

Supporting Information

Electrochemical Regioselective C–H Selenylation of 2*H*-Indazole Derivatives

Shengsheng Lin,⁺ Xiaomei Cheng,⁺ Balati Hasimujiang, Zhongnan Xu, Fengtan Li,
Zhixiong Ruan*

Key Laboratory of Molecular Target & Clinical Pharmacology and the State & NMPA
Key Laboratory of Respiratory Disease, School of Pharmaceutical Sciences & the
Fifth Affiliated Hospital, Guangzhou Medical University, Guangzhou, 511436,
P.R.China.

Email: zruan@gzhmu.edu.cn

⁺ These authors contributed equally to this work.

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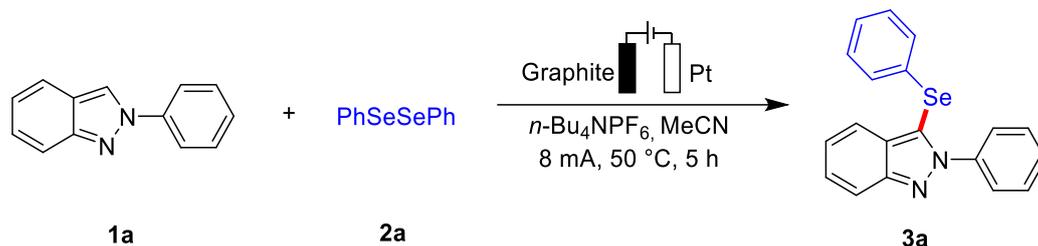
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General Remarks

Electrochemical reactions were performed under air using undivided glassware cell. The substrate **1a–1z** and diselenides were synthesized according to previously described methods.^[1-3] Other chemicals were obtained from commercial sources and were used without further purification. Platinum electrodes are commercially available from Tianjin Aida. Graphite plates are commercially available from Beijing Jinglong Special Carbon Technology Co., Ltd. Electrochemical reactions were conducted using an AXIOMET AX-3003P potentiostat in constant current mode. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ¹H-NMR. TLC: Macherey-Nagel, TLC plates Alugram®Sil G/UV254. Detection under UV light at 254 nm. Chromatography separations were carried out on silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China). High resolution mass spectrometry (HRMS) was measured on Thermo-DFS mass spectrometer. NMR spectra were recorded on JEOL 400 NMR (¹H 400 MHz; ¹³C 100 MHz; ¹⁹F 376 MHz) in CDCl₃. If not otherwise specified, chemical shifts (δ) are given in ppm.

Optimization Studies

Table S1. Optimization of the reaction conditions^a



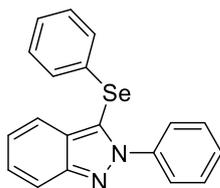
Entry	Deviation from standard conditions	Yield (%) ^b
1	none	85
2	No <i>n</i> -Bu ₄ NPF ₆	0
3	MeCN/DCE (2:1) as solvent	30
4	MeOH as solvent	0
5	<i>n</i> -Bu ₄ NClO ₄ instead of <i>n</i> -Bu ₄ NPF ₆	29
6	MeCN/THF (2:1) as solvent	0
7	LiClO ₄ instead of <i>n</i> -Bu ₄ NPF ₆	38
8	C(+)-C(-)	78
9	Pt plate as anode	31
10	16 mA instead of 8 mA	75
11	MeCN/HFIP (2:1) as solvent	trace
12	RT instead of 50 °C	21
13	Ni plate as cathode	76
14	80 °C instead of 50 °C	50
15	<i>n</i> -Bu ₄ NBF ₄ instead of <i>n</i> -Bu ₄ NPF ₆	22
16	No electricity	0
17	2a (0.24 mmol) instead of 2a (0.3 mmol)	45
18	2a (0.4 mmol) instead of 2a (0.3 mmol)	83
19	4 h instead of 5 h	68

^aReaction conditions: undivided cell, graphite anode (1.5 cm × 1 cm × 0.2 cm), Pt cathode (1 cm × 1 cm × 0.01 cm), **1a** (0.2 mmol), **2a** (0.3 mmol), *n*-Bu₄NPF₆ (0.5 mmol), MeCN (5.0 mL), constant current = 8.0 mA, 5 h, under air, 50 °C. ^bYields of isolated products. RT = room temperature

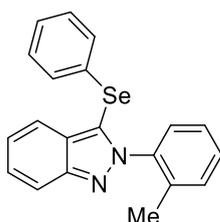
General Procedure for Electrochemical Reactions

General Procedures A: In an undivided cell (20 mL) equipped with a stirring bar, a mixture of 2*H*-Indazole derivatives (0.2 mmol), diphenyl diselenide (0.3 mmol, 93.6 mg), *n*-Bu₄NPF₆ (0.5 mmol, 194 mg) and MeCN (5.0 mL) were added. The cell was equipped with graphite (1.5 cm × 1 cm × 0.2 cm) as the anode and platinum plate (1 cm × 1 cm × 0.01 cm) as the cathode, and connected to a DC power supply. The reaction mixture was stirred and electrolyzed at 50 °C under a constant current of 8 mA for 5 h. After the reaction was completed, the residue was purified by silica gel column chromatography to afford the desired product **3**.

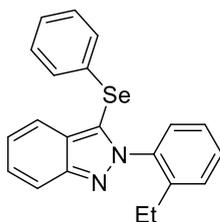
General procedure B: In an undivided cell (20 mL) equipped with a stirring bar, a mixture of 2-Phenyl-2*H*-indazole (0.2 mmol, 38.8 mg), diphenyl diselenide derivative (0.3 mmol), *n*-Bu₄NPF₆ (0.5 mmol, 194 mg) and MeCN (5.0 mL) were added. The battery was equipped with graphite (1.5 cm × 1 cm × 0.2 cm) as the anode and platinum plate (1 cm × 1 cm × 0.01 cm) as the cathode, and connected to a DC power supply. The reaction mixture was stirred and electrolyzed at 50 °C under a constant current of 8 mA for 5 h. After the reaction was completed, the residue was purified by silica gel column chromatography to afford the desired product **4**.



2-Phenyl-3-(phenylselanyl)-2H-indazole (3a). The general procedure **A** was followed using substrate **1a** (0.2 mmol, 39 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3a** (60 mg, 85%) as white solid. Mp: 77.6–78.8 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.84 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.48 – 7.44 (m, 3H), 7.40 (dd, *J* = 8.5, 7.9 Hz, 1H), 7.21 (dd, *J* = 8.7, 7.9 Hz, 1H), 7.17 – 7.09 (m, 5H). ¹³C NMR (100 MHz, CDCl₃): δ = 149.4, 140.3, 131.4, 130.5, 129.6, 129.1, 128.8, 128.1, 127.3, 127.3, 126.6, 123.5, 121.1, 120.0, 118.4. HRMS (ESI) *m/z* calcd for C₁₉H₁₅N₂Se [M+H]⁺ 351.0395, found 351.0397.

