Nanoscale 1,3,5,7-Tetrasubstituted Adamantanes and *p*-Substituted Tetraphenylmethanes for AFM Applications

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Supporting Information

Experimental procedures and AFM conditions, ^{1}H NMR spectra for **5**, **7**, **8**, **10—20**, ^{13}C NMR spectra for **5**, **10—20**.

General methods. Reagent grade solvents were used without further purification. All reagents were purchased from Aldrich Chemical Co. or Lancaster Co. and were used as received. Tetrahydrofuran (99.9%, anhydrous, inhibitor free) and triethylamine (99.5%) were purchased in Aldrich Sure/Seal™ bottles and were well deoxygenated with argon or nitrogen before use in Sonogashira coupling reactions. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$. Chemical shifts are in δ units (ppm) referenced to residual proton signals in the deuterated solvents. Coupling constants (*J*) are reported in Hertz (Hz). NMR splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. Brine refers to a saturated aqueous solution of NaCl. Column chromatography was carried out on Davisil silica gel (60–200 mesh). Analytical TLC was performed on Kieselgel 60 F_{254} glass plates. Spots were rendered visible by exposing the plate to UV light. Radial chromatography (RC) was performed on a Chromatotron 7924T using 1, 2 and 4 mm disks covered with silica gel 60PF_{254} containing gypsum. Mass spectra were recorded on an Agilent 1100 Series LC/MSD. High resolution, MALDI and FAB mass spectra were measured by Dr. Brian Arbogast at Oregon State University. Elemental analyses were performed by Robertson Microlit Laboratories, Inc. Madison, NJ.

1,3,5,7-Tetraphenyladamantane (3). 1-Bromoadamantane (3.00 g, 13.9 mmol) was dissolved in benzene (30 mL). Then *t*-BuBr (3.2 mL, 27.9 mmol) and $AlCl_3$ (0.16 g, 0.12 mmol) was added. The mixture was refluxed for 2 h. The mixture was cooled to rt, filtered, and the residue was washed with benzene (20 mL), water (20 mL) and $CHCl_3$ (50 mL). The residue was dried and then purified by washing with $CHCl_3$ in a Soxhlet apparatus for 24 h. The insoluble residue was dried, affording pure 1,3,5,7-tetraphenyladamantane as a white solid (4.70 g, 77%), mp >250 °C (lit.[1] mp 417-419 ºC). HR EI MS Calcd for $C_{34}H_{32}$ 440.25040, found 440.25008.

1,3,5,7-Tetrakis-(4-iodophenyl)adamantane (5). Iodine (2.30 g, 9.06 mmol) was added to a suspension of 1,3,5,7-tetraphenyladamantane (**3**) (2.00 g, 4.54 mmol) in $CHCl_3$ (50 mL). The mixture was stirred until all iodine dissolved. Then [bis(trifluoroacetoxy)iodo]benzene (**4**)[2] (3.90 g, 9.06 mmol) was added and the resulting suspension was flushed with N_2 and stirred for 24 h. The suspension was filtered to remove a pink solid. The $CHCl_3$ solution was washed with 5% aqueous $NaHSO_3$ (50 mL), water (50 mL) and brine (50 mL). The solution was dried over anhydrous $MgSO_4$ and concentrated to dryness giving crude **5**, which was crystallized from 9:1 $CHCl_3$/MeOH yielding tetraiodide **5** (2.34 g, 46%) as colorless crystals, which were pure by NMR and TLC: mp 320-322 °C (lit.[1] 345 °C), R_f = 0.5 (1:1 $CHCl_3$/hexanes); ^{1}H NMR δ 2.06 (s, 12H), 7.18 (d, *J* = 8.6 Hz, 8H), 7.67 (d, *J* = 8.6 Hz, 8H); ^{13}C NMR δ 39.30, 46.94, 91.99, 127.38, 137.78, 148.66; MS Calcd for $C_{34}H_{28}I_4$ (M^+) 943.8, found 943.9. Anal. Calcd for $C_{34}H_{28}I_4$: C, 43.25; H, 2.99. Found: C, 43.52; H, 2.89.

4-Trityl-iodobenzene (7). 4-Tritylaniline (2.50 g, 7.45 mmol) was added to acetone (70 mL). It dissolved upon addition of concentrated HCl (7 mL) in water (10 mL). The solution was cooled to 0 °C and then sodium nitrite (0.800 g, 11.6 mmol) in water (5 mL) was added dropwise with stirring. The solution was stirred at 0°C for another 30 min and then potassium iodide (2.00 g, 12.1 mmol) in water (7 mL) was added dropwise. The resulting solution was stirred at 0 °C for 1 h, then at rt for 1h and then at 60 °C for 2 h. Sodium bisulfite (1 g) was added to consume any iodine that may have formed in the

reaction. The mixture was extracted with ether (150 mL). The extract was washed with water (60 mL) followed by brine (2 × 60 mL). The extract dried over anhydrous $MgSO_4$ and concentrated on the rotary evaporator giving crude **7**. Purification by chromatography on silica gel and elution with 1:1 hexanes/CH_2Cl_2 gave **7** (3.1 g, 94%) as a yellow powder, mp ~180-230 ºC (dec. color change to gray), which was pure by TLC and NMR: ^{1}H NMR($CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.20 (m, 15H), 6.97 (d, *J* = 8.4 Hz, 2H); MS Calcd for $C_{25}H_{18}I$ (M-1) 445.1, found 445.2.

Tetra(4-iodophenyl)methane (8). A mixture of 4-trityl-iodobenzene **7** (1.29 g, 2.90 mmol), [bis(trifluoroacetoxy) iodo]benzene (2.24 g, 5.21 mmol) and iodine (1.10 g, 4.34 mmol) in $CHCl_3$ (30 mL) was stirred at rt for 3 h and filtered. The filtrate was concentrated to dryness and the residue was triturated with $CHCl_3$ (20 mL) and filtered. The resulting solid was combined with the solid obtained from the original filtration and then boiled in $CHCl_3$ (40 mL) for 10 h. The suspended solid was collected by filtration and dried in vacuum to give tetraiodide **8** (0.50 g, 28%) as a colorless solid, mp >250 ºC (lit.[3] mp not reported), which was pure by TLC and NMR: ^{1}H NMR($CDCl_3$) δ 6.88 (d, *J* = 8.7 Hz, 8H), 7.58 (d, *J* = 8.7 Hz, 8H); MS Calcd for $C_{25}H_{16}I_4$ (M^+) 823.7, found, 823.6.

***N,N*-Bis(2-hydroxyethyl)-4-iodoaniline (10).** Ethylene oxide (12 mL) was condensed at –78 °C and added to *p*-iodoaniline (7.00 g, 32.0 mmol) in methanol (10 mL) at 0 °C in a thick walled reaction tube. The tube was sealed with a Teflon screw cap and stirred at 55 °C for 24 h. The mixture was allowed to cool to rt, and the solvent was evaporated. The residue was chromatographed on silica gel with 1-10% MeOH in $CHCl_3$ as a eluent to give diol **10** (8.80 g, 90%) as colorless crystals, mp 76-78 °C, which were pure by TLC and NMR: ^{1}H NMR δ 3.53 (t, *J* = 4.8 Hz, 4H), 3.65 (bs, 1H, disappeared with D_2O exchange), 3.80 (t, *J* = 4.9 Hz, 4H), 6.46 (d, *J* = 9.0 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR δ 55.13, 60.35, 77.60, 114.67, 137.72, 147.24; MS Calcd for $C_{10}H_{15}INO_2$ $(M+1)^+$ 308.0, found 308.0. Anal. Calcd for $C_{10}H_{14}INO_2$: C, 39.11; H, 4.59; N, 4.56. Found: C, 39.21; H, 4.58, N 4.48.

***N,N*-Bis(2-chloroethyl)-4-iodoaniline (11).** A solution of *N,N*-bis(2-hydroxyethyl)-4-iodoaniline **10** (4.0 g, 13 mmol) in pyridine (5 mL) was added dropwise to a stirred solution of phosphorus oxychloride (2.4 mL, 26 mmol) in pyridine (5 mL) at 0°C. The mixture was stirred at rt for 30 min and then at reflux temperature for 1.5 h. The mixture was allowed to stir overnight at rt. The solvent was evaporated and the residue was mixed with water (50 mL) and extracted with ether (2 × 50 mL). The combined extracts were washed with brine (2 × 50 mL), dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by chromatography on silica gel with 20% CH_2Cl_2 in hexane as an eluent to afford dichloride **11** (3.4 g, 76%) as colorless crystals, mp 68.5-69.5 °C, which were pure by TLC and NMR: ^{1}H NMR δ 3.58-3.73 (m, 8H), 6.47 (d, *J* = 9.3 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR δ 40.13, 53.31, 78.70, 114.22, 138.23, 145.68; MS Calcd for $C_{10}H_{13}Cl_2IN$ $(M+1)^+$ 343.9, found, 343.9. Anal. Calcd for $C_{10}H_{12}Cl_2IN$: C, 34.91; H, 3.52; N, 4.07. Found: C, 35.20; H, 3.38; N, 4.01.

***N,N*-Bis(2-thiocyanatoethyl)-4-iodoaniline (12).** A solution of *N,N*-bis(2-chloroethyl)-4-iodoaniline **11** (2.10 g, 6.10 mmol) and potassium thiocyanate (11.85 g, 122 mmol) in ethanol and water (3 mL) was heated with stirring for 72 h at 125 °C. The solvent was evaporated and the residue was mixed with water (80 mL). The mixture was extracted with ether (100 mL) and chloroform (2 × 60 mL). The combined organic extracts were washed with brine (2 × 60 mL) and water (60 mL), dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by chromatography on silica gel with $CHCl_3$ as an eluent to give **10** (1.2 g, 55%) as colorless crystals, mp 89.5-91 °C, which were pure by TLC and NMR: ^{1}H NMR δ 3.11 (t, *J* = 6.9 Hz, 4H), 3.82 (t, *J* = 6.9 Hz, 4H), 6.56 (d, *J* = 9.3 Hz, 2H), 7.56 (d, *J* = 9.3 Hz, 2H); ^{13}C NMR δ 30.65, 51.60, 81.05, 111.43, 115.80, 138.61, 144.79; MS Calcd for $C_{12}H_{13}IN_3S_2$ $(M+1)^+$ 389.95, found 389.9. Anal. Calcd for $C_{12}H_{12}IN_3S_2$: C, 37.02, H, 3.11, N, 10.79. Found: C, 36.94, H, 3.03, N, 10.63.

5-(4-Iodophenyl)-[1,2,5]dithiazepane (13). A. From 12. A solution of *N,N*-bis(2-thiocyanatoethyl)-4-iodoaniline (**12**) (1.1 g, 2.83 mmol) and potassium thiocyanate (10.23 g, 5.66 mmol) in 90% ethanol (30 mL) was heated with stirring at 125 °C for 2 h. The solvent was evaporated and the residue was mixed with water (60 mL). The mixture was extracted with ether (2 × 50 mL) and chloroform (50 mL). The combined organic extracts were washed with brine (2 × 50 mL), dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by chromatography on silica gel with 1:4 $CHCl_3$/hexanes as an eluent to give **13** (0.865 g, 91%) as colorless crystals, mp 98-100 °C (dec.).

B. From 11. A suspension of dichloride **11** (6.69 g, 19.4 mmol) and potassium thiocyanate (37.8 g, 389 mmol) in 10:1 ethanol/water (110 mL) was heated with stirring for 36 h in a 125 °C bath. The solvent was removed and the residue was treated with water (60 mL) and extracted with ether (50 mL) and then chloroform (2 × 60 mL). The combined organic extracts were washed with brine (2 × 50 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a brown oil, which was purified by chromatography over a short column of silica gel. Elution with 1:4 $CHCl_3$/hexanes gave **13** (4.64 g, 71%) as colorless crystals, mp 99-101 °C (from 1:10 $CHCl_3$/hexanes): R_f = 0.75 ($CHCl_3$); ^{1}H NMR δ 3.06 (t, *J* = 5.6 Hz, 4H), 3.93 (t, *J* = 5.6 Hz, 4H), 6.42 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR δ 36.58, 52.25, 77.13, 113.54, 138.01, 145.90; MS Calcd for $C_{10}H_{13}INS_2$ $(M+1)^+$ 337.9, found 338.0. Anal. Calcd for $C_{10}H_{12}INS_2$: C, 35.61; H, 3.59; N, 4.15. Found: C, 35.79; H, 3.53; N 4.07.

5-(4-Trimethylsilanylethynylphenyl)-[1,2,5]dithiazepane (14). Iodide **13** (1.00 g, 2.97 mmol), trimethylsilylacetylene (2.91 g, 29.70 mmol), $Pd(PPh_3)_2Cl_2$ (0.104 g, 0.149 mmol) and CuI (0.056 g, 0.297 mmol) were added to degassed triethylamine (5 mL) and THF (5 mL) in a thick walled reaction tube. The tube was sealed with a Teflon screw cap and the contents were stirred at 70 °C for 24 h. The reaction mixture was filtered and the solid was washed with diethyl ether (60

mL). The organic phases were combined and evaporated to give crude **14**, which was purified by chromatography on silica gel. Elution with 1:4 ether/hexanes gave **14** (0.83 g, 91%) as a yellow crystalline solid, which was pure by TLC and NMR: mp 100-101 °C (from 1:6 Et_2O/hexanes); R_f = 0.4 (1:4 Et_2O/hexanes); ^{1}H NMR δ 0.23 (s, 9H), 3.06 (t, *J* = 5.6 Hz, 4H), 3.95 (t, *J* = 5.6 Hz, 4H), 6.53 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR 0.17, 36.67, 52.40, 91.46, 106.14, 110.32, 110.94, 133.57, 146.46; MS Calcd for $C_{21}H_{22}NS_2Si$ (M+1) 308.1, found 308.1. Anal. Calcd for $C_{15}H_{21}NS_2Si$ (307.55): C, 58.58; H, 6.88; N, 4.55. Found: C, 58.31; H, 6.84; N, 4.34.

5-(4-Ethynylphenyl)-[1,2,5]dithiazepane (15). To a stirred solution of TMS derivative **14** (1.30 g, 4.23 mmol) in tetrahydrofuran (6 mL) at -20 °C, a 1 M solution of *n*-Bu_4NF in tetrahydrofuran (4.2 mL, 4.2 mmol) was added. After 30 min, the mixture was diluted with water (50 mL) and extracted with CH_2Cl_2 (50 mL) and then ether (50 mL). The combined organic extracts were washed with brine (2 × 50 mL), dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by chromatograph on silica gel. Elution with 1:9 ether/hexane gave **15** (0.85 g, 86%) as a colorless crystalline solid, which was pure by TLC and NMR: mp 119-121 °C (from 1:1 $CHCl_3$/hexanes); R_f = 0.25 (1:9 Et_2O/hexanes); ^{1}H NMR δ 2.97 (s, 1H), 3.07 (t, *J* = 5.6 Hz, 4H), 3.97 (t, *J* = 5.6 Hz, 4H), 6.56 (d, *J* = 9 Hz, 2H), 7.37 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR δ 36.64, 52.39, 74.97, 84.49, 109.19, 119.96, 133.66, 146.63; MS Calcd for $C_{12}H_{14}NS_2$ $(M+1)^+$ 236.0, found 236.0. Anal. Calcd for $C_{12}H_{13}NS_2$: C, 61.23; H, 5.57; N 5.95. Found: C, 61.35; H, 5.53; N 5.95.

5-[4-(4-Trimethylsilanylethynylphenylethynyl)phenyl]-[1,2,5]dithiazepane (16). 5-(4-Ethynylphenyl)-[1,2,5]dithiazepane **15** (0.77g, 3.28 mmol), 4-iodophenylethynyltrimethylsilane (1.08 g, 3.60 mmol), $Pd(PPh_3)_2Cl_2$ (0.569 g, 0.811 mmol) and CuI (0.308 g, 1.617 mmol) were added to degassed triethylamine (10 mL) and tetrahydrofuran (5 mL) in a thick walled reaction tube. The tube was sealed with a Teflon screw cap and stirred at 40-45 °C for 2 h, then at rt for 14 h. The reaction mixture was filtered and the solid was washed with diethyl ether (50 mL). The combined organic solutions were evaporated. The residue was chromatographed on silica gel with 10% ether in hexane as a eluent to give compound **16** (0.83 g, 91%) as colorless crystals, mp 188-190 °C, which were pure by TLC and NMR: ^{1}H NMR δ 7.41 (s, 4H), 7.40 (d, *J* = 9.2 Hz, 2H), 6.59 (d, *J* = 9.2 Hz, 2H), 3.98 (t, *J* = 5.6 Hz, 4H), 3.08 (t, *J* = 5.6 Hz, 4H), 0.26 (s, 9H); ^{13}C NMR δ 146.51, 133.24, 131.81, 130.02, 124.18, 121.98, 111.14, 110.15, 104.87, 95.76, 92.43, 87.31, 52.45, 36.68, -0.07; MS Calcd for $C_{23}H_{26}HS_2Si$ (M+1) 408.1, found 408.1. Anal. Calcd for $C_{23}H_{25}NS_2Si$: C, 67.76; H, 6.18; N, 3.44. Found: C, 67.51; H, 5.98; N, 3.45.

5-[4-(4-Ethynylphenylethynyl)phenyl]-[1,2,5]dithiazepane (17). Dithiazepane **16** (0.37g, mmol) was mixed with potassium carbonate (0.5 g, mmol) in $CHCl_3$ (4 mL) and CH_3OH (12 mL). The suspension was stirred at rt for 3 h and then diluted with ether (100 mL). The organic phase was washed with brine (2 × 30 mL) and water (30 mL), then dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by chromatorgraph on silca gel with 10% ether in hexane as the eluent to give **17** (1.098 g, 82%) as yellow crystals, mp 159-161 °C, which were pure by TLC and NMR: ^{1}H NMR δ 7.41 (s, 4H), 7.40 (d, *J* = 9.15 Hz, 2H), 6.59 (d, *J* = 9.15 Hz, 2H), 3.98 (t, *J* = 5.55 Hz, 4H), 3.08 (t, 4H, *J* = 5.55 Hz), 0.26 (s, 9H); ^{13}C NMR δ 146.55, 133.25, 131.97, 131.09, 124.60, 120.92, 111.12, 99.94, 92.51, 87.12, 83.46, 78.50, 52.45, 36.67; MS Calcd for $C_{20}H_{18}NS_2$ (M+1) 336.1, found 336.1. Anal. Calcd for $C_{20}H_{17}NS_2$ (335.49): C, 71.60; H, 5.11; N 4.18. Found: C, 71.37; H, 4.96; N, 3.99.

Tetrakis-{4-[4-(5-[1,2,5]dithiazepanyl)phenylethynyl]phenyl}methane (Molecular Tip 18). Tetra(4-iodophenyl)-methane (**8**, 41.2 mg, 0.0500 mmol), 5-(4-ethynylphenyl)-[1,2,5]-dithiazepane **15** (56.4 mg, mmol), $Pd(PPh_3)_2Cl_2$ (22 mg, 0.033 mmol) and CuI (12.1 mg, 0.062 mmol) were added to degassed triethylamine (8 mL) and tetrahydrofuran (2 mL) in a thick walled reaction tube which was then flushed with N_2 and capped with a self sealing rubber-lined Teflon screw cap. The mixture was stirred at rt for 2 h, then at 50-60 °C for 4 h. The reaction mixture was filtered and the solid was washed with $CHCl_3$ (30 mL). The filtrate was evaporated to dryness and the residue was purified by chromatography over a short column of silica gel. Elution with $CHCl_3$ gave crude **18**, which was further purified by radial chromatography (1 mm disk). Sequential elution with 30% chloroform in hexanes, 50% chloroform in hexanes and 80% chloroform in hexanes afforded **18** (21 mg, 21%) as a yellow glass, which was pure by TLC and NMR: R_f = 0.3 (80% $CHCl_3$ in hexanes); ^{1}H NMR δ 3.09 (t, *J* = 5.6 Hz, 16H), 3.98 (t, *J* = 5.6 Hz, 16H), 6.59 (d, *J* = 9.2 Hz, 8H), 7.15 (d, *J* = 8.6 Hz, 8H), 7.388 (d, *J* = 9.2 Hz, 8H), 7.394 (d, *J* = 8.6 Hz, 8H); ^{13}C NMR δ 36.74, 52.43, 77.20, 87.16, 90.54, 110.10, 110.48, 121.89, 130.63, 130.86, 133.20, 145.40, 146.30. MS Calcd for $C_{73}H_{64}N_4S_8$ $(M+1)^+$ 1253.3, found 1253.3.

