Synthesis of the Spiroiminal Moiety of Marineosins A and B

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General Experimental Methods. Reactions were conducted in flame- or oven-dried glassware under a nitrogen atmosphere and were stirred magnetically. The phrase "concentrated" refers to removal of solvents by means of a rotary evaporator attached to a diaphragm pump (15-60 Torr) followed by removal of residual solvents at < 1 Torr with a vacuum pump. Flash chromatography was performed on silica gel 60 (230-400 mesh). Analytical thin layer chromatography (TLC) was performed using silica gel 60 F-254 pre-coated glass plates (0.25 mm). TLC Plates were analyzed by short wave UV illumination, or by dipping in vanillin stain (27 g of vanillin in 380 mL of EtOH, 50 mL of water and 20 mL of concentrated sulfuric acid) and heating on a hot plate. THF and ether were dried and purified by distillation from sodium/benzophenone. Et_3N was distilled from CaH_2. ^1H and ^{13}C NMR spectra were obtained on a 400 MHz spectrometer in $CDCl_3$ with $CHCl_3$ as an internal standard (δ 7.26, $CDCl_3$ at δ 77.00) unless otherwise indicated. Chemical shifts are reported in δ (ppm downfield from tetramethylsilane). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet) and br (broad). IR spectra were acquired on an FT-IR spectrometer and are reported in wave numbers (cm^{-1}). High resolution mass spectra were obtained using the following ionization techniques: chemical ionization (CI), electron impact (EI), electrospray ionization analyzed by quadrupole time of flight (QTof).

Benzaldehyde Oxime (S1). A solution of benzaldehyde (530 mg, 5.0 mmol) in 20 mL of EtOH was treated with a mixture of NaOH (300 mg, 7.50 mmol) and $NH_2OH•HCl$ (783 mg, 11.4 mmol) in 10 mL of H_2O. The reaction mixture was stirred at 25 °C for 6 h, concentrated to remove EtOH, diluted with CH_2Cl_2, washed with brine, and dried (Na_2SO_4). Flash chromatography on silica gel (8:1 hexanes/EtOAc) gave 482 mg (84%) of **S1** with data identical to those previously reported.[12]

1-[[2-(Trimethylsilyl)ethoxy]methyl]-1*H*-pyrrole-2-carboxaldehyde (S2) was prepared by the literature procedure.[10] A solution of pyrrole-2-carboxaldehyde (245 mg, 2.57 mmol) in anhydrous THF (2 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 124 mg, 3.09 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min and SEMCl (0.50 mL, 2.83 mmol) was added by syringe over 3 min. The reaction was warmed to 25 °C and stirred for 2 h. The mixture was quenched with saturated aqueous NH_4Cl (3 mL). The aqueous layer was extracted with EtOAc and the combined organic layers were dried (Na_2SO_4) and concentrated. Flash chromatography on silica gel (8:1 hexanes/EtOAc) gave 538 mg (93%) of **S2**: ^{1}H NMR 9.58 (s, 1), 7.15-7.13 (m, 1), 6.96 (dd, 1, *J* = 1.5, 3), 6.30 (dd, 1, *J* = 3, 4), 5.70 (s, 2), 3.54 (t, 2, *J* = 8.1), 0.89 (t, 2, *J* = 8.1), -0.04 (s, 9); ^{13}C NMR 179.3, 131.6, 130.8, 125.0, 110.2, 76.2, 65.8, 17.5, -1.7 (3 C); IR (neat) 1671.

1-[[2-(Trimethylsilyl)ethoxy]methyl]-1*H*-pyrrole-2-carboxaldehyde Oxime (S3). A solution of aldehyde **S2** (538 mg, 2.39 mmol) in 11 mL of 10:1 MeOH/H_2O was treated with NH_2OH•HCl (183 mg, 2.63 mmol) and NaOAc (295 mg, 3.59 mmol). The resulting mixture was stirred at 25 °C for 2.5 h, concentrated to remove MeOH, diluted with CH_2Cl_2, washed with brine, dried (Na_2SO_4), and concentrated. Flash chromatography on silica gel (8:1 hexanes/EtOAc) gave 482 mg (84%) of **S3**: ^{1}H NMR 8.92 (s, 1, OH), 8.20 (s, 1), 6.87-6.85 (m, 1), 6.52 (dd, 1, *J* = 1.2, 2.5), 6.19 (dd, 1, *J* = 3, 4), 5.46 (s, 2), 3.50 (t, 2, *J* = 8.2), 0.91 (t, 2, *J* = 8.2), -0.03 (s, 9); ^{13}C NMR 142.3, 126.2, 125.2, 115.0, 109.1, 76.9, 65.5, 17.5, -1.6 (3 C); IR (neat) 3376, 1624; HRMS (EI) calc for $C_{11}H_{20}N_2O_2Si$ (M^+) 240.1294, found 240.1298.

7-Hydroxy-1-octen-3-one (18) was prepared by the literature procedure.[6] A solution of 6-Methyltetrahydropyran-2-one (**17**) (0.92 g, 8.76 mmol) in anhydrous THF (15 mL) was treated with vinylmagnesium bromide (1 M in THF, 10.51 mL, 10.51 mmol) by syringe over 15 min under nitrogen at -78 °C. The resulting solution was stirred at -78 °C for 4 h. The mixture was quenched with saturated aqueous NH_4Cl, diluted with EtOAc, washed with brine, dried (Na_2SO_4), and concentrated to give 1.11 g of crude **18**. Flash chromatography on MeOH-deactivated silica gel (4:1 hexanes/EtOAc) gave 1.06 g (85%) of **18**: ^{1}H NMR 6.36 (dd, 1, *J* = 10.4, 17.4), 6.24 (d, 1, *J* = 17.4), 5.85 (d, 1, *J* = 10.4), 3.81-3.76 (m, 1), 2.64 (t, 2, *J* = 6.7), 2.37 (s, 1, OH), 1.75-1.65 (m, 2), 1.50-1.43 (m, 2), 1.19 (d, 3, *J* = 6.7); ^{13}C NMR 201.0, 136.3, 128.2, 67.3, 39.2, 38.4, 23.3, 19.8; IR (neat) 3452 (br), 1729.

7-Triethylsilyloxy-1-octen-3-one (19). A solution of alcohol **18** (836 mg, 5.88 mmol) in 15 mL of THF was treated with Et_3N (1.36 mL, 9.41 mmol), DMAP (69 mg, 0.59 mmol), and TESCl (1.58 mL, 9.41 mmol). The mixture was stirred at 25 °C for 3 h. The reaction was then diluted with Et_2O (10 mL) and washed with brine (3 × 5 mL). The organic layer was dried ($MgSO_4$) and concentrated to give 1.78 g of crude **19**. Flash chromatography on silica gel (18:1 hexanes/EtOAc) gave 1.45 g (96%) of **19**: ^{1}H NMR 6.34 (dd, 1, *J* = 10.6, 17.6), 6.21 (d, 1, *J* = 17.6), 5.81 (d, 1, *J* = 10.6), 3.82-3.78 (m, 1), 2.59 (t, 2, *J* = 6.4), 1.72-1.58 (m, 2), 1.46-1.39 (m, 2), 1.14 (d, 3, *J* = 6.4), 0.95 (t, 9, *J* = 7.6), 0.58 (q, 6, *J* = 7.6); ^{13}C NMR 200.8, 136.5, 127.9, 68.2, 39.6, 39.1, 23.8, 20.3, 6.9 (3 C), 4.9 (3 C); IR (neat) 1682; HRMS (EI) calc for $C_{14}H_{27}O_2Si$ ($M-H^+$) 255.1780, found 255.1787.

1-(4,5-Dihydro-3-phenyl-5-isoxazolyl)-5-triethylsilyloxy-1-hexanone (20a). A solution of *N*-chlorosuccinimide (220 mg, 1.65 mmol) in anhydrous THF (3 mL) was added dropwise by syringe over 20 min to a solution of benzaldehyde oxime (**S1**) (170 mg, 1.40 mmol) in THF (6 mL). The mixture was stirred at 25 °C for 5 h, cooled to -78 °C, and treated with a solution of enone **19** (300 mg, 1.17 mmol) in THF (2 mL) and then Et_3N (240 μL, 1.65 mmol). The mixture was gradually warmed to 25 °C and stirred for 3 h. The reaction mixture was diluted with EtOAc, washed with brine, dried (Na_2SO_4), and concentrated. Flash chromatography on MeOH-deactivated silica gel (12:1 hexanes/EtOAc) gave 341 mg (78%) of **20a** as a 1:1 mixture of diastereomers: ^{1}H NMR 7.67 (d, 2, *J* = 6.1), 7.43-7.39 (m, 3), 5.03 (dd, 1, *J* = 6.1, 12.1), 3.79 (tq, 1, *J* = 6.1, 6.1), 3.64 (dd, 1, *J* = 6.1, 16.8), 3.48 (dd, 1, *J* = 12.1, 16.8), 2.73 (t, 2, *J* = 7.3), 1.73-1.52 (m, 2), 1.50-1.34 (m, 2), 1.12 (d, 3, *J* = 5.5), 0.94 (t, 9, *J* = 6.6), 0.57 (q, 6, *J* = 6.6); ^{13}C NMR 209.5, 156.6, 130.5, 128.8 (2 C), 128.5, 126.8 (2 C), 84.1, 68.1, (38.96, 38.94), (38.82, 38.81), (37.28, 37.25), 23.7, (19.30, 19.27), 6.8 (3 C), 4.9 (3 C); IR (neat) 1721, 1595; HRMS (EI) calc for $C_{19}H_{28}O_3NSi$ ($M^+-CH_2CH_3$) 346.1838, found 346.1837.

1-[4,5-Dihydro-3-[[2-(trimethylsilyl)ethoxy]methyl]-1*H*-pyrrole-5-isoxazolyl]-5-triethylsilyloxy-1-hexanone (20c). A mixture of oxime **S3** (440 mg, 1.83 mmol) and enone **19** (610 mg, 2.28 mmol) in CH_2Cl_2 (15 mL) was treated with bleach (5.25% aqueous NaOCl, 5.15 mL, 271 mg of NaOCl, 3.66 mmol) and Et_3N (40 µL, 0.28 mmol) at 0 °C. The resulting mixture was warmed to 25 °C and stirred for 3 h. The reaction was then diluted with CH_2Cl_2, washed with brine, dried (Na_2SO_4), and concentrated. Flash chromatography on MeOH-deactivated silica gel (12:1 hexanes/EtOAc) gave 661 mg (73%) of **20c** as a mixture of diastereomers: ^{1}H NMR 7.00-6.98 (m, 1), 6.46-6.44 (m, 1), 6.23-6.12 (m, 1), 5.67 (d, 1, J = 10.4), 5.60 (d, 1, J = 10.4), 4.87 (dd, 1, J = 6.2, 11.3), 3.79 (tq, 1, J = 6.1, 6.1), 3.60 (dd, 1, J = 6.2, 16.3), 3.53-3.46 (m, 3), 2.78-2.63 (m, 2), 1.72-1.50 (m, 2), 1.48-1.34 (m, 2), 1.12 (d, 3, J = 6.1), 0.94 (t, 9, J = 7,8), 0.89 (t, 2, J = 7.9), 0.57 (q, 6, J = 7.8), -0.04 (s, 9); ^{13}C NMR 209.7, 150.1, 127.5, 121.3, 116.0, 109.3, 82.4, 77.4, 68.1, 65.7, 39.4, 39.0, 38.8, (23.72, 23.70), 19.3, 17.7, 6.9 (3 C), 4.9 (3 C), -1.5 (3 C); IR (neat) 1721, 1598; HRMS (EI) calc for $C_{25}H_{46}O_4N_2Si_2$ (M^+) 494.2996, found 494.2989.

3,4-Dihydro-2,3-dimethoxy-2-(4-triethylsilyloxypentyl)-4-phenyl-2*H*-pyrrole (22a). A solution of isoxazoline **20a** (178 mg, 0.47 mmol) in 10 mL of MeOH was treated with a wet slurry of Raney nickel 2800 (~50 mg) and the suspension was stirred at 25 °C under H_2 (1 atm) for 35 min. The mixture was then diluted with EtOAc and filtered. The filtrate was washed with brine (3 × 5 mL), dried ($MgSO_4$), and concentrated to give 174 mg of crude hydroxy hemi-iminal **21a** as a mixture of four diastereomers that was used for the next step.

A solution of crude **21a** in anhydrous THF (2 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 152 mg, 3.80 mmol) in THF (5 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min and MeI (237 µL, 3.80 mmol) was then added by syringe over 3 min. The resulting mixture was warmed to 25 °C and stirred for 4 h. The reaction was quenched with saturated aqueous NH_4Cl (3 mL). The aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated to give 163 mg of crude **22a**. Flash chromatography on silica gel (18:1 hexanes/EtOAc) gave 110 mg (58% for two steps) of **22a** as a mixture of four diastereomers: ^{1}H NMR (major (75-80%) pair of diastereomers with either cis or trans methoxy groups) 7.87 (d, 2, J = 7.3), 7.46-7.39 (m, 3), 3.96-3.91 (m, 1), 3.84-3.75 (m, 1), 3.48 (s, 6), 3.20 (dd, 1, J = 7.3, 17.4), 3.02 (dd, 1, J = 3.0, 17.4), 1.96-1.82 (m, 1), 1.67-1.35 (m, 5), 1.14 (d, 3, *J* = 6.1), 0.93 (t, 9, *J* = 7.8), 0.58 (q, 6, *J* = 7.8); ^{1}H NMR (minor (20-25%) pair of diastereomers with either trans or cis methoxy groups) 3.48-3.24 (m, 2 or 3); IR (neat) 2955, 1619, 1449; HRMS (EI) calc for $C_{23}H_{39}O_3NSi$ (M^+) 405.2699, found 405.2710.

3,4-Dihydro-2,3-dimethoxy-2-(4-triethylsilyloxypentyl)-4-(1-[[2-(trimethylsilyl)-ethoxy]methyl]-1*H*-pyrrol-2-yl)-2*H*-pyrrole (22c). A solution of isoxazoline **20c** (203 mg, 0.41 mmol) in 12 mL of 5:1 MeOH/H_2O was treated with a wet slurry of Raney nickel 2800 (~50 mg) and the suspension was stirred at 25 °C under H_2 (1 atm) for about 50 min. The mixture was then diluted with EtOAc and filtered. The filtrate was washed with brine (3 × 5 mL), dried (Na_2SO_4), and concentrated to give 191 mg of crude hydroxy hemi-iminal **21c**.

A solution of crude **21c** in THF (2 mL) was added dropwise to a suspension of NaH (60% in mineral oil, 130 mg, 3.24 mmol) in THF (5 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min and MeI (203 μL, 3.24 mmol) was added dropwise by syringe over 3 min. The resulting mixture was warmed to 25 °C and stirred for 4 h. The reaction was quenched with saturated aqueous NH_4Cl (3 mL) and the aqueous layer was extracted with EtOAc. The combined organic layers were dried (Na_2SO_4), and concentrated to give 151 mg of crude **22c**. Flash chromatography on silica gel (15:1 hexanes/EtOAc) gave 91 mg (42% for two steps) of **22c** as a mixture of four diastereomers in which two predominate: ^{1}H NMR 7.03-7.01 (m, 1), 6.58-6.56 (m, 1), 6.21-6.19 (m, 1), 5.93 (d, 1, *J* = 10.4), 5.90 (d, 1, *J* = 10.4), 3.80-3.77 (m, 2), 3.54 (t, 2, *J* = 7.9), 3.44 (s, 3), 3.43 (s, 3), 3.12 (dd, 1, *J* = 6.7, 17.1), 2.96 (dd, 1, *J* = 2.4, 17.1), 1.83-1.77 (m, 1), 1.55-1.37 (m, 5), 1.13 (d, 3, *J* = 6.1), 0.94 (t, 9, *J* = 7.8), 0.87 (t, 2, *J* = 7.9), 0.57 (q, 6, *J* = 7.8), -0.05 (s, 9); IR (neat) 2954, 1617; HRMS (EI) calc for $C_{27}H_{52}O_4N_2Si_2$ (M^+) 524.3466, found 524.3475.

3-Methoxy-α-methyl-5-phenyl-1*H*- pyrrole-2-butanol (23a) and (4*S*, 5*R*, 7*R*)-*rel*-4-Methoxy-7-methyl-2-phenyl-6-oxa-1-azaspiro[4.5]dec-1-ene (24a), (4*R*, 5*R*, 7*R*)-*rel*-4-Methoxy-7-methyl-2-phenyl-6-oxa-1-azaspiro[4.5]dec-1-ene (25a), (4*R*, 5*S*, 7*R*)-*rel*-4-Methoxy-7-methyl-2-phenyl-6-oxa-1-azaspiro[4.5]dec-1-ene (27a). A solution of **22a** (101 mg, 243 μmol) in 6 mL of 1:1 CH_3CN/THF was treated with 2 M HCl (2.49 mL, 4.98 mmol) at 0 °C.

The resulting mixture was stirred at 0 °C for 40 min. Saturated $NaHCO_3$ (5 mL) was added to bring the pH to 7. The reaction was extracted with EtOAc and the organic layer was washed with brine, dried (Na_2SO_4), and concentrated. Flash chromatography on MeOH-deactivated silica gel (7:1 to 2:1 hexanes/EtOAc) gave 26 mg (41%) of **24a**, followed by 8.1 mg (13%) of **25a**, 7.4 mg (12%) of **27a,** and then 5.2 mg (8%) of **23a.**

The data for **23a**: ^{1}H NMR[13] (recorded in C_6D_6 because the compound is unstable in $CDCl_3$) 7.83 (br, 1, NH), 7.30 (d, 2, *J* = 7.3), 7.20 (t, 2, *J* = 7.3), 7.04 (t, 1, *J* = 7.3), 6.30 (d, 1, *J* = 2.5), 3.60 (s, 3), 3.58-3.48 (m, 1), 2.61 (t, 2, *J* = 7.4), 1.69-1.51 (m, 2), 1.38-1.25 (m, 2), 0.92 (d, 3, *J* = 6.1); ^{13}C NMR (C_6D_6) 146.0, 133.9, 129.0 (2 C), 126.9, 125.5, 123.4 (2 C), 117.5, 95.0, 67.8, 58.5, 38.3, 26.3, 24.5, 24.0; IR (neat) 3316, 2934, 1630; HRMS (EI) calc for $C_{16}H_{21}O_2N$ (M^+) 259.1572, found 259.1523; HRMS (EI) calc for $C_{16}H_{19}O_2N$ (M^+-2H) 257.1416, found 257.1407.

The data for **24a**: ^{1}H NMR 7.84 (d, 2, *J* = 6.7), 7.44-7.38 (m, 3), 4.43-4.39 (m, 1, H-7), 3.88 (dd, 1, *J* = 7.0, 7.0, H-4), 3.46 (s, 3), 3.30 (dd, 1, *J* = 17.1, 7.0, H-3), 2.77 (dd, 1, *J* = 16.4, 7.0, H-3), 2.07 (br ddd, 1, *J* = 11, 11, 11, H-9ax), 1.79 (ddd, 1, *J* = 11, 11, 3, H-10ax), 1.77-1.69 (m, 2, H-8eq, H-9eq), 1.51 (br d, 1, *J* = 11, H-10eq), 1.36 (br ddd, 1, *J* = 11, 11, 11, H-8ax), 1.16 (d, 3, *J* = 6.1, H-7 Me); ^{13}C NMR 169.6, 134.8, 130.8, 128.4 (2 C), 127.6 (2 C), 103.8, 87.2, 68.7, 58.2, 39.1, 33.6, 28.7, 22.4, 19.8; IR (neat) 2932, 1615, 1448; HRMS (EI) calc for $C_{16}H_{21}O_2N$ (M^+) 259.1572, found 259.1560. A 1D NOESY experiment with irradiation of the H-4 at δ 3.88 showed NOEs to the protons at δ 3.46 (OMe), 3.30 (H-3), and 2.77 (H-3). A 1D NOESY experiment with irradiation of H-7 at δ 4.43-4.39 showed NOEs to protons at δ 2.07 (H-9ax), δ 1.77-1.69 (H-8eq) and 1.16 (H-7 Me).

The data for **25a**: ^{1}H NMR 7.86 (d, 2, *J* = 7.3), 7.46-7.36 (m, 3), 4.49-4.42 (m, 1, H-7), 3.77 (dd, 1, *J* = 6.1, 4.0, H-4), 3.50 (s, 3), 3.13 (dd, 1, *J* = 17.1, 6.1, H-3), 3.05 (dd, 1, *J* = 17.1, 4.0, H-3), 2.12 (br ddd, 1, *J* = 11, 11, 11, H-9ax), 1.77 (ddd, 1, *J* = 11, 11, 3, H-10ax), 1.76-1.68 (m, 2, H-8eq, H-9eq), 1.48 (br d, 1, *J* = 11, H-10eq), 1.40 (br ddd, 1, *J* = 11, 11, 11, H-8ax), 1.23 (d, 3, *J* = 6.7, H-7 Me); ^{13}C NMR 170.3, 134.8, 130.7, 128.3 (2 C), 127.7 (2 C), 101.7, 85.4, 68.6, 58.8, 39.6, 34.7, 33.3, 22.3, 20.4; IR (neat) 2930, 1616, 1448; HRMS (EI) calc for $C_{16}H_{21}O_2N$ (M^+) 259.1572, found 259.1570. A 1D NOESY experiment with irradiation of H-4 at δ 3.77 showed NOEs to the protons at δ 3.50 (OMe), 3.13 (H-3), 3.05 (H-3), 1.77 (H-10ax) and 1.48 (H-10eq).

The data for **27a**: ^{1}H NMR 7.90 (d, 2, *J* = 7.4), 7.44-7.36 (m, 3), 4.11 (dd, 1, *J* = 6.7, 3.6, H-4), 3.83-3.76 (m, 1, H-7), 3.40 (s, 3), 3.36 (dd, 1, *J* = 17.4, 6.7, H-3), 2.94 (dd, 1, *J* = 17.4, 3.6, H-3), 2.06-2.01 (m, 1), 1.88-1.75 (m, 3), 1.62 (br d, 1, *J* = 11), 1.46-1.38 (m, 1), 1.23 (d, 3, *J* = 6.1); ^{13}C NMR 171.9, 134.0, 131.1, 128.2 (2 C), 128.1 (2 C), 105.4, 83.8, 69.9, 57.7, 40.1, 32.2, 28.9, 22.3, 20.6; IR (neat) 2930, 1627, 1448; HRMS (EI) calc for $C_{16}H_{21}O_2N$ (M^+) 259.1572, found 259.1556. A 1D NOESY experiment with irradiation of H-4 at δ 4.11 showed NOEs to the protons at δ 3.83-3.76 (H-7), 3.40 (OMe), 3.36 (H-3) and 2.94 (H-3).

