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Experimental Section

General: Solvents were purified according to the guidelines in *Purification of Common Laboratory Chemicals* (Perin, Armarego, and Perin, Pergamon: Oxford, 1966). Reagent grade DMF, EtOH (anhydrous), pyridine, methanol and acetone were purchased and used without further purification. Trichloroacetonitrile was fractionally distilled prior to use and 2,6-lutidine was distilled from CaH_2 and stored over oven dried 4 Å molecular sieves and under nitrogen. The reagents: PCC (ACROS) and O-benzyhydoxyl-amine•HCl (TCI) were purchased and used without further purification. Samarium diiodide was freshly prepared by a modification of the Imamoto and Ono method.[1] The titer of nBuLi was determined by the method of Eastham and Watson.[2] 1-Amino-2-phenylaziridine reagent was prepared using the method of Eschenmosher,[3] and Ph_3SnH was prepared from Ph_3SnCl and LAH using the method of Kuivila.[4] Bu_3SnH (Aldrich) and Ph_3SnH were flushed through a small column of activated alumina prior to use. All other reagents were used without further purification. Yields were calculated for material judged homogeneous by thin layer chromatography and NMR. Thin layer chromatography was performed on Merck Kieselgel 60 F_{254} plates eluting with the solvents indicated, visualized by a 254 nm UV lamp, and stained with either a ethanolic solution of 12-Molybdophosphoric acid, p-anisaldehyde or cerium sulfate. Flash column chromatography was performed with Davisil 62 silica gel, slurry packed with 4% EtOAc/ hexanes in glass columns, and flushed with hexanes prior to use or slurry packed with 1% MeOH/ $CHCl_3$ in glass columns, and flushed with chloroform. Preparative chromatography was also carried out using a Chromatotron using glass plates coated with silica gel (P. F. 254 60) of 2 and 4 mm thickness (RPLC). Nuclear magnetic resonance spectra were acquired on a variable temperature equipped Unity 500 spectrometer at 500 MHz for ^{1}H, 125 MHz for ^{13}C, and 470 MHz ^{19}F. Chemical shifts for proton nuclear magnetic resonance ^{1}H NMR) spectra are reported in parts per million downfield from tetramethylsilane (TMS). Chemical shifts for carbon nuclear magnetic resonance (^{13}C NMR) spectra are reported in parts per million downfield relative to the center line of the triplet of $CDCl_3$ at 77.2 ppm. Chemical shifts for fluorine nuclear magnetic resonance (^{19}F NMR) spectra are reported in parts per million downfield from trifluorotoluene. The abbreviations s, d, t, q, br s, br t, and ABq stand for the resonance multiplicities singlet, doublet, triplet, quartet, broad singlet, broad triplet, and AB quartet, respectively. IR spectra were obtained from a Mattson FT-IR GL-3020 spectrometer. Mass spectra analysis was performed on a Finnigan MAT 95 High resolution gas chromatography / mass spectrometer. Optical rotations were obtained on a Perkin Elmer 241 mc polarimeter (Na D line) using a micro cell with a 1 dm path length. Concentrations are reported in g/100 mL. Melting points were obtained on an Electro thermal melting point apparatus and are uncorrected. Analytical C & H analysis were performed by Atlantic Microlab, Inc., Norcross, Georgia. Glassware for all reactions was oven dried at 125 °C and cooled in a desiccator prior to use. Liquid reagents and solvents were introduced by oven dried syringes through septa sealed flasks under a nitrogen atmosphere. In the reactions involving oxime ethers or lactols, a mixture of oxime isomers or anomers was used. However, for characterization purposes the major oxime isomer or anomer was separated and fully characterized utilizing the separation method described in the experimental section of that compound.

Preparation of 5S-(6-Iodo-3,4-methylenedioxybenzyl ether)-6-O-tert-butyldimethylsiloxy-2,3-O-isopropylidene-D-gulonolactone (**20**): To a stirring suspension of sodium hydride (43 mg, 1.1 mmol), (obtained from a 60% dispersion in mineral oil, washed twice with 6 mL of hexanes) in 30 mL of Et_2O at 0 °C (ice/ water bath) was added the alcohol[5] **19** (2.0 g, 7.2 mmol) followed by trichloroacetonitrile (0.9 mL, 1.2 g, 8.6 mmol). After 4 minutes the reaction was warmed to rt and stirred for 1 h before being concentrated *via* a continuous stream of nitrogen being blown over the reaction mixture. The reaction was quenched with 84 mL of a 20:1 hexanes: MeOH mixture, concentrated under reduced pressure and used without further purification.

To crude trichloroacetaimidate prepared above in 30 mL of Et_2O at 0 °C (ice/ water bath) was added a solution of alcohol[6] **11** (2.9 g, 8.6 mmol in 25 mL of Et_2O, 5 mL wash) *via* cannula followed by triflic acid (159 uL, 270 mg, 1.8 mmol). After 1.5 h the reaction was quenched cold with 30 mL of a saturated solution of $NaHCO_3$, then diluted with 100 mL of Et_2O. The layers were separated and the organic layer was washed successively with a saturated solution of $NaHCO_3$ (2x30 mL), and brine (1x10 mL). The organic layer was dried over $MgSO_4$, filtered through a pad of Celite, and concentrated under reduced pressure. Purification of this material was accomplished by column flash chromatography using a 2.5x20 cm column, eluting with a gradient of 200 mL each of 5%, 10%, 15%, 20% and 25% EtOAc/ hexanes, collecting 20 mL fractions. The product containing fractions (23-32) were collected and concentrated under reduced pressure to give the lactone **20** (3.2 g, 75% over 2 steps) as a clear colorless viscous oil: $[\alpha]_D^{22}$ = -38.7° (c 0.95, $CHCl_3$); R_f 0.50 (35% EtOAc/ hexanes); 500 MHz ^1H NMR ($CDCl_3$) δ 7.19 (s, 1H), 7.07 (s, 1H), 5.94 (s, 2H), 4.83 (d, J = 5.4 Hz, 1H), 4.80 (dd, J =

5.4, 3.4 Hz, 1H), 4.70 (dd, J = 8.1, 3.4 Hz, 1H), 4.59 (ABq, $\Delta\nu$ = 8.1 Hz, J_{AB} = 12.2 Hz, 2H), 3.94 (d, J = 3.0 Hz, 2H), 3.82 (dt, J = 8.3, 2.9 Hz, 1H), 1.46 (s, 3H), 1.38 (s, 3H), 0.89 (s, 9H), 0.064 (s, 3H), 0.061 (s, 3H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 173.6, 148.3, 147.7, 133.9, 118.1, 113.9, 109.5, 101.5, 85.2, 80.1, 79.1, 76.4, 76.0, 62.3, 26.8, 25.9, 25.8, 18.2, -5.4, -5.6; IR (neat) 3079, 2951, 1794, 1478, 1384, 1231, 837 cm^{-1}; Anal. Calcd for $C_{23}H_{33}O_8ISi$: C, 46.02; H, 5.61. Found: C, 46.55; H, 5.63.

Preparation of 5S-(6-Iodo-3,4-methylenedioxybenzyl ether)-2R, 3R-O-isopropylidene-6-tert-butyldimethylsiloxy-4R-(hydroxyl)-hexanal-O-benzyl oxime (**21**): To a stirring solution of the lactone **20** (2.6 g, 4.4 mmol) in 44 mL of THF at -78 °C (acetone/ CO_2) was added a solution of L-Selectride (6.6 mL, 6.6 mmol, 1.0 M in THF) down the side of the flask over a 4 minute period. After 1 h the reaction was quenched cold by the slow addition of 30 mL of water and then allowed to warm to rt. The mixture was diluted with 200 mL of EtOAc and the layers were separated. The aqueous layer was back extracted with EtOAc (3x50 mL) and the combined organic layers were dried over $MgSO_4$, filtered through a pad a Celite (1x6 cm) and concentrated under reduced pressure to give the corresponding lactol as a viscous oil which was used without further purification.

To a stirring solution of crude lactol prepared above in 22 mL of pyridine was added O-benzylhydroxylamine•HCl (1.0 g, 6.6 mmol) in one portion. After 21.5 h the reaction was concentrated under reduced pressure to near dryness, diluted with 200 mL of EtOAc and washed with 25 mL of each: H_2O, saturated solution of $CuSO_4$, H_2O, saturated solution of $CuSO_4$, H_2O, 2% HCl and finally brine. The organic layer was dried over $MgSO_4$ filtered through a pad of Celite and concentrated under reduced pressure.

Purification of this material was accomplished by column flash chromatography on a 2.5x20 cm column and eluting with a solvent gradient of 300 mL each of 10% and 20% EtOAc/hexanes, collecting 20 mL fractions. The product containing fractions (10-20) were collected and concentrated under reduced pressure to give alcohol **21** (3.0 g, 96% yield over 2 steps) as a clear colorless oil and a 1:1 mixture of oxime isomers (inseparable): R_f 0.32 (20% EtOAc/ hexanes); IR (neat) 3549, 3087, 2963, 1949, 1860, 1737, 1620, 1381, 1045, 935, 841 cm^{-1}; Anal. Calcd for $C_{30}H_{42}O_8ISi$: C, 51.50; H, 6.05; N, 2.00. Found: C, 51.45; H, 6.05; N, 1.94.

<u>Preparation of 5S-(6-Iodo-3,4-methylenedioxybenzyl ether)-2R, 3R-O-isopropylidene-4R-tert-butyldimethylsiloxy-6-(hydroxyl)-hexanal-O-benzyl oxime (**22**):</u> To a stirring solution of alcohol **21** (3.20 g, 4.58 mmol) in 30 mL of CH_2Cl_2 at 0 °C (ice/ water bath) was added 2,6-lutidine (2.10 mL, 1.91 g, 17.8 mmol). After 15 minutes TBS-OTf (3.78 mL, 4.30 g, 16.5 mmol) was added dropwise down the side of the flask over a 7 minute period. After 4 h the reaction was quenched cold with 25 mL of a saturated solution of $NaHCO_3$ and diluted with 200 mL of CH_2Cl_2. The layers were separated and the organic layer was washed with 0.5 N $NaHSO_4$, (3x25 mL), brine (1x25 mL) then dried over $MgSO_4$, filtered through a pad of Celite (1x4 cm) and concentrated under reduced pressure to give a light yellow oil which was used without further purification.

To a stirring solution of crude bis-TBS-ether prepared above in 153 mL of THF at 0 °C (ice/ water bath) was added a solution at 0 °C (ice-water bath) consisting of HF•pyridine (27.0 g), pyridine (54.0 mL) and 220 mL of THF. The reaction mixture was allowed to warm to rt and stir 9 h, at which time it was diluted with Et_2O and slowly quenched with 200 mL of saturated $NaHCO_3$, and further neutralized with 92 g of solid $NaHCO_3$. The layers were separated and the organic layer was washed with saturated $NaHCO_3$ (2x100 mL), and brine (100 mL). The combined aqueous layers were back extracted with Et_2O (3x100 mL). The combined organic layers were dried over $MgSO_4$, filtered through a pad of Celite (1x6 cm) and concentrated under reduced pressure. Purification of this material was accomplished by column gravity chromatography on a 4.5x25 cm column, eluting with a gradient of 300 mL each of 5%, 10%, 20% and 25% EtOAc/ hexanes, collecting 20 mL fractions. The product containing fractions (31-67) were collected and concentrated to give the alcohol **22** (2.70 g, 84% yield over 2 steps) as a colorless oil and a 1.4:1 mixture of oxime isomers: (major oxime isomer) $[\alpha]_D^{22}$ = -21.1° (c 1.1, $CHCl_3$); R_f 0.28, 0.32 (20% EtOAc/ hexanes) (minor, major oxime isomers respectively); (major oxime isomer) 500 MHz ^1H NMR ($CDCl_3$) δ 7.46 (d, J = 8.2 Hz, 1H), 7.40-7.32 (m, 5H), 7.27 (s, 1H), 6.96 (s, 1H), 5.98 (s, 2H), 5.09 (s, 2H), 4.59 (dd, J = 8.2, 6.3 Hz, 1H), 4.52 (d, J = 12.1 Hz, 1H), 4.50 (dd, J = 6.0, 6.0 Hz, 1H), 4.40 (d, J = 12.1 Hz, 1H), 3.90 (dd, J = 6.0, 3.6, 1H), 3.75 (dd, J = 6.3, 5.5 Hz, 2H), 3.45 (dt, J = 5.0, 3.9 Hz, 1H), 2.14 (t, J = 6.6 Hz, 1H), 1.50 (s, 3H), 1.38 (s, 3H), 0.93 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 148.7, 148.3, 148.0, 137.7, 133.9, 128.7, 128.6, 128.2, 118.7, 109.9, 109.3, 101.9, 86.6, 78.6, 78.0, 76.3, 75.5, 74.9, 70.9, 60.9, 27.9, 26.2, 25.6, 18.5, -3.9, -4.1; IR (neat) 3484(br), 3087, 2930, 1619, 1477, 1380, 1245, 1110, 836 cm^{-1}; Anal. Calcd for $C_{30}H_{42}INO_8Si$: C, 51.50; H, 6.05; N, 2.00. Found: C, 51.40; H, 6.01; N, 1.97.

