7: To a suspension of Cp_2ZrClH (4.00 g, 15.5 mmol) in anhydrous CH_2Cl_2 (24 mL) was added 2,2-dimethylpentyne (**5**, 1.86 mL, 13.2 mmol) via syringe. The heterogeneous mixture was protected from light and was stirred at room temperature until all the solid had dissolved (*ca.* 2-3 h). The bright yellow solution was cooled to 0 °C, solid *N*-iodosuccinimide (3.74 g, 16.8 mmol) was added in one portion, and the mixture was stirred for 1 h at room temperature. The brown mixture was diluted with pentane, and the solution was washed with 5% aq. $NaHCO_3$, satd. $Na_2S_2O_3$ and brine, and dried over Na_2SO_4. The solution was concentrated to a volume of *ca.* 5 mL, which was immediately subjected to flash chromatography on silica gel, eluting with pentane. The pentane eluent was carefully concentrated to a volume of *ca.* 5 mL and immediately used for the next step. An analytical sample of **6** showed: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (s, 9H), 2.53 (1H, d, J = 1.1 Hz), 6.21 (1H, q, J = 1.1 Hz); ^{13}C NMR (75 MHz,$CDCl_3$) δ 30.2, 30.7, 36.8, 95.2, 151.2; IR (film) 1242, 1363, 1463 cm^{-1}; MS (EI *m/z* 224 (M^+), 97 (100%); EI-HRMS *m/z* (M^+) calcd. for $C_7H_{13}I$ 224. 0063, found 224.0062.

A 100 mL round-bottom flask equipped with a reflux condenser and side arms with septa was charged with cut magnesium ribbon (2.44 g, 100 mmol). A solution of EtBr (5.9 mL) in anhydrous THF (30 mL) was added slowly, and after the initial exothermic reaction had subsided a further portion of THF (30 mL) was added. The mixture was heated at reflux for 1 h, then allowed to cool to room temperature. The gray solution of ethylmagnesium bromide (*ca.* 1.3 M) was transferred via canula to an oven-dried 100 mL round-bottom flask, and propyne gas was bubbled through the stirred mixture for 15 min. To the pale green solution of propynylmagnesium bromide was added the pentane solution of **6** prepared above, followed by freshly prepared $Pd(PPh_3)_4$ (700 mg, 2.5 mol %). The mixture was stirred at room temperature for 1 h, poured into satd. NH_4Cl/ice, and extracted with pentane (3x). The combined organic extract was washed with water

(3x) and brine (1x), dried over Mg_2SO_4, and evaporated. The residue was purified by flash chromatograpy on silica gel, eluting with pentane, to yield **7** as a colorless oil (957 mg, 68%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (s, 9H), 1.88 (3H, d, *J* = 1.0 Hz), 1.91 (3H, s), 5.8 (1H, d, *J* = 1.0 Hz); ^{13}C NMR (75 Mhz, $CDCl_3$) δ 4.0, 18.7, 30.5, 33.0, 80.4, 84.2, 117.5, 146.5; IR (film) 2955, 2911, 2359, 1463, 1365 cm^{-1}; MS (EI) *m/z* 136 (M^+), 121 (100%); EI-HRMS *m/z* (M^+) calcd. for $C_{10}H_{16}$ 136.1252, found 136.1252.

9: To a suspension of CuCN (919 mg, 20.5 mmol) in THF (40 mL) was added *n*-BuLi (13.3 mL, 1.6 M in hexanes, 20.5 mmol) at -50 °C. The mixture was stirred for 15 min to yield a homogeneous solution. Bu_3SnH (5.45 mL, 20.5 mmol) was added and the bright yellow solution was stirred for 30 min at -50 °C. A solution of enyne **7** (1.00 g, 7.34 mmol) in anhydrous THF (8 mL) was added, the reaction was stirred at -50 °C for 3 h, and degassed MeOH (22 mL) was added. The deep red solution was stirred at -10 °C overnight, poured into satd. NH_4Cl/ice and extracted with pentane (3x). The combined organic extract was washed with water (2x) and brine (1x), dried over Na_2SO_4, and evaporated to give **8** as a yellow oil (6.6 g). To a stirred solution of crude dienylstannane **8** (3.3 g, 3.67 mmol) in anhydrous Et_2O (25 mL) was added a solution of I_2 (2.0 g) in Et_2O (10 mL) at 0 °C until the brown iodine color persisted. The mixture was immediately quenched with an ice-cold aqueous solution of satd. $NaHCO_3$/satd. $Na_2S_2O_3$ (1:1) and extracted with pentane (3x). The combined organic extract was washed with water (2x) and brine (1x), dried over Na_2SO_4, and evaporated. The residue was purified by flash column chromatography on silica gel, eluting with pentane, to give **9** as a colorless oil (504 mg, 52%) which is light and air sensitive, and which was immediately dissolved in 5 mL of benzene and stored over argon and copper wire at -20 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (s, 9H), 1.79 (3H, d, *J* = 1.2 Hz), 2.53 (3H, d, *J* = 1.6 Hz), 5.30 (1H, t, *J* = 1.4, 1.0 Hz), 6.61 (1H, s); ^{13}C NMR (75 MHz,$CDCl_3$) δ 17.3, 29.0, 30.7, 32.7, 95.8, 131.6, 141.6, 146.4; IR (film) 2956, 2865, 1069 cm^{-1}; MS (EI)

m/z 264 (M^+), 137 (100%); EI-HRMS *m/z* (M^+) calcd. for $C_{10}H_{17}I$ 264.0373; found 264. 0369.

11: A 100 mL round bottom flask fitted with a stirring bar was charged with $CeCl_3 \cdot 7H_2O$ (3.08 g, 8.3 mmol), slowly heated to 160 °C, and kept at this temperature overnight under high vacuum. The flask was allowed to cool to room temperature, THF (13 mL) was added, and the suspension was stirred vigorously for 5 h at room temperature. A separate 25 mL round bottom flask was charged with Mg (211 mg, 8.6 mmol) and a crystal of I_2. The flask was gently warmed and then allowed to cool to room temperature, after which a solution of Me_3SiCH_2Cl (1.16 mL, 8.28 mmol) in THF (5 mL) was added dropwise. The resulting gray solution was stirred for 2 h at room temperature and was added via canula to the $CeCl_3$ suspension at -78 °C. The resulting off-white suspension was stirred at -78 °C for 1 h. A solution of **10** (285 mg, 1.65 mmol) in THF (3 mL) was added and the resulting mixture was allowed to warm to room temperature overnight. The gray mixture was diluted with ether and poured into satd. NH_4Cl/ice. The aqueous layer was extracted with ether (3x), and the combined ether extract was washed with satd. $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated. The residue was dissolved in CH_2Cl_2 (5 mL) and silica gel (1.8 g) was added. After stirring the mixture overnight, the silica gel was filtered off and the filtrate was concentrated to yield **11** as a colorless oil (470 mg, 99%): $[\alpha]^{25}_D$ -19.0 (c 0.80, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.03 (9H, s), 0.06 (6H, s), 0.89 (9H, s), 1.04 (3H, d, J = 7.0 Hz),1.55 (2H, d, J = 4.9 Hz), 2.05-2.15 (1H, m), 3.31 (1H, dd, J =8.0, 9.8 Hz), 3.65 (1H, dd, J = 5.0, 9.8 Hz), 4.58 (1H, d, J = 0.8 Hz), 4.59 (1H, d, J = 0.8 Hz); ^{13}C NMR (75 MHz,$CDCl_3$) δ -5.3, -1.3, 16.7, 18.4, 26.0, 27.1, 43.5, 67.9, 106.2, 149.9; IR (film) 1471, 1249 cm^{-1}; MS (EI) *m/z* 285 (M^+-1, 5), 270 (100%); EI-HRMS *m/z* (M^+) calcd. for $C_{14}H_{30}O_1Si_2$ 270.1835, found 270.1834.

13: A solution of **11** (74.1 mg, 0.26 mmol) in CH_2Cl_2 (2 mL) was treated with a solution of 1,3-dithenium tetrafluoroborate **12**, 80.4 mg, 0.39 mmol) in CH_3NO_2 (0.7 mL). After stirring the brown mixture at 0 °C for 40 min, $BF_3{\cdot}Et_2O$ (0.033 mL, 0.26 mmol) was added, and the mixture was stirred for 35 min at 0 °C before being quenched with satd. $NaHCO_3$ solution. The biphasic mixture was stirred for 35 min, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extract was dried over $MgSO_4$ and evaporated. The residue was purified by flash column chromatography on silica gel, eluting with ethyl acetate - hexanes (1:4), to give **13** as a pale yellow oil (40 mg, 0.18 mmol, 69 %): $[\alpha]^{25}_D$ -18.6 (c 0.52, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 1.05 (3H, d, *J* = 7.6 Hz), 1.8 -1.9 (1H, m), 2.10 - 2.16 (1H, m), 2.37 -2.43 (1H, m), 2.49 (2H, d, *J* = 7.3 Hz), 2.79 - 2.91 (4H, m), 3.53 - 3.62 (2H, m), 4.22 (1H, t, *J* = 7.6 Hz), 4.58 (1H, d, *J* = 0.8 Hz), 4.59 (1H, d, *J* = 0.8 Hz), 5.04 (1H, s), 5.09 (1H, dd, *J* = 0.9, 1.95 Hz); ^{13}C NMR (75 MHz,$CDCl_3$) δ 16.9, 22.8, 26.0, 29.4, 30.6, 30.7, 41.4, 41.7, 45.8, 66.5, 114.3, 146.3; IR (neat) 1422, 3424 cm^{-1}; MS (CI) *m/z* 218 (M^+), 119 (100%); EI-HRMS *m/z* (M^+) calcd. for $C_{10}\ H_{18}\ O_1S_2$ 218.0799, found 218.0799.

3: To a solution of **13** (106 mg, 0.485 mmol) in THF (5 mL) was added a 1M solution of IBX in DMSO (1.45 mL, 1.46 mmol). The solution was stirred at room temperature for 45 min, poured into pH 7.0 buffer / ice and extracted with ethyl acetate (3x). The combined organic extract was washed with pH 7 buffer (2x) and brine (1x), dried over Na_2SO_4, and evaporated. The residue was dissolved in ethyl acetate (5 mL), filtered, and evaporated to yield **3** as a colorless oil (73 mg, 70%). This material was used immediately for the next step.

14: To a solution of **9** (238 mg, 0.901 mmol) in THF (11 mL) was added a 1.45 M solution of *t*-BuLi in heptane (0.62 mL, 0.901 mmol) at -78 °C. The clear solution was stirred at -78 °C for 20 min, and a solution of **3** (65 mg, 0.30 mmol) in THF (5 mL) was

added. The mixture was stirred for 20 min at -78 °C, quenched with satd. NH_4Cl and extracted with ethyl acetate (3x). The combined organic extract was washed with pH 7 buffer (1x) and brine (1x), dried over Na_2SO_4, and evaporated. The residue was purified by flash column chromatography on silica gel, eluting with ethyl acetate - hexanes (1:4), to yield **14** as a colorless oil (64 mg, 60%): $[\alpha]^{25}_D$ +110.5 (c 0.2, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (3H, d, *J* = 6.8 Hz), 1.13 (9H, s), 1.71 (3H, s), 1.79 (3H, s), 1.77-1.91 (1H, m), 2.11-2.18 (1H, m), 2.43-2.58 (3H, m), 2.80-2.93 (4H, m), 4.00 (1H, d, *J* = 4.6 Hz), 4.19 (1H, dd, *J* = 14.8, 7.5 Hz), 5.04 (1H, s), 5.08 (1H, s), 5.28 (1H, s), 5.90 (1H, s); ^{13}C NMR (75 MHz,$CDCl_3$) δ 13.0, 14.7, 18.0, 25.8, 30.5, 30.6, 31.0, 32.6, 41.4, 42.4, 45.9, 77.1, 114.1, 130.9, 131.4, 134.0, 139.9, 147.1; IR (film) 1008, 2900, 2953, 3448 cm^{-1}; MS (EI) *m/z* 354 (M^+), 119 (100%); EI-HRMS *m/z* (M^+) calcd. for $C_{20}H_{34}O_1S_2$ 354.2051, found 354.2051.

15: To a solution of **14** (34 mg, 0.096 mmol) in pyridine (0.9 mL) was added Ac_2O (0.45 mL) at 0 °C. The clear solution was stirred at room temperature, poured into 10% aq. HCl/ice, and extracted with ethyl acetate (3x). The combined organic extract was washed with H_2O (2x), 5% $NaHCO_3$ (1x), H_2O (1x) and brine (1x), dried over Na_2SO_4, and evaporated to yield **15** as a clear oil (31 mg, 100 %). The crude product was used for the next step without further purification. An analytical sample was obtained by flash column chromatography on silica gel, eluting with ethyl acetate - hexanes (1:4): $[\alpha]^{25}_D$ -65.2 (c 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (3H, d, *J* = 6.9 Hz), 1.13 (9H, s), 1.72 (3H, s), 1.77 (3H, s), 1.77-1.92 (1H, m), 2.05 (3H, s), 2.06-2.15 (1H, m), 2.46 (2H, d, *J* = 7.2 Hz), 2.49 - 2.57 (1H, m), 2.78 - 2.93 (4H, m), 4.15 (1H, t, *J* = 7.2 Hz), 5.01 (1H, s), 5.03 (1H, s), 5.14 (1H, d, *J* = 6.9Hz), 5.25 (1H, s), 5.79 (1H, s); ^{13}C NMR (75 MHz,$CDCl_3$) δ 14.5, 15.2, 17.9, 21.1, 25.8, 30.5, 30.6, 30.7, 30.9, 32.6, 41.3, 45.8, 80.6, 114.2, 130.6, 130.9, 133.7, 140.4, 146.0, 170.1; IR (CCl_4) 2958, 2902, 1740.4,

1718, 1550, 1239cm^{-1}; MS (EI) *m/z* 396 (M^+), 119 (100%); EI-HRMS *m/z* (M^+) calcd. for $C_{22}H_{36}O_2S_2$ 396.2153, found 396.2155.

