Supporting Information

Straightforward Synthesis of Photoactive Chalcogen Functionalized Benzimidazo[1,2-*a*]quinolines

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General information. Hydrogen Nuclear Magnetic Resonance (¹H NMR) and Carbon-13 Nuclear Magnetic Resonance (¹³C NMR) spectra were recorded in CDCl₃ or DMSO-d₆ solutions on a Varian 300 MHz, Varian 400 MHz Bruker 400 MHz and Varian 500 MHz spectrometers. Chemical shifts (d) are given in part per million from the peak of tetramethylsilane (δ = 0.00 ppm) as internal standard in ¹H NMR or from the solvent peak of CDCl₃ (δ = 77.23 ppm) in ¹³C NMR. Data are reported as follows: chemical shift (δ) , multiplicity, coupling constant (J) in Hertz and integrated intensity. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), quint (quintet), sext (sextet), td (triplet of doublet) and m (multiplet). High resolution mass spectra (HMRS) were recorded on a Micromass Q-Tof spectrometer, using electrospray ionization (ESI). Melting points were determined on a Buchi Melting Point M-545. Column chromatography was performed using silica gel (230-400 mesh). Thin layer chromatography (TLC) was performed using silica gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapour, or acidic vanillin. Air- and moisture-sensitive reactions were conducted in oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry argon. Reagents and solvents were handled using standard syringe techniques. Spectroscopic grade solvents were used in the photophysical characterization. UV-Vis absorption spectra were acquired on a Shimadzu UV-2450 spectrophotometer at a concentration of 10⁻⁵ M, and the steady-state fluorescence spectra were measured on a Shimadzu spectrofluorometer model RF-5301PC. The maximum absorption wavelength (WL) was used as the excitation WL for fluorescence emission measurements. The relative quantum yield of fluorescence (ϕ_{FL}) was determined in the dilute optical method. Quinine sulphate in H₂SO₄ ($\phi_{FL}=0.55$) was used as the quantum yield standard.¹ All measurements were performed at room temperature $(25^{\circ}C)$.

General procedure for preparation of 2-(bromomethyl)-1*H*-benzimidazole 3.Erro! Indicador não definido. Monochloroacetic acid (0.236 g, 1.7 mmol) and 1,2phenylenediamine (0.108 g, 1.0 mmol) were refluxed in 10 mL of HCl (4 mol.L⁻¹) for 7.5 h with stirring. The reaction mixture was then neutralized with K₂CO_{3 (aq)}. The precipitated product was collected by vacuum filtration, and the yellow solid was obtained in 80 % of yield after drying. ¹H NMR (300 MHz, DMSO-*d*₆) δ : 7.62 – 7.59 (m, 2H), 7.28 – 7.24 (m, 2H), 4.98 (s, 2H). ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ : 149.5, 138.5, 122.2, 115.2, 38.3.

General procedure for preparation of chalcogen 1*H*-benzimidazoles 5a-k. Under an argon atmosphere, sodium borohydride (0.028 g, 0.75 mmol) was added to a solution of the diorganyl dichalcogenides (4) (0.5 mmol) in THF (7.5 mL). EtOH (2.5 mL) was then dropwise added and the clear solution formed was stirred at room temperature for 20 min. After this time a solution of the 2-(bromomethyl)-1*H*benzo[*d*]imidazole **3** (0.211 g, 1.0 mmol) in THF was added dropwise, and the reaction mixture was heated at reflux for 24 h. The solution was washed with NH₄Cl _(aq) (2 x 30 mL) and extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuum. The crude product was purified by silica gel chromatography (eluent: hexane/ethyl acetate).

2-[(Phenylselenyl)methyl]-1*H***-benzo[***d***]imidazole (5a). Yield: 81%. Pale yellow solid. M.p.: 86 – 89°C. ¹H NMR (300 MHz, CDCl₃) \delta: 7.53 – 7.50 (m, 2H), 7.49 – 7.46 (m, 2H), 7.26 – 7.20 (m, 5H), 4.31 (s, 2H). ¹³C NMR (75.5 MHz, CDCl₃) \delta: 151.8, 133.1, 131.5, 129.4, 129.2, 127.9, 122.7, 115.0, 23.7. HRMS (ESI) calcd for C₁₄H₁₃N₂Se (M+H)⁺ requires 289.0238, found 289.0244.**

2-[(4-Tolylselenyl)methyl]-1*H*-benzo[*d*]imidazole (5b). Yield: 54%. Yellow solid. M.p.: 130 - 133°C. ¹H NMR (400 MHz, CDCl₃) δ : 7.50 – 7.49 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.20 (m, 2H), 7.01 – 6.99 (m, 2H), 4.25 (s, 2H), 2.27 (s, 3H). ¹³C NMR (75.5 MHz, CDCl₃) δ : 151.3, 137.1, 132.7, 131.3, 129.1, 124.2, 121.6, 113.9, 23.0, 20.1. HRMS (ESI) calcd for C₁₅H₁₅N₂Se (M+H)⁺ requires 303.0395, found 303.0387.

2-[((4-Methoxyphenyl)selenyl)methyl]-1*H*-benzo[*d*]imidazole (5c). Yield: 44%. Yellow oil. ¹H NMR (300 MHz, CDCl₃) δ : 7.51 - 7.48 (m, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.23 - 7.20 (m, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 4.19 (s, 2H), 3.68 (s, 3H). ¹³C NMR (75.5 MHz, CDCl₃) δ : 160.0, 152.6, 138.7, 136.4, 122.7, 122.7, 119.0, 115.1, 55.4, 24.8. HRMS (ESI) calcd for C₁₅H₁₅N₂OSe (M+H)⁺ requires 319.0344, found 319.0350.

