lutidine ring. To achieve this, **4a** was treated with LDA (1.3 equiv) at −78 °C and reacted with

Table 1
Selected bond distances (Å) and angles (°) for **5**.

Se(1)–C(1)	1.917(9)	Se(1)–Se(1)#1	2.352(2)
C(7)–C(2)	1.480(12)	C(7)–H(02A)	0.9600
C(5)–N(1)	1.353(12)	C(5)–C(4)	1.387(11)
C(5)–H(004)	0.9300	C(3)–C(4)	1.404(12)
C(1)–Se(1)–Se(1)#1	92.9(2)	C(2)–C(7)–H(02A)	109.5
N(1)–C(1)–Se(1)	117.7(6)	C(3)–C(2)–C(7)	123.5(7)

Symmetry transformations used to generate equivalent atoms for 5: #1 $-x+1, -y, -z+1$.

Table 2
Comparative torsion angles (°), bond angles (°) and bond lengths (Å) in **5**, and various 2,2′-dipyridyl diselenides.

Compound	C–Se–Se–C torsion angle	X–C–Se–Se (X = C or N) torsion angle	Se–Se bond length	C (sp^2)–Se bond length	C(1)–Se(1)–Se(1) bond angle
5	−180 (4)	176.7 (7) and −1.9 (6)	2.352 (2)	1.917 (9)	92.9 (2)
2,2′-Dipyridyl diselenide	84.3 (2)	−0.8 (6) and 178.8 (4)	2.2969 (9)	1.932 (6)	102.8 (2)
4,4′-Dimethyl-2,2′-dipyridyl diselenide	−89.2 (18)	4.3 (4) and −176.5 (3)	2.2973 (7)	1.938 (4)	102.6 (12)
6,6′-Dimethyl-2,2′-dipyridyl diselenide	90.1	−1.8 (4) and 178.2 (3)	2.2935 (11)	1.929 (5)	104.4 (14)

elemental selenium. The thio-selenolate dianion thus formed was quenched with an equivalent amount of iodomethane (Scheme 2) to give 6-selenomethyl-2-thiomethyl-3,5-lutidine (**9**) in low yield (25%). Increasing the amount of LDA from 1.3 equiv to 2.0 equiv did not show any substantial improvement in the yield of **9**. The same result was obtained when the time for the lithiation reaction of **4a** was increased from 15 min to 60 min.

2.4. Reaction of *2* with 3.3 equiv of LDA

To further elaborate on this methodology, 3.3 equiv of LDA was reacted with **2**. The usual insertion of selenium followed by reaction with iodomethane (Scheme 1) yielded a clear solution containing the product. To our surprise, this solution, when kept on anhydrous sodium sulphate, got decomposed with the precipitation of red amorphous selenium. This was contrary to our previous experiments where very little decomposition had been noticed during the work-up procedure. On purification of the decomposed products, we were able to isolate 3-(carbylseleno methyl)-2,6-bis(selenomethyl)-5-picoline (**10**) in very low yield (5%) along with **7** in a substantial amount (40%). The low yield of **10** is primarily due to its instability, especially when present in the form of solution. The compounds containing CH_2–Se bond, e.g. the picolyl [13] and benzyl [16] seleniums, are known to be highly unstable.

It is pertinent to mention here that no product corresponding to the 3rd lithiation at the γ-position of the lutidine ring was noticed in this reaction. This clearly establishes that the lithiation of the methyl group is preferred over lithiation at the γ-position of the lutidine ring even after complexation of **1** with boron trifluoride.

2.5. Solid state structural features of *5* and *7*

In order to understand the structural features of **5** and **7** single-crystal X-ray studies were carried out. The structure of **5** is shown in Fig. 1 and the selected bond length and angles are presented in Table 1. The most striking feature about **5** is that it has a rare C–Se–Se–C torsion angle of 180°(4) (Table 2). Intramolecular non-bonded interactions were noticed between selenium and hydrogen of the ortho-methyl group [Se(1)···H(02A), 2.481 Å], and between selenium attached to one ring and nitrogen of the other lutidine ring [Se···N(1)#1, 2.901 Å], these distances are significantly shorter than the sum of van der Waals radii of 3.1 Å and 3.4 Å respectively.

