Supporting Information

Intramolecular Reactions of 2-Indolylacyl Radicals: Access to 1,2-Fused Ring Indole Derivatives

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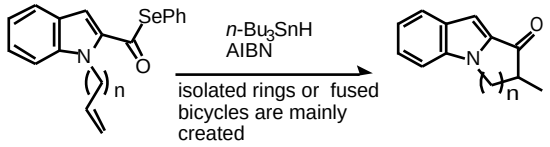
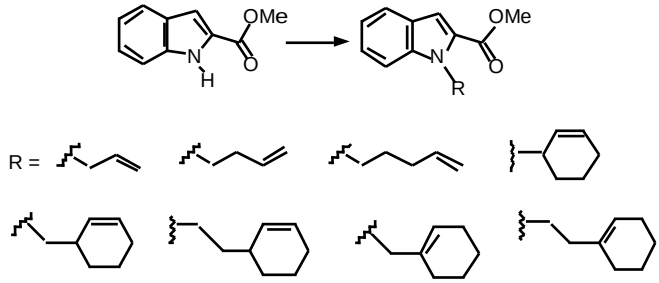


Contents:

A. Methyl 1-Alkyl-2-indolecarboxylates. General Procedure



A solution of methyl 2-indolecarboxylate (1 g, 5.71 mmol) in anhydrous DMF (10 mL) was added dropwise under Ar to a suspension of NaH (6.85 mmol) in anhydrous THF (5 mL). After stirring at rt for 1 h, the mixture was cooled to 0 ºC and the appropriate alkylating agent (see below, 6.85 mmol) was added. The mixture was allowed to warm to rt overnight, then was quenched with cold water and extracted with Et_2O (3 x 40 mL). The organic extracts were washed with H_2O (5 x 100 mL), dried and concentrated to give crude esters, which were purified by flash chromatography (SiO_2). Eluent, yields and NMR data ($CDCl_3$) are given below.

Methyl 1-Allyl-2-indolecarboxylate: alkylating agent, allyl bromide; 80% yield; elution with 2:8 hexanes-AcOEt; ^{1}H NMR (200 MHz) δ 3.86 (s, 3H), 4.86 (dddd, *J* = 1.4, 1.6, 1.6, 17 Hz, 1H), 5.07 (dddd, *J* = 1.4, 1.6, 1.6, 10.2 Hz, 1H), 5.19 (m, 1H), 5.98 (m, 1H), 7.13 (m, 1H), 7.32 (m, 3H), 7.62 (d, *J* = 8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 46.8 (CH_2), 51.7 (CH_3), 110.6 (CH), 110.8 (CH), 116.0 (CH_2), 120.7 (CH), 122.7 (CH), 125.1 (CH), 126.0 (C), 127.0 (C), 133.8 (CH), 139.1 (C), 162.3 (C).

Methyl 1-(3-Butenyl)-2-indolecarboxylate: alkylating agent, 3-butenyl bromide; 40% yield; elution with 3:7 hexanes-AcOEt.

Spectroscopic data of the corresponding carboxylic acid (see below): ^{1}H NMR (200 MHz) δ 2.58 (d, *J* = 7.2 Hz, 2H), 4.60 (t, *J* = 7.2 Hz, 2H), 5.02 (m, 2H), 5.50 (br s, 1H), 5.80 (m, 1H), 7.16 (m, 1H), 7.35 (m, 2H), 7.42 (s, 1H), 7.66 (d, *J* = 8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 34.9 (CH_2), 44.1 (CH_2), 110.5 (CH), 111.9 (CH), 116.9 (CH_2), 120.5 (CH), 122.7 (CH), 125.1 (CH), 125.9 (C), 128.0 (C), 134.8 (CH), 139.2 (C), 167.0 (C).

Methyl 1-(4-Pentenyl)-2-indolecarboxylate: alkylating agent, 4-pentenyl bromide; 45% yield; elution with 9:1 hexanes-CH_2Cl_2; ^{1}H NMR (300 MHz) δ 1.88 (m, 2H), 2.10 (q, *J* = 6.9 Hz, 2H), 3.87 (s, 3H), 4.54 (t, *J* = 7.2 Hz, 2H), 5.0 (m, 2H), 5.82 (m, 1H), 7.12 (m, 1H), 7.28 (s, 1H), 7.32 (m, 2H), 7.65 (d, *J* = 8 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 29.6 (CH_2), 31.1 (CH_2), 44.2 (CH_2), 51.5 (CH_3), 110.4 (CH), 110.6 (CH), 115.2 (CH_2), 120.5 (CH), 122.7 (CH), 124.9 (CH), 126.0 (C), 127.0 (C), 137.6 (CH), 139.0 (C), 162.2 (C).

Methyl 1-(2-Cyclohexenyl)-2-indolecarboxylate: alkylating agent**,** 2-cyclohexenyl bromide; 40% yield; elution with 5:5 hexanes-CH_2Cl_2; ^{1}H NMR (200 MHz) δ 1.8-2.2 (m, 6H), 3.90 (s, 3H), 5.95 (m, 2H), 6.25 (m,1H), 7.12 (m, 1H), 7.28 (m, 3H), 7.68 (d, *J* = 8 Hz, 1H).

