Supporting Information for Organic Letters

“Precipiton Reagents for Solution Phase Reductions”

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General Experimental

Proton (^1H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded on Bruker Avance 300 at 300 MHz and 75 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta scale (δ). The solvent peak was used as the reference value. For ^1H NMR: CDCl_3 = 7.27 ppm; $\text{DMSO}-d_6$ = 2.49 ppm; $\text{THF}-d_8$ = 3.58 ppm; $\text{MeOH}-d_4$ = 3.31; CD_2Cl_2 = 5.32; CD_3CN = 1.94. For ^{13}C NMR: CDCl_3 = 77.23 ppm; $\text{DMSO}-d_6$ = 39.51 ppm; $\text{THF}-d_8$ = 67.57; $\text{MeOH}-d_4$ = 49.15; CD_2Cl_2 = 54.00. Abbreviations for NMR data: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; dt = doublet of triplets; dq = doublet of quartets; tt = triplet of triplets; m = multiplet; br = broad; app = apparent, ABq = AB quartet.

High resolution and low resolution mass spectra were recorded on a VG 7070 spectrometer. Infrared (IR) spectra were collected on Mattson Cygnus 100 and IBM IR/32 spectrometers. Samples for IR were prepared either as a thin film on a NaCl plate by dissolving the sample in CH_2Cl_2 and then evaporating the CH_2Cl_2 or as a KBr pellet. Melting points were determined using a Thomas Hoover capillary melting point apparatus and are uncorrected. UV-Vis spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer.

Thin layer chromatography (TLC) was performed using E. Merck silica gel 60F-254 (0.25 mm) analytical glass plates. Silica gel columns for flash chromatography, according to the method of Still,¹ were prepared with E. Merck silica gel 60 (230-240 mesh ASTM).

Dry solvents were distilled shortly before use from an appropriate drying agent under nitrogen atmosphere. Tetrahydrofuran (THF), diethyl ether (Et_2O), and toluene were distilled from sodium and benzophenone. Ethyl acetate was dried over 4 Å

molecular sieves for at least 24 hours prior to use. Pyridine was distilled from calcium hydride and stored over 4 Å molecular sieves. Hexane refers to the mixed hydrocarbon fraction (bp 68-70 °C), principally *n*-hexane, and was purified as follows: the commercial solvent was stirred over concentrated H₂SO₄ for at least 24 hours, decanted, stirred over anhydrous NaHCO₃ for at least 6 hours, decanted, and distilled. Benzene, methylene chloride (CH₂Cl₂), and triethylamine (TEA) were distilled from CaH₂. Anhydrous dimethylsulfoxide (DMSO), methanol, *N,N*-Dimethylformamide (DMF), and acetonitrile (CH₃CN) were purchased from Acros and used as is.

Other commercially available reagents and solvents were reagent grade and were used without further purification. Alkyl lithium reagents were titrated according to Juaristi's procedure prior to use.²

Reactions run under a nitrogen atmosphere were arranged with a mercury or oil bubbler so that the system could be alternately evacuated and filled with nitrogen and left under positive pressure. Syringes and reaction flasks were dried in an oven at 120 °C and cooled in a desiccator over calcium sulphate prior to use. Reactions at "room temperature" were conducted under ambient laboratory conditions: T = 20-27 °C, p = 720-770 mmHg. References to "removal of volatiles *in vacuo*" or "removal of volatiles *in vacuo*" refer to rotary evaporation of the sample at 25-65 °C *in vacuo* (18-25 mmHg), followed by removal of residual volatile materials under vacuum (0.05-0.5 mm Hg) at room temperature. Unless otherwise noted, irradiations were conducted with 350 nm light in a Rayonet photoreactor. The internal temperature of the photoreactor was 40 °C.

(Z)-4-[4-(*tert*-Butyldimethylsilyloxymethyl)phenyl]-4'-phenylstilbene (1Z). To a solution of (Z)-4-[4-(Hydroxymethyl)phenyl]-4'-phenylstilbene³ (1.81 g, 5.0 mmol) in CH₂Cl₂ (10 mL) at 23 °C was added TBSCl (830 mg, 5.5 mmol), followed by imidazole (375 mg, 5.5 mmol). The solution was stirred at 23 °C for 1 h then diluted with Et₂O (50 mL) and filtered. The filtrate was

washed with 1 M HCl (25 mL), sat aq NaHCO₃ (3 x 25 mL), dried with MgSO₄, and filtered. Volatile components of the filtrate were removed *in vacuo* to afford a residue that was purified by flash chromatography (SiO₂, 9:1 Hex:EtOAc) to afford TBS ether **1Z** as a white solid (2.09 g, 88%): *R_f* 0.50 (19:1 Hex:EtOAc); mp 69-70 °C; IR (neat) 2926, 2851, 1487, 1252, 1057, 1004, 836, 775 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.63-7.56 (m, 4 H), 7.52-7.31 (m, 13 H), 6.66 (s, 2 H), 4.79 (s, 2 H), 0.96 (s, 9 H), 0.12 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 140.8, 140.0, 139.9, 139.5, 136.5, 136.4, 130.2, 130.1, 129.6, 129.0, 127.5, 127.1, 127.0, 126.7, 64.5, 26.2, 18.6, -5.0; HRMS *m/e* calcd for C₃₃H₃₆OSi 476.2535, found 476.2512.

