A Novel Kumada Coupling Reaction to access Cyclic (2-Azaallyl)stannanes. Cycloadditions of Cyclic Nonstabilized 2-Azaallyllithium Species derived from the Cyclic (2-Azaallyl)stannanes.

Douglas M. Mans and William H. Pearson[†]*

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, USA

Email: wpearson@berryassoc.com

[†] Current Address: Berry and Associates, Inc., 2434 Bishop Circle East, Dexter, MI, 48130 USA.

Supporting Information

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EXPERIMENTAL

General Methods. All reactions were performed under an atmosphere of dry nitrogen or argon in flame-dried glassware equipped with tightly fitting rubber septa. All syringes and needles were oven-dried and cooled in a dessicator prior to use. Reactions at 0 °C were carried out in an ice/water bath. Reactions at –78 °C were carried out in a dry ice/acetone bath. Solvents were freshly prepared before use. Benzene, toluene, methylene chloride (CH₂Cl₂), pyridine, triethylamine and diisopropylamine were distilled from calcium hydride. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone ketyl. Dimethylformamide (DMF) was distilled from barium oxide under reduced pressure. *n*-Butyllithium was titrated with diphenylacetic acid prior to use.

2-Thiomethoxy-5-(tri-*n*-butylstannyl)-1-pyrroline (2b): Stannyl lactam **11**^{1b} (523 mg, 1.4 mmol) and Lawesson's reagent (274 mg, 0.68 mmol) were combined in THF (10 mL) and heated under reflux. After 30 min, the reaction was diluted with ethyl acetate, washed with 10% NaOH (aq), dried (MgSO₄), filtered, and concentrated to provide a thick oil. Chromatography (0-5% ethyl acetate/hexanes gradient) afforded 330 mg (60%) of the stannyl thiolactam as a nearly colorless oil. *R*_f = 0.4 (20% ethyl acetate/hexanes); ¹H NMR (200 MHz, CDCl₃) δ 9.08 (br s, 1 H), 3.76 (t, 1 H, *J* = 7.9 Hz), 3.08-2.72 (m, 2 H), 2.60-2.43 (m, 1 H), 2.32-2.12 (m, 1 H), 1.60-1.40 (m, 6 H), 1.40-1.24 (m, 6 H), 1.08-0.89 (m, 15 H); ¹³C NMR (90 MHz, CDCl₃) δ 201.6, 50.3, 44.1, 29.0 (*J* = 21 Hz), 28.6, 27.3 (*J* = 54 Hz), 13.6, 9.1 (*J* = 310 Hz); IR (neat) 3134 (br, m), 1524 (s) cm⁻¹; MS (CI,

CH₄) m/z (rel int) 392 (100), 291 (26), 118 (21), 102 (66), 84 (67); HRMS (CI, CH₄) calcd for C₁₆H₃₄NSSn (M+H)⁺ 392.1434; found 392.1414.

The stannyl thiolactam (340 mg, 0.87 mmol) and dimethyl sulfate (90 μ L, 0.95 mmol) were mixed neat. After 12 h, the reaction was diluted with ether, washed with 10% K₂CO₃ (aq), dried (Na₂SO₄), filtered, and concentrated to provide an oil of mass 323 mg (92%). The product was used without further purification. Data for (**2b**): ¹H NMR (360 MHz, CDCl₃) δ 4.20 (dt, 1 H, J = 8.7, 2.0 Hz, $^2J(^{119/117}\text{Sn}-^1\text{H})$ = 35.9 Hz), 2.63 (ddd, 1 H, J = 16.0, 10.0, 3.1 Hz), 2.50-2.20 (m, 5 H), 2.14 (ddt, 1 H, J = 12.1, 9.4, 2.2 Hz), 1.53-1.45 (m, 6 H), 1.37-1.25 (m, 6 H), 0.95-0.80 (m, 15 H); ¹³C NMR (90 MHz, CDCl₃) δ 165.0, 63.7, 38.4, 29.4, 29.1 (J = 20 Hz), 27.4 (J = 52 Hz), 13.7, 9.3; IR (neat) 1741 (w) cm⁻¹; MS (CI, NH₃) m/z (rel int) 406 (7, [M+H]), 291 (33), 235 (75), 233 (58), 179 (100), 114 (83), 84 (78); HRMS (CI, NH₃) calcd for C₁₇H₃₆NSSn [M+H]⁺ 406.1590; found 406.1588.

5-Phenyl-2-(tri-*n*-butylstannyl)-3,4-dihydro-2H-pyrrole (19): To a flask containing stannane **2b** (50.0 mg, 0.12 mmol) and [1,1'-*bis*(diphenylphosphino)ferrocene]dichloropalladium (II) (2.50 mg, 0.0031 mmol) in toluene (1.3 mL) was added phenylmagnesium bromide in a dropwise fashion (62.0 μ L of a 3.0 M solution in Et₂O, 0.18 mmol). After 4 h, the mixture was diluted with water and extracted with ether (3x). The combined organic phases were dried (Na₂SO₄) and concentrated. Chromatography (5% ethyl acetate/hexanes) yielded 29.0 mg (55%) of **19** as an oil. Data for **19**: R_f = 0.82 (20% ethyl acetate/hexanes); ¹H NMR (500 MHz,

CDCl₃) δ 7.80 (dd, 2 H, J = 8.5, 2.0 Hz), 7.41-7.36 (m, 3 H), 4.48 (ddd, 1 H, J = 8.5, 8.5, 2.0 Hz), 3.11 (ddd, 1 H, J = 16.0, 10.0, 2.0 Hz), 2.65 (dddd, 1 H, J = 17.0, 14.0, 10.0, 2.5 Hz), 2.52 (ddt, 1 H, J = 12.5, 10.5, 9.0 Hz), 2.23 (ddt, 1 H, J = 12.5, 4.0, 2.0 Hz), 1.55-1.49 (m, 6 H), 1.36-1.29 (m, 6 H), 0.91 (dd, 6 H, J = 8.0 Hz), 0.88 (t, 9 H, J = 7.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 166.2, 135.2, 129.2, 128.2, 127.0, 65.0, 34.5, 29.2 ($J_{\text{Sn}}^{117/119}$ = 10.5 Hz), 28.7, 27.4 ($J_{\text{Sn}}^{117/119}$ = 26.4 Hz), 13.7, 9.6 ($J_{\text{Sn}}^{117/119}$ = 147.5 Hz); IR (CHCl₃) 1596 (w), 1569 (w), 1494 (w) cm⁻¹; MS (EI, 70 eV) m/z (rel int) 435.0 (3, M⁺) 378.0 (9), 322.0 (29), 291.0 (32), 268.9 (78), 143.0 (100); HRMS (EI, 70 eV) calcd for C₂₂H₃₇NSn (M⁺) 435.1948; found 435.1935.

