Ethylene in Organic Synthesis. Repetitive Hydrovinylation of Alkenes for Highly Enantioselective Syntheses of Pseudopterosins

Daniel J. Mans, G. Adam Cox, T. V. RajanBabu*
Department of Chemistry, The Ohio State University, Columbus, OH 43210, USA

Supporting Online Material

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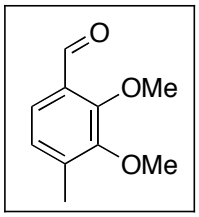
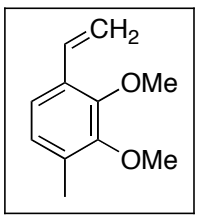
General methods. Reactions requiring air–sensitive manipulations were conducted under an inert atmosphere of nitrogen using Schlenk techniques or in a Vacuum Atmospheres glovebox. Dichloromethane (DCM) was distilled from calcium hydride under a dry atmosphere and stored over molecular sieves. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl. The ligands[1] and $Na^+[[3,5\text{-}(CF_3)_2C_6H_3]_4B]^-$ (NaBARF)[2] were prepared according to the literature. Ethylene (99.5%) was purchased from Matheson Inc., and passed through Drierite® before use. Analytical TLC was performed on precoated (0.25 mm) silica gel 60 F254 plates. Flash column chromatography was carried out on silica gel 40. Enantiomeric excesses of chiral compounds were determined by chiral stationary phase gas chromatographic analyses, which were performed with Cyclodex B (25 m x 0.25 mm, 0.12 mm film thickness), Chiraldex B-PH (30 m × 0.25 mm, 0.12 μm film thickness), or Cyclosil (25 m x 0.25 mm, 0.12 μm film thickness) capillary GC columns. Optical rotations were recorded the sodium D line in chloroform.

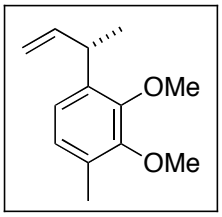


2,3-Dimethoxy-4-methylbenzaldehyde: A 500 mL three-necked flask equipped with a magnetic stirring bar, stopper, addition funnel and nitrogen inlet was flame-dried and purged with nitrogen. The flask was charged with 2,3-dimethoxytoluene (10.0 mL, 67.35 mmol) and freshly distilled *N,N,N',N'*-tetramethylethylenediamine TMEDA (2.52 mL, 16.84 mmol, 0.25 equiv.) dissolved in anhydrous hexanes (200 mL). A 1.7 M solution of *t*-butyl lithium in pentane (47.5 mL, 80.82 mmol, 1.2 equiv.) was added dropwise via addition funnel over 30 min. The resulting cloudy yellow solution was allowed to stir at room temperature overnight (16 h). The reaction vessel was cooled to 0° C and freshly distilled, degassed, anhydrous DMF (10.4 mL, 134.70 mmol, 2.0 equiv.) was added dropwise over 10 min. The reaction vessel was warmed to room temperature and allowed to stir for 1 h. The reaction was quenched by the slow addition of water (20 mL) followed by the addition of 2 N HCl until the pH of the solution was neutral. The reaction mixture was poured into water (200 mL) and extracted with ether (3 x 50 mL). The organic layers were combined and dried over $MgSO_4$, filtered, and evaporated to give the crude aldehyde which was purified via flash column chromatography (R_f = 0.40, hexanes-ethyl acetate, 9:1) to yield the product as a pale yellow oil (8.95 g, 49.68 mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.47 (d, 1H, *J* = 8.0 Hz), 6.99 (d, 1H, *J* = 8.0 Hz), 3.98 (s, 3H), 3.85 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 156.4, 151.7, 140.6, 128.6, 126.3, 123.0, 62.2, 60.4, 16.7. IR (neat) 2855, 2743, 1688, 1596, 1464, 1257, 1253, 1071, 1023 cm^{-1}.



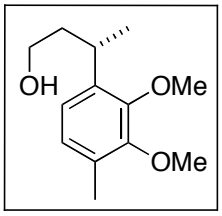
2,3-Dimethoxy-1-methyl-4-vinylbenzene (6): A 500 mL three-necked flask equipped with magnetic stirring bar, stoppers and reflux condenser fitted with a nitrogen inlet was flame-dried and purged with nitrogen. The flask was charged with KHMDS (5.486 g, 27.50 mmol, 1.2 equiv.) dissolved in anhydrous THF (170 mL). Methyltriphenylphosphonium bromide (9.824 g, 27.50 mmol, 1.2 equiv.) was added in small portions and the reaction mixture was allowed to stir for 1 h. A solution of the aldehyde from the previous step (4.130 g, 22.92 mmol) in anhydrous THF (50 mL) was added dropwise via syringe and then heated to reflux in

an oil bath. The reaction was allowed to reflux overnight (16 h). The vessel was allowed to cool to room temperature, then the reaction mixture was diluted with pentane (150 mL) and cooled to 0° C to induce precipitation of triphenylphosphine oxide. The reaction mixture was then passed through a plug of Celite, followed by rinsing of the reaction vessel with pentane (3 x 50 mL). The crude styrene was purified via flash column chromatography (R_f = 0.36, hexanes-ethyl acetate, 19:1) to yield **6** as a colorless oil (3.78 g, 20.98 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, 1H, J = 8.0 Hz), 6.98 (dd, 1H, J = 10.8, 17.7 Hz), 6.88 (d, 1H, J = 8.0 Hz), 5.72 (dd, 1H, J = 1.4, 17.7 Hz), 5.25 (dd, 1H, $J_{1,2}$ = 1.4, 10.8 Hz), 3.84 (s, 6H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 150.9, 132.1, 131.4, 130.2, 126.0, 120.8, 114.4, 61.0, 60.4, 16.1. IR (neat) 1824, 1625, 1601, 1567, 1284, 1222, 1066, 1024 cm^{-1}. HRMS (ESI); *m/z* 201.0898 ([M + Na]); exact mass calculated for $C_{11}H_{14}O_2Na$, 201.0891.

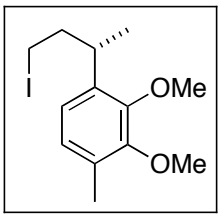


(*S*)-1-(But-3-en-2-yl)-2,3-dimethoxy-4-methylbenzene (7): *Precatalyst preparation*: In a glovebox, NaBARF (56.0 mg, 0.063 mmol, 1.4 mol%), (*R*)-2,2'-binaphthoyl-benzyl-(*S*)-[1-(1-naphthylethyl)]aminoylphosphine (**L1**, 36.4 mg, 0.063 mmol, 1.4 mol%), and $[(allyl)NiBr]_2$ (10.2 mg, 0.032 mmol, 0.7 mol%) were weighed into separate glass vials. The phosphoramidite ligand was dissolved in anhydrous DCM (1.0 mL) and transferred to the vial containing $[(allyl)NiBr]_2$, followed by 1.0 mL rinsing of the source vial. The resulting yellow solution of phosphoramidite ligand and $[(allyl)NiBr]_2$ was transferred to the vial containing NaBARF, followed by 1.0 mL rinsing of the source vial. The resulting orange-yellow solution was diluted with DCM (10.0 mL) and allowed to stand for 1.5 h. *Asymmetric hydrovinylation*: A 100 mL three-necked flask equipped with a rubber septum, flow-controlled nitrogen inlet, thermometer, and magnetic stirring bar was flame-dried and purged with nitrogen. The vessel was charged with anhydrous DCM (35 mL). The catalyst solution prepared above was transferred to the reaction vessel via cannula, followed by 2.0 mL rinsing of the source vial. The system was closed at the flow-controlled stopcock and cooled to -80 °C in a dry ice/acetone bath, creating a small vacuum. A strong flow of dry ethylene was introduced via needle through the septum to relieve the vacuum and then the atmosphere of the vessel was evacuated three times via syringe to remove any remaining nitrogen. The flow of ethylene was adjusted to maintain a pressure of 1 atm by releasing excess gas through an oil bubbler. A solution of the styrene from previous experiment (**6**) (806.0 mg, 4.52 mmol) in anhydrous DCM (3.0 mL), followed by 1.0 mL rinsing of the source vial was introduced via syringe as to not increase the reaction temperature above -80 °C. The reaction mixture was allowed to stir at -80 °C for 2 h. The ethylene needle was then removed and the reaction was exposed to air and water (10 mL) was added to quench the reaction. The resulting mixture was poured into water (30 mL) and extracted with ether (3 x 15 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated to give the crude hydrovinylation product, which was then eluted through a plug of silica with pentane to remove any nickel salts. The eluent was concentrated to yield (**7**) as a colorless oil (931.7 mg, 4.52 mmol, >99%, >95% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90-6.83 (AB quartet, 2H, ν_A = 6.89, ν_B = 6.84, J_{AB} = 8.0 Hz), 6.04 (ddd, 1H, J= 6.0, 10.4, 16.6 Hz), 5.08-5.03 (m, 2H), 3.92-3.81 (m, 7H, containing 3.87 (s, 3H), 3.85 (s, 3H)), 2.26 (s, 3H), 1.34 (d, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 150.8, 143.5, 137.5, 130.2, 125.8, 122.4, 113.0, 60.9, 60.1, 36.0, 20.6, 15.9. $[\alpha]_D^{20}$ -35.0 (*c* 1.24, $CHCl_3$), IR (neat) 1636, 1461, 1277,

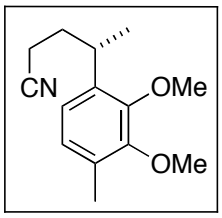
1025 cm^{-1}. HRMS (ESI); *m/z* 229.1191 ([M + Na]); exact mass calculated for $C_{13}H_{18}O_2Na$, 229.1199. GC (Cyclodex B-Ph, 85 °C isotherm): t_R = 99.07 (*R*), 100.74 min (*S*).



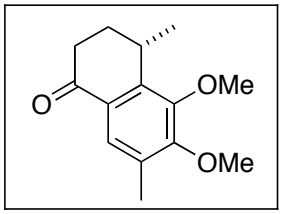
(*S*)-3-(2,3-Dimethoxy-4-methylphenyl)butan-1-ol: A 100 mL three-necked flask equipped with magnetic stirring bar, stopper, thermometer, and nitrogen inlet was flame-dried and purged with nitrogen. The flask was charged with olefin **7** (771.0 mg, 3.74 mmol) dissolved in anhydrous THF (40 mL). 9-BBN dimer (913.0 mg, 3.74 mmol, 1.0 equiv.) was added in small portions and the reaction mixture was allowed to stir at room temperature for 2 h. The vessel was cooled to 0 °C in an ice/water bath and 4 M NaOH (7.5 mL) was added dropwise, maintaining the internal temperature of the vessel below 5 °C. A solution of ~30% H_2O_2 (4.7 mL) was then added dropwise, maintaining the internal temperature of the vessel below 5 °C. The vessel was allowed to warm to room temperature and stir for an additional 0.5 h. The mixture was then diluted with ether (20 mL) and neutralized with 10% H_2SO_4 until pH ~7 was achieved. The whole was poured into water (20 mL) and extracted with ether (3 x 15 mL). The organic layers were combined and dried over $MgSO_4$, and concentrated to give the crude alcohol as a colorless oil. The crude alcohol was purified via flash column chromatography (R_f = 0.40, hexanes-ethyl acetate, 2:1) to yield the product as a colorless oil (826 mg, 3.68 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91-6.83 (AB quartet, 2H, ν_A = 6.90, ν_B = 6.84, J_{AB} = 8.0 Hz), 3.86 (s, 3H), 3.82 (s, 3H), 3.55-3.47 (m, 1H), 3.37-3.28 (m, 2H), 2.31 (bs, 1H), 2.24 (s, 3H), 1.94-1.86 (m, 1H), 1.63-1.55 (m, 1H), 1.27 (d, 3H, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 150.8, 137.8, 130.0, 126.4, 121.6, 61.1 (2 x C), 60.2, 41.4, 28.1, 21.9, 15.8. $[\alpha]_D^{20}$ +32.1 (*c* 3.35, $CHCl_3$), IR (neat) 3421, 1603, 1574, 1277, 1221, 1069, 1024 cm^{-1}. HRMS (ESI); *m/z* 247.1308 ([M + Na]); exact mass calculated for $C_{13}H_{20}O_3Na$, 247.1310.



(*S*)-1-(4-Iodobutan-2-yl)-2,3-dimethoxy-4-methylbenzene (8): A 50 mL three-necked flask equipped with magnetic stirring bar, stopper, thermometer, and nitrogen inlet was flame-dried and purged with nitrogen. The flask was charged with alcohol the alcohol from the previous step (0.74 g, 3.26 mmol) dissolved in anhydrous THF (10 mL). Imidazole (0.44 g, 6.52 mmol, 2.0 equiv.) and triphenylphosphine (0.94 g, 3.59 mmol, 1.1 equiv.) were added in sequence and then the vessel was cooled to 0 °C in an ice/water bath. Iodine crystals (0.91 g, 3.59 mmol, 1.1 equiv.) were added in small portions until a red solution persisted. The vessel was allowed to warm to room temperature and then concentrated. The crude residue was purified via flash column chromatography (R_f = 0.40, hexanes-ethyl acetate, 19:1) to yield the iodide as a colorless oil (1.08 g, 3.23 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88-6.80 (AB quartet, 2H, ν_A = 6.88, ν_B = 6.80, J_{AB} = 8.0 Hz), 3.86 (s, 3H), 3.82 (s, 3H), 3.25 (sextet, 1H, *J* = 7.2 Hz)), 3.09 (t, 2H, *J* = 8.0 Hz), 2.24 (s, 3H), 2.19-2.05 (m, 2H), 1.22 (d, 3H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 151.2, 137.2, 130.4, 126.0, 121.7, 61.0, 60.1, 41.7, 33.8, 21.4, 15.9, 5.1. $[\alpha]_D^{20}$ +25.1 (*c* 1.25, $CHCl_3$), IR (neat) 1461, 1278, 1066, 813 cm^{-1}. HRMS (ESI); *m/z* 357.0331 ([M + Na]); exact mass calculated for $C_{13}H_{19}O_2INa$, 357.0327.

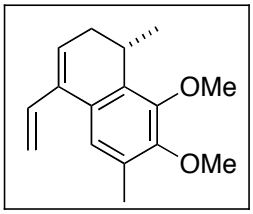


(*S*)-4-(2,3-Dimethoxy-4-methylphenyl)pentanenitrile (9): A 50 mL single-necked flask equipped with a magnetic stirring bar and reflux condenser fitted with a nitrogen inlet was flame-dried and purged with nitrogen. The flask was charged with the iodide from the previous step iodide (833 mg, 2.49 mmol) and NaCN (244 mg, 4.98 mmol, 2.0 equiv.) dissolved in anhydrous dimethylsulfoxide (DMSO, 10 mL). The reaction vessel was heated to 60 °C in an oil bath and allowed to stir for 2 h. The vessel was then cooled to room temperature and the whole was poured into water (30 mL) and extracted with ether (3 x 15 mL). The organic layers were combined and dried over $MgSO_4$, and concentrated to give the crude nitrile, which was purified via flash column chromatography (R_f = 0.23, hexanes-ethyl actetate, 9:1) to yield **9** as a colorless oil (578 mg, 2.48 mmol, >99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90-6.77 (AB quartet, 2H, ν_A = 6.89, ν_B = 6.78, J_{AB} = 7.6 Hz), 3.86 (s, 3H), 3.82 (s, 3H), 3.24 (sextet, 1H, J = 6.8 Hz), 2.24-2.20 (m, 5H containing 2.24 (s, 3H)), 1.98-1.87 (m, 2H), 1.26 (d, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 151.2, 136.2, 130.8, 126.1, 121.4, 120.1, 60.8, 60.1, 33.3, 32.0, 21.6, 15.9, 15.7. $[\alpha]_D^{20}$ +22.1 (*c* 0.70, $CHCl_3$), IR (neat) 2245, 1461, 1278, 1024 cm^{-1}. HRMS (ESI); *m/z* 256.1304 ([M + Na]); exact mass calculated for $C_{14}H_{19}NO_2Na$, 256.1313.

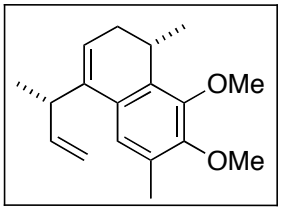


(*S*)-5,6-Dimethoxy-4,7-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (10): A 250 mL single-necked flask equipped with a magnetic stirring bar and reflux condenser fitted with a nitrogen inlet was purged with nitrogen. The flask was charged with the nitrile **9** (581 mg, 2.49 mmol) dissolved in methanol (65 mL). Sodium hydroxide (6.47 g, 161.8 mmol, 65 equiv.) and water (30 mL) were added in sequence and the vessel was heated to reflux in an oil bath. The reaction was allowed to reflux overnight (16 h) and then cooled to room temperature. Concentrated HCl (~14 mL) was added until the pH of the reaction mixture was ~1. The whole was poured into water (25 mL) and extracted with ethyl acetate (3 x 15 mL). The organic layers were combined and dried over $MgSO_4$, and concentrated to give the crude acid as a pale yellow oil. The crude oil was azeotroped with benzene (3 x 15 mL) and dried overnight with a vacuum pump. *Friedel-Crafts Acylation*: A 50 mL three-necked flask equipped with a magnetic stirring bar, stopper, thermometer, and nitrogen inlet was flame-dried and purged with nitrogen. The flask was charged with the crude acid dissolved in anhydrous DCM (10 mL). The vessel was then cooled to 0 °C in an ice/water bath and a 2.0 M solution of oxalyl chloride in DCM (1.4 mL, 2.74 mmol, 1.1 equiv.) was added dropwise. The vessel was allowed to warm to room temperature and stir for 2 h. The vessel was then re-cooled to 0 °C and $AlCl_3$ (498 mg, 3.74 mmol, 1.5 equiv.) was added in a single portion. The vessel was allowed to warm to room temperature and stir for 1 h. The vessel was re-cooled to 0 °C and the reaction was quenched by the slow addition of water (5 mL). The whole was poured into water (25 mL) and extracted with ether (3 x 15 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated to give the crude ketone which was purified via flash column chromatography (R_f = 0.21, hexanes-ethyl acetate, 9:1) to yield **10** as a pale yellow oil (563 mg, 2.40 mmol, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.41-3.38 (m, 1H), 2.77 (ddd, 1H, J = 5.4, 14.8, 18.0 Hz), 2.52 (ddd, 1H, J = 2.4, 4.4, 18.0 Hz), 2.28-2.19 (m, 4H containing 2.25 (s, 3H)), 2.00-1.94 (m, 1H), 1.32 (d, 3H, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 156.3, 149.8, 142.0, 130.8, 127.8, 125.0, 60.7, 60.0, 33.4, 29.4, 26.9,

19.8, 16.0. $[\alpha]_D^{20}$ -23.6 (*c* 3.10, $CHCl_3$). IR (neat) 1684, 1599, 1411, 1220, 1029 cm^{-1}. HRMS (ESI); *m/z* 257.1156 ([M + Na]); exact mass calculated for $C_{14}H_{18}O_3Na$, 257.1154.

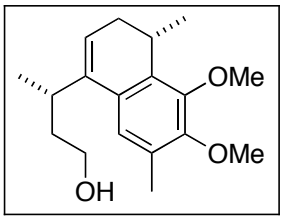


(*S*)-7,8-Dimethoxy-1,6-dimethyl-4-vinyl-1,2-dihydronaphthalene (11): A 100 mL three-necked flask equipped with a magnetic stirring bar, stopper, addition funnel, and nitrogen inlet was flame-dried and purged with nitrogen. The flask was charged with KHMDS (503 mg, 2.52 mmol, 1.05 equiv.) dissolved in anhydrous THF (10 mL) and a solution of **10** (563 mg, 2.40 mmol) in anhydrous THF (10 mL) was added dropwise via addition funnel. The reaction was allowed to stir at room temperature for 1 h, followed by the addition of *N*-phenylbis(trifluoromethanesulfonimide) (900 mg, 2.52 mmol, 1.05 equiv.). The reaction was allowed to stir at room temperature for 1.5 h, then LiCl (204 mg, 4.81 mmol, 2.0 equiv.), triphenylarsine (147 mg, 0.48 mmol, 0.20 equiv.), $Pd_2dba_3{\cdot}CHCl_3$ (124 mg, 0.12 mmol, 0.05 equiv.), and tri-*n*-butyl(vinyl)tin (0.74 mL, 2.52 mmol, 1.05 equiv.) were added in sequence and the vessel was allowed to stir at room temperature overnight (16 h). A solution of saturated aqueous KF (20 mL) was added and the reaction was allowed to stir for 2 h. The whole was poured into water (25 mL) and extracted with ether (3 x 15 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated to give the crude diene which was purified via flash column chromatography (R_f = 0.36, hexanes-ethyl acetate, 19:1) to yield **11** as a colorless oil (505 mg, 2.07 mmol, 86%). ^1H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.62 (dd, 1H, *J* = 11.2, 16.8 Hz), 5.99-5.97 (m, 1H), 5.50 (dd, 1H, *J* = 1.4, 17.6 Hz), 5.17 (dd, 1H, *J* = 1.4, 10.8 Hz), 3.90 (s, 3H), 3.84 (s, 3H), 3.30 (quintet, 1H, *J* = 7.2 Hz), 2.49 (dd, 1H, *J* = 7.2, 16.8 Hz), 2.25-2.20 (m, 4H containing 2.25 (s, 3H)), 1.10 (d, 3H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 149.8, 136.0, 135.6, 133.9, 129.4, 129.3, 123.1, 122.1, 115.2, 60.9, 60.1, 30.6, 25.6, 20.1, 16.0. $[\alpha]_D^{20}$ -51.4 (*c* 5.42, $CHCl_3$), IR (neat) 3082, 1250, 1040, 910, 820 cm^{-1}. HRMS (ESI); *m/z* 267.1356 ([M + Na]); exact mass calculated for $C_{16}H_{20}O_2Na$, 267.1361.

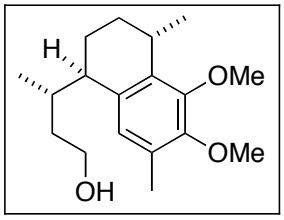


(*S*)-4-((*S*)-But-3-en-2-yl)-7,8-dimethoxy-1,6-dimethyl-1,2-dihyrdonaphthalene (12a): *Precatalyst preparation*: In a glovebox, NaBARF (43.5 mg, 0.049 mmol, 5.0 mol%), (*R*)-2,2'-binaphthoyl-(*S,S*)-di(1-phenylethyl)aminoylphosphine (**L2**, 26.5 mg, 0.049 mmol, 5.0 mol%), and $[(allyl)NiBr]_2$ (7.9 mg, 0.025 mmol, 2.5 mol%) were weighed into separate glass vials. The phosphoramidite ligand was dissolved in anhydrous DCM (1.0 mL) and transferred to the vial containing $[(allyl)NiBr]_2$, followed by 1.0 mL rinsing of the source vial. The resulting yellow solution of phosphoramidite ligand and $[(allyl)NiBr]_2$ was transferred to the vial containing NaBARF, followed by 1.0 mL rinsing of the source vial. The resulting orange-yellow solution was allowed to stand for 1.5 h. *Asymmetric hydrovinylation*: A 25 mL three-necked flask equipped with a rubber septum, flow-controlled nitrogen inlet, thermometer, and magnetic stirring bar was flame-dried and purged with nitrogen. The catalyst solution prepared above was transferred to the reaction vessel via cannula, followed by 1.0 mL rinsing of the source vial. The system was closed at the flow-controlled stopcock and cooled to 0 °C in an ice/water bath, creating a small vacuum. A strong flow of dry ethylene was introduced via needle through the septum to relieve the vacuum and then the atmosphere of the vessel was evacuated three times via syringe to remove any remaining

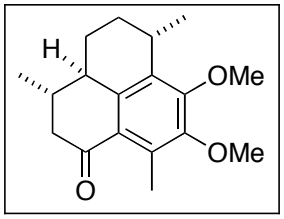
nitrogen. The flow of ethylene was adjusted to maintain a pressure of 1 atm by releasing excess gas through an oil bubbler. A solution of the diene (**10**, 200.0 mg, 0.82 mmol) in anhydrous DCM (2.0 mL), followed by 1.0 mL rinsing of the source vial was introduced via syringe as to not increase the reaction temperature above 0 °C. The reaction mixture was allowed to stir at 0 °C for 4 h. The ethylene needle was then removed and the reaction was exposed to air and water (5 mL) was added to quench the reaction. The resulting mixture was poured into water (10 mL) and extracted with ether (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated to give the crude hydrovinylation product, which was then eluted through a plug of silica with pentane-ether (19:1) to remove any nickel salts. The eluent was concentrated to yield (**12a + 12b**) as a colorless oil (223 mg, 0.82 mmol, 92% (8% isomerization based on GC), 92% de). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 5.93 (ddd, 1H, J = 6.0, 10.4, 16.8 Hz), 5.73 (d, 1H, J = 6.4 Hz), 5.12-5.01 (m, 2H), 3.92 (s, 3H), 3.86 (s, 3H), 3.52 (quintet, 1H, J = 6.4 Hz), 3.30 (quintet, 1H, J = 6.8 Hz), 2.48 (dd, 1H, $J_{1,2}$ = 5.2, 16.8 Hz), 2.28 (s, 3H), 2.24-2.18 (m, 1H), 1.35 (d, 3H, J = 6.8 Hz), 1.10 (d, 3H, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 149.6, 143.2, 138.3, 133.8, 129.8, 128.9, 121.4, 120.8, 113.4, 60.9, 60.1, 38.0, 30.4, 25.3, 20.0, 19.2, 16.2. $[\alpha]_D^{20}$ -36.0 (*c* 0.86, $CHCl_3$). HRMS (ESI); *m/z* 295.1665 ([M + Na]); exact mass calculated for $C_{18}H_{24}O_2Na$, 295.1669.



(*S*)-3-((*S*)-5,6-Dimethoxy-4,7-dimethyl-3,4-dihydronaphthalen-1-yl)butan-1-ol (13): A 50 mL three-necked flask equipped with magnetic stirring bar, stopper, thermometer, and nitrogen inlet was flame-dried and purged with nitrogen. The flask was charged with the olefin **12a** (231.8 mg, 0.85 mmol) dissolved in anhydrous THF (20 mL). 9-BBN dimer (519.1 mg, 2.13 mmol, 2.5 equiv.) was added in small portions and the reaction mixture was allowed to stir at room temperature for 2 h. The vessel was cooled to 0 °C in an ice/water bath and 4 M NaOH (2.0 mL) was added dropwise, maintaining the internal temperature of the vessel below 5 °C. A solution of ~30% H_2O_2 (1.5 mL) was then added dropwise, maintaining the internal temperature of the vessel below 5 °C. The vessel was allowed to warm to room temperature and stir for an additional 0.5 h. The vessel was then diluted with ether (10 mL) and neutralized with 10% H_2SO_4 until pH ~7 was achieved. The whole was poured into water (15 mL) and extracted with ether (3 x 10 mL). The organic layers were combined and dried over $MgSO_4$, and concentrated to give crude **13**, which was purified via flash column chromatography (R_f = 0.42, hexanes-ethyl acetate, 2:1) to yield the product as a colorless oil (245.3 mg, 0.85mmol, >99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 5.69 (d, 1H, J = 6.4 Hz), 3.88 (s, 3H), 3.83 (s, 3H), 3.72-3.63 (m, 2H), 3.27 (quintet, 1H, J = 6.8 Hz), 2.95 (sextet, 1H, J = 6.8 Hz), 2.42 (dd, 1H, J = 6.8, 16.8 Hz), 2.25 (s, 3H), 2.17 (dd, 1H, J = 6.8, 10.0 Hz), 1.87 (sextet, 1H, J = 6.8 Hz), 1.66 (sextet, 1H, J = 6.8 Hz), 1.22 (d, 3H, J = 6.8 Hz), 1.05 (d, 3H, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 149.7, 139.9, 133.7, 130.0, 129.0, 120.5, 119.3, 61.4, 60.8, 60.0, 39.8, 30.3, 25.2, 22.8, 20.4, 19.9, 16.2. $[\alpha]_D^{20}$ -30.4 (*c* 0.63, $CHCl_3$). HRMS (ESI); *m/z* 313.1780 ([M + Na]); exact mass calculated for $C_{18}H_{26}O_3Na$, 313.1780.

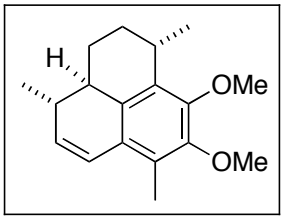


(*S*)-3-((1*R*,4*S*)-5,6-Dimethoxy-4,7-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)butan-1-ol (14a): An oven dried 50 mL three necked flask was equipped with a magnetic stirring bar, septum, stopper, and an oven dried cold finger with an attached balloon. The flask was charged with the alcohol **13** (187.8 mg, 0.65 mmol) dissolved in a minimal amount of THF (~ 1 mL). The vessel was cooled to -78 °C in a dry ice/acetone bath and ammonia (passed through a drying tube of barium oxide) was condensed into the vessel (*ca*. 20 mL). Lithium metal (40% dispersion in mineral oil) (168 mg, 9.69 mmol, 15 equiv.) was added, resulting in the formation of a blue solution, which was stirred for an additional 15 min. at -78 °C. The reaction was slowly quenched with methanol (10 mL) resulting in a cloudy white mixture. Water (10 mL) was slowly added to the reaction mixture and the whole was poured into a separatory funnel and extracted with ether (3 x 10 mL). The organic layers were combined and dried over $MgSO_4$, and concentrated to give the crude product (**14a** + **14b**), which was purified via flash column chromatography (R_f = 0.24, hexanes-ethyl acetate, 3:1) to get the product as a colorless oil (188.3 mg, 0.64 mmol, >99%). *Note*: ammonia:THF ratio is critical to diastereoselectivity of the reduction. A high ammonia:THF ratio and large excess of lithium gives the best selectivities (>95% *de* determined by GC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (s, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 3.78-3.67 (m, 2H), 3.16 (quintet, 1H, *J* = 6.0 Hz), 2.62 (q, 1H, *J* = 6.0 Hz), 2.22 (s, 3H), 2.11 (quintet, 1H, *J* = 6.5 Hz), 1.89-1.19 (m, 2H), 1.76-1.65 (m, 2H), 1.64-1.48 (m, 3H), 1.17 (d, 3H, *J* = 7.0 Hz), 0.76 (d, 3H, *J* = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 149.2, 135.2, 135.1, 128.9, 125.8, 61.8, 60.6, 60.0, 40.4, 38.8, 35.6, 28.1, 27.5, 22.5, 18.9, 16.5, 16.0. $[\alpha]_D^{20}$ +2.51 (*c* 2.11, $CHCl_3$). IR (neat) 3360, 1614, 1236, 1014 cm^{-1}. HRMS (ESI); *m/z* 315.1910 ([M + Na]); exact mass calculated for $C_{18}H_{28}O_3Na$, 315.1936.

