A General Synthesis of *N*-Vinyl Nitrones

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SUPPORTING INFORMATION

Contents:

General Experimental	S2
Literature Procedures	S3
Preparation of Nitroalkene 24f	S4
Preparation of 2-Selenenyl Nitroalkanes 25	S6
Preparation of Nitron Selenides 27	S19
Preparation of <i>N</i> -Vinyl Nitrones 28	S31
Preparation of Nitron 32	S44
¹ H NMR Spectra of all Compounds	S47
Tables of Atomic Coordinates for PM3 Calculations	S52
References	S73

General Experimental

All reactions were performed in oven (140 °C) and/or flame dried glassware under an atmosphere of dry nitrogen or argon. Reaction solvent methylene chloride (unstabilized HPLC grade) was dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvents ethanol and ethyl acetate (spectrophotometric grade) were used without further purification. Solvents for filtration and chromatography were certified ACS grade. “Brine” refers to a saturated solution of sodium chloride. All reaction temperatures correspond to internal temperatures measured with Teflon coated thermocouples unless noted as bath temperature.

^1H and ^{13}C NMR spectra were recorded at (500 MHz, ^1H ; 126 MHz, ^{13}C). Spectra were referenced to residual chloroform (7.26 ppm, ^1H ; 77.0 ppm, ^{13}C) or benzene (7.15 ppm, ^1H ; 128.0 ppm ^{13}C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), sextet, m (multiplet) and br (broad). Coupling constants, J , are reported in Hertz. COSY, HMQC, and/or HMBC 2D experiments were utilized to make assignments when needed. Spectra available upon request to denmark@scs.uiuc.edu. Electron Impact (EI) mass spectral data are reported in the form of m/z (intensity relative to the base peak = 100). Infrared spectra (IR) are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%), w (weak, 0-33%). Melting points (mp) were determined in sealed capillary melting point tubes and are corrected. Kugelrohr distillation and boiling points correspond to uncorrected air bath temperatures (ABT). Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV(254) or potassium permanganate (KMnO_4). Column chromatography was performed using 230-400 mesh silica gel purchased from EM Science.

Benzaldehyde was distilled before use. Diisopropylamine was distilled from CaH_2 before use. SnCl_4 was distilled over copper before use. *meta*-Chloroperoxybenzoic acid was washed with a phosphate buffer before use. Aluminum (200 mesh), HgCl_2 , NaOH , nitroethane, NH_4OAc , MgSO_4 , diphenyl diselenide, EtOH , NaBH_4 , glacial acetic acid, Celite, and Na_2CO_3 were used as received.

Literature Procedures

The following compounds were prepared by literature methods: 2-nitropropene (**24a**),¹ nitrostyrene (**24b**),² (*E*)- α -methylnitrostyrene (**24c**),³ methyl 2-nitro-3-phenylacrylate (**24d**),⁴ 5-nitro-3,4-dihydro-2H-pyran (**24e**),⁵ 2-(3-butenyl)-benzaldehyde.⁶

(E)-1-(3-Butenyl)-2-(2-nitro-1-propenyl)benzene (24f)

2-(3-Butenyl)benzaldehyde (1.76 g, 11.0 mmol) was dissolved in nitroethane (22 mL) in a 50-mL, single-neck, round-bottom flask equipped with a reflux condenser with Ar inlet and a magnetic stir bar. Ammonium acetate (848 mg, 11.0 mmol, 1.0 equiv) was added and the reaction flask was lowered into an oil bath maintained at 124 °C. The reaction mixture was heated to reflux for 4 h then was allowed to cool to room temperature. Most (~15 mL) of the excess nitroethane was removed by rotary evaporation (45 °C, 10 mmHg) and the reaction mixture was diluted with EtOAc (50 mL) and was poured into 1/1 H₂O/brine (150 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were dried (MgSO₄) and concentrated (25 °C, 10 mmHg) to give an oil. The crude product was purified by silica gel column chromatography (30 mm x 10 cm column, hexanes/EtOAc, 19/1) to provide 2.17 g (91%) of nitroalkene **24f** as a pale yellow oil. A small portion of the material (200 mg) was distilled (Kugelrohr, 150 °C ABT, 1 mmHg) to provide an analytical sample.

Data for 24f:

bp: 150 °C (ABT, 1 mm Hg)

¹H NMR: (500 MHz, CDCl₃)

8.22 (s, 1 H, HC(2)), 7.35 (td, *J* = 7.6, 1.2, 1 H, HC(6)), 7.25-7.30 (m, 2 H, HC(4), HC(5)), 7.22 (dd, *J* = 5.8, 1.4, 1 H, HC(7)), 5.80 (ddt, *J* = 17.1, 10.2, 6.6,

1 H, HC(11)), 4.96-5.03 (m, 2 H, H₂C(12)), 2.74 (t, $J = 7.6$, 2 H, H₂C(9)), 2.32 (d, $J = 0.7$, 3 H, H₃C(13)), 2.24-2.33 (m, 2 H, H₂C(10)).

¹³C NMR: (126 MHz, CDCl₃)

148.5 (C(1)), 141.5 (C(8)), 137.1 (C(11)), 132.7 (C(2)), 131.3 (C(3)), 129.68 (C(6)), 129.66 (C(4)), 129.0 (C(7)), 126.2 (C(5)), 115.6 (C(12)), 34.9 (C(10)), 33.1 (C(9)), 13.8 (C(13)).

IR: (neta)

3072 (m), 3022 (m), 3000 (m), 2978 (m), 2933 (s), 2865 (m), 2844 (m), 1931 (w), 1825 (w), 1659 (s), 1641 (s), 1601 (s), 1519 (s), 1484 (s), 1442 (s), 1389 (s), 1326 (s), 1225 (m), 985 (s), 914 (s), 872 (s), 839 (m), 757 (s), 605 (s).

MS: (EI, 70 eV)

217 (M⁺, 2), 200 (3), 170 (5), 162 (15), 145 (11), 130 (100), 115 (38), 103 (4), 91 (14), 77 (8), 63 (6).

TLC: R_f 0.28 (hexanes/EtOAc, 19/1) [silica gel, UV]

Analysis: C₁₃H₁₅NO₂ (217.26)

Calcd: C, 71.87; H, 6.96; N, 6.45 %

Found: C, 71.82; H, 6.86; N, 6.68 %

Preparation of 2-Selenenyl Nitroalkanes 25**(2-Nitropropyl)(phenyl)selane (25a)**

Diphenyl diselenide (1.17 g, 3.75 mmol, 0.75 equiv) was suspended in EtOH (20 mL) in a 100-mL, two-neck, round-bottom flask equipped with a septum, Ar inlet, and magnetic stir bar. A solution of sodium borohydride (378 mg, 10 mmol, 2.0 equiv) in EtOH (20 mL) was added dropwise via cannula to the bright yellow reaction mixture over 10 min. The addition was stopped (after ~15 mL had been added) when all the yellow color dissipated to give a colorless solution. The reaction flask was then cooled in a 0 °C bath (ice/H₂O) for 5 min and glacial acetic acid (1.14 mL, 20 mmol, 4.0 equiv) was added dropwise via syringe. Next, nitropropene **24a** (435 mg, 5 mmol) was added in EtOH (2 mL) via cannula, the reaction was stirred 5 min at 0 °C, then the cold bath was removed. After stirring for 2 h at room temperature, the reaction mixture was poured into H₂O (200 mL) and was extracted with Et₂O (2 x 200 mL). The combined organic layers were washed with brine (200 mL), dried (MgSO₄), and concentrated (25 °C, 10 mmHg) to give a yellow oil. The crude product was purified by silica gel column chromatography (30 mm x 12 cm column, gradient elution, hexanes until diphenyl diselenide came off (bright yellow band) then hexanes/EtOAc, 9/1) to provide 981 mg, (80%) of nitro selenide **25a** as a light yellow oil. A 227 mg portion was further purified via distillation (Kugelrohr, 215 °C ABT, 1.2 mmHg) to provide 220 mg (97% recovery) of an analytical sample.

Data for 25a:

bp: 215 °C (ABT, 1.2 mmHg)

¹H NMR: (500 MHz, CDCl₃)

7.54-7.57 (m, 2 H, HC(5)), 7.28-7.33 (m, 3 H, HC(6), HC(7)), 4.61 (sextet, $J = 6.8$, 1 H, HC(2)), 3.41 (dd, $J = 13.1, 7.0$, 1 H, $HHC(1)$), 3.10 (dd, $J = 13.2, 6.8$, 1 H, $HHC(1)$), 1.63 (d, $J = 6.6$, 3 H, H₃C(3)).

¹³C NMR: (126 MHz, CDCl₃)

134.0 (C(5)), 129.5 (C(6)), 128.2 (C(7)), 128.0 (C(4)), 82.9 (C(2)), 30.7 (C(1)), 19.4 (C(3)).

IR: (neat)

3072 (m), 3058 (m), 2990 (m), 2938 (m), 2899 (w), 1954 (w), 1881 (w), 1806 (w), 1578 (s), 1552 (s), 1478 (s), 1454 (m), 1438 (s), 1405 (m), 1384 (s), 1357 (s), 1301 (m), 1220 (m), 1126 (m), 1072 (m), 1022 (s), 1000 (m), 831 (m), 740 (s), 692 (s).

MS: (EI, 70 eV)

245 (M⁺, 38), 199 (54), 172 (15), 156 (100), 117 (17), 91 (13), 77 (45), 65 (11).

TLC: R_f 0.25 (hexanes/EtOAc, 9/1) [silica gel, UV]

Analysis: C₉H₁₁NO₂Se (244.15)

Calcd: C, 44.27; H, 4.54; N, 5.74; Se, 32.34 %

Found: C, 44.40; H, 4.55; N, 5.86; Se, 33.50 %

(2-Nitro-1-phenylethyl)(phenyl)selane (25b)

Diphenyl diselenide (2.34 g, 7.50 mmol, 0.75 equiv) was suspended in EtOH (40 mL) in a 250-mL, three-neck, round-bottom flask equipped with a septum, Ar inlet, and magnetic stir bar. A solution of sodium borohydride (757 mg, 20 mmol, 2.0 equiv) in EtOH (40 mL) was added dropwise via cannula to the bright yellow reaction mixture over 10 min. The addition was stopped (after ~30 mL had been added) when all the yellow color dissipated to give a colorless solution. The reaction flask was then cooled in a 0 °C bath (ice/H₂O) for 5 min and glacial acetic acid (2.29 mL, 40 mmol, 4.0 equiv) was added dropwise via syringe. Next, nitrostyrene **24b** (1.49 g, 10 mmol) was added in one portion and the reaction was stirred 5 min at 0 °C, then the cold bath was removed and the reaction mixture was allowed to warm to room temperature. Solid precipitated and more EtOH (100 mL) was added to facilitate stirring. After being stirred for 1.5 h at room temperature, the reaction mixture was poured into H₂O (500 mL) and was extracted with Et₂O (3 x 100 mL). The combined organic layers were washed with brine (200 mL) and the combined aqueous layers were back-extracted with E₂O (100 mL). The combined organic layers were dried (MgSO₄), and concentrated (25 °C, 10 mmHg) to give a crude solid product. The material was dissolved in hot hexane (150 mL) and a hot filtration was performed. Then, the filtrate was allowed to cool to room temperature. Crystals formed after about 2 h. The filtrate was then cooled in the freezer for 20 min to complete crystallization. The fine, white

needles were isolated by suction filtration with a sintered glass funnel to give 2.28 g of nitro selenide **25b**. A second crop gave 419 mg additional **25b** for a total of 88% yield.

