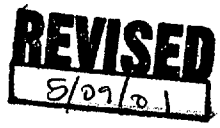

SUPPLEMENTARY MATERIAL

for
the
communication
entitled

Stereoselective *trans* and *cis*-Dihydroxylations of 2*H*-Pyranyl and Dihydropyridinyl Heterocycles Synthesized from Formal [3 + 3]–Cycloaddition Reactions of α,β-Unsaturated Iminium Ions with 1,3-Dicarbonyl Equivalents.

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EXPERIMENTAL PROCEDURES:

Epoxidation Procedure

To a solution of the alkene [83.1 mg, 0.43 mmol] in CH_2Cl_2 (9 ml) at - 10 °C was added a mixture of *m*-CPBA [145.2 mg, 77%, 0.65 mmol] and K_2CO_3 [26.0 mg, 0.19 mmol]. After 1.5 h at rt, the mixture was diluted with CH_2Cl_2 [25 mL] and washed with saturated aqueous $NaHCO_3$ [3 X 50 mL]. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified via silica gel column chromatography [Gradient Eluent: 1:4 to 1:2 ethyl acetate in hexane] to give an inseparable mixture of diastereomers.

General Procedure for *trans*-Dihydroxylation

To a solution of olefin [52.8 mg, 0.28 mmol] in isopropanol [3 mL] was added MMPP [magnesium monoperoxyphthalate] [200.0 mg, 0.40 mmol] as a solution in H_2O [6.5 mL]. After 8 h at 50 °C, [or 72 h at 0 °C] the mixture was diluted with saturated aqueous $NaHCO_3$ (10 mL) and extracted with ether [3 x 20 mL] and CH_2Cl_2 [3 x 20 mL]. The combined organic layers were dried over Na_2SO_4, concentrated under reduced presssure, and purified via silica gel column chromatography [Gradient Eluent: 1:1 ethyl acetate-hexanes to 3:1 ethyl actetate-hexanes].

General Procedure for *Cis*-Dihydroxylation

To a solution of olefin [45.4 mg, 0.21 mmol] in *t*-BuOH [5 mL] and H_2O [5 mL] at 0 °C was added K_2CO_3 [86.2 mg, 0.62 mmol], $K_2Fe(CN)_6$ [206 mg, 0.62 mmol], and osmium tetroxide [0.50 mg, 0.0020 mmol]. After TLC showed the reaction was complete, the mixture was diluted with H_2O [20 mL] and extracted with Et_2O [2 x 30 mL] and CH_2Cl_2 [2 x 30 mL]. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified via silica gel column chromatography [Gradient Eluent: 1:1 ethyl acetate-hexanes].

Asymmetric dihydroxylation

To a stirred solution of pyrone **12** [38.6 mg, 0.2 mmol] in 2 mL *t*-BuOH/H_2O [1:1] at 0 °C was added $K_3Fe(CN)_6$ [200.0 mg, 0.60 mmol], K_2CO_3 [83.0 mg, 0.60 mmol], $MeSO_2NH_2$ [38.0 mg, 0.40 mmol] and $(DHQD)_2PYR$ [two dihydroquinidine ligands linked with pyrimidine] [2.5 mg, 1.4 mol%]. Osmium tetraoxide [3 drops, 2.5 wt% in *t*-BuOH] was then added and the mixture was stirred vigourously at 0 °C for 15 hours, then at room temperature for an additional 15 hours. The reaction was quenched by the addition of Na_2SO_3, and extracted with ethyl acetate and water. Following an aqueous 2 *M* KOH wash, the organic extract was dried over Na_2SO_4 and solvent removed *in vacuo* to afford diol **19-*cis*** in 66% yield as a clear oil.

An identical procedure was carried using $[DHQ]_2PHAL$ [two dihydroquinine ligands linked with phthalazine] to obtain ***ent*-19-*cis***.

Synthesis of Mono-Alcohol 33

Hydrogenation Protocol:

To a solution of 20.0 mg of diol **30** [0.053 mmol] in 0.5 ml of Ac_2O in a 5 mL round bottom flask, Pd/C [10 %w, 14 mg, 25%mol] was added. After three vacumn-H_2 flushing cycles, the mixture was stirred at

RT and under H_2 atmosphere for 3 h. The resulting mixture was poured on the top of a short pipet-column directly. The solvent- Ac_2O was removed by washing with hexane. The pure product **33** was obtained in 74% yield after purification via silica gel column chromatography [Gradient Eluent: 0-50% EtAc in hexane].

Reductive Protocol:
To a suspension of 55.0 mg of diol **30** [0.15 mmol]in 2.5 mL of triethylsilane, trifloroacetic acid [12.0 equiv, 0.14 mL] was added dropwise at rt. The mixture was stirred for 20 h at rt. The yellow precipitate was dissolved by adding 10 mL of CH_2Cl_2. The reaction was quenched with 3 mL of sat. $NaHCO_3$ and followed by normal aqueous work-up procedure. The product **33** was obtained in 77 % yield after purification via silica gel column chromatography [Gradient Eluent: 0-50% EtAc in hexane].

Synthesis of Thiolcarbomate 34
To a solution of diol **30** [48.2 mg, 0.17 mmol] in CH_2Cl_2 (6 mL) was added 1,1'-carbonyldiimidazole [56.2 mg, 0.35 mmol] and DMAP [10.0 mg, 0.082 mmol]. After 1.5 h at rt, the reaction mixture was filtered through a SiO_2 filter cake eluted with 1:1 ethyl acetate in hexane, dried over Na_2SO_4, and concentrated under reduced pressure to give the thiolcarbonate **34** in 92% yield as a white powder.

Barton-Type Deoxygenation Protocol:
In a 25 mL seal-tube, thiolcarbomate **34** [21.0 mg, 0.05 mmol], AIBN [~1-2 mg], and 0.35 mL $^nBu_3SnH$ were mixed, sealed and heated to 130 °C for 2 h. The cooled reaction mixture was purified directly, and the product **33** was obtained in 78 % yield after purification via silica gel column chromatography [Gradient Eluent: 0-50% EtAc in hexane].

SPECTROSCOPIC CHARACTERIZATIONS:

Benzoate 14
R_f = 0.40 (50% EtOAc in hexane)
trans-**Isomer:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 3 H), 1.49 (s, 3 H), 2.22 (s, 3 H), 4.04 (d, 1 H, J = 4.5 Hz), 5.80 (s, 1 H), 6.21 (d, 1 H, J = 4.5 Hz), 7.36 (t, 1 H, J = 7.8 Hz), 7.53 (d, 1 H, J = 7.8 Hz), 7.89 (d, 1 H, J = 7.5 Hz), 7.93 (s, 1 H);
mass spectrum (GCMS): m/e (%relative intensity) 208 (100) M^+-HOBz*, 180 (15), 165 (53), 150 (18), 139 (31), 122 (51), 94 (42), 85 (27), 69 (27), 51 (18);
cis-**Isomer:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 3 H), 1.47 (s, 3 H), 2.22 (s, 3 H), 3.96 (d, 1 H, J = 4 Hz), 5.81 (s, 1 H), 5.90 (d, 1 H, J = 3.5 Hz), 7.36 (t, 1 H, J = 7.8 Hz), 7.53 (d, 1 H, J = 7.8 Hz), 7.89 (d, 1 H, J = 7.5 Hz), 7.93 (s, 1 H);
mass spectrum (GCMS): m/e (%relative intensity) 208(1) M^+-HOBz*, 205 (9), 149 (100);
1:1 Mixture ^{13}C NMR (MHz, $CDCl_3$) δ 20.0, 20.1, 20.6, 22.8, 24.0, 26.0, 65.4, 68.5, 71.5, 80.7, 80.8, 94.0, 94.6, 100.2, 100.4, 128.0, 128.1, 128.2, 129.7, 129.8, 129.9, 130.1, 133.2, 134.5, 163.0, 163.1, 163.4, 165.6, 165.8, 166.7;

Benzoate 15

***trans*-Isomer:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (s, 6H), 3.93 (s, 6H), 4.01 (d, 1H, J = 3.3 Hz), 5.97 (d, 1H, J = 3.0 Hz), 6.36 (s, 1H), 6.89 (s, 1H), 7.26-7.52 (m, 4H), 7.87-7.98 (m, 2H);

***cis*-Isomer:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51 (s, 6H), 3.92 (s, 6H), 4.10 (d, 1H, J = 4.2Hz), 6.28 (d, 1H, J = 4.2 Hz), 6.36 (s, 1H), 6.92 (s, 1H), 7.26-7.52 (m, 4H), 7.87-7.98 (m, 2H);

1:1 Mixture ^{13}C NMR (75MHz, $CDCl_3$) δ 20.8, 22.7, 24.1, 26.0, 56.0, 56.1, 65.6, 68.8, 71.5, 71.7, 80.9, 94.4, 94.8, 96.2, 96.4, 108.3, 111.0, 119.4, 123.5, 123.6, 128.0, 128.1, 129.7, 129.9, 131.4, 133.3, 134.5, 149.2, 151.7, 161.0, 161.2, 162.4, 162.7, 165.7, 166.0, 166.7;

IR (thin film) cm^{-1} 3445 (m), 3092 (w), 2981 (m), 2938 (m), 1722 (s), 1632 (m), 1570 (s), 1517 (s), 1266 (s), 1135 (s), 808 (w), 769 (w), 734 (m).

Diol 19-*trans*

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (s, 3H), 1.51 (s, 3H), 2.22 (s, 3H), 2.68 (s, 1H), 3.69 (dd, 1H, J = 3.0, 7.5 Hz), 4.37 (s, 1H), 4.53 (d, 1H, J = 7.5Hz), 5.79 (s, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 19.5, 19.9, 25.8, 66.2, 74.6, 81.9, 98.5, 100.6, 162.2, 163.6, 164.9;

IR (thin film) cm^{-1} 3402 (br), 2980 (w), 2932 (w), 1694 (s), 1650 (m), 1580 (s), 1450 (m).

Diol 19-*cis*

R_f = 0. 155 (50% EtOAc in hexane)

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (s, 3 H), 1.45 (s, 3 H), 2.15 (s, 3 H), 3.12 (s, 1 H), 3.72 (d, 1 H, J = 4.5 Hz), 4.73 (d, 1 H J = 4.5 Hz), 4.85 (s, 1 H), 5.75 (s, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 19.8, 23.4, 23.7, 61.8, 69.4, 81.1, 96.6, 100.7, 161.8, 164.2, 165.7;

IR (thin film) cm^{-1} 3450 (m), 2982 (w), 2923 (w), 1692 (s), 1649 (m), 1578 (s);

mass spectrum (CI): m/e (%relative intensity); 227 (100) $M + H^+$, 209 (16);

m+1/e calcd for $C_{11}H_{15}O_5$ 227.0920, found 227.0909.

