Photoinduced, Additive- and Photosensitizer-free

Multi-component Synthesis of

Naphthoselenazol-2-amines With Air in Water

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1. General Information

Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification. GC yield was detected by Agilent GC-MS 8890/5977B. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel. ¹H NMR spectra were recorded at 500 MHz and ¹³C NMR spectra were recorded at 125 MHz by using a Bruker Avance 500 spectrometer. ¹⁹F NMR data were collected at 471 MHz with complete proton decoupling. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (¹H NMR: CDCl₃ 7.26 ppm, ¹³C NMR: CDCl₃ 77.16 ppm,), the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet, dd = doublet of doublets, br = broad. Mass spectra were performed on a spectrometer operating on ESI-TOF. UV/Vis spectra were recorded using a Shimadzu UV-2600 spectrophotometer. The crude products were purified by HPLC (LaboACE LC-5060, Japan Analytical Industry Co., Ltd., Japan) equipped with Jaigel 2.5 HR columns with dichloromethane as the eluent. Cyclic voltammetry was performed on a CHI 660E potentiostat, and the conditions are as follow: a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl (0.3 M in MeCN) as counter and reference electrode. The fluorescence emission intensities were recorded on a Hitachi F-7100 fluorescence spectrophotometer.

Photographic depiction of the reaction setup:

Manufacturer: Beijing Rogertech Ltd.

Model: RLR-22CU

Value: 5836.430 µW/cm²/nm

Energy peak wavelength: 453 nm

Peak width at half-height: 22.1 nm

Material of the irradiation vessel: Schlenk flask

Not use any filters





Figure S1 LED spectrum test report



Figure S2 Photographic depiction of the reaction setup

2. Experimental Section

2.1 General Experimental Procedures for Compounds 4



To a 10 mL Schlenk flask equipped with a stirring bar were added 2-isocyanonaphthalene **1** (0.20 mmol), selenium powder **2** (0.24 mmol), amine **3** (0.24 mmol) and H₂O (2.0 mL). The reaction mixture was stirred and irradiatted by 10 W blue LEDs (455 nm) under room temperature for 12 hrs. After completion, the reaction mixture was extracted with 5 mL ethyl acetate, organic phase was dried and concentrated under reduced pressure. The pure products **4** were purified and obtained by flash chromatography on silica gel (elute: petroleum ether/ethyl acetate, 10:1 to 5:1).

2.2 Large Scale Synthesis of 4aa



To an Schlenk flask (50 mL) equipped with a stirring bar were added 2-isocyanonaphthalene **1a** (5.0 mmol), selenium powder **2** (6.0 mmol), *N*-methylaniline **3a** (6.0 mmol), and H₂O (30.0 mL). The reaction mixture was stirred and irradiatted by 10 W blue LEDs (455 nm) under room temperature. After completion, the reaction mixture was extracted with ethyl acetate, organic phase was dried and concentrated under reduced pressure. The pure products **4aa** were purified by HPLC in a yield of 81% (1.37 g).



Figure S3 Photographic depiction of Gram-scale synthesis





- (a) Under the standard conditions, the intermediate 5aa was added to 2 mL H₂O, the reaction was monitored by TLC. Upon completion, the reaction mixture was analyzed by GC and a 98% GC yield of 4aa was detected.
- (b) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added 2-isocyanonaphthalene 1a (0.2 mmol), selenium powder 2 (0.24 mmol), and N-methylaniline 3a (0.24 mmol), radical scavengers (TEMPO, 0.4 mmol) and H₂O (2.0 mL). Then the reaction mixture was stirred and irradiated by 10 W blue LEDs at ambient temperature for 12 hrs. The reaction mixture was analyzed by GC and a 72% GC yield of 4aa was detected.