Preparation of 5S-(6-Iodo-3,4-methylenedioxybenzyl ether)-2R, 3R-O-isopropylidene-4R-tert-butyldimethylsiloxy-6-(2-phenyl-N-aziridinyl imine)-hexanal-O-benzyl oxime (23): To a stirring solution of the alcohol **22** (1.2 g, 1.7 mmol) in 17 mL of CH_2Cl_2 was added 4Å MS (1.2 g), N-methyl-morpholine-N-oxide (0.30 g, 2.6 mmol) followed by tetrapropylammonium perruthenate (0.030 g, 0.087 mmol). After 53 min the reaction was filtered through a pad of $MgSO_4$ (0.2x6 cm), Celite (0.2x6 cm) and silica (1x6 cm). The filter pad was washed with 300 mL of EtOAc/ hexanes and the filtrate was concentrated under reduced pressure to give a light yellow viscous oil that was used without further purification.

To a stirring solution of aldehyde prepared above in 17 mL of EtOH at 0 °C (ice/ water bath) was added a solution of 1-amino-2-phenylaziridine (6.9 ml 3.4 mmol, 0.50 M in CH_2Cl_2) dropwise. After complete addition the reaction was warmed to rt and stirred 3 h before being quenched with 30 mL of water and diluted with 100 mL of CH_2Cl_2. The layers were separated and the aqueous layer was back extracted with CH_2Cl_2 (3x50 mL). The combined organic layers were dried over $MgSO_4$ and filtered through a pad of Celite and concentrated under reduced pressure. Purification of this material was accomplished by RPLC using a 4 mm disk, eluting with a gradient of 200 mL each of 5% and 10% acetone/ hexanes, collecting 8 mL fractions. The product containing fractions (26-36) were collected and concentrated to give **23** (1.2 g, 83% yield over 2 steps) of an inseparable mixture of oxime isomers, aziridinyl imine isomers as well as diastereomers and as a clear colorless oil: R_f 0.39 (20% EtOAc/ hexanes); IR (neat) 2985, 2856, 1948, 1875, 1808, 1602, 1501, 1477, 1232, 1039, 836 cm^{-1}; Anal. Calcd for $C_{38}H_{48}IN_3O_7Si$: C, 56.08; H, 5.95; N, 5.16. Found: C, 56.18; H, 5.94; N, 5.18.

Preparation of (1R, 2R, 3R, 4S, 4aR, 11bR)1-N-Benzyloxyamine-1, 2, 3, 4, 4a, 11b-hexahydro-2, 3-O-isopropylidene-4-tert-butyldimethylsilyloxy-6H-[1, 3]benzodioxolo[5, 6-c][1]bezopyran (**24**): To a stirring solution of the aziridinyl imine **23** (0.82 g, 1.0 mmol) in 20.3 mL of benzene (deoxygenated with N_2 for 15 minutes) at 77-80 °C was added a solution of triphenyl tin hydride (0.71 g, 2.0 mmol) and 2,2-azobis[2-methyl-propionitrile] (0.33 g, 0.20 mmol) in 5 mL of benzene (deoxygenated with N_2 for 15 minutes) *via* syringe pump over 5 h, including the contents of the syringe needle. The reaction was allowed to stir an additional 1.5 h before being concentrated under reduced pressure. Purification of this material was accomplished by column flash chromatography on a 3.5x18 cm column, eluting with a gradient of 200 mL each of 5%, 10% and 15% EtOAc/ hexanes, collecting 8 mL fractions. The product containing fractions (75-100) were collected and concentrated to give **24** (0.44 g, 79% yield) as a single isomer and as a light yellow foam: $[\alpha]_D^{22}$ = +37.0° (c 1.5, $CHCl_3$); R_f 0.35 (25% EtOAc/ hexanes); 500 MHz ^{1}H NMR ($CDCl_3$) δ 7.41–7.31 (m, 5H), 6.95 (s, 1H), 6.48 (s, 1H), 6.01 (bs, 1H), 5.93 (s, 2H), 4.88 (ABq, Δν = 15.5 Hz, J_{AB} = 11.3 Hz, 2H), 4.79 (ABq, Δν = 41.0 Hz, J_{AB} = 11.3 Hz, 2H), 4.62 (dd, J = 8.8, 5.5 Hz, 1H), 4.24 (dd, J = 3.3, 3.0 Hz, 1H), 4.21 (ddd, J = 5.3, 3.3, 0.8 Hz, 1H), 3.77 (dd, J = 2.5, 2.5 Hz, 1H), 3.10 (dd, J = 11.3, 2.2 Hz, 1H), 3.00 (dd, J = 11.3, 8.8 Hz, 1H), 1.49 (s, 3H), 1.40 (s, 3H), 0.90 (s, 9H), 0.15 (s, 3H), 0.10 (s, 3H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 146.9, 146.2, 137.7, 128.5, 128.2, 127.9, 127.8, 127.0, 110.3, 109.0, 104.6, 101.0, 78.2, 78.2, 77.0, 73.9, 70.6, 68.9, 63.1, 34.7, 28.4, 26.2, 25.8, 18.1, -4.8, -4.9; IR($CHCl_3$) 3063, 2952, 1503, 1484, 1370, 1112, 1040, 838 cm^{-1}; Anal. Calcd for $C_{30}H_{41}NO_7Si$: C, 64.84; H, 7.44; N, 2.52. Found: C, 64.59; H, 7.47; N, 2.79.

Preparation of (1R, 2R, 3R, 4S, 4aR, 11bR)-1, 2, 3 ,4a, 11b-Hexahydro-2, 3-O-isopropylidene-4-tert-butyldimethylsiloxy-1-[(2,2,2-trifluoroacetyl)-amino]-benzodioxolo-[5, 6-c][1]benzopyran (25): To a stirring solution of hydroxylamine **24** (0.23 g, 0.41 mmol) in 8.4 mL of THF was added dropwise a freshly prepared solution of samarium diiodide (9.2 mL, 0.92 mmol, 0.10 M in THF), prepared by heating samarium metal (0.33 g, 2.2 mmol) and iodine (0.40 g, 1.8 mmol) in 16 mL of THF at 60 °C for 4 h prior to cooling to rt. After 2 h the faint blue-green reaction mixture was quenched with trifluroacetic anhydride (235 uL, 0.35 g, 1.7 mmol) and was allowed to stir for 3 h before 10 mL of saturated solution of $Na_2S_2O_3$ was added. The resulting mixture was stirred 0.5 h before being diluted with 50 mL of EtOAc. The layers were separated and the organic layer was washed with a saturated solution of $Na_2S_2O_3$ (3x10 mL) and brine (1x10 mL). The organic layer was dried over $MgSO_4$, filtered through a pad of Celite and concentrated under reduced pressure. Purification was accomplished by column flash chromatography, using a 1.5x16 cm column packed with 20% EtOAc/ hexanes, eluting with 200 mL of 20% EtOAc/ hexanes, collecting 8 mL fractions. The product containing fractions (9-16) were collected and concentrated to give **25** (0.20 g, 88% yield) as colorless solid flakes: mp 189-192 (dec); $[\alpha]_D^{21}$ = -20.5° (c 0.43, $CHCl_3$); R_f 0.31 (25% EtOAc/ hexanes); 500 MHz ^{1}H NMR ($CDCl_3$) δ 6.49 (bd, J = 9.3 Hz, 1H), 6.46 (s, 1H), 6.45 (s, 1H), 5.88 (ABq, $\Delta\nu$ = 12.1 Hz, J_{AB}= 1.7 Hz, 2H), 4.93 (d, J = 15.1 Hz, 1H), 4.78 (d, J = 14.8 Hz, 1H), 4.33 (dd, J = 2.8, 2.5 Hz, 1H), 4.31 (dd, J = 9.3, 5.2 Hz, 1H), 4.25 (ddd, J = 11.3, 9.3, 9.3 Hz, 1H), 4.19 (ddd, J = 4.9, 2.1, 0.7 Hz, 1H), 3.82-3.80 (bm, 1H), 2.88 (dd, J = 11.5, 1.9 Hz, 1H), 1.49 (s, 3H), 1.35 (s, 3H), 0.92 (s, 9H), 0.14 (s, 3H), 0.10 (s, 3H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 157.5 (q, $J_{C\text{-}F}$ = 37.1 Hz), 147.3, 146.2, 127.5, 126.9, 116.3 (q, $J_{C\text{-}F}$ = 288.4 Hz), 109.7, 109.4, 104.8, 101.5, 78.4, 77.4, 76.0, 69.6, 69.0, 54.1, 37.0, 28.7, 26.2, 25.9, 18.2, -4.9; 470 MHz ^{19}F NMR ($CDCl_3$) δ 117.8; IR (CHCl3) 3291, 2943, 2911, 1719, 1559, 1497 cm^{-1}; Anal. Calcd for $C_{25}H_{34}F_3NO_7Si$: C, 55.03; H, 6.28; N, 2.57. Found: C, 54.98; H, 6.25; N, 2.61.

Preparation of (1R, 2R, 3R, 4S, 4aR, 11bR)-1, 2, 3 ,4a, 11b-Hexahydro-2, 3-O-isopropylidene-4-tert-butyldimethylsiloxy-1-[(2,2,2-trifluoroacetyl)-amino]-benzodioxolo-[5, 6-c][1]benzopyran-6-one (**26**): To a stirring solutions of benzyl ether **25** (94.0 mg, 0.172 mmol) in 1.7 mL of CH_2Cl_2 was added pyridinium chlorochromate (PCC) (37.2 mg, 0.172 mmol) and then heated to 60 °C in a sealed vial. After 1 h and 1 h interval thereafter the reaction was cooled to rt and an additional amount of PCC (37.2 mg, 0.172 mmol) was added and reheated to 60 °C, (a total of 5 equivalents of PCC was added). After of a total of 9 h the reaction was cooled to rt and purified. Purification of this material was accomplished by column flash chromatography using a 1x8 cm column packed with 20% EtOAc/ hexanes, eluting with 200 mL of 20 % EtOAc/ hexanes, collecting 8 mL fractions. The product containing fractions (11-30) were collected and concentrated to give the lactone **26** (75.3 mg, 78% yield) as a colorless solid: mp 269-272 °C (dec.); $[\alpha]_D^{21}$ = +18.8° (c 1.3, CHCl3); R_f 0.22 (25% EtOAc/ hexanes); 500 MHz ^{1}H NMR ($CDCl_3$) δ 7.44 (s, 1H), 6.72 (d, J = 8.5 Hz, 1H), 6.65 (s, 1H), 6.05 (s, 2H), 4.55 (m, 1H), 4.52 (dd, J = 9.1, 5.0 Hz, 1H), 4.50 (m, 1H), 4.26 (bd, J = 5.0 Hz, 1H), 3.82

(ddd, J = 11.8, 9.1, 9.0 Hz, 1H), 3.43 (dd, J = 12.0, 2.5 Hz, 1H), 1.48 (s, 3H), 1.37 (s, 3H), 0.90 (s, 9H), 0.17 (s, 3H), 0.10 (s, 3H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 163.7, 157.7 (q, $J_{C\text{-}F}$ = 37.1 Hz), 152.7, 148.4, 135.8, 118.5, 115.7 (q, $J_{C\text{-}F}$ = 288.5 Hz), 110.3, 109.9, 108.0, 102.4, 79.4, 78.2, 74.7, 68.1, 53.9, 35.9, 28.4, 26.1, 25.8, 18.1, -4.8, -4.9; 470 MHz ^{19}F NMR ($CDCl_3$) δ 117.8; IR (CHCl3) 3416, 2973, 2944, 1717, 1716, 1487, 1171 cm^{-1}; Anal. Calcd for $C_{25}H_{32}F_3NO_8Si$: C, 53.66; H, 5.76; N, 2.50. Found: C, 53.67; H, 5.76; N, 2.53.

Preparation of (+)-7-Deoxypancratistatin or [(+)-(1R, 2S, 3S, 4S, 4aR, 11bR)]-1,3,4,4a,11b-Hexahydro-1,2,3,4-tetrahyroxy-[1,3]dioxolo[4,5-j]phenanthridin-6[(2H)-one (1): To a stirring solution of the amide **26** (24.3 mg, 0.0434 mmol) in 1.3 mL of $CHCl_3$ was added $BF_3{\bullet}OEt_2$ (110 uL, 123 mg, 0.868 mmol). After 16 h the reaction was concentrated under high vacuum pressure to give a colorless paste that was used without further purification.

To a stirring solution of triol prepared above in 1.3 mL of MeOH was added K_2CO_3 (70.0 mg, 0.506 mmol) and heated to 70 °C in a sealed vial. After 23 h the reaction was cooled to rt, diluted with 1.5 mL of MeOH and acidified with excess DOWEX H^+ resin (300 mg) to pH = 4-5 by litmus paper. The solution was filtered through scintered glass funnel and concentrated. Purification of this material was accomplished by column flash chromatography on a 0.6x5 cm column, eluting with a gradient of 5 mL each of 10%, 20%, 40%, 60%, and 80% MeOH/$CHCl_3$, collecting 0.7 mL fractions. The product containing fractions (9-27) were collected and concentrated under reduced pressure to give a yellow solid which was further purified by dissolving in the tetra-ol in MeOH and filtering it through a pad of alumina, washing the pad with several portions of MeOH. The filtrate was concentrated under reduced pressure to give (+)-7-deoxypancratistatin **1** (11.8 mg, 88% over 2 steps) as a colorless solid: $[\alpha]_D^{20}$ = +60.0° (c 0.85, DMF);. R*f* 0.44 (30% MeOH/ $CHCl_3$); 500 MHz ^{1}H NMR (DMSO d_6) δ 7.31 (s, 1H), 6.90 (s, 1H), 6.90 (s, 1H), 6.07 (s, 2H), 5.41 (d, *J* = 4.4 Hz, 1H), 5.15 (d, *J* = 6.3 Hz, 1H), 5.12 (d, *J* = 5.9 Hz, 1H), 4.85 (d, *J* = 7.3 Hz, 1H), 4.32-4.30 (m, 1H), 3.97 (dd, *J* = 6.8, 3.3 Hz, 1H), 3.88-3.86 (m, 1H), 3.76-3.66 (m, 2H), 2.98 (br dd, *J* = 11.7, 2.4 Hz, 1H); 125 MHz ^{13}C NMR (DMSO d_6) δ 164.0, 150.5, 145.8, 135.4, 123.8, 106.7, 105.5, 101.5, 73.4, 70.3, 70.1, 68.7, 50.4, 40.1.