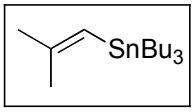


(3*S*,3a*R*,6*S*)-7,8-Dimethoxy-3,6,9-trimethyl-2,3,3a,4,5,6-hexahydro-1*H*-phenalen-1-one (16): A 25 mL three-necked flask equipped with a magnetic stirring bar, septum, thermometer, and nitrogen inlet was flame-dried and purged with nitrogen. The flask was charged with anhydrous DCM (2.0 mL) and dimethyl sulfoxide (0.03 mL) and cooled to -78 °C via dry ice/acetone bath. A 2.0 M solution of oxalyl chloride (0.13 mL) was added and allowed to stir for 15 min. A solution of alcohol **14** (70.5 mg, 0.21 mmol) in anhydrous DCM (1.0 mL) was added and allowed to stir for 30 min. Triethylamine (0.13 mL) was added and allowed to stir for 15 min. The vessel was allowed to warm to room temperature and the whole was poured into water (10 mL) and extracted with ether (3 x 10 mL). The organic layers were combined and dried over $MgSO_4$, and concentrated to give the crude aldehyde, which was used for the next reaction without further purification. Flash column chromatography of the crude aldehyde (**15**) led to the formation of a cyclized product. The crude aldehyde was dissolved in THF (1.0 mL) and *t*-butyl alcohol (1.0 mL) in a 5 dram vial. A solution of 1.0 M tetramethylethylene (1.0 mL) was added to the vial followed by a solution of $NaClO_2$ (65.4 mg, 0.72 mmol, 3.0 equiv.) and NaH_2PO_4 (86.7 mg, 0.72 mmol, 3.0 equiv.) dissolved in deionized water (1.0 mL). The reaction mixture was allowed to stir for 1 h then the whole was poured into water (10 mL) and extracted with ether (3 x 10 mL). The organic layers were combined and dried over $MgSO_4$, concentrated, and azeotroped with benzene to ensure all water has been removed. A 25 mL three-necked flask equipped with a magnetic stirring bar,

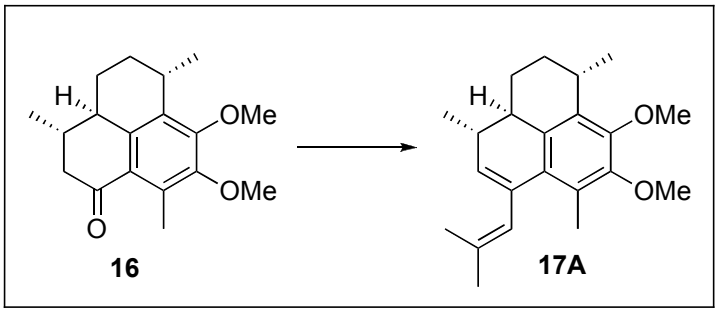
septum, thermometer, and nitrogen inlet was flame-dried and purged with nitrogen. The flask was charged with crude acid dissolved in anhydrous DCM (3.0 mL) and cooled to 0 °C via ice/water bath. A 2.0 M solution of oxalyl chloride in DCM (0.14 mL, 0.29 mmol, 1.2 equiv.) was added and the vessel was allowed to warm to room temperature and stir for 1 h. The vessel was re-cooled to 0 °C and $AlCl_3$ (48.2 mg, 0.36 mmol, 1.5 equiv.) was added. and subsequently was allowed to warm to room temperature and stir for 30 min. The vessel was re-cooled to 0 °C and the reaction was quenched by the slow addition of water (5 mL). The whole was poured into water and extracted with ether (3 x 10 mL). The organic layers were combined and dried over $MgSO_4$, and concentrated to give crude ketone **16** which was purified via flash column chromatography (R_f = 0.29, hexanes-ethyl acetate, 9:1) to get a mixture of diastereomers (depending on the selectivity of the liquid ammonia reduction) as a colorless oily solid. Recrystallization from methanol afforded colorless needles as a single diastereomer of **16** (28.9 mg, 0.10 mmol, 47 % from the alcohol **14**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 3.75 (s, 3H), 3.23 (sextet, 1H, *J* = 7.2 Hz), 2.62 (dd, 1H, *J* = 3.8, 16.4 Hz), 2.52 (s, 3H), 2.36-2.26 (m, 2H), 2.18-2.12 (m, 2H), 1.80-1.77 (m, 1H), 1.42-1.37 (m, 1H), 1.23 (d, 3H, *J* = 6.8 Hz), 1.13-1.09 (m, 4H containing 1.12 (d, 3H, 6.4 Hz)). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 155.3, 150.3, 142.6, 133.7, 133.2, 127.7, 60.6, 60.2, 49.3, 43.8, 35.6, 31.3, 28.6, 27.2, 23.7, 19.6, 14.0. mp = 101.5-103.5 °C, $[\alpha]_D^{20}$ +59.4 (*c* 1.33, $CHCl_3$). IR (neat) 1673, 1448, 1254, 1071 cm^{-1}. HRMS (ESI); *m/z* 311.1624 ([M + Na]); exact mass calculated for $C_{18}H_{24}O_3Na$, 311.1623.



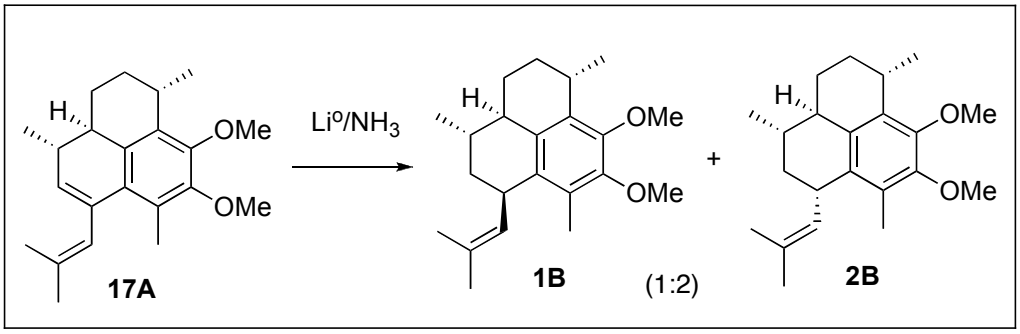
(1*S*,3a*R*,4*S*)-8,9-Dimethoxy-1,4,7-trimethyl-2,3,3a,4-tetrahydro-1*H*-phenalene (17): Ketone **16** (16 mg, 0.055 mmol) was dissolved in ethanol (1.0 mL) in a 5 dram vial. $NaBH_4$ (6 mg, 0.165 mmol, 3.0 equiv.) was added to the reaction mixture and was allowed to stir at room temperature for 3.5 h. The whole was poured into water and extracted with ether (3 x 10 mL). The organic layers were combined and dried over $MgSO_4$, and concentrated to give the crude alcohol which was used in the subsequent reaction without further purification. The crude alcohol was dissolved in anhydrous DCM (1.0 mL) in an oven-dried 5 dram vial. Camphorsulfonic acid (3.0 mg, 0.011 mmol, 0.20 equiv.) was added and the reaction was allowed to stir at room temperature for 45 min. The whole was poured into water and extracted with ether (3 x 10 mL). The organic layers were dried over $MgSO_4$, and concentrated to give crude vinylarene **17** which was purified via flash column chromatography (R_f = 0.36, hexanes-ethyl acetate, 19:1) to get the pure product as a colorless oil (15 mg, 0.055 mmol, >99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (dd, 1H, *J* = 2.8, 9.6 Hz), 5.75 (dd, 1H, *J* = 2.0, 9.6 Hz), 3.86 (s, 3H), 3.79 (s, 3H), 3.11 (sextet, 1H, *J* = 6.8 Hz), 2.31-2.23 (m, 4H containing 2.23 (s, 3H)), 2.14-2.02 (m, 3H), 1.39-1.26 (m, 5H containing 1.27 (d, 3H, *J* = 6.8 Hz)), 1.19 (d, 3H, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 149.7, 134.6, 133.5, 132.3, 128.3, 125.2, 123.9, 60.4, 60.3, 41.2, 34.7, 31.8, 29.4, 26.5, 22.6, 19.8, 11.4. $[\alpha]_D^{20}$ +25.9 (*c* 0.92, $CHCl_3$). HRMS (ESI); *m/z* 295.1692 ([M + Na]); exact mass calculated for $C_{18}H_{24}O_2Na$, 295.1674.



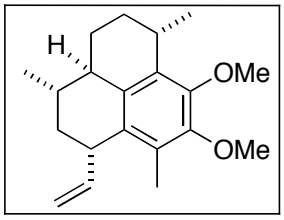
2-Methyl-1-tri-*n*-butylstannylpropene: A 3-necked 25 mL round bottomed flask equipped with magnetic stir bar, gas inlet, thermometer adapter and rubber septum was flame-dried, purged with nitrogen, and charged with dry tetrahydrofuran (6.5 mL) which was cooled internally to -78 °C. *t*-BuLi (2.3 mL, 3.9 mmol, 1.7 M in pentane) was added *via* syringe, followed by isocrotyl bromide (0.20 mL, 1.95 mmol) over a temperature range of -78 °C-55 °C, then was allowed to recool to -78 °C. Tributyltin iodide (0.56 mL, 1.95 mmol) was added neat *via* syringe, keeping the temperature below -65 °C and forming a yellow milky color. The cooling bath was removed and the reaction warmed to rt, stirring for 23 h. The mixture was poured into water, washed with saturated KF, and extracted with ether. The organic phases were combined, dried ($MgSO_4$) and concentrated to an oil of the vinylstannane, which was of sufficient purity to not warrant any further isolation techniques: 679.8 mg, 1.97 mmol, *ca*. 100%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (s, 1H), 1.90 (d, 3H, *J* 1.2 Hz), 1.77 (s, 3H), 1.51-1.47 (m, 6H), 1.35-1.27 (m, 6H), 0.94-0.88 (m, 15H).



(1*S*,3a*R*,4*S*)-8,9-Dimethoxy-1,4,7-trimethyl-6-(2-methylprop-1-enyl)-2,3,3a,4-tetrahydro-1*H*-phenalene (17A). A three-necked 25 mL round bottomed flask equipped with magnetic stir bar, gas inlet, rubber septum, and glass stopper was flame-dried, purged with nitrogen, and charged with solid KHMDS (19.3 mg, 0.097 mmol). Dry tetrahydrofuran (1.0 mL) was added *via* syringe, and the clear colorless solution was stirred at 25 °C while being treated dropwise with a solution of *enantiopure* ketone **16** (19.9 mg, 0.069 mmol) in THF (1.0 mL plus 1.0 mL rinse), forming a red clear solution that was stirred for one hour. Solid *N*-phenylbis(triflouromethanesulfonimide) (25.9 mg, 0.073 mmol) was added under a stream of nitrogen in a single portion, causing the solution to gradually become a clear pale yellow. The reaction was stirred for one hour. Lithium chloride (5.8 mg, 0.138 mmol), triphenylarsine (2.1 mg, 10 mol%), and $Pd_2dba_3.CHCl_3$ (3.6 mg, 5 mol%) were added in sequence, followed by a solution of the vinylstannane from the previous experiment (39 mg, 0.113 mmol) in THF (0.5 mL plus 0.5 mL rinse). The reaction was monitored by GC (methyl silicone, 170 °C for one minute, then 5 °C per minute to 250 °C; t_R triflate = 16.125, t_R 1,3-diene = 17.906) and judged complete after 6.5 h at rt. The whole was treated with saturated NaF and stirred for 5 minutes, then extracted with ether. The organic extracts were combined, dried ($MgSO_4$) and concentrated *in vacuo* to a brown oil, which was purified by prep TLC (97.5:2.5 petroleum ether:diethyl ether) to afford clean 1,3-diene (**17A**, 16.6 mg, 0.051 mmol, 74% from ketone **16**). R_f 0.31 (2.5:97.5 ether:petroleum ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (s, 1H), 5.63 (s, 1H), 3.86 (s, 3H), 3.77 (s, 3H), 3.09-3.05 (m, 1H), 2.19 (s, 3H), 2.14-2.04 (m, 3H), 1.91-1.87 (m, 1H), 1.81 (s, 3H), 1.71 (s, 3H), 1.32-1.23 (m, 1H), 1.28 (d, 3H, *J* 7 Hz), 1.17-1.09 (m, 1H), 1.14 (d, 3H, *J* 7 Hz). ^{13}C (125 MHz, $CDCl_3$) d 150.59, 149.88, 135.83, 135.43, 135.11, 132.62, 131.89, 131.37, 127.43, 126.68, 60.03, 59.82, 43.06, 34.32, 32.17, 29.68, 26.33, 26.01, 23.20, 19.53, 18.80, 14.06. $[\alpha]_D$ (*c* 1.107, + 222.8, $CHCl_3$). IR (neat) 1560, 1458, 1260, 1072 cm^{-1}. UV ($CHCl_3$) λ_{max} 274 nm (ε 1543).

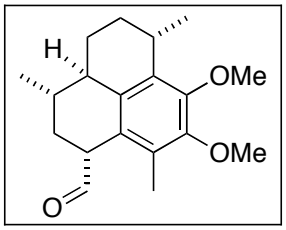


(1*S*,3*S*,3a*R*,6*S*)-7,8-Dimethoxy-3,6,9-trimethyl-1-(2-methylprop-1-enyl)-2,3,3a,4,5,6-hexahydro-1*H*-phenalene (1B+2B). An oven-dried three-necked 25 mL round bottomed flask was equipped (under air) with a dry magnetic stir bar, oven-dried cold finger with gas inlet, a glass stopper, and a drying tube packed with barium oxide. A solution of diene **17A** (16.1 mg, 0.049 mmol) in dry THF (1.0 mL plus 1.0 mL rinse) was added *via* pipette, and ammonia (*ca*. 10 mL, passed through a drying tube packed with barium oxide) was condensed into the vessel. Lithium metal (40% dispersion in mineral oil, *ca*. 10-fold excess) was added, forming a blue solution which was stirred for 15 minutes, then was slowly quenched with methanol until a white cloudy mixture formed. The cooling bath was removed and the mixture poured into a large beaker containing dry ether cooled by an ice bath. Excess methanol was added, and the mixture was swirled with addition of a few drops of water (*CAUTION*!). More water was added until all the excess lithium had been killed, leaving behind a clear colorless solution, which was poured into a separatory funnel and extracted from water with ether. The organics were combined, dried ($MgSO_4$) and concentrated *in vacuo* to a white oily mix, which was filtered through a column of silica gel eluting with isocratic hexane to remove the mineral oil, then with 95:5 hexane:ether to afford a mixture of **1B** and **2B**. Purification by prep TLC (97.5:2.5 petroleum ether:diethyl ether) and analysis by ^{1}H and ^{13}C NMR revealed this to be 1:2 mixture of *R*:*S* epimers at the newly created stereogenic center (12.7 mg, 80%). See attached spectra. ^{1}H and ^{13}C of compound **1B**[3] and close analogs of **2B**[4] have been reported in the literature. The compound **2B** was also confirmed by comparison of the spectra with those a sample prepared according to the scheme shown in Scheme 3.

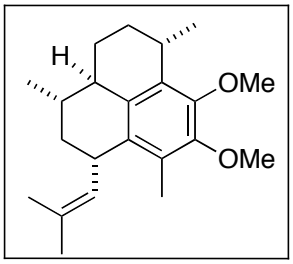


(1*S*,3*S*,3a*R*,6*S*)-7,8-Dimethoxy-3,6,9-trimethyl-1-vinyl-2,3,3a,4,5,6-hexahydro-1*H*-phenalene (18): *Precatalyst preparation*: In a glovebox, NaBARF (1.3 mg, 0.002 mmol, 2.0 mol%), (*R*)-2,2'-binaphthoyl-(*S,S*)-di(1-phenylethyl)aminoylphosphine (0.8 mg, 0.002 mmol, 2.0 mol%), and $[(allyl)NiBr]_2$ (0.3 mg, 0.001 mmol, 1.0 mol%) were weighed into separate glass vials. The phosphoramidite ligand was dissolved in anhydrous DCM (0.5 mL) and transferred to the vial containing $[(allyl)NiBr]_2$, followed by 0.5 mL rinsing of the source vial. The resulting yellow solution of phosphoramidite ligand and $[(allyl)NiBr]_2$ was transferred to the vial containing NaBARF, followed by 0.5 mL rinsing of the source vial. The resulting orange-yellow solution was allowed to stand for 1.5 h. *Asymmetric hydrovinylation*: A 25 mL three-necked flask equipped with a rubber septum, flow-controlled nitrogen inlet, thermometer, and magnetic stirring bar was flame-dried and purged with nitrogen. The catalyst solution prepared above was

transferred to the reaction vessel via cannula, followed by 0.5 mL rinsing of the source vial. The system was closed at the flow-controlled stopcock and a strong flow of dry ethylene was introduced via needle through the septum and then the atmosphere of the vessel was evacuated three times via syringe to remove any remaining nitrogen. The flow of ethylene was adjusted to maintain a pressure of 1 atm by releasing excess gas through an oil bubbler. A solution of the olefin (**17**, 20.5 mg, 0.075 mmol) in anhydrous DCM (0.5 mL), followed by 0.5 mL rinsing of the source vial was introduced via syringe. The reaction mixture was allowed to stir at room temperature for 2.5 h. The ethylene needle was then removed and the reaction was exposed to air and water (2 mL) was added to quench the reaction. The resulting mixture was poured into water (10 mL) and extracted with ether (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated to give the crude hydrovinylation product, which was then eluted through a plug of silica with pentane-ether (19:1) to remove any nickel salts. The eluent was concentrated to yield (**18**) as a colorless oil (22.5 mg, 0.075 mmol, >99%, >99% de). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (ddd, 1H, *J* = 7.5, 10.0, 17.5 Hz), 4.95-4.91 (m, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 3.65 (q, 1H, *J* = 8.0 Hz), 3.20 (sextet, 1H, *J* = 7.5 Hz), 2.16 (s, 3H), 2.09-2.02 (m, 4H), 1.38-1.34 (m, 2H), 1.29-1.24 (m, 5H containing 1.26 (d, 3H, *J* = 6.5 Hz)), 1.06 (d, 3H, *J* = 6.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 144.0 (2 x C), 135.6, 133.4, 132.7, 128.5, 112.9, 60.4, 60.1, 43.2, 42.0, 40.5, 34.4, 31.2, 28.7, 27.0, 24.0, 20.5, 12.8. $[\alpha]_D^{20}$ +29.3 (*c* 0.75, $CHCl_3$). HRMS (ESI); *m/z* 323.1977 ([M + Na]); exact mass calculated for $C_{20}H_{28}O_2Na$, 323.1987.



(1*S*,3*S*,3a*R*,6*S*)-7,8-Dimethoxy-3,6,9-trimethyl-1-formyl-2,3,3a,4,5,6-hexahydro-1*H*-phenalene: The olefin **18** (22.2 mg, 0.074 mmol) was dissolved in anhydrous DCM (2.0 mL) in a 5 dram vial. The vessel was cooled to -78 °C via acetone/dry ice bath and ozone was introduced via bubbling through a glass pipette until a persistent blue color was observed throughout the solution. The flow of ozone was stopped and nitrogen was bubbled through the solution until the blue color was no longer observed. Dimethyl sulfide (0.1 mL, 1.48 mmol, 20.0 equiv.) was added and the reaction mixture was allowed to warm to room temperature. The whole was poured into water (10 mL) and extracted with ether (3 x 10 mL). The organic layers were combined and dried over $MgSO_4$, and concentrated to give the crude aldehyde which was eluted through a small plug of neutral alumina with pentane-ether (19:1) to yield the aldehyde (17.1 mg, 0.565 mmol, 76%). *Note*: Elution on a silica gel column resulted in significant loss of product most likely due to what appears to be products from aldehyde enolization. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (d, 1H, *J* = 3.6 Hz), 3.86 (s, 3H), 3.86-3.76 (m, 5H containing 3.79 (s, 3H)), 3.22 (sextet, 1H, *J* = 7.2 Hz), 2.16-2.04 (m, 6H containing 2.10 (s, 3H)), 2.02-1.94 (m, 2H), 1.60-1.52 (m, 2H), 1.25 (d, 3H, *J* = 6.8 Hz), 1.11 (d, 3H, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 150.8, 149.8, 136.3, 134.4, 128.8, 125.3, 60.4, 60.2, 51.4, 43.3, 33.4, 32.0, 31.0, 28.5, 27.0, 24.0, 20.2, 12.8. $[\alpha]_D^{20}$ +5.0 (*c* 0.25, $CHCl_3$). HRMS (ESI); *m/z* 325.1761 ([M + Na]); exact mass calculated for $C_{19}H_{26}O_3Na$, 325.1774.



(1*S*,3*S*,3a*R*,6*S*)-7,8-Dimethoxy-3,6,9-trimethyl-1-(2-methylprop-1-enyl)-2,3,3a,4,5,6-hexahydro-1*H*-phenalene (2B): A 25 mL three-necked flask equipped with a magnetic stirring bar, septum, stopper, and nitrogen inlet was flame-dried and purged with nitrogen. The flask was charged with KHMDS (8.8 mg, 0.044 mmol, 1.1 equiv.) dissolved in anhydrous THF (1.0 mL). Isopropyl triphenylphosphonium bromide

(23.3 mg, 0.060 mmol, 1.5 equiv.) was added and the reaction mixture was allowed to stir at room temperature for 2 h. The reaction mixture was transferred dropwise to a vessel containing the aldehyde from the previous step (12.2 mg, 0.040 mmol) dissolved in anhydrous THF (1.0 mL) at 0 °C via cannula. The reaction mixture was allowed to stir at 0 °C for 30 min., then allowed to warm to room temperature and to stir for an additional 2 h. The reaction mixture was poured into water (10 mL) and extracted with ether (3 x 10 mL). The organic layers were combined and dried over $MgSO_4$, and concentrated to give the crude olefin which was purified via flash column chromatography (R_f = 0.32, hexanes-ethyl acetate, 19:1) to give **2B** (10.0 mg, 0.030 mmol, 75%, dr [**2B:1B**] 87:13) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (d, 1H, *J* = 9.2 Hz), 3.84 (s, 3H), 3.77 (s, 3H), 3.69 (q, 1H, *J* = 9.2 Hz), 3.22 (sextet, 1H, *J* = 7.2 Hz), 2.12-2.03 (m, 6H containing 2.07 (s, 3H)), 1.98-1.93 (m, 1H), 1.73 (s, 3H), 1.68 (s, 3H), 1.40-1.31 (m, 2H), 1.25-1.19 (m, 5H containing 1.24 (d, 3H, *J* = 7.2 Hz)), 1.03 (d, 3H, *J* = 6.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 149.3, 135.5, 134.2, 133.3, 131.1, 128.8, 128.6, 60.4, 60.1, 44.2, 40.3, 37.5, 34.3, 31.5, 28.5, 27.8, 25.6, 24.6, 20.3, 17.8, 12.3. $[\alpha]_D^{20}$ +29.0 (*c* 0.55, $CHCl_3$). HRMS (ESI); *m/z* 351.2302 ([M + Na]); exact mass calculated for $C_{22}H_{32}O_2Na$, 351.2295. The structure was confirmed by comparison of ^{1}H and ^{13}C NMR spectra and chromatographic behavior with those of authentic sample prepared earlier via the Stille route.

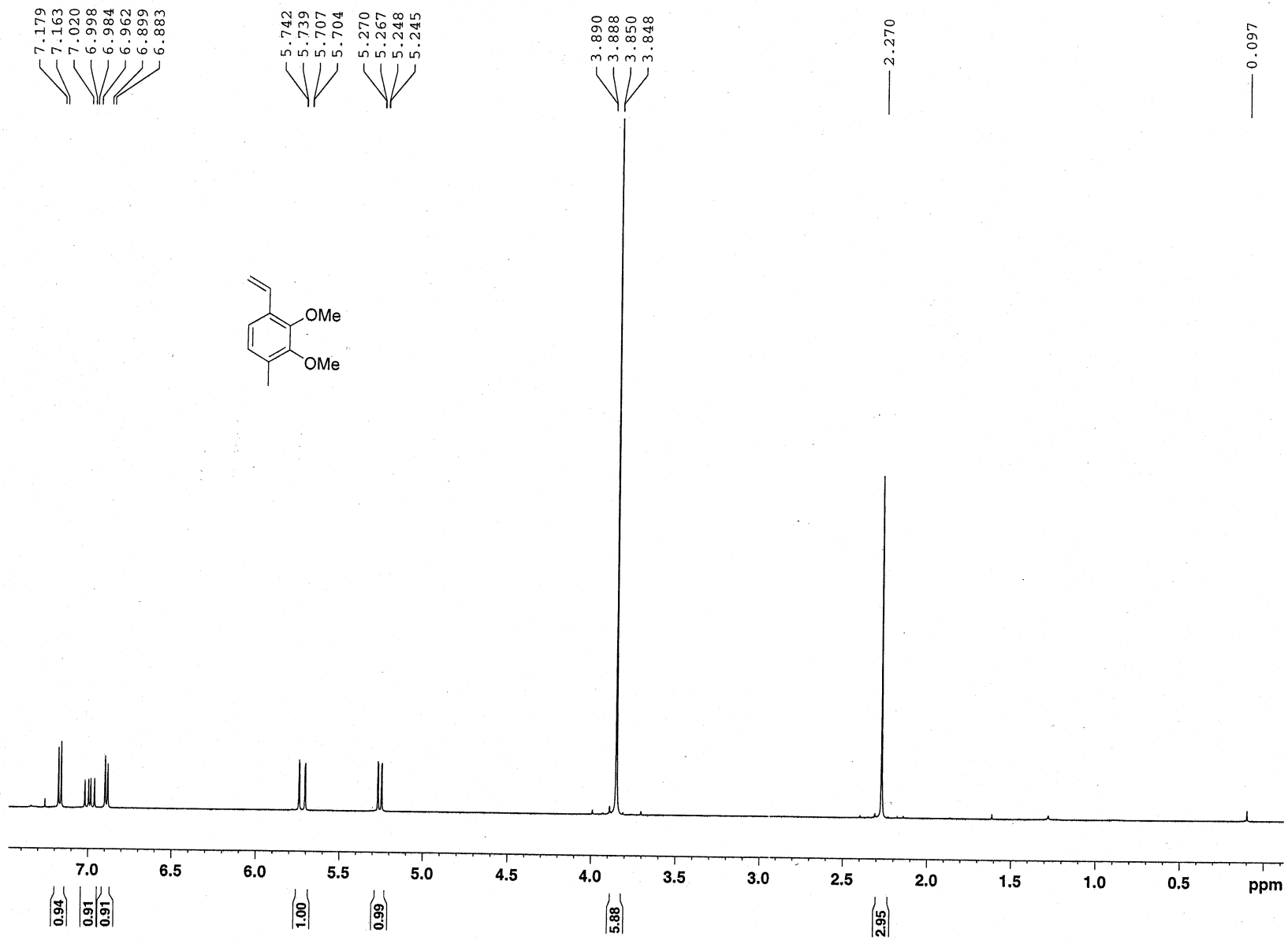
References

1. (a) Smith, C. R.; Mans, D.; RajanBabu, T. V. *Org. Synth.* **2008**, *85*, 238. (b) Arnold, L. A.; Imbos, R.; Mandoli, A.; de Vries, A. H. M.; Naasz, R.; Feringa, B. L. *Tetrahedron*, **2000**, *56*, 2865.

2. (a) Smith, C. R.; Zhang, A.; Mans, D.; RajanBabu, T. V. *Org. Synth.* **2008**, *85*, 248-266. (b) Kobayashi, H.; Sonoda, A.; Iwamoto, H.; Yoshimura, M. *Chem. Lett.* **1981**, *10*, 579. (c) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics*, **1992**, *11*, 3920-3922.

3. Majdalani, A.; Schmalz, H.-G. *Synlett*, **1992**, 1303.

4. S. E. Lazerwith, T. W. Johnson, E. J. Corey, *Org. Lett.* **2000**, *2*, 2389.



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PROCNO	1

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FIDRES	0.157632 Hz
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RG	80.6
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DE	6.00 usec
TE	298.2 K
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MCWRK	0.01500000 sec

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F2 - Processing parameters

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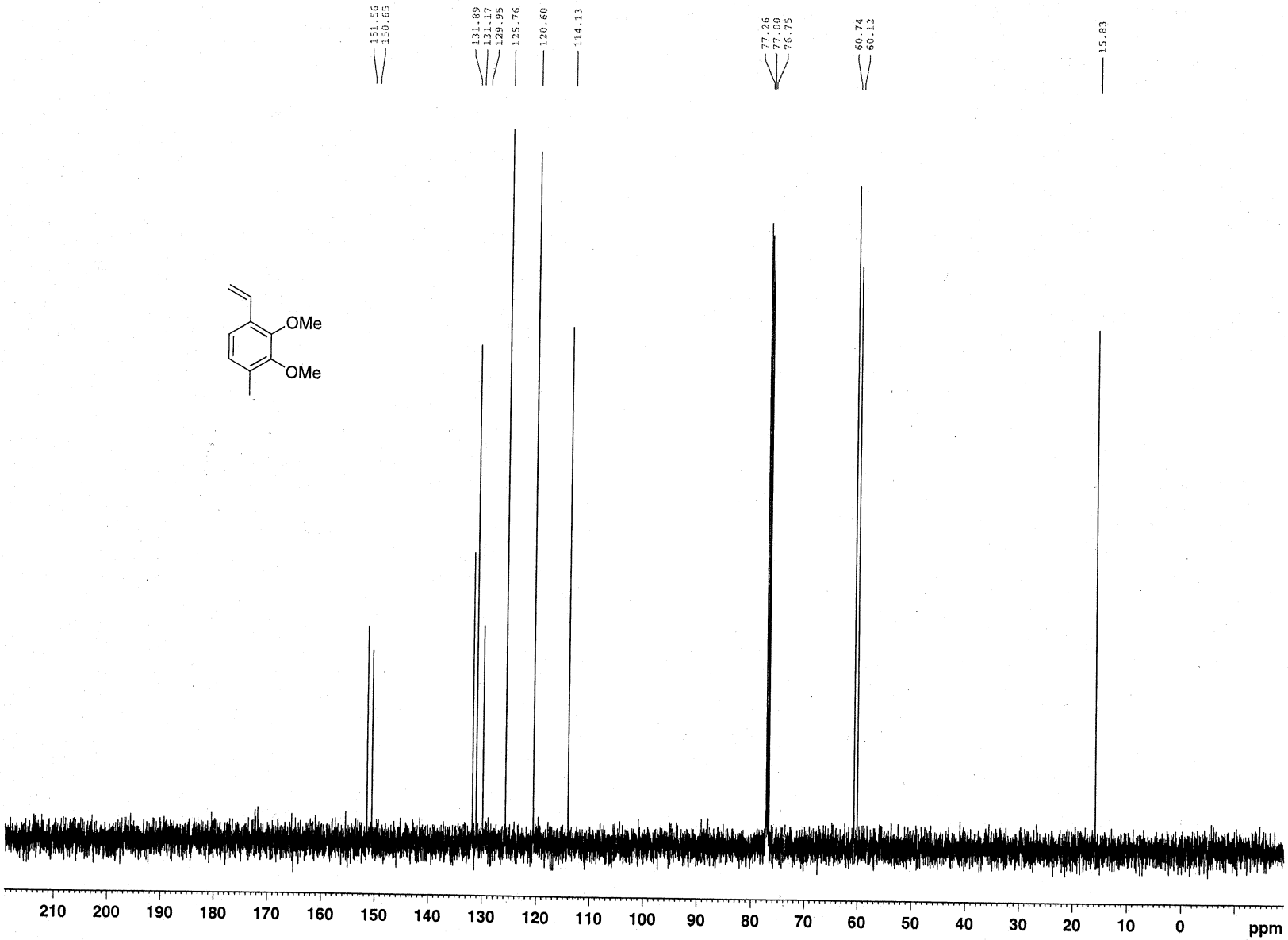

BRUKER

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PROCNO                   1

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TE                  298.2 K
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d11             0.03000000 sec
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MCREST          0.00000000 sec
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PL1                  3.00 dB
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======== CHANNEL f2 ========
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PCPD2              100.00 usec
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PL12                18.80 dB
PL13                22.50 dB
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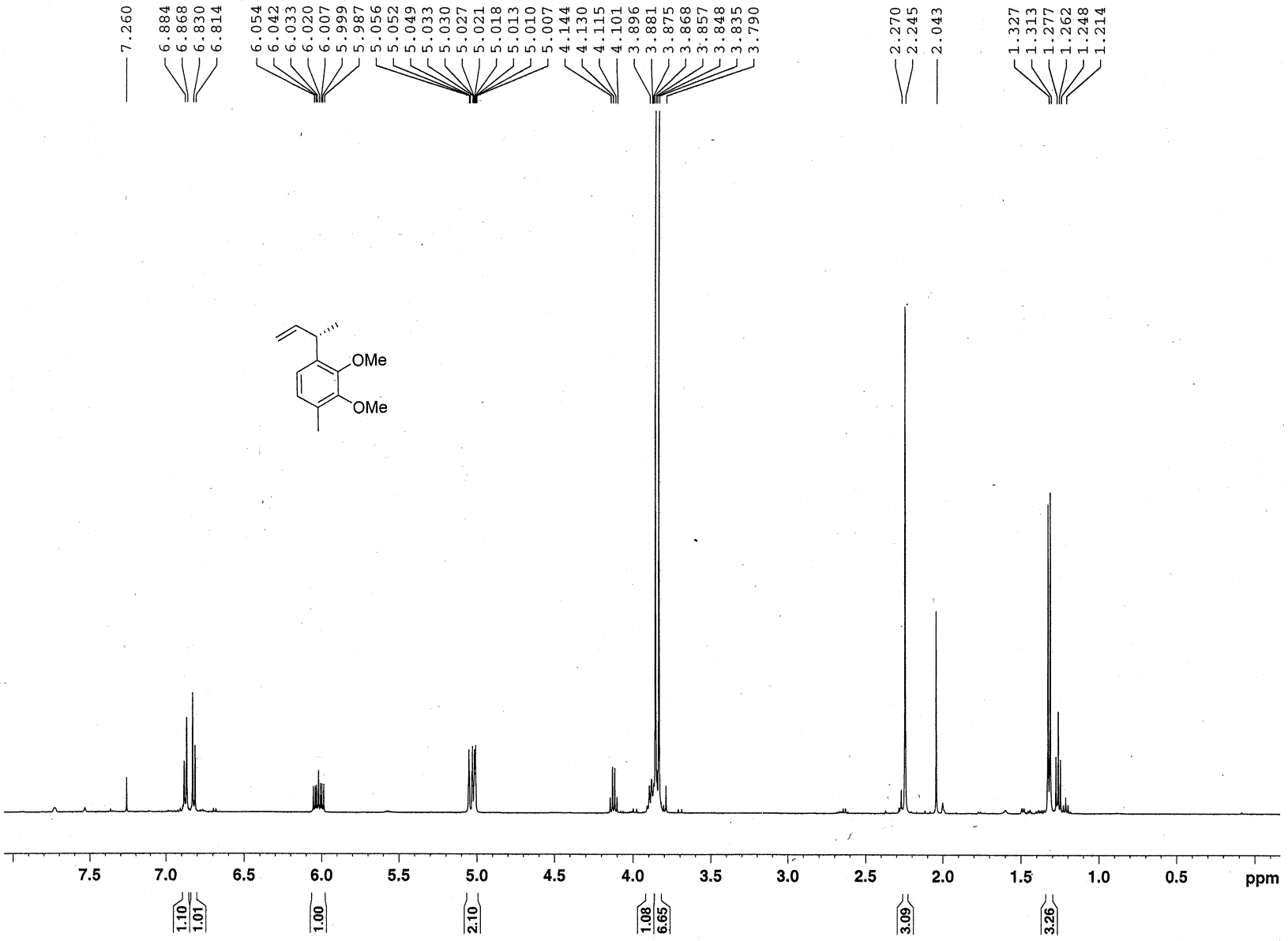