Equilibration of 25a and 27a. A solution of **25a** in 0.6 mL of $CDCl_3$ (containing HCl/DCl from decomposition of $CDCl_3$) equilibrated to a 3:1 mixture of **25a** and **27a.** The percentage of **25a** in the mixture was determined as a function of time by ^{1}H NMR spectroscopy: initial, 100%; 7 days, 90%; 14 days, 80%; 20 days, 75%. The spectrum did not change at longer times. A solution of **27a** in 0.6 mL of $CDCl_3$ (containing HCl/DCl from decomposition of $CDCl_3$) equilibrated to a 3:1 mixture of **25a** and **27a.** The percentage of **25a** in the mixture was determined as a function of time by ^{1}H NMR spectroscopy: initial, <2%; 5 days, 25%; 10 days, 60%, 15 days, 75%. The spectrum did not change at longer times.

Equilibration of 24a and 26a. A solution of **24a** in 0.6 mL of $CDCl_3$ (containing HCl/DCl from decomposition of $CDCl_3$) was monitored by ^{1}H NMR for 14 days, at which time a 19:1 mixture of **24a** and **26a** was present. Partial data for **26a** were determined from the mixture: ^{1}H NMR 4.13 (d, 1, *J* = 4.9, H-4), 3.80-3.74 (m, 1, H-7), 3.36 (s, 3, OMe), 3.20 (d, 1, *J* = 17.4, H-3), 2.99 (dd, 1, *J* = 17.4, 4.9, H-3).

(4*S*, 5*R*, 7*R*)-*rel*-4-Methoxy-7-methyl-2-(1-[[2-(trimethylsilyl)ethoxy]methyl]-1*H*-pyrrol-2-yl)-6-oxa-1-azaspiro[4.5]dec-1-ene (24c), and (4*R*, 5*R*, 7*R*)-*rel*-, (4*R*, 5*S*, 7*R*)-4-*rel*-Methoxy-7-methyl-2-(1-[[2-(trimethylsilyl)ethoxy]methyl]-1*H*-pyrrol-2-yl)-6-oxa-1-

azaspiro[4.5]dec-1-ene (25c, 27c). A solution of **22c** (78 mg, 149 μmol) in 8 mL of 3:1 CH_3CN/THF was treated with aqueous 2 M HCl (1.49 mL, 2.98 μmol) at 25 °C. The resulting mixture was stirred at 25 °C for 11 h. Saturated $NaHCO_3$ (3 mL) was added to bring the pH to 7. The reaction was extracted with EtOAc and the organic layer was washed with brine, dried (Na_2SO_4), and concentrated to give 77 mg of a mixture of spiroiminals. Flash chromatography on MeOH-deactivated silica gel (18:1 to 2:1 hexanes/EtOAc) gave 19 mg (34%) of isomer **24c** followed by 19 mg (34%) of an inseparable 3:2 mixture of isomers **25c** and **27c.**

The data for **24c**: ^{1}H NMR 7.02-7.00 (m, 1), 6.57-6.55 (m, 1), 6.21-6.19 (m, 1), 6.01 (d, 1, *J* = 10.1), 5.88 (d, 1, *J* = 10.1), 4.29-4.22 (m, 1, H-7), 3.77 (dd, 1, *J* = 6.9, 6.9, H-4), 3.55 (t, 2, *J* = 8.2), 3.43 (s, 3), 3.23 (dd, 1, *J* = 6.9, 16.3, H-3), 2.76 (dd, 1, *J* = 6.9, 16.3, H-3), 1.98 (br ddd, 1, *J* = 11, 11, 11, H-9ax), 1.76 (ddd, 1, *J* = 11, 11, 3, H-10ax), 1.76-1.64 (m, 2, H-8eq, H-9eq), 1.49 (br d, 1, *J* = 11, H-10eq), 1.34 (br ddd, 1, *J* = 11, 11, 11, H-8ax), 1.13 (d, 3, *J* = 6.1), 0.88 (t, 2, *J* = 8.2), -0.05 (s, 9); ^{13}C NMR 162.6, 127.6, 127.5, 116.6, 108.9, 104.3, 86.2, 76.8, 68.6, 65.5, 58.2, 40.5, 33.6, 29.0, 22.4, 20.0, 18.0, -1.5 (3 C); IR (neat) 1610; HRMS (EI) calc for $C_{20}H_{34}O_3N_2Si$ (M^+) 378.2339, found 378.2325.

The data for **25c** and **27c:** ^{1}H NMR 7.03-7.01 (m, 0.6 × 1, **25c**), 7.01-6.99 (m, 0.4 × 1, **27c**), 6.57-6.55 (m, 1), 6.38 (d, 0.4 × 1, *J* = 10.4, **27c**), 6.20-6.17 (m, 1), 6.16 (d, 0.6 × 1, *J* = 10.1, **25c**), 5.74 (d, 0.6 × 1, *J* = 10.1, **25c**), 5.54 (d, 0.4 × 1, *J* = 10.4, **27c**), 4.35-4.29 (m, 0.6 × 1, **25c**), 3.97 (dd, 0.4 × 1, *J* = 6.0, 3.1, **27c**), 3.81-3.75 (m, 0.4 × 1, **27c**), 3.67 (dd, 0.6 × 1, *J* = 6.0, 4.8, **25c**), 3.56 (t, 0.6 × 2, *J* = 8.5, **25c**), 3.51 (t, 0.4 × 2, *J* = 8.5, **27c**), 3.47 (s, 0.6 × 3, **25c**), 3.36 (s, 0.4 × 3, **27c**), 3.28 (dd, 0.4 × 1, *J* = 16.8, 6.0, **27c**), 3.06 (dd, 0.6 × 1, *J* = 17.2, 6.0, **25c**), 3.01 (dd, 0.6 × 1, *J* = 17.2, 4.8, **25c**), 2.86 (dd, 0.4 × 1, *J* = 16.8, 3.1, **27c**), 2.06-1.99 (m, 1), 1.78-1.35 (m, 5), 1.21 (d, 3, *J* = 6.1), 0.90-0.85 (m, 2), -0.04 (s, 0.4 × 9, **27c**), -0.05 (s, 0.6 × 9, **25c**); ^{13}C NMR 164.8 (**27c**), 162.9 (**25c**), 127.6 (**25c, 27c**), 127.4 (**25c, 27c**), 117.0 (**27c**), 116.7 (**25c**), 108.9 (**25c, 27c**), 106.2 (**27c**), 102.0 (**25c**), 84.3 (**25c**), 82.0 (**27c**), 70.1 (**27c**), 68.6 (**25c**), 65.6 (**25c, 27c**), 58.6 (**25c**), 57.4 (**27c**), 41.2 (**27c**), 40.8 (**25c**), 34.8 (**25c**), 33.4 (**25c**), 32.2 (**27c**), 29.4 (**27c**), 22.4 (**27c**), 22.3 (**25c**), 20.6 (**25c**), 20.5 (**27c**), 18.0 (**25c**), 17.9 (**27c**), -1.5 (3 C, **25c, 27c**), (one peak for each compound is obscured by the $CDCl_3$ triplet at δ 77.0) ; IR ($CDCl_3$) 1613; HRMS (EI) calc for $C_{20}H_{34}O_3N_2Si$ (M^+) 378.2339, found 378.2350.

(4*S*, 5*R*, 7*R*)-*rel*-4-Methoxy-7-methyl-2-(1*H*-pyrrol-2-yl)-6-oxa-1-azaspiro[4.5]dec-1-ene (24b). A mixture of **24c** (19 mg, 50.2 μmol) and molecular sieves (4 Å, 100 mg) in freshly distilled THF (3 mL) was treated with TBAF (1 M in THF, 1.01 mL, 1.01 mmol) dropwise at 50 °C. The resulting mixture was stirred at 60 °C for 3 h. The reaction was cooled, diluted with Et_2O (15 mL), washed with brine (2 × 5 mL) and H_2O (3 × 5 mL). The organic layer was dried ($MgSO_4$) and concentrated to give 59 mg crude of **24c**. Flash chromatography on MeOH-deactivated silica gel (4:1 hexanes/EtOAc) gave 5.7 mg (54%) of isomer A (**24b**): ^{1}H NMR 6.94-6.91 (m, 1), 6.57-6.54 (m, 1), 6.25-6.23 (m, 1), 4.26-4.20 (m, 1), 3.82 (dd, 1, *J* = 6.7, 6.1), 3.43 (s, 3), 3.19 (dd, 1, *J* = 16.4, 6.7), 2.73 (dd, 1, *J* = 16.4, 6.1), 1.97 (br ddd, 1, *J* = 11, 11, 11, H-9ax), 1.81-1.66 (m, 3, H-10ax, H-8eq, H-9eq), 1.54 (br d, 1, *J* = 11, H-10eq), 1.32 (br ddd, 1, *J* = 11, 11, 11, H-8ax), 1.12 (d, 3, *J* = 6.1, H-7 Me), the pyrrole NH was not observed; ^{13}C NMR 162.8, 127.7, 122.1, 113.7, 109.8, 103.4, 86.9, 68.5, 58.1, 38.5, 33.4, 28.7, 22.4, 19.7; IR ($CDCl_3$) 2930, 1607, 1432, 743; HRMS (EI) calc $C_{14}H_{20}N_2O_2$ (M^+) 248.1525, found 248.1532.

(4*R*, 5*R*, 7*R*)-*rel*-, (4*R*, 5*S*, 7*R*)-*rel*-4-Methoxy-7-methyl-2-(1*H*-pyrrol-2-yl)-6-oxa-1-azaspiro[4.5]dec-1-ene (25b, 27b). A mixture of **25c** and **27c** (19 mg, 50.2 μmol), and molecular sieves (4 Å, 100 mg) in freshly distilled THF (3 mL) was treated with TBAF (1 M in THF, 1.01 mL, 1.01 mmol) dropwise at 50 °C. The resulting mixture was then stirred at 60 °C for 3 h. The reaction was cooled, diluted with Et_2O (15 mL), washed with brine (2 × 5 mL) and H_2O (3 × 5 mL). The organic layer was dried ($MgSO_4$) and concentrated to give 65 mg crude of **25b** and **27b**. Flash chromatography on MeOH-deactivated silica gel (4:1 to 2:1 hexanes/EtOAc) gave 5.9 mg (56%) of an inseparable 7:3 mixture of **25b** and **27b**: ^{1}H NMR 6.94-6.92 (m, 0.7 × 1, **25b**), 6.92-6.90 (m, 0.3 × 1, **27b**), 6.56-6.54 (m, 1), 6.25-6.21 (m, 1), 4.31-4.23 (m, 0.7 × 1, **25b**), 4.07 (dd, 0.3 × 1, *J* = 6.1, 3.0, **27b**), 3.81-3.73 (m, 0.3 × 1, **27b**), 3.70 (dd, 0.7 × 1, *J* = 6.1, 4.3, **25b**), 3.48 (s, 0.7 × 3, **25b**), 3.38 (s, 0.3 × 3, **27b**), 3.24 (dd, 0.3 × 1, *J* = 17.0, 6.1, **27b**), 3.03 (dd, 0.7 × 1, *J* = 16.4, 6.1, **25b**), 2.97 (dd, 0.7 × 1, *J* = 16.4, 4.3, **25b**), 2.85 (dd, 0.3 × 1, *J* = 17.0, 3.0,

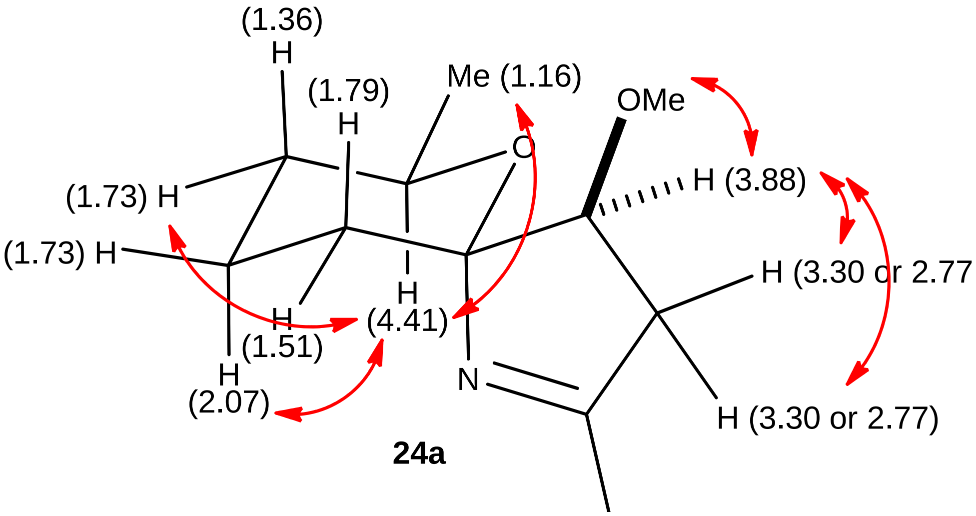
27b), 2.08-1.98 (m, 1), 1.81-1.32 (m, 5), 1.21 (d, 0.3 × 3, *J* = 6.1, **27b**), 1.19 (d, 0.7 × 3, *J* = 6.1, **25b**), the pyrrole NHs were not observed; ^{13}C NMR 164.4 (**27b**), 163.1 (**25b**), (127.8, 127.1), (122.5, 122.2), (114.2, 113.6), (109.9, 109.8), 105.0 (**27b**), 100.7 (**25b**), 85.3 (**25b**), 83.1 (**27b**), 70.1 (**27b**), 68.4 (**25b**), 58.8 (**25b**), 57.5 (**27b**), 39.4 (**27b**), 38.6 (**25b**), 34.3 (**25b**), 33.3 (**25b**), 32.3 (**27b**), 29.1 (**27b**), 22.4 (**27b**), 22.3 (**25b**), 20.7 (**27b**), 20.3 (**25b**); IR ($CDCl_3$) 2933, 1612, 1434, 744; HRMS (EI) calc $C_{14}H_{20}N_2O_2$ (M^+) 248.1525, found 248.1533. A similar reaction on a 6:5 mixture of **25c** and **27c** gave a 1.3:1 mixture of **25b** and **27b**.

References and Notes

12. Jain, N.; Kumar, A.; Chauhan, S. M. S. *Tetrahedron Lett.* **2005**, *46*, 2599-2602.
13. The spectral data correspond well with those of a related 2,5-disubstituted 3-methoxypyrrole. In 2-methyl-3-methoxy-5-phenylpyrrole, the pyrrole NH absorbs at δ 7.8 (br), the pyrrole hydrogen absorbs at δ 6.26 (d, *J* = 3 Hz) and the methoxy group absorbs at δ 3.8. See: Berner, H.; Schulz, G.; Reinshagen, H. *Monat. Chem.* **1978**, *109*, 137-145.

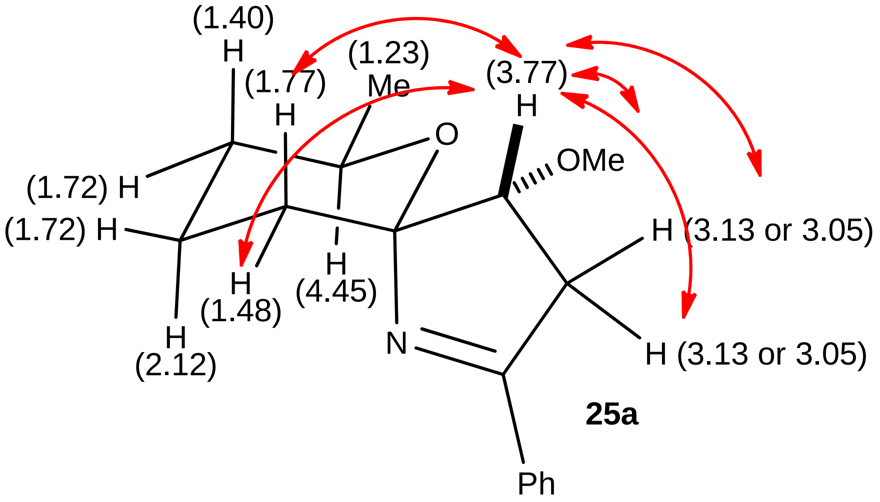
Conformations, Chemical Shift Assignments and NOEs in Spiroiminals 24a, 25a, and 27a.

The chemical shifts of all the protons of spiroiminal **24a**, which were assigned from the coupling pattern and the COSY spectra, are indicated in the figure below. Molecular mechanics calculations suggest that this compound exists as a single tetrahydropyran chair conformer with an equatorial methyl group and axial nitrogen. NOEs are indicated by red arrows and are only seen within the dihydropyrrole and tetrahydropyran rings as required by the structure.



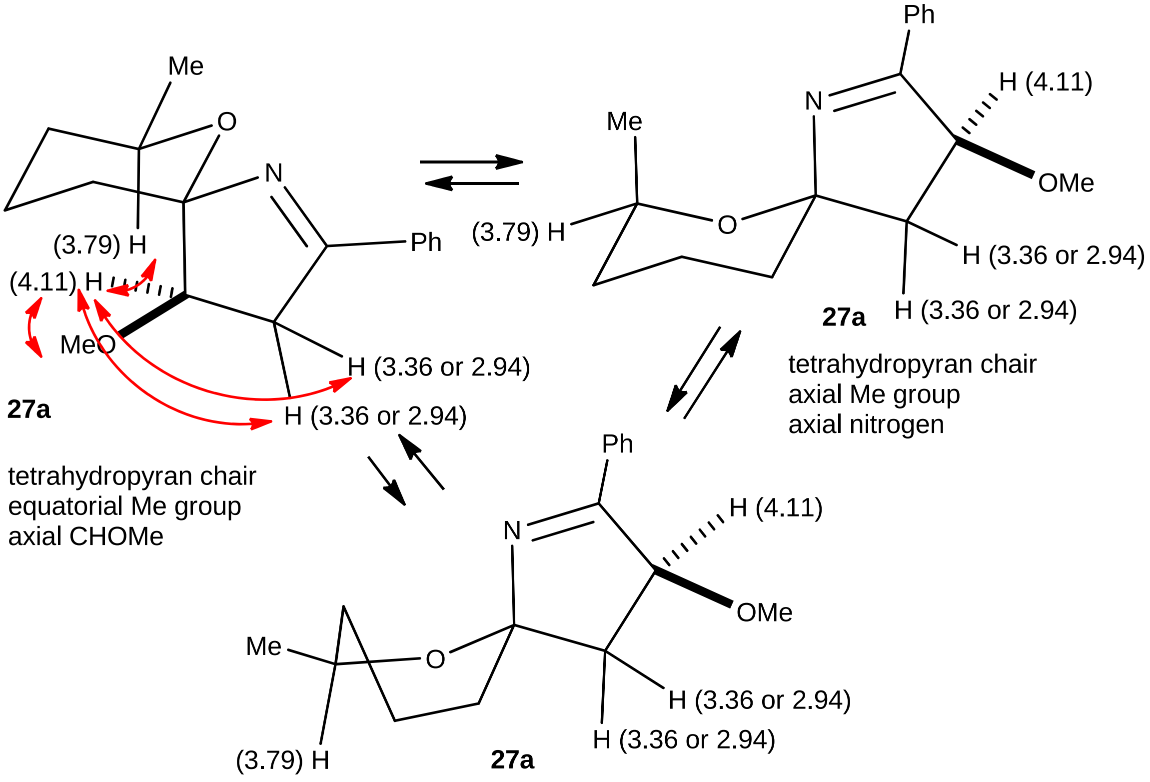
24a

The chemical shifts of all the protons of spiroiminal **25a**, which were assigned from the coupling pattern and the COSY spectra, are indicated in the figure below. Molecular mechanics calculations suggest that this compound exists as a single tetrahydropyran chair conformer with an equatorial methyl group and axial nitrogen. NOEs are indicated by red arrows and seen most significantly between the proton adjacent to the methoxy group at δ 3.77 and the methylene group at δ 1.77 and 1.48.



25a

The chemical shifts of all the protons of spiroiminal **27a** that can be assigned from the coupling pattern and the COSY spectra are indicated in the figure below. Molecular mechanics calculations suggest that this compound exists as several conformers, a tetrahydropyran chair conformer with an equatorial methyl group and axial CHOMe group, a tetrahydropyran chair conformer with an axial methyl group and an equatorial nitrogen and a tetrahydropyran boat conformer with a pseudoaxial nitrogen and a pseudoequatorial methyl group. NOEs are indicated by red arrows and seen most significantly between the proton adjacent to the methoxy group at δ 4.11 and the proton adjacent to the methyl group at δ 3.79. These protons are close (2.1-2.5 Å) in the tetrahydropyran chair conformer of **27a** with an equatorial methyl group and an axial CHOMe group and far apart in other conformers of **27a** and all conformers of **24a-26a**.



