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# Diastereoselective Synthesis of Enantiopure Morpholines by Electrophilic Selenium-Induced 6-*exo* Cyclizations on Chiral 3-Allyl-2-hydroxymethylperhydro-1,3-benzoxazine Derivatives.

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General Methods: All reactions were carried out in anhydrous solvents, under argon atmosphere, and in oven-dried glassware. <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) were registered in CDCl<sub>3</sub> as solvent and chemical shifts are given relative to TMS as internal reference. Specific rotations were determined on a digital polarimeter using a Na lamp and concentration is given in g per 100 mL. Melting points were determined in open capillary tubes and are uncorrected. Solvents were dried by standard methods. TLC was performed on glass-backed plates coated with silica gel 60 with F254 indicator; the chromatograms were visualized under UV light and/or by staining with a Ce/Mo reagent. Flash chromatography was carried out on silica gel 60 (230-240 mesh).

Compounds  $\mathbf{2}$ , <sup>31</sup>  $\mathbf{3a}$ , <sup>23c</sup>  $\mathbf{3b}$ , <sup>31</sup>  $\mathbf{3c}$ , <sup>23b</sup>  $\mathbf{3e}$ , <sup>31</sup>  $\mathbf{4g}^{33}$  and  $\mathbf{4h}^{31}$  have been previously described.

General Procedure for Selenocyclization Reactions. Method A. To a stirred solution of PhSeCl (0.46 g, 2.4 mmol) in anhydrous  $CH_2Cl_2$  (15 mL) cooled to -78 °C, a solution of SnCl<sub>4</sub> in  $CH_2Cl_2$  ( 2.4 mL of 1.0 M solution, Aldrich) was added dropwise under nitrogen atmosphere. The mixture was stirred for 20 min, and then it was added dropwise to a solution of the appropriate alcohol **4a-h** (2.0 mmol) in  $CH_2Cl_2$  (5 mL) cooled to -78 °C. Stirring was continued for 2 h at -78 °C and then the mixture was treated with a 10 % aqueous solution of NaOH (30 mL). The layers were separated and the aqueous was extracted with  $CH_2Cl_2$  (3 x 20 mL). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, concentrated at reduced pressure, and the residue was purified by flash chromatography on silica gel, using hexanes-ethyl acetate as eluent.

**Method B**. To a mixture of the appropriate alcohol **4a-h** (2.0 mmol), solid anhydrous  $K_2CO_3$  (415 mg, 3 mmol) and  $CH_2Cl_2$  (10 mL) at 0 °C was slowly added a solution of of PhSeCl (0.46 g, 2.4 mmol) in  $CH_2Cl_2$  (12 mL). The stirring was continued for 5 h at 0

°C and then a 10 % aqueous solution of NaOH (30 ml) was added and the products were isolated as described in the method A.

**Method C**. To a mixture of the appropriate alcohol **4a-h** (2.0 mmol), anhydrous THF (10 mL) and MeOH (0.5 mL) cooled to -78 °C, a solution of PhSeCl in THF (10 mL) was added dropwise under nitrogen atmosphere. The mixture was stirred for 8 h at -78 °C and then treated with a 10 % aqueous solution of NaOH (30 mL). The THF was evaporated *in vacuo* and the remained aqueous phase was extracted with  $CH_2Cl_2$  and the products isolated as described for methods A and B.

General Method for Elimination of the Menthol Appendage. A solution of the appropriate aminomenthol derivative (1.2 mmol) and PCC (1.3 g, 6.0 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and 3 Å molecular sieves (2.5 g) was stirred under a nitrogen atmosphere until the oxidation was finished (TLC 5-9 h). The mixture was then treated with a 10 % aqueous solution of NaOH (50 mL) and extracted with CHCl<sub>3</sub> (5 x 20 mL). The organic phase was washed with brine, dried over anhydrous MgSO<sub>4</sub> and the solvent were removed under reduced pressure. The residue was redisolved in THF (16 mL) and MeOH (8 ml), an aqueous solution of KOH 2.5M (8 mL) was added, and the mixture stirred at room temperature for 4 h. After elimination of the THF and MeOH under reduced pressure, the residue was acidified with a 1 M solution of HCl to pH 1 and extracted twice with Et<sub>2</sub>O (2 x 20 mL). The aqueous solution was neutralized to pH 12 with a 10% aqueous solution of NaOH and extracted with CHCl<sub>3</sub> (4 x 20 mL). The organic layer was washed with H<sub>2</sub>O, dried over MgSO<sub>4</sub>, and the solvent eliminated under vacuum. The morpholine obtained in this way was characterized as N-tosyl derivative that was obtained pure by treatment with an excess of tosyl chloride and diisopropylethylamine in ethyl acetate for 50 h, elimination of the solvent under vacuum and cromatography on silica gel using hexanes/EtOAc as eluent.

[(2S,4aS,7R,8aR)-3-(Cyclohex-1-en-1-ylmethyl)-4,4,7-trimethyl-**Synthesis** of octahydro-2H-benzo[e][1,3]oxazin-2-yl](phenyl)methanone (3d). A mixture of benzoxazine 2 (3.0 g, 14.1 mmol), potassium carbonate (3.9 g, 28.0 mmol) and 1-(bromomethyl)cyclohexene<sup>39</sup> (2.7 g, 15.5 mmol) in acetonitrile (8 mL) was heated in an oil bath at 80-90 °C until the reaction was complete (TLC, 60 h). The reaction mixture was diluted with ethyl acetate, and the solid was separated by filtration and washed with hot ethyl acetate (3 x 25 mL). The solvents were evaporated under vacuum and the residue was purified by flash chromatography on silica gel with hexanes/ethyl acetate 1:20 as eluent. Yield: 81%. Colorless solid. Mp: 95-96 °C (from ethanol).  $\left[\alpha\right]_{D}^{25} = -25.3$  $(c = 1.0, CHCl_3)$ . <sup>1</sup>H-NMR ( $\delta$ ): 0.93-1.10 (m, 6H); 0.94 (d, 3H, J = 6.5 Hz); 1.20 (s, 3H); 1.21 (m, 1H); 1.38 (s, 3H); 1.47-1.54 (m, 4H); 1.63-1.74 (m, 4H); 1.98 (m, 1H); 3.01 (d, 1H, J = 16.0 Hz); 3.30 (d, 1H, J = 16.0 Hz); 3.58 (td, 1H,  $J_1 = 10.5$  Hz,  $J_2 = 4.1$ Hz); 5.17 (m, 1H); 5.68 (s, 1H); 7.28-7.55 (m, 3H); 8.12-8.15 (m, 2H). <sup>13</sup>C-NMR (δ): 19.1 (CH<sub>3</sub>); 21.9 (2 CH<sub>2</sub>); 22.1 (CH<sub>3</sub>); 24.9 (2 CH<sub>2</sub>); 25.9 (CH<sub>2</sub>); 27.0 (CH<sub>3</sub>); 31.2 (CH); 34.8 (CH<sub>2</sub>); 41.1 (CH<sub>2</sub>); 46.8 (CH); 49.4 (CH<sub>2</sub>); 57.6 (C); 75.9 (CH); 88.3 (CH); 125.8 (CH); 127.6 (2 CH); 129.1 (2 CH); 132.4 (CH); 134.7 (C); 135.3 (C); 194.5 (C=O). IR (Nujol dispersion): 3050; 1690; 1600; 800; 760; 700 cm<sup>-1</sup>. Anal. Calcd. for C<sub>25</sub>H<sub>35</sub>NO<sub>2</sub>: C, 78.70; H, 9.25; N, 3.67. Found: C, 78.84; H, 9.12; N, 3.78.

Reduction of ketones 3a-e with NaBH<sub>4</sub>. General Procedure. To a solution of the corresponding ketone 3a-e (10.0 mmol) in ethanol (60 mL) cooled at -10 °C, NaBH<sub>4</sub> (200 mg, 5.2 mmol) was added with magnetic stirring. After 2 h stirring, additional NaBH<sub>4</sub> (100 mg) was added and the mixture was further stirred for 3 h at 0 °C. Then 150 mL of H<sub>2</sub>O was added, and the mixture was stirred for 1 h at room temperature. The

ethanol was removed under vacuum and the remaining water was extracted with ethyl acetate (4 x 35 mL). The combined organic layers were washed with brine, dried over  $MgSO_4$ , concentrated at reduced pressure and the resulting residue was purified by flash chromatography on silica gel using hexanes-ethyl acetate 45:1 as eluent and/or recristallyzation.

(S)-[(2S,4aS,7R,8aR)-3-Allyl-4,4,7-trimethyl-octahydro-2*H*-benzo[*e*][1,3]oxazin-2yl](phenyl)methanol (4a). Yield: 93%. Colorless oil.  $[\alpha]_{D}^{25} = -64.2$  (c = 2.5, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.84-1.07 (m, 3H); 0.86 (d, 3H, *J* = 6.5 Hz); 1.19 (s, 3H); 1.29 (s, 3H); 1.35 (m, 1H); 1.46 (m,1H); 1.57 (m, 1H); 1.61-1.77 (m, 2H); 3.12 (s, 1H); 3.24 (td, 1H, *J*<sub>1</sub> = 10.6 Hz, *J*<sub>2</sub> = 4.0 Hz); 3.38 (ddt, 1H, *J*<sub>1</sub> = 17.9 Hz, *J*<sub>2</sub> = 4.7 Hz, *J*<sub>3</sub> = 1.7 Hz); 3.63 (ddt, 1H, *J*<sub>1</sub> = 17.9 Hz, *J*<sub>2</sub> = 6.1 Hz, *J*<sub>3</sub> = 1.7 Hz); 4.53 (s, 2H); 5.08 (dq, 1H, *J*<sub>1</sub> = 10.2 Hz, *J*<sub>2</sub> = 1.7 Hz); 5.28 (dq, 1H, *J*<sub>1</sub> = 17.2 Hz, *J*<sub>2</sub> = 1.7 Hz); 6.04 (m, 1H); 7.21-7.32 (m, 3H); 7.41-7.49 (m, 2H). <sup>13</sup>C-NMR ( $\delta$ ): 22.2 (CH<sub>3</sub>); 22.6 (CH<sub>3</sub>); 25.0 (CH<sub>2</sub>); 26.9 (CH<sub>3</sub>); 31.3 (CH); 35.1 (CH<sub>2</sub>); 41.0 (CH<sub>2</sub>); 44.5 (CH<sub>2</sub>); 45.1 (CH); 57.6 (CH); 71.7 (CH); 77.1 (CH); 90.5 (CH); 114.6 (CH<sub>2</sub>); 127.2 (2 CH); 127.4 (CH); 127.8 (2 CH); 140.5 (CH); 141.1 (C). IR (Nujol dispersion): 3500 (broad); 3030;1630; 1590; 750; 720; 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>21</sub>H<sub>31</sub>NO<sub>2</sub>: C, 76.55; H, 9.48; N, 4.25. Found: C, 76.43; H, 9.61; N, 4,12.