Table 3
Selected bond distances (Å) and angles (°) for **7**.

Se(1)–C(1)	1.930(5)	Se(1)–C(8)	1.953(5)
C(4)–C(7)	1.510(7)	C(6)–H(6A)	0.9600
C(3)–H(3)	0.9300	C(8)–H(8B)	0.9600
C(5)–Se(2)–C(9)	97.6(2)	C(2)–C(6)–H(6A)	109.5
H(6A)–C(6)–H(6B)	109.5	N(1)–C(1)-Se(1)	116.7(4)
C(2)–C(1)–Se(1)	117.9(4)	C(4)–C(5)–Se(2)	118.4(4)
C(4)–C(7)–H(7A)	109.5	Se(1)–C(8)–H(8A)	109.5

These non-bonded interactions are probably responsible for the observed C–Se–Se–C torsion angle. All the substituted and unsubstituted 2,2′-dipyridyl diselenides have the C–Se–Se–C torsion angle of 80–90° [7,10,11,17] and none of these compounds exhibits the types of non-bonded interactions discussed above. Also, the X–C–Se–Se torsion angles in **5** and various other 2,2′-dipyridyl diselenides is near 180° (Table 2). The C–Se–Se–C torsion angle of 180°(4) in **5** allows strong interaction of selenium lone pair electrons with the π^* molecular orbital of the lutidine ring. This is evident from the longer C–C and C–N bond length in the lutidine (pyridine) rings compared to that found in 2,2′-dipyridyl diselenide [10]. The reduction in the Se···N (adjacent ring) lone pair–lone pair repulsion in **5**, leads to a smaller C(1)–Se(1)–Se(1)#1 bond angle (92.9°, Table 2). In **5,** the Se–Se bond length is longer and the Se–C bond length is shorter compared to that in 2,2′-dipyridyl diselenide. The geometry around the selenium atom is different, the nitrogen atoms are in *cis*,*cis* position with respect to the Se(1)–Se(2) group.

Selected bond length and angles of **7** are given in Table 3 and its molecular structures with atom numbering scheme is shown in Fig. 2. A very weak interaction between selenium and hydrogen of the ortho-methyl group is observed in **7** (Se···H distance of 3.012 Å). No interaction between selenium attached to one ring and nitrogen of the other lutidine ring was observed. The geometry around the selenium atom in **7** is the same as in tris(2-pyridylseleno)methane [7]. The nitrogen atoms are in *cis*,*cis* position with respect to the Se(1)–C(8) group. It is evident from Table 3 that the geometry around C(8) and C(9) is perfectly tetrahedral, whereas, the geometry around C(1) in tris(2-pyridylseleno) methane is slightly distorted tetrahedral due to lone pair–lone pair repulsions between three selenium atoms. All the bond angles and bond lengths of the lutidine (pyridine) ring are consistent with the value reported for 2,2′-dipyridyl diselenides [10]. Short intermolecular distances were observed between H(9B)···H(7B) [2.254 Å], C(9)···H(7B) [2.680 Å], C(1)···H(8B) [2.805 Å] and C(9)···H(8A) [2.787 Å], which are significantly shorter than sum of van der Waals radii of 2.4 Å (H···H) and 2.9 Å (C···H).

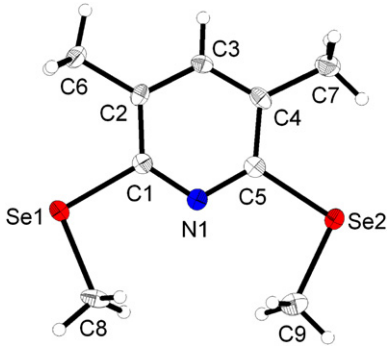


Fig. 2. Ortep diagram of and 2,6-bis(selenomethyl)-3,5-lutidine (**7**) with atom numbering scheme.

Table 4
Crystal data collection and structure refinement parameters of compound **5** and **7**.