27a

tetrahydropyran chair
equatorial Me group
axial CHOMe

27a

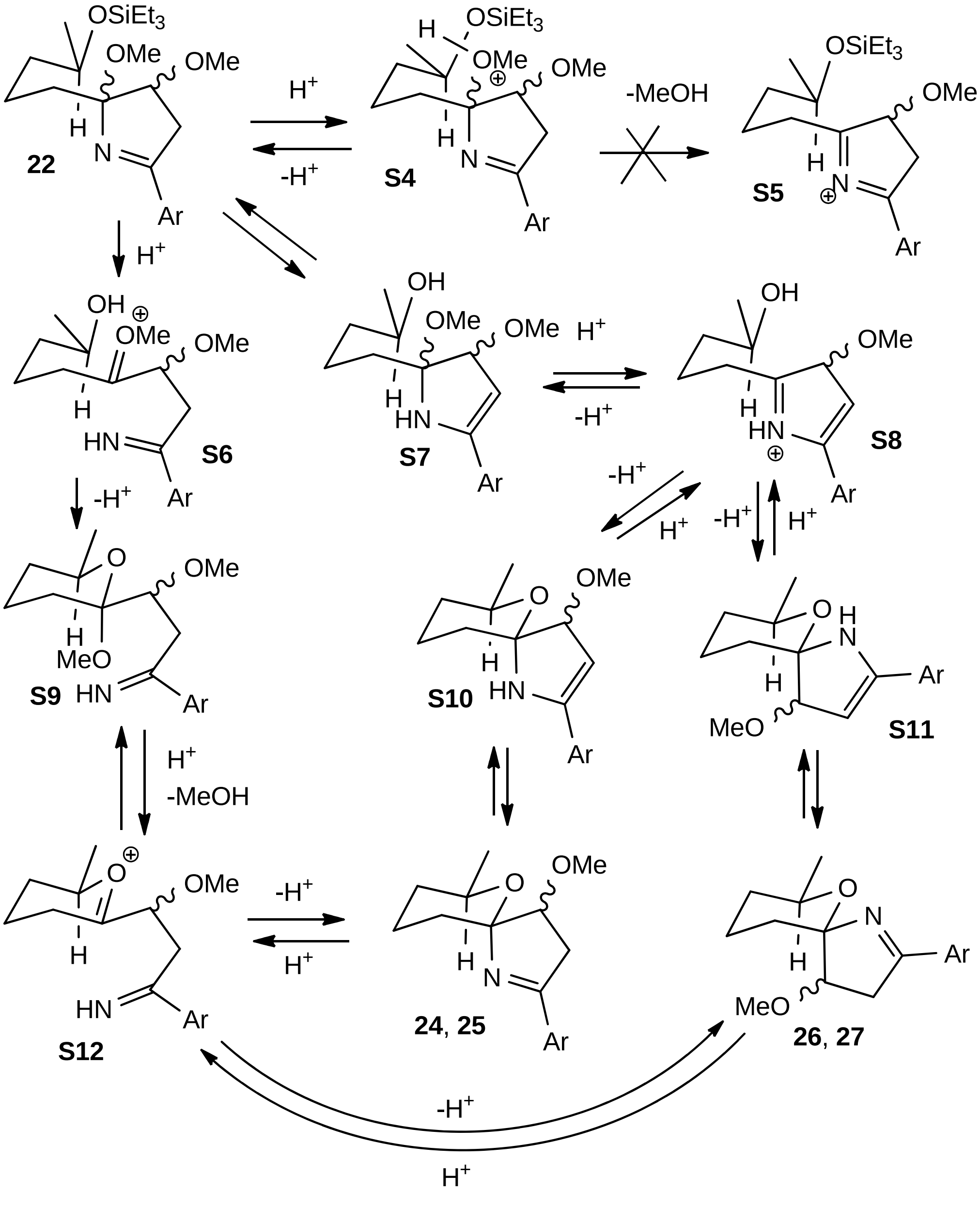
tetrahydropyran chair
axial Me group
axial nitrogen

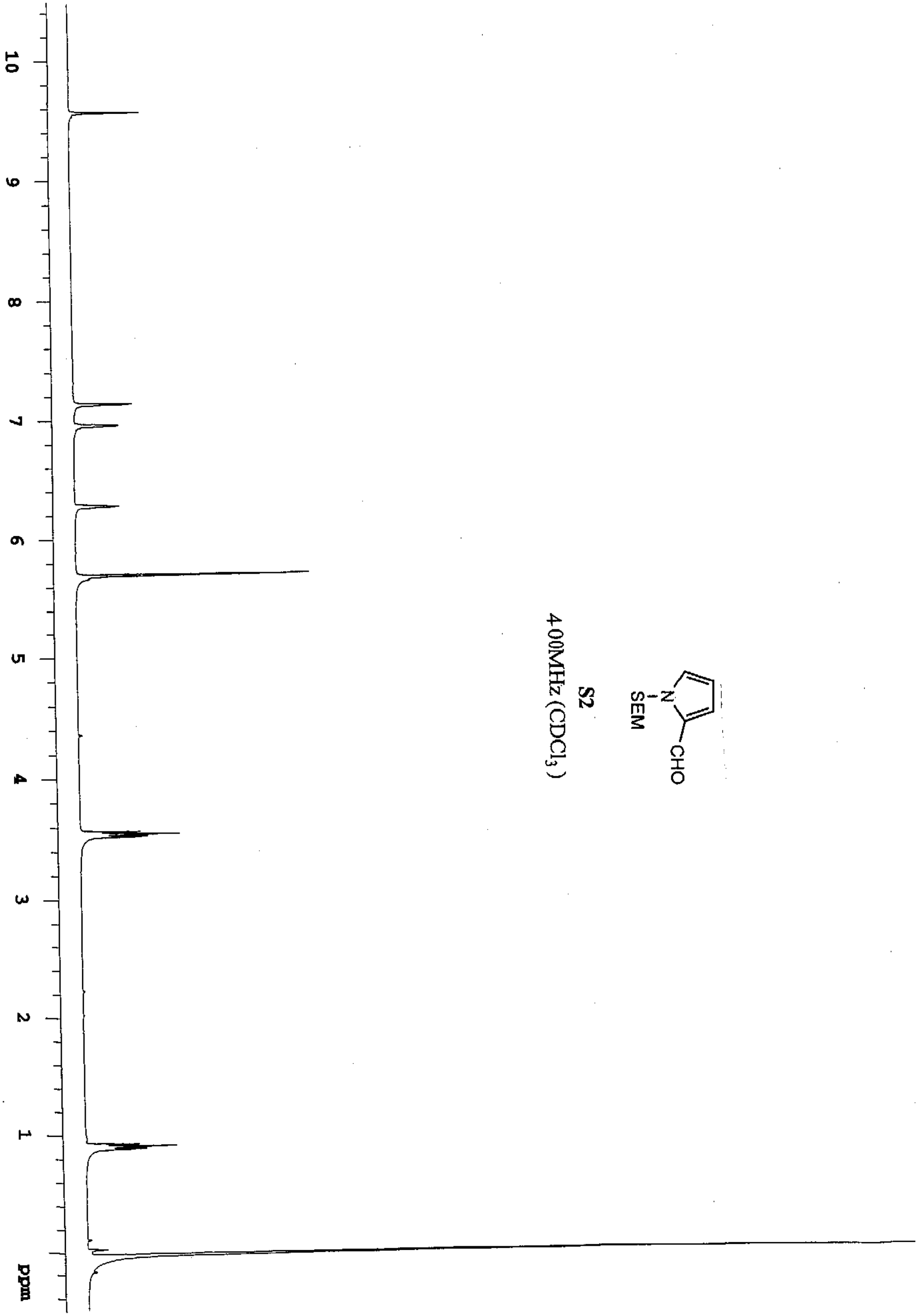
27a

tetrahydropyran boat
pseudoequatorial Me group
pseudoaxial nitrogen

Formation of 24-27

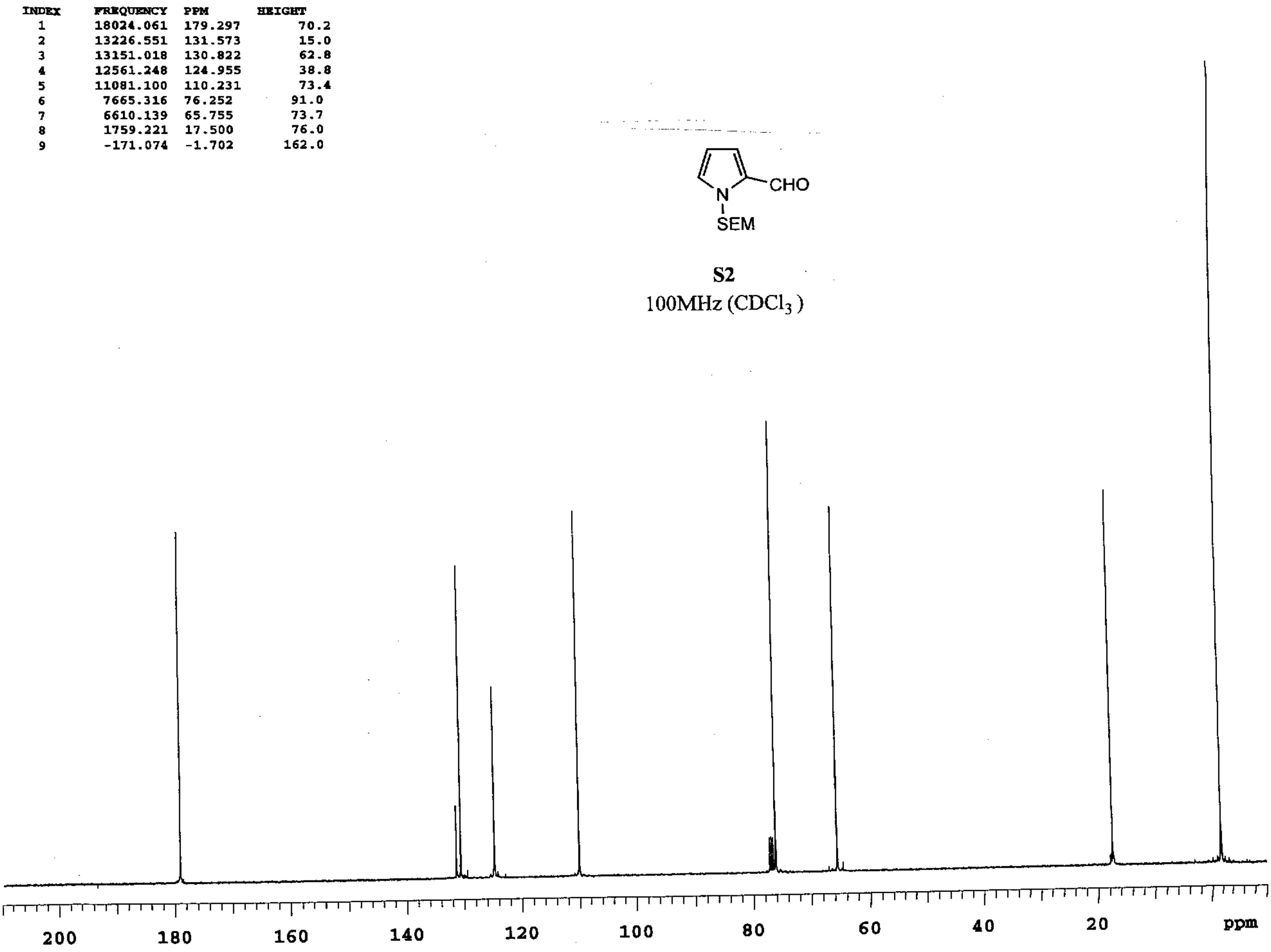
Protonation of **22** on the methoxy group will give **S4**, which is unlikely to lose methanol to give **S5**. The nitrogen lone pair can't stabilize the cation by resonance because $C=N^+=C$ is in a five-membered ring. Protonation of **22** on the nitrogen and ring opening will give imine cation **S6**, which can cyclize and lose a proton to give imine tetrahydropyran **S9**. Protonation of the methoxy group and loss of MeOH will give imine cation **S12**, which can cyclize to give **24-27**. Equilibration of spiroiminal **25** with **27** and spiroiminal **24** with **26** will also occur through imine cation **S12**. Alternatively, **22** can tautomerize to enamine **S7**, which can lose MeOH after protonation to give cation **S8**. Tetrahydropyran formation will give the unsaturated spiroaminals **S10** and **S11**, which can tautomerize to **24-27**.





S2

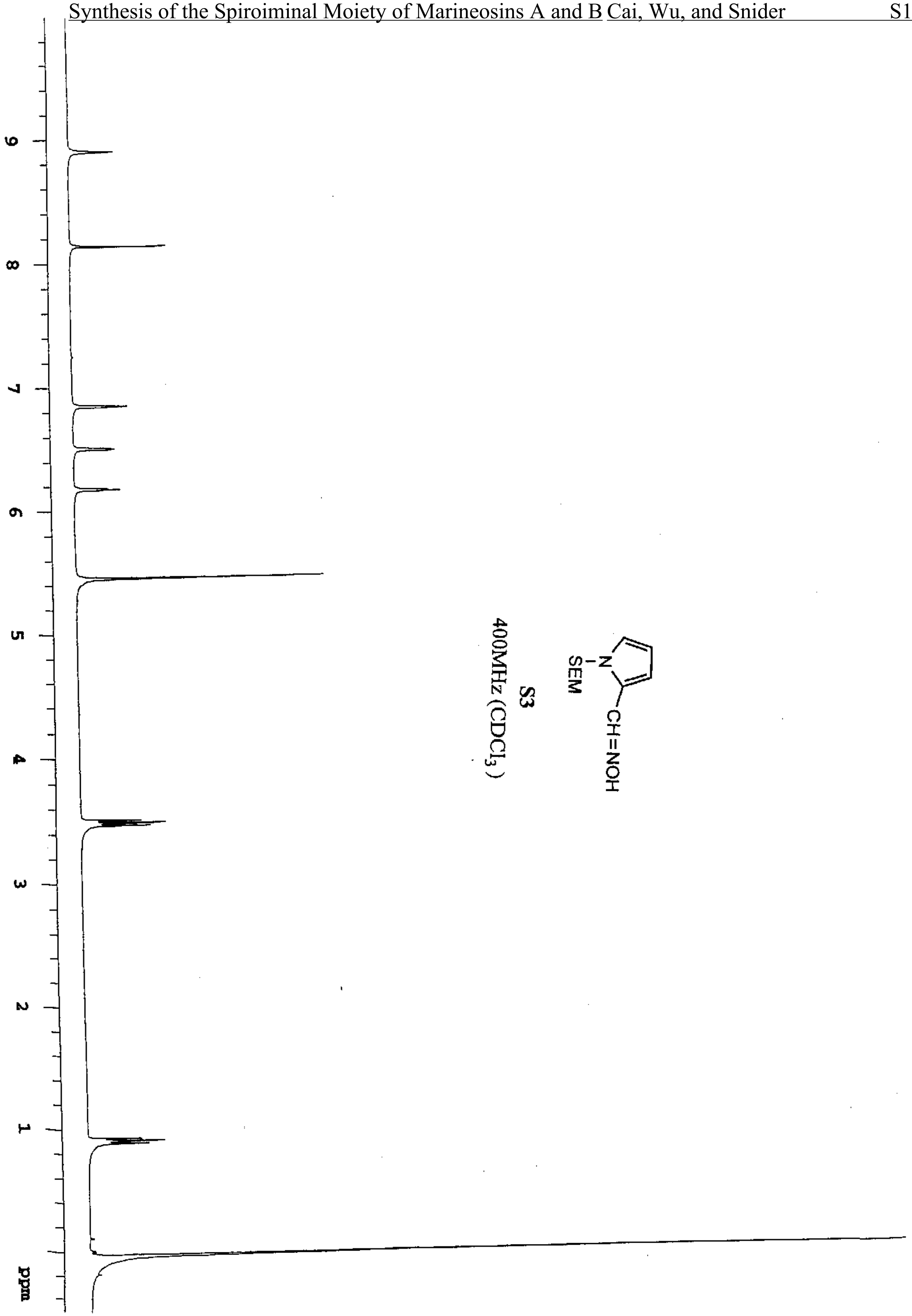
400MHz ($CDCl_3$)



INDEX	FREQUENCY	PPM	HEIGHT
1	18024.061	179.297	70.2
2	13226.551	131.573	15.0
3	13151.018	130.822	62.8
4	12561.248	124.955	38.8
5	11081.100	110.231	73.4
6	7665.316	76.252	91.0
7	6610.139	65.755	73.7
8	1759.221	17.500	76.0
9	-171.074	-1.702	162.0

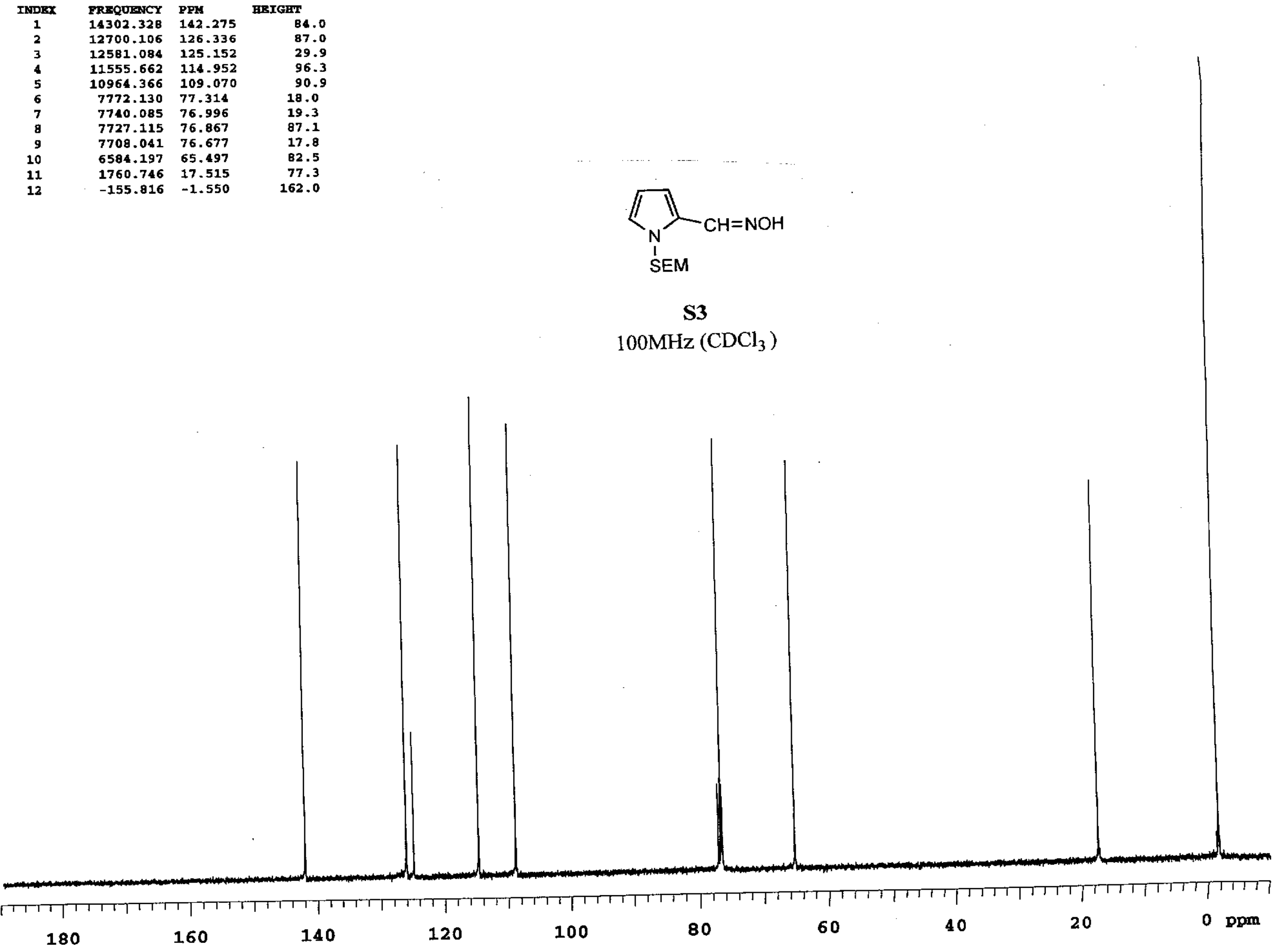
S2

100MHz ($CDCl_3$)



S3

400MHz ($CDCl_3$)



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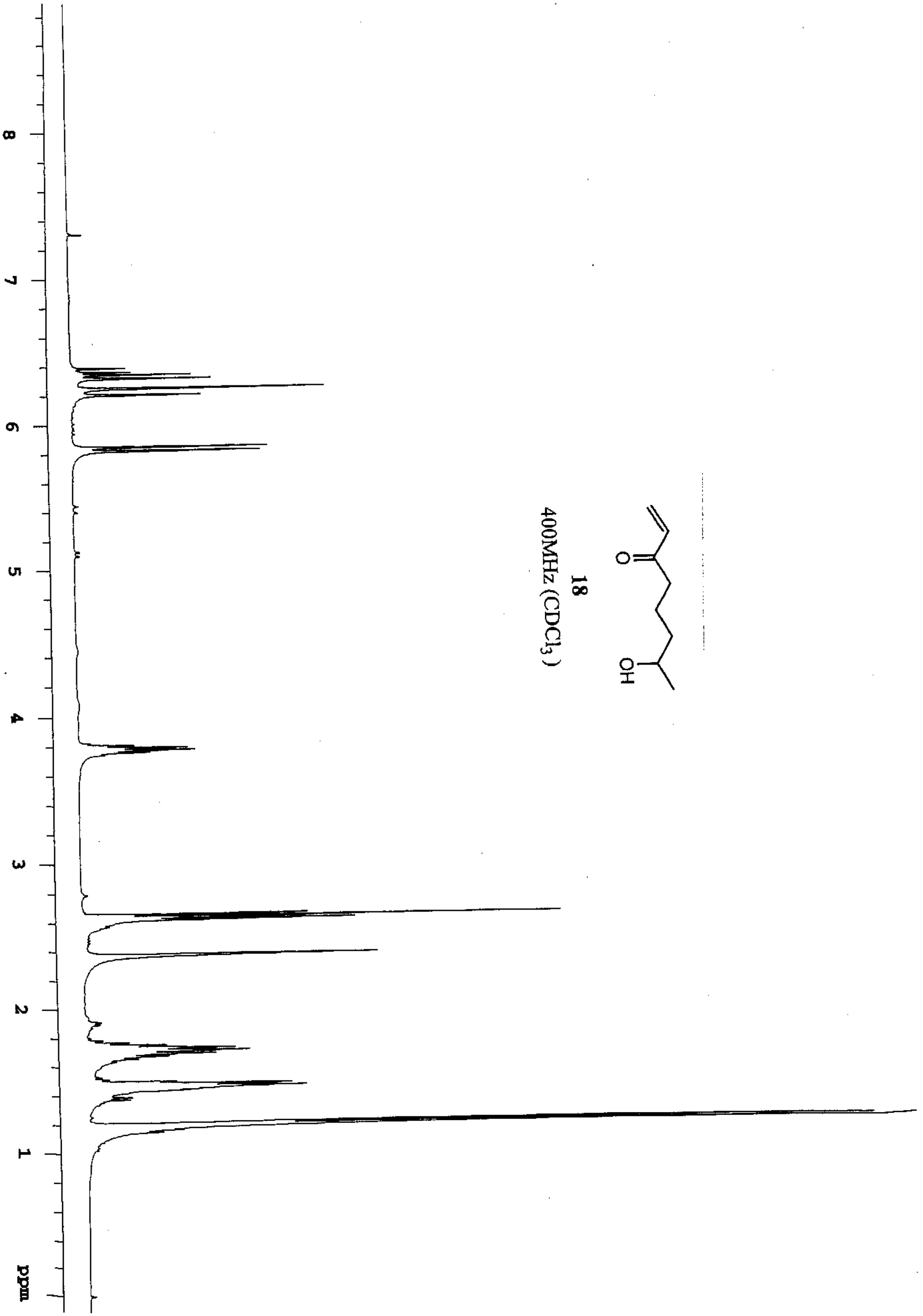
1	14302.328	142.275	84.0
2	12700.106	126.336	87.0
3	12581.084	125.152	29.9
4	11555.662	114.952	96.3
5	10964.366	109.070	90.9
6	7772.130	77.314	18.0
7	7740.085	76.996	19.3
8	7727.115	76.867	87.1
9	7708.041	76.677	17.8
10	6584.197	65.497	82.5
11	1760.746	17.515	77.3
12	-155.816	-1.550	162.0

