Supporting Information

Novel 7- and 8-Endo 2-Indolylacyl Radical Cyclizations: Efficient Construction of Azepino- and Azocinoindoles

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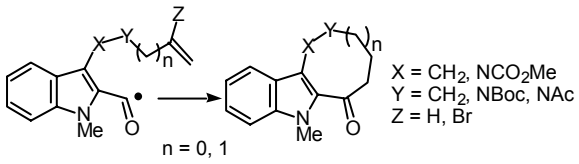
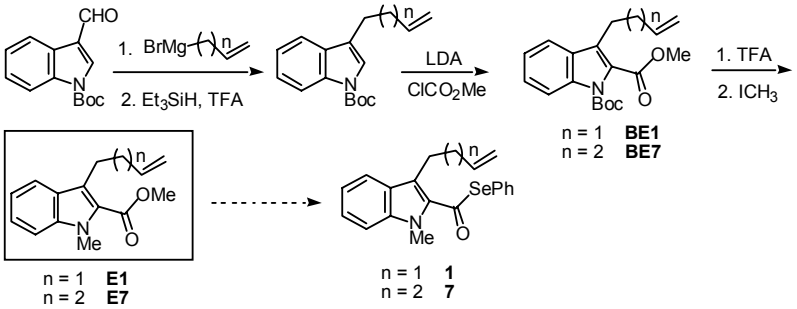


Contents

Reaction courses and product mixtures were routinely monitored by TLC on silica gel (precoated F_{254} Merck plates). Drying of organic extracts during the workup of reactions was performed over anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure with a rotary evaporator. Flash chromatography was carried out on SiO_2 (silica gel 60, SDS, 0.04-0.06 mm). Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution, using TMS as an internal reference.

1. Preparation of the Starting Carboxylic Esters

A. Methyl 3-Alkenylindole-2-carboxylates (E1 and E7).



Methyl 3-(3-Butenyl)-1-(*tert*-butoxycarbonyl)indole-2-carboxylate (**BE1**). Allylmagnesium bromide (1 M in Et_2O, 4 mL, 4.0 mmol) was added dropwise to a cooled (–78°C) solution of 1-(*tert*-butoxycarbonyl)indole-3-carbaldehyde[1] (0.75 g, 3.06 mmol) in anhydrous THF (30 mL) and the resulting mixture was stirred at –78°C for 1 h. The reaction mixture was poured into a saturated aqueous NH_4Cl solution (50 mL) and extracted with Et_2O (3 x 40 mL). The organic extracts were concentrated to give the crude carbinol. Et_3SiH (0.97 mL, 6.12 mmol) and TFA (0.47 mL, 6.12 mmol) were added to a cooled (0°C) solution of the above carbinol in CH_2Cl_2 (30 mL). After stirring at 0°C for 2 h, the reaction mixture was washed with 2 M aqueous Na_2CO_3 solution (3 x 20 mL), dried and concentrated. The crude product was chromatographed (98:2 hexanes-AcOEt) to give **1-(*tert*-butoxycarbonyl)-3-(3-butenyl)indole**: 0.55 g (67%); ^1H NMR (300 MHz) δ 1.66 (s, 9H), 2.47 (q, J = 7.2 Hz, 2H), 2.78 (t, J = 7.2 Hz, 2H), 5.02 (dq, J = 1.2, 1.2, 1.2, 10.2, 1H), 5.09 (dq, J = 1.5, 1.5, 1.5, 16.8, 1H), 5.92 (m, 1H), 7.24 (m, 1H), 7.30 (m, 1H), 7.37 (s, 1H), 7.52 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 7.5 Hz, 1H).

n-BuLi (1.6 M in hexane, 2.45 mL, 3.93 mmol) was added under Ar to a cooled (–78°C) solution of diisopropylamine (0.55 mL, 3.93 mmol) in anhydrous THF (22 mL), and the resulting solution was stirred at –78°C for 30 min. Then, the above 3-substituted indole (0.71 g, 2.62 mmol) in anhydrous THF (22 mL) was added, and the resulting red mixture was stirred at –78°C for 40 min. Methyl chloroformate (0.30 mL, 3.93 mmol) was added, and the mixture was allowed to slowly warm to rt. The reaction mixture was poured into a saturated aqueous NH_4Cl solution (50 mL) and extracted with AcOEt (3 x 45 mL). The organic extracts were

concentrated. The crude product was chromatographed (98:2 hexanes-AcOEt) to give **BE1** as a pale yellow oil: 0.65 g (75%); ^{1}H NMR (300 MHz) δ 1.61 (s, 9H), 2.40 (q, *J* = 7.8 Hz, 2H), 2.92 (t, *J* = 7.8 Hz, 2H), 3.92 (s, 3H), 4.97 (dm, *J* = 10.2 Hz, 1H), 5.03 (dq, *J* = 1.8, 1.8, 1.8, 17.1 Hz, 1H), 5.85 (m, 1H), 7.28 (m, 1H), 7.40 (m, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 23.9 (CH_2), 27.9 (CH_3), 34.2 (CH_2), 52.0 (CH_3), 84.2 (C), 115.0 (CH_2), 115.2 (CH_2), 120.1 (CH), 122.8 (CH), 126.6 (CH, C), 126.7 (C), 128.5 (C), 136.7 (C), 137.6 (CH), 149.3 (C), 163.0 (C). Anal. Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.50; H, 7.15; N, 4.26.

Methyl 3-(3-Butenyl)-1-methylindole-2-carboxylate (E1). A solution of indole **BE1** (0.49 g, 1.50 mmol) in TFA (9 mL) was stirred at rt for 2 h. The reaction mixture was concentrated to dryness and the residue was dissolved in CH_2Cl_2 (25 mL). The organic solution was washed with 2 M aqueous Na_2CO_3 solution (3 x 20 mL), dried and concentrated to give the crude *N*-unsubstituted indole. A solution of the above indole in anhydrous DMF (6 mL) was added dropwise under Ar to a suspension of NaH (1.95 mmol) in anhydrous DMF (4 mL). After stirring at rt for 1 h, the mixture was cooled to 0°C and MeI (0.38 mL, 6.0 mmol) was added dropwise. The mixture was allowed to warm to rt for 5 h, then was quenched with cold H_2O (20 mL) and extracted with AcOEt (3 x 20 mL). The organic extracts were washed with H_2O (5 x 35 mL), dried and concentrated. The crude product was chromatographed (9:1 hexanes-AcOEt) to give **E1** as an oil: 0.22 g (62%); ^{1}H NMR (300 MHz) δ 2.38 (q, *J* = 6.6 Hz, 2H), 3.15 (m, 2H), 3.94 (s, 3H), 4.00 (s, 3H), 4.96 (dm, *J* = 10.2 Hz, 1H), 5.05 (dq, *J* = 1.8, 1.8, 1.8. 16.8 Hz, 1H), 5.91 (m, 1H), 7.14 (m, 1H), 7.35 (m, 2H), 7.68 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 25.1 (CH_2), 32.0 (CH_3), 35.4 (CH_2), 51.3 (CH_3), 110.1 (CH), 114.5 (CH_2), 119.7 (CH), 120.7 (CH), 124.6 (C), 124.8 (C), 125.2 (CH), 126.5 (C), 138.6 (CH), 138.7 (C), 163.2 (C). Anal. Calcd for: $C_{15}H_{17}NO_2$ C, 74.05; H, 7.04; N, 5.76. Found: C, 74.34; H, 6.89; N, 5.31.