$[\alpha]_D^{23}$ = (+) 44.5 (c = 0.35, EtOH)

Diol 20-*trans*:

R_f = 0.21 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (m, 1H), 1.49 (m, 1H,), 1.69 (m, 7H), 2.04 (m, 1H), 2.27 (s, 3H), 3.69 (d, 1H, J = 7.5 Hz), 4.43 (brs, 1H), 4.61 (d, 1H, J = 7.5 Hz), 5.38 (s, 1H), 5.91 (d, 1H, J = 0.6 Hz);

^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8, 20.8, 25.0, 26.9, 32.7 65.8, 74.6, 82.5, 98.5, 100.5, 162.1, 163.3, 164.8 (missing one upfield signal due to overlap);

IR (neat) cm^{-1} 3428 (brs), 2933 (s), 2861 (m), 1694 (s), 1651 (s), 1580 (s), 1320 (w);

mass spectrum (EI): m/e (%relative intensity) 266 (7) M^+, 155 (100), 112 (70), 94 (19); m/e calcd for $C_{14}H_{18}O_5$ 266.1154, found 266.1149.

Diol 20-*cis*:

R_f = 0.35 (50% EtOAc in hexane);

^{1}H NMR (300 MHz, $CDCl_3$) *syn* δ 1.34 (m, 1H), 1.41 (m, 1H), 1.53 (m, 2H), 1.62 (m, 6H), 2.21 (s, 3H), 3.07 (s, 1H), 3.85 (d, 1H, J = 4.5 Hz), 4.78 (d, 1H, J = 4.5 Hz), 4.92 (s, 1H), 5.87 (s, 1H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8, 20.9, 21.1, 25.2, 30.9, 31.8, 61.8, 68.7, 82.1, 96.8, 100.9, 161.9, 164.2, 165.8;
IR (neat) cm^{-} 3450 (brs), 2933 (s), 2861 (m), 1687 (s), 1648 (m), 1579 (s), 1427 (m), 1351 (w);
mass spectrum (EI): m/e (%relative intensity) 266 (8) M^+, 155 (100), 139 (5), 112 (85); m/e calcd for $C_{14}H_{18}O_5$ 266.1154, found 266.1157.

Olefin 24

R_f = 0. 488 (50% EtOAc in hexane)
^{1}H NMR (500MHz, $CDCl_3$) δ 1.31 (qt, 1 H, J = 4.0, 13.5 Hz), 1.44 (qt, 1 H, J = 3.5, 14.0 Hz), 1.72 (m, 2 H), 1.87 (m, 1 H), 1.96 (m, 1 H), 2.11 (m, 1 H), 2.15 (s, 3 H), 2.39 (m, 1 H), 5.00 (dd, 1 H, J = 5.5, 11.5 Hz), 5.68 (s, 1 H), 6.03 (s, 1 H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 20.1, 24.5, 26.9, 33.1, 35.1, 79.7, 97.3, 99.8, 109.1, 133.1, 161.4, 162.6, 163.3;
IR (thin film) cm^{-1} 2933 (m), 2864 (w), 1714 (s), 1639 (m), 1566 (s);
mass spectrum (GCMS): m/e (%relative intensity) 218 (73) M^+, 189 (100), 139 (18), 91 (15);
m/e calcd for $C_{13}H_{15}O_3$ 219.1021 $(M + H)^+$, measd 219.1008

Olefin 25

R_f = 0. 405 (50% EtOAc in hexane)
^{1}H NMR (500MHz, $CDCl_3$) δ 1.34 (q, 1 H, J = 13.0 Hz), 1.47 (q, 1 H, J = 13.5 Hz), 1.78 (m, 2 H), 1.91 (m, 1 H), 2.01 (m, 1 H), 2.16 (m, 1 H), 2.43 (d, 1 H, J = 14.0 Hz), 3.90 (s, 3 H), 3.92 (s, 3 H), 5.05 (dd, 1 H, J = 4.0, 10.5 Hz), 6.11 (s, 1 H), 6.26 (s, 1 H), 6.87 (d, 1 H, J = 8.7 Hz), 7.28 (d, 1 H, J = 2.3 Hz), 7.34 (dd, 1 H, J = 2.3, 8.7 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 24.5, 26.9, 33.2, 35.2, 56.0, 56.1, 79.7, 96.1, 98.0, 108.1, 109.3, 111.0, 118.8, 124.1, 133.5, 149.1, 151.2, 159.2, 161.9, 163.3;
IR (thin film) cm^{-1} 2936 (m), 2858 (w), 1704 (s), 1556 (s), 1515 (s), 1268 (s);
mass spectrum (EI): m/e (%relative intensity) 340 (100) M^+, 311 (35), 261 (10), 165 (97), 149 (12)
m/e calcd for $C_{20}H_{21}O_5$ 341.1389 $(M + H)^+$, measd 341.1412

Diol 26

R_f = 0.09 (50% EtOAc in hexane)
MP = 172-174 °C
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 (d, 3 H, J = 6.7 Hz), 2.23 (s, 3 H), 2.91 (d, 1 H, J = 7.5 Hz), 3.65 (br, 1 H), 3.67 (ddd, 1 H, J = 3.1, 7.5, 8.2 Hz), 4.29 (dddd, 1 H, J = 6.7, 6.7, 6.7, 8.2 Hz), 4.75 (d, 1 H, J = 3.1 Hz), 5.81 (s, 1 H);
^{13}C NMR (75 MHz, CD_3OD) δ 17.9, 19.9, 62.5, 71.9, 73.9, 100.8, 101.3, 164.4, 166.7, 167.8;
IR (thin film) cm^{-1} 3392 (br), 2962 (m), 1697 (s), 1648 (m), 1581 (s), 1260 (vs);
mass spectrum (CI): m/e (%relative intensity) 213 (100) $M+H^+$, 195 (14), 122 (9);
m/e calcd for $(M + H)^+C_{10}H_{13}O_5$ 213.0763, measd 213.0763

Diol 27

R_f=0.091 (50% EtOAc in hexane)

^{1}H NMR (500MHz, $CDCl_3$) δ 0.97 (t, 3H, J=7.5 Hz), 1.45 (m, 1H), 1.61 (m, 2H), 1.83 (m, 1H), 2.21 (s, 3H), 3.07 (d, 1H, J=7.0 Hz), 3.72 (ddd, 1H, J=4.2, 7.0, 8.2 Hz), 4.07 (d, 1H, J=2.7 Hz), 4.18 (dddd, 1H, J= 3.0, 8.2, 8.2, 8.2 Hz), 4.73 (dd, 1H, J=2.7, 4.2 Hz) 5.82 (s, 1H);
^{13}C NMR(125MHz, $CDCl_3$) δ 13.9, 18.3, 19.9, 32.7, 60.8, 67.7, 77.4, 98.8, 100.3, 162.4, 165.2, 165.5;
IR (thin film) cm^{-1} 3396 (s), 1698 (s), 1650 (m), 1582 (s), 1452 (m), 1080 (m), 1066 (m), 1037 (m);

Diol 28

R_f = 0.08 (50% EtOAc in hexane)
^{1}H NMR (300 MHz, CD_3OD) δ 2.24 (d, 3 H, J = 0.9 Hz), 3.88 (dd, 1 H, J = 3.4, 10.5 Hz), 4.67 (d, 1 H, J = 3.4 Hz), 5.08 (d, 1 H, J = 10.5 Hz), 6.03 (m, 1H), 7.36-7.48 (m, 5 H);
^{13}C NMR (75 MHz, CD_3OD) δ 19.9, 62.9, 71.1, 79.6, 100.9, 101.2, 129.4, 129.5, 129.9, 138.7, 164.6, 166.6, 167.8;
mass spectrum (CI): m/e (%relative intensity) 275 (100) $M+H^+$, 274 (25), 257 (31), 172 (73), 155 (28), 138 (20), 127 (10);
m/e calcd for $(M + H)^+$ $C_{15}H_{15}O_5$ 275.0919, measd 275.0941

Diol 29

R_f = 0.175 (50% EtOAc in hexane)
^{1}H NMR (500MHz, CD_3OD) δ 1.25 (m, 1 H) 1.40 (m, 1 H), 1.50 (m, 3 H), 1.74 (m, 1 H), 1.91 (m, 1 H), 2.01 (m, 1 H), 2.23 (s, 3 H), 4.06 (s, 1 H), 4.20 (s, 1 H), 6.00 (s, 1 H);
^{13}C NMR (125 MHz, CD_3OD) δ 18.4, 19.2, 19.6, 25.3, 29.2, 65.2, 67.3, 74.2, 99.5, 99.8, 162.9, 165.3, 165.6;
IR (thin film) cm^{-1} 3417 (m), 2931 (m), 1694 (s), 1650 (m), 1584 (s), 1422 (m);
mass spectrum (GCMS): m/e (%relative intensity) 234 (96) M^+-H_2O, 205 (48), 192 (77), 179 (100), 163 (53), 150 (47), 140 (29);
m/e calcd for $(M + H)^+$ $C_{13}H_{17}O_5$ 253.1076, measd 253.1073

Diol 30

R_f = 0.143 (50% EtOAc in hexane)
^{1}H NMR (500MHz, $CDCl_3$) δ 1.47 (m, 5 H), 1.72 (m, 1 H), 1.85 (m, 1 H), 2.06 (m, 1 H), 3.57 (s, 1 H), 3.89 (s, 3 H), 3.90 (s, 3 H), 4.22 (s, 1 H), 4.38 (s, 1 H), 4.39 (s, 1 H), 6.33 (d, 1 H, J = 2 Hz), 6.87 (dd, 1 H, J = 3.5, 8.3 Hz), 7.23 (s, 1 H), 7.35 (dd, 1 H, J = 2.0, 8.3 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ 20.4, 20.5, 26.2, 30.5, 56.1, 56.2, 64.8, 67.6, 76.3, 96.5, 100.0, 108.5, 111.2, 119.4, 123.8, 149.3, 151.7, 160.5, 164.9, 165.5;
IR (thin film) cm^{-1} 3422 (m), 2932 (w), 1690 (m), 1568 (m), 1515 (s), 1269 (m);
mass spectrum (EI): m/e (%relative intensity) 374 (9) M^+, 278 (16), 277 (100), 165 (45), 98 (11)
m/e calcd for $(M + H)^+$ $C_{20}H_{22}O_7Na$ 397.1263, measd 397.1265

Diol 32

R_f = 0.58 (EtOAc)
^{1}H NMR (300 MHz, $CDCl_3$) δ -0.47 (s, 3 H), 0.09 (s, 3 H), 0.12 (d, 3 H, J = 7 Hz), 0.62 (s, 9 H), 1.12 (m, 1H), 1.62 (m, 2 H), 1.74 (ddd, 1 H, J = 6, 6, 16.5 Hz), 2.08 (m, 4 H), 3.82 (t, 1 H, J = 4, Hz), 3.99

(dddd, 1 H, J = 4, 7, 7, 7, Hz), 4.55 (d, 1 H, J = 4 Hz), 5.20 (d, 1 H, J = 8.5 Hz), 5.24 (d, 1 H, J = 8.5 Hz), 7.27 (m, 3 H), 7.37 (m, 5 H), 7.66 (dd, 2 H, J = 2, 7.5 Hz);
^{13}C NMR (75 MHz, $CDCl_3$) δ -5.1, -4.1, 11.8, 15.6, 17.8, 21.2, 25.6, 27.0, 35.9, 43.6, 52.9, 62.9, 68.3, 73.2, 127.9, 128.0, 128.1, 128.3, 128.5, 130.8 (missing one aromatic signal due to overlap);
IR (thin film) cm^{-1} 3400 (m, br), 2929(m), 2856 (m), 1536 (s), 1443 (s), 1255 (s), 1170 (s);
mass spectrum (EI): m/e (%relative intensity) 508(34) M + H^+, 506 (15), 490 (34), 474 (70), 311 (80), 286 (100), 252 (30), 180 (18);
m/e calcd for $(M + H)^+$ $C_{30}H_{42}NO_4Si$, 508.2883, measd 508.2885;
$[\alpha]_D^{23}$ = (+) 162 (c = 0.32, EtOH);
mp = 146-148 (dec)