### (S)-[(2S,4aS,7R,8aR)-3-((E)-But-2-enyl)-4,4,7-trimethyl-octahydro-2H-1,3-

**benzo**[*e*][1,3]oxazin-2-yl](phenyl)methanol (4b). Yield: 90 % .Colorless oil.  $[\alpha]_D^{25} = -$ 87.5 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.84-1.08 (m, 3H); 0.89 (d, 3H, *J* = 6.5 Hz); 1.20 (s, 3H); 1.21 (s, 3H); 1.31 (m, 1H); 1.42 (m, 1H); 1.55 (m, 1H); 1.59-1.76 (m, 2H); 1.70 (d, 3H, *J* = 4.6 Hz); 3.09-3.40 (m, 3H); 3.58 (dd, 1H, *J*<sub>1</sub> = 16.5 Hz, *J*<sub>2</sub> = 5.2 Hz); 4.50 (d, 1H, *J* = 8.5 Hz); 4.55 (d, 1H, *J* = 8.5 Hz); 5.58-5.67 (m, 2H); 7.17-7.30 (m, 3H); 7.47-7.49 (m, 2H). <sup>13</sup>C-NMR ( $\delta$ ): 17.8 (CH<sub>3</sub>); 22.2 (CH<sub>3</sub>); 22.6 (CH<sub>3</sub>); 24.9 (CH<sub>2</sub>); 27.0

(CH<sub>3</sub>); 31.3 (CH); 35.1 (CH<sub>2</sub>); 41.0 (CH<sub>2</sub>); 43.6 (CH<sub>2</sub>); 45.1 (CH); 57.4 (C); 71.6 (CH); 77.0 (CH); 90.6 (CH); 125.4 (CH); 127.1 (2 CH); 127.3 (CH); 127.7 (2 CH); 133.1 (CH); 141.2 (C). IR (Film): 3450 (broad); 3020; 1590; 750; 720; 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>22</sub>H<sub>33</sub>NO<sub>2</sub>: C, 76.92; H, 9.68; N, 4.08. Found: C, 77.02; H, 9.79; N, 4.16.

#### (S)-[(2S,4aS,7R,8aR)-3-(2-methylallyl)-4,4,7-trimethyl-octahydro-2H-1,3-

**benzo**[*e*][1,3]oxazin-2-yl](phenyl)methanol (4c). Yield: 92 % .Colorless solid. Mp: 94-95 °C (from ethanol). [α]<sub>D</sub><sup>25</sup> = -57.9 (c = 1.2, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (δ) : 0.84-1.09 (m, 3H); 0.85 (d, 3H, J = 6.5 Hz); 1.13 (s, 3H); 1.27 (s, 3H); 1.30-1.48 (m, 2H); 1.58 (m, 1H); 1.61-1.75 (m, 2H); 1.77 (s, 3H); 3.05 (s, 1H); 3.21 (d, 1H, J = 19.1 Hz); 3.28 (td, 1H,  $J_1 = 10.5$  Hz,  $J_2 = 4.0$  Hz); 3.53 (d, 1H, J = 19.1 Hz); 4.07 (d, 1H, J = 7.1 Hz); 4.12 (d, 1H, J = 7.1 Hz); 4.95 (s, 1H); 5.31 (s, 1H); 7.20-7.36 (m, 3H); 7.43-7.46 (m, 2H). <sup>13</sup>C-NMR (δ) : 20.9 (CH<sub>3</sub>); 22.1 (CH<sub>3</sub>); 22.5 (CH<sub>3</sub>); 24.9 (CH<sub>2</sub>); 26.0 (CH<sub>3</sub>); 31.3 (CH); 35.1 (CH<sub>2</sub>); 41.0 (CH<sub>2</sub>); 45.2 (CH); 47.2 (CH<sub>2</sub>); 47.3 (C); 72.5 (CH); 77.0 (CH); 90.6 (CH); 109.8 (CH<sub>2</sub>); 127.1 (2 CH); 127.3 (CH); 127.7 (2 CH); 141.1 (C); 147.7 (C). IR (Nujol dispersion): 3500; 3080; 3020; 1610; 760; 720; 700 cm-1. Anal. Calcd. for C<sub>22</sub>H<sub>33</sub>NO<sub>2</sub>: C, 76.92; H, 9.68; N, 4.08. Found: C, 76.81; H, 9.74; N, 4.19.

(S)-[(2S,4aS,7R,8aR)-3-(Cyclohex-1-en-1-ylmethyl)-4,4,7-trimethyl-octahydro-2*H*-1,3-benzo[*e*][1,3]oxazin-2-yl](phenyl)methanol (4d). Yield: 89 % .Colorless oil.  $[\alpha]_{D}^{25}$ = -31.1 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.84-1.06 (m, 3H); 0.85 (d, 3H, *J* = 6.5 Hz); 1.14 (s, 3H); 1.26 (s, 3H); 1.27-1.47 (m, 2H); 1.51-1.72 (m, 7H); 1.95-2.08 (m, 4H); 3.09 (s, 1H); 3.15 (d, 1H, *J* = 18.4 Hz); 3.28 (td, 1H, *J*<sub>1</sub> = 10.5 Hz, *J*<sub>2</sub> = 4.0 Hz); 3.50 (d, 1H, *J* = 18.4 Hz); 4.43 (d, 1H, *J* = 8.4 Hz); 4.55 (d, 1H, *J* = 8.4 Hz); 5.95 (m, 1H); 7.21-7.33 (m, 3H); 7.42-7.45 (m, 2H). <sup>13</sup>C-NMR ( $\delta$ ): 22.2 (CH<sub>3</sub>); 22.4 (CH<sub>3</sub>); 22.7 (CH<sub>2</sub>); 22.8 (CH<sub>2</sub>); 24.9 (2 CH<sub>2</sub>); 26.4 (CH<sub>3</sub>); 27.3 (CH<sub>2</sub>); 31.3 (CH); 35.1 (CH<sub>2</sub>); 41.0 (CH<sub>2</sub>); 45.4 (CH); 47.1 (CH<sub>2</sub>); 57.2 (C); 72.5 (CH); 76.9 (CH); 90.6 (CH); 121.0 (CH); 127.2 (2 CH); 127.3 (CH); 127.7 (2 CH); 139.6 (C); 141.2 (C). IR (Film): 3490; 3020; 1590; 715; 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>25</sub>H<sub>37</sub>NO<sub>2</sub>: C, 78.28; H, 9.72; N, 3.65. Found: C, 78.36; H, 9.84; N, 3.69.

#### (S)-[(2S,4aS,7R,8aR)-3-(3-Methylbut-2-enyl)-4,4,7-trimethyl-octahydro-2H-1,3-

**benzo[e][1,3]oxazin-2-yl](phenyl)methanol (4e).** Yield: 90 % .Colorless solid. Mp: 103-104 °C (from ethanol).  $[α]_D^{25} = -97.1$  (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (δ): 0.86–1.08 (m, 3H); 0.87 (d, 3H, J = 6.5 Hz); 1.20 (s, 3H); 1.22 (s, 3H); 1.37 (m, 1H); 1.48 (m, 1H); 1.56 (m, 1H); 1.62-1.78 (m, 2H); 1.69 (s, 3H); 1.71 (s, 3H); 3.24 (td, 1H  $J_1 = 10.6$  Hz,  $J_2 = 4.0$  Hz); 3.25 (s, 1H); 3.28 (dd, 1H,  $J_1 = 17.3$  Hz,  $J_2 = 4.7$  Hz); 3.65 (dd, 1H  $J_1 = 17.3$  Hz,  $J_2 = 7.1$  Hz); 4.5 (s, 2H); 5.38 (dd, 1H,  $J_1 = 7.1$  Hz,  $J_2 = 4.7$  Hz); 7.22-7.37 (m, 3H); 7.42-7.48 (m, 2H). <sup>13</sup>C-NMR (δ): 18.0 (CH<sub>3</sub>); 22.1 (CH<sub>3</sub>); 22.7 (CH<sub>3</sub>); 24.9 (CH<sub>2</sub>); 25.8 (CH<sub>3</sub>); 27.0 (CH<sub>3</sub>); 31.3 (CH); 35.1 (CH<sub>2</sub>); 40.0 (CH<sub>2</sub>); 41.0 (CH<sub>2</sub>); 45.0 (CH); 57.4 (C); 71.5 (CH); 77.1 (CH); 90.6 (CH); 126.8 (CH); 127.1 (2 CH); 127.3 (CH); 127.8 (2 CH); 131 (C); 141.2 (C). IR (Nujol dispersion): 3480; 3060; 3020; 1600; 760; 730; 700 cm<sup>-1</sup>. Anal. Calcd. for C<sub>23</sub>H<sub>35</sub>NO<sub>2</sub>: C, 77.27; H, 9.87; N, 3.92. Found: C, 77.14; H, 9.99; N, 4.03.

Synthesis of (S)-1-[(2S,4aS,7R,8aR)-3-(3-Methylbut-2-enyl)-4,4,7-trimethyloctahydro-2*H*-1,3-benzo[*e*][1,3]oxazin-2-yl]-1-phenylethanol (4f). To a stirred solution of the ketone 3e (3.0 g, 8.4 mmol) in anhydrous ethyl ether (50 mL) cooled to -10 °C, an ethereal 3.0 M solution of methylmagnesium iodide (4.2 mL of 3.0 M solution, Aldrich) was added dropwise under a nitrogen atmosphere. Stirring was continued until disappearance of the starting ketone (TLC, 25 min.).The mixture was quenched with saturated aqueous NH<sub>4</sub>Cl (50 mL), the layers were separated and the aqueous was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, concentrated at reduced pressure; and residue was purified by flash chromatography on silica gel, using hexanes-ethyl acetate 40:1 as eluent. Yield: 87 %. Colorless oil.  $[\alpha]_D^{25} = + 1.0$  (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.88-1.18 (m, 4H); 0.93 (s, 3H); 0.95 (d, 3H, J = 6.5 Hz); 1.20 (s, 3H); 1.42 (s, 6H); 1.44-1.59 (m, 2H); 1.53 (s, 3H); 1.69 (m, 1H); 1.96 (m, 1H); 3.08 (dd, 1H,  $J_1 = 17.5$  Hz,  $J_2 = 6.4$  Hz); 3.28 (s, 1H); 3.52-3.63 (m, 2H); 4.20 (m, 1H); 4.89 (s, 1H); 7.17 (m, 1H); 7.20-7.30 (m, 2H); 7.41-7.44 (m, 2H). <sup>13</sup>C-NMR ( $\delta$ ): 17.5 (CH<sub>3</sub>); 22.2 (CH<sub>3</sub>); 22.3 (CH<sub>3</sub>) 24.9 (CH<sub>2</sub>); 25.4 (CH<sub>3</sub>); 26.0 (CH<sub>3</sub>); 31.3 (CH); 32.5 (CH<sub>3</sub>); 35.1 (CH<sub>2</sub>); 40.8 (CH<sub>2</sub>); 41.5 (CH<sub>2</sub>); 45.0 (CH); 57.0 (C); 74.9 (C); 77.4 (CH); 90.3 (CH); 125.3 (2 CH); 125.6 (CH); 126.3 (C); 127.0 (2 CH); 128.9 (CH); 145.0 (C). IR (Film): 3500; 1590; 745; 690; 645 cm<sup>-1</sup>. Anal. Calcd. for C<sub>24</sub>H<sub>37</sub>NO<sub>2</sub>: C, 77.58; H, 10.04; N, 3.77. Found: C, 77.66; H, 9.97; N, 3.86.

