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Synthesis, characterization and X-ray structure of 3,4-lutidinyl-, 3-/4-picolyl- and pyridylselenium compounds

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ABSTRACT

Bis(4,5-dimethyl-2-pyridyl)-, bis(5-methyl-2-pyridyl)- and bis(4-methyl-2-pyridyl) diselenide have been synthesized directly from 3,4-lutidine (**1a**), 3-picoline (**1b**) and 4-picoline (**1c**) respectively via BF_3 aided lithiation reaction. The lithiation of 3,4-lutidinium-, 3- and 4-picolinium-BF_3 adduct (**2a**/**2b**/**2c**) gives the corresponding carbanion (**3a**/**3b**/**3c**) which on subjecting to selenium insertion reaction followed by aerial oxidation affords the related diselenide in good yield. Reaction of BF_3 complexed pyridylselenolate anion (**4a**/**4b**/**4c**) with diiodomethane gives the corresponding bis(2-pyridylseleno)methane. The dilithiation of 4-picolinium-/pyridinium-BF_3 adduct (**2c**/**2d**) followed by reaction with 2.2 equiv. of selenium and iodomethane affords the related 2,6-bis(methylselenenyl)pyridine and 2-(methylselenenyl)pyridine in varying proportions. Preparation of tris(methylselenenyl) derivatives of **1a** and **1c** have been given in the present study. $LiAlH_4$ has also been utilized to synthesize unsymmetrical monoselenides from the corresponding diselenides. Single crystal X-ray studies of bis(4,5-dimethyl-2-pyridyl) diselenide (**5a**), 3,4-dimethyl-2,6-bis(methylselenenyl)pyridine (**9a**), 4-methyl-2,6-bis(methylselenenyl)pyridine (**9c**), 2,6-bis(methylselenenyl)pyridine (**9d**) and 4-methyl-2,6-bis(methylselenenyl)-4-(methylselenenylmethyl)pyridine (**12a**) have also been carried out. The crystal data of these compounds reveals that the instances of Se···Se secondary interactions decreases with the increase in the number of methyl group attached to the pyridine ring.

1. Introduction

Interest in the field of organoselenium chemistry has increased over a period of time as it offers some unique advantages in the field of material and biochemical sciences [1,2]. The metal selenolates have been used as precursors for the low temperatures synthesis of semiconducting materials [3,4] that are finding applications in the solar [5] and thermoelectric [6,7] devices. In biology, organoseleniums are being used as mimics of glutathione peroxidase, an enzyme which shows antioxidant property [8,9]. These compounds are also being tested for their role as potential anticarcinogenic [10,11], anti-hyperglycemic [12] and antimicrobial agents [13]. Therefore, there have been constant efforts by chemists worldwide to come up with novel methodologies for efficiently synthesizing known and unknown organoselenium compounds. Due to lack of systematic study on the lutidinylchalcogen compounds we have focused our attention on the chemistry of these compounds. We have successfully reported the synthesis of 3,5-lutidinylchalcogen and -dichalcogen compounds directly from 3,5-lutidine [14].

In this paper, we have reported the synthesis of 3,4-lutidinyl, 3-/4-picolyl- and pyridylselenium compounds starting from 3,4-lutidine (**1a**), 3-picoline (**1b**) 4-picoline (**1c**) and pyridine (**1d**), respectively. The methodology involves BF_3 aided lithiation, dilithiation and trilithiation of the aforementioned pyridine derivatives. The potential of this methodology has been explored towards the synthesis of a series of compounds having more than one selenium atom attached to the pyridine ring. $LiAlH_4$ has also been utilized to synthesize unsymmetrical monoselenides from the corresponding diselenides. Single crystal X-ray studies of bis(4,5-dimethyl-2-pyridyl) diselenide (**5a**), 3,4-dimethyl-2,6-bis(methylselenenyl)-pyridine (**9a**), 4-methyl-2,6-bis(methylselenenyl)pyridine (**9c**), 2,6-bis(methylselenenyl)pyridine (**9d**) and 4-methyl-2,6-bis(methylselenenyl)-4-(methylselenenylmethyl)pyridine (**12a**) have also been reported.

2. Experimental

2.1. General

All experiments were carried out in dry oxygen-free nitrogen atmosphere. All the solvents were dried before use [15]. Lithium

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diisopropylamide (LDA) was made by adding *n*-BuLi (6.6 ml, 2.5 N, 16.5 mmol) to a solution of diisopropylamine (1.66 g, 2.32 ml, 16.5 mmol) in diethyl ether (30 ml) at −10 °C [16]. ^{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.

2.2. General procedure 1: Synthesis of bis(lutidinyl/picolyl) diselenides

A solution of **1a** (1.60 g, 1.68 ml, 15.0 mmol) or **1b** (1.396 g, 1.46 ml, 15.0 mmol) or **1c** (1.396 g, 1.46 ml, 15.0 mmol) in diethyl ether (50 ml) was cooled to 0 °C in a three-necked 100 ml round bottom flask (RBF) and a solution of boron trifluoride ($BF_3{\cdot}Et_2O$) in diethyl ether (2.34 g, 2.07 ml, 16.5 mmol) was added to it. A white suspension was formed due to the formation of 3,4-lutidinium- /3-picolinium- /4-picolinium-BF_3 adduct (**2a**/**2b**/**2c**). The temperature of the suspension was lowered to −78 °C and LDA (16.5 mmol) was added slowly to it via cannula. The resulting red brown solution containing the BF_3-complexed carbanion (**3a**/**3b**/**3c**) was further stirred for 15–20 min at −78 °C. Elemental selenium (1.30 g, 16.5 mmol) was added to this solution at −78 °C. The temperature was slowly raised till all of the selenium got dissolved indicating the formation of the corresponding selenolate anions (**4a**/**4b**/**4c**). The reaction mixture containing **4a**/**4b**/**4c** was hydrolyzed and exposed to aerial oxidation for 30 min. The organic layer was extracted with diethyl ether, washed with water, brine solution and again with water and then dried over anhydrous sodium sulfate. The solvent was removed and the crude product was purified by column chromatography using 60–120 mesh silica gel and hexane–ethyl acetate as an eluent.

2.2.1. Bis(4,5-dimethyl-2-pyridyl) diselenide (**5a**)

Yield: 3.17 g (57%), m.p. 95–98 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.16 (s, 2H), 7.56 (s, 2H), 2.20 (s, 6H), 2.19 (s, 6H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 151.2, 149.4, 147.7, 130.3, 124.3, 19.3, 15.8. MS (ESI): 372 ([M]$^+$, ^{80}Se). *Anal.* Calc. 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%.

2.2.2. Bis(5-methyl-2-pyridyl) diselenide (**5b**) [17]

Yield: 3.8 g (73%), m.p. 65–66 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.28 (s, 2H), 7.68–7.70 (d, J = 8.16 Hz, 2H), 7.34–7.36 (dd, J = 1.92 Hz, 8.12 Hz, 2H), 2.29 (s, 6H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 150.8, 149.8, 138.2, 130.9, 123.4, 17.8. MS (ESI): 344 ([M].+, ^{80}Se). *Anal.* Calc. for $C_{12}H_{12}N_2Se_2$: C, 42.12; H, 3.53; N, 8.18. Found: C, 41.87; H, 3.56; N, 8.10%.

2.2.3. Bis(4-methyl-2-pyridyl) diselenide (**5c**) [17]

Yield: 3.5 g (68%), m.p. 96–98 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.31–8.29 (d, J = 4.90 Hz, 2H), 7.65 (s, 2H), 6.90–6.91 (d, J = 4.10 Hz, 2H), 2.29 (s, 6H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 154.1, 149.1, 148.9, 123.9, 122.4, 21.0. MS (EI, 70 eV) *m*/*z* (relative intensity): 344 (10, [M].+, ^{80}Se), 263 (5), 183 (59), 92 (99), 80 (6), 65 (100), 51 (7).

2.3. General procedure 2: Synthesis of bis(lutidinyl/picolylseleno)methanes

Diiodomethane (4.42 g, 1.32 ml, 16.5 mmol) was added to the solution containing **4a**/**4b**/**4c** at −78 °C. The reaction mixture was stirred for half an hour at −78 °C and then slowly warmed to room temperature and stirred for additional half an hour. The reaction mixture was then hydrolyzed and worked-up as described for the diselenides.

2.3.1. Bis(4,5-dimethyl-2-pyridylseleno)methane (**6a**)

Yield: 1.8 g (32%), m.p. 65–66 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.14 (s, 2H), 7.04 (s, 2H), 4.72 (s, 2H), 2.11 (s, 12H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 151.9, 150.1, 146.1, 129.4, 126.0, 19.0, 16.1, 15.9. MS (ESI): 386 ([M].+, ^{80}Se). *Anal.* Calc. for $C_{15}H_{18}N_2Se_2$: C, 46.63; H, 4.66; N, 7.25. Found: C, 46.94; H, 4.42; N, 7.48%.