16: To a mixture of **15** (17.0 mg, 0.0428 mmol) and calcium carbonate (77 mg, 0.77 mmol) in aqueous 90% CH_3CN (5 mL) was added CH_3I (1.54 mL, 16.6 mmol). The mixture was stirred at room temperature overnight, diluted with EtoAc, and filtered through a plug of glass wool. The filtrate was washed with brine (2x), dried over Na_2SO_4, and concentrated. The resultant crude aldehyde was dissolved in a mixture of *t*-BuOH and 2-methyl-2-butene (3:1, 6 mL), and a solution of $NaClO_2$ (250 mg) and NaH_2PO_4 (250 mg) in water (2 mL) was added during 5 min. The mixture was stirred at room temperature for 1 h, poured into water/ice, and extracted with ethyl acetate (3x). The combined organic extract was washed with water (2x) and brine (1x), dried over Na_2SO_4, and evaporated. The residue was purified by flash column chromatography on silica gel, eluting with CH_2Cl_2 - MeOH (95:5), to yield 16 as a pale yellow oil (12.5 mg, 91%). An analytical sample of **16** was obtained by dissolving the product in 5% aqueous Na_2CO_3 and washing the aqueous layer with hexanes (2x). The aqueous layer was acidified with concd HCl at 0 °C and was extracted with ethyl acetate (3x). The extract was washed with water (2x), dried over Na_2SO_4, and concentrated to give pure **16**: $[\alpha]^{25}_D$ +75.1 (c 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (3H, d, J = 7.2 Hz), 1.13 (9H, s), 1.72 (3H, d, J = 1.3 Hz), 1.77 (3H, d, J = 0.9 Hz), 2.06 (3H, s), 2.61-2.70 (1H, m), 3.11 (2H, s), 5.07 (2H, s), 5.17 (1H, d, J = 6.6 Hz), 5.24 (1H, t, J = 1.2 Hz), 5.79 (1H, s); ^{13}C NMR (75 MHz,$CDCl_3$) δ 14.2, 14.5, 17.8, 21.0, 30.8, 32.5, 40.2, 41.3, 80.0, 115.8, 130.4, 130.6, 133.5, 140.4, 142.9, 170.2, 176.6; IR (CCl_4) 1239, 1550, 1718, 1740, 2901, 2958 cm^{-1}; MS (EI) *m/z* 322 (M^+), 280, 262, 149 (100%); EI-HRMS *m/z* (M^+) calcd. for $C_{19}H_{30}O_4$ 322.2143, found 322.2142.

17: A mixture of **16** (3.0 mg, 0.0093 mmol) and K_2CO_3 (20 mg, 0.145 mmol) in MeOH (0.5 mL) was stirred at room temperature for 3 h, poured into 5% $KHSO_4$/ice, and

extracted with ethyl acetate (3x). The combined organic extract was washed with brine (2x), dried over Na_2SO_4, and evaporated to yield a colorless oil (2.8 mg). The latter was dissolved in CH_2Cl_2 (0.3 mL) and a crystal of CSA was added. The solution was stirred at room temperature for 15 min, poured into 5% Na_2CO_3/ice, and extracted with ethyl acetate (3x). The combined organic extract was washed with brine (2x), dried over Na_2SO_4, and evaporated. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/hexanes (1:3), to give **17** as a pale yellow oil (1 mg, 43%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (3H, d, J = 7.0 Hz), 1.14 (9H, s), 1.71 (3H, d, J = 1.0 Hz), 1.81 (3 H, d, J = 1.4 Hz), 2.80-2.91 (1H, m), 3.36 (2H, m), 4.73 (1H, d, J = 3.0 Hz), 4.95 (1H, s), 4.99 (1H, s), 5.28 (1H, t, J = 1.4 Hz), 6.03 (1H, s); ^{13}C NMR (75 MHz,$CDCl_3$) δ 13.4, 15.1, 17.9, 30.9, 32.6, 36.9, 37.5, 83.9, 111.3, 128.0, 130.5, 132.7, 140.5, 142.1, 170.0; IR (CCl_4) 1237, 1545, 1712, 1742 cm^{-1}; MS (EI) *m/z* 262 (M^+), 68 (100%); EI-HRMS *m/z* (M^+) calcd. for $C_{17}H_{26}O_2$ 262.1932, found 262.1928.

19: A solution of **18** (300 mg, 1.13 mmol), glycine methyl ester hydrochloride (156 mg, 1.24 mmol), and BroP (505 mg, 1.30 mmol) in anhydrous CH_2Cl_2 (5 mL) was cooled to 0 °C and treated with DIPEA (0.79 mL, 4.52 mmol). The mixture was stirred for 5 min at 0 °C and for 1.5 h at room temperature, poured into 5% $KHSO_4$/ice, and extracted with ethyl acetate (3x). The combined extract was washed with water (2x), 5% $NaHCO_3$ (1x), water (2x) and brine (1x), dried over Na_2SO_4, and evaporated. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate - hexanes (1:1), to give **19** as a pale yellow oil (351 mg, 93%): $[\alpha]^{25}_D$ -97.3 (c 0.2, $CHCl_3$); ^{1}H NMR of major rotamer (300 MHz, $CDCl_3$) δ 0.87 (3H, d, J = 6.2 Hz), 0.97 (3H, d, J = 6.4 Hz), 2.22-2.39 (1H, m), 2.90 (3H, s), 3.71 (3H, s), 3.97 (2H, d, J = 5.4 Hz), 4.18 (1H, d, J = 11.2 Hz), 5.16 (2H, s), 6.70 (1H, br. s), 7.35-7.41 (5H, m); ^{13}C NMR (75 MHz,$CDCl_3$) δ 18.5, 19.5, 25.9, 29.8, 40.8, 52.1, 64.9, 67.5, 127.5, 127.9, 128.4, 136.4, 157.6, 169.9, 170.6; IR (CCl_4) 1217, 1240, 1545, 1695, 1742, 2956, 3363.cm^{-1}; FAB-MS *m/z* 337

(M^++1), 176 (100%); FAB-HRMS *m/z* (M^++1) calcd. $C_{17}H_{24}N_2O_5$ 337.1764, found 337.1765.

20: A mixture of **19** (100 mg, 0.30 mmol) and 5% Pd on carbon (10 mg) in MeOH (5 mL) was exposed to a H_2 atmosphere (1 atm) for 2 h at room temperature. The mixture was filtered and the filtrate was concentrated to give the free amine as a colorless oil (60 mg, ~100%). The crude amine and Troc-AlaOH (118 mg, 0.45 mmol) were dissolved in DMF (2 mL), and DIPEA (0.155 mL, 0.9 mmol) followed by HATU (170 mg, 0.45 mmol) was added at 0 °C. The yellow solution was stirred at 0°C for 30 min and at room temperature overnight, poured into 5% citric acid/ice, and extracted with ethyl acetate (3x). The combined extract was washed with water (2x), 5% $NaHCO_3$ (1x), water (2x), and brine (1x), dried over Na_2SO_4, and evaporated. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate - hexanes (2:1), to give **20** as a pale yellow oil (97 mg, 70%): $[\alpha]^{25}_D$ -105° (c 0.2, $CHCl_3$); ^1H NMR of major rotamer (300 MHz, $CDCl_3$): δ 0.83 (3H, d, *J* = 6.7 Hz), 0.97 (3H, d, *J* = 6.5 Hz), 2.22-2.39 (1H, m), 3.05 (3H, s), 3.71 (3H, s), 3.86 (1H, dd, *J* = 17.9, 5.2 Hz), 4.08 (1H, dd, *J* = 17.9, 6.4 Hz), 3.8-4.10 (4H, m), 4.52-4.70 (3H, m), 6.10 (1H, br d, *J* = 8.0 Hz), 6.78 (1H, s); ^{13}C NMR (75 MHz,$CDCl_3$) δ 18.1, 18.4, 19.5, 25.5, 30.5, 40.7, 47.5, 52.2, 62.7, 74.5, 95.4, 153.8, 170.0 (2x), 173.5; IR (CCl_4) 1217, 1240, 1545, 1742, 1718, 2955, 3340, 3417 cm^{-1}; FAB-MS *m/z* (M^++1) 448, 86 (100%); FAB-HRMS *m/z* (M^++1) calcd. for $C_{15}H_{25}Cl_3N_3O_6$ 448.0809, found 448.0820.

21: A solution of **20** (90 mg, 0.201 mmol) in THF (4.5 mL) was cooled to 0 °C and treated with a 0.31M aqueous solution of LiOH (0.87 mL, 0.26 mmol). The cloudy mixture was stirred at room temperature for 10 min, poured into 5% $KHSO_4$/ice, and extracted with ethyl acetate (3x). The combined organic extract was washed with brine

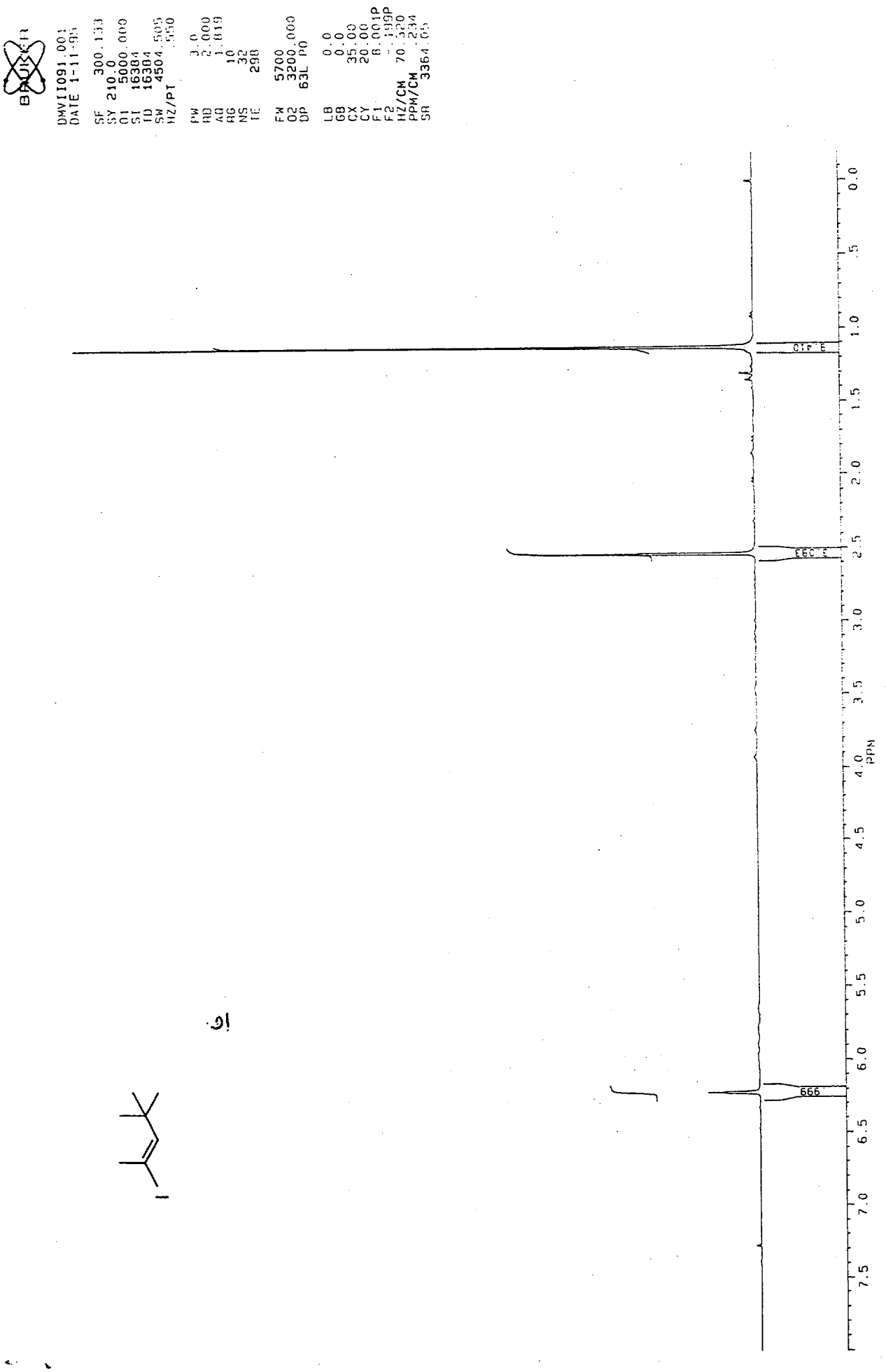
(2x), dried over Na_2SO_4, and evaporated to yield **21** as a colorless oil (83 mg, 98%) which was used without further purification for the next step.