Data for **25b**:

mp: 90.1-91.1 °C (hexane)

¹H NMR: (500 MHz, CDCl₃)

7.51-7.54 (m, 2 H, HC(8)), 7.22-7.40 (m, 8 H, HC(4), HC(5), HC(6), HC(9), HC(10)), 5.03 (dd, $J = 13.0, 10.8$, 1 H, HHC(1)), 4.95 (dd, $J = 10.6, 5.1$, 1 H, HC(2)), 4.71 (dd, $J = 12.9, 5.1$, 1 H, HHC(1)).

¹³C NMR: (126 MHz, CDCl₃)

136.7 (C(3)), 135.9 (C(8)), 129.5 (C(9)), 129.1 (C(6)), 128.9 C(5)), 128.3 (C(10)), 127.4 (C(4)), 127.2 (C(7)), 78.9 (C(1)), 42.2 (C(2)).

IR: (KBr plate)

3071 (w), 3051 (w), 2992 (w), 2959 (w), 2940 (w), 2926 (w), 2874 (w), 1950 (w), 1881 (w), 1537 (s), 1473 (m), 1461 (w), 1438 (m), 1369 (m), 1350 (m), 1221 (m), 1199 (m), 1121 (m), 1088 (m), 1040 (m), 1024 (s), 996 (m), 874 (m), 744 (s), 692 (m).

MS: (EI, 70 eV)

307 (M⁺, 7), 261 (4), 183 (11), 157 (24), 155 (13), 150 (13), 104 (100), 78 (24), 77 (32).

TLC: R_f 0.36 (hexanes/EtOAc, 9/1) [silica gel, UV]

Analysis: C₁₄H₁₃NO₂Se (306.22)

Calcd: C, 54.91; H, 4.28; N, 4.57; Se, 25.79 %

Found: C, 54.94; H, 4.13; N, 4.62; Se, 26.91 %

(2-Nitro-1-phenylpropyl)(phenyl)selane (25c)

Diphenyl diselenide (1.17 g, 3.75 mmol, 0.75 equiv) was suspended in EtOH (20 mL) in a 100-mL, three-neck, round-bottom flask equipped with a septum, Ar inlet, and magnetic stir bar. A solution of sodium borohydride (378 mg, 10 mmol, 2.0 equiv) in EtOH (20 mL) was added dropwise via cannula to the bright yellow reaction mixture over 10 min. The addition was stopped (after ~15 mL had been added) when all the yellow color dissipated to give a colorless solution. The reaction flask was then cooled in a 0 °C bath (ice/H₂O) for 10 min and glacial acetic acid (1.14 mL, 20 mmol, 4.0 equiv) was added dropwise via syringe. Next, solid nitrostyrene **24c** (816 mg, 5.0 mmol) was added in one portion and the reaction was stirred 10 min at 0 °C, then the cold bath was removed. After being stirred for 2 h at room temperature, the reaction mixture was poured into H₂O (200 mL) and was extracted with Et₂O (2 x 100 mL). The combined organic layers were washed with brine (200 mL) and the combined aqueous washes were back extracted with Et₂O (100 mL). The combined organic layers were dried (MgSO₄) and silica gel (~5 g) was added. The solvent was removed via rotary evaporation (25 °C, 10 mmHg) to dry load a silica gel column (30 mm x 14 cm column, gradient elution, hexanes until PhSeSePh came off (bright yellow band) then hexanes/EtOAc, 9/1). The purification provided 1.52 g (95%) of **25c** as a yellowish solid and as a 1.25:1 ratio of diastereomers. Recrystallization from hexane (60 °C, 20 mL) provided the *syn* isomer selectively as fine, white needles. The first

crop gave 135 mg (>25/1 *syn/anti*) and the second crop provided 499 mg (~5/1 *syn/anti*). The mother liquor was then enriched in the *anti* isomer (1/4 *syn/anti*).

Data for *syn*-25c:

mp: 78.6-79.6 °C hexane

¹H NMR: (500 MHz, CDCl₃)

7.29-7.35 (m, 3 H, HC(7), HC(9)), 7.18-7.23 (m, 5 H, HC(6), HC(10), HC(11)),
7.05-7.07 (m, 2 H, HC(5)), 5.11 (dq, *J* = 10.7, 6.6, 1 H, HC(2)), 4.57 (d, *J* = 10.7,
1 H, HC(3)), 1.85 (d, *J* = 6.6, 3 H, H₃C(1)).

¹³C NMR: (126 MHz, CDCl₃)

138.0 (C(4)), 136.1 (C(9)), 129.1 (C(10)), 128.8 C(7)), 128.5 (C(6)), 127.9
(C(11)), 127.5 (C(5)), 127.4 (C(8)), 87.3 (C(2)), 50.7 (C(3)), 19.7 (C(1)).

IR: (KBr plate)

3060 (w), 3028 (w), 2982 (w), 2936 (w), 2885 (w), 1955 (w), 1880 (w), 1549 (s),
1537 (s), 1475 (m), 1451 (m), 1437 (m), 1385 (m), 1353 (m), 1281 (m), 1121 (w),
1088 (w), 1066 (w), 1020 (m), 999 (m), 860 (m), 778 (m), 743 (s), 694 (s).

MS: (EI, 70 eV)

321 (M⁺, 9), 319 (5), 275 (5), 197 (7), 164 (5), 157 (13), 118 (100), 117 (47), 115
(14), 91 (16), 77 (12).

TLC: *R_f* 0.29 (hexanes/EtOAc, 9/1) [silica gel, UV]

Analysis: C₁₅H₁₅NO₂Se (320.25)

Calcd: C, 56.26; H, 4.72; N, 4.37; Se, 24.66 %

Found: C, 56.16; H, 4.69; N, 4.37; Se, 26.36 %

Methyl 2-Nitro-3-phenyl-3-(phenylselanyl)propanoate (25d)

Diphenyl diselenide (1.17 g, 3.75 mmol, 0.75 equiv) was suspended in EtOH (20 mL) in a 100-mL, three-neck, round-bottom flask equipped with a septum, Ar inlet, and magnetic stir bar. A solution of sodium borohydride (378 mg, 10 mmol, 2.0 equiv) in EtOH (20 mL) was added dropwise via cannula to the bright yellow reaction mixture over 10 min. The addition was stopped (after ~15 mL had been added) when all the yellow color dissipated to give a colorless solution. The reaction flask was then cooled in a 0 °C bath (ice/H₂O) for 5 min and glacial acetic acid (1.14 mL, 20 mmol, 4.0 equiv) was added dropwise via syringe. Next, solid nitroalkene **24d** (1.04 g, 5.0 mmol) was added in one portion and the reaction was stirred 10 min at 0 °C, then the cold bath was removed. After being stirred for 1 h at room temperature, a small aliquot was taken for ¹H NMR analysis which showed complete reaction and a 1.4:1 mixture of diastereomers. The reaction mixture was then poured into H₂O (200 mL) and was extracted with Et₂O (2 x 150 mL). The combined organic layers were washed with brine (200 mL) and dried (MgSO₄). Then, silica gel (~5 g) was added. The solvent was removed via rotary evaporation (25 °C, 10 mmHg) to dry load a silica gel column (30 mm x 12 cm column, gradient elution, hexanes until PhSeSePh came off (bright yellow band) then hexanes/EtOAc, 9/1). The purification provided 1.36 g (75%, ~87% pure) of **25d** as a yellow oil and as a 1.6:1 ratio of diastereomers. The purified material was contaminated with ~13% of a 1.6:1 ratio of diastereomers of the starting nitroalkene **24d** which reformed upon purification.

Data for 25d:

¹H NMR: (500 MHz, CDCl₃)

7.18-7.44 (m, 8 H, HC(5), HC(6), HC(8), HC(9), HC(10)), 6.97-7.03 (m, 2 H, HC(4)), 5.69 (d, $J = 11.8$, 0.6 H, HC(1)), 5.65 (d, $J = 10.1$, 0.4 H, HC(1)), 5.03 (d, $J = 12.1$, 0.6 H, HC(2)), 4.95 (d, $J = 10.0$, 0.4 H, HC(2)), 3.84 (s, 1.8 H, H₃C(12)), 3.61 (s, 1.2 H, H₃C(12)).

¹³C NMR: (126 MHz, CDCl₃)

163.3, 162.8 (C(11)), 136.4, 136.2 (C(3)), 137.1, 136.7, 129.40, 129.36, 129.12, 129.10, 128.64, 128.61, 128.2, 128.1, 127.9, 127.3 (C(4), C(5), C(6), C(8), C(9), C(10)), 126.9, 125.8 (C(7)), 91.7, 90.9 (C(1)), 53.8, 53.6 (C(12)), 45.6, 43.9 (C(2)).

IR: (neat)

3089 (m), 3062 (m), 3034 (m), 2956 (m), 2910 (w), 2847 (w), 1756 (s), 1645 (m), 1600 (m), 1563 (s), 1538 (s), 1496 (m), 1478 (s), 1453 (s), 1437 (s), 1360 (s), 1277 (s), 1205 (s), 1171 (s), 1022 (m), 1001 (m), 782 (w), 743 (s), 681 (s), 616 (m).

MS: (EI, 70 eV)

365 (M⁺, 15), 319 (3), 259 (27), 207 (29), 179 (23), 162 (88), 131 (75), 115.1 (41), 102 (99), 91 (42), 78 (100), 59 (87).

TLC: R_f 0.14 (hexanes/EtOAc, 9/1) [silica gel, UV]

HRMS: C₁₆H₁₅NO₄Se (364.25)

Calcd: 365.0166

Found: 365.0166

3-Nitro-2-(phenylselanyl)tetrahydro-2H-pyran (25e)

Diphenyl diselenide (1.17 g, 3.75 mmol, 0.75 equiv) was suspended in EtOH (20 mL) in a 100-mL, three-neck, round-bottom flask equipped with a septum, Ar inlet, and magnetic stir bar. A solution of sodium borohydride (378 mg, 10 mmol, 2.0 equiv) in EtOH (20 mL) was added dropwise via cannula to the bright yellow reaction mixture over 10 min. The addition was stopped (after ~15 mL had been added) when all the yellow color dissipated to give a colorless solution. The reaction flask was then cooled in a 0 °C bath (ice/H₂O) for 5 min and glacial acetic acid (1.14 mL, 20 mmol, 4.0 equiv) was added dropwise via syringe. Next, nitroalkene **24e** (646 mg, 5.0 mmol) was added in EtOH (2 mL) via cannula and the reaction was stirred 5 min at 0 °C, then the cold bath was removed. After being stirred for 3 h at room temperature, the reaction mixture was poured into H₂O (200 mL) and was extracted with Et₂O (200 mL). The organic layer was washed with H₂O (200 mL) and the combined aqueous washes were back extracted with Et₂O (200 mL). The combined organic layers were then washed with brine (200 mL), dried (MgSO₄), and concentrated (25 °C, 10 mmHg) to give crude **25e**. The crude material was purified by silica gel column chromatography (30 mm x 15 cm column, gradient elution, hexanes until PhSeSePh came off (bright yellow band) then hexanes/EtOAc, 20/1 to 9/1) to give 947 mg (66%) of *trans*-**25e** and 252 mg of a mixture of *cis*-**25e** and nitroalkene **24e**. The nitroalkene **24e** was not present in the ¹H spectrum of the crude material. Recrystallization of *trans*-**25e** from hot hexane (30 mL) gave fine, white needles (822 mg).

