Facile synthesis of 4*H*-naphtho[2,3-*e*] derivatives of 1,3-thiazines and 1,3-selenazines and naphtho[2',3':4,5] derivatives of selenolo[2,3-*b*]pyridines and thieno[2,3-*b*]pyridines *via* 2,3-didehydronaphthalene

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Abstract

Thiaazadienes (**2a**–**e**), selenoazadienes (**6a**–**f**), Barton selenium esters (**8a**–**e**) and Barton sulphur esters (10a–d) react with 2,3-didehydronaphthalene (4) generated from (phenyl)[(3-trimethylsilyl)-2-naphthyl]iodonium triflate (3) at 0°C to give 4H-naphtho[2,3-e]-1,3-thiazines (**5a-e**), 4H-naphtho[2,3-e]-1,3-selenazines (7a-f), naphtho[2',3':4,5]selenolo[2,3-b]pyridines (9a-e) and naphtho[2',3':4,5]thieno[2,3-b]pyridines (**11a-d**).

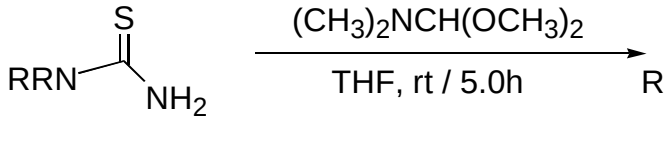
Keywords: Benzyne cycloaddition, nucleophilic addition, 1,3-thiazines, selenolo[2,3-*b*]pyridines, thieno[2,3-*b*]pyridines

Introduction

Substituted naphthalenes and 1,4-naphthoquinones show a variety of biological activity, such as antihypotensive1,2, β-adrenergic antagonists[3], Ca^{2+} channel blocker[3], antitumour4, antifunga[15-8] and antivira.[14] In the present study new fused naphthalenes are synthesized by the benzyne reaction starting from the selenazadienes, thiaazadienes and Barton esters. Recently, benzyne was found to undergo 1,4 addition reactions with 2-pyridones9. These novel results suggested that the reaction of the corresponding selenium and sulfur derivatives, such as Barton esters with arynes under similar conditions, might be worthy of study. Earlier we have reported the 4H-1,3-benzoselenazines10, benzo[4,5]thieno[2,3-b]pyridines[11] and benzo[4,5]selenolo[2,3-b]pyridines[12] by the reaction of various benzynes with the respective selenium, sulfur containing Barton esters and selenoazadienes.[10] We report herein a facile synthesis of 4H-naphtho[2,3-b]1,3-thiazines (**5a**–**e**), 4H-naphtho [2,3-b]-1,3-selenazines (**7a**–**f**), naphtho[2',3':4,5]selenolo[2,3-b]pyridines (**9a**–**e**) and naphtho[2',3':4,5]thieno[2,3-b]pyridines (**11a-d**).

The required (phenyl)[(3-trimethylsilyl)-2-naphthyl]iodonium triflate (3) was prepared from 2,3-dibromonaphthalene.[13] The thiaazabutadienes (**2a**–**e**)[14] and the selenoazadienes (**6a-f**)[15] were prepared by literature procedures. With the exception of thiaazadiene (**2e**) the thiaazadienes (**2a-d**) are new compounds and their % yields are shown in Scheme 1. The Barton selenium esters (**8a**–**e**) were prepared from 2-chloropyridines[12] and the Barton sulfur esters (**10a**–**d**) were prepared by the Barton method.[16]

