Supporting information for

Synthesis of Chiral Cyclic Oligothiazolines: A Novel Chiral Structural Motif of Macrocyclic Molecule

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1. General procedure for the synthesis of cyclooligothiazolines 22, 23 and 25

BOP-Cl (2.0 eq.) and Et$_3$N (4.0 eq.) were added to a solution of thiol carboxylic acid 19 (106 mg, 0.20 mmol) or 24 (135 mg, 0.31 mmol) in anhydrous CH$_2$Cl$_2$ (4 mmol/L), and the mixture was stirred at ambient temperature for 18 to 20 h. The solution was then washed with 5% aq. NaHCO$_3$ and brine. Organic layer was dried over MgSO$_4$, concentrated and purified by flash column chromatography (Hexane/EtOAc, 2:1) on silica gel to give a mixture of cyclooligomerization products (dimer and trimer in the case of 19, trimer and tetramer in the case of 24). The mixture was then treated with neat TFA at room temperature for 20 min, evaporated to dryness. The residue was dissolved in benzene and refluxed for 4 h, then evaporated to leave the crude products. The crude products were purified by PTLC (hexane/EtOAc 1:3) to give pure 22 (22.5 mg) and 23 (15.1 mg) in the case of 19, and 23 (37.0 mg) and 25 (3.0 mg) in the case of 24.

2. Spectra data of compounds 22, 23 and 25

Cyclic octa-(4-β-methyl)thiazoline 22: \([\alpha]_D^{25} = -220 (c 0.50, \text{CHCl}_3)\); IR (film, cm$^{-1}$) 2974, 2927, 2861, 1621, 1432, 1365, 1268, 1178, 1009, 908; $^1$H-NMR (400 MHz, CDCl$_3$, 25 °C, TMS) $\delta = 3.70$ (d, $J = 10.8$ Hz, 8 H), 3.19 (d, $J = 10.8$ Hz, 8 H), 1.63 (s, 24 H); $^{13}$C-NMR (100 MHz, CDCl$_3$, 25 °C) $\delta = 175.7, 83.1, 43.6, 25.2$; FABMS: [M$^+$]: 793; HRMS Calcd. for C$_{32}$H$_{41}$N$_8$S$_8$: 793.1220; Found: 793.1205.
Cyclic dodeca-(4-\(\beta\)-methyl)thiazoline 23: \([\alpha]_D^{25} = -283\) (c 0.22, CHCl\(_3\)); IR (film, cm\(^{-1}\)) 2975, 2927, 2860, 1624, 1432, 1366, 1247, 1178, 1010, 907; \(^1\)H-NMR (400 MHz, CDCl\(_3\), 25 °C, TMS) \(\delta = 3.76\) (d, \(J = 10.8\) Hz, 12 H), 3.01 (d, \(J = 10.8\) Hz, 12 H), 1.76 (s, 36 H); \(^13\)C-NMR (100 MHz, CDCl\(_3\), 25 °C) \(\delta = 176.6, 83.4, 43.0, 25.9\); FABMS: [M]: 1188; HRMS Calcd. for C\(_{48}\)H\(_{60}\)N\(_{12}\)S\(_{12}\): 1188.1712; Found: 1188.1730.

Cyclic nona-(4-\(\beta\)-methyl)thiazoline 25: \([\alpha]_D^{25} = -223\) (c 0.50, CHCl\(_3\)); IR (film, cm\(^{-1}\)) 2975, 2927, 2861, 1622, 1431, 1366, 1264, 1179, 1009, 907; \(^1\)H-NMR (400 MHz, CDCl\(_3\), 25 °C, TMS) \(\delta = 3.75\) (d, \(J = 11.2\) Hz, 9 H), 3.22 (d, \(J = 11.2\) Hz, 9 H), 1.62 (s, 27 H); \(^13\)C-NMR (100 MHz, CDCl\(_3\), 25 °C) \(\delta = 175.7, 83.5, 43.3, 25.7\); FABMS: [M\(^+\)]: 892; HRMS Calcd. for C\(_{36}\)H\(_{46}\)N\(_9\)S\(_9\): 892.1362; Found: 892.1318.
**Figure 1.** $^1$H-NMR of octathiazoline 22

**Figure 2.** Variable-temperature $^1$H-NMR of dodecathiazoline 23 at: a) 0 °C; b) –30 °C; and c) –60 °C.
Figure 3. $^{13}\text{C}$-NMR of octathiazoline 22
Figure 4. $^1$H-NMR of dodecathiazoline 23
Figure 5. $^{13}$C-NMR of dodecatiazoline 23
Figure 6. $^1$H-NMR of nonathiazoline 25
Figure 7. $^{13}$C-NMR of nonathiazoline 25