Compound	**5**	**7**
Empirical formula	$C_{14}H_{16}N_2Se_2$	$C_{7.20}H_{10.40}N_{0.80}Se_{1.60}$
E. formula weight	370.21	234.50
Temperature	100 K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*n*	*P*2(1)/*n*
a	8.748(11) Å	12.367(5) Å
b	8.904(11) Å	6.655(5) Å
c	8.924(11) Å	12.680(5) Å
α	90°	90.000(5)°
β	99.185(19)°	91.968(5)°
γ	90°	90.000(5)°
Volume	686.2(14) Å^3	1043.0(10) Å^3
Z	2	5
Density (calculated)	1.792 Mg/m^3	1.867 Mg/m^3
Absorption coefficient	5.372 mm^{-1}	7.038 mm^{-1}
F(000)	364	568
Crystal size	0.24 × 0.20 × 0.18 mm^3	0.26 × 0.24 × 0.22 mm^3
Theta range for data collection	4.23–25.50°	2.34–26.50°
Index ranges	$-10 \le h \le 10$, $0 \le k \le 10$, $0 \le l \le 10$	$-15 \le h \le 11$, $-8 \le k \le 7$, $-15 \le l \le 15$
Reflections collected	1025	5687
Independent reflections	1281 [R(int) = 0.072]	2143 [R(int) = 0.0406]
Completeness to theta	25.50°, 80.0%	26.50°, 99.0%
Absorption correction	Semi-empirical from equivalents	None
Max. and min. transmission	0.4447 and 0.3588	0.3066 and 0.2619
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1281/57/82	2143/0/109
Goodness-of-fit on F^2	0.995	1.075
Final R indices [$I>2\sigma(I)$]	$R1 = 0.0705$, $wR2 = 0.1812$	$R1 = 0.0414$, $wR2 = 0.1092$
R indices (all data)	$R1 = 0.0847$, $wR2 = 0.1917$	$R1 = 0.0530$, $wR2 = 0.1296$
Largest diff. peak and hole	1.834 and −1.796 e Å^{-3}	1.070 and −0.833 e Å^{-3}

3. Conclusion

Synthesis of a number of monochalcogen and dichalcogen derivatives of 3,5-lutidine has been achieved by a method involving selective ring lithiation and dilithiation of 3,5-lutidine. The uniqueness of this methodology is that it allows the incorporation of two same or two different chalcogen atoms in the lutidine ring in a procedure involving one-step purification.

4. Experimental

4.1. General

All experiments were carried out in dry oxygen-free nitrogen atmosphere. All the solvents were dried before use. TMP and 3,5-lutidine were purchased from Merck. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrophotometer in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. The ESI mass spectra were taken on Water Q-TOF Micro spectrometer. EI mass spectra were taken by using Shimadzu GC–Mass Spectrometer [GCMS QP-2010 plus] with Rtx-1MS (30 m × 0.25 mm ID × 0.25 μm) capillary column.

4.2. General procedure 1: lithiation of 3,5-lutidine

3,5-Lutidine (0.96 g, 1.0 ml, 9.0 mmol) was added to a three-necked 100 ml RBF containing diethyl ether (30 ml) under inert atmosphere. Boron trifluoride ($BF_3 \cdot Et_2O$) in diethyl ether (1.38 g, 1.23 ml, 9.9 mmol) was added to it at 0 °C. The resulting curdy white suspension was stirred for 10 min. In another three-necked 100 ml RBF, *n*-BuLi (7.6 ml, 1.3 N, 9.9 mmol) was added slowly to a solution of TMP (1.38 g, 1.7 ml, 9.9 mmol) or DIPA (0.99 g, 1.4 ml, 9.9 mmol) in diethyl ether (20 ml) at −10 °C to form LTMP or LDA respectively. The temperature of the RBF containing BF_3-complexed lutidine was lowered to −78 °C and LTMP or LDA was added slowly via cannula. Color of suspension changed from white to orange brown in about 10 min. The orange brown solution, indicating the lithiation of the lutidine, was stirred for 15–20 min at −78 °C.