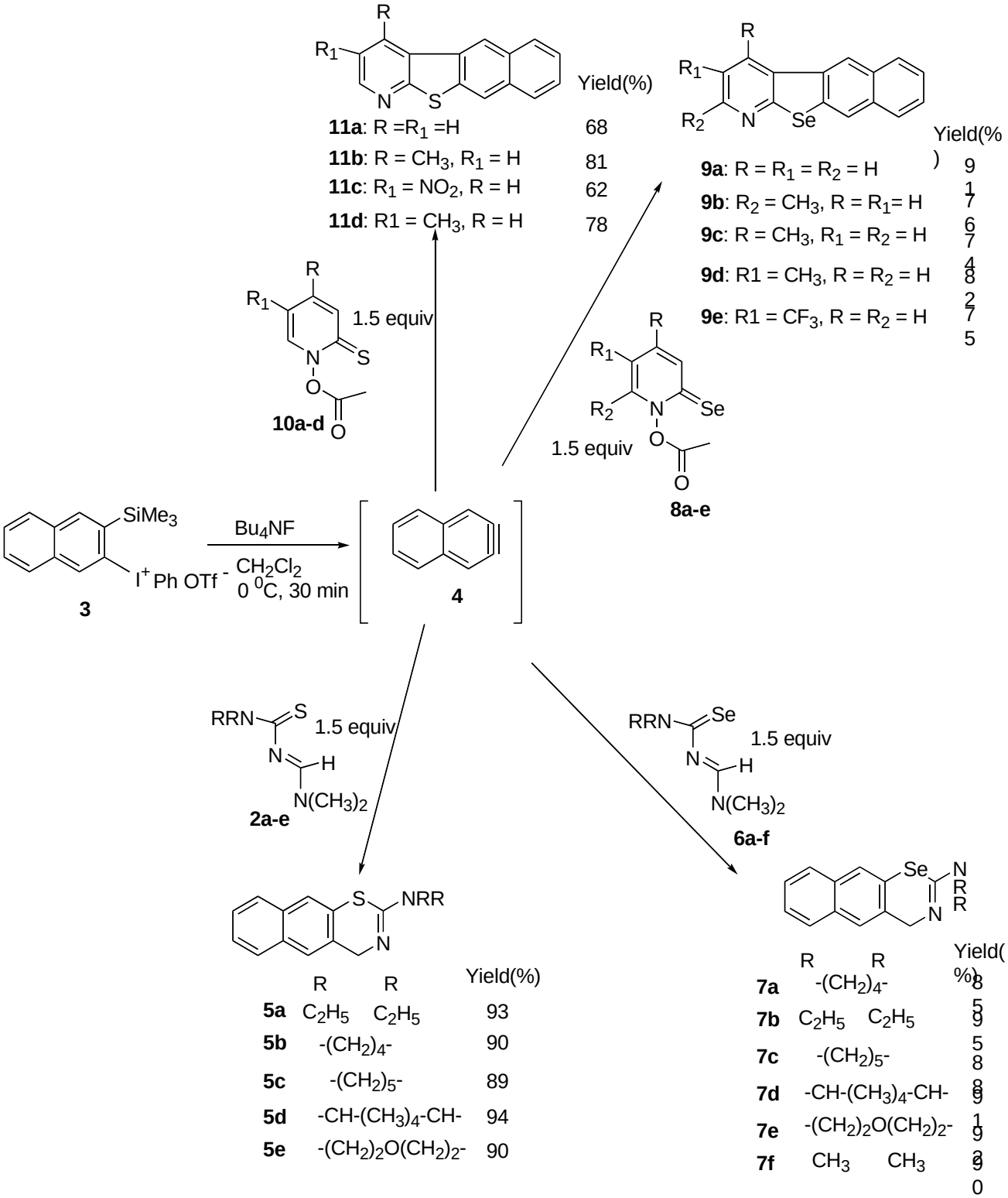
With the dienes on hand, the reactions listed in Scheme 2 were performed. The generation of 2,3-didehydronaphthalene (**4**) was carried out by simply adding Bu4NF to a solution of the precursor 3 at



	R	R		R	R	Yield(%)
1a:	C_2H_5	C_2H_5	**2a**:	C_2H_5	C_2H_5	77
1b:	$-(CH_2)_4-$		**2b**:	$-(CH_2)_4-$		75
1c:	$-(CH_2)_5-$		**2c**:	$-(CH_2)_5-$		68
1d:	$-CH-(CH_3)_2$	$(CH_3)_2CH-$	**2d**:	$-CH-(CH_3)_2$	$(CH_3)_2CH-$	81
1e:	$-(CH_2)_2O(CH_2)_2-$		**2e**:	$-(CH_2)_2O(CH_2)_2-$		79

Scheme 1

0 °C in the presence of 1.5 equiv of the diene. As shown, thiaazadienes (**2a**–**e**) reacted with 4 to give 4*H*-naphtho[2,3-*b*]-1,3-thiazines (**5a**–**e**) in 89-94% yields. Selenazadienes (**6a**–**f**) reacted with 4 to afford 4*H*-naphtho[2,3-*e*]-1,3-selenazines (**7a**–**f**) in 85-92% yields. Similiarly, 4 reacted



Scheme 2

with Barton selenium esters (**8a**–**e**) supplying naphtho[2',3':4,5]selenolo[2,3-*b*]pyridines (**9a**–**e**) in 74-91% yields and with Barton sulfur esters (**10a**–**d**) to give naphtho[2',3':4,5]thieno[2,3-

b]pyridines (**11a**–**d**) in 62- 81% yields. The products were identified on the basis of ^{1}H NMR and ^{13}C NMR spectroscopy. Additionally, 2-(morpholin-4-yl)-4*H*-naphtho[2,3-*b*]-1,3-thiazine (**5e**) and 2-diethylamino-4*H*-naphtho[2,3-*b*]-1,3-selenazine (**7b**) were determined by single x-ray crystallography. An ORTEP drawing for 7b and 5e are shown in Figures 1 and 2, respectively.

