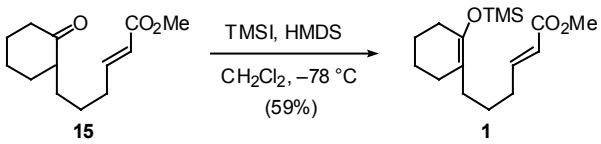
Supplementary Material

General. All Reactions were carried out under an inert atmosphere. Dichloroethane, HMDS, benzene, DMSO and DMF were distilled from CaH_2 under atmospheric or reduced pressure. Et_3N was distilled from KOH under atmospheric pressure. Triethylsilane was distilled and passed through Al_2O_3 before using. Unless otherwise described, other materials were obtained from commercial suppliers and used without further purification. Organic extracts were dried over $MgSO_4$ or Na_2SO_4, filtered and concentrated under reduced pressure using an evaporator. All melting points are uncorrected. The ^1H and ^{13}C NMR spectra were reported in ppm downfield from TMS ($\delta = 0$) for the ^1H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.00$) for the ^{13}C NMR.

Preparation of 1 (Scheme S-1)

Scheme S-1.



Methyl (2*E*)-6-(2-Trimethylsilyloxy-1-cyclohexenyl)-2-hexenoate (1). To a solution of **15** (512 mg, 2.28 mmol) and HMDS (1.15 mL, 5.45 mmol) in CH_2Cl_2 (6.0 mL) was added TMSI (0.39 mL, 2.74 mmol) at –78 °C. After 5 minutes, to the reaction mixture was added to Et_2O and one portion of brine. The organic layer was washed with brine, dried and concentrated. The residue was purified by column chromatography on silica gel with 20% AcOEt/hexane to give **1** (400 mg, 59%) as colorless oil. IR (neat) ν 2930, 2858, 2838, 1727, 1679, 1658, 1436, 1269, 1252, 1171, 929, 844; ^1H NMR (300 MHz, $CDCl_3$) 7.12 (dt, 1H, J = 15.7, 6.9 Hz), 5.83 (dt, 1H,

J = 15.7, 1.5 Hz), 3.72 (s, 3H), 2.18 (dddd, 2H, *J* = 6.9, 6.9, 6.9, 1.5 Hz), 2.07–2.00 (m, 4H), 1.94 (t, 2H, *J* = 5.9 Hz), 1.69–1.40 (m, 6H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 150.0, 143.7, 120.8, 114.9, 51.2, 32.0, 30.2, 29.5, 27.5, 25.9, 23.5, 22.9, 0.59; LRMS (EI) *m/z* 296 (M^+). HRMS *m/z* calcd. for $C_{16}H_{28}O_3Si$, 296.1806; found 296.1822.

(1*S,2*R**,3*R**,7*S**)-1-Hydroxy-2-methoxycarbonyltricyclo[5.4.0.0^{3,7}]undecane (2b).** Colorless oil: IR (neat, cm^{-1}) 3436 (br), 2931, 2856, 1730, 1714, 1436, 1272, 1215; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.69 (s, 3H), 2.62 (d, 1H, *J* = 7.8 Hz), 2.44 (dd, 1H, *J* = 7.8, 5.5 Hz), 2.29–2.20 (m, 1H), 1.89–1.44 (m, 10H), 1.42–1.20 (m, 4H); LRMS (EI) *m/z* 224 (M^+). HRMS *m/z* calcd. for $C_{13}H_{20}O_3$, 224.1412; found 224.1409.

(1*R,6*S**,8*R**)-1-(*tert*-Butyldimethylsiloxy)-8-(pentafluorophenoxycarbonyl)bicyclo[4.2.0]octane (*trans*-6d)**. Colorless oil; IR (neat, cm^{-1}) 2931, 1779, 1520, 1465, 1293, 1252, 1191, 1104, 1075, 1006, 836, 775; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.24 (dd, 1 H, *J* = 10.2, 8.2 Hz), 2.41 (m, 1H), 1.96–1.42 (m, 8H), 1.40–1.22 (m, 2H), 0.89 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 76.8, 49.5, 41.2, 31.8, 25.5, 23.4, 21.1, 20.3, 18.6, 17.8, –2.96; LRMS (EI) *m/z* 435 (M^+–15); *Anal* calcd for $C_{21}H_{27}F_5O_3Si$: C, 55.99; H, 6.04, found C, 56.30; H, 6.05.

(1*R,6*S**,8*R**)-1-(*tert*-Butyldimethylsiloxy)-8-(pentachlorophenoxycarbonyl)bicyclo[4.2.0]octane (*trans*-6e)**. Colorless oil; IR (neat, cm^{-1}) 2928, 1773, 1520, 1361, 1104, 1075, 1005, 834, 774, 668; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.24 (dd, 1 H, *J* = 10.2, 8.2 Hz), 2.38 (m, 1H), 1.97–1.72 (m, 3H), 1.65–1.20 (m, 7H), 0.88 (s, 9H),

0.18 (s, 3H), 0.16 (s, 3H); LRMS (EI) *m/z* 475 (M^+–57); *Anal* calcd for $C_{21}H_{27}Cl_5O_3Si$: C, 47.34; H, 5.11, found C, 47.05; H, 5.21.

(1*R,6*S**,8*R**)-1-(*tert*-Butyldimethylsiloxy)-8-(1,1,1,3,3,3-hexafluoroisopropoxycarbonyl)bicyclo[4.2.0]octane (6f).** Colorless oil: IR (neat, cm^{-1}) 2932, 2860, 1771, 1465, 1386, 1360, 1291, 1233, 1202, 1111, 837, 775, 690; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (m, 1H), 3.06 (dd, 1H, *J* = 10.2, 8.2 Hz), 2.37 (m, 1H), 1.89–1.42 (m, 8H), 1.36–1.20 (m, 2H), 0.88 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ169.1, 120.6 (q, *J* = 278 Hz), 76.7, 66.1, 49.3, 41.0, 31.8, 25.3, 21.1, 20.2, 18.5, 17.8, –3.0, –3.1; LRMS (EI) *m/z* 377 (M^+–57); *Anal* calcd for $C_{18}H_{28}F_6O_3Si$: C, 49.76; H, 6.50, found C, 49.65; H, 6.40.

(1*R,6*S**,8*S**)-1-Hydroxy-8-hydroxymethylbicyclo[4.2.0]octane (*trans*-7).** To a solution of *trans*-**6a** (100 mg, 0.335 mmol) in CH_2Cl_2 (3.4 mL) at –78 °C was added 1M DIBALH-hexane (0.74 mL, 0.740 mmol), and the mixture was stirred for 90 min at –78 °C. After addition of MeOH (0.5 mL) and Et_2O (3.0 mL), the mixture was stirred for 1.5 h at ambient temperature, filtered through Celite and evaporated.

A solution of the crude alcohol in 1M TBAF-THF (0.7 mL,0.70 mmol) was refluxed for 18 h. The resulting mixture was diluted with AcOEt, washed with H_2O and brine, dried and concentrated. The residue was purified by column chromatography on silica gel with AcOEt to give *trans*-**7** (24 mg, 46% for 2 steps) as colorless crystals; mp 92–94 °C; IR (KBr, cm^{-1}) 3332 (br.), 3266, 2940, 2910, 1458, 1237, 1031, 611; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.74–3.55 (m, 2H), 2.93 (br. s, 1H), 2.56 (br. s, 1H), 2.32–1.90 (m, 2H), 1.80–1.18 (m, 9H), 1.01 (q, 1H, *J* = 10.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.5, 62.1, 48.7, 40.0, 29.4, 23.4, 21.5, 20.1, 19.3;

LRMS (EI) *m/z* 138 (M^+–18). *Anal* calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32, found C, 69.00; H, 9.99.

(1*R,6*S**,8*R**)-1-Hydroxy-8-hydroxymethylbicyclo[4.2.0]octane (*cis*-7).** *Cis*-**7** was prepared from *cis*-**6a** by same method as that of preparation of *trans*-**7** (79% for 2 steps); Colorless oil; IR (neat, cm^{-1}) 3348 (br.), 2929, 2855, 1437, 1285, 1178, 1036, 668; ^1H NMR (300 MHz, $CDCl_3$) δ 3.98 (dd, 1H, *J* = 11.2, 9.2 Hz), 3.74 (dd, 1H, *J* = 11.2, 4.7 Hz), 2.86 (br s, 2H), 2.47 (m, 1H), 2.24 (m, 1H), 1.88–1.22 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.4, 63.4, 45.3, 40.1, 31.2, 24.4, 21.2, 20.7, 19.2; LRMS (EI) *m/z* 156 (M^+). HRMS calcd for $C_9H_{16}O_2$, 156.1150; found 156.1194.

(1*R,6*R**,8*S**)-3,3-Dimethyl-2,4-dioxotricyclo[6.4.0.0^{1,6}]undecane (8).** To a solution of *cis*-**7** (11 mg, 70 μmol) and a small amount of TsOH in DMF (0.6 mL) was added 2,2-dimethoxybutane (0.08 mL, 650 μmol) and the mixture was stirred for 8 h at 80 °C. The mixture was cooled to room temperature and quenched with saturated aqueous $NaHCO_3$ (a few drops), then H_2O was added. Aqueous layer was extracted with Et_2O and the combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography on silica gel with 10% Et_2O/hexane to afford **8** (9.4 mg, 68%) as pale yellow oil; IR (neat, cm^{-1}) 2934, 2856, 1449, 1378, 1367, 1241, 1191, 1120, 966, 845; ^1H NMR (300 MHz, $CDCl_3$) δ 4.00 (dd, 1H, *J* = 12.4, 3.8 Hz), 3.58 (dd, 1H, *J* = 12.4, 2.2 Hz), 2.41–2.26 (m, 2H), 2.18–2.06 (m, 1H), 2.02–1.88 (m, 2H), 1.69–1.11 (m, 7H), 1.43 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 96.6, 76.5, 59.9, 39.0, 35.3, 32.3, 30.1, 29.6, 26.0, 24.0, 22.6, 22.4; LRMS (EI) *m/z* 196 (M^+). HRMS calcd for $C_{12}H_{20}O_2$, 196.1463; found196.1502.

(1*R,6*S**,8*S**)-1-(Triehtylsiloxy)-8-(1,1,1,3,3,3-hexafluoroisopropoxycarbonyl)bicyclo[4.2.0]octane (6h).** Colorless oil (dr 89 : 11); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (m, 1H), 3.31 (dd, 0.1H, *J* = 7.6, 7.6 Hz), 3.06 (dd, 0.9H, *J* = 10.2, 8.2 Hz), 2.48 (m, 0.1H), 2.36 (m, 0.9H), 2.04–1.42 (m, 8H), 1.38–1.15 (m, 2H), 0.97 (t, 8.1H, *J* = 7.7 Hz), 0.93 (t, 0.9H, *J* = 7.8 Hz), 0.63 (q, 5.4H, *J* = 7.7 Hz), 0.61 (q, 0.6H, 7.8 Hz); LRMS (EI) *m/z* 405 (M^+–27). HRMS calcd for $C_{16}H_{25}O_3F_6Si$, 405.1321; found 405.1327.

(1*R,6*S**,8*S**)-1-(Triisopropylsiloxy)-8-(1,1,1,3,3,3-hexafluoroisopropoxycarbonyl)bicyclo[4.2.0]octane (6i).** Colorless oil: IR (neat, cm^{-1}) 2944, 2868, 1771, 1464, 1386, 1291,1202, 1111, 882, 690; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 (m, 1H), 3.11 (dd, 1H, *J* = 10.2, 8.2 Hz), 2.40 (m, 1H), 1.91–1.24 (m, 13H), 1.08 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 120.5 (q, *J* = 278 Hz), 76.4, 66.2 (quint, *J* = 32 Hz), 49.9, 41.5, 32.4, 23.3, 21.1, 20.4, 18.3, 18.0, 13.0; LRMS (EI) *m/z* 433 (M^+–43). HRMS calcd for $C_{18}H_{27}F_6O_3Si$, 433.1634; found 433.1635.

(1*R,6*S**,8*S**)-8-(1,1,1,3,3,3-Hexafluoroisopropoxycarbonyl) -1-methoxybicyclo[4.2.0]octane (6j).** Colorless oil: IR (neat, cm^{-1}) 2937, 1769, 1457, 1387, 1360, 1289, 1231, 1202, 1110, 907, 690; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (m, 1H), 3.31 (s, 3H), 3.16 (dd, 1H, *J* = 10.4, 8.2 Hz), 2.43 (m, 1H), 1.98–1.74 (m, 3H), 1.66–1.14 (m, 7H); LRMS (EI) *m/z* 334 (M^+). HRMS calcd for $C_{13}H_{16}F_6O_3$, 334.1004; found 334.1003.

(1*R,5*S**,7*R**)- and (1*R**,5*S**,7*S**)-1-(*tert*-Butyldimethylsiloxy)-7-(1,1,1,3,3,3-hexafluoroisopropoxycarbonyl)bicyclo[4.2.0]heptane (10a).** Colorless oil (dr 60 : 40); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84–5.68 (m, 1H), 3.39 (dd, 0.6H, *J* = 9.9, 9.9 Hz), 3.14 (dd, 0.4H, *J* = 8.8, 6.3 Hz), 2.67–2.54 (m, 1H), 2.18 (dt, 0.6H, *J* = 12.6, 9.9 Hz), 1.98–1.28 (m, 7.4H), 0.87 (s, 5.4H), 0.84 (s, 3.6H), 0.12 (s, 1.8H), 0.10 (s, 1.8H), 0.09 (s, 1.2H), 0.03 (s, 1.2H); LRMS (EI) *m/z* 405 (M^+–15). HRMS calcd for $C_{16}H_{23}F_6O_3Si$, 405.1319; found 405.1324.

(1*R,7*S**,9*R**)-1-(*tert*-Butyldimethylsiloxy)-9-(1,1,1,3,3,3-hexafluoroisopropoxycarbonyl)bicyclo[5.2.0]nonane (10b).** Colorless oil: IR (neat, cm^{-1}) 2930, 2857, 1771, 1463, 1386, 1289, 1203, 1111, 837, 775, 690; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (m, 1H), 3.25 (t, 1H, *J* = 9.6 Hz), 2.40 (m, 1H), 2.14 (dt, 1H, *J* = 11.8, 9.3 Hz), 1.96 (m, 1H), 1.87–1.50 (m, 6H), 1.29–1.10 (m, 4H), 0.91 (s, 9H), 0.19 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 120.6 (q, *J* = 278 Hz), 82.7, 66.3 (quint, *J* = 32 Hz), 47.9, 47.3, 34.4, 33.0, 31.9, 26.5, 25.6, 23.6, 21.8, 18.0, –3.1, –3.3; LRMS (EI) *m/z* 391 (M^+–57). *Anal* calcd for $C_{19}H_{30}F_6O_3Si$: C, 50.88; H, 6.74, found C, 50.52; H, 6.65.

(1*R,8*S**,10*R**)-1-(*tert*-Butyldimethylsiloxy)-10-(1,1,1,3,3,3-hexafluoroisopropoxycarbonyl)bicyclo[6.2.0]decane (10c).** Cololess solids: mp 40–41 °C; IR (neat, cm^{-1}) 2932, 2857, 1772, 1387, 1356, 1289, 1232, 1032, 1023, 1111, 923, 834, 775, 668; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (m, 1H), 3.35 (dd, 1H, *J* = 10.4, 10.4 Hz), 2.13 (m, 1H), 2.03 (m, 1H), 1.80–1.27 (m, 12H), 1.08 (m, 1H), 0.90 (s, 9H), 0.19 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 120.6 (q, *J* = 278 Hz), 82.2, 66.3 (quint, *J* = 32 Hz), 48.9,

47.1, 31.3, 28.8, 26.7, 25.7, 24.6, 24.1, 20.8, 18.2, –2.6, –3.1; LRMS (EI) *m/z* 405 (M^+–57). HRMS calcd for $C_{20}H_{32}F_6O_3Si$, 405.1321; found 405.1308.

(1*R,6*S**,8*S**)-1-(*tert*-Butyldimethylsiloxy)-8-methoxycarbonyl–6-methylbicyclo[4.2.0]octane (10d).** Cololess oil; IR (neat, cm^{-1}) 2960, 2858, 1732, 1464, 1292, 1223, 1178, 1097, 837, 775; ^1H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 3.16 (t, 1H, *J* = 8.8 Hz), 1.83 (t, 1H, *J* = 10.4 Hz), 1.67 (m, 2H), 1.57–1.14 (m, 7H), 1.08 (s, 3H), 0.89 (s, 9H), 0.15 (s, 3H), 0.10 (s, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 50.9, 48.3, 41.1, 33.1, 32.0, 26.6, 25.9, 25.7, 24.6, 21.4, 20.0, 18.3, –3.2, –3.5; LRMS (EI) *m/z* 255 (M^+–57). *Anal* calcd for $C_{17}H_{32}O_3Si$: C, 65.33; H, 10.32, found C, 65.38; H, 10.11.

(1*R,6*S**,8*S**) -1-(*tert*-Butyldimethylsiloxy)-8-(1,1,1,3,3,3-hexafluoroisopropoxycarbonyl) –6-methylbicyclo[4.2.0]octane (10d').** Cololess oil; IR (neat, cm^{-1}) 2931, 2860, 1771, 1468, 1387, 1360, 1290, 1227, 1105, 907, 837, 777, 689; ^1H NMR (400 MHz, $CDCl_3$) δ □ □ septet, 1H, *J* = 6.1 Hz), 3.30 (t, 1H, *J* = 8.0 Hz), 1.88 (t, 1H, *J* = 10.7 Hz), 1.80 (m, 1H), 1.66–1.18 (m, 8H), 1.11 (s, 3H), 0.88 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 120.6 (q, *J* = 278 Hz), 77.9, 66.2 (quint, *J* = 32 Hz), 48.2, 41.7, 33.0, 31.9, 26.7, 25.6, 24.5, 21.3, 20.0, 18.3, –3.3, –3.6; LRMS (EI) *m/z* 391 (M^+–57). HRMS calcd for $C_{15}H_{21}F_6O_3Si$, 391.1164; found 391.1164.

(1*R,2*R**)-1-(*tert*-Butyldimethylsiloxy)-1-phenyl-2-(1,1,1,3,3,3-hexafluoroisopropoxycarbonyl)cyclobutane (*trans*-10e).** Colorless oil; IR (neat, cm^{-1}) 2960, 2932, 2860, 1774, 1771, 1473, 1386, 1289, 1233, 1200, 1111, 831, 777, 700, 690; ^1H NMR

(300 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.34–7.21 (m, 3H), 5.41 (m, 1H), 3.67 (t, 1H, *J* = 9.2 Hz), 2.83 (dddd, 1H, *J* = 11.9, 8.2, 3.8, 0.8 Hz), 2.44 (dt, 1H, *J* = 11.9, 9.7 Hz), 2.23–2.04 (m, 2H), 0.93 (s, 9H), 0.047 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 141.3, 128.2, 127.9, 125.8, 80.9, 66.2(quint, *J* = 32 Hz), 53.9, 33.9, 25.6, 17.9, 15.6, -3.1, -3.3; LRMS (EI) *m/z* 456 (M^+). HRMS calcd for $C_{20}H_{26}F_6O_3Si$, 456.1555; found 456.1518.

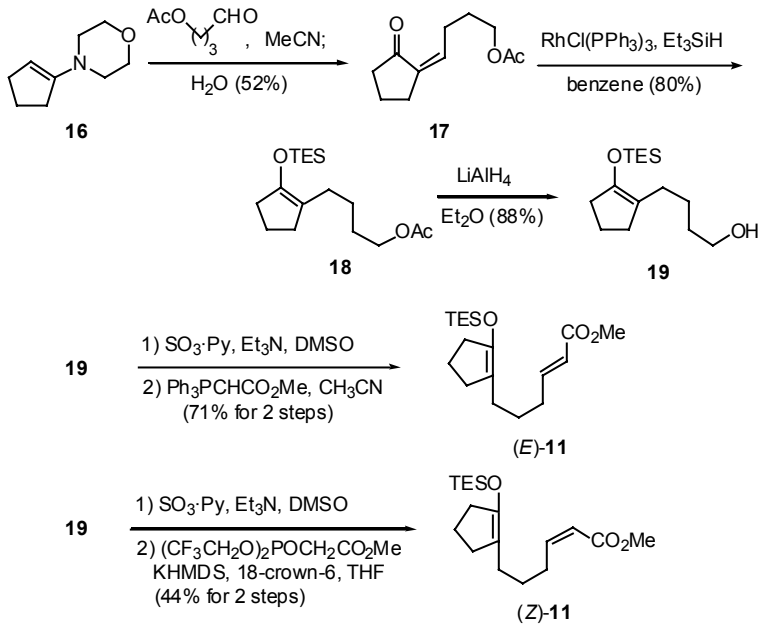
Estrone analogue (10g). Colorless solids (dr 58 : 42); ^{1}H NMR (300 MHz, $CDCl_3$) 7.24 (d, 0.4H, *J* = 8.7 Hz), 7.18 (d, 0.6H, *J* = 8.5 Hz), 6.73 (dd, 0.4H, *J* = 9.2, 2.6 Hz), 6.70 (dd, 0.6H, *J* = 8.9, 2.6 Hz), 6.65 (m, 0.4H), 6.63 (m, 0.6H), 5.76 (m, 0.6H), 5.63 (m, 0.4H), 3.78 (s, 1.2H), 3.77 (s, 1.8H), 3.54 (dd, 0.4H, *J* = 8.8, 8.8 Hz), 3.46 (dd, 0.6H, *J* = 11.4, 8.9 Hz), 2.96–2.60 (m, 3H), 2.46–2.10 (m, 2H), 2.04–1.86 (m, 1H), 1.80–1.20 (m, 13H), 0.92 (s, 5.4H), 0.84 (s, 3.6H), 0.32 (s, 1.2H), 0.26 (s, 1.8H), 0.16 (s, 1.8H), 0.12 (s, 1.2H); LRMS (EI) *m/z* 620 (M^+). *Anal* calcd for $C_{31}H_{42}F_6O_4Si$: C, 58.98; H, 6.82, found C, 58.92; H, 6.78.

(1*R,6*S**,7*S**,8*R**)-1-(*tert*-Butyldimethylsiloxy)-7-methyl-8-(pentafluorophenoxycarbonyl)bicyclo[4.2.0]octane (10h).** Colorless oil: IR (neat, cm^{-1}) 2931, 2859, 1776, 1520, 1290, 1244, 1195, 1079, 1004, 836, 775; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.81 (d, 1H, *J* = 10.3 Hz), 2.04 (m, 1H), 1.94 (dd, 1H, *J* = 10.4, 3.3 Hz), 1.84 (br d, 1H, *J* = 14.6 Hz), 1.71–1.46 (m, 5H), 1.39–1.20 (m, 2H), 1.17 (d, 3H, *J* = 6.0 Hz), 0.89 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 74.3, 57.0, 49.0, 32.7, 27.5, 25.5, 22.1, 21.6, 10.6, 18.9, 17.8, –3.0; LRMS (EI) *m/z* 407 (M^+–57). HRMS calcd for $C_{19}H_{20}F_5O_3Si$, 407.1102; found 407.1107.

(1*R,6*S**,8*R**)-1-(*tert*-Butyldimethylsiloxy)-8-methyl-8-(hexafluoroisopropoxycarbonyl)bicyclo[4.2.0]octane (10i).** Colorless oil: IR (neat, cm^{-1}) 2934, 2859, 1790, 1465, 1387, 1355, 1292, 1223, 1200, 1111, 1096, 836, 774, 689; ^1H NMR (300 MHz, $CDCl_3$) δ 5.74 (m, 1H), 2.44 (m, 1H), 1.92 (dd, 1H, *J* = 12.3, 12.3 Hz), 1.83 (d, 1H, *J* = 12.3 Hz), 1.67–1.16 (m, 8H), 1.41 (s, 3H), 0.90 (s, 9H), 0.141 (s, 3H), 0.135 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 120.6 (q, *J* = 278 Hz), 75.8, 66.1 (quint, *J* = 32 Hz), 52.1, 38.0, 33.6, 25.6, 25.4, 23.3, 21.0, 18.73, 18.65, 18.3, –2.8; LRMS (EI) *m/z* 391 (M^+–57). HRMS calcd for $C_{15}H_{21}F_6O_3Si$, 391.1164; found 391.1154.

Preparation of (*E*)- and (*Z*)-11 (Scheme S-2)

Scheme S-2.



2-(4-Acetoxybutylene)cyclopentan-1-one (17). The solution of 4-(1-cyclopeneten-1-yl)morpholine **16** (650 mg, 4.25 mmol) and 4-acetoxybutanal (580 mg, 4.25 mmol) in MeCN (8.5 mL) was refluxed for 17 h. After addition of H_2O (1.0 mL), the resulting mixture was further refluxed for 1 h. After dilution with Et_2O, organic layer was washed with saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$ and brine, dried and concentrated. The residue was purified by column chromatography on silica gel with 20% AcOEt/hexane to afford **17** (464 mg, 52%) as colorless oil: IR (neat, cm^{-1}) 2960, 1740, 1719, 1650, 1367, 1239, 1182, 1043, 824; ^1H NMR (300 MHz, $CDCl_3$) δ 6.52 (tt, 1 H, J = 7.7, 2.7 Hz), 4.08 (t, 2H, J = 7.0 Hz), 2.58 (m, 2H), 2.34 (t, 2H, J = 7.7 Hz), 2.24 (q, 2H, J = 7.0 Hz), 2.05 (s, 3H), 1.94 (quint, 2H, J = 7.7 Hz), 1.81 (quint, 2H, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.1, 171.1, 138.0, 134.3, 63.5, 38.3, 27.2, 26.5, 26.0, 20.7, 19.5; LRMS (EI) *m/z* 197 (M^++1). HRMS *m/z* calcd. for $C_{11}H_{17}O_3$, 197.1177; found 197.1206.

2-(4-Acetoxybutyl)-1-triethylsiloxy-1-cyclopentene (18). To a solution of **17** (1.94 g, 9.89 mmol) in bezene (10 mL) was added Et_3SiH (1.74 mL, 10.9 mmol) at 0 °C and stirred for 1 h. After addition of $RhCl(PPh_3)_3$ (9 mg, 0.1 mol%), the resulting mixture was stirred at 50 °C for 6 h and concentrated. The residue was purified by column chromatography on silica gel with 20% AcOEt/hexane to afford **18** (2.47 g, 80%) as colorless oil: IR (neat, cm^{-1}) 2954, 1742, 1683, 1365, 1241, 1017, 859, 730; ^1H NMR (300 MHz, $CDCl_3$) δ 4.06 (t, 2 H, *J* = 6.6 Hz), 2.30 (br t, 2H, *J* = 7.3 Hz), 2.18 (br t, 2H, *J* = 7.3 Hz), 2.05 (br t, 2H, *J* = 7.3 Hz), 2.04 (s, 3H), 1.79 (quint, 2H, *J* = 7.3 Hz), 1.61 (quint, 2H, *J* = 7.3 Hz), 1.41 (quint, 2H, *J* = 7.3 Hz), 0.98 (t, 9H, *J* = 7.8 Hz), 0.64 (q, 6H, *J* = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 147.0, 115.9, 64.5, 33.6, 30.7, 28.4, 25.6, 23.8, 20.8, 19.7, 6.46, 5.25; LRMS (EI) *m/z* 312 (M^+). HRMS *m/z* calcd. for $C_{17}H_{32}O_3Si$, 312.2121; found 312.2143.

2-(4-Hydroxybutyl)-1-triethylsiloxy-1-cyclopentene (19). After refluxing the solution of $LiAlH_4$ (0.45 g, 11.9 mmol) in Et_2O (70 mL), a solution of **18** (2.45 g, 7.84 mmol) in Et_2O (70 mL) was added slowly with gentle reflux without heating, and resulting mixture was heated under reflux for 30 min. After the reaction was over, H_2O (0.5 mL), 15% NaOH (0.5 mL) and H_2O (0.8 mL) were added slowly at 0 °C. The mixture was dried and concentrated. The residue was purified by column chromatography on silica gel with 20% AcOEt/hexane to afford **19** (1.86 g, 88%) as colorless oil: IR (neat, cm^{-1}) 3385 (br.), 2936, 2876, 1683, 1556, 1348, 1304, 1210, 1017, 859, 730; ^1H NMR (300 MHz, $CDCl_3$) δ 3.64 (t, 2H, *J* = 6.4 Hz), 2.29 (br t, 2H, *J* = 7.3 Hz), 2.18 (br t, 2H, *J* = 7.3 Hz), 2.05 (t, 2H, *J* = 7.4 Hz), 1.78 (quint, 2H, *J* = 7.3 Hz), 1.54 (quint, 2H, *J* = 7.0 Hz), 1.41 (quint, 2H, *J* = 7.0 Hz), 0.97 (t, 9H, *J* = 7.8 Hz), 0.64 (q, 6H, *J* =

7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8, 116.3, 62.9, 33.7, 32.5, 30.7, 25.7, 23.7, 19.7, 6.5, 5.3;.LRMS (EI) *m/z* 270 (M^+). HRMS *m/z* calcd. for $C_{15}H_{30}O_2Si$, 270.2013; found 270.2014.

Methyl (2*E*)-6-(2-Triethylsilyloxy-1-cyclopentenyl)-2-hexenoate ((*E*)-11). To the mixture of **19** (1.86 g, 6.88 mmol) in DMSO (14 mL) was added Et_3N (5.8 mL, 41.6 mmol) and the mixture was stirred for 1 h. To the mixture, SO_3·Py (3.3 g, 20.7 mmol) was added and stirred for 30 min. The resulting mixture was quenched with H_2O and extracted 3 times with Et_2O. Combined organic layer was washed with saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$ and brine, dried and concentrated to afford crude aldehyde, which was used in the next rection without futher purification.

A mixture of the above aldehyde and methyl (triphenylphosphoranylidene)acetate (2.8 g, 8.37 mmol) in MeCN (30 mL) was stirred for 16 h at rt, and concenrated. The residue was purified by column chromatography on silica gel with 5% Et_2O/hexane to afford (*E*)-**11** (1.59 g, 71% for 2 steps) as colorless oil: IR (neat, cm^{-1}) 2953, 1728, 1682, 1659, 1435, 1269, 1005, 858, 731; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (dt, 1H, *J* = 15.7, 6.9 Hz), 5.81 (dt, 1H, *J* = 15.7, 1.5 Hz), 3.72 (s, 3H), 2.29 (t, 2H, *J* = 7.2 Hz), 2.32–2.12 (m, 4H), 2.05 (t, 2H, *J* = 7.6 Hz), 1.78 (quint, 2H, *J* = 7.2 Hz), 1.50 (quint, 2H, *J* = 7.6 Hz), 0.97 (t, 9H, *J* = 8.0 Hz), 0.63 (q, 6H, *J* = 8.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 149.9, 147.3, 120.8, 115.6, 51.2, 33.6, 32.0, 30.7, 25.6, 19.7, 6.46, 5.27; LRMS (EI) *m/z* 324 (M^+); *Anal* calcd for $C_{18}H_{32}O_3Si$: C, 66.62; H, 9.94; found C, 66.57; H, 9.95.

Methyl (2*Z*)-6-(2-Triethylsilyloxy-1-cyclopentenyl)-2-hexenoate ((*Z*)-11). To the mixture of **19** (150 mg, 0.555 mmol) in DMSO (1.1 mL) was added Et_3N (0.77 mL, 5.52 mmol) and the

mixture was stirred for 30 min. To the mixture, SO_3·Py (440 mg, 2.76 mmol) was added and stirred for 2 h. The resulting mixture was quenched with H_2O and extracted 3 times with Et_2O. Combined organic layer was washed with saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$ and brine, dried and concentrated to afford crude aldehyde, which was used in the next reaction without further purification.

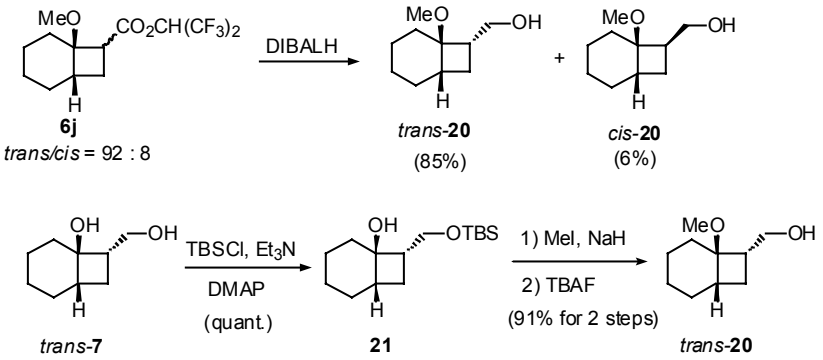
To a solution of $(CF_3CH_2O)_2POCH_2CO_2Me$ (0.120 mL, 0.567 mmol) and 18-crown-6 (730 mg, 2.76 mmol) in THF (10.0 mL) was added 0.5 M KHMDS-toluene (1.1 mL, 0.550 mmol) and solution of the above aldehyde in THF (1.0 mL) at –78 °C and the mixture was stirred for 1.5 h. The resulting mixture was quenched with saturated aqueous NH_4Cl, extracted with Et_2O. Combined organic layer was dried and concentrated. The residue was purified by column chromatography on silica gel with 2% Et_2O/hexane to afford (*Z*)-**11** (79.5 mg, 44% for 2 steps) as colorless oil: IR (neat, cm^{-1}) 2954, 2876, 1727, 1681, 1646, 1437, 1198, 1174, 1017, 729; ^1H NMR (300 MHz, $CDCl_3$) 6.26 (dt, 1H, *J* = 11.5, 5.8 Hz), 5.76 (dt, 1H, *J* = 11.5, 1.6 Hz), 3.70 (s, 3H), 2.63 (dddd, 2H, *J* = 7.5, 7.5, 7.5, 1.6 Hz), 2.30 (br t, 2H, *J* = 6.3 Hz), 2.19 (br t, 2H, *J* = 7.1 Hz), 2.07 (br t, 2H, *J* = 7.6 Hz), 1.85–1.72 (m, 2H), 1.60–1.35 (m, 2H), 0.98 (t, 9H, *J* = 7.8 Hz), 0.64 (q, 6H, *J* = 7.8 Hz); LRMS (EI) *m/z* 324 (M^+). HRMS *m/z* calcd. for $C_{18}H_{32}O_3Si$, 324.2121; found 324.2148.

(1*S, 2*R**, 3*R**, 7*S**)-2-Methoxycarbonyl-1-(triethylsiloxy)tricyclo[5. 3. 0. $0^{3,7}$]decane (12).** IR (neat, cm^{-1}) 2952, 1733, 1435, 1201, 1222, 1121, 745, 668; ^1H NMR (300 MHz, $CDCl_3$) δ 3.69 (s, 3H), 2.63 (dd, 1H, *J* = 6.3, 1.2 Hz), 2.22 (br t, 1H, *J* = 6.3 Hz), 1.97–1.86 (m, 2H), 1.85–1.62 (m, 4H), 1.61–1.42 (m, 4H), 1.32–1.18 (m, 2H), 0.96 (t, 9H, *J* = 8.0 Hz), 0.61 (q, 6H, *J* = 8.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 82.3, 58.8, 53.8, 50.9, 38.2, 37.6, 35.2,

32.2, 30.2, 25.8, 24.2, 6.84, 5.95; LRMS (EI) *m/z* 324 (M^+); *Anal* calcd for $C_{18}H_{32}O_3Si$; C, 66.62; H, 9.94, found C, 66.34; H, 9.88.

Determination of Relative Stereochemistry of Cyclobutanes (selected examples).

Scheme S-3.



Stereochemistry of 6j (Scheme S-3); A diastereomeric mixture of *trans*- and *cis*-**6j** was reduced to afford two diastereomeric alcohols, which are separable. The major product was consistent with *trans*-**20** which was prepared from *trans*-**7**. Hence, the stereochemistry of the major diastereomer of **6j** was assigned as a *trans* isomer.

***trans*-20 from 6j;** To a solution of **6j** (120 mg, 0.359 mmol) in CH_2Cl_2 (1.0 mL) was added 1 M DIBALH–hexane (0.90 mL, 0.90 mmol) at –78 °C and stirred for 10 h at room temperature. After addition of MeOH (1.0 mL) and Et_2O (6.0 mL), the mixture was stirred for 3 h, filtered through Celite and evaporated. The residue was purified by column chromatography on silica gel with 50% Et_2O/hexane to give *trans*-**20** (52.0 mg, 85%) and *cis*-**20** (3.8 mg, 6%) as colorless oil. *trans*-**20**; IR (neat, cm^{-1}) 3386 (br), 2932, 2856, 1463, 1288, 1188, 1138, 1100, 1041, 989; ^1H NMR (300 MHz, $CDCl_3$) δ 3.74–3.52 (m, 2H), 3.26 (s, 3H), 2.42–2.25 (m, 2H), 1.84 (brd, 1H, J = 11.8 Hz), 1.73 (q, 1H, J = 9.2 Hz), 1.68 (brs, 1H), 1.64–1.18 (m, 7H), 1.09 (q, 1H, J = 10.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 78.5, 62.4, 50.5, 43.7, 36.3, 25.2, 24.0, 21.4, 20.2, 19.7; LRMS (EI) *m/z* 152 (M^+–18). HRMS calcd for $C_{10}H_{16}O$, 152.1201; found152.1214.

***trans*-20 from *trans*-7.** To a solution of *trans*-**7** (218 mg, 1.40 mmol), Et_3N (0.30 nL, 2.15 mmol) and DMAP (catalytic amount) in CH_2Cl_2 (3.0 mL) was added TBSCl (230 mg, 1.53 mmol) at 0 °C and stirred for 1 d at ambient temperature. The resulting mixture was quenched with H_2O, extracted with AcOEt, dried and concentrated. The residue was purified by column chromatography on silica gel with 30% AcOEt/hexane to give **21** (378 mg, quant.) as colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70–3.56 (m, 2H), 2.24–2.04 (m, 2H), 1.77 (ddd, 1H, J = 13.6, 13.6, 3.6 Hz), 1.69–1.00 (m, 10H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.7, 62.6, 48.7, 40.0, 30.2, 25.8, 23.5, 21.6, 20.2, 19.6, 18.1, 5.5; LRMS (EI) *m/z* 213 (M^+–57). HRMS calcd for $C_{11}H_{21}O_2Si$, 213.1311; found 213.1331.

To a solution of NaH (60% oil dispersion, 35 mg, 0.875 mg) in THF (1.0 mL) was added **21** (150 mg, 0.555 mmol) and MeI (0.35 mL, 5.62 mL) and stirred for 1.5 h at room temperature. The resulting mixture was cooled to 0 °C, quenched with saturated aqueous NH_4Cl, extracted with Et_2O, washed with brine, dried and concentrated to give crude oil of methyl ether.

The above crude oil was dissolved in THF (1.0 mL) and 1 M TBAF–THF (1.0 mL, 1.0 mmol) was added. After 16 h, the mixture was quenched with H_2O, extracted with AcOEt, dried and concentrated. The residue was purified by column chromatography on silica gel with 60% AcOEt/hexane to give *trans*-**20** (86.3 mg, 91% for 2 steps) as colorless oil.

NOESY experiment; For example, NOESY results of reduced-**10e**, **10h** and **10i** are shown in Figure S-1.

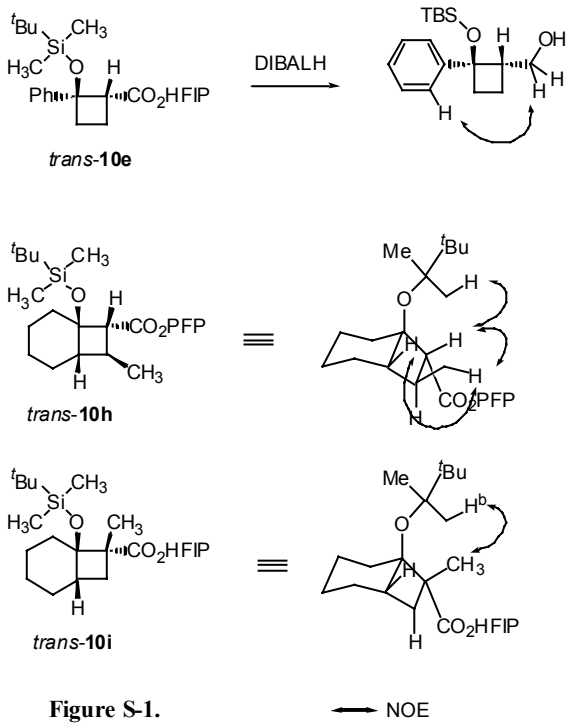
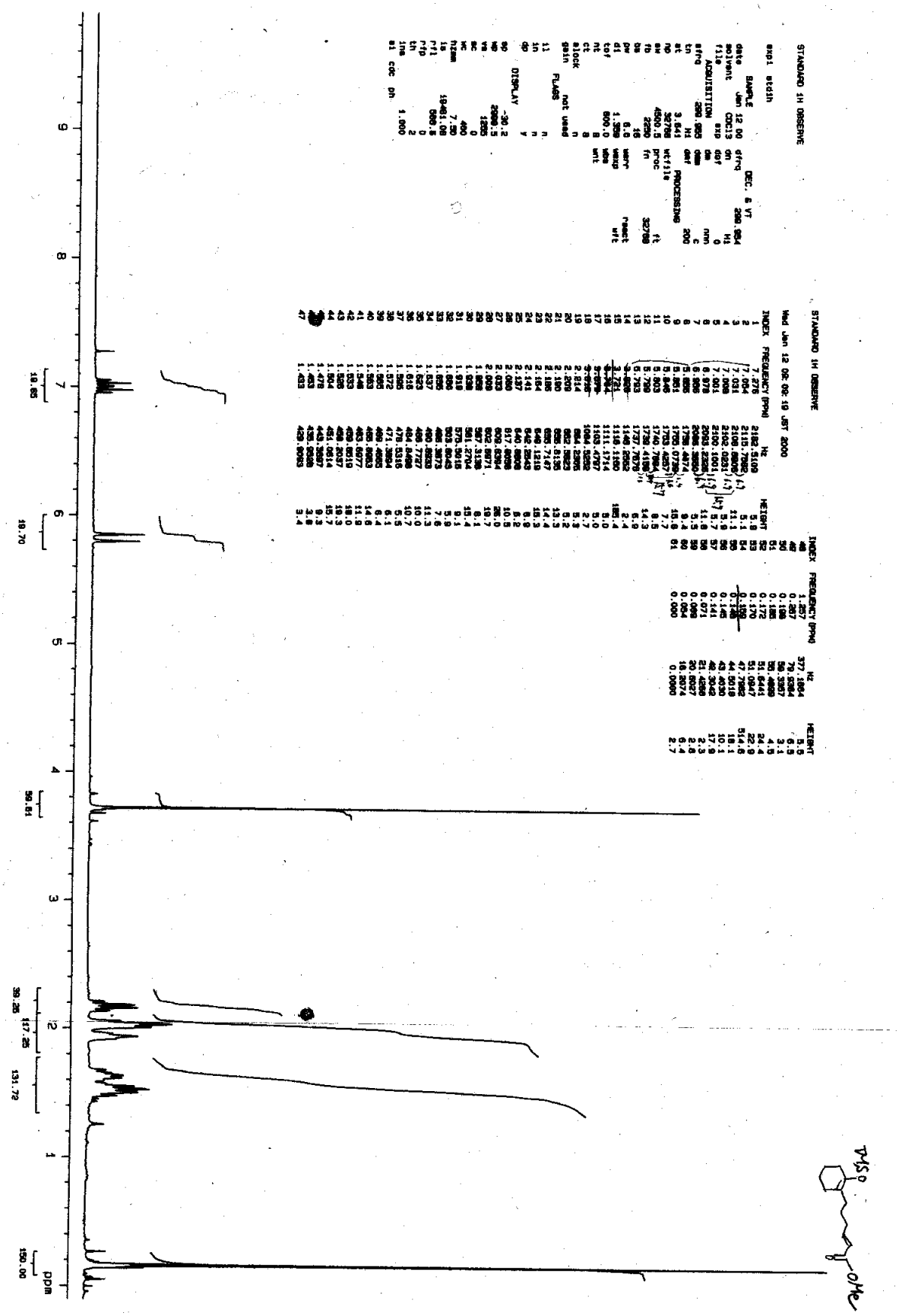


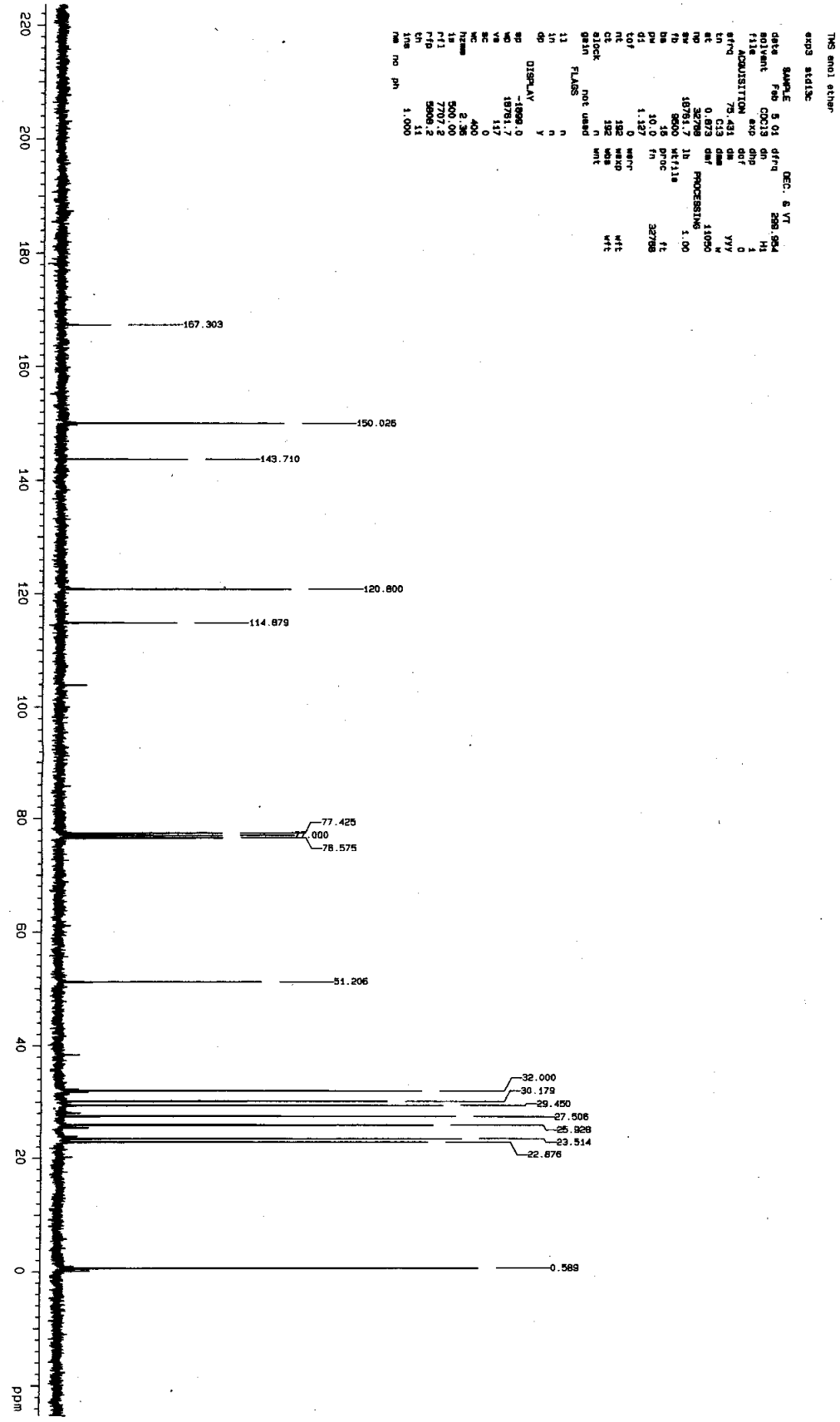
Figure S-1.

^{1}H and ^{13}C NMR Data for Compounds 1, 2b, *trans*-6a, *cis*-6a, 6i–j, *cis*-7, 8, 10a, 10c, 10d', 10e, 10h, 10i and *Z*-11. (For compounds lacking of elemental analysis data)

1 (^{1}H-NMR)



1 (^{13}C-NMR)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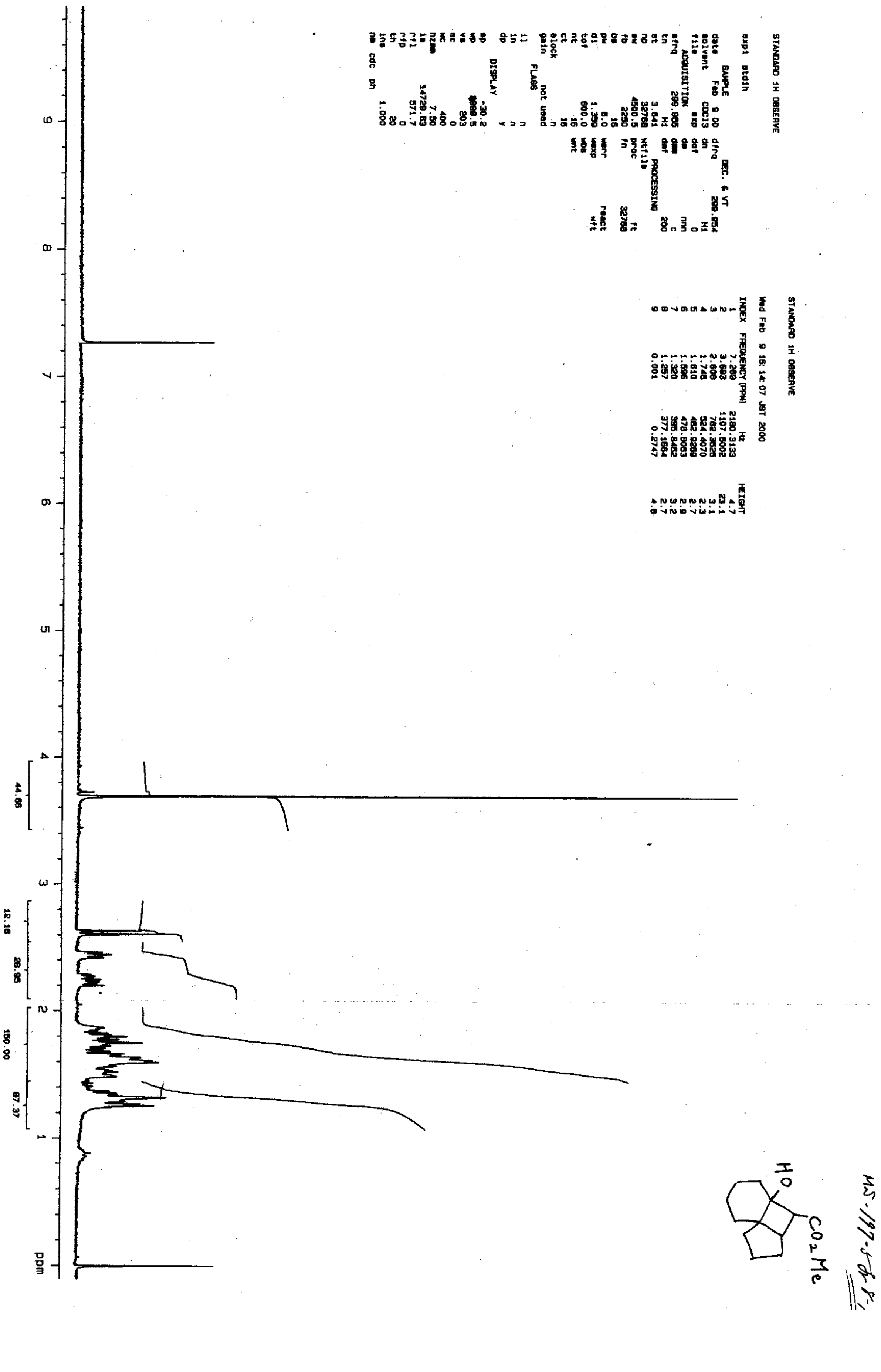
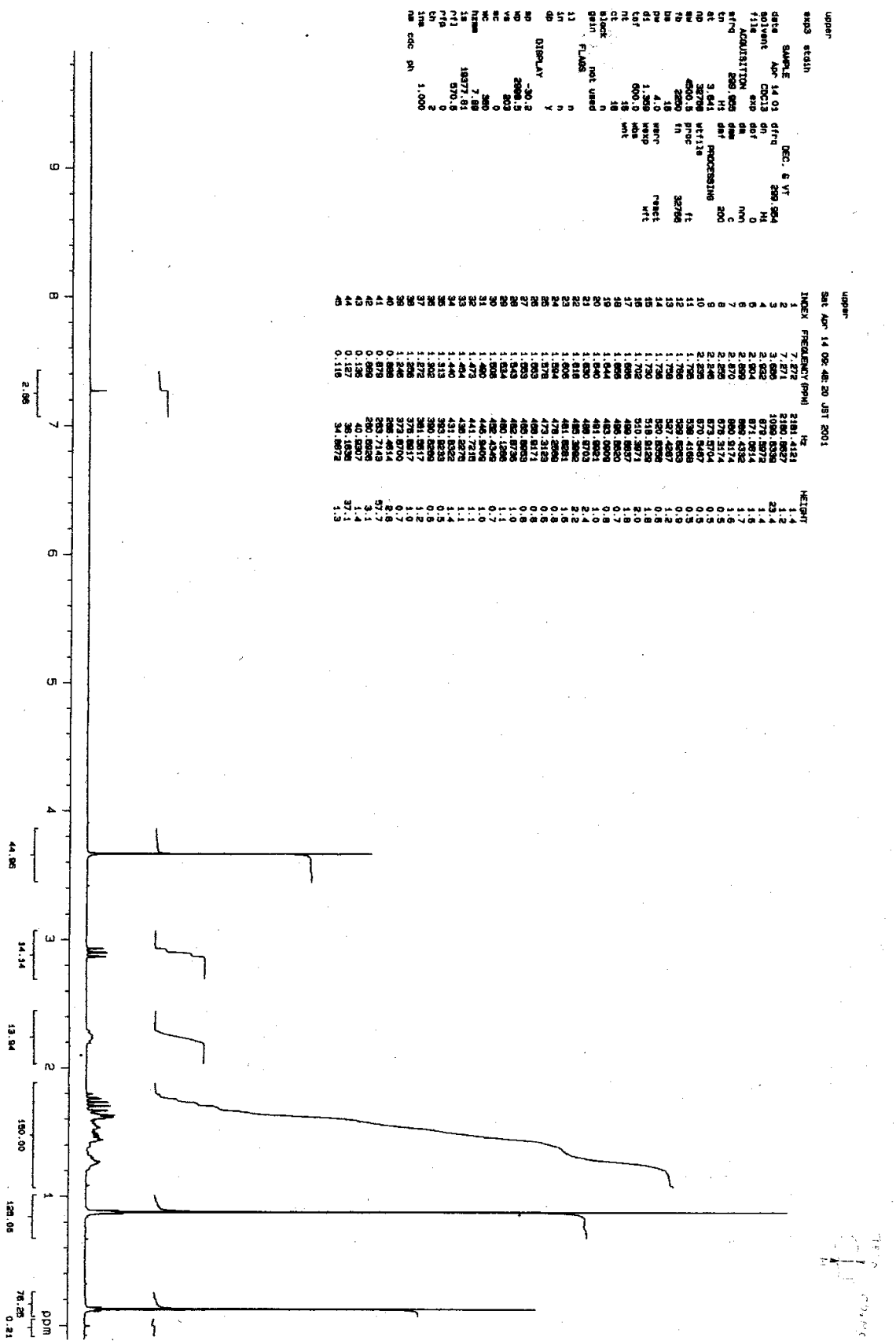
ppm

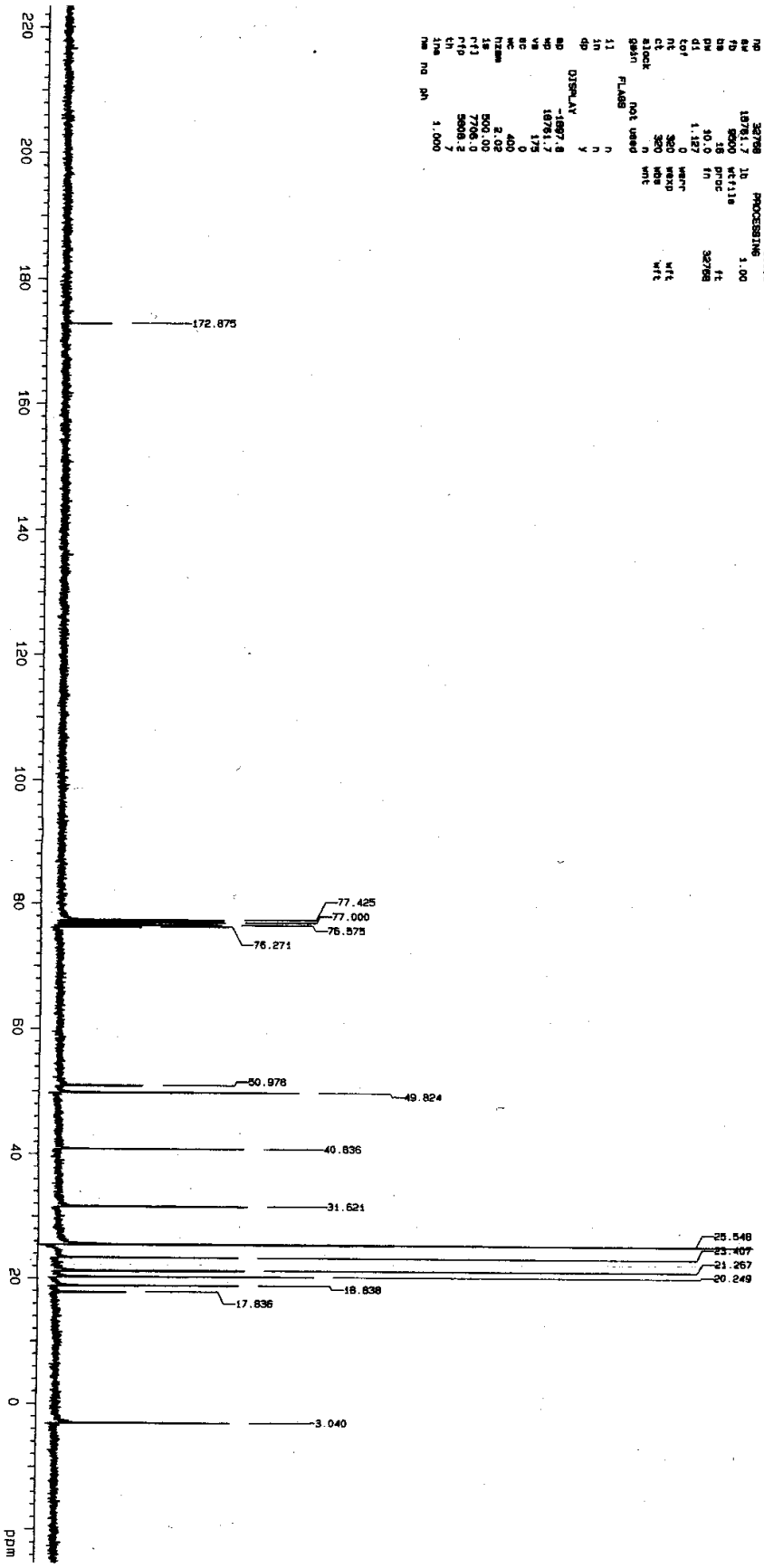
2 (^{1}H-NMR)



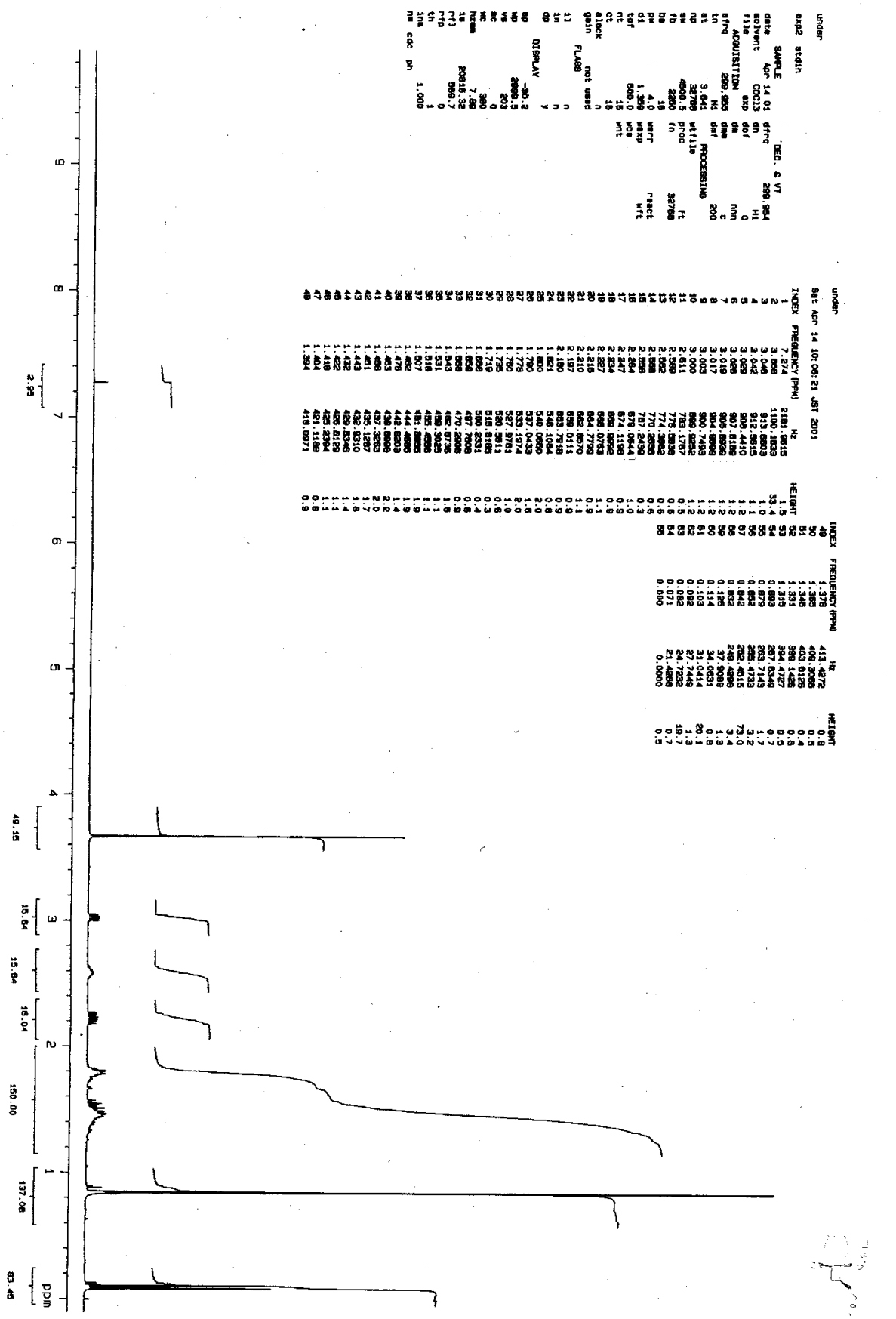
trans-**6a** (^{1}H-NMR)



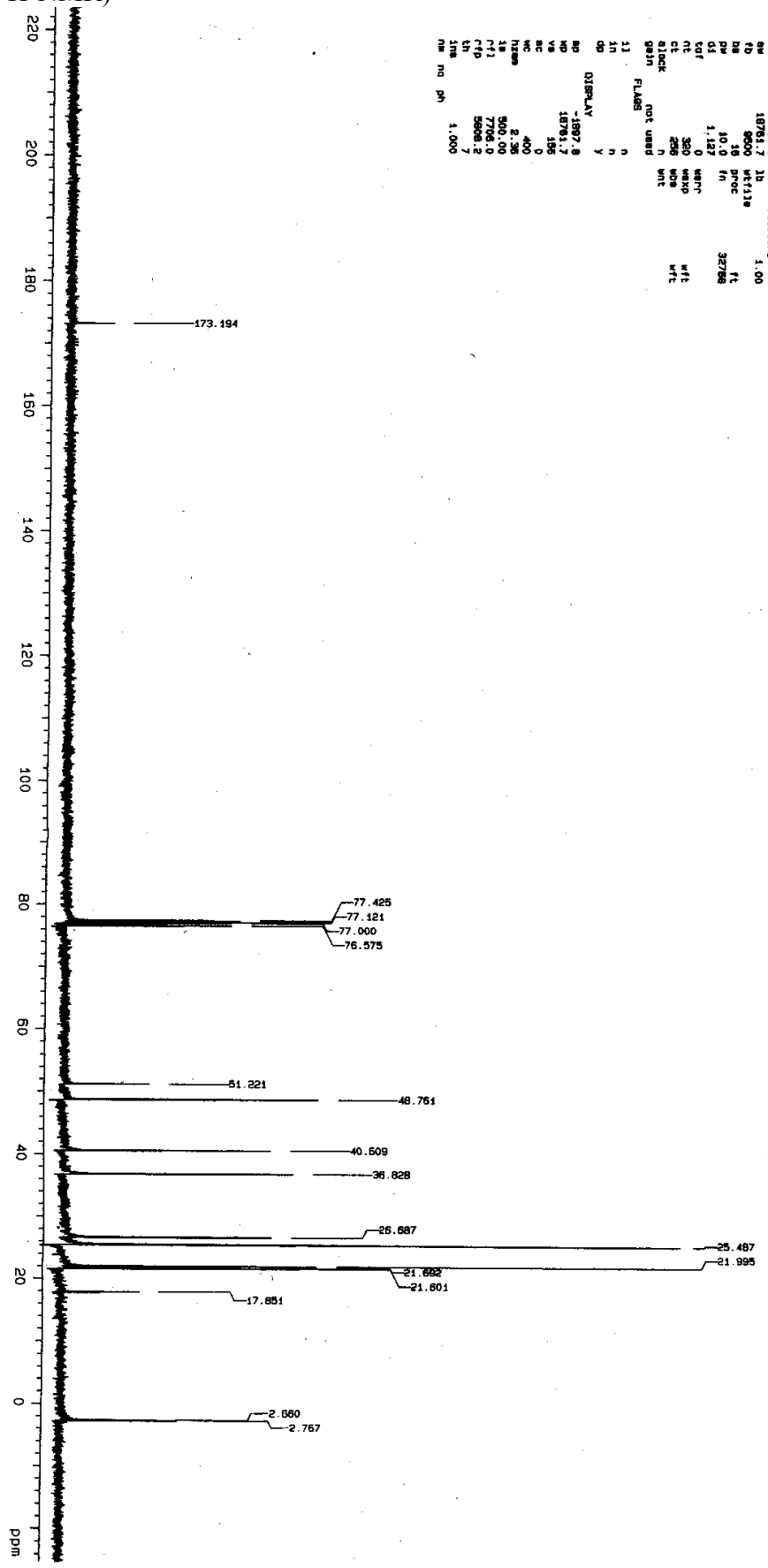
trans-**6a** (^{13}C-NMR)



cis-**6a** (^{1}H-NMR)



cis-**6a** (^{1}H-NMR)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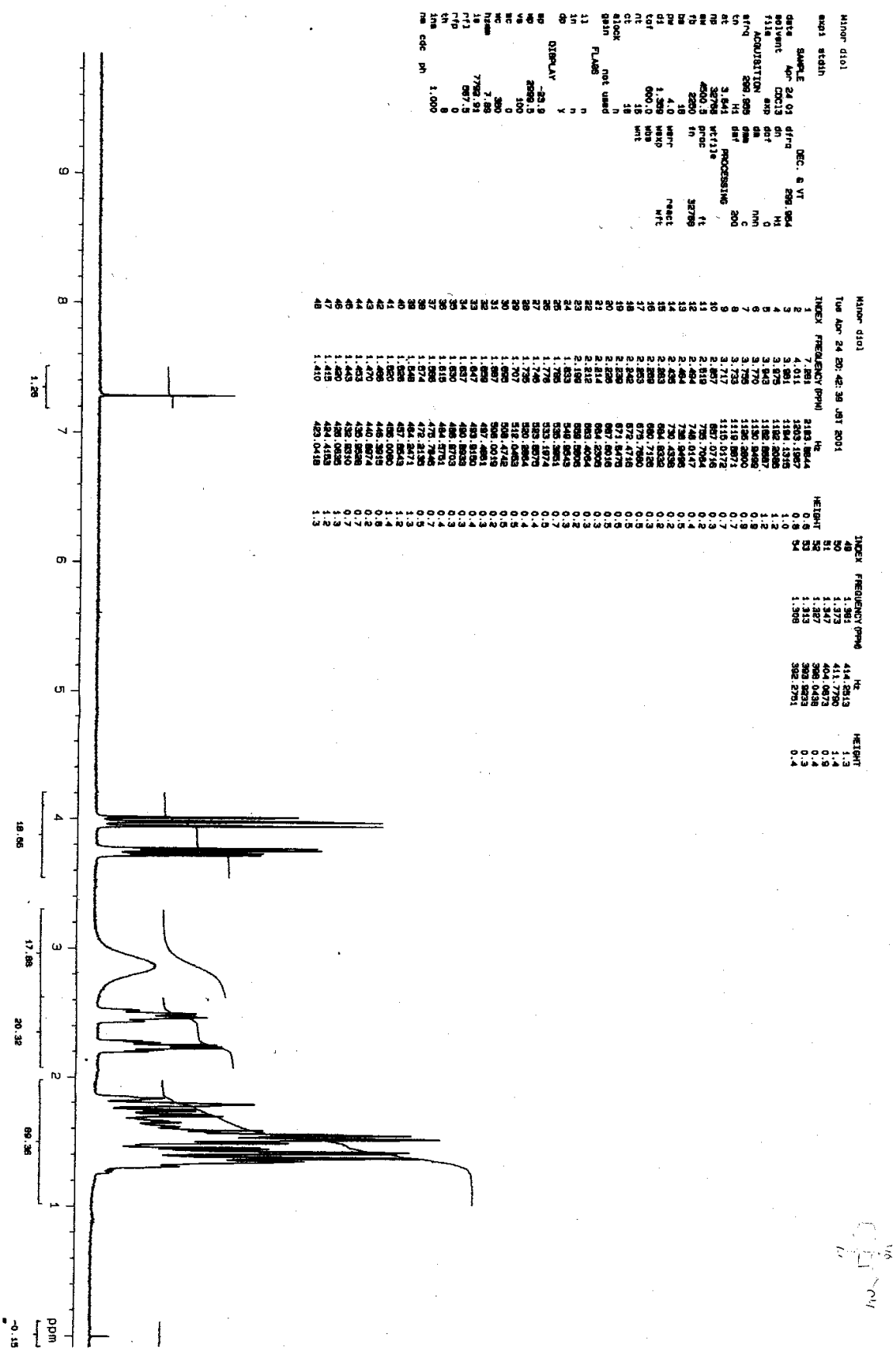
cis-**7** (^{1}H-NMR)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Tue Apr 24 20:42:39 JST 2001
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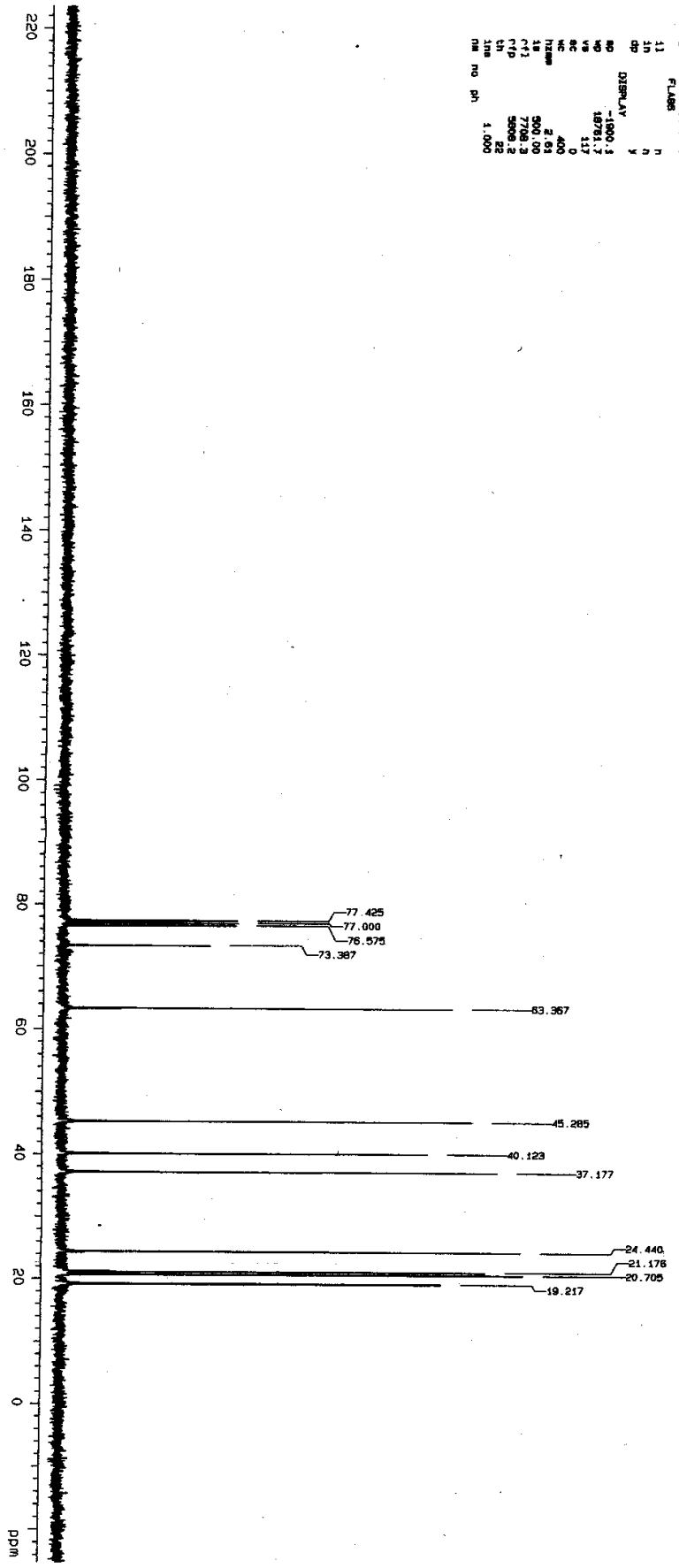
INDEX FREQUENCY (PPM) Hz HEIGHT
ppm

cis-**7** (^{13}C-NMR)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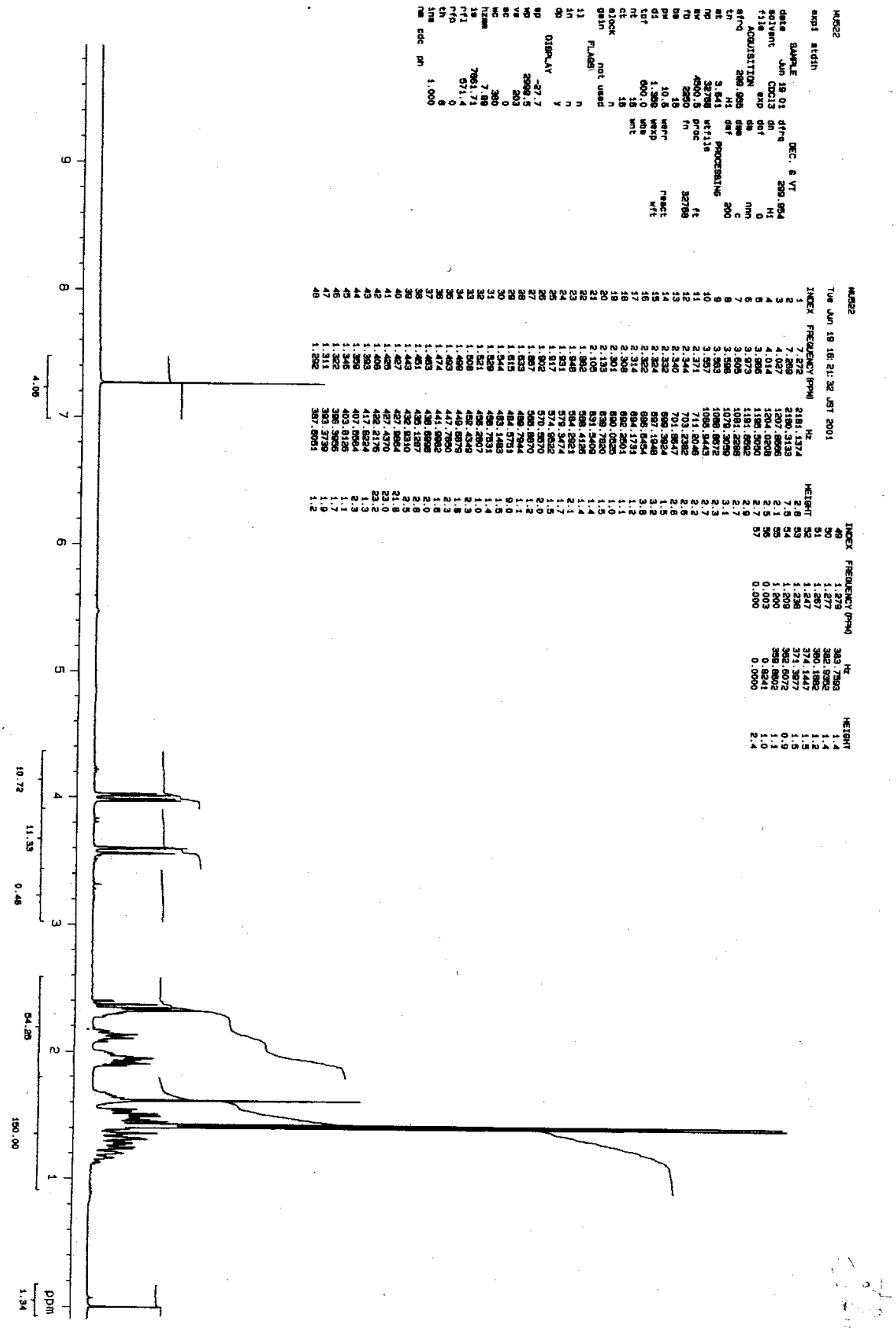
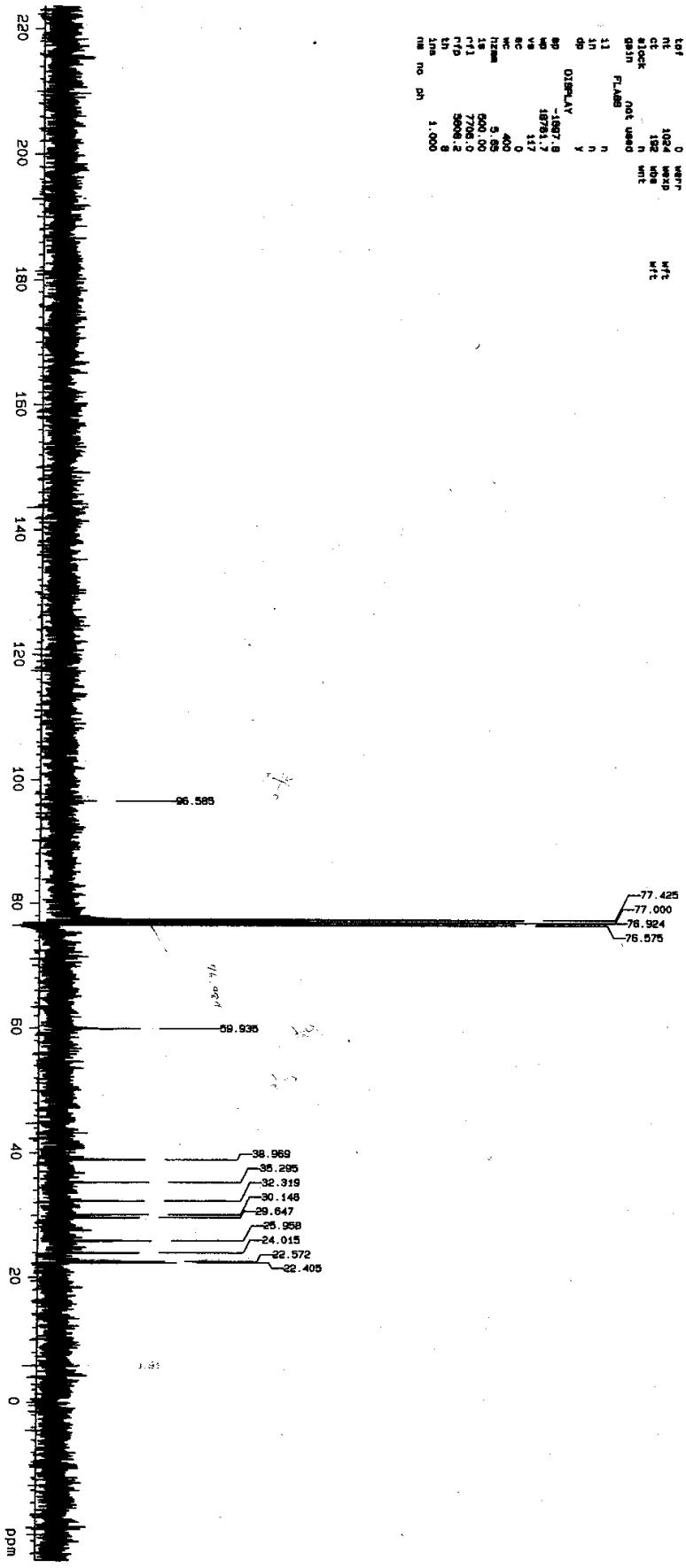
8 (^{1}H-NMR)



8 (^{13}C-NMR)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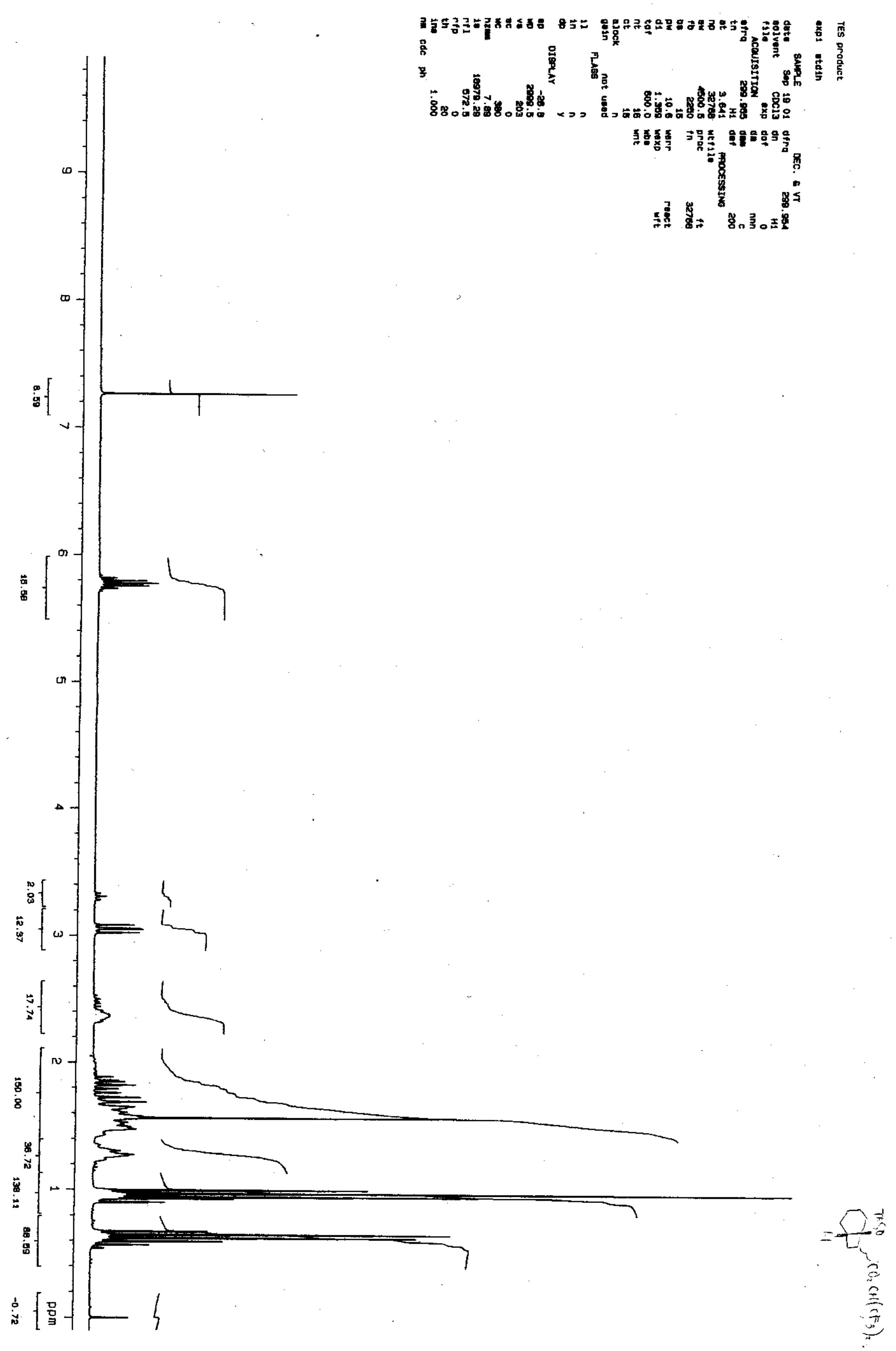
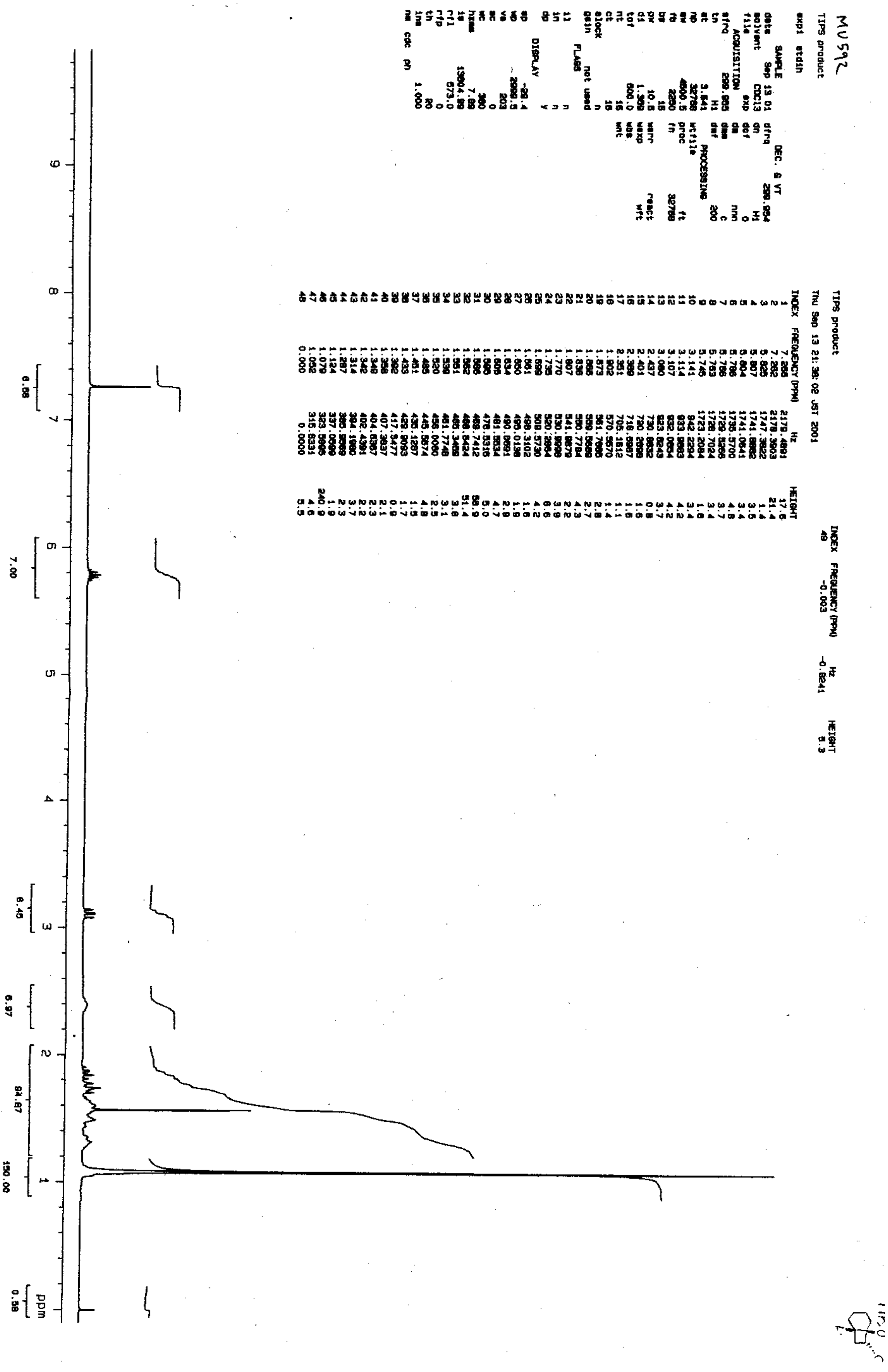
22.405
ppm

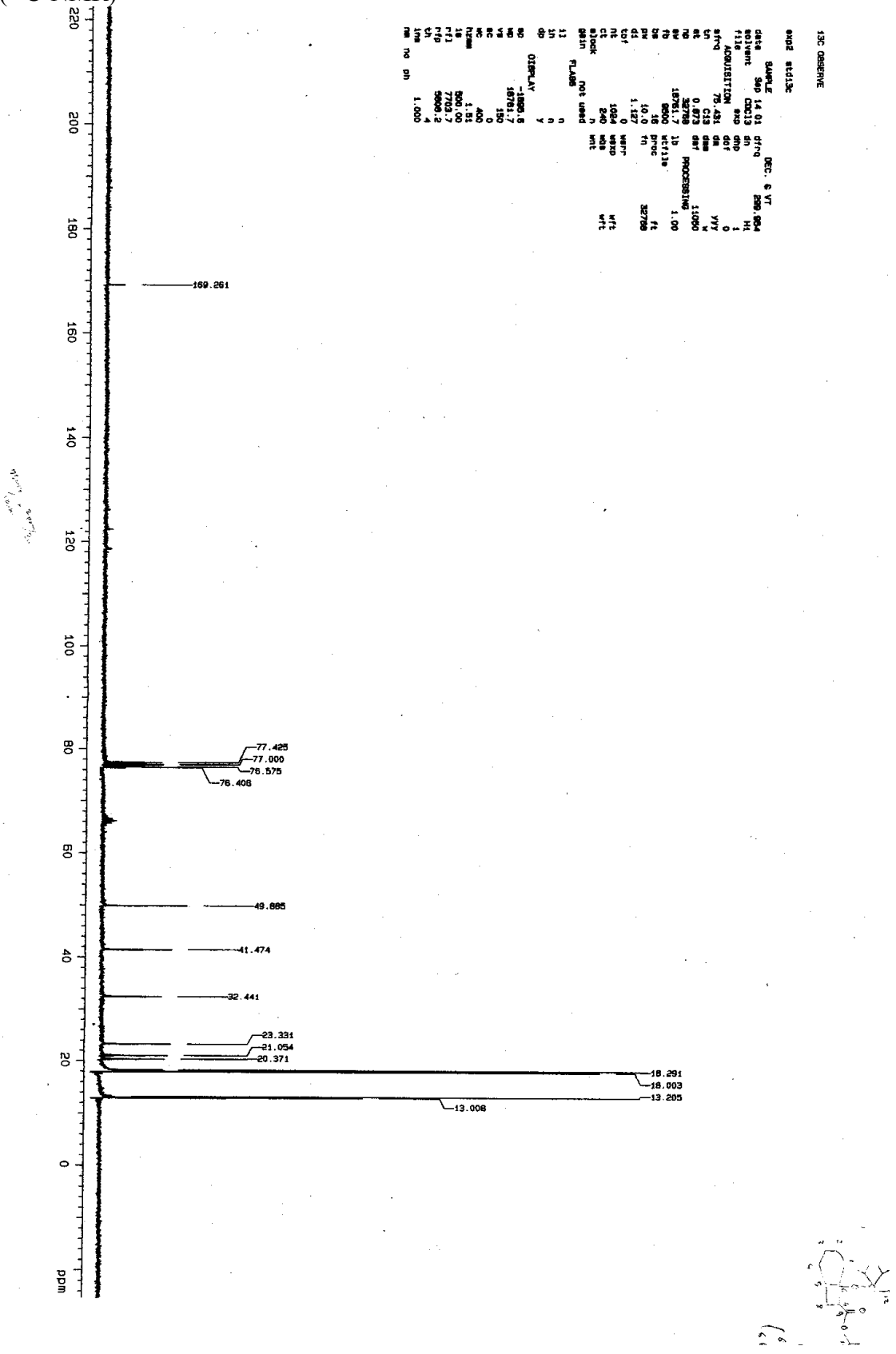
6h (^{1}H-NMR)



6i (^{1}H-NMR)



6i (^{13}C-NMR)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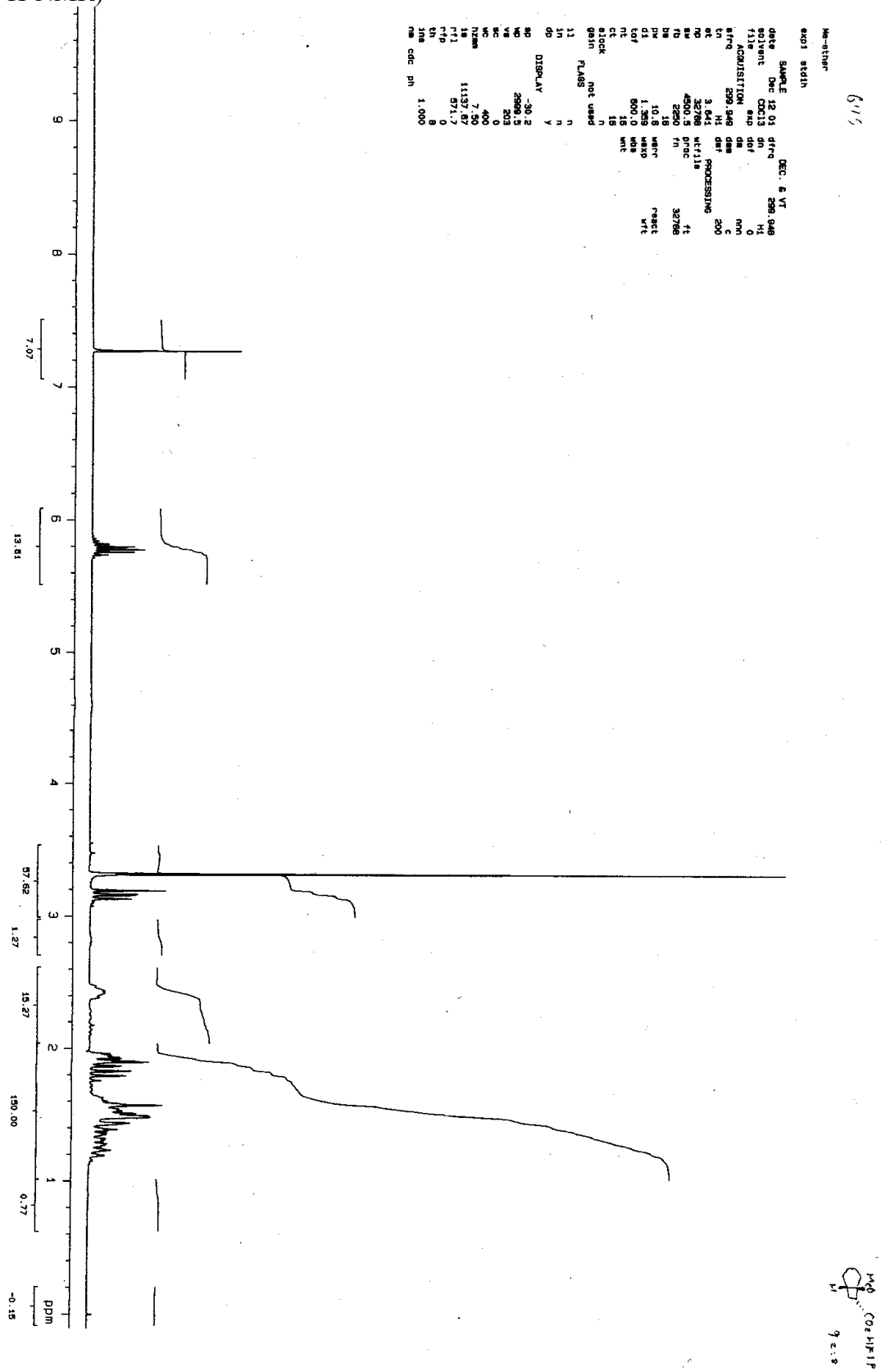
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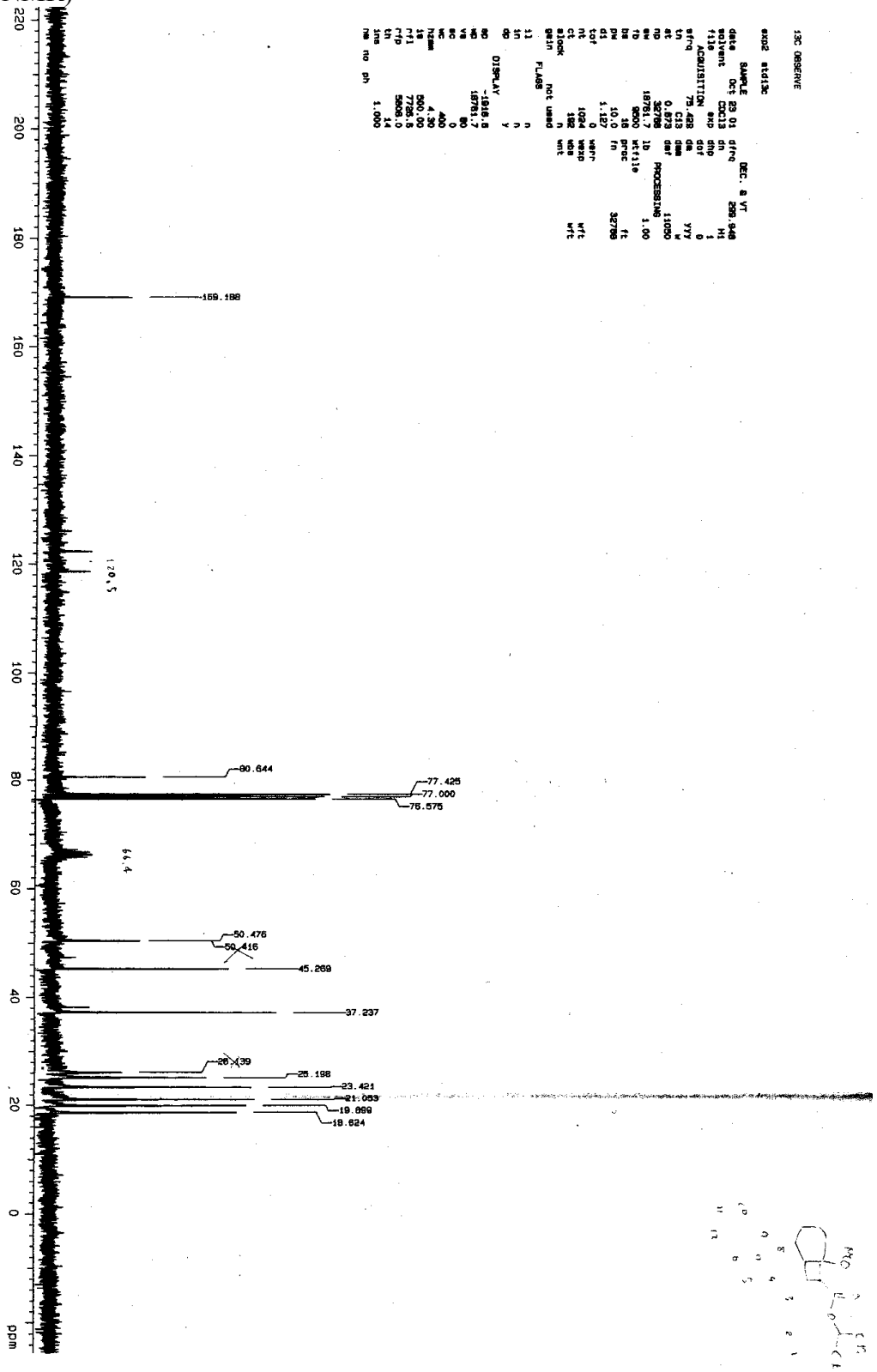
6j (^{13}C-NMR)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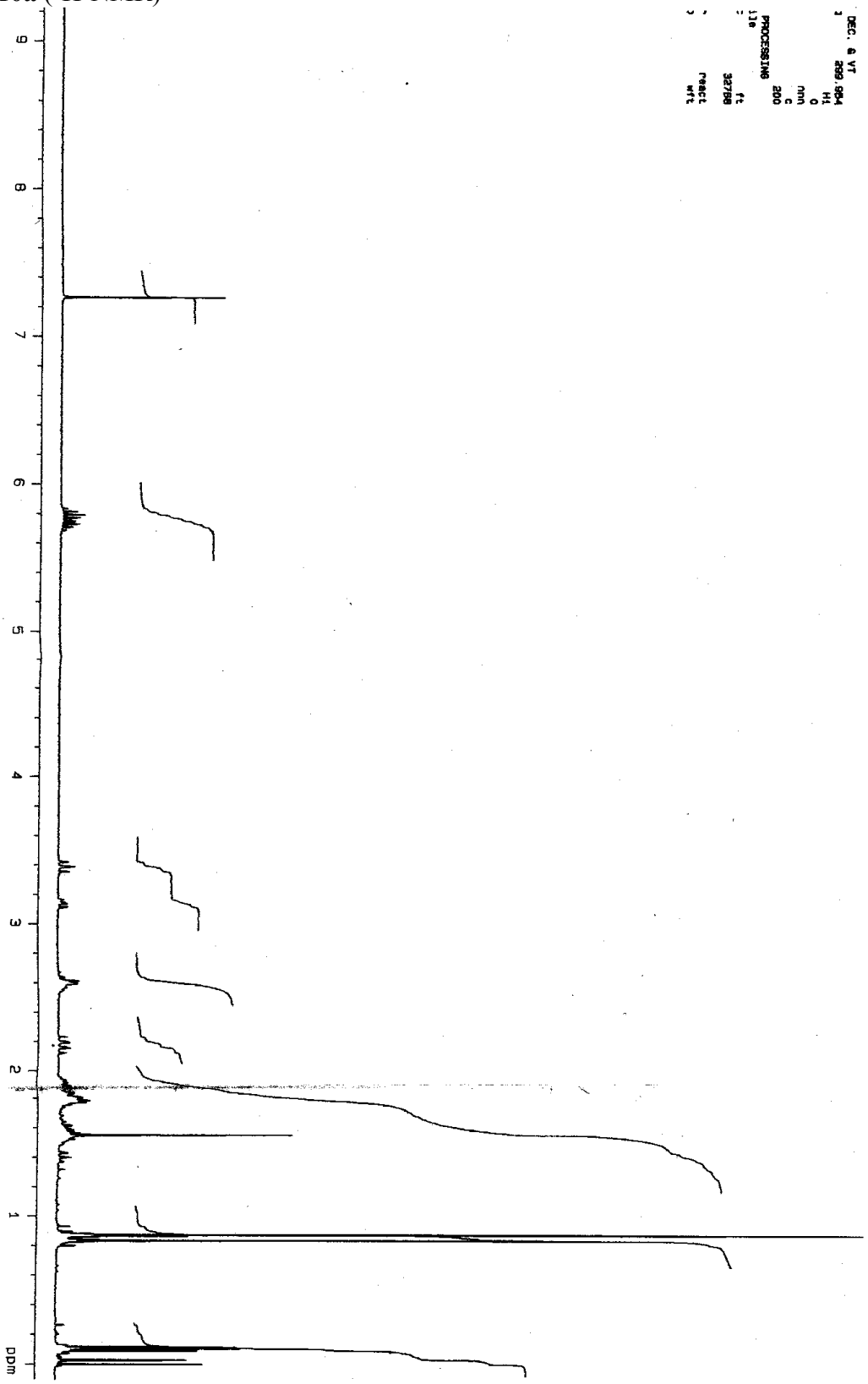
ppm

10a (^{1}H-NMR)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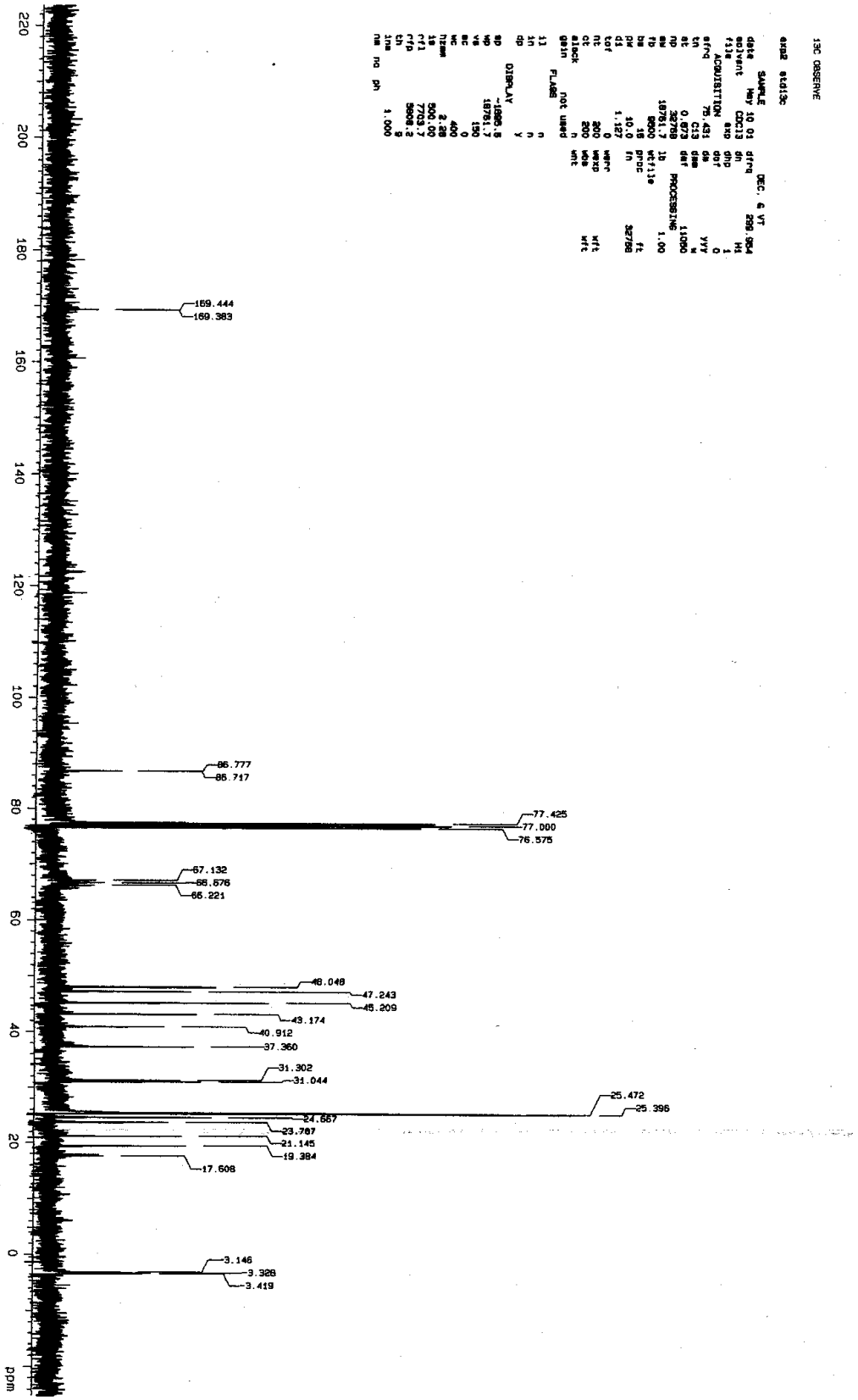
10a (^{13}C-NMR)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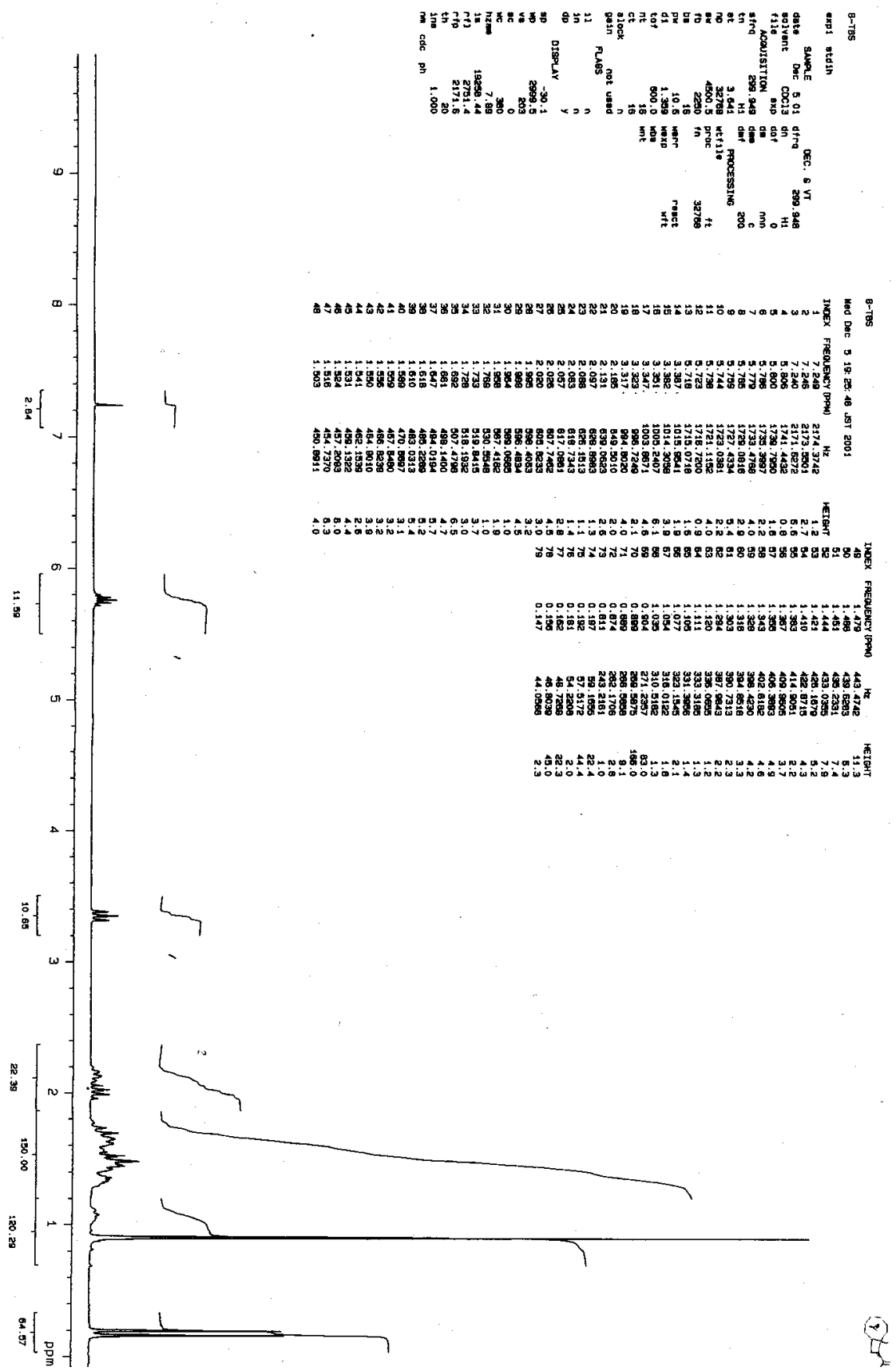
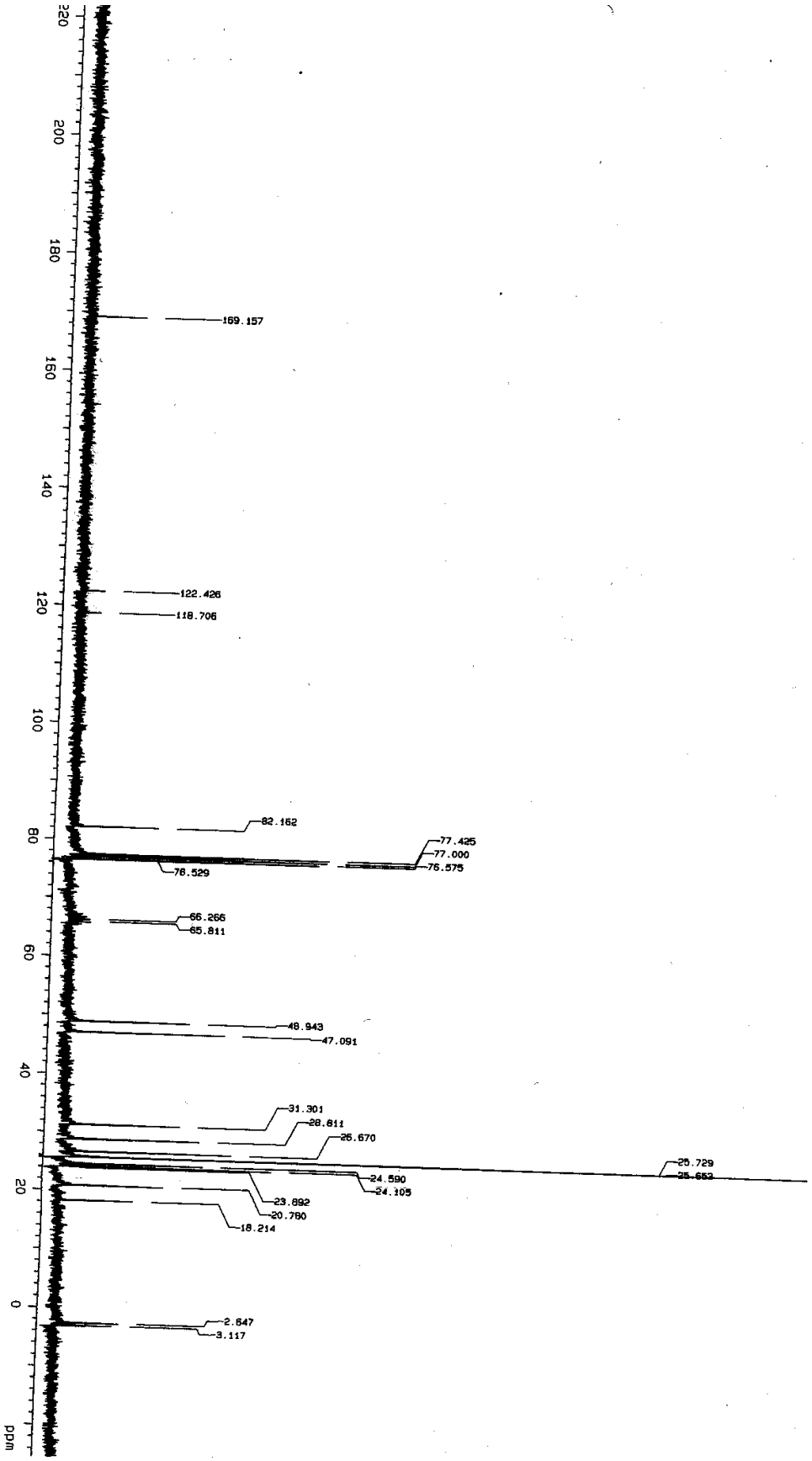
45.209
43.174
40.912
37.360
31.302
31.044
25.472
25.396
24.657
23.787
21.145
19.384
17.606
3.146
3.328
3.419
ppm

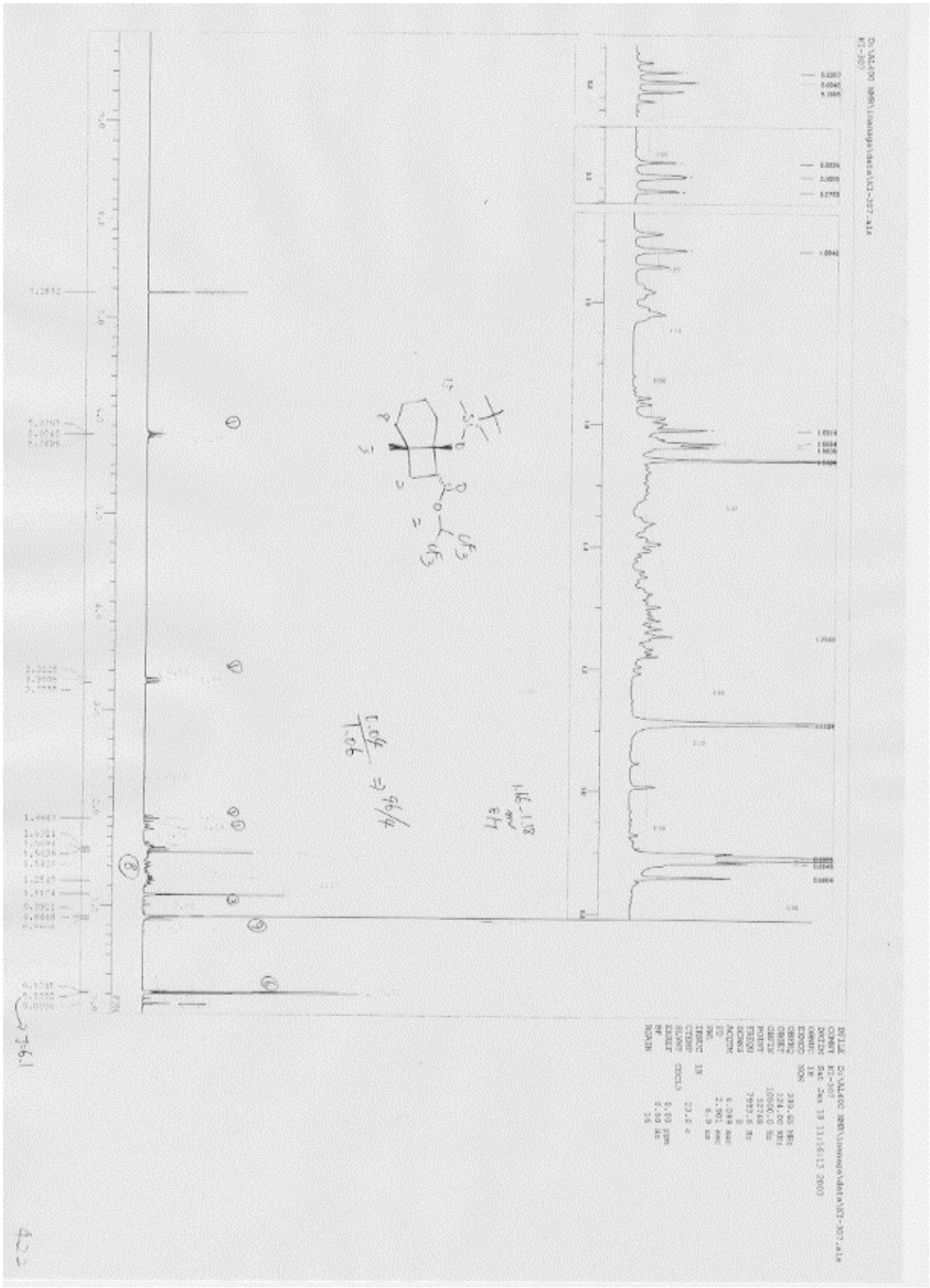
10c (^{1}H-NMR)



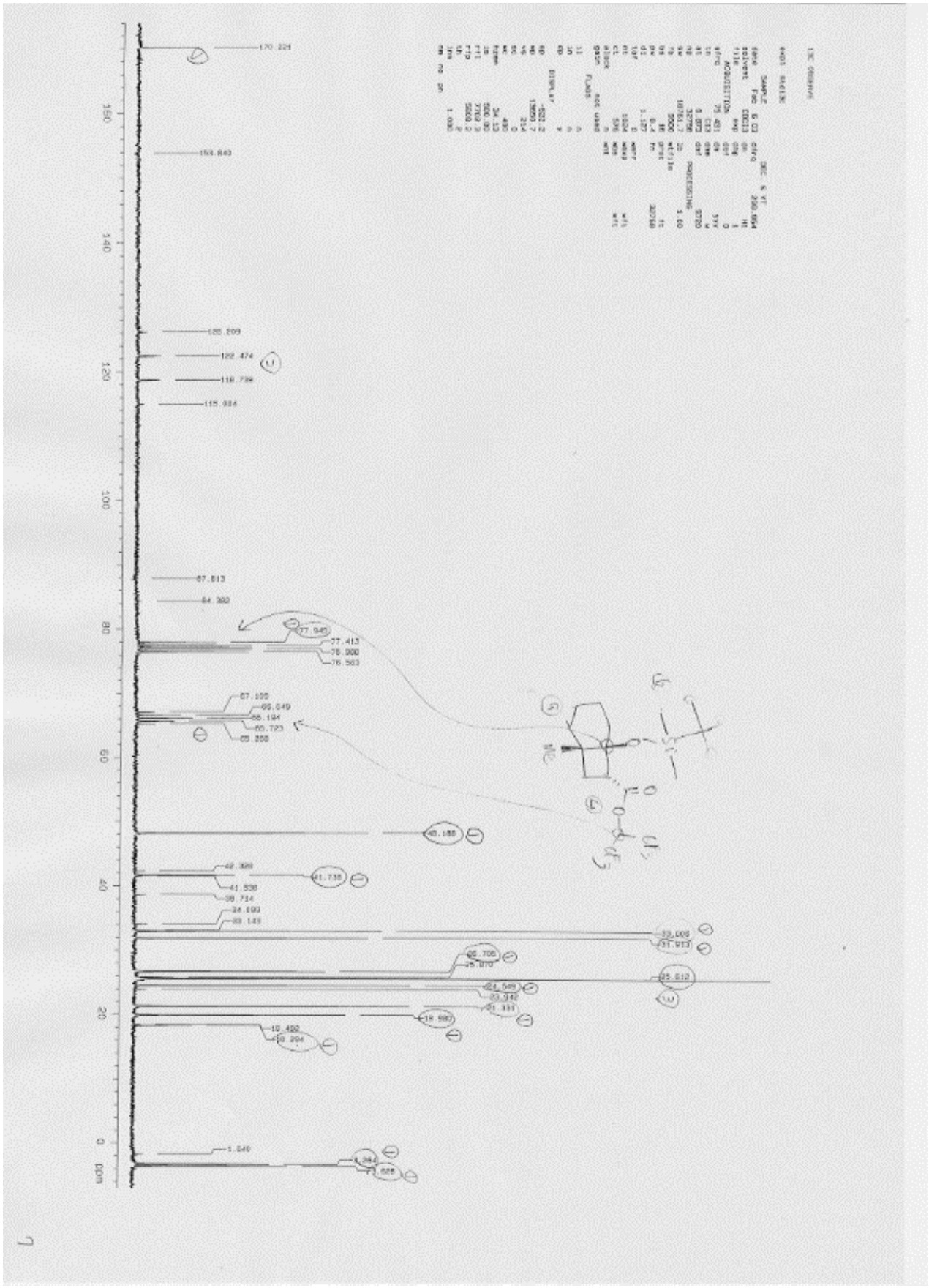
10c (^{13}C-NMR)


220
200
180
160
140
120
100
80
60
40
20
0
ppm
169.157
122.426
118.706
82.162
77.425
77.000
76.575
76.529
66.266
65.811
48.943
47.091
31.301
28.811
26.670
25.729
25.653
24.590
24.105
23.892
20.780
18.214
2.647
3.117

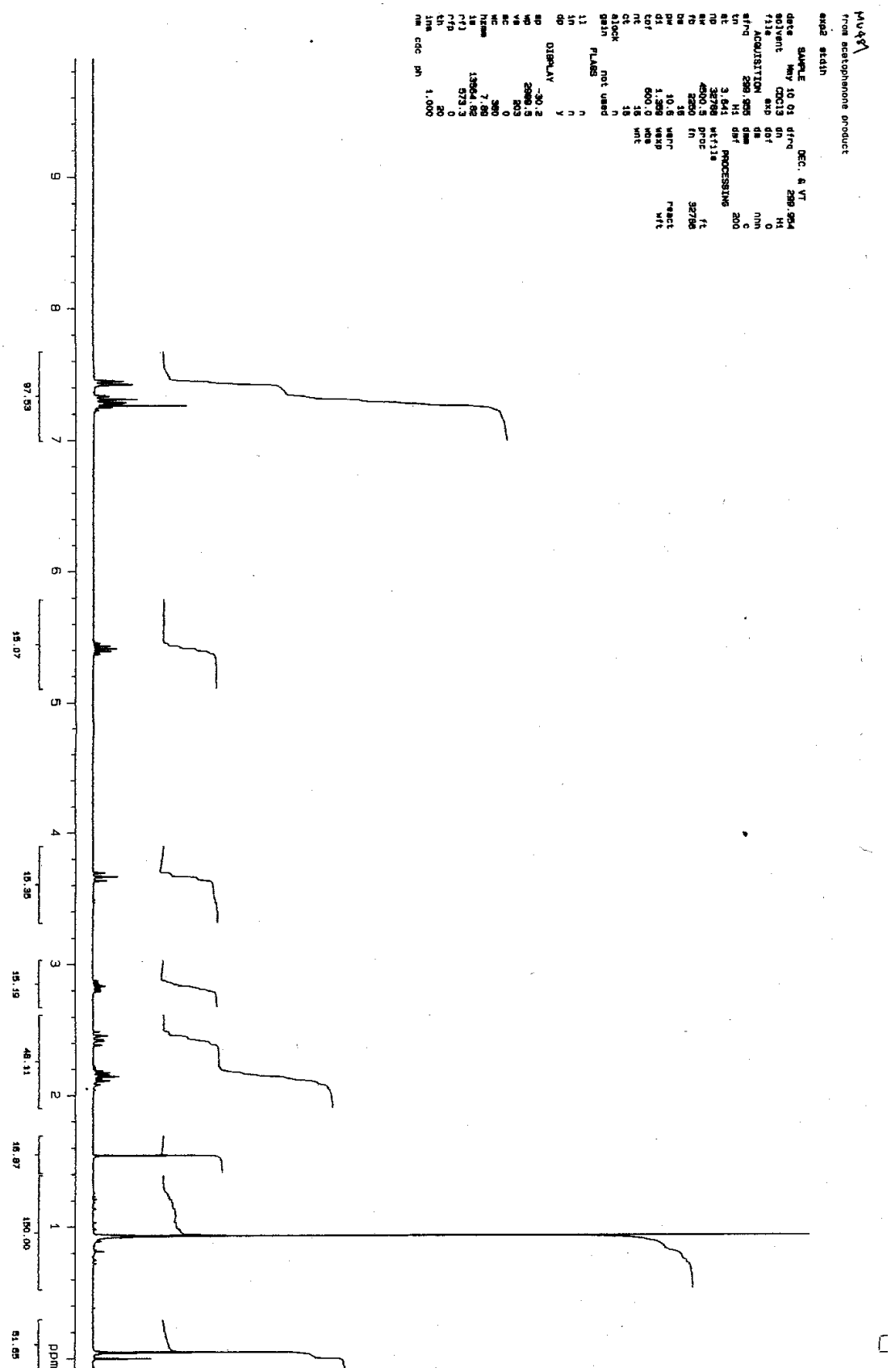
10d' (^{1}H-NMR)



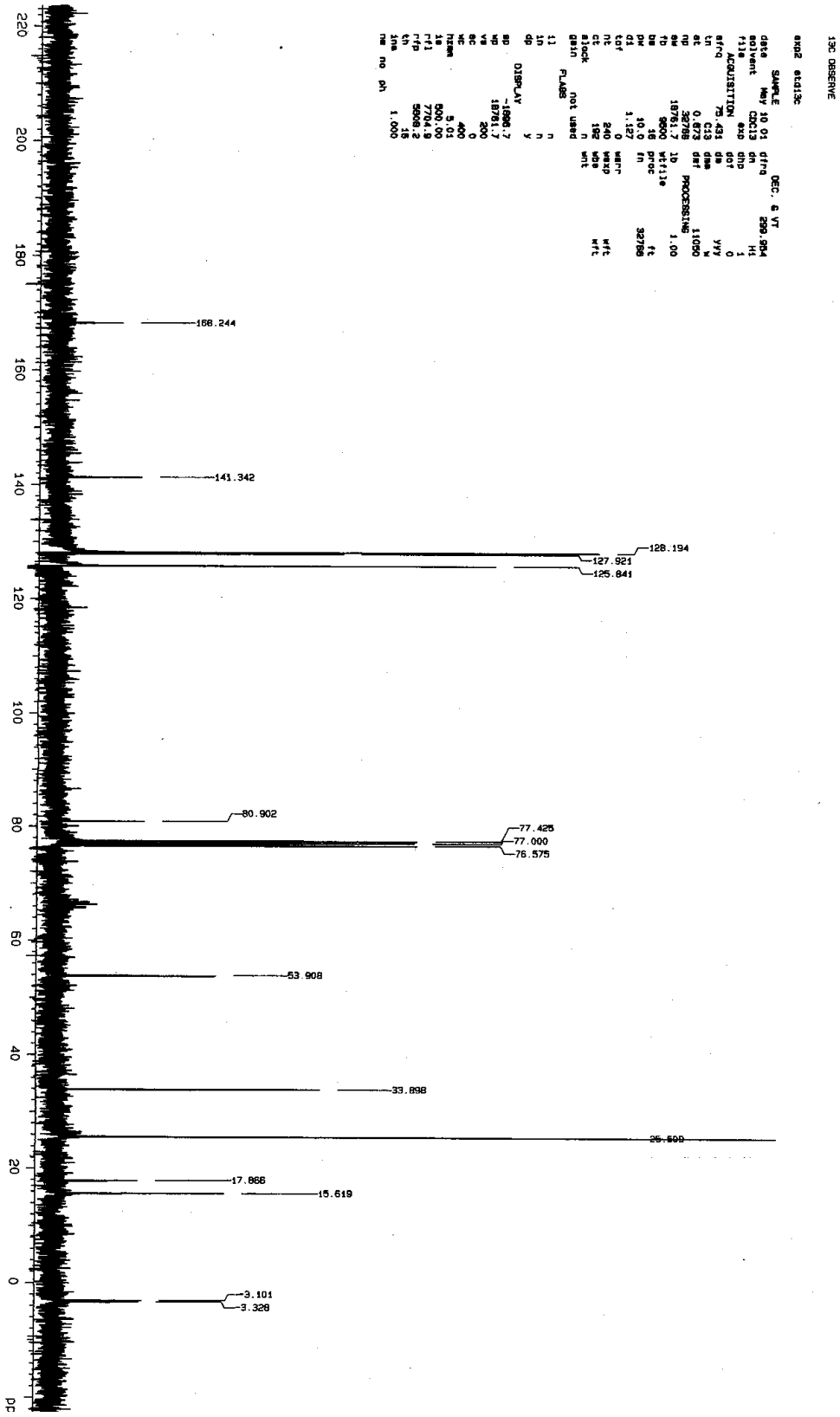
10d' (^{13}C-NMR)



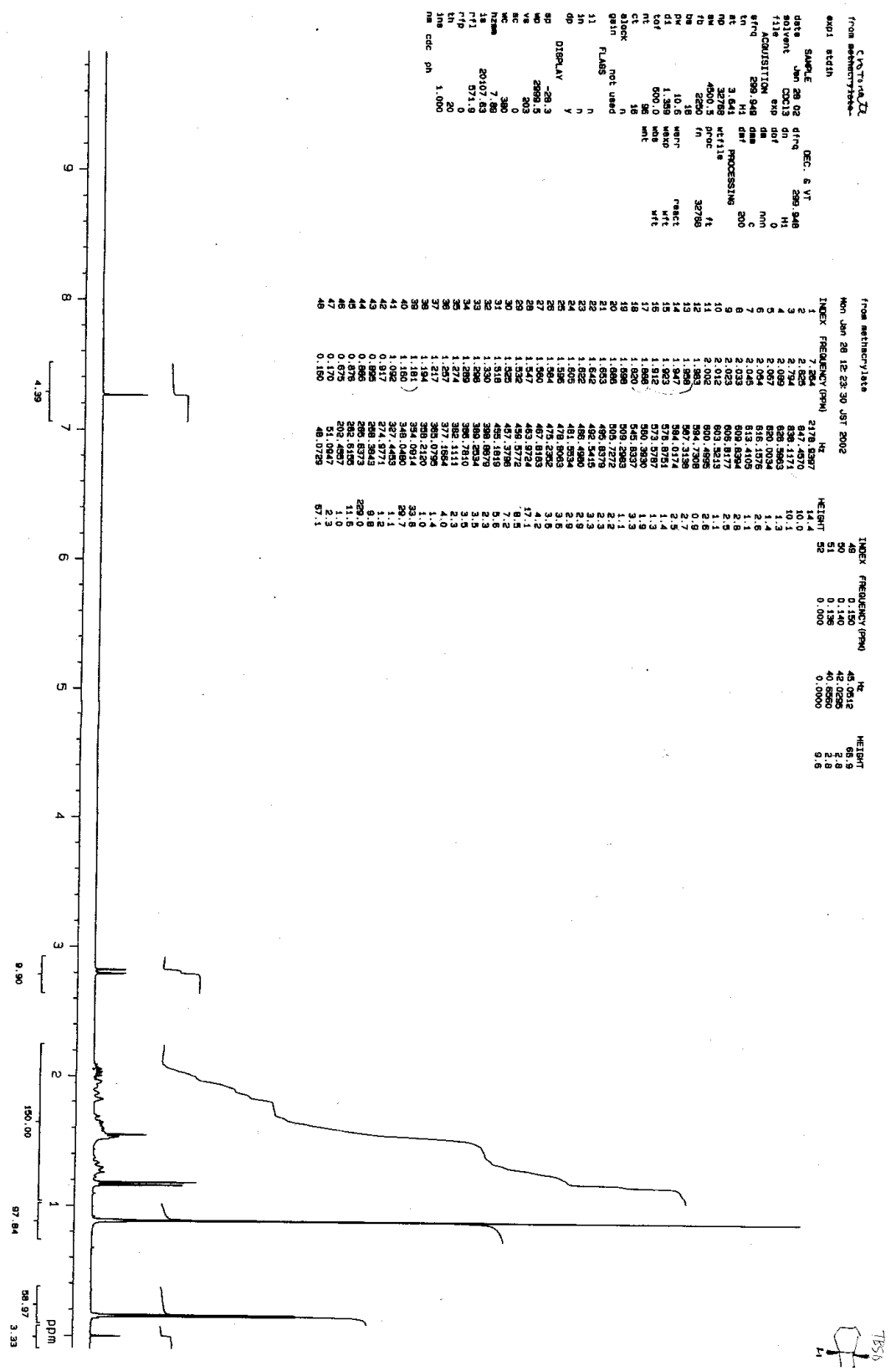
10e (^{1}H-NMR)


MU489
from acetophenone product
exp2 stdsh
SAMPLE
date May 10 01
solvent CDCl3
file ACQUISITION
DEC. & VT
PROCESSING
ppm
97.53
15.07
15.35
15.19
48.11
16.87
150.00
51.65

