Tandem Overmann Rearrangement and Intramolecular Amidomercuration Reaction. Stereocontrolled Synthesis of *cis* and *trans* 2,6-Dialkylpiperidines

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Supporting Information

General: Melting points were recorded on MEL-TEMP melting point apparatus in open capillaries and are uncorrected. NMR (^1H & ^{13}C) spectra were recorded on Advance Varian-500 at 500 MHz instrument using residual solvent as internal standard. TLC was performed with silica gel GF₂₅₄ precoated aluminum plates and spots were visualized with UV and/ or staining with KMnO_4 .

THF was distilled from benzophenone and sodium metal while CH_2Cl_2 from CaH_2 . All other solvents and reagents were of reagent grade and were used without further purification.

***trans* 2,7-Octadienal:** To a suspension of PCC (15 mmol) and celite (10.0 g) in CH_2Cl_2 (50 mL) was added a mixture of *cis* and *trans* 2,7-octadienol (1.26 g, 10 mmol) drop wise with stirring. The resulting suspension was further stirred for 1 hr. After the disappearance of alcohol (TLC), ether (100 mL) was added, solution was filtered and residue was washed with ether (100 mL). The combined filtrates were concentrated under reduced pressure to afford brown oily mass which was dissolved in ether and passed through a small pad of silica gel to furnish *trans* 2,7-octadienal in almost quantitative yield (1.2 g). $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 9.54 (d, 1H, $J = 7.5$ Hz), 6.84 (dt, 1H), $J = 7.0$ & 16.0 Hz), 6.12 (ddt, 1H, $J = 1.5, 7.5$ & 16.0 Hz), 5.80 (m, 1H), 4.98 (m, 2H), 2.37 (m, 2H), 2.06 (m, 2H), 1.60 (m, 2H).

***trans* 2,7-Octadienol:** To a cooled solution of aldehyde (1.24 g; 10 mmol) at -78°C in ether (50 mL) was added DIBAL-H (12 mL; 12 mmol, 1 M solution in hexane) drop wise with constant stirring during 10 min. The mixture was further stirred for 25 min at -78°C and then slowly brought to room temperature. Methanol (10 mL) was added and mixture was further stirred for 1.5 hr. Saturated solution of potassium sodium tartarate was added and mixture was stirred till layers separate. The organic layer was separated and aqueous layer was further extracted with ether (2x50 mL) and combined organic phase was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to afford *trans* 2,7-octadienol (1.1 g, 90%), $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.82-5.73 (m, 1H), 5.69-5.58 (m, 2H), 5.00-4.92 (m, 2H), 4.05 (d, 2H, $J = 5.0$ Hz), 2.06-2.02 (m, 4H), 1.49-1.43 (m, 2H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 138.48, 132.62, 129.15, 114.49, 63.41, 33.08, 31.47, 28.20

2,7-Octadiene trichloroacetimidate (1): A mixture of *trans* 2,7-octadienol (1.26 g; 1 mmol) and DBU (300 mg; 20 mol%) in dry CH₂Cl₂ was cooled to 0°C and trichloroacetonitrile (2.16 g; 1.5 mmol) was added drop wise for 15 min. The reaction mixture was slowly brought to room temperature. After stirring for 2 hrs at room temperature, the reaction mixture was concentrated under reduced pressure and residue was dissolved in hexane which was purified by column chromatography on silica gel (Devisil, pH 7.0) using 5% ethyl acetate: hexane as eluent to afford pure 2,7-octadiene trichloroacetimidate (**1**) 2.43 g (yield 90%) as colorless oil. ¹H-NMR (500 MHz, CDCl₃): δ 8.23 (brs, 1H), 5.92-5.70 (m, 2H), 5.67-5.58 (m, 1H), 5.04-4.95 (m, 2H), 4.72 (d, 2H, *J* = 7.0 Hz), 2.16-2.04 (m, 4H), 152-1.46 (m, 2H); ¹³C-NMR (125 MHz, CDCl₃): 162.44, 138.33, 136.46, 123.31, 114.67, 91.48, 69.79, 33.03, 31.57, 27.94.