Thiolcarbomate 34
R_f = 0.66 (66% EtOAc in hexane);
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.61-2.02 (m, 8 H), 3.92 (s, 3H), 3.95 (s, 3H), 4.54 (dd, J = 4.0, 4.0 Hz, 1H), 4.74 (s, 1H), 6.41(br, 1H), 6.91 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.39 (dd, J = 2.0, 8.5 Hz, 1H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 19.8, 21.9, 26.3, 31.4, 46.6, 56.1, 56.2, 73.4, 81.6, 95.8, 97.0, 108.4, 111.1, 119.5, 123.2, 149.3, 152.0, 160.9, 162.9, 164.6, 171.0;
IR (thin film) cm^{-1} 2941 (w), 1714 (br, s), 1634 (m), 1571 (s), 1515 (s), 1271 (s), 1022 (m), 1006 (m), 914 (m), 806 (m), 731 (s);
mass spectrum (EI): m/e (%relative intensity) 417 (36) M + H^+, 307 (36), 289 (18), 154 (100), 136 (75), 120 (12);
m/e calcd for $(M+H)^+$: $C_{21}H_{22}O_7S$, 417.1008, measd 417.1008;

Mono-Alcohol 33
R_f = 0.14 (Hexane/EtOAc=1/2);
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43-2.02 (m, 8 H), 2.44 (d, J = 17.1 Hz, 1H), 2.74 (d, J = 17.1 Hz, 1H), 3.92 (s, 3H), 3.93 (s, 3H), 4.13 (dd, J = 3.4, 8.8 Hz, 1H), 6.31(br, 1H), 6.88 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.34 (dd, J = 2.0, 8.5 Hz, 1H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 22.3, 28.3, 29.8, 35.8, 55.9, 56.1, 67.2, 80.9, 96.1, 96.5, 108.2, 111.0, 118.7, 124.0, 149.1, 151.1, 158.4, 163.3, 164.5;
IR (thin film) cm^{-1}2359 (w), 1682 (s), 1638 (m), 1572 (s), 1516 (s), 141 (w), 1264 (s), 1144 (w), 1024 (m), 914 (w), 729 (m);
mass spectrum (EI): m/e (%relative intensity) 359 (88) M + H^+, 341 (100), 307 (16), 289 (36), 177 (52), 154 (78), 136 (64), 107 (26);
m/e calcd for $(M+H)^+$: $C_{20}H_{23}O_6$, 359.1497, measd 359.1496;

SUPPLEMENTARY ^{1}H NMR SPECTRA

for the

article

entitled

Stereoselective *trans* and *cis*-Dihydroxylations of 2*H*-Pyranyl and Dihydropyridinyl Heterocycles Synthesized from Formal [3 + 3]–Cycloaddition Reactions of α,β-Unsaturated Iminium Ions with 1,3-Dicarbonyl Equivalents.

authored by

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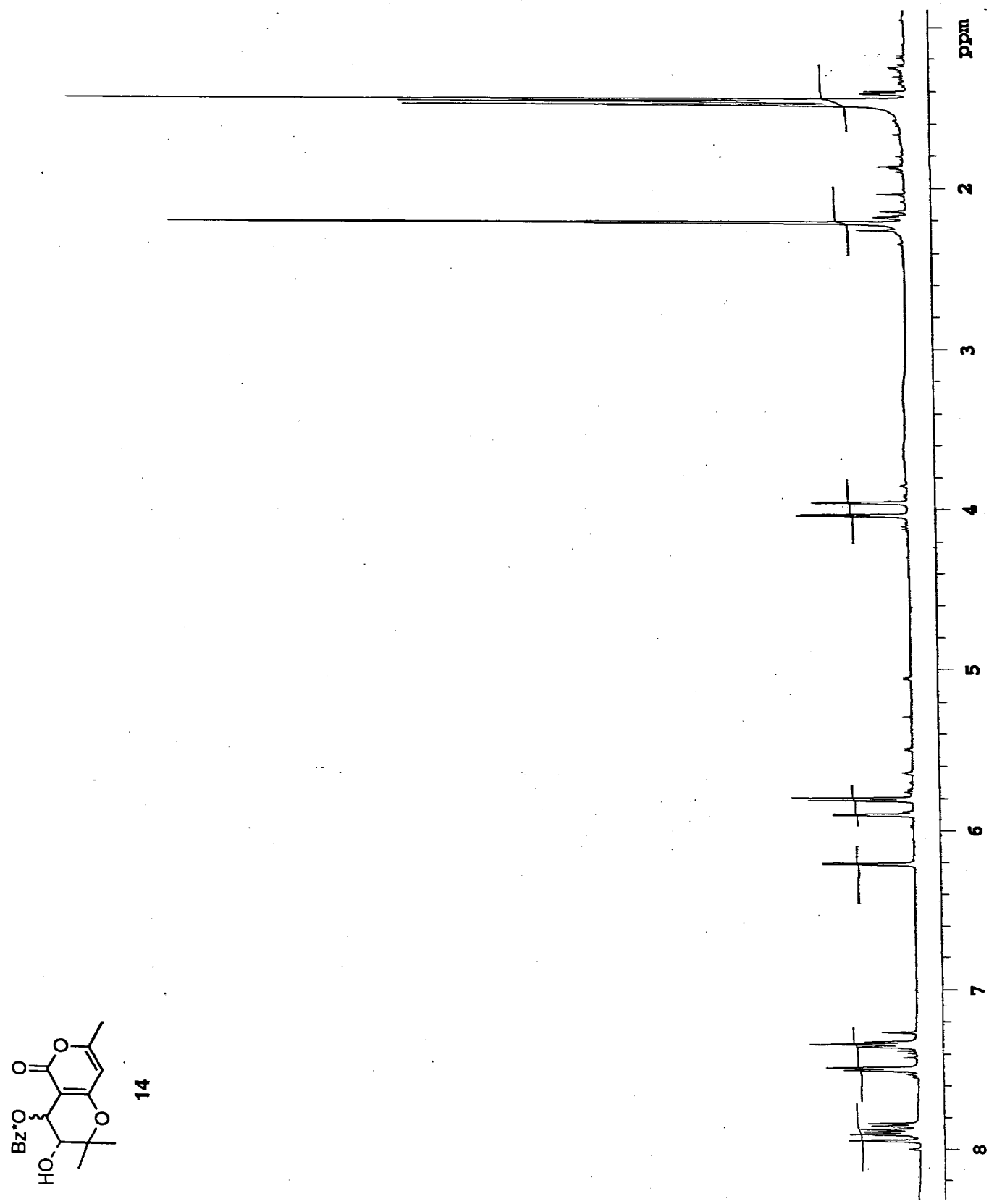

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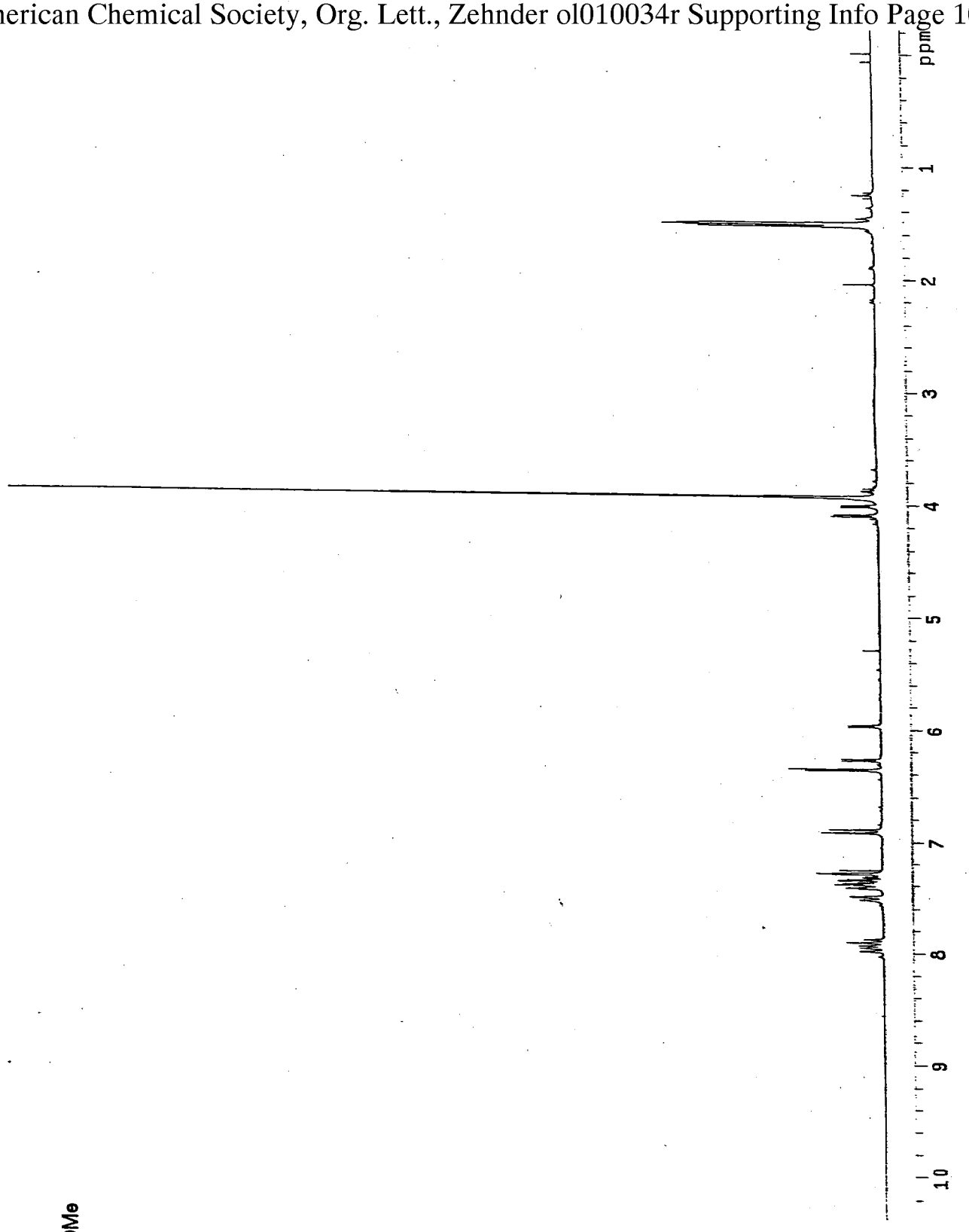
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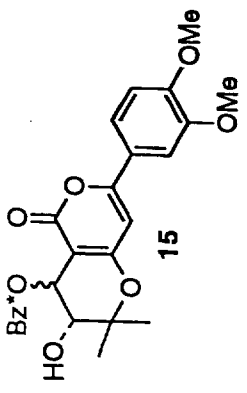
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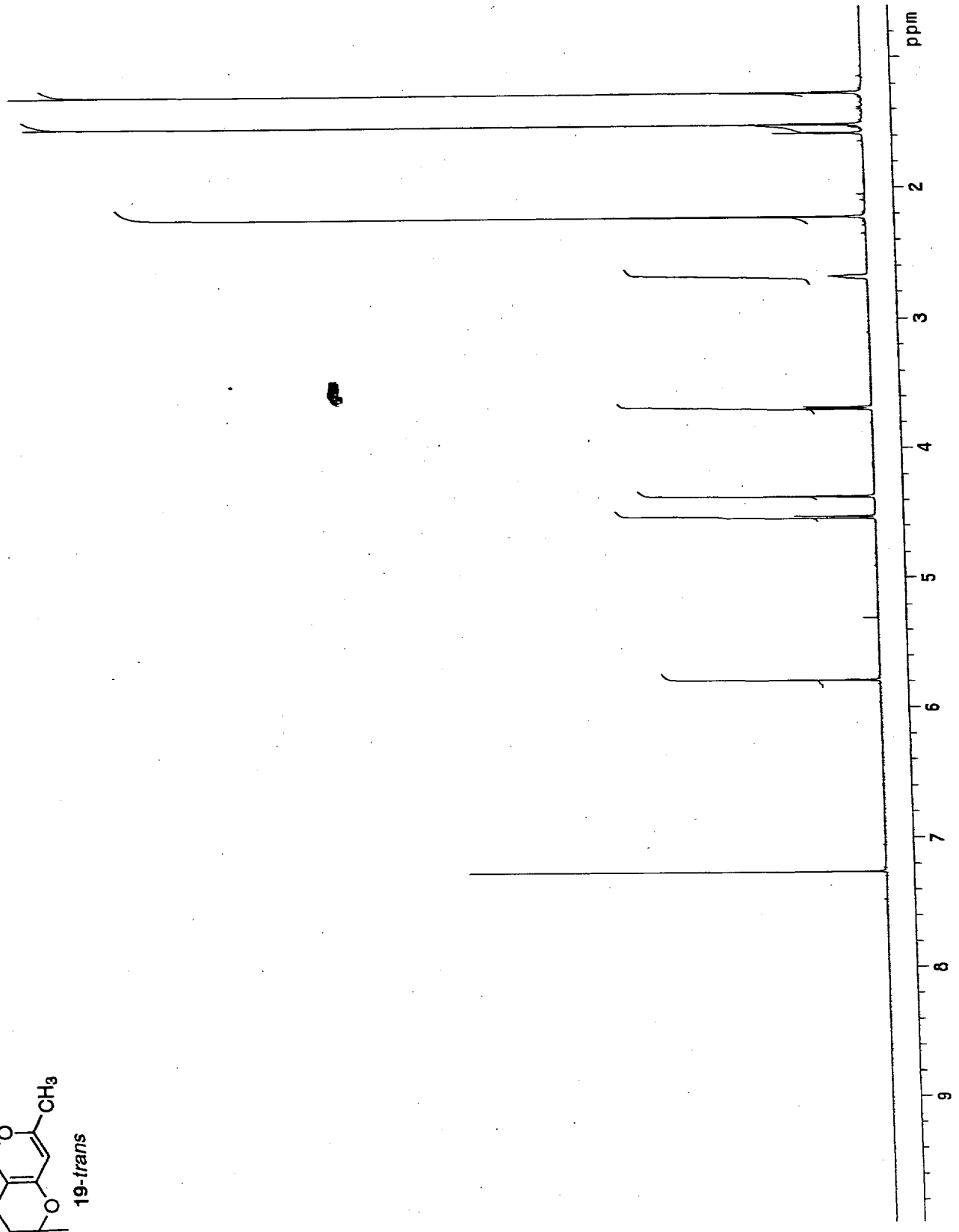

