Supporting Information for:

“Model Study on Trapping of Protein Selenenic Acids by Utilizing a Stable Synthetic Congener”

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1. Experimental Section

General experimental methods: Unless otherwise stated, all operations were performed by using high-vacuum and standard Schlenk techniques under an argon atmosphere. THF (anhydrous) was purchased from Kanto Chemical and passed through a Kayama Oxygen solvent purification system prior to use. Other solvents were purchased from commercial sources and used as received. S1, S2, S3, and cyclooctyne (14) were prepared according to the literature procedure. Other chemicals were purchased from commercial sources and used as received. Silica gel column chromatography was performed using Kanto silica gel N60 or Merck silica gel 60. Preparative thin layer chromatography (PTLC) was performed using Merck silica gel 60 PF254. 1H NMR spectra were recorded on a JEOL ECS-400, a JEOL ECX-500, or a JEOL ECZ-500, and the chemical shifts of 1H are referenced to the residual proton signal of CDCl$_3$ (δ 7.25) or C$_6$D$_6$ (δ 7.15). 13C NMR spectra were recorded on JEOL ECS-400, a JEOL ECX-500, or a JEOL ECZ-500, and the chemical shifts of 13C are referenced to the signal of CDCl$_3$ (δ 77.0) or C$_6$D$_6$ (δ 128.0). 77Se NMR spectra were recorded on a JEOL ECX-500, and the chemical shifts of 77Se are referenced to the diphenyl diselenide (δ 480) as external standard. All spectra were assigned with the aid of DEPT, COSY, HMQC, and HMBC NMR experiments. IR spectra were recorded on a JASCO FT/IR-4100 by utilizing a KBr disk. Mass spectra were measured on a JEOL JMS-T100GCv “AccuTOF GCv” using a field desorption probe. Melting points were measured with a Yanaco MP-S3 and are uncorrected.

Synthesis of quinquephenyl bromide S3.

![Synthesis diagram](image)

To a Grignard reagent prepared by the reaction of 2-bromo-1,3-diisopropylbenzene (S1) (12.97 g, 27.2 mmol) and magnesium turnings (0.9476 g, 39.0 mmol) in THF (50 mL) was added a solution of 1,3,5-tribromo-2-iodobenzene (S2) (4.179 g, 9.48 mmol) over 30 min at 75 °C. The reaction mixture was stirred at 75 °C overnight and then treated with 1 M HCl at 0 °C. After extraction with ether, the combined organic layer was dried over MgSO$_4$ and evaporated in vacuo. To the resulting oily mixture was added EtOH to precipitate white solids, which was collected by filtration. It was purified by silica gel column chromatography (hexane:CHCl$_3$ = 7:1) to give quinquephenyl bromide S3 (6.923 g, 7.29 mmol, 80%) as colorless crystals.

S3: colorless crystals; M.p. >300 °C; 1H NMR (400 MHz, CDCl$_3$) δ 1.04 (d, J = 6.8 Hz, 24H), 1.14 (d, J = 6.8 Hz, 24H), 2.73 (sept, J = 6.8 Hz, 8H), 7.03 (t, J = 1.5 Hz, 2H), 7.19 (d, J = 7.7 Hz, 8H), 7.32 (t, J = 7.7 Hz, 4H), 7.39 (d, J = 1.5 Hz, 4H), 7.69 (d, J = 1.5 Hz, 2H), 7.73 (t, J = 1.5 Hz, 1H); 13C NMR (100 MHz,
Synthesis of arylboronic acid pinacol ester 4.

To a solution of S3 (6.923 g, 7.29 mmol) in THF (30 mL) was added n-BuLi (1.5 M in hexane, 5.2 mL, 7.8 mmol) at –78 °C over 30 min. After the reaction mixture was stirred for 30 min at –78 °C, trimethyl borate (0.86 mL, 7.7 mmol) was added at –78 °C, and it was allowed to warm to room temperature and stirred overnight. The reaction mixture was treated with 1 M HCl and extracted with Et₂O. The combined organic layer was dried over MgSO₄, and the solvent was evaporated in vacuo. To the resulting residue was added THF (15 mL) and pinacol (0.860 g, 7.28 mmol), and it was stirred at 78 °C overnight. After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography (hexane:CHCl₃ = 7:1) to give 4 (4.072 g, 4.09 mmo, 69%) as colorless crystals.