General Procedure for Reductive Deselenylation of Compounds 5a-d, 5f, 5g, 6a-e, 6g, 6h, 7e, 7h and 8h. A mixture of AIBN (33 mg, 0.2 mmol), triphenyltin hydride (0.9 g, 2.6 mmol) and degassed toluene (15 mL) was added dropwise to a refluxing solution of the appropriated selenylated compound (1.7 mmol) in degassed toluene (15 mL) under argon atmosphere. The mixture was refluxed until disappearance of the starting product (TLC, 1-5 h). The solvent was removed *in vacuo* and the residue was chromatographed on silica gel using hexanes/AcOEt as eluent.

# (1S,3S,6aS,9R,10aR,11aS)-1-Phenyl-3,6,6,9-tetramethyl-decahydro-3H,7H-

[1,4]oxazino[3,4-*b*][1,3]benzoxazine (9a). Yield: 95%. Colorless oil.  $[\alpha]_D^{25} = -45.2$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.87-1.03 (m, 2H); 0.91 (d, 3H, *J* = 6.5 Hz); 1.12 (s, 3H); 1.16 (s, 3H); 1.21 (d, 3H, *J* = 6.4 Hz); 1.32-1.56 (m, 3H); 1.61 (m, 1H); 1.72 (m, 1H); 1.90 (m, 1H); 2.63 (dd, 1H, *J*<sub>1</sub> = 10.9 Hz, *J*<sub>2</sub> = 3.0 Hz); 2.87 (dd, 1H, *J*<sub>1</sub> = 10.9 Hz, *J*<sub>2</sub> = 7.7 Hz); 3.45 (td, 1H, *J*<sub>1</sub> = 10.5 Hz, *J*<sub>2</sub> = 4.2 Hz); 3.82 (dqd, 1H, *J*<sub>1</sub> = 7.7 Hz, *J*<sub>2</sub> = 6.4 Hz, *J*<sub>3</sub> = 3.0 Hz); 4.71 (s, 2H); 7.21-7.31 (m, 3H); 7.50-7.54 (m, 2H). <sup>13</sup>C-NMR ( $\delta$ ):

18.2 (CH<sub>3</sub>); 18.3 (CH<sub>3</sub>); 22.2 (CH<sub>3</sub>); 25.1 (CH<sub>2</sub>); 26.2 (CH<sub>3</sub>); 31.3 (CH); 34.9 (CH<sub>2</sub>); 41.2 (CH<sub>2</sub>); 45.3 (CH); 46.5 (CH<sub>2</sub>); 55.5 (C); 66.4 (CH); 75.7 (CH); 76.1 (CH); 82 8 (CH); 127.3 (CH); 127.9 (2 CH); 128.2 (2 CH); 139.2 (C). IR (Film): 3040, 3020, 1590, 730, 700, 690 cm<sup>-1</sup>. Anal. Calcd. for  $C_{21}H_{31}NO_2$ : C, 76.55; H, 9.48; N, 4.25. Found: C, 76.68; H, 9.32; N, 4.37.

#### (1S,3S,6aS,9R,10aR,11aS)-1-Phenyl-3-ethyl-6,6,9-trimethyl-decahydro-3H,7H-

**[1,4]oxazino[3,4-***b***][1,3]benzoxazine (9b).** Yield: 92%. Colorless oil.  $[α]_D^{25} = -5.4$  (c = 1.3, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (δ): 0.88 (t, 3H, *J* = 7.5 Hz); 0.86-1.01 (m, 2H); 0.90 (d, 3H, *J* = 6.5 Hz); 1.11 (s, 3H); 1.15 (s, 3H); 1.20-1.83 (7H, m); 1.88 (m, 1H); 2.64 (dd, 1H, *J*<sub>1</sub> = 11.0 Hz, *J*<sub>2</sub> = 3.1 Hz); 2.90 (dd, 1H, *J*<sub>1</sub> = 11.0 Hz, *J*<sub>2</sub> = 7.2 Hz); 3.43 (td, 1H, *J*<sub>1</sub> = 10.6 Hz, *J*<sub>2</sub> = 4.1 Hz); 3.54 (m, 1H); 4.67 (s, 2H); 7.15-7.38 (m, 3H); 7.49-7.53 (m, 2H). <sup>13</sup>C-NMR (δ): 10.0 (CH<sub>3</sub>); 17.6 (CH<sub>3</sub>); 22.2 (CH<sub>3</sub>), 24.9 (CH<sub>2</sub>); 25.0 (CH<sub>2</sub>); 26.2 (CH<sub>3</sub>); 31.3 (CH); 34.9 (CH<sub>2</sub>); 41.2 (CH<sub>2</sub>); 44.8 (CH<sub>2</sub>); 45.7 (CH); 55.5 (C); 72.1 (CH); 75.6 (CH); 75.7 (CH); 83.3 (CH); 127.3 (CH); 127.9 (2 CH); 128 (2 CH); 139.5 (C). IR (Film): 3040, 3060, 1595, 755,725, 695 cm<sup>-1</sup>. Anal. Calcd. for C<sub>22</sub>H<sub>33</sub>NO<sub>2</sub>: C, 76.92; H, 9.68; N, 4.08. Found: C, 77.06; H, 9.79; N, 3.94.

## (1S,6aS,9R,10aR,11aS)-1-Phenyl-3,3,6,6,9-pentamethyl-decahydro-3H,7H-

**[1,4]oxazino[3,4-***b***][1,3]benzoxazine (9c).** Yield: 96% from **5c**, 93% from **6c**. Colorless solid. Mp:115-116 °C (from ethanol).  $[\alpha]_D^{25} = -11.5$  (c = 1.6, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.83-0.99 (m, 2H); 0.85 (d, 3H, J = 6.5 Hz); 0.85 (s, 3H); 1.02 (m, 1H); 1.11 (s, 3H); 1.26 (s, 3H); 1.27-1.45 (m, 2H); 1.48 (s, 3H); 1.61-1.70 (m, 2H); 1.78 (m, 1H); 2.35 (d, 1H, J = 11.5 Hz); 2.69 (d, 1H, J = 11.5 Hz); 3.12 (dt, 1H,  $J_1 = 10.6$  Hz,  $J_2 = 4.2$  Hz); 3.75 (d, 1H, J = 7.8 Hz); 4.46 (d, 1H, J = 7.8 Hz); 7.24-7.32 (m, 3H); 7.43-7.46 (m, 2H). <sup>13</sup>C-NMR ( $\delta$ ): 11.4 (CH<sub>3</sub>); 21.7 (CH<sub>3</sub>); 22.1 (CH<sub>3</sub>); 25.0 (CH<sub>2</sub>); 25.8 (CH<sub>3</sub>); 28.3 (CH<sub>3</sub>); 31.0 (CH); 34.6 (CH<sub>2</sub>); 40.9 (CH<sub>2</sub>); 49.7 (CH); 52.3 (CH<sub>2</sub>); 54.9 (C); 71.9 (C);

73.7 (CH); 75.8 (CH); 87.6 (CH); 127.4 (CH); 127.6 (2 CH); 128.0 (2 CH); 140.2 (C). IR (Nujol): 3020, 1595, 745, 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>22</sub>H<sub>33</sub>NO<sub>2</sub>: C, 76.92; H, 9.68; N, 4.08. Found: C, 76.83; H, 9.57; N, 4.18.

#### (1'S,6'aS,9'R,10'aR,11'aS)-1'-Phenyl-6',6',9'-trimethyl-decahydro-3'H,7'H-

spiro[cyclohexane-1,3'-[1,4]oxazino[3,4-*b*][1,3]benzoxazine] (9d). Yield: 90% from 5d, 88% from 6d. Colorless oil.  $[\alpha]_D^{25} = -8.7$  (c = 0.6, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.80-1.08 (m, 3H); 0.86 (d, 3H, *J* = 6.4 Hz); 0.87 (s, 3H); 1.11 (s, 3H); 1.25-1.82 (m, 14H); 2.16 (m, 1H); 2.20 (d, 1H, *J* = 10.7 Hz); 2.88 (d, 1H, *J* = 10.7 Hz); 3.12 (td, 1H, *J*<sub>1</sub> = 10.5 Hz, *J*<sub>2</sub> = 4.5 Hz); 3.75 (d, 1H, *J* = 7.8 Hz); 4.45 (d, 1H, *J* = 7.8 Hz); 7.21-7.34 (m, 3H); 7.42-7.50 (m, 2H). <sup>13</sup>C-NMR ( $\delta$ ): 11.4 (CH<sub>3</sub>); 21.8 (CH<sub>2</sub>); 22.1 (CH<sub>2</sub>, CH<sub>3</sub>); 25.0 (CH<sub>2</sub>); 25.8 (CH<sub>3</sub>); 26.3 (CH<sub>2</sub>); 29.6 (CH<sub>2</sub>); 30.9 (CH); 34.6 (CH<sub>2</sub>); 37.2 (CH<sub>2</sub>); 40.9 (CH<sub>2</sub>); 49.7 (CH); 50.5 (CH<sub>2</sub>); 54.9 (C); 72.6 (C); 73.8 (CH); 74.3 (CH); 87.8 (CH); 127.2 (CH); 127.5 (2 CH); 127.9 (2 CH); 140.6 (C). IR (Film): 3020, 750, 740, 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>25</sub>H<sub>37</sub>NO<sub>2</sub>: C, 78.28; H, 9.72; N, 3.65. Found: C, 78.39; H, 9.65; N, 3.80.