2-[((2-Methoxyphenyl)selenyl)methyl]-1*H*-benzo[*d*]imidazole (5d). Yield: 58%. Yellow solid. M.p.: $108 - 111^{\circ}$ C. ¹H NMR (400 MHz, CDCl₃) δ : 7.51 - 7.49 (m, 2H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.19 - 7.14 (m, 3H), 6.78 - 674 (m, 2H), 4.31 (s, 2H), 3.71

(s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 158.0, 152.5, 138.9, 132.9, 129.1, 122.6, 121.8, 118.5, 115.1, 110.8, 55.9, 21.7. HRMS (ESI) calcd for C₁₅H₁₅N₂OSe (M+H)⁺ requires 319.0344, found 319.0320.

2-[((4-Chlorophenyl)selenyl)methyl]-1*H*-benzo[*d*]imidazole (5e). Yield: 60%. Yellow solid. M.p.: 157 – 159°C. ¹H NMR (400 MHz, CDCl₃) δ : 7.53 – 7.52 (m, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.25 – 7.23 (m, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 4.29 (s, 2H). ¹³C NMR (75.5 MHz, CDCl₃) δ : 165.2, 151.6, 134.7, 134.4, 129.7, 127.2, 123.0, 115.2, 24.1. HRMS (ESI) calcd for C₁₄H₁₂ClN₂Se (M+H)⁺ requires 322.9849, found 322.9852.

2-[((3-(Trifluoromethyl)phenyl)selenyl)methyl]-1*H*-benzo[*d*]imidazole (5f). Yield: 58%. Yellow oil. ¹H NMR (300 MHz, CDCl₃) δ : 7.67 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.21 (m, 3H), 4.35 (s, 2H). ¹³C NMR (75.5 MHz, CDCl₃) δ : 151.2, 138.8, 136.2, 131.6 (q, ²*J*_{C-F}= 32.5 Hz), 130.2, 129.8, 129.8 (q, ³*J*_{C-F}= 3.8 Hz), 124.8 (q, ³*J*_{C-F}= 3.8 Hz), 123.7 (q, ¹*J*_{C-F}= 273.3 Hz), 123.1, 115.2, 23.9. HRMS (ESI) calcd for C₁₂H₁₅F₃N₂Se (M+H)⁺ requires 357.0112, found 357.0118.

2-[(Mesitylselenyl)methyl]-1*H***-benzo**[*d*]**imidazole** (**5***g*)**.** Yield: 52%. White solid. M.p.: $199 - 201^{\circ}$ C. ¹H NMR (400 MHz, CDCl₃) δ : 7.48 – 7.47 (m, 2H), 7.22 – 7.20 (m, 2H), 6.90 (s, 2H), 4.00 (s, 2H), 2.37 (s, 6H), 2.25 (s, 3H). ¹³C NMR (75.5 MHz, CDCl₃) δ : 152.6, 143.6, 143.6, 139,4, 128.9, 127.1, 122.7, 115.1, 24.4, 22.9, 21.1. HRMS (ESI) calcd for C₁₇H₁₉N₂Se (M+H)⁺ requires 331.0708, found 331.0714.

2-[(Butylselenyl)methyl]-1*H***-benzo[***d***]imidazole (5h). Yield: 68%. Yellow solid. M.p.: 140 - 142^{\circ}C. ¹H NMR (400 MHz, CDCl₃) \delta: 7.57 – 7.55 (m, 2H), 7.24 – 7.22 (m, 2H), 4.00 (s, 2H), 2.61 (t,** *J* **= 7.4 Hz, 2H), 1.56 (quint,** *J* **= 7.4 Hz, 2H), 1.29 (sex,** *J* **= 7.3 Hz, 2H), 0.81 (t,** *J* **= 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) \delta: 153.2, 139.5, 122.7, 115.0, 32.2, 25.2, 23.0, 18.8, 13.7. HRMS (ESI) calcd for C₁₂H₁₇N₂Se (M+H)⁺ requires 269.0551, found 269.0519.**

2-[(Phenylthio)methyl]-1*H***-benzo[***d***]imidazole (5i). Yield: 43%. Yellow solid. M.p.: 130 – 133°C. ¹H NMR (300 MHz, CDCl₃) δ: 7.52 – 7.50 (m, 2H), 7.22 – 7.19 (m, 4H), 7.13 – 7.08 (m, 3H), 4.36 (s, 2H). ¹³C NMR (75.5 MHz, CDCl₃) δ: 151.5, 134.8, 134.8, 129.5, 129.3, 127.0, 122.8, 113.1, 32.2. HRMS (ESI) calcd for C₁₄H₁₃N₂S (M+H)⁺ requires 241.0794, found 241.0788.**

2-[((4-Methoxyphenyl)thio)methyl]-1*H***-benzo**[*d*]**imidazole (5j).** Yield: 62%. Yellow solid. M.p.: 148 – 150°C. ¹H NMR (400 MHz, CDCl₃) δ : 7.52 – 7.52 (m, 2H), 7.26 – 7.21 (m, 4H), 6.73 (d, *J* = 8.9 Hz, 2H), 4.27 (s, 2H), 3.71 (s, 3H). ¹³C NMR (100

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MHz, CDCl₃) δ : 159.7, 151.7, 133.5, 126.1, 124.7, 122.8, 115.0, 115.0, 55.5, 34.2. HRMS (ESI) calcd for C₁₅H₁₅N₂OS (M+H)⁺ requires 271.0900, found 271.0898.

