

## Supporting Information

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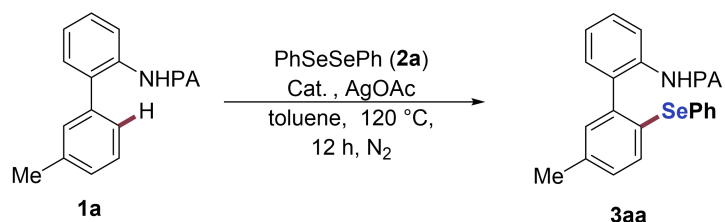
General Remarks	S2
Optimized reaction conditions	S3
Representative procedures for the palladium-catalyzed C-H chalcogenation	S4
Representative procedures for 8-membered N, Se(S)-heterocycles	S5
Preparation and characterization data of products <b>3</b> , <b>5</b> and <b>7</b>	S6
Scaled-up experiment	S38
Removal of the directing group	S39
H/D exchanged experiment	S39
Competition experiments	S40
Radical trap experiments	S41
X-Ray crystallographic data of <b>3ea</b> , <b>3ka'</b> and <b>7e</b>	S41
References	S46
<sup>1</sup> H, <sup>13</sup> C and <sup>19</sup> F NMR	S47

## General Remarks

Catalytic reactions were carried out under an ambient atmosphere of nitrogen. The starting materials were prepared according to previously described methods [1-3]. The reagents and solvents were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be >95 % pure as determined by <sup>1</sup>H-NMR. TLC: Macherey-Nagel, TLC plates Alugram R Sil G/UV254. Detection under UV light at 254 nm. Chromatography: Separations were carried out on Merck Silica 60(0.040–0.063 mm, 70–230 mesh ASTM). EI-MS: Finnigan MAT 95, 70eV; ESI-MS: Finnigan LCQ. High resolution mass spectrometry (HRMS): APEX IV 7T FTICR, Bruker Daltonic. M. p. Stuart R Melting Point Apparatus SMP3 melting point apparatus, values are uncorrected. <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F-spectra were recorded at 600 (<sup>1</sup>H), 150 (<sup>13</sup>C) and 565 (<sup>19</sup>F) respectively, on BRUKER instruments in CDCl<sub>3</sub> solutions. If not otherwise specified, chemical shifts ( $\delta$ ) are given in ppm.

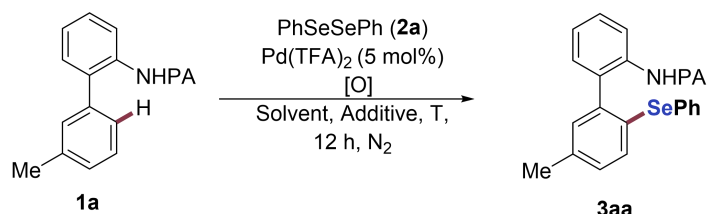
## Optimized reaction conditions

**Table S1.** Palladium-catalyzed C–H selenylations



Entry	Catalyst	Solvent	Oxidant	3aa
1	Co(OAc) <sub>2</sub> (20 mol%)	toluene	AgOAc	--
2	Co(acac) <sub>2</sub> (20 mol%)	toluene	AgOAc	--
3	NiCl <sub>2</sub> (20 mol%)	toluene	AgOAc	--
4	Cu(OAc) <sub>2</sub> (20 mol%)	toluene	AgOAc	--
5	Pd(TFA) <sub>2</sub> (5 mol%)	toluene	AgOAc	71
6	Pd(OAc) <sub>2</sub> (5 mol%)	toluene	AgOAc	60
7	PdCl <sub>2</sub> (5 mol%)	toluene	AgOAc	46
8	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (5 mol%)	toluene	AgOAc	42

**Table S2.** Palladium-catalyzed C–H selenylations

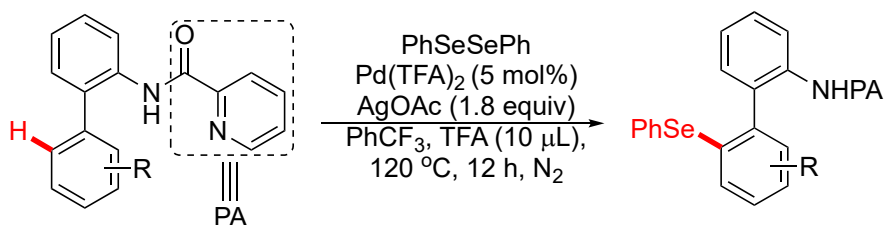


Entry	Solvent	Oxidant	Additive	3aa
1	DMSO	AgOAc	-	23
2	DMF	AgOAc	-	88
3	1,4-dioxane	AgOAc	-	40
4	CH <sub>3</sub> CN	AgOAc	-	80
5	DCE	AgOAc	-	85
6	TFE	AgOAc	-	20
7	HFIP	AgOAc	-	trace
8	Toluene	AgOAc	--	71
9	PhCF <sub>3</sub>	AgOAc	-	89

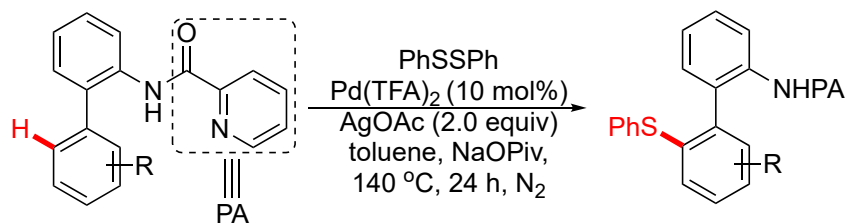
10	PhCF <sub>3</sub>	Ag <sub>2</sub> O	-	72
11	PhCF <sub>3</sub>	AgNO <sub>3</sub>	-	87
12	PhCF <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	-	75
13	PhCF <sub>3</sub>	AgOPiv	-	88
14	PhCF <sub>3</sub>	Cu(OAc) <sub>2</sub>	-	<10
15	PhCF <sub>3</sub>	PhI(OAc) <sub>2</sub>	-	75
16	PhCF <sub>3</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	-	33
17	PhCF <sub>3</sub>	-	-	25
18	PhCF <sub>3</sub>	AgOAc	PivOH	80
19	PhCF <sub>3</sub>	AgOAc	TfOH	87
20	PhCF <sub>3</sub>	AgOAc	1-AdmCO <sub>2</sub> H	81
21	PhCF <sub>3</sub>	AgOAc	TFA	93
22	PhCF <sub>3</sub>	AgOAc	TFA	83 <sup>b</sup>
23	PhCF <sub>3</sub>	AgOAc	TFA	74 <sup>c</sup>
24	PhCF <sub>3</sub>	AgOAc	TFA	-- <sup>d</sup>

<sup>a</sup>Reaction conditions: **1a** (0.20 mmol), **2a** (1.0 equiv, 0.20 mmol), Pd(TFA)<sub>2</sub> (5.0 mol %), oxidant (1.8 equiv), solvent (2.0 mL), 120 °C, 12 h, under N<sub>2</sub>. <sup>b</sup>1.5 equiv AgOAc. <sup>c</sup>100 °C. <sup>d</sup>without catalyst

### Representative procedures for the palladium-catalyzed C-H chalcogenation

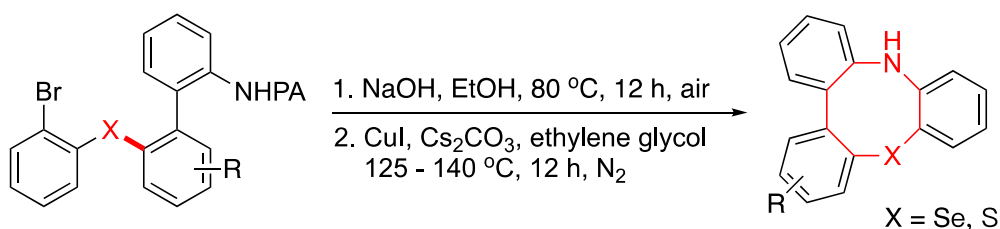


**Representative Procedure A:** A suspension of *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.4 mg, 0.20 mmol), Pd(TFA)<sub>2</sub> (3.3 mg, 5.0 mol%), AgOAc (60.1 mg, 0.36 mmol), TFA (10 μL) in anhydrous PhCF<sub>3</sub> (2.0 mL) was stirred in seal tube under nitrogen at 120 °C for 12 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents in *vacuo*, the crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 30/1→15/1) to yield **3aa** (82.8 mg, 93 %) as a white solid.



**Representative Procedure B:** A suspension of *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-diphenyldisulfane (**5a**) (43.7 mg, 0.20 mmol), Pd(TFA)<sub>2</sub> (6.6 mg, 10.0 mol%), AgOAc (66.8 mg, 0.40 mmol), NaOPiv (12.4 mg, 0.10 mmol) in anhydrous toluene (2.0 mL) was stirred in seal tube under nitrogen at 140 °C for 24 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents in *vacuo*, the crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 30/1→15/1) to yield **5aa** (56.3 mg, 71 %) as a white solid.

#### Representative procedures for the 8-membered N, Se(S)-heterocycles

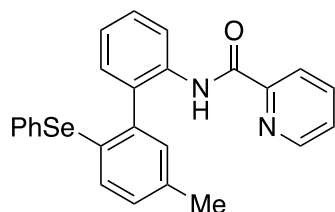


#### Representative Procedure C:

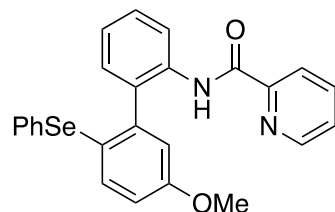
A suspension of *N*-(2'-((2-bromophenyl)selanyl)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**3ad**) (52.2 mg, 0.1 mmol), NaOH (60.0 mg, 1.5 mmol) in EtOH (1.5 mL) was stirred in Schlenk tube under air at 80 °C for 12 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with DCM (3 x 15 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated to give the crude product of amine. A suspension of the crude product, CuI (9.5 mg, 0.05 mmol), Cs<sub>2</sub>CO<sub>3</sub> (65.2 mg, 0.20 mmol) in ethylene glycol (2.0 mL) was stirred in Schlenk tube under nitrogen at 125 °C for 12 h. At ambient temperature, the reaction mixture was quenched with the saturated aqueous NH<sub>4</sub>Cl (10 mL) and

extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents in *vacuo*, the crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 40/1) to yield **6a** (16.2 mg, 48 %) as a colorless oil.

### Preparation and Characterization Data of Products 3, 5 and 7

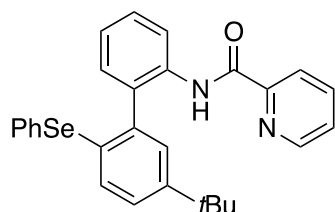


***N*-(5'-methyl-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3aa)**. The general procedure **A** was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.4 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3aa** (82.8 mg, 93 %) as a white solid. M.p = 96 – 97 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.02 (s, 1H), 8.58 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.35 – 8.34 (m, 1H), 8.24 – 8.22 (m, 1H), 7.85 – 7.82 (m, 1H), 7.46 – 7.43 (m, 1H), 7.39 – 7.36 (m, 1H), 7.36 – 7.35 (m, 1H), 7.35 – 7.34 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.17 (m, 2H), 7.17 – 7.15 (m, 1H), 7.14 – 7.12 (m, 2H), 7.11 – 7.10 (m, 2H), 2.34 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 162.0, 150.2, 148.0, 139.3, 137.5, 135.2, 134.5, 134.5, 132.7, 132.1, 131.8, 130.5, 130.3, 130.3, 130.0, 129.2, 129.0, 127.7, 126.2, 123.9, 122.4, 120.5, 21.1. HR-MS(ESI) *m/z* calcd for: C<sub>25</sub>H<sub>21</sub>N<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 445.0814, found 445.0818.

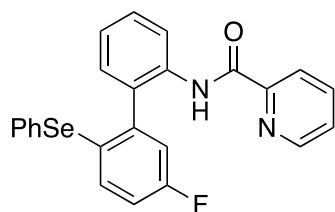


***N*-(5'-methoxy-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3ba)**. The general procedure **A** was followed by using *N*-(3'-methoxy-[1,1'-biphenyl]-2-yl)picolinamide (**1b**) (60.5 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.5 mg, 0.20

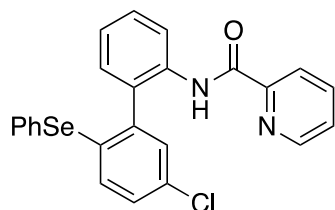
mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→7/1) yielded **3ba** (84.4 mg, 92 %) as a pink solid. M.p = 123 – 124 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.99 (s, 1H), 8.58 – 8.56 (m, 1H), 8.35 – 8.34 (m, 1H), 8.22 – 8.20 (m, 1H), 7.84 – 7.81 (m, 1H), 7.47 – 7.46 (m, 1H), 7.45 – 7.41 (m, 1H), 7.37 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.26 – 7.25 (m, 1H), 7.16 – 7.14 (m, 1H), 7.13 (dd, *J* = 7.0, 1.1 Hz, 1H), 7.12 – 7.09 (m, 1H), 7.06 – 7.02 (m, 2H), 6.92 – 6.88 (m, 2H), 3.78 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.9, 159.7, 150.1, 148.0, 141.8, 137.6, 135.8, 135.2, 133.3, 132.2, 131.5, 130.1, 129.0, 129.0, 127.2, 126.2, 123.8, 123.4, 122.3, 120.4, 116.1, 115.8, 55.6. HR-MS(ESI) *m/z* calcd for: C<sub>25</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub><sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 461.0763, found 461.0769.



***N*-(5'-(*tert*-butyl)-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3ca).** The general procedure **A** was followed by using *N*-(3'-(*tert*-butyl)-[1,1'-biphenyl]-2-yl)picolinamide (**1c**) (66.0 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.4 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→7/1) yielded **3ca** (56.3 mg, 58 %) as a white solid. M.p = 144 – 145 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.99 (s, 1H), 8.63 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.29 – 8.28 (m, 1H), 8.23 – 8.21 (m, 1H), 7.84 – 7.81 (m, 1H), 7.47 – 7.44 (m, 1H), 7.37 – 7.34 (m, 3H), 7.34 – 7.32 (m, 3H), 7.30 – 7.28 (m, 1H), 7.20 – 7.16 (m, 2H), 7.12 – 7.08 (m, 2H), 1.29 (s, 9H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.9, 150.8, 150.2, 147.8, 138.7, 137.5, 135.4, 134.6, 132.6, 132.2, 130.6, 130.5, 130.4, 129.2, 129.0, 128.0, 127.7, 126.3, 126.2, 123.8, 122.3, 120.4, 34.7, 31.4. HR-MS(ESI) *m/z* calcd for: C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 487.1283, found 487.1288.