Tetrakis-{4-(4-[4-(5-[1,2,5]dithiazepanyl)phenylethynyl]phenyl)ethynylphenyl}methane (Molecular Tip 19). 5-[4-(4-Ethynylphenylethynyl)phenyl]-[1,2,5] dithiazepane (**17**, 50 mg, 1.64 mmol), tetra(4-iodophenyl)methane (**8**, 21 mg, 0.025 mmol), $Pd(PPh_3)_2Cl_2$ (11 mg, 0.017 mmol) and CuI (6.1 mg, 0.031 mmol) were added to degassed triethylamine (3 mL) and tetrahydrofuran (3 mL) in a thick walled reaction tube. The tube was sealed with a Teflon screw cap and stirred at 100-105 °C for 3 h, then at rt for 12 h. The reaction mixture was filtered and the solid was washed with diethyl ether (25 mL). The combined organic phase was evaporated. The residue was chromatographed on silica gel with 10% hexanes in chloroform as the eluent to give a solid, which was crystallized by vapor diffusion of hexanes into a chloroform solution. Molecular tip **19** (5.8 mg, 15%) was thus obtained as a yellow crystalline solid, mp >250 °C, which was pure by TLC and NMR: ^{1}H NMR δ 7.46 (s, 16H), 7.45 (d, *J* = 9 Hz, 8H), 7.41 (d, *J* = 9 Hz, 8H), 7.21 (d, *J* = 8.6 Hz, 8H), 6.60 (d, *J* = 8.6 Hz, 8H), 3.99 (t, *J* = 5.5 Hz, 16H), 3.09 (t, *J* = 5.5 Hz, 16H); ^{13}C NMR δ 36.71, 52.48, 77.21, 87.40, 89.78, 90.49, 92.41, 110.23,

111.15, 121.26, 122.09, 124.02, 130.91, 131.09, 131.18, 131.49, 133.26, 145.95, 146.51. MS MALDI Calcd for $C_{105}H_{82}N_4S_8$ (M+2) 1654.4, found 1654.4. Anal. Calcd for $C_{105}H_{80}N_4S_8 \cdot H_2O$: C, 75.41; H, 4.94; N, 3.35. Found: C, 75.22; H, 4.67; N, 3.18.

Tetrakis{4-(4-[(5-[1,2,5]dithiazepanyl)phenyl]ethynyl)phenyl}adamantane (Molecular Tip 20). 5-(4-Ethynyl-phenyl)-[1,2,5]dithiazepane **15** (51 mg, 0.22 mmol), tetra-(4-iodophenyl)adamantane (**5**, 40 mg, 0.042 mmol), $Pd(PPh_3)_2Cl_2$ (6 mg, 0.09 mmol) and CuI (3.4 mg, 0.018 mmol) were added to degassed triethylamine (8 mL) and tetrahydrofuran (2 mL) in a thick walled reaction tube. The tube was sealed with a Teflon screw cap and stirred at 80-85 ^oC for 5 h, then at rt for 12 h. The reaction mixture was filtered and the solid was washed with $CHCl_3$ (30 mL). The filtrate was evaporated to dryness and the residue was purified by chromatography on silica gel with 70% chloroform in hexanes as the eluent to give **20** (6.8 mg, 12%) as a yellow glass, which was pure by TLC and NMR: R_f = 0.8 ($CHCl_3$); ^1H NMR δ 2.15 (s, 12 H), 3.09 (t, J = 5.5 Hz, 16H), 3.98 (t, J = 5.5 Hz, 16H), 7.39-7.50 (m, 24H); ^{13}C NMR δ 36.76, 39.27, 46.90, 52.44, 87.39, 90.01, 110.63, 111.12, 121.90, 125.01 131.35, 133.18, 146.26, 148.60; MS FAB Calcd for $C_{82}H_{77}N_4S_8$ 1373.4 (M+1), found 1373.5.

Atomic Force Microscopy Experiments. AFM measurements were carried out with a Nanoscope IIIa Multimode AFM (Digital Instruments, Santa Barbara, CA) using a 10 μm scanner. Tapping mode AFM (TMAFM) scans were performed in air with NANO*SENSORS* silicon cantilevers/tips: type NCH, cantilever resonance frequency f_0 = 289-332 kHz and force constant 24.0-37.0 N/m.

The instrument was operated at frequencies slightly lower than the natural resonance frequency in air. All data were recorded in height mode. Set point values were chosen so that the interaction of the tip and sample provided a good compromise between stability and resolution, without damaging the tip or the sample. Scan rates ranged from 1 to 3 Hz. Images were taken at a 512 × 512-pixel resolution to increase the detail in the images. All TMAFM studies were carried out on freshly cleaved muscovite mica, grade V-4 (Structure Probe, Inc.). The average sizes of height and width of nanometer sized features and their standard deviation were determined by counting the features on at least three different areas of the same sample and taking the average.

Sample Preparation. Spectroscopic grade solvents were used for sample preparation. *Molecular tip **19** on mica.* One drop of a 0.06 µM, 0.25 µM or 1 µM solution of molecular tip **19** in CH_2Cl_2 was spin-coated onto freshly cleaved mica (cleaved with Scotch tape) for 15-20 s under ambient conditions at a speed of 2000 rpm. Scanning of the sample by AFM began immediately after completion of the spin-coating step.

*DNA/molecular tip **19** on mica.* λ DNA *Hind* III digest fragments were purchased from New England BioLabs and used without additional purification. Prior to imaging, the DNA was diluted to a concentration of 0.33 µg/mL in HEPES buffer (pH = 7.4), containing 4 mM HEPES, 10 mM NaCl, 2 mM $MgCl_2$. An aliquot (20 µL) of the solution was deposited onto freshly cleaved mica. The sample was incubated for 10-15 min in air. The sample was then rinsed well with deionized water, blotted at the edges and allowed to dry under a flow of argon. Next, a 0.25 µM solution of molecular tip **19** in CH_2Cl_2 was spin-coated over the DNA on mica for 15-20 s under ambient conditions at a speed of 2000 rpm. Scanning of the sample by AFM began immediately after completion of the spin-coating step.

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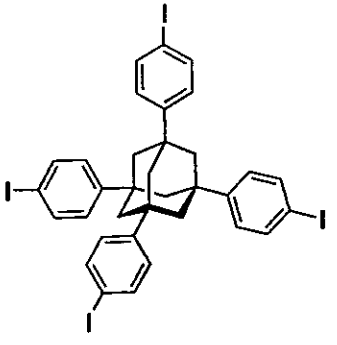
(3) Su, D.; Menger, F. M. *Tetrahedron Lett.* **1997**, *38*, 1485-1488.

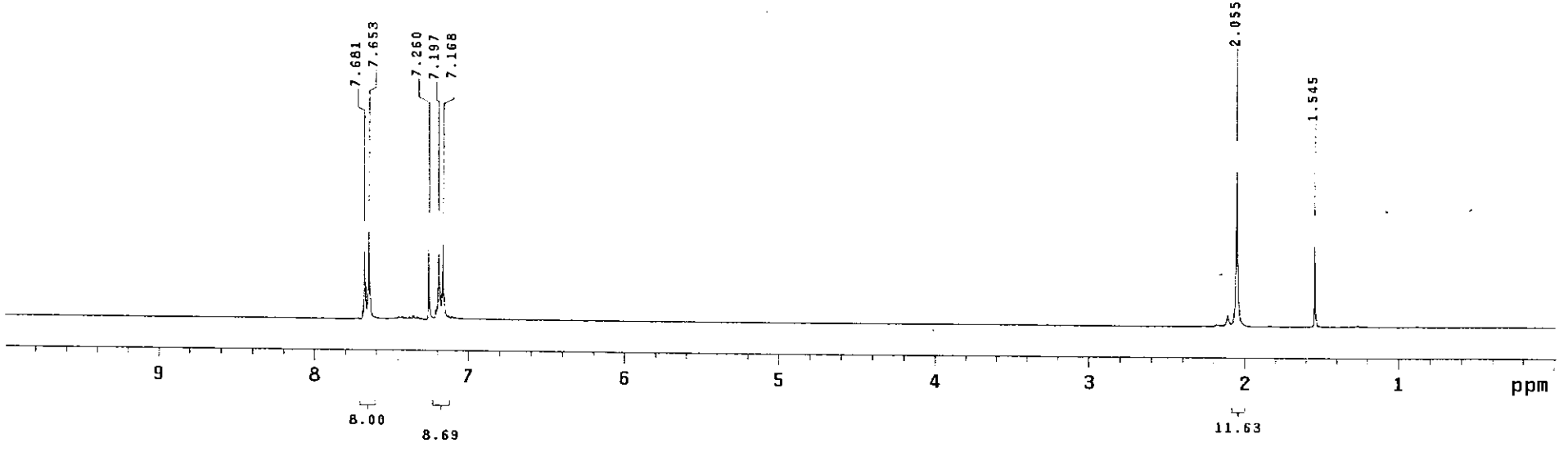
quanli020130a

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 37.9 degrees
Acq. time 2.501 sec
Width 4799.0 Hz
8 repetitions
OBSERVE H1, 299.9468612 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 28 sec

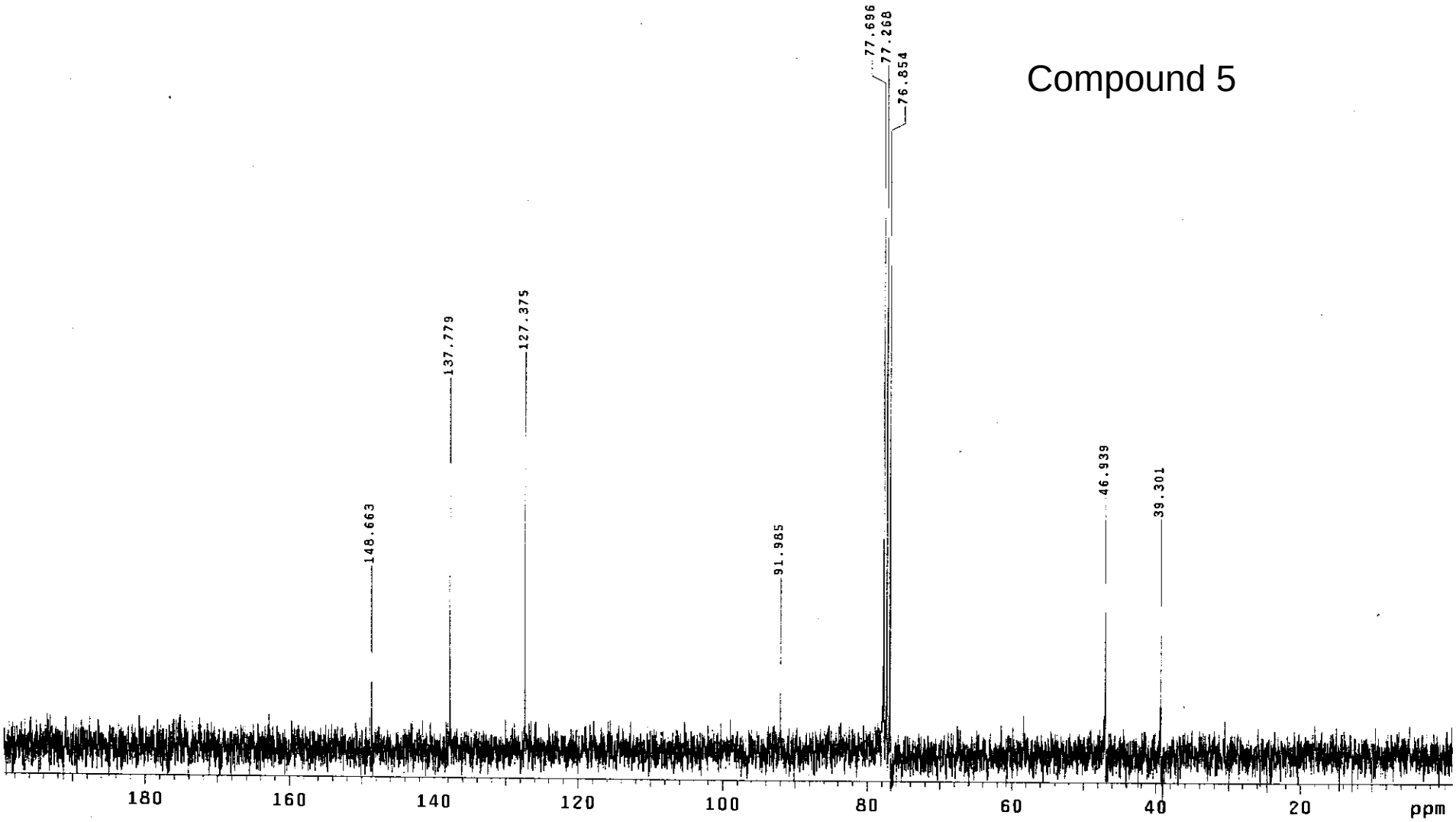


5



quanli020130b

Pulse Sequence: s2pul



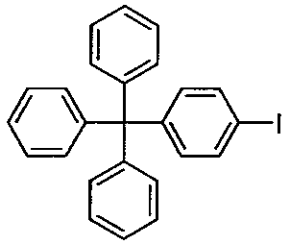
Compound 5

quanli011211b

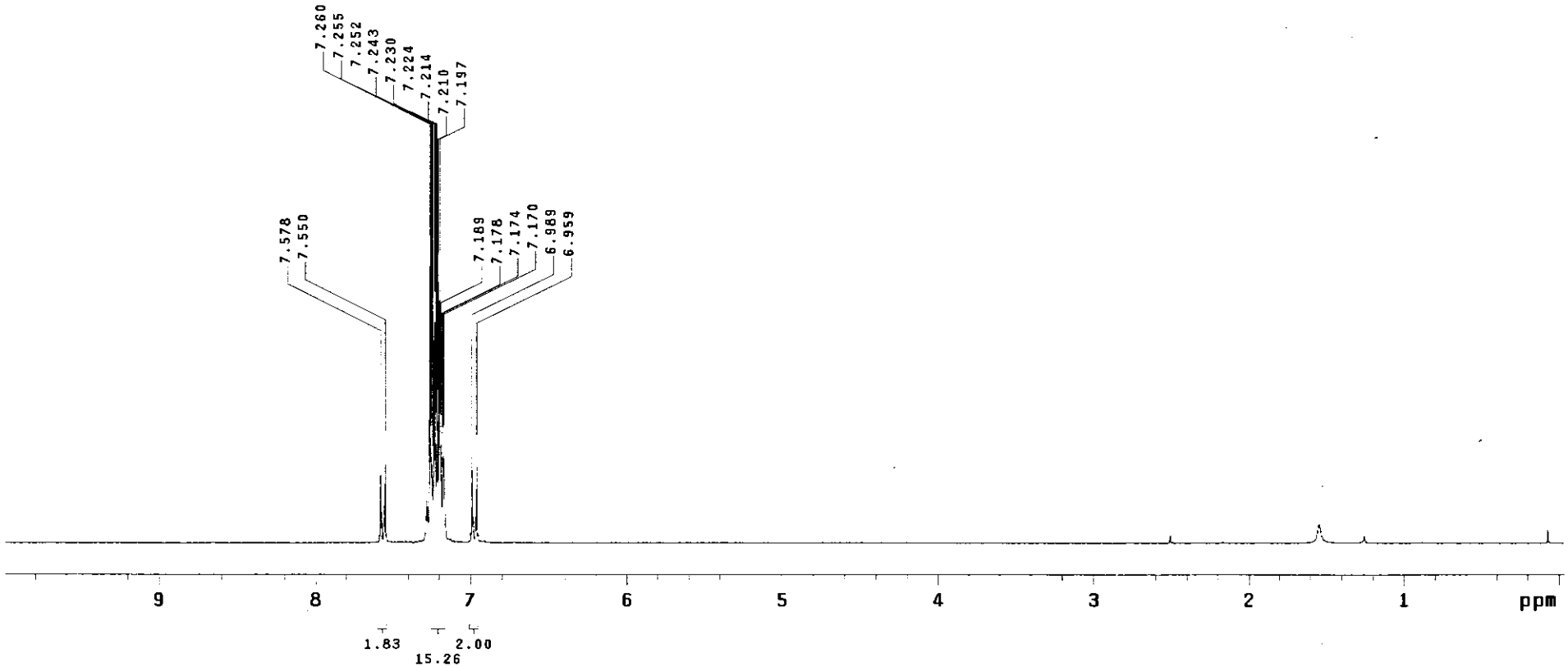
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 37.9 degrees
Acq. time 2.501 sec
Width 4799.0 Hz
8 repetitions
OBSERVE H1, 299.9468612 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 28 sec



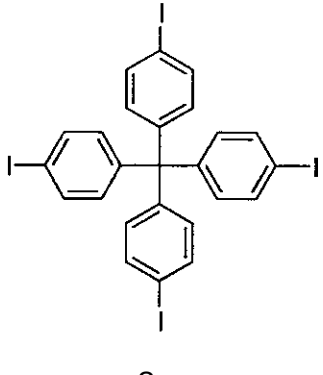
7



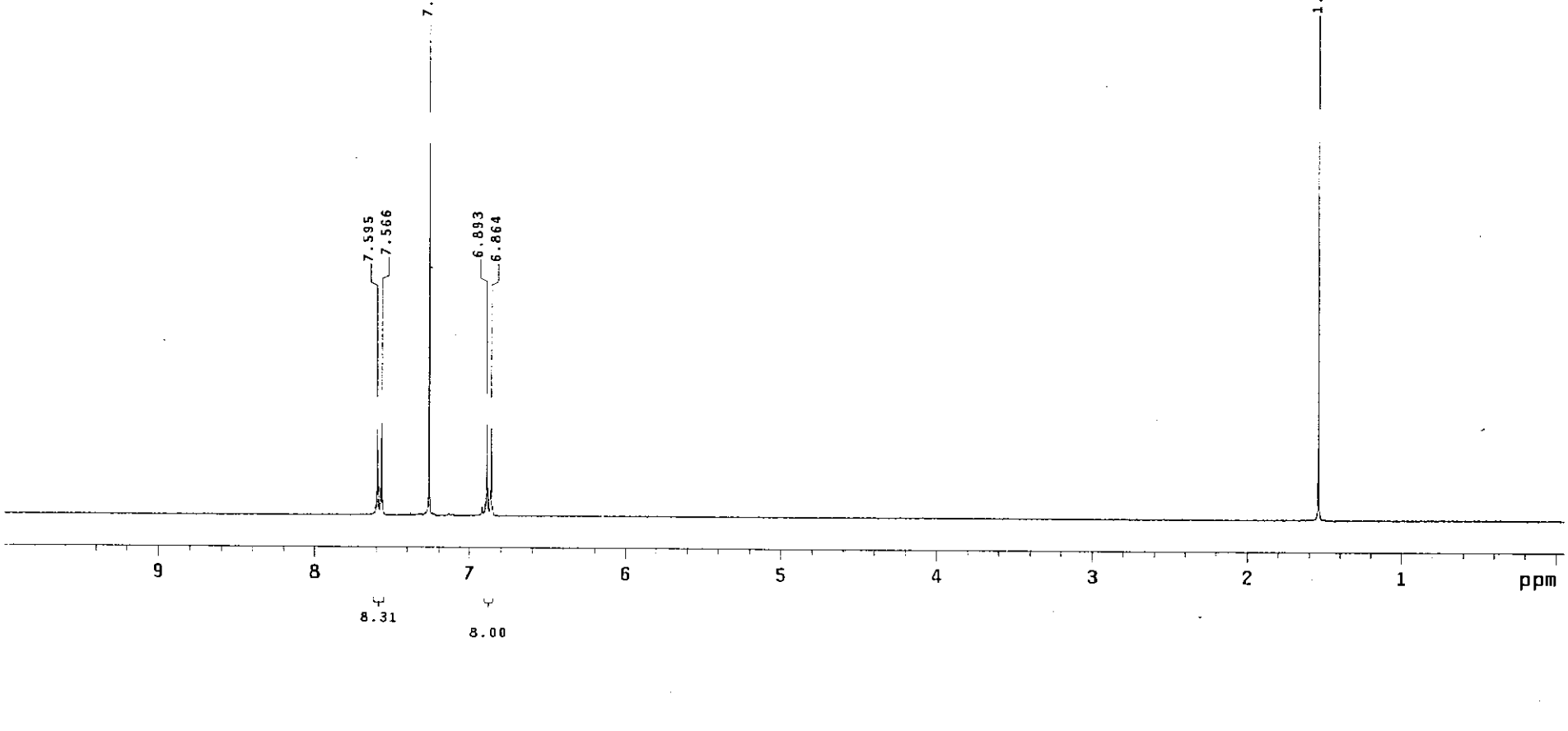
quanli011226a

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: qli011226a
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 37.9 degrees
Acq. time 2.501 sec
Width 4799.0 Hz
8 repetitions
OBSERVE H1, 299.9468609 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 28 sec

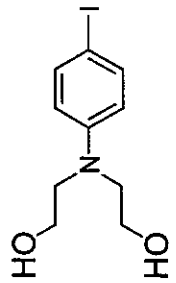


8

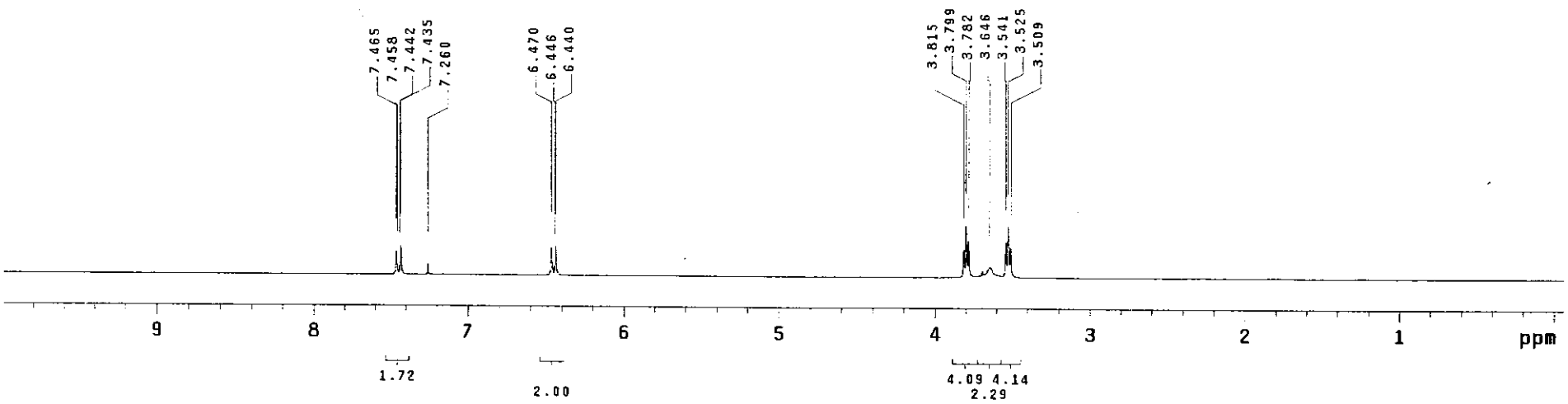


STANDARD 1H OBSERVE

Pulse Sequence: s2pul



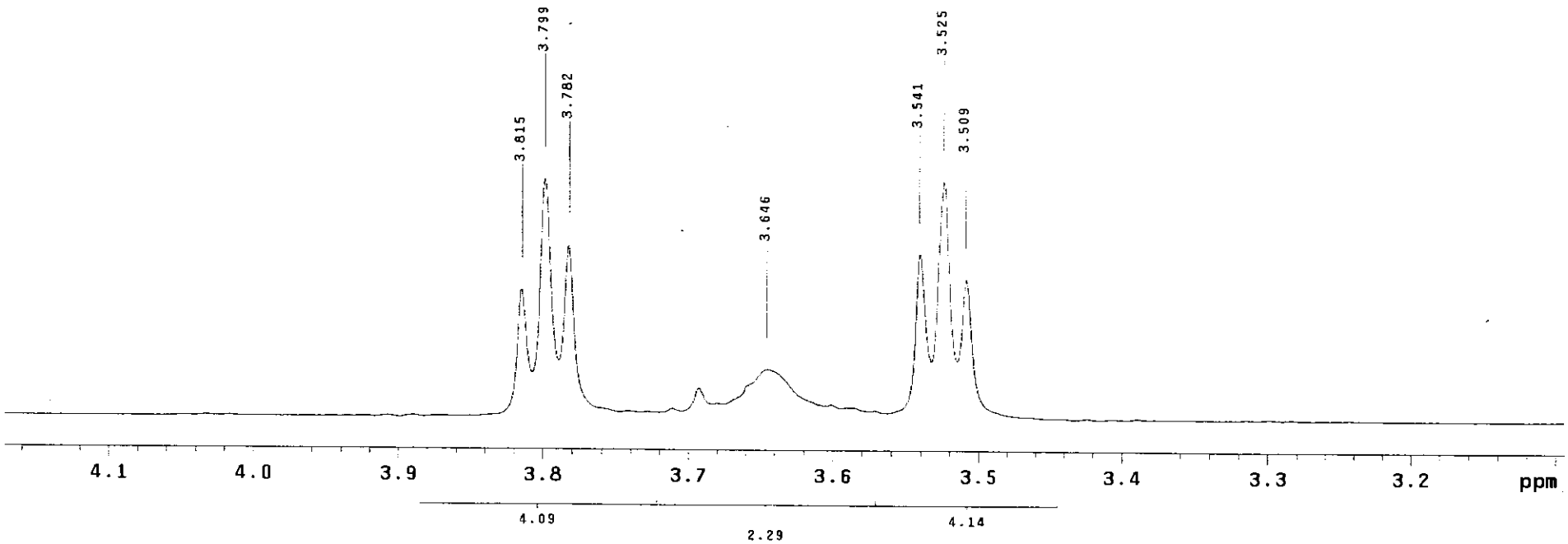
10



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

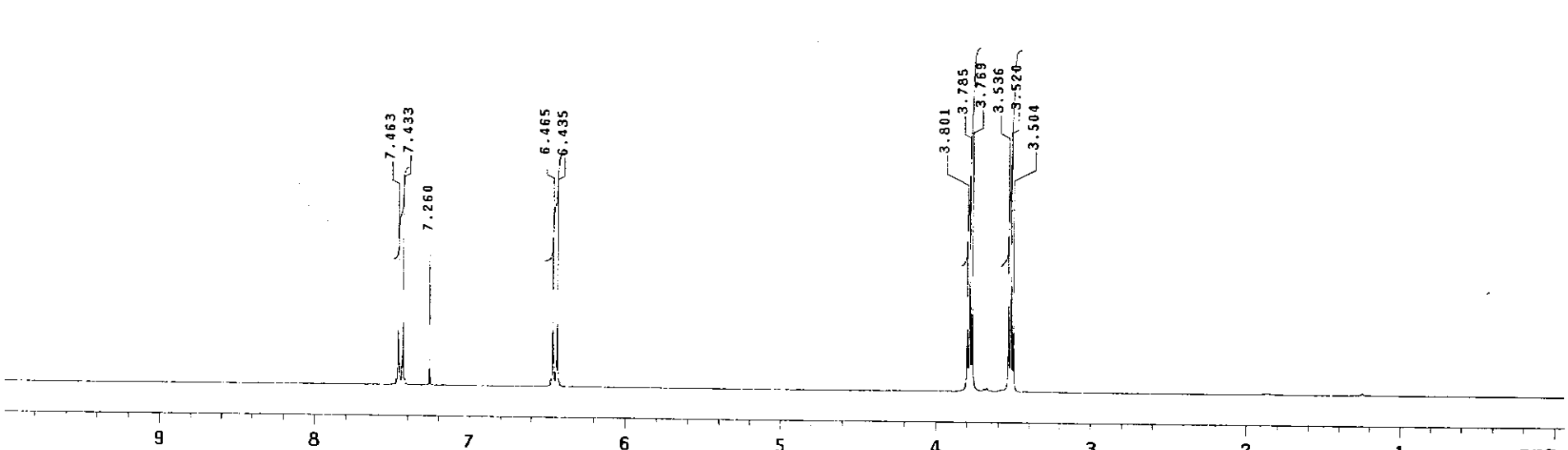
Compound 10



ql1011017 D2O exchange

Pulse Sequence: s2pul

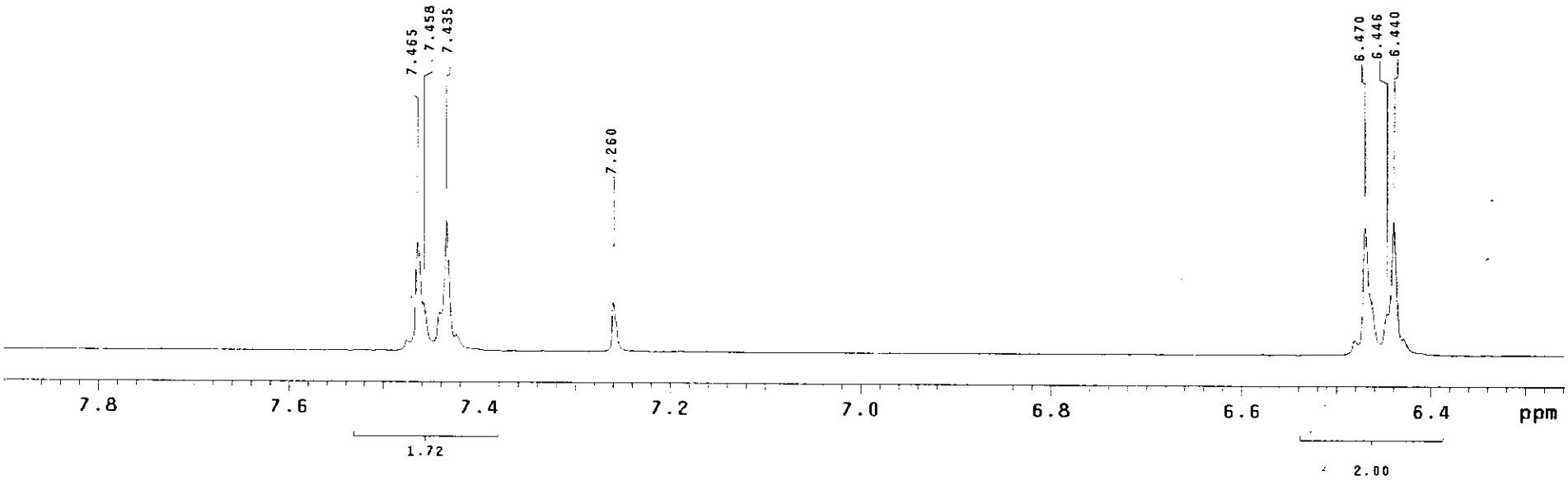
Compound 10



STANDARD IH OBSERVE

Pulse Sequence: s2pul

Compound 10

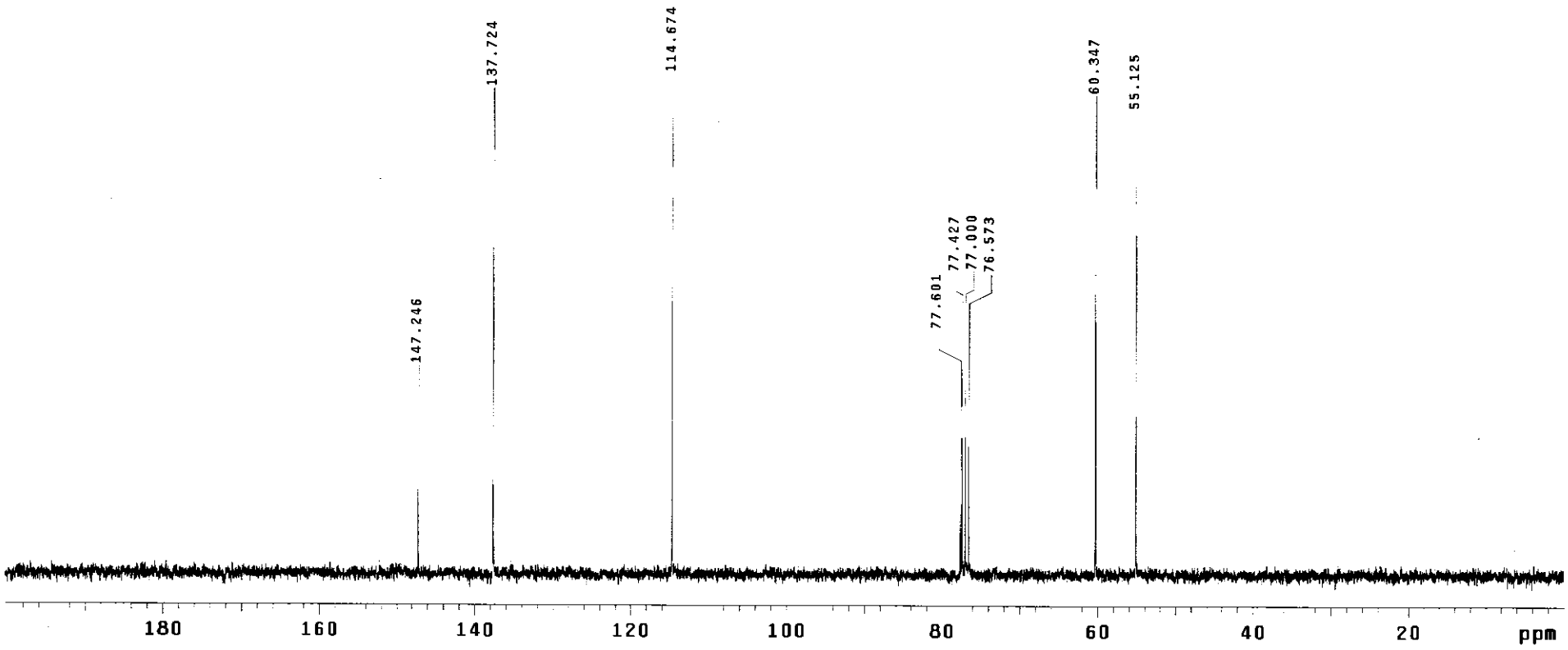


Compound10

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
INOVA-300 "sunofnmr"

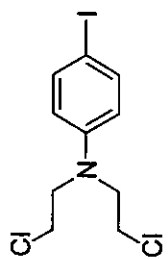
PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 42.6 degrees
 Acq. time 0.599 sec
 Width 16501.7 Hz
 80 repetitions
OBSERVE C13, 75.4217031 MHz
DECOUPLE H1, 299.9478514 MHz
 Power 32 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 32768
Total time 8 min, 2 sec

Compound 10

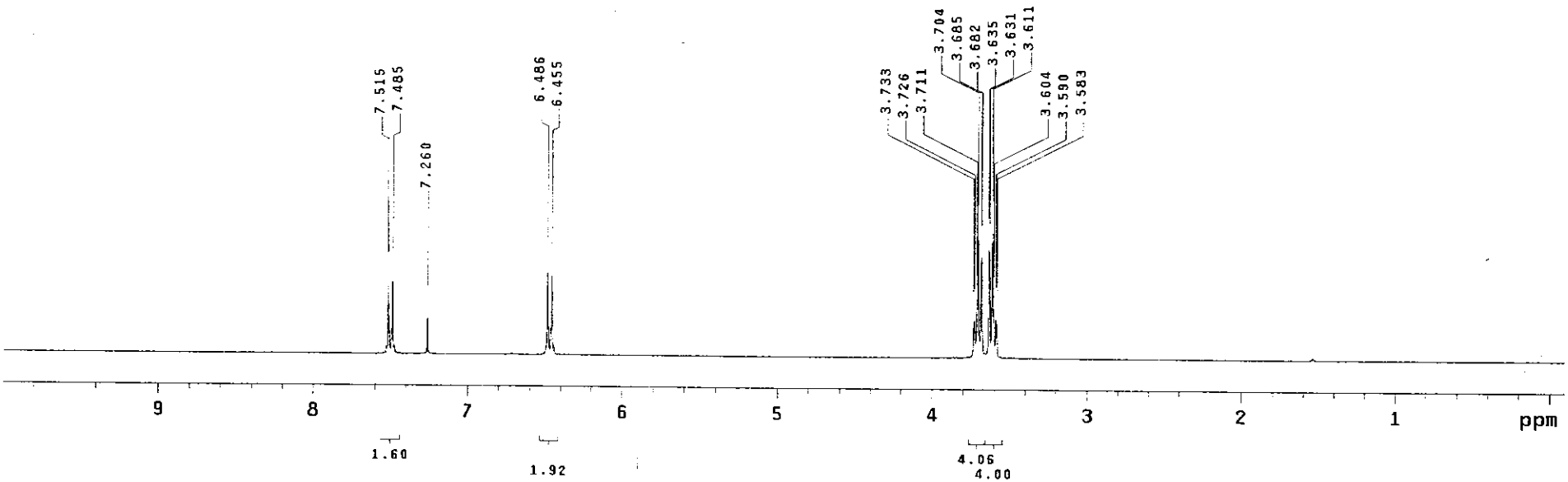


qli011022a

Pulse Sequence: s2pul



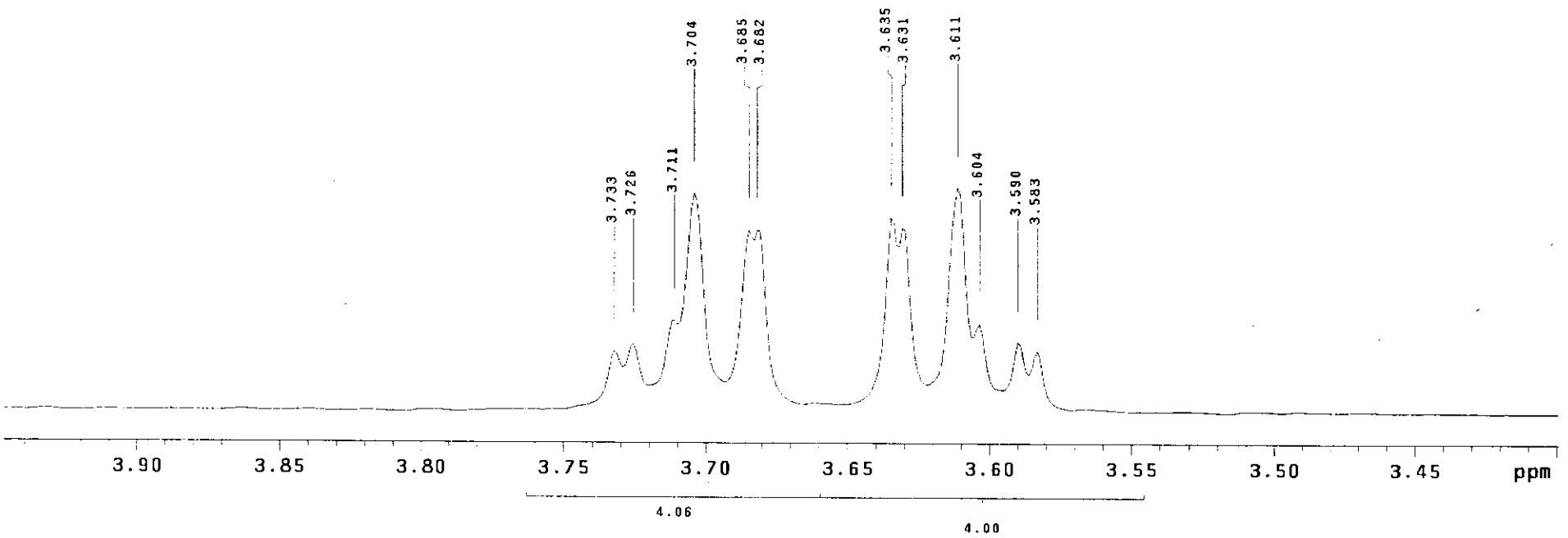
11



qli011022a

Pulse Sequence: s2pul

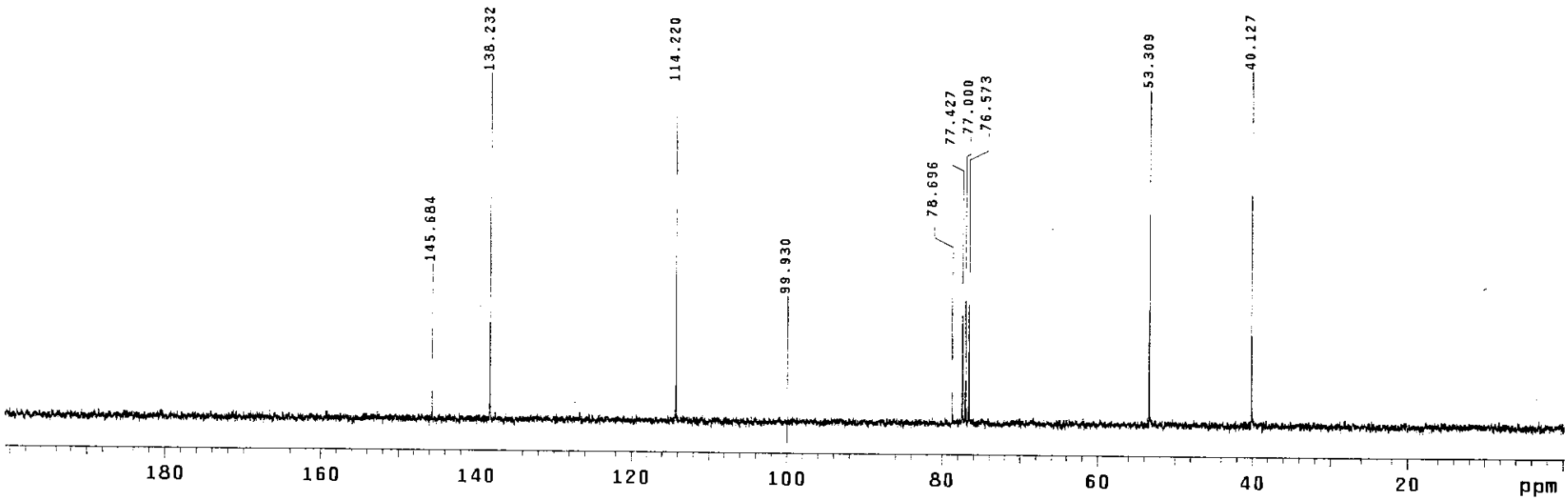
Compound 11



qli011022d

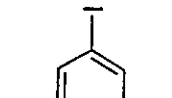
Pulse Sequence: s2pul

Compound 11

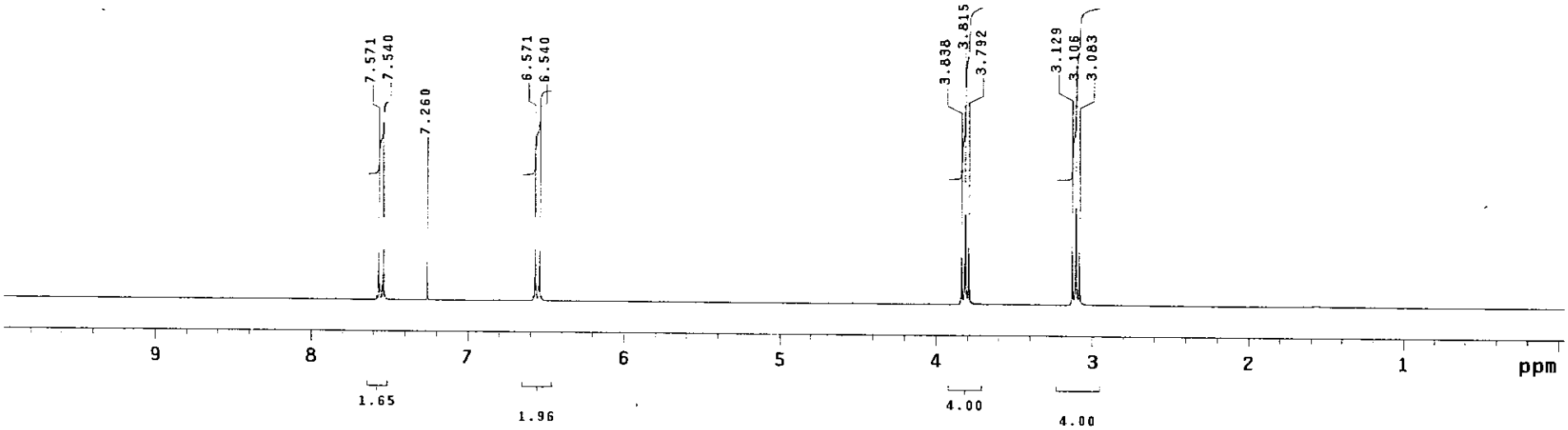


qli011030a

Pulse Sequence: s2pul



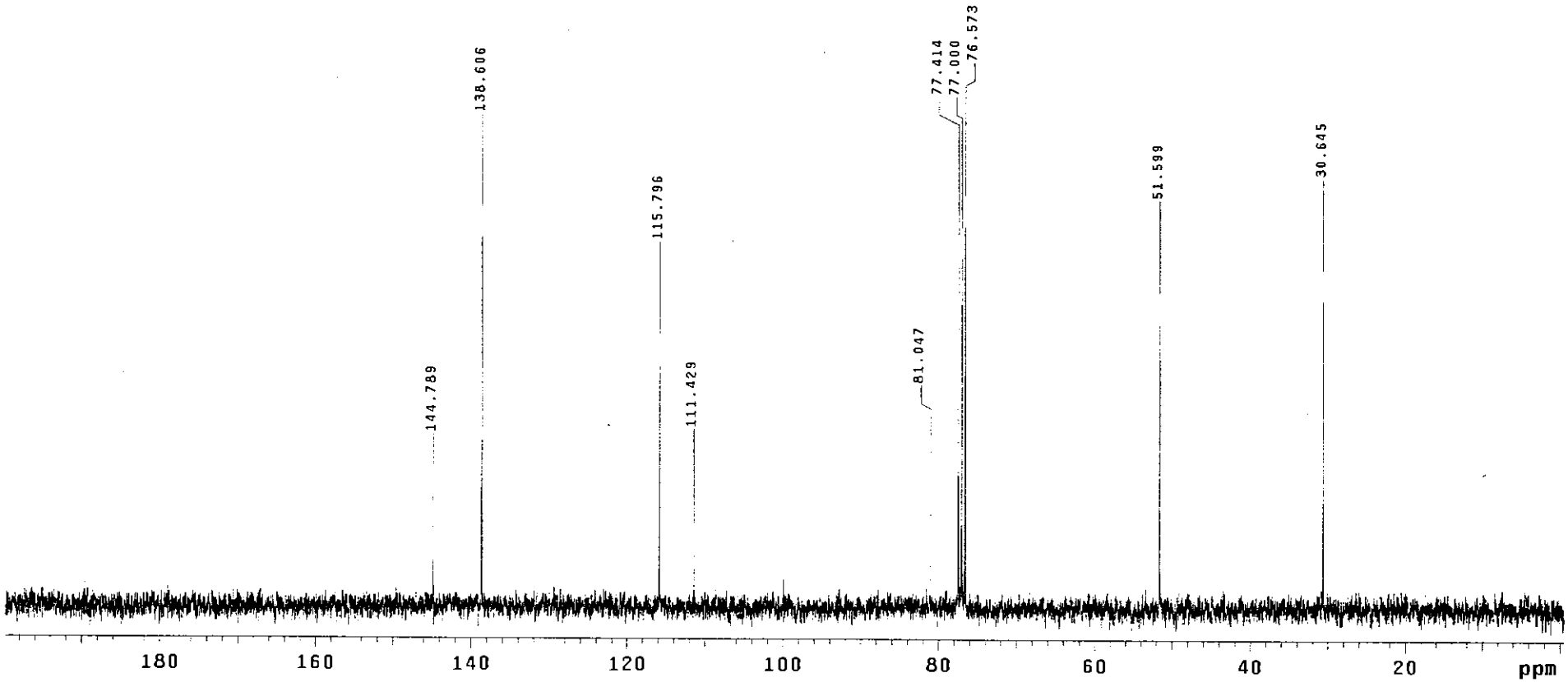
12



qli011030b

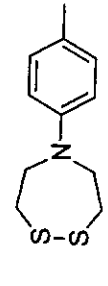
Pulse Sequence: s2pul

Compound 12

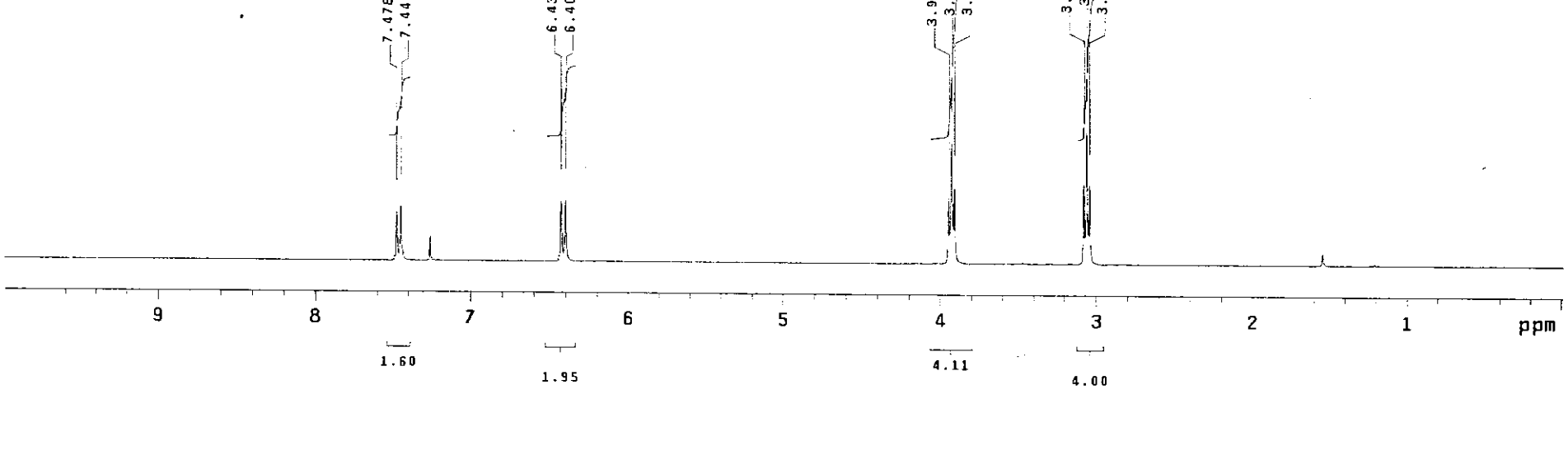


qli011106a

Pulse Sequence: s2pul



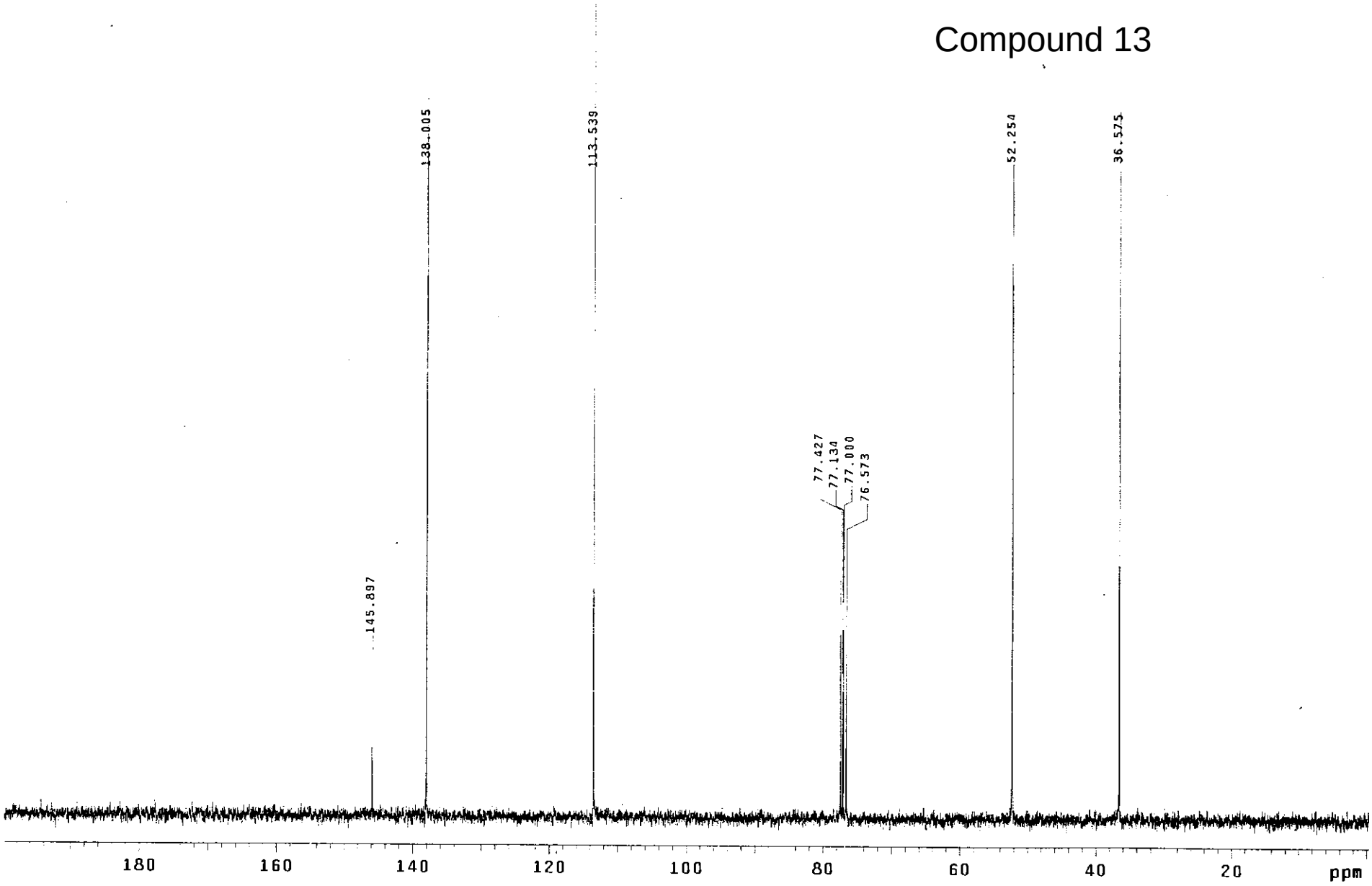
13



qli011106b

Pulse Sequence: s2pul

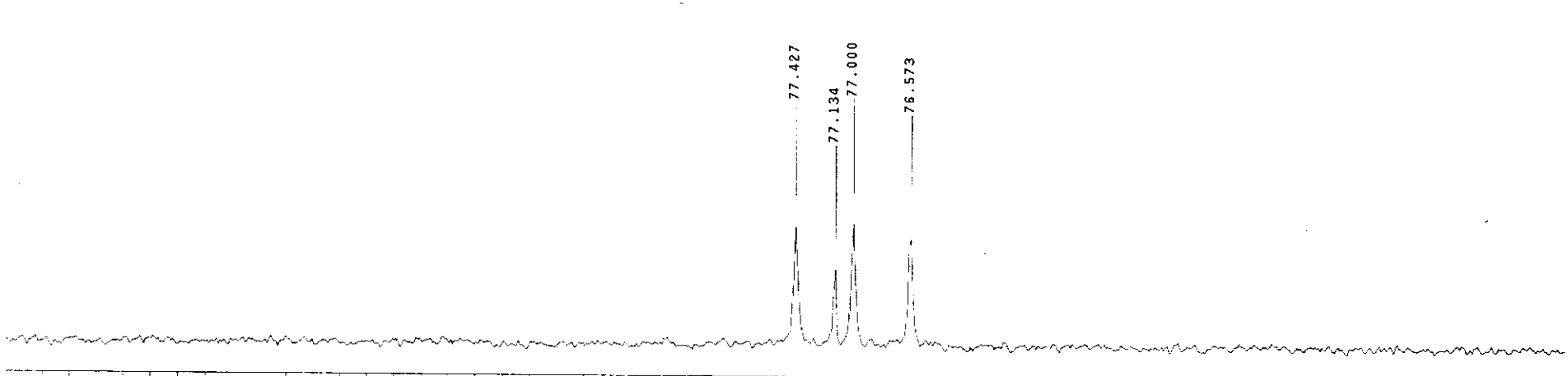
Compound 13



qli011106b

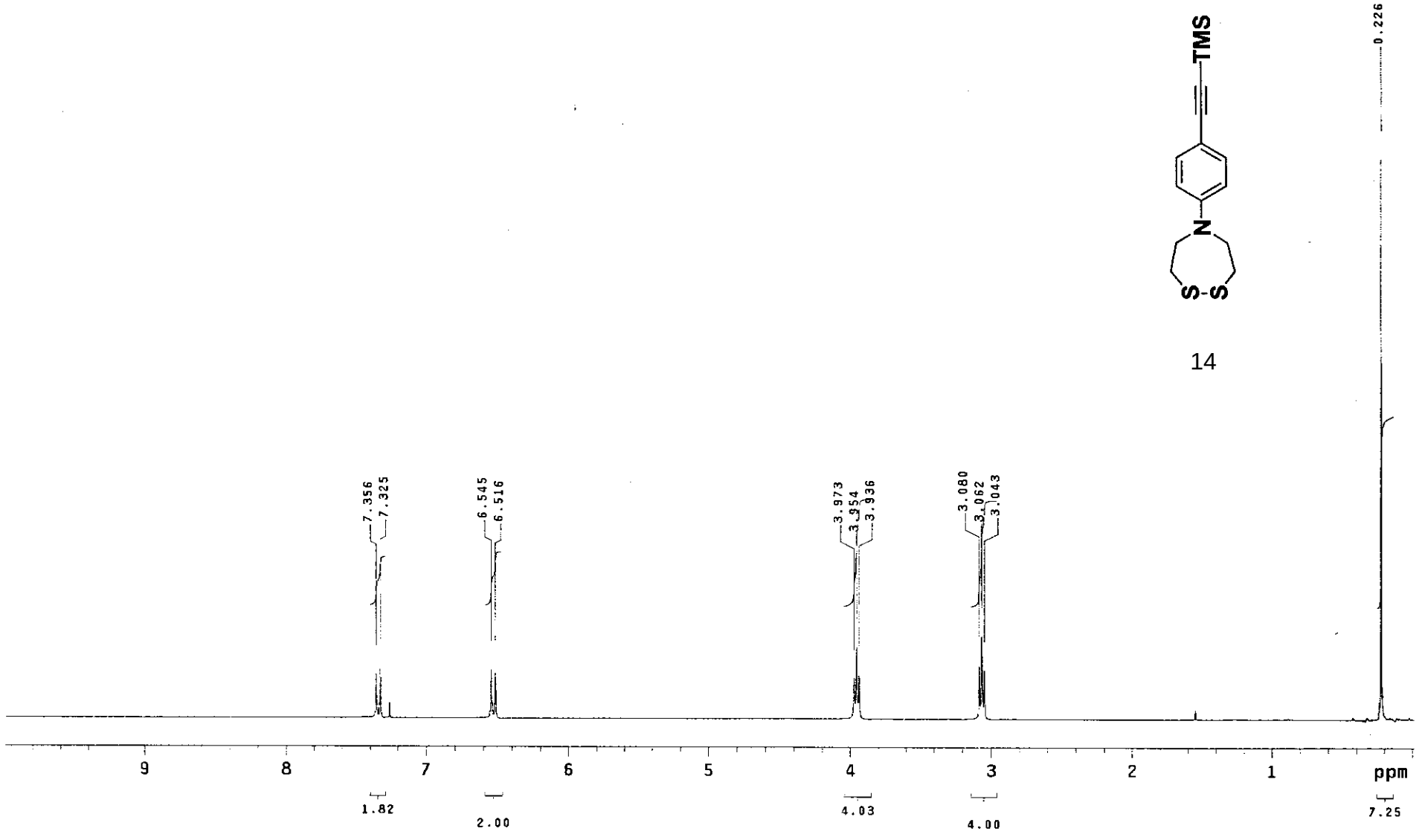
Pulse Sequence: s2pul

Compound 13



qli011108a

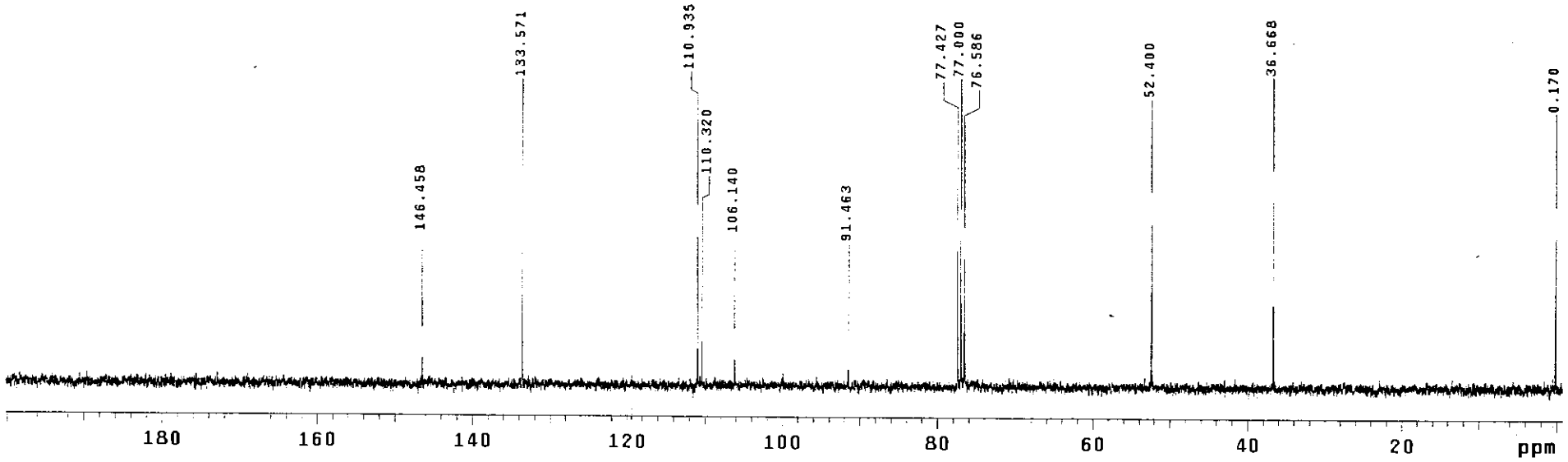
Pulse Sequence: s2pul



qli01108b

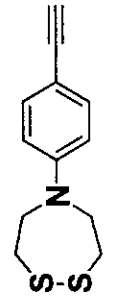
Pulse Sequence: s2pul

Compound 14

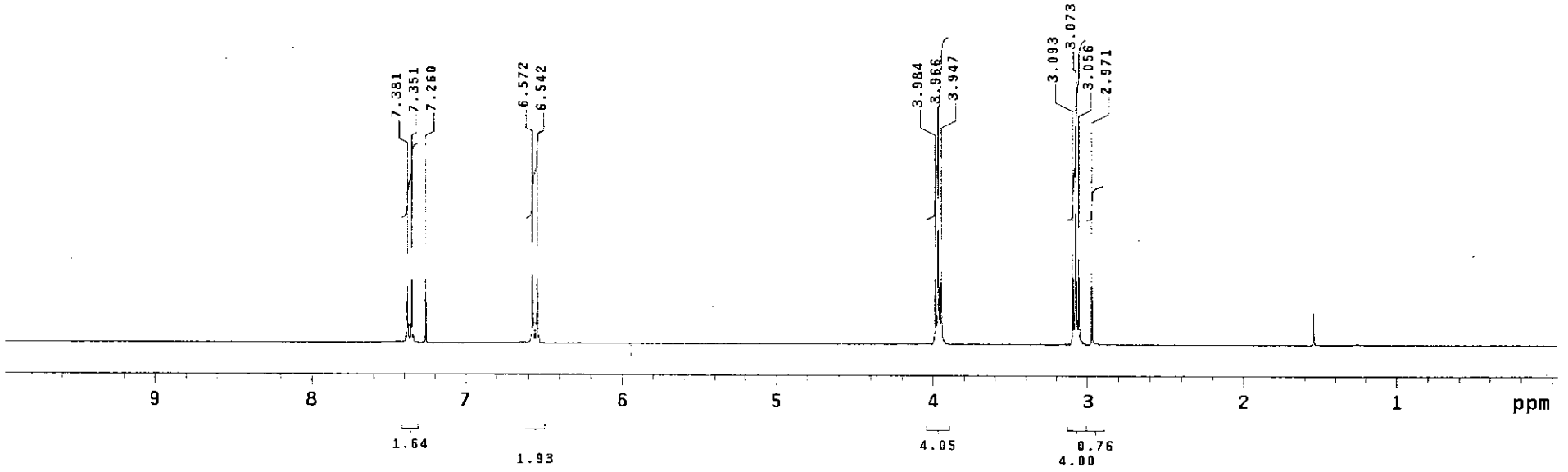


qli011112a

Pulse Sequence: s2pul



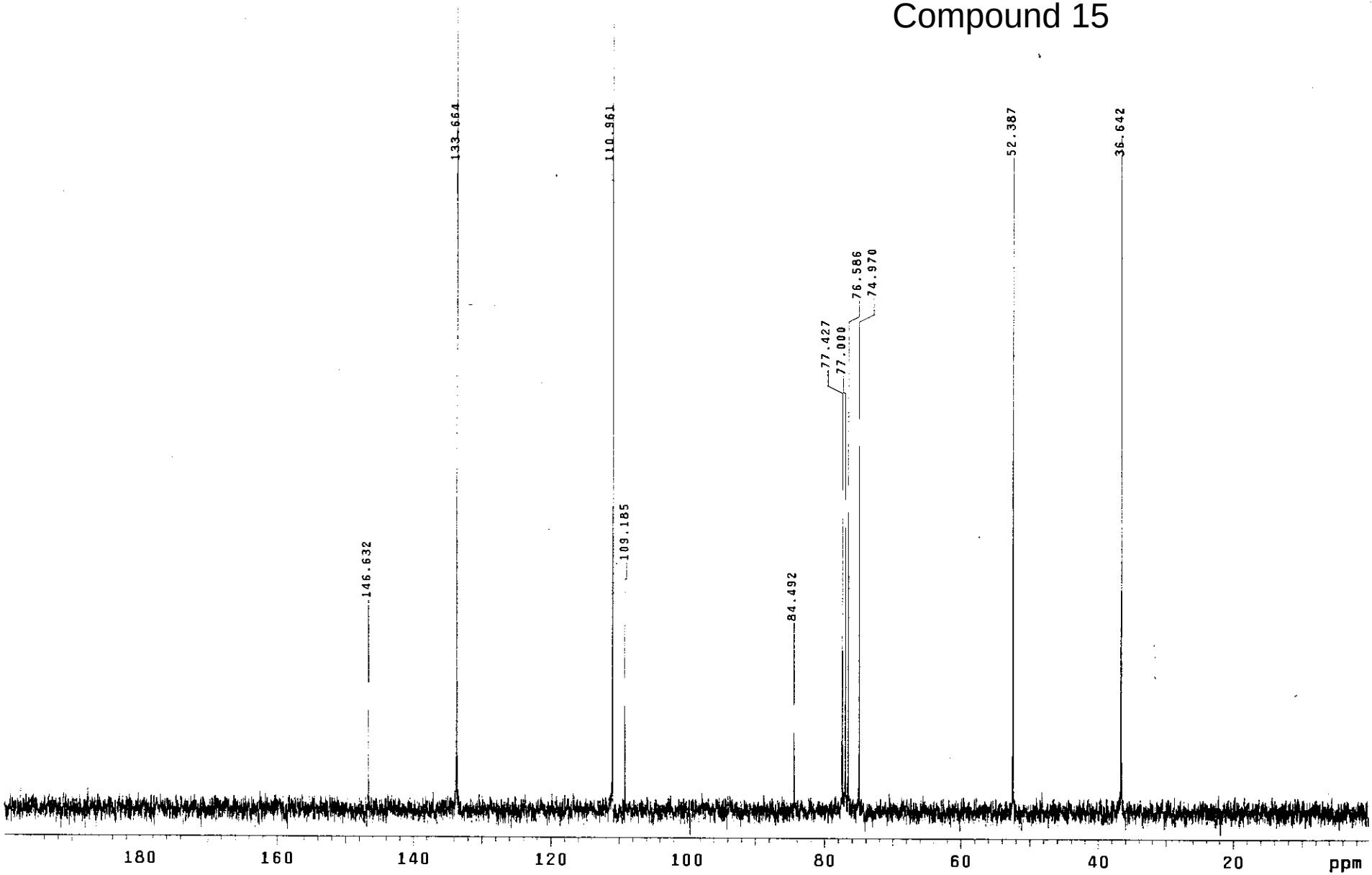
15



qli0111112b

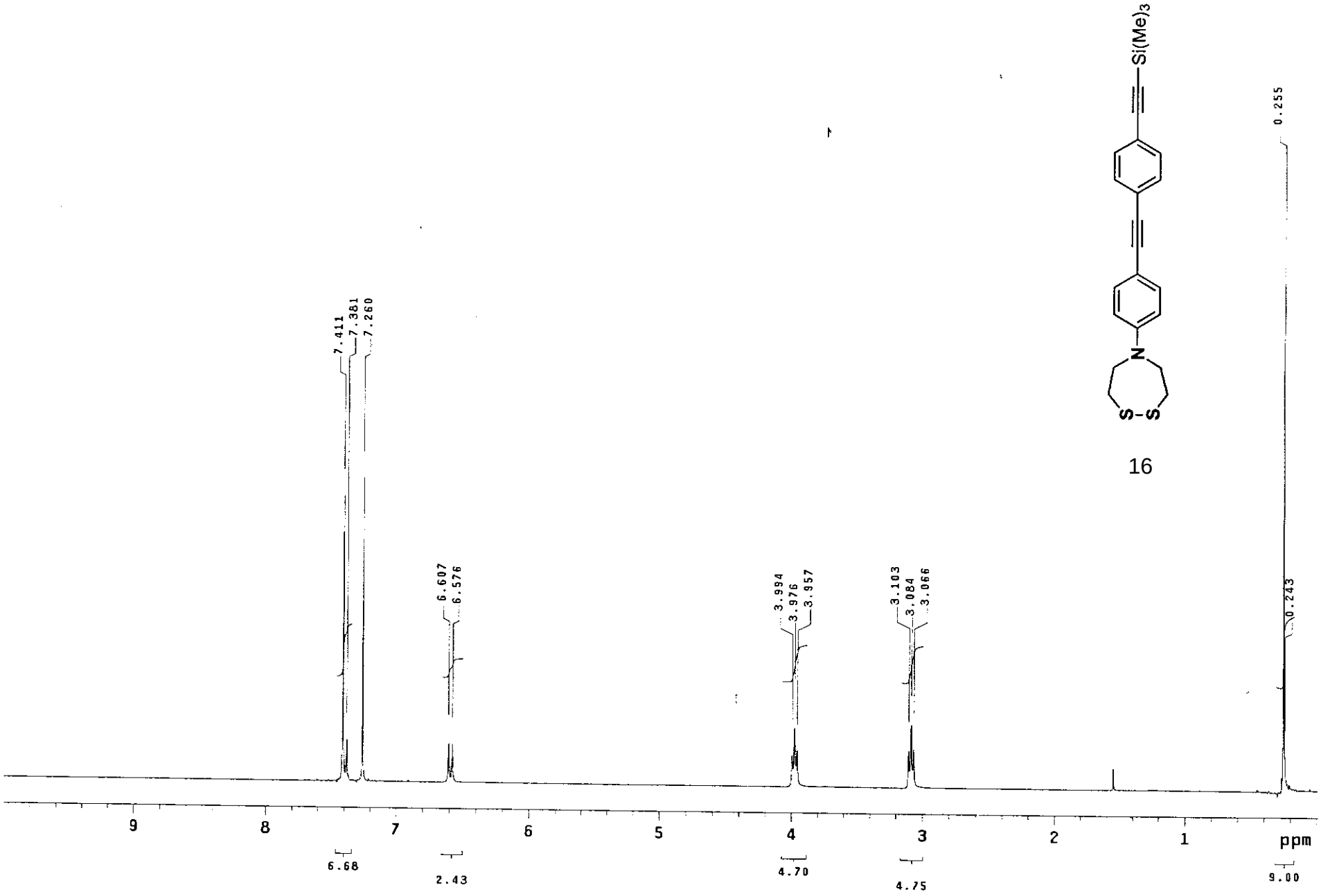
Pulse Sequence: s2pul

Compound 15



qli011128a

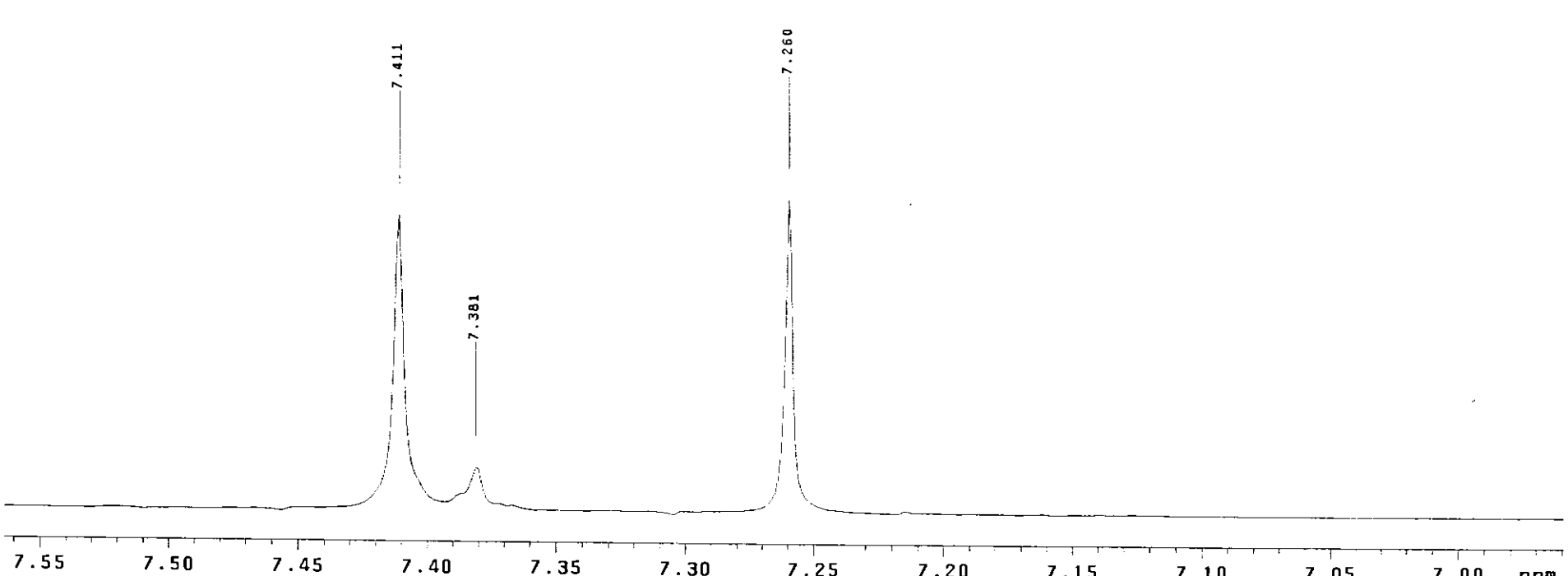
Pulse Sequence: s2pul



qli011128a

Pulse Sequence: s2pul

Compound 16



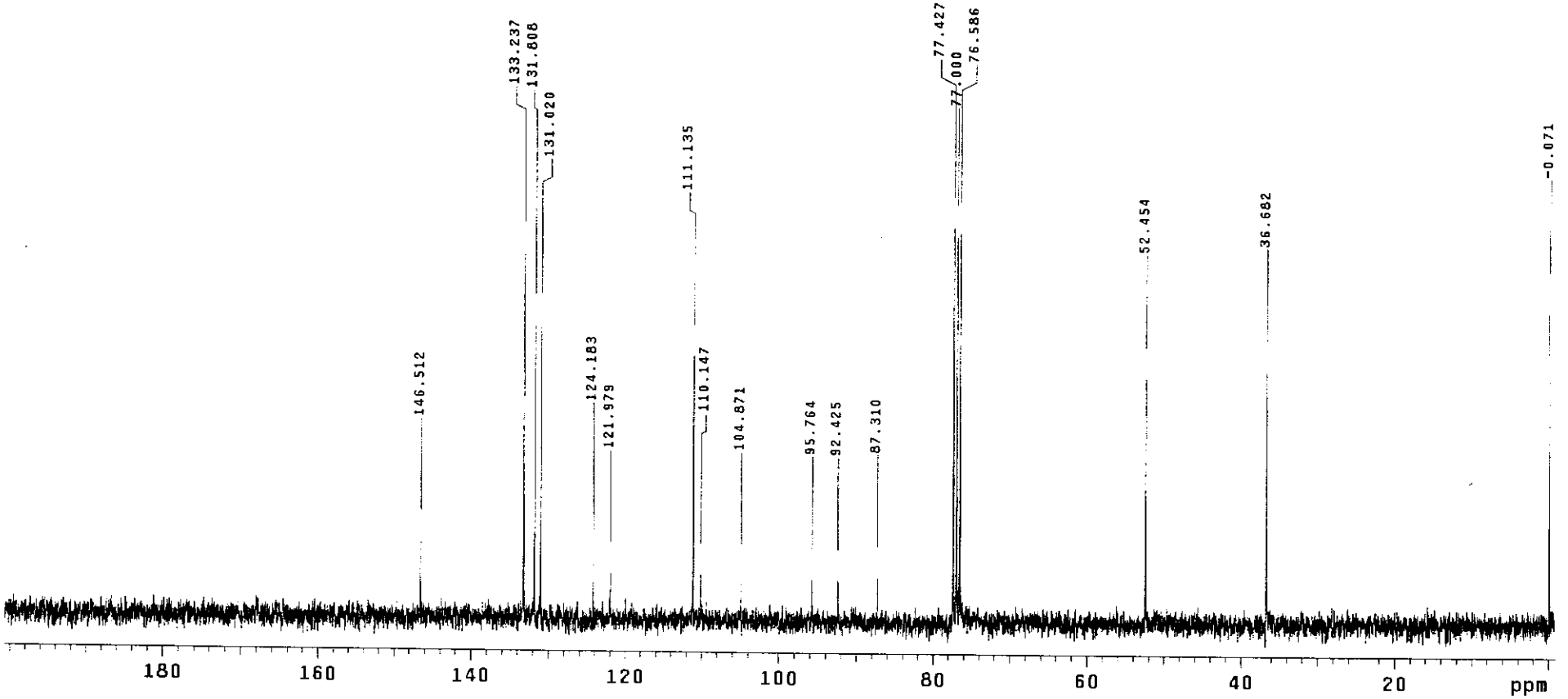
qli011128

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"

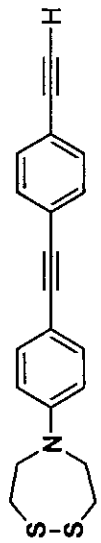
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 42.6 degrees
Acq. time 0.599 sec
Width 16501.7 Hz
500 repetitions
OBSERVE C13, 75.4216991 MHz
DECOUPLE H1, 299.9478514 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 13 min, 24 sec

Compound 16

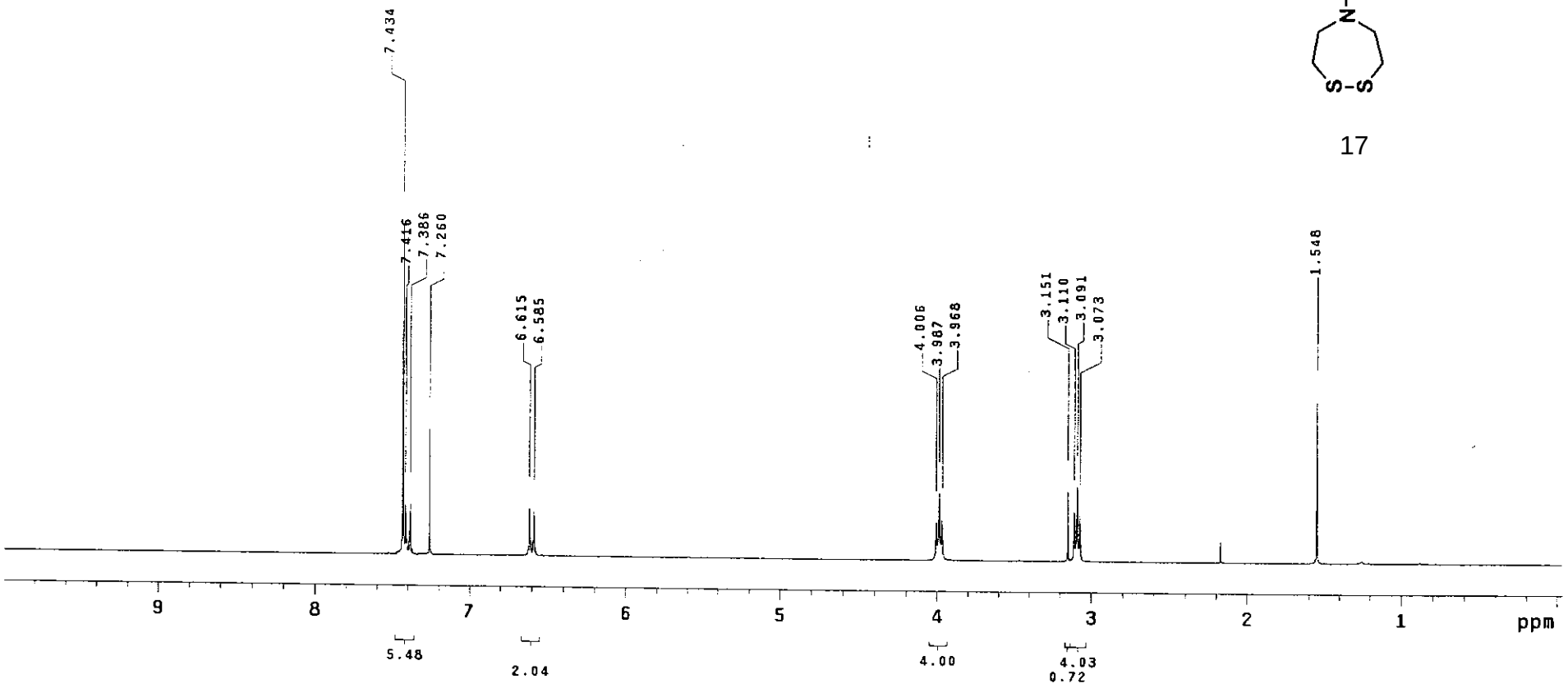


ql1011204a

Pulse Sequence: s2pul



17



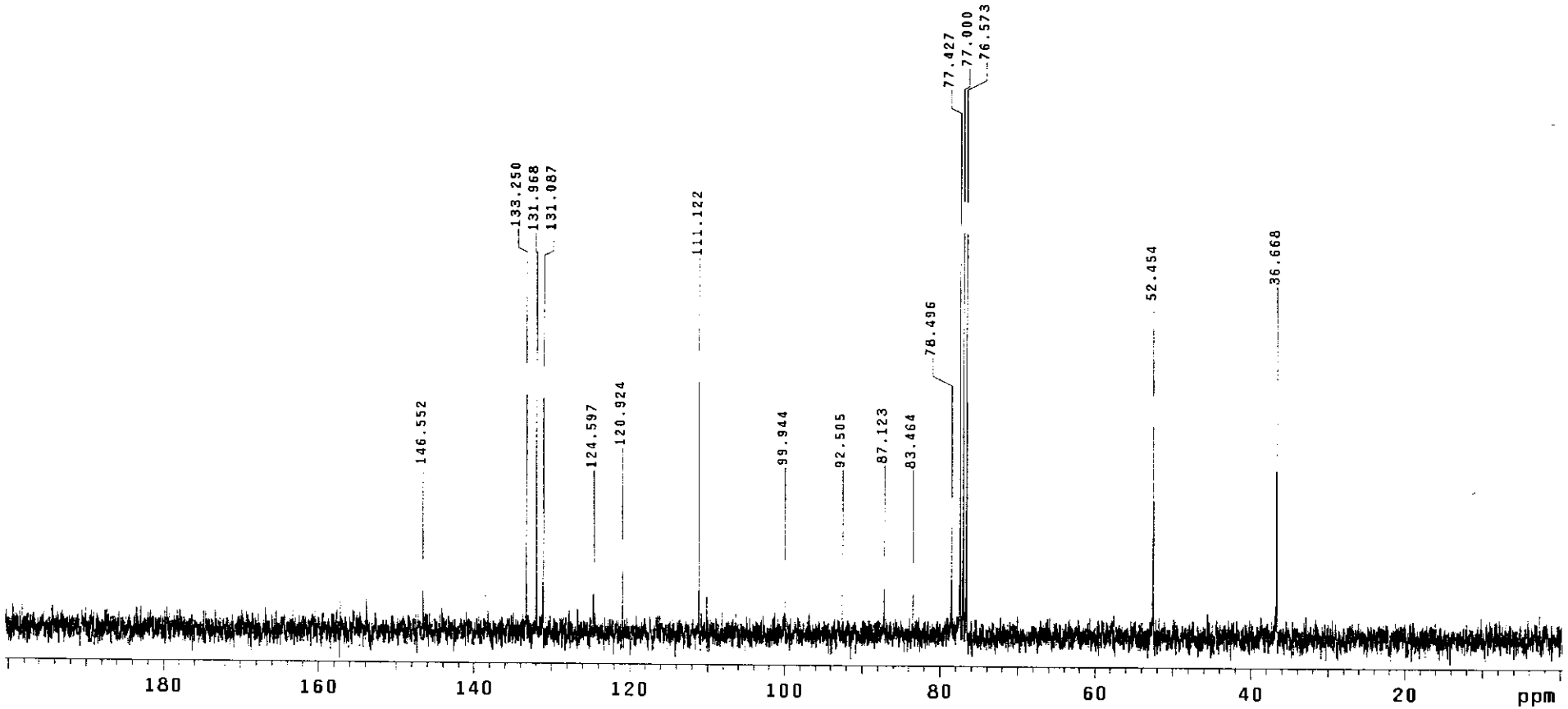
qli011204b

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 42.6 degrees
Acq. time 0.599 sec
Width 16501.7 Hz
300 repetitions
OBSERVE C13, 75.4217001 MHz
DECOUPLE H1, 299.9478514 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 8 min, 2 sec

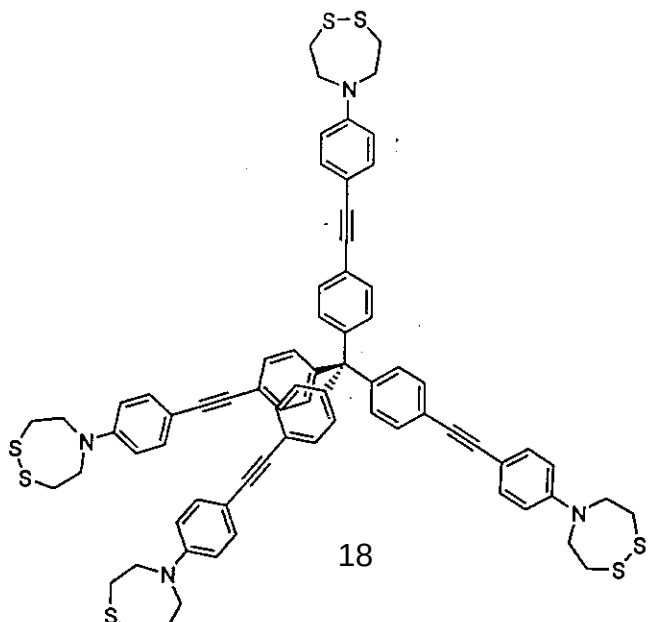
Compound 17



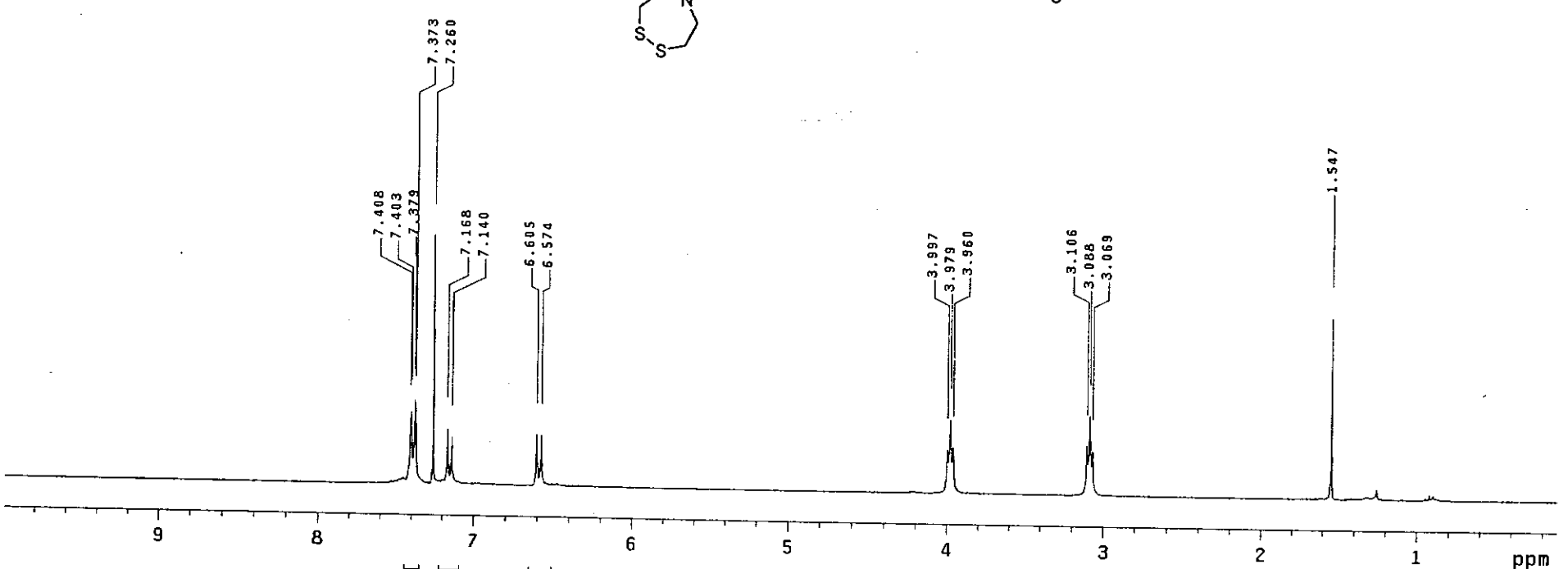
quanli020327b

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 37.9 degrees
Acq. time 2.501 sec
Width 4799.0 Hz
8 repetitions
OBSERVE H1, 299.9468615 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 28 sec



18

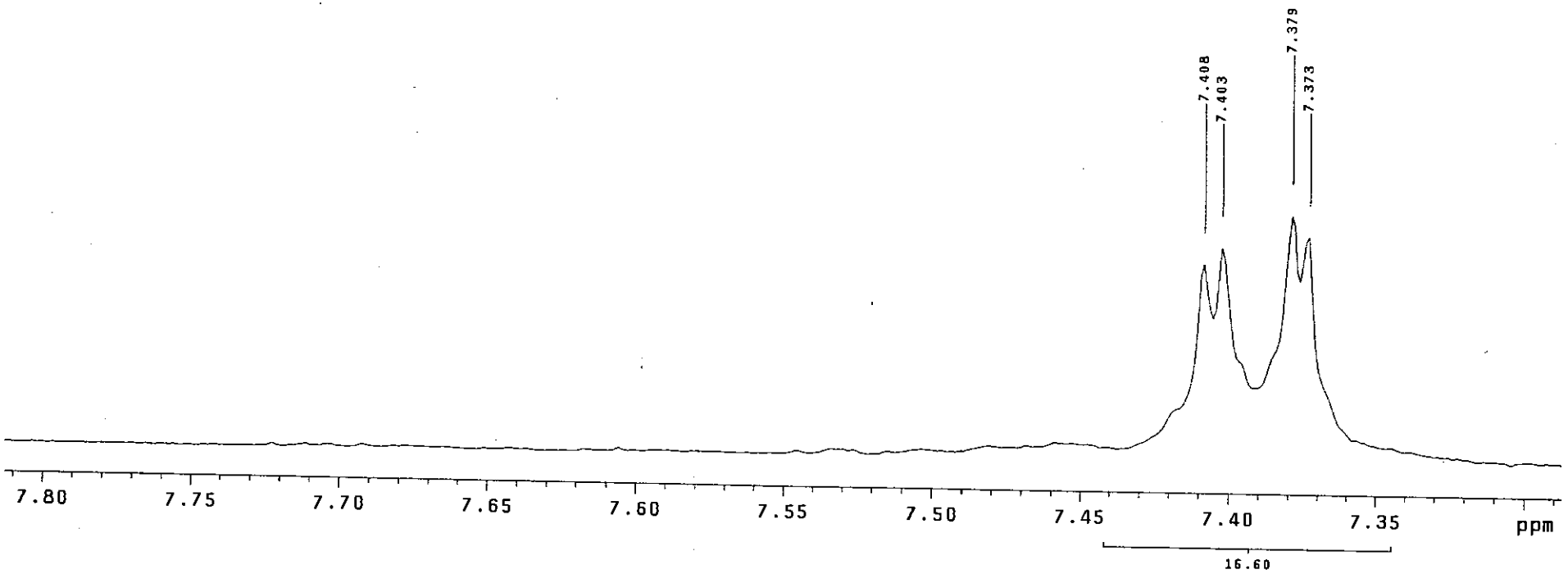


quanli020327b

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 37.9 degrees
Acq. time 2.501 sec
Width 4799.0 Hz
8 repetitions
OBSERVE H1, 299.9468615 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 28 sec

Compound 18

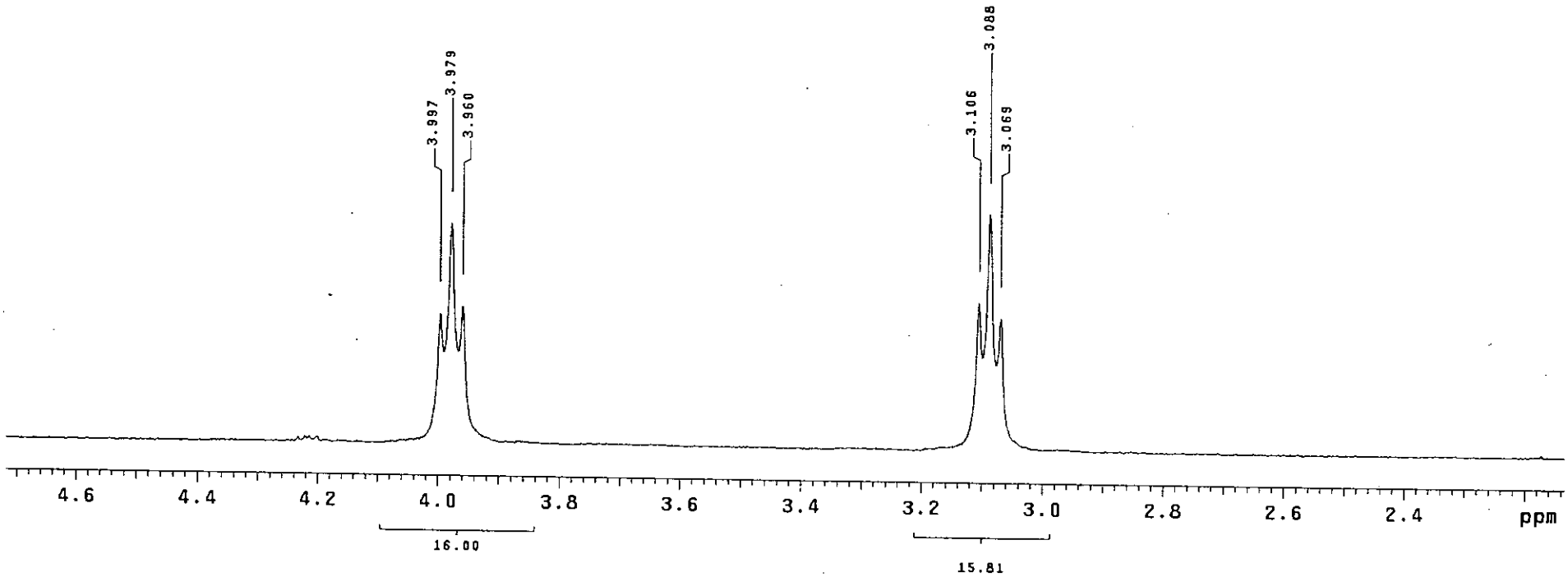


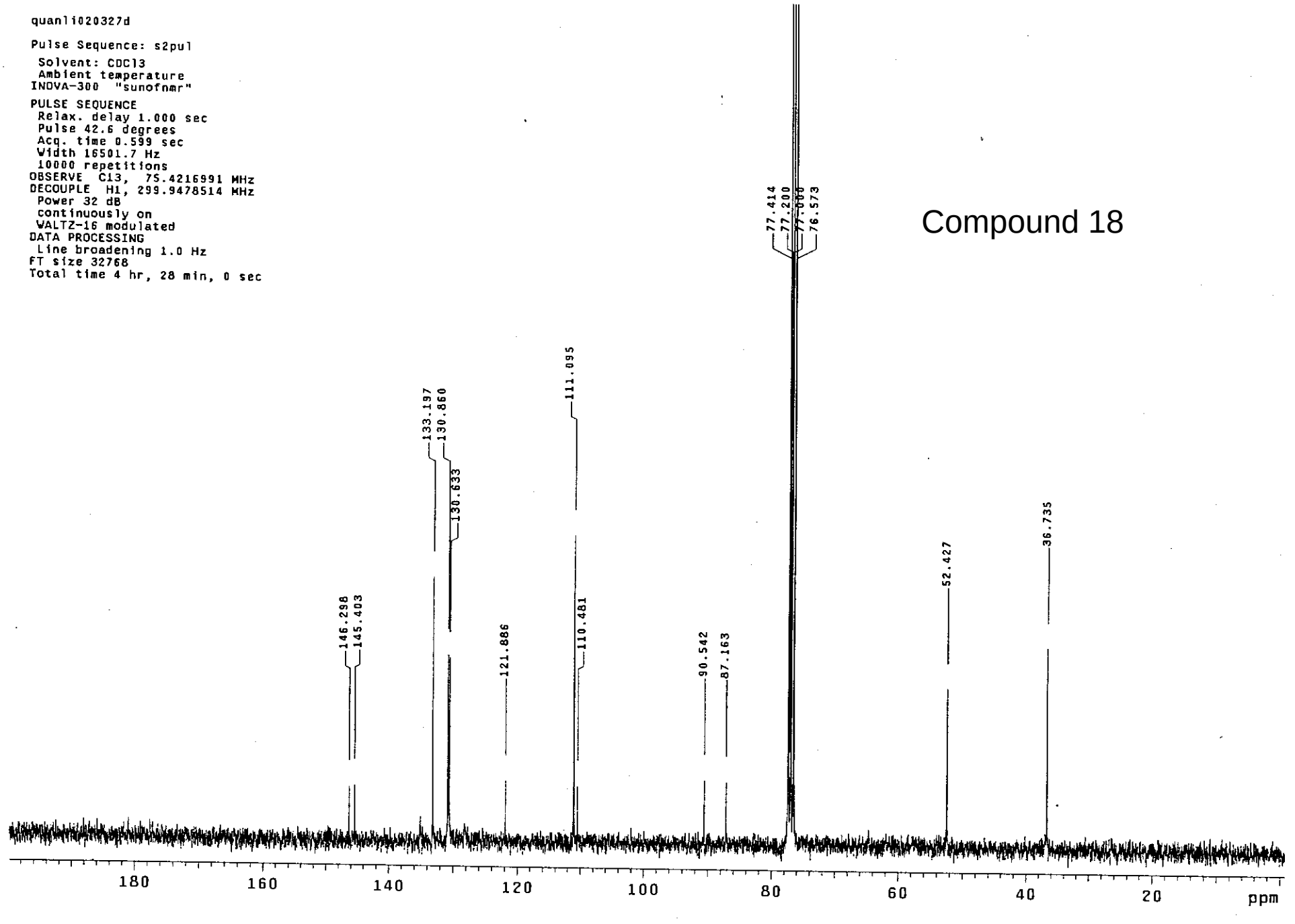
quanli020327b

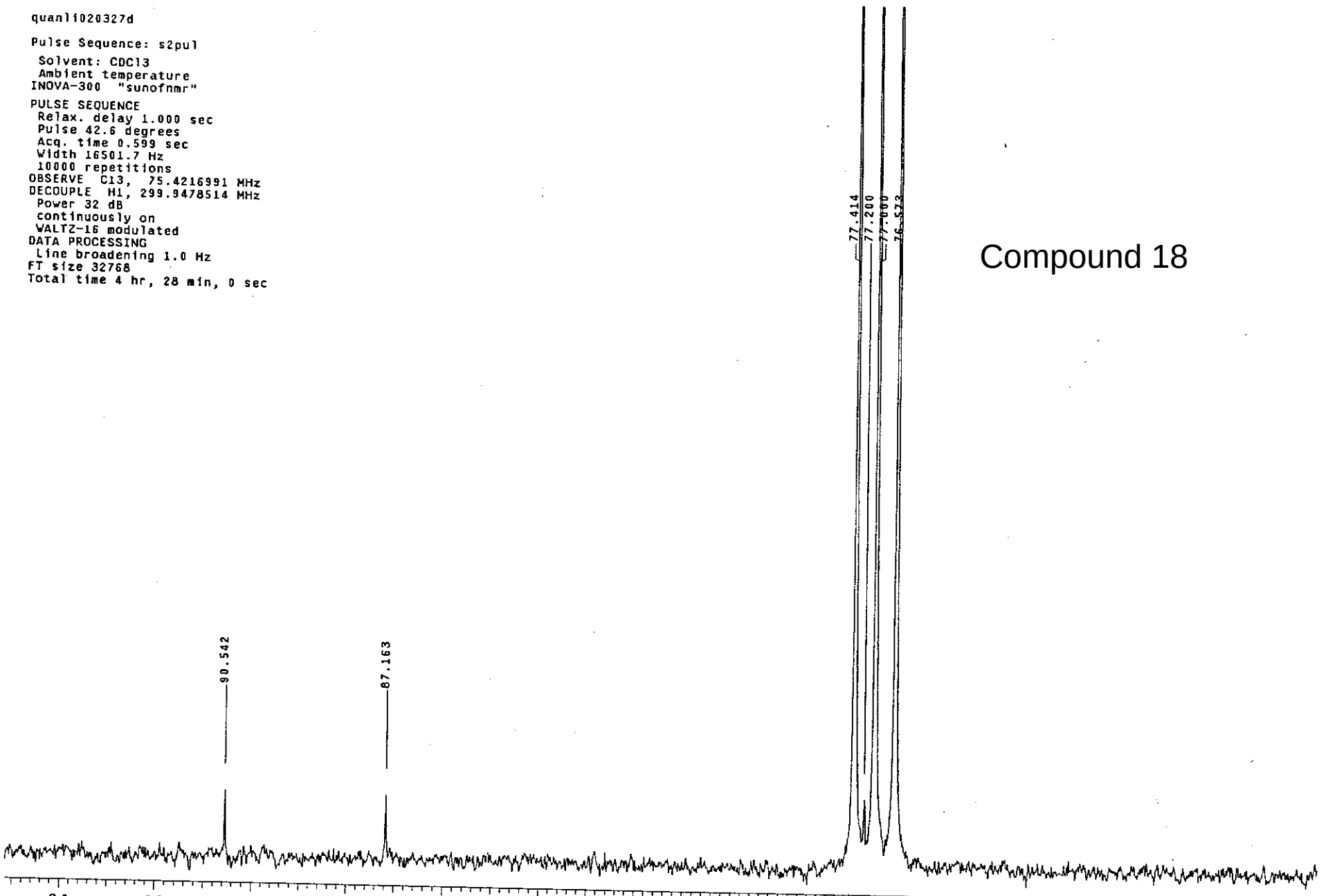
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 37.9 degrees
Acq. time 2.501 sec
Width 4799.0 Hz
8 repetitions
OBSERVE H1, 299.9468615 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 28 sec

Compound 18




quanli020327d
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 42.6 degrees
Acq. time 0.599 sec
Width 16501.7 Hz
10000 repetitions
OBSERVE C13, 75.4216991 MHz
DECOUPLE H1, 299.9478514 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 4 hr, 28 min, 0 sec
Compound 18
146.298
145.403
133.197
130.860
130.633
121.886
111.095
110.481
90.542
87.163
77.414
77.200
77.000
76.573
52.427
36.735
180
160
140
120
100
80
60
40
20
ppm

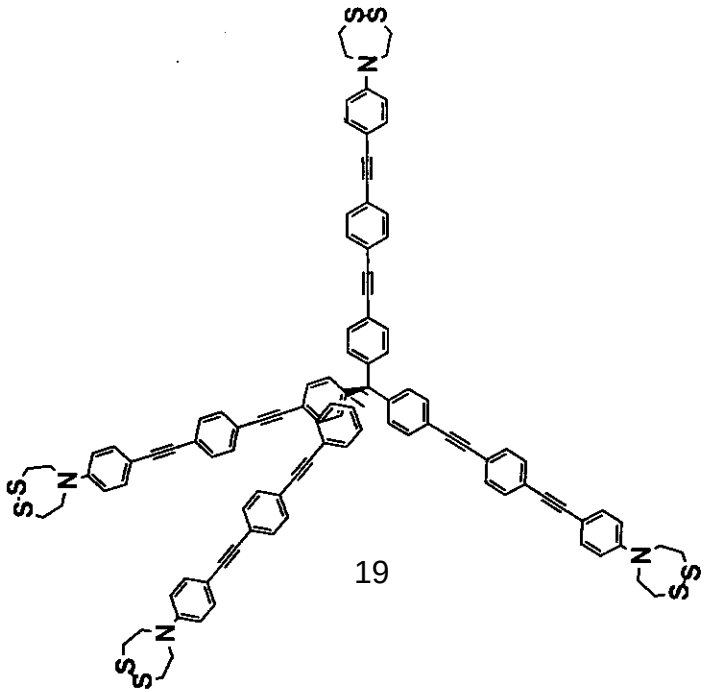

quanli020327d
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 42.6 degrees
Acq. time 0.599 sec
Width 16501.7 Hz
10000 repetitions
OBSERVE C13, 75.4216991 MHz
DECOUPLE H1, 299.9478514 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 4 hr, 28 min, 0 sec
77.414
77.200
77.000
76.573
90.542
87.163
94
92
90
88
86
84
82
80
78
76
74
72
70
ppm

Compound 18

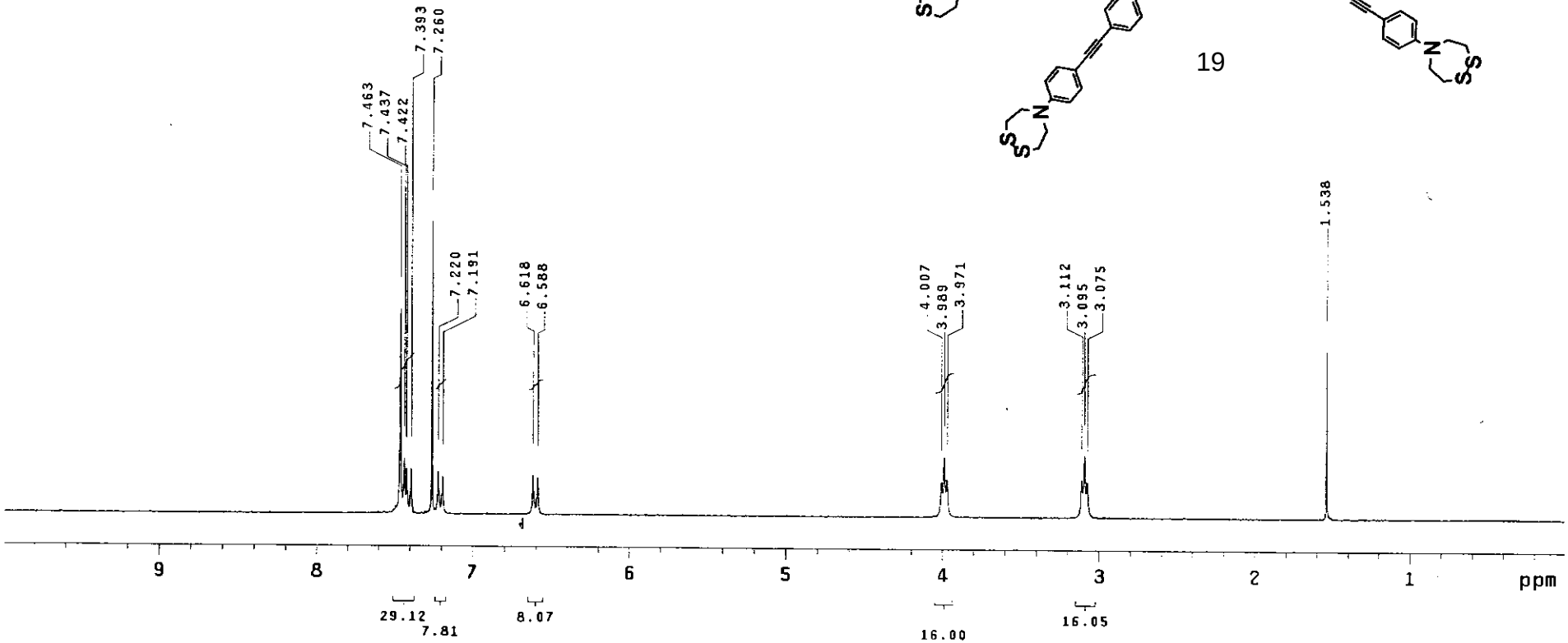
qli011210b

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 37.9 degrees
Acq. time 2.501 sec
Width 4799.0 Hz
8 repetitions
OBSERVE H1, 299.9468618 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 28 sec



19

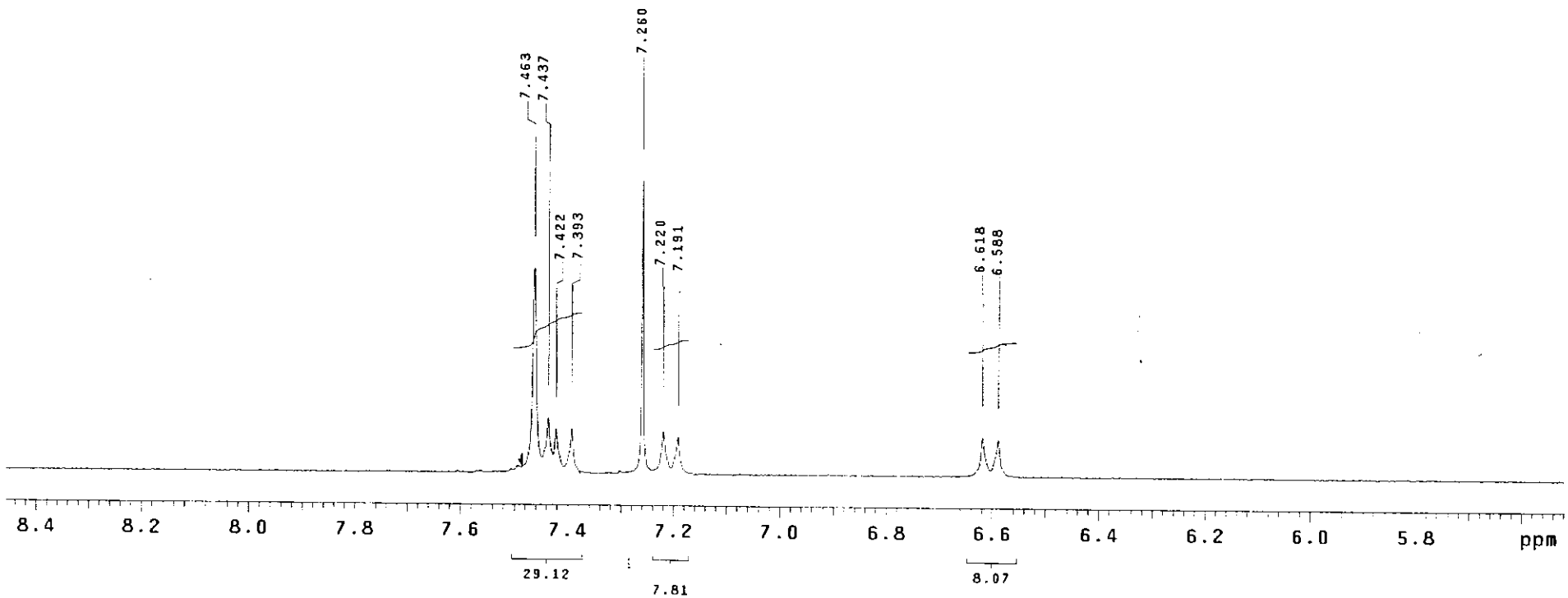


qli011210b

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 37.9 degrees
Acq. time 2.501 sec
Width 4799.0 Hz
8 repetitions
OBSERVE H1, 299.9468618 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 28 sec

Compound 19

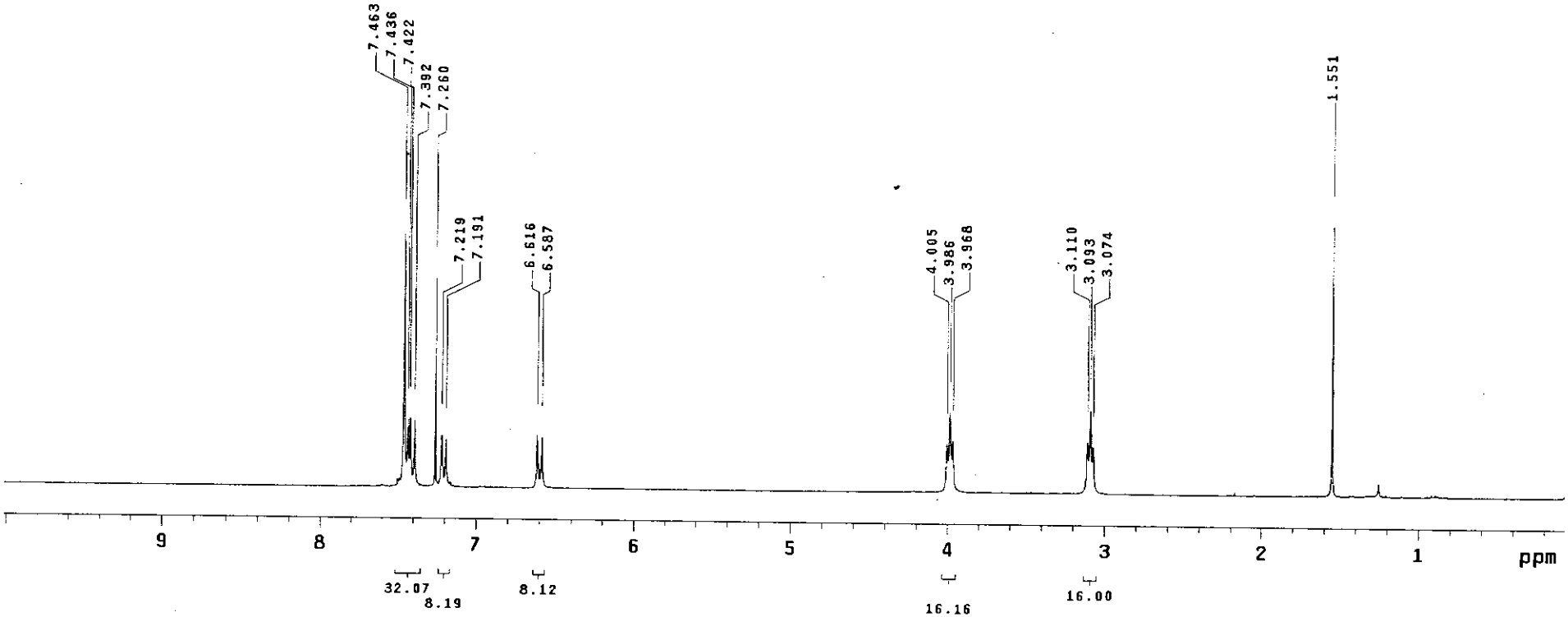


quanlitip19a

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: quanli020603a
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 37.9 degrees
Acq. time 2.501 sec
Width 4799.0 Hz
8 repetitions
OBSERVE H1, 299.9468618 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 28 sec

Compound 19



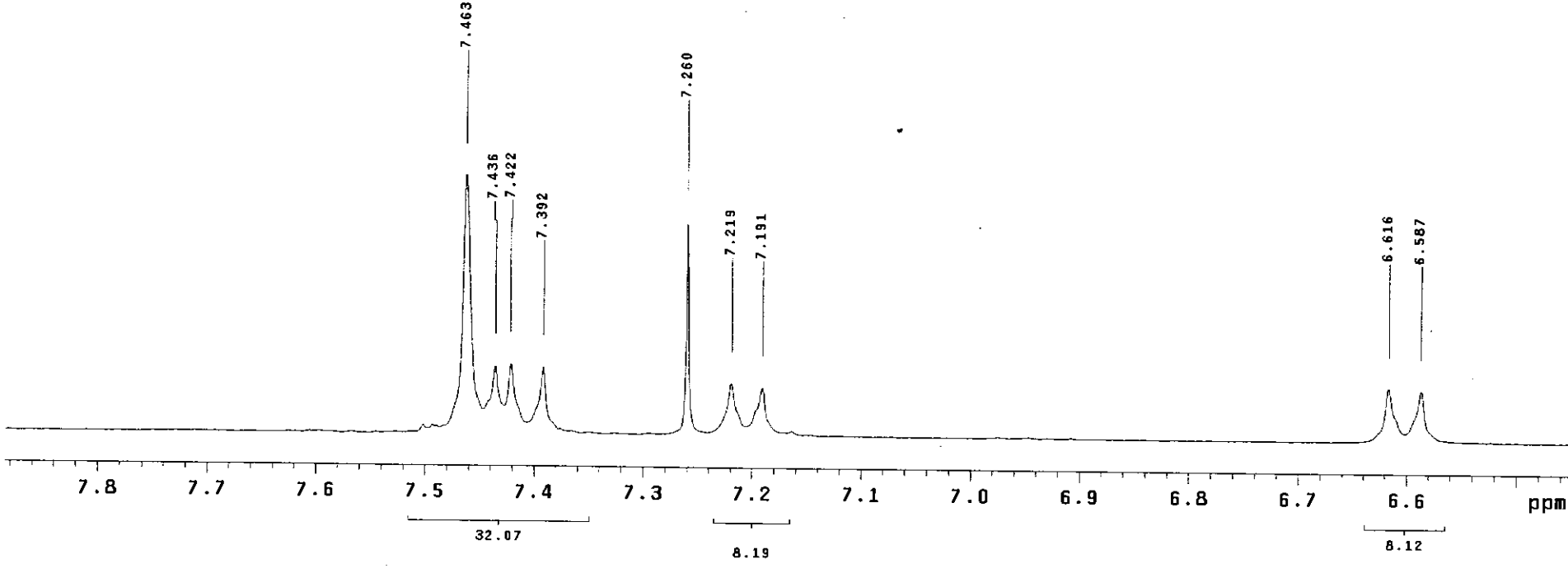
quanlitip19a

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: quanli020603a
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 37.9 degrees
Acq. time 2.501 sec
Width 4799.0 Hz
8 repetitions
OBSERVE H1, 299.9468618 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 28 sec

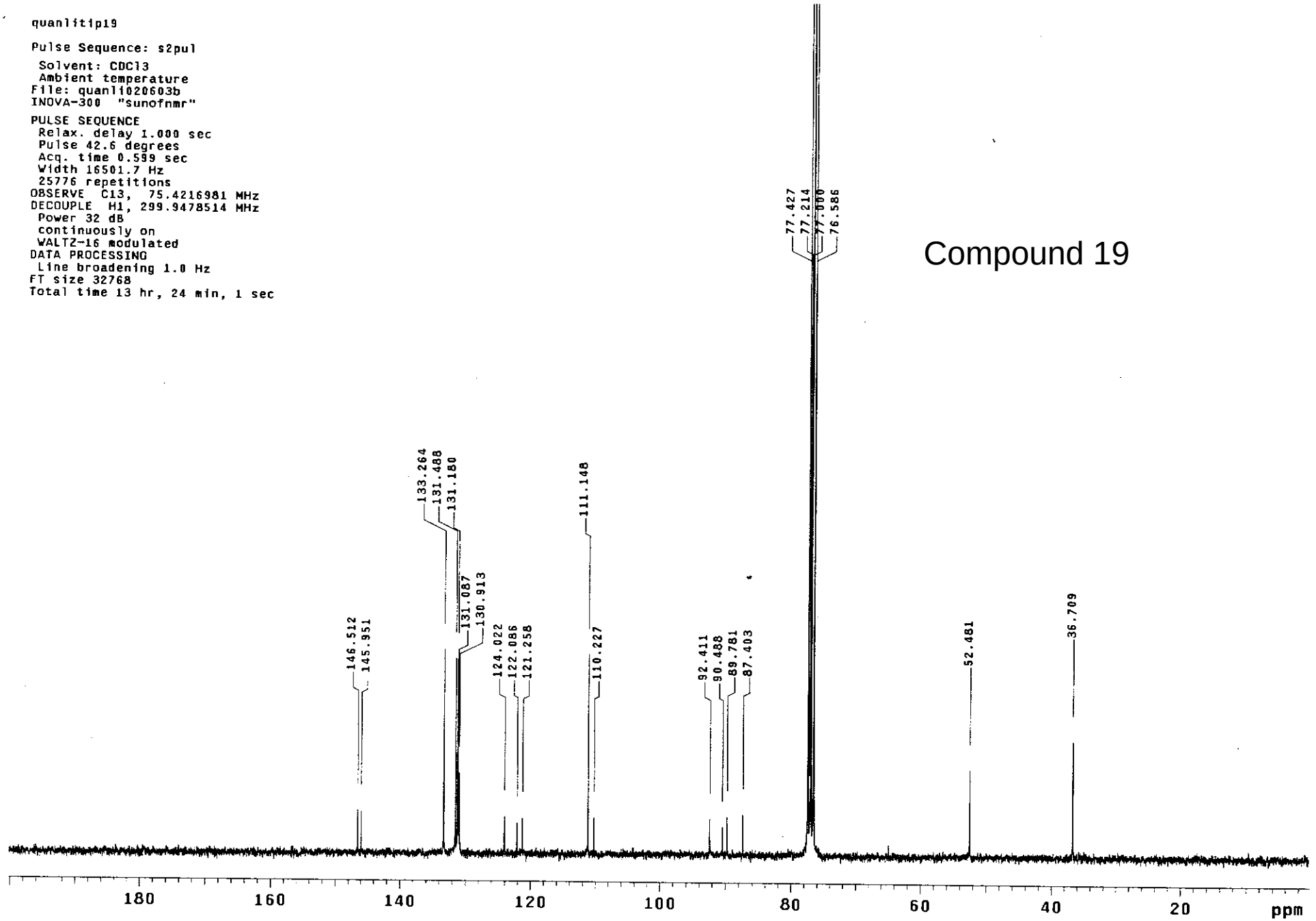
Compound 19



quanlitip19

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: quanli020603b
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 42.6 degrees
Acq. time 0.599 sec
Width 16501.7 Hz
25776 repetitions
OBSERVE C13, 75.4216981 MHz
DECOUPLE H1, 299.9478514 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 13 hr, 24 min, 1 sec



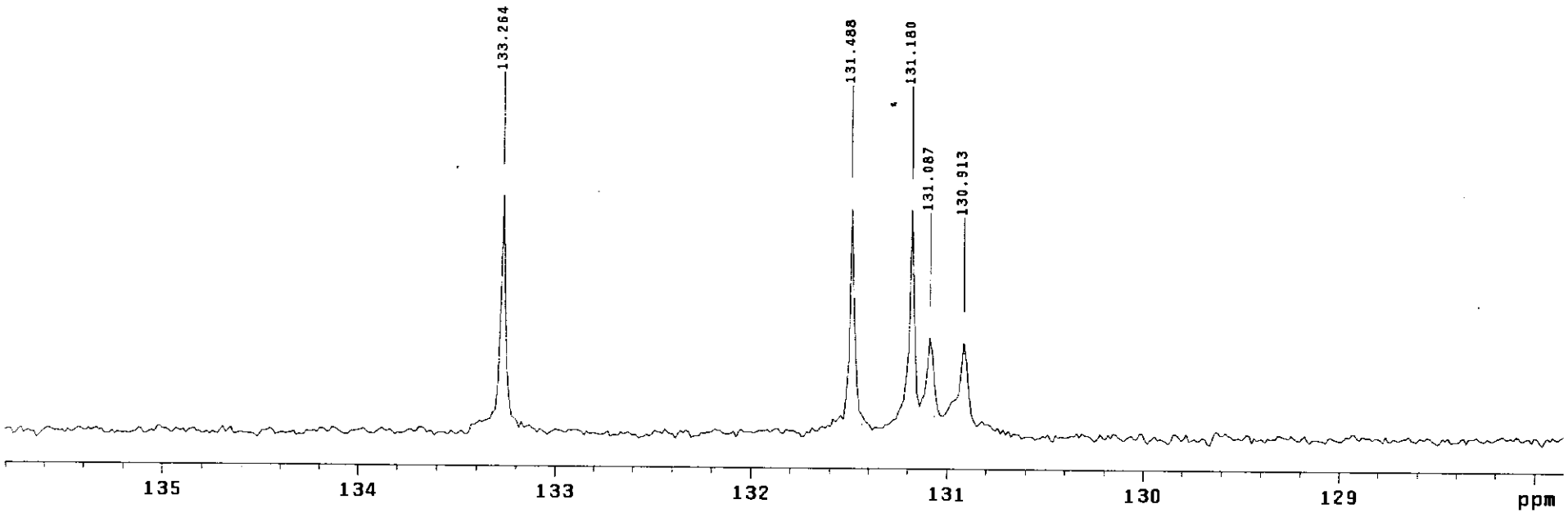
Compound 19

quanlitip19

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: quanli020603b
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 42.6 degrees
Acq. time 0.599 sec
Width 16501.7 Hz
25776 repetitions
OBSERVE C13, 75.4216981 MHz
DECOUPLE H1, 299.9478514 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 13 hr, 24 min, 1 sec

Compound 19



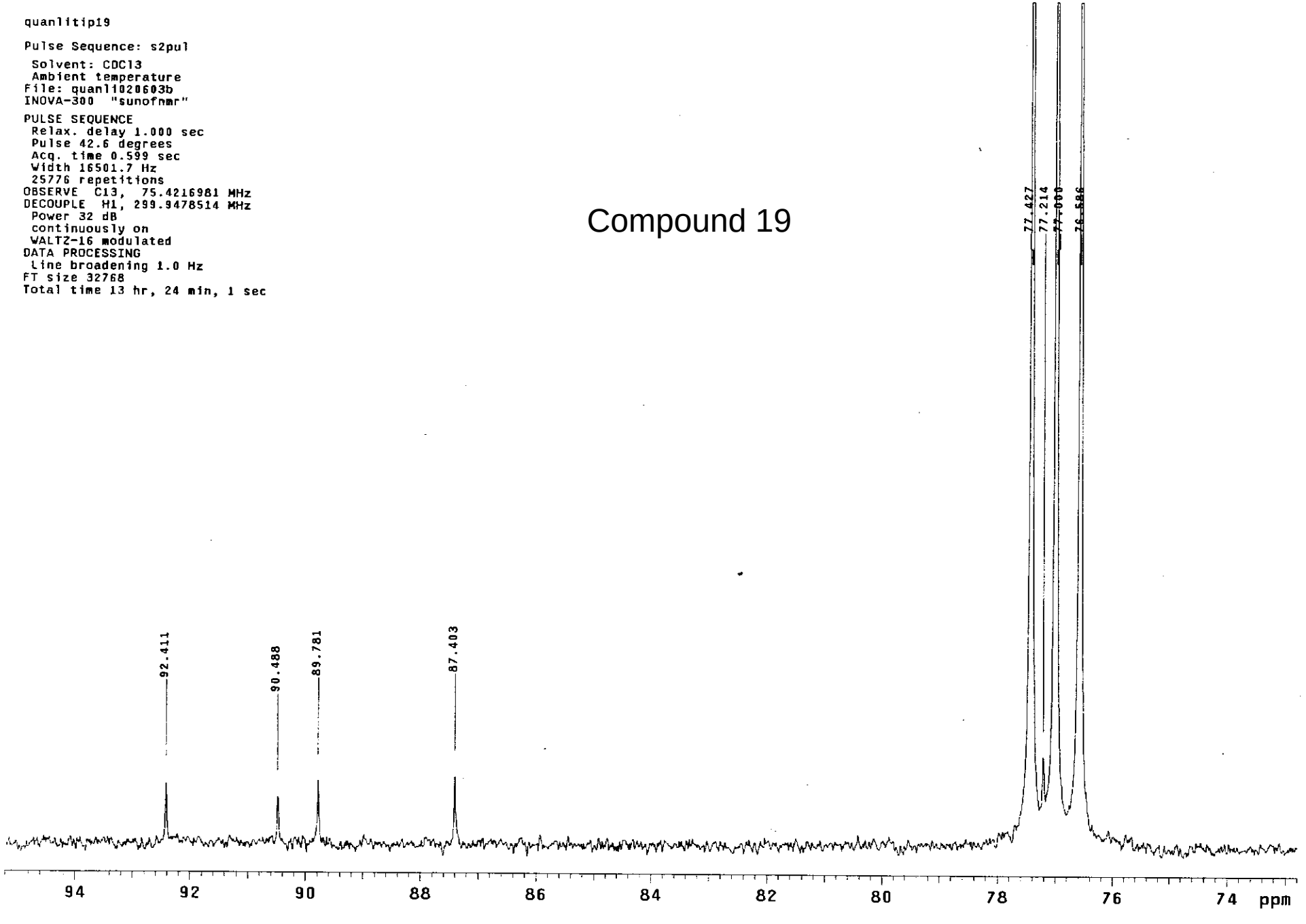
quanlitip19

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: quanl1020603b
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 42.6 degrees
Acq. time 0.599 sec
Width 16501.7 Hz
25776 repetitions
OBSERVE C13, 75.4216981 MHz
DECOUPLE H1, 299.9478514 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 13 hr, 24 min, 1 sec

Compound 19

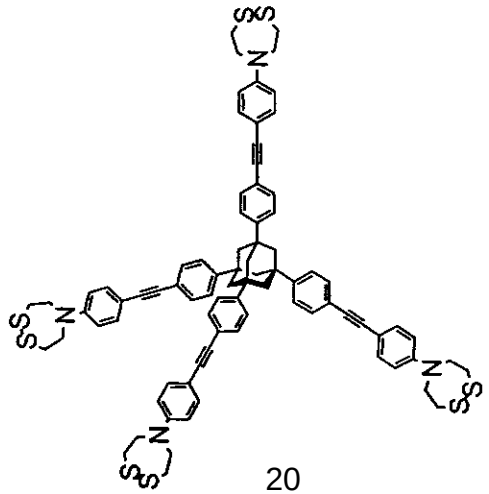


quanli020301spot3a

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: quanli020301spot3a
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 37.9 degrees
Acq. time 2.501 sec
Width 4799.0 Hz
8 repetitions
OBSERVE H1, 299.9468615 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 28 sec

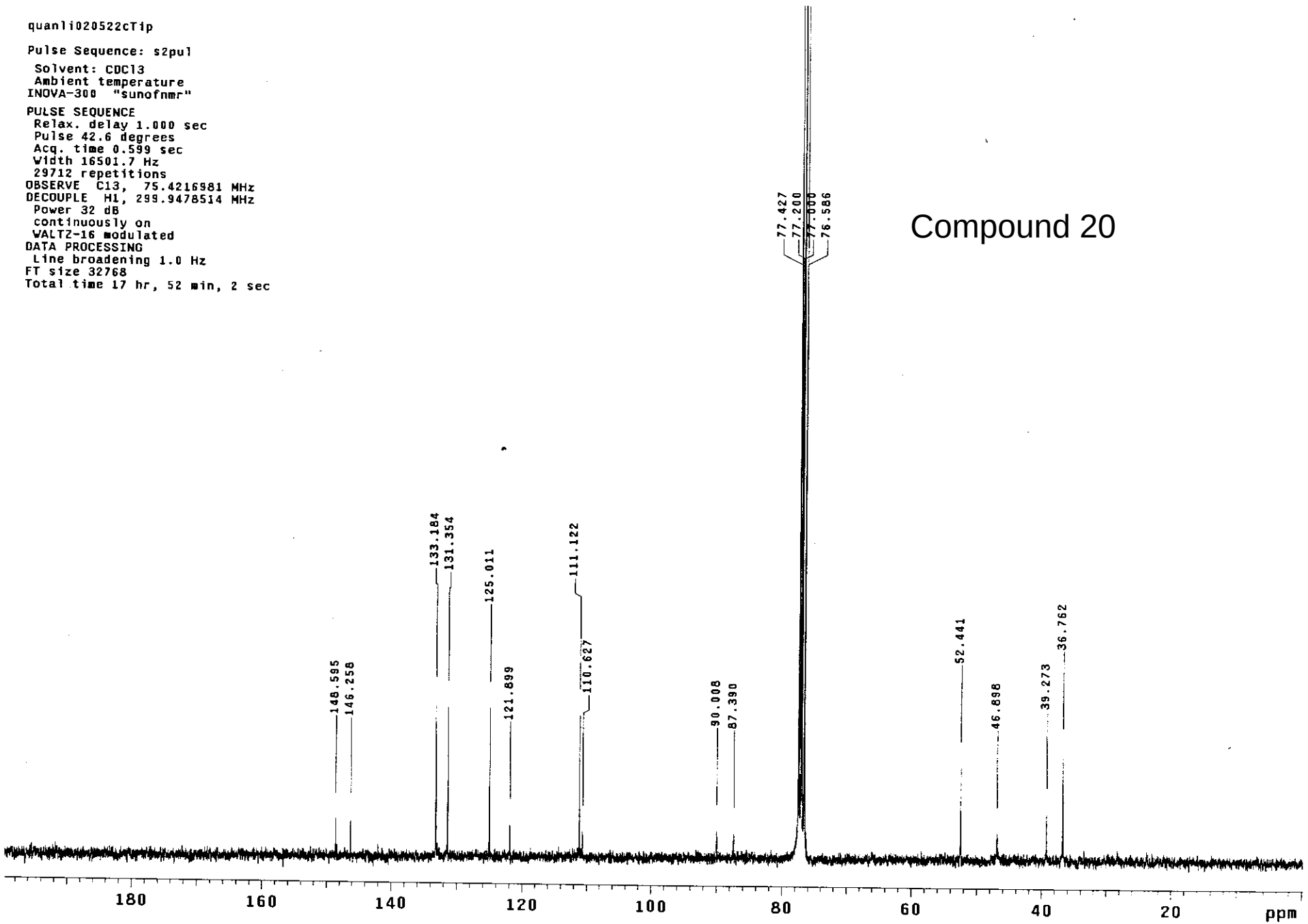


20

quanli020522cTip

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 42.6 degrees
Acq. time 0.599 sec
Width 16501.7 Hz
29712 repetitions
OBSERVE C13, 75.4216981 MHz
DECOUPLE H1, 299.9478514 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 17 hr, 52 min, 2 sec



Compound 20

quanli020522cTip

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-300 "sunofnmr"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 42.6 degrees
Acq. time 0.599 sec
Width 16501.7 Hz
29712 repetitions
OBSERVE C13, 75.4216981 MHz
DECOUPLE H1, 299.9478514 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 17 hr, 52 min, 2 sec

Compound 20