- (c) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added 2-isocyanonaphthalene 1a (0.2 mmol), selenium powder 2 (0.24 mmol), and N-methylaniline 3a (0.24 mmol), radical scavengers (BHT, 0.4 mmol) and H₂O (2.0 mL). Then the reaction mixture was stirred and irradiated by 10 W blue LEDs at ambient temperature for 12 hrs. The reaction mixture was analyzed by GC and a 69% GC yield of 4aa was detected.
- (d) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added 2-isocyanonaphthalene 1a (0.2 mmol), selenium powder 2 (0.24 mmol), and N-methylaniline 3a (0.24 mmol), scavengers (DBACO, 0.4 mmol) and H₂O (2.0 mL). Then the reaction mixture was stirred and irradiated by 10 W blue LEDs at ambient temperature for 12 hrs. The reaction mixture was analyzed by GC and a 94% GC yield of 4aa was detected.
- (e) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added 2-isocyanonaphthalene 1a (0.2 mmol), selenium powder 2 (0.24 mmol), and N-methylaniline 3a (0.24 mmol), scavengers (benzoquinone, 1 mmol) and H₂O (2.0 mL). Then the reaction mixture was stirred and irradiated by 10 W blue LEDs at ambient temperature for 12 hrs. The reaction mixture was analyzed by GC and a trace amount of 4aa was detected.
- (f) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added 2-isocyanonaphthalene 1a (0.2 mmol), selenium powder 2 (0.24 mmol), and N-methylaniline 3a (0.24 mmol), scavengers (K₂S₂O₈, 0.4 mmol) and H₂O (2.0 mL). Then the reaction mixture was stirred and irradiated by 10 W blue LEDs at ambient temperature for 12 hrs. The reaction mixture was analyzed by GC and a trace amount of 4aa was detected.

2.4 Effect of Visible Light Irradiation

The reaction between 1a (0.2 mmol), 2 (0.24 mmol) and 3a (0.24 mmol) was conducted under the standard conditions on a 0.2 mmol scale. The mixture was subjected to sequential periods of stirring under visible light irradiation (10 W blue LEDs) under an air atmosphere at room temperature with 3 hrs and followed by stirring in the absence of light with 3 hrs. At each time point, one reaction system was suspended and the yield was detected by GC.



Figure S4 Visible light irradiation on/off experiments

2.5 UV/Vis Absorption Experiment



Figure S5 UV/Vis spectroscopic measurements

The UV/Vis absorption spectra of **1a**, **4aa** and selenourea **5aa** were recorded in 1 cm path quartz cuvettes in a concentration of 0.003 M by using a Shimadzu UV-2600 spectrophotometer, respectively.

2.6 Fluorescence Quenching Experiments

The fluorescence emission intensities were measured using a Hitachi F-7100 fluorescence spectrophotometer at an excitation wavelength of 385 nm. The samples consisted of **4aa** (1 mM), the in-situ-formed complex (a mixture of **4aa** and **5aa**) dissolved in THF. The resulting emission intensity data were collected.



Figure S6 Fluorescence quenching experiments

2.7 Cyclic voltammetry studies

CV measurements were performed on a CHI 660E potentiostat, and the conditions are as follow: a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl as counter and reference electrode. Cyclic voltammograms of reactants and their mixtures in 0.3 M tetrabutylammonium bromide glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl (0.1 M in EtOH) as counter and reference electrode at 100 mV/s scan rate: a) 5 mM of **4aa** in MeCN (10 mL) (black line), (2) 5 mM of **5aa** in MeCN (10 mL) (red line).



Figure S7 Cyclic voltammogram experiments of **4aa** and **5aa** in an electrolyte of ^{*n*}Bu₄NBr (0.3 M) in MeCN from -2 V to +2 V at room temperature

2.8 Calculation of Apparent Quantum Yield

$$E_{photon} = \frac{hc}{\lambda_{inc}(455 \text{ nm})} = \frac{6.63 \times 10^{-34} \text{ J.Sx} 3 \times 10^8 \text{ m.s}^{-1}}{455 \times 10^{-9} \text{ m}} = 4.37 \times 10^{-19} \text{ J}$$

 E_{total} =PSt = 17.47x 10⁻³ W.cm⁻²x4.78 cm² x12x3600s = 3.6x10³ J

Number of incident photons = $\frac{E_{photon}}{E_{tota}}$ = $\frac{3.6 \times 10^3 \text{ J}}{4.37 \times 10^{-19} \text{ J}}$ =8.24x10²¹=13.58 mmol A.Q.Y(%) = $\frac{\text{Number of Product}}{\text{Number of incident photons}}$ = $\frac{0.194 \text{mmol}}{13.58 \text{ mmol}}$ =1.4 %< 1

Figure S8 Apparent Quantum Yield

Where h (J·s) is Planck's constant, c $(m \cdot s^{-1})$ is the speed of light and λ inc (m) is the wavelength of the incident light. P $(W \cdot cm^{-2})$ is the power density of the incident light, S (cm^2) is the irradiation area and t (s) is the photoreaction time.