Methyl 1-(2-Cyclohexenylmethyl)-2-indolecarboxylate: alkylating agent, (2-cyclohexenyl)methyl methanesulfonate; 45% yield; elution with 9:1 hexanes-AcOEt; ^{1}H NMR (200 MHz) δ 1.4-1.8 (m, 4H), 2.0 (m, 2H), 2.70 (m, 1H), 3.91 (s, 3H), 4.47 (m, 2H), 5.46 (dd, *J* = 2.2, 10.4 Hz, 1H), 5.75 (m, 1H), 7.14 (m, 1H), 7.32 (m, 1H), 7.33 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 20.9 (CH_2), 25.4 (CH_2), 26.8 (CH_2), 37.0 (CH), 49.4 (CH_2), 51.7 (CH_3), 110.9 (CH), 111.0 (CH), 120.4 (CH), 122.6 (CH), 124.8 (CH), 125.8 (C), 127.2 (C), 128.1 (CH), 128.7 (CH), 139.6 (C), 162.4 (C).

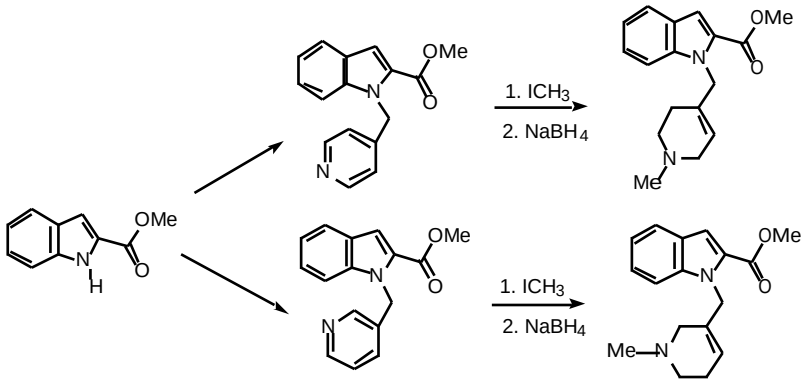
Methyl 1-[2-(2-Cyclohexenyl)ethyl)]-2-indolecarboxylate: alkylating agent, 2-(2-cyclohexenyl)ethyl methanesulfonate; 70% yield; elution with 95:5 hexanes-AcOEt; ^{1}H NMR (200 MHz) δ 1.4-2.0 (m, 8H), 2.10 (m, 1H), 3.88 (s, 3H), 4.59 (t, *J* = 8 Hz, 2H), 5.63 (d, *J* = 12.2 Hz, 1H), 5.72 (m, 1H), 7.12 (m, 1H), 7.30 (m, 2H), 7.35 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 1H);

^{13}C NMR (50.3 MHz) δ 21.5 (CH_2), 25.3 (CH_2), 29.0 (CH_2), 33.4 (CH), 36.7 (CH_2), 42.8 (CH_2), 51.6 (CH_3), 110.3 (CH), 110.6 (CH), 120.5 (CH), 122.7 (CH), 124.9 (CH), 126.0 (C), 126.9 (C), 127.7 (CH), 130.9 (CH), 138.8 (C), 162.3 (C).

Methyl 1-(1-Cyclohexenyl)methyl)-2-indolecarboxylate: alkylating agent, (1-cyclohexenyl)methyl bromide; 75% yield; elution with 8:2 hexanes-CH_2Cl_2; ^{1}H NMR (300 MHz) δ 1.52 (m, 4H), 1.87 (m, 4H), 3.86 (s, 3H), 5.09 (s, 2H), 5.19 (m, 1H), 7.12 (m, 1H), 7.28 (m, 1H), 7.30 (s, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 22.2 (CH_2), 22.4 (CH_2), 24.7 (CH_2), 26.0 (CH_2), 49.9 (CH_2), 51.5 (CH_3), 110.4 (CH), 111.0 (CH), 120.4 (CH), 121.9 (CH), 122.3 (CH), 124.7 (CH), 125.7 (C), 127.3 (C), 133.9 (C), 139.4 (C), 162.2 (C).

Methyl 1-[2-(1-Cyclohexenyl)ethyl)]-2-indolecarboxylate: alkylating agent, 2-(1-cyclohexenyl)ethyl methanesulfonate; 45% yield; elution with 8:2 hexanes-AcOEt. Spectroscopic data of the corresponding carboxylic acid (see below): ^{1}H NMR (200 MHz) δ 1.55 (m, 4H), 1.95 (m, 4H), 2.38 (t, *J* = 7.2 Hz, 2H) 4.65 (t, *J* = 7.2 Hz, 2H), 5.32 (br s,1H), 7.16 (m, 1H), 7.42 (m, 2H), 7.45 (s, 1H), 7.70 (d, *J* = 8 Hz, 1H).

B. Methyl 1-Alkyl-2-indolecarboxylates. Tetrahydropyridine Series



A solution of methyl 2-indolecarboxylate (1.5 g, 8.57 mmol) in anhydrous DMF (20 mL) was added dropwise under Ar to a suspension of NaH (22.3 mmol) in anhydrous THF (10 mL). After stirring at rt for 1 h, the mixture was cooled to 0 ºC and 3 or 4-chloromethylpyridine hydrochloride (1.74 g, 10.3 mmol) was added in portions. The mixture was allowed to warm to rt overnight, then was quenched with cold H_2O and extracted with CH_2Cl_2 (3 x 40 mL). The organic extracts were washed with H_2O (5 x 100 mL), dried and concentrated, and the resulting residue was chromatographed (SiO_2, 1.1 hexanes-AcOEt) to give methyl 1-(pyridylmethyl)-2-indolecarboxylates.

