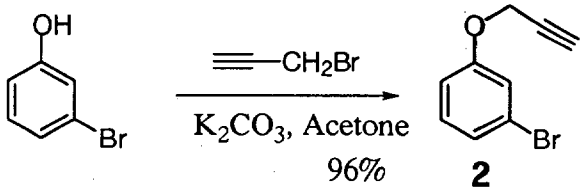
Experimental Section

All melting points and boiling points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a JEOL LA-400 (400 MHz for ^1H and 100 MHz for ^{13}C NMR analysis) spectrometer. All NMR spectra were taken in $CDCl_3$ solutions and are reported in parts per million (δ) downfield from TMS, which was used as an internal standard. The FT-IR spectra (cm^{-1}) were measured with a JASCO Model FT/IR-5300 Fourier transform infrared spectrophotometer. High-resolution mass spectra were obtained with a JEOL HX-100 spectrometer. Optical rotations were measured on a JASCO DIP-370 polarimeter. TLC was conducted by using Merck precoated kieselgel 60F-254 plates (0.25 mm). Preparative TLC was carried out on 2-mm-thick Merck kieselgel 60PF-254. Column chromatography was done on Wakogel C-300 and, for flash chromatography, Merck kieselgel (230-400 mesh) was employed.

All reactions were performed in an oven-dried glassware under a positive pressure of N_2 or Ar. Air- and moisture-sensitive compounds were introduced via syringe or cannula through a rubber septum. All solvents were dried immediately before use. Et_2O, THF, and toluene were distilled from sodium/benzophenone ketyl; $BF_3{\cdot}OEt_2$, Et_3N, $PhNEt_2$, CH_2Cl_2, CH_3CN, and DMF were distilled from CaH_2.

3-Bromophenyl Propargyl Ether (2).



2

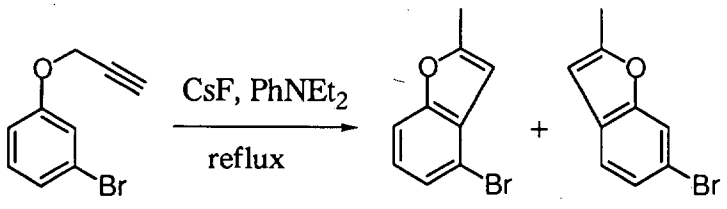
A mixture of 3-bromophenol (1.50 g, 8.7 mmol), propargyl bromide (1.15mL, 13 mmol), and K_2CO_3 (1.94 g, 14 mmol) in acetone (15 mL) was refluxed for 1.5 h. The mixture was filtered and diluted with Et_2O. The organic layer was washed with 5M NaOH and brine, dried (Na_2SO_4), and concd *in vacuo*. The crude product was purified by column chromatography (hexane / AcOEt, 6 : 1) to give **2** (1.76 g, 96%) as a colorless oil.

2: Colorless oil; R_f 0.52 (hexane / AcOEt = 5 : 1).

FTIR (neat) ν 3297, 2124, 1589, 1476, 1219, 1030; ^1H NMR (400 MHz, $CDCl_3$) δ 2.54 (1H, t, J = 2.4 Hz), 4.68 (2H, d, J = 2.4 Hz), 6.92 (1H, dt, J = 7.3, 2.0 Hz), 7.11-7.19 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 76.0, 77.9, 113.7, 118.2, 122.6, 124.6, 130.5, 158.1; MS *m/z* (rel intensity) 211 (M^+ + 1, 100), 170 (8), 132 (37), 102 (17), 91 (4), 41 (17), 32 (12).

HRMS calcd for C_9H_7BrO + H 210.9740, found 210.9759.

Preparation of Bromobenzofuran Derivatives 3 and 4.



2 → 3 + 4

72% (72 : 28)

A mixture of 2 (27.4 g, 0.13 mol) and CsF (25.6 g, 0.168 mol) in $PhNEt_2$ (130 mL) was refluxed overnight. After filtration through Celite, the filtrate was diluted with Et_2O and washed with 5% HCl. The aqueous phase was reextracted with Et_2O and the combined extracts were washed with brine, dried (Na_2SO_4), and concd *in vacuo*. The crude product was purified by column chromatography (hexane to hexane / Et_2O = 4:1) to give 3 and 4 (72 : 28 ratio by GC; 21.8 g, 72%) as an inseparable mixture.

3: Colorless oil; R_f 0.38 (hexane); Bp 84-87 °C / 4 mmHg.

FTIR (neat) ν 1603, 1578, 1472, 1424, 1258, 1165, 907, 768; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (3H, s), 6.42 (1H, t, J = 1.0 Hz), 7.06 (1H, t, J = 8.1 Hz), 7.32, 7.34 (each 1H, dd, J = 8.1, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 102.8, 109.7, 112.9, 124.0, 125.4, 130.6, 154.4, 156.2; MS *m/z* (rel intensity) 212 (M^++ 2, 99), 210 (M^+, 100), 131 (42), 103 (25), 77 (36), 66 (36), 51 (81).

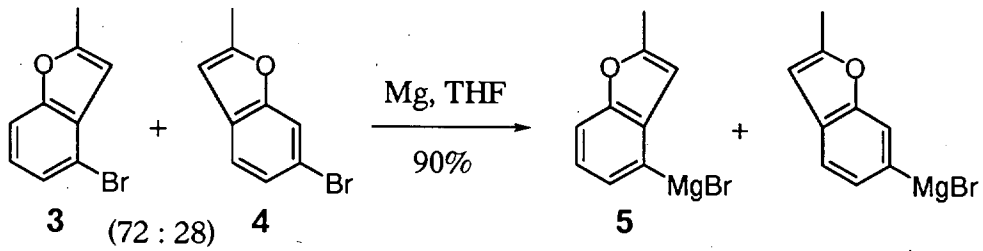
HRMS calcd for C_9H_7BrO 209.9680, found 209.9673.

4: Colorless plates; R_f 0.38 (hexane); Mp 29.0-29.5 °C; Bp 72-75 °C / 4 mmHg.

FTIR (KBr) ν 1605, 1464, 1420, 1289, 937, 820; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (3H, s), 6.32 (1H, t, J = 0.7 Hz), 7.28 (1H, ddd, J = 8.3, 1.4, 0.7 Hz), 7.30 (1H, d, J = 8.3 Hz), 7.55 (1H, dd, J = 1.4, 0.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 102.5, 114.1, 116.1, 120.9, 125.7, 128.2, 155.0, 156.2; MS *m/z* (rel intensity) 212 (M^++ 2, 92), 210 (M^+, 100), 160 (47), 146 (22), 132 (100), 102 (16), 83 (14), 59 (21), 42 (23).

Anal. Calcd for C_9H_7BrO: C, 51.22%; H, 3.34%. Found: C, 50.84%; H, 3.38%.

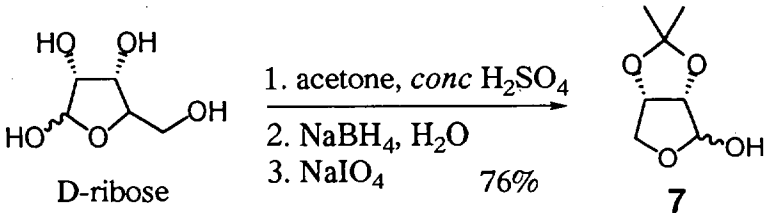
Praparation of the Grignard Reagent 5.



3 (72 : 28) 4 → 5

A two-necked round-bottomed flask fitted with a dropping funnel was charged with Mg (2.5 g, 103 mg atom), THF (10 mL), and a catalytic amount of I_2. After being strirred for 5 min, a solution of **3** and **4** (16.9 g, 80 mmol) in THF (100 mL) was added dropwise over 4 h and the mixture was further stirred for 3 h at rt. The resulting green solution was diluted with THF (90 mL) and titrated as a 0.38 M (90% yield) solution of the Grignard reagent **5**.

2,3-*O*-Isopropyridene-L-erythrose (7).



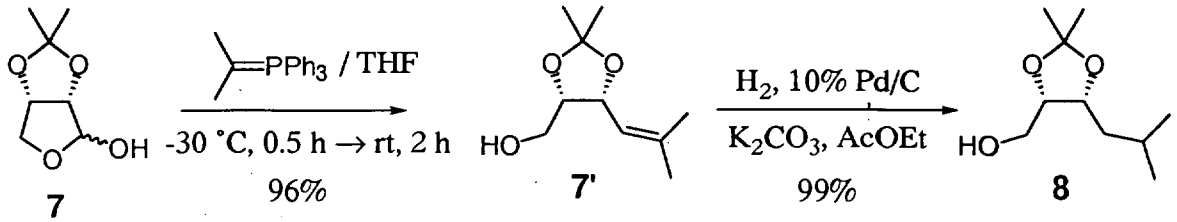
To an ice cooled suspension of D-ribose (11.4 g, 76 mmol) in acetone (300 mL) was added conc H_2SO_4 (200 μL). The clear solution was obtained after 0.5 h, then the mixture was neutralized by addition of $Ca(OH)_2$. The salt was removed by filtration through Celite and the filtrate was concd in *vacuo* to give the crude product (16.1 g) as a colorless oil.

To an ice cooled solution of this product in H_2O (300 mL) was added a solution of $NaBH_4$ (5.0 g, 0.13 mol) in H_2O (200 mL). After being stirred for 1 h at rt, the mixture was adjusted to pH 6 by dropwise addition of AcOH. Then $NaIO_4$ (14.4 g, 67 mmol) was added at 0 ℃ and the mixture was stirred for 2 h. After concentration and filtration through Celite, the filtrate was extracted with AcOEt. The combined extracts were washed with satd $NaHCO_3$ and brine, dried (Na_2SO_4), filtered, and concd *in vacuo*. The crude product was purified by column chromatography (hexane / Et_2O, from 2 : 1 to Et_2O only) to give 9.2 g (76%) of **7**.

7: Colorless prisms; Mp 29.5-31.0 °C; $[\alpha]^{22}_D$ +74.8 (*c* 0.96, $CHCl_3$).

FTIR (neat) ν 3422, 1377, 1211, 1100, 1071; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33, 1.48 (each 3H, s), 2.59 (1H, d, J = 2.0 Hz), 4.03 (1H, d, J = 10.7 Hz), 4.08 (1H, dd, J = 10.7, 3.9 Hz), 4.59 (1H, d, J = 5.9 Hz), 4.84 (1H, dd, J = 5.9, 3.9 Hz), 5.43 (1H, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 26.2, 71.9, 80.0, 85.2, 101.8, 112.3.

(4*S*, 5*R*)-2,2-Dimethyl-4-(hydroxymethyl)-5-(2'-methylpropyl)-1,3-dioxolane (8).



To a suspension of ^{i}PrPPh$_3$I (15.1 g, 35 mmol) in THF (50 mL) at -55 °C was added dropwise n-BuLi (1.62 M in hexane; 24 mL, 39 mmol) and the mixture was stirred for 0.5 h. To the resultant reddish solution was added a solution of **7** (2.8 g, 17.5 mmol) in THF (5 mL) at the same temperature. After being stirred for 0.5 h, the mixture was allowed to warm to rt and stirred for 2 h. The mixture was quenched by addition of H_2O and the insoluble substance was removed by filtration through Celite. After removal of the solvent, the residue was diluted with Et_2O, washed with H_2O and brine, dried (Na_2SO_4), and concd *in vacuo*. The crude product was purified by column chromatography (hexane / AcOEt = 2 : 1) to give alcohol **7'** (3.13 g, 96%) as a colorless oil.

7': Colorless oil; $[\alpha]^{23}_D$ -54.9 (*c* 1.1, $CHCl_3$).

FTIR (neat) ν 3457, 1452, 1379, 1217, 1046; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40, 1.50 (each 3H, s), 1.72, 1.77 (each 3H, d, *J* = 1.2Hz), 1.86(1H, dd, *J* = 6.8, 5.8 Hz), 3.55 (1H, ddd, *J* = 11.4, 6.8, 4.9 Hz), 3.58 (1H, ddd, *J* = 11.4, 6.8, 5.8 Hz), 4.20 (1H, dt, *J* = 6.8, 4.9 Hz), 4.94 (1H, dd, *J* = 9.0, 6.8 Hz), 5.25 (1H, d of septet, *J* = 9.0, 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 25.2, 25.8, 27.9, 62.2, 73.8, 78.1, 108.1, 119.2, 138.7; MS *m/z* (rel intensity) 187 (M^+ + 1, 3), 169 (57), 129 (100), 126 (28), 111 (61), 93 (11), 83 (6), 59 (6), 43 (3).

HRMS calcd for $C_{10}H_{19}O_3$ + H 187.1334, found 187.1320.

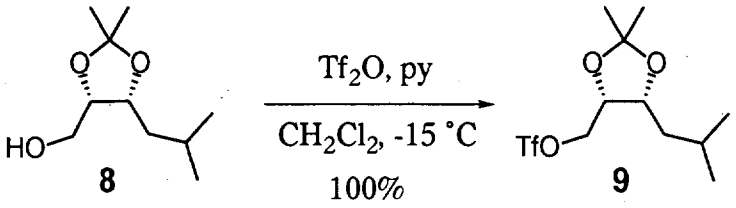
A mixture of **7'** (503 mg, 2.7 mmol) and 10% Pd-C (15 mg) in the presence of K_2CO_3 (10 mg; protection from acetonide shift) was stirred for 9 h at rt under H_2. The mixture was filtered through Celite and the filtrate was concd *in vacuo*. The crude product was purified by column chromatography (benzene / AcOEt, from 4 : 1 to 1 : 1) to give **8** (503 mg, 99%) as a colorless oil.

8: Collorless oil; $[\alpha]^{24}_D$ -29.0 (*c* 1.0, $CHCl_3$).

FTIR (neat) ν 3443, 1370, 1219, 1044; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93, 0.96 (each 3H, d, *J* = 6.6 Hz), 1.23 (1H, ddd, *J* = 13.6, 8.5, 4.0 Hz), 1.37, 1.47 (each, 3H, s), 1.55 (1H, ddd, *J* = 13.6, 9.9, 5.6 Hz), 1.77 (1H, dd of septet, *J* = 8.5, 6.6, 5.6 Hz), 1.91 (1H, dd, *J* = 7.3, 4.9 Hz), 3.60 (2H, m), 4.13 (1H, ddd, *J* = 6.8, 6.1, 4.9 Hz), 4.26 (1H, ddd, *J* = 9.9, 6.1, 4.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 23.4, 25.3, 25.5, 28.2, 37.4, 61.8,75.0, 78.1, 107.9; MS *m/z* (rel intensity) 189 (M^+ + 1, 22), 173 (37), 157 (25), 131 (72), 113 (36), 95 (100), 85 (10), 69 (11), 59 (30), 57 (20), 43 (24), 41 (35).

HRMS calcd for $C_{10}H_{21}O_3$ + H 189.1491, found 189.1462.

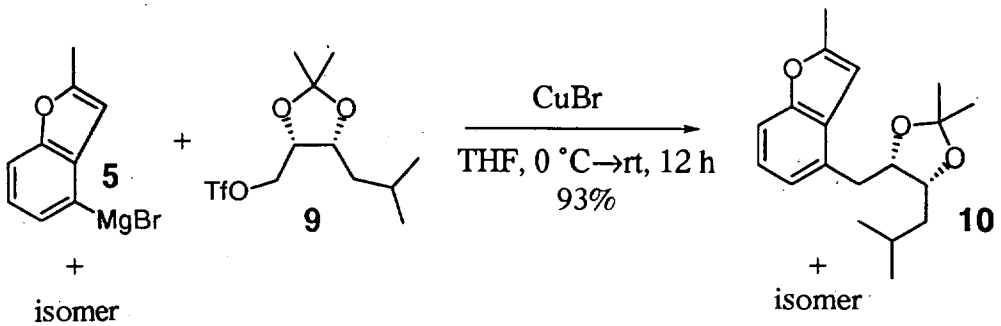
(4*S*, 5*R*)-2,2-Dimethyl-4-(trifluoromethanesulfonyloxymethyl)-5-(2'-methylpropyl)-1,3-dioxolane (9).



To a solution of **8** (940 mg, 5.0 mmol) and pyridine (0.8 mL, 10 mmol) in CH_2Cl_2 (2 mL) at -15 ℃ was added dropwise Tf_2O (2.1 g, 7.44 mmol) and the mixture was stirred for 20 min. After quenching by addition of H_2O, the mixture was extracted with CH_2Cl_2. The extracts were washed with satd $NaHCO_3$ and brine, dried (Na_2SO_4), and filtered through a short silica gel pad. The filtrate was concd to give **9** (1.6 g, 100%) as a pale yellow oil.

R_f 0.41 (hexane / Et_2O = 10 : 1).

(4*R*, 5*S*)-2,2-Dimethyl-5[(2'-methylbenzo[b]furan-4'-yl)methyl]-4-(2''-methylpropyl)-1,3-dioxolane (10).