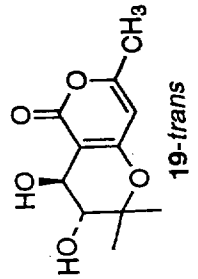

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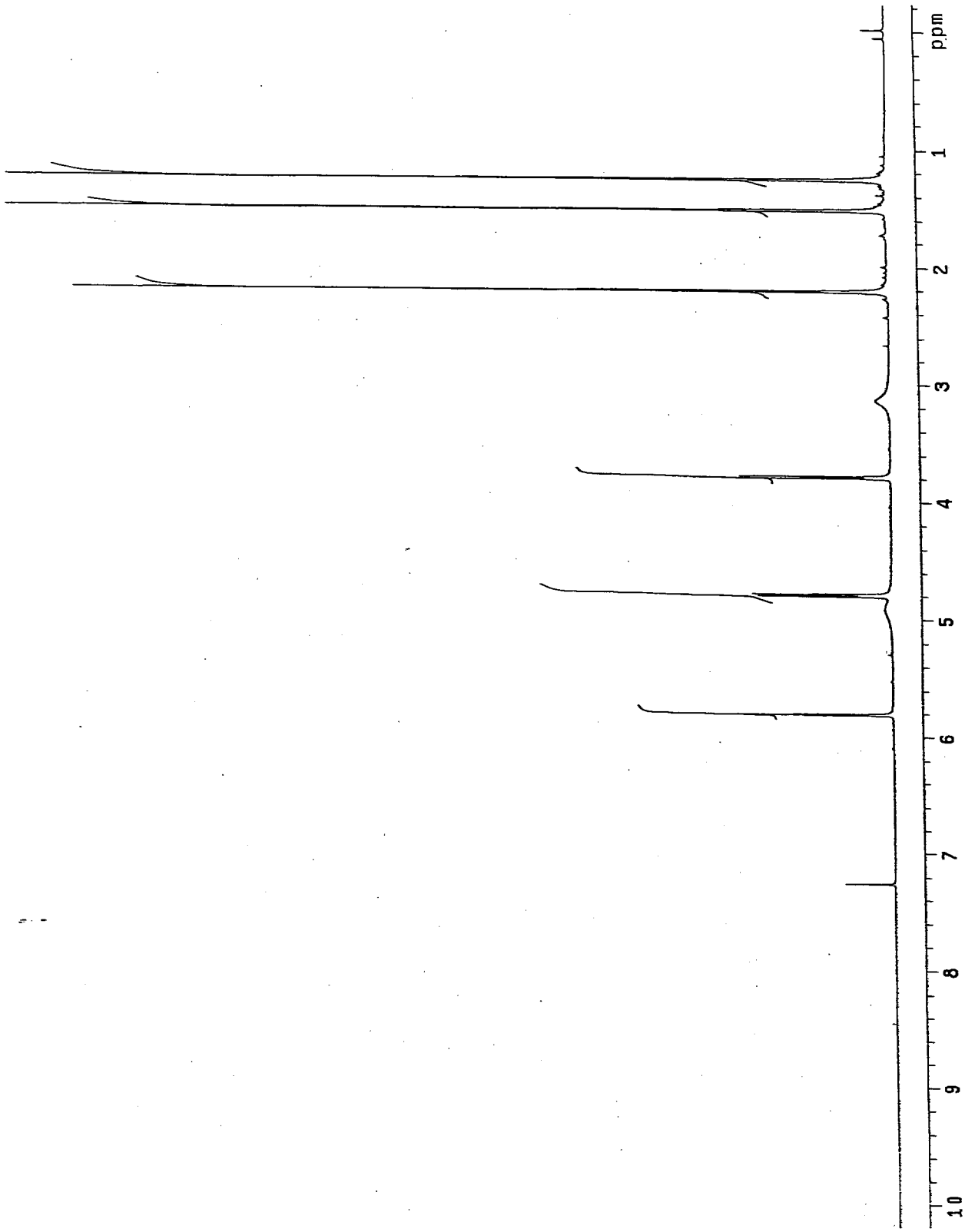

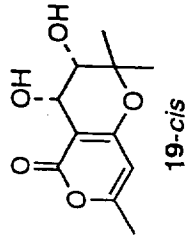

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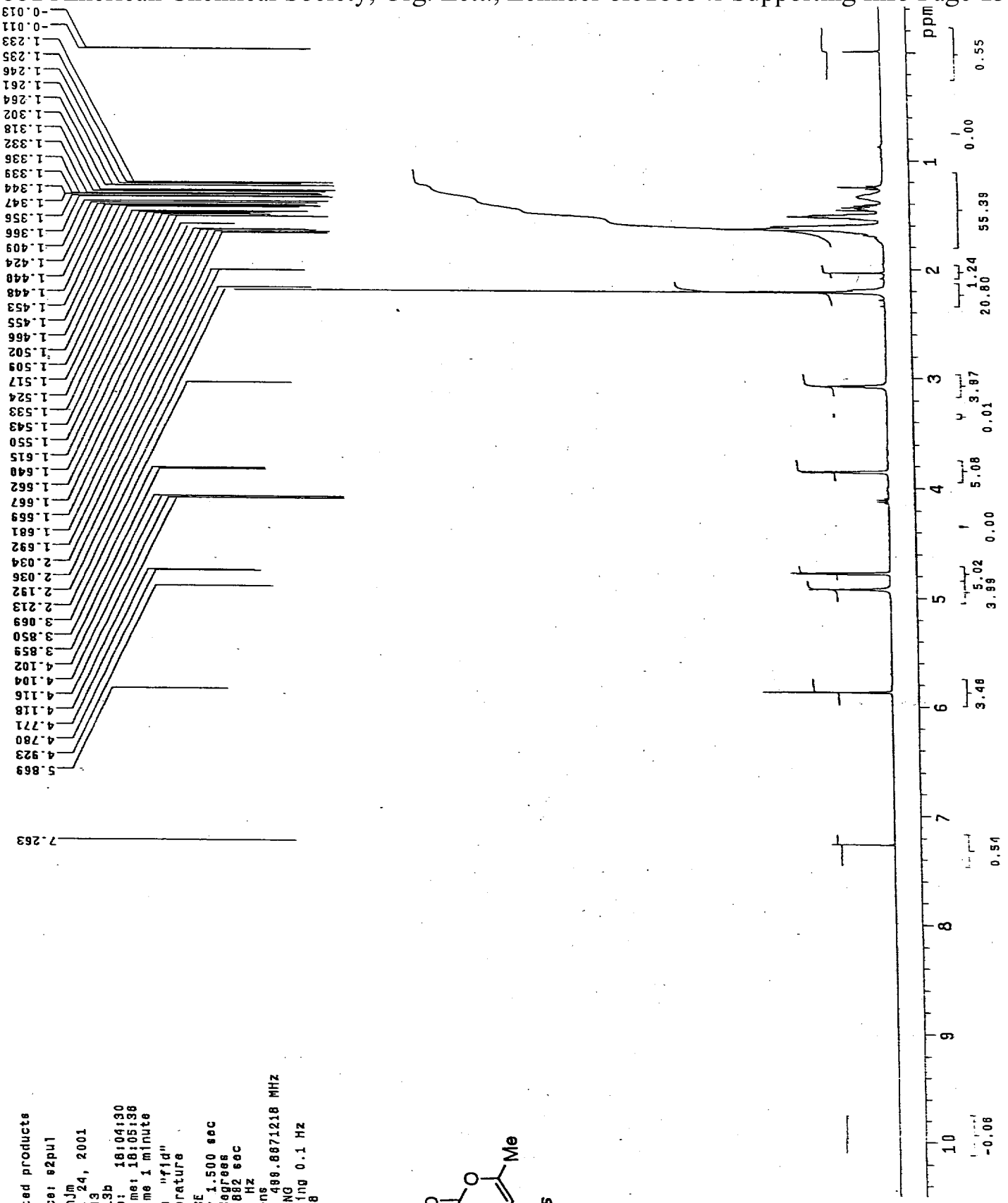

