Supporting Information for Org. Lett.

Intramolecular Catalytic Friedel–Crafts Reactions with Allenyl Cations for the Synthesis of Quinolines and Their Analogues

Teruhiko Ishikawa[†]*, Shinobu Manabe[‡], Toshiaki Aikawa[‡],
Takayuki Kudo[‡], and Seiki Saito[‡]*

Department of Bioscience and Biotechnology, School of Engineering[‡] and School of Education,[†] Okayama University, Tsushima, Okayama, Japan 700-8530

E-mail: seisaito@biotech.okayama-u.ac.jp

Experimental Section

Instrumentation. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Mercury-300 (300 MHz for proton and 75 MHz for carbon-13) instrument. The chemical shifts are given in δ units relative to internal $CHCl_3$ (7.26 ppm for ^{1}H) or $CDCl_3$ (77 ppm for ^{13}C). All NMR experiments were performed using deuteriochloroform as a solvent unless otherwise indicated.

Analytical Procedure and Data Presentation. Analytical thin layer chromatography was performed on Merck pre-coated silica gel 60 F-254 (0.25 mm thickness). ^{1}H-NMR spectral data were indicated in the form: δ-value of signal (peak multiplicity, integrated number of protons and coupling constant (if any)). Splitting patterns are abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad.

General Reaction Procedure. All reactions, unless otherwise noted, were conducted under a nitrogen or an argon atmosphere. Liquid reagents were transferred via a dry hypodermic syringe from sure seal bottles to a reaction flask through a rubber septa wired on to the reaction flask. The septa can also serve to permit evacuation to eliminate air and introduce the inert gas by means of a steady stream of inert gas flowing system. Organic extracts were concentrated by evaporation with a rotary evaporator evacuated at around 60 mmHg. Column chromatography, unless otherwise specified, was performed on a Merck silica gel 60 7734 using an appropriate ratio of ethyl acetate-hexane mixed solvent and abbreviated as CC.

Materials. Unless otherwise noted, materials were obtained from commercial suppliers and reagent grade materials were used without further purification. Dimethyl sulfoxide (DMF) and dichloromethane (CH_2Cl_2) were freshly distilled from CaH_2 prior to use. Methanol (MeOH) and ethanol (EtOH) were distilled from magnesium turnings under argon. Tetrahydrofuran (THF) was distilled from benzophenone/ketyl prior to use.

***N*-(5-Trimethylsiloxy-5,5-diphenyl-3-pentynyl)-*N*-(*p*-toluenesulfonyl)-*m*-methoxyaniline (1a)**. To a solution of *m*-anisidine (3.29 g, 26.7 mmol) in THF (30 ml) was added Et_3N (4.46 mL, 32.0 mmol) followed by the addition of *p*-toluenesulfonyl chloride (5.09 g, 26.7 mmol) at room temperature. The mixture was stirred at room temperature for 15 h, quenched by the addition of water,

and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave *N*-tosylanisidine (**A**) as a yellow solid. (7.03 g, 95 %).

To a solution of **A** (1.52 g, 5.48 mmol) in THF (25 ml) were added triphenylphosphine (1.87 g, 7.12 mmol) and 3-butyn-1-ol (0.50 ml, 6.58 mmol) at room temperature followed by the addition of diethyl azodicarboxylate (1.04 ml, 6.58 mmol) dropwise at 0 ℃. The mixture was stirred at room temperature for 15 min, quenched by the addition of water, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave *N*-(3-butynyl)-*N*-tosylanisidine (**B**) as a yellow oil. (980 mg, 54 %).

To a solution of **B** (442 mg, 1.34 mmol) in THF (5 ml) was added BuLi (1.05 ml, 1.61 mmol) dropwise at 0 ℃ followed by the addition of benzophenone (245 mg, 1.34 mmol) at 0 ℃. The mixture was stirred at 0 ℃ for 30 min, quenched by the addition of water, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave *N*-(5-hydroxy-5,5-diphenyl-3-pentynyl)-*N*-tosylanisidine (**C**) as a yellow oil. (531 mg, 77 %).

To a solution of **C** (531 mg, 1.04 mmol) in DMF (7 ml) were added imidazole (353 mg, 5.19 mmol) and chlorotrimethylsilane (0.33 ml, 2.59 mmol) at rt. The mixture was stirred at rt for 30 min, quenched by the addition of water, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave **1a** as a white solid. (606 mg, 99 %); ^{1}H NMR δ 0.08 (s, 9H), 2.43 (s, 3H), 2.54 (t, 2H, J = 7.7 Hz), 3.69 (s, 3H), 3.54 (t, 2H, J = 7.7 Hz), 6.60–6.54 (m, 1H), 6.68 (t, 1H, J = 2.2 Hz), 6.86 (dd, 1H, J = 2.5, 8.2 Hz), 7.31–7.15 (m, 9H), 7.60–7.50 (m, 6H); ^{13}C NMR δ 1.6, 19.5, 21.5, 49.4, 55.3, 75.5, 84.6, 85.0, 114.2, 114.7, 120.4, 126.0, 127.0, 127.7, 127.9, 129.4, 129.6, 135.0, 139.8, 143.5, 146.7, 160.0; IR (neat) 2239, 1352 cm^{-1}; R_f = 0.70 (hexane : AcOEt = 3 : 1).

The following compounds (**1b**—**h**, **9**, **10**) were synthesized by the similar procedure as that for **1a**.

***N*-(5-Trimethylsiloxy-5,5-diphenyl-3-pentynyl)-*N*-(*p*-toluenesulfonyl)-*p*-methoxyaniline (1b)**. ^{1}H NMR δ 0.14 (s, 9H), 2.48 (s, 3H), 2.61 (t, 2H, J = 7.7 Hz), 3.79 (t, 2H, J = 7.7 Hz), 3.85 (s, 3H), 6.8–6.83 (m, 2H), 7.03–6.98 (m, 2H), 7.38–7.23 (m, 8H), 7.63–7.54 (m, 6H); ^{13}C NMR δ 1.5, 19.5, 21.5, 49.6, 55.4, 75.5, 84.7, 84.9, 114.3, 126.0, 127.0, 127.7, 127.8, 129.4, 130.1, 131.1, 135.1, 143.4, 146.7, 159.1; IR (neat) 2242, 1350 cm^{-1}; R_f = 0.58 (hexane : AcOEt = 3 : 1).

***N*-(5-Trimethylsiloxy-5,5-diphenyl-3-pentynyl)-*N*-(*p*-toluenesulfonyl)-*m*-methylaniline (1c)**. ^{1}H NMR δ 0.08 (s, 9H), 2.29 (s, 3H), 2.44 (s, 3H), 2.55 (t, 2H, J = 7.4 Hz), 3.76 (t, 2H, J = 7.4 Hz), 6.74–6.80 (m b, 1H), 6.95 (b, 1H), 7.14–7.39 (m, 10 H), 7.50–7.65 (m, 6H); ^{13}C NMR δ 1.6, 19.6, 21.2, 21.5, 49.5, 75.5, 84.7, 84.9, 125.3, 126.0, 127.0, 127.7, 127.9, 128.8, 129.0, 129.4, 130.0, 135.2, 138.6, 139.1, 143.5, 146.7; IR (neat) 2243, 1352 cm^{-1}; R_f = 0.67 (hexane : AcOEt = 3 : 1).

***N*-(6-Methyl-5-trimethylsiloxy-5-phenyl-3-heptynyl)-*N*-(*p*-toluenesulfonyl)-*m*-methylaniline (1d)**. ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9H), 0.73 (d, 3H, J = 6.9 Hz), 0.92 (d, 3H, J = 6.6 Hz), 1.92 (m, 1H), 2.31 (s, 3H), 2.43 (s, 3H), 2.56–2.49 (m, 2H), 3.77–3.69 (m, 2H), 6.82–6.75 (m, 1H), 6.99–6.96 (m, 1H) 7.31–7.09 (m, 7H), 7.52–7.45 (m, 4H); ^{13}C NMR δ 1.5, 17.5, 17.7, 19.5, 21.2, 21.5,

42.0, 49.7, 78.3, 83.4, 83.8, 125.2, 126.3, 126.8, 127.4, 127.7, 128.8, 129.0, 129.4, 130.0, 135.2, 138.7, 139.1, 143.4, 145.2; IR (neat) 2237, 1354 cm^{-1}; R_f = 0.57 (hexane : AcOEt = 3 : 1).

***N*-(5-Trimethylsiloxy-5-phenyl-3-hexynyl)-*N*-(*p*-toluenesulfonyl)-*m*-methoxyaniline (1e)**. ^{1}H NMR δ 0.12 (s, 9H), 1.68 (s, 3H), 2.45 (s, 3H), 2.56–2.48 (m, 2H), 3.77–3.69 (m, 5H), 6.63–6.59 (m, 1H), 6.70–6.68 (m, 1H), 7.35–7.21 (m, 8H), 7.60–7.51 (m, 5H); ^{13}C NMR δ 1.7, 19.5, 21.5, 35.9, 49.6, 55.3, 71.2, 82.1, 85.9, 114.1, 114.8, 120.5, 125.0, 127.0, 127.7, 127.9, 129.4, 129.6, 135.2, 140.0, 143.5, 147.0, 160.0; IR (neat) 2240, 1352 cm^{-1}; R_f = 0.73 (hexane : AcOEt = 3 : 1).

***N*-(5-Trimethylsiloxy-5-phenyl-3-pentynyl)-*N*-(*p*-toluenesulfonyl)-*m*-methoxyaniline (1f)**. ^{1}H NMR δ 0.16 (s, 9H), 2.41 (s, 3H), 2.45 (t, 2H, *J* = 7.8 Hz), 3.67 (t, 2H, *J* = 7.8 Hz), 3.70, (s, 3H), 5.41 (s, 1H), 6.53–6.64 (m, 2H), 6.81–6.86 (m, 1H), 7.14–7.52 (m, 10 H); ^{13}C NMR δ 0.18, 19.5, 21.5, 49.6, 55.2, 64.6, 82.3, 82.6, 114.0, 114.8, 120.6, 126.3, 127.6, 127.7, 128.3, 129.4, 129.5, 135.2, 139.9, 141.5, 143.4, 159.9.

***N*-(5-Trimethylsiloxy-5,5-diphenyl-3-pentynyl)-*N*-(*p*-toluenesulfonyl)aniline (1g)**. ^{1}H NMR δ 0.06 (s, 9H), 2.41 (s, 3H), 2.54 (t, 2H, *J* = 7.7 Hz), 3.54 (t, 2H, *J* = 7.7 Hz), 7.07–7.00 (m, 2H), 7.32–7.15 (m, 11H), 7.54–7.45 (m, 6H); ^{13}C NMR δ 1.6, 19.6, 21.5, 49.5, 84.6, 85.0, 126.0, 127.0, 127.7, 127.9, 128.1, 128.8, 129.1, 129.4, 135.1, 138.8, 143.5, 146.7; IR (KBr) 2243, 1339 cm^{-1}; R_f = 0.67 (hexane : AcOEt = 3 : 1).

***N*-(5-Trimethylsiloxy-5,5-diphenyl-3-pentynyl)-*N*-(*p*-toluenesulfonyl)-*m*-chloroaniline (1h)**. ^{1}H NMR δ 0.08 (s, 9H), 2.44 (s, 3H), 2.55 (t, 2H, *J* = 7.1 Hz), 3.74 (t, 2H, *J* = 7.1 Hz), 6.98–6.93 (m, 1H), 7.06 (t, 1H, *J* = 2.2 Hz), 7.32–7.17 (m, 10H), 7.56–7.46 (m, 6H), 7.60–7.51 (m, 5H); ^{13}C NMR δ 1.7, 19.6, 21.5, 49.3, 84.3, 85.2, 125.9, 126.97, 127.03, 127.6, 127.9, 128.4, 128.9, 129.5, 130.0, 134.5, 134.6, 140.0, 143.9, 146.6; IR (neat) 2240, 1354 cm^{-1}; R_f = 0.70 (hexane : AcOEt = 3 : 1).

***N*-(7-Trimethylsiloxy-6,6-diphenyl-4-hexynyl)-*N*-(*p*-toluenesulfonyl)-*m*-methoxyaniline (9)**. ^{1}H NMR δ 0.05 (s, 9H), 1.75 (quin, 2H, *J* = 7.1 Hz), 2.44–2.37 (m, 5H), 3.62 (t, 2H, *J* = 6.3 Hz), 3.71 (s, 3H), 6.56–6.52 (m, 1H), 6.66–6.62 (m, 1H), 6.8–6.60 (m, 1H), 7.27–7.11 (m, 9H), 7.52–7.43 (m, 6H); ^{13}C NMR δ 1.5, 16.2, 21.5, 27.4, 49.9, 55.2, 75.5, 83.8, 87.3, 113.8, 114.7, 120.4, 125.9, 126.9, 127.7, 129.3, 129.5, 135.0, 140.3, 143.3, 146.9, 159.9 ; IR (neat) 2235, 1352 cm^{-1}; R_f = 0.63 (hexane : AcOEt = 3 : 1).

***N*-(7-Trimethylsiloxy-7,7-diphenyl-5-heptynyl)-*N*-(*p*-toluenesulfonyl)-*m*-methoxyaniline (10)**. ^{1}H NMR δ 0.07 (s, 9H), 1.70–1.51 (m, 4H), 2.42 (s, 3H), 3.00 (s, 3H), 3.58–3.50 (m, 2H), 3.72 (s, 3H), 6.65–6.57 (m, 2H), 6.86–6.80 (m, 1H), 7.29–7.13 (m, 9H), 7.63–7.48 (m, 6H); ^{13}C NMR δ 1.5, 18.4, 21.5, 25.2, 27.4, 49.8, 55.2, 75.5, 83.5, 88.1, 113.6, 114.6, 120.5, 125.9, 126.8, 127.7, 127.8, 129.3, 129.4, 135.1, 140.1, 143.3, 147.0, 159.8; IR (neat) 2235, 1350 cm^{-1}; R_f = 0.67 (hexane : AcOEt = 3:1).

7-Methoxy-4-(2,2-diphenylvinylidene)-1-(*p*-toluenesulfonyl)-1,2,3,4-tetrahydroquinoline (2a). To a solution of **1a** (60 mg, 0.10 mmol) in CH_2Cl_2 (1.5 ml) was added BF_3•OEt_2 (0.0026 ml, 0.021 mmol) dropwise at 0 ℃. The mixture was stirred at 0 ℃ for 10 min, neutralized with aqueous $NaHCO_3$ at 0 ℃, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and

concentrated by a rotary evaporator to give a yellow gum, which, on CC, gave a mixture of **2a** and **3a** (10:1, inseparable by SiO_2 column) as a white solid (49 mg, 99 %); **2a**: ^{1}H NMR δ 2.38 (s, 3H), 2.47–2.40 (m, 2H), 3.84 (s, 3H), 4.00–3.93 (m, 2H), 6.73 (dd, 1H, J =2.8, 8.8 Hz), 7.45–7.11 (m, 14H), 7.57–7.52 (m, 2H); ^{13}C NMR δ 21.6, 25.6, 45.7, 55.5, 100.2, 110.0, 113.6, 114.0, 117.0, 126.7, 127.0, 127.5, 127.9, 128.2, 128.3, 128.4, 129.7, 136.5, 136.7, 137.4, 143.7, 159.0, 204.5; IR (neat) 1356 cm^{-1}; R_f = 0.50 (hexane : AcOEt = 3 : 1).

The following compounds (**2b**—**e**,**g**,**h**, **11a**, **12**) were synthesized by the similar procedure as that for **2a** and were obtained as a mixture of 7- (**2**) and 5-substituted (**3**) isomers except for **2b**,**g**. These mixtures were inseparable by SiO_2 column chromatography. The spectroscopic data only for the major isomer (**2**) were listed, which were carefully read from the corresponding spectra of the mixtures.

6-Methoxy-4-(2,2-diphenylvinylidene)-1-(*p*-toluenesulfonyl)-1,2,3,4-tetrahydroquinoline (2b). ^{1}H NMR δ 2.44–2.36 (m, 5H), 3.76 (s, 3H), 3.96–3.90 (m, 2H), 6.83 (dd, 1H, J = 2.7, 9.1 Hz), 7.03 (d, 1H, J = 2.8 Hz), 7.36–7.17 (m, 12H), 7.52–7.46 (m, 2H), 7.73 (d, 1H, J = 9.1 Hz); ^{13}C NMR δ 21.6, 25.0, 45.5, 55.3, 100.3, 110.8, 114.0, 114.3, 126.4, 127.1, 127.6, 128.1, 128.3, 128.4, 129.1, 129.7, 136.0, 137.4, 143.6, 157.4, 205.1; IR (neat) 1350 cm^{-1}; R_f = 0.55 (hexane : AcOEt = 3 : 1). Exact Mass: exact mass, m/z 493.17122 (calcd for $C_{31}H_{27}NO_3S$ m/z 493.17116). Anal. Calcd for $C_{31}H_{27}NO_3S$: C, 75.43; H, 5.51; N, 2.84. Found: C, 75.30; H, 5.50; N, 2.80.