Data for *trans*-25e:

mp: 57.6-59.6 °C (hexane)

¹H NMR: (500 MHz, CDCl₃)

7.61-7.64 (m, 2 H, HC(7)), 7.29-7.37 (m, 3 H, HC(8), HC(9)), 6.04 (dd, $J = 3.7$, 1.0, 1 H, HC(1)_{eq}), 4.63 (q, $J = 4.6$, 1 H, HC(2)_{eq}), 4.16 (ddd, $J = 12.0$, 9.5, 3.2, 1 H, HC(5)_{ax}), 3.74 (dt, $J = 11.0$, 4.4, 1 H, HC(5)_{eq}), 2.52 (dq, $J = 13.4$, 4.4, 1.2, 1 H, HC(3)_{eq}), 2.23 (ddt, $J = 14.7$, 10.3, 4.4, 1 H, HC(3)_{ax}), 1.90 (dtt, $J = 14.2$, 9.8, 4.2, 1 H, HC(4)_{ax}), 1.63 (dpent, $J = 13.7$, 4.6, 1 H, HC(4)_{eq}).

¹³C NMR: (126 MHz, CDCl₃)

134.6 (C(7)), 129.3 (C(8)), 128.4 (C(9)), 127.9 (C(6)), 83.3 (C(2)), 81.7 (C(1)), 64.1 (C(5)), 24.9 (C(3)), 21.5 (C(4)).

IR: (KBr plate)

3058 (w), 3028 (w), 2909 (w), 1954 (w), 1881 (w), 1553 (s), 1543 (s), 1494 (w), 1476 (w), 1455 (m), 1430 (m), 1437 (m), 1375 (m), 1302 (w), 1192 (w), 1083 (w), 1020 (w), 999 (w), 902 (w), 794 (w), 747 (m), 742 (m), 696 (s), 635 (m).

MS: (EI, 70 eV)

287 (M⁺, 4), 157 (19), 155 (11), 130 (70), 84 (100), 83 (18), 78 (11), 77 (15), 56 (10), 55 (21).

TLC: R_f 0.26 (hexanes/EtOAc, 9/1) [silica gel, UV]

Analysis: C₁₁H₁₃NO₃Se (286.19)

Calcd: C, 54.91; H, 4.28; N, 4.57 %

Found: C, 54.94; H, 4.13; N, 4.62 %

(1-(2-(3-Butenyl)phenyl)-2-nitropropyl)(phenyl)selane (25f)

Diphenyl diselenide (2.11 g, 6.75 mmol, 0.75 equiv) was suspended in EtOH (36 mL) in a 250-mL, three-neck, round-bottom flask equipped with a septum, Ar inlet, internal temperature probe, and magnetic stir bar. A solution of sodium borohydride (681 mg, 18 mmol, 2.0 equiv) in EtOH (36 mL) was added dropwise via cannula to the bright yellow reaction mixture over 10 min. The addition was stopped (after ~30 mL had been added) when all the yellow color dissipated to give a colorless solution. The reaction flask was then cooled in a -78 °C bath (CO_{2(s)}/IPA) until the internal temperature reached -75 °C. Then, nitroalkene **23f** (1.95 g, 9.00 mmol) was added in EtOH (3 mL) dropwise via cannula. The reaction mixture was stirred at -75 °C (internal) for 1 h then glacial acetic acid (2.06 mL, 36.0 mmol, 4.0 equiv) was added via syringe. The acetic acid froze into small particles upon addition. Next, the cold bath was removed and the reaction mixture was allowed to warm to room temperature and stir for 1 h. Then, the reaction mixture was poured into H₂O (150 mL) and was extracted with Et₂O (2 x 150 mL). The combined organic layers were washed with brine (150 mL), dried (MgSO₄), and concentrated (25 °C, 10 mmHg) to give an oil (4.6:1 dr from ¹H NMR). The crude **25f** was mixed with ~5 g silica gel and 200 mL Et₂O and the solvent was removed by rotary evaporation. The powder was loaded onto a silica gel column for purification (gradient elution, pentane until PhSeSePh came off (bright yellow band) then pentane/Et₂O, 19/1). 2.99 g (89%) of **25f** was obtained as a pale yellow oil with a diastereomeric ratio of 4.3/1 *syn/anti*.

Data for 25f:

¹H NMR: (500 MHz, CDCl₃)

6.97-7.35 (m, 8 H, HC(4), HC(5), HC(6), HC(14), HC(15), HC(16)), 6.87 (d, $J = 7.6$, 0.81 H, HC(7)), 6.56 (d, $J = 7.3$, 0.19 H, HC(7)), 5.69-5.96 (m, 1 H, HC(11)), 5.10-5.21 (m, 1 H, HC(1)), 5.00-5.12 (m, 2 H, H₂C(12)), 4.84 (d, $J = 10.8$, 0.81 H, HC(2)), 4.81 (d, $J = 10.8$, 0.19 H, HC(2)), 2.65-2.83 (m, 2 H, H₂C(9)), 2.30-2.46 (m, 2 H, H₂C(10)), 1.85 (d, $J = 6.6$, 2.43 H, H₃C(17)), 1.42 (d, $J = 6.8$, 0.57 H, H₃C(17)).

¹³C NMR: (126 MHz, CDCl₃)

139.5, 139.1 (C(3)), 137.9, 137.5, 137.3, 136.2, 130.8, 129.8, 129.12, 129.12, 129.06, 129.0, 128.93, 128.89, 127.7, 127.5, 126.13, 126.09 (C(4), C(5), C(6), C(7), C(11), C(14), C(15), C(16)), 135.3, 134.8 (C(8)), 126.2 (C(13)), 115.5, 115.1 (C(12)), 87.5, 87.2 (C(1)), 45.1 (C(2)), 34.7, 34.2 (C(10)), 32.0, 31.8 (C(9)), 20.0, 19.0 (C(17)).

IR: (KBr plate)

3073 (m), 3019 (m), 2979 (m), 2938 (m), 2875 (m), 1954 (w), 1812 (w), 1689 (m), 1640 (s), 1551 (s), 1476 (s), 1438 (s), 1385 (s), 1356 (s), 1284 (m), 1156 (m), 1022 (s), 1000 (2), 915 (s), 862 (s), 741 (s), 692 (s), 612 (s).

MS: (EI, 70 eV)

375 (M⁺, 6), 314 (2), 219 (2), 188 (3), 171 (34), 157 (17), 143 (51), 130 (64), 119 (100), 104 (10), 91 (94), 78 (15), 65 (21).

TLC: R_f 0.35 (hexanes/EtOAc, 9/1) [silica gel, UV]

HRMS: C₁₉H₂₁NO₂Se (374.34)

Calcd: 375.0738

Found: 375.0733

Aluminum Amalgam (Al-Hg)

Solid aluminum metal (200 mesh, 0.1 to 3.0 g, ~150 mg/mmol of nitro compound) was placed in a 50-mL, single-neck, round-bottom flask equipped with a magnetic stir bar and open to the atmosphere. Aqueous sodium hydroxide solution (10% wt, 2 mL) was added the mixture was stirred until H₂ bubbles were observed (~ 2 sec). The liquid phase was removed via pipette and H₂O (2 mL) was added. The mixture was stirred for 5 sec, then the liquid phase was removed via pipette and aqueous HgCl₂ solution was added (0.5% wt, 2 mL). The mixture was stirred for 1.5 min, then the liquid phase was removed via pipette. The entire sequence was repeated again (NaOH, H₂O, HgCl₂) then the solid was washed with H₂O, EtOH, and EtOAc (2 x 2 mL each). The stir bar was removed from the reaction flask and concentration via rotary evaporation (25 °C, 10 mmHg) removed the final traces of solvent. A bright silver solid remained that was used immediately to reduce nitro compounds to hydroxylamines.

Preparation of Nitrone Selenides 27**(Z)-N-Benzylidene-1-(phenylselenanyl)propan-2-amine N-Oxide (27a)**

Nitro selenide **25a** (733 mg, 3.00 mmol) was dissolved in water-saturated EtOAc (9 mL) in a 50-mL, single-neck, round-bottom flask equipped with an Ar inlet and magnetic stir bar. The reaction flask was lowered into a room temperature water bath and aluminum amalgam (450 mg, 150 mg/mmol) was added in one portion. The cloudy, grey suspension was stirred for 15 min then was filtered through a pad of Celite (40 mm x 1 cm) with filter paper on top, eluting with EtOAc (50 mL). The filtrate was dried (Na₂SO₄) and concentrated to give crude hydroxylamine (643 mg). The residue was dissolved in EtOH (10 mL) in a 100 mL single-neck round-bottom flask equipped with a septum with an Ar inlet (needle) and a magnetic stir bar. Benzaldehyde (1.52 mL, 15.0 mmol, 5.0 equiv) was added via syringe and the reaction mixture was stirred for 2 h at room temperature. EtOAc (20 mL) and silica gel (3.5 g) were added to the reaction flask and the mixture was concentrated (25 °C, 10 mmHg) to give silica bound crude **27a**. Purification by silica gel column chromatography (30 mm x 15 cm column, dry loaded, hexanes/EtOAc, 2/1) provided 725 mg (76%, 2 steps) of nitrone **27a** as a heavy, colorless oil that became partially crystalline upon storage.

Data for 27a:

mp: 54.1-55.1 °C (hexane)

¹H NMR: (500 MHz, CDCl₃)

8.19-8.22 (m, 2 H, HC(6)), 7.49-7.52 (m, 2 H, HC(10)), 7.40-7.42 (m, 3 H, HC(11), HC(12)), 7.32 (s, 1 H, HC(4)), 7.24-7.26 (m, 3 H, HC(7), HC(8)), 4.05-4.15 (m, 1 H, HC(2)), 3.54 (dd, $J = 13.2, 8.6$, 1 H, *H*HC(1)), 3.14 (dd, $J = 13.2, 4.9$, 1 H, *H*HC(1)), 1.59 (d, $J = 6.6$, 3 H, H₃C(3)).

¹³C NMR: (126 MHz, CDCl₃)

133.9 (C(4)), 132.9, 130.4, 129.2, 128.8, 128.4, 127.3 (C(6), C(7), C(8), C(10), C(11), C(12)), 130.2, 129.1 (C(5), C(9)), 71.9 (C(2)), 31.3 (C(1)), 19.4 C(3)).

IR: (KBr plate)

3071 (w), 2978 (w), 2932 (w), 1961 (w), 1941 (w), 1582 (m), 1565 (m), 1479 (m), 1462 (m), 1437 (m), 1407 (m), 1312 (m), 1302 (m), 1144 (s), 1111 (m), 1071 (m), 1010 (m), 933 (m), 897 (m), 854 (w), 844 (m), 758 (m), 734 (s), 689 (s), 669 (m).

MS: (EI, 70 eV)

319 (M⁺, 4), 303 (2), 198 (100), 183 (16), 156 (37), 132 (19), 117 (23), 105 (11), 91 (15), 77 (34), 65 (15).