4.2.1. Bis(3,5-dimethyl-2-pyridyl) diselenide (**5**)

Elemental selenium (0.780 g, 9.9 mmol) was added to the solution containing **3** at −78 °C. The temperature was slowly raised till all of the selenium dissolved. The reaction mixture was then hydrolyzed and exposed to aerial oxidation for 30 min. The organic layer was extracted with diethyl ether, washed with water, brine solution and then dried over anhydrous sodium sulphate. The solvent was removed and the crude product was refrigerated. Dark red solid was obtained the following day and it was later purified by column chromatography using 60–120 mesh silica gel and using hexane–ethyl acetate as an eluent (5:1). Yield: 1.0 g, 60% (LTMP), 1.2 g, 72% (LDA); m.p. 115–117 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.04 (2H, s), 7.08 (2H, s), 2.35 (6H, s), 2.18 (6H, s); ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 149.83, 148.15, 137.94, 133.89, 131.92, 20.86, 17.68. MS (ESI): 372 [M^{+}, ^{80}Se]. Anal. (%) Calcd for $C_{14}H_{16}N_2Se_2$: C, 45.43, H, 4.36, N, 7.57. Found: C, 45.97, H, 4.76, N, 7.40.

4.2.2. 3,5-Lutidin-2-thiol (**5a**)

Elemental selenium in the above procedure was replaced with elemental sulfur. Yield: 0.63 g, 50% (LDA), mp 184–188 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 11.52 (1H, s), 7.60 (1H, s), 7.30 (1H, s), 2.42 (3H, s), 2.19 (3H, s); ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 148.71, 139.56, 139.33, 129.52, 20.15, 18.05. MS (EI, 70 eV) *m*/*z* (relative intensity): 139 (100), 138 (27), 106 (9), 92 (6), 77 (11). Anal. (%) Calcd for C_7H_9NS: C, 60.43, H, 6.47, N, 10.07. Found: C, 59.85, H, 6.22, N, 9.25.

4.2.3. 2-Selenomethyl-3,5-lutidine (**6b**)

Iodomethane (1.38 g, 0.60 ml, 9.9 mmol) was added to selenolate anion formed in the above reaction. The reaction mixture was

slowly brought to room temperature and hydrolyzed. Yield: 1.26 g, (70%), viscous oil. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8. 05 (2H, s), 7.05 (2H, s), 2.36 (3H, s), 2.11 (6H, s). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 152.01, 147.36, 137.07, 132.57, 129.06, 19.39, 17.60, 5.21. MS (EI, 70 eV) *m*/*z* (relative intensity): 201 (100), 186 (64), 121 (99), 106 (75), 92 (25), 77 (61). Anal. (%) Calcd for $C_8H_{11}NSe$: C, 48.02, H, 5.54, N, 7.00. Found: C, 48.33, H, 5.75, N, 7.13.

4.2.4. 2-Thiomethyl-3,5-lutidine (**6a**)

Elemental selenium in the above procedure was replaced with elemental sulfur. Yield: 0.72 g, (52%), viscous oil. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.06 (2H, s), 7.05 (2H, s), 2.48 (3H, s), 2.15 (3H, s), 2.13 (3H, s). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 155.08, 146.47, 137.54, 130.38, 128.29, 18.35, 17.61, 13.05. MS (EI, 70 eV) *m*/*z* (relative intensity): 153 (82), 138 (16), 120 (100), 106 (40), 92 (26), 77 (38).

4.2.5. 2-Telluromethyl-3,5-lutidine (**6c**)

Elemental selenium in the procedure 4.2.3 was replaced with elemental tellurium. Yield: 1.36 g, (61%), viscous oil. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.18 (2H, s), 7.08 (2H, s), 2.30 (3H, s), 2.22 (3H, s), 2.19 (3H, s). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 148.45, 139.58, 136.91, 136.11, 129.87, 21.82, 17.58, −15.34. MS (EI, 70 eV) *m*/*z* (relative intensity): 251 (25, ^{130}Te), 236 (22), 121 (70), 106 (100), 77 (56).

4.3. General procedure 2: dilithiation of 3,5-lutidine

LDA (26.4 mmol) was added slowly to the BF_3-complexed 3,5-lutidine (2, 12 mmol) via cannula. The color of suspension changed from white to orange brown in about 10 min. The orange brown solution was stirred for 15 min at −78 °C.