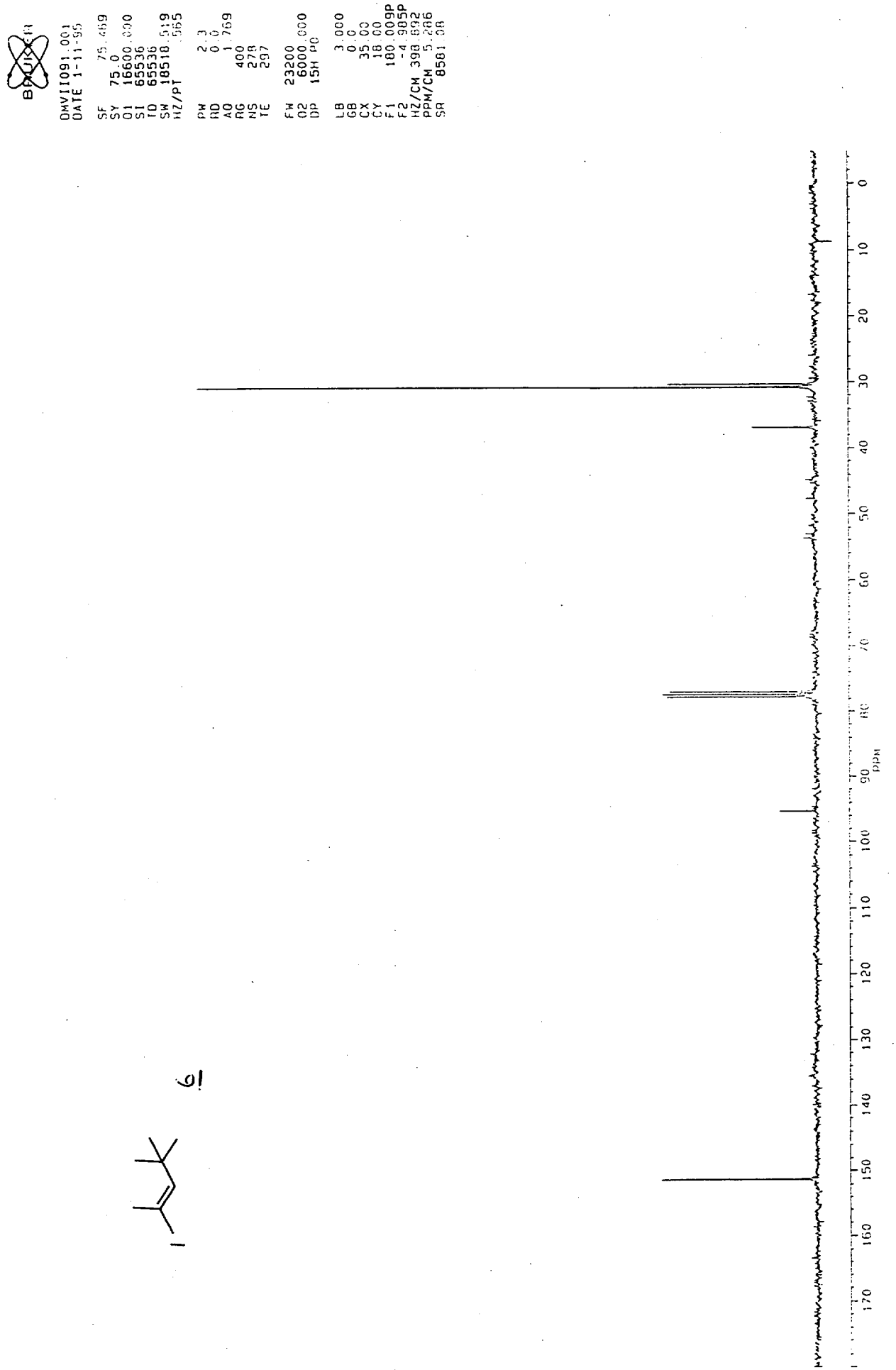
23: To a solution of **14** (10.5 mg, 0.0296 mmol) and **21** (15.4 mg, 0.0355 mmol) in CH_2Cl_2 (0.15 mL) was added EDC (6.8 mg, 0.0355 mmol) and DMAP (7.2 mg, 0.0592 mmol). The solution was stirred at room temperature overnight, poured into 5% $KHSO_4$/ice, and extracted with ethyl acetate (3x). The combined organic extract was washed with water (2x), 5% $NaHCO_3$ (1x), water (2x) and brine (1x), and dried over Na_2SO_4. Evaporation gave a mixture of **14** and **23** (*ca.* 3:1 according to ^{1}H-NMR), which was resubmitted 3 more times to the above esterification conditions. The crude product was dissolved in MeCN/H_2O (9:1, 2 mL), and Ca_2CO_3 (53 mg, 0.53 mmol) and MeI (1.5 mL, 24.1 mmol) were added. The mixture was stirred at room temperature for 8 h and diluted with ethyl acetate. The solution was filtered through a plug of glass wool, and the filtrate was washed with brine (2x), dried over sodium sulfate, and evaporated. The crude aldehyde was immediately dissolved in a mixture of *t*-BuOH and 2-methyl-2-butene (3:1, 4.8 mL), and water (1.45 mL) and NaH_2PO_4 (193 mg) were added, followed by $NaClO_2$ (193 mg). The mixture was stirred at room temperature for 2 h, poured into water/ice, and extracted with ethyl acetate (3x). The combined organic extract was washed with brine (2x), dried over Na_2SO_4, and evaporated. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate - hexane (1:1) and CH_2Cl_2 - MeOH (8:2), to yield **23** as a colorless oil (15.5 mg, 75%): $[\alpha]^{25}_D$ - 66.0 (0.2, $CHCl_3$); ^{1}H NMR of major rotamer (300 MHz, $CDCl_3$) δ 0.84 (3H, d, J = 6.5 Hz), 0.97 (3H, d, J = 6.3 Hz), 1.06 (3H, d, J = 6.9 Hz), 1.12 (9H, s), 1.37 (3H, d, J = 6.7 Hz), 1.69 (3H, s), 1.75 (3H, s), 2.28-2.38 (1H, m), 2.62-2.70 (1H, m), 3.02.-3.10 (2H, m), 3.04 (3H, s), 3.79 (1H, dd, J = 17.9, 5.0 Hz), 4.17 (1H, dd, J = 17.9, 6.8 Hz), 4.55-4.81 (4H, m), 5.07 (2H, s), 5.15 (1H, d, J = 5.8 Hz), 5.21 (1H, s), 5.71 (1H, s), 6.01 (1H, br d, J = 7.9 Hz), 6.68-6.75 (1H, br m); ^{13}C NMR (75 MHz,$CDCl_3$) δ 14.1, 14.5, 18.0 (2x),

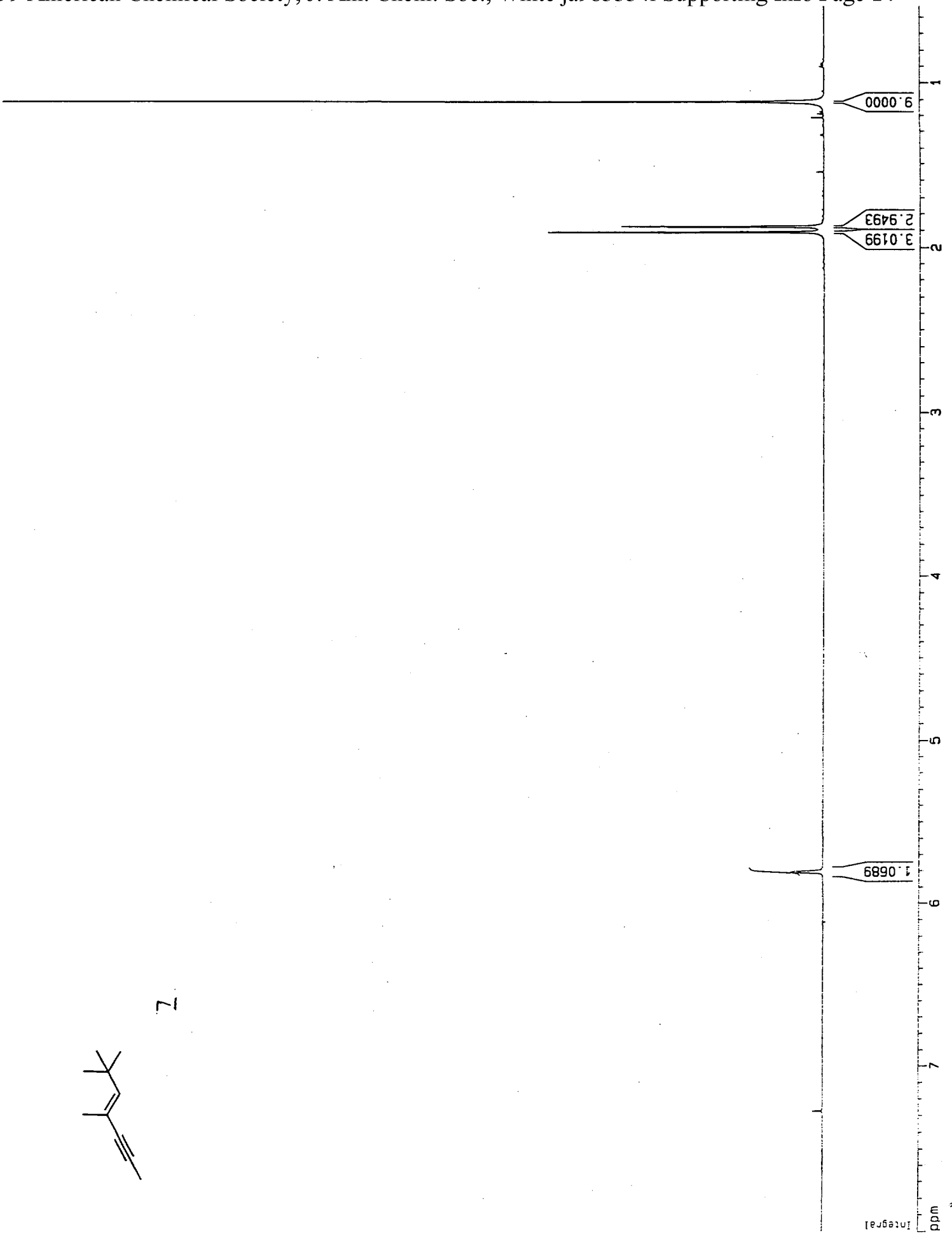
18.4, 19.5, 25.4, 30.6, 30.9, 32.6, 40.1, 41.0, 41.7, 47.6, 62.9, 74.6, 81.8, 95.5, 116.6, 130.3 (2x), 133.4, 140.7, 143.2, 153.8, 168.4, 170.3, 173.8, 174.5; IR (CCl_4) 1218, 1240, 1545, 1718, 1741, 2978 cm^{-1}; FAB-MS *m/z* (M^++1) 696, 359 (100%); Negative FAB-HRMS *m/z* (M^++1) calcd. for $C_{31}H_{47}Cl_3N_3O_8$ 694.2429, found 694.2433.

1: To a solution of **23** (5.0 mg, 0.00717 mmol) in THF (0.5 mL) was added activated Zn (250 mg) followed by a 1M aqueous solution of KH_2PO_4 (0.5 mL). The mixture was stirred at room temperature overnight and diluted with ethyl acetate, and filtered through a plug of glass wool. The aqueous layer was extracted with ethyl acetate (2x), and the combined organic extract was evaporated. The residue was diluted with ethyl acetate (2 mL), the solution was filtered and the filtrate was evaporated and dried azeotropically with benzene (2x). The residue (4.7 mg) was dissolved in DMF (1.25 mL) and DIPEA (0.0062 mL, 0.0359 mmol) was added at 0 °C followed by HATU (8.1 mg, 0.0215 mmol). The yellow solution was stirred at 0 °C for 15 min and at room temperature for 2 h, poured into 5% citric acid/ice, and extracted with ethyl acetate (3x). The combined extract was washed with water (2x), 5% $NaHCO_3$ (1x), water (2x) and brine (1x), dried over Na_2SO_4, and evaporated. The residue was purified by flash chromatography on silica gel, eluting with CH_2Cl_2 - MeOH (98:2) to give **1** as a colorless oil (2.2 mg, 60%): $[\alpha]^{25}_D$ -52.5 (0.07, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.84 (3H, d, *J* = 6.7 Hz), 0.97 (3H, d, *J* = 7.4 Hz), 0.98 (3H, d, *J* = 6.4 Hz), 1.11 (9H, s), 1.38 (3H, d, *J* = 6.6 Hz), 1.64 (3H, s), 1.74 (3H, s), 2.35-2.44 (1H, m), 2.65-2.78 (1H, m), 2.90 (1H, d, *J* = 15.5 Hz), 2.91 (3H, s), 3.13 (1H, d, *J* = 15.5 Hz), 3.57 (1H, dd, *J* = 17.5, 1.4 Hz), 4.15 (1H, d, *J* = 10.8 Hz), 4.70 (1H, dd, *J* = 9.5, 17.5 Hz), 5.16 (1H, s), 5.18-5.22 (3H, m), 5.32-5.41 (1H, m), 5.55 (1H, s), 6.39 (1H, d, *J* = 9.5 Hz), 7.98 (1H, d, *J* =9.0 Hz); ^{13}C NMR (100 MHz,$CDCl_3$) δ 14.9, 15.7, 18.0, 18.1, 18.7, 19.4, 26.9, 28.8, 30.9, 32.6, 40.8, 41.6, 42.5, 44.6, 67.0, 80.4, 119.8, 129.8, 130.3, 131.9, 140.3, 144.7, 168.0, 168.1, 171.2, 171.6; IR (CCl_4) 1218, 1240, 1550, 1718, 1741, 2983 cm^{-1}; FAB-MS *m/z* (M^++1) 504, 86

IR (CCl_4) 1218, 1240, 1550, 1718, 1741, 2983 cm^{-1}; FAB-MS *m/z* (M^++1) 504, 86 (100%); FAB-HRMS *m/z* (M^++1) calcd. for $C_{28}H_{46}N_3O_5$ 504.3438, found 504.3447.