Preparation of [(+)-(1R, 2S, 3S, 4S, 4aR, 11bR)]-1,3,4,4-Tetraacetoxy-1,2,3,4a,5,11b-hexahydro-[1,3]dioxolo[4,5-j]phenanthridin-6-(2H)-one: To a stirring solution of 7-deoxypancratistatin **1** (11.2 mg, 0.04 mmol) in 0.5 mL of pyridine was added 0.5 mL of acetic anhydride. The reaction mixture was stirred 12 h then concentrated under high vacuum pressure to give a thin film. Purification of this material was accomplished by column flash chromatography using a 0.5x8 cm column, eluting with a gradient of 5 mL each of 30%, 40%, 50%, 60% and 80% EtOAc/hexanes, collecting 0.7 mL fractions. The product containing fractions (21-31) were collected and concentrated to give the tetraacetate (12.1 mg, 70% yield) as a colorless solid: $[\alpha]_D^{20}$ = +71.4° (c 0.95, $CHCl_3$), 500 MHz ^{1}H NMR ($CDCl_3$) δ 7.57 (s, 1H), 6.57 (s, 1H), 6.45 (br s, 1H), 6.04 (ABq, $\Delta\nu$ = 8.4 Hz, J_{AB}= 1.4 Hz, 2H), 5.59 (dd, *J* = 2.5, 2.5 Hz, 1H), 5.47 (dd, *J* = 3.0, 3.0 Hz, 1H), 5.23 (dd, *J* = 2.9, 2.9 Hz, 1H), 5.19 (dd, *J* = 11.0, 3.6 Hz, 1H), 4.31 (dd, *J* = 12.9, 10.7, 1H), 3.46 (dd, *J* = 13.2, 3.0 Hz, 1H), 2.17 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.05

(s, 3H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 170.0, 169.9, 169.1, 168.3, 165.0, 151.8, 147.3, 131.5, 123/3, 108.5, 103.7, 101.9, 71.6, 67.7, 66.9, 66.3, 48.2, 39.5, 20.8, 20.7, 20.6, 20.5.

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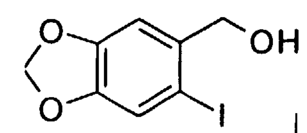
5. (a) This material was prepared by oxidation of iodopiperonal, which in turn is available in three steps from bromopiperonal using the method of Charlton: Bogucki, D. E.; Charlton, J. L. *J. Org. Chem.* **1995**, *60*, 588. (b) A preparation of 6-iodopiperonol is also described in this paper.

6. This material was prepared in three steps from D-gulonolactone using the general procedure of Fleet: Fleet, G. W. J.; Ramsden, N. G.; Witty, D. R. *Tetrahedron* **1989**, *45*, 319.



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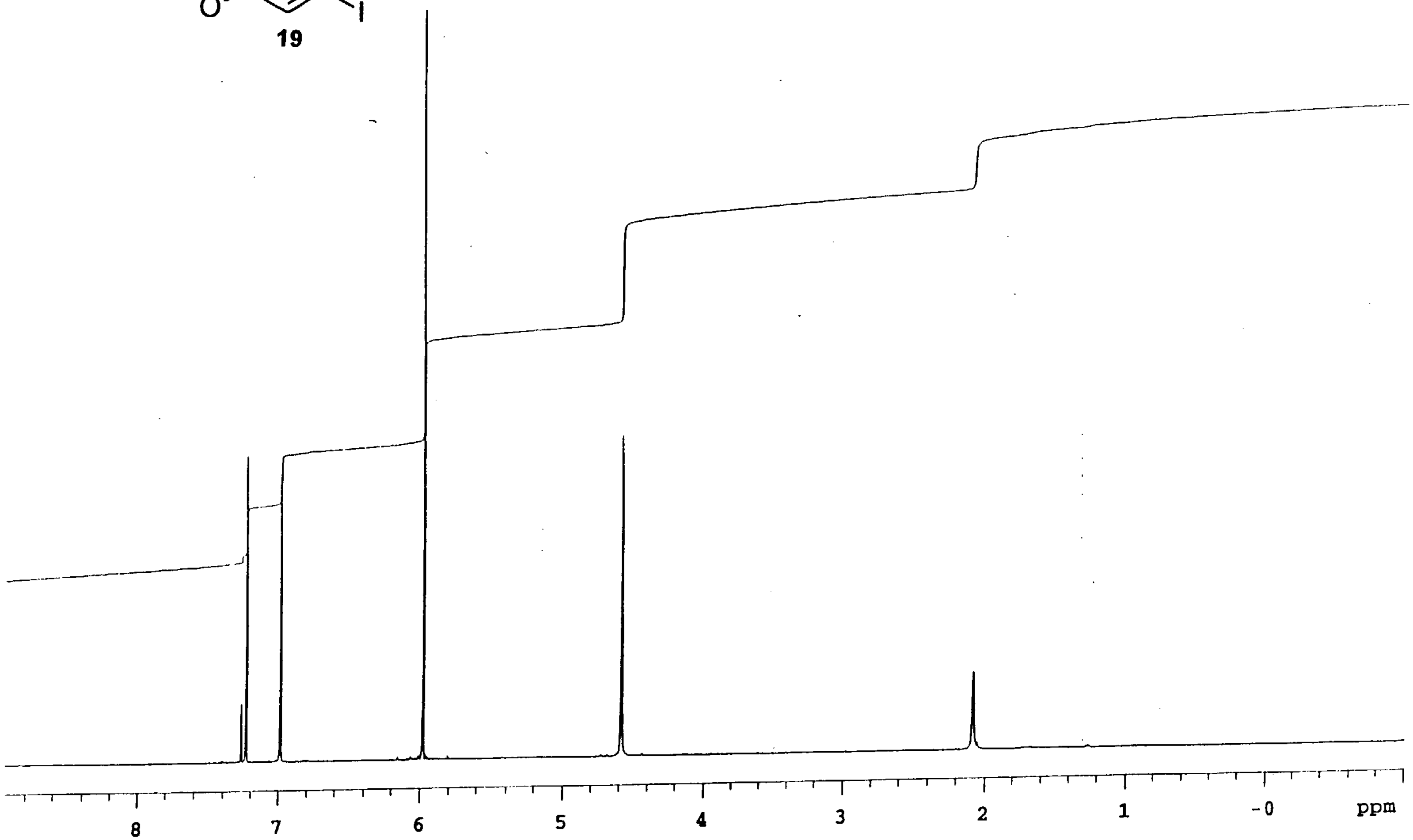

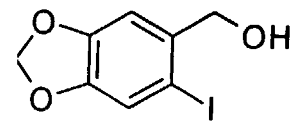

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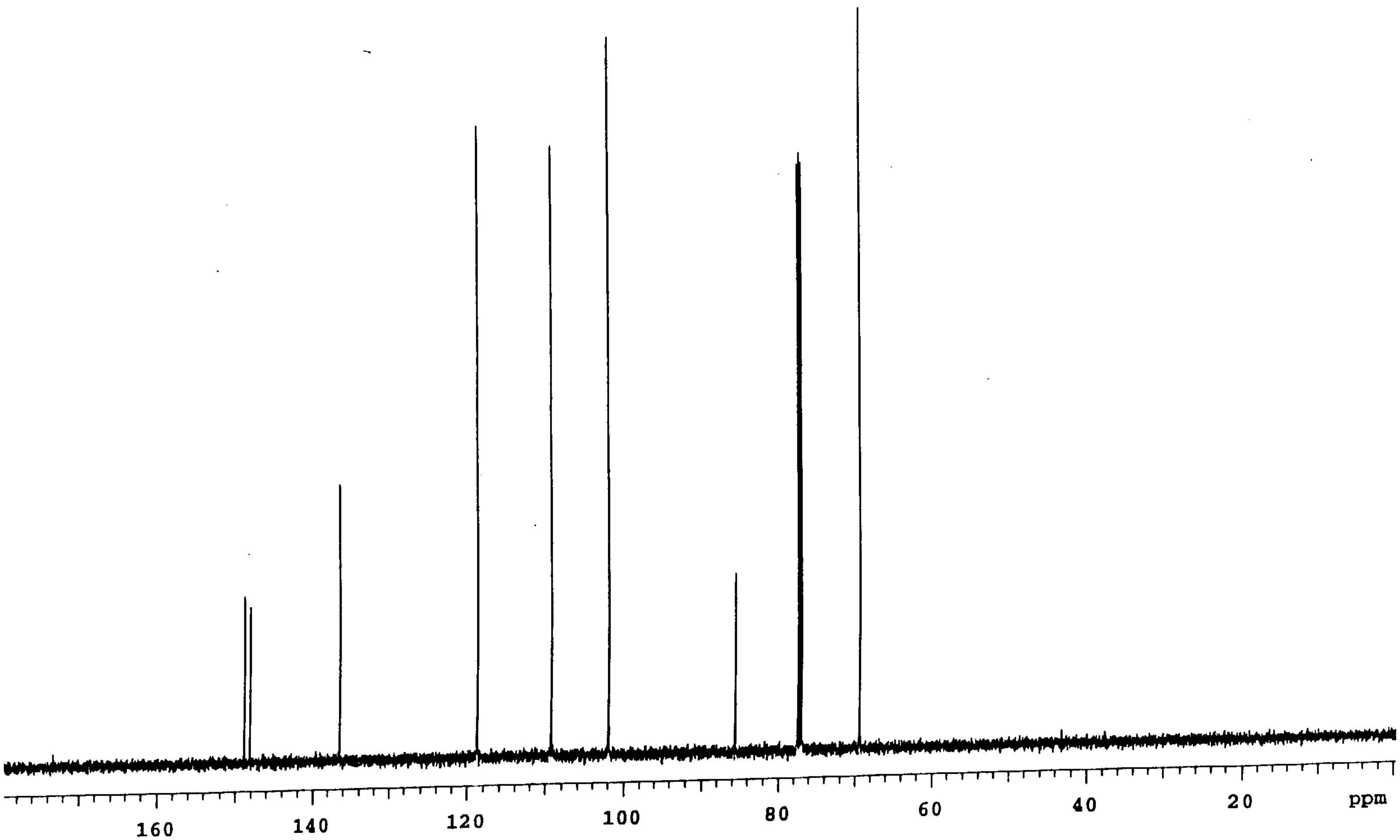