2-[((3-(Trifluoromethyl)phenyl)thio)methyl]-1*H*-benzo[*d*]imidazole (5k). Yield: 69%. Yellow solid. M.p.: 119 – 121°C. ¹H NMR (400 MHz, CDCl₃) δ : 7.53 – 7.51 (m, 2H), 7.47 (s, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.23 – 7.21 (m, 2H), 7.17 (t, *J* = 7.9 Hz, 1H), 4.43 (s, 2H). ¹³C NMR (75.5 MHz, CDCl₃) δ : 150.4, 138.6, 136.3, 131.9, 131.5 (q, ²*J*_{C-F}= 32.6 Hz), 129.8, 125.9 (q, ³*J*_{C-F}= 3.9 Hz), 123.7 (q, ¹*J*_{C-F}= 272.8 Hz), 123.6 (q, ³*J*_{C-F}= 3.8 Hz), 121.9, 115.3, 31.9. HRMS (ESI) calcd for C₁₅H₁₂F₃N₂S (M+H)⁺ requires 309.0668, found 309.0673.

General procedure for the preparation of 6-(phenylselenyl)benzo[4,5] imidazo[1,2-*a*]quinoline 7a-r. A mixture of 2-fluorobenzaldehyde 6a (0.148 g, 1.2 mmol), 2-[(phenylselenyl)methyl]-1*H*-benzo[*d*]imidazole 5a (0.287 g, 1.0 mmol), and Cs₂CO₃ (0.325g, 3.0 mmol) in DMF (5.0 mL) was stirred at 80°C for 8 h. After the end of the reaction, the mixture was cooled to room temperature and diluted with water. The resulting mixture was extracted with ethyl acetate. The combined organic layer was washed with water, dried over MgSO₄ and the solvent was removed under vacuo. The residue was purified by silica gel chromatography (eluent: hexane/ethyl acetate= 9/1) to afford 6-(phenylselenyl)benzo[4,5]imidazo[1,2-*a*]quinoline 7a in 77 % yield.

6-(phenylselenyl)benzo[4,5]imidazo[1,2-*a***]quinoline (7a). Yield: 77%. Pale yellow solid. M.p.: 155 - 157^{\circ}C. ¹HNMR (400 MHz, CDCl₃) \delta: 8.43 (d, J = 8.5 Hz, 1H), 8.31 (d, J = 8.2 Hz, 1H), 8.11 - 8.09 (m, 1H), 7.83 - 7.80 (m, 2H), 7.61 - 7.57 (m, 1H), 7.54 - 7.52 (m, 1H), 7.51 - 7.44 (m, 5H), 7.33 - 7.29 (m, 1H), 7.03 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) \delta: 146.8, 144.5, 137.2, 134.1, 131.4, 130.1, 129.6, 128.7, 128.3, 127.9, 126.3, 125.3, 124.6, 124.2, 124.0, 123.1, 121.0, 115.1, 114.1. HRMS (ESI) calcd for C₂₁H₁₅N₂Se (M+H)⁺ requires 375.0395, found 375.0391.**

6-(Phenylselenyl)-3-(trifluoromethyl)-11,11a-dihydrobenzo[4,5]imidazo[1,2*a*]**quinoline (7b).** Yield: 73%. Yellow solid. M.p.: 146 – 148°C. ¹H NMR (400 MHz, CDCl₃) δ : 8.47 (d, J = 8.8 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H), 8.09 – 8.07 (m, 1H), 7.86 – 7.82 (m, 2H), 7.81 - 7.79 (m, 1H), 7.71 (s, 1H), 7.58 – 7.46 (m, 5H), 6.97 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 146.6, 144.5, 137.5, 135.7, 131.2, 130.3, 130.0, 128.2, 126.3, 126.3 (q, ²*J*_{C-F}= 33.3 Hz), 125.6, 125.4 (q, ³*J*_{C-F} = 4.0 Hz), 125.2, 124.7 (q, ³*J*_{C-F}= 3.4 Hz), 123.8, 123.9 (q, ¹*J*_{C-F}= 270.0 Hz), 123.7 121.4, 115.5, 113.9. HRMS (ESI) calcd for C₂₂H₁₄F₃N₂Se (M+H)⁺ requires 443.0269, found 443.0228.

2-Bromo-6-(phenylselenyl)-11,11a-dihydrobenzo[4,5]imidazo[1,2-

a]quinoline (7c). Yield: 58%. Yellow solid. M.p.: 197 – 199°C. ¹H NMR (400 MHz, CDCl₃) δ : 8.55 (s, 1H), 8.22 (d, *J* = 7.9 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.83 – 7.80 (m, 2H), 7.56 – 7.45 (m, 5H), 7.43 – 7.40 (m, 1H), 7.32 – 7.29 (m, 1H), 6.94 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 146.6, 144.5, 137.3, 134.7, 131.1, 130.2, 129.8, 129.3, 127.5, 126.8, 126.3, 126.1, 125.0, 123.6, 122.8, 122.3, 121.3, 118.1, 113.9. HRMS (ESI) calcd for C₂₁H₁₄BrN₂Se (M+H)⁺ requires 452.9500, found 452.9478.