7-Methyl-4-(2,2-diphenylvinylidene)-1-(*p*-toluenesulfonyl)-1,2,3,4-tetrahydroquinoline (2c). ^{1}H NMR δ 2.37 (s, 3H), 2.38 (s, 3H), 2.47–2.40 (m, 2H), 3.96–3.89 (m, 2H), 6.98–6.93 (m, 1H), 7.49–7.07 (m, 12H), 7.42 (d, 1H, J = 8.0 Hz), 7.57–7.50 (m, 2H), 7.63 (s, 1H); ^{13}C NMR δ 21.4, 21.5, 25.5, 45.5, 100.3, 110.8, 114.0, 121.9, 126.5, 126.7, 126.97, 127.01, 127.3, 127.5, 128.28, 128.33, 128.4, 129.59, 129.64, 135.6, 136.3, 137.5, 137.9, 143.6, 204.8; IR (neat) 1356 cm^{-1}; R_f = 0.67 (hexane : AcOEt = 3 : 1).

4-(2-Isopropyl-2-phenylvinylidene)-7-methyl-1-(*p*-toluenesulfonyl)-1,2,3,4-tetrahydroquinoline (2d). ^{1}H NMR δ 0.99 (d, 3H, J = 6.3 Hz), 1.07 (d, 3H, J = 6.6 Hz), 2.40–2.29 (m, 8H), 2.96–2.82 (m, 1H), 4.10–3.78 (m, 2H), 6.97–6.92 (m, 1H), 7.36–7.18 (m, 8H), 7.54–7.48 (m, 2H) 7.63 (s, 1H); ^{13}C NMR δ 21.3, 21.5, 22.2, 22.4, 25.4, 29.1, 45.7, 101.2, 117.6, 123.1, 126.2, 126.4, 126.6, 126.8, 126.9, 127.0, 127.1, 128.4, 128.4, 129.6, 135.3, 136.0, 137.4, 137.5, 143.5 201.9; IR (neat) 1348 cm^{-1}; R_f = 0.57 (hexane : AcOEt = 3 : 1).

7-Methoxy-4-(2-methyl-2-phenylvinylidene)-1-(*p*-toluenesulfonyl)-1,2,3,4-tetrahydroquinoline (2e). ^{1}H NMR δ 2.10 (s, 3H), 2.3–2.32 (m, 2H), 2.42 (s, 3H), 3.83 (s, 3H), 4.04–3.86 (m, 2H), 6.70 (dd, 1H, J = 8.8, 2.7 Hz), 7.40–7.13 (m, 9H), 7.60–7.54 (m, 2H); ^{13}C NMR δ 16.7, 21.6, 25.5, 45.9, 55.5, 98.9, 104.8, 109.9, 113.5, 117.8, 118.3, 125.67, 125.74, 126.1, 126.9, 127.06, 127.13, 128.0, 128.1, 128.3, 129.7, 136.5, 137.4, 143.7, 158.7, 202.6; IR (neat) 1352 cm^{-1}; R_f = 0.53 (hexane : AcOEt = 3 : 1).

4-(2,2-Diphenylvinylidene)-1-(*p*-toluenesulfonyl)-1,2,3,4-tetrahydroquinoline (2g). ^{1}H NMR δ 2.37 (s, 3H), 2.51–2.45 (m, 2H), 4.00–3.93 (m, 2H), 7.36–7.09 (m, 14H), 7.56–7.50 (m, 3H), 7.79 (dd, 1H, J = 1.4, 8.2 Hz); ^{13}C NMR δ 21.6, 25.7, 45.5, 100.4, 114.1, 124.9, 125.8, 126.1, 126.95, 127.04, 127.6, 127.8, 128.3, 128.4, 129.7, 135.8, 136.1, 137.4, 143.7, 205.1; IR ($CHCl_3$) 1356 cm^{-1}; R_f = 0.67 (hexane : AcOEt) = 3 : 1). Exact Mass: exact mass, m/z 463.16045 (calcd for $C_{30}H_{25}NO_2S$ m/z

463.16060). Anal. Calcd for $C_{30}H_{25}NO_2S$: C, 77.72; H, 5.44; N, 3.02. Found: C, 77.58; H, 5.31; N, 2.99.

7-Chlolo-4-(2,2-diphenylvinylidene)-1-(*p*-toluenesulfonyl)-1,2,3,4-tetrahydroquinoline (2h). ^{1}H NMR δ 2.38 (s, 3H), 2.50–2.41 (m, 2H), 3.97–3.88 (m, 2H), 7.50–7.05 (m, 13H), 7.84 (d, 1H, J = 1.9 Hz), 7.53–7.11 (m, 12H), 7.49–7.42 (m, 2H), 7.68 (d, 2H); ^{13}C NMR δ 21.6, 25.0, 45.5, 55.3, 100.3, 110.8, 114.0, 114.3, 126.4, 127.1, 127.7, 127.9, 128.1, 128.3, 129.1, 129.7, 136.1, 137.4, 143.6, 157.4, 205.1; IR ($CHCl_3$) 1358 cm^{-1}; R_f = 0.60 (hexane : AcOEt = 3 : 1).

8-Methoxy-5-(2,2-diphenylvinylidene)-1-(*p*-toluenesulfonyl)-2,3,4,5-tetrahydro-1-benzazepine (11a). ^{1}H NMR δ 2.01 (quin, 2H, J = 6.0 Hz), 2.37 (s, 3H), 2.51–2.44 (m, 2H), 3.74 (s, 3H), 3.88 (t, 2H, J = 6.0 Hz), 6.71 (dd, 1H, J = 2.5, 8.5 Hz), 6.97 (d, 1H, J = 2.5 Hz), 7.12 (d, 1H, J = 8.0 Hz), 7.40–7.26 (m, 11H), 7.75–7.49 (m, 2H); ^{13}C NMR δ 21.5, 28.2, 29.6, 50.6, 55.3, 107.2, 110.3, 112.6, 113.5, 126.0, 127.2, 127.3, 128.4, 128.4, 129.6, 130.7, 136.8, 138.2, 139.0, 143.3, 159.0, 206.3; IR (neat) 1346 cm^{-1}; R_f = 0.47 (hexane : AcOEt = 3 : 1). Exact Mass: exact mass, m/z 507.18677 (calcd for $C_{32}H_{29}NO_3S$ m/z 507.18681). Anal. Calcd for $C_{32}H_{29}NO_3S$: C, 75.71; H, 5.76; N, 2.76. Found: C, 75.77; H, 5.71; N, 2.74.

9-Methoxy-6-(2,2-diphenylvinylidene)-1-(*p*-toluenesulfonyl)-1,2,3,4,5,6-hexahydro-2-benzazocine (12). ^{1}H NMR δ 1.67–1.56 (m, 2H), 1.99–1.87 (m, 2H), 2.43 (s, 3H), 3.12–3.04 (m, 2H), 3.61 (s, 3H) 3.69–3.63 (m, 2H), 6.26 (d, 1H, J = 2.7 Hz), 6.79 (dd, 1H, J = 2.7, 9.1 Hz), 7.45–7.23 (m, 12H), 7.55 (d, 2H, J = 8.8 Hz), 7.78–7.73 (m, 2H); ^{13}C NMR δ 21.5, 23.9, 27.6, 31.2, 51.3, 55.2, 107.8, 109.8, 113.6, 115.0, 127.1, 127.6, 128.3, 128.4, 129.6, 129.8, 130.7, 136.4, 136.8, 137.7, 143.3, 159.2, 208.4; IR ($CHCl_3$) 1346 cm^{-1}; R_f = 0.38 (hexane : AcOEt = 3:1). Exact Mass: exact mass, m/z 521.20233 (calcd for $C_{33}H_{31}NO_3S$ m/z 521.20246). Anal. Calcd for $C_{33}H_{31}NO_3S$: C, 75.98; H, 5.99; N, 2.68. Found: C, 75.79; H, 6.06; N, 2.54.

7-Methoxy-4-(2,2-diphenylvinyl)-1-(*p*-toluenesulfonyl)-1,2-dihydroquinoline (4a). To a solution of **1a** (75 mg, 0.13 mmol) in CH_2Cl_2 (1.5 ml) was added BF_3•OEt_2 (0.0033 ml, 0.026 mmol) at 0 ℃. The mixture was stirred at 0 ℃ for 1 h, neutralized with aqueous $NaHCO_3$ at 0 ℃, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave a mixture of **4a** and **5a** (10 : 1; inseparable by SiO_2 column) as a yellow oil. (63 mg, 99 %). Data for **4a**: ^{1}H NMR δ 2.46 (s, 3H), 3.88 (S, 3H), 4.16–4.09 (m, 2H), 4.95–4.90 (m, 1H), 5.86–5.83 (m, 1 H), 6.78 (dd, 1H, J = 2.8, 8.5 Hz), 7.05–7.00 (m, 2H), 7.25–7.10 (m, 8H), 7.50–7.26 (m, 6H); ^{13}C NMR δ 21.5, 45.3, 55.6, 112.0, 113.2, 120.4, 124.2, 124.3, 125.6, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 128.06, 128.13, 129.0, 129.7, 133.6, 136.1, 136.8, 139.6, 142.6, 143.2, 145.5, 159.3; IR ($CHCl_3$) 1352 cm^{-1}; R_f = 0.50 (hexane : AcOEt = 3 : 1).**4-(2,2-Diphenylvinyl)-1-(*p*-toluenesulfonyl)-1,2-dihydroquinoline (4g)**. To a solution of **2g** (65 mg, 0.14 mmol) in EtOH (5 ml) was added *p*-toluenesulfonic acid monohydrate (27 mg, 0.14 mmol) at room temperature. The mixture was stirred at 78 ℃ for 24 h, neutralized with aqueous $NaHCO_3$ at 0 ℃, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave **4g** as a yellow gum (64 mg, 99 %); ^{1}H NMR δ 2.47 (s, 3H), 4.18–4.13 (m, 2H), 5.10–5.04 (m, 1H), 5.88–5.84 (m, 1H), 7.08–7.00 (m, 2H), 7.37–7.10

(m, 15H), 7.74–7.69 (m, 1H); ^{13}C NMR δ 21.5, 45.2, 123.2, 123.9, 124.6, 126.8, 127.1, 127.4, 127.5, 127.7, 127.8, 128.08, 128.13, 128.2, 129.0, 129.7, 131.3, 133.8, 135.4, 136.1, 139.5, 142.5, 143.2, 145.6; IR (neat) 1354 cm^{-1}; R_f = 0.67 (hexane : AcOEt = 3 : 1). Exact Mass: exact mass, m/z 463.16066 (calcd for $C_{30}H_{25}NO_2S$ m/z 463.16060). Anal. Calcd for $C_{30}H_{25}NO_2S$: C, 77.72; H, 5.44; N, 3.02. Found: C, 77.61; H, 5.42; N, 3.10.

The following compound was prepared in a similar way as that described for **4g**.

5-(2,2-Diphenylvinyl)-8-methoxy-1-*p*-toluenesulfonyl-2,3-dihydro-1-benzazepine (11b). ^{1}H NMR ($CDCl_3$) δ 2.06–1.98 (m, 2H), 2.44 (s, 3H), 3.83 (s, 3H), 4.06–3.95 (b, 2H), 5.46–5.38 (m, 1H), 5.79 (d, 1H, *J* = 1.1 Hz), 6.85–6.78 (m, 1H), 7.33–7.08 (m, 14H), 7.51–7.47 (m, 2H); ^{13}C NMR δ 21.6, 27.5, 55.5, 55.7, 114.3, 115.9, 126.9, 127.4, 127.6, 128.0, 128.1, 129.0, 129.2, 129.8, 129.9, 130.1, 131.0, 137.0, 137.7, 138.3, 140.0, 142.8, 143.0, 143.1, 159.0; R_f = 0.47 (hexane : AcOEt = 3:1). Exact Mass: exact mass, m/z 507.18693 (calcd for $C_{32}H_{29}NO_3S$ m/z 507.18681). Anal. Calcd for $C_{32}H_{29}NO_3S$: C, 75.71; H, 5.76; N, 2.76. Found: C, 75.62; H, 5.69; N, 2.70.

7-Methoxy-4-(2,2-diphenylvinyl)quinoline (6a) and 5-methoxy-4-(2,2-diphenylvinyl)-quinoline (7a). To a solution of a mixture of **4a** and **5a** (60 mg, 0.12 mmol) in MeOH (5 ml) was added potassium hydroxide (95 mg, 1.69 mmol) at room temperature. The mixture was stirred at 64 ℃ for 30 h, quenched by the addition of water, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave **6a** (29 mg, 72 %) and **7a** (4 mg, 9 %) both as a yellow gum. **6a**: ^{1}H NMR δ 3.96 (s, 3H), 6.74 (d, 1H, *J* = 4.7 Hz), 7.10–7.04 (m, 2H), 7.20–7.15 (m, 4H), 7.45–7.34 (m, 7H), 8.03 (d, 1H, *J* = 9.1 Hz), 8.50 (d, 1H, *J* = 4.7 Hz); ^{13}C NMR δ 55.5, 107.7, 119.4, 119.6, 122.6, 123.3, 125.6, 127.8, 128.17, 128.25, 128.31, 128.35, 130.3, 139.2, 142.5, 143.5, 147.7, 148.9, 150.0, 150.1, 160.4; R_f = 0.17 (hexane : AcOEt = 3 : 1); Exact Mass: exact mass, m/z 337.14660 (calcd for $C_{24}H_{19}NO$ m/z 337.14666). Anal. Calcd for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15. Found: C, 85.29; H, 5.62; N, 4.11.

7a: ^{1}H NMR δ 3.90 (s, 3H), 6.78 (dd, 1H, *J* = 1.1, 4.7 Hz), 6.78 (dd, 1H, *J* = 1.1, 7.7 Hz), 7.20–7.04 (m, 4H), 7.44–7.30 (m, 5H), 7.72–7.59 (m, 3H), 8.47 (d, 1H, *J* = 4.7 Hz); ^{13}C NMR δ 56.1, 105.6, 120.5, 122.4, 122.9, 127.2, 127.6, 128.06, 128.09, 128.2, 128.9, 129.6, 130.9, 139.6, 141.7, 142.9, 144.2, 149.7, 150.2, 150.1, 157.2; R_f = 0.27 (hexane : AcOEt = 3 : 1).

4-(2,2-Diphenylvinyl)quinoline (6g). To a solution of **4g** (75 mg, 0.16 mmol) in MeOH (5 ml) was added potassium hydroxide (95 mg, 1.69 mmol) at room temperature. The mixture was stirred at 64 ℃ for 30 h, quenched by the addition of water, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave **6g** (47 mg, 94 %) as a yellow gum: ^{1}H NMR δ 6.87 (d, 1H, *J* = 4.4 Hz), 7.12–7.06 (m, 2H), 7.30–7.14 (m, 3H), 7.47–7.34 (m, 6H), 7.57–7.49 (m, 1H), 7.74–7.67 (m, 1H), 8.18–8.09 (m, 2H), 8.59 (d, *J* = 4.7 Hz); ^{13}C NMR δ 121.5 123.1, 124.3, 126.4, 127.6, 127.8, 128.1, 128.26, 128.33, 129.2, 129.9, 130.3, 139.1, 142.4, 143.6, 147.8, 148.3, 149.7; R_f = 0.33 (hexane : AcOEt = 3 : 1). Exact Mass: exact mass, m/z 307.13601 (calcd for $C_{23}H_{17}N$ m/z 307.13610). Anal. Calcd for $C_{23}H_{17}N$: C, 89.87; H, 5.57; N, 4.56. Found: C, 89.77; H, 5.51; N, 4.59.