Irradiation of TBS ether **1Z at 350 nm.** A solution of TBS ether **1Z** (750 mg, 1.58 mmol) in THF (65 mL) was irradiated at 350 nm for 18 h. Volatile components of the reaction mixture were removed *in vacuo* to afford a crude solid that was purified by flash chromatography (SiO₂, 98:2 Hex:EtOAc) to generate an inseparable and indistinguishable mixture of *syn* cyclobutanes **2** and **3** (460 mg, 61%) and an inseparable and indistinguishable mixture of *anti* cyclobutanes **4** and **5** (54 mg, 7%): ***syn* Cyclobutanes **2** and **3**:** *R_f* 0.13 (18:1 Hex:EtOAc); UV-Vis (THF) λ_{max} 265 nm; IR (neat) 3027, 2953, 2928, 2855, 1498, 1487, 1255, 1113, 1090, 1006, 837, 776 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.55-7.49 (m, 8 H), 7.45-7.29 (m, 18 H), 7.27-7.23 (m, 8 H), 4.76 (s, 4 H), 4.59 (s, 4 H), 0.95 (s, 18 H), 0.11 (s, 12 H); ¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, *J* = 7.7 Hz, 4 H), 7.50 (d, *J* = 8.1 Hz, 4 H), 7.43 (d, *J* = 8.0 Hz, 8 H), 7.39 (app t, *J* = 7.6 Hz, 4 H), 7.35 (d, *J* = 8.1 Hz, 4 H), 7.29 (app t, *J* = 7.3 Hz, 2 H), 7.25 (d, *J* = 8.1 Hz, 4 H), 7.24 (d, *J* = 8.1 Hz, 4 H), 4.76 (s, 4 H), 4.59 (s, 4 H), 0.95 (s, 4 H), 0.11 (s, 12 H); ¹³C NMR (125 MHz, CDCl₃) δ 141.03, 140.48,

140.11, 139.94, 139.66, 138.92, 138.80, 128.87, 128.78, 127.22, 127.12, 126.94, 126.85, 126.62, 64.84, 47.65, 26.05, 18.52, -5.13. **anti Cyclobutanes 4 and 5:** R_f 0.20 (18:1 Hex:EtOAc); UV-Vis (THF) $\lambda_{\max}$ 267 nm; IR (neat) 2954, 2926, 2854, 1499, 1487, 1255, 1113, 1090, 838, 812, 777, 762 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.63-7.57 (m, 16 H), 7.48-7.35 (m, 18 H), 4.80 (s, 2 H), 3.84 (s, 2 H), 0.98 (s, 18 H), 0.14 (s, 12 H); ^1H NMR (500 MHz, CDCl_3) δ 7.62-7.56 (m, 18 H), 7.47-7.44 (m, 12 H), 7.41 (d, $J = 8.1$ Hz, 7.35 (app t, $J = 7.3$ Hz, 2 H), 4.81 (s, 4 H), 3.85 (s, 4 H), 0.97 (s, 18 H), 0.13 (s, 12 H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.75, 141.59, 141.15, 140.64, 139.82, 139.75, 139.69, 128.97, 127.74, 127.54, 127.44, 127.35, 127.22, 127.06, 126.69, 64.96, 51.74, 26.19, 18.67, -4.99.

[4'-(2-Biphenyl-4-yl-vinyl)-biphenyl-4-yl]-diphenyl-

phosphane (7). A solution of bromide **6**⁴ in THF was cooled to -78 °C. To this solution was added a solution of *tert*-butyl lithium dropwise. The dark red solution was stirred for 5 min at -78 °C then treated with trimethylborate dropwise and allowed to warm to 23 °C over 30 min. The solution was stirred overnight to afford boronic acid as a white powdery solid. To a solution of boronic acid (750 mg, 2.49 mmol) in THF (9 mL) and 50% aq Cs_2CO_3 (3 mL) was added 4-bromophenyldiphenylphosphine (500 mg, 1.46 mmol) and tetrakis(triphenylphosphine)palladium (0) (85 mg, 0.07 mmol). The solution was heated at reflux for 21 h then cooled to 23 °C and extracted with degassed (by N_2 purge) EtOAc (50 mL), dried with MgSO_4 , and filtered. To filtrate was added SiO_2 (2 g) and volatiles were removed *in vacuo*. Flash chromatography (SiO_2 , 95:5 Hex:EtOAc) afforded **7** as a white foamy solid (253 mg, 34%): $R_f = 0.37$ (Hex); mp 57-60 °C; IR (neat) 3051, 3026, 1485, 1433, 1091, 882, 837, 817, 773, 742, 695 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.64-7.60 (m, 4 H), 7.55-7.34 (m, 23 H), 6.69 (s, 2 H); ^1H NMR (300 MHz, $\text{THF}-d_8$) δ 7.64-7.60 (m, 4 H), 7.57-7.51 (m, 4 H), 7.41-7.25 (m, 19 H), 6.65 (s, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.1, 140.8, 140.0, 139.2, 137.3, 137.2, 136.8, 136.4,

134.5, 134.3, 134.1, 133.8, 130.3, 130.1, 129.6, 129.56, 129.0, 128.8, 128.7, 127.5, 127.1; ^{13}C NMR (75 MHz, THF- d_8) δ 138.9, 138.6, 138.0, 137.1, 135.8, 135.6, 134.9, 134.8, 134.5, 132.4, 132.1, 131.8, 131.6, 128.1, 127.8, 127.5, 127.4, 126.7, 127.65, 126.5, 126.4, 125.2, 124.7, 124.6; ^{31}P NMR (121.4 MHz, CDCl_3) δ -4.76; ^{31}P NMR (121.4 MHz, THF- d_8) δ -6.68; HRMS m/e calcd for $\text{C}_{38}\text{H}_{29}\text{P}$ 516.2007, found 516.2024.