Iodomethane (1 mL, 16.64 mmol) in anhydrous benzene (1 mL) was added to a solution of the above esters (1.10 g, 4.16 mmol) in anhydrous acetone (6 mL). After stirring at rt for 5 h, the precipitated pyidiridinium salts were collected by filtration.

$NaBH_4$ (145 mg, 3.85 mmol) was added in two portions to an ice-cooled suspension of the above pyridinium salts (1.57 g, 3.85 mmol) in EtOH (40 mL). After stirring at rt for 5 h, the solvent was removed and the resulting residue was partitioned between CH_2Cl_2 and saturated aqueous Na_2CO_3, and extracted with CH_2Cl_2. The organic extracts were dried, filtered and concentrated to give the corresponding tetrahydropyridines.

Methyl 1-(1-Methyl-1,2,5,6-tetrahydro-4-pyridylmethyl)-2-indolecarboxylate: 48% overall yield; ^{1}H NMR (200 MHz) δ 2.09 (m, 2H), 2.29 (s, 3H), 2.49 (t, *J* = 5.8 Hz, 2H), 2.82 (m, 2H), 3.88 (s, 3H), 5.10 (m, 1H), 5.15 (s, 2H), 7.14 (m, 1H), 7.33 (m, 2H), 7.31 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 27.1 (CH_2), 45.6 (CH_3), 49.0 (CH_2), 51.6 (CH_2), 51.6 (CH_3), 54.0 (CH_2), 110.7 (CH), 111.0 (CH), 119.7 (CH), 120.6 (CH), 122.4 (CH), 125.0 (CH), 125.7 (C), 127.3 (C), 132.6 (C), 139.4 (C), 162.2 (C).

Methyl 1-(1-Methyl-1,2,5,6-tetrahydro-3-pyridylmethyl)-2-indolecarboxylate: 52% overall yield; ^{1}H NMR (200 MHz) δ 2.10 (m, 2H), 2.31 (s, 3H), 2.43 (t, *J* = 6 Hz, 2H), 2.81 (m, 2H),

3.90 (s, 3H), 5.15 (br s, 2H), 5.24 (m, 1H), 7.14 (m, 1H), 7.32 (s, 1H), 7.35 (m, 2H), 7.68 (d, J = 7.6 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 25.2 (CH_2), 45.4 (CH_3), 47.7 (CH_2), 51.4 (CH_2), 51.6 (CH_3), 54.8 (CH_2), 110.8 (CH), 110.9 (CH), 120.2 (CH), 120.6 (CH), 122.4 (CH), 125.1 (CH), 125.8 (C), 127.1 (C), 132.4 (C), 139.4 (C), 162.2 (C).

C. Hydrolysis to 1-Alkyl-2-indolecarboxylic Acids.

A solution of the corresponding methyl 1-alkyl-2-indolecarboxylate (4 mmol) in a 1:1:1 mixture of aqueous 2N KOH:MeOH:dioxane (15 mL) was refluxed for 2 h. The reaction mixture was concentrated and acidified with aqueous 2N HCl. The precipitated carboxylic acid was collected by filtration.

D. Phenyl Selenoesters 1-6. General Procedure.

A suspension of the above carboxylic acid (4 mmol) in anhydrous CH_2Cl_2 (15 mL) was treated with a solution of Et_3N (4 mmol for selenoesters **1**-**4**; 8 mmol for selenoesters **5** and **6**) in CH_2Cl_2 (5 mL). After stirring at rt for 10 min, the mixture was concentrated to give the corresponding triethylammonium salts.

In another flask, tributylphosphine (6 mmol) was added under Ar to a solution of PhSeCl (6 mmol) in anhydrous THF (15 mL), and the mixture was stirred at rt for 10 min (yellow solution). To this solution, the above triethylammonium salt in THF (15 mL) was added and the resulting mixture was stirred overnight. The reaction mixture was partitioned between Et_2O (40 mL) and H_2O (40 mL) and extracted with Et_2O (3 x 25 mL). The solvent was removed and the crude product was purified by flash chromatography (SiO_2, unless otherwise indicated). Eluents, yields and NMR data ($CDCl_3$) are given below.

***Se*-Phenyl 1-Allyl-2-indolecarboselenoate (1a):** 90% yield; elution with 9:1 hexanes-AcOEt; ^{1}H NMR (200 MHz) δ 4.86 (d, J = 17.2 Hz, 1H), 5.07 (m, 3H) 5.95 (m, 1H), 7.20 (m, 1H), 7.35-7.45 (m, 5H), 7.60 (s, 1H), 7.62 (m, 2H), 7.75 (d, J = 8.2 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 47.1 (CH_2), 110.8 (CH), 112.3 (CH), 116.2 (CH_2), 121.2 (CH), 122.9 (CH), 125.8 (C), 126.0 (C), 126.3 (CH), 129.0 (CH), 129.3 (CH), 133.2 (CH), 134.3 (C), 136.3 (CH), 139.5 (C), 184.4 (C). Anal. Calcd for $C_{18}H_{15}NOSe$: C, 63.26; H, 4.51; N, 4.08. Found: C, 63.20; H, 4.48; N, 4.09.

