

Supporting Information

General Experimental. Reactions were run under an atmosphere of argon. Flash chromatography was performed using E. Merck Silica Gel 60 (70-230 mesh.). Preparative TLC was done with EM Silica Gel 60 PF254. THF was distilled from sodium/benzophenone ketyl. Methylene chloride was distilled from calcium hydride, and was deoxygenated with argon before use.

2,6-Dimethylbenzenesulfinyl Chloride. Excess sulfur dioxide was bubbled through a solution of 2,6-dimethylbenzenemagnesium bromide (1.0 M in THF, 20 mL) at 0 °C in a fume hood allowing for adequate venting of SO₂. After 2-3 h, the reaction mixture was diluted with ice-cold 5% HCl. The aqueous layer was then extracted with 20 mL of methylene chloride. The organic extracts were combined, dried over MgSO₄, and concentrated *in vacuo* to afford 2,6-dimethylbenzenesulfinic acid as a white solid (3.3 g, 95%). This material was used without further purification.

To a solution of the above 2,6-dimethylbenzenesulfinic acid (3.3 g in 7 mL of THF) was added dropwise 1.7 mL of thionyl chloride at rt. After 3 h, the solvent was removed under reduced pressure and excess thionyl chloride was evaporated *in vacuo*. The resulting 2,6-dimethylbenzenesulfinyl chloride (3.4 g, 95%) was used without further purification (dark green liquid). ¹H NMR (200 MHz) 7.35 (br t, *J*=7.6 Hz, 1H), 7.13 (br d, *J*=7.6 Hz, 2H), 2.66 (s, 6H).

General Procedure for Radical Cyclization Reactions. To a solution of the oxime (0.3 mmol) and radical trap (TEMPO: 0.45 mmol; diphenyl diselenide: 0.6 mmol; diphenyl disulfide: 6 mmol; 1,4-cyclohexadiene: 9 mmol) in methylene chloride (7.5 mL) at -50 °C was added *N,N*-diisopropylethylamine (0.6 mmol) and 2,6-dimethylbenzenesulfinyl chloride (0.6 mmol). The mixture was then warmed slowly to rt, and stirred for about 5 h. The solution was concentrated and the residue was purified by flash column chromatography (hexane/ethyl acetate, 80/20 0/100) to give the cyclization product.

2-(2,2,6,6-Tetramethylpiperidin-1-yloxy)methyl-3,3a,4,5,6,7-hexahydro-2H-indole (8a): ¹H NMR (360 MHz) 4.15 (m, 0.4H), 4.03 (dd, *J* = 8.2, 4.6 Hz, 0.6H), 4.01 (m, 0.6H), 3.89-3.82 (m, 1H), 3.76 (dd, *J* = 8.6, 4.6 Hz, 0.4H), 2.66-2.58 (m, 2H), 2.20-2.03 (m, 3H), 1.94-1.86 (m, 1H), 1.78-1.68 (m, 1H), 1.48-0.92 (m, 22H); ¹³C NMR (90 MHz) 180.1, 179.4, 79.7, 78.7, 70.3, 69.9, 59.8, 59.7, 48.7, 48.0, 39.6, 39.5, 34.8, 34.7, 33.1, 32.95, 32.9, 31.8, 31.7, 26.8, 26.7, 25.4, 25.3, 20.3, 17.1, 17.0. HRMS (C₁₈H₃₂N₂O): Calcd. 293.2593 (MH⁺), Found 293.2587.

Anal. Calcd for C₁₈H₃₂N₂O: C, 61.64; H, 6.55, N, 4.79;. Found: C, 61.42; H, 6.41; N, 4.71.

2-Phenylselenylmethyl-3,3a,4,5,6,7-hexahydro-2H-indole (8b): ¹H NMR (360 MHz) 7.58-7.54 (m, 2H), 7.29-7.24 (m, 3H), 4.38 (m, 0.4H), 4.10 (m, 0.6H), 3.44 (dd, *J* = 11.8, 5.4 Hz, 0.6H), 3.25 (dd, *J* = 12.2, 5.0 Hz, 0.4H), 3.05 (dd, *J* = 11.8, 8.2 Hz, 0.6H), 2.94 (dd, *J* = 12.2, 7.8 Hz, 0.4H), 2.78-2.54 (m, 2H), 2.40 (ddd, *J* = 12.8, 9.1, 7.3 Hz, 0.6H), 2.21-1.97 (m, 3H), 1.88-1.78 (m, 1H), 1.68 (ddd, *J* = 13.2, 8.7, 6.8 Hz), 1.50-1.09 (m,

4H); ^{13}C NMR (75 MHz) 180.5, 179.9, 132.3, 132.3, 130.6, 129.0, 126.6, 70.6, 70.5, 48.9, 48.0, 36.7, 34.9, 34.8, 34.6, 34.2, 31.9, 31.7, 26.96, 26.5, 25.3, 25.1. HRMS ($\text{C}_{15}\text{H}_{19}\text{NSe}$): Calcd. 292.0769 (MH^+), Found 292.0760.