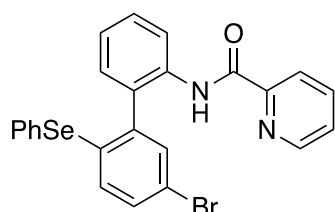
***N*-(5'-fluoro-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3da).** The general procedure A was followed by using *N*-(3'-fluoro-[1,1'-biphenyl]-2-yl)picolinamide (**1d**) (58.4 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.4 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3da** (63.4 mg, 71 %) as a white solid. M.p = 100 – 101 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.95 (s, 1H), 8.57 (d, *J* = 8.2 Hz, 1H), 8.35 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.23 (d, *J* = 7.7 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.49 – 7.45 (m, 1H), 7.41 – 7.38 (m, 1H), 7.37 – 7.33 (m, 3H), 7.22 – 7.18 (m, 1H), 7.18 – 7.16 (m, 2H), 7.14 – 7.11 (m, 2H), 7.05 (dd, *J* = 9.0, 2.8 Hz, 1H), 7.03 – 7.00 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 162.3 (d, *J* = 249.2 Hz), 161.9, 150.0, 148.0, 141.3 (d, *J* = 7.3 Hz), 137.7, 135.1, 134.6, 134.3 (d, *J* = 7.8 Hz), 131.0, 130.0, 129.5, 129.4, 129.0, 129.0, 128.0, 126.4, 124.1, 122.4, 120.8, 118.1 (d, *J* = 21.7 Hz), 116.3 (d, *J* = 21.2 Hz). <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ = -114.85 – -114.89 (m). HR-MS(ESI) *m/z* calcd for: C<sub>24</sub>H<sub>18</sub>FN<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 449.0563, found 449.0567.



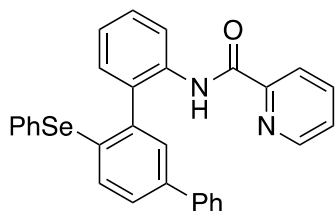
***N*-(5'-chloro-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3ea).** The general procedure A was followed by using *N*-(3'-chloro-[1,1'-biphenyl]-2-yl)picolinamide (**1e**) (62.1 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.4 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3ea** (79.9 mg, 86 %) as a white solid. M.p = 112 – 113 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.02 (s, 1H), 8.58 (d, *J* = 8.2 Hz, 1H), 8.39 – 8.37 (m, 1H), 8.26 – 8.24 (m, 1H), 7.88 – 7.85 (m, 1H), 7.50 – 7.47 (m, 1H), 7.42 – 7.40 (m, 3H), 7.29 (d,



$J = 2.3$  Hz, 1H), 7.28 – 7.26 (m, 1H), 7.23 (dd,  $J = 8.5, 2.3$  Hz, 1H), 7.20 – 7.19 (m, 2H), 7.19 – 7.17 (m, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 162.0, 150.0, 148.0, 140.2, 137.6, 135.4, 135.1, 133.4, 133.0, 132.7, 130.8, 130.6, 130.1, 129.6, 129.5, 129.2, 129.1, 128.4, 126.4, 124.2, 122.4, 120.9$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{24}\text{H}_{18}\text{ClN}_2\text{O}^{80}\text{Se}^+ [\text{M}+\text{H}]^+$  465.0267, found 465.0269.

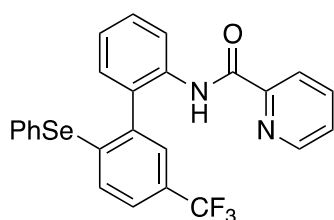


***N*-(5'-bromo-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3fa).** The general procedure A was followed by using *N*-(3'-bromo-[1,1'-biphenyl]-2-yl)picolinamide (**1f**) (70.9 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.7 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3fa** (80.3 mg, 79 %) as a white solid. M.p = 111 – 112 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 10.04$  (s, 1H), 8.59 (d,  $J = 8.2$  Hz, 1H), 8.39 – 8.38 (m, 1H), 8.25 (d,  $J = 7.8$  Hz, 1H), 7.87 – 7.84 (m, 1H), 7.51 – 7.47 (m, 1H), 7.45 – 7.43 (m, 1H), 7.43 – 7.38 (m, 3H), 7.38 – 7.35 (m, 1H), 7.28 – 7.27 (m, 1H), 7.20 – 7.18 (m, 4H), 7.10 (d,  $J = 8.7$  Hz, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 162.0, 150.0, 148.0, 140.3, 137.6, 135.5, 135.1, 134.2, 133.6, 132.7, 132.0, 130.4, 130.1, 129.6, 129.5, 128.9, 128.5, 126.3, 124.2, 122.3, 120.8, 120.8$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{24}\text{H}_{18}\text{BrN}_2\text{O}^{80}\text{Se}^+ [\text{M}+\text{H}]^+$  508.9762, found 508.9760.



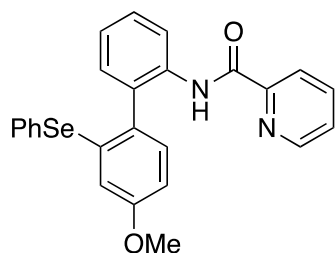
***N*-(6'-(phenylselanyl)-[1,1':3',1''-terphenyl]-2-yl)picolinamide (3ga).** The general procedure A was followed by using *N*-([1,1':3',1''-terphenyl]-2-yl)picolinamide (**1g**) (70.0 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.7 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3ga** (81.1 mg, 80 %) as a white solid. M.p = 137 – 138 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta =$

10.16 (s, 1H), 8.64 (d,  $J = 8.2$  Hz, 1H), 8.28 – 8.26 (m, 1H), 8.23 (d,  $J = 7.5$  Hz, 1H), 7.84 – 7.81 (m, 1H), 7.59 – 7.57 (m, 2H), 7.55 (d,  $J = 2.1$  Hz, 1H), 7.51 – 7.48 (m, 2H), 7.46 – (m, 2H), 7.40 – 7.39 (m, 1H), 7.37 (s, 1H), 7.37 – 7.35 (m, 1H), 7.34 – 7.32 (m, 1H), 7.32 – 7.29 (m, 2H), 7.27 – 7.24 (m, 1H), 7.22 – 7.20 (m, 1H), 7.20 – 7.17 (m, 2H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 162.0, 150.2, 148.0, 140.2, 139.0, 137.6, 135.3, 135.3, 133.8, 132.2, 131.6, 130.4, 129.6, 129.5, 129.4, 129.3, 129.0, 129.0, 128.2, 127.7, 127.6, 127.0, 126.2, 124.0, 122.3, 120.6$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{30}\text{H}_{23}\text{N}_2\text{O}^{80}\text{Se}^+ [\text{M}+\text{H}]^+$  507.0970, found 507.0977.

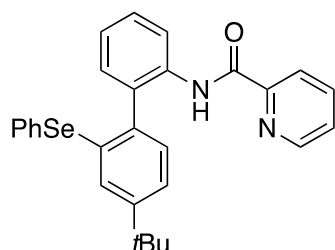


***N*-(2'-(phenylselanyl)-5'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)picolinamide (3ha).**

The general procedure **A** was followed by using *N*-(3'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)picolinamide (**1h**) (68.0 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.6 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3ha** (47.5 mg, 48 %) as a yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 10.06$  (s, 1H), 8.64 (d,  $J = 8.3$  Hz, 1H), 8.33 – 8.32 (m, 1H), 8.26 – 8.24 (m, 1H), 7.87 – 7.84 (m, 1H), 7.54 – 7.51 (m, 2H), 7.52 – 7.49 (m, 2H), 7.46 – 7.44 (m, 1H), 7.39 (ddd,  $J = 7.6, 4.7, 1.2$  Hz, 1H), 7.38 – 7.35 (m, 1H), 7.31 – 7.30 (m, 1H), 7.29 – 7.27 (m, 2H), 7.25 – 7.23 (m, 1H), 7.21 (d,  $J = 8.4$  Hz, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 162.1, 150.0, 148.0, 141.4, 138.0, 137.7, 136.5, 135.2, 130.2, 130.2, 130.1, 130.0, 129.9, 129.2, 128.8$  (q,  $J = 32.9$  Hz), 127.9, 127.5 (q,  $J = 3.9$  Hz), 126.4, 125.6 (q,  $J = 3.7$  Hz), 124.4, 124.2 (q,  $J = 271.7$  Hz), 122.4, 121.0.  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta = -62.34$ . (s) HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{25}\text{H}_{18}\text{F}_3\text{N}_2\text{O}^{80}\text{Se}^+ [\text{M}+\text{H}]^+$  499.0531, found 499.0533.

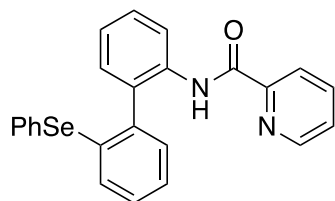


***N*-(4'-methoxy-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3ia).** The general procedure **A** was followed by using *N*-(4'-methoxy-[1,1'-biphenyl]-2-yl)picolinamide (**1i**) (60.6 mg, 0.20 mmol), 1,2-diphenyldiselane (**2a**) (62.8 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3ia** (85.3 mg, 93 %) as a pink solid. M.p = 126 – 127 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.98 (s, 1H), 8.57 (d, *J* = 8.2 Hz, 1H), 8.36 – 8.33 (m, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.38 – 7.36 (m, 1H), 7.27 – 7.25 (m, 2H), 7.17 – 7.12 (m, 2H), 7.12 – 7.09 (m, 1H), 7.06 – 7.03 (m, 2H), 6.92 – 6.88 (m, 2H), 3.78 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.9, 159.7, 150.1, 148.0, 141.8, 137.6, 135.8, 135.1, 133.3, 132.2, 131.5, 130.1, 129.0, 129.0, 127.2, 126.2, 123.8, 123.4, 122.3, 120.4, 116.1, 115.8, 55.6. HR-MS(ESI) *m/z* calcd for: C<sub>25</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub><sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 461.0763, found 461.0767.

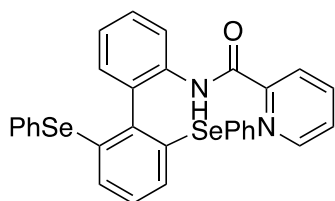


***N*-(4'-(*tert*-butyl)-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3ja).** The general procedure **A** was followed by using *N*-(4'-(*tert*-butyl)-[1,1'-biphenyl]-2-yl)picolinamide (**1j**) (65.9 mg, 0.20 mmol), 1,2-diphenyldiselane (**2a**) (62.6 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3ja** (78.9 mg, 81 %) as a yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.98 (s, 1H), 8.60 (d, *J* = 8.2 Hz, 1H), 8.25 – 8.20 (m, 2H), 7.84 – 7.81 (m, 1H), 7.46 – 7.43 (m, 1H), 7.40 (d, *J* = 2.2 Hz, 1H), 7.37 – 7.35 (m, 4H), 7.24 – 7.20 (m, 2H), 7.20 – 7.13 (m, 2H), 7.13 – 7.10 (m, 2H), 1.27 (s, 9H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ =

161.8, 152.1, 150.2, 147.7, 137.6, 136.2, 135.5, 134.7, 133.8, 131.8, 130.6, 130.3, 130.2, 129.6, 129.2, 129.0, 127.8, 126.2, 124.5, 123.8, 122.3, 120.1, 34.9, 31.3. HR-MS(ESI)  $m/z$  calcd for:  $C_{28}H_{27}N_2O^{80}Se^+$   $[M+H]^+$  487.1283, found 487.1288.

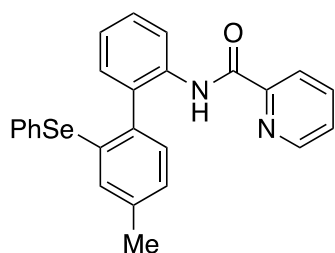


***N*-(2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3ka')**. The general procedure A was followed by using *N*-([1,1'-biphenyl]-2-yl)picolinamide (**1k**) (54.7 mg, 0.20 mmol), 1,2-diphenyldiselane (**2a**) (63.2 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3ka'** (66.4 mg, 77 %) as a white solid. M.p = 106 – 107 °C.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  = 10.00 (s, 1H), 8.60 (d,  $J$  = 8.3 Hz, 1H), 8.33 – 8.31 (m, 1H), 8.23 (d,  $J$  = 7.8 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.48 – 7.45 (m, 1H), 7.42 – 7.40 (m, 2H), 7.37 (ddd,  $J$  = 7.5, 4.8, 1.2 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.29 – 7.26 (m, 2H), 7.24 – 7.22 (m, 2H), 7.19 (dd,  $J$  = 7.4, 1.2 Hz, 1H), 7.17 – 7.14 (m, 2H).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  = 162.0, 150.2, 148.0, 138.8, 137.6, 135.3, 134.7, 131.9, 131.7, 131.0, 130.3, 129.7, 129.4, 129.4, 129.2, 129.1, 128.1, 127.2, 126.2, 124.1, 122.4, 120.6. HR-MS(ESI)  $m/z$  calcd for:  $C_{24}H_{19}N_2O^{80}Se^+$   $[M+H]^+$  431.0657, found 431.0556.

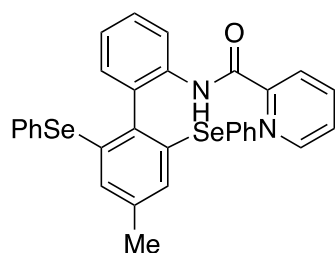


***N*-(2',6'-bis(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3ka'')**. The general procedure A was followed by using *N*-([1,1'-biphenyl]-2-yl)picolinamide (**1k**) (54.7 mg, 0.20 mmol), 1,2-diphenyldiselane (**2a**) (63.2 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3ka''** (22.3 mg, 19 %) as a white solid. M.p = 120 – 121 °C.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  = 10.04 (s, 1H), 8.69 (d,  $J$  = 8.2 Hz, 1H), 8.34 – 8.32 (m, 1H), 8.26 (d,  $J$  = 7.8 Hz, 1H), 7.87 – 7.85 (m, 1H), 7.55 – 7.52 (m, 1H), 7.43 (d,  $J$  = 7.5 Hz, 4H), 7.41 – 7.39 (m,

1H), 7.26 – 7.25 (m, 1H), 7.25 – 7.23 (m, 3H), 7.19 – 7.15 (m, 4H), 7.03 – 7.02 (m, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.9, 150.3, 147.9, 137.6, 137.3, 136.8, 135.7, 135.2, 130.6, 130.1, 130.0, 129.8, 129.6, 129.5, 128.8, 128.4, 126.2, 124.4, 122.4, 120.6. HR-MS(ESI) m/z calcd for: C<sub>30</sub>H<sub>23</sub>N<sub>2</sub>O<sup>80</sup>Se<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> 587.0135, found 587.0143.

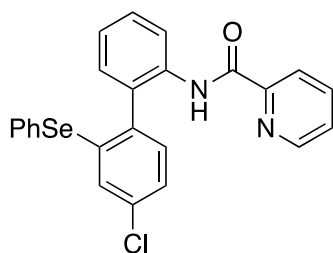


***N*-(4'-methyl-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3la')**. The general procedure **A** was followed by using *N*-(4'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**II**) (57.5 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.6 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3la'** (66.8 mg, 75 %) as a colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.99 (s, 1H), 8.57 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.35 – 8.34 (m, 1H), 8.23 – 8.22 (m, 1H), 7.84 – 7.81 (m, 1H), 7.45 – 7.43 (m, 1H), 7.39 – 7.36 (m, 3H), 7.22 – 7.20 (m, 1H), 7.19 – 7.18 (m, 2H), 7.17 (s, 1H), 7.16 – 7.11 (m, 4H), 2.32 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 162.0, 150.2, 148.0, 139.0, 137.5, 136.2, 135.4, 134.8, 133.9, 132.8, 132.0, 130.8, 130.5, 130.1, 129.3, 128.9, 128.3, 127.8, 126.2, 124.0, 122.4, 120.5, 21.3. HR-MS(ESI) m/z calcd for: C<sub>25</sub>H<sub>21</sub>N<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 445.0814, found 445.0818.