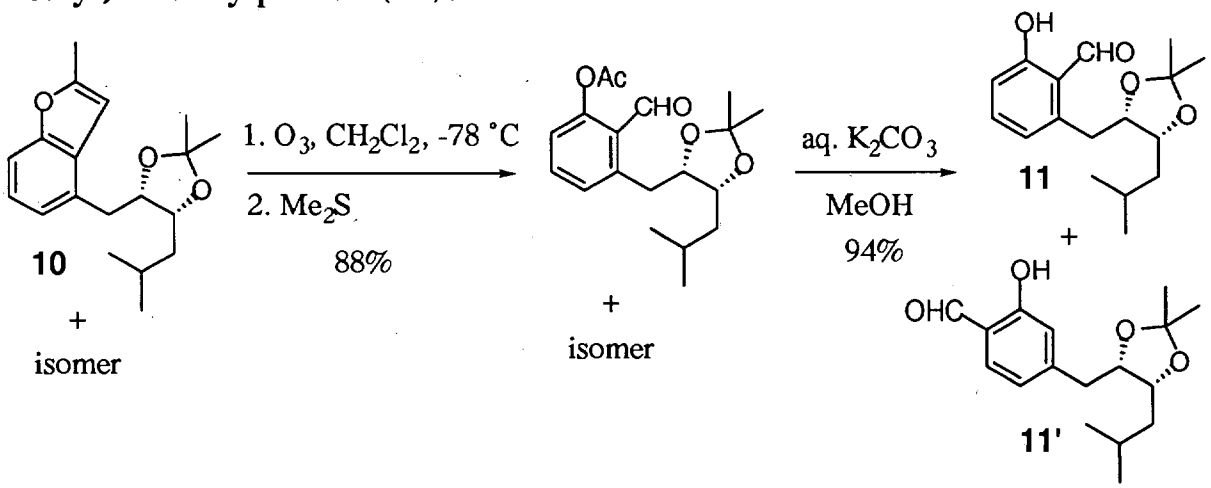


To a suspension of CuBr (37 mg, 0.26 mmol) in THF (1 mL) was added the Grignard reagent **5** (0.38 M in THF, 3.55 mL, 1.35 mmol). To this solution at 0 °C was added a solution of **9** (300 mg, 0.94 mmol) in THF (8.5 mL) and the mixture was allowed to warm to rt with stirring for 12 h. After quenching by addition of satd NH_4Cl/aq NH_3 (9 : 1), the insoluble substance was removed by filtration through Celite and rinsed with AcOEt. After removal of the solvent, the residue was diluted with AcOEt and washed with satd $NaHCO_3$ and brine, dried (Na_2SO_4), and concd *in vacuo*. The crude product was purified by column chromatography (hexane / Et_2O = 99 : 1 to 9 : 1) to give **10** (263 mg, 93%) as an inseparable mixture.

10: Pale yellow oil; R_f 0.49 (hexane / Et_2O = 10 : 1).

FTIR (neat) ν 1609, 1591, 1431, 1379, 1252, 1217, 1055; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.93, 0.99 (each 3H, d *J* = 6.6 Hz), 1.32, 1.52 (each 3H, s), 1.25-1.35 (1H, m), 1.67 (1H, ddd, *J* = 13.7, 10.0, 5.1 Hz), 1.75-1.88 (1H, m), 2.45 (3H, s), 2.8-3.0 (2H, m), 4.2-4.3 (1H, m), 4.4-4.5 (1H, m), 6.41 (1H, d, *J* = 0.7 Hz), 7.04 (1H, d, *J* = 7.8 Hz), 7.14 (1H, t, *J* = 7.8 Hz), 7.27 (1H, dd, *J* = 7.8, 0.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 14.1, 21.9, 23.7, 25,2, 25.9, 28.7, 34.0, 38.5, 76.1, 78.1, 101.2, 108.8, 122.8, 123.1, 128.8, 130.7, 154.7, 155.0.

(1'*S*, 5'*R*)-3-{[3', 3'-Dimethyl-5'-(2''-methylpropyl)(2', 4'-dioxolanyl)]-methyl}-2-formylphenol (11).



To a solution of **10** (600 mg, 1.98 mmol) in CH_2Cl_2 (20 mL) at -78 °C was bubbled O_3 for 12 min (until the color of the solution turned light blue) and the mixture was quenched by addition of Me_2S (1 mL). After evaporation of the solvent, the crude product was purified by column chromatography (hexane / Et_2O = 2 : 1 to 1 : 1) to give the acetate (584 mg, 88%) as an inseparable mixture.

R_f 0.28 (hexane / Et_2O = 2 : 1).

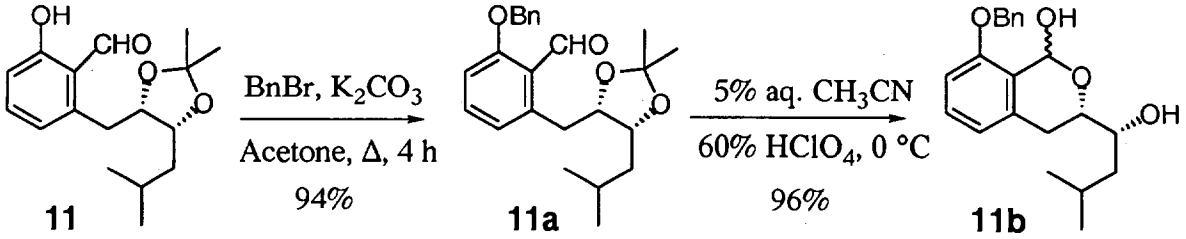
The product obtained above was dissolved in MeOH (6 mL) and K_2CO_3 (480 mg, 3.47 mmol) in water (1.5 mL) was added. After being stirred for 15 min at rt, the mixture was concd *in vacuo*. The residue was neutralized with 1M HCl and acidified with aq NH_4Cl. Then the solution was diluted with brine and extracted with AcOEt. The combined extracts were washed with brine, dried (Na_2SO_4), and concd *in* vacuo. The crude product was purified by column chromatography (hexane / Et_2O = 2 : 1) to give **11** (327 mg, 64%) and **11'** (143 mg, 28%).

11: Light yellow oil; R_f 0. 35 (hexane / Et_2O = 4 : 1); $[\alpha]^{23}_D$ -12.9 (*c* 1.16, $CHCl_3$). FTIR (neat) ν 1647, 1578, 1454; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98, 1.02 (each 3H, d, *J* = 6.7 Hz), 1.28 (3H, s), 1.29 (1H, ddd, *J* = 13.7, 8.8, 3.6 Hz), 1.49 (3H, s), 1.65 (1H, ddd, *J* = 13.7, 10.0, 4.9 Hz), 1.86 (1H. m), 2.89 (1H, dd, *J* = 14.1, 2.6 Hz), 3.13 (1H, dd, *J* = 14.1, 10.5 Hz), 4.20 (1H, ddd, *J* = 10.5, 6.1, 2.6 Hz), 4.31 (1H, ddd, *J* = 10.0, 6.1, 3.6 Hz), 6.76 (1H, d, *J* = 7.6 Hz), 6.86 (1H, d, *J* = 8.3 Hz),7.43 (1H, dd, *J* = 8.3, 7.6 Hz), 10.33 (1H, s), 12.01 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 23.7, 25.2, 25.3, 28.2, 32.4; 38.7, 75.8, 79.0, 108.0, 116.5, 118.7, 121.6, 137.0, 143.5, 163.2, 195.7; MS *m/z* (rel intensity) 292 (M^+, 2), 277 (14), 234 (56), 157 (100), 148 (24), 99 (27), 81 (50), 59 (33), 43 (24).

HRMS calcd for $C_{17}H_{24}O_4$ 292.1674, found 292.1660.

11': Light yellow oil; R_f 0.27 (hexane / Et_2O = 4 : 1); $[\alpha]^{22}_D$ -93.2 (*c* 1.04, $CHCl_3$). FTIR (neat) ν 1659, 1572, 1507, 1453; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96, 1.00 (each 3H, d, *J* = 6.6 Hz), 1.26 (1H, ddd, *J* = 13.6, 9.3, 5.3 Hz), 1.33 (3H, s), 1.51 (3H, s), 1.62 (1H, ddd, *J* = 13.6, 8.8, 3.8 Hz), 1.82 (1H, m), 2.70 (1H, dd, *J* = 13.9, 3.4 Hz), 2.76 (1H, dd, *J* = 13.9, 9.5 Hz), 4.28 (2H, m), 6.88 (1H, d, *J* = 1.5 Hz), 6.91 (1H, dd, *J* = 7.8, 1.5 Hz), 7.48 (1H, d, *J* = 7.8 Hz), 9.85 (1H, s), 11.03 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 23.6, 25.2, 25.8, 28.6, 37.2, 38.3, 75.9, 78.0, 107.9, 118.0, 119.2, 121.1, 133.6, 149.6, 161.6, 195.9; MS *m/z* (rel intensity) 292 (M^+, 4), 277 (15), 235 (13), 157 (100), 133 (7), 99 (11), 81 (29), 59 (19), 43 (16).
HRMS calcd for $C_{17}H_{24}O_4$ 292.1674, found 292.1680.

(1'*S*, 5'*R*)-6-{[3', 3'-Dimethyl-5'-(2''-methylpropyl)(2', 4'-dioxolanyl)]-methyl}-2-(phenylmethoxy)benzaldehyde



11 **11a** **11b**

A mixture of salicylaldehyde **11** (1.29 g, 4.4 mmol), benzyl bromide (1.5 g, 8.8 mmol), and K_2CO_3 (1.22 g, 8.8 mmol) in acetone (22 mL) was refluxed for 3 h. After filtration, the mixture was concd *in vacuo*. The crude product was purified by column chromatography (hexane / Et_2O = 4 : 1) to give **11a** (1.59 g, 94%).

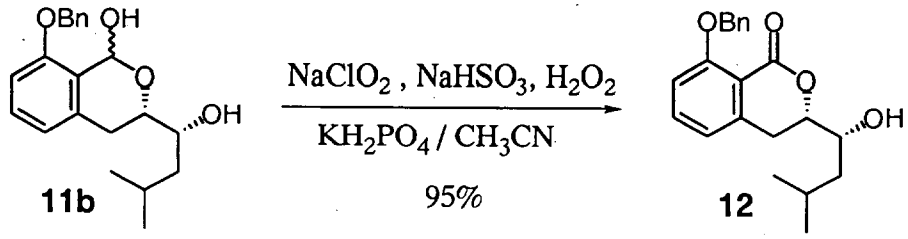
11a: Colorless oil; R_f 0.33 (hexane:Et_2O = 4:1); $[\alpha]^{24}_D$ -124.9 (*c* 1.43, $CHCl_3$). FTIR (neat) ν 1686, 1600, 1578; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00, 1.02 (each 3H, d, *J* = 6.6 Hz), 1.29 (3H, s) 1.47 (1H, ddd, *J* = 13.8, 8.6, 3.2 Hz), 1.52 (3H, s), 1.62 (1H, ddd, *J* = 13.8, 9.3, 5.4 Hz), 1.92 (1H, m), 2.61 (1H, dd, *J* = 13.1, 10.0 Hz), 3.48 (1H, dd, *J* = 13.1, 1.5 Hz), 4.30 (2H, m), 5.15 (2H, s), 6.91 (1H, d, *J* = 7.8 Hz), 6.95 (1H, d, *J* = 8.3 Hz), 7.34-7.45 (6H, m), 10.71 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 23.6, 25.2, 25.8, 28.6, 35.0, 38.2, 70.6, 76.2, 78.2, 107.4, 111.0, 123.2, 125.3, 127.2 (×2), 128.1, 128.6 (×2), 134.4, 136.1, 142.9, 162.6, 192.3; MS *m/z* (rel intensity) 382 (M^+, 11), 367 (21), 325 (100), 307 (24), 267 (10), 226 (14), 157 (54), 91 (58), 81 (6), 59 (7).
HRMS calcd for $C_{24}H_{30}O_4$ 382.2144, found 382.2114.

To a solution of **11a** (535 mg, 1.40 mmol) in 5% aq CH_3CN (7 mL) was added 6 drops of 60% $HClO_4$ at rt and the mixture was stirred for 15 min. After dilution with AcOEt, the organic layer was washed with satd $NaHCO_3$ and brine, dried (Na_2SO_4), and concd *in vacuo*.

The crude product was purified by column chromatography (hexane / AcOEt = 9 : 1) to give **11b** (460 mg, 96%) as a colorless oil.

11b: Colorless oil; R_f 0.40 (hexane / AcOEt = 9 : 1); $[\alpha]^{24}_D$ -42.0 (*c* 1.24, $CHCl_3$). FTIR (neat) ν 1589, 1470, 1265, 1049; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89, 0.91 (each 3H, d, *J* = 6.7 Hz), 1.23 (1H, ddd, *J* = 13.4, 7.8, 5.6 Hz), 1.41 (1H, ddd, *J* = 13.4, 8.8, 6.4 Hz), 1.57 (1H, s), 1.72 (1H, m), 2.35 (1H, br), 2.78 (1H, d, *J* = 17.6 Hz), 3.31 (1H, dd, *J* = 17.6, 5.6 Hz), 4.24 (1H, dt, *J* = 8.8, 5.6 Hz), 4.27 (1H, t, *J* = 5.6 Hz), 5.04, 5.12 (each 1H, d, J_{AB} = 11.9 Hz), 6.49 (1H, s), 6.71 (1H, d, *J* = 8.0 Hz), 6.72 (1H, d, *J* = 8.0 Hz), 7.12 (1H, t, *J* = 8.0 Hz), 7.28-7.45 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 23.1, 26.0, 29.0, 40.2, 70.1, 74.9, 77.3, 94.6, 109.9, 120.8, 127.1 (×2), 127.7, 128.3, 128.4 (×2), 128.7, 132.8, 136.9, 153.9.
MS *m/z* (rel intensity) 325 (M^+-17, 100), 267 (21), 238 (20), 218 (26), 147 (5), 120 (8), 99 (6), 91 (58).

(1'*R*, 3*S*)-3-(1'-Hydroxy-3'-methylbutyl)-8-(benzyloxy)isochroman-1-one (12).



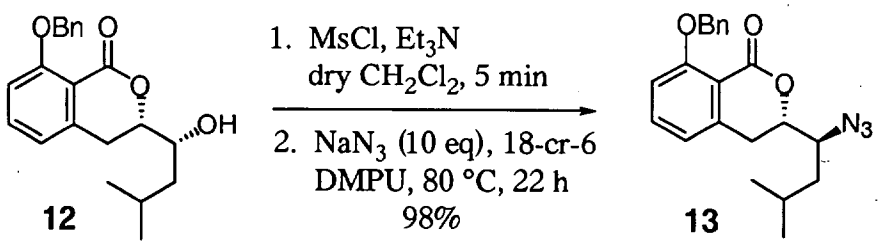
To a mixture of $NaH_2PO_4 \cdot 2H_2O$ (57 mg, 0.365 mmol), 30% H_2O_2 (24 mg, 0.219 mmol), and 80% $NaClO_2$ (27 mg, 0.292 mmol) in water (0.5 mL) at 0 ℃ was added portionwise $NaHSO_3$ (15 mg, 0.146 mmol). Then this solution was added to a solution of hemiacetal **11b** (50 mg, 0.146 mmol) in CH_3CN (1.5 mL) at rt. After 2 h, freshly prepared aq solution (1mL) of $NaH_2PO_4 \cdot 2H_2O$ (137 mg, 0.876 mmol), 30% H_2O_2 (66 mg, 0.584 mmol), 80% $NaClO_2$ (40 mg, 0.438 mmol), and $NaHSO_3$ (61 mg, 0.584 mmol) was added. After 2 h, additional 80% $NaClO_2$ (40 mg, 0.438 mmol), $NaHSO_3$ (30 mg, 0.292 mmol) in water (0.5 mL) was added. After 20 h, most of the solvent was removed and diluted with AcOEt. The organic layer was washed with water and the aqueous phase was reextracted with AcOEt. The combined extracts were washed with satd $NaHCO_3$ and brine, dried (Na_2SO_4), and concd *in vacuo*. The crude product was purified by column chromatography (hexane / AcOEt = 2 : 1) to give **12** (47 mg, 95%) as a colorless oil.

12: Colorless oil; R_f 0.54 (hexane / AcOEt = 1 : 2); $[\alpha]^{25}_D$ -110.1 (*c* 1.38, $CHCl_3$). FTIR (KBr) ν 3430, 1725, 1599, 1586, 1474, 1453; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95, 0.98 (each 3H, d, *J* = 6.6 Hz), 1.29 (1H, ddd, *J* = 14.4, 9.0, 3.4 Hz), 1.52 (1H, ddd, *J* = 14.4, 10.0, 4.6 Hz), 1.87 (1H, m), 2.27 (1H, br s), 2.79 (1H, dd, *J* = 16.2, 2.7 Hz), 3.20 (1H, dd, *J* = 16.2, 12.4 Hz), 4.07 (1H, m), 4.32 (1H, dt, *J* = 12.4, 2.7 Hz), 5.23,

5.30 (each 1H, d, J_{AB}= 12.7 Hz), 6.85 (1H, d, J = 8.1 Hz), 6.93 (1H, d, J = 8.1 Hz), 7.29 (1H, t, J = 7.6 Hz), 7.38 (2H, t, J = 7.6 Hz), 7.41 (1H, t, J = 8.1 Hz), 7.53 (2H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 23.4, 24.5, 28.1, 40.7, 69.8, 70.4, 80.9, 112.5, 114.1, 119.9, 126.6 (×2), 127.6, 128.5 (×2), 134.4, 136.4, 142.0, 160.0, 162.1; MS *m/z* (rel intensity) 340 (M^+, 47), 322 (6), 253 (13), 248 (7), 222 (18), 148 (7), 91 (100), 65 (5).