2-Phenylsulfenylmethyl-3,3a,4,5,6,7-hexahydro-2H-indole (8c): ^1H NMR (360 MHz) 7.32-7.28 (m, 2H), 7.21-7.16 (m 2H), 7.08 (br. t, $J = 7.3$ Hz, 1H), 4.21 (m, 0.4H), 3.97 (m, 0.6H), 3.40 (dd, $J = 12.6, 5.4$ Hz, 0.6H), 3.20 (dd, $J = 12.8, 4.7$ Hz, 0.4H), 2.89 (dd, $J = 12.6, 8.2$ Hz, 0.6H), 2.76 (dd, $J = 12.8, 8.0$ Hz), 2.65-2.45 (m, 2H), 2.30 (ddd, $J = 12.9, 8.6, 7.5$ Hz, 0.6H), 2.12-1.87 (m, 3H), 1.78-1.69 (m, 1H), 1.58 (ddd, $J = 13.3, 8.4, 6.6$ Hz), 1.40-0.90 (m, 4H); ^{13}C NMR (90 MHz) 180.7, 180.1, 136.7, 136.6, 128.9, 128.9, 128.8, 125.7, 125.7, 69.8, 69.8, 48.6, 47.8, 40.3, 39.4, 36.1, 34.8, 34.7, 34.2, 31.8, 31.7, 26.9, 26.4, 25.3, 25.1. HRMS ($\text{C}_{15}\text{H}_{19}\text{NS}$): Calcd. 246.1316 (MH^+), Found 246.1318.

2-[1-Methyl-1-(2,2,6,6-tetramethylpiperidin-1-yloxy)-ethyl]-3,3a,4,5,6,7-hexahydro-2H-indole (10a): ^1H NMR (300 MHz) 4.37 (m, 0.4H), 4.14 (m, 0.6H), 2.68-2.62 (m, 1H), 2.56-2.47 (m, 1H), 2.33 (m, 0.6H), 2.22-2.06 (m, 2.4H), 2.02-1.97 (m, 1H), 1.84-1.76 (m, 1H), 1.58-0.92 (m, 28H); ^{13}C NMR (90 MHz) 180.2, 178.8, 80.6, 80.3, 80.2, 80.0, 59.3, 59.2, 48.7, 48.0, 40.9, 40.9, 35.4, 34.8, 34.8, 34.7, 34.6, 34.4, 32.0, 31.78, 31.1, 30.0, 27.2, 26.6, 25.5, 25.3, 24.5, 23.9, 22.7, 21.97, 20.8, 20.7, 20.39, 20.37, 17.1. HRMS ($\text{C}_{20}\text{H}_{36}\text{N}_2\text{O}$): Calcd. 321.2906 (MH^+), Found 321.2924.

2-(1-Methyl-1-phenylselenylethyl)-3,3a,4,5,6,7-hexahydro-2H-indole (10b): ^1H NMR (300 MHz) 7.58 (br. t, $J = 7.8$ Hz, 2H), 7.29-7.18 (m, 3H), 4.10-4.03 (m, 0.4H), 3.88-3.80 (m, 0.6H), 2.60-2.45 (m, 2H), 2.20-2.02 (m, 3H), 1.96-1.87 (m, 1H), 1.76-1.68 (m, 1H), 1.58-1.14 (m, 10H); ^{13}C NMR (75 MHz) 181.7, 180.3, 168.5, 138.6, 133.4, 128.6, 128.49, 128.45, 128.37, 80.2, 79.97, 51.6, 50.5, 48.7, 48.2, 35.2, 34.3, 32.6, 32.0, 31.7, 27.9, 27.7, 27.1, 26.9, 26.7, 26.6, 26.5, 25.7, 25.3, 25.1. HRMS ($\text{C}_{17}\text{H}_{23}\text{NSe}$): Calcd. 318.1101 (MH^+), Found 318.1080.