TLC: R_f 0.27 (hexanes/EtOAc, 1/1) [silica gel, KMnO₄]

Analysis: C₁₆H₁₇NOSe (318.27)

Calcd: C, 60.38; H, 5.38; N, 4.40 %

Found: C, 60.50; H, 5.32; N, 4.42 %

(Z)-N-Benzylidene-2-phenyl-2-(phenylselenanyl)ethanamine N-Oxide (27b)

Nitro selenide **25b** (1.23 g, 4.00 mmol) was dissolved in water-saturated EtOAc (12 mL) in a 50-mL, single-neck, round-bottom flask equipped with an Ar inlet and magnetic stir bar. The reaction flask was lowered into a room temperature water bath and aluminum amalgam (600 mg, 150 mg/mmol) was added in one portion. The cloudy, grey suspension was stirred for 30 min then was filtered with a Buchner funnel through hardened filter paper, eluting with EtOAc (80 mL). The filtrate was dried (K_2CO_3) and concentrated (25 °C, 10 mmHg) to give crude hydroxylamine (944 mg). The residue was dissolved in EtOH (13.3 mL) in a 50-mL, single-neck, round-bottom flask equipped with a septum with an Ar inlet (needle) and a magnetic stir bar. Benzaldehyde (2.03 mL, 20.0 mmol, 5.0 equiv) was added via syringe and the reaction mixture was stirred for 3 h at room temperature. The reaction mixture was concentrated (25 °C, 10 mmHg) to give crude **27b**. Purification by silica gel column chromatography (30 mm x 15 cm column, hexanes/EtOAc, 4/1) provided 650 mg (43%, 2 steps) of nitrone **27b** as a white solid. Recrystallization from hot hexane/EtOAc (~2/1, 30 mL) gave 567 mg (87% recovery) of **27b** as white, hair-like needles.

Data for 27b:

mp: 128.7-129.7 °C (hexane/EtOAc)

¹H NMR: (500 MHz, CDCl₃)

8.07 (dd, 2 H, HC(5)), 7.50 (dd, $J = 6.6, 1.3$, 2 H, HC(13)), 7.19-7.39 (m, 11 H, HC(6), HC(7), HC(9), HC(10), HC(11), HC(14), HC(15)), 7.12 (s, 1 H, HC(3)), 5.15 (dd, $J = 8.5, 6.6$, 1 H, HC(1)), 4.45 (dd, $J = 12.2, 8.6$, 1 H, *HHC*(2)), 4.38 (dd, $J = 12.2, 6.4$, 1 H, *HHC*(2)).

¹³C NMR: (126 MHz, CDCl₃)

138.6, 130.0, 128.4 (C(4), C(8), C(12)), 135.3 (C(3)), 134.8, 130.4, 129.1, 128.7, 128.5, 128.3, 128.2, 127.8, 127.7 (C(5), C(6), C(7), C(9), C(10), C(11), C(13), C(14), C(15)), 71.7 (C(2)), 43.9 (C(1)).

IR: (KBr plate)

3065 (w), 3034 (w), 2992 (w), 2942 (w), 1946 (w), 1881 (w), 1801 (w), 1755 (w), 1582 (m), 1567 (w), 1500 (w), 1456 (s), 1432 (s), 1318 (m), 1194 (m), 1161 (m), 1147 (s), 932 (s), 916 (m), 853 (m), 752 (m), 741 (s), 728 (m), 691 (s).

MS: (EI, 70 eV)

381 (M⁺, 2), 365 (5), 260 (83), 208 (42), 157 (27), 130 (15), 117 (24), 103 (100), 91 (37), 77 (62).

TLC: R_f 0.24 (hexanes/EtOAc, 2/1) [silica gel, UV]

Analysis: C₂₁H₁₉NOS_e (380.34)

Calcd: C, 66.32; H, 5.04; N, 3.68 %

Found: C, 66.34; H, 4.99; N, 3.79 %

(Z)-N-Benzylidene-1-phenyl-1-(phenylselenanyl)propan-2-amine N-Oxide (27c)

Nitro selenide **25c** (1.50 g, 4.68 mmol) was dissolved in water-saturated EtOAc (14 mL) in a 100-mL, single-neck, round-bottom flask equipped with an Ar inlet and magnetic stir bar. The reaction flask was lowered into a room temperature water bath and aluminum amalgam (703 mg, 150 mg/mmol) was added in one portion. The cloudy, grey suspension was stirred for 30 min then was filtered with a Buchner funnel through Celite with hardened filter paper (2 cm x 30 mm pad, with filter paper on top), eluting with EtOAc (80 mL). The filtrate was dried (K₂CO₃) and concentrated (25 °C, 10 mmHg) to give crude hydroxylamine (1.36 g). The residue was dissolved in EtOH (15.6 mL) in a 100-mL, single-neck, round-bottom flask equipped with a septum with an Ar inlet (needle) and a magnetic stir bar. Benzaldehyde (2.38 mL, 23.4 mmol, 5.0 equiv) was added via syringe and the reaction mixture was stirred for 20 h at room temperature. The reaction mixture was concentrated to give crude **27c** (*syn/anti*, 1.6/1). Purification by silica gel column chromatography (30 mm x 15 cm column, hexanes/EtOAc, 4/1) provided 1.22 g (66%, 2 steps) of nitrone **27c** as a white solid with a 1.6/1 *syn/anti* diastereomeric ratio. Recrystallization of 220 mg of **27c** from hot hexane (5 mL) gave 190 mg (86% recovery) of **27c** as white needles with a 1.3/1 *syn/anti* diastereomeric ratio.

Data for 27c:

mp: 104.7-106.2 °C (hexane)

¹H NMR: (500 MHz, CDCl₃)

8.20-8.22 (m, 0.87 H, HC(6)), 7.94-7.96 (m, 1.13 H, HC(6)), 7.00-7.51 (m, 14 H, HC(4), HC(7), HC(8), HC(10), HC(11), HC(12), HC(14), HC(15), HC(16)), 4.79-4.85 (m, 1 H, HC(1)), 4.45-4.55 (m, 1 H, HC(2)), 1.82 (d, $J = 6.5$, 1.69 H, H₃C(3)), 1.43 (d, $J = 6.6$, 1.31 H, H₃C(3)).

¹³C NMR: (126 MHz, CDCl₃)

139.7, 139.4 (C(4)), 135.2, 135.0, 134.1, 133.6, 130.22, 130.20, 130.0, 128.9, 128.8, 128.75, 128.5, 128.4, 128.3, 128.2, 128.12, 128.10, 127.9, 127.7, 127.6, 127.3, 127.2 (C(5), C(6), C(7), C(8), C(9), C(10), C(11), C(12), C(13), C(14), C(15), C(16)), 76.5, 76.0 (C(2)), 51.8, 51.0 (C(1)), 18.8, 18.5 (C(3)).

IR: (KBr plate)

3057 (m), 2981 (w), 2933 (w), 1954 (w), 1578 (m), 1564 (m), 1475 (m), 1449 (m), 1438 (m), 1364 (m), 1298 (m), 1147 (s), 1112 (w), 1077 (w), 1023 (m), 999 (w), 899 (w), 809 (m), 744 (s), 722 (m), 692 (s), 671 (m), 649 (m).

MS: (EI, 70 eV)

395 (M⁺, 1), 313 (1), 274 (43), 238 (4), 222 (16), 197 (5), 157 (10), 132 (20), 117 (100), 91 (25), 77 (28), 65 (12).

TLC: R_f 0.27 (hexanes/EtOAc, 2/1) [silica gel, UV]

Analysis: C₂₂H₂₁NOSe (394.37)

Calcd: C, 67.00; H, 5.37; N, 3.55 %

Found: C, 67.08; H, 5.34; N, 3.69 %

(Z)-N-Benzylidene-1-methylcarboxylate-2-phenyl-2-(phenylselenanyl)-2-ethanamine N-Oxide
(27d)

Nitro selenide **25d** (1.09 g, 3.00 mmol) was dissolved in water-saturated EtOAc (9 mL) in a 25-mL, single-neck, round-bottom flask equipped with an Ar inlet and magnetic stir bar. The reaction flask was lowered into a room temperature water bath and aluminum amalgam (450 mg, 150 mg/mmol) was added in one portion. The cloudy, grey suspension was stirred for 20 min then was filtered with a Buchner funnel through Celite with hardened filter paper (1 cm x 30 mm pad, with filter paper on top), eluting with EtOAc (50 mL). The filtrate was dried (Na₂SO₄) and concentrated (25 °C, 10 mmHg) to give crude hydroxylamine (970 mg). The residue was dissolved in EtOH (10 mL) in a 100-mL, single-neck, round-bottom flask equipped with a septum with an Ar inlet (needle) and a magnetic stir bar. Benzaldehyde (1.52 mL, 15.0 mmol, 5.0 equiv) was added via syringe and the reaction mixture was stirred for 20 h at room temperature. Solid precipitated at around 7.5 h of reaction time. The reaction mixture was filtered and the solid was washed with EtOH (10 mL). The solid (440 mg) was identified as **227d** and was recrystallized from hot EtOH (50 mL) to give 420 mg (32%, 2 steps) of nitron **27d** (*syn* isomer only) as a white powder. The mother liquor contained a mixture of isomers of **27d**, benzaldehyde, and other unknown products.

Data for syn-27d:

mp: 175.8-176.8 °C (EtOH)

¹H NMR: (500 MHz, CDCl₃)

7.98 (d, $J = 7.1$, 2 H, HC(7)), 7.04-7.36 (m, 14 H, HC(5), HC(8), HC(9), HC(11), HC(12), HC(13), HC(15), HC(16), HC(17)), 5.14 (s, 2 H, HC(1), HC(2)), 3.84 (s, 3 H, H₃C(4)).

¹H NMR: (500 MHz, acetone-*d*₆)

8.04 (dd, $J = 5.8, 1.4$, 2 H, HC(7)), 7.81 (s, 1 H, HC(5)), 7.02-7.39 (m, 13 H, HC(8), HC(9), HC(11), HC(12), HC(13), HC(15), HC(16), HC(17)), 5.54 (d, $J = 11.7$, 1 H, HC(2)), 5.20 (d, $J = 11.9$, 1 H, HC(1)), 3.77 (s, 3 H, H₃C(4)).

¹³C NMR: (126 MHz, CDCl₃)

166.9 (C(3)), 137.1, 129.6, 126.7 (C(6), C(10), C(14)), 136.9, 135.4, 130.6, 128.92, 128.89, 128.7, 128.31, 128.29, 127.6, 127.5 (C(5), C(7), C(8), C(9), C(11), C(12), C(13), C(15), C(16), C(17)), 81.2 (C(5)), 53.3 (C(4)), 45.0 (C(1)).

IR: (KBr plate)

3068 (w), 3031 (w), 3004 (w), 2949 (w), 1974 (w), 1904 (w), 1830 (w), 1761 (s), 1580 (m), 1564 (m), 1459 (m), 1436 (m), 1298 (m), 1287 (m), 1253 (m), 1197 (m), 1169 (s), 1140 (s), 1130 (s), 945 (m), 742 (s), 737 (s), 704 (s), 694 (s), 621 (m).

MS: (EI, 70 eV)

439 (M⁺, 2), 408 (1), 318 (100), 282 (16), 259 (26), 222 (4), 206 (22), 178 (14), 161 (82), 131 (97), 103 (53), 78 (80).