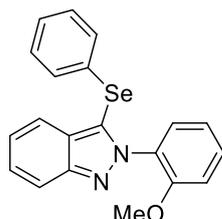


3-(Phenylselanyl)-2-(*o*-tolyl)-2H-indazole (3b). The general procedure **A** was followed using substrate **1b** (0.2 mmol, 42 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3b** (54 mg, 74%) as colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 7.82 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.32 – 7.28 (m, 1H), 7.25 – 7.20 (m, 2H), 7.17 (m, 1H), 7.14 – 7.08 (m, 5H), 1.86 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 149.3, 139.6, 135.9, 131.8, 130.8, 130.3, 129.8, 129.4, 128.0, 127.6, 127.0, 126.9, 126.1, 123.3, 121.6, 121.0, 118.5, 17.3. HRMS (ESI) *m/z* calcd for C₂₀H₁₇N₂Se [M+H]⁺ 365.0551, found 365.0541.

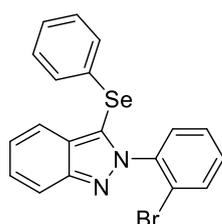


2-(2-Ethylphenyl)-3-(phenylselanyl)-2H-indazole (3c). The general procedure **A** was followed using substrate **1c** (0.2 mmol, 45 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3c** (63 mg, 84%) as colorless liquid.

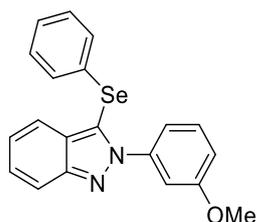
^1H NMR (400 MHz, CDCl_3): δ = 7.82 (d, J = 8.7 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.49 – 7.36 (m, 3H), 7.25 – 7.16 (m, 3H), 7.15 – 7.11 (m, 4H), 7.07 (dd, J = 7.8, 1.2 Hz, 1H), 2.16 (q, J = 7.4 Hz, 2H), 1.00 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 149.2, 141.5, 139.0, 131.6, 130.4, 130.0, 129.4, 128.9, 128.0, 127.5, 127.0, 126.9, 126.0, 123.3, 121.8, 121.0, 118.5, 23.8, 14.3. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{N}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 379.0708, found 379.0702.



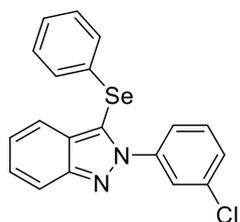
2-(2-Methoxyphenyl)-3-(phenylselanyl)-2H-indazole (3d). The general procedure A was followed using substrate **1d** (0.2 mmol, 45 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3d** (46 mg, 60%) as colorless liquid. ^1H NMR (400 MHz, CDCl_3): δ = 7.82 (d, J = 8.7 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.40 (dd, J = 8.5, 7.4 Hz, 1H), 7.32 (dd, J = 7.9, 1.8 Hz, 1H), 7.20 – 7.10 (m, 6H), 7.08 – 6.98 (m, 2H), 3.59 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 154.7, 149.5, 131.1, 130.9, 130.8, 130.7, 129.4, 129.2, 129.0, 127.0, 126.9, 123.1, 122.5, 121.0, 120.5, 118.5, 111.7, 55.6. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{OSe}$ $[\text{M}+\text{H}]^+$ 381.0501, found 381.0493.



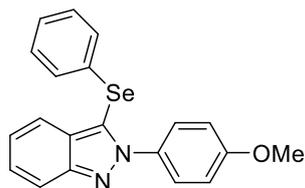
2-(2-Bromophenyl)-3-(phenylselanyl)-2H-indazole (3e). The general procedure A was followed using substrate **1e** (0.2 mmol, 55 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3e** (38 mg, 44%) as yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.83 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 7.7 Hz, 2H), 7.45 – 7.32 (m, 3H), 7.25 – 7.19 (m, 2H), 7.15 (d, J = 6.8 Hz, 5H). ^{13}C NMR (100 MHz, CDCl_3): δ = 149.6, 139.9, 133.3, 131.4, 131.2, 130.5, 129.8, 129.4, 127.8, 127.5, 127.4, 127.0, 123.6, 122.4, 122.3, 121.1, 118.6. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{BrN}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 428.9500, found 428.9494.



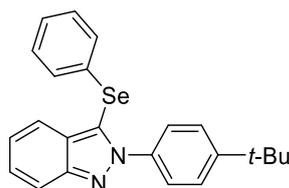
2-(3-Methoxyphenyl)-3-(phenylselanyl)-2H-indazole (3f). The general procedure A was followed using substrate **1f** (0.2 mmol, 45 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3f** (52 mg, 68%) as yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.86 (d, J = 8.7 Hz, 1H), 7.73 (d, J = 8.6 Hz, 1H), 7.41 (dd, J = 8.6, 7.5, 1H), 7.36 (t, J = 8.2 Hz, 1H), 7.21 (dd, J = 8.7, 7.5, 1H), 7.15 – 7.12 (m, 6H), 7.07 – 7.04 (m, 1H), 7.01 (dd, J = 8.5, 1.3 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 159.7, 149.2, 141.2, 131.5, 130.2, 129.5, 129.4, 128.2, 127.3, 127.1, 123.5, 121.0, 119.8, 118.8, 118.3, 115.6, 111.6, 55.4. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{OSe}$ $[\text{M}+\text{H}]^+$ 381.0501, found 381.0501. Analytical data for compound **3f** was consistent with the literature.^[1]



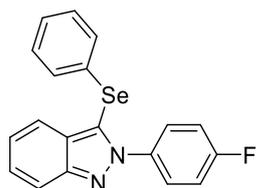
2-(3-Chlorophenyl)-3-(phenylselanyl)-2H-indazole (3g). The general procedure A was followed using substrate **1g** (0.2 mmol, 46 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3g** (70 mg, 91%) as colorless liquid. ^1H NMR (400 MHz, CDCl_3): δ = 7.82 (d, J = 8.7 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.44 – 7.38 (m, 3H), 7.22 (dd, J = 8.7, 7.4, 1H), 7.14 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3): δ = 149.5, 138.8, 135.1, 131.2, 130.4, 129.8, 129.7, 129.0, 128.4, 127.8, 127.6, 127.4, 123.8, 122.2, 121.1, 120.1, 118.4. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{ClN}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 385.0005, found 384.9994. Analytical data for compound **3g** was consistent with the literature.^[1]



2-(4-Methoxyphenyl)-3-(phenylselanyl)-2H-indazole (3h). The general procedure **A** was followed using substrate **1h** (0.2 mmol, 45 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3h** (51 mg, 67%) as colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 7.82 (d, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.22 – 7.10 (m, 6H), 6.98 – 6.93 (m, 2H), 3.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 160.0, 149.2, 133.5, 131.5, 130.4, 129.6, 128.0, 127.8, 127.2, 127.2, 123.4, 121.1, 120.1, 118.3, 113.9, 55.7. HRMS (ESI) *m/z* calcd for C₂₀H₁₇N₂OSe [M+H]⁺ 381.0501, found 381.0500. Analytical data for compound **3h** was consistent with the literature.^[1]

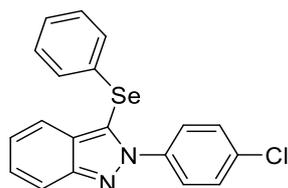


2-(4-(*tert*-Butyl)phenyl)-3-(phenylselanyl)-2H-indazole (3i). The general procedure **A** was followed using substrate **1i** (0.2 mmol, 50 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3i** (80 mg, 90%) as colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 7.84 (d, *J* = 8.7 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.49 – 7.44 (m, 4H), 7.42 – 7.36 (m, 1H), 7.22 – 7.12 (m, 6H), 1.37 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ = 152.2, 149.3, 137.8, 131.5, 130.4, 129.5, 128.0, 127.1, 126.0, 125.7, 123.4, 121.1, 119.7, 118.4, 34.9, 31.4. HRMS (ESI) *m/z* calcd for C₂₃H₂₃N₂Se [M+H]⁺ 407.1021, found 407.1019.

