Supporting Information

A De Novo Approach to the Synthesis of Glycosylated Methymycin Analogues with Structural and Stereochemical Diversity

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Section A: General Information

Section B: Experimental Procedures

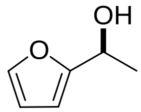
Section C: ^{1}H and ^{13}C NMR Spectra

Section A: General Information:

General methods and materials: ^{1}H and ^{13}C spectra were recorded on Joel 270 and Varian 600 spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) or CD_3OD (δ 4.78 ppm) or acetone-d_6 (δ 2.05 ppm) for ^{1}H and $CDCl_3$ (δ 77.0 ppm) or CD_3OD (δ 49.0 ppm) or acetone-d_6 (δ 29.92 ppm) for ^{13}C. Optical rotations were measured with a Jasco DIP-370 digital polarimeter in the solvent specified. Infrared (IR) spectra were obtained on a prospect MIDAC FT-IR spectrometer. Flash column chromatography was performed on ICN reagent 60 (60-200 mesh) silica gel. Analytical thin-layer chromatography was performed with precoated glass-backed plates (Whatman K6F 60, F254) and visualized by quenching of fluorescence and by charring after treatment with panisaldehyde or phosphomolybdic acid or potassium permanganate stain. R_f values were obtained by elution in the stated solvent ratios (v/v). Ether, THF, methylene chloride and triethylamine were dried by passing through activated alumina (8 x 14 mesh) column with Argon gas pressure. Commercial reagents were used without purification unless otherwise noted. Air and/or moisture-sensitive reactions were carried out under an atmosphere of argon/nitrogen using oven/flamed-dried glassware and standard syringe/septa techniques.

Section B: Experimental Procedures:

(*S*)-1-(2-Furyl)-ethanol 15 (*S*).[1]



To a 25 ml flask was added furan ketone **14** (800 mg, 7.27 mmol), CH_2Cl_2 (3.7 ml), formic acid/triethylamine (1:1, 9.71 ml) and Noyori asymmetric transfer hydrogenation catalyst (*R*)-Ru(η^6-mesitylene)-(*S, S*)-TsDPEN (22.2 mg, 0.5 mol%). The resulting solution was stirred at room temperature for 24 h. The reaction mixture was diluted with water (10 ml) and extracted with EtOAc (3 x 25 ml). The combined organic layers were washed with saturated $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography eluting with 30% EtOAc/hexane to give furan alcohol **15 (S)** (745 mg, 6.76 mmol, 93%): colorless oil; R_f (30% EtOAc/hexane) = 0.41; $[\alpha]^{25}_D = +21$ (c = 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 3360, 2980, 2935, 1668, 1505, 1467, 1370, 1229, 1149, 1007, 877, 734; ^{1}H NMR (600 MHz $CDCl_3$) δ 7.30 (d, J = 1.8, 1H), 6.26 (dd, J = 3.0, 1.8 Hz, 1H), 6.15 (d, J = 3.0, 1H), 4.78 (dq, J =6.6, 6.6 Hz, 1H), 3.11 (s, 1H), 1.46 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 141.6, 109.9, 104.9, 63.3, 21.1.

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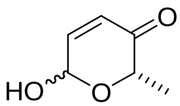
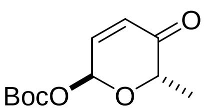
[1] Ohkuma, T.; Koizumi, M.; Yoshida, M.; Noyori R. *Org. Lett.,* **2000**, *2*, 1749-1751.

(2*S*)-6-Hydroxy-2- methyl-2*H*-Pyran-3 (6*H*)-one A (*S*).



Compound furan alcohol **15 (*S*)** (8.30 g, 74.1 mmol), 184.5 mL of THF, and 61.5 mL of H_2O were added to a round bottom flask and cooled to 0 °C. Solid $NaHCO_3$ (12.4 g, 148.2 mmol), $NaOAc•3H_2O$ (10.1 g, 74.1 mmol), and NBS (13.1 g, 74.1 mmol) were added to the solution and the mixture was stirred for 1 h at 0 °C. The reaction was quenched with saturated $NaHCO_3$ (200 mL), extracted (3 x 200 mL) with Et_2O, dried (Na_2SO_4), concentrated under reduced pressure and purified by silica gel chromatography eluting with 25% EtOAc/hexane to give pyranone **A (*S*)** (8.56 g, 67.4 mmol, 91%): R_f (60% EtOAc/hexane) = 0.29; $[\alpha]^{25}_{D}$ = + 44 (c = 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 3381, 2988, 2942, 1692, 1447, 1373, 1232, 1021, 937; ^1H NMR (600 MHz, $CDCl_3$) major isomer δ 6.82 (dd, J = 10.2, 3.0 Hz, 1H), 5.96 (d, J = 10.2, 1H), 5.48 (d, J = 3.0 Hz, 1H), 3.99 (q, J = 7.2 Hz, 1H), 1.23 (d, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) major isomer δ 197.6, 145.3, 126.6, 87.2, 74.8, 15.1.

(2*S*, 6*S*)-*tert*-butyl -5,6-dihydro-6-methyl-5-oxo-2*H*-pyran-2-yl carbonate (13a).

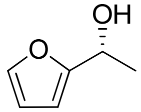


To a solution of 7.4 g pyranone alcohol **A** (57.8 mmol) in 80 mL CH_2Cl_2 was added 528 mg DMAP (4.33 mmol) at -78 °C. A pre-cooled solution of 25.2 g $(Boc)_2O$ (115.6 mmol) in 30 mL CH_2Cl_2 was dropwised into the reaction mixture via a cannula. The reaction mixture was stirred at -78 °C for 12 hours. The reaction was quenched by 100 mL saturated aqueous $NaHCO_3$ and then extracted with Et_2O (300 mL × 3). The organic layers were pooled, then washed by 70 mL saturated aqueous NaCl, dried over Na_2SO_4 and concentrated under reduced pressure to give a residue. Flash chromatography on silica gel eluting with hexane-Et_2O (100:7) gave Boc protected α-pyranone **13a** (7.8 g, 60%). Elution with hexane-Et_2O (10:1) gave β-isomer **13b** (2.5g, 19%).

α-pyranone **13a**: R_f = 0.67 (33% EtOAc/hexane); $[\alpha]_D^{25}$ = +98 (*c* 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 2984, 2942, 1752, 1703, 1371, 1273, 1254, 1153, 938, 838; ^1H NMR (600 MHz, $CDCl_3$) δ 6.78 (dd, J = 10.2, 3.6 Hz, 1H), 6.22 (d, J = 3.6 Hz, 1H), 6.09 (d, J = 10.2 Hz, 1H), 4.53 (q, J = 6.6 Hz, 1H), 1.40 (s, 9H), 1.28 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150.8 MHz, CDCl3) δ 195.5, 151.7, 140.9, 128.2, 89.1, 83.3, 72.0, 27.5, 15.1;

β -pyranone **13b**: R_f = 0.60 (33% EtOAc/hexane); $[\alpha]_D^{25}$ = -35 (*c* 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 2984, 1752, 1702, 1371, 1276, 1254, 1161, 1068, 939, 854; ^1H NMR (600 MHz, $CDCl_3$) δ 6.88 (dd, J = 10.2, 2.4 Hz, 1H), 6.36 (dd, J = 2.4, 1.2 Hz, 1H), 6.20 (dd, J = 10.2, 1.2 Hz, 1H), 4.37 (q, J = 7.2 Hz, 1H), 1.51 (s, 9H), 1.50 (d, J = 7.2 Hz, 3H); ^{13}C NMR (150.8 MHz, CDCl3) δ 196.1, 152.0, 143.0, 128.5, 90.1, 83.6, 75.9, 27.9 (3C), 18.8.

(R)-1-(furan-2-yl)ethanol (15 (*R*))



To a solution of 15 g acylfuran **14** (136.4 mmol) in 20 mL CH_2Cl_2 was added a prepared solution of formic acid/triethylamine (40 mL, 2:1(mol/mol)) and Noyori asymmetric transfer hydrogenation catalyst (*R*)-Ru(η^6-mesitylene)-(*R*, R)-TsDPEN (0.2 g, 0.25 mol%). The resulting solution was stirred at room temperature for 24 h. Then it was diluted with water (90 mL) and extracted with Et_2O (200 mL x 3). The pooled organic layer was washed with 50 mL saturated $NaHCO_3$, 50 mL saturated brine, dried over Na_2SO_4 and then concentrated under reduced pressure to give a residue. Flush chromatograph on silica gel eluting with hexane-Et_2O (7:3) gave furan alcohol **15 (*R*)** (15.0 g, 98%):[2] Colorless oil; R_f = 0.38 (7:3 (v/v) Hexane/EtOAc); $[\alpha]_D^{25}$ = +20.8° (c = 1.20, $CHCl_2$); ^1H NMR (270 MHz CDCl$_3$) δ 7.36 (d, *J* = 1.7, 1H), 6.31 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.22 (d, *J* = 3.2, 1H), 4.87 (dq, *J* = 6.4, 6.4 Hz, 1H), 2.19 (bs, 1H), 1.53 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 157.7, 141.6, 109.9, 104.9, 63.3, 21.1.

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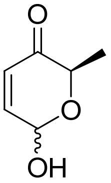
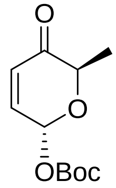
[2] These known compounds were characterized based on the comparison with authentic sample that our group prepared before: (a) Guo, H.; O'Doherty, G. A. *Org. Lett.* **2005**, *7*, 3921-3924. (b) Li, M.; Scott, J. G.; O'Doherty, G. A. *Tetrahedron Lett.* **2004**, *45*, 1005-1009.

(2R,6S)-6-hydroxy-2-methyl-2H-pyran-3(6H)-one (B)



To a solution of 13.0 g furan alcohol **15 (*R*)** (116 mmol) in 386 mL THF-H_2O (3:1) was added 19.5 g $NaHCO_3$ (232 mmol), 15.8 g NaOAc•$3H_2O$ (116 mmol), and 20.7 g NBS (116 mmol) at 0 ^oC. The reaction mixture was kept stirring at this temperature for 1 hour, then at 0 ^oC 200 mL saturated $NaHCO_3$ was added to quench the reaction. The reaction mixture was directly extracted with Et_2O (300 mL × 3) and the organic layer was pooled, washed by 100 mL saturated brine, dried over Na_2SO_4 and then concentrated reduced pressure to give a residue, which was rapidly subjected to flush chromatography on silica gel. Elution with hexane-EtOAc (1:1) afforded pyranone alcohol **B** (13.5 g, 91%, α:β=2.8:1): White solid; R_f = 0.17 (7:3 (v/v) hexane/EtOAc); ^1H NMR (270 MHz, $CDCl_3$) major isomer (α): δ 6.89 (dd, *J* = 10.4, 3.5 Hz, 1H), 6.11 (d, *J* = 10.4, 1H), 5.64 (dd, *J* = 4.2, 3.5 Hz, 1H), 4.71 (q, *J* = 6.9 Hz, 1H), 3.04 (d, *J* = 4.7 Hz, 1H), 1.39 (d, *J* = 6.7 Hz, 3H); minor isomer (β): δ 6.94 (dd, *J* = 10.4, 1.5 Hz, 1H), 6.16 (dd, *J* = 10.2, 1.5, 1H), 5.67 (dd, *J* = 5.7, 1.2 Hz, 1H), 4.23 (dq, *J* = 6.7, 1.2 Hz, 1H), 3.28 (d, *J* = 7.4 Hz, 1H), 1.46 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) major isomer (α): δ 197.4, 144.9, 126.9, 87.4, 70.3, 15.2. minor isomer (β): δ 196.8, 148.5, 128.2, 87.2, 75.1, 16.1.

(2R,6R)-*t*-butyl-5,6-dihydro-6-methyl-5-oxo -2H-pyran-2-yl carbonate (13c)

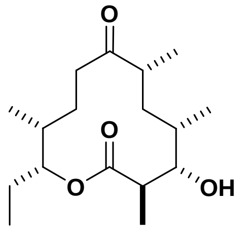


To a solution of 29.7 g pyranone alcohol **B** (190 mmol) in 130 mL CH_2Cl_2 was added 1.74 g DMAP (14.2 mmol) at -78 ^oC. A pre-cooled solution of 83.0 g $(Boc)_2O$ (380 mmol) in 50 mL CH_2Cl_2 was dropwised into the reaction mixture via a cannula. The reaction mixture was stirred at -78 ^oC for 12 hours. The reaction was quenched by 200 mL saturated $NaHCO_3$ and then extracted with Et_2O (300 mL × 3). The organic layers were pooled, then washed by 70 mL saturated NaCl, dried over Na_2SO_4 and concentrated under reduced pressure to give a residue. Flush chromatograph on silica gel eluting with 6% and 8% hexane/Et_2O gave two diastereomers (35.7g, 73%) of Boc protected *α*-pyranone **13c** and *β*-pyranone **13D** (**α:β=**3:1).

Boc protected *α*-pyranone **13c:** R_f = 0.57 (7:3 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ = -97° (c = 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 2986, 1752, 1703, 1633, 1278, 1258, 1159, 1090, 1058, 1029, 944; ^1H NMR (600 MHz, $CDCl_3$) δ 6.79 (dd, J = 10.2, 4.2 Hz, 1H), 6.24 (d, J = 4.2 Hz, 1H), 6.10 (d, J = 10.2 Hz, 1H), 4.55 (q, J = 6.6 Hz, 1H), 1.40 (s, 9H), 1.30 (d, J = 6.7 Hz, 3H); ^{13}C NMR (150.8 MHz, CDCl3) δ 195.4, 151.7, 140.9, 128.1, 89.1, 83.2, 71.9, 27.4, 15.0; HRMS (CI) : calcd for $[C_{11}H_{16}O_5Na]^+$: 251.0890, Found 251.0884.

Boc protected *β*-pyranone **13d:** R_f = 0.52 (7:3 (v/v) hexane/EtOAc); mp: 43-43.5 °C; $[\alpha]_D^{25}$ = +42.3 (c = 1.3, $CHCl_3$); IR (thin film, cm^{-1}) 2986, 1752, 1703, 1633, 1278, 1258, 1159, 1090, 1058, 1029, 944; ^1H NMR (600 MHz, $CDCl_3$) δ 6.82 (dd, J = 10.2, 2.4 Hz, 1H), 6.28 (dd, J = 4.2, 1.2 Hz, 1H), 6.11 (dd, J = 10.2, 1.2 Hz, 1H), 4.27 (q, J = 6.6 Hz, 1H), 1.42 (s, 9H), 1.39 (d, J = 6.9 Hz, 3H); ^{13}C NMR (150.8 MHz, CDCl3) δ 195.6, 151.6, 142.7, 128.0, 89.7, 83.3, 75.5, 27.4, 18.3; HRMS (CI): calcd for $[C_{11}H_{16}O_5 + Na]^+$: 251.0890, Found 251.0883.

(16):



The enone compound **III**[3] (100 mg, 0.34 mmol) and *o*-$NO_2C_6H_4SO_2NHNH_2$ (414 mg, 2.04 mmol) were dissolved in 3.4 mL of CH_2Cl_2 in a round bottom flask and cooled 0 °C under nitrogen atmosphere then triethylamine (393 μL, 2.72 mmol) was added and the reaction mixture was stirred at 0 °C for 12 hours and on completion, as monitored by TLC. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. The crude product was purified using silica gel flash

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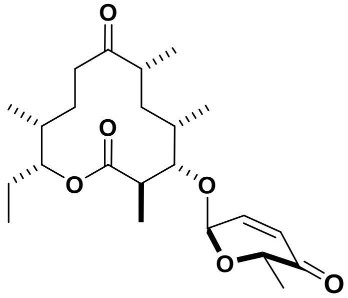
[3] The macrolactone III was purified as previously reported from the fermentation broth of S. venezuelae KdesI-80 mutant, whose desosamine biosynthetic genes had been partially disrupted (Borisova, S. A.; Zhao, L.; Sherman, D. H.; Liu, H.-w. Org. Lett. 1999, 1, 133–136).

chromatography eluting with EtOAc/hexanes (15:85) to give deoxy ketone **16** (96 mg, 0.32 mmol, 95 %) as viscous oil. *R_f* (33% EtOAc/Hexane) = 0.47; $[\alpha]^{25}_{D}$ = -17.48 (*c* = 1.7, $CHCl_3$); IR (thin film, cm^{-1}) 3504, 2971, 2940, 2882, 1725, 1701, 1462, 1373, 1171, 1147, 1093, 992, 898, 731; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.69 (ddd, *J* = 7.8, 5.4, 2.4 Hz, 1H), 3.49 (ddd, *J* = 10.2, 5.4, 1.2 Hz, 1H), 3.10 (ddd, *J* = 18.6, 12.6, 2.4 Hz, 1H), 2.69 (dq, *J* = 12.6, 6.6 Hz, 1H), 2.54 (dqd, *J* = 13.2, 6.6, 4.2 Hz, 1H), 2.12 (ddd, *J* = 18.6, 5.4, 2.4 Hz, 1H), 1.90-1.79 (m, 3H), 1.70 (d, *J* = 5.4 Hz, 1H), 1.54-1.49 (m, 2H), 1.42 (dddd, *J* = 13.8, 11.4, 5.4, 2.4 Hz, 1H), 1.36 (ddd, *J* = 13.2, 12.6, 3.6 Hz, 1H), 1.26 (d, *J* = 6.6 Hz, 3H), 1.20-1.15 (m, 1H), 1.16 (d, *J* = 7.2 Hz, 3H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.5, 174.8, 81.2, 79.2, 46.1, 44.0, 34.2, 34.1, 33.7, 32.4, 24.5, 20.8, 19.6, 18.2, 17.2, 15.6, 11.0; CIHRMS calcd for $[C_{17}H_{30}O_4 + Na]^+$: 321.2041, Found 321.2037.

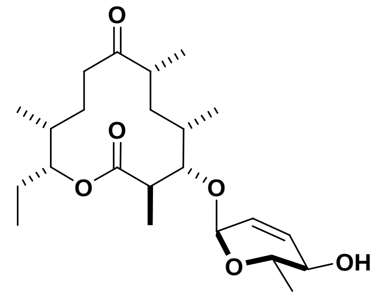
(12):



A CH_2Cl_2 (0.6 mL) solution of Boc-enone **13a** (93 mg, 0.40 mmol) and 10-deoxymethynolide alcohol **16** (60 mg, 0.20 mmol) was cooled to 0 °C. A CH_2Cl_2 (0.2

mL) solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (21 mg, 2.5 mol%) and PPh_3 (22 mg, 10 mol%) was added to the reaction mixture at 0 °C. The reaction mixture was stirred at 0 °C for 5 hours. The reaction mixture was quenched with 5 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 20% EtOAc/hexanes to give enone **12** (75 mg, 0.18 mmol, 90%) as viscous oil. R_f (50% EtOAc/hexanes) = 0.50; $[\alpha]_D^{25}$ = -65 (*c* = 0.3, MeOH); IR (thin film, cm^{-1}) 2965, 2930, 1724, 1701, 1459, 1171, 1019, 974; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.85 (dd, *J* = 10.8, 3.0 Hz, 1H), 6.07 (d, *J* = 10.2 Hz, 1H), 5.24 (d, *J* = 3.6 Hz, 1H), 4.70 (ddd, *J* = 7.8, 5.4, 2.4 Hz, 1H), 4.60 (q, *J* = 6.6 Hz, 1H), 3.65 (dd, *J* = 10.2, 1.2 Hz, 1H), 3.09 (ddd, *J* = 19.6, 11.4, 2.4 Hz, 1H), 2.87 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.56 (dqd, *J* = 13.8, 6.6, 4.2 H), 2.13 (ddd, *J* = 18.6, 5.4, 3.0 Hz, 1H), 1.91-1.82 (m, *3*H), 1.55-1.50 (m, 2H), 1.48-1.43 (m, 1H), 1.36 (d, *J* = 6.6 Hz, 3H), 1.38-1.32 (m, 1H), 1.24-1.16 (m, 1H), 1.24 (d, *J* = 7.2 Hz, 3H), 1.14 (d, *J* = 7.2 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.1, 196.8, 174.1, 142.5, 126.9, 95.8, 88.5, 81.1, 70.6, 45.8, 44.1, 34.7, 34.3, 33.8, 32.3, 24.2, 20.6, 17.9, 17.1, 15.3, 14.9, 10.8; CIHRMS calcd for $[C_{23}H_{36}O_6 + Na]^+$: 431.2409, Found 431.2405.

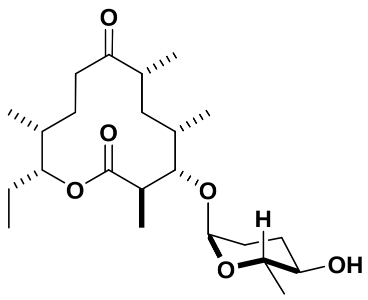
(17):



The enone compound **12** (60 mg, 0.15 mmol) was dissolved in 0.2 mL of CH_2Cl_2 and 0.2 mL MeOH in round bottom flask and cooled -78 °C then NaBH$_4$ (6.1 mg, 0.15 mmol) was added and the reaction mixture was stirred at -78 °C for 3 hours and on completion, monitored by TLC, reaction mixture was diluted with ether and was quenched with 2 mL of satd. aq. NaHCO$_3$, extracted (3 x 5 mL) with Et$_2$O, dried (Na$_2$SO$_4$), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 25% EtOAc/hexanes to give allylic alcohol **17** (56 mg, 0.14 mmol, 92%) as viscous oil. R_f (50% EtOAc/hexanes) = 0.35; $[\alpha]_D^{25}$ = - 14 (*c* = 0.25, MeOH); IR (thin film, cm^{-1}) 3444, 2968, 2934, 1726, 1704, 1460, 1171, 1039, 899; ^{1}H NMR (600 MHz, CDCl$_3$) δ 5.94 (d, *J* = 10.2 Hz, 1H), 5.78 (dt, *J* = 10.2, 2.4 Hz, 1H), 4.98 (br s, 1H), 4.68 (ddd, *J* = 7.2, 4.8, 2.4 Hz, 1H), 3.81 (d, *J* = 8.4 Hz, 1H), 3.67 (dq, *J* = 9.6, 6.0 Hz, 1H), 3.57 (d, *J* = 10.2 Hz, 1H), 3.10 (ddd, *J* = 18.6, 12.6, 2.4 Hz, 1H), 2.83 (dq, *J* = 9.6, 6.6 Hz, 1H), 2.55(dqd, *J* = 13.8, 6.6, 4.2 Hz, 1H), 2.14 (ddd, *J* = 18.6, 5.4, 2.4 Hz, 1H), 1.91-1.81 (m, 3H), 1.66 (br s, 1H), 1.54-1.49 (m, 2H), 1.48-1.40 (m, 1H), 1.39-1.35 (m, 1H), 1.29 (d, *J* = 6.0 Hz, 3H), 1.25-1.23 (m, 1H), 1.21 (d, *J* = 7.2 Hz, 3H), 1.14 (d, *J* = 7.2

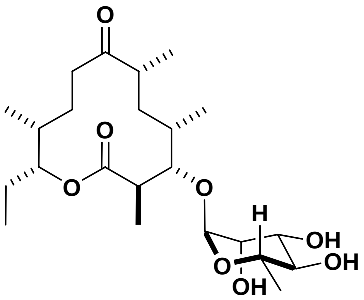
Hz, 3H), 1.07 (d, $J = 6.6$ Hz, 3H), 0.95 (d, $J = 6.6$ Hz, 3H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.4, 174.4, 133.4, 126.0, 96.4, 86.8, 80.9, 69.2, 68.0, 45.9, 44.3, 34.8, 34.0, 33.8, 32.2, 29.6, 24.2, 20.5, 17.9, 17.6, 17.1, 15.3, 10.8; CIHRMS calcd for $[C_{23}H_{38}O_6 + Na]^+$: 433.2566, Found 433.2560.

(1):



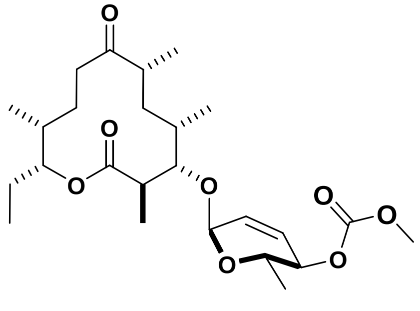
The enol compound **17** (40 mg, 0.10 mmol) and *o*-$NO_2C_6H_4SO_2NHNH_2$ (120 mg, 0.60 mmol) were dissolved in 1.0 mL of CH_2Cl_2 in a round bottom flask and cooled 0 °C under nitrogen atmosphere then triethylamine (114 μL, 0.80 mmol) was added and the reaction mixture was stirred at 0 °C for 12 hours and on completion, as monitored by TLC. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. The crude product was purified using silica gel flash chromatography eluting with EtOAc/hexanes (30:70) to give deoxy alcohol **1** (40 mg, 0.09 mmol, 96 %) as viscous oil. R_f (50% EtOAc/Hexane) = 0.26; $[\alpha]_D^{25} = -34$ (*c* 0.25, CH_2Cl_2); IR (thin film, cm^{-1}) 3449, 2963, 2928, 1726, 1703, 1459, 1170, 1019, 940, 898; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.74 (d, $J = 2.4$ Hz, 1H), 4.67 (ddd, $J = 8.4, 5.4, 1.8$ Hz, 1H), 3.70 (dq, *J* = 9.0, 6.0 Hz, 1H), 3.48 (d, *J* = 10.2 Hz, 1H), 3.28 (ddd, *J* = 10.2, 9.0, 4.2 Hz, 1H), 3.10 (ddd, *J* = 18.6, 12.6, 2.4 Hz, 1H), 2.79 (dq, *J* = 10.2, 7.2 Hz, 1H), 2.55 (dqd, *J* = 13.2, 6.6, 4.2 Hz, 1H), 2.12 (ddd, *J* = 18.6, 5.4, 2.4 Hz, 1H), 1.93-1.81 (m, 5H), 1.78-1.67 (m, 2H), 1.45-1.37 (m, 2H), 1.25-1.22 (m, 1H), 1.21 (d, *J* = 6.6 Hz, 3H), 1.17 (d, *J* = 7.2 Hz, 3H), 1.15 (d, *J* = 7.2 Hz, 3H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.3, 174.5, 99.2, 80.8, 72.0, 70.2, 45.9, 44.3, 34.7, 34.3, 33.8, 32.2, 29.9, 29.6, 27.6, 24.2, 20.6, 19.2, 18.0, 17.5, 17.0, 15.5, 10.7; CIHRMS calcd for $[C_{23}H_{40}O_6 + Na]^+$: 435.2722, Found 435.2717.

(2):



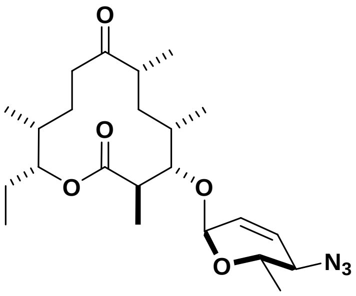
To a CH_2Cl_2 (0.2 mL) solution of allylic alcohol **17** (10 mg, 0.02 mmol) at 0 °C was added a solution of (50% w/v) of *N*-methyl morpholine *N*-oxide / water (10 μL). Crystalline OsO_4 (2.0 mg, 10 mol %) was added and the reaction was stirred for 12 h. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. Impurities were eluted with ether and the product was eluted with MeOH/EtOAc/hexanes (10:40:50). Pure fractions were combined and concentrated to afford triol **2** (9.7 mg, 0.02 mmol, 91 %) as viscous oil. *R*$_f$ (90% EtOAc/MeOH) = 0.30; $[\alpha]_D^{25}$ = - 39 (*c* = 0.3, MeOH); IR (thin film, cm^{-1}) 3390, 2965, 2929, 1723, 1702, 1458, 1173, 1062, 899, 735; ^{1}H NMR (600 MHz, CDCl$_3$) δ 4.80 (d, *J* = 1.2 Hz, 1H), 4.67 (ddd, *J* = 8.4, 4.8, 1.8 Hz, 1H), 4.02 (br s, 1H), 3.78 (dq, *J* = 9.6, 6.0 Hz, 1H), 3.71 (m, 1H), 3.51 (d, *J* = 10.2 Hz, 1H), 3.47 (dd, *J* = 10.2, 9.0 Hz, 1H), 3.09 (ddd, *J* = 18.6, 12.0, 2.4 Hz, 1H), 2.81 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.54 (dqd, *J* = 13.8, 7.2, 4.2 Hz, 1H), 2.43 (m, 1H), 2.23 (m, 1H), 2.14 (ddd, *J* = 18.6, 5.4, 2.4 Hz, 1H), 1.88-1.82 (m, 2H), 1.55-1.50 (m, 2H), 1.47-1.42 (m, 1H), 1.35-1.30 (m, 1H), 1.29 (d, *J* = 6.0 Hz, 3H), 1.27-1.25(m, 1H), 1.22 (d, *J* = 6.6 Hz, 3H), 1.16 (d, *J* = 6.6 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 214.1, 174.2, 102.6, 89.5, 81.1, 73.4, 71.8, 71.2, 68.4, 45.8, 44.1, 34.6, 34.2, 33.8, 32.3, 24.2, 20.6, 19.2, 18.0, 17.1, 16.9, 15.5, 10.7; CIHRMS calcd for $[C_{23}H_{40}O_8 + Na]^+$: 467.2620, Found 467.2616.

(18):



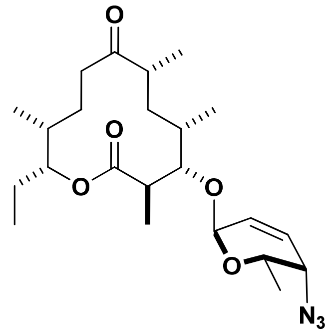
To a solution of allylic alcohol **17** (60 mg, 0.15 mmol) in dry CH$_2$Cl$_2$ (1.0 mL) at 0 °C, was added pyridine (59 μL, 0.73 mmol), DMAP (3.6 mg), and methyl chloroformate (57 mg, 0.73 mmol). After stirring 24 h at room temperature, water (1 mL) was added and then the mixture was extracted with EtOAc (3 x 5 mL), dried (Na_2SO_4), concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with EtOAc/hexane (20:80) to give carbonate **18** (60.2 mg, 0.13 mmol, 88%) as viscous oil. R_f (50% EtOAc/hexane) = 0.50; $[\alpha]_D^{25}$ = - 12 (c = 0.5, CH_2Cl_2); IR (thin film, cm^{-1}) 2962, 2924, 1752, 1701, 1459, 1261, 1045, 970; ^1H NMR (600 MHz, $CDCl_3$) δ 5.94 (d, J = 10.2 Hz, 1H), 5.85 (ddd, J = 9.6, 2.4, 2.4 Hz, 1H), 5.01 (br s, 1H), 4.85 (dd, J = 9.0, 1.8 Hz, 1H), 4.69 (ddd, J = 8.4, 5.4, 1.8 Hz, 1H), 3.95 (dq, J = 9.0, 6.0 Hz, 1H), 3.81 (s, 3H), 3.65 (dd, J = 10.2, 1.2 Hz, 1H), 3.10 (ddd, J = 18.6, 12.6, 2.4 Hz, 1H), 2.84 (dq, J = 10.2, 6.6 Hz, 1H), 2.54 (dqd, J = 13.8, 7.2, 4.2 Hz, 1H), 2.12 (ddd, J = 18.6, 6.0, 2.4 Hz, 1H), 1.90-1.81 (m, 3H), 1.54-1.49 (m, 2H), 1.43 (ddd, J = 13.8, 5.4, 1.8 Hz, 1H), 1.36 (ddd, J = 13.8, 12.6, 4.2 Hz, 1H), 1.24 (d, J = 6.0 Hz, 3H), 1.21 (d, J = 7.2 Hz, 3H), 1.17-1.12(m, 1H), 1.15 (d, J = 7.2 Hz, 3H), 1.05 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 7.2 Hz, 3H), 0.88 (t, J = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.5, 174.5, 155.5, 129.3, 127.8, 96.5, 87.2, 81.1, 74.5, 64.9, 55.2, 46.1, 44.4, 34.9, 34.2, 34.0, 32.4, 24.4, 20.8, 19.5, 18.1, 17.8, 17.3, 15.4, 11.0; CIHRMS calcd for $[C_{25}H_{40}O_8 + Na]^+$: 491.2620, Found 491.2615.

(19):



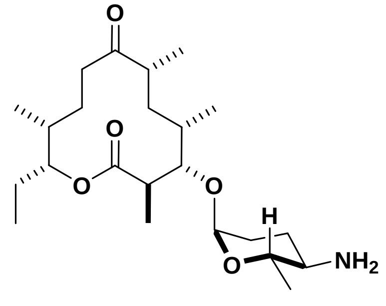
To a mixture of carbonate **18** (55 mg, 0.12 mmol), allylpalladium chloride dimer (6.4 mg, 0.02 mmol) and 1,4-bis(diphenylphosphino)butane (30 mg, 0.08 mmol) in anhydrous THF (0.20 mL) was added TMSN$_3$ (77 μg, 0.59 mmol) under argon atmosphere. The solution was stirred at room temperature for 3 h. Then the mixture was evaporated under reduced pressure, purified using silica gel flash chromatography eluting with EtOAc/hexane (15:85) to give allylic azide **19** (43 mg, 0.10mmol, 85%) as viscous oil. R_f (30% EtOAc/hexane) = 0.60; $[\alpha]_D^{25}$ = - 45 (c = 1, CH$_2$Cl$_2$); IR (thin film, cm^{-1}) 2968, 2934, 2103, 1725, 1703, 1459, 1170, 1041, 984; ^{1}H NMR (600 MHz, CDCl$_3$) δ 5.96 (d, J = 10.8 Hz, 1H), 5.93 (ddd, J = 9.6, 2.4, 2.4 Hz, 1H), 5.00 (br s, 1H), 4.69 (ddd, J = 7.2, 6.6, 2.4 Hz, 1H), 3.74 (dq, J = 10.2, 6.6 Hz, 1H), 3.57 (d, J = 10.2 Hz, 1H), 3.55 (d, J = 9.6 Hz, 1H), 3.10 (ddd, J = 18.6, 12.6, 2.4 Hz, 1H), 2.84 (dq, J = 10.8, 7.2 Hz, 1H), 2.55 (dqd, J = 13.2, 6.6, 4.2 Hz, 1H), 2.13 (ddd, J = 18.6, 6.0, 2.4 Hz, 1H), 1.90-1.81 (m, 3H), 1.54-1.49 (m, 2H), 1.46-1.41 (m, 1H), 1.35 (ddd, J = 13.2, 13.2, 4.2), 1.30 (d, J = 6.6 Hz, 3H), 1.21 (d, J = 7.2 Hz, 3H), 1.19-1.12 (m, 1H), 1.15 (d, J = 6.6 Hz, 3H), 1.05 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 7.2 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 214.5, 174.5, 128.6, 128.2, 94.4, 87.3, 81.1, 66.3, 60.2, 46.1, 44.4, 34.9, 34.2, 34.0, 32.4, 24.4, 20.8, 19.5, 18.3, 18.1, 17.4, 15.5, 11.0; CIHRMS calcd for $[C_{23}H_{37}N_3O_5 + Na]^+$: 458.2630, Found 458.2625.

(21):



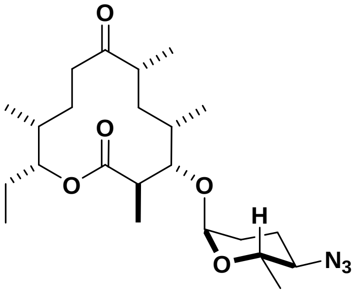
To a solution of allylic alcohol **17** (15 mg, 0.03 mmol) and methanesulphonyl chloride (4 μL, 0.05 mmol) in dry CH_2Cl_2 (0.3 mL) at 0 °C, was added triethylamine (6 μL, 0.04 mmol). After stirring 8 h at room temperature, water (1 mL) was added and then the mixture was extracted with EtOAc (3 x 5 mL), dried (Na_2SO_4), concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with EtOAc/hexane (15:85) to give mesylate **20**. To a solution mesylate **20** (15 mg, 0.12 mmol) in THF (0.3 mL) was added NaN_3 (3.0 mg, 0.05 mmol) under argon atmosphere. The solution was stirred at room temperature for 2 h. Then the mixture was evaporated under reduced pressure, purified using silica gel flash chromatography eluting with EtOAc/hexane (20:80) to give allylic azide **21** (10 mg, 0.02 mmol, 80%) as viscous oil. R_f (30% EtOAc/hexane) = 0.55; $[\alpha]_D^{25}$ = + 73 (c = 0.3, CH_2Cl_2); IR (thin film, cm^{-1}) 2967, 2932, 2100, 1725, 1702, 1460, 1170, 1041, 972; ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.16 (dd, *J* = 10.2, 3.0 Hz, 1H), 6.10 (dd, *J* = 10.2, 6.0 Hz, 1H), 5.06 (d, *J* = 2.4 Hz, 1H), 4.69 (ddd, *J* = 7.8, 5.4, 2.4 Hz, 1H), 4.22 (qd, *J* = 6.0, 2.4 Hz, 1H), 3.62 (d, *J* = 10.2 Hz, 1H), 3.13 (dd, *J* = 5.4, 2.4 Hz, 1H), 3.09 (ddd, *J* = 18.6, 12.6, 2.4 Hz, 1H), 2.84 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.54 (dqd, *J* = 12.6, 7.2, 4.2 Hz, 1H), 2.13 (ddd, *J* = 18.6, 5.4, 3.0 Hz, 1H), 1.91-1.82 (m, 3H), 1.54-1.49 (m, 2H), 1.47-1.42 (m, 1H), 1.38-1.30 (m, 1H), 1.32 (d, *J* = 6.0 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 1.20-1.14 (m, 1H), 1.14 (d, *J* = 7.2 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 214.2, 174.2, 129.8, 124.9, 96.3, 86.7, 80.9, 66.4, 55.1, 45.9, 44.2, 34.7, 34.1, 33.8, 32.2, 24.2, 20.6, 19.3, 17.9, 17.2, 16.9, 15.3, 10.8; CIHRMS calcd for $[C_{23}H_{37}N_3O_5 + Na]^+$: 458.2630, Found 458.2631.