Methyl quinoline-4-carboxylate (**8g**). To a solution of **6g** (47 mg, 0.15 mmol) in THF (3 ml) was added potassium permanganate (121 mg, 0.76 mmol) dissolved in H_2O (1 ml) at 0 ℃. The mixture was stirred at 0 ℃ for 5 h, neutralized with aqueous $NaHCO_3$ at 0 ℃, and concentrated by a rotary evaporator to give an oil. To a solution of the oil in MeOH (5 ml) was added chlorotrimethylsilane (0.50 ml 3.93 mmol) at room temperature. The mixture was stirred at 55 ℃ for 3 days, neutralized with aqueous $NaHCO_3$ at 0 ℃, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave **8g** (17 mg, 60 %) as a colorless oil: ^{1}H NMR δ 4.04 (s, 3H), 7.70–7.63 (m, 1H), 7.81–7.74 (m, 1H), 7.91 (d, 1H, J = 4.4 Hz), 8.20–8.15 (m, 1H), 8.80–8.74 (m, 1H), 9.20 (d, 1H, J = 4.4 Hz); ^{13}C NMR δ 52.7, 122.2, 125.0, 125.6, 128.2, 129.7, 130.0, 134.8, 149.1, 149.8, 166.6; IR (neat) 1728 cm^{-1}; R_f = 0.33 (hexane : AcOEt = 3 : 1). Exact Mass: exact mass, m/z 187.06333 (calcd for $C_{11}H_9NO_2$ m/z 187.06333). Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48; O, 17.09. Found: C, 70.50; H, 4.90; N, 7.42.

***N*-Methoxy-*N*-(4-trimethylsiloxy-4,4-diphenyl-2-butynyl)-(*m*-methoxybenzyl)amine (13a)**. To a solution of 3-methoxybenzyl bromide (3.00 ml, 21.4 mmol) in DMF (50 ml) was added *N,N*-diisopropylethylamine (8.96 mL, 64.3 mmol) followed by the addition of $MeONH_2$·HCl (2.15 g, 25.7 mmol) at room temperature. The mixture was stirred at room temperature for 19 h, quenched by the addition of water, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which on, CC, gave *N*-(3-methoxybenzyl)-*O*-methylhydroxylamine (**D**) as a yellow oil (2.06 g, 58 %).

To a solution of **D** (1.65 g, 9.84 mmol) in DMF (20 ml) was added *N,N*-diisopropylethylamine (2.51 ml, 14.8 mmol) followed by the addition of propargyl bromide (0.89 ml, 11.8 mmol) at room temperature. The mixture was stirred at 60 ℃ for 15 h, quenched by the addition of water, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave *N*-(3-methoxybenzyl)-*N*-(2-propynyl)-*O*-methylhydroxylamine (**E**) as a yellow oil (1.98 g, 98 %).

To a solution of **E** (520 mg, 2.44 mmol) in THF (12 ml) was added BuLi (2.05 ml, 3.17 mmol) dropwise at 0 ℃ followed by the addition of benzophenone (532 mg, 2.92 mmol) at 0 ℃. The mixture was stirred at 0 ℃ for 30 min, quenched by the addition of water, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave *N*-(3-methoxybenzyl)-*N*-(4-hydroxy-4,4-diphenyl-2-propynyl)-*O*-methyl-hydroxylamine (**F**) as a yellow oil (709 mg, 75 %).

To a solution of **F** (709 mg, 1.83 mmol) in DMF (12 ml) was added imidazole (747 mg, 10.1 mmol) and chlorotrimethylsilane (0.70 ml, 5.49 mmol) at room temperature. The mixture was stirred at rt for 1 h, quenched by the addition of water, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which on, CC, gave **13a** as a yellow oil. (808 mg, 96 %); ^{1}H NMR δ 0.13 (s, 9H), 3.42 (s, 3H), 3.72 (s, 2H), 3.79 (s, 3H), 3.92 (s, 2H), 6.86–6.80 (m, 1H), 6.95–6.90 (m, 2H), 7.32–7.18 (m, 7H), 7.62–7.58 (m, 4H); ^{13}C NMR δ 1.5,

46.3, 55.2, 60.7, 61.3, 75.6, 83.7, 87.4, 113.1, 114.8, 121.9, 126.1, 127.1, 127.9, 129.2, 138.6, 146.7, 159.5; IR (neat) 2349 cm^{-1}; R_f = 0.77 (hexane : AcOEt = 3 : 1).

The following compounds were synthesized by the similar procedure as that for **13a**.

***N*-Methoxy-*N*-(4-trimethylsiloxy-4,4-diphenyl-2-butynyl)-(*m*-methylbenzyl)amine (13b)**. ^{1}H NMR δ 0.18 (s, 9H), 2.39 (s, 3H), 3.46 (s, 3H), 3.75 (s, 2H), 3.98 (s, 2H), 7.39-7.10 (m, 10H), 7.69–7.63 (m, 4H); ^{13}C NMR δ 1.5, 21.3, 46.2, 60.6, 61.2, 75.6, 83.8, 87.3, 126.1, 126.6, 127.1, 127.9, 128.1, 130.3, 136.8, 137.8, 146.7; IR (neat) 2341 cm^{-1}; R_f = 0.80 (hexane : AcOEt = 3 : 1).

2,7-Dimethoxy-4-(2,2-diphenylvinylidene)-1,2,3,4-tetrahydroisoquinoline (14a). To a solution of **13a** (127 mg, 0.28 mmol) in CH_2Cl_2 (1.5 ml) was added TMSOTf (0.05 ml, 0.28 mmol) dropwise at –30 ℃. The mixture was stirred at –25 ℃ for 45min, neutralized with aqueous $NaHCO_3$ at 0 ℃, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave **14a** as a yellow gum. (91 mg, 89 %); ^{1}H NMR δ 3.65 (s, 3H), 3.80 (s, 3H), 2.39 (s, 3H), 4.40–4.00 (b, 4H), 6.69 (d, 1H, J = 2.5 Hz), 6.78 (dd, 1H, J = 2.5, 8.5 Hz), 7.56–7.26 (m, 11H); ^{13}C NMR δ 54.9, 55.3, 57.2, 59.6, 100.7, 111.7, 114.0, 114.5, 121.1, 127.4, 128.4, 133.2, 136.6, 159.3, 204.1; R_f = 0.53 (hexane : AcOEt = 3 : 1). Exact Mass: exact mass, m/z 369.17276 (calcd for $C_{25}H_{23}NO_2$ m/z 369.17288). Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27; N, 3.79. Found: C, 81.22; H, 6.30; N, 3.69.

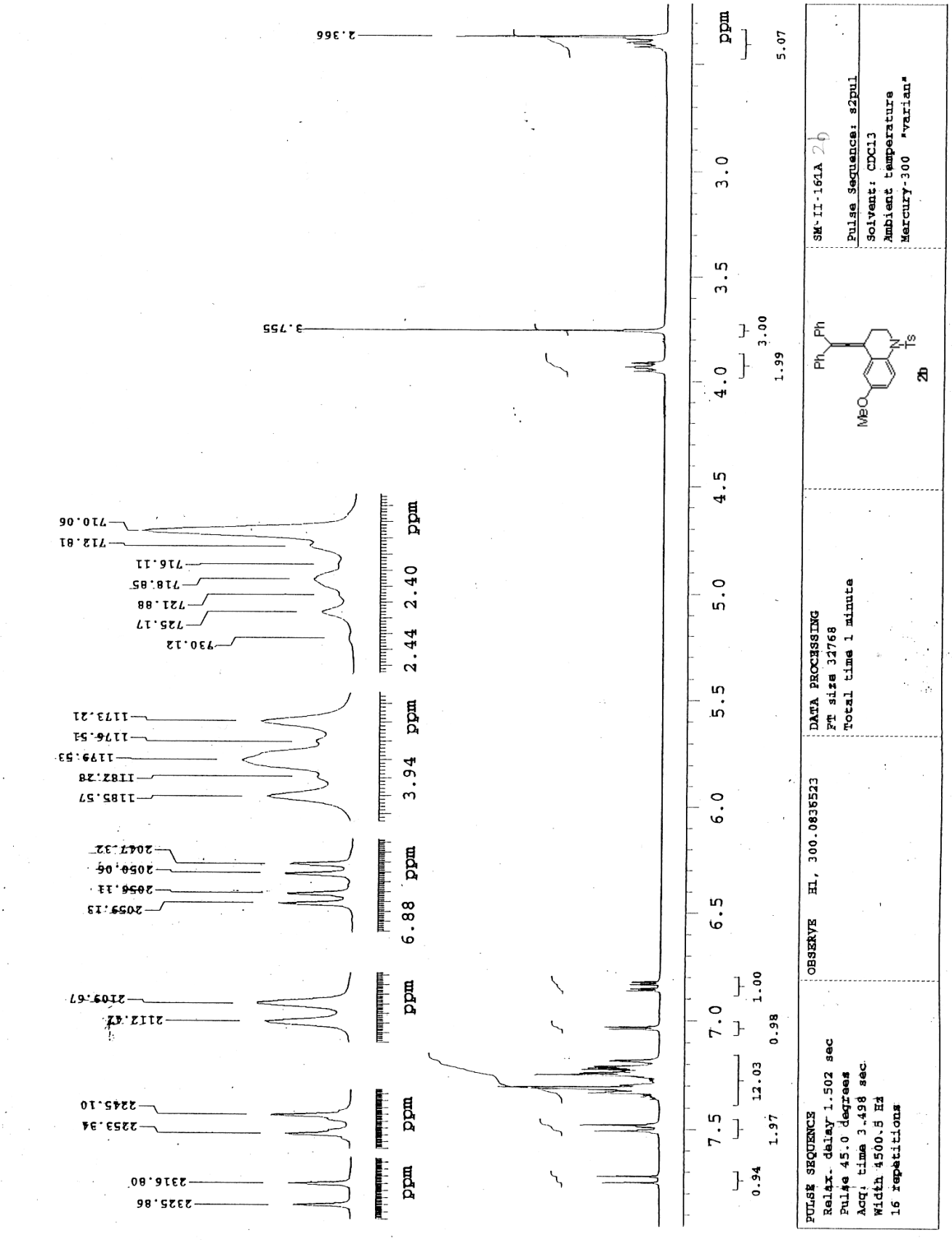
The following compound was synthesized by the similar procedure as that for **14a**.

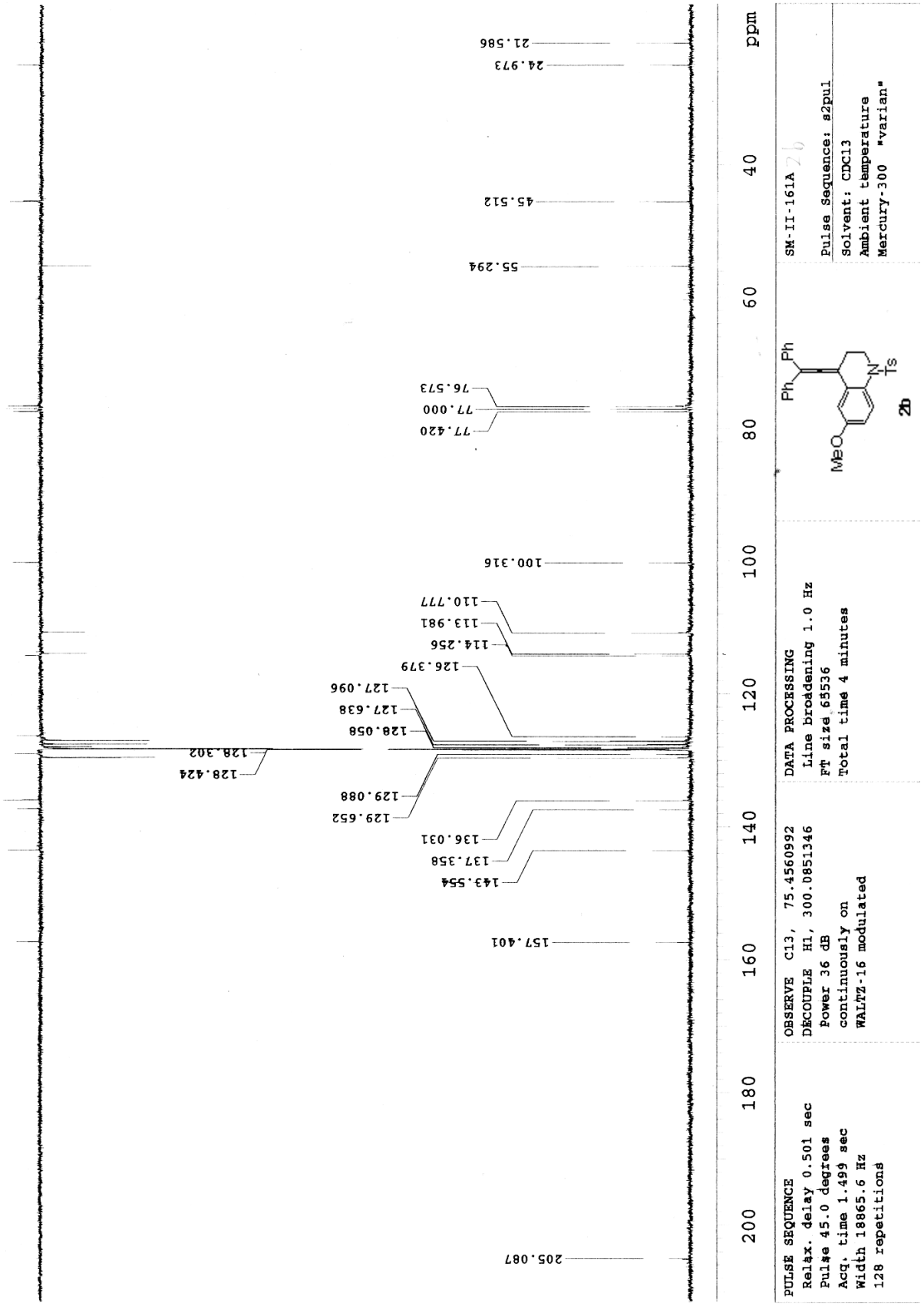
2-Methoxy-7-methyl-4-(2,2-diphenylvinylidene)-1,2,3,4-tetrahydroisoquinoline (14b). ^{1}H NMR δ 2.31 (s, 3H), 3.63 (s, 3H), 4.40–3.98 (b, 4H), 7.05–6.93 (m, 2H), 7.47–7.26 (m, 11H); ^{13}C NMR δ 21.2, 55.0, 57.0, 59.5, 101.1, 114.5, 125.8, 125.9, 127.2, 127.4, 127.8, 128.1, 128.4, 131.7, 136.5, 137.6, 204.4; R_f = 0.67 (hexane : AcOEt = 3 : 1).