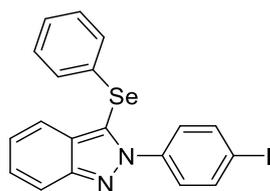


2-(4-Fluorophenyl)-3-(phenylselanyl)-2H-indazole (3j). The general procedure **A** was followed using substrate **1j** (0.2 mmol, 42 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3j** (59 mg, 80%) as colorless liquid.

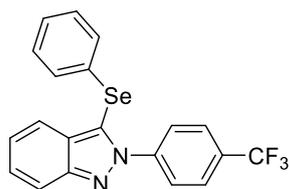
^1H NMR (400 MHz, CDCl_3): δ = 7.82 (d, J = 8.7 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.40 (dd, J = 8.4, 7.5, 1H), 7.22 (dd, J = 8.7, 7.5, 1H), 7.19 – 7.08 (m, 7H). ^{13}C NMR (100 MHz, CDCl_3): δ = 162.8 (d, $^1J_{\text{C-F}}$ = 249.2 Hz), 149.4, 136.4 (d, $^4J_{\text{C-F}}$ = 3.2 Hz), 131.2, 130.5, 129.6, 128.4 (d, $^3J_{\text{C-F}}$ = 8.2 Hz), 128.2, 127.5, 127.4, 123.7, 121.1, 120.3, 118.4, 115.8 (d, $^2J_{\text{C-F}}$ = 23.1 Hz). ^{19}F NMR (376 MHz, CDCl_3): δ = -111.73. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{FN}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 369.0301, found 369.0296.



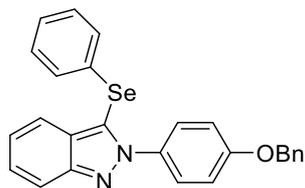
2-(4-Chlorophenyl)-3-(phenylselanyl)-2H-indazole (3k). The general procedure **A** was followed using substrate **1k** (0.2 mmol, 46 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3k** (58 mg, 76%) as yellow oil. ^1H NMR (400 MHz, CDCl_3) δ = 7.82 (d, J = 8.7 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.46 – 7.34 (m, 4H), 7.25 – 7.20 (m, 1H), 7.20 – 7.11 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3): δ = 149.4, 141.2, 134.4, 131.0, 130.7, 129.7, 129.6, 129.2, 128.3, 127.6, 127.5, 126.9, 124.7, 123.8, 121.1, 120.3, 118.4. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{ClN}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 385.0005, found 385.0000.



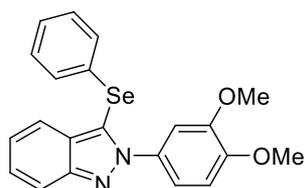
2-(4-Iodophenyl)-3-(phenylselanyl)-2H-indazole (3l). The general procedure **A** was followed using substrate **1l** (0.2 mmol, 64 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3l** (83 mg, 87%) as white solid. Mp: 84.2–86.3 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.72 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 8.5 Hz, 1H), 7.30 (dd, J = 8.5, 7.4 Hz, 1H), 7.18 (d, J = 8.6 Hz, 2H), 7.11 (dd, J = 8.8, 7.4 Hz, 1H), 7.09 – 6.97 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3): δ = 149.5, 140.0, 137.9, 131.2, 130.4, 129.7, 128.4, 128.2, 127.6, 127.4, 123.8, 121.1, 119.9, 118.4, 94.7. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{IN}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 476.9361, found 476.9358.



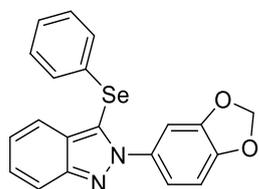
3-(Phenylselanyl)-2-(4-(trifluoromethyl)phenyl)-2H-indazole (3m). The general procedure **A** was followed using substrate **1m** (0.2 mmol, 52 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3m** (79 mg, 95%) as white solid. Mp: 108.9–109.9 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.83 (d, *J* = 8.8 Hz, 1H), 7.76 – 7.67 (m, 5H), 7.42 (dd, *J* = 8.8, 7.6 Hz, 1H), 7.23 (dd, *J* = 8.5, 7.6 Hz, 1H), 7.20 – 7.09 (m, 5H). ¹³C NMR (100 MHz, CDCl₃): δ = 149.6, 143.0, 131.0, 130.9 (q, ²*J*_{C-F} = 32.3 Hz), 130.4, 129.7, 128.6, 127.8, 127.5, 126.9, 126.0 (q, ³*J*_{C-F} = 3.4 Hz), 124.0, 123.8 (q, ¹*J*_{C-F} = 272.2 Hz), 121.1, 120.1, 118.4. ¹⁹F NMR (376 MHz, CDCl₃): δ = -62.42. HRMS (ESI) *m/z* calcd for C₂₀H₁₄F₃N₂OSe [M+H]⁺ 419.0269, found 419.0262.



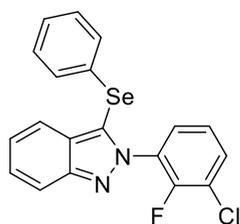
2-(4-(Benzyloxy)phenyl)-3-(phenylselanyl)-2H-indazole (3n). The general procedure **A** was followed using substrate **1n** (0.2 mmol, 60 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3n** (85 mg, 93%) as yellow solid. Mp: 106.6–108.8 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.86 (d, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.45 – 7.34 (m, 3H), 7.26 – 7.21 (m, 3H), 7.20 – 7.12 (m, 4H), 7.12 – 7.08 (m, 2H), 7.08 – 7.01 (m, 4H), 4.99 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 153.8, 149.5, 136.4, 131.0, 131.0, 130.8, 130.0, 129.2, 129.1, 127.8, 127.0, 126.9, 126.7, 123.0, 122.6, 121.0, 120.9, 118.4, 113.8, 70.6. HRMS (ESI) *m/z* calcd for C₂₆H₂₁N₂OSe [M+H]⁺ 457.0814, found 457.0808.



2-(3,4-Dimethoxyphenyl)-3-(phenylselanyl)-2H-indazole (3o). The general procedure **A** was followed using substrate **1o** (0.2 mmol, 51 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3o** (51 mg, 62%) as white solid. Mp: 131.6–133.4 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.83 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.40 (ddd, *J* = 8.6, 8.5, 1.1 Hz, 1H), 7.21 (ddd, *J* = 8.6, 8.5, 1.1 Hz, 1H), 7.18 – 7.11 (m, 5H), 7.08 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.94 (d, *J* = 2.5 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 3.94 (s, 3H), 3.67 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 149.9, 149.5, 149.1, 133.8, 132.2, 130.5, 129.9, 128.6, 127.6, 127.5, 123.9, 121.4, 120.2, 119.1, 118.7, 110.8, 110.4, 56.6, 56.2. HRMS (ESI) *m/z* calcd for C₂₁H₁₉N₂O₂Se [M+H]⁺ 411.0606, found 411.0608.