(3):



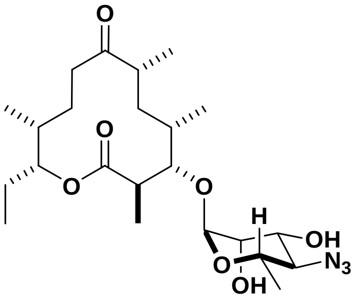
To a solution of allylic azide **19** (15 mg, 0.04 mmol) in dry MeOH (0.3 mL) was added Pd/C (10 mg) and the mixture was stirred under H_2 at an 100 psi pressure for 8 h at room temperature. The catalyst was filtered off through a short pad of Celite, concentrated under reduced pressure. The resulting crude product was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. Impurities were eluted with ether and the product was eluted with MeOH/EtOAc/hexanes (200:40:40). Pure fractions were combined and concentrated to afford deoxy amine **3** (13.2 mg, 0.03 mmol, 92 %) as viscous oil. R_f (90% EtOAc/MeOH) = 0.30; $[\alpha]_D^{25}$ = - 38 (c = 0.5, MeOH); IR (thin film, cm^{-1}) 3345, 2964, 2929, 1728, 1705, 1457, 1167, 1016, 983, 897; ^1H NMR (600 MHz, $CDCl_3$) δ 4.71 (d, J = 3.0 Hz, 1H), 4.61 (ddd, J = 9.0, 4.2, 1.8 Hz, 1H), 3.92 (dq, J = 9.6, 6.6 Hz, 1H), 3.40 (d, J = 10.2 Hz, 1H), 3.12 (ddd, J = 19.2, 12.6, 2.4 Hz, 1H), 2.79 (dq, J = 10.2, 7.2 Hz, 1H), 2.48 (dqd, J = 13.8, 7.2, 4.2 Hz, 1H), 2.24-2.18 (m, 5H), 1.96-1.89 (m, *2*H), 1.79-1.63 (m, 4H), 1.55-1.45 (m, 3H), 1.36 (ddd, J = 14.4, 12.0, 4.2 Hz, 1H), 1.15 (d, J = 7.2 Hz, 3H), 1.14 (d, J = 6.0 Hz, 3H), 1.12 (d, J = 7.2 Hz, 3H), 1.10-1.04 (m, 1H), 1.03 (d, J = 6.0 Hz, 3H), 0.90 (d, J = 7.2 Hz, 3H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 217.1, 176.6, 101.2, 82.6, 68.9, 66.8, 49.7, 47.4, 45.9, 41.0, 36.3, 35.9, 35.2, 33.7, 31.5, 25.4, 21.7, 19.5, 19.2, 17.8, 16.2, 16.1, 11.3; CIHRMS calcd for $[C_{23}H_{41}NO_5 + H]^+$: 412.3063, Found 412.3061.

(4):



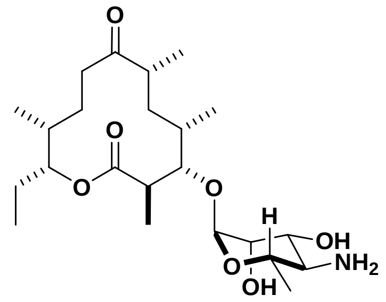
The allylic azide compound **19** (20 mg, 0.04 mmol) and *o*-$NO_2C_6H_4SO_2NHNH_2$ (56 mg, 0.27 mmol) were dissolved in 0.4 mL of CH_2Cl_2 in a round bottom flask and cooled 0 °C under nitrogen atmosphere then triethylamine (60 μL, 0.36 mmol) was added and the reaction mixture was stirred at 0 °C for 12 hours and on completion, as monitored by TLC. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. The crude product was purified using silica gel flash chromatography eluting with EtOAc/hexanes (15:85) to give deoxy azide **4** (18 mg, 0.04 mmol, 90 %) as viscous oil. R_f (50% EtOAc/Hexane) = 0.65; $[\alpha]_D^{25}$ = - 13 (c = 0.5, CH_2Cl_2); IR (thin film, cm^{-1}) 2965, 2930, 1724, 1701, 1459, 1171, 1019, 974; ^1H NMR (600 MHz, $CDCl_3$) δ 4.78 (d, J = 3.0 Hz, 1H), 4.68 (ddd, J = 6.6, 6.0, 2.4 Hz, 1H), 3.73 (dq, J = 9.6, 6.6 Hz, 1H), 3.48 (d, J = 10.8 Hz, 1H), 3.10 (ddd, J = 19.2, 12.6, 2.4 Hz, 1H), 3.04 (ddd, J = 10.8, 10.2, 4.2 Hz, 1H), 2.80 (dq, J = 10.8, 7.2 Hz, 1H), 2.56 (dqd, J = 13.2, 6.6, 4.2 Hz, 1H), 2.14 (ddd, J = 19.2, 5.4, 3.0 Hz, 1H), 1.97-1.75(m, 7H), 1.54-1.49 (m, 2H), 1.48-1.42 (m, 1H), 1.39-1.33 (m, 1H), 1.21 (d, J = 6.6 Hz, 3H), 1.18 (d, J = 6.0 Hz, 3H), 1.17 (d, J = 6.6 Hz, 3H), 1.18-1.11(m, 1H), 1.03 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.3, 174.4, 99.1, 88.3, 80.9, 68.2, 62.6, 45.9, 44.3, 34.7, 34.5, 33.8, 32.2, 29.5, 24.5, 23.9, 20.6, 19.2, 18.3, 18.0, 17.0, 15.5, 10.7; CIHRMS calcd for $[C_{23}H_{39}N_3O_5 + Na]^+$: 460.2787, Found 460.2783.

(5):



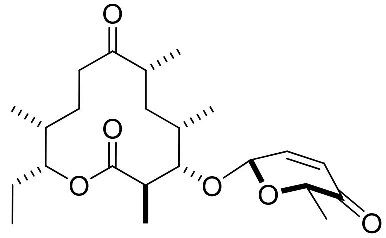
To a CH_2Cl_2 (0.3 mL) solution of allylic azide **19** (15 mg, 0.3 mmol) at 0 °C was added a solution of (50% w/v) of *N*-methyl morpholine *N*-oxide / water (17 μL). Crystalline OsO_4 (1.0 mg, 10 mol %) was added and the reaction was stirred for 12 h. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. Impurities were eluted with ether and the product was eluted with MeOH/EtOAc/hexanes (2:48:50). Pure fractions were combined and concentrated to afford diol **5** (15 mg, 0.03 mmol, 90 %) as viscous oil. R_f (50% EtOAc/hexanes) = 0.20; $[\alpha]_D^{25}$ = - 62 (*c* = 0.5, MeOH); IR (thin film, cm^{-1}) 3411, 2968, 2933, 2108, 1725, 1703, 1459, 1174, 1051, 997, 900; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.81 (d, *J* = 1.2 Hz, 1H), 4.67 (ddd, *J* = 7.8, 5.4, 2.4 Hz, 1H), 4.00 (ddd, *J* = 4.8, 3.0, 1.8 Hz, 1H), 3.78 (ddd, *J* = 10.2, 7.2, 3.0 Hz, 1H), 3.69 (dd, *J* = 10.2, 6.6 Hz, 1H), 3.51 (d, *J* = 10.2 Hz, 1H), 3.31 (dd, *J* = 10.2, 9.6 Hz, 1H), 3.07 (ddd, *J* = 18.6, 6.6, 2.4 Hz, 1H), 2.80 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.55 (m, 2H), 2.35 (br s, 1H), 2.14 (ddd, *J* = 19.2, 6.0, 3.0 Hz, 1H), 1.87-1.80 (m, 3H), 1.54-1.49 (m, 2H), 1.44 (dddd, *J* = 14.4, 12.0, 5.4, 3.0 Hz, 1H), 1.32 (d, *J* = 6.0 Hz, 3H), 1.28-1.24 (m, 1H), 1.20 (d, *J* = 6.6 Hz, 3H), 1.18-1.14 (m, 1H), 1.15 (d, *J* = 6.0 Hz, 3H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.1, 174.1, 102.4, 89.6, 81.1, 70.5, 67.4, 65.8, 60.3, 45.8, 44.1, 34.6, 34.2, 33.7, 32.3, 24.2, 20.5, 19.2, 18.0, 17.0, 15.6, 14.1, 10.7; CIHRMS calcd for $[C_{23}H_{39}N_3O_7 + Na]^+$: 492.2685, Found 492.2684.

(6):



To a solution of dihydroxy azide **5** (10 mg, 0.02 mmol) in dry MeOH (0.2 mL) was added Pd/C (2 mg) and the mixture was stirred under H_2 at an 100 psi pressure for 6 h at room temperature. The catalyst was filtered off through a short pad of Celite, concentrated under reduced pressure. The resulting crude product was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. Impurities were eluted with ether and the product was eluted with MeOH/EtOAc/hexanes (20:40:40). Pure fractions were combined and concentrated to afford dihydroxy amine **6** (8.5 mg, 0.02 mmol, 90 %) as viscous oil. R_f (90% EtOAc/MeOH) = 0.20; $[\alpha]_D^{25}$ = -130 (c = 0.5, MeOH); IR (thin film, cm^{-1}) 3373, 2967, 2933, 1721, 1702, 1458, 1366, 1173, 1032, 984; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.71 (d, J = 2.4 Hz, 1H), 4.63 (ddd, J = 8.4, 4.8, 1.8 Hz, 1H), 3.85 (dd, J = 3.0, 1.8 Hz, 1H), 3.69 (dq, J = 9.6, 6.6 Hz, 1H), 3.48 (dd, J = 10.2, 3.0 Hz, 1H), 3.42 (d, J = 10.8 Hz, 1H), 3.13 (ddd, J = 19.2, 12.0, 2.4 Hz, 1H), 2.83 (dq, J = 10.2, 6.6 Hz, 1H), 2.76 (dd, J = 10.2, 9.6 Hz, 1H), 2.49 (ddd, J = 13.8, 6.6, 4.2 Hz, 1H), 2.21 (ddd, J = 19.2, 5.4, 3.0 Hz, 1H), 1.88 (dd, J = 12.6, 12.6 Hz, 1H), 1.81-1.73 (m, 3H), 1.57-1.47 (m, 3H), 1.55 (ddd, J = 13.8, 12.0, 4.2 Hz, 1H), 1.20 (d, J = 7.2 Hz, 3H), 1.19 (d, J = 6.0 Hz, 3H), 1.16 (d, J = 7.2 Hz, 3H), 1.13-1.10 (m, 1H), 1.04 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 217.1, 176.3, 105.5, 82.7, 72.1, 71.5, 71.1, 55.3, 47.4, 45.8, 35.9, 35.8, 35.1, 33.6, 31.4, 25.4, 21.7, 19.5, 18.3, 18.1, 17.6, 16.0, 11.3; CIHRMS calcd for $[C_{23}H_{41}NO_7 + H]^+$: 444.2961, Found 444.2955.

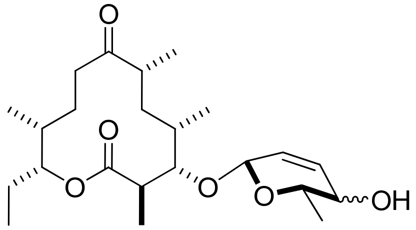
(22):



A CH_2Cl_2 (0.5 mL) solution of Boc-enone **13b** (60 mg, 0.26 mmol) and 10-deoxymethynolide alcohol **16** (52 mg, 0.0.17 mmol) was cooled to 0 °C. A CH_2Cl_2

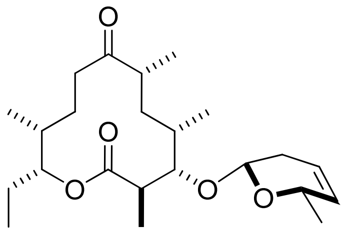
(0.5 mL) solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (9 mg, 5 mol%) and PPh_3 (9 mg, 20 mol%) was added to the reaction mixture at 0 °C. The reaction mixture was stirred at 0 °C for 12 hours. The reaction mixture was quenched with 2 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 10% EtOAc/hexanes to give enone **22** (62 mg, 87%): Pale yellow solid, mp: 142.7-143.1 ºC; R_f (33% EtOAc/hexanes) = 0.65; $[\alpha]^{25}_{D}$ = + 8.85 (c = 0.7, $CHCl_3$); IR (thin film, cm^{-1}) 2966, 2934, 1722, 1701, 1458, 1372, 1168, 1141, 1095, 1052, 986, 905; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90 (dd, J = 10.2, 1.2 Hz, 1H), 6.10 (dd, J = 10.2, 1.8 Hz, 1H), 5.34 (ddd, J = 1.8, 1.2, 1.2 Hz, 1H), 4.65 (ddd, J = 7.8, 5.4, 1.8 Hz, 1H), 4.10 (qd, J = 6.6, 1.8 Hz, 1H), 3.70 (dd, J = 10.2, 0.6 Hz, 1H), 3.08 (ddd, J = 18.6, 12.6, 2.4 Hz, 1H), 2.77 (dq, J = 10.2, 6.6 Hz, 1H), 2.53 (dqd, J = 14.4, 6.6, 4.2 Hz, 1H), 2.12 (ddd, J = 18.6, 5.4, 2.4 Hz, 1H), 1.91 (ddd, J = 12.6, 12.6, 1.8 Hz, 1H), 1.87-1.80 (m, 2H), 1.53-1.47 (m, 2H), 1.41 (d, J = 6.6 Hz, 3H), 1.44-1.35 (m, 2H), 1.29 (d, J = 6.6 Hz, 3H), 1.26-1.20 (m, 1H), 1.15 (d, J = 6.6 Hz, 3H), 1.06 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.4, 196.7, 175.1, 147.5, 129.2, 98.7, 87.9, 81.5, 75.4, 45.9, 43.3, 35.0, 34.5, 34.0, 32.5, 24.5, 20.8, 19.5, 18.1, 18.0, 16.1, 15.9, 11.0; HRMS (ESI) calcd. for $[C_{23}H_{36}O_6 + Na]^+$: 431.2410, Found 431.2409.

(23):



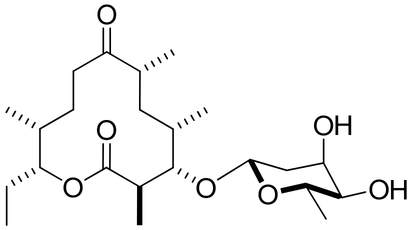
The enone compound **22** (150 mg, 0.36 mmol) was dissolved in 0.8 mL of CH_2Cl_2 and 0.2 mL MeOH in round bottom flask and cooled -78 °C then NaBH$_4$ (15 mg, 0.41 mmol) was added and the reaction mixture was stirred at -78 °C for 3 hours and on completion, monitored by TLC, reaction mixture was diluted with ether and was quenched with 5 mL of satd. aq. NaHCO$_3$, extracted (3 x 10 mL) with Et$_2$O, dried (Na$_2$SO$_4$), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 15% EtOAc/hexanes to give allylic alcohol **23** (141 mg, 93%): white solid; R_f (33% EtOAc/hexanes) = 0.32; $[\alpha]^{25}_{D}$ = + 5.46 (*c* = 1.5, CHCl$_3$); IR (thin film, cm^{-1}) 3487, 2967, 2934, 2878, 1722, 1703, 1458, 1373, 1333, 1168, 1059, 982, 909; ^{1}H NMR (600 MHz, CDCl$_3$) δ 5.91 (ddd, *J* = 10.2, 1.8, 1.2 Hz, 1H), 5.79 (ddd, *J* = 10.2, 1.2, 1.2 Hz, 1H), 5.08 (br s, 1H), 4.65 (ddd, *J* = 7.2, 4.8, 1.8 Hz, 1H), 3.93 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 3.61 (d, *J* = 10.2 Hz, 1H), 3.47 (dq, *J* = 7.8, 6.6 Hz, 1H), 3.08 (ddd, *J* = 18.6, 12.6, 1.8 Hz, 1H), 2.74 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.52 (dqd, *J* = 13.8, 6.6, 4.2 Hz, 1H), 2.10 (ddd, *J* = 19.2, 5.4, 2.4 Hz, 1H), 1.91-1.80 (m, 3H), 1.77 (d, *J* = 7.2 Hz, 1H), 1.54-1.48 (m, *2*H), 1.44-1.37 (m, 2H), 1.33 (d, *J* = 6.0 Hz, 3H), 1.31 (d, *J* = 6.6 Hz, 3H), 1.20-1,16 (m, 1H), 1.14 (d, *J* = 7.2 Hz, 3H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 214.7, 175.4, 133.4, 128.9, 99.8, 87.6, 81.3, 74.8, 69.3, 45.9, 43.4, 35.0, 34.6, 33.9, 32.5, 24.4, 20.8, 19.5, 18.3, 18.1, 17.8, 16.1, 11.0; HRMS (ESI) calcd. for [$C_{23}H_{38}O_6$ + Na]$^+$: 433.2566, Found 433.2565.

(24):



A flask was charged with dry N-methyl morpholine (NMM) 0.8 mL, triphenyl phosphine (95 mg, 0.36 mmol) and was cooled to -30 °C under Ar atmosphere. Diisopropylazodicarboxylate (70 µL, 0.33 mmol) was added and the reaction was stirred for 25 min, Allylic alcohol **23** (45 mg, 0.11 mmol) was added and the reaction mixture was stirred for 10 min, followed by addition of o-nitrobenzenesulfonyl hydrazide (NBSH) (72 mg, 0.33 mmol). The reaction was stirred at -30 °C for 2h and was monitored by TLC, upon consumption of starting material, warm up to room temperature and stirred for another 4h. The reaction mixture was diluted with ether (10 mL) and was quenched with 5 mL of satd aq NaHCO$_3$, extracted (3 x 5 mL) with Et$_2$O, dried (Na$_2$SO$_4$), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 5% EtOAc/hexanes to give **24** (26 mg, 60%) of viscous product: R_f = 0.84 (33% EtOAc/hexanes); $[\alpha]^{25}_D$ = + 22.39 (*c* = 1.0, CHCl$_3$); IR (thin film, cm^{-1}) 2967, 2933, 2882, 1725, 1703, 1458, 1367, 1153, 1067, 1032, 901; ^{1}H NMR (600 MHz, CDCl$_3$) δ 5.64 (dddd, *J* = 9.6, 4.8, 2.4, 2.4 Hz, 1H), 5.56 (dddd, *J* = 9.6, 2.4, 1.2, 1.2 Hz, 1H), 4.67 (ddd, *J* = 7.8, 5.4, 2.4 Hz, 1H), 4.63 (dd, *J* = 8.4, 3.6 Hz, 1H), 4.29-4.27 (m, 1H), 3.59 (dd, *J* = 10.2, 1.2 Hz, 1H), 3.11 (ddd, *J* = 19.2, 12.6, 2.4 Hz, 1H), 2.76 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.54 (dqd, *J* = 14.4, 6.6, 4.2 Hz, 1H), 2.22-2.11 (m, *2*H), 2.11 (ddd, *J* = 12.6, 5.4, 2.4 Hz, 1H), 1.93-1.82 (m, 3H), 1.55-1.50 (m, 2H), 1.46-1.41 (m, 1H), 1.38 (ddd, *J* = 14.4, 12.6, 4.2 Hz, 1H), 1.33 (d, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 1.19-1.14 (m, 1H), 1.15 (d, *J* = 6.6 Hz, 3H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 214.7, 175.6, 131.5, 122.9, 101.2, 86.1, 81.1, 71.4, 46.0, 43.4, 35.0, 34.6, 33.9, 32.5, 31.4, 24.5, 21.1, 20.8, 19.5, 18.2, 17.9, 16.1, 11.0; HRMS (ESI) calcd for [$C_{23}H_{38}O_5$ + Na]$^+$: 417.2612, Found 417.2613.

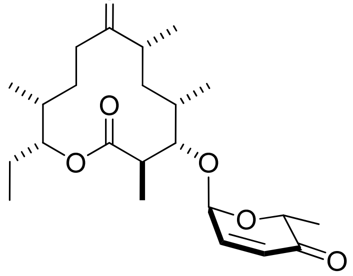
(7):



To a CH$_2$Cl$_2$ (0.7 mL) solution of ene **24** (17 mg, 0.04 mmol) at 0 °C was added a solution of (50% w/v) of *N*-methyl morpholine *N*-oxide/water (70 μL). Catalytic amount of crystalline OsO$_4$ (~1 mg) was added and the reaction was stirred for 12 h. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH$_2$Cl$_2$

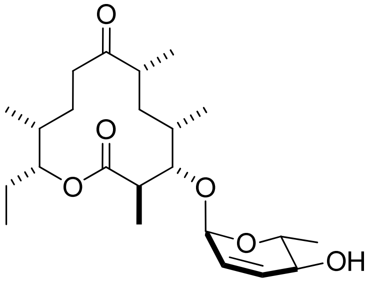
(1 mL) in three portions. Chromatography eluting with 35% EtOAc/hexanes afforded diol **7** (16.3 mg, 87%): amorphous white solid; R_f (50% EtOAc/hexane) = 0.24; $[\alpha]^{25}_{D} = +27.49$ (c = 0.47, MeOH); IR (thin film, cm^{-1}) 3477, 3348, 2930, 1721, 1708, 1458, 1329, 1169, 1081, 1066, 1017, 902, 734; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.80 (dd, J = 9.6, 1.8 Hz, 1H), 4.65 (ddd, J = 6.0, 5.4, 1.8 Hz, 1H), 4.10 (ddd, J = 3.0, 3.0, 2.5 Hz, 1H), 3.67 (dq, J = 9.6, 6.6 Hz, 1H), 3.56 (d, J = 10.2 Hz, 1H), 3.28 (dd, J = 9.6, 3.0 Hz, 1H), 3.09 (ddd, J = 18.6, 12.6, 2.4 Hz, 1H), 2.72 (dq, J = 10.8, 6.6 Hz, 1H), 2.53 (dqd, J = 13.8, 6.6, 4.2 Hz, 1H), 2.15 (ddd, J = 13.8, 3.6, 2.4 Hz, 1H), 2.11 (ddd, J = 16.8, 5.4, 2.4 Hz, 1H), 1.90-1.80 (m, 3H), 1.68 (ddd, J = 13.8, 10.2, 3.0 Hz, 1H), 1.54- 1.49 (m, 2H), 1.44- 1.39 (m, 1H), 1.35 (ddd, J = 13.8, 12.6, 3.6 Hz, 1H), 1.29 (d, J = 6.0 Hz, 3H), 1.28 (d, J = 6.0 Hz, 3H), 1.18-1.14 (m, 1H), 1.14 (d, J = 7.2 Hz, 3H), 1.03 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 7.2 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.7, 175.5, 99.7, 86.8, 81.2, 73.3, 69.6, 68.5, 45.9, 43.4, 38.2, 35.0, 34.6, 33.9, 32.5, 24.5, 20.8, 19.5, 18.23, 18.16, 17.8, 16.0, 11.0; HRMS (ESI) calcd for $[C_{23}H_{40}O_7 + Na]^+$: 451.2666, Found 451.2669.

(25):



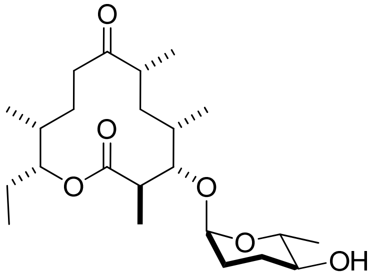
A CH_2Cl_2 (1.3 mL) solution of Boc-enone **13c** (303 mg, 1.32 mmol) and 10-deoxymethynolide alcohol **16** (198 mg, 0.66 mmol) was cooled to 0 °C. A CH_2Cl_2 (0.2 mL) solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (34 mg, 0.03 mmol) and PPh_3 (34.6 mg, 0.13 mmol) was added to the reaction mixture at 0 °C. The reaction mixture was stirred at 0 °C for 5 hours. The reaction mixture was quenched with 5 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure to give a residue. Chromatograph on silica gel eluting with 15% EtOAc/hexanes to give enone **25** (230 mg, 85%): white solid, mp: 156.9-157.6 °C; R_f = 0.63 (33% EtOAc/hexanes); $[\alpha]^{25}_D$ = -19.21 (*c* = 0.51, $CHCl_3$); IR (thin film, cm^{-1}) 2966, 2935, 1722, 1700, 1459, 1371, 1171, 1101, 1079, 1017, 973; ^1H NMR (600 MHz, $CDCl_3$) δ 6.83 (dd, *J* = 10.2, 3.6 Hz, 1H), 6.07 (d, *J* = 10.2 Hz, 1H), 5.25 (d, *J* = 3.6 Hz, 1H), 4.67 (ddd, *J* = 7.2, 6.6, 2.4 Hz, 1H), 4.60 (q, *J* = 6.6 Hz, 1H), 3.69 (dd, *J* = 10.2, 0.6 Hz, 1H), 3.08 (ddd, *J* = 19.2, 12.6, 2.4 Hz, 1H), 2.81 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.54 (dqd, *J* = 12.6, 6.6, 4.2 Hz, 1H), 2.13 (ddd, *J* = 18.6, 5.4, 2.4 Hz, 1H), 1.91-1.81 (m, 3H), 1.55-1.50 (m, 2H), 1.45-1.40 (m, 1H), 1.35 (d, *J* = 7.2 Hz, 3H), 1.32 (ddd, *J* = 13.8, 12.0, 4.2 Hz,, 1H), 1.30 (d, *J* = 6.6 Hz, 3H), 1.27-1.22 (m, 1H), 1.15 (d, *J* = 7.2 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.3, 196.9, 174.7, 142.7, 127.1, 95.9, 88.4, 81.5, 70.9, 45.8, 43.3, 35.1, 34.5, 34.0, 32.5, 24.4, 20.8, 19.5, 18.1, 17.8, 15.7, 15.1, 11.0; HRMS (ESI) calcd for $[C_{23}H_{36}O_6 + Na]^+$: 431.2404, Found: 431.2410.

(26):



The enone compound **25** (23 mg, 0.057 mmol) was dissolved in 0.4 mL of CH_2Cl_2 and 0.3 mL MeOH in round bottom flask and cooled -78 °C, then NaBH$_4$ (2.2 mg, 0.057 mmol) was added and the reaction mixture was stirred at -78 °C for 3 hours and on completion, monitored by TLC, reaction mixture was diluted with ether and was quenched with 2 mL of satd. aq. NaHCO$_3$, extracted (3 x 5 mL) with Et$_2$O, dried (Na$_2$SO$_4$), and concentrated under reduced pressure to give a residue. Chromatograph on silica gel eluting with 25% EtOAc/hexanes gave allylic alcohol **26** (19 mg, 83%): white solid, mp: 155.0-156.5 °C; R_f = 0.38 (33% EtOAc/hexanes); $[\alpha]^{25}_D$ = + 34.5 (*c* = 0.41, MeOH); IR (thin film, cm^{-1}) 3500, 2964, 2936, 1725, 1703, 1460, 1172, 1096, 1026, 1004, 900; ^{1}H NMR (600 MHz, CDCl$_3$) δ 5.95 (ddd, *J* = 10.2, 1.2, 1.2 Hz, 1H), 5.79 (dt, *J* = 10.2, 2.4 Hz, 1H), 5.02 (brs, 1H), 4.68 (ddd, *J* = 7.8, 6.0, 2.4 Hz, 1H), 3.82 (ddd, *J* = 9.0, 7.2, 1.2 Hz, 1H), 3.67 (dq, *J* = 9.0, 6.0 Hz, 1H), 3.64 (dd, *J* = 10.2, 0.6 Hz, 1H), 3.10 (ddd, *J* = 19.2, 12.6, 2.4 Hz, 1H), 2.67 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.54 (dqd, *J* = 13.2, 6.6, 4.2 Hz, 1H), 2.12 (ddd, *J* = 18.6, 4.8, 2.4 Hz, 1H), 1.92-1.81 (m, 3H), 1.55-1.50 (m, 2H), 1.46 (d, *J* = 7.8 Hz, 1H), 1.45-1.40 (m, 1H), 1.36 (ddd, *J* = 14.4, 12.6, 4.2 Hz, 1H), 1.30 (d, *J* = 6.6 Hz, 3H), 1.28 (d, *J* = 6.6 Hz, 3H), 1.22-1.17 (m, 1H), 1.15 (d, *J* = 6.6 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 7.2 Hz, 3H), 0.90 (dd, *J* = 7.8, 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.5, 175.0, 133.8, 126.2, 96.6, 86.7, 81.2, 69.5, 68.5, 45.9, 43.2, 35.2, 34.7, 34.0, 32.5, 24.4, 20.8, 19.5, 18.1, 17.9, 17.8, 15.7, 11.0; HRMS (ESI) calcd for $[C_{23}H_{38}O_6 + Na]^+$: 433.2561, Found: 433.2566.

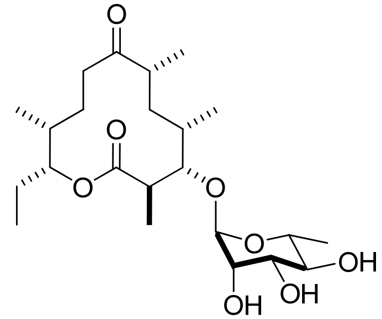
(8):



The enol compound **26** (6 mg, 0.015 mmol) and *o*-$NO_2C_6H_4SO_2NHNH_2$ (25 mg, 0.12 mmol) were dissolved in 0.5 mL of CH_2Cl_2 in a round bottom flask and cooled 0 °C under nitrogen atmosphere then triethylamine (20 µL, 0.15 mmol) was added and the reaction mixture was stirred at 0 °C for 12 hours and on completion, as monitored by TLC. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. Chromatography on silica gel eluting with 25% EtOAc/hexanes gave deoxy alcohol **8** (5.4 mg, 90 %) as viscous oil. R_f (50% EtOAc/Hexane) = 0.59; $[\alpha]^{25}_D = + 3.75$ (*c* = 0.16, $CHCl_3$); IR (thin film, cm^{-1}) 3490, 2964, 2933, 1728, 1702, 1459, 1330, 1262, 1171, 1004, 898; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.79

(d, J = 3.0 Hz, 1H), 4.66 (ddd, J = 7.8, 6.0, 2.4 Hz, 1H), 3.72 (dq, J = 9.0, 6.6 Hz, 1H), 3.52 (dd, J = 10.2, 0.6 Hz, 1H), 3.30 (ddd, J = 9.6, 9.6, 4.8 Hz, 1H), 3.10 (ddd, J = 18.6, 12.6, 2.4 Hz, 1H), 2.77 (dq, J = 10.2, 6.6 Hz, 1H), 2.53 (dqd, J = 13.8, 6.6, 4.2 Hz, 1H), 2.12 (ddd, J = 19.2, 5.4, 2.4 Hz, 1H), 1.93-1.82 (m, 4H), 1.78-1.69 (m, 2H), 1.54-1.50 (m, 2H), 1.45 (d, J = 5.4 Hz, 1H), 1.45-1.40 (m, 1H), 1.35 (ddd, J = 13.8, 12.6, 4.2 Hz, 1H), 1.29 (d, J = 7.2 Hz, 3H), 1.26 (brs, 1H), 1.23 (d, J = 6.0 Hz, 3H), 1.20-1.16 (m, 1H), 1.16 (d, J = 7.2 Hz, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.94 (d, J = 7.2 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 214.5, 175.3, 99.2, 87.9, 81.3, 72.2, 70.4, 46.0, 43.6, 35.3, 34.8, 33.9, 32.5, 30.1, 27.6, 24.5, 20.8, 19.5, 18.2, 18.1, 17.9, 15.9, 11.0; HRMS (ESI) calcd for [$C_{23}H_{40}O_6$ + Na]$^+$: 435.2717, Found: 435.2723

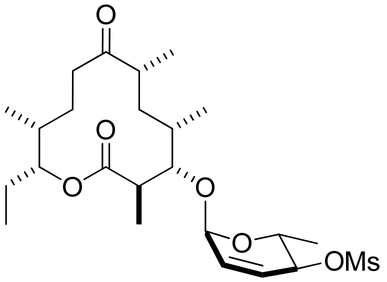
(9):



To a CH$_2$Cl$_2$ (0.3 mL) solution of allylic alcohol **26** (5.8 mg, 0.014 mmol) at 0 °C was added a solution of (50% w/v) of N-methyl morpholine N-oxide / water (10 μL). Crystalline OsO$_4$ (2.0 mg, 0.008) was added and the reaction was stirred for 12 h. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using

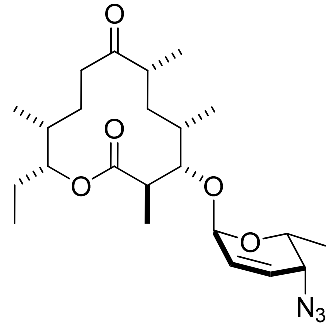
CH_2Cl_2 (1 mL) in three portions. Impurities were eluted with ether and the product was eluted with 80% EtOAc/hexanes. Pure fractions were combined and concentrated to afford triol **9** (5.3 mg, 85 %) as viscous oil. R_f (70% EtOAc/Hexane) = 0.10; $[\alpha]^{25}_{D}$ = + 22.4 (*c* = 0.25, $CHCl_3$); IR (thin film, cm^{-1}) 3380, 2964, 2931, 1720, 1702, 1458, 1372, 1261, 1174, 1062, 1036, 989, 803, 731; ^1H NMR (600 MHz, $CDCl_3$) δ 4.82 (d, *J* = 1.2 Hz, 1H), 4.65 (ddd, *J* = 6.6, 6.6, 1.8 Hz, 1H), 4.02 (ddd, *J* = 4.8, 3.0, 1.8 Hz, 1H), 3.80 (dq, *J* = 9.6, 6.0 Hz, 1H), 3.73 (ddd, *J* = 9.6, 7.2, 3.6 Hz, 1H), 3.54 (d, *J* = 10.2 Hz, 1H), 3.47 (ddd, *J* = 9.6, 9.0, 3.0 Hz, 1H), 3.07 (ddd, *J* = 18.6, 12.6, 2.4 Hz, 1H), 2.76 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.53 (ddd, *J* = 13.2, 7.2, 4.2 Hz, 1H), 2.46 (d, *J* = 7.2 Hz, 1H), 2.21 (d, *J* = 3.0 Hz, 1H), 2.16 (d, *J* = 5.4 Hz, 1H), 2.13 (ddd, *J* = 19.2, 6.0, 2.4 Hz, 1H), 1.89-1.84 (m, 3H), 1.55-1.50 (m, 2H), 1.30 (d, *J* = 6.0 Hz, 3H), 1.28 (d, *J* = 7.2 Hz, 3H), 1.26 (br s, 1H), 1.23-1.20 (m, 1H), 1.16 (d, *J* = 6.6 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 6.6Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.3, 174.9, 102.7, 89.6, 81.5, 73.7, 71.9, 71.4, 68.6, 45.9, 43.6, 35.2, 34.6, 33.9, 32.6, 24.5, 20.8, 19.5, 18.2, 18.0, 17.4, 15.8, 11.0; HRMS (ESI) calcd for $[C_{23}H_{40}O_8 + Na]^+$: 467.2615, Found: 467.2621.