2.3.2. Bis(5-methyl-2-pyridylseleno)methane (**6b**)

Yield: 3.21 g (60%), m.p. 70–72 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.29–8.31 (d, J = 2.33 Hz, 2H), 7.14–7.22 (m, 3H), 6.88–6.91 (dd, J = 4.84 Hz, 2.6 Hz, 2H), 4.72 (s, 2H), 2.19 (s, 3H), 2.12 (s, 3H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 155.8, 151.7, 150.4, 147.0, 136.9, 136.2, 133.1 129.9, 124.8, 120.0, 19.2, 16.2 15.4. MS (EI, 70 eV) *m*/*z* (relative intensity): 358 (2, [M].+, ^{80}Se), 264 (3), 186 (61), 173 (18), 143 (2), 106 (28), 92 (63), 80 (5), 65 (100), 51 (7). *Anal.* Calc. for $C_{13}H_{14}N_2Se_2$: C, 43.83; H, 3.96; N, 7.86. Found: C, 43.91; H, 3.89; N, 8.11%.

2.3.3. Bis(4-methyl-2-pyridylseleno)methane (**6c**)

Yield: 2.9 g (54%), m.p. 58–60 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.26–8.28 (d, J = 5.12 Hz, 2H), 7.09 (s, 2H), 6.78–6.80 (d, J = 5.12 Hz, 2H), 4.78 (s, 2H), 2.19 (s, 6H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 155.1, 149.6, 147.2, 125.8, 121.8, 20.8, 15.8. MS (EI, 70 eV) *m*/*z* (relative intensity): 358 (1, [M].+, ^{80}Se), 266 (1), 186 (66), 173 (21), 145 (2), 107 (2), 92 (83), 80 (10), 65 (100), 54 (1). *Anal.* Calc. for $C_{13}H_{14}N_2Se_2$: C, 43.83; H, 3.96; N, 7.86. Found: C, 43.79; H, 4.01; N, 7.72%.

2.3.4. 2-(Benzylselenenyl)-4-methylpyridine (**7c**)

(Chloromethyl)benzene (2.08 g, 1.89 ml, 16.5 mmol) was added to the solution containing **4c** at −78 °C. The reaction mixture was stirred for half an hour at −78 °C and then slowly warmed to room temperature and stirred for additional half an hour. The reaction mixture was then hydrolyzed and worked-up as described for the diselenides. Yield: 2.3 g (59%), yellow viscous liquid. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.30–8.31 (d, J = 5.04 Hz, 1H), 7.12–7.34 (m, 5H), 7.06 (s, 1H), 6.78–6.79 (dd, J = 0.92 Hz, 4.98 Hz, 1H), 4.42 (s, 2H), 2.17 (s, 3H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 155.3, 149.6, 147.2, 139.2, 128.6, 128.5, 126.9, 126.0, 121.9, 29.2, 20.8 MS (EI, 70 eV) *m*/*z* (relative intensity): 263 (9, [M].+, ^{80}Se), 182 (40), 167 (5), 91 (100), 65 (59). *Anal.* Calc. for $C_{13}H_{13}NSe$: C, 59.54; H, 4.99; N, 5.34. Found: C, 59.90; H, 4.69; N, 5.46%.

2.3.5. 2-Iodo-5-methyl-4-((4-methylpyridin-2-selenenyl)methyl)pyridine (**8c**)

2-Iodo-4-(iodomethyl)-5-methylpyridine (1.19 g, 3.3 mmol) was added to the solution containing **4c** at −78 °C. Rest of the procedure remained as above. Yield: 0.8 g (67%), yellow viscous liquid. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.36–8.37 (d, J = 5.08 Hz, 1H), 8.08 (s, 1H), 7.61 (s, 1H), 7.10 (s, 1H), 6.91–6.92 (dd, J = 1.08 Hz, 4.98 Hz, 1H), 4.28 (s, 2H), 2.27 (s, 6H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 153.1, 151.5, 149.6, 148.9, 147.6, 134.7, 131.6, 126.3, 122.4, 114.9, 24.4, 20.7, 15.7. MS (EI, 70 eV) *m*/*z* (relative intensity): 404 (16, [M].+, ^{80}Se), 323 (60), 277 (17), 262 (8), 196 (28), 173 (48), 104 (70), 92 (91), 77 (52), 65 (100). *Anal.* Calc. for $C_{13}H_{13}N_2SeI$: C, 38.73; H, 3.25; N, 6.94. Found: C, 38.82; H, 3.13; N, 6.96%.

2.4. General procedure 3: Reaction of 4-picolinium-BF_3 (**2c**) and pyridinium-BF_3 (**2d**) adduct with 2.2 equiv. of LDA

4-Picolinium-BF_3 (**2c**) was made by adding BF_3–Et_2O (2.34 g, 2.07 ml, 16.5 mmol) to a solution of **1c** (1.396 g, 1.45 ml, 15 mmol) in dry diethyl ether at 0 °C. Pyridinium-BF_3 (**2d**) adduct (15 mmol) was made by adding BF_3–Et_2O (16.5 mmol) to **1d** (1.185 g, 1.21 ml,

15 mmol) at 0 °C [18]. A solution of LDA (33.0 mmol) was added slowly to **2c**/**2d** at −78 °C via cannula. The color of the suspension changed from white to orange brown in about 10 min. The orange brown solution was stirred for 15 min at −78 °C and then elemental selenium (2.60 g, 33.0 mmol) was added to it. The temperature was raised slowly until complete dissolution of selenium took place. The reddish brown solution was again cooled to −78 °C and iodomethane (4.68 g, 2.0 ml, 33.0 mmol) was added to it. The reaction mixture was slowly brought to the room temperature, hydrolyzed and worked up. Two compounds, **9c** and **10c**, were isolated from the reaction involving **2c** whereas, **9d** and **10d**, were isolated from the reaction involving **2d**.

*2.4.1. 4-Methyl-2,6-bis(methylselenenyl)pyridine (**9c**)*

Yield: 0.22 g (7%), m.p. 64–66 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 6.78–6.79 (s, 2H), 2.39 (s, 6H), 2.12 (s, 3H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 154.1, 145.6, 120.6, 19.4, 4.4. MS (EI, 70 eV) *m*/*z* (relative intensity): 281 (66, [M]**.**+, ^{80}Se), 266 (2), 201 (100), 184 (23), 170 (10), 144 (10), 120 (72), 107 (78), 91 (40), 79 (28), 63 (25), 51 (7). *Anal.* Calc. for $C_8H_{11}NSe_2$: C, 34.40; H, 3.95; N, 5.01. Found: C, 34.77; H, 3.81; N, 5.25%.

*2.4.2. 4-Methyl-2-(methylselenenyl)pyridine (**10c**) [19]*

Yield: 0.98 g (35%), light brown viscous oil. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.19–8.20 (d, *J* = 5.08 Hz, 1H), 7.02 (s, 1H) 6.72–6.73 (d, *J* = 5.04 Hz, 1H), 2.34 (s, 3H), 2.16 (s, 3H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 155.6, 149.5, 147.0, 125.0, 121.3, 20.7, 5.4. MS (EI, 70 eV) *m*/*z* (relative intensity): 187 (13, [M]**.**+, ^{80}Se), 117 (1), 107 (100), 93 (27), 79 (6), 65 (34), 51 (5).

*2.4.3. 2,6-Bis(methylselenenyl)pyridine (**9d**)*

Yield: 1.56 g (39%), m.p. 45–47 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 7.04–7.08 (t, *J* = 7.40 Hz, 7.96 Hz, 1H), 6.90–6.92 (d, *J* = 7.7 Hz, 2H), 2.37 (s, 6H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 155.6, 135.4, 120.6, 5.5. MS (EI, 70 eV) *m*/*z* (relative intensity): 267 (49, [M]**.**+, ^{80}Se), 187 (70), 172 (22), 157 (13), 130 (20), 106 (50), 93 (100), 65 (15), 51 (15). *Anal.* Calc. for $C_7H_9NSe_2$: C, 31.71; H, 3.42; N,5.28. Found: C, 31.48;H, 3.40; N, 5.26%.