***Se*-Phenyl 1-(3-Butenyl)-2-indolecarboselenoate (1b):** 75% yield; elution with 9:1 hexanes-AcOEt; ^{1}H NMR (200 MHz) δ 2.45 (q, J = 7.2 Hz, 2H), 4.47 (t, J = 7.2 Hz, 2H), 5.0 (m, 2H), 5.75 (m, 1H), 7.19 (m, 1H), 7.36-7.44 (m, 5H), 7.57 (s, 1H), 7.62 (m, 2H), 7.70 (d, J = 8.2 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 34.8 (CH_2), 44.5 (CH_2), 110.8 (CH), 112.4 (CH), 117.3 (CH_2), 121.1 (CH), 123.0 (CH), 126.0 (C), 126.1 (C), 126.2 (CH), 129.1 (CH), 129.4 (CH), 134.3 (C), 134.5 (CH), 136.4 (CH), 139.5 (C), 184.5 (C). Anal. Calcd for $C_{19}H_{17}NOSe$: C, 64.41; H, 4.84; N, 3.95. Found: C, 64.27; H, 4.50; N, 4.01.

***Se*-Phenyl 1-(4-Pentenyl)-2-indolecarboselenoate (1c):** 65% yield; elution with 9:1 hexanes-AcOEt; ^{1}H NMR (200 MHz) δ 1.86 (m, 2H), 2.05 (m, 2H), 4.43 (t, J = 7.4 Hz, 2H), 5.0 (m, 2H), 5.79 (m, 1H), 7.17 (m, 1H), 7.37-7.45 (m, 5H), 7.59 (s, 1H), 7.64 (m, 2H), 7.74 (d, J = 8.2 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 29.4 (CH_2), 30.8 (CH_2), 44.5 (CH_2), 110.6 (CH), 112.2 (CH), 115.1 (CH_2), 120.9 (CH), 122.9 (CH), 125.9 (C), 126.1 (C), 126.1 (CH), 128.9 (CH), 129.2 (CH), 134.2 (C), 136.3 (CH), 137.4 (CH), 139.4 (C), 184.2 (C). Anal. Calcd for $C_{20}H_{19}NOSe$: C, 65.22; H, 5.20; N, 3.80. Found: C, 65.12; H, 5.03; N, 3.76.

***Se*-Phenyl 1-(2-Cyclohexenyl)-2-indolecarboselenoate (2):** 70% yield; elution with 8:2 hexanes-CH_2Cl_2; ^{1}H NMR (200 MHz) δ 1.6-1.9 (m, 2H), 2.20 (m, 4H), 5.7-6.0 (m, 3H), 7.18 (m, 1H), 7.25 (m, 1H), 7.45 (m, 3H), 7.60-7.75 (m, 5H); ^{13}C NMR (50.3 MHz) δ 22.1 (CH_2), 24.6 (CH_2), 28.9 (CH_2), 53.9 (CH), 112.8 (CH), 114.0 (CH), 120.8 (CH), 123.0 (CH), 125.4 (CH), 126.2 (C), 126.8 (C), 128.9 (CH), 129.1 (CH), 129.4 (CH), 129.7 (CH), 134.3 (C), 136.4 (CH), 139.2 (C), 185.3 (C); HRMS calcd for $C_{21}H_{19}NOSe$ 381.0632, found 381.0625.

***Se*-Phenyl 1-(2-Cyclohexenylmethyl)-2-indolecarboselenoate (3a):** 86% yield; elution with 7:3 hexanes-CH_2Cl_2; ^{1}H NMR (200 MHz) δ 1.2-1.8 (m, 4H), 1.97 (br s, 2H), 2.65 (br s, 1H), 4.33 (m, 2H), 5.38 (d, J = 11.6 Hz, 1H), 5.72 (m, 1H), 7.16 (m, 1H), 7.40 (m, 5H), 7.61 (s, 1H), 7.62 (m, 2H), 7.71 (d, J = 7.8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 20.9 (CH_2), 25.4 (CH_2), 26.7

(CH_2), 36.8 (CH), 49.7 (CH_2), 111.4 (CH), 112.6 (CH), 121.0 (CH), 122.9 (CH), 126.0 (C), 126.1 (C), 126.1 (CH), 128.9 (CH), 129.1 (2 CH), 129.4 (CH), 134.6 (C), 136.4 (CH), 140.1 (C), 184.3 (C); HRMS calcd for $C_{22}H_{21}NOSe$ 395.0788, found 395.0794.

***Se*-Phenyl 1-[2-(2-Cyclohexenyl)ethyl)]-2-indolecarboselenoate (3b):** 65% yield; elution with 7:3 hexanes-CH_2Cl_2; pale yellow solid, mp 79-81 °C; ^{1}H NMR (200 MHz) δ 1.3-2.0 (m, 8H), 2.10 (m, 1H), 4.48 (t, *J* = 7.6 Hz, 2H), 5.56 (dd, *J* = 1.8, 12.4 Hz, 1H), 5.70 (m, 1H), 7.17 (m, 1H), 7.38-7.46 (m, 5H), 7.58 (s, 1H), 7.64 (m, 2H), 7.73 (d, *J* = 8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 21.5 (CH_2), 25.3 (CH_2), 29.0 (CH_2), 33.2 (CH), 36.6 (CH_2), 43.2 (CH_2), 110.6 (CH), 112.3 (CH), 121.0 (CH), 123.1 (CH), 126.2 (2C), 126.2 (CH), 127.7 (CH), 129.1 (CH), 129.4 (CH), 130.8 (CH), 134.4 (C), 136.4 (CH), 139.4 (C), 184.2 (C). Anal. Calcd for $C_{23}H_{23}NOSe$: C, 67.65; H, 5.65; N, 3.43. Found: C, 67.10; H, 5.70; N, 3.27.