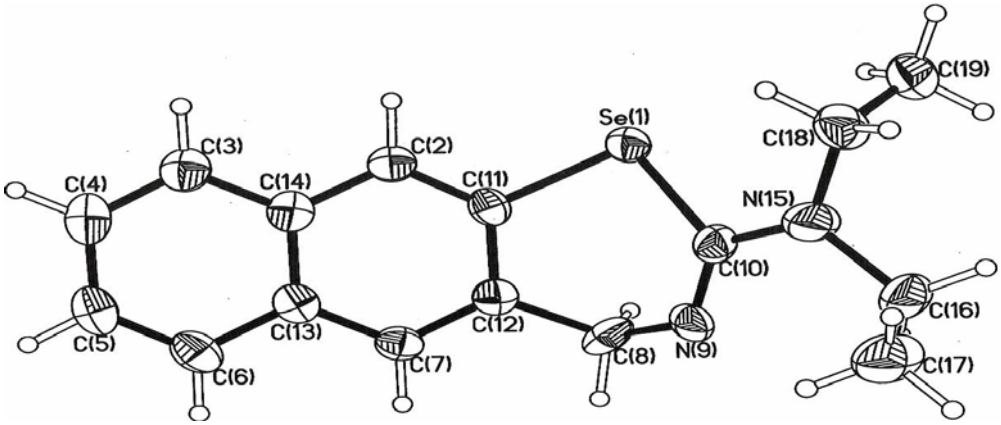


Figure 1. ORTEP of compound (**7b**).

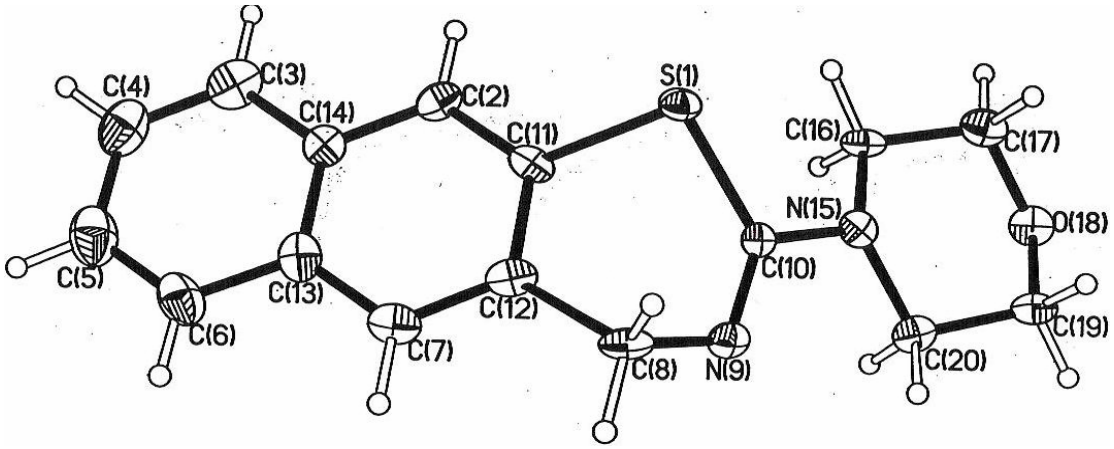
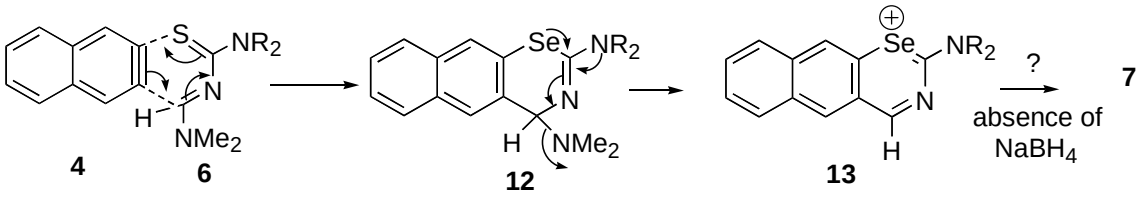


Figure 2. ORTEP of compound (**5e**).