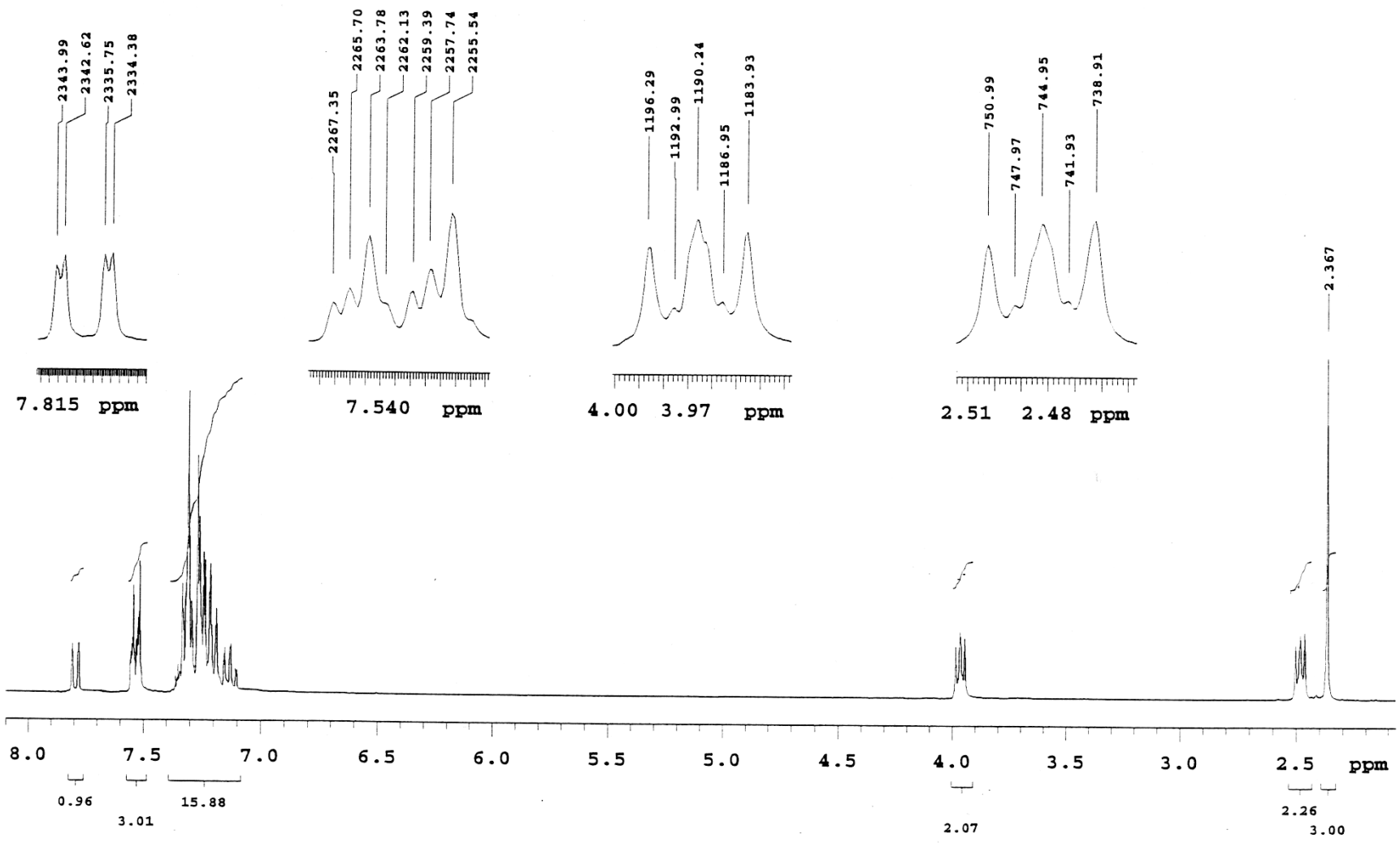
7-Methoxy-4-(2,2-diphenylvinyl)isoquinoline (16a). To a solution of **14a** containing **15a** (230 mg, 0.62 mmol) in EtOH (8 ml) was added *p*-toluenesulfonic acid (107 mg, 1.0 equiv) at room temperature. The mixture was stirred at 78 ℃ for 24 h, neutralized with aqueous $NaHCO_3$ at 0 ℃, and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated by a rotary evaporator to give an oil, which, on CC, gave **16a** as a brown gum. (190 mg, 91 %); ^{1}H NMR δ 3.95 (s, 3H), 7.22–7.04 (m, 6H), 7.45–7.28 (m, 7H), 8.02–7.95 (m, 2H), 8.94 (s, 1H); ^{13}C NMR δ 55.4, 105.0, 122.5, 123.3, 125.4, 127.5, 128.0, 128.1, 128.2, 128.3, 128.7, 129.3, 130.4, 139.5, 142.3, 142.8, 146.5, 149.5, 158.2; R_f = 0.20 (hexane : AcOEt = 3 : 1). Exact Mass: exact mass, m/z 337.14659 (calcd for $C_{24}H_{19}NO$ m/z 337.14666). Anal. Calcd for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15. Found: C, 85.29; H, 5.64; N, 4.14.

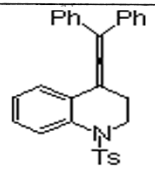
The following compound was synthesized by the similar procedure as that for **16a**.

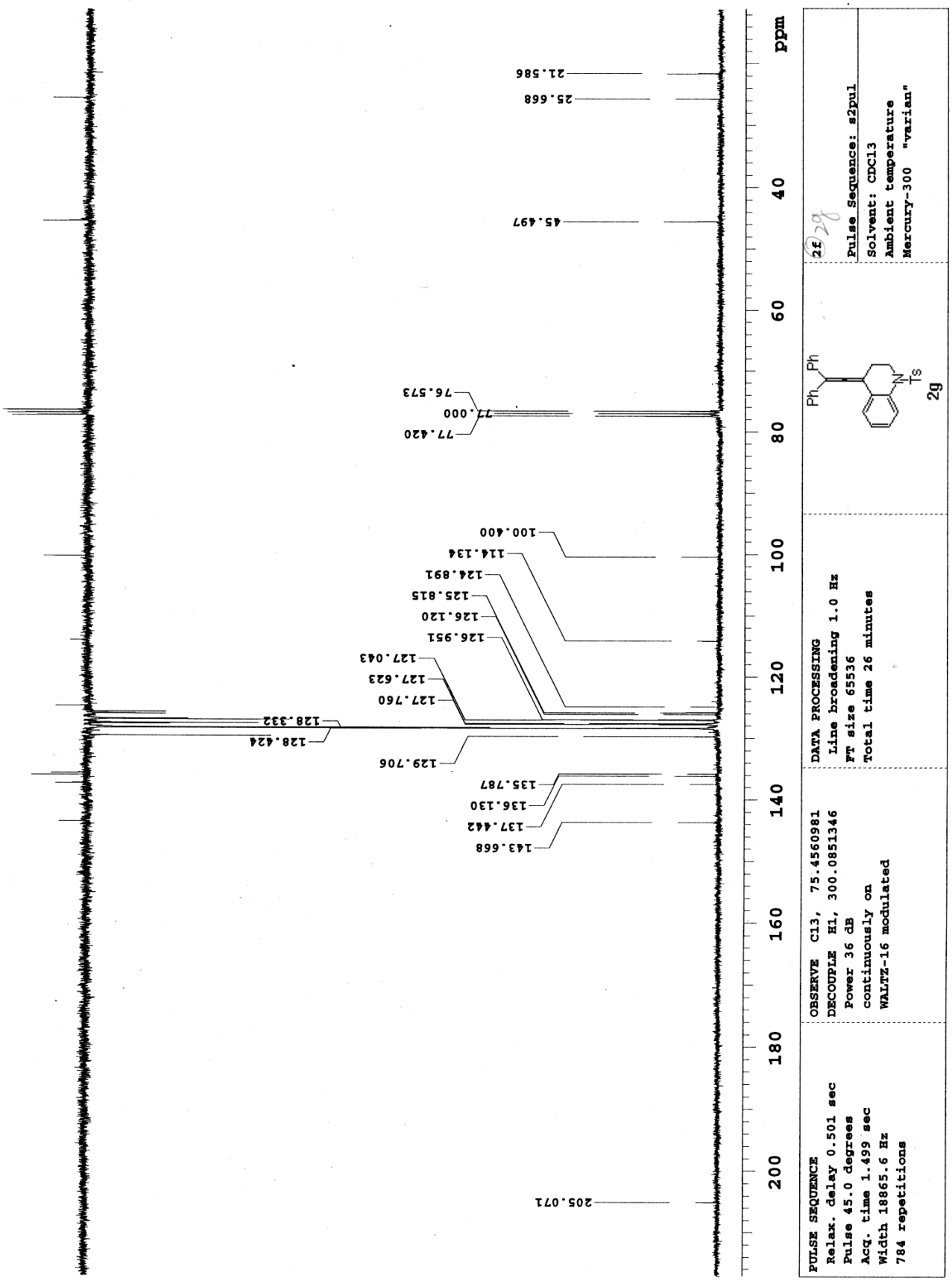
7-Methyl-4-(2,2-diphenylvinyl)isoquinoline (16b) and 5-methyl-4-(2,2-diphenylvinyl)-isoquinoline (17b) (5:1). ^{1}H NMR δ 2.55 (s, 3H), 7.20–7.04 (m, 5H), 7.55–7.28 (m, 7H), 7.72 (s, 1H), 8.05–7.97 (m, 2H), 8.95 (s, 1H); ^{13}C NMR δ 21.6, 122.5, 123.5, 126.8, 127.5, 128.0, 128.1, 128.2, 128.3, 128.40, 128.44, 128.6, 129.9, 130.4, 132.6, 133.1, 137.0, 139.6, 142.9, 143.2, 146.4, 150.3; R_f = 0.43 (hexane : AcOEt = 3 : 1).

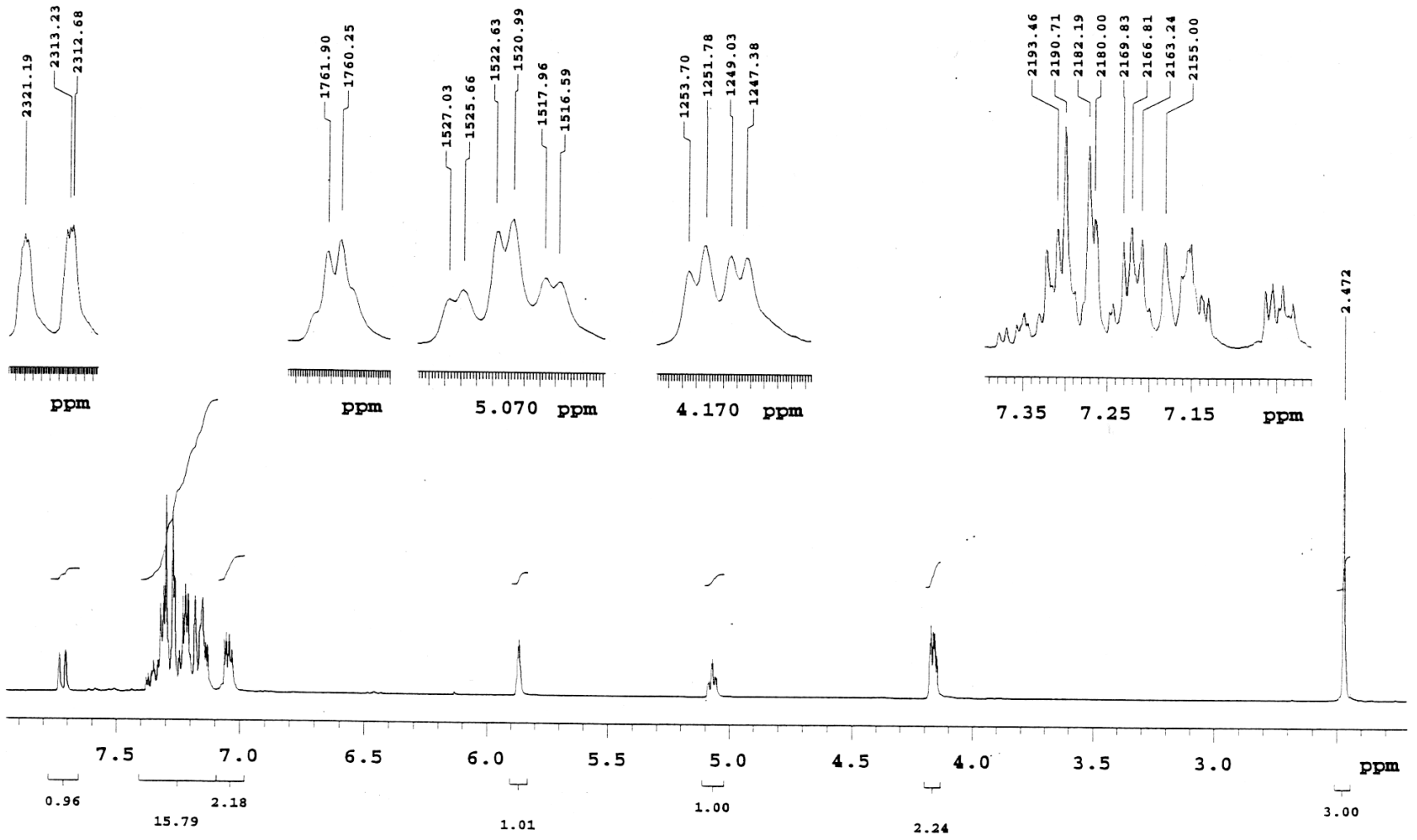

2.366
3.755
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
0.94
12.03
1.00
1.97
0.98
3.00
1.99
5.07
6.88 ppm
3.94 ppm
2.44 2.40 ppm
2325.86
2316.80
2253.34
2245.10
2112.47
2109.67
2059.13
2056.11
2050.06
2047.32
1185.57
1182.78
1179.53
1176.54
1173.21
730.12
725.17
721.88
718.85
716.11
712.81
710.06
PULSE SEQUENCE
Relax. delay 1.502 sec
Pulse 45.0 degrees
Acq. time 3.498 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.0836523
DATA PROCESSING
FT size 32768
Total time 1 minute
Ph
Ph
MeO
N
Ts
2b
SM-II-161A 2b
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "varian"

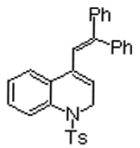

21.586
24.973
45.512
55.294
76.573
77.000
77.420
100.316
110.777
113.981
114.256
126.379
127.096
127.638
128.058
128.302
128.424
129.088
129.652
136.031
137.358
143.554
157.401
205.087
200
180
160
140
120
100
80
60
40
ppm
PULSE SEQUENCE
Relax. delay 0.501 sec
Pulse 45.0 degrees
Acq. time 1.499 sec
Width 18865.6 Hz
128 repetitions
OBSERVE C13, 75.4560992
DECOUPLE H1, 300.0851346
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 4 minutes
SM-II-161A 2b
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "varian"
Ph
Ph
N
Ts
MeO
2b