HRMS calcd for $C_{21}H_{24}O_4$ 340.1674, found 340.1691.

(1'*S*, 3*S*)-3-(1'-Azido-3'-methylbutyl)-8-(benzyloxy)isochroman-1-one (13).



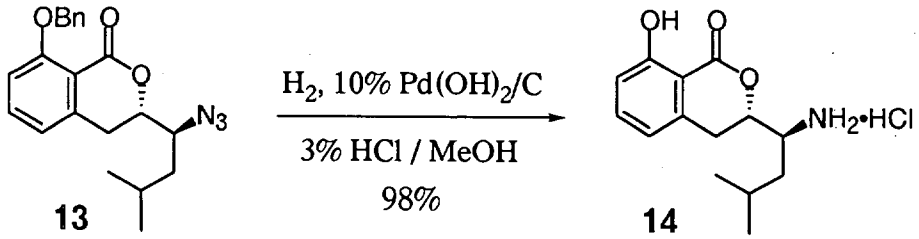
To a stirred solution of alcohol **12** (374 mg, 1.10 mmol) and Et_3N (310 μL, 2.22 mmol) in CH_2Cl_2 (10 mL) at 0 ℃ was added a solution of MsCl (344 mg, 3.00 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred for 5 min. The mixture was diluted with CH_2Cl_2, washed with aq $NaHCO_3$ and brine, dried (Na_2SO_4), and concd *in vacuo*. Then the crude mesylate was dissolved in DMPU (11 mL) and treated with NaN_3 (715 mg, 11.0 mmol) in the presence of a catalytic amount of 18-crown-6. After being stirred for 22 h at 80 °C, the mixture was diluted with Et_2O, washed with water, satd $NaHCO_3$, and brine, dried (Na_2SO_4), and concd *in vacuo*. The crude product was purified by column chromatography (hexane / AcOEt = 4 : 1) to give azido **13** (394 mg, 98%) as colorless needles.

13: Colorless needles; R_f 0.57 (hexane / AcOEt = 1 : 1); Mp 94.5-95.0 °C (from CH_2Cl_2 / hexane); $[\alpha]^{22}_D$ -175.0 (*c* 1.00, $CHCl_3$).

FTIR (KBr) ν 2097, 1723, 1601, 1588, 1476, 1454; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98, 1.00 (each 3H, d, J = 6.3 Hz), 1.53 (1H, ddd, J = 13.7, 9.2, 4.0 Hz), 1.77 (1H, ddd, J = 13.7, 10.2, 5.3 Hz), 1.87 (1H, m), 2.77 (1H, dd, J = 16.1, 2.4 Hz), 3.21 (1H, dd, J = 16.2, 12.4 Hz), 3.47 (1H, dt, J = 10.2, 4.0 Hz), 4.42 (1H, ddd, J = 12.4, 4.0, 2.4 Hz), 5.20, 5.28 (each 1H, d, J_{AB} = 12.4 Hz), 6.83 (1H, d, J = 7.6 Hz), 6.96 (1H, d, J = 8.3 Hz), 7.29 (1H, t, J = 7.6 Hz), 7.38 (2H, t, J = 7.6 Hz), 7.42 (1H, dd, J = 8.3, 7.6 Hz), 7.56 (2H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 23.1, 24.8, 31.3, 38.3, 61.3, 70.4, 79.0, 112.7, 114.0, 119.6, 126.6 (×2), 127.7, 128.5 (×2), 134.5, 136.3, 141.3, 160.1, 161.1.

Anal. Calcd for $C_{21}H_{23}N_3O_3$: C, 69.02%; H, 6.34%; N, 11.50%. Found: C, 68.91%; H, 6.37%; N, 11.42%.

(1'*S*, 3*S*)-3-(1'-Amino-3'-methylbutyl)-8-hydroxyisochroman-1-one (14).

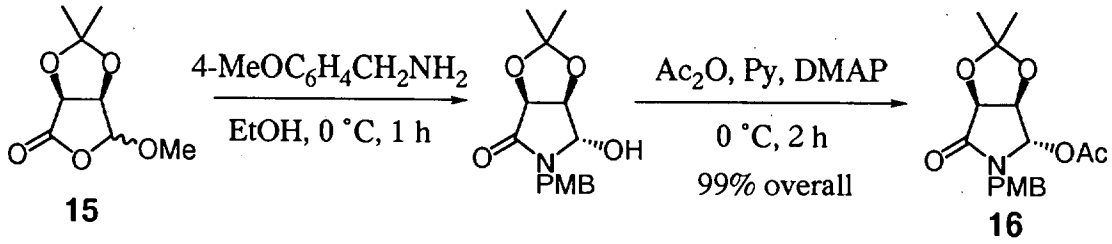


A mixture of azido **13** (404 mg, 1.11 mmol), 10% $Pd(OH)_2/C$ (10 mg), and 3% HCl/MeOH (2 mL) in CH_2Cl_2 (2 mL) was stirred for 5 h at rt under H_2. The mixture was filtered through Celite and washed with MeOH. The filtrate was concd to give the crude product as a white solid, which was triturated with Et_2O to give **14** (310 mg, 98%).

14: Colorless needles; Mp 203.0-205.0 °C (from EtOH); $[\alpha]^{22}_D$ -55.4 (*c* 1.01, MeOH). FTIR (KBr) ν 3424, 3057, 1678, 1618, 1588, 1512, 1462; ^{1}H NMR (400 MHz, CD_3OD) δ 1.01, 1.03 (each 3H, d, *J* = 6.3 Hz), 1.68 (2H, m), 1.83 (1H, m), 3.14 (1H, dd, *J* = 16.3, 4.1 Hz), 3.19 (1H, dd, *J* = 16.3, 12.0 Hz), 3.61 (1H, m), 4.76 (1H, ddd, *J* = 12.0, 5.4, 4.1 Hz), 6.87 (1H, d, *J* = 7.3 Hz), 6.89 (1H, d, *J* = 7.8 Hz), 7.50 (1H, dd, *J* = 7.8, 7.3 Hz); ^{13}C NMR (100 MHz, CD_3OD) δ 22.1, 23.2, 25.3, 30.6, 39.4, 53.4, 79.5, 109.1, 117.2, 119.8, 137.9, 140.2, 163.3, 169.6.

Anal. Calcd for $C_{14}H_{20}NO_3Cl$ C, 58.84%; H, 7.05%; N, 4.90%. Found: C, 58.75%; H, 7.17%; N, 4.96%.

(3*S*, 4*R*)-*N*-(*p*-Methoxybenzyl)-5-acetoxy-3,4-isopropylidenedioxy-2-pyrrolidinone (16).



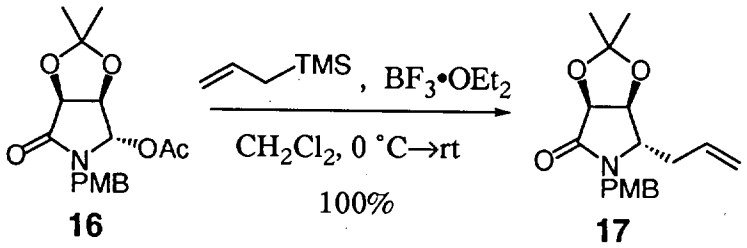
To a stirred solution of **15** (350 mg, 1.86 mmol) in EtOH (3 mL) at 0 ℃ was added *p*-methoxybenzylamine (365 μL, 2.79 mmol) and the mixture was stirred for 1 h at rt. After evaporation of the solvent, the residue was dissolved in pyridine (1.5 mL) and treated with Ac_2O (530 μL, 5.62 mmol) in the presence of a catalytic amount of DMAP. After being stirred for 0.5 h at rt, the mixture was diluted with Et_2O and washed with 5% aq $CuSO_4$ and water. The aqueous phase was reextracted with Et_2O. The combined extracts were washed with satd $NaHCO_3$ and brine, dried (Na_2SO_4), and concd *in vacuo*. The crude product was purified by column chromatography (AcOEt / hexane = 1 : 4) to give acetate **16** (618 mg, 99%) as colorless plates.

16: Colorless plates; Mp 106.0-107.0 ℃; R_f 0.47 (Et_2O / hexane = 4 : 1); $[\alpha]^{25}_D$ -36.9 (*c* 1.03, $CHCl_3$).

FTIR (KBr) ν 1746, 1717, 1615, 1514, 1246, 1227; ^1H NMR (400 MHz, $CDCl_3$) δ 1.35, 1.96 (each 3H, s), 3.79 (3H, s), 4.14 (1H, d, *J* = 14.6 Hz), 4.50 (1H, d, *J* = 5.6 Hz), 4.70 (1H, d, *J* = 14.6 Hz), 4.85 (1H, d, *J* = 5.6 Hz), 5.92 (1H, s), 6.84 (2H, d, *J* = 8.5 Hz), 7.20 (2H, d, *J* = 8.5 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ 18.1, 23.2, 24.3, 41.7, 52.6, 81.9, 111.0, 111.4 (×2), 124.6, 127.2 (×2), 156.7, 169.9, 171.9; MS *m/z* (rel intensity) 335 (M^+, 17), 321 (6), 275 (64), 260 (9), 218 (16), 189 (19), 161 (21), 121 (100), 101 (5), 85 (10), 43 (20).

Anal. Calcd for $C_{17}H_{21}NO_6$: C, 60.89%; H, 6.31%; N, 4.18%. Found: C, 60.86%; H, 6.36%; N, 4.20%.

(3*S*, 4*S*, 5*S*)-*N*-(*p*-Methoxybenzyl)-3,4-isopropylidenedioxy-5-allyl-2-pyrrolidinone (17).



16 **17**

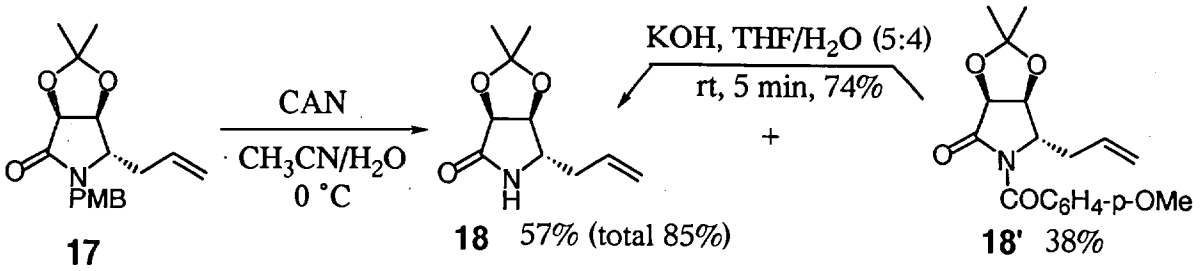
Allyltrimethylsilane (230 μL, 1.45 mmol) was added to a solution of BF_3•OEt_2 (120 μL, 0.95 mmol) in CH_2Cl_2 (1 mL) at 0 °C. After being stirred for 10 min, a solution of acetate **16** (162 mg, 0.48 mmol) in CH_2Cl_2 (3 mL) was added and the mixture was stirred at rt for 30 min. The mixture was diluted with CH_2Cl_2, washed with satd $NaHCO_3$ and brine, dried (Na_2SO_4), and concd *in vacuo*. The crude product was purified by column chromatography (AcOEt / hexane = 1 : 2) to give **17** (153 mg, 100%) as a colorless oil which was crystallized in a refrigerator.

17: Colorless solid; R_f 0.37 (AcOEt / hexane = 1 : 1); $[\alpha]^{25}_D$ -41.0 (*c* 1.12, $CHCl_3$); Mp 52.0-53.0 ℃ (unrecrystallized).

FTIR (KBr) ν 1688, 1613, 1516, 1451, 1256; ^1H NMR (400 MHz, $CDCl_3$) δ 1.35, 1.40 (each 3H, s), 2.27 (1H, ddd, *J* = 14.9, 7.3, 7.1 Hz), 2.38 (1H, ddd, *J* = 14.9, 7.3, 3.4 Hz), 3.53 (1H, dd, *J* = 7.1, 3.4 Hz), 3.80 (3H, s), 3.90 (1H, d, J_{AB} = 15.0 Hz), 4.40 (1H, d, *J* = 5.6 Hz), 4.67 (1H, d, *J* = 5.6 Hz), 5.00 (1H, d, J_{AB} = 15.0 Hz), 5.15 (1H, d, *J* = 17.0 Hz), 5.18 (1H, d, *J* = 9.8 Hz), 5.59 (1H, ddt, *J* = 17.0, 9.8, 7.3 Hz), 6.85 (2H, d, *J* = 8.5 Hz), 7.18 (2H, d, *J* = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 27.1, 34.7, 43.7, 55.2, 59.7, 76.7, 77.3, 111.9, 114.1 (×2), 119.9, 127.2, 129.4 (×2), 131.5, 159.2, 171.0; MS *m/z* (rel intensity) 317 (M^+, 63), 302 (6), 276 (10), 259 (6), 242 (7), 210 (9), 121 (100), 41 (76).

Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.12%; H, 7.30%; N, 4.41%. Found: C, 68.35%; H, 7.48%; N, 4.49%.

CAN Oxidation of 17.



17 **18** 57% (total 85%) **18'** 38%

To an ice-cooled solution of **17** (91 mg, 0.287 mmol) in CH_3CN (3 mL) was added a solution of ceric ammonium nitrate (CAN; 472 mg, 0.861 mmol) in water (4 mL) and the mixture was stirred at rt for 30 min. After dilution with water, the most of the organic solvent was evaporated. The aqueous phase was extracted with CH_2Cl_2 and the extracts were washed with satd $NaHCO_3$ and brine, dried (K_2CO_3), and concd *in vacuo*. The crude product was purified by column chromatography (AcOEt / hexane, from 1 : 2 to 4 : 1) to give **18** (32 mg, 57%) and **18'** (36 mg, 38%).

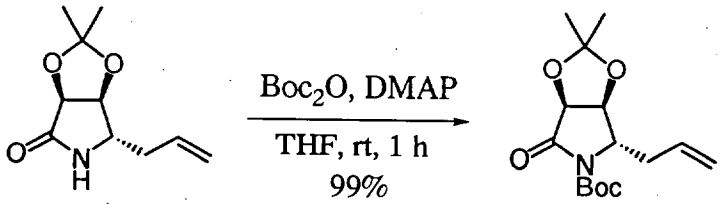
18: Light yellow oil; R_f 0.23 (acetone / hexane = 1 : 2); $[\alpha]^{25}_D$ +26.0 (*c* 1.00, $CHCl_3$). FTIR (neat) ν 3233, 1713, 1642; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37, 1.47 (each 3H, s), 2.24 (1H, dt, *J* = 14.2, 6.5 Hz), 2.35 (1H, dt, *J* = 14.2, 6.5 Hz), 3.73 (1H, t, *J* = 6.5 Hz), 4.45, 4.60 (each 1H, d, *J* = 6.0 Hz), 5.18 (1H, dd, *J* = 17.1, 1.5 Hz), 5.20 (1H, dd, *J* = 10.2, 1.5 Hz), 5.74 (1H, ddt, *J* = 17.1, 10.2, 6.5 Hz), 6.70 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 26.9, 38.8, 57.6, 76.6, 78.8, 112.5, 119.6, 132.1, 174.2; MS *m/z* (rel intensity) 198 (M^+ + 1, 100), 182 (28), 156 (44), 140 (50), 128 (15), 85 (19), 83 (28), 59 (8), 43 (6).
HRMS calcd for $C_{10}H_{15}NO_3$ + H 198.1130, found 198.1131.

18': Colorless oil; R_f 0.35 (Et_2O / hexane = 2 : 1); $[\alpha]^{25}_D$ +124.2 (*c* 0.76, $CHCl_3$). FTIR (neat) ν 1750, 1678, 1605, 1512; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39, 1.46 (each 3H, s), 2.57 (2H, m), 3.86 (3H, s), 4.54, 4.78 (each 1H, d, *J* = 5.4 Hz), 4.72 (1H, dd, *J* = 6.3, 4.6 Hz), 5.21 (1H, dd, *J* = 17.1, 1.5 Hz), 5.23 (1H, dd, *J* = 10.2, 1.5 Hz), 5.77 (1H, ddt, *J* = 17.1, 10.2, 7.3 Hz), 6.90 (2H, d, *J* = 8.9 Hz), 7.62 (2H, d, *J* = 8.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 27.1, 36.2, 55.4, 59.1, 76.0, 78.1, 112.5, 113.3 (×2), 120.5, 125.8, 131.6, 131.7 (×2), 163.2, 169.4, 171.6; MS *m/z* (rel intensity) 331 (M^+, 16), 182 (3), 156 (5), 135 (100), 107 (4), 85 (25), 83 (37), 77 (5), 47 (6).
HRMS calcd for $C_{18}H_{21}NO_5$ + H 332.1498, found 332.1501.

Base Hydrolysis of 18'.