BRUKER

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EXPNO                     1
PROCNO                    1

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TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
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FIDRES           0.157632 Hz
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RG                     128
DW                48.400 usec
DE                 6.00 usec
TE                 300.2 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

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NUC1                   1H
P1                 14.80 usec
PL1                -1.00 dB
SFO1          500.0230878 MHz

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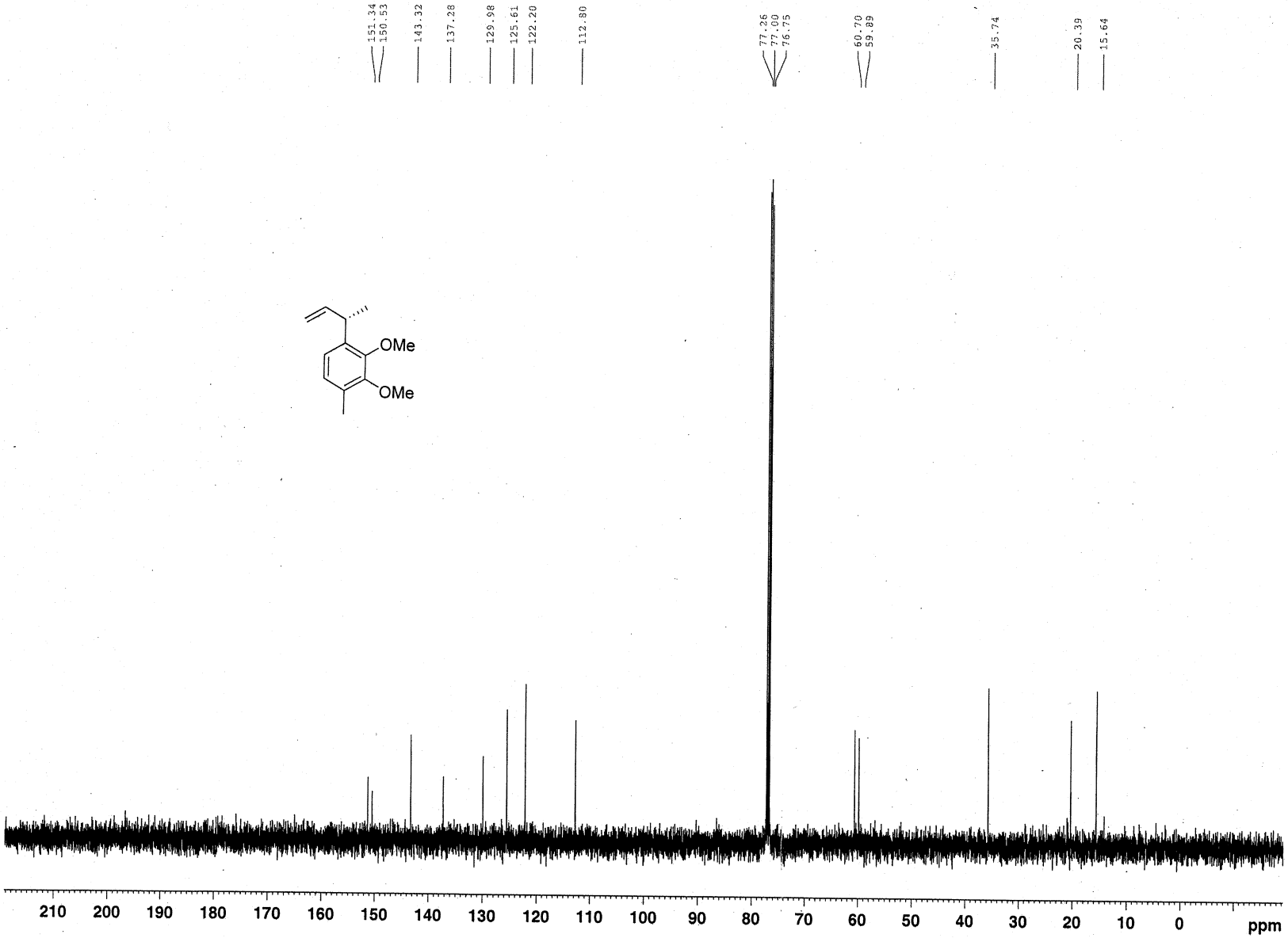

BRUKER

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PROCNO 1

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FIDRES 0.458222 Hz
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RG 3251
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DE 6.00 usec
TE 300.2 K
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d11 0.03000000 sec
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MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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NUC1 13C
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PL1 3.00 dB
SFO1 125.7427020 MHz

======== CHANNEL f2 ========
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NUC2 1H
PCPD2 100.00 usec
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PL12 18.80 dB
PL13 120.00 dB
SFO2 500.0220001 MHz

F2 - Processing parameters
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SF 125.7301313 MHz
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GB 0
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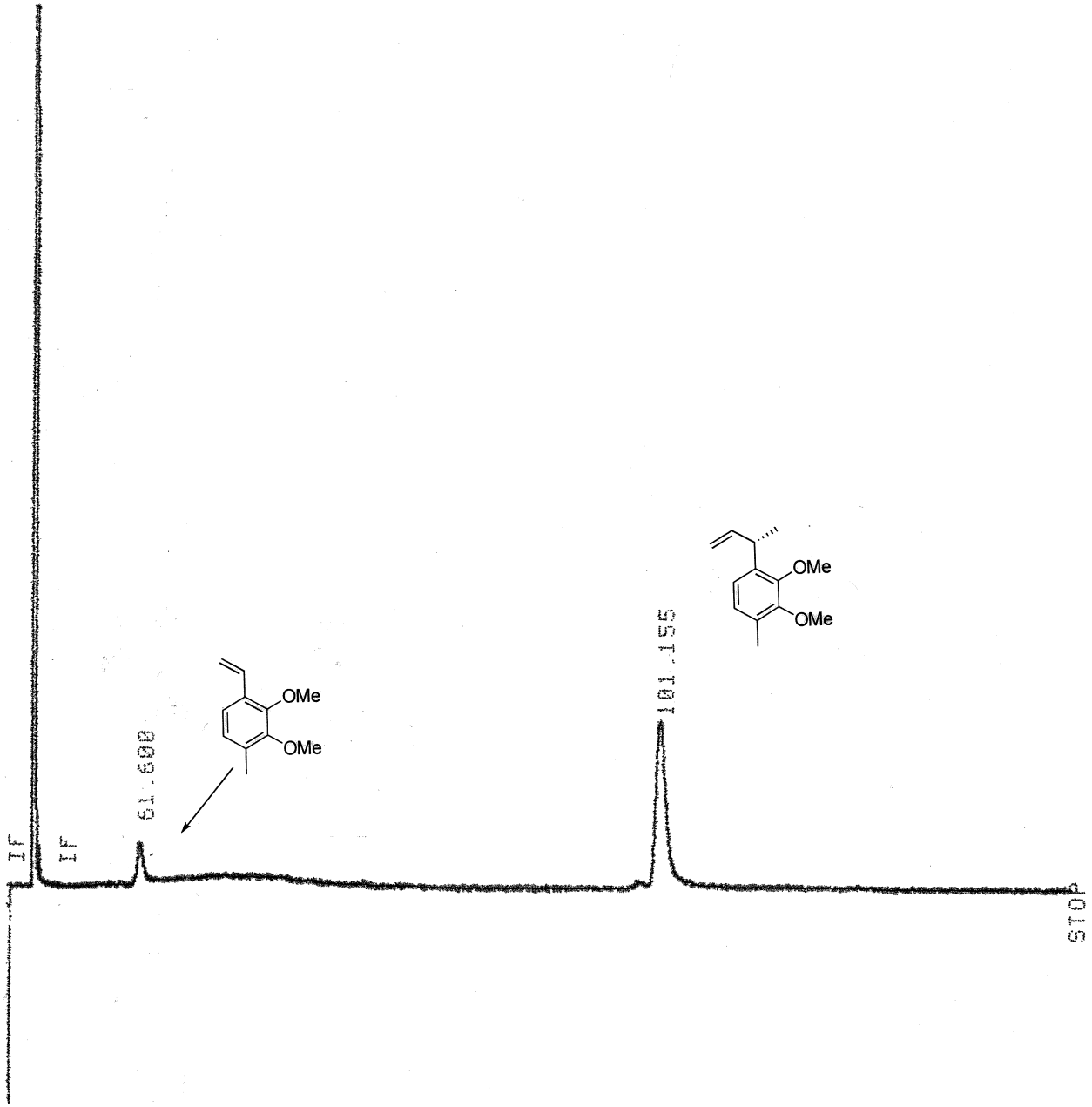
Column B (85°C isothermal) IV-281



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RUN# 2707 FEB 6, 2006 10:11:23

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	101.155	9121 PU	.287	82.72266

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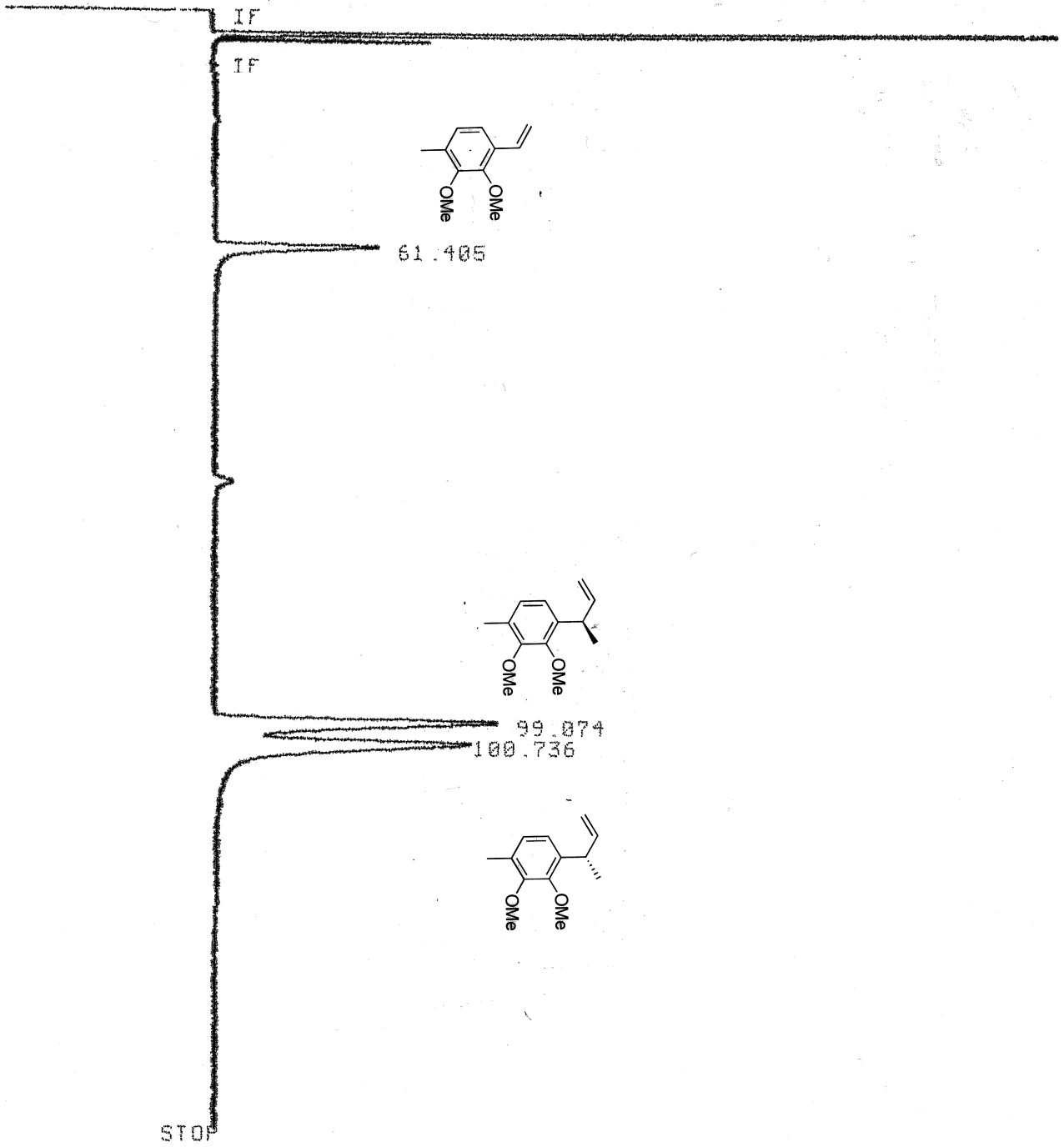

Racemic + IV-281 85°C isothermal

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Closing signal file M:SIGNAL   .BNC

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SIGNAL FILE: M:SIGNAL.BNC
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   61.405      21734   BV    .520    51.11117
   99.074      19803   PV    .297    46.57010
  100.736        108 I PB    .017      .25398

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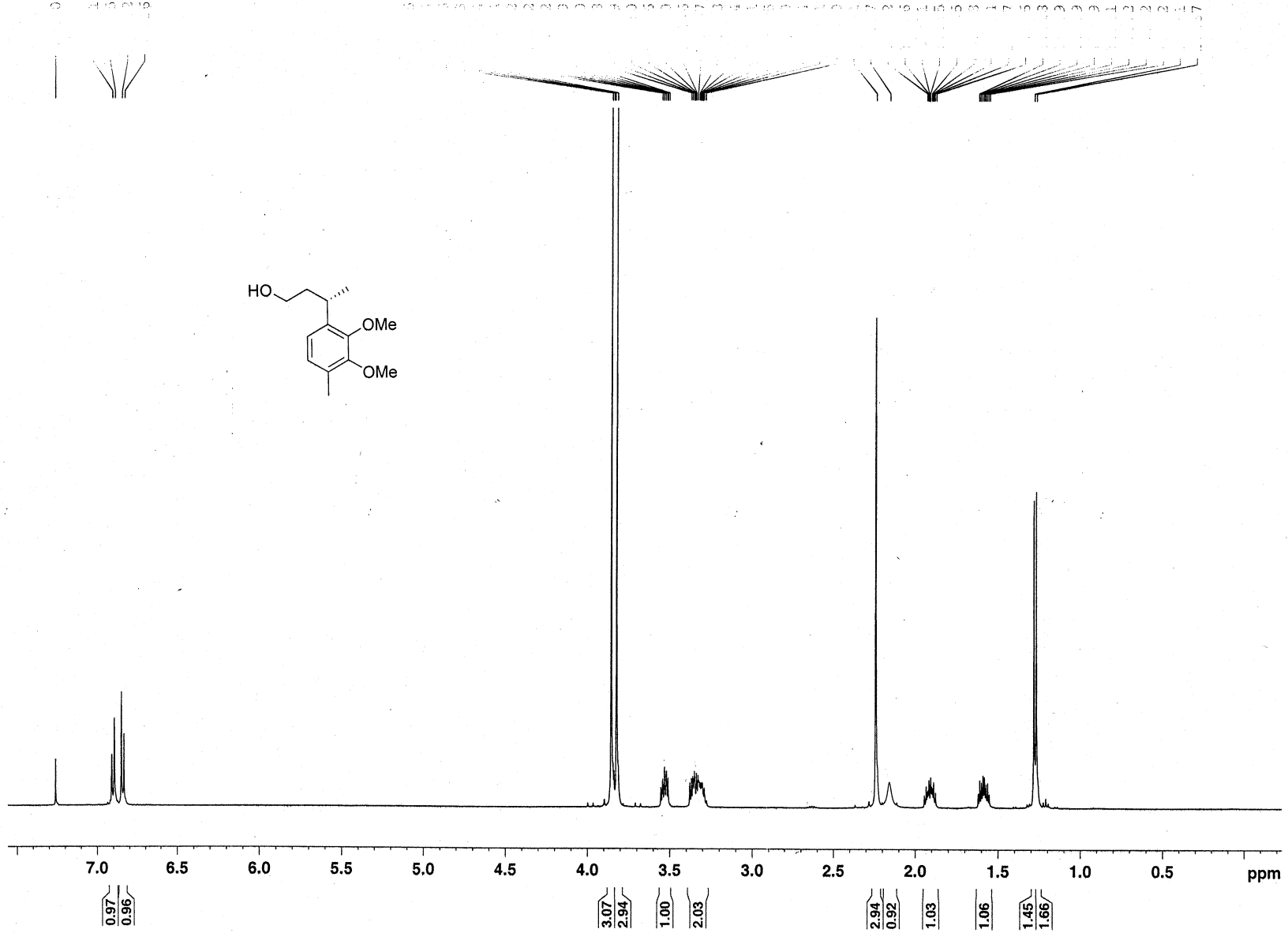


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PROCNO                         1

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SFO1                500.0230878 MHz

F2 - Processing parameters
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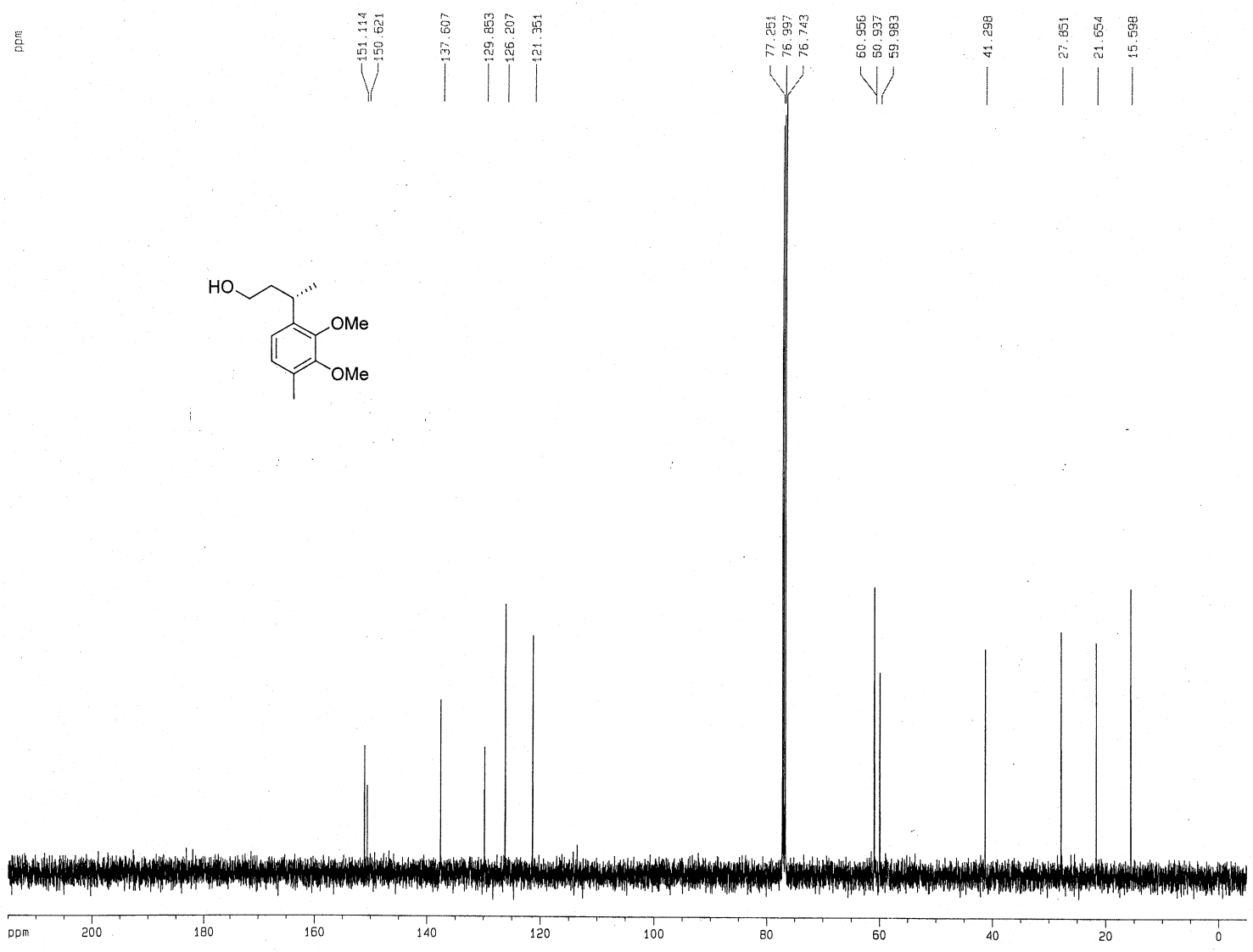

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PROCNO	1

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F2 - Processing parameters

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CY	19.00 cm
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F2P	-5.000 ppm
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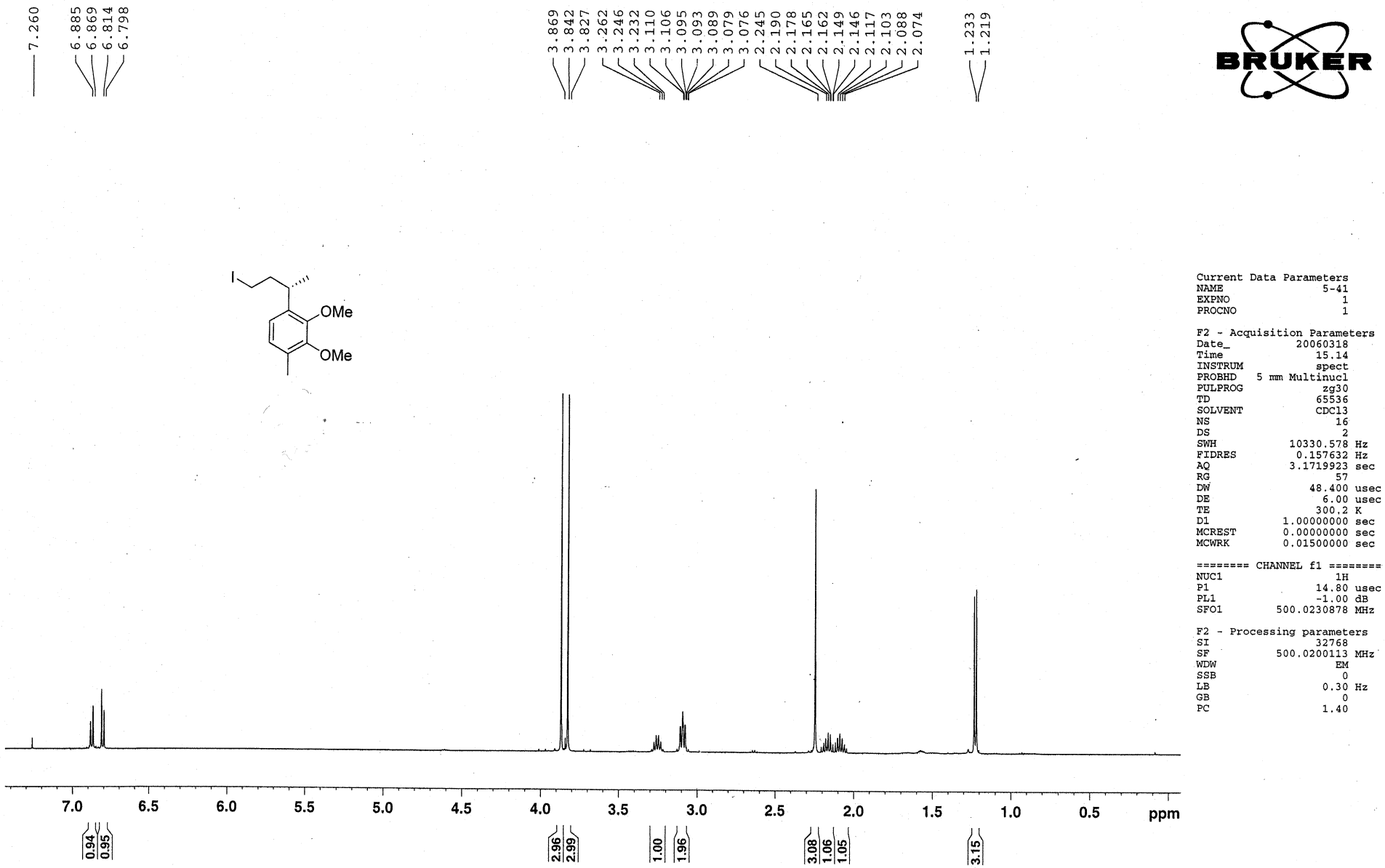


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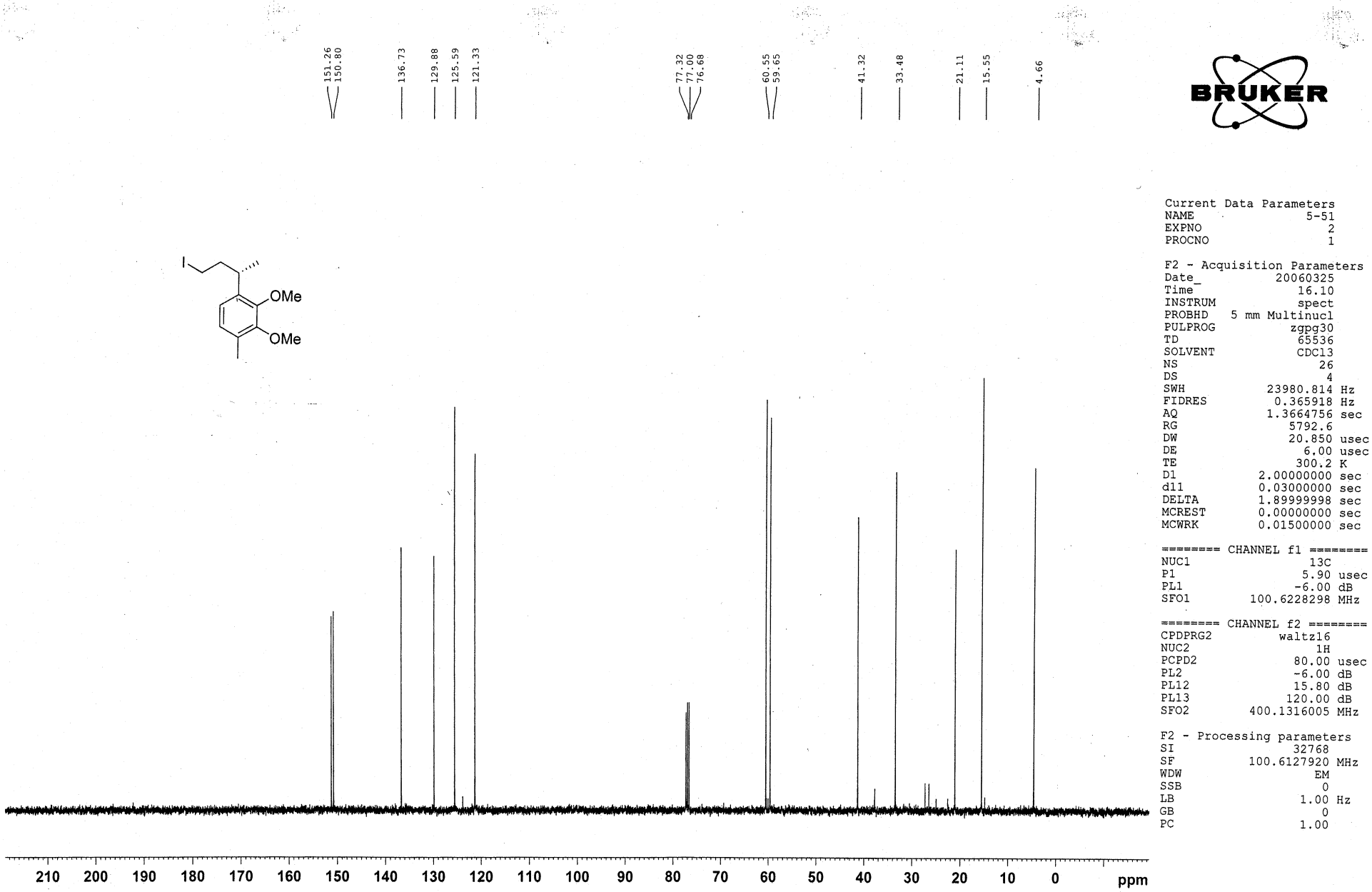

BRUKER

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PROCNO 1

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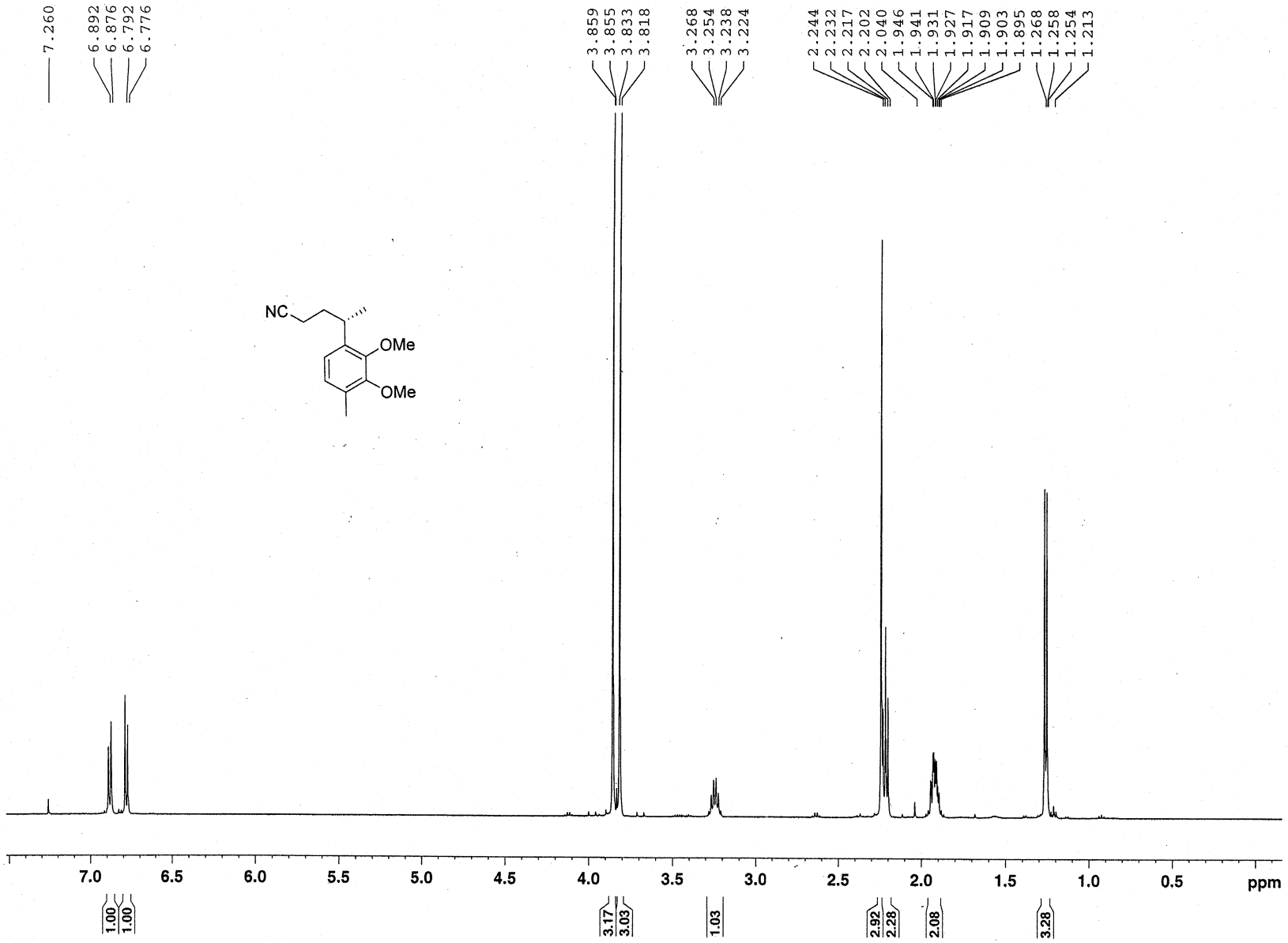