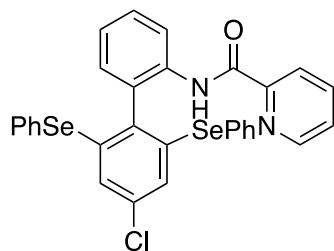


***N*-(4'-methyl-2',6'-bis(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3la'')**. The general procedure **A** was followed by using *N*-(4'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**II**) (57.5 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.6 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1)

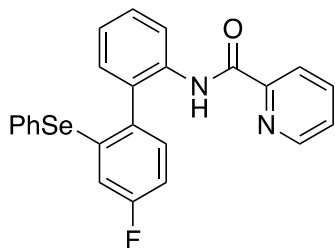
yielded **3la''** (19.1 mg, 16 %) as a yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.01 (s, 1H), 8.66 (d,  $J$  = 8.3 Hz, 1H), 8.35 (s, 1H), 8.25 (d,  $J$  = 7.9 Hz, 1H), 7.87 – 7.85 (m, 1H), 7.52 – 7.49 (m, 1H), 7.43 – 7.39 (m, 5H), 7.24 – 7.17 (m, 3H), 7.17 – 7.14 (m, 5H), 6.91 (s, 2H), 2.15 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 161.9, 150.3, 147.9, 139.8, 137.6, 136.0, 135.4, 135.3, 135.2, 130.9, 130.3, 130.2, 129.9, 129.7, 129.4, 128.2, 126.2, 124.2, 122.4, 120.4, 21.3. HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{31}\text{H}_{25}\text{N}_2\text{O}^{80}\text{Se}_2^+$   $[\text{M}+\text{H}]^+$  601.0292, found 601.0295.



***N*-(4'-chloro-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3ma')**. The general procedure **A** was followed by using *N*-(4'-chloro-[1,1'-biphenyl]-2-yl)picolinamide (**1m**) (61.4 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.4 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3ma'** (72.1 mg, 78 %) as a white solid. M.p = 100 – 101 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.98 (s, 1H), 8.57 (d,  $J$  = 8.3 Hz, 1H), 8.39 (d,  $J$  = 4.7 Hz, 1H), 8.24 (d,  $J$  = 7.8 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.51 – 7.47 (m, 1H), 7.45 – 7.43 (m, 2H), 7.42 – 7.39 (m, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.22 (m, 2H), 7.21 – 7.19 (m, 3H), 7.17 (s, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 162.0, 150.0, 148.1, 137.6, 137.1, 136.7, 135.8, 135.2, 135.0, 131.9, 130.7, 130.3, 129.7, 129.7, 129.5, 128.8, 128.5, 127.1, 126.4, 124.3, 122.4, 121.0. HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{24}\text{H}_{18}\text{ClN}_2\text{O}^{80}\text{Se}^+$   $[\text{M}+\text{H}]^+$  465.0267, found 465.0266.

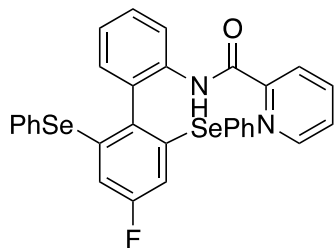


*N*-(4'-chloro-2',6'-bis(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (**3ma''**). The general procedure A was followed by using *N*-(4'-chloro-[1,1'-biphenyl]-2-yl)picolinamide (**1m**) (61.4 mg, 0.20 mmol), 1,2-diphenyldiselane (**2a**) (62.4 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3ma''** (19.5 mg, 16 %) as a white solid. M.p = 151 – 152 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.04 (s, 1H), 8.69 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.41 – 8.39 (m, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.90 – 7.87 (m, 1H), 7.57 – 7.54 (m, 1H), 7.46 – 7.44 (m, 4H), 7.44 – 7.42 (m, 1H), 7.33 – 7.30 (m, 2H), 7.25 – 7.22 (m, 4H), 7.22 – 7.20 (m, 2H), 6.88 (s, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 162.0, 150.2, 148.1, 138.7, 137.7, 136.1, 135.7, 135.3, 134.8, 130.7, 130.4, 129.8, 129.0, 128.9, 128.5, 127.4, 126.4, 124.6, 122.5, 120.8. HR-MS(ESI) *m/z* calcd for: C<sub>30</sub>H<sub>22</sub>ClN<sub>2</sub>O<sup>80</sup>Se<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> 620.9746, found 620.9748.



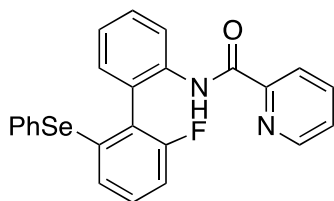
*N*-(4'-fluoro-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (**3na'**). The general procedure A was followed by using *N*-(4'-fluoro-[1,1'-biphenyl]-2-yl)picolinamide (**1n**) (58.0 mg, 0.20 mmol), 1,2-diphenyldiselane (**2a**) (62.9 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3na'** (67.0 mg, 75 %) as a white solid. M.p = 91 – 92 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.02 (s, 1H), 8.59 (d, *J* = 8.2 Hz, 1H), 8.39 – 8.37 (m, 1H), 8.25 (dd, *J* = 7.9, 2.5 Hz, 1H), 7.88 – 7.85 (m, 1H), 7.51 – 7.49 (m, 1H), 7.47 – 7.46 (m, 2H), 7.42 – 7.40 (m, 1H), 7.34 – 7.31 (m, 1H), 7.25 – 7.17 (m, 5H), 7.00 – 6.97 (m, 1H), 6.86 (d, *J* = 9.4 Hz, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 163.0 (d, *J* = 249.9 Hz), 162.0, 150.1, 148.0, 137.7, 137.7, 136.1, 135.5, 133.8 (d, *J* = 3.2 Hz), 132.2 (d, *J* = 8.1 Hz), 130.7, 130.5, 129.8, 129.5, 128.9, 128.4, 126.4, 124.3, 122.4, 120.9, 117.2 (d, *J* = 23.9

Hz), 113.8 (d,  $J = 21.7$  Hz).  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta = -112.78 - -112.82$  (m). HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{24}\text{H}_{18}\text{FN}_2\text{O}^{80}\text{Se}^+ [\text{M}+\text{H}]^+$  449.0563, found 449.0568.



***N*-(4'-fluoro-2',6'-bis(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3na'')**

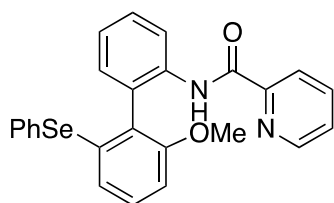
The general procedure **A** was followed by using *N*-(4'-fluoro-[1,1'-biphenyl]-2-yl)picolinamide (**1n**) (58.0 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.9 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3na''** (23.0 mg, 19 %) as a white solid. M.p = 154 – 155 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 10.07$  (s, 1H), 8.72 (d,  $J = 7.9$  Hz, 1H), 8.41 – 8.38 (m, 1H), 8.29 (d,  $J = 7.8$  Hz, 1H), 7.90 – 7.87 (m, 1H), 7.58 – 7.56 (m, 1H), 7.48 – 7.46 (m, 4H), 7.43 (ddd,  $J = 7.6, 4.7, 1.2$  Hz, 1H), 7.34 – 7.31 (m, 2H), 7.26 – 7.24 (m, 3H), 7.24 (s, 2H), 7.23 (d,  $J = 0.8$  Hz, 1H), 6.59 – 6.58 (m, 2H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 163.2$  (d,  $J = 252.2$  Hz), 162.0, 150.2, 148.0, 139.2 (d,  $J = 7.2$  Hz), 137.7, 136.4, 135.6, 131.8, 131.0, 130.4, 129.8, 129.1, 128.8, 128.4, 126.4, 124.5, 122.5, 120.8, 114.4 (d,  $J = 24.2$  Hz).  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta = -111.68 - -111.71$  (m). HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{30}\text{H}_{22}\text{FN}_2\text{O}^{80}\text{Se}_2^+ [\text{M}+\text{H}]^+$  605.0041, found 605.0049.



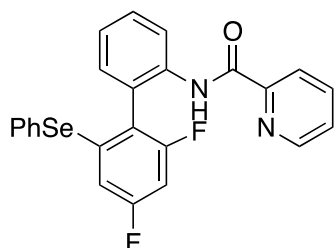
***N*-(2'-fluoro-6'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3oa)**. The general procedure **A** was followed by using *N*-(2'-fluoro-[1,1'-biphenyl]-2-yl)picolinamide (**1o**) (57.6 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.4 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3oa** (64.4 mg, 72 %) as a white solid. M.p = 123 – 124 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 10.00$  (s, 1H), 8.64 (dd,  $J = 8.3, 1.2$  Hz, 1H), 8.33 – 8.32 (m, 1H),



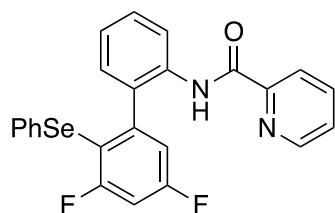
8.25 – 8.23 (m, 1H), 7.86 – 7.83 (m, 1H), 7.53 – 7.50 (m, 1H), 7.45 – 7.43 (m, 2H), 7.38 (ddd,  $J = 7.6, 4.7, 1.2$  Hz, 1H), 7.30 – 7.28 (m, 1H), 7.27 (d,  $J = 1.5$  Hz, 1H), 7.25 – 7.23 (m, 1H), 7.23 – 7.21 (m, 1H), 7.21 – 7.18 (m, 2H), 7.06 – 7.03 (m, 1H), 7.00 (dd,  $J = 8.0, 1.1$  Hz, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 161.9, 160.3$  (d,  $J = 249.2$  Hz), 150.1, 147.9, 138.0, 137.6, 135.8, 135.8, 130.8, 130.4 (d,  $J = 8.5$  Hz), 129.9, 129.6, 128.9, 128.6, 126.5, 126.3, 125.5 (d,  $J = 18.3$  Hz), 124.9, 124.2, 122.4, 120.8, 113.8 (d,  $J = 22.5$  Hz).  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta = -111.29 - -111.32$  (m). HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{24}\text{H}_{18}\text{FN}_2\text{O}^{80}\text{Se}^+$   $[\text{M}+\text{H}]^+$  449.0563, found 449.0568.



***N*-(2'-methoxy-6'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3pa).** The general procedure **A** was followed by using *N*-(2'-methoxy-[1,1'-biphenyl]-2-yl)picolinamide (**1p**) (60.7 mg, 0.20 mmol), 1,2-diphenyldiselenane (**2a**) (62.7 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3pa** (38.4 mg, 47 %) as a brown oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 10.03$  (s, 1H), 8.64 – 8.61 (m, 1H), 8.35 – 8.33 (m, 1H), 8.25 – 8.23 (m, 1H), 7.85 – 7.82 (m, 1H), 7.50 – 7.47 (m, 1H), 7.46 – 7.43 (m, 2H), 7.37 (ddd,  $J = 7.6, 4.7, 1.2$  Hz, 1H), 7.29 (dd,  $J = 7.6, 1.7$  Hz, 1H), 7.26 – 7.25 (m, 1H), 7.24 – 7.21 (m, 2H), 7.20 – 7.17 (m, 2H), 6.88 (d,  $J = 8.3$  Hz, 1H), 6.80 (d,  $J = 8.0$  Hz, 1H), 3.70 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 161.9, 157.6, 150.4, 147.9, 137.5, 137.2, 135.8, 135.7, 131.0, 130.0, 129.6, 129.4, 129.2, 128.3, 127.9, 126.4, 126.1, 124.1, 123.2, 122.3, 120.5, 109.0, 56.0$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{25}\text{H}_{21}\text{N}_2\text{O}_2^{80}\text{Se}^+$   $[\text{M}+\text{H}]^+$  461.0763, found 461.0763.

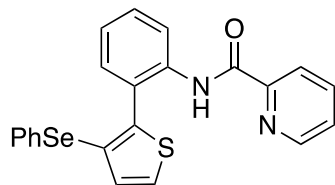


***N*-(2',4'-difluoro-6'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3qa).** The general procedure A was followed by using *N*-(2',4'-difluoro-[1,1'-biphenyl]-2-yl)picolinamide (**1q**) (62.1 mg, 0.20 mmol), 1,2-diphenyldiselane (**2a**) (62.4 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3qa** (62.4 mg, 67 %) as a blue oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.01 (s, 1H), 8.64 (d, *J* = 8.3 Hz, 1H), 8.38 (d, *J* = 4.8 Hz, 1H), 8.26 (d, *J* = 7.7 Hz, 1H), 7.88 – 7.85 (m, 1H), 7.55 – 7.53 (m, 1H), 7.50 – 7.47 (m, 2H), 7.41 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.31 – 7.25 (m, 4H), 6.80 – 6.76 (m, 1H), 6.63 – 6.60 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 163.1 (dd, *J* = 251.8, 12.8 Hz), 161.9, 160.4 (dd, *J* = 250.8, 12.2 Hz), 150.0, 148.0, 140.4 (dd, *J* = 9.3, 3.0 Hz), 137.7, 136.5, 136.0, 131.0, 130.2, 129.9, 129.3, 127.6, 126.4, 124.4, 123.9, 122.4, 121.0, 120.8 (d, *J* = 18.3 Hz), 112.6 (dd, *J* = 23.9, 3.6 Hz), 102.0 (dd, *J* = 26.2, 26.0 Hz). <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ = -107.63 – -107.66 (m), -109.02 – -109.06 (m). HR-MS(ESI) *m/z* calcd for: C<sub>24</sub>H<sub>17</sub>F<sub>2</sub>N<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 467.0469, found 467.0472.

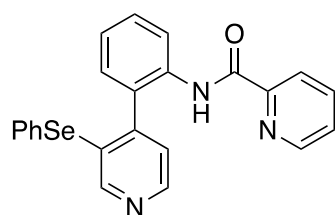


***N*-(3',5'-difluoro-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3ra).** The general procedure A was followed by using *N*-(3',5'-difluoro-[1,1'-biphenyl]-2-yl)picolinamide (**1r**) (62.1 mg, 0.20 mmol), 1,2-diphenyldiselane (**2a**) (62.4 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3ra** (63.7 mg, 68 %) as a white solid. M.p = 80 – 81 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.76 (s, 1H), 8.51 (d, *J* = 8.2 Hz, 1H), 8.37 – 8.34 (m, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.45 – 7.42 (m, 1H), 7.39 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.13 – 7.09 (m, 3H), 7.04 – 7.03 (m, 1H), 7.02 – 6.97 (m, 3H), 6.93 – 6.91 (m, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 163.6 (dd, *J* = 247.8, 13.1 Hz), 163.5 (dd, *J* = 252.2, 13.0 Hz), 161.7, 149.8, 148.0, 146.2 (dd, *J* = 10.1, 2.8 Hz), 137.6, 135.1, 132.0, 130.9, 130.8, 129.9, 129.4, 128.9, 127.1, 126.4, 123.9, 122.3, 120.6, 114.8 (dd, *J* =

22.4, 4.5 Hz), 114.6 (dd,  $J = 21.3, 3.7$  Hz), 104.3 (dd,  $J = 29.4, 25.4$  Hz).  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta = -92.03 - -92.07$  (m),  $-107.77 - -107.82$  (m). HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{24}\text{H}_{17}\text{F}_2\text{N}_2\text{O}^{80}\text{Se}^+ [\text{M}+\text{H}]^+$  467.0469, found 467.0475.