4: colorless crystals; M.p. >300 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.06 (d, J = 6.9 Hz, 24H), 1.16 (d, J = 6.9 Hz, 24H), 1.32 (s, 12H), 2.79 (sept, J = 6.9 Hz, 8H), 7.02 (d, J = 1.2 Hz, 2H), 7.22 (d, J = 7.6 Hz, 8H), 7.35 (t, J = 7.6 Hz, 4H), 7.48 (d, J = 1.6 Hz, 4H), 7.94 (d, J = 1.6 Hz, 1H), 8.04 (d, J = 1.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 24.1 (q), 24.4 (q), 24.9 (q), 30.4 (d), 84.0 (s), 122.5 (d), 126.6 (d), 127.9 (d), 129.2 (d), 129.8 (d), 132.8 (d), 139.1 (s), 140.77 (s), 140.83 (s), 121.1 (s), 146.7 (s). Anal. Calcd. for C₅₆H₅₇BrO₂: C, 87.03; H, 7.43. Found: C, 87.13; H, 7.72.

Synthesis of BpsCHO 5.

Toluene and H₂O were degassed through bubbling of argon for 1 h prior to use. A mixture of 4 (1.798 g, 1.804 mmol), 5 (0.267 g, 1.01 mmol), Pd(PPh₃)₄ (0.225 g, 0.195 mmol), and Ba(OH)₂•8H₂O (2.842 g, 9.01 mmol) in a mixed solvent of THF (36 mL), THF (4.5 mL), and H₂O (4.5 mL) was stirred at 91 °C for 21 h. After cooling to room temperature, the reaction mixture was passed through a pad of celite, and the solvent was evaporated in vacuo. The crude mixture was purified by silica gel column chromatography
(hexane:CHCl₃ = 4:1) to give BpsCHO 6 (1.633 g, 0.886 mmol, 98%) as colorless crystals.

6: colorless crystals; M.p. 275.2-277.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.03 (d, J = 6.8 Hz, 4H), 1.10 (d, J = 6.8 Hz, 4H), 2.74 (sept, J = 6.8 Hz, 16H), 6.99 (t, J = 1.6 Hz, 4H), 7.17 (d, J = 7.8 Hz, 16H), 7.31 (t, J = 7.8 Hz, 8H), 7.43 (d, J = 1.6 Hz, 8H), 7.46 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 1.6 Hz, 4H), 7.59 (t, J = 8.4 Hz, 2H), 7.86 (t, J = 1.6 Hz, 2H), 10.13 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 24.1 (q), 24.3 (q), 30.4 (d), 122.5 (d), 125.3 (d), 126.4 (d), 127.5 (d), 127.9 (d), 130.3 (d), 131.8 (d), 133.0 (s), 139.0 (s), 140.1 (s), 140.8 (s), 141.1 (s), 141.5 (s), 144.1 (s), 146.7 (s), 193.6 (d); LRMS (FD) m/z 1843 [M⁺]. Anal. Calcd for C₁₃₉H₁₄₈O: C, 90.50; H, 8.63. Found: C, 90.48, H, 8.34.

**Synthesis of BpsCH₂OH 7.**

To a mixture of LiAlH₄ (101.2 mg, 2.67 mmol) in THF (12 mL) was added a solution of 6 (0.572 g, 0.310 mmol) in THF (8 mL) at 0 °C over 15 min. The reaction mixture was allowed to warm to room temperature and stirred for 3 h, and then 1 M aq. HCl was carefully added at 0 °C. After extraction with CHCl₃, the combined organic layer was dried over MgSO₄, and the solvent was evaporated in vacuo. The crude mixture was recrystallized from hexane/acetonitrile to give 7 (0.544 g, 0.295 mmol, 95%) as colorless crystals.