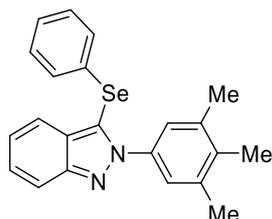


2-(Benzo[d][1,3]dioxol-5-yl)-3-(phenylselanyl)-2H-indazole (3p). The general procedure **A** was followed using substrate **1p** (0.2 mmol, 48 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3p** (61 mg, 77%) as colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 7.81 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.39 (dd, *J* = 8.4, 7.6 Hz, 1H), 7.22 – 7.12 (m, 6H), 6.97 – 6.93 (m, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.05 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 149.2, 148.3, 147.7, 134.4, 131.3, 130.5, 129.6, 128.0, 127.3, 127.3, 123.5, 121.1, 120.5, 120.3, 118.3, 107.9, 107.8, 102.1. HRMS (ESI) *m/z* calcd for C₂₀H₁₅N₂O₂Se [M+H]⁺ 395.0293, found 395.0289.

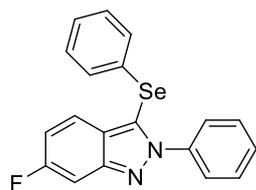


2-(3-Chloro-2-fluorophenyl)-3-(phenylselanyl)-2H-indazole (3q). The general procedure **A** was followed using substrate **1q** (0.2 mmol, 53 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3q** (32 mg, 40%) as colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 7.81 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H),

7.54 (ddd, $J = 8.6, 7.3, 1.3$ Hz, 1H), 7.41 (ddd, $J = 8.6, 7.3, 1.3$ Hz, 1H), 7.28 – 7.19 (m, 2H), 7.19 – 7.07 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.4$ (d, $^1J_{\text{C-F}} = 254.8$ Hz), 149.9, 131.9, 131.1, 130.1, 129.6 (d, $^3J_{\text{C-F}} = 12.7$ Hz), 129.5, 127.7 (d, $^2J_{\text{C-F}} = 21.2$ Hz), 127.7, 127.2, 124.4 (d, $^4J_{\text{C-F}} = 3.9$ Hz), 123.8, 122.7, 122.4 (d, $^3J_{\text{C-F}} = 13.7$ Hz), 121.0, 118.4. ^{19}F NMR (376 MHz, CDCl_3): $\delta = -120.74$. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{13}\text{ClFN}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 402.9911, found 402.9905.

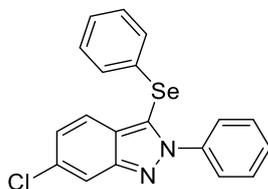


3-(Phenylselanyl)-2-(3,4,5-trimethylphenyl)-2H-indazole (3r). The general procedure **A** was followed using substrate **1r** (0.2 mmol, 47 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3r** (54 mg, 69%) as white solid. Mp: 114.3-116.9 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.82$ (d, $J = 8.7$ Hz, 1H), 7.70 (d, $J = 8.5$ Hz, 1H), 7.38 (dd, $J = 8.5, 7.4$ Hz, 1H), 7.22 – 7.15 (m, 6H), 7.10 (s, 2H), 2.28 (s, 6H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 149.1, 137.3, 137.0, 136.3, 131.9, 130.6, 129.5, 128.0, 127.2, 127.0, 125.3, 123.3, 121.0, 119.9, 118.3, 20.7, 15.5$. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 393.0864, found 393.0861.

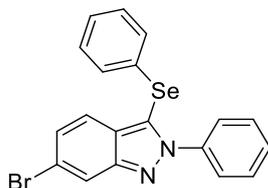


6-Fluoro-2-phenyl-3-(phenylselanyl)-2H-indazole (3s). The general procedure **A** was followed using substrate **1s** (0.2 mmol, 42 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3s** (55 mg, 72%) as colorless liquid. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.65$ (dd, $J = 9.1, 5.3$ Hz, 1H), 7.52 – 7.45 (m, 5H), 7.40 (dd, $J = 9.7, 2.2$ Hz, 1H), 7.20 – 7.09 (m, 5H), 6.99 (ddd, $J = 9.7, 9.6, 2.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 162.7$ (d, $^1J_{\text{C-F}} = 245.4$ Hz), 149.4 (d, $^3J_{\text{C-F}} = 13.3$ Hz), 140.5, 131.2, 131.1, 130.0, 129.6, 129.2, 127.8, 126.8, 125.5, 123.4 (d, $^3J_{\text{C-F}} = 11.0$ Hz), 121.3, 115.5 (d, $^2J_{\text{C-F}} = 28.2$ Hz), 101.8 (d, $^2J_{\text{C-F}} = 23.8$ Hz). ^{19}F NMR

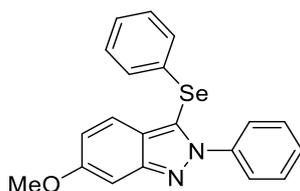
(376 MHz, CDCl₃): $\delta = -112.68$. HRMS (ESI) m/z calcd for C₁₉H₁₄FN₂Se [M+H]⁺ 369.0301, found 369.0303.



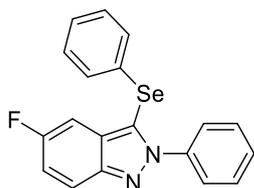
6-Chloro-2-phenyl-3-(phenylselanyl)-2H-indazole (3t). The general procedure A was followed using substrate **1t** (0.2 mmol, 46 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3t** (51 mg, 66%) as white solid. Mp: 77.6–79.5 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.80$ (s, 1H), 7.62 (d, $J = 8.9$ Hz, 1H), 7.51 – 7.45 (m, 5H), 7.22 – 7.09 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 149.4$, 140.1, 133.2, 130.8, 130.8, 129.7, 129.4, 128.9, 127.6, 126.5, 126.4, 125.0, 122.5, 121.1, 117.3. HRMS (ESI) m/z calcd for C₁₉H₁₄ClN₂Se [M+H]⁺ 385.0005, found 384.9992.



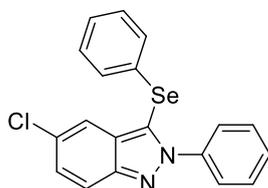
6-Bromo-2-phenyl-3-(phenylselanyl)-2H-indazole (3u). The general procedure A was followed using substrate **1u** (0.2 mmol, 55 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3u** (51 mg, 60%) as white solid. Mp: 71.5–74.2 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.00$ (s, 1H), 7.56 (d, $J = 8.9$ Hz, 1H), 7.51 – 7.45 (m, 5H), 7.29 – 7.23 (m, 1H), 7.19 – 7.09 (m, 5H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 149.9$, 140.1, 130.8, 130.8, 129.7, 129.4, 128.9, 127.6, 127.3, 126.6, 126.5, 122.6, 121.3, 121.2, 120.7. HRMS (ESI) m/z calcd for C₁₉H₁₄BrN₂Se [M+H]⁺ 428.9500, found 428.9492.



6-Methoxy-2-phenyl-3-(phenylselanyl)-2H-indazole (3v). The general procedure A was followed using substrate **1v** (0.2 mmol, 45 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3v** (33 mg, 44%) as colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 8.42 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 9.1 Hz, 1H), 7.45 (m, 4H), 7.35 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.18 – 7.13 (m, 3H), 7.03 (d, *J* = 9.1 Hz, 1H), 3.90 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 158.9, 151.9, 140.6, 132.5, 131.1, 129.5, 128.8, 127.9, 126.0, 122.8, 121.2, 121.1, 119.4, 112.6, 102.7, 57.7. HRMS (ESI) *m/z* calcd for C₂₀H₁₇N₂OSe [M+H]⁺ 381.0501, found 381.0496.