(Z,Z)- and (Z,E)-1,4-Bis[4-(bromo)styryl]benzene. A solution of terephthalaldehyde (670 mg, 5.0 mmol), (4-bromobenzyl)-triphenylphosphonium bromide (6.43 g, 11.0 mmol), and 18-crown-6 (290 mg, 1.0 mmol) in CH_2Cl_2 (20 mL) was cooled to -78°C . To solution was added freshly powdered potassium hydroxide (1.23 g, 22.0 mmol) and the solution was stirred at -78°C for 2 h then warmed to 23°C and stirred for 1 h. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and filtered. The filtrate was washed with saturated NH_4Cl (75 mL), dried with MgSO_4 , and filtered. Volatile components of the filtrate were removed *in vacuo* to afford a pale yellow solid that was purified by flash chromatography (SiO_2 , Hex) to afford isomeric bromides as a white solid (*Z,Z*:*Z,E*-1.35:1.00, 1.70 g, 77%). **(Z,Z) isomer:** R_f 0.15 (Hex); mp 122°C ; IR (neat) 3006, 1506, 1483, 1417, 1068, 1009, 888, 832, 816, 808, 741 cm^{-1} ; UV-Vis (THF, $10\text{ }\mu\text{M}$) λ_{max} 322 nm, ϵ $14,800\text{ M}^{-1}\text{cm}^{-1}$; ^1H NMR (300 MHz, CDCl_3) δ 7.35 (d, $J = 8.4\text{ Hz}$, 4 H), 7.12 (d, $J = 8.4\text{ Hz}$, 4 H), 7.10 (s, 4 H), 6.59 (d, $J = 12.2\text{ Hz}$, 2 H), 6.50 (d, $J = 12.2\text{ Hz}$, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 136.3, 136.0, 131.6, 130.8, 130.7, 129.3, 129.0, 121.2; HRMS m/e calcd for $\text{C}_{22}\text{H}_{16}\text{Br}$ 437.9619, found 437.9633. **(Z,E) isomer:** R_f 0.10; mp 164°C ; IR ; UV-Vis (THF, $10\text{ }\mu\text{M}$) λ_{max} 341 nm, ϵ $37,000\text{ M}^{-1}\text{cm}^{-1}$; ^1H NMR (300 MHz, CDCl_3) δ 7.48 (d, $J = 8.6\text{ Hz}$, 2 H), 7.40-7.36 (m, 6 H), 7.23 (d, $J = 8.2\text{ Hz}$, 2 H), 7.15 (d, $J = 8.2\text{ Hz}$, 2 H), 7.07 (d, $J = 16.4\text{ Hz}$, 1 H), 7.01 (d, $J = 16.4\text{ Hz}$, 1 H), 6.62 (d, $J = 12.2\text{ Hz}$, 1 H), 6.53 (d, $J = 12.2\text{ Hz}$, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 136.6, 136.4, 136.2, 132.0, 131.6, 130.7, 129.5, 129.4, 129.1, 128.2, 127.7, 127.0, 121.6, 121.2; HRMS m/e calcd for $\text{C}_{22}\text{H}_{16}\text{Br}$ 437.9619, found 437.9633.

(Z,Z)- and (Z,E)-1,4-Bis[4-(diphenylphosphino)

styryl]benzene 8. A solution of above **(Z,Z)** and **(Z,E)** bromides (1.70 g, 3.86 mmol) in THF (38.6 mL) was cooled to -78 °C. To this solution was added a solution of *n*-butyl lithium (1.6 M, 5.8 mL, 9.27 mmol) dropwise. The resulting dark yellow solution was stirred for 5 min at -78 °C then treated with chlorodiphenylphosphine (1.7 mL, 9.66 mmol) and allowed to warm to 23 °C over 30 min. The reaction mixture was treated with SiO₂ (5.7 g) and volatiles were removed *in vacuo*. Flash chromatography (SiO₂, Hex to 98:2 Hex:EtOAc) afforded phosphine **8** (*Z,Z*:*Z,E*-1.35:1.00) as a pale yellow foam (1.86 g, 74%). **(Z,Z) isomer:** *R_f* 0.19 (24:1 Hex:EtOAc); mp 51-54 °C; IR (neat) 3050, 3010, 1478, 1433, 1089, 889, 833, 742, 696 cm⁻¹; ¹H NMR (300 MHz, THF-*d*₈) δ 7.35-7.21 (m, 24 H), 7.16-7.11 (m, 8 H), 6.55 (s, 4 H); ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.26 (m, 20 H), 7.24 (d, *J* = 8.1 Hz, 4 H), 7.16 (d, *J* = 7.9 Hz, 4 H), 7.13 (s, 4 H), 6.55 (s, 4 H); ¹³C NMR (75 MHz, THF-*d*₈) δ 138.8, 138.6, 138.5, 137.7, 137.6, 137.3, 134.8, 134.6, 134.3, 131.5, 130.7, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4; ³¹P NMR (121.4 MHz, THF-*d*₈) δ -6.4; HRMSm/e calcd for C₄₆H₃₆P₂ 650.2292, found 650.2312. **(Z,E) isomer:** *R_f* 0.13 (24:1 Hex:EtOAc); mp 67-70 °C; IR (neat) cm⁻¹; ¹H NMR (300 MHz, THF-*d*₈) δ 7.55-7.49 (m, 3 H), 7.44-7.41 (m, 3 H), 7.35-7.13 (m, 28 H), 6.61 (d, *J* = 12.9 Hz, 1 H), 6.57 (d, *J* = 12.9 Hz, 1 H); ¹H NMR (300 MHz, CDCl₃) δ 7.51-7.25 (m, 29 H), 7.20-7.15 (m, 2 H), 7.15 (s, 1 H), 7.08 (s, 2 H), 6.60 (s, 2 H); ¹³C NMR (75 MHz, THF-*d*₈) δ 139.2, 139.0, 238.8, 138.7, 138.6, 138.5, 138.0, 137.8, 137.7, 137.6, 137.58, 135.1, 134.8, 134.6, 134.57, 134.4, 131.5, 130.6, 130.2, 130.0, 129.96, 129.9, 129.7, 129.5, 129.4, 129.1, 127.6, 127.5, 127.47; ³¹P NMR (121.4 MHz, THF-*d*₈) δ -6.4; HRMSm/e calcd for C₄₆H₃₆P₂ 650.2292, found 650.2312.