Overmann rearrangement of 2,7-Octadiene trichloroacetimidate with different mercury(II) salts: To a solution of 2,7-octadiene trichloroacetimidate (135 mg; 0.5 mmol) in dry THF (10 mL) was added mercury(II) salt (0.6 mmol) slowly with constant stirring. After disappearance of starting material, the reaction mixture was quenched with saturated KBr solution (3 mL) and mixture was stirred for 1 hr. The solution was extracted with CHCl₃ and organic layer was washed with water and dried. The solvent was distilled off and residue was triturated with hexane to yield a solid material which was characterized by ¹H-NMR.

***trans* (N-Trichloroacetyl-6-vinylpiperidin-2-yl)methylmercuric bromide:** $^1\text{H-NMR}$ (500 MHz, CD_3NO_2): δ 6.11 (ddd, 1H, $J = 7.0, 11.0$ & 17.0 Hz), 5.54 (dd, 1H, $J = 1.5$ & 17.0 Hz), 5.52 (dd, 1H, $J = 1.5$ & 11.0 Hz), 4.40 (m 1H), 4.14-4.08 (m, 1H), 2.47 (d, 2H, $J = 7.0$ Hz), 2.22-2.16 (m, 1H), 2.08-2.00 (m, 1H), 1.99-1.93 (m, 1H), 1.90-1.81 (m, 3H).

1-(2-Trichloromethyl-4,5dihydrooxazol-4-yl)-hex-5-enylmercuric bromide: The compound was obtained as thick oil, yield 70%; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 5.81-5.73 (m, 1H), 5.04-4.98 (m, 2H), 4.89-4.85 (m, 1H), 4.67 (t, 1H, $J = 9.5$ Hz), 4.39 (dd, 1H, $J = 7.0$ & 9.5 Hz), 3.09 (dt, 1H, $J = 4.0$ & 11.0 Hz), 2.18-2.09 (m, 2H), 1.96-1.89 (m, 1H), 1.78-1.53 (m, 3H).

Demercuration of (N-Trichloroacetyl-6-vinylpiperidin-2-yl)methylmercuric bromide with sodium amalgam: Synthesis of *trans*-N-Benzoyloxycarbonyl-6-methyl-2-vinylpiperidine (4): To a solution of (N-trichloroacetyl-6-vinyl-piperidin-2-yl)methylmercuric bromide (385 mg; 0.7 mmol) in THF-water (9:1; 30 mL) was added sodium-amalgam (10%, 2 g) and reaction mixture was stirred at room temperature for 40 hrs. To the above mixture benzyl chloroformate (0.5 mL) was added drop wise and mixture was further stirred for 3 hrs. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with water (2 x 25 mL). The organic layer was dried over anhydrous sodium sulfate and solvent was distilled off under reduced pressure. The residue was purified by flash chromatography over silica gel using ethyl acetate: hexane

(04:96) as eluent to give 3-benzyloxycarbonylamino-1,7-octadiene (36 mg; 20%) and *trans*-*N*-benzyloxycarbonyl-6-methyl-2-vinylpiperidine (127 mg; 70%); $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.39-7.27 (m, 5H), 5.91 (ddd, 1H, $J = 5.0, 10.0$ & 17.0 Hz), 5.20-5.04 (m, 4H), 4.52-4.48 (m, 1H), 4.18-4.10 (m, 1H), 2.04-1.88 (m, 2H), 1.86-1.76 (m, 1H), 1.72-1.60 (m, 2H), 1.57-1.48 (m, 1H), 1.28 (d, 3H, $J = 6.5$ Hz); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 155.82, 140.04, 137.02, 128.32, 127.73, 127.71, 113.73, 66.64, 53.33, 47.55, 26.34, 25.36, 20.55, 13.66 ; EI-MS (m/z): 260 ($M+1$, 10%), 259 (M^+ , 10%), 244 (11), 200 (36), 168 (45), 124 (15), 91 (100).