4.3.1. 2,6-Bis(selenomethyl)-3,5-lutidine (**7**)

Elemental selenium (2.08 g, 26.4 mmol) was added to the above solution at −78 °C. The temperature was raised slowly until complete dissolution of selenium took place. The blackish brown solution was again cooled to −78 °C and iodomethane (3.74 g, 1.64 ml, 26.4 mmol) was added to it. The reaction mixture was slowly brought to the room temperature, hydrolyzed and purified. Yield: 2.6 g, (64%), mp 79–80 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 6.94 (1H, s), 2.50 (6H, s), 2.16 (6H, s). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 151.34, 136.90, 128.65, 18.48, 5.40. MS (EI, 70 eV) *m*/*z* (relative intensity): 295 (35), 280 (7), 214 (100), 200 (23), 185 (8), 120 (36), 105 (30), 90 (8), 77 (81). Anal. (%) Calcd for $C_9H_{13}NSe_2$: C, 36.89, H, 4.47, N, 4.78. Found: C, 36.98, H, 4.25, N, 4.54.

4.4. 6-Selenomethyl-2-thiomethyl-3,5-lutidine (**9**)

To a reaction mixture containing **4a** (12 mmol), LDA (13.2 mmol) was added in a drop-wise manner via cannula at −78 °C. The solution turned from viscous yellow to yellowish brown. Elemental selenium (1.04 g, 13.2 mmol) was added to the reaction mixture and after all the selenium had dissolved, iodomethane (3.74 g, 1.64 ml, 26.4 mmol) was added at −78 °C. The reaction mixture was slowly brought to the room temperature, hydrolyzed and purified. Yield: 0.75 g, (25%), mp 70–71 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 6.96 (1H, s), 2.61 (3H, s), 2.49 (3H, s), 2.16 (3H, s), 2.15 (3H, s). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 154.59, 150.80, 137.22, 127.77, 126.27, 18.50, 17.45, 13.24, 5.35. MS (EI, 70 eV) *m*/*z* (relative intensity): 247 (58), 215 (5), 166 (100), 152 (26), 137 (7), 105 (10), 92 (18), 77 (47). Anal. (%) Calcd for $C_9H_{13}NSSe$: C, 43.72, H, 5.26, N, 5.66. Found: C, 44.28, H, 4.98, N, 5.33.

4.5. 3-(Carbylselenomethyl)-2,6-bis(selenomethyl)-5-picoline (**10**)

LDA (27.9 mmol) was added slowly to the BF_3-complexed 3,5-lutidine (**2**, 9 mmol) in a drop-wise manner via cannula. Elemental selenium (2.20 g, 27.9 mmol) was added to the orange brown solution at −78 °C. After the complete dissolution of selenium, the blackish brown solution was cooled to −78 °C and iodomethane (3.96 g, 1.73 ml, 27.9 mmol) was added to it. The reaction mixture was slowly brought to the room temperature and hydrolyzed. Yield 0.18 g, (5%). ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 6.92 (1H, s), 3.58 (2H, s), 2.43 (3H, s), 2.42 (3H, s), 2.09 (3H, s), 1.88 (3H, s). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 152.10, 150.27, 136.13, 131.55, 128.04, 24.39, 18.24, 4.94, 4.49, 4.08. MS (EI, 70 eV) *m*/*z* (relative intensity): 389 (16), 294 (100), 279 (32), 198 (33), 118 (33), 103 (55), 93 (37), 88 (16), 77 (70). Anal. (%) Calcd for $C_{10}H_{15}NSe_3$: C, 31.12, H, 3.91, N, 3.62. Found: C, 30.92, H, 3.15, N, 3.52.

4.6. Crystal structure determination and refinement

Single-crystal X-ray data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on "Bruker SMART APEX CCD diffractometer" at 100 K. The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* [18]. The program SMART [19] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The data integration and reduction were processed with SAINT [19] software. An empirical absorption correction was applied to the collected reflections with SADABS [20] using XPREP [21]. All the structures were solved by the direct method using the program SHELXS-97 [22] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters in all the structure. All other relevant information about the data collection and refinement are presented in Table 4.

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Appendix A. Supplementary material

CCDC 786929 and 786928 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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