Z-4,4'-bromostilbene. A solution of 4-bromobenzaldehyde (41.44 g, 224 mmol), (4-bromobenzyl)-triphenylphosphonium bromide (149.2 g, 291 mmol), and 18-crown-6 (7.68 g, 29.1 mmol) in CH₂Cl₂ (600 mL) was cooled to -78 °C. To solution

was added freshly powdered potassium hydroxide (32.60 g, 582 mmol) and the solution was stirred at -78 °C for 1.5 h then warmed to 23 °C and stirred for 3 h. The reaction mixture filtered and the filtrate was washed with saturated NH₄Cl (300 mL), dried with MgSO₄, and filtered. Volatile components of the filtrate were removed *in vacuo* to afford a pale yellow solid that was extracted with hexanes (1.5 L) and filtered. Volatile components of the filtrate were removed *in vacuo* to afford a pale yellow solid that was purified by flash chromatography (SiO₂, Hex) to afford bromide as a white solid (59.0 g, 78%): *R*_f 0.32 (Hex); mp 51-53 °C; IR (neat) 3003, 1480, 1412, 1388, 1065, 1007, 826 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.37 (dd, *J* = 8.8, 2.2 Hz, 4 H), 7.09 (dd, *J* = 8.8, 2.2 Hz, 4 H), 6.55 (s, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 135.8, 131.6, 130.6, 129.8, 121.4; HRMS *m/e* calcd for C₁₄H₁₀Br₂ 335.9149, found 335.9142.

Z-4,4'-formylstilbene. A solution of Z-4,4'-bromostilbene (2.0 g, 5.9 mmol) in THF (25 mL) was cooled to -78 °C. To solution was added a solution of *n*-butyl lithium (1.6 M, 8.9 mL, 14.2 mmol) dropwise. The resulting anion solution was stirred for 5 min at -78 °C then treated with *N,N*-dimethylformamide (4.6 mL, 59.0 mmol) and allowed to warm to 0 °C over 15 min. The reaction mixture was then treated with saturated NH₄Cl (20 mL), extracted with ether (100 mL), washed with water (3 x 75 mL), dried with MgSO₄, and filtered. Volatile components of the filtrate were removed *in vacuo* to afford a residue that was purified by flash chromatography (SiO₂, 4:1 Hex:EtOAc) to afford formylstilbene as a pale yellow solid (1.23 g, 88%): *R*_f 0.36 (2:1 Hex:EtOAc); mp 99-102 °C; IR (neat) 2829, 2737, 1694, 1602, 1305, 1209, 1163, 840 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 9.98 (s, 2 H), 7.77 (d, *J* = 8.3 Hz, 4 H), 7.38 (d, *J* = 8.3 Hz, 4 H), 6.79 (s, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 191.7, 142.9, 135.4, 131.6, 129.9, 129.6; HRMS *m/e* calcd for C₁₆H₁₂O₂ 236.0837, found 236.0835.

(Z,Z,Z)- and (Z,Z,E)-4,4'-Bis[4-(bromo)styryl]stilbene. A solution of Z-4,4'-formystilbene (1.39 g, 5.89 mmol), (4-bromobenzyl)-triphenylphosphonium bromide (6.64 g, 12.96 mmol), and 18-crown-6 (343 mg, 1.30 mmol) in CH₂Cl₂ (26 mL) was cooled to -78 °C. To solution was added freshly powdered potassium hydroxide (1.45 g, 25.92 mmol) and the solution was stirred at -78 °C for 2 h then warmed to 23 °C and stirred for 1 h. The reaction mixture was diluted with CH₂Cl₂ (150 mL) and filtered. The filtrate was washed with saturated NH₄Cl (75 mL), dried with MgSO₄, and filtered. Volatile components of the filtrate were removed *in vacuo* to afford a pale yellow solid that was purified by flash chromatography (SiO₂, Hex to 97:3 Hex:EtOAc to 93:7 Hex:EtOAc) to afford isomeric bromides as a yellow solid (Z,Z,Z:Z,Z,E-1.07:1.00, 2.13 g, 67%). **(Z,Z,Z) isomer:** *R_f* 0.08 (Hex); mp 131-133 °C; UV-Vis (THF, 10 μM) λ_{max} 342 nm, ε 25,500 M⁻¹cm⁻¹; IR (neat) 1653, 1586, 1485, 1070, 1011, 890, 812 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.34 (d, *J* = 8.4 Hz, 4 H), 7.14-7.07 (m, 12 H), 6.59 (d, *J* = 12.2 Hz, 2 H), 6.54 (s, 2 H), 6.50 (d, *J* = 12.2 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 136.5, 136.4, 135.9, 131.5, 130.9, 130.7, 130.3, 129.2, 129.0, 128.9, 121.2; HRMS *m/e* calcd for C₃₀H₂₂Br₂ 540.0088, found 540.0112. **(Z,Z,E) isomer:** *R_f* 0.24 (24:1 Hex:EtOAc); mp 173-175 °C; UV-Vis (THF, 10 μM) λ_{max} 352 nm, ε 37,600 M⁻¹cm⁻¹; IR (neat) 3005, 1484, 1412, 1070, 1007, 970, 895, 836, 810, 727 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.48 (d, *J* = 8.3 Hz, 2 H), 7.39-7.34 (m, 6 H), 7.26 (d, *J* = 8.3 Hz, 2 H), 7.18-7.09 (m, 6 H), 7.07 (d, *J* = 16.7 Hz, 1 H), 7.01 (d, *J* = 16.7 Hz, 1 H), 6.60 (d, *J* = 12.2 Hz, 1 H), 6.57 (s, 2 H), 6.50 (d, *J* = 12.2 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 137.0, 136.5, 136.4, 136.3, 136.0, 135.9, 132.0, 131.5, 130.9, 130.7, 130.24, 130.18, 129.5, 129.2, 129.12, 129.06, 128.9, 128.2, 127.5, 126.6; HRMS *m/e* calcd for C₃₀H₂₂Br₂ 540.0088, found 540.0084.

(*Z,Z,Z*)- and (*Z,Z,E*)-4,4'-Bis[4-

(diphenylphosphino)styryl]stilbene **9**. To a solution of above bromides (2.13 g, 3.93 mmol) in THF (40 mL) was cooled to -78 °C. To this solution was added a solution of *n*-butyl lithium (1.6 M solution in hexanes, 5.9 mL, 9.43 mmol) dropwise. The resulting dark yellow solution was stirred at -78 °C for 5 min then treated with chlorodiphenylphosphine (1.8 mL, 9.83 mmol) and allowed to warm to 23 °C over 30 min. The reaction mixture was treated with SiO₂ (6 g) and volatiles were removed *in vacuo*. Flash chromatography (SiO₂, Hex to 96:4 Hex:EtOAc) gave phosphine **9** (*Z,Z,Z*:*Z,Z,E*-1.25:1.00) as a yellow foam (1.50 g, 51%). (*Z,Z,Z*) isomer: *R_f* 0.24 (24:1 Hex:EtOAc); mp 61-64 °C; IR (neat) 3052, 3011, 1434, 1115, 1090, 888, 834, 785, 743, 696 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.27 (m, 20 H), 7.23 (dd, *J* = 1.5, 8.0 Hz, 4 H), 7.17-7.09 (m, 12 H), 6.54 (s, 4 H), 6.52 (s, 2 H); ¹H NMR (300 MHz, THF-*d*₈) δ 7.30-7.27 (m, 20 H), 7.23 (dd, *J* = 1.4, 8.1 Hz, 4 H), 7.16-7.08 (m, 12 H), 6.55 (s, 4 H), 6.50 (s, 2 H); ¹³C NMR (75 MHz, THF-*d*₈) δ 138.8, 138.6, 138.4, 137.6, 137.4, 137.3, 137.1, 134.7, 134.44, 134.39, 134.2, 131.4, 130.7, 130.5, 129.8, 129.7, 129.6, 129.5, 129.3, 129.2; ³¹P NMR (121.4 MHz, THF-*d*₈) δ -6.3; HRMS (ES, *M* + *H*) *m/e* calcd for C₅₄H₄₃P₂ 753.2840, found 753.2808. (*Z,Z,E*) isomer: *R_f* 0.15 (24:1 Hex:EtOAc); mp 68-71 °C; IR (neat) 3050, 3012, 1478, 1433, 1090, 832, 743, 696 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.46 (dd, *J* = 1.3, 8.3 Hz, 2 H), 7.38-7.23 (m, 28 H), 7.19-7.12 (m, 6 H), 7.07 (s, 2 H), 6.59 (d, *J* = 12.3 Hz, 1 H), 6.56 (s, 2 H), 6.55 (d, *J* = 12.3 Hz, 1 H); ¹H NMR (300 MHz, THF-*d*₈) δ 7.57-7.10 (m, 38 H), 6.63-6.47 (m, 4 H); ¹³C NMR (75 MHz, THF-*d*₈) δ 139.1, 138.9, 138.8, 138.6, 138.5, 137.9, 137.8, 137.7, 137.6, 137.5, 137.2, 135.1, 134.8, 134.6, 134.4, 131.6, 130.9, 130.8, 130.7, 130.2, 130.1, 130.0, 129.8, 129.70, 129.65, 129.5, 129.4, 129.0, 127.6, 127.5; HRMS (ES, *M* + *H*) *m/e* calcd for C₅₄H₄₃P₂ 753.2840, found 753.2873.

1-(3-Azido-propoxy)-4-tert-butyl-benzene. A solution of 4-*tert*-butylphenol (900 mg, 6.0 mmol), 3-bromopropanol (450 μ L, 5.0 mmol), and triphenylphosphine (1.57 g, 6.0 mmol) in THF (30 mL) was cooled to 0 °C. To this solution was added diisopropylazodicarboxylate (1.2 mL, 6.0 mmol) dropwise. The solution was stirred at 0 °C for 1.5 h then treated with SiO₂ (5.5 g). Volatile components were removed *in vacuo* followed by flash chromatography (SiO₂, 9:1 Hex:EtOAc) to afford 3-(4-*tert*-butylphenoxy)propyl bromide⁵ as a clear residue (1.19 g, 73%): *R_f* 0.53 (9:1 Hex:EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.32 (d, *J* = 8.8 Hz, 2 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 4.10 (t, *J* = 5.8 Hz, 2 H), 3.62 (t, *J* = 6.4 Hz, 2 H), 2.32 (m, 2 H), 1.32 (s, 9 H). To a solution of 3-(4-*tert*-butylphenoxy)propyl bromide (1.19 g, 4.4 mmol) in DMSO (20 mL) was added sodium azide (345 mg, 5.3 mmol). The solution was heated at 60 °C for 1 h then cooled to 23 °C and extracted with hexanes (2 x 75 mL), washed with water (1 x 75 mL), dried with MgSO₄, and filtered. Volatile components of the filtrate were removed *in vacuo* to afford 3-(4-*tert*-butylphenoxy)propyl azide as a colorless oil (832 mg, 81%): *R_f* 0.48 (Hex); IR (neat) 3040, 2962, 2870, 2088, 1609, 1580, 1511, 1474, 1392, 1364, 1295, 1244, 1184, 1046, 829 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.31 (d, *J* = 8.8 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 4.04 (t, *J* = 8.8 Hz, 2 H), 3.52 (t, *J* = 5.9 Hz, 2 H), 3.52 (t, *J* = 6.7 Hz, 2 H), 2.05 (m, 2 H), 1.31 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 156.5, 143.6, 126.4, 114.0, 64.5, 48.4, 34.2, 31.6, 28.9; HRMS *m/e* calcd for C₁₃H₁₉N₃O 233.1528, found 233.1536.

***cis*-2-Azido-1-methoxy-indan.** To a solution of *trans*-2-bromo-1-indanol (1.065 g, 5.0 mmol) in DMSO (20 mL) was added sodium azide (390 mg, 6.0 mmol). The reaction mixture was heated at 60 °C for 1 h then cooled 23 °C and extracted with ether (100 mL), washed with water (4 x 50 mL) dried with MgSO₄, and filtered. Volatile components of the filtrate were removed *in vacuo* to afford a solid that was purified by flash chromatography (SiO₂, 4:1 Hex:EtOAc) to give *cis*-2-azido-1-indanol⁶ as a white solid (798 mg, 91%): *R_f* 0.38 (2:1 Hex:EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.46-7.43 (m, 1 H), 7.32-7.26 (m, 3 H), 5.16 (dd, *J* = 5.0, 8.3 Hz, 1 H), 4.35 (dd, *J* = 5.0,

9.8 Hz, 1 H), 3.18-3.4 (m, 2 H), 2.32 (d, $J = 8.6$ Hz, 1 H). A solution of *cis*-2-azido-1-indanol (510 mg, 2.91 mmol), methyl iodide (500 μ L, 7.48 mmol), and silver(I)oxide (750 mg, 3.22 mmol) in acetonitrile (3 mL) was heated at reflux for 3 h. The reaction mixture was cooled to 23 °C and filtered through celite. Volatile components of the filtrate were removed *in vacuo* to afford a brown residue that was purified by flash chromatography (SiO₂, 98:2 Hex:EtOAc) to give azide as a white solid (480 mg, 87%): R_f 0.29 (19:1 Hex:EtOAc); mp 44-45 °C; IR (neat) 2998, 2941, 2836, 2101, 1474, 1460, 1357, 1112, 1084, 754, 732, 646 cm^{-1} ; ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.39 (m, 1 H), 7.35-7.25 (m, 3 H), 4.72 (d, $J = 5.0$ Hz, 1 H), 4.16-4.10 (m, 1 H), 3.55 (s, 3 H), 3.20 (dd, $J = 6.0, 15.7$ Hz, 1 H), 3.11 (dd, $J = 6.5, 15.7$ Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 140.0, 139.9, 129.2, 127.1, 125.32, 125.27, 84.8, 62.9, 57.5, 35.4; HRMS m/e calcd for C₁₀H₁₀NO (M-N₂)⁺ 160.0762, found 160.0756.