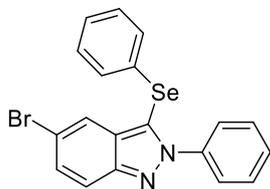


5-Fluoro-2-phenyl-3-(phenylselanyl)-2H-indazole (3w). The general procedure A was followed using substrate **1w** (0.2 mmol, 42 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3w** (70 mg, 95%) as white solid. Mp: 81.7–83.5 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.81 (dd, *J* = 9.1, 4.5 Hz, 1H), 7.54 – 7.44 (m, 5H), 7.29 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.23 – 7.09 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ = 159.4 (d, ¹*J*_{C-F} = 243.0 Hz), 146.7, 140.2, 131.1, 130.5, 129.6, 129.3, 128.9, 128.0 (d, ³*J*_{C-F} = 12.4 Hz), 127.4, 126.5, 120.6 (d, ³*J*_{C-F} = 10.2 Hz), 120.1 (d, ⁴*J*_{C-F} = 6.9 Hz), 119.0 (d, ²*J*_{C-F} = 27.3 Hz), 103.7 (d, ²*J*_{C-F} = 24.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ = -117.05. HRMS (ESI) *m/z* calcd for C₁₉H₁₄FN₂Se [M+H]⁺ 369.0301, found 369.0297.

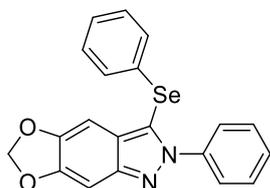


5-Chloro-2-phenyl-3-(phenylselanyl)-2H-indazole (3x). The general procedure A was followed using substrate **1x** (0.2 mmol, 46 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3x** (70 mg, 91%) as white solid. Mp: 108.9–109.8 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.76 (d, *J* = 9.1 Hz, 1H), 7.69 (s, 1H), 7.53 – 7.43 (m, 5H), 7.32 (dd, *J* = 9.1, 1.9 Hz, 1H), 7.22 – 7.13 (m, 3H), 7.13 – 7.08 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 147.7, 140.1, 130.9, 130.6, 129.7,

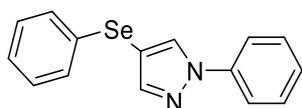
129.4, 129.3, 128.9, 128.8, 128.7, 127.5, 126.5, 120.0, 119.9, 119.9. HRMS (ESI) m/z calcd for $C_{19}H_{14}ClN_2Se$ $[M+H]^+$ 385.0005, found 385.0006. Analytical data for compound **3x** was consistent with the literature.^[1]



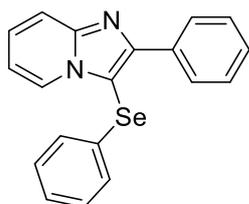
5-Bromo-2-phenyl-3-(phenylselanyl)-2H-indazole (3y). The general procedure **A** was followed using substrate **1y** (0.2 mmol, 55 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3y** (76 mg, 88%) as yellow solid. Mp: 122.5–124.9 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 7.89 (s, 1H), 7.71 (d, J = 9.1 Hz, 1H), 7.52 – 7.43 (m, 6H), 7.19 – 7.08 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.7, 140.0, 131.0, 130.8, 130.6, 129.7, 129.4, 129.3, 128.9, 127.5, 126.5, 123.3, 120.2, 119.7, 117.2. HRMS (ESI) m/z calcd for $C_{19}H_{14}BrN_2Se$ $[M+H]^+$ 428.9500, found 428.9491.



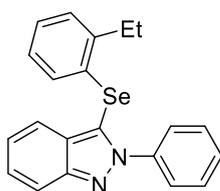
2-Phenyl-3-(phenylselanyl)-2H-[1,3]dioxolo[4,5-f]indazole (3z). The general procedure **A** was followed using substrate **1z** (0.2 mmol, 48 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3z** (50 mg, 63%) as colorless liquid. 1H NMR (400 MHz, $CDCl_3$): δ = 7.51 – 7.47 (m, 2H), 7.44 – 7.40 (m, 3H), 7.18 – 7.14 (m, 3H), 7.13 – 7.08 (m, 2H), 7.07 (s, 1H), 6.91 (s, 1H), 6.00 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 147.0, 146.7, 140.4, 131.6, 130.0, 129.6, 128.8, 128.7, 127.1, 126.3, 124.8, 118.7, 101.3, 95.9, 94.6. HRMS (ESI) m/z calcd for $C_{20}H_{15}N_2O_2Se$ $[M+H]^+$ 395.0293, found 395.0298.



1-Phenyl-5-(phenylselanyl)-1*H*-pyrazole (3aa). The general procedure **A** was followed using substrate **1aa** (0.2 mmol, 29 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3aa** (37 mg, 62%) as white solid. Mp: 98.6–101.3 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.09 (s, 1H), 7.81 (s, 1H), 7.74 – 7.67 (m, 2H), 7.47 (dd, *J* = 7.9 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.25 – 7.14 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 146.7, 139.7, 132.8, 132.5, 129.6, 129.3, 127.1, 126.5, 119.2, 103.7. HRMS (ESI) *m/z* calcd for C₁₅H₁₃N₂Se [M+H]⁺ 301.0238, found 301.0235.

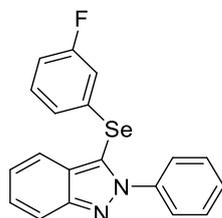


2-Phenyl-3-(phenylselanyl)imidazo[1,2-*a*]pyridine (3ab). The general procedure **A** was followed using substrate **1ab** (0.2 mmol, 39 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **3ab** (56 mg, 80%) as colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 8.35 (d, *J* = 6.8 Hz, 1H), 8.15 (d, *J* = 7.4 Hz, 2H), 7.76 – 7.69 (m, 1H), 7.44 (m, *J* = 7.4 Hz, 2H), 7.38 (m, *J* = 7.3 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.17 (d, *J* = 5.1 Hz, 3H), 7.11 (m, *J* = 7.0, 2.1 Hz, 2H), 6.85 (m, *J* = 6.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 152.0, 147.9, 133.9, 131.0, 129.8, 128.9, 128.6, 128.4, 128.3, 126.8, 126.6, 125.7, 117.6, 113.1, 102.9. HRMS (ESI) *m/z* calcd for C₁₉H₁₅N₂Se [M+H]⁺ 351.0395, found 351.0386. Analytical data for compound **3ab** was consistent with the literature.^[4]

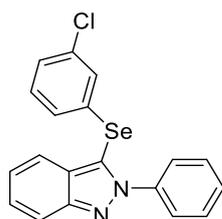


3-((2-Ethylphenyl)selanyl)-2-phenyl-2*H*-indazole (4a). The general procedure **B** was followed using substrate **2a** (0.3 mmol, 111 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **4a** (30 mg, 40%) as colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 7.84 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.44 – 7.37 (m, 4H), 7.19 (dd, *J* = 8.5, 7.6 Hz, 1H), 7.16 – 7.09 (m, 2H), 6.89 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.17 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 149.4, 143.3,

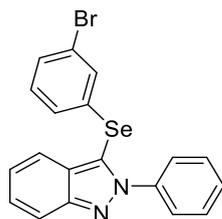
140.4, 131.8, 130.6, 129.1, 128.8, 128.8, 128.5, 127.4, 127.3, 127.1, 126.5, 123.5, 121.1, 119.7, 118.5, 28.6, 14.8. HRMS (ESI) m/z calcd for $C_{21}H_{19}N_2Se$ $[M+H]^+$ 379.0708, found 379.0705.



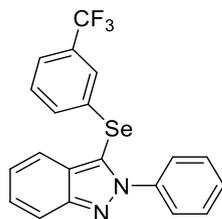
3-((3-Fluorophenyl)selanyl)-2-phenyl-2H-indazole (4b). The general procedure **B** was followed using substrate **2b** (0.3 mmol, 104 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **4b** (68 mg, 93%) as colorless liquid. 1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.54 – 7.45 (m, 5H), 7.41 (dd, J = 8.4, 7.3 Hz, 1H), 7.23 (dd, J = 8.7, 7.3 Hz, 1H), 7.14 – 7.07 (m, 1H), 6.89 – 6.82 (m, 2H), 6.81 – 6.77 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.0 (d, $^1J_{C-F}$ = 251.2 Hz), 149.4, 140.2, 133.2 (d, $^3J_{C-F}$ = 6.9 Hz), 130.8 (d, $^3J_{C-F}$ = 7.7 Hz), 129.3, 128.9, 128.2, 127.4, 126.6, 125.7 (d, $^4J_{C-F}$ = 2.8 Hz), 123.9, 120.8, 119.0, 118.6, 117.1 (d, $^2J_{C-F}$ = 23.3 Hz), 114.3 (d, $^2J_{C-F}$ = 21.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -110.95. HRMS (ESI) m/z calcd for $C_{19}H_{14}FN_2Se$ $[M+H]^+$ 369.0301, found 369.0294.



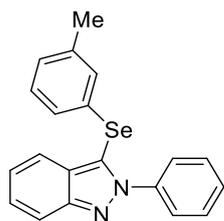
3-((3-Chlorophenyl)selanyl)-2-phenyl-2H-indazole (4c). The general procedure **B** was followed using substrate **2c** (0.3 mmol, 114 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **4c** (48 mg, 62%) as colorless liquid. 1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.53 – 7.45 (m, 5H), 7.41 (dd, J = 8.4, 7.6 Hz, 1H), 7.23 (dd, J = 8.7, 7.6 Hz, 1H), 7.16 – 7.11 (m, 1H), 7.09 (s, 1H), 7.07 – 7.01 (m, 1H), 6.97 – 6.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.4, 140.2, 135.2, 132.9, 130.5, 130.0, 129.3, 128.9, 128.4, 128.2, 127.5, 127.4, 126.6, 123.9, 120.9, 119.1, 118.6. HRMS (ESI) m/z calcd for $C_{19}H_{14}ClN_2Se$ $[M+H]^+$ 385.0005, found 384.9996.



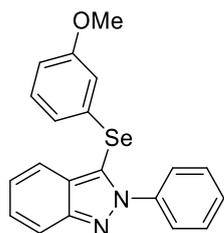
3-((3-Bromophenyl)selanyl)-2-phenyl-2H-indazole (4d). The general procedure **B** was followed using substrate **2d** (0.3 mmol, 141 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **4d** (52 mg, 61%) as colorless liquid. ^1H NMR (400 MHz, CDCl_3): δ = 7.85 (d, J = 8.7 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.53 – 7.45 (m, 5H), 7.41 (dd, J = 8.7, 7.7 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.26 – 7.20 (m, 2H), 7.02 – 6.96 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 149.4, 140.2, 133.2, 132.8, 130.9, 130.4, 129.3, 128.9, 128.9, 128.1, 127.4, 126.6, 123.9, 123.3, 120.8, 119.1, 118.5. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{BrN}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 428.9500, found 428.9492.



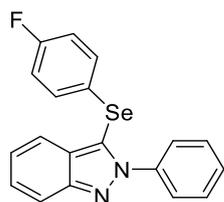
2-Phenyl-3-((3-(trifluoromethyl)phenyl)selanyl)-2H-indazole (4e). The general procedure **B** was followed using substrate **2e** (0.3 mmol, 134 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **4e** (35 mg, 42%) as colorless liquid. ^1H NMR (400 MHz, CDCl_3): δ = 7.85 (d, J = 8.7 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.50 – 7.44 (m, 5H), 7.44 – 7.34 (m, 3H), 7.26 – 7.17 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 149.4, 140.1, 133.8, 132.3, 131.7 (q, $^2J_{\text{C-F}}$ = 31.6 Hz), 129.9, 129.4, 128.9, 128.1, 127.5, 127.1 (q, $^3J_{\text{C-F}}$ = 4.1 Hz), 126.6, 124.2 (q, $^3J_{\text{C-F}}$ = 3.7 Hz), 124.0, 123.5 (q, $^1J_{\text{C-F}}$ = 272.5 Hz), 120.7, 118.9, 118.6. ^{19}F NMR (376 MHz, CDCl_3): δ = -62.77. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{14}\text{F}_3\text{N}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 419.0269, found 419.0266.



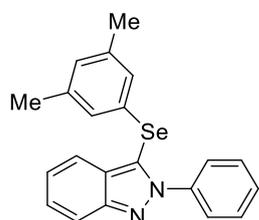
2-Phenyl-3-(*m*-tolylselanyl)-2*H*-indazole (4f). The general procedure **B** was followed using substrate **2f** (0.3 mmol, 102 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **4f** (67 mg, 92%) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.84 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.49 – 7.44 (m, 3H), 7.40 (dd, *J* = 8.5, 7.2 Hz, 1H), 7.20 (dd, *J* = 8.7, 7.2 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.99 – 6.95 (m, 2H), 6.91 (d, *J* = 7.5 Hz, 1H), 2.21 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 149.3, 140.4, 139.4, 131.1, 131.0, 129.3, 129.0, 128.8, 128.2, 128.1, 127.6, 127.2, 126.6, 123.4, 121.2, 120.1, 118.3, 21.4. HRMS (ESI) *m/z* calcd for C₂₀H₁₇N₂Se [M+H]⁺ 365.0551, found 365.0547.



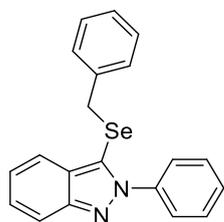
3-((3-Methoxyphenyl)selanyl)-2-phenyl-2*H*-indazole (4g). The general procedure **B** was followed using substrate **2g** (0.3 mmol, 112 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **4g** (43 mg, 56%) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.83 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.50 – 7.44 (m, 3H), 7.39 (dd, *J* = 8.5, 7.3 Hz, 1H), 7.21 (dd, *J* = 8.7, 7.3 Hz, 1H), 7.06 (dd, *J* = 9.1, 7.9 Hz, 1H), 6.73 – 6.65 (m, 3H), 3.65 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 160.1, 149.3, 140.3, 132.4, 130.3, 129.1, 128.8, 128.2, 127.3, 126.6, 123.6, 122.5, 121.1, 119.8, 118.4, 115.7, 112.9, 55.3. HRMS (ESI) *m/z* calcd for C₂₀H₁₇N₂OSe [M+H]⁺ 381.0501, found 381.0496.



3-((4-Fluorophenyl)selanyl)-2-phenyl-2H-indazole (4h). The general procedure **B** was followed using substrate **2h** (0.3 mmol, 104 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **4h** (45 mg, 61%) as colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 7.82 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.45 (m, 5H), 7.38 (dd, *J* = 8.5, 7.7 Hz, 1H), 7.21 (dd, *J* = 8.7, 7.7 Hz, 1H), 7.14 – 7.07 (m, 2H), 6.88 – 6.80 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 162.6 (d, ¹*J*_{C-F} = 247.6 Hz), 149.3, 140.3, 133.2 (d, ³*J*_{C-F} = 7.9 Hz), 129.2, 128.9, 127.8, 127.3, 126.7, 125.4 (d, ⁴*J*_{C-F} = 3.2 Hz), 123.6, 120.9, 120.4, 118.5, 116.7 (d, ²*J*_{C-F} = 21.9 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ = -113.88. HRMS (ESI) *m/z* calcd for C₁₉H₁₄N₂Se [M+H]⁺ 369.0301, found 369.0301.

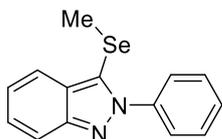


3-((3,5-Dimethylphenyl)selanyl)-2-phenyl-2H-indazole (4i). The general procedure **B** was followed using substrate **2i** (0.3 mmol, 111 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **4i** (19 mg, 25%) as colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 7.84 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.50 – 7.45 (m, 3H), 7.43 – 7.37 (m, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.80 (s, 1H), 6.75 (s, 2H), 2.16 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ = 149.3, 140.4, 139.2, 130.6, 129.2, 129.0, 128.7, 128.3, 128.1, 127.2, 126.7, 123.3, 121.3, 120.3, 118.3, 21.3. HRMS (ESI) *m/z* calcd for C₂₁H₁₉N₂Se [M+H]⁺ 379.0708, found 379.0704.

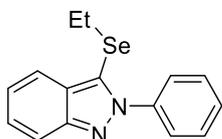


3-(Benzylselanyl)-2-phenyl-2H-indazole (4j). The general procedure **B** was followed using substrate **2j** (0.3 mmol, 102 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **4j** (51 mg, 70%) as colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 7.78 (d, *J* = 8.7 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.40 (m,

3H), 7.40 – 7.31 (m, 3H), 7.20 – 7.14 (m, 1H), 7.13 – 7.05 (m, 3H), 6.80 (d, $J = 7.0$ Hz, 2H), 3.86 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 149.2, 140.3, 137.7, 128.9, 128.7, 128.7, 128.6, 128.1, 127.3, 127.1, 126.8, 123.0, 121.0, 120.4, 118.3, 33.8$. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 365.0551, found 365.0554.

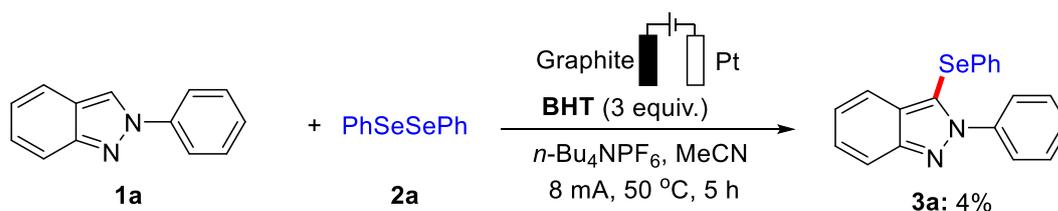


3-(Methylselanyl)-2-phenyl-2H-indazole (4k). The general procedure **B** was followed using substrate **2k** (0.3 mmol, 56 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **4k** (39 mg, 68%) as colorless liquid. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.78$ (dd, $J = 9.3, 8.9$ Hz, 2H), 7.70 – 7.63 (m, 2H), 7.60 – 7.49 (m, 3H), 7.37 (dd, $J = 8.6, 7.3$ Hz, 1H), 7.20 (dd, $J = 8.8, 7.3$ Hz, 1H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 149.3, 140.6, 129.1, 129.0, 127.2, 127.2, 126.6, 122.8, 121.2, 121.1, 118.3, 10.2$. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 289.0238, found 289.0239.



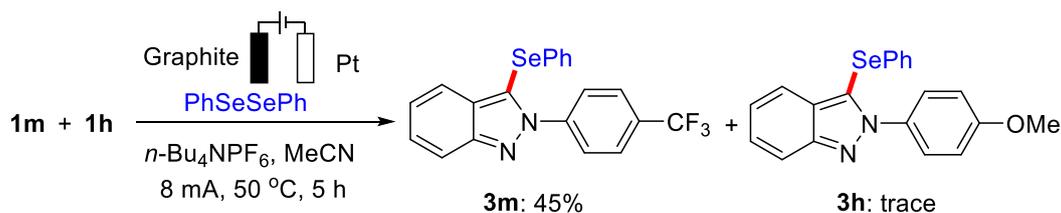
3-(Ethylselanyl)-2-phenyl-2H-indazole (4l). The general procedure **B** was followed using substrate **2l** (0.3 mmol, 65 mg). Isolation by column chromatography (PE/EtOAc: 30/1→15/1) yielded **4l** (25 mg, 41%) as yellow oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.83 - 7.73$ (m, 2H), 7.68 – 7.62 (m, 2H), 7.57 – 7.47 (m, 3H), 7.38 (dd, $J = 8.8, 7.4$ Hz, 1H), 7.20 (dd, $J = 8.4, 7.4$ Hz, 1H), 2.66 (q, $J = 7.5$ Hz, 2H), 1.18 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 148.9, 140.3, 128.7, 128.5, 127.8, 126.8, 126.5, 122.6, 121.0, 120.1, 117.9, 23.8, 15.6$. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{Se}$ $[\text{M}+\text{H}]^+$ 303.0395, found 303.0396.

Radical Scavenger Experiments



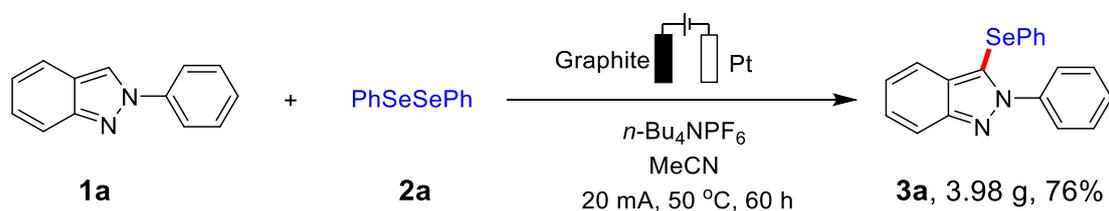
In an undivided cell (20 mL) equipped with a stirring bar, a mixture of **1a** (0.2 mmol), **2a** (0.3 mmol), BHT (3 equiv.), $n\text{-Bu}_4\text{NPF}_6$ (0.5 mmol) and MeCN (5 mL) were added. The cell was equipped with graphite plate (1.5 cm \times 1 cm \times 0.2 cm) as the anode and platinum plate (1 cm \times 1 cm \times 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 50 °C (heating module) for 5 h. When the reaction was finished, the mixture was concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate: 15/1) yielded product **3a** (3 mg, 4%) as white solid.