7: colorless crystals; M.p. >300 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.03 (d, J = 6.8 Hz, 4H), 1.09 (d, J = 6.8 Hz, 4H), 2.74 (sept, J = 6.8 Hz, 16H), 4.63 (d, J = 6.0 Hz, 2H), 6.99 (t, J = 1.5 Hz, 4H), 7.17 (d, J = 6.8 Hz, 16H), 7.32 (t, J = 6.8 Hz, 8H), 7.45 (d, J = 1.6 Hz, 8H), 7.71 (d, J = 1.6 Hz, 4H), 7.85 (t, J = 1.6 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 24.1 (q), 24.3 (q), 30.4 (d), 122.5 (d), 125.3 (d), 126.4 (d), 127.5 (d), 127.9 (d), 130.0 (d), 130.2 (d), 135.2 (d), 139.0 (s), 140.3 (s), 141.1 (s), 141.6 (s, two singlets are overlapped, judged by HMBC), 142.3 (s), 143.2 (s), 146.7 (s); LRMS (FD) m/z 1845 [M⁺].

**Synthesis of BpsCH₂Br 8.**

To a solution of 7 (52.3 mg, 28.3 µmol) in 1,4-dioxane (1.5 mL) was added PBr₃ (7.8 µL, 83 µmol), and
the resulting solution was stirred at 85 °C for 18 h. After the reaction mixture was cooled to room temperature, ice-cooled water was added, and the resulting pale yellow solution was stirred at room temperature until it became colorless. After extraction with CHCl₃, the combined organic layer was dried over MgSO₄, and the solvent was evaporated in vacuo. The crude mixture was recrystallized from hexane to give 8 (44.0 mg, 23.1 µmol, 81%) as colorless crystals.

8: colorless crystals; M.p. >300 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.04 (d, J = 6.8 Hz, 48H), 1.09 (d, J = 6.8 Hz, 48H), 2.75 (sept, J = 6.8 Hz, 16H), 4.38 (s, 2H), 7.00 (t, J = 1.6 Hz, 4H), 7.18 (d, J = 8.0 Hz, 16H), 7.32 (t, J = 7.6 Hz, 8H), 7.30-7.45 (m, 11H), 7.36 (t, J = 7.6 Hz, 2H), 7.50 (d, J = 1.6 Hz, 8H), 7.77 (d, J = 1.6 Hz, 4H), 7.89 (t, J = 1.6 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 24.1 (q), 24.3 (q), 30.3 (d), 67.1 (t), 122.5 (d), 125.5 (d), 126.4 (d), 127.3 (d), 127.9 (d), 128.2 (d), 130.03 (d), 130.2 (d), 132.9 (s), 139.0 (s), 140.2 (s), 141.0 (s), 141.3 (s), 141.6 (s), 143.5 (s), 146.7 (s); LRMS (FD) m/z 1907 [M⁺].

Synthesis of BpsCH₂SeCN 9.

To a mixture of potassium selenocyanate (145.8 mg, 1.03 mmol) in THF (4 mL) was added a solution of 8 (574.6 mg, 0.301 mmol) in THF (4 mL) at 0 °C over 10 min. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. After addition of water, the mixture was extracted with toluene. The organic layer was washed with brine and dried over MgSO₄. After evaporation of solvent in vacuo, the crude mixture was recrystallized from hexane to give 9 (518.7 mg, 0.268 mmol, 89%) as colorless crystals.

9: colorless crystals; M.p. >300 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.03 (d, J = 6.8 Hz, 48H), 1.09 (d, J = 6.8 Hz, 48H), 2.75 (sept, J = 6.8 Hz, 16H), 4.37 (s, 2H), 7.00 (t, J = 1.6 Hz, 4H), 7.17 (d, J = 7.6 Hz, 16H), 7.32 (t, J = 7.6 Hz, 8H), 7.33 (t, J = 7.2 Hz, 1H), 7.37 (d, J = 7.2 Hz, 2H), 7.45 (d, J = 1.6 Hz, 8H), 7.58 (d, J = 1.6 Hz, 4H), 7.89 (t, J = 1.6 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 24.2 (q), 24.3 (q), 30.4 (d), 77.2 (t), 100.8 (s), 122.5 (d), 126.0 (d), 126.4 (d), 127.0 (d), 127.9 (d), 128.3 (d), 130.1 (d), 130.2 (s), 130.3 (d), 138.9 (s), 140.1 (s), 141.1 (s), 141.2 (s), 141.9 (s), 143.5 (s), 146.7 (s); ⁷⁷Se NMR (95 MHz, CDCl₃) δ 244; IR (KBr) 2152 cm⁻¹ (ν(CN)); LRMS (FD) m/z 1934 [M⁺].
Synthesis of BpsCH₂SeH 10.