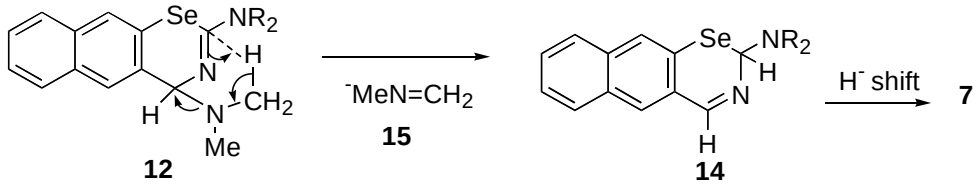
Possible mechanisms for the reactions reported here are worthy of discussion. The reaction of benzyne (**4**) with the esters **8** and **10** giving **9** and **11**, respectively, probably proceeds by the usual cycloaddition pathway previously reported.[11] However, the reaction of **4** with thiaazabutadienes (**2**) and with selenoazadienes (**6**) to give **5** and **7** is worthy of discussion. We[12] have shown that the reaction of selenoazadienes with benzynes generated by the reaction of 2-trimethylsilylphenyl triflates with CsF at room temperature gave extremely polar compounds which LC/MS showed to be N-oxide derivatives. By adding $NaBH_4$, the desired 4*H*-1,3-benzoselenazines were obtained. We proposed a somewhat controversial mechanism involving the formation of a Diels-Alder adduct intermediate which could aromatize by the electron release from S and NR_2 displacing the NMe_2 anion. What is left behind is a reasonably stable aromatic

cation which gets reduced by $NaBH_4$ giving the observed product. However, in this study we found that by generating benzyne (**4**) from the reaction of (phenyl)[(3-trimethylsilyl)-2-naphthyl]iodonium triflate (**3**) with Bu_4NF, the desired products **5** and **7** are obtained without the aid of the $NaBH_4$ reducing agent. This dilemma is shown in Scheme 3.



Scheme 3

Thus, it is unlikely that the proposed reduction mechanism in Scheme 3 is operative. One of the referees of this paper suggested the possibility that the electrons in **12** flow the other way in which the heterocyclic ring is reduced to **14** and the dimethylamine moiety is oxidized to $CH_3N{=}CH_2$ (**15**). This possibility is illustrated in Scheme 4. A 1,3-hydride shift would lead to the observed product **7**.



Scheme 4

Exactly the same process could apply to the reaction of 4 +2 going to 5. To date we have not been able to trap **15** and have insufficient information to support this mechanism. However, it appears to be a reasonable mechanism, and we are studying its validity.

In summary, we have synthesized a large number of naphthalene derivatives using 2,3-bis(trimethylsilyl)naphthalene with a $PhI(OAc)_2$/TfOH-reagent system which behaves as a highly efficient 2,3-didehydronaphthalene precursor. Compared with currently available aryne precursors, the hypervalent iodine reagent **3** not only generates arynes under neutral conditions at low temperatures but also reacts with dienes to give adducts in very good yields. This process represents a very powerful tool for the preparation of complex molecules, which might be difficult to prepare by any other present methodology.

Experimental Section

General Procedures. Melting points were taken on a Mel-Temp capillary apparatus and are uncorrected with respect to stem correction. ^{1}H-, and ^{13}C-NMR Spectra were recorded on a 400MHz Bruker AVANCE DRX-400 Multi-nuclear NMR spectrometer. Chemical shifts are reported in reference to TMS as internal standard. Elemental analyses were obtained from SMU Analytical Laboratories. HRMS analyses were provided by the Washington University Mass spectrometry Resource, an NIH Research Resource (Grant No. P41RR0954). Barton esters were stored in an amber bottle in a refrigerator. The glassware was heated overnight in an oven at 125°C prior to use. All the benzyne reactions were done under an atmosphere of dryO_2–free Ar via balloon.

General procedure for the synthesis of *N*^{1},*N*^{1}-diethyl-*N*^{2}-(dimethylaminomethylidene) thiourea (**2a**)

Dimethylformamide acetal (1.93mL, 14.5 mmol) was added to a THF solution (30mL) of diethylthiourea (**1a**) (1.60g, 12.1 mmol). The reaction mixture was stirred at rt for 5h. The mixture was evaporated to dryness. The residue was purified by flash chromatography in silica gel with hexane: ethyl acetate (7:3) to give **2a** 1.75g (77 %) as a light red color liquid; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.19 (t, *J* = 7.0Hz, CH_3), 1.29 (t, *J* = 7.1Hz, CH_3), 3.06 (s, CH_3), 3.15 (s, CH_3), 3.76 (q, *J* = 7.0Hz, CH_2), 4.01 (q, *J* = 7.0Hz), 8.81 (s, N=CH); ^{13}C NMR (100Hz, $CDCl_3$): δ 12.7, 13.7, 35.8, 41.5, 44.4, 47.5, 162.3, 189.9; Anal. Calcd for $C_8H_{17}N_3S$: C, 51.30; H, 9.15; N, 22.43. Found C, 51.45; H, 9.26; N, 22.64.

***N*^{1},*N*^{1}- Dimethyl-*N*^{2}-(pyrrolidinothiacarbonyl)formamidine (2b).** mp: 96–97 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.94 (m, CH_2), 3.05 (s, CH_3), 3.16 (s, CH_3), 3.65 (t, J = 7.5Hz, CH_2), 3.89 (t, J = 7.3Hz, CH_2), 8.74 (s, N=CH); ^{13}C NMR (100MHz, $CDCl_3$): δ 23.4, 24.61, 36.3, 40.7, 48.5, 53.3, 164.5, 184.8; Anal. Calcd for $C_8H_{15}N_3S$: C, 51.86; H, 8.16; N, 22.68. Found C, 51.38; H, 8.49; N, 22.87.