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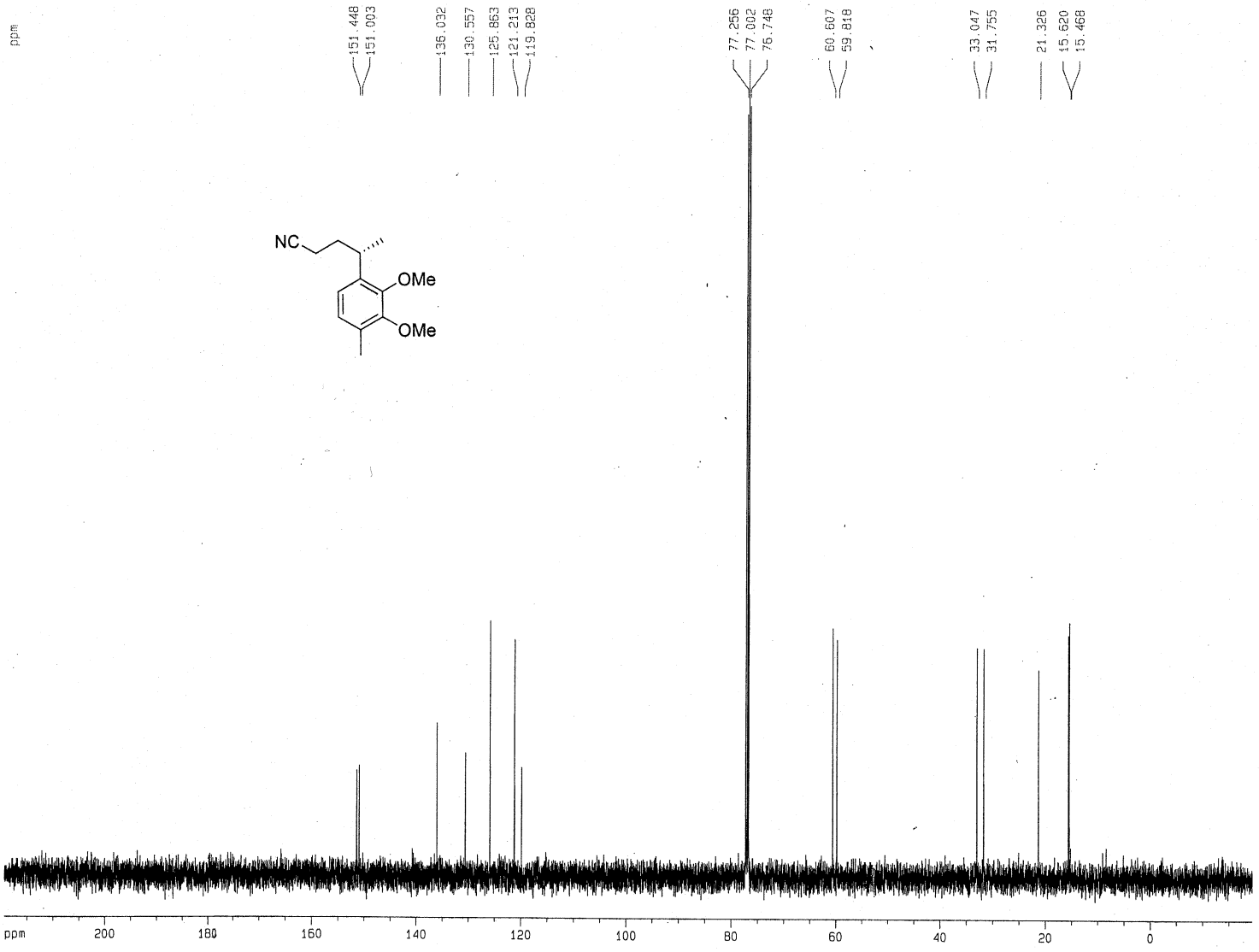


Current Data Parameters

NAME	5-43
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20060320
Time	15.10
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	51
DS	4
SWH	30030.029 Hz
FIDRES	0.458222 Hz
AQ	1.0912244 sec
RG	2048
DW	16.650 usec
DE	6.00 usec
TE	300.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

NUC1	13C
P1	13.00 usec
PL1	3.00 dB
SFO1	125.7427020 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	-1.00 dB
PL12	18.80 dB
PL13	120.00 dB
SFO2	500.0220001 MHz

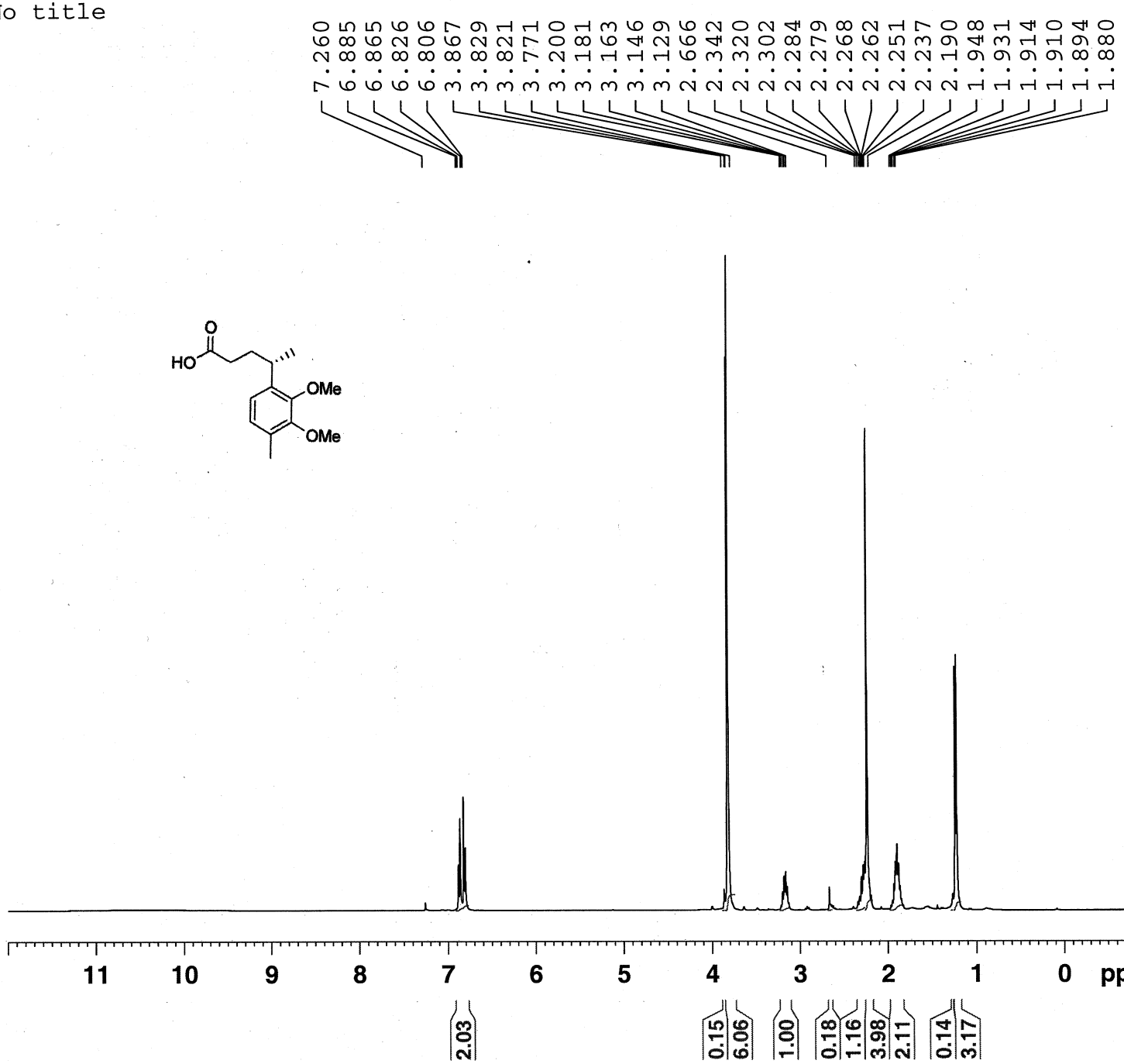
F2 - Processing parameters

SI	32768
SF	125.7301340 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	30.00 cm
CY	19.00 cm
F1P	219.383 ppm
F1	27583.03 Hz
F2P	-19.462 ppm
F2	-2447.00 Hz
PPMCM	7.96150 ppm/cm
HZCM	1001.00098 Hz/cm

No title



Current Data Parameters

NAME	6.85
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20060912
Time	10.32
INSTRUM	spect
PROBHD	5 mm QNP 1H/1
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8250.825 Hz
FIDRES	0.125898 Hz
AQ	3.9715922 sec
RG	32
DW	60.600 usec
DE	6.00 usec
TE	300.3 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

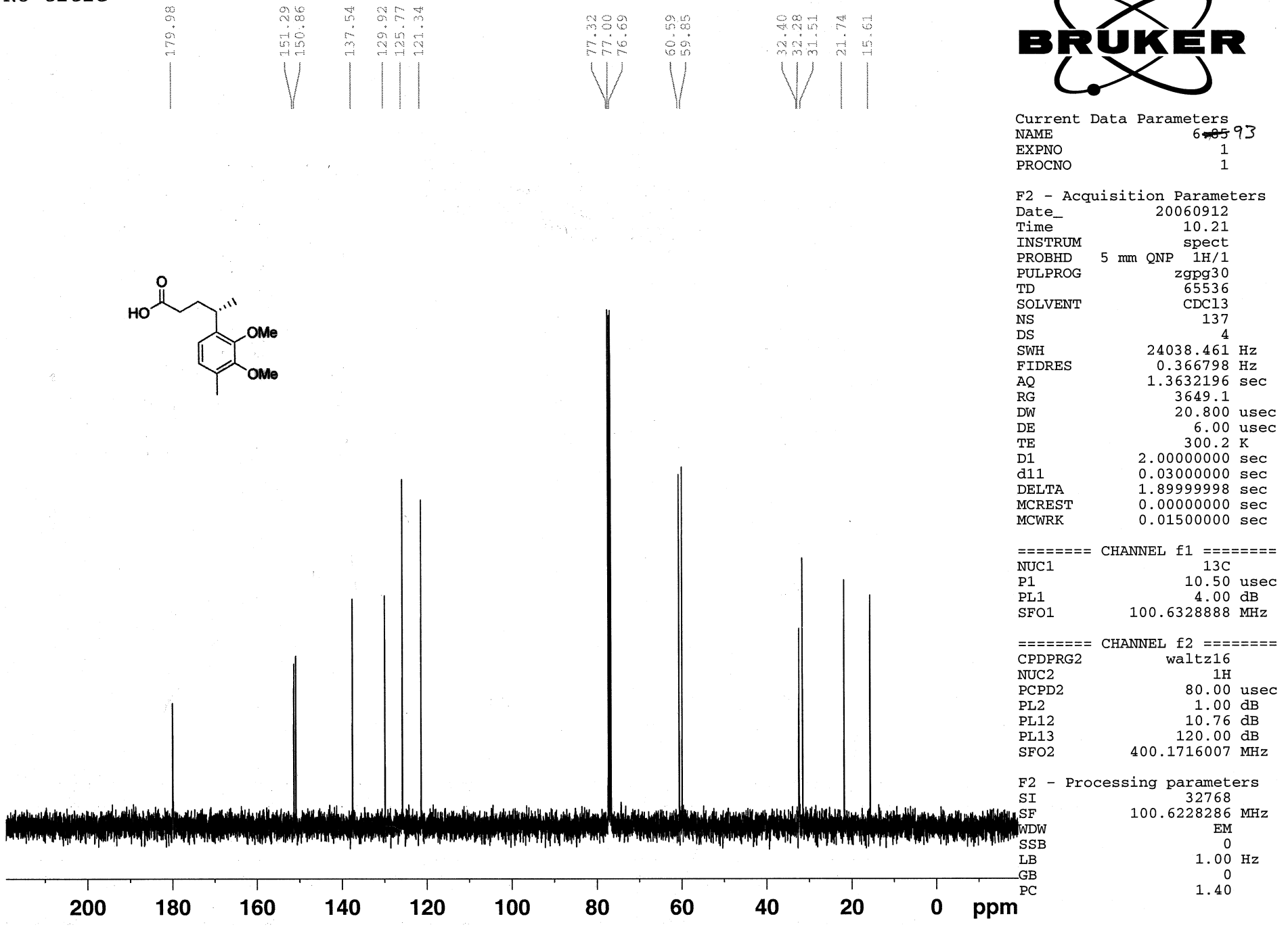
======== CHANNEL f1 ========

NUC1	1H
P1	26.00 usec
PL1	1.00 dB
SFO1	400.1724712 MHz

F2 - Processing parameters

SI	32768
SF	400.1700074 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

No title



Current Data Parameters

NAME	6~~.85~~93
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20060912
Time	10.21
INSTRUM	spect
PROBHD	5 mm QNP 1H/1
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	137
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3632196 sec
RG	3649.1
DW	20.800 usec
DE	6.00 usec
TE	300.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

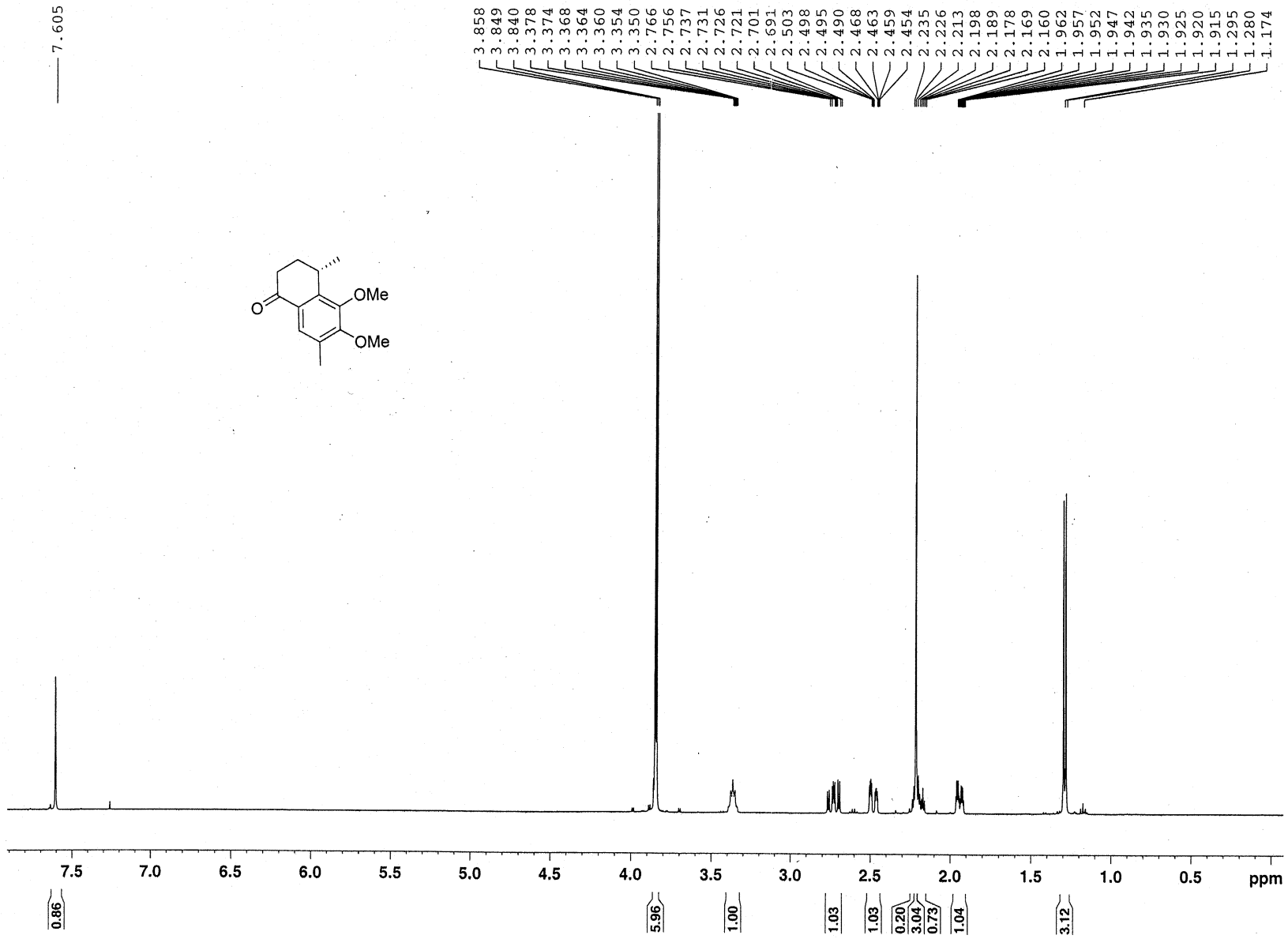
NUC1	13C
P1	10.50 usec
PL1	4.00 dB
SFO1	100.6328888 MHz

======== CHANNEL f2 ========

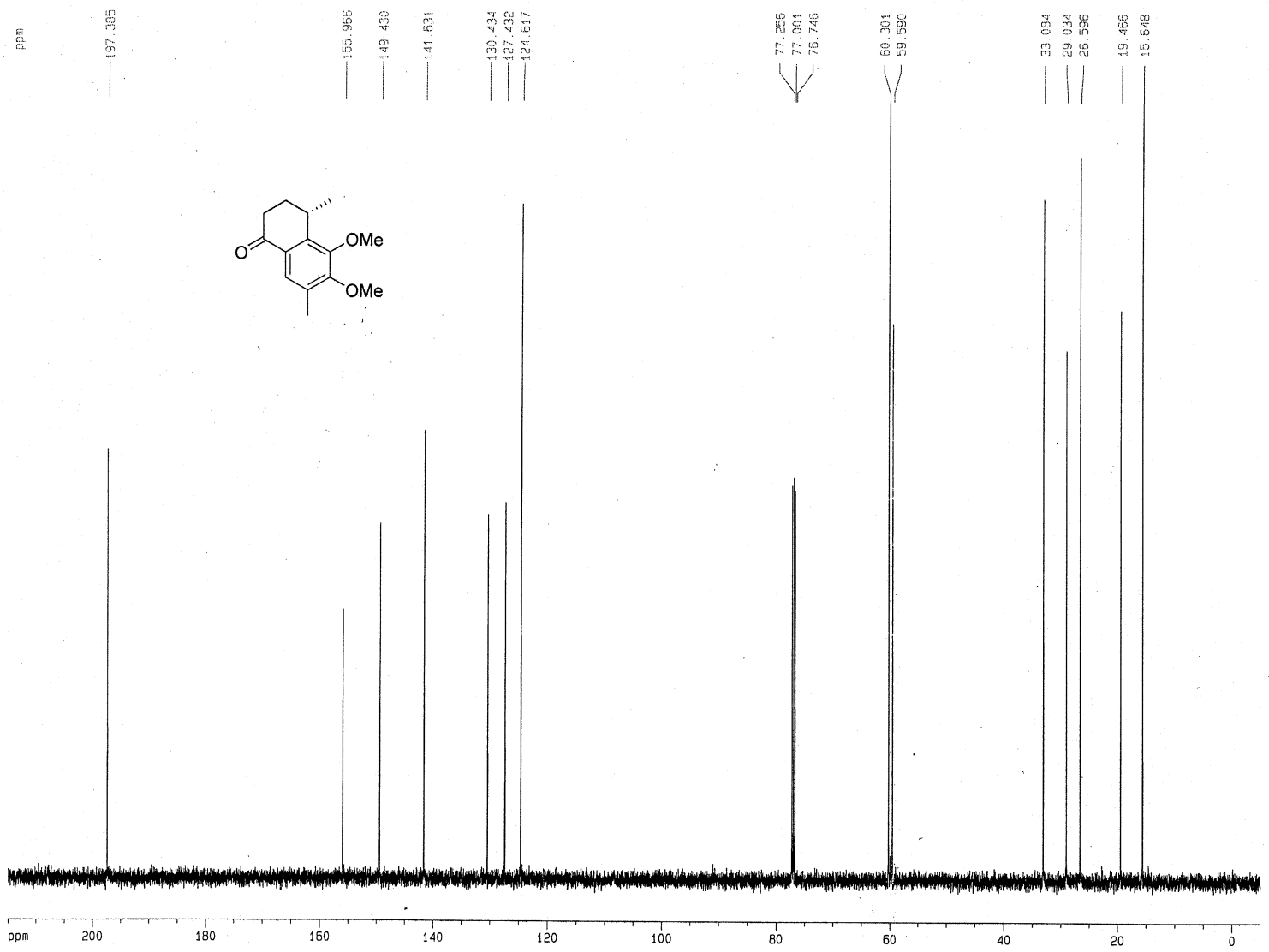
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.00 dB
PL12	10.76 dB
PL13	120.00 dB
SFO2	400.1716007 MHz

F2 - Processing parameters

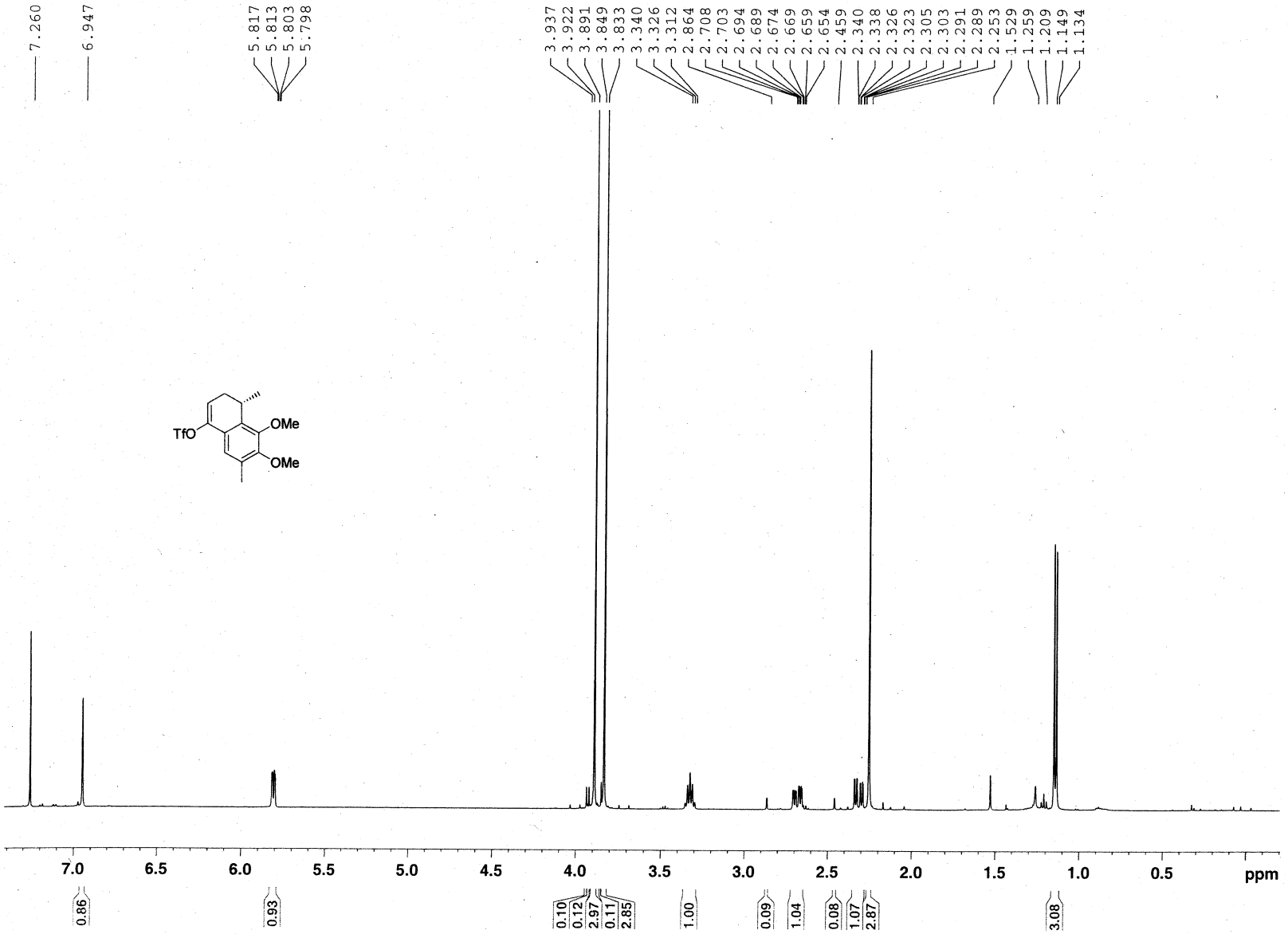
SI	32768
SF	100.6228286 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



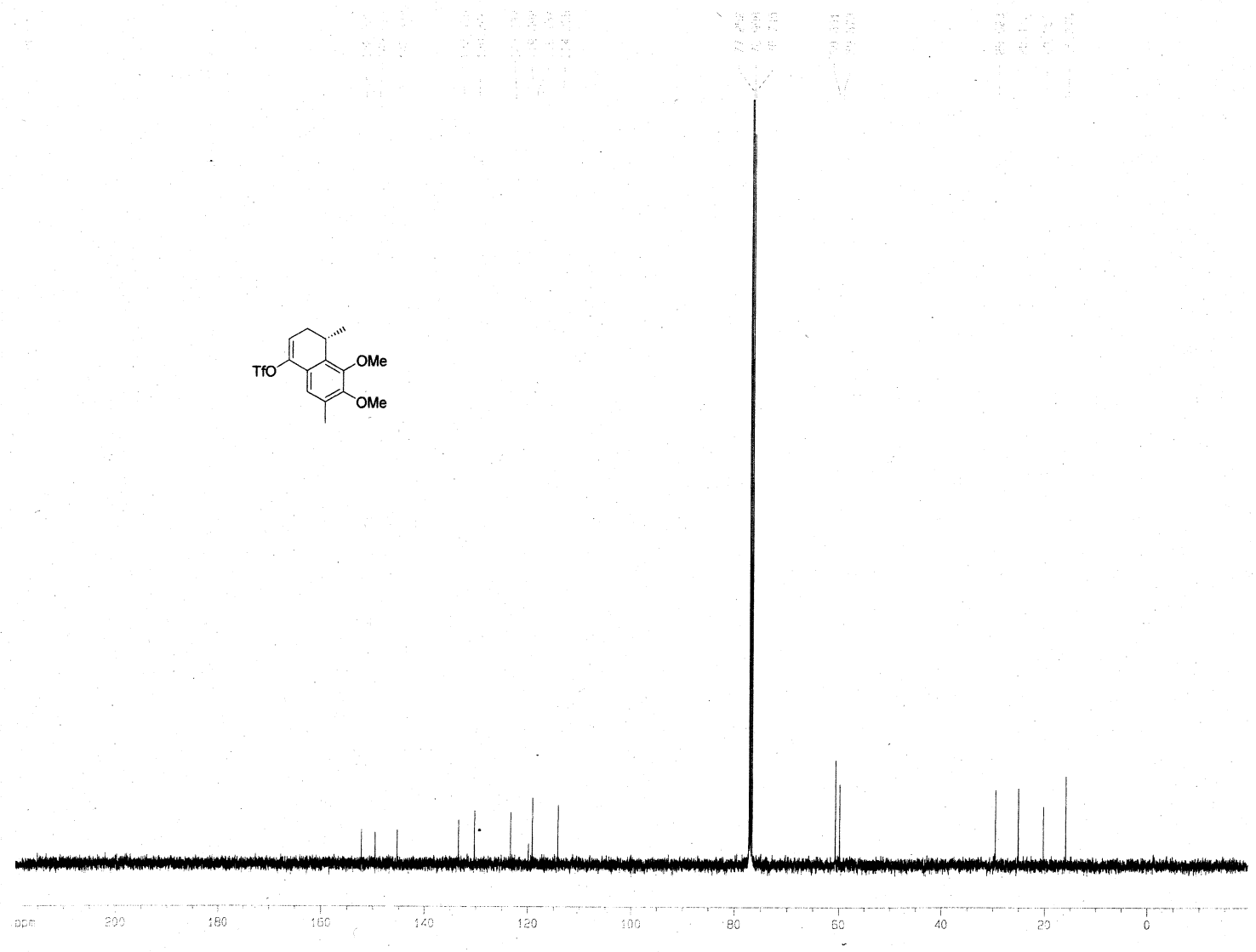

```
Current Data Parameters
NAME                  5-59
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20060328
Time                 13.15
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              10330.578 Hz
FIDRES               0.157632 Hz
AQ                3.1719923 sec
RG                    28.5
DW                   48.400 usec
DE                    6.00 usec
TE                   300.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.80 usec
PL1                  -1.00 dB
SFO1           500.0230878 MHz

F2 - Processing parameters
SI                      32768
SF             500.0200110 MHz
WDW                      EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



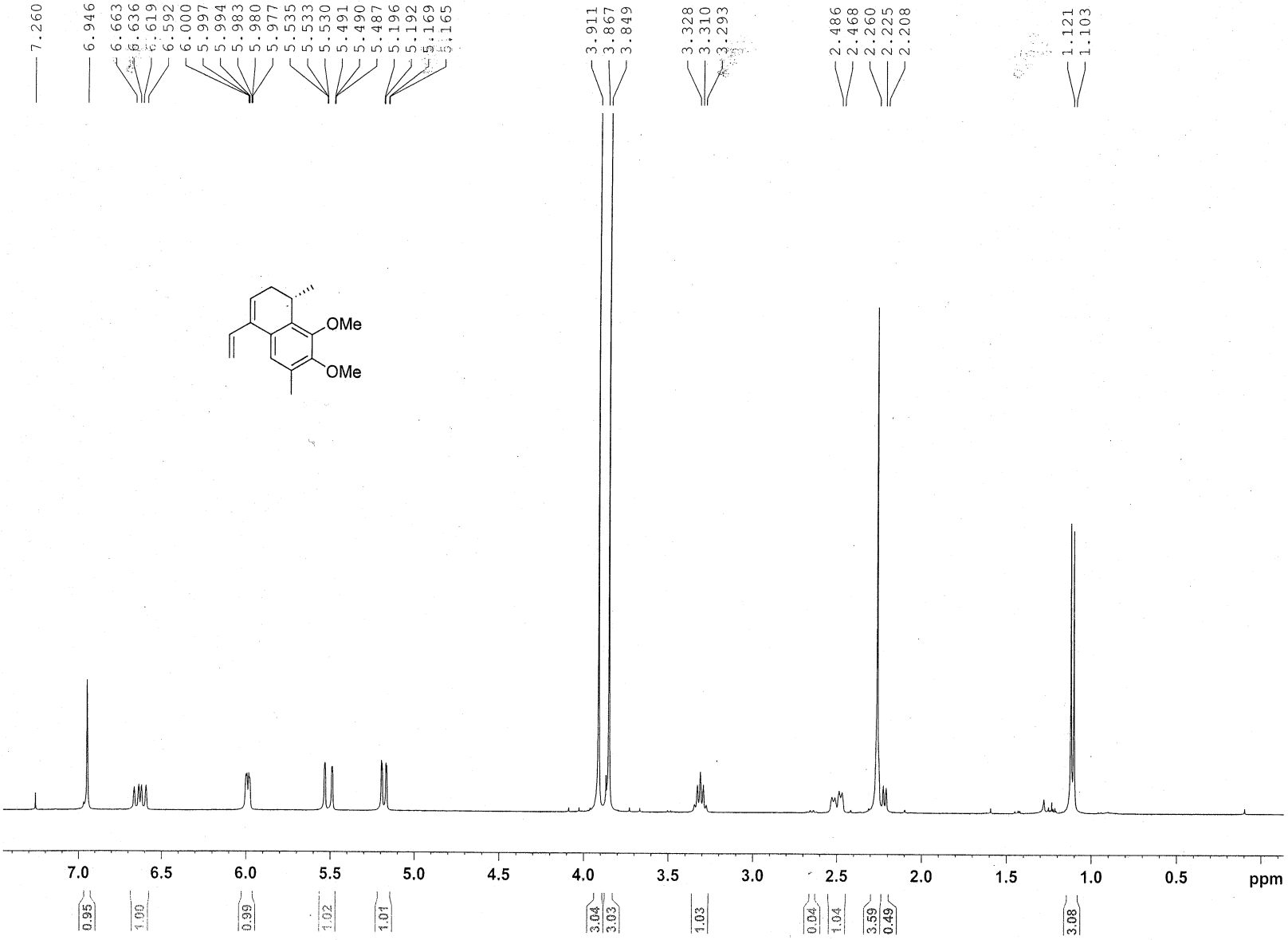

```
Current Data Parameters
NAME                  5-59
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20060328
Time                 13.18
INSTRUM              spect
PROBHD    5 mm Multinucl
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       46
DS                        4
SWH              30030.029 Hz
FIDRES           0.458222 Hz
AQ               1.0912244 sec
RG                  11585.2
DW                   16.650 usec
DE                    6.00 usec
TE                   300.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                   13.00 usec
PL1                   3.00 dB
SFO1           125.7427020 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  -1.00 dB
PL12                 18.80 dB
PL13                120.00 dB
SFO2           500.0220001 MHz

F2 - Processing parameters
SI                    32768
SF             125.7301422 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   30.00 cm
CY                   19.00 cm
F1P                215.000 ppm
F1                27031.98 Hz
F2P                 -5.000 ppm
F2                -628.65 Hz
PPMCM              7.33333 ppm/cm
HZCM             922.02100 Hz/cm
```




```
Current Data Parameters
NAME                  5-51
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20060324
Time                 11.07
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719923 sec
RG                  456.1
DW                 48.400 usec
DE                  6.00 usec
TE                 300.2 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.80 usec
PL1                -1.00 dB
SFO1          500.0230878 MHz

F2 - Processing parameters
SI                     32768
SF            500.0200116 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.40
```




```
Current Data Parameters
NAME                  5-51
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20060324
Time                 11.11
INSTRUM              spect
PROBHD    5 mm Multinucl
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     370
DS                       4
SWH              30030.029 Hz
FIDRES           0.458222 Hz
AQ               1.0912244 sec
RG                  5792.6
DW                 16.650 usec
DE                  6.00 usec
TE                 300.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                  13.00 usec
PL1                  3.00 dB
SFO1          125.7427020 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -1.00 dB
PL12                18.80 dB
PL13               120.00 dB
SFO2          500.0220001 MHz

F2 - Processing parameters
SI                    32768
SF            125.7301290 MHz
WDW                      EM
SSB                       0
LB                   1.00 Hz
GB                        0
PC                    1.40