The following reaction and workup were performed under argon atmosphere. A solution of 9 (58.7 mg, 30.3 µmol) in THF (2 mL) was degassed through three freeze-pump-thaw cycles, and the flask was flushed with argon. To a solution of NaBH₄ (3.3 mg, 87 µmol) in MeOH (2 mL), which was degassed through three freeze-pump-thaw cycles, was added the degassed solution of 9 at –3 °C over 5 min. After the reaction mixture was stirred at room temperature for 2 h, degassed water (0.5 mL) was added. Extraction was performed by using CHCl₃ that was degassed through bubbling of argon and then pre-cooled at 0 °C. The combined organic layer was dried over MgSO₄, and the solvent was evaporated in vacuo. The crude mixture was recrystallized from hexane to give 10 (48.7 mg, 25.5 µmol, 84%) as colorless crystals.

10: colorless crystals; M.p. 293.8-296.0 °C (dec); ¹H NMR (400 MHz, CDCl₃) δ –0.13 (t, J = 6.4 Hz, 1H), 1.03 (d, J = 6.8 Hz, 48H), 1.09 (d, J = 6.8 Hz, 48H), 2.76 (sept, J = 6.8 Hz, 16H), 3.74 (d, J = 6.4 Hz, 2H), 7.00 (t, J = 1.4 Hz, 4H), 7.17 (d, J = 1.4 Hz, 4H), 7.12-7.17 (m, 11H), 7.48 (d, J = 6.8 Hz, 2H), 7.69 (d, J = 1.4 Hz, 4H), 7.88 (t, J = 1.4 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 16.9 (t), 24.2 (q), 24.4 (q), 30.5 (d), 122.6 (d), 125.2 (d), 126.6 (d), 126.8 (d), 127.3 (d), 128.0 (d), 130.0 (d), 130.3 (d), 136.5 (s), 139.1 (s), 140.2 (s), 141.1 (s), 141.5 (s), 142.2 (s), 142.5 (s), 146.8 (s); ⁷⁷Se NMR (95 MHz, CDCl₃) δ 95; LRMS (FD) m/z 1909 [M⁺].

Synthesis of BpsCH₂SeOH 3.

A stock solution of H₂O₂ (30%, 30 µL, 0.26 mmol) in THF (1 mL) and that of NaOH (94.3 mg, 2.36 mmol) in H₂O (8.0 mL) were prepared prior to the reaction. To a solution of 10 (69.0 mg, 36.1 µmol) in THF (2 mL) were added 0.12 mL of the stock solution of NaOH (36 µmol) and 125 µL of that of H₂O₂ (36 µmol) at 0 °C, and the reaction mixture was stirred for 2 h at 0 °C. Then, the solvent was evaporated in vacuo, and NMR measurement of the crude mixture in C₆D₆ showed that selenenic acid 3 was formed in 99% yield. Selenenic acid 3 can also be prepared from oxidation of 10 with NaBO₃. To a solution of 10 (16.9 mg, 8.9 µmol) was added an aqueous solution of NaBO₃ (0.18 M, 106 µL, 19 µmol) at –2 °C. The solution was
stirred at the same temperature at the same temperature for 30 min and then at room temperature for 1 h. After treatment with 3% aq. NaHSO₃, the mixture was extracted with CHCl₃ under an argon atmosphere. The combined organic layer was dried over MgSO₄ and evaporated in vacuo. ¹H NMR measurement of the crude mixture in C₆D₆ showed that 3 was formed quantitatively.

3: colorless crystals; M.p. 250.0-251.5 °C; ¹H NMR (400 MHz, C₆D₆) δ 1.07 (d, J = 6.8 Hz, 48H), 2.03 (s, 1H), 2.99 (sept, J = 6.9 Hz, 16H), 4.18 (s, 2H), 6.91-7.02 (A₂B pattern, 3H), 7.10 (t, J = 1.6 Hz, 4H), 7.20 (d, J = 7.6 Hz, 16H), 7.34 (t, J = 7.6 Hz, 8H), 7.48 (d, J = 1.6 Hz, 4H), 8.06 (d, J = 1.6 Hz, 2H); ¹³C NMR (125 MHz, C₆D₆) δ 24.4 (q), 24.6 (d), 30.8 (d), 35.5 (t), 122.0 (d), 126.5 (d), 127.2 (d), 128.4 (d), 130.1 (d), 130.9 (d), 132.8 (d), 139.4 (s), 141.6 (s), 141.9 (s), 142.1 (s), 142.3 (s), 142.8 (s), 143.1 (s), 146.9 (s); ⁷⁷Se NMR (95 MHz, C₆D₆) ν 3511 cm⁻¹ (OH). Anal. Calcd. for C₁₃₉H₁₆₀OSe: C, 86.69; H, 8.37. Found: C, 86.43; H, 8.43.