2-(1-Methyl-1-phenylsulfenylethyl)-3,3a,4,5,6,7-hexahydro-2H-indole (10c): ^1H NMR (300 MHz) 7.48 (br. t, $J = 7.2$ Hz, 2H), 7.29-7.22 (m, 3H), 3.98-3.92 (m, 0.4H), 3.81-3.73 (m, 0.6H), 2.60-2.42 (m, 2H), 2.24 (m, 0.6H), 2.18-2.00 (m, 2.4H), 1.97-1.85 (m, 1H), 1.76-1.65 (m, 1H), 1.53-1.02 (m, 10H); ^{13}C NMR (90 MHz) 181.2, 180.1, 137.7, 137.6, 131.8, 131.6, 128.6, 128.6, 128.4, 128.3, 79.2, 79.0, 53.1, 51.9, 48.7, 48.2, 35.2, 34.3, 32.0, 31.8, 31.7, 31.5, 27.3, 27.1, 27.0, 26.6, 25.3, 25.1, 24.9, 23.8. HRMS ($\text{C}_{17}\text{H}_{23}\text{NS}$): Calcd. 274.1629 (MH^+), Found 274.1651.

2-Isopropyl-3,3a,4,5,6,7-hexahydro-2H-indole (10d): ^1H NMR (300 MHz) 3.90-3.80 (m, 0.4H), 3.55-3.49 (m, 0.6H), 2.70-2.45 (m, 3H), 2.18-2.04 (m, 3H), 2.00-1.89 (m, 1H), 1.82-1.71 (m, 2H), 1.50-1.08 (m, 3H), 1.04 (d, $J = 6.7$ Hz, 1.8H), 0.93 (d, $J = 6.8$ Hz, 1.2H), 0.85 (d, $J = 6.7$ Hz, 1.8H), 0.79 (d, $J = 6.8$ Hz, 1.2H); ^{13}C NMR (75 MHz) 178.8, 178.4, 77.2, 76.8, 48.4, 48.1, 35.2, 34.7, 33.4 (2), 33.1, 31.8, 31.8, 31.5, 27.2, 26.6, 25.5, 25.2, 20.3, 19.5, 18.7, 18.2. HRMS ($\text{C}_{11}\text{H}_{19}\text{N}$): Calcd. 166.1596 (MH^+), Found 166.1584.

4,4-Dimethyl-2-phenylselenylmethyl-3,4-dihydro-2H-pyrrole (12b): ^1H NMR (360 MHz) 7.58-7.49 (m, 2H), 7.32-7.16 (m, 4H), 4.31 (m, 1H), 3.35 (dd, $J = 11.9, 5.9$ Hz,

1H), 3.01 (dd, $J = 11.9, 7.8$ Hz, 1H), 1.96 (dd, $J = 12.9, 7.3$ Hz, 1H), 1.40 (dd, $J = 12.9, 7.7$ Hz), 1.19 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (90 MHz) 175.3, 132.5, 130.4, 129.0, 126.8, 72.2, 49.9, 43.6, 34.3, 26.2, 24.8. HRMS ($\text{C}_{13}\text{H}_{17}\text{NSe}$): Calcd. 262.0664 (MH^+), Found 262.0646.

4,4-Dimethyl-2-phenylsulfenylmethyl-3,4-dihydro-2H-pyrrole (12c): ^1H NMR (360 MHz) 7.34 (br. d, $J = 8.0$ Hz, 1H), 7.25-7.20 (m, 3H), 7.10 (br. t, $J = 7.3$ Hz, 1H), 4.22 (m, 1H), 3.38 (dd, $J = 12.7, 5.6$ Hz), 2.91 (dd, $J = 12.7, 8.1$ Hz), 1.92 (dd, $J = 12.9, 7.4$ Hz), 1.43 (dd, $J = 12.9, 7.7$ Hz), 1.16 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (90 MHz) 175.5, 136.4, 129.2, 128.9, 125.9, 71.5, 49.9, 42.9, 40.0, 26.2, 24.8. HRMS ($\text{C}_{13}\text{H}_{17}\text{NS}$): Calcd. 220.1160 (MH^+), Found 220.1170.

5-Methyl-2-[1-methyl-1-(2,2,6,6-tetramethylpiperidin-1-yloxy)-ethyl]-3,4-dihydro-2H-pyrrole (14a): ^1H NMR (360 MHz) 4.30-4.25 (m, 1H), 2.49-2.44 (m, 2H), 2.01 (d, $J = 1.7$ Hz, 3H), 2.04-1.92 (m, 2H), 1.51 (s, 3H), 1.50-1.42 (m, 4H), 1.31-1.24 (m, 2H), 1.15 (s, 3H), 1.13 (s, 3H), 1.07 (2, 3H), 1.06 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (90 MHz) 174.5, 82.1, 80.5, 59.3, 40.9, 40.9, 39.3, 34.7, 24.4, 23.7, 22.3, 20.8, 20.4, 19.8, 17.1. HRMS ($\text{C}_{17}\text{H}_{32}\text{N}_2\text{O}$): Calcd. 281.2593 (MH^+), Found 281.2599.