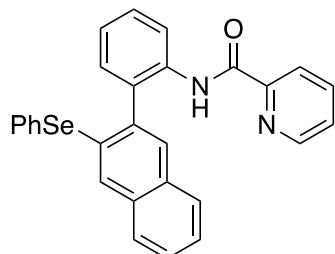


***N*-(2-(3-(phenylselanyl)thiophen-2-yl)phenyl)picolinamide (3sa).** The general procedure **A** was followed by using *N*-(2-(thiophen-2-yl)phenyl)picolinamide (**1s**) (56.4 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.4 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3sa** (49.1 mg, 56 %) as a pink solid. M.p = 109 – 110 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 10.18$  (s, 1H), 8.61 – 8.59 (m, 1H), 8.41 – 8.40 (m, 1H), 8.24 (d,  $J = 7.8$  Hz, 1H), 7.86 – 7.83 (m, 1H), 7.48 – 7.45 (m, 2H), 7.40 (ddd,  $J = 7.5, 4.8, 1.1$  Hz, 1H), 7.29 – 7.27 (m, 3H), 7.15 – 7.13 (m, 1H), 7.11 (d,  $J = 5.3$  Hz, 1H), 7.10 – 7.07 (m, 1H), 7.06 – 7.04 (m, 1H), 7.04 – 7.02 (m, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 162.0, 150.0, 148.1, 138.6, 137.6, 136.5, 133.2, 132.4, 131.9, 131.3, 130.0, 129.0, 127.2, 127.1, 126.3, 125.2, 124.1, 123.8, 122.4, 120.6$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{22}\text{H}_{17}\text{N}_2\text{OS}^{80}\text{Se}^+ [\text{M}+\text{H}]^+$  437.0221, found 437.0225.

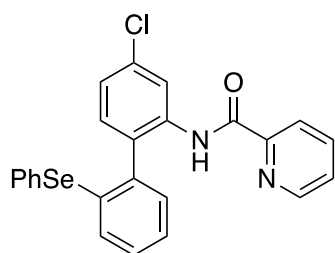


***N*-(2-(3-(phenylselanyl)pyridin-4-yl)phenyl)picolinamide (3ta).** The general procedure **A** was followed by using *N*-(2-(pyridin-4-yl)phenyl)picolinamide (**1t**) (54.9 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.5 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→3/1) yielded **3ta** (58.5 mg, 68 %) as a white solid. M.p = 117 – 118 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 9.87$  (s, 1H), 8.57 – 8.51 (m, 3H), 8.38 – 8.36 (m, 1H), 8.23 (d,  $J = 7.5$  Hz, 1H), 7.87 – 7.84 (m, 1H), 7.52 – 7.49 (m, 1H), 7.42 – 7.41 (m, 1H), 7.39 – 7.38 (m, 2H), 7.25 – 7.22

(m, 2H), 7.22 – 7.20 (m, 1H), 7.18 – 7.14 (m, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 162.0, 152.3, 149.8, 148.2, 148.1, 147.4, 137.7, 135.1, 134.5, 131.5, 129.9, 129.7, 129.6, 129.4, 128.5, 128.1, 126.5, 125.5, 124.5, 122.4, 121.4. HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{23}\text{H}_{18}\text{N}_3\text{O}^{80}\text{Se}^+$   $[\text{M}+\text{H}]^+$  432.0610, found 432.0612.

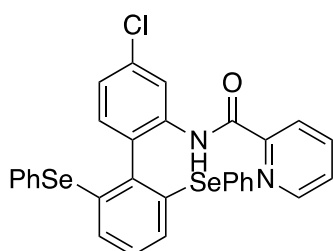


***N*-(2-(3-(phenylselanyl)naphthalen-2-yl)phenyl)picolinamide (3ua)**. The general procedure **A** was followed by using *N*-(2-(naphthalen-2-yl)phenyl)picolinamide (**1u**) (64.3 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (63.6 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3ua** (75.4 mg, 79 %) as a yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.07 (s, 1H), 8.59 (d,  $J$  = 8.3 Hz, 1H), 8.20 (d,  $J$  = 7.8 Hz, 1H), 8.10 – 8.08 (m, 1H), 7.80 – 7.77 (m, 4H), 7.68 (d,  $J$  = 6.9 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.42 – 7.41 (m, 2H), 7.29 – 7.24 (m, 3H), 7.20 – 7.16 (m, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 162.0, 150.1, 147.9, 137.5, 136.8, 135.7, 135.2, 133.8, 132.5, 132.5, 131.7, 130.8, 130.7, 130.1, 129.8, 129.4, 129.2, 128.2, 128.0, 127.1, 126.8, 126.3, 126.1, 124.0, 122.3, 120.8. HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{28}\text{H}_{21}\text{N}_2\text{O}^{80}\text{Se}^+$   $[\text{M}+\text{H}]^+$  481.0814, found 481.0817.



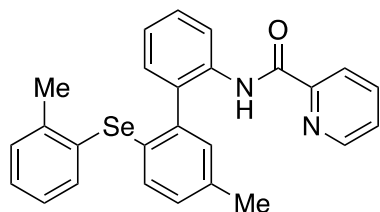
***N*-(4-chloro-2'-(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3va')**. The general procedure **A** was followed by using *N*-(4-chloro-[1,1'-biphenyl]-2-yl)picolinamide (**1v**) (60.7 mg, 0.20 mmol), 1,2-diphenyldisilane (**2a**) (62.7 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3va'** (68.6 mg, 74 %) as a white solid. M.p = 126 – 127 °C.  $^1\text{H}$  NMR (600

MHz, CDCl<sub>3</sub>)  $\delta$  = 9.99 (s, 1H), 8.71 (d,  $J$  = 1.9 Hz, 1H), 8.32 – 8.31 (m, 1H), 8.22 (d,  $J$  = 7.7 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.40 – 7.38 (m, 2H), 7.38 – 7.37 (m, 1H), 7.35 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.22 (m, 2H), 7.16 – 7.15 (m, 1H), 7.15 – 7.14 (m, 1H), 7.14 (d,  $J$  = 1.9 Hz, 1H), 7.13 (s, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  = 162.0, 149.7, 148.0, 137.8, 137.7, 136.3, 135.1, 134.8, 134.6, 132.2, 131.1, 131.0, 130.0, 129.6, 129.4, 129.4, 128.2, 127.5, 126.5, 124.0, 122.4, 120.4. HR-MS(ESI)  $m/z$  calcd for: C<sub>24</sub>H<sub>18</sub>ClN<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 465.0267, found 465.0269.



***N*-(4-chloro-2',6'-bis(phenylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3va'')**

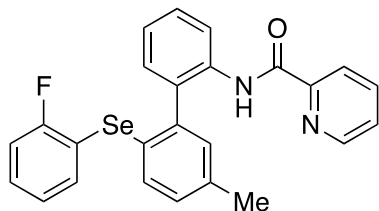
The general procedure **A** was followed by using *N*-(4-chloro-[1,1'-biphenyl]-2-yl)picolinamide (**1v**) (60.7 mg, 0.20 mmol), 1,2-diphenyldiselane (**2a**) (62.7 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3va''** (8.8 mg, 7 %) as a pink solid. M.p = 105 – 106 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.01 (s, 1H), 8.78 (d,  $J$  = 2.1 Hz, 1H), 8.33 – 8.31 (m, 1H), 8.25 (d,  $J$  = 7.8 Hz, 1H), 7.90 – 7.87 (m, 1H), 7.42 – 7.39 (m, 5H), 7.26 – 7.23 (m, 2H), 7.20 – 7.18 (m, 2H), 7.18 – 7.15 (m, 3H), 7.09 (d,  $J$  = 8.1 Hz, 1H), 7.07 – 7.05 (m, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  = 161.9, 149.8, 147.9, 137.7, 136.7, 136.4, 136.3, 135.6, 131.5, 130.0, 129.5, 129.5, 129.3, 129.2, 128.5, 128.2, 126.5, 124.4, 122.5, 120.5. HR-MS(ESI)  $m/z$  calcd for: C<sub>30</sub>H<sub>22</sub>ClN<sub>2</sub>O<sup>80</sup>Se<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> 620.9746, found 620.9740.



***N*-(5'-methyl-2'-(*o*-tolylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3ab).**

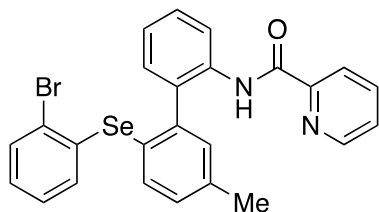
The general procedure **A** was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-di-*o*-tolylldiselane (**2b**) (69.3 mg, 0.20

mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3ab** (70.4 mg, 77 %) as a brown oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.01 (s, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 8.33 – 8.32 (m, 1H), 8.24 – 8.21 (m, 1H), 7.85 – 7.82 (m, 1H), 7.46 – 7.43 (m, 1H), 7.38 – 7.34 (m, 2H), 7.21 – 7.18 (m, 1H), 7.18 – 7.15 (m, 1H), 7.15 – 7.13 (m, 1H), 7.13 – 7.11 (m, 2H), 7.11 – 7.07 (m, 2H), 6.93 – 6.90 (m, 1H), 2.34 (s, 3H), 2.16 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 162.0, 150.2, 147.9, 141.5, 139.0, 137.5, 137.1, 135.9, 135.3, 132.0, 131.8, 130.8, 130.2, 130.2, 130.2, 130.1, 130.0, 129.0, 128.4, 126.6, 126.2, 124.0, 122.3, 120.5, 22.5, 21.1. HR-MS(ESI) *m/z* calcd for: C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 459.0970, found 459.0973.



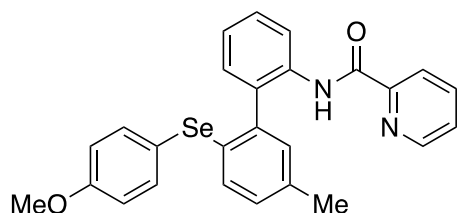
***N*-(2'-((2-fluorophenyl)selanyl)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**3ac**).**

The general procedure **A** was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-bis(2-fluorophenyl)diselane (**2c**) (70.9 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3ac** (83.6 mg, 91 %) as a white solid. M.p = 103 – 104 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.99 (s, 1H), 8.59 (d, *J* = 8.2 Hz, 1H), 8.33 (d, *J* = 4.6 Hz, 1H), 8.21 (d, *J* = 7.7 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.46 – 7.42 (m, 1H), 7.38 – 7.35 (m, 2H), 7.21 – 7.17 (m, 2H), 7.17 – 7.12 (m, 4H), 6.92 – 6.90 (m, 1H), 6.82 – 6.80 (m, 1H), 2.36 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.9, 161.8 (d, *J* = 244.6 Hz), 150.1, 148.0, 140.0, 138.2, 137.5, 135.7, 135.3, 133.7, 131.9, 131.9, 130.2, 130.1, 129.8 (d, *J* = 7.7 Hz), 129.0, 128.1, 126.2, 124.7 (d, *J* = 3.8 Hz), 123.9, 122.3, 120.4, 117.7 (d, *J* = 21.8 Hz), 115.6 (d, *J* = 23.3 Hz), 21.1. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ = -102.50 – -102.55 (m). HR-MS(ESI) *m/z* calcd for: C<sub>25</sub>H<sub>20</sub>FN<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 463.0719, found 463.0720.



***N*-(2'-((2-bromophenyl)selanyl)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (3ad).**

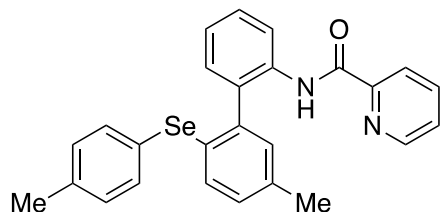
The general procedure **A** was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.6 mg, 0.20 mmol), 1,2-bis(2-bromophenyl)diselane (**2d**) (95.0 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3ad** (91.4 mg, 88 %) as a white solid. M.p = 139 – 140 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.98 (s, 1H), 8.57 (d, *J* = 8.2 Hz, 1H), 8.34 (d, *J* = 4.9 Hz, 1H), 8.21 (d, *J* = 7.7 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.23 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.16 – 7.15 (m, 1H), 7.12 – 7.10 (m, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.94 – 6.92 (m, 1H), 6.87 – 6.84 (m, 1H), 2.39 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.8, 150.1, 147.9, 141.3, 139.1, 137.6, 135.6, 135.2, 135.2, 133.3, 132.8, 132.2, 132.1, 130.4, 130.1, 129.0, 128.3, 128.1, 127.6, 126.2, 126.0, 123.8, 122.3, 120.4, 21.2. HR-MS(ESI) *m/z* calcd for: C<sub>25</sub>H<sub>20</sub>BrN<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 522.9919, found 522.9920.



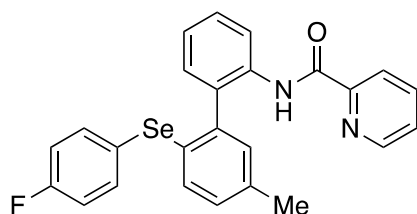
***N*-(2'-((4-methoxyphenyl)selanyl)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (3ae).**

The general procedure **A** was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-bis(4-methoxyphenyl)diselane (**2e**) (75.3 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3ae** (64.0 mg, 68 %) as a white solid. M.p = 149 – 150 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.04 (s, 1H), 8.61 (d, *J* = 8.3 Hz, 1H), 8.34 – 8.32 (m, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.48 – 7.45 (m, 1H), 7.36 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.35 – 7.32 (m, 2H),

7.23 (dd,  $J = 7.5, 1.7$  Hz, 1H), 7.20 – 7.17 (m, 1H), 7.12 (d,  $J = 8.1$  Hz, 1H), 7.08 – 7.07 (m, 1H), 7.07 – 7.04 (m, 1H), 6.71 – 6.69 (m, 2H), 3.75 (s, 3H), 2.31 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 162.0, 159.9, 150.3, 147.9, 138.1, 137.5, 137.4, 136.7, 135.3, 132.0, 131.7, 131.6, 131.0, 130.3, 129.9, 129.0, 126.2, 124.0, 122.3, 120.5, 119.6, 115.0, 55.3, 21.0$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{26}\text{H}_{23}\text{N}_2\text{O}_2^{80}\text{Se}^+$   $[\text{M}+\text{H}]^+$  475.0919, found 475.0925.



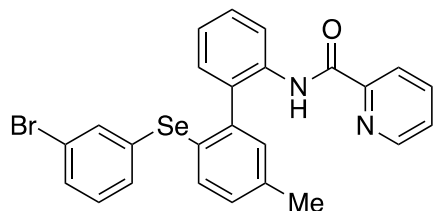
***N*-(5'-methyl-2'-(*p*-tolylselanyl)-[1,1'-biphenyl]-2-yl)picolinamide (3af).** The general procedure A was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-di-*p*-tolylselane (**2f**) (69.3 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3af** (59.4 mg, 65 %) as a white solid. M.p = 148 – 149 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 10.03$  (s, 1H), 8.60 (d,  $J = 8.3$  Hz, 1H), 8.39 – 8.33 (m, 1H), 8.24 – 8.22 (m, 1H), 7.85 – 7.82 (m, 1H), 7.50 – 7.43 (m, 1H), 7.37 (ddd,  $J = 7.0, 4.5, 0.9$  Hz, 1H), 7.31 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 7.14 – 7.06 (m, 2H), 6.96 – 6.94 (m, 2H), 2.32 (s, 3H), 2.27 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 162.0, 150.3, 147.9, 138.7, 138.0, 137.5, 137.0, 135.3, 135.2, 132.1, 131.8, 131.6, 131.0, 130.3, 130.1, 129.9, 129.0, 126.2, 126.2, 124.0, 122.3, 120.5, 21.3, 21.0$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{26}\text{H}_{23}\text{N}_2\text{O}^{80}\text{Se}^+$   $[\text{M}+\text{H}]^+$  459.0970, found 459.0976.