***N*^{1},*N*^{1}-Dimethyl-*N*^{2}-(piperidinothiacarbonyl)formamidine (2c).** mp: 84–85 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.57 (m, CH_2), 1.68 (m, CH_2), 3.06 (s, CH_3), 3.15 (s, CH_3), 4.02 (m, CH_2), 4.26 (m, CH_2) 8.82 (s, N=CH); ^{13}C NMR (100MHz, CDC_{l3}): δ 25.1, 26.1, 26.6, 35.90, 41.5, 47.8, 51.4, 163.0, 189.7; Anal. Calcd for $C_9H_{17}N_3S$: C, 54.23; H, 8.60; N, 21.08. Found C, 54.17; H, 8.25; N, 21.16.

***N*^{1},*N*^{1}-Diisopropyl-*N*^{2}-(dimethylaminomethylidene)thiourea (2d).** mp: 79–80 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.22 (s, CH_3), 1.24 (s, CH_3), 1.48 (s, CH_3), 1.50 (s, CH_3), 1.59 (m, N-CH), 3.09 (s, CH_3), 3.15 (s, CH_3) 8.81 (s, N=CH); ^{13}C NMR (100MHz, $CDCl_3$): δ 20.0, 22.3, 36.4, 41.4, 48.8, 53.9, 161.7, 190.8; Anal. Calcd for $C_{10}H_{21}N_3S$: C, 55.77; H, 9.83; N, 19.51. Found C, 55.86; H, 9.58; N, 19.67.

General procedure for synthesis of diethylamino-4*H*-naphtho[2,3-*e*]-1,3-thiazine (5a)

To a solution of **3** (0.20g, 0.39 mmol), and N1,N1-diethyl-N2-(dimethylaminomethylidene)thiourea (**2a**) (0.10g, 0.53 mmol) in dichloromethane (10 mL) was added a tetrahydrofuran solution of Bu_4NF (1M,

0.57 mL) at 00C. After the mixture was stirred for 30 min at 0 °C, water was added and the product was extracted with dichloromethane. After evaporation of the solvent, the product was separated by column chromatography on silica gel (hexane/ethyl acetate 8:2) to give diethylamino-4H-naphtho[2,3-e]-1,3-thiazine (5a) 0.93g (93%) as a pale yellow solid, mp: 74–75 °C: 1H NMR (400MHz, $CDCl_3$) δ 1.23 (t, J = 6.0Hz, 6H), 3.56 (q, J = 6.2Hz, 4H), 4.62 (s, 2H), 7.47 (m, 2H), 7.85 (bs, 2H); 13C NMR ($CDCl_3$): δ 14.1, 44.3, 54.27, 124.9, 125.9, 126.3, 126.4, 127.3, 128.1, 130.4, 132.9, 133.0, 134.1, 156.6. Anal. Calcd for $C_{16}H_{18}N_2S$: C, 71.07, H, 6.71, N, 10.36. Found: C, 71.19, H, 6.70, N, 10.30.

2-(Pyrrolidin-1-yl)-4*H*-naphtho[2,3-*e*]-1,3-thiazine (5b). Light brown solid, mp: 86–87°C: ^{1}H NMR (400MHz, $CDCl_3$) δ 1.97 (m, 4H), 3.58 (m, 4H), 4.63 (s, 2H), 7.46 (m, 2H), 7.76 (m, 2H), 7.82 (bs, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 25.7, 48.7, 54.2, 125.1, 125.7, 126.3, 126.4, 127.3, 128.1, 130.0, 132.9, 133.0, 133.4,154.7. Anal. Calcd for $C_{16}H_{16}N_2S$: C, 71.61, H, 6.01, N, 10.44. Found: C, 71.55, H, 6.04, N, 10.65.

2-(Piperidin-2-yl)-4*H*-naphtho[2,3-*e*]-1,3-thiazine (5c). Yellow solid, mp: 106–107°C: ^{1}H NMR (400MHz, $CDCl_3$) δ 1.60 (m, 6H), 3.57 (m, 4H), 4.62 (s, 2H), 7.46 (m, 2H), 7.77 (m, 2H), 7.81 (s, 1H), 7.84 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 25.3, 26.1, 49.2, 54.4, 1245.0, 126.0, 126.1, 126.4, 127.3, 128.1, 130.3, 132.9, 133.0, 133.9, 158.5. Anal. Calcd for $C_{17}H_{18}N_2S$: C, 72.30, H, 6.42, N, 9.92. Found: C, 72.24, H, 6.52, N, 9.72.