*2.4.4. 2-(Methylselenenyl)pyridine (**10d**) [17]*

Yield: 0.57 g (22%), yellow viscous liquid. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.45–8.46 (dd, *J* = 1.72 Hz, 1.32 Hz, 4.62 Hz, 1H), 7.43–7.47 (dt, *J* = 1.88 Hz, 8.68 Hz, 1H), 7.30–7.32 (dd, *J* = 1.40 Hz, 7.48 Hz, 1H), 7.00–7.03 (m, *J* = 1.08 Hz, 4.96 Hz, 7.36 Hz, 1H) 2.46 (s, 3H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 156.0, 150.0, 135.8, 124.5, 120.0, 5.6. MS (EI, 70 eV) *m*/*z* (relative intensity): 173 (12, [M]**.**+, ^{80}Se), 158 (1), 93 (100), 78 (47), 65 (7), 51 (51).

*2.4.5. 2,6-Bis(benzylselenenyl)pyridine (**11d**)*

(Chloromethyl)benzene (4.17 g, 3.79 ml, 33.0 mmol) was added in place of iodomethane in the reaction discussed in the Section 2.4.3. Yield: 0.68 g (11%), m.p. 113–115 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 7.34–7.37 (m, 4H), 7.24–7.28 (m, 4H), 7.17–7.21 (m, 3H), 7.03–7.05 (d, *J* = 7.56, 2H), 4.49 (s, 4H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 155.7, 138.7, 135.9, 128.9, 128.6, 127.0, 121.6, 29.3. MS (EI, 70 eV) *m*/*z* (relative intensity): 419 (3, [M]**.**+, ^{80}Se), 339 (2), 247 (4), 167 (9), 91 (100), 65 (30). *Anal.* Calc. for $C_{19}H_{17}NSe_2$: C, 54.69; H, 4.10; N, 3.35. Found: C, 54.46; H, 4.53; N, 3.17%.

*2.4.6. 2-(Benzylselenenyl)pyridine (**12d**)*

2-(Benzylselenenyl)pyridine was isolated from the reaction discussed in Section 2.4.5. Yield: 2.0 g (55%), Red brown viscous oil. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.42–8.62 (d, *J* = 8.00 Hz, 1H), 7.40–7.43 (m, 2H), 7.17–7.29 (m, 5H), 7.00–7.02 (d, *J* = 7.56 Hz, 1H), 4.45 (s, 2H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 155.6, 150.0, 139.0, 136.0, 129.0, 128.4, 126.9, 125.4, 120.5, 29.3. MS (EI, 70 eV) *m*/*z* (relative intensity): 249 (6, [M]**.**+, ^{80}Se), 168 (43), 91 (100), 78 (18), 65 (34). *Anal.* Calc. for $C_{12}H_{11}NSe$: C, 58.07; H, 4.46; N, 5.64. Found: C, 57.61; H, 4.79; N, 5.76%.

*2.5. Reaction of 3,4-lutidinium-BF_3 adduct (**2a**) with 3.3 equiv. of LDA*

The 3,4-lutidinium-BF_3 adduct (**2a**) was made by adding $BF_3{\cdot}Et_2O$ (2.34 g, 2.07 ml, 16.5 mmol) to a solution of **1a** (1.60 g, 1.68 ml, 15.0 mmol) in diethyl ether. LDA (49.5 mmol) was added slowly to a suspension containing **2a** in a drop-wise manner via cannula. Elemental selenium (3.90 g, 49.5 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 (7.02 g, 3.07 ml, 49.5 mmol) was added to it. The reaction mixture was slowly brought to the room temperature, hydrolyzed and purified. Following compounds were isolated from the crude product.

*2.5.1. 3,4-Dimethyl-2,6-bis(methylselenenyl)pyridine (**9a**) [20]*

Yield: 0.22 g (5%), m.p. 72–75 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 6.87 (s, 1H), 2.46 (s, 6H), 2.18 (s, 3H), 2.13 (s, 3H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 155.1, 150.7, 144.7, 128.0, 122.2 19.5, 15.2, 6.1, 5.4. MS (EI, 70 eV) *m*/*z* (relative intensity): 295 (40, [M]**.**+, ^{80}Se), 280 (12), 265 (6), 214 (100), 199 (23), 186 (12), 120 (23), 104 (23), 93 (23), 77 (35).

*2.5.2. 4,5-Dimethyl-2-(methylselenenyl)pyridine (**10a**) [20]*

Yield: 1.66 g (55%), red viscous oil. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.16 (s, 1H), 7.08 (s, 1H), 2.42 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 152.3, 149.9, 146.0, 128.9, 125.1, 19.0, 15.9, 5.5. MS (EI, 70 eV) *m*/*z* (relative intensity): 201 (35, [M]**.**+, ^{80}Se), 186 (1), 121 (100), 106 (27), 91 (7), 77 (24).

*2.5.3. 3-Methyl-2,6-bis(methylselenenyl)-4-(methylselenenylmethyl)pyridine (**12a**)*

Yield 0.875 g (15%), m.p. 85–88 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 6.83 (s, 1H), 3.55 (s, 2H), 2.47 (s, 6H), 2.18 (s, 3H), 1.94 (s, 3H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 156.5, 150.9, 146.7, 144.9, 121.3, 24.8, 15.01, 6.2, 5.4, 4.7. MS (EI, 70 eV) *m*/*z* (relative intensity): 389 (54, [M]**.**+, ^{80}Se), 387 (62), 372 (3), 294 (40), 213 (100), 198 (29), 182 (11), 157 (10), 118 (29), 104 (43), 93 (47), 77 (52), 51 (28). *Anal.* Calc. for $C_{10}H_{15}NSe_3$: C, 31.12; H, 3.91; N, 3.62. Found: C, 30.92; H, 3.65; N, 3.52%.

*2.5.4. 3-Methyl-2,6-bis(methylselenenyl)-4-pyridinecarboxaldehyde (**13a**)*

Yield 0.23 g (5%), m.p. 60–62 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 10.25 (s, 1H), 7.34 (s, 1H), 2.51 (s, 6H), 2.49 (s, 3H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 191.7, 153.0, 148.9, 141.7, 128.9, 29.7, 6.4. MS (EI, 70 eV) *m*/*z* (relative intensity): 309 (73, [M]**.**+, ^{80}Se), 305 (36), 281 (17), 228 (100), 200 (17), 186 (17), 170 (14), 144 (14), 120 (15), 106 (32), 93 (45), 78 (29), 63 (37), 51 (11). *Anal.* Calc. for $C_9H_{11}NOSe_2$: C, 34.95; H, 3.55; N, 4.53. Found: C, 34.92; H, 3.15; N, 4.42%.

*2.6. Reaction of 4-picolinium-BF_3 adduct (**2c**) with 3.3 equiv. of LDA*

LDA (49.5 mmol) was added slowly to the suspension containing 4-picolinium-BF_3 adduct (**2c**, 16.5 mmol) in a drop-wise manner via cannula. Elemental selenium (3.90 g, 49.5 mmol) was added to the orange brown solution at −78 °C. Rest of the procedure remained same as for the reaction involving **2a**, Section 2.5. 4-Methyl-2,6-bis(methyl selenenyl)pyridine (**9c**) and 4-methyl-2-(methylselenenyl)pyridine (**10c**) were isolated in 21% (0.887 g)

and 22% (0.632 g) yields respectively along with 4-methyl-2,6-bis(methylselenenyl)-4-(methylselenenylmethyl)pyridine (**12c**) in 9% yield.

2.6.1. 2,6-Bis(methylselenenyl)-4-(methylselenenylmethyl)pyridine (*12c*)

Yield 0.5 g (9%), dark brown viscous liquid. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 7.19 (s, 1H), 3.58 (s, 2H), 2.45 (s, 6H), 1.92 (s, 3H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 156.1, 150.3, 148.3, 124.2, 120.6, 26.5, 7.5, 5.6, 4.9. MS (EI, 70 eV) *m*/*z* (relative intensity): 375 (10, [M]**.**+, ^{80}Se), 280 (65), 265 (14), 185 (100), 170 (15), 90 (29), 76 (3), 51 (22).

2.7. Reaction of pyridine-BF_3 adduct (*2d*) with 3.3 equiv. of LDA

LDA (49.5 mmol) was added slowly to the suspension containing pyridinium-BF_3 adduct (**2a**, 16.5 mmol) in a drop-wise manner via cannula. Elemental selenium (3.90 g, 49.5 mmol) was added to the orange brown solution at −78 °C. Rest of the procedure remained same as for **2a** (Section 2.5). 2,6-Bis(methylselenenyl)pyridine (**9d**, 2.53 g, 63%) was the only compound isolated from the crude mixture.