***N*-(2'-((4-fluorophenyl)selanyl)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (3ag).** The general procedure A was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-bis(4-fluorophenyl)diselane (**2g**) (70.9 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc:

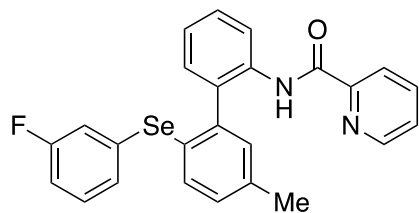


30/1→20/1) yielded **3ag** (48.1 mg, 52 %) as a white solid. M.p = 130 – 131 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.98 (s, 1H), 8.59 (d, *J* = 8.3 Hz, 1H), 8.32 – 8.31 (m, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.46 – 7.44 (m, 1H), 7.37 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.16 (s, 1H), 7.16 – 7.14 (m, 1H), 7.12 – 7.10 (m, 2H), 6.82 – 6.78 (m, 2H), 2.34 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 162.8 (d, *J* = 244.5 Hz), 161.9, 150.2, 147.9, 139.1, 137.6, 137.6, 136.9 (d, *J* = 8.0 Hz), 135.2, 132.3, 131.9, 131.9, 130.5, 130.2, 130.0, 129.0, 126.2, 124.8 (d, *J* = 3.4 Hz), 124.0, 122.4, 120.5, 116.4 (d, *J* = 21.6 Hz), 21.1. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ = -113.54 – -113.58 (m). HR-MS(ESI) *m/z* calcd for: C<sub>25</sub>H<sub>20</sub>FN<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 463.0719, found 463.0724.



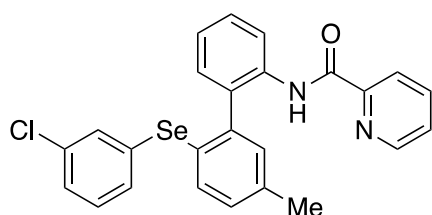
***N*-(2'-((3-bromophenyl)selanyl)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**3ah**).**

The general procedure **A** was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-bis(3-bromophenyl)diselane (**2h**) (95.3 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3ah** (56.0 mg, 54 %) as a yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.98 (s, 1H), 8.57 (d, *J* = 8.3 Hz, 1H), 8.36 (d, *J* = 3.4 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.45 – 7.41 (m, 2H), 7.39 – 7.36 (m, 2H), 7.26 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.20 (d, *J* = 7.8 Hz, 1H), 7.16 – 7.12 (m, 4H), 6.94 – 6.92 (m, 1H), 2.36 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.9, 150.1, 148.1, 139.9, 138.3, 137.6, 136.3, 135.2, 133.5, 132.7, 132.5, 132.1, 131.9, 130.6, 130.4, 130.2, 130.2, 129.3, 129.0, 126.3, 123.9, 122.9, 122.3, 120.4, 21.1. HR-MS(ESI) *m/z* calcd for: C<sub>25</sub>H<sub>20</sub>BrN<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 522.9919, found 522.9920.



***N*-(2'-((3-fluorophenyl)selanyl)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (3ai).**

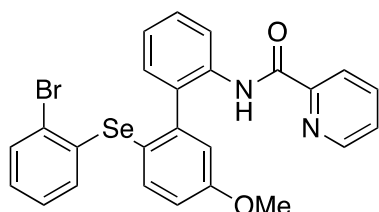
The general procedure A was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.6 mg, 0.20 mmol), 1,2-bis(3-fluorophenyl)diselane (**2i**) (69.5 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3ai** (70.9 mg, 77 %) as a white solid. M.p = 101 – 102 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.97 (s, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.37 – 8.35 (m, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.45 – 7.42 (m, 1H), 7.40 – 7.37 (m, 2H), 7.17 – 7.13 (m, 4H), 7.08 – 7.04 (m, 2H), 7.04 – 7.01 (m, 1H), 6.84 – 6.81 (m, 1H), 2.37 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 162.8 (d, *J* = 247.5 Hz), 161.9, 150.1, 148.0, 140.1, 138.4, 137.6, 135.2, 133.8, 132.9 (d, *J* = 6.8 Hz), 132.1, 132.0, 130.3, 130.2, 130.2, 129.2, 129.1, 129.0, 126.3, 123.9, 122.3, 120.5, 120.3 (d, *J* = 22.2 Hz), 114.4 (d, *J* = 21.3 Hz), 21.2. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ = -111.93 – -111.97 (m). HR-MS(ESI) *m/z* calcd for: C<sub>25</sub>H<sub>20</sub>FN<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 463.0719, found 463.0726.



***N*-(2'-((3-chlorophenyl)selanyl)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (3aj).**

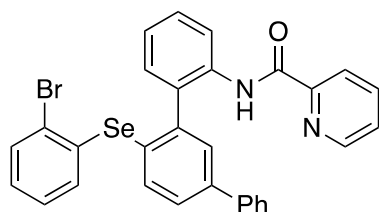
The general procedure A was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-bis(3-chlorophenyl)diselane (**2j**) (77.8 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **3aj** (72.6 mg, 76 %) as a white solid. M.p = 92 – 93 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.98 (s, 1H), 8.57 (d, *J* = 8.2 Hz, 1H), 8.36 (d, *J* = 4.7 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.46 – 7.42 (m, 1H), 7.38 – 7.36 (m,

2H), 7.29 – 7.26 (m, 1H), 7.17 – 7.13 (m, 5H), 7.11 (d,  $J = 8.1$  Hz, 1H), 7.02 – 6.97 (m, 1H), 2.36 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 161.9, 150.1, 148.1, 139.9, 138.3, 137.6, 135.2, 134.7, 133.6, 133.4, 132.5, 132.0, 131.9, 131.9, 130.2, 130.2, 130.1, 129.3, 129.0, 127.7, 126.3, 123.9, 122.3, 120.4, 21.1$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{25}\text{H}_{20}\text{ClN}_2\text{O}^{80}\text{Se}^+ [\text{M}+\text{H}]^+$  479.0424, found 479.0427.



***N*-(2'-((2-bromophenyl)selenanyl)-5'-methoxy-[1,1'-biphenyl]-2-yl)picolinamide**

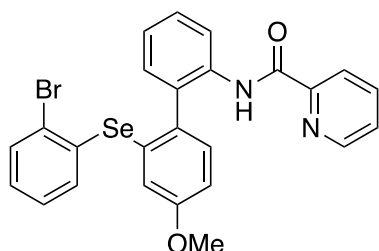
**(3bd)**. The general procedure **A** was followed by using *N*-(3'-methoxy-[1,1'-biphenyl]-2-yl)picolinamide (**1b**) (60.6 mg, 0.20 mmol), 1,2-bis(2-bromophenyl)diselane (**2d**) (94.2 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→7/1) yielded **3bd** (92.5 mg, 86 %) as a white solid. M.p = 124 – 125 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 9.99$  (s, 1H), 8.58 – 8.55 (m, 1H), 8.38 – 8.36 (m, 1H), 8.22 – 8.19 (m, 1H), 7.85 – 7.82 (m, 1H), 7.67 – 7.64 (m, 1H), 7.43 – 7.40 (m, 1H), 7.38 (dd,  $J = 7.4, 4.1$  Hz, 1H), 7.35 – 7.32 (m, 1H), 7.14 – 7.13 (m, 1H), 7.12 – 7.08 (m, 1H), 7.01 – 6.98 (m, 2H), 6.92 – 6.88 (m, 2H), 6.83 – 6.79 (m, 1H), 3.82 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 161.8, 160.6, 150.0, 148.0, 143.9, 138.7, 137.6, 136.2, 135.1, 132.7, 132.2, 131.8, 129.9, 129.1, 127.5, 127.5, 126.3, 124.6, 123.8, 122.3, 121.4, 120.4, 116.5, 116.2, 55.7$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{25}\text{H}_{20}\text{BrN}_2\text{O}_2^{80}\text{Se}^+ [\text{M}+\text{H}]^+$  538.9868, found 538.9870.



***N*-(6'-((2-bromophenyl)selenanyl)-[1,1':3',1''-terphenyl]-2-yl)picolinamide** (**3gd**).

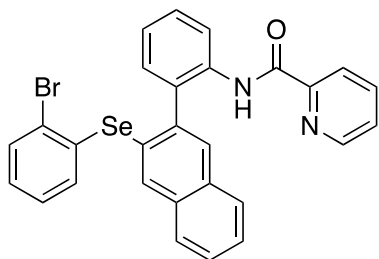
The general procedure **A** was followed by using *N*-([1,1':3',1''-terphenyl]-2-yl)picolinamide (**1g**) (70.3 mg, 0.20 mmol), 1,2-bis(2-bromophenyl)diselane (**2d**) (94.8 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc:

30/1→10/1) yielded **3gd** (107.2 mg, 92 %) as a white solid. M.p = 133 – 134 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.13 (s, 1H), 8.62 (d, *J* = 7.2 Hz, 1H), 8.28 – 8.25 (m, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.64 (d, *J* = 2.1 Hz, 1H), 7.63 – 7.61 (m, 1H), 7.61 – 7.59 (m, 2H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.42 – 7.40 (m, 2H), 7.36 – 7.32 (m, 2H), 7.27 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.18 – 7.16 (m, 1H), 7.03 – 7.00 (m, 1H), 6.95 – 6.92 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.9, 150.0, 148.0, 141.4, 140.9, 140.0, 137.6, 135.3, 134.9, 134.5, 134.2, 133.1, 131.6, 130.2, 129.9, 129.3, 129.0, 129.0, 128.8, 128.0, 127.9, 127.8, 127.1, 127.1, 126.3, 124.0, 122.3, 120.5. HR-MS(ESI) *m/z* calcd for: C<sub>30</sub>H<sub>22</sub>BrN<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 585.0075, found 585.0077.



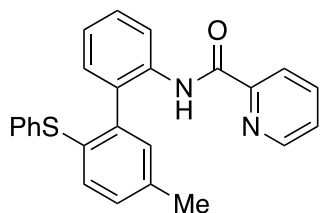
***N*-(2'-((2-bromophenyl)selanyl)-4'-methoxy-[1,1'-biphenyl]-2-yl)picolinamide**

**(3id).** The general procedure **A** was followed by using *N*-(4'-methoxy-[1,1'-biphenyl]-2-yl)picolinamide (**1i**) (60.9 mg, 0.20 mmol), 1,2-bis(2-bromophenyl)diselane (**2d**) (95.0 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→7/1) yielded **3id** (93.8 mg, 87 %) as a white solid. M.p = 123 – 124 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.99 (s, 1H), 8.56 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.37 – 8.36 (m, 1H), 8.21 – 8.20 (m, 1H), 7.85 – 7.82 (m, 1H), 7.65 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.38 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.34 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.14 – 7.13 (m, 1H), 7.11 – 7.08 (m, 1H), 7.00 – 6.98 (m, 2H), 6.92 – 6.88 (m, 2H), 6.82 – 6.79 (m, 1H), 3.82 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.8, 160.6, 150.0, 148.0, 143.9, 138.7, 137.6, 136.2, 135.1, 132.7, 132.2, 131.8, 129.9, 129.1, 127.5, 127.5, 126.3, 124.6, 123.8, 122.3, 121.4, 120.4, 116.5, 116.2, 55.7. HR-MS(ESI) *m/z* calcd for: C<sub>25</sub>H<sub>20</sub>BrN<sub>2</sub>O<sub>2</sub><sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 538.9868, found 538.9866.



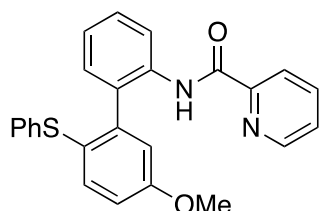
***N*-(2-(3-((2-bromophenyl)selanyl)naphthalen-2-yl)phenyl)picolinamide (3ud).**

The general procedure **A** was followed by using *N*-(2-(naphthalen-2-yl)phenyl)picolinamide (**1u**) (64.7 mg, 0.20 mmol), 1,2-bis(2-bromophenyl)diselane (**2d**) (94.0 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **3ud** (83.2 mg, 75 %) as a yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.04 (s, 1H), 8.58 (d, *J* = 7.3 Hz, 1H), 8.18 (d, *J* = 6.9 Hz, 1H), 8.07 – 8.06 (m, 1H), 8.02 (s, 1H), 7.88 (s, 1H), 7.84 (dd, *J* = 6.4, 3.2 Hz, 1H), 7.79 – 7.76 (m, 2H), 7.55 – 7.51 (m, 2H), 7.48 – 7.42 (m, 2H), 7.29 – 7.24 (m, 1H), 7.24 – 7.20 (m, 1H), 7.18 – 7.12 (m, 2H), 7.01 – 6.98 (m, 1H), 6.92 – 6.89 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.9, 150.0, 147.9, 137.9, 137.5, 135.6, 134.4, 134.1, 133.9, 133.1, 133.0, 131.6, 130.5, 130.2, 129.2, 128.7, 128.1, 127.8, 127.4, 127.0, 127.0, 126.9, 126.1, 123.9, 122.3, 120.6. HR-MS(ESI) *m/z* calcd for: C<sub>28</sub>H<sub>20</sub>BrN<sub>2</sub>O<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 558.9919, found 558.9919.

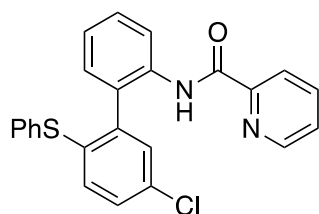


***N*-(5'-methyl-2'-(phenylthio)-[1,1'-biphenyl]-2-yl)picolinamide (5aa).** The general procedure **B** was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-diphenyldisulfane (**5a**) (44.3 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **5aa** (56.3 mg, 71 %) as a white solid. M.p = 82 – 83 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.02 (s, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.37 (d, *J* = 4.6 Hz, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.43 – 7.40 (m, 1H), 7.39 – 7.37 (m, 1H), 7.27 –

7.25 (m, 1H), 7.20 – 7.15 (m, 4H), 7.14 – 7.12 (m, 2H), 7.12 – 7.07 (m, 3H), 2.36 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.9, 150.2, 147.9, 138.8, 137.6, 137.6, 135.5, 135.3, 133.3, 132.1, 131.8, 131.8, 131.4, 130.4, 129.9, 129.0, 128.8, 127.1, 126.2, 124.0, 122.4, 120.6, 21.1. HR-MS(ESI) m/z calcd for: C<sub>25</sub>H<sub>21</sub>N<sub>2</sub>OS<sup>+</sup> [M+H]<sup>+</sup> 397.1369, found 397.1372.

