Supplementary Material (ESI) for Chemical Communications

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_3N (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_2Cl_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, $CHCl_3$); IR (film, cm^{-1}) 2974, 2927, 2861, 1621, 1432, 1365, 1268, 1178, 1009, 908; ^{1}H-NMR (400 MHz, $CDCl_3$, 25 ˚C, TMS) δ = 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) δ = 175.7, 83.1, 43.6, 25.2; FABMS: [M^+]: 793; HRMS Calcd. for $C_{32}H_{41}N_8S_8$: 793.1220; Found: 793.1205.

Cyclic dodeca-(4-β-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) δ = 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) δ = 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-β-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) δ = 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) δ = 175.7, 83.5, 43.3, 25.7; FABMS: [M^+]: 892; HRMS Calcd. for $C_{36}H_{46}N_9S_9$: 892.1362; Found: 892.1318.

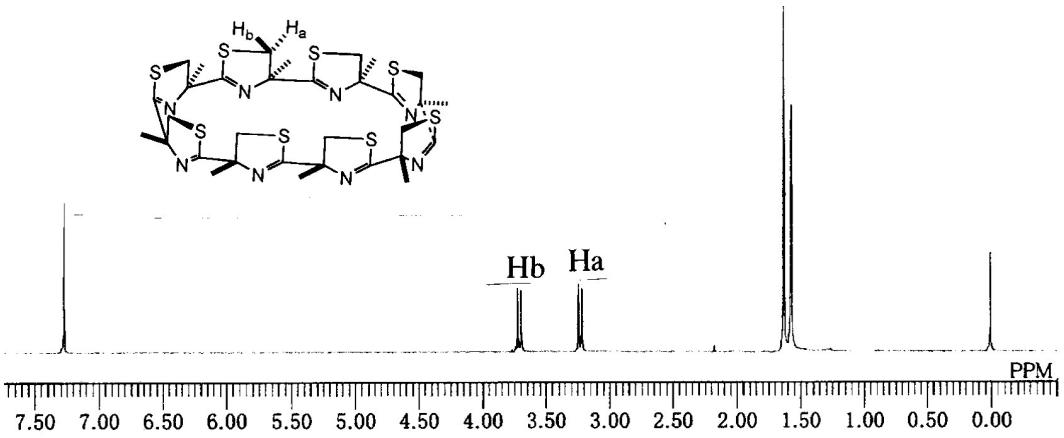

Figure 1. ^{1}H-NMR of octathiazoline **22**

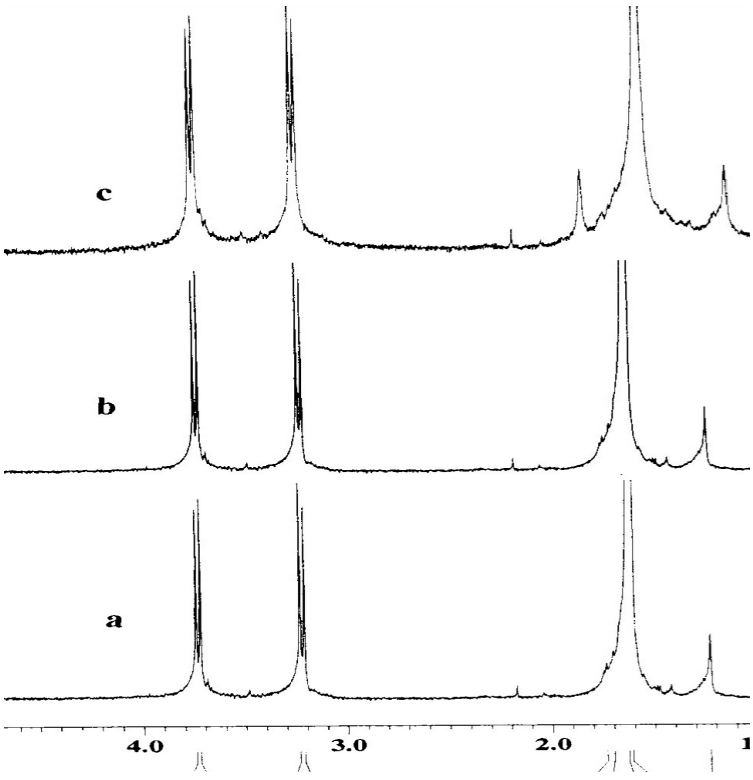

Figure 2. Variable-temperature ^{1}H-NMR of dodecathiazoline **23** at : a) 0 ˚C; b) –30 ˚C; and c) –60 ˚C.