5-Benzyl-2-(tri-*n*-butylstannyl)-3,4-dihydro-2H-pyrrole (20): A deoxygenated solution of benzylzinc bromide (4.0 mmol of a 0.5 M solution in THF, 2.0 mmol) was transferred via cannula to a flask containing *tetrakis*(triphenylphosphine)palladium (0) (0.012 g, 0.01 mmol) and stannane **2b** (0.388 g, 0.95 mmol) under argon. The mixture was heated to 60 °C for 24 h then cooled to room temperature and diluted with ethyl acetate. The combined organic phases were washed with 10% aqueous sodium bicarbonate. Back extracted the aqueous layer with ethyl acetate (2x). Organics were combined, dried (Na₂SO₄) and concentrated. Chromatography (0-20% ethyl acetate/hexanes gradient) yielded 0.193 g, (45%) of the title compound **20** as a clear yellow oil. Data for **20**: R_f = 0.24 (20% ethyl acetate/hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.20 (m, 5 H), 4.15 (d, 1 H, J = 9.0 Hz), 3.66 (bs, 2 H), 2.45-2.39 (m, 1 H), 2.22-1.94 (m, 3 H), 1.53-1.44 (m, 6 H), 1.29 (quint, 6 H, J = 7.5 Hz), 0.88 (t, 9 H, J =

7.5 Hz), 0.85-0.76 (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 138.0, 129.2, 128.7, 126.6, 63.3, 40.9, 36.4, 29.4 ($J_{\text{Sn}}^{117/119} = 10.5$ Hz), 28.8, 27.7 ($J_{\text{Sn}}^{117/119} = 26.8$ Hz), 13.9, 9.3 ($J_{\text{Sn}}^{117/119} = 151.8$ Hz); IR (CHCl_3) 1622 (w), 1602 (w), 1495 (w) cm^{-1} ; MS (DCI w/ NH_3) m/z (rel int) 450.5 (60, $[\text{M}+\text{H}]^+$), 392.4 (35), 336.3 (19), 158.2 (52), 91.1 (100); HRMS (DCI w/ NH_3) calcd for $\text{C}_{23}\text{H}_{40}\text{NSn}$ ($[\text{M}+\text{H}]^+$) 450.2183; found 450.2177.

5-Butyl-2-(tri-*n*-butylstannyl)-3,4-dihydro-2H-pyrrole (21): *n*-Butylmagnesium chloride (81 μL of a 2.0 M solution in THF, 0.16 mmol) was added in a dropwise fashion to a mixture of [1,3-*bis*(diphenylphosphinopropene)]dichloronickel (II) (3.6 mg, 0.0066 mmol) and toluene (1.0 mL) placed in a water bath. After 5 min. a solution of stannane **2b** (60 mg, 0.15 mmol) and toluene (0.5 mL) was added in a dropwise fashion. The reaction was allowed to stir for 15 min. and then was diluted with water and extracted with hexanes (4x). The combined organic phases were dried (Na_2SO_4) and concentrated. Chromatography (5% ethyl acetate/hexanes) yielded 50 mg (80%) of **21** as a clear slightly brown oil. Data for **21**: $R_f = 0.4$ (20% ethyl acetate/hexanes); ^1H NMR (500 MHz, CDCl_3) δ 4.12 (dt, 1 H, $J = 9.0, 1.8$ Hz, $J_{\text{Sn}}^{117/119} = 19.0$ Hz), 2.52 (ddd, 1 H, $J = 17.0, 10.0, 3.0$ Hz), 2.37-2.25 (m, 3 H), 2.17-2.09 (m, 1 H), 2.03 (ddt, 1 H, $J = 12.0, 5.0, 2.5$ Hz), 1.58-1.46 (m, 8 H), 1.39-1.27 (m, 8 H), 0.94-0.85 (m, 18 H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 63.1, 37.1, 29.4, 29.3 ($J_{\text{Sn}}^{117/119} = 10.6$ Hz), 28.4, 27.7 ($J_{\text{Sn}}^{117/119} = 27.3$), 23.0, 14.1, 13.9, 9.3 ($J_{\text{Sn}}^{117/119} = 147.6$ Hz); IR (CHCl_3) 1624 (w) cm^{-1} ; MS (CI w/

NH₃) m/z (rel int) 416.2 (100, [M+H]⁺), 308.1 (3), 124.1 (49); HRMS (CI w/ NH₃) calcd for C₂₀H₄₂NSn ([M+H]⁺) 416.2339; found 416.2326.

5-Methyl-2-(tri-*n*-butylstannyl)-3,4-dihydro-2*H*-pyrrole (22): Methylmagnesium chloride (64 μ L of a 2.57 M solution in THF, 0.165 mmol) was added in a dropwise fashion to a mixture of [1,3-*bis*(diphenylphosphinopropane)]dichloronickel (II) (4.0 mg, 0.0075 mmol) and toluene (1.0 mL) placed in a water bath. After 5 min. a solution of stannane **2b** (60 mg, 0.15 mmol) and toluene (0.5 mL) was added in a dropwise fashion. After 15 min the reaction mixture was diluted with water and extracted with hexanes (4x). The combined organic phases were dried (Na₂SO₄) and concentrated. Chromatography (0-5% ethyl acetate/hexanes gradient) yielded 41.8 mg (75%) of **22** as a clear yellowish oil. Data for **22**: R_f = 0.2 (20% ethyl acetate/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 4.11 (dd, 1 H, J = 8.8, 2.0 Hz), 2.51 (ddd, 1 H, J = 16.4, 10.4, 2.8 Hz), 2.34-2.11 (m, 2 H), 2.10-2.00 (m, 1 H), 2.00 (s, 3 H), 1.53-1.45 (m, 6 H), 1.35-1.29 (m, 6 H), 0.89 (t, 9 H, J = 7.6 Hz), 0.86 (dd, 6 H, J = 9.2, 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 168.0, 63.4, 38.9, 29.4 ($J_{\text{Sn}}^{117/119}$ = 10.6 Hz), 28.9, 27.7 ($J_{\text{Sn}}^{117/119}$ = 26.9 Hz), 19.6, 13.9, 9.3 ($J_{\text{Sn}}^{117/119}$ = 151.8 Hz); IR (CHCl₃) 1630 (w) cm⁻¹; MS (EI, 70 eV) m/z (rel int) 374.2 (2, M⁺), 316.2 (18), 260.2 (29), 204.1 (40), 179.1 (100), 121.0 (37), 85.1 (40), 57.2 (85); HRMS (EI, 70 eV) calcd for C₁₃H₂₆NSn ([M-C₄H₉]⁺) 316.1087; found 316.1102.