3. Characterization data of products



N-phenyl-N-methylnaphtho[2,1-d][1,3]selenazol-2-amine (4aa): 97%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, J = 8.0 Hz, 1H), 7.83-7.75 (m, 2H), 7.50 (d, J = 4.4 Hz, 5H), 7.46-7.33 (m, 3H), 3.69 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.58, 152.23, 147.08, 130.44, 130.12, 129.77, 129.56, 128.68, 127.64, 126.69, 126.51, 125.89, 125.82, 123.89, 120.81, 40.38; HRMS: calcd for C₁₈H₁₅N₂Se [M+H]⁺ 339.0395, found 339.0393.



N-methyl-N-(p-tolyl)naphtho[2,1-d][1,3]*selenazol-2-amine (4ab)*: 87%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.7 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.48 (d, J = 8.1 Hz, 1H), 7.46-7.39 (m, 1H), 7.38-7.34 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 3.66 (s, 3H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.93, 152.32, 144.58, 137.75, 130.71, 130.42, 129.73, 129.45, 128.64, 126.62, 126.46, 125.84, 125.76, 123.78, 120.72, 40.32, 21.12; HRMS: calcd for C₁₉H₁₇N₂Se [M+H]⁺ 353.0551, found 353.0545.



N-(4-methoxyphenyl)-*N*-methylnaphtho[2,1-d][1,3]selenazol-2-amine (4ac): 86%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.82-7.73 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.38-7.3 (m, 3H), 7.02-6.96 (m, 2H), 3.85 (s, 3H), 3.63 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.48, 158.98, 152.57, 140.12, 130.50, 129.98, 129.44, 128.64, 127.79, 126.61, 126.45, 125.78, 123.75,

120.78, 115.26, 55.44, 40.41; HRMS: calcd for $C_{19}H_{17}N_2OSe [M+H]^+$ 369.0501, found 369.0501.



N-methyl-N-(4-(methylthio)phenyl)naphtho[2,1-d][1,3]selenazol-2-amine (4ad): 84%, black oil. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.53-7.48 (m, 2H), 7.45 (t, *J* = 6.9 Hz, 1H), 7.41-7.34 (m, 3H), 3.54 (s, 3H), 2.52 (s, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 169.06, 152.19, 143.41, 137.99, 130.01, 129.21, 129.08, 128.65, 127.20, 127.03, 126.79, 126.49, 125.81, 124.13, 120.66, 40.27, 14.66; HRMS: calcd for C₁₉H₁₇N₂SSe [M+H]⁺ 385.0272, found 385.0275.



N-methyl-N-(4-(trifluoromethoxy)phenyl)naphtho[2,1-d][1,3]selenazol-2-amine (*4ae*): 90%, yellow oil. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.93 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.7 Hz, 1H), 7.79-7.74 (d, 2H), 7.72 (d, J = 8.7 Hz, 1H), 7.66 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.51-7.44 (m, 1H), 7.40 (t, J = 7.5 Hz, 1H), 3.59 (s, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 168.58, 151.95, 146.78, 145.35, 129.98, 129.36, 129.19, 128.68, 127.74, 127.12, 126.93, 125.91, 124.33, 122.78, 121.12, 120.75, 119.08 (q, J = 257.04 Hz), 40.60. ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -56.88; HRMS: calcd for C₁₉H₁₄F₃N₂OSe [M+H]⁺ 423.0218, found 423.0217.



N-(4-fluorophenyl)-*N*-methylnaphtho[2,1-d][1,3]selenazol-2-amine (4af): 85%, black oil. ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.78 (q, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.46-7.41 (m, 3H), 7.38-7.35 (m, 1H), 7.22-7.14 (m, 2H), 3.63 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.68, 162.51, 160.53 (t, *J* = 10.0 Hz), 152.26, 143.03, 143.00, 136.40, 130.40, 130.02, 129.53, 128.68, 128.22, 128.15 (d, J = 8.82 Hz), 126.77, 126.58 (d, J = 23.94 Hz), 125.79, 123.97, 120.81, 117.12, 116.94 (d, J = 22.68 Hz), 40.54. ¹⁹F NMR (471 MHz, CDCl₃) δ -112.76; HRMS: calcd for C₁₈H₁₄FN₂Se [M+H]⁺ 357.0301, found 357.0304.