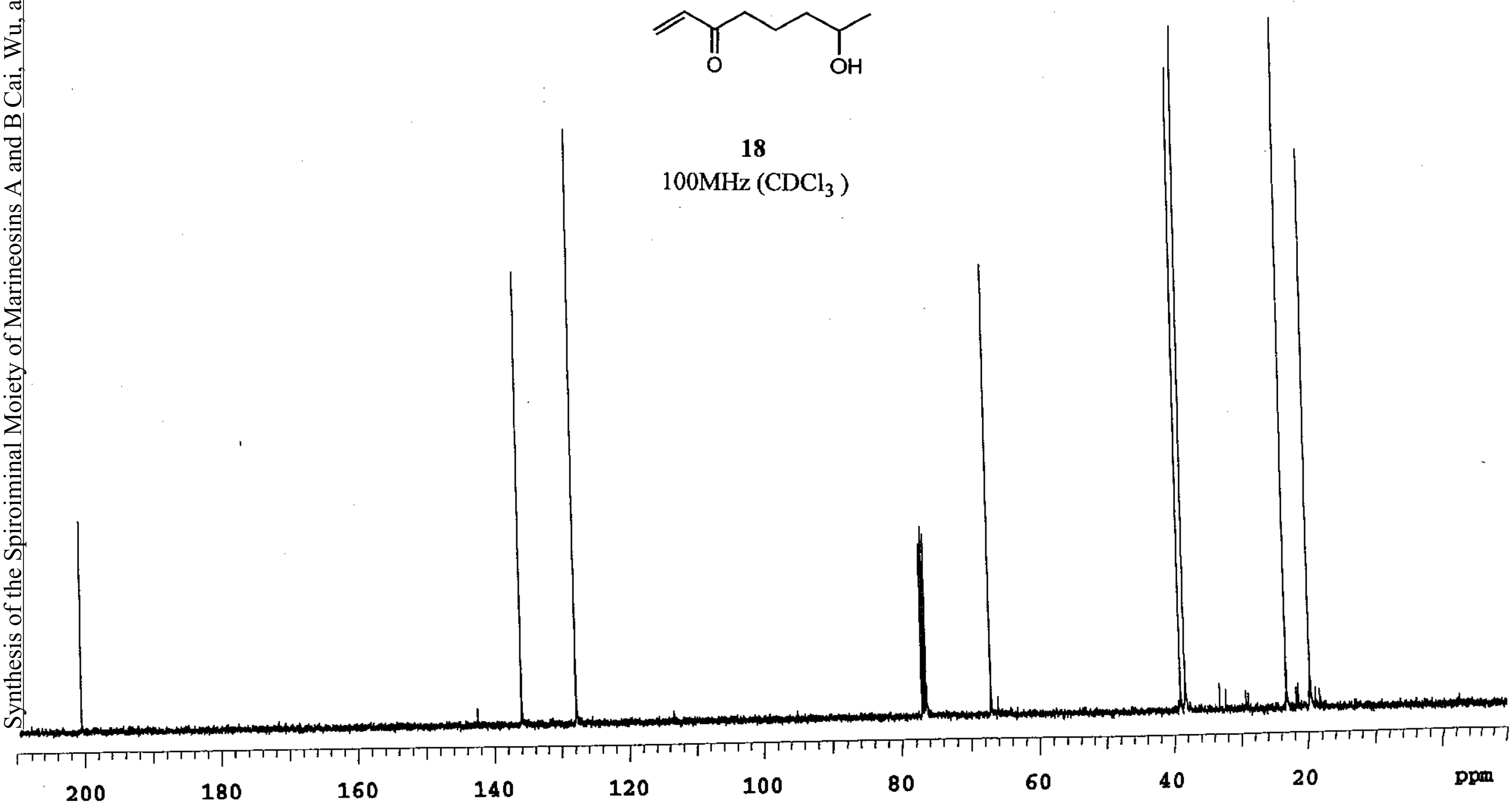
S3

100MHz ($CDCl_3$)



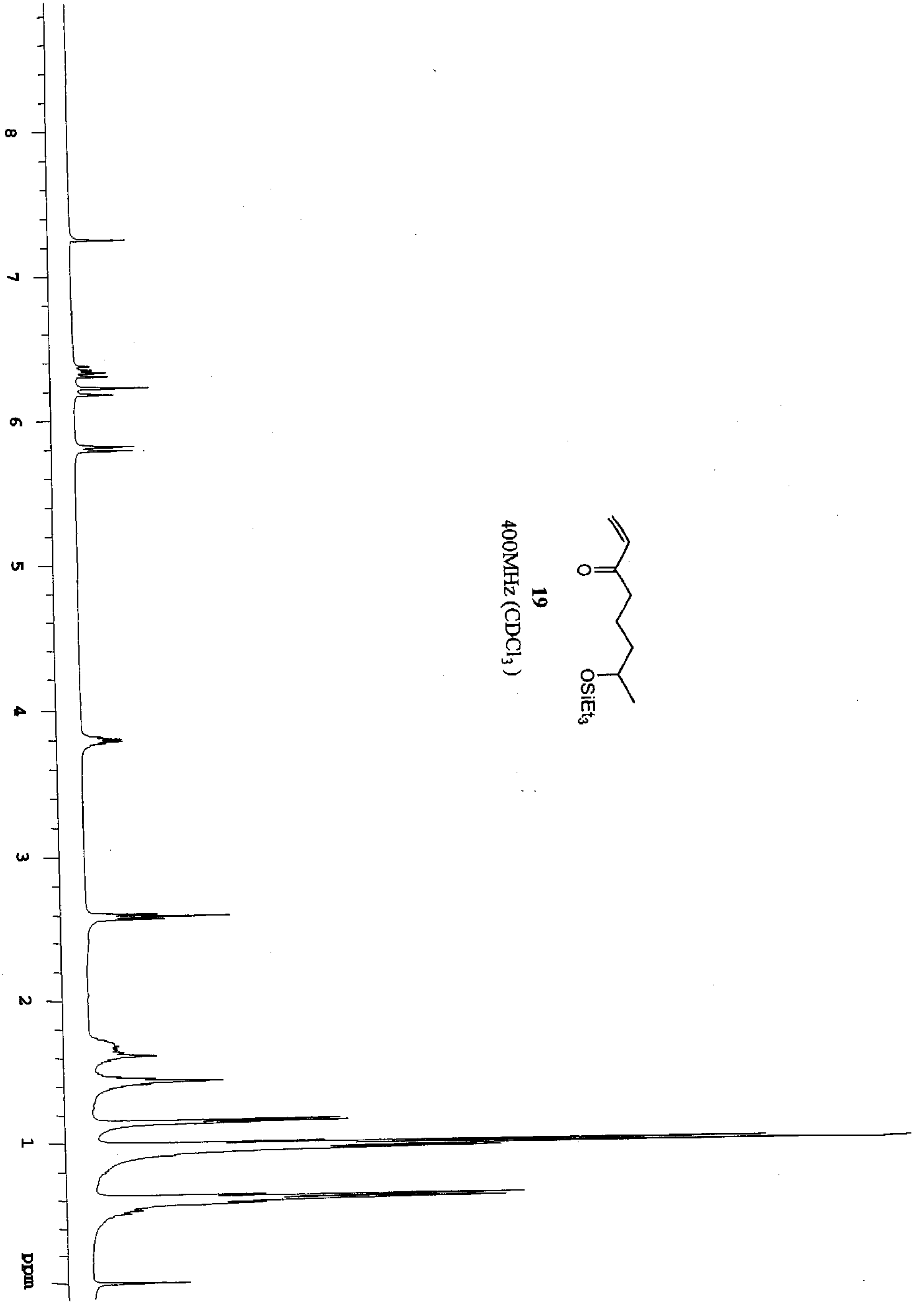
18
400MHz (CDCl$_3$)

INDEX	FREQUENCY	PPM	HEIGHT
1	20208.094	201.023	36.6
2	13703.837	136.321	78.0
3	12886.703	128.192	102.3
4	7772.564	77.319	30.5
5	7740.520	77.000	33.4
6	7708.475	76.681	32.1
7	6766.979	67.316	78.3
8	3940.965	39.203	111.8
9	3863.906	38.437	118.9
10	2341.795	23.295	120.0
11	1987.781	19.774	97.3



18

100MHz ($CDCl_3$)



19

400MHz ($CDCl_3$)