A solution of **18'** (285 mg, 0.86 mmol) in THF (4.8 mL) was treated with KOH (48 mg, 0.86 mmol) in water (3.8 mL) for a short period. The solution was diluted with water and extracted with CH_2Cl_2. The extracts were washed with satd $NaHCO_3$. The aqueous phase was reextracted with CH_2Cl_2. The combined extracts were washed with brine, dried (K_2CO_3), and concd *in vacuo*. The crude product was purified by column chromatography (AcOEt / hexane, from 1 : 2 to 4 : 1) to give **18** (125 mg, 74%).

(3*S*, 4*S*, 5*S*)-*N*-Boc-3,4-isopropylidenedioxy-5-allyl-2-pyrrolodinone (19).



18 **19**

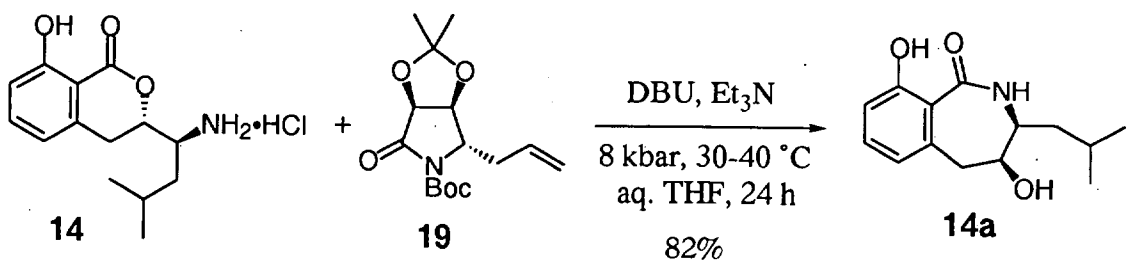
A mixture of **18** (1.27 g, 6.44 mmol), Boc_2O (1.54 g, 7.06 mmol) and a catalytic amount of DMAP in THF (50 mL) was stirred at rt overnight. After evaporation of the solvent, the residue was purified by column chromatography (AcOEt / hexane, 1 : 4) to give *N*-Boc lactam **19** (1.90 g, 99%) as colorless plates.

19: Colorless plates; R_f 0.42 (AcOEt / hexane = 1 : 2); Mp 65.5-67.0 °C (from Et_2O / hexane); $[\alpha]^{25}_D$ +89.5 (*c* 0.98, $CHCl_3$).

FTIR (KBr) ν 1752, 1721, 1379, 1312, 1159, 1101; ^1H NMR (400 MHz, $CDCl_3$) δ 1.37, 1.45 (each 3H, s), 1.55 (9H, s), 2.40 (1H, dt, *J* = 14.1, 7.8 Hz), 2.54 (1H, ddd, *J* = 14.1, 6.8, 3.4 Hz), 4.27 (1H, dd, *J* = 7.8, 3.4 Hz), 4.41, 4.61 (each 1H, d, *J* = 5.4 Hz), 5.18 (1H, dd, *J* = 16.8, 1.2 Hz), 5.21 (1H, dd, *J* = 8.9, 1.2 Hz), 5.71 (1H, dddd, *J* = 16.8, 8.9, 7.8, 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 27.0, 27.9 (×3), 36.2, 59.6, 75.5, 77.2, 83.7, 112.4, 120.2, 131.4, 149.6, 170.8.

Anal. Calcd for $C_{15}H_{23}NO_5$: C, 60.59%; H, 7.80%; N, 4.71%. Found: C, 60.66%; H, 7.72%; N, 4.85%.

High-Pressure Condensation of 14 with 19.

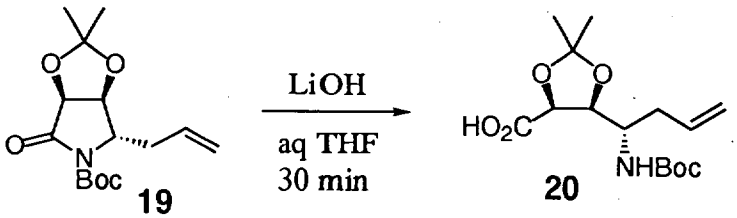


14 **19** **14a**

A mixture of **14** (18 mg, 0.063 mmol), **19** (19 mg, 0.064 mmol), Et_3N (18 μL, 0.13 mmol), and DBU (9.6 μL, 0.064 mmol) in THF / H_2O (2.5 mL, 9 : 1) was placed in a Teflon reaction vessel and reacted at 8 kbar and 30-40 °C for 24 h. After evaporation of the solvent, the residue was purified by preparative TLC (hexane / AcOEt = 1 : 1) to give **14a** (13 mg, 83%) and **19** (19 mg).

14a: Colorless oil; R_f 0.29 (hexane / AcOEt = 1 : 1); $[\alpha]^{22}_D$ -7.4 (*c* 1.35, $CHCl_3$).
FTIR (KBr) ν 3277, 1638, 1611, 1462; ^1H NMR (400 MHz, $CDCl_3$) δ 0.82, 0.88 (each 3H, d, *J* = 6.3 Hz), 1.50 (1H, ddd, *J* = 13.9, 8.1, 5.9 Hz), 1.61 (1H, ddd, *J* = 13.9, 8.8, 6.3 Hz), 1.72 (1H, m), 2.63 (1H, br), 2.76 (1H, dd, *J* = 13.2, 9.8 Hz), 3.12 (1H, dd, *J* = 13.2, 7.1 Hz), 3.22 (1H, m), 4.11 (1H, ddd, *J* = 9.8, 7.1, 2.9 Hz), 6.71 (1H, d, *J* = 7.3 Hz), 6.89 (1H, d, *J* = 8.3 Hz), 7.07 (1H, br), 7.27 (1H, dd, *J* = 8.3, 7.3 Hz), 10.14 (1H, br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 22.8, 24.6, 38.6, 41.5, 54.9, 75.7, 116.1, 116.7, 120.7, 133.2, 137.7, 159.7, 174.5; MS *m/z* (rel intensity) 249 (M^+, 95), 206 (100), 188 (7), 163 (50), 146 (24), 135 (27), 86 (41), 44 (12).
HRMS calcd for $C_{14}H_{19}NO_3$ 249.1365, found 249.1343.

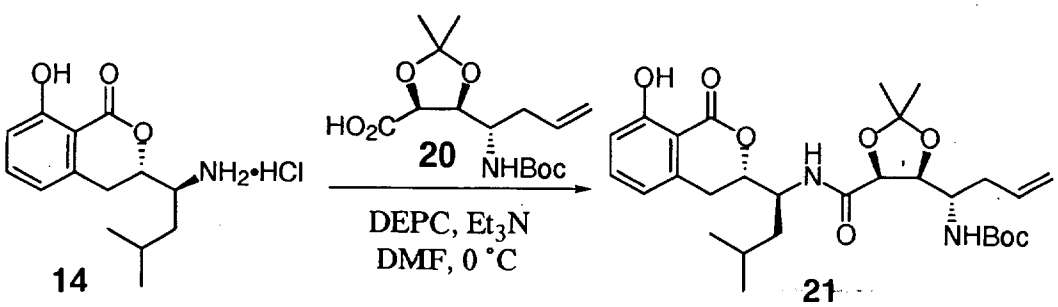
Base Hydrolysis of *N*-Boc Lactam 19.



19 **20**

To a solution of **19** (419 mg, 1.4 mmol) in THF (15 mL) was added dropwise 1M aq LiOH (4.2 mL, 4.2 mmol) at 0 °C. After being stirred for 30 min, the solvent was evaporated *in vacuo*. The aqueous phase was carefully acidified (pH 4) by addition of 10% aq AcOH at 0 °C and extracted with Et_2O. The combined extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave **20** as a colorless oil. This sample was used immediately for the next reaction.

Coupling Reaction of 14 with 20.



14 **21**

To a stirred suspention of **14** (403 mg, 1.41 mmol), **20** (generated as above), and diethyl phosphorocyanidate (DEPC; 277 mg, 1.70 mmol) in DMF (15 mL) at 0 ℃ was added dropwise Et_3N (429 μL, 3.08 mmol) over 2 h. After being stirred for additional 10 h at the same temperature, the mixture was diluted with benzene/AcOEt (2 : 1), and the organic layer was wahsed with 10% aq citric acid and brine, dried (Na_2SO_4), and concd *in vacuo*. The crude product was purified by column chromatography (hexane/AcOEt = 5 : 3) to give **21** (594 mg, 77%).

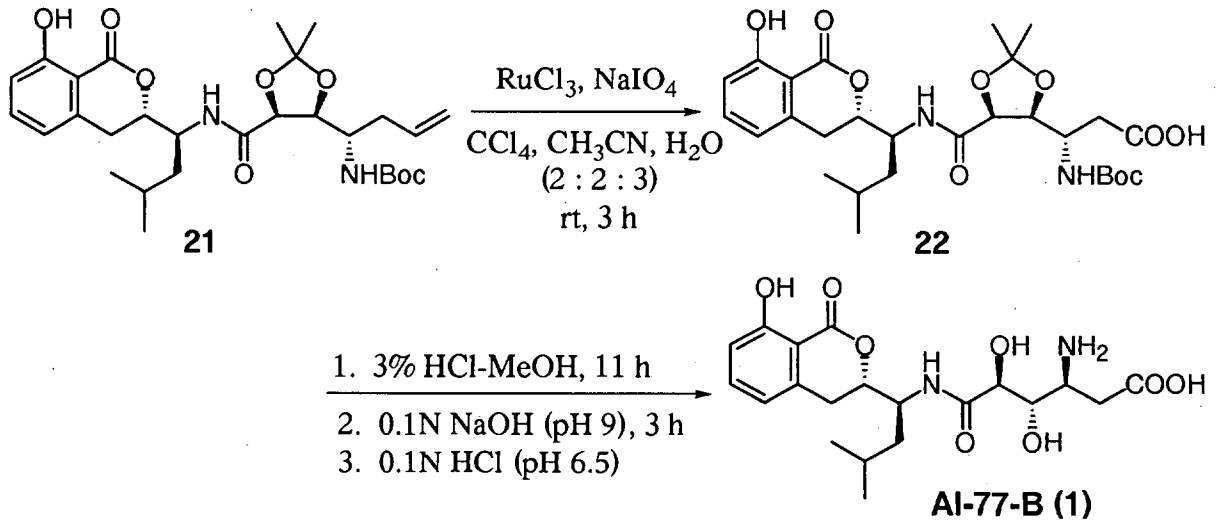
21: Colorless solid; R_f 0.51 (hexane / AcOEt = 1 : 1); Mp 121.0-122.5 °C (unrecrystallized); $[\alpha]^{23}_D$ -20.5 (*c* 1.71, $CHCl_3$).

FTIR (KBr) ν 3318, 1692, 1669, 1620, 1507; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (3H, d, *J* = 6.1 Hz), 0.96 (3H, d, *J* = 6.6 Hz), 1.37 (3H, s), 1.43 (9H, s), 1.50-1.65 (2H, m), 1.75 (1H, m), 1.56 (3H, s), 2.30 (1H, br), 2.44 (1H, br), 2.84 (1H, dd, *J* = 16.6, 2.9 Hz), 3.04 (1H, dd, *J* = 16.6, 13.1 Hz), 3.96 (1H, m), 4.36 (1H, m), 4.56 (2H, s), 4.64 (1H, ddd, *J* = 13.1, 2.7, 1.5 Hz), 4.92 (1H, br), 5.06 (1H, dd, *J* = 10.2, 1.2 Hz), 5.10 (1H, dd, *J* = 17.3, 1.2 Hz), 5.77 (1H, dddd, *J* = 17.3, 10.2, 7.8, 6.1 Hz), 6.70 (1H, d, *J* = 7.6 Hz), 6.86 (1H, d, *J* = 10.0 Hz), 6.89 (1H, d, *J* = 8.5 Hz), 7.42 (1H, dd, *J* = 8.5, 7.6 Hz), 10.82 (1H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 22.8, 24.5, 24.7, 26.7, 28.4 (×3), 30.4, 34.4, 40.5, 48.6, 50.2, 75.7, 77.2, 79.1, 80.7, 108.1, 109.6, 116.2, 117.3, 118.2, 134.8, 136.5, 139.4, 155.4, 162.2, 169.6, 170.0.

Anal. Calcd for $C_{29}H_{42}N_2O_8$: C, 63.72%; H, 7.74%; N, 5.12%. Found: C, 63.86%; H, 8.03%; N, 4.86%.

AI-77-B (1).



To a vigorously stirring mixture of **21** (94 mg, 0.172 mmol) and $NaIO_4$ (221 mg, 1.03 mmol) in a mixed solvent of CCl_4 (0.6 mL), CH_3CN (0.6 mL), and H_2O (1 mL) at 0 ℃ was

added $RuCl_3 \cdot xH_2O$ (0.7 mg, 0.004 mmol) and the mixture was stirred at rt for 11 h. After dilution with H_2O, the mixture was extracted with CH_2Cl_2. The combined extracts were dried (Na_2SO_4) and concd *in vacuo*. To complete the oxidation (the aldehyde component was detected by TLC), the crude product was retreated with a catalytic amount of $RuCl_3 \cdot xH_2O$ and $NaIO_4$ (18 mg, 0.086 mmol) in CCl_4 (0.6 mL), CH_3CN (0.6 mL), and H_2O (1 mL). After being stirred for 30 min, the mixture was worked up again similarly as above. The crude carboxylic acid **22** was used for the next reaction without further purification.

22: Colorless solid; R_f 0.38 ($CHCl_3$ / MeOH = 9 : 1).

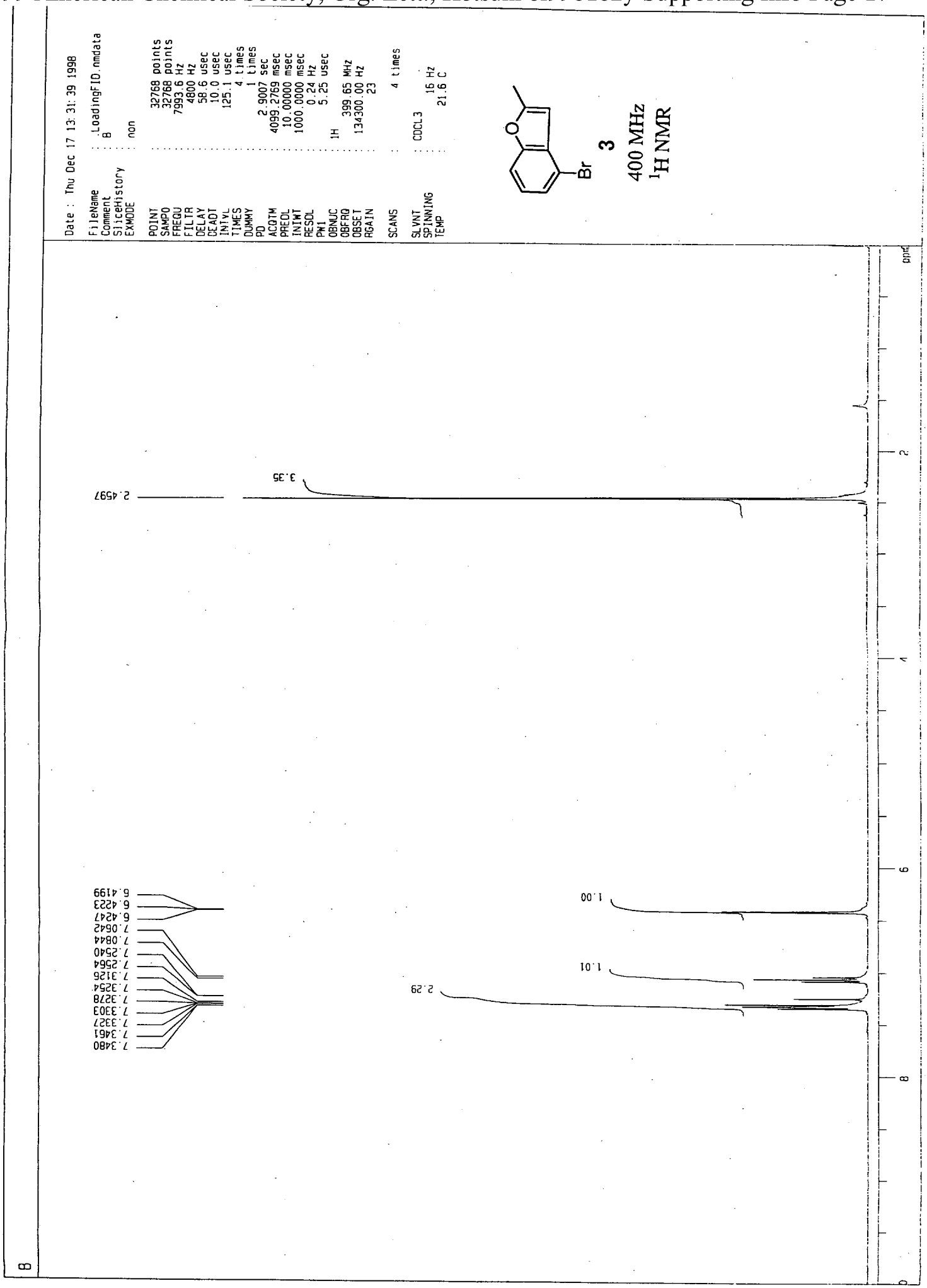
The protected AI-77-B **22** was treated with 3% HCl-MeOH (1.5 mL) at rt for 11 h. After dilution with 50% aq MeOH (1 mL), 0.1M aq. NaOH was added dropwise maintaining at pH 9 with stirring. After 3 h, the pH was adjusted to 6.5 by dropwise addition of 0.1M HCl. Then the mixture was charged on an Amberlite XAD-2 column (20 mL in water) and eluted with MeOH. Fractions containing AI-77-B (**1**) were combined and concd *in vacuo* to give **1** (62 mg, 85%) as a colorless solid.