Reaction of 3 with dimeredone (1).

To 3 (15.0 mg, 7.8 µmol) in an NMR tube with a J-young valve was added a solution of 1 (5.5 mg, 39 µmol) in C₆D₆ (0.6 mL) at room temperature, and the tube was carefully sealed. In the ¹H NMR measurement after 5 min, selenide 11 was formed quantitatively. After extraction with CHCl₃, the combined organic layer was dried over MgSO₄, and the solvent was evaporated in vacuo. The crude mixture was purified by PTLC (hexane:CHCl₃ = 2:1) to afford 11 (8.0 mg, 3.9 µmol, 50%) as colorless crystals

11: colorless crystals; M.p. 225.0-228.0 °C; ¹H NMR (400 MHz, C₆D₆) δ 0.46 (s, 6H), 1.06 (d, J = 6.8 Hz, 48H), 1.14 (d, J = 6.8 Hz, 48), 1.63 (s, 2H), 1.69 (s, 2H), 3.02 (sept, J = 6.8 Hz, 16H), 3.81 (s, 2H), 6.80 (s, 1H), 6.92-6.99 (A₂B pattern, 3H), 7.10 (t, J = 1.4 Hz, 4H), 7.18 (d, J = 7.2 Hz, 16H), 7.32 (t, J = 7.2 Hz, 8H), 7.81 (d, J = 1.4 Hz, 8H), 8.01 (d, J = 1.4 Hz, 4H), 8.16 (t, J = 1.4 Hz, 2H); ¹³C NMR (100 MHz, C₆D₆) δ 24.5 (q), 24.6 (q), 27.8 (q), 29.0 (s), 30.8 (d), 41.2 (t), 50.3 (t), 106.3 (s), 122.9 (d), 126.2 (d), 127.1 (d), 128.5 (d), 128.6 (d), 130.6 (d), 130.9 (d), 132.0 (d), 139.6 (s), 141.8 (s), 142.4 (s), 142.66 (s), 142.74 (s), 143.8 (s), 147.0 (s), 147.6 (s), 190.6 (s); ⁷⁷Se NMR (95 MHz, C₆D₆) ν 79.

Reaction of 3 with acetylacetone (12).

To 3 (15.0 mg, 7.8 µmol) in an NMR tube with a J-young valve was added a solution of 12 (5 eq) in THF (0.6 mL) at room temperature, and the tube was carefully sealed. In the ¹H NMR measurement after 8 min, selenide 13a was formed quantitatively. After extraction with CHCl₃, the combined organic layer was dried over MgSO₄, and the solvent was evaporated in vacuo. The crude mixture was purified by PTLC (hexane:CHCl₃ = 2:1) to afford 13a (86%) as colorless crystals

13a: colorless crystals; M.p. 225.0-228.0 °C; ¹H NMR (400 MHz, C₆D₆) δ 0.46 (s, 6H), 1.06 (d, J = 6.8 Hz, 48H), 1.14 (d, J = 6.8 Hz, 48), 1.63 (s, 2H), 1.69 (s, 2H), 3.02 (sept, J = 6.8 Hz, 16H), 3.81 (s, 2H), 6.80 (s, 1H), 6.92-6.99 (A₂B pattern, 3H), 7.10 (t, J = 1.4 Hz, 4H), 7.18 (d, J = 7.2 Hz, 16H), 7.32 (t, J = 7.2 Hz, 8H), 7.81 (d, J = 1.4 Hz, 8H), 8.01 (d, J = 1.4 Hz, 4H), 8.16 (t, J = 1.4 Hz, 2H); ¹³C NMR (100 MHz, C₆D₆) δ 24.5 (q), 24.6 (q), 27.8 (q), 29.0 (s), 30.8 (d), 41.2 (t), 50.3 (t), 106.3 (s), 122.9 (d), 126.2 (d), 127.1 (d), 128.5 (d), 128.6 (d), 130.6 (d), 130.9 (d), 132.0 (d), 139.6 (s), 141.8 (s), 142.4 (s), 142.66 (s), 142.74 (s), 143.8 (s), 147.0 (s), 147.6 (s), 190.6 (s); ⁷⁷Se NMR (95 MHz, C₆D₆) ν 79.