2.8. Formation of 2-(benzylselenenyl)-4,5-dimethylpyridine (*7a*) and 2-(benzylselenenyl)-4-methylpyridine (*7c*) by cleavage of Se–Se bond in *5a* and *5c*, respectively

To a vigorously stirred solution of **5a**/**5c** (0.4 mmol) in dry THF at 0 °C, powdered $LiAlH_4$ (0.16 g, 0.44 mmol) was added in small instalments. The reaction mixture was slowly brought to room temperature and stirred for two hours. The pale yellow solution was again cooled to 0 °C and (chloromethyl)benzene (1.0 g, 0.92 ml, 0.88 mmol) was added drop-wise. The resulting solution was stirred overnight and hydrolyzed with 20 ml of water the next day. The organic layer was extracted with diethyl ether, washed with water, and then dried over anhydrous sodium sulfate. The solvent was removed and the crude product was purified by column chromatography using 60–120 mesh silica gel and hexane–ethyl acetate as an eluent (20:1). **7a** and **7c** were obtained in 80% and 85% yield, respectively.

2.8.1. 2-(Benzylselenenyl)-4,5-dimethylpyridine (*7a*)

Yield: 0.18 g (80%), m.p. 122–124 °C. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.16 (s, 1H), 7.56 (s, 1H) 7.13–7.24 (m, 5H), 4.27 (s, 2H), 2.21 (s, 3H), 2.19 (s, 3H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 151.4, 149.4, 143.0, 139.2, 132.4, 129.0, 128.8, 128.4, 121.1, 27.8, 19.8, 16.6 MS (EI, 70 eV) *m*/*z* (relative intensity): 277 (18, [M]**.**+, ^{80}Se), 197 (52), 106 (22), 91 (100), 77 (24), 65 (49). *Anal.* Calc. for $C_{14}H_{15}NSe$: C, 60.87; H, 5.47; N, 5.07. Found: C, 61.05; H, 4.95; N, 5.39%.

2.8.2. 2-(Butylselenenyl)-4-methylpyridine (*14c*)

Iodobutane (1.46 g, 0.9 ml, 0.88 mmol) was added to the pale yellow solution containing species formed by the reaction of **5c** with $LiAlH_4$. Rest of the procedure was same as for **7a**. Yield: 0.17 g (93%), very light brown viscous liquid. ^{1}H NMR: $CDCl_3$, 400 MHz δ (ppm): 8.26–8.28 (d, J = 5.12 Hz, 1H), 7.12 (s, 1H), 6.79–6.80 (dd, J = 0.84 Hz, 4.98 Hz, 1H), 3.12–3.19 (t, 2H), 2.23 (s, 3H), 1.71–1.79 (m, 2H), 1.37–1.49 (m, 2H), 0.87–0.96 (m, 3H). ^{13}C NMR: $CDCl_3$, 400 MHz δ (ppm): 155.4, 149.5, 146.8, 125.9, 121.4, 32.3, 25.4, 23.1, 20.7, 13.6. MS (EI, 70 eV) *m*/*z* (relative intensity): 229 (100, [M]**.**+, ^{80}Se), 200 (99), 187 (98), 171 (99), 148 (99), 134 (43), 120 (93), 107 (92), 92 (71), 80 (12), 65 (54). *Anal.* Calc. for $C_{10}H_{15}NSe$: C, 52.63; H, 6.62; N, 6.13. Found: C, 52.19; H, 6.70; N, 6.26%.

2.9. Crystal structure determination and refinement

The single crystal X-ray data of the selenium compounds were collected on a CCD Bruker APEX II using graphite monochromatized Mo Kα radiation (α = 0.71073 Å) at 150(2) K for **5a**, **9a**, **9d** and **12a** and at 180(2) K for **9c**. The crystals of all the aforementioned compounds were grown in the solution of hexane and dichloromethane. The selected crystal of each compound was positioned at a suitable distance from CCD and the spots were measured using an appropriate counting time. For all compounds, the data reduction together with the corresponding multi-scan absorption correction was carried out using the SAINT-NT from Bruker AXS. The structures were solved by means of direct methods followed of successive Fourier difference syntheses using SHELXS-97. The structures were refined on F^2 by full-matrix least squares with SHELXL-97. All these calculations were carried out with SHELX-97 suite [21]. The hydrogen atoms were included in the structure refinement at geometrical positions. Anisotropic thermal parameters were used for all non-hydrogen atoms while the hydrogen atoms were refined with isotropic parameters equivalent 1.2 times those of the atom to which they are attached. Final *R* values together with pertinent crystallographic data are summarized in Table 1. Molecular diagrams were drawn with ORTEP-3 [22] and PYMOL [23] graphical packages.

3. Results and discussion

3.1. Preparation of symmetrical and unsymmetrical 4,5-lutidinyl-, 3-picolyl- and 4-picolyl diselenides/-selenides by the monolithiation procedure

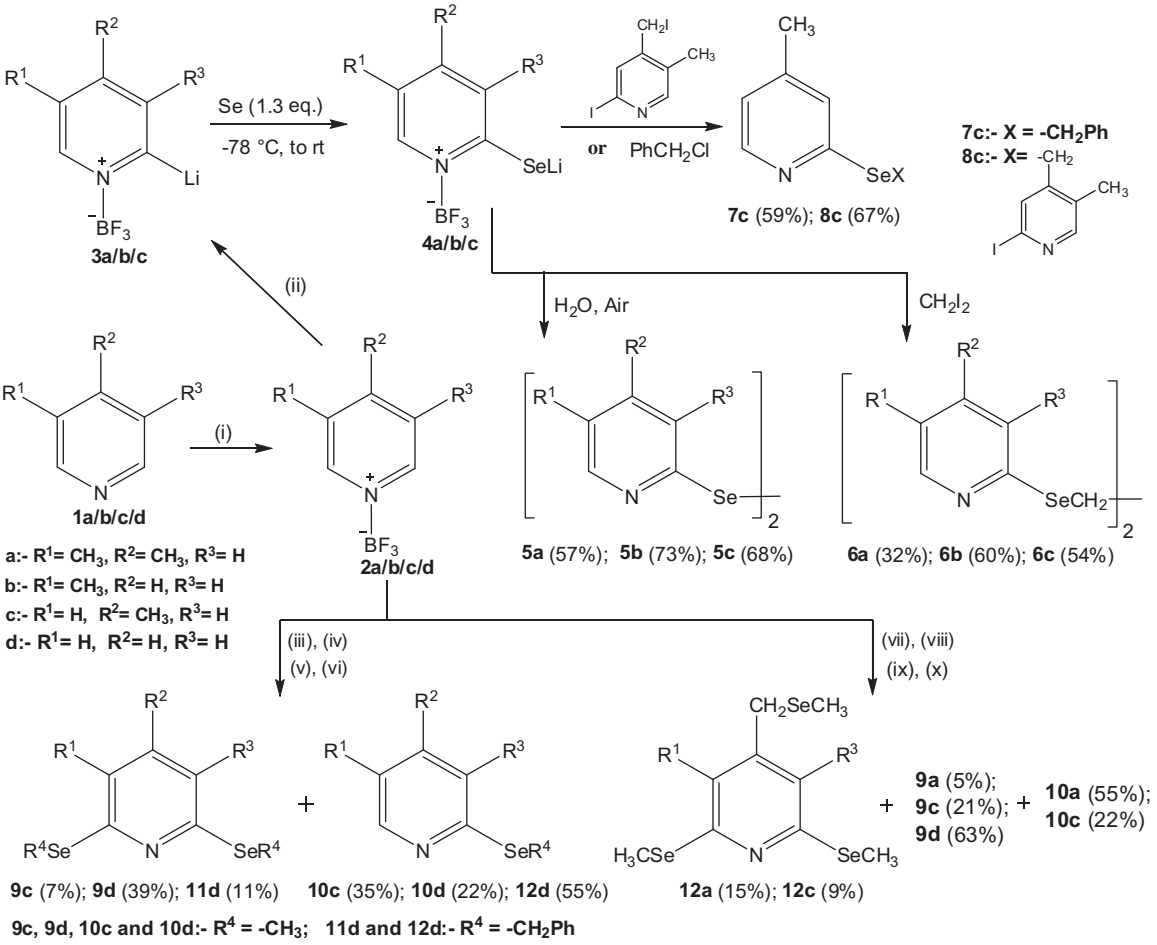
Treatment of **1a** with BF_3–Et_2O gives the 3,4-lutidinium-BF_3 adduct, **2a**, in dry diethyl ether at 0 °C. This adduct undergoes lithium-hydrogen abstraction reaction with lithium diisopropylamide (LDA) at −78 °C. Addition of selenium to the carbanion **3a** leads to the formation of the selenolate anion, **4a**[20]. The selenolate anion on aerial oxidation and hydrolysis affords hither to unknown bis(4,5-dimethyl-2-pyridyl) diselenide (**5a**) in good yield (Scheme 1). In another variation, reaction of **4a** with diiodomethane affords a novel compound, **6a**, in 32% yield. Similar to **2a**, the reaction of 3-picolinium-BF_3 adduct (**2b**) with LDA followed by selenium insertion and aerial oxidation leads to bis(5-methyl-2-pyridyl) diselenide (**5b**) in excellent yield. The quenching of **4b** with diiodomethane affords **6b** in 60% yield. Complexation of 4-Picoline (**1c**) with BF_3 etherate and its subsequent reaction with LDA affords the selenolate anion, **4c**, which on aerial oxidation or reaction with diiodomethane gives bis(4-methyl-2-pyridyl) diselenide (**5c**, 68%) and bis(4-methyl-2-pyridylseleno)methane (**6c**, 54%), respectively (Scheme 1). Further, the reaction of **4c** either with (chloromethyl) benzene or with 2-iodo-4-(iodomethyl)-3-methylpyridine affords 2-(benzylselenenyl)-4-methylpyridine (**7c**) and 2-iodo-5-methyl-4-((4-methylpyridin-2-selenenyl)methyl)pyridine (**8c**) respectively in good yields. Interestingly, the reaction of **4c** with 2-chloropropane, 1-bromopropane 1,2-dibromoethane and 2-iodo-4,5-lutidine did not lead to the formation of the related monoselenide instead, in all cases **5c** was the only product obtained.