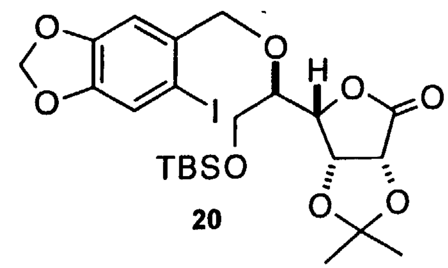

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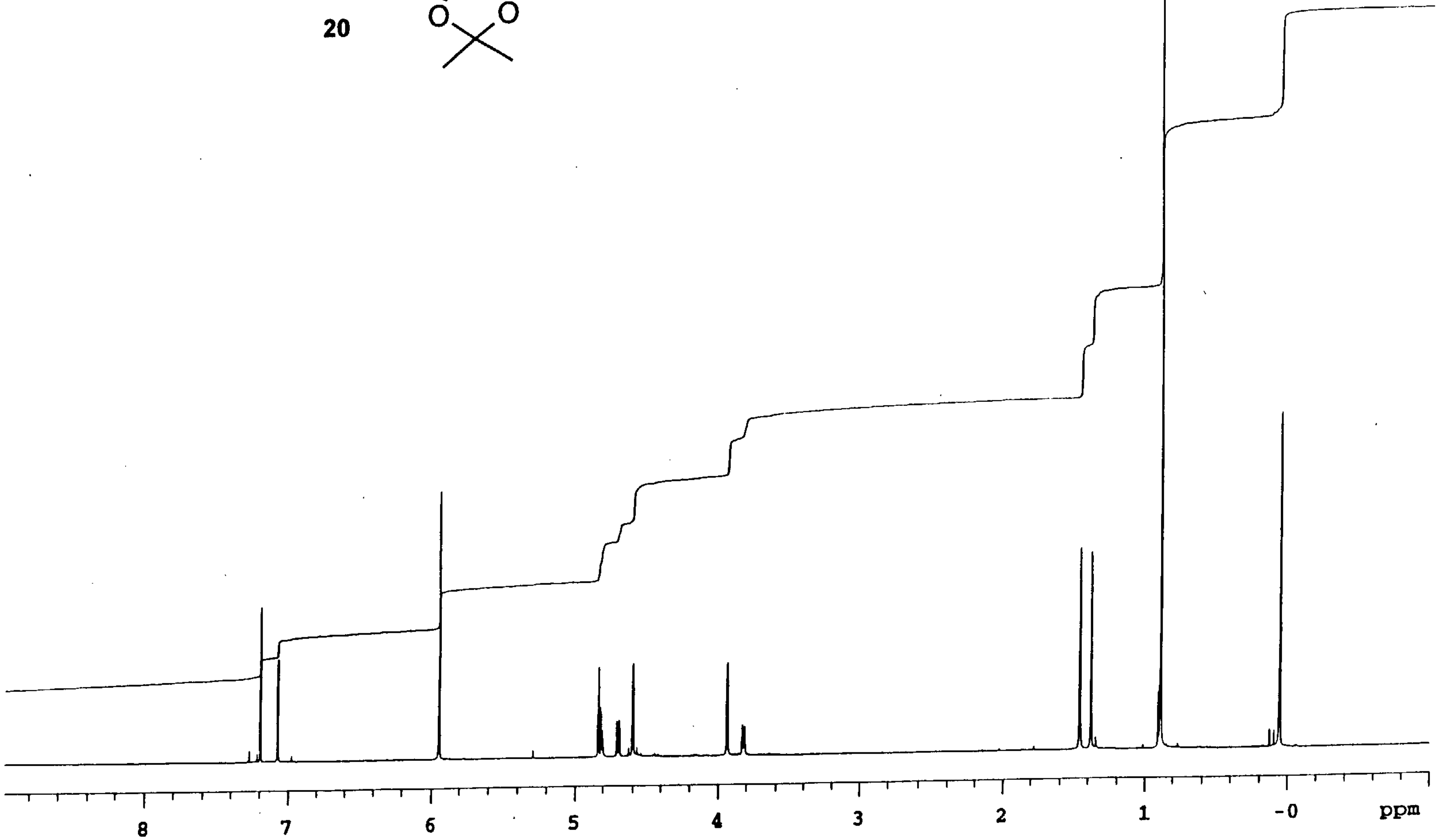

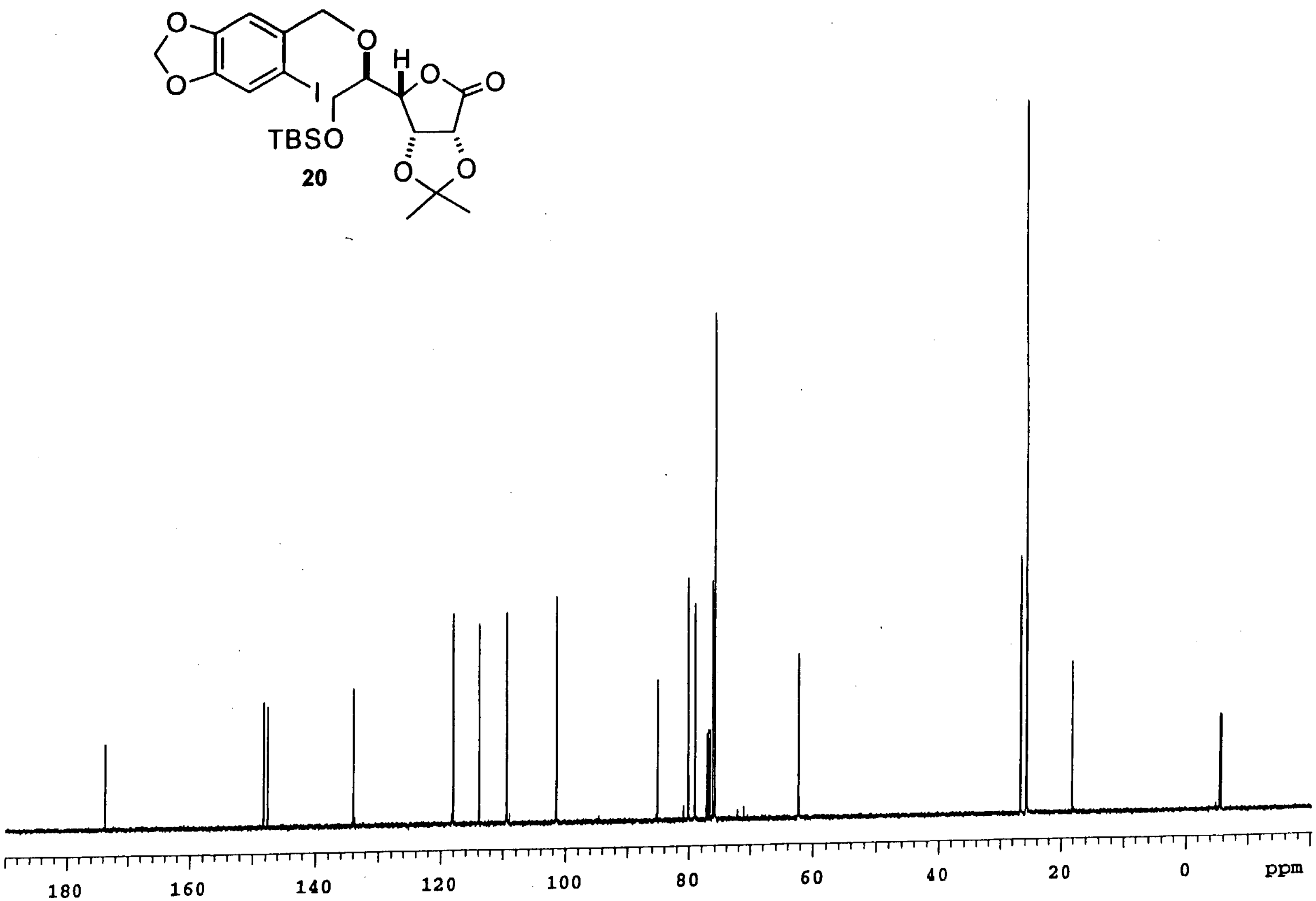

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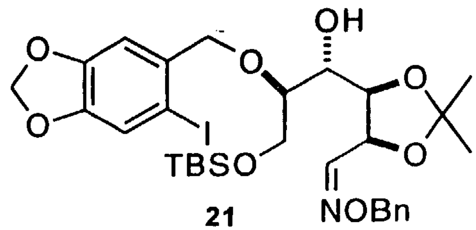

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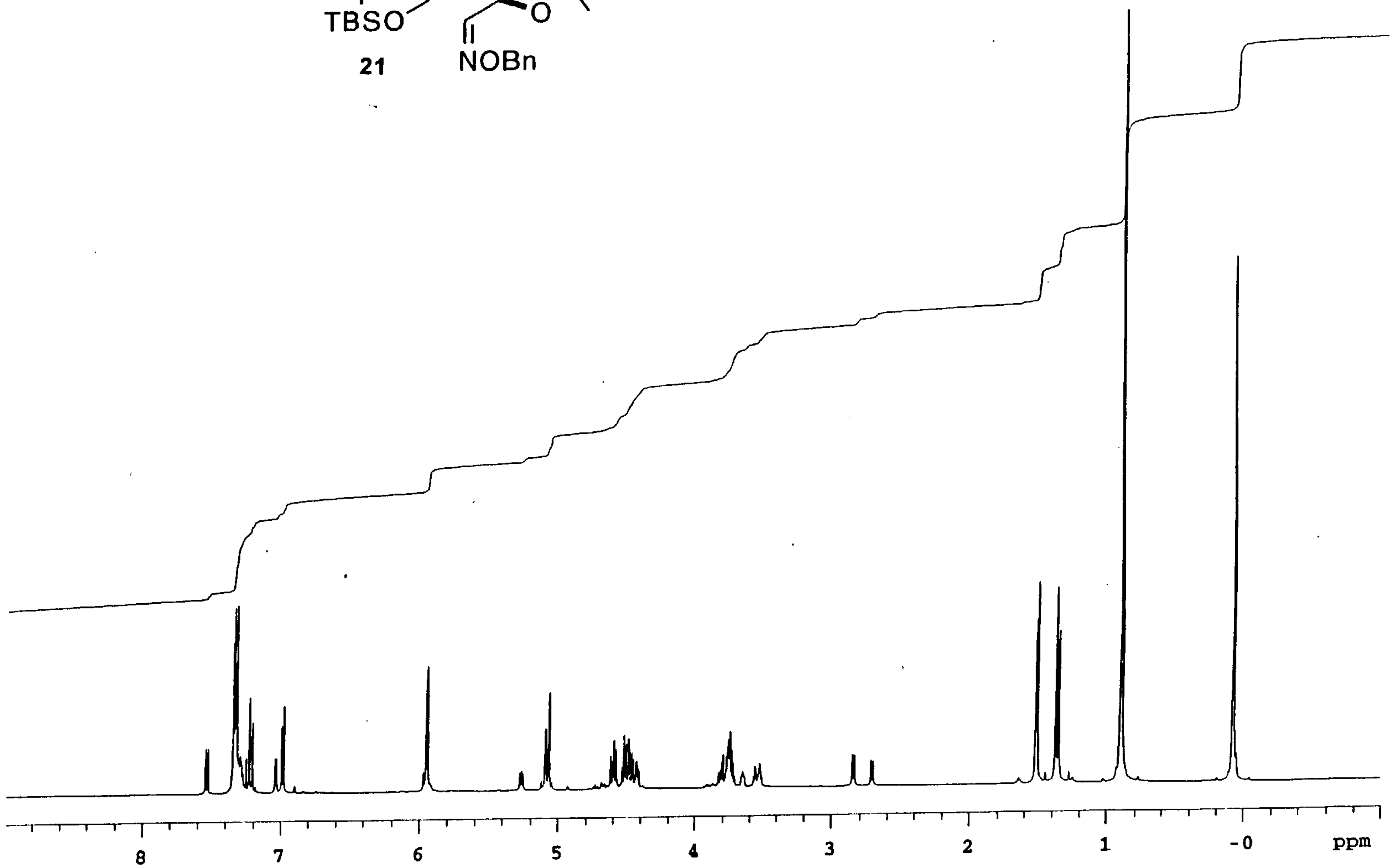

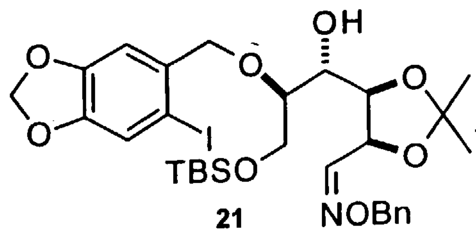

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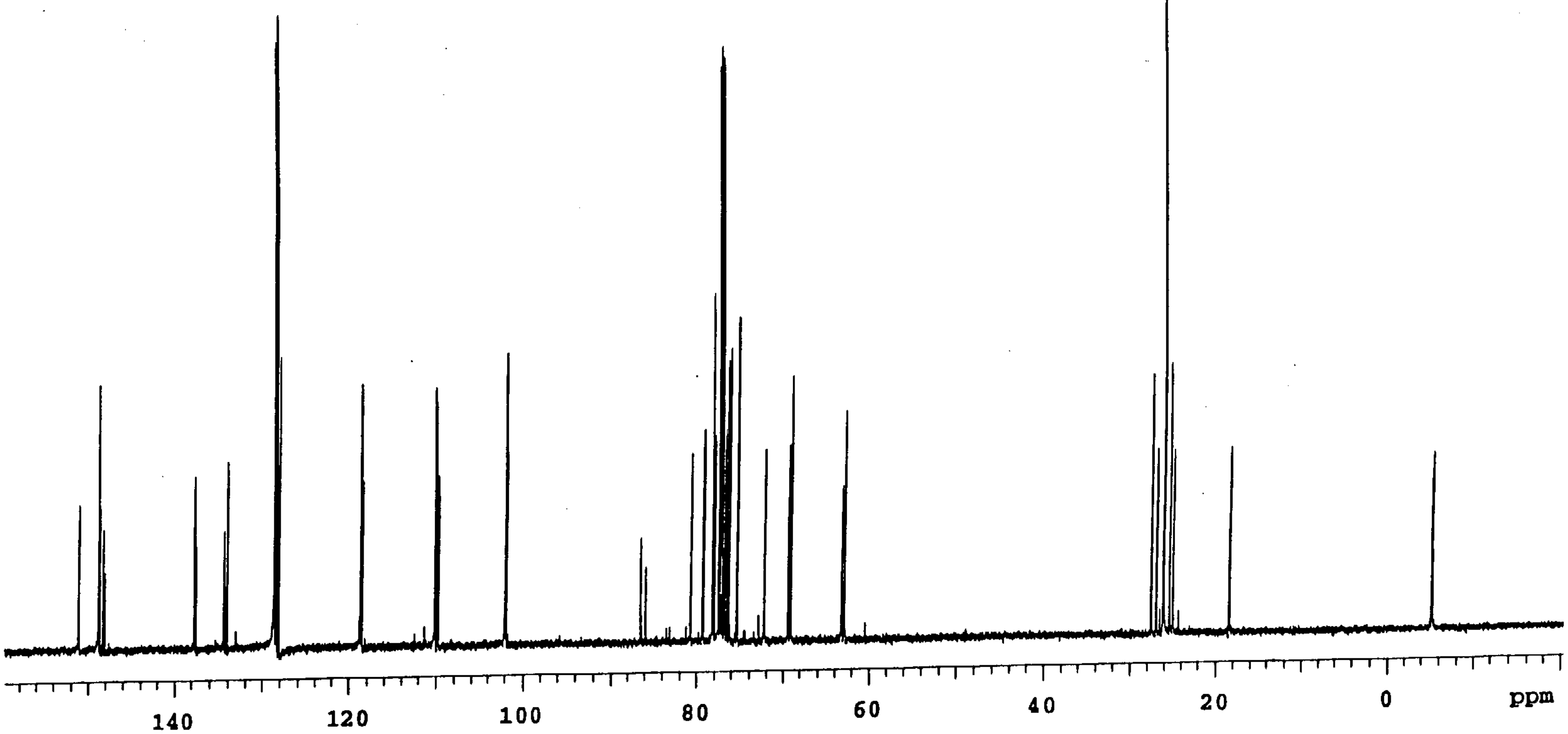

