Supporting Information

Synthesis and photophysical properties of selenopheno[2,3-*b*]quinoxaline and selenopheno[2,3-*b*]pyrazine heteroacenes

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List of the Content:

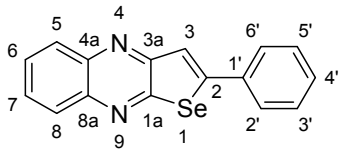
Experimental: General

All solvents and reagents were purchased from the suppliers and used without further purification. IR spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Reactions were monitored by TLC on silica plates using UV-light or Iodine chamber for visualization. Evaporation and condensation were carried out *in vacuo*. NMR spectra were recorded with JEOL JNM-ECS 400 spectrometers with tetramethylsilane as an internal standard. Chemical shifts δ and coupling constants *J* are given in ppm (parts per million) and Hz (hertz), respectively. The abbreviations were used as follows: s: singlet, d: doublet, t: triplet, m: multiplet. All known compound data are in consistent with the given literature reports. Scale up reactions also performed as per the given general procedure without any deviation. Melting points were measured by a Yanaco micromelting point apparatus. The HRMS were recorded with the Acquity XEVO QTof MS analyzer. UV-vis spectra were taken on a Hitachi U4100 spectrophotometer. Fluorescence spectra were measured on a FP-8600 spectrofluorometer. Fluorescence quantum yields were recorded on a Quantaurus-QY.

General procedure and spectral data for compounds 4a-4f.

NaSeH was prepared *in situ* by reactions of elemental selenium (1.0 equiv.) and sodium borohydride (2.0 equiv.) in ethanol (0.75 mL) / water (1.5 mL) mixture at 0°C for 15 min, after confirming that the solution changed from black to colorless and transparent (white), to this freshly prepared NaseH solution, compounds **3a-3f** (1.0 equiv.) and ethanol (1 mL) was added, and the mixture was stirred under reflux for 1 hour. After confirming the completion of the reaction by TLC (Hexane:EtOAc = 7:3), the reaction mixture was cooled to room temperature, and the obtained solution was extracted with ethyl acetate and water. Thereafter, the organic layer was washed with a brine solution and dried over anhydrous sodium sulfate. The residue was purified by silica gel column chromatography (Hexane:EtOAc = 19:1) afforded the corresponding 2-arylselenopheno[2,3-*b*]quinoxaline derivatives **4a-4f** in 69-95% yields.

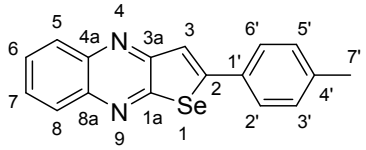
2-Phenylselenopheno[2,3-*b*]quinoxaline (4a)



4a

Yield: 83%; Melting point: 134-135˚C; IR (ATR): 1442, 1330, 1044, 753 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14-8.08 (2H, m, H-5 and H-8), 7.88 (1H, s, H-3), 7.79-7.72 (4H, m, H-6, H-7, H-2' and H-6'), 7.50-7.44 (3H, m, H-3', H-4' and H-5'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 155.2, 155.1, 141.2, 140.2, 135.0, 130.3, 129.3 (2C), 129.26, 129.23, 128.3, 127.1 (2C), 120.2; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 488.9; HRESIMS: *m/z* 311.0065 $[M+H]^+$ (calcd. for $C_{16}H_{11}N_2Se$, 311.0087).

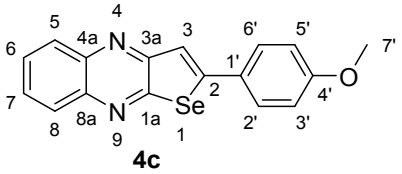
2-(*p*-Tolyl)selenopheno[2,3-*b*]quinoxaline (4b)



4b

Yield: 77%; Melting point: 174-175˚C; IR (ATR): 3039, 2910, 1555, 1138, 1043, 801, 751, 461 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.06 (2H, m, H-5 and H-8), 7.80 (1H, s, H-3), 7.75-7.71 (2H, m, H-6 and H-7), 7.58 (2H, d, *J* = 8.2 Hz, H-2' and H-6'), 7.23 (2H, d, *J* = 8.2 Hz, H-3' and H-5'), 2.37 (3H, s, H-7'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 155.4, 141.3, 140.8, 140.2, 132.3, 130.0 (2C), 129.3, 129.1, 128.4, 127.1 (2C), 119.5, 21.5; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 486.9; HRESIMS: *m/z* 325.0226 $[M+H]^+$ (calcd. for $C_{17}H_{13}N_2Se$, 325.0244).