3.2. Reaction of 4-picolinium- and pyridinium-BF_3 adduct with 2.2 equiv. of LDA

We next attempted the dilithiation of **2c** with 2.2 equiv. of LDA at −78 °C followed by *in situ* quenching of the resulting species with 2.2 equiv. of elemental selenium and iodomethane. It was found that 4-methyl-2,6-bis(methylselenenyl)pyridine (**9c**) was

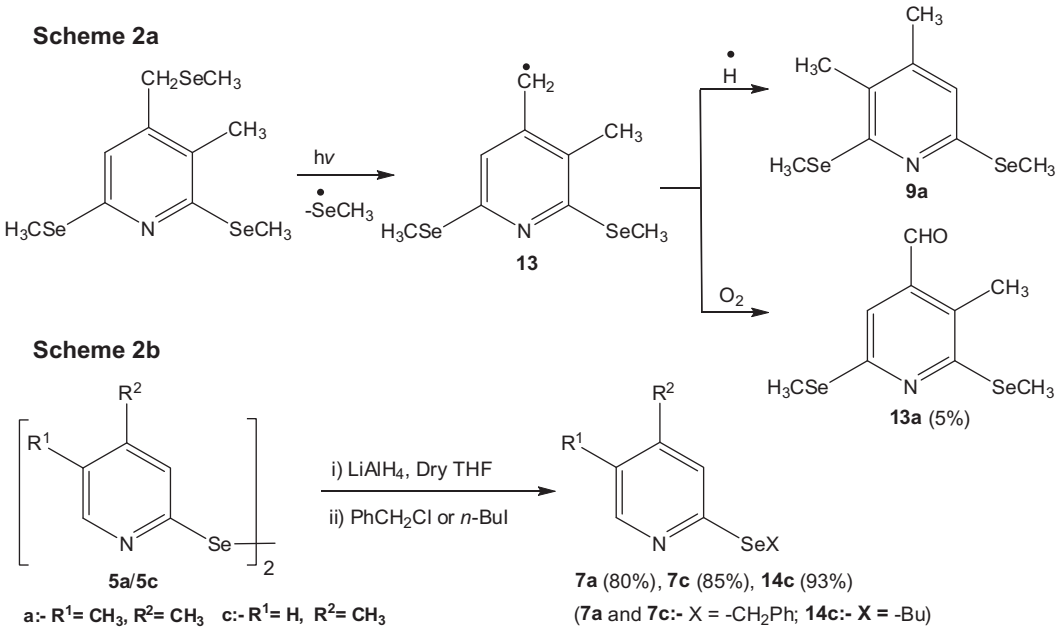
Table 1
Crystal data collection and selected structure refinement details for compounds **5a**, **9a**, **9c**, **9d** and **12a**.

Compound	**5a**	**9a**	**9c**	**9d**	**12a**
Empirical formula	$C_{14}H_{16}N_2Se_2$	$C_9H_{13}NSe_2$	$C_8H_{11}NSe_2$	$C_7H_9NSe_2$	$C_{10}H_{15}NSe_3$
Formula weight	370.21	293.12	279.10	265.07	386.11
Temperature (K)	150	180	150	150	150
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/n$
a (Å)	10.3650(4)	5.3120(3)	8.1417(5)	10.321(3)	5.2757(2)
b (Å)	6.6892(2)	16.3259(8)	21.6308(14)	5.3769(17)	27.3034(12)
c (Å)	21.1397(7)	12.3903(6)	5.6145(3)	15.617(4)	9.0001(4)
α (°)	90	90	90	90	90
β (°)	95.182(2)	101.301(2)	100.286(2)	90	101.042(2)
γ (°)	90	90	90	90	90
Volume (Å^3)	1459.70(9)	1053.69(9)	972.89(10)	866.7(4)	1272.41(9)
Z	4	4	4	4	4
D_{calc} (mg m^{-3})	1.685	1.848	1.905	2.031	2.016
μ (mm^{-1})	5.050	6.966	7.540	8.458	8.637
Reflections collected	12906	7135	7470	10286	13158
Independent reflections (R_{int})	3935 (0.0321)	2307 (0.0449)	1839 (0.0390)	2360 (0.0313)	3446 (0.0209)
Final R indices					
R_1, wR_2, [$I > 2(I)$]	0.0263, 0.0547 (3139)	0.0376, 0.1029, (1962)	0.0463, 0.1437, (1636)	0.0213, 0.0479, (2201)	0.0261, 0.0586 (3021)
R_1, wR_2 (all data)	0.0404, 0.0586	0.0460, 0.1179	0.0520, 0.1479	0.0243, 0.0486	0.0326, 0.0606



Scheme 1. Monolithiation of **1a**, **1b** and **1c**; (i) $BF_3{\cdot}Et_2O$ (1.3 equiv.), 0 °C, dry diethyl ether, (ii) LDA (1.3 equiv.), −78 °C. Dilithiation of **2c** and **2d**; (iii) LDA (2.2 equiv.), −78 °C; (iv) Se (2.2 equiv.), −78 °C to rt; (v) CH_3I (2.2 equiv.), −78 °C; (vi) H_2O. Trilithiation of **2a**, **2c** and **2d**; (vii) LDA (3.3 equiv.), −78 °C; (viii) Se (3.3 equiv.), −78 °C to rt; (ix) CH_3I (3.3 equiv.), −78 °C; (x) H_2O.

formed in minor quantity (7%) whereas, 4-methyl-2-(methylselenenyl)pyridine (**10c**) was the major product formed (Scheme 1). Combining these results with our earlier reported result on the dilithiation of 3-picoline, 3,4-lutidine and 3,5-lutidine [14,20], it appears that the 4-methyl substituted pyridines (3,4-lutidine and 4-picoline) are not conducive to dilithiation when compared with 3-methyl substituted pyridines (3,5-lutidine and 3-picoline). The dilithiation of pyridinium-BF_3 adduct (**1d**) [18] with LDA (2.2 equiv.) followed by quenching with elemental selenium and iodomethane gave the disubstituted product, 2,6-bis(methylselenenyl)pyridine (**9d**), in major quantity (39%) along with the monosubstituted product, **10d** (22%, Scheme 1). However, when



Scheme 2. (a) Probable route to the formation of 3-methyl-2,6-bis(methylselenenyl)-4-pyridine-carboxaldehyde (**13a**). (b) Cleavage of Se–Se bond in **5a** and **5c** with $LiAlH_4$.

(chloromethyl)benzene was used as the electrophile in the later reaction the yield of the products got reversed. 2,6-Bis(benzylselenenyl) pyridine (**11d**, 11%) corresponding to dilithiation of **1d** was formed in lesser quantity than the monosubstituted product, 2-(benzylselenenyl)pyridine (**12d**, 55%).

3.3. Reaction of 3,4-lutidinium-, 4-picolinium- and pyridinium-BF_3 adduct with 3.3 equiv. of LDA

We also examined the trilithiation of 3,4-lutidinium-BF_3 adduct (**2a**) with 3.3 equiv. of LDA. In this reaction, 3,4-dimethyl-2,6-bis(methylselenenyl)pyridine (**9a**) was formed only in a minute quantity and 4,5-dimethyl-2-(methylselenyl)pyridine (**10a**) was the main product formed (Scheme 1). In addition to these compounds, we were also able to isolate two hitherto unknown compounds, 4-methyl-2,6-bis(methylselenenyl)-4-(methylselenenylmethyl)pyridine (**12a**) and 3-methyl-2,6-bis(methylselenenyl)-4-pyridinecarboxaldehyde (**13a**), from the reaction mixture. The isolation of **12a** evinces the trilithiation of **2a** with 3.3 equiv. of LDA. The compound **12a** appears to be photochemically labile, especially when present in the form of solution and decomposes to give red amorphous selenium. It is probable that the photochemical decomposition of **12a** might have generated picolyl type radical **13** which on reaction with oxygen or hydrogen radical affords **13a** and **9a**, respectively (Scheme 2a). The compounds containing $ArCH_2$–SeR bond are known to undergo photochemical decomposition to give the benzyl/picolyl radical [24,25]. The resonance stabilization of this radical appears to be the driving force for the lability of the $ArCH_2$–SeR bond.