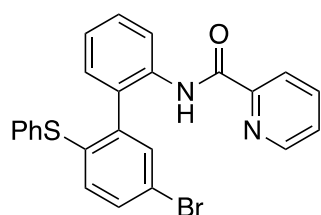


***N*-(5'-methoxy-2'-(phenylthio)-[1,1'-biphenyl]-2-yl)picolinamide (5ba).** The general procedure **B** was followed by using *N*-(3'-methoxy-[1,1'-biphenyl]-2-yl)picolinamide (**1b**) (60.1 mg, 0.20 mmol), 1,2-diphenyldisulfane (**5a**) (43.7 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **5ba** (39.2 mg, 48 %) as a yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.98 (s, 1H), 8.53 – 8.52 (m, 1H), 8.38 – 8.37 (m, 1H), 8.22 – 8.21 (m, 1H), 7.85 – 7.82 (m, 1H), 7.47 (d, *J* = 8.7 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.40 – 7.37 (m, 1H), 7.13 – 7.09 (m, 2H), 7.07 – 7.05 (m, 2H), 7.04 – 7.01 (m, 3H), 6.97 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.90 (d, *J* = 2.8 Hz, 1H), 3.80 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.9, 159.8, 150.2, 148.0, 141.9, 137.6, 137.0, 135.4, 135.2, 131.4, 130.2, 130.2, 128.9, 128.8, 128.8, 126.4, 126.2, 123.9, 122.4, 120.5, 116.4, 115.7, 55.7. HR-MS(ESI) m/z calcd for: C<sub>25</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 413.1318, found 413.1323.

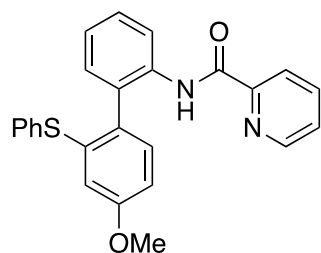


***N*-(5'-chloro-2'-(phenylthio)-[1,1'-biphenyl]-2-yl)picolinamide (5ea).** The general procedure **B** was followed by using *N*-(3'-chloro-[1,1'-biphenyl]-2-yl)picolinamide (**1e**) (61.0 mg, 0.20 mmol), 1,2-diphenyldisulfane (**5a**) (43.7 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1)

yielded **5ea** (44.2 mg, 53 %) as a white solid. M.p = 120 – 121 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.02 (s, 1H), 8.54 (d, *J* = 8.2 Hz, 1H), 8.40 (d, *J* = 4.4 Hz, 1H), 8.25 – 8.24 (m, 1H), 7.87 – 7.84 (m, 1H), 7.48 – 7.45 (m, 1H), 7.41 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.26 (s, 1H), 7.23 – 7.20 (m, 1H), 7.20 – 7.16 (m, 4H), 7.13 (d, *J* = 8.4 Hz, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 162.0, 150.1, 148.0, 139.3, 137.7, 136.8, 135.2, 133.6, 133.2, 132.6, 131.2, 131.1, 130.2, 129.9, 129.5, 129.4, 129.1, 128.1, 126.4, 124.3, 122.5, 121.0. HR-MS(ESI) *m/z* calcd for: C<sub>24</sub>H<sub>18</sub>ClN<sub>2</sub>OS<sup>+</sup> [M+H]<sup>+</sup> 417.0823, found 417.0827.

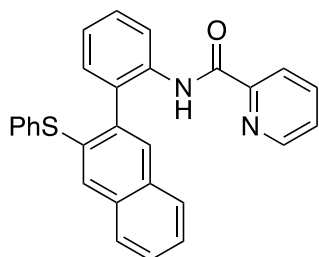


***N*-(5'-bromo-2'-(phenylthio)-[1,1'-biphenyl]-2-yl)picolinamide (5fa)**. The general procedure **B** was followed by using *N*-(3'-bromo-[1,1'-biphenyl]-2-yl)picolinamide (**1f**) (70.1 mg, 0.20 mmol), 1,2-diphenyldisulfane (**5a**) (43.9 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **5fa** (52.3 mg, 57 %) as a white solid. M.p = 120 – 121 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.04 (s, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 8.44 – 8.39 (m, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.87 – 7.85 (m, 1H), 7.50 – 7.44 (m, 2H), 7.43 – 7.40 (m, 2H), 7.30 – 7.23 (m, 3H), 7.22 (d, *J* = 6.2 Hz, 1H), 7.20 – 7.18 (m, 4H), 7.05 – 7.03 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 162.0, 150.1, 148.0, 139.4, 137.7, 137.6, 135.2, 133.9, 133.4, 133.3, 132.0, 131.1, 130.3, 129.8, 129.5, 129.4, 128.2, 126.4, 124.3, 122.5, 121.0, 120.4. HR-MS(ESI) *m/z* calcd for: C<sub>24</sub>H<sub>18</sub>BrN<sub>2</sub>OS<sup>+</sup> [M+H]<sup>+</sup> 461.0318, found 461.0316.



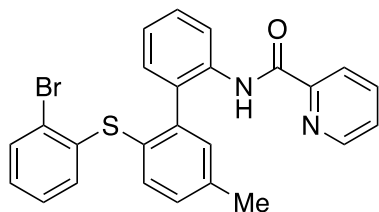
***N*-(4'-methoxy-2'-(phenylthio)-[1,1'-biphenyl]-2-yl)picolinamide (5ia)**. The general procedure **B** was followed by using *N*-(4'-methoxy-[1,1'-biphenyl]-2-yl)

picolinamide (**1i**) (60.1 mg, 0.20 mmol), 1,2-diphenyldisulfane (**5a**) (43.8 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→10/1) yielded **5ia** (49.8 mg, 60 %) as a yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.98 (s, 1H), 8.53 – 8.52 (m, 1H), 8.38 – 8.37 (m, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.47 (d, *J* = 8.7 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.40 – 7.37 (m, 1H), 7.14 – 7.10 (m, 2H), 7.08 – 7.05 (m, 2H), 7.04 – 7.01 (m, 3H), 6.97 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.90 (d, *J* = 2.8 Hz, 1H), 3.80 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.9, 159.8, 150.1, 148.0, 141.8, 137.6, 137.0, 135.4, 135.2, 131.4, 130.2, 128.9, 128.8, 128.8, 126.4, 126.3, 126.3, 123.9, 122.4, 120.5, 116.4, 115.7, 55.7. HR-MS(ESI) *m/z* calcd for: C<sub>25</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 413.1318, found 413.1321.



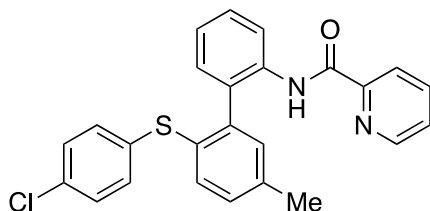
***N*-(2-(3-(phenylthio)naphthalen-2-yl)phenyl)picolinamide (5ua)**. The general procedure **B** was followed by using *N*-(2-(naphthalen-2-yl)phenyl)picolinamide (**1u**) (64.5 mg, 0.20 mmol), 1,2-diphenyldisulfane (**5a**) (43.9 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **5ua** (40.2 mg, 46 %) as a brown oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 10.07 (s, 1H), 8.53 (d, *J* = 8.3 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.16 – 8.12 (m, 1H), 7.80 – 7.77 (m, 3H), 7.72 – 7.71 (m, 2H), 7.50 – 7.45 (m, 3H), 7.31 – 7.22 (m, 4H), 7.21 – 7.13 (m, 4H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 162.1, 150.1, 147.9, 137.5, 136.2, 135.7, 135.6, 134.2, 133.6, 133.0, 132.4, 131.0, 130.8, 130.7, 129.3, 129.2, 129.1, 128.0, 127.8, 127.2, 126.9, 126.4, 126.1, 124.1, 122.3, 120.9. HR-MS(ESI) *m/z* calcd for: C<sub>28</sub>H<sub>21</sub>N<sub>2</sub>O<sup>+</sup> [M+H]<sup>+</sup> 433.1369, found 433.1368.





***N*-(2'-((2-bromophenyl)thio)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (5ab).**

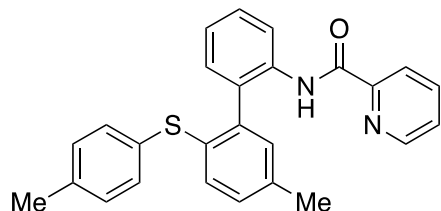
The general procedure **B** was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.6 mg, 0.20 mmol), 1,2-bis(2-bromophenyl)disulfane (**5b**) (75.6 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **5ab** (55.0 mg, 58 %) as a white solid. M.p = 117 – 118 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.98 (s, 1H), 8.53 (d, *J* = 7.3 Hz, 1H), 8.35 – 8.34 (m, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.42 – 7.35 (m, 3H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.11 – 7.09 (m, 1H), 7.05 – 6.99 (m, 1H), 6.92 – 6.89 (m, 2H), 2.38 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 161.9, 150.2, 148.0, 140.0, 138.6, 137.7, 137.6, 135.3, 133.4, 133.1, 132.4, 132.0, 131.3, 131.0, 130.2, 130.2, 128.9, 127.9, 127.6, 126.2, 125.1, 123.9, 122.4, 120.5, 21.2. HR-MS(ESI) *m/z* calcd for: C<sub>25</sub>H<sub>20</sub>BrN<sub>2</sub>OS<sup>+</sup> [M+H]<sup>+</sup> 475.0474, found 475.0477.



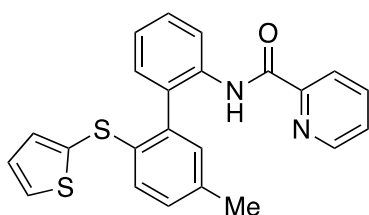
***N*-(2'-((4-chlorophenyl)thio)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (5ac).**

The general procedure **B** was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.4 mg, 0.20 mmol), 1,2-bis(3-chlorophenyl)disulfane (**5c**) (57.6 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **5ac** (63.0 mg, 73 %) as a white solid. M.p = 59 – 60 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.94 (s, 1H), 8.54 (d, *J* = 8.2 Hz, 1H), 8.34 (d, *J* = 4.7 Hz, 1H), 8.22 (d, *J* = 7.7 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.43 – 7.41 (m, 1H), 7.40 – 7.38 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.16 (s, 1H), 7.13 – 7.11 (m, 2H), 7.08 – 7.04 (m, 2H), 7.04 – 6.98 (m, 2H), 2.37 (s, 3H). <sup>13</sup>C NMR (150 MHz,

CDCl<sub>3</sub>)  $\delta$  = 161.9, 150.1, 147.9, 139.3, 138.2, 137.6, 135.2, 134.4, 133.0, 132.7, 132.6, 132.3, 132.3, 131.2, 130.3, 130.0, 129.0, 128.9, 126.3, 124.0, 122.4, 120.5, 21.2. HR-MS(ESI)  $m/z$  calcd for: C<sub>25</sub>H<sub>20</sub>ClN<sub>2</sub>OS<sup>+</sup> [M+H]<sup>+</sup> 431.0979, found 431.0988.

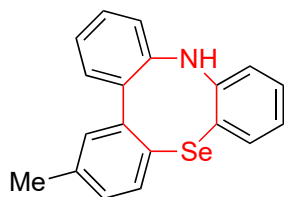


***N*-(5'-methyl-2'-(*p*-tolylthio)-[1,1'-biphenyl]-2-yl)picolinamide (5ad).** The general procedure **B** was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.4 mg, 0.20 mmol), 1,2-di-*p*-tolylidysulfane (**5d**) (50.0 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **5ad** (60.1 mg, 73 %) as a brown solid. M.p = 123 – 124 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.03 (s, 1H), 8.55 (d,  $J$  = 8.3 Hz, 1H), 8.37 – 8.36 (m, 1H), 8.23 (d,  $J$  = 7.7 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.45 – 7.42 (m, 1H), 7.38 (ddd,  $J$  = 7.6, 4.7, 1.2 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.15 – 7.14 (m, 1H), 7.14 – 7.12 (m, 3H), 7.10 (s, 1H), 6.96 – 6.94 (m, 2H), 2.34 (s, 3H), 2.26 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  = 162.0, 150.3, 147.9, 137.8, 137.6, 137.5, 136.8, 135.3, 134.5, 133.0, 131.9, 131.4, 131.0, 130.4, 130.4, 129.9, 129.8, 128.9, 126.2, 124.0, 122.4, 120.6, 21.2, 21.1. HR-MS(ESI)  $m/z$  calcd for: C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>OS<sup>+</sup> [M+H]<sup>+</sup> 411.1526, found 411.1531.

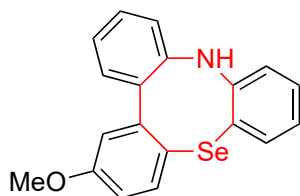


***N*-(5'-methyl-2'-(thiophen-2-ylthio)-[1,1'-biphenyl]-2-yl)picolinamide (5ae).** The general procedure **B** was followed by using *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.4 mg, 0.20 mmol), 1,2-di(thiophen-2-yl)disulfane (**5e**) (48.0 mg, 0.20 mmol). Purification by column chromatography (Petroleum ether /EtOAc: 30/1→15/1) yielded **5ae** (43.1 mg, 54 %) as a brown oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.09 (s, 1H), 8.61 (dd,  $J$  = 8.3, 1.2 Hz, 1H), 8.36 – 8.35 (m, 1H), 8.25 – 8.24 (m, 1H), 7.85 – 7.83 (m, 1H), 7.50 – 7.46 (m, 1H), 7.39 – 7.36 (m, 1H), 7.36 (dd,  $J$  = 5.4,

1.2 Hz, 1H), 7.27 (dd,  $J = 7.6, 1.7$  Hz, 1H), 7.23 – 7.20 (m, 1H), 7.14 – 7.12 (m, 1H), 7.08 – 7.07 (m, 1H), 7.03 (d,  $J = 8.2$  Hz, 1H), 7.01 (dd,  $J = 3.6, 1.3$  Hz, 1H), 6.94 (dd,  $J = 5.3, 3.5$  Hz, 1H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta = 162.1, 150.2, 148.1, 137.5, 136.5, 136.3, 135.9, 135.6, 135.5, 131.7, 131.3, 131.0, 130.6, 130.5, 129.9, 129.1, 127.9, 127.8, 126.2, 124.2, 122.3, 120.7, 21.0$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{23}\text{H}_{19}\text{N}_2\text{OS}_2^+ [\text{M}+\text{H}]^+$  403.0933, found 403.0936.

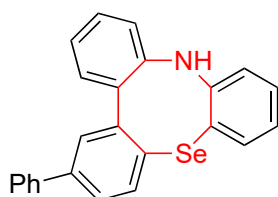


**2-methyl-10H-tribenzo[*b,e,g*][1,4]selenazocine (7a).** The general procedure C was followed by using *N*-(2'-((2-bromophenyl)selanyl)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**3ad**) (52.2 mg, 0.10 mmol), CuI (9.5 mg, 0.05 mmol) at 125 °C for 12 h. Purification by column chromatography (Petroleum ether/EtOAc: 40/1) yielded **7a** (16.2 mg, 48 %) as a colorless oil.  $^1\text{H}$  NMR (600 MHz,  $d_6$ -DMSO)  $\delta = 7.68$  (d,  $J = 7.8$  Hz, 1H), 7.43 – 7.40 (m, 1H), 7.34 (dd,  $J = 7.7, 1.6$  Hz, 1H), 7.33 – 7.30 (m, 2H), 7.26 (dd,  $J = 7.5, 1.7$  Hz, 1H), 7.19 – 7.15 (m, 2H), 7.09 – 7.06 (m, 1H), 7.01 (s, 1H), 6.98 (dd,  $J = 8.0, 1.4$  Hz, 1H), 6.71 – 6.68 (m, 1H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $d_6$ -DMSO)  $\delta = 148.5, 147.6, 144.6, 139.6, 139.2, 136.3, 133.7, 129.7, 129.3, 128.5, 128.2, 128.1, 127.9, 126.1, 122.5, 120.0, 119.8, 115.5, 20.9$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{19}\text{H}_{16}\text{N}^{80}\text{Se}^+ [\text{M}+\text{H}]^+$  338.0442, found 338.0446.