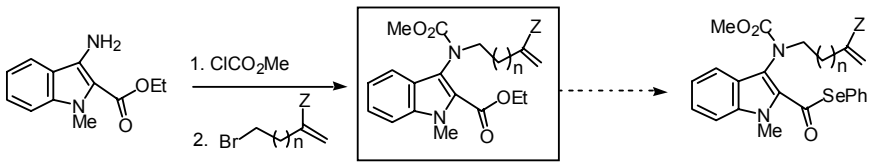
Methyl 1-(*tert*-Butoxycarbonyl)-3-(4-pentenyl)indole-2-carboxylate (BE7). 4-Bromo-1-butene (1.55 mL, 15 mmol) was added dropwise at rt to a suspension of magnesium turnings (0.45 g, 18 mmol) in anhydrous THF (18 mL), and the mixture was stirred at rt for 2 h. 1-(*tert*-Butoxycarbonyl)indole-3-carbaldehyde[1] (0.75 g, 3.06 mmol) was dissolved in anhydrous THF (10 mL) and cooled to –40°C. The freshly prepared Grignard reagent was added dropwise to the aldehyde solution and the mixture was allowed to slowly warm to rt for 4 h. The reaction mixture was poured into a saturated aqueous NH_4Cl solution (50 mL) and extracted with Et_2O (3 x 40 mL). The organic extracts were concentrated to give the crude carbinol. Et_3SiH (0.97 mL, 6.12 mmol) and TFA (0.47 mL, 6.12 mmol) were added to a cooled (0°C) solution of the above carbinol in CH_2Cl_2 (30 mL). After stirring at 0°C for 30 min, the reaction mixture was washed with 2 M aqueous Na_2CO_3 solution (3 x 20 mL), dried and concentrated. The crude

product was chromatographed (95:5 hexanes-AcOEt) to give **1-(*tert*-butoxycarbonyl)-3-(4-pentenyl)indole**: 0.70 g (80%); ^{1}H NMR (300 MHz) δ 1.66 (s, 9H), 1.81 (m, 2H), 2.16 (q, *J* = 6.9 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 5.02 (m, 2H), 5.86 (m, 1H), 7.22 (m, 1H), 7.30 (m, 1H), 7.35 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H).

n-BuLi (1.6 M in hexane, 1.55 mL, 2.48 mmol) was added under Ar to a cooled (–78°C) solution of diisopropylamine (0.35 mL, 2.48 mmol) in anhydrous THF (14 mL), and the resulting solution was stirred at –78°C for 30 min. Then, the above 3-substituted indole (0.47 g, 1.66 mmol) in anhydrous THF (14 mL) was added, and the resulting red mixture was stirred at –78°C for 40 min. Methyl chloroformate (0.19 mL, 2.48 mmol) was added, and the mixture was allowed to slowly warm to rt. The reaction mixture was poured into a saturated aqueous NH_4Cl solution (40 mL) and extracted with AcOEt (3 x 35 mL). The organic extracts were concentrated. The crude product was chromatographed (98:2 hexanes-AcOEt) to give **BE7** as a pale yellow oil: 0.35 g (62%); ^{1}H NMR (300 MHz) δ 1.61 (s, 9H), 1.76 (m, 2H), 2.13 (q, *J* = 6.9 Hz, 2H), 2.84 (t, *J* = 7.8 Hz, 2H), 3.92 (s, 3H), 5.01 (m, 2H), 5.83 (m, 1H), 7.26 (ddd, *J* = 1.2, 6, 8.1 Hz, 1H), 7.40 (ddd, *J* = 1.2, 6.9, 8.1 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 23.7 (CH_2), 27.9 (CH_3), 29.3 (CH_2), 33.4 (CH_2), 52.1 (CH_3), 84.2 (C), 114.8 (CH_2), 115.0 (CH), 120.2 (CH), 122.8 (CH), 126.5 (C), 126.6 (CH), 127.3 (C), 128.6 (C), 136.8 (C), 138.2 (CH), 149.4 (C), 163.1 (C). Anal. Calcd for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.34; N, 4.08. Found: C, 70.07; H, 7.48; N, 4.02.

Methyl 1-Methyl-3-(4-pentenyl)indole-2-carboxylate (E7). A solution of indole **BE7** (0.51 g, 1.50 mmol) in TFA (9 mL) was stirred at rt for 2 h. The reaction mixture was concentrated to dryness and the residue was dissolved in CH_2Cl_2 (25 mL). The organic solution was washed with 2 M aqueous Na_2CO_3 solution (3 x 20 mL), dried and concentrated to give the crude *N*-unsubstituted indole. A solution of the above indole in anhydrous DMF (6 mL) was added dropwise under Ar to a suspension of NaH (1.95 mmol) in anhydrous DMF (4 mL). After stirring at rt for 1 h, the mixture was cooled to 0°C and MeI (0.38 mL, 6.0 mmol) was added dropwise. The mixture was allowed to warm to rt for 5 h, then was quenched with cold H_2O (20 mL) and extracted with AcOEt (3 x 20 mL). The organic extracts were washed with H_2O (5 x 35 mL), dried and concentrated. The crude product was chromatographed (9:1 hexanes-AcOEt) to give **E7** as an oil: 0.30 g (78%); ^{1}H NMR (300 MHz) δ 1.97 (m, 2H), 2.37 (q, *J* = 6.6 Hz, 2H), 3.30 (m, 2H), 4.14 (s, 3H), 4.20 (s, 3H), 5.23 (m, 2H), 6.09 (m, 1H), 7.35 (m, 1H), 7.55 (m, 2H), 7.89 (dt, *J* = 1.2, 1.2, 7.8 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 24.8 (CH_2), 30.4 (CH_2), 32.0 (CH_3), 33.8 (CH_2), 51.3 (CH_3), 110.0 (CH), 114.5 (CH_2), 119.6 (CH), 120.7 (CH), 124.5 (C), 125.2 (CH), 125.5 (C), 126.6 (C), 138.8 (CH, C), 163.2 (C). Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.44; H, 7.67; N, 5.42.

B. Ethyl 3-(*N*-Alkenylamino)indole-2-carboxylates (E4a, E4b, and E11)



Z = H, n = 0 **E4a**
Z = Br, n = 0 **E4b**
Z = H, n = 1 **E11**

Z = H, n = 0 **4a**
Z = Br, n = 0 **4b**
Z = H, n = 1 **11**

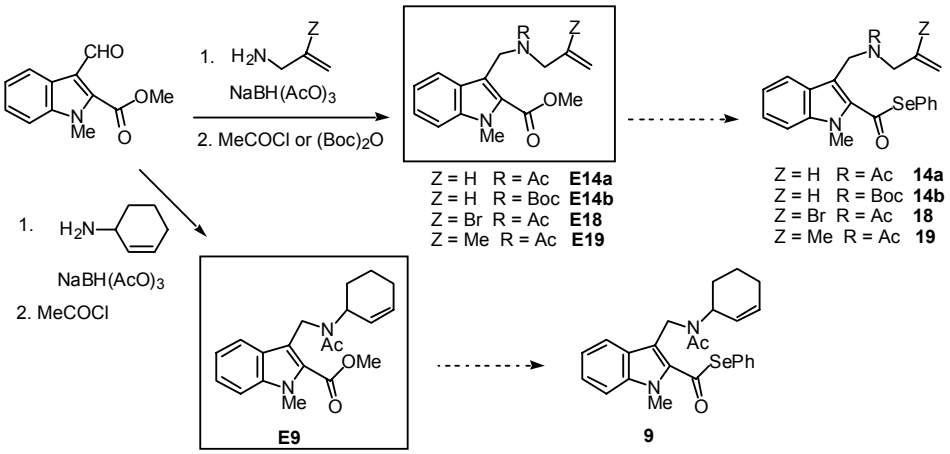
General Procedure. Methyl chloroformate (0.38 mL, 4.90 mmol) in anhydrous THF (5 mL) was added dropwise to a solution of ethyl 3-amino-1-methylindole-2-carboxylate[2] (1.0 g, 4.59 mmol) and anhydrous pyridine (0.85 mL, 9.63 mmol) in anhydrous THF (15 mL). After stirring at rt for 12 h, the reaction mixture was concentrated and the resulting residue was dissolved in CH_2Cl_2 (80 mL). The organic solution was washed with 2 N aqueous HCl solution (2 x 50 mL), dried and concentrated to give crude methylcarbamate. Cs_2CO_3 (4.48 g, 13.77 mmol) and TBAI (5.12 g, 13.77 mmol) were added to a solution of the above methyl carbamate in anhydrous DMF (50 mL). After stirring at rt for 30 min, the respective alkylbromide (13.77 mmol) was added to the suspension. The reaction mixture was stirred at rt for 5 h, poured into H_2O (50 mL) and extracted with AcOEt (3 x 70 mL). The combined organic extracts were washed with H_2O (3 x 50 mL) and brine (50 mL), dried, and concentrated, and the resulting residue was chromatographed. Eluents, yields, NMR data and elemental analyses are given below.