(C):



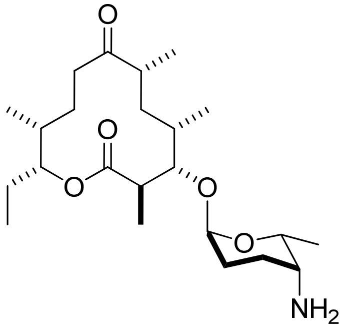
To a solution of allylic alcohol **26** (124.8 mg, 0.30 mmol) and methanesulphonyl chloride (40 μL, 0.52 mmol) in dry CH_2Cl_2 (1.0 mL) at 0 °C, was added triethylamine (55 μL, 0.73 mmol). After stirring 7 h at room temperature, water (1 mL) was added and then the mixture was extracted with EtOAc (3 x 5 mL), dried (Na_2SO_4), concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 20% EtOAc/hexane to give mesylate **C** (134 mg, 90%) as viscous oil; R_f = 0.45 (33% EtOAc/hexanes); $[\alpha]^{25}_{D}$ = + 50.66 (*c* = 0.45, $CHCl_3$); IR (thin film, cm^{-1}) 2966, 2934, 1720, 1701, 1459, 1359, 1175, 1013, 952, 901; ^1H NMR (600 MHz, $CDCl_3$) δ 6.06 (ddd, *J* = 10.2, 1.2, 1.2 Hz, 1H), 5.90 (ddd, *J* = 10.2, 2.4, 1.8 Hz, 1H), 5.05 (brs, 1H), 4.82 (dddd, *J* = 9.0, 1.8, 1.8, 1.2 Hz, 1H), 4.68 (ddd, *J* = 6.6, 6.6, 1.8 Hz, 1H), 3.97 (dq, *J* = 9.0, 6.0 Hz, 1H), 3.63 (d, *J* = 9.6 Hz, 1H), 3.09 (ddd, *J* = 18.6, 12.6, 2.4 Hz, 1H), 3.06 (s, 3H), 2.77 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.54 (dqd, *J* = 14.4, 6.6, 4.2 Hz, 1H), 2.12 (ddd, *J* = 18.6, 5.4, 2.4 Hz, 1H), 1.91-1.82 (m, 3H), 1.55-1.50 (m, 2H), 1.46-1.41 (m, 1H), 1.35 (ddd, *J* = 13.8, 12.0, 3.6 Hz, 1H), 1.32 (d, *J* = 6.0 Hz, 3H), 1.26 (d, *J* = 7.2 Hz, 3H), 1.24-1.18 (m, 1H), 1.16 (d, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 7.2 Hz, 3H), 0.91 (dd, *J* = 7.8, 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.4, 174.9, 129.1, 128.7, 96.4, 87.2, 81.3, 76.8, 65.1, 45.9, 43.1, 38.9, 35.2, 34.6, 34.0, 32.5, 24.4, 20.8, 19.5, 18.1, 17.9, 17.7, 15.7, 11.0; HRMS (ESI) calcd for $[C_{24}H_{40}O_8S + Na]^+$: 511.2336, Found: 511.2342.

(27):



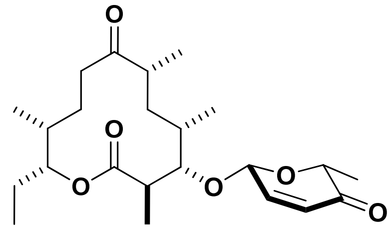
To a solution mesylate **C** (127.5 mg, 0.26 mmol) in 2.0 mL of actone-H_2O (6:1) was added NaN_3 (84.8 mg, 1.31 mmol) under argon atmosphere. The solution was stirred at room temperature for 12 h. Water (1 mL) was added and then the mixture was extracted with EtOAc (3 x 5 mL), dried (Na_2SO_4), and then concentrated under reduced pressure to give a residue. Chromatography on silica gel eluting with 5% EtOAc/hexane gave allylic azide **27** (95 mg, 84%): white amorphous solid; R_f = 0.61 (33% EtOAc/hexane); $[\alpha]^{25}_D$ = -152.59 (*c* = 0.27, $CHCl_3$); IR (thin film, cm^{-1}) 2964, 2934, 2100, 1722, 1702, 1458, 1172, 1093, 1013, 900; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.17 (dd, *J* = 9.6, 3.0 Hz, 1H), 6.10 (ddd, *J* = 9.6, 5.4, 1.2 Hz, 1H), 5.08 (d, *J* = 2.4 Hz, 1H), 4.68 (ddd, *J* = 6.6, 6.6, 1.8 Hz, 1H), 4.22 (qd, *J* = 6.6, 2.4 Hz, 1H), 3.68 (d, *J* = 10.2 Hz, 1H), 3.14 (dd, *J* = 5.4, 2.4 Hz, 1H), 3.08 (ddd, *J* = 18.6, 12.6, 2.4 Hz, 1H), 2.76 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.55 (dqd, *J* = 14.4, 6.6, 4.2 Hz, 1H), 2.12 (ddd, *J* = 18.6, 5.4, 2.4 Hz, 1H), 1.91-1.81 (m, *3*H), 1.54-1.50 (m, 2H), 1.45-1.40 (m, 1H), 1.35 (ddd, *J* = 13.8, 12.6, 4.2 Hz, 1H), 1.32 (d, *J* = 6.6 Hz, 3H), 1.26 (d, *J* = 6.6 Hz, 3H), 1.24-1.19 (m, 1H), 1.15 (d, *J* = 6.6 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.3, 174.8, 130.0, 125.2, 96.5, 86.8, 81.3, 66.7, 55.3, 45.9, 43.2, 35.2, 34.6, 34.0, 32.5, 24.4, 20.8, 19.5, 18.1, 17.9, 17.1, 15.7, 11.0; HRMS (ESI) calcd. for $[C_{23}H_{37}N_3O_5 + Na]^+$: 458.2625, Found: 458.2631.

(10):



To a solution of allylic azide **27** (86 mg, 0.19 mmol) in dry MeOH (2.0 mL) was added Pd/C (50 mg) and the mixture was stirred under H_2 at an 100 psi pressure for 7 h at room temperature. The catalyst was filtered off through a short pad of Celite, concentrated under reduced pressure. The resulting crude product was pipetted directly on to a reversed phase column eluting with 80% MeOH/H_2O to afford deoxy amine **10** (51 mg, 63 %) as viscous oil. R_f (80% MeOH /H_2O) = 0.17(reversed phase TLC); $[\alpha]^{25}_D = +57.85$ (c = 0.81, MeOH); IR (thin film, cm^{-1}) 3383, 2964, 2933, 2878, 1723, 1702, 1456, 1367, 1170, 1004, 899; ^{1}H NMR (600 MHz, CD_3OD) δ 4.85 (d, J = 3.0 Hz, 1H), 4.62 (ddd, J = 9.0, 4.2, 1.8 Hz, 1H), 4.13 (qd, J = 6.6, 1.8 Hz, 1H), 3.50 (dd, J = 10.2, 1.2 Hz, 1H), 3.15 (ddd, J = 19.2, 12.0, 1.8 Hz, 1H), 2.80 (dq, J = 9.6, 6.6 Hz, 1H), 2.76 (br s, 1H), 2.50 (dqd, J = 15.0, 7.2, 4.2 Hz, 1H), 2.24 (ddd, J = 18.6, 4.8, 2.4 Hz, 1H), 2.05 (dddd, J = 13.2, 13.2, 4.2, 4.2 Hz, 1H), 1.95-1.89 (m, 2H), 1.84-1.76 (m, 2H), 1.65-1.55 (m, 4H), 1.50 (dddd, J = 15.0, 12.0, 5.4, 3.6 Hz, 1H), 1.39 (ddd, J = 13.8, 12.0, 4.2 Hz, 1H), 1.26 (d, J = 7.2 Hz, 3H), 1.18 (d, J = 7.2 Hz, 3H), 1.16-1.12 (m, 1H), 1.10 (d, J = 6.6 Hz, 3H), 1.02 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 217.1, 177.1, 101.2, 88.6, 82.9, 68.3, 49.6, 47.3, 44.8, 36.7, 35.9, 35.1, 33.7, 26.8, 25.5, 25.2, 21.7, 19.6, 18.4, 18.3, 17.6, 16.4, 11.4; HRMS (ESI) calcd for $[C_{23}H_{41}NO_5 + H]^+$: 412.3058, Found 412.3061.

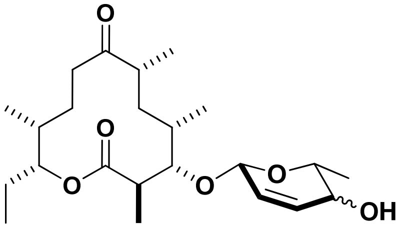
(28):



A CH_2Cl_2 (1.5 mL) solution of Boc-enone **13d** (366 mg, 1.60 mmol) and 10-deoxymethynolide alcohol **16** (120 mg, 0.41 mmol) was cooled to 0 °C. A CH_2Cl_2 (1.5 mL) solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (41 mg, 2.5 mol%) and PPh_3 (42 mg, 10 mol%) was added to the reaction mixture at 0 °C. The reaction mixture was stirred at 0 °C for 2 hours.

The reaction mixture was quenched with 10 mL of satd. aq. $NaHCO_3$, extracted (3 x 10 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 20% EtOAc/hexanes to give enone **28** (131 mg, 0.32 mmol, 80%) as viscous oil. R_f (50% EtOAc/hexanes) = 0.45; $[\alpha]_D^{25}$ = -12 (*c* = 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 2967, 2934, 1725, 1703, 1459, 1171, 1018, 899; ^1H NMR (600 MHz, $CDCl_3$) δ 6.92 (dd, *J* = 10.2, 1.2 Hz, 1H), 6.12 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.34 (d, *J* = 1.2 Hz, 1H), 4.70 (ddd, *J* = 7.2, 6.6, 1.8 Hz, 1H), 4.14-4.10 (m, 1H), 4.11 (m, 6.6, 1.2), 3.68 (dd, *J* = 10.2, 1.2 Hz, 1H), 3.11 (ddd, *J* = 18.6, 12.6, 2.4 Hz, 1H), 2.92 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.56 (dqd, *J* = 13.8, 6.6, 4.2 Hz, 1H), 2.14 (ddd, *J* = 18.6, 5.4, 2.4 Hz, 1H), 1.89-1.82 (m, 3H), 1.55-1.51 (m, 2H), 1.48-1.39 (m, 2H), 1.42 (d, *J* = 6.6 Hz, 3H), 1.26 (d, *J* = 6.6 Hz, 3H), 1.18-1.14 (m, 1H), 1.13 (d, *J* = 6.6 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.5, 196.6, 174.4, 147.5, 129.2, 98.6, 88.2, 81.3, 75.3, 46.0, 44.1, 34.6, 34.3, 34.0, 32.4, 24.4, 20.8, 19.4, 18.1, 17.1, 15.9, 15.8, 11.0; CIHRMS calcd for $[C_{23}H_{36}O_6 + Na]^+$: 431.2409, Found 431.2403.

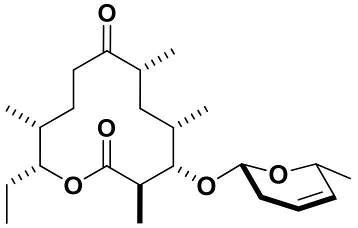
(29):



The enone compound **28** (90 mg, 0.22 mmol) was dissolved in 0.3 mL of CH_2Cl_2 and 0.3 mL MeOH in round bottom flask and cooled -78 °C then NaBH$_4$ (9.2 mg, 0.24 mmol) was added and the reaction mixture was stirred at -78 °C for 3 hours and on completion, monitored by TLC, reaction mixture was diluted with ether and was quenched with 2 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 25% EtOAc/hexanes to give allylic alcohol **29** (77 mg, 0.19 mmol, 85%) as viscous oil. R_f (50% EtOAc/hexanes) = 0.35; $[\alpha]_D^{25}$ = + 7 (c = 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 3329, 2939, 22834, 1721, 1697, 1456, 1172, 1032, 900; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.92 (ddd, J = 10.2, 2.4, 1.8 Hz, 1H), 5.82 (ddd, J = 10.2, 1.8, 1.2 Hz, 1H), 5.06 (br s, 1H), 4.70 (ddd, J = 5.4, 5.4, 2.4 Hz, 1H), 3.93 (ddd, J = 7.8, 7.2, 1.8 Hz, 1H), 3.60 (d, J = 10.8 Hz, 1H), 3.50 (m, 1H), 3.10 (ddd, J = 18.6, 12.6, 2.4 Hz, 1H), 2.85 (dq, J = 10.2, 6.6 Hz, 1H), 2.55 (dqd, J = 13.8, 6.6, 4.2 Hz, 1H), 2.11 (ddd, J = 18.6, 5.4, 3.0 Hz, 1H), 1.88-1.82 (m, 3H), 1.54 -1.50 (m, 2H), 1.46-1.40 (m, 1H), 1.33 (d, J = 6.0 Hz, 3H), 1.27-1.23 (m, 1H), 1.23 (d, J = 6.6 Hz, 3H), 1.14-1.09 (m, 1H), 1.13 (d, J = 7.2 Hz, 3H), 1.09 (d, J = 6.0 Hz, 3H), 0.93 (d, J = 7.2 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C

NMR (150 MHz, $CDCl_3$) δ 214.5, 174.5, 132.8, 128.9, 99.4, 87.5, 80.9, 74.5, 69.0, 45.9, 44.0, 34.5, 34.2, 33.8, 32.2, 24.2, 20.6, 19.2, 18.1, 18.0, 16.9, 15.5, 10.7; CIHRMS calcd for $[C_{23}H_{38}O_6 + Na^+]$: 433.2566, Found 433.2559.

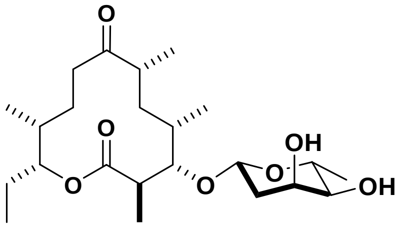
(30):



A flask was charged with dry N-methyl morpholine (NMM) 0.8 mL, triphenyl phosphine (126 mg, 0.48 mmol) and was cooled to -30 °C under Ar atmosphere. Diethylazodicarboxylate (69 μL, 0.44 mmol) was added and the reaction was stirred for 25 min, Allylic alcohol **29** (60 mg, 0.15 mmol) was added in a 1M solution of NMM and the reaction mixture was stirred for 10 min, followed by addition of o-nitrobenzenesulfonyl hydrazide (NBSH) (89 mg, 0.44 mmol). The reaction was stirred at -30 °C for 2h and was monitored by TLC, upon consumption of starting material, warm up to room temperature and stirred for another 4h. The reaction mixture was diluted with ether (10 mL) and was quenched with 5 mL of satd aq $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 30% EtOAc/hexanes to give **30** (29 mg, 0.07 mmol, 40%) of viscous product: R_f (50% EtOAc/hexanes) = 0.60; $[\alpha]_D^{25} = +20$ ($c = 0.5$, CH_2Cl_2);

IR (thin film, cm^{-1}) 2959, 2932, 1756, 1700, 1429, 1131, 1017, 985; ^1H NMR (600 MHz, $CDCl_3$) δ 5.64 (dddd, *J* = 10.2, 4.8, 2.4, 2.4 Hz, 1H), 5.57 (dt, *J* = 10.2, 1.2 Hz, 1H), 4.69 (ddd, *J* = 7.8, 5.4, 2.4 Hz, 1H), 4.60 (dd, *J* = 8.4, 3.6 Hz, 1H), 4.27 (m, 1H), 3.54 (d, *J* = 10.2 Hz, 1H), 3.12 (ddd, *J* = 19.2, 12.0, 2.4 Hz, 1H), 2.85 (dd, *J* = 10.2, 6.6 Hz, 1H), 2.57 (dqd, *J* = 13.8, 6.6, 4.2 Hz, 1H), 2.20-2.15 (m, 2H), 2.11 (ddd, *J* = 19.2, 5.4, 3.0 Hz, 1H), 1.89-1.81 (m, 3H), 1.55-1.44 (m, 4H), 1.24 (d, *J* = 7.2 Hz, 3H), 1.23 (d, *J* = 6.6 Hz, 3H), 1.22 (d, *J* = 6.6 Hz, 3H), 1.14-1.08 (m, 1H), 1.13 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.6, 174.6, 131.3, 122.7, 100.9, 86.4, 80.8, 71.1, 45.9, 44.1, 34.5, 34.1, 33.8, 32.1, 31.0, 24.2, 20.7, 20.6, 19.2, 18.0, 16.9, 15.4, 10.7; CIHRMS calcd for $[C_{23}H_{38}O_5 + Na]^+$: 417.2617, Found 417.2613.

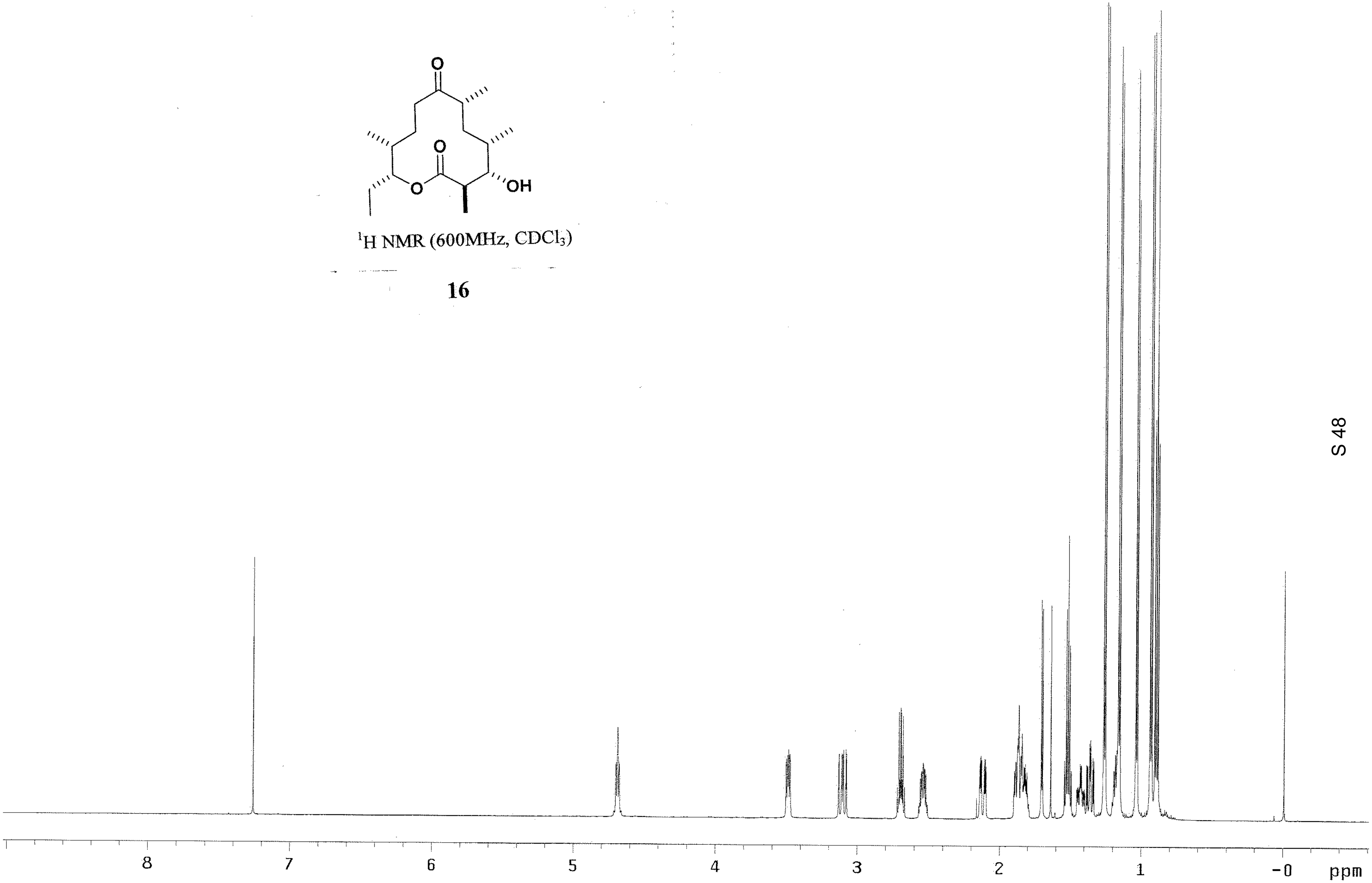
(11):



To a CH_2Cl_2 (0.5 mL) solution of ene **30** (10 mg, 0.03 mmol) at 0 °C was added a solution of (50% w/v) of *N*-methyl morpholine *N*-oxide / water (10 μL). Crystalline OsO_4 (0.3 mg, 10 mol %) was added and the reaction was stirred for 12 h. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. Impurities were eluted with ether and the product was eluted with

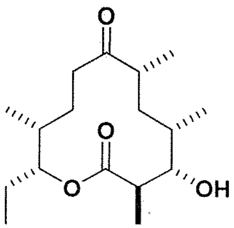
MeOH/EtOAc/hexanes (10:40:50). Pure fractions were combined and concentrated to afford diol **11** (8 mg, 0.02 mmol, 70 %) as viscous oil. R_f (90% EtOAc/MeOH) = 0.20; $[\alpha]_D^{25}$ = - 12 (c = 0.5, CH_2Cl_2); IR (thin film, cm^{-1}) 3442, 2928, 2919, 1741, 1711, 1459, 1167, 1080, 989, 734; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.78 (dd, J = 9.6, 1.8 Hz, 1H), 4.67 (ddd, J = 7.8, 5.4, 1.8 Hz, 1H), 4.10 (d, J = 3.6 Hz, 1H), 3.68 (dq, J = 9.6, 6.6 Hz, 1H), 3.50 (d, J = 10.8 Hz, 1H), 3.28 (dd, J = 3.6, 3.6 Hz, 1H), 3.10 (ddd, J = 18.6, 12.6, 2.4 Hz, 1H), 2.80 (dq, J = 10.2, 6.6 Hz, 1H), 2.54 (dqd, J = 13.8, 6.6, 4.2 Hz, 1H), 2.49 (s, 1H), 1.29 (d, J = 5.4 Hz, 1H), 2.14 (ddd, J = 13.8, 3.6, 2.4 Hz, 1H), 2.10 (ddd, J = 18.6, 5.4, 3.0 Hz, 1H), 1.84 (m, 3H), 1.69 (ddd, J = 13.8, 10.2, 2.4 Hz, 1H), 1.53-1.48 (m, 2H), 1.45-1.38 (m, 2H), 1.26 (d, J = 6.0 Hz, 3H), 1.21 (d, J = 6.6 Hz, 3H), 1.12 (d, J = 7.2 Hz, 3H), 1.10-1.05 (m, 1H), 1.06 (d, J = 6.0 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.6, 174.6, 99.4, 86.9, 80.8, 73.0, 69.2, 68.3, 45.9, 44.0, 37.8, 34.5, 34.1, 33.8, 32.1, 24.2, 20.6, 19.2, 17.9, 16.9, 15.4, 10.7; CIHRMS calcd for $[C_{23}H_{40}O_7 + Na]^+$: 451.2671, Found 451.2665.

Section C: ^{1}H and ^{13}C NMR Spectra



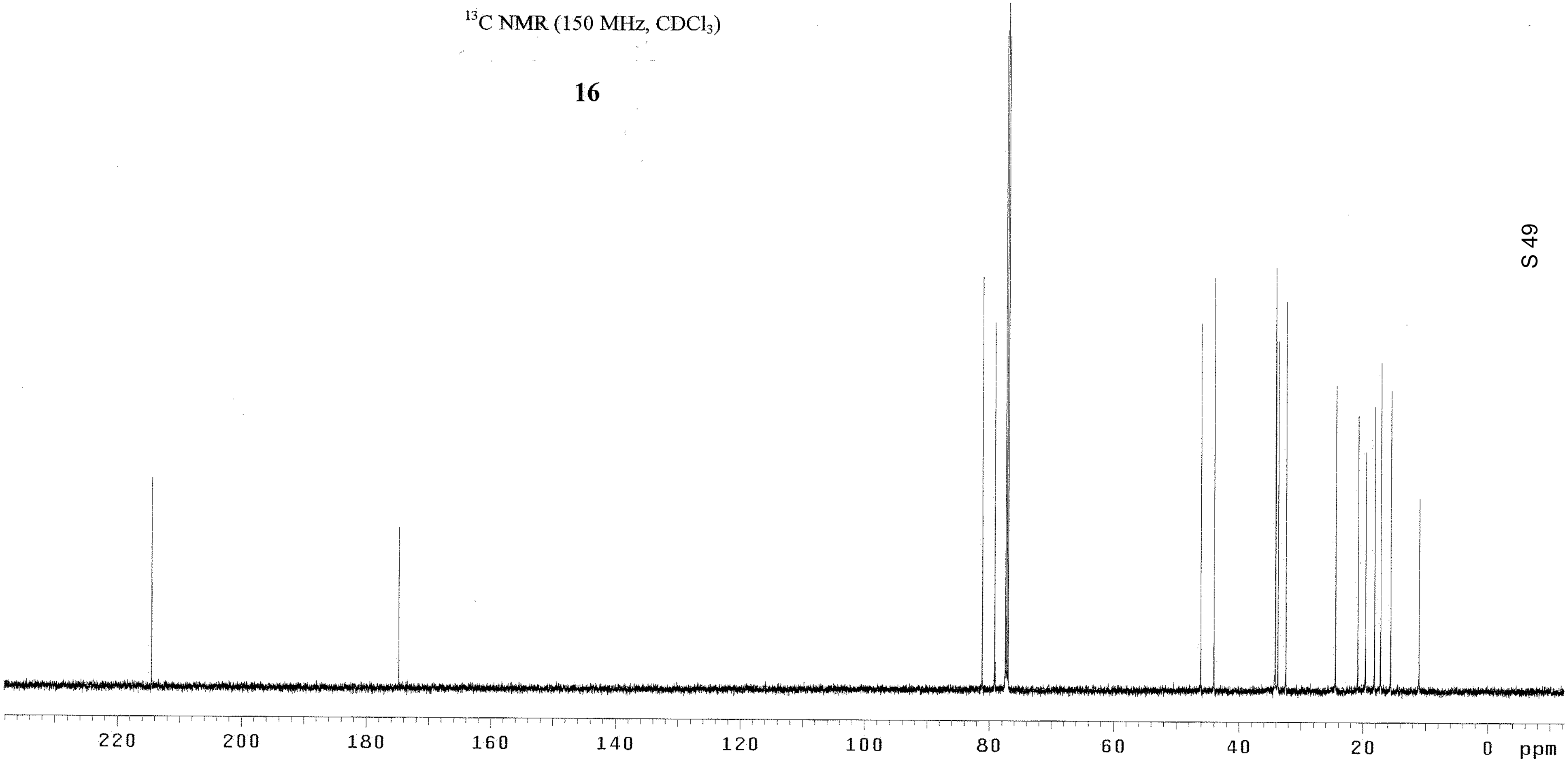
^{1}H NMR (600MHz, CDCl$_3$)

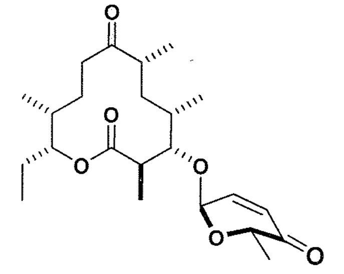
16



^{13}C NMR (150 MHz, CDCl$_3$)

16





^{1}H NMR (600MHz, CDCl$_3$)

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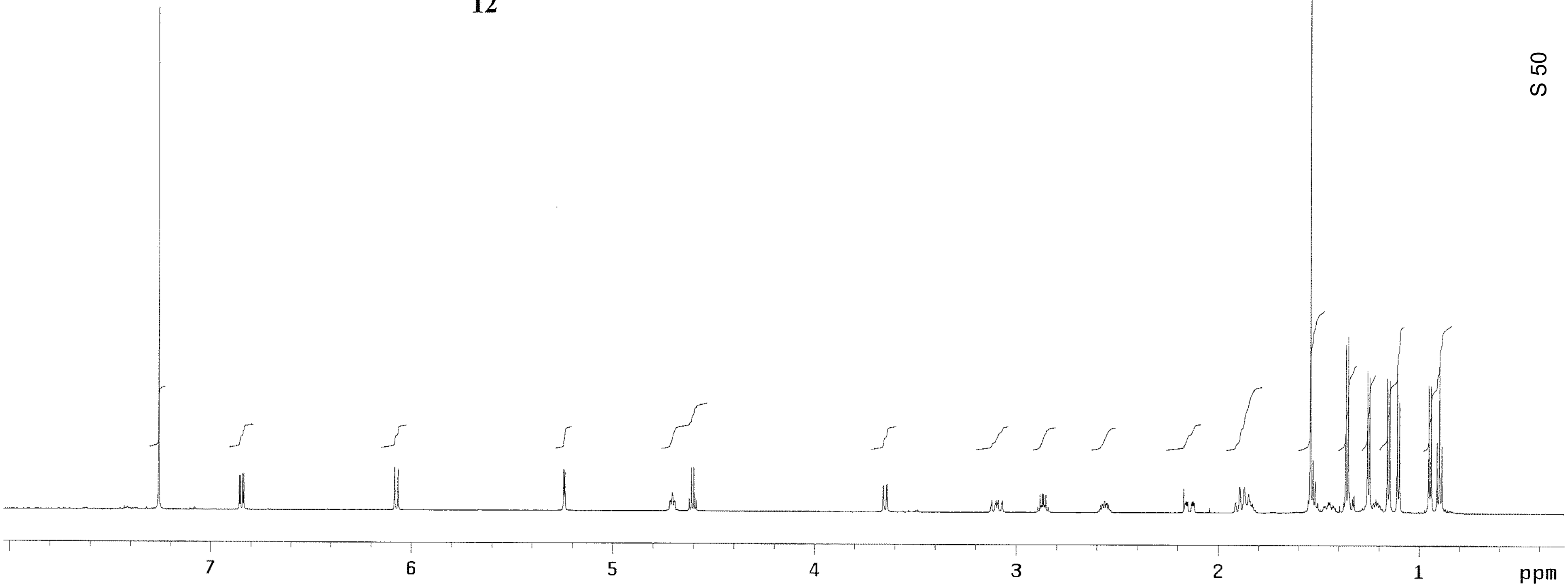

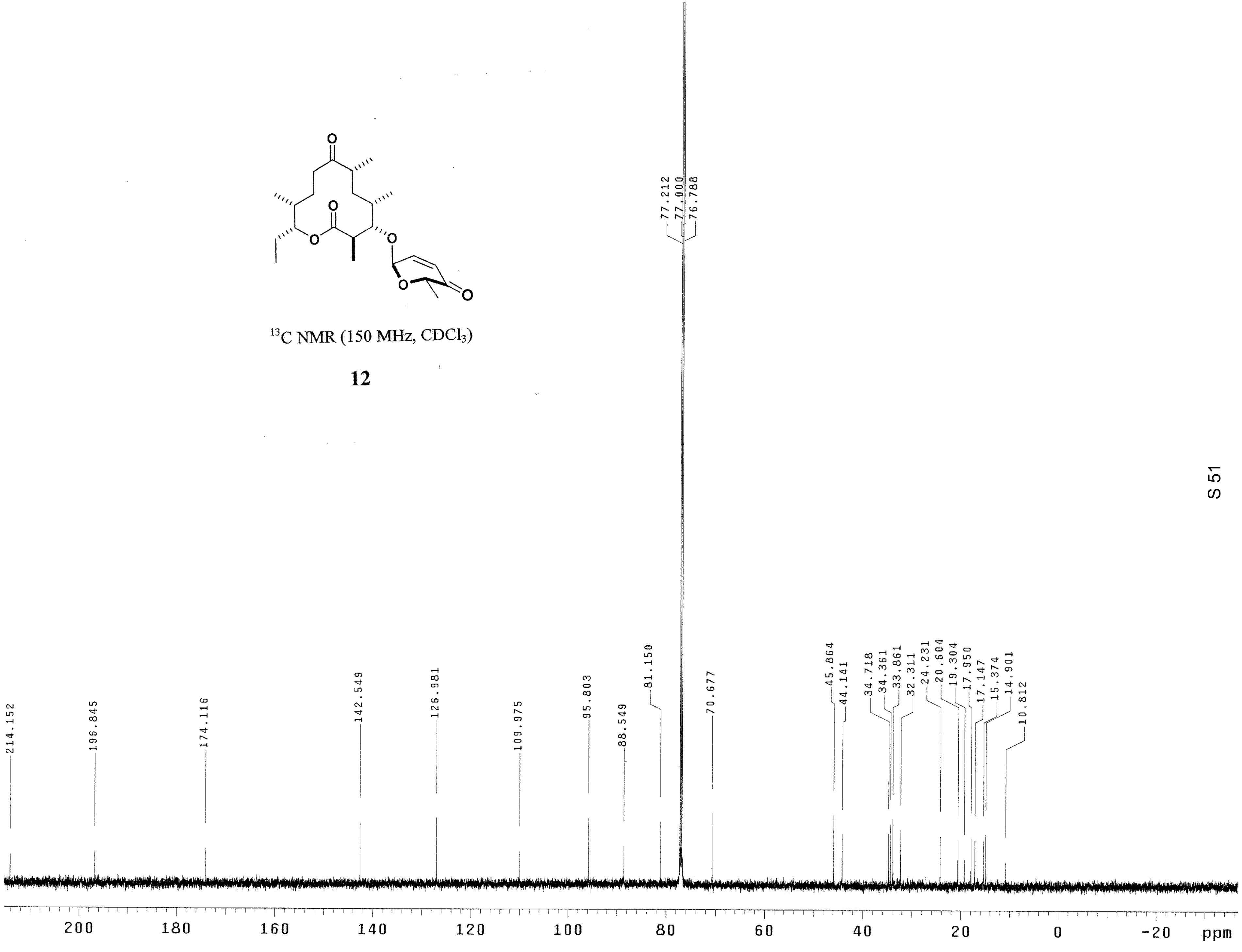

^{13}C NMR (150 MHz, CDCl$_3$)

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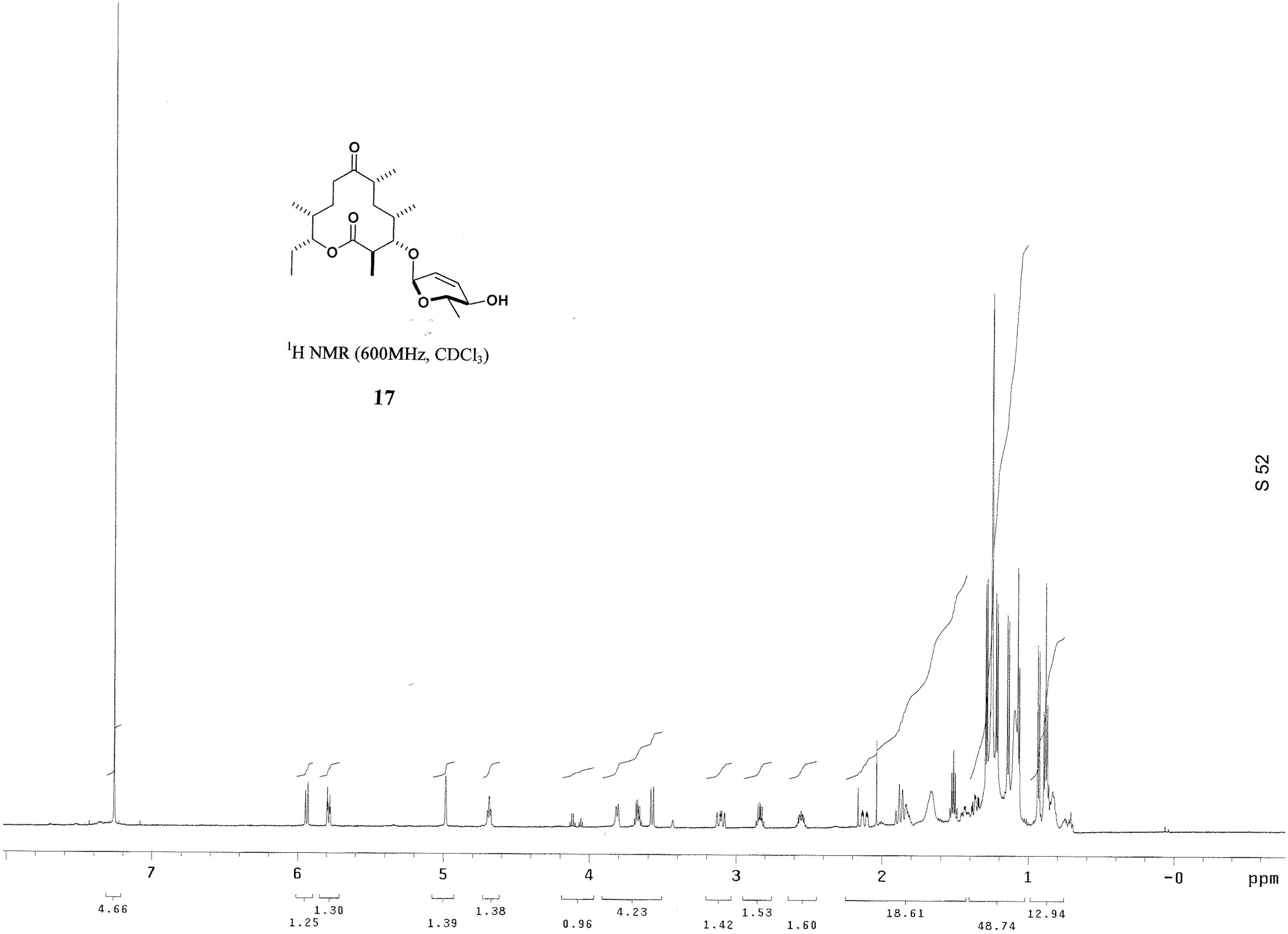