2-Diisopropylamino-4*H*-naphtho[2,3-*e*]-1,3-thiazine (5d). Yellow solid, mp: 88–89°C: ^{1}H NMR (400MHz, $CDCl_3$) δ 1.32 (t, *J* = 6.5Hz, 12H), 4.18 (m, 2H), 4.62 (s, 2H), 7.31 (s, 1H), 7.48 (m, 2H), 7.80 (m, 2H), 7.86 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 21.9, 22.1, 49.4, 53.8, 54.6, 125.0, 126.0, 126.4, 127.4, 128.2, 129.8, 134.6, 136.5, 152.6. Anal. Calcd for $C_{18}H_{22}N_2S$: C, 72.44, H, 7.43, N, 9.29. Found: C, 72.31; H, 7.54; N, 9.38.

2-(Morpholin-4-yl)-4*H*-naphtho[2,3-*e*]-1,3-thiazine (5e). Colorless solid, mp: 123–124°C: ^{1}H NMR (400MHz, $CDCl_3$) δ 3.58 (m, 4H), 3.76 (m, 4H), 4.65 (d, *J* = 5.3Hz, 2H), 7.48 (m, 2H), 7.76 (m, 2H), 7.83 (bs, 2H), 7.99 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 48.5, 54.3, 67.0, 125.2, 126.1, 126.5, 126.6, 127.3, 128.1, 129.4, 133.0, 133.1, 133.3, 158.8. Anal. Calcd for $C_{16}H_{16}N_2OS$: C, 67.58, H, 5.87, N, 9.85. Found: C, 67.78, H, 5.69; N, 9.73.

2-(Pyrrolidin-1-yl)-4*H*-naphtho[2,3-*e*]-1,3-selenazine (7a). Light yellow solid, mp: 87–89°C: ^{1}H NMR (400MHz, $CDCl_3$) δ 1.96 (m, 4H), 3.54 (m, 4H), 4.58 (s, 2H), 7.47 (m, 2H), 7.76 (s, 1H), 7.83 (m, 2H), 7.98 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 25.5, 49.5, 58.0, 125.7, 126.3, 126.4, 127.2, 128.2, 128.5, 128.5, 133.2, 133.8, 153.0. Anal. Calcd for $C_{16}H_{16}N_2Se$: C, 60.95, H, 5.12, N, 8.89. Found: C, 61.09, H, 5.32, N, 8.85.

2-Diethylamino-4*H*-naphtho[2,3-*e*]-1,3-selenazine (7b). Brown solid, mp: 62–63°C: ^{1}H NMR (400MHz, $CDCl_3$) δ 1.18 (t, *J* = 6.8Hz, 6H), 3.50 (q, *J* = 6.6Hz, 4H), 4.56 (d, *J* = 6.6Hz, 2H), 7.46 (m, 2H), 7.80 (s, 1H), 7.83 (m, 2H), 7.98 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 14.2, 45.1, 58.1, 125.5, 126.3, 126.4, 127.2, 128.2, 128.7, 128.8, 133.2, 133.4, 154.8. Anal. Calcd for $C_{16}H_{18}N_2Se$: C, 60.57, H, 5.72, N, 8.83. Found: C, 60. 88, H, 5.88, N, 8.96.

2-(Piperidin-2-yl)-4*H*-naphtho[2,3-*e*]-1,3-selenazine (7c). Light yellow solid, mp: 93–94°C: ^{1}H NMR (400MHz, $CDCl_3$) δ 1.59 (m, 6H), 3.55 (m, 4H), 4.59 (s, 2H), 7.47 (m, 2H), 7.76 (m, 2H),

7.82 (s, 1H), 7.99 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 26.1, 50.0, 58.1, 125.6, 126.3, 126.4, 127.2, 128.2, 128.7, 128.8, 133.2, 134.2, 145.9, 157.3. Anal. Calcd for $C_{17}H_{18}N_2Se$: C, 62.01, H, 5.51, N, 8.51. Found: C, 62.18, H, 5.52, N, 8.47.

2-Diisopropylamino-4*H*-naphtho[2,3-*e*]-1,3-selenazine (7d). Yellow solid, mp: 110–111°C: ^{1}H NMR (400MHz, $CDCl_3$) δ 1.32 (t, *J* = 6.7 Hz, 12H), 4.06 (dd, *J* = 13.3, 6.6 Hz, 2H), 4.56 (s, 2H), 7.47 (dd, *J* = 6.6, 3.3Hz, 2H), 7.77 (m, 2H), 7.83 (s, 1H), 8.00 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 21.5, 21.8, 50.1, 50.3, 58.0, 125.3, 126.2, 127.2, 128.2, 128.8, 129.6, 133.2, 134.5, 153.1. Anal. Calcd for $C_{18}H_{22}N_2Se$: C, 62.60, H, 6.42, N, 8.11. Found: C, 62.70, H, 6.57, N, 8.08.