### (1S,3S,6aS,9R,10aR,11aS)-3-Isopropyl-1-phenyl-1,6,6,9-tetramethyl-decahydro-

**3H,7H-[1,4]oxazino[3,4-***b***][1,3]benzoxazine (9f).** Yield: 91%. Colorless oil.  $[\alpha]_D^{25} = -144.1$  (c = 0.5, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.79 (d, 3H, J = 6.7 Hz); 0.86-1.08 (m, 2H); 0.93 (d, 3H, J = 6.5 Hz); 1.06 (d, 3H, J = 6.1 Hz); 1.07 (s, 3H); 1.19 (m, 1H); 1.31 (s, 3H); 1.39 (s, 3H); 1.45-1.62 (m, 3H); 1.64-1.80 (m, 2H); 1.98 (m, 1H); 2.58 (dd, 1H,  $J_1 = 10.4$  Hz,  $J_2 = 2.5$  Hz); 2.84 (t, 1H, J = 10.4 Hz); 3.05 (ddd, 1H,  $J_1 = 10.8$  Hz,  $J_2 = 10.4$  Hz,  $J_3 = 2.5$  Hz); 3.58 (td, 1H,  $J_1 = 10.5$  Hz,  $J_2 = 4.0$  Hz); 5.10 (s, 1H); 7.21 (m, 1H); 7.24-7.32 (m, 2H); 7.33-7.42 (m, 2H). <sup>13</sup>C-NMR ( $\delta$ ): 18.6 (CH<sub>3</sub>); 19.4 (CH<sub>3</sub>); 21.4 (CH<sub>3</sub>); 22.3 (CH<sub>3</sub>); 25.2 (CH<sub>2</sub>); 26.4 (CH<sub>3</sub>); 29.3 (CH<sub>3</sub>); 31.5 (CH); 31.7 (CH); 35.1 (CH<sub>2</sub>); 41.3 (CH<sub>2</sub>); 42.5 (CH<sub>2</sub>); 43.4 (CH); 56.3 (C); 75.5 (CH); 77.2 (CH); 77.3 (C); 82.5 (CH); 125.9 (2 CH); 126.3 (CH); 128.0 (2 CH); 145.5 (C). IR (Film): 3040, 3060,

1600, 1370, 770, 700, 670 cm<sup>-1</sup>. Anal. Calcd. for C<sub>24</sub>H<sub>37</sub>NO<sub>2</sub>: C, 77.58; H, 10.04; N, 3.77. Found: C, 77.71; H, 10.18; N, 3.65.

#### (3S,6aS,9R,10aR,11aS)-3,6,6,9-tetramethyl-decahydro-3H,7H-[1,4]oxazino[3,4-

*b*][1,3]benzoxazine (9g). Yield: 92%. Colorless solid. Mp: 104-105 °C (from ethanol).  $[\alpha]_{D}^{25} = -62.8 (c = 0.8, CH_{2}Cl_{2}).$  <sup>1</sup>H-NMR ( $\delta$ ): 0.79-0.92 (m, 2H); 0.84 (d, 3H, J = 6.5Hz); 1.02 (s, 3H); 1.13 (m, 1H); 1.10 (s, 3H); 1.11 (d, 3H, J = 6.2 Hz); 1.33-1.53 (m, 3H); 1.62 (m, 1H); 1.86 (m, 1H); 2.50 (dd, 1H,  $J_{1} = 10.5$  Hz,  $J_{2} = 2.3$  Hz); 2.76 (t, 1H, J = 10.5 Hz); 3.41 (td, 1H,  $J_{1} = 10.5$  Hz,  $J_{2} = 4.0$  Hz); 3.54 (dd, 1H,  $J_{1} = 11.8$  Hz,  $J_{2} = 1.6$ Hz); 3.55 (m, 1H); 3.80 (dd, 1H,  $J_{1} = 11.8$  Hz,  $J_{2} = 1.6$  Hz); 4.44 (t, 1H, J = 1.6 Hz). <sup>13</sup>C-NMR ( $\delta$ ): 19.2 (CH<sub>3</sub>); 21.2 (CH<sub>3</sub>); 22.2 (CH<sub>3</sub>); 25.0 (CH<sub>2</sub>); 26.2 (CH<sub>3</sub>); 31.3 (CH); 34.9 (CH<sub>2</sub>); 41.2 (CH<sub>2</sub>); 43.1 (CH); 46.7 (CH<sub>2</sub>); 55.5 (C); 69.9 (CH<sub>2</sub>); 72.3 (CH); 76.1 (CH); 79.5 (CH). IR (Nujol): 920, 880, 780, 735, 680 cm<sup>-1</sup>. Anal. Calcd. for C<sub>15</sub>H<sub>27</sub>NO<sub>2</sub>: C, 71.10; H, 10.74; N, 5.53. Found: C, 71.24; H, 10.66; N, 5.60.

## (3S,6aS,9R,10aR,11aS)-3-Isopropyl-6,6,9-trimethyl-decahydro-3H,7H-

[1,4]oxazino[3,4-*b*][1,3]benzoxazine (9h). Yield: 90%. Colorless oil.  $[\alpha]_D^{25} = -13.3$  (c = 0.9, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.86-1.01 (m, 2H); 0.90 (d, 3H, J = 6.5 Hz); 0.96 (d, 3H, J = 6.7 Hz); 1.01 (d, 3H, J = 6.7 Hz); 1.11 (s, 3H); 1.12 (m, 1H); 1.20 (s, 3H); 1.39-1.59 (m, 3H); 1.62-1.81 (m, 2H); 1.90 (m, 1H); 2.70 (dd, 1H J<sub>1</sub> = 10.7 Hz, J<sub>2</sub> = 2.5 Hz); 2.84 (dd, 1H, J<sub>1</sub> = 10.7 Hz, J<sub>2</sub> = 10.1 Hz); 3.13 (ddd, 1H, J<sub>1</sub> = 10.1 Hz, J<sub>2</sub> = 7.6 Hz, J<sub>3</sub> = 2.5 Hz); 3.50 (td, 1H, J<sub>1</sub> = 10.3 Hz, J<sub>2</sub> = 4.0 Hz); 3.59 (dd, 1H, J<sub>1</sub> = 11.9 Hz, J<sub>2</sub> = 2.0 Hz); 3.90 (dd, 1H, J<sub>1</sub> = 11.9 Hz, J<sub>2</sub> = 1.6 Hz); 4.52 (dd, 1H, J<sub>1</sub> = 2.0 Hz, J<sub>2</sub> = 1.6 Hz). <sup>13</sup>C-NMR ( $\delta$ ): 18.6 (CH<sub>3</sub>); 18.9 (CH<sub>3</sub>); 21.2 (CH<sub>3</sub>); 22.2 (CH<sub>3</sub>); 25.1 (CH<sub>2</sub>); 26.2 (CH<sub>3</sub>); 31.3 (2 CH); 35.0 (CH<sub>2</sub>); 41.3 (CH<sub>2</sub>); 43.1 (CH<sub>2</sub>); 43.2 (CH); 55.7 (C); 70.0 (CH<sub>2</sub>); 76.1 (CH); 79.8 (CH); 81.5 (CH). IR (Film): 2910, 2820, 1445, 720 cm<sup>-1</sup>. Anal. Calcd. for C<sub>17</sub>H<sub>31</sub>NO<sub>2</sub>: C, 72.55; H, 11.10; N, 4.98. Found: C, 72. 67; H, 11.23; N, 5.14.

#### (1S,3R,6aS,9R,10aR,11aS)-1-phenyl-3,6,6,9-tetramethyl-decahydro-3H,7H-

[1,4]oxazino[3,4-*b*][1,3]benzoxazine (10a). Yield: 94%. Colorless oil.  $[\alpha]_D^{25} = -33.8$ (c= 0.7, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.82-0.98 (m, 2H); 0.85 (d, 3H, *J* = 6.4 Hz); 0.92 (s, 3H); 1.00 (m, 1H); 1.16 (s, 3H); 1.22 (d, 3H, *J* = 6.2 Hz); 1.23-1.41 (m, 2H); 1.51-1.78 (m, 3H); 2.28 (dd, 1H, *J*<sub>1</sub> = 11.5 Hz, *J*<sub>2</sub> = 10.3 Hz); 2.91 (dd, 1H, *J*<sub>1</sub> = 11.5 Hz, *J*<sub>2</sub> = 1.9 Hz); 3.15 (td, 1H, *J*<sub>1</sub> = 10.5 Hz, *J*<sub>2</sub> = 4.1 Hz); 3.83 (d, 1H, *J* = 7.7 Hz); 3.91 (dqd, 1H, *J*<sub>1</sub> = 10.3 Hz, *J*<sub>2</sub> = 6.2 Hz, *J*<sub>3</sub> = 1.9 Hz); 4.29 (d, 1H, *J* = 7.7 Hz); 7.20-7.32 (m, 3H); 7.40-7.47 (m, 2H). <sup>13</sup>C-NMR ( $\delta$ ): 11.3 (CH<sub>3</sub>); 19.1 (CH<sub>3</sub>); 22.1 (CH<sub>3</sub>); 25.0 (CH<sub>2</sub>); 25.6 (CH<sub>3</sub>); 31.1 (CH); 34.7 (CH<sub>2</sub>); 41.0 (CH<sub>2</sub>); 49.2 (CH<sub>2</sub>); 50.0 (CH); 55.6 (C); 72.3 (CH); 74.3 (CH); 81.1 (CH); 86.3 (CH); 127.6 (CH); 127.7 (2 CH); 127.9 (2 CH); 139.6 (C). IR (Film): 3020, 3040, 750, 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>21</sub>H<sub>31</sub>NO<sub>2</sub>: C, 76.55; H, 9.48; N, 4.25. Found: C, 76.66; H, 9.39; N, 4.40.

## (1S,3R,6aS,9R,10aR,11aS)-1-phenyl-3-ethyl-6,6,9-trimethyl-decahydro-3H,7H-

**[1,4]oxazino[3,4-***b***][1,3]benzoxazine (10b).** Yield: 90%. Colorless solid. Mp: 69-70 °C (from ethanol).  $[α]_{D}^{25} = -3.4$  (c = 1.5, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (δ): 0.85-1.05 (m, 3H); 0.86 (d, 3H, J = 6.5 Hz); 0.92 (s, 3H); 0.96 (t, 3H, J = 7.3 Hz); 1.17 (s, 3H); 1.19-1.70 (m, 7H); 2.27 (t, 1H, J = 10.3 Hz); 2.94 (dd, 1H,  $J_1 = 10.3$  Hz,  $J_2 = 2.5$  Hz); 3.16 (td, 1H,  $J_1 = 10.5$  Hz,  $J_2 = 3.9$  Hz); 3.65 (m, 1H); 3.82 (d, 1H, J = 7.8 Hz); 4.27 (d, 1H, J = 7.8 Hz); 7.14-7.28 (m, 3H); 7.38-7.42 (m, 2H). <sup>13</sup>C-NMR (δ): 10.0 (CH<sub>3</sub>); 11.3 (CH<sub>3</sub>); 22.1 (CH<sub>3</sub>); 24.9 (CH<sub>2</sub>); 25.6 (CH<sub>3</sub>); 26.6 (CH<sub>2</sub>); 31.0 (CH); 34.6 (CH<sub>2</sub>); 41.0 (CH<sub>2</sub>); 47.3 (CH<sub>2</sub>); 50.0 (CH); 55.6 (C); 74.2 (CH); 77.3 (CH); 80.8 (CH); 86.6 (CH); 127.4 (CH); 127.5 (2 CH); 127.8 (2 CH); 139.7 (C). IR (Nujol): 3040, 3020, 1600, 760, 730, 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>22</sub>H<sub>33</sub>NO<sub>2</sub>: C, 76.92; H, 9.68; N, 4.08. Found: C, 76.89; H, 9.80; N, 4.20.