^{1}H NMR (600MHz, CDCl$_3$)

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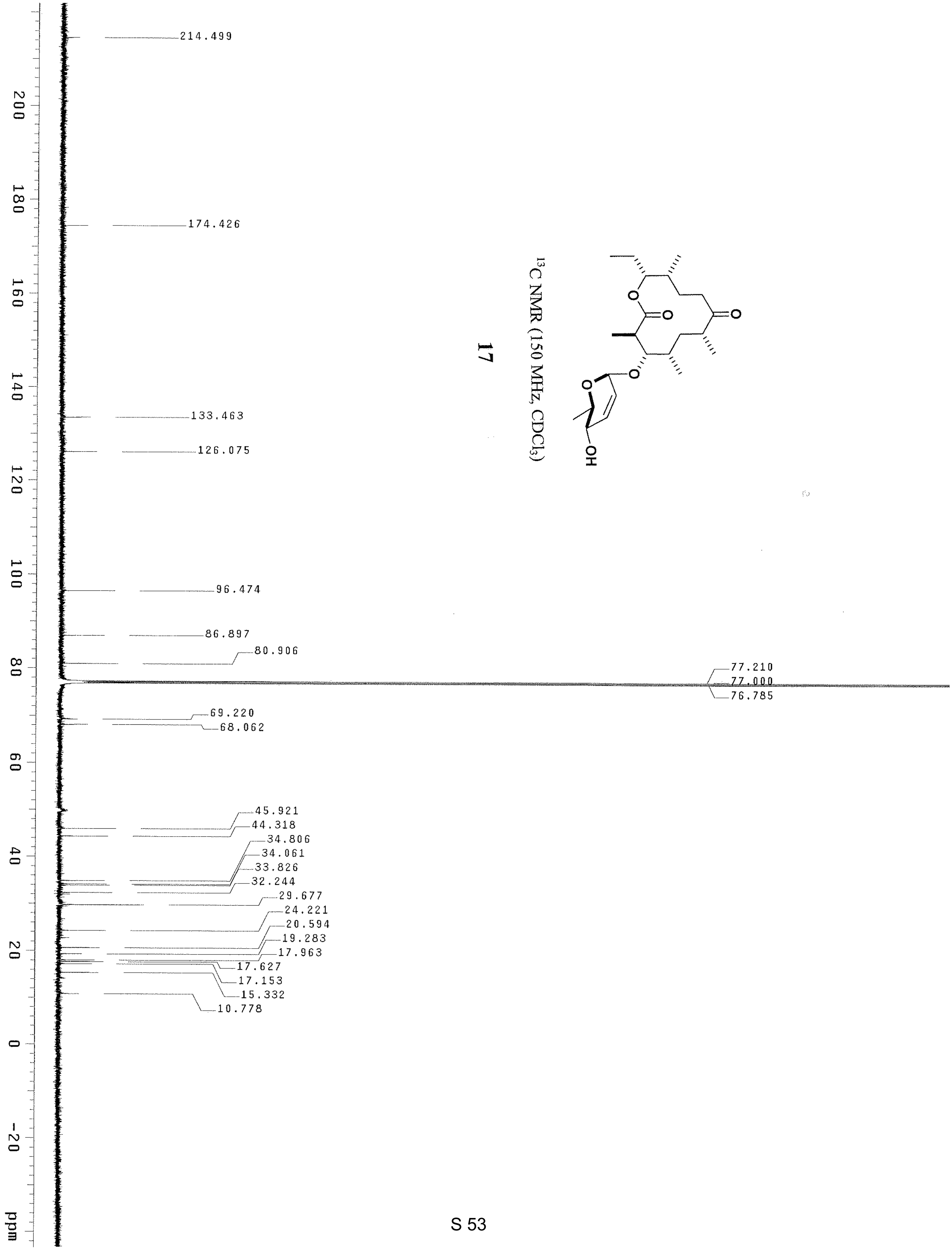

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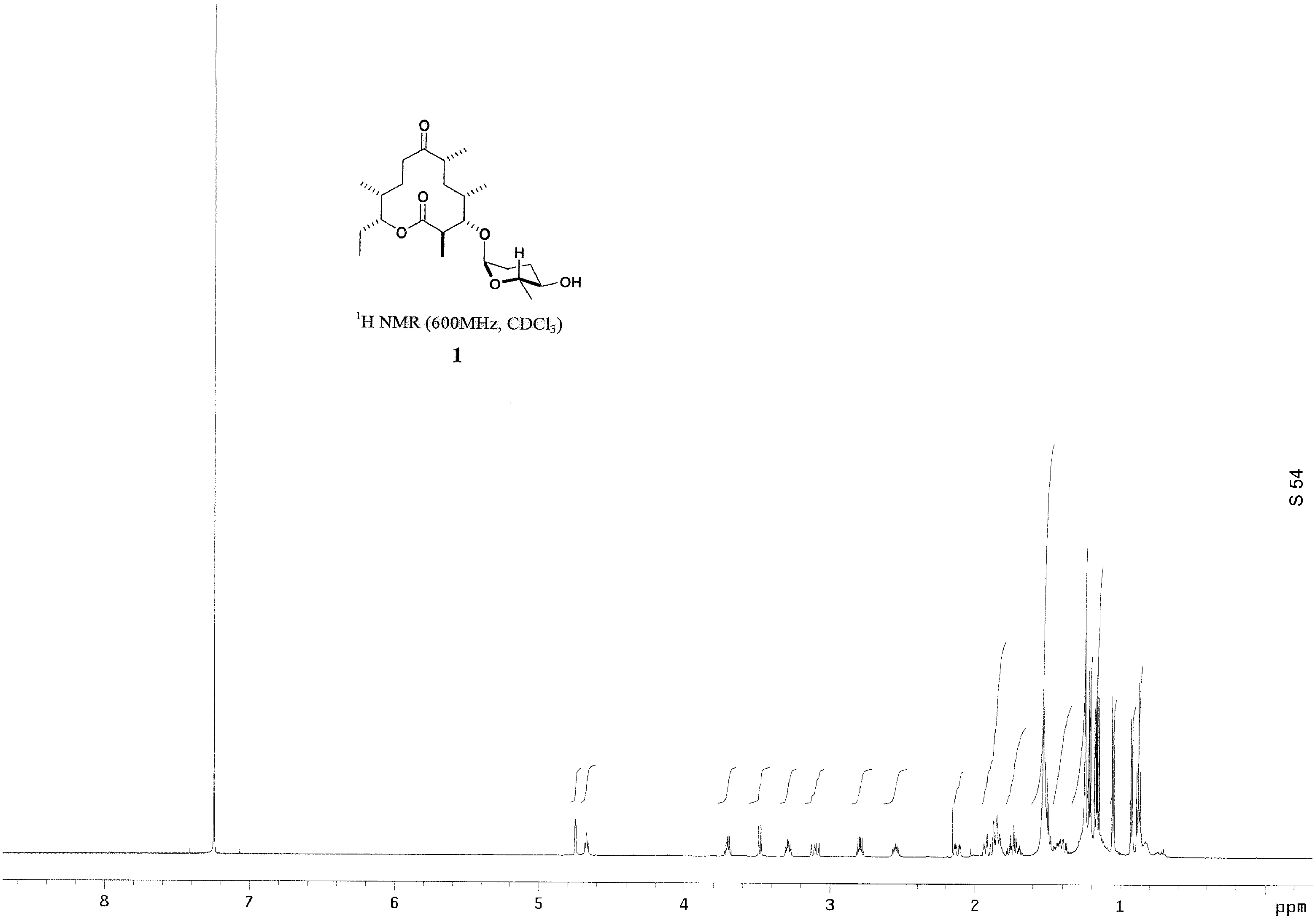
^{13}C NMR (150 MHz, CDCl$_3$)



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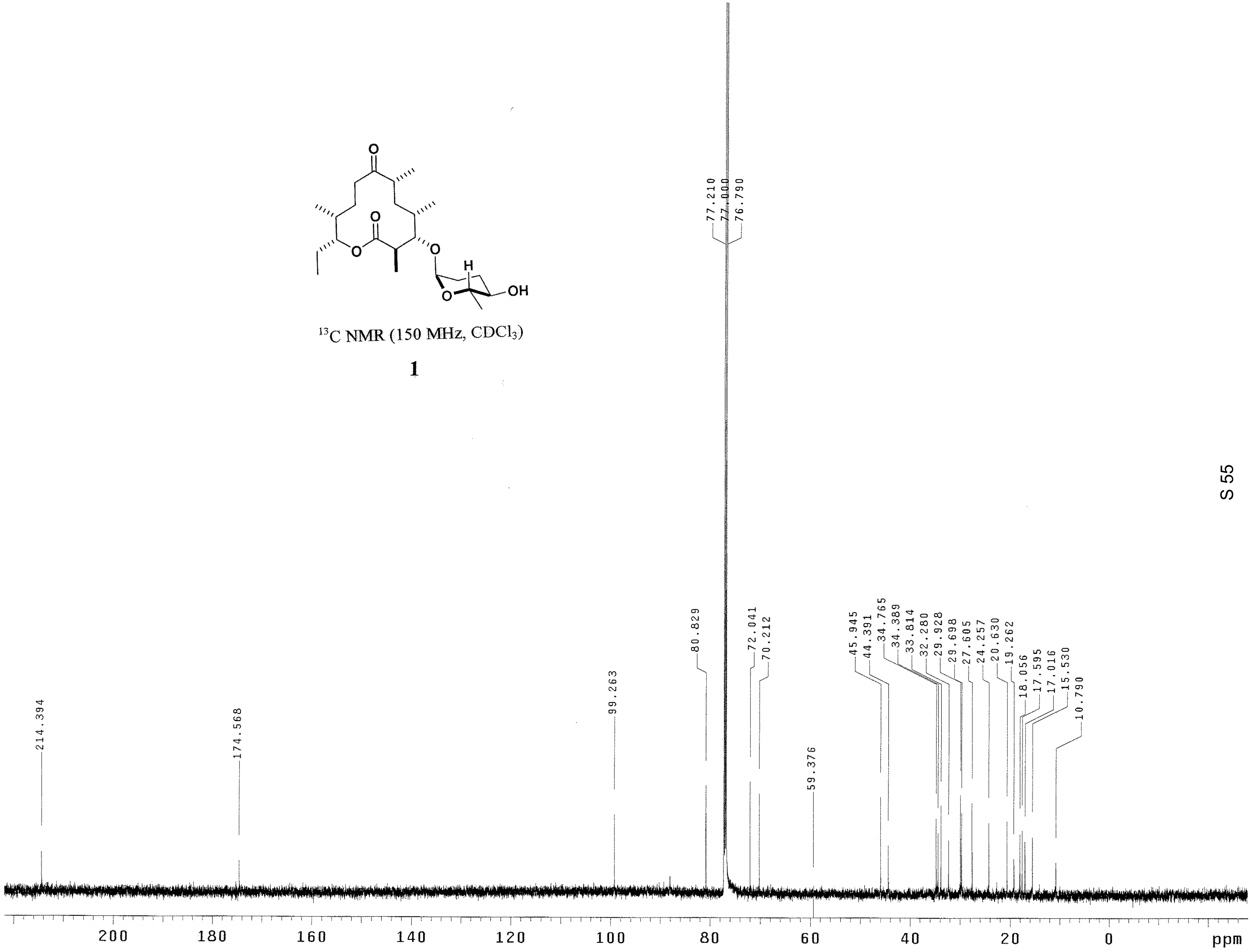

^{13}C NMR (150 MHz, CDCl$_3$)

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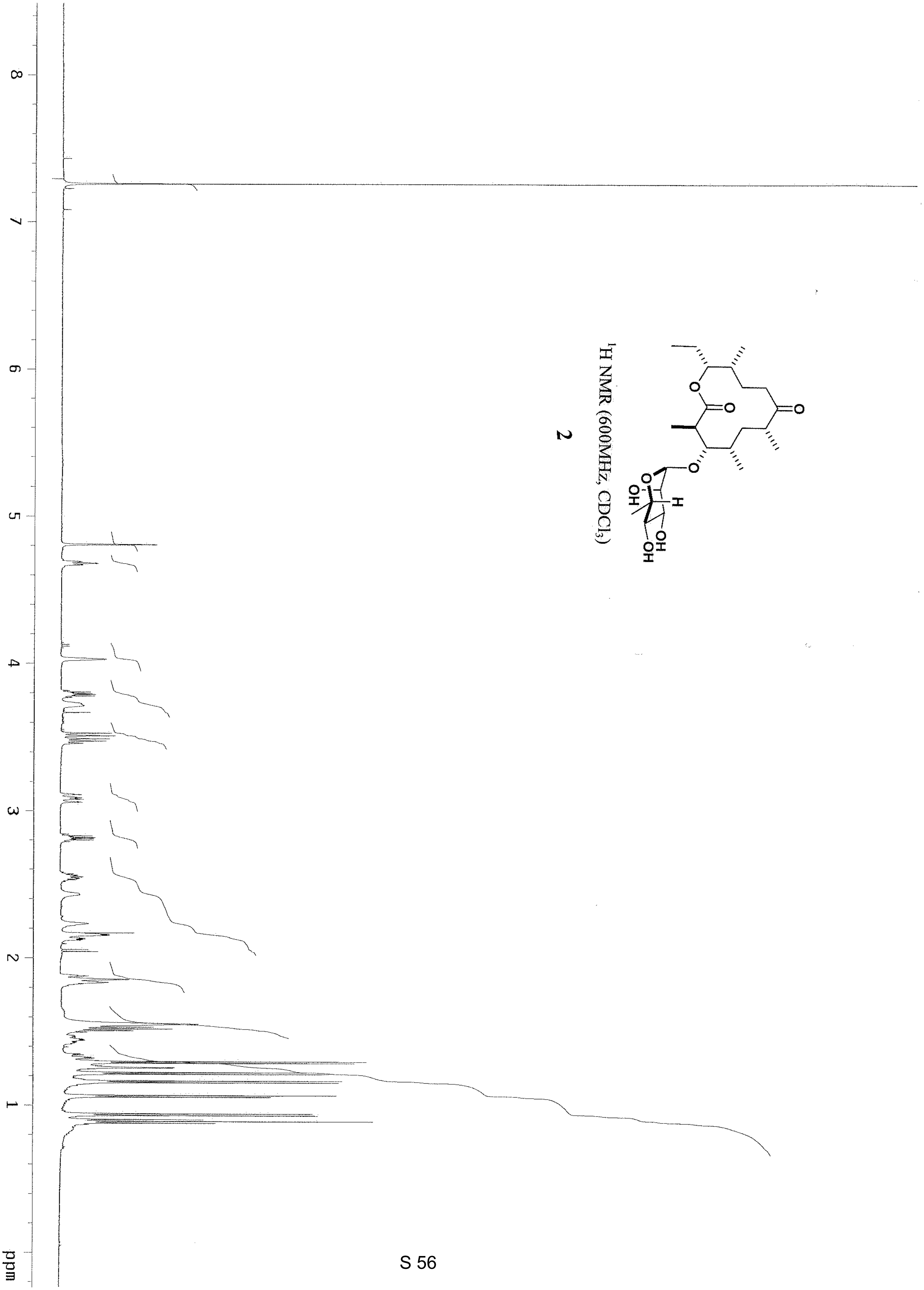

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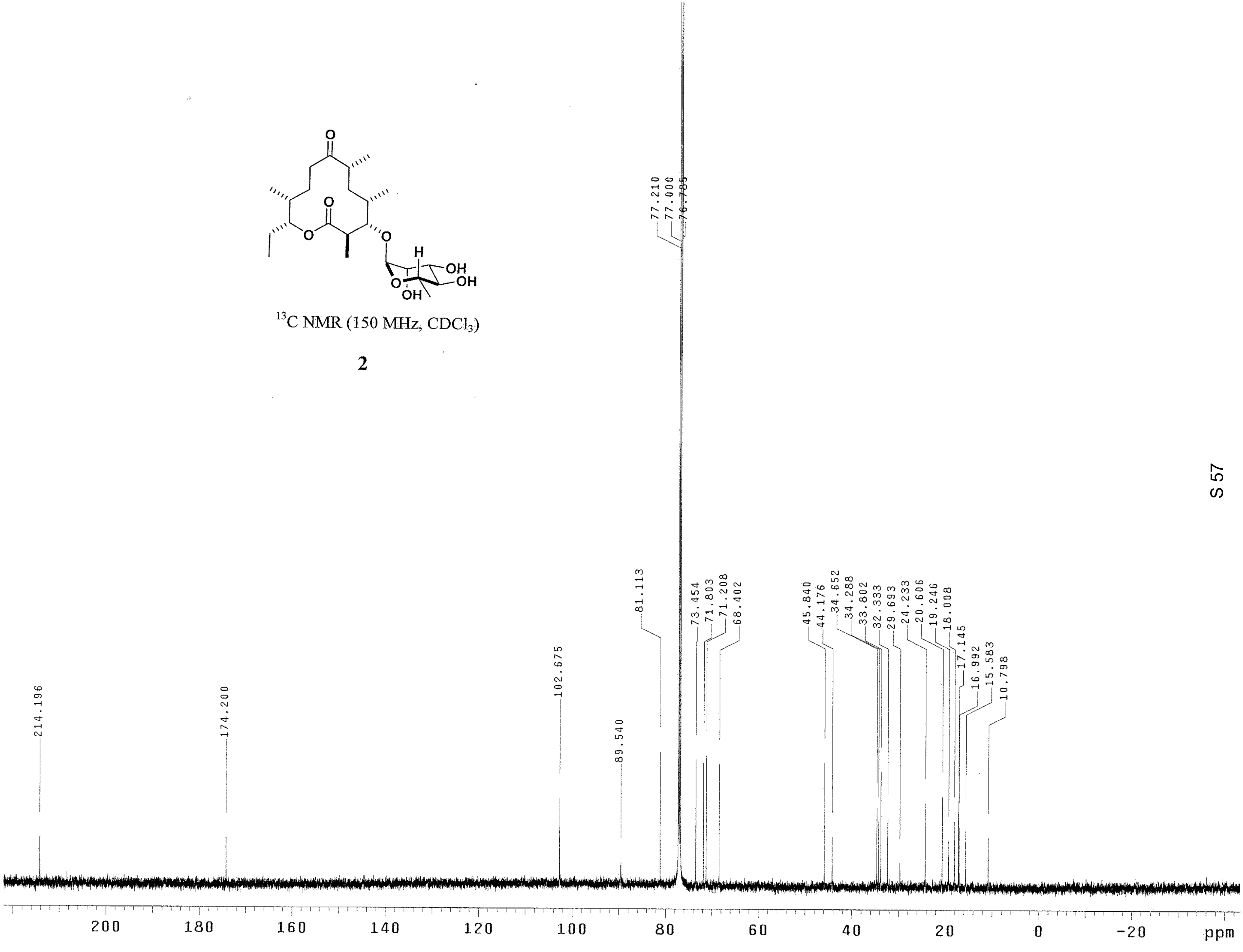

^{13}C NMR (150 MHz, CDCl$_3$)

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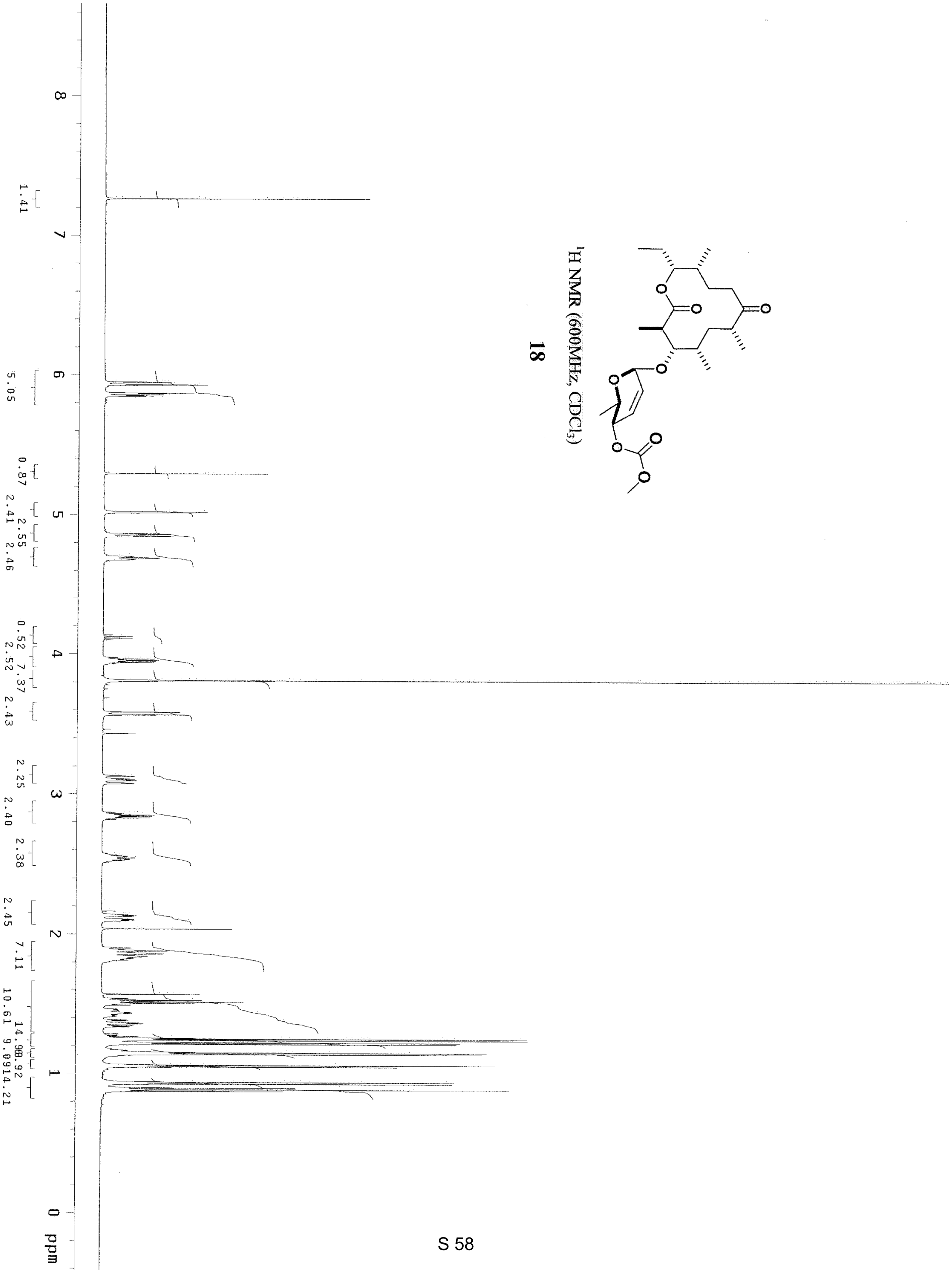

^{1}H NMR (600MHz, CDCl$_3$)

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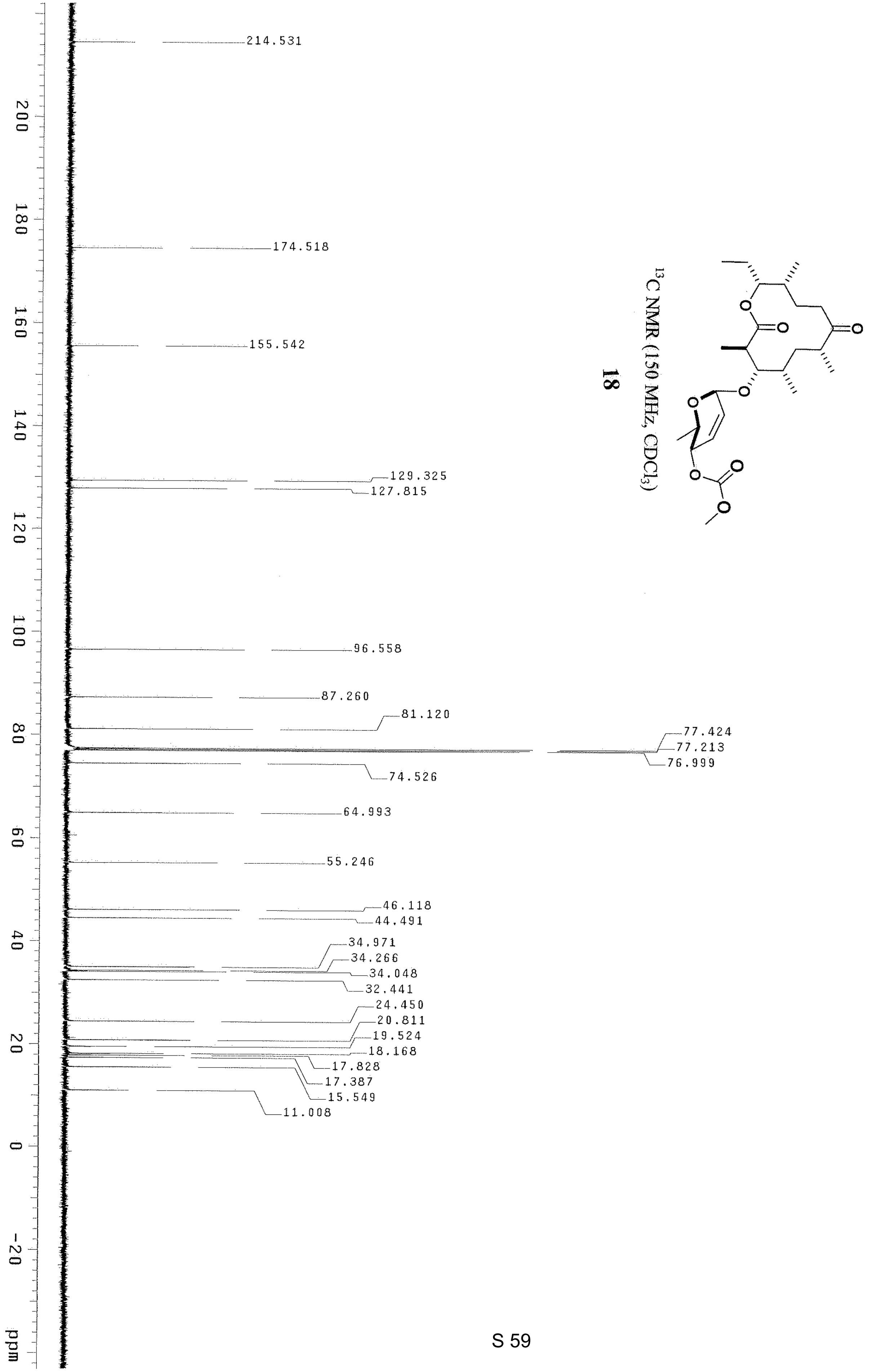

^{13}C NMR (150 MHz, CDCl$_3$)

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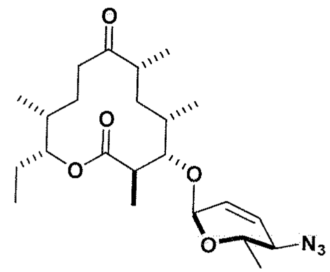

^{1}H NMR (600MHz, CDCl$_3$)

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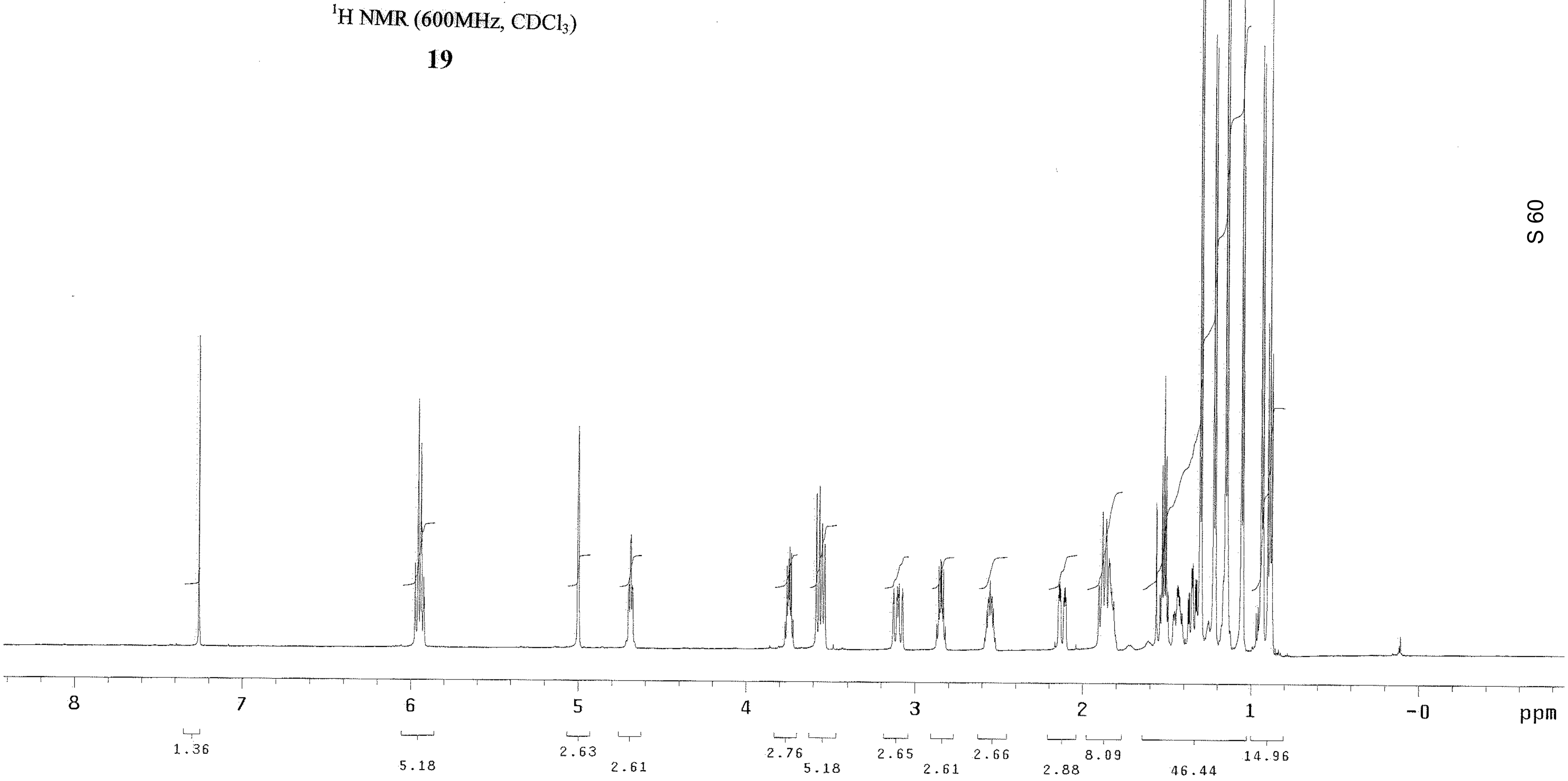

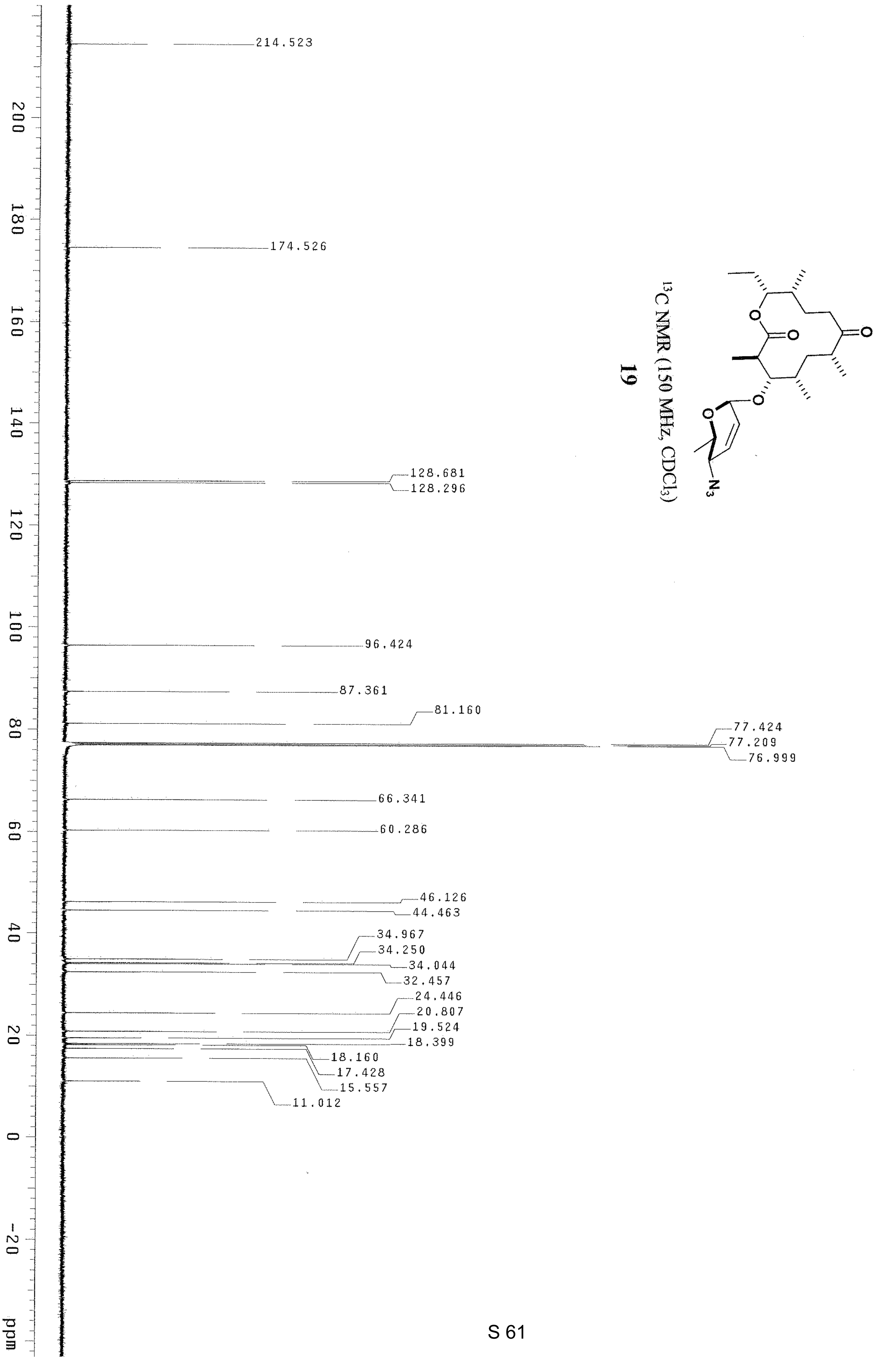

^{13}C NMR (150 MHz, CDCl$_3$)

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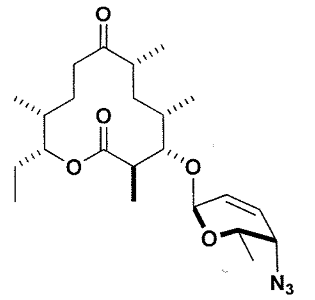

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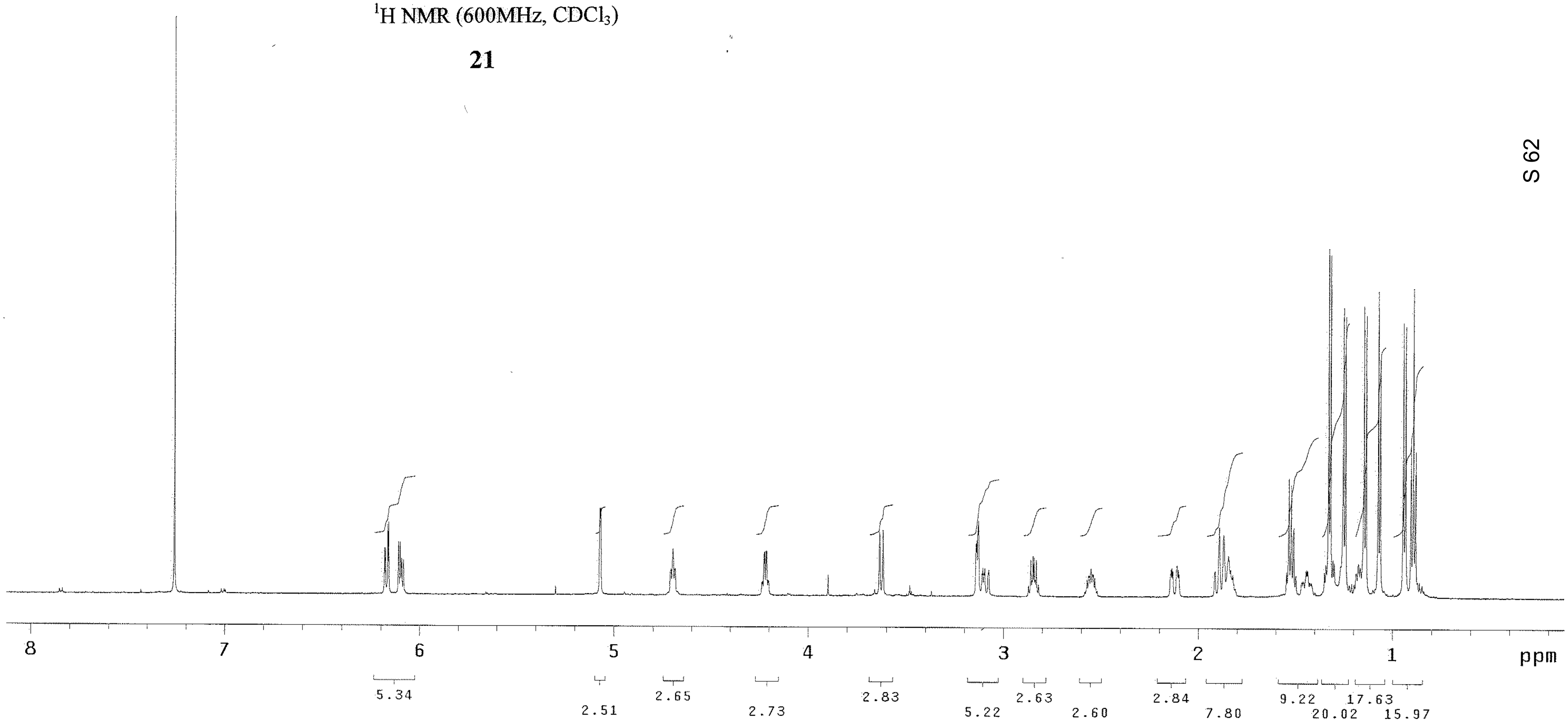

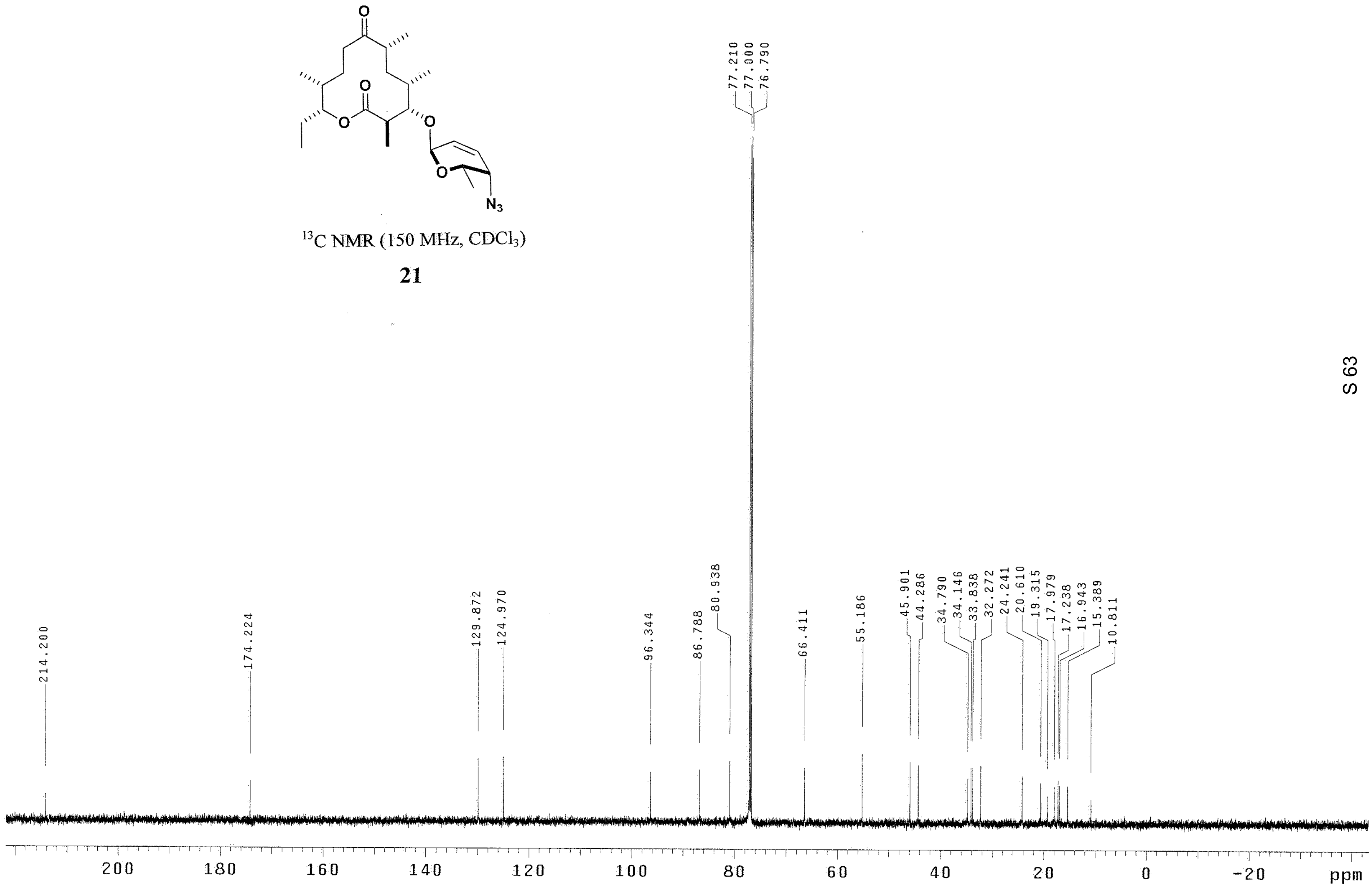

^{13}C NMR (150 MHz, CDCl$_3$)

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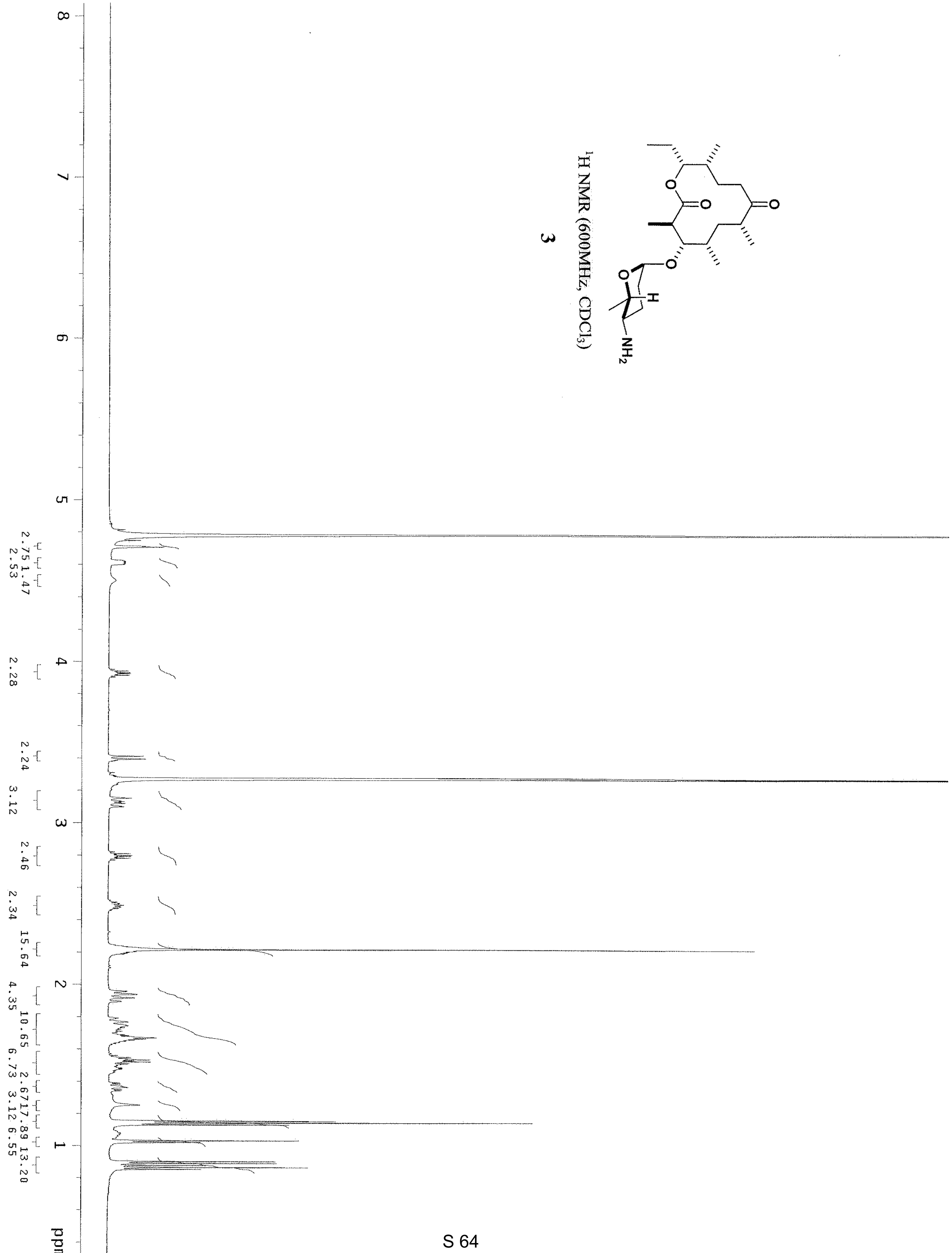

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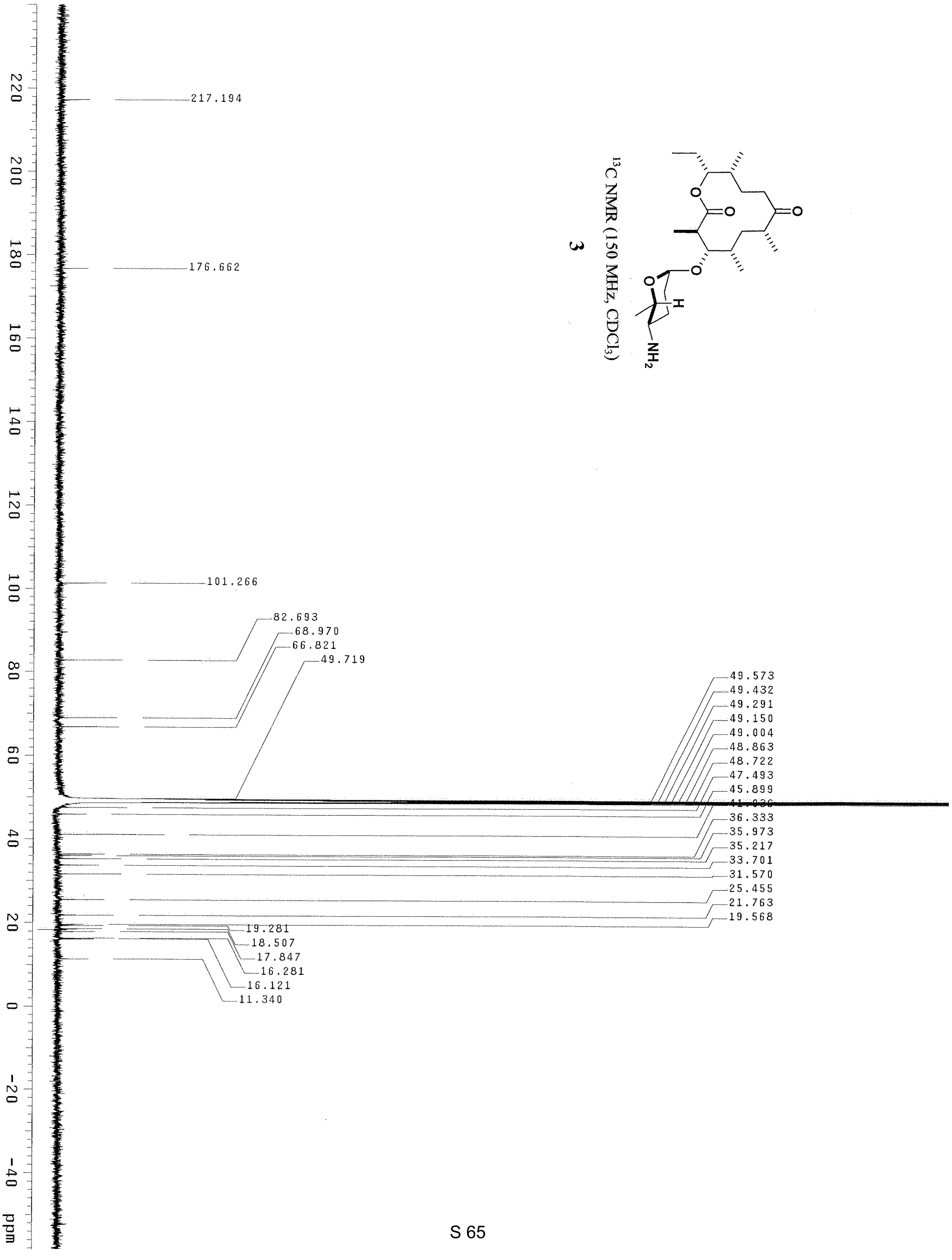

^{13}C NMR (150 MHz, CDCl$_3$)

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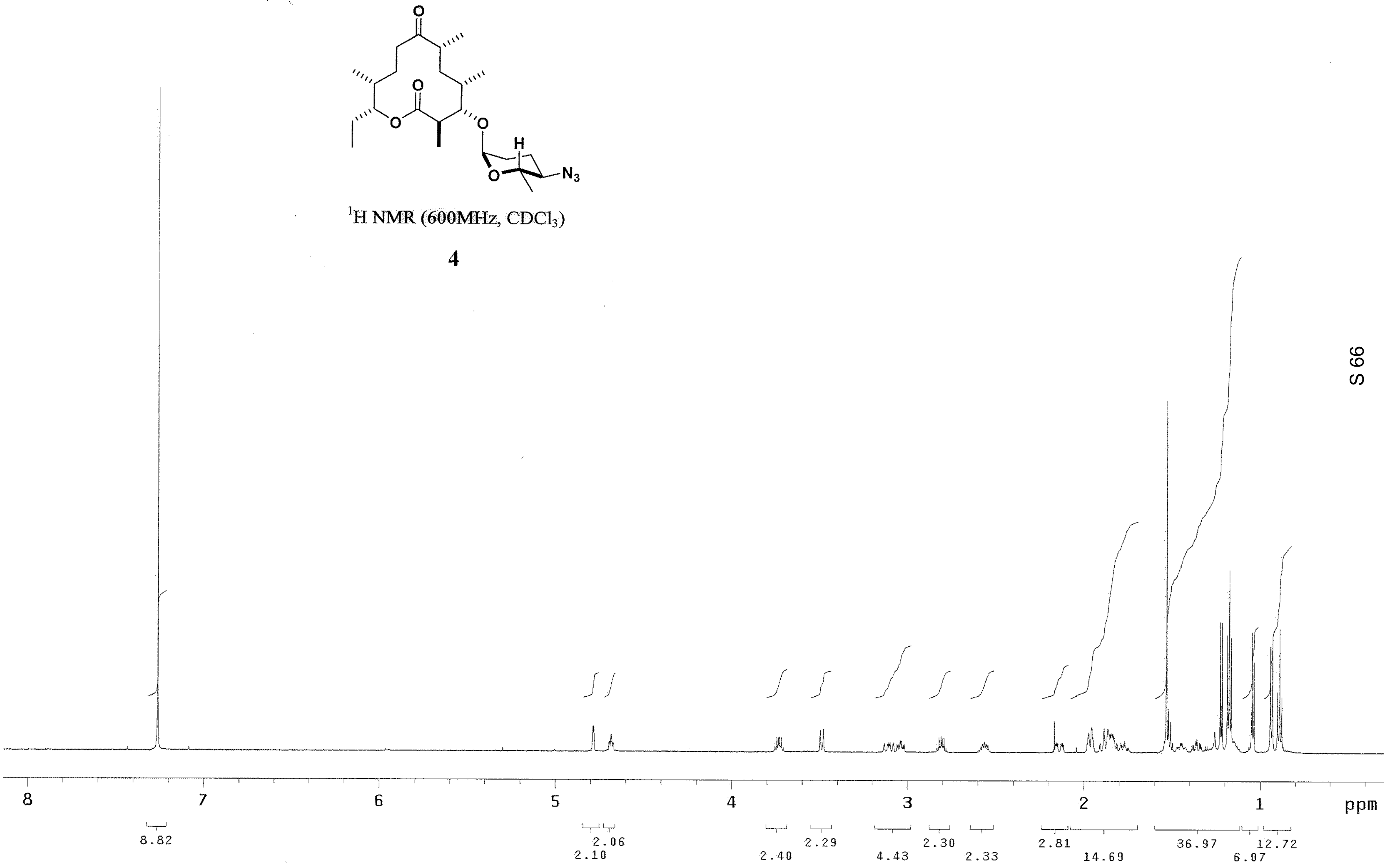

^{1}H NMR (600MHz, CDCl$_3$)

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^{13}C NMR (150 MHz, CDCl$_3$)

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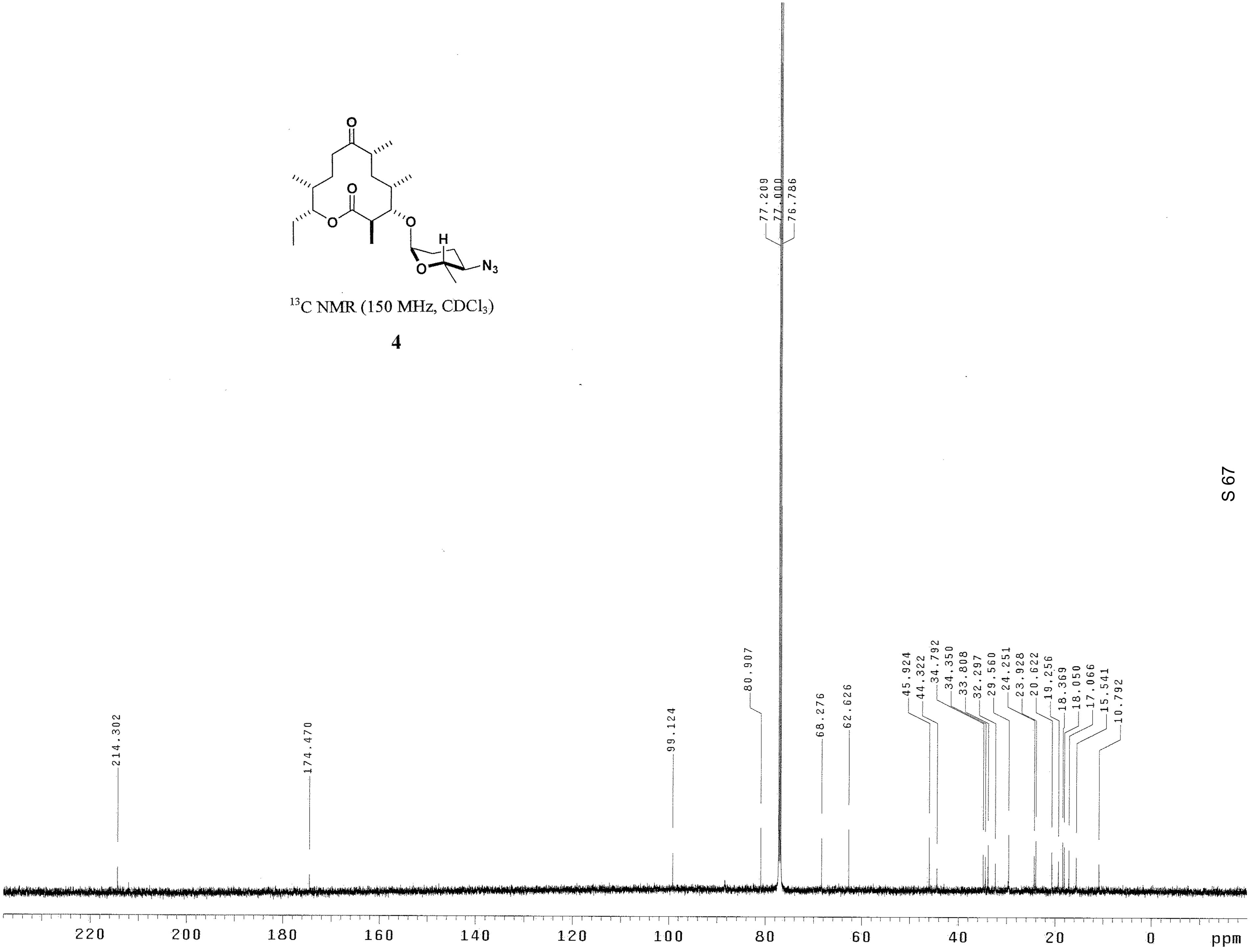

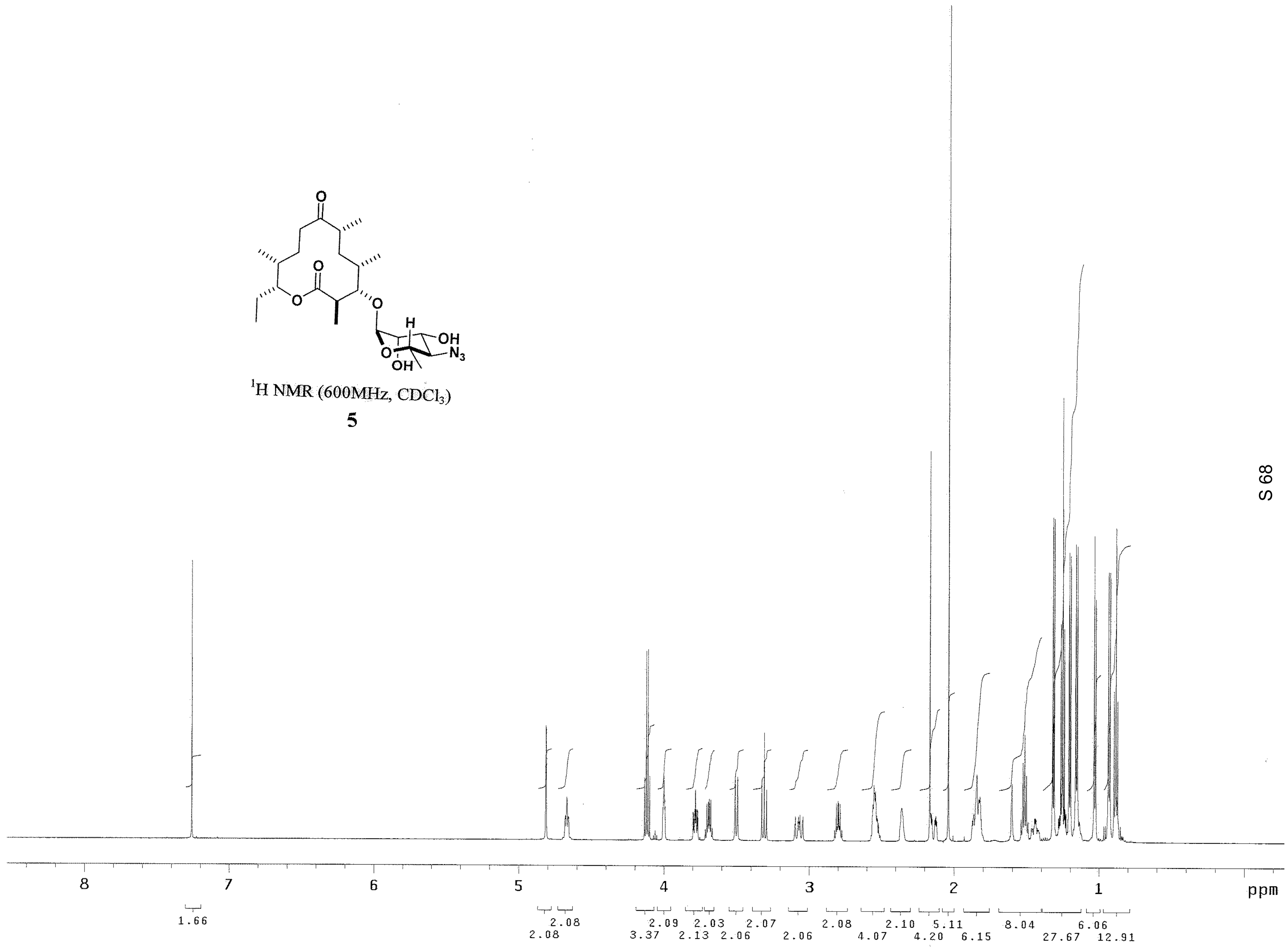

^{1}H NMR (600MHz, $CDCl_3$)

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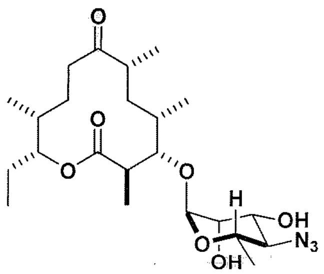

^{13}C NMR (150 MHz, CDCl$_3$)

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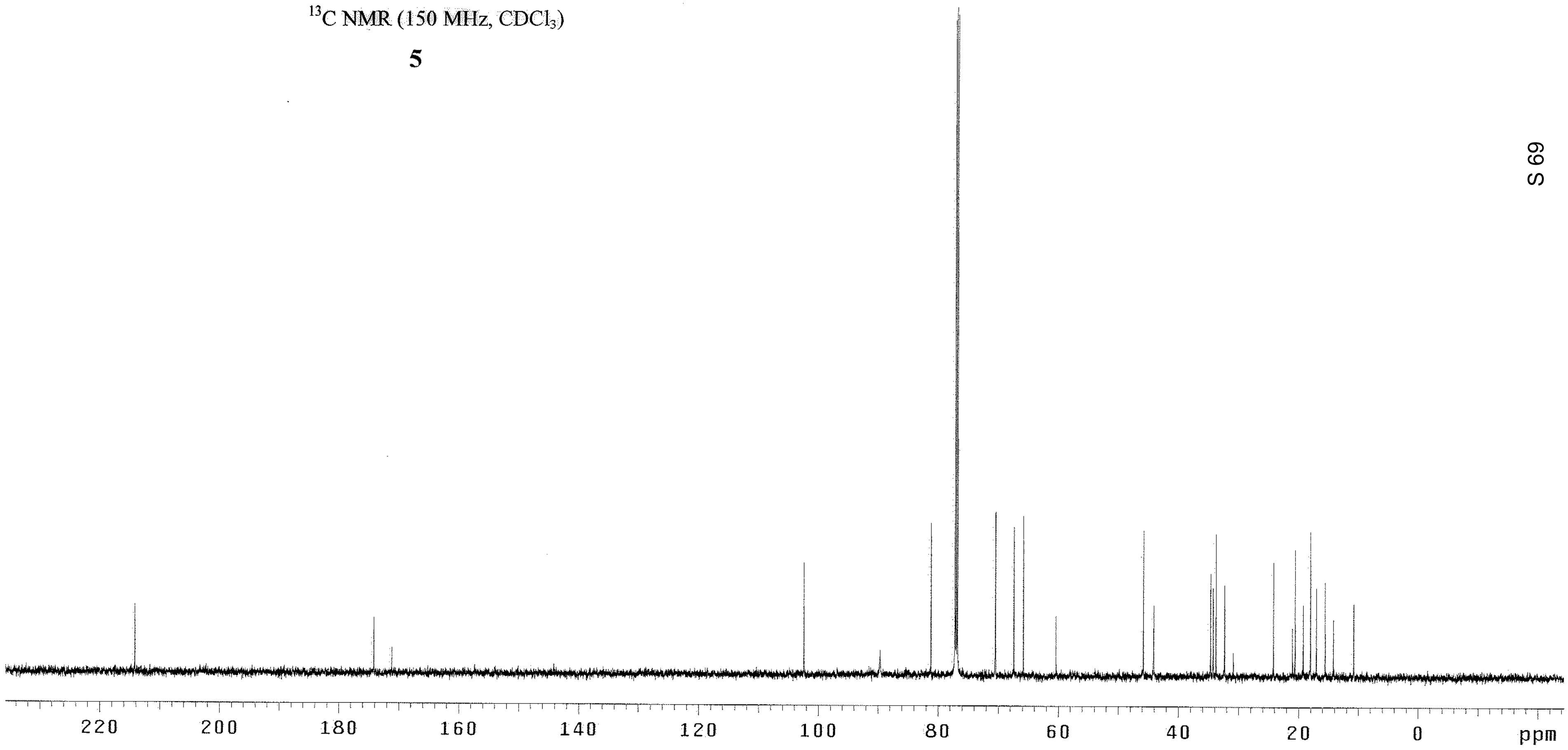

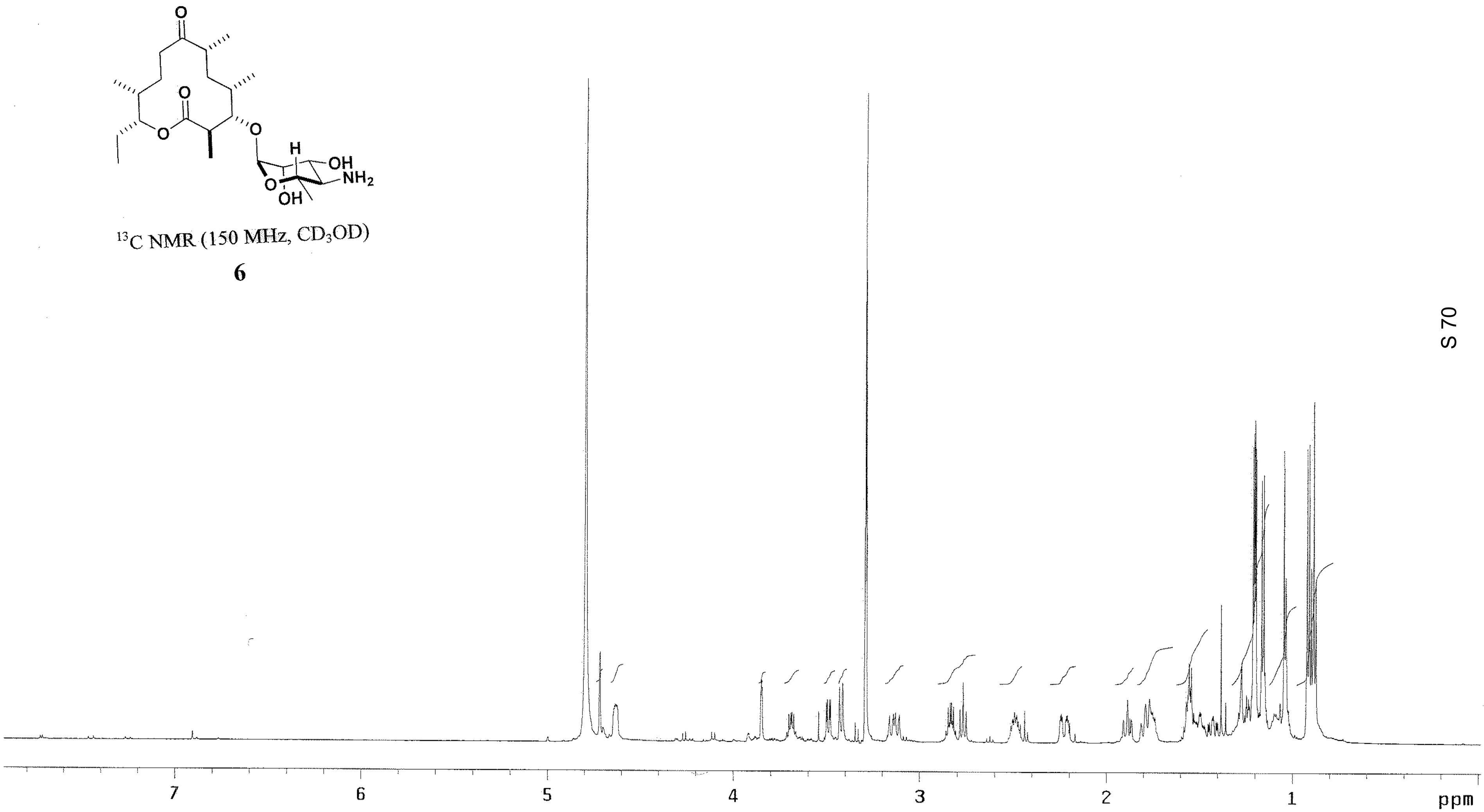

^{13}C NMR (150 MHz, CD_3OD)

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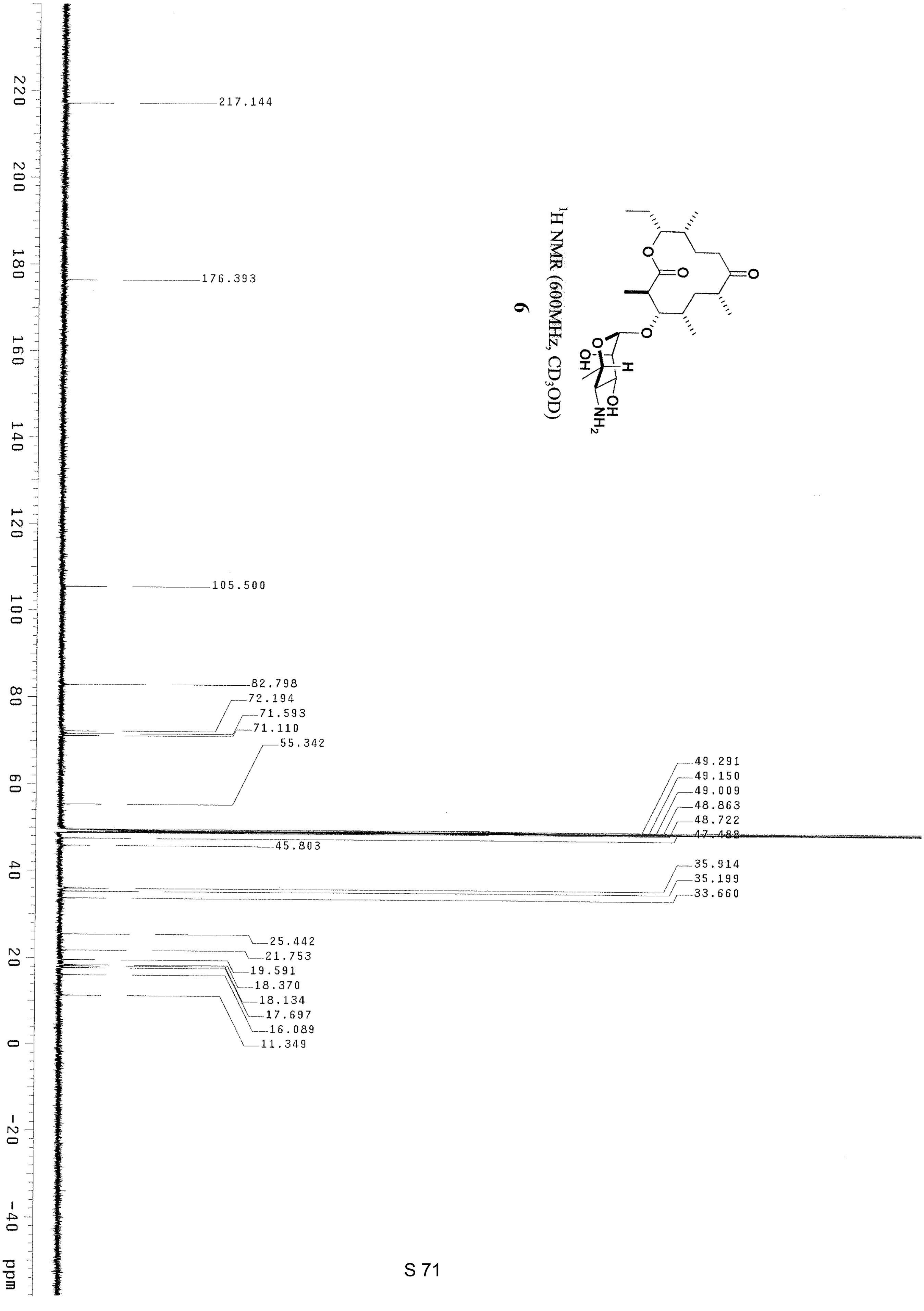

^{1}H NMR (600MHz, CD$_3$OD)

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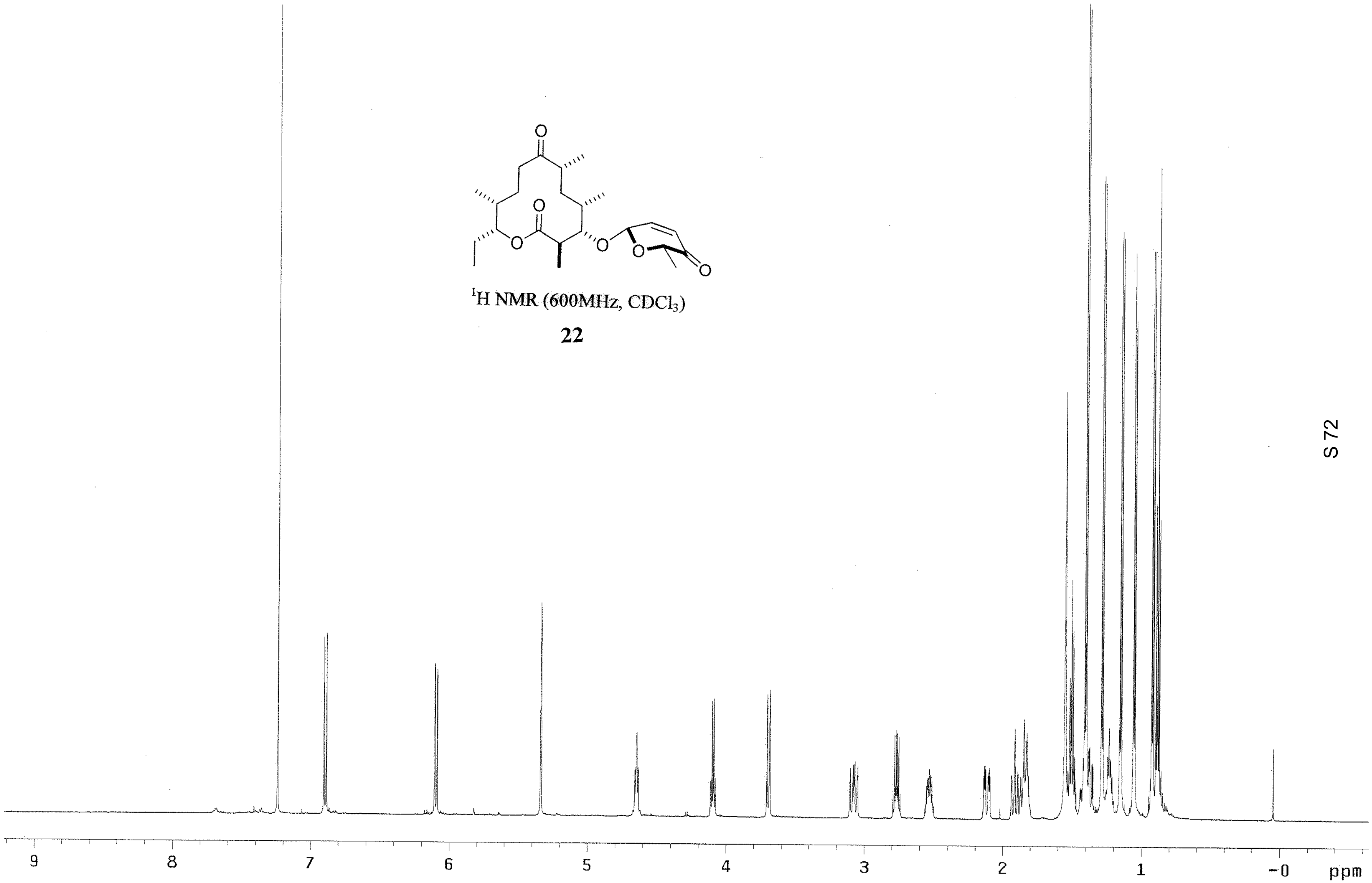
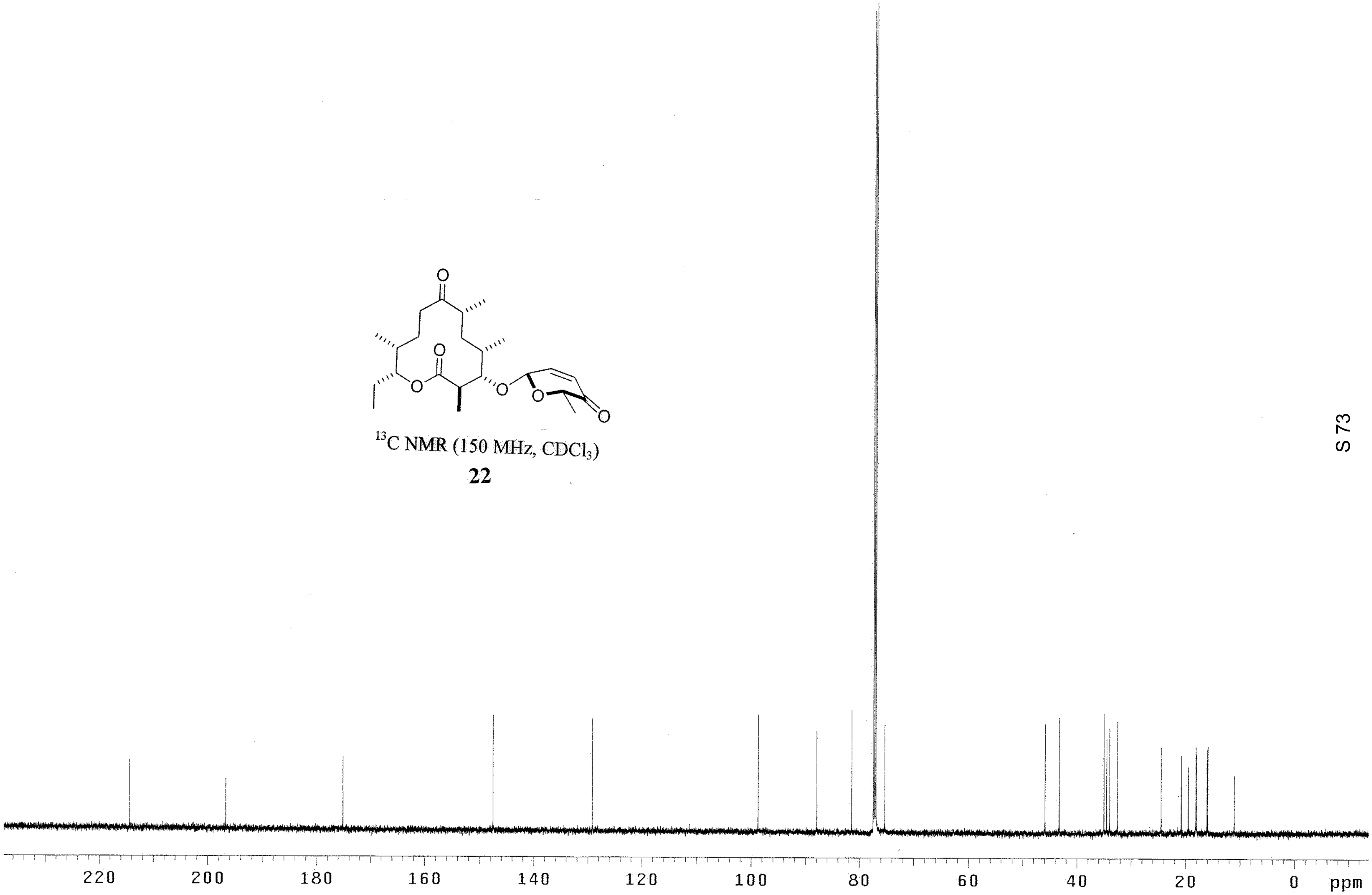


^{1}H NMR (600MHz, CDCl$_3$)

22



^{13}C NMR (150 MHz, CDCl$_3$)

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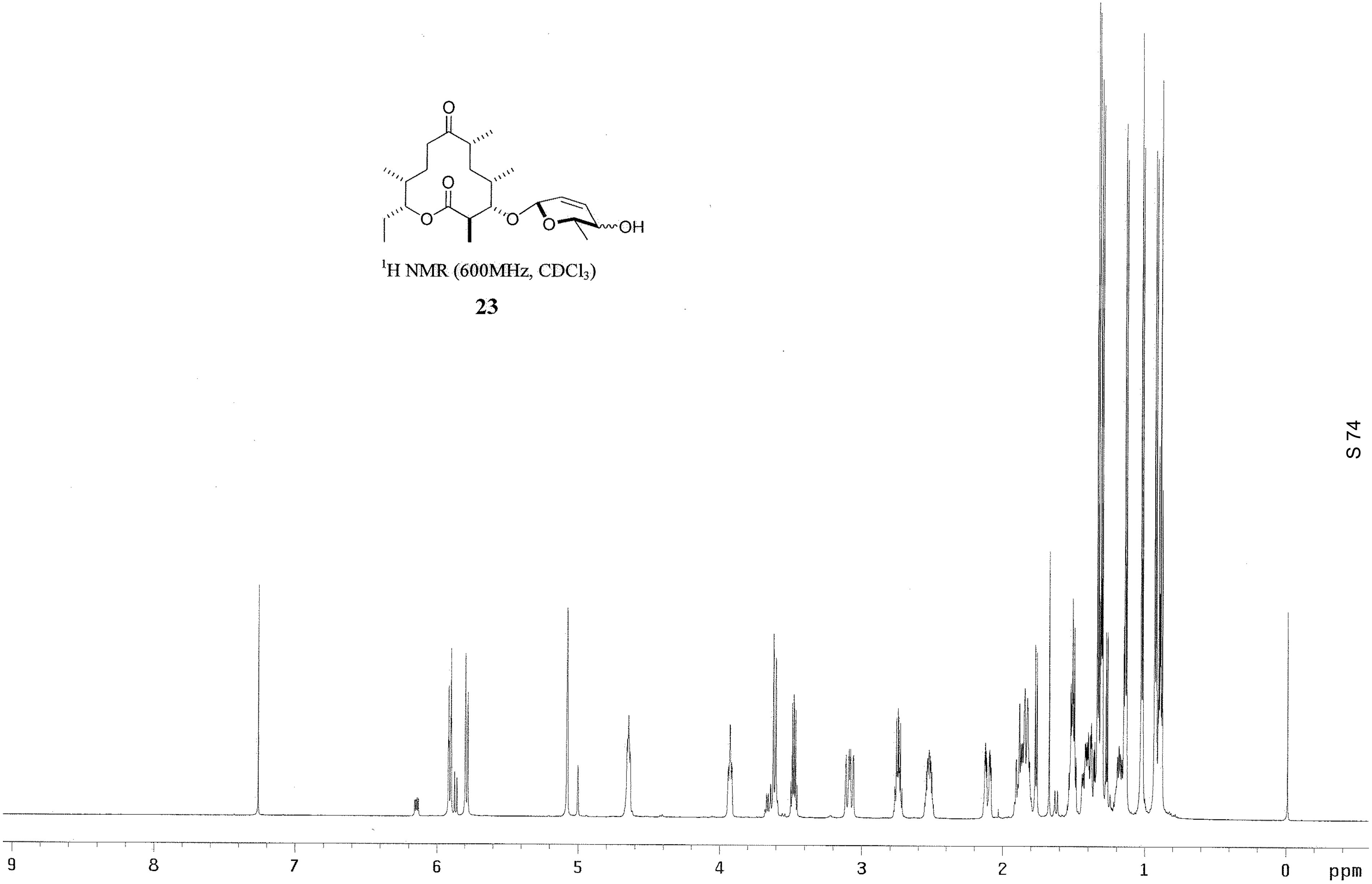

^{1}H NMR (600MHz, CDCl$_3$)

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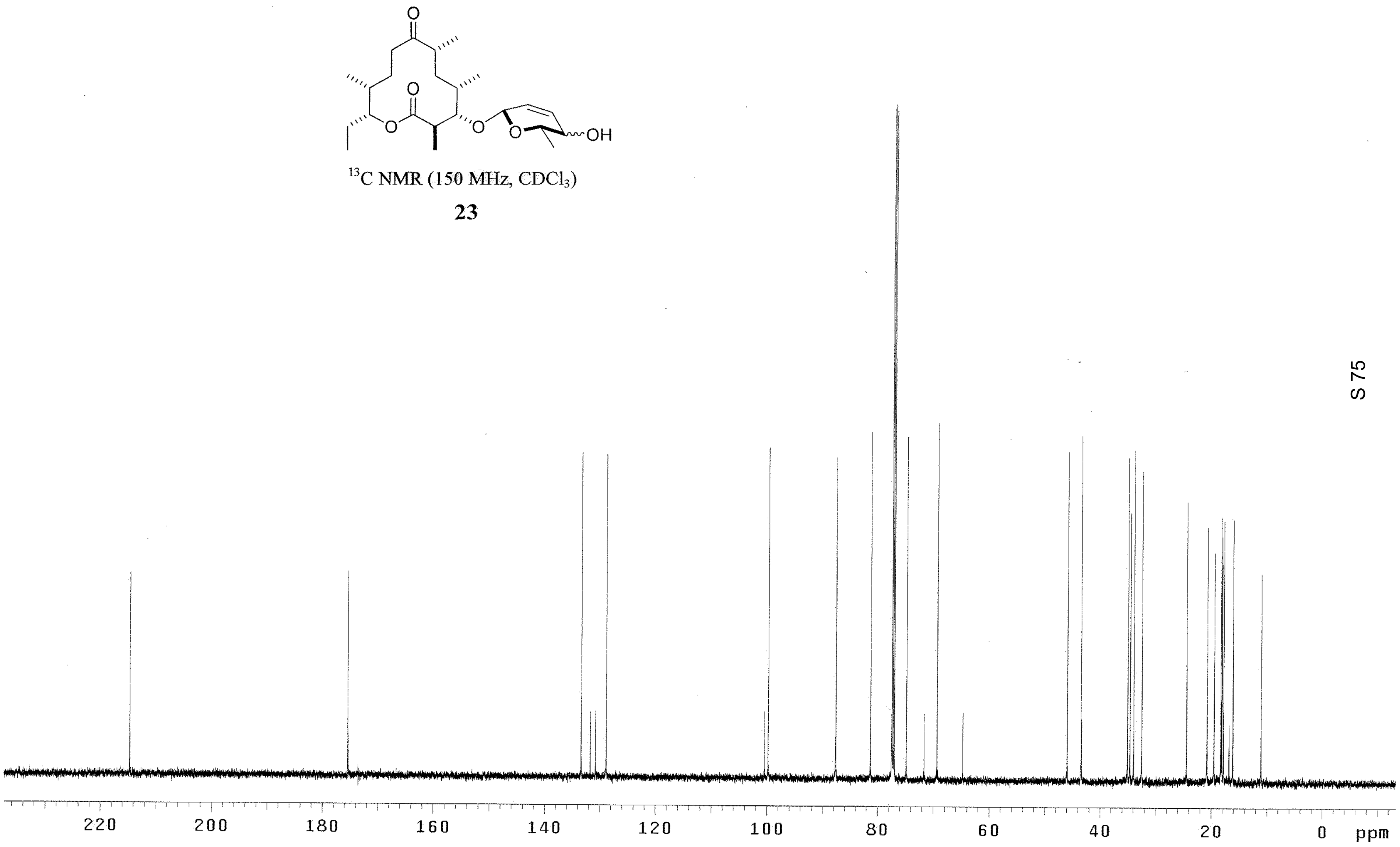

^{13}C NMR (150 MHz, CDCl$_3$)

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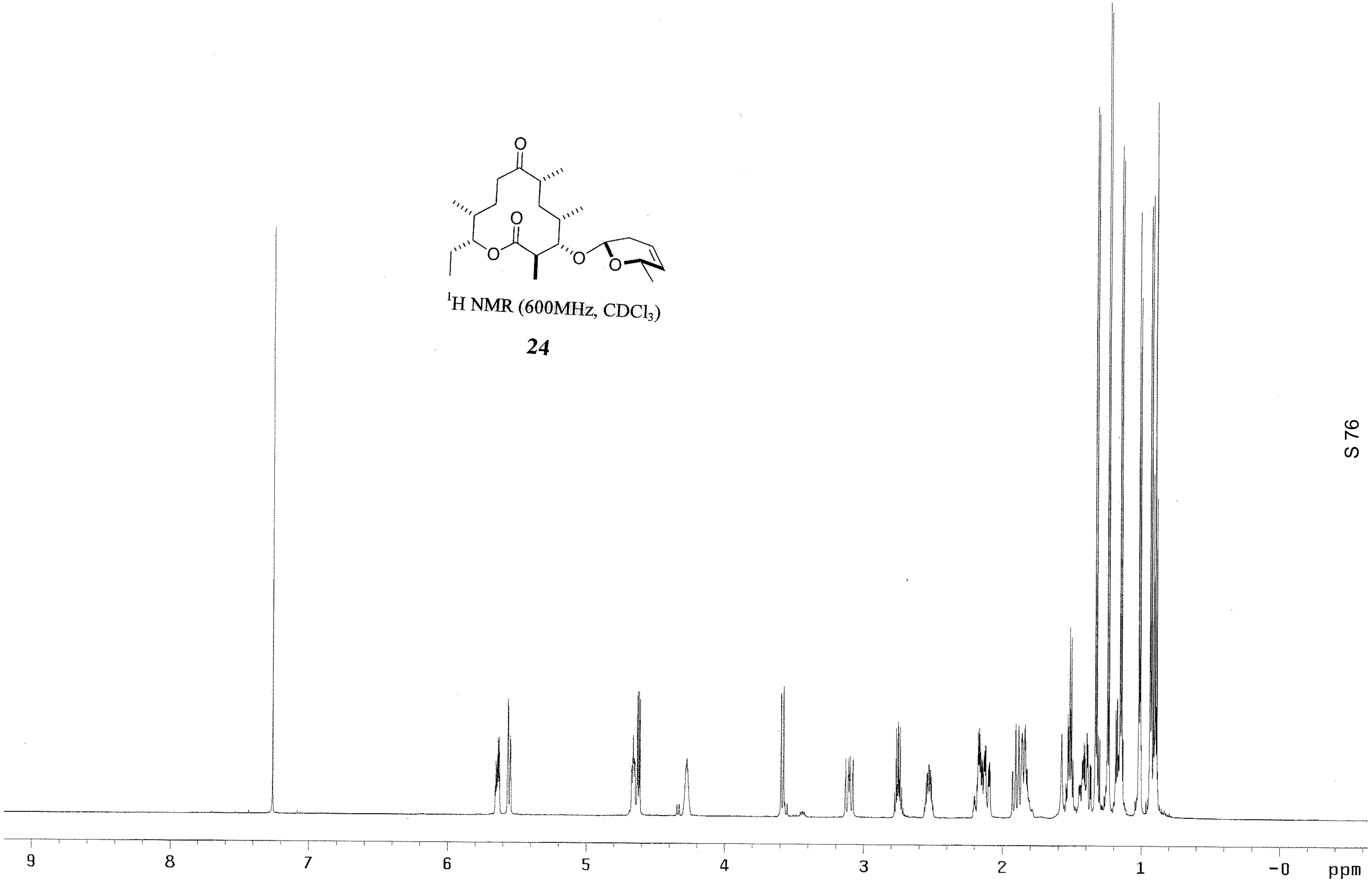

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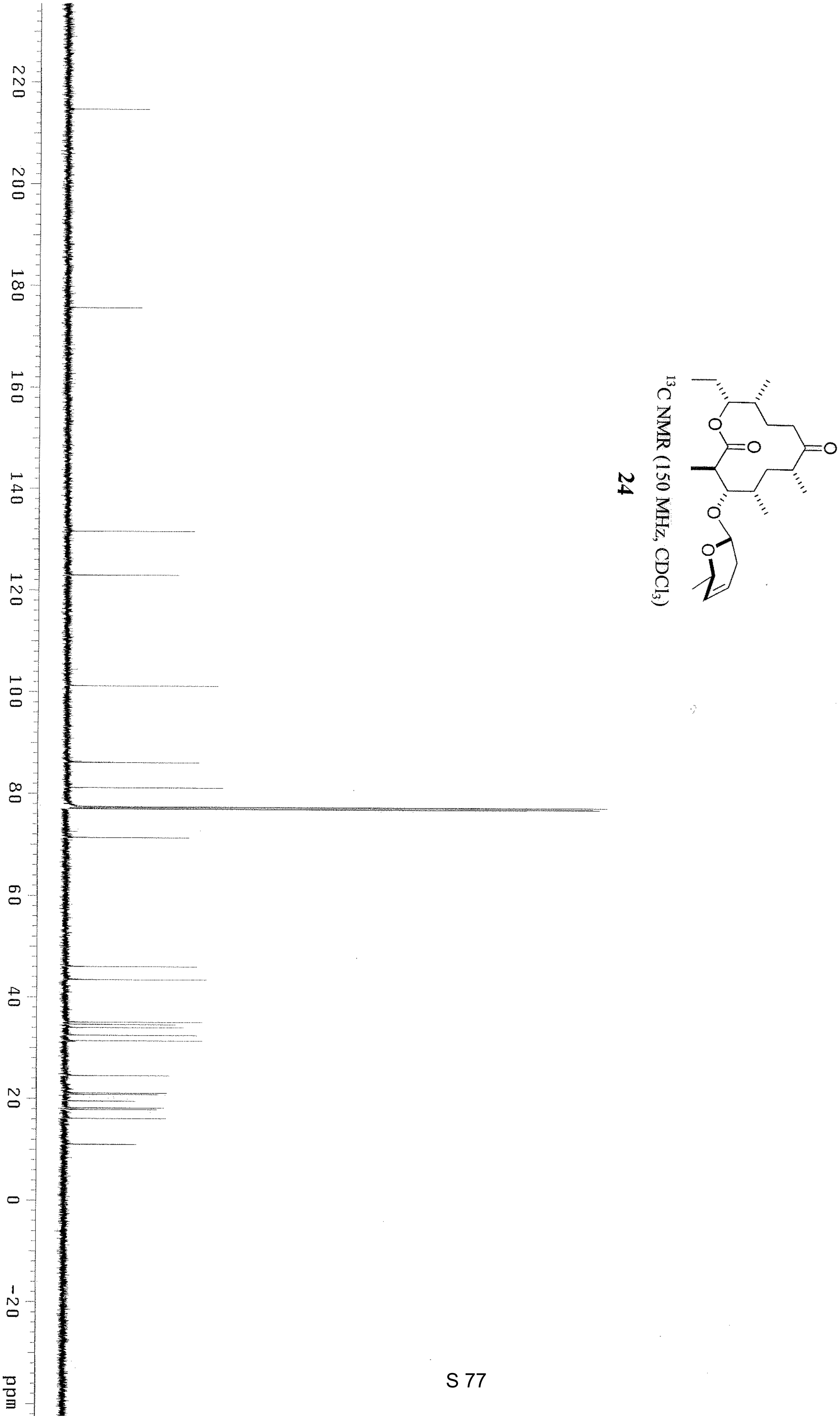

^{13}C NMR (150 MHz, CDCl$_3$)

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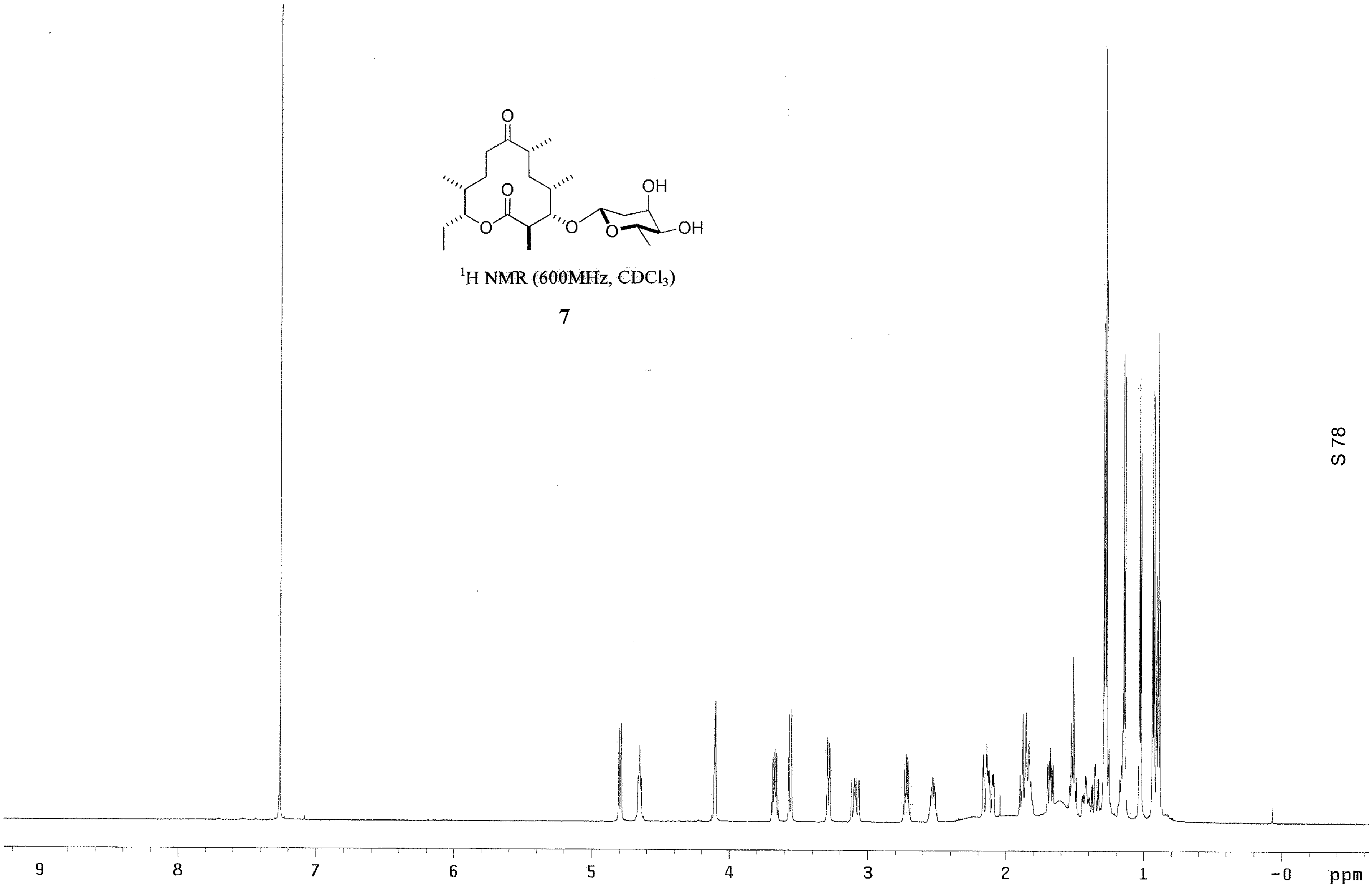
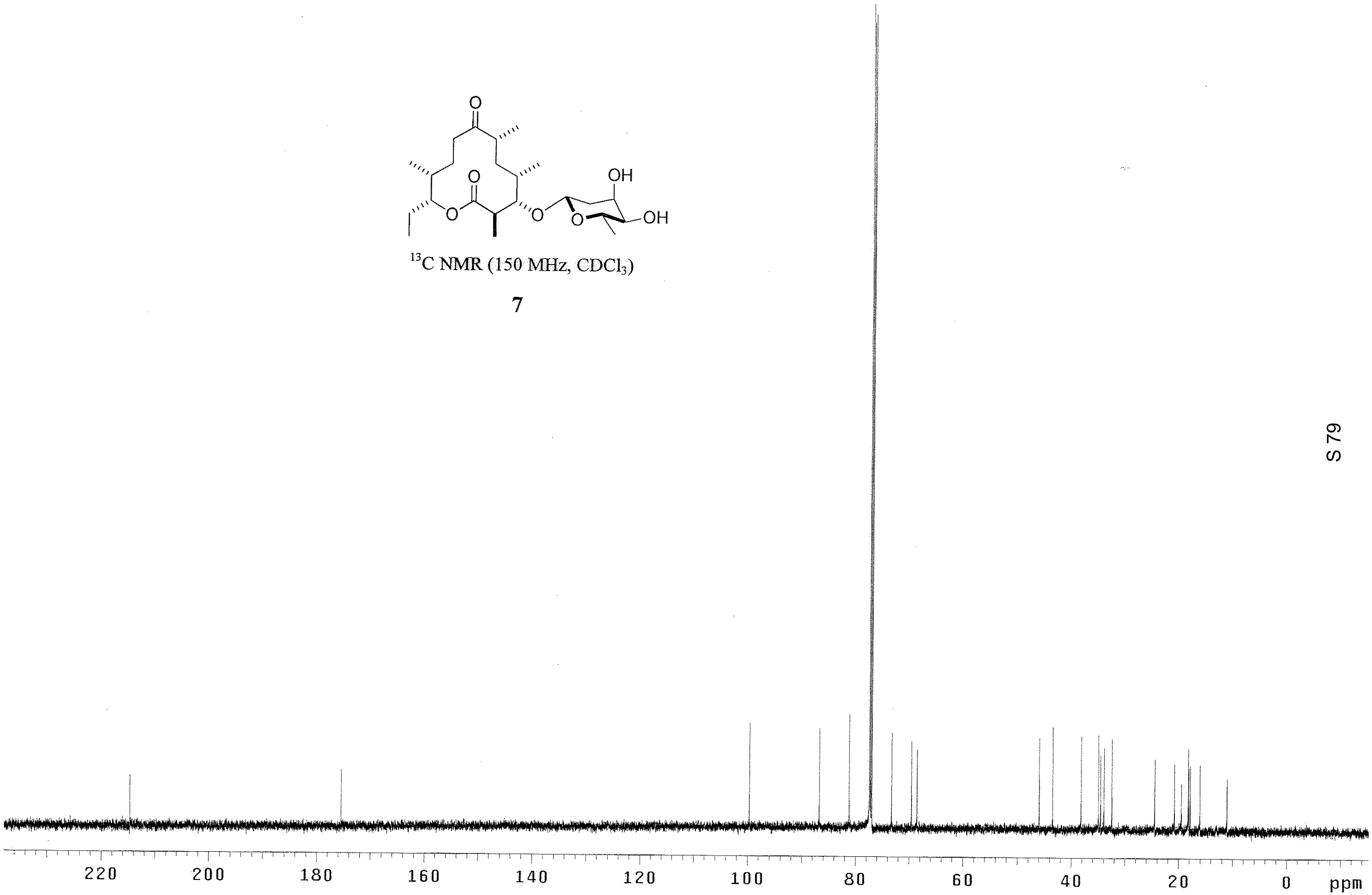


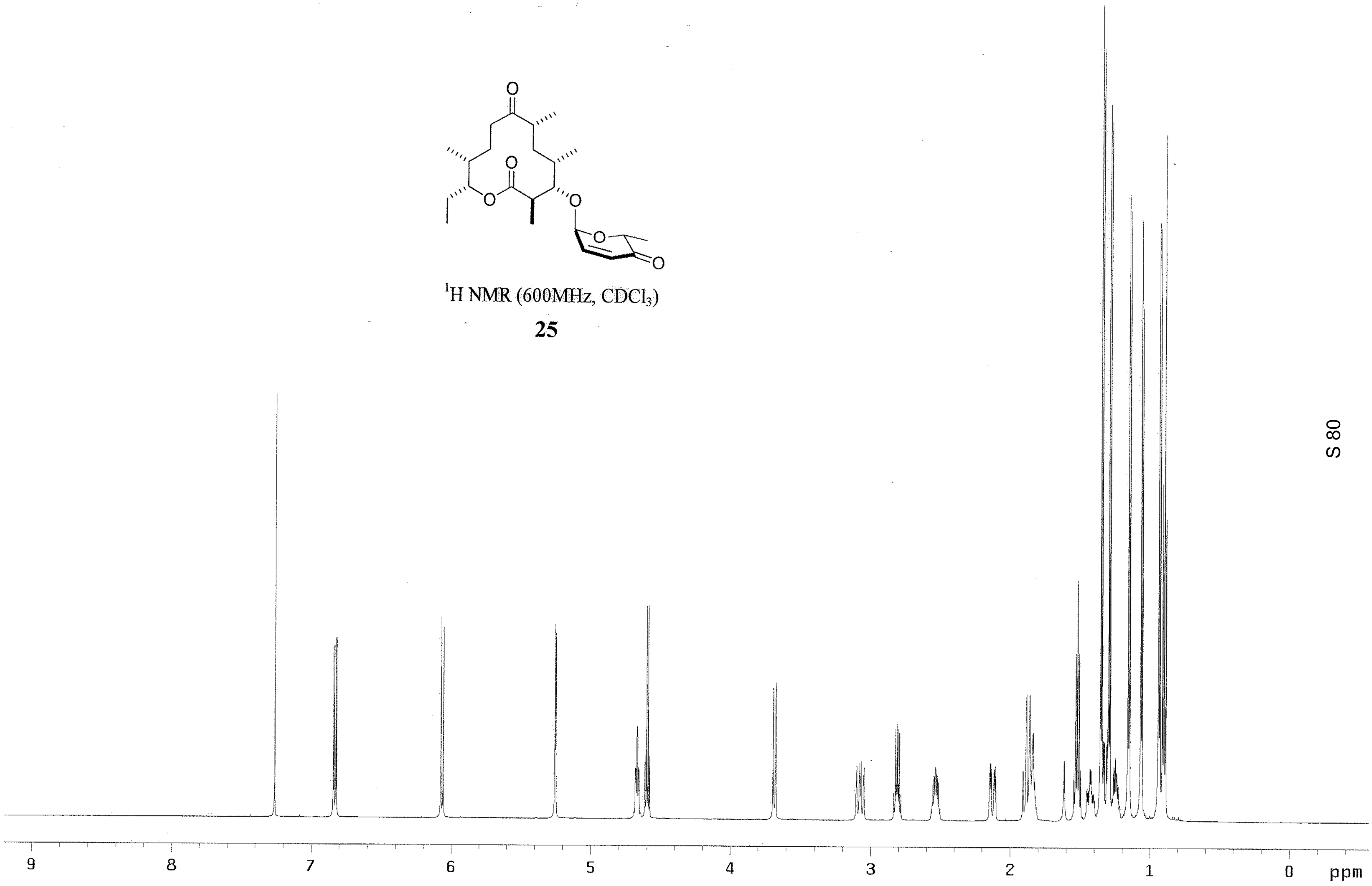
^{1}H NMR (600MHz, $CDCl_3$)

7

^{13}C NMR (150 MHz, CDCl$_3$)

7





^{1}H NMR (600MHz, CDCl$_3$)

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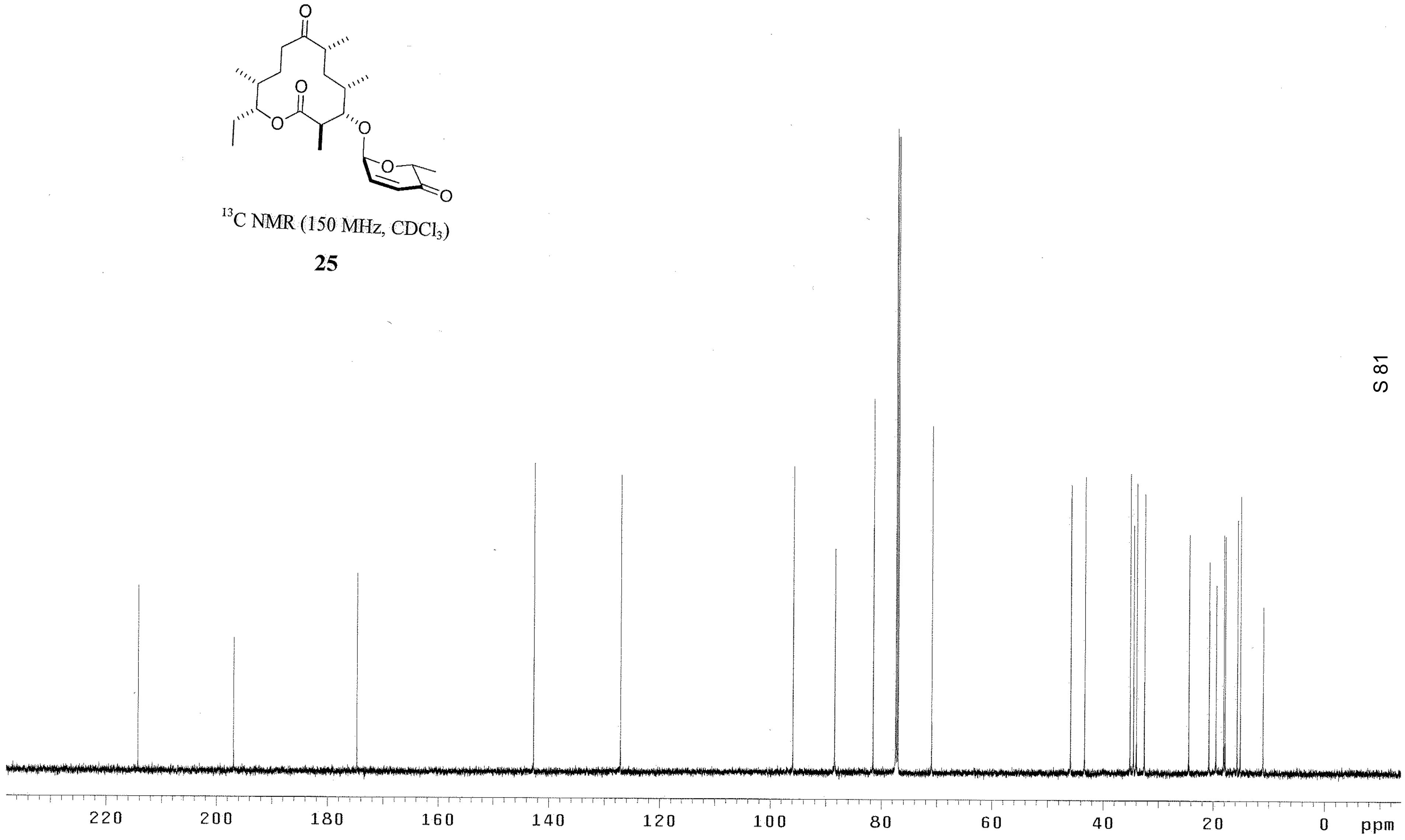

^{13}C NMR (150 MHz, CDCl$_3$)

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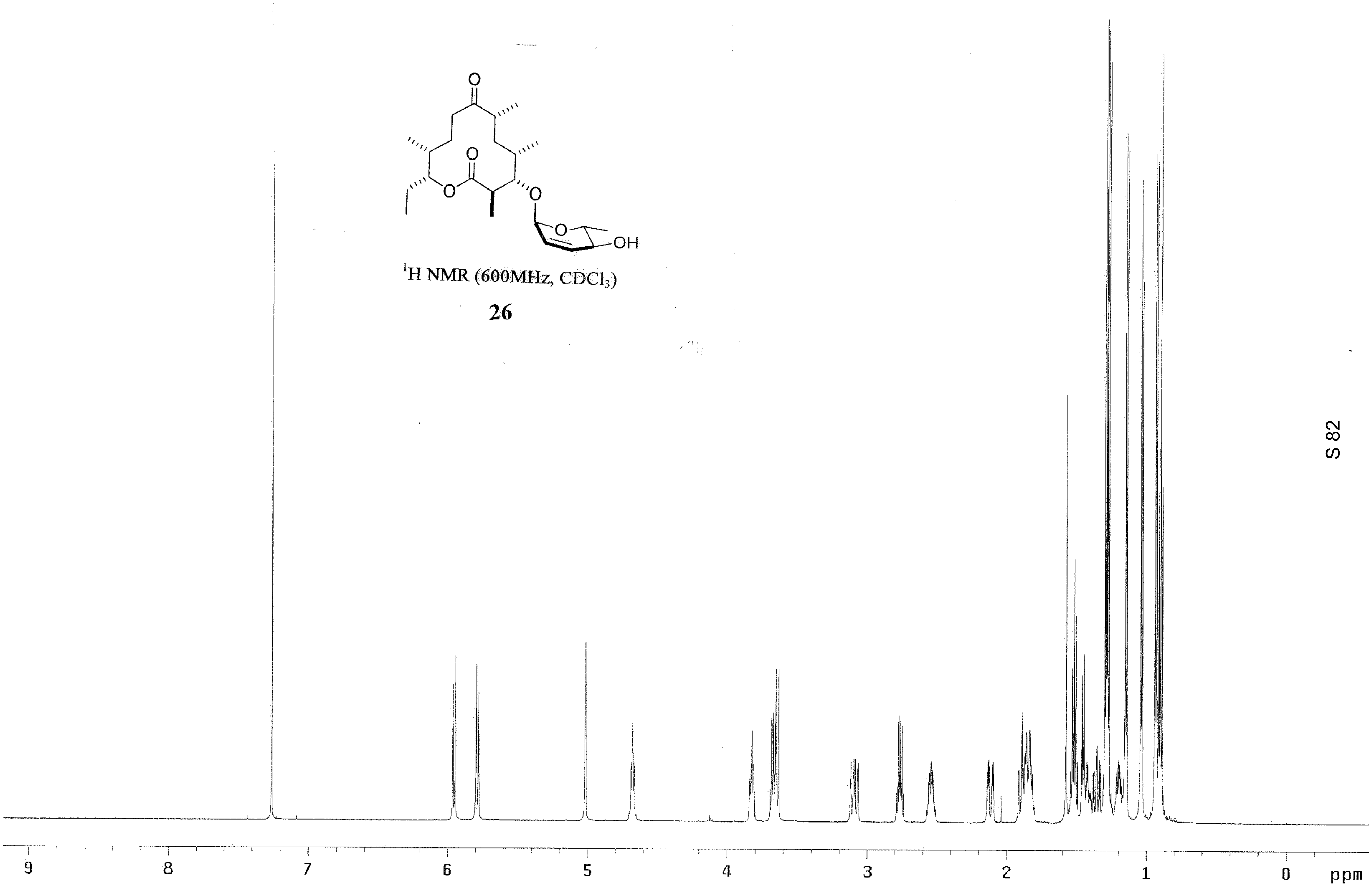

^{1}H NMR (600MHz, CDCl$_3$)

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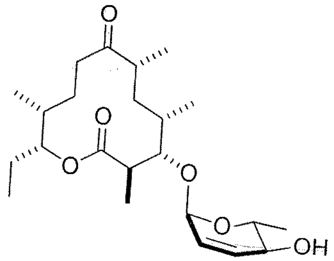

^{13}C NMR (150 MHz, CDCl$_3$)

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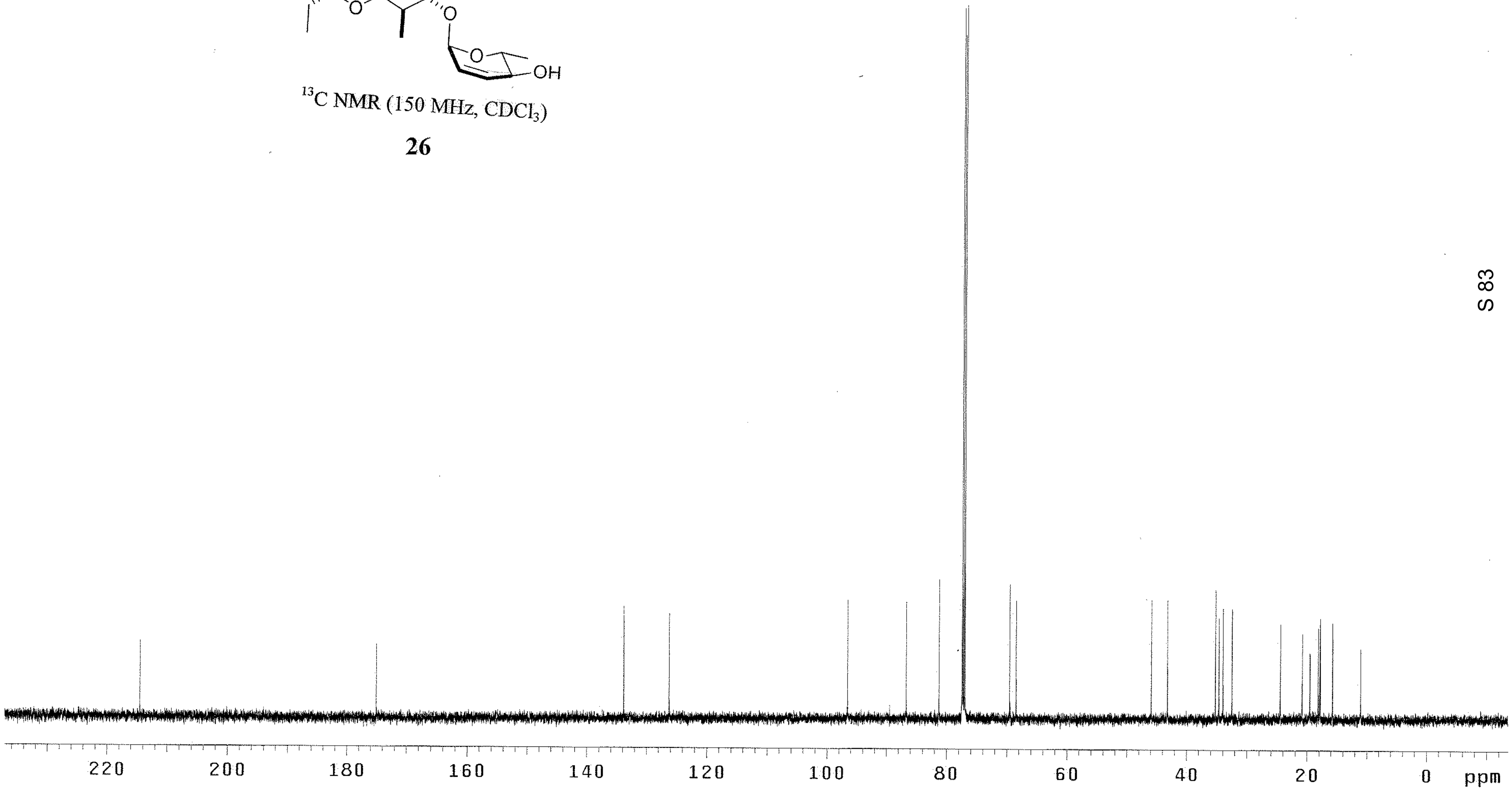

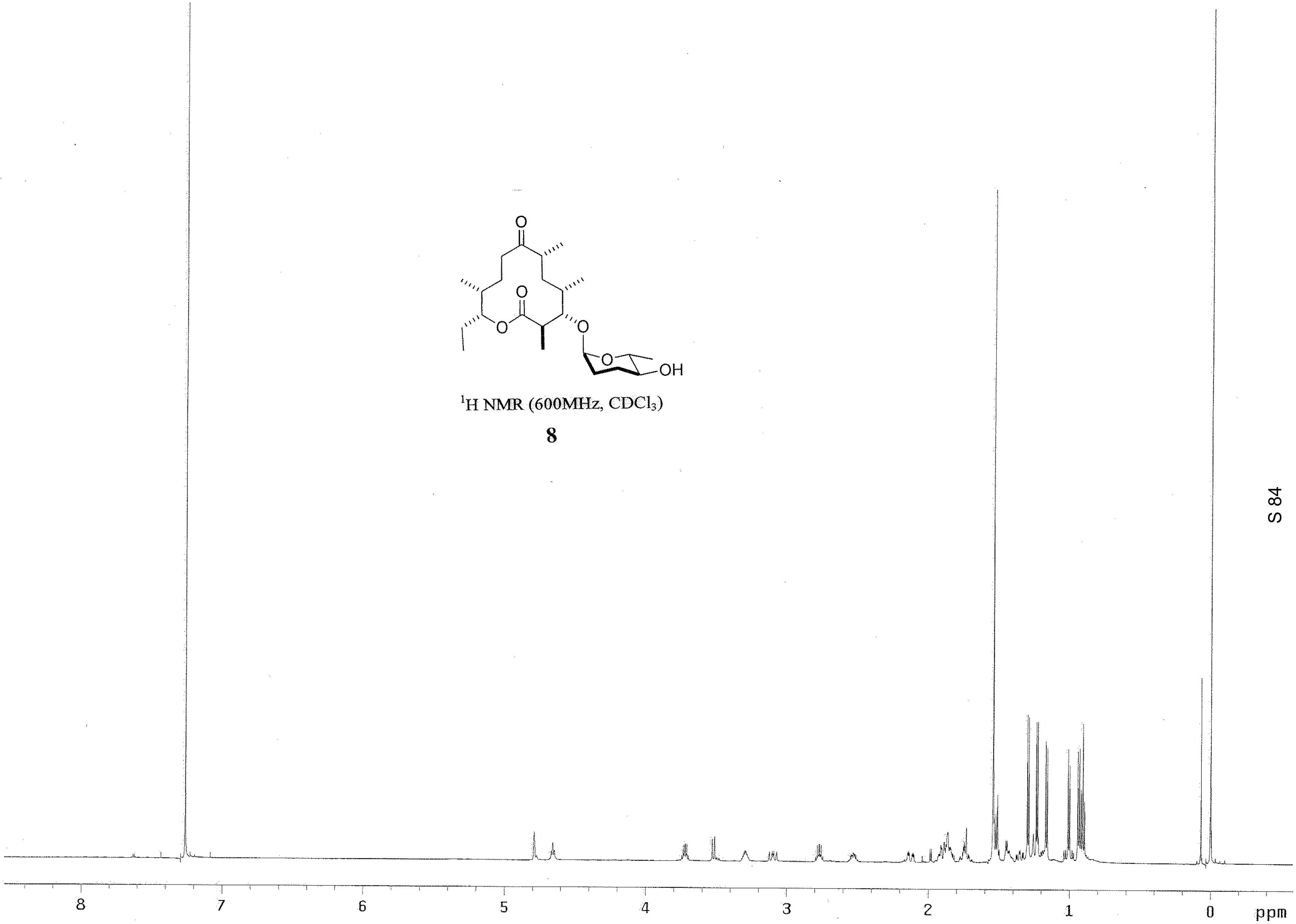

^{1}H NMR (600MHz, CDCl$_3$)

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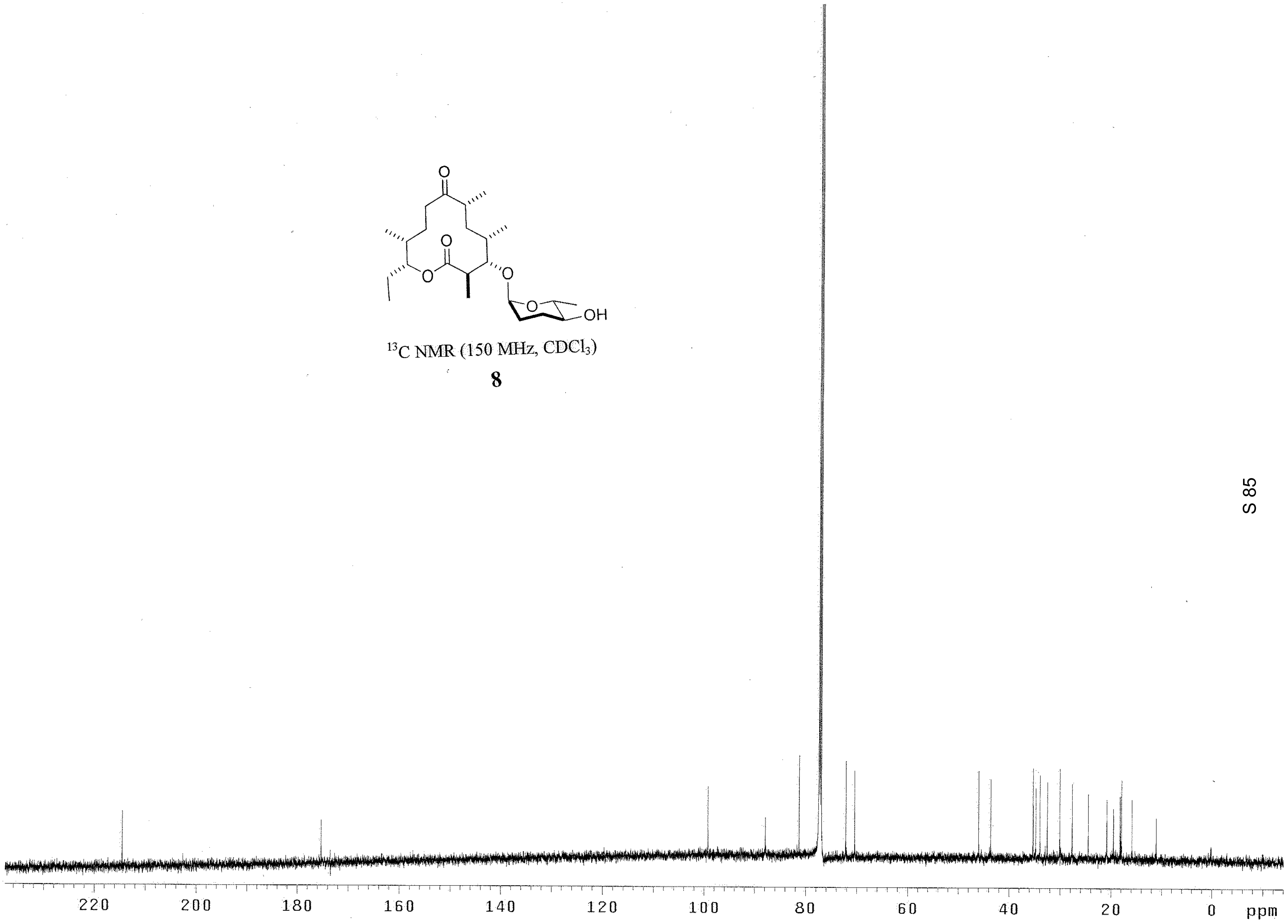

^{13}C NMR (150 MHz, CDCl$_3$)

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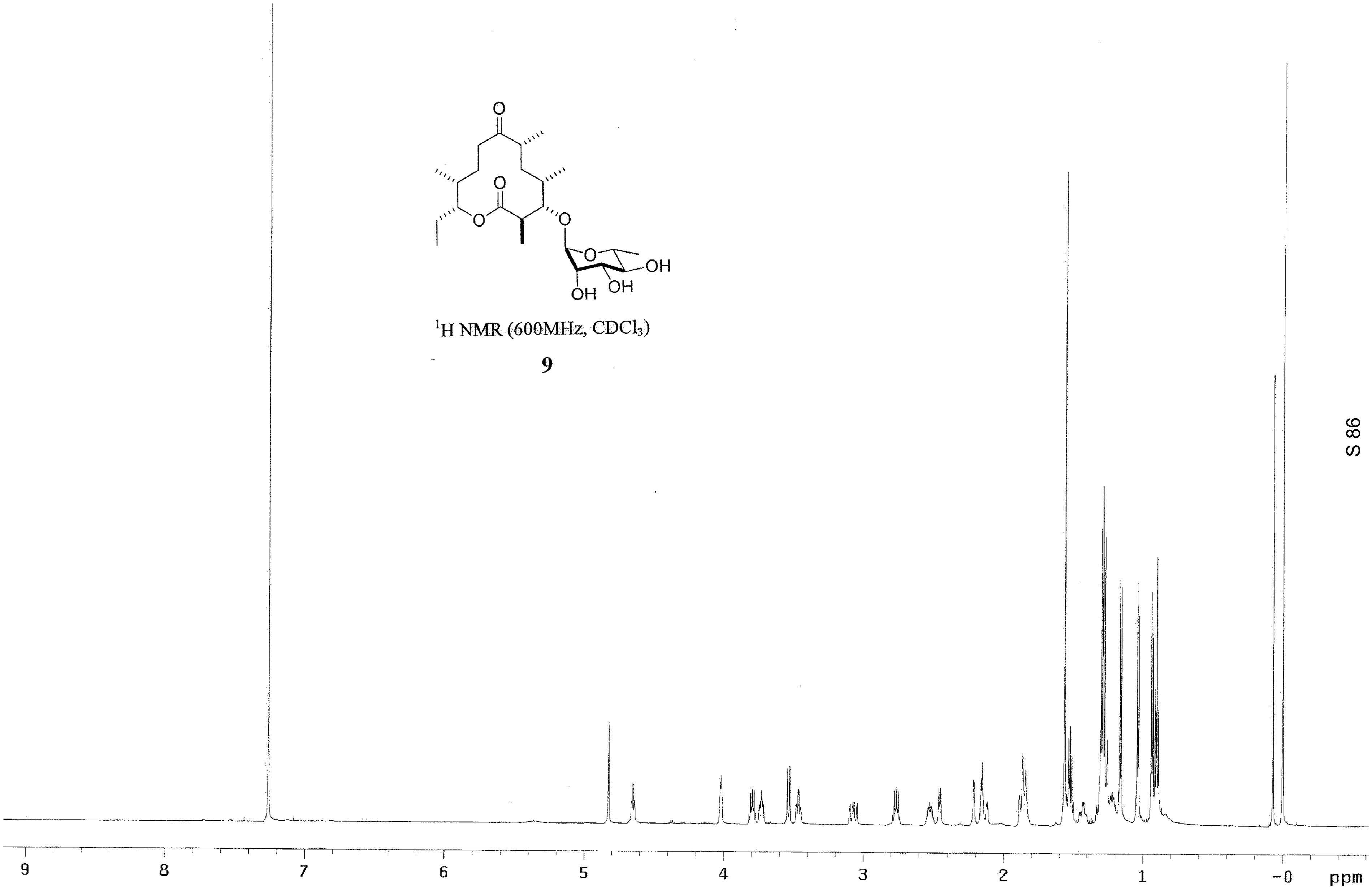

^{1}H NMR (600MHz, CDCl$_3$)

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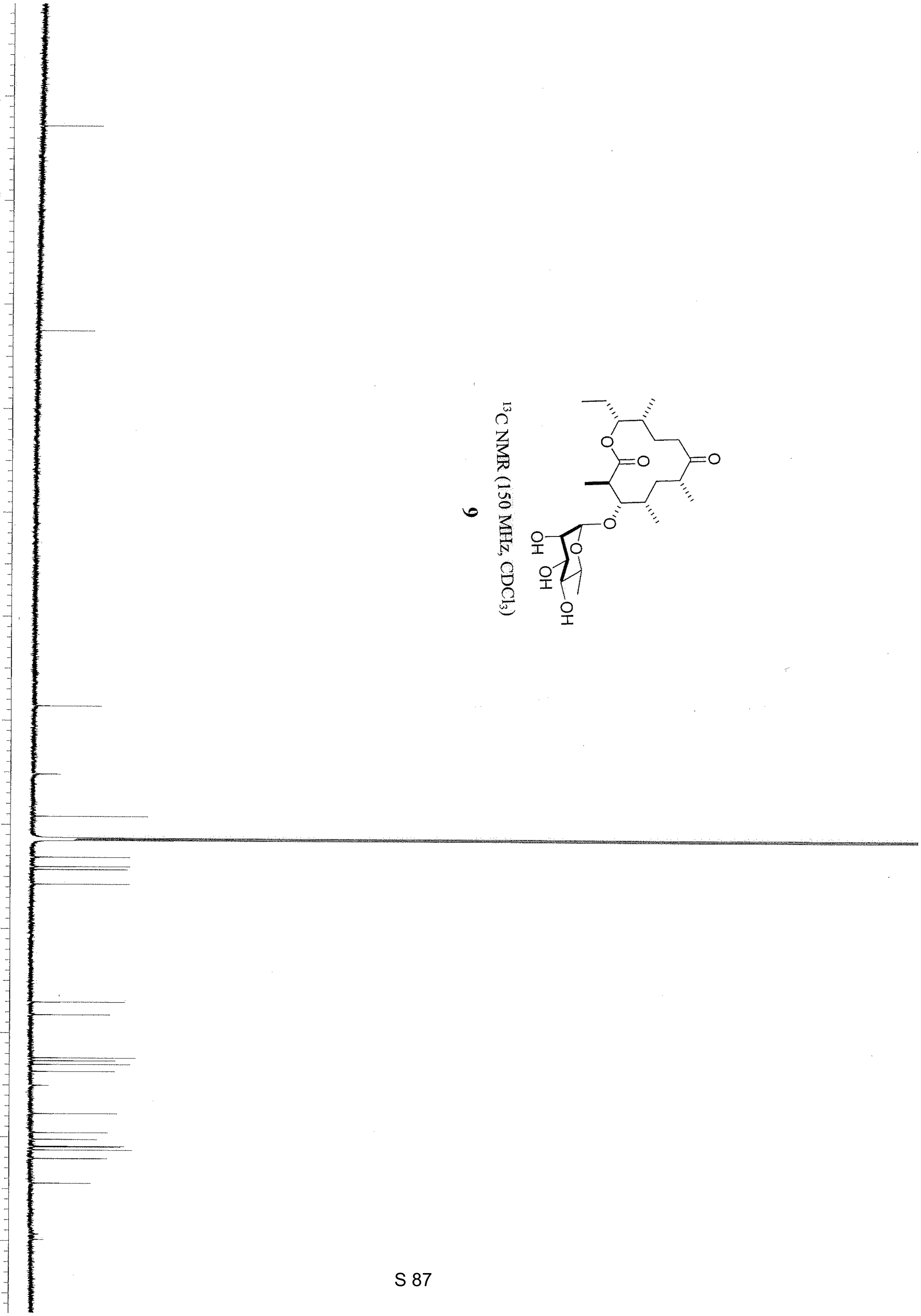

^{13}C NMR (150 MHz, CDCl$_3$)

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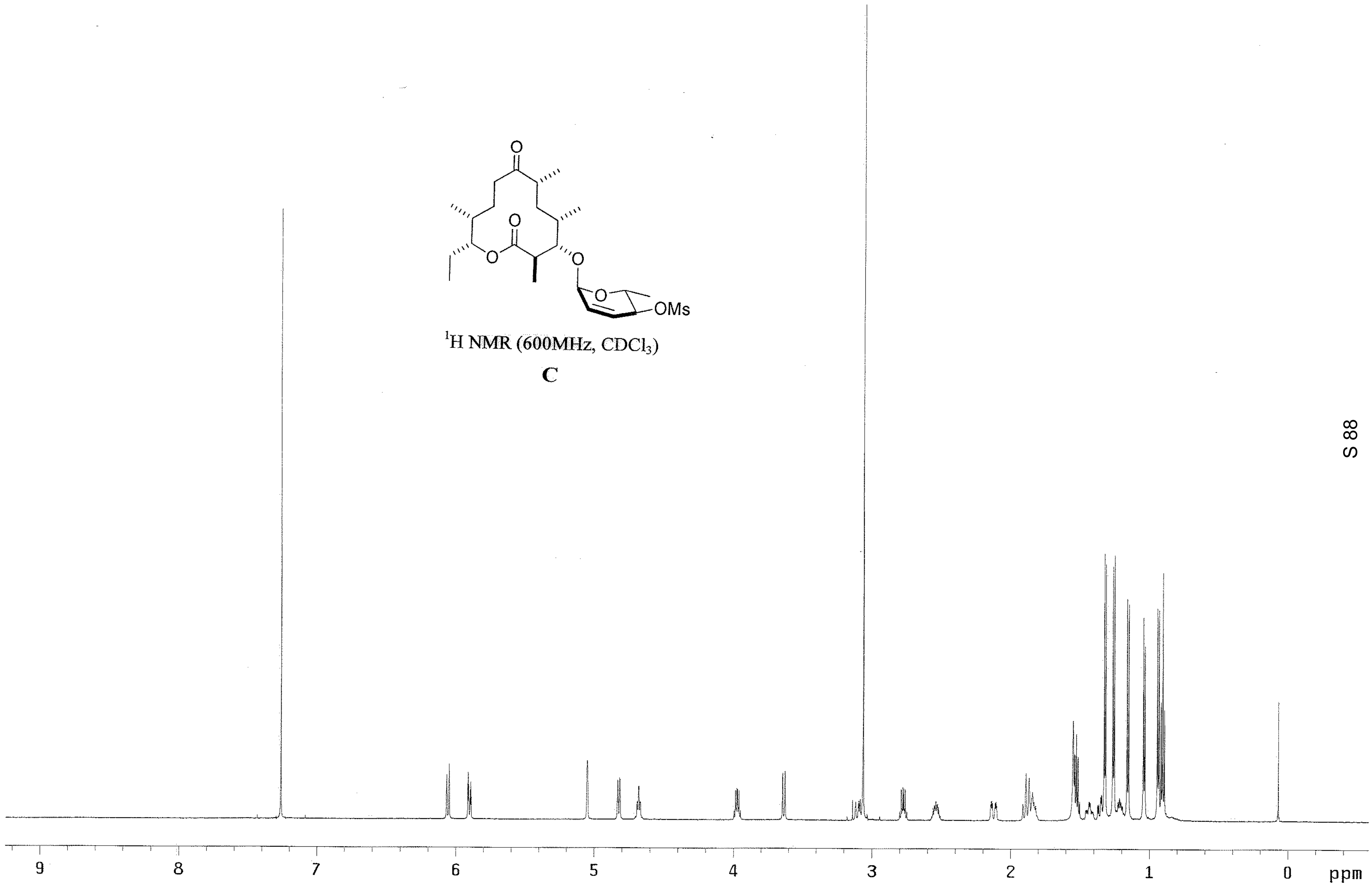

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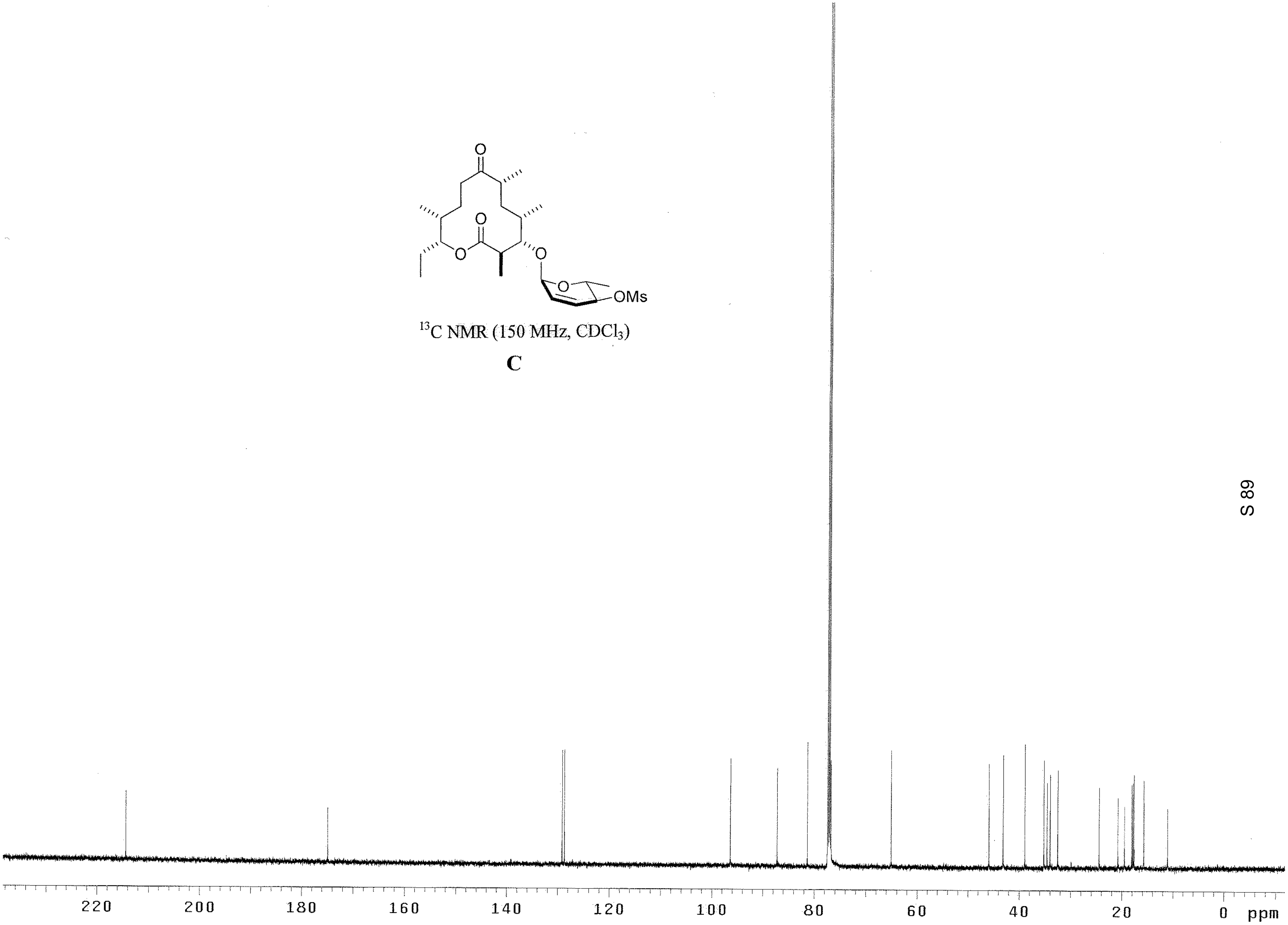

^{13}C NMR (150 MHz, CDCl$_3$)

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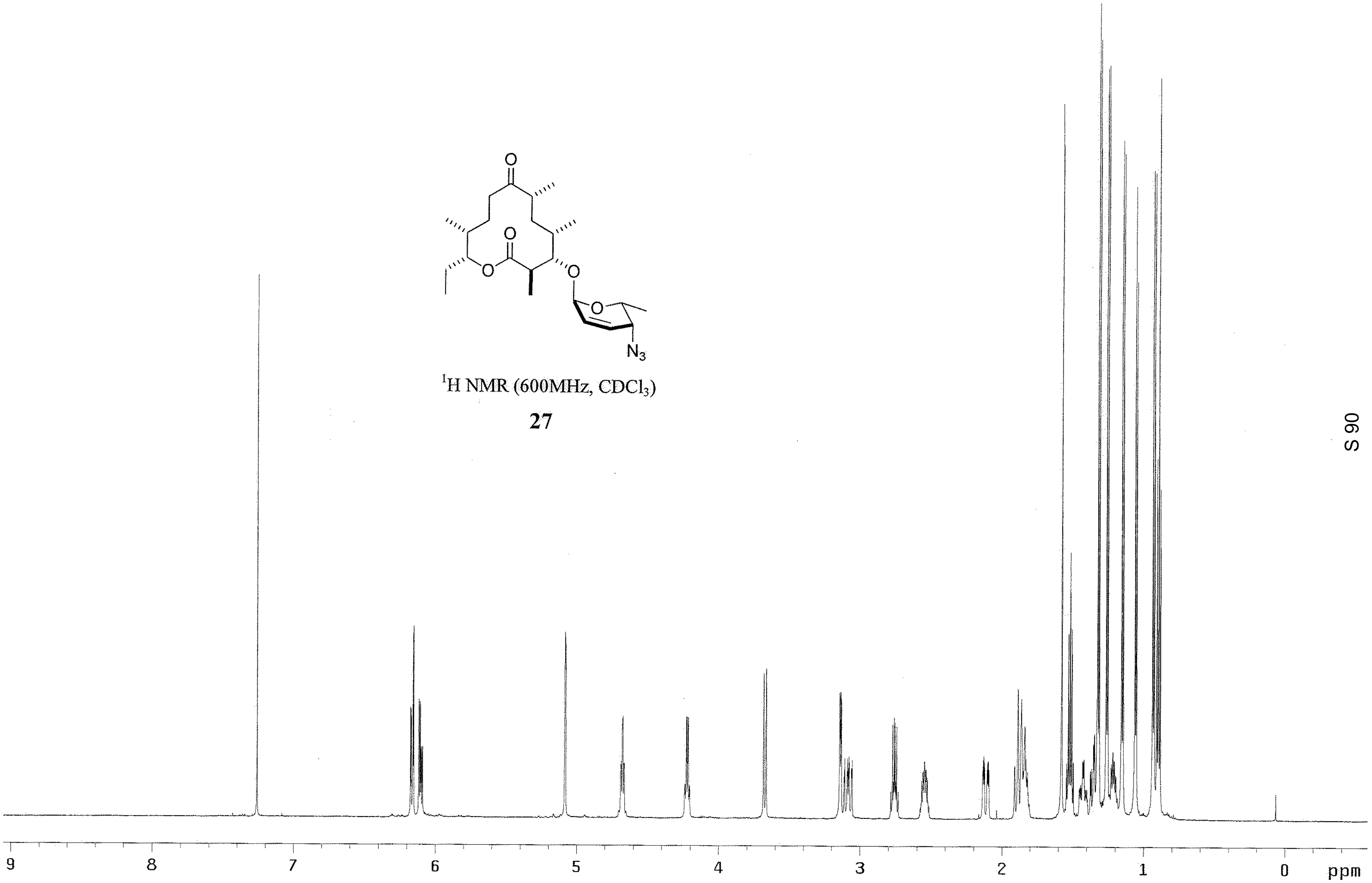

^{1}H NMR (600MHz, CDCl$_3$)