TLC: R_f 0.22 (hexanes/EtOAc, 2/1) [silica gel, UV]

Analysis: C₂₃H₂₁NO₃Se (438.38)

Calcd: C, 63.02; H, 4.83; N, 3.20 %

Found: C, 62.81; H, 4.72; N, 3.31 %

(Z)-N-Benzylidene-2-(phenylselenanyl)-tetrahydro-2H-pyran-3-amine N-Oxide (27e)

Nitro selenide **25e** (859 mg, 3.00 mmol) was dissolved in water-saturated EtOAc (9 mL) in a 50-mL, single-neck, round-bottom flask equipped with an Ar inlet and magnetic stir bar. The reaction flask was lowered into a room temperature water bath and aluminum amalgam (450 mg, 150 mg/mmol) was added in one portion. The cloudy, grey suspension was stirred for 30 min then was filtered using a Buchner funnel through a pad of Celite (40 mm x 1 cm) with hardened filter paper on top, eluting with EtOAc (50 mL). The filtrate was dried (Na₂SO₄) and concentrated (25 °C, 10 mmHg) to give the crude hydroxylamine (767 mg). The residue was dissolved in EtOH (10 mL) in a 100-mL, single-neck, round-bottom flask equipped with a septum with an Ar inlet (needle) and a magnetic stir bar. Benzaldehyde (1.52 mL, 15.0 mmol, 5.0 equiv) was added via syringe and the reaction mixture was stirred for 8 h at room temperature. EtOAc (20 mL) and silica gel (3.5 g) were added to the reaction flask and the mixture was concentrated (25 °C, 10 mmHg) to give silica-bound product **27e**. Purification by silica gel column chromatography (30 mm x 10 cm column, dry loaded, gradient elution, hexanes/EtOAc, 2/1 to 1/1) provided 748 mg (69%, 2 steps) of nitronium **27e** as a white solid.

Recrystallization from hot hexanes/EtOAc (200 mL / 2 mL) gave 720 mg (96% recovery) of **27e** as colorless needles.

Data for 27e:

mp: 99.7-101.2 °C (hexane/EtOAc)

¹H NMR: (500 MHz, CDCl₃)

8.20 (dd, $J = 7.3, 3.7$, 2 H, HC(8)), 7.63 (dd, $J = 8.1, 1.0$, 2 H, HC(12)), 7.26-7.43 (m, 6 H, HC(9), HC(10), HC(13), HC(14)), 7.24 (s, 1 H, HC(6)), 5.57 (d, $J = 8.3$, 1 H, HC(1)), 4.11 (dt, $J = 11.4, 4.1$, 1 H, *HHC*(5)), 3.95 (ddd, $J = 10.2, 8.5, 3.9$, 1 H, HC(2)), 3.64 (td, $J = 10.8, 3.0$, 1 H, *HHC*(5)), 2.52-2.61 (m, 1 H, *HHC*(3)), 2.14-2.19 (m, 1 H, *HHC*(3)), 1.73-1.88 (m, 2 H, H₂C(4)).

¹³C NMR: (126 MHz, CDCl₃)

135.1, 130.5, 129.0, 128.8, 128.5, 128.2 (C(8), C(9), C(10), C(12), C(13), C(14)), 134.8 (C(6)), 130.2 (C(7)), 127.7 (C(11)), 82.6 (C(1)), 74.2 (C(2)), 68.4 (C(5)), 27.6 (C(3)), 23.8 (C(4)).

IR: (KBr plate)

3067 (w), 2955 (w), 2935 (w), 2902 (w), 2870 (w), 2845 (w), 1961 (w), 1897 (w), 1577 (m), 1560 (m), 1475 (m), 1452 (m), 1439 (m), 1336 (w), 1295 (m), 1268 (m), 1152 (m), 1062 (s), 1031 (m), 989 (m), 933 (m), 912 (m), 825 (m), 742 (s), 692 (s).

MS: (EI, 70 eV)

361.1 (M⁺, 0.4), 345.1 (0.1), 313.9 (0.8), 240.0 (6), 204.1 (100), 188.1 (14), 157.0 (9), 104.0 (18), 83.0 (31), 77.0 (23), 55.1 (22).

TLC: R_f 0.13 (hexanes/EtOAc, 2/1) [silica gel, UV]

Analysis: C₁₈H₁₉NO₂Se (360.31)

Calcd: C, 60.00; H, 5.32; N, 3.89 %

Found: C, 60.01; H, 5.30; N, 3.98 %

(Z)-N-Benzylidene-1-(2-(3-butenyl)phenyl)-1-(phenylselenanyl)propan-2-amine N-Oxide

(27f)

Nitro selenide **25f** (2.62 g, 6.99 mmol) was dissolved in water-saturated EtOAc (21 mL) in a 100-mL, single-neck, round-bottom flask equipped with an Ar inlet and magnetic stir bar. The reaction flask was lowered into a room temperature water bath and aluminum amalgam (1.05 g, 150 mg/mmol) was added in one portion. The cloudy, grey suspension was stirred for 30 min then was filtered through a pad of Celite (30 mm x 3 cm) with hardened filter paper on top, eluting with EtOAc (300 mL). The filtrate was dried (K₂CO₃) and concentrated (25 °C, 10 mmHg) to give crude hydroxylamine (2.25 g). The residue was dissolved in EtOH (23.3 mL) in a 100-mL, single-neck, round-bottom flask equipped with a septum with an Ar inlet (needle) and a magnetic stir bar. Benzaldehyde (3.55 mL, 34.9 mmol, 5.0 equiv) was added via syringe and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was then concentrated (25 °C, 10 mmHg) to give crude **27f**. Purification by silica gel column chromatography (30 mm x 12 cm column, hexanes/EtOAc, 6/1) provided 2.56 g (82%, 2 steps)

of nitron **27f** as a partially solid oil. Recrystallization from hot hexanes (200 mL) gave 1.81 g of *syn*-**27f** (white powder) and a second crop provided 537 mg additional *syn*-**27f** for a total of 75% yield after recrystallization.

Data for *syn*-**27f**:

mp: 101.2-101.7 °C (hexane)

¹H NMR: (500 MHz, CDCl₃)

7.95 (dd, *J* = 6.6, 2.0, 2 H, HC(15)), 6.94-7.46 (m, 13 H, HC(4), HC(5), HC(6), HC(7), HC(13), HC(16), HC(17), HC(19), HC(20), HC(21)), 5.80 (ddt, *J* = 15.9, 9.8, 6.4, 1 H, HC(11)), 5.15 (d, *J* = 10.3, 1 H, HC(2)), 4.90-5.00 (m, 2 H, H₂C(12)), 4.57 (dq, *J* = 10.3, 6.4, 1 H, HC(1)), 2.60-2.81 (m, 2 H, H₂C(10)), 2.14-2.34 (m, 2 H, H₂C(9)), 1.79 (d, *J* = 6.4, 3 H, H₃C(22)).

¹³C NMR: (126 MHz, CDCl₃)

140.0, 137.6, 130.3, 127.0 (C(3), C(8), C(14), C(18)), 138.3 (C(11)), 135.2, 129.9, 129.7, 129.0, 128.3, 128.20, 128.16, 127.0, 125.9 (C(4), C(5), C(6), C(7), C(15), C(16), C(17), C(19), C(20), C(21)), 133.3 (C(13)), 114.8 (C(12)), 76.9 (C(1)), 46.3 (C(2)), 34.3 (C(9)), 31.7 (C(10)), 19.0 (C(22)).

IR: (KBr plate)

3056 (m), 3024 (w), 2974 (m), 2933 (w), 1953 (w), 1819 (w), 1640 (m), 1580 (m), 1566 (m), 1464 (m), 1453 (m), 1438 (m), 1369 (w), 1314 (m), 1299 (m), 1143 (s), 1024 (m), 902 (m), 755 (m), 739 (s), 689 (s).

MS: (EI, 70 eV)

449 (M⁺, 0.5), 433 (2), 328 (4), 292 (4), 276 (100), 234 (6), 171 (25), 132 (63), 91 (36), 57 (50).

TLC: R_f 0.14 (hexanes/EtOAc, 6/1) [silica gel, UV]

Analysis: $C_{26}H_{27}NOSe$ (448.46)

Calcd: C, 69.63; H, 6.07; N, 3.12 %

Found: C, 69.77; H, 6.06; N, 3.16 %

Preparation of *N*-Vinyl Nitrones **28**

(*Z*)-*N*-Benzylidene-1-propen-2-amine Oxide (**28a**)

Nitron **27a** (318 mg, 1.00 mmol) was dissolved in CH_2Cl_2 (2 mL) in a 25-mL, single-neck, round-bottom flask equipped with a septum with an Ar inlet (needle) and a magnetic stir bar. The reaction flask was cooled in a $-78\text{ }^{\circ}C$ cold bath ($CO_{2(s)}/IPA$) for 10 min and *meta*-chloroperoxybenzoic acid (207 mg, 1.20 mmol, 1.2 equiv) was added in CH_2Cl_2 (3 mL) dropwise via cannula over 5 min. The reaction mixture was stirred for 5 min and diisopropylamine (182 μ L, 1.30 mmol, 1.3 equiv) was added via syringe. Then, the cold bath was removed and the reaction mixture was allowed to warm to room temperature and stir for 30 min. Next, the reaction mixture was poured into sat. aq. $NaHCO_3$ solution (50 mL) and was extracted with CH_2Cl_2 (2 x 25 mL). The combined organic layers were dried ($MgSO_4$) and concentrated ($25\text{ }^{\circ}C$, 10 mmHg) to give crude selenoxide. The residue was dissolved in benzene (10 mL) in a 25-mL, conical flask and diisopropylamine (182 μ L, 1.30 mmol, 1.3 equiv) was added. The resulting solution was transferred dropwise via cannula to a 25-mL, round-bottom

flask equipped with a reflux condenser containing 1 mL of refluxing benzene (85 °C oil bath). The reaction mixture was heated to reflux for 30 min and then concentrated (25 °C, 10 mmHg). The residue was purified by silica gel column chromatography (20 mm x 12 cm column, EtOAc/hexane, 3/1) to provide 95.4 mg (59%) of **28a** as a yellow oil. **28a** was not stable to prolonged storage.

Data for **28a**:

¹H NMR: (500 MHz, CDCl₃)

8.32 (dd, $J = 7.1, 3.7$, 2 H, HC(6)), 7.68 (s, 1 H, HC(4)), 7.42-7.45 (m, 3 H, HC(7), HC(8)), 5.67 (s, 1 H, HHC(1)), 5.07 (s, 1 H, HHC(1)), 2.25 (s, 3 H, H₃C(3)).

¹³C NMR: (126 MHz, CDCl₃)

151.1 (C(2)), 133.3 (C(4)), 130.8 (C(8)), 130.4 (C(5)), 129.2 (C(6)), 128.5 (C(7)), 109.4 (C(1)), 18.2 (C(3)).

IR: (neat)

3134 (w), 3057 (m), 3026 (w), 2993 (w), 2927 (w), 1962 (w), 1896 (w), 1817 (w), 1657 (m), 1575 (m), 1550 (m), 1493 (m), 1445 (s), 1409 (s), 1369 (s), 1322 (m), 1304 (m), 1260 (m), 1205 (m), 1158 (m), 1125 (s), 941 (m), 910 (m), 755 (s), 692 (s).

MS: (EI, 70 eV)

161 (M⁺, 52), 144 (20), 130 (4), 120 (7), 104 (30), 89 (18), 77 (50), 65 (13), 55 (100).