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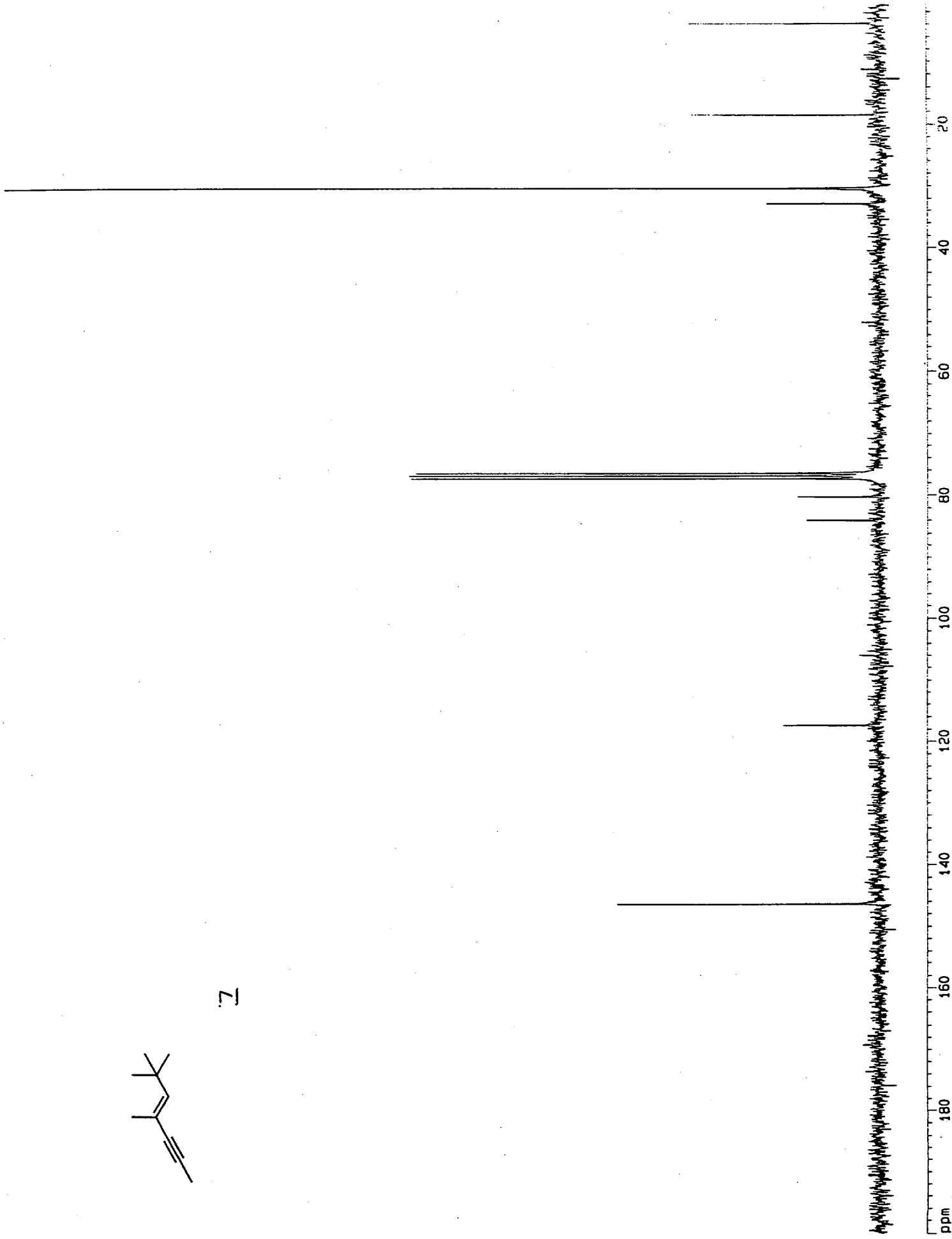

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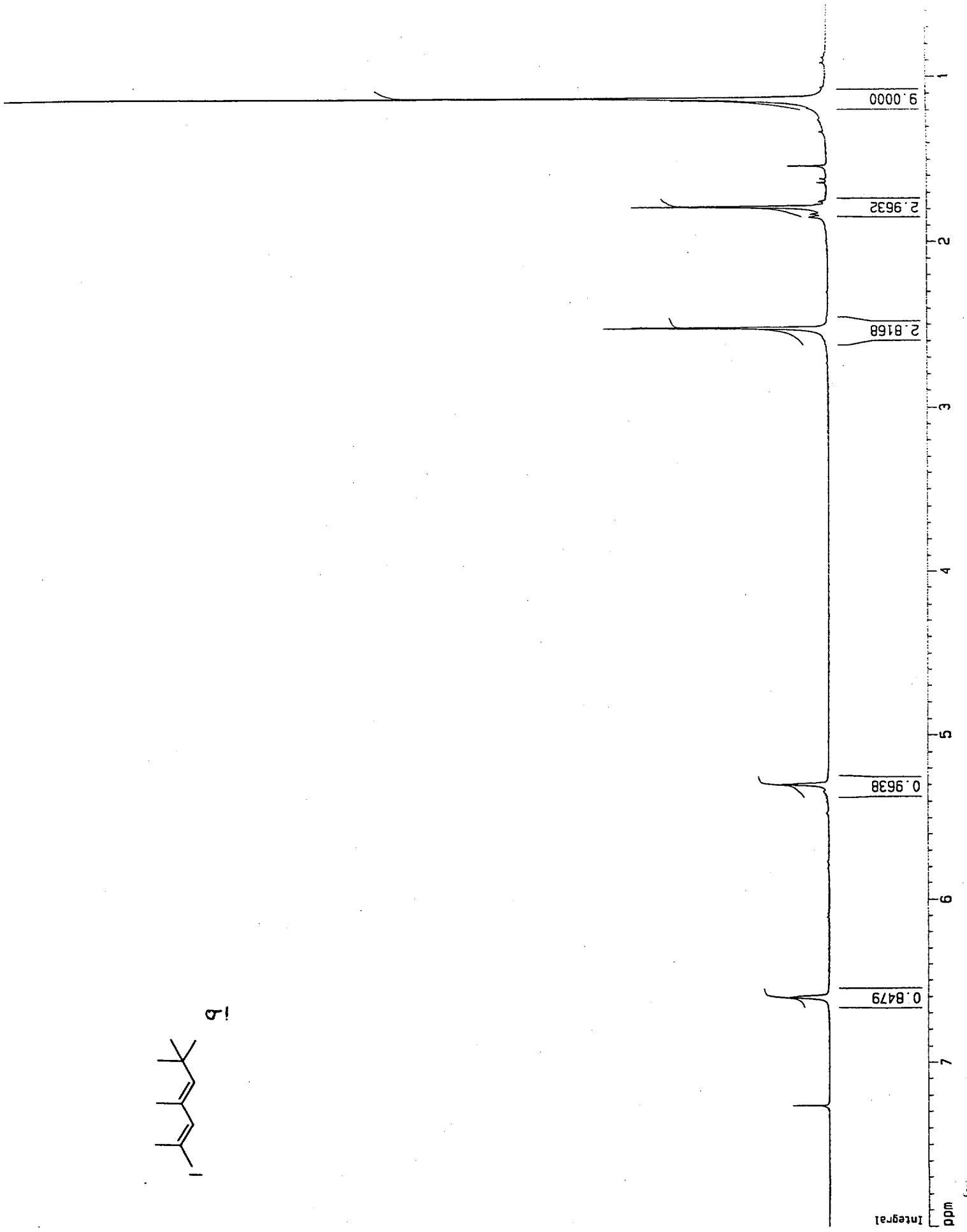