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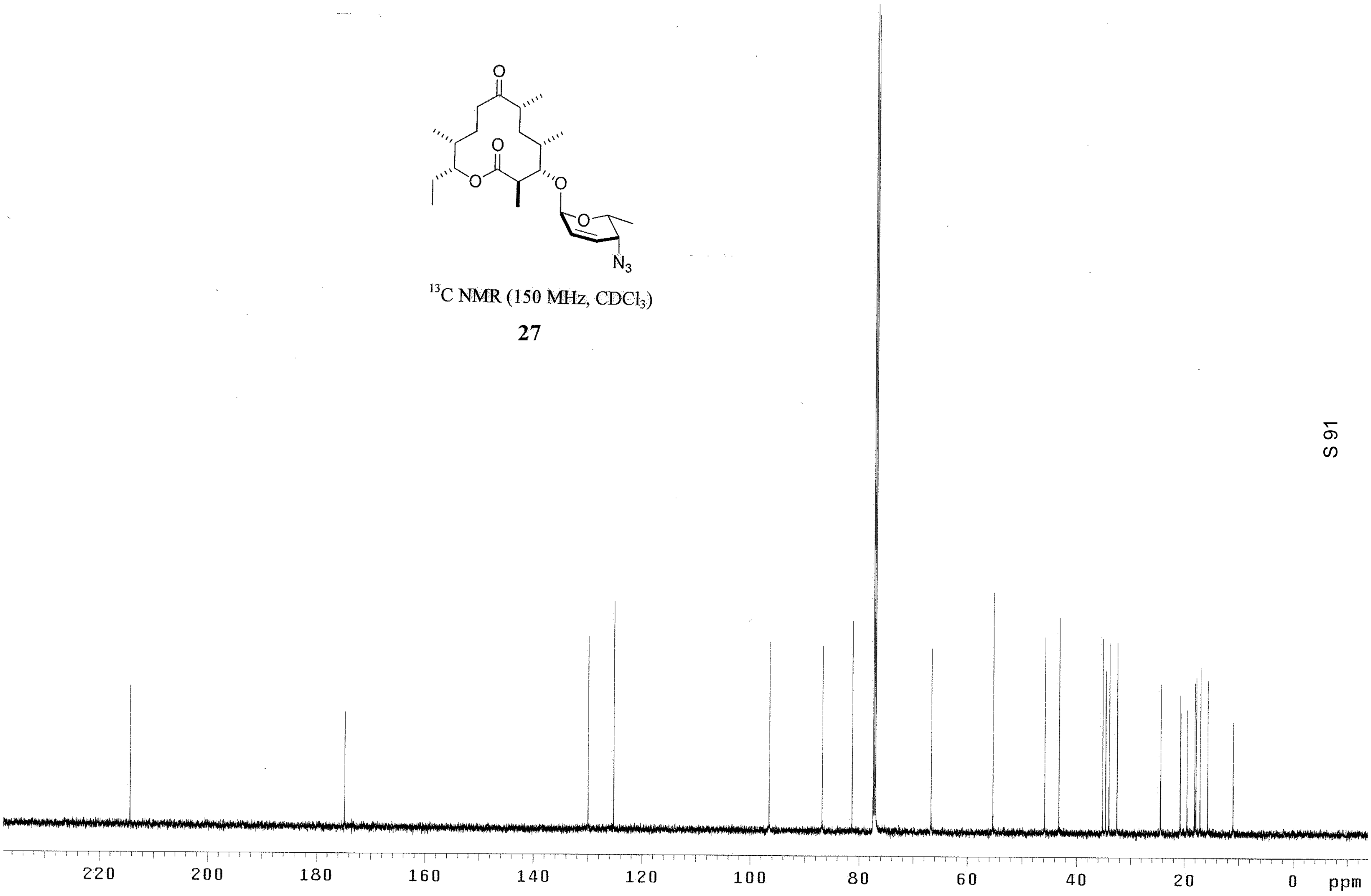

^{13}C NMR (150 MHz, $CDCl_3$)

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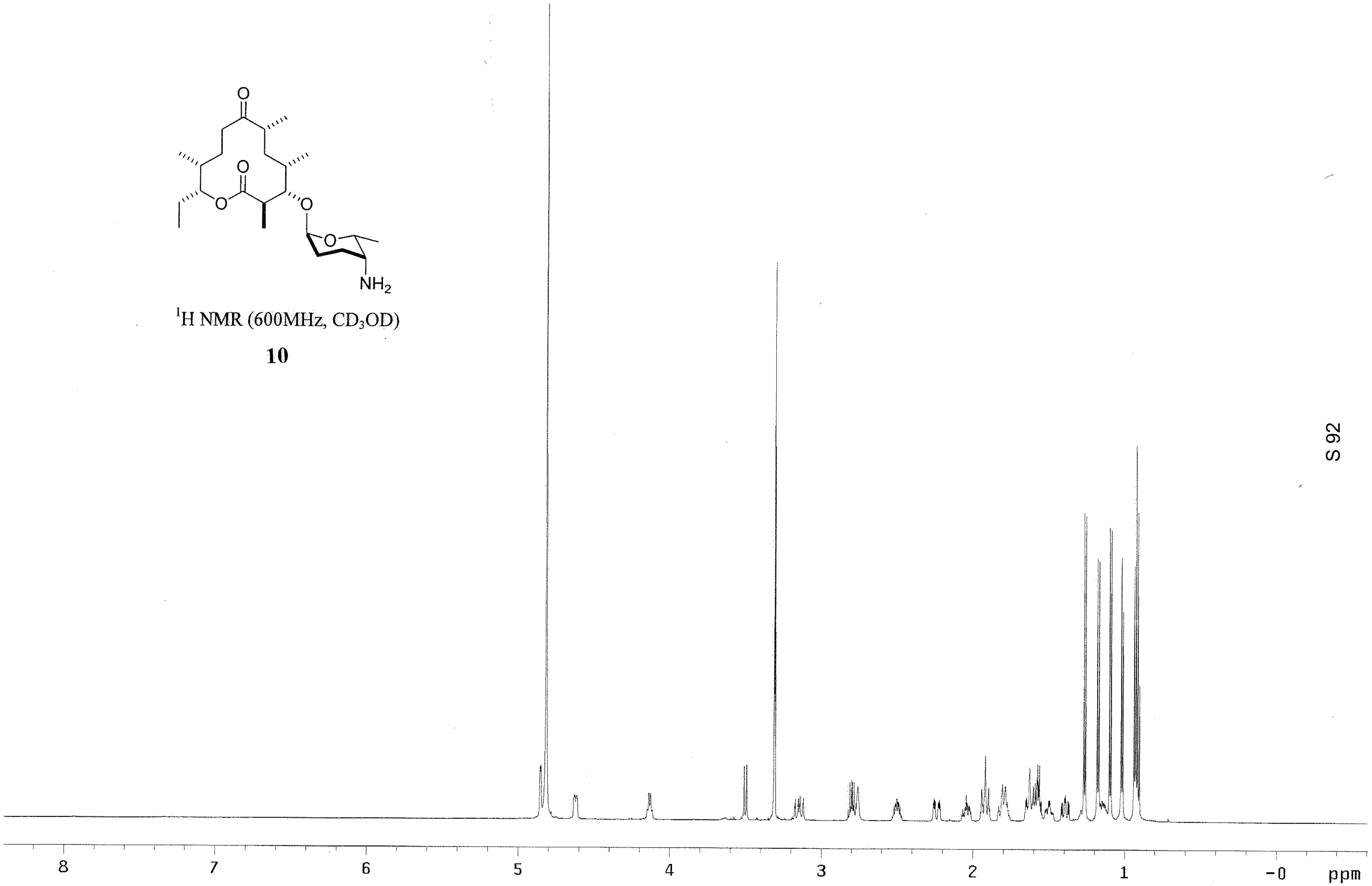

^{1}H NMR (600MHz, CD_3OD)

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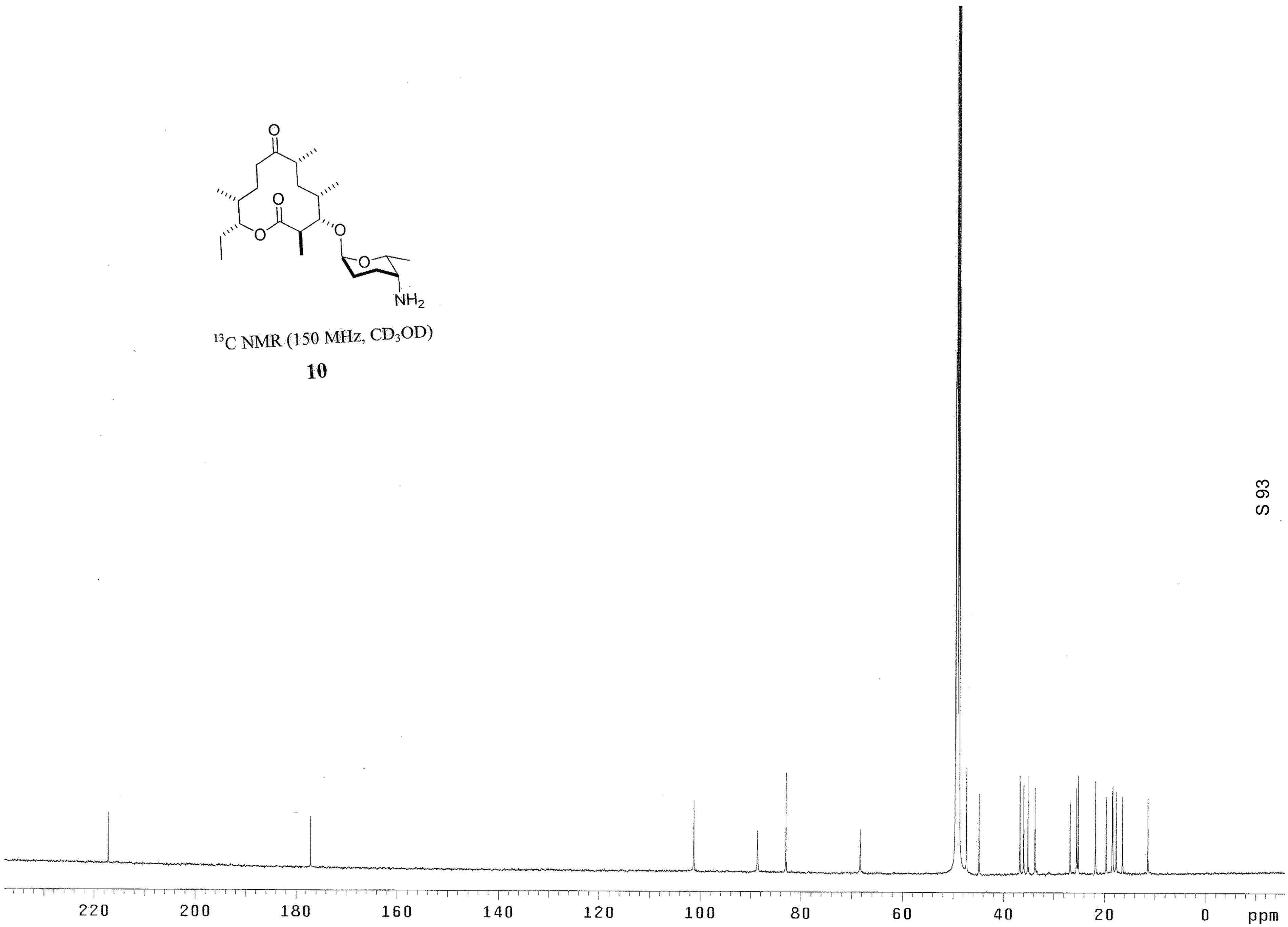

^{13}C NMR (150 MHz, CD$_3$OD)

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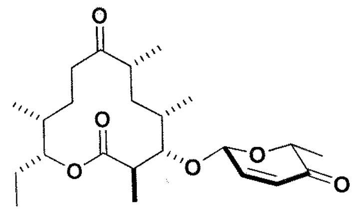

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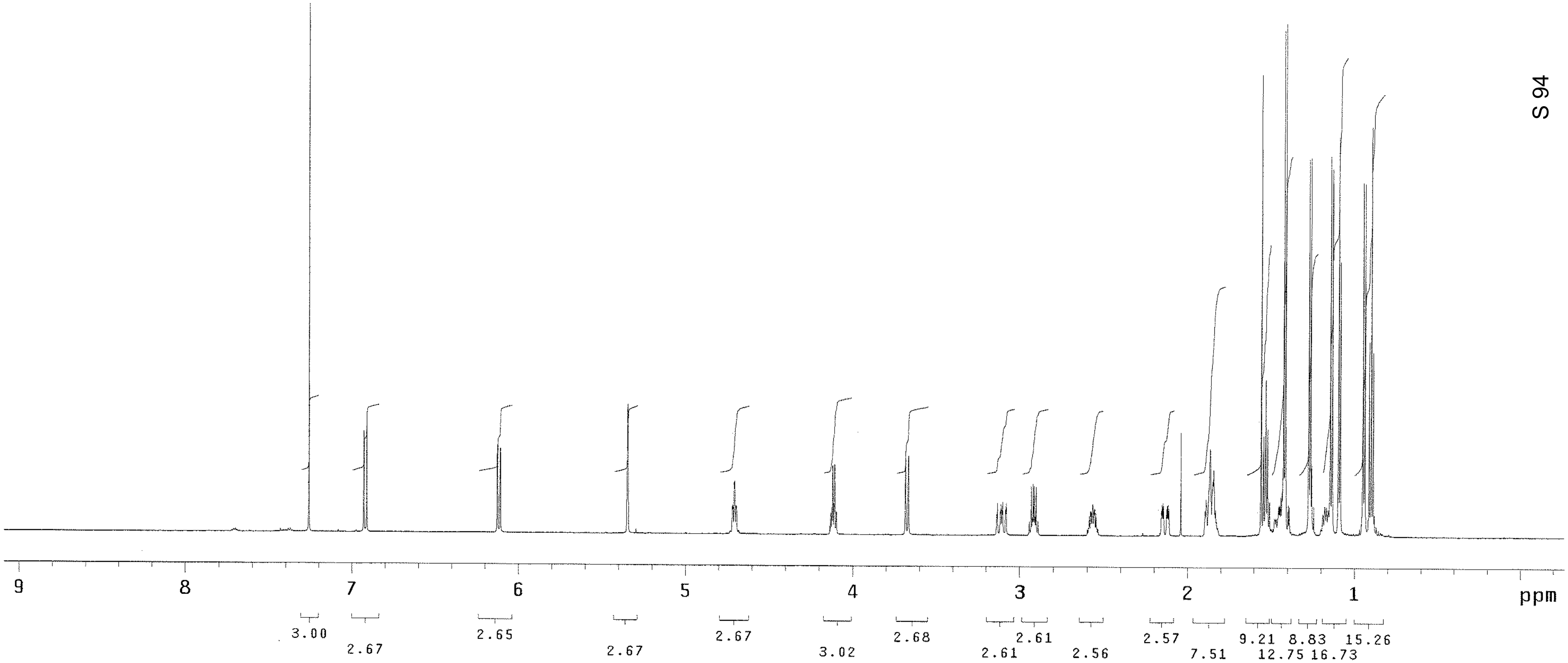

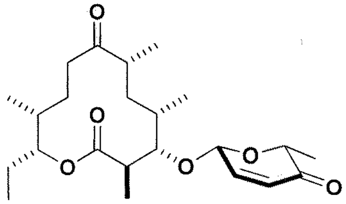

^{13}C NMR (150 MHz, CDCl$_3$)

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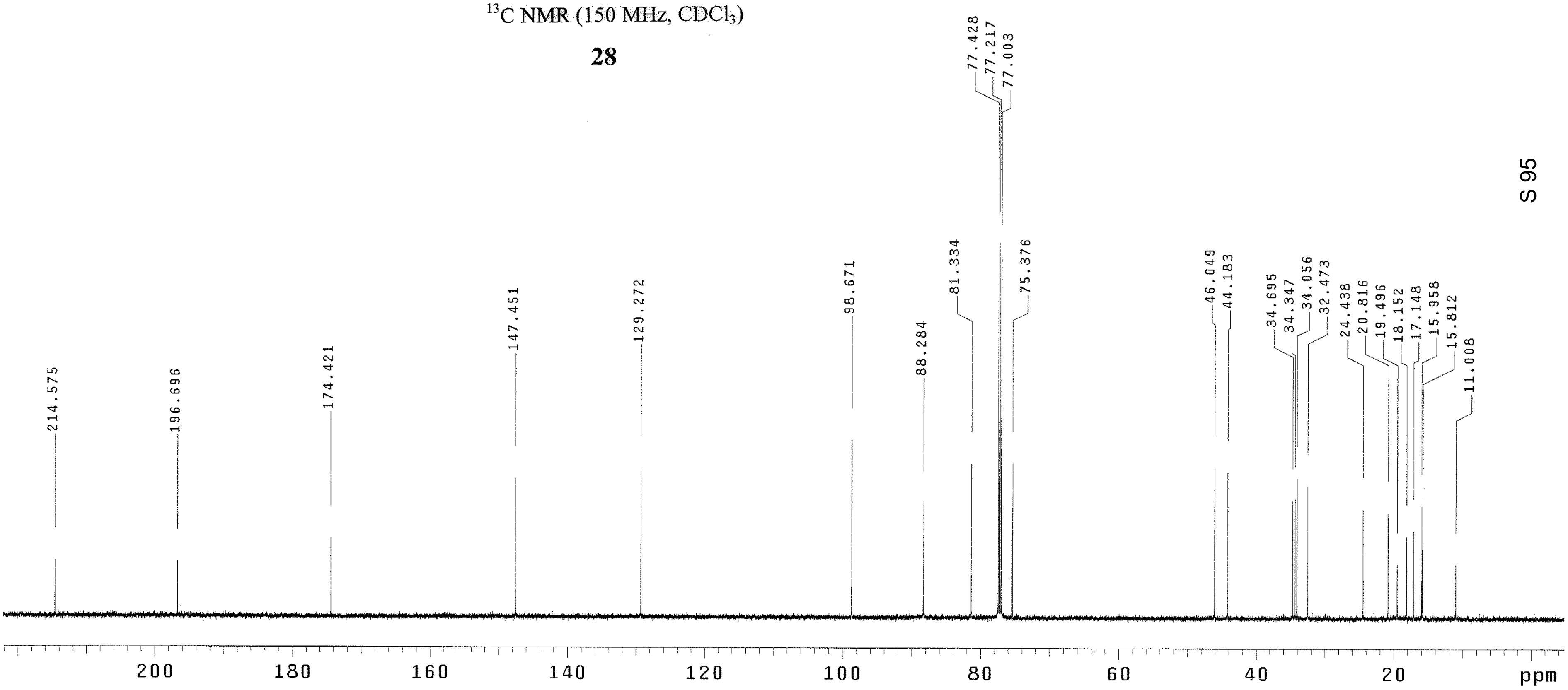

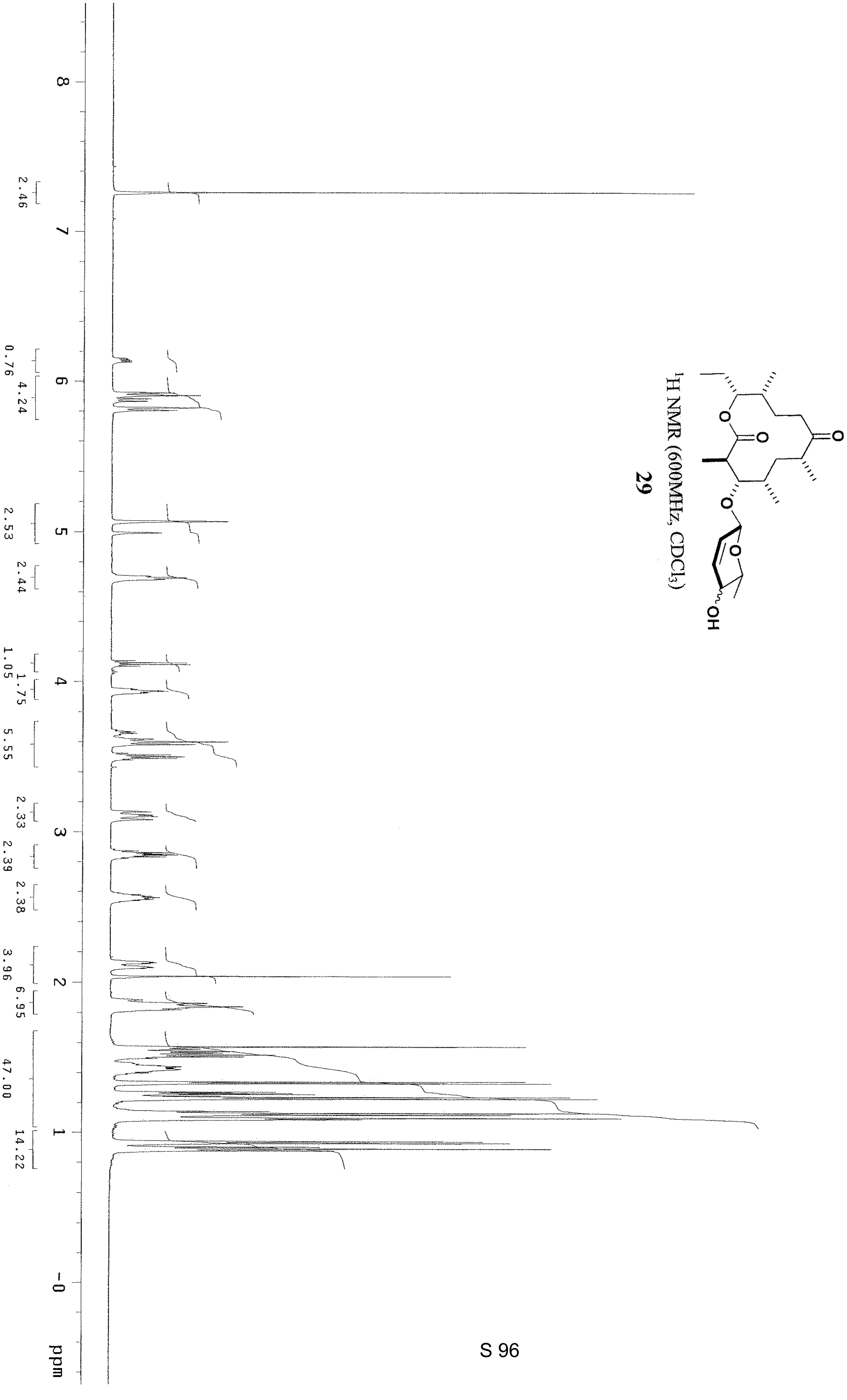

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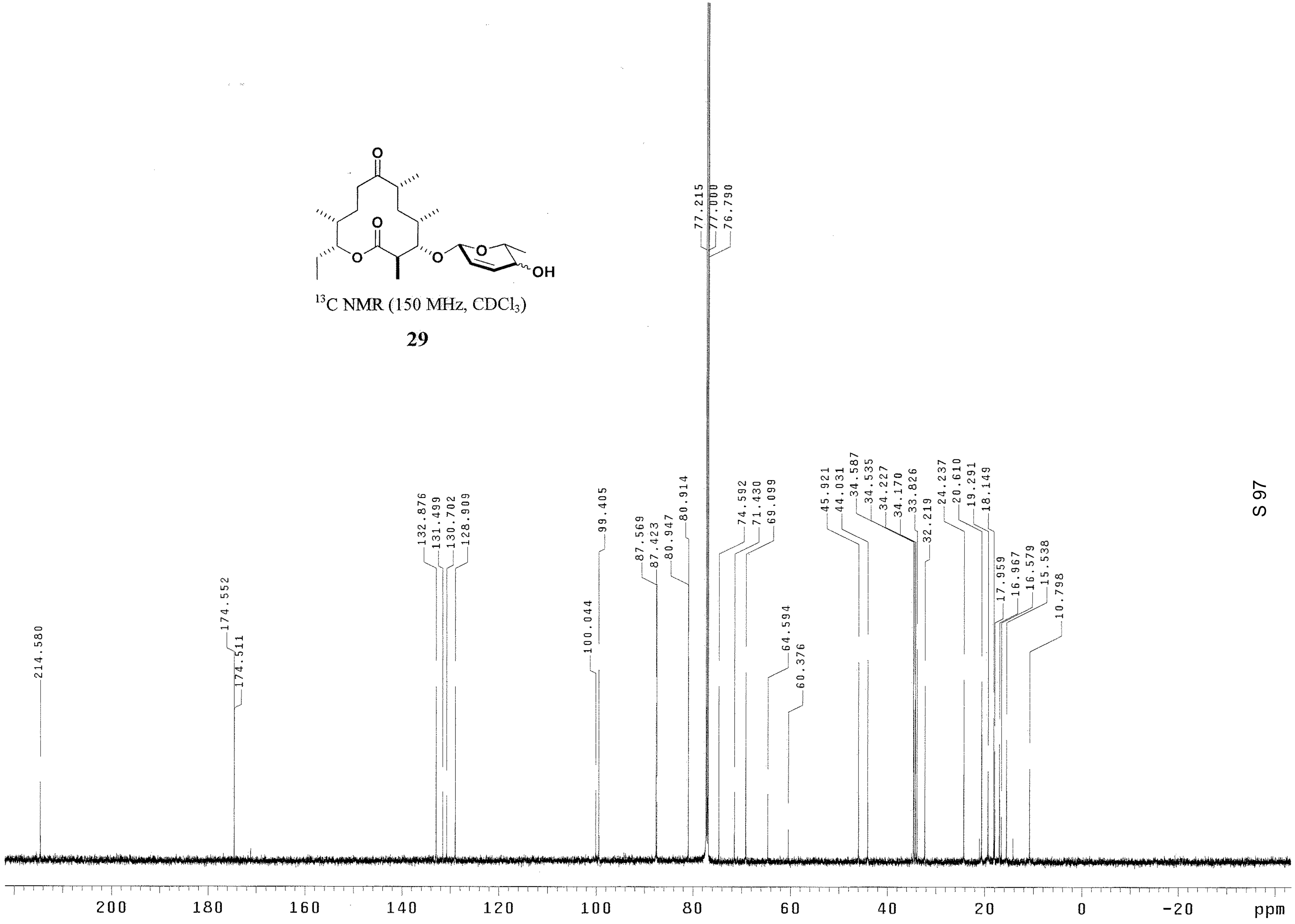

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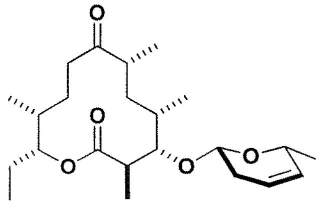

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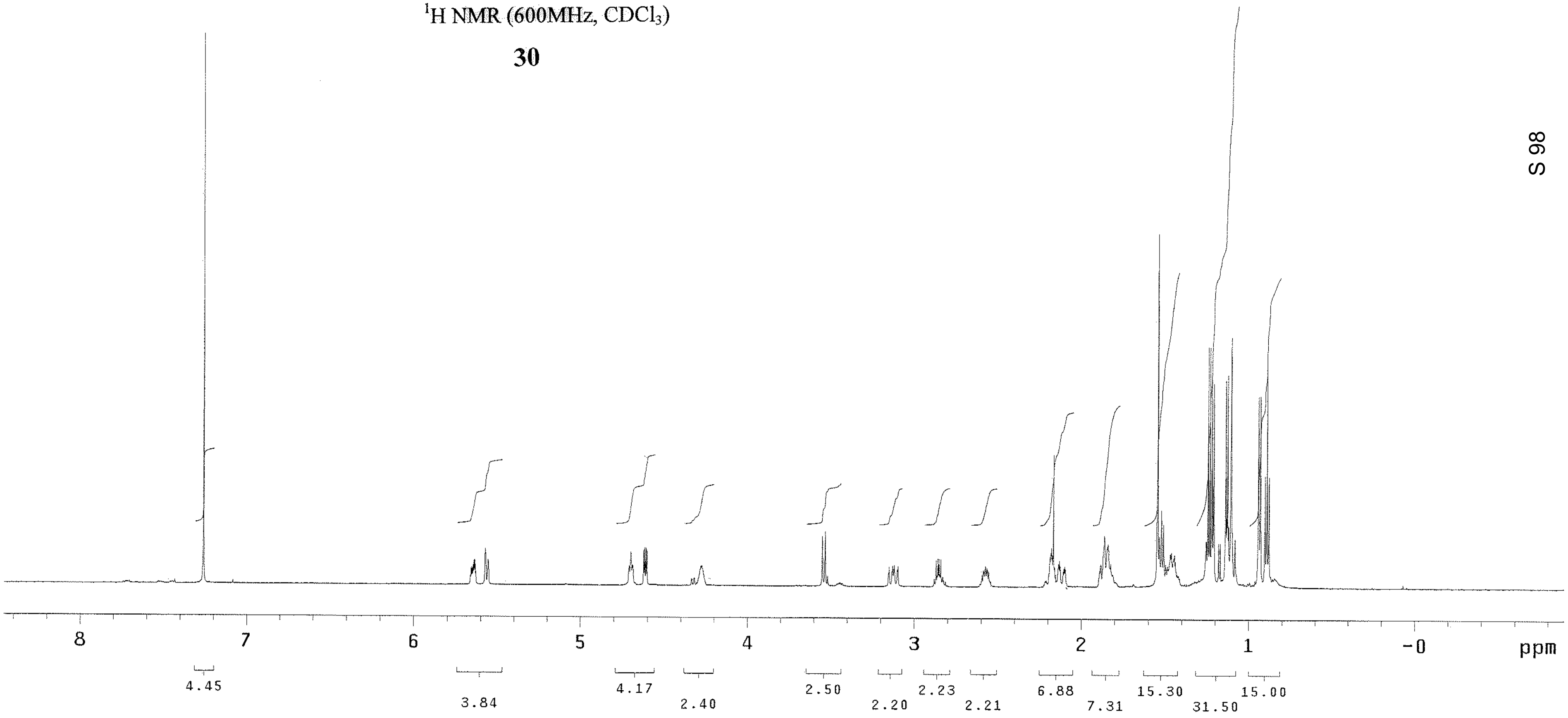

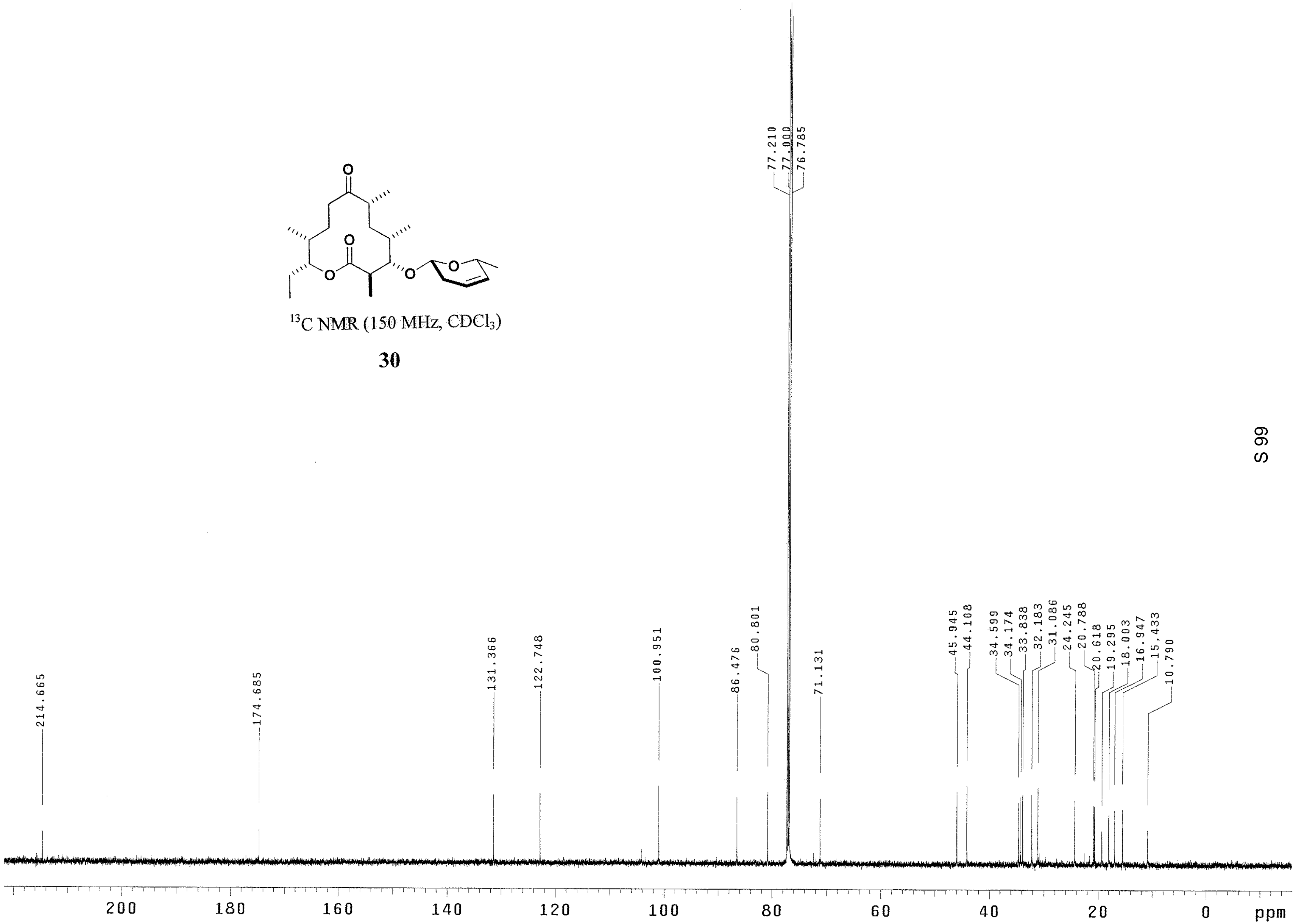

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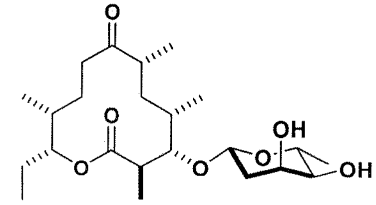

^{1}H NMR (600MHz, CDCl$_3$)

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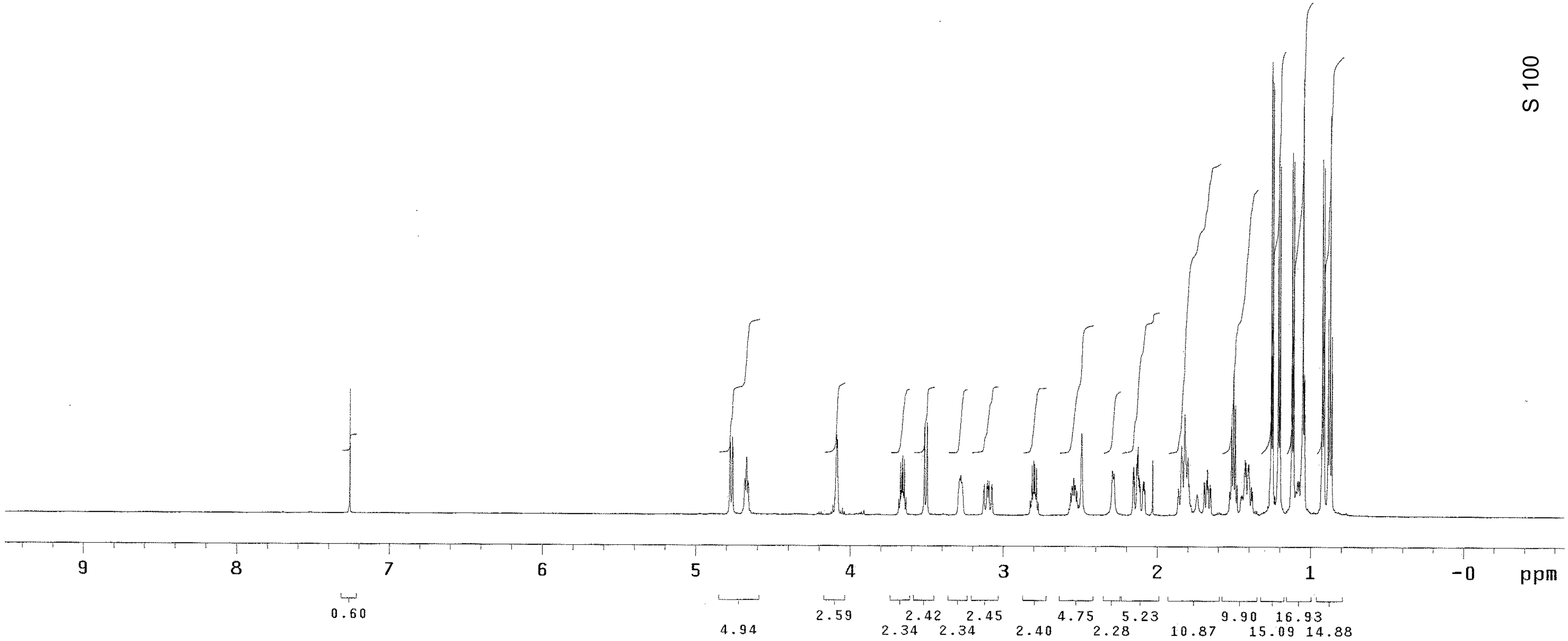

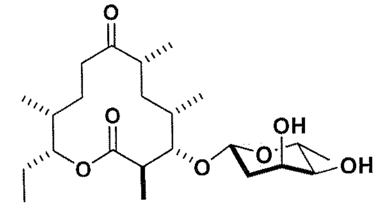

^{13}C NMR (150 MHz, CDCl$_3$)

11