4A413b isolated products

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User: rhsmjm
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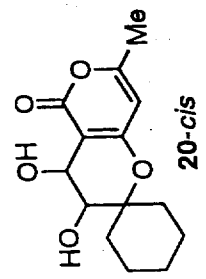
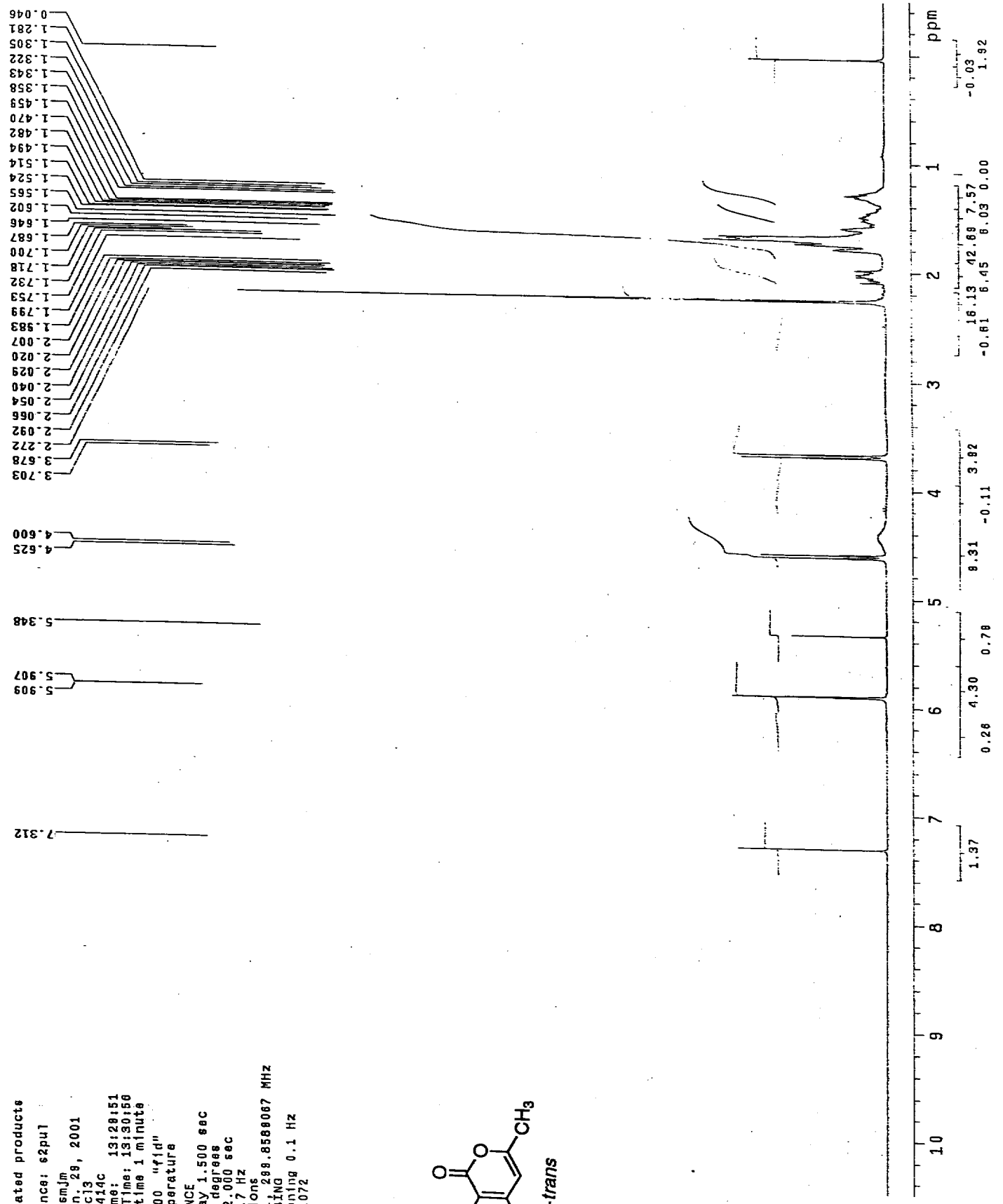
Solvent: cdcl3
File: 4A413b
Starting Time: 18:04:30
Completion Time: 18:05:38
Total acq. time 1 minute

UNITYplus-500 "f1d"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.882 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8871218 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768



20-*cis*



4A414c isolated products

Pulse Sequence: s2pul

User: rhsmjm
Date: Jan. 29, 2001
Solvent: cdcl3
File: 4A414c
Starting Time: 13:28:51
Completion Time: 13:30:50
Total acq. time 1 minute

UNITYplus-500 "ftd"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 2.000 sec
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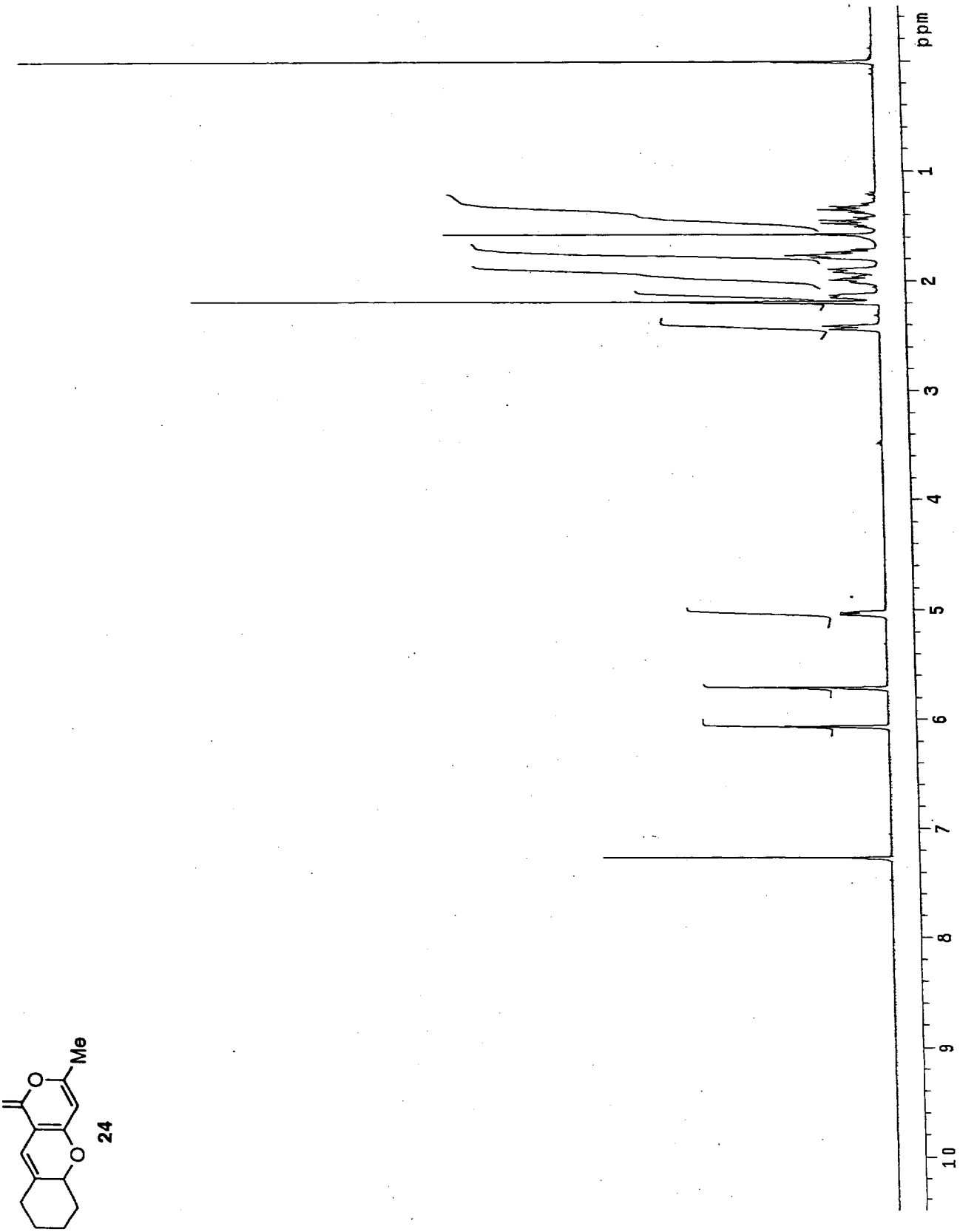
16 repetitions
OBSERVE H1, 299.8588087 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 131072

20-*trans*



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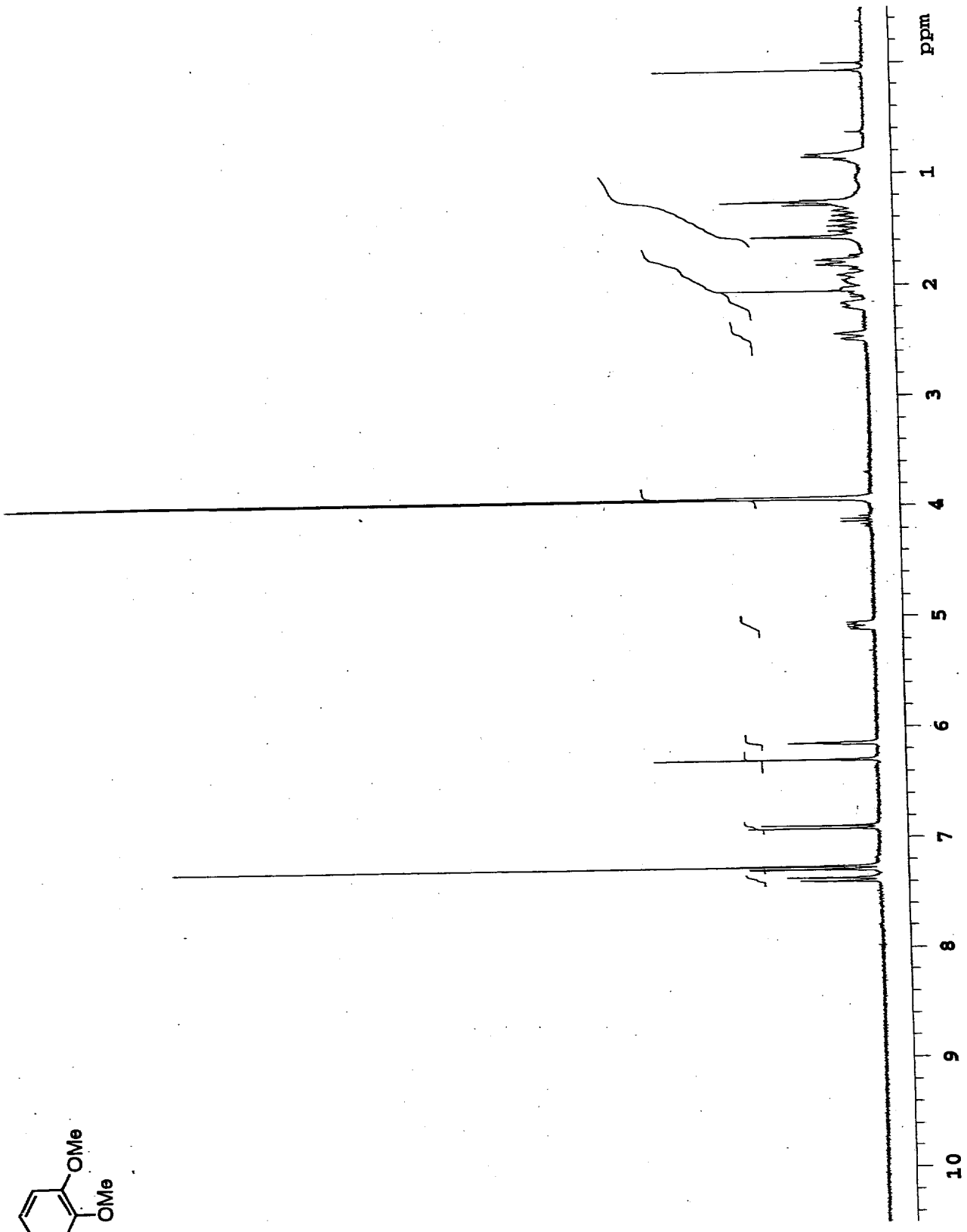