1D NMR plot parameters
CX                   30.00 cm
CY                   19.00 cm
F1P                219.423 ppm
F1                27588.03 Hz
F2P                -19.423 ppm
F2                -2442.00 Hz
PPMCM              7.96150 ppm/cm
HZCM           1001.00104 Hz/cm
```



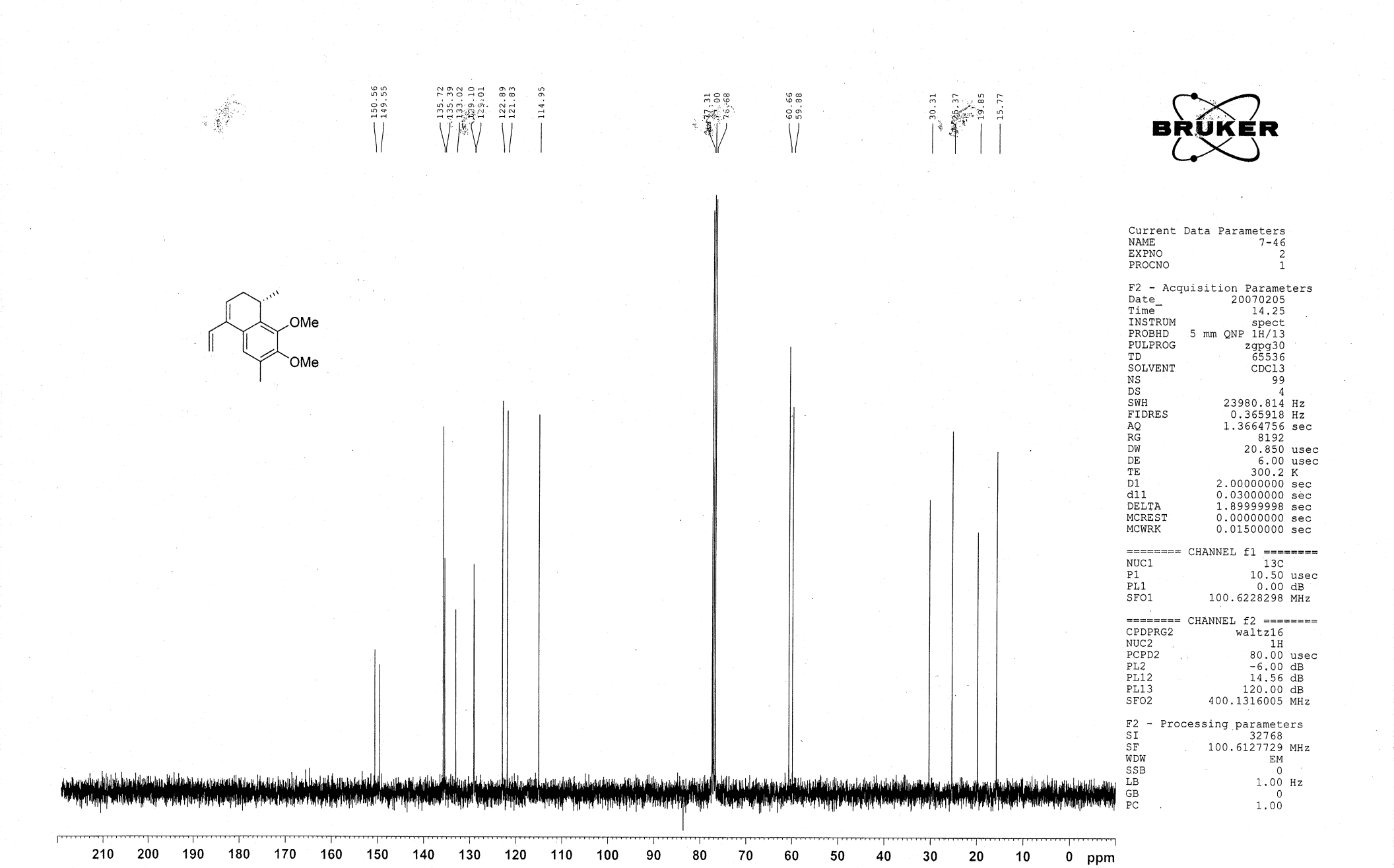
BRUKER

Current Data Parameters
NAME 7-43
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070205
Time 14.17
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 45.3
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



BRUKER

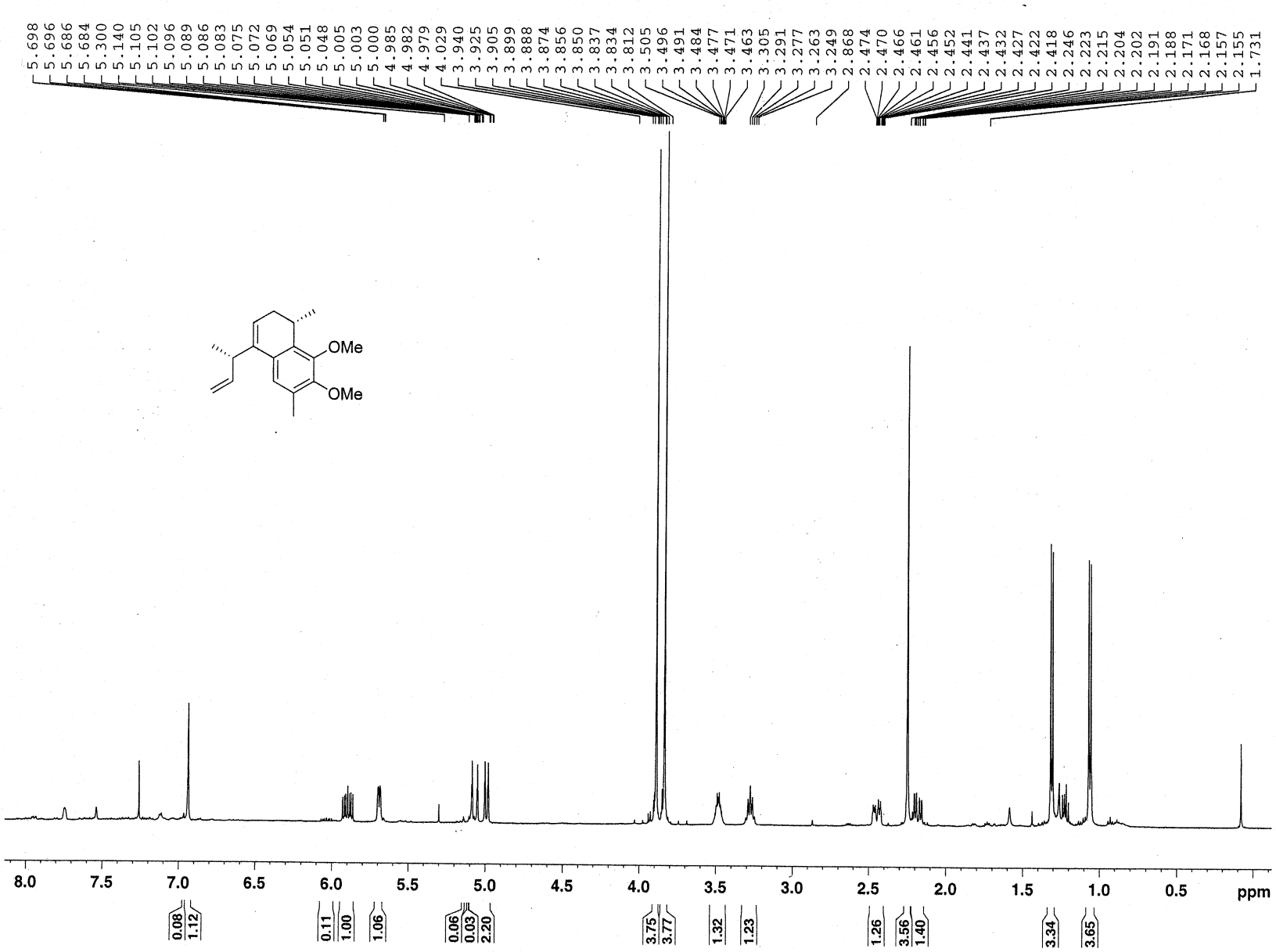
Current Data Parameters
NAME 7-46
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070205
Time 14.25
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 99
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 8192
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

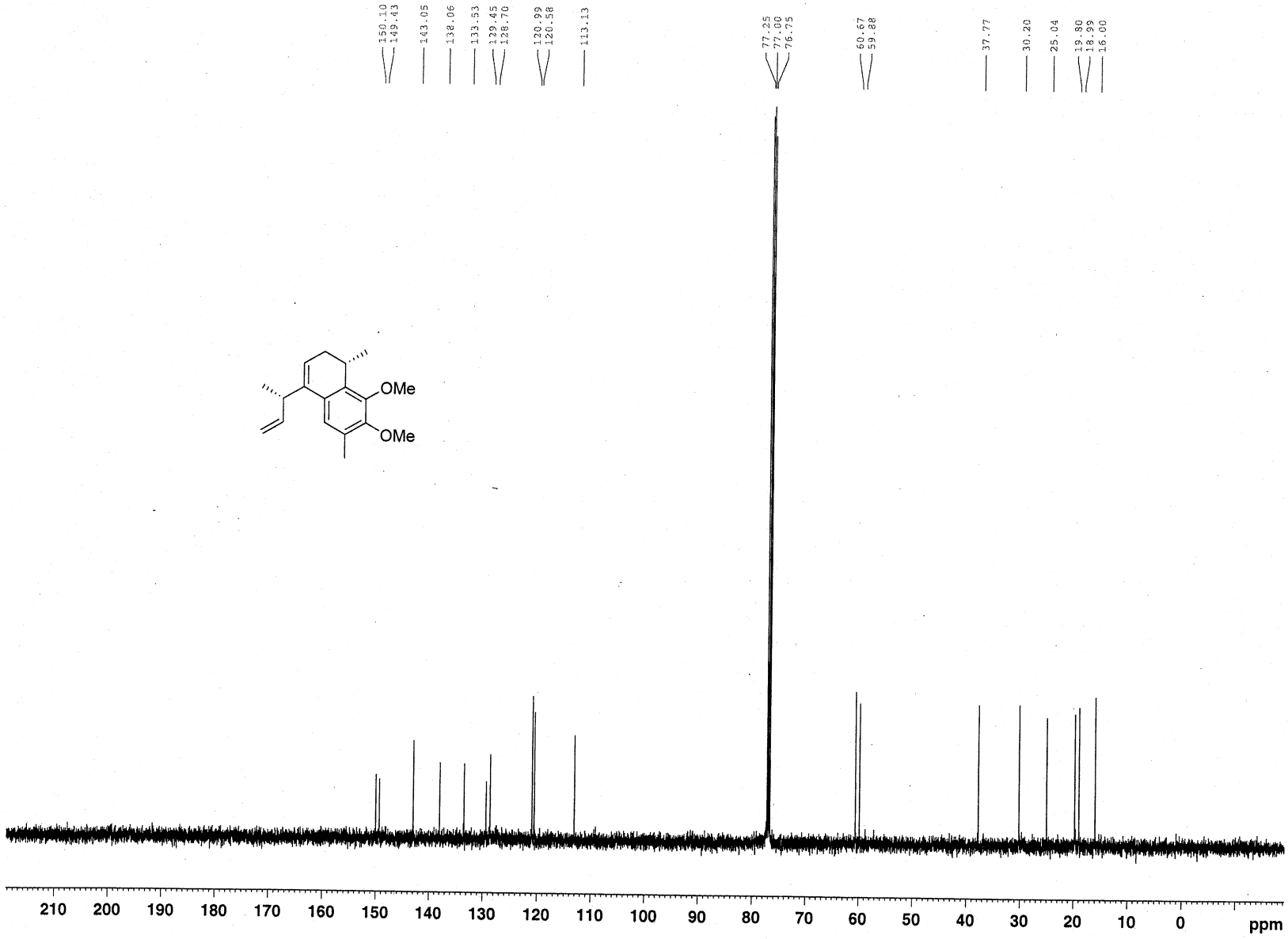
======== CHANNEL f1 ========
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 14.56 dB
PL13 120.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127729 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00




```
Current Data Parameters
NAME                  8-51
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20070702
Time                 15.37
INSTRUM              spect
PROBHD    5 mm Multinucl
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             10330.578 Hz
FIDRES              0.157632 Hz
AQ                3.1719923 sec
RG                    143.7
DW                   48.400 usec
DE                    6.00 usec
TE                   294.2 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.80 usec
PL1                 -1.00 dB
SFO1          500.0230878 MHz

F2 - Processing parameters
SI                    32768
SF            500.0200119 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.40
```



BRUKER

Current Data Parameters
NAME 8-51
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070702
Time 15.42
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 299
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912244 sec
RG 3649.1
DW 16.650 usec
DE 6.00 usec
TE 295.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 13.00 usec
PL1 3.00 dB
SFO1 125.7427020 MHz

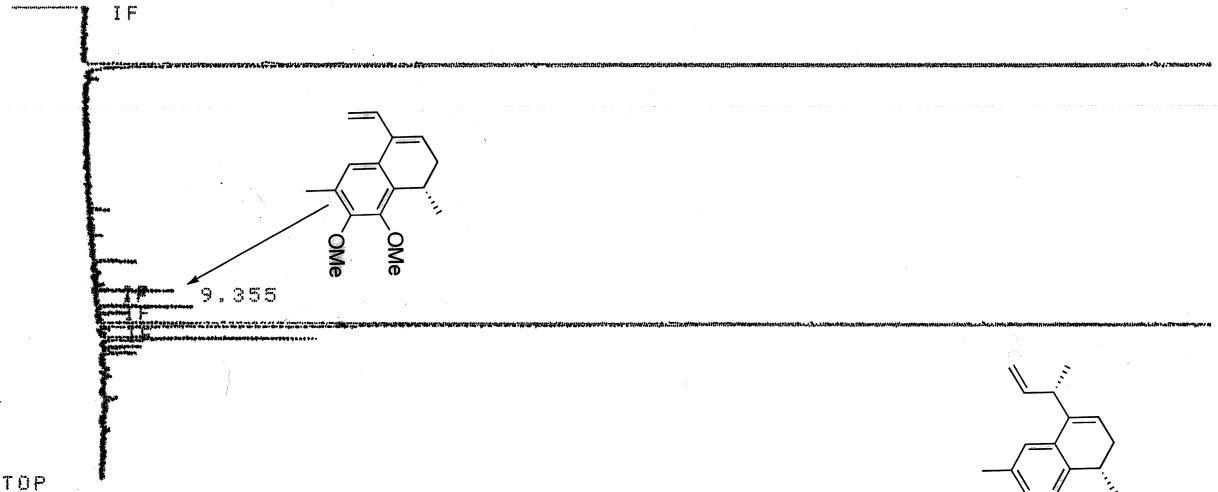
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -1.00 dB
PL12 18.80 dB
PL13 22.50 dB
SFO2 500.0220001 MHz

F2 - Processing parameters
SI 32768
SF 125.7301331 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

VIII-51, 150°C/1°/10°C/min/250°C

* RUN # 199 MAR 23, 1901 16:23:49

START



STOP

Closing signal file M:SIGNAL .BNC

RUN# 199 MAR 23, 1901 16:23:49

SIGNAL FILE: M:SIGNAL.BNC

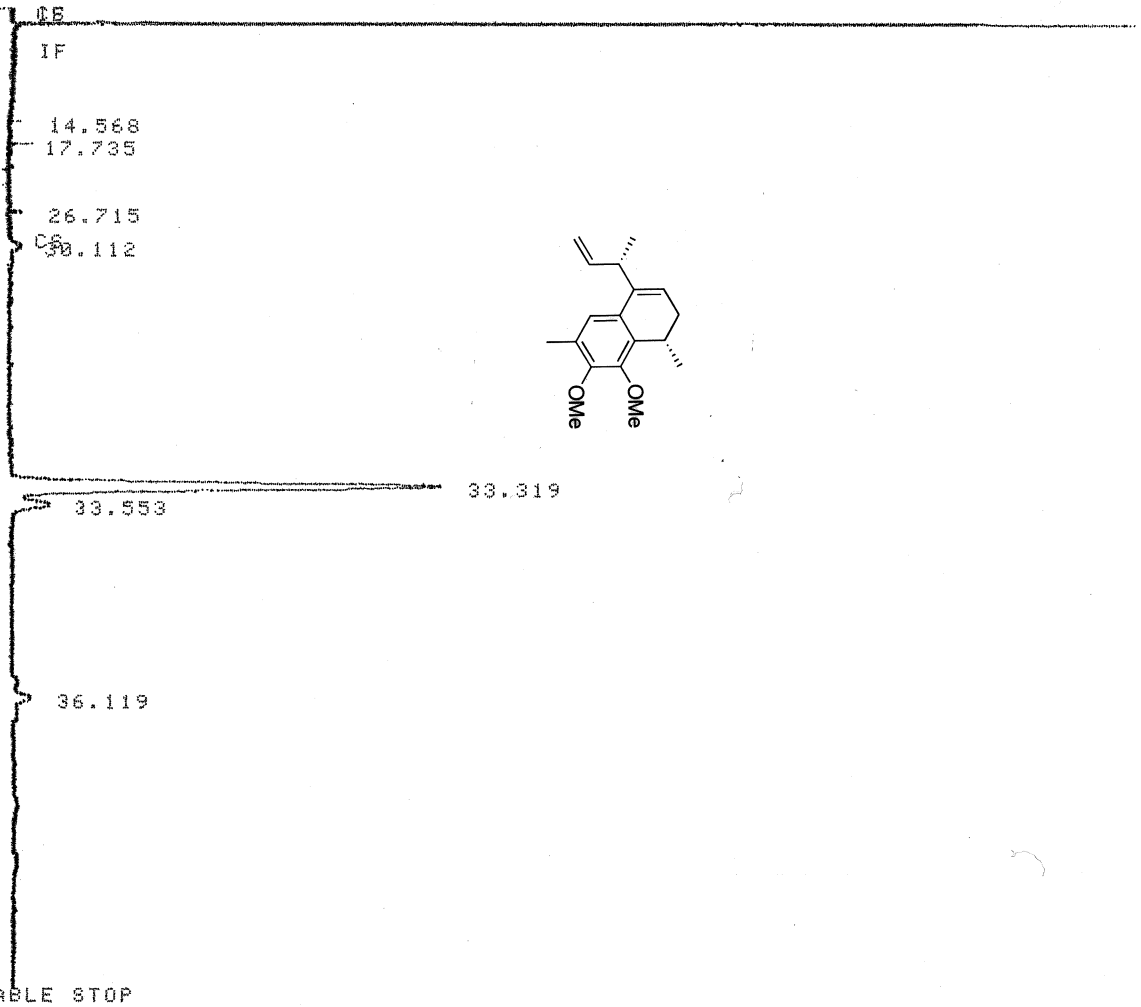
AREA%

RT	AREA	TYPE	WIDTH	AREA%
9.355	4584	I BH	.034	1.72280
10.480	261494	PV	.037	98.27718

TOTAL AREA= 266078

MUL FACTOR=1.0000E+00

*AN
RUN # 215 MAR 25, 1901 20:43:36
START



TIMETABLE STOP

Error storing signal to M:SIGNAL .BNA
ATTEMPTED WRITE PAST END OF FILE

RUN# 215 MAR 25, 1901 20:43:36

AREA%

RT	AREA	TYPE	WIDTH	AREA%
33.319	85069	VV	.115	91.73939
33.553	7660	VV	.115	8.26063

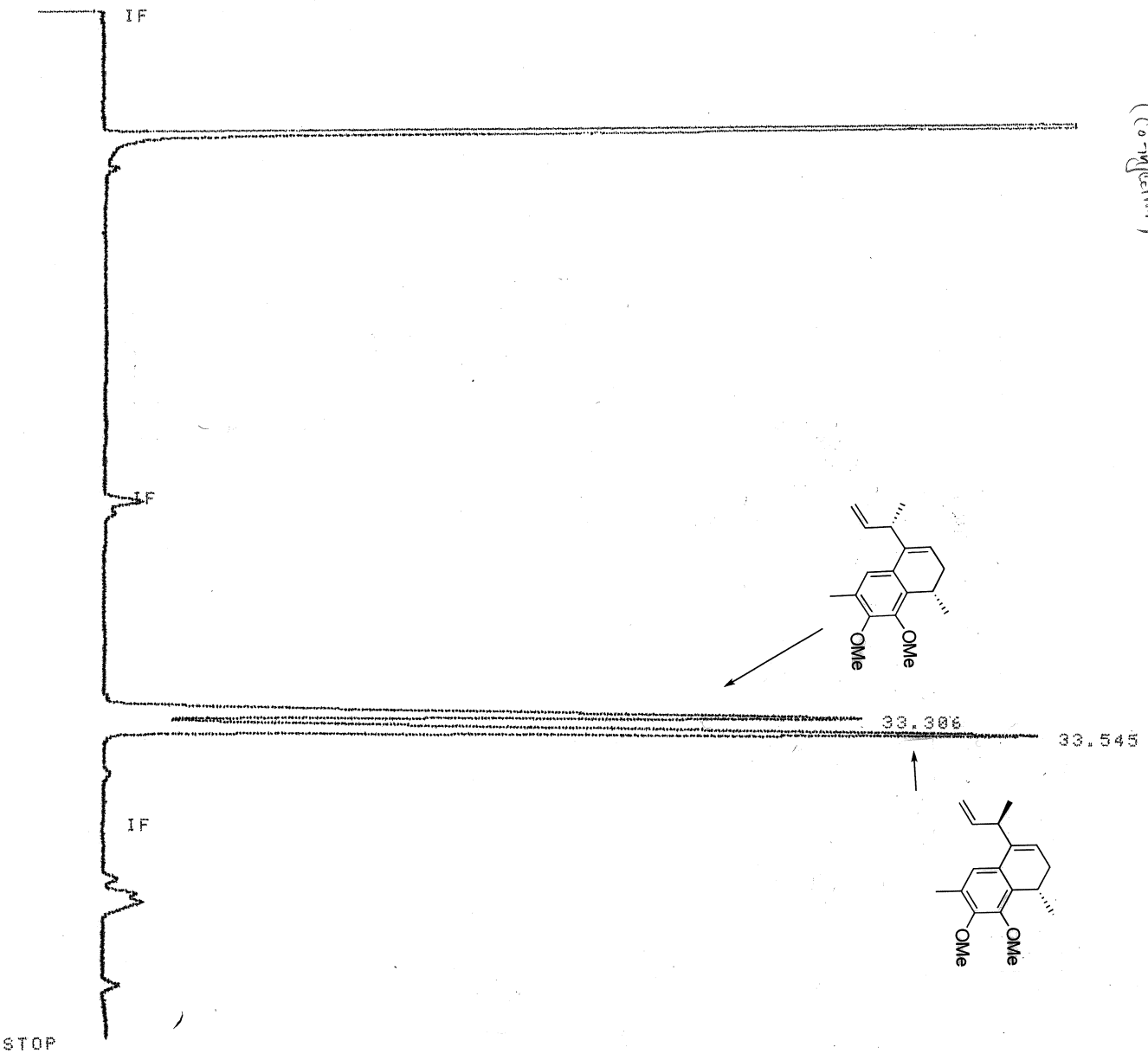
TOTAL AREA= 92729
MUL FACTOR=1.0000E+00

VIII-51
150 °C/15'/1.8°C/min/250°C

150°C/15'/1.8°C/min/250°C
(Co-injection)

* RUN # 213 MAR 25, 1901 18:41:15

START



STOP

Closing signal file M:SIGNAL .BNC

RUN# 213 MAR 25, 1901 18:41:15

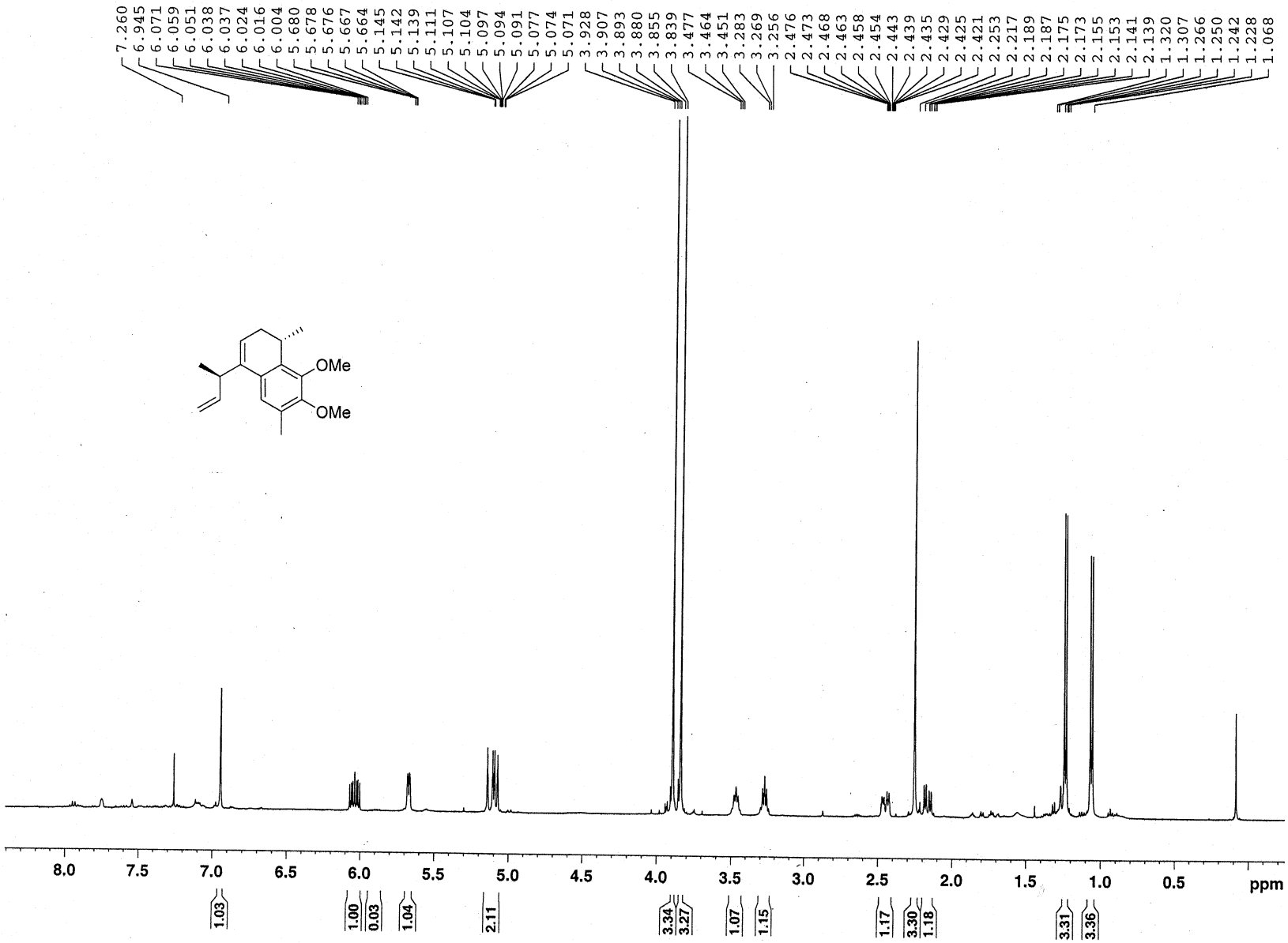
SIGNAL FILE: M:SIGNAL.BNC

AREA%

RT	AREA	TYPE	WIDTH	AREA%
33.306	175332	VV	.117	45.28144
33.545	211873	VP	.115	54.71856

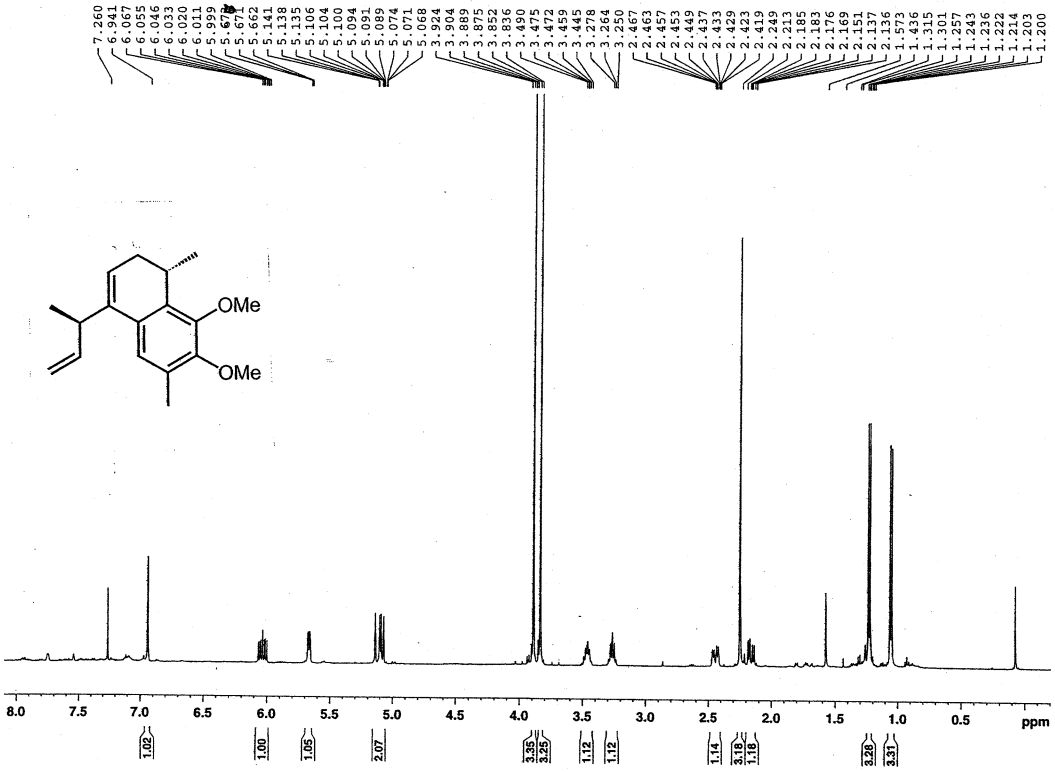
TOTAL AREA= 387205

MUL FACTOR=1.0000E+00



BRUKER

```
Current Data Parameters
NAME                  8-49
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_              20070706
Time                 12.09
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH             10330.578 Hz
FIDRES              0.157632 Hz
AQ                3.1719923 sec
RG                    143.7
DW                   48.400 usec
DE                    6.00 usec
TE                   298.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

========= CHANNEL f1 =========
NUC1                     1H
P1                   14.80 usec
PL1                  -1.00 dB
SFO1           500.0230878 MHz