#### (1S,3R,6aS,9R,10aR,11aS)-3-Isopropyl-1-phenyl-3-6,6,9-trimethyl-decahydro-

**3H**,7*H*-[1,4]oxazino[3,4-*b*][1,3]benzoxazine (10e). Yield: 89%. Colorless solid. Mp: 78-79 °C. (from ethanol). [α]<sub>D</sub><sup>25</sup> = -16.1 (c = 1.0; CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (δ): 0.87-1.10 (m, 3H); 0.92 (d, 3H, J = 6.5 Hz); 0.97 (s, 3H); 1.01 (d, 3H, J = 6.9 Hz); 1.04 (d, 3H, J = 6.9 Hz); 1.22 (s, 3H); 1.28-1.46 (m, 3H); 1.62-1.85 (m, 3H); 2.31 (dd, 1H,  $J_1 = 11.0$  Hz,  $J_2 = 10.6$  Hz); 2.96 (dd, 1H,  $J_1 = 11.0$  Hz,  $J_2 = 1.8$  Hz); 3.16 (td, 1H,  $J_1 = 10.6$  Hz,  $J_2 = 4.1$  Hz); 3.48 (ddd, 1H,  $J_1 = 10.6$  Hz,  $J_2 = 6.1$  Hz,  $J_3 = 1.8$  Hz); 3.77 (d, 1H, J = 7.8 Hz); 4.26 (d, 1H, J = 7.8 Hz); 7.26-7.34 (m, 3H); 7.43-7.51 (m, 2H). <sup>13</sup>C-NMR (δ): 11.3 (CH<sub>3</sub>); 18.7 (2 CH<sub>3</sub>); 22.1 (CH<sub>3</sub>); 25.0 (CH<sub>2</sub>); 25.5 (CH<sub>3</sub>); 31.0 (CH); 31.4 (CH); 34.6 (CH<sub>2</sub>); 41.0 (CH<sub>2</sub>); 44.8 (CH<sub>2</sub>); 50.0 (CH); 55.8 (C); 74.2 (CH); 80.5 (CH); 80.6 (CH); 86.7 (CH); 127.3 (CH); 127.5 (2 CH); 127.8 (2 CH); 140.0 (C). IR (Nujol): 3020, 3040, 1595, 750, 730, 695 cm<sup>-1</sup>. Anal. Calcd. for C<sub>23</sub>H<sub>35</sub>NO<sub>2</sub>: C, 77.27; H, 9.87; N, 3.92. Found: C, 77.40; H, 10.0; N, 3.81.

#### (3R,6aS,9R,10aR,11aS)-3,6,6,9-Tetramethyl-decahydro-3H,7H-[1,4]oxazino[3,4-

*b*][1,3]benzoxazine (10g). Yield: 92%. Colorless oil.  $[\alpha]_D^{25} = +7.3$  (c = 0.9; CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.84-1.12 (m, 3H); 0.92 (d, 3H, J = 6.6 Hz); 0.93 (s, 3H); 1.12 (s, 3H); 1.15 (d, 3H, J = 6.2 Hz); 1.40 (m, 1H); 1.52 (m, 1H); 1.64-1.78 (m, 2H); 1.91 (m, 1H); 2.11 (dd, 1H,  $J_1 = 11.5$  Hz,  $J_2 = 10.0$  Hz); 2.82 (dd, 1H,  $J_1 = 11.5$  Hz,  $J_2 = 2.0$  Hz); 3.33 (dd, 1H,  $J_1 = 10.8$  Hz,  $J_2 = 8.8$  Hz); 3.38 (td, 1H,  $J_1 = 10.6$  Hz,  $J_2 = 4.2$  Hz); 3.69 (dqd, 1H,  $J_1 = 10.0$  Hz,  $J_2 = 6.2$  Hz,  $J_3 = 2.0$  Hz); 3.83 (dd, 1H,  $J_1 = 10.8$  Hz,  $J_2 = 3.8$  Hz); 4.06 (dd, 1H  $J_1 = 8.8$  Hz,  $J_2 = 3.8$  Hz). <sup>13</sup>C-NMR ( $\delta$ ): 11.1 (CH<sub>3</sub>); 18.8 (CH<sub>3</sub>); 22.0 (CH<sub>3</sub>); 24.8 (CH<sub>2</sub>); 25.2 (CH<sub>3</sub>); 31.0 (CH); 34.5 (CH<sub>2</sub>); 41.0 (CH<sub>2</sub>); 48.8 (CH<sub>2</sub>); 50.0 (CH); 55.1 (C); 69.6 (CH<sub>2</sub>); 72.5 (CH); 74.3 (CH); 81.2 (CH). IR (Film): 2930, 2665, 1455, 770, 730 cm<sup>-1</sup>. Anal. Calcd. for C<sub>15</sub>H<sub>27</sub>NO<sub>2</sub>: C, 71.10; H, 10.74; N, 5.53. Found: C, 71.23; H, 10.60; N, 5.45.

#### (,3R,6aS,9R,10aR,11aS)-3-Isopropyl-6,6,9-trimethyl-decahydro-3H,7H-

**[1,4]oxazino[3,4-***b***][1,3]benzoxazine (10h).** Yield: 85%. Colorless oil.  $[α]_D^{25} = +12.3$  (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (δ): 0.82-1.06 (m, 3H); 0.86 (d, 3H, *J* = 6.6 Hz); 0.88 (d, 3H, *J* = 6.7 Hz); 0.89 (s, 3H); 0.91 (d, 3H, J = 6.7 H); 1.08 (s, 3H); 1.25-1.47 (m, 2H); 1.57-1.71 (m, 3H); 1.87 (m, 1H); 2.10 (dd, 1H, J<sub>1</sub> = 11.3 Hz, J<sub>2</sub> = 10.3 Hz); 2.84 (dd, 1H, J<sub>1</sub> = 11.3 Hz, J<sub>2</sub> = 2.0 Hz); 3.19 (m,1H); 3.23 (dd, 1H, J<sub>1</sub> = 10.7 Hz, J<sub>2</sub> = 8.8 Hz); 3.33 (td, 1H, J<sub>1</sub> = 10.4 Hz, J<sub>2</sub> = 4.1 Hz); 3.81 (dd, 1H J<sub>1</sub> = 10.7 Hz, J<sub>2</sub> = 3.7 Hz); 3.99 (dd, 1H J<sub>1</sub> = 8.8 Hz, J<sub>2</sub> = 3.7 Hz). <sup>13</sup>C-NMR (δ): 11.2 (CH<sub>3</sub>); 18.6 (CH<sub>3</sub>); 18.8 (CH<sub>3</sub>); 22.0 (CH<sub>3</sub>); 24.8 (CH<sub>2</sub>); 25.2 (CH<sub>3</sub>); 31.0 (CH); 31.1 (CH); 34.5 (CH<sub>2</sub>); 41.1 (CH<sub>2</sub>); 44.7 (CH<sub>2</sub>); 50.1 (CH); 55.2 (C); 69.7 (CH<sub>2</sub>); 74.2 (CH); 81.4 (CH); 81.5 (CH). IR (Film): 2920, 1450, 725 cm<sup>-1</sup>. Anal. Calcd. for C<sub>17</sub>H<sub>31</sub>NO<sub>2</sub>: C, 72.55; H, 11.10; N, 4.98. Found: C, 72.46; H, 11.23; N, 5.12.

#### (1S,7aS,10R,11aR,12aS)-1-Phenyl-3,3,7,7,10-pentamethyl-decahydro-3H,7H-

[1,4]oxazepino[3,4-*b*][1,3]benzoxazine (11e). Yield: 40%. Colorless oil.  $[\alpha]_D^{25} = -28.5$ (c = 0.8, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.80-0.96 (m, 3H); 0.81 (d, 3H, *J* = 6.5 Hz, CH<sub>3</sub>); 0.98 (s, 3H, CH<sub>3</sub>); 1.17 (s, 3H, CH<sub>3</sub>); 1.18 (s, 3H, CH<sub>3</sub>); 1.20-1.33 (m, 3H); 1.22 (s, 3H, CH<sub>3</sub>); 1.51-1.68 (m, 2H); 1.82 (dd, 1H, *J*<sub>1</sub> = 14.9 Hz, *J*<sub>2</sub> = 8.1 Hz); 2.00 (dd, 1H, *J*<sub>1</sub> = 14.9 Hz, *J*<sub>2</sub> = 8.6 Hz); 2.63 (dd, 1H, *J*<sub>1</sub> = 13.2 Hz, *J*<sub>2</sub> = 8.6 Hz); 2.94 (dd, 1H, *J*<sub>1</sub> = 13.2 Hz, *J*<sub>2</sub> = 8.1 Hz); 3.12 (td, 1H, *J*<sub>1</sub> = 10.6 Hz, *J*<sub>2</sub> = 4.2 Hz); 4.10 (d, 1H, *J* = 7.7 Hz); 4.50 (d, 1H, *J* = 7.7 Hz); 7.18-7.30 (m, 3H); 7.32-7.39 (m, 2H). <sup>13</sup>C-NMR ( $\delta$ ): 13.3 (CH<sub>3</sub>); 22.0 (CH<sub>3</sub>); 25.3 (CH<sub>2</sub>); 26.0 (CH<sub>3</sub>); 26.8 (CH<sub>3</sub>); 29.2 (CH<sub>3</sub>); 31.0 (CH); 34.8 (CH<sub>2</sub>); 37.6 (CH<sub>2</sub>); 40.8 (CH<sub>2</sub>); 42.1 (CH<sub>2</sub>); 49.6 (CH); 57.4 (C); 74.4 (CH); 75.2 (CH); 76.0 (C); 89.7 (CH); 126.6 (CH); 127.4 (2 CH); 127.5 (2 CH); 142.1 (C). IR (Film): 3020, 3040, 1590, 750, 725, 700, 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>23</sub>H<sub>35</sub>NO<sub>2</sub>: C, 77.27; H, 9.87; N, 3.92. Found: C, 77.36; H, 9.72; N, 4.04.