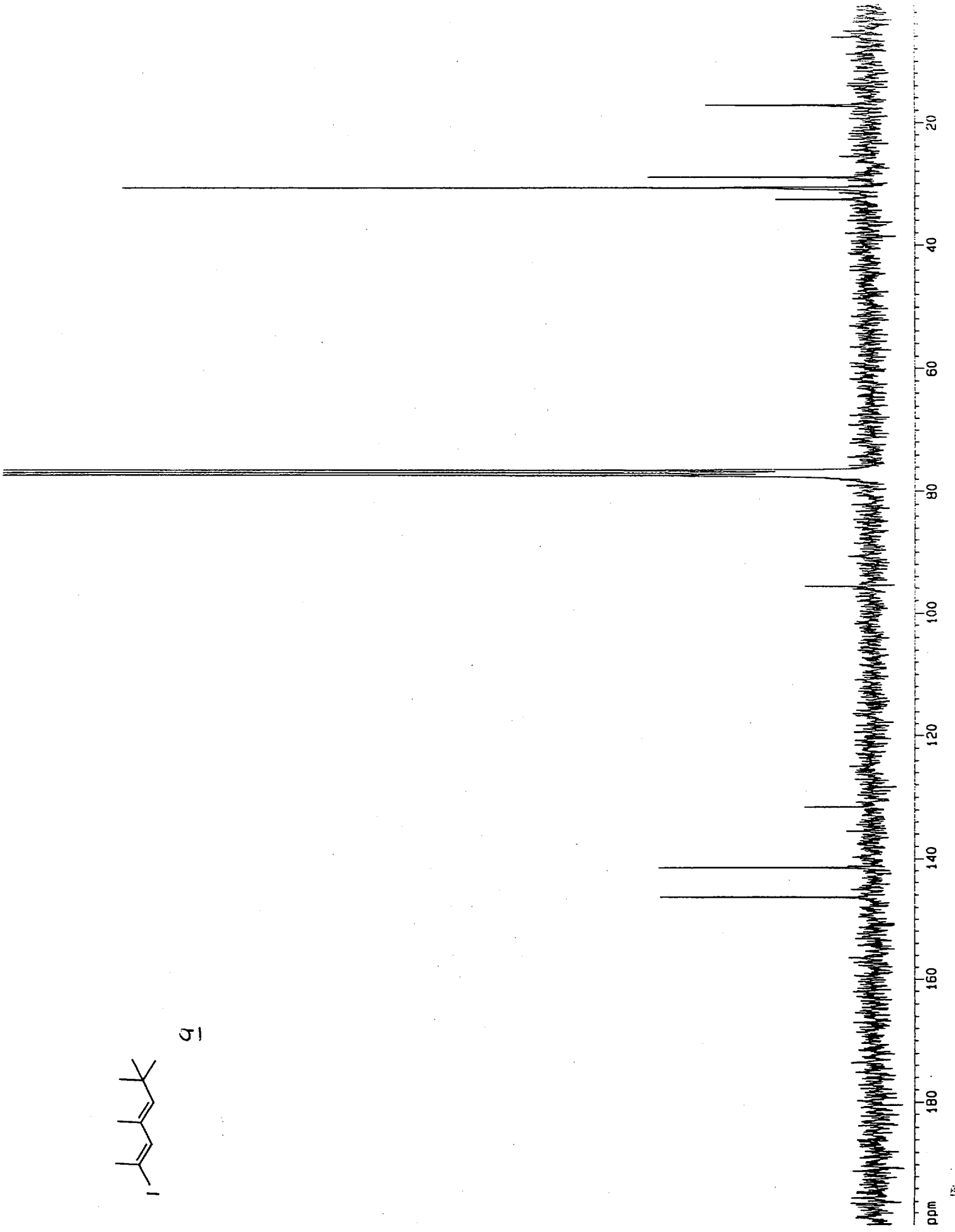

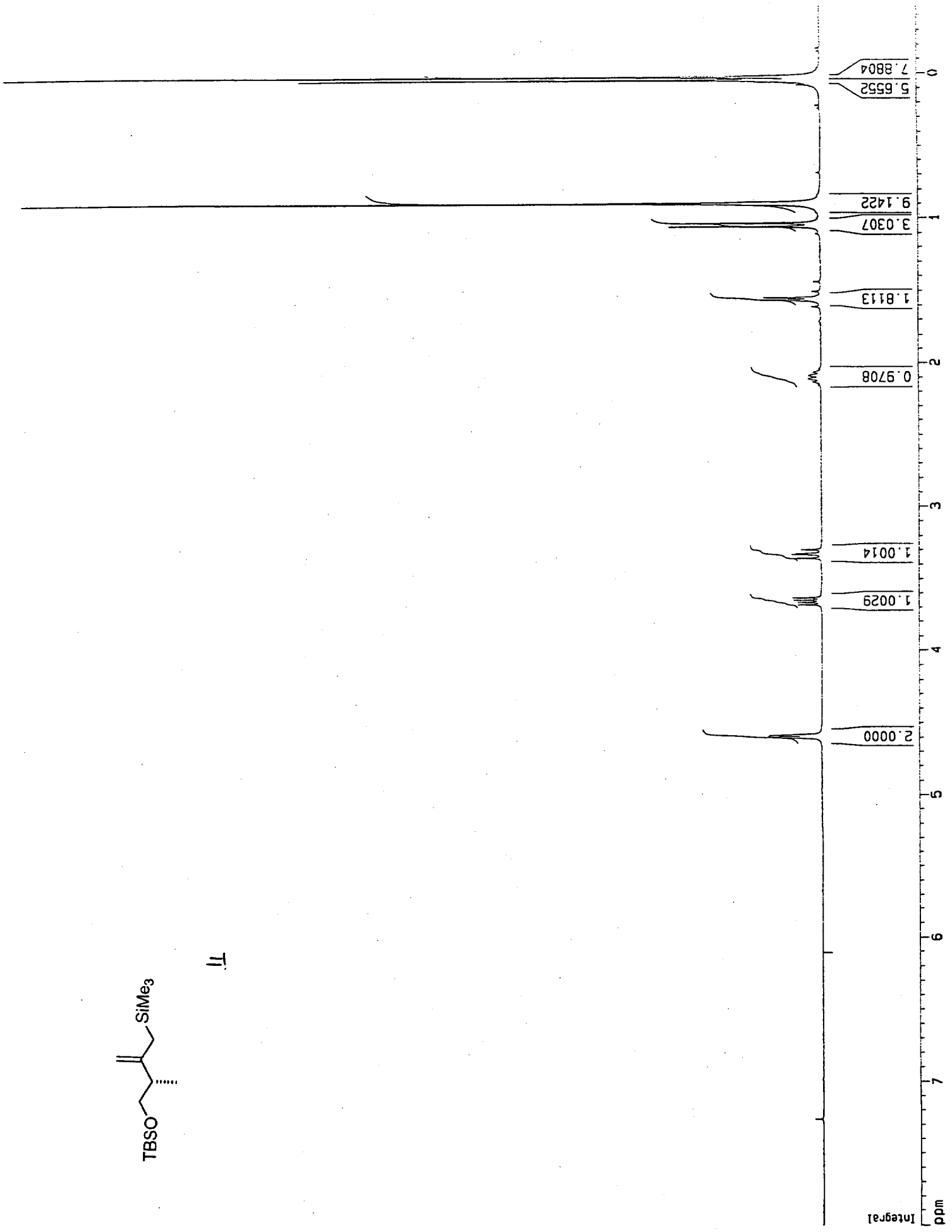

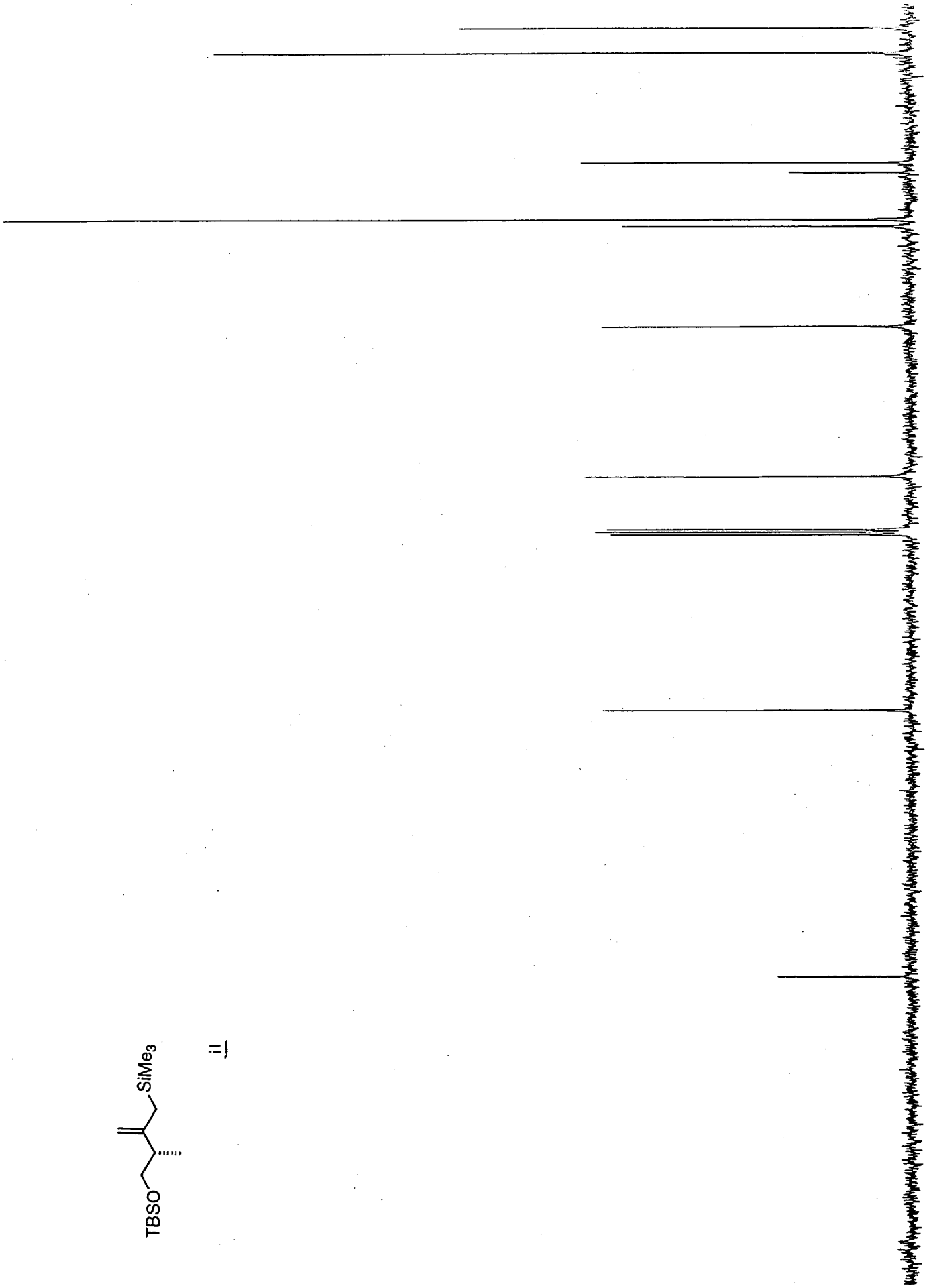

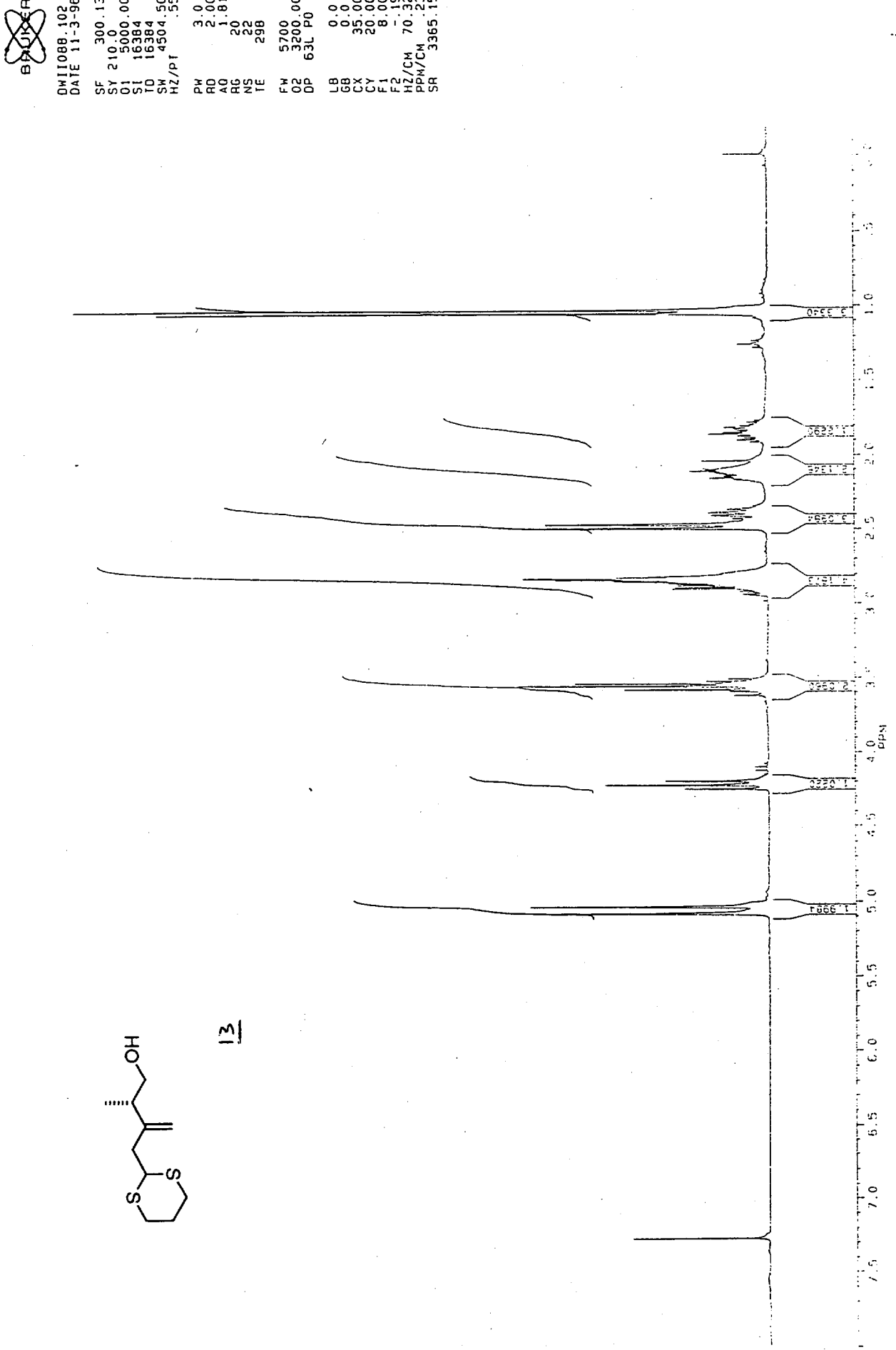

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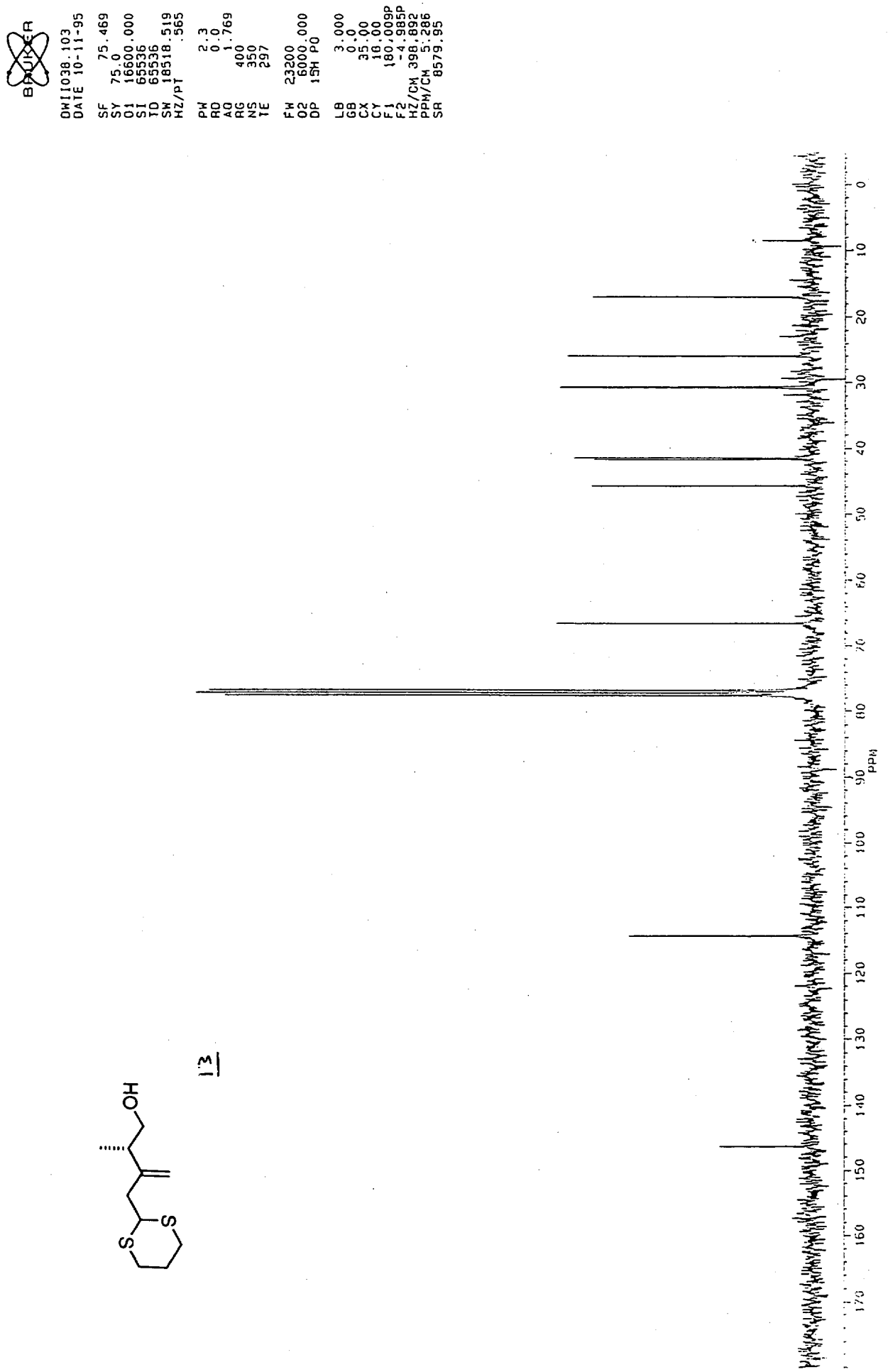

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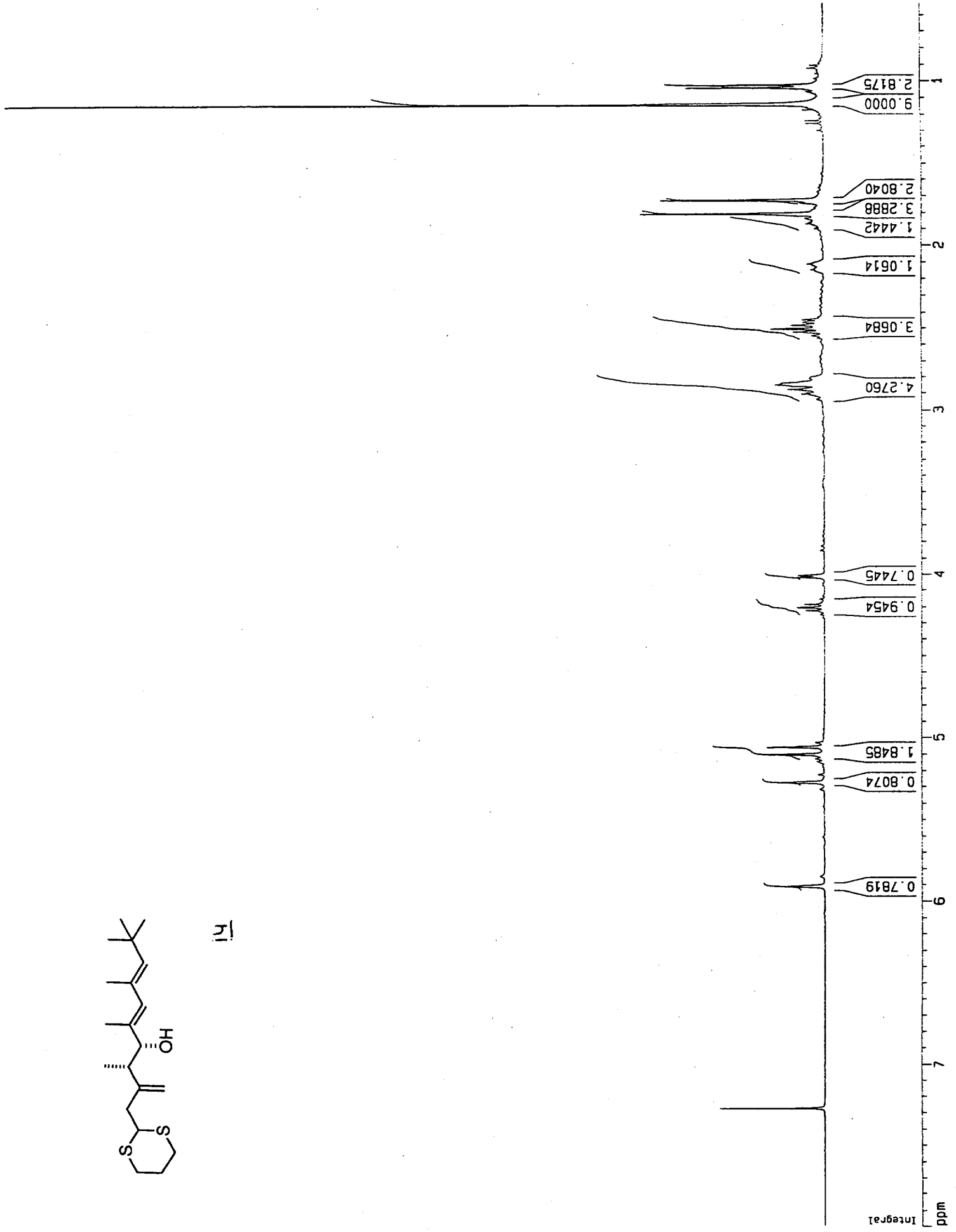

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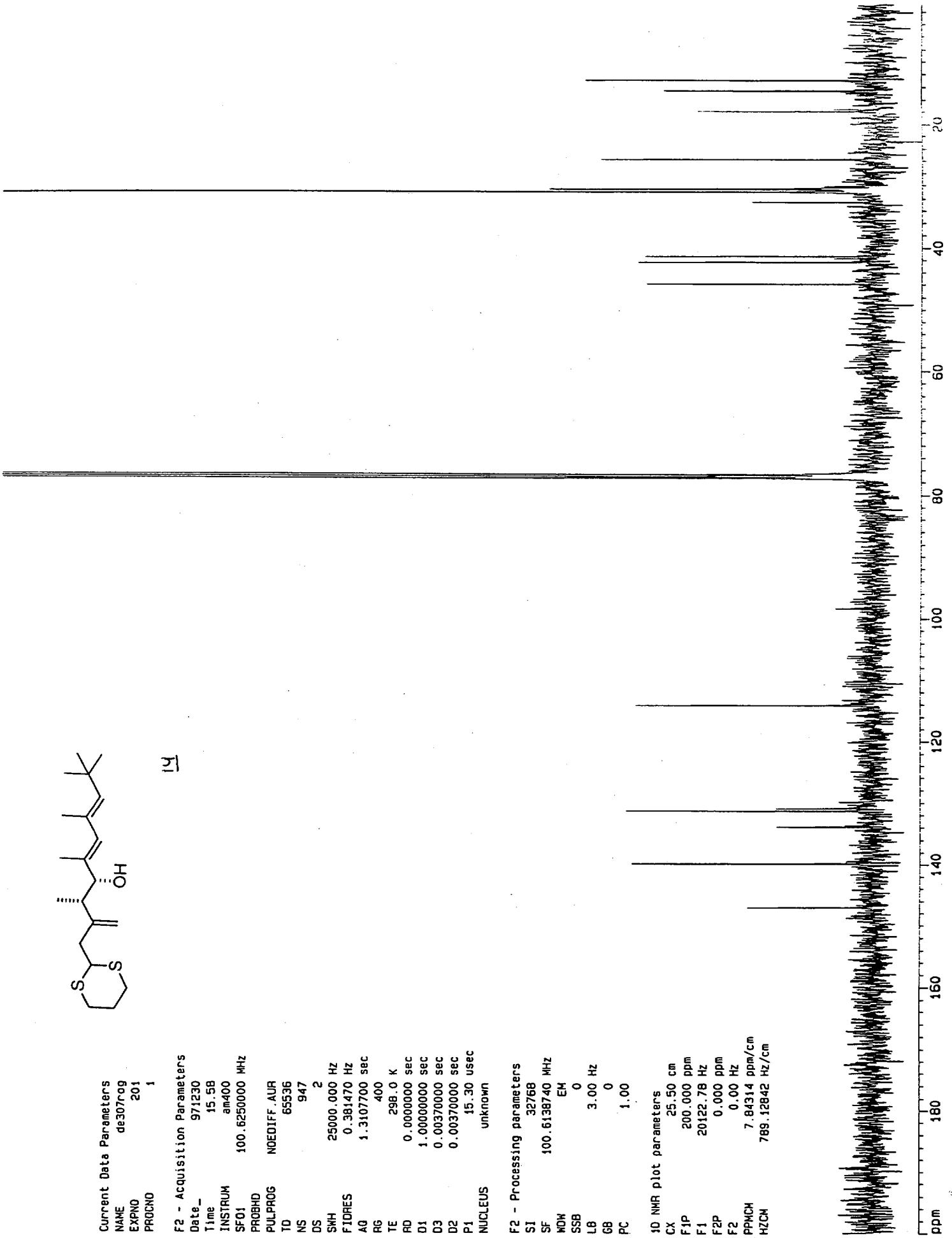

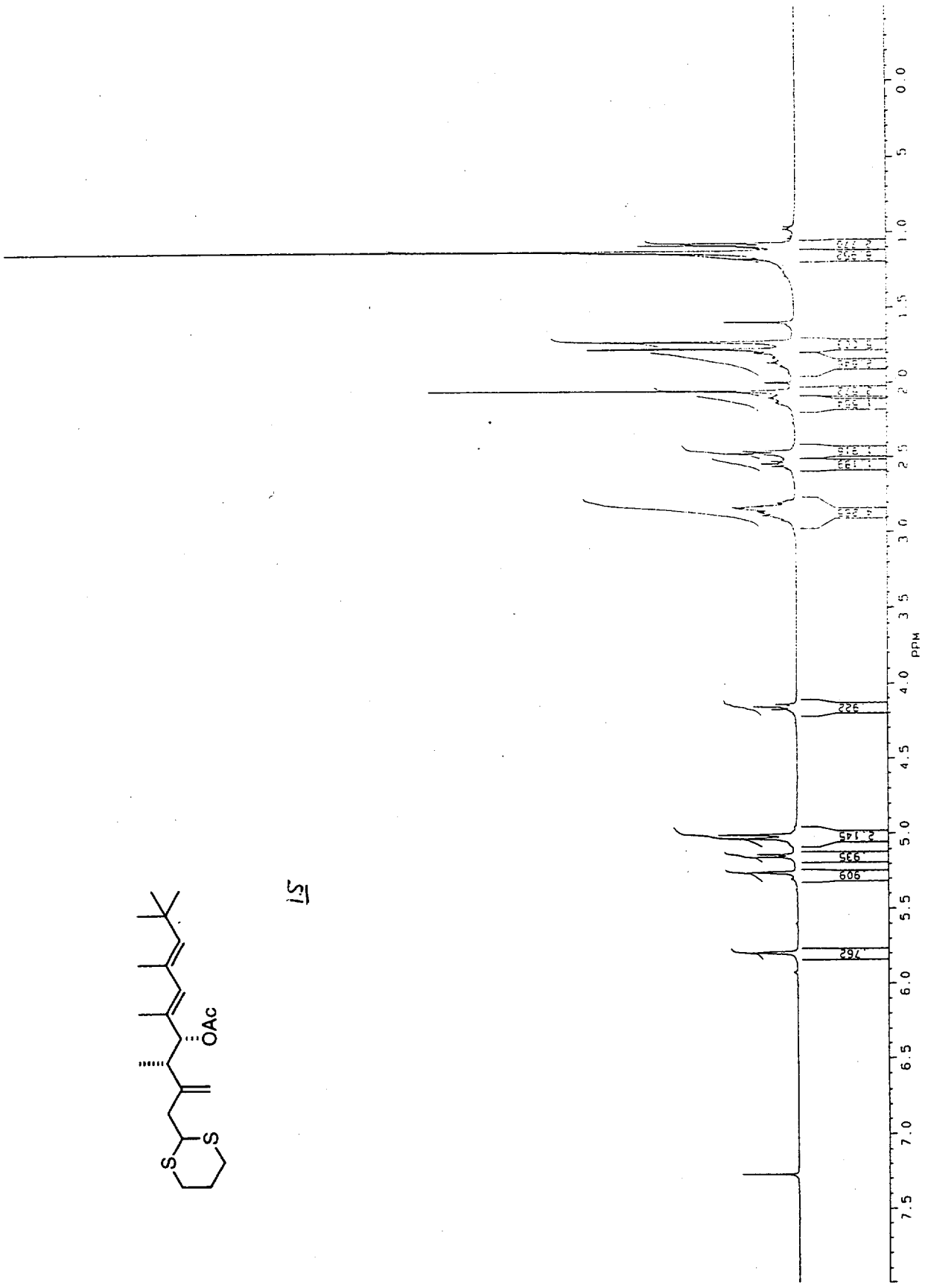

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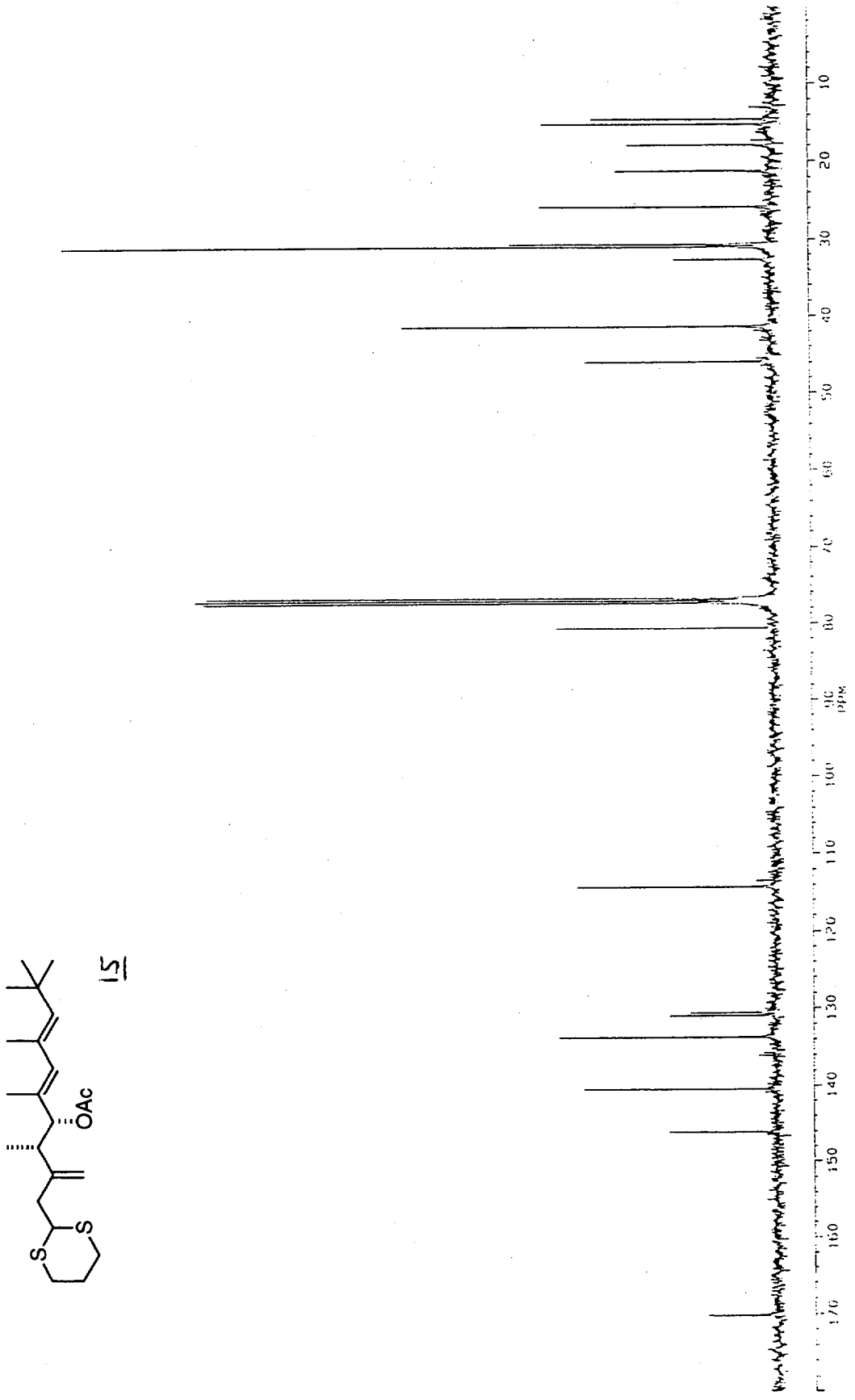

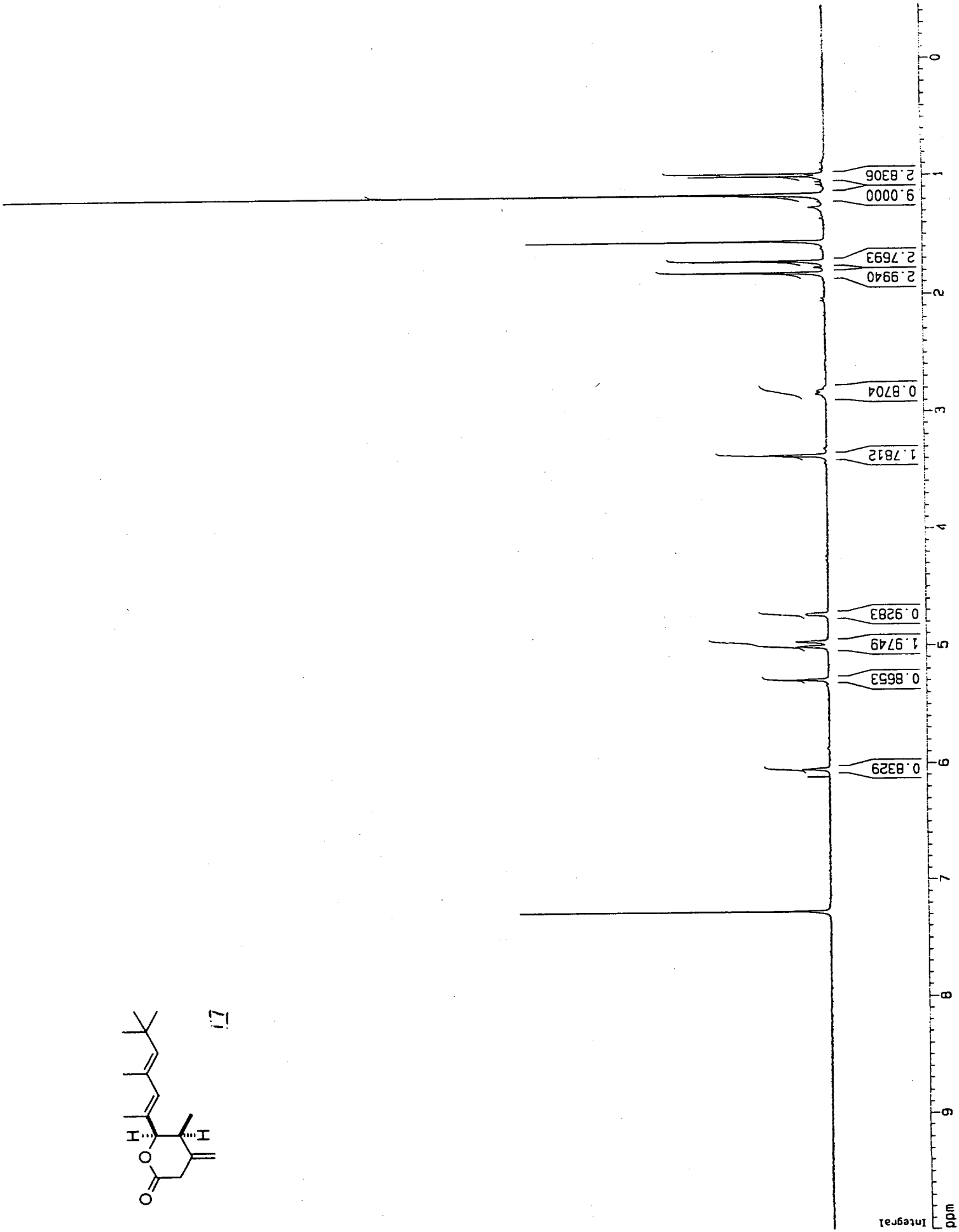

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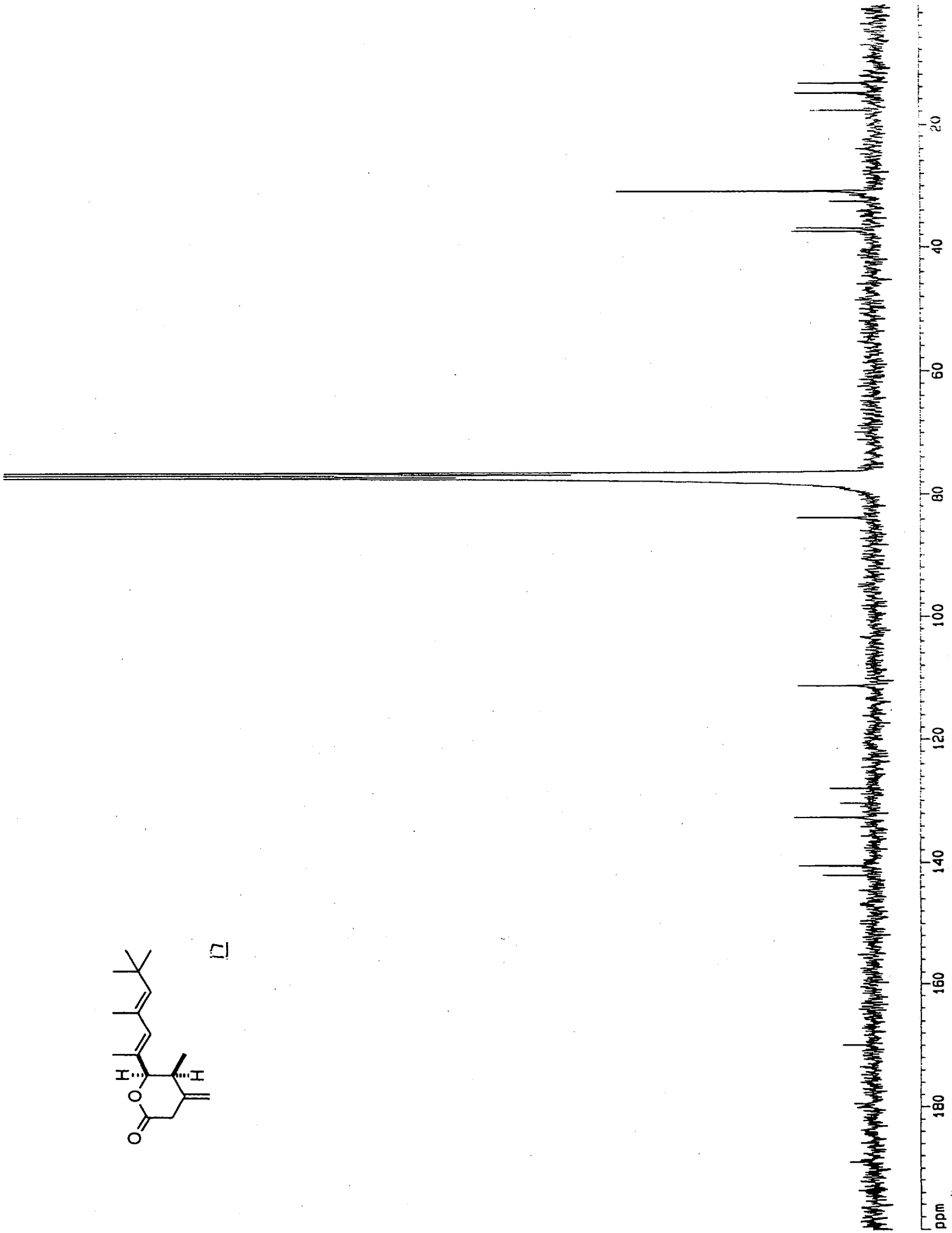

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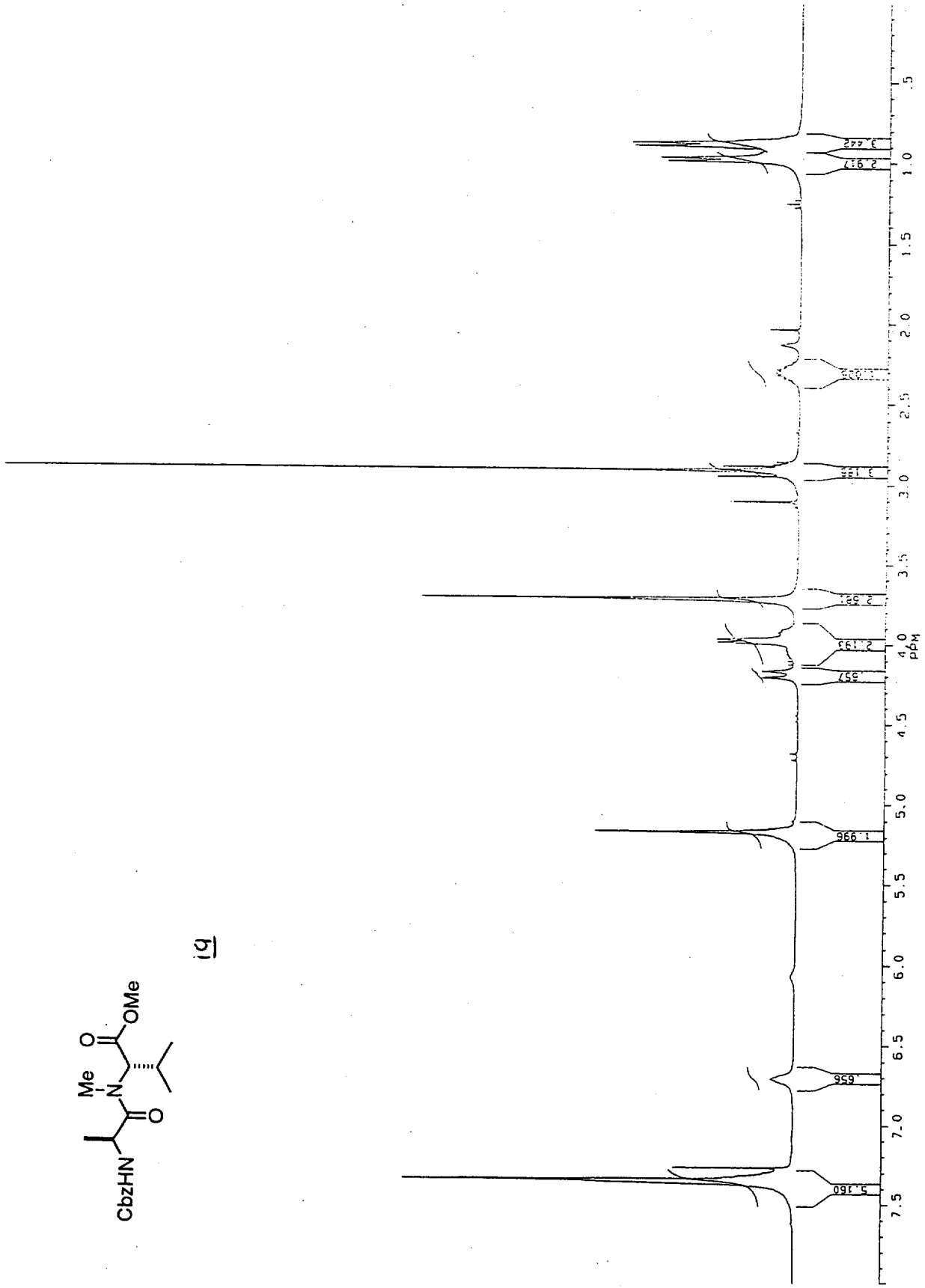
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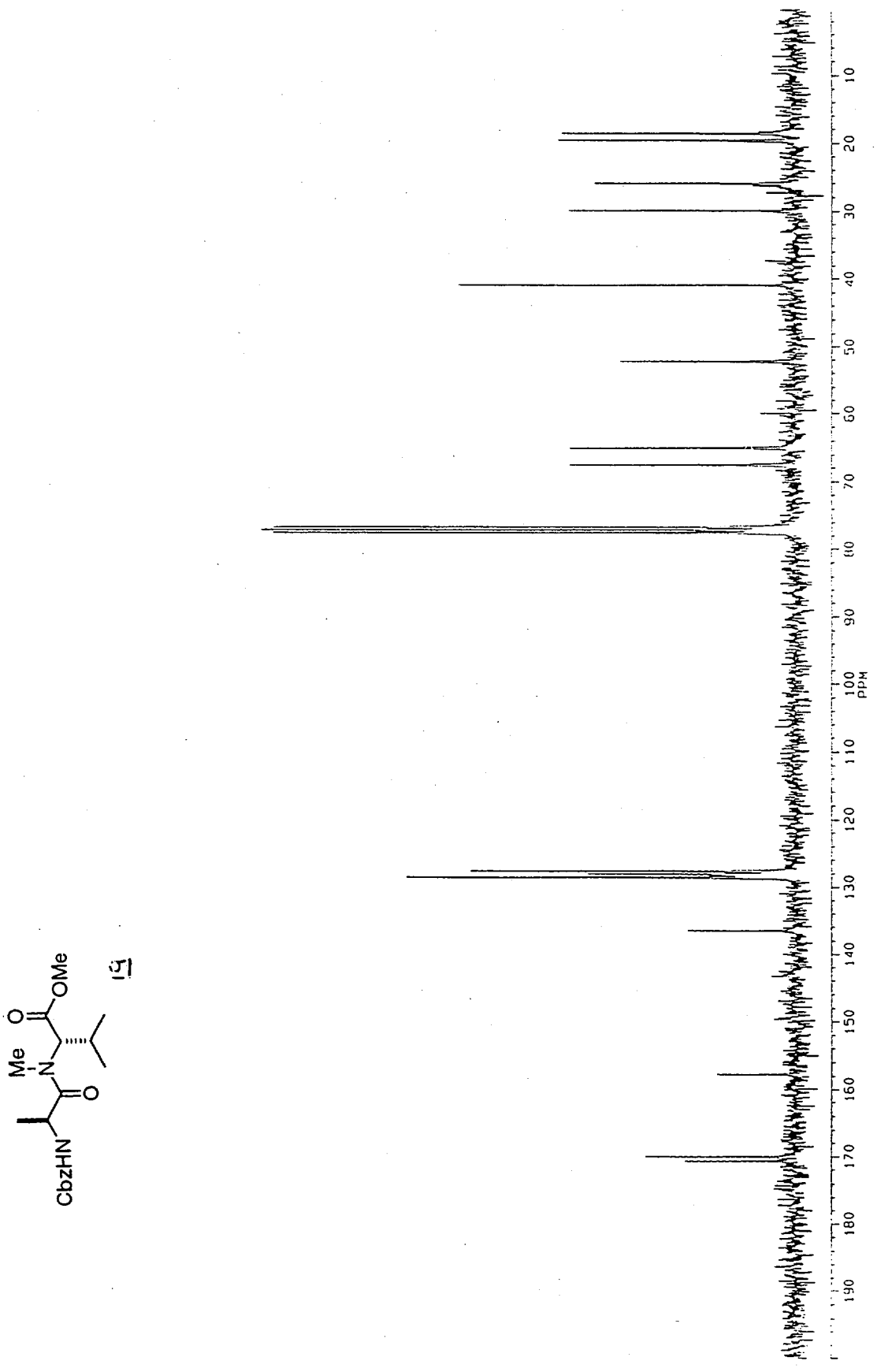