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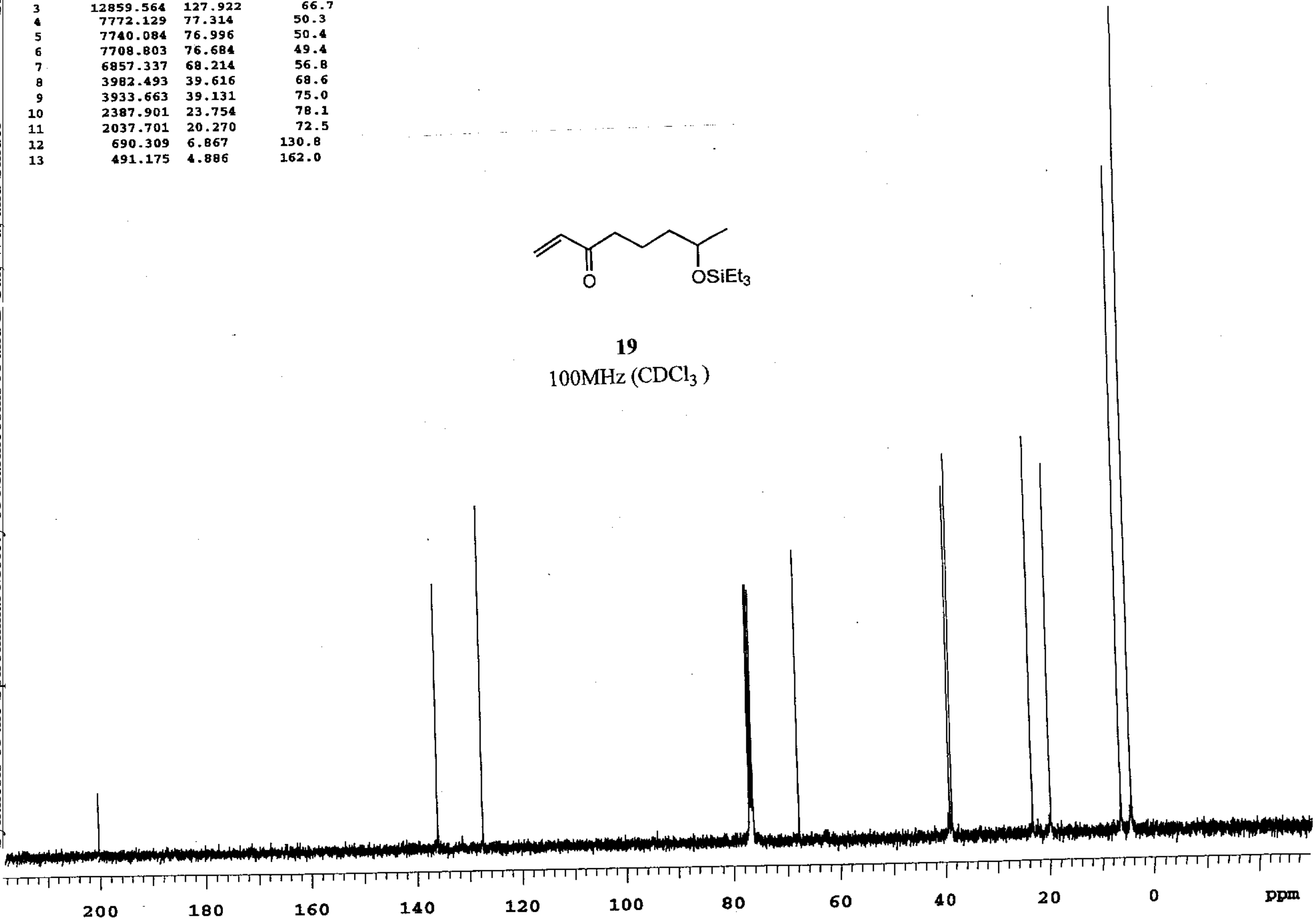
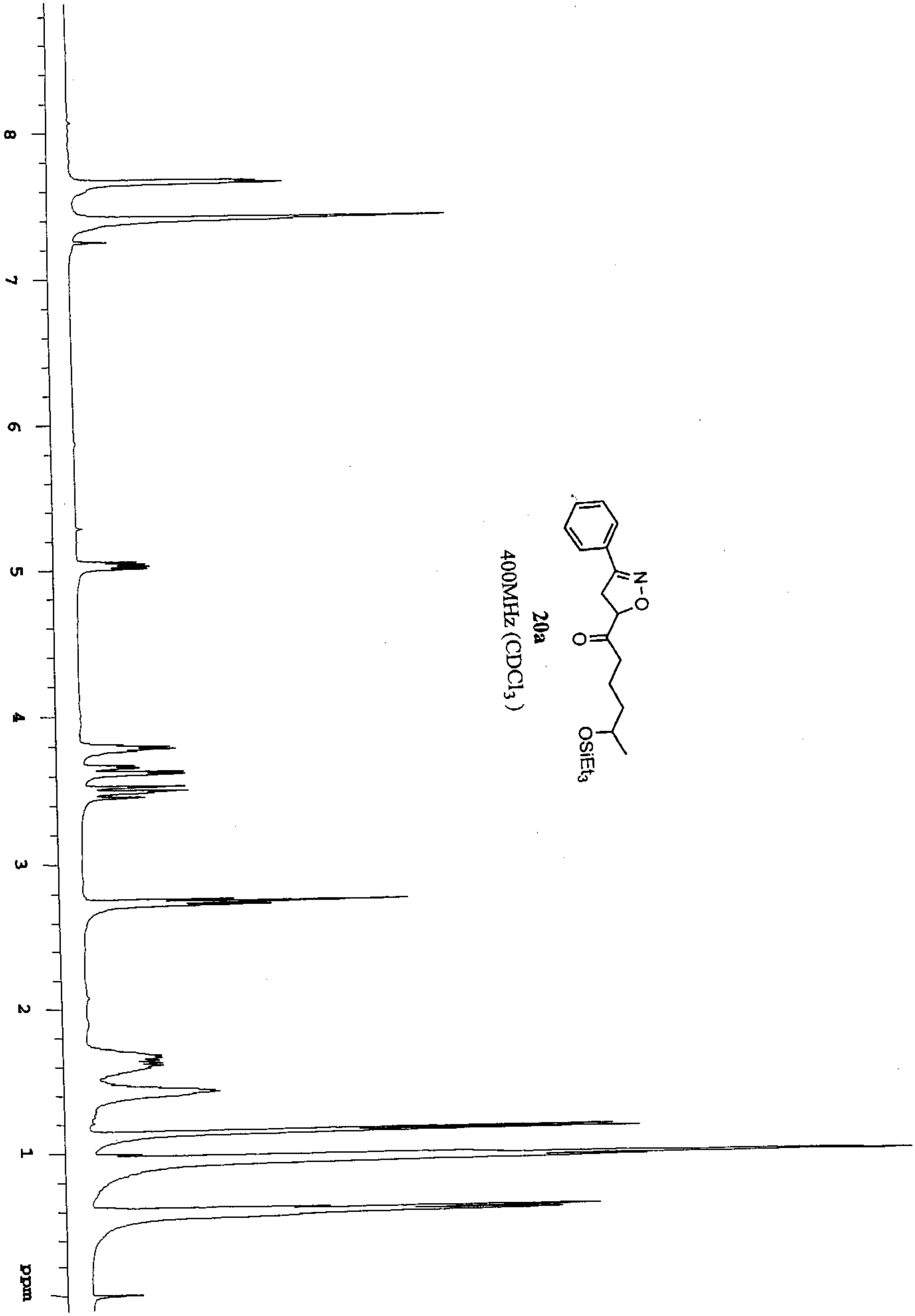
INDEX   FREQUENCY    PPM      HEIGHT
  1     20190.873   200.852     12.8
  2     13722.475   136.506     51.8
  3     12859.564   127.922     66.7
  4      7772.129    77.314     50.3
  5      7740.084    76.996     50.4
  6      7708.803    76.684     49.4
  7      6857.337    68.214     56.8
  8      3982.493    39.616     68.6
  9      3933.663    39.131     75.0
 10      2387.901    23.754     78.1
 11      2037.701    20.270     72.5
 12       690.309     6.867    130.8
 13       491.175     4.886    162.0
```



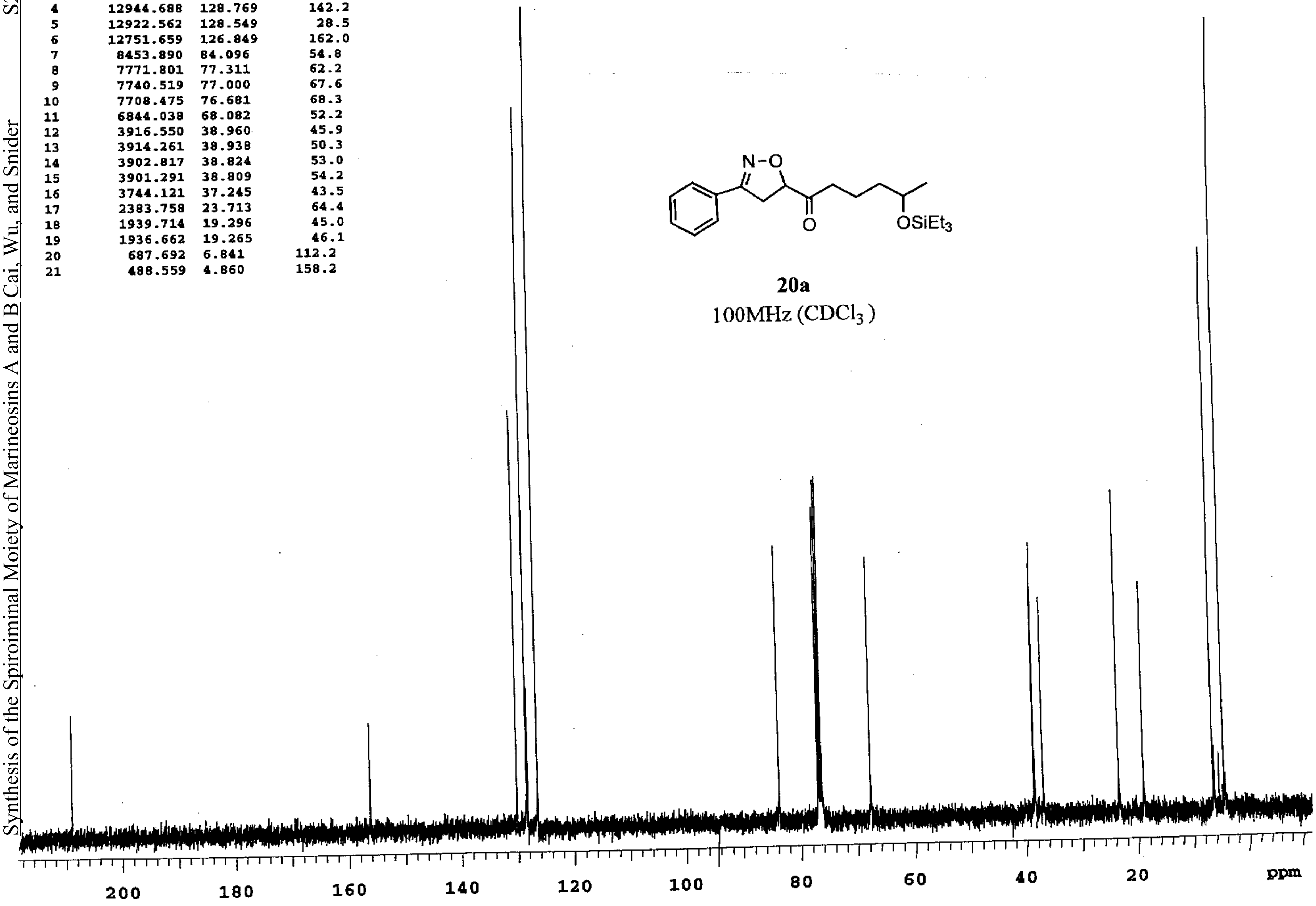
19
100MHz (CDCl$_3$)



20a

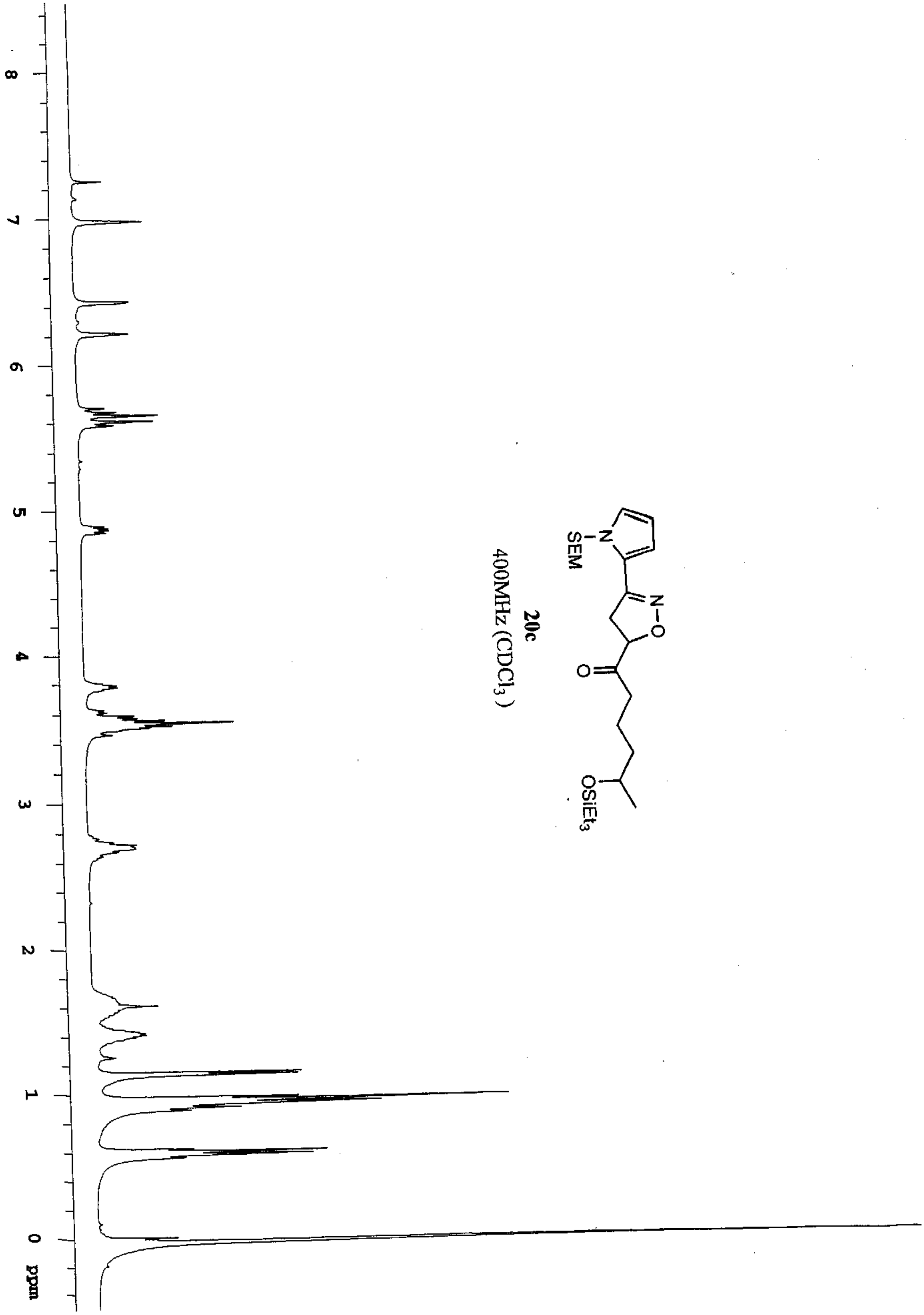
400MHz ($CDCl_3$)

INDEX	FREQUENCY	PPM	HEIGHT
1	21059.560	209.493	24.7
2	15742.473	156.601	22.0
3	13120.170	130.515	82.7
4	12944.688	128.769	142.2
5	12922.562	128.549	28.5
6	12751.659	126.849	162.0
7	8453.890	84.096	54.8
8	7771.801	77.311	62.2
9	7740.519	77.000	67.6
10	7708.475	76.681	68.3
11	6844.038	68.082	52.2
12	3916.550	38.960	45.9
13	3914.261	38.938	50.3
14	3902.817	38.824	53.0
15	3901.291	38.809	54.2
16	3744.121	37.245	43.5
17	2383.758	23.713	64.4
18	1939.714	19.296	45.0
19	1936.662	19.265	46.1
20	687.692	6.841	112.2
21	488.559	4.860	158.2



20a

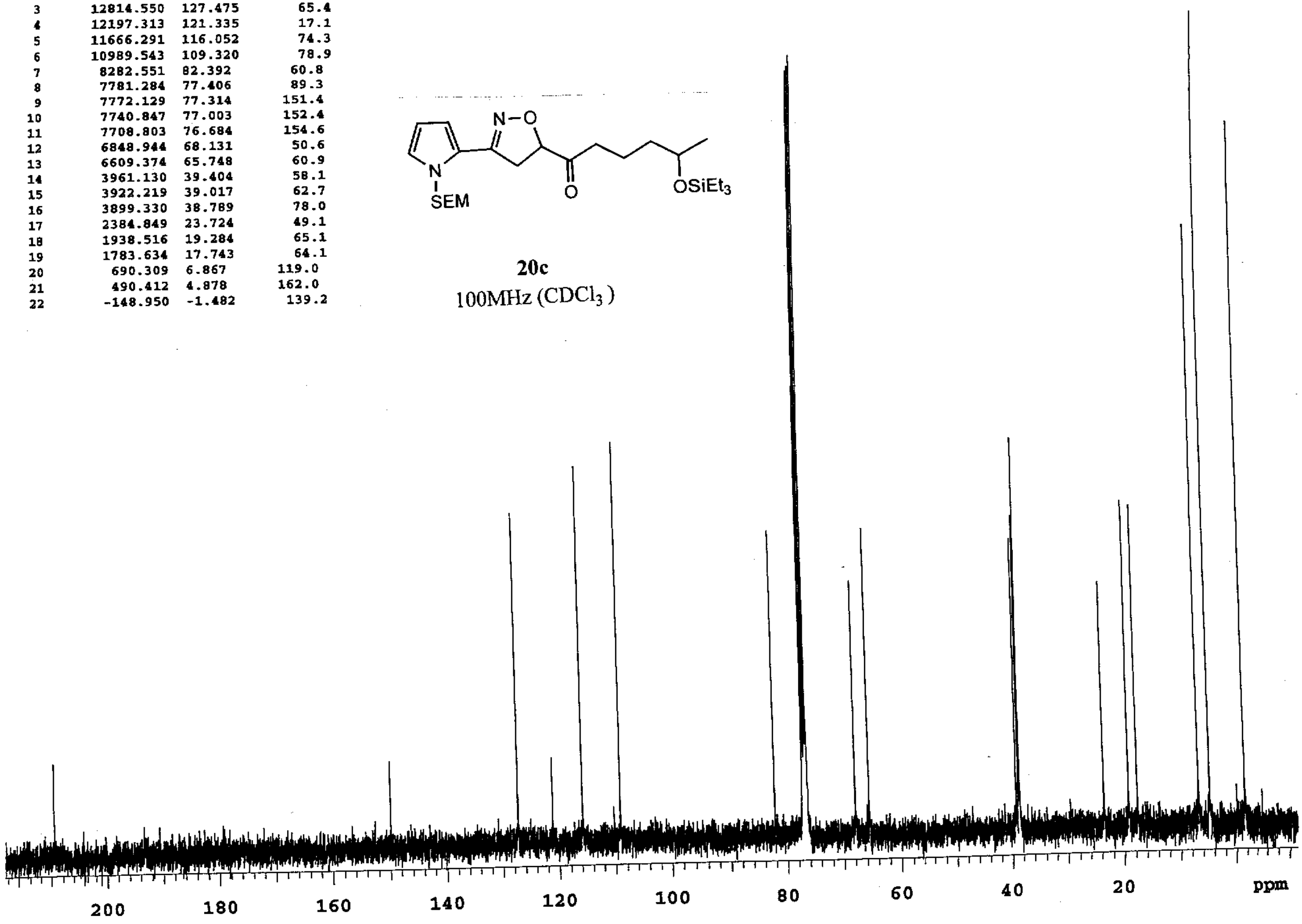
100MHz ($CDCl_3$)



20c

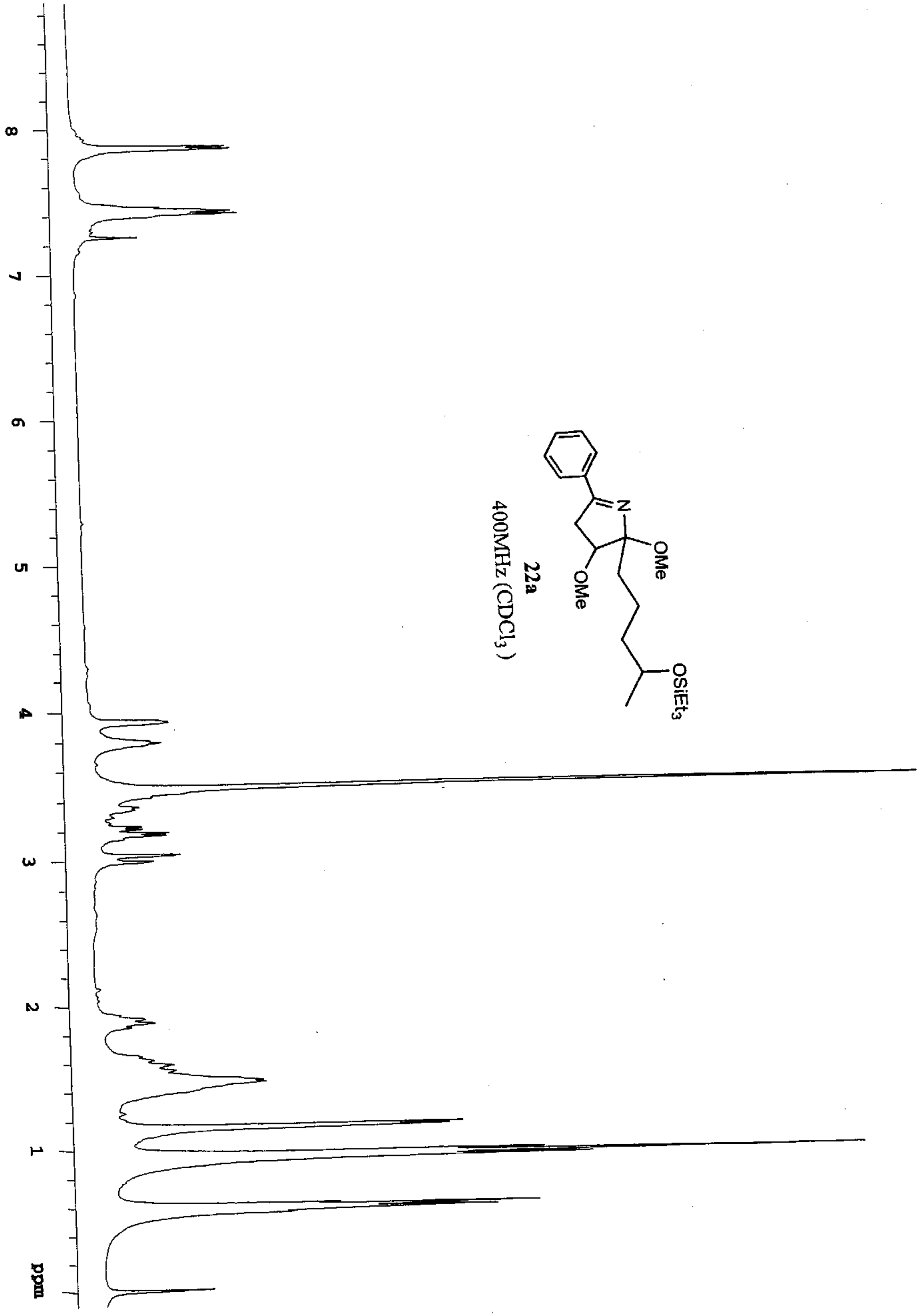
400MHz ($CDCl_3$)

INDEX	FREQUENCY	PPM	HEIGHT
1	21085.066	209.747	18.1
2	15089.704	150.107	17.3
3	12814.550	127.475	65.4
4	12197.313	121.335	17.1
5	11666.291	116.052	74.3
6	10989.543	109.320	78.9
7	8282.551	82.392	60.8
8	7781.284	77.406	89.3
9	7772.129	77.314	151.4
10	7740.847	77.003	152.4
11	7708.803	76.684	154.6
12	6848.944	68.131	50.6
13	6609.374	65.748	60.9
14	3961.130	39.404	58.1
15	3922.219	39.017	62.7
16	3899.330	38.789	78.0
17	2384.849	23.724	49.1
18	1938.516	19.284	65.1
19	1783.634	17.743	64.1
20	690.309	6.867	119.0
21	490.412	4.878	162.0
22	-148.950	-1.482	139.2



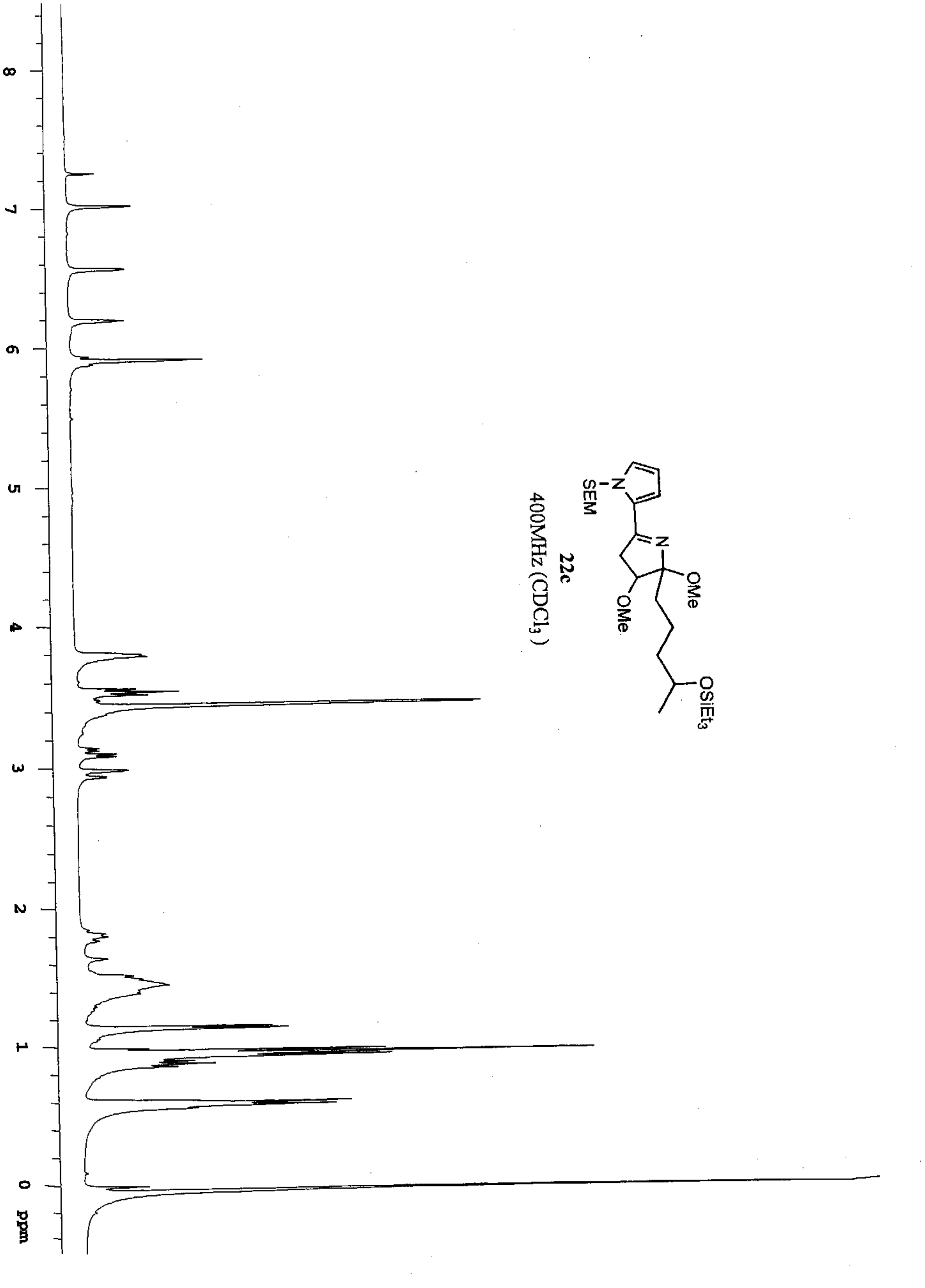
20c

100MHz ($CDCl_3$)



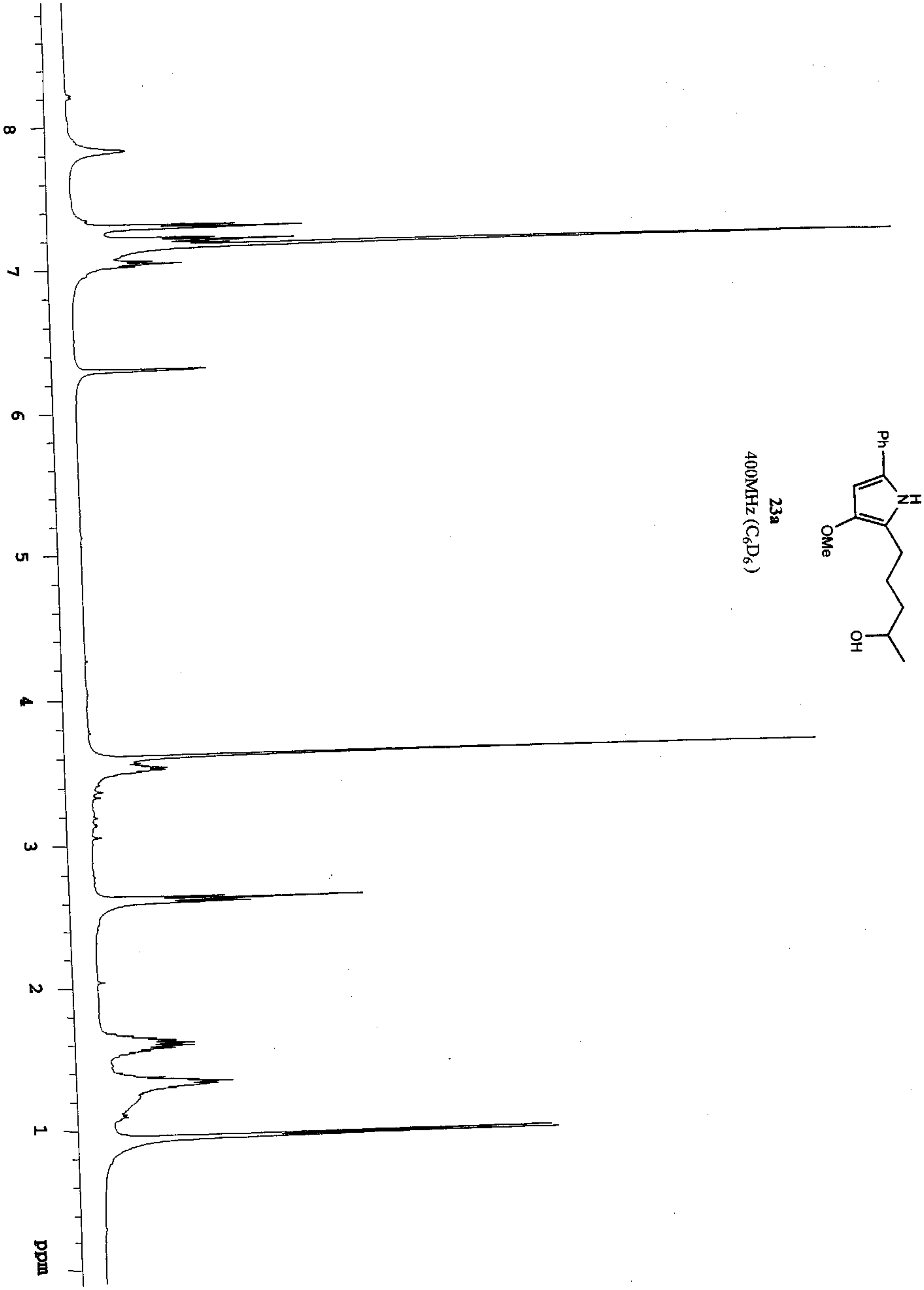
22a