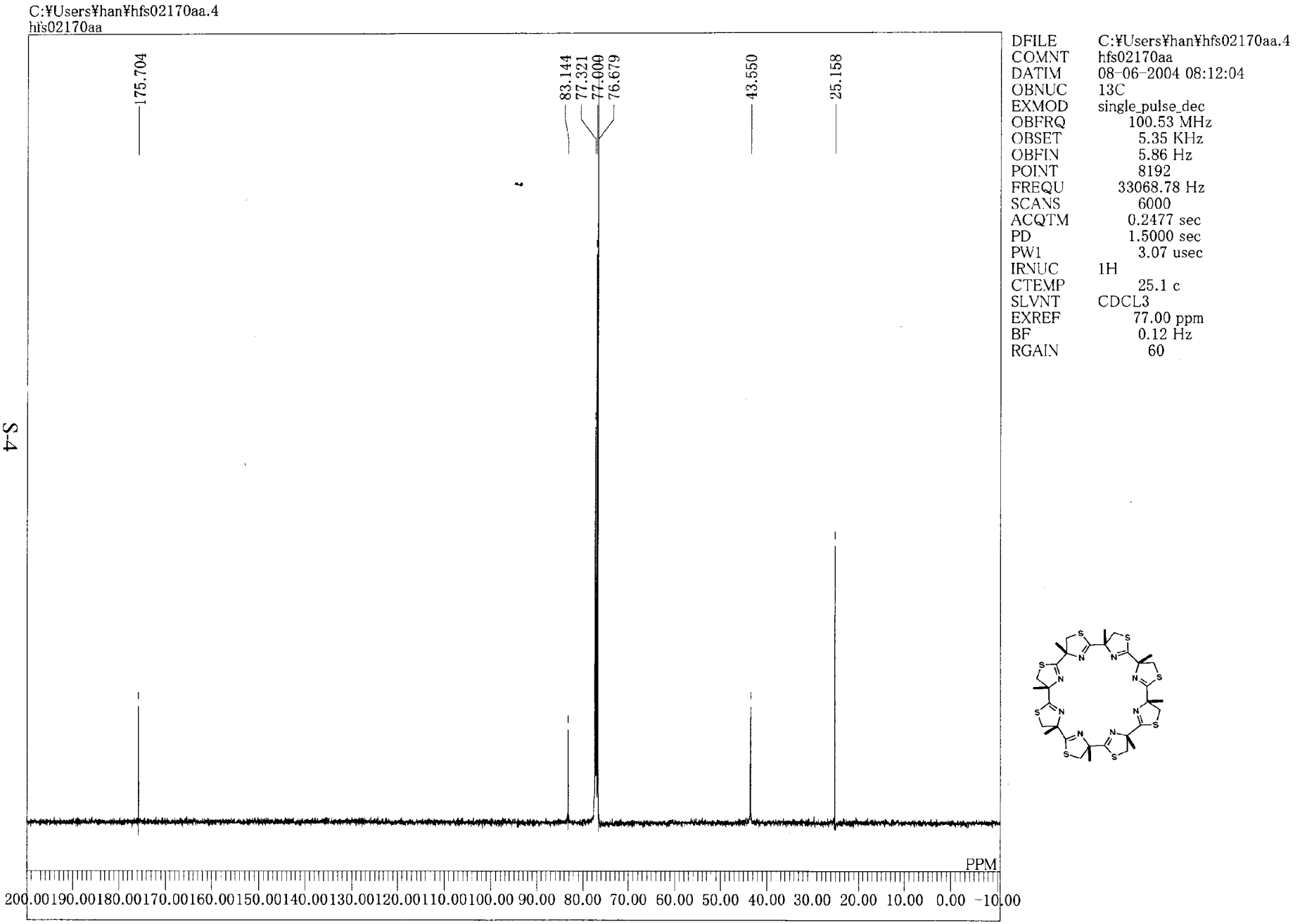

Figure 3. ^{13}C-NMR of octathiazoline **22**