***Se*-Phenyl 1-(1-Cyclohexenyl)methyl)-2-indolecarboselenoate (4a):** 76% yield; elution with 8:2 hexanes-CH_2Cl_2; ^{1}H NMR (200 MHz) δ 1.50 (m, 4H), 1.78 (m, 2H), 1.89 (m, 2H). 4.96 (s, 2H), 5.21 (m, 1H), 7.16 (m, 1H), 7.35 (m, 2H), 7.42 (m, 3H), 7.58 (s, 1H), 7.62 (m, 2H), 7.71 (d, *J* = 8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 22.3 (CH_2), 22.4 (CH_2), 24.8 (CH_2), 25.9 (CH_2), 50.5 (CH_2), 111.5 (CH), 112.1 (CH), 121.0 (CH), 122.5 (CH), 122.8 (CH), 126.0 (C), 126.0 (CH), 126.1 (C), 129.0 (CH), 129.3 (CH), 133.6 (C), 134.9 (C), 136.3 (CH), 140.0 (C), 184.3 (C); HRMS calcd for $C_{22}H_{21}NOSe$ 395.0788, found 395.0801.

***Se*-Phenyl 1-[2-(1-Cyclohexenyl)ethyl)]-2-indolecarboselenoate (4b):** 65% yield; elution with 8:2 hexanes-CH_2Cl_2; ^{1}H NMR (200 MHz) δ 1.50 (m, 4H), 1.85 (m, 4H), 2.30 (t, *J* = 7.2 Hz, 2H) 4.51 (t, *J* = 7.2 Hz, 2H), 5.21 (br s,1H), 7.16 (m, 1H), 7.37 (m, 2H), 7.43 (m, 3H), 7.57 (s, 1H), 7.63 (m, 2H), 7.72 (d, *J* = 8 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 22.2 (CH_2), 22.8 (CH_2), 25.3 (CH_2), 28.6 (CH_2), 38.4 (CH_2), 44.0 (CH_2), 110.8 (CH), 112.1 (CH), 120.9 (CH), 122.9 (CH), 123.6 (CH), 126.0 (C), 126.0 (CH), 126.1 (C), 129.0 (CH), 129.3 (CH), 134.1 (C), 134.5 (C), 136.3 (CH), 139.5 (C), 184.1 (C); HRMS calcd for $C_{22}H_{23}NOSe$ 409.0945, found 409.0955.

***Se*-Phenyl 1-(1-Methyl-1,2,5,6-tetrahydro-4-pyridylmethyl)-2-indolecarboselenoate (5):** 34% yield; elution with 8:2 hexanes-AcOEt (Al_2O_3); ^{1}H NMR (200 MHz) δ 2.05 (m, 2H), 2.31 (s, 3H), 2.51 (t, *J* = 5.8 Hz, 2H), 2.87 (m, 2H), 5.02 (s, 2H), 5.09 (m, 1H), 7.17 (m, 1H), 7.34 (m, 2H), 7.44 (m, 3H), 7.60 (s, 1H), 7.62 (m, 2H), 7.72 (d, *J* = 8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 26.6 (CH_2), 45.1 (CH_3), 49.3 (CH_2), 51.3 (CH_2), 53.6 (CH_2), 111.2 (CH), 112.4 (CH), 119.5 (CH), 121.2 (CH), 122.8 (CH), 125.9 (C), 126.3 (CH), 126.3 (C), 129.0 (CH), 129.3 (CH), 132.2 (C), 134.6 (C), 136.3 (CH), 139.9 (C), 184.3 (C); HRMS calcd for $C_{22}H_{22}N_2OSe$ 410.0897, found 410.0905.

***Se*-Phenyl 1-(1-Methyl-1,2,5,6-tetrahydro-3-pyridylmethyl)-2-indolecarboselenoate (6):** 40% yield; elution with 8:2 hexanes-AcOEt (Al_2O_3); ^{1}H NMR (200 MHz) δ 2.24 (m, 2H), 2.44 (s, 3H), 2.64 (t, *J* = 5.6 Hz, 2H), 3.02 (s, 2H), 5.02 (s, 2H), 5.35 (m, 1H), 7.19 (m, 1H), 7.37 (m, 2H), 7.44 (m, 3H), 7.61 (s, 1H), 7.62 (m, 2H), 7.73 (d, *J* = 8 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 23.8 (CH_2), 44.1 (CH_3), 47.6 (CH_2), 50.5 (CH_2), 53.5 (CH_2), 110.8 (CH), 112.3 (CH), 120 .2 (CH), 121.1 (CH), 122.6 (CH), 125.6 (C), 125.7 (C), 126.3 (CH), 128.8 (CH), 129.0 (CH), 130.4 (C), 134.1 (C), 136.0 (CH), 139.7 (C), 184.1 (C); HRMS calcd for $C_{22}H_{22}N_2OSe$ 410.0897, found 410.0901.