5-(Prop-1-enyl)-2-(tri-*n*-butylstannyl)-3,4-dihydro-2*H*-pyrrole (24): To a flask containing stannane **2b** (60 mg, 0.15 mmol) and [1,3-*bis*(diphenylphosphinopropane)]dichloronickel (II) (4 mg, 0.0075 mmol) in toluene (1.5 mL) was added allylmagnesium bromide in a dropwise fashion (0.22 mL of a 0.817 M solution in diethyl ether, 0.18 mmol). After 15 min., the mixture was diluted with water and extracted with hexanes (4x). The combined organic phases were dried (Na₂SO₄), filtered, and concentrated. Chromatography (0-5% ethyl acetate/hexanes gradient) yielded 18.7 mg (31%) of the title compound **24** as a clear colorless oil. Data for **24**: R_f = 0.48 (20% ethyl acetate/hexanes); ¹H NMR (500 MHz, CDCl₃) δ 6.40 (d, 1 H, J = 14.5 Hz), 6.06-5.99 (m, 1 H), 4.28 (d, 1 H, J = 8.5 Hz), 2.75 (ddd, 1 H, J = 16.0, 9.5, 2.5 Hz), 2.38-2.30 (m, 1 H), 2.21-2.12 (m, 4 H), 1.87 (d, 3 H, J = 6.5 Hz), 1.53-1.46 (m, 6 H), 1.34-1.27 (m, 6 H), 0.91-0.86 (m, 15 H); ¹³C NMR (125 MHz, CDCl₃) δ 167.4, 134.0, 128.9, 64.0, 33.7, 29.2, 28.3, 27.4, 18.5, 13.7, 9.4; IR (CHCl₃) 1652 (w) cm⁻¹; MS (EI, 70 eV), m/z (rel int) 399.1 (2, M⁺), 342.0 (4), 291.0 (5), 235.0 (16), 150.1 (100), 108.1 (35); HRMS (EI, 70 eV) calcd for C₁₉H₃₇NSn (M⁺) 399.1948; found 399.1953.

5-*n*-Butyl-3,4-dihydro-2*H*-pyrrole (34): Thioimide **33**²³ (23 mg, 0.20 mmol), [1,3-*bis*(diphenylphosphinopropane)]dichloronickel (II) (5 mg, 0.01 mmol) were added to toluene (2.0 mL) *n*-Butylmagnesium chloride (0.11 mL of a 2.0 M solution in THF, 0.22 mmol) was added in a dropwise fashion. After 30 min., the mixture was diluted with

water and extracted with pentane (3x). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated. Chromatography (0-50% ethyl acetate/hexanes gradient) provided 19 mg (75%) of **34** as a clear colorless oil. ^1H NMR matched that as reported in the literature.¹⁰

5-Phenyl -3,4-dihydro-2H-pyrrole (35): Thioimide **33**²³ (23 mg, 0.20 mmol), [1,3-*bis*(diphenylphosphinopropene)]dichloronickel (II) (5 mg, 0.01 mmol) were added to toluene (2.0 mL) *n*-Butylmagnesium chloride (0.11 mL of a 2.0 M solution in THF, 0.22 mmol) was added in a dropwise fashion. After 30 min., the mixture was diluted with water and extracted with pentane (3x). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated. Kugelrohr distillation (100 °C @ 20 mm Hg) provided 23 mg (80%) of **35** as a clear colorless oil. ^1H NMR matched that as reported in the literature.¹⁰

(1*R,2*S**,3*S**,4*S**)-1-Butyl-2,3-diphenyl-7-azabicyclo[2.2.1]heptane (43a) and (1*R**2*R**,3*R**,4*S**)-1-Butyl-2,3-diphenyl-7-azabicyclo[2.2.1]heptane (43b):** *n*-Butyllithium (17 μL of a 2.5 M solution in hexanes, 0.043 mmol) was added to a solution of stannane **21** (15 mg, 0.036 mmol) and *trans*-stilbene (13 mg, 0.072 mmol) in THF (0.36 mL) cooled to -78 °C. After 30 min., the reaction was quenched with 0.1 mL of methanol and warmed to room temperature. The solvent was removed *in vacuo* and the residue columned directly (10-50% ethyl acetate:hexanes gradient) to give 5.4 mg of **43a**

and 4.2 mg of **43b** (86% combined yield, 1.3:1) as clear oils. Data for **43a**: R_f = 0.11 (20% ethyl acetate/hexanes); ^1H NMR (500 Mhz, CDCl_3) δ 7.34-7.24 (m, 10 H), 3.78 (d, 1 H, J = 5.0 Hz), 3.22 (d, 1 H, J = 6.5 Hz), 3.06 (dd, 1 H, J = 6.5, 2.0 Hz), 1.97 (br s, 1 H), 1.92 (dddd, 1 H, J = 12.7, 12.5, 5.0, 5.0 Hz), 1.83 (ddd, 1 H, J = 10.6, 9.3, 5.0 Hz), 1.72-1.64 (m, 2 H), 1.56-1.47 (m, 2 H), 1.39-1.28 (m, 4 H), 0.90 (t, 3 H, J = 7.0 Hz); ^{13}C NMR (100 Mhz, CDCl_3) δ 129.1, 128.7, 128.4, 126.9, 126.7, 71.2, 63.1, 62.7, 55.4, 33.1, 33.1, 27.7, 27.2, 23.6, 14.3; IR (neat) 3393 (br, m), 1600 (w), 1495 (w), 1449 (w) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 305.3 (5, M^+), 205.2 (38), 125.1 (100), 82.1 (54); HRMS (EI, 70 eV) calcd for $\text{C}_{22}\text{H}_{27}\text{N}$ (M^+) 305.2143; found 305.2147. Data for **43b**: R_f = 0.06 (20% ethyl acetate/hexanes); ^1H NMR (500 Mhz, CDCl_3) δ 7.41 (d, 2 H, J = 7.0 Hz), 7.30-7.20 (m, 8 H), 3.89 (dd, 1 H, J = 4.5, 4.0 Hz), 3.61 (dd, 1 H, J = 5.5, 5.5 Hz), 2.98 (d, 1 H, J = 7.0 Hz), 2.12 (br s, 1 H), 1.70-1.50 (m, 4 H), 1.41-1.38 (m, 1 H), 1.30 (ddd, 1 H, J = 12.5, 11.3, 6.0 Hz), 1.24-1.15 (m, 2 H), 1.10 (hex, 1 H, J = 7.5 Hz), 0.99 (hex, 1 H, J = 7.5 Hz), 0.67 (t, 3 H, J = 7.5 Hz); ^{13}C NMR (100 Mhz, CDCl_3) δ 129.2, 128.4, 128.3, 128.1, 126.9, 126.4, 126.3, 72.0, 61.0, 59.5, 55.5, 36.9, 32.9, 27.1, 26.2, 23.4, 13.9; IR (neat) 3400 (br, m), 1600 (w), 1495 (w), 1454(w) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 305.3 (4, M^+), 205.2 (25), 125.1 (100), 82.1 (44), 49.0 (46); HRMS (EI, 70 eV) calcd for $\text{C}_{22}\text{H}_{27}\text{N}$ (M^+) 305.2143; found 305.2141.