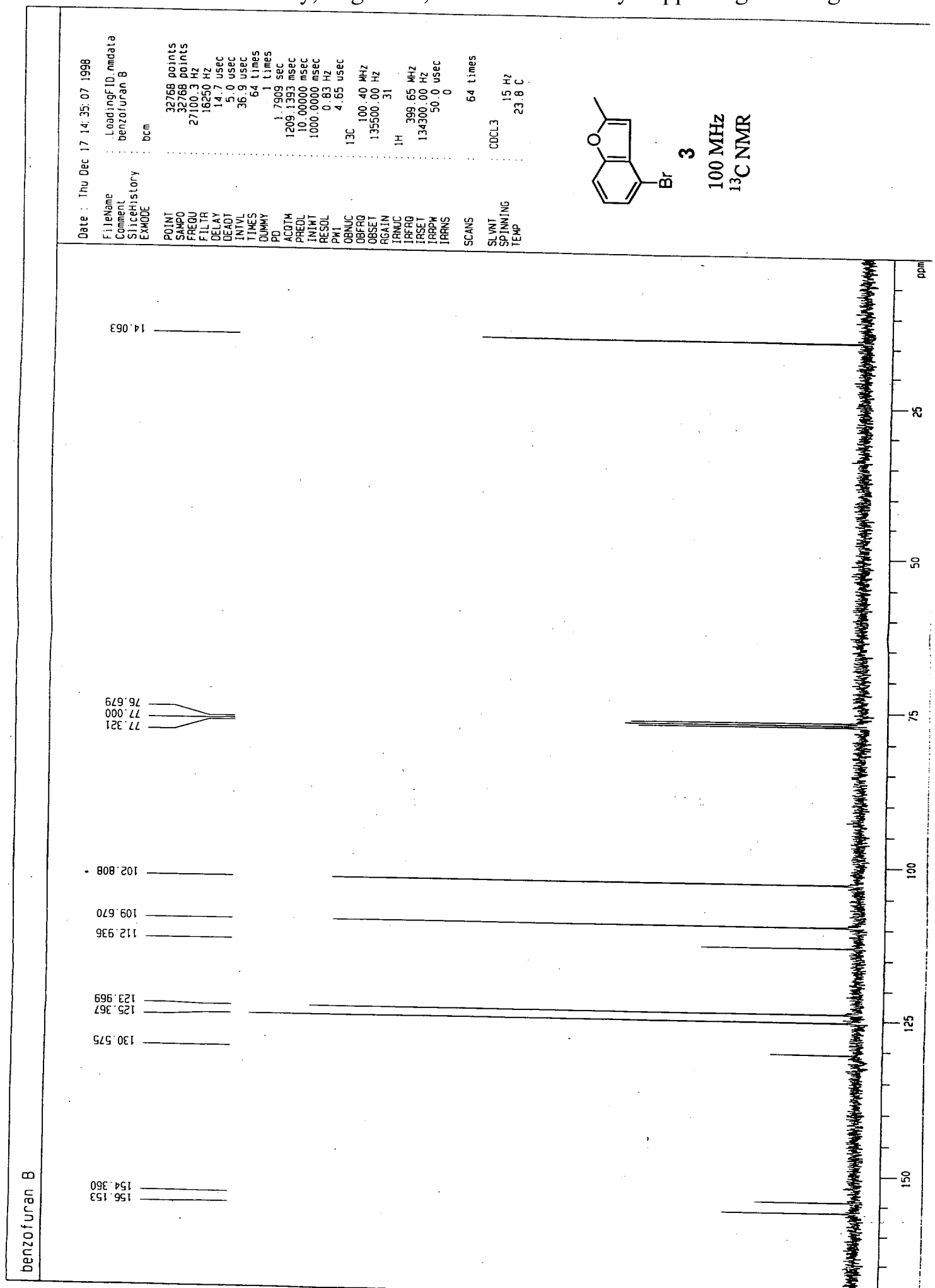
AI-77-B (**1**): Colorless plates; R_f 0.57 (*n*-BuOH / H_2O / pyridine / AcOH = 4 : 2 : 1 : 1); Mp 144.5-145.0 °C (from MeOH); $[\alpha]^{23}_D$ -76.1 (*c* 0.09, MeOH).

FTIR (KBr) ν 3437, 3331, 3144, 1653, 1462, 1389, 1235; ^{1}H NMR (400 MHz, **DMSO-d6**) δ 0.84 (3H, d, *J* = 6.3 Hz), 0.89 (3H, d, *J* = 6.1 Hz), 1.31 (1H, m), 1.58-1.72 (2H, m), 2.13, (1H, dd, *J* = 16.6, 9.8 Hz), 2.26 (1H, dd, *J* = 16.6, 3.6 Hz), 2.84 (1H, dd, *J* = 16.7, 2.8 Hz), 3.07 (1H, dd, *J* = 16.7, 12.8 Hz), 3.26 (1H, m), 3.66 (1H, m), 3.92 (1H, d, *J* = 7.6 Hz), 4.19 (1H, m), 4.68 (1H, ddd, *J* = 12.8, 2.8, 2.4 Hz), 6.80 (1H, d, *J* = 7.3 Hz), 6.84 (1H, d, *J* = 8.5 Hz), 7.47 (1H, dd, *J* = 8.5, 7.3 Hz), 7.90 (1H, br); ^{13}C NMR (100 MHz, **DMSO-d6**) δ 21.5, 23.3, 24.0, 29.0, 33.8, 38.9, 48.0, 50.1, 71.6, 72.1, 81.0, 108.3, 115.2, 118.5, 136.3, 140.7, 160.9, 169.0, 172.7, 173.6; ^{1}H NMR (400 MHz, **CD_3OD**) δ 0.93, 0.97 (each 3H, d, *J* = 6.6 Hz), 1.43 (1H, ddd, *J* = 13.7, 9.8, 3.7 Hz), 1.71 (1H, m), 1.83 (1H, ddd, *J* = 13.7, 11.0, 4.1 Hz), 2.51, (1H, dd, *J* = 17.1, 10.2 Hz), 2.61 (1H, dd, *J* = 17.1, 3.9 Hz), 2.92 (1H, dd, *J* = 16.6, 3.2 Hz), 3.08 (1H, dd, *J* = 16.6, 12.1 Hz), 3.60 (1H, ddd, *J* = 10.2, 4.1, 3.9 Hz), 3.93 (1H, dd, *J* = 7.0, 4.1 Hz), 4.13 (1H, d, *J* = 7.0 Hz), 4.34 (1H, dt, *J* = 11.0, 3.7 Hz), 4.66 (1H, ddd, *J* = 12.1, 3.7, 3.2 Hz), 6.78 (1H, d, *J* = 7.3 Hz), 6.83 (1H, d, *J* = 8.3 Hz), 7.44 (1H, dd, *J* = 8.3, 7.3 Hz); ^{13}C NMR (100 MHz, **CD_3OD**) δ 22.0, 23.8, 25.8, 30.9, 34.3, 40.7, 50.4, 52.6, 72.7, 73.0, 82.7, 109.4, 116.7, 119.5, 137.5, 141.5, 163.2, 171.0, 175.2 (×2).

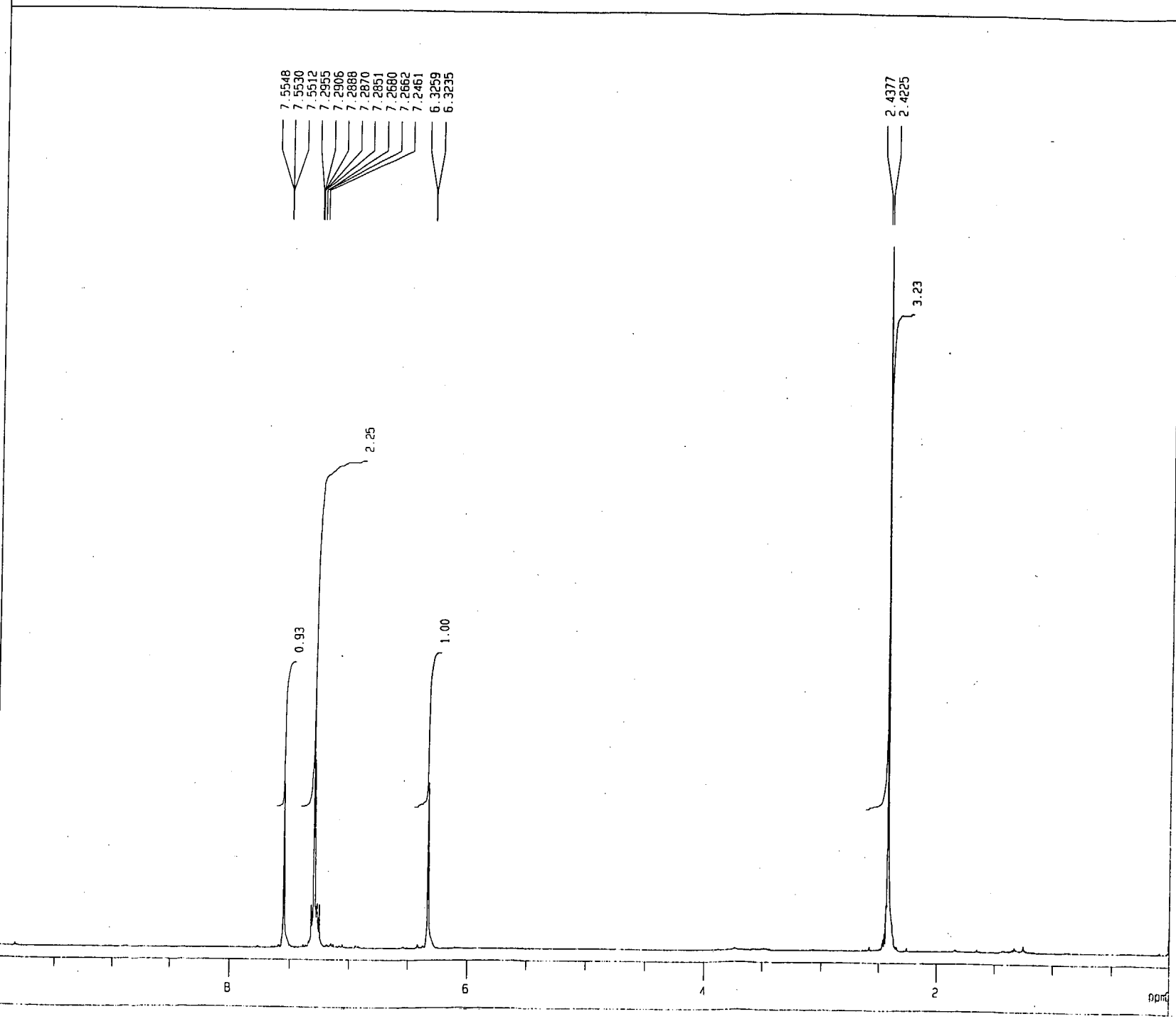
HRMS (FAB) calcd for $C_{20}H_{28}N_2O_8$ + H 425.1924, found 425.1905.

Anal. Calcd for $C_{20}H_{28}N_2O_8$: C, 56.59%; H, 6.65%; N, 6.60%. Found: C, 56.19%; H, 6.81%; N, 6.63%.





benzofuran A



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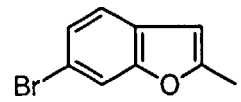
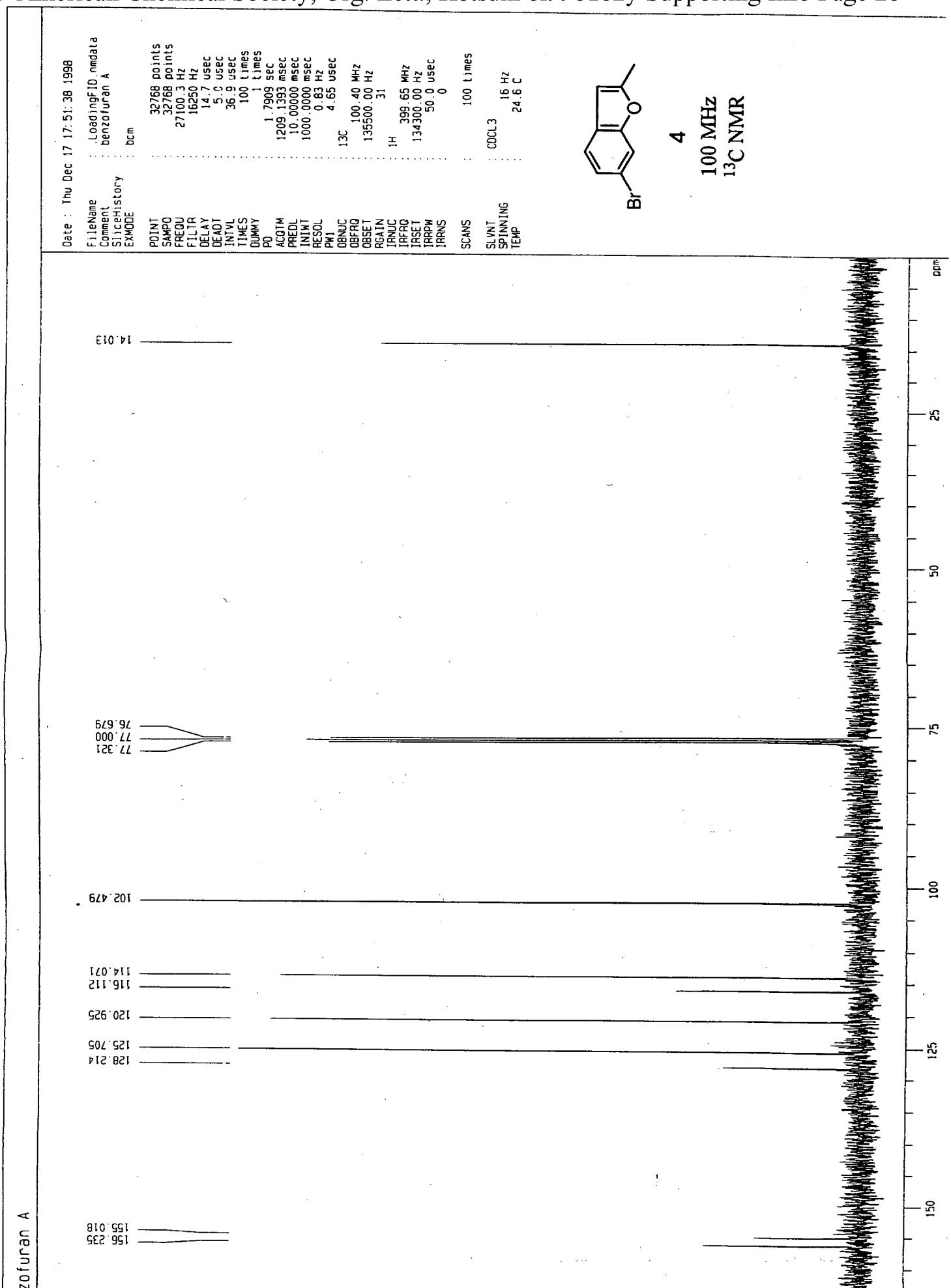
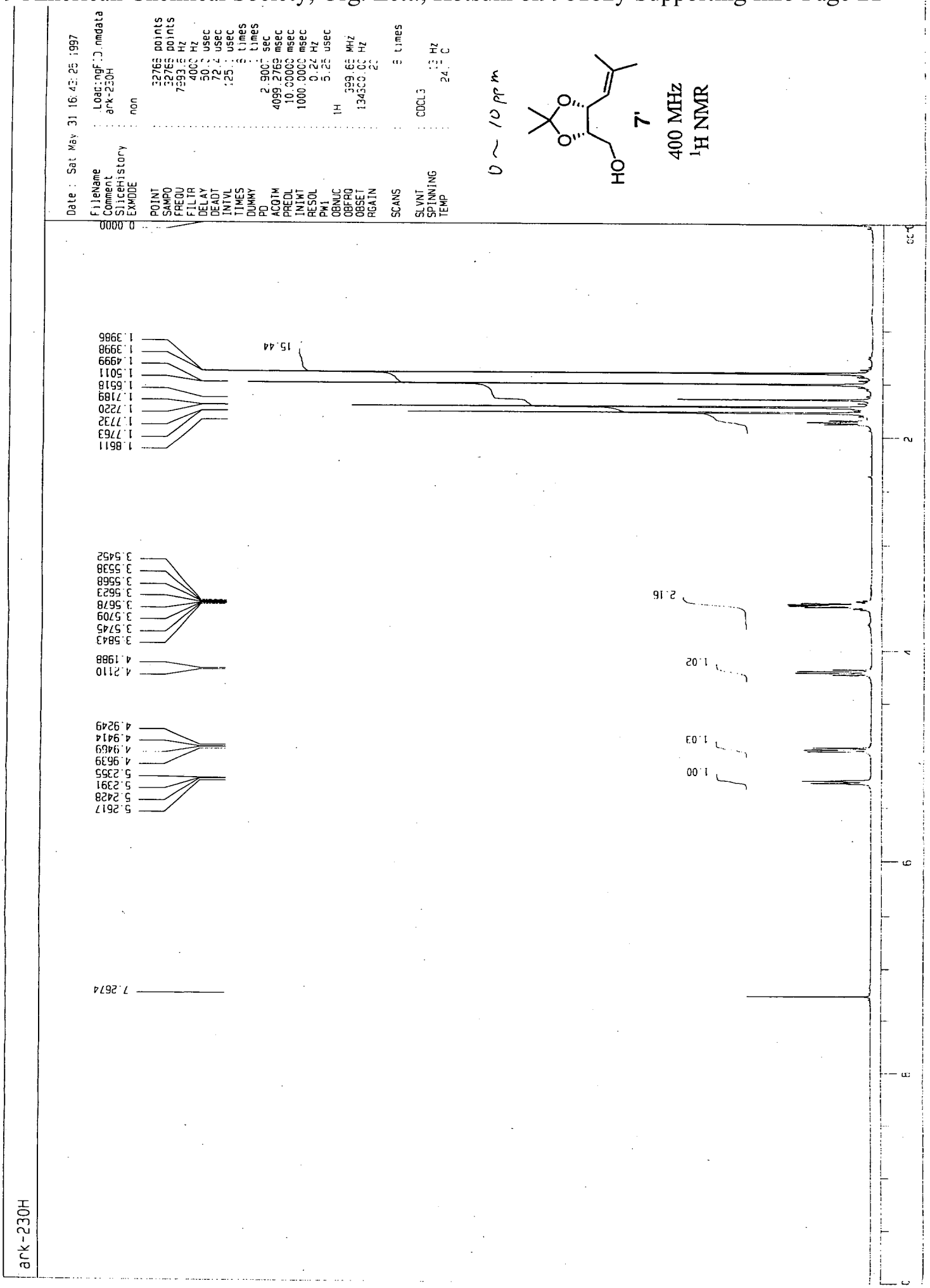