E. General Procedure for Cyclization Reactions of Phenyl Selenoesters 1-6.

n-Bu_3SnH (0.52 mmol) in C_6H_6 (2 mL) was added over a period of 1h (syringe pump) to a heated (reflux) solution of selenoesters **1-6** (0.4 mmol) and AIBN (0.04 mmol) in C_6H_6 (4 mL). After additional 2-3 h at reflux, the solution was concentrated and the residue was chromatographed (SiO_2). Yields, eluents and NMR data ($CDCl_3$) are given below.

2,3-Dihydro-2-methyl-1*H*-pyrrolo[1,2-*a*]indol-1-one (7): 84% yield; elution with 7:3 hexanes-AcOEt; mp 100-102 °C; ^{1}H NMR (200 MHz) δ 1.45 (d, *J* = 7.8 Hz, 3H), 3.28 (ddddd, *J* = 4.6, 7.8, 7.8, 7.8, 8.0 Hz, 1H), 3.97 (dd, *J* = 4.6, 11 Hz, 1H), 4.66 (dd, *J* = 8, 11 Hz, 1H), 7.02 (s, 1H), 7.21 (m, 1H), 7.40 (m, 2H), 7.76 (d, *J* = 8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 15.6 (CH_3), 45.5 (CH), 47.9 (CH_2), 99.2 (CH), 110.5 (CH), 121.4 (CH), 124.1 (CH), 125.0 (CH), 132.1 (C), 135.0 (C), 135.1 (C), 196.1 (C); HRMS calcd for $C_{12}H_{11}NO$ 185.0841, found

185.0842. Anal. Calcd for $C_{12}H_{11}NO.1/3H_2O$: C, 75.39; H, 6.15; N, 7.33. Found: C, 75.30; H, 5.90; N, 7.23.

6,7,8,9-Tetrahydro-8-methylpyrido[1,2-*a*]indol-9-one (8): 70% yield; elution with 9:1 hexanes-AcOEt; mp 145-147 °C; ^{1}H NMR (200 MHz) δ 1.35 (d, *J* = 6.8 Hz, 3H), 2.18 (m, 1H), 2.44 (dddd, *J* = 4.1, 4.4, 4.5, 13.8 Hz, 1H), 2.74 (m, 1H), 4.15 (ddd, *J* = 4.1, 10.6, 12.5 Hz, 1H), 4.41 (ddd, *J* = 4.4, 4.5, 12.5 Hz, 1H), 7.16 (m, 1H), 7.30 (s, 1H), 7.36 (m, 2H), 7.72 (d, *J* = 8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 14.9 (CH_3), 31.1 (CH_2), 40.9 (CH_2), 41.1 (CH), 105.6 (CH), 110.2 (CH), 121.0 (CH), 123.3 (CH), 125.4 (CH), 126.9 (C), 133.4 (C), 137.1 (C), 192.8 (C); Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 77.93; H, 6.69; N, 6.96.

***cis*-2,3,4,4a,11,11a-Hexahydro-1*H*-indolo[1,2-*a*]indol-11-one (13)**: 70% yield; elution with 9:1 hexanes-AcOEt; mp 93-94 °C; ^{1}H NMR (300 MHz) δ 1.2-1.8 (m, 6H), 2.40 (m, 2H), 3.29 (ddd, *J* = 3.2, 6.8, 7.2 Hz, 1H), 4.91 (ddd, *J* = 7.2, 7.2, 8.1 Hz, 1H), 7.00 (d, *J* = 0.8 Hz, 1H), 7.17 (ddd, *J* = 0.8, 6.8, 8 Hz, 1H), 7.35 (ddd, *J* = 1.2, 6.8, 8.4 Hz, 1H), 7.47 (dd, *J* = 0.8, 8.4 Hz, 1H), 7.77 (dd, *J* = 1.2, 8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 20.6 (CH_2), 21.5 (CH_2), 22.4 (CH_2), 30.2 (CH_2), 51.0 (CH), 53.1 (CH), 99.1 (CH), 111.0 (CH), 121.2 (CH), 124.3 (CH), 124.8 (CH), 132.0 (C), 134.8 (C), 135.0 (C), 195.1 (C); Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.21. Found: C, 79.92; H, 6.75; N, 6.30.

***cis*-6,6a,7,8,9,10,10a,11-Octahydroisoquinolino[2,3-*a*]indol-11-one (14)**: 70% yield; elution with 6:4 hexanes-AcOEt; mp 98-100 °C; ^{1}H NMR (400 MHz) δ 1.45-1.70 (m, 7H), 2.37 (m, 1H), 2.59 (m, 1H), 2.83 (q, *J* = 4.8 Hz, 1H), 4.21 (dd, *J* = 4.8, 12.4 Hz, 1H), 4.25 (dd, *J* = 4.8, 12.4 Hz, 1H), 7.15 (m, 1H), 7.31 (s, 1H), 7.37 (m, 2H), 7.72 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 22.9 (CH_2), 24.3 (CH_2), 25.2 (CH_2), 27.9 (CH_2), 36.1 (CH), 45.4 (CH_2), 46.9 (CH), 105,4 (CH), 110.2 (CH), 120.9 (CH), 123.2 (CH), 125.3 (CH), 126.9 (C), 133.0 (C), 137.3 (C), 192.2 (C). This compound was quantitatively converted into **16** (see below) by treatment with MeONa (2 equivalents) in MeOH.