4-Azidomethyl-6-benzyloxy-2,2-dimethyl-tetrahydro-furo[3,4-d][1,3]dioxole. To a solution of (6-Benzyloxy-2,2-dimethyl-tetrahydro-furo[3,4-d][1,3]dioxol-4-yl)-methanol⁷ (980 mg, 3.5 mmol) and triphenylphosphine (917 mg, 3.5 mmol) in THF (12 mL) was added DEAD (554 μ L, 3.5 mmol), followed by DPPA (754 μ L, 3.5 mmol). The reaction mixture was stirred overnight at 23 °C. The solution was treated with SiO₂ (3.0 g) and volatile components of the reaction mixture were removed *in vacuo*. Flash chromatography (SiO₂, 2:1 Hex:EtOAc) afforded azide⁷ as an oil (885 mg, 83%): ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.27 (m, 5 H), 5.12 (s, 1 H), 4.74 (dd, $J = 3.7, 5.9$ Hz, 1 H), 4.71 (d, $J = 11.8$ Hz, 1 H), 4.67 (d, $J = 5.9$ Hz, 1 H), 4.17 (ddd, $J = 3.7, 5.3, 7.4$ Hz, 1 H), 3.61 (dd, $J = 7.4, 12.8$ Hz, 1 H), 3.52 (dd, $J = 5.3, 12.8$ Hz, 1 H), 1.47 (s, 3 H), 1.32 (s, 3 H).

Citronelly azide. To a solution of citronellol (780 mg, 5.0 mmol) and triphenylphosphine (1.310 g, 5.0 mmol) in THF (25 mL) was added di-*tert*-butylazodicarboxylate (1.15 g, 5.0 mmol), followed by DPPA (1.1 mL, 5.0 mmol). The reaction mixture was stirred overnight at 23 °C. The reaction mixture was triturated with hexanes (100 mL) and filtered through Celite. Volatile components of

the filtrate were removed *in vacuo* to afford a crude oil that was purified by flash chromatography (SiO₂, 99:1 Hex:EtOAc) to afford azide⁸ as an oil (765 mg, 85%): ¹H NMR (300 MHz, CDCl₃) δ 5.13-5.07 (m, 1 H), 3.35-3.24 (m, 2 H), 2.07-1.90 (m, 2 H), 1.69 (s, 3 H), 1.71-1.53 (m, 2 H), 1.62 (s, 3 H), 1.43-1.31 (m, 3 H), 1.25-1.15 (m, 2 H), 0.92 (d, *J* = 6.5 Hz, 3 H).

Precipiton Staudinger Reactions

General Procedure: A solution of azide (1.0 eq) and phosphine (1.1 eq for **7** and 0.55 eq for **8** and **9**) in THF (0.1 M) was heated at reflux for 2 h. The solution was treated with water (100 μL/0.1 mmol of azide) and heated at reflux overnight. The solution was cooled to 23 °C then diluted with THF (0.02 M relative to phosphine) and treated with erythrosin B (5 mol% relative to phosphine). The solution was irradiated with a 250 W sunlamp (4 h for **7**, 2 h for **8**, 1 h for **9**). After irradiation, the solution was treated with MP-Carbonate (50 eq relative to erythrosin B) and the reaction mixture was stirred for 2 h to remove erythrosin B. Volatile components of the reaction mixture were removed *in vacuo*. The amines were extracted from the crude solids with Et₂O (1-3 mL/0.1 mmol of azide) and filtered through a 0.45 μm filter. Volatile components of the filtrate were removed *in vacuo* to leave remaining the amines (yields indicated in Tables 1 and 2).

3-(4-tert-Butyl-phenoxy)-propylamine:⁹ ¹H NMR (300 MHz, CDCl₃) δ 7.31 (d, *J* = 8.9 Hz, 2 H); 6.85 (d, *J* = 8.9 Hz, 2 H); 4.04 (t, *J* = 6.1 Hz, 2 H); 2.91 (t, *J* = 6.8 Hz, 2 H); 1.97-1.90 (m, 2 H), 1.31 (s, 9 H);

1-Methoxy-indan-2-ylamine. Colorless oil: IR (neat) 3424, 2926, 1637, 1460, 1087, 753 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.37 (d, *J* = 7.0 Hz, 1 H), 7.31-7.19 (m, 3 H), 4.39 (d, *J* = 5.1 Hz, 1 H), 3.72 (dt, *J* = 5.1, 6.7 Hz, 1 H), 3.47 (s, 3 H), 3.05 (dd, *J* = 6.7, 15.5 Hz, 1 H), 2.81 (dd, *J* = 6.7, 15.5 Hz, 1 H); ¹³C NMR (75 MHz,

CDCl₃) δ 142.3, 141.3, 128.8, 126.5, 125.8, 125.6, 85.1, 56.9, 56.0, 39.6; HRMS *m/e* calcd for C₁₀H₁₃NO 163.0997, found 163.0994.

C-(6-Benzyloxy-2,2-dimethyl-tetrahydro-furo[3,4-d][1,3]dioxol-4-yl)-methylamine. White solid: mp 52 °C; IR (neat) 3387, 3064, 3031, 2987, 2937, 2876, 1587, 1455, 1373, 1209, 1086, 1020, 976, 870, 738, 700 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.37-7.29 (m, 5 H), 5.11 (s, 3 H), 4.76 (dd, *J* = 3.7, 5.9 Hz, 1 H), 4.69 (d, *J* = 11.8 Hz, 1 H), 4.67 (d, *J* = 5.9 Hz, 1 H), 4.50 (d, *J* = 11.8 Hz, 1 H), 4.02 (dt, *J* = 3.7, 6.2 Hz, 1 H), 3.11-2.98 (m, 2 H), 1.71 (br s, 2 H), 1.46 (s, 3 H), 1.31 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ 137.6, 128.6, 128.2, 127.9, 112.6, 105.3, 85.4, 81.2, 80.1, 69.1, 41.0, 26.1, 24.8; HRMS *m/e* calcd for C₁₅H₂₂NO₄ 280.1549, found 280.1563.