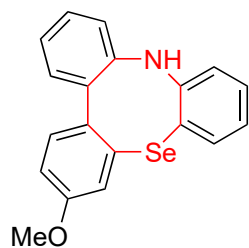


**2-methoxy-10H-tribenzo[*b,e,g*][1,4]selenazocine (7b).** The general procedure C was followed by using *N*-(2'-((2-bromophenyl)selanyl)-5'-methoxy-[1,1'-biphenyl]-2-yl)picolinamide (**3bd**) (53.8 mg, 0.10 mmol), CuI (9.7 mg, 0.05 mmol) at 130 °C for 12 h. Purification by column chromatography (Petroleum ether/EtOAc: 30/1) yielded **7b** (15.7 mg, 45 %) as a colorless oil.  $^1\text{H}$  NMR (600 MHz,  $d_6$ -DMSO)  $\delta = 7.72 - 7.68$  (m,

1H), 7.44 – 7.40 (m, 1H), 7.34 (dd,  $J = 7.7, 1.5$  Hz, 1H), 7.32 (dd,  $J = 7.3, 1.2$  Hz, 1H), 7.30 – 7.28 (m, 1H), 7.19 – 7.15 (m, 1H), 7.10 – 7.05 (m, 1H), 7.05 – 7.03 (m, 1H), 7.01 – 7.00 (m, 1H), 7.00 – 6.97 (m, 1H), 6.93 (dd,  $J = 8.5, 3.0$  Hz, 1H), 6.71 – 6.68 (m, 1H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $d_6$ -DMSO)  $\delta = 160.4, 149.2, 148.4, 144.5, 139.2, 137.6, 133.5, 129.4, 128.6, 128.1, 127.8, 126.1, 120.0, 119.9, 116.7, 115.7, 114.4, 113.3, 55.4$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{19}\text{H}_{16}\text{NO}^{80}\text{Se}^+$   $[\text{M}+\text{H}]^+$  354.0392, found 354.0394.

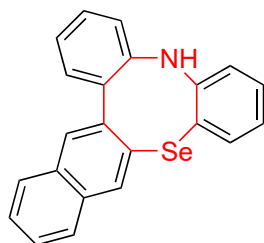


**2-phenyl-10H-tribenzo[*b,e,g*][1,4]selenazocine (7c).** The general procedure C was followed by using *N*-(6'-((2-bromophenyl)selanyl)-[1,1':3',1''-terphenyl]-2-yl) picolinamide (**3gd**) (58.4 mg, 0.10 mmol), CuI (9.6 mg, 0.05 mmol) at 130 °C for 12 h. Purification by column chromatography (Petroleum ether/EtOAc: 60/1) yielded **7c** (18.7 mg, 47 %) as a colorless oil.  $^1\text{H}$  NMR (600 MHz,  $d_6$ -DMSO)  $\delta = 7.89$  (d,  $J = 7.9$  Hz, 1H), 7.75 – 7.74 (m, 2H), 7.74 – 7.73 (m, 1H), 7.65 (dd,  $J = 8.0, 2.2$  Hz, 1H), 7.49 – 7.47 (m, 2H), 7.46 – 7.44 (m, 1H), 7.41 – 7.38 (m, 3H), 7.36 – 7.34 (m, 1H), 7.22 – 7.19 (m, 1H), 7.12 – 7.07 (m, 2H), 7.02 (dd,  $J = 8.0, 1.4$  Hz, 1H), 6.74 – 6.71 (m, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $d_6$ -DMSO)  $\delta = 148.4, 148.3, 144.5, 141.7, 139.3, 139.2, 137.1, 133.7, 129.5, 129.1, 128.6, 128.3, 128.0, 127.2, 127.0, 127.0, 126.2, 125.6, 124.9, 120.1, 120.0, 115.4$ . HR-MS(ESI)  $m/z$  calcd for:  $\text{C}_{24}\text{H}_{18}\text{N}^{80}\text{Se}^+$   $[\text{M}+\text{H}]^+$  400.0599, found 400.0591.

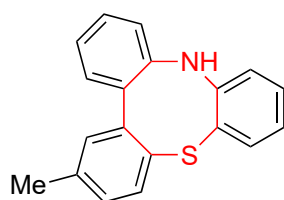


**3-methoxy-10H-tribenzo[*b,e,g*][1,4]selenazocine (7d).** The general procedure C was followed by using *N*-(2'-((2-bromophenyl)selanyl)-4'-methoxy-[1,1'-biphenyl]-2-yl)

picolinamide (**3id**) (53.8 mg, 0.10 mmol), CuI (9.5 mg, 0.05 mmol) at 130 °C for 12 h. Purification by column chromatography (Petroleum ether/EtOAc: 40/1) yielded **7d** (16.1 mg, 46 %) as a colorless oil. <sup>1</sup>H NMR (600 MHz, *d*<sub>6</sub>-DMSO)  $\delta$  = 7.41 (d, *J* = 8.3 Hz, 1H), 7.39 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.31 – 7.29 (m, 1H), 7.25 – 7.22 (m, 1H), 7.18 – 7.15 (m, 1H), 7.12 – 7.09 (m, 1H), 7.09 – 7.07 (m, 1H), 7.06 – 7.04 (m, 1H), 7.01 – 6.99 (m, 1H), 6.72 – 6.69 (m, 1H), 3.78 (s, 3H). <sup>13</sup>C NMR (150 MHz, *d*<sub>6</sub>-DMSO)  $\delta$  = 159.3, 148.4, 144.1, 140.0, 139.2, 133.8, 129.0, 128.4, 128.3, 128.2, 128.1, 126.4, 126.1, 121.2, 120.0, 119.8, 115.6, 115.1, 55.4. HR-MS(ESI) *m/z* calcd for: C<sub>19</sub>H<sub>16</sub>N<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 354.0392, found 354.0392.

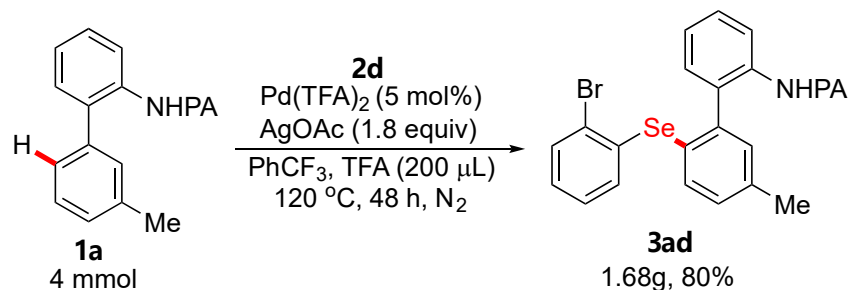


**5H-dibenzo[*b,e*]naphtho[2,3-*g*][1,4]selenazocine (7e).** The general procedure **C** was followed by using *N*-(2-(3-((2-bromophenyl)selenanyl)naphthalen-2-yl)phenyl)picolinamide (**3ud**) (55.8 mg, 0.10 mmol), CuI (9.5 mg, 0.05 mmol) at 130 °C for 12 h. Purification by column chromatography (Petroleum ether/EtOAc: 60/1) yielded **7e** (19.7 mg, 53 %) as a white solid. M.p = 162 – 163 °C. <sup>1</sup>H NMR (600 MHz, *d*<sub>6</sub>-DMSO)  $\delta$  = 8.47 (s, 1H), 8.03 – 8.00 (m, 2H), 7.98 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.56 – 7.53 (m, 1H), 7.48 – 7.45 (m, 1H), 7.43 – 7.40 (m, 2H), 7.39 – 7.36 (m, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.10 – 7.08 (m, 1H), 7.02 (d, *J* = 7.1 Hz, 1H), 6.95 (s, 1H), 6.76 – 6.73 (m, 1H). <sup>13</sup>C NMR (150 MHz, *d*<sub>6</sub>-DMSO)  $\delta$  = 148.6, 144.7, 144.4, 139.6, 136.3, 133.5, 133.4, 133.2, 129.5, 128.8, 128.4, 127.9, 127.8, 127.6, 127.4, 126.4, 126.3, 125.6, 125.0, 120.5, 120.1, 117.9. HR-MS(ESI) *m/z* calcd for: C<sub>22</sub>H<sub>16</sub>N<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 374.0442, found 374.0446.



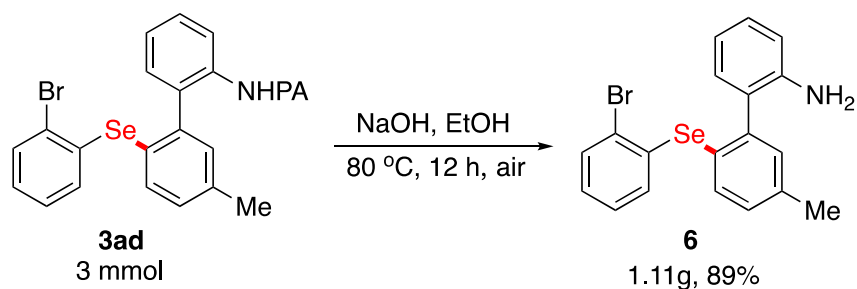
**2-methyl-10*H*-tribenzo[*b,e,g*][1,4]thiazocine (7f).** The general procedure C was followed by using *N*-(2'-((2-bromophenyl)thio)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**5ab**) (47.5 mg, 0.10 mmol), CuI (19.5 mg, 0.10 mmol) at 140 °C for 12 h. Purification by column chromatography (Petroleum ether/EtOAc: 40/1) yielded **7f** (19.4 mg, 67 %) as a colorless oil. <sup>1</sup>H NMR (600 MHz, *d*<sub>6</sub>-DMSO) δ = 7.54 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.33 – 7.28 (m, 3H), 7.26 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.23 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.22 – 7.21 (m, 1H), 7.18 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.93 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.69 – 6.67 (m, 1H), 2.37 (s, 3H). <sup>13</sup>C NMR (150 MHz, *d*<sub>6</sub>-DMSO) δ = 148.3, 147.3, 141.8, 139.7, 139.5, 135.3, 133.2, 129.8, 129.4, 128.5, 128.4, 128.2, 127.4, 125.9, 125.8, 119.1, 118.9, 118.3, 20.9. HR-MS(ESI) *m/z* calcd for: C<sub>19</sub>H<sub>16</sub>NS<sup>+</sup> [M+H]<sup>+</sup> 290.0998, found 290.1000.

### Scheme S1: Scale-up experiment



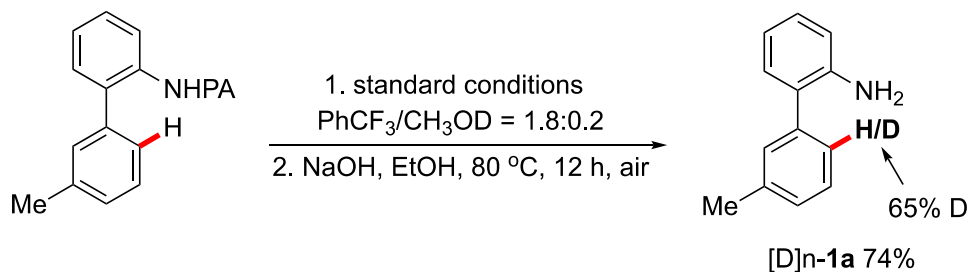
A suspension of *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (1153.0 mg, 4.0 mmol), 1,2-bis(2-bromophenyl)diselane (**2d**) (1878.9 mg, 4.0 mmol), Pd(TFA)<sub>2</sub> (66.7 mg, 5.0 mol%), AgOAc (1200.7 mg, 7.2 mmol), TFA (200 μL) in anhydrous PhCF<sub>3</sub> (20.0 mL) was stirred in Schlenk tube under nitrogen at 120 °C for 48 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (20 mL) and extracted with EtOAc (3 x 35 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents in *vacuo*, the crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 30/1→15/1) to yield **3ad** (1678.4 mg, 80 %) as a white solid.

## Scheme S2: Removal of the directing group



A suspension of *N*-(2'-((2-bromophenyl)selanyl)-5'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**3ad**) (1567.0 mg, 3.0mmol), NaOH (1801.0 mg, 45.0 mmol) in EtOH (42.9 mL) was stirred in Schlenk tube under air at 80 °C for 12 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (30 mL) and extracted with DCM (3 x 50 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents in *vacuo*, the crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 50/1→20/1) to yield **6** (1116.5 mg, 89 %) as a brown solid. M.p = 108 – 109 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.49 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.19 (s, 1H), 7.17 – 7.14 (m, 2H), 7.11 – 7.09 (m, 2H), 7.07 – 7.03 (m, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.75 – 6.73 (m, 2H), 3.37 (brs, 2H), 2.37 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 143.8, 142.2, 138.8, 135.4, 134.8, 133.6, 133.0, 132.0, 130.1, 129.9, 129.1, 128.3, 128.2, 127.9, 127.6, 126.4, 118.4, 115.6, 21.2. HR-MS(ESI) *m/z* calcd for: C<sub>19</sub>H<sub>17</sub>BrN<sup>80</sup>Se<sup>+</sup> [M+H]<sup>+</sup> 417.9704, found 417.9708.

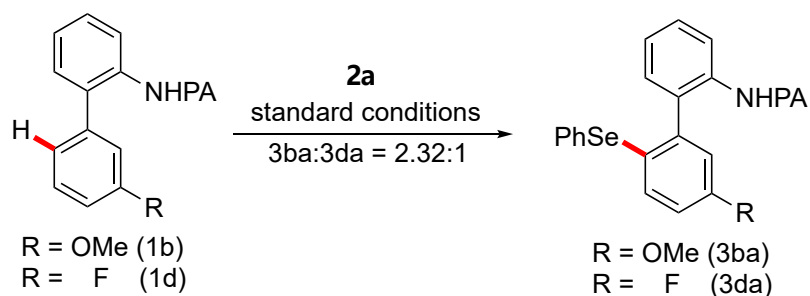
## Scheme S3: H/D Exchanged Experiment



A suspension of *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), Pd(TFA)<sub>2</sub> (3.3 mg, 5.0 mol %), AgOAc (60.1 mg, 0.36 mmol), TFA (10 μL)

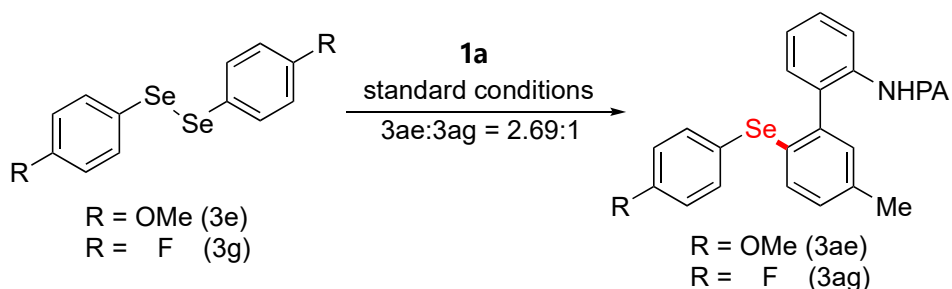
in a mixture solvent of anhydrous PhCF<sub>3</sub> and CH<sub>3</sub>OD (1.8/0.2 mL) was stirred in seal tube under nitrogen at 120 °C for 12 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with DCM (3 x 25 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated to give the crude product. A suspension of the crude product, NaOH (120.0 mg, 3.0 mmol) in EtOH (2.9 mL) was stirred in Schlenk tube under air at 80 °C for 12 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with DCM (3 x 15 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents in *vacuo*, the crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 50/1→20/1) to yield [D]<sub>n</sub>-**1a** (42.7 mg, 74 %) as a brown oil. The D-incorporation in [D]<sub>n</sub>-**1a** was estimated by <sup>1</sup>H-NMR spectroscopy.