Ethyl 3-[*N*-Allyl-*N*-(methoxycarbonyl)amino]-1-methylindole-2-carboxylate (E4a): alkylating agent, allyl bromide; elution with 6:4 hexanes-AcOEt, oil; yield 78%; ^{1}H NMR (300 MHz, major rotamer) δ 1.39 (t, J = 7.5 Hz, 3H), 3.59 (s, 3H), 4.05 (s, 3H), 4.19, (m, 1H), 4.36 (m, 1H), 4.34 (q, J = 7.5 Hz, 2H), 5.05 (m, 2H), 5.95 (m, 1H), 7.18 (m, 1H), 7.38 (m, 2H), 7.56 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75.4 MHz, major rotamer) δ 14.3 (CH_3), 32.0 (CH_3), 52.9 (CH_3), 53.9 (CH_2), 60.8 (CH_2), 110.3 (CH), 117.9 (CH_2), 119.9 (CH), 120.9 (CH), 123.1 (C), 123.5 (C), 125.5 (CH), 133.6 (CH), 137.2 (C), 156.8 (C), 161.5 (C), C-2 not observed. Anal. Calcd for $C_{17}H_{20}N_2O_4$: C, 64.54; H, 6.37; N, 8.85. Found: C, 64.36; H, 6.45; N, 8.71.

Ethyl 3-[*N*-(2-Bromo-2-propenyl)-*N*-(methoxycarbonyl)amino]-1-methylindole-2-carboxylate (E4b): alkylating agent, 2,3-dibromopropene; elution with 96:4 hexanes-AcOEt, oil; yield 85%; ^{1}H NMR (300 MHz, major rotamer) δ 1.39 (t, J = 7.5 Hz, 3H), 3.62 (s, 3H), 4.06 (s, 3H), 4.20 (d, J = 15.9 Hz, 1H), 4.39 (m, 2H), 4.90 (d, J = 15.3 Hz, 1H), 5.49 (d, J = 1.5 Hz, 1H), 5.70 (as, 1H), 7.18 (m, 1H), 7.38 (m, 2H), 7.72 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75.4 MHz, major rotamer) δ 14.2 (CH_3), 32.0 (CH_3), 53.1 (CH_3), 59.3 (CH_2), 60.9 (CH_2), 110.2 (CH), 119.9 (CH_2), 120.5 (CH), 120.9 (CH), 122.7 (C), 123.6 (C), 123.7 (C), 125.5 (CH), 128.7 (C), 137.0 (C), 156.9 (C), 161.2 (C). Anal. Calcd for $C_{17}H_{19}BrN_2O_4$: C, 51.66; H, 4.85; N, 7.09. Found: C, 51.43; H, 4.98; N, 7.26.

Ethyl 3-[*N*-(3-Butenyl)-*N*-(methoxycarbonyl)amino]-1-methylindole-2-carboxylate (E11): alkylating agent, 4-bromo-1-butene; elution with 9:1 hexanes-AcOEt, oil; yield 82%; ^{1}H NMR (300 MHz, major rotamer) δ 1.39 (t, *J* = 7.2 Hz, 3H), 2.35 (q, *J* = 7.8 Hz, 2H), 3.58 (s, 3H), 3.64 (m, 1H), 3.87 (m, 1H), 4.06 (s, 3H), 4.36, (m, 2H), 5.01 (m, 2H), 5.73 (m, 1H), 7.19 (ddd, *J* = 2.1, 6.3, 8.4 Hz, 1H), 7.40 (m, 2H), 7.56 (dt, *J* = 1.2, 1.2, 7.8 Hz, 1H); ^{13}C NMR (75.4 MHz, major rotamer) δ 14.3 (CH_3), 31.2 (CH_3), 32.6 (CH_2), 50.7 (CH_2), 52.8 (CH_3), 60.8 (CH_2), 110.4 (CH), 116.4 (CH_2), 119.8 (CH), 120.9 (CH), 122.9 (C), 123.5 (C), 123.7 (C), 125.5 (CH), 135.2 (CH), 137.2 (C), 156.7 (C), 161.4 (C). Anal. Calcd for $C_{18}H_{22}N_2O_4 \cdot 1/4\ H_2O$: C, 64.55; H, 6.77; N, 8.36. Found: C, 64.33; H, 6.73; N, 8.48.

C. Methyl 3-(*N*-Alkenylaminomethyl)indole-2-carboxylates



***N*-Acetyl Derivatives E9, E14a, E18 and E19. General Procedure.** A solution of methyl 3-formyl-1-methylindole-2-carboxylate[3] (1.0 g, 4.61 mmol), the respective amine (9.20 mmol), $NaBH(AcO)_3$ (2.93 g, 13.82 mmol) and AcOH (0.25 mL, 4.61 mmol) in anhydrous CH_2Cl_2 (25 mL) was stirred at rt for 12 h. The reaction mixture was washed with saturated aqueous Na_2CO_3 solution (3 x 20 mL). The solvent was removed and the resulting residue (crude secondary amine) was dissolved in anhydrous CH_2Cl_2 (45 mL). Acetyl chloride (0.39 mL, 5.53 mmol) and Et_3N (0.70 mL, 5.07 mmol) were added to the above cooled (0°C) solution. After stirring at rt until no starting amine was detected by TLC (2-4 h), the reaction mixture was poured into H_2O (25 mL) and washed with 2 N aqueous HCl solution (2 x 25 mL). The solvent was removed and the crude product was chromatographed. Eluents, yields, NMR data and elemental analyses are given below.

Methyl 3-[*N*-Acetyl-*N*-(2-cyclohexenyl)aminomethyl]-1-methylindole-2-carboxylate (E9): amine, 2-cyclohexenylamine; elution with 7:3 hexanes-AcOEt, oil; yield 70%; ^{1}H NMR (300 MHz) δ 1.45-1.75 (m, 4H), 1.95 (m, 2H), 2.05 and 2.22 (2 s, 3H), 3.95 and 4.03 (2 s, 3H), 3.98 (s, 3H), 4.31 and 5.30 (2 m, 1H), [4.92 (d, *J* =18.9 Hz), 5.03 (d, *J* =18.9 Hz), 5.12 (d, *J* =15.3 Hz) and 5.35 (d, *J* =15.3 Hz), 2H], [5.30 (m) and 5.48 (d, *J* = 9 Hz), 1H], 5.65 and 5.75 (2 m,

1H), 7.12 (m, 1H), 7.36 (m, 2H), [7.72 (d, J = 8.4 Hz) and 7.83 (d, J = 7.8 Hz), 1H]; ^{13}C NMR (75.4 MHz) δ 21.3 and 22.0 (CH_2), 22.7 and 22.8 (CH_3), 24.2 and 24.6 (CH_2), 27.0 and 27.9 (CH_2), 32.1 and 32.2 (CH_3), 38.3 and 44.2 (CH_2), 51.6 and 55.4 (CH), 51.7 (CH_3), 109.9 and 110.4 (CH), 120.4 and 120.9 (CH), 121.0 and 121.4 (C), 121.6 and 122.1 (CH), 123.6 and 124.9 (C), 125.2 and 125.3 (CH), 126.0 (C), 127.7 and 129.0 (CH), 129.4 and 131.5 (CH), 138.7 and 138.8 (C), 162.7 and 162.9 (C), 171.0 and 172.0 (C). Anal. Calcd for $C_{20}H_{24}N_2O_3$: C, 70.56; H, 7.11; N, 8.23. Found: C, 70.34; H, 7.31; N, 8.02.

Methyl 3-(*N*-Acetyl-*N*-allylaminomethyl)-1-methylindole-2-carboxylate (E14a): amine, allylamine; elution with 6:4 hexanes-AcOEt; yield 68%; mp 92-3°C; ^{1}H NMR (300 MHz, major rotamer) δ 2.13 (s, 3H), 3.75 (m, 2H), 3.92 (s, 3H), 4.01 (s, 3H), 5.05 (m, 1H), 5.16 (m, 1H), 5.22 (s, 2H), 5.70 (m, 1H), 7.16 (m, 1H), 7.37 (m, 2H), 7.89 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75.4 MHz, major rotamer) δ 21.5 (CH_3), 32.1 (CH_3), 37.7 (CH_2), 48.4 (CH_2), 51.7 (CH_3), 109.9 (CH), 115.4 (CH_2), 119.1 (C), 120.7 (CH), 121.9 (CH), 125.5 (CH), 126.4 (C), 126.6 (C), 132.9 (CH), 138.6 (C) 162.7 (C), 170.6 (C). Anal. Calcd for $C_{17}H_{20}N_2O_3 \cdot 1/4H_2O$: C, 66.98; H, 6.78; N, 9.19. Found: C, 66.72; H, 6.64; N, 9.11.