TLC: R_f 0.22 (EtOAc/hexanes, 3/1) [silica gel, UV]

Analysis: C₁₀H₁₁NO (161.2)

Calcd: C, 74.51; H, 6.88; N, 8.69 %

Found: C, 74.19; H, 6.85; N, 8.50 %

(1E)-N-Benzylidene-2-phenylethenamine N-Oxide (28b)

Nitron **27b** (380 mg, 1.00 mmol) was dissolved in CH₂Cl₂ (2 mL) in a 25-mL, two-neck round-bottom flask equipped with a septum, Ar inlet, and a magnetic stir bar. The reaction flask was cooled in a -78 °C cold bath (CO_{2(s)}/IPA) for 10 min and *meta*-chloroperoxybenzoic acid (207 mg, 1.20 mmol, 1.2 equiv) was added in CH₂Cl₂ (3 mL) dropwise via cannula over 5 min. The reaction mixture was stirred for 5 min and diisopropylamine (182 µL, 1.30 mmol, 1.3 equiv) was added via syringe. Then, the cold bath was removed and the reaction mixture was allowed to warm to room temperature and stir for 1 h. Next, the reaction mixture was poured into sat. aq. NaHCO₃ solution (75 mL) and was extracted with CH₂Cl₂ (3 x 25 mL). The combined organic layers were dried (MgSO₄) and concentrated (25 °C, 10 mmHg) to give **28b**. The residue was purified by silica gel column chromatography (20 mm x 12 cm column, dry loaded, gradient elution, hexanes until PhSeSePh eluted off the column (bright yellow band) then hexanes/EtOAc, 14/1 to 2/1) to provide 189 mg (85%) of **28b** as a powdery white solid. **28b** was not stable to heating or in CDCl₃ solution.

Data for 28b:

mp: decomp >90 °C

¹H NMR: (500 MHz, benzene-*d*₆)

8.49 (dd, *J* = 7.7, 1.3, 2 H, HC(9)), 8.04 (d, *J* = 13.3, 1 H, HC(2)), 7.20 (t, *J* = 7.5, 2 H, HC(10)), 7.01-7.16 (m, 6 H, HC(5), HC(6), HC(7), HC(11)), 6.78 (d, *J* = 13.1, 1 H, HC(3)), 6.70 (s, 1 H, HC(1)).

¹³C NMR: (126 MHz, benzene-*d*₆)

136.5 (C(3)), 135.8 (C(1)), 134.3 (C(4)), 132.1 (C(8)), 130.9 (C(11)), 129.7 (C(9)), 129.38 (C(7)), 129.36 (C(6)), 129.1 (C(10)), 128.3 (C(5)), 127.8 (C(2)).

IR: (KBr plate)

3058 (m), 3023 (m), 1542 (w), 1489 (w), 1444 (s), 1425 (m), 1326 (w), 1270 (w), 1199 (w), 1149 (m), 1076 (w), 965 (m), 956 (m), 943 (m), 833 (w), 815 (w), 749 (s), 688 (s), 638 (w).

MS: (EI, 70 eV)

223 (M⁺, 4), 207 (100), 178 (8), 165 (3), 130 (77), 117 (23), 105 (60), 91 (28), 77 (80), 63 (10).

TLC: *R*_f 0.25 (hexanes/EtOAc, 2/1) [silica gel, UV]

HRMS: C₁₅H₁₃NO (223.27)

Calcd: 223.0997

Found: 223.1001

(1*E*)-*N*-Benzylidene-1-phenyl-1-propen-2-amine *N*-Oxide ((*E*)-28c) and

(1*Z*)-*N*-benzylidene-1-phenyl-1-propen-2-amine *N*-Oxide ((*Z*)-28c)

Nitro compound **27c** (725 mg, 1.84 mmol, 1.6/1 dr) was dissolved in CH_2Cl_2 (2 mL) in a 25-mL, two-neck, round-bottom flask equipped with a septum, Ar inlet, and a magnetic stir bar. The reaction flask was cooled in a $-78\text{ }^\circ\text{C}$ cold bath ($\text{CO}_2(\text{s})/\text{IPA}$) for 10 min and *meta*-chloroperoxybenzoic acid (349 mg, 2.02 mmol, 1.1 equiv) was added in CH_2Cl_2 (7 mL) dropwise via cannula over 5 min. The reaction mixture was stirred for 5 min and diisopropylamine (309 μL , 2.21 mmol, 1.2 equiv) was added via syringe. Then, the cold bath was removed and the reaction mixture was allowed to warm to room temperature and stir for 1 h. Next, the reaction mixture was poured into sat. aq. sodium bicarbonate solution (100 mL) and was extracted with CH_2Cl_2 (2 x 75 mL). The combined organic layers were washed with brine (75 mL) and the combined aqueous layers were back extracted with CH_2Cl_2 (50 mL). The combined organic layers were then dried (MgSO_4) and concentrated ($25\text{ }^\circ\text{C}$, 10 mmHg) to give crude **28c**. The residue was purified by silica gel column chromatography (30 mm x 15 cm column, hexanes/EtOAc, 1/1) to provide 103 mg (24%) of (*E*)-**28c** and 166 mg (38%) of (*Z*)-**28c**. Both were recrystallized from hot hexane. (*E*)-**28c** gave 94 mg (91% recovery) of a white powdery solid. (*Z*)-**28c** gave 156 mg (94% recovery) of colorless needles.

Data for (E)-28c:

mp: 98.1-99.2 °C (hexane)

¹H NMR: (500 MHz, CDCl₃)

8.35 (dd, $J = 7.8, 4.2$, 2 H, HC(9)), 7.80 (s, 1 H, HC(1)), 7.31-7.50 (m, 8 H, HC(5), HC(6), HC(7), HC(10), HC(11)), 7.23 (s, 1 H, HC(3)), 2.42 (d, $J = 0.7$, 3 H, H₃C(12)).

¹³C NMR: (126 MHz, CDCl₃)

145.5 (C(2)), 134.5 (C(4)), 133.8 (C(1)), 130.9, 129.23, 128.62, 128.55, 128.0 (C(5), C(6), C(7), C(10), C(11)), 130.7 (C(8)), 129.2 (C(9)), 124.9 (C(3)), 15.1 (C(12)).

IR: (KBr plate)

3101 (w), 3041 (w), 2966 (w), 1959 (w), 1897 (w), 1571 (w), 1540 (m), 1485 (w), 1444 (s), 1404 (s), 1375 (m), 1319 (w), 1300 (w), 1168 (s), 1160 (s), 1096 (s), 1074 (m), 924 (m), 900 (m), 810 (m), 752 (s), 701 (s), 690 (s).

MS: (EI, 70 eV)

237 (M⁺, 19), 221 (20), 206 (10), 194 (19), 179 (13), 167 (11), 144 (18), 131 (74), 115 (59), 105 (75), 90 (100), 77 (51), 63 (24).

TLC: R_f 0.37 (hexanes/EtOAc, 1/1) [silica gel, UV]

Analysis: C₁₆H₁₅NO (237.3)

Calcd: C, 80.98; H, 6.37; N, 5.90 %

Found: C, 81.10; H, 6.37; N, 6.04 %

Data for (Z)-28c:

mp: 112.2-112.9 °C (hexane)

¹H NMR: (500 MHz, CDCl₃)

8.17 (dd, $J = 7.3, 1.7$, 2 H, HC(9)), 7.33-7.42 (m, 5 H, HC(6), HC(10), HC(11)),
7.33 (s, 1 H, HC(1)), 7.14-7.24 (m, 3 H, HC(5), HC(7)), 6.26 (s, 1 H, HC(3)),
2.35 (d, $J = 1.3$, 3 H, H₃C(12)).

¹³C NMR: (126 MHz, CDCl₃)

143.9 (C(2)), 137.0 (C(1)), 133.2 (C(4)), 130.8, 128.8, 128.7, 128.5, 128.0, 127.9
(C(5), C(6), C(7), C(9), C(10), C(11)), 130.4 (C(8)), 121.9 (C(3)), 20.8 (C(12)).

IR: (KBr plate)

3144 (w), 3045 (m), 2984 (w), 2961 (w), 1897 (w), 1670 (w), 1581 (m), 1564
(m), 1488 (m), 1446 (s), 1409 (s), 1325 (m), 1175 (s), 1100 (s), 1009 (m), 932
(m), 905 (m), 879 (m), 766 (s), 756 (s), 704 (s), 689 (s), 624 (m), 608 (m).

MS: (EI, 70 eV)

237 (M⁺, 43), 221 (11), 208 (21), 194 (45), 178 (9), 160 (15), 144 (12), 133.1
(65), 115 (52), 105 (100), 90 (89), 77 (50), 63 (23).

TLC: R_f 0.16 (hexanes/EtOAc, 1/1) [silica gel, UV]

Analysis: C₁₆H₁₅NO (237.3)

Calcd: C, 80.98; H, 6.37; N, 5.90 %

Found: C, 81.06; H, 6.34; N, 6.04 %

(1Z)-N-Benzylidene-2-methylcarboxylate-1-phenyl-1-ethen-2-amine N-Oxide (28d)

Nitron **27d** (395 mg, 0.90 mmol) was dissolved in CH₂Cl₂ (6 mL) in a 25-mL two-neck, round-bottom flask equipped with a septum, Ar inlet, and a magnetic stir bar. The reaction flask was cooled in a -78 °C cold bath (CO_{2(s)}/IPA) for 10 min and *meta*-chloroperoxybenzoic acid (171 mg, 0.99 mmol, 1.1 equiv) was added in CH₂Cl₂ (4 mL) dropwise via cannula over 5 min. The reaction mixture was stirred for 5 min and diisopropylamine (151 μL, 1.08 mmol, 1.2 equiv) was added via syringe. Then, the cold bath was removed and the reaction mixture was allowed to warm to room temperature and stir for 30 min. Next, the reaction mixture was poured into sat. aq. sodium bicarbonate solution (50 mL) and was extracted with CH₂Cl₂ (2 x 50 mL). The combined organic layers were washed with brine (25 mL) and the combined aqueous layers were back extracted with CH₂Cl₂ (25 mL). The combined organic layers were then dried (MgSO₄) and concentrated (25 °C, 10 mmHg) to give crude **28d**. The residue was purified by silica gel column chromatography (30 mm x 12 cm column, hexanes/EtOAc, 1/1) to provide 235 mg (93%) of **28d** as a powdery solid. The material was recrystallized from hot hexane/EtOAc (5/1, 10 mL) to provide 230 mg (98% recovery) of **28d** as fine, white needles.

Data for 28d:

mp: 149.8-151.3 °C (hexane/EtOAc)

¹H NMR: (500 MHz, CDCl₃)

8.31 (dd, $J = 7.5, 1.5$, 2 H, HC(6)), 7.64 (s, 1 H, HC(1)), 7.61 (dd, $J = 7.1, 1.3$, 2 H, HC(10)), 7.30-7.50 (m, 7 H, HC(4), HC(7), HC(8), HC(11), HC(12)), 3.90 (s, 3 H, H₃C(13)).

¹³C NMR: (126 MHz, CDCl₃)

162.8 (C(3)), 139.5 (C(4)), 136.2 (C(2)), 134.8 (C(1)), 131.4, 131.3, 130.2, 129.19, 129.18, 128.6 (C(6), C(7), C(8), C(10), C(11), C(12)), 130.6, 130.1 (C(5), C(9)), 53.2 (C(13)).