2-(Morpholin-4-yl)-4*H*-naphtho[2,3-*e*)]-1,3-selenazine (7e). Colorless solid, mp: 122–123°C: ^{1}H NMR (400MHz, $CDCl_3$) δ 3.56 (m, 4H), 3.74 (m, 4H), 4.62 (s, 2H), 7.30 (m, 2H), 7.49 (s, 1H), 7.80 (m, 2H), 7.99 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 49.3, 58.0, 67.0, 125.8, 126.5, 126.6, 127.2, 127.9, 128.2, 128.8, 133.2, 133.6, 145.9, 157.7. Anal. Calcd for $C_{16}H_{16}N_2OSe$: C, 58.01, H, 4.87, N, 8.46. Found: C, 58.18; H, 4.62, N, 8.26.

2-Dimethylamino-4*H*-naphtho[2,3-*e*]-1,3-selenazine (7f). Yellow solid, mp: 65–67°C: ^{1}H NMR (400MHz, $CDCl_3$) δ 3.10 (s, 6H), 4.58 (s, 2H), 7.47 (dd, *J* = 6.0, 3.1Hz, 2H), 7.77 (m, 2H), 7.83 (s, 1H), 7.99 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 40.4, 58.1, 125.6, 126.3, 126.4, 127.2, 128.2, 128.5, 128.6, 133.2, 133.2, 133.8, 156.7. Anal. Calcd for $C_{14}H_{14}N_2Se$: C, 58.14, H, 4.88, N, 9.69. Found: C, 58.35, H, 4.97, N, 9.45.

General procedure for synthesis of naphtho[2',3':4,5]selenolo(2,3-*b*)pyridine (9a)

To a solution of **3** (0.20 g, 0.39 mmol) and a Barton ester (**8a**, 0.12 g, 0.57 mmol) in dichloromethane (10 mL) was added a tetrahydrofuran solution of Bu_4NF (1M, 0.57mL) at 0 °C, and the mixture was stirred for 30 min. Water was added and the resulting mixture was extracted with CH_2Cl_2. After evaporation of the solvent, the product was purified by column chromatography on silica gel (hexane : ethyl acetate 9:1) to yield 0.91g, (91%) of a colorless liquid identified as naphtho[2',3':4,5]selenolo[2,3-*b*]pyridines (**9a**). ^{1}H NMR (400MHz, $CDCl_3$) δ 6.73 (d, *J* = 8.0Hz, 1H), 7.00 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.32 (dd , *J* = 7.9 , 2.2Hz , 1H), 7.56 (m , 1H), 7.81 (d, *J* = 7.4Hz , 1H), 7.91 (d, *J* = 7.0Hz, 1H), 8.13 (s, 1H), 8.33 (s, 1H) and 8.46 (t, *J* = 4.67, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 120.4, 123.9, 127.5, 127.6, 127.9, 128.52, 130.7, 133.1, 134.9, 137.0, 137.2, 139.4, 144.0, 150.1, 161.5. HRMS (*m/z*): Calcd for $C_{15}H_9NSe$: 282.9900. Found: 282.9896.

2-Methylnaphtho[2',3':4,5]selenolo[2,3-*b*]pyridines (9b). Colorless liquid: ^{1}H NMR (400MHz, $CDCl_3$) δ 2.57 (s, CH_3), 6.48 (d, *J* = 7.9Hz, 1H), 6.85 (d, *J* = 7.5Hz, 1H), 7.54–7.57 (m , 2H), 7.79 (t , *J* = 9.0Hz, 1H), 7.91 (t, *J* = 8.6Hz, 1H), 8.31 (s, 1H) and 8.33 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 24.7, 119.9, 120.7, 127.4, 127.5, 127.8, 128.5, 130.9, 133.1, 134.9, 137.1, 137.2, 139.3, 144.1, 159.0, 160.9. HRMS (*m/z*): Calcd for $C_{16}H_{11}NSe$: 297.0143. Found : 297.0156.

4-Methylnaphtho[2',3':4,5]selenolo[2,3-*b*]pyridine (9c). Colorless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 2.11 (s, CH_3), 6.60 (s, 1H), 6.83 (d, *J* = 4.9Hz, 1H), 7.54–7.59 (m , 2H), 7.82 (t , *J* =

9.0Hz, 1H), 7.91 (dd, *J* = 2.9, 2.2Hz, 1H), 8.13 (s, 1H) and 8.32 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 21.4, 121.8, 124.6, 127.3, 127.4, 127.9, 128.5, 130.8, 133.7, 134.8, 137.1, 139.2, 143.9, 148.4, 149.7, 160.8. HRMS(*m/z*): Calcd for $C_{16}H_{11}NSe$: C, 297.0143. Found : 297.0153.

3- Methylnaphtho[2',3':4,5]selenolo[2,3-*b*]pyridine (9d). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, CH_3), 6.67 (d, *J* = 8.1Hz, 1H), 7.15 (dd, *J* = 2.0, 2.0Hz, 1H), 7.53–7.58 (m , 2H), 7.78 (t , *J* = 6.9Hz, 1H), 7.90 (t, *J* = 8.7Hz, 1H), 8.11 (s, 1H) and 8.30 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 18.3, 123.8, 127.4, 127.4, 127.8, 128.5, 120.0, 131.2, 133.0, 134.9, 137.0, 137.9, 139.0, 143.9, 150.5, 157.3. HRMS(*m/z*): Calcd for $C_{16}H_{11}NSe$: 297.0176. Found : 297.0186.

3-Trifluoromethylnaphtho[2',3':4,5]selenolo[2,3-*b*]pyridine (9e). Colorless solid. mp. 190–191°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (d, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 1H), 7.44 (m, 1H), 7.62 (m , 1H), 8.11 (bs, 1H), 8.19 (bs, 1H), 8.29 (bs, 1H) and 8.65 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.7, 125.7, 128.0 (q, *J* = 256.3Hz), 128.7 (q, *J* = 3.8Hz), 130.2, 131.7, 133.5, 134.8 (q, *J* = 3.8 Hz), 135.07 (q, *J* = 35.1 Hz), 136.2, 138.0, 140.0, 143.9, 158.5 170.5. HRMS (*m/z*): Calcd for $C_{16}H_8F_3NSe$: 350.9893. Found: 350.9890.

Naphtho[2',3':4,5]thieno[2,3-*b*]pyridines (11a). Colorless solid, mp 190-191°C:^{1}H NMR (400 MHz, $CDCl_3$) 7.42 (dd, *J* = 6.3, 4.8 Hz, 1H), 7.94 (d, *J* = 7.4 Hz, 1H), 8.00 (d, *J* = 7.8 Hz , 1H), 8.31 (s, 1H), 8.45 (dd, *J* = 7.8, 0.9 Hz, 1H), 8.65 (s, 1H) and 8.66 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 120.0, 121.3, 121.5, 125.9, 126.9, 127.6, 128.8, 129.4, 129.7, 131.3, 132.7, 133.3, 136.2, 149.4, 163.3. HRMS (*m/z*): Calcd for $C_{15}H_9F_3NS$: 235.0456. Found: 235.0459.

4-Methylnaphtho[2',3':4,5]thieno[2,3-*b*]pyridine (11b). Colorless solid, mp 165 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.01 (s, CH_3) 7.21 (d, *J* = 4.6 Hz, 1H), 7.53–7.61 (m, 2 H), 7.94 (d, *J* = 7.8 Hz, 1H), 8.06 (d , *J* = 7.7 Hz, 1 H), 8.33 (s, 1H), 8.51 (d, *J* = 4.7 Hz, 1H) and 8.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.3, 121.2, 122.6, 125.0, 125.7, 126.9, 127.2, 128.2, 129.1, 131.3, 132.4, 133.9, 136.2, 144.1, 148.4, 163.3. HRMS (*m/z*): Calcd for $C_{16}H_{11}NS$: 249.0612. Found: 249.0615.

3-Nitronaphtho[2',3':4,5]thieno[2,3-*b*]pyridine (11c). Colorless solid, mp 181–182°C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.77 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.97 (d , *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 8.24 (s, 1 H) and 9.13 (d, *J* = 2.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.9, 121.6, 124.4, 127.9, 128.4, 128.5, 128.8, 131.2,131.2, 134.4, 134.4, 134.7, 136.9, 142.0, 162.5. HRMS (*m/z*): Calcd for $C_{15}H_8NO_2S$: 280.0306. Found: 280.0303.

3-Methylnaphtho[2',3':4,5]thieno[2,3-*b*]pyridine (11d). Colorless solid, mp 146–147 °C: ^{1}H NMR (400MHz, $CDCl_3$) δ 2.55 (s, CH_3), 7.53–7.59 (m, 2H), 7.94 (dd, *J* = 4.7, 1.2Hz, 1H), 8.03 (d, *J* = 7.3Hz, 1H), 8.28 (d , *J* = 1.0 Hz, 1H), 8.30 (s, 1H), 8.50 (d, *J* = 1.5Hz, 1H) and 8.58 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 121.2, 121.5, 125.8, 126.8, 127.5, 128.7, 129.5, 129.6, 129.9, 131.3, 132.7, 133.2, 136.7, 150.2, and 160.3. HRMS (*m/z*): Calcd for $C_{16}H_{11}NS$: 249.0612. Found: 249.0611.

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