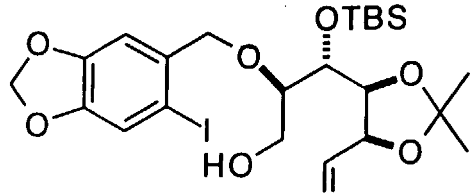

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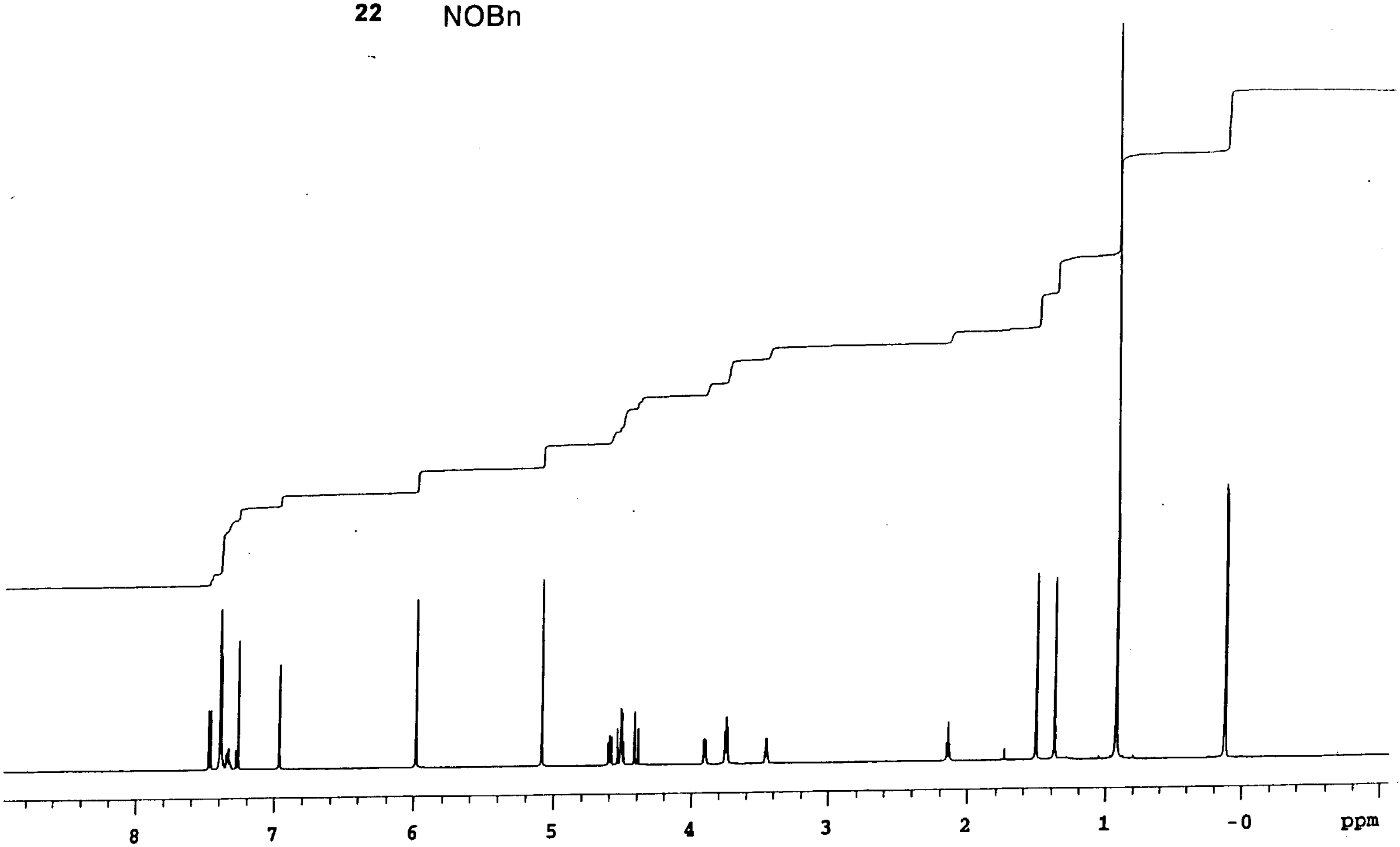

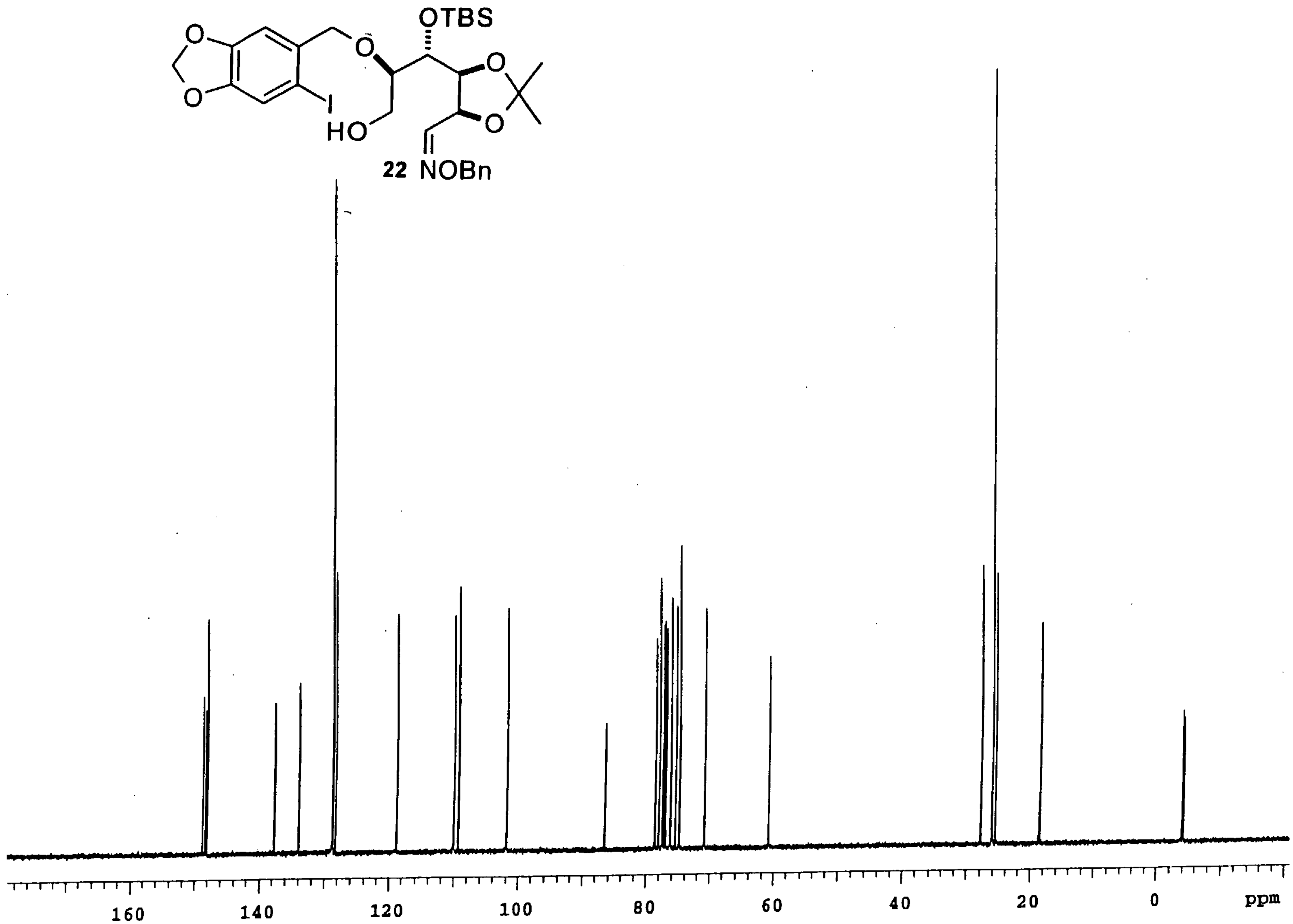
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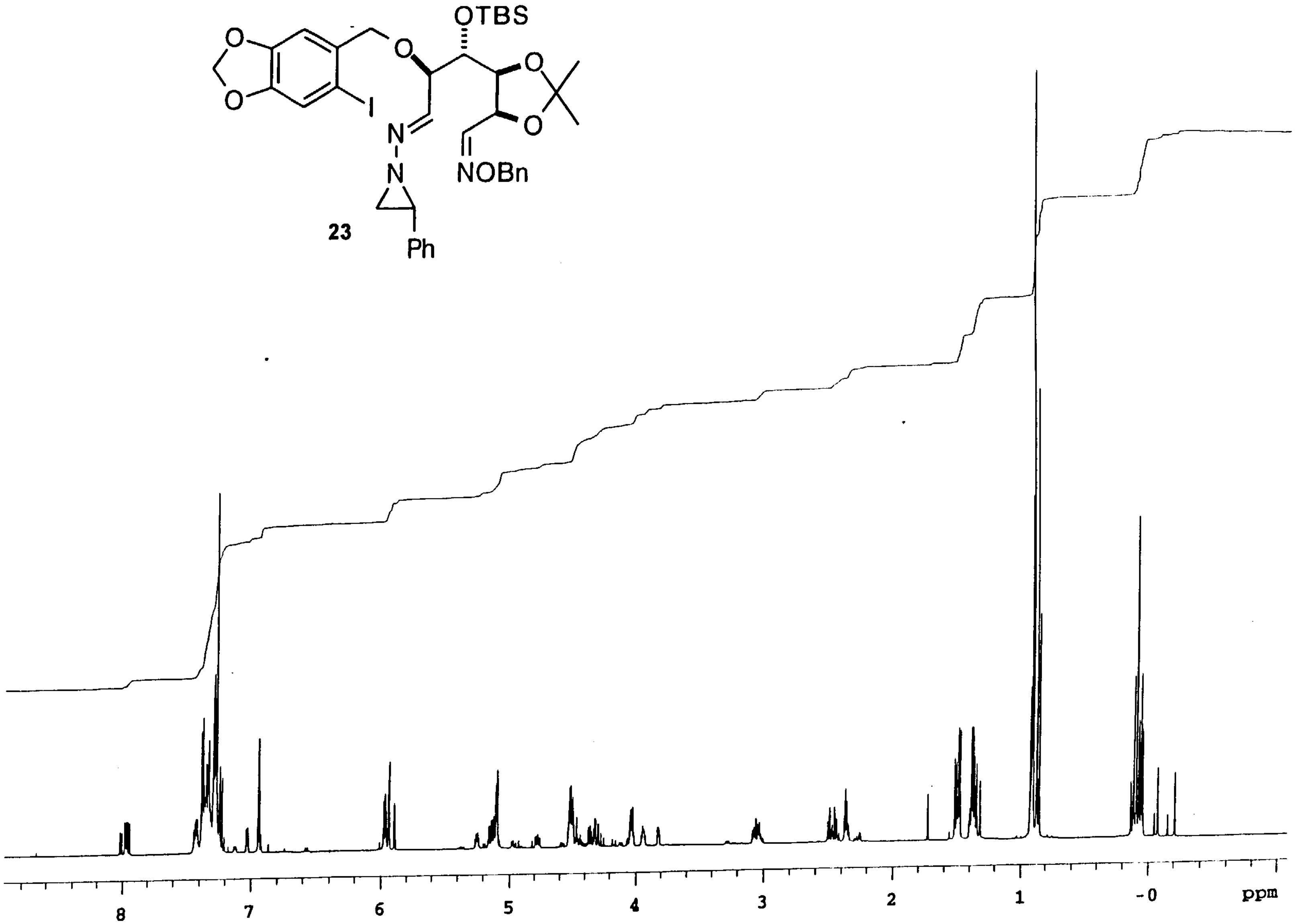

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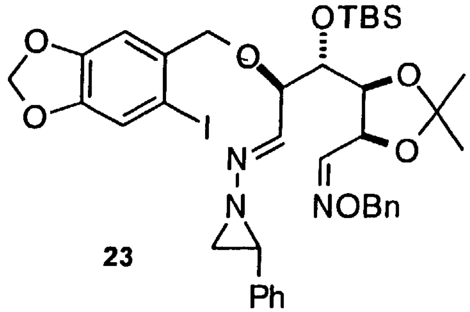