Encouraged by the isolation of **12a**, we also examined the trilithiation of **1c** and **1d** with 3.3 equiv. of LDA. The *in situ* quenching of the resulting lithiated species of **2c** with selenium and iodomethane gave 2,6-bis(methylselenenyl)-4-(methylselenenylmethyl)pyridine (**12c**), **10c** and **9c** whereas, the lithiated species of **2d** gave the disubstituted product, **9d** (63%) only (Scheme 1). We were not able to isolate any triselenated product in the reaction involving **1d** although a very minute quantity of it was noticed in the GC chromatogram. Similar to the dilithiation reaction involving **1d** and (chloromethyl)benzene, treatment of **1d** with 3.3 equiv. of LDA followed by addition of elemental selenium and (chloromethyl)benzene afforded **12d** in major amount and **11d** only in a very minor quantity. It appears that the nature of the electrophile plays a crucial role in the formation of the bis(selenenyl) derivatives of **1d**.

3.4. Treatment of the diselenides with $LiAlH_4$

We next thought of studying the reductive cleavage of selenium-selenium bond in **5a** and **5c** with $LiAlH_4$. Addition of $LiAlH_4$ powder to a solution of **5a** in dry THF immediately leads to the change in color of the solution from dark orange to pale yellow with the evolution of hydrogen gas indicating the cleavage of Se–Se bond and the formation of selenolate anion. Addition of (chloromethyl)benzene to this solution affords 2-(benzylselenenyl)-4,5-dimethylpyridine (**7a**) in excellent yield (Scheme 2b). Similar to **5a**, the reduction of **5c** with $LiAlH_4$ followed by reaction with (chloromethyl)benzene or 1-iodobutane leads to the formation of **7c** and 2-(butylselenenyl)-4-methylpyridine (**14c**) respectively in excellent yields.

3.5. Spectroscopic studies

All the synthesized compounds were characterized by elemental analysis, NMR (^1H and ^{13}C), and mass spectral techniques. The ^1H NMR spectra of **5a** and **6a** shows two singlets whereas, the spectra of **5b**, **5c**, **6b** and **6c** shows three signals in the aromatic region indicating deprotonation of the parent compound (**1a**–**1c**). The spectra of the aforementioned compounds show singlet between 2.1 and 2.5 δ ppm due to the methyl group attached to the pyridine ring. The signal corresponding to the protons of the methyl group attached to the selenium atom in compounds **9a**–**9d**, **10a**–**10d**, **12a** and **13a** also appear in the range 2.1–2.5 δ ppm as singlet and is invariably flanked by selenium satellites due to NMR active ^{77}Se. The signal due to Se-C**H**$_2$–Se protons in **6a**–**6c**, **7c**–**8c** and **11d**–**12d** is also flanked by selenium satellites and appears as singlet in the range 4.78–4.28 δ ppm. However, the Se–C**H**$_2$-py group in **12a** appears upfield at 3.55 δ ppm. A signal at 10.25 δ ppm in the ^1H NMR spectrum of **13a** establishes the presence of aldehydic

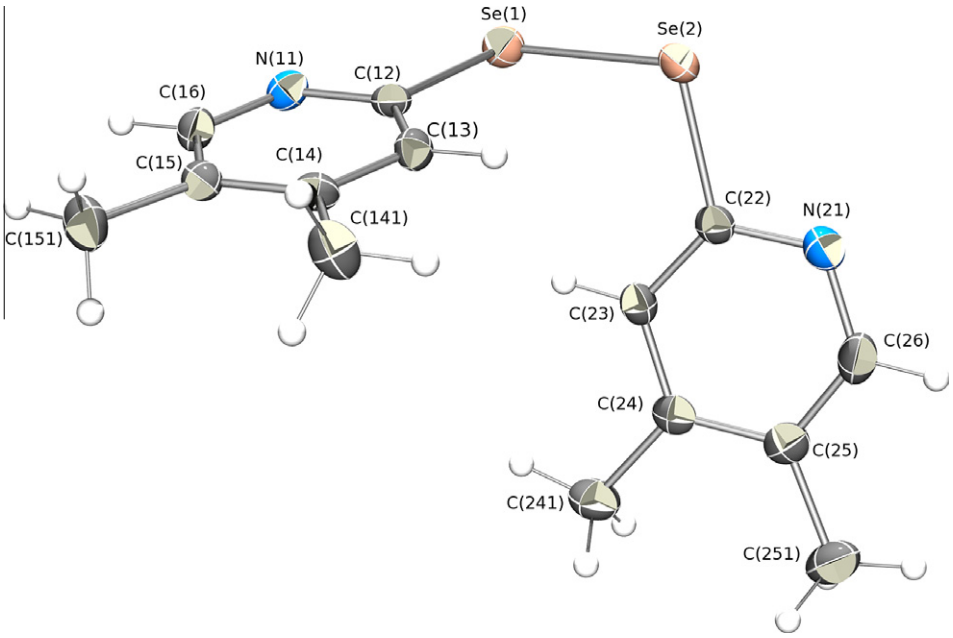


Fig. 1. ORTEP view of **5a** with thermal ellipsoids drawn at 50% probability level. Se(1)–Se(2) 2.3010(3); Se(1)–C(12) 1.934(2); C(12)–Se(1)–Se(2) 104.20(6); C(22)–Se(2)–Se(1) 102.74(7); N(11)–C(12)–Se(1) 109.25(15); C(13)–C(12)–Se(1) 126.24(16); N(21)–C(22)–Se(2) 111.06(15); C(23)–C(22)–Se(2) 124.73(16).

proton. In the ^{13}C NMR spectra of **12a** and **12c**, the signal due to Se–**C**H$_2$-py appears at 24.8 and 26.5 δ ppm, respectively whereas, the signals for methyl carbon attached to selenium atoms appear at three different positions ranging from 7.1 to 4.7 δ ppm. As expected, the H**C**O signal in **13a** appears at 191.7 δ ppm. The ESI mass spectra of **5a**, **5b** and **6a** shows molecular ion peak [M.+, ^{80}Se] at *m/z* 372, 344 and 386, respectively. The EI mass spectra of all other compounds gave distinct molecular ion peaks with characteristic selenium isotopic patterns. In addition to the molecular ion peak, the mass spectra of **9c**, **10a** and **10c** exhibit base ion peak corresponding to a fragment formed due to the removal of ^{80}Se˙ from the molecular ion peak. However, base ion peak in **9a** appears due the removal of ^{80}SeH from the molecular ion peak. The molecular ion peak in **12a** is at *m/z* 389 and its base ion peak appears at *m/z* 213 due to the fragment [$C_9H_{11}NSe^+$].

3.6. Solid state structural features of *5a*

The molecular structure of **5a** and its crystallographic numbering scheme is shown in Fig. 1. **5a** adopts a *gauche* conformation with a C–Se–Se–C torsion angle of 82°(4). The two pyridine rings are almost orthogonal to each other with the angle of 76.0°. The two N–C–Se–Se torsion angles of 177.8° and 171.8° indicate that the selenium atoms lie in the plane of the related pyridine ring. This geometric arrangement around the Se–Se bond is comparable to that reported in substituted and unsubstituted 2,2′-dipyridyl diselenide [17,26]. However, this arrangement is opposite to that found in bis(3,5-dimethyl-2-pyridyl) diselenide [14]. The later

Table 2
Selected bond distances (Å) and angles (°) for selenium compounds **9a**, **9c**, **9d** and **12a**.