Spiro Compound (15): 10% yield; elution with 1:1 hexanes-CH_2Cl_2; ^{1}H NMR (200 MHz) δ 1.35-1.90 (m, 10H), 4.28 (s, 2H), 7.02 (d, *J* = 0.6 Hz, 1H), 7.18 (m, 1H), 7.37 (m, 1H), 7.44 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 23.1 (CH_2), 25.0 (CH_2), 33.0 (CH_2), 54.8 (C), 51.4 (CH_2), 99.4 (CH), 110.4 (CH), 121.3 (CH), 124.1 (CH), 124.9 (CH), 132.1 (C), 134.9 (C), 135.1 (C), 198.3 (C); HRMS calcd for $C_{16}H_{17}NO$ 239.1310, found 239.1312.

***trans*-6,6a,7,8,9,10,10a,11-Octahydroisoquinolino[2,3-*a*]indol-11-one (16)**: 75% yield; obtained directly from the crude by trituration with hexanes; mp 180-182 °C; ^{1}H NMR (300 MHz) δ 1.35 (m, 4H), 1.87 (m, 1H), 2.0 (m, 2H), 2.20 (m, 1H), 2.28 (ddd, *J* = 4, 12, 12 Hz, 1H), 2.51 (d, *J* = 13.2 Hz, 1H), 3.78 (dd, *J* = 4.5, 12 Hz, 1H), 4.38 (dd, *J* = 11.7, 12 Hz, 1H), 7.16 (m, 1H), 7.28 (s, 1H), 7.36 (m, 2H), 7.72 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 25.1 (CH_2), 25.2 (CH_2), 25.5 (CH_2), 30.8 (CH_2), 39.5 (CH), 47.6 (CH_2), 50.4 (CH), 105,2 (CH), 110.1 (CH), 120.9 (CH), 123.3 (CH), 125.3 (CH), 126.7 (C), 133.4 (C), 137.0 (C), 191.8 (C); Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.05; H, 7.17; N, 5.85.

Spiro Compound (17): 27% yield; elution with 95:4:1 CH_2Cl_2-MeOH-DEA; ^{1}H NMR (300 MHz) δ 1.33 (m, 1H), 1.72 (m, 2H), 2.17 (m, 3H), 2,38 (s, 3H), 3.02 (m, 2H), 4.27 (s, 2H), 7.03 (d, *J* = 0.6, 1H), 7.19 (m, 1H), 7.37 (m, 1H), 7.43 (m, 1H), 7.77 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 32.9 (CH_2), 46.3 (CH_3), 51.3 (CH_2), 51.9 (C), 52.4 (CH_2), 99.7 (CH), 110.4 (CH), 121.4 (CH), 124.1 (CH), 125.1 (CH), 132.1 (C), 134.7 (C), 135.1 (C), 197.1 (C); HRMS calcd for $C_{16}H_{18}N_2O$ 254.1419, found 254.1460.

***trans*-1,2,3,4,4a,5,12,12a-Octahydro-2-methylpyrido[3',4':4,5]pyrido[1,2-*a*]indol-12-one (18)**: 25% yield; elution with 95:4:1 CH_2Cl_2-MeOH-DEA; ^{1}H NMR (300 MHz) δ 1.81 (dddd, *J* = 3.9, 12.3, 12.3, 12.3 Hz, 1H), 1.92 (m, 1H), 1.95 (m, 1H), 2.01 (dd, *J* = 11.7, 12.3 Hz, 1H), 2.17 (ddddd, *J* = 3.9, 4.5, 10.8, 12, 12.3 Hz, 1H), 2.42 (s, 3H), 2.69 (ddd, *J* = 3.9, 10.8, 12.3 Hz, 1H), 3.01 (dddd, *J* = 1.2, 1.8, 1.8, 11.7 Hz, 1H), 3.59 (ddd, *J* = 1.2, 3.9, 12.3 Hz, 1H), 3.83 (t, *J* = 12 Hz, 1H), 4.45 (dd, *J* = 4.5, 12 Hz, 1H), 7.16 (ddd, *J* = 1.8, 6, 8.1 Hz, 1H), 7.31 (s, 1H), 7.36 (m, 2H), 7.73 (ddd, *J* = 0.9, 1.2, 7.8 Hz, 1H); ^{13}C NMR (50.3 MHz) δ 29.6 (CH_2), 37.5 (CH), 46.4 (CH_3), 47.1 (CH_2), 49.0 (CH), 54.5 (CH_2), 54.6 (CH_2), 105,6 (CH), 110.1 (CH), 121.1 (CH), 123.4 (CH), 125.6 (CH), 126.6 (C), 130.3 (C), 137.0 (C), 189.6 (C); HRMS calcd for $C_{16}H_{18}N_2O$ 254.1419, found 254.1424.