IR: (KBr plate)

3050 (w), 2996 (w), 2965 (w), 2947 (w), 1718 (s), 1643 (s), 1580 (m), 1447 (m), 1435 (m), 1414 (m), 1324 (m), 1280 (s), 1205 (s), 1145 (s), 1057 (m), 962 (m), 894 (m), 772 (m), 755 (m), 692 (s).

MS: (EI, 70 eV)

281 (M⁺, 41), 265 (19), 204 (36), 194 (18), 176 (21), 156 (8), 143 (17), 128 (21), 116 (100), 105 (40), 89 (58), 77 (61), 59 (48).

TLC: R_f 0.23 (hexanes/EtOAc, 1/1) [silica gel, UV]

Analysis: C₁₇H₁₅NO₃ (281.31)

Calcd: C, 72.58; H, 5.37; N, 4.98 %

Found: C, 72.63; H, 5.30; N, 5.07 %

(Z)-N-Benzylidene-5,6-dihydro-4H-pyran-3-amine N-Oxide (28e)

Nitrone **27e** (360 mg, 1.00 mmol) was dissolved in CH₂Cl₂ (1 mL) in a 25-mL two-neck, round-bottom flask equipped with a septum, Ar inlet, and a magnetic stir bar. The reaction flask was cooled in a -78 °C cold bath (CO₂(s)/IPA) for 10 min and *meta*-chloroperoxybenzoic acid (190 mg, 1.10 mmol, 1.1 equiv) was added in CH₂Cl₂ (4 mL) dropwise via cannula over 5 min. The reaction mixture was stirred for 5 min and diisopropylamine (168 μL, 1.20 mmol, 1.2 equiv) was added via syringe. Then, the cold bath was removed and the reaction mixture was allowed to warm to room temperature and stir for 1 h. Next, the reaction mixture was poured into sat. aq. sodium bicarbonate solution (50 mL) and was extracted with CH₂Cl₂ (2 x 50 mL). The combined organic layers were washed with brine (50 mL) and the combined aqueous layers were back extracted with CH₂Cl₂ (50 mL). The combined organic layers were then dried (MgSO₄) and concentrated (25 °C, 10 mmHg) to give crude **28e**. The residue was purified by silica gel column chromatography (20 mm x 12 cm column, hexanes/EtOAc, 3/2) to provide 182 mg (90%) of **28e** as a crystalline solid. The material was recrystallized from hot hexane/EtOAc (10 mL/2 mL) to provide 121 mg of **28e** as fine, colorless needles. A second crop gave 56 mg additional **28e** for a total recovery of 97%.

Data for 28e:

mp: 120.9-122.2 °C (hexane/EtOAc)

¹H NMR: (500 MHz, CDCl₃)

8.29 (dd, $J = 8.1, 2.4$, 2 H, HC(8)), 7.60 (s, 1 H, HC(1)), 7.39-7.44 (m, 4 H, HC(6), HC(9), HC(10)), 4.04 (t, $J = 5.1$, 2 H, H₂C(5)), 2.62 (td, $J = 6.3, 0.9$, 2 H, H₂C(3)), 2.03 (pent, $J = 6.1$, 2 H, H₂C(4)).

¹³C NMR: (126 MHz, CDCl₃)

143.7 (C(1)), 131.2 (C(6)), 130.8 (C(7)), 130.3 (C(10)), 129.0 (C(9)), 128.5 (C(8)), 126.9 (C(2)), 66.0 (C(5)), 21.3 (C(3)), 21.1 (C(4)).

IR: (KBr plate)

3092 (w), 3059 (w), 2983 (w), 2955 (w), 2926 (w), 2877 (w), 1966 (w), 1904 (w), 1651 (s), 1546 (m), 1446 (m), 1410 (m), 1232 (s), 1178 (s), 1090 (m), 1060 (m), 1048 (m), 930 (m), 868 (m), 802 (s), 750 (m), 694 (s).

MS: (EI, 70 eV)

203 (M⁺, 39), 187 (8), 174 (5), 158 (7), 146 (2), 130 (20), 117 (9), 105 (17), 97 (100), 89 (24), 77 (47), 68 (59).

TLC: R_f 0.10 (hexanes/EtOAc, 1/1) [silica gel, UV]

Analysis: C₁₂H₁₃NO₂ (203.24)

Calcd: C, 70.92; H, 6.45; N, 6.89 %

Found: C, 70.78; H, 6.44; N, 6.87 %

(1Z)-N-Benzylidene-1-(2-(3-butenyl)phenyl)-1-propen-2-amine N-Oxide (28f)

Nitron **27f** (1.55 g, 3.46 mmol) was dissolved in CH_2Cl_2 (3.5 mL) in a 50-mL, two-neck, round-bottom flask equipped with a septum, Ar inlet, and a magnetic stir bar. The reaction flask was cooled in a $-78\text{ }^\circ\text{C}$ cold bath ($\text{CO}_2(\text{s})/\text{IPA}$) for 10 min and *meta*-chloroperoxybenzoic acid (656 mg, 3.80 mmol, 1.10 equiv) was added in CH_2Cl_2 (7 mL) dropwise via cannula over 5 min. The reaction mixture was stirred for 10 min and diisopropylamine (581 μL , 4.15 mmol, 1.2 equiv) was added via syringe. Then, the cold bath was removed and the reaction mixture was allowed to warm to room temperature and stir for 1 h. Next, the reaction mixture was poured into sat. aq. sodium bicarbonate solution (100 mL) and was extracted with CH_2Cl_2 (2 x 75 mL). The combined organic layers were washed with brine (75 mL), dried (MgSO_4), and concentrated ($25\text{ }^\circ\text{C}$, 10 mmHg) to give crude selenoxide mixed with **28f**. The residue was dissolved in benzene (20 mL) in a 50-mL, round-bottom flask and diisopropylamine (581 μL , 4.15 mmol, 1.2 equiv) was added. The resulting solution was heated in a $60\text{ }^\circ\text{C}$ oil bath for 30 min then was cooled to room temperature and concentrated ($25\text{ }^\circ\text{C}$, 10 mmHg). The residue was purified by silica gel column chromatography (30 mm x 12 cm column, hexanes/EtOAc, 4/1) to provide 896 mg (89%) of **28f** as a heavy, pale-yellow oil.

Data for 28f:

¹H NMR: (500 MHz, CDCl₃)

8.06 (dd, $J = 7.3, 1.2$, 2 H, HC(15)), 7.40 (d, $J = 7.6$, 1 H, HC(5)), 7.30-7.38 (m, 3 H, HC(16), HC(17)), 7.09-7.17 (m, 2 H, HC(7), HC(8)), 7.13 (s, 1 H, HC(1)), 7.00 (td, $J = 7.5, 1.4$, 1 H, HC(6)), 6.42 (s, 1 H, HC(3)), 5.89 (ddt, $J = 17.1, 10.2, 6.6$, 1 H, HC(12)), 5.02-5.13 (m, 2 H, H₂C(13)), 2.78 (t, $J = 8.1$, 2 H, H₂C(10)), 2.37-2.43 (m, 2 H, H₂C(11)), 2.38 (d, $J = 1.2$, 3 H, H₃C(18)).

¹³C NMR: (126 MHz, CDCl₃)

144.9 (C(2)), 139.2 (C(9)), 137.7 (C(12)), 137.3 (C(1)), 132.2 (C(4)), 130.7 (C(5)), 130.3 (C(14)), 129.2 (C(8)), 128.8 (C(15)), 128.3 (C(17)), 128.2 (C(16)), 128.1 (C(7)), 126.6 (C(6)), 120.3 (C(3)), 115.4 (C(13)), 34.7 (C(11)), 32.9 (C(10)), 20.3 (C(18)).

IR: (neat)

3064 (m), 3025 (m), 2977 (m), 2922 (m), 1957 (w), 1818 (w), 1703 (m), 1640 (m), 1601 (m), 1576 (m), 1557 (m), 1487 (m), 1446 (s), 1403 (s), 1326 (m), 1300 (m), 1228 (m), 1171 (s), 1113 (s), 997 (m), 884 (s), 811 (s), 753 (s), 622 (s).

MS: (EI, 70 eV)

291 (M⁺, 3), 274 (43), 232 (16), 171 (8), 162 (44), 145 (99), 129 (86), 115 (53), 105 (100), 91 (83), 77 (88), 65 (18).

TLC: R_f 0.31 (hexanes/EtOAc, 1/1) [silica gel, UV]

Analysis: C₂₀H₂₁NO (291.39)

Calcd: C, 82.44; H, 7.26; N, 4.81 %

Found: C, 82.53; H, 7.25; N, 4.90 %

1-Methyl-3-phenyl-3,4,4a,5,6,10b-hexahydrobenzo[h]isoquinoline 2-N-Oxide (32)

N-Vinyl nitrone **28f** (370 mg, 1.27 mmol) was dissolved in CH_2Cl_2 (12.7 mL) in a 100-mL, two-neck, round-bottom flask equipped with a septum, Ar inlet, and a magnetic stir bar. The reaction flask was cooled in a $-78\text{ }^\circ\text{C}$ cold bath ($\text{CO}_2(\text{s})/\text{IPA}$) over 5 min and tin(IV) tetrachloride (446 μL , 3.81 mmol, 3.0 equiv) was added dropwise via syringe. The solution turned bright yellow. The reaction mixture was stirred for 5 min at $-78\text{ }^\circ\text{C}$, then the cold bath was removed and the reaction mixture was allowed to warm to room temperature and stir for 2 h. Then, sat. aq. sodium bicarbonate solution (20 mL) was added slowly to quench the reaction and the entire mixture was poured into sat. aq. sodium bicarbonate solution (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL) and the combined organic layers were dried (MgSO_4) and concentrated to give **32**. The crude material was purified by silica gel column chromatography (20 mm x 10 cm column, acetone) to provide 317 mg (86%) of nitrone **32** as a foamy solid. ^1H NMR analysis showed the product to be ~90% pure. The contaminant was either another diastereomer or decomposition products. Nitrone **32** was not stable upon storage in the freezer under Ar.

Data for 32:

¹H NMR: (500 MHz, CDCl₃)

7.38 (t, $J = 7.2$, 2 H, HC(8)), 7.29 (tt, $J = 7.5$, <1 , 1 H, HC(9)), 7.18-7.25 (m, 4 H, HC(7), HC(14), HC(15)), 7.17 (dd, $J = 5.8$, 3.0, 1 H, HC(16)), 7.12 (dd, $J = 5.8$, 2.8, 1 H, HC(13)), 5.09 (s (br), 1 H, HC(5)), 3.75 (d, $J = 5.4$, 1 H, HC(2)), 2.72 (dt, $J = 15.4$, 5.1, 1 H, HHC(11)), 2.64 (ddd, $J = 15.0$, 11.2, 5.6, 1 H, HHC(11)), 2.40-2.48 (m, 1 H, HC(3)), 2.42 (s, 3 H, H₃C(18)), 2.08 (dddd, $J = 13.5$, 8.0, 5.6, 4.1, 1 H, HHC(10)), 2.03 (ddd, $J = 13.9$, 10.5, 5.8, 1 H, HHC(4)), 1.94 (dt, $J = 14.2$, 3.0, 1 H, HHC(4)), 1.16 (dddd, $J = 13.0$, 11.0, 7.0, 5.5, 1 H, HHC(10)).