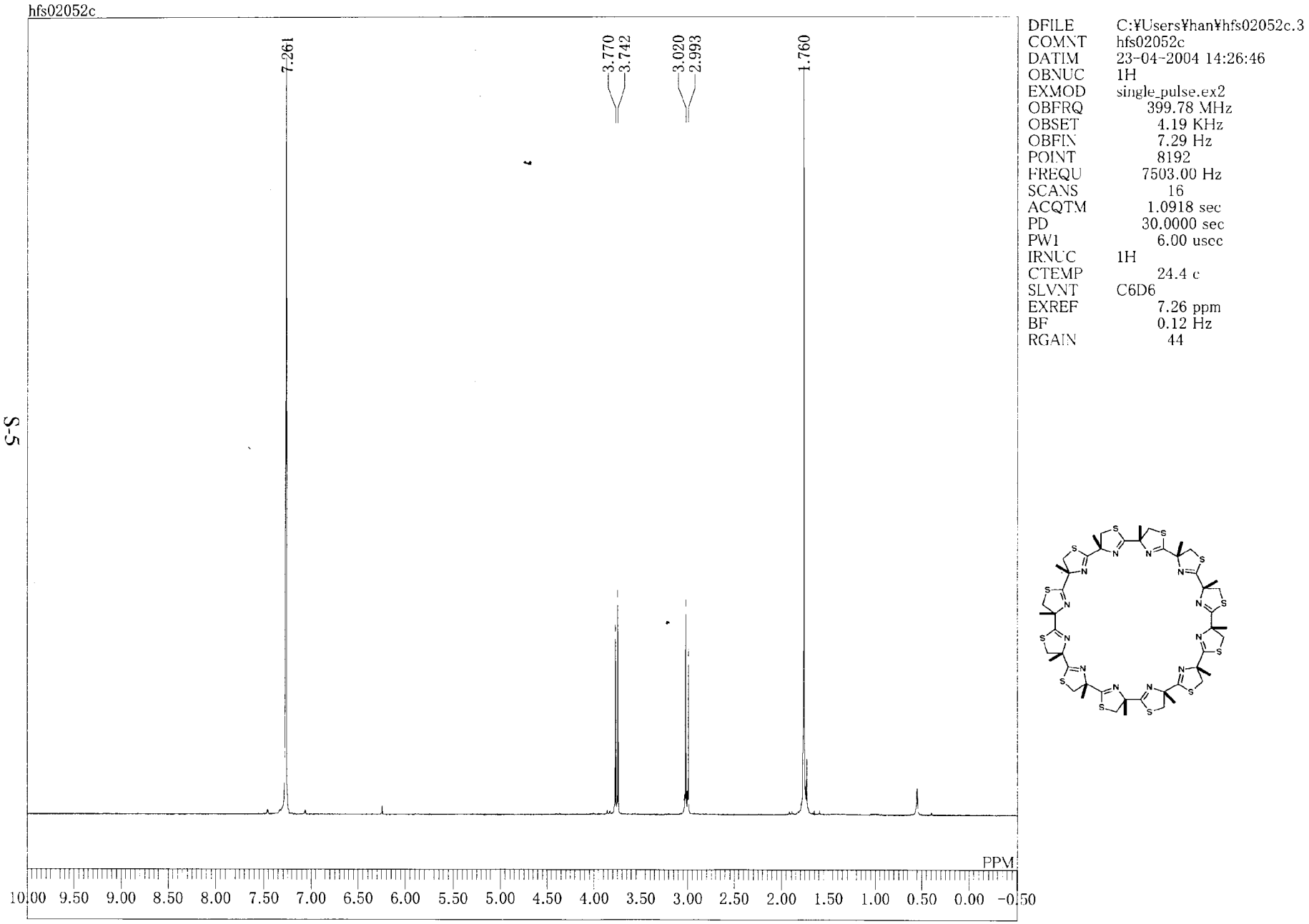

Figure **4.** ^{1}H-NMR of dodecathiazoline **23**