Spiro Compound (19): 30% yield; elution with 95:5 CH_2Cl_2-MeOH; ^{1}H NMR (400 MHz) δ 1.80 (m, 4H), 2.05 (m, 1H), 2.30 (m, 1H), 2.32 (br s, 3H), 2.75 (m, 1H), 2.95 (m, 1H), 4.26 (d, *J* = 11.4 Hz, 1H), 4.65 (br s 1H), 6.97 (s, 1H), 7.12 (ddd, *J* = 1.2, 6.8, 8 Hz, 1H), 7.31 (ddd, *J* = 0.8, 6.8, 8.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8 Hz, 1H); ^{13}C NMR (100.6 MHz) δ 22.8 (CH_2), 30.6 (CH_2), 46.6 (CH_3), 51.5 (CH_2), 55.08 (C), 55.14 (CH_2), 61.7 (CH_2), 99.6 (CH), 110.6 (CH), 121.4 (CH), 124.1 (CH), 125.2 (CH), 132.1 (C), 134.8 (C), 135.2 (C), 196.0 (C). **19.HCl**; mp 166-168 °C; ^{1}H NMR (DMSO-d_6, 200 MHz) δ 1.8-2.0 (m, 4H), 2.73 and 2.76 (2s, 3H), 3.03 (m, 1H), 3.16 (t, *J* = 10.6 Hz, 1H), 3.38 (m, 1H), 3.64 (d, *J* = 12.6 Hz, 1H), 4.47 (d, *J* = 11.8 Hz, 1H), 4.89 (d, *J* = 11.8 Hz, 1H), 7.11 (d, *J* = 0.8 Hz, 1H), 7.19 (ddd, *J* = 1, 6.8, 8 Hz, 1H), 7.41 (ddd, *J* = 1.2, 6.8, 8.2 Hz, 1H), 7.53 (dd, *J* = 0.8, 8.2 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 10.57 (br s, 1H); Anal. Calcd for $C_{16}H_{18}N_2O$.HCl.1/2H_2O: C, 64.32; H, 6.41; N, 9.38. Found: C, 64.12; H, 6.53; N, 9.44.

***trans*-1,2,3,4,4a,5,12,12a-Octahydro-2-methylpyrido[4',3':4,5]pyrido[1,2-*a*]indol-5-one (20)**: 35% yield; elution with 95:4:1 CH_2Cl_2-MeOH-DEA; mp 155-157 °C; ^{1}H NMR (300 MHz) δ 1.71 (dddd, *J* = 4.2, 11.4, 11.4, 12.6 Hz, 1H), 2.05 (dd, *J* = 10.8, 11.4 Hz, 1H), 2.08 (ddd, *J* = 2.4, 11.4, 11.4 Hz, 1H), 2.26 (ddd, *J* = 3.9, 11.1, 11.4 Hz, 1H), 2.38 (s, 3H), 2.43 (m, 1H), 2.54 (ddddd, *J* = 3.9, 4.8, 11.1, 11.4, 11.7 Hz, 1H), 3.09 (m, 1H), 3.13 (m, 1H), 3.80 (t, *J* = 11.7 Hz, 1H), 4.39 (dd, *J* = 4.8, 11.7 Hz, 1H), 7.17 (ddd, *J* = 1.5, 6.3, 8.1 Hz, 1H), 7.31 (s, 1H), 7.35 (m, 2H), 7.73 (ddd, *J* = 0.9, 1.2, 8.1 Hz, 1H); ^{13}C NMR (75.4 MHz) δ 24.9 (CH_2), 38.4 (CH), 45.0 (CH_2), 46.2 (CH_3), 48.2 (CH), 55.5 (CH_2), 59.0 (CH_2), 105,6 (CH), 110.1 (CH), 121.1 (CH), 123.4 (CH), 125.6 (CH), 126.8 (C), 133.2 (C), 137.1 (C), 190.4 (C). Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.27; H, 7.15; N, 10.80.

F. Cyclization-Intermolecular Addition Cascade Reaction from Phenyl Selenoester 1a.

n-Bu_3SnH (0.1 mL, 0.38 mmol) in C_6H_6 (2 mL) was added over a period of 1h (syringe pump) to a heated (reflux) solution of selenoester **1a** (0.1 g, 0.29 mmol), methyl acrylate (0.13 mL, 1.45 mmol) and AIBN (5 mg, 0.03 mmol) in C_6H_6 (29 mL). After additional 2 h at reflux, the solution was concentrated and the residue was chromatographed (SiO_2, 8:2 hexanes-AcOEt) to give **12** (35 mg, 45%) and **7** (11 mg, 20%).

Methyl 4-[2,3-Dihydro-1-oxo-1*H*-pyrrolo[1,2-*a*]indole]-2-butanoate (12): mp 75-77 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.79 (m, 2H), 2.10 (m, 2H), 2.40 (t, *J* = 7 Hz, 2H), 3.24 (m, 1H), 3.68 (s, 3H), 4.12 (dd, *J* = 4.2, 11 Hz, 1H),), 4.65 (dd, *J* = 8, 11 Hz, 1H), 7.01 (s, 1H), 7.19 (m, 1H), 7.40 (m, 2H), 7.76 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.5 (CH_2), 30.3 (CH_2), 33.7 (CH_2), 46.0 (CH_2), 50.5 (CH), 51.7 (CH_3), 99.3 (CH), 110.5 (CH), 121.4 (CH), 124.1 (CH), 125.1 (CH), 132.1 (C), 135.1 (C), 135.2 (C), 173.5 (C), 195.0 (C). Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.58; H, 6.30; N, 5.14.