Methyl 3-[*N*-Acetyl-*N*-(2-bromo-2-propenyl)aminomethyl]-1-methylindole-2-carboxylate (E18): amine, 2-bromo-2-propenylamine;[4] elution with 7:3 hexanes-AcOEt; yield 64%; mp 65-7°C; ^{1}H NMR (300 MHz, major rotamer) δ 2.14 (s, 3H), 3.95 (s, 3H), 3.96 (s, 2H), 4.03 (s, 3H), 5.22 (s, 2H), 5.63 (m, 1H), 5.70 (m, 1H), 7.18 (m, 1H), 7.37 (m, 2H), 7.88 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75.4 MHz, major rotamer) δ 21.4 (CH_3), 32.2 (CH_3), 37.6 (CH_2), 51.8 (CH_2), 53.7 (CH_3), 110.0 (CH), 115.5 (CH_2), 118.2 (C), 120.9 (CH), 121.9 (CH), 125.6 (CH), 125.7 (C), 126.8 (C), 128.5 (C), 138.7 (C) 162.6 (C), 170.7 (C). Anal. Calcd for $C_{17}H_{19}BrN_2O_3 \cdot 1/4\ H_2O$: C, 53.21; H, 5.12; N, 7.30. Found: C, 53.04; H, 4.89; N, 7.23.

Methyl 3-[*N*-Acetyl-*N*-(2-methyl-2-propenyl)aminomethyl]-1-methylindole-2-carboxylate (E19): amine, 2-methyl-2-propenylamine; elution with 1:1 hexanes-AcOEt; yield 65%; mp 90-1°C; ^{1}H NMR (300 MHz, major rotamer) δ 1.65 (s, 3H), 2.09 (s, 3H), 3.60 (s, 2H), 3.89 (s, 3H), 4.01 (s, 3H), 4.78 (s, 1H), 4.93 (s, 1H), 5.20 (s, 2H), 7.16 (m, 1H), 7.37 (m, 2H), 7.90 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75.4 MHz, major rotamer) δ 20.2 (CH_3), 21.3 (CH_3), 32.1 (CH_3), 37.7 (CH_2), 51.2 (CH_2), 51.5 (CH_3), 109.4 (CH_2), 109.9 (CH), 119.1 (C), 120.7 (CH), 121.9 (CH), 125.5 (CH), 126.4 (C), 126.7 (C), 138.6 (C), 139.9 (C), 162.7 (C), 170.8 (C). Anal. Calcd for $C_{18}H_{22}N_2O_3$: C, 68.77; H, 7.05; N, 8.91. Found: C, 68.41; H, 6.93; N, 8.84.

Methyl 3-(*N*-Allyl-*N*-*tert*-butoxycarbonylaminomethyl)-1-methylindole-2-carboxylate (E14b). Methyl 3-formyl-1-methylindole-2-carboxylate (1.0 g, 4.61 mmol) was allowed to react as above with allylamine (0.69 mL, 9.20 mmol). $(Boc)_2O$ (1.31 g, 5.95 mmol), Et_3N (0.64 mL, 4.61 mmol) and DMAP (0.14 g, 1.14 mmol) were added to the crude amine in anhydrous

CH_2Cl_2 (40 mL). After stirring at rt for 5 h, the reaction mixture was poured into H_2O (25 mL) and washed with 2 N aqueous HCl solution (2 x 25 mL). The solvent was removed and the crude product was chromatographed (95:5 hexanes-AcOEt) to give **E14b** (1.17 g, 71% yield); mp 98-100°C; ^{1}H NMR (300 MHz) δ 1.50 (br s, 9H), 3.63 (br m, 2H), 3.92 (s, 3H), 4.01 (s, 3H), 5.01 (m, 2H), 5.03 (s, 2H), 5.69 (m, 1H), 7.15 (m, 1H), 7.37 (m, 2H), 7.88 (br m,1H); ^{13}C NMR (75.4 MHz) δ 28.4 (CH_3), 32.1 (CH_3), 39.4 and 41.0 (CH_2), 47.2 (CH_2), 51.6 (CH_3), 79.4 (C), 110.0 (CH), 115.2 (CH_2), 119.7 (C), 120.4 (CH), 121.8 (CH), 125.3 (CH), 126.3 (C), 126.5 (C), 134.0 (CH), 138.7 (C), 155.5 (C), 162.9 (C). Anal. Calcd for $C_{20}H_{26}N_2O_4$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.23; H, 7.36; N, 7.76.

2. Preparation of Phenyl Selenoesters

General Procedure. A solution of the respective carboxylic ester (1.0 mmol) and $LiOH·H_2O$ (50 mg, 1.20 mmol) in a 3:1 mixture of THF-H_2O (10 mL) was stirred at 65°C for 5 h. The reaction mixture was concentrated and acidified with aqueous 1 N HCl solution. The precipitated carboxylic acid was collected by filtration. When no solid appeared, the solution was extracted with CH_2Cl_2 (3 x 15 mL), and the combined organic extracts were dried and concentrated. A suspension of the carboxylic acid (1.0 mmol) in anhydrous CH_2Cl_2 (7 mL) was treated with Et_3N (0.27 mL, 2.0 mmol). After 15 min at rt, the mixture was concentrated under reduced pressure to give the respective triethylammonium salt. In another flask, tributylphosphine (1.22 mL, 5.0 mmol) was added under Ar to a solution of PhSeCl (0.96 g, 5.0 mmol) in anhydrous THF (7 mL), and the mixture was stirred at rt for 10 min (yellow solution). The above triethylammonium salt in THF (7 mL) was added to this solution and the resulting mixture was stirred overnight. The reaction mixture was partitioned between Et_2O (25 mL) and H_2O (25 mL) and extracted with Et_2O (3 x 15 mL). The solvent was removed and the crude product was purified. Method of purification, yields, NMR data and elemental analyses are given below.

***Se*-Phenyl 1-Methyl-3-(3-butenyl)indole-2-carboselenoate (1):** flash chromatography (9:1 hexanes-AcOEt); yield 75%; mp 63-5°C; ^{1}H NMR (300 MHz) δ 2.56 (q, J = 6.6 Hz, 2H), 3.36 (m, 2H), 3.86 (s, 3H), 5.05 (dm, J = 10.5 Hz, 1H), 5.17 (dq, J = 1.8, 1.8, 1.8, 17.1 Hz, 1H), 6.01 (m, 1H), 7.16 (m, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.37 (m, 1H), 7.44 (m, 3H), 7.63 (m, 2H), 7.70 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 25.4 (CH_2), 32.3 (CH_3), 35.9 (CH_2), 110.3 (CH), 115.2 (CH_2), 120.2 (CH), 121.1 (CH), 123.5 (C), 126.0 (CH), 126.2 (C), 126.8 (C), 129.1 (CH), 129.4 (CH), 133.3 (C), 136.3 (CH), 137.9 (CH), 138.7 (C), 185.4 (C). Anal. Calcd for $C_{20}H_{19}NOSe.1/2H_2O$: C, 63.66; H, 5.34; N, 3.71. Found: C, 63.77; H, 5.17; N, 3.44.

***Se*-Phenyl 3-[*N*-Allyl-*N*-(methoxycarbonyl)amino]-1-methylindole-2-carboselenoate (4a):**

flash chromatography (8:2 hexanes-AcOEt), oil; yield 68%; ^{1}H NMR (300 MHz) δ 3.71 (br s, 3H), 3.95 (s, 3H), 4.08 (m, 1H), 4.77 (m, 1H), 5.10 (dm, *J* = 10.2 Hz, 1H), 5.14 (dq, *J* = 1.5, 1.5, 1.5, 16.8 Hz, 1H), 6.09 (m, 1H), 7.18 (ddd, *J* = 1.5, 6, 7.8 Hz, 1H), 7.35-7-45 (m, 5H), 7.55-7.65 (m, 3H); ^{13}C NMR (75.4 MHz) δ 32.4 (CH_3), 53.4 (CH_3), 54.7 (CH_2), 110.5 (CH), 119.2 (CH_2), 120.5 (CH), 121.3 (CH), 123.7 (C), 124.4 (C), 125.7 (C), 126.6 (CH), 129.2 (CH), 129.3 (CH), 129.8 (C), 133.0 (CH), 136.5 (CH), 137.2 (C), 156.3 (C), 187.3 (C). Anal. Calcd for $C_{21}H_{20}N_2O_3Se$: C, 59.02; H, 4.72; N, 6.56. Found: C, 58.67; H, 4.79; N, 6.35.