Compound	9a	9c	9d	12a
Se(21)–C(2)	1.925(4)	1.919(6)	1.914(2)	1.924(2)
Se(21)–C(22)	1.941(4)	1.938(6)	1.936(3)	1.940(3)
Se(42)–C(41)	–	–	–	1.963(2)
Se(42)–C(43)	–	–	–	1.943(3)
Se(61)–C(6)	1.918(4)	1.921(5)	1.919(2)	1.911(2)
Se(61)–C(62)	1.942(4)	1.935(6)	1.937(3)	1.938(3)
C(2)–Se(21)–C(22)	98.45(17)	98.9(2)	99.98(12)	98.26(11)
C(6)–Se(61)–C(62)	98.64(19)	98.7(3)	97.71(12)	98.85(12)
C(43)–Se(42)–C(41)	–	–	–	97.41(11)
N(1)–C(2)–Se(21)	116.4(3)	117.9(4)	118.72(18)	116.56(18)
C(3)–C(2)–Se(21)	118.7(3)	117.8(4)	117.63(18)	118.70(18)
N(1)–C(6)–Se(61)	119.1(3)	118.0(4)	118.96(17)	–
C(5)–C(6)–Se(61)	118.0(3)	117.7(4)	117.40(18)	–

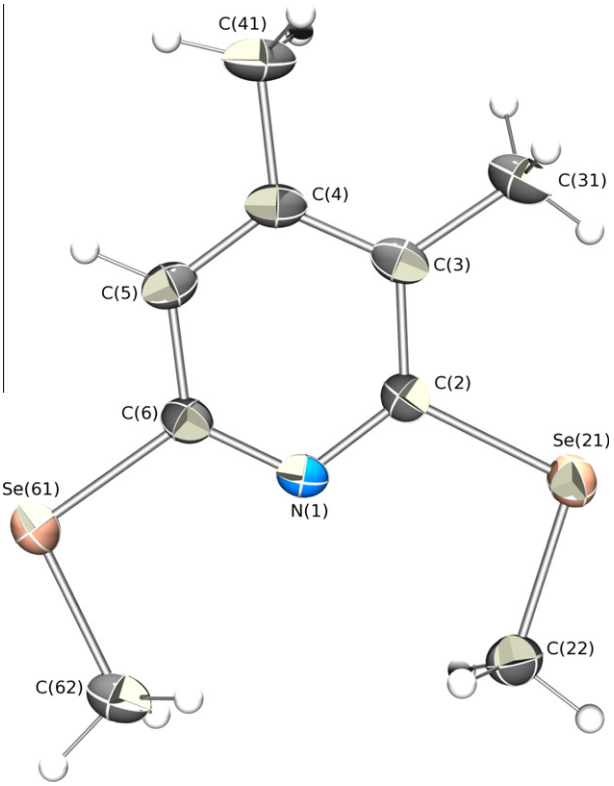


Fig. 2. ORTEP diagrams of **9a** with ellipsoids drawn at 50% probability level.

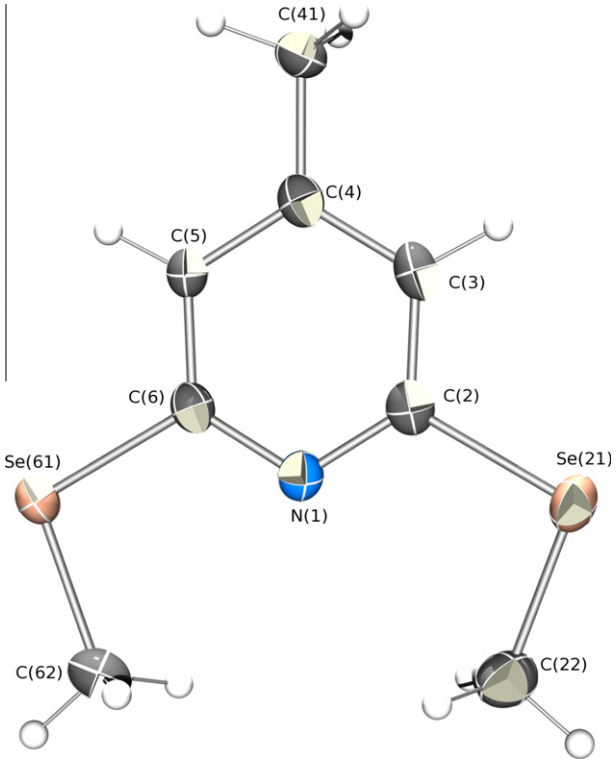


Fig. 3. ORTEP diagrams of **9c** with ellipsoids drawn at 50% probability level.

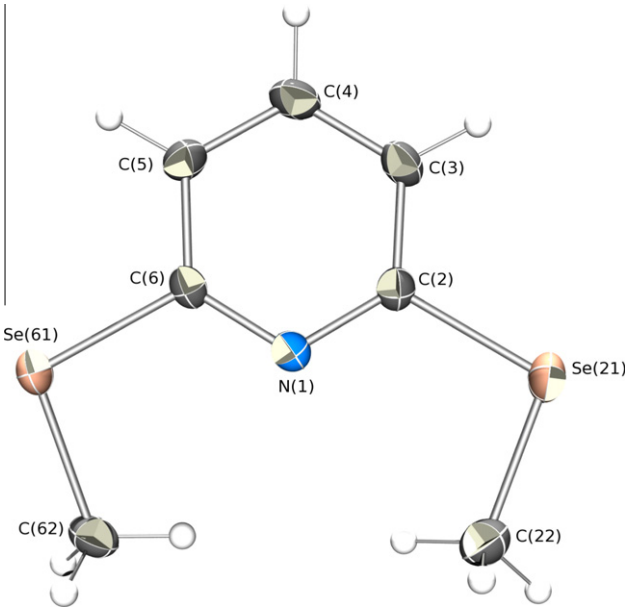


Fig. 4. ORTEP diagrams of **9d** with ellipsoids drawn at 50% probability level.

compound adopts anti conformation with two pyridyl rings completely coplanar with the Se–Se bridge. The Se–Se distance of 2.301(3) Å is within the range of 2.275–2.415 Å for the related diselenides [14,17,26]. The analysis of the short intermolecular contacts indicates that the discrete molecules of **5a** are not involved in Se···Se secondary interactions.

3.7. Solid state structural features of *9a*, *9c* and *9d*

Selected bond lengths and angles of **9a**, **9c** and **9d** are also given Table 2 and their molecular structures with atomic numbering schemes are shown in Figs. 2–4, respectively. The Se–C(sp^2) and Se–C(sp^3) bond lengths in these compounds are slightly shorter

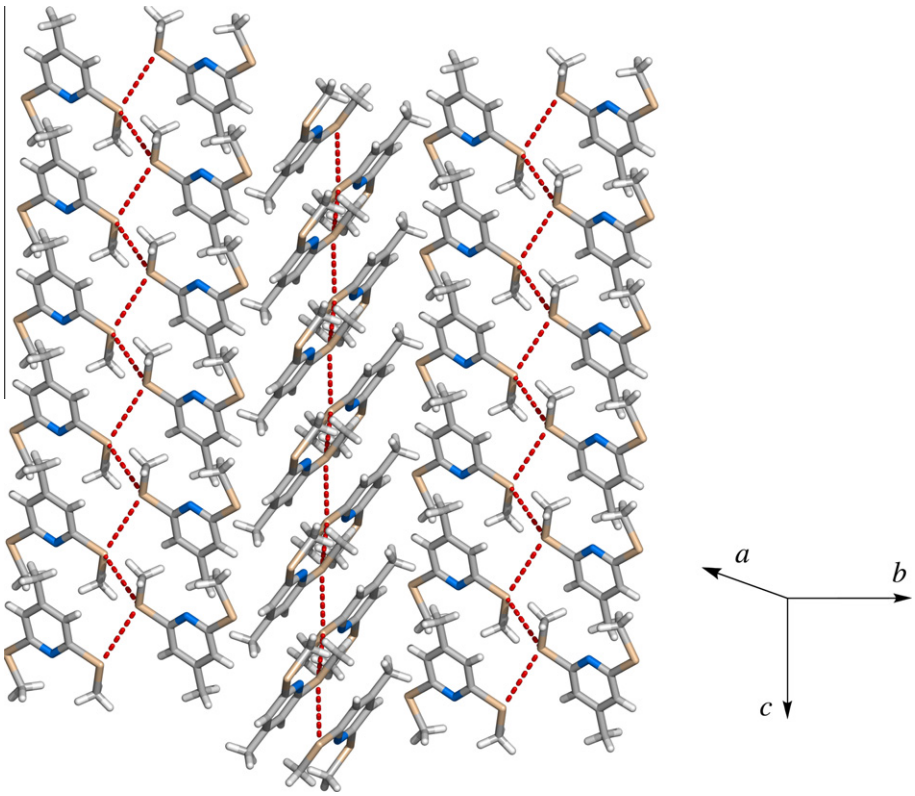


Fig. 5. Crystal packing diagram of **9c** showing the helical assembling in solid sate through the Se···Se interactions, which are represented as red dashed lines.