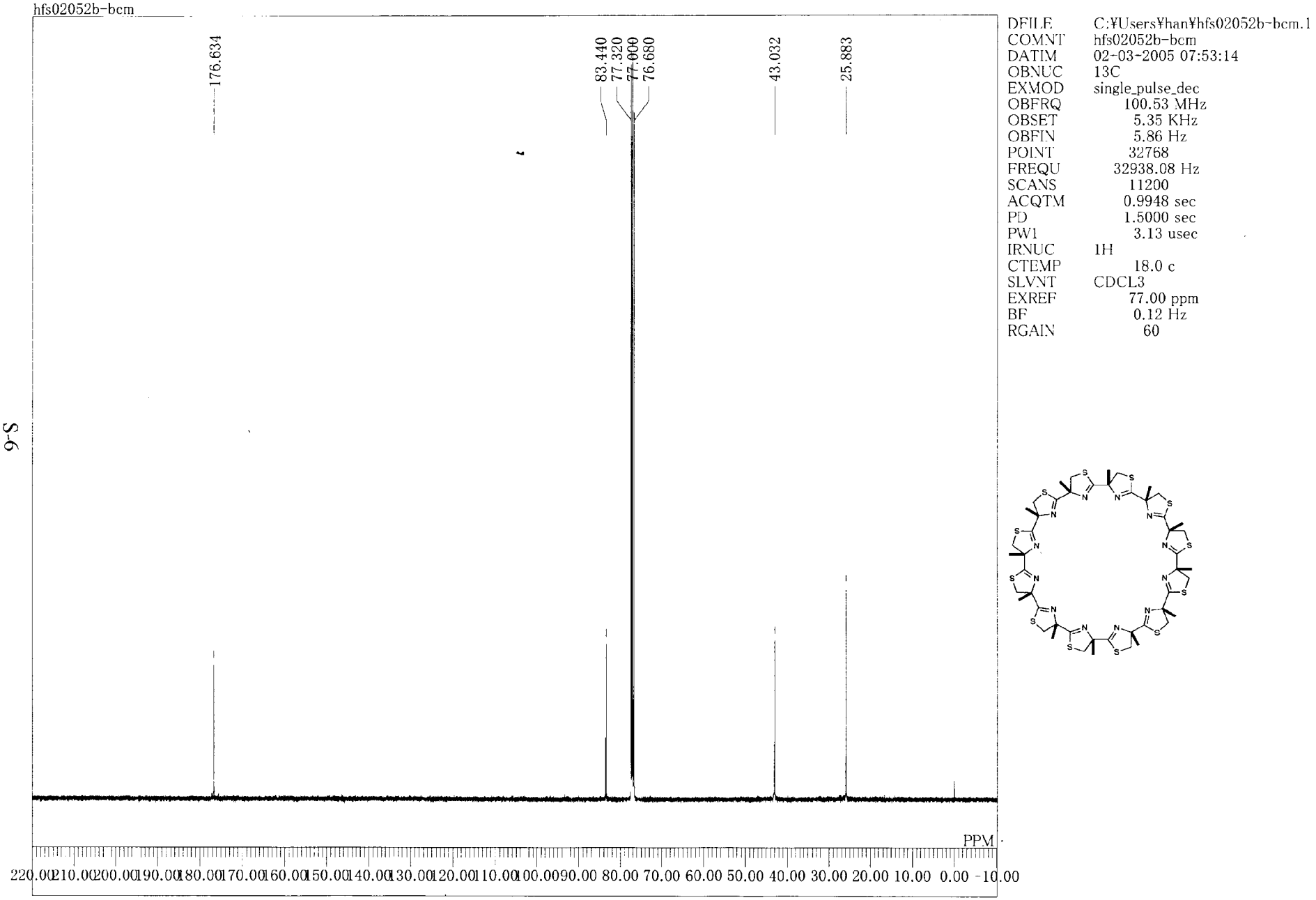

Figure **5.** ^{13}C-NMR of dodecathiazoline **23**