Estimated by ¹H NMR.
To a solution of 3 (169 mg, 88.0 µmol) in THF (6.6 mL) was added 12 (45 µL, 0.44 µmol) at room temperature. After the reaction mixture was allowed to react for 8 min, the solvent was evacuated in vacuo to afford a mixture of 13a and 13b (13a:13b = 86:14, estimated by ¹H NMR). The crude mixture was purified by silica gel column chromatography (hexane:CHCl₃ = 3:1), and subsequent reprecipitation from hexane afforded a mixture of 13a and 13b (110 mg, 54.7 µmol, 63%; 13a:13b = 93:7, estimated by ¹H NMR).

13a: ¹H NMR (500 MHz, CDCl₃) δ 1.02 (d, J = 6.9 Hz, 48H), 1.09 (d, J = 6.9 Hz, 48H), 1.66 (s, 6H), 2.73 (sept, J = 6.9 Hz, 16H), 3.89 (s, 2H), 3.84 (s, 2H), 6.99 (t, J = 1.4 Hz, 3H), 7.17 (d, J = 7.8 Hz, 16H), 7.25-7.33 (m, 11H), 7.42 (d, J = 1.7 Hz, 8H), 7.62 (d, J = 1.7 Hz, 4H), 7.78 (t, J = 1.7 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 24.39 (q), 24.54 (q), 25.39 (q), 28.72 (t), 30.64 (d), 99.93 (s), 125.54 (d), 126.94 (d), 127.67 (d), 128.20 (d), 130.36 (d), 130.43 (d), 132.67 (s), 139.18 (s), 140.67 (s), 141.36 (s), 142.71 (s), 143.21 (s), 197.16 (s); ⁷⁷Se NMR (95 MHz, CDCl₃) δ 247.

13b: ¹H NMR (500 MHz, CDCl₃) δ 1.03 (d, J = 6.6 Hz, 48H), 1.08 (d, J = 6.8 Hz, 48H), 1.62 (s, 6H), 2.73 (sept, J = 6.9 Hz, 16H), 3.64 (s, 2H), 3.83 (s, 2H), 6.99 (t, J = 1.4 Hz, 3H), 7.17 (d, J = 7.8 Hz, 16H), 7.27-7.33 (m, 11H), 7.42 (d, J = 1.5 Hz, 8H), 7.59 (d, J = 1.5 Hz, 4H), 7.80 (t, J = 1.5 Hz, 2H); ⁷⁷Se NMR (95 MHz, CDCl₃) δ 329.

The following data were obtained for a mixture of 13a and 13b (13a:13b = 92:8); M.p. >300 ºC; LRMS (FD) m/z 2007 [M⁺]; Anal. Calcd. for C₁₄₄H₁₆₆O₂Se C, 86.14; H, 8.33. Found: C, 86.11; H, 8.39.

Reaction of 3 with cyclooctyne (14).

A stock solution of cyclooctyne (14) (5.4 µL, 43 µmol) in C₆D₆ (0.40 mL) was prepared. To a solution of 2 (14.0 mg, 7.3 µmol) in C₆D₆ (0.40 mL) was added a part of the stock solution of 14 (0.20 mL, 22 µmol as 14) at room temperature. In the ¹H NMR measurement after 5 min, it was found that 15 was formed quantitatively. The reaction mixture was extracted with CHCl₃, and the combined organic layer was dried over MgSO₄. After evaporation of the solvent in vacuo, the resulting crude mixture was purified by PTLC (hexane:CHCl₃ = 2:1) to afford 15 (9.5 mg, 4.7 µmol, 65%) as colorless solids.

15: colorless solids; M.p. 227.0-229.0 ºC; ¹H NMR (400 MHz, C₆D₆) δ 1.07 (d, J = 6.6 Hz, 48H), 1.12 (d, J = 6.8 Hz, 48H), 1.01-1.03 (m, 8H), 1.44-1.55 (m, 1H), 1.66-1.91 (m, 3H), 2.99 (sept, J = 6.8 Hz, 16H), 3.71 (d, J = 12.0 Hz, 1H), 3.83 (d, J = 12.0 Hz, 1H), 5.88 (t, J = 8.0 Hz, 1H), 6.92-7.04 (A,B pattern, 3H), 7.10 (brs, 4H), 7.18 (d, J = 7.6 Hz, 16H), 7.31 (t, J = 7.6 Hz, 8H), 7.65-8.01 (br, 12H), 8.17 (t, J = 1.6 Hz, 2H); ¹³C NMR (125 MHz, C₆D₆) δ 24.1 (q), 24.3 (q), 24.7 (t), 25.3 (t), 25.8 (t), 26.3 (t), 28.1 (t), 29.4 (t), 30.6 (d), 51.6 (t), 122.6 (d), 125.5 (d), 126.9 (d), 127.1 (d), 128.2 (d), 129.2 (d), 130.2 (d), 130.9 (d), 132.5 (d), 139.2
(s), 141.1 (s), 141.6 (s), 142.1 (s), 142.5 (s), 142.9 (s), 143.5 (s), 146.6 (s), 146.7 (s); $^{77}$Se NMR (95 MHz, C$_6$D$_6$) δ 920; IR (KBr) ν 1055 cm$^{-1}$ (Se=O).

Reactions of 3 with acetamide (16).

(i) Under acidic conditions

The reaction was carried out in an NMR tube with a J-young valve. To a solution of 3 (13.5 mg, 7.0 µmol) in C$_6$D$_6$ (0.6 mL) was added acetamide 16 (2.2 mg, 37 µmol), benzoic acid (4.4 mg, 36 µmol), and bis(trimethylsilyl)methane (1 drop, internal standard). The tube was carefully sealed, and the reaction at room temperature was monitored by $^1$H NMR spectroscopy. After 25 h, N-selenoamide 17 was formed in 85% yield, which was confirmed by $^1$H NMR measurement. The reaction mixture was opened in air and extracted with chloroform. The combined organic layer was dried over MgSO$_4$, and the solvent was evaporated in vacuo. The resulting crude mixture was purified by PTLC (hexane:CHCl$_3$ = 1:1) to give 17 (5.0 mg, 2.5 µmol, 36%).

(ii) Under basic conditions

The reaction was carried out in an NMR tube with a J-young valve at room temperature. To a solution of 3 (22.8 mg, 11.9 µmol) in C$_6$D$_6$ (0.6 mL) was added acetamide 16 (2.7 mg, 46 µmol), triethylamine (4.7 µL, 47 µmol), and bis(trimethylsilyl)methane (1 drop, internal standard). The tube was carefully sealed, and the reaction at room temperature was monitored by $^1$H NMR spectroscopy. After 6 h, 17 was formed in 92% yield, which was confirmed by $^1$H NMR measurement. The reaction mixture was opened in air and extracted with chloroform. The combined organic layer was dried over MgSO$_4$, and the solvent was evaporated in vacuo. The crude mixture was purified by PTLC (hexane:CHCl$_3$ = 1:1) to give 17 (12.4 mg, 6.3 µmol, 53%).

17: colorless solids; Mp 227.0-229.0 ºC; $^1$H NMR (500 MHz, CDCl$_3$, 320 K) δ 1.05 (d, J = 6.8 Hz, 48H), 1.12 (d, J = 6.8 Hz, 48H), 1.48 (s, 3H, CH$_3$C(=O)NH), 2.77 (sept, J = 6.8 Hz, 16H), 4.26 (brs, 2H, CH$_2$Se), 5.27 (s, 1H, NH), 7.01(t, J =1.2 Hz, 4H), 7.18 (d, J = 7.8 Hz, 16H), 7.29-7.37 (m, 10H), 7.47 (d, J = 1.2 Hz),
7.62 (br, 4H), 7.88 (br, 2H); $^{13}$C NMR (500 MHz, CDCl$_3$, 320 K) δ 21.2 (br, q), 24.2 (q), 24.3 (q), 30.5 (d), 34.8 (br, t), 122.6 (d, one doublet overlapped), 125.4 (br, d), 126.5 (d), 127.4 (d), 128.0 (d), 130.0 (d), 130.5 (d), 139.0 (s, one singlet overlapped), 140.2 (s), 141.3 (s), 141.7 (s), 142.6 (br, s), 146.8 (s), 170.6 (br, s, C=O); $^{77}$Se NMR (95 MHz, CDCl$_3$, 320 K) δ 690.