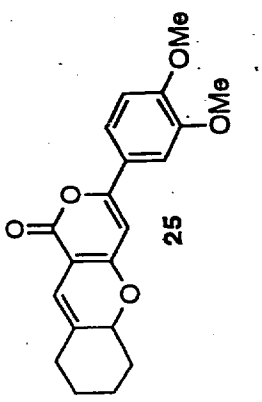

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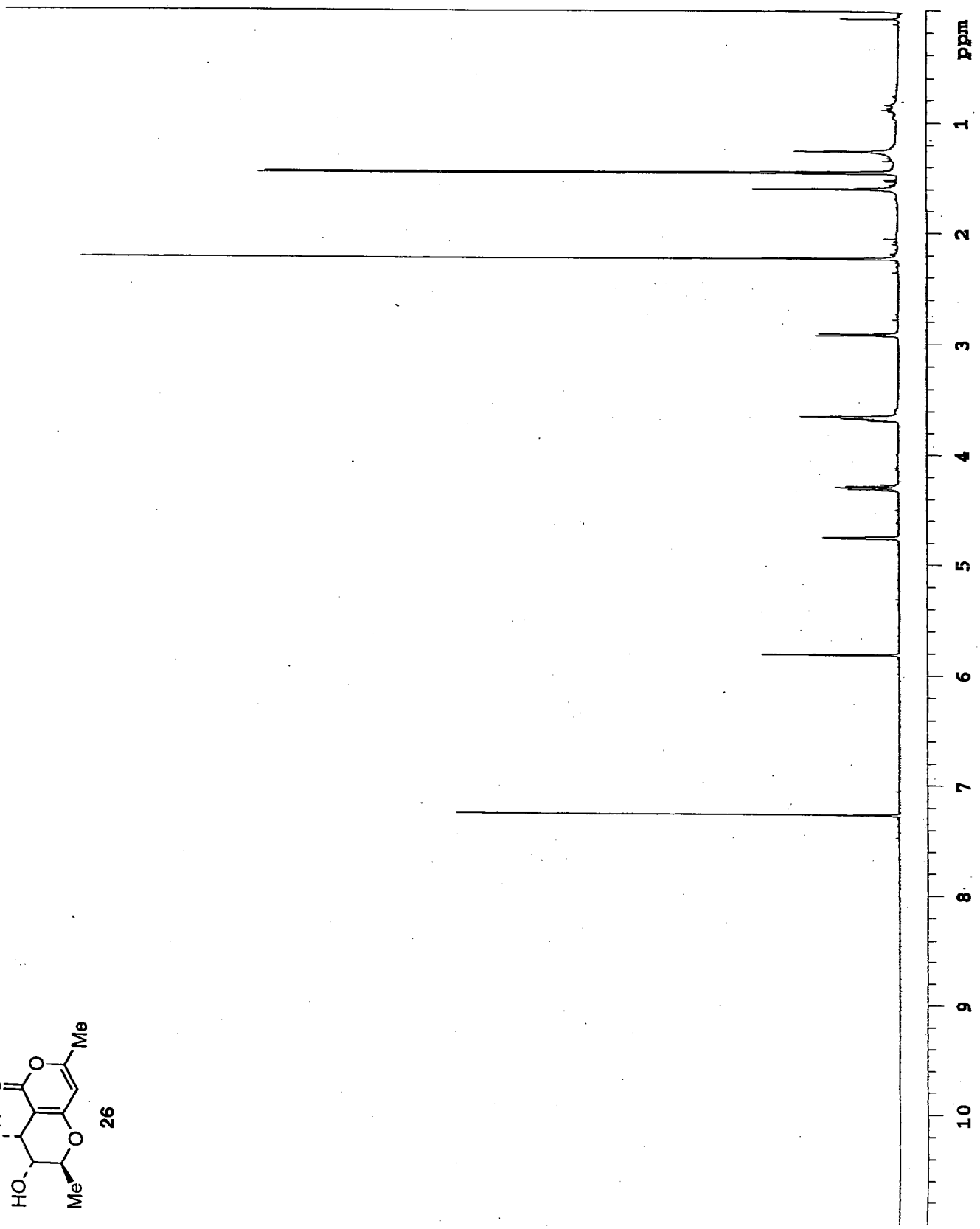

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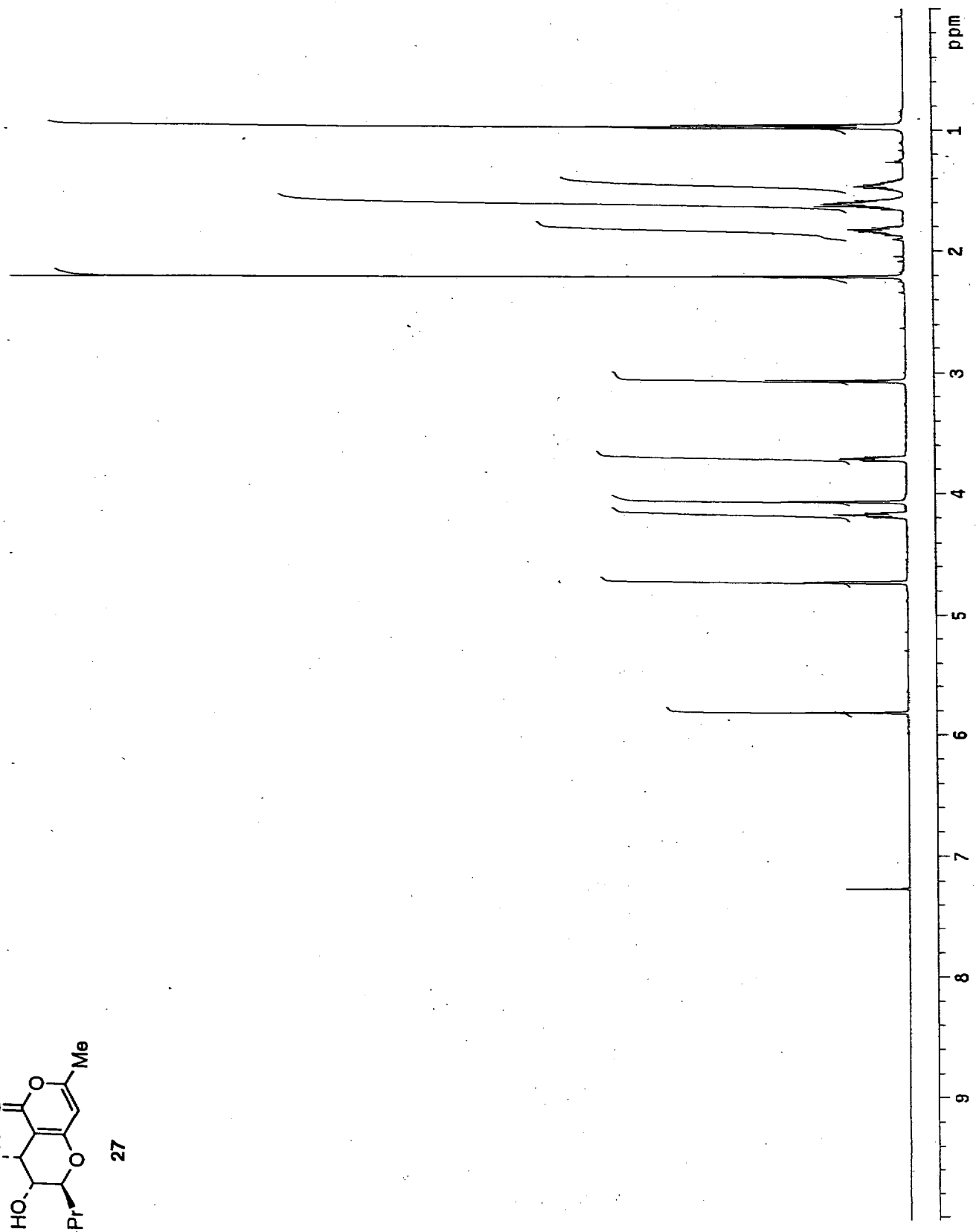