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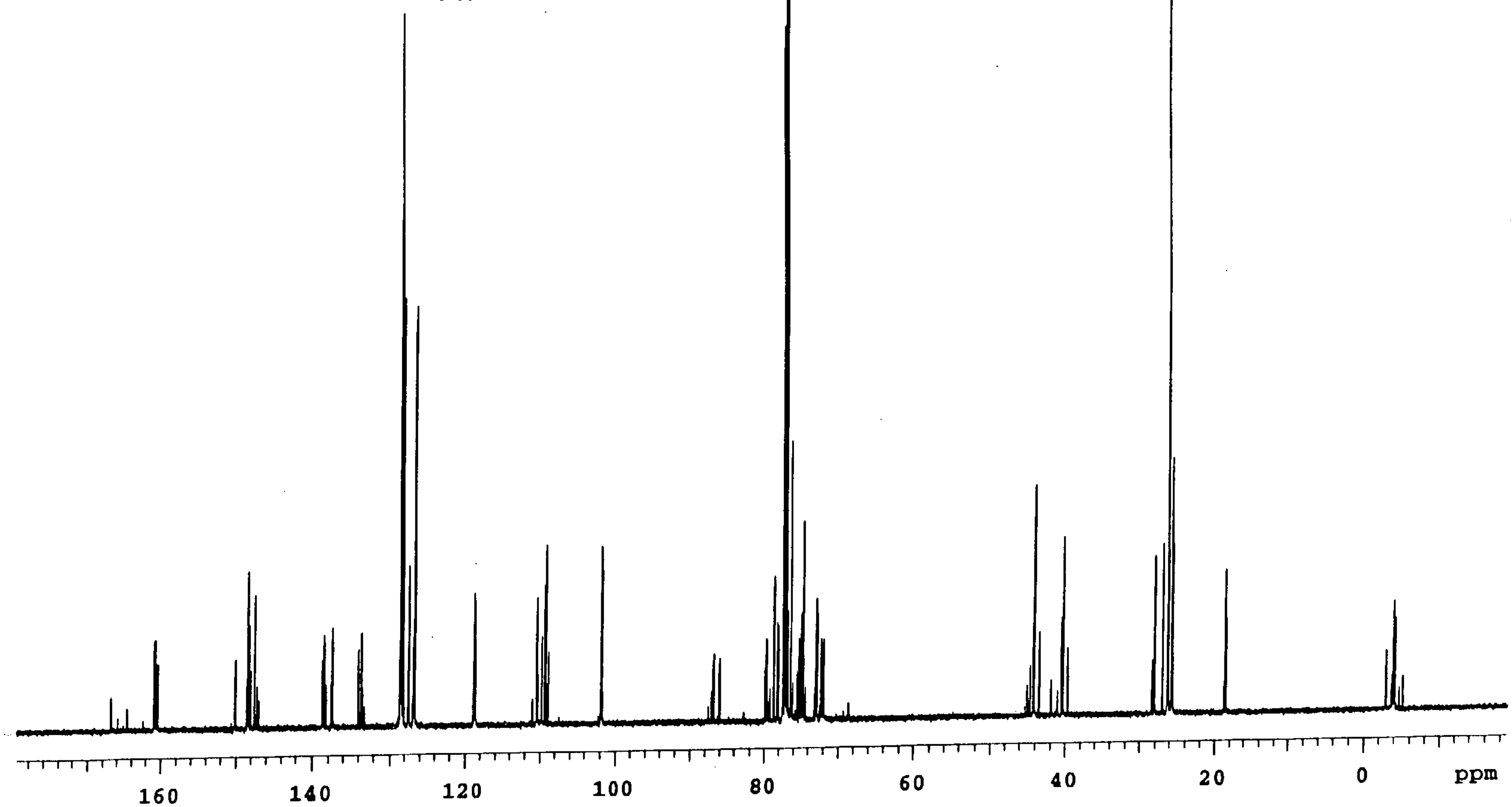

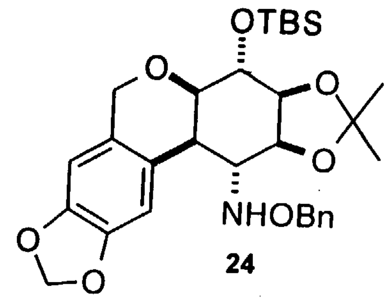

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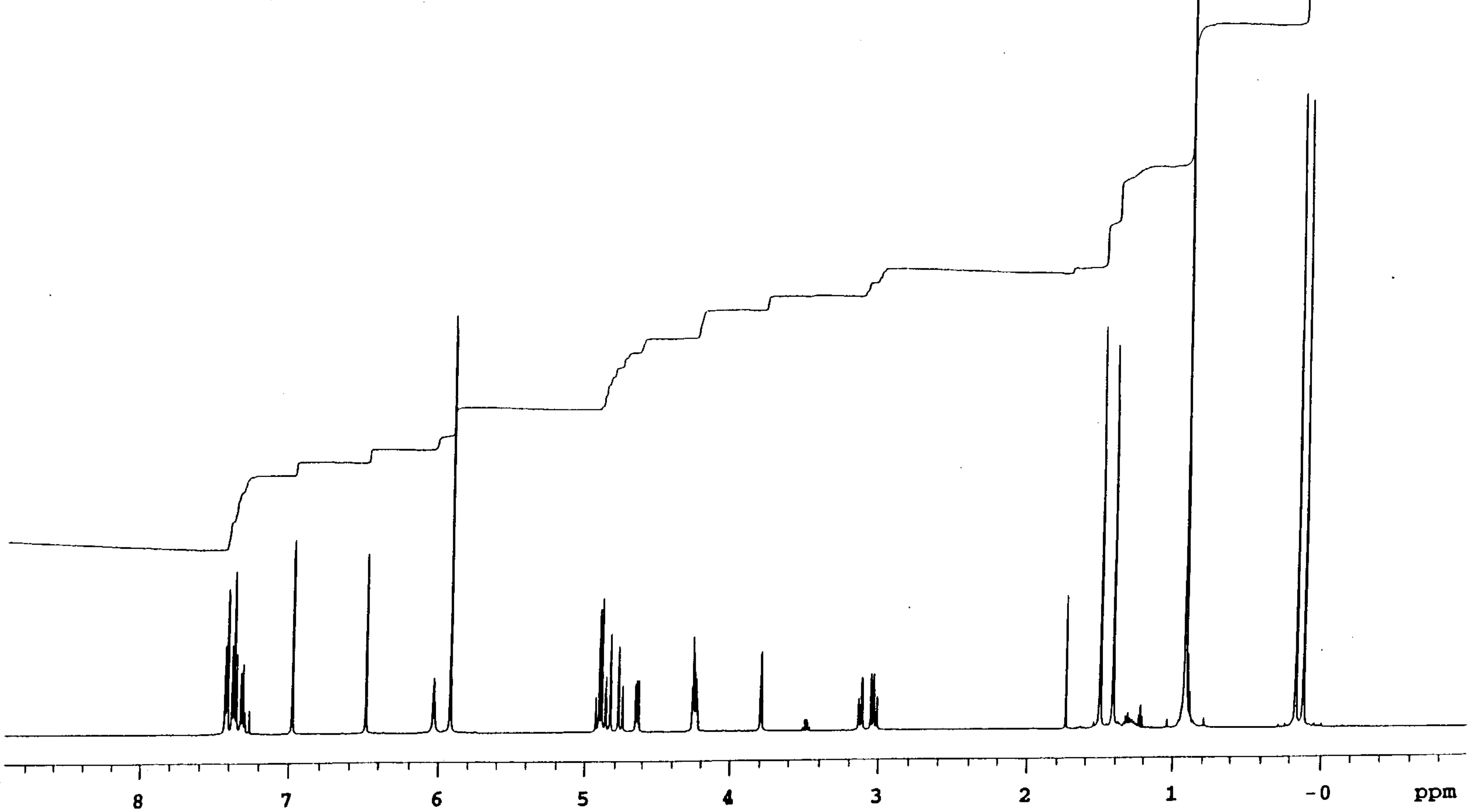

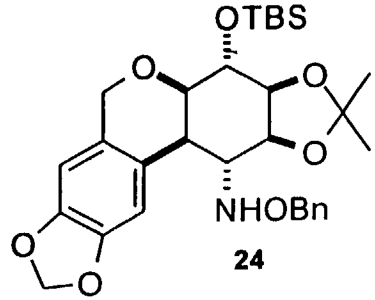

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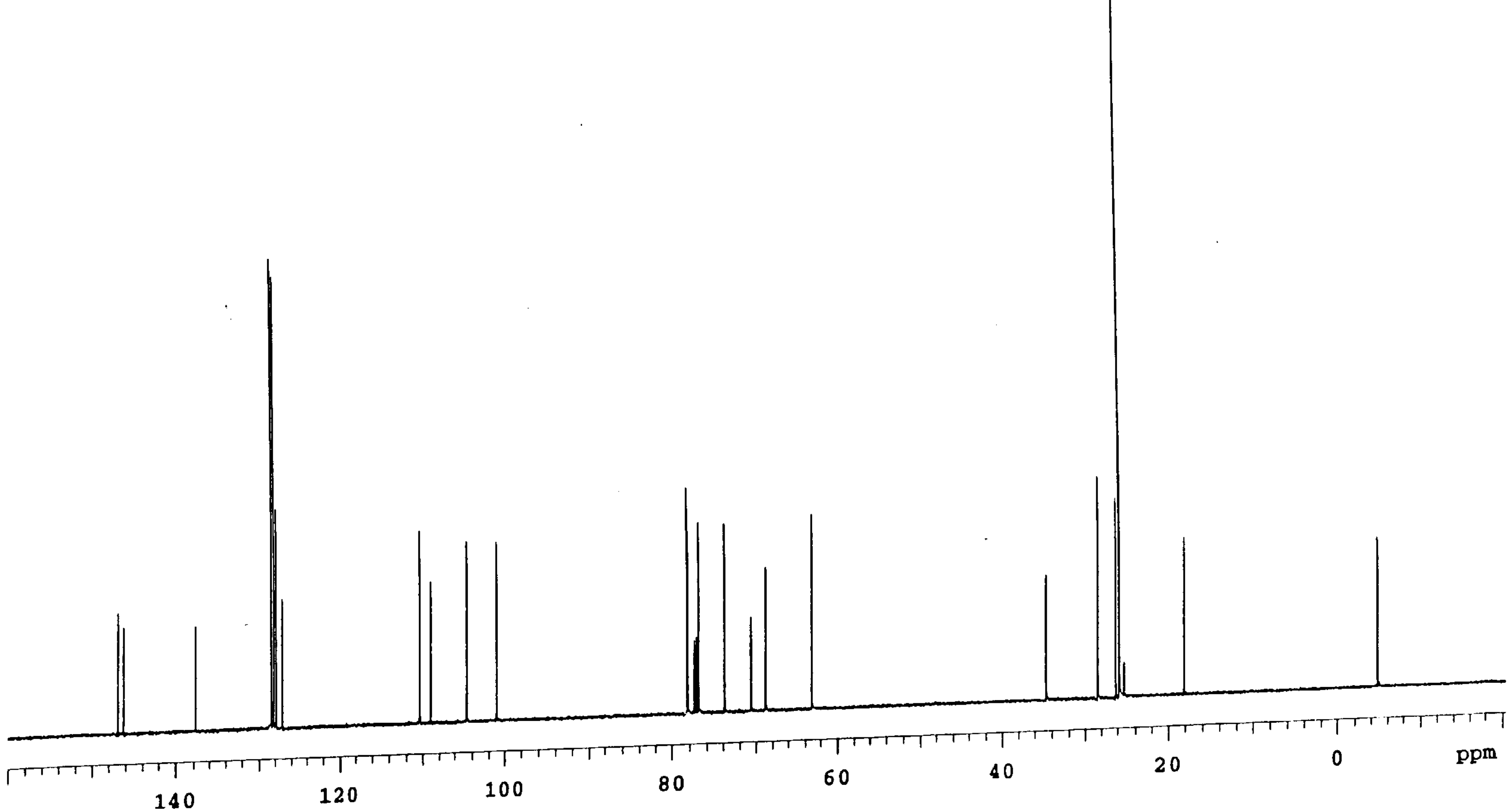