**Reaction of 3 with benzylamine.**

The reaction was carried out in an NMR tube with a J-young valve at room temperature. To a solution of 3 (8.2 mg, 4.3 µmol) in C$_6$D$_6$ (0.6 mL) was added benzylamine (6.0 µL, 55 µmol) and bis(trimethylsilyl)methane (1 drop, internal standard). The tube was carefully sealed, and the reaction was monitored by $^1$H NMR spectroscopy. After 30 min, selenenamide 18 was formed quantitatively, which was confirmed by $^1$H NMR measurement. Purification by PTLC was unsuccessful due to complete decomposition of 18. Isolation of 18 was accomplished in another experiment through precipitation from CHCl$_3$/CH$_3$CN, where 18 (51.5 mg, 25.5 µmol, 68%) was obtained from 3 (72.6 mg, 37.7 µmol) and benzylamine (21 µL, 0.19 mmol).

18: white crystals; Mp 226.5-228.0 °C; $^1$H NMR (400 MHz, C$_6$D$_6$) δ 1.02 (d, J = 6.8 Hz, 48H), 1.07 (d, J = 6.8 Hz, 48H), 2.94 (sept, J = 6.8 Hz, 16H), 3.50 (s, 2H), 3.66 (s, 2H), 6.73-6.75 (m, 3H), 6.80-6.92 (m, 5H), 7.04 (t, J = 1.5 Hz, 4H), 7.13 (d, J = 7.6 Hz, 16H), 7.28 (t, J = 7.6 Hz, 8H), 7.63 (d, J = 1.5 Hz, 8H), 7.82 (d, J = 1.6 Hz, 4H), 8.00 (t, J = 1.6 Hz); $^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 24.1 (q), 24.3 (q), 30.6 (d), 58.8 (t), 86.7 (t), 122.7 (d), 125.4 (d), 126.3 (s), 126.9 (d), 127.8 (d), 128.0 (d), 128.2 (d), 128.3 (d), 128.5 (d), 129.8 (d), 130.7 (d), 134.0 (d), 139.2 (s), 140.9 (s), 141.3 (s), 141.7 (s), 141.9 (s), 142.8 (s), 142.9 (s), 146.7 (s); $^{77}$Se NMR (95 MHz, C$_6$D$_6$) δ 709.
2. NMR data

\( ^1H \text{ NMR (400 MHz, CDCl}_3 \) 

\( ^{13}C \text{ NMR (100 MHz, CDCl}_3 \)
$^1$H NMR (400 MHz, CDCl$_3$)

\[ \begin{align*}
\text{X : parts per Million : Proton} \\
10 & 9 & 8 & 7 & 6 & 5 & 4 & 3 & 2 & 1 & 0
\end{align*} \]

\[ \begin{align*}
\end{align*} \]

$^1$C NMR (100 MHz, CDCl$_3$)

\[ \begin{align*}
\text{X : parts per Million : Carbon13} \\
220 & 210 & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0 & -10 & -20
\end{align*} \]

\[ \begin{align*}
193.589 & 146.698 & 144.085 & 141.454 & 141.053 & 140.844 & 140.119 & 138.956 & 133.025 & 131.824 & 130.832 & 130.279 & 127.915 & 127.495 & 126.408 & 125.531 & 122.499 & 77.324 & 77.000 & 76.676 & 30.376 & 24.293 & 24.121
\end{align*} \]
H NMR (400 MHz, CDCl₃)

C NMR (100 MHz, CDCl₃)
$^1$H NMR (400 MHz, C$_6$D$_6$)

11

$^{13}$C NMR (100 MHz, C$_6$D$_6$)

11
$^1$H NMR (400 MHz, $C_6D_6$)

BpsCH$_2$Se$\sim$H$\sim$Ph

$^{13}$C NMR (100 MHz, $C_6D_6$)

BpsCH$_2$Se$\sim$H$\sim$Ph

X : parts per Million : Proton

X : parts per Million : Carbon13
References