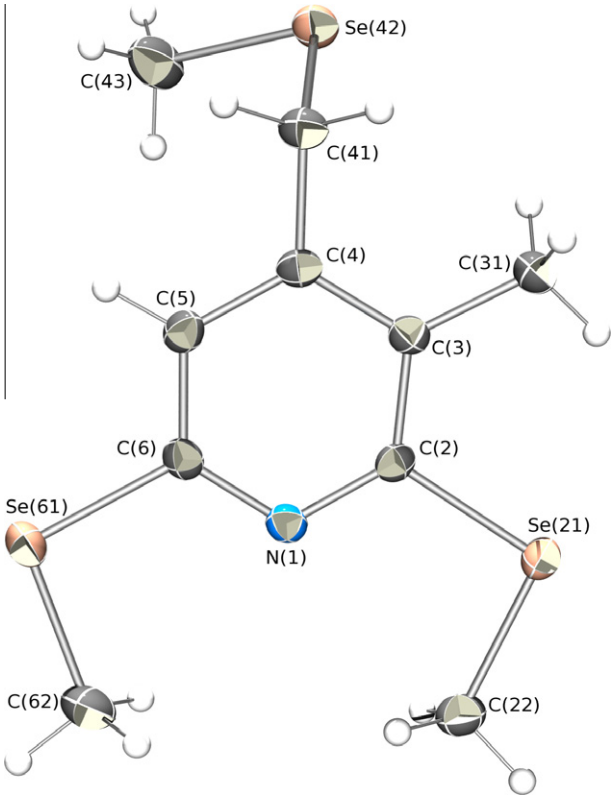


Fig. 6. ORTEP diagram of **12a** with ellipsoids drawn at 50% probability level.

than that found in 3,5-dimethyl-2,6-bis(methylselenenyl)pyridine [14]. Of these compounds, **9d** has the shortest average Se–C(sp^2) bond length (Table 2). Similar to 3,5-dimethyl-2,6-bis(methyl selenenyl)pyridine, no Se···Se short intermolecular distances were observed in crystal structure of **9a**. Indeed, the shortest Se···Se distances in **9a** are 3.883 and 4.063 Å which are slightly longer than the sum of their Van der Waals radii (3.8 Å) [27]. However, the crystal packing diagram (Fig. 5) of **9c** shows two independent short Se(61)···Se(61) intermolecular distances of 3.733 and 3.774 Å between one of the two selenium atoms attached to the molecule and other selenium atoms of the two neighboring rings leading to the formation of pillars composed of two rows assembled around the 2_1 helical crystallographic axis thorough the Se···Se interactions.

In case of **9d**, the crystal packing analysis shows the presence of Se···Se intermolecular interactions occurring at short distances of 3.761 Å involving both the selenium atoms. Comparing the crystal structure of **9a**, **9c** and **9d** it is clear that instances of Se···Se secondary interactions decreases with the increase in number of methyl group at the pyridine ring. The attachment of methyl group(s) to the pyridine ring decreases the electronegativity of the pyridine moiety attached to the selenium atom. This result is consistent with the reported result that decrease in the electronegativity of the group attached directly to the selenium atom decreases the chalcogen···selenium interactions [28].

3.8. Solid state structural features of *12a*

To the best of our knowledge, this is the first ever reported crystal structure of a molecule having two selenium atoms directly attached to the pyridine moiety and a third selenium atom bonded to a side-chain. This fact was confirmed by a search carried out on Cambridge Structural Database [29]. Selected bond distances and angles of **12a** are given in Table 2 and its molecular structure with atomic numbering scheme is shown in Fig. 6. The two Se–C(sp^2) bond lengths in **12a** are not equivalent. Indeed, the Se(61)–C(6) bond length (*ortho* to the methyl group) is slightly longer than Se(21)–C(2) bond length (Table 2). In contrast, the Se–C(sp^3) bond length at both the positions is almost of equal length. The Se(42)–CH_2 bond length is slightly greater than the Se(42)–CH_3 bond length. The crystal packing analysis of **12a** reveals Se···Se secondary intermolecular interactions between the three independent selenium atoms. The Se(61)···Se(61) and Se(21)···Se(42) distances are 3.613 and 3.712 Å, respectively.

4. Conclusion

Synthesis of a number of 3,4-lutidinyl, 3-/4-picolyl- and 2-pyridylselenium compounds has been achieved by a procedure involving directed ring lithiation, dilithiation and trilithiation of the corresponding pyridyl derivative. Reduction of selenium-selenium bond in various diselenides with $LiAlH_4$ is an effective method to form unsymmetrical monoselenides at room temperature. A comparative study of the crystal structure of some of the prepared compounds indicates that the instances of Se···Se secondary interactions decreases with the increase in the number of methyl group attached to the pyridine ring.

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Appendix A. Supplementary material

CCDC 836311, 836312, 836313, 836314 and 836315 contain the supplementary crystallographic data for complexes **5a**, **9a**, **9c**, **9d** and **12a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.03.043.

References

[1] Y. Wei, J. Yang, A.W.H. Lin, J.Y. Ying, Chem. Mater. 22 (2010) 5672.
[2] A.J. Mukherjee, S.S. Zade, H.B. Singh, R.B. Sunoj, Chem. Rev. 110 (2010) 4357.
[3] R.K. Beri, P.K. Khanna, V. Singh, B.R. Mehta, Curr. Appl. Phys. 11 (2011) 809.
[4] S. Dey, V.K. Jain, J. Singh, V. Trehan, K.K. Bhasin, B. Varghese, Eur. J. Inorg. Chem. (2003) 744.
[5] Y. Xie, X. Zheng, X. Jiang, J. Lu, L. Zhu, Inorg. Chem. 41 (2002) 387.
[6] F. Gascoin, A. Maignan, Chem. Mater. 23 (2011) 2510.
[7] M.-F. Wang, W.-H. Huang, C.-S. Lee, Inorg. Chem. 48 (2009) 6402.
[8] W. Hassan, S. Pinton, J.T. da Rocha, A.M. Deobald, A.L. Braga, C.W. Nogueira, A.S. Latini, J.B.T. Rocha, Chem. Biol. Interact. 190 (2011) 35.
[9] A.S. Hodage, P.P. Phadnis, A. Wadawale, K.I. Priyadarsini, V.K. Jain, Org. Biomol. Chem. 9 (2011) 2992.
[10] J.T. Pinto, J.-I. Lee, R. Sinha, M.E. MacEwan, A.J.L. Cooper, Amino Acids 41 (2011) 29.
[11] R. Terazawa, D.R. Garud, N. Hamada, Y. Fujita, T. Itoh, Y. Nozawa, K. Nakane, T. Deguchi, M. Koketsu, M. Ito, Bioorg. Med. Chem. 18 (2010) 7001.
[12] N.B. Barbosa, J.B. Rocha, D.C. Wondracek, J. Perottoni, G. Zeni, C.W. Nogueira, Chem. Biol. Interact. 163 (2006) 230.
[13] B.S. Kumar, S.K. Tiwari, R. Saikant, G. Manoj, A. Kunwar, G. Sivaram, Z. Abid, A. Ahmad, K.I. Priyadarsini, A.A. Khan, J. Trace Elem. Med Biol. 24 (2010) 263.
[14] J.S. Dhau, A. Singh, R. Dhir, J. Organomet. Chem. 696 (2011) 2008.
[15] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, third ed., Pergamon Press, Oxford, 1988.
[16] A.P. Smith, J.J.S. Lamba, C.L. Fraser, Org. Synth. Coll. 10 (2004) 107.
[17] K.K. Bhasin, J. Singh, J. Organomet. Chem. 658 (2002) 71.
[18] S.V. Kessar, P. Singh, K.N. Singh, M. Dutt, Chem. Commun. (1991) 570.
[19] K.K. Bhasin, V.K. Jain, H. Kumar, S. Sharma, S.K. Mehta, J. Singh, Synth. Commun. 33 (2003) 977.
[20] J. Dhau, A. Singh, Y. Kasetti, P.V. Bharatam, Eur. J. Org. Chem. 2012 (2012) 1746.

[21] G.M. Sheldrick, Acta. Crystallogr., Sect. A 64 (2008) 112.
[22] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[23] The PYMOL Molecular Graphics System, Version 1.2r3pre, Schrödinger, LLC.
[24] W. Stanley, M.R. Van De Mark, P.L. Kumler, Chem. Commun. (1974) 700.
[25] K.K. Bhasin, J. Singh, K.N. Singh, Phosphorus, Sulfur Silicon Relat. Elem. 177 (2002) 597.
[26] C.O. Kienitz, C. Thöne, P.G. Jones, Inorg. Chem. 35 (1996) 3990.
[27] M. Mantina, A.C. Chamberlin, R. Valero, C.J. Cramer, D.G. Truhlar, J. Phys. Chem. A 113 (2009) 5806.
[28] C. Santi, S. Santoro, M. Tiecco, in: Proceedings of the 15th Int. Electron. Conf. Synth. Org. Chem., Sciforum Electronic Conferences Series, 2011.
[29] F.H. Allen, Acta. Crystallogr., Sect. B 58 (2002) 380.