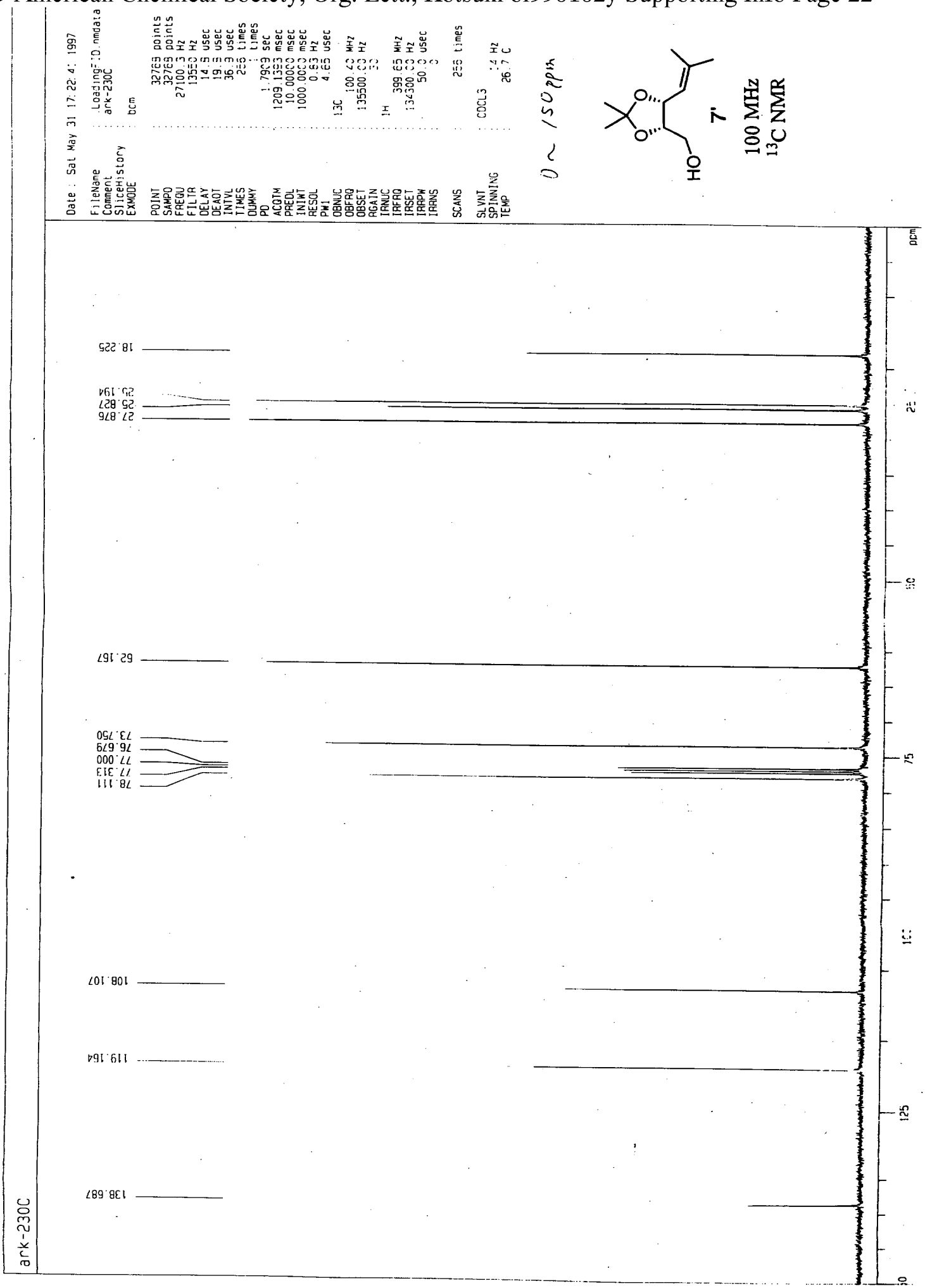
4

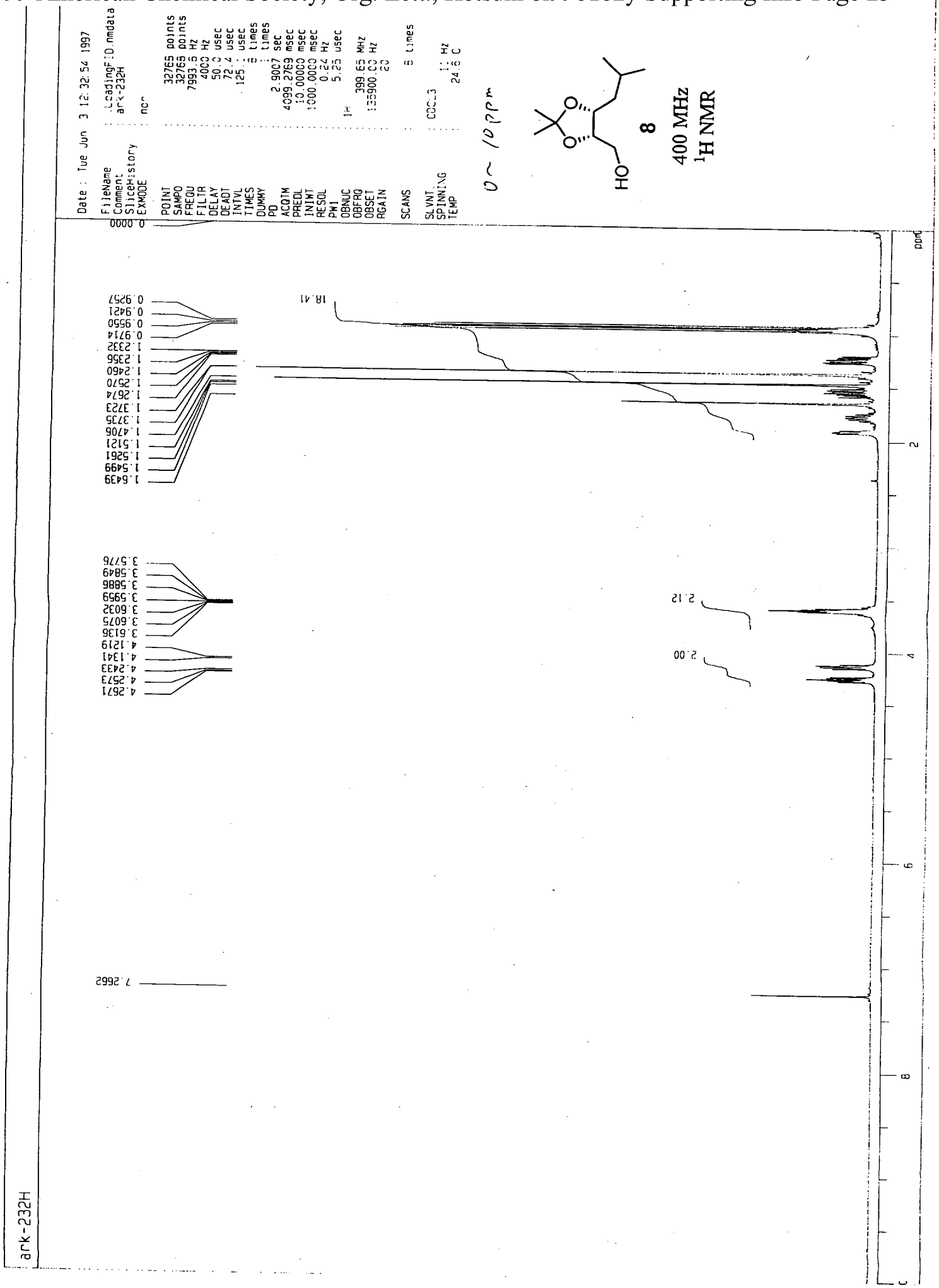
400 MHz

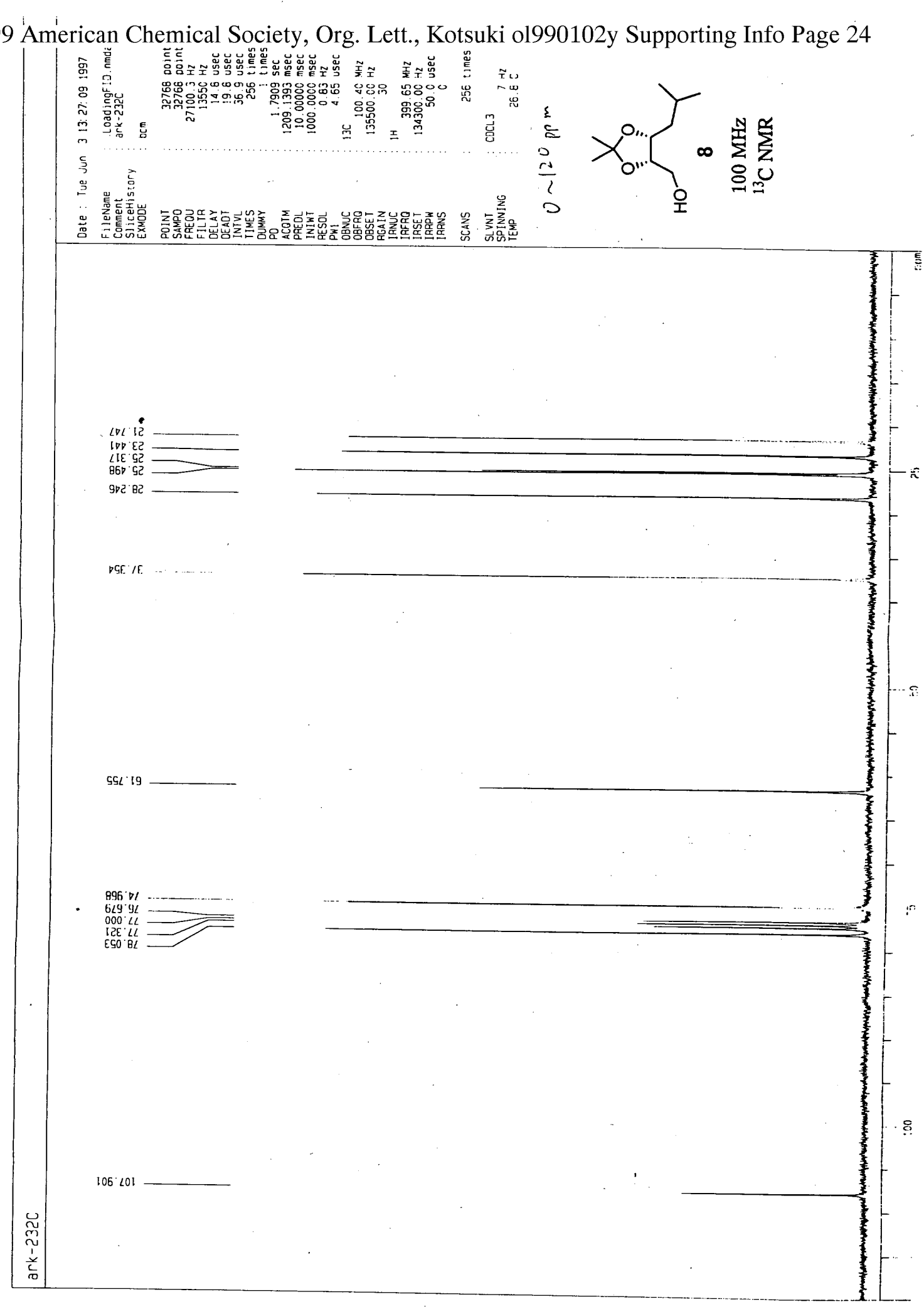
^{1}H NMR

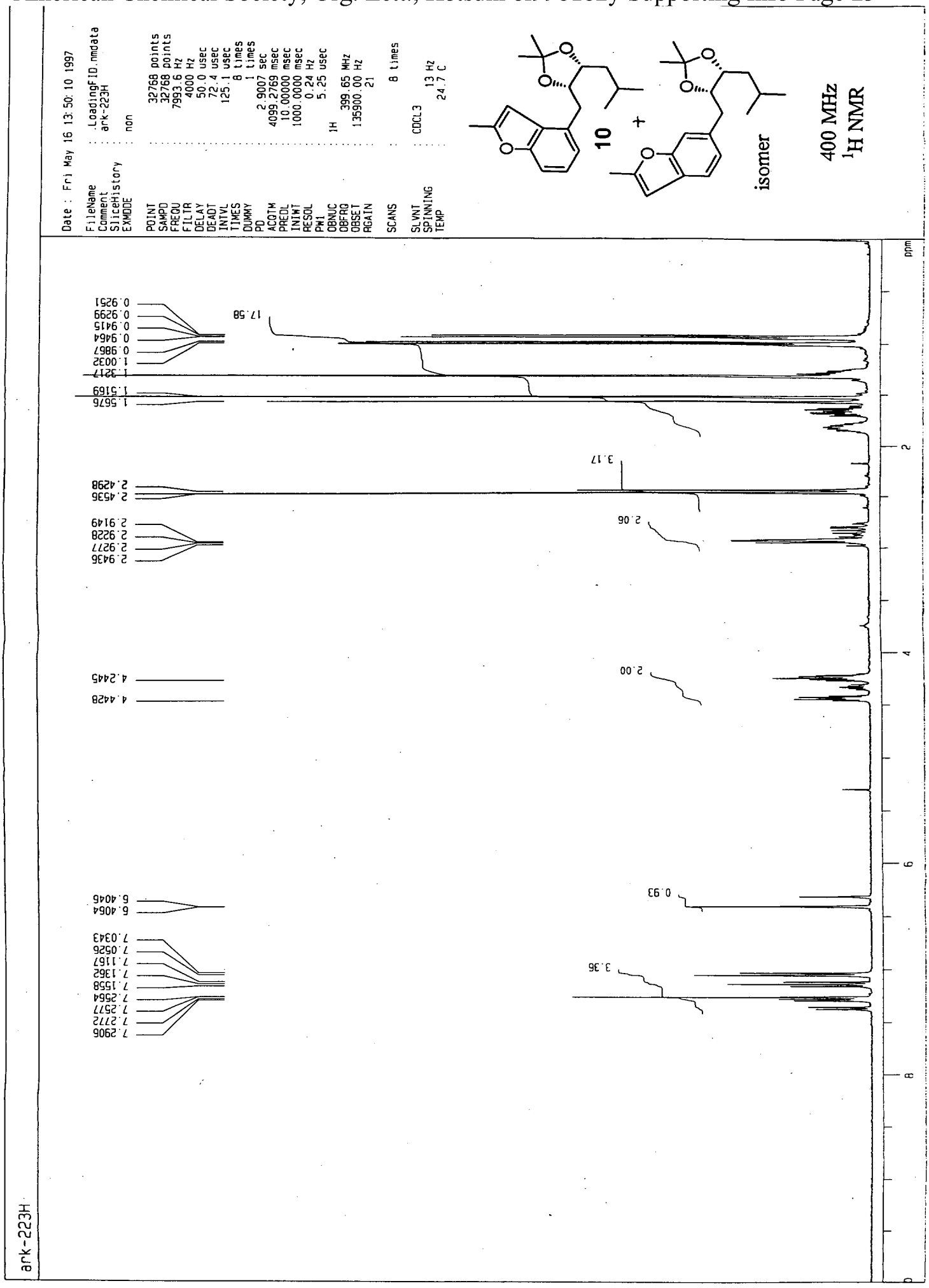


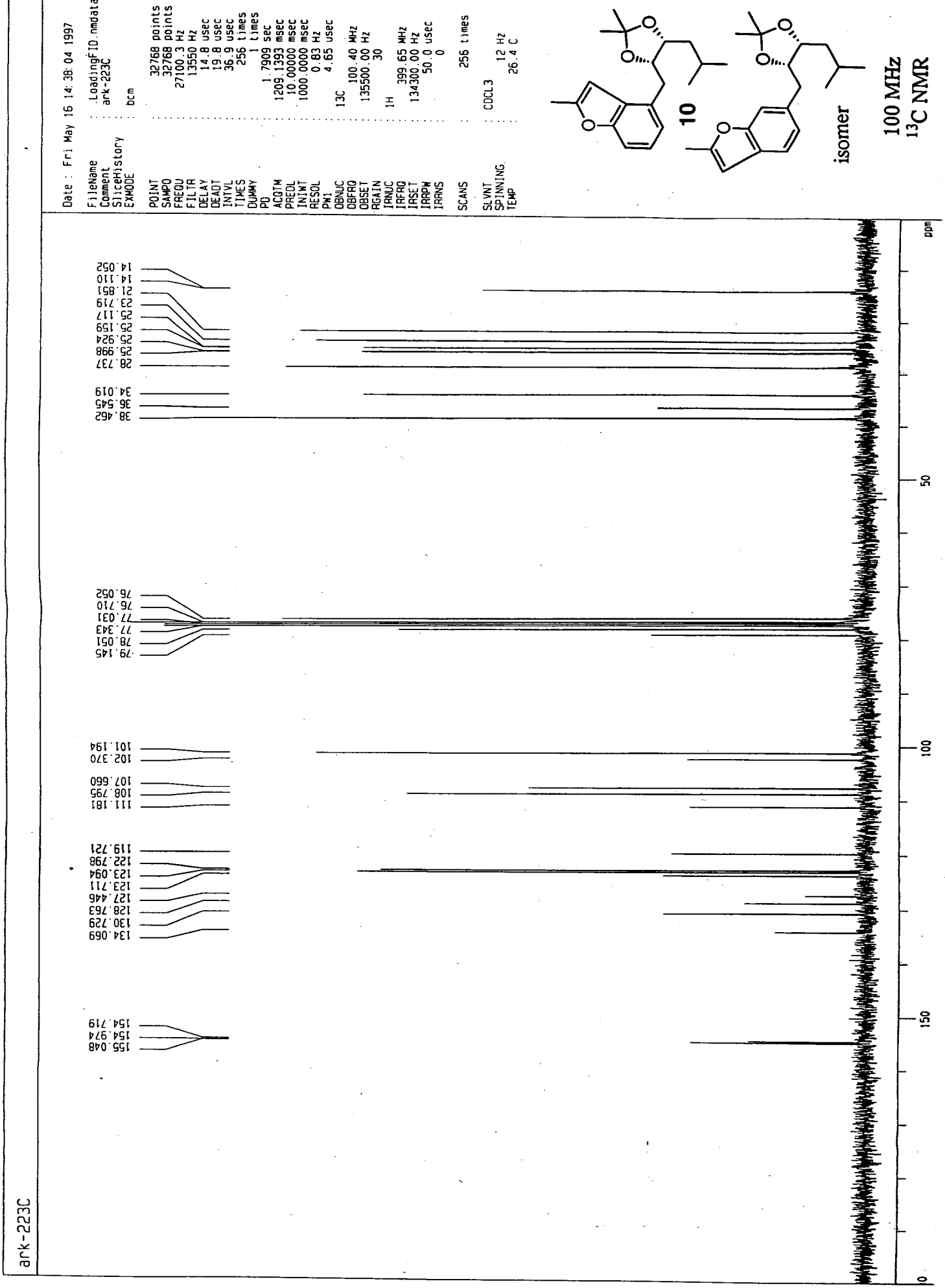