***trans* 2-Ethyl-6-methylpiperidine hydrochloride:** To a solution of *trans*-*N*-benzyloxycarbonyl-6-methyl-2-vinylpiperidine (52 mg; 0.2 mmol) in MeOH (10 mL) was added Pd/C (20 mg; 10%) and mixture was hydrogenated using H_2 balloon. After completion of reaction (12 hrs), the mixture was filtered through celite and washed with MeOH (10 mL). Hydrochloric acid (1N, 1 mL) was added to the combined methanol solution and concentrated under reduced pressure to yield *trans* 2-ethyl-6-methylpiperidine hydrochloride (32 mg, 98%) as white solid. $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 9.20 (br m, 2H), 3.50 (m, 1H), 3.16 (m, 1H), 2.00-1.88 (m, 3H), 1.74-1.67 (m, 1H), 1.63-1.54 (m, 4H), 1.42 (d, 3H, $J = 6.5$ Hz), 0.94 (t, 3H, $J = 6.5$ Hz); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 53.07, 47.96, 28.79, 25.64, 23.82, 17.23, 16.77, 10.22

3-Trichloroacetylamino-1,7-octadiene: A solution of 2,7-octadiene trichloroacetimidate (2.70 g, 10 mmol) in xylene (10 mL) was heated under reflux for 8 hrs. After the

disappearance of starting material on TLC, the reaction mixture was concentrated under reduced pressure and residue was purified over silica gel using ethyl acetate hexane (5: 95) as eluent to afford 3-trichloroacetyl-amino-1,7-octadiene (2.3 g; 85%) as an oil. ^1H -NMR (500 MHz, CDCl_3): δ 6.62 (d, 1H, $J = 6.5$ Hz), 5.81-5.70 (m, 2H), 5.23-5.15 (m, 2H), 5.01-4.93 (m, 2H), 4.41-4.36 (m, 1H), 2.09-2.04 (m, 2H), 1.70-1.56 (m, 2H), 1.48-1.41 (m, 2H); ^{13}C -NMR (125 MHz, CDCl_3): δ 161.07, 137.82, 136.49, 116.03, 115.06, 92.72, 53.42, 33.63, 33.08, 24.71.

3-Amino-1,7-octadiene hydrochloride: To solution of 3-trichloroacetyl-amino-1,7-octadiene (2.70 g; 10 mmol) in MeOH (20 mL) was added sodium hydroxide (2N, 10 mL) and resultant mixture was stirred at room temperature for 6 hrs. After completion of the reaction (TLC), the mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (3x50 mL). The organic layer was washed with water (10 mL) and dried over anhydrous sodium sulfate. Concentrated HCl (2 mL) was added to the CH_2Cl_2 extract and concentrated under reduced pressure to provide 3-amino-1,7-octadiene hydrochloride as white solid (1.60 g; 98%); ^1H -NMR (500 MHz, CDCl_3): δ 8.44 (brs, 3H), 5.88-5.81 (m, 1H), 5.77-5.69 (m, 1H), 5.42 (d, 1H, $J = 17.0$ Hz), 5.33 (d, 1H, $J = 9.5$ Hz), 5.00-4.92 (m, 2H), 3.69 (m, 1H), 2.08-2.00 (m, 2H), 1.91-1.83 (m, 1H), 1.76-1.67 (m 1H), 1.47-1.42 (m, 2H); ^{13}C -NMR (125 MHz, CDCl_3): δ 137.55, 133.33, 120.75, 115.16, 54.44, 33.89, 32.31, 24.48

3-Benzyloxycarbonylamino-1,7-octadiene: To solution of 3-amino-1,7-octadiene hydrochloride (1.2 g; 7.34 mmol) in CH_2Cl_2 (50 mL) was added saturated aqueous

potassium carbonate (5 mL) and stirred. To the above mixture benzyl chloroformate (1.8 mL) was added drop wise and mixture was further stirred for 2 hrs. After completion of reaction, the reaction mixture was diluted with CH₂Cl₂ (50mL) and washed with water (2x25 mL). The organic layer was dried and solvent was distilled off under reduced pressure to furnish 3-benzyloxycarbonylamino-1,7-octadiene, which was purified by column chromatography over silica gel using ethyl acetate hexane (05: 95) as eluent as pure product as an colorless oil (1.82 g; 96%); ¹H-NMR (500 MHz, CDCl₃): δ 7.38-7.29 (m, 5H), 5.70-5.82 (m, 2H), 4.97-5.18 (m, 6H), 4.52 (brs, 1H), 4.08-4.10 (m, 1H), 2.02-2.10 (m, 2H), 1.40-1.58 (m, 4H), ¹³C-NMR (125 MHz, CDCl₃): δ 155.69, 138.51, 138.20, 136.47, 128.40, 127.98, 114.75, 114.63, 66.58, 53.15, 34.38, 33.28, 24.81.

Cyclization of 3-Bezyloxycarbonylamino-1,7-octadiene with Mercury(II) trifluoroacetate in nitromethane: Synthesis of *cis*-(*N*-Benzyloxycarbonyl-2-vinylpiperidin-6-yl)methylmercuric bromide: To a solution of 3-benzyloxycarbonylamino-1,7-octadiene (259 mg; 1 mmol) in nitromethane (25 mL) was added mercury(II) trifluoroacetate (512 mg; 1.2 mmol) at room temperature and reaction mixture was further stirred at room temperature for 2 hrs. The reaction mixture was quenched by the addition of saturated potassium bromide solution (3 mL) and further stirred for 1 hr. Water (50 mL) was added and mixture was extracted with ethyl acetate (2x50 mL). The combined organic phase was washed with water (2x25 mL) and dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure and residue was purified by flash chromatography over silica gel using ethyl acetate: hexane (05:95) as eluent to yield 3-benzyloxycarbonylamino-1,7-octadiene (52 mg; 20%) and *cis*-(*N*-benzyloxycarbonyl-2-vinylpiperidin-6-yl)methylmercuric bromide (375 mg; 75%); ¹H-NMR (500 MHz, CDCl₃): δ 7.40-7.29 (m, 5H), 5.95 (ddd, 1H, *J* = 6.0, 10.5 & 16.5 Hz), 5.25 (d, 1H, *J* = 12.0 Hz), 5.17-5.10 (m, 3H), 4.81-4.78 (m, 1H), 4.6-4.55 (m, 1H), 2.30

(dd, 1H, $J = 11.0$ & 12.0 Hz), 1.92-1.88 (m, 2H), 1.82-1.73 (m, 2H), 1.68-1.61 (m, 2 H), 1.54-1.40 (m, 1H); ^{13}C -NMR (125 MHz, CDCl_3): δ 155.42, 139.57, 136.23, 128.40, 128.16, 127.97, 116.05, 67.45, 51.44, 50.65, 40.08, 32.03, 27.24, 13.92.

Cyclization of 3-Benzylloxycarbonylamino-1,7-octadiene with Mercury(II) trifluoroacetate in THF: Synthesis of *cis*- and *trans*-(*N*-Benzylloxycarbonyl-2-vinylpiperidin-6-yl)methylmercuric bromide (7:3): To a solution of 3-benzylloxycarbonylamino-1,7-octadiene (259 mg; 1 mmol) in THF (35 mL) was added mercury(II) trifluoroacetate (512 mg; 1.2 mmol) at room temperature and reaction mixture was further stirred at room temperature for 5 hrs. The reaction mixture was worked up as above and mixture was purified to afford 3-benzylloxycarbonylamino-1,7-octadiene (51 mg; 20%) and an inseparable mixture of *cis*- and *trans*-(*N*-benzylloxycarbonyl-2-vinylpiperidin-6-yl)methylmercuric bromide (375 mg; 70%) in ratio of 7:3; ^1H -NMR (500 MHz, CDCl_3): δ 7.40-7.29 (m, 5H), 5.99-5.90* (m, 1H), 5.90-5.82** (m, 1H), 5.26-5.05 (m, 4), 4.79* (brs, 1H), 4.58* (m, 1H), 4.49** (brs, 1H), 4.31** (m, 1H), 2.30* (t, 1H, $J = 11.0$ Hz), 2.18** (t, 1H, $J = 11.0$ Hz), 2.12-1.95 (m, 1H), 1.94-1.84 (m, 2H), 1.82-1.47 (m, 4 H).

Demercuration of (*N*-Benzylloxycarbonyl-2-vinylpiperidin-6-yl)methylmercuric bromide with sodium-amalgam: Synthesis of *cis* *N*-Benzylloxycarbonyl-6-methyl-2-vinylpiperidine (11): To a solution of *cis* (*N*-benzylloxycarbonyl-6-vinylpiperidin-2-yl)methylmercuric bromide (300 mg; 0.56 mmol) in THF-water (9:1; 30 mL) was added sodium-amalgam (10%, 2 g) and reaction mixture was stirred at room temperature for 24 hrs. Water (30 mL) was added and reaction mixture was extracted with ethyl acetate (2x35 mL). The combined organic phase was washed with water and dried over

The NMR signals of *cis* isomer are presented with *, *trans* isomer with ** while the signals due to both isomers are without any asterisk.

anhydrous sodium sulfate. The solvent was distilled off under reduced pressure and residue was purified by flash chromatography over silica gel using ethyl acetate hexane (05:95) as eluent to afford *cis* *N*-benzyloxycarbonyl-6-methyl-2-vinylpiperidine as colorless oil (129 mg; 89%); $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.39-7.29 (m, 5H), 5.98-5.90 (m, 1H), 5.13-5.07 (m, 2H), 5.15 (s, 2H), 4.81-4.77 (m, 1H), 4.46-4.40 (m, 1H), 1.93-1.87 (m, 1H), 1.76-1.61 (m, 3H), 1.57-1.52 (m, 1H), 1.50-1.44 (m, 1H), 1.19 (d, 3H, $J = 6.5\text{Hz}$); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 155.72, 139.87, 136.93, 128.23, 127.73, 127.67, 114.77, 66.83, 51.69, 46.50, 30.04, 27.80, 20.32, 14.18; EI-MS (m/z): 260 ($M+1$, 5%), 259 (M^+ , 5%), 244 (8), 200 (37), 168 (63), 124 (20), 91 (100).

***cis* 2-Ethyl-6-methylpiperidine hydrochloride:** To a solution of *cis*-*N*-benzyloxycarbonyl-6-methyl-2-vinylpiperidine (39 mg; 0.15 mmol) in MeOH (10 mL) was added Pd/C (15 mg; 10%) and mixture was hydrogenated under atmosphere of hydrogen using balloon. After completion of reaction (12 hrs), the mixture was filtered through celite and washed with MeOH (10 mL). Hydrochloric acid (1N, 1 mL) was added to the combined methanol solution and concentrated under reduced pressure to afford *cis* 2-ethyl-6-methylpiperidine hydrochloride (24 mg, 98%) as white solid. $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 9.24 (br s, 1H), 8.89 (br s, 1H), 3.04 (m, 1H), 2.83-2.76 (m, 1H), 2.13-2.06 (m, 1H), 1.91-1.82 (m, 2H), 1.77-1.68 (m, 3H), 1.59-1.50 (m, 1H), 1.48 (d, 3H, $J = 6.5\text{ Hz}$), 1.43-1.35 (m, 1H). 0.90 (t, 3H, $J = 6.5\text{ Hz}$); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 59.49, 54.44, 30.35, 26.72, 26.14, 22.67, 19.18 and 9.89.

***trans* N-Benzoyloxycarbonyl-6-methyl-2-(undec-1-enyl)piperidine (E:Z* = 9:1):** To a solution of *trans*-N-benzyloxycarbonyl-6-methyl-2-vinylpiperidine (52 mg; 0.2 mmol) in CH₂Cl₂ (1 mL) was added 1-undecene (45 mg; 0.3 mmol) and 2nd generation Grubbs catalyst (17 mg, 0.002 mmol) under nitrogen atmosphere. The reaction mixture was heated on an oil bath at 40-45°C for 4 hrs. After 4 hrs, another lot of 1-undecene (45 mg) was further added and mixture was again heated for 4 hrs. The solvent was distilled under reduced pressure and residue was purified by flash chromatography over silica gel using ethyl acetate hexane (04:96) as eluent to furnish *trans* N-benzyloxycarbonyl-6-methyl-2-(undec-1-enyl)piperidine (62 mg; 80%) as a mixture of E:Z (9:1). ¹H-NMR (500 MHz, CDCl₃): δ 7.38-7.28 (m, 5H), 5.51-5.41 (m, 2H), 5.17 (d, 1H, *J* = 12.5 Hz), 5.10 (d, 1H, *J* = 12.5 Hz), 4.49-4.47 (m, 1H), 4.12-4.07 (m, 1H), 2.01-1.91 (m, 4H), 1.78-1.73 (m, 1H), 1.68-1.61 (m, 2H), 1.53-1.47 (m, 1H), 1.33-1.26 (m, 17H), 0.88 (t, 3H, *J* = 6.5 Hz); ¹³C-NMR (125 MHz, CDCl₃): δ 155.77, 137.13, 131.25, 130.35, 128.29, 127.72, 127.65, 66.53, 52.66, 47.47, 32.22, 31.86, 29.52, 29.43, 29.28, 29.25, 29.13, 26.40, 25.65, 22.65, 20.68, 14.07, 13.66.

Solenopsin A hydrochloride (*trans* 6-Methyl-2-undecanypiperidine hydrochloride):

To a solution of *trans* N-benzyloxycarbonyl-6-methyl-2-(undec-1-enyl)piperidine (58 mg; 0.15 mmol) in MeOH (10 mL) was added Pd/C (15 mg; 10%) and mixture was hydrogenated under atmospheric pressure of hydrogen. After completion of reaction (12 hrs), the mixture was filtered through celite and washed with MeOH (10 mL). Hydrochloric acid (1N, 1 mL) was added to the combined methanol solution and concentrated under reduced pressure to yield *trans* 6-methyl-2-undecylpiperidine hydrochloride (Solenopsin A hydrochloride; 42 mg, 97%) as white solid; mp 152-53°C; ¹H-NMR (500 MHz, CDCl₃): δ 9.30 (brm, 2H), 3.51 (m, 1H), 3.25 (m, 1H), 1.95 (m, 3H), 1.73-1.54 (m, 5H), 1.45 (d, 3H, *J* = 6.5 Hz), 1.22 (s, 18H), 0.85 (t, 3H, *J* = 6.5 Hz);

^{13}C -NMR (125 MHz, CDCl_3): δ 51.68, 47.87, 31.81, 30.68, 29.54, 29.40, 29.43, , 29.26, 28.81 26.10, 25.78, 22.60, 17.29, 16.80, 14.03.

***cis* N-Benzyloxycarbonyl-6-methyl-2-(undec-1-enyl)piperidine (E:Z= 10:1):** *cis* N-Benzyloxycarbonyl-6-methyl-2-(undec-1-enyl)piperidine was synthesized from *cis*-N-benzyloxycarbonyl-6-methyl-2-vinylpiperidine (52 mg, 0.2 mmol) and 1-undecene 2nd generation Grubbs' catalyst (17 mg, 0.02 mmol) as described above. Yield 65 mg (85%), ^1H -NMR (500 MHz, CDCl_3): δ 7.37-7.28 (m, 5H), 5.53 (brs, 2H), 5.16 (d, 1H, J = 11.0 Hz), 5.12 (d, 1H, J = 11.0Hz), 4.76 (m, 1H), 4.40 (m, 1H), 1.98 (m 2H), 1.85-1.80 (m, 1H), 1.78-1.71 (m, 1H), 1.68-1.1.59 (m, 2H), 1.57-1.1.51 (m, 1H), 1.49-1.41 (m, 1H), 1.37-1.24 (m, H), 1.18 (d, 3H, J = 6.5 Hz), 0.88 (t, 3H, J = 7.0 Hz); ^{13}C -NMR (125 MHz, CDCl_3): δ 155.72, 137.08, 131.22, 131.14, 128.32, 127.69, 127.67, 66.74, 51.18, 46.42, 32.38, 31.86, 30.12, 29.54, 29.44, 29.28, 29.14, 29.14, 28.61, 22.64, 20.48, 14.24, 14.08.

Isosolenopsin A hydrochloride (*cis* 6-Methyl-2-undecanylpiperidine hydrochloride): Isosolenopsin A hydrochloride was synthesized from *cis* N-benzyloxycarbonyl-6-methyl-2-(undec-1-enyl)piperidine (58 mg; 0.15 mmol) and Pd/C (15 mg; 10%) as described for solenopsin A. Yield 42 mg (97%), mp 152-53°C; ^1H -NMR (500 MHz, CDCl_3): δ 9.40 (brs, 1H), 9.01 (brs, 1H), 3.07 (m, 1H), 2.89 (m, 1H), 2.13 (m, 1H), 1.96-1.88 (m, 2H), 1.77 (m 3H), 1.64-1.52 (m, 4H), 1.47-1.32 (m, 2H), 1.22 (s, 17H), 0.86 (t, 3H, J = 6.5 Hz); ^{13}C -NMR (125 MHz, CDCl_3): δ 58.60, 54.49, 33.23, 31.85, 30.72, 29.58, 29.51, 29.34, 29.29, 27.45, 25.67, 22.85, 22.63, 19.48, 14.07.

2,7-Octadiene trichloroacetimidate

2,7-Octadiene trichloroacetimidate

1-(2-Trichloromethyl-4,5-dihydrooxazol-4-yl)-hex-5-enylmercuric bromide

trans-N-Benzyloxycarbonyl-6-methyl-2-vinylpiperidine

trans-N-Benzyloxycarbonyl-6-methyl-2-vinylpiperidine

trans 2-Ethyl-6-methylpiperidine Hydrochloride

trans 2-Ethyl-6-methylpiperidine Hydrochloride

3-Trichloroacetylamino-1,7-octadiene

3-Trichloroacetylamino-1,7-octadiene

3-Benzyloxycarbonylamino-1,7-octadiene

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3-Benzyloxycarbonylamino-1,7-octadiene

cis-(N-Benzyloxycarbonyl-2-vinylpiperidin-6-yl)methylmercuric bromide

cis-(N-Benzyloxycarbonyl-2-vinylpiperidin-6-yl)methylmercuric bromide

Mixture of cis and trans-(N-Benzoyloxycarbonyl-2-vinylpiperidin-6-yl)methylmercuric bromide

cis N-Benzyloxycarbonyl-6-methyl-2-vinylpiperidine

cis N-Benzyloxycarbonyl-6-methyl-2-vinylpiperidine

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cis 2-Ethyl-6-methylpiperidine Hydrochloride

cis 2-Ethyl-6-methylpiperidine Hydrochloride

trans N-Benzoyloxycarbonyl-6-methyl-2-(undec-1-enyl)piperidine

trans N-Benzoyloxycarbonyl-6-methyl-2-(undec-1-enyl)piperidine

Solenopsin A Hydrochloride

Solenopsin A Hydrochloride

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cis N-Benzoyloxycarbonyl-6-methyl-2-(undec-1-enyl)piperidine

cis N-Benzyloxycarbonyl-6-methyl-2-(undec-1-enyl)piperidine

Isosolenopsin A Hydrochloride

Isosolenopsin A Hydrochloride