(1*R,3*R**,4*S**)-1-Butyl-3-phenylsulfanyl-7-azabicyclo[2.2.1]heptane (44a) and (1*R**,2*S**,4*S**)-1-Butyl-2-phenylsulfanyl-7-azabicyclo[2.2.1]heptane (44b):** *n*-

Butyllithium (17 μL of a 2.5M solution in hexanes, 0.043 mmol) was added in a

dropwise fashion to a solution of stannane **21** (15 mg, 0.036 mmol) and phenyl vinyl sulfide (9.4 μ L, 9.8 mg, 0.072 mmol) in THF (0.36 mL) cooled to -78 $^{\circ}$ C. After 30 min., 0.1 mL of methanol was added and the mixture was warmed to room temperature. The solvent was removed *in vacuo* and the residue was subjected to column chromatography directly (10-50% ethyl acetate/hexanes gradient) to yield 2.3 mg of **44a** and 1.7 mg of **44b** (43% combined yield, 1.3:1) both as colorless oils. Data for **44a**: R_f = 0.04 (20% ethyl acetate/hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.27 (m, 4 H), 7.21-7.18 (m, 1 H), 3.48 (dd, 1 H, J = 7.8, 3.5 Hz), 3.39 (d, 1 H, J = 5.0 Hz), 2.06 (dd, 2 H, J = 13.0, 8.0 Hz), 1.85-1.83 (m, 1 H), 1.74-1.70 (m, 2 H), 1.37-1.33 (m, 6 H), 1.15 (dt, 2 H, J = 13.0, 4.0 Hz), 0.92 (t, 3 H, J = 7.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 129.9, 129.2, 126.4, 125.7, 61.3, 43.0, 35.2, 33.6, 30.5, 29.9, 29.7, 28.1, 23.6, 14.3; IR (neat) 3360 (br, w), 3080 (w), 1580 (w) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 261.2 (18, M^+), 205.2 (100), 125.1 (79), 82.1 (56), 57.1 (34); HRMS (EI, 70 eV) calcd for $\text{C}_{16}\text{H}_{23}\text{NS}$ (M^+) 261.1551; found 261.1540. Data for **44b**: R_f = 0.14 (20% ethyl acetate/hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.33 (m, 2 H), 7.28-7.25 (m, 2 H), 7.18-7.14 (m, 1 H), 4.05 (t, 1 H, J = 7.5 Hz), 3.11 (ddd, 1 H, J = 13.0, 9.5, 6.0 Hz), 3.04 (ddd, 1 H, J = 12.6, 9.8, 5.5 Hz), 2.46-2.41 (m, 1 H), 2.32 (t, 1 H, J = 8.0 Hz), 2.06 (dddd, 1 H, J = 12.7, 9.5, 8.0, 5.0 Hz), 1.99-1.91 (m, 1 H), 1.81-1.75 (m, 1 H), 1.59-1.52 (m, 4 H), 1.33 (hex, 2 H, J = 7.5 Hz), 0.92 (t, 3 H, J = 7.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 129.1, 129.0, 125.9, 71.7, 37.2, 36.5, 33.9, 31.1, 30.5, 29.9, 29.0, 22.8, 14.1; IR (neat) 3206 (br, w), 1641 (m), 1583 (m) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 261.2 (11, M^+), 205.1 (100), 125.1 (56), 82.1 (55), 57.1 (31); HRMS (EI, 70 eV) calcd for $\text{C}_{16}\text{H}_{23}\text{NS}$ (M^+) 261.1551; found 261.1542.

(1R*, 2S*, 4S*)-1-Butyl-2-phenylselanyl-7-azabicyclo[2.2.1]heptane (45a) and (1R*, 3R*, 4S*)-1-Butyl-3-phenylselanyl-7-azabicyclo[2.2.1]heptane (45b): *n*-Butyllithium (48.0 μ L of a 2.5 M solution in hexanes, 0.12 mmol) was added in a dropwise fashion to a solution of stannane **21** (25.0 mg, 0.060 mmol) and phenyl vinyl selenide (22.0 mg, 0.12 mmol) in THF (0.60 mL) at -78°C . After 30 min., 0.1 mL of methanol was added and the solution warmed to room temperature. Solvent was removed *in vacuo* and the residue columned (1-2% methanol/methylene chloride gradient) to give 7.3 mg of **45a** and 6.5 mg of **45b** as oils (74% combined yield, 1.1:1). Data for **45a**: $R_f = 0.25$ (5% methanol/methylene chloride); ^1H NMR (500 MHz, CDCl_3) δ 7.50-7.49 (m, 2 H), 7.26-7.21 (m, 3 H), 4.02 (t, 1 H, $J = 7.5$ Hz), 3.06 (ddd, 1 H, $J = 12.0, 9.5, 6.0$ Hz), 3.01 (ddd, 1 H, $J = 12.0, 9.5, 6.0$ Hz), 2.50 (dq, 1 H, $J = 17.0, 5.0, 2.0$ Hz), 2.41 (dt, 1 H, $J = 17.0, 9.5$ Hz), 2.31 (t, 2 H, $J = 9.0$ Hz), 2.07-1.98 (m, 2 H), 1.86-1.79 (m, 1 H), 1.54 (quint, 2 H, $J = 7.0$ Hz), 1.42-1.38 (m, 1 H), 1.34 (hex, 2 H, $J = 7.0$ Hz), 0.91 (t, 3 H, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 132.6, 129.2, 126.8, 72.6, 37.5, 37.4, 33.9, 28.9, 28.7, 25.1, 22.8, 14.1; IR (neat) 3266 (w), 1640 (s), 1578 (s), 1477 (s), 1436 (s) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 309.2 (24, M^+), 232.1 (20), 138.2 (49), 125.1 (98), 82.1 (100); HRMS (EI, 70 eV) calcd for $\text{C}_{16}\text{H}_{23}\text{NSe}$ (M^+) 309.0996; found 309.0997. Data for **45b**: $R_f = 0.13$ (5% methanol/methylene chloride); ^1H NMR (500 MHz, CDCl_3) δ 7.51 (dd, 2 H, $J = 7.3, 2.5$ Hz), 7.29-7.26 (m, 3 H), 3.56 (dd, 1 H, $J = 8.0, 4.0$ Hz), 3.44 (d, 1 H, $J = 5.0$ Hz), 2.07 (dd, 1 H, $J = 13.5, 8.0$ Hz), 1.88-1.84 (m, 1 H), 1.72 (quint, 2 H, $J = 5.0$ Hz), 1.46-1.34 (m, 7 H), 1.25 (t, 1 H, $J = 3.5$ Hz), 1.22 (t, 1 H, $J = 3.5$ Hz), 0.93 (t, 3 H, $J = 6.5$ Hz); ^{13}C

NMR (125 MHz, CDCl_3) δ 133.4, 131.1, 129.3, 127.3, 67.7, 61.9, 47.4, 43.2, 35.2, 33.6, 30.4, 28.1, 23.6, 14.3; IR (neat) 3239 (w), 1578 (m), 1476 (s), 1436 (s) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 309.2 (3, M^+), 152.2 (12), 125.2 (13), 84.0 (100), 49.0 (99); HRMS (EI, 70 eV) calcd for $\text{C}_{16}\text{H}_{23}\text{Nse}$ (M^+) 309.0996, found 309.1001.