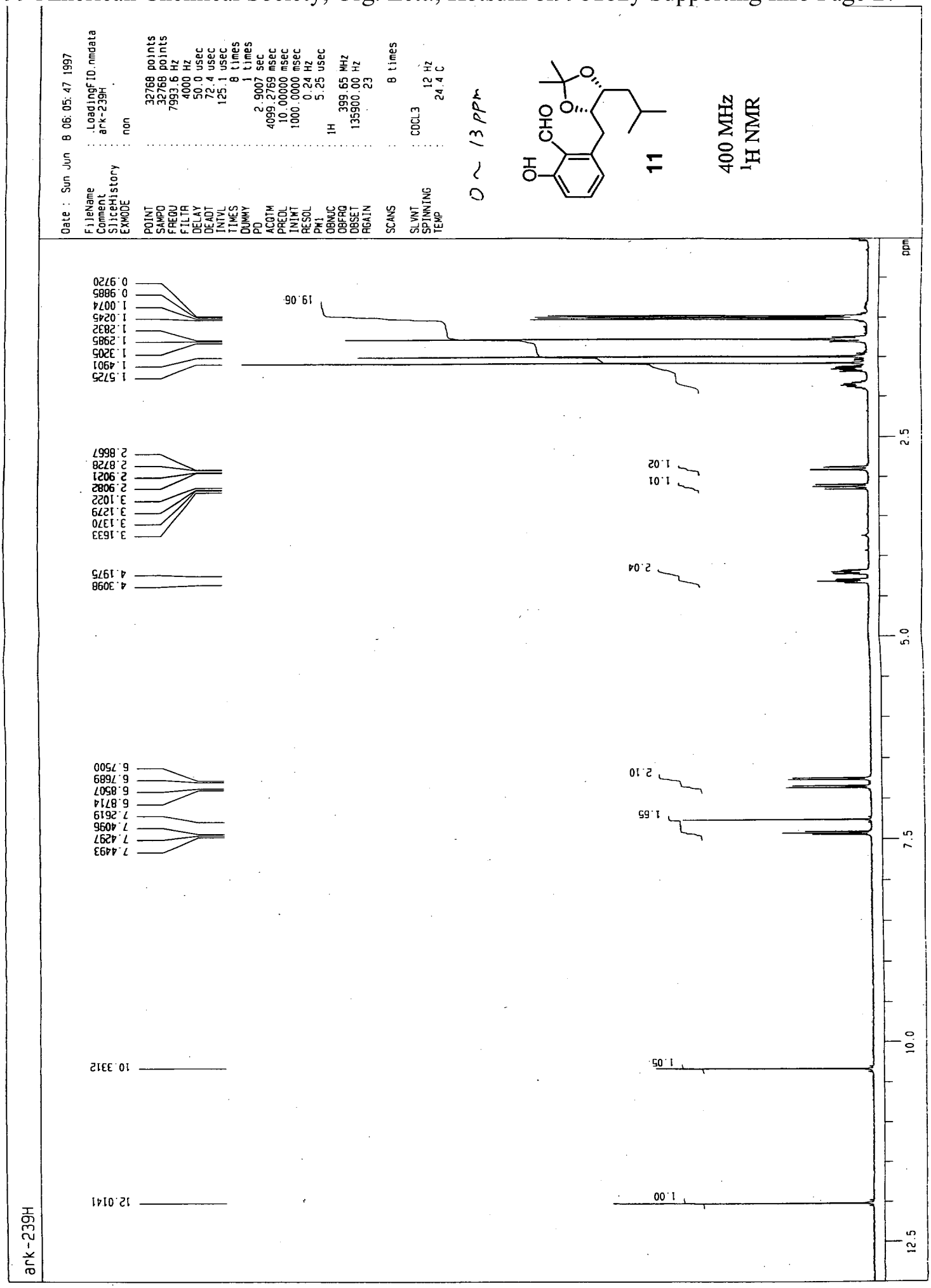


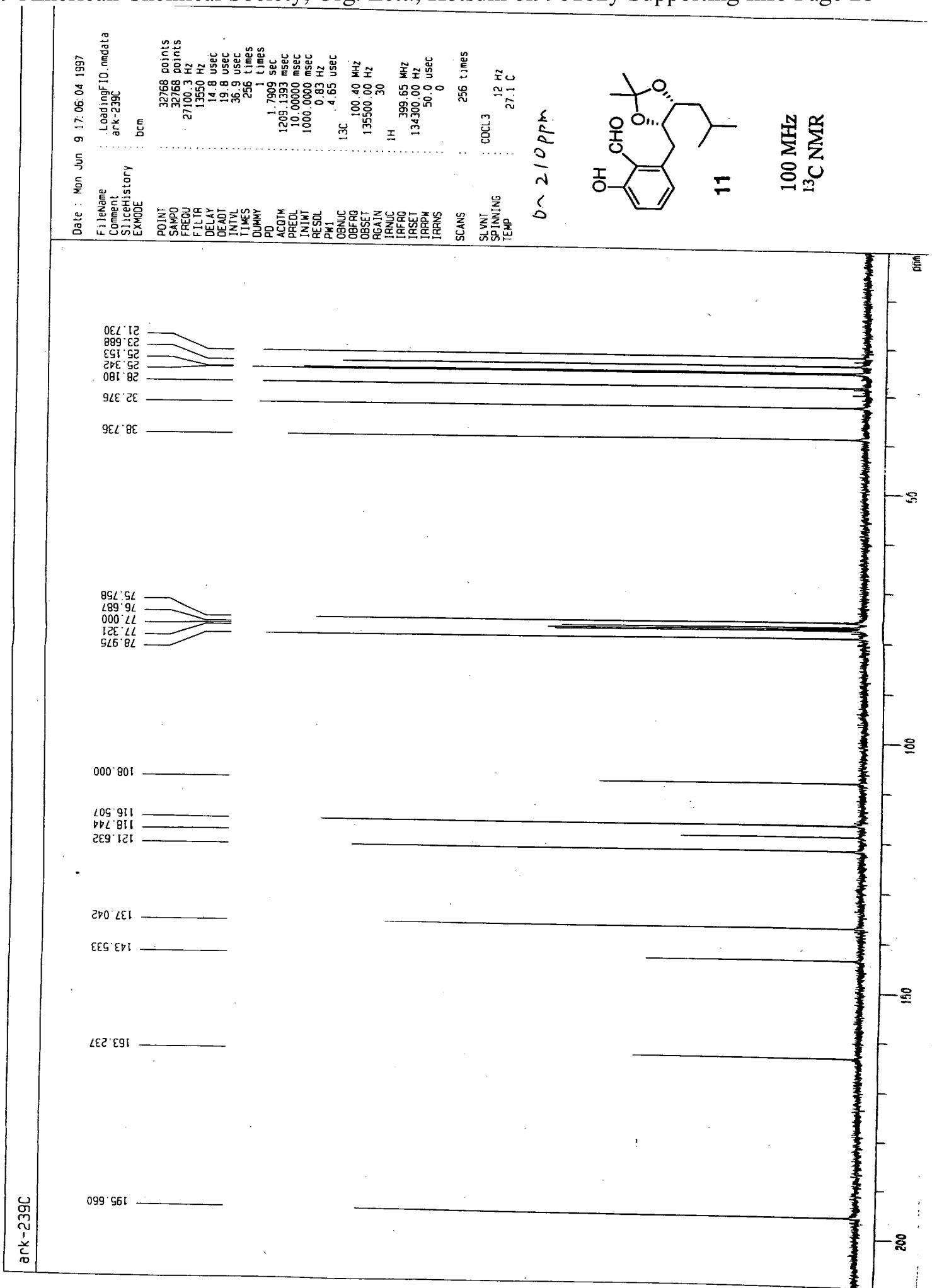


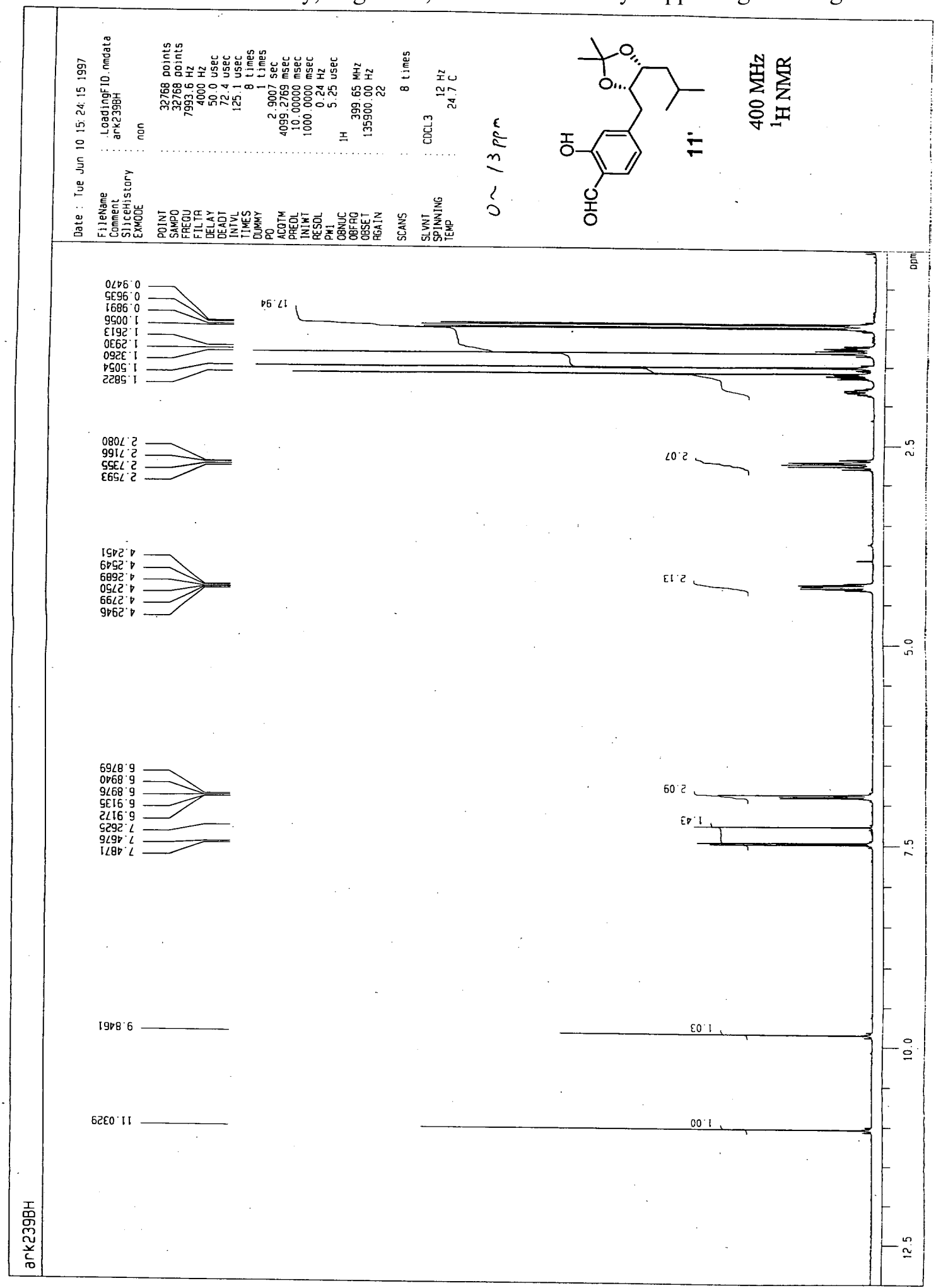


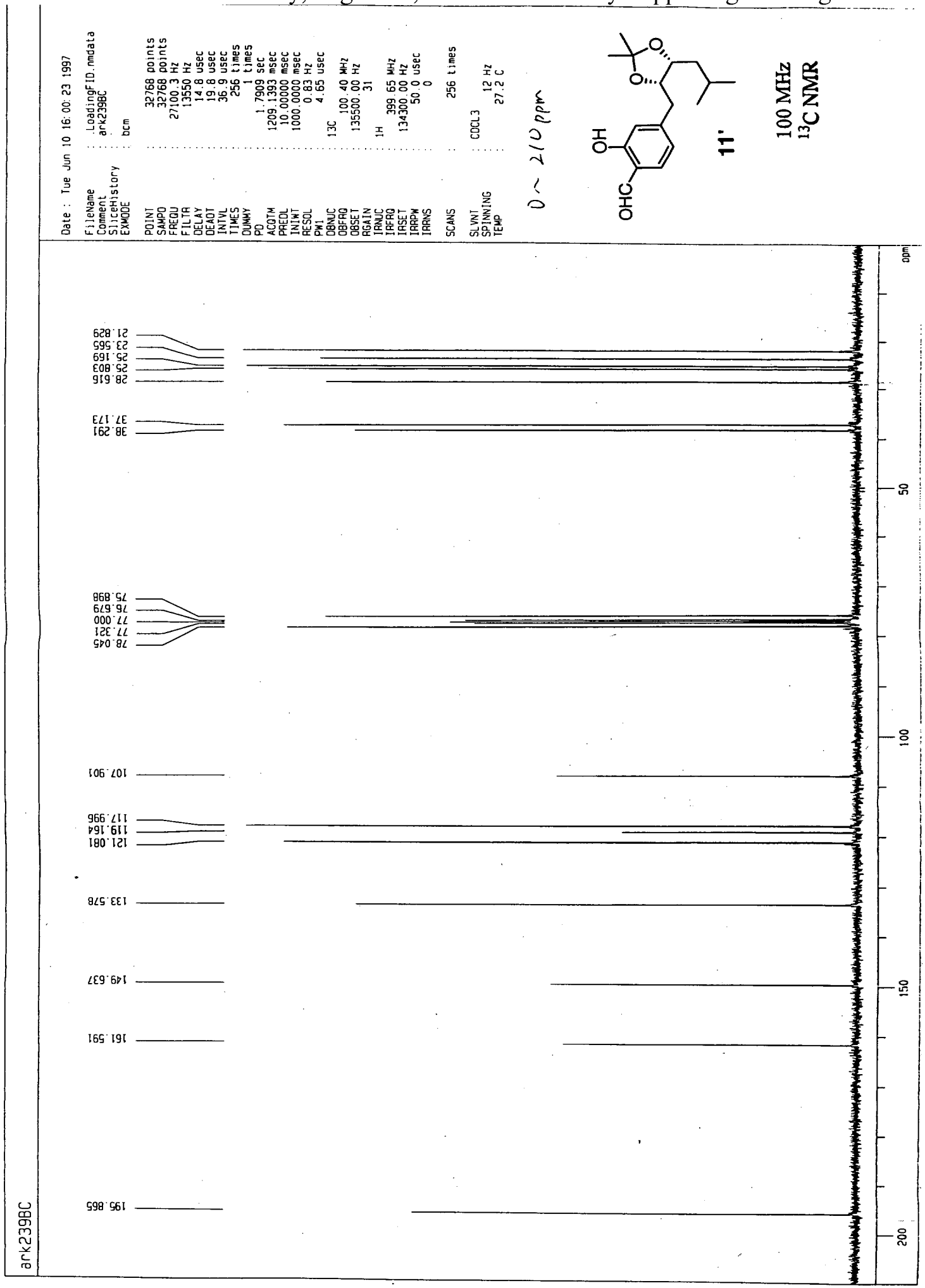


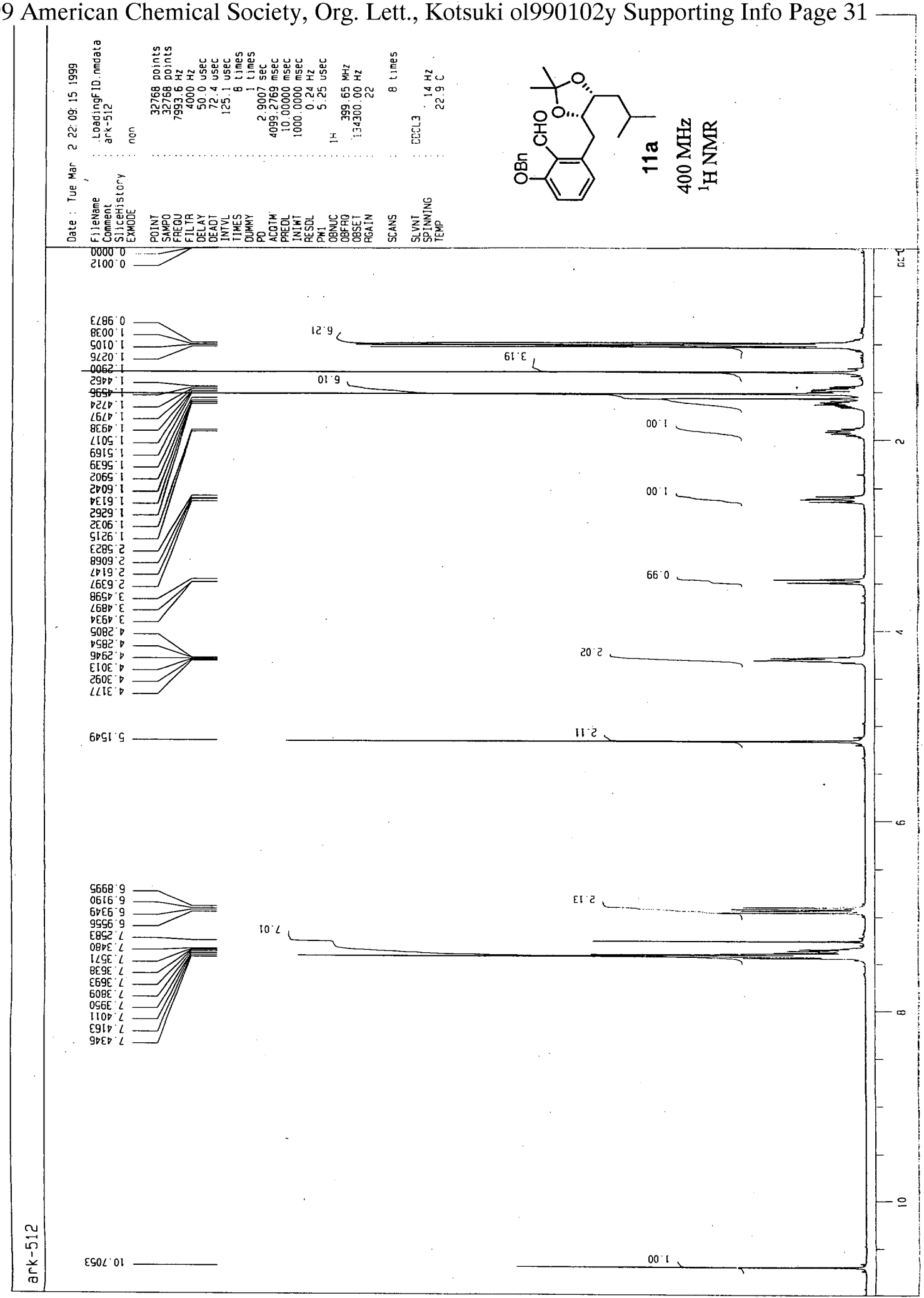