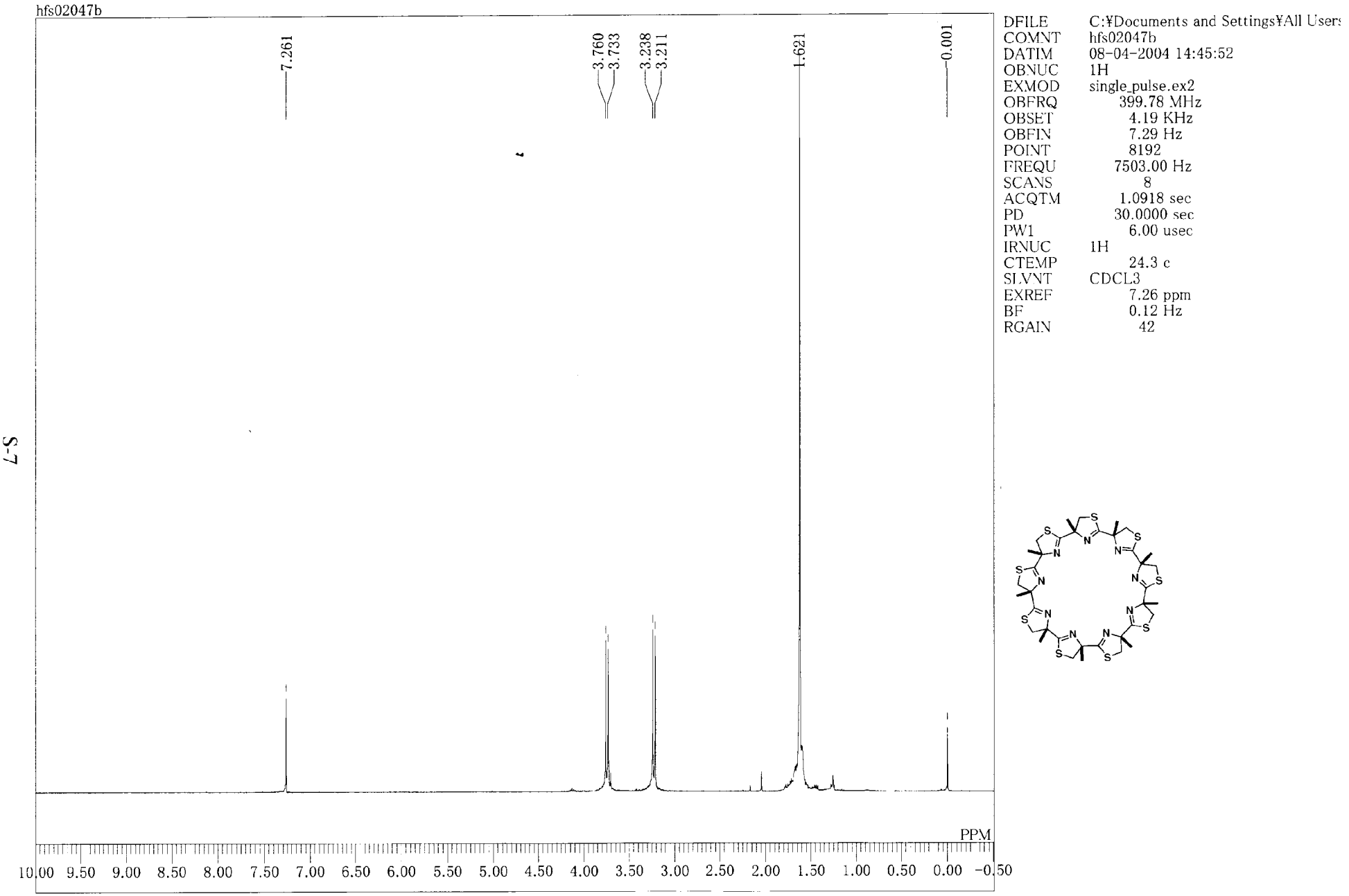

Figure **6.** ^{1}H-NMR of nonathiazoline **25**