5-Butyl-2-(trimethylsilyl)-3,4-dihydro-2H-pyrrole (46): *n*-Butyllithium was added in a dropwise fashion to a solution of stannane **21** (25.0 mg, 0.060 mmol) and trimethylsilyl phenyl acetylene (21.0 mg, 0.12 mmol) in THF (0.60 mL) at -78°C . After 30 min., the mixture was quenched with 0.1 mL of methanol and warmed to room temperature. The solvent was removed *in vacuo* and the residue columned (0-5% methanol/methylene chloride gradient) to give 6.5 mg (55%) of **46** as an oil. Data for **46**: R_f = 0.36 (5% methanol/methylene chloride); ^1H NMR (500 MHz, CDCl_3) δ 3.57-3.54 (m, 1 H), 2.50 (dd, 1 H, J = 11.3, 4.5 Hz), 2.46 (dd, 1 H, J = 11.3, 5.5 Hz), 2.42-2.28 (m, 2 H), 2.05-1.96 (m, 1 H), 1.80 (ddd, 1 H, J = 12.9, 10.0, 5.0 Hz), 1.57-1.47 (m, 2 H), 1.35 (hex, 2 H, J = 7.5 Hz), 0.91 (t, 3 H, J = 7.5 Hz), 0.01 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.6, 64.6, 37.6, 33.7, 29.4, 24.6, 22.9, 14.1, -3.3; IR (neat) 1634 (w) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 197.2 (6, M^+), 182.2 (8), 154.1 (64), 73.1 (100); HRMS (EI, 70 eV) calcd for $\text{C}_{11}\text{H}_{23}\text{Nsi}$ (M^+) 197.1600; found 197.1597.

(1*R,2*R**,5*S**,6*S**)-2-Butyl-12-azatricyclo[4.4.1.1^{2,5}]dodeca-7,9-diene (47a) and 5-Butyl-2-cyclohepta-2',5'-dienyl-3,4-dihydro-2H-pyrrole (47b):** *n*-Butyllithium (17 μL

of a 2.5 M solution in hexanes, 0.043 mmol) was added in a dropwise fashion to a solution of stannane **21** (15 mg, 0.036 mmol) and cycloheptatriene (11 μ L, 9.9 mg, 0.11 mmol) in THF (0.36 mL) cooled to -78°C . After 30., min 0.1 mL of methanol was added and the solution was warmed to room temperature. The solvent was removed *in vacuo* and the residue was columned directly to yield 2.9 mg of **47a** and 2.3 mg of **47b** (67% combined yield, 1.3:1) both as clear oils. Data for **47a**: R_f = 0.06 (20% ethyl acetate/hexanes); ^1H NMR (500 MHz, CDCl_3) δ 6.01-5.96 (m, 2 H), 5.89-5.84 (m, 2 H), 3.38 (d, 1 H, J = 7.0 Hz), 2.46-2.44 (m, 1 H), 2.38-2.33 (m, 2 H), 2.10 (tdd, 1 H, J = 12.3, 7.0, 6.5 Hz), 1.89 (dd, 1 H, J = 9.3, 4.0 Hz), 1.86 (dd, 1 H, J = 9.3, 5.0 Hz), 1.74 (ddd, 1 H, J = 12.6, 9.3, 4.5 Hz), 1.68 (ddd, 1 H, J = 12.3, 12.3, 4.5 Hz), 1.58-1.49 (m, 2 H), 1.41-1.30 (m, 4 H), 0.90 (t, 3 H, J = 7.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 136.7, 135.6, 126.8, 68.8, 61.2, 43.2, 42.4, 39.8, 35.1, 30.5, 29.5, 27.4, 23.7, 23.4, 14.3; IR (neat) 3312 (br, w), 1456 (m) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 217.2 (44, M^+), 125.1 (89), 82.1 (100); HRMS (EI, 70 eV) calcd for $\text{C}_{15}\text{H}_{23}\text{N}$ (M^+) 217.1830; found 217.1831. Data for **47b**: R_f = 0.24 (20% ethyl acetate/hexanes); ^1H NMR (500 MHz, CDCl_3) δ 5.75-5.62 (m, 4 H), 3.98 (d, 1 H, J = 6.5 Hz), 2.97-2.91 (m, 1 H), 2.80-2.75 (m, 2 H), 2.53-2.32 (m, 4 H), 2.24-2.17 (m, 1 H), 2.13-2.09 (m, 1 H), 1.96 (dddd, 1 H, J = 12.8, 9.8, 7.8, 4.5 Hz), 1.58-1.50 (m, 3 H), 1.35 (hex, 2 H, J = 7.5 Hz), 0.92 (t, 3 H, J = 7.5 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 159.7, 134.34, 129.9, 128.3, 42.6, 37.4, 34.0, 30.5, 29.2, 29.1, 28.6, 26.0, 22.9, 14.1; IR (neat) 1642 (m), 1460 (m) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 217.3 (27, M^+), 188.2 (98), 175.2 (48), 124.2 (95), 82.1 (100); HRMS (EI, 70 eV) calcd for $\text{C}_{15}\text{H}_{23}\text{N}$ (M^+) 217.1830; found 217.1828.