F2 - Processing parameters
SI                    32768
SF             500.0200116 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.40
```

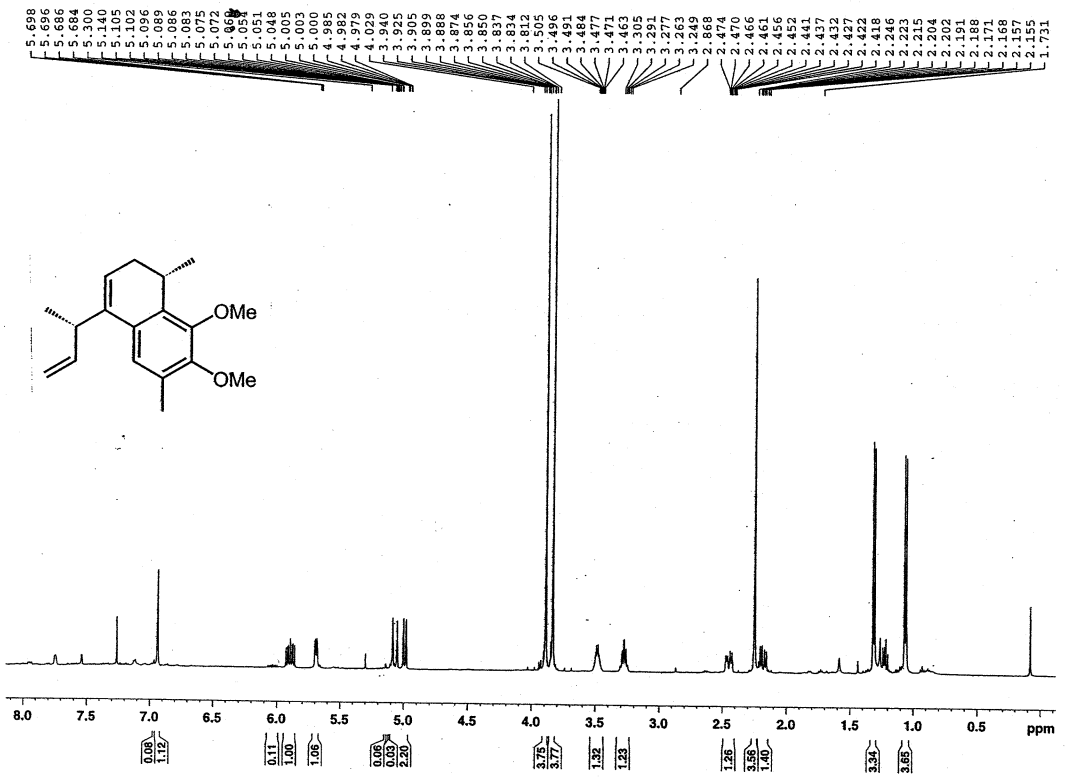


Current Data Parameters
NAME 8-49
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070702
Time 8.09
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 203.2
DW 48.400 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 14.80 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz

F2 - Processing parameters
SI 32768
SF 500.0200119 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

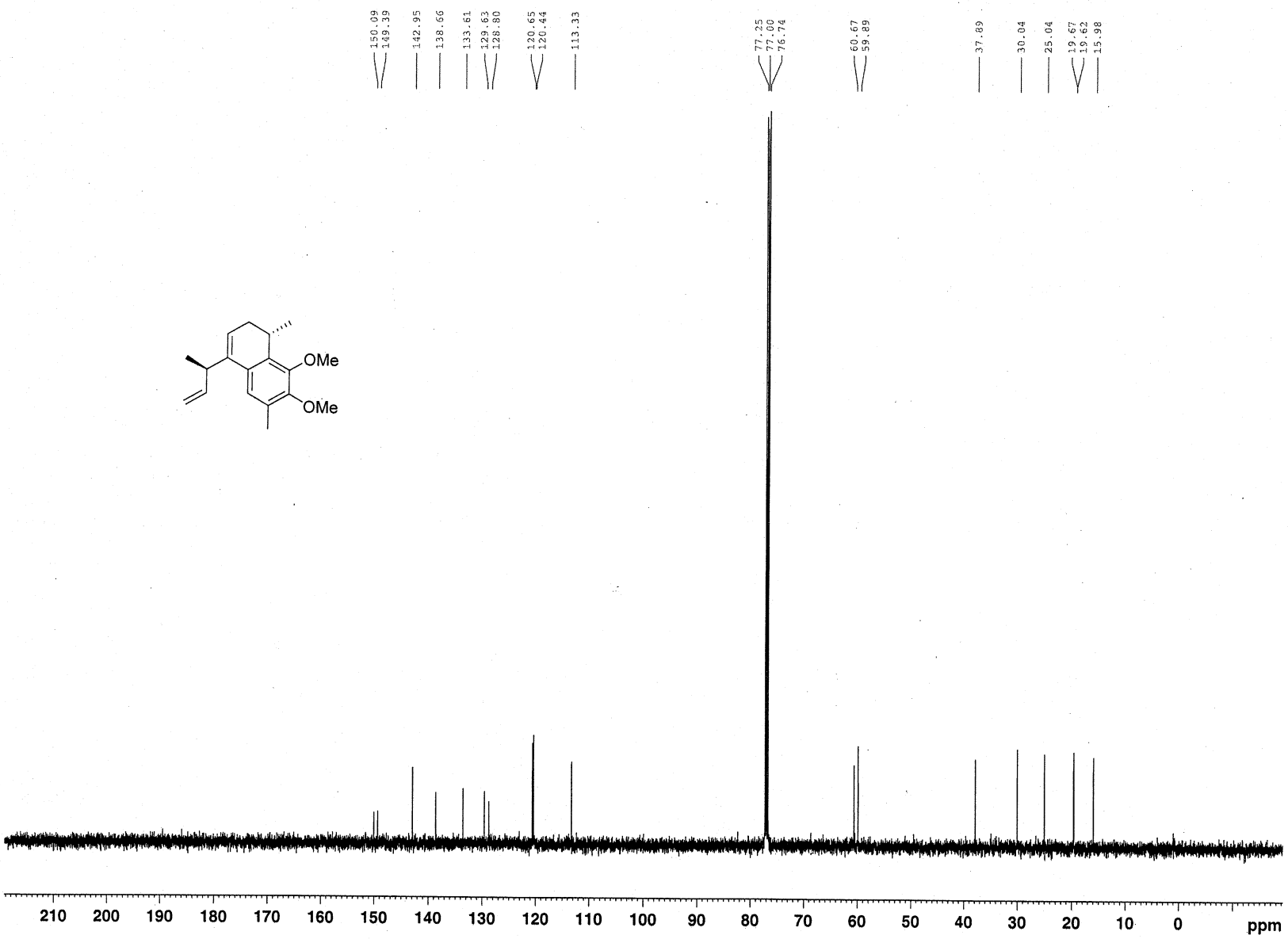


Current Data Parameters
NAME 8-51
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070702
Time 15.37
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 143.7
DW 48.400 usec
DE 6.00 usec
TE 294.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 14.80 usec
PL1 -1.00 dB
SFO1 500.0230878 MHz

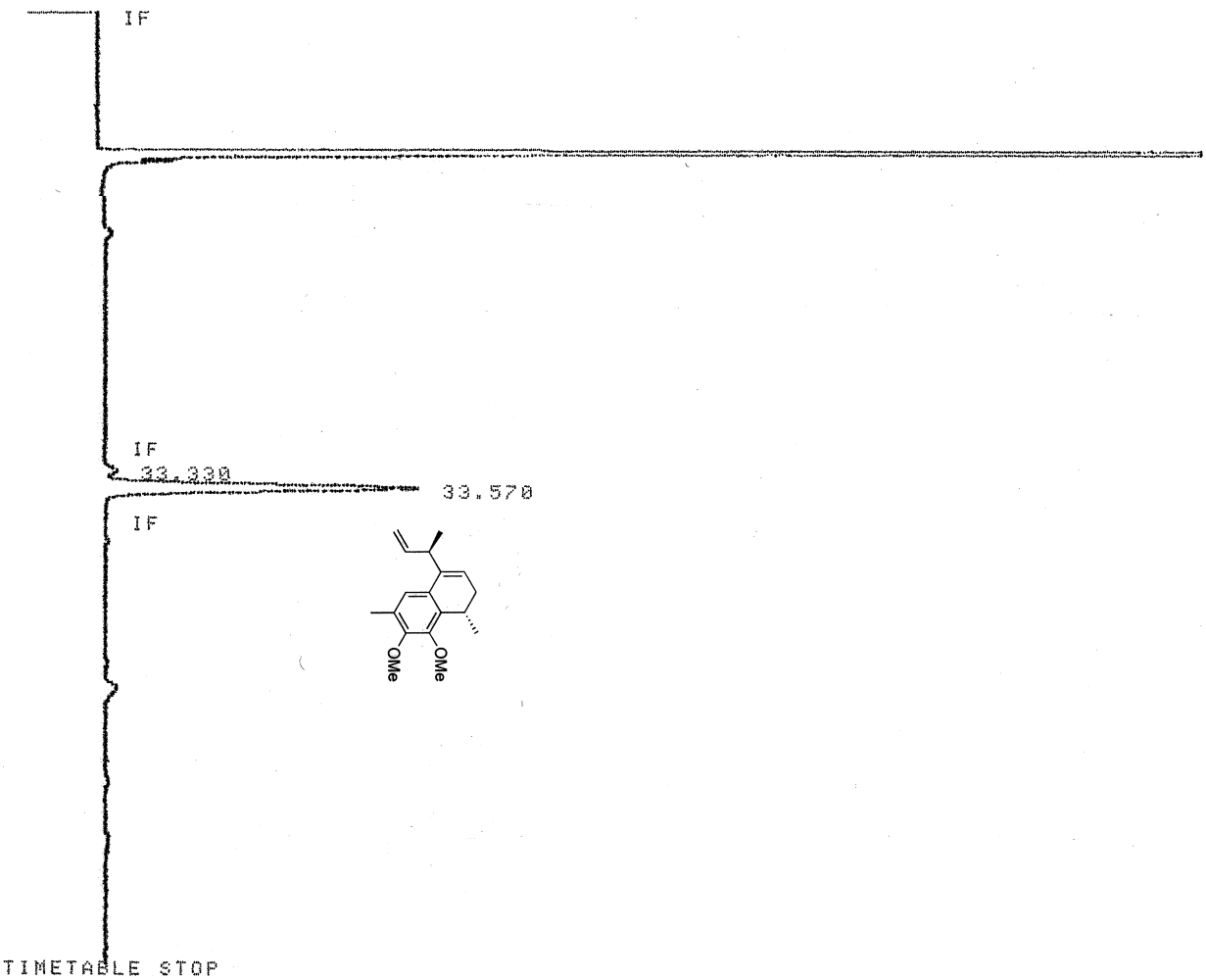
F2 - Processing parameters
SI 32768
SF 500.0200119 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



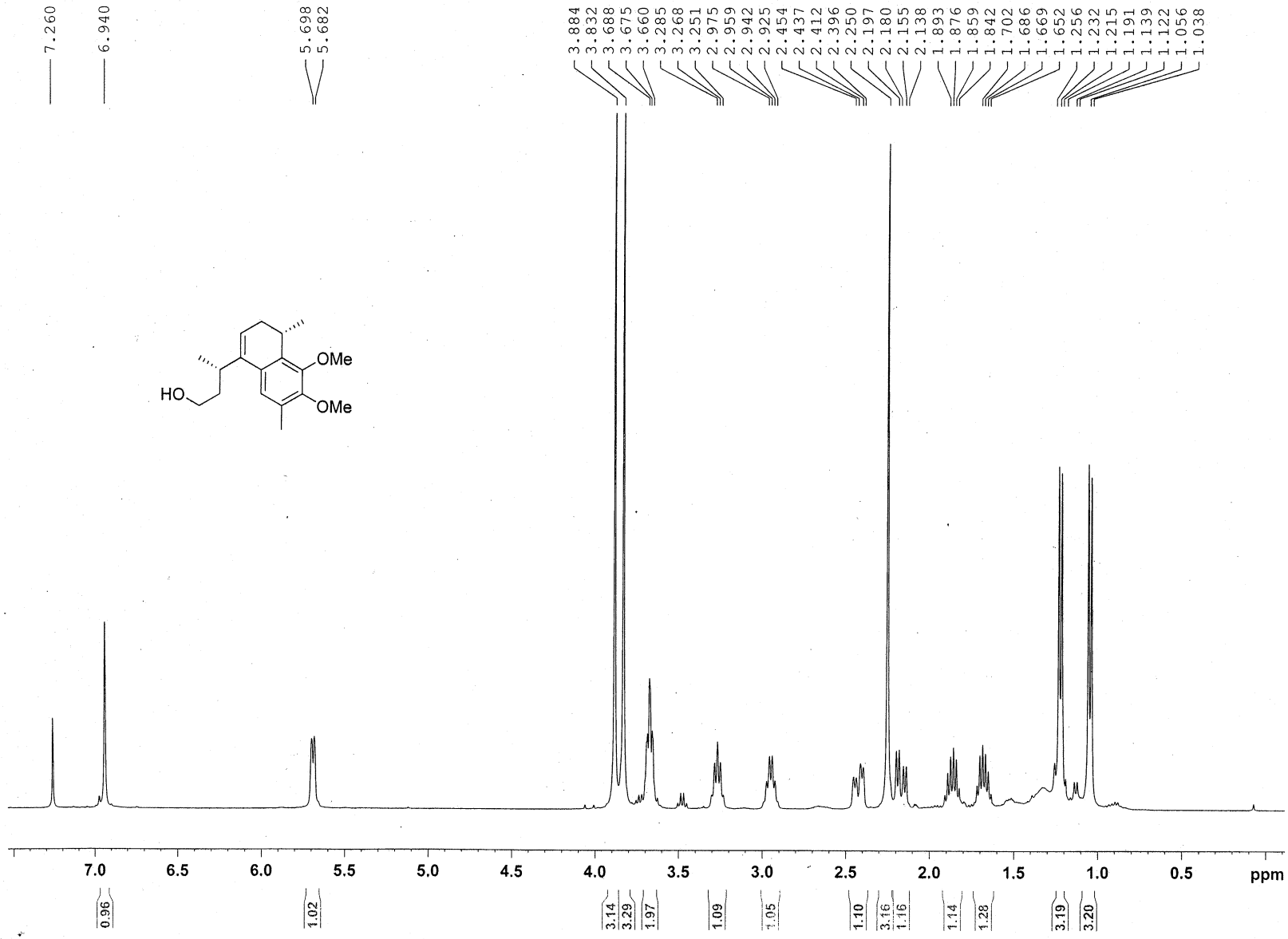
BRUKER

```
Current Data Parameters
NAME                  8-49
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20070702
Time                 8.13
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   285
DS                     4
SWH           30030.029 Hz
FIDRES         0.458222 Hz
AQ             1.0912244 sec
RG                1625.5
DW                16.650 usec
DE                 6.00 usec
TE                293.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                13.00 usec
PL1                3.00 dB
SFO1         125.7427020 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -1.00 dB
PL12              18.80 dB
PL13              22.50 dB
SFO2         500.0220001 MHz

F2 - Processing parameters
SI                 32768
SF           125.7301349 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.00
```

```
*  AR REJ 1000  @
*  DELETE  TIME   @

*  TIME .01  INTG # 9  @
*  TIME 33,0  INTG # -9  @
*  TIME 34  INTG # 9  @
*  TIME 40  STOP
*  LIST: TIME   @

   0.010 INTG # =  9
  33.000 INTG # = -9
  34.000 INTG # =  9
  40.000 STOP


*  RUN #  220      MAR 26, 1901  14:34:42
START
```




```
TIMETABLE STOP

Closing signal file M:SIGNAL  .BNC

RUN#   220          MAR 26, 1901  14:34:42

SIGNAL FILE: M:SIGNAL.BNC
AREA%
      RT       AREA TYPE  WIDTH       AREA%
  33.330       2339   PV   .120     3.53430
  33.570      63841   VV   .117    96.46570

TOTAL AREA=  66180
MUL FACTOR=1.0000E+00
```



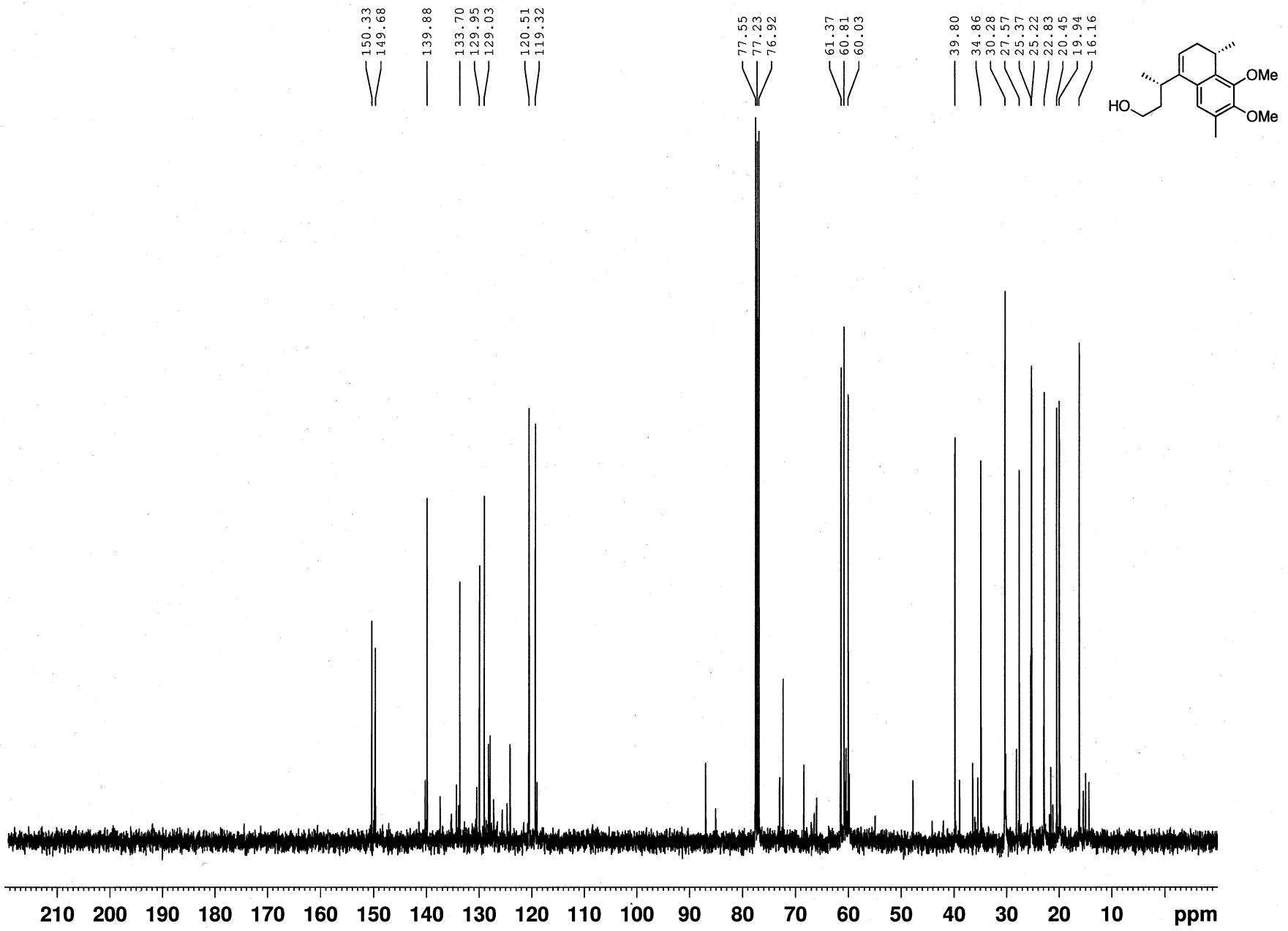
BRUKER

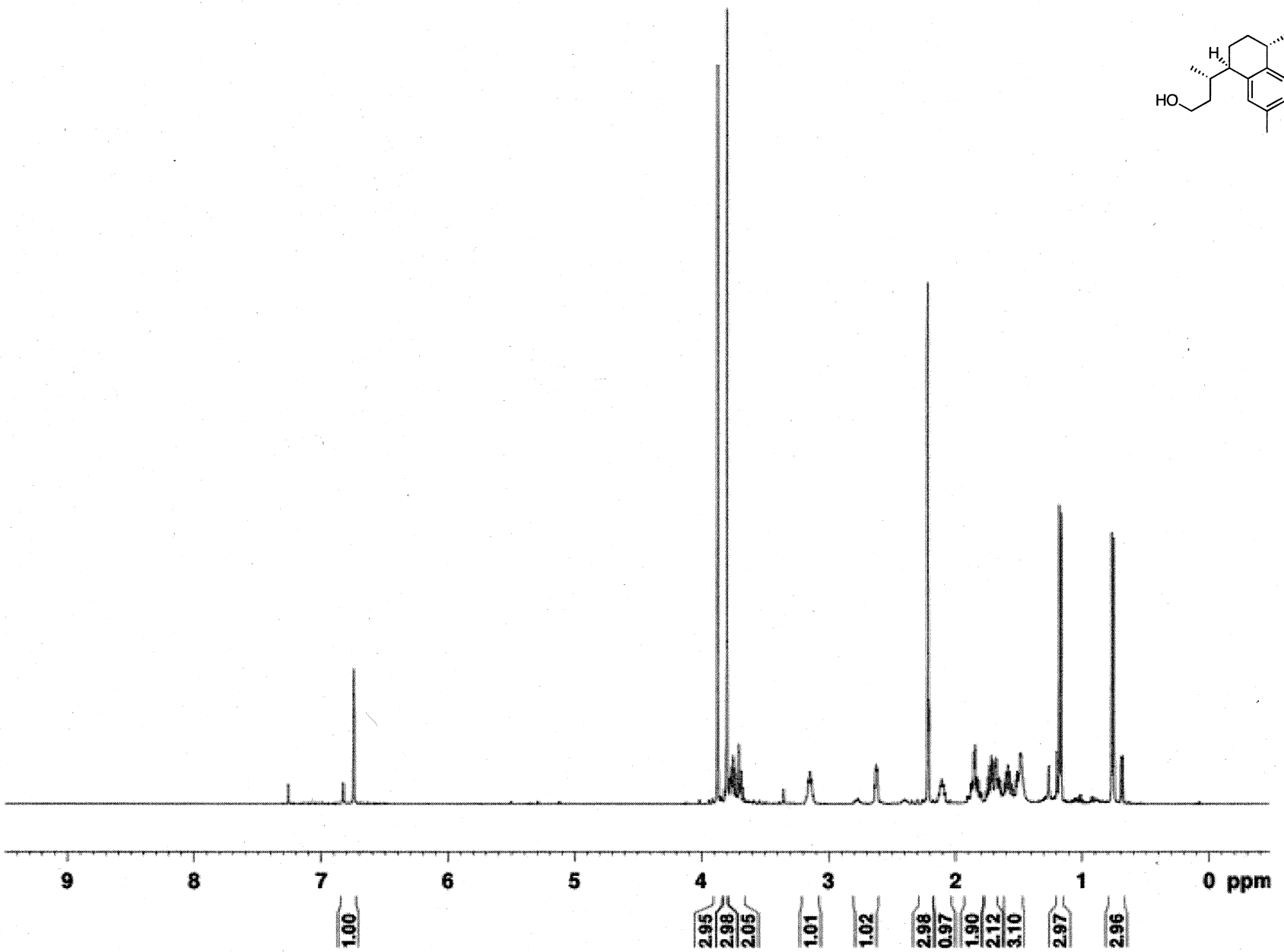
Current Data Parameters
NAME 8-265
EXPNO 9
PROCNO 1

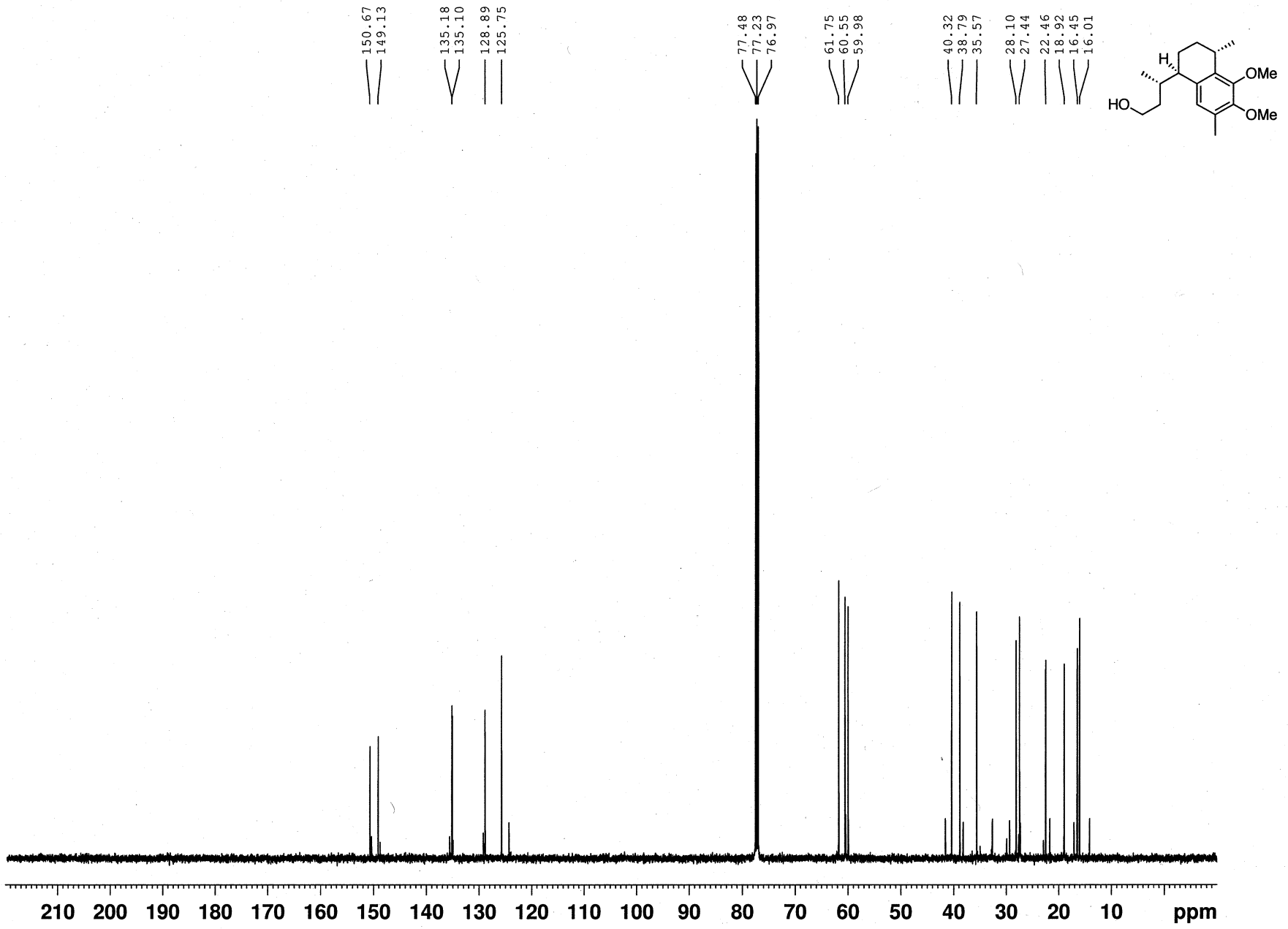
F2 - Acquisition Parameters
Date_ 20071015
Time 12.49
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 128
DW 60.400 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

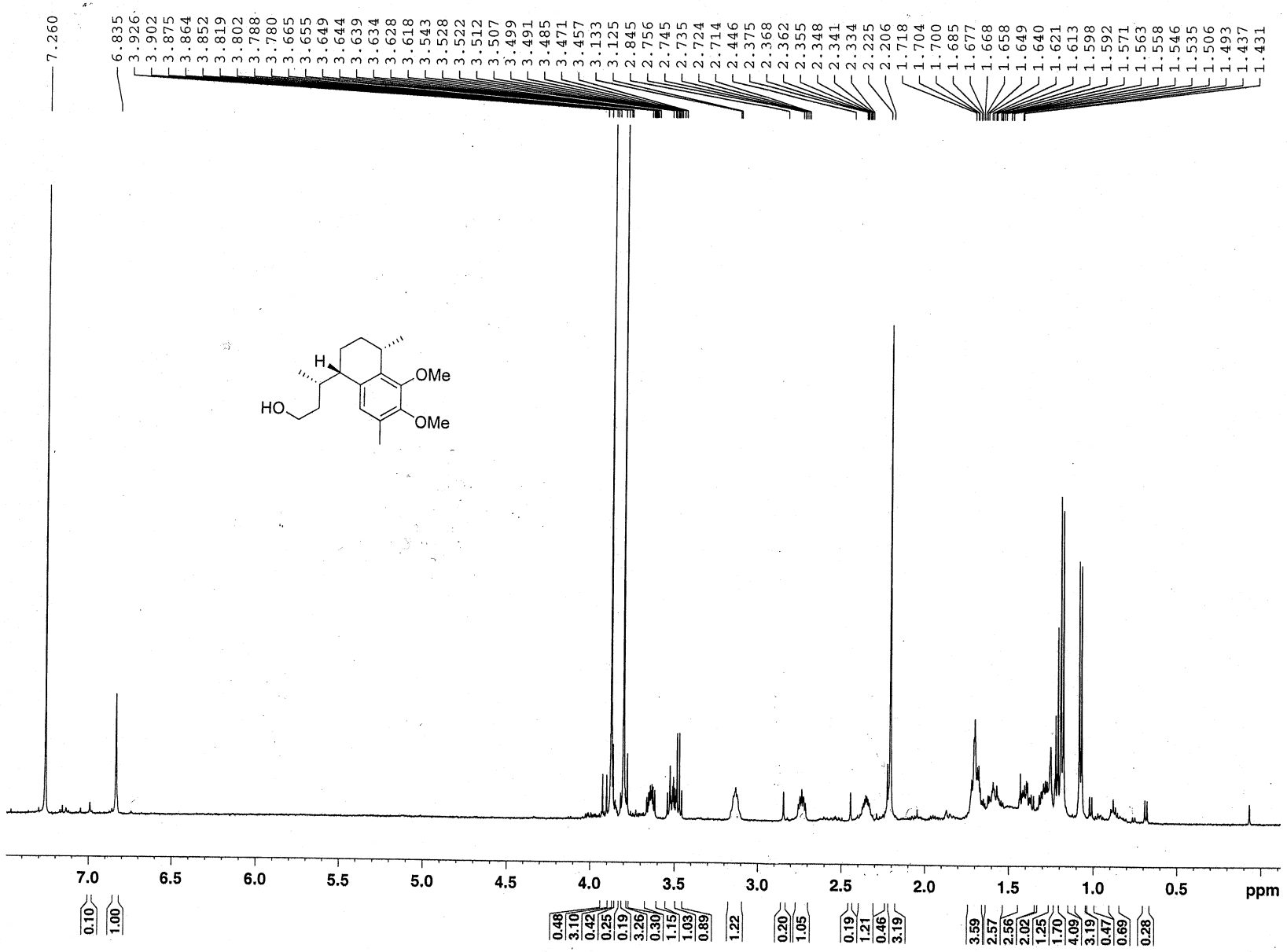
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300101 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

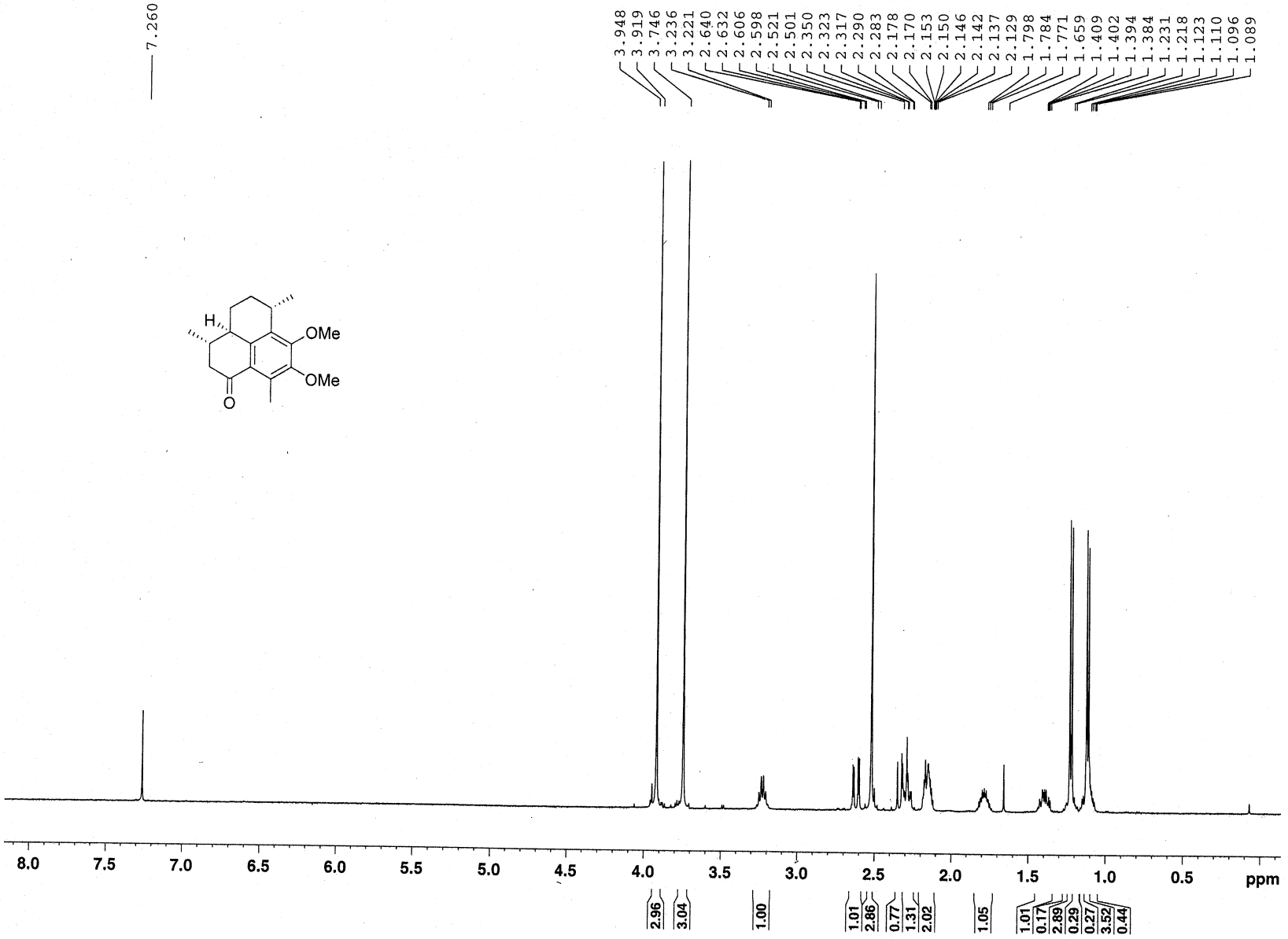

150.33
149.68
139.88
133.70
129.95
129.03
120.51
119.32
77.55
77.23
76.92
61.37
60.81
60.03
39.80
34.86
30.28
27.57
25.37
25.22
22.83
20.45
19.94
16.16
HO
OMe
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


H
OMe
OMe
HO
9
8
7
6
5
4
3
2
1
0 ppm
1.00
2.95
2.98
2.05
1.01
1.02
2.98
0.97
1.90
2.12
3.10
2.97
2.96

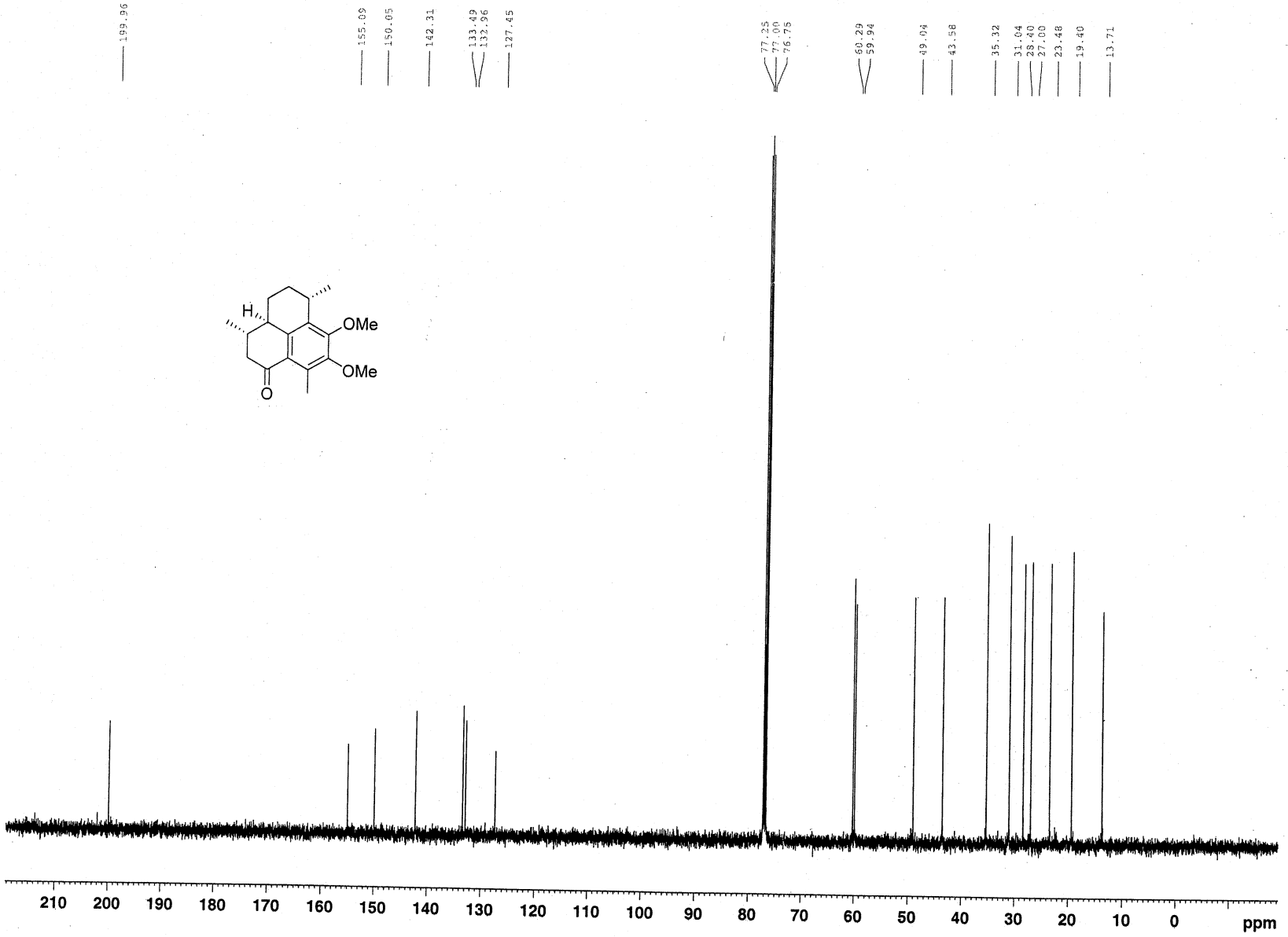

150.67
149.13
135.18
135.10
128.89
125.75
77.48
77.23
76.97
61.75
60.55
59.98
40.32
38.79
35.57
28.10
27.44
22.46
18.92
16.45
16.01
H
OMe
OMe
HO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm




```
Current Data Parameters
NAME                  7-157
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20070403
Time                  9.47
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH             10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719923 sec
RG                   645.1
DW                48.400 usec
DE                 6.00 usec
TE                295.2 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.80 usec
PL1                -1.00 dB
SFO1          500.0230878 MHz

F2 - Processing parameters
SI                    32768
SF            500.0200116 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```




```
Current Data Parameters
NAME                  8-283
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20071022
Time                 12.42
INSTRUM              spect
PROBHD   5 mm TXI 13C Z
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH             10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719923 sec
RG                    1024
DW                48.400 usec
DE                 6.00 usec
TE                295.2 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.70 usec
PL1                0.00 dB
SFO1          500.0230878 MHz

F2 - Processing parameters
SI                   32768
SF            500.0200110 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```



BRUKER

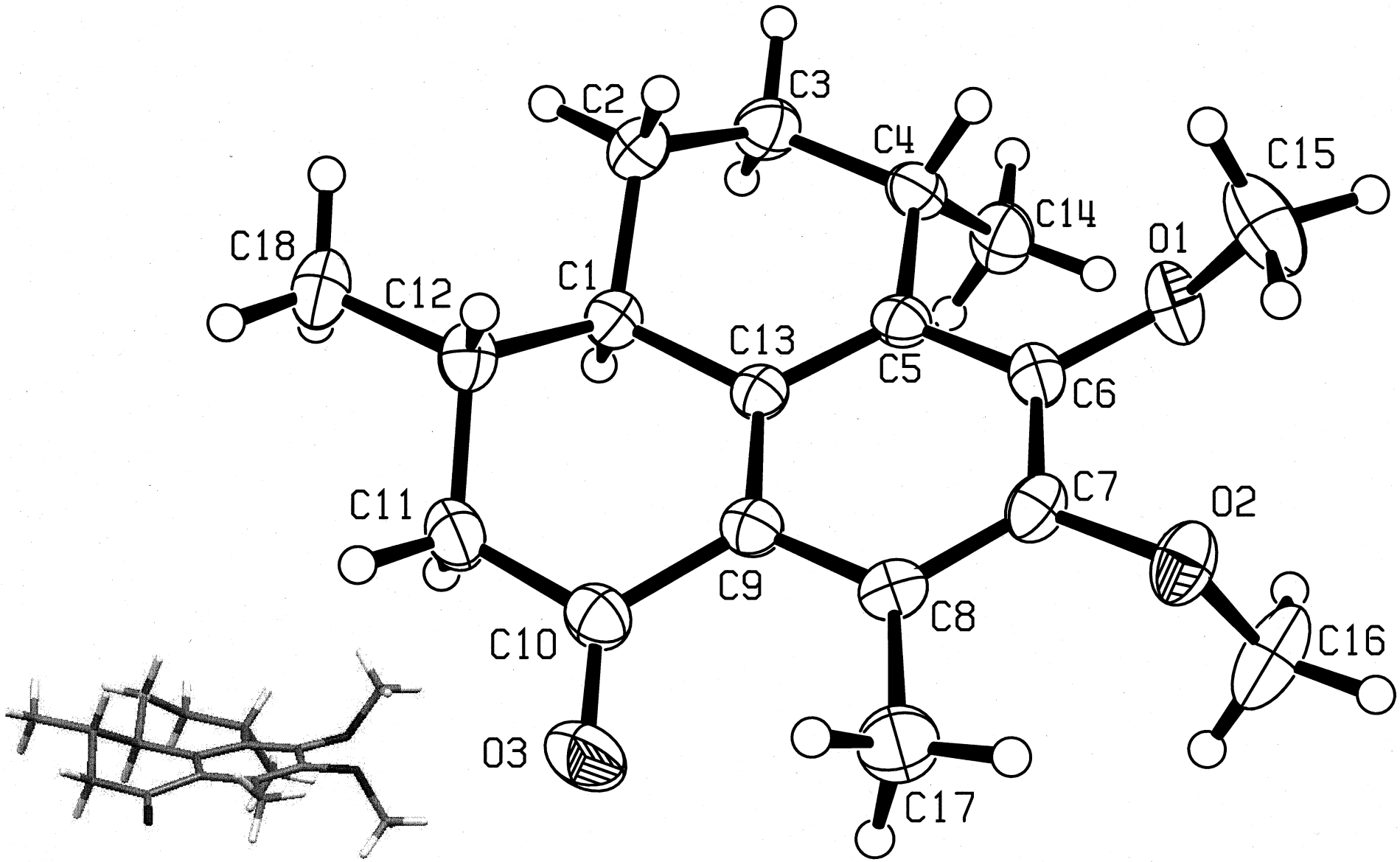
Current Data Parameters
NAME Tricyclic Ketone
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070815
Time 9.47
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 157
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912244 sec
RG 3649.1
DW 16.650 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

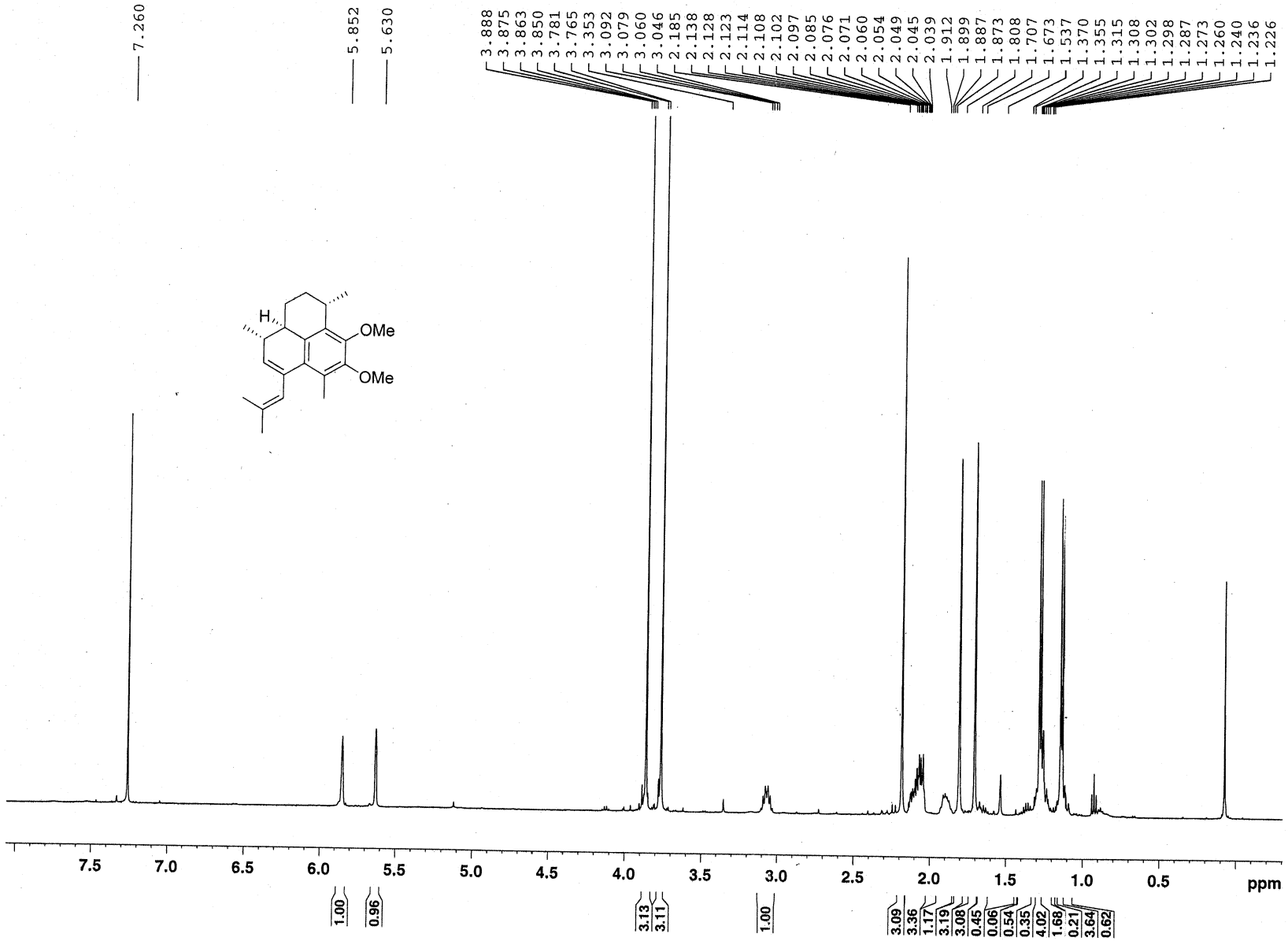
======== CHANNEL f1 ========
NUC1 13C
P1 13.00 usec
PL1 3.00 dB
SFO1 125.7427020 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -1.00 dB
PL12 18.80 dB
PL13 22.50 dB
SFO2 500.0220001 MHz

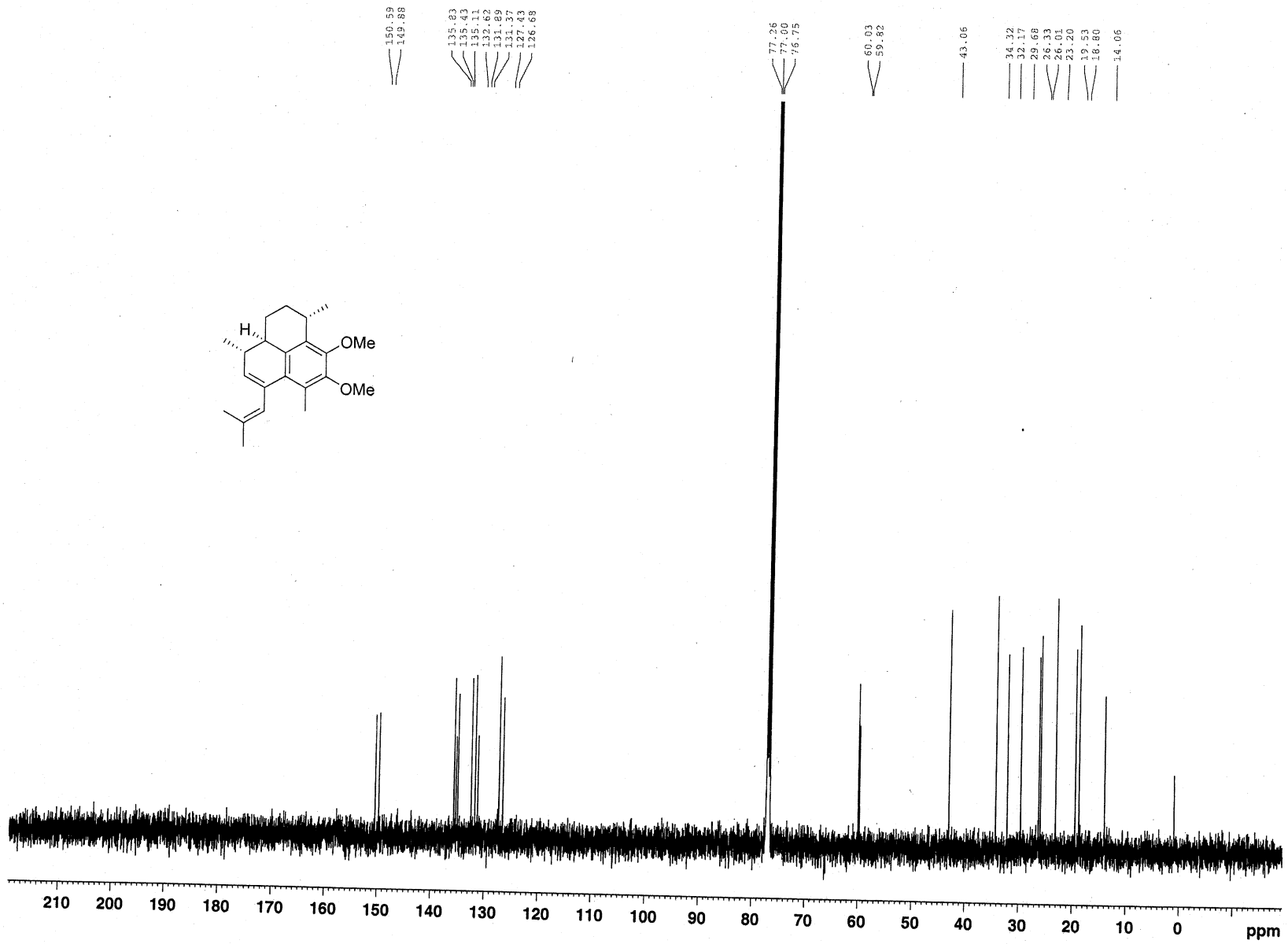
F2 - Processing parameters
SI 32768
SF 125.7301322 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



ORTEP diagram and Conformation of the Ketone 16




```
Current Data Parameters
NAME                  8-285
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20071024
Time                  2.37
INSTRUM              spect
PROBHD   5 mm TXI 13C Z
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               10330.578 Hz
FIDRES                0.157632 Hz
AQ                3.1719923 sec
RG                      181
DW                   48.400 usec
DE                    6.00 usec
TE                   300.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                    9.70 usec
PL1                   0.00 dB
SFO1          500.0230878 MHz

F2 - Processing parameters
SI                       32768
SF            500.0200113 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```



BRUKER

Current Data Parameters

NAME	8-285
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20071024
Time	2.44
INSTRUM	spect
PROBHD	5 mm TXI 13C Z
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8873
DS	4
SWH	30030.029 Hz
FIDRES	0.458222 Hz
AQ	1.0912244 sec
RG	4096
DW	16.650 usec
DE	6.00 usec
TE	300.2 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

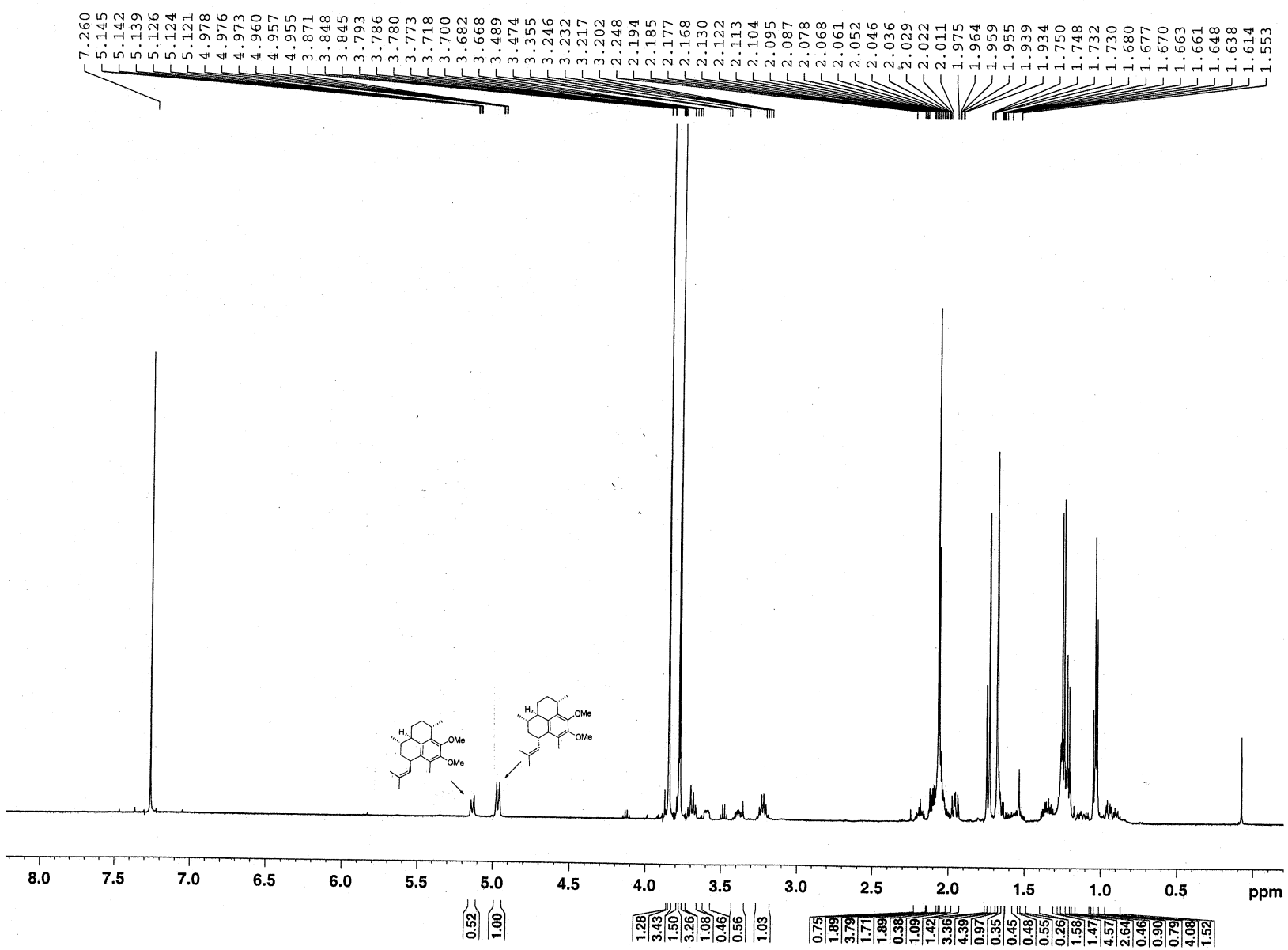
NUC1	13C
P1	14.20 usec
PL1	0.00 dB
SFO1	125.7427020 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	-1.00 dB
PL12	15.59 dB
PL13	22.50 dB
SFO2	500.0220001 MHz

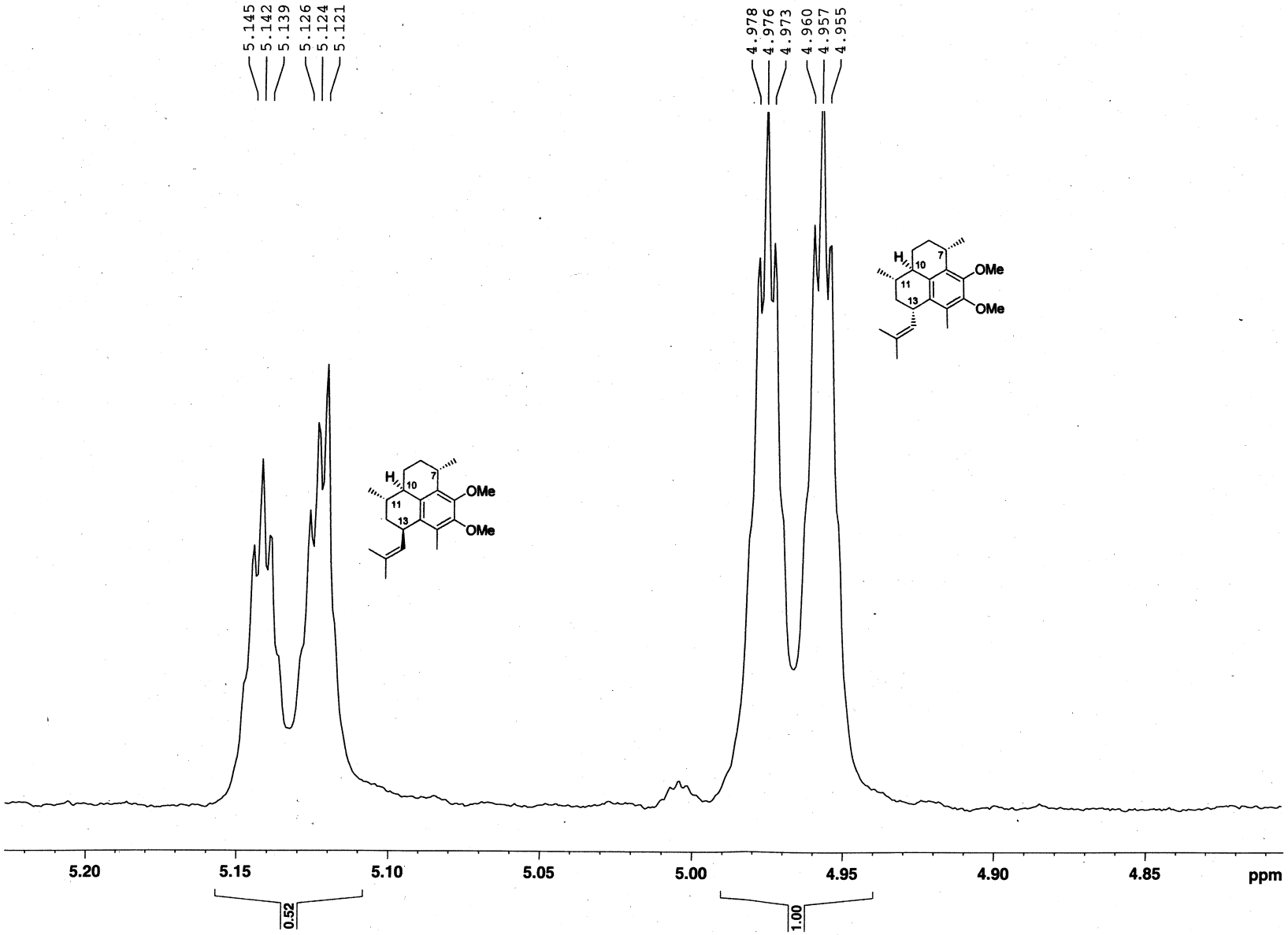
F2 - Processing parameters

SI	32768
SF	125.7301285 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

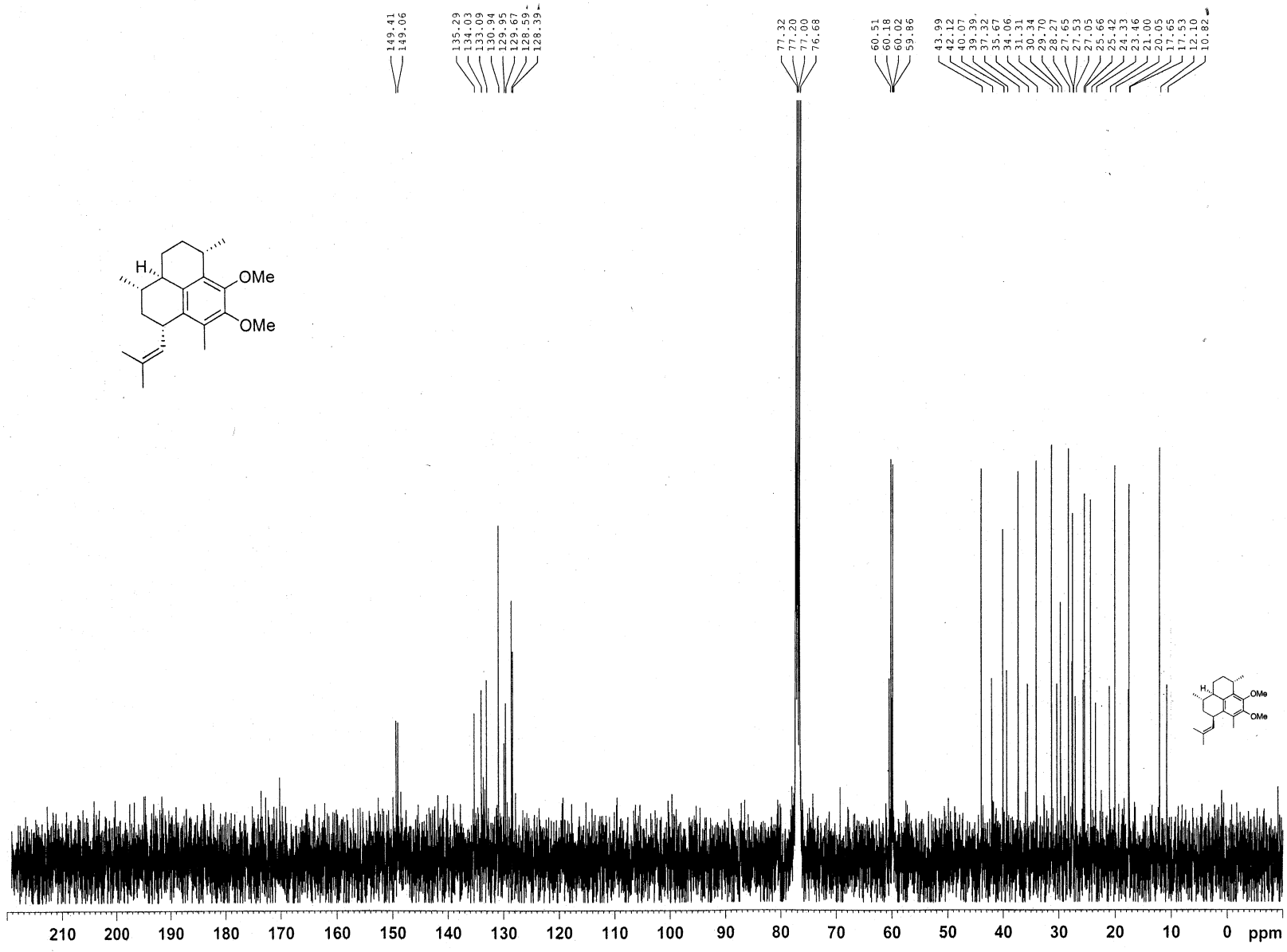


BRUKER

```
Current Data Parameters
NAME                  8-287
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20071024
Time                 23.55
INSTRUM              spect
PROBHD   5 mm TXI 13C Z
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ                3.1719923 sec
RG                   161.3
DW                  48.400 usec
DE                   6.00 usec
TE                  300.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    9.70 usec
PL1                   0.00 dB
SFO1          500.0230878 MHz

F2 - Processing parameters
SI                    32768
SF            500.0200110 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```

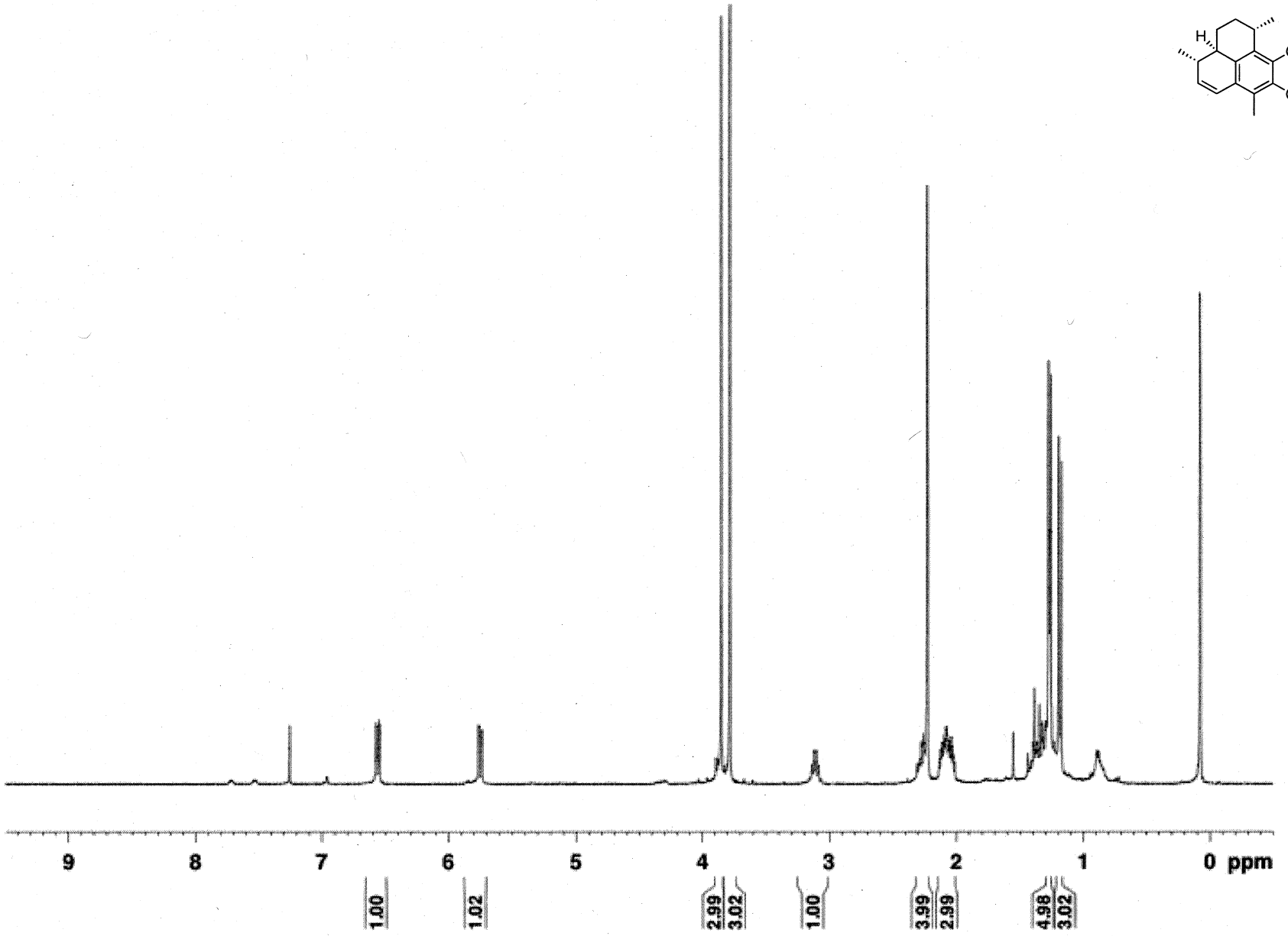


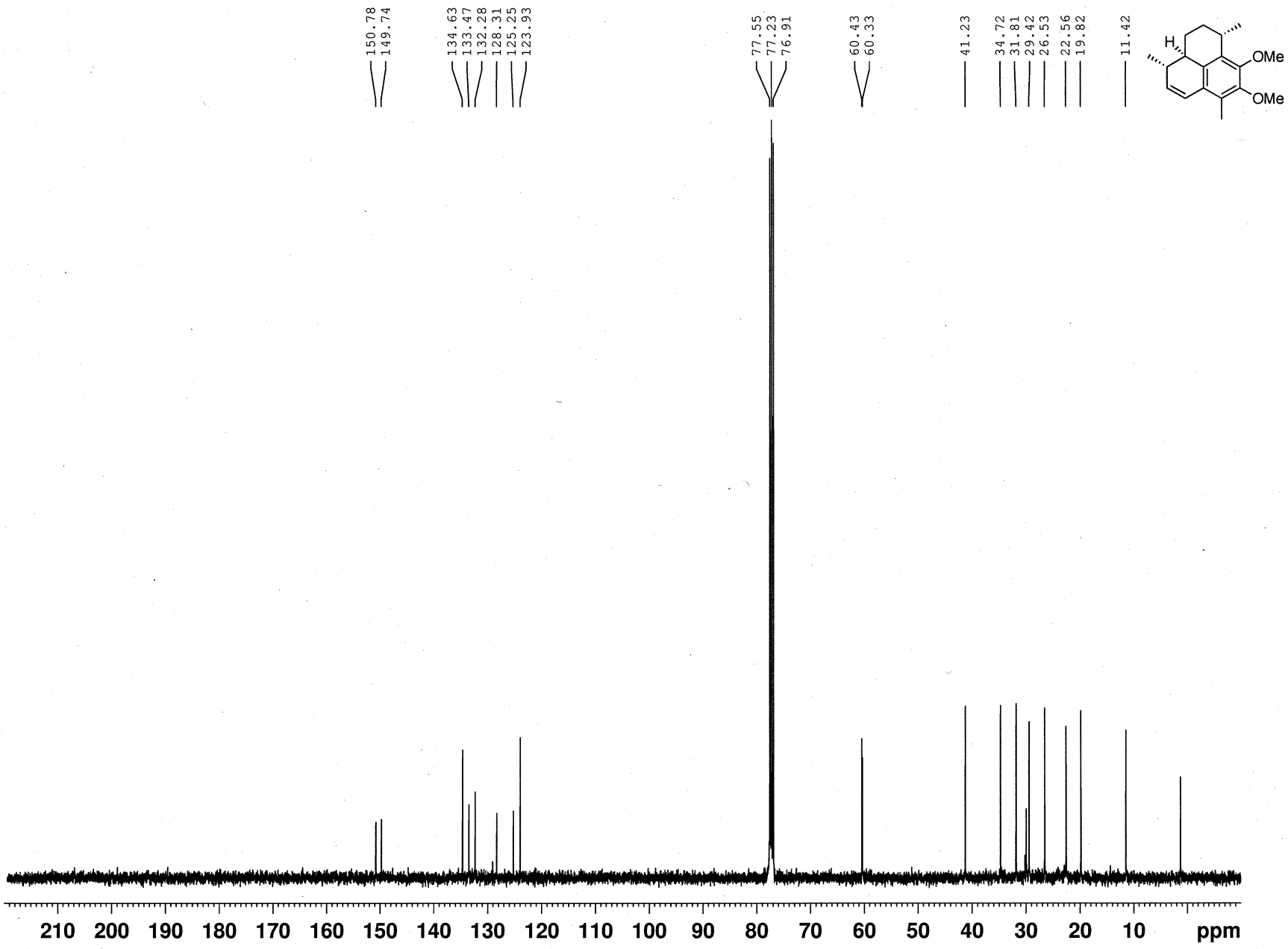