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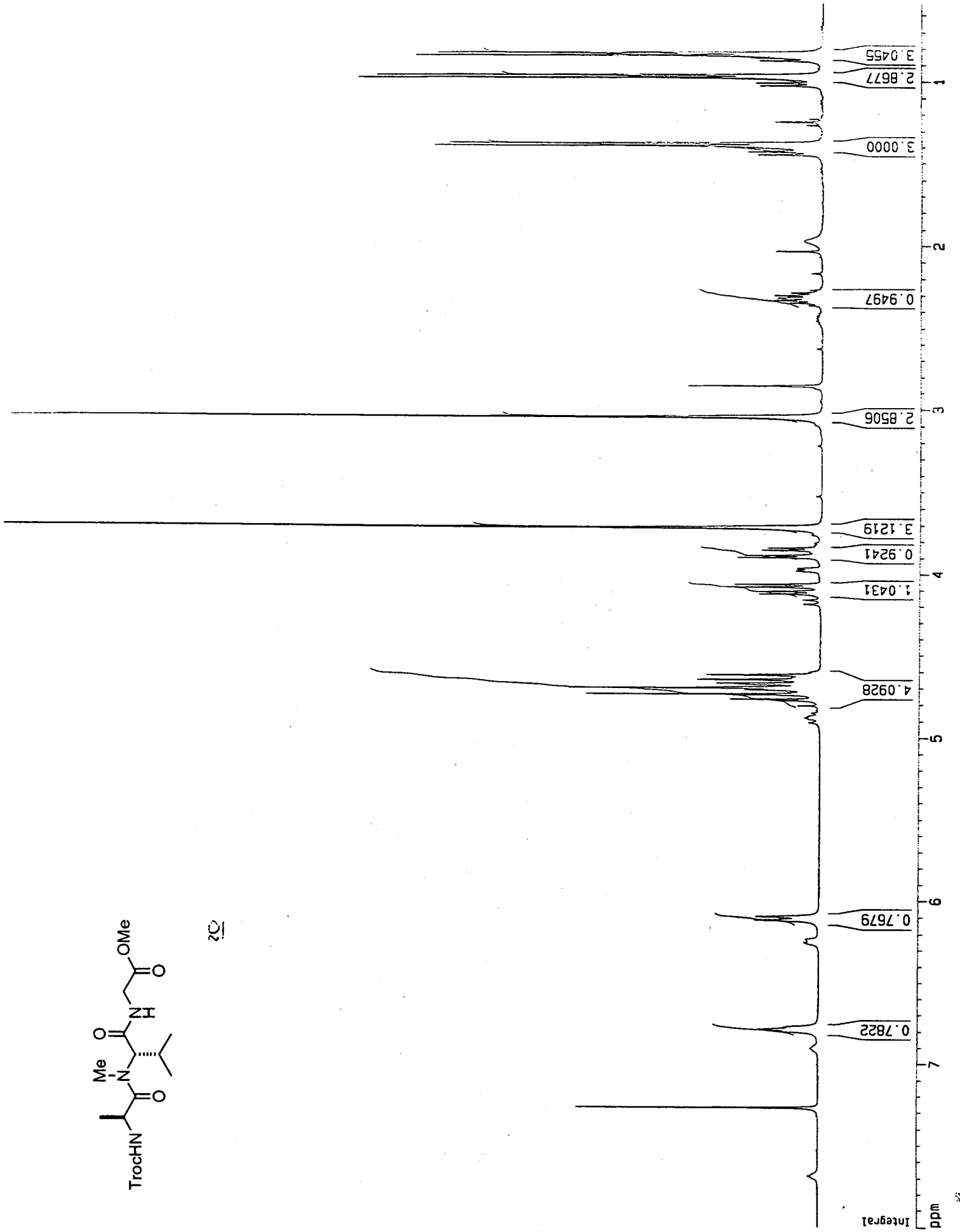

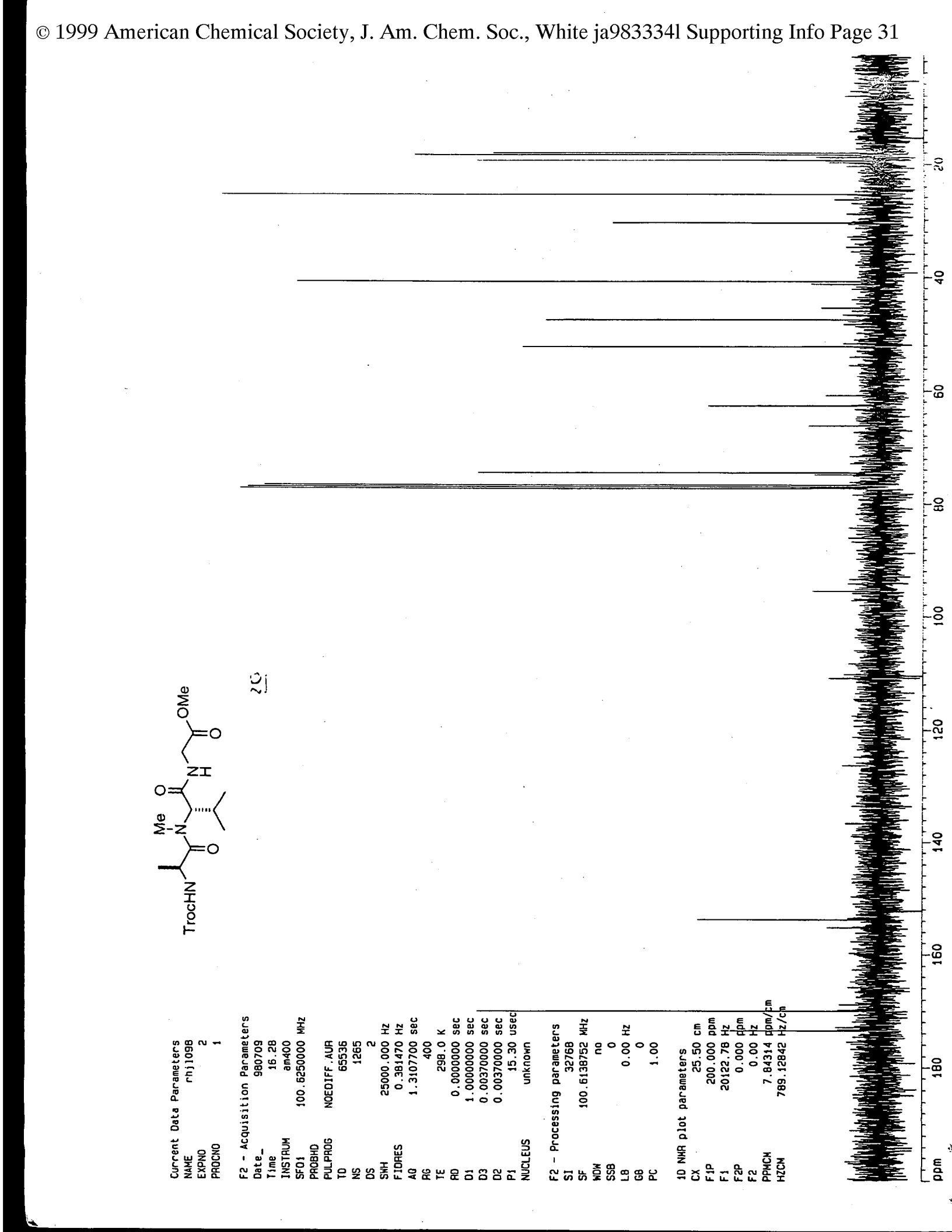

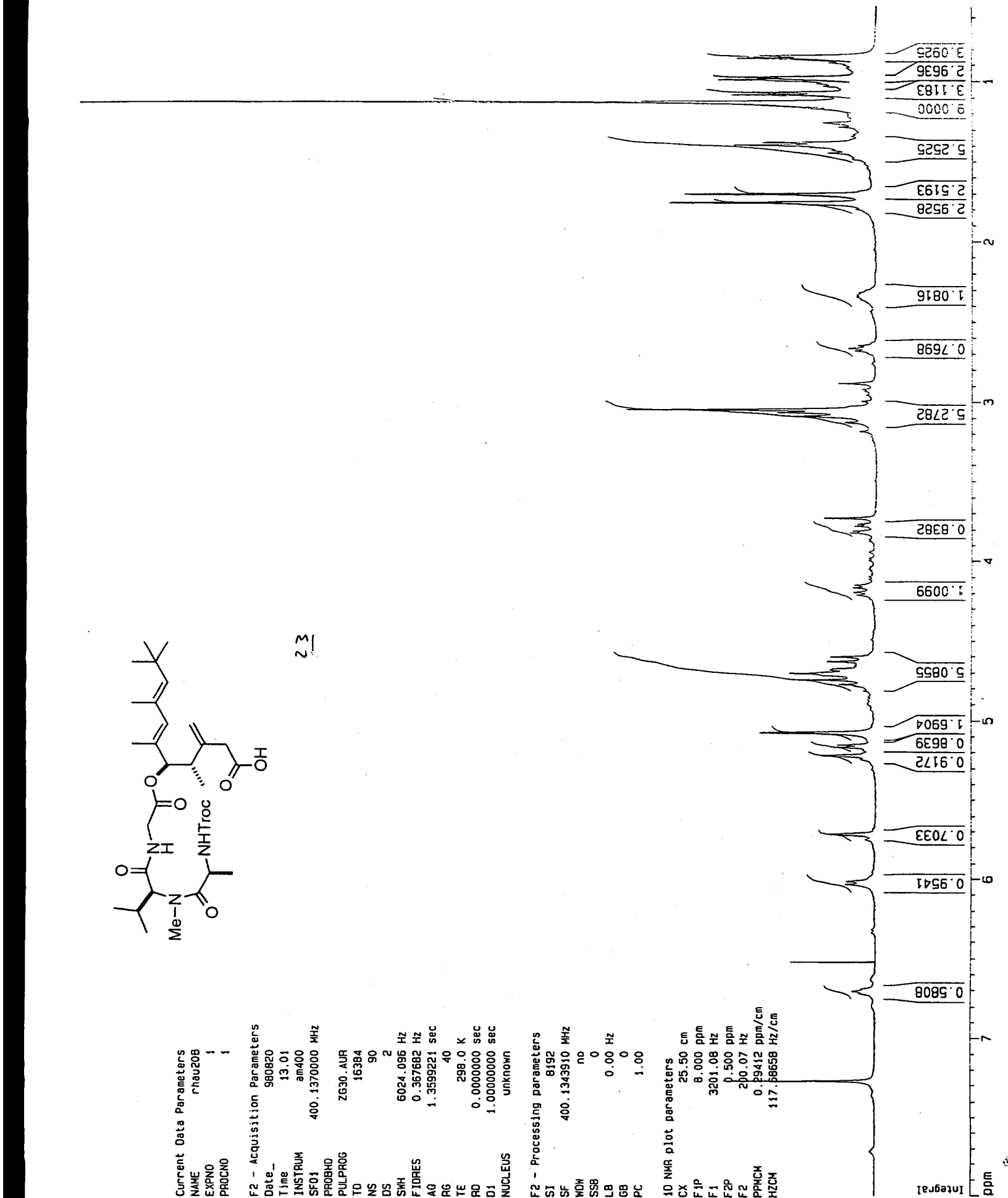

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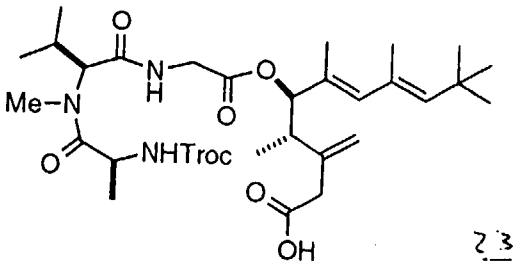

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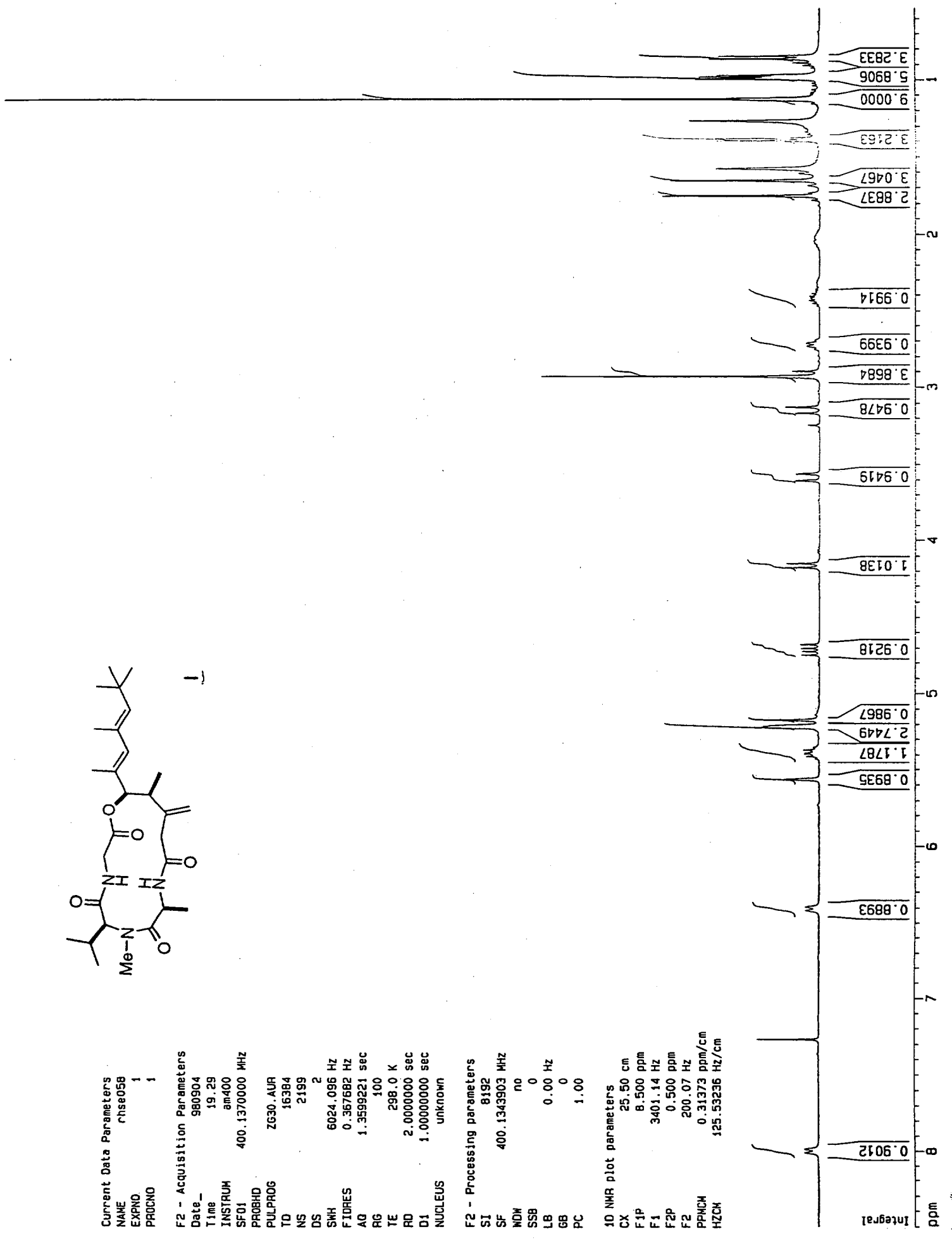

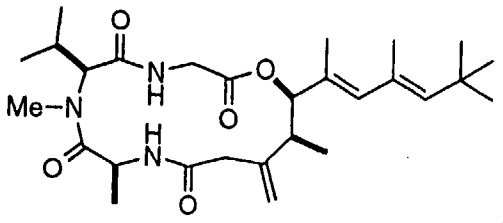

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