(1*R,4*S**,4*aS**,8*aS**)-4-Butyl-1,2,3,4,4*a*,5,6,8*a*-octahydro-1,4-**

epiazanonaphthalenium picrate (48a) and (1*R,4*S**,4*aR**,8*aR**)-1-Butyl-**

1,2,3,4,4*a*,5,6,8*a*-octahydro-1,4-epiazanonaphthalenium picrate (48b): *n*-

Butyllithium (48 μ L of a 2.5 M solution in hexanes, 0.12 mmol) was added in a dropwise fashion to a solution of stannane **21** (25 mg, 0.060 mmol) and 1,3-cyclohexadiene (17 μ L, 14 mg, 0.18 mmol) in THF (0.60 mL) cooled to -78 $^{\circ}$ C. After 30 min., 0.1 mL of methanol was added and the solution warmed to room temperature. Picric acid (0.3 mL of a 0.2M solution in ethanol, 0.060 mmol) was added in a dropwise fashion. The mixture was then concentrated and the residue was columned (0-1% methanol/methylene chloride) to give 18 mg (68% combined yield) of the picrate salts **48a** and **48b** (1.5:1 by 1 H NMR) as a yellow oil. Data for **48a/b**: R_f = 0.4 (10% MeOH/ CH_2Cl_2); 1 H NMR (500 MHz, CDCl_3) δ 8.86 (s, 2 H), 6.18 (dddd, 0.60 H, J = 10.3, 4.4, 4.3, 2.0 Hz), 5.99-5.95 (m, 0.40 H), 5.71 (ddd, 0.60 H, J = 10.3, 1.8, 1.5 Hz), 5.63-5.61 (m, 0.40 H), 3.93 (d, 0.4 H, J = 4.5 Hz), 3.91 (d, 0.60 H, J = 4.0 Hz), 2.62-2.57 (m, 1 H), 2.42-2.21 (m, 2 H), 2.16-1.71 (m, 9 H), 1.53-1.29 (m, 6 H), 0.94 (t, 1.8 H, J = 7.0 Hz), 0.93 (t, 1.2 H, J = 7.5 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 161.9, 141.9, 133.8, 132.5, 128.7, 126.7, 126.4, 124.4, 75.9, 75.2, 64.5, 64.0, 42.0, 41.5, 40.3, 32.2, 31.5, 30.0, 29.3, 28.7, 27.6, 27.4, 27.2, 25.1, 23.3, 23.2, 22.3, 21.9, 21.4, 14.0; IR (neat) 3213 (w), 1628 (s), 1607 (s), 1566 (s), 1538

(s), 1316 (s) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 205.2 (17, $[\text{M}-\text{H}]^+$), 125.1 (91), 82.1 (100), 68.1 (34), 55.1 (18); HRMS (ES, positive cation) calcd for $\text{C}_{14}\text{H}_{24}\text{N}$ ($[\text{M}+\text{H}]^+$) 206.1909; found 206.1910.

5-(Tri-*n*-butylstannyl)-2-pyrroline (49): Stannane **56** (346 mg, 0.70 mmol) and hydrazine monohydrate (1.80 mL, 37.1 mmol) were dissolved in ethanol (15 mL) and heated under reflux. After 5 h, the reaction was concentrated, diluted with ether, washed with water (3x), dried (Na_2SO_4), filtered, and concentrate to provide an oil. Chromatography (0-5% ethyl acetate/hexanes gradient) afforded 193 mg (78%) of **49** as an oil. Data for **49**: R_f = 0.28 (10% ethyl acetate/hexanes); ^1H NMR (360 MHz, CDCl_3) δ 7.32 (s, 1 H, $^4J(^{117/119}\text{Sn}-^1\text{H}) = 16.8$ Hz), 4.22-4.04 (m, 1 H), 2.63-2.55 (m, 1 H), 2.37-2.26 (m, 1 H), 2.10-1.93 (m, 2 H), 1.58-1.41 (m, 6 H), 1.28 (hex, 6 H, $J = 7.4$ Hz), 0.98-0.68 (m, 15 H); ^{13}C NMR (90 MHz, CDCl_3) δ 160.0, 63.5, 36.3, 29.1, 27.4, 26.4, 13.6, 9.0; IR (neat) 1708 (w), 1596 (m); MS (CI, NH_3) m/z (rel int) 360 (100, $\text{M}+\text{H}$); HRMS (CI, NH_3) calcd for $\text{C}_{16}\text{H}_{34}\text{NSn}$ $[\text{M}+\text{H}]^+$ 360.1713; found 360.1701.

(1*R,2*S**,3*S**,4*S**)-1,2,3-Triphenyl-7-azabicyclo[2.2.1]heptane (50):** *n*-Butyllithium (118 μL of a 1.7 M solution in hexanes, 0.20 mmol) was added in a dropwise fashion to a solution of stannane **19** (29.0 mg, 0.067 mmol) and *trans*-stilbene (24.1 mg, 0.13 mmol) in THF (0.70 mL) at -78 $^\circ\text{C}$. After 30 min., the reaction was quenched with 0.1 mL methanol and warmed to 25 $^\circ\text{C}$. The solvent was removed *in vacuo* and the organic

residue was purified by chromatography (0-10% ethyl acetate/hexanes gradient) to give 9.2 mg (40%) of **50** as an oil. Data for **50**: R_f = 0.32 (20% ethyl acetate/hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.50 (d, 2 H, J = 7.0 Hz), 7.29-7.18 (m, 11 H), 6.89 (dd, 2 H, J = 8.0, 2.8 Hz), 3.90 (d, 1 H, J = 5.0 Hz), 3.26-3.23 (m, 2 H), 2.31 (ddd, 1 H, J = 12.7, 8.5, 5.0 Hz), 2.06-1.93 (m, 2 H), 1.52 (tdd, 1 H, J = 12.5, 5.0, 2.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 146.5, 142.4, 138.5, 129.3, 128.6, 128.1, 127.9, 127.4, 127.3, 127.0, 126.8, 126.3, 74.1, 66.8, 63.2, 54.2, 34.0, 29.5; IR (neat) 1599 (m), 1495 (m), 1447 (m) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 325.2 (1, M^+), 202.2 (13), 145.1 (100), 104.1 (12), 77.1 (7); HRMS (ES, pos. ion) calcd for $\text{C}_{24}\text{H}_{24}\text{N}$ [$\text{M}+\text{H}$] $^+$ 326.1909; found 326.1906.