¹³C NMR: (126 MHz, CDCl₃)

148.8 (C(1)), 140.0 (C(17)), 138.9 (C(12)), 135.5 (C(6)), 128.6 (C(8)), 127.8, 127.7 (C(13), C(16)), 127.4 (C(9)), 127.1 (C(7)), 126.33, 126.27 (C(14), C(15)), 70.7 (C(5)), 44.2 (C(2)), 36.2 (C(4)), 27.8 (C(11)), 27.0 (C(10)), 25.5 (C(18)), 20.2 (C(3)).

IR: (neat)

3045 (s), 3031 (s), 2934 (s), 2869 (s), 1962 (w), 1884 (w), 1817 (w), 1591 (s), 1574 (m), 1480 (m), 1451 (s), 1375 (m), 1222 (s), 1195 (m), 1152 (s), 1077 (m), 1036 (m), 973 (m), 928 (m), 834 (m), 806 (w), 752 (s), 703 (s), 678 (s), 622 (s).

MS: (EI, 70 eV)

291 (M⁺, 2), 275 (54), 260 (14), 198 (5), 170 (35), 157 (4), 146 (15), 130 (100), 115 (15), 104 (6), 91 (13), 77 (7).

TLC: R_f 0.13 (acetone) [silica gel, KMnO₄ or UV]

HRMS: C₂₀H₂₁NO (291.39)

Calcd: 291.1623

Found: 291.1618

Tables of Atomic Coordinates for PM3 Calculations

All PM3 level calculations performed with CAChe WorkSystem Pro Version 6.1.12.33 (Fujitsu Ltd., 2004). Heterodienes were constrained to have a planar, *s-cis* diene system.

Nitroethylene 1 (HOMO -12.03 eV, LUMO -0.97 eV)

CARTESIAN COORDINATES

NO.	ATOM	X	Y	Z
1	C	0.00000000	0.00000000	0.00000000
2	N	1.48103500	0.00000000	0.00000000
3	O	2.09373546	1.09455918	0.00000000
4	C	-0.70901011	1.13841468	0.00000000
5	O	2.02257136	-1.13583901	-0.00000347
6	H	-1.80320277	1.10298832	-0.00000632
7	H	-0.20989823	2.11253343	0.00000695
8	H	-0.41007714	-1.01247125	0.00000262

N-Vinyl nitron 4 (HOMO -9.57 eV, LUMO -0.63 eV)

CARTESIAN COORDINATES

NO.	ATOM	X	Y	Z
1	C	0.00000000	0.00000000	0.00000000
2	N	1.47989500	0.00000000	0.00000000
3	C	2.09296223	1.17223107	0.00000000
4	C	-0.74221895	1.10496556	0.00000000
5	O	2.04159157	-1.11242030	-0.00028321
6	H	-1.82732169	1.06987577	-0.00031900
7	H	1.54526906	2.11560865	0.00080410
8	H	-0.31193999	2.10943141	-0.00006674
9	H	-0.45623756	-1.00408413	0.00015839
10	H	3.17709987	1.24991062	0.00016612

Methyl vinyl ether (HOMO -9.52 eV, LUMO 1.30 eV)

CARTESIAN COORDINATES

NO.	ATOM	X	Y	Z
1	C	-0.01904000	-0.05547600	0.00001700
2	C	0.03353000	1.29188500	0.00007100
3	O	1.22873900	1.98816100	0.00007400
4	C	1.10653900	3.43136800	0.00000200
5	H	0.88826600	-0.66830000	-0.00004700
6	H	-0.99074200	-0.55583500	0.00003900
7	H	-0.87984700	1.90590000	0.00014200
8	H	0.58095900	3.79751500	-0.90358900
9	H	0.58082200	3.79759300	0.90347700
10	H	2.13742600	3.81654000	0.00006700

Ethylene (HOMO (-10.64 eV, LUMO 1.23 eV)

CARTESIAN COORDINATES

NO.	ATOM	X	Y	Z
1	C	0.02069800	0.67284400	0.00000000
2	C	-0.02061500	-0.67284700	0.00000000
3	H	0.96996500	1.22435800	0.00000100
4	H	-0.89254500	1.28211300	-0.00000100
5	H	-0.96998700	-1.22412900	0.00000100
6	H	0.89248500	-1.28233800	-0.00000100

Acrolein (HOMO -10.69 eV, LUMO -0.19 eV)

CARTESIAN COORDINATES

NO.	ATOM	X	Y	Z
1	C	-0.00095000	0.00030400	-0.00001200
2	C	-0.04822100	-1.35226400	0.00001800
3	H	2.21006700	0.10932600	-0.00009900
4	H	-0.91444400	0.61048000	0.00000300
5	H	0.86687800	-1.95848400	0.00000900
6	H	-1.00134800	-1.89361000	0.00005900
7	C	1.28352000	0.74263700	-0.00004600
8	O	1.36140000	1.97591400	-0.00001600

Cycloadduct **32** **32** global minimum (Hf = 197.8 kJ/mol)

CARTESIAN COORDINATES

NO.	ATOM	X	Y	Z
1	C	-0.14459800	-0.97920600	1.08324800
2	C	-1.52440700	-0.47443800	0.69951900
3	N	-1.69822500	0.37685700	-0.23588200
4	O	-3.11269000	0.67371600	-0.57116300
5	C	-0.67606400	1.03805900	-1.02750400
6	C	-0.67774600	2.54870000	-0.87742000
7	C	-1.14059500	3.18300000	0.28192100
8	C	-1.10863400	4.57297700	0.39319800
9	C	-0.61616900	5.34847000	-0.65394600
10	C	-0.16007900	4.73049800	-1.81569200
11	C	-0.19262700	3.34104300	-1.92593900
12	C	-2.75048900	-0.98376100	1.43282500

13	C	0.29199300	-2.29867300	0.47203800
14	H	-0.14555900	-1.12467300	2.18850300
15	C	1.63707700	-2.55448100	0.14913700
16	H	-0.91614100	0.80433900	-2.09126600
17	H	-1.55520300	2.59617500	1.11788200
18	H	-1.48669600	5.06085000	1.30720700
19	H	-0.59929300	6.44788300	-0.56849300
20	H	0.21973100	5.34160800	-2.65156200
21	H	0.16705400	2.86942100	-2.85578600
22	H	-3.42279200	-1.56632500	0.76370200
23	H	-2.46809500	-1.64744100	2.27978400
24	H	-3.33954500	-0.14560400	1.86841900
25	C	1.99809400	-3.79074200	-0.39981600
26	C	1.04450500	-4.77673800	-0.63261300
27	C	-0.28483700	-4.53408500	-0.30812000
28	C	-0.65270300	-3.30916900	0.24430600
29	H	3.05120100	-3.98886900	-0.66110800
30	H	1.34106800	-5.74444700	-1.07124300
31	H	-1.04683800	-5.31144800	-0.48696100
32	H	-1.71301800	-3.15699100	0.49592200
33	C	0.74134300	0.51048900	-0.71782000
34	C	0.86673700	0.13854700	0.76717500
35	C	2.28005800	-0.31659000	1.15582300
36	C	2.73268800	-1.53600900	0.34649900
37	H	1.51380600	1.26809000	-0.98454600
38	H	0.93919500	-0.38286100	-1.35206800
39	H	0.61635800	1.03821400	1.37908200
40	H	2.28937500	-0.57233000	2.24105400
41	H	3.00641800	0.51842300	1.02211400
42	H	3.09154800	-1.20281700	-0.65434900
43	H	3.60479500	-2.00966100	0.85394300

32 local minimum depicted in Figure 2 (Hf = 208.0 kJ/mol)

CARTESIAN COORDINATES

NO.	ATOM	X	Y	Z
1	C	-0.07919000	-0.76191300	1.63898200
2	C	-1.31939000	0.09535700	1.50605200
3	N	-1.40769200	0.90471200	0.52466400
4	O	-2.67590900	1.66171400	0.40200900
5	C	-0.30744200	1.07467500	-0.41106100
6	C	-0.37652500	2.19612200	-1.43116600
7	C	-0.84826500	3.46703200	-1.08381600
8	C	-0.87244600	4.49928700	-2.02097800
9	C	-0.41754800	4.27630000	-3.31845700
10	C	0.05834300	3.01704900	-3.67649300
11	C	0.07862400	1.98463700	-2.73899600
12	C	-2.46817100	-0.10010700	2.47511500
13	C	-0.03759500	-2.02897300	0.81402800
14	H	-0.07180400	-1.11181400	2.69775600
15	C	1.14615100	-2.77824400	0.83972600
16	H	-0.25452600	0.11875600	-0.98167900
17	H	-1.22298400	3.66148900	-0.06461300

18	H	-1.26142000	5.49076400	-1.73481000
19	H	-0.44083200	5.09211000	-4.06005800
20	H	0.41665100	2.83704600	-4.70381000
21	H	0.46310900	0.99645800	-3.04153600
22	H	-2.83603800	-1.14939000	2.43686600
23	H	-2.12985400	0.09543700	3.51682100
24	H	-3.34269100	0.56025700	2.29025600
25	C	1.23099000	-3.97832400	0.13031700
26	C	0.13580100	-4.44512000	-0.59303200
27	C	-1.04504700	-3.70714500	-0.61667700
28	C	-1.13225500	-2.50519100	0.08399300
29	H	2.16830100	-4.55916300	0.13362300
30	H	0.20444200	-5.39538500	-1.14883300
31	H	-1.91397500	-4.07739900	-1.18671800
32	H	-2.08423300	-1.94910800	0.05908900
33	C	0.99573600	1.22675300	0.39510100
34	C	1.19126600	0.11235000	1.45808300
35	C	2.45686900	-0.72751800	1.14057700
36	C	2.32963700	-2.19457800	1.56798600
37	H	0.98535800	2.21571900	0.91025500
38	H	1.86684300	1.25754400	-0.29838900
39	H	1.37098600	0.62317100	2.43476500
40	H	3.34842400	-0.26376000	1.62338300
41	H	2.65184100	-0.71163400	0.04334900
42	H	3.26462500	-2.74723500	1.31892100
43	H	2.18183500	-2.27274200	2.66940200

¹H NMR Spectra of all Compounds

28e

References

- (1) Miyashita, M.; Yanami, T.; Yoshikoshi, A. In *Organic Synthesis Collective Volume VII*; Freeman, J. P., Ed.; John Wiley & Sons: New York, 1990, p 396.
- (2) Worral, D. E. In *Organic Synthesis Collective Volume I*; Blatt, A. H., Ed.; John Wiley & Sons, Inc.: New York, 1941, p 413.
- (3) Kawai, Y.; Inaba, Y.; Tokitoh, N. *Tetrahedron Asymmetry* **2001**, *12*, 309-318.
- (4) Melot, J. M.; Texier-Boullet, F.; Foucaud, A. *Tetrahedron* **1988**, *44*, 2215-2224.
- (5) Menicagli, R.; Malanga, C.; Guagnano, V. *Tetrahedron Lett.* **1992**, *33*, 2867-2870.
- (6) Bailey, W. F.; Wachter-Jurcsak, N. M.; Pineau, M. R.; Ovaska, T. V.; Warren, R. R.; Lewis, C. E. *J. Org. Chem.* **1996**, *61*, 8216-8228.