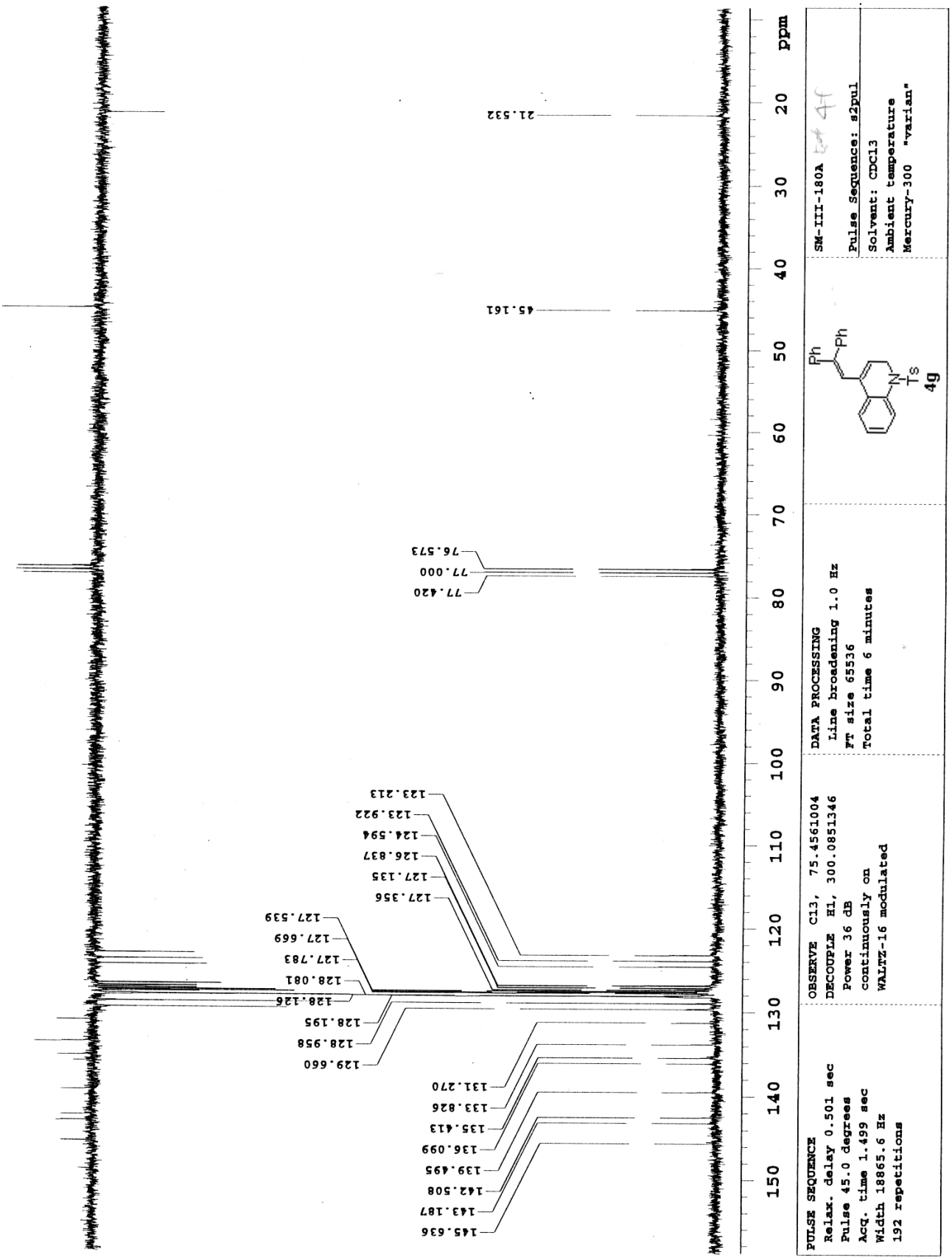


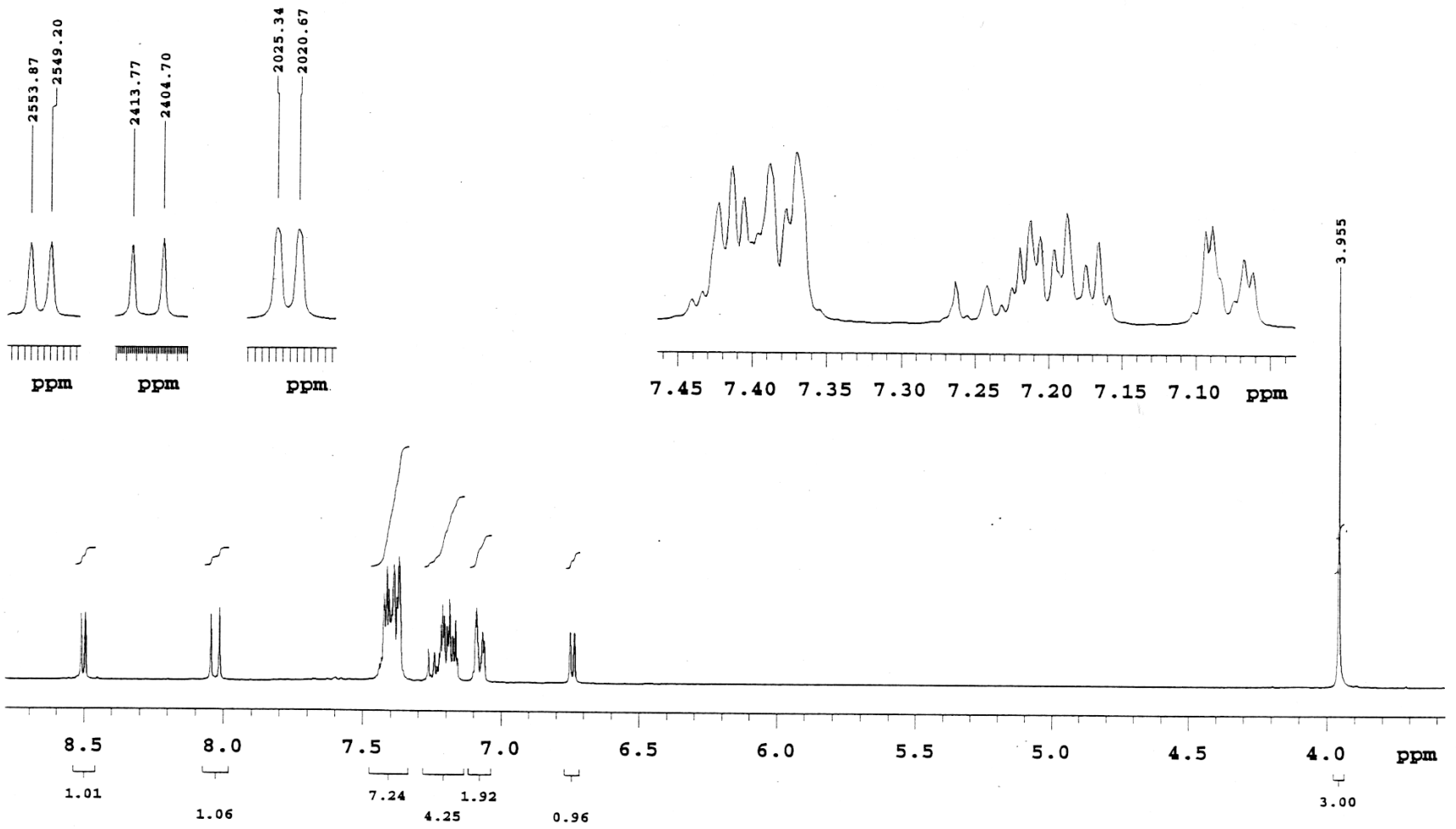
PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 40 repetitions	OBSERVE H1, 300.0836536	DATA PROCESSING FT size 32768 Total time 3 minutes	 2g	2f 2g Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"

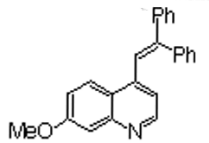

205.071
143.668
137.442
136.130
135.787
129.706
128.424
128.332
127.760
127.623
127.043
126.951
126.120
125.815
124.891
114.134
100.400
77.420
77.000
76.573
45.497
25.668
21.586
ppm
200
180
160
140
120
100
80
60
40
PULSE SEQUENCE
Relax. delay 0.501 sec
Pulse 45.0 degrees
Acq. time 1.499 sec
Width 18865.6 Hz
784 repetitions
OBSERVE C13, 75.4560981
DECOUPLE H1, 300.0851346
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 26 minutes
Ph
Ph
N
Ts
2g
2g
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "varian"

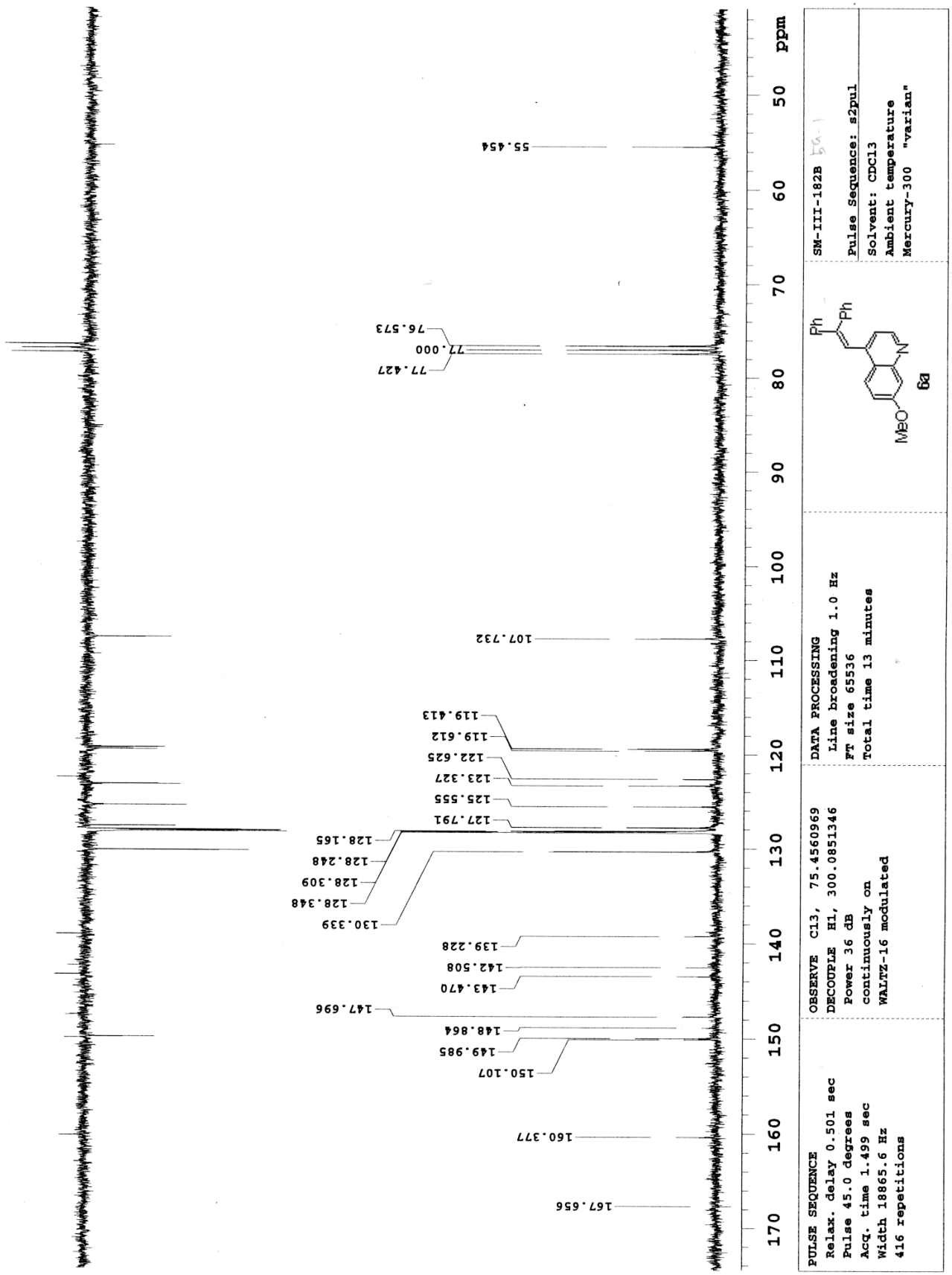


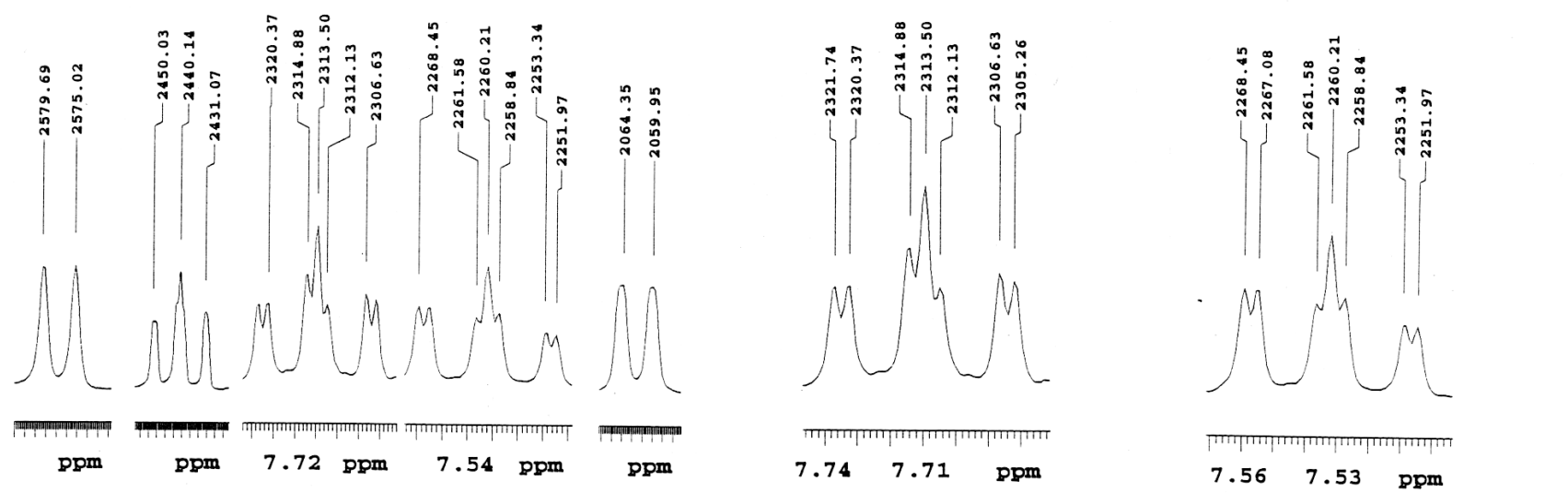
PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 20 repetitions	OBSERVE H1, 300.0836520	DATA PROCESSING FT size 32768 Total time 1 minutes	 4g	SM-III-180A Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"

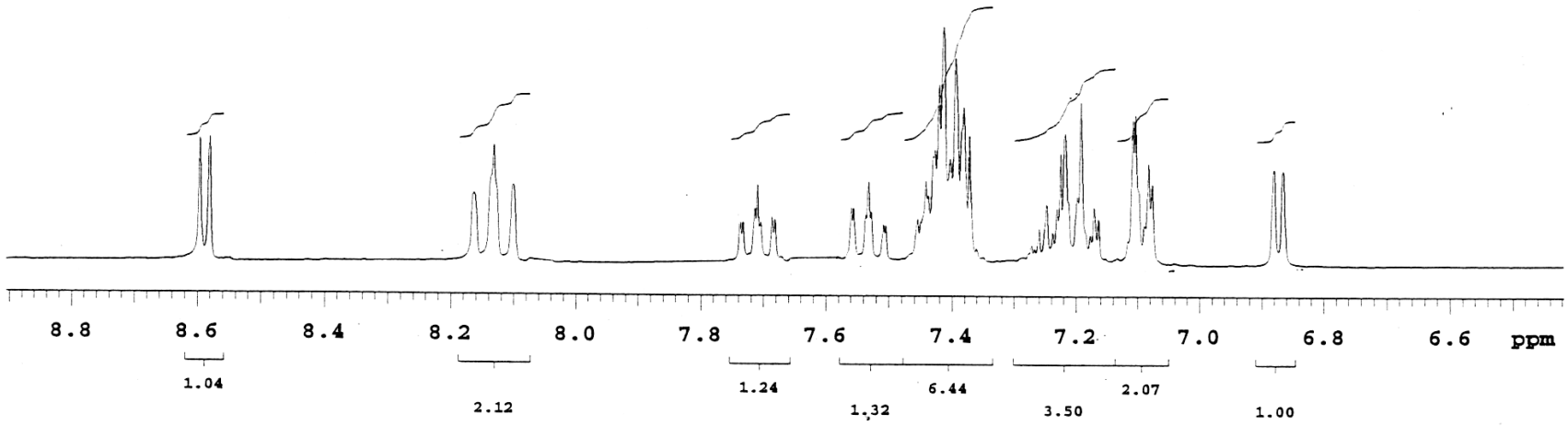

21.532
45.161
76.573
77.000
77.420
123.213
123.922
124.594
126.837
127.135
127.356
127.539
127.669
127.783
128.081
128.126
128.195
128.958
129.660
131.270
133.826
135.413
136.099
139.495
142.508
143.187
145.636
ppm
PULSE SEQUENCE
Relax. delay 0.501 sec
Pulse 45.0 degrees
Acq. time 1.499 sec
Width 18865.6 Hz
192 repetitions
OBSERVE C13, 75.4561004
DECOUPLE H1, 300.0851346
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6 minutes
Ph
Ph
N
Ts
4g
SM-III-180A
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "varian"

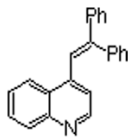


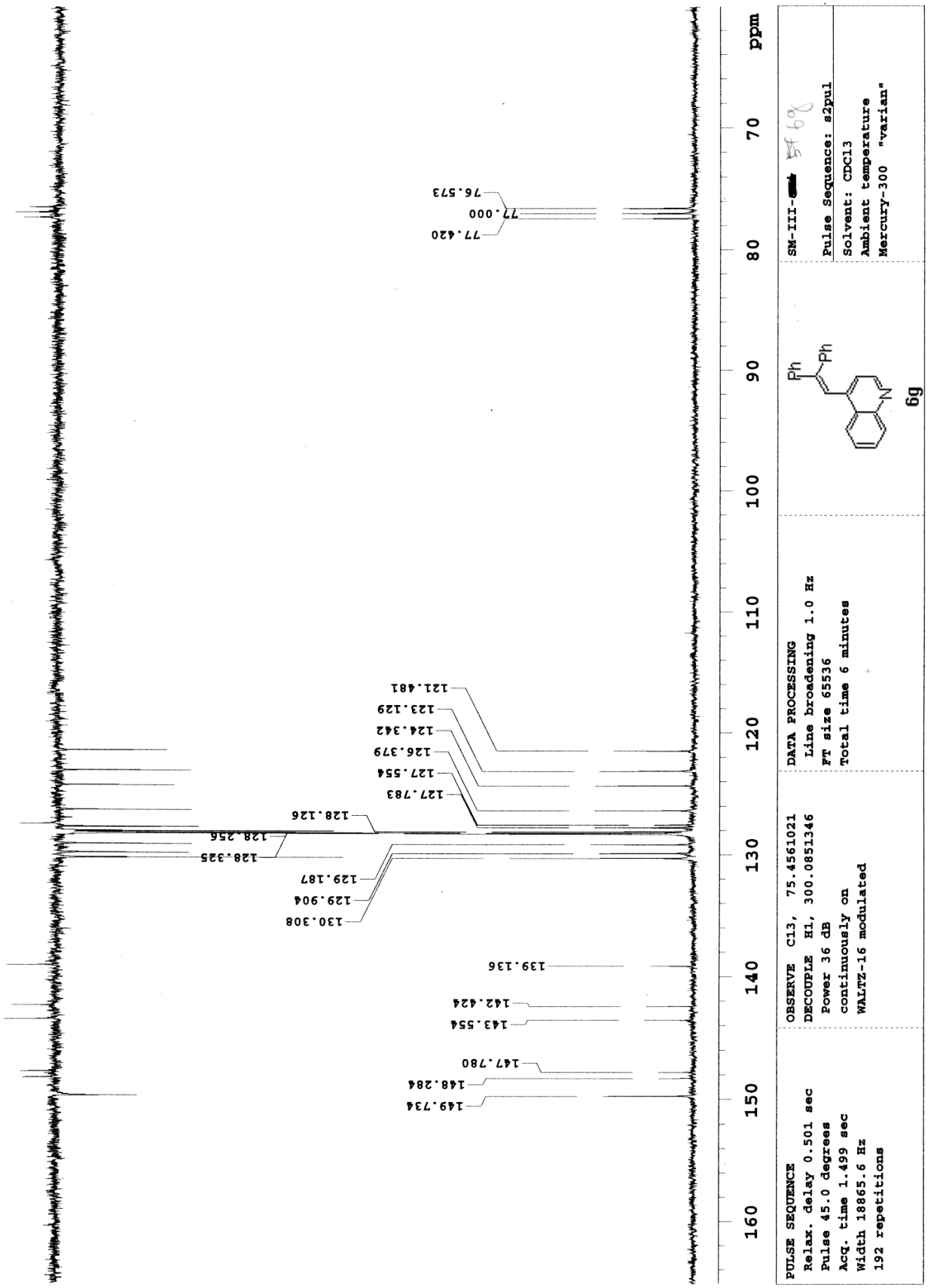
PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 28 repetitions	OBSERVE H1, 300.0836514	DATA PROCESSING FT size 32768 Total time 2 minutes	 6a	SM-III-182B 5A-1 Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"

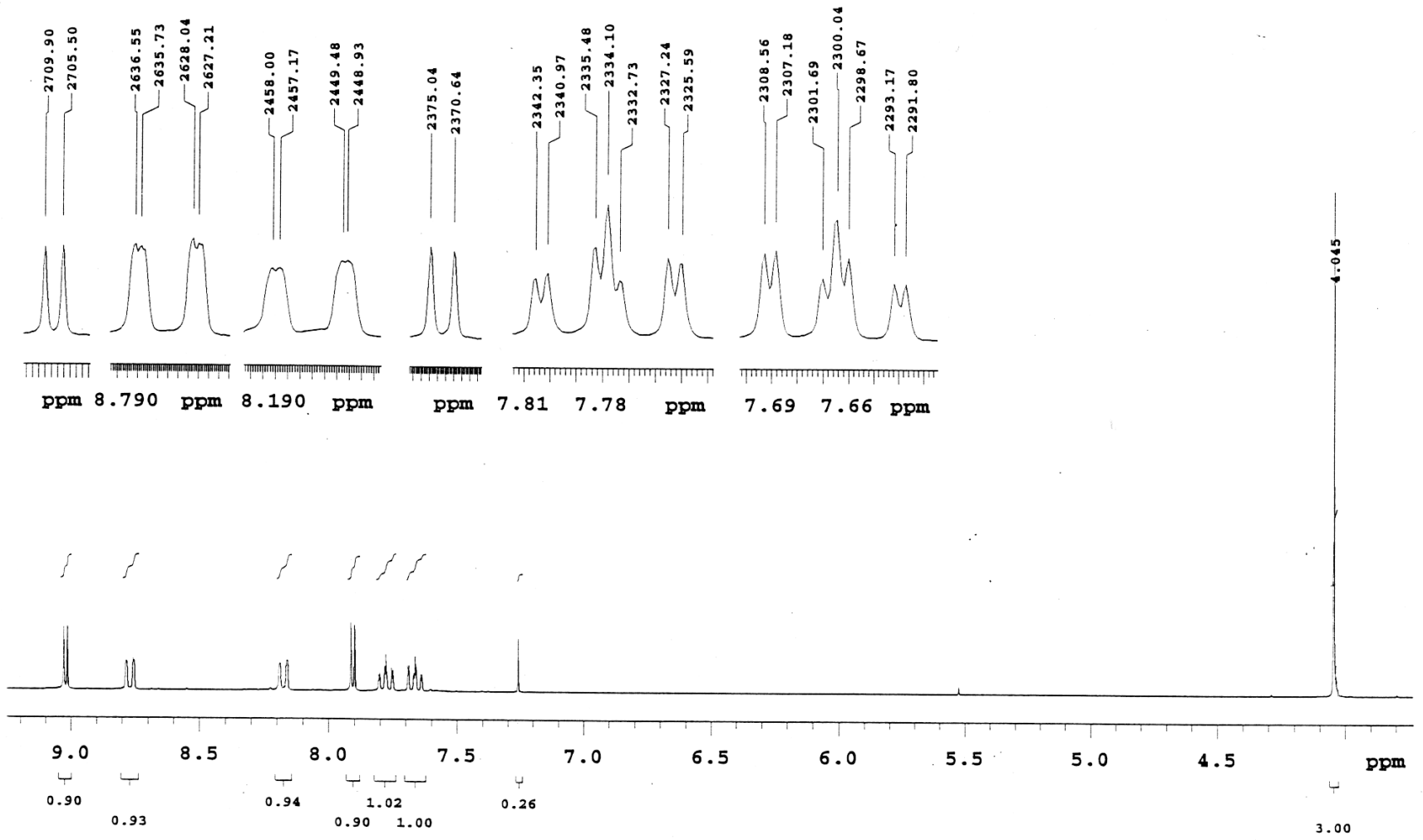

55.454
76.573
77.000
77.427
107.732
119.413
119.612
122.625
123.327
125.555
127.791
128.165
128.248
128.309
128.348
130.339
139.228
142.508
143.470
147.696
148.864
149.985
150.107
160.377
167.656
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm
PULSE SEQUENCE
Relax. delay 0.501 sec
Pulse 45.0 degrees
Acq. time 1.499 sec
Width 18865.6 Hz
416 repetitions
OBSERVE C13, 75.4560969
DECOUPLE H1, 300.0851346
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 13 minutes
Ph
Ph
N
MeO
6a
SM-III-182B EG-1
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "varian"

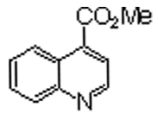


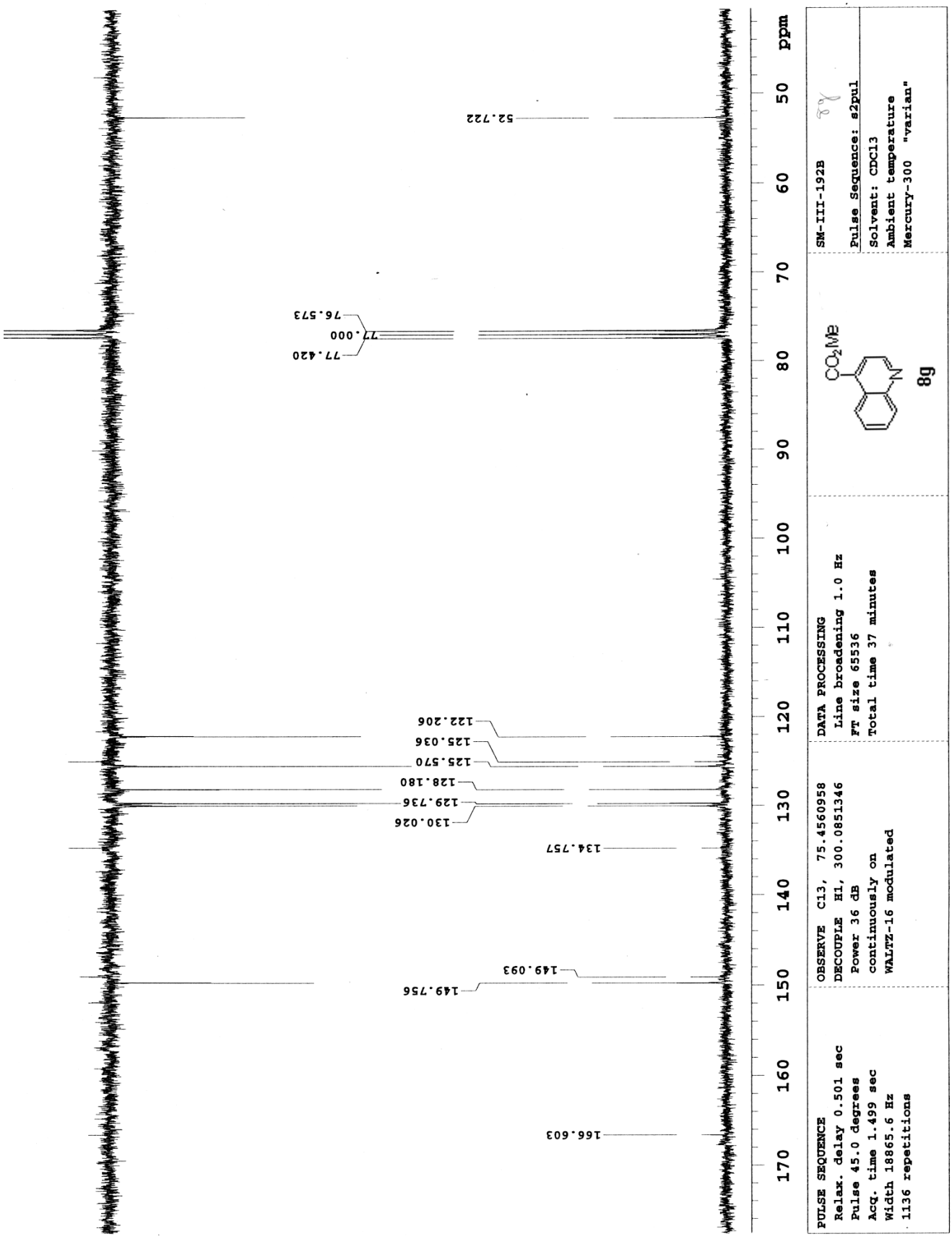


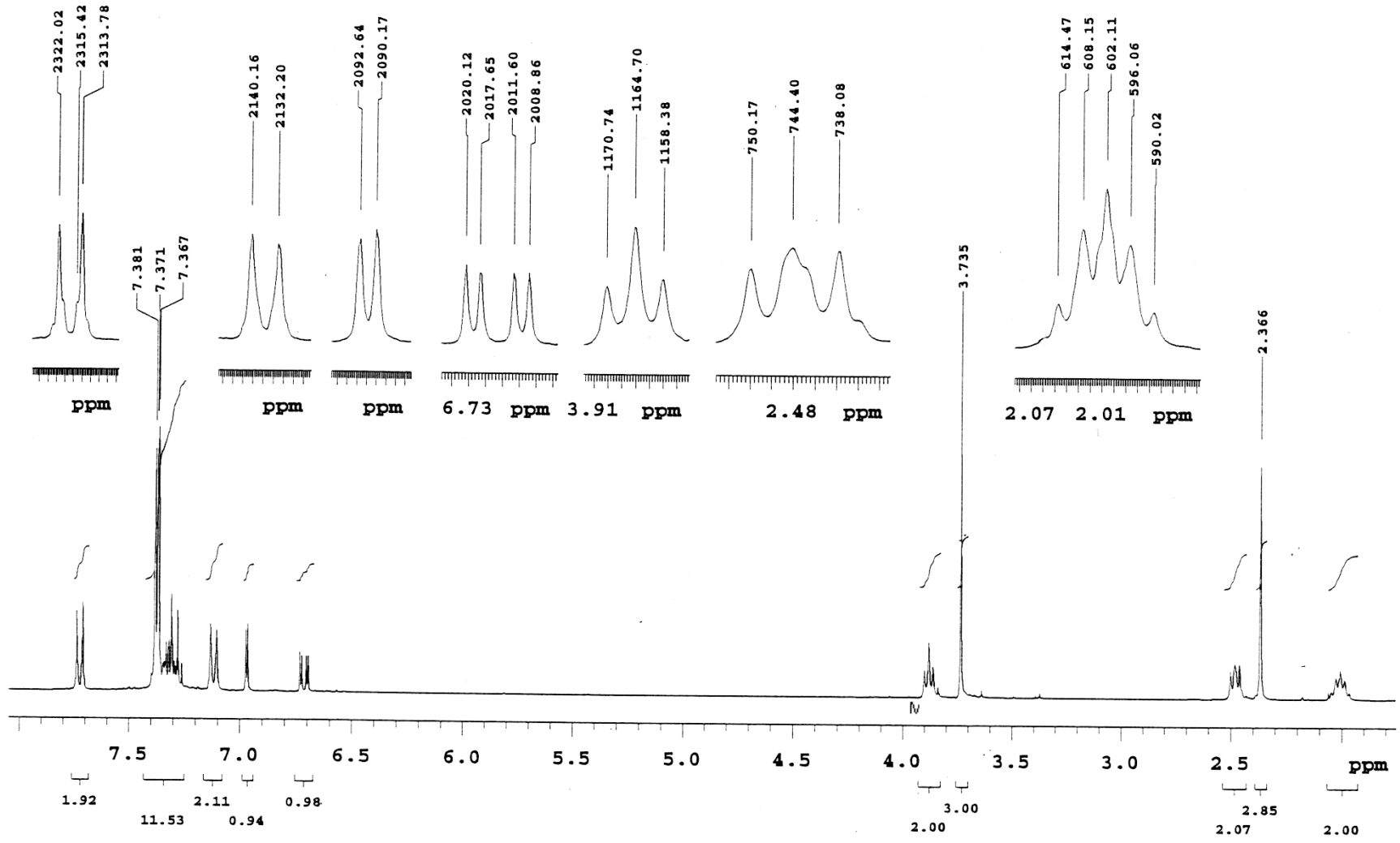
PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 20 repetitions	OBSERVE H1, 300.0836534	DATA PROCESSING FT size 32768 Total time 1 minutes	 6g	SM-III-[redacted] 6g) Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"

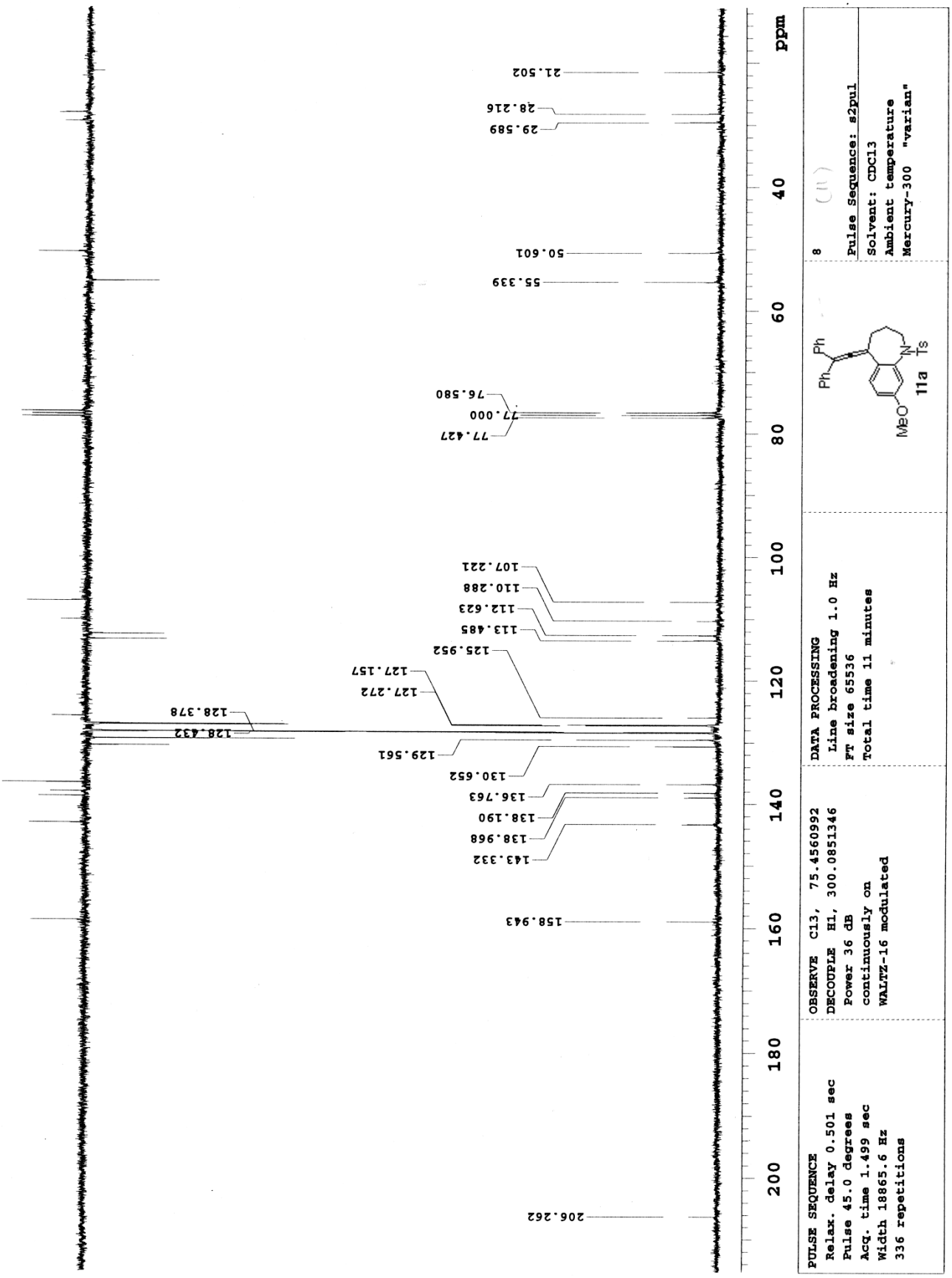

77.420
77.000
76.573
121.481
123.129
124.342
126.379
127.554
127.783
128.126
128.256
128.325
129.187
129.904
130.308
139.136
142.424
143.554
147.780
148.284
149.734
ppm
PULSE SEQUENCE
Relax. delay 0.501 sec
Pulse 45.0 degrees
Acq. time 1.499 sec
Width 18865.6 Hz
192 repetitions
OBSERVE C13, 75.4561021
DECOUPLE H1, 300.0851346
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6 minutes
Ph
Ph
N
SM-III-
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "varian"
6g