(1R*,2S*,3S*,4R*)-1-Methyl-2,3-diphenyl-7-azabicyclo[2.2.1]heptane (51a) and (1R*,2R*,3R*,4S*)-1-Methyl-2,3-diphenyl-7-azabicyclo[2.2.1]heptane (51b): *n* -

Butyllithium (50 μL of a 2.5 M solution in hexanes, 0.12 mmol) was added to a solution of stannane **22** (25 mg, 0.062 mmol) and *trans*-stilbene (22 mg, 0.12 mmol) in THF (0.62 mL) cooled to $-78\text{ }^{\circ}\text{C}$. After 30 min., the reaction was quenched with 0.1 mL of methanol and warmed to room temperature. The solvent was removed *in vacuo* and the residue columned directly (2-5% methanol/methylene chloride gradient) to give 15 mg of **51a** and **51b** (89% combined yield, 1.5:1) as a clear oil. Data for **51a/b**: R_f = 0.36 (10% methanol/methylene chloride); ^1H NMR (500 MHz, CDCl_3) δ 7.40-7.14 (m, 10 H), 3.91 (t, 0.41 H, J = 4.5 Hz), 3.80 (d, 0.59 H, J = 5.0 Hz), 3.68 (t, 0.41 H, J = 5.5 Hz), 3.25 (d, 0.59 H, J = 6.5 Hz), 2.97 (dd, 0.59 H, J = 6.5, 2.5 Hz), 2.93 (d, 0.41 H, J = 6.5 Hz), 2.02-1.60 (m, 2 H), 1.51 (td, 1 H, J = 11.8, 7.0 Hz), 1.32 (s, 1.76 H), 1.17-1.12 (m, 1 H), 0.98

(s, 1.24 H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.2, 141.3, 139.7, 129.0, 128.8, 128.7, 128.5, 128.4, 128.1, 126.9, 126.8, 126.5, 126.3, 126.2, 68.7, 68.3, 65.0, 62.8, 61.4, 58.8, 56.6, 55.1, 40.2, 33.5, 30.1, 26.5, 20.1, 19.7; IR (neat) 3273 (br, w), 1600 (w), 1495 (m), 1448 (m) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 263.3 (4, M^+), 179.2 (9), 115.1 (5), 83.1 (100); HRMS (EI, 70 eV) calcd for $\text{C}_{19}\text{H}_{21}\text{N}$ (M^+) 263.1674; found 263.1676.

(2*R,3*R**)-Diphenyl-7-azabicyclo[2.2.1]heptane (52):** *n*-Butyllithium (0.41 mL of a 2.12 M solution in hexanes, 0.87 mmol) was added in a dropwise fashion to a solution of stannyl imine **36** (0.26 g, 0.73 mmol) and *trans*-stilbene (0.30 g, 1.6 mmol) in THF (2.0 mL) cooled to $-78\text{ }^{\circ}\text{C}$. After 30 min., saturated aqueous ammonium chloride was added and the mixture was diluted with ether then acid/base extracted with 2 M aqueous HCl and 2 M aqueous NaOH. The combined organic phases were dried (Na_2SO_4) and concentrated to an oil. Chromatography (10% methanol/methylene chloride) gave 59 mg (33%) of **52** as an oil. Data for **52**: R_f = 0.30 (10% methanol/methylene chloride); ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.17 (m, 10 H), 3.92 (t, 1 H, J = 5.0 Hz), 3.80 (d, 1 H, J = 5.0 Hz), 3.46 (dd, 1 H, J = 7.0, 5.0 Hz), 3.05 (d, 1 H, J = 7.0 Hz), 2.39 (br s, 1 H), 1.77-1.68 (m, 1 H), 1.64-1.57 (m, 2 H), 1.53-1.43 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.0, 140.5, 128.7, 128.6, 128.3, 127.2, 126.5, 126.4, 64.4, 62.1, 58.4, 52.3, 31.9, 24.0; IR (neat) 3366 (w), 1603 (m), 1493 (s) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 249.2 (2, M^+), 180.1 (5), 69.1 (100); HRMS (EI, 70 eV) calcd for $\text{C}_{18}\text{H}_{19}\text{N}$ (M^+) 249.1517; found 249.1509.

***N*-[4-(*tert*-Butyldimethylsilyloxy)-1-(tri-*n*-butylstannyl)butyl]phthalimide (**55**):** *n*-Butyllithium (44.0 mL of a 1.75 M solution in hexanes, 77.0 mmol) was added to a solution of diisopropylamine (11.0 mL, 7.9 g, 78.9 mmol) in THF at 0 °C. After 30 min., (tri-*n*-butyl)tin hydride (30 mL, 32.5 g, 112 mmol) was added in a dropwise fashion to afford a pale green-yellow solution. After 30 min., the solution was cooled to –78 °C and 4-(*tert*-butyldimethylsilyloxy)butyraldehyde (10.0 g, 51.2 mmol) in THF (25 mL) was added. After 20 min. at –78 °C, saturated aqueous ammonium chloride was added. The mixture was diluted with ether, washed with saturated aqueous ammonium chloride, dried (MgSO₄), filtered, and concentrated to provide an oil. The crude oil was then dissolved in THF (200 mL) and cooled to 0 °C. Triphenylphosphine (14.8 g, 56.4 mmol), phthalimide (8.30 g, 56.4 mmol), and diethyl azodicarboxylate (9.0 mL, 57.2 mmol) were added sequentially. The reaction was allowed to warm to room temperature while stirring overnight. The mixture was concentrated and the residue triturated with hexanes. Concentration of the extracts yielded a yellow oil. Chromatography (0-5% ethyl acetate/hexanes gradient) afforded 14.2 g (45%) of **55** as a bright yellow oil. Data for **55**: R_f = 0.45 (10 % ethyl acetate/hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.77 (ddd, 2 H, J = 5.2, 2.9, 0.7 Hz), 7.65 (ddd, 2 H, J = 5.4, 3.2, 0.8 Hz), 3.91 (dd, 1 H, J = 10.1, 5.9 Hz), 3.60-3.56 (m, 2 H), 2.00-1.78 (m, 2 H), 1.50-1.39 (m, 8 H), 1.26 (hex, 6 H, J = 7.0 Hz), 1.02-0.70 (m, 24 H), 0.01 (s, 3 H), -0.01 (s, 3 H); ¹³C NMR (90 MHz, CDCl₃) δ

159.1, 133.7, 132.1, 122.8, 62.4, 37.1, 31.4, 29.2, 29.0, 27.4, 25.9, 18.3, 13.6, 10.3, -5.4; IR (neat) 1772 (w), 1706 (s), 1466 (m), 1388 (m), 1255 (m), 1100 (m); MS (CI, CH₄) *m/z* (rel int) 608 (12, M-CH₄), 566 (100), 1887 (72), 149 (51), 127 (30), 99 (39); HRMS (CI, CH₄) calcd for C₂₉H₅₀NO₃SiSn [M-CH₃]⁺ 608.2582; found 608.2570.