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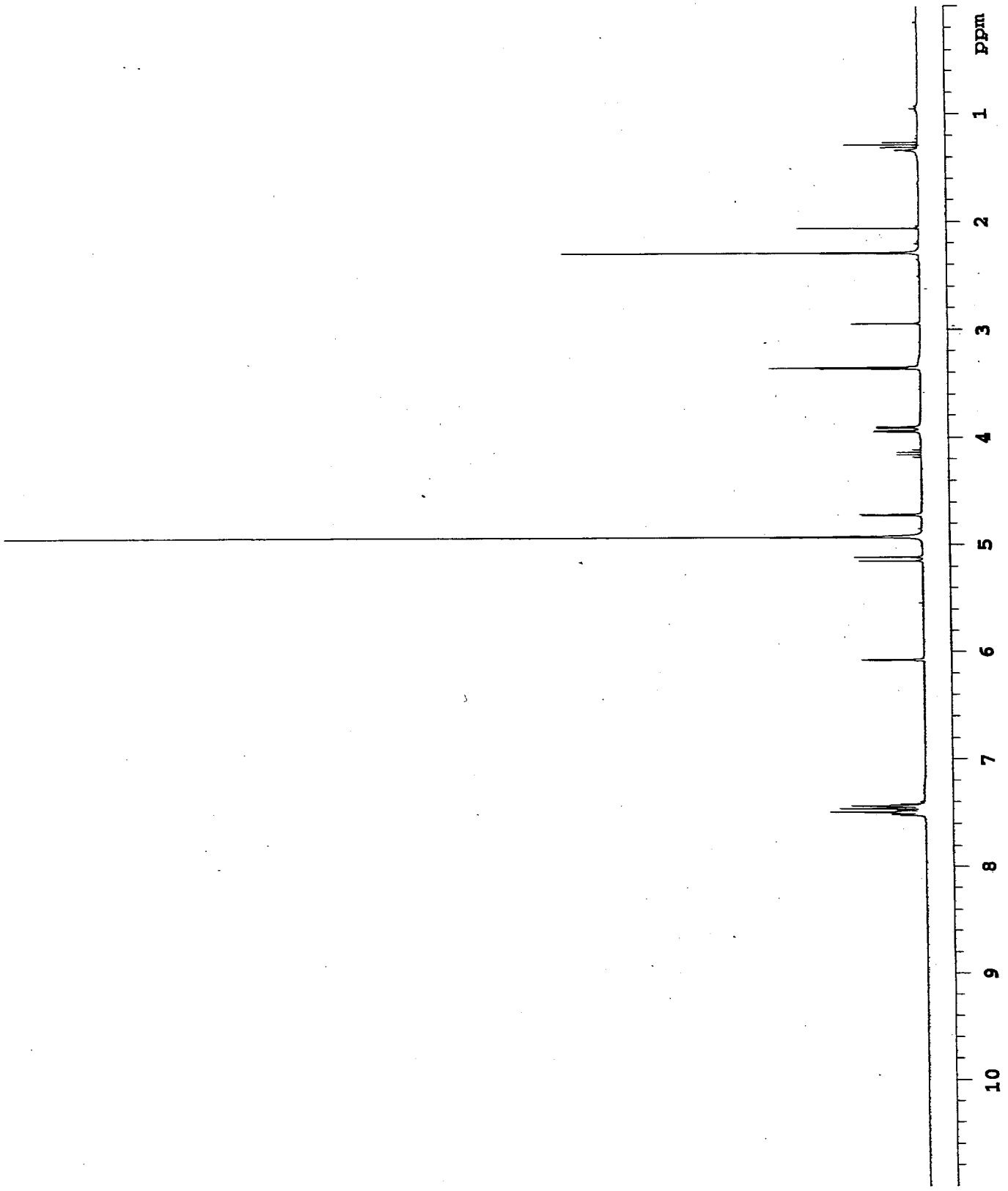

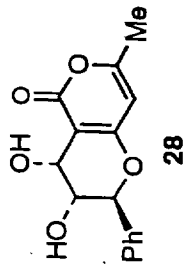

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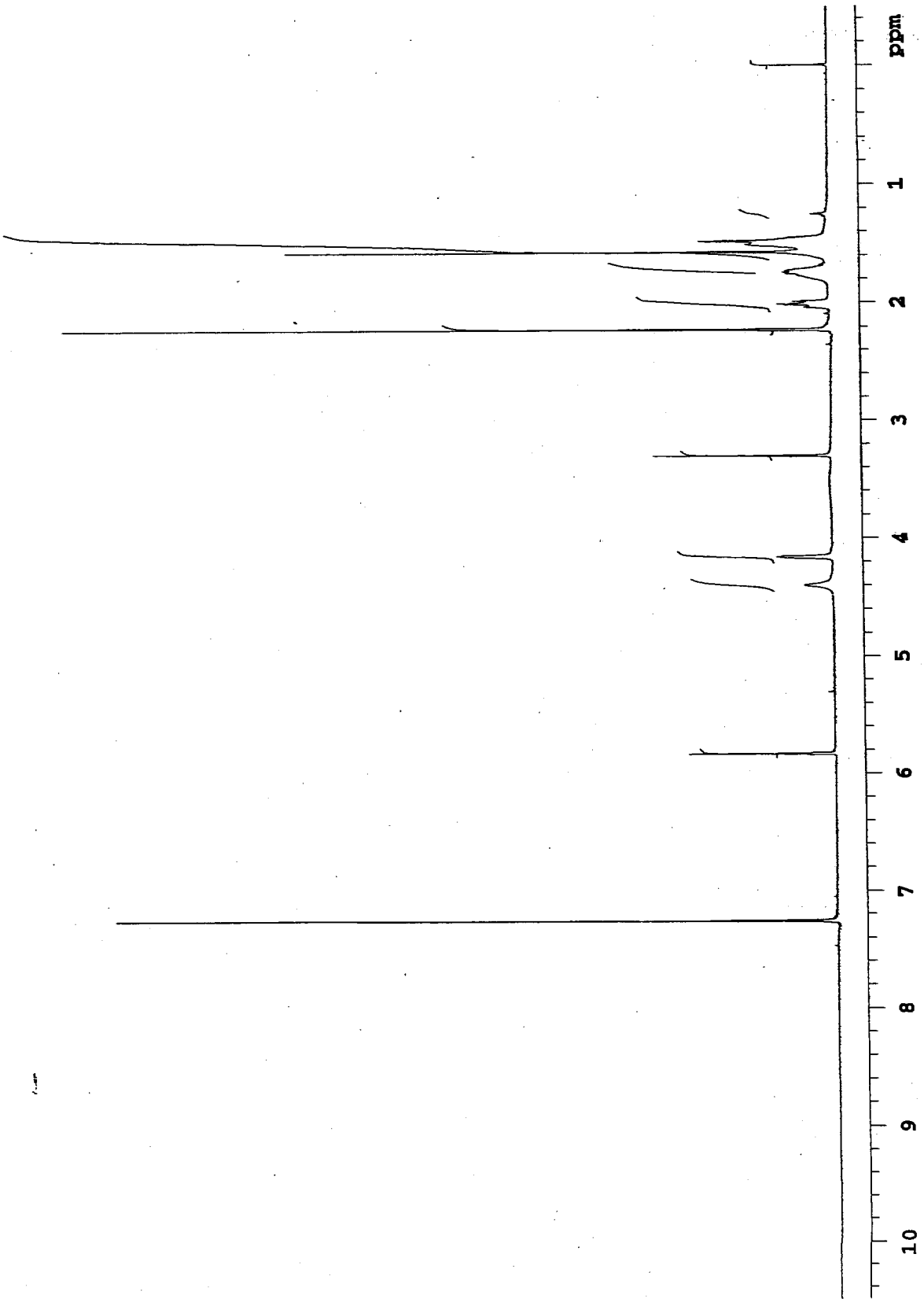

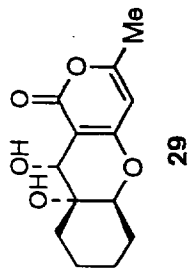

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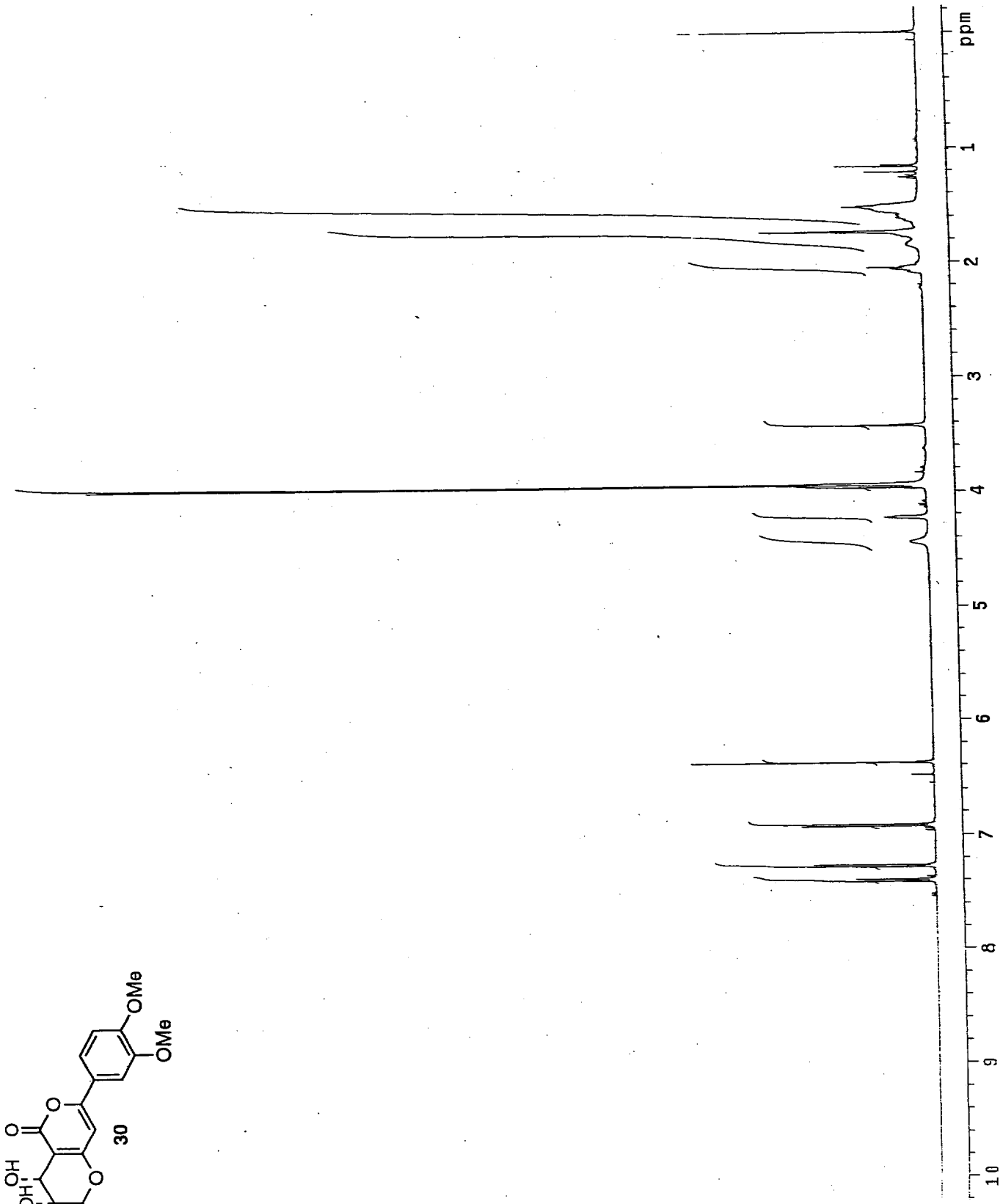
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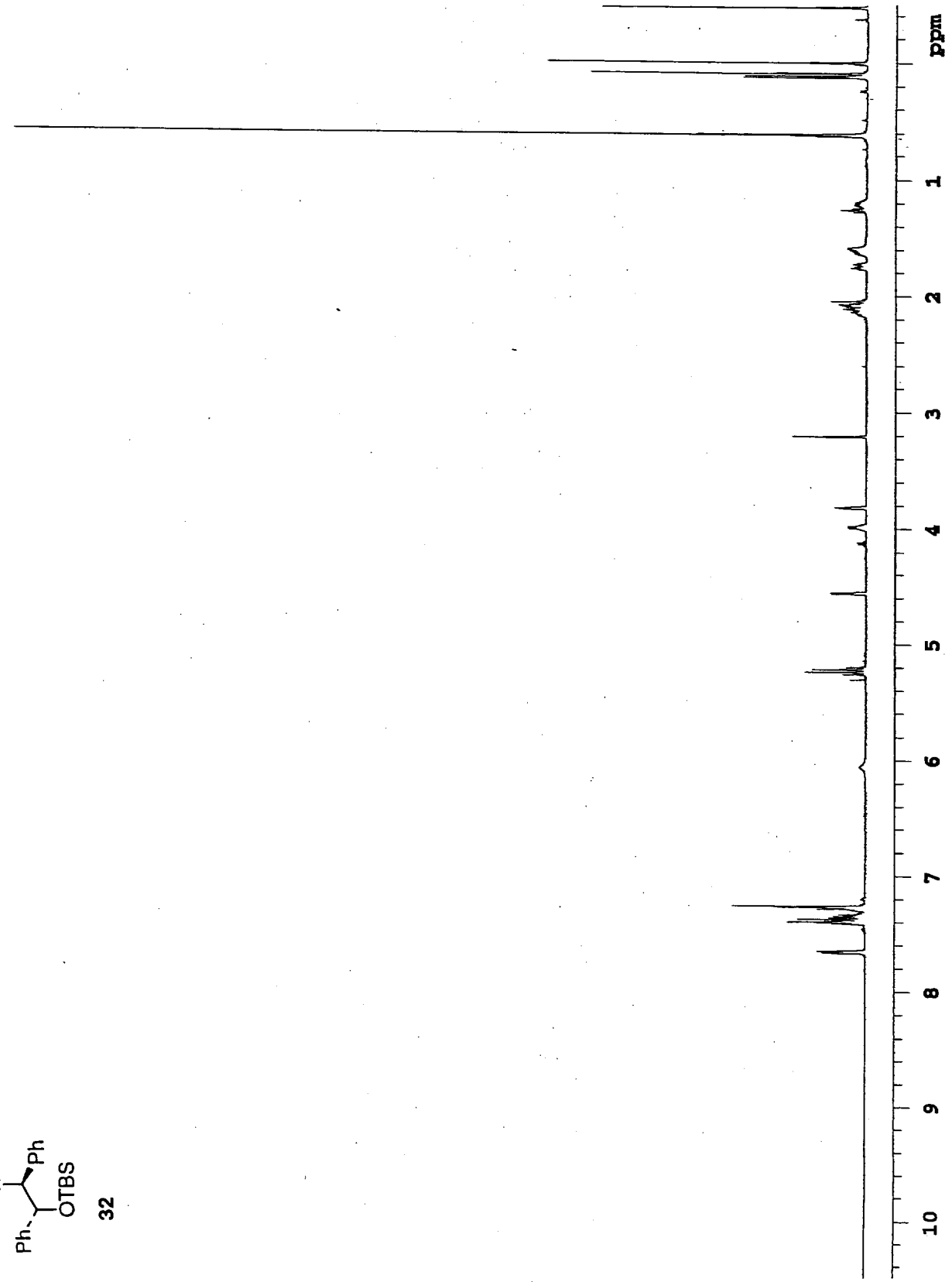

