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Enantioselective Syntheses of ^{13}C-Labeled 2*R*- and 2*S*-Phytochromobilin Dimethyl Ester

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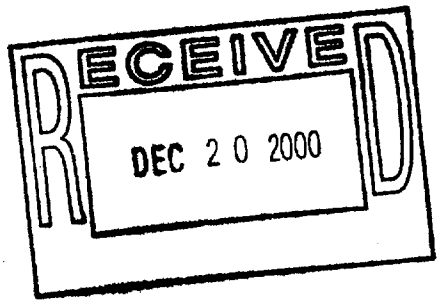
SUPPORTING INFORMATION

Experimental procedures and spectral data for all new compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.



Experimental Section

All reactions were carried out in oven-dried glassware under an inert atmosphere of nitrogen or argon. Air- and moisture-sensitive compounds were introduced *via* syringe or cannula and weighed in a dry-box. Reactions involving light sensitive compounds were carried out wrapped in foil. Melting points are uncorrected and were measured on a Fisher-Jones melting point apparatus. ^{1}H NMR spectra were recorded at 500 MHz and are expressed as ppm downfield from tetramethylsilane as an internal standard.

***Z*3-[5-(3*E*-Ethylidene-4*R*-methyl-5-oxo-pyrrolidin-2-ylidenemethyl)-2-formyl-4-methyl-1*H*-pyrrol-3-yl]-propionic acid methylester (10).** A solution of 534 mg (1.22 mmol, 1.00 eq) of lactone **14** in 10 ml of freshly distilled THF was fitted with a dry ice/acetone condenser, cooled to -78 °C under argon, and treated dropwise with 10 mL of dry liquid NH_3. After addition was complete, the orange reaction solution was maintained at reflux (-33 °C) for 1.5 h, and then allowed to warm slowly to rt to evaporate excess NH_3. The remaining solution was concentrated to dryness under an argon stream and without purification was disolved in 20 mL of $CHCl_3$, treated with 44.3 mg (100 µL, 1.22 mmol, 1.00 eq) of 12 N HCl and stirred vigorously at rt under argon for 24 hr. The reaction mixture was then partitioned between CH_2Cl_2 and ice cold NaH_2PO_4/Na_2HPO_4 buffer (pH 7) and the aqueous layer was extracted with 3 x 5 mL of CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4), filtered, concentrated under reduced pressure and chromatographed (silica gel; 30-60% EtOAc/pet ether) to afford 383 mg (95 %) of **10**. Recrystallization from EtOAc/pet ether afforded **10** as yellow-green needles, mp 185-86 °C; $[\alpha]^{28}_D$ - 6.47° (*c* =27.1, $CHCl_3$); R_f 0.50 (silica gel, 50% EtOAc/pet ether); UV-vis (MeOH) λ_{max}nm (log ε): 262 (4.05), 384 (4.40); IR (film) 3320, 1720, 1610, 1290 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$) δ 1.42 (d, *J* = 7.5 Hz, 3H), 1.88 (d, *J* = 6.5 Hz, 3H), 2.07 (s, 3H), 2.59 (t, *J* = 8.0 Hz, 2H), 3.06 (t, *J* = 7.5 Hz, 2H), 3.24 (q, *J* = 7.5 Hz, 1H), 3.67 (s, 1H), 5.76 (s, 1H), 6.26 (dq, *J* = 7.5 Hz, *J* = 2.0 Hz, 1H), 9.55 (s, 1H); 125 MHz NMR ($CDCl_3$) δ 9.21, 14.87, 16.38, 19.49, 35.82, 38.36, 51.90, 85.37, 120.47, 129.56, 135.88, 136.58, 136.67, 137.25, 172.97, 175.62, 180.29; Anal. Calcd for $C_{18}H_{22}N_2O_4$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.33; H, 6.65; N, 8.39.

Pyrromethenone $^{13}C_{10}$-10. This material was prepared in 95% yield in identical fashion as for pyrromethenone **10** above, employing 76 mg (0.17 mmol, 1.0 eq) of lactone $^{13}C_{10}$-**14**, and 3 mL of condensed NH_3 in 3 mL of THF for 1.5 hr, then treated with 6.3 mg (14 µL, 0.17 mmol, 1.0 eq) of 12N HCl in 7 mL of $CHCl_3$ for 24 hr. Chromatography afforded 54 mg (95%) of $^{13}C_{10}$-**10** as a yellow-green solid, mp 184-85 °C; R_f 0.50 (silica gel, 50% EtOAc/pet ether); UV-vis (MeOH) λ_{max}nm (log ε): 260 (4.02), 380 (4.45); IR (film) 3320, 1730, 1570, 1440 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$) δ 1.42 (d, *J* = 7.7 Hz, 3H), 1.88 (d, *J* = 7.3 Hz, 3H), 2.07 (s, 3H), 2.59 (t, *J* = 7.5 Hz, 2H), 3.06 (t, *J* = 7.5 Hz,.2H), 3.24 (q, *J* = 7.7 Hz, 1H), 3.67 (s, 3H), 5.76 (s, 1H), 6.28 (dq, *J* = 7.3 Hz, *J* = 2.0 Hz, 1H), 9.51 (d, *J* = 174.5 Hz, 1H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 9.22, 14.88, 16.38, 19.50, 35.79, 38.33, 51.91, 85.31, 120.65, 121.16, 129.18, 129.78, 136.29, 136.54, 136.64, 137.51, 172.95, 175.04, 180.26.

Pyrromethenone *ent*-10. This material was prepared in 93% yield in identical fashion as for pyrromethenone **10** above, employing 244 mg (0.555 mmol, 1.00 eq) of lactone *ent*-**14** and 5 mL of condensed NH_3 in 5 mL of THF for 1.5 hr, then treated with 20 mg (46 µL, 0.56 mmol, 1.0 eq) of 12 N HCl for 24 hr. Chromatography afforded 171 mg (93%) of *ent*-**10** as yellow/green solid, mp 185-186 °C; $[\alpha]^{28}_D$ + 6.49° (*c* = 17.9, $CHCl_3$). IR and ^{1}H NMR are identical to those of pyrromethenone **10**.

Pyrromethenone *ent*-$^{13}C_{10}$-10. This material was prepared in 91% yield in identical fashion as *ent*-**10** above, employing 102 mg (0.231 mmol, 1.00 eq) of lactone *ent*-$^{13}C_{10}$ **14** and 3 mL condensed NH_3 in 3 mL of THF for 1.5 hr, then treated 8.5 mg (19 µL, 0.23 mmol, 1.0 eq) of 12N HCl for 32 hr.

Chromatography afforded 70 mg (91%) of *ent*-$^{13}C_{10}$-**10** as yellow green solid, mp 184-85 °C; having IR and ^{1}H NMR that are identical to those of pyrromethenone $^{13}C_{10}$-**10.**

3-[4-Methyl-5-(3-methyl-5-oxo-4-vinyl-1,5-dihydro-pyrrol-2-ylidenemethyl)-1*H*-pyrrol-3-yl]-propionic acid methylester (11). A solution of 32 mg (0.065 mmol, 1.0 eq) of selanylpyrromethenone **20** in 5.0 mL of dry THF was cooled to –78 °C and treated dropwise with a 0 °C solution of 11 mg (0.065 mmol, 1.0 eq) of *m*-CPBA in 0.5 mL of dry THF. The resulting solution was stirred at –78 C for 45 min, diluted with 50 mL of CH_2Cl_2 and treated with K_2HPO_4/KOH buffer pH 12. The frozen mixture was slowly warmed to 0°C and stirred for additional 2 hr, then partitioned between CH_2Cl_2 and ice cold pH 12 K_2HPO_4/KOH buffer. The organic layer was washed with H_2O, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (silca gel, 30:70 EtOAc/pet ether) to afford 19 mg (99%) of yellow solid, mp 152-53 °C; R_f 0.40 (30% EtOAc/pet ether); 500 MHz ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3H), 2.23 (s, 3H), 2.58 (t, *J* = 7.3, 2H), 2.79 (t, *J* = 7.3 Hz, 2H), 3.70 (s, 3H), 5.48 (dd, *J* = 11.6 Hz, *J* = 2.4 Hz, 1H), 6.26 (s, 1H), 6.33 (dd, *J* = 17.46 Hz, *J* = 2.2 Hz, 1H), 6.62 (dd, *J* = 17.7 Hz, *J* = 11.5 Hz, 1H), 6.83 (d, *J* = 2.8 Hz), 10.31 (bs, 1NH), 11.00 (bs, 1NH); Anal. Calcd for $C_{17}H_{20}N_2O_3$: C, 67.98; H, 6.71; N, 9.33. Found: C, 67.92; H,6.67; N, 9.36.

3-(2-Formyl-5-iodo-4-methyl-1*H*-pyrrol-3-yl)-propionic acid methylester (^{13}C-13).[1] A solution of 266 mg (1.05 mmol, 1.00 eq) of 5-^{13}C-Formyl-4-(2-methoxycarbonyl-ethyl)-3-methyl-1*H*-pyrrole-2-carboxylic acid[2] in 20 mL of MeOH was treated with a solution of 605 mg (7.20 mmol, 6.5 eq) of $NaHCO_3$ in 20 mL of H_2O, stirred at rt for 20 min to which was added dropwise a solution of 267 mg (1.05 mmol, 1.00 eq) of I_2 in 20 mL of MeOH. After addition was complete, the reaction mixture was stirred at rt for an additional 2.5 hr, treated with ice cold 1.0 M $Na_2S_2O_3$ and partitioned between CH_2Cl_2 and ice cold $NaHCO_3$. The aqueous phase was extracted with 2 x 25 mL CH_2Cl_2 and the combined organic extracts were dried (Na_2SO_4), filtered, concentrated under reduced pressure and chromatographed (silica gel, 10-30 % EtOAc/ pet ether) to afford 314 mg (89%) of ^{13}C- labeled iodopyrrole ^{13}C-**13**,[1] mp 92°C; R_f 0.45 (30% EtOAc/pet ether); 500 MHz ^{1}H NMR ($CDCl_3$) δ 2.01 (s, 3H), 2.57 (t, *J* = 7.6, 2H), 3.06 (t, *J* =7.6, 2H), 9.43 (d, *J* = 176.2, 1H), 9.50 (bs, 1H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 11.83, 19.75, 35.36, 52.10, 126.41, 132. 69, 133.43, 133.93, 172.83, 176.63.

3*R*-{5-[3*S*-(1-Benzyloxy-ethyl)-4*R*-methyl-5-oxo-dihydro-furan-2-ylidenemethyl]-2-formyl-4-methyl-1*H*-pyrrol-3-yl}-propionic acid methylester (14). A solution of 450 mg (1.40 mmol, 1.00 eq) of iodopyrrole **13**,[1] 380 mg (1.54 mmol, 1.10 eq) of alkyne acid **12**, 162 mg (0.140 mmol, 0.100 eq) of $Pd(PPh_3)_4$, and 319 mg (1.40 mmol, 1.00 eq) of $BnNEt_3Cl$ in 11.0 mL of dry CH_3CN and 1.95 mL (14.0 mmol, 10.0 eq) of Et_3N was degassed under argon for 10 min, and was then subjected to 5 freeze-thaw cycles and covered with Argon. The mixture was heated to reflux (oil bath: 58 °C) for 18 hours, cooled to rt and solvent was removed under reduced pressure. The resulting dark brown residue was partitioned between CH_2Cl_2 and H_2O, and the aqueous phase extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, 10-30% EtOAc/hexanes) to afford 534 mg (87%) of enelactone **14**[6] as a light yellow oil. R_f 0.50 (50% EtOAc/pet ether); UV-vis (MeOH) λ_{max}nm (log ε): 212 nm (4.15); 340 nm (4.10); IR (film) 3270, 1810, 1730, 1640 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$) δ 1.32 (d, *J* = 7.5 Hz, 3H), 1.38 (d, *J* = 6.0 Hz, 3H), 2.01 (s, 3H), 2.55 (t, *J* = 7.5 Hz, 2H), 3.00 (t, *J* = 7.5Hz, 1H), 3.59 (m, 1H), 3.68 (s, 3H), 4.64 (dd, *J* =103.5 Hz, *J* = 11.5 Hz, 2H), 6.38 (s, 1H), 7.30 (m, 4H), 9.46 (s, 1H), 10.80 (s, 1H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 8.82, 16.88, 18.04, 19.43, 35.63, 39.98, 51.90, 53.24, 71.79, 75.38, 101.59, 120.53, 128.31, 128.40, 128.81, 129.07, 130.61, 133.17, 136.44, 151.35, 173.11, 176.10, 176.92; HRMS (FAB) Calcd for ($C_{25}H_{29}NO_6$ + H)([M + H]$^+$): 440.2073; found 439.2073.

Enelactone $^{13}C_{10}$-14. This material was prepared in 84% yield in identical fashion as for enelactone **14** above, employing 150 mg (0.465 mmol, 1.00 eq) of ^{13}C-**13**,[1] 127 mg (0.516 mol, 1.10 eq) of alkyne acid **12**, 54 mg (0.047 mmol, 0.10 eq) of $Pd(PPh_3)_4$, and 106 mg (0.465 mmol, 1.00 eq) of $BnNEt_3Cl$ in 3.75 mL of dry CH_3CN and 0.650 mL (4.7 mmol, 10 eq) of Et_3N for 18 hr. Chromatography afforded 173 mg (84%) of lactone $^{13}C_{10}$-**14** as a light yellow oil. R_f 0.50 (50% EtOAc/Petroleum Ether); UV-vis (MeOH) λ_{max}nm (log ε): 208 nm (4.12); 338 nm (4.08); (film) 3300, 1820, 1720, 1650 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$): δ 1.35 (d, *J* = 7.5 Hz, 3H), 1.41 (d, *J* = 6.0 Hz, 3H), 2.03 (s, 3H), 2.58 (t, *J* = 8.0 Hz, 2H), 3.03 (t, *J* = 8.0 Hz, 2H), 3.62 (m, 1H), 3.70 (s, 3H), 4.67 (dd, *J* = 102.7 Hz, *J* = 12.1 Hz, 2H), 6.41 (s, 1H), 7.33 (m, 4H), 9.49 (d, *J* = 172.5 Hz, 1H), 10.84 (s, 1H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 8.76, 16.82, 17.90, 19.36, 35.55, 39.83, 51.81, 53.05, 71.69, 101.41, 120.44, 128.22, 128.31, 128.52, 29.25, 130.56, 133.11, 136.43, 151.36, 173.03, 176.06, 176.85.

Enelactone *ent*-14. This material was prepared in 88% yield in identical fashion as for enelactone **14** above, employing 450 mg (1.40 mmol, 1.0 eq) of iodopyrrole **13**,[1] 380 mg (1.54 mmol, 1.10 eq) of alkyne acid *ent*-**12**, 162 mg (0.140 mmol, 0.100 eq) of $Pd(PPh_3)_4$, and 319 mg (1.40 mmol, 1.00 eq) of $BnNEt_3Cl$ in 11.0 mL of dry CH_3CN and 2.0 mL (14 mmol, 10 eq) of Et_3N for 18 hours. Chromatography afforded 539 mg (88%) of lactone *ent*-**14** as a light yellow oil having IR and ^{1}H NMR identical to those of enelactone **14**.

Enelactone *ent*^{1}-$^{13}C_{10}$-14. This material was prepared in 84% yield in identical fashion as for enelactone *ent*-**14** above, employing 138 mg (0.428 mmol, 1.00 eq) of iodopyrrole ^{13}C-**13**, 127 mg (0.516 mmol, 1.20 eq) of alkyne acid **12**, 50 mg (0.043 mmol, 0.10 eq) of $Pd(PPh_3)_4$, and 98 mg (0.43 mmol, 1.0 eq) of $BnNEt_3Cl$ in 3.5 mL of dry CH_3CN and 0.60 mL (4.3 mmol, 10 eq) of Et_3N for 18 hr. Chromatography afforded 159 mg (84%) of lactone $^{13}C_{10}$-**14**. 500 MHz ^{1}H NMR ($CDCl_3$) δ 1.33 (d, *J* = 7.5 Hz, 3H), 1.40 (d, *J* = 6.0 Hz, 3H), 2.01 (s, 3H), 2.57 (t, *J* = 8.0 Hz, 2H), 3.02 (t, *J* = 8.0 Hz, 2H), 3.60 (m, 1H), 3.68 (s, 3H), 4.67 (dd, *J* = 103 Hz, *J* = 12.0 Hz, 2H), 6.38 (s, 1H), 7.31 (m, 4H), 9.47 (d, *J* = 172.7 Hz, 1H), 10.83 (s, 1H); IR and^{13}C NMR identical to those of enelactone $^{13}C_{10}$-**14.**

Pyrroloaldehyde ^{13}C-17.[4] 0.300 mL (290 mg, 3.88 mmol, 2.00 eq) of $Me_2N^{13}CHO$ was cooled to 0°C and treated dropwise with 0.360 mL (590 mg, 3.86 mmol, 2.00 eq) of $POCl_3$ for 30 min. The solution was diluted with 4 mL of CH_2Cl_2, warmed to rt and treated dropwise with a solution of 520 mg (1.95 mmol, 1.00 eq) of 3-(2-Methoxycarbonyl-ethyl)-4-methyl-1*H*-pyrrole-2-carboxylic acid *tert*-butyl ester[4] in 5 mL of CH_2Cl_2. The reaction solution was heated to reflux for 1 hr, then cooled to rt and diluted with 20 mL of CH_2Cl_2. After cooling, the reaction was treated with 15 mL of pH 8 NaOH/H_2O solution, stirred at rt for 2 hr, then partitioned between $NaHCO_3/H_2O$ and aqueous phase extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4), filtered, concentrated under reduced pressure and chromatographed (silica gel; 10-30 % EtOAc/pet ether) to yield 548 mg (95%) of pyrroloaldehyde ^{13}C-**17**[4]. mp 77-8°C; R_f 0.40 (30% EtOAc/pet ether); (500 MHz ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 9H), 2.33 (s, 3H), 2.56 (t, *J* = 7.8 Hz, 2H), 3.02 (t, *J* = 7.8 Hz, 2H), 3.68 (s, 3H), 9.42 (bs, 1H), 9.76 (d, *J* = 176 Hz, 1H).

Aldol adducts 19a-d.[5] A solution of 1.63g (5.52 mmol, 1.00 eq) of pyrroloaldehyde **17**[4] in 40 mL of dry CH_2Cl_2 was cooled to -78 °C under Ar, and was treated dropwise with vigorous stirring with 1.05g (607μL, 5.52 mmol, 1.00 eq) of $TiCl_4$. The resulting orange/red suspension was stirred for an additional 15 min at -78 °C to ensure thorough mixing, and was then treated portionwise with a solution of 2.93g (5.54 mmol, 1.00 eq) of silyloxypyrrole **18**[5] in 30 mL of dry CH_2Cl_2. The resulting dark red solution was stirred for an additional 10 min and was then quenched with sat'd $NaHCO_3$ at -78 °C, warmed to 0 °C, and extracted with CH_2Cl_2. The combined organic extracts were washed with H_2O and brine, dried (Na_2SO_4), concentrated under reduced pressure, and chromatographed (silica gel, 10% EtOAc/pet ether) to

afford 1.81 g **19a**, 170 mg **19b**, 1.93 g **19c** and 160 mg **19d** (combined yield 4.07g, 97%), relative stereochemistry not assigned.

Aldol aducts ^{13}C-19a-d. This material was prepared in 97% overal yield in identical fashion as for aldol adducts **19a-19d**, employing 140 mg (0.47 mmol, 1.0 eq) of formylpyrrole^{13}C-**17**, 250 mg (0.47 mmol, 1.0 eq) of siloxypyrrole **18**, 90 mg (52 μL, 0.47 mmol, 1.0 eq) of $TiCl_4$ in 5 mL of dry CH_2Cl_2 for 10 min. Chromatography afforded 104 mg **^{13}C-19a**, 36 mg mixture **^{13}C-19a** and **^{13}C-19b**, 132 mg **^{13}C-19c**, and 10 mg **^{13}C-19d** (combined yield 282 mg, 97%), relative stereochemistry not assigned.