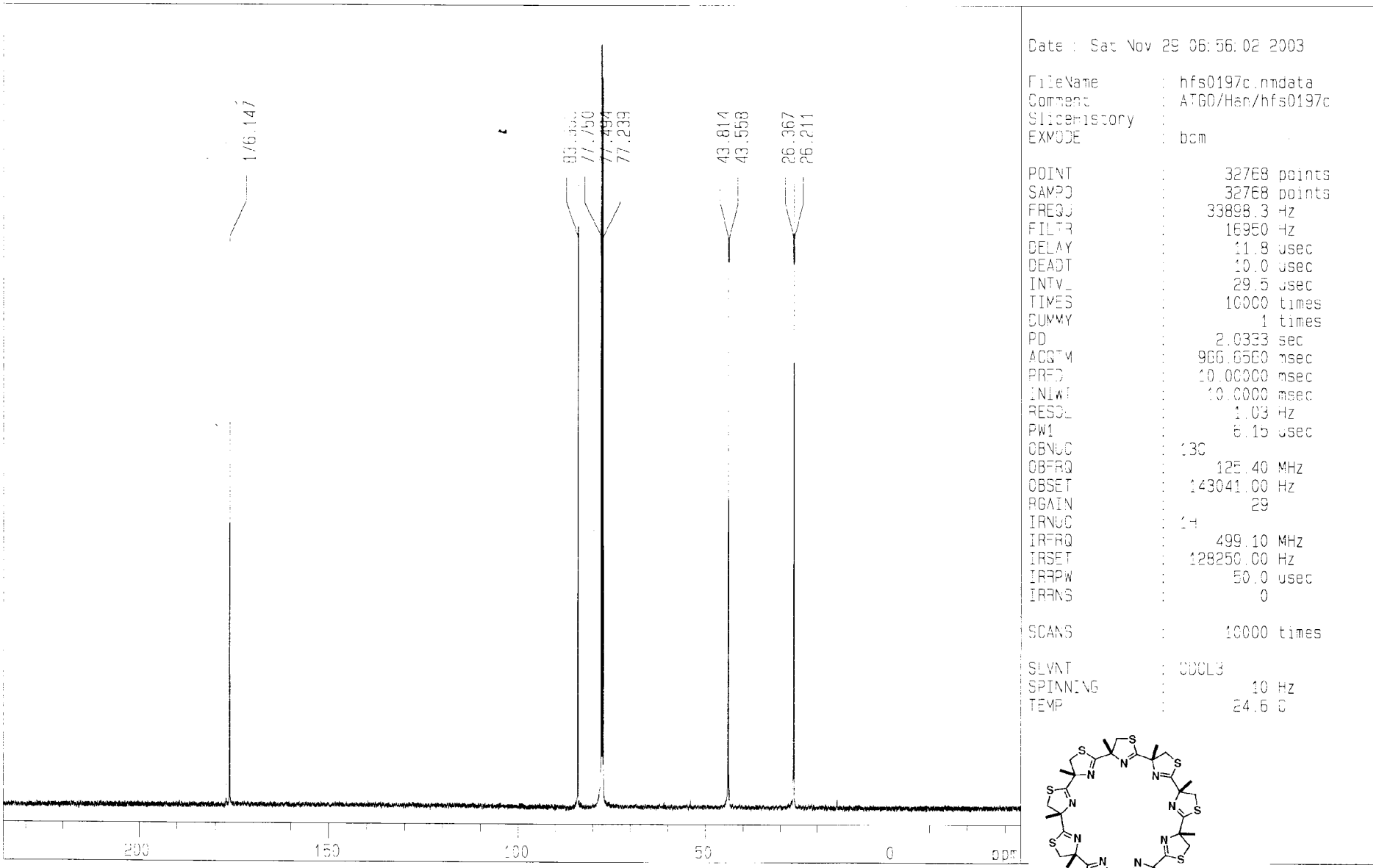

Figure 7. ^{13}C-NMR of nonathiazoline **25**