#### (7aS,10R,11aR,12aS)-3,3,7,7,10-Pentamethyl-decahydro-3H,7H-

**[1,4]oxazepino[3,4-***b***]<b>[1,3]benzoxazine** (**11h**). Yield: 72% from **7h**, 82% from **8h**. Colorless oil.  $[\alpha]_D^{25} = -2.9$  (c = 0.9, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.80-0.95 (m, 2H); 0.91 (d, 3H, *J* = 6.5 Hz); 0.95 (s, 3H); 1.04 (m, 1H); 1.13 (s, 3H); 1.16 (s, 3H); 1.17 (s, 3H); 1.24-1.49 (m, 2H); 1.68-1.79 (m, 3H); 1.88-1.96 (m, 2H); 2.39 (dd, 1H, *J*<sub>1</sub> = 13.3 Hz, *J*<sub>2</sub> = 8.7 Hz); 2.84 (dd, 1H, *J*<sub>1</sub> = 13.3 Hz, *J*<sub>2</sub> = 8.3 Hz); 3.37 (dt, 1H, *J*<sub>1</sub> = 10.4 Hz, *J*<sub>2</sub> = 4.2 Hz); 3.53 (dd, 1H, *J*<sub>1</sub> = 13.2 Hz, *J*<sub>2</sub> = 3.1 Hz); 3.60 (dd, 1H, *J*<sub>1</sub> = 13.2 Hz, *J*<sub>2</sub> = 7.5 Hz); 4.13 (dd, 1H, *J*<sub>1</sub> = 7.5Hz, *J*<sub>2</sub> = 3.1 Hz). <sup>13</sup>C-NMR ( $\delta$ ): 12.9 (CH<sub>3</sub>); 22.0 (CH<sub>3</sub>); 25.1 (CH<sub>2</sub>); 26.4 (CH<sub>3</sub>); 26.6 (CH<sub>3</sub>); 28.3 (CH<sub>3</sub>); 31.0 (CH); 34.6 (CH<sub>2</sub>); 37.2 (CH<sub>2</sub>); 41.1 (CH<sub>2</sub>); 41.5 (CH<sub>2</sub>); 49.4 (CH); 56.5 (C); 66.2 (CH<sub>2</sub>); 74.3 (C); 75.2 (CH); 86.3 (CH). IR (Film): 2905, 1450, 880, 735 cm<sup>-1</sup>. Anal. Calcd. for C<sub>17</sub>H<sub>31</sub>NO<sub>2</sub>: C, 72.55; H, 11.10; N, 4.98. Found: C, 72.99; H, 10.99; N,5.09 .

General Method for 1,3-Oxazine Ring Opening by Aluminum Hydride. To a suspension of LiAlH<sub>4</sub> (0.57 g, 15.0 mmol) in anhydrous THF (25 mL) cooled to -10 °C and under nitrogen atmosphere was added, in portions, dry AlCl<sub>3</sub> (0.67 g, 5.0 mmol). The mixture was stirred for 15 min at -15 °C and a solution of the corresponding benzoxazine (1.5 mmol) in dry THF (15 mL) was slowly added. The reaction mixture was stirred for 30-60 min at 0 °C (TLC) and quenched by addition of 10 % aqueous solution of NaOH (1.5 mL). The resulting mixture was filtered, the solid was washed with hot EtOAc, an the organic layer was dried over anhydrous MgSO<sub>4</sub>. The solvent was eliminated under reduced pressure, and the residue was chromatographed on silica gel using hexanes/EtOAc as eluent. Additional reflux for 25 min was necessary for reduction of oxazine **5d**.

(2S,6S)-7,7-Dimethyl-4-(8-mentholyl)-2-phenyl-6-phenylselenyl-1,4-oxazepane (12). Yield: 90%. Colorless solid. Mp: 138-139 °C (from hexane-ethyl acetate).  $[\alpha]_D^{25} =$  +41.5 (c = 0.9, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (333 K) ( $\delta$ ): 0.68-0.97 (m, 3H); 0.72 (s, 3H); 0.80 (s, 3H); 0.84 (d, 3H, *J* = 6.5 Hz); 1.28-1.47 (m, 2H); 1.31 (s, 3H); 1.53-1.60 (m, 2H); 1.61 (s, 3H); 1.91 (m, 1H); 2.75 (dd, 1H, *J*<sub>1</sub> = 11.3 Hz, *J*<sub>2</sub> = 4.4 Hz); 3.10 (dd, 1H, *J*<sub>1</sub> = 14.8 Hz, *J*<sub>2</sub> = 10.8 Hz); 3.17 (dd, 1H, *J*<sub>1</sub> = 11.3 Hz, *J*<sub>2</sub> = 10.1 Hz); 3.27 (dd, 1H, *J*<sub>1</sub> = 14.8 Hz, *J*<sub>2</sub> = 2.7 Hz); 3.40 (dd, 1H, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 2.7 Hz); 3.48 (td, 1H, *J*<sub>1</sub> = 10.4 Hz, *J*<sub>2</sub> = 4.0 Hz); 4.87 (dd, 1H, *J*<sub>1</sub> = 10.1 Hz, *J*<sub>2</sub> = 4.4 Hz); 7.165 (broad s, 1H); 7.21-7.41 (m, 8H); 7.63-7.67 (m, 2H). <sup>13</sup>C-NMR (333 K) ( $\delta$ ): 19.7 (CH<sub>3</sub>); 20.9 (CH<sub>3</sub>); 21.4 (CH<sub>3</sub>); 21.9 (CH<sub>3</sub>); 26.1 (CH<sub>2</sub>); 31.0 (CH<sub>3</sub>); 31.2 (CH); 35.0 (CH<sub>2</sub>); 44.2 (CH<sub>2</sub>); 46.7 (CH); 48.9 (CH<sub>2</sub>); 54.8 (CH<sub>2</sub>); 58.4 (CH); 61.7 (C); 71.9 (CH); 72.6 (CH); 77.1 (C); 126.0 (2 CH); 127.1 (CH); 127.8 (CH); 128.1 (2 CH); 129.0 (2 CH); 129.3 (C); 135.5 (2 CH); 142.8 (C). IR (Nujol): 3200 (broad), 3020, 1595 cm<sup>-1</sup>. Anal. Calcd. for C<sub>29</sub>H<sub>41</sub>NO<sub>2</sub>Se: C, 67.69; H, 8.03; N, 2.72. Found: C, 67.83; H, 7.90; N, 2.80.

(2S,6S)-4-(8-MentholyI)-6-methyl-2-phenyl-morpholine (13a). Yield: 87%. Colorless solid. Mp: 162-163 °C (from hexane).  $[\alpha]_D^{25} = -33.8$  (c = 0.7, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.87-1.039 (m, 3H); 0.92 (d, 3H, *J* = 6.5 Hz); 0.93 (s, 3H); 1.15 (s, 3H); 1.41 (m, 1H); 1.42 (d, 3H, *J* = 6.8 Hz); 1.54-1.60 (m, 2H); 1.69 (m, 1H); 1.96 (m, 1H); 2.39 (m, 1H); 2.62 (dd, 1H, *J*<sub>1</sub> = 11.5 Hz, *J*<sub>2</sub> = 4.0 Hz); 2.88 (m, 1H); 2.99 (m, 1H); 3.60 (td, 1H, *J*<sub>1</sub> = 10.0 Hz, *J*<sub>2</sub> = 4.0 Hz); 4.23 (m, 1H); 4.84 (dd, 1H, *J*<sub>1</sub> = 9.7 Hz, *J*<sub>2</sub> = 2.5 Hz); 7.212-7.40 (m, 5H); 7.64 (broad s, 1H). <sup>13</sup>C-NMR ( $\delta$ ): 16.9 (CH<sub>3</sub>); 17.8 (CH<sub>3</sub>); 20.6 (CH<sub>3</sub>); 21.9 (CH<sub>3</sub>); 25.9 (CH<sub>2</sub>); 30.9 (CH); 35.1 (CH<sub>2</sub>); 44.8 (CH<sub>2</sub>); 46.7 (CH); 49.4 (CH<sub>2</sub>); 52.2 (CH<sub>2</sub>); 60.7 (C); 69.0 (CH); 71.8 (CH); 72.5 (CH); 126.2 (2 CH); 127.5 (CH); 128.2 (2 CH); 140.6 (C). IR (Film): 3140 (broad), 1595, 750, 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>21</sub>H<sub>33</sub>NO<sub>2</sub>: C, 76.09; H, 10.03; N, 4.23. Found: C, 76.22; H, 10.12; N, 4.14.

(2S)-6,6-Dimethyl-4-(8-mentholyl)-2-phenyl-morpholine (13c). Yield: 95%. Colorless solid. Mp: 138-139 °C (from hexane).  $[\alpha]_{D}^{25} = -9.5$  (c = 1.1, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H- NMR ( $\delta$ ): 0.88 (s, 3H); 0.89-1.09 (m, 3H); 0.92 (d, 3H, J = 6.4 Hz); 1.15 (s, 3H); 1.30 (s, 3H); 1.40 (s, 3H); 1.42 (m, 1H); 1.510-1.73 (m, 3H); 1.98 (m, 1H); 2.07-2.20 (m, 2H); 2.92 (d, 1H, J = 11.3 Hz); 3.01 (d, 1H, J = 11.3 Hz); 3.62 (m, 1H); 4.75 (dd, 1H,  $J_1 = 9.1$  Hz,  $J_2 = 2.0$  Hz); 7.18-7.38 (m, 5H); 7.78 (broad s, 1H). <sup>13</sup>C-NMR ( $\delta$ ): 17.7 (CH<sub>3</sub>); 20.8 (CH<sub>3</sub>); 21.8 (CH<sub>3</sub>); 22.1 (CH<sub>3</sub>); 25.9 (CH<sub>2</sub>); 29.2 (CH<sub>3</sub>); 30.8 (CH); 35.1 (CH<sub>2</sub>); 44.8 (CH<sub>2</sub>); 46.5 (CH); 52.5 (CH<sub>2</sub>); 55.1 (CH<sub>2</sub>); 60.7 (C); 71.9 (C); 72.5 (CH); 72.8 (CH); 126.3 (2 CH); 127.5 (CH); 128.1 (2 CH); 140.9 (C). IR (Nujol): 3170 (broad), 1595, 745, 740, 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>22</sub>H<sub>35</sub>NO<sub>2</sub>: C, 76.47; H, 10.21; N, 4.05. Found: C, 76.56; H, 10.09; N, 4.14.