Aldol aduct 19a. Recrystallization from EtOAc/pet ether afforded **19a** as a white solid, mp 106-7 °C; R_f 0.90 (silica gel, 30% EtOAc/pet ether); UV-vis (MeOH) λ_{max}nm (log ε): 208 (4.24), 226 (4.23); 280 (4.13); IR (film): 3467, 1777, 1739, 1705 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 3H), 0.19 (s, 3H), 0.93 (s, 9H), 1.50 (s, 9H), 1.57 (s, 9H), 1.83 (s, 3H), 2.12 (s, 3H), 2.28 (m, 1H), 2.33-2.51 (m, 2H), 2.40 (t, *J* = 8.8 Hz, 2H), 2.65 (m, 1H), 2.82 (m, 1H), 2.96 (m, 1H), 3.65 (s, 3H), 4.53 (d, *J* = 3.9 Hz, 1H), 5.60 (d, *J* = 3.9 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz), 8.49 (s, 1H); 125 MHz ^{13}C NMR ($CDCl_3$) δ -5.19, -4.88, 8.76, 15.21, 18.22, 20.81, 24.17, 24.59, 25.93, 28.35, 28.58, 35.25, 51.67, 67.23, 68.30, 81.10, 83.26, 117.80, 119.46, 128.21, 128.49, 129.19, 129.38, 132.93, 133.49, 133.55, 150.06, 153.45, 160.90, 168.10, 173.67; Anal. Calcd. for $C_{39}H_{57}ClN_2O_8SeSi$: C, 56.82; H, 6.97; N, 3.39. Found: C, 57.07; H, 6.84; N 3.40; relative stereochemistry not assigned.

Aldol aduct $^{13}C_{15}$-19a. Recrystallization from EtOAc/pet ether afforded **$^{13}C_{15}$-19a** as a white solid, mp 106-7 °C; R_f 0.90 (silica gel, 30% EtOAc/pet ether); 500 MHz ^{1}H NMR ($CDCl_3$) δ 0.060 (s, 3H), 0.24 (s, 3H), 0.98 (s, 9H), 1.56 (s, 9H), 1.63 (s, 9H), 1.88 (s 3H), 2.17 (s, 3H), 2.33 (m, 1H), 2.46 (m, 4H), 2.70 (m, 1H), 2.87 (m, 1H), 3.01 (m, 1H), 3.71 (s, 3H), 4.58 (dd, *J* = 6.0 Hz, *J* =2.0 Hz, 1H), 5.65 (dd, *J* =148 Hz, *J* = 4.0 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 8.54 (s, 1H); 125 MHz ^{13}C NMR ($CDCl_3$) δ -5.14, -4.83, 8.82, 15.27, 18.27, 20.86, 24.23, 24.63, 25.98, 28.40, 28.63, 35.31, 51.74, 67.00, 68.34 (m, enriched *meso*-C), 81.17, 83.34, 117.84 (d, *J* = 21 Hz), 119.52, 128.25, 128.53, 129.01, 129.44, 132.98, 133.53, 133.60, 150.12, 153.54, 160.98, 168.18, 173.76; Anal. Calcd. for $C_{38}{}^{13}CH_{57}ClN_2O_8SeSi$: C, 56.87; H, 6.96; N, 3.39. Found: C, 57.11; H, 6.89; N, 3.28; relative stereochemistry not assigned.

Aldol aduct 19b. Column chromatography afforded **19b** as a clear gel: R_f 0.80 (silica gel 30% EtOAc/pet ether); UV-vis (MeOH) λ_{max}nm (log ε): 208 (4.24), 224 (4.23); 272 (4.13); IR (film): 3480, 3470, 1780, 1740, 1710, 1680 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$) δ -0.02 (s, 3H), 0.03 (s, 3H), 0.87 (s, 9H), 1.31 (s, 3H), 1.56 (s, 9H), 1.61 (s, 9H), 2.14 (s, 3H), 2.52-2.65 (m, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.93-3.03 (m, 2H), 3.06 (m, 1H), 3.13 (m, 1H), 3.66 (s, 3h), 4.54 (br s, 1H), 5.59 (d, *J* = 1.9 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 8.77 (s, 1H); 125 MHz ^{13}C NMR ($CDCl_3$) δ -5.08, -5.00, 9.50, 13.32, 18.25, 20.75, 24.85, 25.42, 25.99, 28.53, 28.69, 35.22, 51.68, 66.99 (2), 80.93, 83.41, 114.79, 118.20, 128.39, 129.41, 130.36, 130.41, 133.03, 133.44, 133.47, 150.19, 153.12, 160.54, 169.22, 173.82; Anal. Calcd. for $C_{39}H_{57}ClN_2O_8SeSi$: C, 56.82; H, 6.97; N, 3.39. Found: C, 57.08; H, 6.82; N, 3.28; relative stereochemistry not assigned.

Aldol aduct 19c. Recrystallization from EtOAc/pet ether afforded **19c** as fine white needles, mp 150-51 °C; R_f 0.40 (silica gel, 30% EtOAc/pet ether); UV-vis (MeOH) λ_{max}nm (log ε): 228 (4.27); 278 (4.17); IR (film): 3418, 1757, 1728, 1680 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 9H), 1.56 (s, 9H), 1.84 (s, 3H), 2.02 (s, 3H), 2.31 (m, 1H), 2.40 (t, *J* = 8.3 Hz, 2H), 2.48 (m, 2H), 2.74 (m, 1H), 2.85 (m, 1H), 2.93 (m, 1H), 3.67 (s, 3H), 4.32 (d, *J* = 2.9 Hz, 1H), 4.68 (d, *J* = 3.6 Hz, 1H), 5.59 (m, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 8.90, 14.67, 20.88, 24.49, 24.59, 28.28, 28.54, 35.23, 51.75, 67.36, 67.80, 81.60, 83.59, 117.73, 119.49, 128.19, 129.04, 129.42, 130.00, 133.01, 133.29, 133.51, 150.31, 153.79, 161.74, 168.38, 173.70;

Anal. Calcd. For $C_{33}H_{43}ClN_2O_8Se$: C, 55.82; H, 6.10; N, 3.94. Found: C, 56.05; H, 6. 09; N, 3.87; relative stereochemistry not assigned.

Aldol aduct $^{13}C_{15}$-19c. Recrystallization from EtOAc/pet ether afforded $^{13}C_{15}$-**19c** as fine white needles, mp 150-51 °C; R_f 0.40 (silica gel, 30% EtOAc/ pet ether); 500 MHz ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 9H), 1.56 (s, 9H), 1.83 (s, 3H), 2.02 (s, 3H), 2.31 (m, 1H), 2.40 (t, *J* =8.0 Hz, 2H), 2.47 (m, 1H), 2.74 (m, 1H), 2.84 (m, 1H), 2.93 (m, 1H), 3.67 (s, 3H), 4.44 (bs, 1H), 4.68 (dd, *J* = 6.0 Hz, *J* = 2.5 Hz, 1H), 5.59 (ddd, *J* = 149 Hz, *J* = 6.0 Hz, *J* = 2.0 Hz, 1H), 7.22 (d, 8.8 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 9.11 (bs, NH) ; 125 MHz ^{13}C NMR ($CDCl_3$) δ 8.89, 14.68, 20.88, 24.48, 24.59, 28.27, 28.53, 35.22, 51.74, 67.69, 67.78 (m, enriched *meso*-C), 81.60, 83.56, 117.70 (d, *J* = 21 Hz), 119.47, (d, *J* = 8 Hz), 128.19, 129.06 (d, *J* = 31 Hz), 129.42, 130.04 (d, *J* = 223 Hz), 133.00, 133.27 (d, *J* = 5 Hz), 133.50, 150.28, 153.80 (d, *J* = 8 Hz), 161.78, 168.39, 173.70. Anal. Calcd. For $C_{32}{}^{13}CH_{43}ClN_2O_8Se$: C, 55.88; H, 6.09, N, 3.94 Found: C, 56.03, H, 6.15, N, 3.98; relative stereochemistry not assigned.

Aldol aduct 19d. Column chromatography afforded **19d** as a pale yellow solid, mp 76-8 °C; R_f = 0.35 (silica gel, 30% EtOAc/pet ether); UV-vis (MeOH) λ_{max}nm (log ε): 220 (4.32); 280 (4.32); IR (film) 3420, 1760, 1730, 1680, 1660 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 3H), 1.56 (s, 9H), 1.58 (s, 9H), 2.05 (s, 3H), 2.51 (t, *J* = 8.4 Hz, 2H), 2.56 (t, *J* = 7.0 Hz, 2H), 2.88-3.08 (m, 4H), 3.66 (s, 3H), 4.63 (s, 1H), 4.72 (br s, 1H), 5.56 (s, 1H), 7.190 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 9.35 (s, 1H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 9.58, 13.31, 20.89, 24.78, 25.00, 28.45, 28.64, 35.33, 551.67, 66.60, 67.20, 81.43, 83.94, 114.92, 118.67, 128.27, 129.33, 129.82, 130.27, 132.97, 133.32, 133.40, 150.32, 152.96, 161.46, 169.40, 173.79; Anal. Calcd. For $C_{33}H_{43}ClN_2O_8Se$; C, 55.82; H, 6.10; N, 3.94. Found: C, 55.95; H, 6.13; N, 3.98; relative stereochemistry not assigned.

3-(5-{4-[2-(4-Chlorophenylselanyl)ethyl]-3-methyl-5-oxo-1,5-dihydropyrrol-2-ylidenemethyl}-4-methyl-1*H*-pyrrol-3-yl)-propionic acid-methyl ester (20). A mixture consisting of 1.00 g (1.21 mmol, 1.0 eq) of silanyloxypyrromethanes **19a** and **19b** and 860 mg (1.21 mmol, 1.00 eq) of hydroxypyrromethanes **19c** and **19d** was treated with 27.6 g (18.6 mL, 240 mmol, 100 eq) of neat TFA under Argon at 23 °C. The resulting deep red solution was kept at rt for 8 hours, and was then partitioned between 50 mL of ice cold H_2O and 50 mL of CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were washed with 2 x 20 mL of H_2O and sat'd $NaHCO_3$, dried over anhydrous Na_2SO_4, concentrated under reduced pressure and chromatographed (silica gel, 30% EtOAc/pet ether) to afford 1.15 g (96%) of pyrromethenone **20** as a yellow-green solid. Recrystallization from EtOAc/pet ether afforded **20** as yellow/green needles, mp 168-69 °C; R_f 0.55 (silica gel, 50% EtOAc/pet ether); UV-vis (MeOH) λ_{max}nm (log ε): 206 (4.16); 226 (4.02); 270 (3.85); 400 (4.44); IR (film) 3372, 1730, 1700, 1640, 1610 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 3H); 2.17 (s, 3H); 2.56 (t, *J* = 7.3 Hz, 2H); 2.78 (t, *J* = 7.3 Hz, 2H); 2.84 (t, *J* = 7.3 Hz, 2H); 3.20 (t, *J* = 7.3 Hz, 2H); 3.70 (s, 3H); 6.19 (s, 1H); 6.76 (d, *J* = 2.7 Hz, 1H); 7.13 (d, *J* = 8.6 Hz, 2H); 7.38 (d, *J* = 8.5 Hz, 2H); 10.34 (s, 1H); 11.01 (s, 1H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 9.65, 10.24, 20.94, 25.10, 26.78, 35.01, 51.83; 102.57, 121.32, 123.18, 124.44, 124.59, 126.63, 128.53, 129.32, 129.51, 133.11, 133.95, 143.04, 173.63, 173.88; Anal. Calcd. for $C_{23}H_{25}ClN_2O_3Se$: C, 56.16; H, 5.12; N, 5.70. Found: C, 55.88; H, 5.11; N, 5.67.

Pyrromethenone $^{13}C_{15}$-20. This material was prepared in 85% yield in identical fashion as for pyrromethenone **20** in 85% yield, employing 200 mg (0.281mmol, 1.0 eq) of $^{13}C_{15}$-**19a** in 3.20 mL (28.1 mmol, 100 eq) of neat TFA for 8 hr. Chromatography afforded 117 mg (85%) of dipyrromethenone $^{13}C_{15}$-**20** as a yellow green powder, mp 167-68°C, R_f 0.55 (silica gel, 50% EtOAc/pet ether); UV-vis (MeOH) λ_{max}nm (log ε): 204 (4.14); 228 (3.98); 272 (3.80); 402 (4.43); IR (film) 3360, 2900, 1740, 1610 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 3H), 2.17 (s, 3H), 2.56 (t, *J* = 7.3 Hz,

2H), 2.78 (t, J = 7.3 Hz, 2H), 2.83 (t, J = 7.3 Hz, 2H), 3.19 (t, J = 7.3 Hz, 2H), 3.70 (s, 3H), 6.18 (d, J = 153 Hz, 1H), 6.76 (d, J = 1.5 Hz, 1H), 7.13 (d, J = 8.5 Hz, 2H); 7.37 (d, J = 8.5 Hz), 10.39 (s, 1H), 11.07 (s, 1H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 9.63 (d, J = 7.0 Hz), 10.20 (d, J = 4.0 Hz), 20.93, 25.08, 26. 75, 35.00, 51.80, 102.55 (m, enriched *meso*-C), 121.31 (d, J = 6.0 Hz), 123.14 (d, J = 14.5 Hz), 124.37 (d, J = 77 Hz), 124.63 (d, J = 216 Hz), 126.58 (d, J = 16 Hz), 128.53, 129.30, 129.43 (d, J = 321 Hz), 133.09, 133. 93, 143.90 (d, J =14 Hz), 173.61 (d, J = 20 Hz), 173.86.

3-[2-[5-(3*E*-Ethylidene-4*R*-methyl-5-oxo-pyrrolidin-2-ylidenemethyl)-3-(2-methoxycarbonyl-ethyl)-4-methyl-1*H*-pyrrol-2-ylmethylene]-5-(4-(4-Chloro-phenylselanyl-ethyl)-3-methyl-5-oxo-1,5-dihydro-pyrrol-2-ylidenemethyl)-4-methyl-2*H*-pyrrol-3-yl]-propionic acid-methyl ester (22). A solution of 60 mg (0.12 mmol, 1.0 eq) of selanylpyrromethenone **20** in 10 mL dry CH_2Cl_2 and 6 mL dry MeOH under Argon atmosphere at rt was treated with 122 μL (0.12 mmol, 1.0 eq) of anhydrous 1.0 M HCl (diethyl ether) followed by dropwise addition of a solution of 41 mg (0.12 mmol, 1.0 eq) of pyrromethenone **10** over 30 minutes. After addition was complete, the reaction solution was stirred at rt for 24 hours then treated with an additional 61 μL (0.61 mmol, 0.50 eq) of 1.0 M HCl and stirred for an additional 8 hr. The reaction solution was partitioned between CH_2Cl_2 and ice cold pH 8 buffer and the aqueous layer extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried (Na_2SO_4), concentrated under reduced pressure and chromatographed (silica gel, 20-50% EtOAc/CCl_4) to afford 75 mg (76%) of tetrapyrrole **22** as a cobalt blue solid. Recrystallized from $CHCl_3$/pet ether afforded **22** as deep cobalt blue crystals, mp 192-93 °C, R_f 0.80 (silica gel, 50% EtOAc/CCl_4); UV-vis (MeOH) λ_{max} (log ε) 272 (4.34), 368 (4.58), 602 (4.06); IR (film) 3420, 1730, 1710, 1580 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$) δ 1.26 (d, J = 7.5 Hz, 3H), 1.86 (d, J =7.3 Hz, 3H), 2.03 (s, 3H), 2.07 (s, 3H), 2.13 (s, 3H), 2.55 (t, J = 7.6 Hz, 4H), 2.65 (m, 2H), 2.89 (t, J = 7.7 Hz, 2H), 2.93 (t, J = 7.5 Hz, 2H), 3.06 (m, 2H), 3.67 (s, 3H), 3.68 (s, 3H), 5.78 (s, 1H), 5.99 (s, 1H), 6.36 (dq, J = 6.7 Hz, J = 2.1 Hz, 1H), 6.59 (s, 1H), 7.19 (d, J = 8.5, 2H), 7.45 (d, J = 8.5 Hz, 2H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 9.52, 10.31, 10.22, 15.15, 15.72, 19.93, 20.12, 25.15, 25.76, 35.42, 35.49, 38.13, 51.95 (2), 87.66, 97.47, 111.35, 123.28, 124.21, 128.92, 129.30, 129.32, 130.11, 131.39, 132.65, 132.82, 133.35, 133.51, 133.56, 135.97, 136.59, 142.12, 142.94, 145.95, 149.39, 166.25, 173.29, 173.39, 178.34; Anal. Calcd. for $C_{41}H_{45}ClN_4O_6Se$: C, 61.23; H, 5.64, N, 6.97. Found: C, 61.39; H, 5.70; N, 6.91.

Tetrapyrrole $^{13}C_{15}$-22. This material was prepared in 73% yield in identical fashion as for **22**, employing 30 mg (0.061 mmol, 1.0 eq) of selanylpyrromethenone $^{13}C_{15}$-**20**, 20 mg (0.061 mmol, 1.00 eq) of pyrromethenone **10**, and 92 μL (0.092 mmol, 1.5 eq) of 1.0 M HCl (diethyl ether) in a solution of 5 mL CH_2Cl_2 and 3 mL of MeOH for 30 hr. Chromatography afforded 36 mg (73%) of tetrapyrrole $^{13}C_{15}$-**22** as a cobalt blue powder, mp 192-92.5°C, R_f 0.80 (silica gel, 50% EtOAc/CCl_4); UV-vis (MeOH) λ_{max} (log ε) 272 (4.38), 368 (4.64), 608 (4.10); IR (film) 3330, 2850, 1730, 1600 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$) δ 1.25 (d, J = 6.3 Hz, 3H), 1.87 (d J = 6.8 Hz, 3H), 2.03 (s, 3H), 2.07 (s, 3H), 2.13 (s, 3H), 2.56 (t, J = 7.8 Hz, 4H), 2.62 (m, 2H), 2.88 (t, J = 8.2 Hz, 2H), 2.93 (t, J = 8.15 Hz, 2H), 3.04 (m, 2H), 3.67 (s, 3H), 3.69 (s,3H), 5.77 (s, 1H), 5.98 (d, J = 160 Hz, 1H), 6.36 (dq, J = 7.5 Hz, J =2.3 Hz, 1H), 6.58 (s, 1H), 7.18 (d, J = 8.4 Hz, 2H), 7.44 (d, J =8.5 Hz, 2H).

Tetrapyrrole $^{13}C_{10}$-22. This material was prepared in 75% yield as in **22**, employing 22mg (0.045 mmol, 1.0 eq) of selanylpyrromethenone **20**, 16 mg (0.048 mmol, 1.1 eq) of pyrromethenone $^{13}C_{10}$-**10**, and 68 μL (0.068 mmol, 1.5 eq) of 1.0 M HCl (diethyl ether) in a solution of 4.0 ml CH_2Cl_2 and 2.5 mL MeOH for 30 hours. Chromatography afforded 27 mg (75%) of tetrapyyrrole $^{13}C_{10}$-**22** as cobalt blue powder, mp 191.5-92°, R_f 0.80 (silica gel, 50% EtOAc/CCl_4); UV-vis (MeOH) λ_{max} (log ε) 272 (4.40), 368 (4.74), 608 (4.12); IR (film) 3220, 2850, 1730, 1700 cm^{-1}; 500 MHz ^{1}H NMR ($CDCl_3$) δ 1.25 (d, 7.7 Hz, 3H), 1.87 (d, J = 6.8 Hz, 3H), 2.04 (s, 3H), 2.08 (s, 3H), 2.14 (s, 3H), 5.77 (s, 1H), 5.99 (s,

1H), 6.36 (dq, J = 7.4 Hz, J = 2.1 Hz, 1H), 7.19 (d, J = 7.8 Hz, 2H), 7.45 (d, J =7.8 Hz, 2H).

3-[2-[5-(3*E*-Ethylidene-4*S*-methyl-5-oxo-pyrrolidin-2-ylidenemethyl)-3-(2-methoxycarbonylethyl)-4-methyl-1*H*-pyrrol-2-ylmethylene]-5-(4-(4-Chloro-phenylselanyl-ethyl)-3-methyl-5-oxo-1,5-dihydro-pyrrol-2-ylidenemethyl)-4-methyl-2*H*-pyrrol-3-yl]-propionic acid-methyl ester (*ent*-**22**). This material was prepared in 72% yield in identical fashion as for tetrapyrrole **22**, employing 27 mg (0.055 mmol, 1.0 eq) of selanylpyrromethenone **20**, 18 mg (0.055 mmol, 1.0 eq) of pyrromethenone *ent*-**10** and 83 µL (0.083 mmol, 1.5 eq) of 1.0 M HCl (diethyl ether) in a solution of 2 mL of CH_2Cl_2 and 1 mL of MeOH for 30 hr. Chromatography afforded 21 mg (72%) of *ent*-**22** as cobalt blue powder, mp 192-93°C; IR (film) 3340, 2850, 1730, 1580 cm^{-1}; IR and ^1H NMR are identical to those of tetrapyrrole **22**.

Tetrapyrrole $^{13}C_{15}$-*ent*-**22**. This material was prepared in 73% yield in identical fashion as for tetrapyrrole **22**, employing 30 mg (0.061 mmol, 1.0 eq) of pyrrolidenone $^{13}C_{15}$-*ent*-**20**, 20 mg (0.061 mmol, 1.0 eq) of formylpyrrole **10**, and 92 µL (0.092 mmol, 1.5 eq) of 1.0 M HCl in a solution of 5 mL CH_2Cl_2 and 3 mL of MeOH for 30 hr. Chromatography afforded 36 mg (73%) of tetrapyrrole $^{13}C_{15}$-**22** as a cobalt blue powder, mp 192-92.5°C, having IR and ^1H NMR identical those of tetrapyrrole $^{13}C_{15}$-**22**.

Tetrapyrrole $^{13}C_{10}$-*ent*-**22**. This material was prepared in 75% yield in identical fashion as for **22**, employing 22 mg (0.045 mmol, 1.0 eq) of pyrrolideneone **20**, 16 mg (0.048 mmol, 1.1 eq) of formylpyrrole $^{13}C_{10}$-*ent*-**10**, and68 µL (0.068 mmol, 1.5 eq) of 1.0 M HCl (diethyl ether) in a solution of 4.0 ml CH_2Cl_2 and 2.5 mL MeOH for 30 hours. Chromatography afforded 27 mg (75%) of tetrapyrrole $^{13}C_{10}$-**22** as cobalt blue powder, mp 191.5-192°C, having IR and ^1H NMR identical to those of tetrapyrrole $^{13}C_{10}$-**22**

4*R*-Phytochromobilin dimethylester (**4**). A solution of 37 mg (0.0 46 mmol, 1.0 eq) of tetrapyrrole **22** in 15 mL of dry CH_2Cl_2 was treated dropwise at -78°C under an Argon atmosphere with a solution of 7.9 mg (0.046 mmol, 1.0 eq) of m-CPBA in 4 mL of dry CH_2Cl_2. After addition was complete, the reaction mixture was stirred at -78°C for an additional 1.5 hr, diluted with 15 mL of precooled CH_2Cl_2 and treated with ice cold K_2HPO_4/KOH pH 12 buffer. The frozen mixture was slowly warmed to 10°C and stirred for additional 2 hr, noting reaction progress by TLC (50% EtOAc/CCl_4), then partitioned between CH_2Cl_2 and ice cold K_2HPO_4/KOH pH 12 buffer. The organic layer was washed with brine, dried (Na_2SO_4), concentrated under reduced pressure, and then chromatographed (silica gel, 20-50% EtOAc/CCl_4) to afford 24 mg (84%) of 4*R*-phytochromobilin dimethylester **4** as a cobalt blue solid. Recrystallized from $CHCl_3$/Petroleum Ether afforded **4** as deep cobalt blue crystals, mp 180-81 °C (*lit.*[3] mp 180°C); R_f 0.75 (silica gel, 50% EtOAc/CCl_4); UV-vis (MeOH) λ_{max} (log ε) 298 (4.30), 372 nm (4.63), 602 (4.22); IR (film) 3340, 2850, 1730, 1680 cm^{-1}; 500 MHz ^1H NMR ($CDCl_3$) δ 1.34 (d, J = 7.4 Hz, 3H), 1.89 (d, J = 7.3 Hz, 3H), 2.06 (s, 3H), 2.14 (s, 3H), 2.22 (s, 3H), 2.56 (t, J = 7.3 Hz, 4H), 2.91 (t, J = 7.8 Hz, 2H), 2.95 (t, J = 7.8 Hz, 2H), 3.13 (q, J =7.8 Hz, 1H), 3.67 (s, 3H), 3.69 (s, 3H), 5.42 (dd, J = 11.6 Hz, J = 2.1 Hz, 1H), 5.85 (s, 1H), 6.10 (s, 1H), 6.24 (dd, J = 17.5 Hz, J = 1.9 Hz, 1H), 6.40 (dq, J = 7.4 Hz, J = 1.8 Hz, 1H), 6.53 (dd, J = 17.6 Hz, J = 11.3 Hz, 1H), 6.64 (s, 1H); Anal. Calcd. for $C_{35}H_{40}N_4O_6$: C, 68.61, H, 6.58, N, 9.14. Found: C, 68.73; H, 6.62; N, 9.02.

$^{13}C_{15}$-**Phytochromobilin dimethylester -5.** This material was prepared in 79 % yield in identical fashion as for tetrapyrrole **4**, employing 30 mg (0.037 mmol, 1.00) of tetrapyrrole $^{13}C_{15}$-**22**, and 6.4 mg (0.037 mmol, 1.00 eq) of m-CPBA in 15 mL of CH_2Cl_2 for 5 hr. Chromatography afforded 18 mg (79%) of tetrapyrrole $^{13}C_{15}$-**5** as a cobalt colored powder, mp 179-80°C; R_f 0.75 (silica gel, 50% EtOAc/CCl_4); UV-vis (MeOH) λ_{max} (log ε) 296 (4.23), 372 (4.49), 604 (4.09); IR (film) 3330, 2860, 1730, 1700; 500 MHz ^1H NMR ($CDCl_3$) δ 1.35 (d, J = 7.6 Hz, 3H), 1.90 (dd, J = 7.2 Hz, J = 0.9, 3H), 2.06 (s, 3H), 2.14 (s, 3H), 2.22 (s, 3H), 2.57 (t, J =7.4 Hz, 4H), 2.92 (t, J = 7.8 Hz, 2H), 2.96 (t, J = 7.6 Hz, 2H), 3.14 (q, J = 7.6 Hz, 1H), 3.68 (s, 3H), 3.69 (s, 3H), 5.42 (dd, J =11.5 Hz, J = 2.0 Hz,

1H), 5.86 (s, 1H), 6.10 (d, J = 159 Hz, 1H), 6.25 (dd, J = 17.6 Hz, J = 2.0 Hz, 1H), 6.42 (dq, J = 7.3 Hz, J = 2.2 Hz, 1H), 6.54 (dd J = 17.6 Hz, J = 11.5 Hz, 1H), 6.66 (s, 1H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 97.4 (enriched $^{13}C_{15}$).[3]

$^{13}C_{10}$-Phytochromobilin dimethylester 6. This material was prepared in 80 % yield in identical fashion as for tetrapyrrole **4** employing 13 mg (0.016 mmol, 1.00) of tetrapyrrole $^{13}C_{10}$-**22**, and 2.8 mg (0.016 mmol, 1.0 eq) of m-CPBA in 3.0 mL of CH_2Cl_2 for 5 hr. Chromatography afforded 8.0 mg (80%) of tetrapyrrole $^{13}C_{15}$-**5** as a cobalt colored powder, mp 179-80°C; R_f 0.75 (silica gel, 50% CCl_4); UV-vis (MeOH) λ_{max} (log ε) 296 (4.32), 372 (4.60), 600 (4.20); 500 MHz ^1H NMR ($CDCl_3$) δ 1.35 (d, J = 7.6 Hz, 3H), 1.90 (dd, 7.2 Hz, J = 1.0 Hz, 3H), 2.06 (s, 3H), 2.14 (s, 3H), 2.22 (s, 3H), 2.57 (t, J = 7.3 Hz, 4H), 2.92 (t, J = 7.8 Hz, 2H), 2.97 (t, J = 7.6 Hz, 2H), 3.14 (q, J = 7.6 Hz, 1H), 3.68 (s, 3H), 3.69 (s, 3H), 5.42 (d, J = 12.0 Hz, 5.86 (s, 1H), 6.10 (s, 1H), 6.25 (d, J = 18.1 Hz, 1H), 6.42 (dq, J = 7.2 Hz, J = 1.4 Hz, 1H), 6.55 (dd, J = 17.9 Hz, J = 10.9 Hz, 1H), 6.65 (d, J = 156 Hz, 1H); 125 MHz ^{13}C NMR ($CDCl_3$) δ 111.1 (enriched $^{13}C_{10}$).[3]

Phytochromobilin dimethylester *ent*-**4.** This material was prepared in 85% yield in identical fashion as for tetrapyrrole **4**, employing 30 mg (0.037 mmol, 1.0) of tetrapyrrole *ent*-**22**, and 6.4 mg (0.037 mmol, 1.0 eq) of m-CPBA in 7.0 mL of CH_2Cl_2 for 5 hr. Chromatography afforded 20 mg (85%) of tetrapyrrole *ent*-**4** as a cobalt colored powder, mp 179-80°C; having IR and ^1H NMR identical to those of tetrapyrrole **4**.

Phytochromobilin dimethylester $^{13}C_{15}$-*ent*-**5.** This material was prepared in 79 % yield in identical fashion as for tetrapyrrole **4**, employing 20 mg (0.025 mmol, 1.0) of tetrapyrrole $^{13}C_{15}$-*ent*-**22**, and 4.3 mg (0.025 mmol, 1.0 eq) of m-CPBA in 7.0 mL of CH_2Cl_2 for 5 hr. Chromatography afforded 12 mg (79 %) of tetrapyrrole $^{13}C_{15}$-*ent*-**5** as a cobalt colored powder, mp 179-80°C; having IR and ^1H NMR identical to those of tetrapyrrole $^{13}C_{15}$-**5**.

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DP-II-236 phytochromobilin dimethlester

exp1 s2pul

SAMPLE		DEC. & VT	
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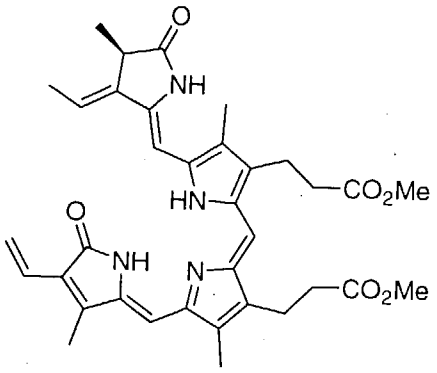
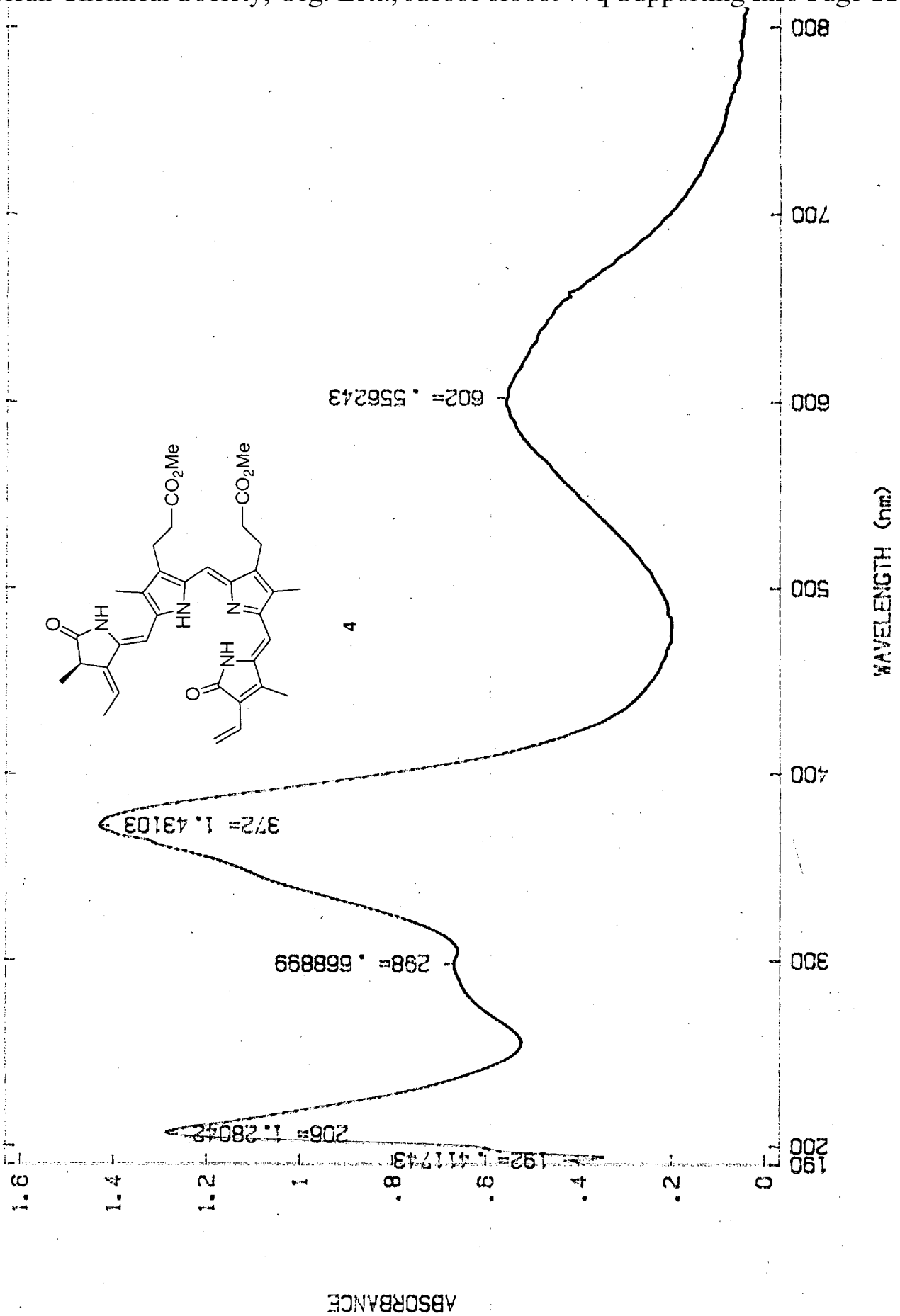
DP500/DP-II-236.ph~	yto2	dof	0
		dm	nnn
ACQUISITION		dmm	c
sfrq	499.875	dmf	11111
tn	H1	dseq	
at	1.500	dres	1.0
np	24000	homo	n
sw	7998.4	temp	23.0
fb	4400	DEC2	
bs	8	dfrq2	0
tpwr	59	dn2	
pw	5.6	dpwr2	1
d1	1.000	dof2	0
tof	513.1	dm2	n
nt	500	dmm2	c
ct	500	dmf2	200
alock	n	dseq2	
gain	not used	dres2	1.0
FLAGS		homo2	n
il	n	PROCESSING	
in	n	lb	0.05
dp	y	wtfile	
hs	nn	proc	ft
DISPLAY		fn	not used
sp	-0.2	math	f
wp	4998.3		
vs	157	werr	
sc	0	wexp	wft aph vsadj
wc	240	wbs	wft
hzmm	20.83	wnt	
is	415.86		
rfl	4640.5		
rfp	3634.1		
th	7		
ins	100.000		
nm	ph		



4

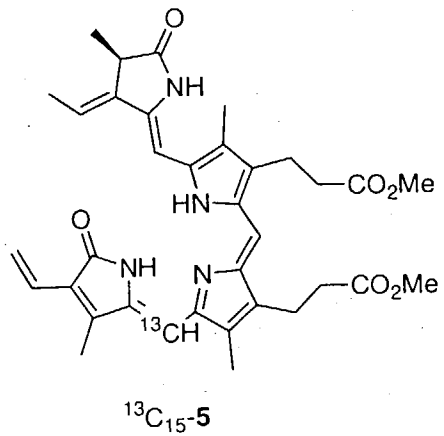

602= .556243
372= 1.43103
298= .668899
206= 1.28042
192= 1.41743
800
700
600
500
400
300
200
190
WAVELENGTH (nm)
1.6
1.4
1.2
1
.8
.6
.4
.2
0
ABSORBANCE
CO2Me
CO2Me
NH
HN
N
NH
O
O

4

DP-III-72 1H 13C/C15 4R phyto-DME

exp3 s2pul

SAMPLE		DEC. & VT	
date	Oct 18 00	dfrq	499.875
solvent	CDCl3	dn	H1
file	/data1/guest/~	dpwr	38
	DP500/DP-III-72.1H~	dof	0
	.13C.C15.2R-phyto	dm	nnn
ACQUISITION		dmm	c
sfrq	499.875	dmf	11111
tn	H1	dseq	
at	2.997	dres	1.0
np	47936	homo	n
sw	7998.4	temp	21.0
fb	4400	DEC2	
bs	8	dfrq2	0
tpwr	59	dn2	
pw	5.6	dpwr2	1
d1	1.000	dof2	0
tof	513.1	dm2	n
nt	1000	dmm2	c
ct	488	dmf2	200
alock	n	dseq2	
gain	not used	dres2	1.0
FLAGS		homo2	n
il	n	PROCESSING	
in	n	lb	0.05
dp	y	wtfile	
hs	nn	proc	ft
DISPLAY		fn	not used
sp	-0.1	math	f
wp	4998.7		
vs	373	werr	
sc	0	wexp	wft aph vsadj
wc	240	wbs	
hzmm	20.83	wnt	
is	95.77		
rfl	4625.7		
rfp	3634.1		
th	13		
ins	100.000		
nm	ph		

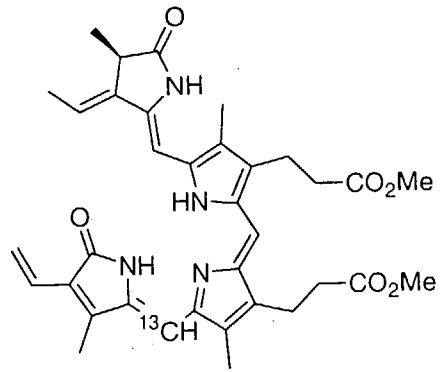


$^{13}C_{15}$-**5**

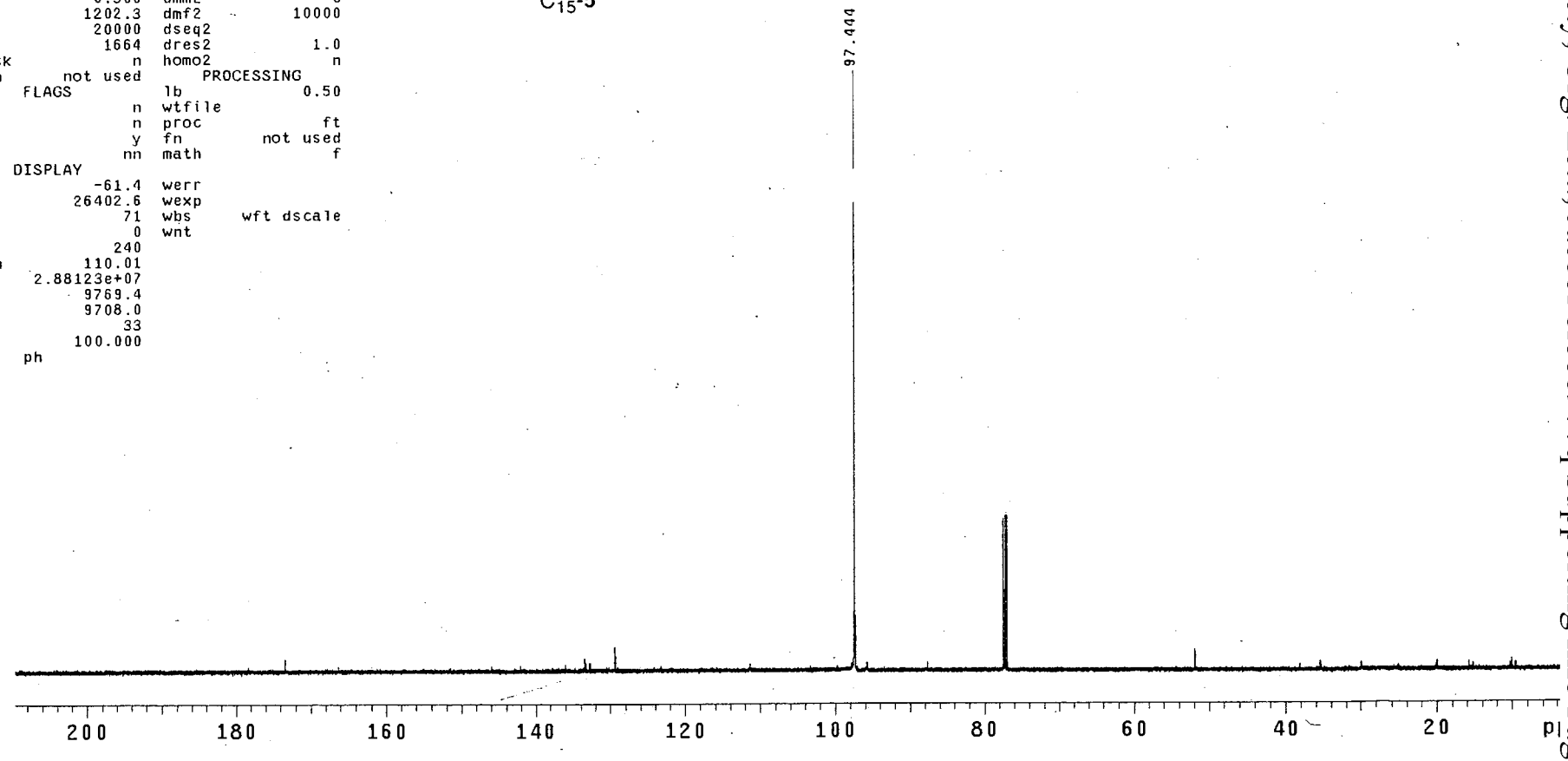
DP-III-67 4R 13C-C15 phyto DME

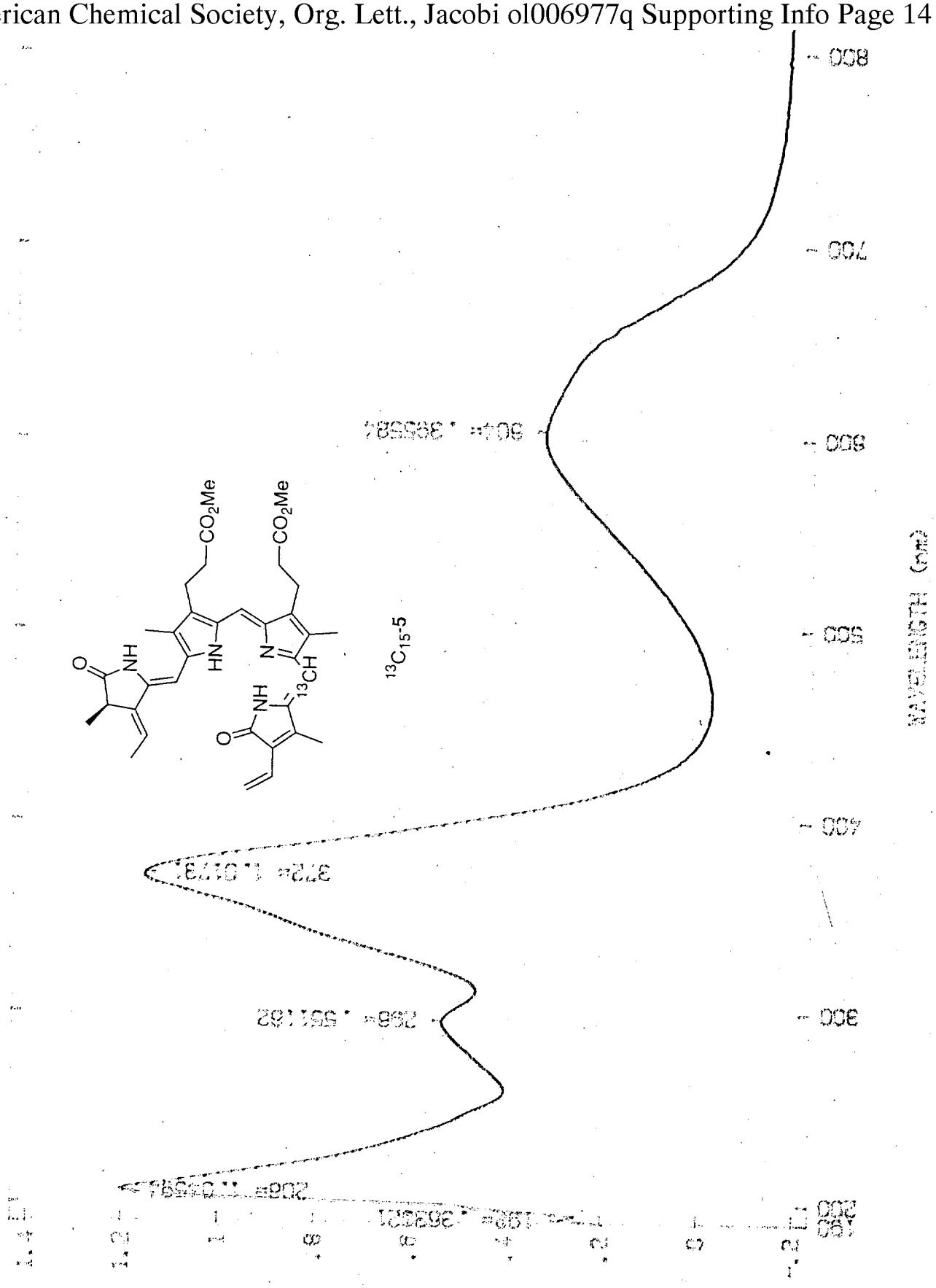
exp5 s2pul

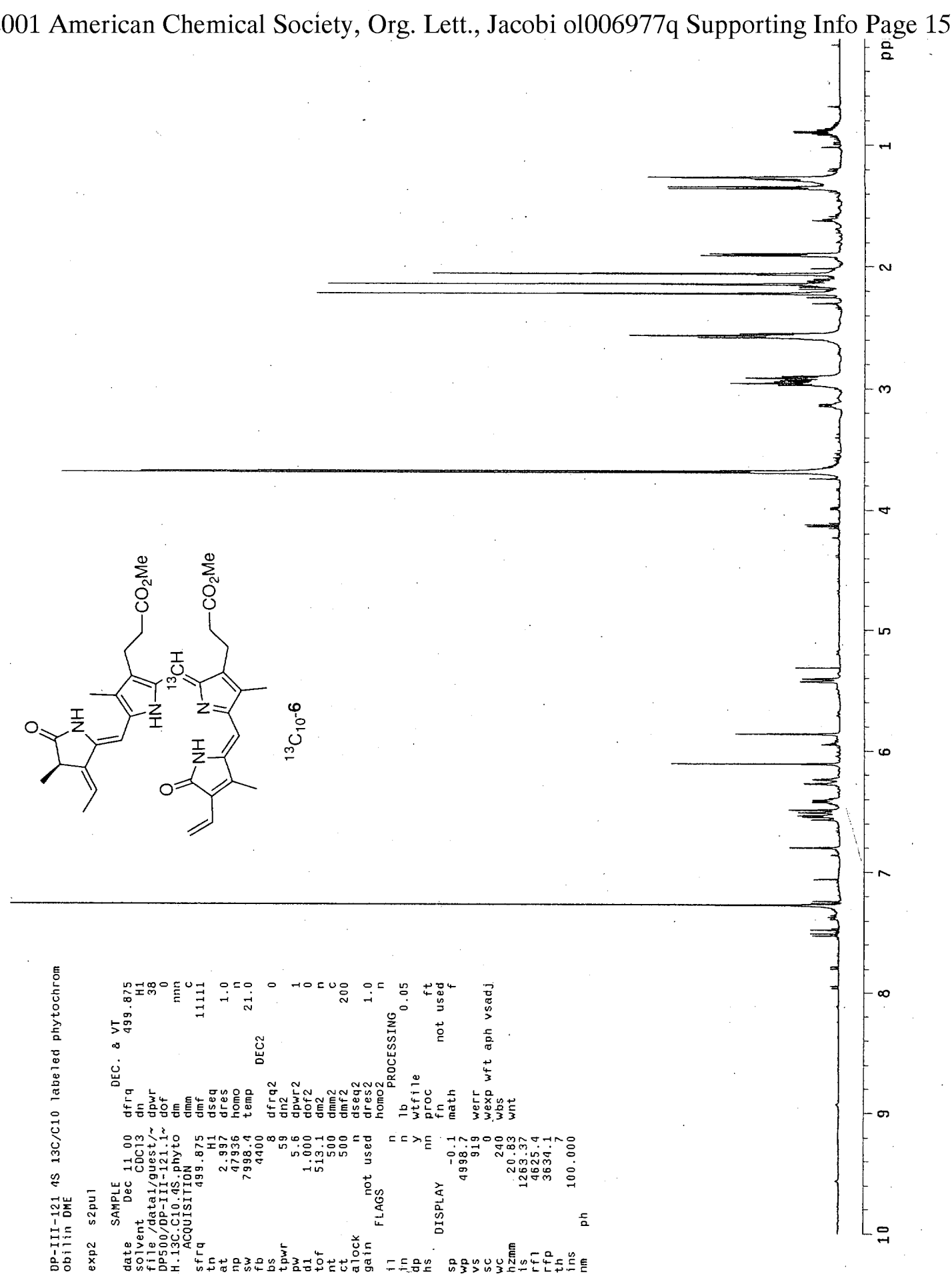
SAMPLE		DEC. & VT	
date	Oct 16 00	dfrq	499.875
solvent	CDCl3	dn	H1
file	/data1/guest/~	dpwr	41
	DP500/DP-III-67.13~	dof	0
	C.13C-C15.4RphytoD~	dm	nyy
	ME	dmm	w
ACQUISITION		dmf	14815
sfrq	125.706	dseq	
tn	C13	dres	1.0
at	1.500	homo	n
np	79232	temp	21.0
sw	26402.6	DEC2	
fb	14600	dfrq2	0
bs	16	dn2	
tpwr	60	dpwr2	1
pw	10.2	dof2	0
d1	1.200	dm2	n
d2	0.300	dmm2	c
tof	1202.3	dmf2	10000
nt	20000	dseq2	
ct	1664	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS		lb	0.50
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-61.4	werr	
wp	26402.6	wexp	
vs	71	wbs	wft dscale
sc	0	wnt	
wc	240		
hzmm	110.01		
is	2.88123e+07		
rfl	9769.4		
rfp	9708.0		
th	33		
ins	100.000		
nm	ph		



$^{13}C_{15}$-**5**



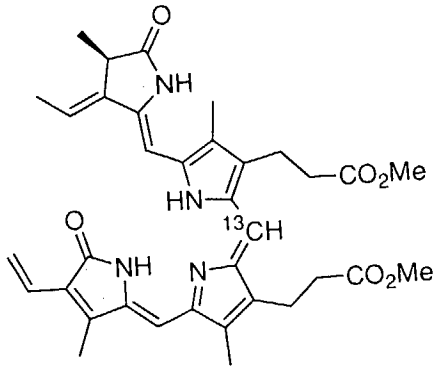




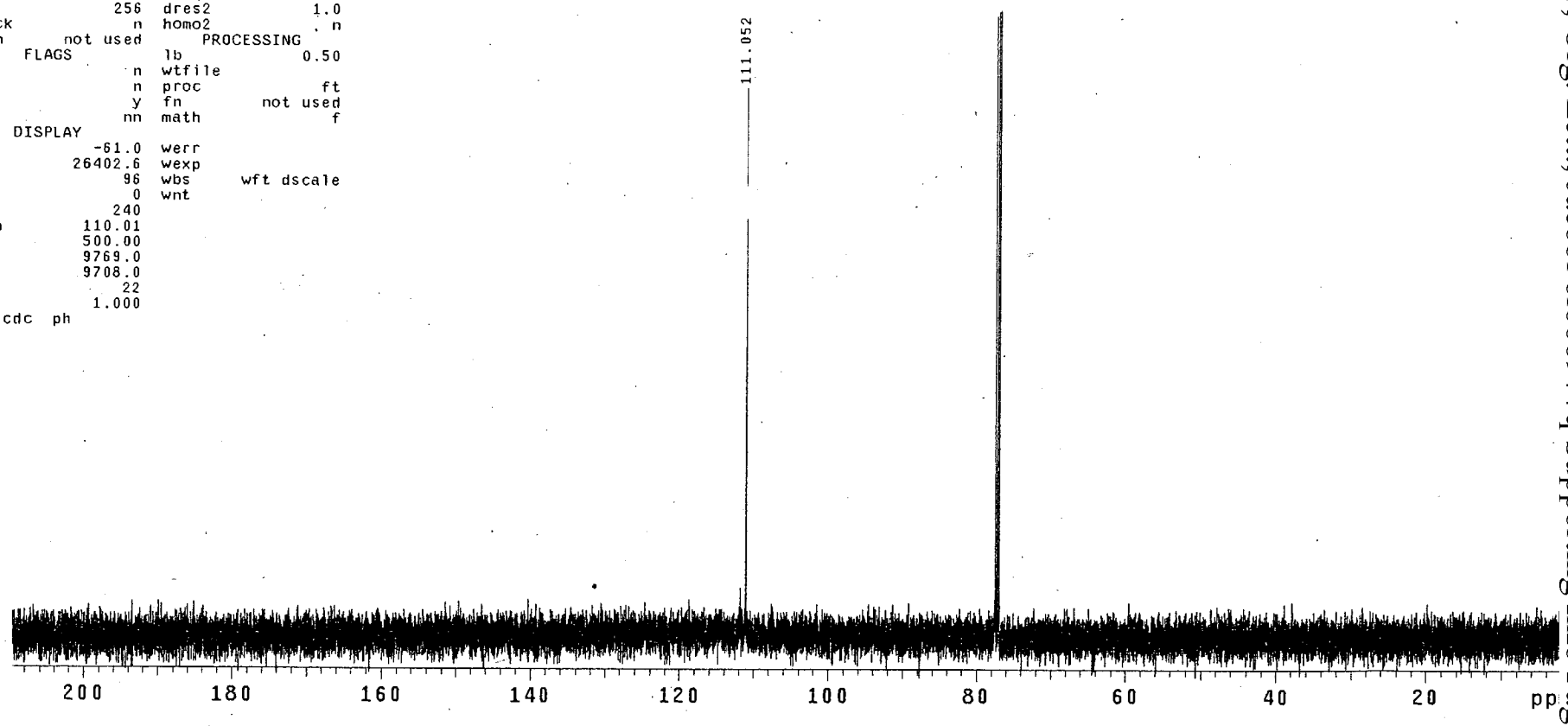
DP-III-121 13C-C10 labeled 4S-phyto DME

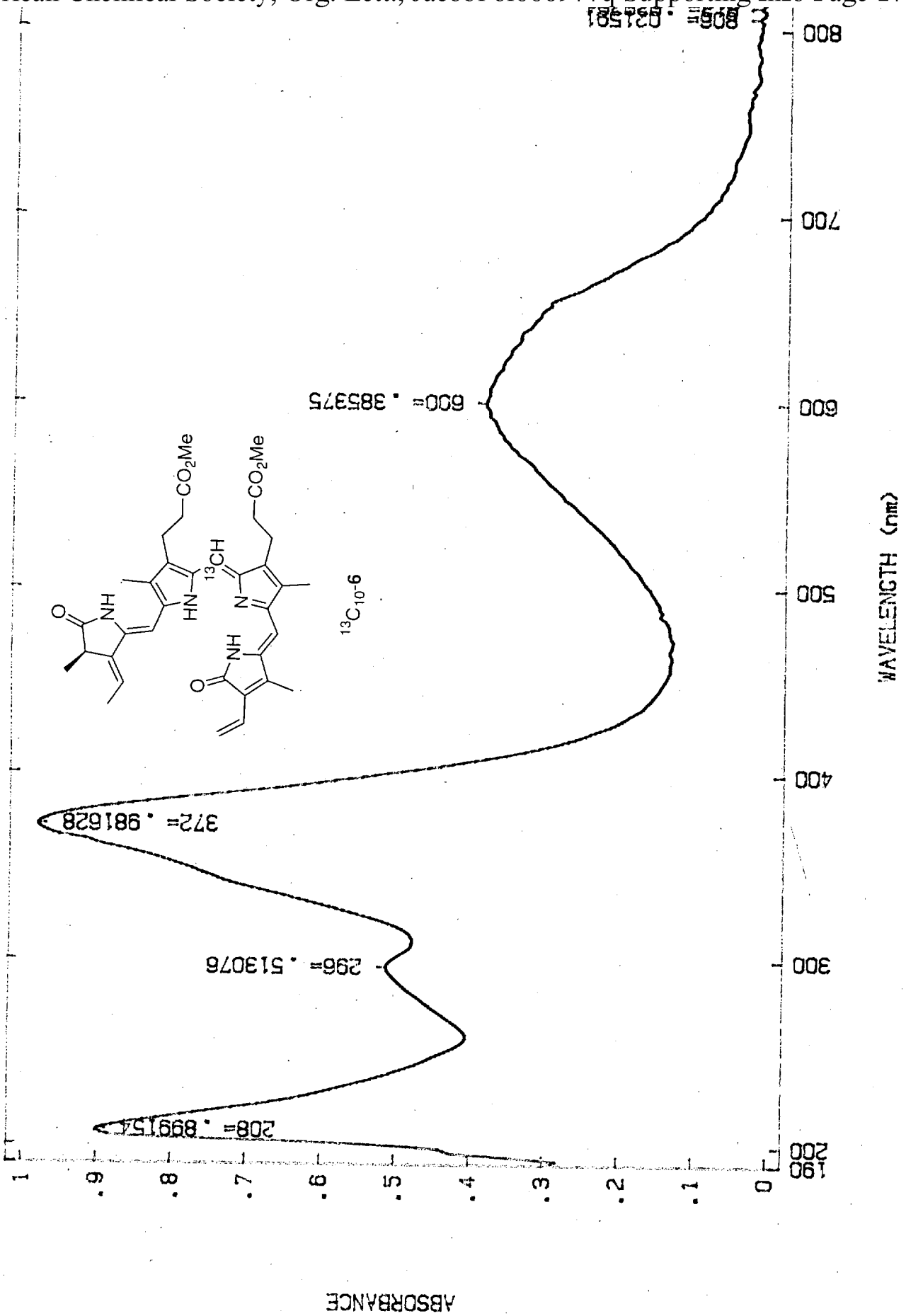
exp6 s2pul

SAMPLE		DEC. & VT	
date	Dec 11 00	dfrq	499.875
solvent	CDCl3	dn	H1
file	/data1/guest/~	dpwr	41
	DP500/DP-III-121.1~	dof	0
	3C.13C-C10.lbld.4S~	dm	nyy
	phyto	dmm	w
ACQUISITION		dmf	14815
sfrq	125.706	dseq	
tn	C13	dres	1.0
at	1.500	homo	n
np	79232	temp	21.0
sw	26402.6	DEC2	
fb	14600	dfrq2	0
bs	32	dn2	
tpwr	60	dpwr2	1
pw	10.2	dof2	0
d1	0.800	dm2	n
d2	0.300	dmm2	c
tof	1202.3	dmf2	10000
nt	1024	dseq2	
ct	256	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS		lb	0.50
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-61.0	werr	
wp	26402.6	wexp	
vs	96	wbs	wft dscale
sc	0	wnt	
wc	240		
hzmm	110.01		
is	500.00		
rfl	9769.0		
rfp	9708.0		
th	22		
ins	1.000		
nm cdc ph			



$^{13}C_{10}$-**6**

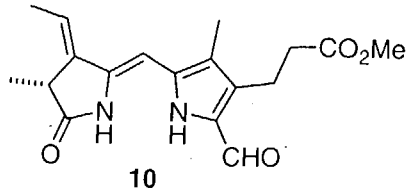




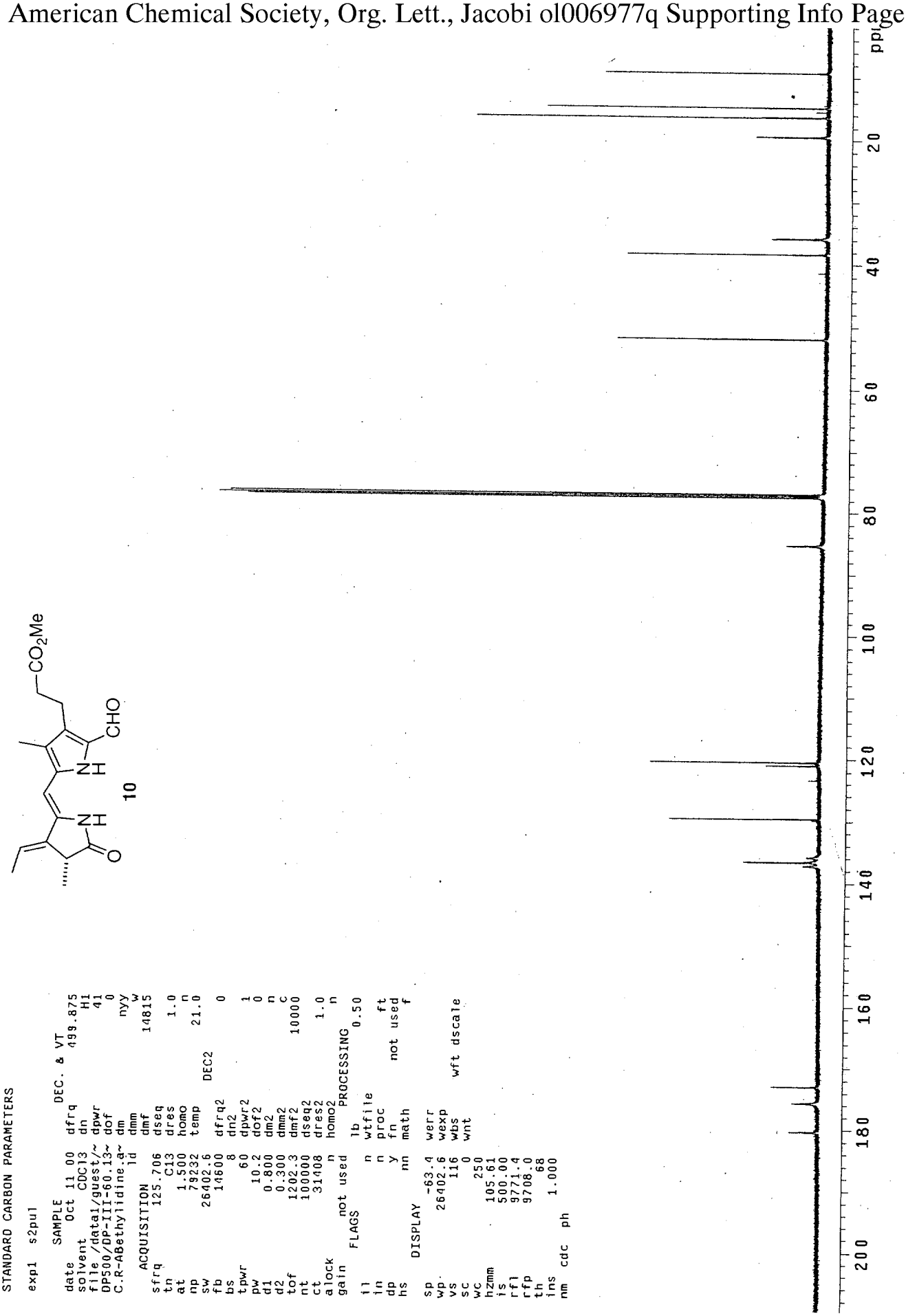
DP-III-19 4R AB ethylidene pyrromethenon
e

exp3 s2pul

SAMPLE		DEC. & VT	
date	Jul 27 00	dfrq	499.875
solvent	CDCl3	dn	H1
file	/data1/guest/~	dpwr	38
	DP500/DP-III-19.R~~	dof	0
	AB-ethylidene.ald	dm	nnn
ACQUISITION		dmm	c
sfrq	499.875	dmf	11111
tn	H1	dseq	
at	3.001	dres	1.0
np	48000	homo	n
sw	7998.4	temp	21.0
fb	4400	DEC2	
bs	8	dfrq2	0
tpwr	59	dn2	
pw	5.6	dpwr2	1
d1	1.000	dof2	0
tof	513.1	dm2	n
nt	500	dmm2	c
ct	98	dmf2	200
alock	n	dseq2	
gain	not used	dres2	1.0
FLAGS		homo2	n
il	n	PROCESSING	
in	n	lb	0.05
dp	y	wtfile	
hs	nn	proc	ft
DISPLAY		fn	not used
sp	-0.1	math	f
wp	5998.5		
vs	143	werr	
sc	0	wexp wft aph vsadj	
wc	240	wbs	
hzmm	24.99	wnt	
is	347137.45		
rfl	4605.8		
rfp	3619.1		
th	7		
ins	100.000		
nm cdc ph			

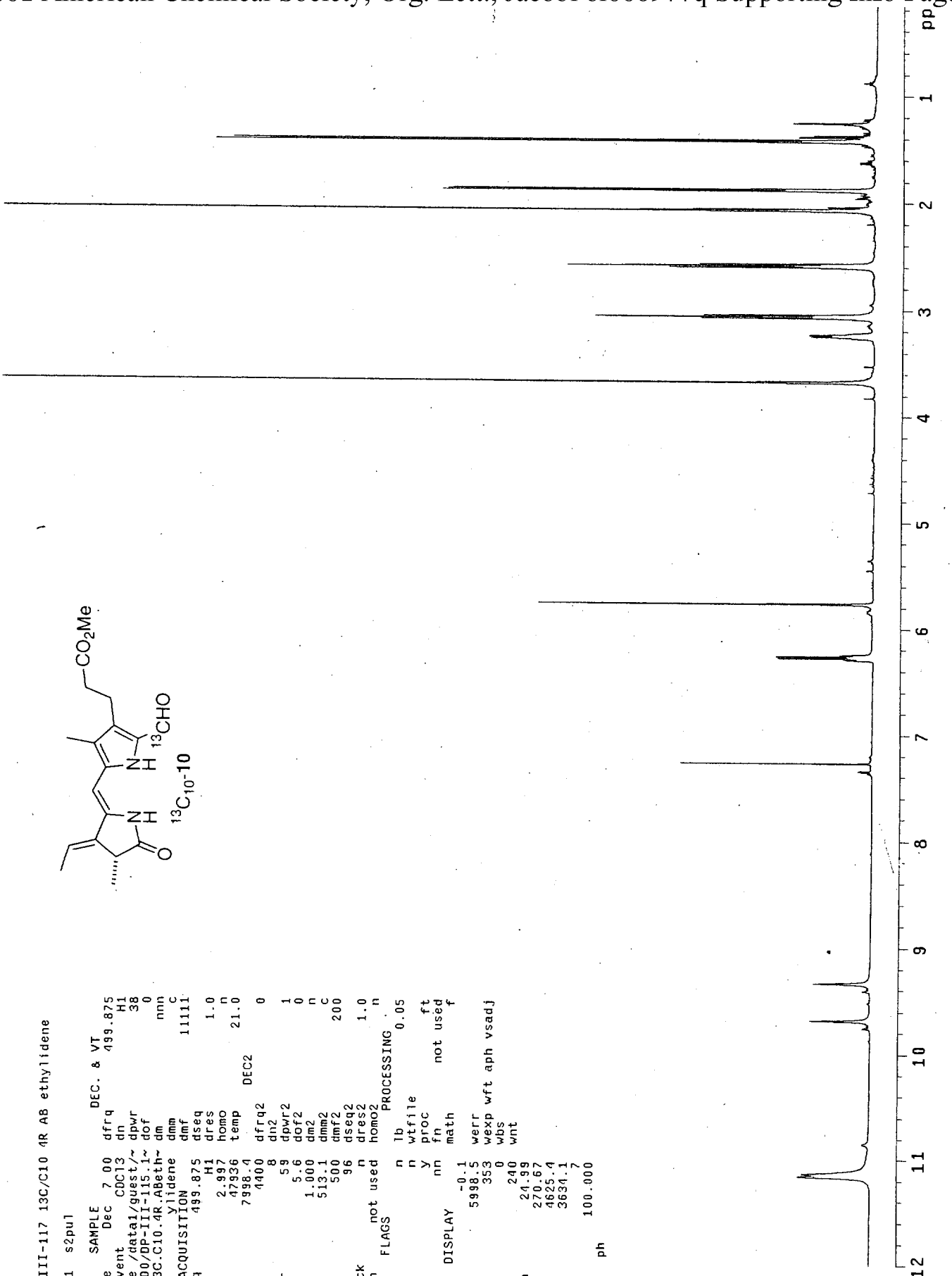


10



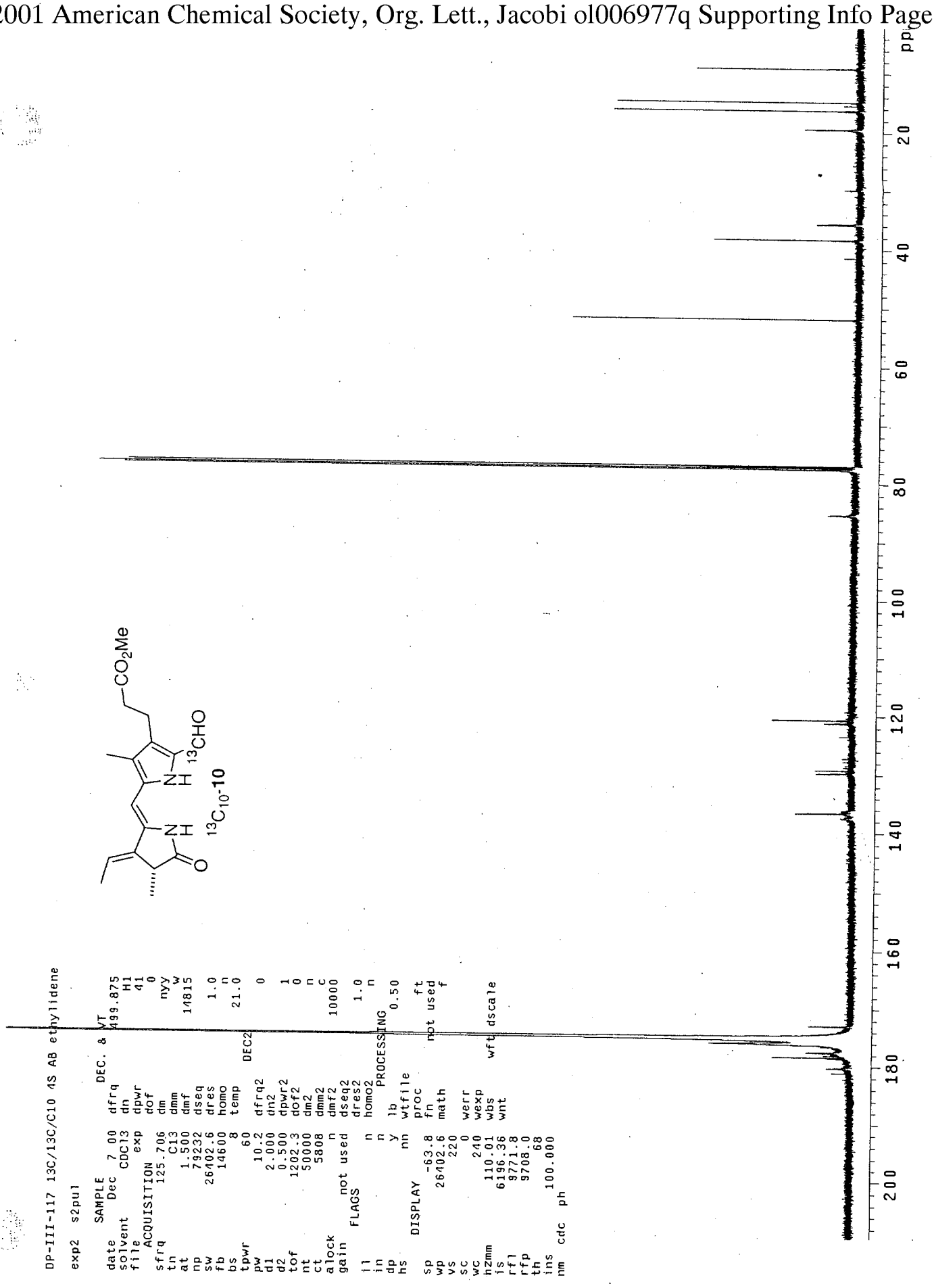
STANDARD CARBON PARAMETERS

```
exp1  s2pul

      SAMPLE                DEC. & VT
date          Oct 11 00   dfrq      499.875
solvent          CDCl3    dn             H1
file /data1/guest/~  dpwr               41
DPS00/DP-III-60.13~  dof                 0
C.R-ABethylidine.a~  dm                nyy
      ACQUISITION   id     dmm            w
sfrq        125.706      dmf        14815
tn              C13      dseq
at              1.500    dres          1.0
np             79232     homo             n
sw          26402.6      temp         21.0
fb             14600     dfrq2            0
bs                 8     dn2
tpwr              60     dpwr2            1
pw              10.2     dof2             0
d1             0.800     dm2              n
d2             0.300     dmm2             c
tof           1202.3     dmf2         10000
nt            100000     dseq2
ct             31408     dres2          1.0
alock              n     homo2            n
gain      not used       PROCESSING
      FLAGS                  lb         0.50
il                 n      wtfile
in                 n      proc             ft
dp                 y      fn         not used
hs                nn      math              f
      DISPLAY
sp             -63.4      werr
wp          26402.6       wexp
vs              116       wbs          wft dscale
sc                0       wnt
wc              250
hzmm         105.61
is           500.00
rfl         9771.4
rfp         9708.0
th                68
ins            1.000
nm  cdc  ph
```



DP-III-117 13C/C10 4R AB ethylidene

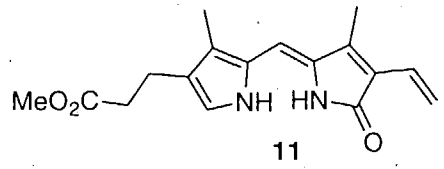
```
exp1  s2pul

      SAMPLE                DEC. & VT
date      Dec  7.00  dfrq        499.875
solvent       CDCl3  dn             H1
file /data1/guest/~  dpwr           38
DP500/DP-III-115.1~  dof             0
H.13C.C10.4R.ABeth~  dm            nnn
      ylidene        dmm             c
  ACQUISITION        dmf         11111
sfrq      499.875    dseq
tn             H1    dres          1.0
at          2.997    homo            n
np          47936    temp         21.0
sw        7998.4                 DEC2
fb          1400    dfrq2            0
bs             8    dn2
tpwr          59    dpwr2            1
pw           5.6    dof2             0
d1         1.000    dm2              n
tof        513.1    dmm2             c
nt           500    dmf2           200
ct            96    dseq2
alock          n    dres2          1.0
gain    not used    homo2            n
      FLAGS                 PROCESSING
il             n    lb             0.05
in             n    wtfile
dp             y    proc             ft
hs            nn    fn         not used
      DISPLAY       math             f
sp         -0.1
wp       5998.5    werr
vs          353    wexp wft aph vsadj
sc            0    wbs
wc          240    wnt
hzmm      24.99
is       270.67
rfl      4625.4
rfp      3634.1
th             7
ins          100.000
nm    ph
```



DP-III-18 CD unsubstituted alkene

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jul 27 00	dfrq	499.875
solvent	CDCl3	dn	H1
file	/data1/guest/~	dpwr	38
	DP500/DP-III-18.CD~	dof	0
	.unsub.vinylquanty~	dm	nnn
	1d	dmm	c
ACQUISITION		dmf	11111
sfrq	499.875	dseq	
tn	H1	dres	1.0
at	2.997	homo	n
np	47936	temp	21.0
sw	7998.4	DEC2	
fb	4400	dfrq2	0
bs	8	dn2	
tpwr	59	dpwr2	1
pw	5.6	dof2	0
d1	1.000	dm2	n
tof	513.1	dmm2	c
nt	10000	dmf2	200
ct	504	dseq2	
alock	n	dres2	1.0
gain	not used	homo2	n
FLAGS		PROCESSING	
il	n	lb	0.05
in	n	wtfile	
dp	y	proc	ft
hs	nn	fn	not used
DISPLAY		math	f
sp	-0.1		
wp	5998.5	werr	
vs	852	wexp	wft aph vsadj
sc	0	wbs	
wc	240	wnt	
hzmm	24.99		
is	16601.56		
rfl	4625.7		
rfp	3634.1		
th	5		
ins	100.000		
nm	ph		



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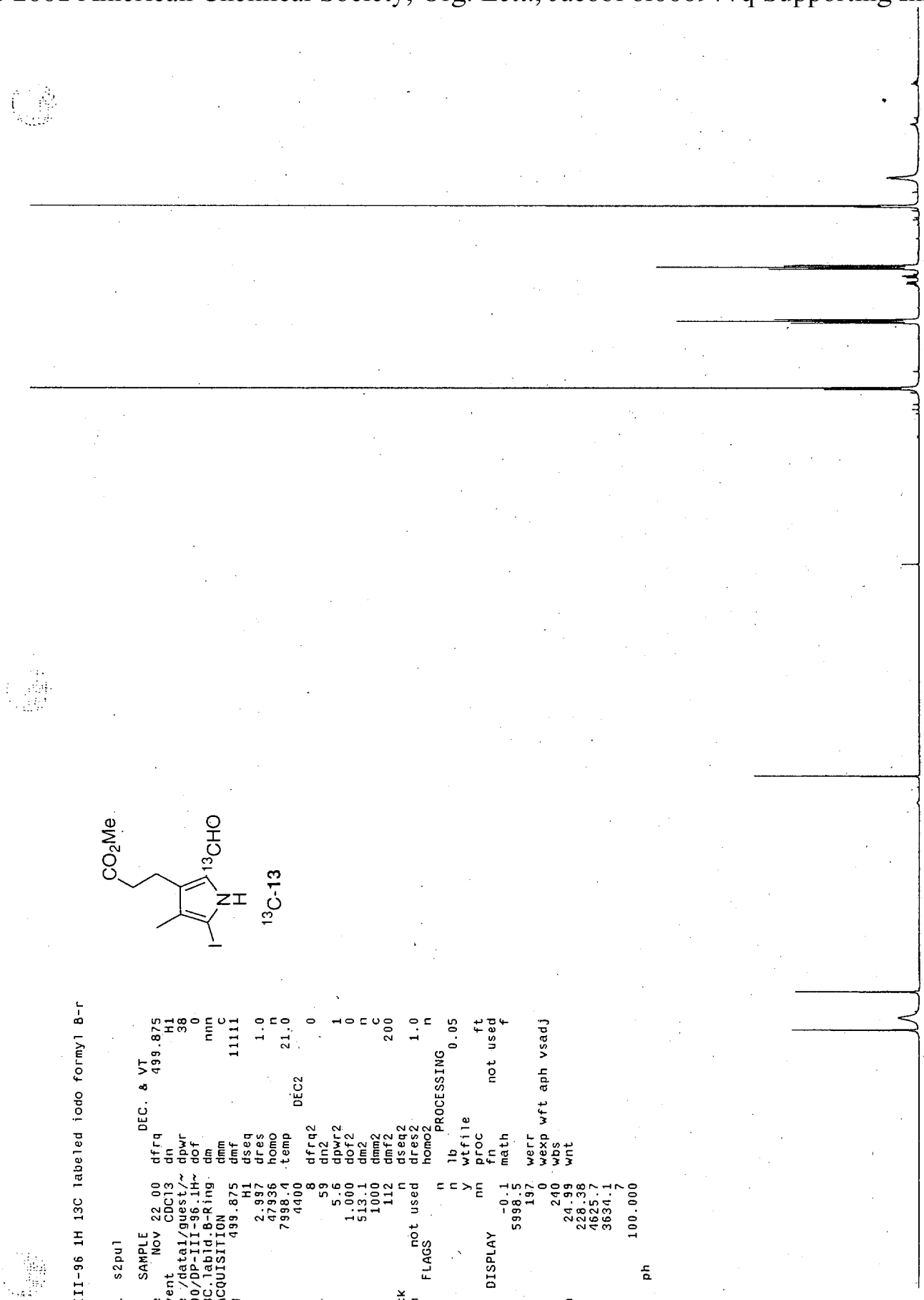
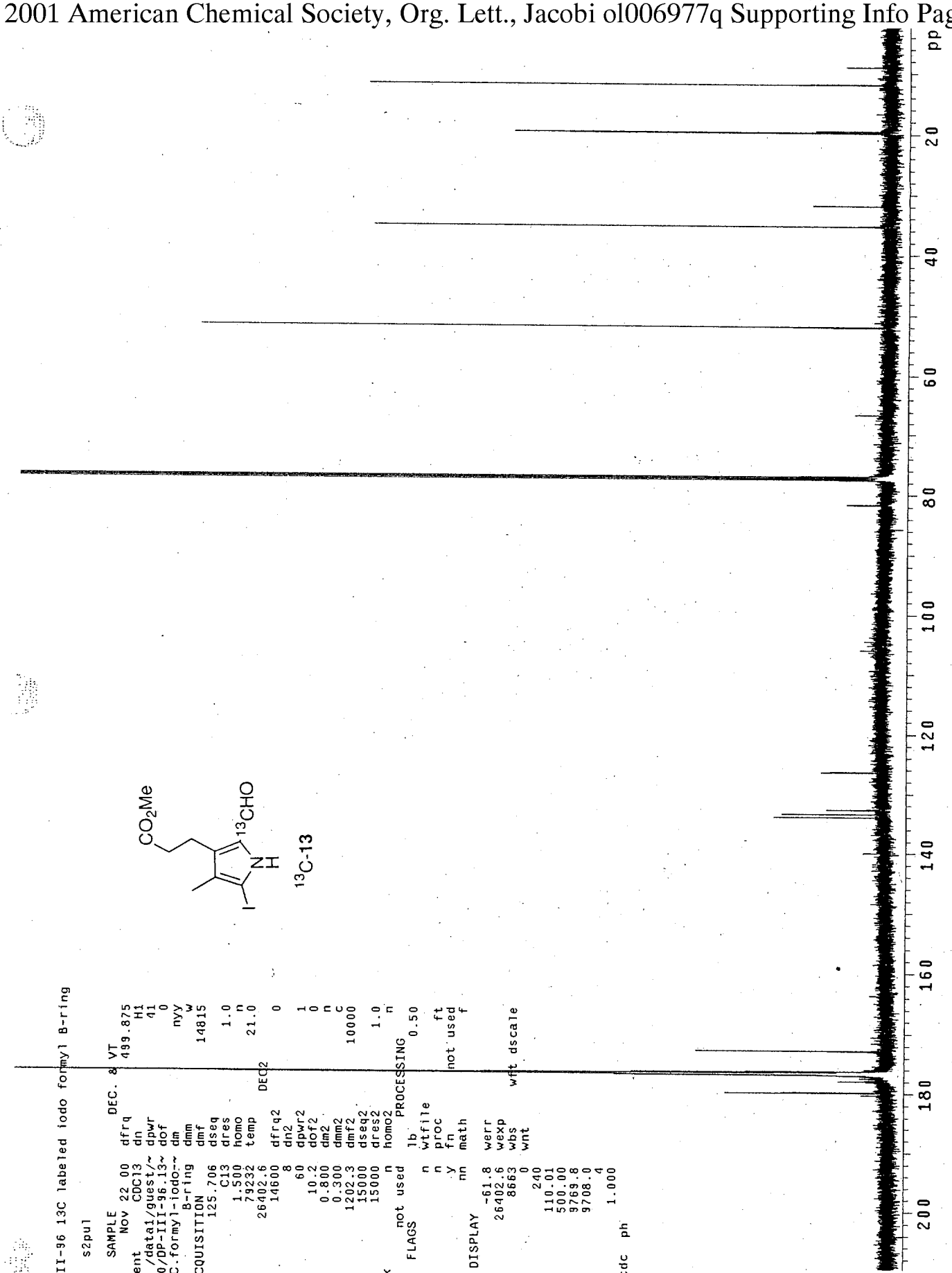
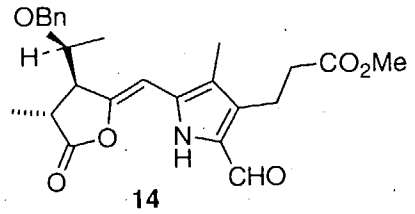




DP-III-69

exp1 s2pul

SAMPLE		DEC. & VT	
date	Nov 1 00	dfrq	499.875
solvent	CDCl3	dn	H1
file	/data1/guest/~	dpwr	38
	DP500/DP-III-69.2R~	dof	0
	-A-Benzyloxy.B-ald~	dm	nnn
ACQUISITION		dmm	c
sfrq	499.875	dmf	11111
tn	H1	dseq	
at	2.997	dres	1.0
np	47936	homo	n
sw	7998.4	temp	21.0
fb	4400	DEC2	
bs	8	dfrq2	0
tpwr	59	dn2	
pw	5.6	dpwr2	1
d1	1.000	dof2	0
tof	513.1	dm2	n
nt	100	dmm2	c
ct	100	dmf2	200
alock	n	dseq2	
gain	not used	dres2	1.0
FLAGS		homo2	n
il	n	PROCESSING	
in	n	lb	0.05
dp	y	wtfile	
hs	nn	proc	ft
DISPLAY		fn	not used
sp	-0.1	math	f
wp	5998.5		
vs	130	werr	
sc	0	wexp	wft aph vsadj
wc	240	wbs	
hzmm	24.99	wnt	
is	342.35		
rfl	4605.8		
rfp	3619.1		
th	7		
ins	100.000		
nm	ph		



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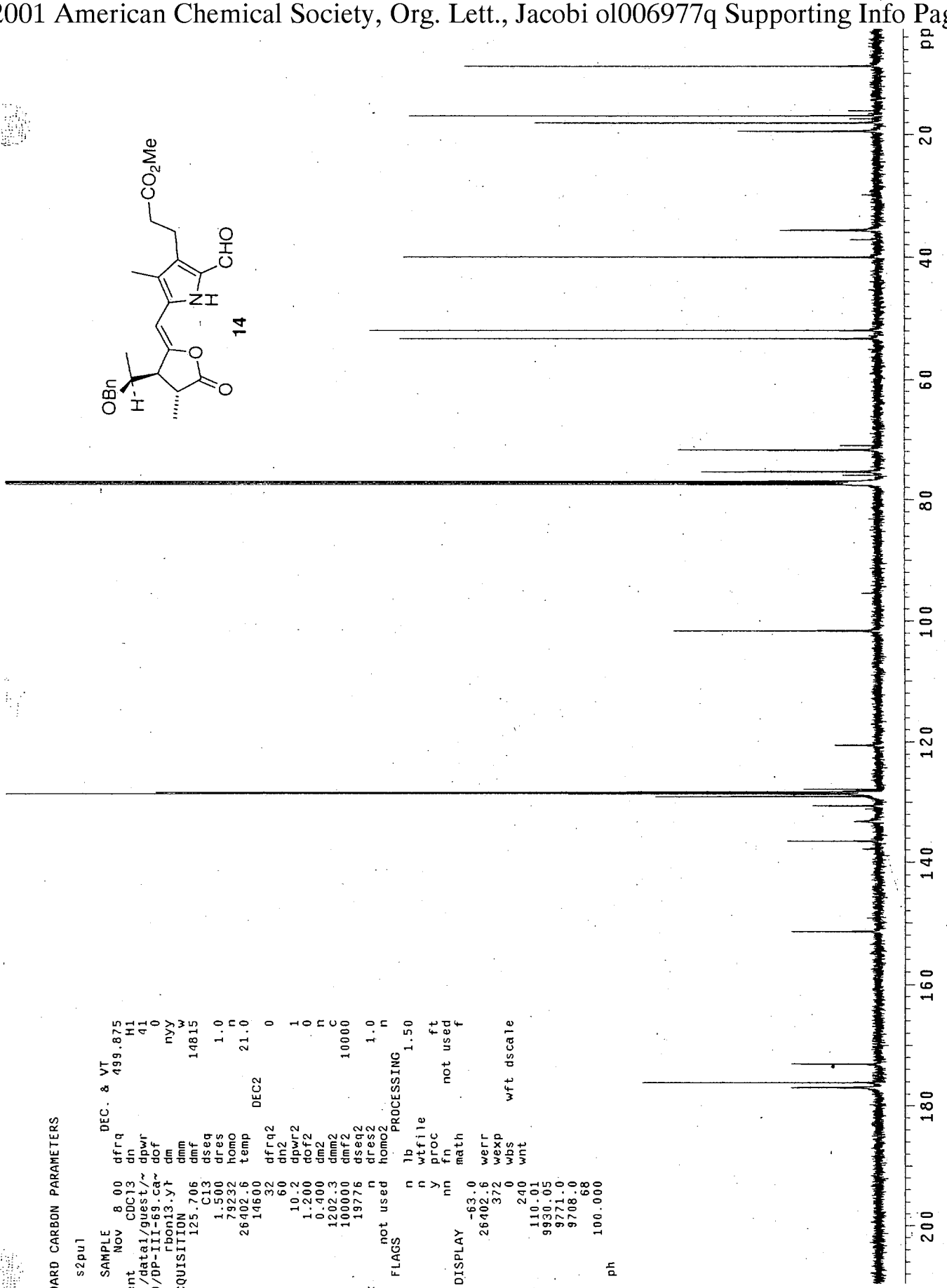
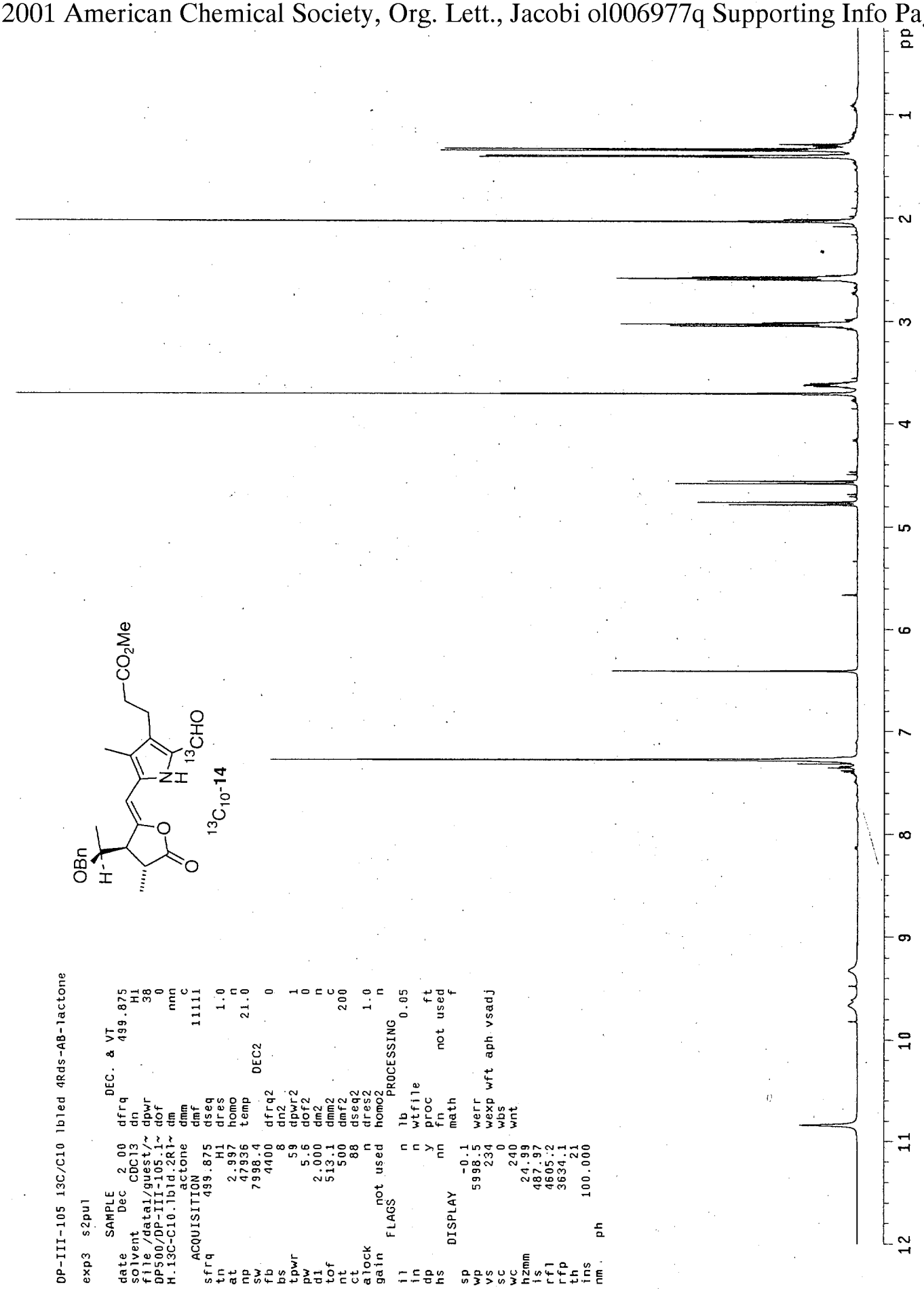
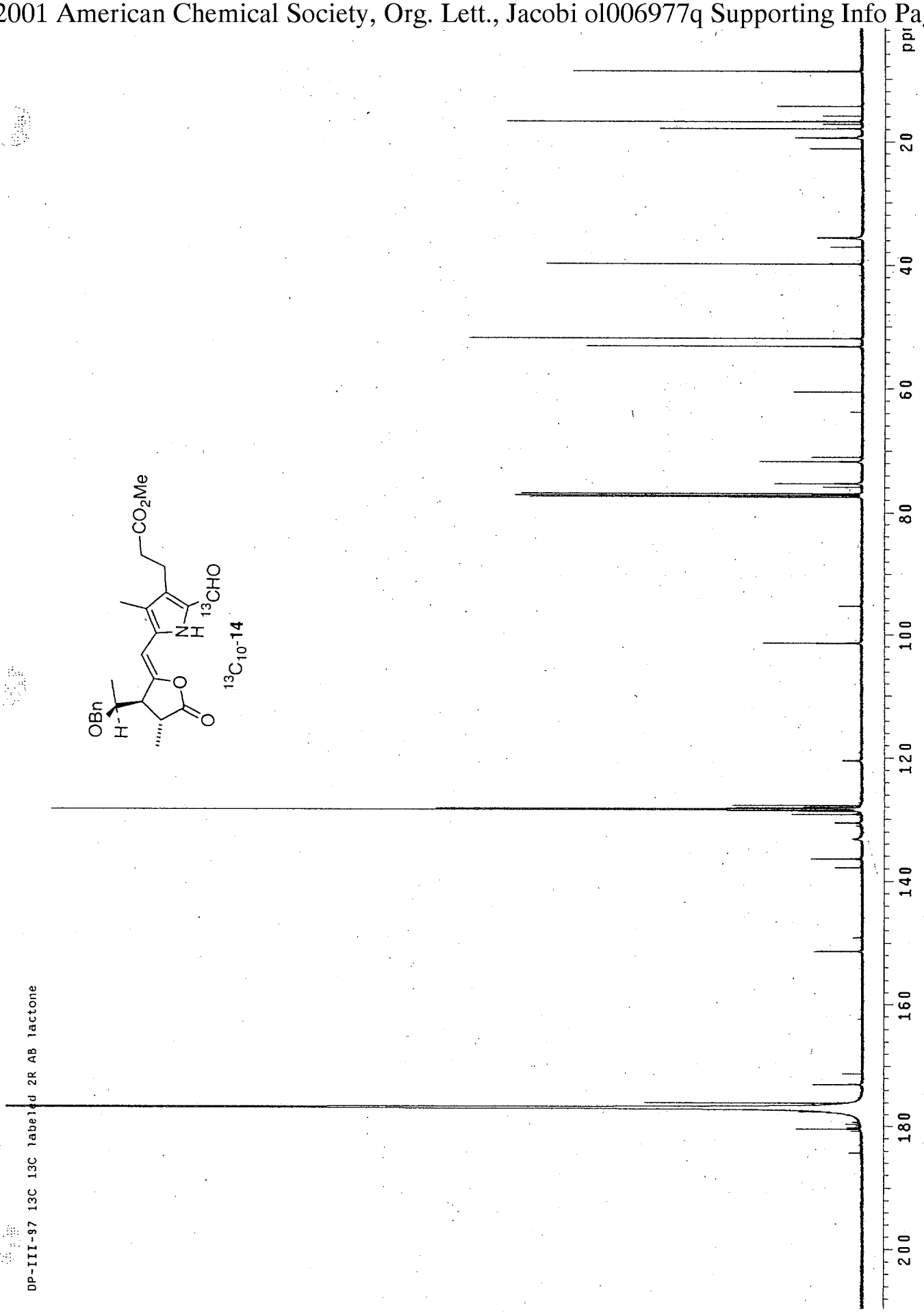
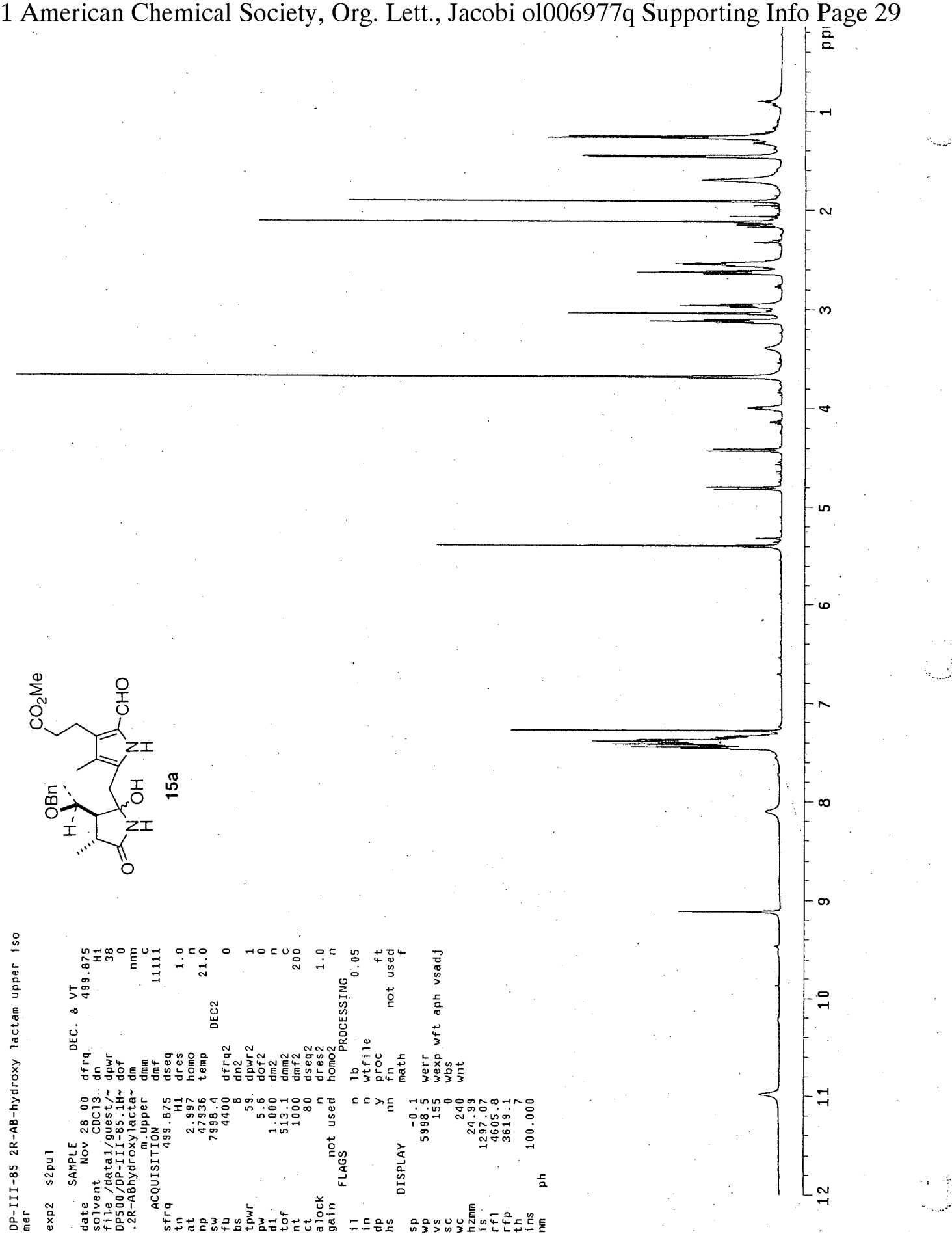


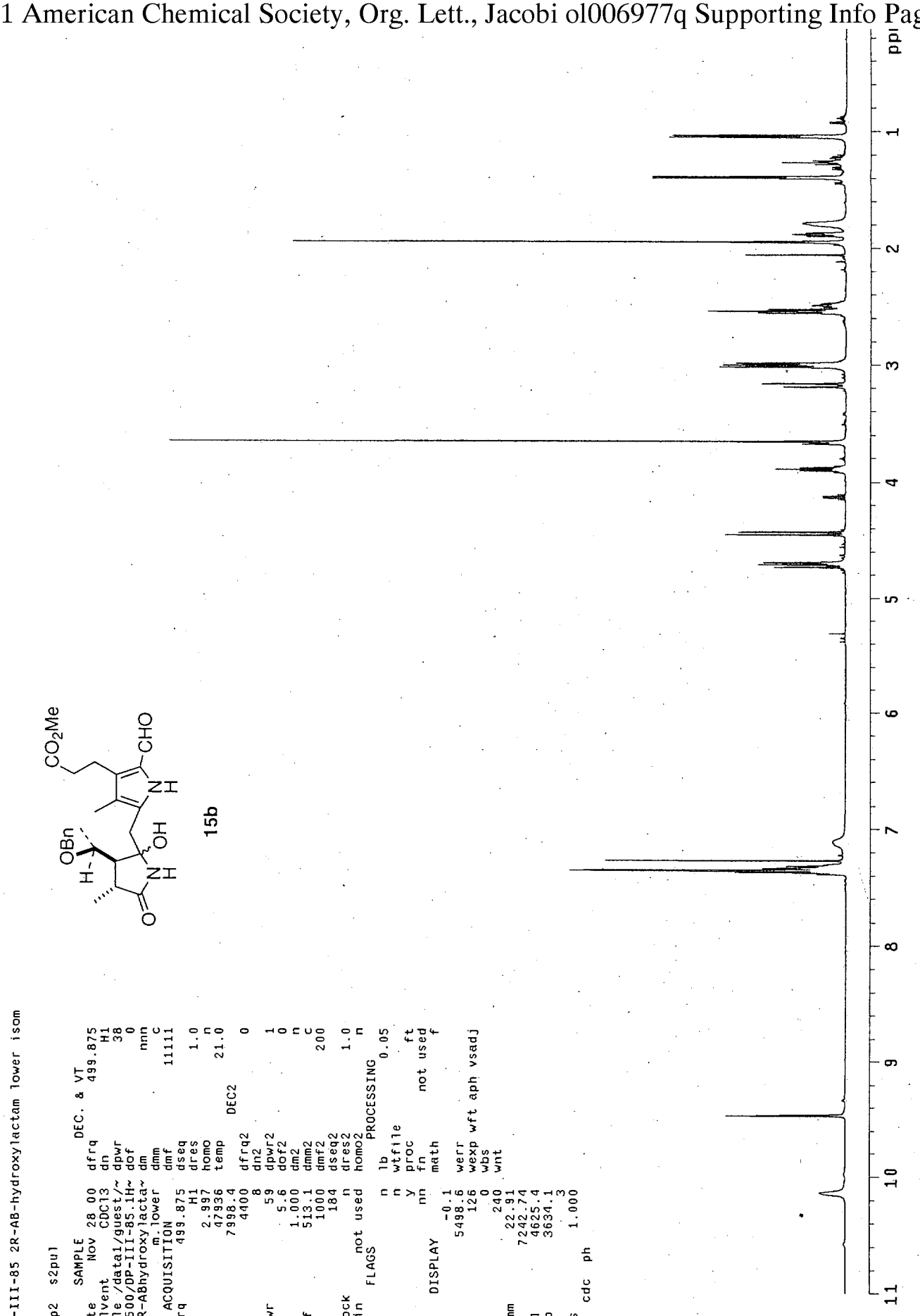

```
STANDARD CARBON PARAMETERS

expl  s2pul

      SAMPLE                DEC. & VT
date      Nov  8 00   dfrq      499.875
solvent           CDCl3   dn           H1
file /data1/guest/~   dpwr           41
DP500/DP-III-69.ca~   dof             0
          rbon13.yf   dm            nyy
    ACQUISITION       dmm             w
sfrq        125.706   dmf         14815
tn              C13   dseq
at            1.500   dres            1.0
np            79232   homo              n
sw         26402.6    temp         21.0
fb           14600   DEC2
bs              32   dfrq2              0
tpwr            60   dn2
pw            10.2   dpwr2              1
d1           1.200   dOf2               0
d2           0.400   dm2                n
tof         1202.3   dmm2               c
nt          100000   dmf2           10000
ct           19776   dseq2
alock            n   dres2            1.0
gain     not used    homo2              n
         FLAGS       PROCESSING
il               n   lb                1.50
in               n   wtfile
dp               y   proc               ft
hs              nn   fn             not used
      DISPLAY        math               f
sp          -63.0
wp        26402.6    werr
vs            372    wexp
sc              0    wbs          wft dscale
wc            240    wnt
hzmm       110.01
is        9930.05
rfl        9771.0
rfp        9708.0
th              68
ins        100.000
nm    ph
```

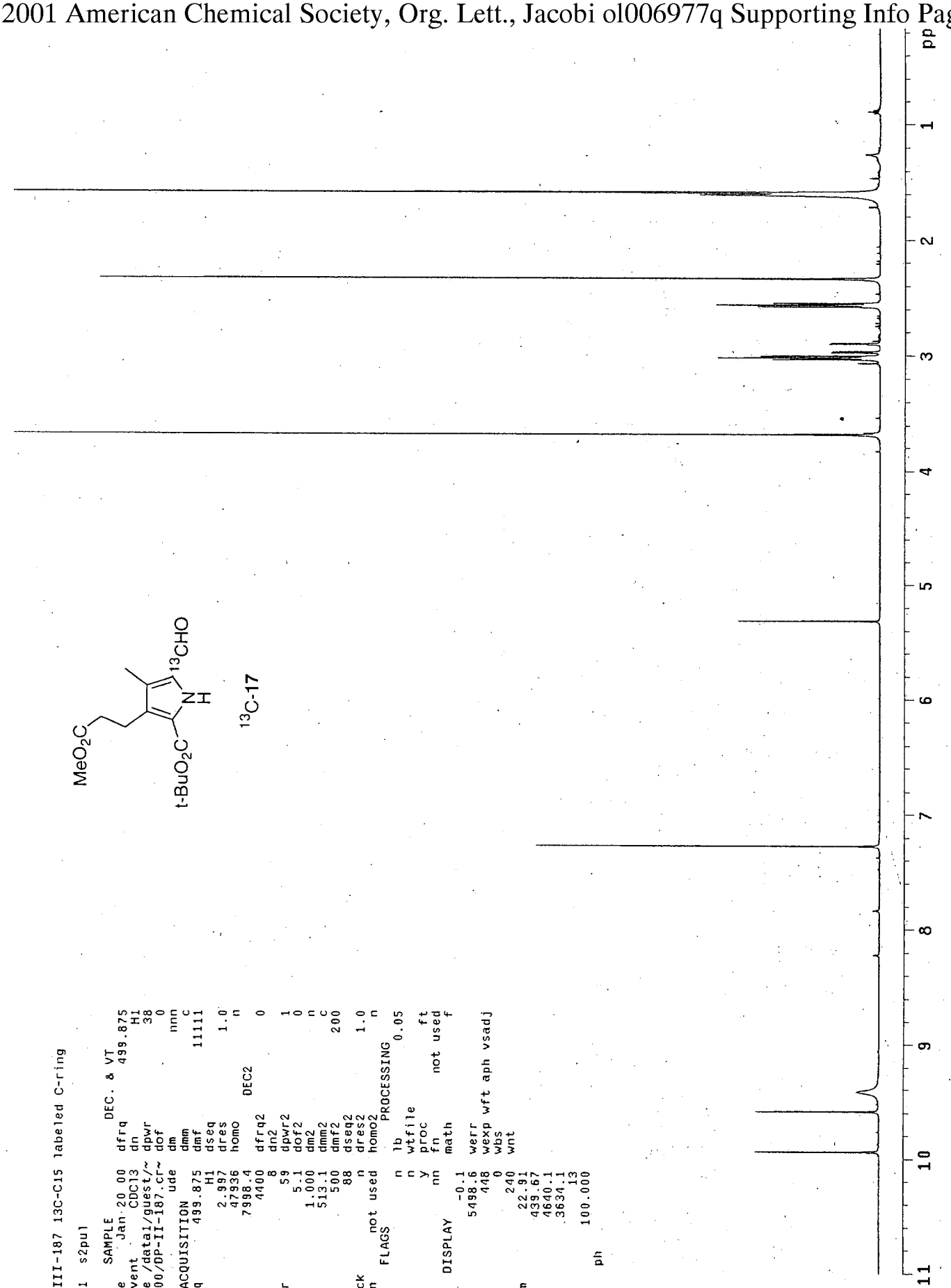



```
DP-III-105 13C/C10 lbled 4Rds-AB-lactone

exp3  s2pul

      SAMPLE                DEC. & VT
date      Dec  2.00  dfrq      499.875
solvent       CDCl3  dn            H1
file /data1/guest/~  dpwr          38
DP500/DP-III-105.1~  dOf            0
H.13C-C10.lbld.2R1~  dm           nnn
          actone     dmm            c
   ACQUISITION       dmf        11111
sfrq        499.875  dseq
tn               H1  dres          1.0
at            2.997  homo            n
np            47936  temp        21.0
sw          7998.4   DEC2
fb            4400   dfrq2          0
bs               8   dn2
tpwr            59   dpwr2          1
pw             5.6   dOf2           0
d1           2.000   dm2            n
tof         5113.1   dmm2           c
nt             500   dmf2         200
ct              88   dseq2
alock            n   dres2        1.0
gain      not used   homo2            n
      FLAGS                PROCESSING
il               n  lb              0.05
in               n  wtfile
dp               y  proc             ft
hs              nn  fn          not used
      DISPLAY       math           f
sp           -0.1
wp         5998.5   werr
vs            234   wexp wft aph vsadj
sc              0   wbs
wc            240   wnt
hzmm        24.99
is         487.97
rfl        4605.2
rfp        3634.1
th              21
ins        100.000
nm   ph
```

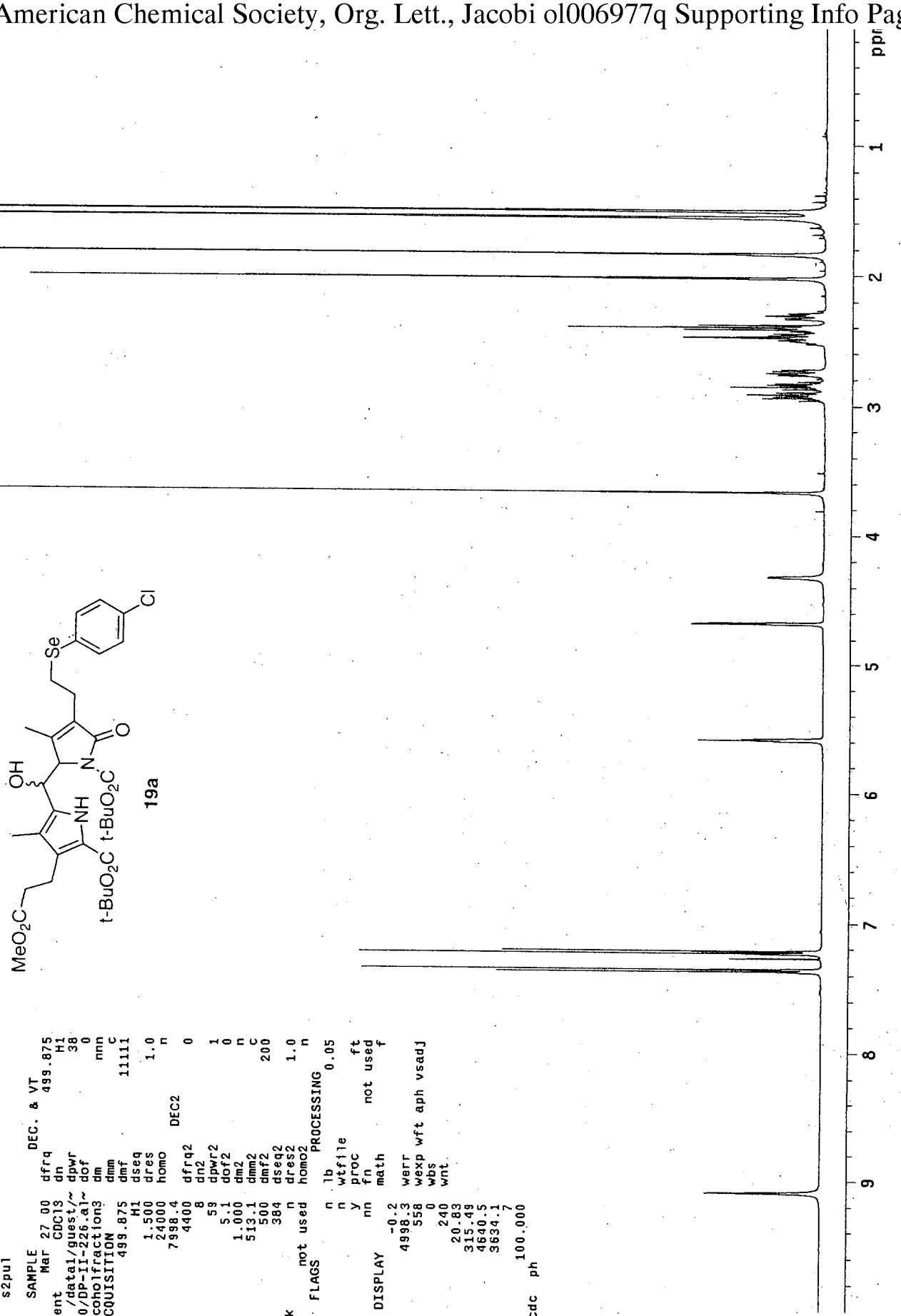

DP-III-97 13C 13C labeled 2R AB lactone
ppm
200
180
160
140
120
100
80
60
40
20
OBn
H
O
O
N
H
13CHO
CO2Me
13C10-14



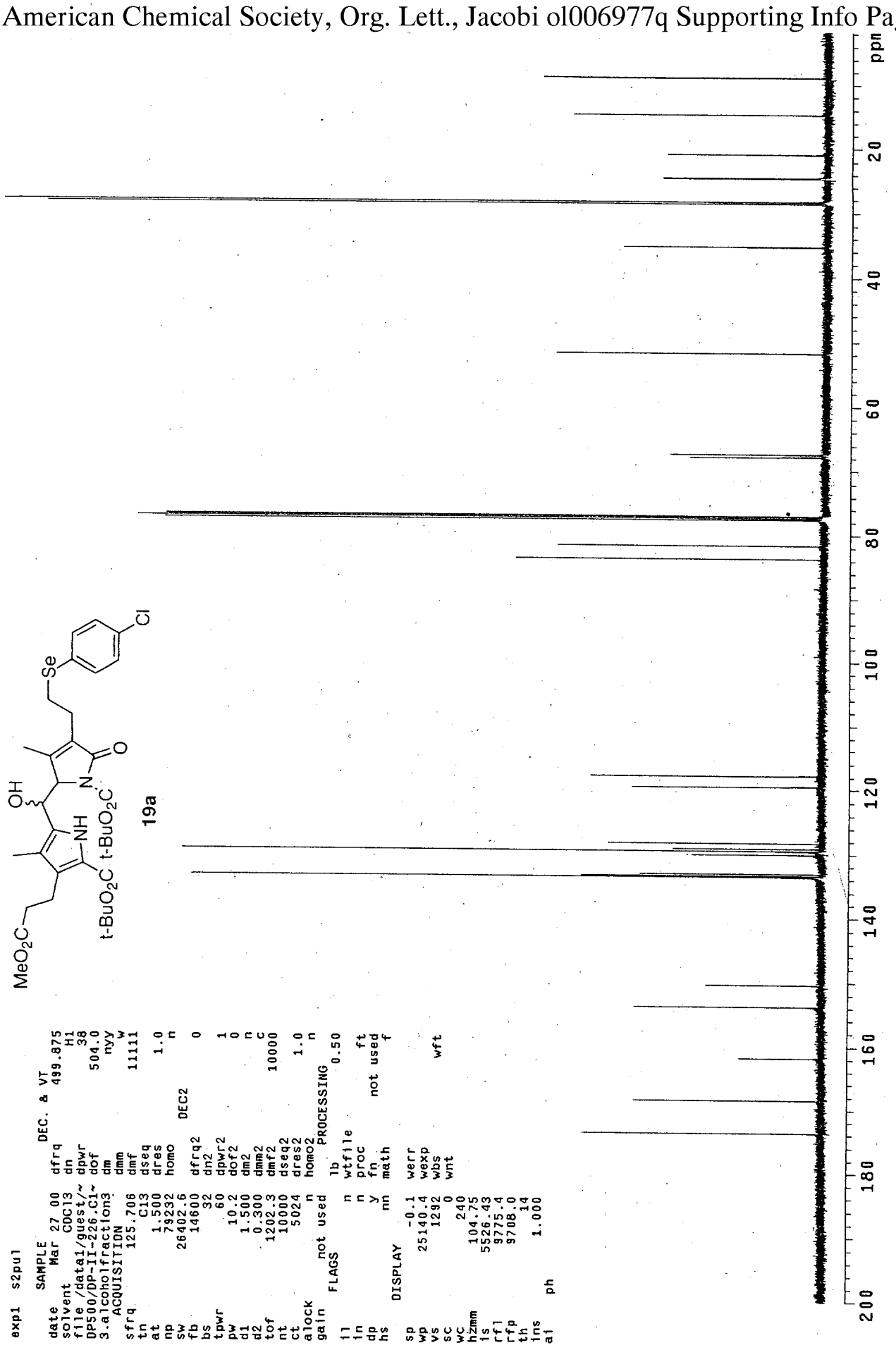


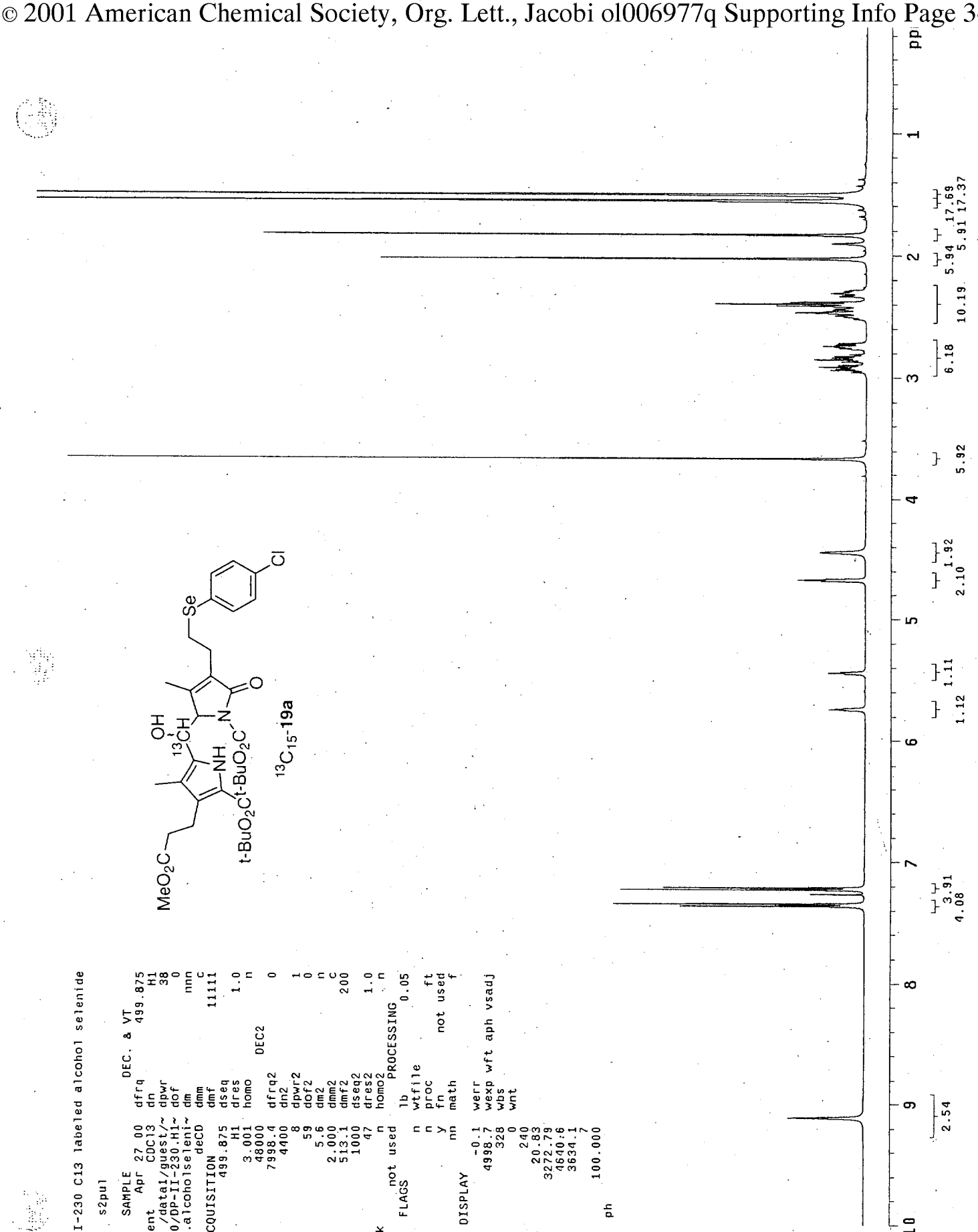


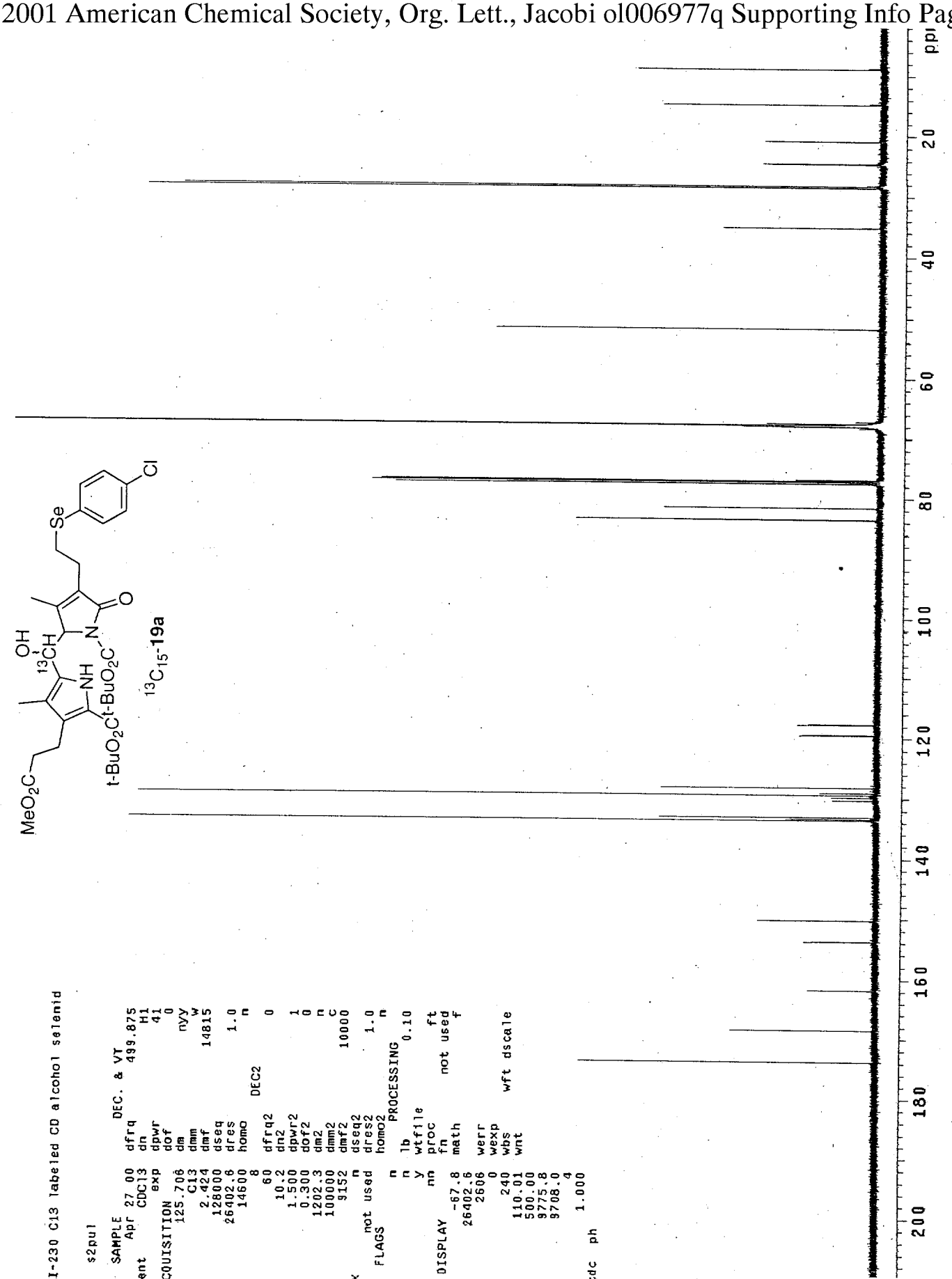

```
DP-III-187 13C-C15 labeled C-ring

  expl  s2pul

        SAMPLE                DEC. & VT
  date    Jan 20 00  dfrq      499.875
  solvent     CDCl3  dn            H1
  file /data1/guest/~  dpwr          38
  DP500/DP-II-187.cr~  dof            0
                 ude  dm           nnn
    ACQUISITION       dmm             c
  sfrq      499.875  dmf         11111
  tn             H1  dseq            1.0
  at          2.997  dres             n
  np          47936  homo      DEC2
  sw         7998.4                   0
  fb           4400  dfrq2
  bs              8  dn2
  tpwr           59  dpwr2            1
  pw            5.1  dof2             0
  d1          1.000  dm2              n
  tof         513.1  dmm2             c
  nt            500  dmf2           200
  ct             88  dseq2
  alock           n  dres2          1.0
  gain     not used  homo2            n
        FLAGS                 PROCESSING
  il              n  lb              0.05
  in              n  wtfile
  dp              y  proc             ft
  hs             nn  fn       not used
        DISPLAY      math             f
  sp          -0.1
  wp        5498.6  werr
  vs           448  wexp wft aph vsadj
  sc             0  wbs
  wc           240  wnt
  hzmm       22.91
  is        439.67
  rfl      4640.1
  rfp      3634.1
  th            13
  ins      100.000
  nm    ph
```



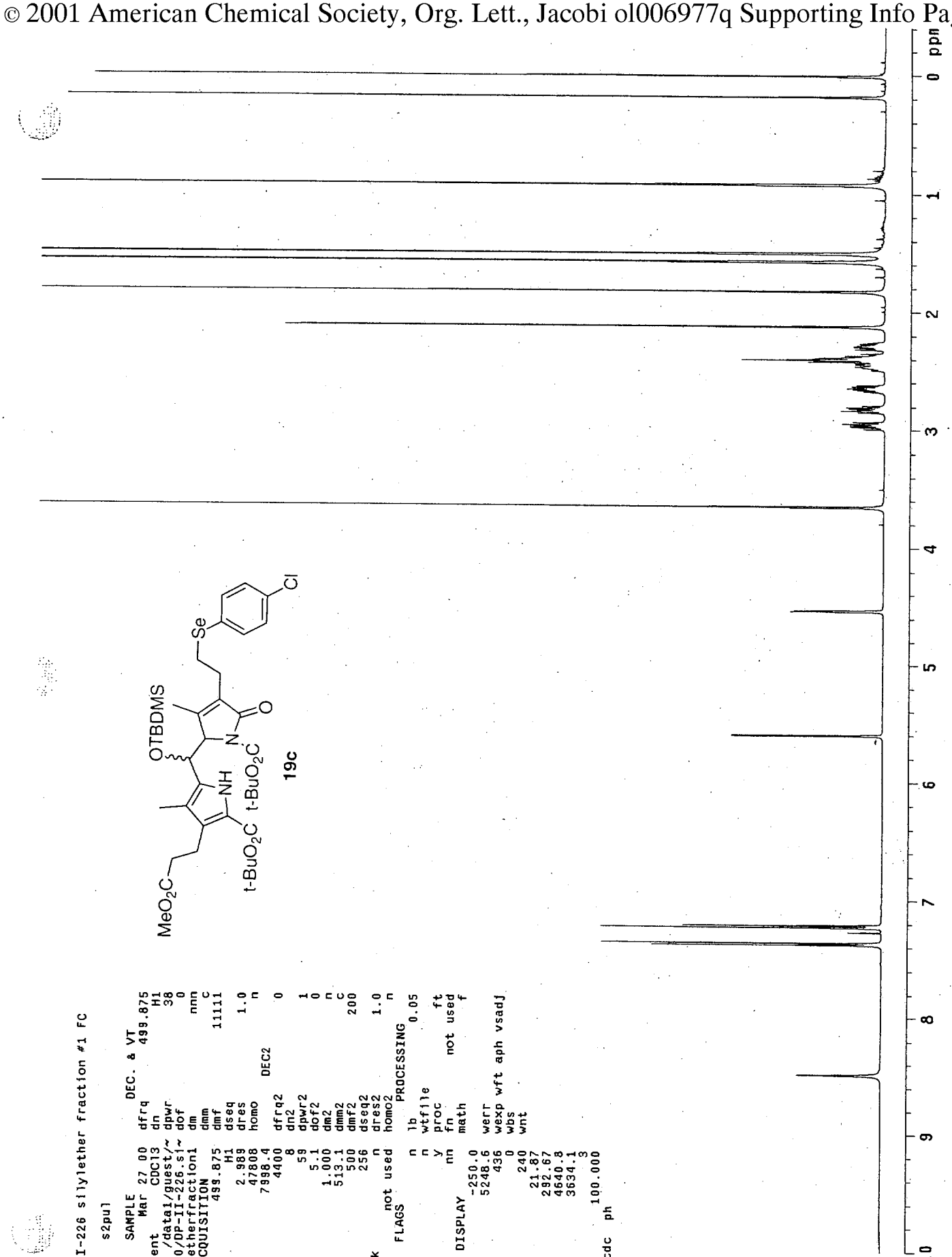

```
DP-II-226 alcohol fraction #3 FC

exp1  s2pul

      SAMPLE                DEC. & VT
date      Mar 27 00  dfrq      499.875
solvent       CDCl3  dn            H1
file /data1/guest/~  dpwr          38
DP500/DP-II-226.a1~  dof            0
     cholfraction3   dm           nnn
    ACQUISITION      dmm            c
sfrq        499.875  dmf        11111
tn               H1  dseq
at            1.500  dres          1.0
np            24000  homo            n
sw          7998.4               DEC2
fb            4400  dfrq2             0
bs               8  dn2
tpwr            59  dpwr2             1
pw             5.1  dof2              0
d1           1.000  dm2               n
tof          513.1  dmm2              c
nt             500  dmf2            200
ct             384  dseq2
alock            n  dres2           1.0
gain      not used  homo2             n
          FLAGS               PROCESSING
il               n  lb             0.05
in               n  wtfile
dp               y  proc             ft
hs      nn  nn      fn       not used  f
        DISPLAY     math
sp          -0.2
wp        4998.3  wexp wft aph vsadj
vs           558  wbs
sc             0  wnt
wc           240
hzmm       20.83
is         315.49
rfl        4640.5
rfp        3634.1
th               7
ins    100.000
nm  cdc  ph
```








```
DP-II-230 C13 labeled CD alcohol selenid
e

exp1  s2pul

        SAMPLE                  DEC. & VT
date      Apr 27 00  dfrq          499.875
solvent       CDCl3  dn               H1
file             exp  dpwr             41
  ACQUISITION        dof               0
sfrq        125.706  dm              nyy
tn              C13  dmm               w
at            2.424  dmf           14815
np           128000  dseq
sw         26402.6  dres             1.0
fb           14600  homo               n
bs               8         DEC2
tpwr            60  dfrq2             0
pw            10.2  dn2
d1           1.500  dpwr2             1
d2           0.300  dof2              0
tof         1202.3  dm2               n
nt          100000  dmm2              c
ct            9152  dmf2          10000
alock              n  dseq2
gain      not used  dres2            1.0
        FLAGS       homo2              n
                                PROCESSING
il                n  lb               0.10
in                n  wtfile
dp                y  proc               ft
hs               nn  fn         not used
        DISPLAY     math              f
sp          -67.8  werr
wp        26402.6  wexp
vs           2606  wbs
sc              0  wnt         wft dscale
wc            240
hzmm       110.01
is         500.00
rfl        9775.8
rfp        9708.0
th               4
ins          1.000
nm  cdc  ph
```

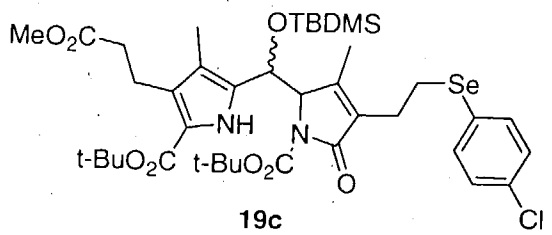


DP-II-226 C13 silylether frac #1

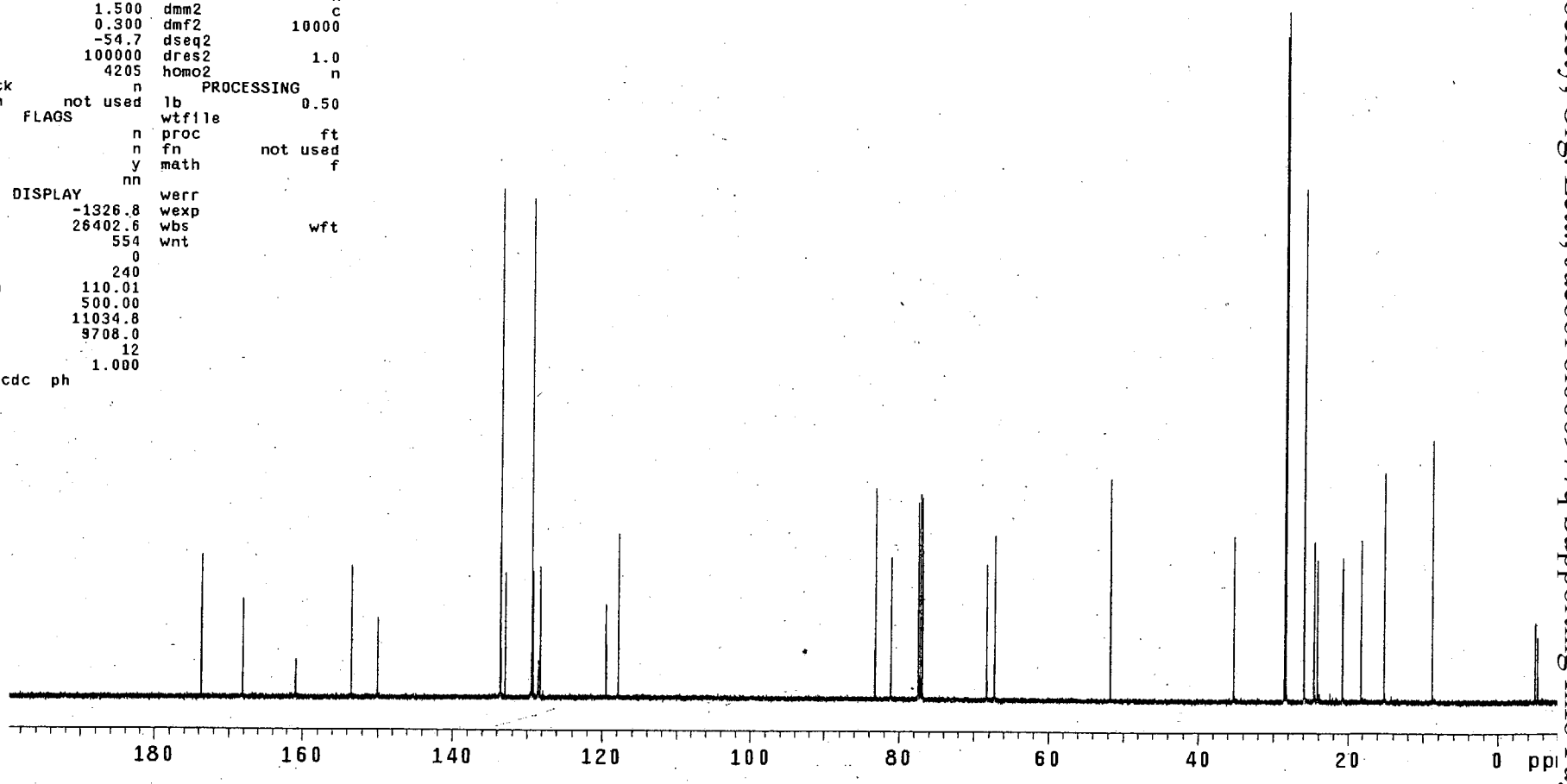
exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 27 00	dfrq	499.875
solvent	CDCl3	dn	H1
file	/data1/guest/~	dpwr	38
	DP500/DP-II-226.C1~	dof	504.0
	3.silyletherfracti~	dm	nyy
	on1	dmm	w
ACQUISITION		dmf	11111
sfrq	125.705	dseq	
tn	C13	dres	1.0
at	1.500	homo	n
np	79232	DEC2	
sw	26402.6	dfrq2	0
fb	14600	dn2	
bs	16	dpwr2	1
tpwr	60	dof2	0
pw	10.2	dm2	n
d1	1.500	dmm2	c
d2	0.300	dmf2	10000
tof	-54.7	dseq2	
nt	100000	dres2	1.0
ct	4205	homo2	n
alock	n	PROCESSING	
gain	not used	lb	0.50
FLAGS		wtfile	
il	n	proc	ft
in	n	fn	not used
dp	y	math	f
hs	nn		
DISPLAY		werr	
sp	-1326.8	wexp	
wp	26402.6	wbs	wft
vs	554	wnt	
sc	0		
wc	240		
hzmm	110.01		
is	500.00		
rfl	11034.8		
rfp	9708.0		
th	12		
ins	1.000		

ai cdc ph



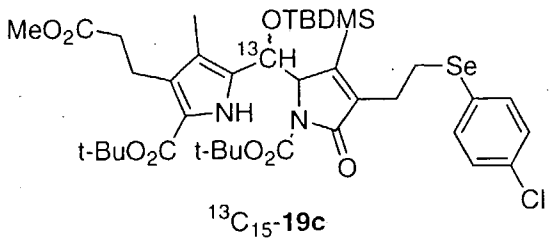
19c



DP-II-230 C13 labeled silyl ether

exp4 s2pul

SAMPLE		DEC. & VT	
date	May 4 00	dfrq	499.875
solvent	CDCl3	dn	H1
file	/data1/guest/~	dpwr	38
	DP500/DP-II-230.H1~	dof	0
	.C13.silyletherfra~	dm	nnn
	c1	dmm	c
ACQUISITION		dmf	11111
sfrq	499.875	dseq	
tn	H1	dres	1.0
at	2.997	homo	n
np	47936	temp	21.0
sw	7998.4	DEC2	
fb	4400	dfrq2	0
bs	8	dn2	
tpwr	59	dpwr2	1
pw	5.6	dof2	0
d1	1.000	dm2	n
tof	513.1	dmm2	c
nt	500	dmf2	200
ct	116	dseq2	
alock	n	dres2	1.0
gain	not used	homo2	n
FLAGS		PROCESSING	
il	n	lb	0.05
in	n	wtfile	
dp	y	proc	ft
hs	nn	fn	not used
DISPLAY		math	f
sp	-250.0		
wp	5248.6	werr	
vs	292	wexp wft aph vsadj	
sc	0	wbs	
wc	240	wnt	
hzmm	21.87		
is	2832.06		
rfl	4640.6		
rfp	3634.1		
th	7		
ins	100.000		
nm	ph		



$^{13}C_{15}$-**19c**