#### Scheme S4: Competition experiments



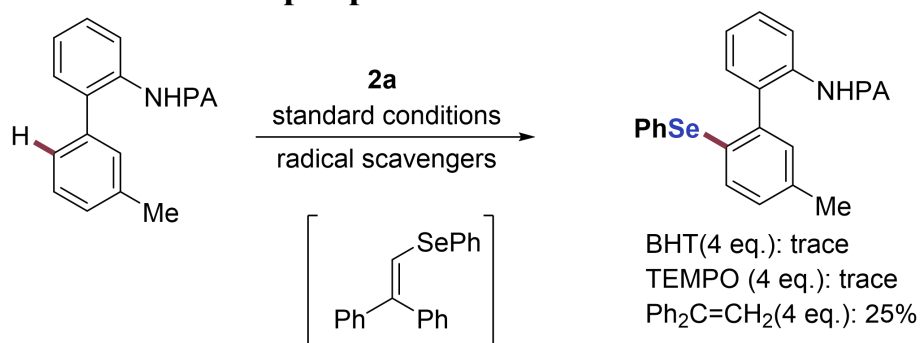
A suspension of *N*-(3'-methoxy-[1,1'-biphenyl]-2-yl)picolinamide (**1b**) (60.5 mg, 0.20 mmol), *N*-(3'-fluoro-[1,1'-biphenyl]-2-yl)picolinamide (**1d**) (58.5 mg, 0.20 mmol), 1,2-diphenyldiselane (**2a**) (62.4 mg, 0.20 mmol), Pd(TFA)<sub>2</sub> (3.3 mg, 5.0 mol %), AgOAc (60.1 mg, 0.36 mmol), TFA (10 μL) in anhydrous PhCF<sub>3</sub> (2.0 mL) was stirred in seal tube under nitrogen at 120 °C for 12 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents in *vacuo*, the crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 30/1→5/1) to yield **3ba** (59.7 mg, 65 %) as a pink solid and yield **3da** (24.6 mg, 28 %) as a white solid.





A suspension of *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-bis(4-methoxyphenyl)diselane (**2e**) (74.7 mg, 0.20 mmol), 1,2-bis(4-fluorophenyl)diselane (**2g**) (69.1 mg, 0.20 mmol), Pd(TFA)<sub>2</sub> (3.3 mg, 5.0 mol %), AgOAc (60.1 mg, 0.36 mmol), TFA (10 μL) in anhydrous PhCF<sub>3</sub> (2.0 mL) was stirred in seal tube under nitrogen at 120 °C for 12 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents in *vacuo*, the crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 30/1→5/1) to yield **3ae** (41.1 mg, 43 %) as a white solid and yield **3ag** (14.7 mg, 16 %) as a white solid.

### Scheme S5: Radical trap experiments

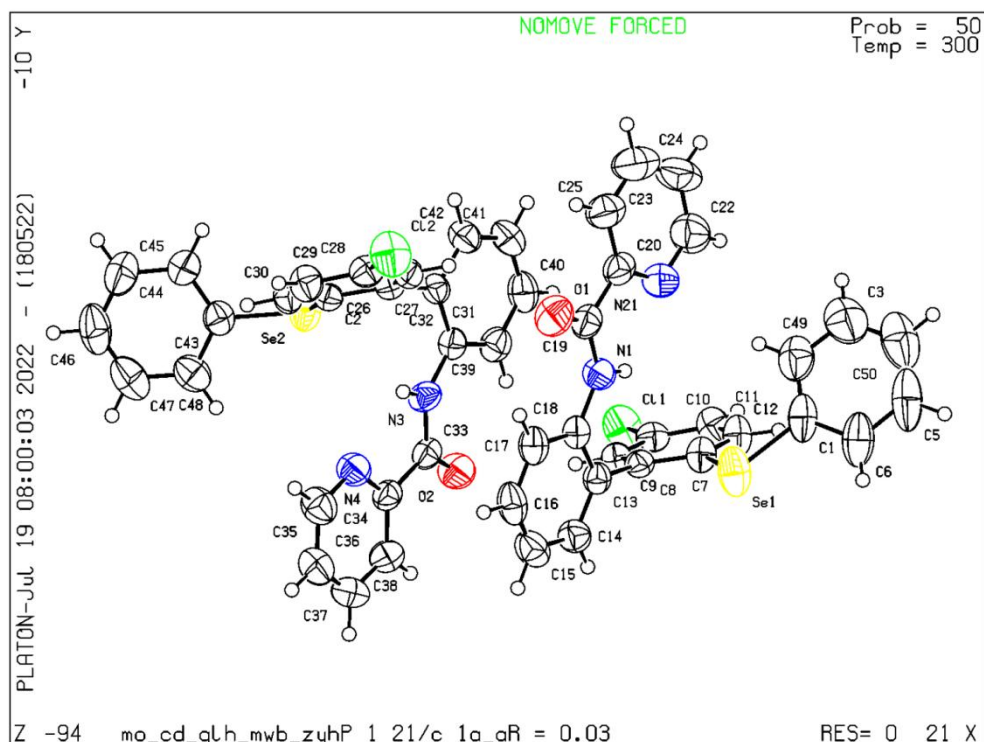


A suspension of *N*-(3'-methyl-[1,1'-biphenyl]-2-yl)picolinamide (**1a**) (57.7 mg, 0.20 mmol), 1,2-diphenyldiselane (**2a**) (62.4 mg, 0.20 mmol), Pd(TFA)<sub>2</sub> (3.3 mg, 5.0 mol%), AgOAc (60.1 mg, 0.36 mmol), TFA (10 μL), the radical scavenger BHT (4 equiv) or TEMPO (4 equiv) or 1,1-diphenylethylene (4 equiv) in anhydrous PhCF<sub>3</sub> (2.0 mL) was stirred in seal tube under nitrogen at 120 °C for 12 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents in *vacuo*, the crude product was

purified by column chromatography on silica gel (Petroleum ether/EtOAc: 30/1→15/1) to yield **3aa** as a white solid.

### **X-Ray crystallographic data of 3ea, 3ka' and 7e**

The structure of **3ea** (CDCC: 2256296), **3ka'** (CDCC: 2256297) and **7e** (CDCC: 2256298) was determined by the X-ray diffraction. Recrystallized from DCM and n-hexane. Further information can be found in the CIF file.



Bond precision: C-C = 0.0045 Å

Wavelength=0.71073

Cell: a=20.765 (5)

b=14.171 (3)

c=15.154 (4)

alpha=90

beta=109.346 (8)

gamma=90

Temperature: 300 K

	Calculated	Reported
Volume	4207.4 (18)	4207.5 (17)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C24 H17 Cl N2 O Se	C24 H17 Cl N2 O Se
Sum formula	C24 H17 Cl N2 O Se	C24 H17 Cl N2 O Se
Mr	463.81	463.80
Dx, g cm <sup>-3</sup>	1.464	1.464
Z	8	8
Mu (mm <sup>-1</sup> )	1.929	1.929
F000	1872.0	1872.0
F000'	1873.02	
h, k, lmax	24, 16, 18	24, 16, 18
Nref	7400	7380
Tmin, Tmax	0.566, 0.654	0.525, 0.746
Tmin'	0.514	

Correction method= # Reported T Limits: Tmin=0.525 Tmax=0.746

AbsCorr = MULTI-SCAN

Data completeness= 0.997

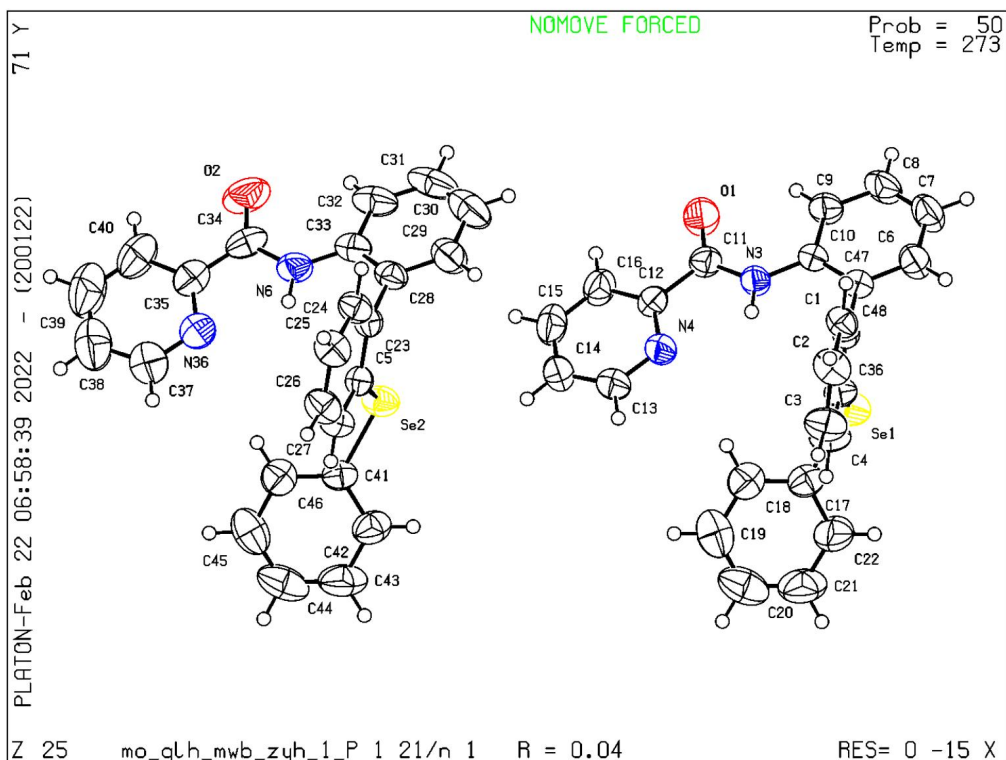
Theta (max)= 24.999

R(reflections)= 0.0334 ( 5162)

wR2(reflections)=  
0.0766 ( 7380)

S = 1.021

Npar= 523



Bond precision: C-C = 0.0049 Å

Wavelength=0.71073

Cell: a=15.2884 (10) b=12.8941 (9) c=21.3671 (16)

alpha=90

beta=106.412 (3)

gamma=90

Temperature: 273 K

	Calculated	Reported
Volume	4040.5 (5)	4040.5 (5)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C24 H18 N2 O Se	C24 H18 N2 O Se
Sum formula	C24 H18 N2 O Se	C24 H18 N2 O Se
Mr	429.36	429.36
Dx, g cm <sup>-3</sup>	1.412	1.412
Z	8	8
Mu (mm <sup>-1</sup> )	1.875	1.875
F000	1744.0	1744.0
F000'	1743.82	
h, k, lmax	19, 16, 27	19, 16, 27
Nref	9357	9312
Tmin, Tmax	0.378, 0.384	0.499, 0.746
Tmin'	0.349	

Correction method= # Reported T Limits: Tmin=0.499 Tmax=0.746

AbsCorr = MULTI-SCAN

Data completeness= 0.995

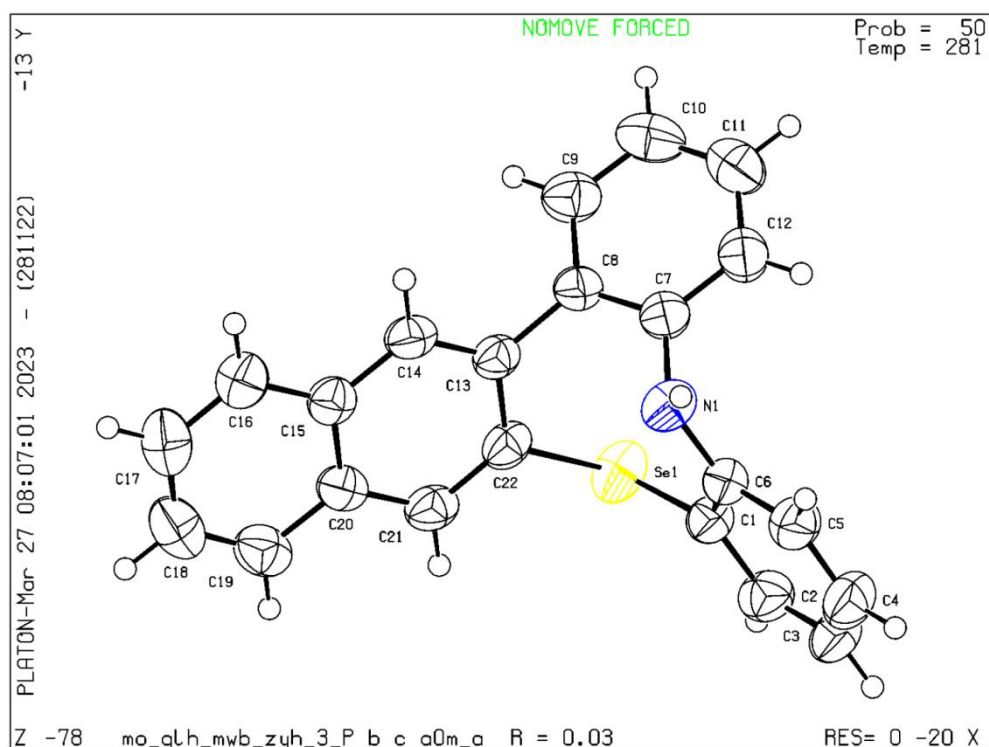
Theta (max)= 27.588

R(reflections)= 0.0433 ( 5176)

wR2(reflections)=  
0.0954 ( 9312)

S = 0.996

Npar= 506



Bond precision: C-C = 0.0042 Å

Wavelength=0.71073

Cell: a=8.3047(2)

b=18.4642(6)

c=21.7070(7)

alpha=90

beta=90

gamma=90

Temperature: 281 K

	Calculated	Reported
Volume	3328.54(17)	3328.54(17)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C22 H15 N Se	C22 H15 N Se
Sum formula	C22 H15 N Se	C22 H15 N Se
Mr	372.31	372.31
Dx, g cm <sup>-3</sup>	1.486	1.486
Z	8	8
Mu (mm <sup>-1</sup> )	2.257	2.257
F000	1504.0	1504.0
F000'	1503.71	
h, k, lmax	9, 21, 25	9, 21, 25
Nref	2915	2915
Tmin, Tmax	0.414, 0.835	0.527, 0.746
Tmin'	0.373	

Correction method= # Reported T Limits: Tmin=0.527 Tmax=0.746

AbsCorr = MULTI-SCAN

Data completeness= 1.000

Theta(max)= 24.999

R(reflections)= 0.0313( 2117)

wR2(reflections)=  
0.0794( 2915)

S = 1.026

Npar= 221

**Reference:**

1. A. Baccalini, S. Vergura, P. Dolui, S. Maiti, S. Dutta, S. Maity, F. F. Khan, G. K. Lahiri, G. Zanoni, D. Maiti, *Org. Lett.*, 2019, **21**, 8842.
2. W. Ma, Y. Zhou, Y. Wang, B. Li, T. Zheng, Z. Cheng, R. Mei, *Adv. Synth. Catal.*, 2022, **364**, 3544.
3. J. L. Kenwright, W. R. J. D. Galloway, D. T. Blackwell, A. Isidro-Llobet, J. Hodgkinson, L. Wortmann, S. D. Bowden, M. Welch, D. R. Spring. *Chem. Eur. J.*, 2011, **17**, 2981.