#### (2S,6S)-6-Isopropyl-4-(8-mentholyl)-2-methyl-2-phenyl-morpholine

(13f). Yield: 87%. Colorless solid. Mp: 121-122 °C (from hexane).  $[\alpha]_{D}^{25} = -108.8$  (c = 0.4, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.86-1.1 (m, 3H); 0.91 (d, 3H, *J* = 6.8 Hz); 0.93 (d, 3H, *J* = 6.8 Hz); 0.94 (s, 3H); 1.03 (d, 3H, *J* = 6.8 Hz); 1.08 (s, 3H); 1.33 (s, 3H); 1.40 (m, 1H); 1.60-1.80 (m, 4H); 1.85 (m, 1H); 2.09 (t, 1H, *J* = 10.5 Hz); 2.27 (d, 1H, *J* = 12.1 Hz); 2.82 (ddd, 1H, *J*<sub>1</sub> = 10.5 Hz, *J*<sub>2</sub> = 2.5 Hz, *J*<sub>3</sub> = 1.6 Hz); 3.26 (ddd, 1H, *J*<sub>1</sub> = 10.5 Hz, *J*<sub>2</sub> = 6.5 Hz, *J*<sub>3</sub> = 2.5 Hz); 3.37 (td, 1H, *J*<sub>1</sub> = 10.4 Hz, *J*<sub>2</sub> = 3.9 Hz); 3.62 (dd, 1H, *J*<sub>1</sub> = 12.1 Hz, *J*<sub>2</sub> = 1.6 Hz); 6.30 (broad s, 1H); 7.14-7.38 (m, 5H). <sup>13</sup>C-NMR ( $\delta$ ): 18.1 (CH<sub>3</sub>); 18.4 (CH<sub>3</sub>); 18.5 (CH<sub>3</sub>); 20.7 (CH<sub>3</sub>); 21.9 (CH<sub>3</sub>); 25.8 (CH<sub>2</sub>); 30.6 (CH); 31.6 (CH); 32.1 (CH<sub>3</sub>); 35.0 (CH<sub>2</sub>); 44.8 (CH<sub>2</sub>); 46.4 (CH); 47.7 (CH<sub>2</sub>); 52.8 (CH<sub>2</sub>); 60.1 (C); 72.1 (CH); 75.1 (CH); 75.7 (C); 125.8 (2 CH); 126.4 (CH); 127.9 (2 CH); 142.8 (C). IR (Nujol): 3180 (broad), 1595, 780, 750, 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>24</sub>H<sub>39</sub>NO<sub>2</sub>: C, 77.16; H, 10.52; N, 3.75. Found: C, 77.02; H, 10.68; N, 3.84.

(2S)-4-(8-Mentholyl)-2-methyl-morpholine (13g). Yield: 90%. Colorless solid. Mp: 93-94 °C (from hexane).  $[\alpha]_D^{25} = -20.4$  (c = 1.2, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (333 K) ( $\delta$ ): 0.83-1.09 (m, 3H); 0.90 (d, 3H, J = 6.3 Hz); 0.91 (s, 3H); 1.12 (d, 3H, J = 6.2 Hz); 1.13 (s, 3H); 1.40 (m, 1H); 1.53-1.64 (m, 2H); 1.70 (m, 1H); 1.91 (m, 1H); 2.04 (dd, 1H,  $J_1 = 11.0$  Hz,  $J_2 = 10.0$  Hz); 2.28 (td, 1H,  $J_1 = 11.5$  Hz,  $J_2 = 3.0$  Hz); 2.85 (dd, 1H,  $J_1 = 11.0$  Hz,  $J_2 = 3.0$  Hz); 2.99 (m, 1H); 3.45-3.62 (m, 3H); 3.84 (dt, 1H,  $J_1 = 11.5$  Hz,  $J_2 = 3.0$  Hz); 7.94 (broad s, 1H). <sup>13</sup>C-NMR (333 K) ( $\delta$ ): 18.0 (CH<sub>3</sub>); 19.1 (CH<sub>3</sub>); 20.4 (CH<sub>3</sub>); 21.9 (CH<sub>3</sub>); 25.9 (CH<sub>2</sub>); 30.9 (CH); 35.1 (CH<sub>2</sub>); 44.6 (CH<sub>2</sub>); 45.3 (CH<sub>2</sub>); 46.7 (CH); 51.8 (CH<sub>2</sub>); 60.4 (C); 66.7 (CH<sub>2</sub>); 72.4 (CH); 72.6 (CH). IR (Nujol): 3200 (broad), 2920, 1455 cm<sup>-1</sup>. Anal. Calcd. for C<sub>15</sub>H<sub>29</sub>NO<sub>2</sub>: C, 70.54; H, 11.45; N, 5.48. Found: C, 70.62; H, 11.55; N, 5.54.

(2S,6R)-4-(8-Mentholyl)-6-methyl-2-phenyl-morpholine (14a). Yield: 90%. Colorless oil.  $[\alpha]_D^{25} = -40.6$  (c = 0.7, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (333 K) ( $\delta$ ): 0.85-1.09 (m, 3H); 0.91 (s, 3H); 0.92 (d, 3H, J = 6.6 Hz); 1.14 (s, 3H); 1.25 (d, 3H, J = 6.2 Hz); 1.41 (m, 1H); 1.57-1.73 (m, 3H); 1.96 (m, 1H); 2.01 (dd, 1H,  $J_1 = 11.3$  Hz,  $J_2 = 10.4$  Hz); 2.21 (dd, 1H,  $J_1 = 11.3$  Hz,  $J_2 = 10.4$  Hz); 3.03 (dt, 1H,  $J_1 = 11.3$  Hz,  $J_2 = 2.1$  Hz); 3.10 (dt, 1H,  $J_1 = 11.3$  Hz,  $J_2 = 2.1$  Hz); 3.65 (1H, td,  $J_1 = 10.4$  Hz,  $J_2 = 4.0$  Hz); 3.79 (dqd, 1H,  $J_1 = 10.4$  Hz,  $J_2 = 6.2$  Hz,  $J_3 = 2.1$  Hz); 4.51 (dd, 1H,  $J_1 = 10.4$  Hz,  $J_2 = 2.1$  Hz); 7.23-7.39 (m, 5H); 8.02 (broad s, 1H). <sup>13</sup>C-NMR (333 K) ( $\delta$ ): 18.1 (CH<sub>3</sub>); 19.1 (CH<sub>3</sub>); 20.6 (CH<sub>3</sub>); 21.8 (CH<sub>3</sub>); 25.9 (CH<sub>2</sub>); 30.9 (CH); 35.1 (CH<sub>2</sub>); 44.5 (CH<sub>2</sub>); 46.6 (CH); 51.8 (2 CH<sub>2</sub>); 60.6 (C); 72,0 (CH); 72.5 (CH); 76.4 (CH); 126.2 (2 CH); 127.6 (CH); 128.2 (2 CH); 140.5 (C). IR (Film): 3180 (broad), 1595, 730 cm<sup>-1</sup>. Anal. Calcd. for C<sub>21</sub>H<sub>33</sub>NO<sub>2</sub>: C, 76.09; H, 10.03; N, 4.23. Found: C, 76.22; H, 10.04; N, 4.31.

(2S,6R)-6-Ethyl-4-(8-mentholyl)-2-phenyl-morpholine (14b). Yield: 92%. Colorless solid Mp: 124-125 °C (from hexane).  $[\alpha]_D^{25} = -2.9$  (c = 0.2, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (333 K) ( $\delta$ ): 0.86-1.08 (m, 3H); 0.91 (s, 3H); 0.92 (d, 3H, *J* = 6.5 Hz); 1.00 (t, 3H, *J* = 7.5 Hz); 1.14 (s, 3H); 1.38-1.71 (m, 6H); 1.94 (m, 1H); 2.03 (dd, 1H, *J*<sub>1</sub> = 11.0 Hz, *J*<sub>2</sub> = 10.4 Hz, Hz); 2.19 (dd, 1H, *J*<sub>1</sub> = 11.0 Hz, *J*<sub>2</sub> = 10.4 Hz, Hz); 3.05 (ddd, 1H, *J*<sub>1</sub> = 11.0 Hz, *J*<sub>2</sub> = 2.4

Hz,  $J_3 = 1.8$  Hz); 3.10 (ddd, 1H,  $J_1 = 11.0$  Hz,  $J_2 = 2.4$  Hz,  $J_3 = 1.8$  Hz); 3.54 (m, 1H); 3.65 (td, 1H,  $J_1 = 10.3$  Hz,  $J_2 = 4.2$  Hz); 4.50 (dd, 1H,  $J_1 = 10.4$  Hz,  $J_2 = 2.4$  Hz); 7.19-7.35 (m, 5H), 8.37 (broad s,1H). <sup>13</sup>C-NMR (333 K) ( $\delta$ ): 9.8 (CH<sub>3</sub>); 18.2 (CH<sub>3</sub>); 20.7 (CH<sub>3</sub>); 22.0 (CH<sub>3</sub>); 25.7 (CH<sub>2</sub>); 26.7 (CH<sub>2</sub>); 30.9 (CH); 35.0 (CH<sub>2</sub>); 44.4 (CH<sub>2</sub>); 46.3 (CH); 49.9 (CH<sub>2</sub>); 52.1 (CH<sub>2</sub>); 60.6 (C); 72.5 (CH); 76.5 (CH); 78.6 (CH); 126.1 (2 CH); 127.6 (CH); 128.2 (2 CH); 140.5(C). IR (Nujol): 3150 (broad), 760, 750, 700, 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>22</sub>H<sub>35</sub>NO<sub>2</sub>: C, 76.47; H, 10.21; N, 4.05. Found: C, 76.56; H, 10.32; N, 3.92.