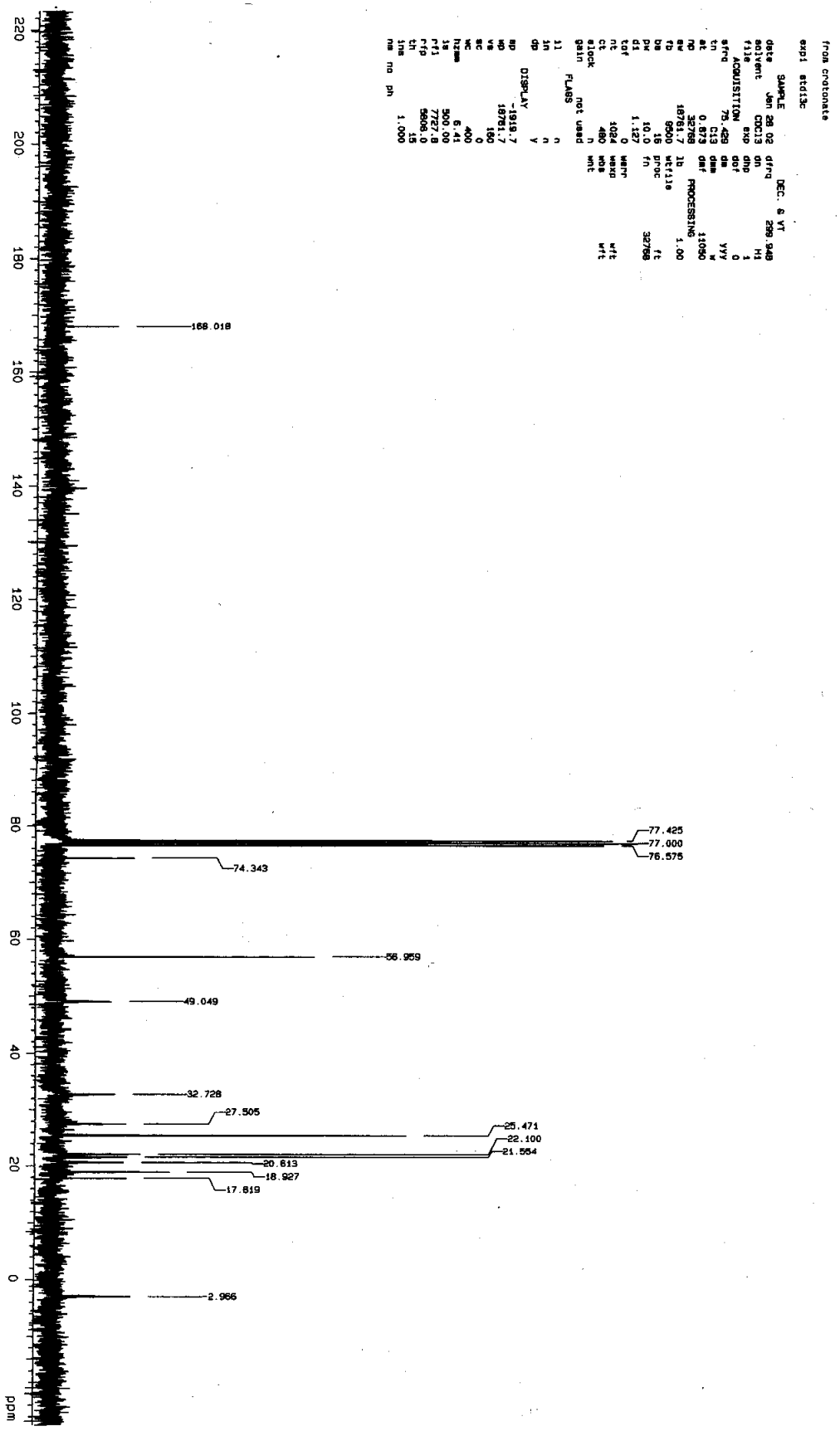
10e (^{13}C-NMR)


168.244
141.342
128.194
127.921
125.841
80.902
77.425
77.000
76.575
53.908
33.898
25.509
17.866
15.619
3.101
3.328

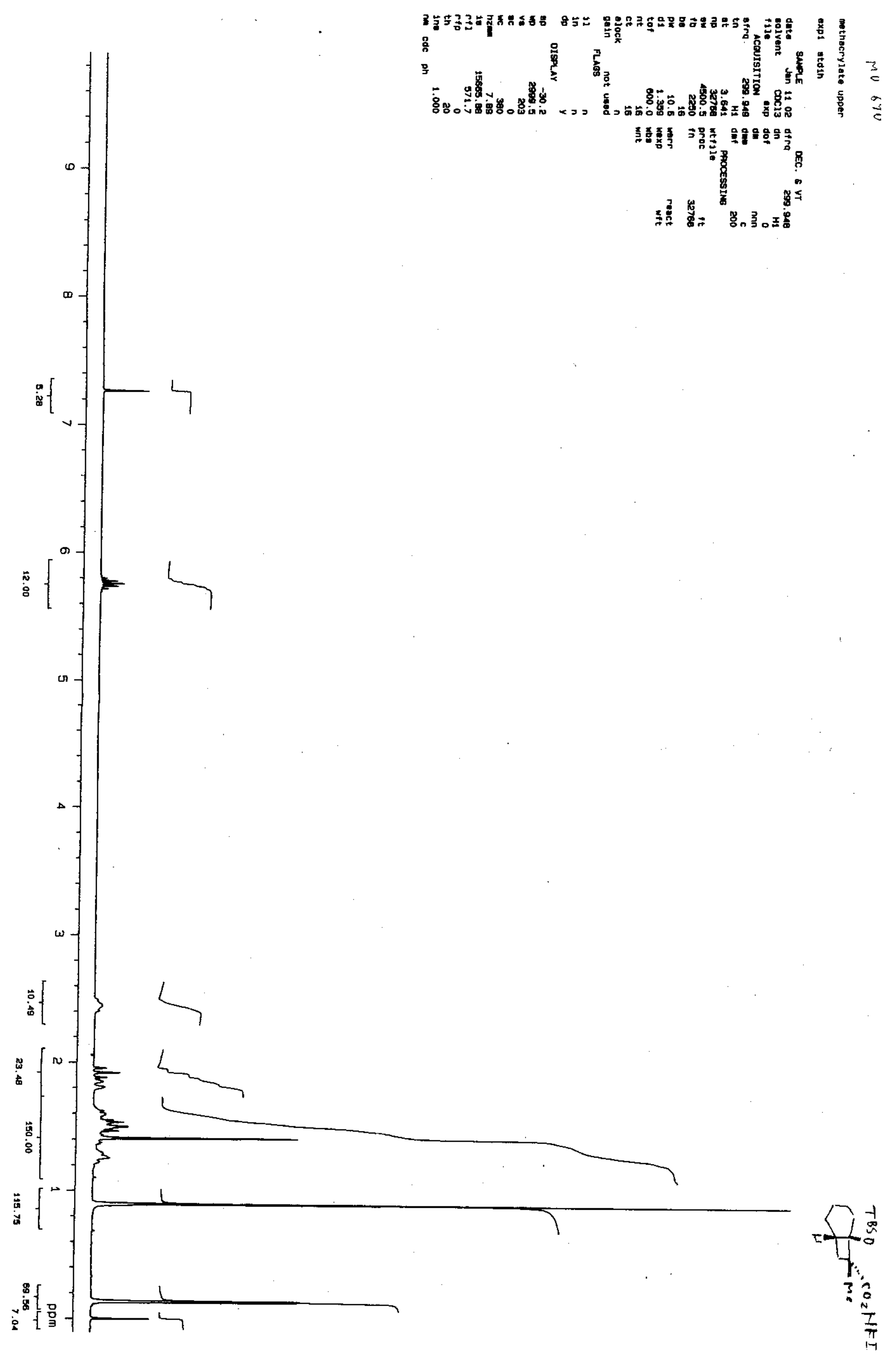
10h (^{1}H-NMR)



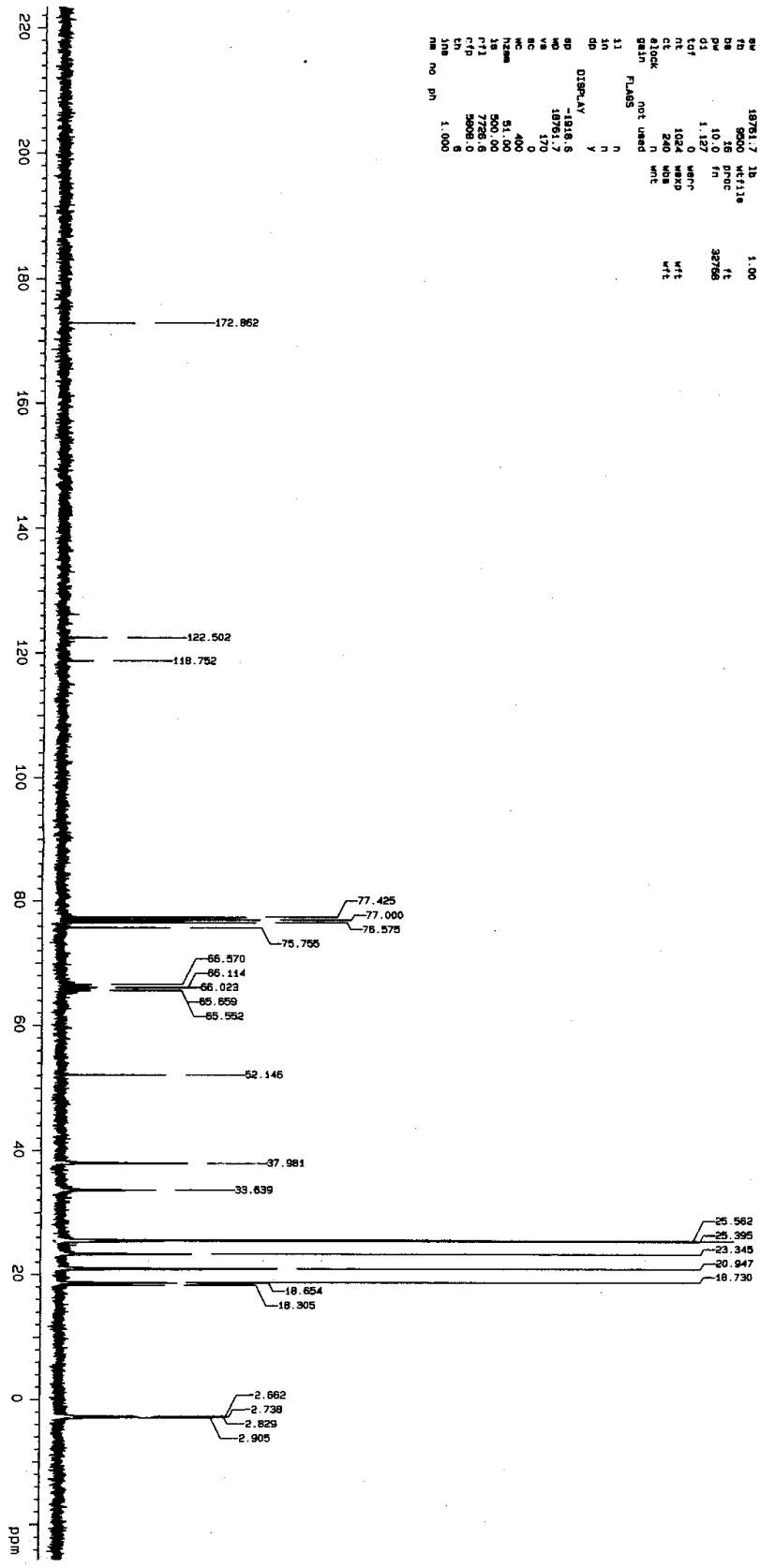
10h (^{13}C-NMR)


168.018
77.425
77.000
76.575
74.343
58.959
49.049
32.728
27.505
25.471
22.100
21.554
20.613
18.927
17.819
2.966
ppm

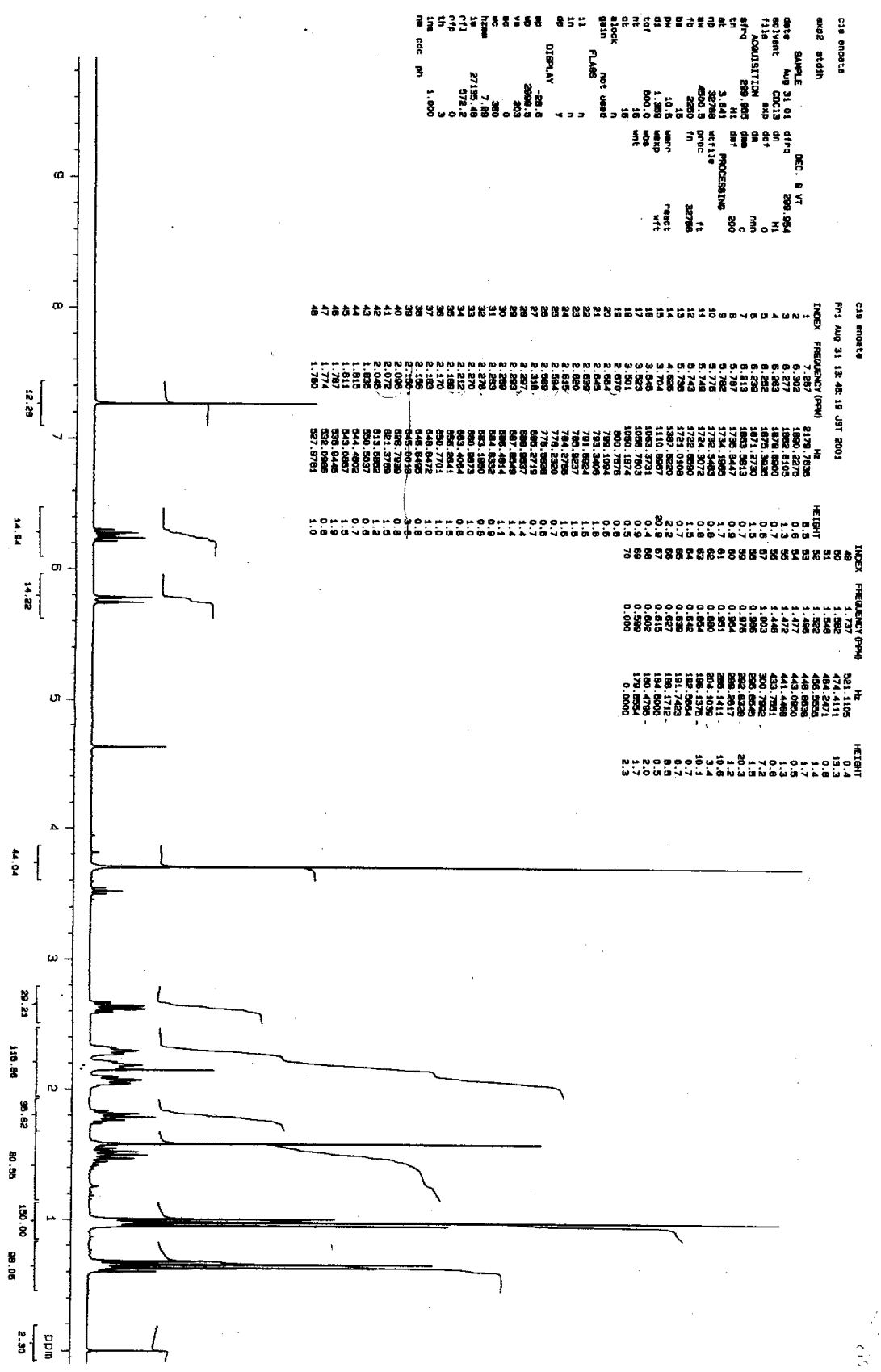
10i ([1]H-NMR)



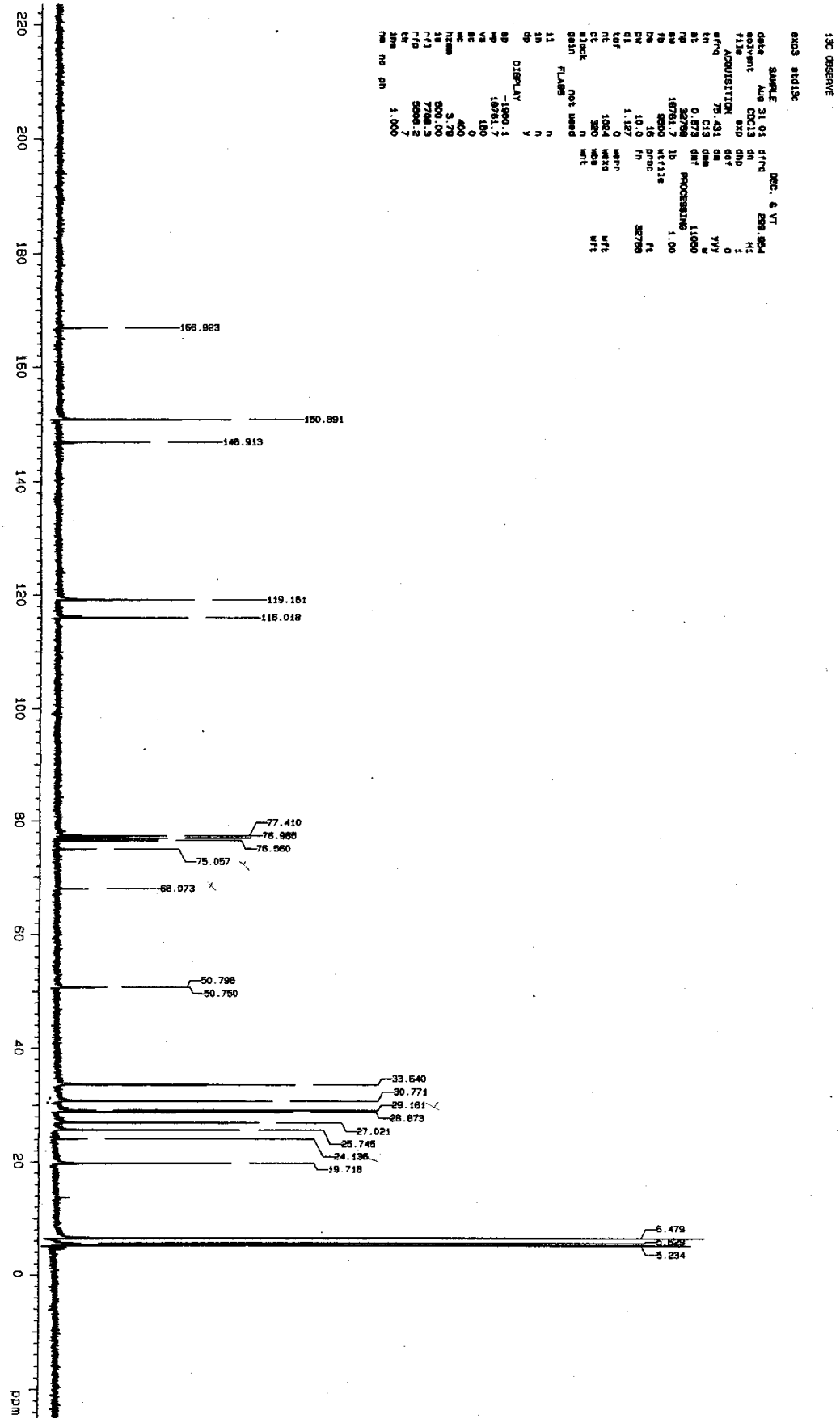
10i (^{13}C-NMR)


172.862
122.502
118.752
77.425
77.000
76.575
75.755
66.570
66.114
66.023
65.659
65.552
52.146
37.981
33.639
25.562
25.395
23.345
20.947
18.730
18.654
18.305
2.662
2.738
2.829
2.905
ppm

(*Z*)-**11** (^{1}H-NMR)



(*Z*)-**11** (^{13}C-NMR)


156.923
150.891
146.913
119.151
116.018
77.410
76.966
76.560
75.057
68.073
50.798
50.750
33.540
30.771
29.161
28.673
27.021
25.745
24.136
19.718
6.479
5.234
ppm