1-Methoxy-6-(phenylselanyl)-11,11a-dihydrobenzo[4,5]imidazo[1,2a]quinoline (7d). Yield: 58%. Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ : 8.32 – 8.29 (m, 1H), 8.06 - 8.03 (m, 1H), 7.83 – 7.80 (m, 2H), 7.53 – 7.43 (m, 4H), 7.39 – 7.35 (m, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.14 – 7.11 (m, 1H), 7.08 – 7.06 (m, 1H), 6.97 (s, 1H), 4.01 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 149.1, 147.5, 144.5, 137.3, 133.8, 130.1, 129.6, 127.4, 126.6, 126.4, 126.3, 125.1, 124.3, 124.1, 121.8, 120.5, 120.3, 118.6, 111.1, 56.1. HRMS (ESI) calcd for C₂₂H₁₇N₂OSe (M+H)⁺ requires 405.0501, found 405.0469.

1-Fluoro-6-(phenylselanyl)benzo[4,5]imidazo[1,2-*a***]quinoline (7e). Yield: 31%. Yellow solid. M.p.: 142 - 145^{\circ}C. ¹H NMR (400 MHz, CDCl₃) \delta: 8.41 – 8.38 (m, 1H), 8.08 – 8.05 (m, 1H), 7.84 – 7.82 (m, 2H), 7.55 – 7.48 (m, 4H), 7.47 – 7.42 (m, 1H), 7.36 (td,** *J***= 8.0 Hz,** *J***= 1.8 Hz, 1H), 7.29 (td,** *J***= 8.0 Hz,** *J***= 4.6 Hz, 1H), 7.26 – 7.23 (m, 1H), 6.97 (d,** *J* **= 1.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) \delta: 151.2 (d, ¹***J***_{C-F}= 248.7 Hz), 146.9, 144.5, 137.5, 132.5, 130.2, 129.8, 129.7, 127.7, 127.0, 126.6, 126.1, 125.0, 123.9 (d, ⁴***J***_{C-F}= 3.1 Hz), 123.2 (d, ³***J***_{C-F}= 5.5 Hz), 122.1 (d, ³***J***_{C-F}= 12.4 Hz), 120.7, 116.3 (d, ²***J***_{C-F}= 35.9 Hz), 115.5 (d, ²***J***_{C-F}= 23.2 Hz). HRMS (ESI) calcd for C₂₁H₁₄FN₂Se (M+H)⁺ requires 393.0301, found 393.0208.**

6-(Phenylthio)-3-(trifluoromethyl)-11,11a-dihydrobenzo[4,5]imidazo[1,2*a*]quinoline (7f). Yield: 79%. Yellow solid. M.p.: 203 – 206°C. ¹H NMR (400 MHz, CDCl₃) δ : 8.45 (d, *J*= 8.8 Hz, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 8.09 – 8.07 (m, 1H), 7.78 – 7.70 (m, 4H), 7.56 – 7.45 (m, 5H), 6.81 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 145.8, 144.5, 136.1, 135.2, 132.3, 131.1, 130.2, 129.1, 126.3 (q, ²*J*_{C-F}= 33.2 Hz), 125.4 (q, ³*J*_{C-F}= 4.0 Hz), 125.2, 124.6 (q, ³*J*_{C-F}= 3.0 Hz), 123.9 (q, ¹*J*_{C-F}= 270 Hz), 123.8, 123.4, 123.0, 122.9, 121.5, 115.4, 113.8. HRMS (ESI) calcd for C₂₂H₁₄F₃N₂S (M+H)⁺ requires 395.0824, found 395.0797.

2-Bromo-6-(phenylthio)-11,11a-dihydrobenzo[4,5]imidazo[1,2-*a***]quinoline (7g). Yield: 85 %. Yellow solid. m.p.: 183 – 186°C. ¹H NMR (500 MHz, CDCl₃) \delta: 8.60 (s, 1H), 8.26 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.73 – 7.71 (m, 2H), 7.57 –** 7.50 (m, 5H), 7.46 – 7.44 (m, 1H), 7.35 (d, J = 8.4 Hz, 1H), 6.84 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ : 145.9, 144.5, 135.8, 134.4, 131.1, 130.5, 130.2, 129.9, 129.8, 129.5, 127.6, 125.1, 123.8, 123.7, 122.5, 122.2, 121.4, 118.1, 113.9. HRMS (ESI) calcd for C₁₂H₁₄BrN₂S (M+H)⁺ requires 405.0056, found 405.0030.

1-Methoxy-6-(phenylthio)-11,11a-dihydrobenzo[4,5]imidazo[1,2-*a*]quinoline (7h). Yield: 82 %. Yellow oil. ¹H NMR (500 MHz, CDCl₃) δ: 8.32 (d, J = 8.6 Hz, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.72 – 7.71 (m, 2H), 7.50 – 7.46 (m, 4H), 7.40 - 7.36 (m, 1H), 7.34 - 7.30 (m, 1H), 7.13 - 7.09 (m, 2H), 6.85 (s, 1H), 4.02 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ: 149.1, 146.9, 144.5, 135.8, 133.8, 130.5, 130.3, 130.0, 129.7, 126.4, 125.2, 124.5, 124.2, 124,0 121.9, 120.6, 120.5, 118.5, 111.1, 56.1. HRMS (ESI) calcd for $C_{22}H_{17}N_2OS (M+H)^+$ requires 357.1056, found 357.1021.