400MHz (CDCl$_3$)



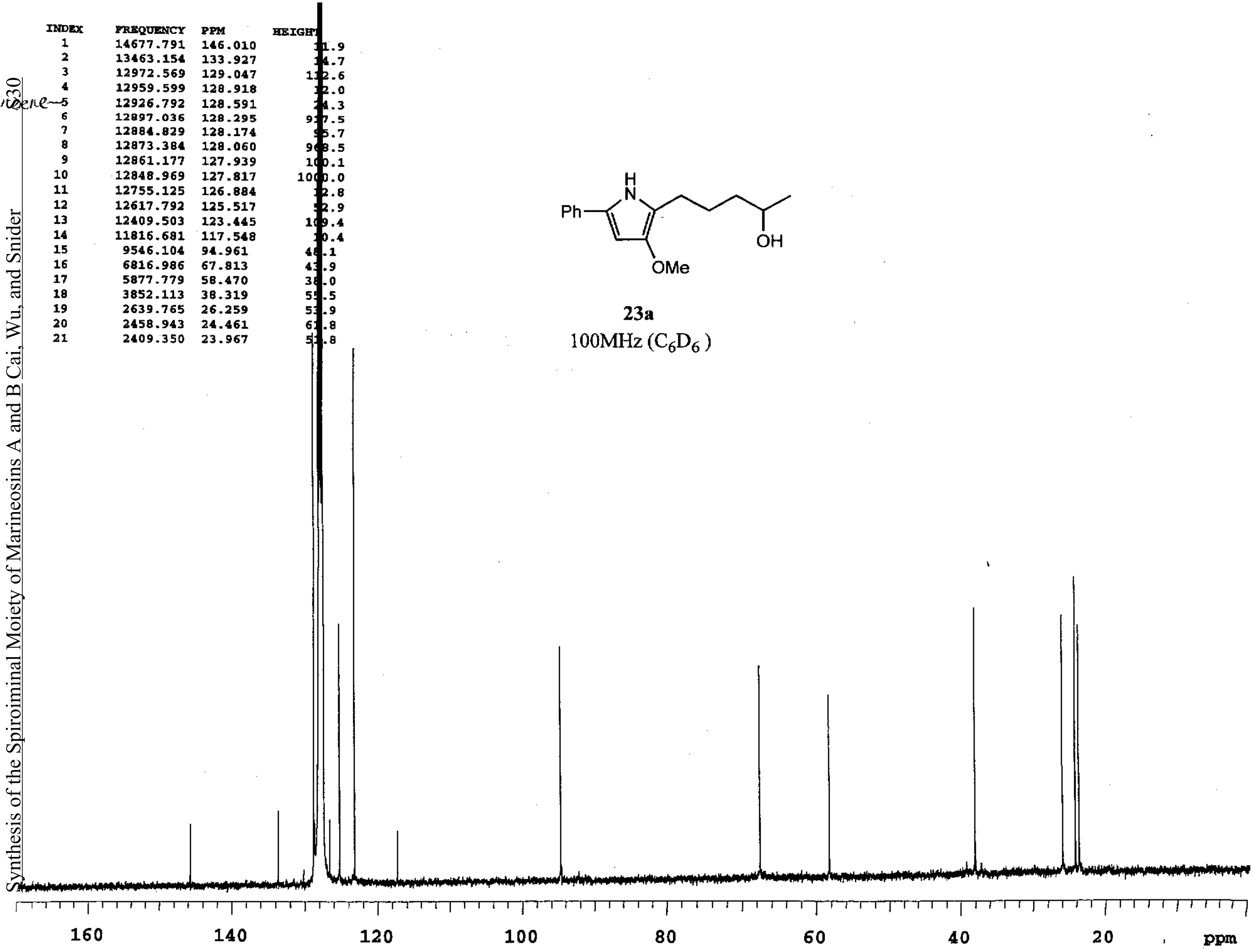
22c

400MHz (CDCl$_3$)



23a

400MHz (C_6D_6)

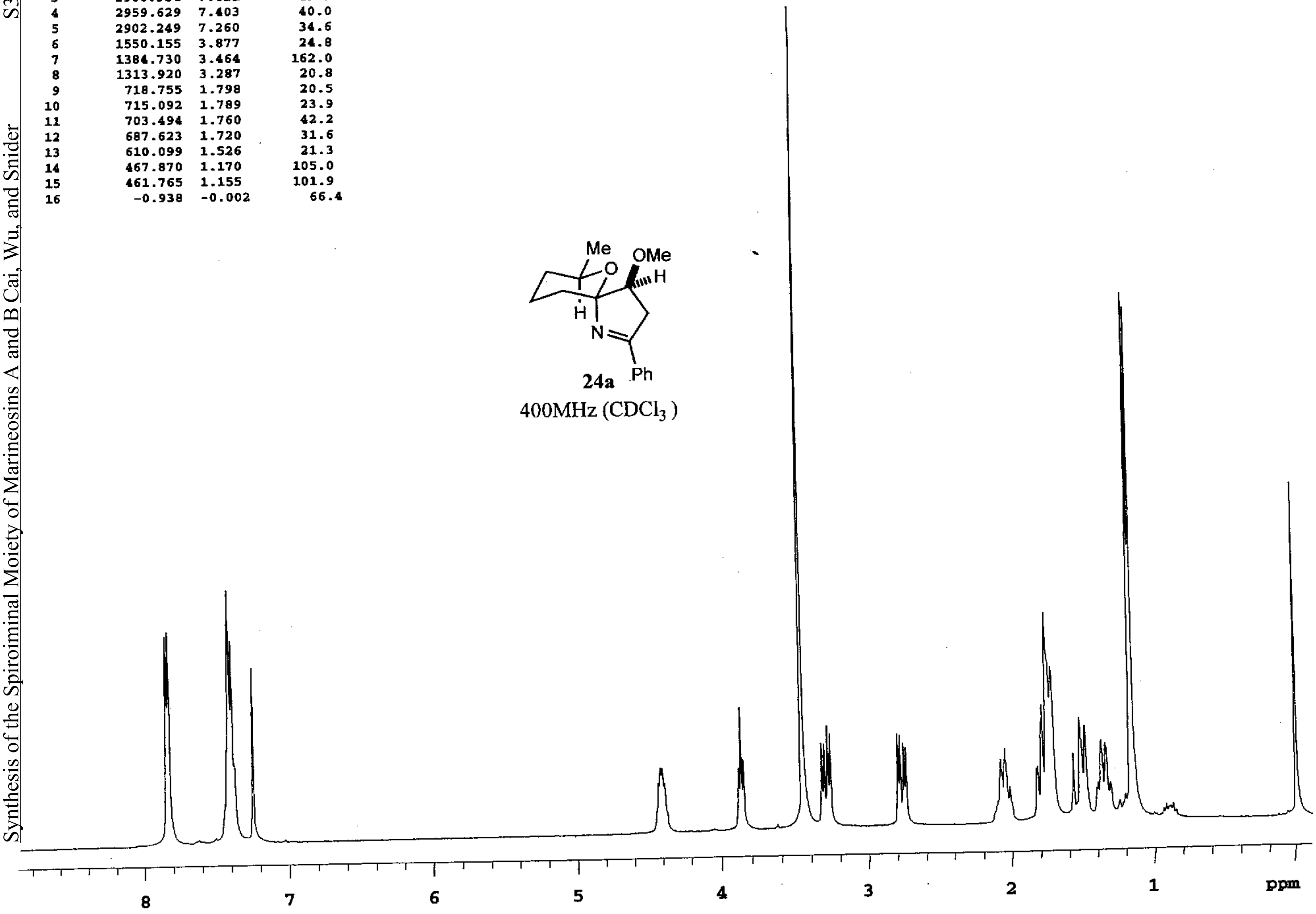


23a
100MHz (C_6D_6)

benzene

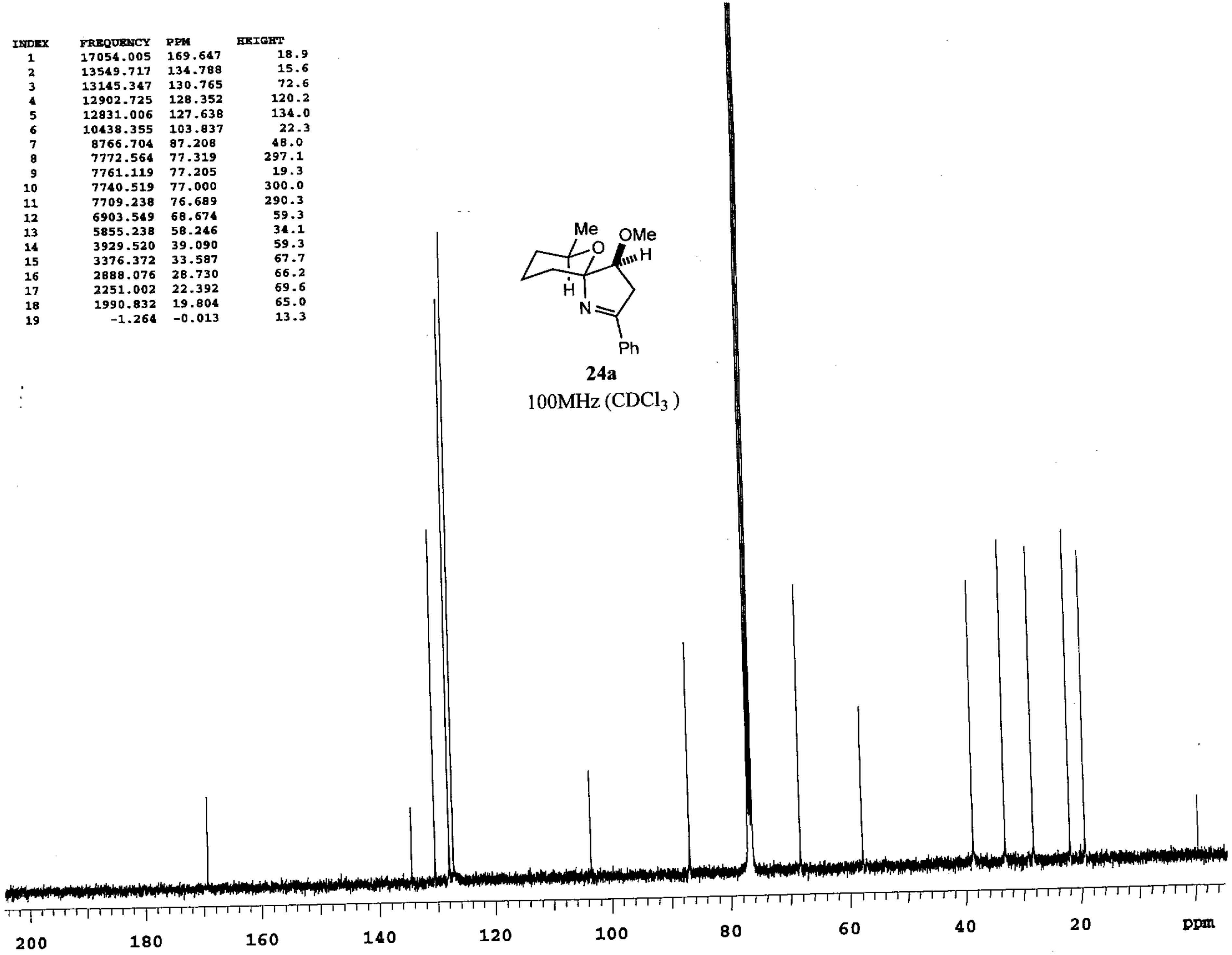
INDEX	FREQUENCY	PPM	HEIGHT
1	14677.791	146.010	11.9
2	13463.154	133.927	14.7
3	12972.569	129.047	112.6
4	12959.599	128.918	12.0
5	12926.792	128.591	24.3
6	12897.036	128.295	917.5
7	12884.829	128.174	95.7
8	12873.384	128.060	968.5
9	12861.177	127.939	100.1
10	12848.969	127.817	1000.0
11	12755.125	126.884	12.8
12	12617.792	125.517	52.9
13	12409.503	123.445	109.4
14	11816.681	117.548	10.4
15	9546.104	94.961	48.1
16	6816.986	67.813	43.9
17	5877.779	58.470	38.0
18	3852.113	38.319	55.5
19	2639.765	26.259	53.9
20	2458.943	24.461	61.8
21	2409.350	23.967	51.8

INDEX	FREQUENCY	PPM	HEIGHT
1	3140.315	7.855	41.0
2	3133.600	7.838	41.9
3	2966.954	7.421	49.9
4	2959.629	7.403	40.0
5	2902.249	7.260	34.6
6	1550.155	3.877	24.8
7	1384.730	3.464	162.0
8	1313.920	3.287	20.8
9	718.755	1.798	20.5
10	715.092	1.789	23.9
11	703.494	1.760	42.2
12	687.623	1.720	31.6
13	610.099	1.526	21.3
14	467.870	1.170	105.0
15	461.765	1.155	101.9
16	-0.938	-0.002	66.4



24a

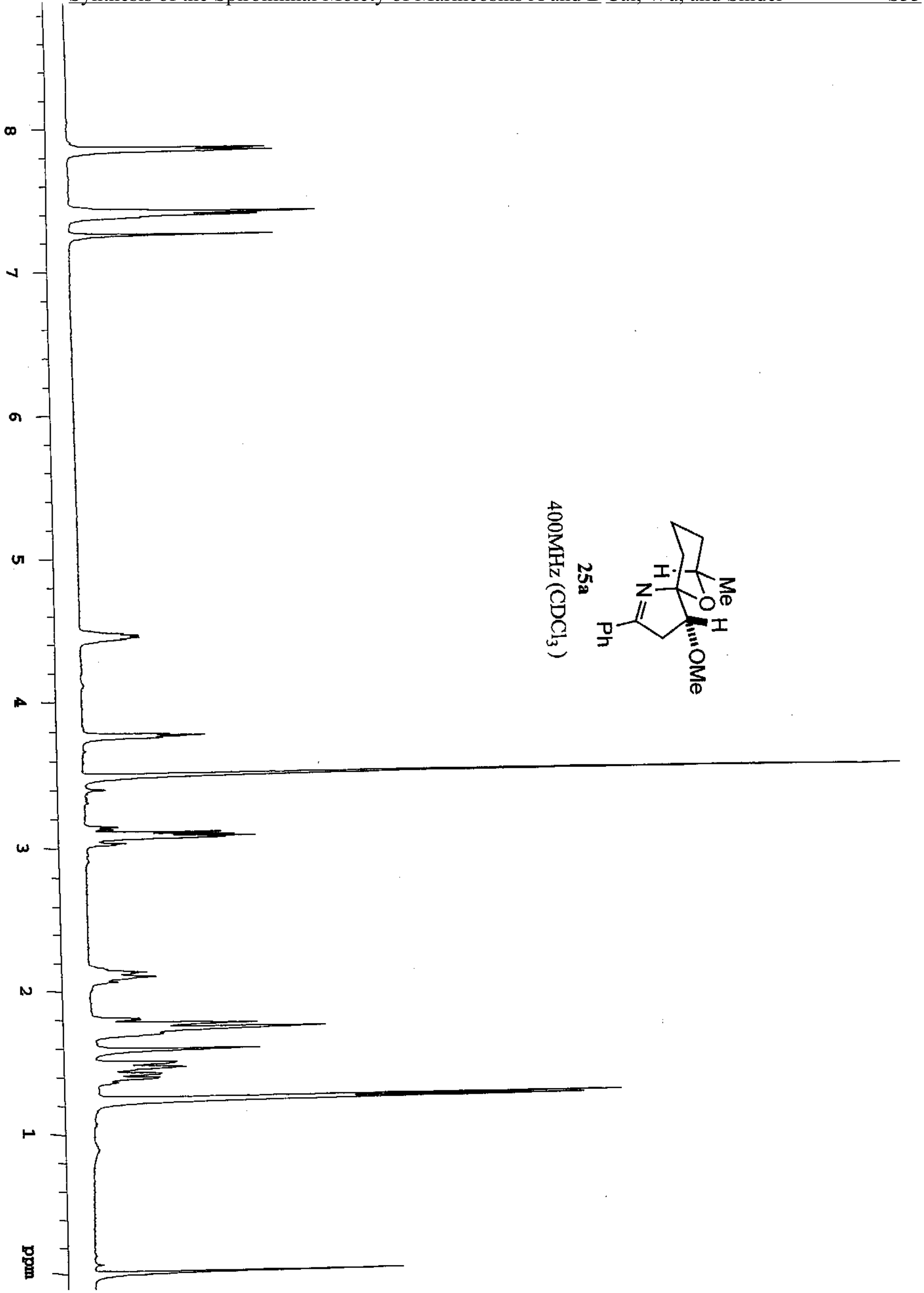
400MHz ($CDCl_3$)



24a

100MHz ($CDCl_3$)

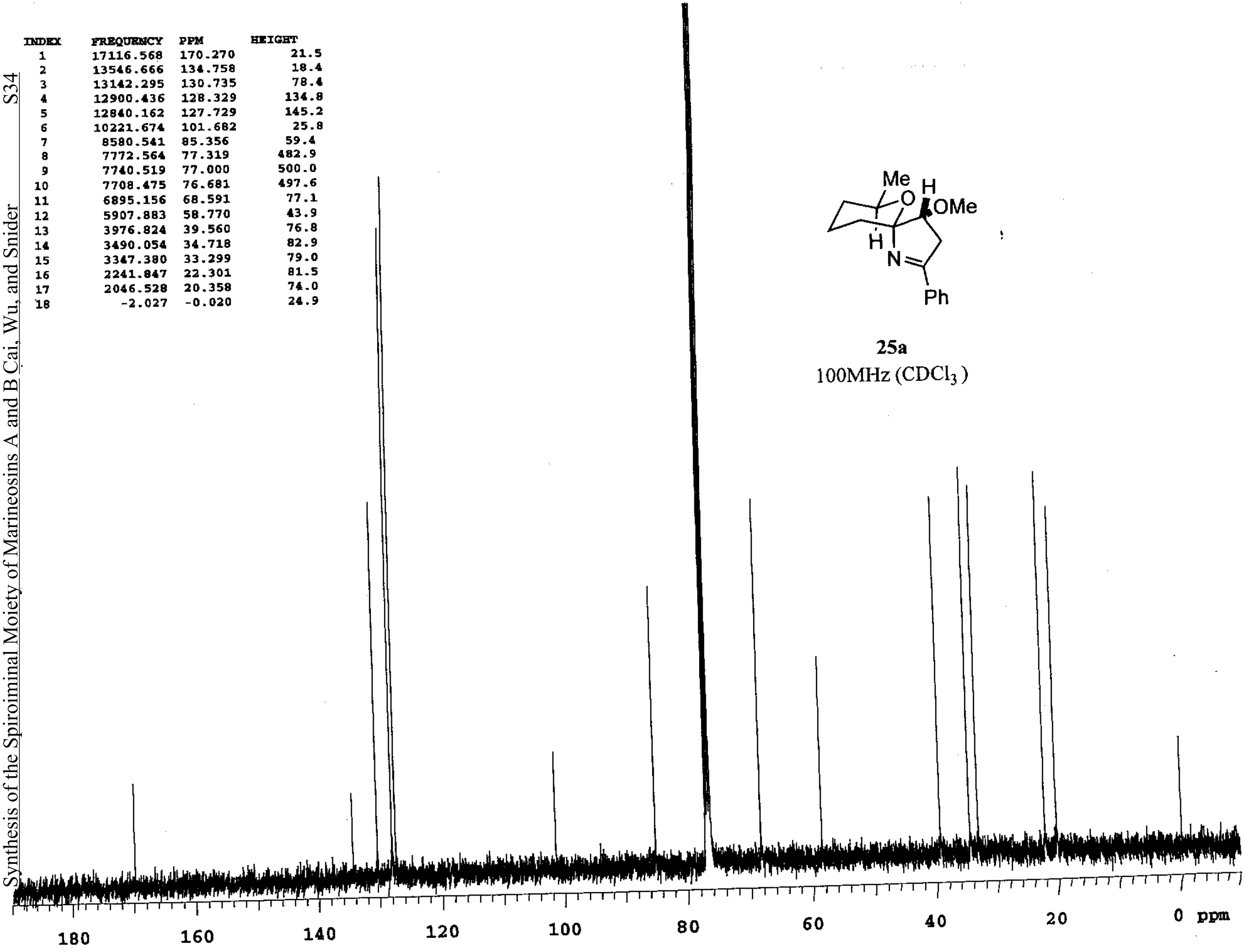
INDEX	FREQUENCY	PPM	HEIGHT
1	17054.005	169.647	18.9
2	13549.717	134.788	15.6
3	13145.347	130.765	72.6
4	12902.725	128.352	120.2
5	12831.006	127.638	134.0
6	10438.355	103.837	22.3
7	8766.704	87.208	48.0
8	7772.564	77.319	297.1
9	7761.119	77.205	19.3
10	7740.519	77.000	300.0
11	7709.238	76.689	290.3
12	6903.549	68.674	59.3
13	5855.238	58.246	34.1
14	3929.520	39.090	59.3
15	3376.372	33.587	67.7
16	2888.076	28.730	66.2
17	2251.002	22.392	69.6
18	1990.832	19.804	65.0
19	-1.264	-0.013	13.3



25a

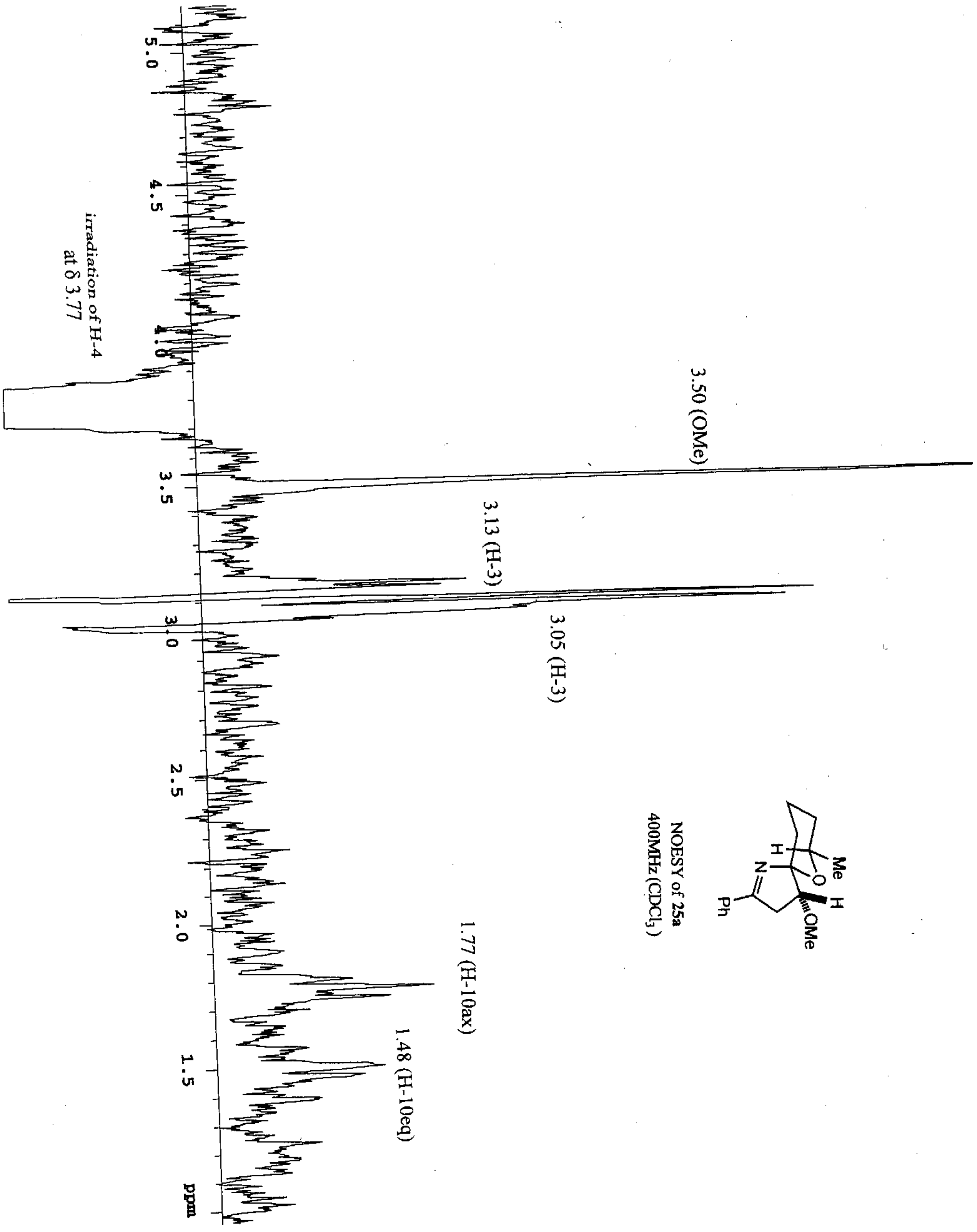
400MHz ($CDCl_3$)

INDEX	FREQUENCY	PPM	HEIGHT
1	17116.568	170.270	21.5
2	13546.666	134.758	18.4
3	13142.295	130.735	78.4
4	12900.436	128.329	134.8
5	12840.162	127.729	145.2
6	10221.674	101.682	25.8
7	8580.541	85.356	59.4
8	7772.564	77.319	482.9
9	7740.519	77.000	500.0
10	7708.475	76.681	497.6
11	6895.156	68.591	77.1