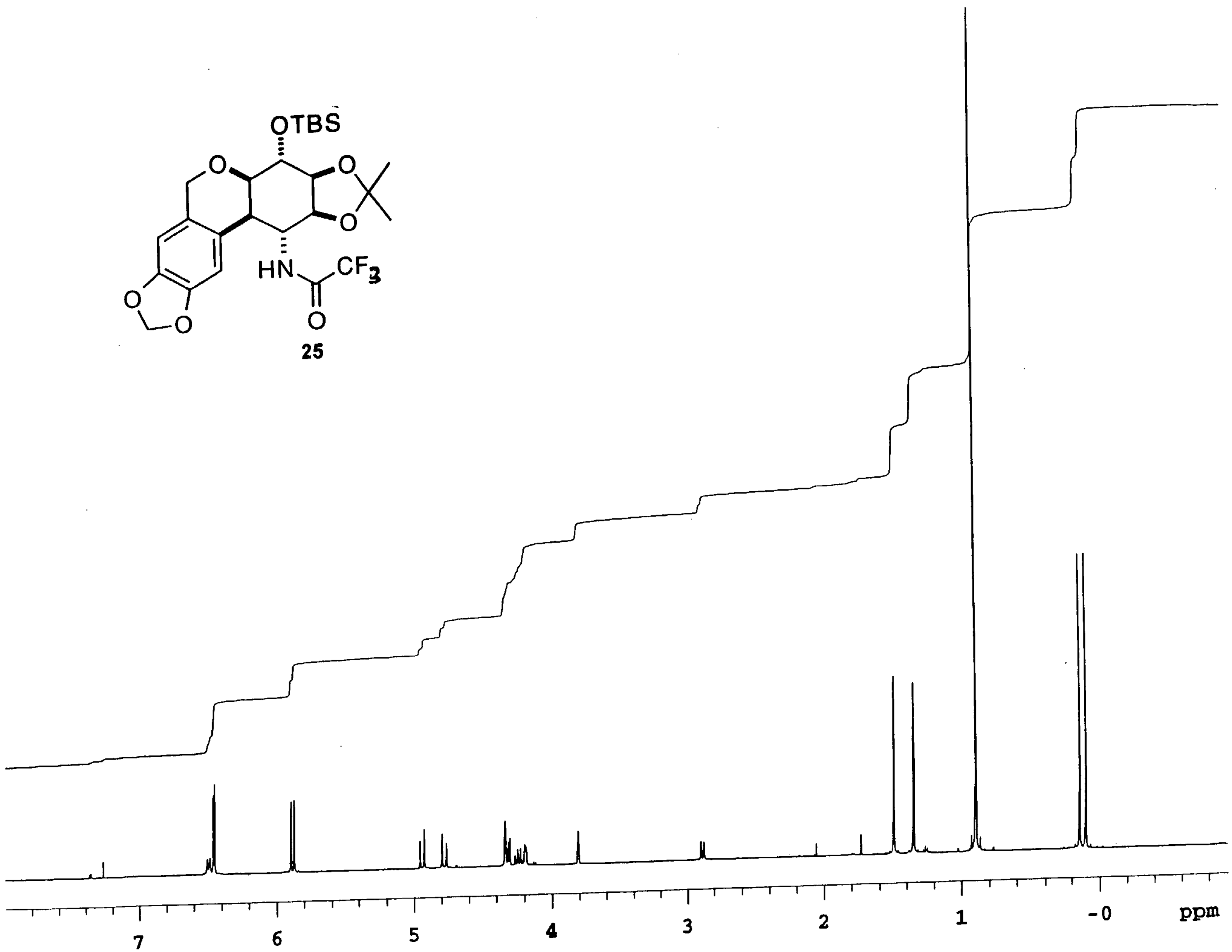

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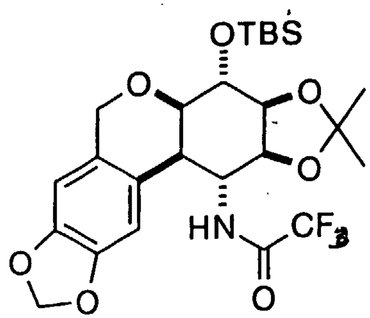

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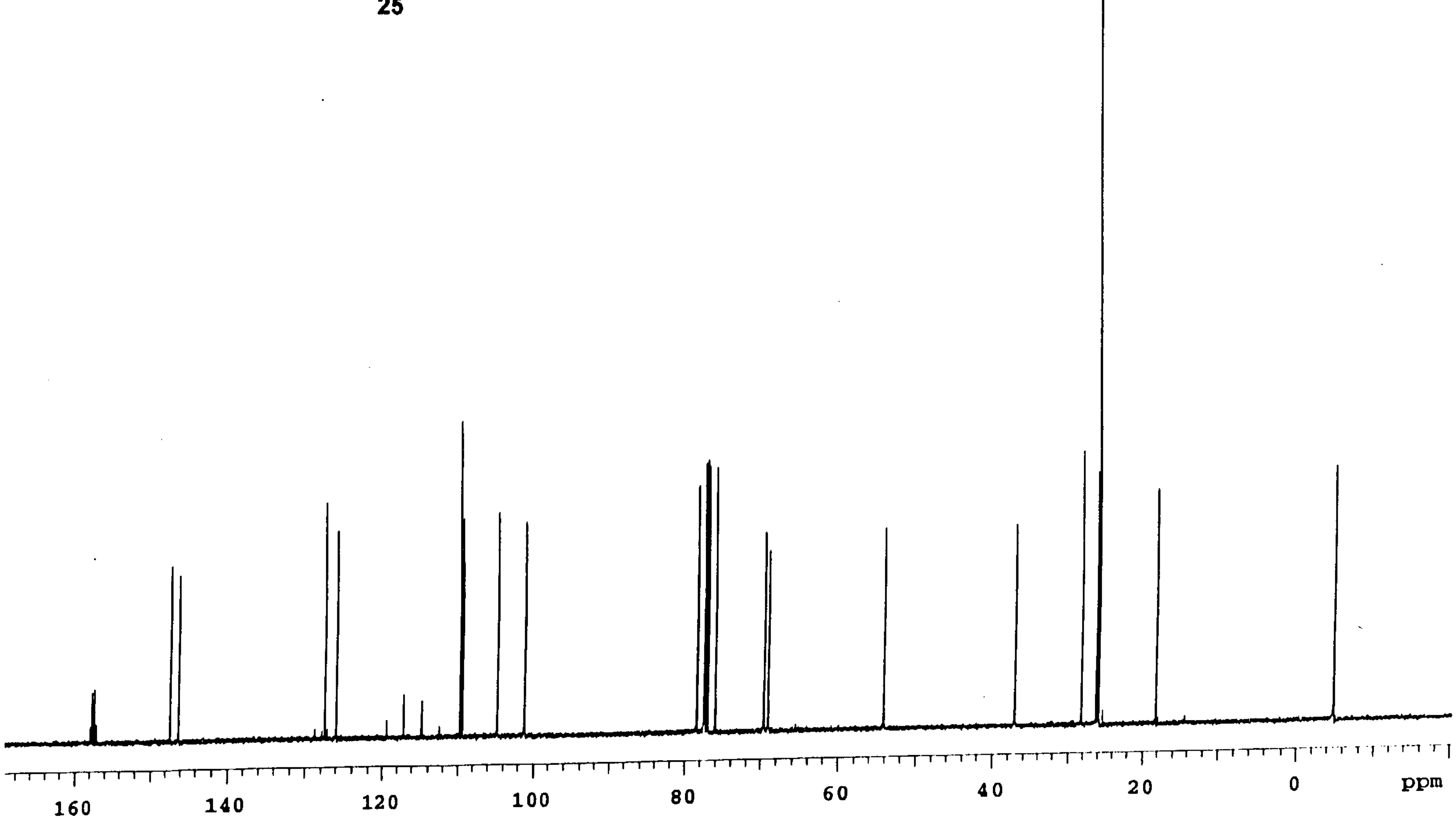

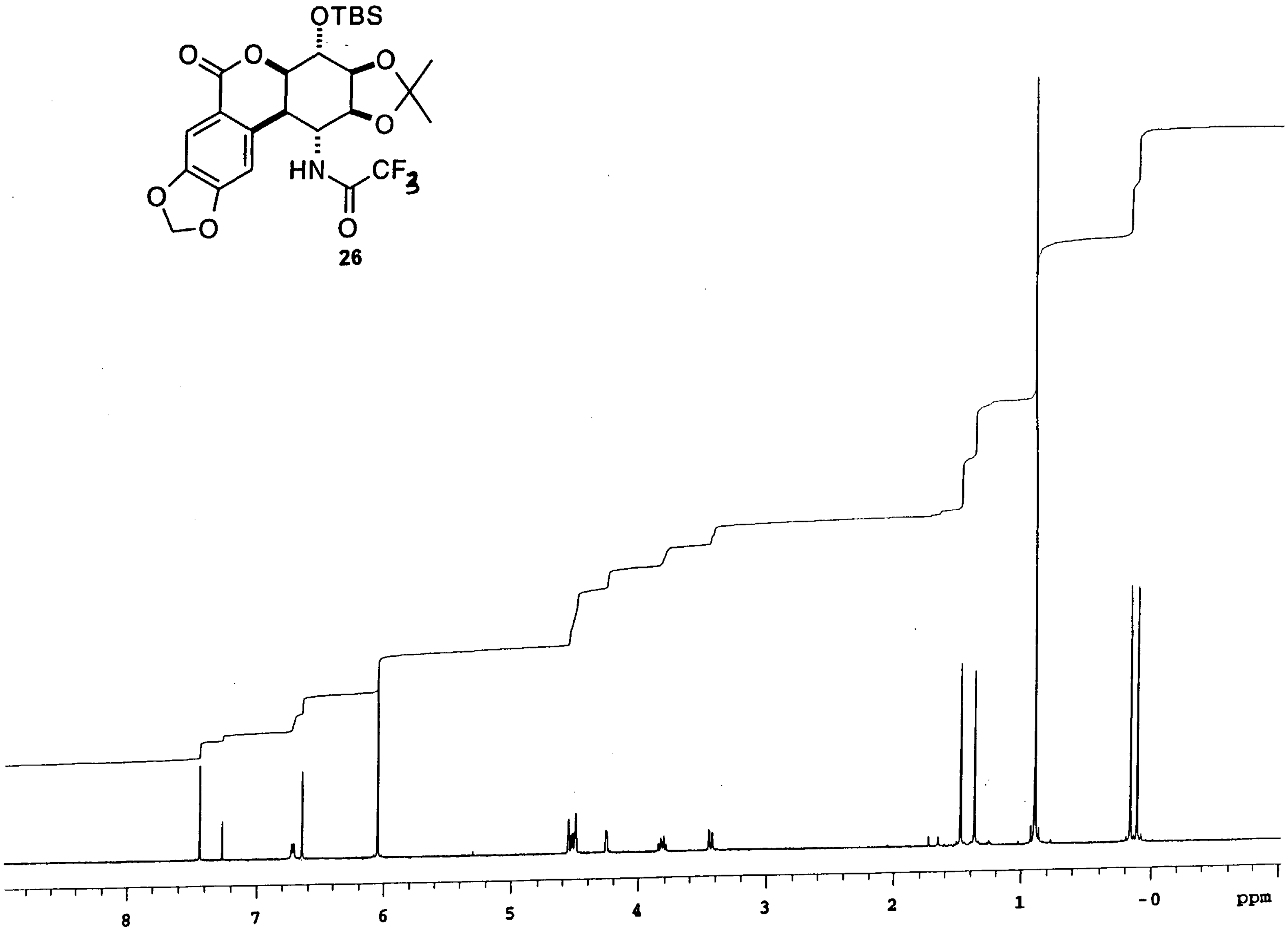
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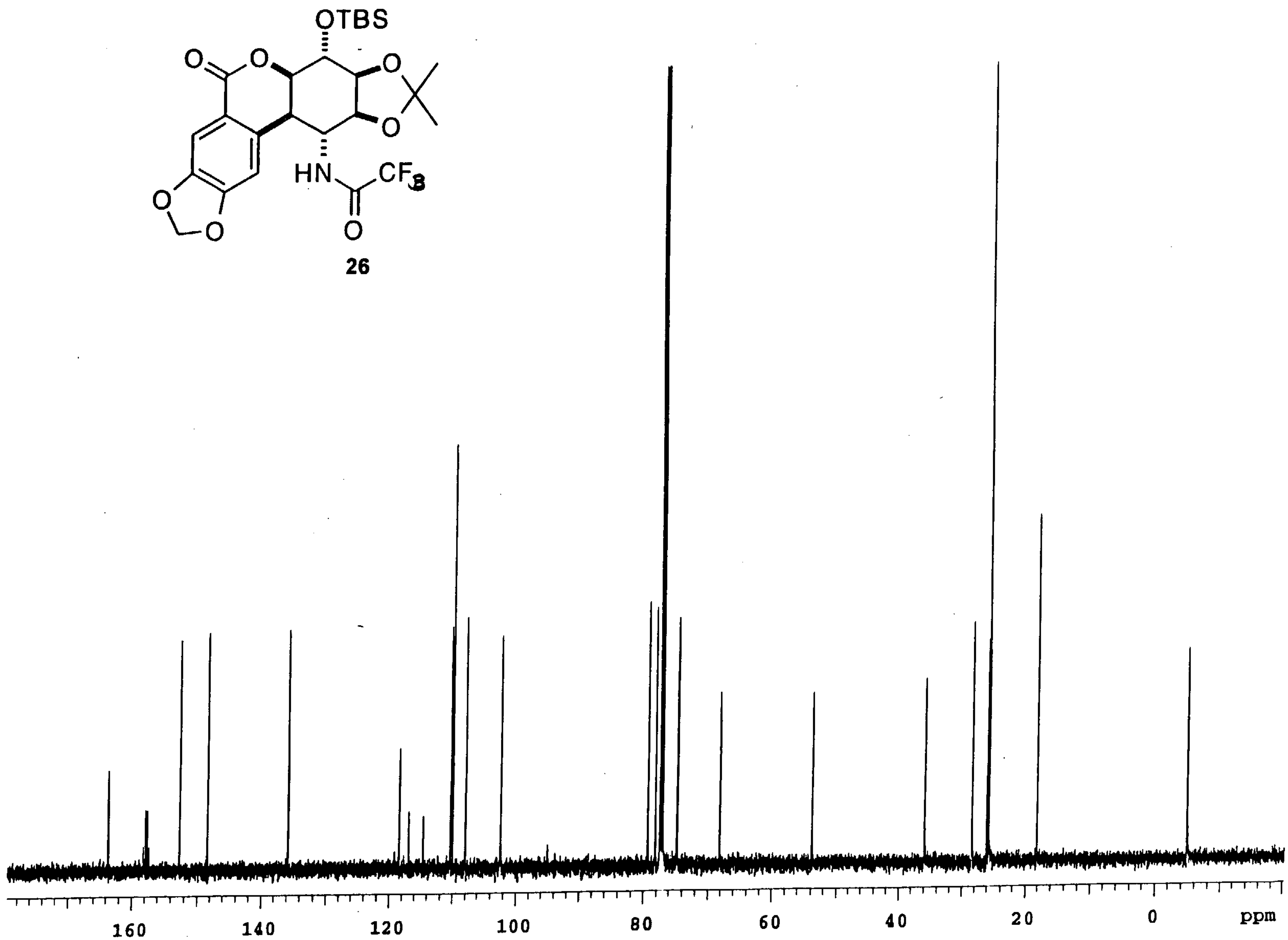