***Se*-Phenyl 3-[*N*-(2-Bromo-2-propenyl)-*N*-(methoxycarbonyl)amino]-1-methylindole-2-carboselenoate (4b):** flash chromatography (9:1 hexanes-AcOEt), oil; yield 60%; ^{1}H NMR (300 MHz) δ 3.76 and 3.95 (2 s, 3H), 3.93 (s, 3H), 4.23 (br d, *J* = 12.9 Hz, 1H), 5.24 (br d, *J* = 14.7 Hz, 1H), 5.49 (d, *J* = 1.8 Hz, 1H), 5.70 (br s, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.37 (m, 2H), 7.45 (m, 3H), 7.60 (m, 2H), 7.80 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 32.3 (CH_3), 53.7 (CH_3), 60.0 (CH_2), 110.4 (CH), 121.1 (CH), 121.3 (CH), 121.7 (CH_2), 123.6 (C), 124.1 (C), 125.3 (C), 126.6 (CH), 128.1 (C), 129.1 (C), 129.3 (CH), 129.4 (CH), 136.4 (CH), 137.0 (C), 156.4 (C), 184.5 (C). Anal. Calcd for $C_{21}H_{19}BrN_2O_3Se$: C, 49.82; H, 3.78; N, 5.53. Found: 49.75; H, 3.86; N, 5.32.

***Se*-Phenyl 1-Methyl-3-(4-pentenyl)indole-2-carboselenoate (7):** flash chromatography (hexanes); yield 77%; mp 60-1°C; ^{1}H NMR (300 MHz) δ 1.92 (m, 2H), 2.27 (q, *J* = 7.2 Hz, 2H), 3.26 (m, 2H), 3.85 (s, 3H), 5.02 (dq, *J* = 2.1, 2.1, 2.1, 10.2 Hz, 1H), 5.09 (dq, *J* = 2.1, 2.1, 2.1, 17.1 Hz, 1H), 5.92 (m, 1H), 7.15 (m, 1H), 7.34 (m, 2H), 7.45 (m, 3H), 7.63 (m, 2H), 7.69 (dt, *J* = 0.9, 0.9, 8.1 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 25.4 (CH_2), 31.0 (CH_2), 32.3 (CH_3), 34.0 (CH_2), 110.3 (CH), 115.0 (CH_2), 120.1 (CH), 121.1 (CH), 124.3 (C), 126.0 (CH), 126.3 (C), 126.8 (C), 129.1 (CH), 129.4 (CH), 133.2 (C), 136.3 (CH), 138.3 (CH), 138.8 (C), 185.4 (C). Anal. Calcd for $C_{21}H_{21}NOSe$: C, 65.97; H, 5.54; N, 3.66. Found: C, 66.08; H, 5.72; N, 3.48.

***Se*-Phenyl 3-[*N*-Acetyl-*N*-(2-cyclohexenyl)aminomethyl]-1-methylindole-2-carboselenoate (9):** flash chromatography (7:3 hexanes-AcOEt); yield 77%; mp 105-7°C; ^{1}H NMR (300 MHz) δ 1.51 (m, 1H), 1.71 (m, 2H), 1.85-2.0 (m, 3H), 2.12 and 2.23 (2 s, 3H), 3.85 and 3.96 (2 s, 3H), 4.31 and 5.27 (2 br m, 1H), [5.00 (d, *J* =18.9 Hz), 5.09 (d, *J* =18.9 Hz), 5.27 (d, *J* =15.3 Hz) and 5.50 (d, *J* =15.3 Hz), 2H], 5.27 and 5.49 (2 m, 1H), 5.63 and 5.79 (2 m, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.35 (m, 2H), 7.47 (m, 3H), 7.62 (m, 2H), [7.74 (d, *J* = 8.1 Hz) and 7.84 (d, *J* = 8.1 Hz), 1H]; ^{13}C NMR (75.4 MHz) δ 21.3 and 21.9 (CH_2), 22.6 and 23.0 (CH_3), 24.2 and 24.6 (CH_2), 27.0 and 28.1 (CH_2), 32.5 and 33.1 (CH_3), 38.1 and 43.8 (CH_2), 52.3 and 55.9 (CH), 110.5 and 111.1 (CH), 119.3 and 119.4 (C), 121.3 and 121.7 (CH), 122.3 and 122.8 (CH), 125.6 and 126.2 (C), 126.1 and 126.3 (CH), 126.7 and 126.8 (C), 128.0 and 128.9 (CH), 129.7 (CH), 129.9 (CH), 130.5 and 132.1 (CH), 133.7 and 135.8 (C), 136.2 and 136.5 (CH), 138.9 and 139.4 (C), 171.5 and 172.2 (C), 186.0 and 187.0 (C). Anal. Calcd for $C_{25}H_{26}N_2O_2Se \cdot 1/2H_2O$: C, 63.29; H,

5.74; N, 5.90. Found: C, 63.43; H, 5.61; N, 5.80.

***Se*-Phenyl 3-[*N*-(3-Butenyl)-*N*-(methoxycarbonyl)amino]-1-methylindole-2-carboselenoate (11):** flash chromatography (8:2 hexanes-AcOEt); yield 71%; mp 143-4°C; ^{1}H NMR (300 MHz) δ 2.47 (m, 2H), 3.52 (m, 1H), 3.71 (s, 3H), 3.96 (s, 3H), 4.26 (m, 1H), 5.06 (m, 2H), 5.78 (m, 1H), 7.21 (ddd, *J* = 1.5, 6.6, 8.1 Hz, 1H), 7.45 (m, 3H), 7.60 (m, 5H); ^{13}C NMR (75.4 MHz) δ 32.4 (CH_3), 32.9 (CH_2), 51.7 (CH_2), 53.4 (CH_3), 110.6 (CH), 116.8 (CH_2), 120.2 (CH), 121.5 (CH), 123.9 (C), 124.5 (C), 125.6 (C), 126.6 (CH), 129.2 (CH), 129.3 (CH), 129.7 (C), 134.7 (CH), 137.2 (C), 136.5 (CH), l.156.3 (C), 184.4 (C). Anal. Calcd for $C_{22}H_{22}N_2O_3Se$: C, 59.87; H, 5.02; N, 6.35. Found: 59.88; H, 4.83; N, 6.22.

***Se*-Phenyl 3-(*N*-Acetyl-*N*-allylaminomethyl)-1-methylindole-2-carboselenoate (14a):** crystallization on standing in the fridge, then washed with hexanes; yield 85%; mp 120-2°C; ^{1}H NMR (300 MHz, major rotamer) δ 2.14 (s, 3H), 3.73 (br s, 2H), 3.87 (s, 3H), 5.13 (m, 2H), 5.32 (s, 2H), 5.70 (m, 1H), 7.19 (m, 1H), 7.38 (m, 2H), 7.47 (m, 3H), 7.61 (m, 2H), 7.86 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75.4 MHz, major rotamer) δ 21.5 (CH_3), 32.1 (CH_3), 38.0 (CH_2), 48.6 (CH_2), 110.1 (CH), 116.4 (CH_2), 117.1 (C), 121.0 (CH), 122.1 (CH), 125.8 (CH), 126.1 (C), 126.4 (C), 129.3 (CH), 129.5 (CH), 132.6 (CH), 135.8 (CH), 136.4 (C), 138.3 (C), 170.7 (C), 187.2 (C). Anal. Calcd for $C_{22}H_{22}N_2O_2Se \cdot 1/2H_2O$: C, 60.83; H, 5.34; N, 6.45. Found: C, 60.83; H, 5.06; N, 6.37.

***Se*-Phenyl 3-(*N*-Allyl-*N*-*tert*-butoxycarbonylaminomethyl)-1-methylindole-2-carboselenoate (14b):** flash chromatography (9:1 hexanes-AcOEt); yield 76%; mp 102-3°C; ^{1}H NMR (300 MHz) δ 1.52 (s, 9H), 3.63 (br s, 2H), 3.86 (s, 3H), 5.03 (m, 2H), 5.16 (s, 2H), 5.69 (m, 1H), 7.17 (m, 1H), 7.36 (m, 2H), 7.46 (m, 3H), 7.60 (m, 2H), 7.88 (br s,1H); ^{13}C NMR (75.4 MHz) δ 28.5 (CH_3), 32.0 (CH_3), 39.6 (CH_2), 47.3 (CH_2), 79.7 (C), 110.1 (CH), 116.1 (CH_2), 117.1 (C), 120.8 (CH), 122.0 (CH), 125.7 (CH), 126.3 (C), 126.5 (C), 129.3 (CH), 129.5 (CH), 133.7 (CH), 135.9 (CH, C), 138.4 (C), 155.5 (C), 187.0 (C). Anal. Calcd for $C_{25}H_{28}N_2O_3Se$: C, 62.11; H, 5.84; N, 5.79. Found: C, 62.13; H, 5.86; N, 5.72.