(2S,6R)-6-Isopropyl-4-(8-mentholyl)-2-phenyl-morpholine (14e). Yield: 87%. Colorless solid. Mp: 101-102 °C (from hexane).  $[\alpha]_{D}^{25} = +1.5$  (c = 0.4, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (333 K) ( $\delta$ ): 0.86-1.07 (m, 3H); 0.90 (s, 3H); 0.92 (d, 3H, J = 6.5 Hz); 1.00 (d, 3H, J = 6.7 Hz; 1.02 (d, 3H, J = 6.7 Hz); 1.15 (s, 3H); 1.38-1.68 (m, 4H); 1.80 (m, 1H); 1.97 (m, 1H), 2.07 (dd, 1H,  $J_1 = 11.0$  Hz,  $J_2 = 10.4$  Hz, Hz); 2.15 (dd, 1H,  $J_1 = 11.0$  Hz,  $J_2 = 10.4$  Hz, Hz); 3.04 (dt, 1H,  $J_1 = 11.0$  Hz,  $J_2 = 2.3$  Hz); 3.09 (dt, 1H,  $J_1 = 11.0$  Hz,  $J_2 =$ = 2.3 Hz); 3.41 (ddd, 1H,  $J_1$  = 10.4 Hz,  $J_2$  = 5.8 Hz,  $J_3$  = 2.3 Hz); 3.65 (td, 1H,  $J_1$  = 10.2 Hz,  $J_2 = 3.9$  Hz); 4.50 (1H, dd,  $J_1 = 10.4$  Hz,  $J_2 = 2.3$  Hz); 7.24-7.40 (m, 5H); 8.43 (broad s, 1H). <sup>13</sup>C-NMR (333 K) (δ): 18.2 (CH<sub>3</sub>); 18.3 (CH<sub>3</sub>); 18.8 (CH<sub>3</sub>); 20.8 (CH<sub>3</sub>); 22.0 (CH<sub>3</sub>); 25.8 (CH<sub>2</sub>); 30.9 (CH); 31.5 (CH); 35.0 (CH<sub>2</sub>); 44.4 (CH<sub>2</sub>); 46.3 (CH); 47.7 (CH<sub>2</sub>); 52.3 (CH<sub>2</sub>); 60.7 (C); 72.5 (CH); 78.4 (CH); 80.1 (CH); 126.0 (2 CH); 127.6 (CH); 128.2 (2 CH); 140.8 (C). IR (Nujol): 3410 (broad), 1595, 735, 690 cm<sup>-1</sup>. Anal. Calcd. for C<sub>23</sub>H<sub>37</sub>NO<sub>2</sub>: C, 76.83; H, 10.37; N, 3.90. Found: C, 76.80; H, 10.52; N, 3.79. (2R)-4-(8-Mentholyl)-2-methyl-morpholine (14g). Yield: 90%. Cololess oil.  $\left[\alpha\right]_{D}^{25} = -$ 4.9 (c = 1.4, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (333 K) ( $\delta$ ): 0.78-1.05 (m, 3H); 0.84 (d, 3H, *J* = 6.5 Hz); 0.87 (s, 3H); 1.09 (d, 3H, J = 6.0 Hz); 1.10 (s, 3H); 1.31 (m, 1H); 1.49-1.72 (m, 3H); 1.85 (m, 1H); 1.92 (dd, 1H,  $J_1 = 11.1$  Hz,  $J_2 = 10.2$  Hz); 2.33 (td, 1H,  $J_1 = 11.3$  Hz}; 2.33 (td, 1H, J\_2 = 10.2 Hz); 2.33 (td, 1H, J\_2 = 10.2 Hz); 2.33 (td, 1H, J\_2 = 10.2 Hz); 2.33 (td, 2H, J\_2 = 10.2 3.0 Hz); 2.78 (m, 1H); 2.99 (m, 1H); 3.48-3.69 (m, 3H); 3.83 (ddd 1H,  $J_1 = 11.6$  Hz,  $J_2 = 3.0$  Hz,  $J_3 = 1.6$  Hz); 8.08 (broad s, 1H). <sup>13</sup>C-NMR (333 K) ( $\delta$ ): 18.1 (CH<sub>3</sub>); 19.0 (CH<sub>3</sub>); 20.4 (CH<sub>3</sub>); 21.8 (CH<sub>3</sub>); 25.9 (CH<sub>2</sub>); 30.9 (CH); 35.0 (CH<sub>2</sub>); 44.5 (CH<sub>2</sub>); 44.7 (CH<sub>2</sub>); 46.4 (CH); 52.2 (CH<sub>2</sub>); 61.0 (C); 67.1 (CH<sub>2</sub>); 71.7 (CH); 72.3 (CH). IR (Film): 3165 (broad), 2950, 2920, 2850, 1455, 825 cm<sup>-1</sup>. Anal. Calcd. for C<sub>15</sub>H<sub>29</sub>NO<sub>2</sub>: C, 70.54; H, 11.45; N, 5.48. Found: C, 70.46; H, 11.60; N, 5.39.

(2R)-2-Isopropyl-4-(8-mentholyl)-morpholine (14h). Yield: 88%. Cololess oil.  $[\alpha]_{D}^{25}$ = -2.5 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.78-1.08 (m, 3H); 0.90 (d, 3H, *J* = 6.3 Hz); 0.91 (s, 3H); 0.93 (d, 3H, *J* = 6.6 Hz); 0.95 (d, 3H, *J* = 6.6 Hz); 1.14 (s, 3H); 1.40 (m, 1H); 1.52-1.73 (m, 4H); 1.88-2.06 (m, 2H); 2.37 (td, 1H, td, 1H, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 2.8 Hz); 2.80 (m, 1H); 3.06 (m, 1H); 3.17 (m, 1H); 3.41-3.65 (m, 2H); 3.92 (ddd, 1H, *J*<sub>1</sub> = 11.3 Hz, *J*<sub>2</sub> = 2.8 Hz, *J*<sub>3</sub> = 1.5 Hz); 8.33 (s, 1H). <sup>13</sup>C-NMR ( $\delta$ ): 18.0 (2 CH<sub>3</sub>); 18.6 (CH<sub>3</sub>); 20.6 (CH<sub>3</sub>); 21.9 (CH<sub>3</sub>); 25.8 (CH<sub>2</sub>); 30.9 (CH); 31.2 (CH); 35.1 (CH<sub>2</sub>); 44.6 (CH<sub>2</sub>); 45.1 (CH<sub>2</sub>); 46.4 (CH); 48.5 (CH<sub>2</sub>); 60.4 (C); 67.3 (CH<sub>2</sub>); 72.4 (CH); 80.5 (CH). IR (Film): 3185 (broad), 1450, 750 cm<sup>-1</sup>. Anal. Calcd. for C<sub>17</sub>H<sub>33</sub>NO<sub>2</sub>: C, 72.03; H, 11.73; N, 4.94. Found: C, 69.90; H, 11.64; N, 5.08.

(1R,2S,6'S)-4'-(8-Mentholyl)-6'-phenyl-2-phenylselenenyl-spiro[cyclohexane-1,2'morpholine] (17). Yield: 68%. Colorless oil.  $[\alpha]_D^{25} = +3.2$  (c = 0.7, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.85 (d, 3H, J = 6.5 Hz); 0.87-0.98 (m, 2H); 0.90 (s, 3H); 1.12-1.46 (m, 5H); 1.20 (s, 3H); 1.51-1.90 (m, 8H); 1.98 (m, 1H); 2.07 (d, 1H, J = 11.1 Hz); 2.15 (dd, 1H,  $J_1 =$ 11.1 Hz,  $J_2 = 10.5$  Hz); 3.13 (ddd, 1H,  $J_1 = 11.1$  Hz,  $J_2 = 2.4$  Hz,  $J_3 = 1.4$  Hz); 3.48 (dd, 1H,  $J_1 = 11.1$  Hz,  $J_2 = 1.4$  Hz); 3.65 (td, 1H,  $J_1 = 10.3$  Hz,  $J_2 = 3.8$  Hz); 4.33 (m, 1H); 4.74 (dd, 1H,  $J_1 = 10.5$  Hz,  $J_2 = 2.4$  Hz); 7.25-7.43 (m, 8H); 7.90-7.98 (m, 2H); 8.10 (s, 1H). <sup>13</sup>C-NMR ( $\delta$ ): 18.6 (CH<sub>3</sub>); 20.0 (CH<sub>2</sub>); 20.5 (CH<sub>2</sub>); 21.0 (CH<sub>3</sub>); 22.1 (CH<sub>3</sub>); 23.9 (CH<sub>2</sub>); 26.0 (CH<sub>5</sub>); 31.1 (CH); 34.2 (CH<sub>2</sub>); 35 1 (CH<sub>2</sub>); 44.0 (CH<sub>2</sub>); 44.9 (CH); 46.0 (CH); 52.9 (CH<sub>2</sub>); 54.9 (CH<sub>2</sub>); 60.6 (C); 71.6 (CH); 73.7 (CH); 74.3 (C); 126.1 (2 CH); 127.4 (CH); 127.6 (CH); 128.2 (2 CH); 128.8 (2 CH); 129.1 (C); 135.5 (2 CH); 140.8 (C). IR (Film): 3250 (broad), 3040, 1600, 1595, 745,690 cm<sup>-1</sup>. Anal. Calcd. for  $C_{31}H_{43}NO_2Se: C, 68.87; H, 8.02; N, 2.59$ . Found: C, 68.99; H, 8.15; N, 2.51.

(2S,6S)-4-(8-Mentholyl)-2-(1-methyl-1-phenylselenenylethy)-6-phenyl-morpholine (18). Yield: 85%. Colorless oil.  $[\alpha]_D^{25} = -5.0$  (c = 0.3, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR ( $\delta$ ): 0.87-1.18 (m, 3H); 0.93 (s, 3H); 0.95 (d, 3H, J = 6.6 Hz); 1.18 (s, 3H); 1.40 (s, 3H); 1.48 (m, 1H); 1.50 (s, 3H); 1.59-1.78 (m, 3H); 2.02 (m, 1H); 2.17 (dd, 1H,  $J_1 = 11.0$  Hz,  $J_2 = 10.5$  Hz); 2.31 (dd, 1H,  $J_1 = 11.0$  Hz,  $J_2 = 10.5$  Hz); 3.05 (m, 1H); 3.58 (dd, 1H,  $J_1 = 11.0$  Hz,  $J_2 =$ 1.7 Hz); 3.67-3.74 (m, 2H); 4.51 (dd,1H,  $J_1 = 10.5$  Hz,  $J_2 = 2.4$  Hz); 7.23-7.40 (m, 8H); 7.73-7.76 (m, 2H); 8.25 (broad s, 1H). <sup>13</sup>C-NMR ( $\delta$ ): 18.4 (CH<sub>3</sub>); 20.9 (CH<sub>3</sub>); 22.1 (CH<sub>3</sub>); 25.7 (CH<sub>3</sub>); 25.8 (CH<sub>2</sub>); 27.5 (CH<sub>3</sub>); 30.9 (CH); 35.1 (CH<sub>2</sub>); 44.6 (CH<sub>2</sub>); 46.6 (CH); 46.8 (CH<sub>2</sub>); 48.4 (C); 52.4 (CH<sub>2</sub>); 60.9 (C); 72.6 (CH); 78.7 (CH); 82.1 (CH); 126.0 (2 CH); 127.2 (C); 127.6 (CH); 128.2 (2 CH); 128.6 (CH); 128.7 (2 CH); 138.6 (2 CH), 140.5 (C). IR (Film): 3120 (broad), 3040, 1600, 1570, 750, 730, 695 cm<sup>-1</sup>. Anal. Calcd. for C<sub>29</sub>H<sub>41</sub>NO<sub>2</sub>Se: C, 67.69; H, 8.03; N, 2.72. Found: C, 67.80; H, 8.15; N, 2.59.