***N*-[4-Oxo-1-(tri-*n*-butylstannyl)butyl]phthalimide (56):** Silane **55** (3.70 g, 5.94 mmol) was dissolved in a 3:1:1 mixture of acetic acid:THF:water (50 mL). After 15 h, the mixture was diluted with ether, washed with water (3x), dried (MgSO₄), filtered, and concentrated to provide an oil. Chromatography (0-20% ethyl acetate/hexanes gradient) afforded 2.35 g (77%) of the alcohol compound as an oil. Data for *N*-[4-hydroxy-1-(tri-*n*-butylstannyl)butyl]phthalimide: *R_f* = 0.60 (50% ethyl acetate/hexanes); ¹H NMR (360 MHz, CDCl₃) δ 7.78 (dd, 2 H, *J* = 5.0, 3.1 Hz), 7.66 (dd, 2 H, *J* = 5.4, 3.0 Hz), 3.92 (dd, 1 H, *J* = 9.2, 5.8 Hz, ²*J*(^{117/119}Sn-¹H) = 35.5 Hz), 3.62 (t, 2 H, *J* = 6.4 Hz), 1.53-1.37 (m, 10 H), 1.24 (hex, 6 H, *J* = 7.3 Hz), 1.05-0.83 (m, 15 H); ¹³C NMR (90 MHz, CDCl₃) δ 169.2, 133.8, 132.0, 122.9, 62.3, 36.9, 31.2, 29.2, 28.9, 27.3, 13.6, 10.3; IR (neat) 3447 (br, m), 1703 (s), 1466 (m), 1068 (m); MS (CI, NH₃) *m/z* (rel int) 452 (100, M-C₄H₉), 235 (41), 88 (31); HRMS (CI, NH₃) calcd for C₂₀H₃₀NO₃Sn [M-C₄H₉]⁺ 452.1248; found 452.1240.

Oxalyl chloride (0.34 mL, 3.90 mmol), dimethyl sulfoxide (0.55 mL, 7.75 mmol), *N*-[4-hydroxy-1-(tri-*n*-butylstannyl)butyl]phthalimide (1.65 g, 3.25 mmol), and triethylamine (2.70 mL, 19.3 mmol) were sequentially dissolved in CHCl₂ (30 mL) at -78 °C over 15

min. intervals. The reaction was allowed to warm to room temperature. The mixture was diluted with ether, was with saturated aqueous ammonium chloride (5x), dried (Na_2SO_4), filtered, and concentrated to provide 1.42 g (86%) of **56** as an oil. The product was used without further purification. Data for **56**: R_f = 0.10 (10% ethyl acetate/hexanes); ^1H NMR (360 MHz, CDCl_3) δ 9.69 (t, 1 H, J = 1.3 Hz), 7.79 (dd, 2 H, J = 5.6, 3.1 Hz), 7.68 (dd, 2 H, J = 5.5, 3.2 Hz), 3.86 (dd, 1 H, J = 11.1, 4.6 Hz), 2.50-2.36 (m, 2 H), 2.30-2.20 (m, 1 H), 2.07-1.98 (m, 1 H), 1.57-1.38 (m, 6 H), 1.31-1.22 (m, 6 H), 1.06-0.80 (m, 15 H); ^{13}C NMR (90 MHz, CDCl_3) δ 201.3, 169.1, 133.9, 131.8, 123.0, 42.8, 36.4, 28.9, 27.3, 25.3, 13.5, 10.4; IR (neat) 1703 (s), 1466 (m), 1388 (s), 1334 (m), 1072 (m); MS (CI, NH_3) m/z (rel int) 507 (18, $\text{M}+\text{H}$), 450 (100), 308 (31), 235 (24), 217 (29), 147 (20); HRMS (CI, NH_3) calcd for $\text{C}_{20}\text{H}_{28}\text{NO}_3\text{Sn}$ [$\text{M}-\text{C}_4\text{H}_9$] $^+$ 450.1078; found 450.1091.

(1*R,2*S**,6*R**)-1-Butyl-4,10-dimethyl-4,10-diazatricyclo[5.2.1.0^{2,6}]decane-3,5-dione**

(57): Stannane **21** (82 mg, 0.20 mmol), methyl iodide (60 μL , 137 mg, 1.0 mmol), *N*-methylmaleimide (44 mg, 0.4 mmol) were dissolved in toluene (2 mL) and heated to 110 $^\circ\text{C}$ for 18 h in a sealed tube. The reaction mixture was diluted with methylene chloride and washed with water (1x). The combined organic phases were dried (Na_2SO_4) and concentrated to an oily solid. Chromatography (0-1% methanol: methylene chloride gradient) gave 20 mg (40%) of **57** as a solid off-white powder. Data for **57**: R_f = 0.11 (2% methanol: methylene chloride); mp = 86-90 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 3.55 (d, 1 H, J = 4.5 Hz), 2.94 (s, 3 H), 2.67 (d, 1 H, J = 7.0 Hz), 2.58 (d, 1 H, J = 7.0 Hz), 2.01 (s, 3 H), 2.00-1.96 (m, 1 H), 1.82-1.77 (m, 2 H), 1.56-1.38 (m, 7 H), 0.97 (t, 3 H, J =

7.5 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 178.9, 177.1, 71.4, 65.1, 50.7, 48.8, 31.8, 30.8, 30.0, 28.1, 26.6, 25.0, 23.7, 14.3; IR (CHCl_3) 1696 (s), 1435 (m), 1287 (m) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 250.3 (13, M^+), 221.2 (26), 208.2 (52), 179.2 (51), 139.2 (52), 96.1 (100); HRMS (EI, 70 eV) calcd for $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_2$ (M^+) 250.1681; found 250.1682.

(1*R,2*R**,6*S**)-4,10-Dimethyl-1-phenyl-4,10-diazatriacylo[5.2.1.0^{2,6}]decane-3,5-dione**

(58): Stannane **19** (43 mg, 0.10 mmol), methyl iodide (30 μL , 68 mg, 0.5 mmol), *N*-methylmaleimide (17 mg, 0.15 mmol) were dissolved in toluene (1 mL) and heated to 110 $^{\circ}\text{C}$ for 18 h in a sealed tube. The reaction mixture was diluted with methylene chloride and washed with water (1x). The combined organic phases were dried (Na_2SO_4) and concentrated to an oily solid. Chromatography (0-1% methanol: methylene chloride gradient) gave 5.0 mg (19%) of **58** as a solid off-white film. Data for **58**: R_f = 0.20 (2% methanol:methylene chloride); ^1H NMR (500 MHz, CDCl_3) δ 7.40-7.20 (m, 5 H), 3.81 (d, 1 H, J = 4.5 Hz), 2.96 (s, 3 H), 2.76 (q, 2 H, J = 7.0 Hz), 2.24-2.18 (m, 1 H), 2.07 (dd, 2 H, J = 8.0, 5.5 Hz), 2.02 (s, 3 H), 1.72-1.67 (m, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 178.4, 176.1, 137.1, 128.6, 128.2, 127.8, 74.9, 64.9, 56.1, 49.5, 32.3, 30.9, 26.4, 25.1; IR (CHCl_3) 1696 (s), 1444 (m), 1290 (m) cm^{-1} ; MS (EI, 70 eV) m/z (rel int) 270.2 (58, M^+), 242.2 (55), 184.2 (32), 159.2 (100), 118.1 (35); HRMS (EI, 70eV) calcd for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2$ (M^+) 270.1368; found 270.1358.