N-(4-chlorophenyl)-N-methylnaphtho[2,1-*d*][1,3]selenazol-2-amine (4ag): 84%, yellow oil. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.68-7.62 (m, 3H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.51-7.44 (m, 1H), 7.42-7.39 (m, 1H), 3.58 (s, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 168.61, 151.98, 145.28, 131.70, 130.15, 129.96, 129.30, 129.16, 128.67, 127.65, 127.10, 126.89, 125.85, 124.28, 120.72, 40.43; HRMS: calcd for C₁₈H₁₄ClN₂Se [M+H]⁺ 373.0005, found 373.0007.



N-(4-bromophenyl)-N-methylnaphtho[2,1-d][1,3]selenazol-2-amine (4ah): 80%, yellow oil. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.74-7.71 (m, 3H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.60-7.52 (m, 2H), 7.51-7.44 (m, 1H), 7.41-7.38 (m, 1H), 3.57 (d, *J* = 1.1 Hz, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 168.48, 151.95, 145.68, 133.07, 129.96, 129.31, 129.17, 128.68, 127.86, 127.10, 126.89, 125.85, 124.29, 120.72, 120.03, 40.40; HRMS: calcd for C₁₈H₁₄BrN₂Se [M+H]⁺ 416.9500, found 416.9503.



N-methyl-N-(m-tolyl)naphtho[2,1-*d*][1,3]selenazol-2-amine (4ai): 88%, yellow oil. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.50-7.31 (m, 5H), 7.23 (d, *J* = 7.5 Hz, 1H), 3.57 (s, 3H), 2.36 (s, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 168.92, 152.11, 146.65, 139.94, 130.04, 130.01, 129.09, 129.02, 128.63, 128.43, 126.97, 126.74, 126.11, 125.82, 124.09, 122.66, 120.65, 40.21, 20.93; HRMS: calcd for C₁₉H₁₇N₂Se [M+H]⁺ 353.0551, found 353.0549.



N-methyl-N-(o-tolyl)naphtho[2,1-d][1,3]selenazol-2-amine (4aj): 83%, yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 7.87-7.74 (m, 3H), 7.46-7.31 (m, 7H), 3.60 (s, 3H), 2.34 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.22, 152.61, 145.30, 136.61, 132.15, 130.53, 130.24, 129.29, 129.14, 128.66, 128.47, 128.08, 126.67, 126.48, 125.74, 123.75, 120.72, 39.26, 17.44; HRMS: calcd for C₁₉H₁₇N₂Se [M+H]⁺ 353.0551, found 353.0555.



Methyl-N-propylnaphtho[2,1-d][1,3]selenazol-2-amine (4ak): 98%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.75-7.74 (m, 1H), 7.64 (s, 2H), 7.50-7.48 (m, 1H), 7.38-7.35 (m, 1H), 7.27-7.24 (m, 1H), 3.39-3.37 (t, J = 5 Hz, 2H), 3.11 (s, 3H), 1.68-1.64 (m, 2H), 0.91-0.88 (t, J = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.47, 152.87, 130.71, 129.37, 129.14, 128.79, 126.76, 126.60, 125.81, 123.63, 120.73, 56.59, 38.84, 20.63, 11.39; HRMS: calcd for C₁₅H₁₇N₂Se [M+H]⁺ 305.0551, found 305.0553.



Methyl-N-octylnaphtho[2,1-d][1,3]selenazol-2-amine (4al): 90%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.89-7.77 (m, 3H), 7.64-7.62 (m, 1H), 7.51-7.48 (m, 1H), 7.40-7.37 (m, 1H), 3.55-3.52 (t, J = 7.5 Hz, 2H), 3.24 (s, 3H), 1.77-1.72 (m, 2H), 1.39-1.32 (m, 10H), 0.94-0.91 (t, J = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.38, 152.85, 130.72, 129.35, 129.14, 128.78, 126.74, 126.58, 125.81, 123.62, 120.73, 55.07, 38.75, 31.85, 29.40, 29.28, 27.29, 26.90, 22.69, 14.16; HRMS: calcd for C₂₀H₂₇N₂Se [M+H]⁺ 375.1334, found 375.1330.



(tert-butyl)-N-methylnaphtho[2,1-d][1,3]selenazol-2-amine (4am): 95%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.90-7.68 (m, 4H), 7.52-7.39 (m, 2H), 3.18 (s, 3H), 1.67 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 168.84, 152.63, 130.60, 129.78, 129.21, 128.75, 126.47, 126.41, 126.32, 123.64, 121.22, 59.37, 39.13, 28.31; HRMS: calcd for C₁₆H₁₉N₂Se [M+H]⁺ 319.0708, found 319.0713.



N-cyclopropyl-N-methylnaphtho[2,1-d][1,3]selenazol-2-amine (4an): 92%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7,90-7.37 (m, 6H), 3.39-3.31 (m, 3H), 2.82-2.27 (m, 1H), 0.98-0.91 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 171.52, 152.17, 130.65, 129.91, 129.32, 128.78, 126.61, 126.56, 125.95, 123.86, 121.00, 38.48, 36.18, 8.89; HRMS: calcd for C₁₅H₁₅N₂Se [M+H]⁺ 303.0395, found 303.0399.



N-cyclohexyl-N-methylnaphtho[2,1-*d*][1,3]selenazol-2-amine (4ao): 65%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.74 (s, 2H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.50-7.44 (m, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 3.85 (s, 1H), 3.11 (s, 3H), 1.97-1.87 (m, 4H), 1.75-1.71 (m, 1H), 1.60-1.41 (m, 4H), 1.21-1.11 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.77, 152.58, 130.57, 129.00, 128.68, 128.59, 126.62, 126.46, 125.66, 123.47, 120.60, 62.23, 33.28, 30.09, 25.75, 25.40; HRMS: calcd for C₁₈H₂₁N₂Se [M+H]⁺ 345.0864, found 345.0867.



N-benzyl-N-methylnaphtho[2,1-*d*][1,3]selenazol-2-amine (4ap): 72%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, J = 8.1 Hz, 1H), 7.78 (s, 2H), 7.61 (d, J = 8.1 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.41-7.28 (m, 6H), 4.81 (s, 2H), 3.18 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.96, 152.60, 136.20, 130.60, 129.71, 129.17, 128.75, 128.72, 127.73, 127.54, 126.80, 126.59, 125.74, 123.72, 120.75, 57.45, 38.90; HRMS: calcd for C₁₉H₁₇N₂Se [M+H]⁺ 353.0551, found 353.0551.



Ethyl N-methyl-N-(naphtho[2,1-d][1,3]selenazol-2-yl)glycinate (4aq): 88%, light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.89-7.35 (m, 6H), 4.44 (s, 2H), 4.28-4.22 (m, 2H), 3.29-3.23 (m, 3H), 1.32-1.27 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.60, 169.12, 152.40, 130.62, 129.31, 128.79, 126.83, 126.68, 125.87, 125.84,

123.96, 121.05, 61.43, 53.74, 41.07, 14.25; HRMS: calcd for C₁₆H₁₇N₂O₂Se [M+H]⁺ 349.0450, found 349.0447.



N-(2,2-dimethoxyethyl)-N-methylnaphtho[2,1-d][1,3]selenazol-2-amine (4ar): 95%, white oil. ¹H NMR (500 MHz, CDCl₃) δ 7.76-7.75 (d, J = 5 Hz, 1H), 7.65 (d, J = 5 Hz, 2H), 7.52-7.50 (d, J = 10 Hz, 1H), 7.39-7.36 (t, J = 7.5 Hz, 1H), 7.28-7.25 (t, J = 7.5 Hz, 1H), 4.63-4.60 (t, J = 7.5 Hz, 1H), 3.60-3.59 (d, J = 5 Hz, 2H), 3.36 (s, 6H), 3.16 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.40, 152.74, 130.68, 129.83, 129.19, 128.79, 126.80, 126.66, 125.85, 123.79, 120.89, 102.98, 55.81, 55.04, 41.31; HRMS: calcd for C₁₆H₁₉N₂O₂Se [M+H]⁺ 351.0606, found 351.0607.



Methyl-N-(pyridin-4-ylmethyl)naphtho[2,1-d][1,3]selenazol-2-amine (4as): 70%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.60-8.54 (m, 2H), 7.89-7.20 (m, 8H), 4.85 (s, 2H), 3.18 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.72, 152.48, 150.20, 145.77, 130.62, 130.23, 129.34, 128.84, 127.03, 126.81, 125.81, 124.05, 122.36, 120.89, 55.70, 39.75; HRMS: calcd for C₁₈H₁₆N₃Se [M+H]⁺ 354.0504, found 354.0500.



Isopropyl-N-phenylnaphtho[2,1-d][1,3]*selenazol-2-amine (4at)*: 72%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.75-7.65 (m, 3H), 7.48-7.43 (m, 3H), 7.35-7.17 (m, 5H),

5.20-5.14 (m, 1H), 1.21 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 170.81, 152.60, 142.20, 130.94, 130.51, 130.16, 129.57, 129.35, 129.16, 128.70, 126.63, 126.45, 125.88, 123.68, 120.85, 51.42, 21.26; HRMS: calcd for C₂₀H₁₉N₂Se [M+H]⁺ 367.0708, found 367.0710.



N,N-diisopropylnaphtho[2,1-d][1,3]selenazol-2-amine (4au): 84%, yellow solid. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.91 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.63-7.61 (m, 2H), 7.51-7.49 (m, 1H), 7.38-7.35 (m, 1H), 3.88-3.80 (m, 2H), 1.42 (d, J = 6.7 Hz, 12H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 165.68, 152.77, 130.05, 128.69, 128.49, 127.34, 126.94, 126.49, 125.75, 123.58, 120.47, 19.97; HRMS: calcd for C₁₇H₂₁N₂Se [M+H]⁺ 333.0864, found 333.0867.



N,N-diethylnaphtho[2,1-*d*][1,3]selenazol-2-amine (4av): 90%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.88-7.82 (m, 1H), 7.74 (s, 2H), 7.59 (d, J = 8.2 Hz, 1H), 7.50-7.44 (m, 1H), 7.39-7.32 (m, 1H), 3.60 (q, J = 7.2 Hz, 4H), 1.33 (t, J = 7.2 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 168.21, 152.81, 130.65, 129.03, 128.94, 128.69, 126.58, 126.46, 125.74, 123.46, 120.59, 46.55, 12.86; HRMS: calcd for C₁₅H₁₇N₂Se [M+H]⁺ 305.0551, found 305.0552.



N,N-dihexylnaphtho[2,1-d][1,3]selenazol-2-amine (4aw): 70%, yellow oil. ¹H NMR (500 MHz, DMSO- d_6) δ 7.90 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.62 (t, J = 8.3 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 3.46 (t, J = 7.5 Hz, 4H), 1.65 (t, J = 7.4 Hz, 4H), 1.28 (q, J = 7.8, 7.0 Hz, 12H), 0.88-0.82 (m, 6H); ¹³C NMR (125 MHz, DMSO- d_6) δ 168.15, 152.63, 130.19, 128.68, 128.55, 128.31, 126.98, 126.63, 125.59, 123.68, 120.41, 31.03, 27.01, 26.00, 22.11, 13.94; HRMS: calcd for C₂₃H₃₃N₂Se [M+H]⁺ 417.1803, found 417.1805.



2-(azetidin-1-yl)naphtho[2,1-d][1,3]selenazole (4ax): 98%, white oil. ¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, J = 8.1 Hz, 1H), 7.75 (s, 2H), 7.58 (d, J = 8.2 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 4.20 (t, J = 7.5 Hz, 4H), 2.53-2.47 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 169.39, 152.54, 130.80, 130.46, 129.27, 128.79, 126.90, 126.70, 125.96, 123.92, 120.76, 53.60, 17.24; HRMS: calcd for C₁₄H₁₃N₂Se [M+H]⁺ 289.0238, found 289.0236.



2-(pyrrolidin-1-yl)naphtho[2,1-d][1,3]selenazole (4ay): 75%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, J = 8.1 Hz, 1H), 7.81-7.72 (m, 2H), 7.60 (d, J = 8.2 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 3.58 (d, J = 6.4 Hz, 4H), 2.11-2.03 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 166.00, 152.76, 130.69, 129.18, 128.94, 128.67, 126.71, 126.48, 125.72, 123.50, 120.62, 50.41, 25.60; HRMS: calcd for C₁₅H₁₅N₂Se [M+H]⁺ 303.0395, found 303.0394.



2-(*piperidin-1-yl*)*naphtho*[2,1-*d*][1,3]*selenazole* (4*az*): 95%, white oil. ¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, J = 8.1 Hz, 1H), 7.77-7.67 (m, 2H), 7.58 (d, J = 8.2 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 3.60 (t, J = 5.2 Hz, 4H), 1.73-1.68 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 170.16, 152.60, 130.67, 129.34, 129.26, 128.79, 126.77, 126.60, 125.85, 123.74, 120.76, 51.01, 25.46, 24.36; HRMS: calcd for C₁₆H₁₇N₂Se [M+H]⁺ 317.0551, found 317.0555.



2-(azepan-1-yl)naphtho[2,1-d][1,3]selenazole (4aA): 84%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, J = 8.1 Hz, 1H), 7.75 (s, 2H), 7.60 (d, J = 8.1 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 3.68 (t, J = 6.1 Hz, 4H), 1.95-1.81 (m, 4H), 1.65-1.61 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 169.08, 152.81, 130.60, 128.93, 128.78, 128.65, 126.58, 126.43, 125.68, 123.40, 120.56, 51.90, 27.83, 27.52; HRMS: calcd for C₁₇H₁₉N₂Se [M+H]⁺ 331.0708, found 331.0706.



2-(4-methylpiperazin-1-yl)naphtho[2,1-d][1,3]selenazole (4aB): 70%, yellow oil. ¹H NMR (500 MHz, DMSO- d_6) δ 7.93 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.6 Hz, 1H), 7.65 (t, J = 7.7 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 3.57 (t, J = 5.1Hz, 4H), 2.45 (t, J = 5.1 Hz, 4H), 2.23 (s, 3H); ¹³C NMR (125 MHz, DMSO- d_6) δ 169.59, 152.16, 130.13, 129.08, 128.82, 128.76, 127.14, 126.84, 125.71, 124.11, 120.62, 53.88, 49.19, 45.68; HRMS: calcd for $C_{16}H_{18}N_3Se [M+H]^+$ 332.0660, found 332.0661.



4-(naphtho[2,1-d][1,3]selenazol-2-yl)morpholine (4aC): 85%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, J = 8.1 Hz, 1H), 7.75 (q, J = 8.7 Hz, 2H), 7.62 (d, J = 8.2 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 3.85 (t, J = 5.0 Hz, 4H), 3.66-3.61 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 170.37, 151.98, 130.47, 129.66, 129.38, 128.76, 126.94, 126.69, 125.80, 124.07, 120.84, 66.24, 49.63; HRMS: calcd for C₁₅H₁₅N₂OSe [M+H]⁺ 319.0344, found 319.0347.



3-(naphtho[2,1-d][1,3]selenazol-2-yl)thiazolidine (4aD): 95%, white oil. ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, J = 8.1 Hz, 1H), 7.77 (s, 2H), 7.61 (d, J = 8.1 Hz, 1H), 7.51-7.48 (m, 1H), 7.41-7.38 (m, 1H), 4.73 (s, 2H), 3.92 (t, J = 6.2 Hz, 2H), 3.22 (t, J = 6.2 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 165.76, 152.16, 130.63, 130.29, 129.43, 128.83, 127.08, 126.79, 125.86, 124.15, 120.96, 53.66, 52.42, 30.69; HRMS: calcd for C₁₄H₁₃N₂SSe [M+H]⁺ 320.9959, found 320.9955.



4-(naphtho[2,1-d][1,3]selenazol-2-yl)thiomorpholine (4aE): 95%, white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.69 (d,

J = 8.7 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 4.00-3.93 (m, 4H), 2.81-2.74 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 169.36, 152.24, 130.57, 129.78, 129.42, 128.84, 126.98, 126.76, 125.82, 124.06, 120.86, 52.65, 26.79; HRMS: calcd for C₁₅H₁₅N₂SSe [M+H]⁺ 335.0116, found 335.0119.



6-(naphtho[2,1-d][1,3]selenazol-2-yl)-2-oxa-6-azaspiro[3.3]heptane (4aF): 96%, white oil. ¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, J = 8.1 Hz, 1H), 7.76 (s, 2H), 7.59 (d, J = 8.1 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 4.86 (s, 3H), 4.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.04, 152.18, 130.95, 130.71, 129.45, 128.84, 127.09, 126.84, 125.97, 124.24, 120.83, 80.77, 62.86, 39.73; HRMS: calcd for C₁₆H₁₅N₂OSe [M+H]⁺ 331.0344, found 331.0347.



2-(3,4-dihydroquinolin-1(2H)-yl)naphtho[2,1-d][1,3]selenazole (4aG): 97%, yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.74-7.65 (m, 2H), 7.49 (d, J = 8.2 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.33-7.26 (m, 1H), 7.20-7.13 (m, 1H), 7.10 (d, J = 7.4 Hz, 1H), 7.03 (t, J = 7.4 Hz, 1H), 4.05 (t, J = 6.2 Hz, 2H), 2.72 (t, J = 6.4 Hz, 2H), 2.04-1.95 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 167.88, 151.23, 141.41, 131.00, 130.37, 129.89, 129.11, 128.99, 128.71, 126.81, 126.70, 126.62, 125.96, 124.50, 124.18, 120.96, 120.51, 49.80, 27.35, 23.45; HRMS: calcd for C₂₀H₁₇N₂Se [M+H]⁺ 365.0551, found 365.0556.



2-(1H-imidazol-1-yl)naphtho[2,1-d][1,3]selenazole (4aH): 60%, yellow oil. ¹H NMR (500 MHz, DMSO- d_6) δ 8.62 (s, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.04 (dd, J = 5.5, 3.0 Hz, 4H), 7.68 (t, J = 7.4 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 1.4 Hz, 1H); ¹³C NMR (125 MHz, DMSO- d_6) δ 157.75, 149.25, 136.90, 134.31, 130.96, 130.55, 129.73, 128.96, 127.97, 127.86, 126.59, 126.49, 122.13, 118.96; HRMS: calcd for C₁₄H₁₀N₃Se [M+H]⁺ 300.0034, found 300.0034.



7-bromo-N-methyl-N-phenylnaphtho[2,1-d][1,3]selenazol-2-amine (4ba): 73%, yellow oil, ¹H NMR (500 MHz, DMSO- d_6) δ 8.22 (s, 1H), 7.83 (d, J = 8.7 Hz, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.65-7.59 (m, 3H), 7.59-7.54 (m, 3H), 7.47-7.42 (m, 1H), 3.60 (s, 3H); ¹³C NMR (126 MHz, DMSO- d_6) δ 169.39, 152.69, 146.56, 130.49, 130.37, 129.73, 129.07, 128.60, 128.03, 127.95, 126.10, 125.83, 121.72, 116.81, 40.37; HRMS: calcd for C₁₈H₁₄BrN₂Se [M+H]⁺416.9500, found 416.9503.



N,7-*dimethyl-N-phenylnaphtho*[2,1-*d*][1,3]*selenazol-2-amine (4ca)*: 84%, yellow oil. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.78-7.64 (m, 3H), 7.62-7.49 (m, 5H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 3.59 (s, 3H), 2.44 (s, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 168.43, 151.44, 146.66, 133.28, 130.20, 129.29, 129.02, 128.99, 128.14, 127.63, 127.53, 126.11, 125.70, 125.68, 120.60, 40.26, 21.02; HRMS: calcd for C₁₉H₁₇N₂Se [M+H]⁺ 353.0551, found 353.0549.

4. Reference

- 1. H. Liu, Z.-L. Ye, Z.-J. Cai and S.-J. Ji, Green Chem., 2023, 25, 4239.
- 2. Y. Fang, Z.-L. Zhu, P. Xu, S.-Y. Wang and S.-J. Ji, Green Chem., 2017, 19, 1613.

5. ¹H, ¹⁹F and ¹³C NMR spectra of products



¹³C NMR of compound **4aa**



¹³C NMR of compound **4ab**



¹³C NMR of compound **4ac**



¹³C NMR of compound **4ad**



¹³C NMR of compound **4ae**



S29



¹³C NMR of compound **4af**







¹³C NMR of compound **4ag**



¹H NMR of compound **4ah**



¹H NMR of compound 4ai



¹H NMR of compound 4aj



S36



¹H NMR of compound **4al**



¹H NMR of compound **4am**



¹H NMR of compound **4an**



S40



¹H NMR of compound **4ap**



¹H NMR of compound **4aq**















¹H NMR of compound **4au**



¹³C NMR of compound **4au**



¹³C NMR of compound **4av**



¹³C NMR of compound **4aw**



S50



¹³C NMR of compound **4ay**



¹³C NMR of compound **4az**



¹H NMR of compound **4aA**



¹H NMR of compound **4aB**



¹H NMR of compound **4aC**



¹H NMR of compound **4aD**



¹³C NMR of compound **4aD**



¹³C NMR of compound **4aE**



¹³C NMR of compound **4aF**



¹H NMR of compound 4aG



¹³C NMR of compound **4aG**



S61

¹H NMR of compound **4aH**



¹H NMR of compound **4ba**



¹H NMR of compound **4ca**



¹³C NMR of compound **4ca**