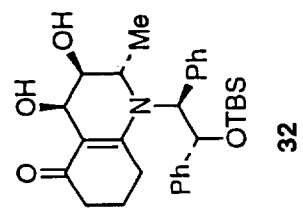

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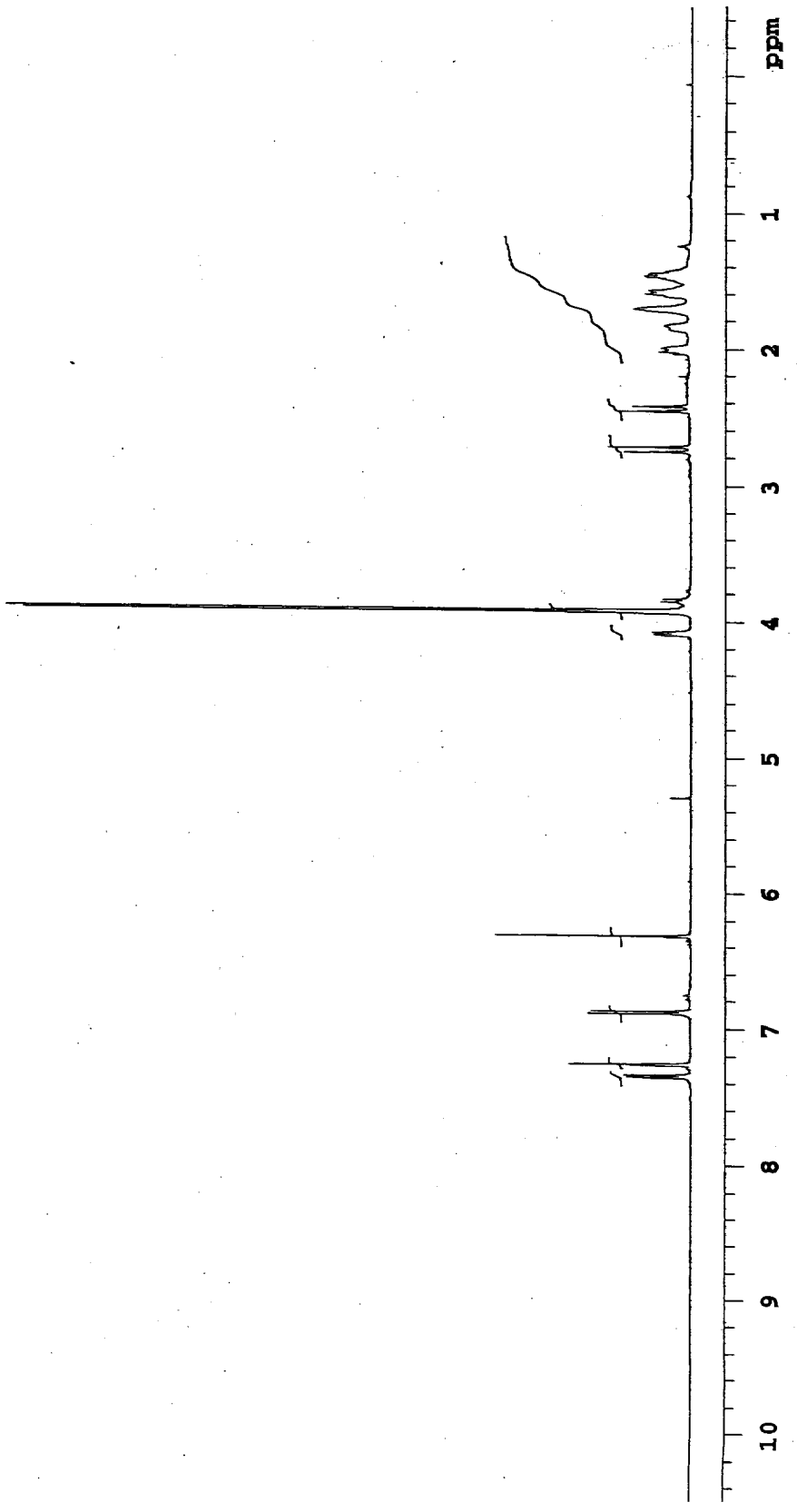

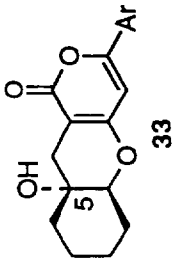

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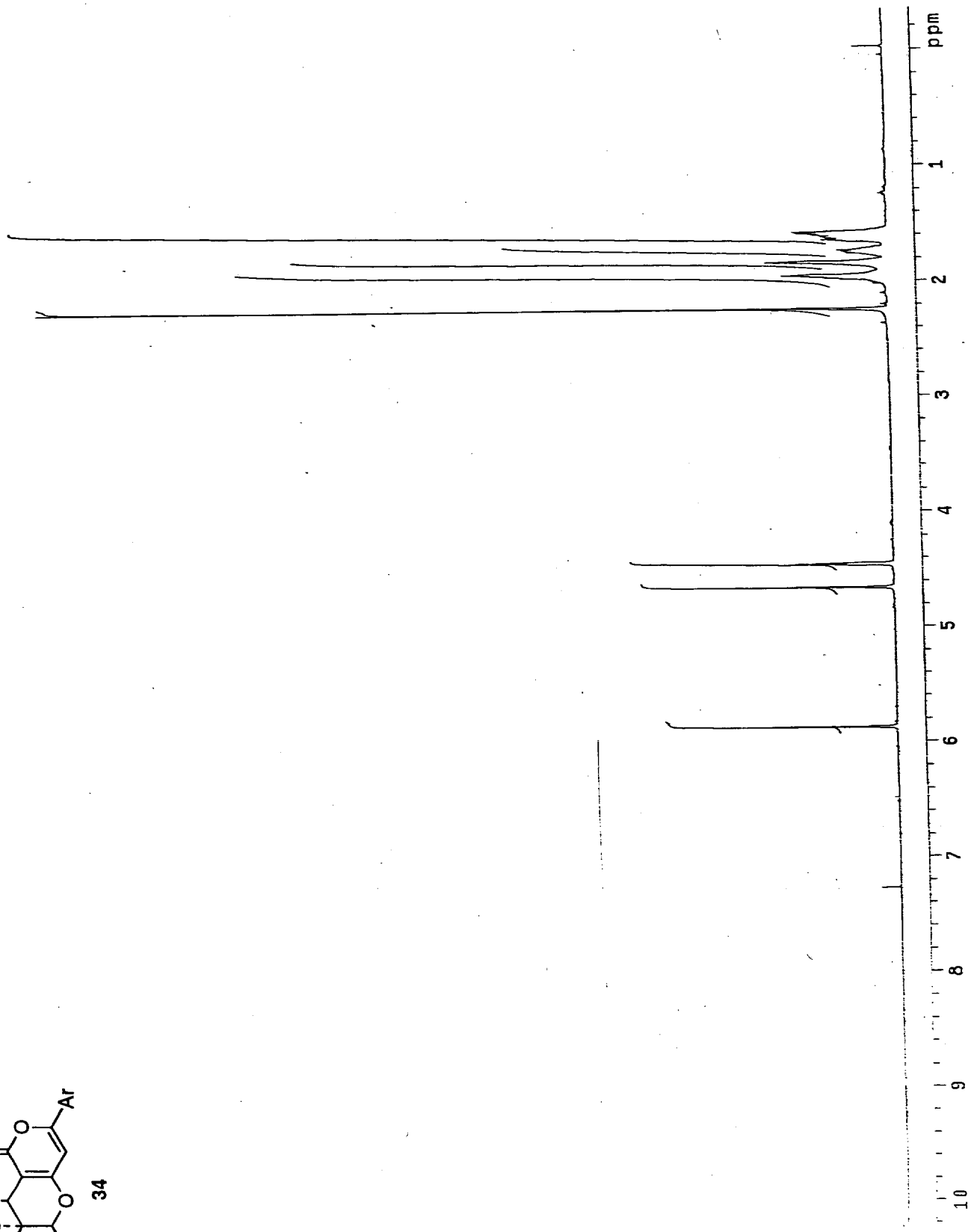

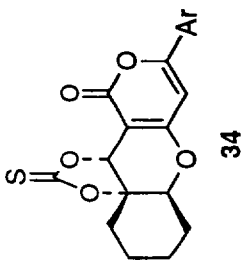

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