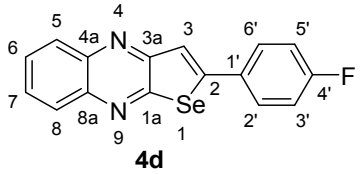
2-(4-Methoxyphenyl)selenopheno[2,3-*b*]quinoxaline (4c)



4c

Yield: 83%; Melting point: 140-142˚C; IR (ATR): 1601, 1505, 1258, 1182, 1036, 748 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.10 (2H, m, H-5 and H-8), 7.78-7.69 (5H, m, H-3, H-6, H-7, H-2' and H-6'), 7.03-7.00 (2H, m, H-3' and H-5'), 3.89 (3H, s, H-7'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 159.5, 155.7, 155.1, 141.3, 140.1, 129.3, 129.0, 128.7, 128.6, 128.4, 127.8, 118.63, 118.58, 114.8, 114.7, 55.6; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 484.8; HRESIMS: *m/z* 341.0182 $[M+H]^+$ (calcd. for $C_{17}H_{13}N_2OSe$, 341.0193).

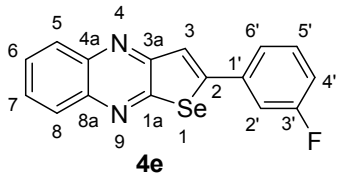
2-(4-Fluorophenyl)selenopheno[2,3-*b*]quinoxaline (4d)



4d

Yield: 95%; Melting point: 179-180˚C; IR (ATR): 3053, 1560, 1503, 1229, 1045, 828, 750 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.04 (2H, m, H-5 and H-8), 7.73 (1H, s, H-3), 7.76-7.71 (2H, m, H-6 and H-7), 7.65-7.62 (2H, m, H-3' and H-5'), 7.12 (2H, t, *J* = 8.5 Hz, H-2' and H-6'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 162.6, 159.4, 155.1, 153.8, 141.2, 140.2, 131.4, 129.40, 129.36, 129.3, 129.27, 129.02, 128.4, 120.3, 116.5, 116.3; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 489.9; ^{19}F-NMR (400 MHz, $CDCl_3$) δ -109.63; HRESIMS: *m/z* 328.9970 $[M+H]^+$ (calcd. for $C_{16}H_{10}N_2SeF$, 328.9993).

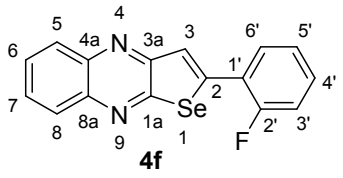
2-(3-Fluorophenyl)selenopheno[2,3-*b*]quinoxaline (4e)



4e

Yield: 69%; Melting point: 169-170˚C; IR (ATR): 3047, 1583, 1476, 1329, 1161, 1045, 780 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.105 (2H, m, H-5 and H-8), 7.82 (1H, s, H-3), 7.76-7.71 (2H, m, H-6 and H-7), 7.46-7.36 (3H, m, H-2', H-4' and H-6'), 7.13-7.09 (1H, m, H-5'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 161.9, 159.3, 154.8, 153.4, 141.3, 140.4, 137.24, 137.16, 131.0, 130.8, 129.6, 129.5, 129.4, 128.4, 123.0, 121.3, 117.2, 117.0, 114.1, 113.8; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 492.8; ^{19}F-NMR (400 MHz, $CDCl_3$) δ -111.57; HRESIMS: *m/z* 328.9970 $[M+H]^+$ (calcd. for $C_{16}H_{10}N_2SeF$, 328.9993).

2-(2-Fluorophenyl)selenopheno[2,3-*b*]quinoxaline (4f)



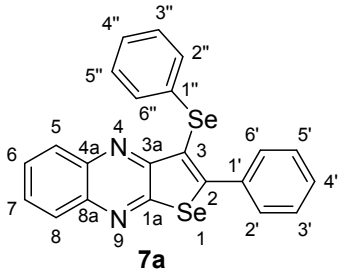
4f

Yield: 95%; Melting point: 125-126˚C; IR (ATR): 3053, 1447, 1102, 1046, 747 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14-8.08 (2H, m, H-5 and H-8), 8.06 (1H, s, H-3), 7.78-7.74 (2H, m, H-6 and H-7), 7.71-7.67 (1H, m, H-4'), 7.40-7.37 (1H, m, H-5'), 7.27-7.18 (2H, m, H-4' and H-6'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 159.61, 159.55, 158.5, 154.6, 147.4, 141.3, 140.4, 131.6, 131.5, 129.8, 129.8, 129.5, 129.41, 129.38, 128.4, 125.0, 124.9, 124.07, 124.00, 123.1, 123.0, 116.9, 116.7; ^{77}Se NMR (75 MHz, $CDCl_3$): 512.5; ^{19}F-NMR (400 MHz, $CDCl_3$) δ -111.66; HRESIMS: *m/z* 328.9966 $[M+H]^+$ (calcd. for $C_{16}H_{10}N_2SeF$, 328.9993).

General procedure and spectral data for compounds 7a-7i.

To a stirred mixture of diorganyl diselenides (1.0 equiv.) and $FeCl_3 \cdot 6H_2O$ (2.0 equiv.) in dichloromethane solvent was added the compounds 2-(methylselanyl)-3-(arylethynyl)quinoxaline **5** (1.0 equiv.) and heated at 45˚C, successfully affording the corresponding 3-(arylselanyl/sulfanyl)-2-arylselenopheno[2,3-*b*]quinoxaline derivatives **7a-7i** in 57-92% yields.

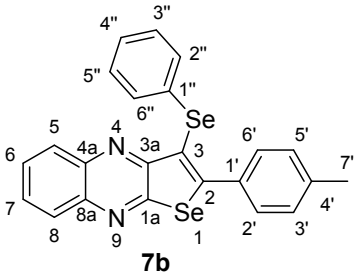
2-Phenyl-3-(phenylselanyl)selenopheno[2,3-*b*]quinoxaline (7a)



7a

Yield: 74%; Melting point: 155-156˚C; IR (ATR): 2920, 1474, 1437, 1063, 1020, 759, 743, 690 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (1H, dd, *J* = 6.9 and 2.9 Hz, H-5 or H-8), 8.13 (1H, dd, *J* = 7.2 and 2.6 Hz, H-5 or H-8), 7.80-7.75 (2H, m, H-6 and H-7), 7.66 (2H, dd, *J* = 6.6 and 3.2 Hz, H-2" and H-6"), 7.44-7.43 (3H, m, H-3", H-4" and H-5"), 7.36-7.34 (2H, m, H-2' and H-6'), 7.10-7.09 (3H, m, H-3', H-4' and H-5'); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 158.4, 154.3, 141.6, 140.9, 135.8, 131.8 (2C), 131.4, 130.1, 130.0 (2C), 129.9, 129.8, 129.3, 129.1 (2C), 128.6 (2C), 128.2, 126.8, 118.8; ^{77}Se NMR (100 MHz, $CDCl_3$): δ 556.7, 303.9; HRESIMS: *m/z* 466.9581 $[M+H]^+$ (calcd. for $C_{22}H_{15}N_2Se_2$, 466.9566).

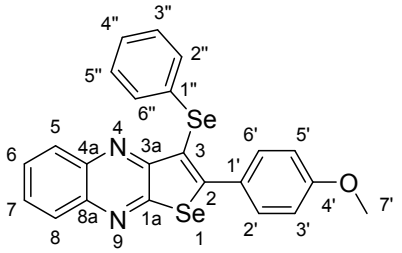
3-(Phenylselanyl)-2-(*p*-tolyl)selenopheno[2,3-*b*]quinoxaline (7b)



7b

Yield: 81%; Melting point: 155-157˚C; IR (ATR): 2922, 1474, 1436, 1185, 1065, 1019, 814, 762, 736, 720, 689 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (1H, dd, *J* = 7.2 and 3.2 Hz, H-5 or H-8), 8.04 (1H, dd, *J* = 6.9 and 2.9 Hz, H-5 or H-8), 7.71-7.66 (2H, m, H-6 and H-7), 7.50 (2H, d, *J* = 8.0 Hz, H-2' and H-6'), 7.28-7.27 (2H, m, H-2" and H-6"), 7.19-7.17 (2H, m, H-3' and H-5'), 7.03-7.01 (3H, m, H-3", H-4" and H-5"), 2.33 (3H, s, H-7'); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 158.9, 154.5, 141.6, 140.8, 140.3, 133.0, 132.0, 131.2 (2C), 130.1, 129.9 (2C), 129.8, 129.33 (2C), 129.25, 129.1 (2C), 128.2, 126.7, 118.1, 21.5; ^{77}Se NMR (100 MHz, $CDCl_3$): δ 553.7, 302.1; HRESIMS: *m/z* 480.9746 $[M+H]^+$ (calcd. for $C_{23}H_{17}N_2Se_2$, 480.9722).

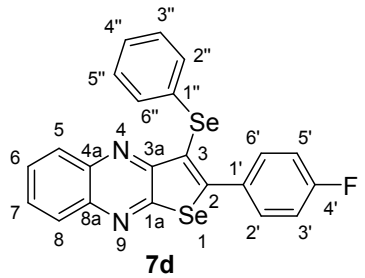
2-(4-Methoxyphenyl)-3-(phenylselanyl)selenopheno[2,3-*b*]quinoxaline (7c)



7c

Yield: 92%; Melting point: 142-144˚C; IR (ATR): 2928, 2832, 1600, 1571, 1473, 1254, 1171, 1025, 829, 822, 764, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22-8.19 (1H, m, H-5 or H-8), 8.13-8.10 (1H, m, H-5 or H-8), 7.77-7.74 (2H, m, H-6 and H-7), 7.66 (2H, d, *J* = 8.7 Hz, H-2' and H-6'), 7.36-7.33 (2H, m, H-2" and H-6"), 7.11-7.09 (3H, m, H-3", H-4" and H-5"), 6.96 (2H, d, *J* = 8.7 Hz, H-3' and H-5'), 3.86 (3H, s, H-7'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 159.0, 158.7, 154.7, 141.6, 140.8, 132.1 (2C), 131.6, 130.9 (2C), 130.0, 129.7, 129.2, 129.1 (2C), 128.2, 128.1, 126.7, 117.4, 114.1 (2C), 55.5; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 550.4, 300.7; HRESIMS: *m/z* 494.9670 $[M+H]^+$ (calcd. for $C_{23}H_{17}N_2OSe_2$, 494.9700).

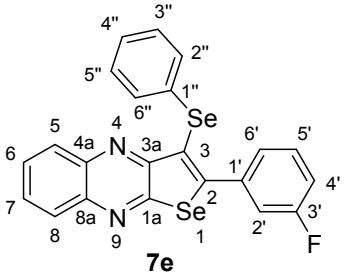
2-(4-Fluorophenyl)-3-(phenylselanyl)selenopheno[2,3-*b*]quinoxaline (7d)



7d

Yield: 69%; Melting point: 155-157˚C; IR (ATR): 3051, 1474, 1062, 1019, 759, 743, 690, 604 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24-8.22 (1H, m, H-5 or H-8), 8.15-8.12 (1H, m, H-5 or H-8), 7.79-7.76 (2H, m, H-6 and H-7), 7.67-7.65 (2H, m, H-2'and H-6'), 7.45-7.43 (2H, m, H-2" and H-6"), 7.36-7.34 (2H, m, H-3'and H-5'), 7.10-7.09 (3H, m, H-3", H-4" and H-5"); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 158.4, 154.3, 148.2, 141.5, 140.9, 135.8, 133.5, 131.8, 131.3 (2C), 130.1, 130.0 (2C), 129.9, 129.8, 129.5, 129.3, 129.1 (2C), 128.6 (2C), 128.2, 126.8, 118.8, 72.7; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 556.7, 303.6; ^{19}F-NMR (400 MHz, $CDCl_3$) δ -109.75; HRESIMS: *m/z* 484.9472 $[M+H]^+$ (calcd. for $C_{22}H_{14}N_2FSe_2$, 484.9471).

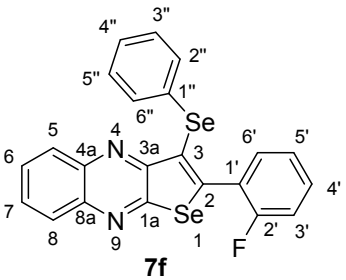
2-(3-Fluorophenyl)-3-(phenylselanyl)selenopheno[2,3-*b*]quinoxaline (7e)



7e

Yield: 61%; Melting point: 127-128˚C; IR (ATR): 3063, 1576, 1474, 1068, 763, 733, 722, 684 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26-8.23 (1H, m, H-5 or H-8), 8.15-8.12 (1H, m, H-5 or H-8), 7.81-7.78 (2H, m, H-6 and H-7), 7.41-7.34 (5H, m, H-2", H-3", H-4", H-5" and H-6"), 7.14-7.09 (4H, m, H-2', H-4', H-5' and H-6'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 161.2, 158.8, 155.8, 154.1, 141.6, 141.0, 137.8, 137.7, 131.7 (2C), 131.3, 130.2, 130.10, 130.07, 129.5, 129.2 (2C), 128.2, 127.0, 125.7, 119.9, 117.1, 116.8, 116.7, 116.5; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 560.2, 308.7; ^{19}F-NMR (400 MHz, $CDCl_3$) δ -112.07; HRESIMS: *m/z* 484.9500 $[M+H]^+$ (calcd. for $C_{22}H_{14}N_2FSe_2$, 484.9471).

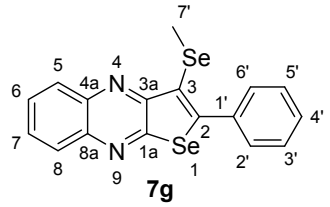
2-(2-Fluorophenyl)-3-(phenylselanyl)selenopheno[2,3-*b*]quinoxaline (7f)



7f

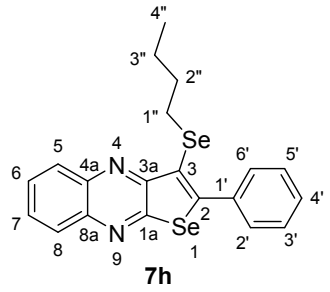
Yield: 88%; Melting point: 110-111˚C; IR (ATR): 3065, 1476, 1437, 1065, 757, 748, 738, 727 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.22 (1H, m, H-5 or H-8), 8.14-8.12 (1H, m, H-5 or H-8), 7.81-7.77 (2H, m, H-6 and H-7), 7.47-7.35 (4H, m, H-3', H-4', H-5' and H-6'), 7.22-7.05 (5H, m, H-2", H-3", H-4", H-5" and H-6"); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 159.3, 157.8, 153.3, 150.1, 141.4, 140.8, 133.5, 132.3 (2C), 131.7, 131.6, 130.8, 130.10, 130.06, 129.4, 128.9 (2C), 128.2, 127.0, 124.19, 124.16, 123.9, 123.8, 122.5, 116.3, 116.1; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 569.5, 319.6; ^{19}F-NMR (400 MHz, $CDCl_3$) δ -110.428; HRESIMS: *m/z* 484.9482 $[M+H]^+$ (calcd. for $C_{22}H_{14}N_2FSe_2$, 484.9471).

3-(Methylselanyl)-2-phenylselenopheno[2,3-*b*]quinoxaline (7g)



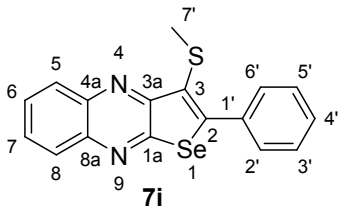
Yield: 66%; Melting point: 118-120˚C; IR (ATR): 3064, 3012, 2924, 1478, 1061.9, 756, 716, 691, 505 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (1H, dd, *J* = 6.4 and 3.2 Hz, H-5 or H-8), 8.14 (1H, dd, *J* = 6.4 and 3.2 Hz, H-5 or H-8), 7.82-7.79 (2H, m, H-6 and H-7), 7.73-7.71 (2H, m, H-2' and H-6'), 7.54-7.48 (3H, m, H-3', H-4' and H-5'), 2.38 (3H, s, H-7'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 154.7, 153.8, 141.3, 140.6, 136.1, 130.0 (2C), 129.79, 129.75, 129.3, 128.7 (2C), 128.2, 119.0, 8.6; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 551.4, 128.9; HRESIMS: *m/z* 404.9413 $[M+H]^+$ (calcd. for $C_{17}H_{13}N_2Se_2$, 404.9409).

3-(Butylselanyl)-2-phenylselenopheno[2,3-*b*]quinoxaline (7h)



Yield: 80%; Sticky; IR (ATR): 3058, 3021, 2954, 2924, 1478, 1440, 1263, 1063, 755, 708, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (1H, dd, *J* = 7.3 and 2.7 Hz, H-5 or H-8), 8.15 (1H, dd, *J* = 7.3 and 2.7 Hz, H-5 or H-8), 7.82-7.79 (2H, m, H-6 and H-7), 7.73-7.70 (2H, m, H-2' and H-6'), 7.51-7.47 (3H, m, H-3', H-4' and H-5'), 3.05 (2H, t, *J* = 7.6 Hz, H-1"), 1.55-1.48 (2H, m, H-2"), 1.30-1.21 (2H, m, H-3"), 0.77 (3H, t, *J* = 7.3 Hz, H-4"); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 154.8, 154.4, 141.2, 140.5, 136.1, 129.91 (2C), 129.85, 129.6, 129.5, 129.1, 128.5 (2C), 128.1, 118.3, 32.2, 27.7, 22.6, 13.5; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 551.1, 204.3; HRESIMS: *m/z* 446.9882 $[M+H]^+$ (calcd. for $C_{20}H_{19}N_2Se_2$, 446.9879).

2-Phenyl-3-(methylthio)selenopheno[2,3-*b*]quinoxaline (7i)



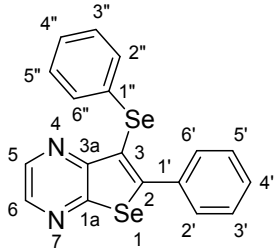
7i

Yield: 57%; Melting point: 115-117˚C; IR (ATR): 2918, 2849, 1124, 1066, 756, 733, 726, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (1H, dd, *J* = 6.6 and 3.4 Hz, H-5 or H-8), 8.15 (1H, dd, *J* = 6.6 and 3.4 Hz, H-5 or H-8), 7.83-7.77 (4H, m, H-6, H-7, H-2' and H-6'), 7.55-7.48 (3H, m, H-3', H-4' and H-5'), 2.55 (3H, s, H-7'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 154.9, 153.5, 141.1, 140.8, 135.3, 130.02 (2C), 129.96, 129.8, 129.4, 128.8 (2C), 128.3, 124.8, 18.1; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 529.3; HRESIMS: *m/z* 356.9951 $[M+H]^+$ (calcd. for $C_{17}H_{13}N_2SSe$, 356.9965).

General procedure and spectral data for compounds 8a-8e.

To a stirred mixture of diorganyl diselenides (1.0 equiv.) and $FeCl_3 \cdot 6H_2O$ (2.0 equiv.) in dichloromethane solvent was added the 2-(methylselanyl)-3-(arylethynyl)quinoxaline **6** (1.0 equiv.) at 45˚C, successfully affording the corresponding 6-phenyl-7-(arylselanyl)selenopheno[2,3-*b*]pyrazine derivatives **8a-8e** in 47-70% yields.

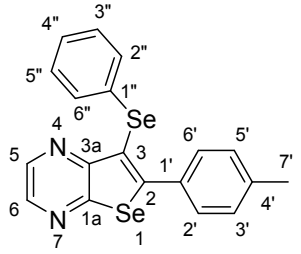
Phenyl-7-(phenylselanyl)selenopheno[2,3-*b*]pyrazine (8a)



8a

Yield: 62%; Melting point: 57-58˚C; IR (ATR): 3052, 3023, 1575, 1475, 1437, 1345, 1180, 732, 706, 687, 667, 629 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (1H, d, *J* = 2.3 Hz, H-5 or H-6), 8.45 (1H, d, *J* = 2.3 Hz, H-5 or H-6), 7.60 (2H, dd, *J* = 6.3 and 3.4 Hz, H-2'' and H-6''), 7.43-7.41 (3H, m, H-3'', H-4'' and H-5''), 7.21-7.20 (2H, m, H-2' and H-6'), 7.11-7.10 (3H, m, H-3', H-4' and H-5'); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 157.8, 153.9, 142.6, 140.8, 135.6, 132.1, 130.3 (2C), 130.0 (2C), 129.6, 129.2 (2C), 128.6 (2C), 126.5, 118.5; ^{77}Se NMR (95 MHz, $CDCl_3$): δ 575.4, 293.2; HRESIMS: *m/z* 416.9402 $[M+H]^+$ (calcd. for $C_{18}H_{13}N_2Se_2$, 416.9409).

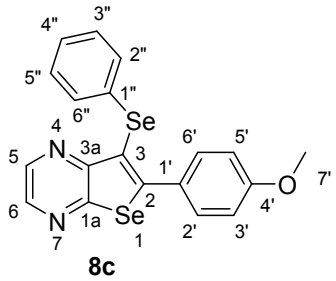
6-(*p*-Tolyl)-7-(phenylselanyl)selenopheno[2,3-*b*]pyrazine (8b)



8b

Yield: 69%; Melting point: 67-68˚C; IR (ATR): 3054, 2916, 1475, 1346, 1185, 1098, 811, 732 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.68 (1H, d, *J* = 2.7 Hz, H-5 or H-6), 8.43 (1H, d, *J* = 2.7 Hz, H-5 or H-6), 7.51 (2H, d, *J* = 7.6 Hz, H-2' and H-6'), 7.26-7.20 (4H, m, H-3', H-5', H-2" and H-6"), 7.11-7.10 (3H, m, H-3", H-4" and H-5"), 2.40 (3H, s, H-7'); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.7, 158.4, 154.1, 142.5, 140.6, 140.0, 132.7, 132.3, 130.1 (2C), 129.9 (2C), 129.3 (2C), 129.2 (2C), 126.4, 117.9, 21.5; ^{77}Se NMR (115 MHz, $CDCl_3$): δ 572.8, 291.6; HRESIMS: *m/z* 430.9554 $[M+H]^+$ (calcd. for $C_{19}H_{15}N_2Se_2$, 430.9566).

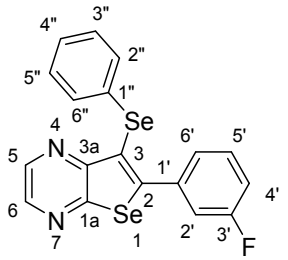
6-(4-Methoxyphenyl)-7-(phenylselanyl)selenopheno[2,3-*b*]pyrazine (8c)



8c

Yield: 70%; Melting point: 118-119˚C; IR (ATR): 2924, 2850, 1601, 1474, 1347, 1291, 1250, 1171, 1020, 831, 741, 690 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.66 (1H, d, *J* = 2.7 Hz, H-5 or H-6), 8.41 (1H, d, *J* = 2.1 Hz, H-5 or H-6), 7.58 (2H, d, *J* = 8.9 Hz, H-3' and H-5'), 7.21-7.20 (2H, m, H-2" and H-6"), 7.11-7.10 (3H, m, H-3", H-4" and H-5"), 6.94 (2H, d, *J* = 8.9 Hz, H-2' and H-6'), 3.84 (3H, s, H-7'); ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.8, 159.6, 158.1, 154.2, 142.5, 140.6, 132.3, 131.5 (2C), 130.0 (2C), 129.2 (2C), 128.0, 126.4, 117.3, 114.1 (2C), 55.5; ^{77}Se NMR (114MHz, $CDCl_3$): δ 570.0, 290.8; HRESIMS: *m/z* 446.9516 $[M+H]^+$ (calcd. for $C_{19}H_{15}N_2OSe_2$, 446.9515).

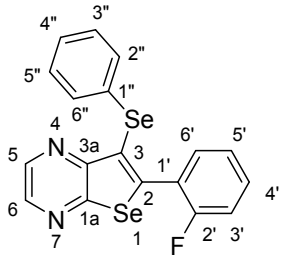
6-(3-Fluorophenyl)-7-(phenylselanyl)selenopheno[2,3-*b*]pyrazine (8d)



8d

Yield: 60%; Sticky; IR (ATR): 3056, 2924, 1578, 1474, 1344, 1146, 1096, 785, 732, 713, 682 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.72 (1H, d, *J* = 2.7 Hz, H-5 or H-6), 8.48 (1H, d, *J* = 2.3 Hz, H-5 or H-6), 7.39-7.30 (3H, m, H-3", H-4" and H-5"), 7.23-7.21 (2H, m, H-2" and H-6"), 7.12-7.11 (4H, m, H-2', H-4', H-5' and H-6'); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.4, 161.5, 159.7, 155.3, 153.7, 142.7, 141.0, 137.6, 137.5, 131.6, 130.7 (2C), 130.2, 130.1, 129.2 (2C), 126.8, 125.8, 119.7, 117.1, 116.9, 116.5, 116.3; ^{77}Se NMR (95 MHz, $CDCl_3$): δ 579.1, 297.8; ^{19}F-NMR (400 MHz, $CDCl_3$) δ -112.10; HRESIMS: *m/z* 434.9307 $[M+H]^+$ (calcd. for $C_{18}H_{12}N_2FSe_2$, 434.9315).

6-(2-Fluorophenyl)-7-(phenylselanyl)selenopheno[2,3-*b*]pyrazine (8e)

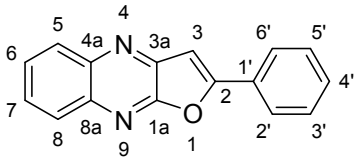


8e

Yield: 47%; Melting point: 73-75˚C; IR (ATR): 3071, 2921, 1468, 1354, 1097, 851, 747, 688, 472 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.71 (1H, d, *J* = 2.3 Hz, H-5 or H-6), 8.48 (1H, d, *J* = 2.3 Hz, H-5 or H-6), 7.41 (2H, t, *J* = 7.2 Hz, H-2" and H-6"), 7.22-7.08 (7H, m, H-3', H-4', H-5', H-6', H-3", H-4" and H-5"); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.4, 160.1, 158.1, 153.0, 149.4, 142.5, 140.9, 131.9, 131.52, 131.45, 131.2 (2C), 129.0 (2C), 126.8, 124.12, 124.09, 123.5, 122.2, 116.2, 116.0; ^{77}Se NMR (75 MHz, $CDCl_3$): δ 587.8, 307.6; ^{19}F-NMR (400 MHz, $CDCl_3$) δ -110.95; HRESIMS: *m/z* 434.9309 $[M+H]^+$ (calcd. for $C_{18}H_{12}N_2FSe_2$, 434.9315).

General procedure and spectral data for 2-phenylfuro[2,3-*b*]quinoxaline 9a

To the solution of 2-chloro-3-(phenylethynyl) quinoxaline **3a** (1.0 equiv.) in dimethyl sulfoxide (0.6 mL) and water (2.4 mL) was added NaOH (5.0 equiv.) are refluxed for 2 hours. After completion of the reaction, monitored by TLC (Hexane:EtOAc = 20:1), the reaction mixture was cooled to room temperature, and the obtained solution was extracted with ethyl acetate and water. Thereafter, the organic layer was washed with a saturated saline solution and dried over anhydrous sodium sulfate. The residue was isolated and purified by silica gel column chromatography (Hexane:EtOAc = 20:1), successfully affording the yellow-white solid 2-phenylfuro [2,3-*b*] quinoxaline **9a** in 34% yield.

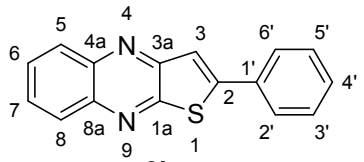


9a

Yield: 34%; Melting point: 188-190˚C; IR (ATR): 3102, 1563, 1386, 1310, 1214, 1013, 891, 767.1, 755, 741, 687, 659 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.18-8.17 (1H, m, H-5 or H-8), 8.12-8.11 (1H, m, H-5 or H-8), 8.03-8.02 (2H, m, H-6 and H-7), 7.74 (2H, dd, *J* = 5.4 and 2.6 Hz, H-2' and H-6'), 7.55-7.51 (3H, m, H-3', H-4' and H-5'), 7.28 (1H, s, H-3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.1, 154.5, 144.7, 142.4, 138.9, 131.4, 129.3 (2C), 128.9, 128.8, 128.6, 128.4, 126.3 (2C), 100.9; HRESIMS: *m/z* 247.0847 $[M+H]^+$ (calcd. for $C_{16}H_{11}N_2O$, 247.0871).

General procedure and spectral data for 2-phenylthieno[2,3-*b*]quinoxaline (9b)

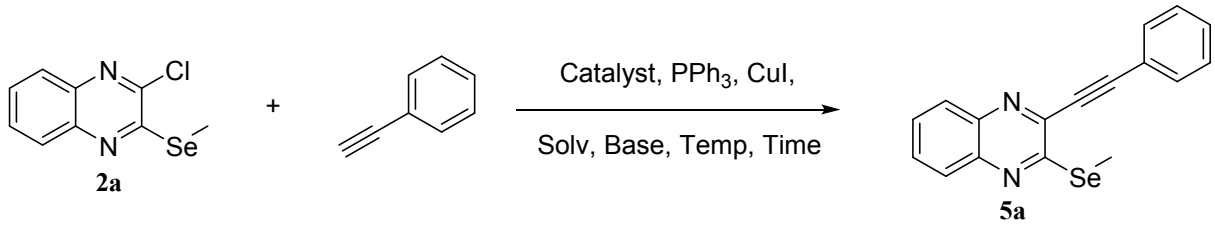
The mixture of 2-chloro-3-(phenylethynyl) quinoxaline **3a** (1.0 equiv.) and $NaSH \cdot xH_2O$ (5.0 equiv.) in dimethylformamide (2 mL) was refluxed for 2 hours. After completion of the reaction by TLC (Hexane:EtOAc = 20:1), the reaction mixture was cooled to room temperature, and the reaction mixture was extracted with ethyl acetate and water. Thereafter, the organic layer was washed with a saturated saline solution and dried over anhydrous sodium sulfate. After removing the solvent with an evaporator, the residue was isolated and purified by silica gel column chromatography (Hexane:EtOAc = 20:1) successfully afforded the resulting yellow-white solid 2-phenylthieno [2,3-*b*] quinoxaline **9b** in 87% yield.



9b

Yield: 87%; Melting point: 177-178˚C; IR (ATR): 1481, 1442, 1278, 1130, 1072, 758, 713, 683, 595 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.15-8.09 (2H, m, H-5 and H-8), 7.80-7.72 (4H, m, H-6, H-7, H-2' and H-6'), 7.71 (1H, s, H-3), 7.49-7.43 (3H, m, H-3', H-4' and H-5'); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 152.5, 152.0, 141.4, 140.3, 133.2, 130.5, 129.3 (2C), 129.2, 128.6, 126.9 (2C), 117.1; HRESIMS: *m/z* 263.0625 $[M+H]^+$ (calcd. for $C_{16}H_{11}N_2S$, 263.0643).

Table S1 Synthesis of 2-(methylselanyl)-3-(phenylethynyl)quinoxaline



Entry	Catalyst	PPh_3 (equiv.)	CuI (equiv.)	Solvent	Base	Temp. (°C)	Time (h)	Yield (%) **5a**
1	$Pd(PPh_3)_2Cl_2$	0.1	0.05	Acetone	Et_3N	70	23	—
2	$Pd(PPh_3)_2Cl_2$	—	0.05	EtOH	Et_3N	rt.	27	—
3	$Pd(PPh_3)_2Cl_2$	—	0.07	EtOH	Et_3N	rt.	14	—
4	$Pd(PPh_3)_2Cl_2$	—	0.5	DMF	K_2CO_3	rt.	14.5	—
5	$Pd(OAc)_2$	0.1	—	DMF	K_2CO_3	rt.	19	—
6	$Pd(PPh_3)_2Cl_2$	—	—	DME	Na_2CO_3	90	20	41