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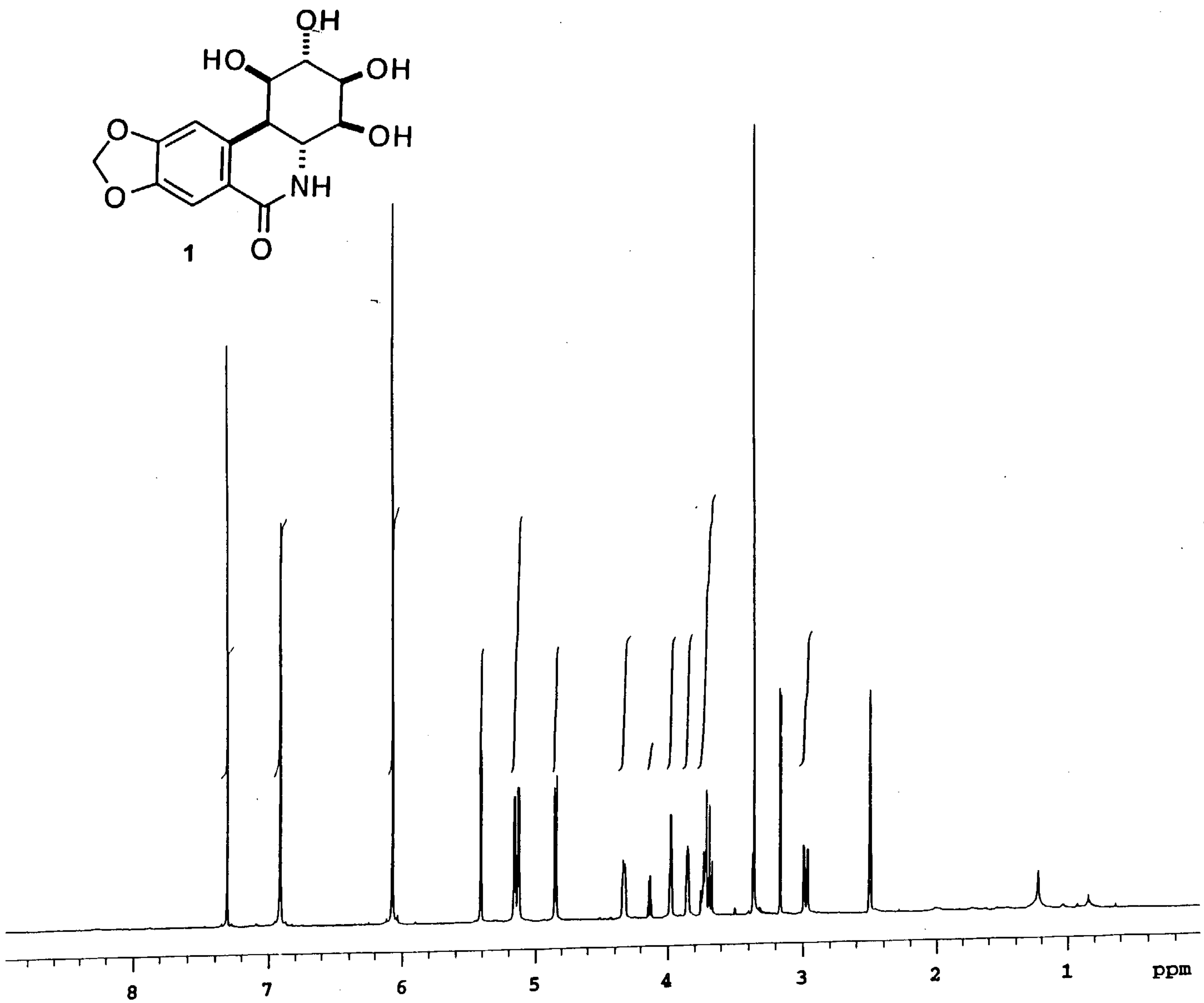

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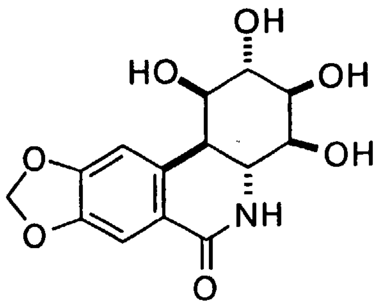

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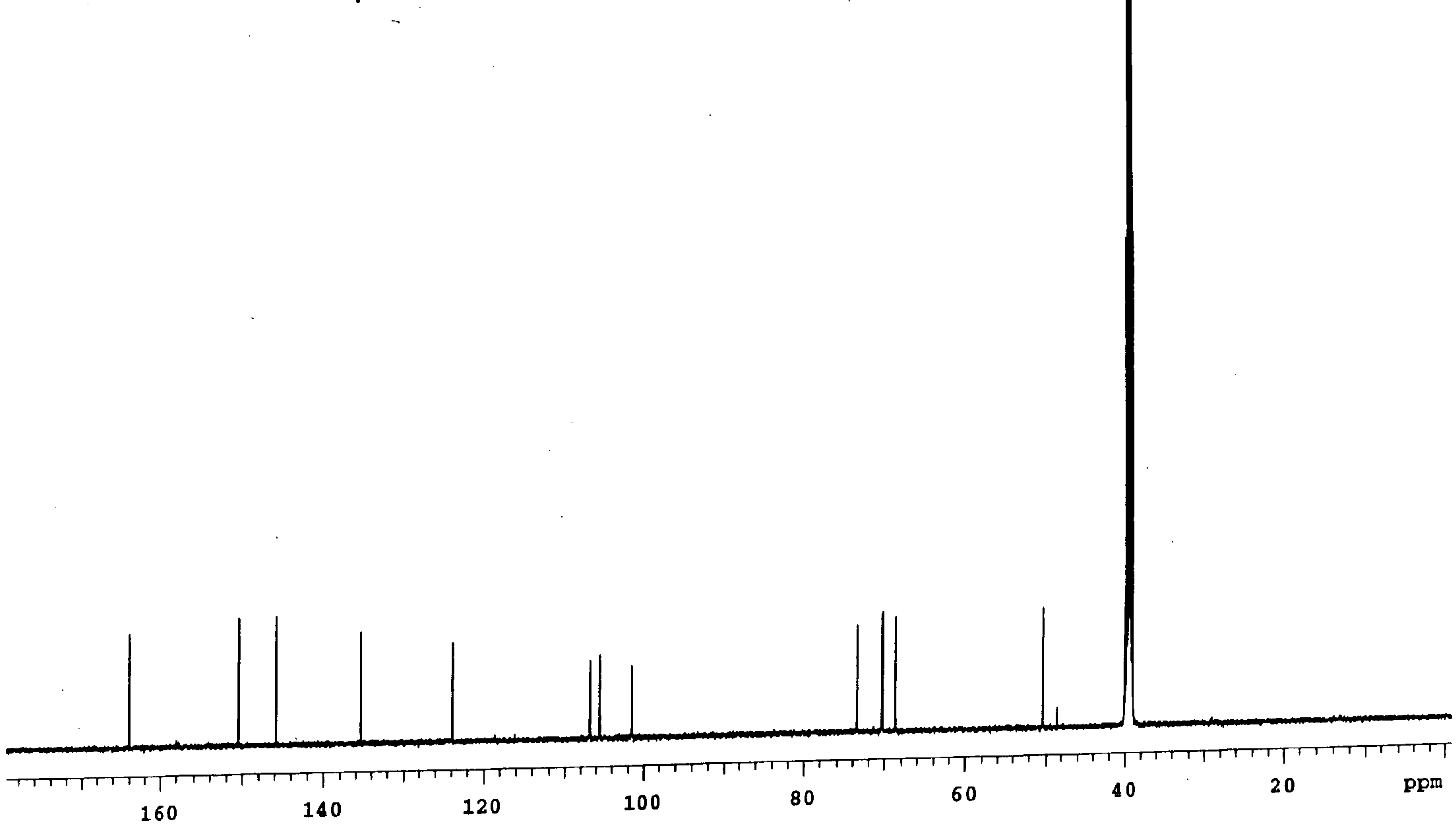

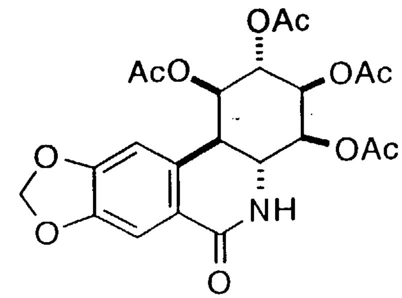

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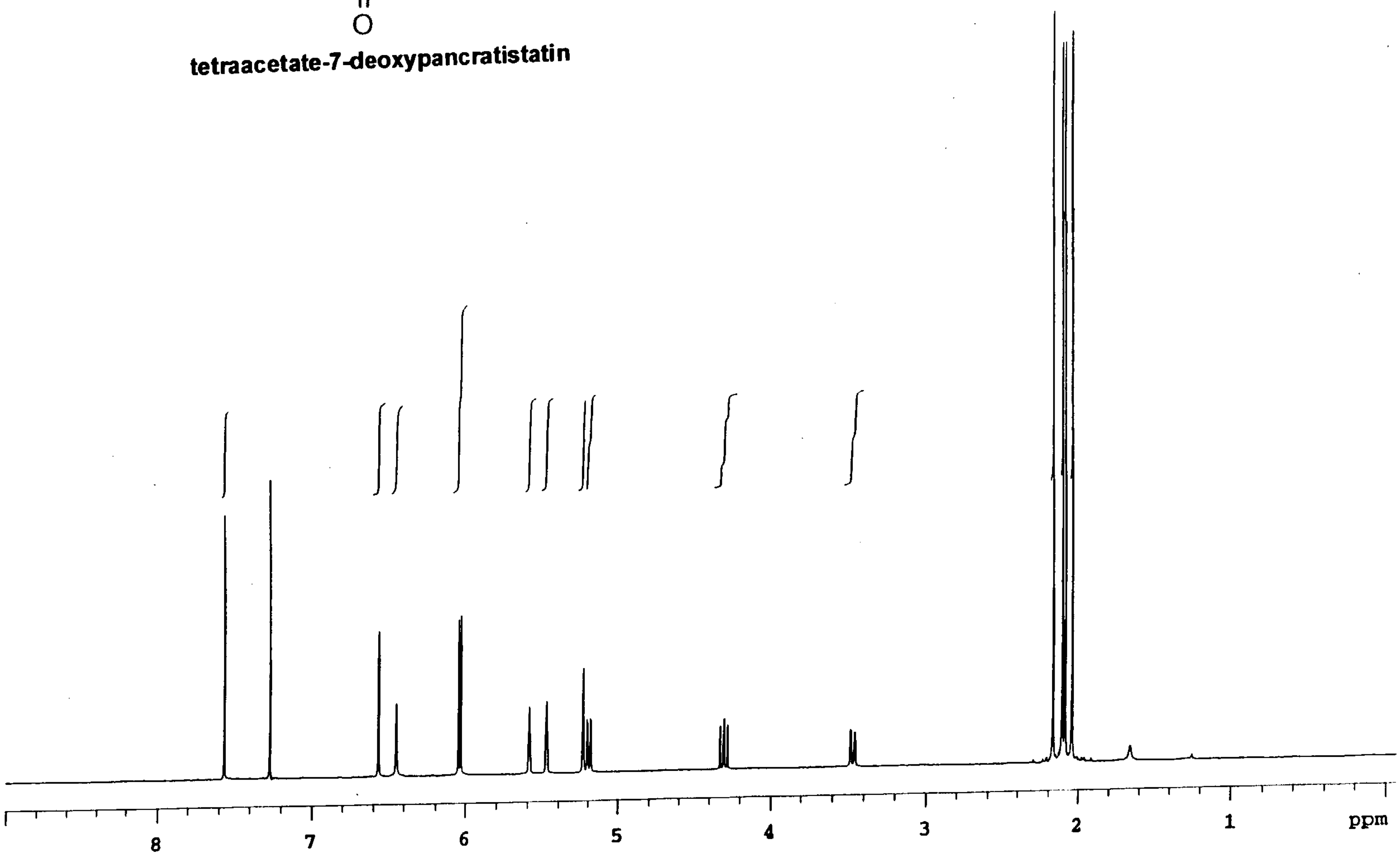

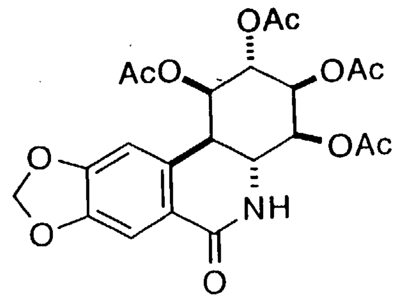

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