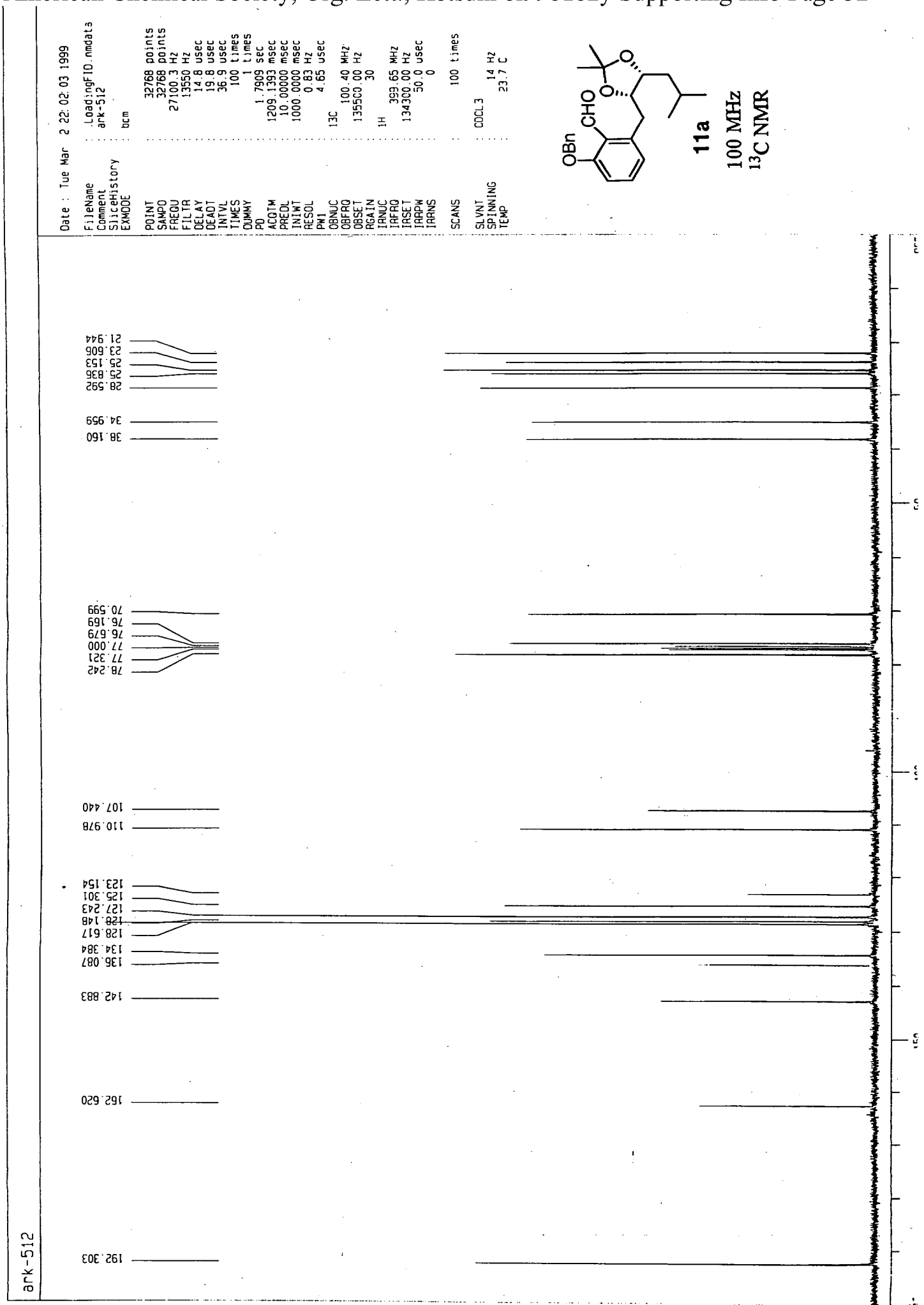








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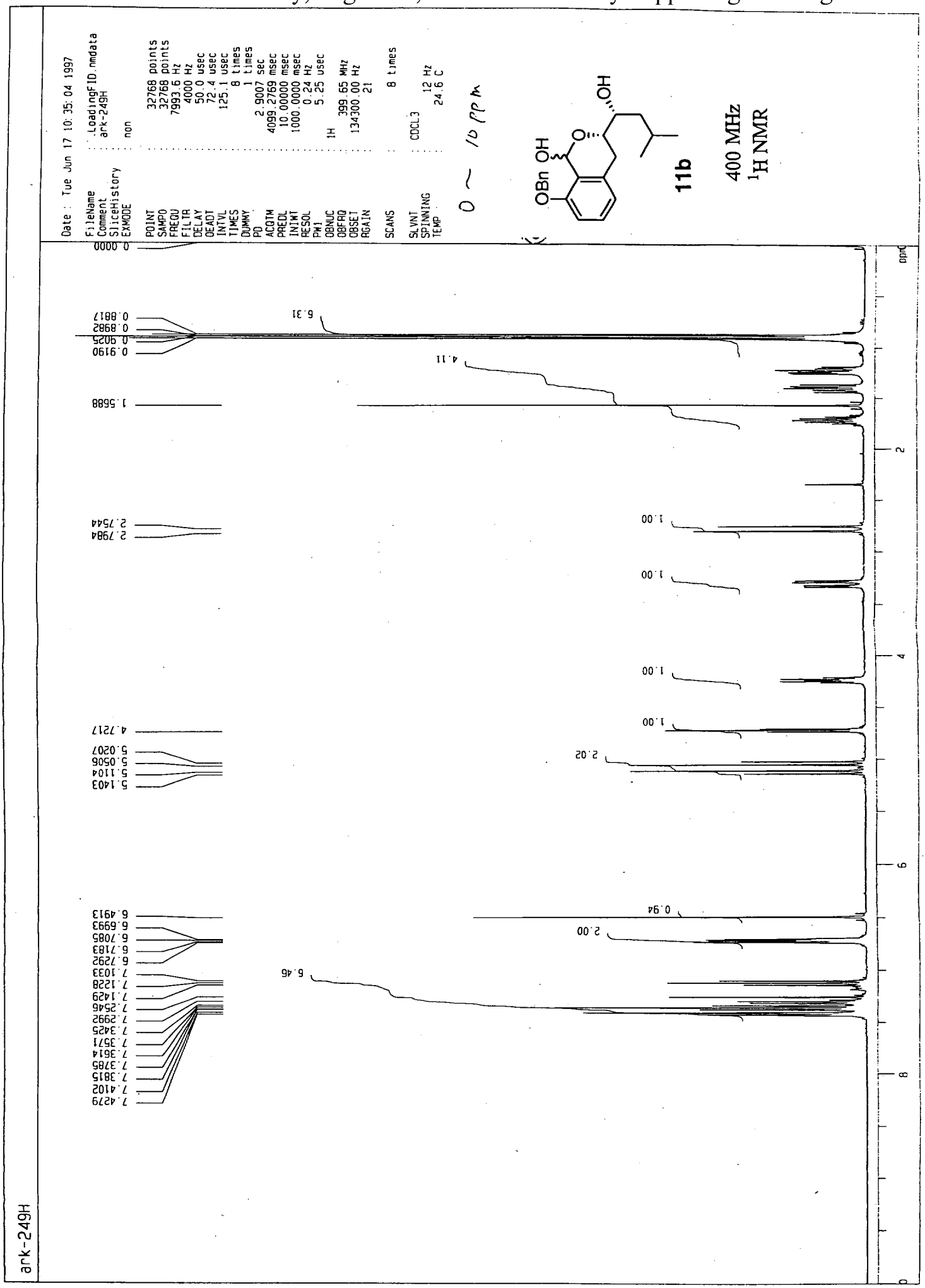

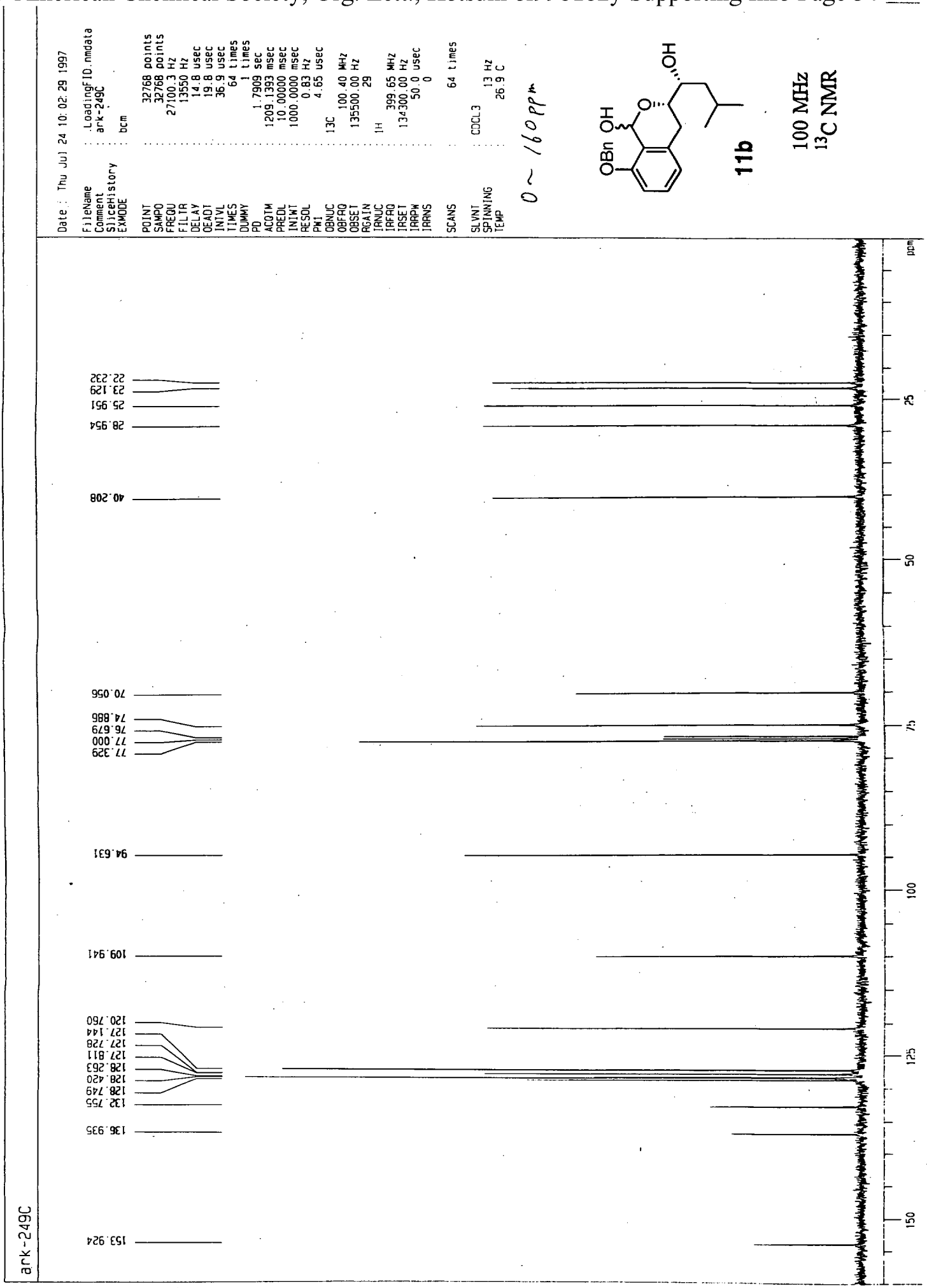
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