6-(4-Tolylselenyl)benzo[4,5]imidazo[1,2-*a***]quinoline (7i). Yield: 78%. Yellow solid. M.p.: 151 - 153^{\circ}C. ¹H NMR (400 MHz, CDCl₃) \delta: 8.41 (d, J = 8.4 Hz, 1H), 8.29 (d, J = 8.2 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.67 – 7.69 (m, 2H), 7.59 – 7.55 (m, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.46 – 7.43 (m, 2H), 7.31 – 7.25 (m, 3H), 7.00 (s, 1H), 2.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) \delta: 146.8, 144.5, 139.8, 137.3, 134.1, 131.4, 130.9, 128.5, 128.3, 127.5, 125.7, 124.6, 124.2, 124.0, 123.0, 122.5, 121.0, 115.1, 114.1, 21.6. HRMS (ESI) calcd for C₂₂H₁₇N₂Se (M+H)⁺ requires 389.0551, found 389.0590.**

6-[(4-Methoxyphenyl)selenyl]benzo[4,5]imidazo[1,2-*a*]**quinoline (7j).** Yield: 42%. Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ : 8.51 (d, *J* = 8.4 Hz, 1H), 8.37 (d, *J* = 8.1 Hz, 1H), 8.13 – 8.11 (m, 1H), 7.76 – 7.72 (m, 2H), 7.66 – 7.61 (m, 1H), 7.56 – 753 (m, 1H), 7.53 – 7.47 (m, 2H), 7.38 – 7.34 (m, 1H), 7.03 – 6.99 (m, 3H), 3.89 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 161.0, 146.9, 144.6, 139.2, 134.2, 131.5, 128.6, 128.4, 127.2, 126.4, 124.7, 124.3, 124.3, 124.2, 123.2, 121.1, 116.3, 115.8, 114.2, 55.5. HRMS (ESI) calcd for C₂₂H₁₇N₂OSe (M+H)⁺ requires 405.0501, found 405.0487.

6-[(2-Methoxyphenyl)selenyl]benzo[4,5]imidazo[1,2-*a***]quinoline (7k). Yield: 48%. Yellow solid. M.p.: 149 - 151^{\circ}C. ¹H NMR (400 MHz, CDCl₃) \delta: 8.42 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.2 Hz, 1H), 8.09 – 8.07 (m, 1H), 7.66 – 7.64 (m, 1H), 7.60 – 7.56 (m, 1H), 7.52 – 7.41 (m, 4H), 7.32 – 7.28 (m, 1H), 7.14 (s, 1H), 7.03 – 7.00 (m, 1H), 6.99 – 6.95 (m, 1H), 3.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) \delta: 159.7, 147.2, 144.5, 137.5, 134.3, 131.4, 131.1, 129.3, 128.7, 128.3, 124.5, 124.1, 124.0, 123.1, 122.9, 121.9, 121.0, 115.9, 115.0, 114.1, 111.5, 56.2. HRMS (ESI) calcd for C₂₂H₁₇N₂OSe (M+H)⁺ requires 405.0501, found 405.0483.**

6-[(4-Chlorophenyl)selenyl]benzo[4,5]imidazo[1,2-*a***]quinoline (71). Yield: 47%. Yellow solid. M.p.: 173 - 176^{\circ}C. ¹H NMR (400 MHz, CDCl₃) \delta: 8.51 (d, J = 8.5 Hz, 1H), 8.37 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.75 - 7.73 (m, 2H), 7.68 - 7.64 (m, 1H), 7.57 - 7.55 (m, 2H), 7.53 - 7.48 (m, 1H), 7.44 - 7.42 (m, 2H), 7.39 (d, J = 7.4 Hz, 1H), 7.08 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) \delta: 146.8, 144.5, 138.4, 136.0, 134.4, 131.5, 130.4, 129.0, 128.5, 128.3, 124.8, 124.7, 124.7, 124.4, 124.0, 123.3, 121.1, 115.2, 114.2. HRMS (ESI) calcd for C₂₁H₁₄ClN₂Se (M+H)⁺ requires 409.0005, found 408.9993.**

6-[(3(Trifluoromethyl)phenyl)selenyl]benzo[4,5]imidazo[1,2-*a***]quinoline (7m). Yield: 41%. Yellow oil. ¹H NMR (500 MHz, CDCl₃) \delta: 8.57 (d, J = 8.5 Hz, 1H), 8.41 (d, J = 8.2 Hz, 1H), 8.13 – 8.12 (m, 1H), 8.10 (s, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.60 – 7.55 (m, 3H), 7.54 – 7.51 (m, 1H), 7.44 – 7.41 (m, 1H), 7.19 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) \delta: 145.9, 143.6, 139.0, 135.2, 133.6, 132.2 (q, ³J_{C-F} = 3.7 Hz), 131.3 (q, ²J_{C-F}= 32.5 Hz), 129.4, 128.9, 128.3, 127.8, 127.1, 125.2 (q, ³J_{C-F}= 3.8 Hz), 123.9, 123.8 (q, ¹J_{C-F}= 271.5 Hz), 123.5, 122.4, 120.2, 120.0, 114.6, 114.3, 113.3. HRMS (ESI) calcd for C₂₂H₁₄F₃N₂Se (M+H)⁺ requires 443.0269, found 443.0293.**

6-(Mesitylselenyl)benzo[4,5]imidazo[1,2-*a***]quinoline (7n). Yield: 78%. Yellow solid. M.p.: 176 - 179^{\circ}C. ¹H NMR (400 MHz, CDCl₃) \delta: 8.44 (d, J = 8.5 Hz, 1H), 8.31 (d, J = 8.2 Hz, 1H), 8.11 - 8.09 (m, 1H), 7.59 - 7.54 (m, 1H), 7.53 - 7.49 (m, 1H), 7.47 - 7.42 (m, 2H), 7.31 - 7.27 (m, 1H), 7.09 (s, 2H), 6.71 (s, 1H), 2.52 (s, 6H), 2.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) \delta: 147.0, 144.5, 140.1, 137.0, 133.9, 131.3, 129.3, 128.6, 128.2, 128.1, 125.1, 124.5, 124.4, 124.2, 124.2, 124.1, 123.0, 120.9, 115.1, 114.1, 24.2, 21.3. HRMS (ESI) calcd for C₂₄H₂₁N₂Se (M+H)⁺ requires 417.0864, found 417.0894.**

6-(Butylselenyl)benzo[4,5]imidazo[1,2-*a***]quinoline (70). Yield: 68%. Yellow solid. M.p.: 108 - 110^{\circ}C. ¹H NMR (400 MHz, CDCl₃) \delta: 8.32 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.3 Hz, 1H), 8.07 - 8.04 (m, 1H), 7.57 - 7.55 (m, 1H), 7.52 - 7.45 (m, 2H), 7.42 - 7.38 (m, 1H), 7.40 (s, 1H), 7.29 - 7.25 (m, 1H), 3.11 (t, J = 7.5 Hz, 2H), 1.87 - 1.79 (m, 2H), 1.57 - 1.48 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) \delta: 147.3, 144.4, 133.9, 131.3, 128.4, 128.0, 127.9, 124.4, 124.1, 123.7, 122.9, 122.7, 120.9, 114.9, 114.1, 31.4, 25.2, 23.3, 13.8. HRMS (ESI) calcd for C₁₉H₁₉N₂Se (M+H)⁺ requires 355.0708, found 355.0699.**

6-(Phenylthio)benzo[4,5]imidazo[1,2-*a***]quinoline (7p).** Yield: 65%. Yellow solid. M.p.: $145 - 148^{\circ}$ C. ¹H NMR (400 MHz, CDCl₃) δ : 8.48 (d, J = 8.5 Hz, 1H), 8.35 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.72 – 7.70 (m, 2H), 7.63 – 7.59 (m, 1H),

7.55 – 7.46 (m, 6H), 7.34 (t, J = 7.5 Hz, 1H), 6.94 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 146.2, 144.5, 135.6, 133.9, 131.4, 130.2, 130.0, 129.7, 129.5, 128.6, 128.5, 125.1, 124.7, 124.4, 123.7, 123.2, 121.2, 115.1, 114.1. HRMS (ESI) calcd for C₂₁H₁₅N₂S (M+H)⁺ requires 327.0950, found 327.0981.

6-[(4-Methoxyphenyl)thio]benzo[4,5]imidazo[1,2-*a***]quinoline (7q). Yield: 42%. Yellow solid. M.p.: 223 – 226°C. ¹H NMR (400 MHz, CDCl₃) \delta: 8.50 (d,** *J* **= 8.4 Hz, 1H), 8.37 (d,** *J* **= 8.1 Hz, 1H), 8.14 – 8.12 (m, 1H), 7.68 – 7.64 (m, 2H), 7.63 – 7.59 (m, 1H), 7.56 – 7.47 (m, 3H), 7.35 (t,** *J* **= 7.5 Hz, 1H), 7.06 – 7.02 (m, 2H), 6.82 (s, 1H), 3.89 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) \delta: 161.2, 146.1, 144.6, 137.9, 133.7, 131.4, 131.0, 129.5, 128.4, 124.7, 124.4, 123.9, 123.6, 123.2, 121.2, 120.0, 115.7, 115.1, 114.1, 55.7. HRMS (ESI) calcd for C₂₂H₁₇N₂OS (M+H)⁺ requires 357.1056, found 357.1094. 6-[(3-(Trifluoromethyl)phenyl)thio]benzo[4,5]imidazo[1,2-***a***]quinoline (7r). Yield: 45%. Yellow solid. M.p.: 168 – 171°C. ¹H NMR (400 MHz, CDCl₃) \delta: 8.42 (d,** *J* **= 8.4 Hz, 1H), 8.28 (d,** *J* **= 8.1 Hz, 1H), 8.09 – 8.07 (m, 1H), 7.93 (s, 1H), 7.79 (d,** *J* **= 7.8 Hz, 1H), 7.68 – 7.66 (m, 1H), 7.62 – 7.58 (m, 1H), 7.55 – 7.43 (m, 4H), 7.34 (m, 1H), 7.09 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) \delta: 146.2, 144.4, 137.4, 134.3, 133.0, 132.2 (q, ²***J***c-F= 32.5 Hz), 131.4, 130.7 (q, ³***J***c-F= 3.9 Hz), 130.3, 129.3, 128.8, 127.9, 126.9, 125.8 (q, ³***J***c-F= 3.8 Hz), 124.8, 124.4, 123.7 (q, ¹***J***c-F= 271.5 Hz), 123.3, 123.3, 121.2, 115.1, 114.1. HRMS (ESI) calcd for C₂₂H₁₄F₃N₂S (M+H)⁺ requires 395.0824, found 395.0881.**

Procedure for *in situ* oxidation of selenylquinolines and monitoring with fluorescence spectroscopy

To a solution of respective selenylquinoline derivative in dicholoromethane (10^{-5} M) , 20 equiv. of benzoyl peroxide was added from a stock solution in DCM (10^{-5} M) under room temperature. The mixture was monitored along ~4h by UV-Vis and Fluorescence spectroscopy.

Spectra of products



¹H NMR (300 MHz, CDCl₃) spectrum of 2-[(phenylselanyl)methyl]-1*H*-benzo[*d*]imidazole **5a**.



¹³C NMR (75.5 MHz, CDCl₃) spectrum of 2-[(phenylselanyl)methyl]-1*H*-benzo[*d*]imidazole **5a**.











¹H NMR (300 MHz, CDCl₃) spectrum of 2-[((4-methoxyphenyl)selenyl)methyl]-1*H*-benzo[*d*]imidazole **5**c.



¹³C NMR (75.5 MHz, CDCl₃) spectrum of 2-[((4-methoxyphenyl)selenyl)methyl]-1*H*-benzo[*d*]imidazole **5**c.



¹H NMR (400 MHz, CDCl₃) spectrum of 2-[((2-methoxyphenyl)selenyl)methyl]-1*H*-benzo[*d*]imidazole **5d**.



¹³C NMR (100 MHz, CDCl₃) spectrum of 2-[((2-methoxyphenyl)selenyl)methyl]-1*H*-benzo[*d*]imidazole **5d**.



¹H NMR (400 MHz, CDCl₃) spectrum of 2-[((4-chlorophenyl)selenyl)methyl]-1*H*-benzo[*d*]imidazole **5e**.



¹³C NMR (75.5 MHz, CDCl₃) spectrum of 2-[((4-chlorophenyl)selenyl)methyl]-1*H*-benzo[*d*]imidazole

5e.













¹³C NMR (75.5 MHz, CDCl₃) spectrum of 2-[(mesitylselenyl)methyl]-1*H*-benzo[*d*]imidazole **5g.**



¹H NMR (400 MHz, CDCl₃) spectrum of 2-[(butylselenyl)methyl]-1*H*-benzo[*d*]imidazole **5h**.



¹³CNMR (100 MHz, CDCl₃) spectrum of 2-[(butylselenyl)methyl]-1*H*-benzo[*d*]imidazole **5h**.



¹H NMR (300 MHz, CDCl₃) spectrum of 2-[(phenylthio)methyl]-1*H*-benzo[*d*]imidazole **5i**.



¹³C NMR (75.5 MHz, CDCl₃) spectrum of 2-[(phenylthio)methyl]-1*H*-benzo[*d*]imidazole **5i**.



¹H NMR (400 MHz, CDCl₃) spectrum of 2-[((4-methoxyphenyl)thio)methyl]-1*H*-benzo[*d*]imidazole **5j.**



¹³C NMR (100 MHz, CDCl₃) spectrum of 2-[((4-methoxyphenyl)thio)methyl]-1*H*-benzo[*d*]imidazole **5j**.







¹H NMR (400 MHz, CDCl₃) spectrum of 6-(phenylselenyl)benzo[4,5]imidazo[1,2-*a*]quinoline **7a**.



¹³C NMR (100 MHz, CDCl₃) spectrum of 6-(phenylselenyl)benzo[4,5]imidazo[1,2-*a*]quinoline **7a**.







¹³C NMR (100 MHz, CDCl₃) spectrum of 6-(phenylselenyl)-3-(trifluoromethyl)-11,11adihydrobenzo[4,5]imidazo[1,2-*a*]quinoline **7b**.











¹H NMR (400 MHz, CDCl₃) spectrum of 1-methoxy-6-(phenylselenyl)-11,11adihydrobenzo[4,5]imidazo[1,2-*a*]quinoline **7d**.







¹H NMR (400 MHz, CDCl₃) spectrum of 1-fluoro-6-(phenylselanyl)benzo[4,5]imidazo[1,2-*a*]quinoline

7e.



¹³C NMR (100 MHz, CDCl₃) spectrum of 1-methoxy-6-(phenylselenyl)-11,11adihydrobenzo[4,5]imidazo[1,2-*a*]quinoline 7d.

¹³C NMR (100 MHz, CDCl₃) spectrum of 1-fluoro-6-(phenylselanyl)benzo[4,5]imidazo[1,2-a]quinoline

7e.



dihydrobenzo[4,5]imidazo[1,2-*a*]quinoline **7f**.





¹H NMR (500 MHz, CDCl₃) spectrum of 2-bromo-6-(phenylthio)-11,11a-dihydrobenzo[4,5]imidazo[1,2*a*]quinoline **7**g.



¹³C NMR (100 MHz, CDCl₃) spectrum of 6-(phenylthio)-3-(trifluoromethyl)-11,11adihydrobenzo[4,5]imidazo[1,2-a]quinoline **7f**.

¹³C NMR (125 MHz, CDCl₃) spectrum of 2-bromo-6-(phenylthio)-11,11a-dihydrobenzo[4,5]imidazo[1,2*a*]quinoline **7g**.



¹H NMR (500 MHz, CDCl₃) spectrum of 1-methoxy-6-(phenylthio)-11,11a dihydrobenzo[4,5]imidazo[1,2-*a*]quinoline **7h**.



¹³C NMR (125 MHz, CDCl₃) spectrum of 1-methoxy-6-(phenylthio)-11,11adihydrobenzo[4,5]imidazo[1,2-*a*]quinoline **7h**.



¹H NMR (400 MHz, CDCl₃) spectrum of 6-(4-tolylselenyl)benzo[4,5]imidazo[1,2-*a*]quinoline 7i.



¹³C NMR (100 MHz, CDCl₃) spectrum of 6-(4-tolylselenyl)benzo[4,5]imidazo[1,2-*a*]quinoline 7i.





¹³C NMR (100 MHz, CDCl₃) spectrum of 6-[(4-methoxyphenyl)selenyl)]benzo[4,5]imidazo



¹H NMR (400 MHz, CDCl₃) spectrum of 6-[(2-methoxyphenyl)selenyl]benzo[4,5]imidazo [1,2-*a*]quinoline **7k**.



¹³C NMR (100 MHz, CDCl₃) spectrum of6-[(2-methoxyphenyl)selenyl]benzo[4,5]imidazo

[1,2-*a*]quinoline **7k.**



¹H NMR (400 MHz, CDCl₃) spectrum of 6-[(4-chlorophenyl)selenyl]benzo[4,5]imidazo[1,2-*a*]quinoline **7**l.



¹³C NMR (100 MHz, CDCl₃) spectrum of 6-[(4-chlorophenyl)selenyl]benzo[4,5]imidazo[1,2-a]quinoline



¹H NMR (500 MHz, CDCl₃) spectrum of 6-[(3(trifluoromethyl)phenyl)selenyl]benzo[4,5]imidazo [1,2-*a*]quinoline **7m**



¹³C NMR (100 MHz, CDCl₃) spectrum of 6-[(3(trifluoromethyl)phenyl)selenyl]benzo[4,5]imidazo [1,2-*a*]quinoline **7m**.



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<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 6-(mesitylselenyl)benzo[4,5]imidazo[1,2-a]quinoline 7n.
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¹³C NMR (100 MHz, CDCl₃) spectrum of 6-(mesitylselenyl)benzo[4,5]imidazo[1,2-*a*]quinoline **7n**.













¹³C NMR (100 MHz, CDCl₃) spectrum of 6-(phenylthio)benzo[4,5]imidazo[1,2-*a*]quinoline **7p**.



¹H NMR (400 MHz, CDCl₃) spectrum of 6-((4-methoxyphenyl)thio)benzo[4,5]imidazo[1,2-a]quinoline

7q.

OMe



¹³C NMR (100 MHz, CDCl₃) spectrum of 6-[(4-methoxyphenyl)thio]benzo[4,5]imidazo[1,2-a]quinoline

7q.



¹H NMR (400 MHz, CDCl₃) spectrum of 6-[(3-(trifluoromethyl)phenyl)thio]benzo[4,5]imidazo [1,2-*a*]quinoline **7r.**



¹³C NMR (100 MHz, CDCl₃) spectrum of 6-[(3-(trifluoromethyl)phenyl)thio]benzo[4,5]imidazo [1,2-*a*]quinoline **7r**.

Additional Photophysical data



UV-Vis spectra of compound **7a** $(1.0 \times 10^{-5} \text{ M})$ in different organic solvents



Fluorescence emission spectra of compound **7a** ($1.0x10^{-5}$ M) in different organic solvents



UV-Vis spectra of compound **7b** $(1.0 \times 10^{-5} \text{ M})$ in different organic solvents



Fluorescence emission spectra of compound **7b** ($1.0x10^{-5}$ M) in different organic solvents



UV-Vis spectra of compound **7c** ($1.0x10^{-5}$ M) in different organic solvents



Fluorescence emission spectra of compound **7c** ($1.0x10^{-5}$ M) in different organic solvents



UV-Vis spectra of compound **7f** $(1.0 \times 10^{-5} \text{ M})$ in different organic solvents



Fluorescence emission spectra of compound **7f** ($1.0x10^{-5}$ M) in different organic solvents



UV-Vis spectra of compound 7g (1.0x10⁻⁵ M) in different organic solvents



Fluorescence emission spectra of compound 7g (1.0x10⁻⁵ M) in different organic solvents



UV-Vis spectra of compound 7i $(1.0x10^{-5} \text{ M})$ in different organic solvents



Fluorescence emission spectra of compound **7i** $(1.0 \times 10^{-5} \text{ M})$ in different organic solvents



UV-Vis spectra of compound **7k** ($1.0x10^{-5}$ M) in different organic solvents



Fluorescence emission spectra of compound 7k (1.0x10⁻⁵ M) in different organic solvents



UV-Vis spectra of compound **7l** $(1.0x10^{-5} \text{ M})$ in different organic solvents



Fluorescence emission spectra of compound **7l** $(1.0 \times 10^{-5} \text{ M})$ in different organic solvents



UV-Vis spectra of compound **7n** ($1.0x10^{-5}$ M) in different organic solvents



Fluorescence emission spectra of compound **7n** ($1.0x10^{-5}$ M) in different organic solvents



UV-Vis spectra of compound **7o** $(1.0 \times 10^{-5} \text{ M})$ in different organic solvents



Fluorescence emission spectra of compound **70** ($1.0x10^{-5}$ M) in different organic solvents



UV-Vis spectra of compound **7p** ($1.0x10^{-5}$ M) in different organic solvents



Fluorescence emission spectra of compound 7p (1.0x10⁻⁵ M) in different organic solvents



UV-Vis spectra of compound $7r (1.0x10^{-5} \text{ M})$ in different organic solvents



Fluorescence emission spectra of compound $7r (1.0x10^{-5} \text{ M})$ in different organic solvents



⁷⁷Se NMR (57 MHz, DMSO) spectrum of 6-(phenylselenyl)benzo[4,5]imidazo[1,2-*a*]quinoline **7a**. The signal in 459 ppm refers to Diphenyl Diselenide, used as reference.



signal in 459 ppm refers to Diphenyl Diselenide, used as reference.

¹. Würth, C.; Grabolle, M.; Pauli, J.; Spieles, M.; Resch-Genger, U. Relative and absolute determination of fluorescence quantum yields of transparent samples. *Nat. Protoc.* **2013**, 8, 1535-1550.