Intermolecular Competition Experiments



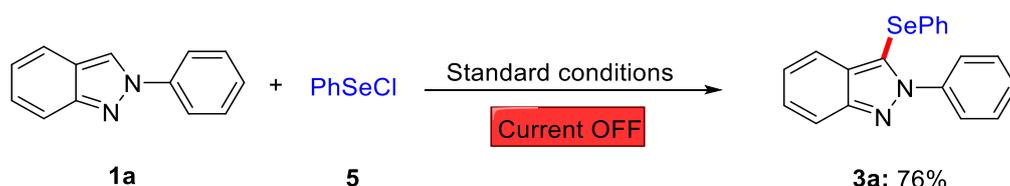
In an undivided cell (20 mL) equipped with a stirring bar, a mixture of **1m** (0.2 mmol), **1h** (0.2 mmol), **2a** (0.2 mmol), $n\text{-Bu}_4\text{NPF}_6$ (0.5 mmol) and MeCN (5 mL) were added. The cell was equipped with graphite plate (1.5 cm \times 1 cm \times 0.2 cm) as the anode and platinum plate (1 cm \times 1 cm \times 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 50 $^\circ\text{C}$ by heating the aluminum block for 5 h. When the reaction was finished, the mixture was concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate: 15/1) yielded solo product **3m** (38 mg, 45%) as white solid.

Gram-scale Synthesis

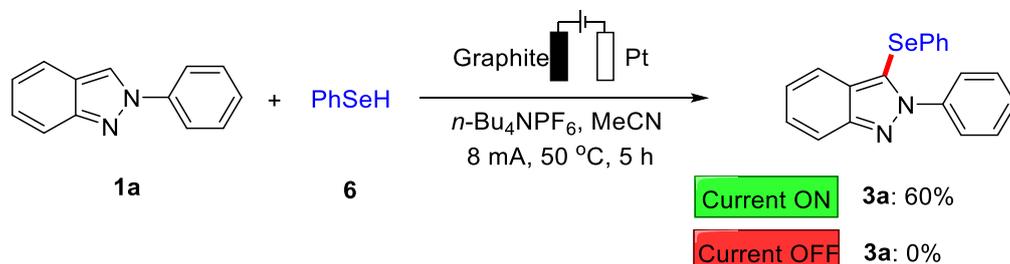


In an undivided cell (250 mL) equipped with a stir bar, a mixture of substrates **1a** (15.0 mmol, 2.91 g), **2a** (22.5 mmol, 7.02 g), $n\text{-Bu}_4\text{NPF}_6$ (15.0 mmol, 5.81 g) and MeCN (150 mL) were added. The cell was equipped with a graphite plate (3 cm \times 3 cm \times 0.6 cm) as the anode and platinum plate (3 cm \times 3 cm \times 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA at 50 $^\circ\text{C}$ in an oil bath for 60 h. When the reaction was finished, the mixture was concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate: 15/1) yielded solo product **3a** (3.98 g, 76%) as white solid.

Control Experiments



In an undivided cell (20 mL) equipped with a stirring bar, a mixture of **1a** (0.2 mmol), **2a** (0.3 mmol), **5** (0.3 mmol), *n*-Bu₄NPF₆ (0.5 mmol) and MeCN (5 mL) were added. The cell was equipped with graphite plate (1.5 cm × 1 cm × 0.2 cm) as the anode and platinum plate (1 cm × 1 cm × 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 50 °C by heating the aluminum block for 5 h. When the reaction was finished, the mixture was concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate: 15/1) yielded product **3a** (58 mg, 82%) as white solid. In addition, when performing the reaction without current, the product **3a** (53 mg, 76%) was also isolated as white solid.



In an undivided cell (20 mL) equipped with a stirring bar, a mixture of **1a** (0.2 mmol), **2a** (0.3 mmol), **6** (0.3 mmol), *n*-Bu₄NPF₆ (0.5 mmol) and MeCN (5 mL) were added. The cell was equipped with graphite plate (1.5 cm × 1 cm × 0.2 cm) as the anode and platinum plate (1 cm × 1 cm × 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 50 °C by heating the aluminum block for 5 h. When the reaction was finished, the mixture was concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate: 15/1) yielded product **3a** (42 mg, 60%) as white solid. In addition, when performing the reaction without current, no product of **3a** was formed.

Cyclic Voltammetry Experiments

Cyclic voltammetry experiments were carried out on an IGS 1230 electrochemical work station (Ingsens instruments, Guangzhou) 0.1 M $n\text{-Bu}_4\text{NPF}_6$ was dissolved in acetonitrile. Working electrode: glassy carbon, counter electrode: Pt, reference electrode: Ag-AgCl (3 M KCl). Scan rate: 100 mV/s.

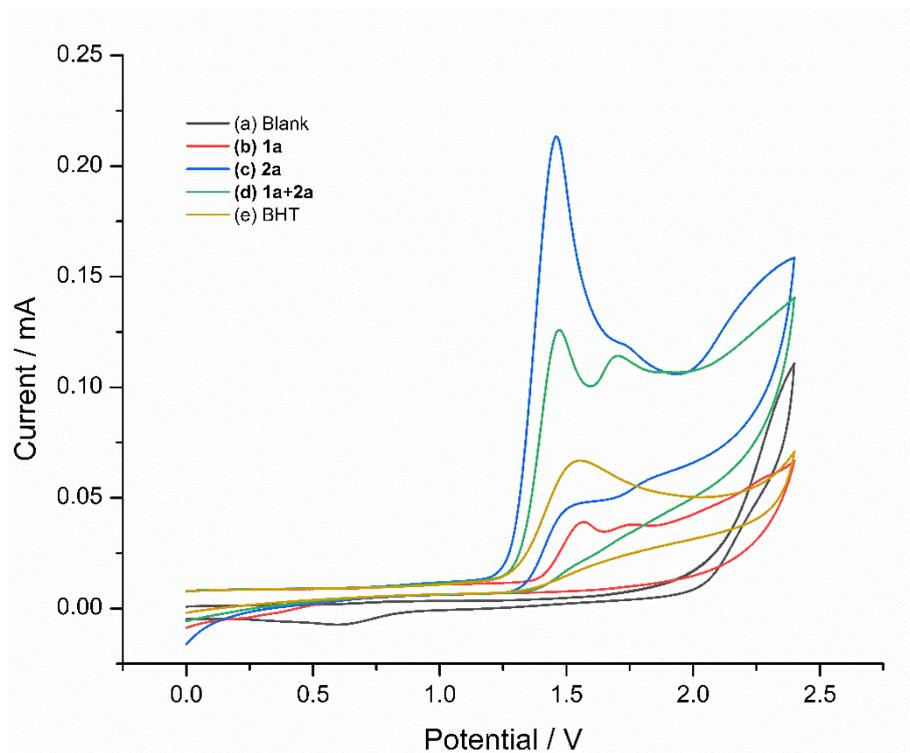


Figure S1. Cyclic voltammograms. Conditions: a glassy carbon working electrode, a Ag/AgCl (3 M KCl) reference electrode, and a platinum wire counter electrode, $n\text{-Bu}_4\text{NPF}_6$ (0.1 M in MeCN), 100mV/s scan rate. (a) Background; (b) **1a** (1 mM); (c) **2a** (1 mM); (d) **1a** (1 mM) + **2a** (1 mM)

References

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^1H -, ^{13}C - and ^{19}F -NMR Spectra