5-Methyl-2-(1-methyl-1-phenylselenylethyl)-3,4-dihydro-2H-pyrrole (14b): ^1H NMR (360 MHz) 7.66-7.64 (m, 2H), 7.36-7.25 (m, 3H), 4.04-4.00 (m 1H), 2.60-2.40 (m, 2H), 2.04 (s, 3H), 2.04-1.85 (m, 2H), 1.39 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (90 MHz) 175.4, 138.4, 128.5, 127.5, 82.1, 51.2, 39.4, 27.7, 26.4, 25.6, 19.8. HRMS ($\text{C}_{14}\text{H}_{19}\text{NSe}$): Calcd. 282.0760 (MH^+), Found 282.0753.

5-Methyl-2-(1-methyl-1-phenylsulfenylethyl)-3,4-dihydro-2H-pyrrole (14c): ^1H NMR (360 MHz) 7.56-7.54 (m, 2H), 7.34-7.29 (m, 3H), 3.99-3.94 (m, 1H), 2.55-2.41 (m, 2H), 2.04 (d, $J = 4.0$ Hz, 3H), 1.90-2.05 (m, 2H), 1.30 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (90 MHz) 175.5, 137.7, 131.7, 128.6, 128.4, 81.0, 52.5, 39.4, 27.0, 24.9, 24.6, 19.8. HRMS ($\text{C}_{14}\text{H}_{19}\text{NS}$): Calcd. 234.1316 (MH^+), Found 234.1321.
Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{NS}$: C, 72.05; H, 8.21, N, 6.00;. Found: C, 71.78; H, 8.15; N, 5.95.

5-Methyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)-4-aza-tricyclo[4.2.1.0^{0,0}]non-4-ene (16a): ^1H NMR (300 MHz) 4.03 (d, $J = 4.6$ Hz, 1H), 3.39 (s, 1H), 2.99 (m, 1H), 2.72 (m, 1H), 2.30 (m, 1H), 1.99 (m, 1H), 1.95 (s, 3H), 1.43 (s, 6H), 1.13 (s, 6H), 1.57-1.13 (m, 9H); ^{13}C NMR (75 MHz) 183.3, 89.0, 79.4, 59.2, 50.8, 47.7, 44.9, 40.1, 34.9, 34.8, 32.7, 20.2, 19.2, 17.2. HRMS ($\text{C}_{18}\text{H}_{30}\text{N}_2\text{O}$): Calcd. 291.2436 (MH^+), Found 291.2436.

5-Methyl-2-phenylselenyl-4-aza-tricyclo[4.2.1.0^{0,0}]non-4-ene (16b): ^1H NMR (300 MHz) 7.48-7.39 (m, 2H), 7.22-7.11 (m, 3H), 4.02 (d, $J = 4.6$ Hz, 1H), 3.05 (m, 1H), 2.99 (s, 1H), 2.41-2.38 (m, 2H), 2.22 (br. d, $J = 10.9$ Hz, 1H), 1.96 (s, 3H), 1.68-1.58 (m, 2H), 1.28 (br. d, $J = 12.6$ Hz, 1H); ^{13}C NMR (75 MHz) 184.2, 132.7, 130.5, 129.1, 126.8, 77.6, 52.3, 48.9, 48.0, 45.6, 37.4, 34.5, 19.4. HRMS ($\text{C}_{15}\text{H}_{17}\text{NSe}$): Calcd. 286.0664 (MH^+), Found 286.0657.

5-Methyl-2-phenylsulfenyl-4-aza-tricyclo[4.2.1.0^{0,0}]non-4-ene (16c): ¹H NMR (300 MHz) 7.35-7.26 (m, 4H), 7.14 (br. t, *J* = 7.2 Hz, 1H), 3.95 (d, *J* = 4.4 Hz, 1H), 3.09 (m, 1H), 2.93 (s, 1H), 2.48-2.41 (m, 2H), 2.28 (br. d, *J* = 5.5 Hz, 1H), 2.03 (s, 3H), 1.67 (ddd, *J* = 12.6, 10.3, 4.1 Hz, 1H), 1.62 (br. d, *J* = 11.0 Hz, 1H), 1.35 (br. d, *J* = 12.6 Hz, 1H); ¹³C NMR (90 MHz) 184.2, 136.1, 129.0, 129.0, 125.7, 77.2, 52.4, 52.2, 48.1, 44.9, 36.7, 34.2, 19.5. HRMS (C₁₅H₁₇NS): Calcd. 244.1160 (MH⁺), Found 244.1150.