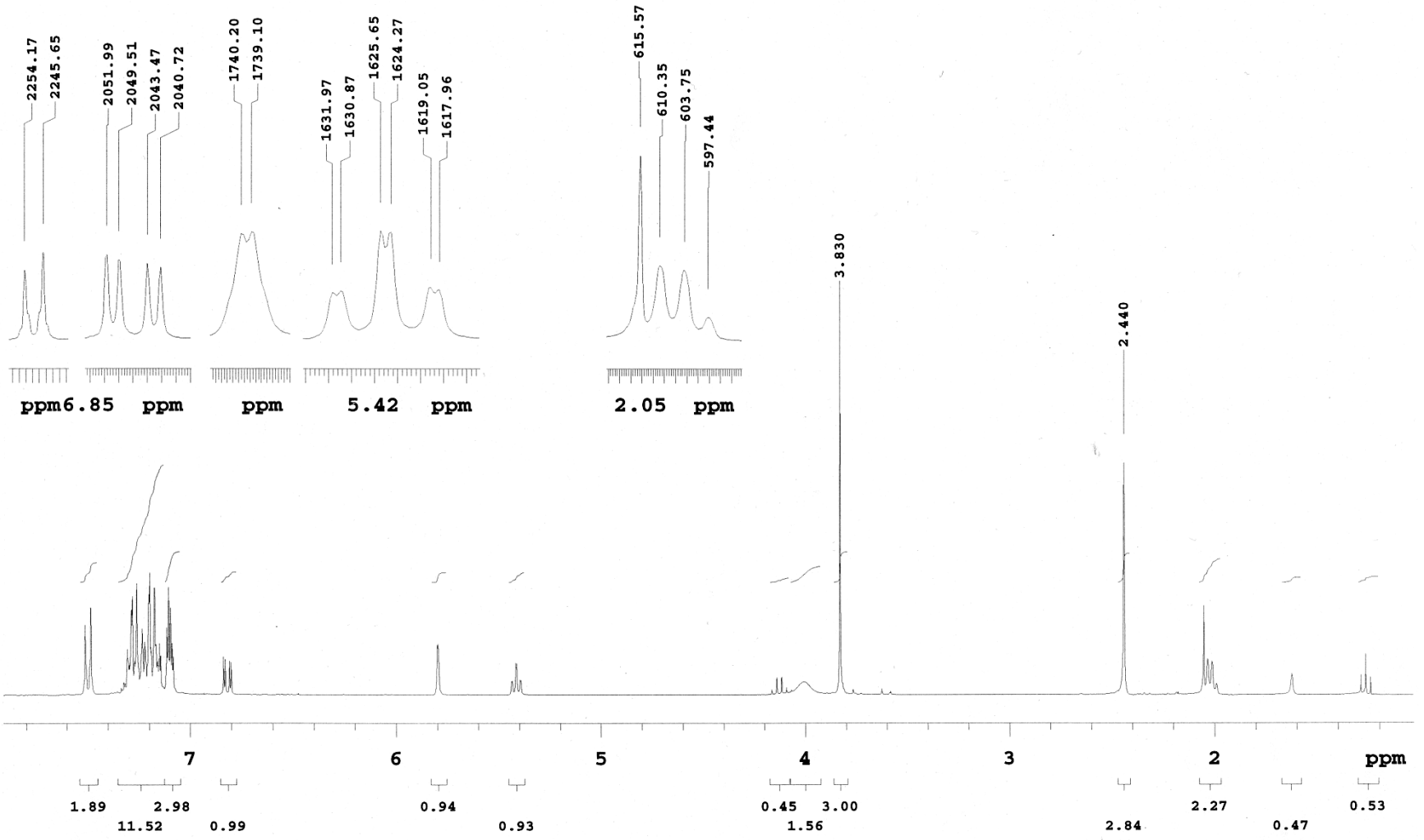


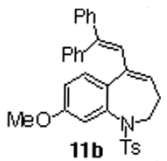
PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 128 repetitions	OBSERVE H1, 300.0836525	DATA PROCESSING FT size 32768 Total time 10 minutes	 8g	SM-III-192A Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"

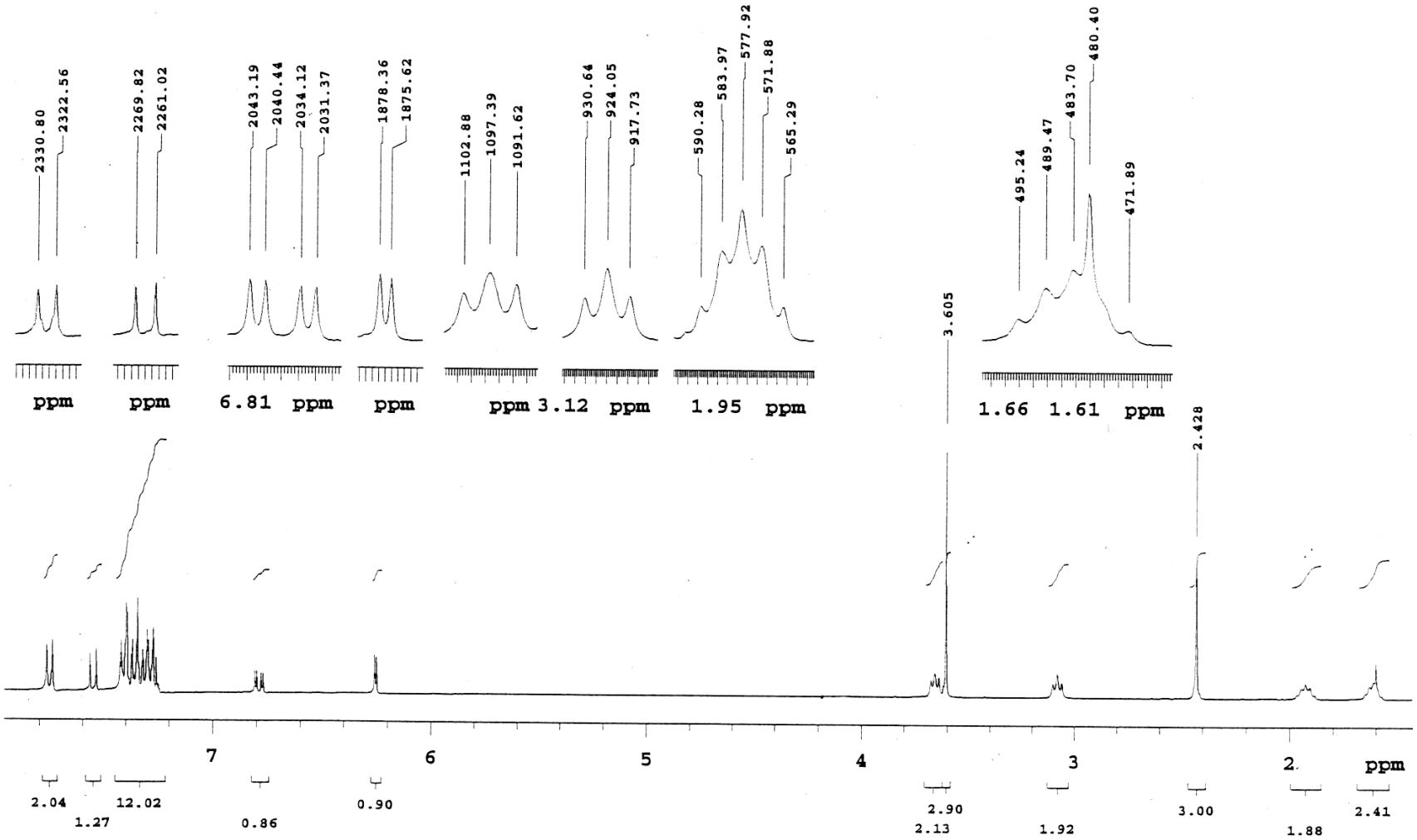

52.722
77.420
77.000
76.573
122.206
125.036
125.570
128.180
129.736
130.026
134.757
149.093
149.756
166.603
ppm
PULSE SEQUENCE
Relax. delay 0.501 sec
Pulse 45.0 degrees
Acq. time 1.499 sec
Width 18865.6 Hz
1136 repetitions
OBSERVE C13, 75.4560958
DECOUPLE H1, 300.0851346
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 37 minutes
CO2Me
8g
SM-III-192B
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "varian"

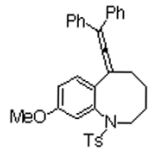

2322.02
2315.42
2313.78
7.381
7.371
7.367
2140.16
2132.20
2092.64
2090.17
2020.12
2017.65
2011.60
2008.86
1170.74
1164.70
1158.38
750.17
744.40
738.08
3.735
614.47
608.15
602.11
596.06
590.02
2.366
ppm
6.73 ppm
3.91 ppm
2.48 ppm
2.07 2.01 ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
1.92
11.53
2.11
0.94
0.98
2.00
3.00
2.07
2.85
2.00
PULSE SEQUENCE
Relax. delay 1.502 sec
Pulse 45.0 degrees
Acq. time 3.498 sec
Width 4500.5 Hz
32 repetitions
OBSERVE H1, 300.0836523
DATA PROCESSING
FT size 32768
Total time 2 minutes
Ph
Ph
tBO
N
Ts
11a
8
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "varian"

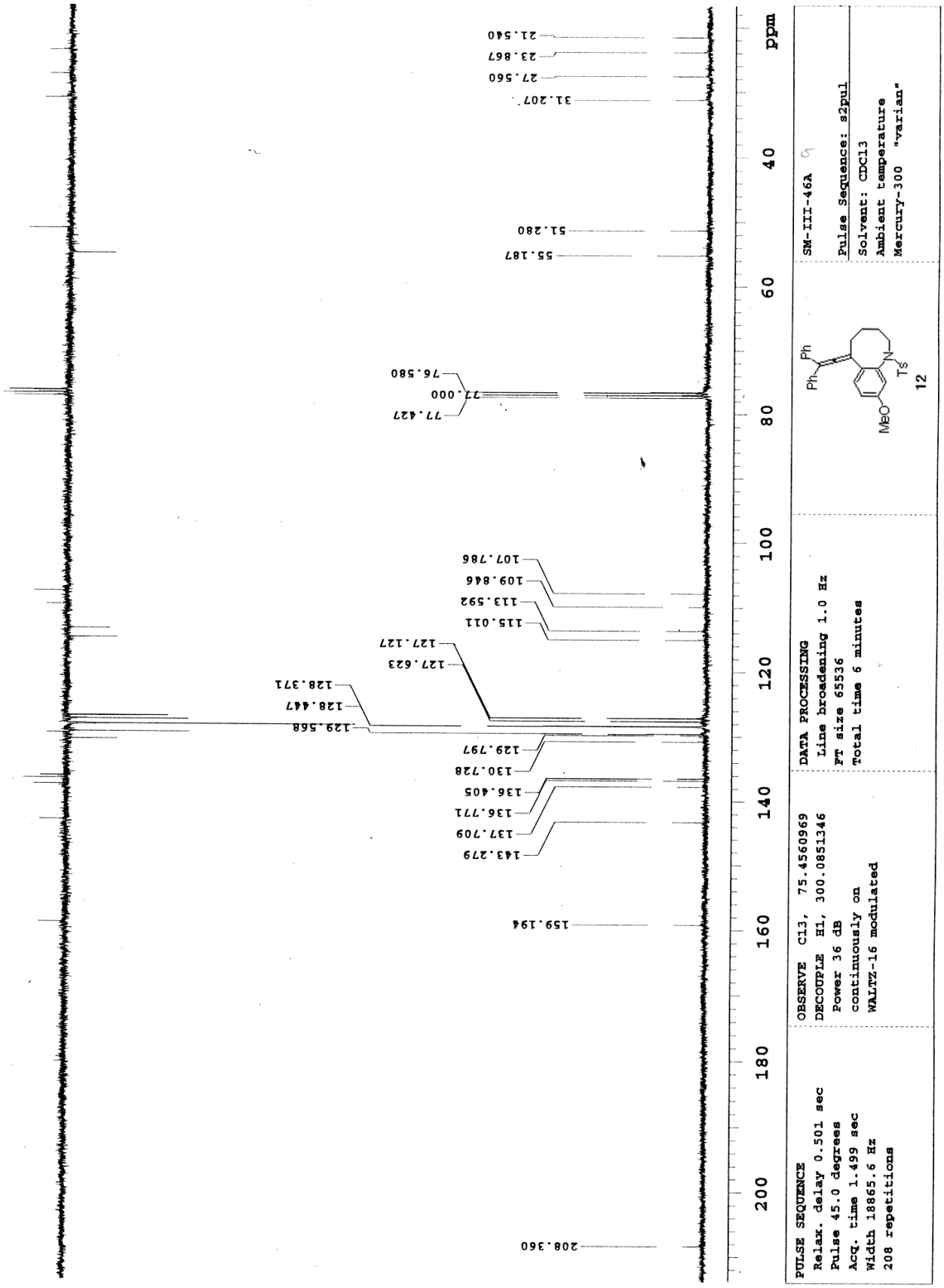

206.262
158.943
143.332
138.968
138.190
136.763
130.652
129.561
128.432
128.378
127.272
127.157
125.952
113.485
112.623
110.288
107.221
77.427
77.000
76.580
55.339
50.601
29.589
28.216
21.502
ppm
PULSE SEQUENCE
Relax. delay 0.501 sec
Pulse 45.0 degrees
Acq. time 1.499 sec
Width 18865.6 Hz
336 repetitions
OBSERVE C13, 75.4560992
DECOUPLE H1, 300.0851346
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 minutes
Ph
Ph
N
Ts
MeO
11a
8
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "varian"

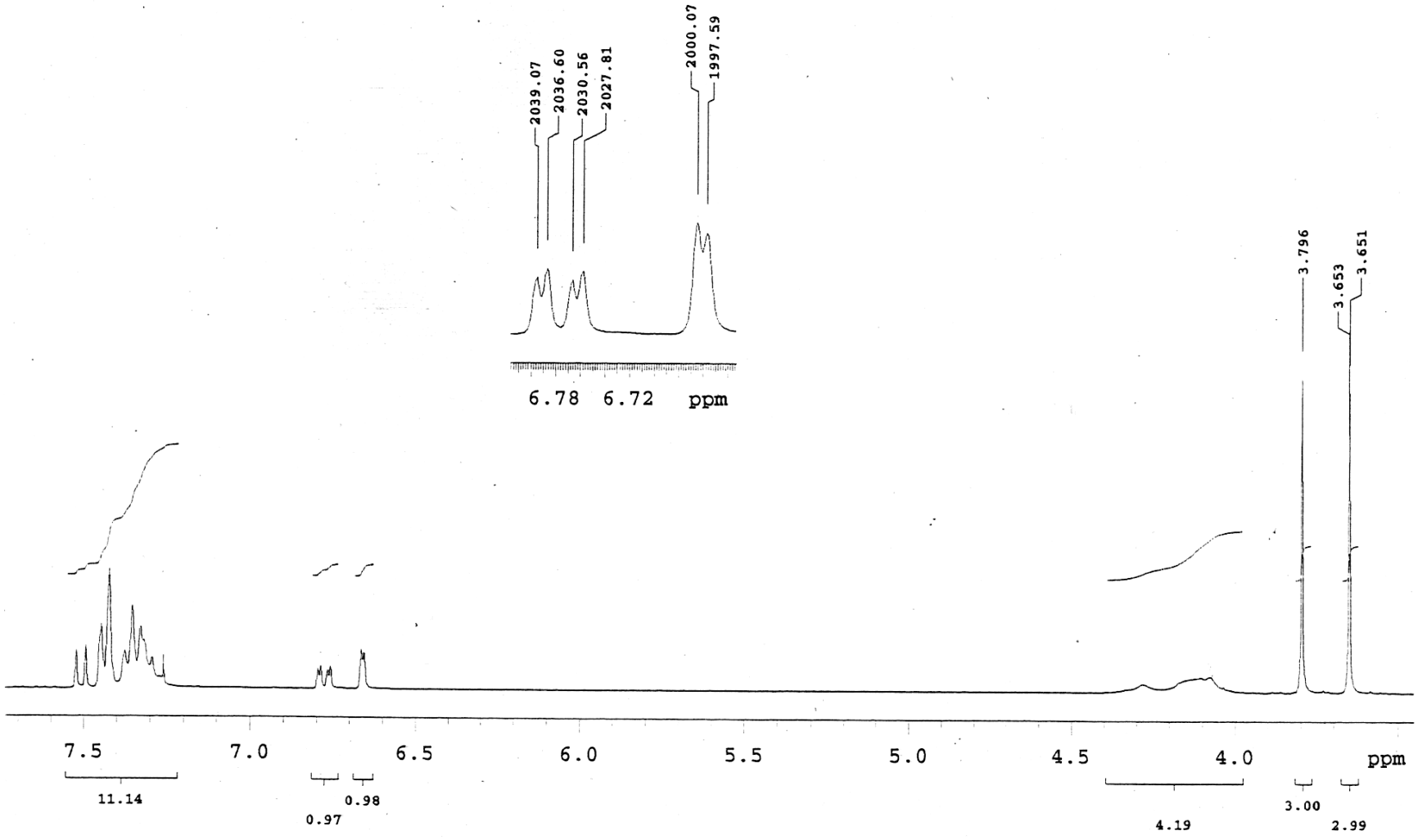


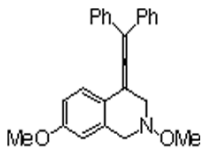
PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 24 repetitions	OBSERVE H1, 300.0836523	DATA PROCESSING FT size 32768 Total time 2 minutes	 11b	SM-III-74cr Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"

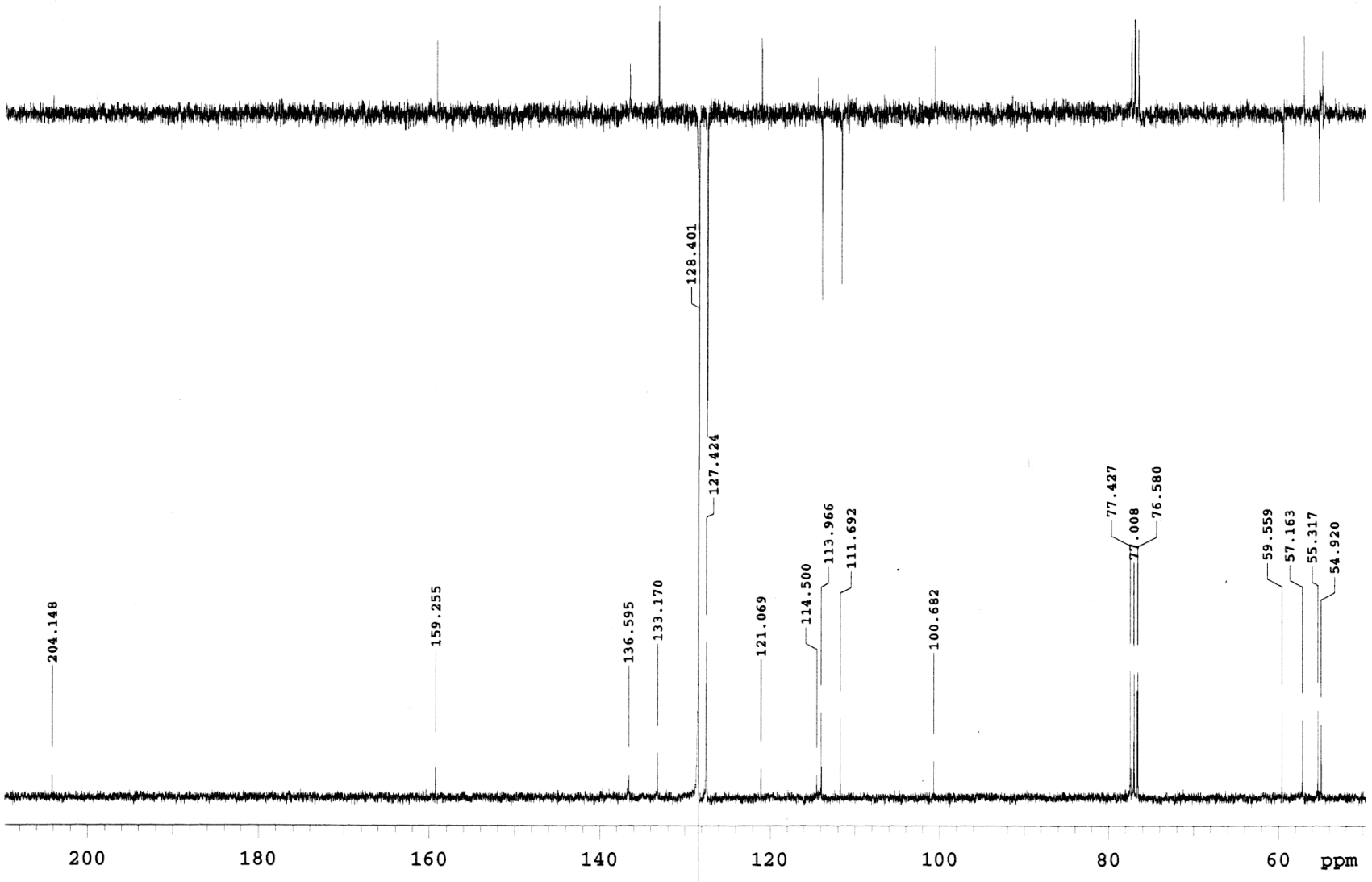


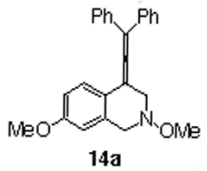
PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 20 repetitions	OBSERVE H1, 300.0836539	DATA PROCESSING FT size 32768 Total time 1 minutes	 12	SM-III-46A 9 (71) 12 Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"

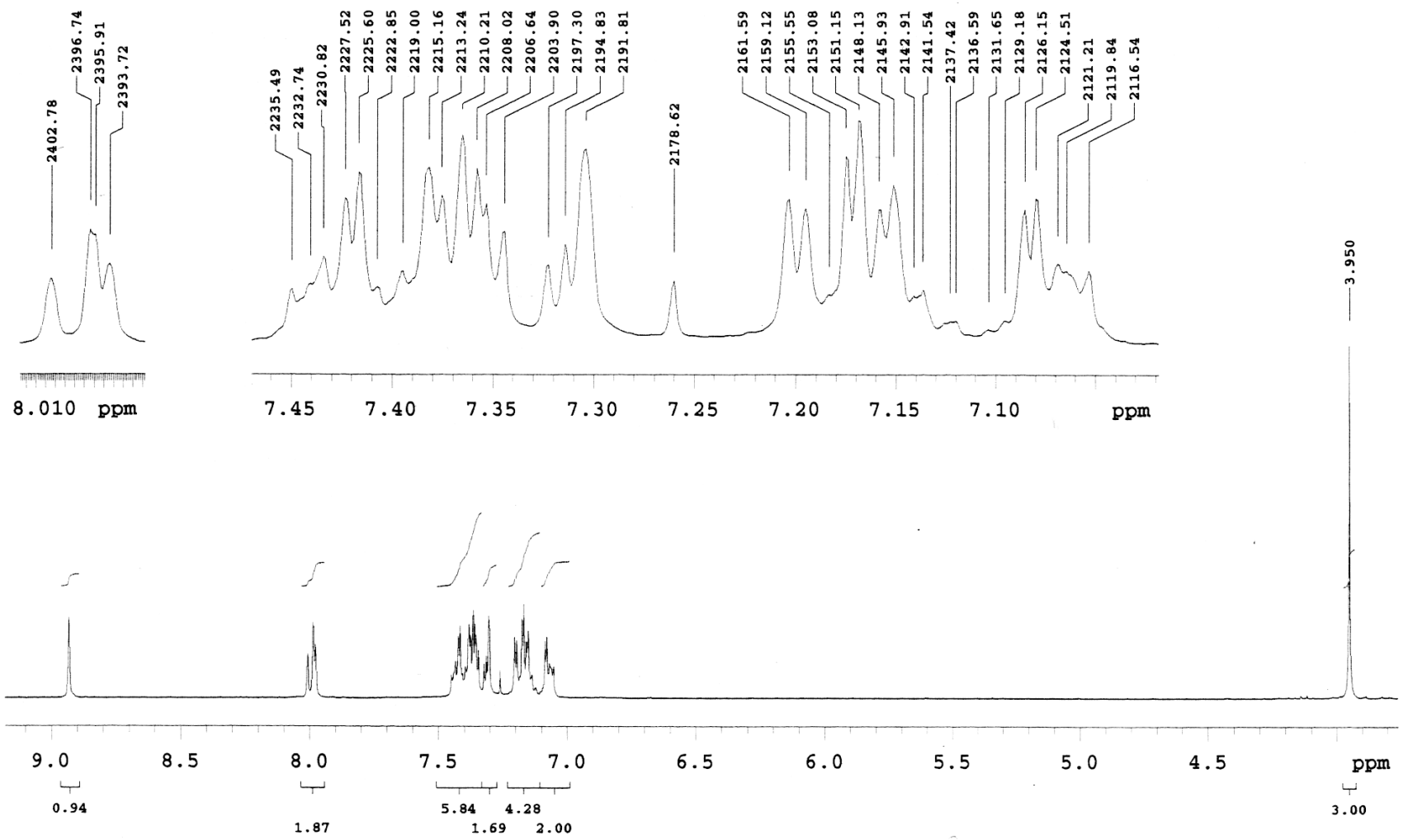

21.540
23.867
27.560
31.207
51.280
55.187
76.580
77.000
77.427
107.786
109.846
113.592
115.011
127.127
127.623
128.371
128.447
129.568
129.797
130.728
136.405
136.771
137.709
143.279
159.194
208.360
ppm
200
180
160
140
120
100
80
60
40
PULSE SEQUENCE
Relax. delay 0.501 sec
Pulse 45.0 degrees
Acq. time 1.499 sec
Width 18865.6 Hz
208 repetitions
OBSERVE C13, 75.4560969
DECOUPLE H1, 300.0851346
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6 minutes
Ph
Ph
N
Ts
MeO
12
SM-III-46A
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "varian"

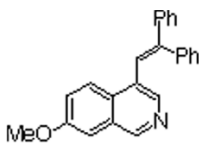


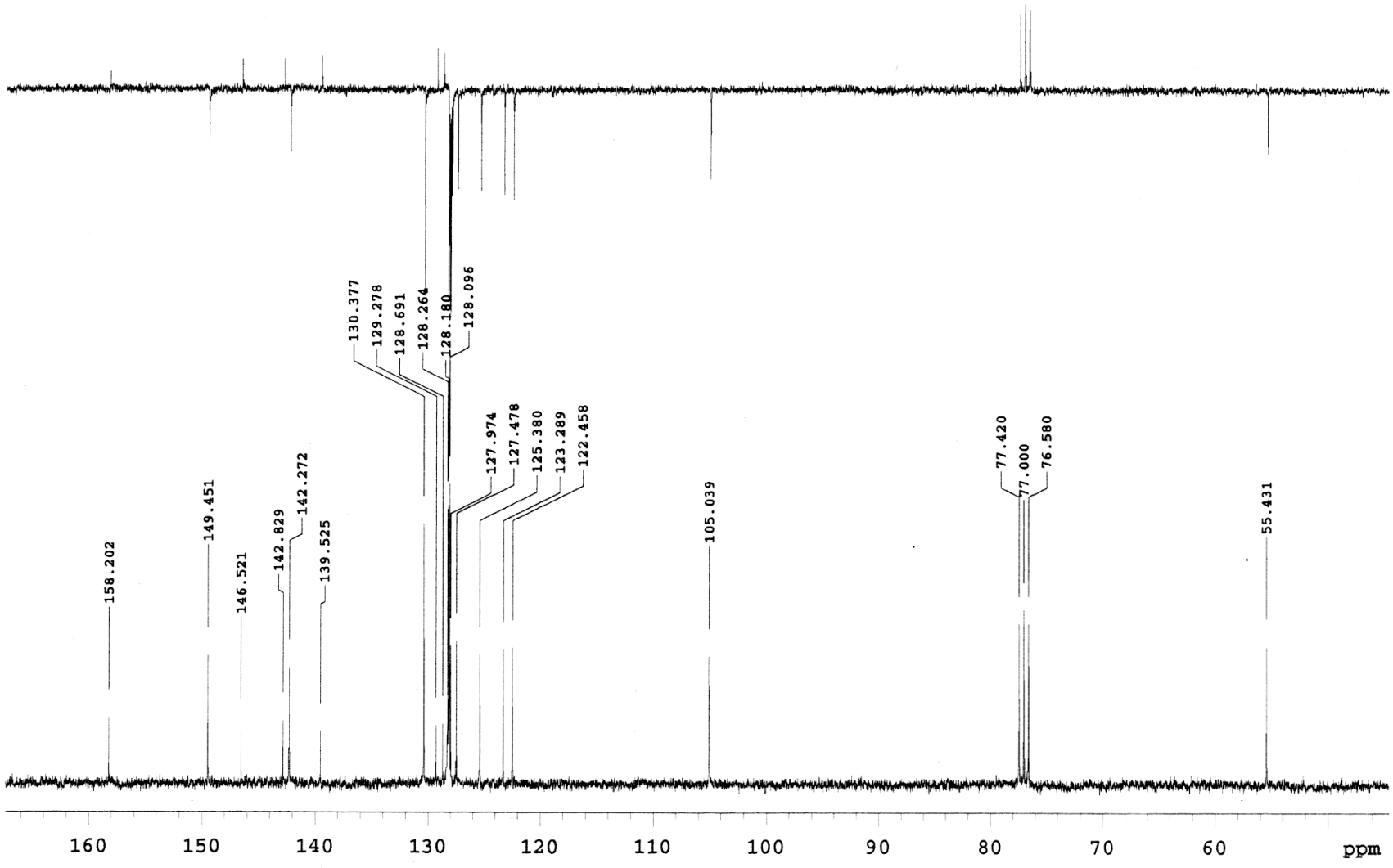
PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 16 repetitions	OBSERVE H1, 300.0836523	DATA PROCESSING FT size 32768 Total time 1 minute	 14a	SM-II-111A ~~7a 11a~~ 14a Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"

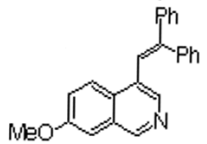


PULSE SEQUENCE Relax. delay 0.501 sec Pulse 45.0 degrees Acq. time 1.499 sec Width 18865.6 Hz 128 repetitions	OBSERVE C13, 75.4560975 DECOUPLE H1, 300.0851346 Power 36 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 4 minutes	 14a	13C OBSERVE Pulse Sequence: s2pul Solvent: CDC13 Ambient temperature Mercury-300 "varian"



PULSE SEQUENCE Relax. delay 1.502 sec Pulse 45.0 degrees Acq. time 3.498 sec Width 4500.5 Hz 16 repetitions	OBSERVE H1, 300.0836523	DATA PROCESSING FT size 32768 Total time 1 minute	 16a	SM-II-112B ~~10~~ ~~11~~ ~~12~~ 16(a) Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"



PULSE SEQUENCE Relax. delay 0.501 sec Pulse 45.0 degrees Acq. time 1.499 sec Width 18865.6 Hz 224 repetitions	OBSERVE C13, 75.4560981 DECOUPLE H1, 300.0851346 Power 36 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 7 minutes	 16a	SM-II-112B 16a Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-300 "varian"