***Se*-Phenyl 3-[*N*-Acetyl-*N*-(2-bromo-2-propenyl)aminomethyl]-1-methylindole-2-carboselenoate (18):** flash chromatography (8:2 hexanes-AcOEt); yield 85%; mp 93-5°C; ^{1}H NMR (300 MHz, major rotamer) δ 2.18 (s, 3H), 3.87 (s, 3H), 3.93 (s, 2H), 5.36 (s, 2H), 5.60 (m, 1H), 5.67 (m, 1H), 7.18 (ddd, *J* = 1.2, 6.6, 8.1 Hz, 1H), 7.37 (m, 2H), 7.46 (m, 2H), 7.62 (m, 3H), 7.82 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75.4 MHz, major rotamer) δ 21.6 (CH_3), 32.1 (CH_3), 37.8 (CH_2), 53.8 (CH_2), 110.2 (CH), 115.5 (C), 117.4 (CH_2), 121.2 (CH), 121.8 (CH), 125.9 (CH), 126.0 (C), 126.3 (C), 128.3 (C), 129.4 (CH), 129.5 (CH), 135.9 (CH), 136.5 (C), 138.3 (C) 170.8 (C), 187.2 (C). Anal. Calcd for $C_{22}H_{21}BrN_2O_2Se$: C, 52.40; H, 4.20; N, 5.56. Found: C, 52.38; H, 4.16; N, 5.45.

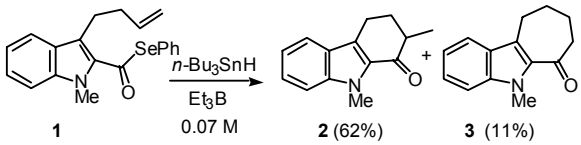
***Se*-Phenyl 3-[*N*-Acetyl-*N*-(2-methyl-2-propenyl)aminomethyl]-1-methylindole-2-**

carboselenoate (19): flash chromatography (75:25 hexanes-AcOEt); yield 72%; mp 109-11 °C; ^{1}H NMR (300 MHz, major rotamer) δ 1.64 (s, 3H), 2.11 (s, 3H), 3.58 (s, 2H), 3.86 (s, 3H), 4.80 (s, 1H), 4.94 (s, 1H), 5.34 (s, 2H), 7.18 (m, 1H), 7.35 (m, 2H), 7.45 (m, 3H), 7.59 (m, 2H), 7.87 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75.4 MHz, major rotamer) δ 20.2 (CH_3), 21.4 (CH_3), 32.0 (CH_3), 38.1 (CH_2), 51.5 (CH_2), 110.0 (CH), 110.5 (CH_2), 116.4 (C), 121.0 (CH), 122.1 (CH), 125.8 (CH), 126.2 (C), 126.4 (C), 129.5 (CH), 129.6 (CH), 135.8 (CH), 136.4 (C), 138.3 (C), 139.8 (C), 171.0 (C), 187.3 (C). Anal. Calcd for $C_{23}H_{24}N_2O_2Se$: C, 62.87; H, 5.51; N, 6.38. Found: C, 62.84; H, 5.30; N, 6.21.

3. Cyclization Reactions

General Procedure. *n*-Bu_3SnH (0.16 mL, 0.60 mmol) and Et_3B (1 M in hexanes, 0.60 mmol) were added to a solution of the respective phenyl selenoester (0.30 mmol, previously dried azeotropically with anhydrous C_6H_6) in anhydrous C_6H_6 (see the hydride concentration below). The reaction mixture was stirred at rt for 2-7 h with constant supply of dry air provided by passing compressed air through a short tube of Drierite. The reaction mixture was concentrated. The residue was eluted with CH_2Cl_2 through a KF/SiO_2 column to remove tin impurities[5] (workup A). Alternatively, the residue was partitioned between hexanes (15 mL) and acetonitrile (15 mL), and the polar layer was washed with hexanes (3 x 15 mL) (workup B). The solvent was removed, and the crude product was chromatographed. Hydride concentration, eluents, yields, NMR data, elemental analyses and HRMS are given below.

From selenoester 1: concn 0.07 M; workup A; 95:5 hexanes-AcOEt



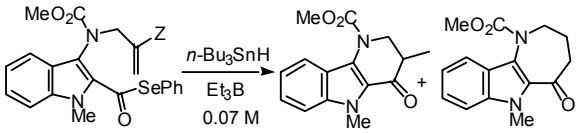
1 **2** (62%) **3** (11%)

2,9-Dimethyl-2,3,4,9-tetrahydrocarbazol-1-one (2): yield 62%; mp 74-5°C; ^{1}H NMR (300 MHz) δ 1.29 (d, J = 7.2 Hz, 3H), 1.98 (m, 1H), 2.30 (dddd, J = 3.9, 4.5, 4.8, 13.2 Hz, 1H), 2.68 (m, 1H), 2.98 (ddd, J = 4.5, 9.6, 16.8 Hz, 1H), 3.11 (ddd, J = 4.5, 4.8, 16.8 Hz, 1H), 4.07 (s, 3H), 7.14 (m, 1H), 7.37 (m, 2H), 7.65 (dt, J = 0.9, 0.9, 8.1 Hz, 1H); ^{13}C NMR (100.6 MHz) δ 15.3 (CH_3), 20.7 (CH_2), 31.5 (CH_3), 32.8 (CH_2), 43.2 (CH), 110.2 (CH), 119.9 (CH), 121.2 (CH), 124.6 (C), 126.4 (CH), 128.5 (C), 130.1 (C), 139.8 (C), 195.2 (C). Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.04; N, 6.57. Found: C, 78.65; H, 7.18; N, 6.35.

5-Methyl-7,8,9,10-tetrahydro-5*H*-cyclohepta[*b*]indol-6-one (3):[6] yield 11%; ^{1}H NMR (300 MHz) δ 1.94 (m, 4H), 2.82 (m, 2H), 3.10 (m, 2H), 4.02 (s, 3H), 7.15 (m, 1H), 7.37 (m, 2H), 7.69 (dt, J = 0.9, 0.9, 8.1 Hz, 1H); ^{13}C NMR (100.6 MHz) δ 21.8 (CH_2), 22.9 (CH_2), 25.3 (CH_2),

31.9 (CH_3), 42.6 (CH_2), 110.2 (CH), 119.8 (CH), 120.8 (CH), 125.9 (C), 126.0 (CH), 126.8 (C), 133.8 (C), 139.1 (C), 196.2 (C).

From selenoesters 4: concn 0.07 M; workup B; 9:1 hexanes-AcOEt.



4a. Z = H
4b. Z = Br

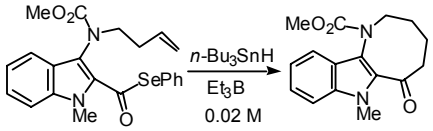
5 (45%)
5 (19%)

6 (29%)
6 (62%)

Methyl 3,5-Dimethyl-4-oxo-2,3,4,5-tetrahydropyrido[3,2-*b*]indole-1-carboxylate (5): yield 45% (from **4a**), 19% (from **4b**); mp 82-4°C; ^{1}H NMR (300 MHz) δ 1.26 (d, *J* = 6.9 Hz, 3H), 2.82 (m, 1H), 3.84 (dd, *J* = 9.3, 13.2 Hz, 1H), 3.90 (s, 3H), 4.05 (s, 3H), 4.39 (dd, *J* = 4.2, 12.9 Hz, 1H), 7.13 (ddd, *J* = 1.2, 6.9, 8.4 Hz, 1H), 7.32 (dt, *J* = 0.9, 0.9, 8.4 Hz, 1H), 7.40 (ddd, *J* = 1.2, 6.6, 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 12.9 (CH_3), 31.3 (CH_3), 42.5 (CH), 53.2 (CH_2), 53.3 (CH_3), 110.2 (CH), 118.7 (C), 120.2 (CH), 121.8 (C), 124.1 (CH), 127.1 (CH), 129.9 (C), 139.0 (C), 154.4 (C), 190.7 (C). Anal. Calcd for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92; N, 10.29. Found: C, 66.20; H, 6.08; N, 10.00.

Methyl 6-Methyl-5-oxo-3,4,5,6-tetrahydro-*2H*-azepino[3,2-*b*]indole-1-carboxylate (6): oil; yield 29% (from **4a**), 62% (from **4b**); ^{1}H NMR (300 MHz, HSQC, HMBC) δ 1.85-2.45 (br m, 2H, H-3), 2.78 (br m, 2H, H-4), 3.10-3.30 (br m, 1H, H-2), 3.74 and 3.90 (2 br s, 3H, OMe), 4.03 (s, 3H, NMe), 4.45-4.70 (br m, 1H, H-2), 7.17 (m, 1H, H-9), 7.39 (m, 2H, H-7,8), [7.52 (d, *J* = 8.1 Hz) and 7.60 (br m), 1H, H-10]; ^{1}H NMR (300 MHz, 50 ºC) δ 2.16 (br m, 2H, H-3), 2.77 (t, *J* = 6.6 Hz, 2H, H-4), 3.40-4.0 (br m, 2H, H-2), 3.76 (br s, 3H, OMe), 4.02 (s, 3H, NMe), 7.16 (m, 1H, H-9), 7.37 (m, 2H; H-7,8), 7.54 (d, *J* = 7.8 Hz, 1H, H-10); ^{13}C NMR (75.4 MHz, HSQC, HMBC) δ 24.4 (C-3), 31.7 (NMe), 40.8 (C-4), 48.2 (C-2), 53.3 (OMe), 110.4 (C-7), 120.7 (C-9), 121.2 (C-10), 121.7 (C-10a), 126.4 (C-8), 127.5 (C-10b), 128.6 (C-5a), 138.1 (C-5b), 155.9 (NCO), 194.0 (C-5). Anal. Calcd for $C_{15}H_{16}N_2O_3 \cdot 3/4\ H_2O$: C, 63.03; H, 6.17; N, 9.80. Found: C, 63.42; H, 5.97; N, 9.49.

From selenoester 11: concn 0.02 M; workup B; 9:1 hexanes-AcOEt.



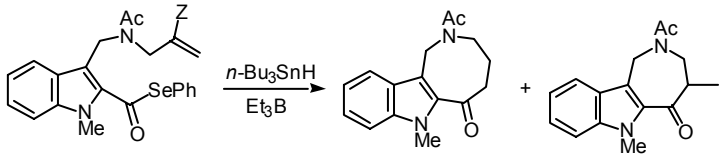
11

12 (54%)

Methyl 7-Methyl-6-oxo-2,3,4,5,6,7-hexahydroazocino[3,2-*b*]indole-1-carboxylate (12): yield 54%; mp 112-4°C; ^{1}H NMR (400 MHz, HSQC, HMBC) δ 1.45-1.85 (br m, 2H, H-4), 1.90 (br m, 2H, H-3), 2.62 and 3.25 (2 br m, 2H, H-5), 3.20 and 4.47 (2 br m, 2H, H-2), 3.66 and 3.90 (2 s, 3H, Me), 4.09 and 4.11 (2 s, 3H, NMe), 7.18 (m, 1H, H-10), 7.42 (m, 2H, H-8,9), 7.46 (d, *J* =

8.1 Hz, 1H, H-11); ^{13}C NMR (100.6 MHz, HSQC, HMBC) δ 23.0 (C-3), 23.8 (C-4), 32.6 (NMe), 40.7 (C-5), 47.6 (C-2), 53.3 (Me), 110.5 (C-8), 120.0 (C-11), 121.0 (C-10), 122.9 (C-11b), 123.2 (C-11a), 126.5 (C-9), 131.0 (C-6a), 138.0 (C-7a), 156.4 (NCO), 194.3 (CO). Anal. Calcd for $C_{16}H_{18}N_2O_3$: C, 67.12; H, 6.34; N, 9.78. Found: C, 66.90; H, 6.37; N, 9.60.

From selenoesters 14a (concn 0.005 M) or **18** (concn 0.02 M); workup B; 3:7 hexanes-AcOEt.

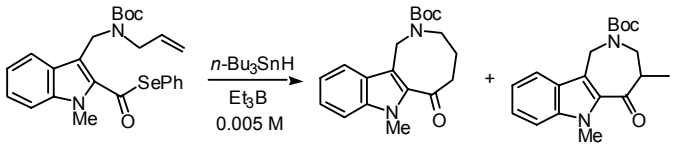


14a Z = H 0.005 M **15a** (55%) **16a** (8%)
18 Z = Br 0.02 M **15a** (75%)

2-Acetyl-7-methyl-1,2,3,4,5,7-hexahydroazocino[4,3-*b*]indol-6-one (15a): oil; yield 55% (from **14a**), 75% (from **18**); ^{1}H NMR (300 MHz, HSQC, HMBC) δ 1.94 and 2.16 (2 s, 3H, Me), 2.01 and 2.11 (2 m, 2H, H-4), 2.91 and 3.02 (2 m, 2H, H-5), [3.53 (t, *J* = 6 Hz) and 3.79 (t, *J* = 6 Hz), 2H, H-3], 3.86 and 4.05 (2 s, 3H, NMe), 4.92 and 5.13 (2 s, 2H, H-1), 7.20 (m, 1H, H-10), 7.40 (m, 2H, H-8,9), [7.61 (d, *J* = 8.1 Hz) and 7.82 (d, *J* = 8.1 Hz), 1H, H-11]; ^{13}C NMR (75.4 MHz, HSQC, HMBC) δ 21.7 and 22.1 (Me), 24.6 and 26.5 (C-4), 31.7 and 32.7 (NMe), 41.0 and 42.2 (C-5), 42.1 and 45.8 (C-1), 45.5 and 46.7 (C-3), 110.2 and 110.5 (C-8), 117.8 and 118.4 (C-11b), 119.3 and 121.0 (C-11), 120.7 and 120.8 (C-10), 124.9 (C-11a), 125.5 and 126.5 (C-9), 133.4 and 134.1 (C-6a), 138.1 and 138.8 (C-6b), 169.9 and 171.0 (NCO), 194.2 and 198.1 (C-6); HRMS $[M+H]^+$ calcd for $C_{16}H_{19}N_2O_2$ 271.1441, found 271.1447.

2-Acetyl-4,6-dimethyl-2,3,4,6-tetrahydro-*1H*-azepino[4,3-*b*]indol-5-one (16a): oil; yield 8% (from **14a**); ^{1}H NMR (300 MHz) δ [1.31 (d, *J* = 6.6 Hz) and 1.34 (d, *J* = 6.9 Hz), 3H, Me], 2.12 and 2.14 (2 s, 3H, MeCO), 3.27 (m, 1H, H-4), [3.47 (dd, *J* = 11.1, 13.2 Hz), 3.66 (dd, *J* = 11.4, 13.5 Hz) and 3.80 (m), 2H, H-3], 3.99 and 4.00 (2 s, 3H, NMe), [4.73 (d, *J* = 16.8 Hz), 4.82 (d, *J* = 17.1 Hz), 5.05 (d, *J* = 16.8 Hz) and 5.59 (d, *J* = 16.8 Hz), 2H, H-1], 7.21 (m, 1H, H-9), 7.35-7.45 (m, 2H, H-7,8), [7.67 (dt, *J* = 1.5, 1.5, 7.8 Hz) and 7.80 (dt, *J* = 1.2, 1.2, 7.8 Hz), 1H, H-10]; HRMS $[M+H]^+$ calcd for $C_{16}H_{19}N_2O_2$ 271.1441, found 271.1449.

From selenoester 14b: concn 0.005 M; workup B; 9:1 hexanes-AcOEt.