Citronellyl amine:¹⁰ ¹H NMR (300 MHz, CDCl₃) δ 5.10 (t, *J* = 7.0 Hz, 1 H), 2.80-2.68 (m, 2 H), 2.10-1.95 (m, 2 H), 1.69 (s, 3 H), 1.61 (s, 3 H), 1.60-1.10 (m, 7 H), 0.90 (d, *J* = 7.0 Hz, 3 H).

Tandem Precipiton Staudinger Imine Formation Reactions

General Procedure: A solution of azide (1.0 eq) and phosphine (0.55 eq of **8** or **9**) in THF (0.1 M) was heated at reflux for 2 h. The solution was treated with water (100 μ L/0.1 mmol of azide) and heated at reflux overnight. The solution was cooled to 23 °C and the volatile components of the reaction mixture were removed *in vacuo*. The crude solid was diluted with CH₃CN (0.03 M relative to phosphine), treated with erythrosin B (5 mol% relative to phosphine), and then irradiated with a 250 W sunlamp for 5 h. Volatile components of the reaction mixture were removed *in vacuo* and the imines were extracted from the crude solid with Et₂O (3 mL/0.1 mmol azide) and filtered through a plug of silica. Volatile components of the filtrate were removed *in vacuo* to leave remaining the imines (yields indicated in Table 2).

***N*-(4-Carboxymethyl-benzyl)-(4-carboxymethyl-benzylidene)-amine:**¹¹ ¹H NMR (300 MHz, CDCl₃) δ 8.47 (s, 1 H), 8.11 (d, J = 8.2 Hz, 2 H), 8.04 (d, J = 8.1 Hz, 2 H), 7.87 (d, J = 8.2 Hz, 2 H), 7.43 (d, J = 8.1 Hz, 2 H), 4.91 (s, 2 H), 3.95 (s, 3 H), 3.92 (s, 3 H).

***N*-(4-Methyl-benzyl)-(4-methyl-benzylidene)-amine:**¹² ¹H NMR (300 MHz, CDCl₃) δ 8.35 (s, 1 H), 7.67 (d, J = 7.8 Hz, 2 H), 7.27-7.14 (m, 6 H), 4.78 (s, 2 H), 2.39 (s, 3 H), 2.35 (s, 3 H).

Reduction of Secondary Ozonides with Precipiton Phosphines

General Procedure: A solution of alkene (1.0 eq) in CH₂Cl₂ (0.07 M) was cooled to -78 °C and treated with a stream of ozone until a blue color persisted. A stream of nitrogen was passed through the solution for 15 min to remove excess ozone from solution. The solution was then treated with phosphine (0.55 eq of **8** or **9**) and allowed to warm to 23 °C over 30 min. Volatile components of the reaction mixture were removed *in vacuo* and crude solid was diluted with THF (0.02 M relative to phosphine), treated with erythrosin B (5 mol% relative to phosphine), and irradiated with a 250 W sunlamp (2 h for **8** and 1 h for **9**). Volatile components of the reaction mixture were removed *in vacuo* and the aldehydes were extracted from the crude solid with Et₂O (3 mL/0.1 mmol alkene) and filtered through a plug of silica. Volatile components of the filtrate were removed *in vacuo* to leave remaining the aldehydes (yields indicated in Table 3).

(*tert*-Butyl-diphenyl-silanyloxy)-acetaldehyde:¹³ ¹H NMR (300 MHz, CDCl₃) δ 9.73 (s, 1 H) 7.68-7.65 (m, 4 H), 7.46-7.37 (m, 6 H), 4.23 (s, 2 H), 1.11 (s, 9 H).

6-(*tert*-Butyl-diphenyl-silanyloxy)-4-methyl-hexanal:¹⁴ ¹H NMR (300 MHz, CDCl₃) δ 9.75 (s, 1 H), 7.69-7.66 (m, 4 H), 7.44-7.37 (m, 6 H), 3.77-3.68 (m, 2 H), 2.44-2.36 (m, 2 H), 1.71-1.30 (m, 5 H), 1.06 (s, 9 H), 0.86 (d, J = 6.2 Hz, 3 H).

6-(tert-Butyl-dimethyl-silanyloxy)-4-methyl-hexanal:¹⁵ ¹H NMR (300 MHz, CDCl₃) δ 9.79 (t, J = 1.9 Hz, 1 H), 3.69- 3.61 (m, 2 H), 2.47-2.42 (m, 2 H), 1.66-1.35 (m, 5 H), 0.93-0.86 (m, 12 H), 0.06 (s, 6 H).

4-Tolyl-acetaldehyde:¹⁶ ¹H NMR (300 MHz, CDCl₃) δ 9.74 (t, J = 2.4 Hz, 1 H), 7.19 (d, J = 8.0 Hz, 2 H), 7.12 (d, J = 8.0 Hz, 2 H), 3.66 (d, J = 2.4 Hz, 2 H), 2.34 (s, 3 H).

(4-Methoxy-phenyl)-acetaldehyde:¹⁷ ¹H NMR (300 MHz, CDCl₃) δ 9.73 (t, J = 2.4 Hz, 1 H), 7.15 (d, J = 8.7 Hz, 2 H), 6.92 (d, J = 8.7 Hz, 2 H), 3.81 (s, 3 H), 3.64 (d, J = 2.4 Hz, 2 H).

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