12	5907.883	58.770	43.9
13	3976.824	39.560	76.8
14	3490.054	34.718	82.9
15	3347.380	33.299	79.0
16	2241.847	22.301	81.5
17	2046.528	20.358	74.0
18	-2.027	-0.020	24.9

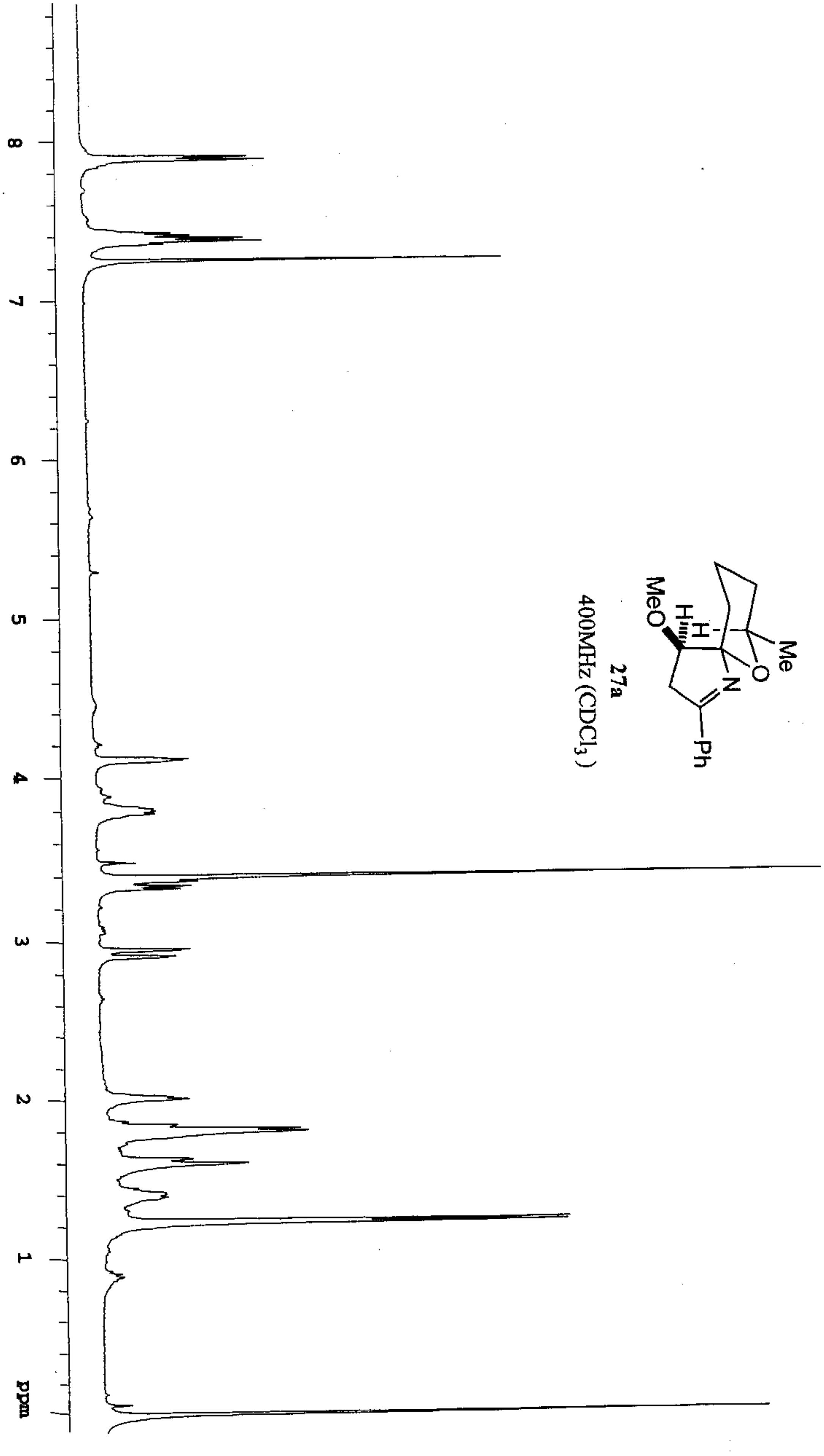


25a

100MHz ($CDCl_3$)



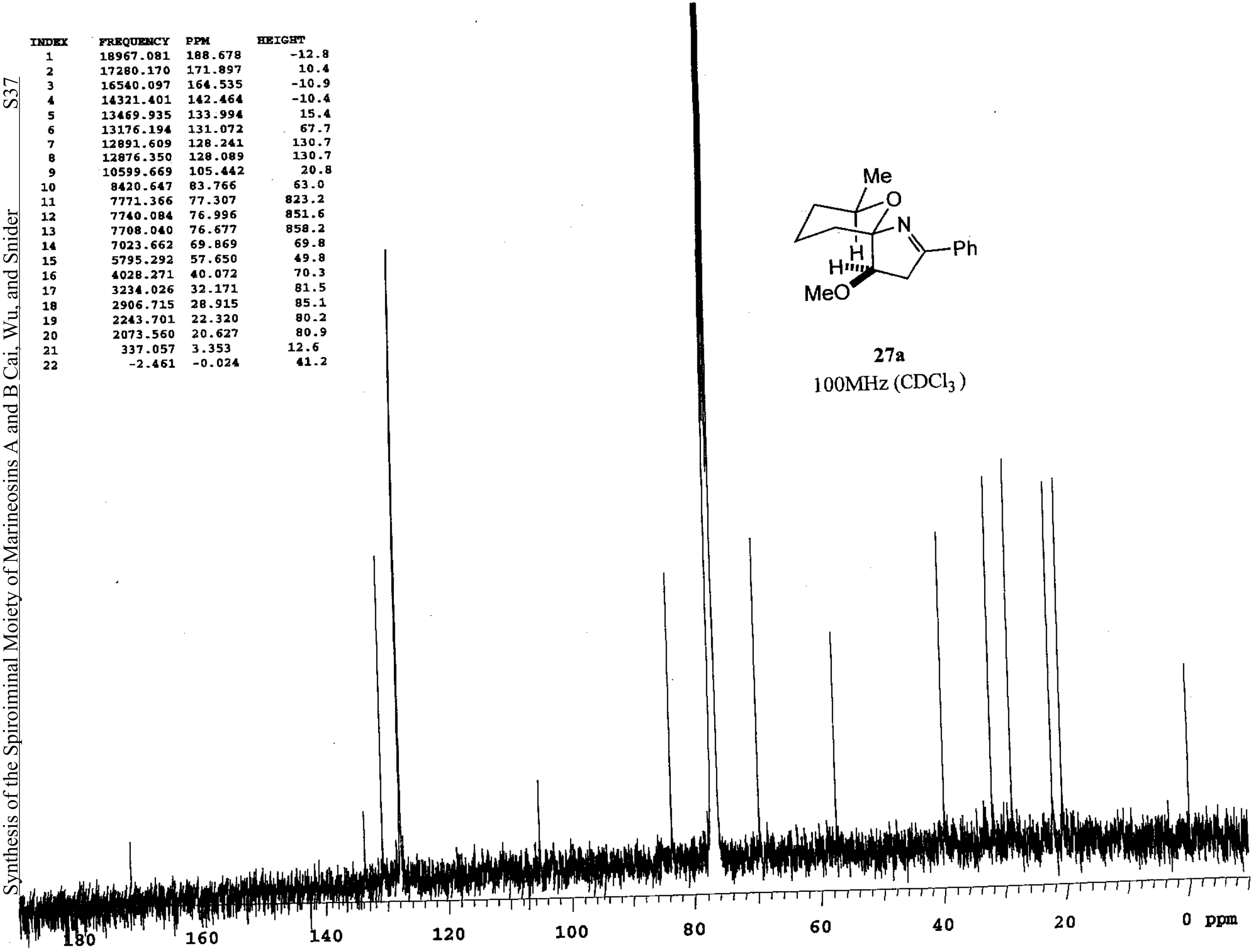
NOESY of **25a**
400MHz (CDCl$_3$)



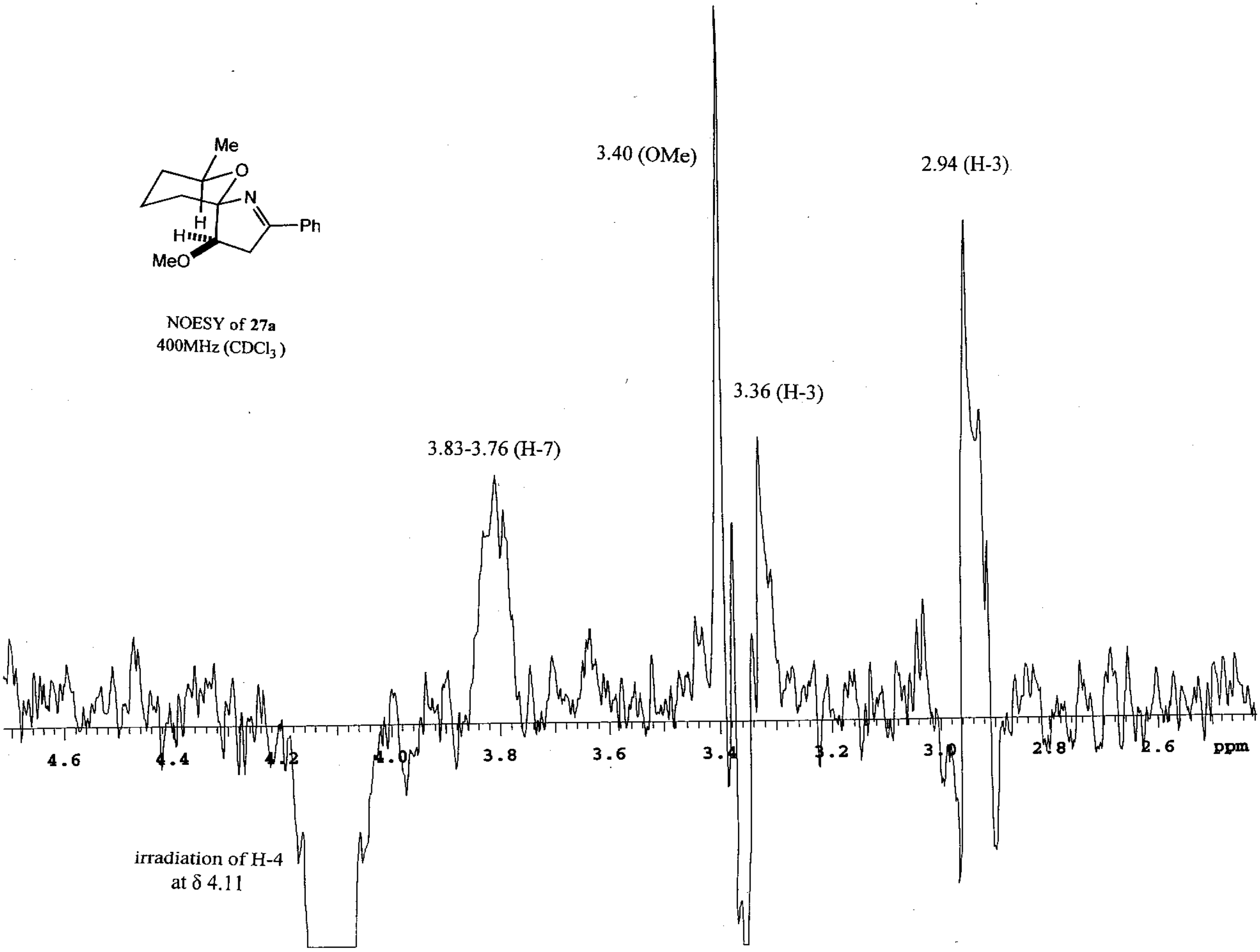
27a

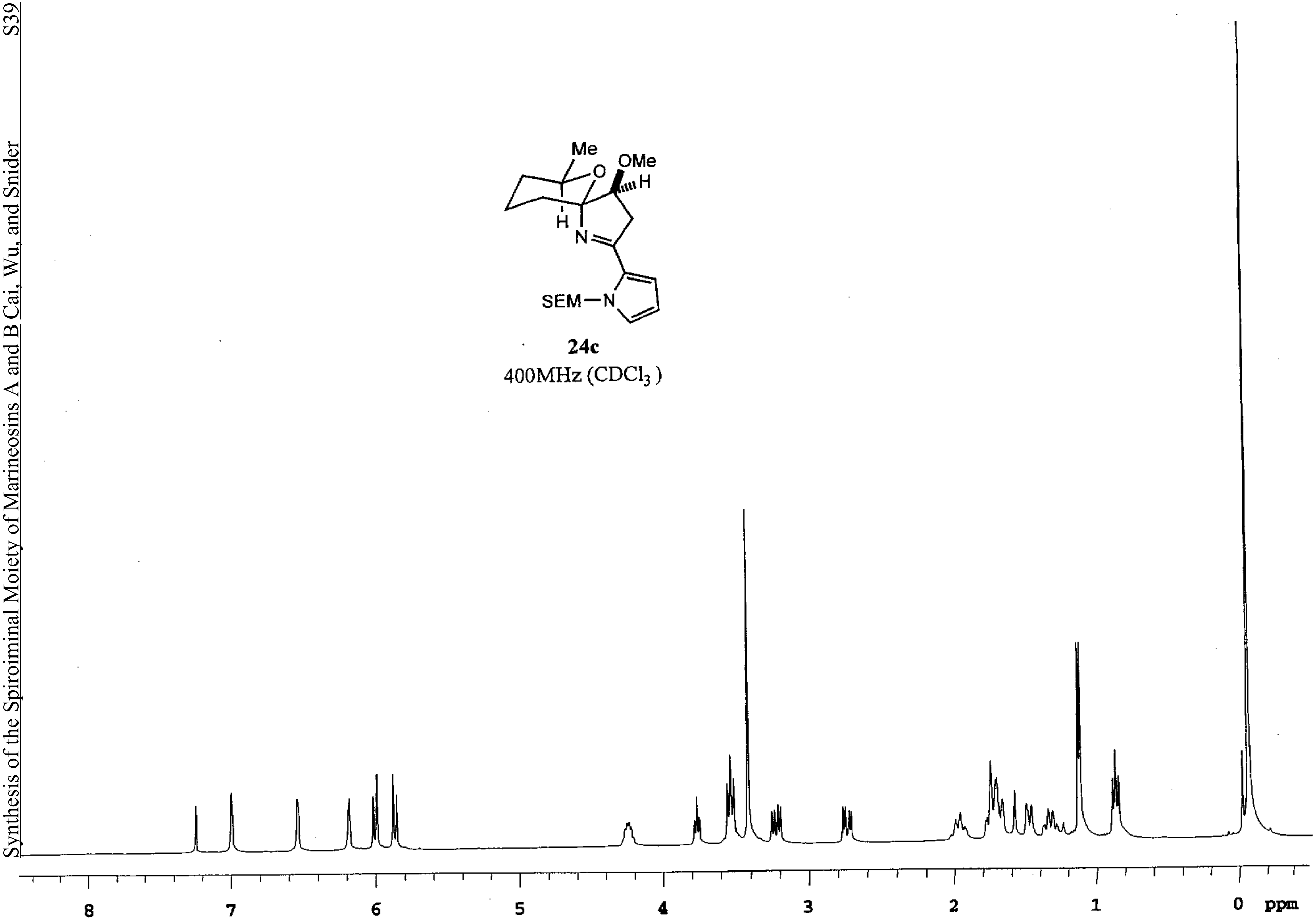
400MHz ($CDCl_3$)

INDEX	FREQUENCY	PPM	HEIGHT
1	18967.081	188.678	-12.8
2	17280.170	171.897	10.4
3	16540.097	164.535	-10.9
4	14321.401	142.464	-10.4
5	13469.935	133.994	15.4
6	13176.194	131.072	67.7
7	12891.609	128.241	130.7
8	12876.350	128.089	130.7
9	10599.669	105.442	20.8
10	8420.647	83.766	63.0
11	7771.366	77.307	823.2
12	7740.084	76.996	851.6
13	7708.040	76.677	858.2
14	7023.662	69.869	69.8
15	5795.292	57.650	49.8
16	4028.271	40.072	70.3
17	3234.026	32.171	81.5
18	2906.715	28.915	85.1
19	2243.701	22.320	80.2
20	2073.560	20.627	80.9
21	337.057	3.353	12.6
22	-2.461	-0.024	41.2



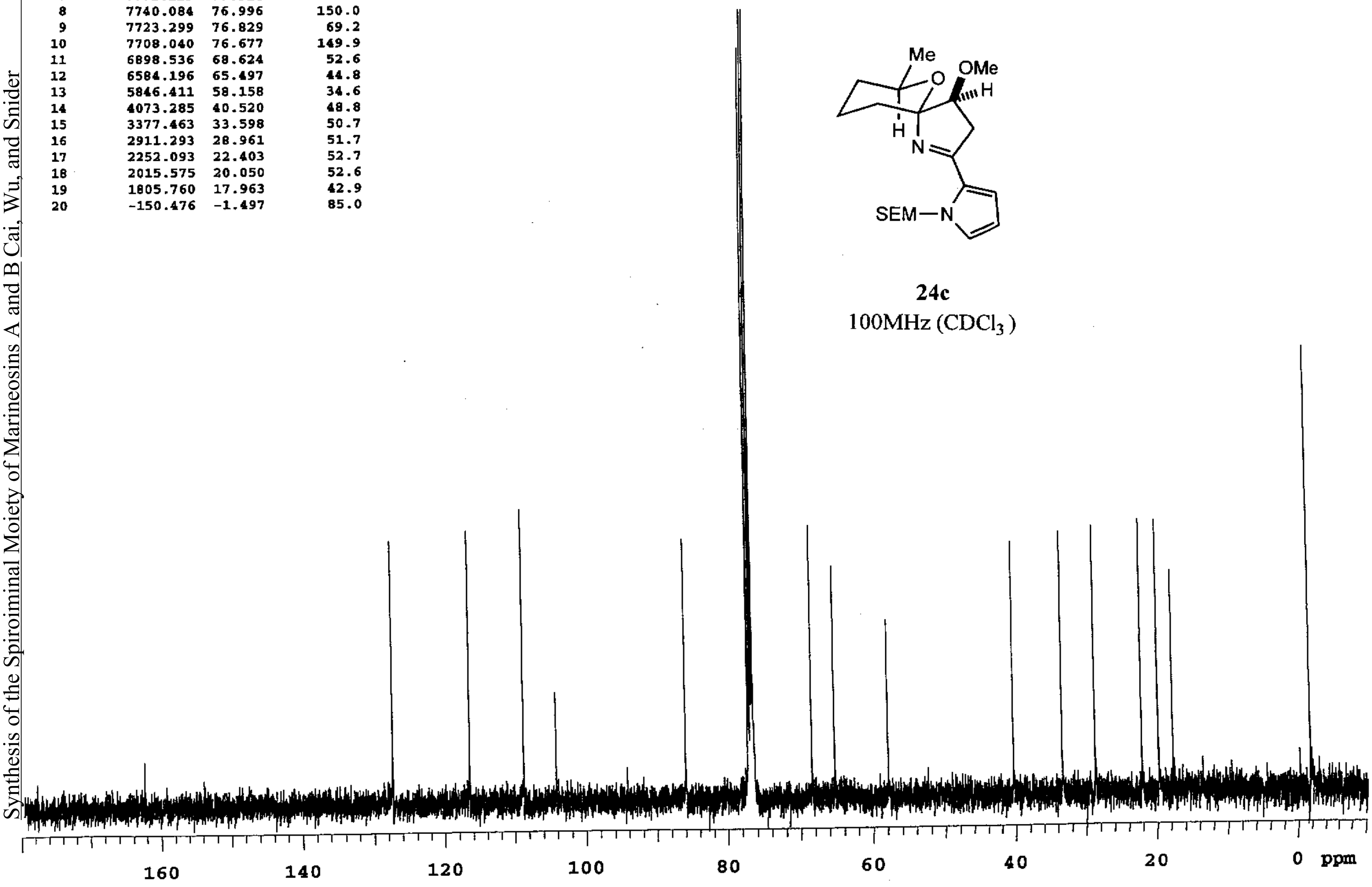
27a
100MHz ($CDCl_3$)


NOESY of **27a**
400MHz ($CDCl_3$)



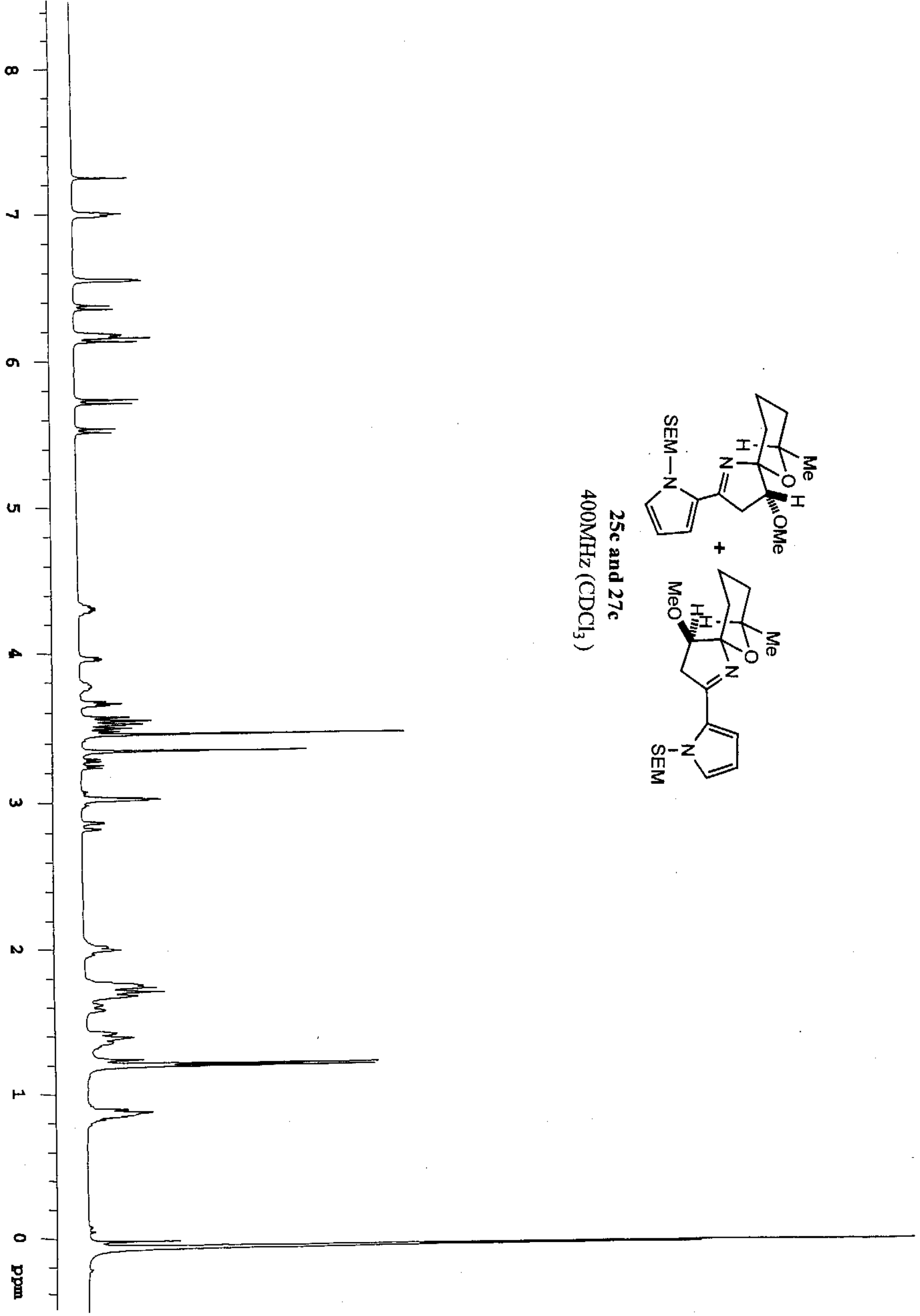
24c
400MHz ($CDCl_3$)

INDEX	FREQUENCY	PPM	HEIGHT
1	16344.015	162.585	10.1
2	12825.994	127.589	50.8
3	11727.328	116.659	52.5
4	10950.632	108.933	56.4
5	10489.802	104.349	21.9
6	8660.980	86.156	50.3
7	7772.129	77.314	142.6
8	7740.084	76.996	150.0
9	7723.299	76.829	69.2
10	7708.040	76.677	149.9
11	6898.536	68.624	52.6
12	6584.196	65.497	44.8
13	5846.411	58.158	34.6
14	4073.285	40.520	48.8
15	3377.463	33.598	50.7
16	2911.293	28.961	51.7
17	2252.093	22.403	52.7
18	2015.575	20.050	52.6
19	1805.760	17.963	42.9
20	-150.476	-1.497	85.0



24c

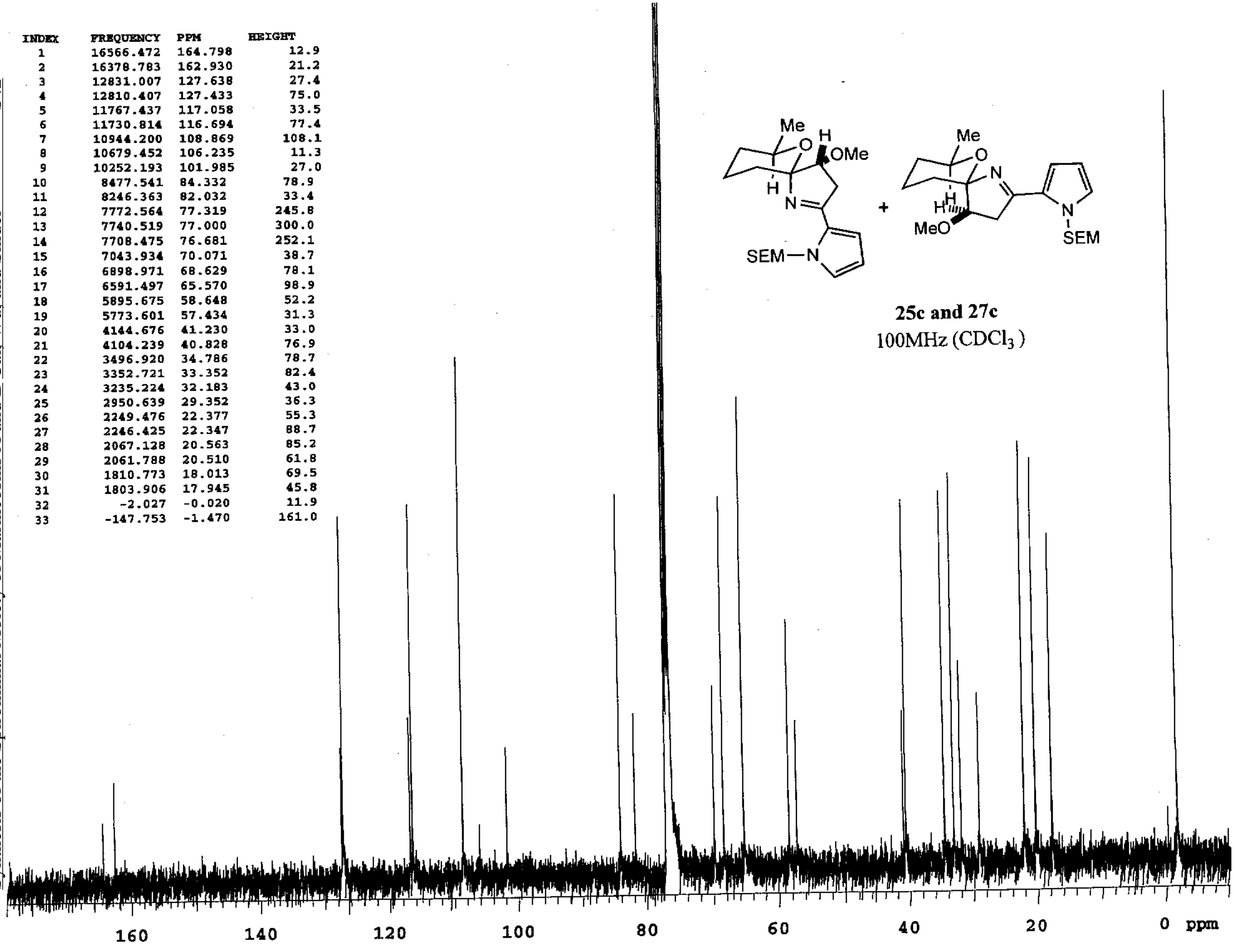
100MHz ($CDCl_3$)



25c and 27c

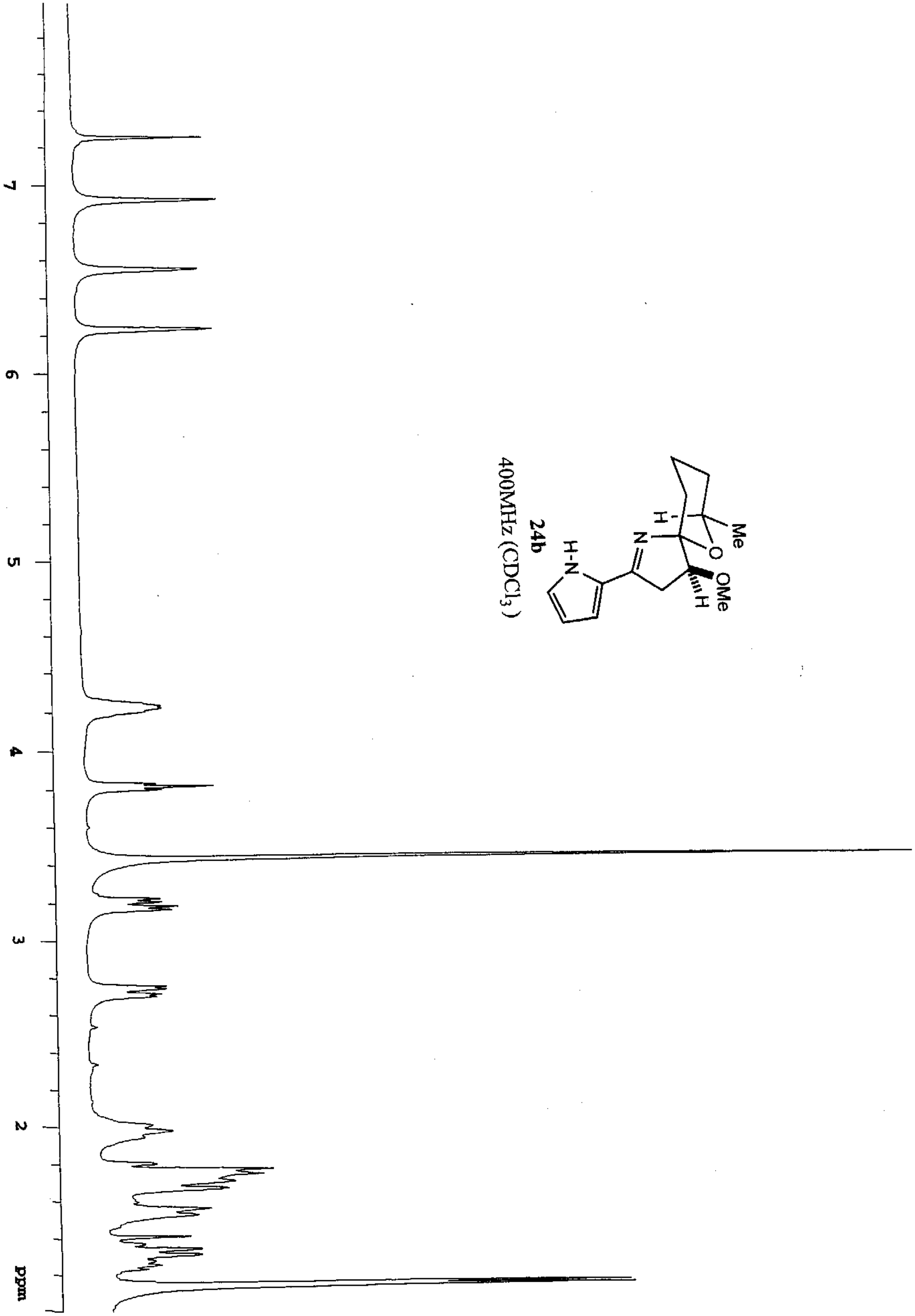
400MHz ($CDCl_3$)

INDEX	FREQUENCY	PPM	HEIGHT
1	16566.472	164.798	12.9
2	16378.783	162.930	21.2
3	12831.007	127.638	27.4
4	12810.407	127.433	75.0
5	11767.437	117.058	33.5
6	11730.814	116.694	77.4
7	10944.200	108.869	108.1
8	10679.452	106.235	11.3
9	10252.193	101.985	27.0
10	8477.541	84.332	78.9
11	8246.363	82.032	33.4
12	7772.564	77.319	245.8
13	7740.519	77.000	300.0
14	7708.475	76.681	252.1
15	7043.934	70.071	38.7
16	6898.971	68.629	78.1
17	6591.497	65.570	98.9
18	5895.675	58.648	52.2
19	5773.601	57.434	31.3
20	4144.676	41.230	33.0
21	4104.239	40.828	76.9
22	3496.920	34.786	78.7
23	3352.721	33.352	82.4
24	3235.224	32.183	43.0
25	2950.639	29.352	36.3
26	2249.476	22.377	55.3
27	2246.425	22.347	88.7
28	2067.128	20.563	85.2
29	2061.788	20.510	61.8
30	1810.773	18.013	69.5
31	1803.906	17.945	45.8
32	-2.027	-0.020	11.9
33	-147.753	-1.470	161.0



25c and 27c

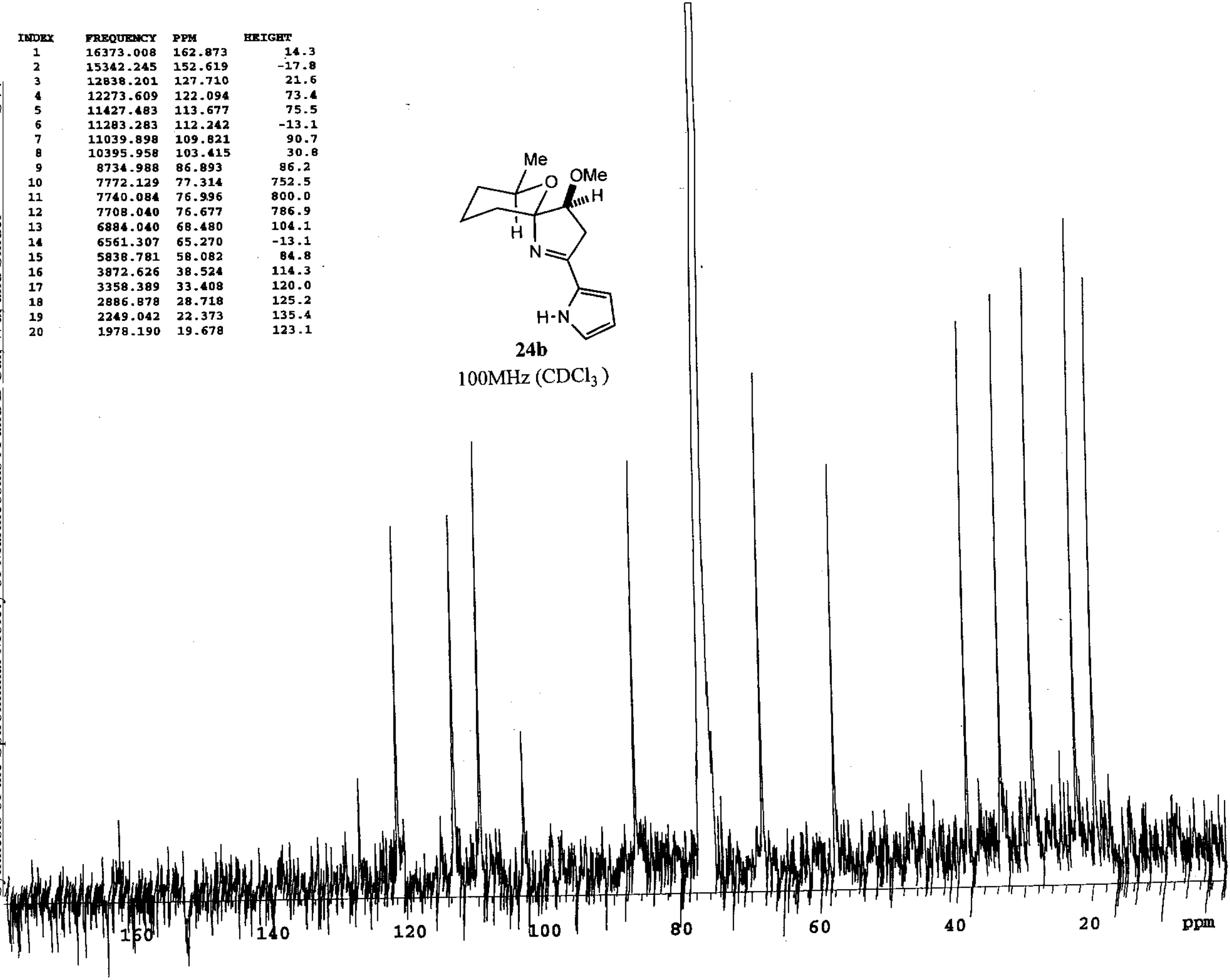
100MHz ($CDCl_3$)



24b

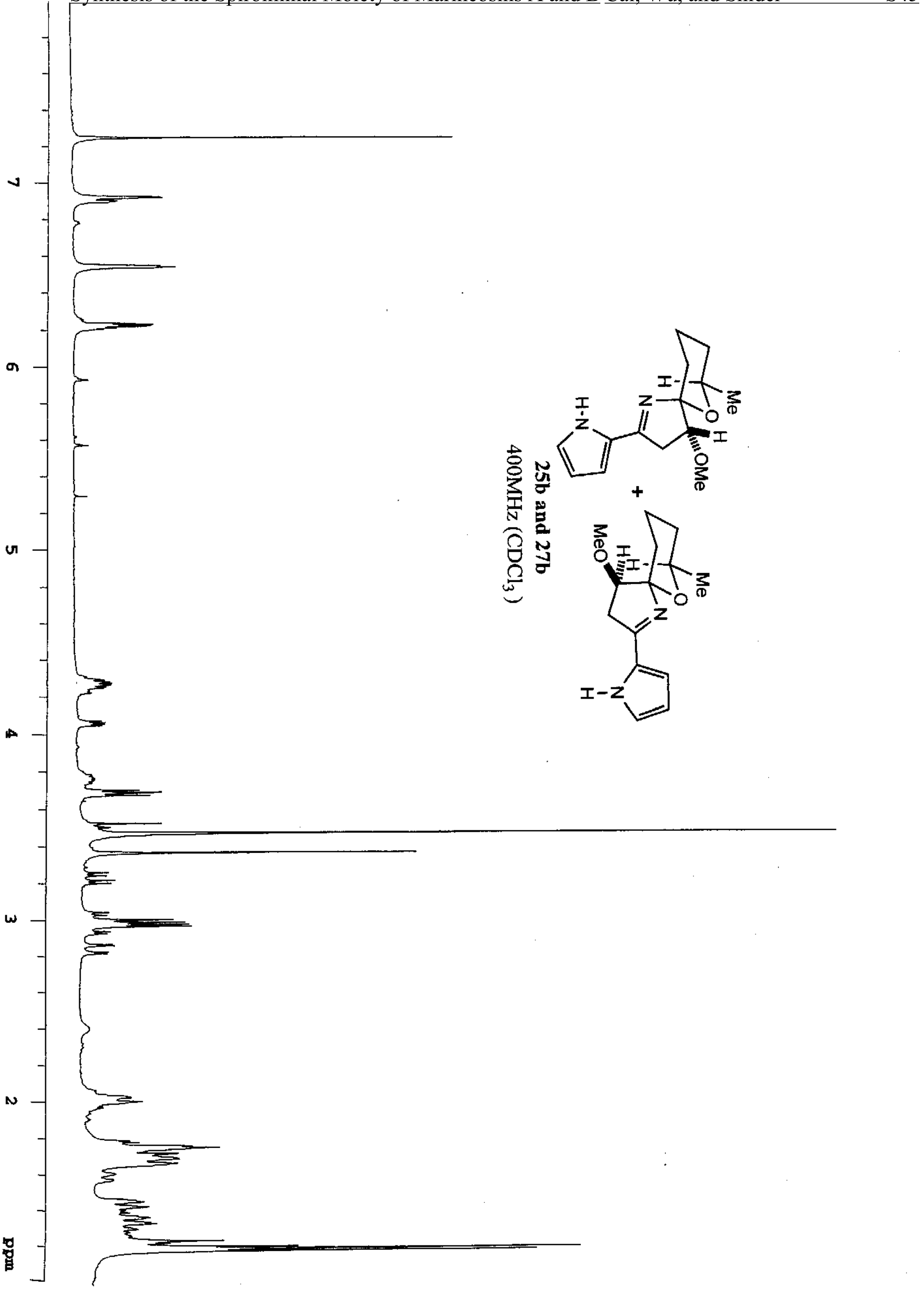
400MHz (CDCl$_3$)

INDEX	FREQUENCY	PPM	HEIGHT
1	16373.008	162.873	14.3
2	15342.245	152.619	-17.8
3	12838.201	127.710	21.6
4	12273.609	122.094	73.4
5	11427.483	113.677	75.5
6	11283.283	112.242	-13.1
7	11039.898	109.821	90.7
8	10395.958	103.415	30.8
9	8734.988	86.893	86.2
10	7772.129	77.314	752.5
11	7740.084	76.996	800.0
12	7708.040	76.677	786.9
13	6884.040	68.480	104.1
14	6561.307	65.270	-13.1
15	5838.781	58.082	84.8
16	3872.626	38.524	114.3
17	3358.389	33.408	120.0
18	2886.878	28.718	125.2
19	2249.042	22.373	135.4
20	1978.190	19.678	123.1



24b

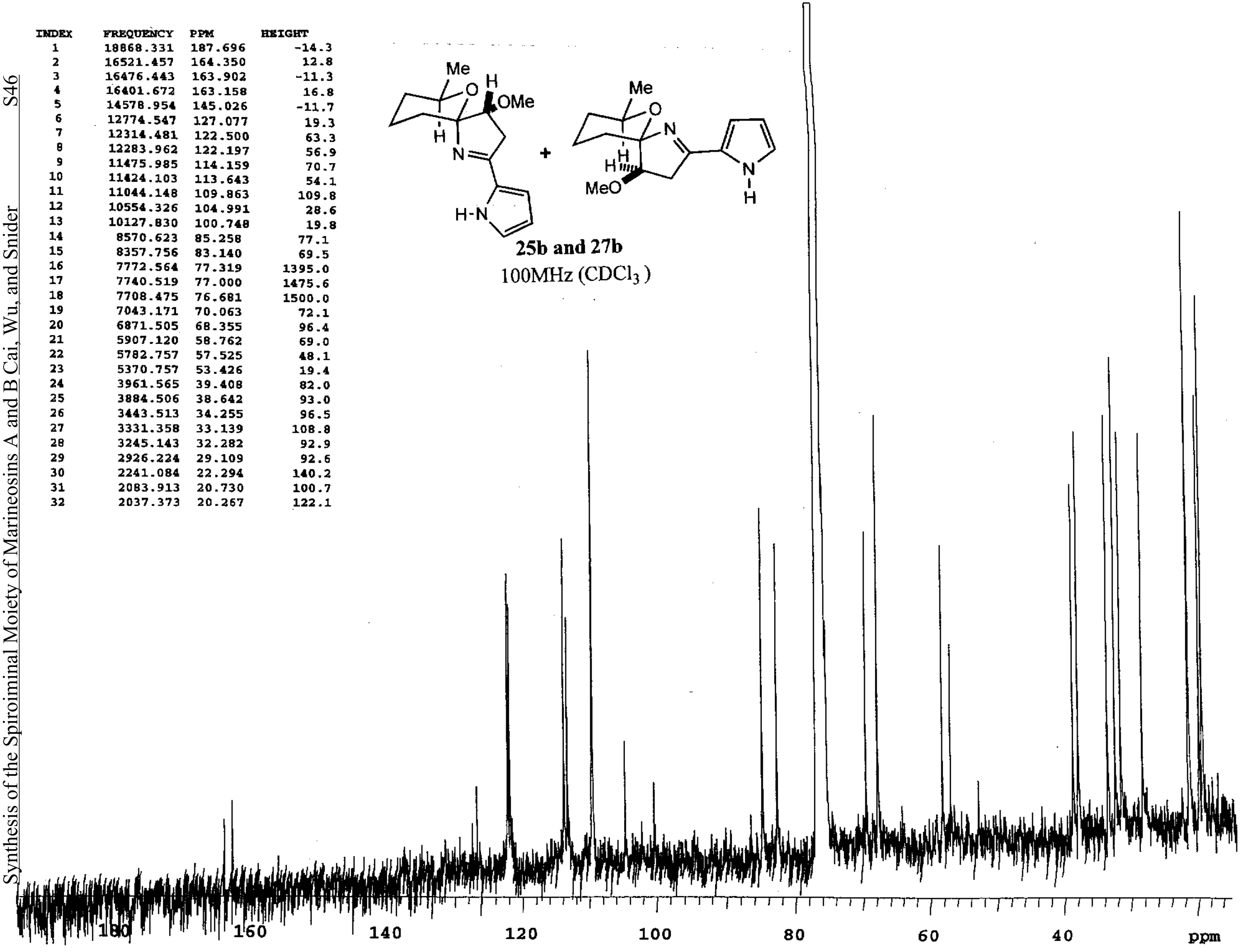
100MHz ($CDCl_3$)



25b and 27b

400MHz ($CDCl_3$)

INDEX	FREQUENCY	PPM	HEIGHT
1	18868.331	187.696	-14.3
2	16521.457	164.350	12.8
3	16476.443	163.902	-11.3
4	16401.672	163.158	16.8
5	14578.954	145.026	-11.7
6	12774.547	127.077	19.3
7	12314.481	122.500	63.3
8	12283.962	122.197	56.9
9	11475.985	114.159	70.7
10	11424.103	113.643	54.1
11	11044.148	109.863	109.8
12	10554.326	104.991	28.6
13	10127.830	100.748	19.8
14	8570.623	85.258	77.1
15	8357.756	83.140	69.5
16	7772.564	77.319	1395.0
17	7740.519	77.000	1475.6
18	7708.475	76.681	1500.0
19	7043.171	70.063	72.1
20	6871.505	68.355	96.4
21	5907.120	58.762	69.0
22	5782.757	57.525	48.1
23	5370.757	53.426	19.4
24	3961.565	39.408	82.0
25	3884.506	38.642	93.0
26	3443.513	34.255	96.5
27	3331.358	33.139	108.8
28	3245.143	32.282	92.9
29	2926.224	29.109	92.6
30	2241.084	22.294	140.2
31	2083.913	20.730	100.7
32	2037.373	20.267	122.1



25b and 27b

100MHz ($CDCl_3$)