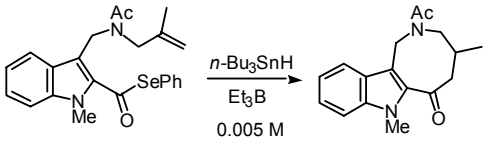


14b **15b** (40%) **16b** (11%)

***tert*-Butyl 7-Methyl-6-oxo-1,3,4,5,6,7-hexahydroazocino[4,3-*b*]indole-2-carboxylate (15b):** oil; yield 40%; ^{1}H NMR (300 MHz) δ 1.22 and 1.47 (2 s, 9H), 2.04 (m, 2H), 2.96 (m, 2H), 3.49 and 3.60 (2 m, 2H), 3.93 and 3.97 (2 s, 3H), 4.87 and 4.97 (2 s, 2H), 7.17 (m, 1H), 7.38 (m, 2H), [7.68 (d, J = 8.1 Hz) and 7.76 (d, J = 7.8 Hz), 1H]; ^{13}C NMR (75.4 MHz) δ 25.5 and 25.9 (CH_2), 28.3 and 28.4 (CH_3), 32.0 and 32.3 (CH_3), 41.6 and 43.2 (CH_2), 41.6 and 43.9 (CH_2), 44.6 and 47.1 (CH_2), 80.0 (C), 110.2 (CH), 118.7 and 122.0 (C), 120.2 and 120.7 (CH), 120.4 and 120.6 (CH), 124.9 (C), 125.6 and 126.9 (CH), 133.5 and 134.0 (C), 138.3 and 138.6 (C), 154.9 and 155.1 (C), 196.2 and 197.3 (C); HRMS $[M+Na]^+$ calcd for $C_{19}H_{24}N_2NaO_3$ 351.1679, found 351.1674.

***tert*-Butyl 4,6-Dimethyl-5-oxo-3,4,5,6-tetrahydro-*1H*-azepino[4,3-*b*]indole-2-carboxylate (16b):** oil; yield 11%; ^{1}H NMR (300 MHz) δ 1.28 (d, J = 6.9 Hz, 3H), 1.38 and 1.46 (2 s, 9H), 3.19 (m, 1H), [3.45 (m) and 3.72 (dd, J = 3.9, 13.8 Hz), 2H], 3.96 and 3.98 (2 s, 3H), [4.72 (d, J = 16.5 Hz), 4.87 (d, J = 17.1 Hz), 5.13 (d, J = 16.8 Hz) and 5.18 (d, J = 16.5 Hz), 2H], 7.19 (m, 1H), 7.40 (m, 2H), 7.65 (m, 1H); ^{13}C NMR (75.4 MHz) δ 14.4 and 14.9 (CH_3), 28.3 and 28.4 (CH_3), 32.1 (CH_3), 42.1 and 42.3 (CH_2), 45.9 and 46.5 (CH), 48.3 and 48.6 (CH_2), 80.2 (C), 110.5 and 110.7 (CH), 120.5 and 120.6 (CH), 120.7 and 121.0 (CH), 122.9 and 123.2 (C), 124.9 (C), 126.4 and 126.5 (CH), 133.2 (C), 139.2 (C), 155.0 (C), 196.4 and 196.9 (C); HRMS $[M+Na]^+$ calcd for $C_{19}H_{24}N_2NaO_3$ 351.1679, found 351.1676.

From selenoester 19: concn 0.005 M; workup B; 4:6 hexanes-AcOEt.



19 **20** (40%)

2-Acetyl-4,7-dimethyl-1,2,3,4,5,7-hexahydroazocino[4,3-*b*]indol-6-one (20): oil; yield 40%; ^{1}H NMR (400 MHz, HSQC, HMBC) δ [1.04 (d, J = 7.2 Hz) and 1.05 (d, J = 6.9 Hz), 3H, Me], 1.96 and 2.17 (2s, 3H, COMe), 2.32 and 2.54 (2 m, 1H, H-4), [2.74 (dd, J = 2.7, 14.4 Hz), 2.90 (m) and 3.07 (dd, J = 4.5, 13.5 Hz), 2H, H-5], [3.18 (dd, J = 9.6, 15.3 Hz), 3.42 (dd, J = 10.8, 13.5 Hz), 3.50 (dd, J = 4.2, 15 Hz), and 3.71 (dd, J = 4.2, 13.8 Hz), 2H, H-3], 3.87 and 4.06 (2 s, 3H, NMe), [4.90 (d, J = 16.8, Hz), 4.95 (d, J = 16.8, Hz), 5.09 (d, J = 15.6 Hz), and 5.20 (d, J = 15.6 Hz), 2H, H-1], 7.20 (m, 1H, H-10), 7.40 (m, 2H, H-8,9), [7.61 (d, J = 8.1 Hz) and 7.79 (d, J = 8.1 Hz), 1H, H-11]; ^{13}C NMR (100.6 MHz, HSQC, HMBC) δ 18.2 and 19.1 (Me), 21.7 and 22.2 (MeCO), 31.0 and 32.6 (C-4), 31.7 and 32.7 (NMe), 41.8 and 46.0 (C-1), 48.0 and 49.9 (C-

5), 50.7 and 52.6 (C-3), 110.3 and 110.6 (C-8), 117.7 and 118.1 (C-11b), 119.3 and 120.8 (C-11), 120.9 and 121.0 (C-10), 124.9 and 126.5 (C-11a), 125.5 and 126.5 (C-9), 134.0 and 134.6 (C-6a), 138.2 and 138.9 (C-6b), 170.2 and 170.9 (NCO), 193.1 and 197.0 (C-6); HRMS $[M+H]^+$ calcd for $C_{17}H_{21}N_2O_2$ 285.1598, found 285.1592.

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4. NMR Data of Aldehydes.

1-Methyl-3-(4-pentenyl)indole-2-carboxaldehyde (8): ^{1}H NMR (300 MHz) δ 1.85 (m, 2H), 2.15 (m, 2H), 3.08 (m, 2H), 4.06 (s, 3H), 5.02 (m, 2H), 5.83 (m, 1H), 7.15 (m, 1H), 7.39 (m, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 10.13 (s, 1H).

3-[*N*-Acetyl-*N*-(2-cyclohexenyl)aminomethyl]-1-methylindole-2-carboxaldehyde (10): ^{1}H NMR (300 MHz) δ 1.50 (m, 2H), 1.69 (m, 2H), 1.92 (m, 2H), 2.11 and 2.23 (2 s, 3H), 4.06 (s, 3H), 4.31 and 5.30 (2 br m, 1H), [4.86 (br s), 5.00 (d, *J* =15.9 Hz), 5.37 (d, *J* =15.6 Hz) and 5.45 (br s), 2H], 5.07 and 5.42 (2 m, 1H), 5.50 and 5.78 (2 m, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.38 (m, 2H), [7.72 (d, *J* = 9 Hz) and 7.86 (d, *J* = 8.4 Hz), 1H], 10.25 (s, 1H).

3-[*N*-(3-Butenyl)-*N*-(methoxycarbonyl)amino]-1-methylindole-2-carboxaldehyde (13): ^{1}H NMR (300 MHz) δ 2.35 (q, *J* = 6.6 Hz, 2H), 3.63 (br s, 3H), 3.79 (m, 2H), 4.09 (s, 3H), 5.04 (m, 2H), 5.74 (m, 1H), 7.20 (m, 1H), 7.42 (m, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 9.95 (s, 1H).

3-(*N*-Acetyl-*N*-allylaminomethyl)-1-methylindole-2-carboxaldehyde (17a): ^{1}H NMR (300 MHz, major rotamer) δ 2.14 (s, 3H), 3.79 (m, 2H), 4.09 (s, 3H), 5.14 (s, 2H), 5.24 (m, 2H), 5.73 (m, 1H), 7.18 (m, 1H), 7.42 (m, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 10.20 (s, 1H).

3-(*N*-Allyl-*N*-*tert*-butoxycarbonylaminomethyl)-1-methylindole-2-carboxaldehyde (17b): ^{1}H NMR (300 MHz) δ 1.45 (s, 9H), 3.64 (br s, 2H), 4.02 (s, 3H), 4.91 (s, 2H), 5.00 (dq, *J* = 1.5, 17.1 Hz, 1H), 5.07 (dm, *J* = 10.2 Hz, 1H), 5.65 (m, 1H), 7.11 (m, 1H), 7.34 (m, 2H), 7.79 (br d, *J* = 6.6 Hz, 1H), 10.13 (s, 1H).

3-[*N*-Acetyl-*N*-(2-methyl-2-propenyl)aminomethyl]-1-methylindole-2-carboxaldehyde (21): ^{1}H NMR (300 MHz) δ 1.69 (s, 3H), 2.12 (s, 3H), 3.66 (s, 2H), 4.09 (s, 3H), 4.83 (s, 1H), 5.00 (s, 1H), 5.13 (s, 2H), 7.18 (m, 1H), 7.41 (m, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 10.17 (s, 1H).