```
Current Data Parameters
NAME                  8-287
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20071024
Time                 23.55
INSTRUM              spect
PROBHD   5 mm TXI 13C Z
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              10330.578 Hz
FIDRES           0.157632 Hz
AQ               3.1719923 sec
RG                   161.3
DW                  48.400 usec
DE                   6.00 usec
TE                  300.2 K
D1               1.00000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   9.70 usec
PL1                  0.00 dB
SFO1          500.0230878 MHz

F2 - Processing parameters
SI                   32768
SF            500.0200110 MHz
WDW                     EM
SSB                      0
LB                   0.30 Hz
GB                       0
PC                    1.00
```



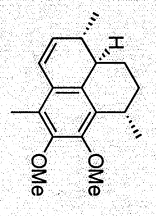
BRUKER

```
Current Data Parameters
NAME                  8-287
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20071030
Time                  22.24
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              23980.814 Hz
FIDRES             0.365918 Hz
AQ                1.3664756 sec
RG                     8192
DW                   20.850 usec
DE                    6.00 usec
TE                     0.0 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                   10.50 usec
PL1                   0.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -6.00 dB
PL12                 14.56 dB
PL13                 16.50 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                     32768
SF            100.6127693 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                      1.00
```

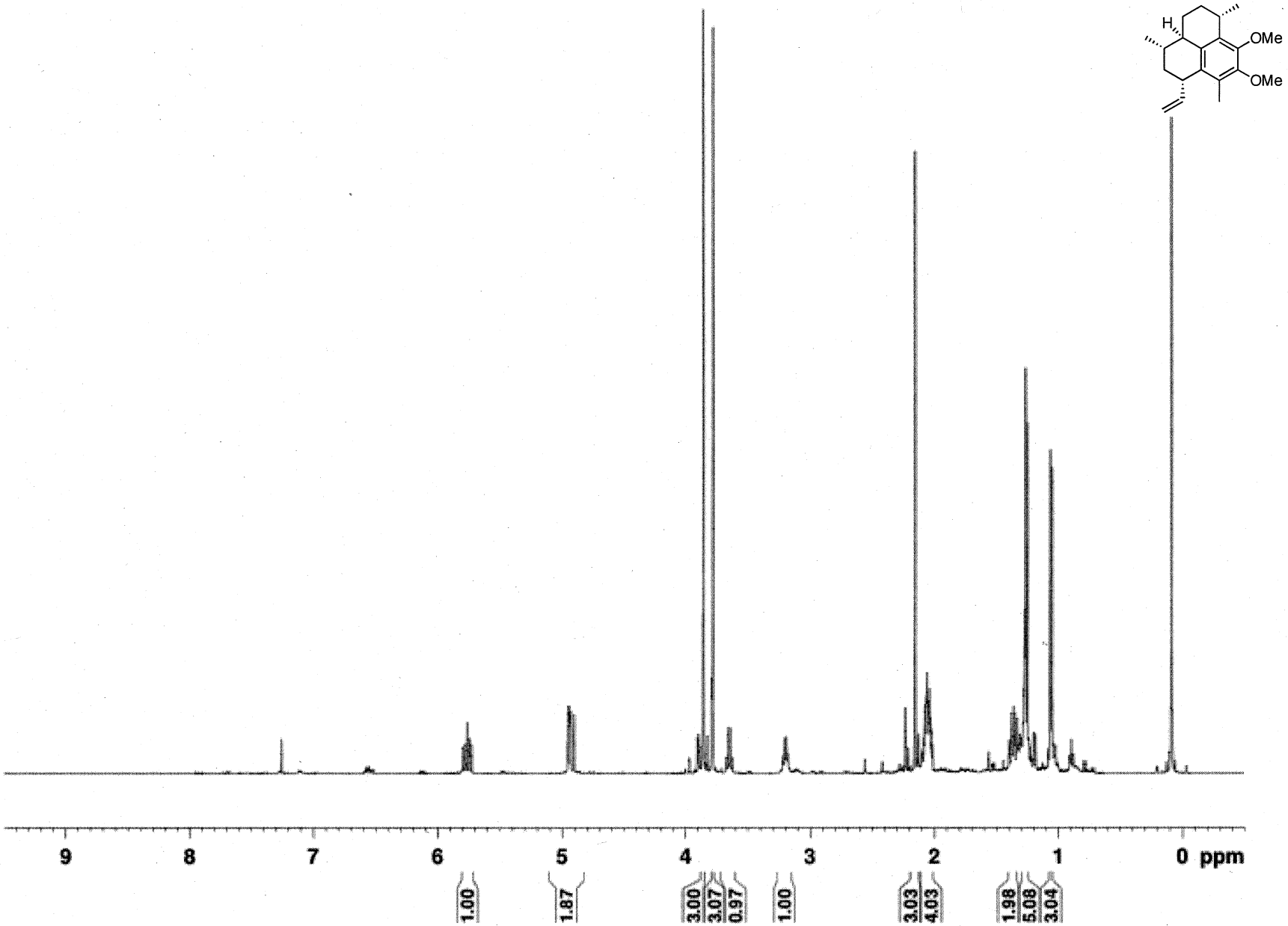

H
OMe
OMe
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.02
2.99
3.02
1.00
3.99
2.99
4.98
3.02

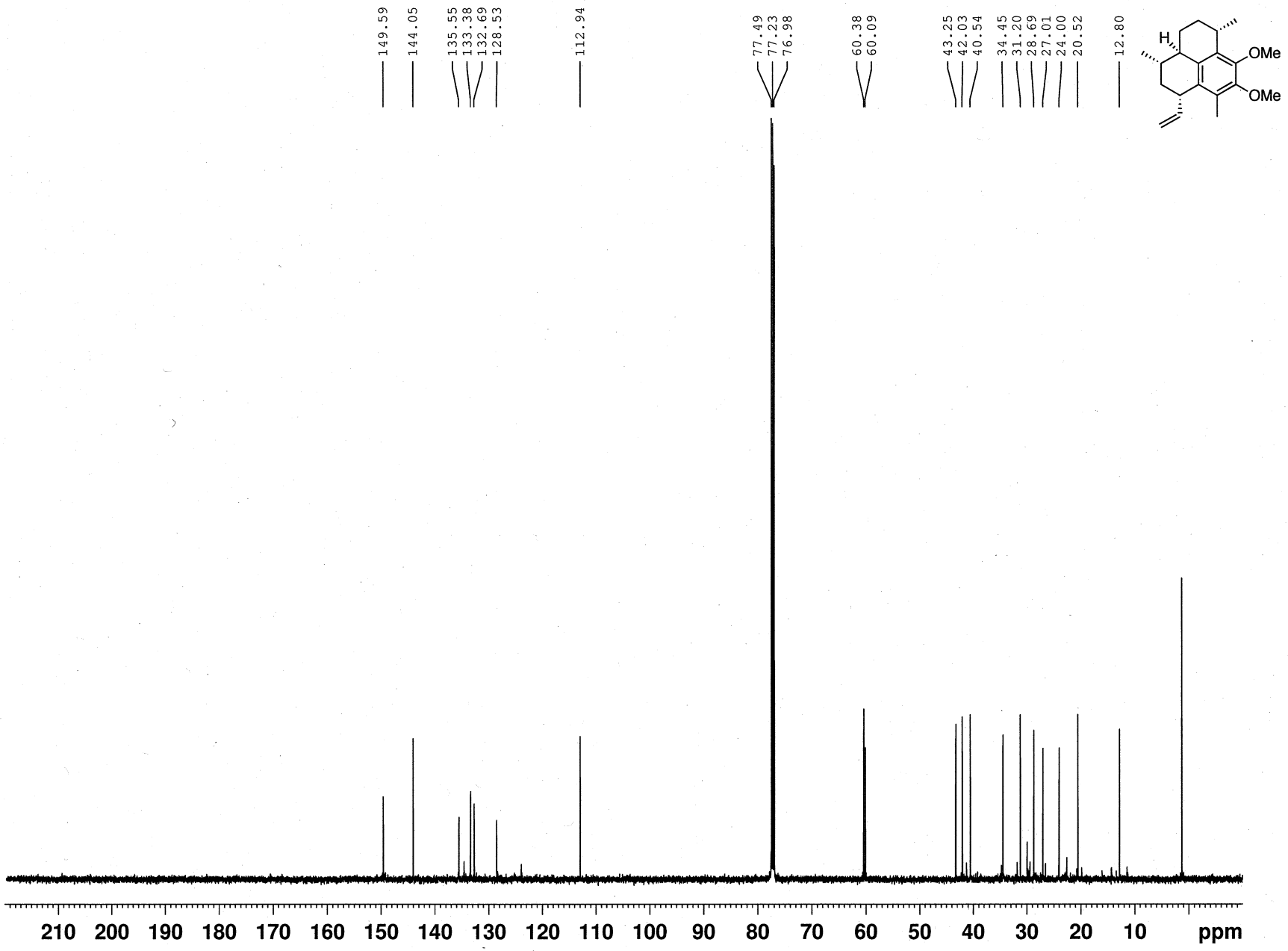

150.78
149.74
134.63
133.47
132.28
128.31
125.25
123.93
77.55
77.23
76.91
60.43
60.33
41.23
34.72
31.81
29.42
26.53
22.56
19.82
11.42
H
OMe
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

```
*  RUN #  276      FEB 27, 1901  13:22:07
START
        IF
        IF
                                                    28.444
TIMETABLE STOP
```

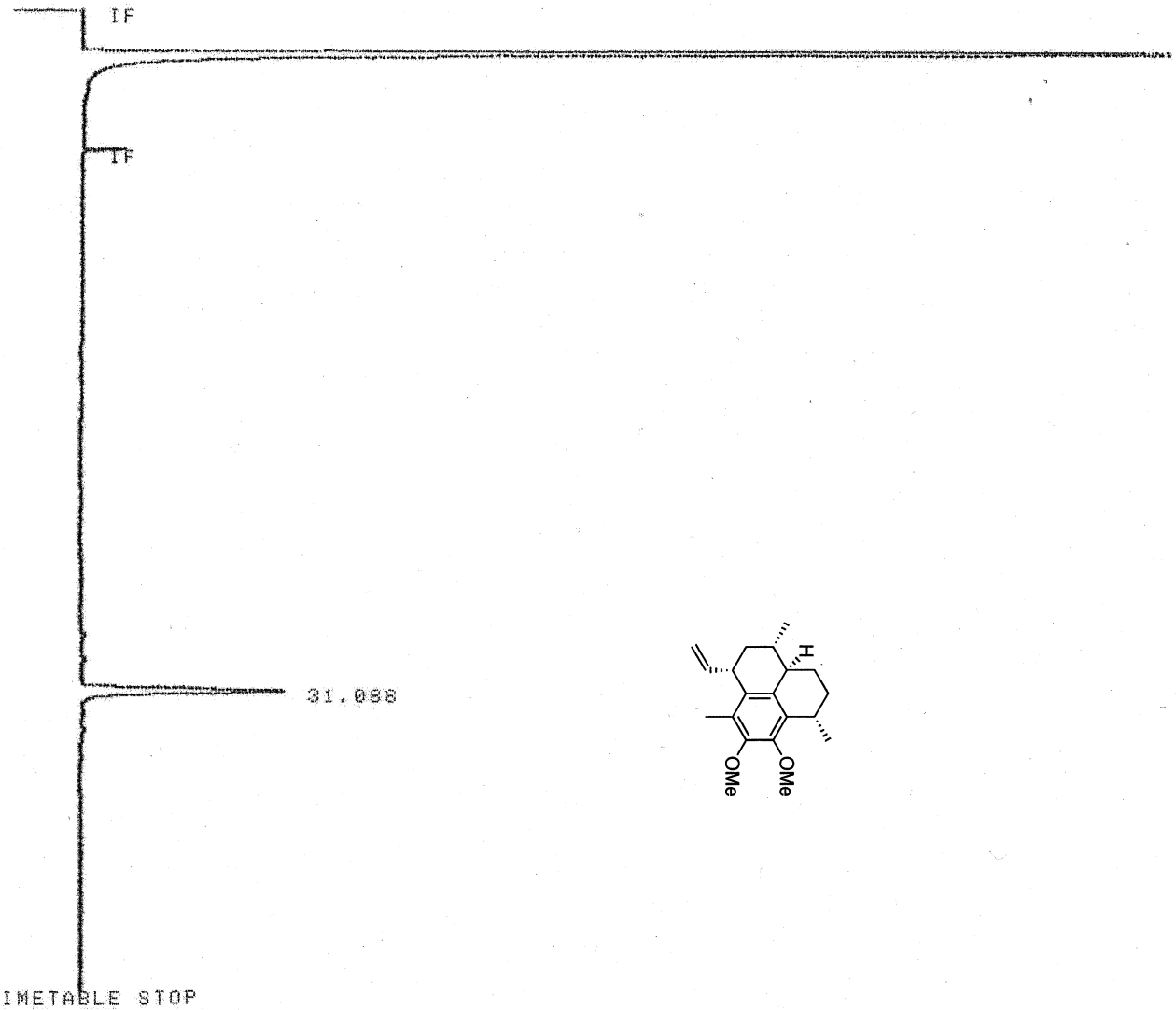



```
RUN#   276           FEB 27, 1901  13:22:07

AREA%
      RT       AREA TYPE  WIDTH       AREA%
  28.444     145537   BP    .240   100.00000

TOTAL AREA= 145537
MUL FACTOR=1.0000E+00
```


H
OMe
OMe
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.87
3.00
3.07
0.97
1.00
3.03
4.03
1.98
5.08
3.04

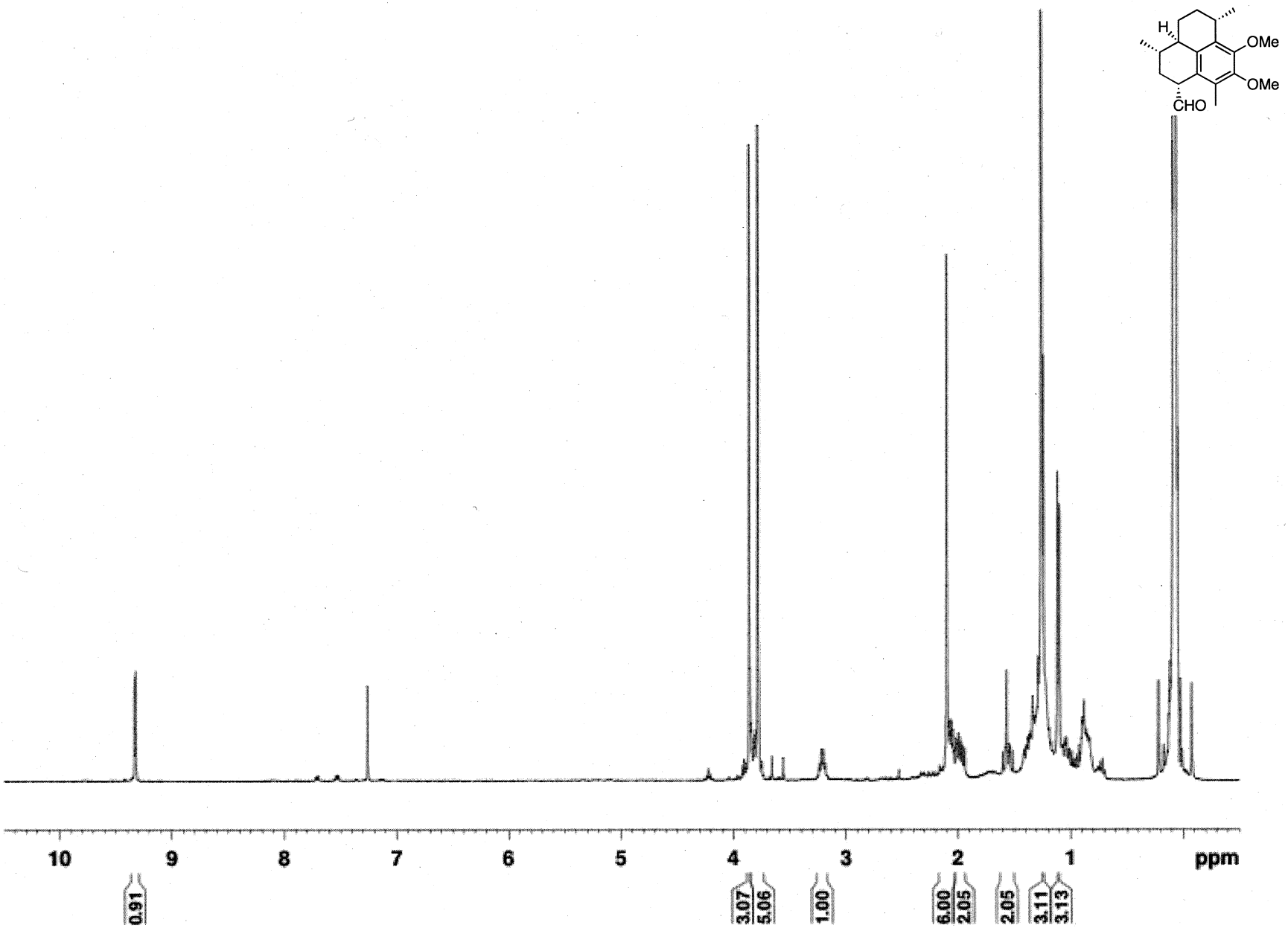

149.59
144.05
135.55
133.38
132.69
128.53
112.94
77.49
77.23
76.98
60.38
60.09
43.25
42.03
40.54
34.45
31.20
28.69
27.01
24.00
20.52
12.80
H
OMe
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

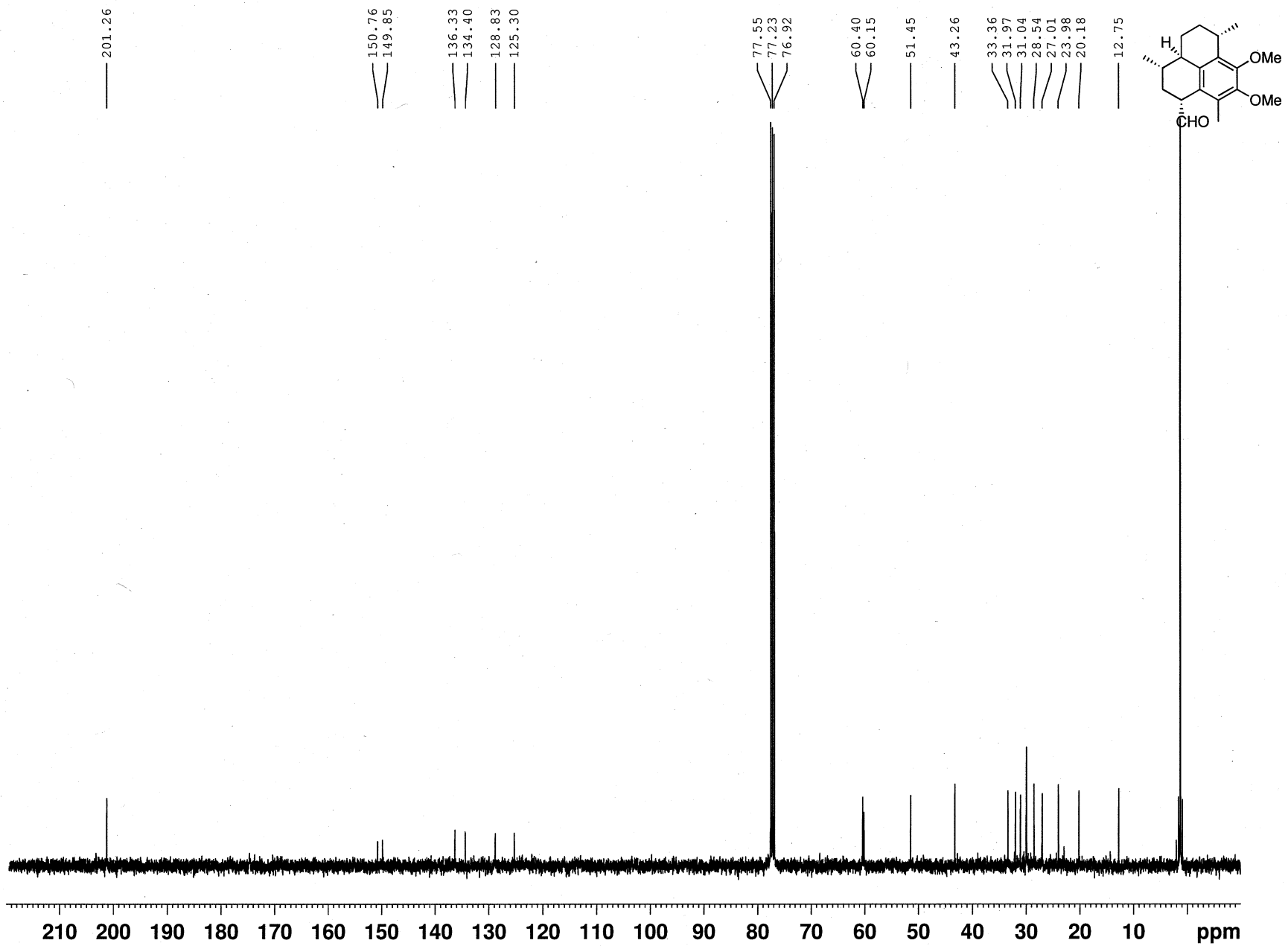
```
*  RUN #  377      MAR 12, 1901  13:33:55
START
```

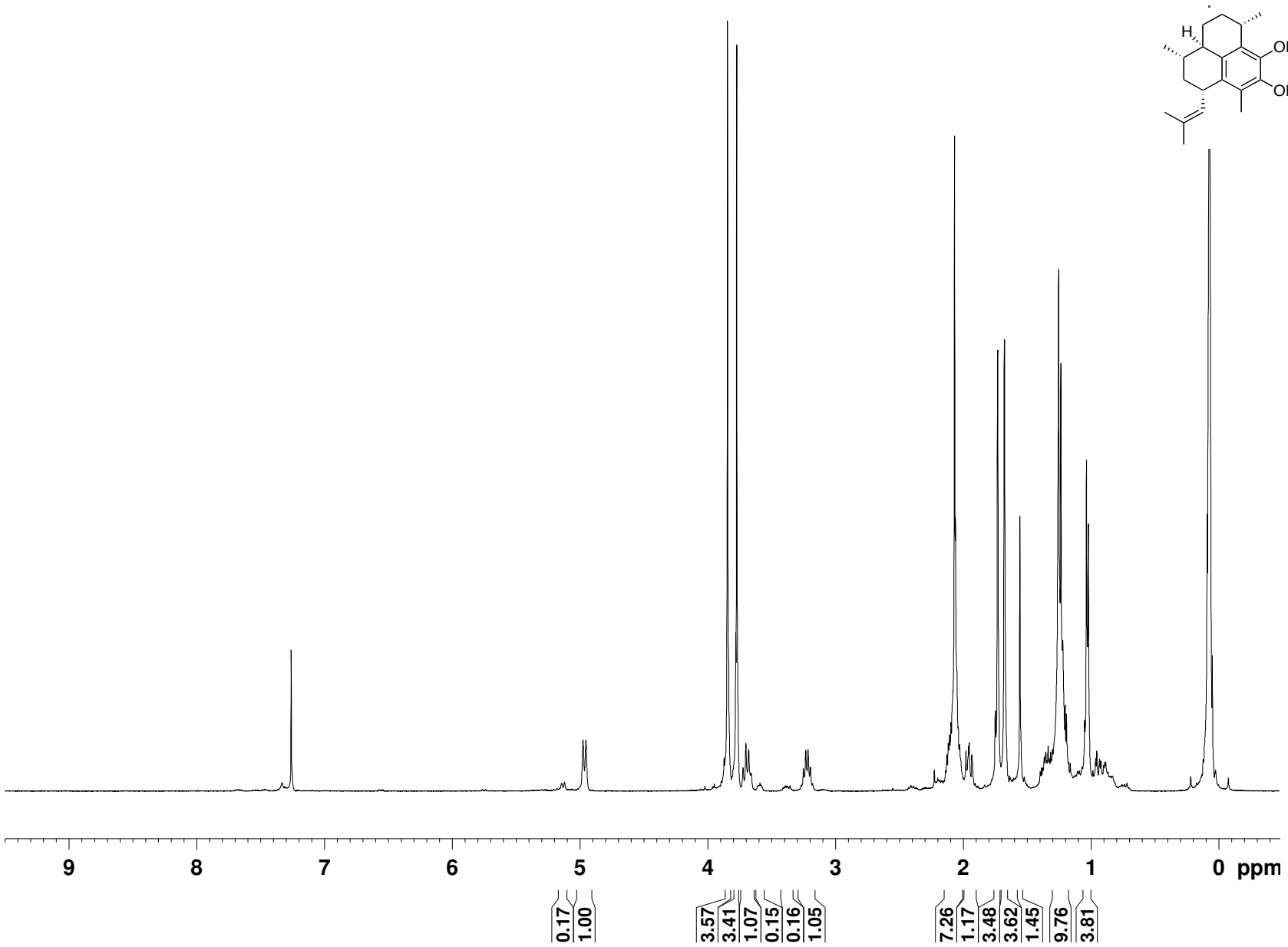


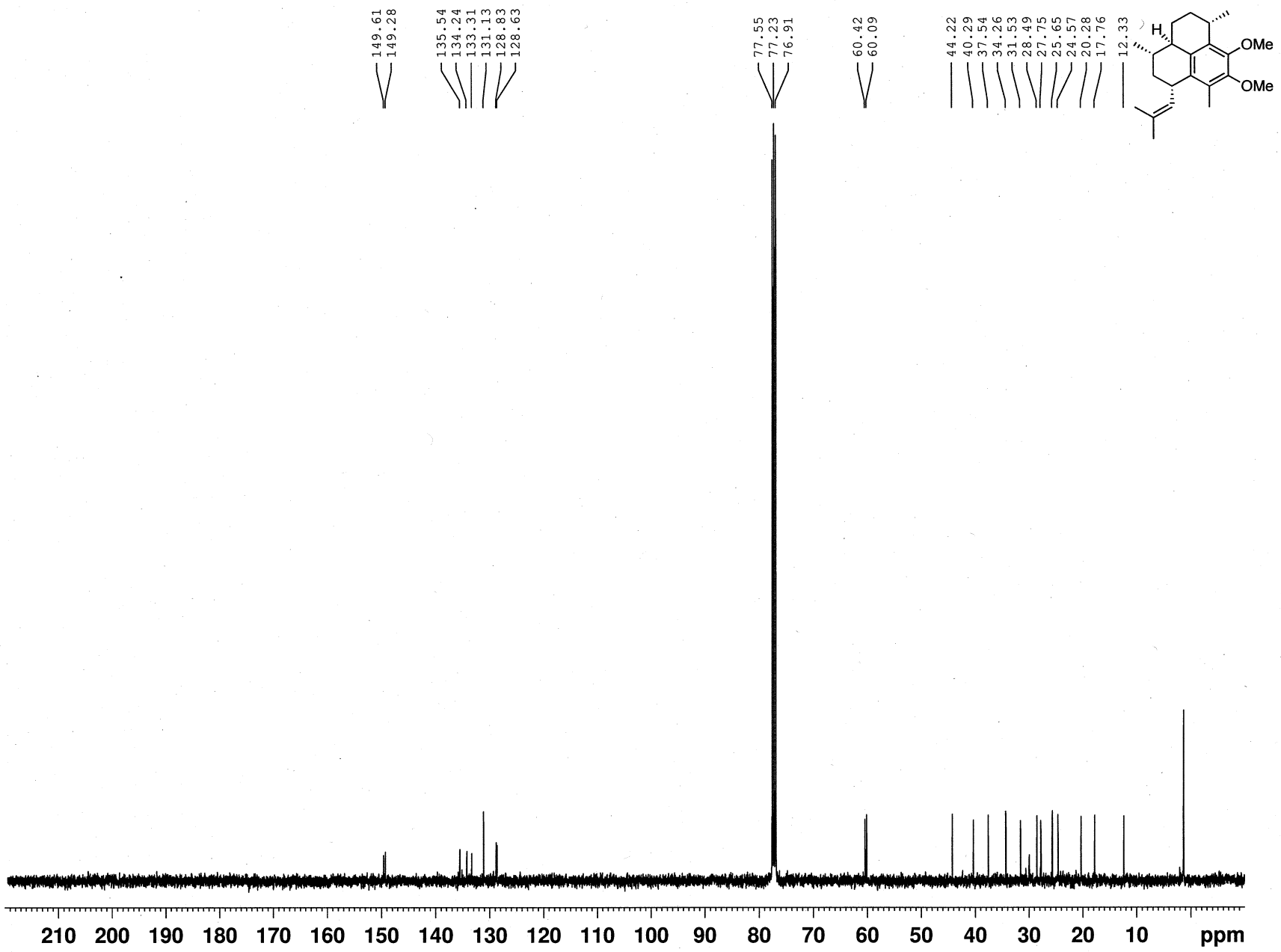

```
TIMETABLE STOP
```

```
RUN#   377          MAR 12, 1901  13:33:55

AREA%
      RT       AREA TYPE  WIDTH       AREA%
  31.088     200559   BV    .278   100.00000

TOTAL AREA=  200559
MUL FACTOR=1.0000E+00
```


H
OMe
OMe
CHO
10
9
8
7
6
5
4
3
2
1
ppm
0.91
3.07
5.06
1.00
6.00
2.05
2.05
3.11
3.13


201.26
150.76
149.85
136.33
134.40
128.83
125.30
77.55
77.23
76.92
60.40
60.15
51.45
43.26
33.36
31.97
31.04
28.54
27.01
23.98
20.18
12.75
H
OMe
OMe
CHO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


H
OMe
OMe
9
8
7
6
5
4
3
2
1
0 ppm
0.17
1.00
3.57
3.41
1.07
0.15
0.16
1.05
7.26
1.17
3.48
3.62
1.45
9.76
3.81


149.61
149.28
135.54
134.24
133.31
131.13
128.83
128.63
77.55
77.23
76.91
60.42
60.09
44.22
40.29
37.54
34.26
31.53
28.49
27.75
25.65
24.57
20.28
17.76
12.33
H
OMe
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm